Asymmetric Friedel–Crafts reaction of unsaturated carbonyl-tethered heteroarenes via vinylogous activation of Pd^0-π-Lewis base catalysis

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Supplementary Information

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1. General methods

^{1}H NMR (400 or 600 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were recorded on Varian INOVA-400/54, Agilent DD2-600/54 or Bruker Ascend™ 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet; td = triple doublet; m = multiplet, br = broad, and coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2, Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. X-ray diffraction experiments were carried out on an Agilent Gemini or Bruker APEX-II CCD diffractometer, and the data obtained were deposited at the Cambridge Crystallographic Data Centre (CCDC 2251805–2251810). In each case, diastereomeric ratio was determined by ^{1}H NMR analysis and enantiomeric excess was determined by HPLC (Agilent Technologies: 1220 Infinity II, 1200 Series, 1260 Infinity) analysis on a chiral column in comparison with authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralpak IA Column (250 × 4.6 mm), Chiralpak IB Column (250 × 4.6 mm), Chiralpak IC Column (250 × 4.6 mm), Chiralpak ID Column (250 × 4.6 mm), Chiralpak IE Column (250 × 4.6 mm), Chiralcel IF Column (250 × 4.6 mm). UV detection was monitored at 254 nm. The specific optical rotation was obtained from Rudolph Research Analytical Autopol I automatic polarimeter in $CHCl_3$ solution at 25 °C. The melting point was obtained from WRX-4 Mel-Temp apparatus. Column chromatography was performed on silica gel (200–300 mesh) eluting with ethyl acetate (EtOAc) and petroleum ether or dichloromethane (DCM)/methanol (MeOH). TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether (60–90 ℃) was redistilled. 2-Indolyl propiolate **1**,[1] enones **2**,[2] enones **5**,[3] 2-indolyl acrylates **7**,[4] imines **8**,[5] 2-pyrrolyl acrylates **10**,[6] 2-furyl acrylate **12**,[7] 1-azadiene **13**,[8] **L2**, **L3**,[9] bifuncational chiral ligands **L6** and **L7**,[10] were synthesized following the literature procedures.

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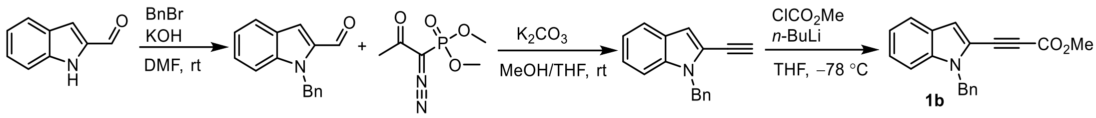
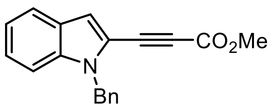
2. Procedure for the preparation of 2-indolyl propiolates



To a stirred solution of 1*H*-indole-2-carbaldehyde (1.45 g, 10.0 mmol, 1.0 equiv) in DMF (10 mL) was added KOH (1.12 g, 20.0 mmol, 2.0 equiv) at 0 ℃. The mixture was stirred for 20 min, and benzyl bromide (1.42 mL, 12.0 mmol, 1.2 equiv) was added dropwise. The resulting mixture was stirred at rt for 2 h before the reaction was quenched by pouring it into ice water. The mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water (20 mL) and brine (30 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, petroleum ether/EtOAc = 20/1) to give 1-benzyl-1*H*-indole-2-carbaldehyde as a colorless oil (2.12 g, 90% yield).

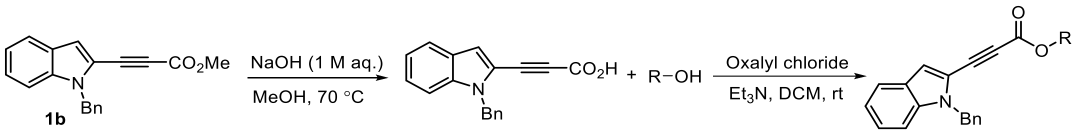
1-Benzyl-1*H*-indole-2-carbaldehyde (2.12 g, 9.00 mmol, 1.0 equiv) was dissolved in MeOH/THF (20/10 mL), and K_2CO_3 (3.73 g, 27.0 mmol, 3.0 equiv) was added at 0 ℃. Then dimethyl (1-diazo-2-oxopropyl)phosphonate (1.62 mL, 10.8 mmol, 1.2 equiv) was added by dropwise before the mixture was allowed to warm to room temperature. The mixture was stirred until completion (monitored by TLC). The reaction was quenched with water and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water (20 mL) and brine (30 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, petroleum ether/EtOAc = 30/1) to give 1-benzyl-2-ethynyl-1*H*-indole as a yellow solid (1.30 g, 62% yield).

To a solution of 1-benzyl-2-ethynyl-1*H*-indole (1.30 g, 5.60 mmol, 1.0 equiv) in THF was added *n*-BuLi (2.4 M, 2.80 mL, 6.72 mmol, 1.2 equiv) dropwise at −78 ℃ under argon atmosphere. The mixture was stirred for 30 min. Methyl chloroformate (0.63 mL, 6.7 mmol, 1.2 equiv) was added and the mixture was stirred at the same temperature for 3 h. Then the solution was warmed to room temperature, quenched with water and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water (20 mL) and brine (30 mL), dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, petroleum ether/EtOAc = 15/1) to give **1b**.



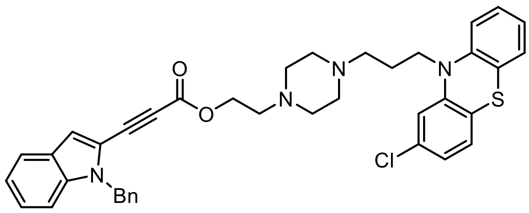
Compound 1b: yellow solid, 1.32 g, 82% yield; mp 113–115 ℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.65 (s, 1H), 7.39–7.23 (m, 5H), 7.22–7.06 (m,

4H), 5.48 (s, 2H), 3.85 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 154.2, 137.6, 137.0, 128.7, 127.7, 127.0, 126.9, 125.0, 121.9, 120.9, 118.2, 113.3, 110.5, 87.4, 79.1, 52.8, 48.3; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}NO_2^+$ 290.1176; Found 290.1186.

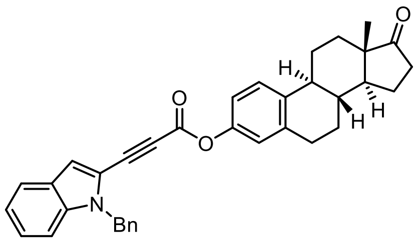


To a stirred solution of **1b** (2.89 g, 10.0 mmol, 1.0 equiv) in MeOH (20 mL) was added aqueous NaOH (1 M, 30 mL, 30 mmol, 3.0 equiv) at rt. The mixture was heated at 70 ℃ for 5 h. After completion, the solvent was removed in vacuo, diluted with water and acidified with aqueous HCl (1 M, 30 mL). The mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated to give crude carboxylic acid (2.56 g, 93% yield).

To a solution of carboxylic acid (275 mg, 1.00 mmol, 1.0 equiv) in DCM (10 mL) and Et_3N (0.26 mL, 2.0 mmol, 2.0 equiv) was added oxalyl chloride (102 μL, 1.30 mmol, 1.3 equiv) dropwise at 0 ℃ under argon atmosphere. The mixture was stirred for 5 min. Estrone or prochlorperazine (1.10 mmol, 1.1 equiv) was added and the mixture was stirred at rt for 1 h. After completion, the solvent was removed in vacuo, and the residue was purified by column chromatography (SiO_2, petroleum ether/EtOAc = 5/1) to give pure product.



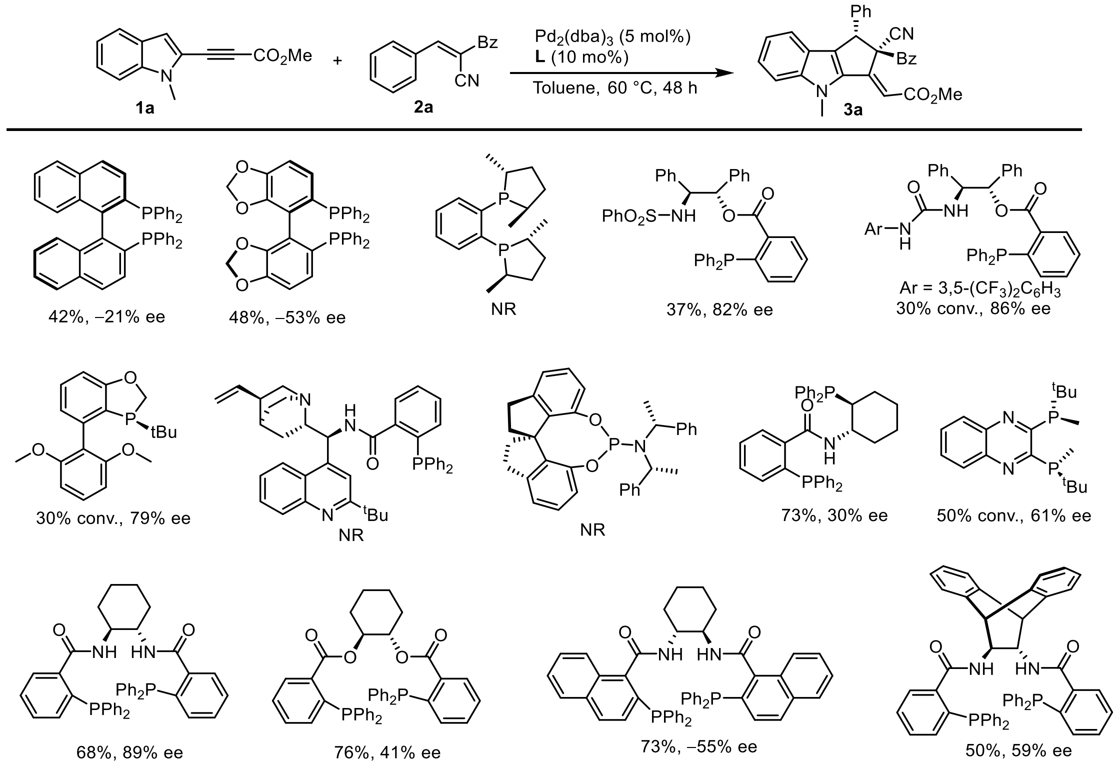
Compound 1l: yellow solid, 426 mg, 64% yield; mp 48–49 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.54 (d, *J* = 8.0 Hz, 1H), 7.22–7.12 (m, 5H), 7.10–6.99 (m, 6H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.86–6.74 (m, 4H), 5.36 (s, 2H), 4.25 (t, *J* = 5.9 Hz, 2H), 3.80 (t, *J* = 6.8 Hz, 2H), 2.60 (t, *J* = 5.9 Hz, 2H), 2.47–2.31 (m, 10H), 1.88–1.78 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 153.6, 146.4, 144.4, 137.6, 136.9, 133.1, 128.7, 127.8, 127.6, 127.43, 127.35, 127.0, 126.8, 125.0, 124.7, 123.4, 122.8, 122.2, 121.9, 120.9, 118.2, 115.8, 115.7, 113.2, 110.4, 87.5, 79.1, 63.3, 56.3, 55.4, 53.3, 53.1, 48.2, 45.3, 24.2; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{38}ClN_4O_2S^+$ 661.2399; Found 661.2402.



Compound 1m: yellow solid, 386 mg, 73% yield; mp 130–132 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.64 (d, *J* = 8.0 Hz, 1H), 7.34–7.21 (m, 6H), 7.20–7.10 (m, 4H), 6.95 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 5.43 (s, 2H), 2.90 (dd, *J* = 9.3, 4.3 Hz, 2H), 2.50 (dd, *J* = 18.9, 8.7 Hz, 1H), 2.44–2.34 (m, 1H), 2.31–2.20 (m, 1H), 2.19–1.92 (m, 4H), 1.69–1.36 (m, 6H), 0.90 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 220.7, 152.5, 148.1, 138.3, 138.1, 137.8, 137.0, 128.8, 127.8, 127.1, 127.0, 126.6, 125.4, 122.1, 121.5, 121.1, 118.7, 118.0, 114.1, 110.6, 87.5, 81.6, 50.5, 48.4, 48.0, 44.2, 38.0, 35.9, 31.6, 29.4, 26.3, 25.8, 21.6, 13.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{33}NO_3Na^+$ 550.2353; Found 550.2359.

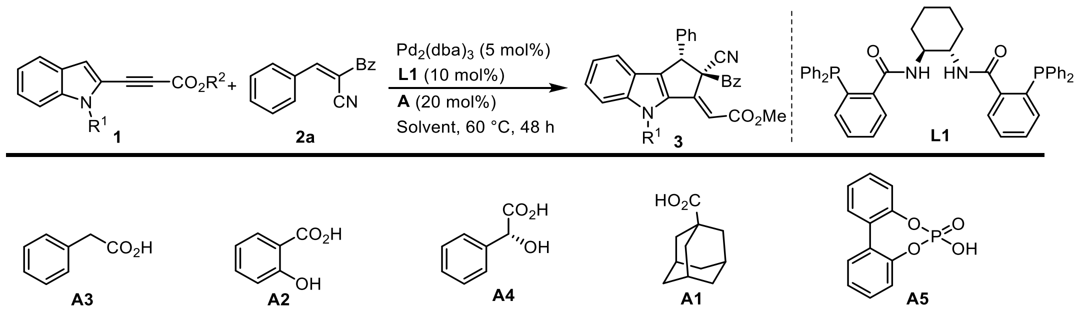
3. Optimisations for the asymmetric [3 + 2] annulations of 2- indolyl propiolates 1 with enone 2a

Table S1. Ligand screenings for the asymmetric [3 + 2] annulation of 2-indolyl propiolate 1a with enone 2a[a]



[a] Reactions were carried out with **1a** (0.025 mmol), **2a** (0.03 mmol), $Pd_2(dba)_3$ (5 mol%) and **L** (10 mol%) in toluene (0.25 mL) at 60 ℃ under Ar.

Table S2. Other condition screenings for the asymmetric [3 + 2] annulations of 2-indolyl propiolates 1 with enone 2a[a]



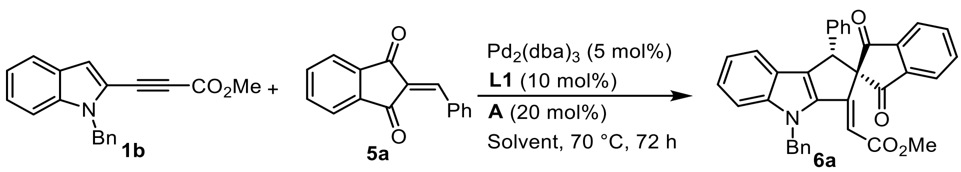
Entry	R^1, R^2	**A**	Solvent	*Temp* (°C)	Yield (%)[b] (conv.)	ee (%)[c]
1	Me, Me	/	Toluene	60	**3a**, 68	89
2	Me, Me	**A3**	Toluene	60	**3a**, (80)	89
3	Me, Me	**A2**	Toluene	60	**3a**, (60)	88
4	Me, Me	**A4**	Toluene	60	**3a**, 52	89
5	Me, Me	**A1**	Toluene	60	**3a**, 49 (90)	90
6	Me, Me	**A5**	Toluene	60	**3a**, nr	/

7	Me, Me	Na_2CO_3	Toluene	60	**3a**, 61	86
8	Me, Me	DIPEA	Toluene	60	**3a**, 42	89
9	Me, Me	TBAB	Toluene	60	**3a**, 86	86
10	Me, Me	/	EtOAc	60	**3a**, 46	81
11	Me, Me	/	MeCN	60	**3a**, 93	30
12	Me, Me	/	*i*-PrOH	60	**3a**, 91	65
13	Me, Me	/	1,4-Dioxane	60	**3a**, 81	89
14	Me, Me	TBAB	1,4-Dioxane	60	**3a**, 89	84
15	Me, *i*-Pr	TBAB	1,4-Dioxane	60	**3ah**, 51	79
16	Me, Bn	TBAB	1,4-Dioxane	60	**3ai**, 48	89
17	Bn, Me	TBAB	1,4-Dioxane	60	**3b**, 70	91
18	Bn, Me	/	1,4-Dioxane	60	**3b**, 49	92
19	Bn, Me	TBAB	1,4-Dioxane	70	**3b**, 70	91
20	Bn, Me	TBAB	1,4-Dioxane	80	**3b**, 69	89
21[d]	Bn, Me	TBAB	1,4-Dioxane	60	**3b**, 81	92
22[d,e]	Bn, Me	TBAB	1,4-Dioxane	60	**3b**, 86	92
23[d,e]	Bn, Me	TBAI	1,4-Dioxane	60	**3b**, 81	91
24[d,e]	Bn, Me	TBAC	1,4-Dioxane	60	**3b**, 76	92
25[d,e]	Bn, Me	TBAHS	1,4-Dioxane	60	**3b**, 79	90
26[d,e]	Bn, Me	KBr	1,4-Dioxane	60	**3b**, 52	92

[a] Unless noted otherwise, reactions were carried out with **1** (0.025 mmol), **2a** (0.03 mmol), $Pd_2(dba)_3$ (5 mol%), **L1** (10 mol%) and additive **A** (20 mol%) in solvent (0.25 mL) at 60 ℃ under Ar. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] C = 0.2 M. [e] The ratio of **1b/2a** was 1/1.3.

4. Optimisations for the asymmetric [3 + 2] annulation of 2-indolyl propiolate 1b with enone 5a

Table S3. Screenings for the asymmetric [3 + 2] annulation of 2-indolyl propiolate 1b with enone 5a[a]



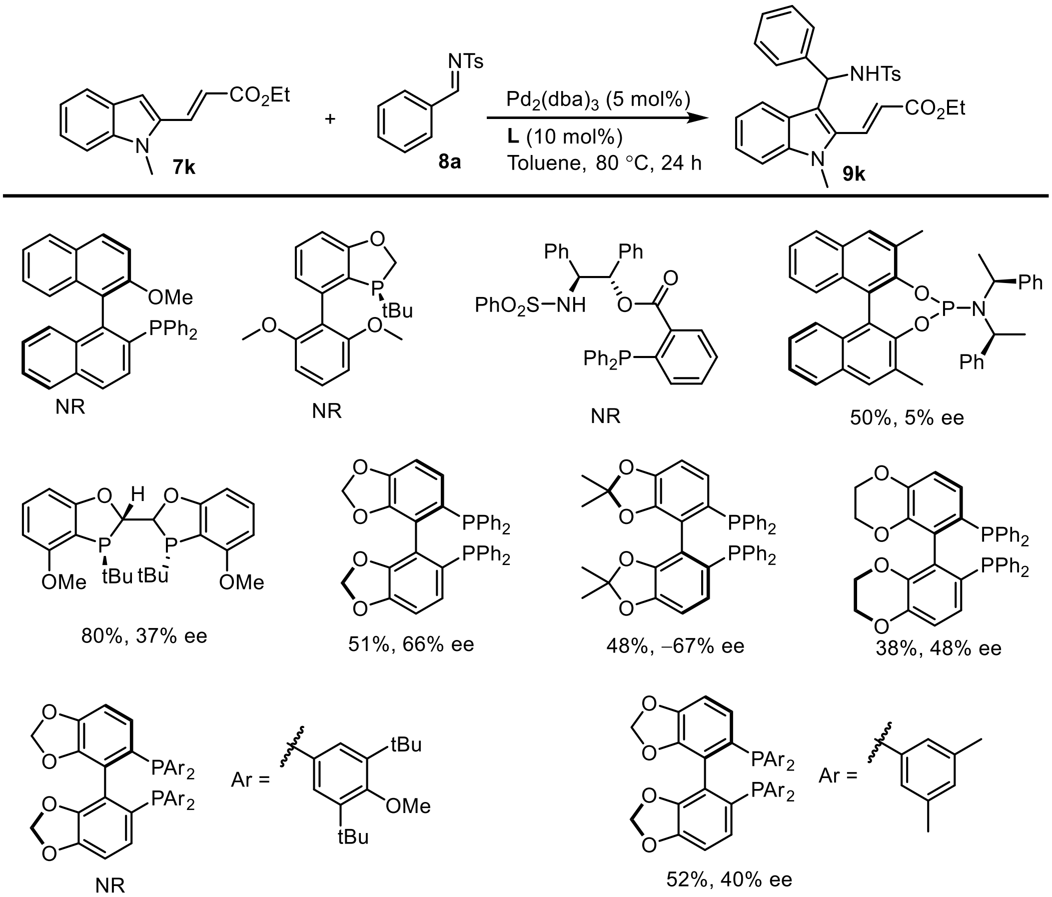
Entry	**A**	Solvent	*Temp* (°C)	Yield (%)[b]	ee (%)[c]
1[d]	/	MeCN	70	62	/
2	/	MeCN	70	60	42
3	/	Toluene	70	84	90
4	/	1,4-Dioxane	70	80	89
5	/	MeOH	70	99	3

6	/	DCE	70	65	69
7[e]	/	Toluene	70	81	90
8[e]	TBAB	Toluene	70	76	89

[a] Unless noted otherwise, reactions were carried out with **1b** (0.025 mmol), **5a** (0.03 mmol), $Pd_2(dba)_3$ (5 mol%), **L1** (10 mol%) and additive **A** (20 mol%) in solvent (0.125 mL) at 70 ℃ under Ar. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] With $Pd(PPh_3)_4$ (10 mol%). [e] On a 0.1 mmol scale.

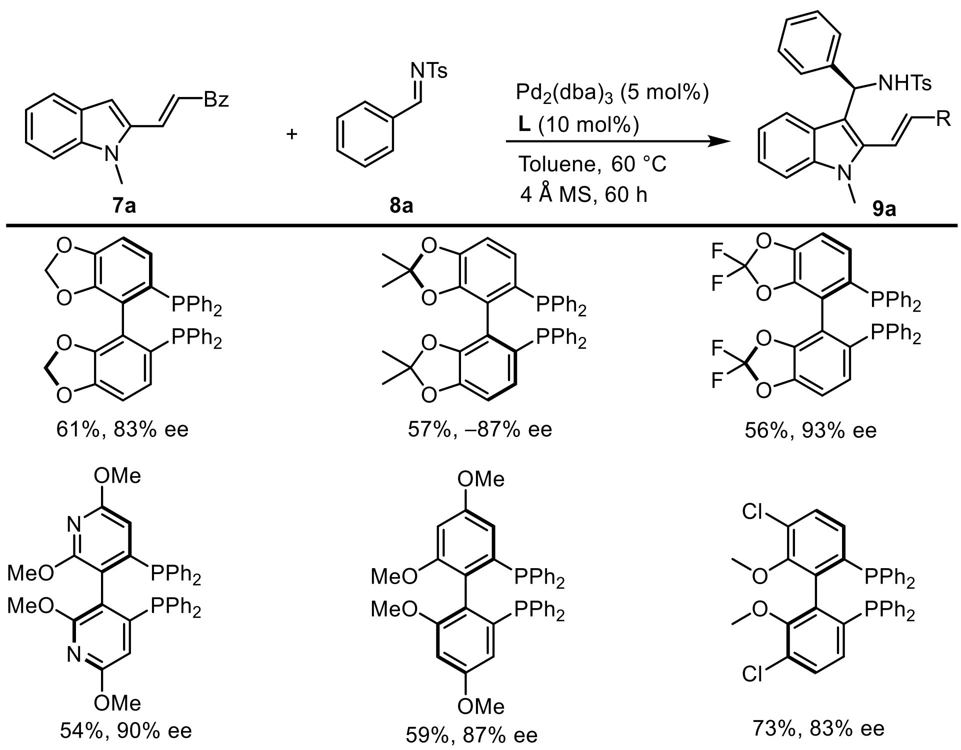
5. Optimisations for the asymmetric Friedel−Crafts reaction of 2-alkenyl indoles 7 with imine 8a

Table S4. Ligand screenings for the asymmetric Friedel−Crafts reaction of 2-alkenyl indole 7k with imine 8a[a]



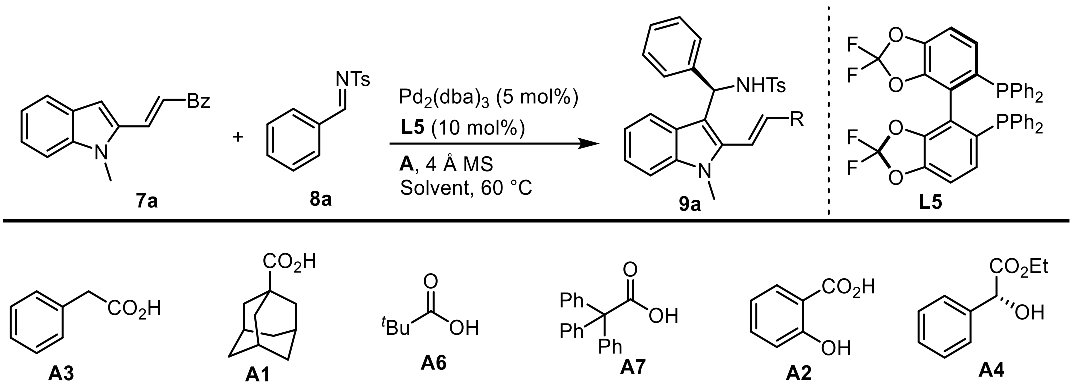
[a] Reactions were carried out with **7k** (0.025 mmol), **8a** (0.05 mmol), $Pd_2(dba)_3$ (5 mol%) and **L** (10 mol%) in toluene (0.25 mL) at 80 ℃ for 24 h under Ar.

Table S5. Ligand screenings for the asymmetric Friedel−Crafts reaction of 2-alkenyl indole 7a with imine 8a[a]



[a] Reactions were carried out with **7a** (0.025 mmol), **8a** (0.05 mmol), $Pd_2(dba)_3$ (5 mol%), **L** (10 mol%) and 4 Å MS (10.0 mg) in toluene (0.25 mL) at 60 ℃ for 60 h under Ar.

Table S6. Other condition screenings for the asymmetric Friedel−Crafts reaction of 2-alkenyl indole 7a with imine 8a[a]



Entry	**A** (mol%)	Solvent	*Temp* (°C)	Yield (%)[b]	ee (%)[c]
1	**A3** (30)	Toluene	60	92	70
2	**A1** (30)	Toluene	60	95	86
3	**A6** (30)	Toluene	60	57	87
4	**A7** (30)	Toluene	60	60	45
5	**A2** (30)	Toluene	60	93	0
6	**A4** (30)	Toluene	60	71	93
7	**A1** (10)	Toluene	60	90	85
8	**A1** (10)	Toluene	50	94	90
9	**A1** (10)	Toluene	40	62	92

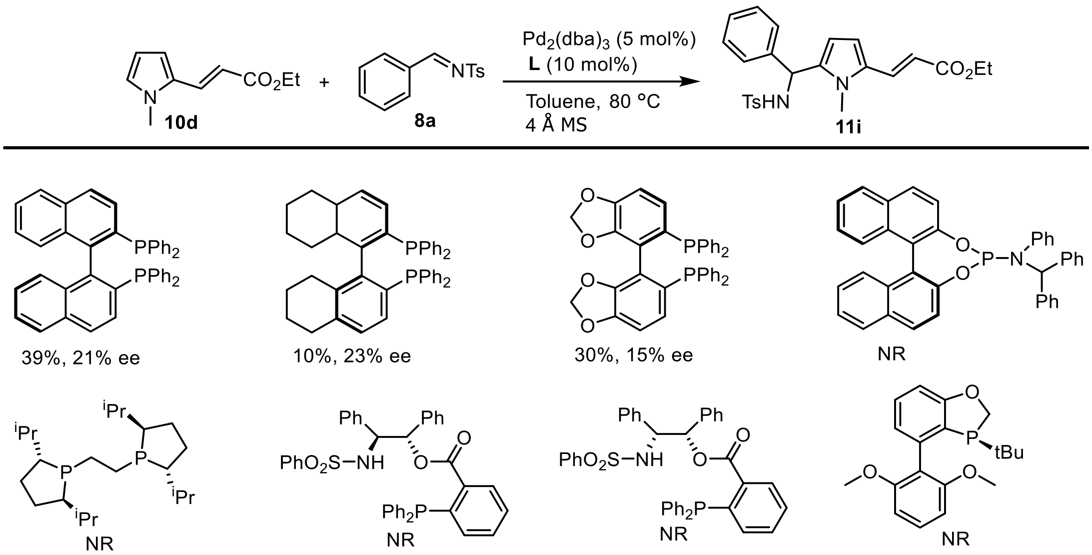
10	**A1** (5)	Toluene	50	90	92
11	**A1** (5)	THF	50	32	92
12	**A1** (5)	$CHCl_3$	50	65	87
13	**A1** (5)	Xylene	50	93	92
14	**A1** (5)	$PhCF_3$	50	97	67

[a] Unless noted otherwise, reactions were carried out with **7a** (0.025 mmol), **8a** (0.05 mmol), $Pd_2(dba)_3$ (5 mol%), **L5** (10 mol%), additive **A** (mol%) and 4 Å MS (10.0 mg) in solvent (0.25 mL) at 60 ℃ for 60 h under Ar. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase.

6. Optimisations for the asymmetric Friedel−Crafts reaction of 2-alkenyl pyrrole 10 with imine 8a

At first, substrate **10d** with an *N*-methyl group was employed for the Friedel−Crafts reaction with **8a** under palladium catalysis. After extensive screenings, only low conversions and poor enantioselectivity were attained. Therefore, some other substrates were tested as well (see Table S7).

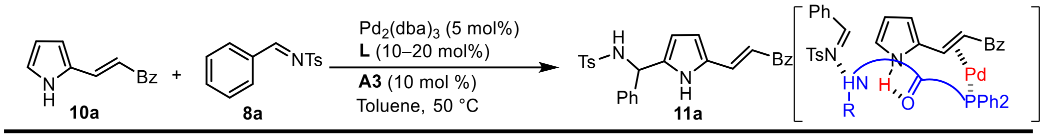
Table S7. Ligand screenings for the asymmetric Friedel−Crafts reaction of 2-alkenyl pyrrole 10d with imine 8a[a]

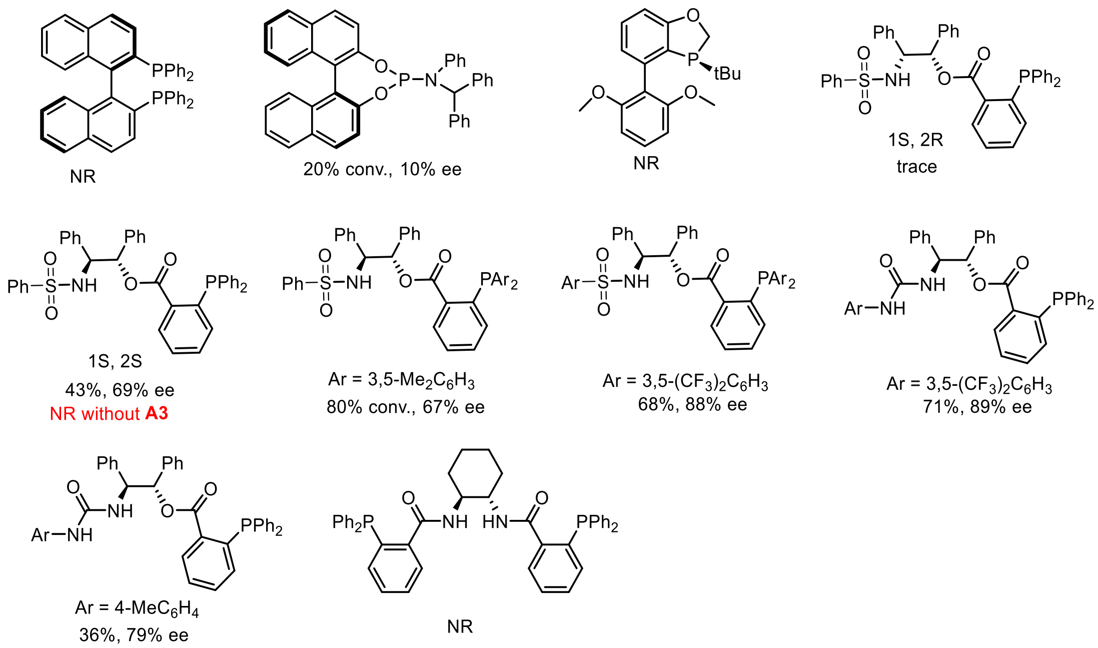


[a] Reactions were carried out with **10d** (0.05 mmol), **8a** (0.05 mmol), $Pd_2(dba)_3$ (5 mol%), **L** (10 mol%) and 4 Å MS (20.0 mg) in toluene (0.5 mL) at 80 ℃ for 60 h under Ar.

It was found that substrate **10a** with a free NH group underwent the desired reaction smoothly in combination with ligands derived from *trans*-1,2-diphenylaminoethanol. It was assumed that the NH of **10a** might interact with the ligands via H-bonding, and the NH of the ligands might also activate imine via H-bonding interaction.

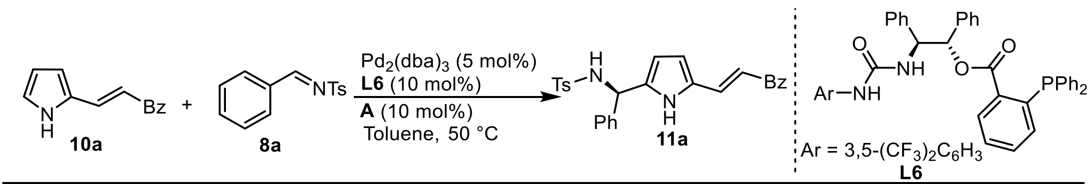
Table S8. Ligand screenings for the asymmetric Friedel−Crafts reaction of 2-alkenyl pyrrole 10a with imine 8a[a]

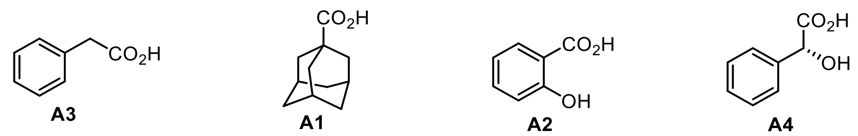




[a] Reactions were carried out with **10a** (0.03 mmol), **8a** (0.025 mmol), $Pd_2(dba)_3$ (5 mol%), **L** (20 mol%), **A3** (10 mol%) and 4 Å MS (10.0 mg) in toluene (0.25 mL) at 50 ℃ for 48 h under Ar.

Table S9. Other condition screenings for the asymmetric Friedel−Crafts reaction of 2-alkenyl pyrrole 10a with imine 8a[a]





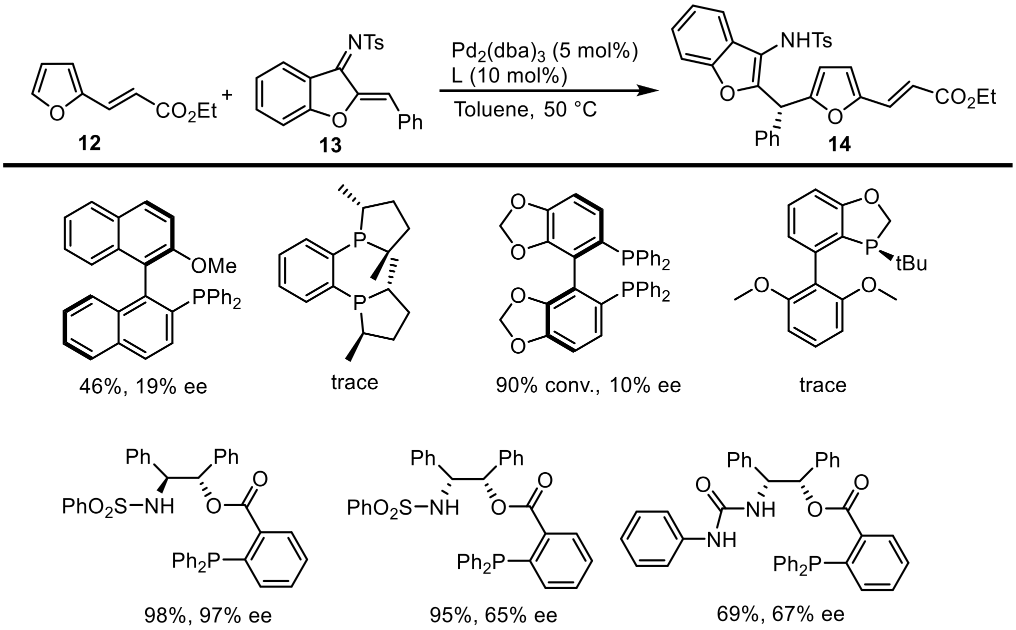
Entry	A	Pd/**L6**	Solvent	Yield (%)[b]	ee (%)[c]
1	**A3**	1/2	Toluene	71	89
2	**A1**	1/2	Toluene	89	88
3	**A2**	1/2	Toluene	82	91
4	**A4**	1/2	Toluene	80	89
5	**A2**	1/2	Xylene	80	81
6	**A2**	1/2	THF	69	85
7	**A2**	1/2	$CHCl_3$	53	78

8	**A2**	1/1	Toluene	82	98
9[d]	**A2**	1/1	Toluene	74	97

[a] Unless noted otherwise, reactions were carried out with **10a** (0.03mmol), **8a** (0.025 mmol), $Pd_2(dba)_3$ (5 mol%), **L6** (10 mol%), additive **A** (10 mol%) and 4 Å MS (10.0 mg) in solvent (0.25 mL) at 50 ℃ for 48 h under Ar. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Performed on a 0.1 mmol scale for 60 h.

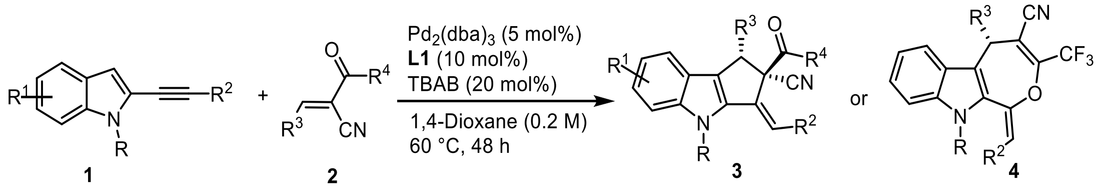
7. Optimisations for the asymmetric Friedel−Crafts reaction of 2-alkenyl furan 12 with 1-azadiene 13

Table S10. Ligand screenings for the asymmetric Friedel−Crafts reaction of 2-alkenyl furan 12 with 1-azadiene 13[a]

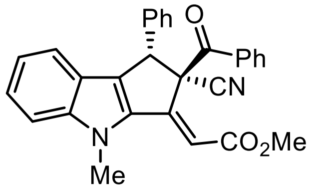


[a] Reactions were carried out with **12** (0.1 mmol), **13** (0.05 mmol), $Pd_2(dba)_3$ (5 mol%), and **L** (10 mol%) in toluene (0.5 mL) at 50 ℃ for 36 h under Ar.

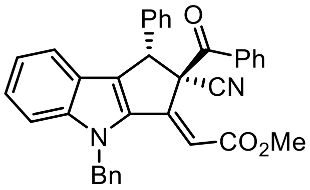
8. General procedure for the asymmetric [3 + 2] or [3 + 4] annulations of 2-indolyl propiolates 1 with enones 2



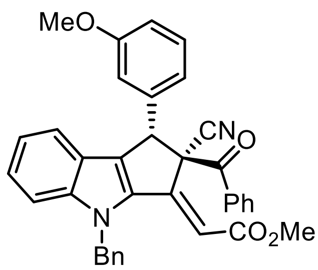
An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1** (0.10 mmol, 1.0 equiv), enone **2** (0.13 mmol, 1.3 equiv) or enone **2h** (0.15 mmol, 1.5 equiv), TBAB (6.4 mg, 0.020 mmol, 20 mol%), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and back-filled three times with argon, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then heated to 60 ℃ or 80 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give product **3** or **4**. Racemic **3** or **4** was obtained under the catalysis of $Pd(PPh_3)_4$ (10 mol%) in MeCN (0.5 mL).



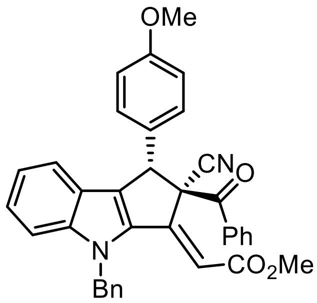
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-2-cyano-4-methyl-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3a): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1a** (22.7 mg, 0.106 mmol, 1.0 equiv), enone **2a** (30.3 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 30/10/1) to give product **3a**: 39.7 mg, as a yellow solid, 89% yield; >19:1 dr; >19:1 *E/Z*; mp 81–83 ℃; $[\alpha]^{25}_D$ = –26.4 (*c* = 0.25, in $CHCl_3$); 84% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 13.39 min, t (minor) = 22.12 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.95 (dd, *J* = 7.2 Hz, 1.3 Hz, 2H), 7.57 (dd, *J* = 7.0, 1.3 Hz, 1H), 7.45–7.33 (m, 7H), 7.22–7.17 (m, 2H), 7.08–6.98 (m, 2H), 6.43 (s, 1H), 5.00 (s, 1H), 4.01 (s, 3H), 3.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.9, 165.8, 147.3, 145.6, 140.2, 136.4, 134.4, 133.3, 130.9, 129.7, 129.2, 128.8, 128.6, 128.4, 126.0, 122.2, 121.0, 120.8, 117.0, 110.3, 108.4, 68.5, 53.7, 51.6, 31.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{22}N_2O_3Na^+$ 469.1523; Found 469.1519.



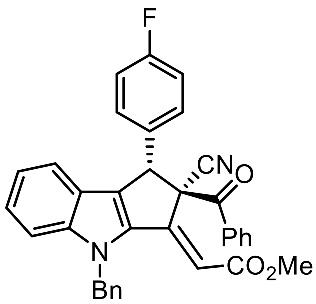
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3b): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2a** (30.3 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–8/1) to give product **3b**: 44.8 mg, as a yellow solid, 86% yield; >19:1 dr; >19:1 *E/Z*; mp 93–94 ℃; $[\alpha]^{25}_D$ = –10.2 (*c* = 0.25, in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 15.21 min, t (minor) = 24.49 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.4 Hz, 2H), 7.55 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.42–7.35 (m, 8H), 7.35–7.30 (m, 2H), 7.26–7.22 (m, 2H), 7.17 (d, *J* = 6.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.05 (ddd, *J* = 7.9, 6.7, 1.2 Hz, 1H), 6.16 (s, 1H), 5.59 (s, 2H), 5.06 (s, 1H), 3.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.7, 165.7, 146.6, 145.5, 140.1, 136.3, 136.2, 134.3, 133.3, 131.4, 129.6, 129.2, 129.0, 128.9, 128.7, 128.4, 128.0, 126.3, 125.9, 122.5, 121.3, 121.1, 116.8, 110.7, 109.0, 68.7, 53.5, 51.5, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{26}N_2O_3Na^+$ 545.1836; Found 545.1841.



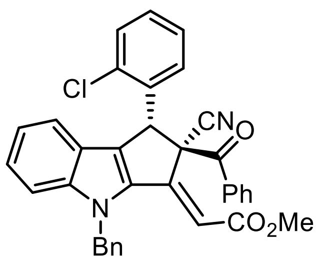
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(3-methoxy phenyl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3c): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2b** (34.2 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3c**: 49.1 mg, as a yellow solid, 89% yield; >19:1 dr; >19:1 *E/Z*; mp 100–102 ℃; $[\alpha]^{25}_{D}$ = –6.4 (*c* = 0.25, in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 15.08 min, t (minor) = 26.63 min]; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.94 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.60–7.52 (m, 1H), 7.43–7.35 (m, 5H), 7.34–7.25 (m, 3H), 7.20–7.13 (m, 3H), 7.06 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 1H), 6.94 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.87–6.79 (m, 1H), 6.78–6.73 (m, 1H), 6.15 (s, 1H), 5.59 (s, 2H), 5.02 (s, 1H), 3.72 (s, 3H), 3.55 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 189.8, 165.7, 159.6, 146.6, 145.5, 140.1, 137.9, 136.3, 134.4, 133.3, 131.4, 129.7, 129.2, 129.1, 128.4, 128.0, 126.3, 125.9, 122.5, 121.9, 121.3, 121.2, 116.9, 115.2, 114.5, 110.7, 109.0, 68.5, 55.2, 53.5, 51.6, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}N_2O_4Na^+$ 575.1942; Found 575.1940.



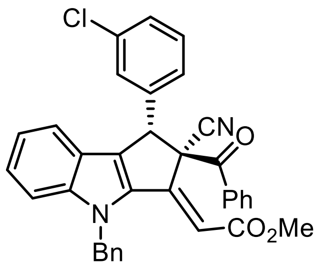
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(4-methoxyphenyl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3d): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2c** (39.4 mg, 0.149 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 80 ℃ for 96 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3d**: 34.9 mg, as a yellow solid, 63% yield; >19:1 dr; >19:1 *E/Z*; mp 108–109 ℃; $[\alpha]^{25}_{D}$ = +34.6 (*c* = 0.1, in $CHCl_3$); 89% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 20.11 min, t (minor) = 37.53 min]; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.2 Hz, 2H), 7.58–7.52 (m, 1H), 7.38 (dd, *J* = 8.2, 6.8 Hz, 7H), 7.19–7.12 (m, 5H), 7.06 (ddd, *J* = 8.0, 6.6, 1.2 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.14 (s, 1H), 5.59 (s, 2H), 5.02 (s, 1H), 3.83 (s, 3H), 3.55 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 189.8, 165.7, 159.9, 146.7, 145.5, 139.9, 136.3, 134.3, 133.3, 131.8, 130.8, 129.2, 129.1, 128.4, 128.2, 128.0, 126.3, 125.9, 122.5, 121.2, 121.1, 117.0, 114.1, 110.7, 109.0, 68.9, 55.2, 53.1, 51.5, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}N_2O_4Na^+$ 575.1942; Found 575.1950.



Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(4-fluoro phenyl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3e): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2d** (32.6 mg, 0130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3e**: 45.6 mg, as a yellow solid, 84% yield; >19:1 dr; >19:1 *E/Z*; mp 112–114 ℃; $[\alpha]^{25}_{D}$ = +36.6 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 11.19 min, t (minor) = 16.97 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.88 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.58–7.52 (m, 1H), 7.43–7.27 (m, 7H), 7.24–7.19 (m, 2H), 7.19–7.15 (m, 2H), 7.14–7.04 (m, 4H), 6.15 (s, 1H), 5.59 (s, 2H), 5.06 (s, 1H), 3.55 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.5, 165.7, 163.1 (d, *J* = 246.6 Hz), 146.3, 145.5, 140.0, 136.2, 134.2, 133.4, 132.1, 131.3 (d, *J* = 8.6 Hz), 130.9, 129.2, 128.9, 128.4, 128.1, 126.4, 125.9, 122.3, 121.4, 121.0, 116.8, 115.8 (d, *J* = 21.5 Hz), 110.8, 109.3, 68.8, 52.7, 51.6, 47.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) −112.64; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{25}FN_2O_3Na^+$ 563.1742; Found 563.1742.

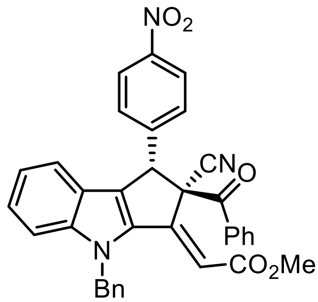


Methyl (*E*)-2-((1S,2*R*)-2-benzoyl-4-benzyl-1-(2-chlorophenyl)-2-cyano-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3f): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2e** (40.2 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 80 ℃ for 96 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3f**: 33.2 mg, as a yellow solid, 60% yield; >19:1 dr; >19:1 *E/Z*; mp 102–104 ℃; $[\alpha]^{25}_{D}$ = –22.2 (*c* = 0.25, in $CHCl_3$); 65% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 13.47 min, t (minor) = 21.42 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.87 (m, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.51–7.47 (m, 1H), 7.42–7.31 (m, 9H), 7.28 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.19–7.14 (m, 2H), 7.05 (dd, *J* = 3.1, 1.0 Hz, 2H), 6.18 (s, 1H), 5.80 (s, 1H), 5.60 (s, 2H), 3.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.3, 165.6, 146.5, 145.5, 140.0, 136.2, 134.6, 134.3, 134.2, 133.3, 131.9, 131.8, 130.0, 129.7, 129.3, 129.1, 128.3, 128.1, 127.2, 126.4, 125.9, 122.1, 121.4, 120.8, 117.0, 110.7, 109.4, 68.2, 51.6, 48.9, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{25}ClN_2O_3Na^+$ 579.1446 (^{35}Cl), 580.1480 (^{37}Cl); Found 579.1447 (^{35}Cl), 580.1471 (^{37}Cl).

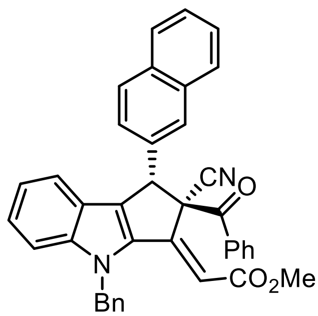


Methyl (*E*)-2-((1S,2*R*)-2-benzoyl-4-benzyl-1-(3-chlorophenyl)-2-cyano-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3g): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2f** (34.8 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3g**: 46.3 mg, as a yellow solid, 83% yield; >19:1 dr; >19:1 *E/Z*; mp 106–108 ℃; $[\alpha]^{25}_{D}$ = +26.0 (*c* = 0.1, in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 11.40 min, t (minor) = 16.89 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.61–7.53 (m, 1H), 7.42–7.36 (m, 6H), 7.36–7.30 (m, 3H), 7.21–7.15 (m, 2H), 7.17–7.09 (m, 3H), 7.08 (ddd, *J* = 8.0, 6.4, 1.2 Hz, 1H), 6.16 (s, 1H), 5.60 (s, 2H), 5.01 (s, 1H), 3.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.4, 165.7, 146.1, 145.5, 140.2, 138.5, 136.1, 134.5, 134.1, 133.5, 130.4, 130.0, 129.7, 129.3, 129.2, 129.0, 128.5, 128.1, 127.8, 126.4, 125.9, 122.3, 121.5, 120.9, 116.7, 110.8, 109.3, 68.4, 52.9, 51.6, 47.9; **HRMS**

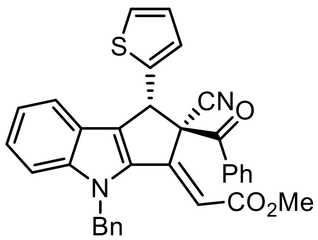
(ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{25}ClN_2O_3Na^+$ 579.1446 (^{35}Cl), 580.1480 (^{37}Cl); Found 579.1449 (^{35}Cl), 580.1475 (^{37}Cl).



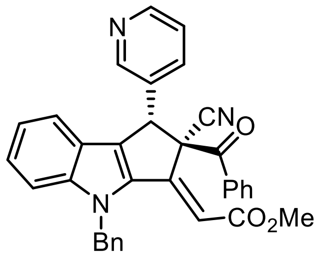
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(4-nitrophenyl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3h): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2g** (36.2 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1–4/1) to give product **3h**: 40.2 mg, as a yellow solid, 71% yield; 10:1 dr; >19:1 *E/Z*; mp 136–138 ℃; $[\alpha]^{25}_D$ = +16.1 (*c* = 0.1, in $CHCl_3$); 89% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 21.73 min, t (minor) = 35.46 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.25 (d, *J* = 8.8 Hz, 2H), 7.89–7.83 (m, 2H), 7.60–7.55 (m, 1H), 7.43–7.35 (m, 9H), 7.17 (d, *J* = 6.9 Hz, 2H), 7.12–7.07 (m, 2H), 6.18 (s, 1H), 5.64 (d, *J* = 17.6 Hz, 1H), 5.59 (d, *J* = 17.6 Hz, 1H), 5.17 (s, 1H), 3.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.1, 165.7, 148.2, 145.6, 145.5, 143.7, 140.3, 136.0, 133.9, 133.6, 130.5, 129.3, 129.2, 128.8, 128.5, 128.2, 126.7, 125.8, 124.0, 122.1, 121.8, 120.7, 116.4, 111.0, 109.8, 68.5, 52.6, 51.7, 48.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{25}N_3O_5Na^+$ 590.1687; Found 590.1688.



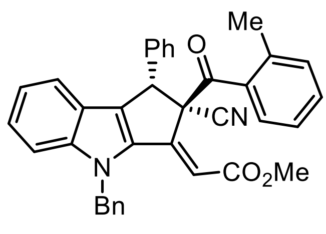
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(naphthalen-2-yl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3i): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2h** (36.8 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8/1–4/1) to give product **3i**: 56.1 mg, as a white solid, 98% yield; >19:1 dr; >19:1 *E/Z*; mp 119–121 ℃; $[\alpha]^{25}_{D}$ = +62.0 (*c* = 0.1, in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 13.09 min, t (minor) = 22.11 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.96 (d, *J* = 7.0 Hz, 2H), 7.85 (dd, *J* = 9.0, 3.6 Hz, 2H), 7.79–7.73 (m, 2H), 7.59–7.54 (m, 1H), 7.52–7.47 (m, 2H), 7.43–7.35 (m, 5H), 7.37–7.27 (m, 3H), 7.20 (dd, *J* = 7.0, 1.8 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.99 (ddd, *J* = 8.0, 6.7, 1.0 Hz, 1H), 6.20 (s, 1H), 5.61 (s, 2H), 5.22 (s, 1H), 3.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.7, 165.7, 146.6, 145.5, 140.1, 136.3, 134.3, 133.9, 133.5, 133.3, 133.2, 131.5, 129.24, 129.15, 128.6, 128.4, 128.1, 128.0, 127.8, 126.8, 126.5, 126.30, 126.28, 125.9, 122.5, 121.3, 121.1, 117.0, 110.7, 109.1, 68.4, 53.7, 51.6, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{39}H_{28}N_2O_3Na^+$ 595.1993; Found 595.2001.



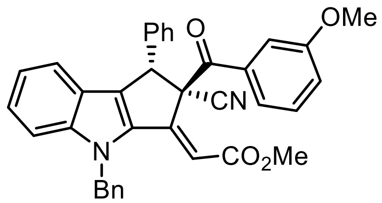
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(thiophen-2-yl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3j): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2i** (31.1 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3j**: 46.7 mg, as a yellow solid, 88% yield; >19:1 dr; >19:1 *E/Z*; mp 87–89 ℃; $[\alpha]^{25}_{D}$ = –4.8 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 15.46 min, t (minor) = 25.33 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.95–7.89 (m, 2H), 7.58–7.51 (m, 1H), 7.42–7.35 (m, 8H), 7.34–7.31 (m, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.19–7.15 (m, 2H), 7.12 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.05 (ddd, *J* = 7.9, 6.6, 1.2 Hz, 1H), 6.16 (s, 1H), 5.59 (s, 2H), 5.06 (s, 1H), 3.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.7, 165.7, 146.6, 145.5, 140.1, 136.33, 136.25, 134.2, 133.3, 131.4, 129.6, 129.2, 129.0, 128.9, 128.7, 128.4, 128.0, 126.3, 125.9, 122.5, 121.3, 121.1, 116.8, 110.7, 109.0, 68.7, 53.5, 51.5, 47.9; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{25}N_2O_3S^+$ 529.1581; Found 529.1590.



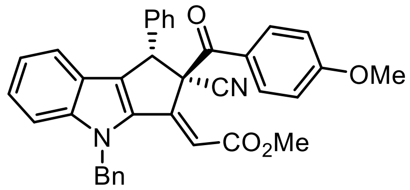
Methyl (*E*)-2-((1*R*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(pyridin-3-yl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3k): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2j** (30.4 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 72 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1–3/1) to give product **3k**: 34.2 mg, as a yellow solid, 65% yield; >19:1 dr; >19:1 *E/Z*; mp 105–107 ℃; $[\alpha]^{25}_{D}$ = +2.4 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 24.50 min, t (minor) = 37.80 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.67 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.50 (d, *J* = 2.3 Hz, 1H), 7.90 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.60–7.52 (m, 2H), 7.44–7.30 (m, 8H), 7.20–7.14 (m, 2H), 7.10–7.06 (m, 2H), 6.18 (s, 1H), 5.61 (s, 2H), 5.07 (s, 1H), 3.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.2, 165.7, 150.5, 150.3, 146.0, 145.5, 140.2, 137.0, 136.1, 134.1, 133.5, 132.5, 129.9, 129.3, 128.9, 128.5, 128.1, 126.5, 125.8, 123.7, 122.1, 121.6, 120.7, 116.8, 110.9, 109.5, 68.4, 51.7, 50.8, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{25}N_3O_3Na^+$ 546.1789; Found 546.1780.



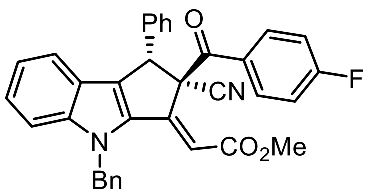
Methyl (*E*)-2-((1*S*,2*R*)-4-benzyl-2-cyano-2-(2-methylbenzoyl)-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3l): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2k** (32.1 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3l**: 43.8 mg, as a yellow solid, 82% yield; >19:1 dr; >19:1 *E/Z*; mp 107–109 ℃; $[\alpha]^{25}_{D}$ = +12.6 (*c* = 0.25, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 11.42 min, t (minor) = 14.81 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.69–7.63 (m, 1H), 7.42–7.28 (m, 10H), 7.26 (d, *J* = 2.1 Hz, 2H), 7.19–7.15 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.10–7.02 (m, 2H), 6.13 (s, 1H), 5.57 (s, 2H), 5.11 (s, 1H), 3.57 (s, 3H), 2.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 191.6, 166.0, 147.1, 145.5, 140.6, 140.3, 136.8, 136.2, 133.5, 132.4, 131.9, 131.8, 129.7, 129.2, 128.8, 128.7, 128.2, 128.0, 126.2, 125.9, 124.6, 122.5, 121.2, 121.1, 116.9, 110.7, 108.5, 69.3, 53.9, 51.7, 47.9, 21.1; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}N_2O_3Na^+$ 559.1993; Found 559.1992.



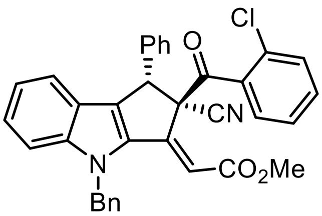
Methyl (*E*)-2-((1*S*,2*R*)-4-benzyl-2-cyano-2-(3-methoxybenzoyl)-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3m): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2l** (34.2 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3m**: 47.5 mg, as a yellow solid, 86% yield; >19:1 dr; >19:1 *E/Z*; mp 93–95 ℃; $[\alpha]^{25}_{D}$ = +8.0 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 13.85 min, t (minor) = 16.79 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.45–7.37 (m, 2H), 7.35–7.27 (m, 6H), 7.25 (dt, *J* = 7.1, 1.9 Hz, 2H), 7.20–7.16 (m, 3H), 7.13–7.08 (m, 2H), 7.03 (dd, *J* = 8.3, 2.0 Hz, 2H), 6.96 (ddd, *J* = 8.0, 6.6, 1.2 Hz, 1H), 6.09 (s, 1H), 5.51 (s, 2H), 4.97 (s, 1H), 3.65 (s, 3H), 3.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.4, 165.8, 159.5, 146.7, 145.5, 140.0, 136.4, 136.2, 135.4, 131.5, 129.7, 129.3, 129.2, 128.9, 128.7, 128.0, 126.3, 125.9, 122.4, 121.4, 121.3, 121.1, 120.3, 116.9, 113.5, 110.7, 108.9, 68.6, 55.3, 53.6, 51.6, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}N_2O_4Na^+$ 575.1942; Found 575.1941.



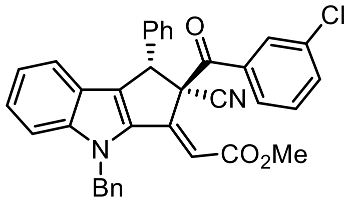
Methyl (*E*)-2-((1*S*,2*R*)-4-benzyl-2-cyano-2-(4-methoxybenzoyl)-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3n): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2m** (34.2 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3n**: 48.8 mg, as a yellow solid, 88% yield; >19:1 dr; >19:1 *E/Z*; mp 162–163 ℃; $[\alpha]^{25}_{D}$ = +6.7 (*c* = 0.25, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 27.80 min, t (minor) = 30.85 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) δ 7.93 (d, *J* = 8.9 Hz, 2H), 7.42–7.35 (m, 6H), 7.35–7.29 (m, 2H), 7.25–7.23 (m, 2H), 7.21–7.16 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.04 (ddd, *J* = 7.9, 6.7, 1.1 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.17 (s, 1H), 5.59 (s, 2H), 5.02 (s, 1H), 3.85 (s, 3H), 3.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.2, 165.6, 163.6, 146.7, 145.5, 140.1, 136.5, 136.3, 131.6, 131.5, 129.7, 129.2, 128.8, 128.7, 128.0, 126.8, 126.2, 125.9, 122.5, 121.2, 121.1, 117.2, 113.7, 110.7, 109.1, 68.4, 55.5, 53.6, 51.5, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}N_2O_4Na^+$ 575.1942; Found 575.1944.



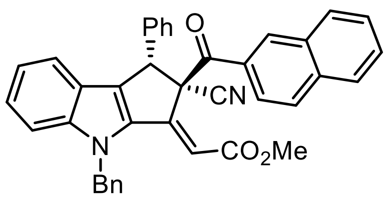
Methyl (*E*)-2-((1*S*,2*R*)-4-benzyl-2-cyano-2-(4-fluorobenzoyl)-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3o): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2n** (32.6 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3o**: 50.3 mg, as a yellow solid, 93% yield; >19:1 dr; >19:1 *E/Z*; mp 107–109 ℃; $[\alpha]^{25}_{D}$ = –26.0 (*c* = 0.1, in $CHCl_3$); 88% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 12.54 min, t (minor) = 23.05 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.99–7.93 (m, 2H), 7.43–7.36 (m, 6H), 7.36–7.30 (m, 2H), 7.23 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.19–7.15 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.08–7.02 (m, 3H), 6.17 (s, 1H), 5.59 (s, 2H), 5.00 (s, 1H), 3.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.3, 165.8, 165.7 (d, *J* = 254.5 Hz), 146.6, 145.6, 140.0, 136.2, 131.9 (d, *J* = 9.2 Hz), 131.5, 130.7 (d, *J* = 3.0 Hz), 129.6, 129.3, 129.0, 128.7, 128.1, 126.4, 125.9, 122.4, 121.3, 121.1, 116.8, 115.7, 115.5, 110.7, 108.9, 68.3, 53.6, 51.6, 47.9; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) –104.17; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{25}FN_2O_3Na^+$ 563.1742; Found 563.1752.



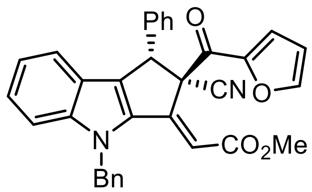
Methyl (*E*)-2-((1*S*,2*R*)-4-benzyl-2-(2-chlorobenzoyl)-2-cyano-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3p): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2o** (34.8 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3p**: 49.7 mg, as a yellow solid, 89% yield; >19:1 dr; >19:1 *E/Z*; mp 99–101 ℃; $[\alpha]^{25}_{D}$ = +140.8 (*c* = 0.25, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 9.82 min, t (minor) = 15.11 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.33 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.58 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.45 (td, *J* = 7.7, 1.6 Hz, 1H), 7.38 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.35–7.25 (m, 7H), 7.22–7.16 (m, 2H), 7.12 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.07–7.01 (m, 3H), 6.23 (s, 1H), 5.57 (s, 2H), 5.27 (s, 1H), 3.68 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.7, 166.2, 145.9, 145.5, 140.3, 137.0, 136.2, 135.3, 132.3, 131.3, 131.0, 130.8, 129.2, 129.1, 128.7, 128.6, 128.0, 126.6, 126.32, 126.25, 125.9, 122.5, 121.2, 121.1, 116.4, 110.7, 108.4, 69.5, 52.0, 51.8, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{25}ClN_2O_3Na^+$ 579.1446 (^{35}Cl), 580.1480 (^{37}Cl); Found 579.1447 (^{35}Cl), 580.1478 (^{37}Cl).



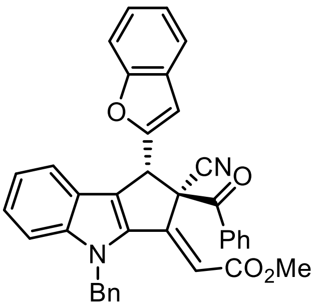
Methyl (*E*)-2-((1*S*,2*R*)-4-benzyl-2-(3-chlorobenzoyl)-2-cyano-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3q): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2p** (34.8 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 36 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3q**: 46.3 mg, as a yellow solid, 83% yield; >19:1 dr; >19:1 *E/Z*; mp 98–99 ℃; $[\alpha]^{25}_{D}$ = –6.4 (*c* = 0.25, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 13.81 min, t (minor) = 32.35 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 1.9 Hz, 1H), 7.77 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.55–7.50 (m, 1H), 7.43–7.27 (m, 10H), 7.22 (s, 1H), 7.20–7.15 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.05 (ddd, *J* = 8.0, 6.4, 1.3 Hz, 1H), 6.15 (s, 1H), 5.59 (s, 2H), 5.02 (s, 1H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.5, 165.9, 146.4, 145.6, 139.9, 136.2, 136.1, 135.9, 134.7, 133.2, 131.4, 129.63, 129.58, 129.3, 129.2, 129.0, 128.8, 128.0, 126.9, 126.4, 125.8, 122.4, 121.3, 121.1, 116.6, 110.7, 108.8, 68.5, 53.6, 51.7, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{25}ClN_2O_3Na^+$ 579.1446 (^{35}Cl), 580.1480 (^{37}Cl); Found 579.1452 (^{35}Cl), 580.1483 (^{37}Cl).



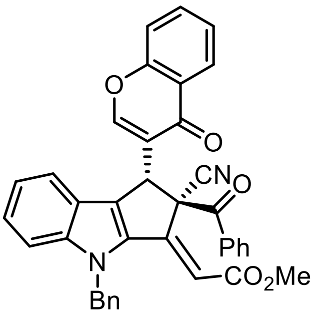
Methyl (*E*)-2-((1*S*,2*R*)-2-(2-naphthoyl)-4-benzyl-2-cyano-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3r): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2q** (36.8 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3r**: 53.8 mg, as a yellow solid, 94% yield; >19:1 dr; >19:1 *E/Z*; mp 85–87 ℃; $[\alpha]^{25}_{D}$ = +64.0 (*c* = 0.1, in $CHCl_3$); 86% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 11.81 min, t (minor) = 14.74 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.48 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 2H), 7.88 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.60 (ddd, *J* = 8.5, 6.8, 1.6 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.42–7.29 (m, 9H), 7.22–7.17 (m, 2H), 7.16–7.10 (m, 3H), 7.06 (ddd, *J* = 7.9, 6.5, 1.3 Hz, 1H), 6.17 (s, 1H), 5.60 (s, 2H), 5.22 (s, 1H), 3.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 191.6, 166.0, 147.0, 145.5, 140.3, 136.8, 136.3, 134.2, 133.2, 131.70, 131.66, 130.8, 129.6, 129.3, 128.8, 128.6, 128.5, 128.0, 127.9, 127.6, 126.5, 126.3, 126.2, 125.9, 123.4, 122.5, 121.3, 121.2, 116.9, 110.7, 108.6, 69.8, 54.0, 51.7, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{39}H_{28}N_2O_3Na^+$ 595.1993; Found 595.1998.



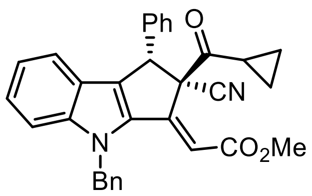
Methyl (*E*)-2-((1*S*,2*R*)-4-benzyl-2-cyano-2-(furan-2-carbonyl)-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3s): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2r** (29.0 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **3s**: 46.1 mg, as a yellow solid, 90% yield; >19:1 dr; >19:1 *E/Z*; mp 82–84 ℃; $[\alpha]^{25}_{D}$ = –60.6 (*c* = 0.1, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 17.84 min, t (minor) = 25.72 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, *J* = 1.8 Hz, 1H), 7.42–7.34 (m, 7H), 7.34–7.29 (m, 2H), 7.24–7.15 (m, 4H), 7.09 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.03 (ddd, *J* = 8.0, 6.6, 1.2 Hz, 1H), 6.55 (dd, *J* = 3.7, 1.7 Hz, 1H), 6.20 (s, 1H), 5.60 (s, 2H), 4.94 (s, 1H), 3.60 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 178.0, 165.8, 149.2, 147.5, 145.50, 145.47, 140.2, 136.4, 136.3, 131.3, 129.6, 129.2, 128.9, 128.6, 128.5, 128.0, 126.2, 126.0, 122.4, 121.2, 121.1, 120.8, 116.5, 112.5, 110.7, 109.0, 67.3, 54.0, 51.7, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{24}N_2O_4Na^+$ 535.1629; Found 535.1627.



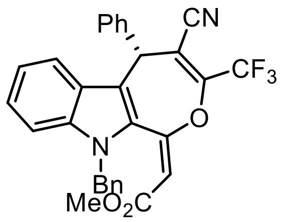
Methyl (*E*)-2-((1*S*,2*R*)-1-(benzofuran-2-yl)-2-benzoyl-4-benzyl-2-cyano-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3t): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2s** (35.5 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3t**: 43.9 mg, as a yellow solid, 78% yield; >19:1 dr; >19:1 *E/Z*; mp 109–110 ℃; $[\alpha]^{25}_{D}$ = +18.4 (*c* = 0.25, in $CHCl_3$); 98% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 13.48 min, t (minor) = 24.29 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.11–8.06 (m, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.50–7.45 (m, 1H), 7.44–7.36 (m, 3H), 7.35–7.20 (m, 7H), 7.17–7.09 (m, 3H), 7.04 (ddd, *J* = 8.1, 6.7, 1.4 Hz, 1H), 6.65 (s, 1H), 6.12 (s, 1H), 5.52 (s, 2H), 5.22 (s, 1H), 3.49 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.6, 165.7, 155.5, 152.8, 145.9, 145.4, 140.2, 136.1, 134.4, 133.4, 129.3, 128.5, 128.1, 127.93, 127.87, 126.3, 125.9, 124.8, 123.0, 122.4, 121.5, 121.4, 120.9, 116.6, 111.5, 110.8, 109.2, 107.5, 66.6, 51.7, 48.0, 47.7; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{26}N_2O_4Na^+$ 585.1785; Found 585.1792.



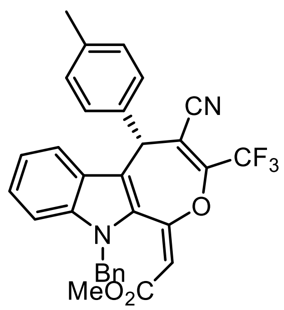
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(4-oxo-4H-chromen-3-yl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3u): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2t** (39.1 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **3u**: 51.5 mg, as a yellow solid, 87% yield; >19:1 dr; >19:1 *E/Z*; mp 99–100 ℃; $[\alpha]^{25}_{D}$ = –96.0 (*c* = 0.25, in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (minor) = 21.50 min, t (major) = 44.83 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.31–8.20 (m, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.81 (s, 1H), 7.70 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.56–7.48 (m, 1H), 7.49–7.43 (m, 2H), 7.43–7.29 (m, 8H), 7.21–7.07 (m, 3H), 6.16 (s, 1H), 5.79 (s, 1H), 5.60 (d, *J* = 2.4 Hz, 2H), 3.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.7, 176.0, 165.4, 156.8, 156.4, 145.9, 145.5, 140.3, 136.1, 134.0, 134.0, 133.2, 129.3, 129.2, 129.0, 128.2, 128.1, 126.5, 126.4, 125.8, 125.6, 123.7, 121.8, 121.6, 121.3, 120.7, 118.3, 117.4, 111.0, 110.0, 69.2, 51.4, 47.9, 42.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{38}H_{26}N_2O_5Na^+$ 613.1734; Found 613.1739.



Methyl (*E*)-2-((1*S*,2*R*)-4-benzyl-2-cyano-2-(cyclopropanecarbonyl)-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate **(3v)**: An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2u** (29.6 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min. then at 80 ℃ for 72 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **3v**: 39.4 mg, as a yellow solid, 81% yield; >19:1 dr; >19:1 *E/Z*; mp 86–87 ℃; $[\alpha]^{25}_{D}$ = –8.0 (*c* = 0.25, in $CHCl_3$); 85% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 9.74 min, t (minor) = 13.65 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.44–7.37 (m, 3H), 7.37–7.33 (m, 2H), 7.33–7.27 (m, 5H), 7.17–7.10 (m, 3H), 7.04 (ddd, *J* = 8.0, 6.2, 1.7 Hz, 1H), 6.15 (s, 1H), 5.54 (s, 2H), 4.88 (s, 1H), 3.67 (s, 3H), 2.46 (tt, *J* = 7.7, 4.5 Hz, 1H), 1.35 (ddt, *J* = 9.1, 4.4, 2.3 Hz, 1H), 1.30–1.23 (m, 1H), 1.21–1.15 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 199.8, 165.8, 145.4, 145.1, 140.4, 137.0, 136.2, 131.4, 129.2, 129.1, 128.80, 128.77, 127.9, 126.1, 125.9, 122.4, 121.2, 121.0, 116.7, 110.7, 108.7, 69.9, 53.9, 51.6, 47.9, 18.4, 13.9, 12.4; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{26}N_2O_3Na^+$ 509.1836; Found 509.1830.

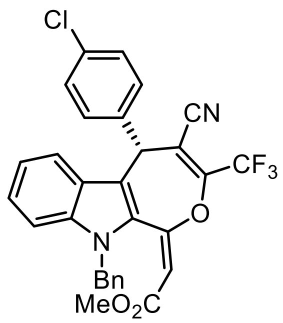


Methyl (*S*,*E*)-2-(10-benzyl-4-cyano-5-phenyl-3-(trifluoromethyl)-5,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-ylidene)acetate (4a): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2v** (33.8 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 24 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give product **4a**: 28.6 mg, as a yellow oil, 56% yield; >19:1 *E/Z*; $[\alpha]^{25}_D$ = –48.0 (*c* = 0.25, in $CHCl_3$); 87% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 10/90, flow rate: 1.0 mL/min, 254 nm, t (minor) = 5.52 min, t (major) = 6.47 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.71 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.41–7.36 (m, 1H), 7.33 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H), 7.26–7.19 (m, 9H), 6.90–6.85 (m, 2H), 5.85 (s, 1H), 5.39–5.33 (m, 2H), 5.17 (d, *J* = 16.5 Hz, 1H), 3.62 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 164.2, 154.6, 149.3 (q, *J* = 35.0 Hz), 138.0, 137.5, 136.7, 128.8, 128.7, 127.8, 127.7, 126.8, 126.3, 125.2, 125.0, 124.4, 121.3, 120.5, 118.9, 118.3 (q, *J* = 275.8 Hz), 115.6, 111.4, 109.2, 103.0, 51.8, 48.0, 41.5; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) −67.79; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{21}F_3N_2O_3Na^+$ 537.1397; Found 537.1395.

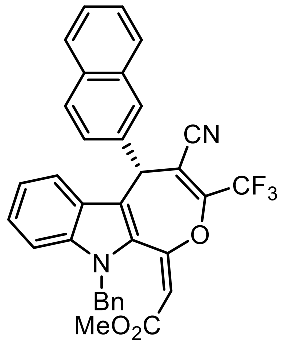


Methyl (*S*,*E*)-2-(10-benzyl-4-cyano-5-(*p*-tolyl)-3-(trifluoromethyl)-5,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-ylidene)acetate (4b): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2w** (35.8 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 24 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give product **4b**: 30.4 mg, as a yellow oil, 57% yield; >19:1 *E/Z*; $[\alpha]^{25}_D$ = –10.9 (*c* = 1.52, in $CHCl_3$); 92% ee, determined by HPLC analysis

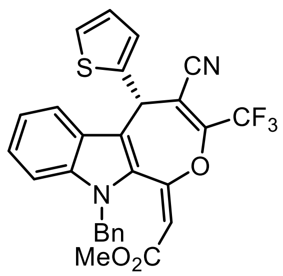
[Chiralpak column ID, *i*PrOH/*n*Hexane = 10/90, flow rate: 1.0 mL/min, 254 nm, t (minor) = 5.89 min, t (major) = 8.07 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 8.1 Hz, 1H), 7.41–7.29 (m, 2H), 7.24–7.18 (m, 4H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.91–6.82 (m, 2H), 5.87 (s, 1H), 5.36 (d, *J* = 16.5 Hz, 1H), 5.31 (s, 1H), 5.17 (d, *J* = 16.5 Hz, 1H), 3.64 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 164.3, 154.7, 149.2 (q, *J* = 35.4 Hz), 137.6, 137.5, 136.8, 135.0, 129.4, 128.8, 127.8, 126.8, 126.3, 125.3, 125.0, 124.5, 121.3, 120.6, 119.0, 118.3 (q, *J* = 275.7 Hz), 115.7, 111.4, 109.1, 103.4, 51.9, 48.1, 41.4, 21.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) −67.81; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{23}F_3N_2O_3Na^+$ 551.1553; Found 551.1559.



Methyl (*S*,*E*)-2-(10-benzyl-5-(4-chlorophenyl)-4-cyano-3-(trifluoromethyl)-5,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-ylidene)acetate (4c): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2x** (38.8 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 24 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give product **4c**: 23.3 mg, as a yellow oil, 43% yield; >19:1 *E/Z*; $[\alpha]^{25}_{D}$ = –14.9 (*c* = 1.16, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 10/90, flow rate: 1.0 mL/min, 254 nm, t (minor) = 5.43 min, t (major) = 7.18 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.70 (d, *J* = 8.1 Hz, 1H), 7.39 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.34 (ddd, *J* = 8.4, 6.7, 1.1 Hz, 1H), 7.25–7.15 (m, 8H), 6.90–6.83 (m, 2H), 5.89 (s, 1H), 5.36 (d, *J* = 16.4 Hz, 1H), 5.30 (s, 1H), 5.15 (d, *J* = 16.4 Hz, 1H), 3.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 164.2, 154.3, 149.6 (q, *J* = 35.6 Hz), 137.6, 136.59, 136.55, 133.7, 128.9, 128.8, 128.3, 127.8, 126.3, 125.4, 124.8, 124.4, 121.4, 119.8, 118.8, 118.2 (q, *J* = 275.9 Hz), 115.5, 111.5, 109.5, 102.5, 51.9, 48.1, 41.0; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) −67.83; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{20}ClF_3N_2O_3Na^+$ 571.1007 (^{35}Cl), 572.1041 (^{37}Cl); Found 571.1016 (^{35}Cl), 572.1046 (^{37}Cl)

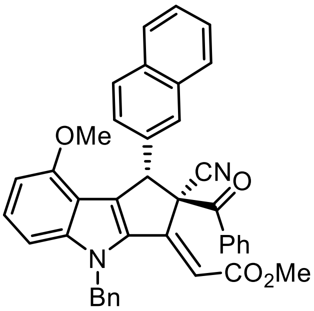


Methyl (*S,E*)-2-(10-benzyl-4-cyano-5-(naphthalen-2-yl)-3-(trifluoromethyl)-5,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-ylidene)acetate (4d): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2y** (41.2 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then stirred at 60 ℃ for 24 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give product **4d**: 31.0 mg, as a yellow oil, 55% yield; >19:1 *E/Z*; $[\alpha]^{25}_{D}$ = +91.3 (*c* = 1.38, in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 10/90, flow rate: 1.0 mL/min, 254 nm, t (minor) = 6.83 min, t (major) = 10.43 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83–7.71 (m, 3H), 7.63 (d, *J* = 6.7 Hz, 2H), 7.52–7.40 (m, 4H), 7.36 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.28–7.18 (m, 4H), 6.94–6.83 (m, 2H), 5.78 (s, 1H), 5.51 (s, 1H), 5.40 (d, *J* = 16.5 Hz, 1H), 5.20 (d, *J* = 16.5 Hz, 1H), 3.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 164.3, 154.8, 149.4 (q, *J* = 35.3 Hz), 137.7, 136.7, 135.2, 133.1, 132.6, 128.84, 128.77, 128.0, 127.8, 127.5, 126.4, 126.33, 126.32, 125.7, 125.3, 125.0, 124.9, 124.6, 121.4, 120.0, 119.0, 118.3 (q, *J* = 275.7 Hz), 115.8, 111.5, 109.0, 103.2, 51.8, 48.0, 41.6; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) –67.81; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{23}F_3N_2O_3Na^+$ 587.1553; Found 587.1562.

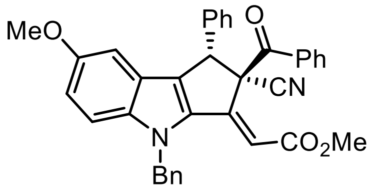


Methyl (*S,E*)-2-(10-benzyl-4-cyano-5-(thiophen-2-yl)-3-(trifluoromethyl)-5,10-dihydro-1*H*-oxepino[3,4-*b*]indol-1-ylidene)acetate (4e): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **2z** (34.6 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 30 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give product **4e**: 25.5 mg, as a yellow oil, 49% yield; >19:1 *E/Z*;

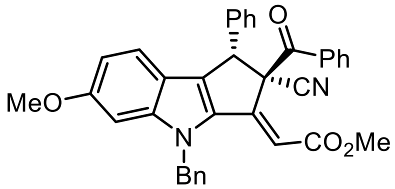
$[\alpha]^{25}_{D}$ = 42.6 (*c* = 1.27, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 10/90, flow rate: 1.0 mL/min, 254 nm, t (minor) = 6.88 min, t (major) = 8.63 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.62 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.30 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.27–7.21 (m, 1H), 7.17–7.10 (m, 5H), 6.86–6.70 (m, 4H), 5.92 (s, 1H), 5.40 (d, *J* = 1.5 Hz, 1H), 5.29 (d, *J* = 16.5 Hz, 1H), 5.11 (d, *J* = 16.4 Hz, 1H), 3.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 164.2, 154.3, 149.8 (q, *J* = 35.4 Hz), 141.7, 137.4, 136.7, 128.9, 127.8, 126.9, 126.4, 126.0, 125.7, 125.3, 124.7, 124.4, 121.4, 119.8, 118.9, 118.3 (q, *J* = 276.0 Hz), 115.2, 111.5, 110.2, 101.9, 52.0, 48.2, 38.1; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) –67.86; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{19}F_3N_2O_3SNa^+$ 543.0961; Found 543.0966.



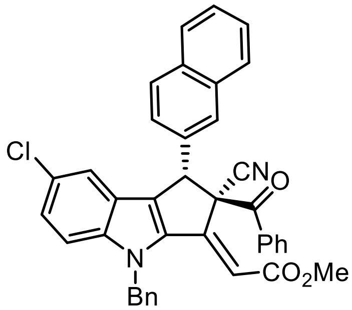
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-8-methoxy-1-(naphthalen-2-yl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene) acetate (3w): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1c** (31.9 mg, 0.0999 mmol, 1.0 equiv), enone **2h** (42.4 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 80 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3w**: 48.3 mg, as a yellow solid, 80% yield; >19:1 dr; >19:1 *E/Z*; mp 140–141 ℃; $[\alpha]^{25}_{D}$ = +112.0 (*c* = 0.25, in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 17.86 min, t (minor) = 34.82 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, *J* = 7.9 Hz, 2H), 7.85–7.79 (m, 3H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.50–7.44 (m, 2H), 7.44–7.36 (m, 5H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.22–7.16 (m, 3H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.32 (d, *J* = 7.8 Hz, 1H), 6.16 (s, 1H), 5.57 (s, 2H), 5.25 (s, 1H), 3.55 (s, 3H), 3.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.8, 165.9, 154.6, 146.9, 146.5, 138.9, 136.3, 134.2, 133.30, 133.26, 133.2, 132.2, 129.3, 129.2, 128.9, 128.6, 128.42, 128.36, 128.0, 127.8, 127.7, 127.5, 127.2, 126.4, 126.0, 125.9, 117.5, 114.2, 107.9, 103.3, 101.1, 68.0, 55.0, 54.4, 51.5, 48.2; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{40}H_{30}N_2O_4Na^+$ 625.2098; Found 625.2088.



Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-7-methoxy-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3x): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1d** (31.9 mg, 0.0999 mmol, 1.0 equiv), enone **2a** (30.3 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3x**: 50.8 mg, as a yellow solid, 92% yield; >19:1 dr; >19:1 *E/Z*; mp 102–104 ℃; $[\alpha]^{25}_{D}$ = –8.0 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 22.03 min, t (minor) = 35.29 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.1 Hz, 2H), 7.59–7.52 (m, 1H), 7.44–7.33 (m, 7H), 7.34–7.30 (m, 1H), 7.29–7.22 (m, 3H), 7.16 (dd, *J* = 7.4, 2.2 Hz, 2H), 6.99 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 6.12 (s, 1H), 5.56 (s, 2H), 5.04 (s, 1H), 3.64 (s, 3H), 3.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.7, 165.7, 154.9, 146.5, 140.8, 140.3, 136.4, 136.2, 134.3, 133.3, 130.5, 129.6, 129.2, 129.0, 128.9, 128.7, 128.4, 128.0, 125.8, 122.8, 117.1, 116.8, 111.6, 108.7, 101.8, 68.8, 55.7, 53.4, 51.5, 48.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}N_2O_4Na^+$ 575.1942; Found 575.1948.

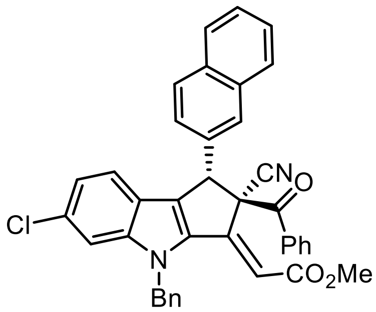


Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-6-methoxy-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3y): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1e** (31.9 mg, 0.0999 mmol, 1.0 equiv), enone **2a** (30.3 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3y**: 52.8 mg, as a yellow solid, 95% yield; >19:1 dr; >19:1 *E/Z*; mp 105–107 ℃; $[\alpha]^{25}_{D}$ = –26.4 (*c* = 0.25, in $CHCl_3$); 86% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 40.89 min, t (minor) = 52.68 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, *J* = 7.0 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42–7.35 (m, 7H), 7.35–7.29 (m, 2H), 7.24–7.21 (m, 1H), 7.19 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 2.1 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.05 (s, 1H), 5.53 (s, 2H), 5.02 (s, 1H), 3.80 (s, 3H), 3.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.7, 165.9, 159.7, 146.9, 146.4, 139.2, 136.4, 136.2, 134.3, 133.2, 132.0, 129.6, 129.2, 129.0, 128.8, 128.6, 128.3, 128.0, 125.9, 122.0, 116.9, 116.8, 111.8, 107.1, 93.6, 68.8, 55.6, 53.4, 51.4, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}N_2O_4Na^+$ 575.1942; Found 575.1945.

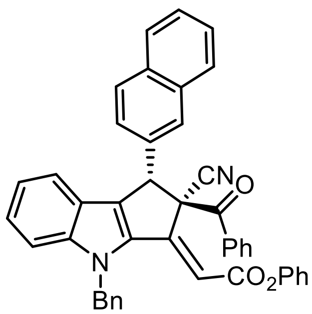


Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-7-chloro-2-cyano-1-(naphthalen-2-yl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene) acetate (3z): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1f** (32.3 mg, 0.0997 mmol, 1.0 equiv), enone **2h** (42.4 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 80 ℃ for 30 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3z**: 39.0 mg, as a yellow solid, 64% yield; >19:1 dr; >19:1 *E/Z*; mp 131–132 ℃; $[\alpha]^{25}_{D}$ = +16.0 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 18.01 min, t (minor) = 39.70 min]; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.99 (d, *J* = 7.8 Hz, 2H), 7.92–7.86 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.74 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.58–7.50 (m, 2H), 7.45–7.39 (m, 4H), 7.36 (dd, *J* = 8.5, 6.0 Hz, 1H), 7.34–7.27 (m, 3H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.04 (s, 1H), 6.24 (s, 1H), 5.61 (s, 2H), 5.18 (s, 1H), 3.58 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 189.7, 165.6, 146.4, 143.7, 141.2, 135.8, 134.3, 133.61, 133.58, 133.5, 133.2, 130.5, 129.4, 129.3, 129.2, 128.8, 128.5, 128.24, 128.15, 127.9, 127.2, 126.8, 126.64, 126.60, 126.5, 125.8, 123.3, 120.2, 116.9, 111.9, 110.0, 68.1, 53.7, 51.7, 48.1; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for

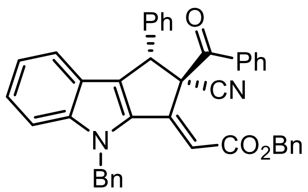
$C_{39}H_{27}ClN_2O_3Na^+$ 629.1603 (^{35}Cl), 630.1636 (^{37}Cl); Found 629.1603 (^{35}Cl), 630.1636 (^{37}Cl).



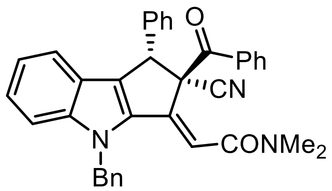
Methyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-6-chloro-2-cyano-1-(naphthalen-2-yl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene) acetate (3aa): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1g** (32.3 mg, 0.0997 mmol, 1.0 equiv), enone **2h** (42.4 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 80 ℃ for 30 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3aa**: 34.5 mg, as a yellow solid, 57% yield; >19:1 dr; >19:1 *E/Z*; mp 138–140 ℃; $[\alpha]^{25}_D$ = +27.2 (*c* = 0.25, in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 14.77 min, t (minor) = 33.84 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.97 (d, *J* = 7.0 Hz, 2H), 7.86 (dd, *J* = 8.8, 4.7 Hz, 2H), 7.79–7.75 (m, 1H), 7.73–7.69 (m, 1H), 7.60–7.55 (m, 1H), 7.53–7.48 (m, 2H), 7.45–7.35 (m, 6H), 7.27 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.19 (d, *J* = 6.9 Hz, 2H), 6.96 (d, *J* = 1.1 Hz, 2H), 6.19 (s, 1H), 5.57 (s, 2H), 5.18 (s, 1H), 3.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.7, 165.6, 146.3, 145.7, 140.8, 135.7, 134.3, 133.7, 133.5, 133.4, 133.2, 132.4, 131.3, 129.4, 129.22, 129.17, 128.7, 128.5, 128.2, 128.1, 127.9, 126.7, 126.6, 126.4, 125.8, 122.3, 121.8, 121.0, 116.9, 110.8, 109.5, 68.2, 53.6, 51.7, 48.1; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{39}H_{27}ClN_2O_3Na^+$ 629.1603 (^{35}Cl), 630.1636 (^{37}Cl); Found 629.1601 (^{35}Cl), 630.1628 (^{37}Cl).



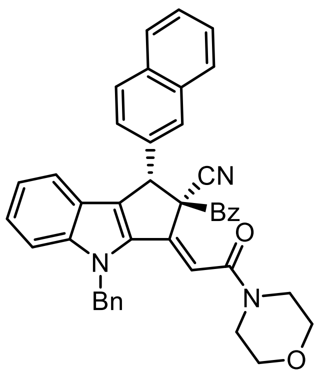
Phenyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-(naphthalen-2-yl)-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3ab): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1h** (35.1 mg, 0.0999 mmol, 1.0 equiv), enone **2h** (42.4 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 80 ℃ for 48 h. After completion, the mixture was concentrated and then purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **3ab**: 39.4 mg, as a yellow solid, 62% yield; >19:1 dr; >19:1 *E/Z*; mp 100–101 ℃; $[\alpha]^{25}_{D}$ = +72.4 (*c* = 0.25, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 13.43 min, t (minor) = 17.00 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.80–7.72 (m, 2H), 7.57–7.47 (m, 3H), 7.46–7.30 (m, 8H), 7.29–7.24 (m, 4H), 7.10 (dd, *J* = 14.6, 7.5 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.97–6.92 (m, 2H), 6.40 (s, 1H), 5.68 (s, 2H), 5.24 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.4, 163.8, 150.2, 148.1, 145.8, 140.1, 136.2, 134.2, 133.9, 133.5, 133.4, 133.2, 132.4, 129.3, 129.3, 129.23, 129.19, 128.6, 128.4, 128.1, 127.9, 126.8, 126.6, 126.5, 126.3, 126.0, 125.7, 122.5, 121.5, 121.44, 121.42, 121.2, 116.8, 110.8, 108.5, 68.4, 53.8, 48.1; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{44}H_{30}N_2O_3Na^+$ 657.2149; Found 657.2152.



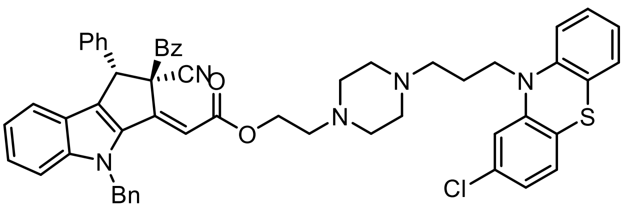
Benzyl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3ac): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1i** (36.5 mg, 0.0999 mmol, 1.0 equiv), enone **2a** (30.3 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/ EtOAc = 10/1–6/1) to give product **3ac**: 48.6 mg, as a yellow solid, 81% yield; >19:1 dr; >19:1 *E/Z*; mp 88–89 ℃; $[\alpha]^{25}_{D}$ = +2.4 (*c* = 0.25, in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 21.62 min, t (minor) = 26.97 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.91–7.85 (m, 2H), 7.57–7.51 (m, 1H), 7.43–7.36 (m, 6H), 7.37–7.33 (m, 4H), 7.32–7.24 (m, 5H), 7.19 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.18–7.14 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 7.04 (ddd, *J* = 8.0, 6.4, 1.4 Hz, 1H), 6.21 (s, 1H), 5.57 (s, 2H), 5.06 (s, 1H), 5.01 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.6, 165.4, 147.0, 145.5, 140.1, 136.4, 136.2, 135.5, 134.3, 133.2, 131.7, 129.7, 129.2, 129.1, 128.9, 128.7, 128.45, 128.39, 128.3, 128.2, 128.0, 126.3, 126.0, 122.5, 121.3, 121.1, 116.9, 110.8, 108.9, 68.7, 66.4, 53.5, 47.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{41}H_{30}N_2O_3Na^+$ 621.2149; Found 621.2148.



(*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)-N,N-dimethylacetamide (3ad): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolamide **1j** (30.2 mg, 0.0999 mmol, 1.0 equiv), enone **2a** (30.3 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/ EtOAc = 3/1–1/1) to give product **3ad**: 41.9 mg, as a yellow solid, 78% yield; >19:1 dr; >19:1 *E/Z*; mp 132–134 ℃; $[\alpha]^{25}_D$ = –22.4 (*c* = 0.25, in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 11.66 min, t (major) = 16.46 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.53–7.46 (m, 1H), 7.44–7.28 (m, 10H), 7.29–7.25 (m, 2H), 7.20–7.12 (m, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.30 (s, 1H), 5.64 (d, *J* = 17.7 Hz, 1H), 5.58 (d, *J* = 17.8 Hz, 1H), 5.06 (s, 1H), 2.74 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.5, 164.9, 145.1, 143.0, 141.1, 136.8, 136.8, 135.0, 132.6, 129.6, 129.3, 129.2, 129.0, 128.6, 128.5, 128.0, 127.9, 125.52, 125.46, 122.6, 121.0, 120.9, 117.4, 110.1, 109.7, 68.3, 53.5, 47.7, 36.8, 35.5; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{29}N_3O_2Na^+$ 558.2152; Found 558.2147.

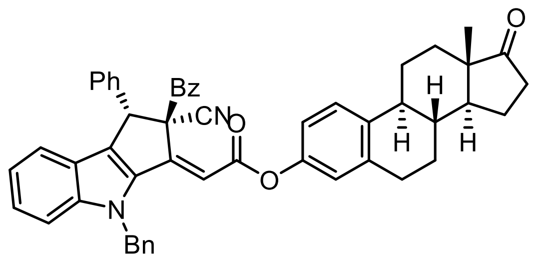


(1*S*,2*R*,*E*)-2-benzoyl-4-benzyl-3-(2-morpholino-2-oxoethylidene)-1-(naphthalen-2-yl)-1,2,3,4-tetrahydrocyclopenta[*b*]indole-2-carbonitrile (3ae): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolamide **1k** (34.4 mg, 0.0999 mmol, 1.0 equiv), enone **2h** (42.4 mg, 0.150 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 80 ℃ for 24 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/ EtOAc = 3/1–1/1) to give product **3ae**: 45.1 mg, as a yellow solid, 72% yield; >19:1 dr; >19:1 *E/Z*; mp 145–147 °C; $[\alpha]^{25}_{D}$ = +2.4 (*c* = 0.25, in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 14.49 min, t (major) = 17.03 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.82–7.75 (m, 2H), 7.55–7.45 (m, 3H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.42–7.39 (m, 1H), 7.38–7.27 (m, 6H), 7.19–7.15 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.03 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1H), 6.17 (s, 1H), 5.66 (d, *J* = 17.8 Hz, 1H), 5.59 (d, *J* = 17.8 Hz, 1H), 5.27 (s, 1H), 3.49–3.40 (m, 1H), 3.37 (m, 2H), 3.33–3.21 (m, 2H), 3.07–2.94 (m, 1H), 2.71 (ddd, *J* = 13.6, 6.5, 3.0 Hz, 1H), 2.59–2.47 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.3, 163.9, 145.2, 143.6, 141.0, 137.1, 134.7, 134.2, 133.5, 133.2, 132.8, 129.30, 129.27, 129.0, 128.9, 128.5, 128.2, 128.1, 127.84, 127.79, 126.9, 126.3, 126.2, 125.7, 125.5, 122.7, 121.2, 121.0, 117.3, 110.1, 109.6, 68.3, 66.7, 66.4, 53.6, 47.6, 45.8, 42.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{42}H_{33}N_3O_3Na^+$ 650.2415; Found 650.2421.



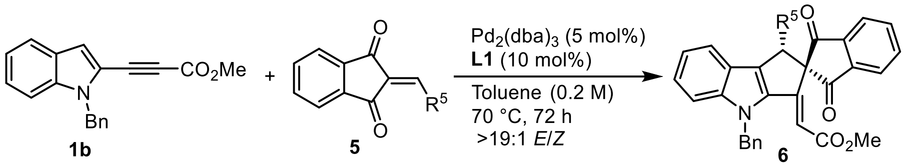
2-(4-(3-(2-chloro-10*H*-phenothiazin-10-yl) propyl)piperazin-1-yl)ethyl (*E*)-2-((1S,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene) acetate (3af): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1l** (66.1 mg, 0.0999 mmol, 1.0 equiv), enone **2a** (30.3 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 48 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 3/1–1/1) to give product **3af**: 50.1 mg, as a yellow solid, 56% yield; 9:1 dr; >19:1 *E/Z*; mp 73–75 °C; $[\alpha]^{25}_{D}$ = –10.2 (*c* = 0.25, in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 13.32 min, t (minor)

= 18.42 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.34–7.26 (m, 8H), 7.28–7.18 (m, 2H), 7.11–7.01 (m, 6H), 6.98 (ddd, *J* = 7.9, 6.3, 1.3 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.87–6.75 (m, 5H), 6.09 (s, 1H), 5.52 (s, 2H), 4.98 (s, 1H), 4.05–3.97 (m, 2H), 3.81 (t, *J* = 6.9 Hz, 2H), 2.42–2.23 (m, 12H), 1.89–1.81 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.6, 165.4, 146.7, 146.5, 145.5, 144.5, 140.1, 136.34, 136.28, 134.4, 133.22, 133.18, 131.5, 129.6, 129.2, 129.1, 128.9, 128.7, 128.3, 128.0, 127.8, 127.5, 127.4, 126.3, 125.9, 124.7, 123.5, 122.9, 122.5, 122.2, 121.3, 121.1, 116.8, 115.81, 115.79, 110.8, 109.2, 68.7, 62.1, 56.3, 55.4, 53.5, 53.2, 53.1, 47.9, 45.3, 29.7, 24.2, 1.0; **HRMS** (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{55}H_{49}ClN_5O_3S^+$ 894.3240; Found 894.3237.

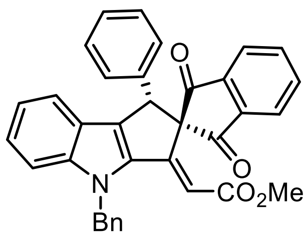


(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl (*E*)-2-((1*S*,2*R*)-2-benzoyl-4-benzyl-2-cyano-1-phenyl-1,4-dihydrocyclopenta[*b*]indol-3(2*H*)-ylidene)acetate (3ag): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1m** (52.7 mg, 0.0999 mmol, 1.0 equiv), enone **2a** (30.3 mg, 0.130 mmol, 1.3 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%) and TBAB (6.4 mg, 0.020 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed 1,4-dioxane (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 72 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **3ag**: 39.1 mg, as a yellow solid, 51% yield; 16:1 dr; >19:1 *E/Z*; mp 148–150 ℃; $[\alpha]^{25}_{D}$ = +2.6 (*c* = 0.25, in $CHCl_3$); determined by H-NMR analysis; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45–7.31 (m, 11H), 7.24–7.20 (m, 3H), 7.20–7.11 (m, 2H), 7.07 (ddd, *J* = 8.0, 6.6, 1.2 Hz, 1H), 6.69 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 6.35 (s, 1H), 5.65 (s, 2H), 5.07 (s, 1H), 2.81 (dd, *J* = 9.1, 4.3 Hz, 2H), 2.48 (dd, *J* = 18.9, 8.6 Hz, 1H), 2.39–2.29 (m, 1H), 2.24–1.84 (m, 6H), 1.64–1.54 (m, 3H), 1.44–1.34 (m, 2H), 0.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 220.9, 189.2, 164.0, 148.0, 147.8, 145.7, 140.1, 137.7, 137.2, 136.3, 136.2, 134.1, 133.3, 132.2, 129.6, 129.3, 129.2, 128.9, 128.7, 128.3, 128.1, 126.6, 126.1, 126.0, 122.5, 121.5, 121.4, 121.2, 118.6, 116.6, 110.8, 108.6, 68.7, 53.5, 50.4, 48.0, 47.9, 44.1, 37.9, 35.8, 31.5, 29.3, 26.3, 25.6, 21.5, 13.8; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{52}H_{44}N_2O_4Na^+$ 783.3194; Found 783.3189.

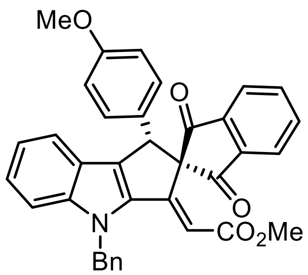
9. General procedure for the asymmetric [3+2] annulations of 2-indolyl propiolate 1b with enones 5



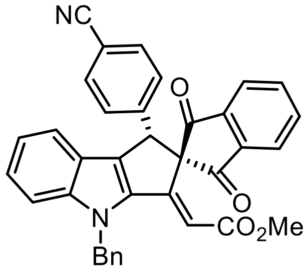
An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1** (0.10 mmol, 1.0 equiv), enone **5** (0.12 mmol, 1.2 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.8 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and back-filled three times with argon, then degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 70 ℃–90 ℃ for 72 h. After completion, the crude product was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give product **6**. Racemic **6** was obtained under the catalysis of $Pd(PPh_3)_4$ (10 mol%) and MeCN (0.5 mL) as solvent.



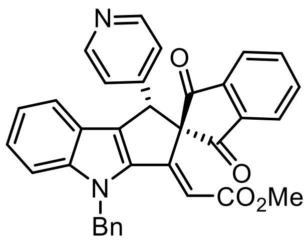
Methyl (*S*,*E*)-2-(4-benzyl-1',3'-dioxo-1-phenyl-1,1',3',4-tetrahydro-3*H*-spiro[cyclopenta[*b*]indole-2,2'-inden]-3-ylidene)acetate (6a): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **5a** (28.1 mg, 0.120 mmol, 1.2 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 70 ℃ for 72 h. After completion, the crude product was directly purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **6a**: 42.3 mg, as a yellow solid, 81% yield; >19:1 *E*/*Z*; mp 213–215 ℃; $[\alpha]^{25}_D$ = +40.0 (c = 0.25, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 10.88 min, t (major) = 13.15 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.07 (d, J = 7.7 Hz, 1H), 7.78 (td, J = 7.5, 1.1 Hz, 1H), 7.62 (td, J = 7.5, 1.1 Hz, 1H), 7.42–7.34 (m, 3H), 7.34–7.29 (m, 2H), 7.29–7.25 (m, 2H), 7.27–7.22 (m, 3H), 7.16–7.07 (m, 1H), 7.09–7.02 (m, 2H), 7.03–6.94 (m, 2H), 6.18 (s, 1H), 5.60 (s, 2H), 4.90 (s, 1H), 3.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 197.3, 196.3, 166.6, 145.7, 145.0, 142.8, 142.5, 141.9, 136.6, 135.9, 134.9, 134.6, 132.5, 129.6, 129.1, 128.0, 127.8, 127.7, 126.1, 125.5, 123.1, 122.7, 122.6, 121.0, 120.7, 110.7, 107.5, 77.2, 54.7, 51.2, 48.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{25}NO_4Na^+$ 546.1676; Found 546.1676.



Methyl (*S*,*E*)-2-(4-benzyl-1-(4-methoxyphenyl)-1',3'-dioxo-1,1',3',4-tetrahydro-3*H*-spiro[cyclopenta[*b*]indole-2,2'-inden]-3-ylidene) acetate (6b): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **5b** (31.7 mg, 0.120 mmol, 1.2 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 80 ℃ for 72 h. After completion, the crude product was directly purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **6b**: 38.6 mg, as a yellow solid, 70% yield; >19:1 *E*/*Z*; mp 218–220 ℃; $[\alpha]^{25}_D$ = +90.4 (c = 0.25, in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 19.31 min, t (major) = 27.07 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.06 (dd, J = 7.5, 1.0 Hz, 1H), 7.78 (td, J = 7.5, 1.1 Hz, 1H), 7.64 (td, J = 7.5, 1.1 Hz, 1H), 7.44–7.35 (m, 4H), 7.34–7.29 (m, 3H), 7.28–7.22 (m, 5H), 7.07 (dt, J = 8.0, 1.0 Hz, 1H), 6.98 (ddd, J = 8.0, 6.7, 1.1 Hz, 1H), 6.17 (s, 1H), 5.59 (s, 2H), 4.86 (s, 1H), 3.70 (s, 3H), 3.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 197.4, 196.5, 166.7, 158.9, 145.8, 145.1, 142.6, 142.6, 141.9, 136.6, 134.9, 134.6, 132.9, 130.7, 129.1, 127.83, 127.75, 126.1, 125.5, 123.1, 122.8, 122.6, 121.0, 120.7, 113.1, 110.6, 107.5, 77.3, 55.1, 54.1, 51.2, 48.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{27}NO_5Na^+$ 576.1782; Found 576.1791.

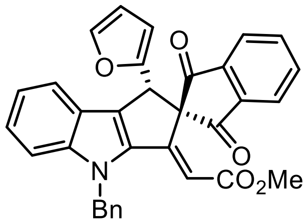


Methyl (*S*,*E*)-2-(4-benzyl-1-(4-cyanophenyl)-1',3'-dioxo-1,1',3',4-tetrahydro-3*H*-spiro[cyclopenta[*b*]indole-2,2'-inden]-3-ylidene) acetate (6c): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **5c** (31.1 mg, 0.120 mmol, 1.2 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min. then at 70 ℃ for 72 h. After completion, the crude product was directly purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **6c**: 51.1 mg, as a yellow solid, 93% yield; >19:1 *E*/*Z*; mp 151–152 ℃; $[\alpha]^{25}_{D}$ = +139.2 (*c* = 0.25, in $CHCl_3$); 87% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 23.66 min, t (major) = 29.42 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.08 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.83 (td, *J* = 7.5, 1.1 Hz, 1H), 7.69 (td, *J* = 7.5, 1.1 Hz, 1H), 7.44–7.38 (m, 3H), 7.38–7.32 (m, 4H), 7.32–7.26 (m, 2H), 7.25–7.20 (m, 2H), 7.06–6.93 (m, 3H), 6.20 (s, 1H), 5.60 (s, 2H), 4.91 (s, 1H), 3.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 196.6, 195.9, 166.6, 145.0, 144.9, 143.0, 142.2, 142.0, 141.7, 136.3, 135.3, 135.1, 130.7, 130.3, 129.1, 127.9, 126.1, 125.8, 123.3, 122.8, 122.2, 121.1, 120.5, 118.5, 111.6, 110.9, 108.0, 76.8, 54.0, 51.4, 48.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{24}N_2O_4Na^+$ 571.1629; Found 571.1639.

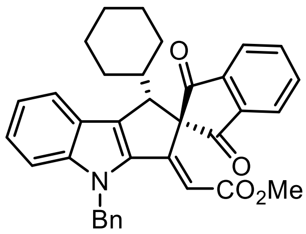


Methyl (*S*,*E*)-2-(4-benzyl-1',3'-dioxo-1-(pyridin-4-yl)-1,1',3',4-tetrahydro-3*H*-spiro[cyclopenta[*b*]indole-2,2'-inden]-3-ylidene) acetate (6d): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **5d** (28.2 mg, 0.120 mmol, 1.2 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 70 ℃ for 72 h. After completion, the crude product was directly purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5/1–2/1) to give product **6d**: 45.8 mg, as a yellow solid, 87% yield; >19:1 *E*/*Z*; mp 95–96 ℃; $[\alpha]^{25}_{D}$ = +29.6 (*c* = 0.25, in $CHCl_3$); 80% ee, determined by HPLC analysis

[Chiralpak column ID, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 27.86 min, t (major) = 36.82 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.35–8.24 (m, 2H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.83 (td, *J* = 7.5, 1.1 Hz, 1H), 7.68 (td, *J* = 7.5, 1.1 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.42–7.38 (m, 1H), 7.36 (d, *J* = 4.8 Hz, 1H), 7.33 (d, *J* = 3.9 Hz, 1H), 7.32–7.26 (m, 2H), 7.25–7.21 (m, 2H), 7.05–6.99 (m, 2H), 6.79–6.56 (m, 2H), 6.20 (s, 1H), 5.60 (s, 2H), 4.83 (s, 1H), 3.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 196.6, 195.8, 166.6, 149.4, 145.5, 145.0, 143.1, 142.3, 141.6, 136.4, 135.3, 135.1, 130.5, 129.1, 128.5, 127.9, 126.1, 125.8, 124.5, 123.3, 122.9, 122.2, 121.1, 120.5, 110.8, 107.9, 76.7, 53.3, 51.3, 48.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{24}N_2O_4Na^+$ 547.1629; Found 547.1627.

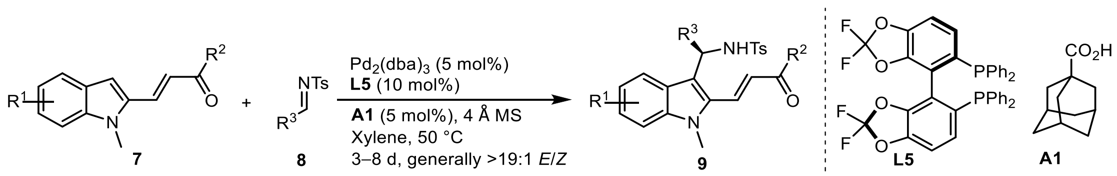


Methyl (*S*,*E*)-2-(4-benzyl-1-(furan-2-yl)-1',3'-dioxo-1,1',3',4-tetrahydro-3*H*-spiro[cyclopenta[*b*]indole-2,2'-inden]-3-ylidene) acetate (6e): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **5e** (26.9 mg, 0.120 mmol, 1.2 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 70 ℃ for 96 h. After completion, the crude product was directly purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–5/1) to give product **6e**: 29.2 mg, as a yellow solid, 57% yield; >19:1 *E*/*Z*; mp 108–109 ℃; $[\alpha]^{25}_{D}$ = –26.4 (*c* = 0.25, in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (minor) = 31.31 min, t (major) = 47.23 min]; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 7.5 Hz, 1H), 7.83 (td, *J* = 7.5, 1.1 Hz, 1H), 7.75 (td, *J* = 7.5, 1.1 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.42–7.33 (m, 2H), 7.33–7.27 (m, 4H), 7.25–7.20 (m, 2H), 7.10–7.04 (m, 1H), 7.00 (d, *J* = 1.8 Hz, 1H), 6.17 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.15 (s, 1H), 5.93 (d, *J* = 3.3 Hz, 1H), 5.57 (s, 2H), 5.01 (s, 1H), 3.34 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 197.1, 195.8, 166.6, 149.9, 145.97, 145.96, 142.5, 142.3, 142.2, 141.8, 136.5, 134.9, 134.7, 129.6, 129.1, 127.8, 126.1, 125.6, 123.4, 122.7, 122.6, 120.9, 120.8, 110.7, 110.6, 110.1, 107.8, 75.9, 51.3, 48.1, 47.5; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{23}NO_5Na^+$ 536.1469; Found 536.1469.

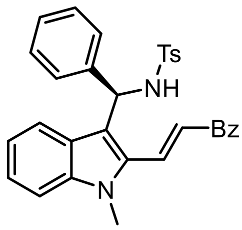


Methyl (*S*,*E*)-2-(4-benzyl-1-cyclohexyl-1',3'-dioxo-1,1',3',4-tetrahydro-3*H*-spiro[cyclopenta[*b*]indole-2,2'-inden]-3-ylidene) acetate (6f): An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (28.9 mg, 0.0999 mmol, 1.0 equiv), enone **5f** (28.8 mg, 0.120 mmol, 1.2 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L1** (6.9 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 90 ℃ for 96 h. After completion, the crude product was directly purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–3/1) to give product **6f**: 16.3 mg, as a yellow solid, 31% yield; >19:1 *E*/*Z*; mp 110–112 ℃; $[\alpha]^{25}_{D}$ = +94.4 (*c* = 0.25, in $CHCl_3$); 81% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 10.89 min, t (major) = 13.21 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 7.93–7.81 (m, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.38–7.30 (m, 2H), 7.30–7.22 (m, 3H), 7.18–7.09 (m, 3H), 6.07 (s, 1H), 5.55 (s, 2H), 3.42 (s, 1H), 3.33 (s, 3H), 1.73 (dd, *J* = 26.8, 13.1 Hz, 2H), 1.67–1.58 (m, 2H), 1.54–1.33 (m, 3H), 1.21–1.05 (m, 2H), 0.96 (ddd, *J* = 17.0, 8.5, 3.8 Hz, 1H), 0.44–0.30 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 197.8, 195.4, 166.7, 145.7, 144.7, 142.91, 142.89, 140.6, 136.7, 135.4, 134.9, 132.3, 129.0, 127.7, 126.0, 125.1, 123.8, 123.7, 123.2, 122.2, 120.6, 110.6, 106.3, 75.1, 55.1, 51.1, 47.8, 41.1, 34.2, 28.7, 27.1, 26.1, 26.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{31}NO_4Na^+$ 552.2146; Found 552.2155.

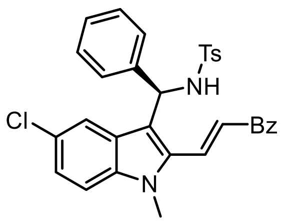
10. General procedure for the asymmetric Friedel−Crafts reaction of 2-alkenyl indole 7 with imines 8



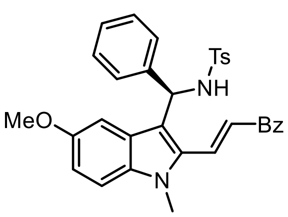
An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7** (0.10 mmol, 1.0 equiv), *N*-sulfonylimine **8** (0.20 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ (monitored by TLC analysis). After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again, and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9** (***The E-products 9 would be converted to the corresponding Z-isomers upon flash chromatography on silica gel, and a mixture of products was generally obtained***). Racemic **9** was obtained under the catalysis of $Pd(PPh_3)_4$ (10 mol%) and using **A3** (30 mol%) as an acidic additive.



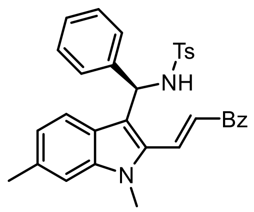
(*R*,*E*)-4-methyl-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)benzenesulfonamide (9a): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 4 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9a**: 44.6 mg, as a yellow solid, 86% yield; >19:1 *E/Z*; mp 203–205 °C; $[\alpha]^{25}_{D} = -16.0$ (c = 0.25, in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 16.31 min, t (major) = 28.02 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 15.6 Hz, 1H), 7.58 (t, *J* = 6.4 Hz, 1H), 7.49–7.38 (m, 4H), 7.35–7.26 (m, 6H), 7.24–7.18 (m, 2H), 7.23 (d, *J* = 15.6 Hz, 1H), 7.00 (t, *J* = 6.4 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.39 (dd, *J* = 8.0, 2.5 Hz, 1H), 3.72 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.7, 142.7, 140.0, 138.5, 137.6, 136.7, 133.1, 133.0, 131.2, 128.73, 128.72, 128.6, 128.5, 127.7, 127.2, 126.9, 125.8, 124.9, 124.2, 120.6, 120.3, 116.6, 109.7, 54.1, 30.6, 21.3.; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{28}N_2O_3SNa^+$ 543.1713; Found 543.1722.



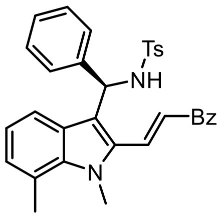
(*R*,*E*)-*N*-((5-chloro-1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (9b): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7b** (29.5 mg, 0.0997 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9b**: 34.8 mg, as a yellow solid, 63% yield; >19:1 *E/Z*; mp 168–169 °C; $[\alpha]^{25}_D = -12.8$ (*c* = 0.25, in $CHCl_3$); 98% ee, determined by HPLC analysis [Chiralpak column IC, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 12.28 min, t (minor) = 15.56 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.79 (m, 2H), 7.75 (d, J = 15.6 Hz, 1H), 7.61–7.53 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.41–7.34 (m, 2H), 7.37–7.27 (m, 5H), 7.28–7.26 (m, 2H), 7.25 (d, J = 15.6 Hz, 1H), 7.16 (dd, J = 8.8, 1.9 Hz, 1H), 7.11 (d, J = 8.8 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 6.15 (d, J = 7.0 Hz, 1H), 5.40 (d, J = 7.0 Hz, 1H), 3.71 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.6, 142.9, 139.6, 137.4, 136.6, 136.5, 134.3, 133.2, 130.8, 128.9, 128.7, 128.6, 128.5, 128.0, 127.2, 126.9, 126.8, 126.1, 126.0, 124.3, 119.6, 115.5, 110.6, 54.1, 30.8, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}ClN_2O_3SNa^+$ 577.1324 (^{35}Cl); 578.1357 (^{37}Cl); Found 577.1327 (^{35}Cl); 578.1363 (^{37}Cl).



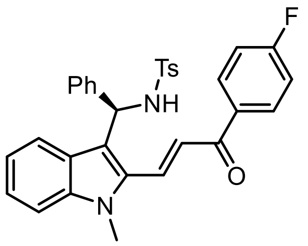
(*R*,*E*)-*N*-((5-methoxy-1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (9c): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7c** (29.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9c**: 51.7 mg, as a yellow solid, 94% yield; >19:1 *E/Z*; mp 96–98 °C; $[\alpha]^{25}_D$ = −12.8 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 19.33 min, t (minor) = 30.61 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 15.6 Hz, 1H), 7.60–7.53 (m, 1H), 7.49–7.41 (m, 4H), 7.35–7.26 (m, 5H), 7.19 (d, J = 15.6 Hz, 1H), 7.08 (d, J = 9.0 Hz, 1H), 6.88 (dd, J = 9.0, 2.4 Hz, 1H), 6.82 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 2.4 Hz, 1H), 6.19 (d, J = 7.8 Hz, 1H), 5.74 (d, J = 7.8 Hz, 1H), 3.69 (s, 3H), 3.68 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.8, 154.5, 142.8, 140.0, 137.7, 136.7, 134.1, 133.2, 133.1, 131.4, 128.8, 128.7, 128.6, 128.5, 127.7, 127.3, 126.9, 126.2, 124.2, 116.2, 115.3, 110.5, 101.0, 55.7, 54.0, 30.8, 21.4; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{30}N_2O_4SNa^+$ 573.1819; Found 573.1823.



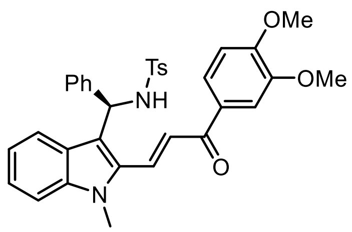
(*R*,*E*)-*N*-((1,6-dimethyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (9d): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7d** (27.5 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9d**: 48.2 mg, as a yellow solid, 90% yield; >19:1 *E/Z*; mp 174–176 °C; $[\alpha]^{25}_D$ = −11.2 (*c* = 0.25, in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 10.42 min, t (major) = 15.82 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 15.6 Hz, 1H), 7.62–7.53 (m, 1H), 7.50–7.38 (m, 4H), 7.33–7.27 (m, 5H), 7.22–7.14 (m, 2H), 6.99 (s, 1H), 6.86–6.81 (m, 3H), 6.15 (d, J = 7.8 Hz, 1H), 5.51 (d, J = 7.8 Hz, 1H), 3.68 (s, 3H), 2.46 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.7, 142.7, 140.0, 139.1, 137.7, 136.6, 134.6, 133.0, 132.4, 131.4, 128.7, 128.6, 128.5, 127.6, 127.2, 126.9, 123.9, 123.7, 122.5, 120.0, 117.0, 109.5, 54.0, 30.6, 22.0, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{30}N_2O_3SNa^+$ 557.1870; Found 557.1878.



(*R*,*E*)-*N*-((1,7-dimethyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (9e): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7e** (27.5 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9e**: 41.6 mg, as a yellow solid, 78% yield; >19:1 *E/Z*; mp 179–180 °C; $[\alpha]^{25}_{D}$ = −6.4 (*c* = 0.25, in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 13.19 min, t (major) = 15.37 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, J = 7.7 Hz, 2H), 7.68 (d, J = 15.6 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.36–7.51 (m, 4H), 7.34–7.24 (m, 5H), 7.20–7.09 (m, 2H), 6.92 (d, J = 7.1 Hz, 1H), 6.89–6.80 (m, 3H), 6.14 (d, J = 8.0 Hz, 1H), 5.53 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 2.72 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.7, 142.7, 140.1, 137.9, 137.6, 136.7, 134.4, 133.2, 131.6, 128.8, 128.7, 128.59, 128.58, 127.7, 127.23, 127.18, 126.9, 126.5, 125.6, 121.5, 120.7, 118.4, 116.5, 54.0, 33.9, 21.4, 20.6; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{30}N_2O_3SNa^+$ 557.1870; Found 557.1875.

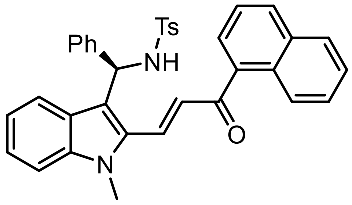


(*R*,*E*)-*N*-((2-(3-(4-fluorophenyl)-3-oxoprop-1-en-1-yl)-1-methyl-1*H*-indol-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (9f): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7f** (27.9 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and wished with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9f**: 46.8 mg, as a yellow solid, 87% yield; >19:1 *E*/*Z*; mp 149–150 °C; $[\alpha]^{25}_{D}$ = −36.0 (*c* = 0.25, in $CHCl_3$); 98% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 14.13 min, t (major) = 25.79 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.86 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.75 (d, *J* = 15.6 Hz, 1H), 7.41 (d, *J* = 6.4 Hz, 2H), 7.35–7.27 (m, 6H), 7.24–7.18 (m, 3H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.21 (d, *J* = 8.0 Hz, 1H), 5.50 (d, *J* = 8.0 Hz, 1H), 3.71 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 187.1, 165.7 (d, *J* = 253.7 Hz), 142.7, 139.9, 138.4, 136.6, 133.9 (d, *J* = 3.0 Hz), 132.9, 131.3 (d, *J* = 21.6 Hz), 131.1, 128.7, 128.6, 127.7, 127.2, 126.8, 125.8, 124.5, 124.2, 120.6, 120.3, 116.5, 115.8 (d, *J* = 21.7 Hz), 109.7, 54.1, 30.5, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) −104.83; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}FN_2O_3SNa^+$ 561.1619; Found 561.1626.



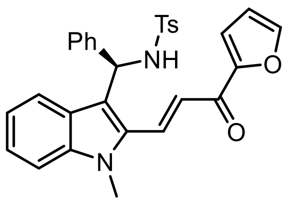
(*R*,*E*)-*N*-((2-(3-(3,4-dimethoxyphenyl)-3-oxoprop-1-en-1-yl)-1-methyl-1*H*-indol-3-yl)(phenyl)methyl)-4-methylbenzene sulfonamide (9g): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7g** (32.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe.

The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 5 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9g**: 54.2 mg, as a yellow solid, 93% yield; >19:1 *E/Z*; mp 201–202 °C; $[\alpha]^{25}_{D}$ = –25.6 (*c* = 0.25, in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 19.41 min, t (major) = 28.93 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.72 (d, *J* = 15.6 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.49–7.39 (m, 3H), 7.34 (d, *J* = 15.6 Hz, 1H), 7.32–7.25 (m, 6H), 7.23–7.15 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.24 (d, *J* = 8.0 Hz, 1H), 5.63 – 5.55 (m, 1H), 3.95 (s, 3H), 3.90 (s, 3H), 3.69 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 186.9, 153.5, 149.2, 142.6, 140.0, 138.3, 136.7, 133.4, 130.7, 130.5, 128.6, 128.5, 127.6, 127.2, 126.7, 125.6, 125.1, 123.9, 123.2, 120.4, 120.1, 115.7, 110.7, 110.2, 109.6, 56.1, 56.0, 54.1, 30.4, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{32}N_2O_5SNa^+$ 603.1925; Found 603.1931.

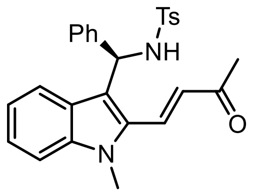


(*R*,*E*)-4-methyl-*N*-((1-methyl-2-(3-(naphthalen-1-yl)-3-oxoprop-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)benzenesulfonamide (9h): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7h** (31.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9h**: 38.4 mg, as a yellow solid, 67% yield; >19:1 *E/Z*; mp 86–87 °C; $[\alpha]^{25}_{D}$ = +16.0 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 23.38 min, t (major) = 32.11 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.45 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.64–7.47 (m, 4H), 7.35–

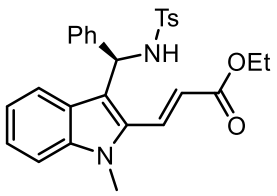
7.22 (m, 7H), 7.22–7.17 (m, 3H), 7.02–6.91 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.11 (d, *J* = 7.6 Hz, 1H), 5.38 (d, *J* = 7.6 Hz, 1H), 3.69 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 193.6, 142.7, 139.7, 138.8, 136.7, 136.3, 133.9, 132.7, 132.3, 132.0, 130.5, 129.0, 128.6, 128.5, 127.8, 127.7, 127.6, 127.1, 126.8, 126.6, 125.6, 125.5, 124.6, 124.4, 120.6, 120.3, 117.4, 109.7, 53.9, 30.9, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{30}N_2O_3SNa^+$ 593.1870; Found 593.1874.



(*R*,*E*)-*N*-((2-(3-(furan-2-yl)-3-oxoprop-1-en-1-yl)-1-methyl-1*H*-indol-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (9i): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7i** (25.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 5 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9i**: 45.5 mg, as a yellow solid, 89% yield; >19:1 *E/Z*; mp 189–191 °C; $[\alpha]^{25}_{D}$ = –41.6 (*c* = 0.25, in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 13.63 min, t (major) = 25.66 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, *J* = 15.8 Hz, 1H), 7.62 (s, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.35–7.21 (m, 6H), 7.23–7.15 (m, 3H), 7.13 (d, *J* = 15.8 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.60–6.54 (m, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 5.54 (d, *J* = 8.0 Hz, 1H), 3.70 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 176.5, 153.3, 147.0, 142.7, 139.9, 138.6, 136.6, 132.8, 130.3, 128.6, 127.6, 127.1, 126.8, 125.5, 124.3, 124.2, 120.5, 120.3, 118.3, 116.9, 112.6, 109.6, 54.0, 30.6, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{26}N_2O_4SNa^+$ 533.1506; Found 533.1512.

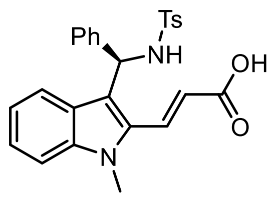


(*R*,*E*)-4-methyl-*N*-((1-methyl-2-(3-oxobut-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)benzenesulfonamide (9j): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7j** (19.9 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **9j**: 38.9 mg, as a yellow solid, 85% yield; *E/Z* = 16:1; mp 117–118 °C; $[\alpha]^{25}_{D}$ = –20.8 (*c* = 0.25, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 10.39 min, t (major) = 16.48 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.43 (d, *J* = 16.4 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.30–7.22 (m, 4H), 7.20 (t, *J* = 7.4 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 2H), 6.36 (d, *J* = 16.4 Hz, 1H), 6.07 (d, *J* = 7.7 Hz, 1H), 5.44 (d, *J* = 7.7 Hz, 1H), 3.67 (s, 3H), 2.30 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 197.3, 142.8, 139.7, 139.0, 136.8, 132.4, 130.1, 129.2, 128.7, 128.6, 127.7, 127.1, 126.8, 125.2, 124.3, 120.6, 120.3, 117.3, 109.7, 53.7, 31.1, 28.0, 21.4; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{26}N_2O_3SNa^+$ 481.1557; Found 481.1565.

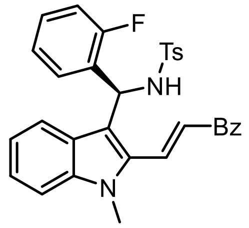


(*R*,*E*)-ethyl-3-(1-methyl-3-(((4-methylphenyl)sulfonamido)(phenyl)methyl)-1*H*-indol-2-yl)acrylate (9k): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7k** (22.9 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **9k**: 32.7 mg, as a yellow solid, 67% yield; *E/Z* = 10:1; mp 141–142 °C; $[\alpha]^{25}_{D}$ = +24.8 (*c* = 0.25, in $CHCl_3$); 76% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 7.39 min, t (major) = 18.63 min]; **^{1}H NMR** (400

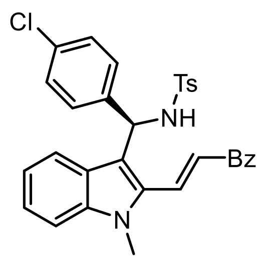
MHz, $CDCl_3$): δ (ppm) 7.51 (d, J = 16.2 Hz, 1H), 7.44–7.38 (m, 2H), 7.32–7.18 (m, 8H), 6.96 (ddd, *J* = 7.9, 6.7, 1.3 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.06–5.99 (m, 2H), 5.41 (d, *J* = 7.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 2.29 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 166.2, 142.7, 139.8, 138.6, 136.6, 132.4, 131.5, 128.6, 128.5, 127.6, 127.1, 126.9, 125.0, 124.0, 121.4, 120.4, 120.2, 116.4, 109.7, 60.8, 53.7, 30.9, 21.4, 14.3; **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{28}H_{28}N_2O_4SNa^+$ 511.1662; Found 511.1660.



(*R*,*E*)-3-(1-methyl-3-(((4-methylphenyl)sulfonamido)(phenyl)methyl)-1*H*-indol-2-yl)acrylic acid (9l): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7l** (20.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (51.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 5 d. After completion, purification by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 20/5/1) to give product **9l**: 31.3 mg, as a faint yellow solid, 68% yield; *E/Z* = 9:1; mp 180–182 ℃; $[\alpha]^{25}_D$ = +20.0 (*c* = 0.1, in $CHCl_3$); 62% ee, determined by HPLC analysis [Chiralpak column IC, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 10.39 min, t (major) = 14.62 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.64 (d, *J* = 16.1 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.37–7.33 (m, 2H), 7.31–7.25 (m, 4H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.09–5.99 (m, 2H), 5.53 (d, *J* = 7.6 Hz, 1H), 3.69 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 170.9, 142.9, 139.7, 139.1, 136.6, 133.6, 131.9, 128.8, 128.6, 127.7, 127.1, 127.0, 125.0, 124.5, 120.6, 120.5, 119.6, 117.8, 109.8, 53.7, 31.2, 21.4; **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{24}N_2O_4SNa^+$ 483,1349; Found 483,1358.

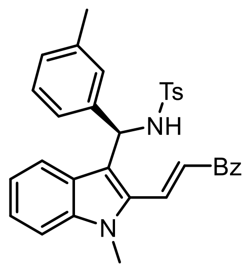


(*R*,*E*)-*N*-((2-fluorophenyl)(1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)methyl)-4-methylbenzenesulfonamide (9m): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8b** (55.5 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 5 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again, and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9m**: 49.5 mg, as a yellow solid, 92% yield; >19:1 *E/Z*; mp 85–87 °C; $[\alpha]^{25}_{D}$ = +151.2 (*c* = 0.25, in $CHCl_3$); 92% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 21.47 min, t (major) = 25.57 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.00 (d, *J* = 7.6 Hz, 2H), 7.76–7.71 (m, 1H), 7.75 (d, *J* = 15.6 Hz, 1H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.55–7.51 (m, 3H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 15.6 Hz, 1H), 7.25–7.20 (m, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.04–6.99 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.30 (dd, *J* = 5.2, 2.5 Hz, 1H), 5.20 (d, *J* = 5.2 Hz, 1H), 3.75 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.8, 160.1 (d, *J* = 245.0 Hz), 143.4, 138.6, 137.7, 136.1, 133.1, 132.6, 131.2, 129.5, 129.4, 129.1, 128.9 (d, *J* = 3.1 Hz), 128.8 , 128.6, 127.3, 127.2, 125.3 (d, *J* = 5.1 Hz), 124.12, 124.10, 120.6, 120.4, 115.8, 115.6, 109.8, 49.5, 31.0, 21.3; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) –115.51; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}FN_2O_3SNa^+$ 561.1619; Found 561.1624.

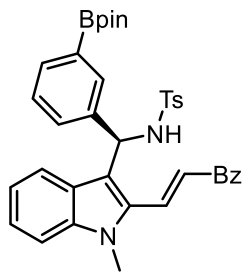


(*R*,*E*)-*N*-((4-chlorophenyl)(1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)methyl)-4-methylbenzenesulfonamide (9n): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8c** (58.7 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 4 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again, and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9n**: 42.1 mg, as a yellow solid, 76%

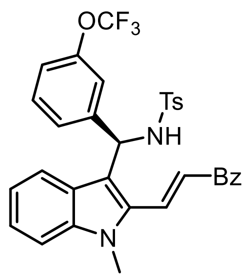
yield; >19:1 *E/Z*; mp 112–114 °C; $[\alpha]^{25}_{D}$ = +24.0 (*c* = 0.25, in $CHCl_3$); 98% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 12.40 min, t (major) = 24.47 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.87 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.29–7.19 (m, 6H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.12 (d, *J* = 8.0 Hz, 1H), 5.36 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.6, 143.0, 138.7, 138.6, 137.5, 136.5, 133.6, 133.3, 133.0, 131.0, 128.81, 128.78, 128.76, 128.6, 128.5, 126.9, 125.3, 124.9, 124.4, 120.8, 120.0, 116.1, 109.8, 53.4, 30.7, 21.4; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}ClN_2O_3SNa^+$ 577.1324 (^{35}Cl), 578.1357 (^{37}Cl); Found 577.1314 (^{35}Cl), 578.1331 (^{37}Cl).



(*R*,*E*)-4-methyl-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(m-tolyl)methyl)benzenesulfonamide (9o): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8d** (54.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 5 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9o**: 35.8 mg, as a yellow solid, 67% yield; >19:1 *E/Z*; mp 84–85 °C; $[\alpha]^{25}_{D}$ = –10.4 (*c* = 0.25, in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 12.74 min, t (major) = 16.14 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.84 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 15.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.27–7.13 (m, 6H), 7.08 (t, *J* = 4.1 Hz, 1H), 7.03–6.97 (m, 1H), 6.82 (d, *J* = 7.6 Hz, 2H), 6.16 (d, *J* = 8.0 Hz, 1H), 5.46 (d, *J* = 8.0 Hz, 1H), 3.71 (s, 3H), 2.28 (s, 3H), 2.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.7, 142.6, 139.9, 138.5, 138.4, 137.6, 136.6, 133.1, 132.9, 131.3, 128.7, 128.6, 128.57, 128.52, 128.4, 127.8, 126.8, 125.9, 124.8, 124.3, 124.1, 120.6, 120.3, 116.7, 109.6, 54.1, 30.5, 21.5, 21.3; **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{33}H_{30}N_2O_3SNa^+$ 557.1870; Found 557.1875.

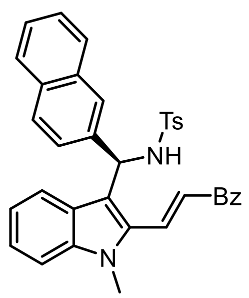


(*R*,*E*)-4-methyl-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl) benzenesulfonamide (9p): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8e** (77.0 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again, and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9p**: 50.3 mg, as a yellow solid, 85% yield; *E/Z* = 8:1; mp 70–71 °C; $[\alpha]^{25}_D$ = +12.8 (*c* = 0.25, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 9.90 min, t (minor) = 11.18 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.99 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 2H), 7.78–7.70 (m, 2H), 7.59–7.54 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.40–7.30 (m, 3H), 7.29 (d, *J* = 2.8 Hz, 1H), 7.24–7.15 (m, 4H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 2H), 6.23 (d, *J* = 7.8 Hz, 1H), 5.44 (dd, *J* = 7.8, 2.4 Hz, 1H), 3.69 (s, 3H), 2.22 (s, 3H), 1.32 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.8, 142.5, 139.1, 138.5, 137.6, 136.6, 134.2, 133.09, 133.07, 133.0, 131.3, 130.1, 128.7, 128.6, 128.5, 128.0, 126.9, 126.8, 125.8, 125.0, 124.1, 120.5, 120.3, 116.5, 109.6, 83.9, 54.1, 30.5, 24.8, 21.3; **HRMS** (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{38}H_{39}BN_2O_5SNa^+$ 669.2565; Found 669.2569.

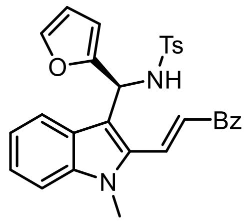


(*R*,*E*)-4-methyl-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(3-(trifluoromethoxy)phenyl)methyl)benzenesulfonamide (9q): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8f** (68.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and

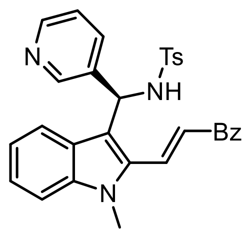
4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 5 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again, and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9q**: 52.6 mg, as a yellow solid, 87% yield; >19:1 *E/Z*; mp 68–69 °C; $[\alpha]^{25}_{D}$ = +5.6 (*c* = 0.25, in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 9.58 min, t (minor) = 10.84 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 15.6 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.39–7.27 (m, 6H), 7.26–7.19 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.05–6.98 (m, 1H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.15 (d, *J* = 7.9 Hz, 1H), 5.44–5.29 (m, 1H), 3.74 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.5, 149.5, 143.1, 142.7, 138.6, 137.5, 136.4, 133.3, 133.1, 131.0, 130.0, 128.9, 128.8, 128.5, 126.9, 125.7, 125.2, 125.0, 124.4, 120.9, 120.4 (q, *J* = 256.0 Hz), 119.9, 119.8, 115.7, 109.9, 53.5, 30.8, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) −72.83; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{27}F_3N_2O_4SNa^+$ 627.1536; Found 627.1532.



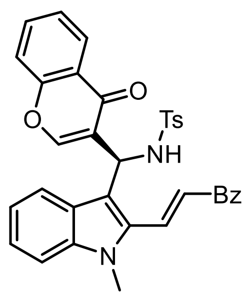
(*R,E*)-4-methyl-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(naphthalen-2-yl)methyl)benzenesulfonamide (9r): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8g** (61.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 8 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again, and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9r**: 48.9 mg, as a yellow solid, 86% yield; >19:1 *E/Z*; mp 157–159 °C; $[\alpha]^{25}_{D}$ = +96.0 (*c* = 0.25, in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 16.21 min, t (major) = 33.57 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89 (s, 1H), 7.82–7.67 (m, 6H), 7.54–7.41 (m, 4H), 7.39–7.29 (m, 5H), 7.26–7.18 (m, 3H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 2H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.67 (d, *J* = 8.0 Hz, 1H), 3.71 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.6, 142.7, 138.4, 137.5, 137.4, 136.7, 135.0, 133.2, 133.0, 132.7, 131.2, 128.6, 128.59, 128.57, 128.4, 128.2, 128.0, 127.5, 126.8, 126.3, 126.2, 125.8, 125.3, 124.9, 124.2, 120.6, 120.3, 116.4, 109.7, 54.2, 30.6, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{30}N_2O_3SNa^+$ 593.1870; Found 593.1876.



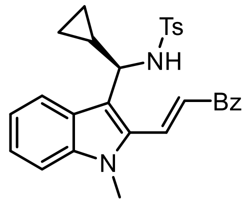
(*R*,*E*)-*N*-(furan-2-yl(1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)methyl)-4-methylbenzenesulfonamide (9s): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8h** (49.8 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **9s**: 49.1 mg, as a yellow solid, 96% yield; >19:1 *E/Z*; mp 56–58 °C; $[\alpha]^{25}_D$ = –20.0 (*c* = 0.25, in $CHCl_3$); 85% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 16.37 min, t (major) = 27.17 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 15.8 Hz, 1H), 7.65–7.57 (m, 1H), 7.57–7.49 (m, 3H), 7.46 (d, *J* = 15.8 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 18.5 Hz, 1H), 7.23–7.15 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.24 (d, *J* = 19.0 Hz, 2H), 6.15 (d, *J* = 6.4 Hz, 1H), 5.56 (s, 1H), 3.71 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.9, 152.2, 142.9, 142.5, 138.4, 137.6, 136.5, 133.3, 133.1, 131.2, 128.8, 128.7, 128.6, 126.9, 125.8, 125.4, 124.1, 120.5, 120.5, 114.1, 110.5, 109.6, 108.2, 49.2, 30.7, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{26}N_2O_4SNa^+$ 533.1506; Found 533.1508.



(*S*,*E*)-4-methyl-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(pyridin-3-yl)methyl)benzenesulfonamide (9t): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8i** (52.0 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 8 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9t**: 38.1 mg, as a yellow solid, 73% yield; >19:1 *E/Z*; mp 88–89 °C; $[\alpha]^{25}_{D}$ = –5.6 (*c* = 0.25, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 19.96 min, t (major) = 31.55 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.55 (d, *J* = 2.4 Hz, 1H), 8.49 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 15.8 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 15.8 Hz, 1H), 7.27–7.18 (m, 4H), 6.98 (ddd, *J* = 8.0, 5.4, 2.5 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.17 (d, *J* = 7.5 Hz, 1H), 5.64 (d, *J* = 7.5 Hz, 1H), 3.74 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 188.6, 148.9, 148.7, 143.2, 138.7, 137.5, 136.4, 135.8, 134.9, 133.3, 133.1, 131.0, 128.9, 128.8, 128.5, 126.9, 125.0, 124.9, 124.4, 123.3, 120.9, 119.9, 115.4, 109.9, 52.1, 30.9, 21.4; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{27}N_3O_3SNa^+$ 544.1666; Found 544.1670.

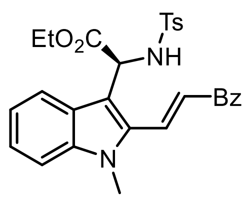


(*S*,*E*)-4-methyl-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(4-oxo-4H-chromen-3-yl)methyl)benzenesulfonamide (9u): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8j** (65.4 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 3 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9u**: 52.9 mg, as a yellow solid, 90% yield; >19:1 *E/Z*; mp 178–180 ℃; $[\alpha]^{25}_{D}$ = +297.6 (*c* = 0.25, in $CHCl_3$); 88% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 12.26 min, t (major) = 15.84 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.49 (s, 1H), 8.19–8.09 (m, 3H), 8.03 (d, *J* = 15.6 Hz, 1H), 7.69 (d, *J* = 9.4 Hz, 2H), 7.66–7.59 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.52–7.43 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28–7.20 (m, 2H), 7.09–7.03 (m, 1H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.01 (d, *J* = 3.5 Hz, 1H), 5.49 (d, *J* = 3.5 Hz, 1H), 3.73 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.6, 177.2, 156.2, 155.4, 143.9, 138.4, 137.6, 135.0, 133.8, 133.5, 133.1, 130.7, 129.5, 128.8, 128.7, 127.4, 126.7, 125.7, 125.2, 125.1, 123.9, 123.8, 122.8, 120.6, 120.2, 118.1, 113.1, 109.9, 48.7, 30.9, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{35}H_{28}N_2O_5SNa^+$ 611.1612; Found 611.1612.

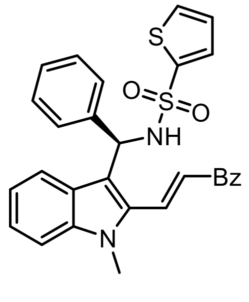


(*R*,*E*)-*N*-(cyclopropyl(1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)methyl)-4-methylbenzenesulfonamide (9v): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8k** (44.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **9v**: 42.8 mg, as a yellow oil, 88% yield; >19:1 *E/Z*; $[\alpha]^{25}_{D}$ = –12.8 (*c* = 0.25, in $CHCl_3$); 88% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 9.15min, t (minor) = 10.66 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.10 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 15.6 Hz, 1H), 7.63 (dd, *J* = 13.0, 7.6 Hz, 2H), 7.60–7.52 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.33 (d, *J* = 4.7 Hz, 1H), 4.30 (dd, *J* = 8.5, 4.7 Hz, 1H), 3.72 (s, 3H), 2.19 (s, 3H), 1.61–1.48 (m, 1H), 0.66–0.56 (m, 1H), 0.49–0.34 (m, 2H), 0.31–0.22 (m, 1H);

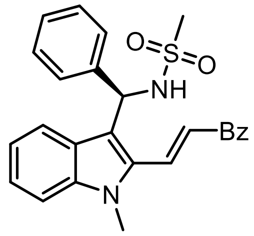
^{13}**C NMR** (150 MHz, $CDCl_3$): δ (ppm) 189.1, 142.6, 138.7, 137.9, 136.7, 133.1, 132.5, 131.7, 128.8, 128.6, 128.4, 126.9, 125.5, 124.2, 124.0, 120.7, 120.2, 117.5, 109.6, 56.2, 30.9, 21.3, 17.3, 5.1, 4.1; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{28}N_2O_3SNa^+$ 507.1713; Found 507.1719.



Ethyl (*S*,*E*)-2-(1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)-2-((4-methylphenyl)sulfonamido)acetate (9w): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8l** (51.0 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 4 d. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **9w**: 31.6 mg, as a yellow oil, 61% yield; *E/Z* = 17:1; $[\alpha]^{25}_D$ = +69.6 (*c* = 0.25, in $CHCl_3$); 96% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 14.91 min, t (major) = 16.87 min]; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.16 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 5.6 Hz, 2H), 7.65–7.53 (m, 4H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.25–7.21 (m, 1H), 7.17 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.07 (ddd, *J* = 8.0, 6.8, 1.1 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 2H), 5.91 (d, *J* = 6.4 Hz, 1H), 5.58 (d, *J* = 6.5 Hz, 1H), 4.20 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.03 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.70 (s, 3H), 2.23 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ (ppm) 188.9, 169.8, 142.9, 138.0, 137.6, 136.3, 134.5, 133.3, 130.9, 128.8, 128.8, 128.6, 126.9, 126.6, 125.2, 124.0, 120.8, 120.1, 110.6, 109.5, 62.5, 52.9, 30.6, 21.3, 14.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{28}N_2O_5SNa^+$ 539.1612; Found 539.1620.



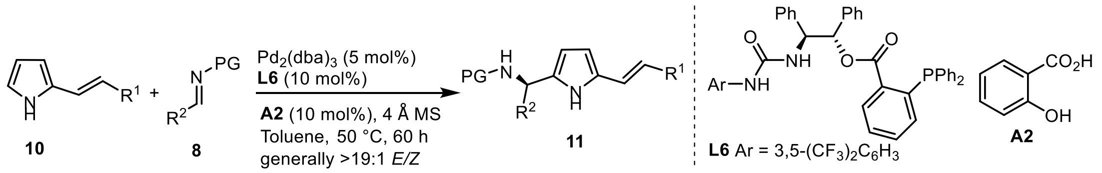
(*R*,*E*)-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)thiophene-2-sulfonamide (9x): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8m** (50.2 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 3 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9x**: 48.2 mg, as a yellow solid, 94% yield; >19:1 *E/Z*; mp 185–187 °C; $[\alpha]^{25}_D$ = –1.6 (*c* = 0.25, in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 7.66 min, t (minor) = 8.47 min]; **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.85 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.32–7.25 (m, 7H), 7.18 (t, *J* = 2.4 Hz, 1H), 7.02 (ddd, *J* = 8.0, 5.9, 2.0 Hz, 1H), 6.68 (t, *J* = 4.3 Hz, 1H), 6.27 (d, *J* = 7.6 Hz, 1H), 5.64 (d, *J* = 7.6 Hz, 1H), 3.77 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 188.8, 140.7, 139.9, 138.6, 137.6, 133.1, 133.0, 132.4, 131.6, 131.3, 128.7, 128.5, 127.7, 127.1, 126.6, 125.7, 125.0, 124.3, 120.7, 120.2, 116.7, 109.9, 54.4, 30.8; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{24}N_2O_3S_2Na^+$ 535.1121; Found 535.1119.



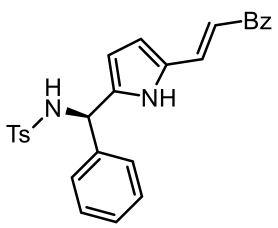
(*R,E*)-*N*-((1-methyl-2-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-indol-3-yl)(phenyl)methyl)methanesulfonamide (9y): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7a** (26.1 mg, 0.0999 mmol, 1.0 equiv), *N*-sulfonylimine **8n** (36.6 mg, 0.200 mmol, 2.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L5** (6.8 mg, 0.010 mmol, 10 mol%), **A1** (0.9 mg, 0.005 mmol, 5 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 7 d. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again and washed with DCM (5 × 5 mL). The filtrate was concentrated to give pure product **9y**: 41.1 mg, as a yellow solid, 92% yield; >19:1 *E/Z*; mp 171–173 °C; $[\alpha]^{25}_D$ = +34.4 (*c* = 0.25, in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 8.86 min, t (major) = 12.03 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, *J* = 15.6 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50–7.41 (m, 5H), 7.42–7.26 (m, 5H), 7.12

(t, J = 7.6 Hz, 1H), 6.41 (d, J = 7.0 Hz, 1H), 5.36 (d, J = 7.1 Hz, 1H), 3.89 (s, 3H), 2.60 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 188.9, 140.2, 138.7, 137.5, 133.1, 133.0, 131.2, 128.9, 128.7, 128.6, 127.9, 127.2, 125.8, 125.6, 124.4, 120.9, 120.5, 116.7, 110.2, 54.4, 41.7, 31.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{24}N_2O_3SNa^+$ 467.1400; Found 467.1408.

11. General procedure for the asymmetric Friedel−Crafts reaction of 2-alkenyl pyrroles 10 with imines 8

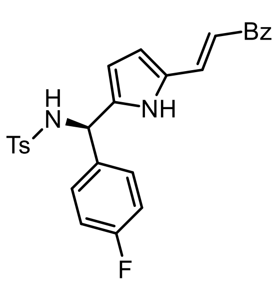


An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10** (0.12 mmol, 1.2 equiv), *N*-sulfonylimine **8** (0.10 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A2** (1.4 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min. then stirred at 50 ℃ (monitored by TLC analysis). After completion, product **11** was obtained by flash chromatography on silica gel (petroleum ether/DCM/EtOAc). Racemic **11** was obtained under the catalysis of $Pd(PPh_3)_4$ (10 mol%) and using **A2** (10 mol%) as an acidic additive.

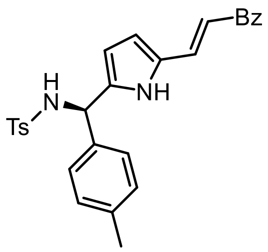


(*R,E*)-4-methyl-*N*-((5-(3-oxo-3-phenylprop-1-en-1-yl)-1H-pyrrol-2-yl)(phenyl)methyl)benzenesulfonamide (11a): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10a** (23.6 mg, 0.120 mmol, 1.2 equiv), *N*-sulfonylimine **8a** (25.9 mg, 0.0999 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A2** (1.4 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 60 h. After completion, purification by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 5/5/1) to give product **11a**: 33.6 mg, as a yellow oil, 74% yield; >19:1 *E/Z*; $[\alpha]^{25}_D$ = +4.6 (c = 0.65, in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 15.07 min, t (minor) = 17.69

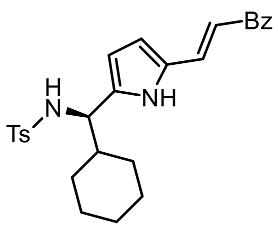
min]; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.66 (s, 1H), 7.89–7.83 (m, 2H), 7.59–7.47 (m, 4H), 7.40 (t, J = 7.6 Hz, 2H), 7.21–7.13 (m, 3H), 7.13–7.04 (m, 4H), 7.00 (d, J = 15.6 Hz, 1H), 6.43 (d, J = 3.0 Hz, 1H), 6.14 (d, J = 8.4 Hz, 1H), 5.80 (d, J = 3.0 Hz, 1H), 5.67 (d, J = 8.4 Hz, 1H), 2.28 (s, 3H); ^{13}**C NMR** (150 MHz, $CDCl_3$): δ (ppm) 191.0, 143.5, 138.4, 138.3, 136.8, 136.4, 134.8, 132.4, 129.8, 129.4, 128.6, 128.5, 128.3, 128.1, 127.2, 127.0, 116.3, 115.7, 111.1, 55.8, 21.4; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{24}N_2O_3SNa^+$ 479.1400; Found 479.1402.



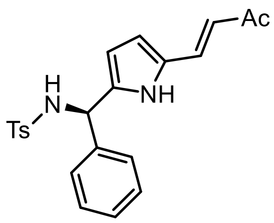
(*R*,*E*)-*N*-((4-fluorophenyl)(5-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-pyrrol-2-yl)methyl)-4-methylbenzenesulfonamide (11b): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10a** (23.6 mg, 0.120 mmol, 1.2 equiv), *N*-sulfonylimine **8o** (27.7 mg, 0.0999 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A2** (1.4 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 60 h. After completion, purification by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 5/5/1) to give product **11b**: 31.9 mg, as a yellow oil, 67% yield; >19:1 *E/Z*; $[\alpha]^{25}_{D}$ = +106.3 (c = 0.16, in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 10/90, flow rate: 1.0 mL/min, 254 nm, t (major) = 29.33 min, t (minor) = 38.20 min]; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.71 (s, 1H), 7.85 (d, J = 7.0 Hz, 2H), 7.57–7.48 (m, 4H), 7.41 (dd, J = 8.3, 7.0 Hz, 2H), 7.11–7.04 (m, 4H), 7.01 (d, J = 15.6 Hz, 1H), 6.82 (t, J = 8.6 Hz, 2H), 6.43 (dd, J = 3.7, 2.5 Hz, 1H), 6.24 (d, J = 8.6 Hz, 1H), 5.77 (dd, J = 3.7, 2.4 Hz, 1H), 5.66 (d, J = 8.6 Hz, 1H), 2.30 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ (ppm) 191.3, 162.3 (d, J = 245.9 Hz), 143.7, 138.3, 136.8, 136.1, 134.9, 134.1 (d, J = 3.4 Hz), 132.5, 129.9, 129.4, 129.1 (d, J = 8.3 Hz), 128.5, 128.3, 127.0, 116.1, 115.9, 115.4 (d, J = 21.5 Hz), 111.2, 55.2, 21.4; ^{19}**F NMR** (376 MHz, $CDCl_3$): δ (ppm) –113.71; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{23}FN_2O_3SNa^+$ 497.1306; Found 497.1305.



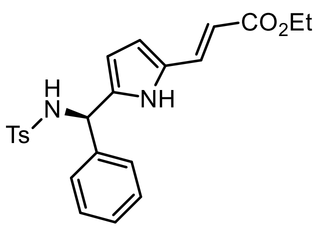
(*R*,*E*)-4-methyl-*N*-((5-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-pyrrol-2-yl)(p-tolyl)methyl)benzenesulfonamide (11c): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10a** (23.6 mg, 0.120 mmol, 1.2 equiv), *N*-sulfonylimine **8p** (27.3mg, 0.0999 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A2** (1.4 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min. then at 50 ℃ for 60 h. After completion, purification by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 5/5/1) to give product **11c**: 27.6 mg, as a yellow oil, 59% yield; >19:1 *E/Z*; $[\alpha]^{25}_D$ = +43.6 (*c* = 0.2, in $CHCl_3$); 93% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 16.84 min, t (minor) = 19.47 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.62 (s, 1H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.58–7.46 (m, 4H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 15.6 Hz, 1H), 6.98–6.93 (m, 4H), 6.43 (d, *J* = 3.7 Hz, 1H), 6.03 (d, *J* = 8.1 Hz, 1H), 5.80 (dd, *J* = 3.7, 2.1 Hz, 1H), 5.60 (d, *J* = 8.1 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 190.8, 143.6, 138.4, 138.1, 136.7, 136.6, 135.2, 134.6, 132.4, 129.7, 129.44, 129.35, 128.5, 128.3, 127.2, 127.0, 116.2, 115.6, 111.0, 55.6, 21.4, 21.0; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{26}N_2O_3SNa^+$ 493.1557; Found 493.1556.



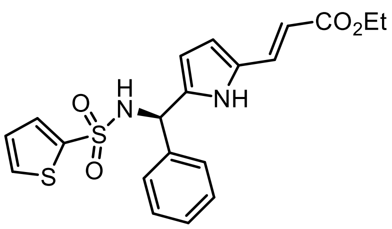
(*R*,*E*)-*N*-(cyclohexyl(5-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-pyrrol-2-yl) methyl)-4-methylbenzenesulfonamide (11d): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10a** (23.6 mg, 0.120 mmol, 1.2 equiv), *N*-sulfonylimine **8q** (26.5 mg, 0.0999 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A2** (1.4 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min. then at 50 ℃ for 60 h. After completion, purification by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 5/5/1) to give product **11d**: 35.4 mg, as a yellow oil, 77% yield; *E/Z* = 17:1; $[\alpha]^{25}_D$ = +175.0 (*c* = 0.84, in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 8.98 min, t (minor) = 12.28 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.74 (s, 1H), 7.91 (d, *J* = 7.1 Hz, 2H), 7.61–7.51 (m, 3H), 7.50–7.41 (m, 3H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 15.5 Hz, 1H), 6.39 (dd, *J* = 3.7, 2.5 Hz, 1H), 6.19 (d, *J* = 9.4 Hz, 1H), 5.89 (dd, *J* = 3.7, 2.2 Hz, 1H), 4.25 (dd, *J* = 9.4, 7.8 Hz, 1H), 2.24 (s, 3H), 1.87 (d, *J* = 12.7 Hz, 1H), 1.67–1.45 (m, 4H), 1.34 (dd, *J* = 12.7, 4.0 Hz, 1H), 1.13–0.95 (m, 3H), 0.97–0.78 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 192.7, 143.1, 138.5, 137.4, 137.2, 135.9, 132.4, 129.2, 128.9, 128.6, 128.4, 126.7, 116.6, 115.4, 110.7, 57.4, 42.9, 29.59, 29.56, 26.0, 25.7, 21.4, 21.39; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{30}N_2O_3SNa^+$ 485.1870; Found 485.1869.



(*R*,*E*)-4-methyl-*N*-((5-(3-oxobut-1-en-1-yl)-1*H*-pyrrol-2-yl)(phenyl) methyl)benzenesulfonamide (11e): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10b** (16.2 mg, 0.120 mmol, 1.2 equiv), *N*-sulfonylimine **8a** (25.9 mg, 0.0999 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A2** (1.4 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 60 h. After completion, purification by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 5/1/1) to give product **11e**: 18.8 mg, as a yellow oil, 48% yield; >19:1 *E/Z*; $[\alpha]^{25}_D$ = +121.4 (*c* = 0.28, in $CHCl_3$); 90% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (minor) = 32.41 min, t (major) = 34.33 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.96 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 3.5 Hz, 1H), 7.26–7.14 (m, 5H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 9.4 Hz, 1H), 6.36 (t, *J* = 3.0 Hz, 1H), 6.23 (d, *J* = 16.2 Hz, 1H), 5.92 (t, *J* = 3.0 Hz, 1H), 5.73 (d, *J* = 9.4 Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 200.4, 143.0, 139.1, 137.2, 137.1, 135.0, 129.1, 128.7, 128.6, 127.8, 127.0, 126.8, 120.4, 117.2, 111.1, 55.7, 25.8, 21.4; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}N_2O_3SNa^+$ 417.1244; Found 417.1237.

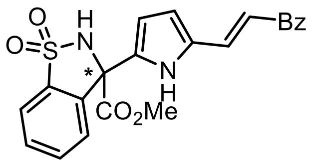


Ethyl (*R*,*E*)-3-(5-(((4-methylphenyl)sulfonamido)(phenyl)methyl)-1*H*-pyrrol-2-yl)acrylate (11f): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10c** (19.8 mg, 0.120 mmol, 1.2 equiv), *N*-sulfonylimine **8a** (25.9 mg, 0.0999 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A2** (1.4 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 60 h. After completion, purification by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 5/1/1) to give product **11f**: 25.2 mg, as a faint red oil, 59% yield; >19:1 *E/Z*; $[\alpha]^{25}_{D}$ = +88.7 (*c* = 0.55, in $CHCl_3$); 91% ee, determined by HPLC analysis [Chiralpak column AD, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (minor) = 12.14 min, t (major) = 17.87 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.25 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 15.9 Hz, 1H), 7.23–7.19 (m, 3H), 7.13 (dd, *J* = 6.6, 2.7 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.29 (t, *J* = 3.1 Hz, 1H), 6.03–5.91 (m, 1H), 5.85 (d, *J* = 15.9 Hz, 1H), 5.77 (t, *J* = 3.0 Hz, 1H), 5.64 (d, *J* = 8.4 Hz, 1H), 4.30–4.01 (m, 2H), 2.33 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 168.1, 143.5, 138.5, 136.9, 135.4, 134.2, 129.4, 128.9, 128.6, 128.0, 127.2, 126.9, 114.9, 111.1, 110.5, 60.5, 55.7, 21.4, 14.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{24}N_2O_4SNa^+$ 447.1349; Found 447.1352.



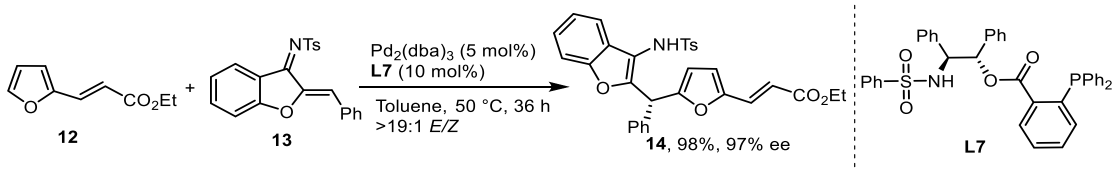
Ethyl (*R*,*E*)-3-(5-(phenyl(thiophene-2-sulfonamido)methyl)-1*H*-pyrrol-2-yl)acrylate (11g): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10c** (19.8 mg, 0.120 mmol, 1.2 equiv), *N*-sulfonylimine **8m** (25.1 mg, 0.0999 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A2** (1.4 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 60 h. After completion, purification by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 5/1/1) to give product **11g**: 35.7 mg, as a faint red oil, 86% yield; >19:1 *E/Z*; $[\alpha]^{25}_{D}$ = +47.2 (*c* = 0.55, in $CHCl_3$); 86% ee, determined by

HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 10/90, flow rate: 1.0 mL/min, 254 nm, t (major) = 17.40 min, t (minor) = 19.34 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.11 (s, 1H), 7.50 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.45–7.37 (m, 2H), 7.32–7.23 (m, 4H), 7.19–7.11 (m, 2H), 6.93 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.34 (t, *J* = 3.1 Hz, 1H), 5.92 (d, *J* = 15.8 Hz, 1H), 5.82–5.76 (m, 2H), 5.68 (dd, *J* = 8.3, 3.7 Hz, 1H), 4.24–4.03 (m, 2H), 1.33–1.21 (m, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 168.0, 140.7, 138.1, 135.1, 134.1, 132.7, 132.3, 129.0, 128.8, 128.4, 127.3, 127.2, 114.9, 111.4, 110.7, 60.6, 56.0, 14.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}N_2O_4S_2Na^+$ 439.0757; Found 439.0760.



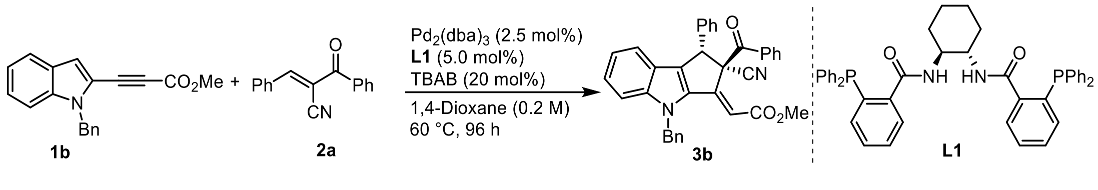
Methyl (*E*)-3-(5-(3-oxo-3-phenylprop-1-en-1-yl)-1*H*-pyrrol-2-yl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (11h): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl pyrrole **10a** (23.6 mg, 0.120 mmol, 1.2 equiv), *N*-sulfonylimine **8r** (22.5 mg, 0.0999 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%), ligand **L6** (7.6 mg, 0.010 mmol, 10 mol%), **A1** (1.8 mg, 0.010 mmol, 10 mol%) and 4 Å MS (40.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (1.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 48 h. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–4/1) to give product **11h**: 35.8 mg, as a yellow oil, 85% yield; *E/Z* = 12:1; $[\alpha]^{25}_{D}$ = +151.1 (*c* = 0.4, in $CHCl_3$); 83% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane =40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 17.05 min, t (minor) = 29.71 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.49 (s, 1H), 7.95–7.89 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81–7.75 (m, 1H), 7.73–7.64 (m, 1H), 7.64–7.56 (m, 2H), 7.54–7.48 (m, 1H), 7.44–7.37 (m, 2H), 7.12 (d, *J* = 15.6 Hz, 1H), 6.55 (dd, *J* = 3.8, 2.7 Hz, 1H), 6.42 (dd, *J* = 3.8, 2.4 Hz, 2H), 3.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.9, 168.0, 138.3, 136.5, 134.0, 133.9, 133.6, 132.5, 132.1, 130.9, 130.2, 128.5, 128.3, 126.4, 121.3, 116.9, 116.1, 110.1, 66.6, 54.8; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}N_2O_5SNa^+$ 445.0829; Found 445.0820.

12. General procedure for the asymmetric Friedel−Crafts reaction of 2-alkenyl furan 12 with 1-azadiene 13

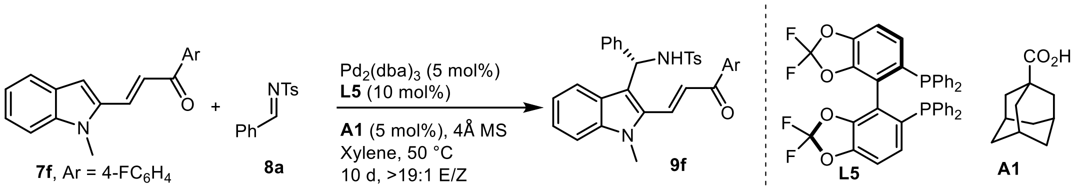


Ethyl (*S,E*)-3-(5-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)furan-2-yl)acrylate (14): An oven-dried 10 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl furan **12** (33.2 mg, 0.200 mmol, 2.0 equiv), aza-diene **13** (37.5 mg, 0.0998 mmol, 1.0 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.0050 mmol, 5 mol%) and ligand **L7** (6.4 mg, 0.010 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times and toluene (0.5 mL) was added via syringe. Then the resulting mixture was stirred at 50 ℃ for 36 h. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **14**: 53.4 mg, as a yellow semisolid, 98% yield; >19:1 *E/Z*; $[\alpha]^{25}_{D}$ = +29.1 (*c* = 0.35, in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 9.95 min, t (major) = 16.76 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.62 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 15.8 Hz, 1H), 7.28–7.25 (m, 2H), 7.25–7.20 (m, 4H), 7.20–7.15 (m, 1H), 7.11–7.07 (m, 3H), 6.75 (s, 1H), 6.48 (d, *J* = 3.4 Hz, 1H), 6.17 (d, *J* = 15.8 Hz, 1H), 6.12 (d, *J* = 3.4 Hz, 1H), 5.62 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 167.1, 155.6, 153.4, 152.5, 150.4, 144.0, 137.3, 136.1, 130.8, 129.6, 128.6, 128.4, 127.5, 127.4, 125.5, 124.7, 123.2, 119.3, 115.6, 115.4, 113.9, 111.6, 110.9, 60.4, 41.9, 21.5, 14.2; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{27}NO_6SNa^+$ 564.1452; Found 564.1444.

13. Asymmetric reaction on a 1.0 mmol scale

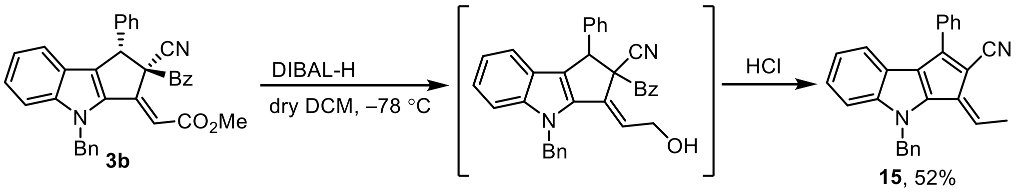


An oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-indolyl propiolate **1b** (289 mg, 1.00 mmol, 1.0 equiv), enone **2a** (303 mg, 1.30 mmol, 1.3 equiv), $Pd_2(dba)_3$ (22.9 mg, 0.0250 mmol, 2.5 mol%), ligand **L1** (34.5 mg, 0.0499 mmol, 5 mol%) and TBAB (64.0 mg, 0.200 mmol, 20 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times and degassed 1,4-dioxane (5.0 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 60 ℃ for 96 h. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–8/1) to give product **3b**: 454.1 mg, as a yellow solid, 87% yield; 92% ee; >19:1 dr; >19:1 *E/Z*.



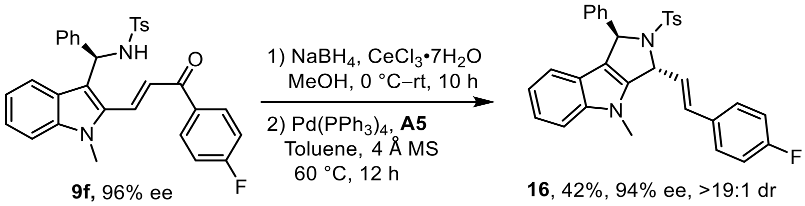
An oven-dried 50 mL test-tube equipped with a septum and a magnetic stir bar was charged with 2-alkenyl indole **7f** (279 mg, 0.999 mmol, 1.0 equiv), *N*-sulfonylimine **8a** (518 mg, 2.00 mmol, 2.0 equiv), $Pd_2(dba)_3$ (45.8 mg, 0.0500 mmol, 5 mol%), ligand **L5** (68.2 mg, 0.100 mmol, 10 mol%), **A1** (9.0 mg, 0.050 mmol, 5 mol%) and 4 Å MS (400 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times and xylene (10 mL) was added via syringe. The resulting solution was stirred at room temperature for 30 min, then at 50 ℃ for 10 d. After completion, Et_2O (10 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered and washed with cold Et_2O (3 × 5 mL). The cake was collected and dissolved in DCM. The mixture was filtered again, and washed with DCM (5 × 5 mL). The filtrate was concentrated to give product **9f**: 516.0 mg, as a yellow solid, 96% yield; 96% ee; >19:1 *E/Z*.

14. Transformations of products



To a solution of compound **3b** (52.2 mg, 0.0998 mmol, 1.0 equiv) in dry DCM, 1.0 M DIBAL-H (0.5 mL, 0.5 mmol, 5.0 equiv) was added drop wise at –78 ℃ under argon atmosphere, and the mixture was stirred for 12 h. Then the solution was warmed to room temperature, quenched with aqueous HCl (1M, 2 mL) and stirred at rt for 30 min. The mixture was extracted with DCM (3 × 2 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After concentration, the residue was purified by column chromatography (petroleum ether/EtOAc = 10/1) to give product **15**: 19.4 mg, as a red semisolid, 52% yield; >19:1 *E/Z*; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.94–7.88 (m, 2H), 7.61 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.51 (dd, *J* = 8.3, 6.5 Hz, 2H), 7.47–7.42 (m, 1H), 7.29–7.21 (m, 4H), 7.17–7.12 (m, 1H), 7.09 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.05–7.00 (m, 2H), 6.64 (q, *J* = 7.7

Hz, 1H), 5.43 (s, 2H), 2.39 (d, *J* = 7.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 156.2, 142.9, 141.7, 136.6, 135.4, 133.3, 131.5, 130.0, 129.1, 128.8, 128.7, 127.9, 125.9, 122.9, 121.6, 121.5, 120.1, 119.9, 119.8, 110.4, 92.6, 48.1, 15.5; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{20}N_2Na^+$ 395.1519; Found 395.1526.

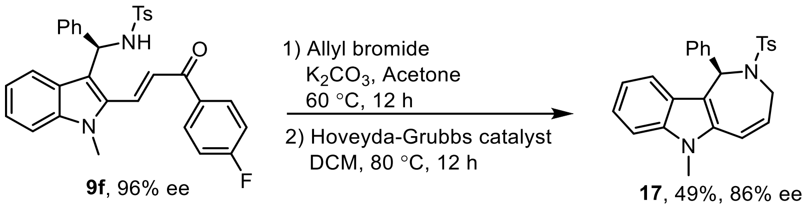


9f, 96% ee

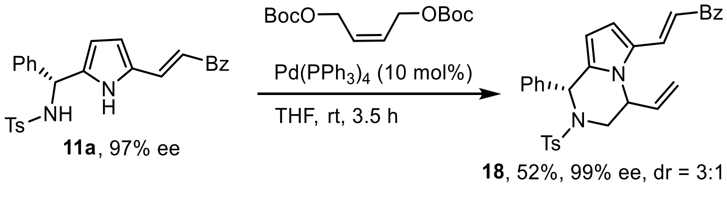
16, 42%, 94% ee, >19:1 dr

To a solution of **9f** (53.8 mg, 0.0999 mmol, 1.0 equiv) in MeOH (1.0 mL) was added $CeCl_3 \cdot 7H_2O$ (149.1 mg, 0.4002 mmol, 4.0 equiv), and $NaBH_4$ (15.1 mg, 0.399 mmol, 4.0 equiv) was added slowly in two batches. The mixture was stirred at rt for 10 h. After completion (monitored by TLC analysis), it was quenched with water (3 mL). Then MeOH was evaporated under reduced pressure and the resulting aqueous phase was extracted with DCM (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and evaporated. The crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 6/1–3/1) to give allyl alcohol product (48.9 mg, 94% yield). Then an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with the allyl alcohol product (40.5 mg, 0.0750 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (8.7 mg, 0.0075 mmol, 10 mol%), **A5** (3.7 mg, 0.015 mmol, 20 mol%) and 4 Å MS (60.0 mg). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed toluene (1.0 mL) was added via syringe. The resulting mixture was stirred at 60 ℃ for 12 h. After completion, the mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **16**: 21.9 mg, as a yellow solid, 42% overall yield; >19:1 dr; >19:1 *E/Z*; mp 101–102 ℃; $[\alpha]^{25}_{D}$ = +11.6 (*c* = 0.25, in $CHCl_3$); 94% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (minor) = 5.66 min, t (major) = 6.33 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.41 (d, *J* = 8.3 Hz, 2H), 7.34–7.29 (m, 2H), 7.29–7.26 (m, 2H), 7.25–7.20 (m, 4H), 7.14 (ddd, *J* = 8.3, 6.9, 1.2 Hz, 1H), 7.09–7.04 (m, 1H), 7.04–6.93 (m, 5H), 6.77 (d, *J* = 14.8 Hz, 1H), 6.18 (d, *J* = 3.4 Hz, 1H), 5.96–5.88 (m, 2H), 3.62 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 162.7 (d, *J* = 246.7 Hz), 142.5, 141.4, 141.2, 138.8, 137.8, 132.2, 131.9 (d, *J* = 3.4 Hz), 129.0, 128.4 (d, *J* = 8.1 Hz), 128.2, 127.6, 127.5, 127.45 (d, *J* = 3.2 Hz), 127.41, 121.8, 121.6, 120.1, 118.6, 116.8, 115.6 (d, *J* = 21.6 Hz), 109.7, 66.1, 63.6, 30.5, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm)

–113.08; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{27}FN_2O_2SNa^+$ 545.1670; Found 545.1679.

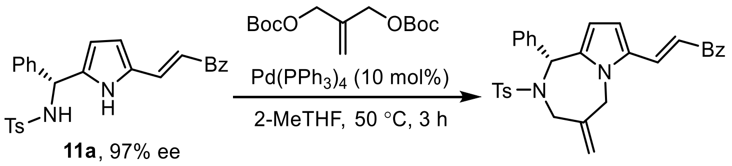


To a solution of **9f** (107.7 mg, 0.1999 mmol, 1.0 equiv) in acetone (1.0 mL) was added K_2CO_3 (110.4 mg, 0.7988 mmol, 4.0 equiv) and 3-bromopropylene (69 μL, 0.80 mmol, 4.0 equiv). The mixture was stirred at 60 ℃ for 12 h. After completion (determined by TLC analysis), solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 6/1) to give product (104.2 mg, 0.1800 mmol, 90% yield). Then an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with the *N*-allyl product (57.8 mg, 0.100 mmol, 1.0 equiv) and Hoveyda-Grubbs catalyst (3.2 mg, 0.0050 mmol, 5 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times, and degassed dried DCM (1.0 mL) was added via syringe. The resulting mixture was stirred at 80 ℃ for 12 h. After completion, the mixture was purified by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 30/30/1) to give product **17**: 23.3 mg, as a yellow solid, 49% overall yield; mp 59–61 °C; $[\alpha]^{25}_D$ = +114.9 (*c* = 0.35, in $CHCl_3$); 86% ee, determined by HPLC analysis [Chiralpak column IA, *i*PrOH/*n*Hexane = 20/80, flow rate: 1.0 mL/min, 254 nm, t (major) = 7.83 min, t (minor) = 9.86 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.35 (d, *J* = 7.9 Hz, 1H), 7.31–7.18 (m, 9H), 7.09–7.01 (m, 1H), 6.82 (s, 1H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.12 (dd, *J* = 12.0, 2.8 Hz, 1H), 5.59 (ddd, *J* = 12.0, 5.8, 2.7 Hz, 1H), 4.50 (ddd, *J* = 19.9, 5.9, 1.9 Hz, 1H), 3.70–3.60 (m, 1H), 3.41 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 142.2, 140.0, 137.0, 136.7, 133.5, 128.7, 128.6, 128.1, 127.8, 127.7, 127.5, 126.7, 122.6, 120.0, 118.4, 118.4, 113.2, 109.0, 57.6, 44.8, 29.1, 21.3; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{24}N_2O_2SNa^+$ 451.1451; Found 451.1454.



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **11a** (45.6 mg, 0.0998 mmol, 1.0 equiv), (*Z*)-but-2-ene-1,4-diyldi-tert-butyl bis(carbonate) (43.2 mg, 0.150

mmol, 1.5 equiv) and $Pd(PPh_3)_4$ (11.5 mg, 0.0100 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times and degassed THF (1.0 mL) was added via syringe. The resulting mixture was stirred at rt for 3.5 h. After completion, the mixture was concentrated and purified by flash chromatography on silica gel (petroleum ether/DCM/EtOAc = 20/10/1) to give product **18**: 26.4 mg, as a yellow oil, 52% yield; 3:1 dr; $[\alpha]^{25}_{D}$ = +8.6 (c = 0.73, in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak column IB, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 5.35 min, t (minor) = 5.69 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.98 (d, J = 7.1 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.58–7.50 (m, 3H), 7.37–7.33 (m, 2H), 7.33–7.28 (m, 6H), 7.20 (d, J = 16.2 Hz, 1H), 6.63 (d, J = 5.0 Hz, 1H), 6.42 (d, J = 5.0 Hz, 1H), 4.99 (dd, J = 9.7, 7.7 Hz, 1H), 4.94–4.84 (m, 2H), 4.70 (s, 1H), 4.11–4.03 (m, 1H), 3.67 (dd, J = 10.9, 8.7 Hz, 1H), 3.54–3.42 (m, 1H), 2.42 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 190.4, 169.3, 152.7, 143.6, 141.4, 137.2, 137.1, 133.4, 131.0, 130.2, 129.3, 128.8, 128.7, 128.4, 128.1, 127.8, 127.0, 126.97, 126.93, 119.4, 94.1, 69.1, 53.1, 47.0, 21.5; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{28}N_2O_3SNa^+$ 531.1713; Found 531.1723.

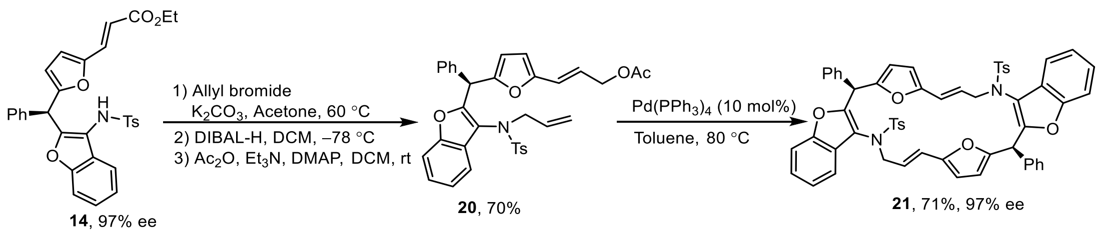


11a, 97% ee

19, 84%, 98% ee

An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **11a** (45.6 mg, 0.0998 mmol, 1.0 equiv), di-tert-butyl (2-methylenepropane-1,3-diyl) bis(carbonate) (43.2 mg, 0.150 mmol, 1.5 equiv) and $Pd(PPh_3)_4$ (11.5 mg, 0.0100 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times and degassed 2-MeTHF (1.0 mL) was added via syringe. The resulting mixture was stirred at 50 ℃ for 3 h. After completion, the mixture was concentrated and then purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to give product **19**: 42.7 mg, as a yellow oil, 84% yield; $[\alpha]^{25}_{D}$ = +241.1 (c = 0.75, in $CHCl_3$); 98% ee, determined by HPLC analysis [Chiralpak column IF, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 15.08 min, t (minor) = 21.54 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, J = 7.2 Hz, 2H), 7.71 (d, J = 15.0 Hz, 1H), 7.59–7.54 (m, 1H), 7.54–7.44 (m, 4H), 7.36–7.25 (m, 4H), 7.19–7.14 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 3.9 Hz, 1H), 6.55 (s, 1H), 6.05 (d, J = 3.7 Hz, 1H), 4.98 (s, 1H), 4.82 (s, 1H), 4.33 (d, J = 14.5 Hz, 1H), 4.29 (d, J = 16.5 Hz, 1H), 4.19 (d, J = 14.4 Hz, 1H), 3.80 (d, J = 15.5 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR**

(100 MHz, $CDCl_3$): δ (ppm) 189.4, 143.4, 138.5, 137.5, 137.4, 136.6, 135.0, 132.6, 131.5, 130.7, 129.3, 128.62, 128.56, 128.2, 127.9, 127.5, 127.3, 119.0, 117.4, 113.0, 111.2, 58.4, 50.0, 49.0, 21.4; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{28}N_2O_3SNa^+$ 531.1713; Found 531.1705.



To a solution of **14** (108.3 mg, 0.1999 mmol, 1.0 equiv) in acetone (1.0 mL) was added K_2CO_3 (110.4 mg, 0.7988 mmol, 4.0 equiv) and 3-bromopropylene (69 μL, 0.80 mmol, 4.0 equiv). The mixture was stirred at 60 ℃ for 12 h. After completion (determined by TLC analysis), the solvent was evaporated under reduced pressure and the crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to give product (101.4 mg, 0.1743 mmol, 87% yield). Diisobutylaluminium hydride (348 μL of a 1.0 M solution in cyclohexane, 0.348 mmol, 2.0 equiv) was added dropwise to a solution of the above product (101.4 mg, 0.1743 mmol, 1.0 equiv) in anhydrous DCM (2.0 mL) under Ar at –78 ℃ over 10 min and the mixture was stirred for 2 h. After completion, the mixture was quenched with aqueous NH_4Cl. The mixture was allowed to warm to rt and stirred for 1 h. The layers were separated and the aqueous layer was extracted with DCM (3 × 5 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure to give the crude allylic alcohol. To a solution of the allylic alcohol and DMAP (2.1 mg, 0.017 mmol, 10 mol%) in DCM (1.0 mL), acetic anhydride (33 μL, 0.35 mmol, 2.0 equiv) and Et_3N (45 μL, 0.35 mmol, 2.0 equiv) was added and the reaction mixture was stirred at rt. After completion, the mixture was purified by flash chromatography on silica gel (petroleum ether/ EtOAc = 10/1) to give allyl acetates product **20**: 81.2 mg, as a yellow oil, 70% yield, over 3 steps; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) (d, J = 8.0 Hz, 2H), 7.40–7.18 (m, 6H), 7.11–6.99 (m, 3H), 6.97–6.79 (m, 1H), 6.73–6.37 (m, 1H), 6.30 (d, J = 14.6 Hz, 1H), 6.18–5.91 (m, 3H), 5.83–5.38 (m, 2H), 4.89–4.65 (m, 2H), 4.57 (d, J = 6.4 Hz, 2H), 4.48–4.15 (m, 1H), 4.03–3.84 (m, 1H), 2.31 (s, 3H), 1.99 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 170.8, 155.9, 153.6, 153.5, 151.3, 143.8, 137.7, 136.4, 132.6, 129.6, 128.9, 128.5, 128.3, 127.7, 127.2, 124.6, 124.2, 122.7, 122.0, 121.2, 119.3, 116.8, 112.0, 109.9, 109.7, 64.6, 53.5, 41.7, 21.5, 20.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{31}NO_6SNa^+$ 604.1765; Found 604.1756.

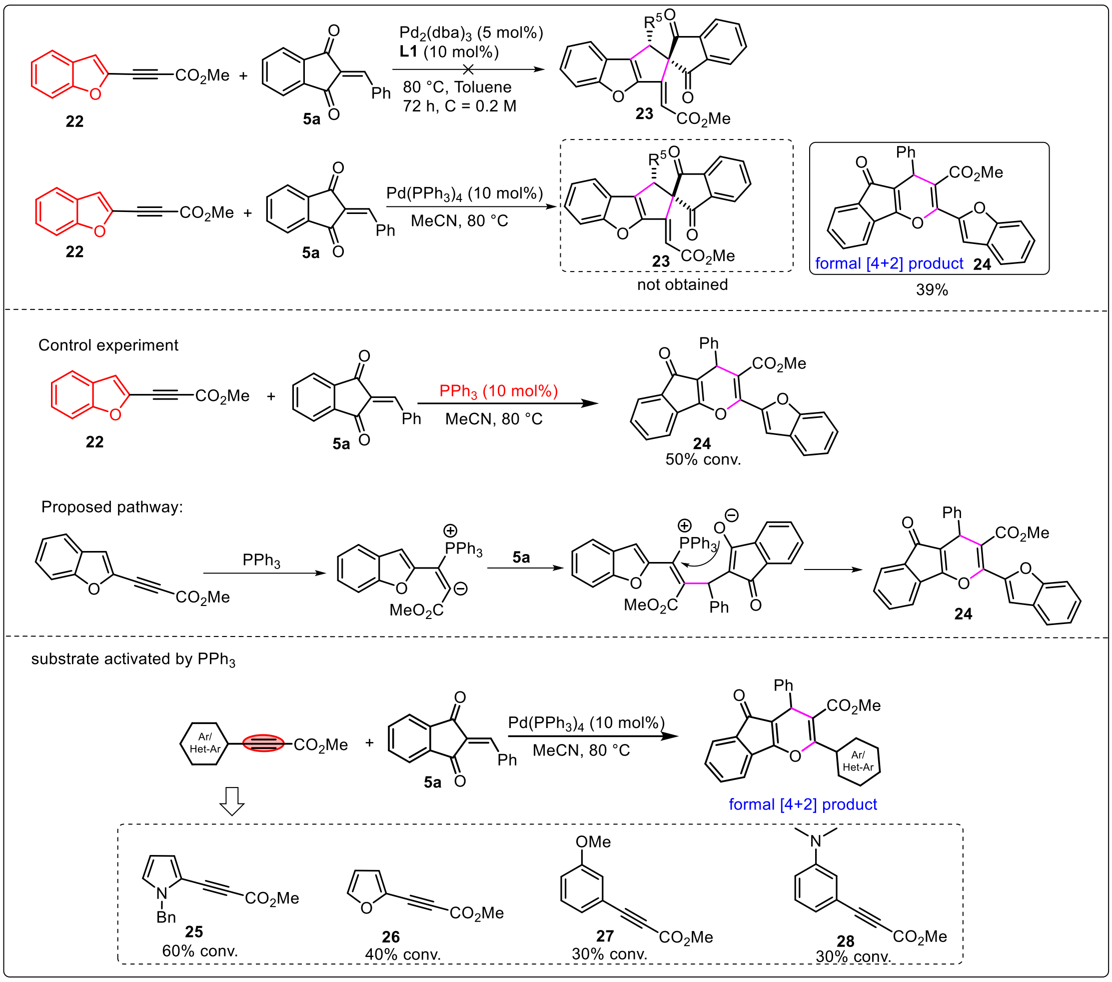
An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **20** (58.1

mg, 0.0998 mmol) and $Pd(PPh_3)_4$ (11.5 mg, 0.0100 mmol, 10 mol%). The tube was then evacuated and filled with argon. This cycle was repeated three times and degassed toluene (1.0 mL) was added via syringe. The mixture was stirred at 80 ℃ for 15 h. After completion, the mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1–6/1) to give product **21**: 34.0 mg, as a yellow solid, 71% yield; mp 155–157 ℃; $[\alpha]^{25}_{D}$ = –44.0 (*c* = 0.25, in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak column ID, *i*PrOH/*n*Hexane = 40/60, flow rate: 1.0 mL/min, 254 nm, t (major) = 28.51 min, t (minor) = 35.14 min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.70 (d, *J* = 8.0 Hz, 4H), 7.46–7.37 (m, 6H), 7.32–7.27 (m, 4H), 7.27–7.17 (m, 8H), 7.03–6.96 (m, 2H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.11 (ddd, *J* = 15.4, 10.4, 4.9 Hz, 2H), 5.98 (d, *J* = 3.3 Hz, 2H), 5.79 (s, 2H), 5.68–5.57 (m, 4H), 4.79 (dd, *J* = 14.2, 4.9 Hz, 2H), 3.49 (dd, *J* = 14.2, 10.4 Hz, 2H), 2.43 (s, 6H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ (ppm) 156.8, 153.9, 153.7, 150.3, 143.9, 138.3, 137.2, 129.8, 128.8, 128.4, 127.8, 127.1, 124.4, 124.2, 123.0, 122.8, 121.0, 119.0, 116.3, 112.1, 110.0, 109.0, 53.0, 41.6, 21.6; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{58}H_{46}N_2O_8S_2Na^+$ 985.2588; Found 985.2590.

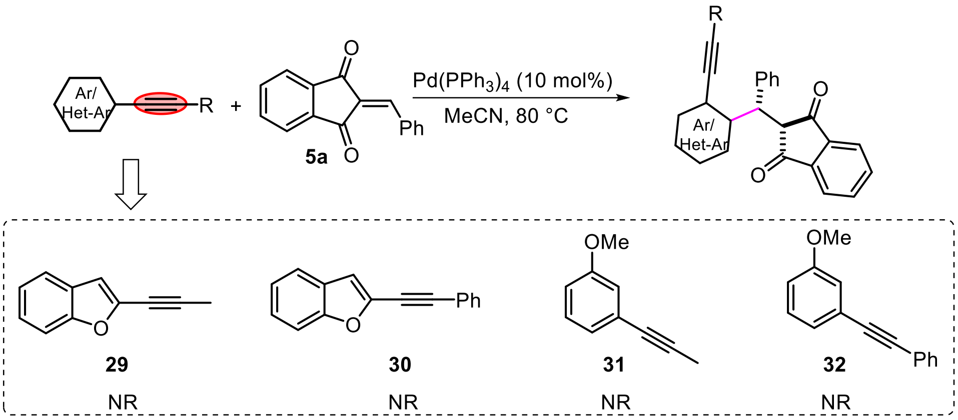
15. More investigation on substrates scope

1) Other aromatic compounds

Benzofuran derivative **22** was applied to the reaction with **5a** under the standard conditions, but it did not work. When the reaction was carried out under the catalysis of $Pd(PPh_3)_4$, **24** was obtained instead of desired **23**. The control experiment indicated that the reaction was catalyzed by PPh_3 via a Rauhut–Currier pathway, followed by annulation to give the formal [4+2] adduct. Similar phenomenon was observed for substrates **25**–**28**.

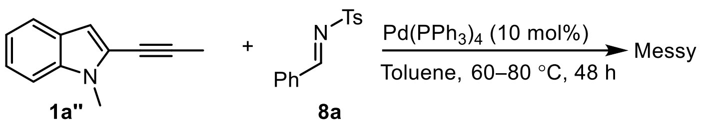


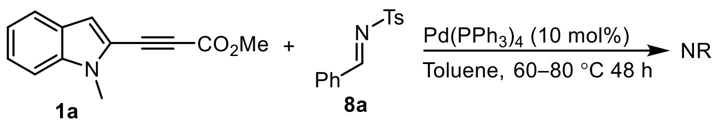
Since the electron-deficient alkynes mentioned above were activated by PPh_3 rather than Pd, some electron-neutral alkyne derivatives were tested. However, compounds **29**–**32** were inert in the reaction.

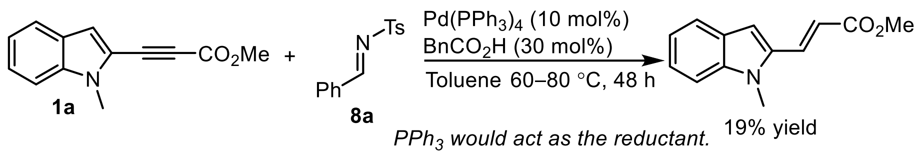


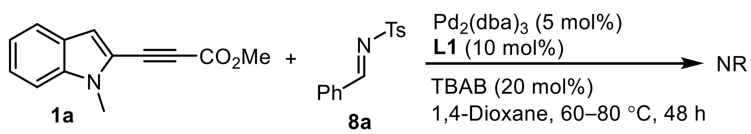
2) Other electrophiles

Imine **8a** was investigated with 2-alkyne indole **1a** or **1a″** under the catalysis of palladium. Unfortunately, those substrates did not undergo the desired FC addition reaction.

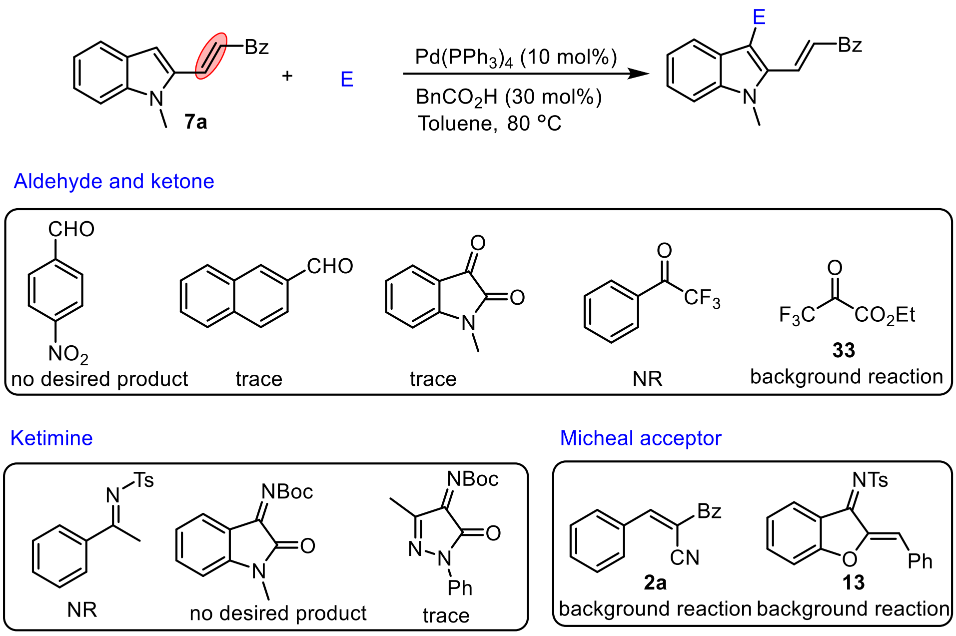






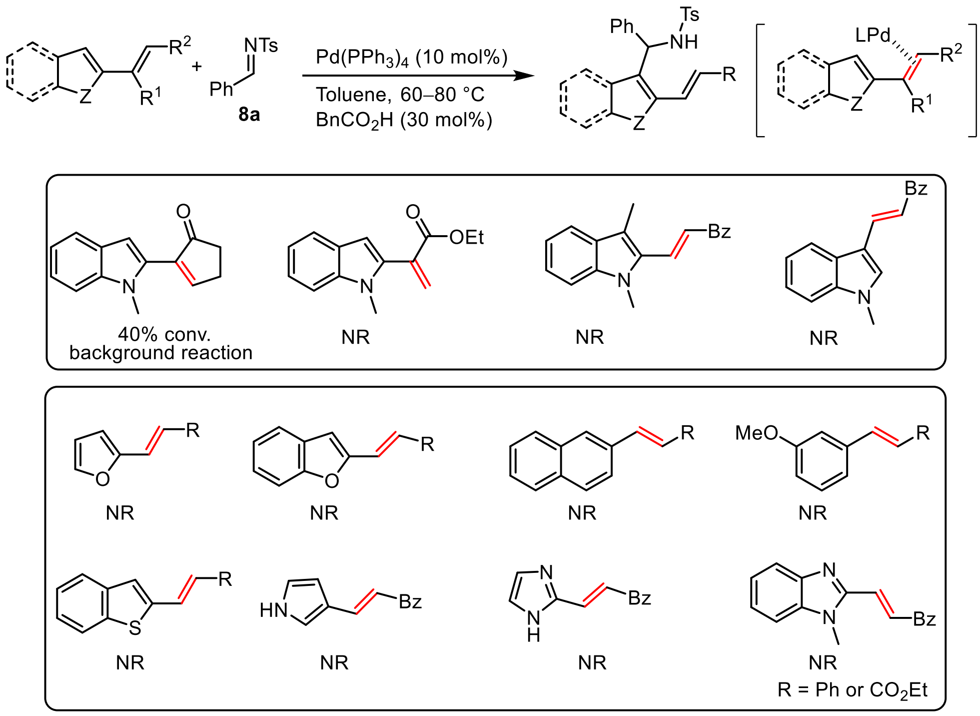


Some other electrophiles, including carbonyls, ketimines and Michael acceptors, were investigated with 2-alkenyl indole **7a** under the catalysis of $Pd(PPh_3)_4$. It was found that most carbonyls and imines listed as below were not reactive. In addition, some compounds, such as **33**, Micheal acceptor **2a** and **13**, could undergo the reaction with **7a** in the absence of Pd^0 (background reaction).



3) Other styrene-type substrates

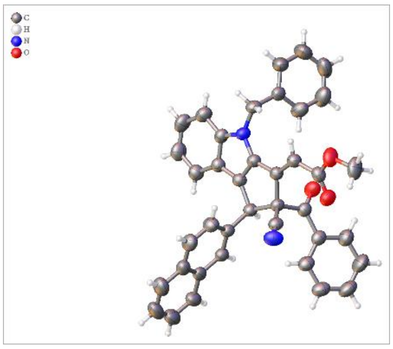
Considering that the aromatic rings are activated by Pd^0 which coordinates to the conjugated unsaturated bond as a π-Lewis base, we applied more styrene-type substrates to the reaction. However, most of the aromatic compounds were inert, probably due to some steric and electronic effects.

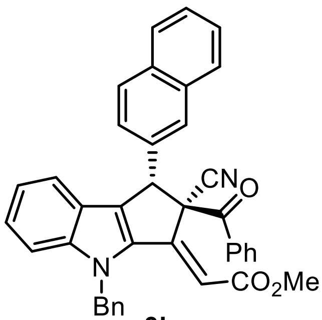


16. X-ray crystallographic data and structural refinement

(1) Crystal data and structural refinement for 3i

Procedure for the recrystallisation of **3i**: To a 10 mL tube containing **3i** (20.0 mg) were added $CHCl_3$ (1.0 mL) and Et_2O (2.0 mL). The mixture was heated until a clear solution was formed, which was kept aside and sealed by a piece of weighing paper with a tiny hole at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of enantiopure **3i**. The data were collected by a Bruker APEX-II CCD diffractometer equipped with a Cu radiation source (Kα = 1.54178 Å) at 273.15 K. CCDC 2251805 (**3i**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





3i

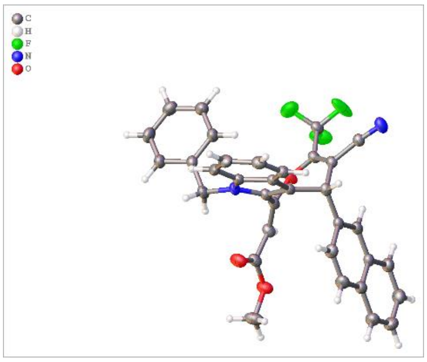
(ellipsoid contour probability 50%)

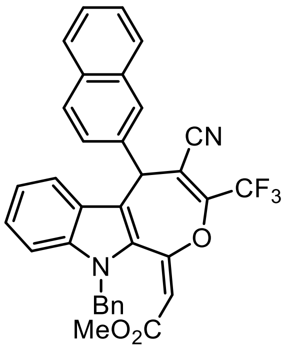
Identification code	**3i**
Empirical formula	$C_{39}H_{28}N_2O_3$
Formula weight	572.63
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.1245(4)
b/Å	10.5529(3)
c/Å	13.5415(5)
α/°	90
β/°	107.914(2)
γ/°	90
Volume/Å^3	1512.64(9)
Z	2
ρcalcg/cm^3	1.257
μ/mm^{-1}	0.632
F(000)	600.0
Crystal size/mm^3	0.27 × 0.19 × 0.04

Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.86 to 126.98
Index ranges	$-12 \leq h \leq 12$, $-11 \leq k \leq 12$, $-14 \leq l \leq 15$
Reflections collected	15015
Independent reflections	4840 [R_{int} = 0.0439, R_{sigma} = 0.0359]
Data/restraints/parameters	4840/1/398
Goodness-of-fit on F^2	1.040
Final R indexes [I> = 2σ (I)]	R1 = 0.0318, wR2 = 0.0838
Final R indexes [all data]	R1 = 0.0355, wR2 = 0.0866
Largest diff. peak/hole / e $Å^{-3}$	0.10/-0.14
Flack parameter	0.08(12)

(2) Crystal data and structural refinement for *rac*-4d

Procedure for the recrystallisation of *rac*-**4d**: To a 10 mL tube containing *rac*-**4d** (10.0 mg) were added $CHCl_3$ (0.5 mL). The mixture was heated until a clear solution was formed, which was kept aside and sealed by a piece of weighing paper with a tiny hole at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine structural refinement for *rac*-**4d**. The data were collected by a Bruker APEX-II CCD diffractometer equipped with a Mo radiation source (Kα = 0.71073 Å) at 150.0 K. CCDC 2251806 (*rac*-**4d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





rac-**4d**

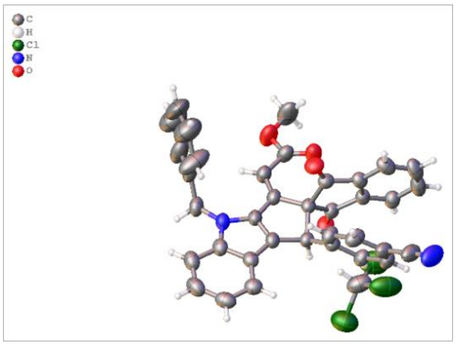
(ellipsoid contour probability 50%)

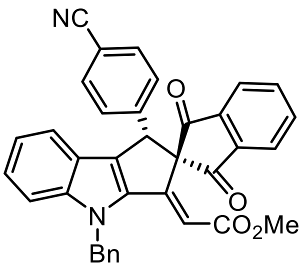
Identification code	*rac*-**4d**
Empirical formula	$C_{34}H_{23}F_3N_2O_3$
Formula weight	564.54
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1

a/Å	10.0380(5)
b/Å	12.1514(6)
c/Å	12.3554(7)
α/°	77.395(2)
β/°	67.131(2)
γ/°	85.909(2)
Volume/$Å^3$	1354.98(12)
Z	2
$\rho_{calc}g/cm^3$	1.384
μ/mm^{-1}	0.103
F(000)	584.0
Crystal size/mm^3	0.28 × 0.21 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/	4.404 to 54.988
Index ranges	-13 ≤ h ≤ 12, -15 ≤ k ≤ 15, -15 ≤ l ≤ 16
Reflections collected	19422
Independent reflections	6096 [R_{int} = 0.0795, R_{sigma} = 0.0713]
Data/restraints/parameters	6096/0/380
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0525, wR_2 = 0.1142
Final R indexes [all data]	R_1 = 0.0971, wR_2 = 0.1319
Largest diff. peak/hole / e $Å^{-3}$	0.48/-0.34

(3) Crystal data and structural refinement for 6c

Procedure for the recrystallisation of **6c**: To a 10 mL tube containing **6c** (20.0 mg) were added $CHCl_3$ (1.0 mL) and Et_2O (2.0 mL). The mixture was heated until a clear solution was formed, which was kept aside and sealed by a piece of weighing paper with a tiny hole at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of enantiopure **6c**. The data were collected by a Bruker APEX-II CCD diffractometer equipped with a Mo radiation source (Kα = 0.71073 Å) at 273.15 K. CCDC 2251807 (**6c**·$CHCl_3$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





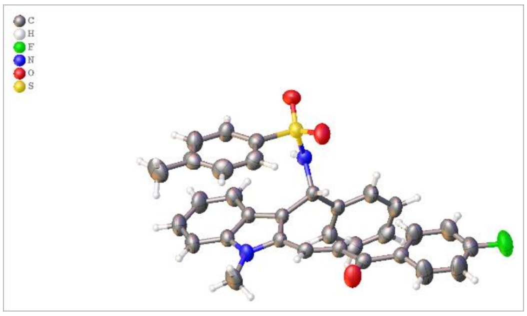
6c·CHCl$_3$

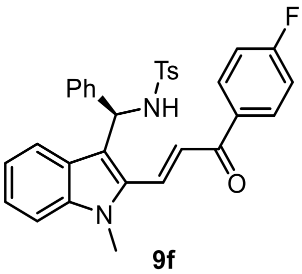
(ellipsoid contour probability 50%)

Identification code	**6c ·CHCl$_3$**
Empirical formula	$C_{37}H_{25}Cl_3N_2O_4$
Formula weight	667.94
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	13.2537(4)
b/Å	8.0062(2)
c/Å	15.7406(5)
α/°	90
β/°	94.6260(10)
γ/°	90
Volume/Å^3	1664.82(8)
Z	2
ρ_{calc}g/cm^3	1.332
μ/mm^{-1}	0.318
F(000)	688.0
Crystal size/mm^3	0.43 × 0.15 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.188 to 55.064
Index ranges	$-17 \le h \le 17$, $-10 \le k \le 10$, $-19 \le l \le 20$
Reflections collected	35129
Independent reflections	7649 [R_{int} = 0.0619, R_{sigma} = 0.0484]
Data/restraints/parameters	7649/13/398
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0667, wR_2 = 0.1763
Final R indexes [all data]	R_1 = 0.1003, wR_2 = 0.2034
Largest diff. peak/hole / e Å^{-3}	0.40/-0.48
Flack parameter	0.05(3)

(4) Crystal data and structural refinement for 9f

Procedure for the recrystallisation of **9f**: To a 10 mL tube containing **9f** (10.0 mg) were added $CHCl_3$ (1.0 mL) and *n*-hexane (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside and sealed by a piece of weighing paper with a tiny hole at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of enantiopure **9f**. The data were collected by a Bruker APEX-II CCD diffractometer equipped with a Mo radiation source (Kα = 0.71073 Å) at 302.0 K. CCDC 2251808 (**9f**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





9f

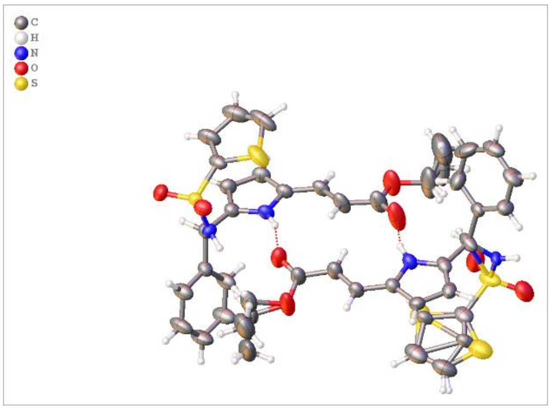
(ellipsoid contour probability 50%)

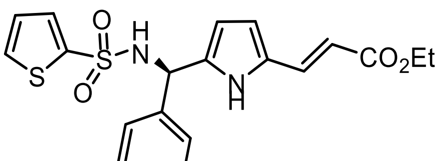
Identification code	**9f**
Empirical formula	$C_{32}H_{27}FN_2O_3S$
Formula weight	538.61
Temperature/K	302.0
Crystal system	triclinic
Space group	P1
a/Å	9.2530(5)
b/Å	9.3566(5)
c/Å	9.9037(6)
α/°	106.668(2)
β/°	101.698(2)
γ/°	117.979(2)
Volume/Å^3	665.24(7)
Z	1
ρ_{calc}g/cm^3	1.344
μ/mm^{-1}	0.166
F(000)	282.0
Crystal size/mm^3	0.41 × 0.25 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.682 to 55.258

Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-12 \leq l \leq 12$
Reflections collected	19634
Independent reflections	6078 [R_{int} = 0.0484, R_{sigma} = 0.0451]
Data/restraints/parameters	6078/4/358
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0386, wR_2 = 0.0881
Final R indexes [all data]	R_1 = 0.0504, wR_2 = 0.0941
Largest diff. peak/hole / e Å^{-3}	0.15/-0.19
Flack parameter	0.01(3)

(5) Crystal data and structural refinement for 11g

Procedure for the recrystallisation of **11g**: To a 10 mL tube containing **11g** (15.0 mg) were added $CHCl_3$ (1.0 mL) and *n*-hexane (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside and sealed by a piece of weighing paper with a tiny hole at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of enantiopure **11g**. The data were collected by a Bruker APEX-II CCD diffractometer equipped with a Mo radiation source (Kα = 0.71073 Å) at 184.0 K. CCDC 2251809 (**11g**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.





11g

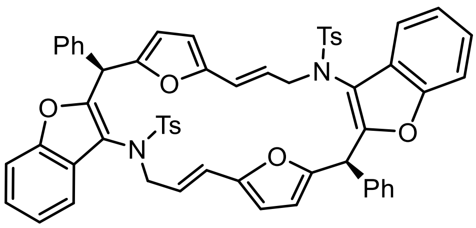
(ellipsoid contour probability 50%)

Identification code	**11g**
Empirical formula	$C_{20}H_{20}N_2O_4S_2$
Formula weight	461.08
Temperature/K	184.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.1003(4)
b/Å	15.1715(5)
c/Å	13.9176(5)

α/°	90
β/°	101.792(2)
γ/°	90
Volume/Å^3	2087.68(13)
Z	2
ρ_{calc}g/cm^3	1.322
μ/mm^{-1}	0.283
F(000)	868.0
Crystal size/mm^3	0.38 × 0.24 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.018 to 55.086
Index ranges	$-13 \le h \le 13$, $-19 \le k \le 19$, $-18 \le l \le 18$
Reflections collected	37794
Independent reflections	9567 [R_{int}= 0.0821, R_{sigma}= 0.0654]
Data/restraints/parameters	9567/38/562
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1156
Final R indexes [all data]	R_1 = 0.0789, wR_2 = 0.1273
Largest diff. peak/hole / e Å^{-3}	0.53/-0.53
Flack parameter	-0.01(4)

(6) Crystal data and structural refinement for 21

Procedure for the recrystallisation of **21**: To a 10 mL tube containing **21** (20.0 mg) were added EtOAc (1.0 mL) and *n*-hexane (1.0 mL). The mixture was heated until a clear solution was formed, which was kept aside and sealed by a piece of weighing paper with a tiny hole at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of enantiopure **21**. The data were collected by a Bruker APEX-II CCD diffractometer equipped with a Mo radiation source (Kα = 0.71073 Å) at 302.0 K. CCDC 2251810 (**21**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



21

(ellipsoid contour probability 50%)

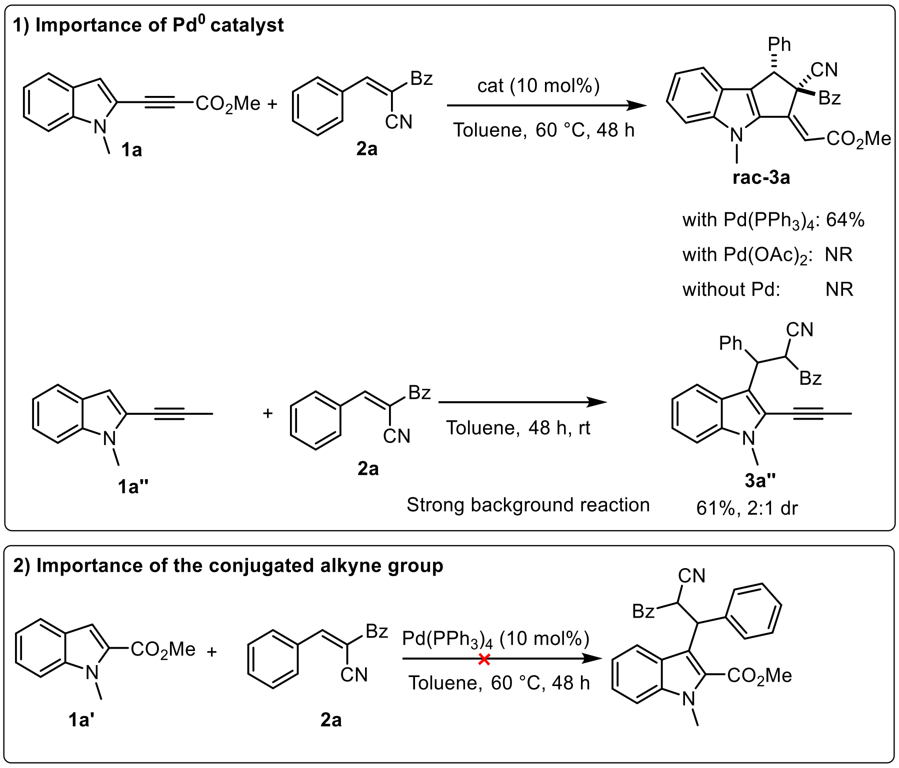
Identification code	**21**
Empirical formula	$C_{58}H_{44}N_2O_8S_2$
Formula weight	961.07
Temperature/K	302.0
Crystal system	monoclinic
Space group	C2
a/Å	32.1431(8)
b/Å	7.1890(2)
c/Å	11.8007(3)
α/°	90
β/°	98.963(2)
γ/°	90
Volume/Å^3	2693.57(12)
Z	2
ρ_{calc}g/cm^3	1.185
μ/mm^{-1}	0.153
F(000)	1004.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.81 to 49.998
Index ranges	$-38 \leq h \leq 38$, $-8 \leq k \leq 8$, $-14 \leq l \leq 14$
Reflections collected	22880
Independent reflections	4626 [R_{int} = 0.0453, R_{sigma} = 0.0315]
Data/restraints/parameters	4626/1/317
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0425, wR_2 = 0.1046
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1151
Largest diff. peak/hole / e Å^{-3}	0.29/-0.17
Flack parameter	0.07(3)

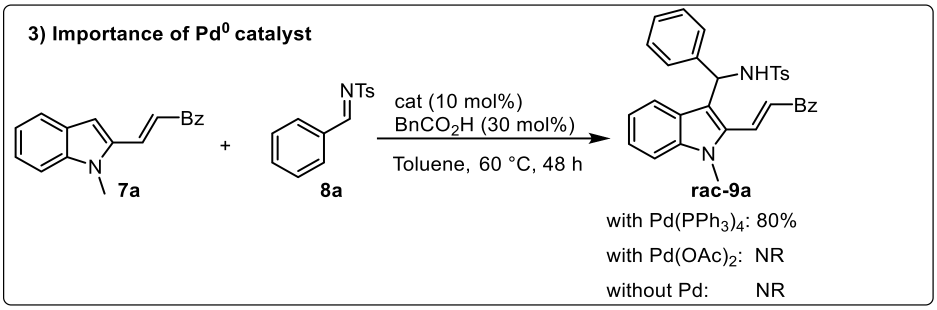
17. Mechanism studies

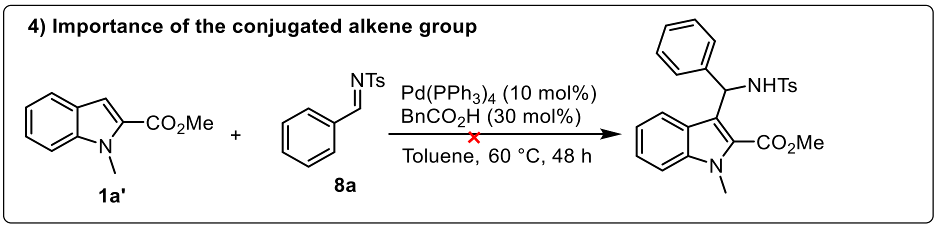
(1) Control experiment

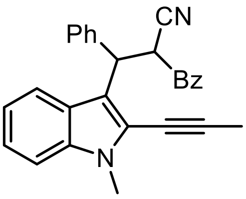
To get more insight into the mechanism, some control experiments were carried out. Substrate **1a′′** without an electron-withdrawing group showed high reactivity, and it could undergo Friedel−Crafts reaction with **2a** in the absence of Pd catalyst. In contrast, **1a** was inert without catalysts, while the reaction proceed smoothly under the catalysis of $Pd(PPh_3)_4$, indicating that there is no background reaction. No reaction occurred with $Pd(OAc)_2$, demonstrating the importance of Pd^0. Besides, indole derivative **1a′** was applied to the reaction with **2a** under the catalysis of $Pd(PPh_3)_4$, but no Friedel−Crafts product was observed, demonstrating the importance of the conjugated alkyne group. Similar phenomenon was observed for the reaction of 2-alkenyl indole **7a** with imine **2a**, implying the importance of Pd^0 and the conjugated alkene group.

1) Control experiment of indole derivetives and enone **2a**.

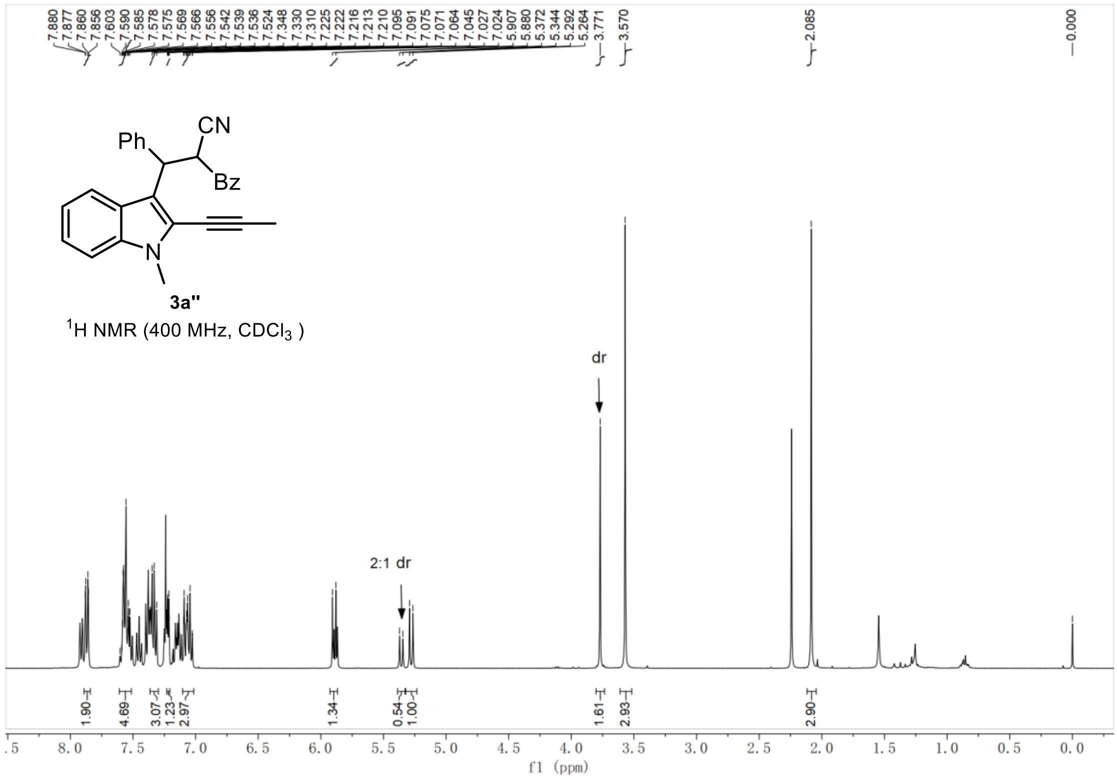




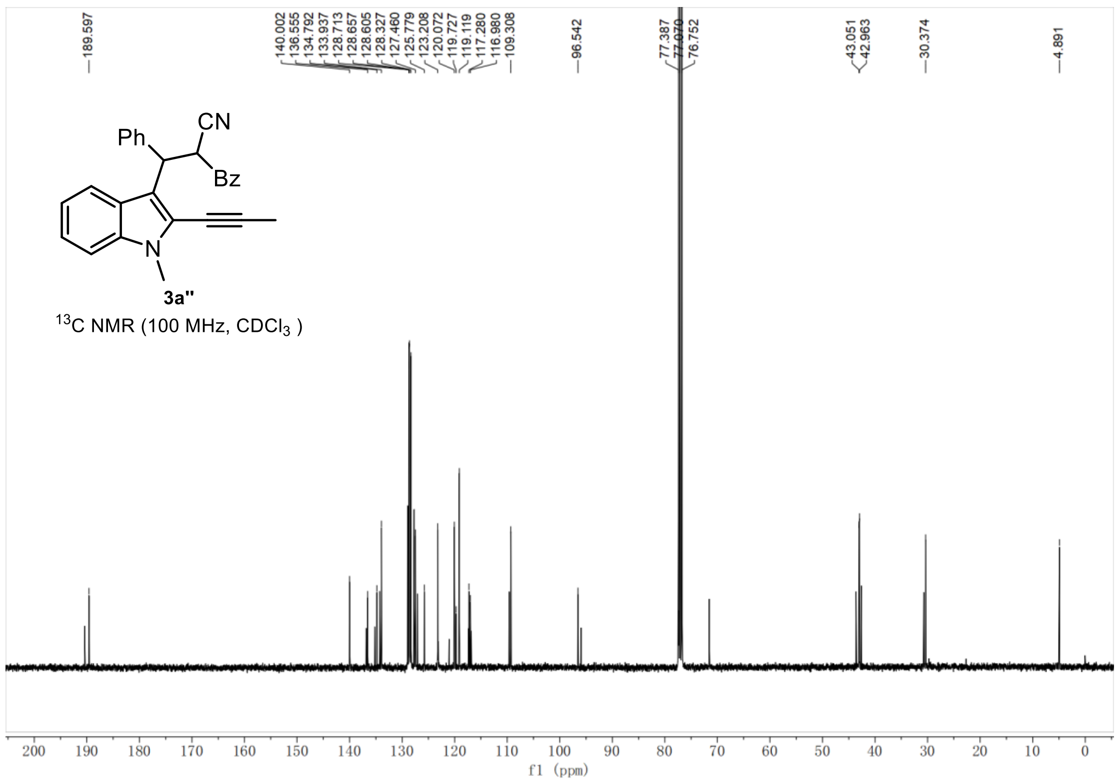




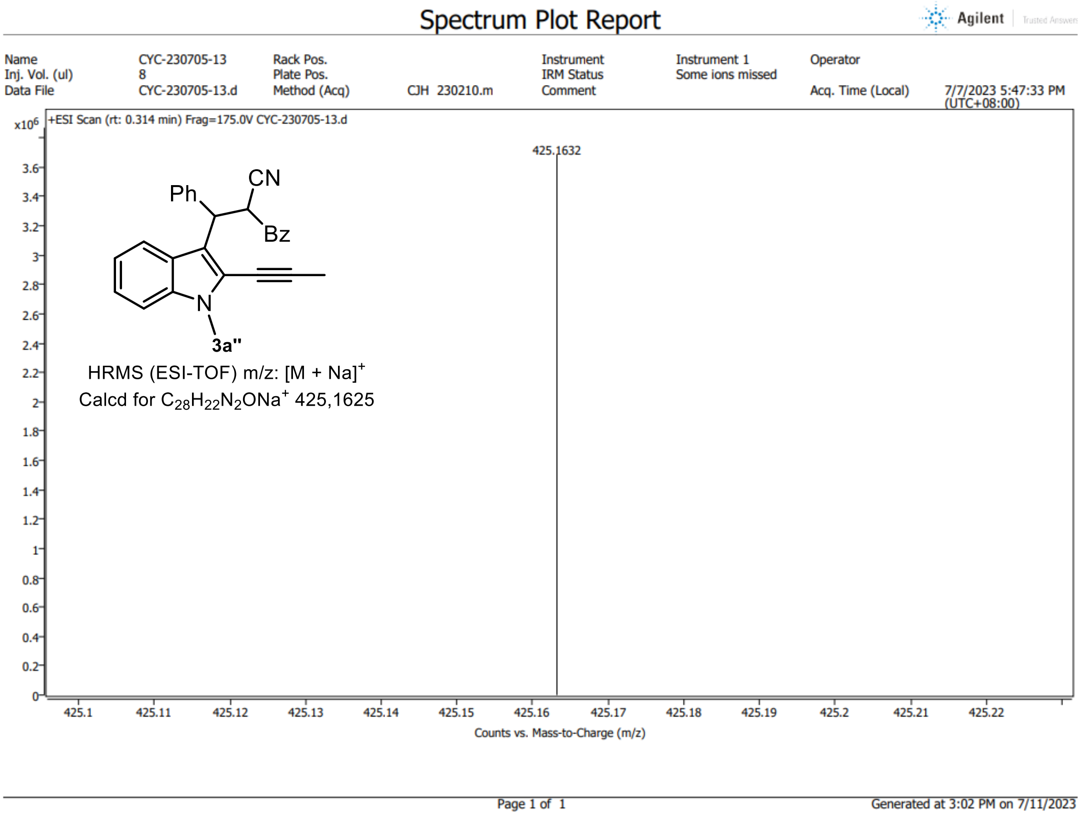
1a″ (8.5 mg, 0.050 mmol) and **2a** (11.6 mg, 0.0500 mmol) were dissolved in toluene (0.5 mL), and the mixture was stirred at rt for 48 h. After completion, it was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give product **3a″**: 15.4 mg, 61% yield, colorless oil; 2:1 dr; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89–7.84 (m, 2H), 7.61–7.51 (m, 5H), 7.36–7.30 (m, 3H), 7.23–7.21 (m, 1H), 7.10–7.01 (m, 3H), 5.89 (d, *J* = 10.9 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 3.57 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) 189.6, 140.0, 136.6, 134.8, 133.9, 128.71, 128.66, 128.6, 128.3, 127.5, 125.8, 123.2, 120.1, 119.7, 119.1, 117.3, 117.0, 109.3, 96.5, 71.6, 43.1, 43.0, 30.4, 4.9; **HRMS** (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{22}N_2ONa^+$ 425.1625, found 425.1632.



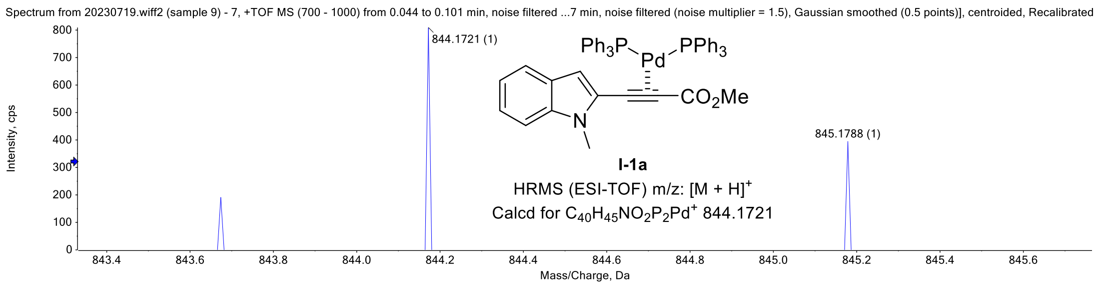
3a''
^{1}H NMR (400 MHz, $CDCl_3$)
2:1 dr
dr
f1 (ppm)

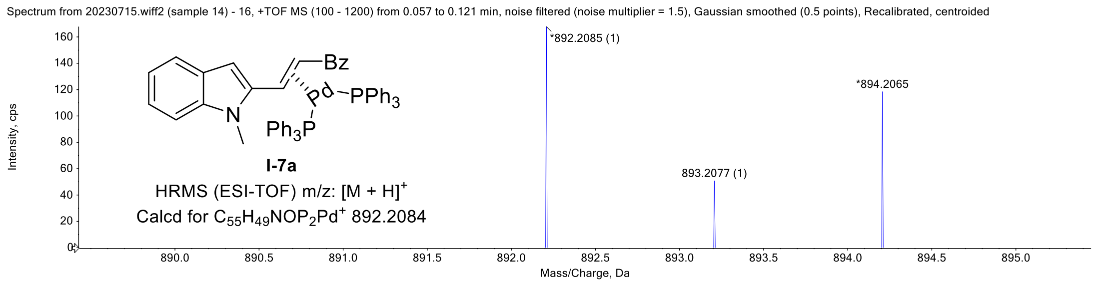


3a''
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

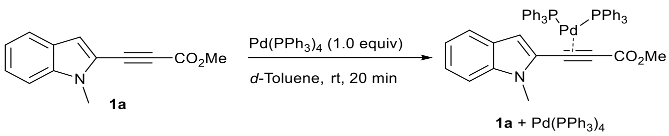


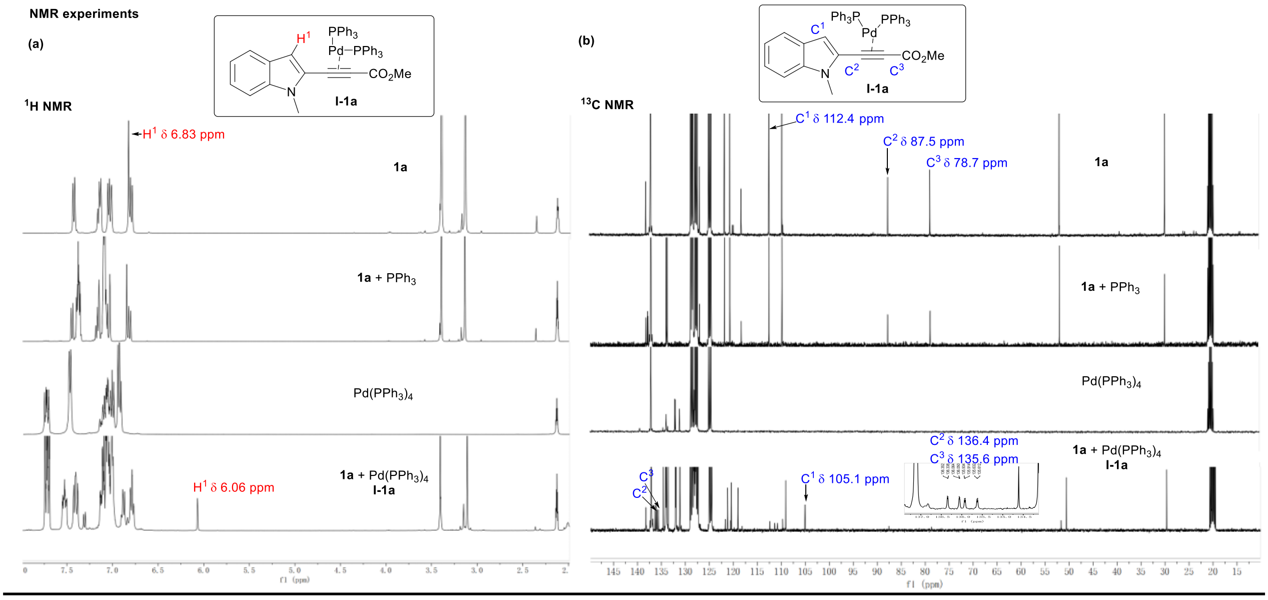
(2) HRMS study

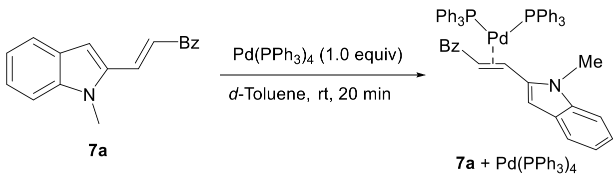


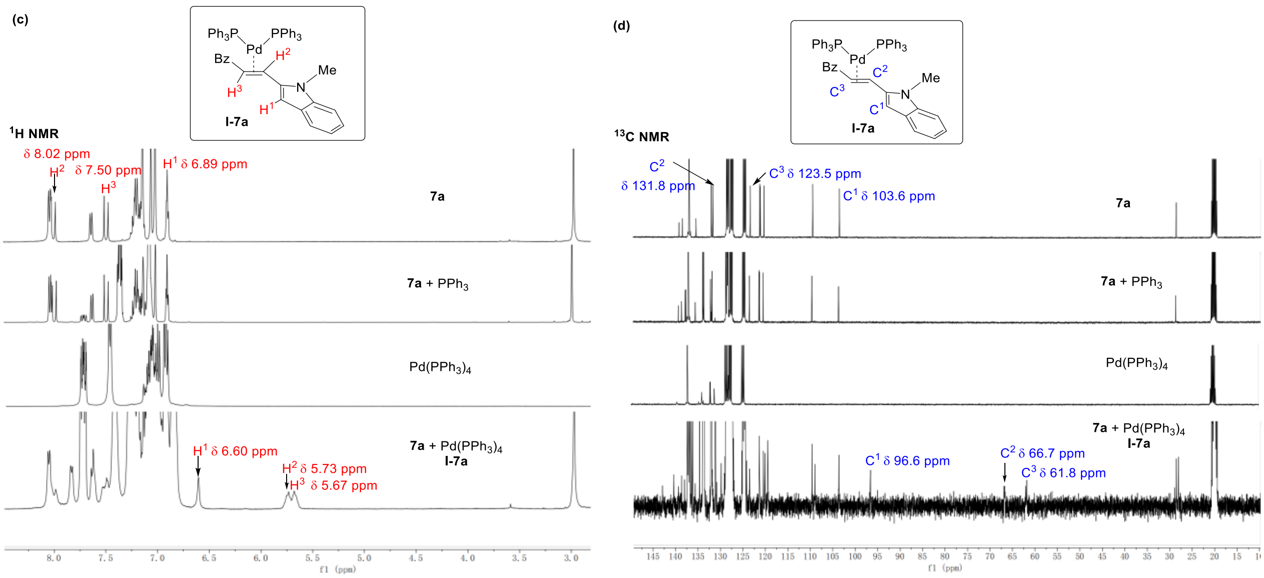


(3) NMR experiments

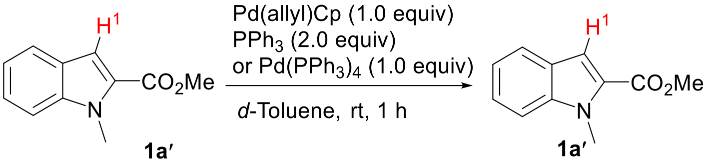


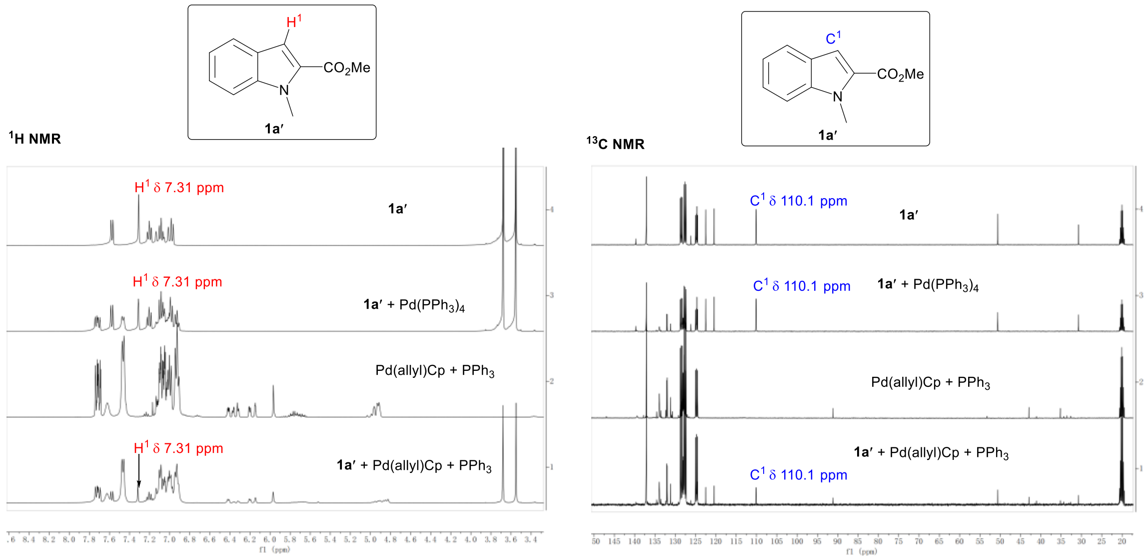






The ^{1}H NMR analysis showed that 3-H (H^1) of **1a** experienced apparent high-field shifts when $Pd(PPh_3)_4$ was added (6.06 *vs* 6.83 ppm). The possible nucleophilic attack of PPh_3 to electron-deficient **1a** was not observed by mixing **1a** and PPh_3 **(a)**. The ^{13}C NMR experiments showed that the signals of the triple bond of **1a** disappeared (around 70−80 ppm) after adding $Pd(PPh_3)_4$, while new peaks were observed at the sp^2-carbon region (C^2 and C^3, around 136 ppm); in contrast, C^1 of **1a** experienced significant high-field shifts (105.1 *vs* 112.4 ppm) **(b)**. Similarly, the signals of H^1, H^2, H^3, C^1, C^2 and C^3 of **7a** were all high-field shifted in the presence of $Pd(PPh_3)_4$, according to the NMR experiments. These results well supported that the proposed complexes **I-1a** and **I-7a** would be formed, and verified the π-Lewis base activation of Pd^0 through the coordination to the unsaturated group **(c** and **d)**.





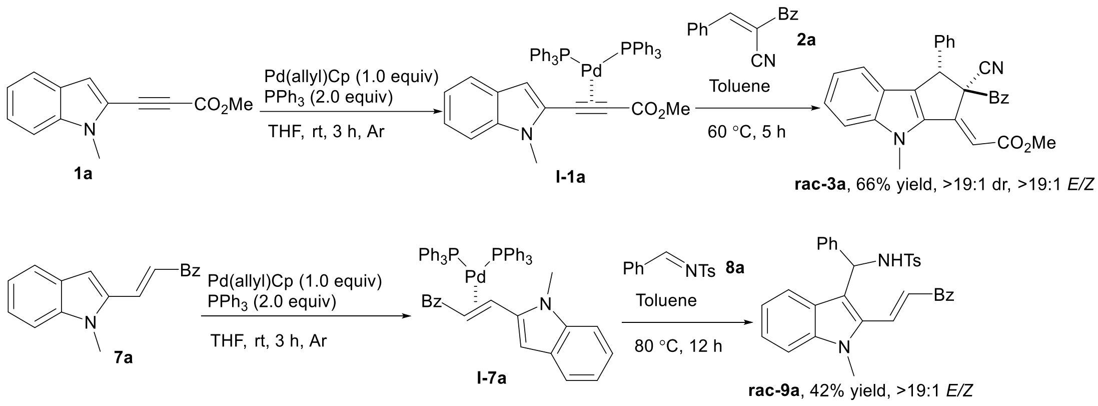
In contrast, no chemical shifts were observed for substrate **1a′** when mixed with $Pd(PPh_3)_4$ or Pd(allyl)Cp, demonstrating the importance of the conjugated triple or double bond.

Procedure of NMR experiments

An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with **1b** (2.9 mg, 0.010 mmol) or **7a** (2.6 mg, 0.010 mmol) and $Pd(PPh_3)_4$ (11.5 mg, 0.0100 mmol). The tube was then evacuated and filled with argon. This cycle was repeated five times, and deuterated toluene (0.5 mL) was added via syringe. The resulting solution was stirred at rt for 20 min. The mixture was analyzed by NMR.

An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with **1a′** (3.8 mg, 0.020 mmol), PPh_3 (10.5 mg, 0.0400 mmol) and Pd(allyl)Cp (4.3 mg, 0.020 mmol). The tube was then evacuated and filled with argon. This cycle was repeated five times, and deuterated toluene (0.5 mL) was added via syringe. The resulting solution was stirred at rt for 1 h. The mixture was analyzed by NMR.

(4) Transformation of η^2-Pd^0-unsaturated indole complexes with electrophiles



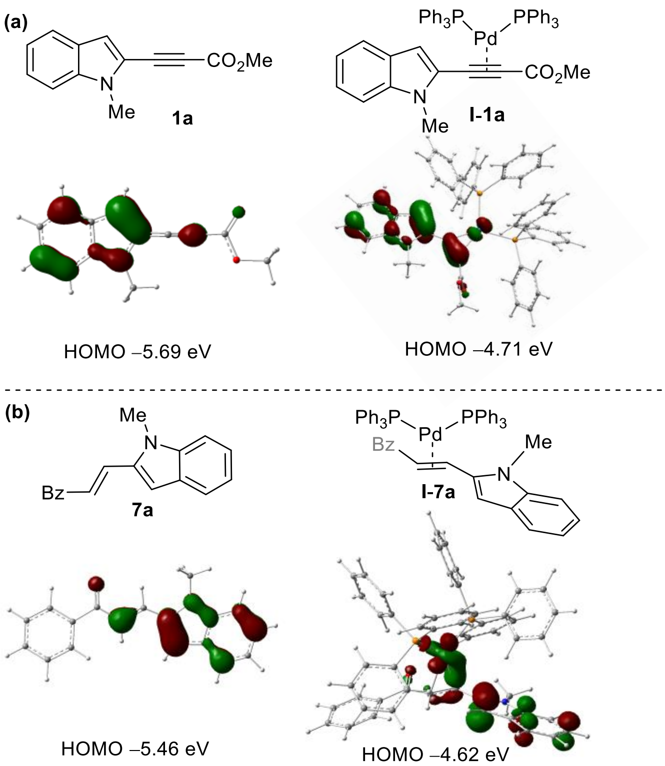
An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with unsaturated indoles **1a** (21.3 mg, 0.100 mmol, 1.0 equiv) or **7a** (26.1 mg, 0.100 mmol, 1.0 equiv), PPh_3 (52.4 mg, 0.200 mmol, 2.0 equiv), Pd(allyl)Cp (21.2 mg, 0.100 mmol, 1.0 equiv). The tube was then evacuated and back-filled three times with argon, and degassed THF (0.5 mL) was added via syringe. The resulting solution was stirred at room temperature for 3 h. After completion, the mixture was concentrated and dried in vacuum to give crude product **I-1a** or **I-7a**. Then **I-1a** and **2a** were added to an oven-dried 10 mL Schlenk tube. After the tube was evacuated and back-filled three times with argon, degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at 60 ℃ for 5 h. After completion, the crude product was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) to give ***rac*-3a** (29.4 mg, 66% yield, >19:1 dr, >19:1 *E/Z*). Similarly, **I-7a** and **8a** were added to an oven-dried 10 mL Schlenk tube. After the tube was evacuated and back-filled three times with argon, degassed toluene (0.5 mL) was added via syringe. The resulting solution was stirred at 80 ℃ for 12 h. After completion, Et_2O (3 mL) was added and the mixture was stirred 30 min at 0 ℃. The precipitates were filtered, and washed with cold Et_2O (3 × 3 mL). The cake was collected and dissolved in DCM. The mixture was filtered again, and washed with DCM (5 × 5 mL). The filtrate was concentrated to give ***rac*-9a** (21.8 mg, 42% yield, >19:1 *E/Z*).

(5) DFT calculations

1) Computational details

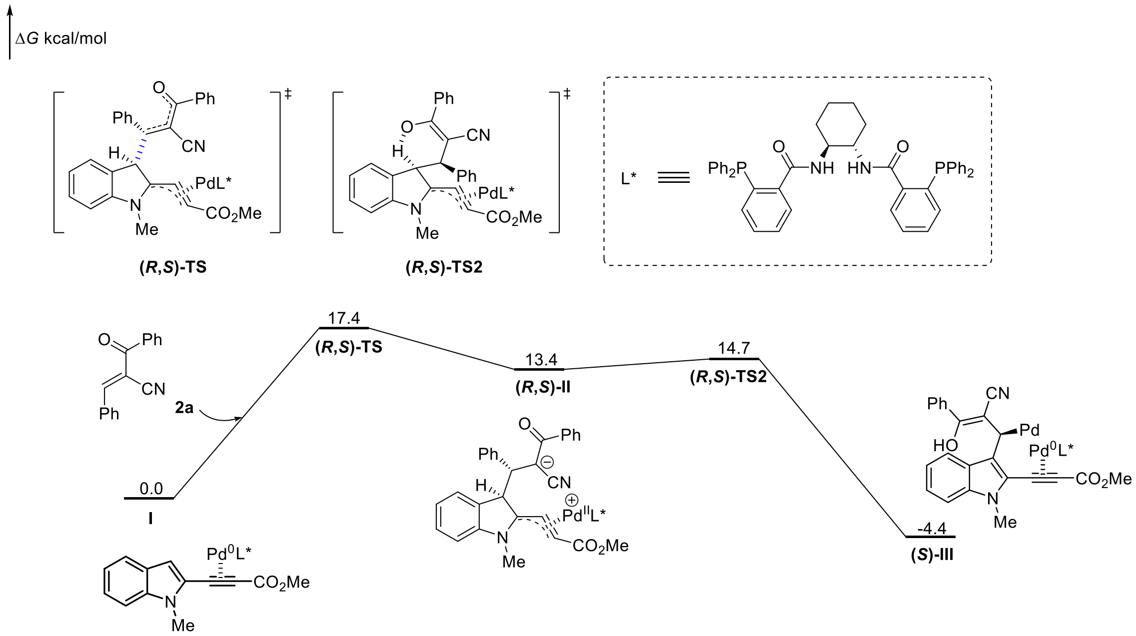
In this work, all geometry optimizations and single-point energy calculations were carried out using Gaussian 09.[11] Geometries of minima and transition states were optimized using the B3LYP functional[12] with basis set 6-31G(d) (SDD for Pd atom) in gas phase. Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum or a transition state structure, as well as deriving the thermochemical corrections for the enthalpies and free energies. Solvation energy corrections were calculated in 1,4-Dioxane with the continuum solvation model (SMD)[13] based on the gas-phase optimized geometries. To gain more accurate results, the M06 functional[14] with basis set 6-311++G(d,p) (SDD for Pd atom) was used for solvation single-point energy calculations. The integration grids defined by the 'Int=Ultrafine' keyword were used for all calculations.

2) DFT calculations on the unsaturated indoles and related η²-Pd⁰-complexes (The calculations were performed at the B3LYP/6-31G(d)(SDD for Pd) (298.15K) level of theory)



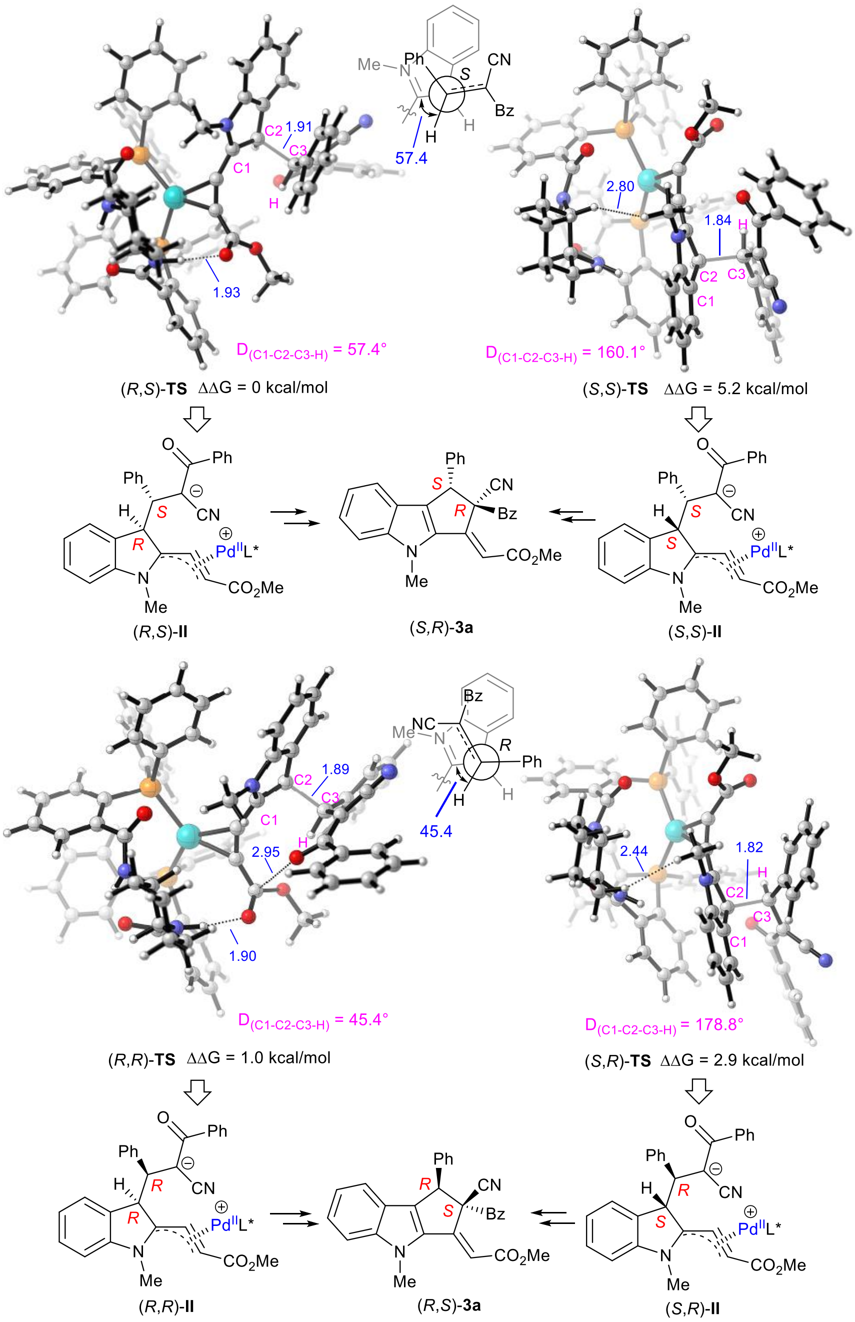
To get more insight into the catalytic mechanism, we conducted frontier molecular orbital (FMO) analysis on the Pd^0 complexes of unsaturated indoles. In comparison with the parent substrate alkyne **1a** (−5.69 eV) or alkene **7a** (−5.46 eV), the HOMO energy of corresponding η^2-Pd^0-complex **I-1a** (−4.71 eV) or **I-7a** (−4.62 eV) is apparently raised, respectively, supporting the π-Lewis back donation of Pd^0 as a Lewis base.

3) Computed energy profiles for the FC step and deprotonation step (The calculations were performed at the M06/6-311++G(d,p)(SDD for Pd)/SMD//B3LYP/6-31G(d)(SDD for Pd) (298.15K) level of theory)



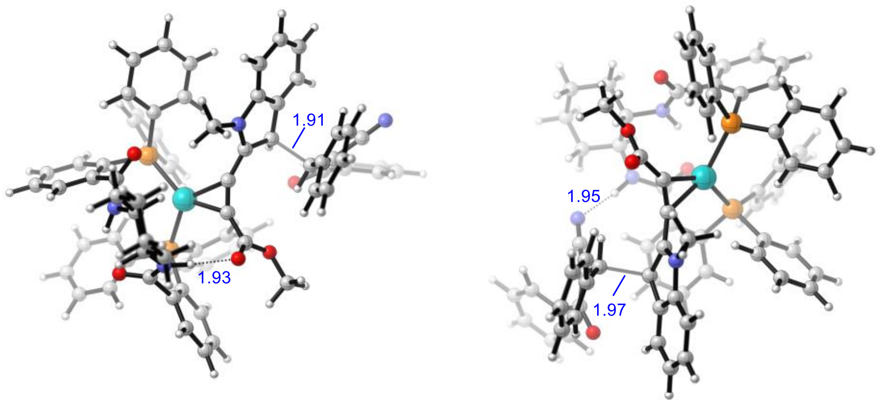
The electrophilic aromatic substitution contains two steps: 1) FC addition step, and 2) deprotonation/aromatisation. Unon the Pd^0-π-Lewis base activation, the FC addition step proceeds via (*R*,*S*)-**TS** to generate intermediate (*R*,*S*)-**II**. The energy barrier for (*R*,*S*)-**TS** is 17.4 kcal/mol, which is the highest in the whole process. Thus this is the rate-determining step. The subsequent deprotonation/aromatisation proceeds via an intramolecular 1,5-proton transfer [via (*R*,*S*)-**TS2**] to give aromatic substituted intermediate (*S*)-**III**. The relative free energy of (*R*,*S*)-**TS2** is 2.7 kcal/mol lower than that of (*R*,*S*)-**TS**, indicating that the FC addition step is irreversible. The subsequent Michael addition is not catalysed by Pd. Therefore, the FC addition step is the stereochemistry-determining step for this electrophilic aromatic substitution.

4) Enantioselectivity of the formation of chiral 3a (The calculations were performed at the M06/6-311++G(d,p)(SDD for Pd)/SMD//B3LYP/6-31G(d)(SDD for Pd) (298.15K) level of theory)



We also investigated the origins of enantioselectivity in the reaction of alkyne **1a** and enone **2a**. The enantiocontrol of this transformation was determined in the FC addition step, in which the first C–C bond was constructed, four transition states were considered. Transition states (*R*,*S*)-**TS** and (*S*,*S*)-**TS** would lead to product (*S*,*R*)-**3a** via (*R*,*S*)-**II** and (*S*,*S*)-**II**, respectively, and the stereogenic centre at 3-C of indole would disappear through deprotonation/aromatisation. On the other hand, (*R*,*R*)-**TS** and (*S*,*R*)-**TS** would lead to enantiomer (*R*,*S*)-**3a** via similar transformations. Notably, H-bonding interaction between the NH group of **L1** and the carbonyl group of **1a** is observed in (*R*,*S*)-**TS** and (*R*,*R*)-**TS**, while the other two transition states without H-bonding interaction exhibit higher energies [5.2 kcal/mol for (*S*,*S*)-**TS**; 2.9 kcal/mol for (*S*,*R*)-**TS**]. The results indicate that the H-bonding is beneficial for the reaction, which is consistent with the experimental results (Table 1, entry 5 *vs* entry 8). Geometric structure analyses show that the forming C−C bond in (*R*,*R*)-**TS** presents a pseudogauche conformation to avoid the steric repulsion between the ester group of **1a** and the carbonyl of **2a**. As a result, the dihedral angle $D_{C1\text{-}C2\text{-}C3\text{-}H}$ is 45.4° with apparent torsional strain. In contrast, (*R*,*S*)-**TS** possesses smaller torsional strain (referring to the corresponding $D_{C1\text{-}C2\text{-}C3\text{-}H}$ = 57.4°), thus leading to lower energy [0 kcal/mol for (*R*,*S*)-**TS** *vs* 1.0 kcal/mol for (*R*,*R*)-**TS**]. Therefore, the most favourable transition state (*R*,*S*)-**TS** would afford (*S*,*R*)-**3a** as the major product after annulation, which is consistent with the experimental observation.

5) Hydrogen bonding mode (The calculations were performed at the M06/6-311++G(d,p)(SDD for Pd)/SMD//B3LYP/6-31G(d)(SDD for Pd) (298.15K) level of theory)

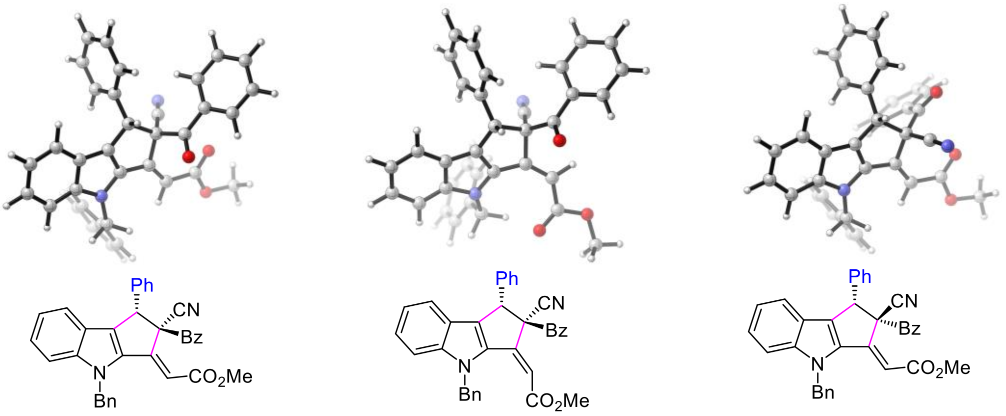


(*R*,*S*)-**TS** $\Delta\Delta G^{\ddagger} = 0$

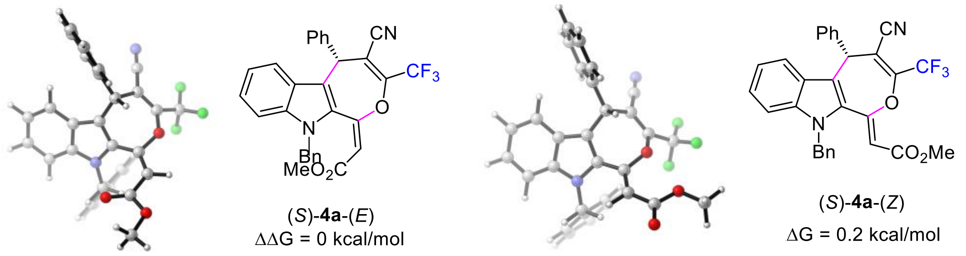
(*R*,*S*)-**TS-II** $\Delta\Delta G^{\ddagger}$ = 9.2 kcal/mol

Since the NH group of **L1** plays an important role for the enantioselectivity, two H-bonding interaction modes were considered. In the first mode, the NH group in **L1** interacts with the ester group of **1a**, forming a chiral binding pocket to achieve stereocontrol [(*R*,*S*)-**TS**]. In the second mode, the NH group in **L1** interacts with the carbonyl of **2a** [(*R*,*S*)-**TS-II**]. According to computational results, the energy of (*R*,*S*)-**TS-II** is 9.2 kcal/mol higher than that of (*R*,*S*)-**TS**, indicating that the first mode is favoured.

6) Thermodynamic stability of several possible stereoselective products (The calculations were performed at the M06/6-311++G(d,p)(SDD for Pd)/SMD//B3LYP/6-31G(d)(SDD for Pd) (298.15K) level of theory)



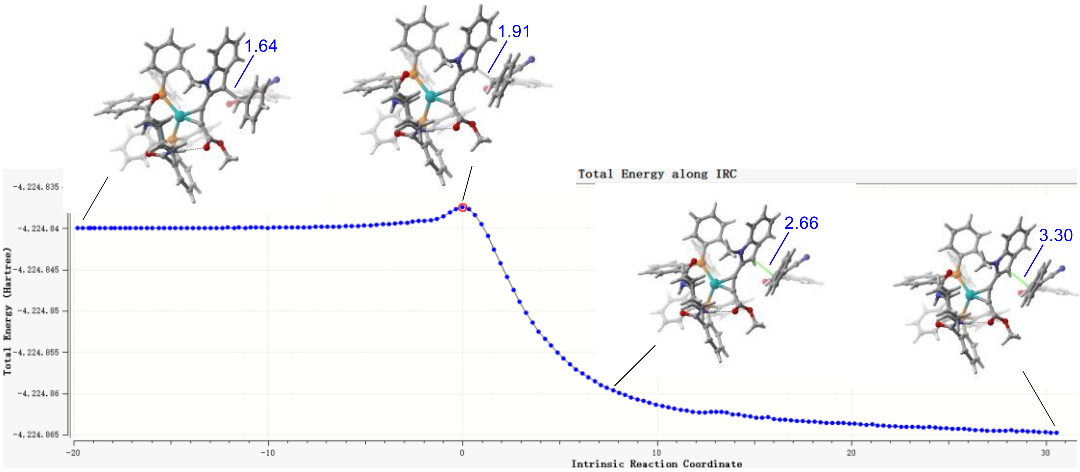
(*S*,*R*)-**3b**-(*E*) ΔΔG = 0 kcal/mol (*S*,*R*)-**3b**-(*Z*) ΔΔG = 6.5 kcal/mol (*S*,*S*)-**3b**-(*E*) ΔΔG = 2.3 kcal/mol



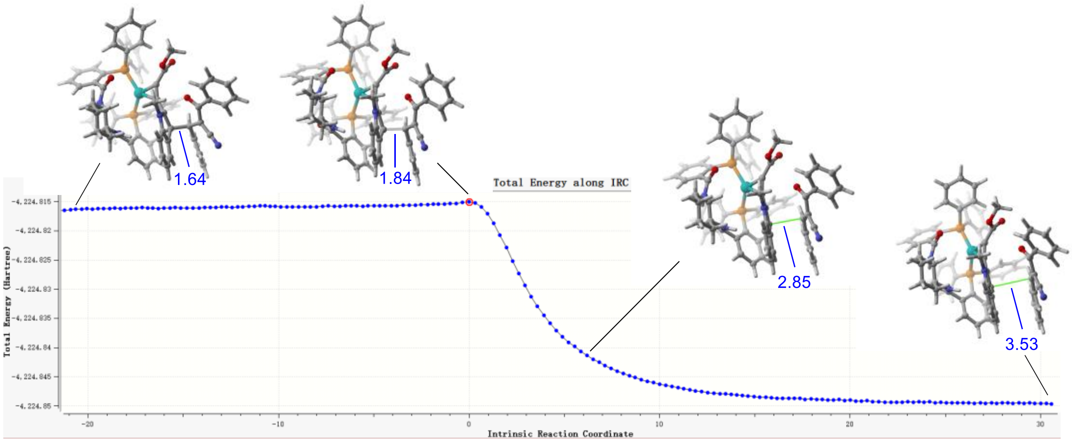
(*S*)-**4a**-(*E*) ΔΔG = 0 kcal/mol (*S*)-**4a**-(*Z*) ΔG = 0.2 kcal/mol

Since the Pd complex would not be involved in the final annulation process, thermodynamic stability of several possible stereoselective products, including (*S*,*R*)-**3b**-(*E*), (*S*,*R*)-**3b**-(*Z*), (*S*,*S*)-**3b**-(*E*), (*S*)-**4a**-(*E*) and (*S*)-**4a**-(*Z*), were calculated via DFT studies. Among the three possible formal [3 + 2] products, (*S*,*R*)-**3b**-(*E*) has the lowest energy; on the other hand, (*S*)-**4a**-(*E*) possesses lower energy compared with (*S*)-**4a**-(*Z*). The results indicates that the two products would be thermodynamicaly more stable, thus they are obtained as the major products in cascade reactions.

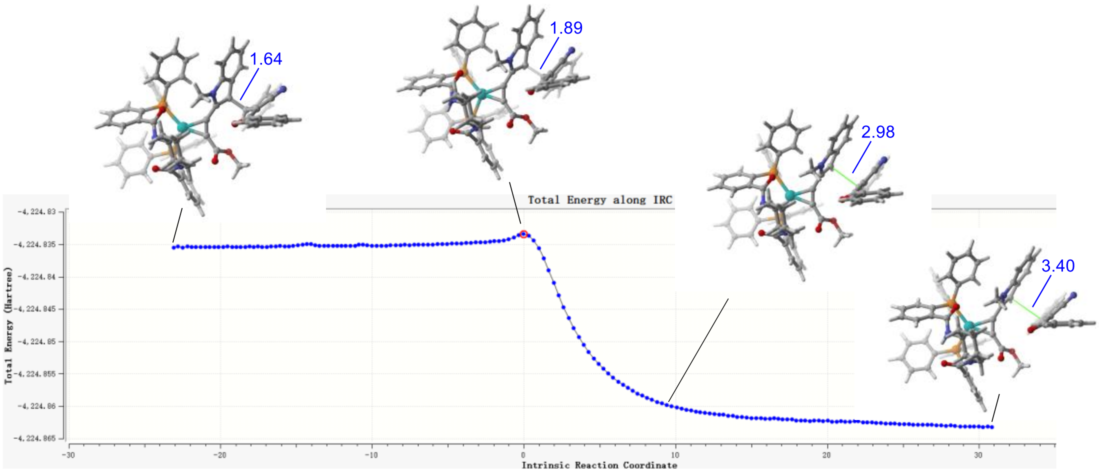
7) IRC calculations for all transition states



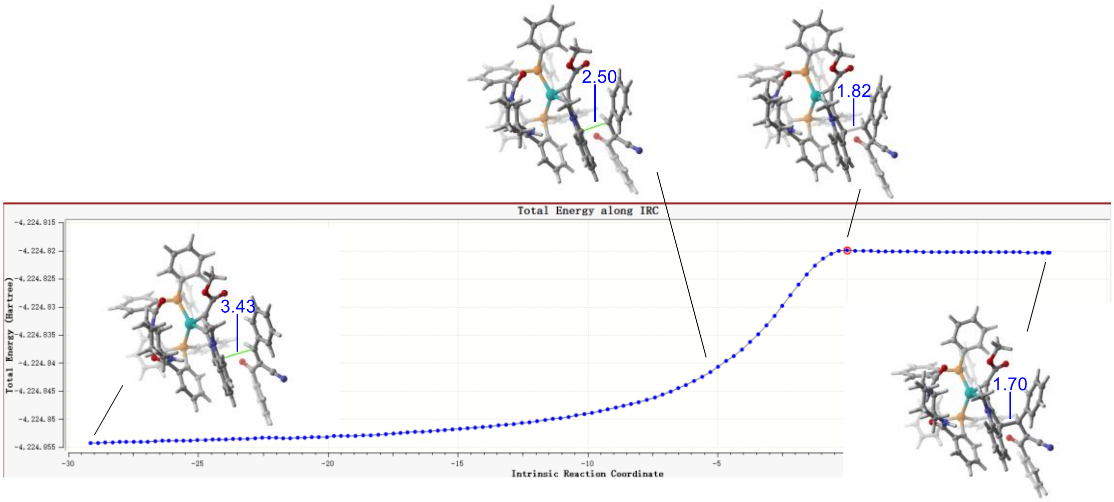
(*R*,*S*)-**TS**



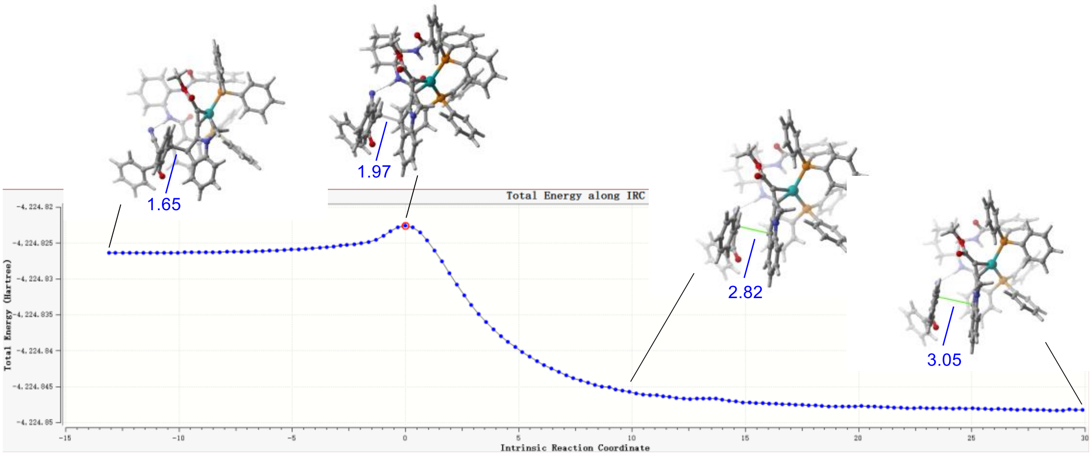
(*S*,*S*)-**TS**



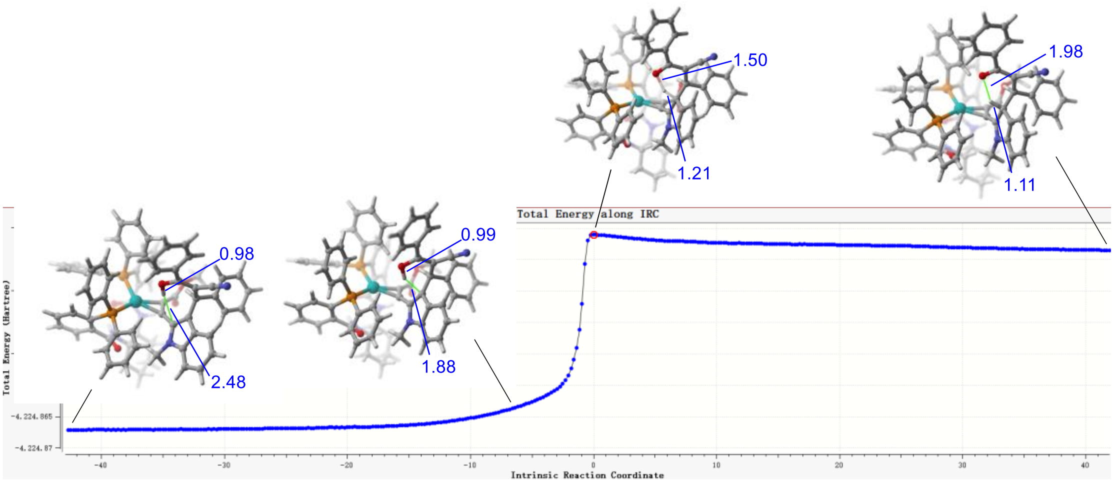
(*R*,*R*)-**TS**



(*S*,*R*)-**TS**



(*R*,*S*)-**TS-II**



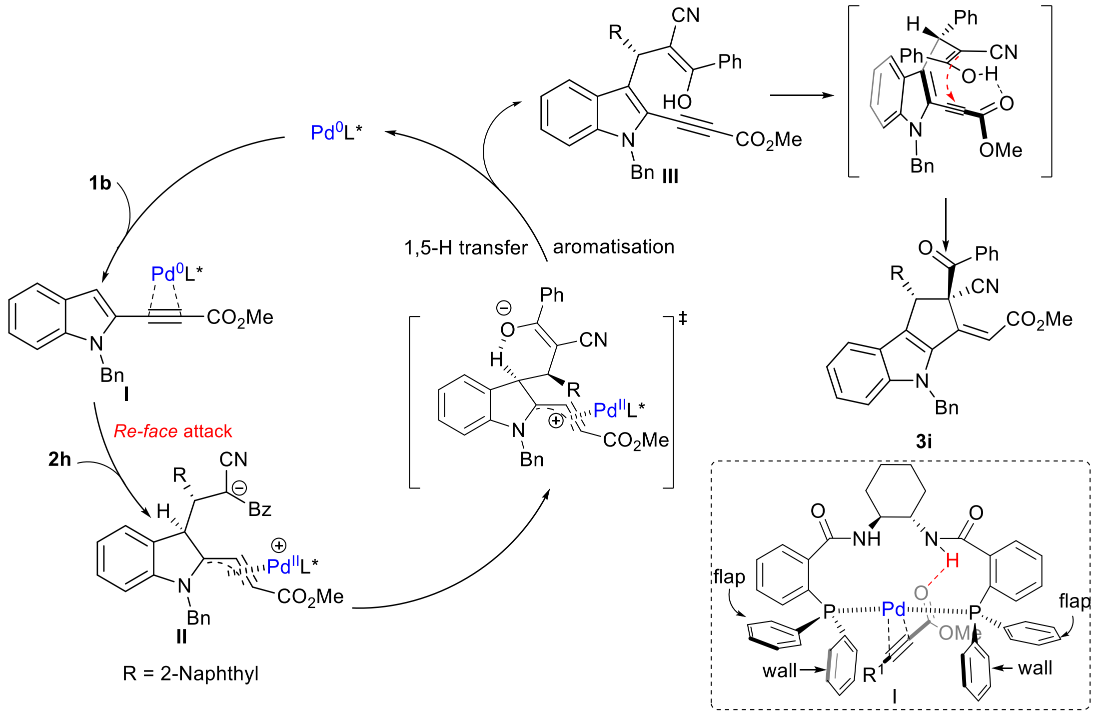
(*R*,*S*)-**TS2**

(7) Proposed mechanism

(a) The reaction of indoles with a 2-alkynyl group

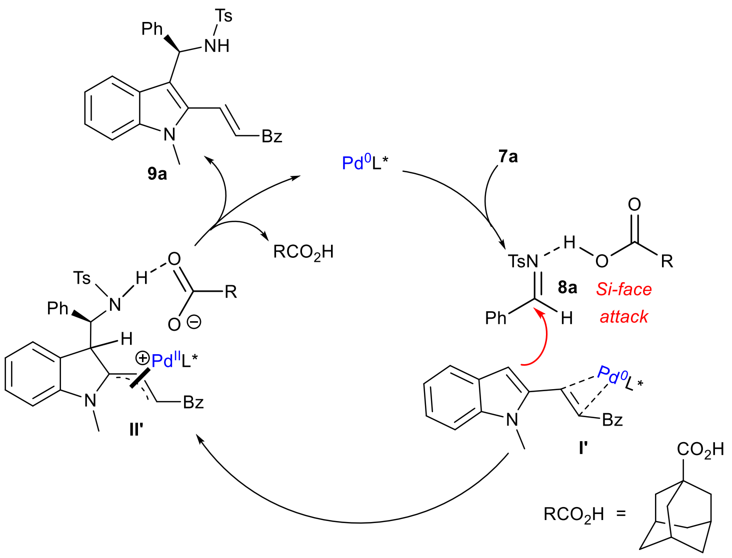
On the basis of the above results and the absolute configuration of enantiopure **3i**, a possible reaction pathway was proposed. Firstly, alkyne **1b** coordinates with Pd(0) to generate HOMO raised η^2-complex **I**, in which the NH group of **L1** interact with the carbonyl group of **1a** via H-bonding. Then the 3-position of the indole attacks enone **2h** from *Re*-face. The resultant η^3-complex **II** would undergoes an intramolecular 1,5-proton transfer to giv intermediate **III**, and the hydroxyl group of the enol moiety might interact with the carbonyl of the propiolate group of **III**, thus facilitating the intramolecular Michael reaction to give thermodynamically more stable product **3i** with an *exo*-*E*-double bond.

Proposed mechanism



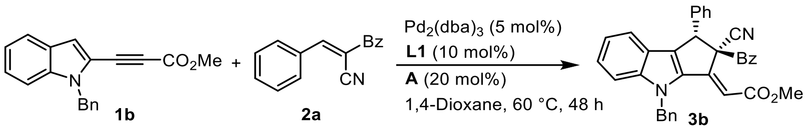
(b) The reaction of indoles with a 2-alkenyl group

Similarly, the mechanism for the FC reaction of **7a** was proposed as well. Firstly, alkene **7a** coordinates with Pd(0) to generate HOMO raised η^2-complex **I′**. Then the 3-position of the indole attacks imine **8a** which is activated by the acid additive from *Si*-face, followed by a β-H elimination or deprotonation process to give final product **9a**.



(8) Influence of ammonium salts

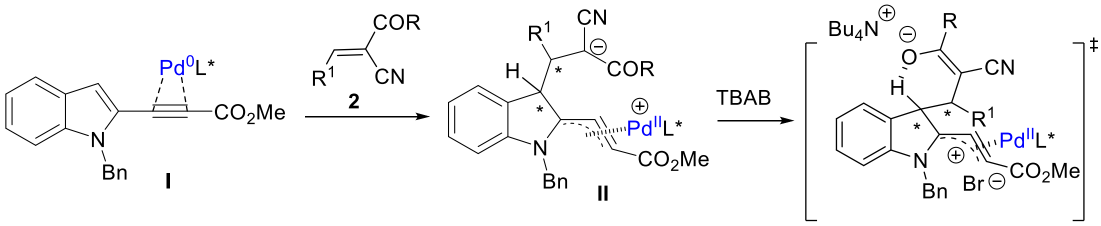
For additive TBAB, we conducted more control experiments to elucidate its role. As shown in the following table, the addition of TBAB significantly imporved the yield (entry 1 *vs* 2). Under the optimised conditions, TBAC, TBAI and even TBAHS (tetrabutylammonium hydrogen sulfate) all provided comparable results (entries 4–6 *vs* entry 3), while KBr showed much lower reactivity (entry 7). The results indicated the ammonium cation was important to the reactivity, while the counter anion had little effect.



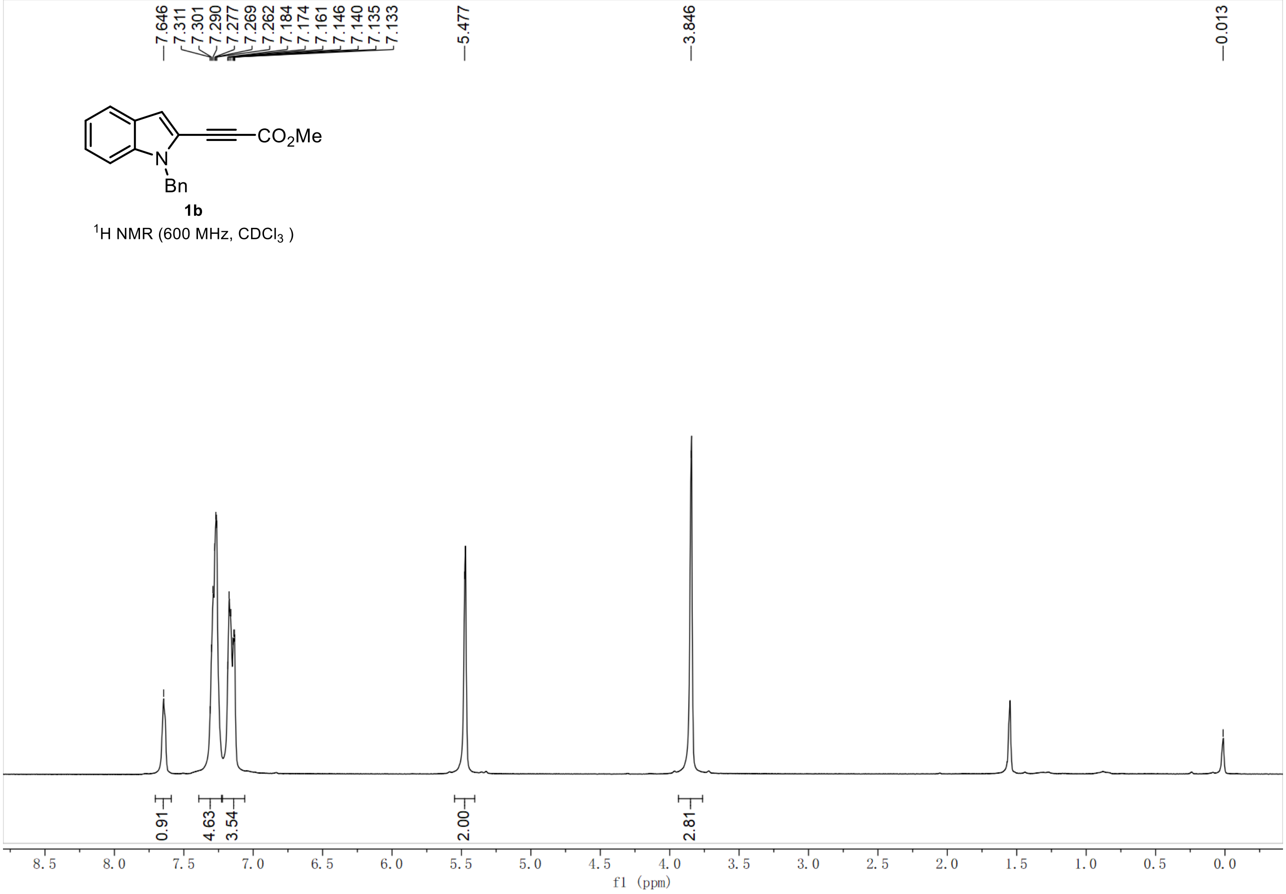
Entry[a]	**A**	Yield (%)[b]	ee (%)[c]
1	/	**3b**, 49	92
2	TBAB	**3b**, 70	91
3[d,e]	TBAB	**3b**, 86	92
5[d,e]	TBAC	**3b**, 76	92
4[d,e]	TBAI	**3b**, 81	91
6[d,e]	TBAHS	**3b**, 79	90
7[d,e]	KBr	**3b**, 52	92

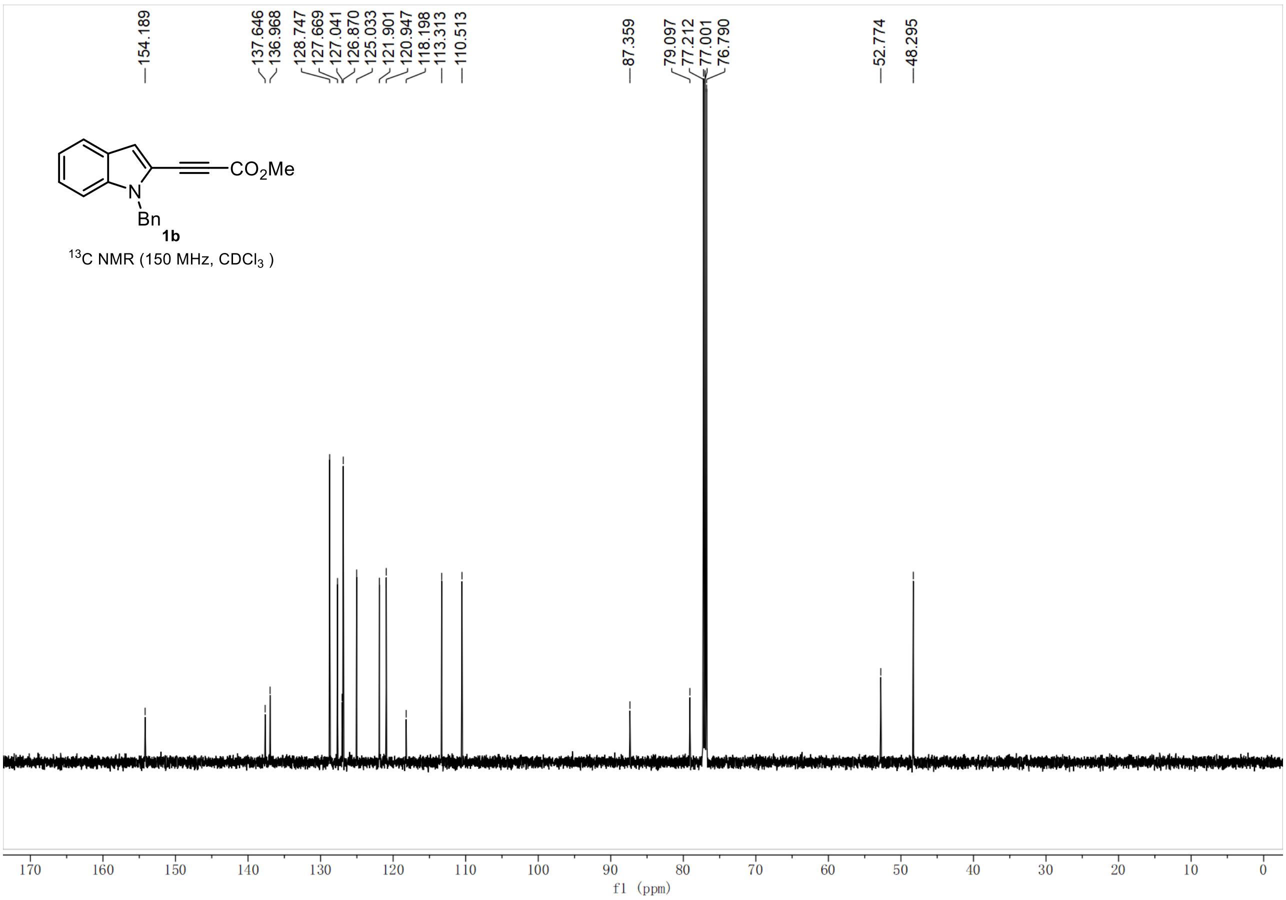
[a]Unless noted otherwise, reactions were carried out with **1b** (0.025 mmol), **2a** (0.03 mmol), $Pd_2(dba)_3$ (5 mol%), **L1** (10 mol%) and additive **A** (20 mol%) in solvent (0.25 mL) at 60 ℃ under Ar. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] C = 0.2 M. [e] The ratio of **1b/2a** was 1/1.3.

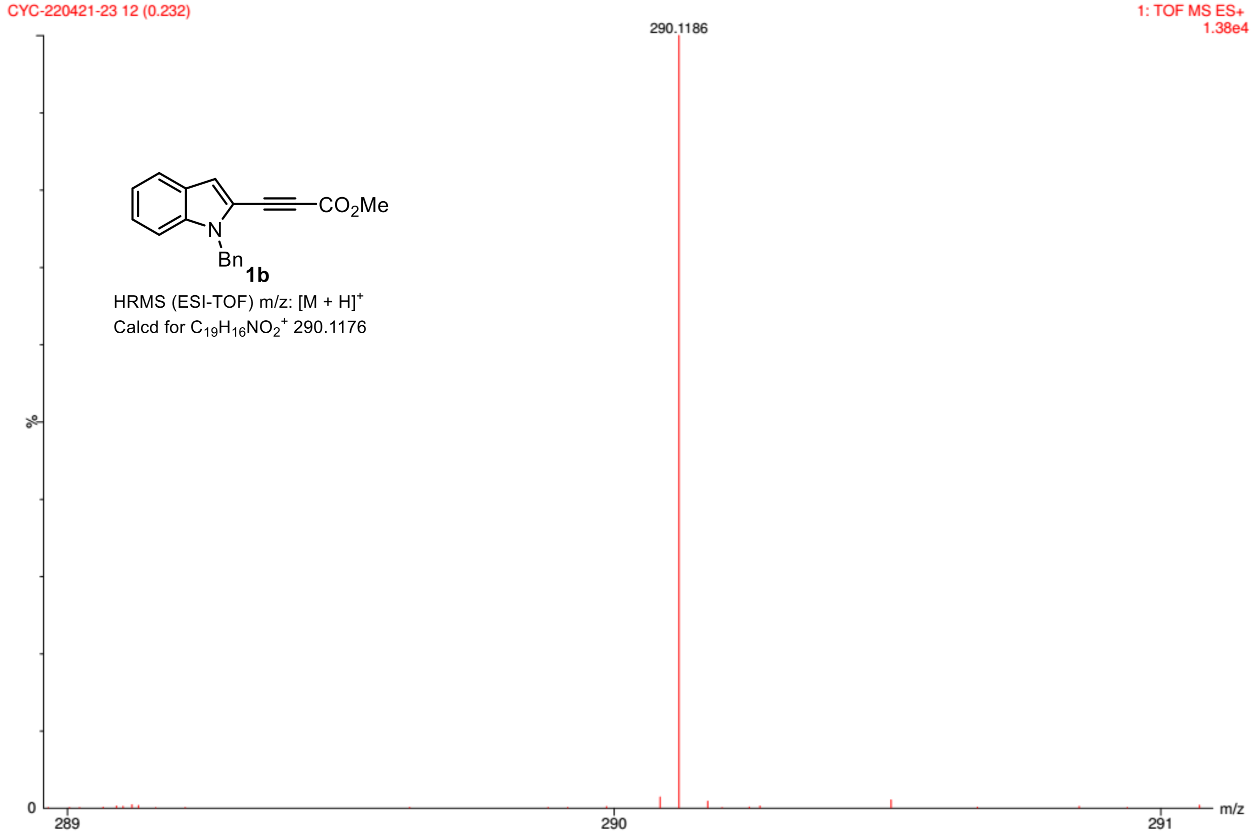
Therefore, we speculated that the ammonium salt might facilitate the reaction by stablilising intermeidate **II** as a counterion for the enolate motif after FC addition to acceptor **2**, as outlined in the following scheme.



18. NMR, HRMS spectra and HPLC chromatograms







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CO2Me
N
Bn
1b
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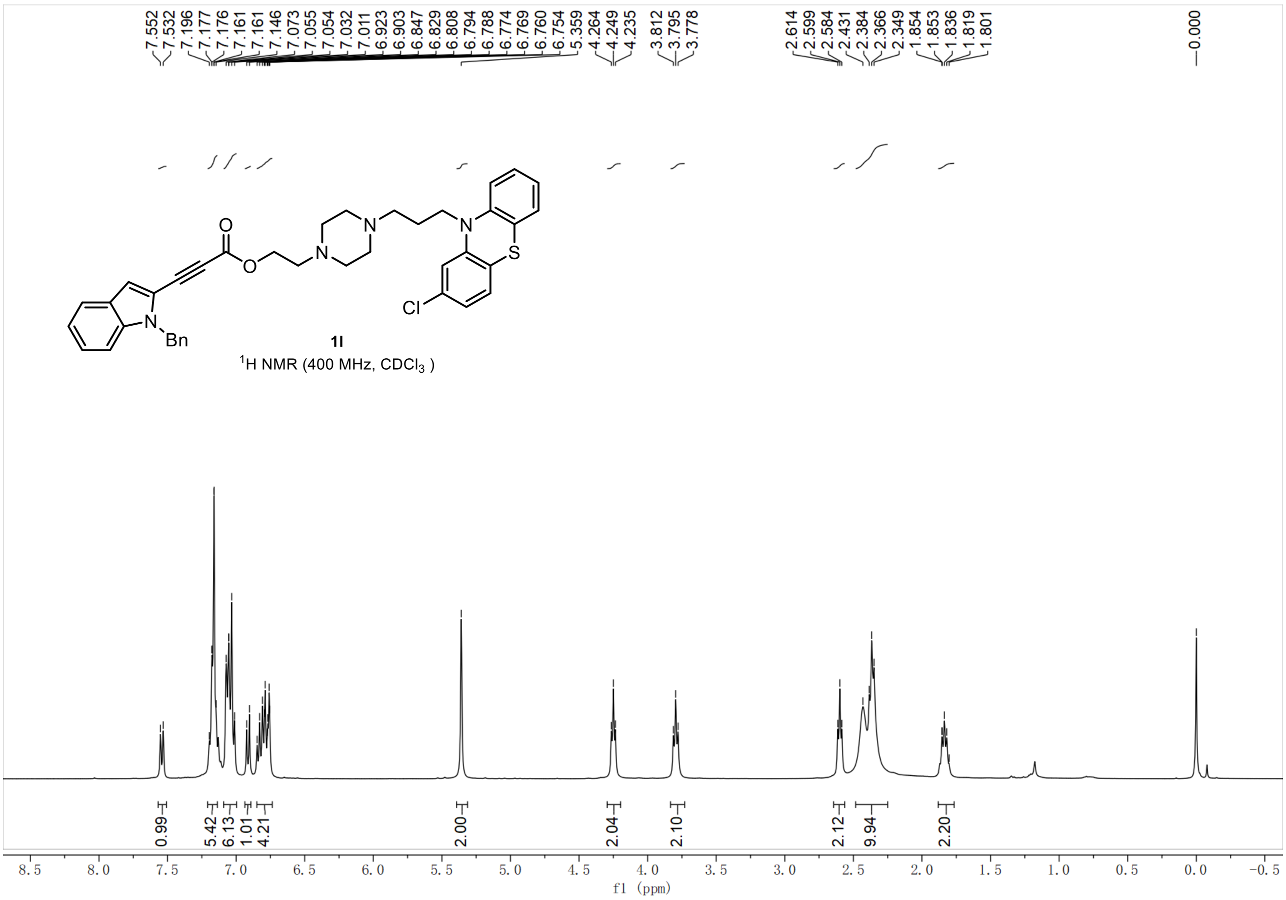
Calcd for C19H16NO2+ 290.1176
%
0
289
290
291
m/z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6.923
6.903
6.847
6.829
6.808
6.794
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6.769
6.760
6.754
5.359
4.264
4.249
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3.812
3.795
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2.614
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2.584
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1.853
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S
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N
O
O
N
Bn
1l
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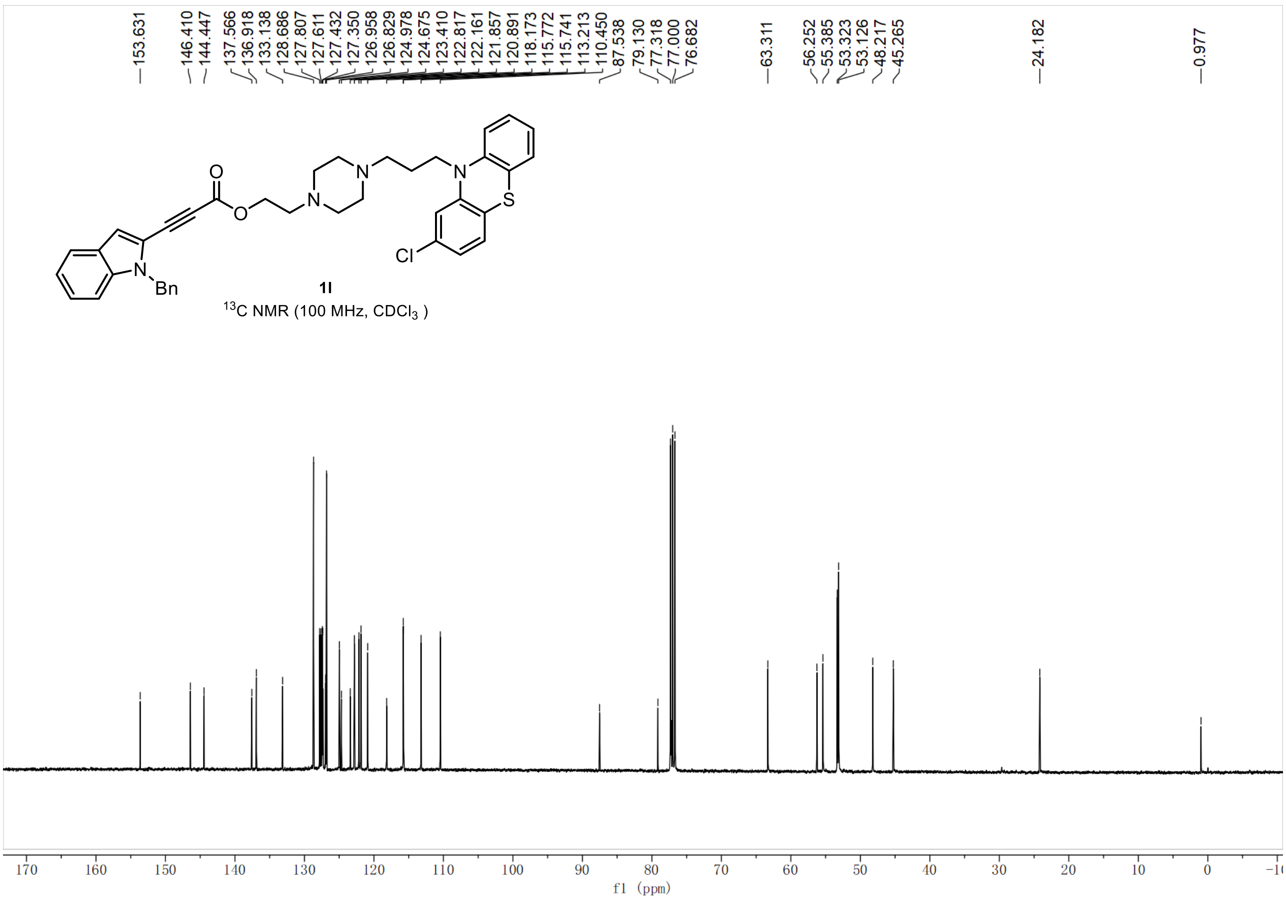
2.00
2.04
2.10
2.12
9.94
2.20
f1 (ppm)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45.265
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S
N
N
O
O
N
Bn
1l
13C NMR (100 MHz, CDCl3)
f1 (ppm)

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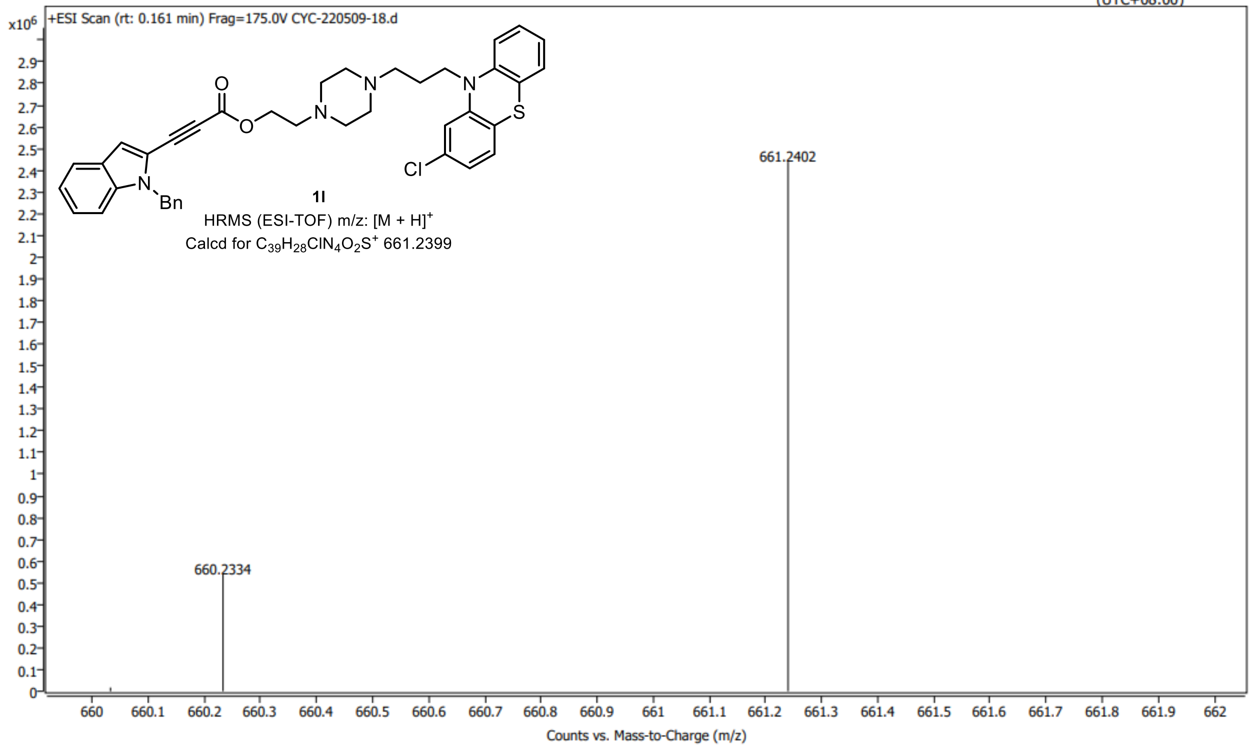

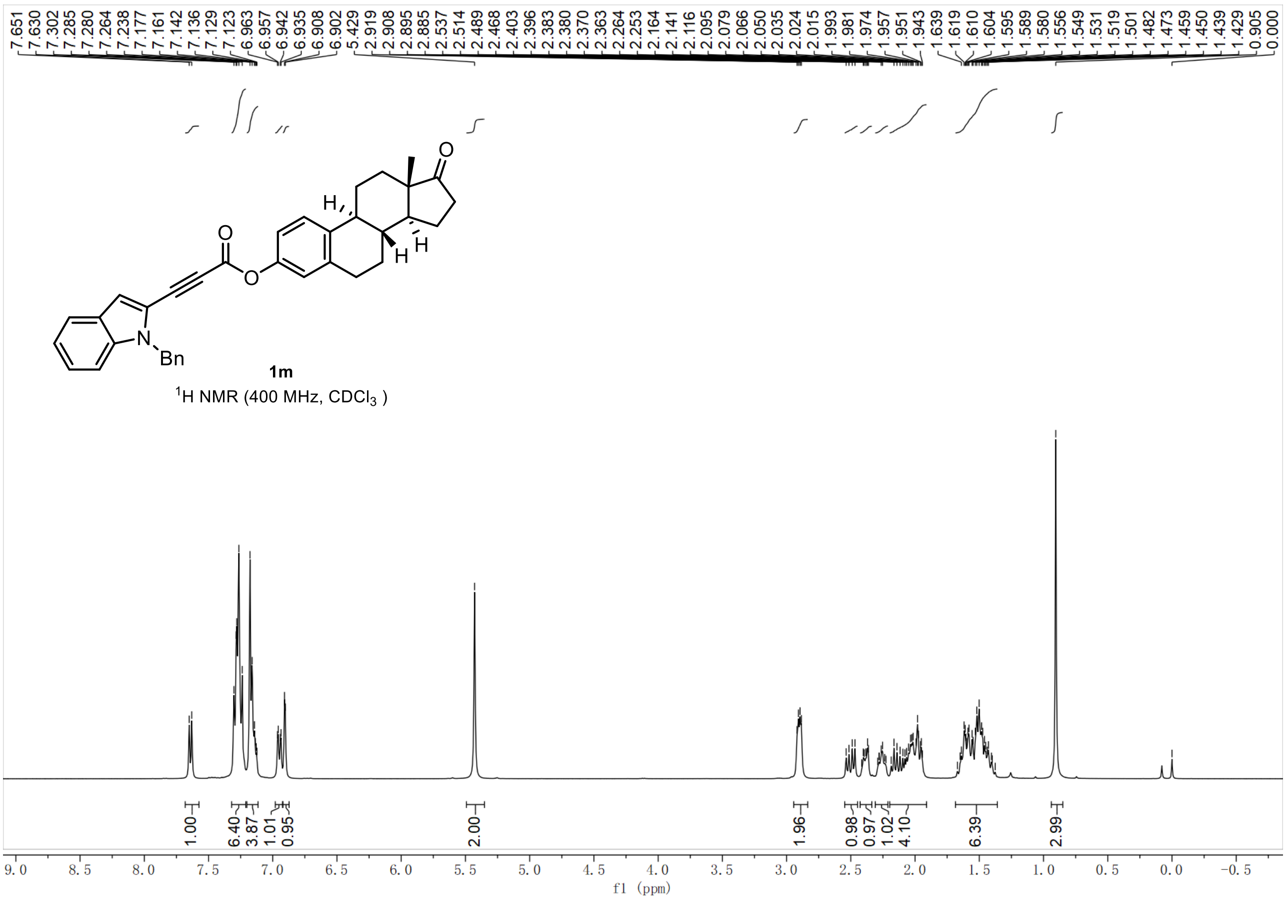
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O
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O
O
H
H
N
Bn
1m
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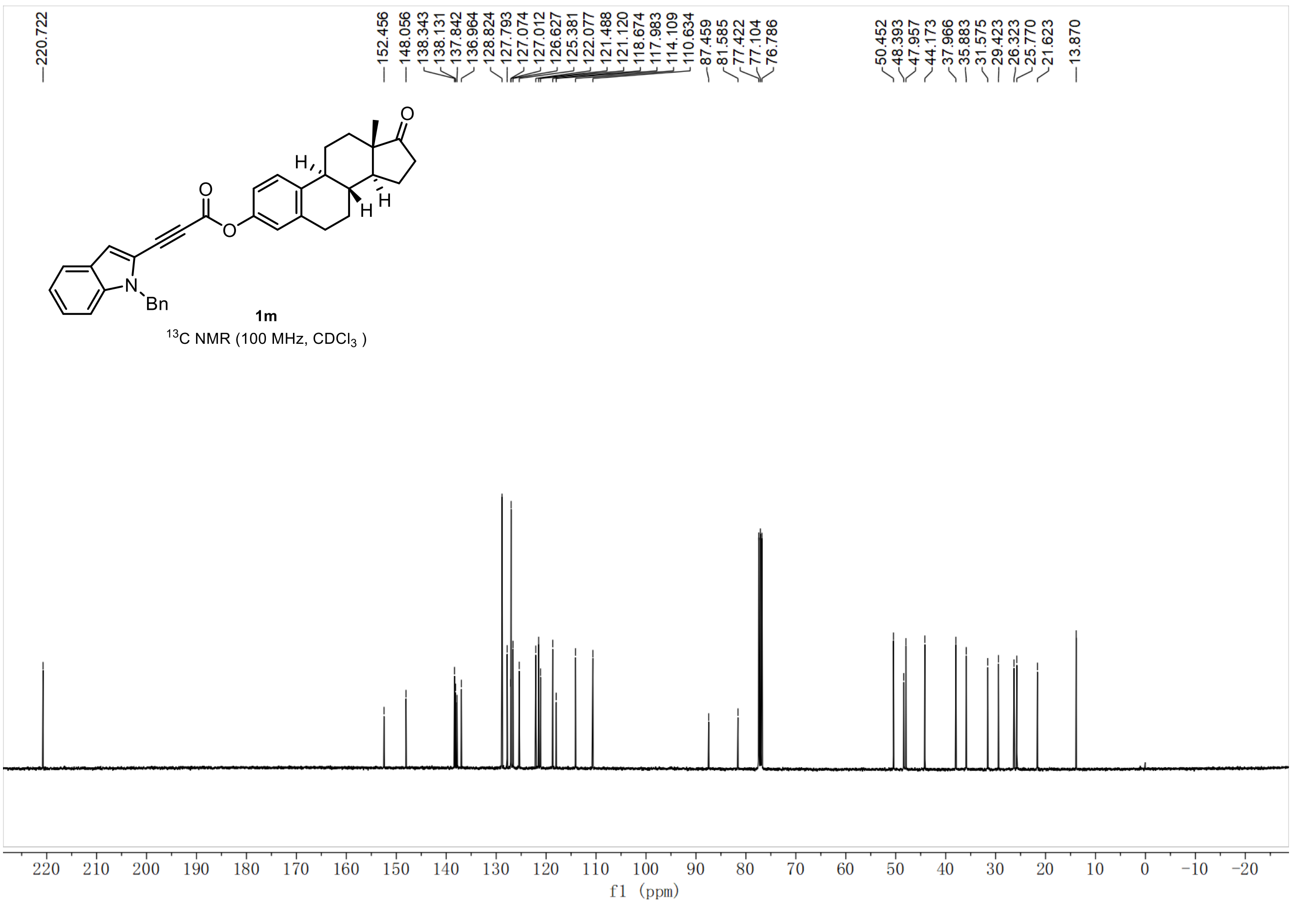
1.00 6.40 3.87 1.01 0.95 2.00 1.96 0.98 0.97 1.02 4.10 6.39 2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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O
H
O
O
H
H
N
Bn
1m
^{13}C NMR (100 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

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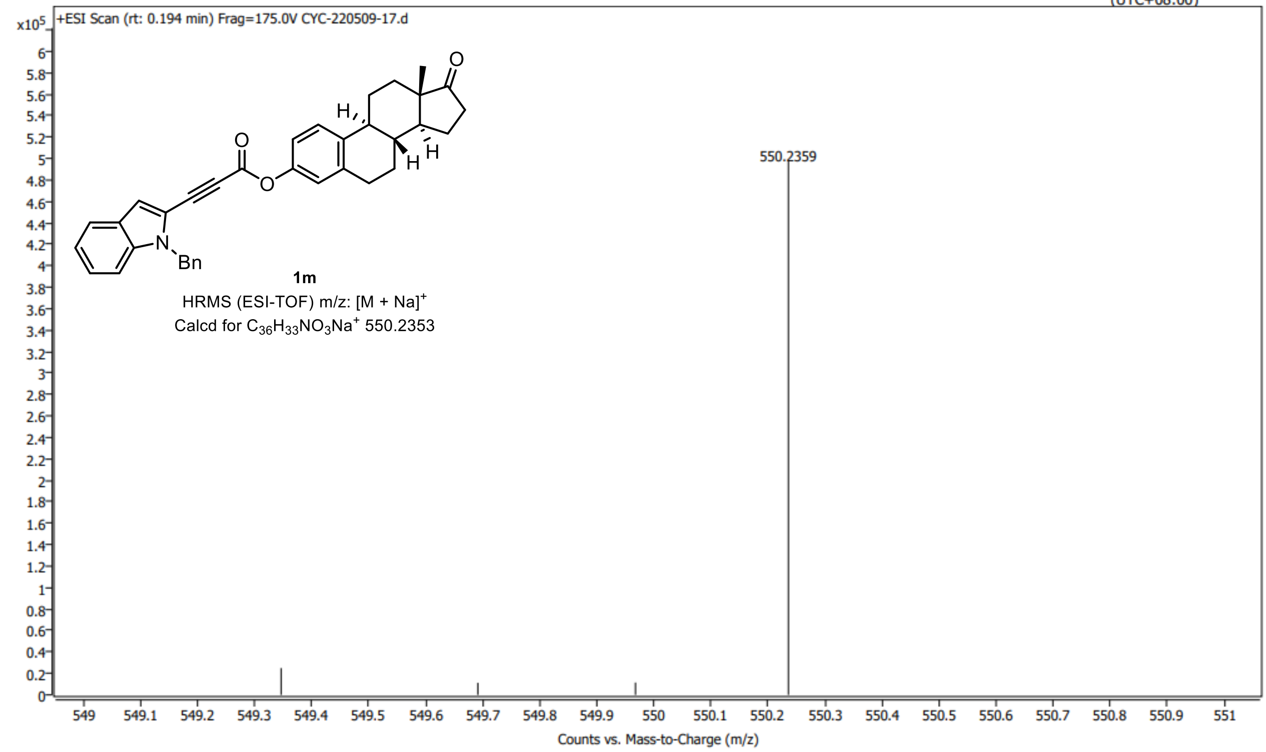

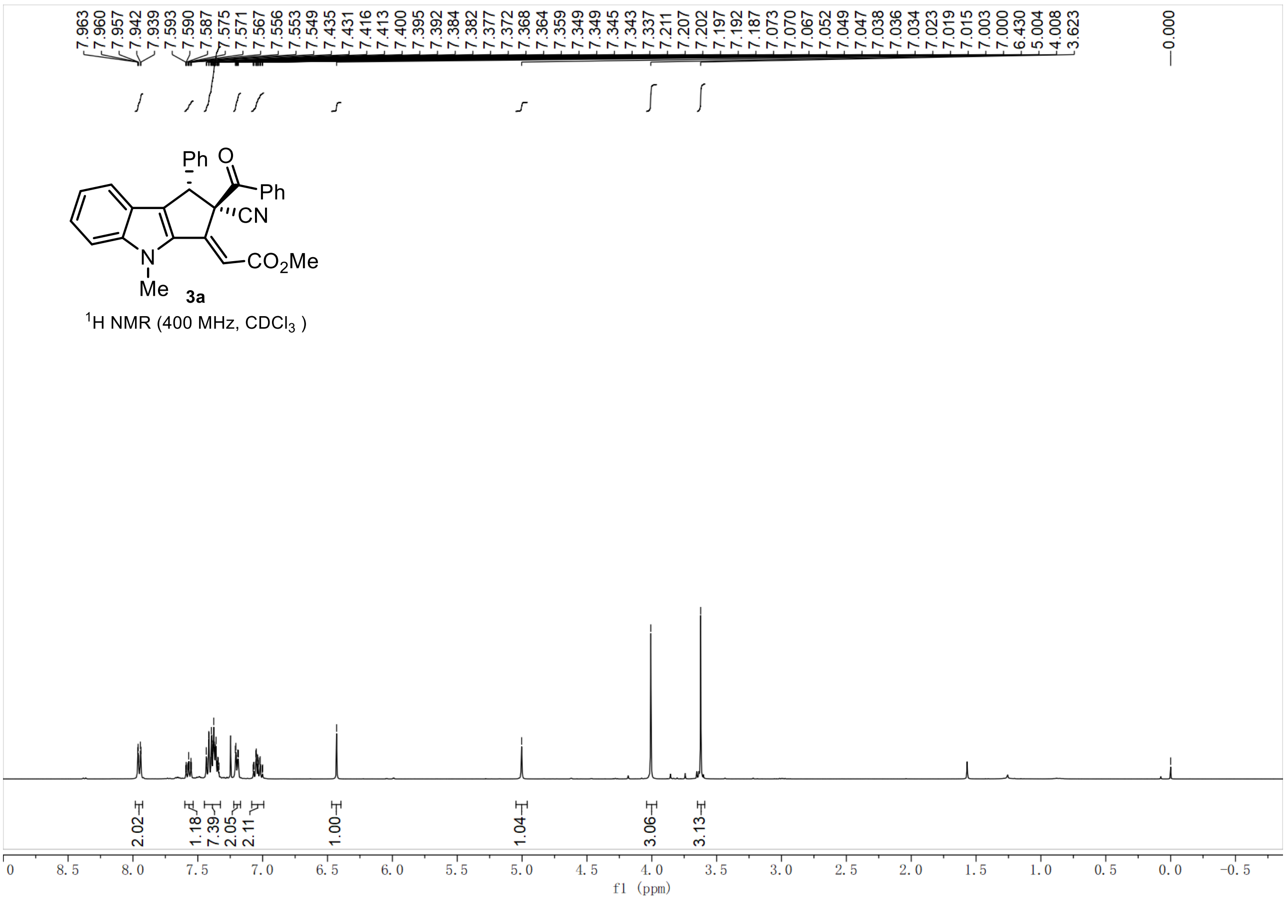
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0.000
Ph
O
Ph
CN
N
Me
CO2Me
3a
1H NMR (400 MHz, CDCl3)
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2.05
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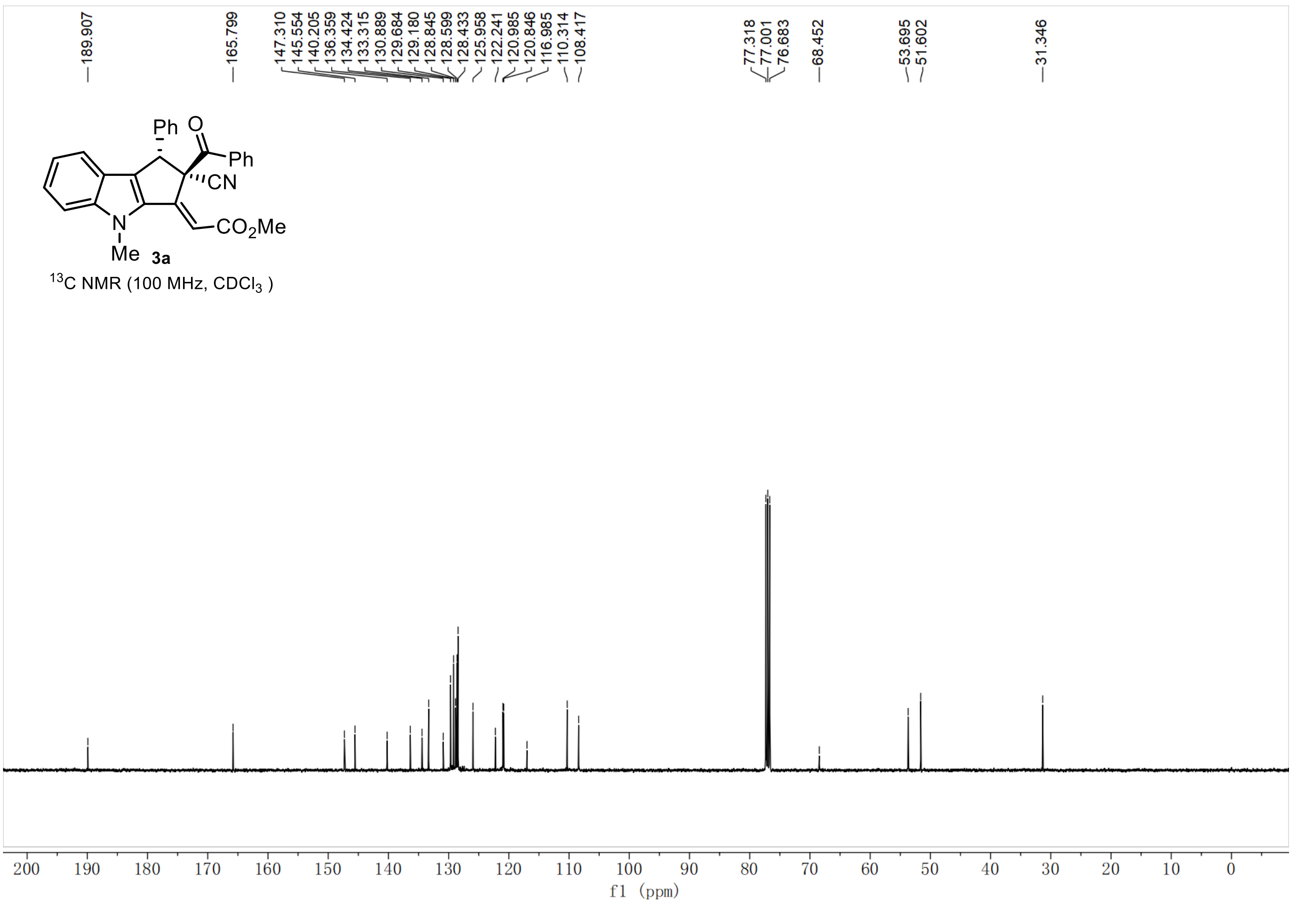
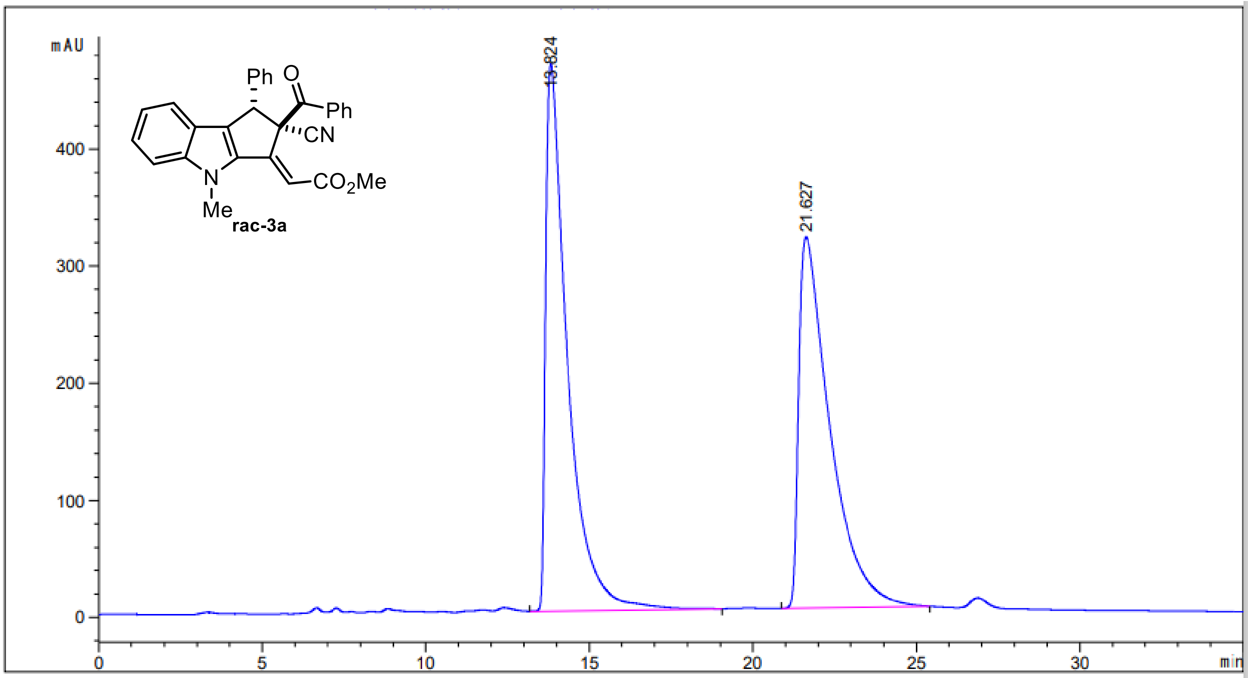
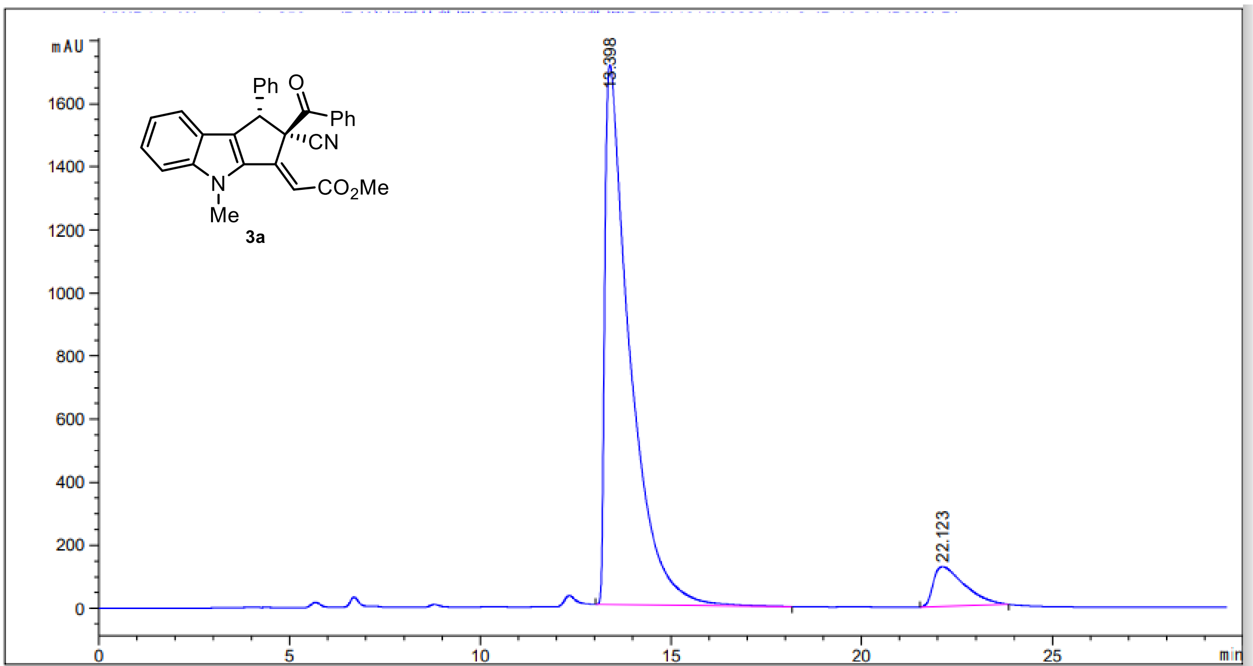
1.00
1.04
3.06
3.13
f1 (ppm)


189.907
165.799
147.310 145.554 140.205 136.359 134.424 133.315 130.889 129.684 129.180 128.845 128.599 128.433 125.958 122.241 120.985 120.846 116.985 110.314 108.417
77.318 77.001 76.683
68.452
53.695 51.602
31.346
Ph
O
Ph
CN
N
Me
CO2Me
3a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

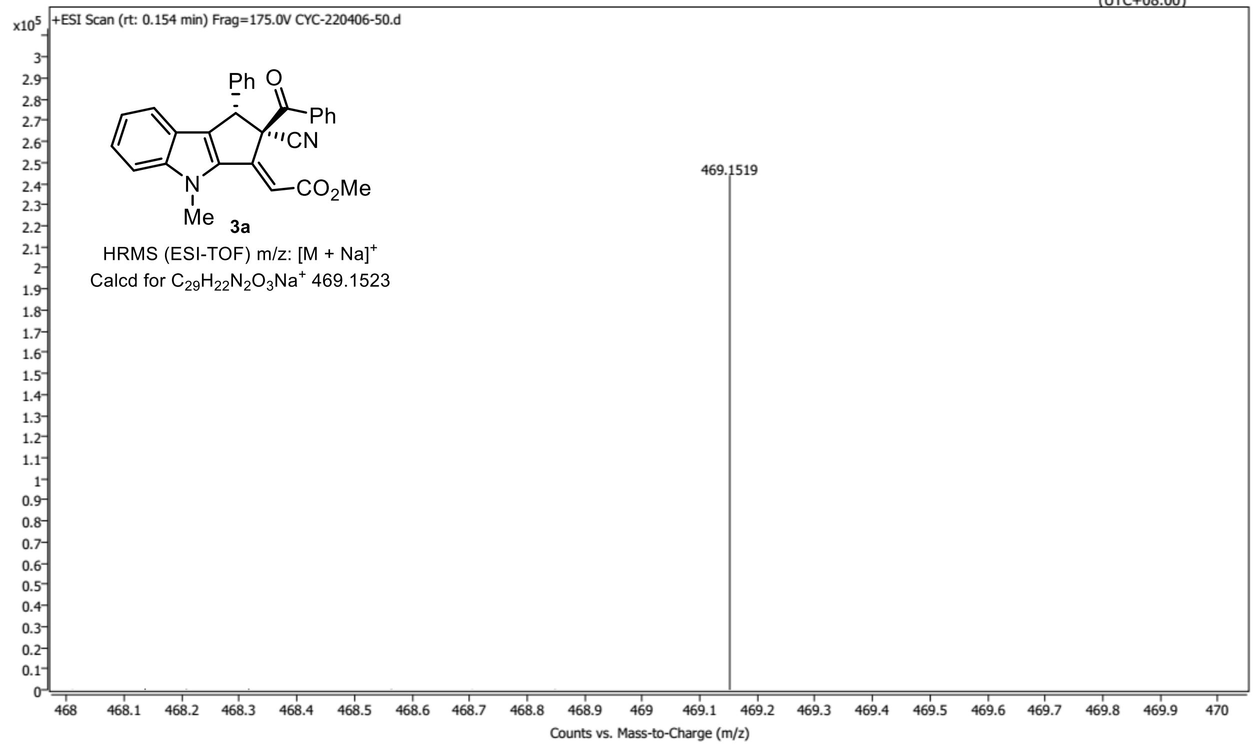


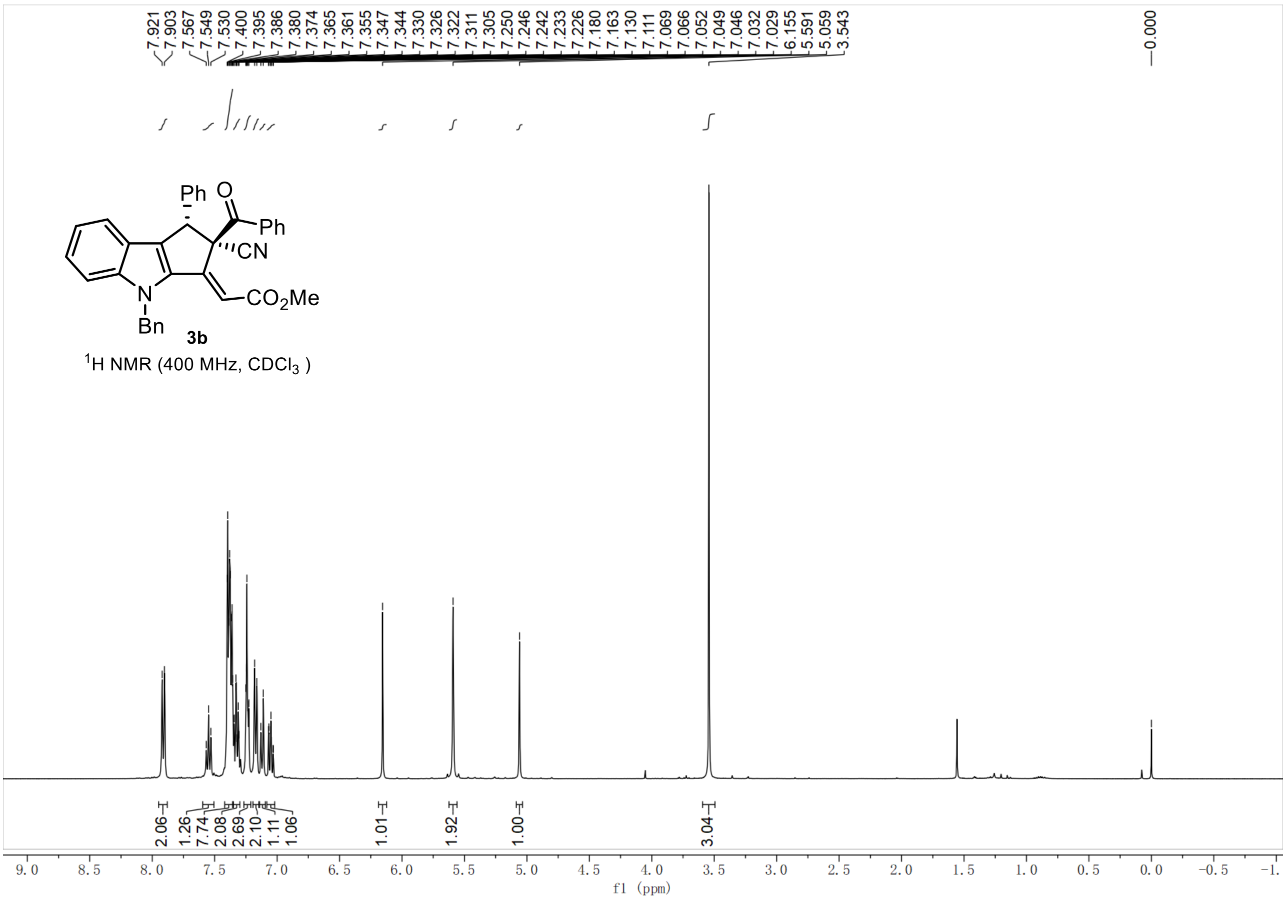
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.824	BB	0.6632	2.16614e4	467.23834	50.6824
2	21.627	BBA	0.9675	2.10781e4	317.18118	49.3176

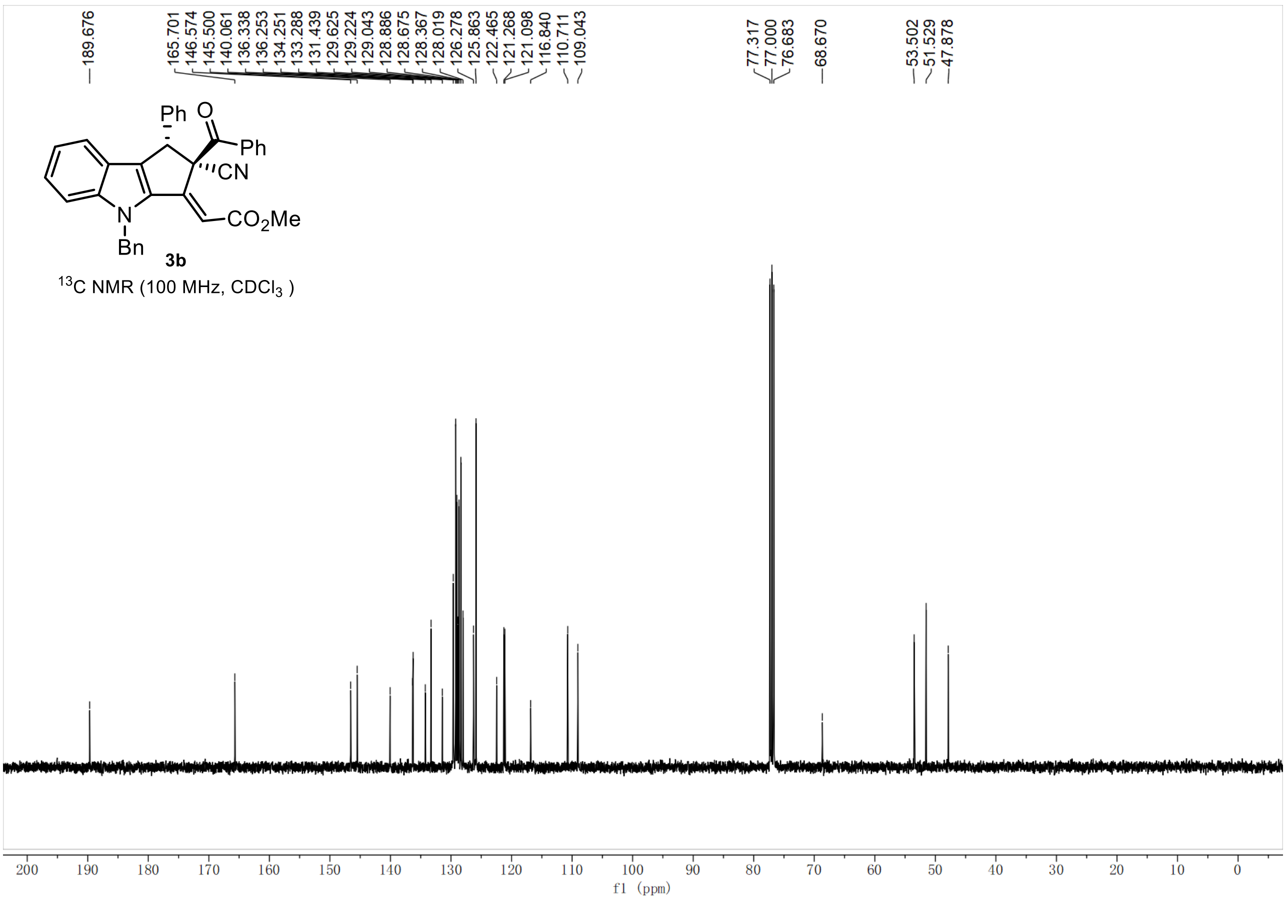


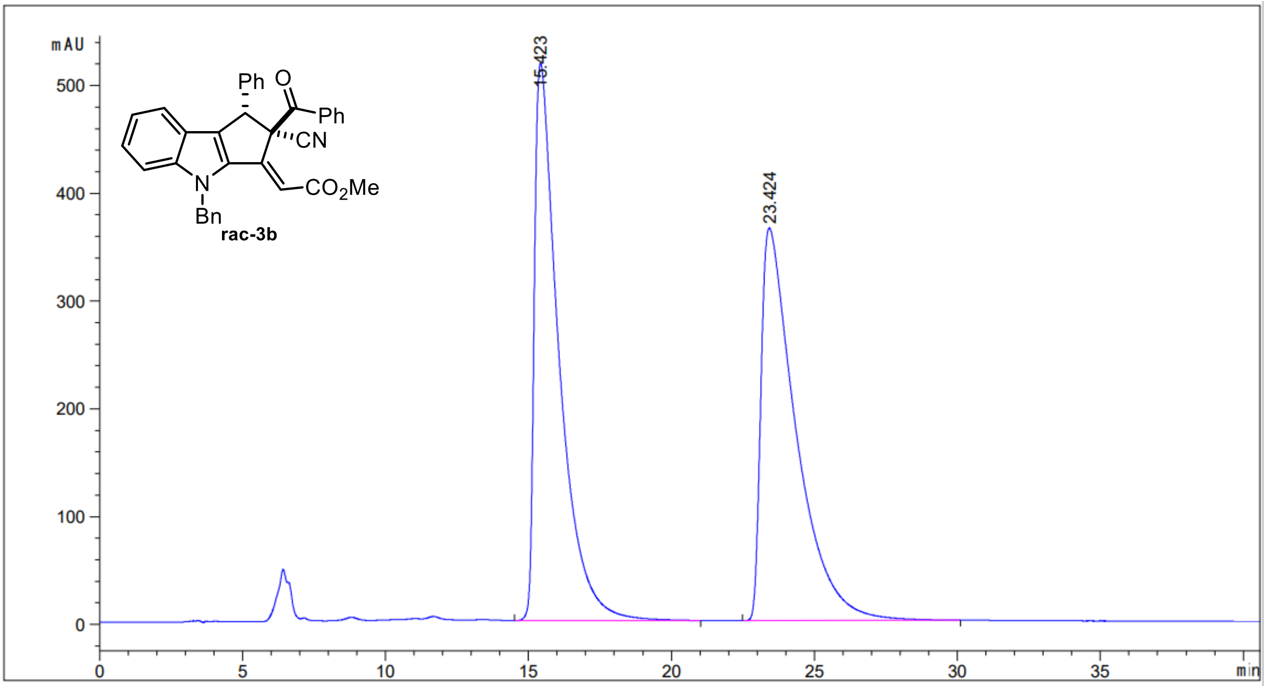
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.398	BBA	0.6518	7.85127e4	1711.18335	91.5957
2	22.123	BBA	0.8601	7203.91016	125.82844	8.4043

Name	CYC-220406-50	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-50.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:30:41 AM (UTC+08:00)

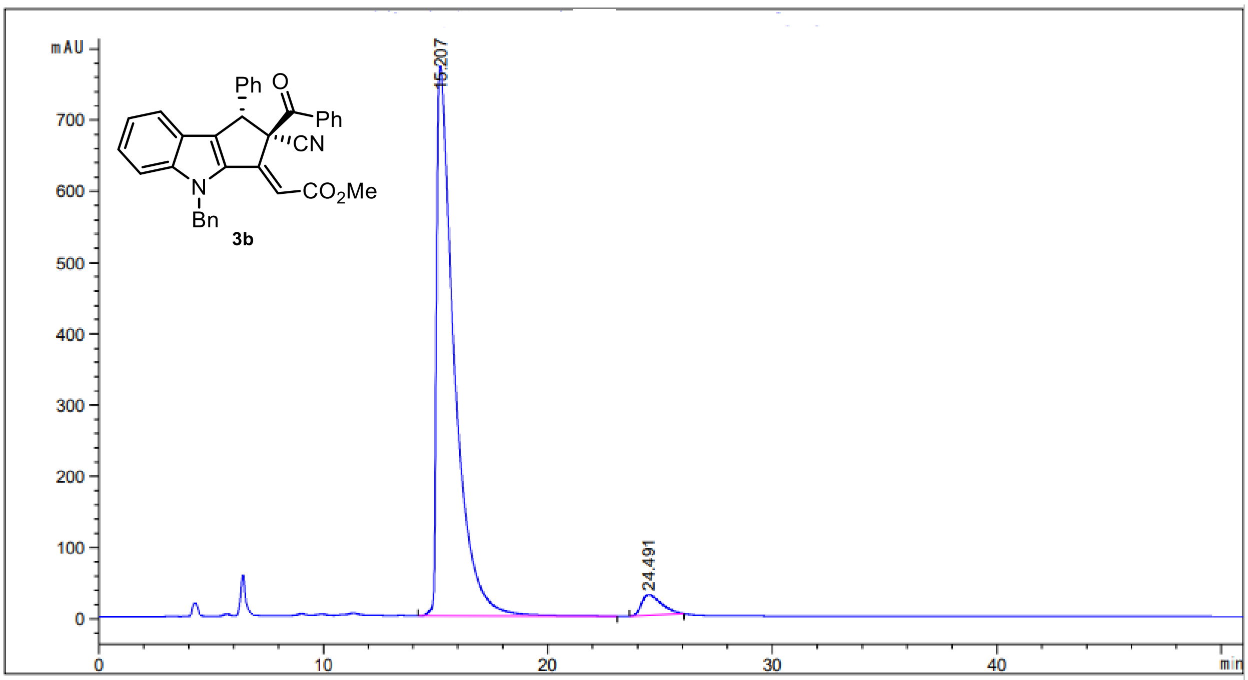



7.921
7.903
7.567
7.549
7.530
7.400
7.395
7.386
7.380
7.374
7.365
7.361
7.355
7.347
7.344
7.330
7.326
7.322
7.311
7.305
7.250
7.246
7.242
7.233
7.226
7.180
7.163
7.130
7.111
7.069
7.066
7.052
7.049
7.046
7.032
7.029
6.155
5.591
5.059
3.543
0.000
Ph
O
Ph
CN
N
CO_2Me
Bn
3b
^1H NMR (400 MHz, $CDCl_3$)
2.06
1.26
7.74
2.08
2.69
2.10
1.11
1.06
1.01
1.92
1.00
3.04
f1 (ppm)


189.676
165.701
146.574
145.500
140.061
136.338
136.253
134.251
133.288
131.439
129.625
129.224
129.043
128.886
128.675
128.367
128.019
126.278
125.863
122.465
121.268
121.098
116.840
110.711
109.043
77.317
77.000
76.683
68.670
53.502
51.529
47.878
Ph
O
Ph
CN
N
CO_2Me
Bn
3b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

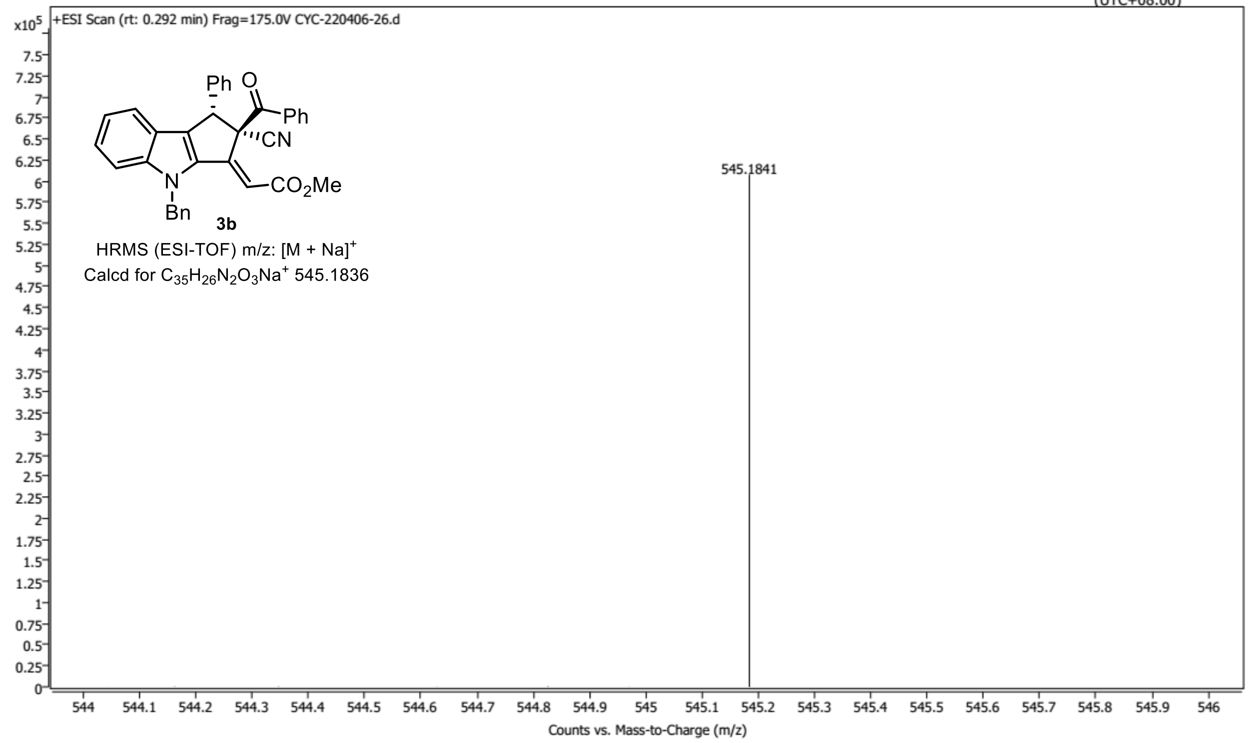


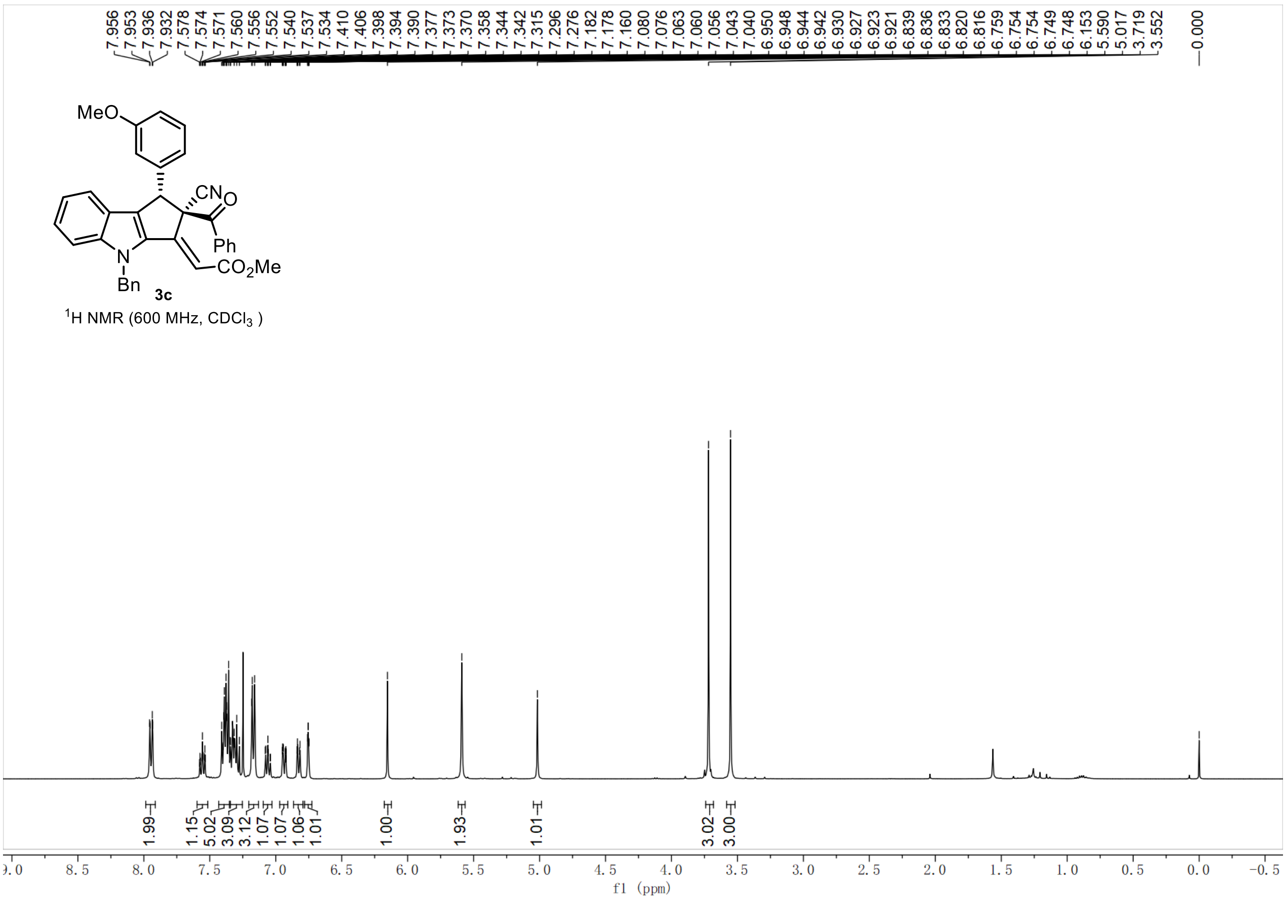
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.423	BB	0.8734	3.10287e4	517.07349	49.9863
2	23.424	BB	1.2271	3.10458e4	364.32623	50.0137

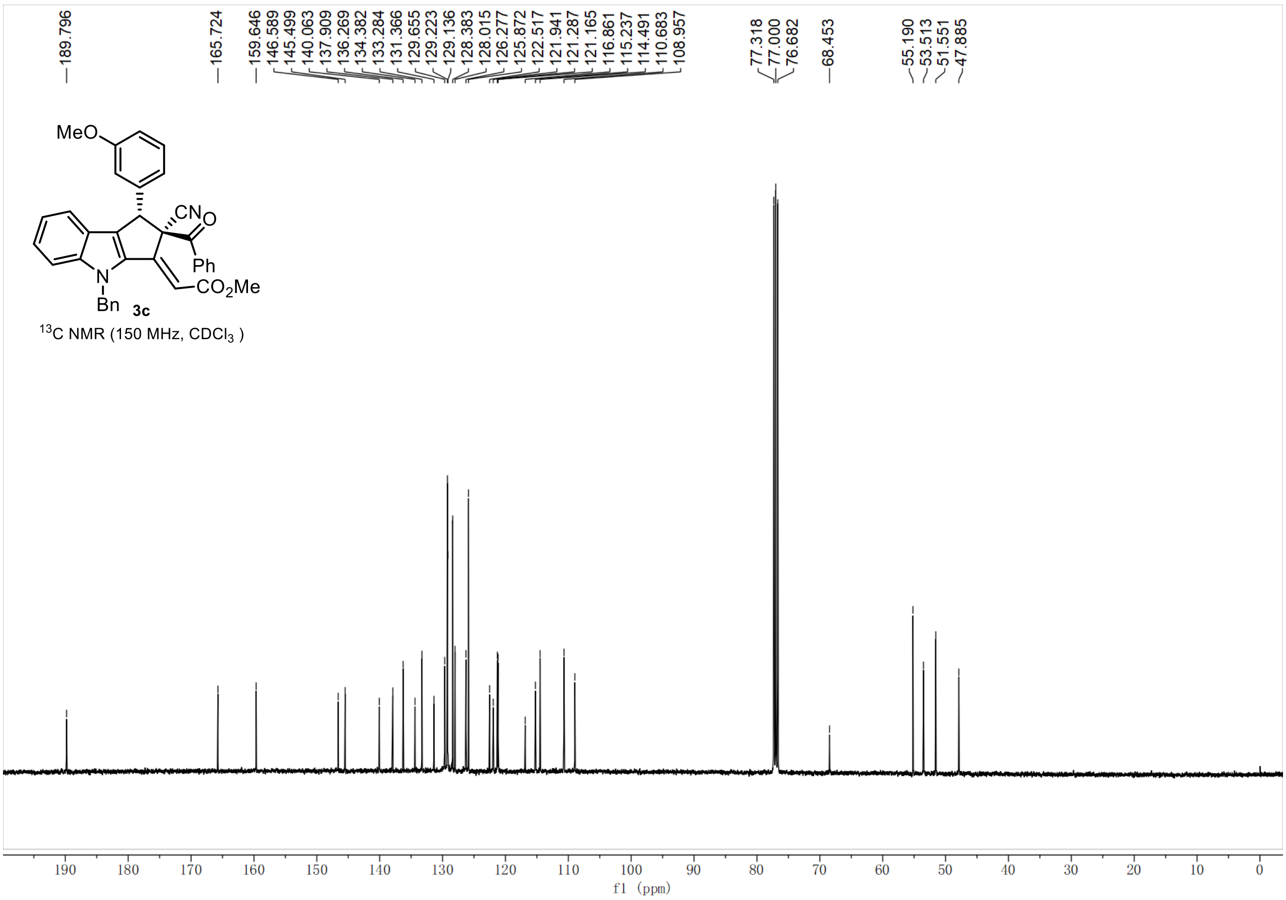


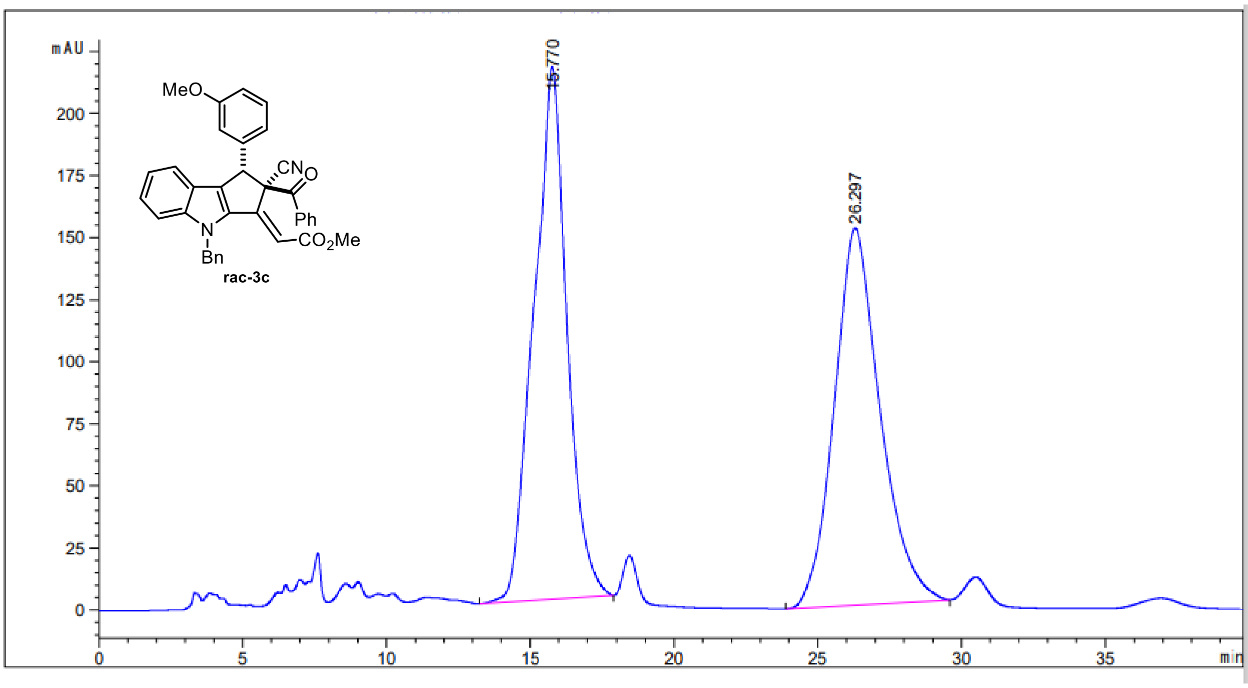
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.207	BB	0.7838	4.24238e4	772.04480	96.0058
2	24.491	BBA	0.9302	1764.99414	28.69467	3.9942

Name	CYC-220406-26	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-26.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 9:50:38 AM (UTC+08:00)

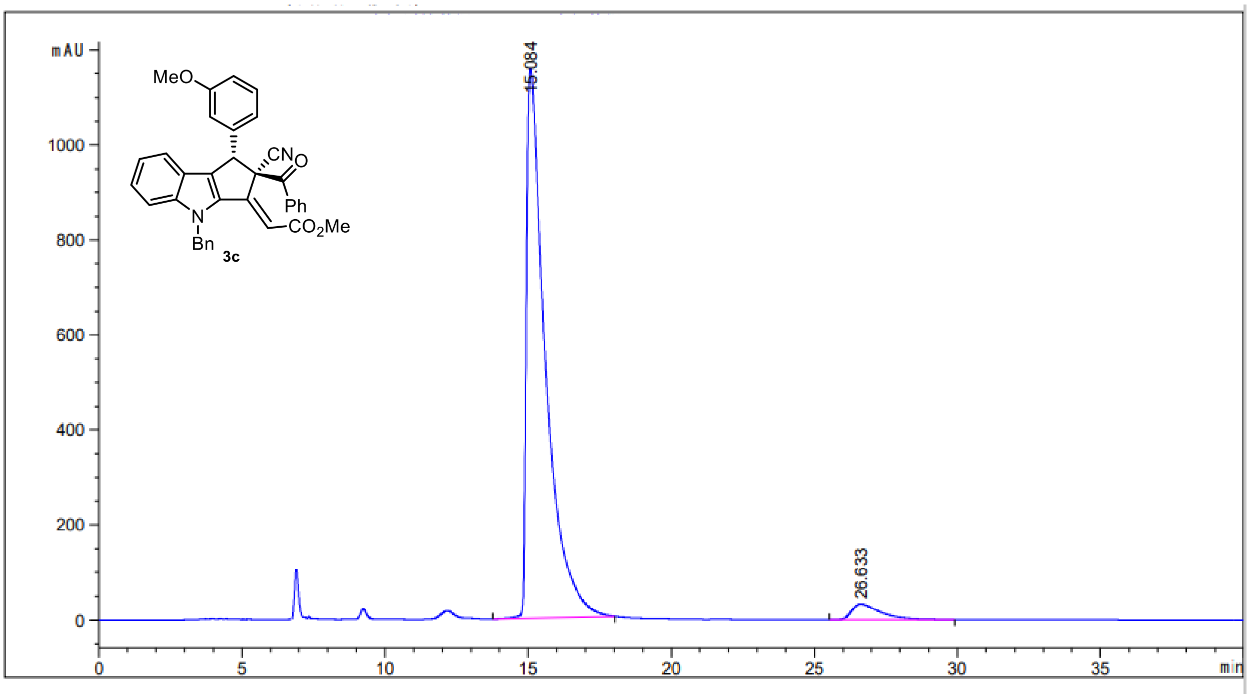






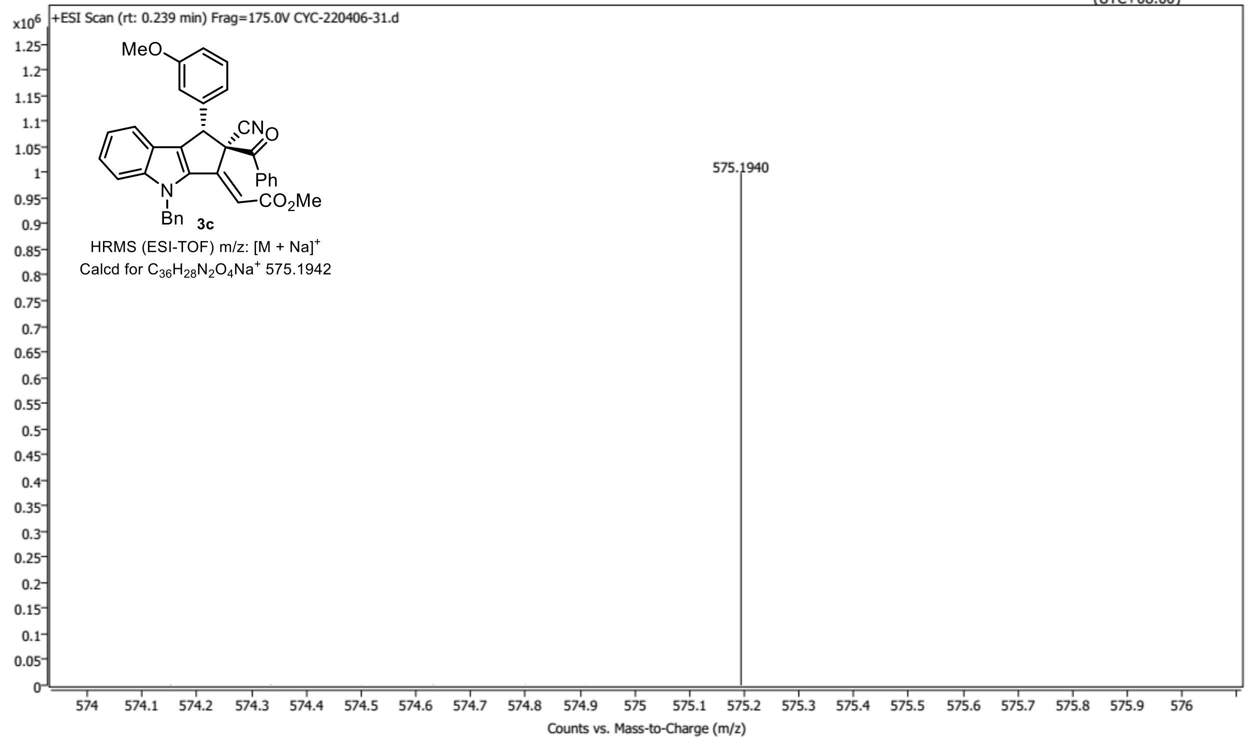


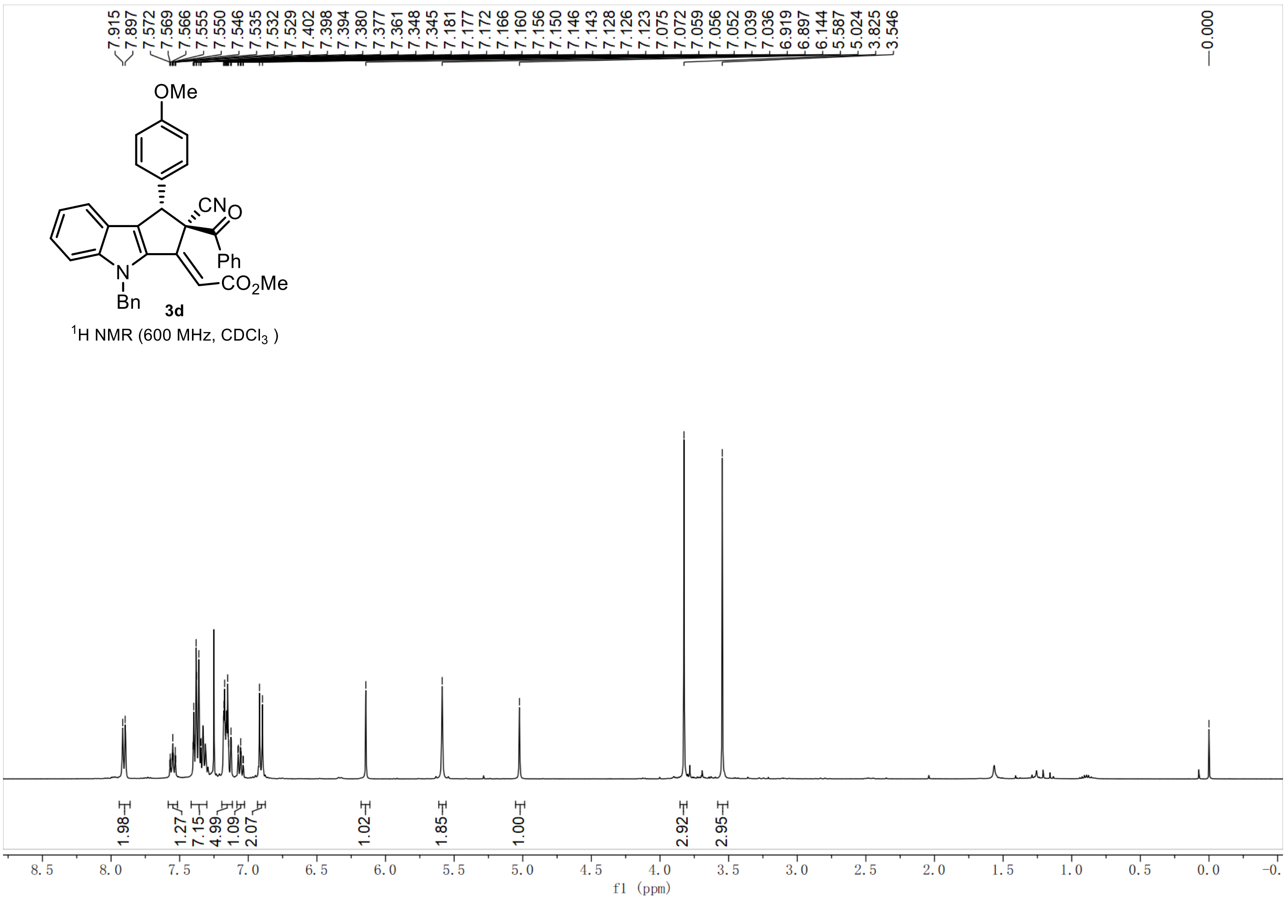
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.770	BB	1.0893	1.71668e4	214.54269	50.4965
2	26.297	BB	1.5712	1.68292e4	151.83821	49.5035



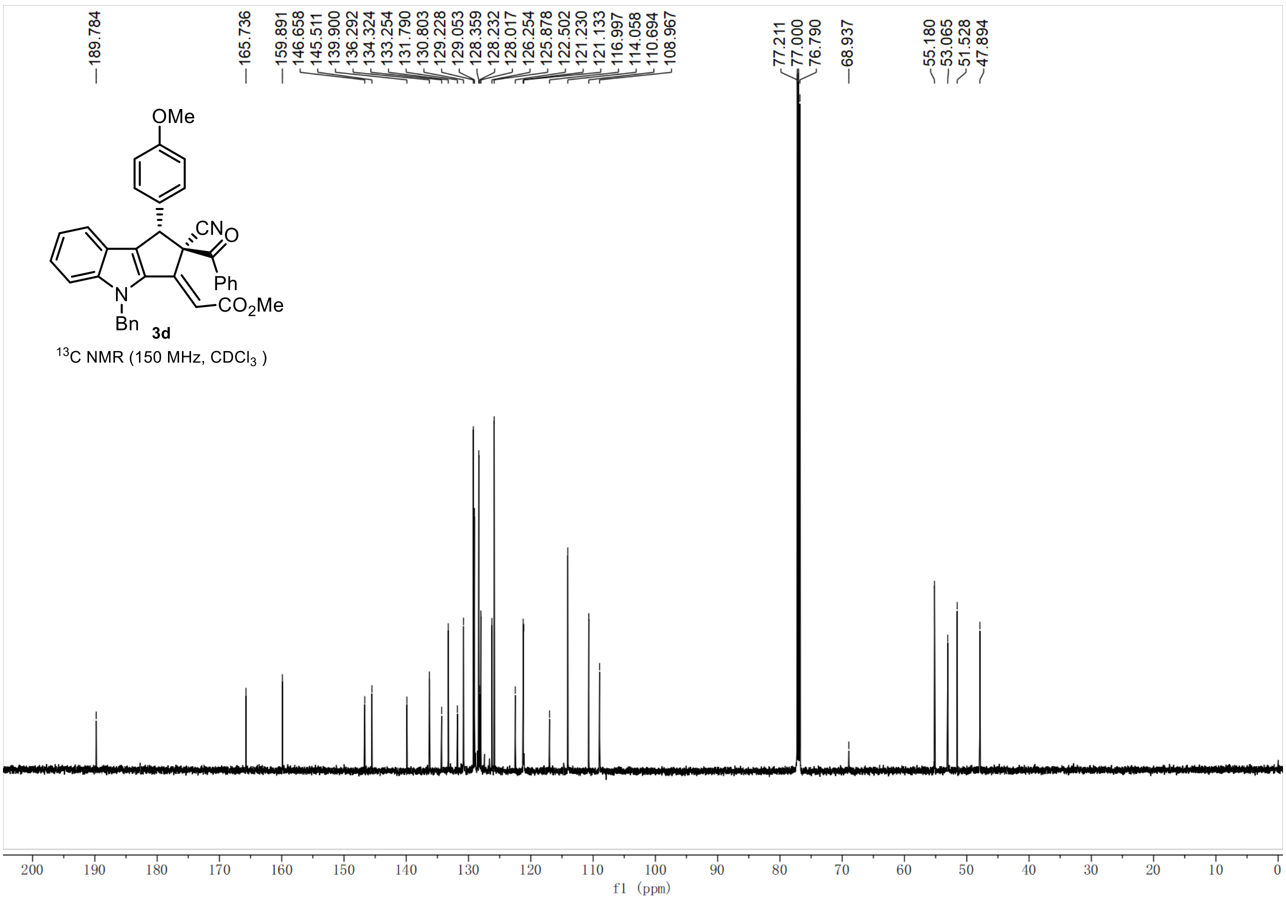
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.084	BBA	0.6656	5.38549e4	1156.43701	95.7896
2	26.633	BBA	1.0401	2367.19531	33.02604	4.2104

Name	CYC-220406-31	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-31.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:05:30 AM (UTC+08:00)

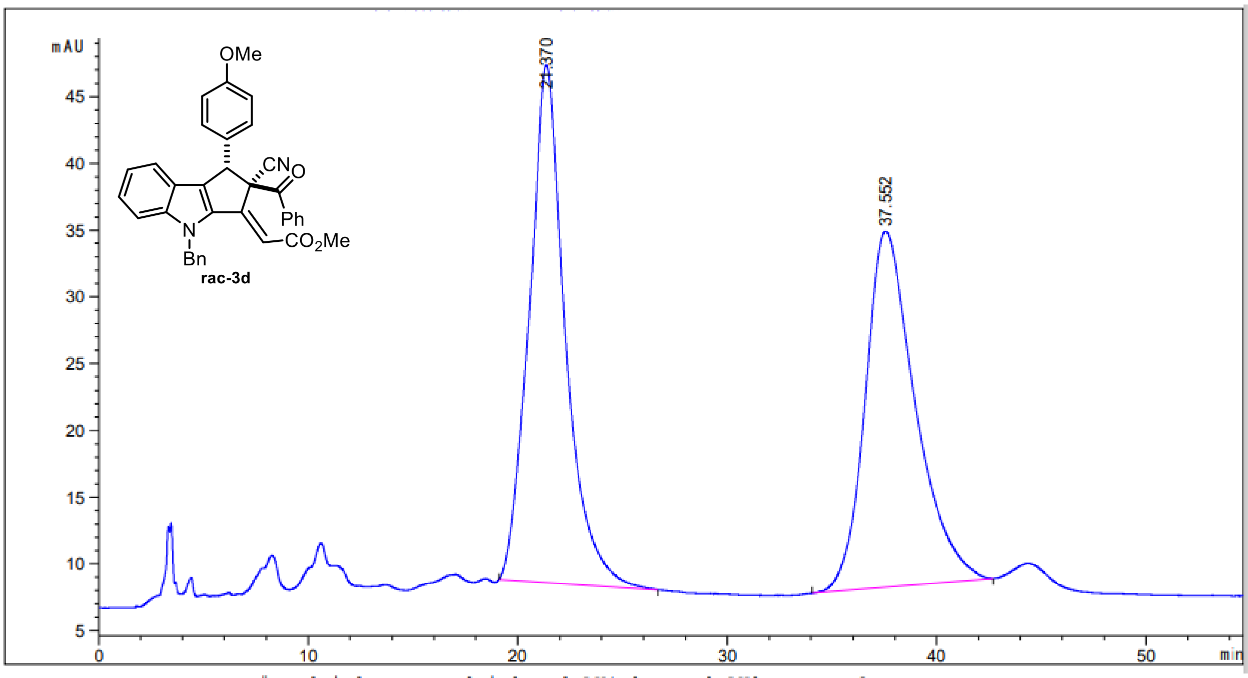




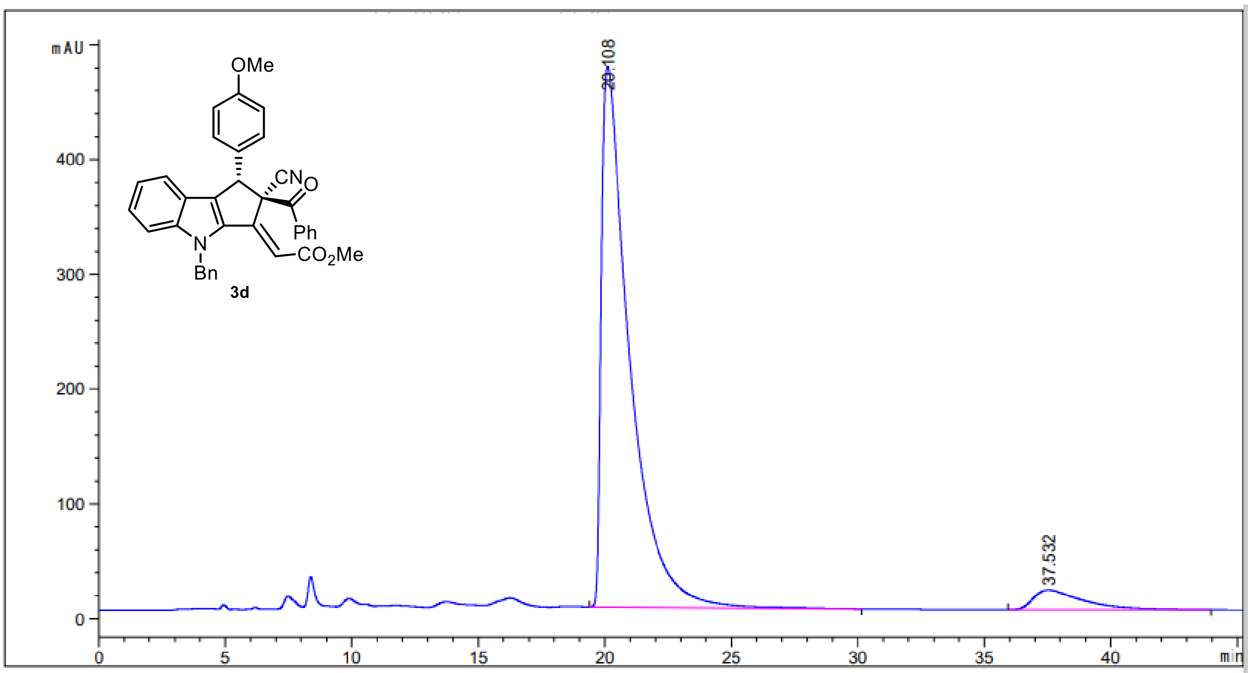
7.915
7.897
7.572
7.569
7.566
7.555
7.550
7.546
7.535
7.532
7.529
7.402
7.398
7.394
7.380
7.377
7.361
7.348
7.345
7.181
7.177
7.172
7.166
7.160
7.156
7.150
7.146
7.143
7.128
7.126
7.123
7.075
7.072
7.059
7.056
7.052
7.039
7.036
6.919
6.897
6.144
5.587
5.024
3.825
3.546
0.000
OMe
CN
O
Ph
N
Bn
CO2Me
3d
1H NMR (600 MHz, CDCl3)
1.98
1.27
7.15
4.99
1.09
2.07
1.02
1.85
1.00
2.92
2.95
f1 (ppm)



189.784
165.736
159.891
146.658
145.511
139.900
136.292
134.324
133.254
131.790
130.803
129.228
129.053
128.359
128.232
128.017
126.254
125.878
122.502
121.230
121.133
116.997
114.058
110.694
108.967
77.211
77.000
76.790
68.937
55.180
53.065
51.528
47.894
OMe
CN
O
Ph
N
Bn
CO2Me
3d
13C NMR (150 MHz, CDCl3)
f1 (ppm)

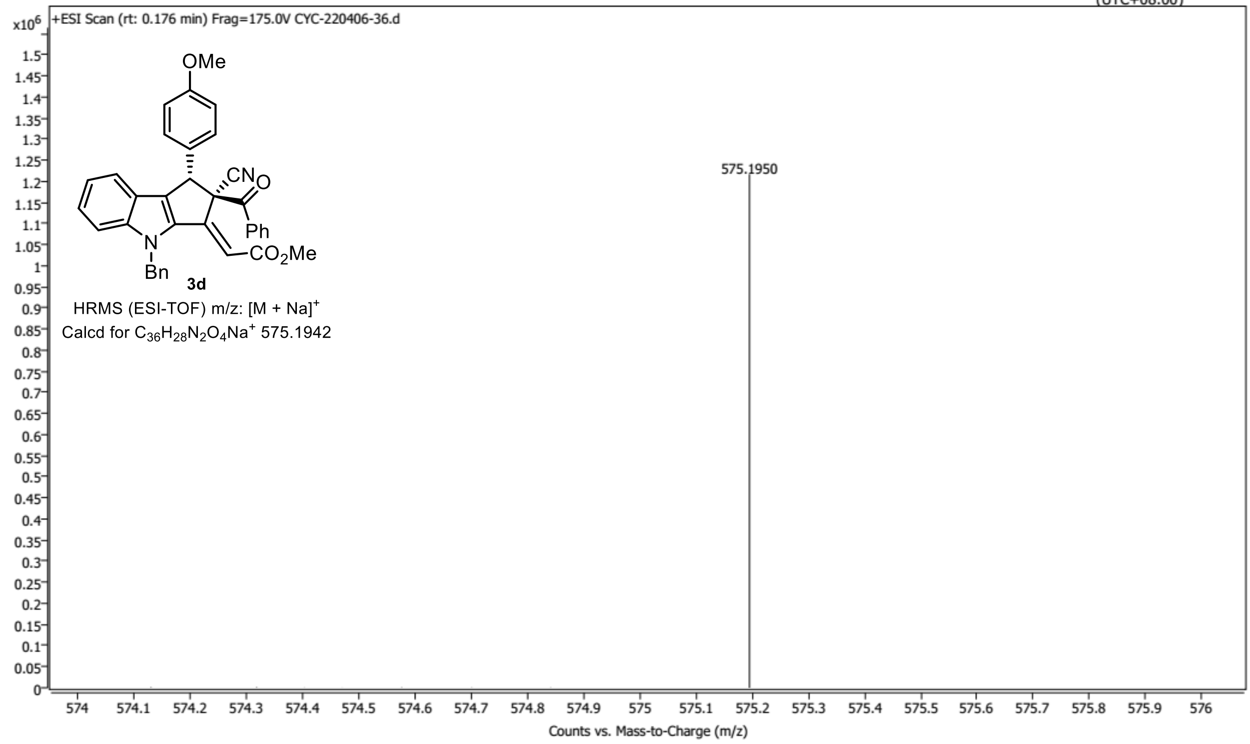


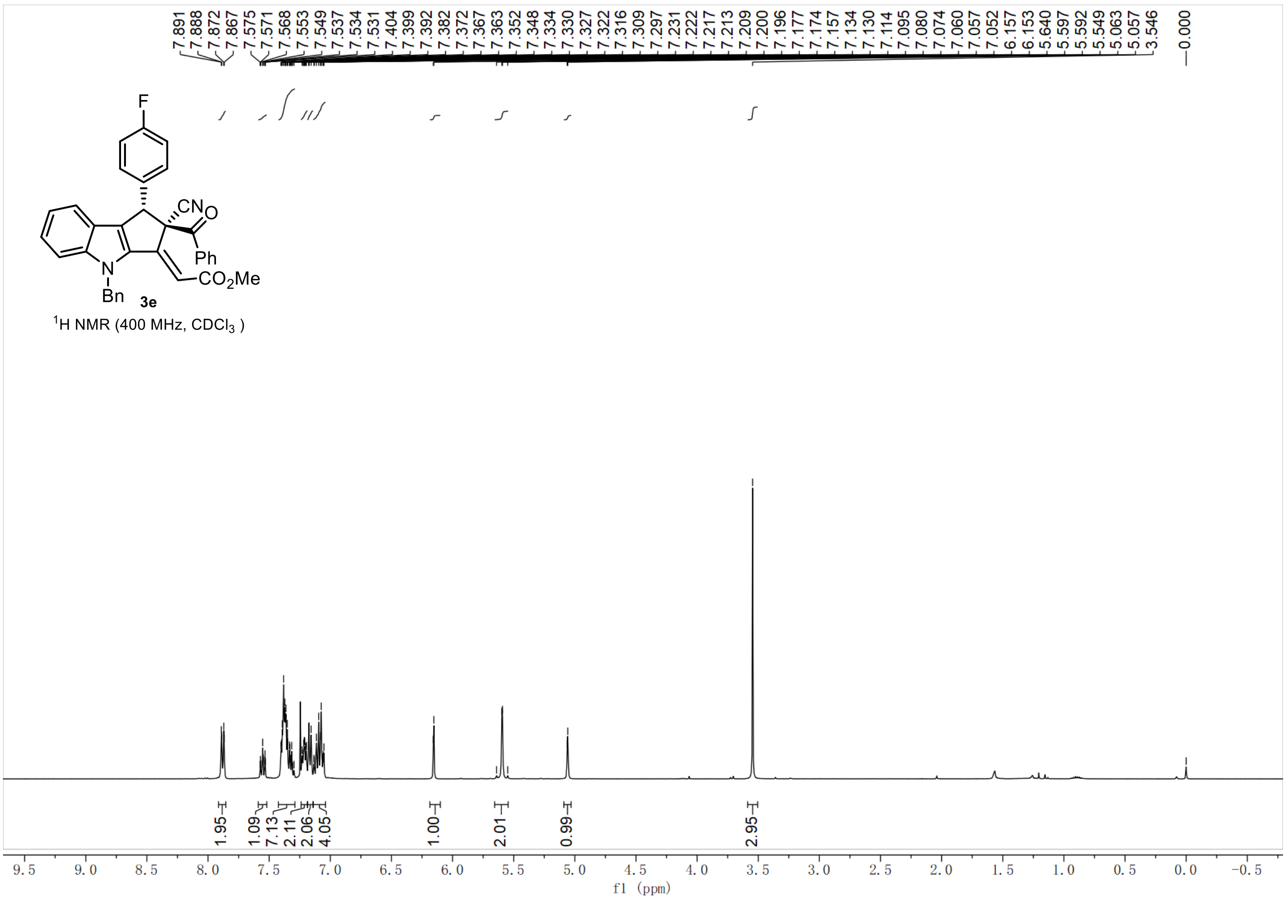
#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.370	BB	1.6519	4642.52393	38.76826	51.2039
2	37.552	BB	2.1829	4424.21533	26.66907	48.7961



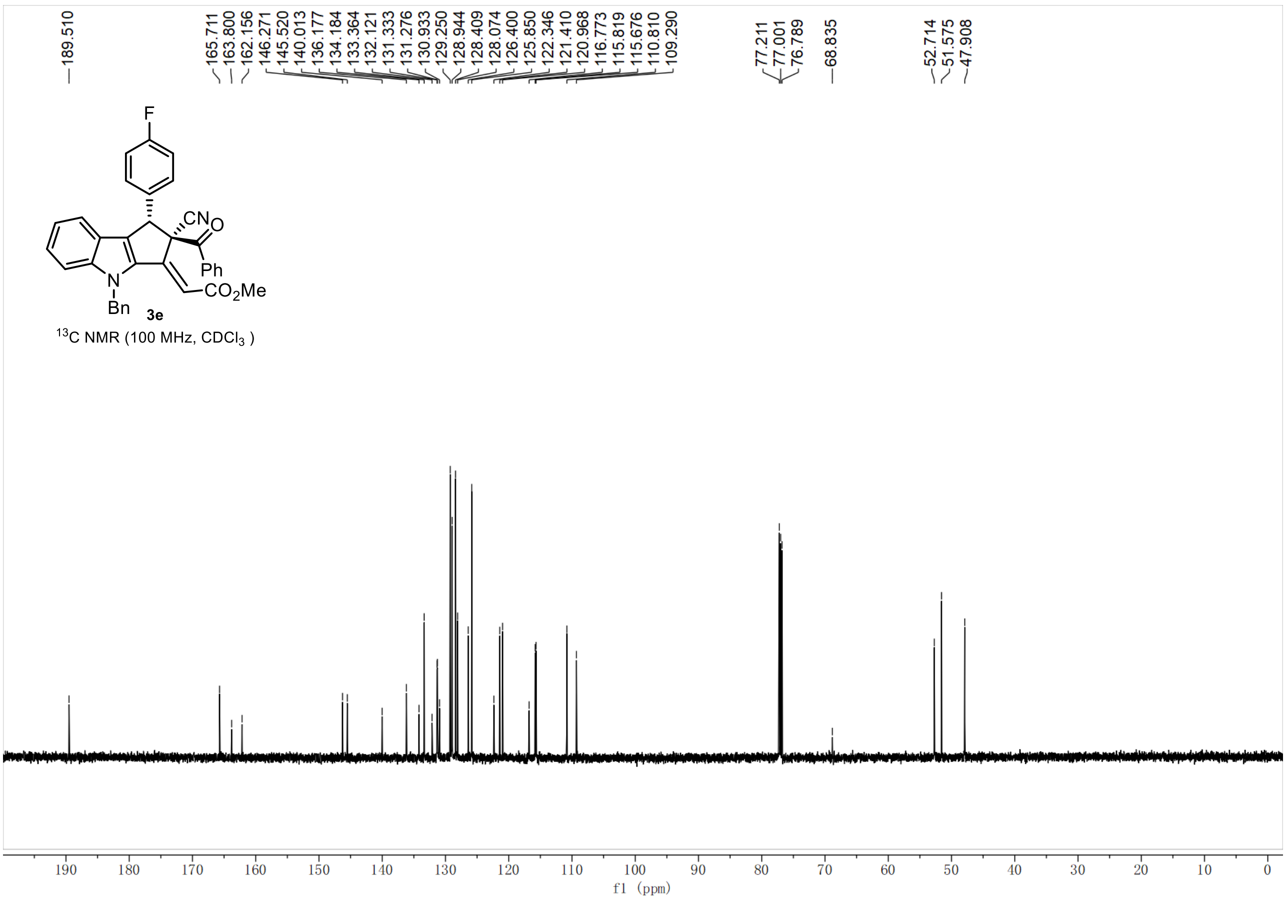
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.108	BB	1.1079	3.67421e4	471.13086	94.1100
2	37.532	BB	1.8515	2299.55078	16.92615	5.8900

Name	CYC-220406-36	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-36.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:20:19 AM (UTC+08:00)

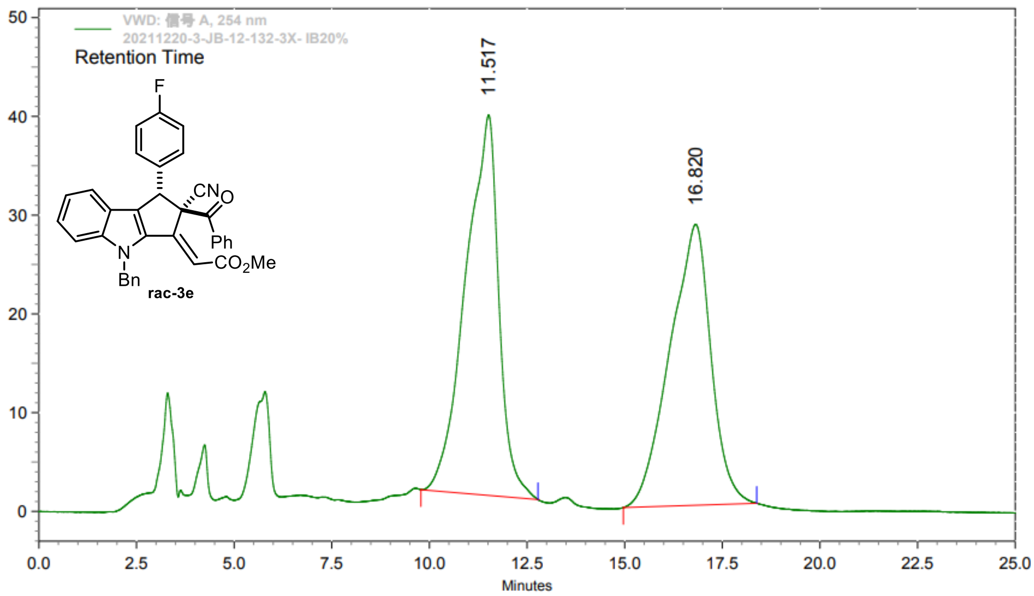




7.891
7.888
7.872
7.867
7.575
7.571
7.568
7.553
7.549
7.537
7.534
7.531
7.404
7.399
7.392
7.382
7.372
7.367
7.363
7.352
7.348
7.334
7.330
7.327
7.322
7.316
7.309
7.297
7.231
7.222
7.217
7.213
7.209
7.200
7.196
7.177
7.174
7.157
7.134
7.130
7.114
7.095
7.080
7.074
7.060
7.057
7.052
6.157
6.153
5.640
5.597
5.592
5.549
5.063
5.057
3.546
0.000
F
CN
O
Ph
N
Bn
CO_2Me
3e
^{1}H NMR (400 MHz, $CDCl_3$)
1.95
1.09
7.13
2.11
2.06
4.05
1.00
2.01
0.99
2.95
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

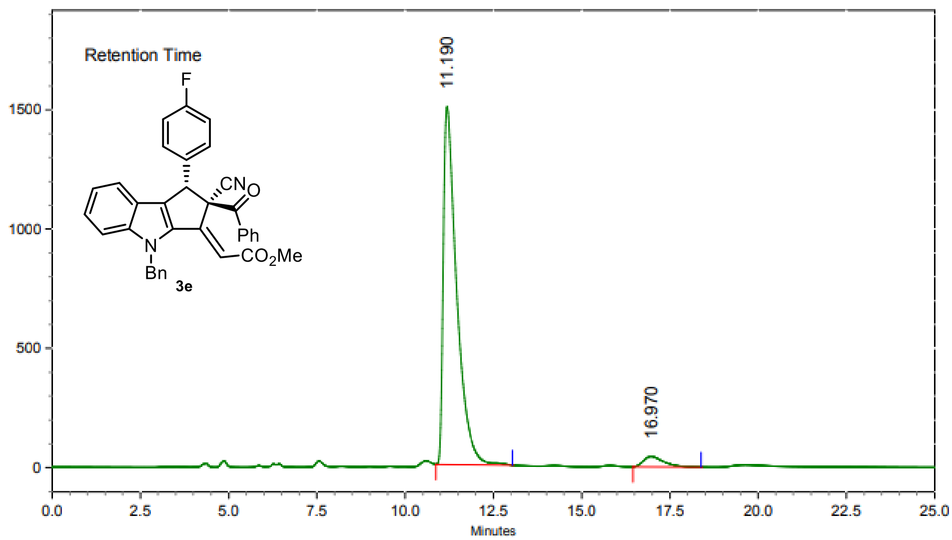


189.510
165.711
163.800
162.156
146.271
145.520
140.013
136.177
134.184
133.364
132.121
131.333
131.276
130.933
129.250
128.944
128.409
128.074
126.400
125.850
122.346
121.410
120.968
116.773
115.819
115.676
110.810
109.290
77.211
77.001
76.789
68.835
52.714
51.575
47.908
F
CN
O
Ph
N
Bn
CO_2Me
3e
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



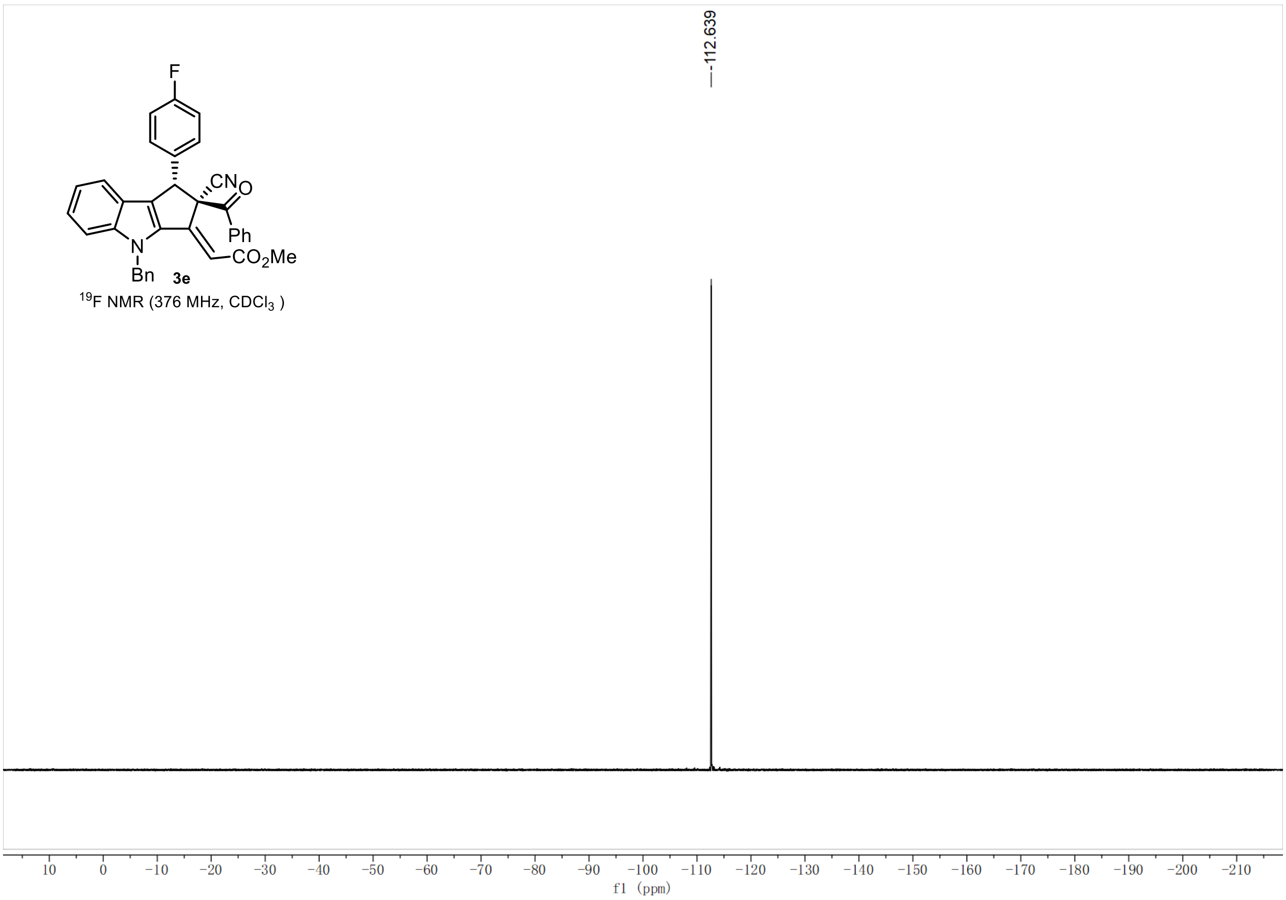
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	11.517	2.997	646287	38198004	52.2167
2	16.820	3.413	477300	34954859	47.7833

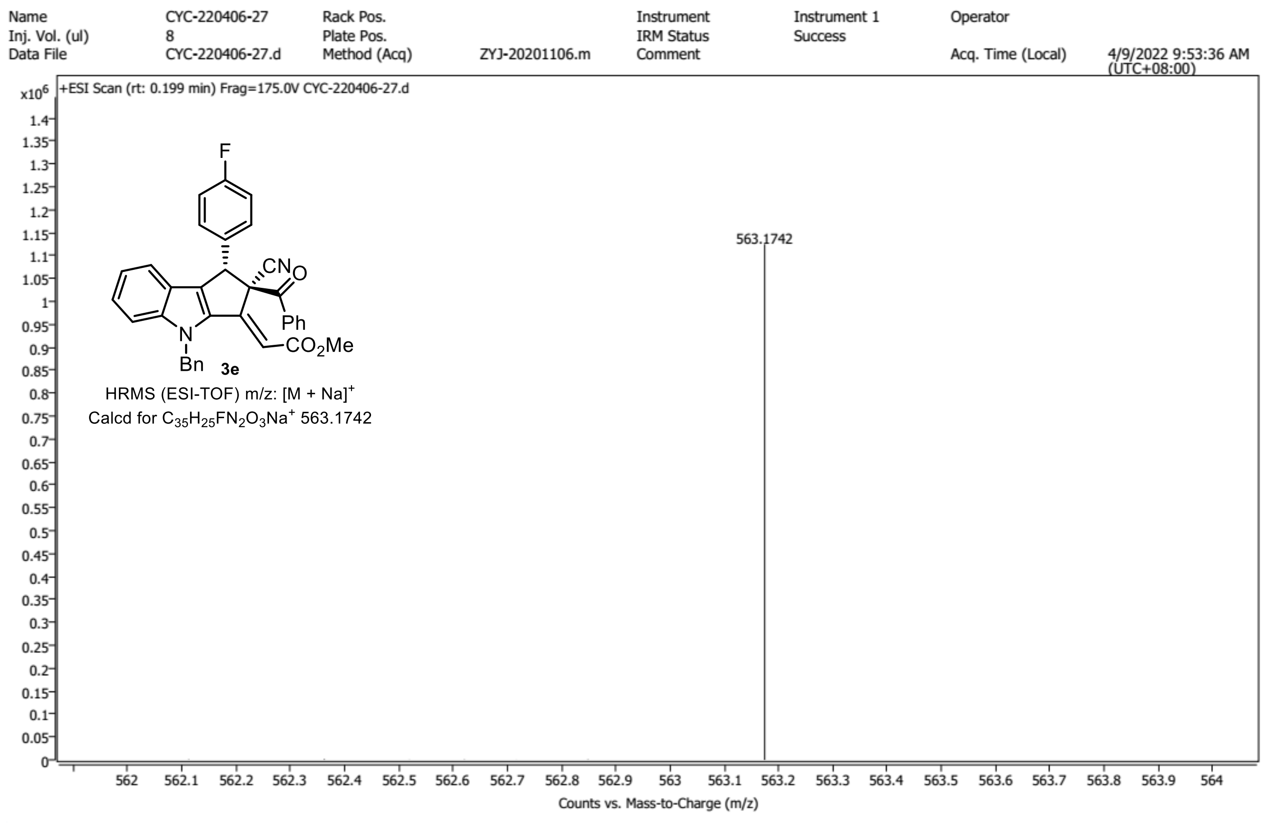


AREA PERCENT REPORT

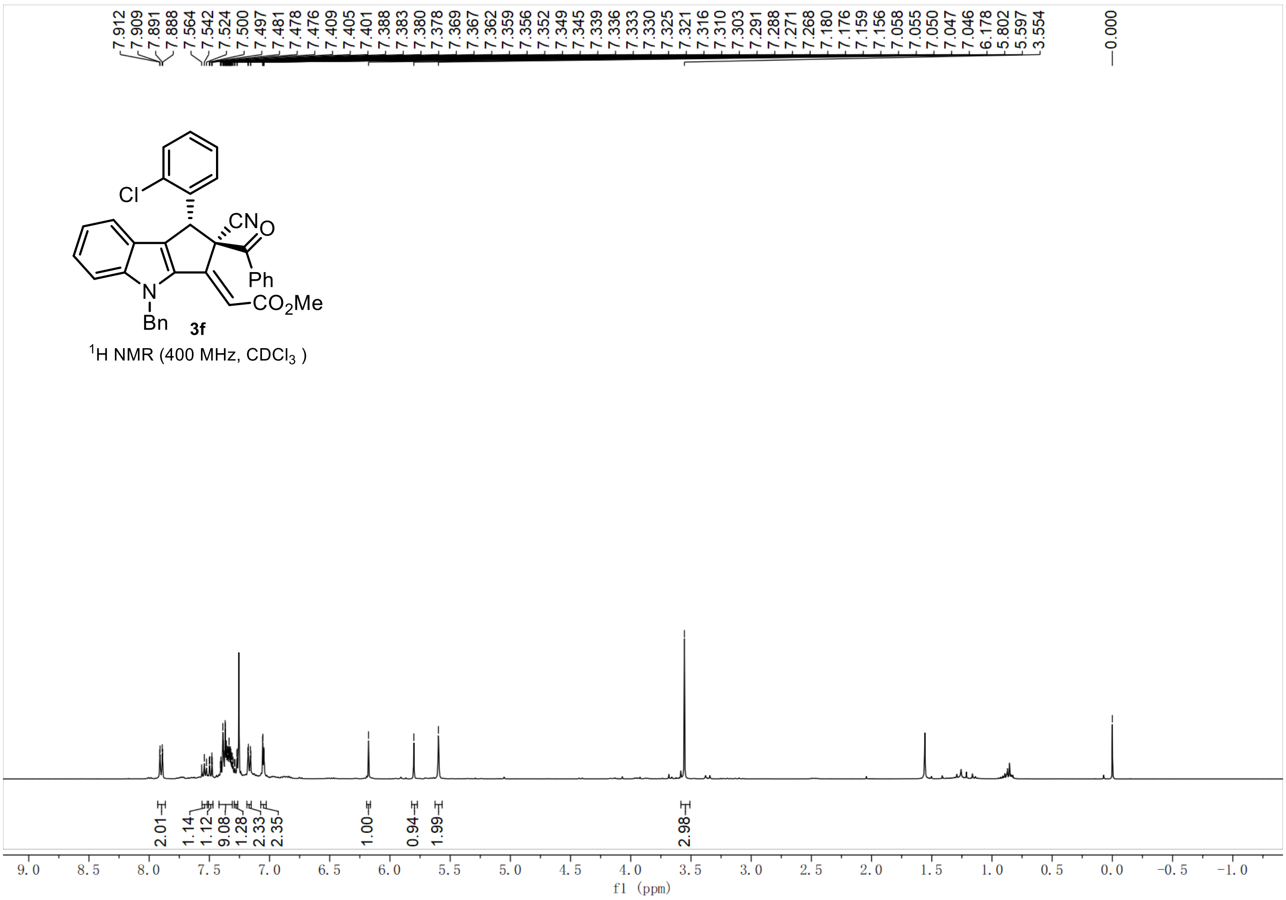
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	11.190	2.170	25194964	657783056	95.6538
2	16.970	1.920	764296	29887205	4.3462

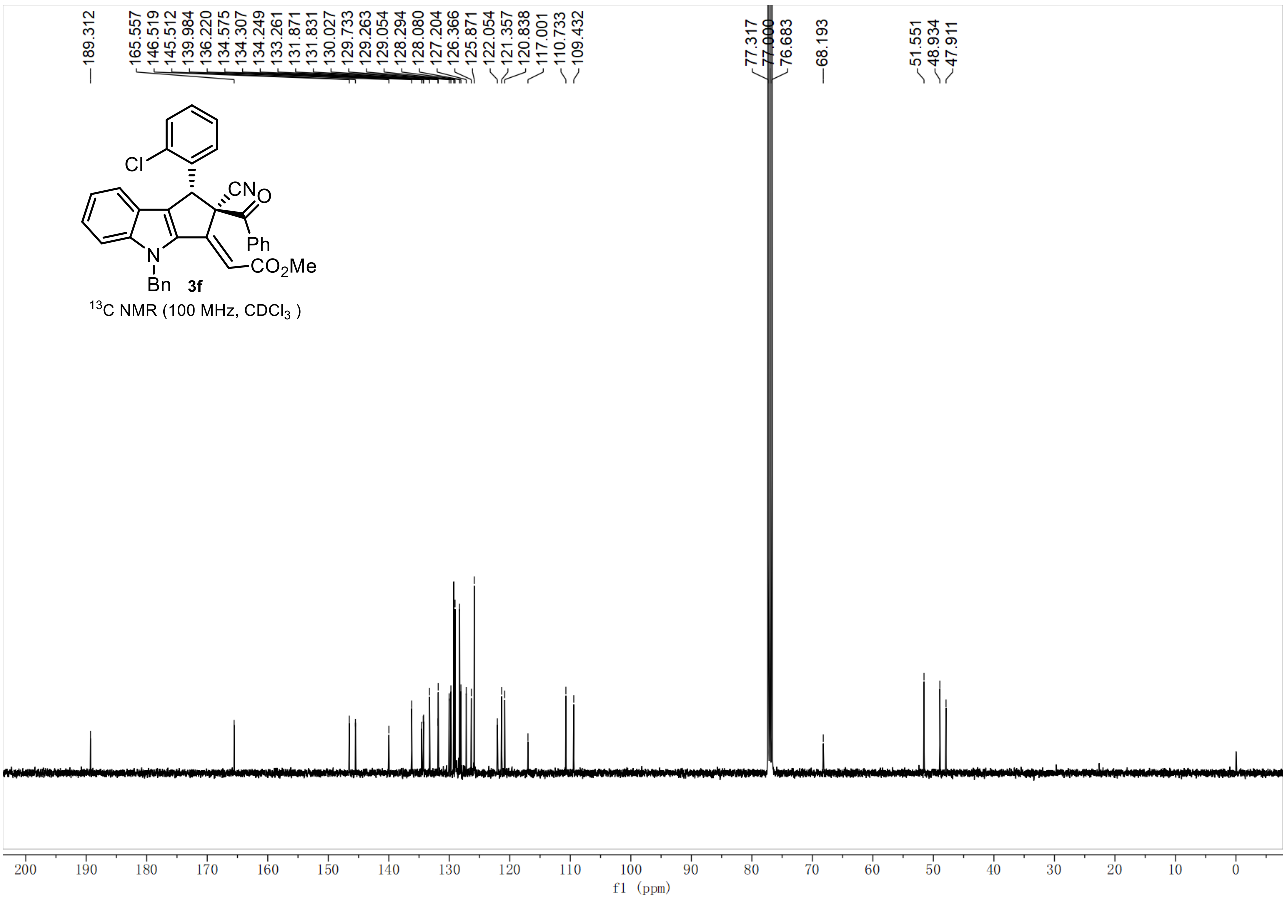


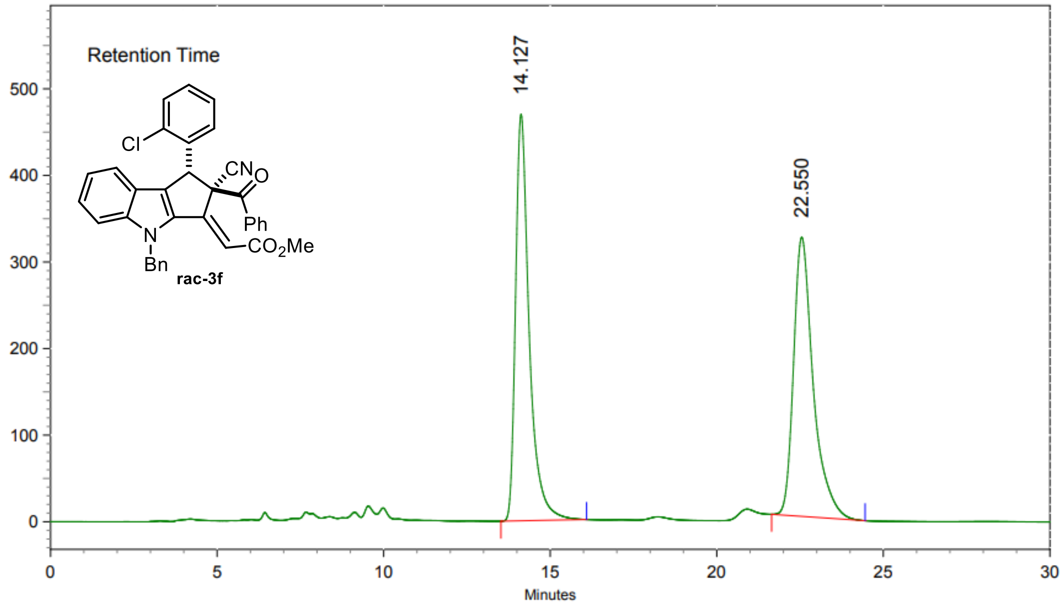
-112.639
F
CN
O
Ph
N
Bn
3e
CO_2Me
^{19}F NMR (376 MHz, $CDCl_3$)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



Name CYC-220406-27
Rack Pos.
Instrument Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status Success
Data File CYC-220406-27.d
Method (Acq) ZYJ-20201106.m
Comment
Acq. Time (Local) 4/9/2022 9:53:36 AM (UTC+08:00)
x10^6
+ESI Scan (rt: 0.199 min) Frag=175.0V CYC-220406-27.d
563.1742
F
CN
O
Ph
N
Bn
3e
CO_2Me
HRMS (ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{35}H_{25}FN_2O_3Na^+$ 563.1742
Counts vs. Mass-to-Charge (m/z)

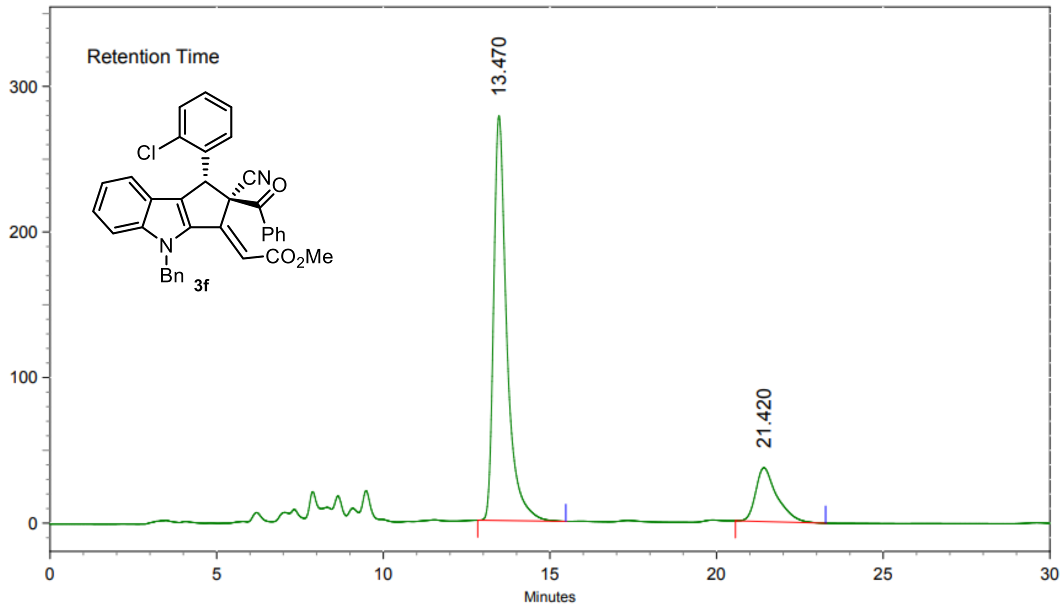

7.912 7.909 7.891 7.888 7.564 7.542 7.524 7.500 7.497 7.481 7.478 7.476 7.409 7.405 7.401 7.388 7.383 7.380 7.378 7.369 7.367 7.362 7.359 7.356 7.352 7.349 7.345 7.339 7.336 7.333 7.330 7.325 7.321 7.316 7.310 7.303 7.291 7.288 7.271 7.268 7.180 7.176 7.159 7.156 7.058 7.055 7.050 7.047 7.046 6.178 5.802 5.597 3.554
0.000
Cl
CN
O
Ph
N
CO2Me
Bn
3f
1H NMR (400 MHz, CDCl3)
2.01 1.14 1.12 9.08 1.28 2.33 2.35 1.00 0.94 1.99 2.98
f1 (ppm)


189.312
165.557 146.519 145.512 139.984 136.220 134.575 134.307 134.249 133.261 131.871 131.831 130.027 129.733 129.263 129.054 128.294 128.080 127.204 126.366 125.871 122.054 121.357 120.838 117.001 110.733 109.432
77.317 77.000 76.683
68.193
51.551 48.934 47.911
Cl
CN
O
Ph
N
CO2Me
Bn
3f
13C NMR (100 MHz, CDCl3)
f1 (ppm)



AREA PERCENT REPORT

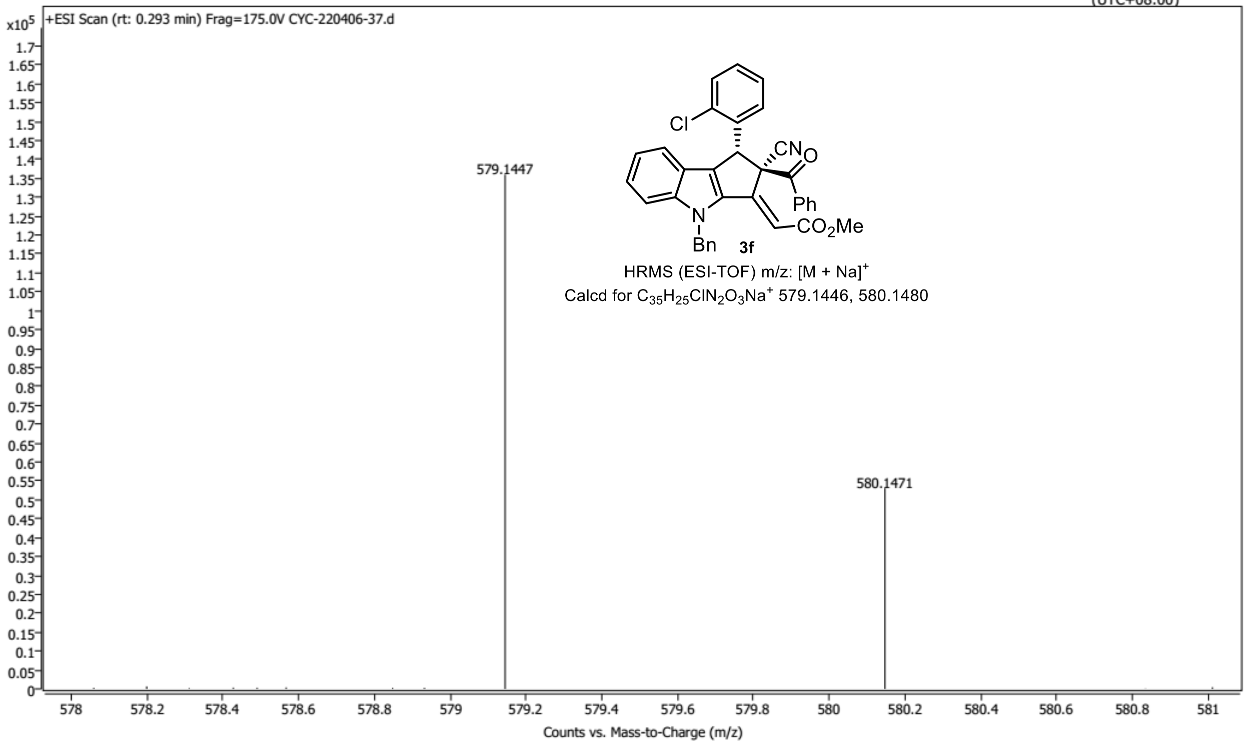
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	14.127	2.573	7877961	224533728	50.2902
2	22.550	2.807	5407970	221942612	49.7098

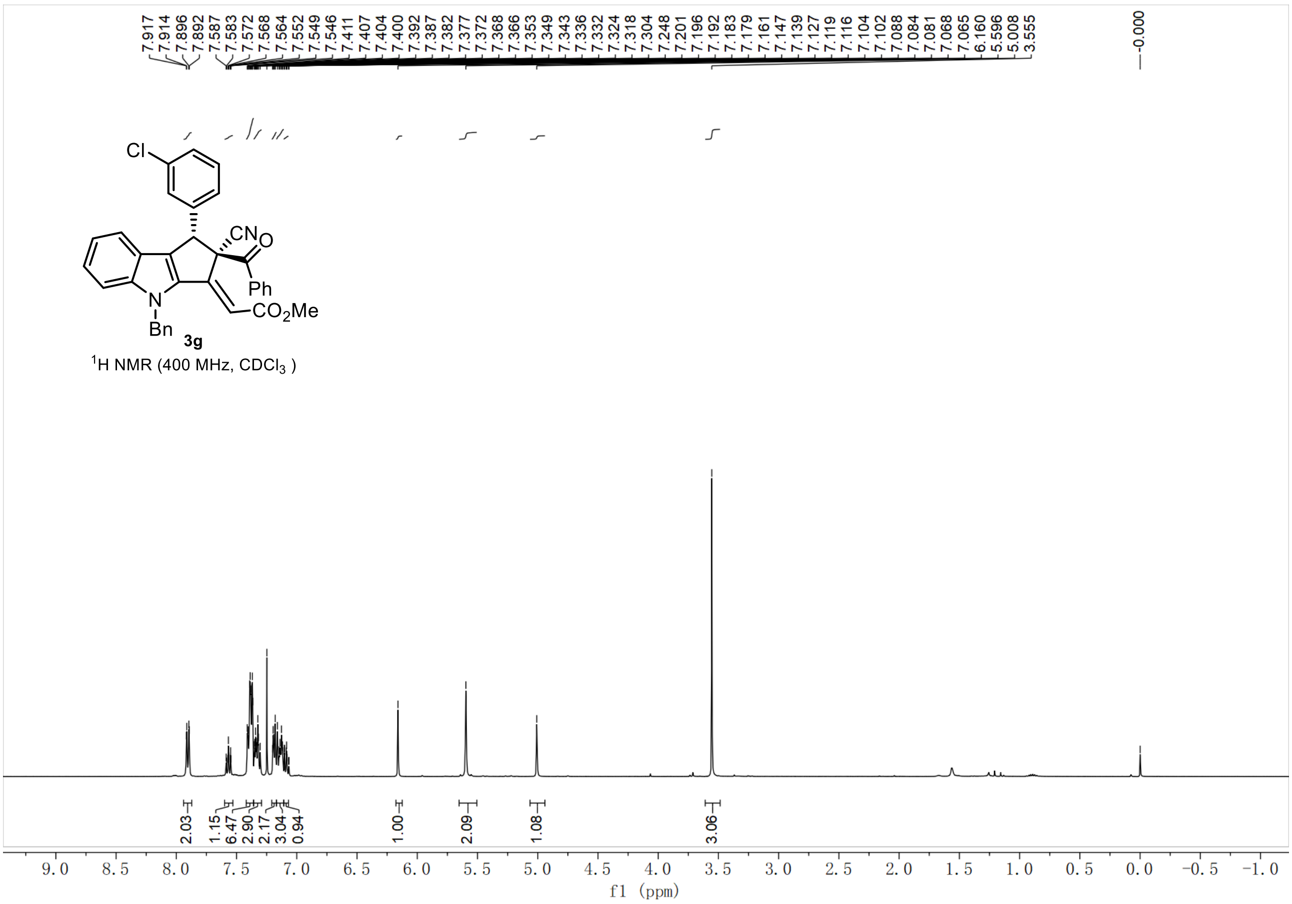


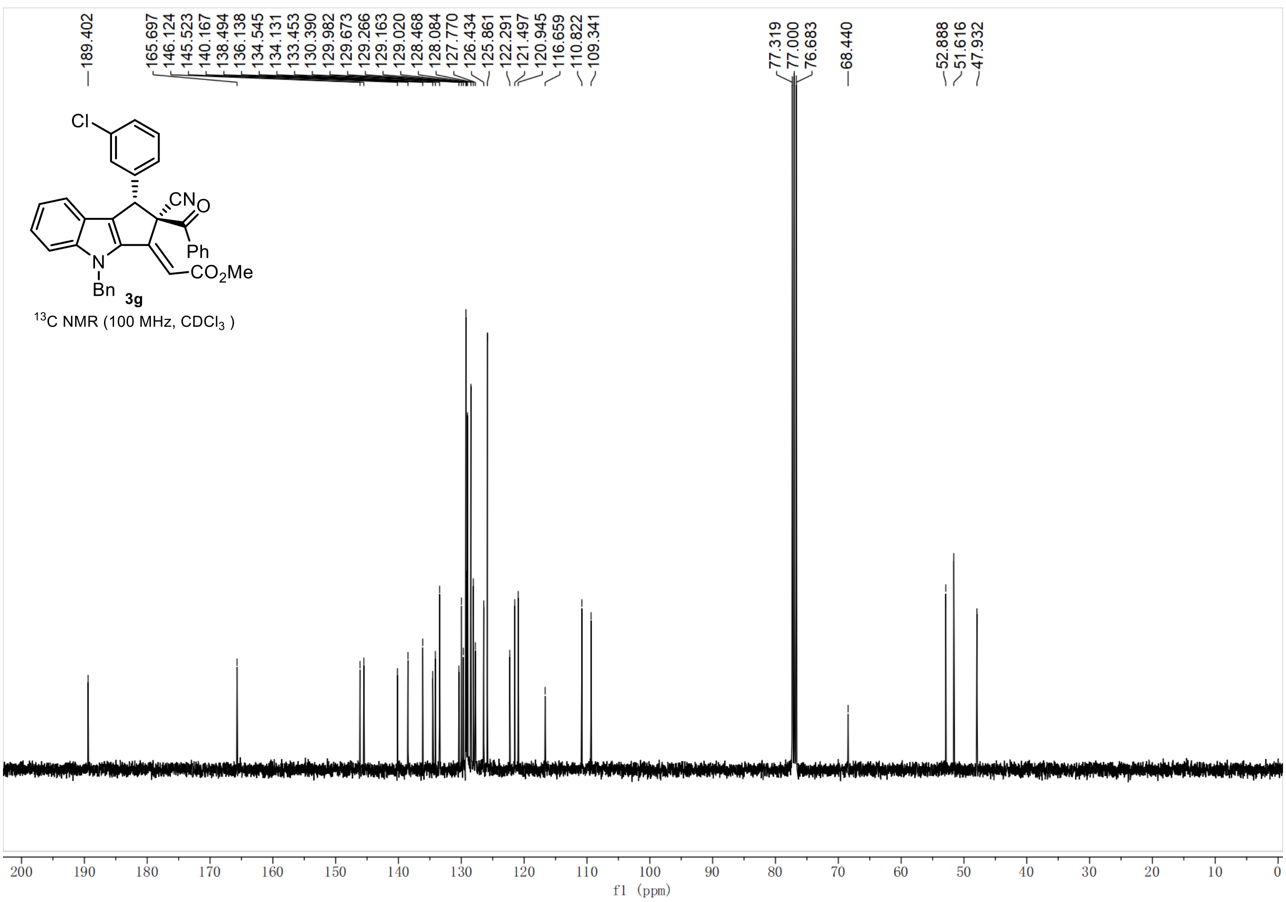
AREA PERCENT REPORT

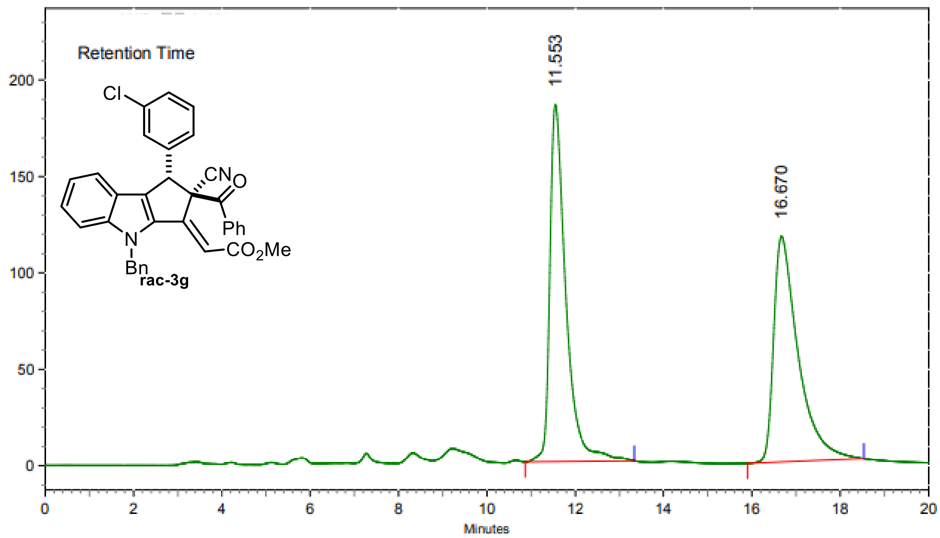
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.470	2.643	4663761	127889900	82.3282
2	21.420	2.707	620541	27451695	17.6718

Name	CYC-220406-37	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-37.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:52:20 AM (UTC+08:00)



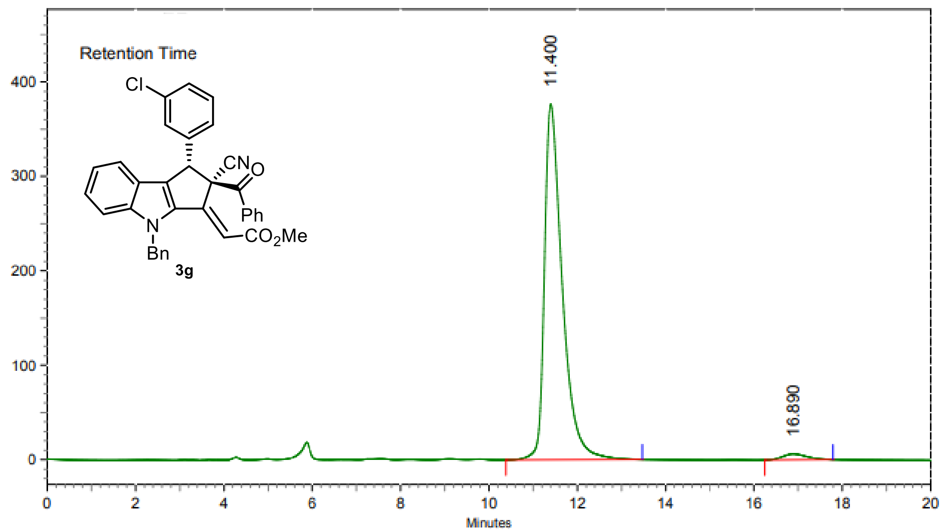

7.917
7.914
7.896
7.892
7.587
7.583
7.572
7.568
7.564
7.552
7.549
7.546
7.411
7.407
7.404
7.400
7.392
7.387
7.382
7.377
7.372
7.368
7.366
7.353
7.349
7.343
7.336
7.332
7.324
7.318
7.304
7.248
7.201
7.196
7.192
7.183
7.179
7.161
7.147
7.139
7.127
7.119
7.116
7.104
7.102
7.088
7.084
7.081
7.068
7.065
6.160
5.596
5.008
3.555
0.000
Cl
CN
O
Ph
N
Bn
3g
CO2Me
1H NMR (400 MHz, CDCl3)
2.03
1.15
6.47
2.90
2.17
3.04
0.94
1.00
2.09
1.08
3.06
f1 (ppm)


189.402
165.697
146.124
145.523
140.167
138.494
136.138
134.545
134.131
133.453
130.390
129.982
129.673
129.266
129.163
129.020
128.468
128.084
127.770
126.434
125.861
122.291
121.497
120.945
116.659
110.822
109.341
77.319
77.000
76.683
68.440
52.888
51.616
47.932
Cl
CN
O
Ph
N
Bn
3g
CO2Me
13C NMR (100 MHz, CDCl3)
f1 (ppm)



AREA PERCENT REPORT

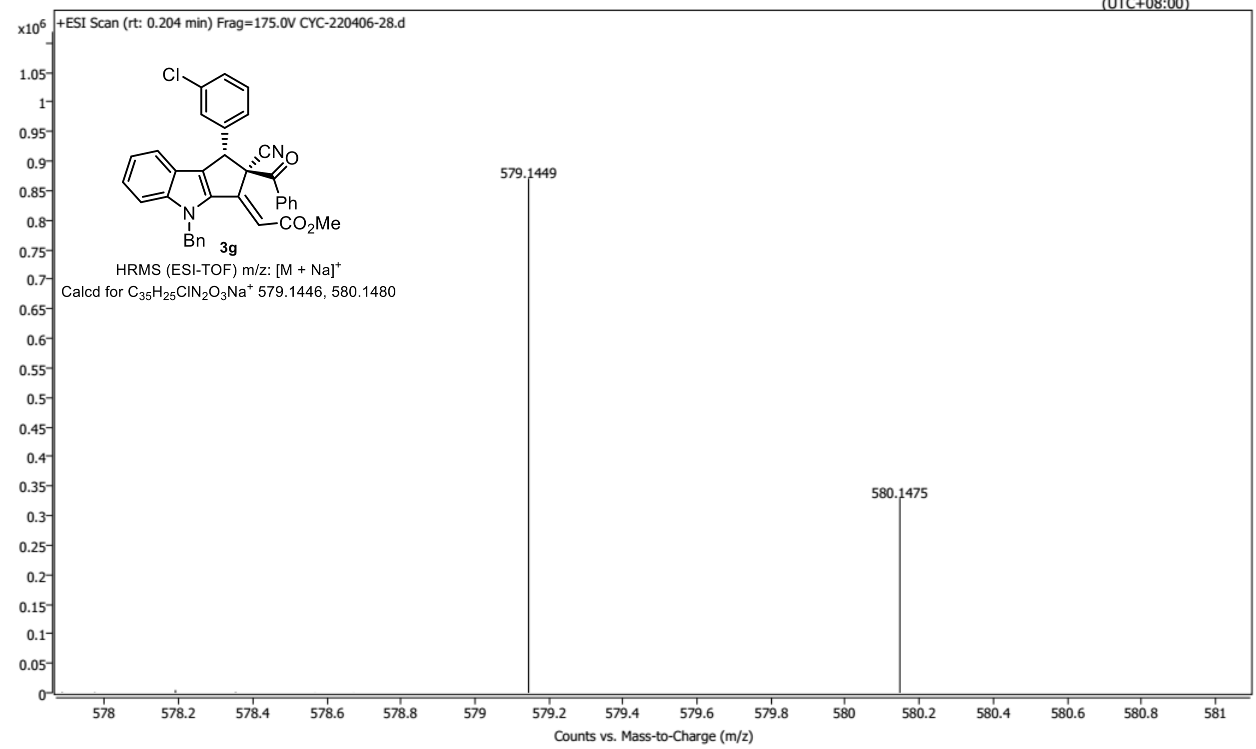
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	11.553	2.473	3107348	77648017	50.4894
2	16.670	2.637	1965246	76142563	49.5106

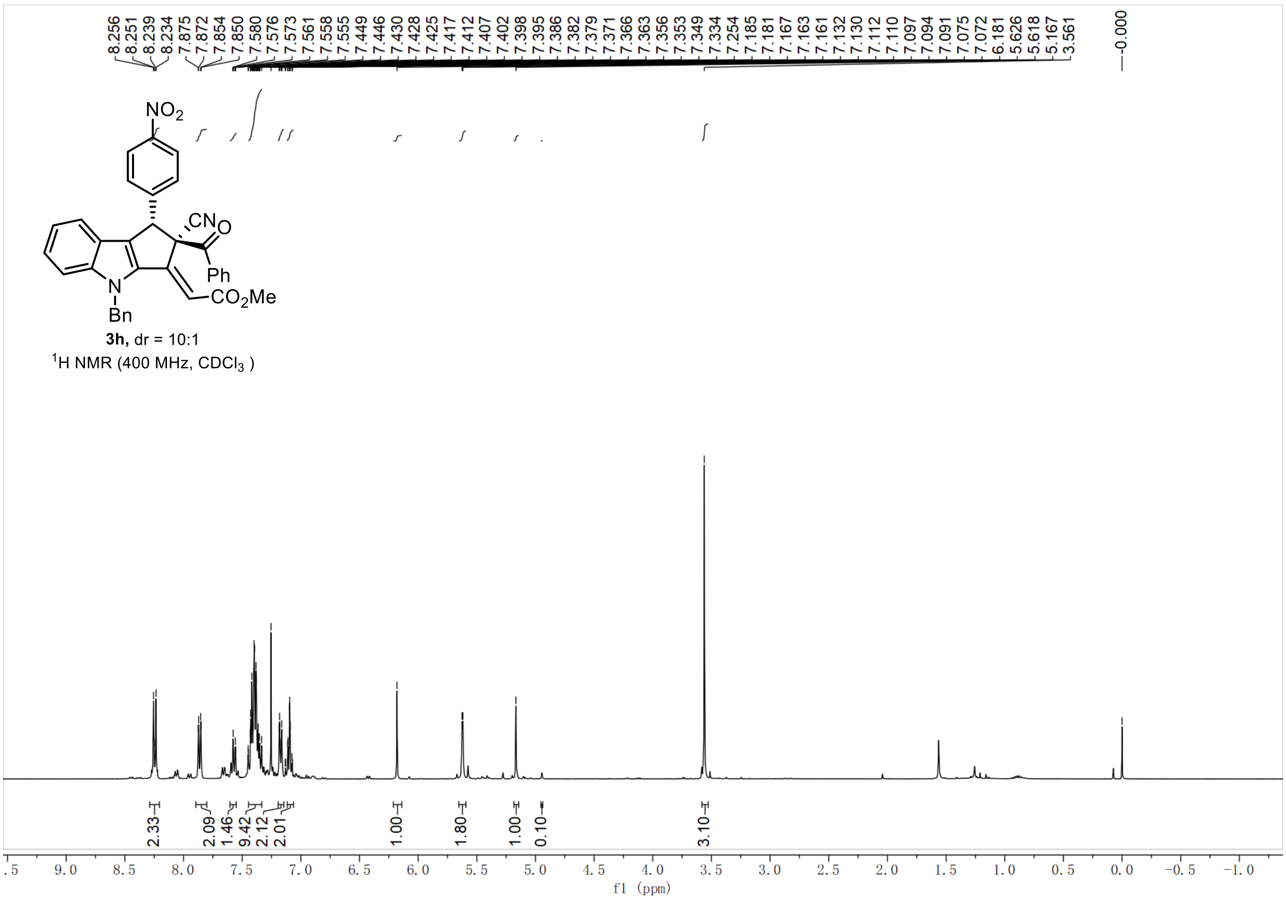


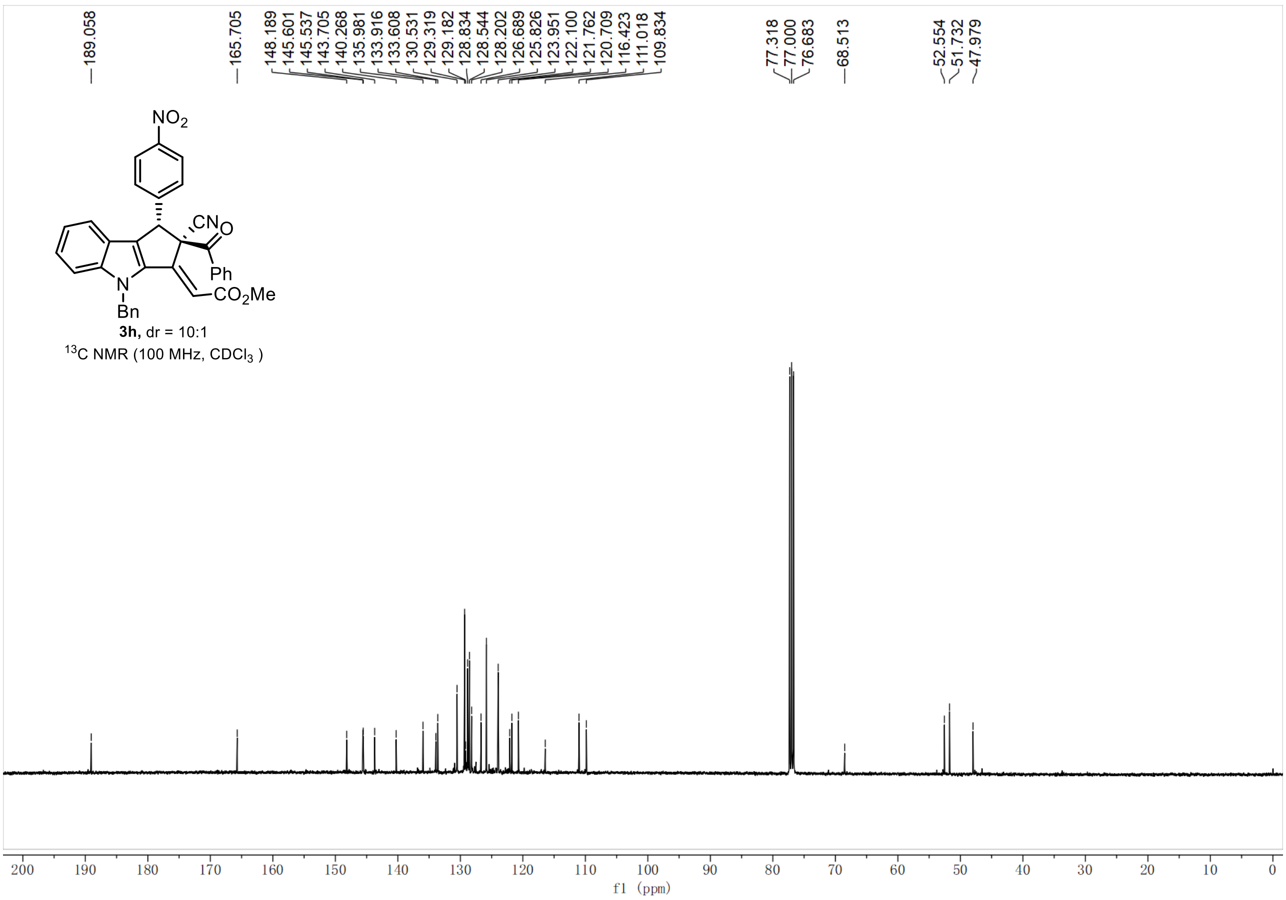
AREA PERCENT REPORT

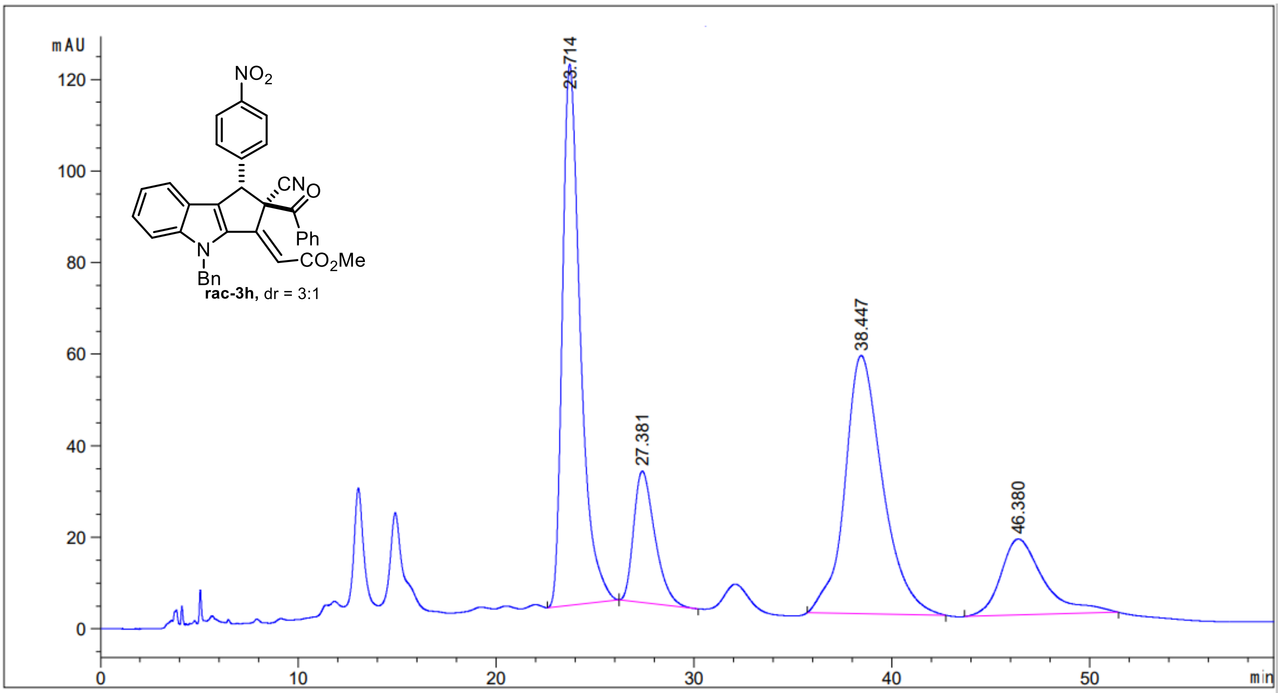
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	11.400	3.093	6316741	179639463	97.6855
2	16.890	1.547	109246	4256232	2.3145

Name	CYC-220406-28	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-28.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 9:56:34 AM (UTC+08:00)

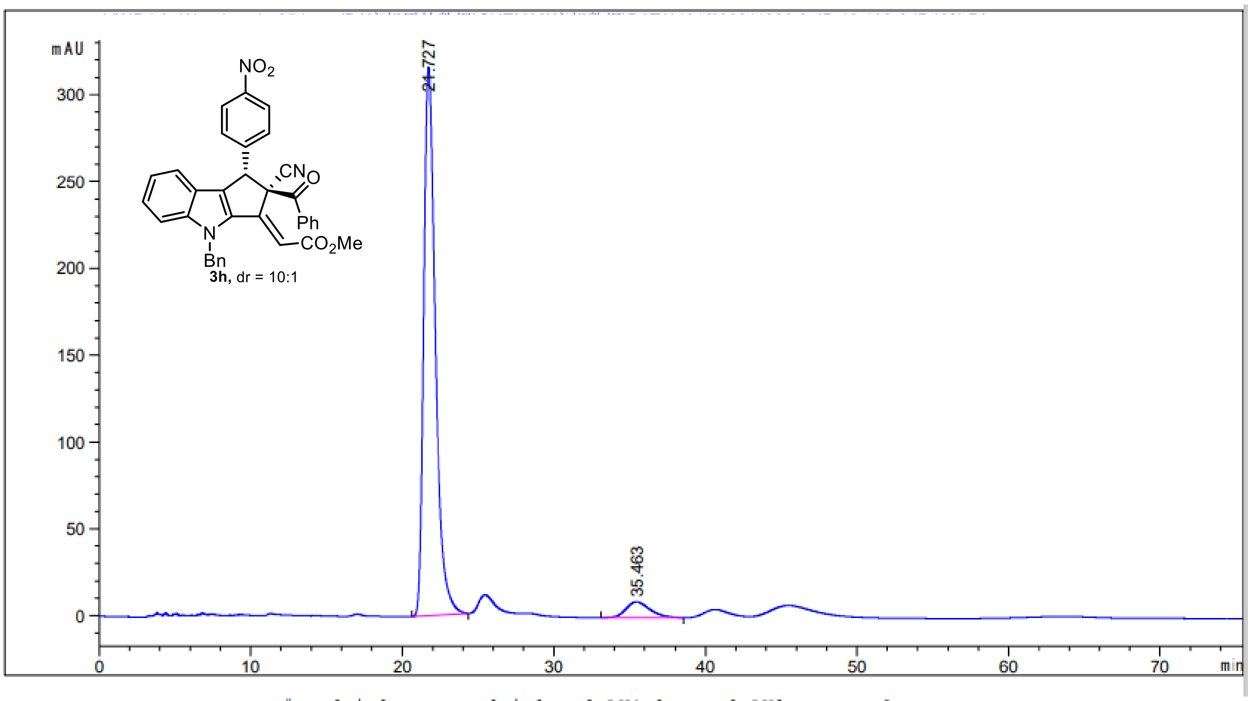



8.256
8.251
8.239
8.234
7.875
7.872
7.854
7.850
7.580
7.576
7.573
7.561
7.558
7.555
7.449
7.446
7.430
7.428
7.425
7.417
7.412
7.407
7.402
7.398
7.395
7.386
7.382
7.379
7.371
7.366
7.363
7.356
7.353
7.349
7.334
7.254
7.185
7.181
7.167
7.163
7.161
7.132
7.130
7.112
7.110
7.097
7.094
7.091
7.075
7.072
6.181
5.626
5.618
5.167
3.561
-0.000
NO2
CN
O
Ph
N
Bn
CO2Me
3h, dr = 10:1
1H NMR (400 MHz, CDCl3)
2.33
2.09
1.46
9.42
2.12
2.01
1.00
1.80
1.00
0.10
3.10
f1 (ppm)


189.058
165.705
148.189
145.601
145.537
143.705
140.268
135.981
133.916
133.608
130.531
129.319
129.182
128.834
128.544
128.202
126.689
125.826
123.951
122.100
121.762
120.709
116.423
111.018
109.834
77.318
77.000
76.683
68.513
52.554
51.732
47.979
NO2
CN
O
Ph
N
Bn
CO2Me
3h, dr = 10:1
13C NMR (100 MHz, CDCl3)
f1 (ppm)

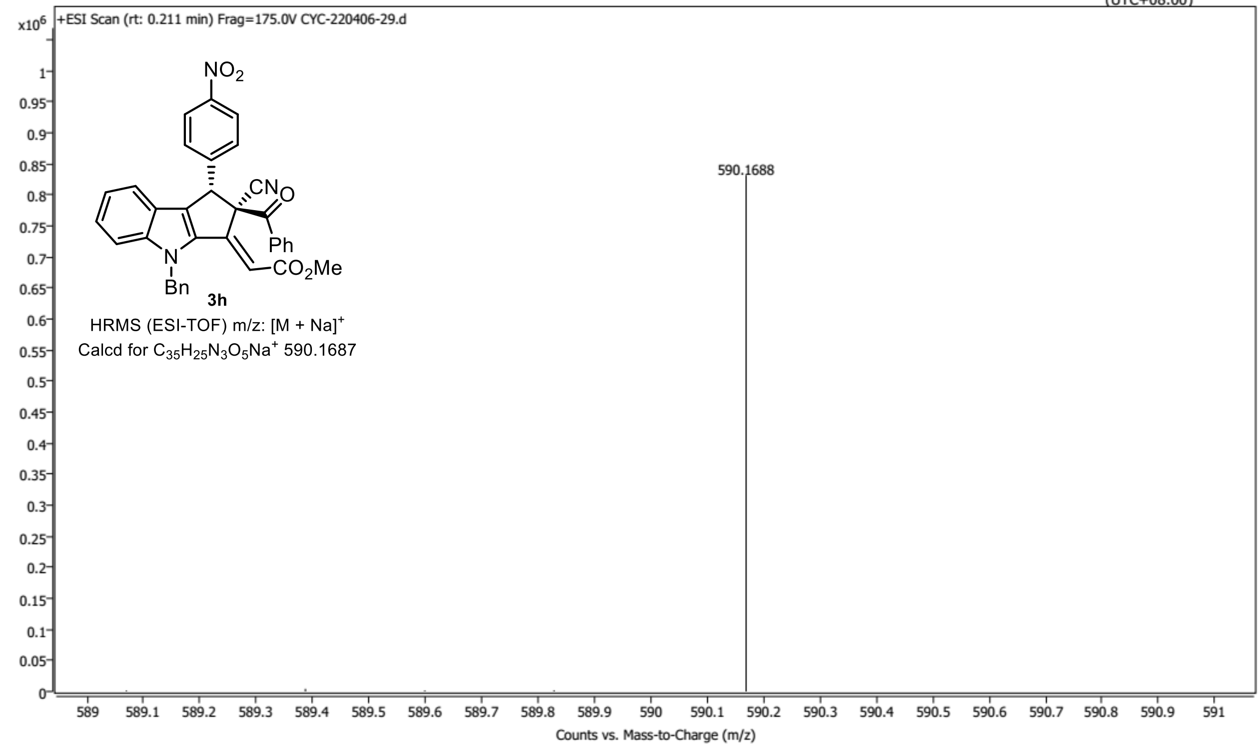


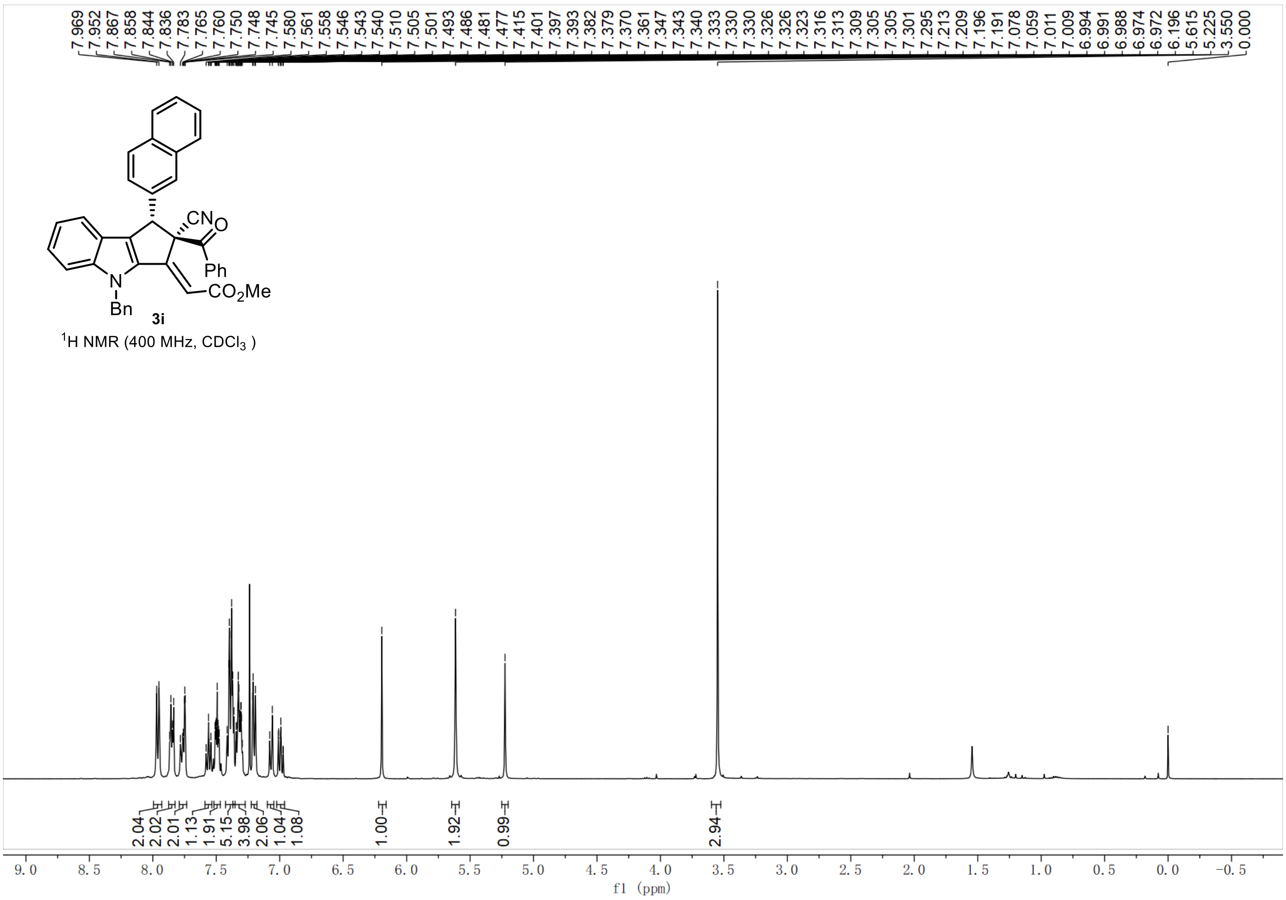
#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.714	BB	0.9631	7482.34961	118.14599	38.1177
2	27.381	BB	1.1014	2142.34985	28.73208	10.9139
3	38.447	BBA	1.9575	7496.09375	56.32394	38.1878
4	46.380	BBA	1.8679	2508.78101	16.61508	12.7806

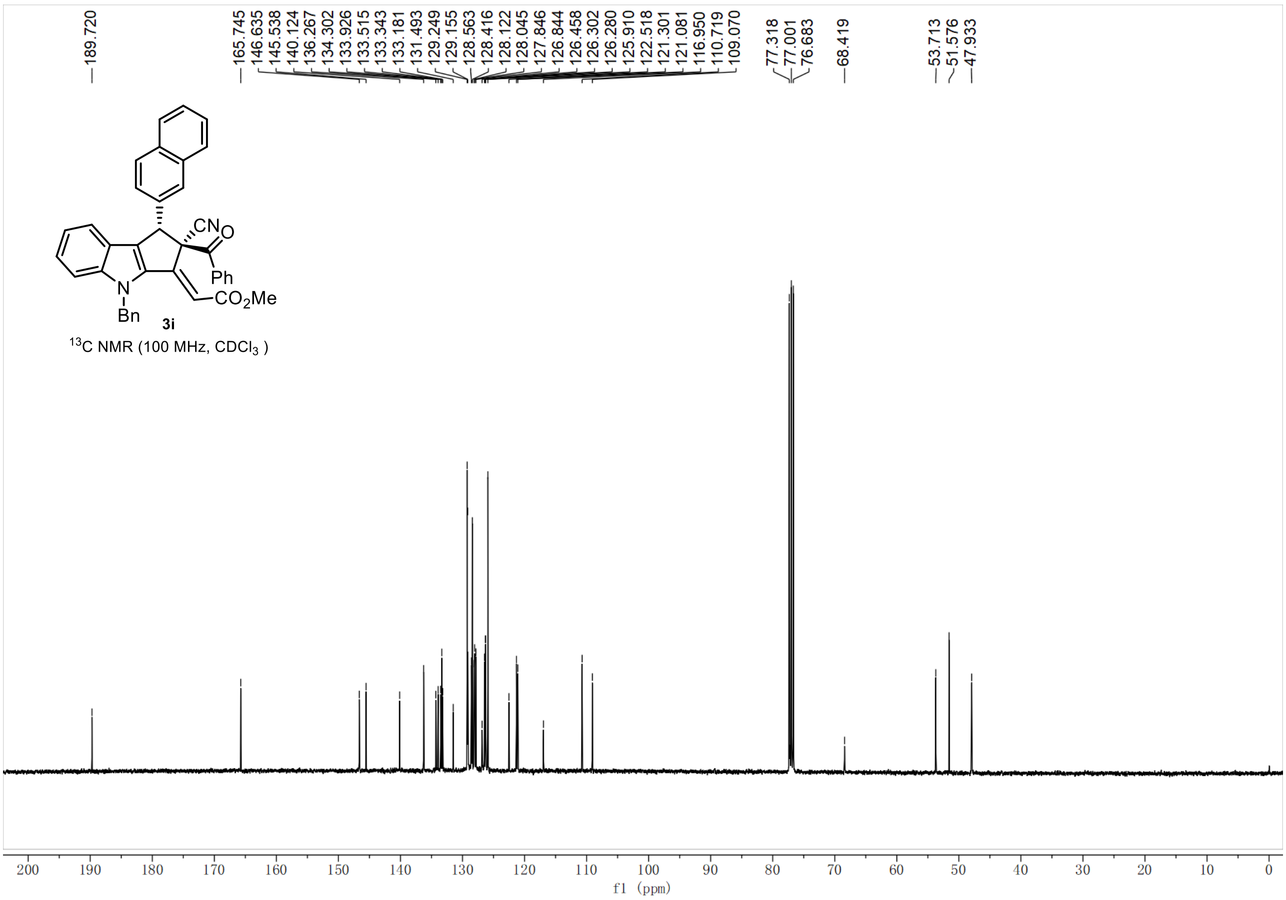


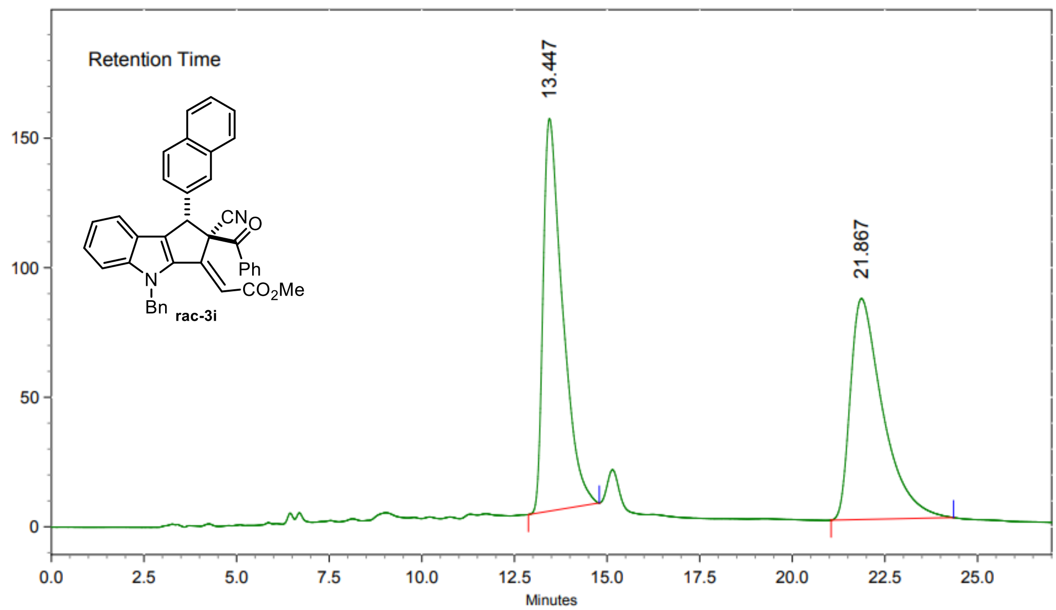
#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.727	BB	0.8111	1.68350e4	315.86215	94.4745
2	35.463	BBA	1.2989	984.63000	9.00523	5.5255

Name	CYC-220406-29	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-29.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 9:59:32 AM (UTC+08:00)



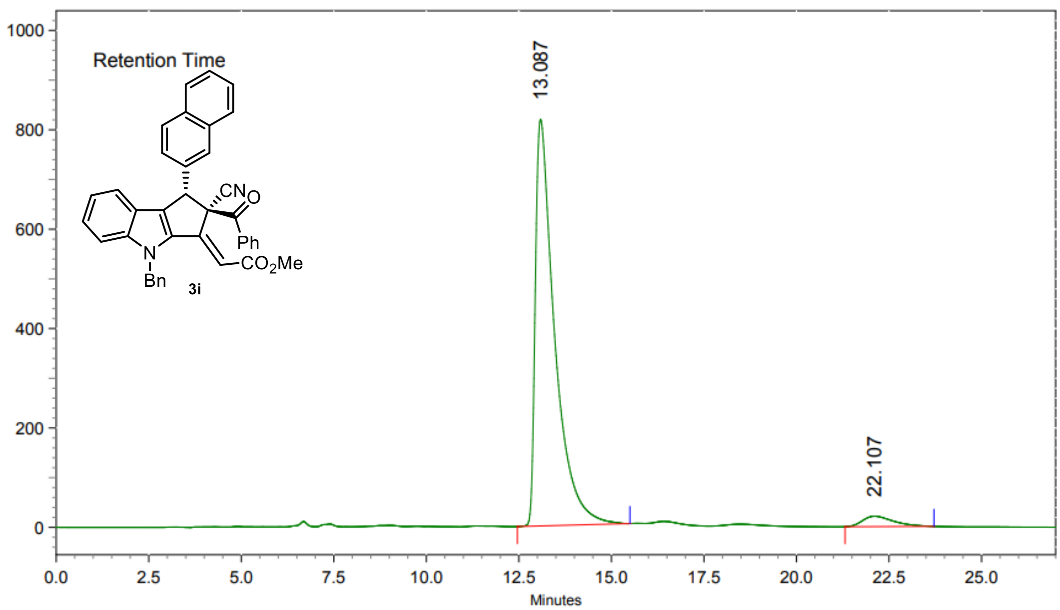

7.969
7.952
7.867
7.858
7.844
7.836
7.783
7.765
7.760
7.750
7.748
7.745
7.580
7.561
7.558
7.546
7.543
7.540
7.510
7.505
7.501
7.493
7.486
7.481
7.477
7.415
7.401
7.397
7.393
7.382
7.379
7.370
7.361
7.347
7.343
7.340
7.333
7.330
7.330
7.326
7.326
7.323
7.316
7.313
7.309
7.305
7.305
7.301
7.295
7.213
7.209
7.196
7.191
7.078
7.059
7.011
7.009
6.994
6.991
6.988
6.974
6.972
6.196
5.615
5.225
3.550
0.000
CN
O
Ph
N
Bn
CO2Me
3i
1H NMR (400 MHz, CDCl3)
2.04
2.02
2.01
1.13
1.91
5.15
3.98
2.06
1.04
1.08
1.00
1.92
0.99
2.94
f1 (ppm)


189.720
165.745
146.635
145.538
140.124
136.267
134.302
133.926
133.515
133.343
133.181
131.493
129.249
129.155
128.563
128.416
128.122
128.045
127.846
126.844
126.458
126.302
126.280
125.910
122.518
121.301
121.081
116.950
110.719
109.070
77.318
77.001
76.683
68.419
53.713
51.576
47.933
CN
O
Ph
N
Bn
CO2Me
3i
13C NMR (100 MHz, CDCl3)
f1 (ppm)



AREA PERCENT REPORT

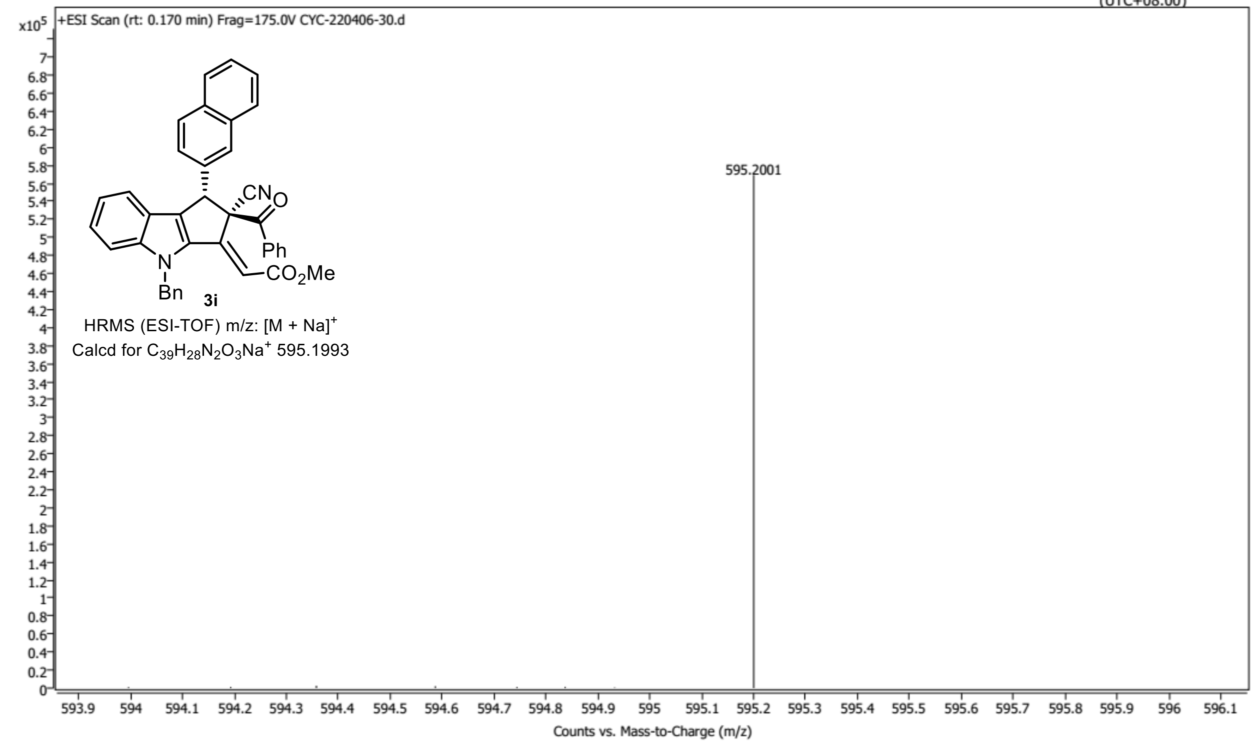
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.447	1.913	2541914	93115451	51.6469
2	21.867	3.307	1431065	87176867	48.3531

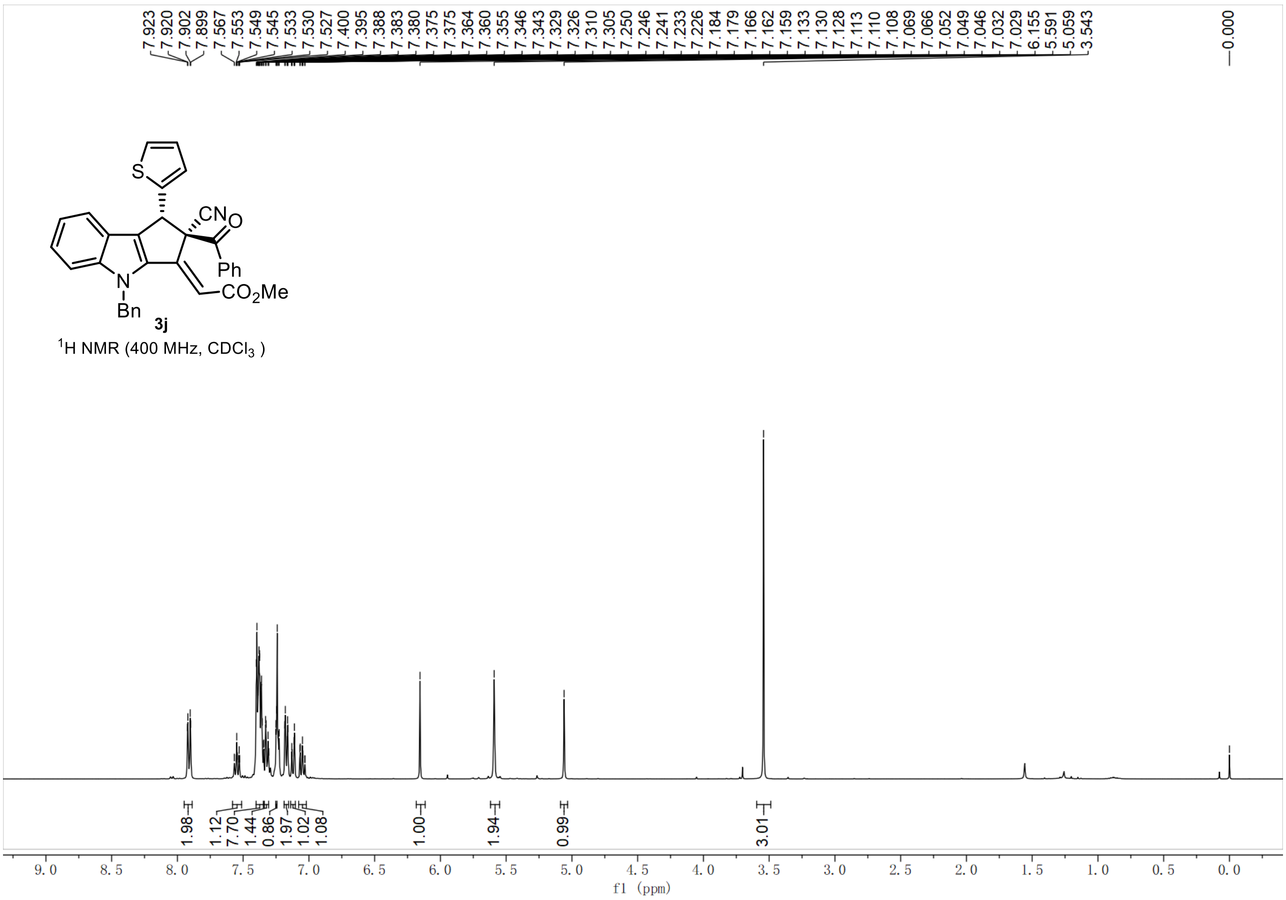


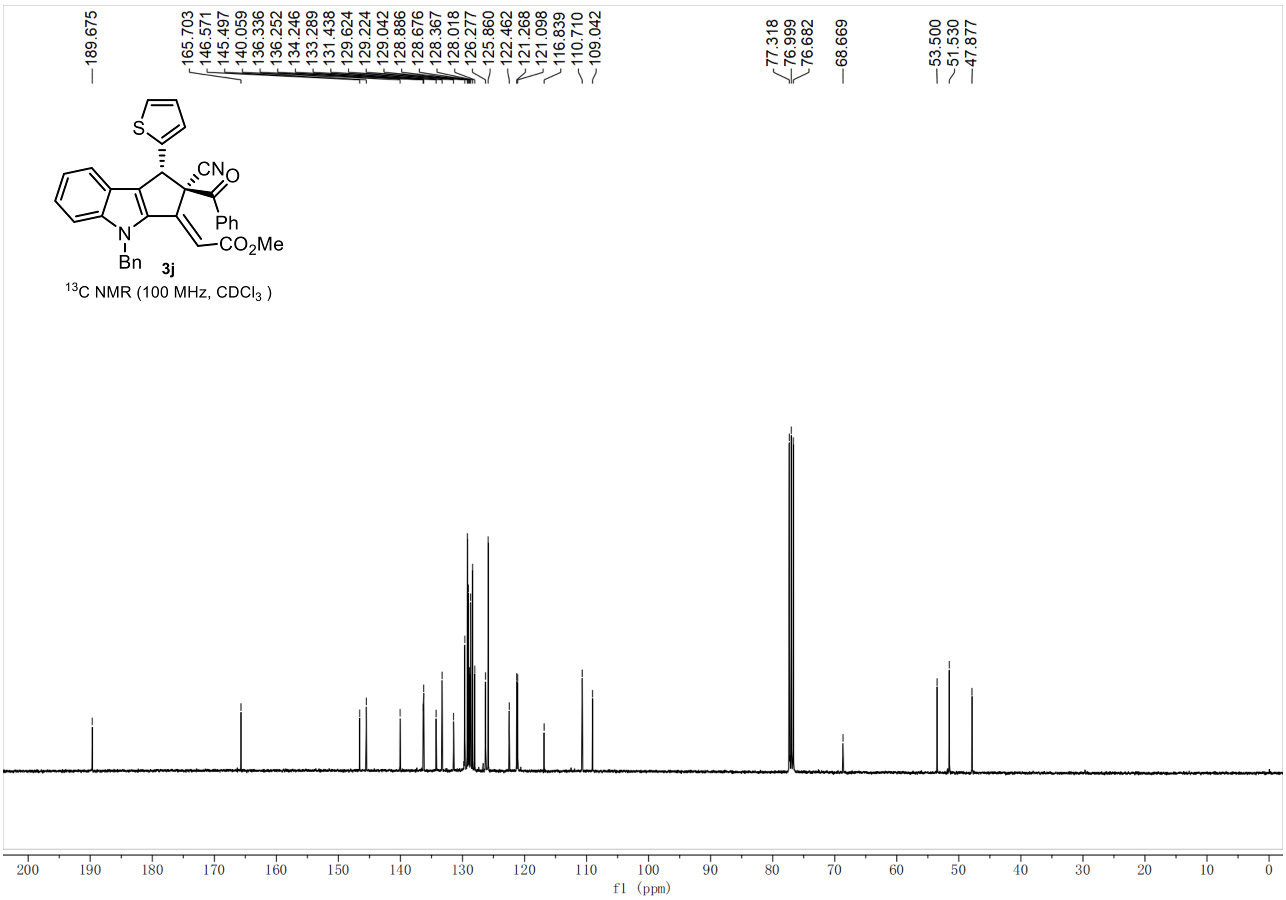
AREA PERCENT REPORT

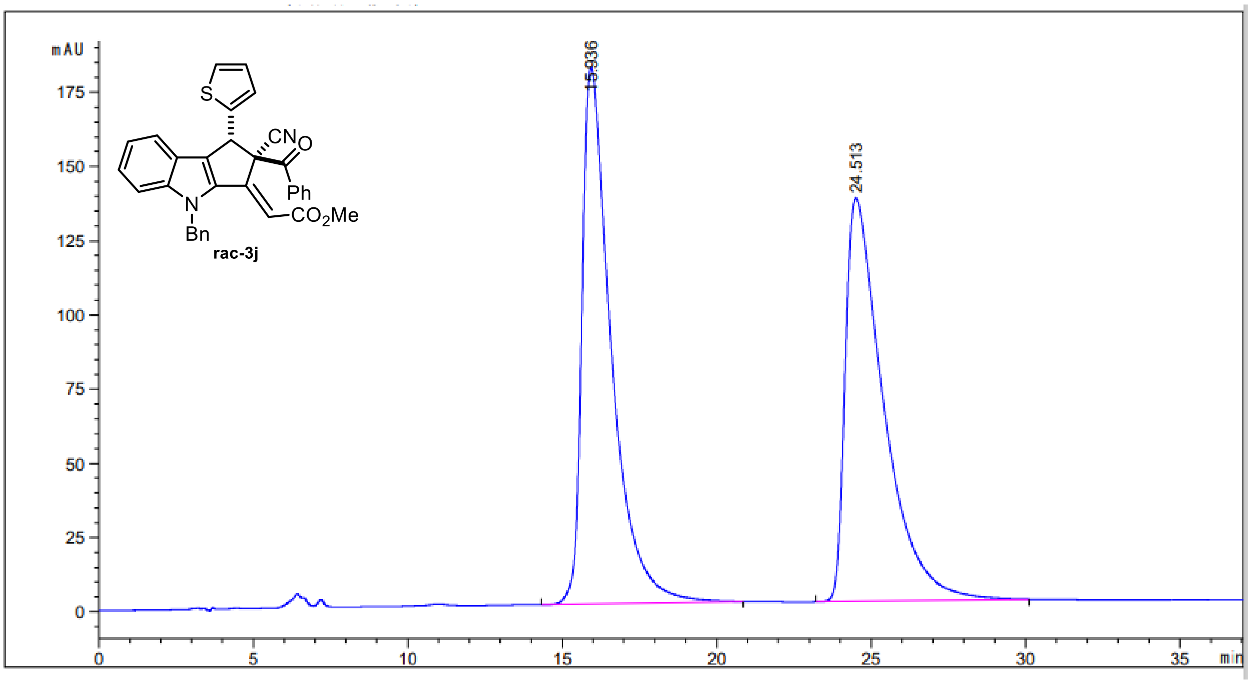
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.087	3.040	13724743	496471446	96.0521
2	22.107	2.400	352219	20405799	3.9479

Name	CYC-220406-30	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-30.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:02:32 AM (UTC+08:00)

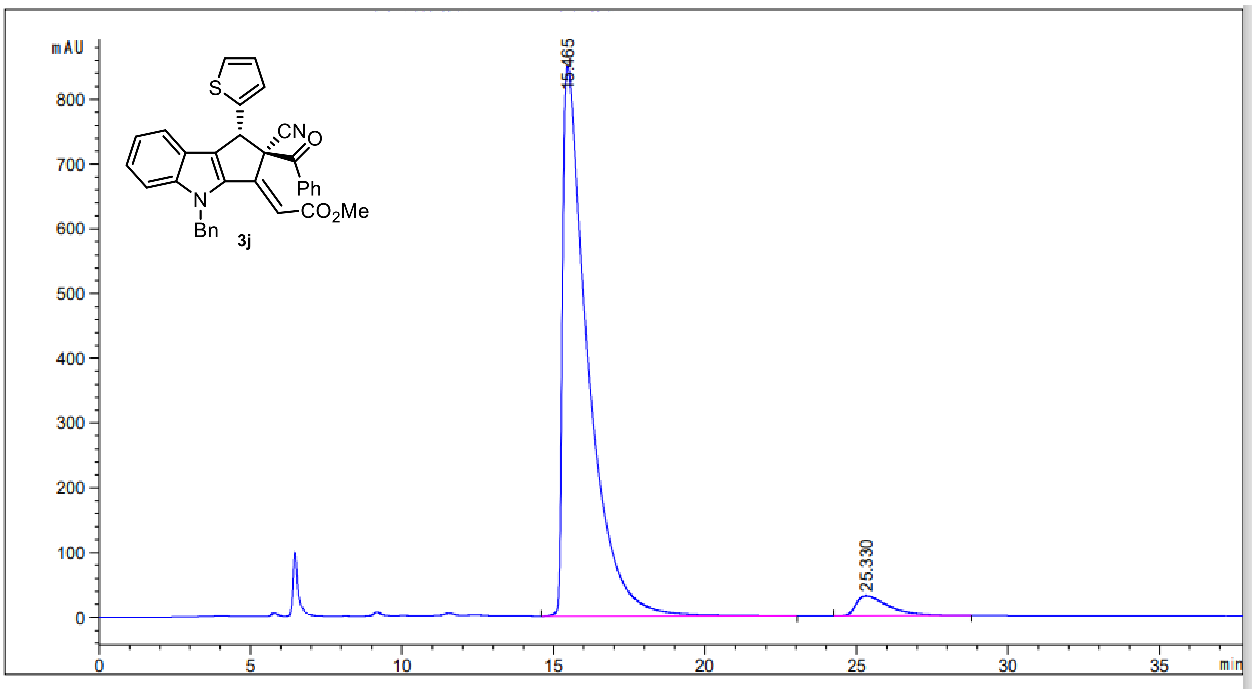



S
CN
O
Ph
N
CO2Me
Bn
3j
1H NMR (400 MHz, CDCl3)
7.923
7.920
7.902
7.899
7.567
7.553
7.549
7.545
7.533
7.530
7.527
7.400
7.395
7.388
7.383
7.380
7.375
7.375
7.364
7.360
7.355
7.346
7.343
7.329
7.326
7.310
7.305
7.250
7.246
7.241
7.233
7.226
7.184
7.179
7.166
7.162
7.159
7.133
7.130
7.128
7.113
7.110
7.108
7.069
7.066
7.052
7.049
7.046
7.032
7.029
6.155
5.591
5.059
3.543
0.000
1.98
1.12
7.70
1.44
0.86
1.97
1.02
1.08
1.00
1.94
0.99
3.01
f1 (ppm)


S
CN
O
Ph
N
CO2Me
Bn
3j
13C NMR (100 MHz, CDCl3)
189.675
165.703
146.571
145.497
140.059
136.336
136.252
134.246
133.289
131.438
129.624
129.224
129.042
128.886
128.676
128.367
128.018
126.277
125.860
122.462
121.268
121.098
116.839
110.710
109.042
77.318
76.999
76.682
68.669
53.500
51.530
47.877
f1 (ppm)

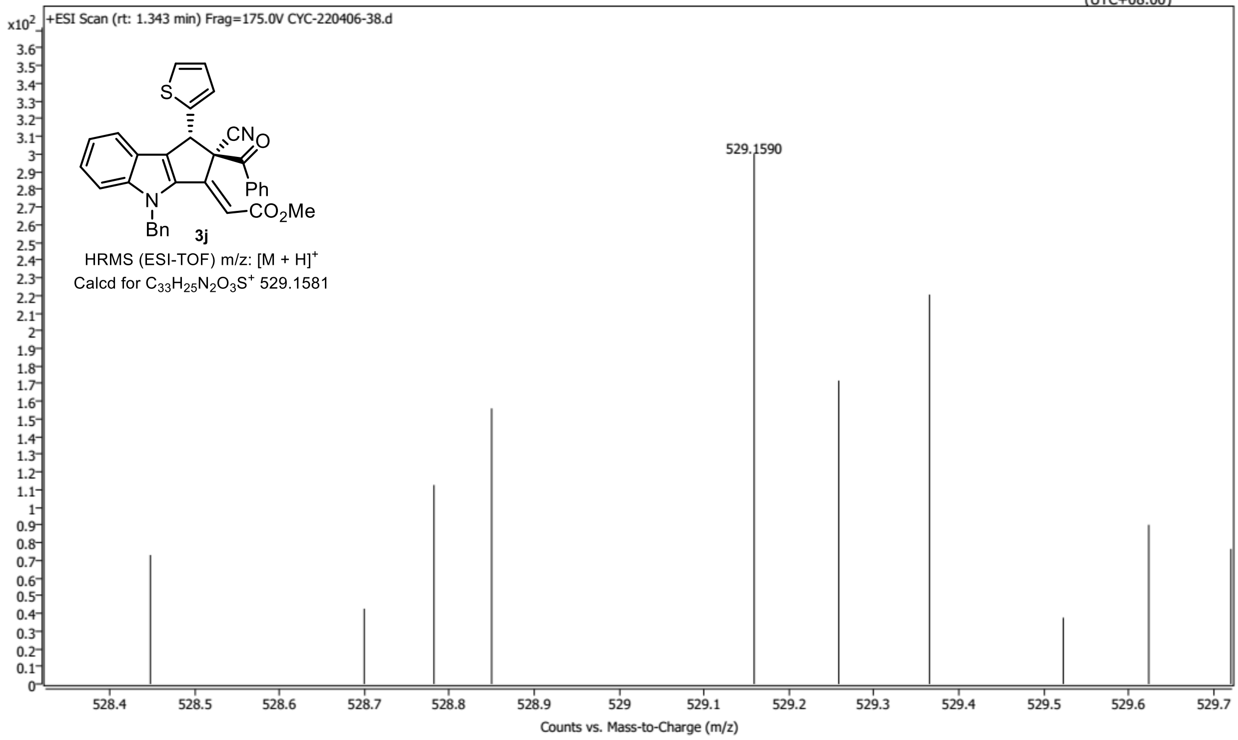


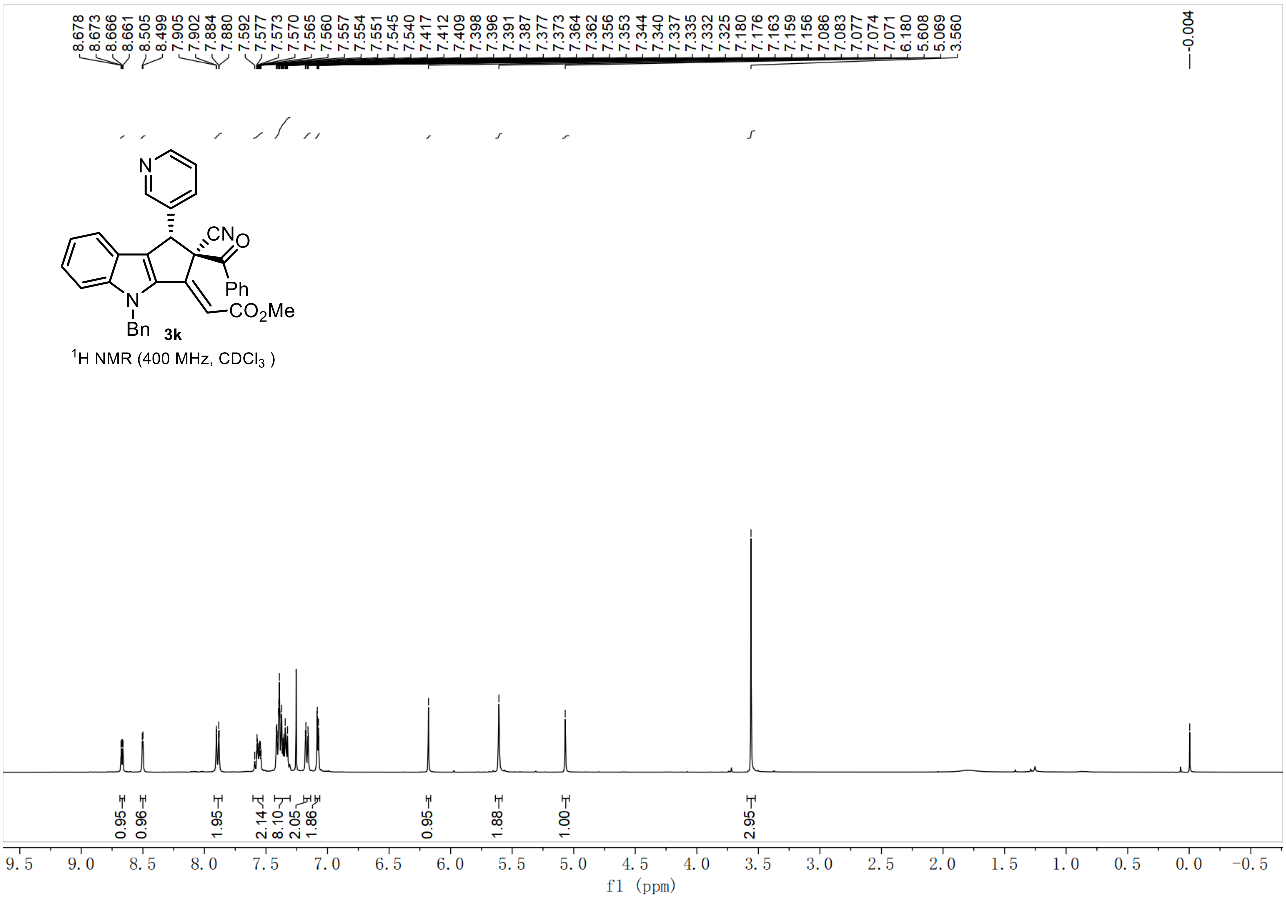
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.936	BB	0.9618	1.18417e4	180.54533	50.1643
2	24.513	BB	1.2725	1.17641e4	135.83820	49.8357



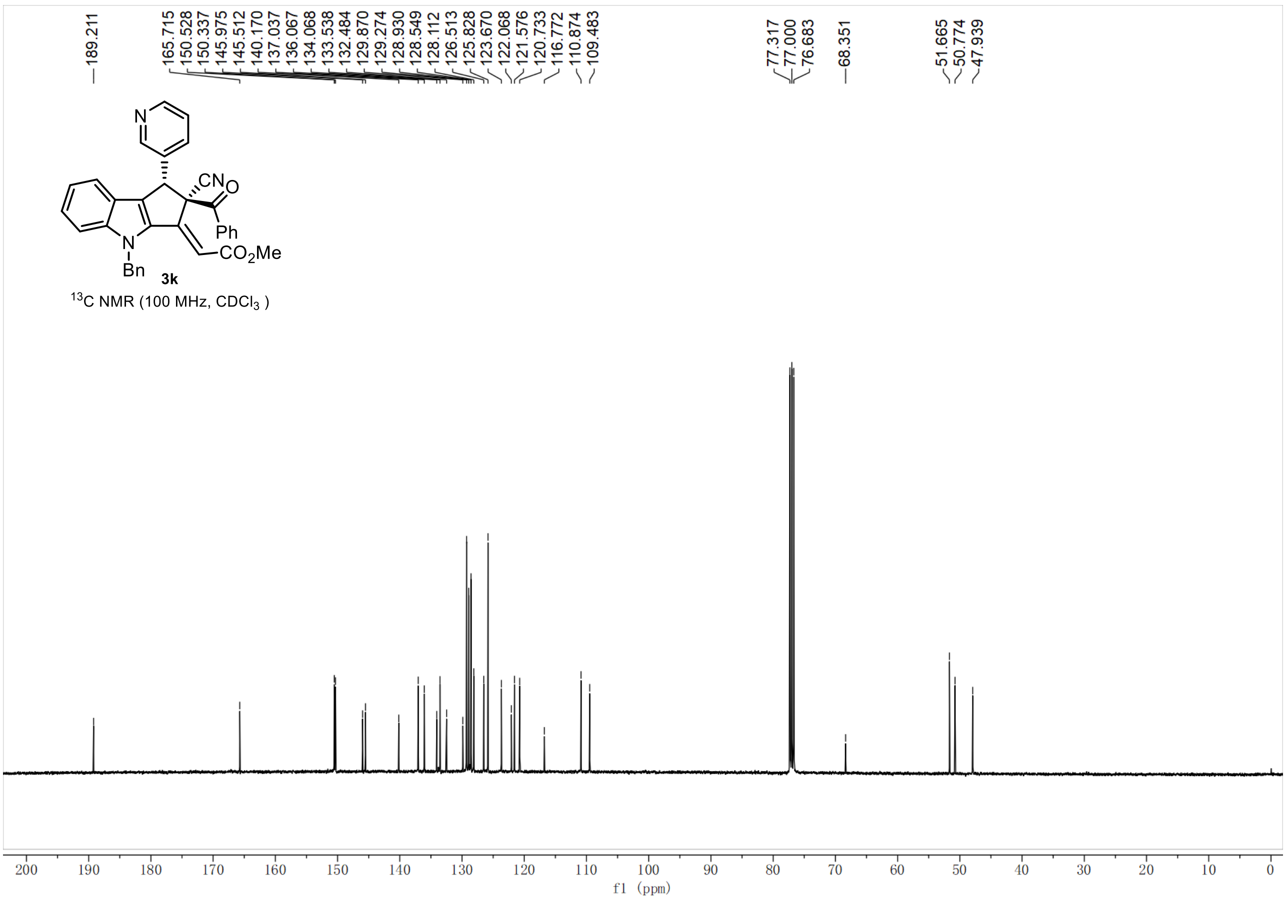
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.465	BB	0.8201	4.93233e4	849.45795	95.5379
2	25.330	BB	1.0859	2303.64648	30.98013	4.4621

Name	CYC-220406-38	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-38.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:55:16 AM (UTC+08:00)

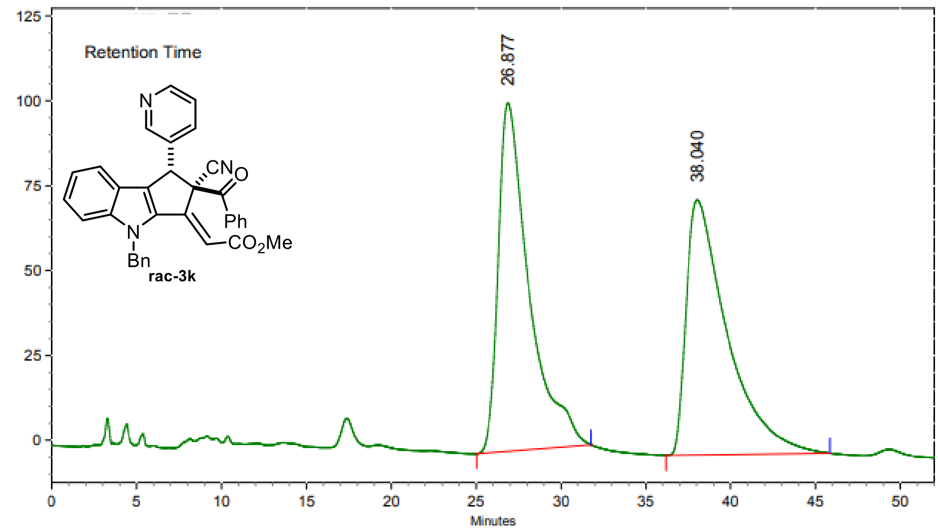




3k
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

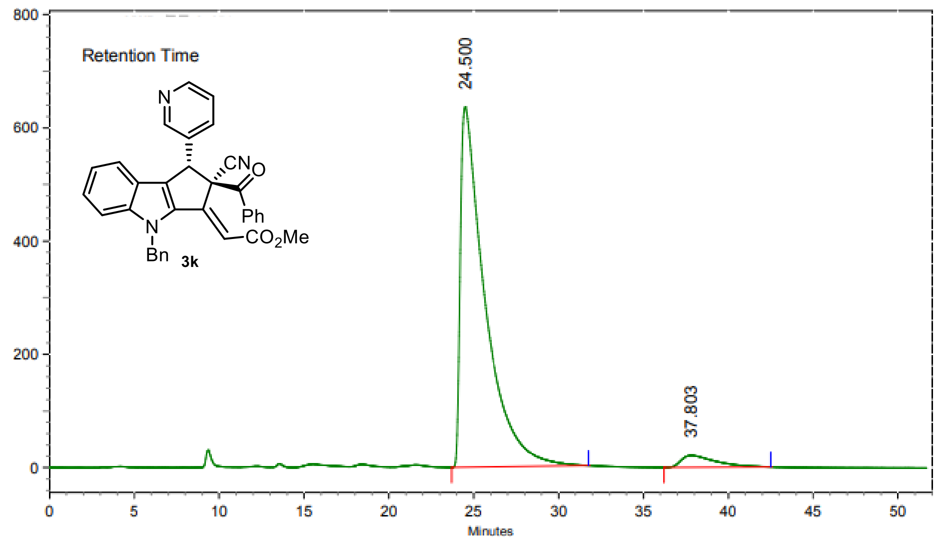


3k
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



AREA PERCENT REPORT

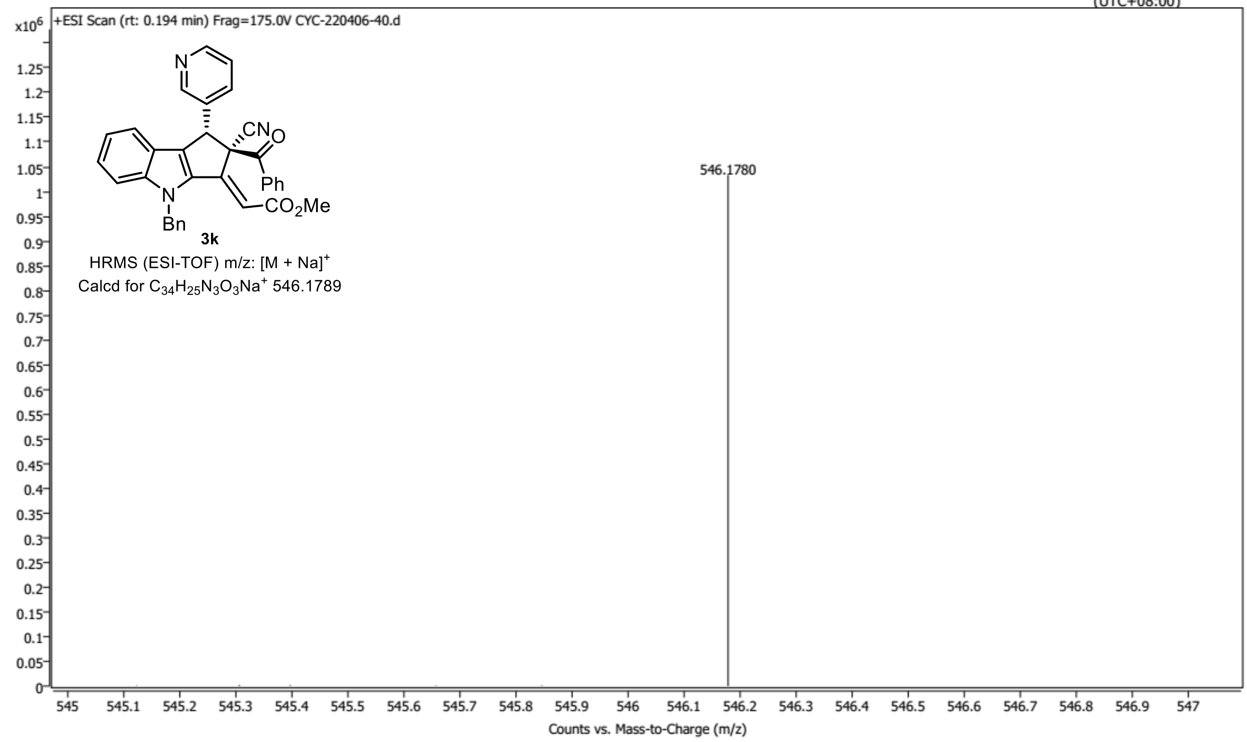
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	26.877	6.743	1720277	216448465	50.5905
2	38.040	9.660	1260471	211395288	49.4095

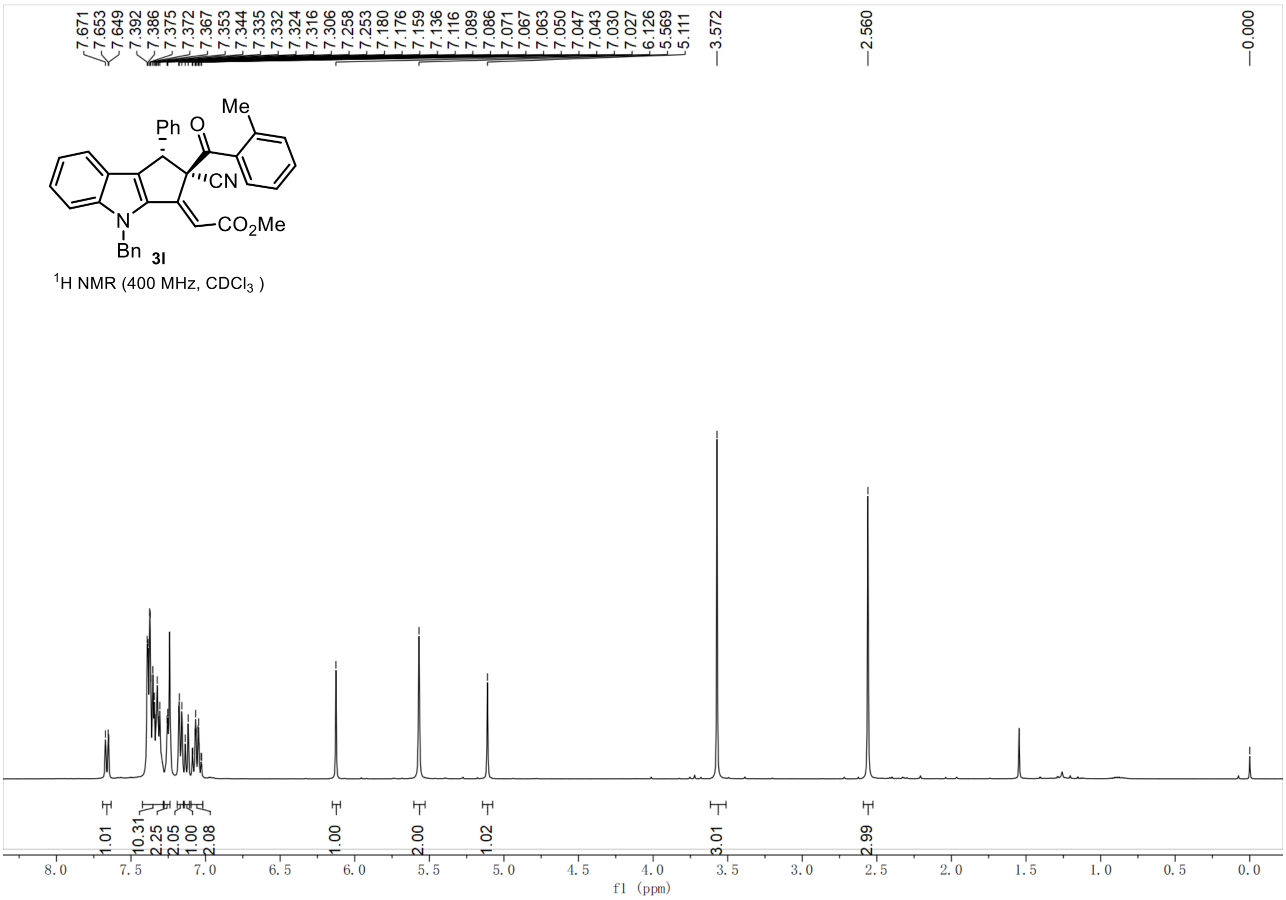


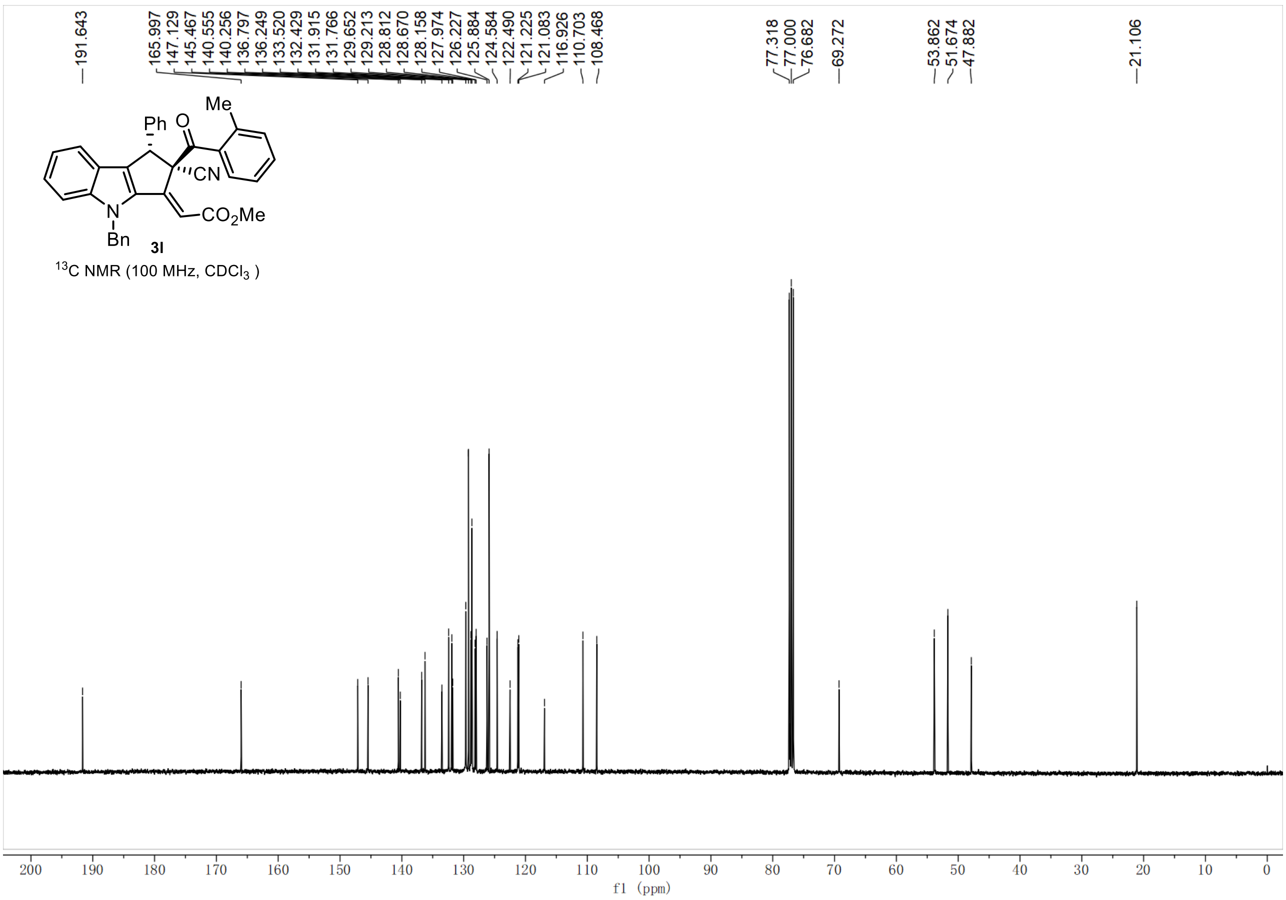
AREA PERCENT REPORT

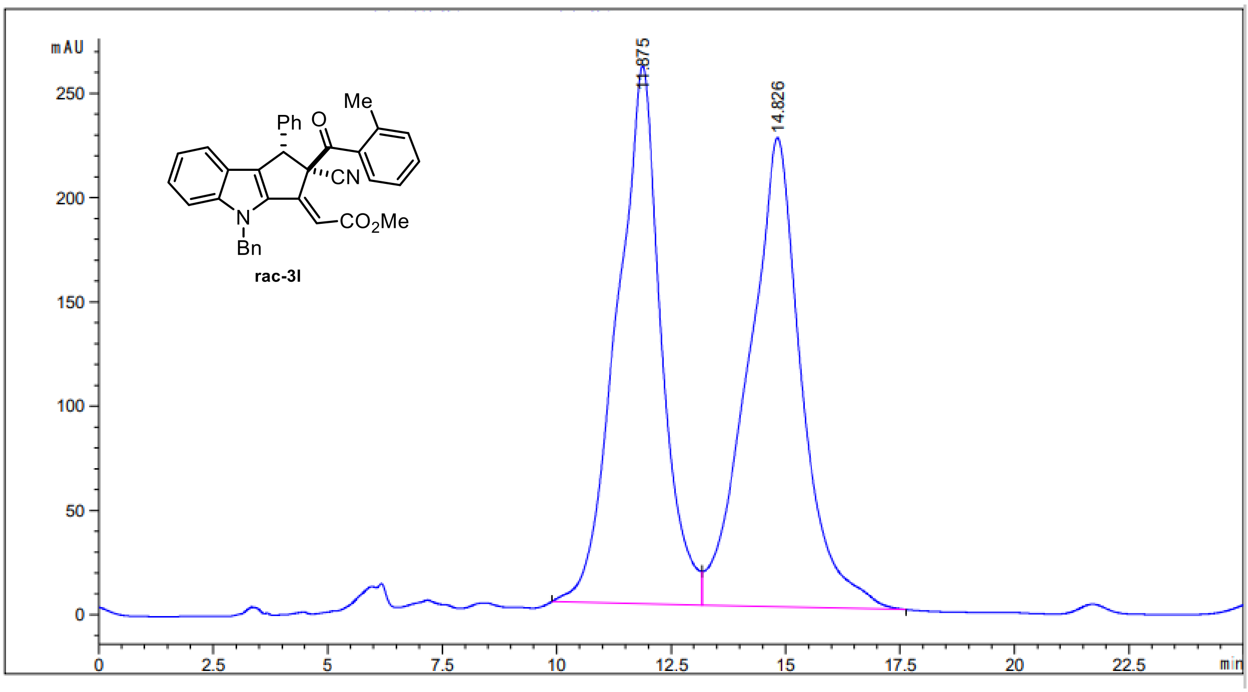
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	24.500	8.080	10668682	1066770812	95.6273
2	37.803	6.267	349035	48779251	4.3727

Name	CYC-220406-40	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-40.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:01:10 AM (UTC+08:00)

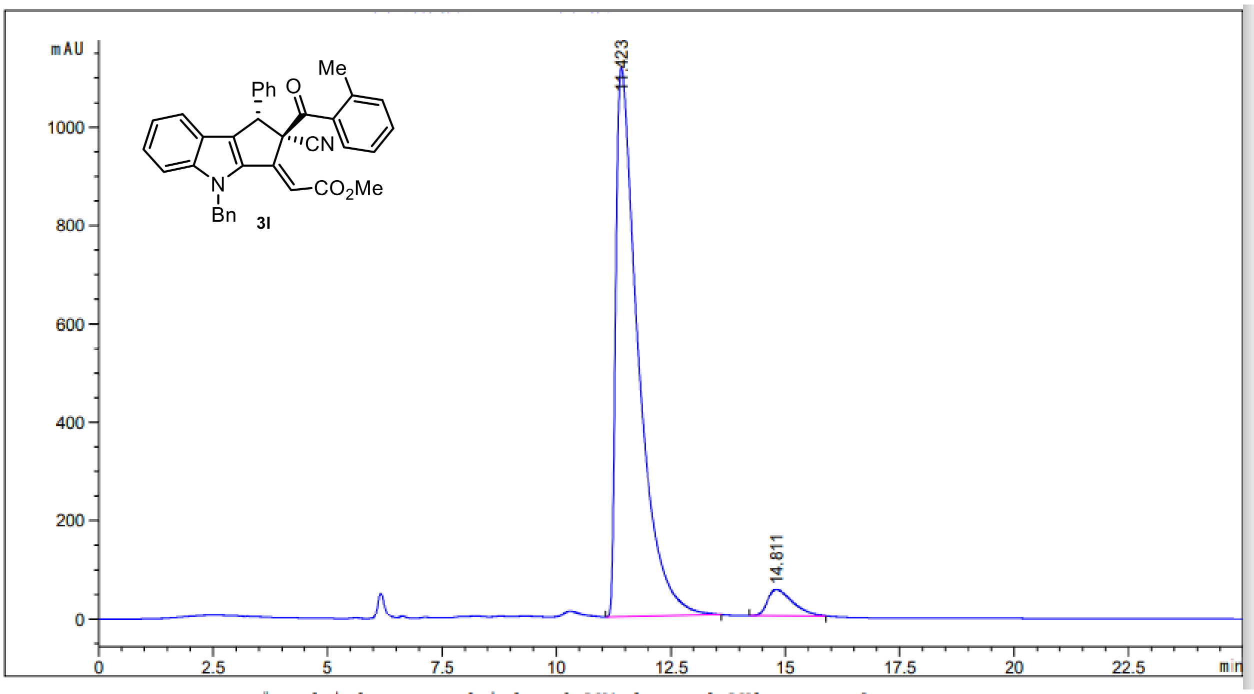



7.671
7.653
7.649
7.392
7.386
7.375
7.372
7.367
7.353
7.344
7.335
7.332
7.324
7.316
7.306
7.258
7.253
7.180
7.176
7.159
7.136
7.116
7.089
7.086
7.071
7.067
7.063
7.050
7.047
7.043
7.030
7.027
6.126
5.569
5.111
3.572
2.560
0.000
Ph
O
Me
CN
N
Bn
CO2Me
3l
1H NMR (400 MHz, CDCl3)
1.01
10.31
2.25
2.05
1.00
2.08
1.00
2.00
1.02
3.01
2.99
f1 (ppm)


191.643
165.997
147.129
145.467
140.555
140.256
136.797
136.249
133.520
132.429
131.915
131.766
129.652
129.213
128.812
128.670
128.158
127.974
126.227
125.884
124.584
122.490
121.225
121.083
116.926
110.703
108.468
77.318
77.000
76.682
69.272
53.862
51.674
47.882
21.106
Ph
O
Me
CN
N
Bn
CO2Me
3l
13C NMR (100 MHz, CDCl3)
f1 (ppm)

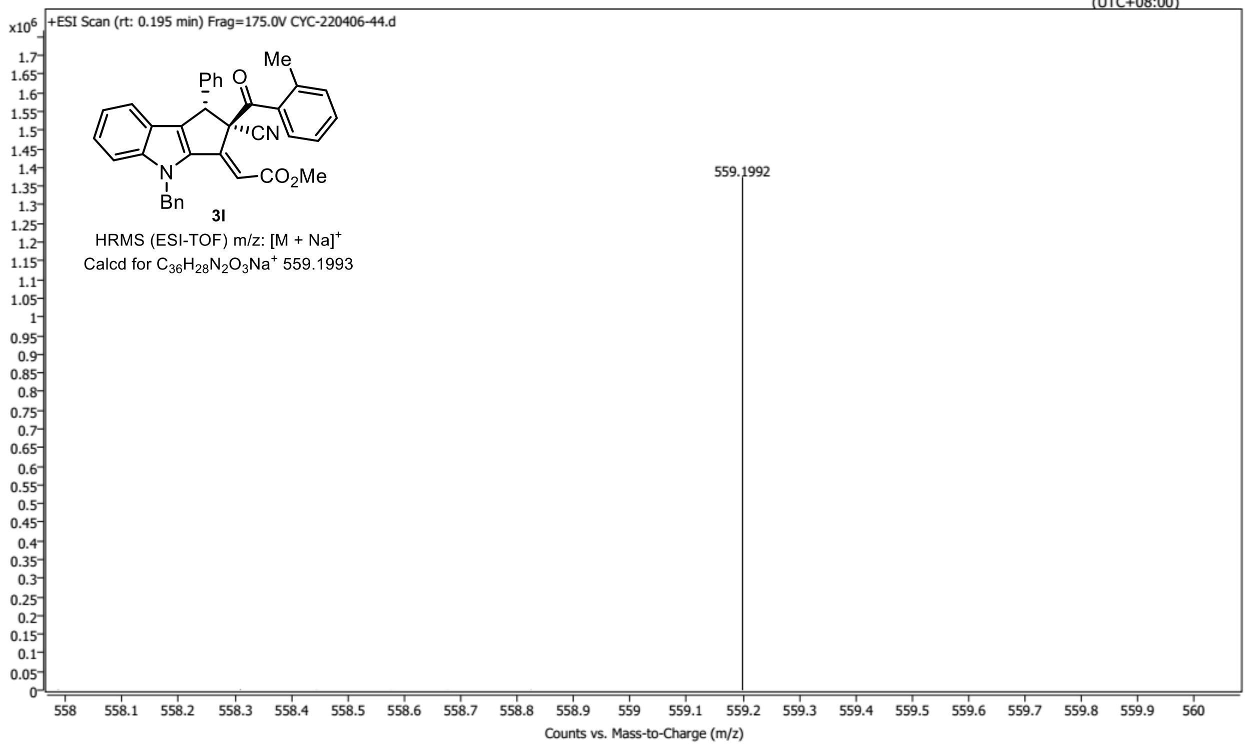


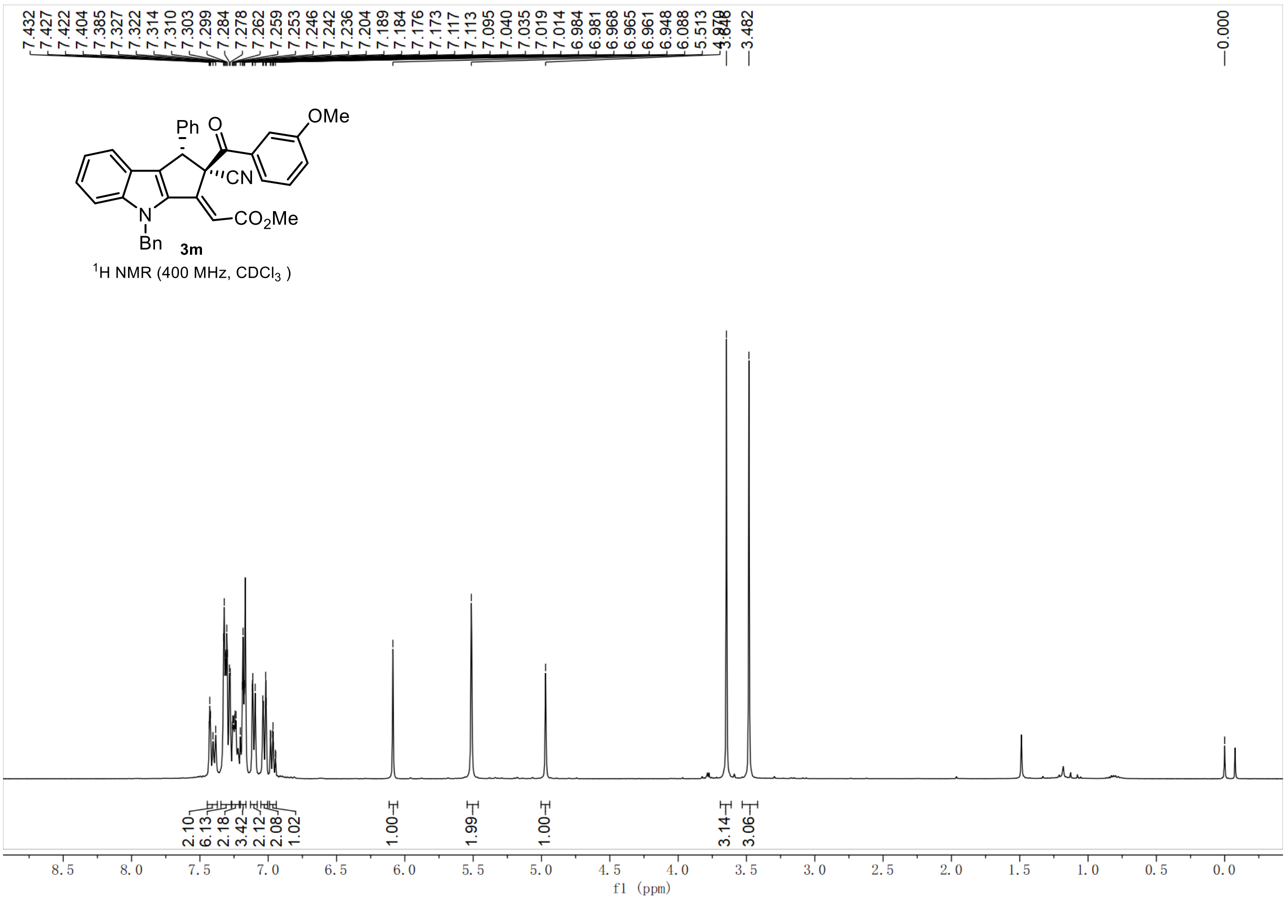
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.875	BV	0.9103	1.73700e4	258.11917	48.8459
2	14.826	VBA	1.1015	1.81908e4	225.10349	51.1541

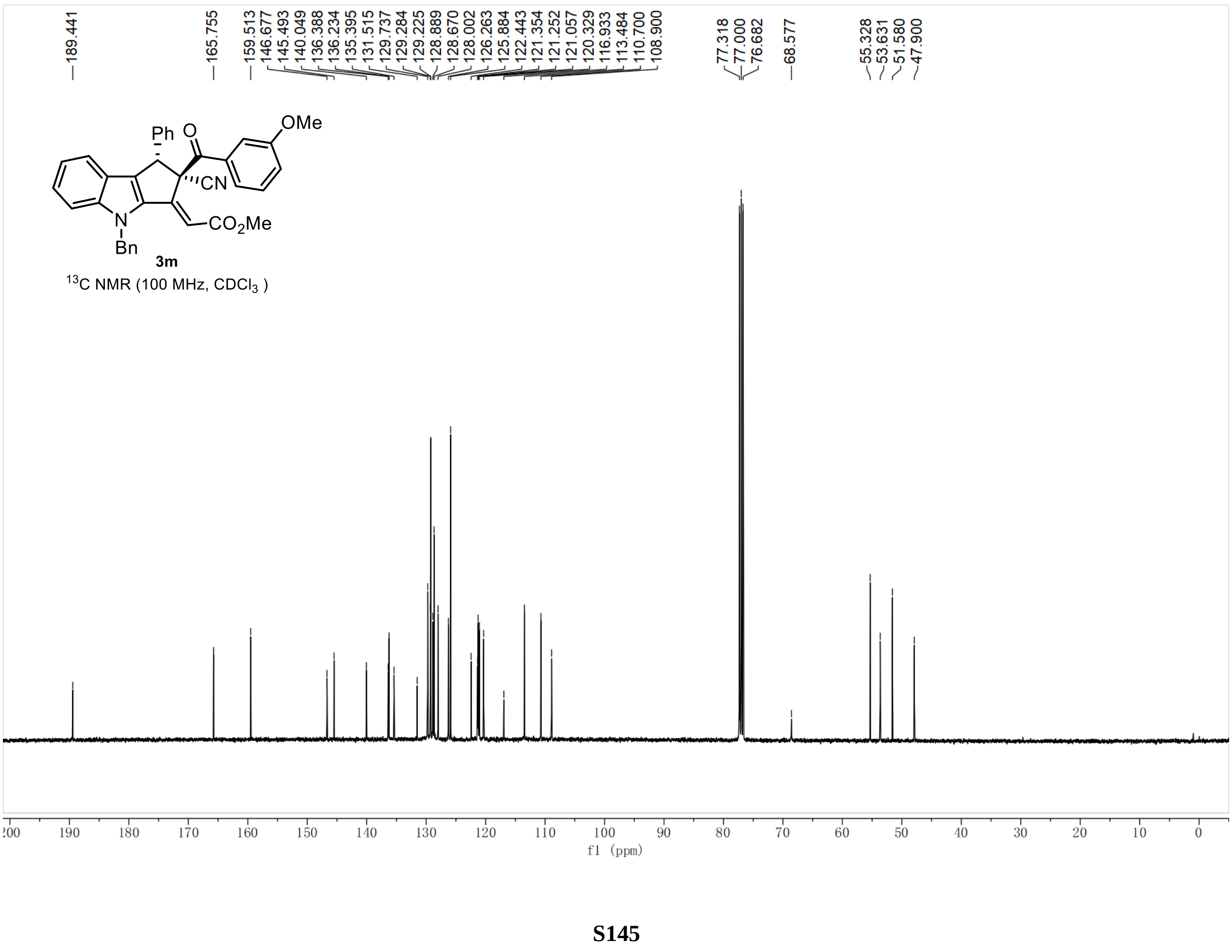


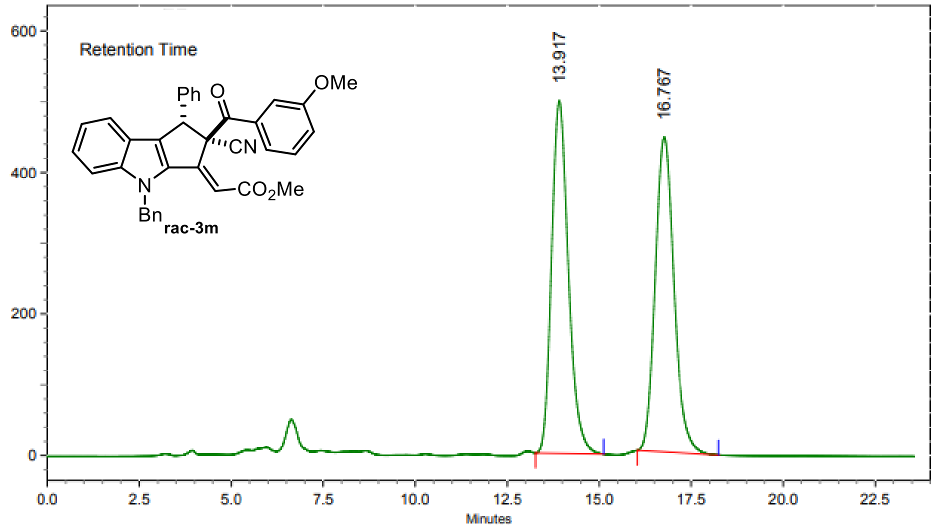
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.423	BBA	0.4923	3.77875e4	1116.81165	94.9573
2	14.811	BBA	0.5643	2006.69128	53.67023	5.0427

Name	CYC-220406-44	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-44.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:12:58 AM (UTC+08:00)



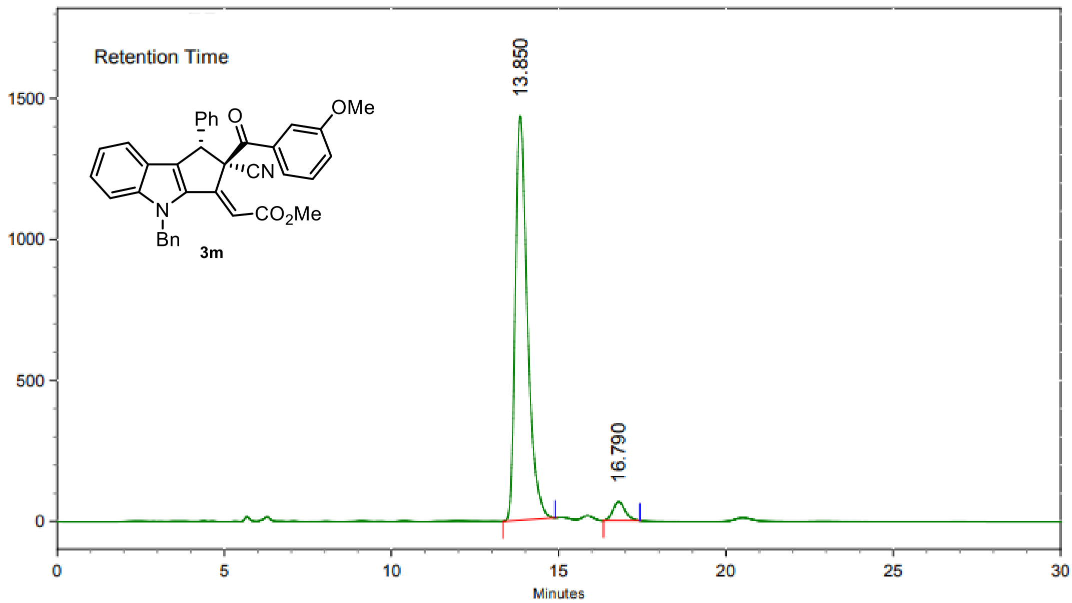






AREA PERCENT REPORT

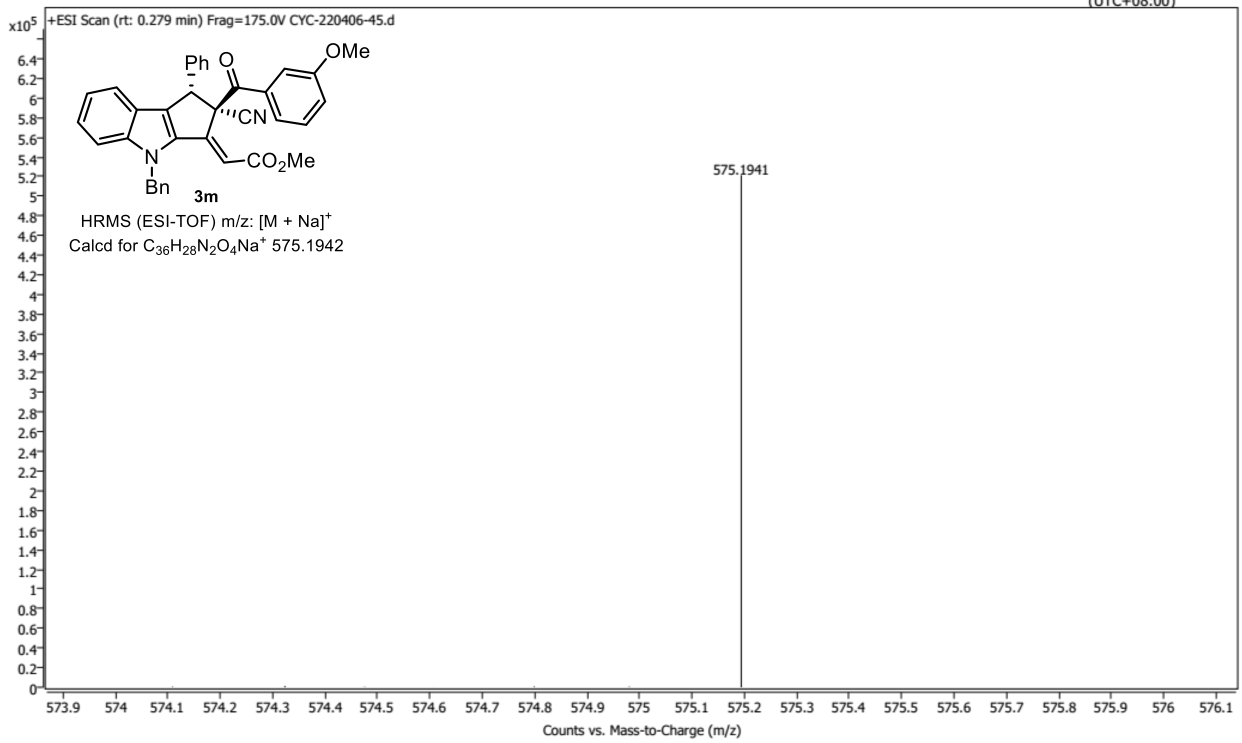
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.917	1.857	8370363	268723777	50.4536
2	16.767	2.200	7463371	263891976	49.5464

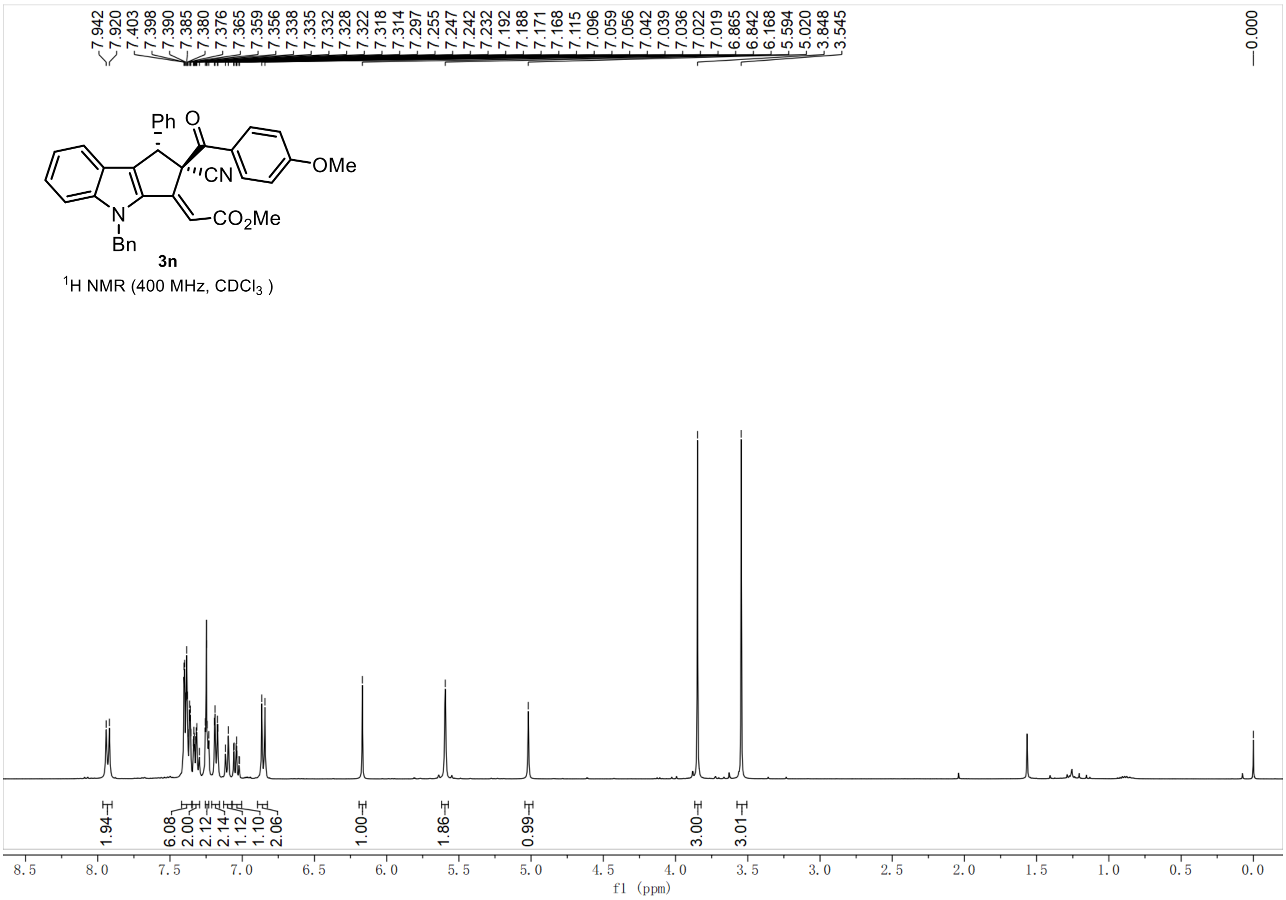


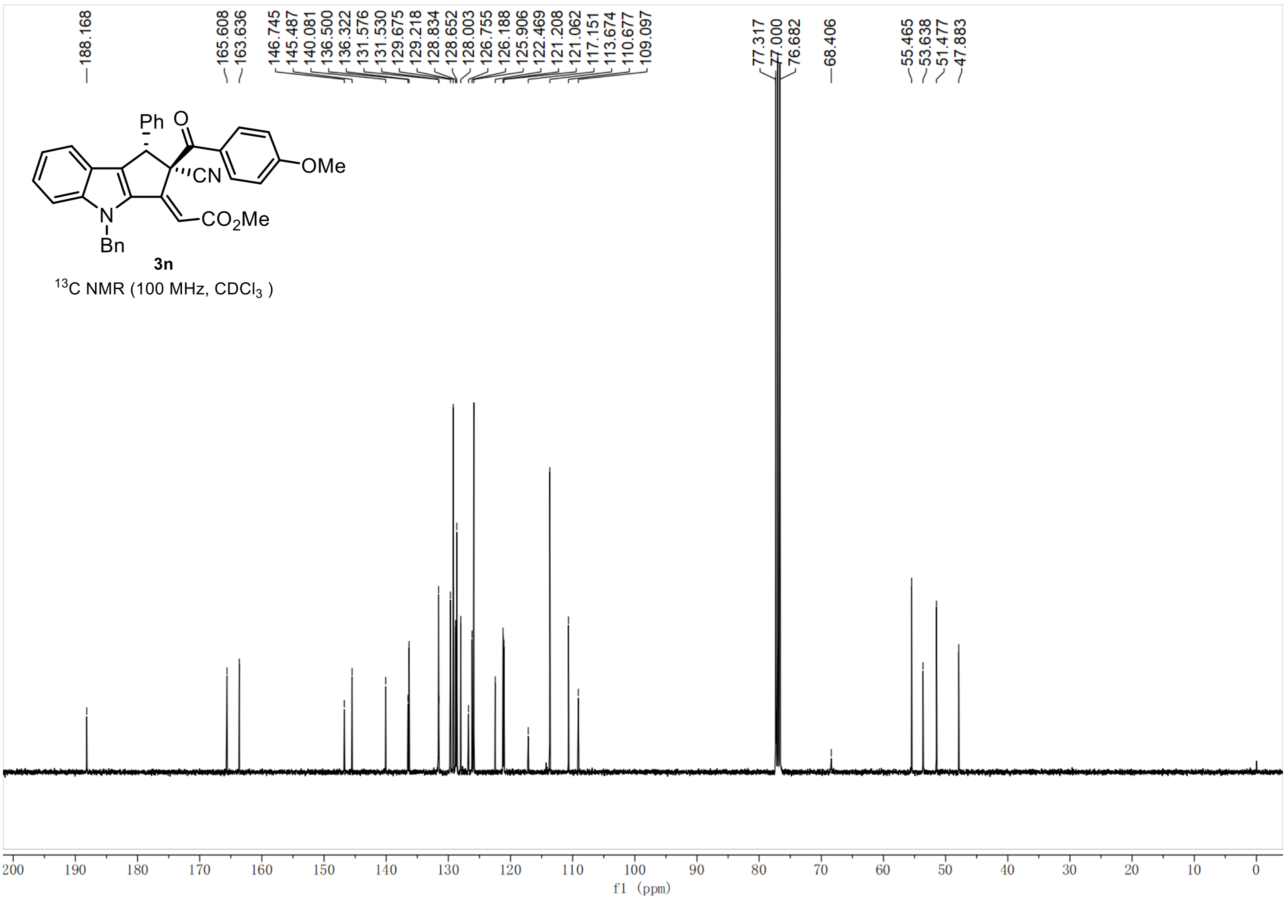
AREA PERCENT REPORT

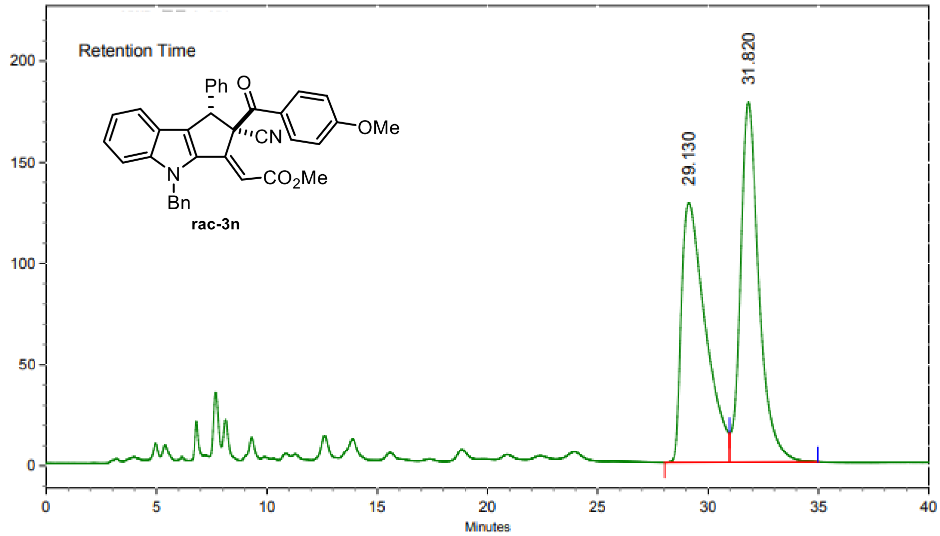
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.850	1.563	24038377	599013966	95.3890
2	16.790	1.080	1114030	28955369	4.6110

Name	CYC-220406-45	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-45.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:15:55 AM (UTC+08:00)



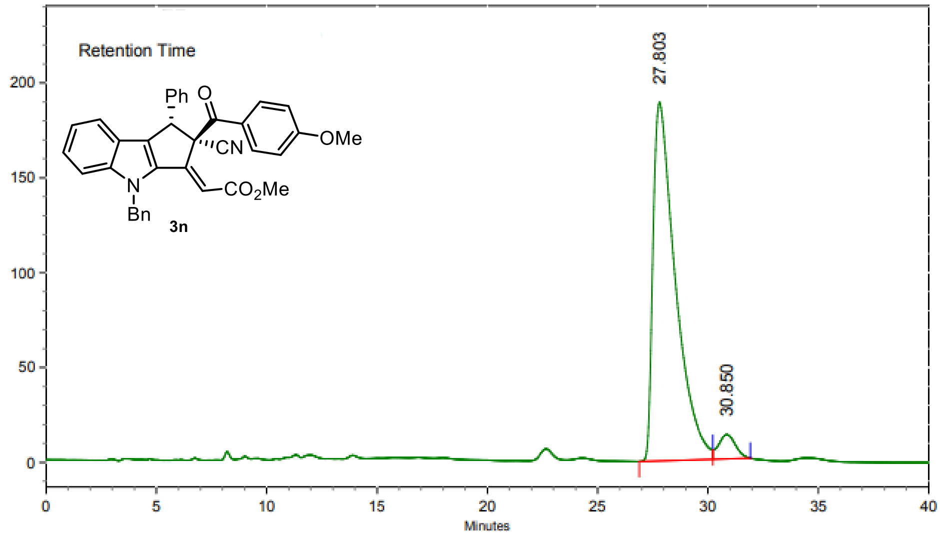






AREA PERCENT REPORT

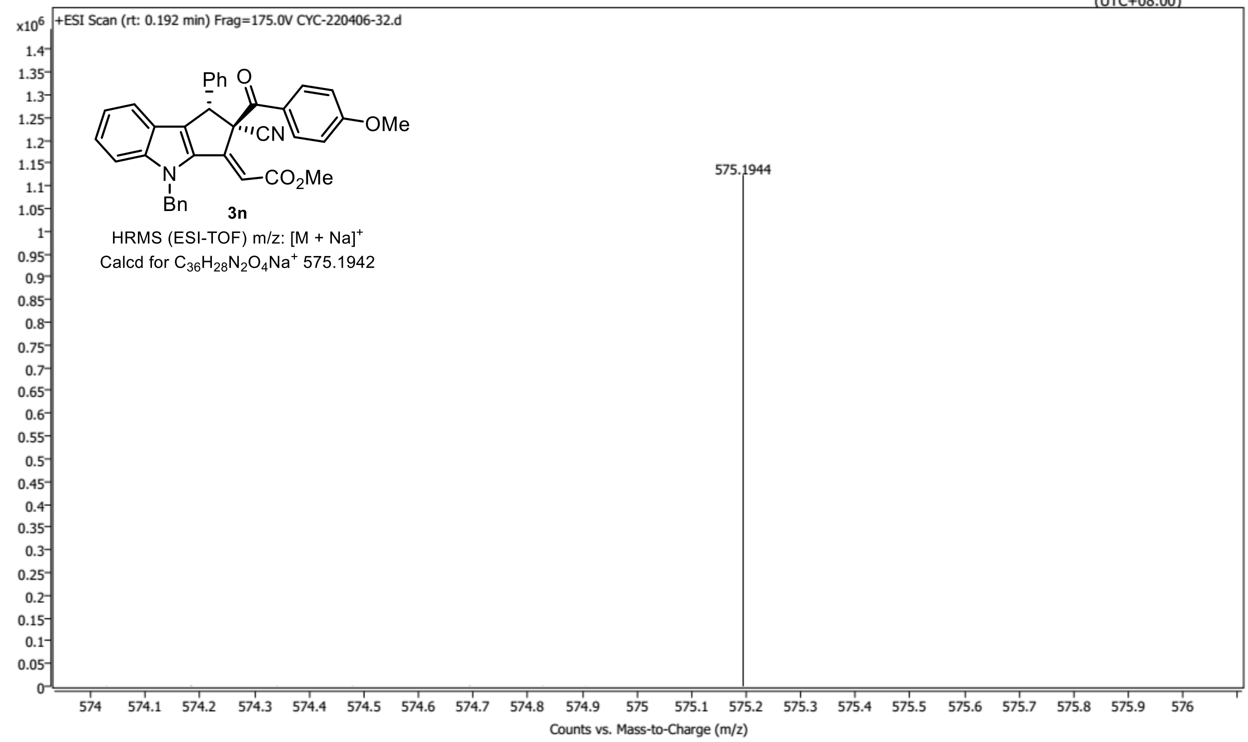
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	29.130	2.943	2151178	162161312	48.1460
2	31.820	3.990	2982721	174650024	51.8540

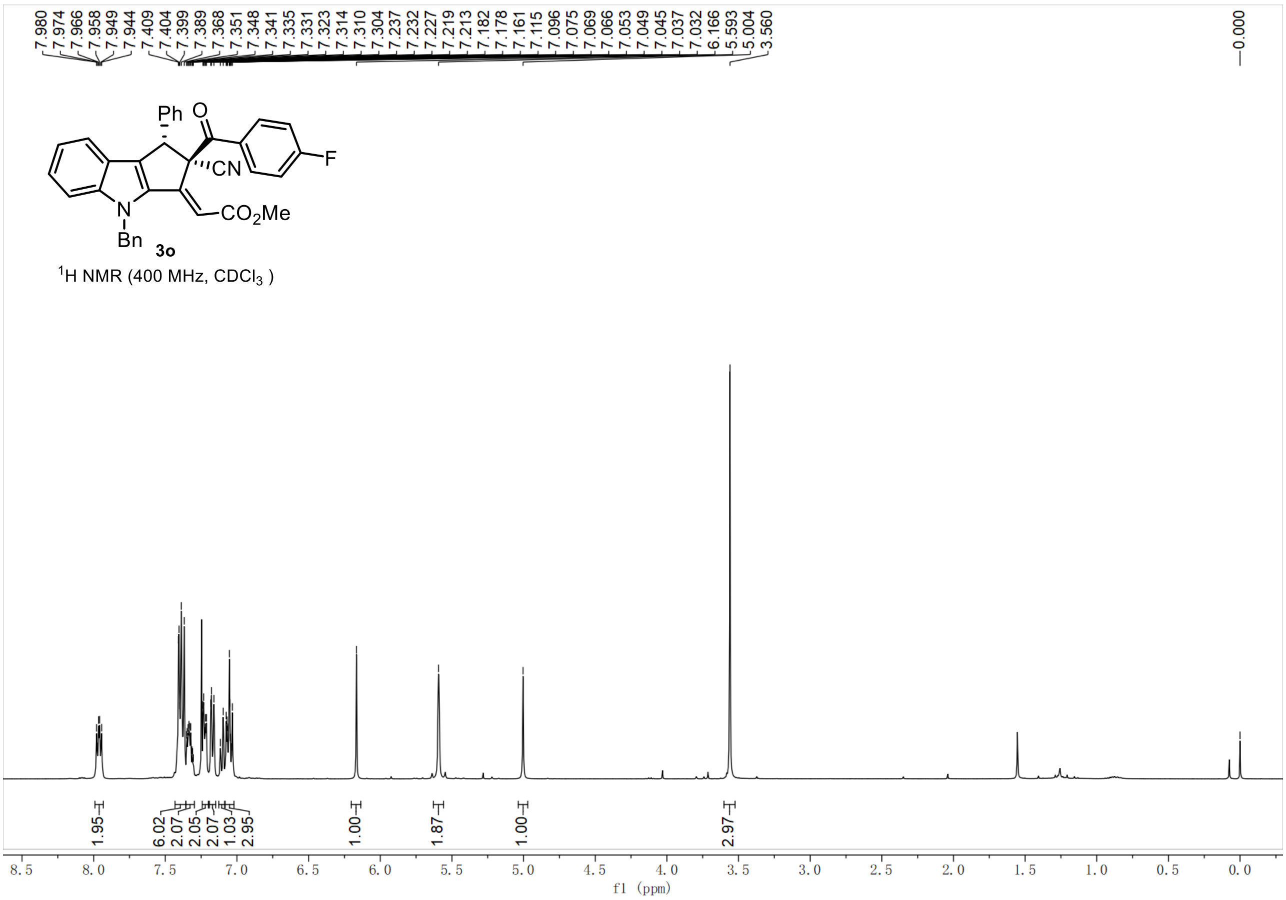


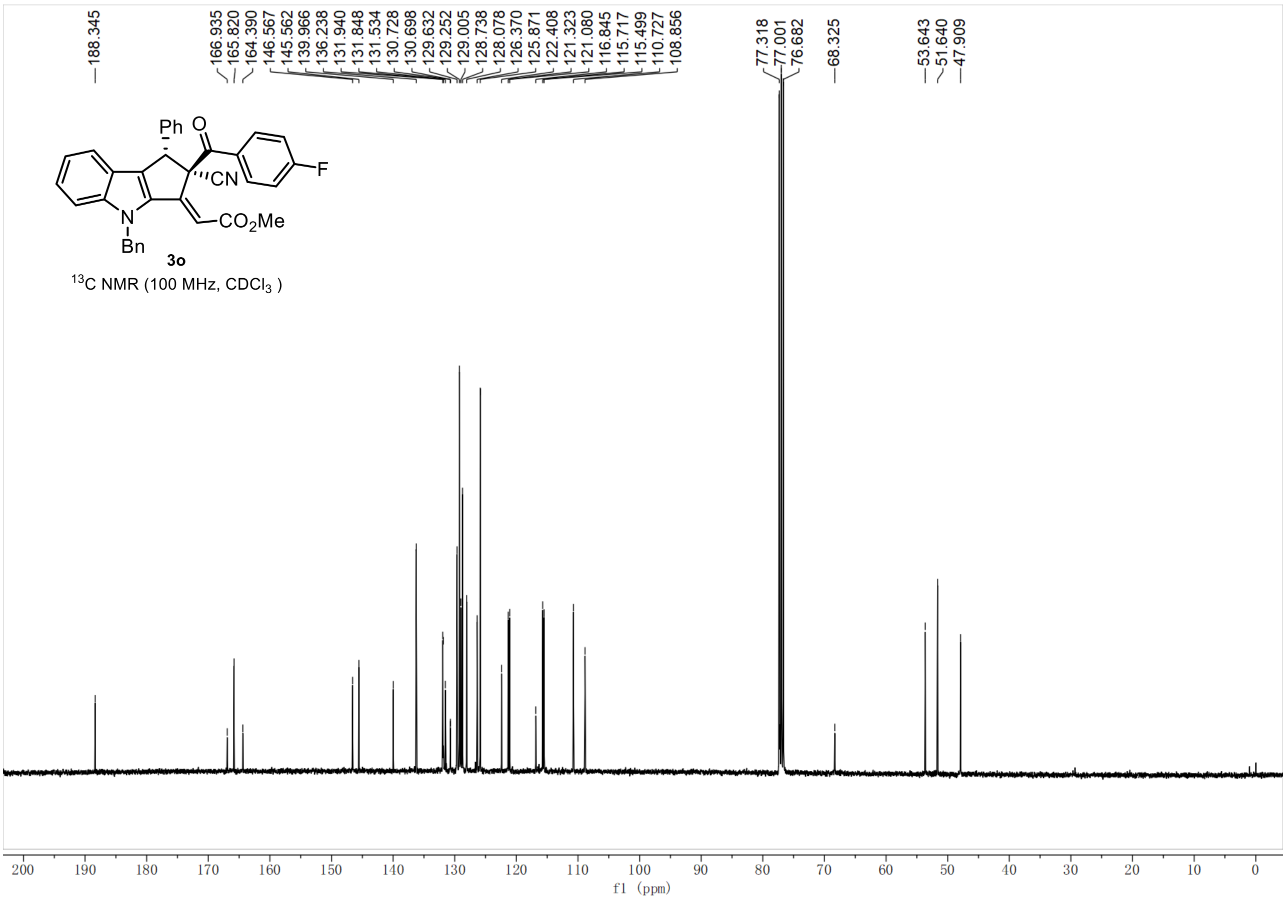
AREA PERCENT REPORT

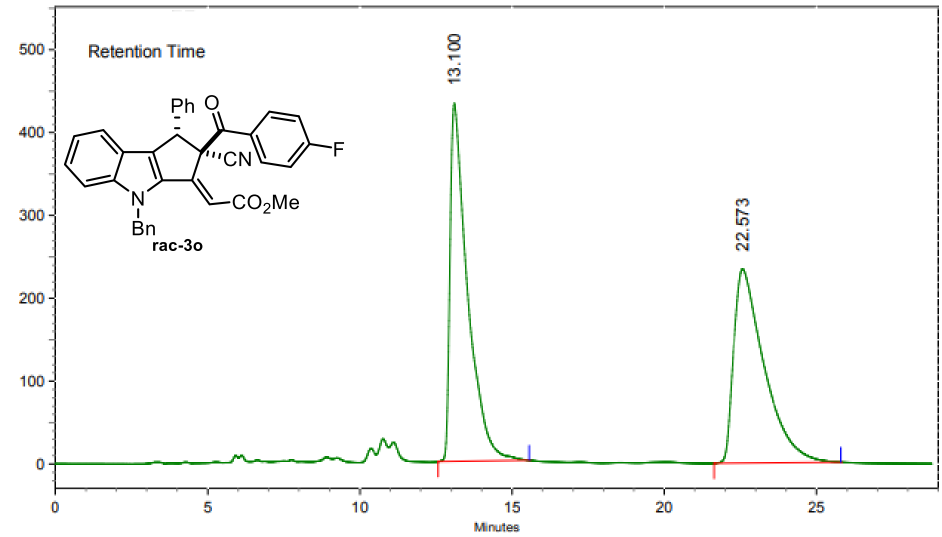
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	27.803	3.337	3173152	225559844	95.1760
2	30.850	1.703	216535	11432497	4.8240

Name	CYC-220406-32	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-32.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:08:28 AM (UTC+08:00)



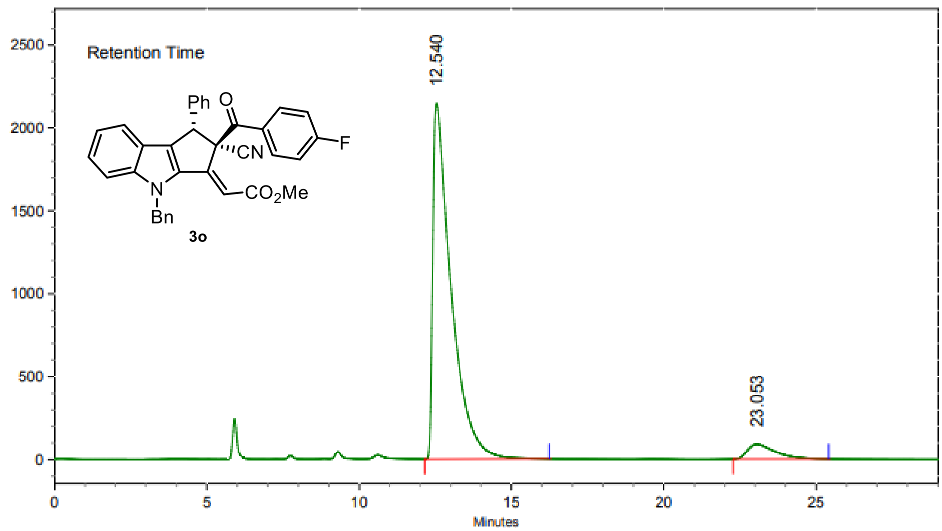

7.980
7.974
7.966
7.958
7.949
7.944
7.409
7.404
7.399
7.389
7.368
7.351
7.348
7.341
7.335
7.331
7.323
7.314
7.310
7.304
7.237
7.232
7.227
7.219
7.213
7.182
7.178
7.161
7.115
7.096
7.075
7.069
7.066
7.053
7.049
7.045
7.037
7.032
6.166
5.593
5.004
3.560
0.000
Ph
O
F
CN
N
CO_2Me
Bn
3o
^{1}H NMR (400 MHz, $CDCl_3$)
1.95
6.02
2.07
2.05
2.07
1.03
2.95
1.00
1.87
1.00
2.97
f1 (ppm)


188.345
166.935
165.820
164.390
146.567
145.562
139.966
136.238
131.940
131.848
131.534
130.728
130.698
129.632
129.252
129.005
128.738
128.078
126.370
125.871
122.408
121.323
121.080
116.845
115.717
115.499
110.727
108.856
77.318
77.001
76.682
68.325
53.643
51.640
47.909
Ph
O
F
CN
N
CO_2Me
Bn
3o
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



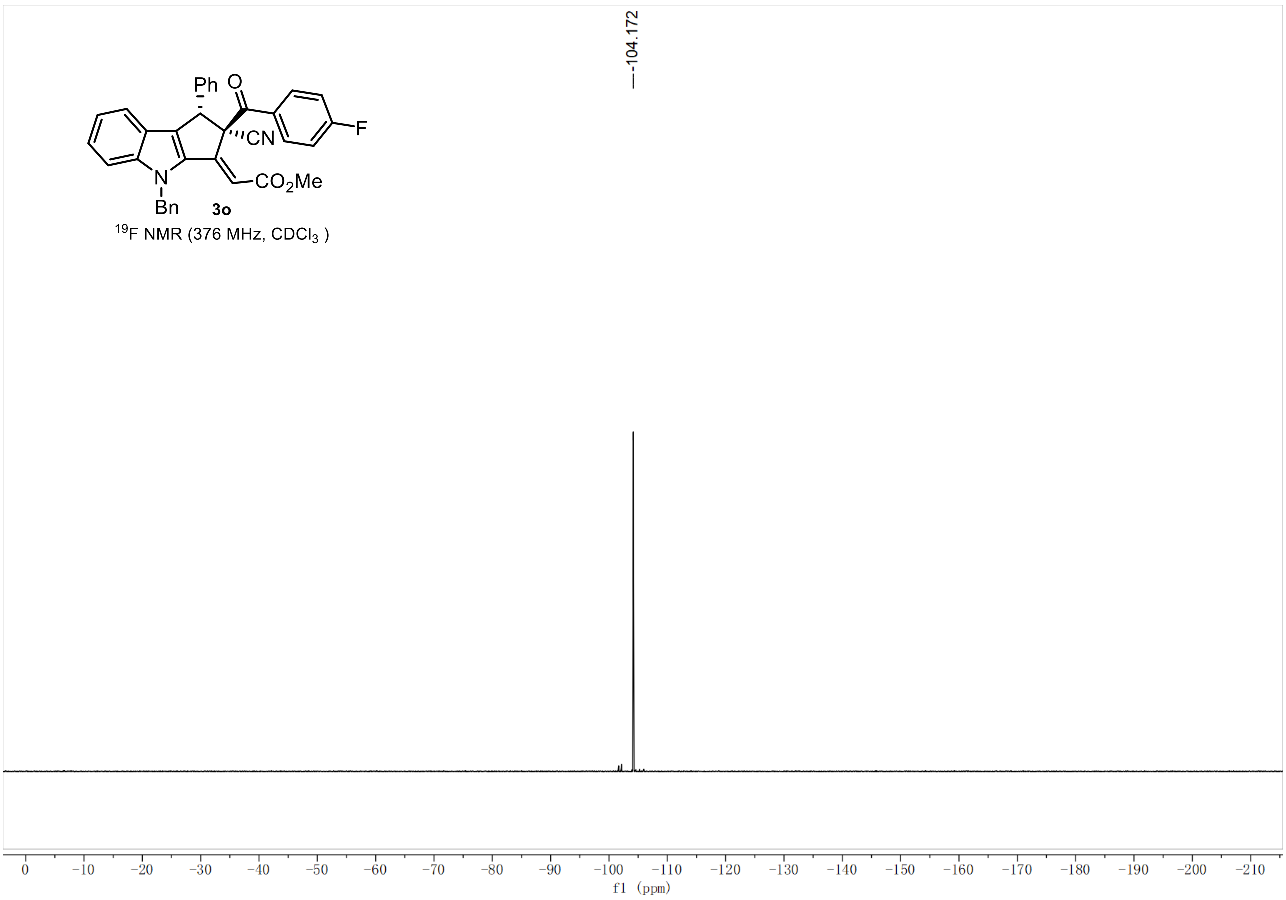
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.100	2.987	7255656	292906758	51.6780
2	22.573	4.160	3934370	273885073	48.3220

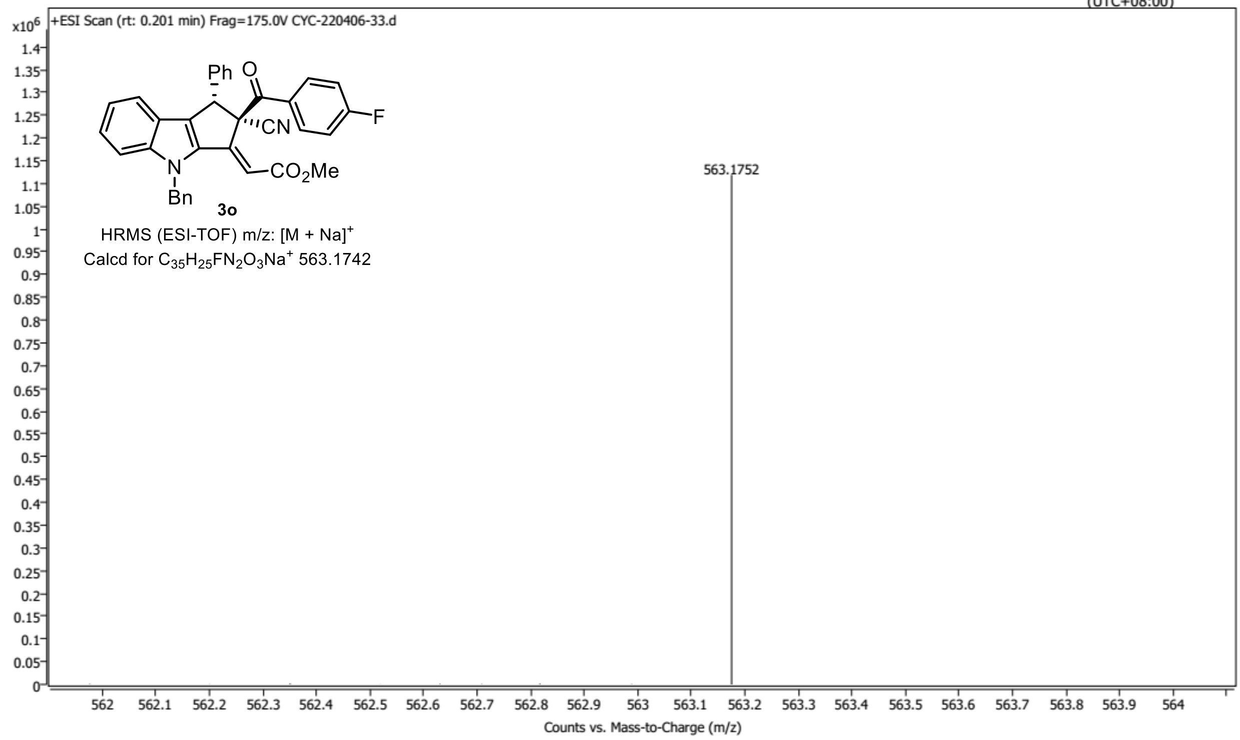


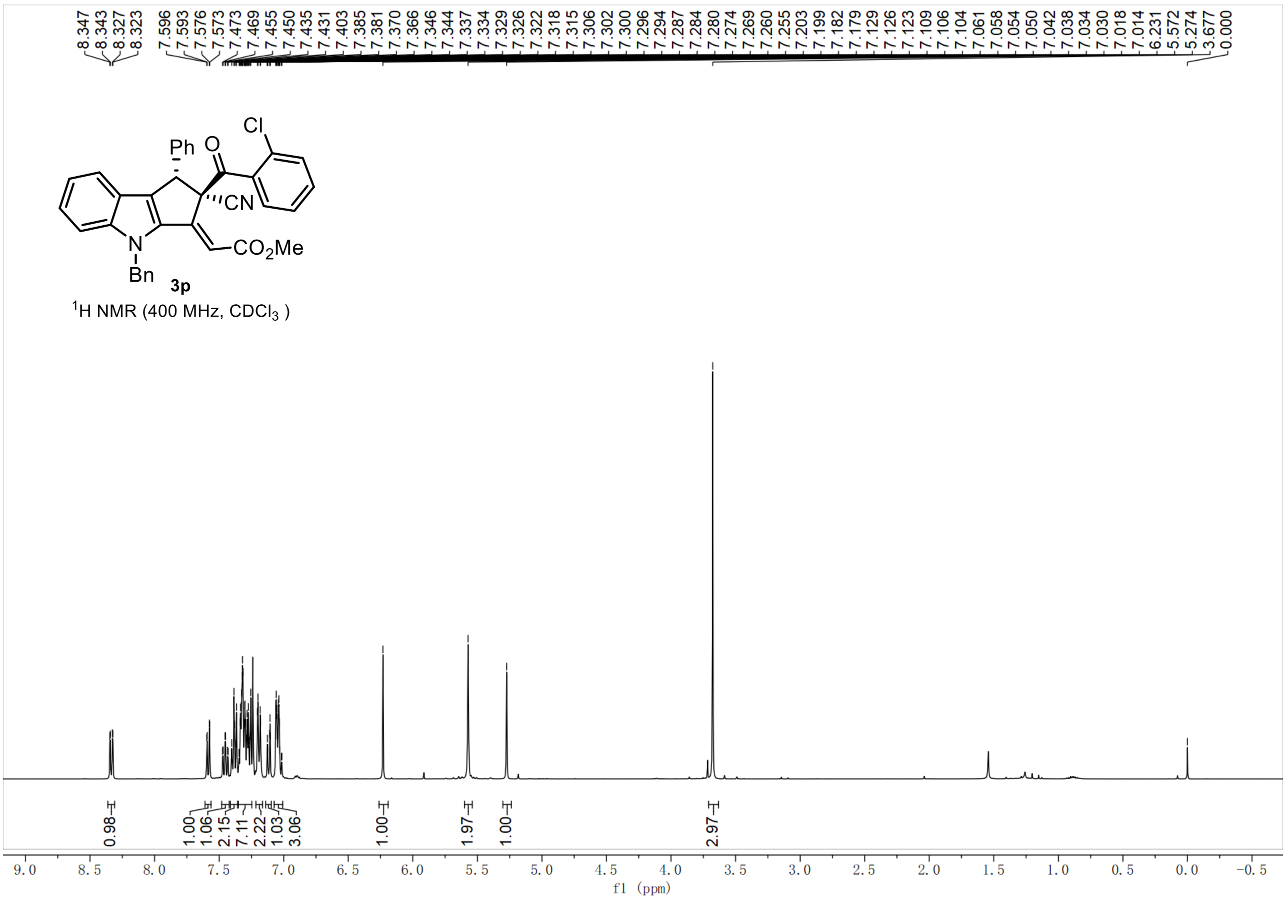
AREA PERCENT REPORT

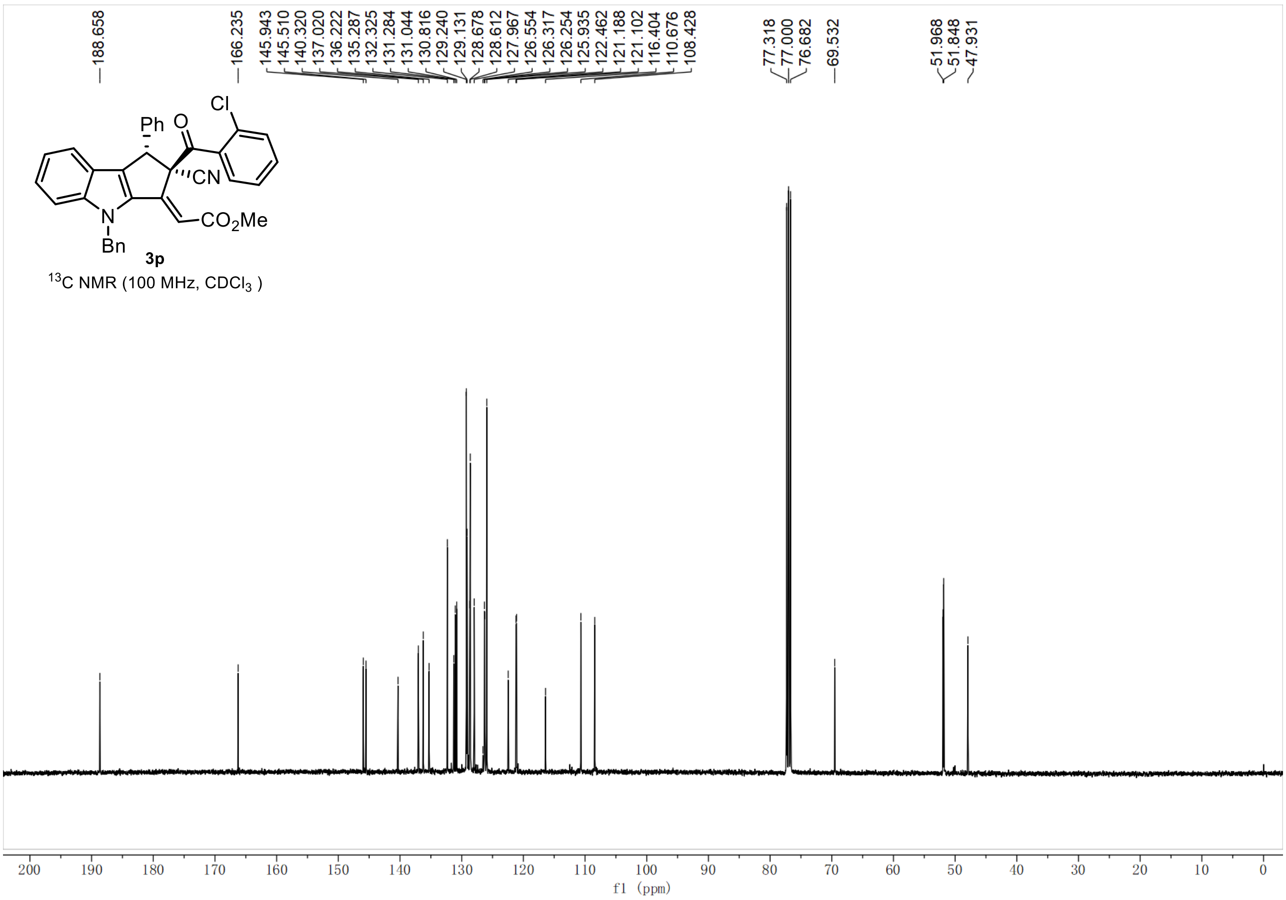
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	12.540	4.093	35980476	1490787818	94.0316
2	23.053	3.147	1498793	94623682	5.9684

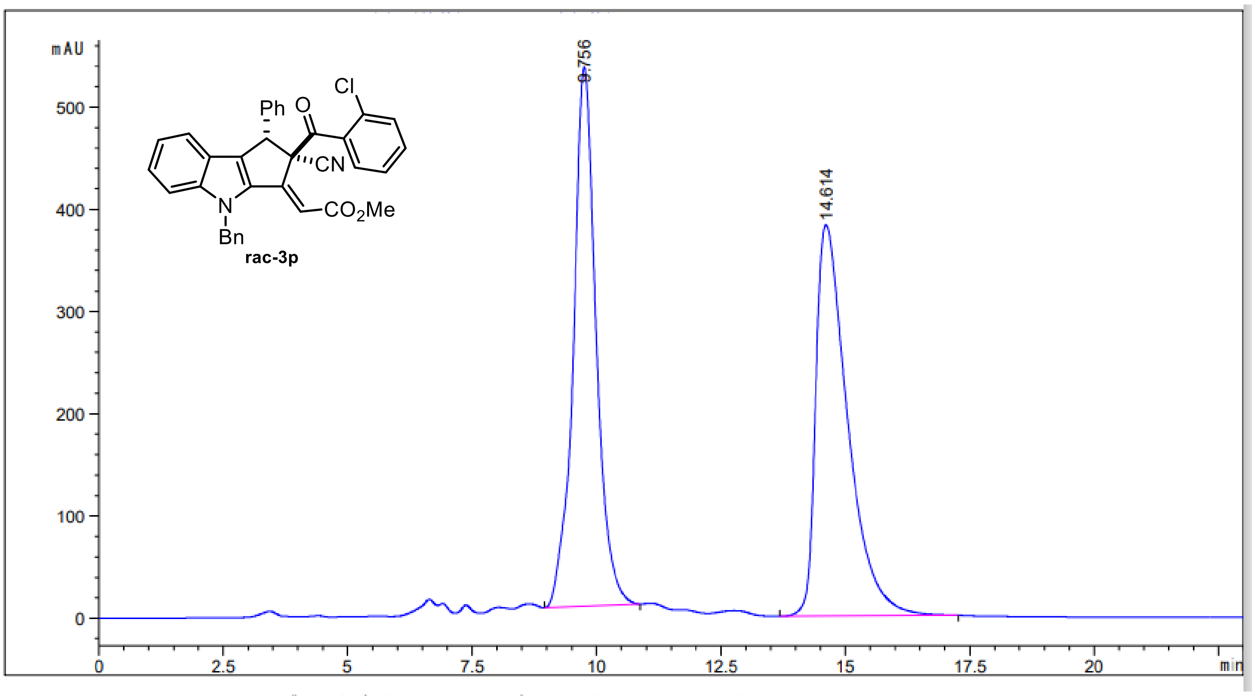


Name	CYC-220406-33	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-33.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:11:26 AM (UTC+08:00)

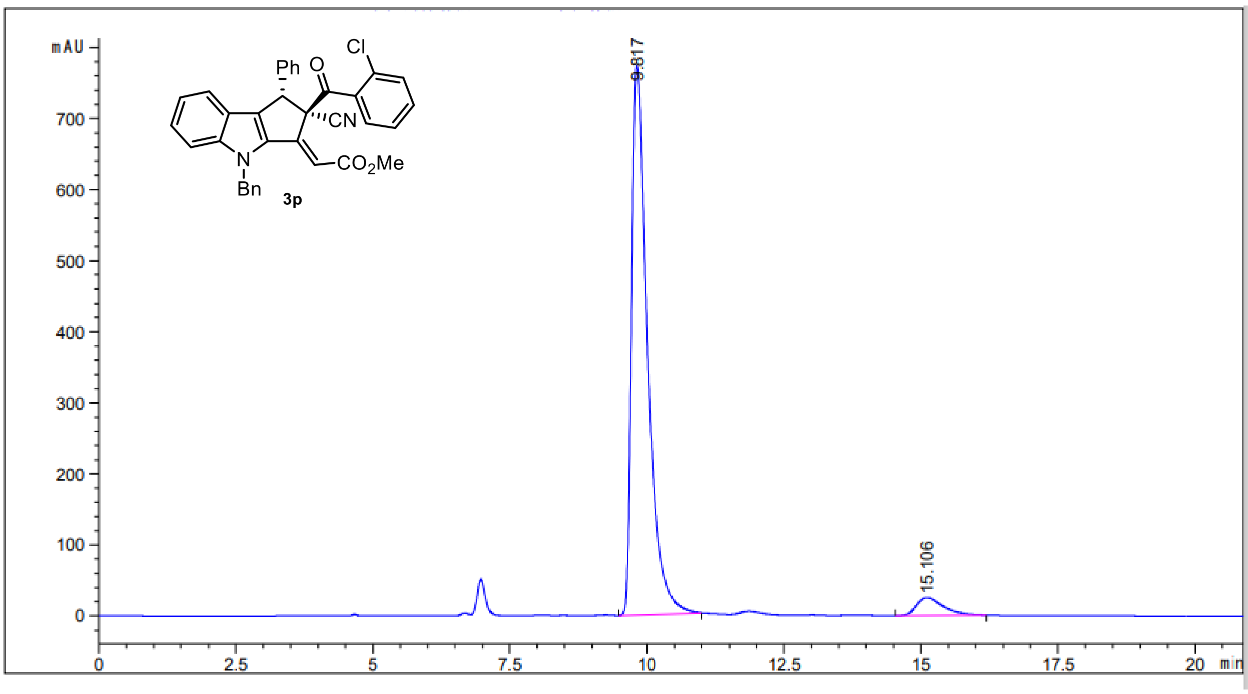



8.347
8.343
8.327
8.323
7.596
7.593
7.576
7.573
7.473
7.469
7.455
7.450
7.435
7.431
7.403
7.385
7.381
7.370
7.366
7.346
7.344
7.337
7.334
7.329
7.326
7.322
7.318
7.315
7.306
7.302
7.300
7.296
7.294
7.287
7.284
7.280
7.274
7.269
7.260
7.255
7.203
7.199
7.182
7.179
7.129
7.126
7.123
7.109
7.106
7.104
7.061
7.058
7.054
7.050
7.042
7.038
7.034
7.030
7.018
7.014
6.231
5.572
5.274
3.677
0.000
Ph
O
Cl
CN
N
Bn
CO_2Me
3p
^1H NMR (400 MHz, $CDCl_3$)
0.98
1.00
1.06
2.15
7.11
2.22
1.03
3.06
1.00
1.97
1.00
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

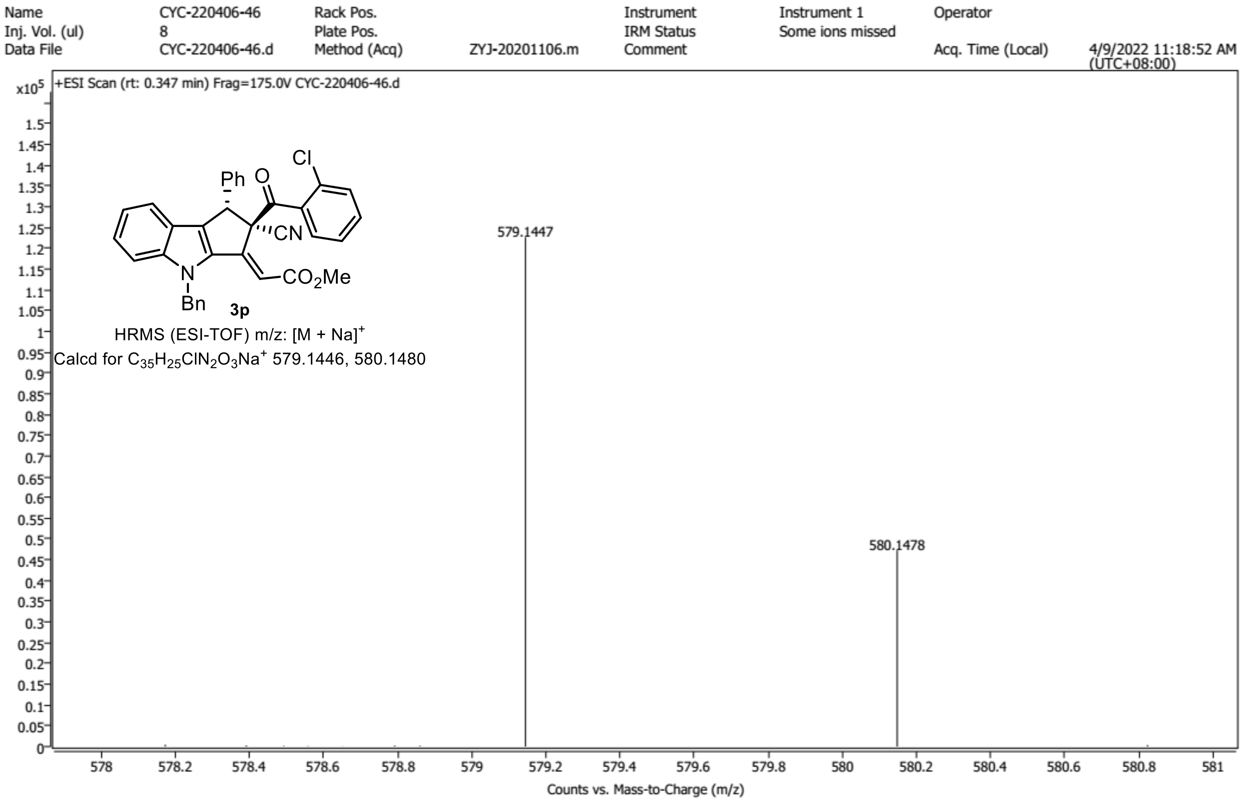

188.658
166.235
145.943
145.510
140.320
137.020
136.222
135.287
132.325
131.284
131.044
130.816
129.240
129.131
128.678
128.612
127.967
126.554
126.317
126.254
125.935
122.462
121.188
121.102
116.404
110.676
108.428
77.318
77.000
76.682
69.532
51.968
51.848
47.931
Ph
O
Cl
CN
N
Bn
CO_2Me
3p
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

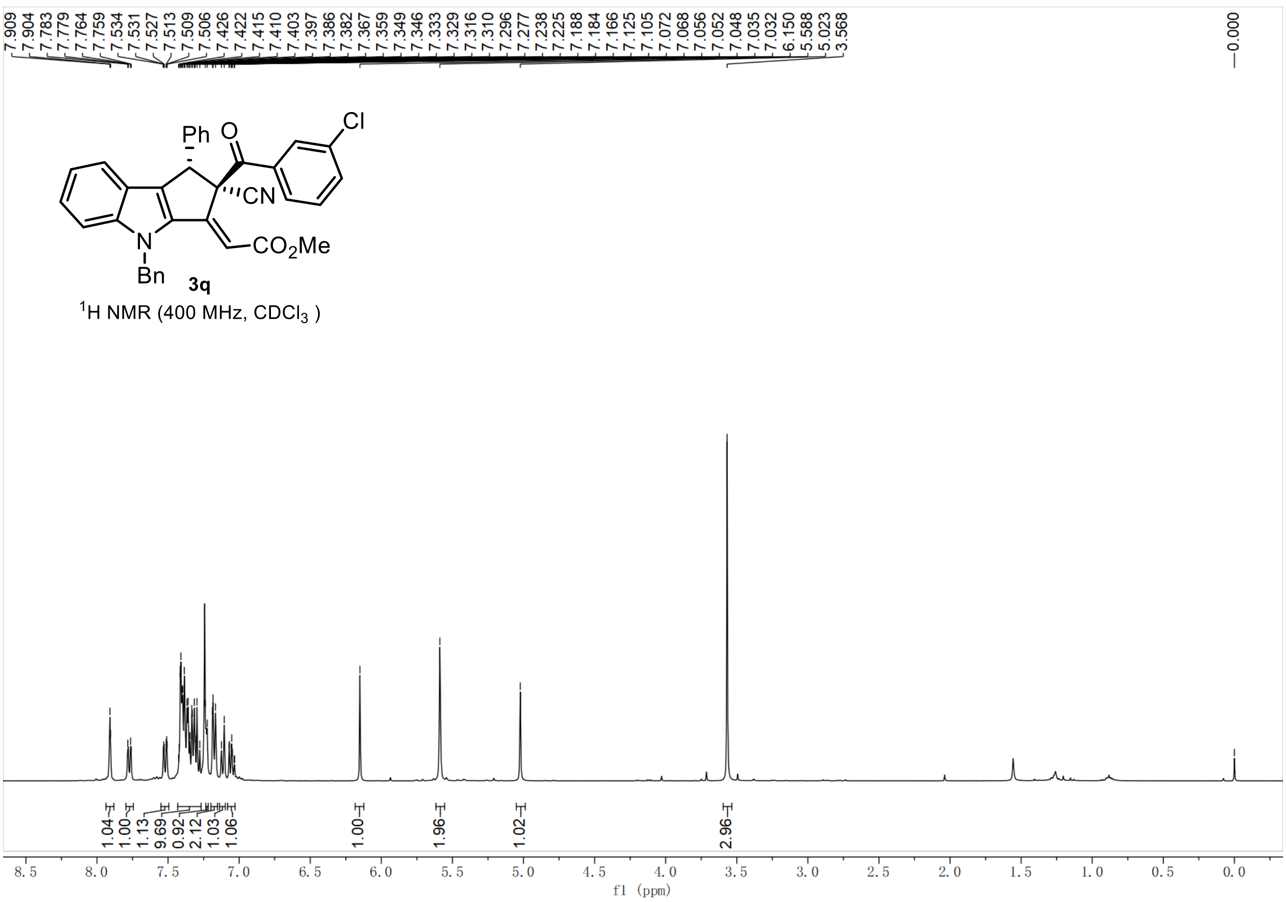


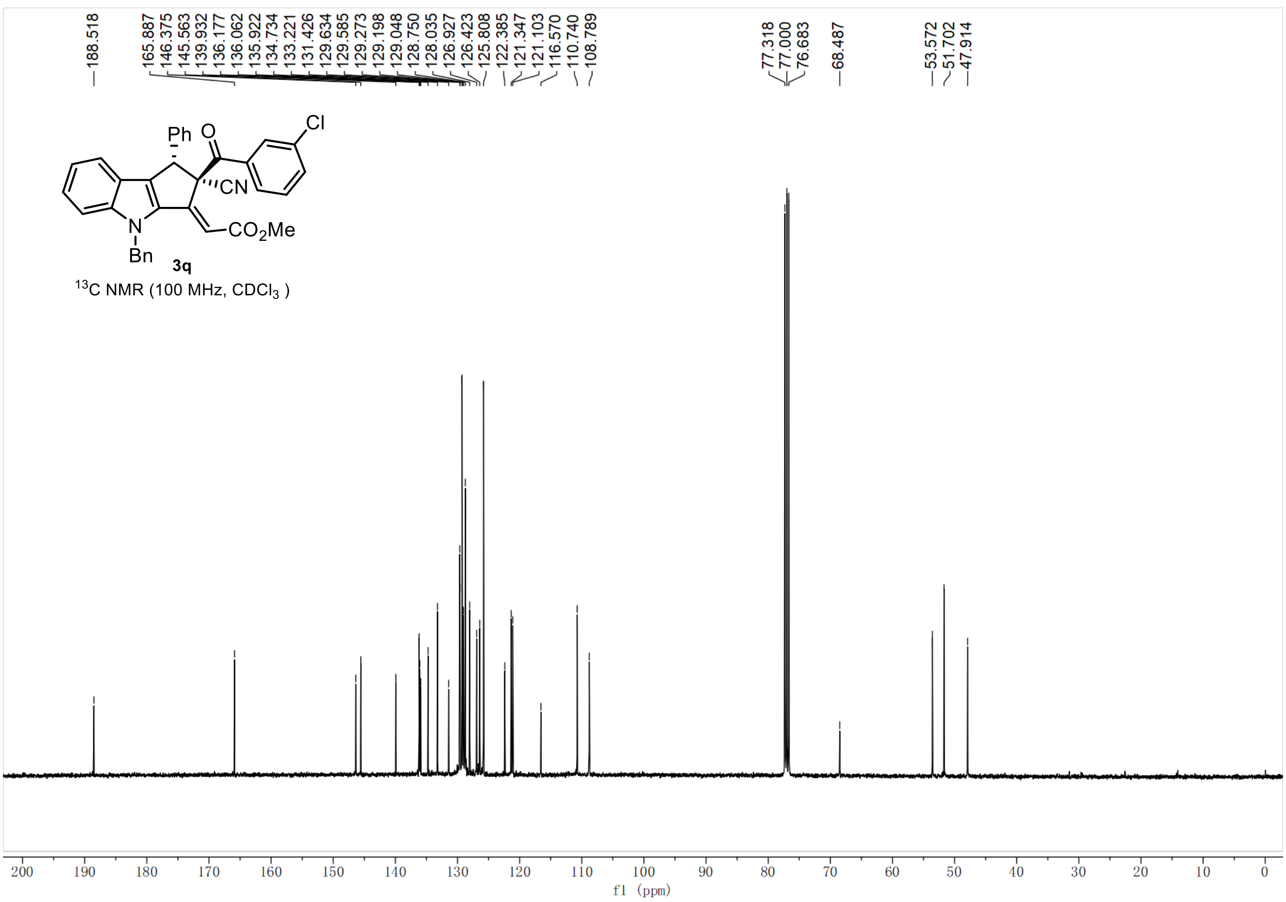
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.756	BB	0.4748	1.67838e4	527.17853	49.5926
2	14.614	BBA	0.6715	1.70595e4	382.72595	50.4074

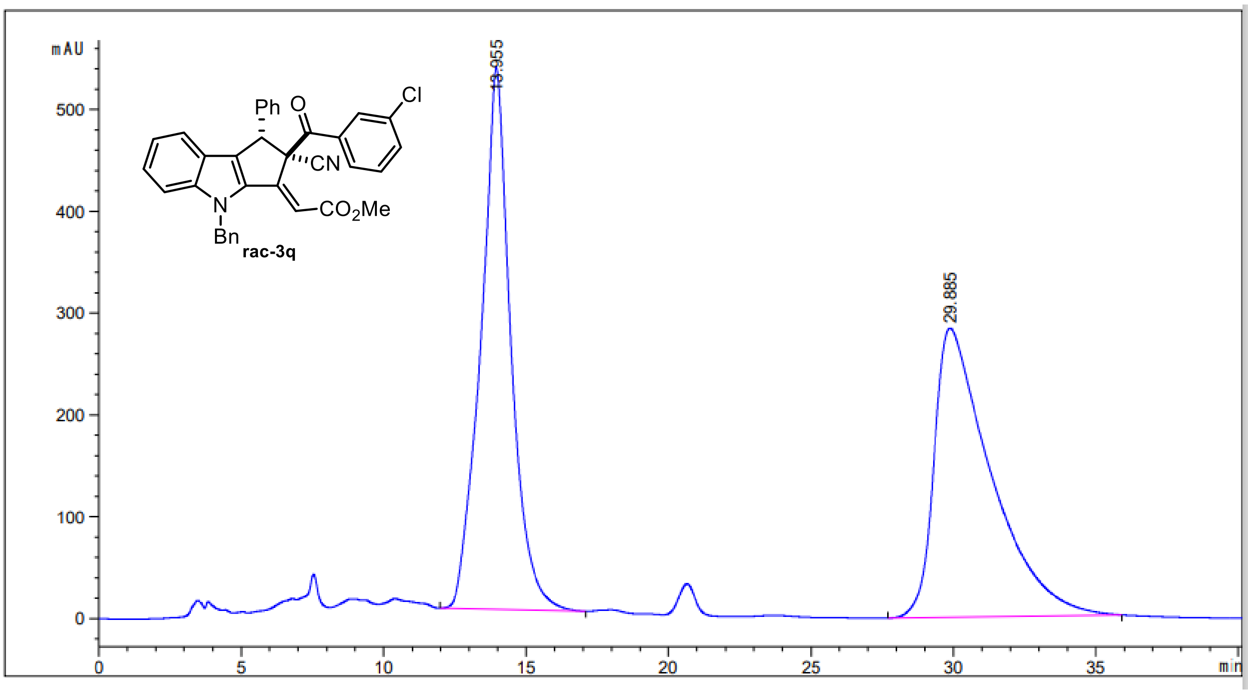


#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.817	BBA	0.2992	1.55849e4	773.43219	94.8097
2	15.106	BBA	0.5153	853.17926	24.95508	5.1903

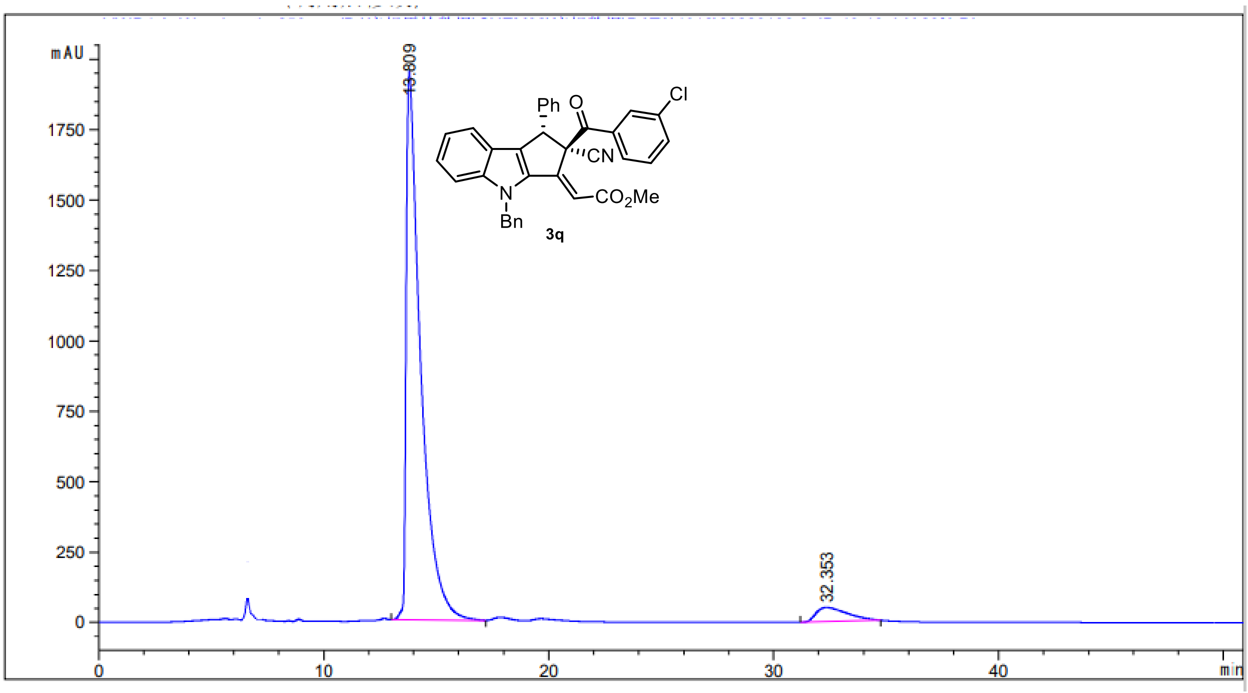

Name CYC-220406-46 Rack Pos. Instrument Instrument 1 Operator
Inj. Vol. (ul) 8 Plate Pos. IRM Status Some ions missed
Data File CYC-220406-46.d Method (Acq) ZYJ-20201106.m Comment Acq. Time (Local) 4/9/2022 11:18:52 AM (UTC+08:00)
x10^5 +ESI Scan (rt: 0.347 min) Frag=175.0V CYC-220406-46.d
Ph
O
Cl
CN
N
Bn
CO2Me
3p
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C35H25ClN2O3Na+ 579.1446, 580.1480
579.1447
580.1478
Counts vs. Mass-to-Charge (m/z)


7.909 7.904 7.783 7.779 7.764 7.759 7.534 7.531 7.527 7.513 7.509 7.506 7.426 7.422 7.415 7.410 7.403 7.397 7.386 7.382 7.367 7.359 7.349 7.346 7.333 7.329 7.316 7.310 7.296 7.277 7.238 7.225 7.188 7.184 7.166 7.125 7.105 7.072 7.068 7.056 7.052 7.048 7.035 7.032 6.150 5.588 5.023 3.568
0.000
Ph
O
Cl
CN
N
CO2Me
Bn
3q
1H NMR (400 MHz, CDCl3)
1.04 1.00 1.13 9.69 0.92 2.12 1.03 1.06
1.00
1.96
1.02
2.96
f1 (ppm)


188.518
165.887 146.375 145.563 139.932 136.177 136.062 135.922 134.734 133.221 131.426 129.634 129.585 129.273 129.198 129.048 128.750 128.035 126.927 126.423 125.808 122.385 121.347 121.103 116.570 110.740 108.789
77.318 77.000 76.683
68.487
53.572 51.702 47.914
Ph
O
Cl
CN
N
CO2Me
Bn
3q
13C NMR (100 MHz, CDCl3)
f1 (ppm)

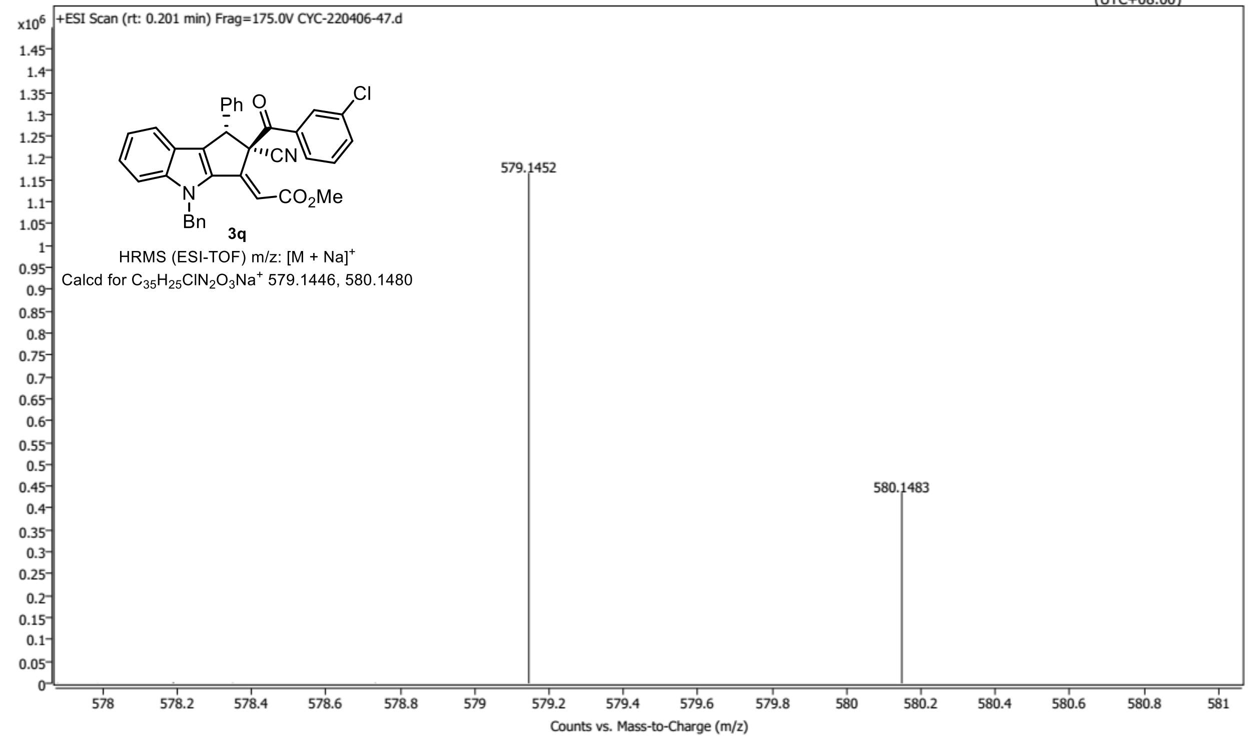


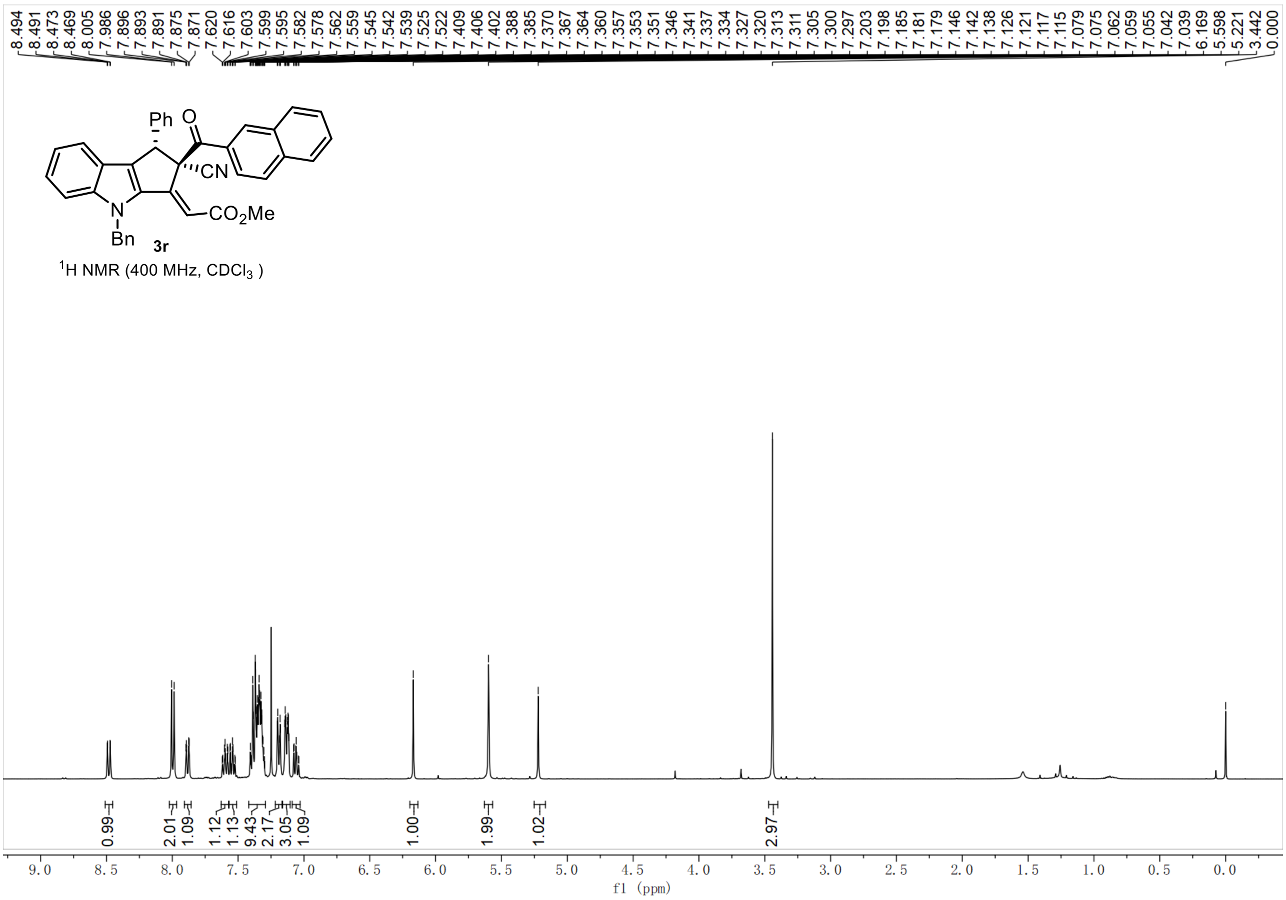
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.955	BBA	1.0123	3.91535e4	532.43646	49.8356
2	29.885	BBA	1.9491	3.94118e4	283.82718	50.1644



#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.809	BB	0.6504	8.86727e4	1948.11304	94.9048
2	32.353	BBA	1.4554	4760.59619	49.69775	5.0952

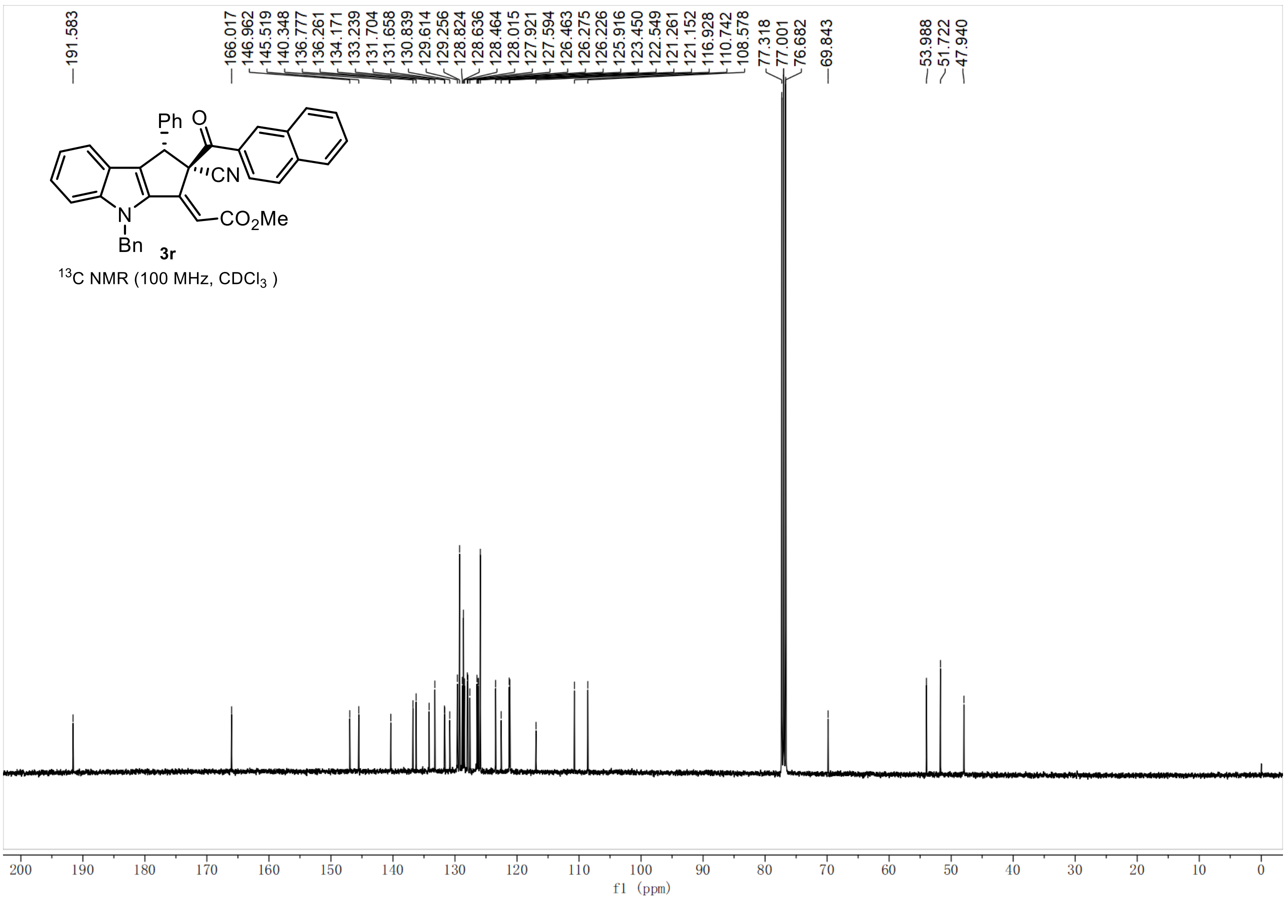
Name	CYC-220406-47	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-47.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:21:49 AM (UTC+08:00)





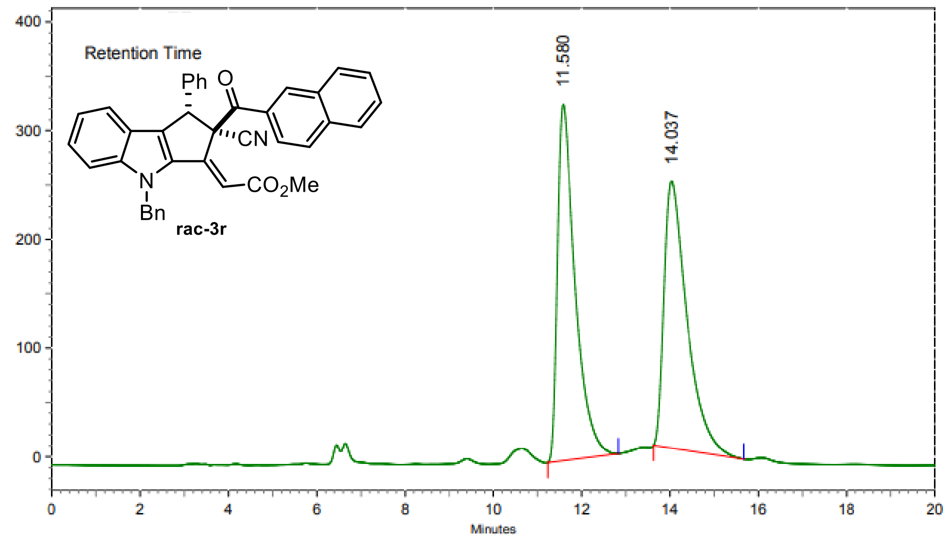
3r

^{1}H NMR (400 MHz, $CDCl_3$)



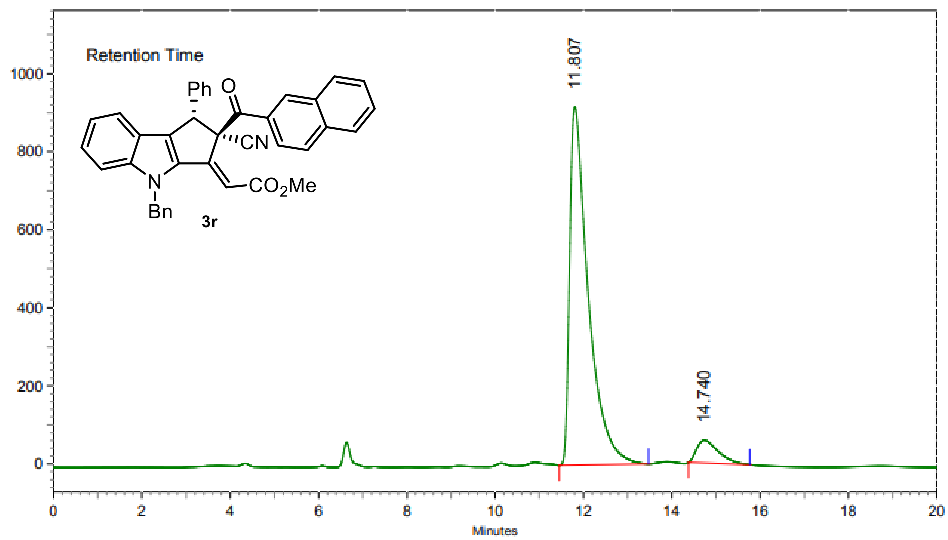
3r

^{13}C NMR (100 MHz, $CDCl_3$)



AREA PERCENT REPORT

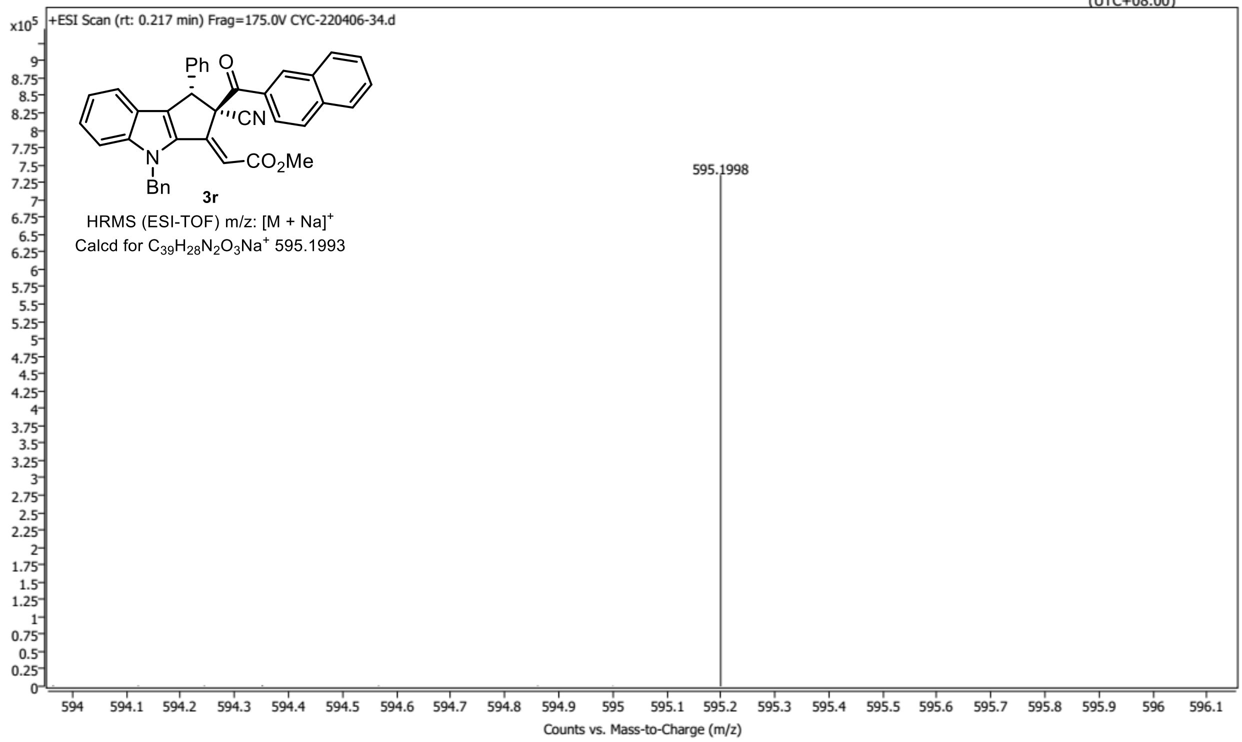
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	11.580	1.600	5492989	153173798	50.8394
2	14.037	2.040	4120141	148115976	49.1606

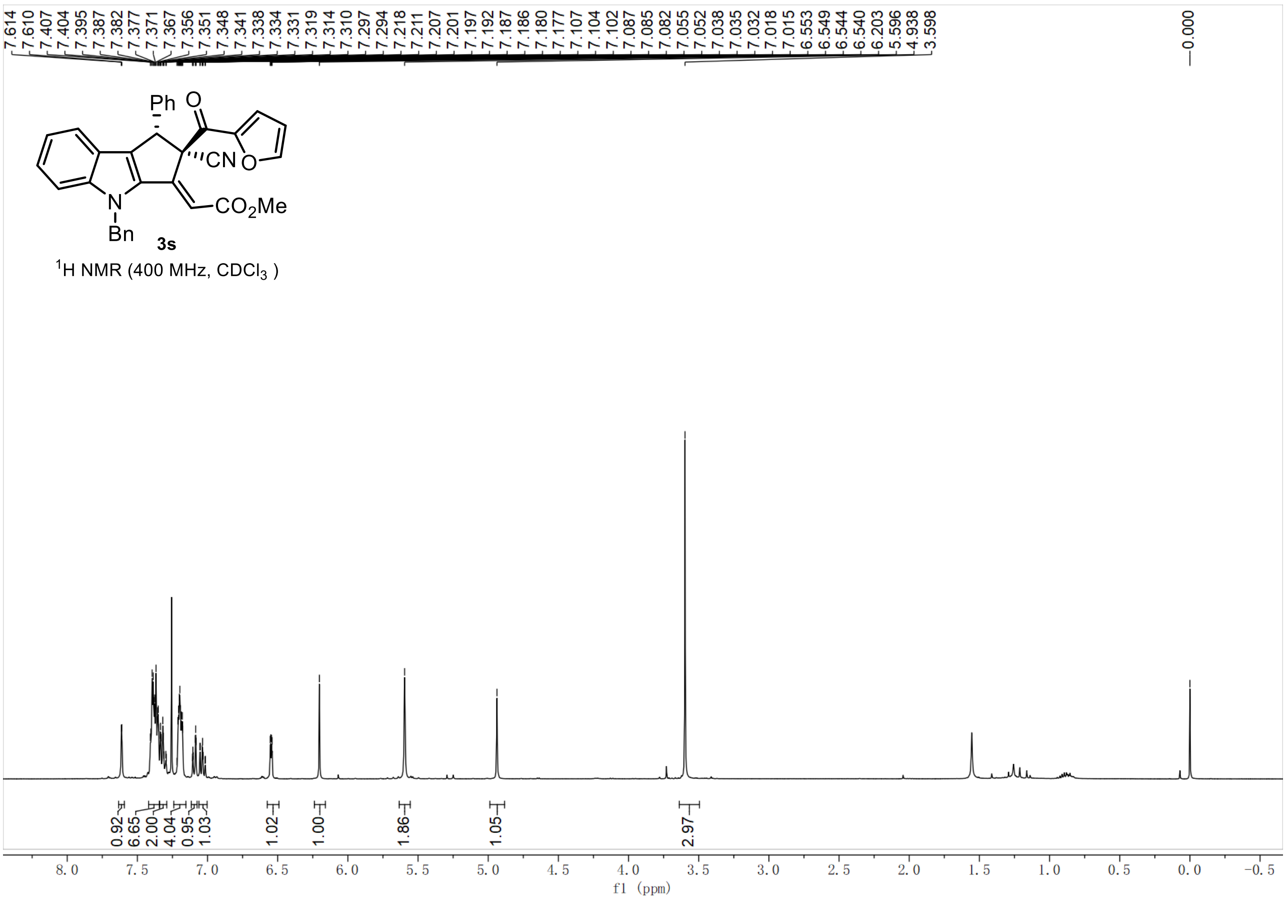


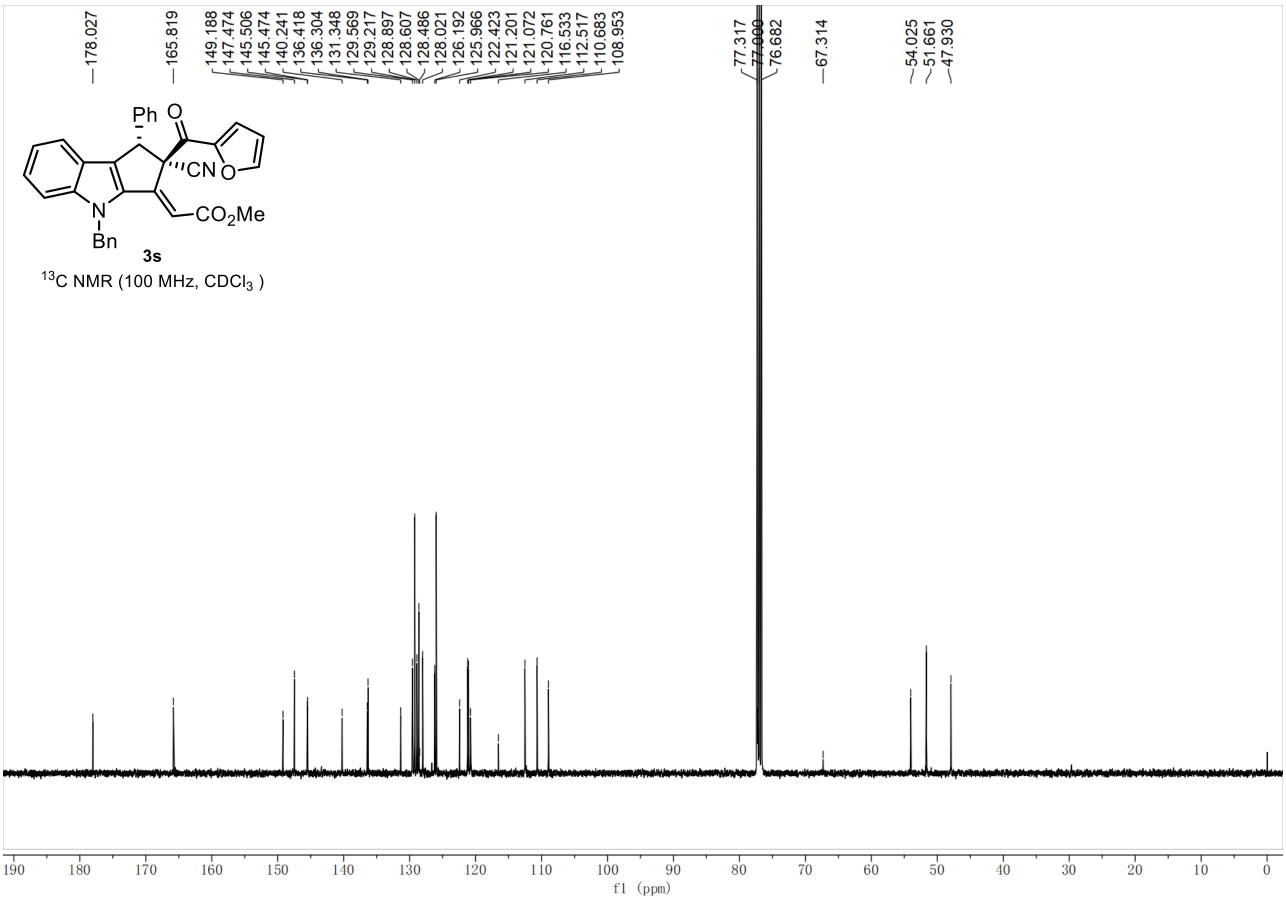
AREA PERCENT REPORT

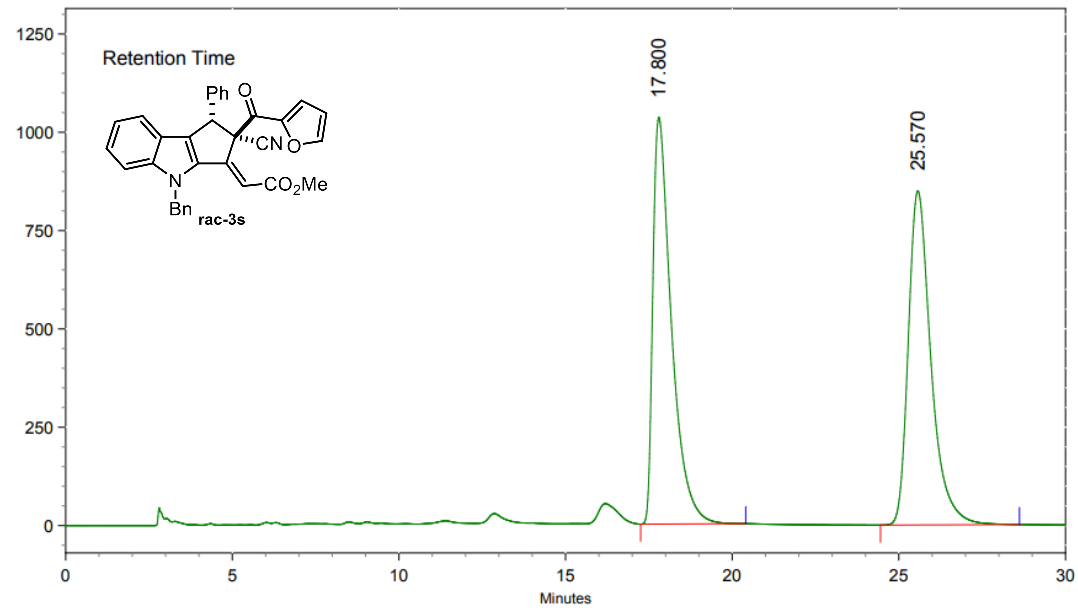
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	11.807	2.020	15395999	452310860	93.1072
2	14.740	1.387	985064	33484779	6.8928

Name	CYC-220406-34	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-34.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:14:24 AM (UTC+08:00)



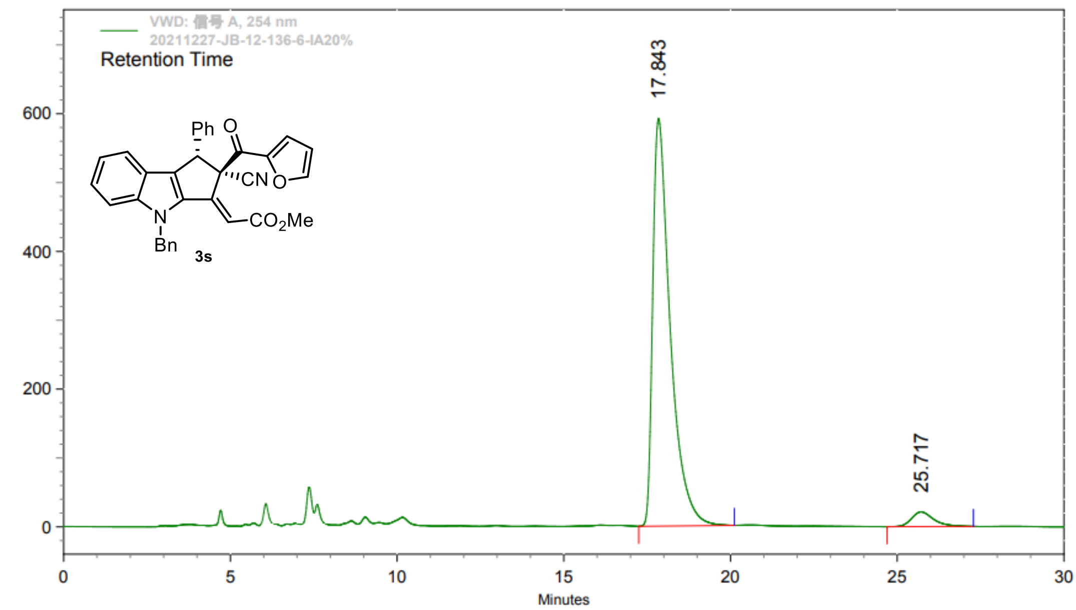

7.614 7.610 7.407 7.404 7.395 7.387 7.382 7.377 7.371 7.367 7.356 7.351 7.348 7.341 7.338 7.334 7.331 7.319 7.314 7.310 7.297 7.294 7.218 7.211 7.207 7.201 7.197 7.192 7.187 7.186 7.180 7.177 7.107 7.104 7.102 7.087 7.085 7.082 7.055 7.052 7.038 7.035 7.032 7.018 7.015 6.553 6.549 6.544 6.540 6.203 5.596 4.938 3.598
0.000
Ph
O
CN
O
N
Bn
CO2Me
3s
1H NMR (400 MHz, CDCl3)
0.92 6.65 2.00 4.04 0.95 1.03 1.02 1.00 1.86 1.05 2.97
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


178.027
165.819
149.188 147.474 145.506 145.474 140.241 136.418 136.304 131.348 129.569 129.217 128.897 128.607 128.486 128.021 126.192 125.966 122.423 121.201 121.072 120.761 116.533 112.517 110.683 108.953
77.317 77.000 76.682
67.314
54.025 51.661 47.930
Ph
O
CN
O
N
Bn
CO2Me
3s
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



AREA PERCENT REPORT

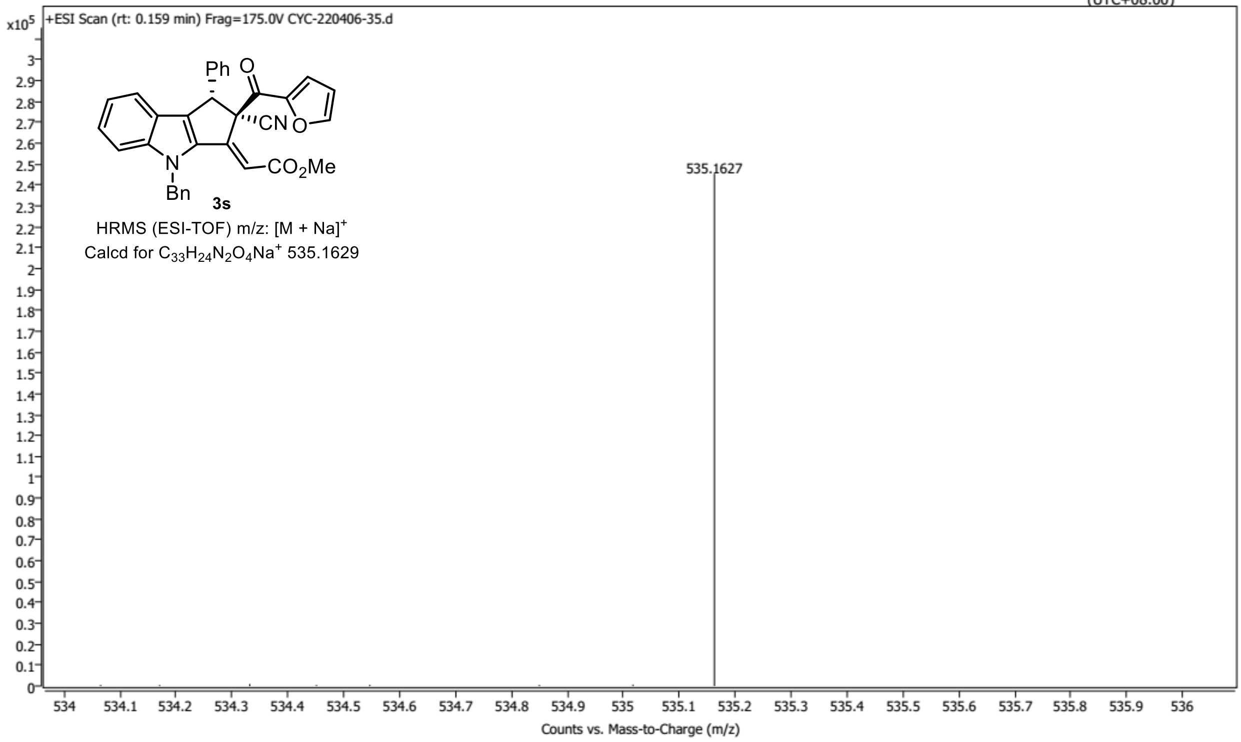
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	17.800	3.153	17351435	670966566	49.9116
2	25.570	4.170	14252623	673342811	50.0884

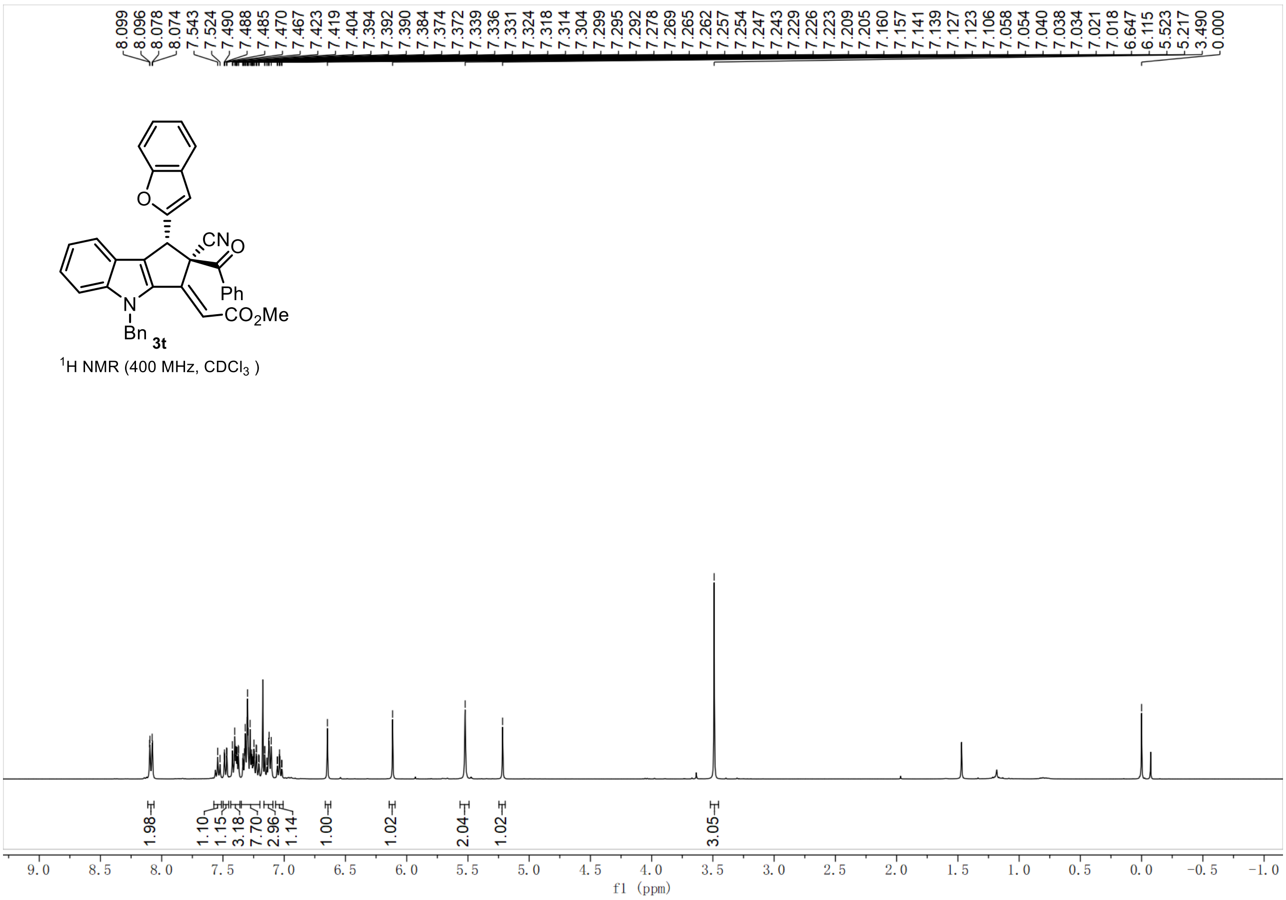


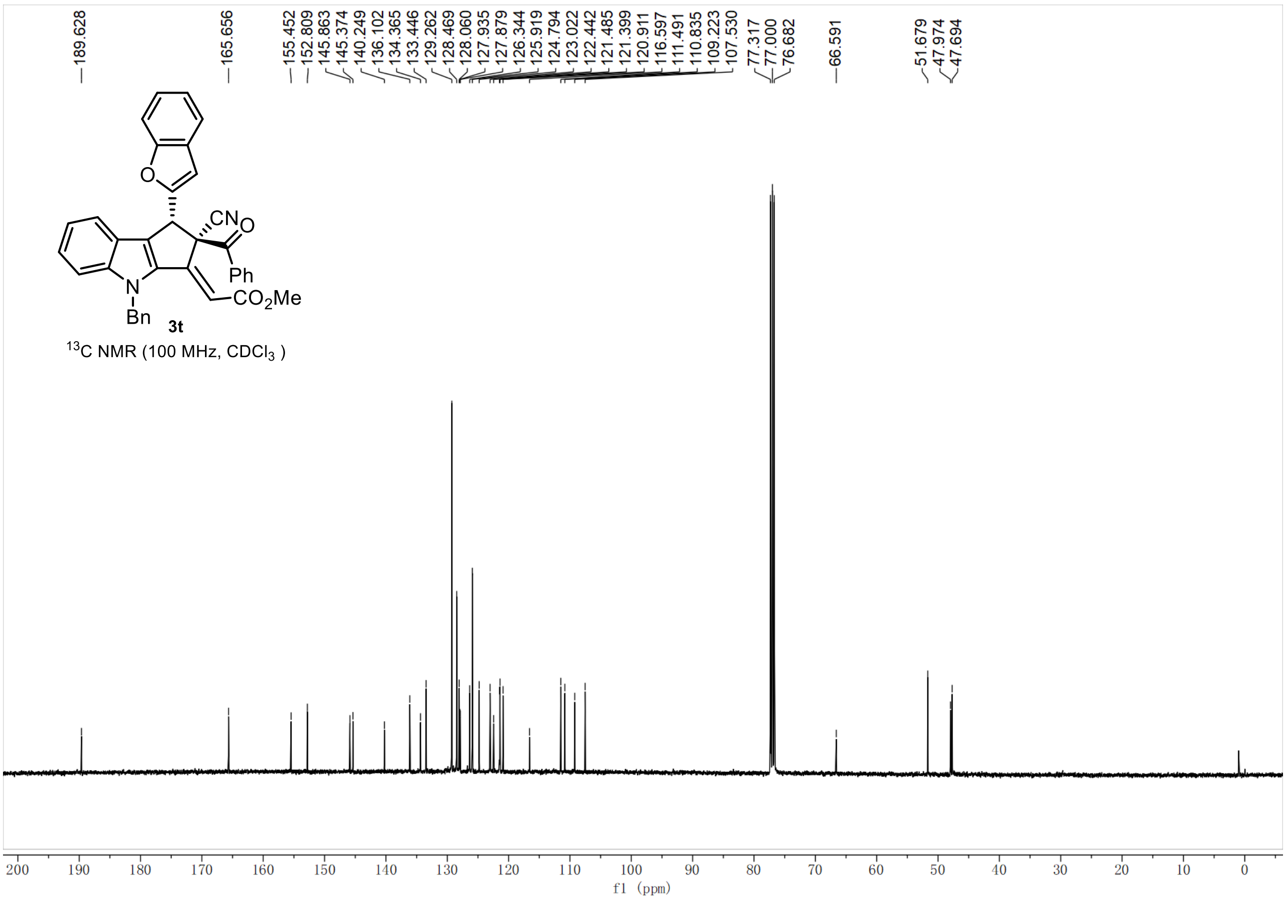
AREA PERCENT REPORT

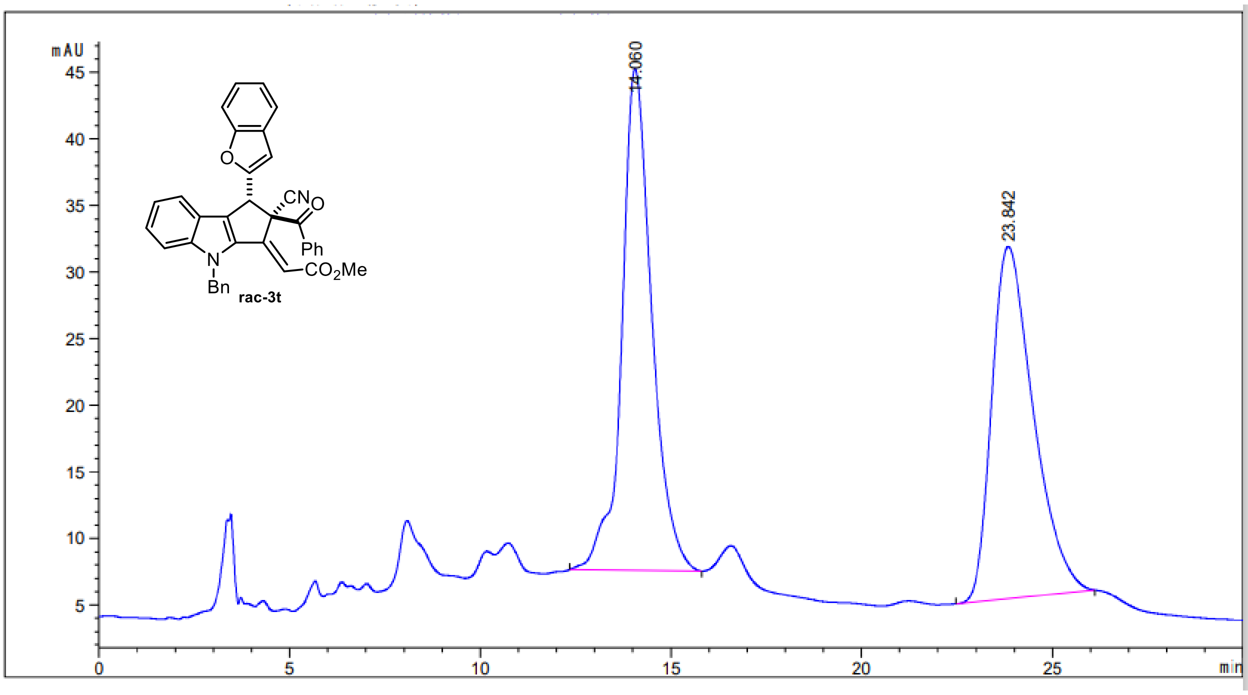
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	17.843	2.867	9932096	362098755	95.6293
2	25.717	2.590	357222	16549756	4.3707

Name	CYC-220406-35	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-35.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:17:22 AM (UTC+08:00)

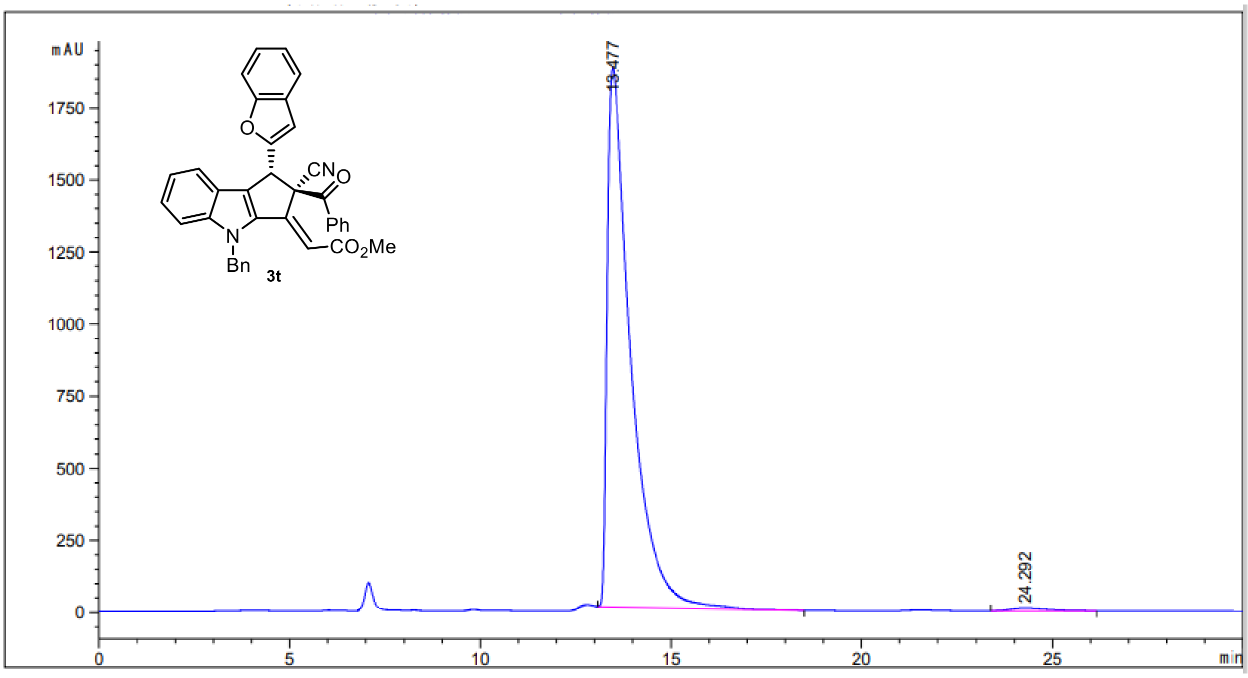



3t
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


3t
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

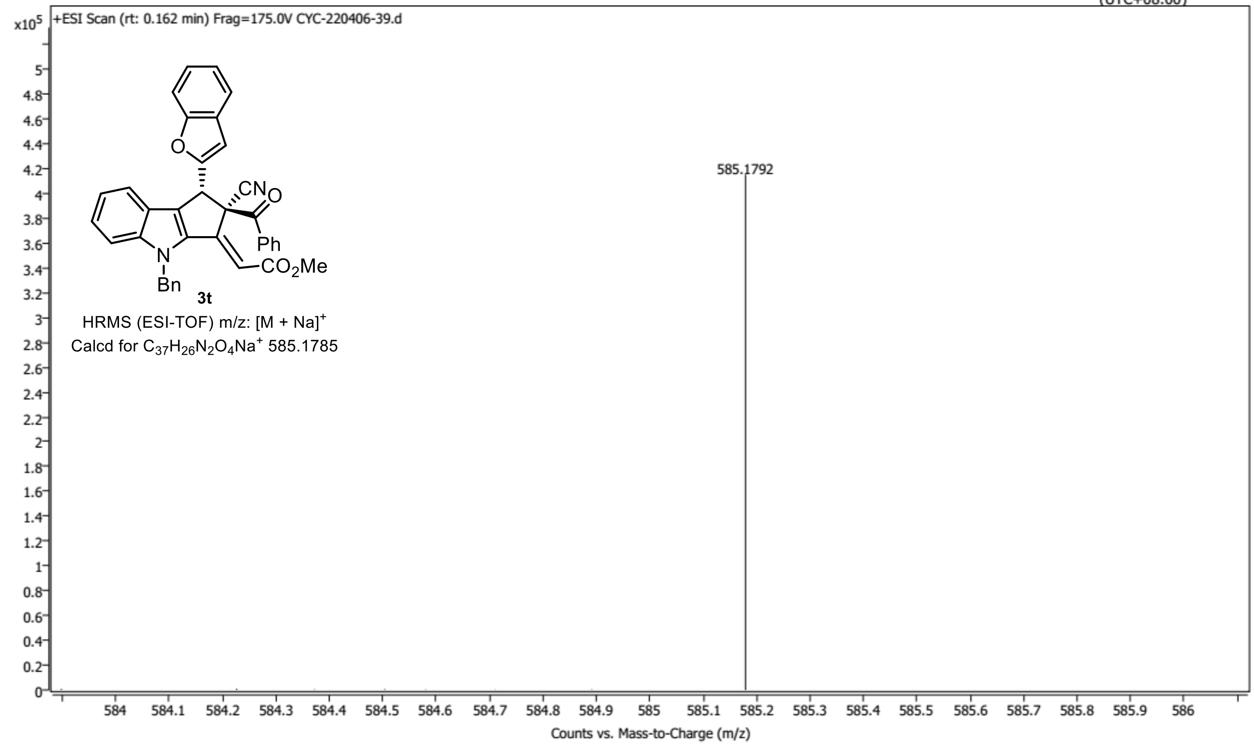


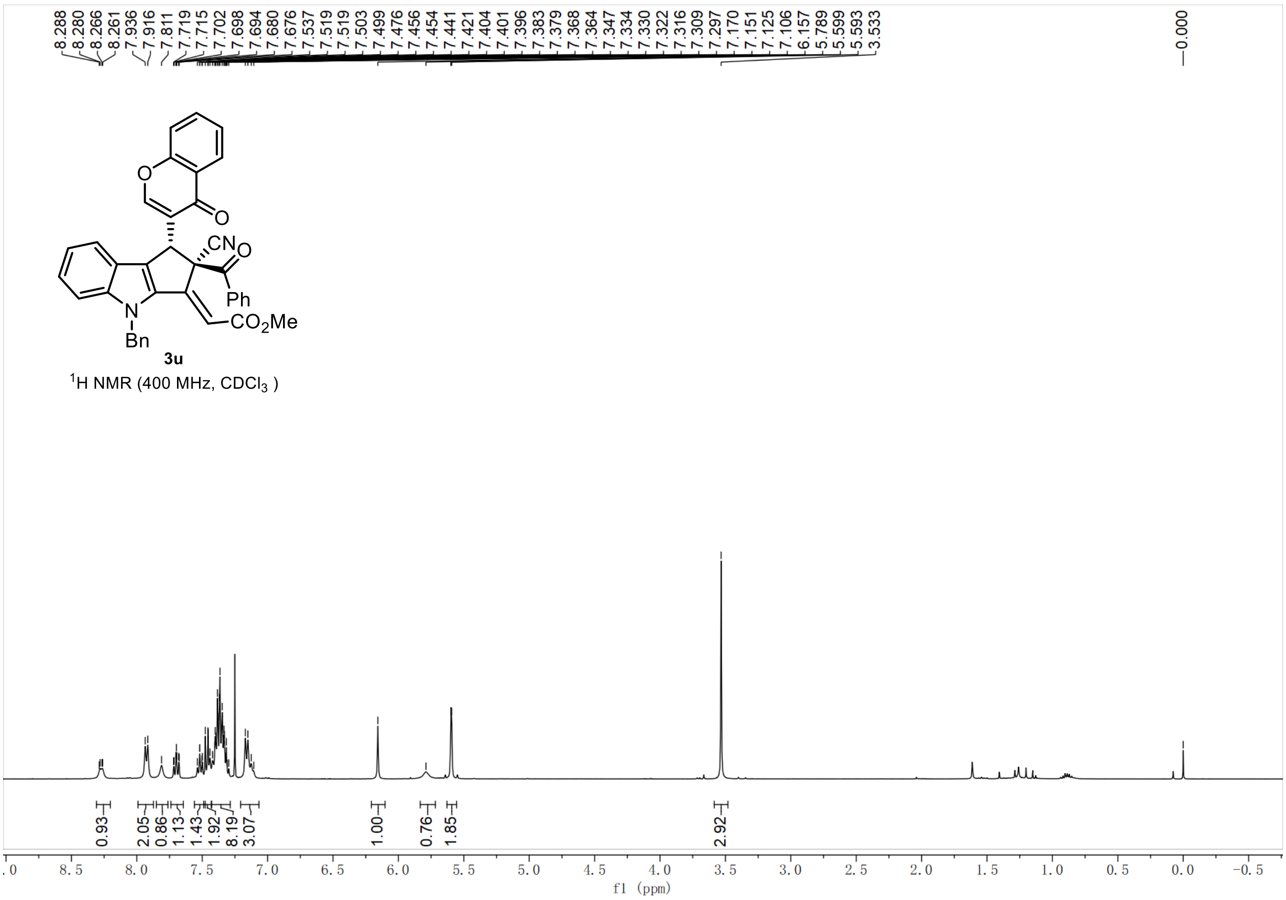
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.060	BB	0.8114	2055.39478	37.66331	50.5917
2	23.842	BBA	1.1414	2007.31409	26.45690	49.4083

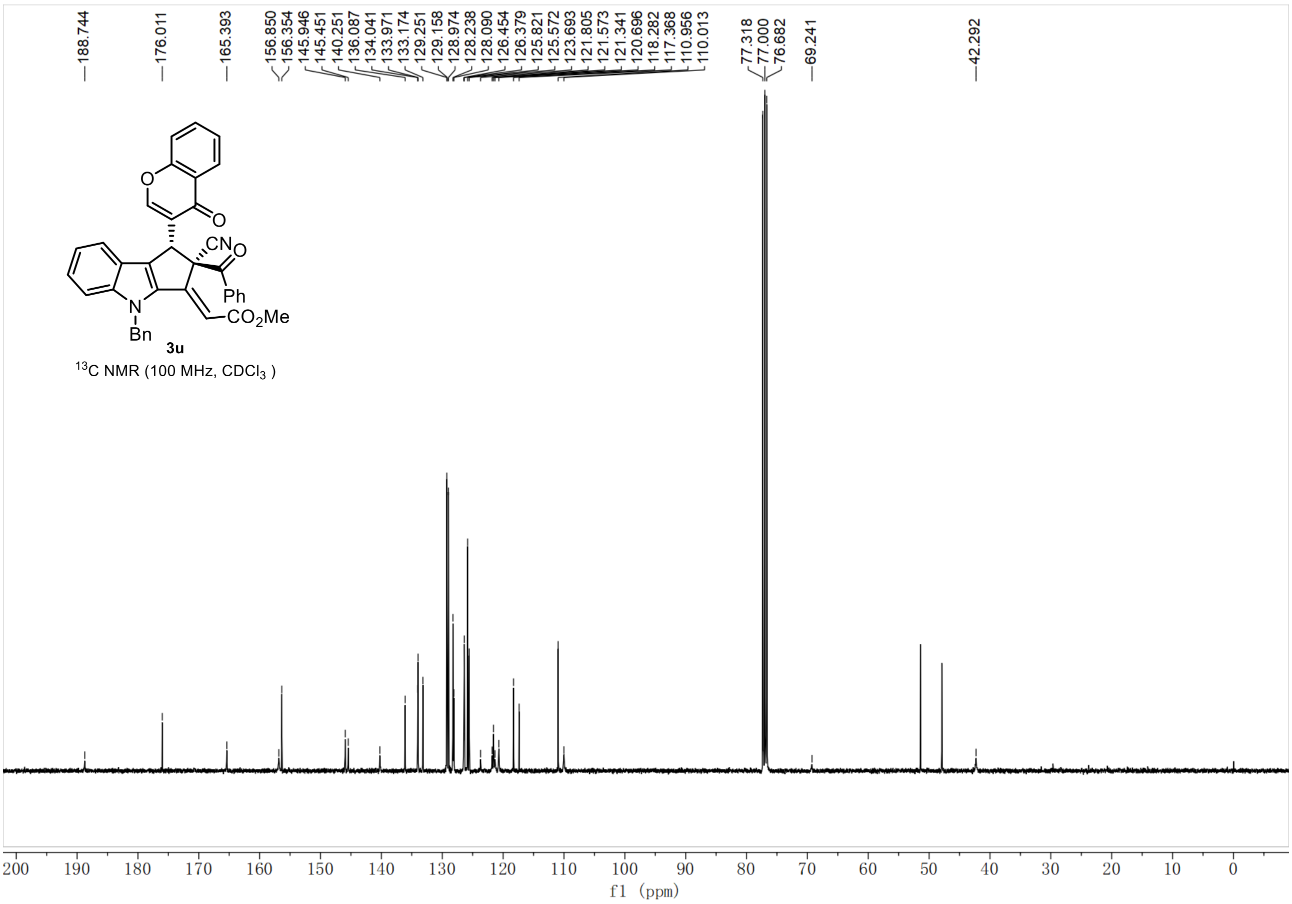


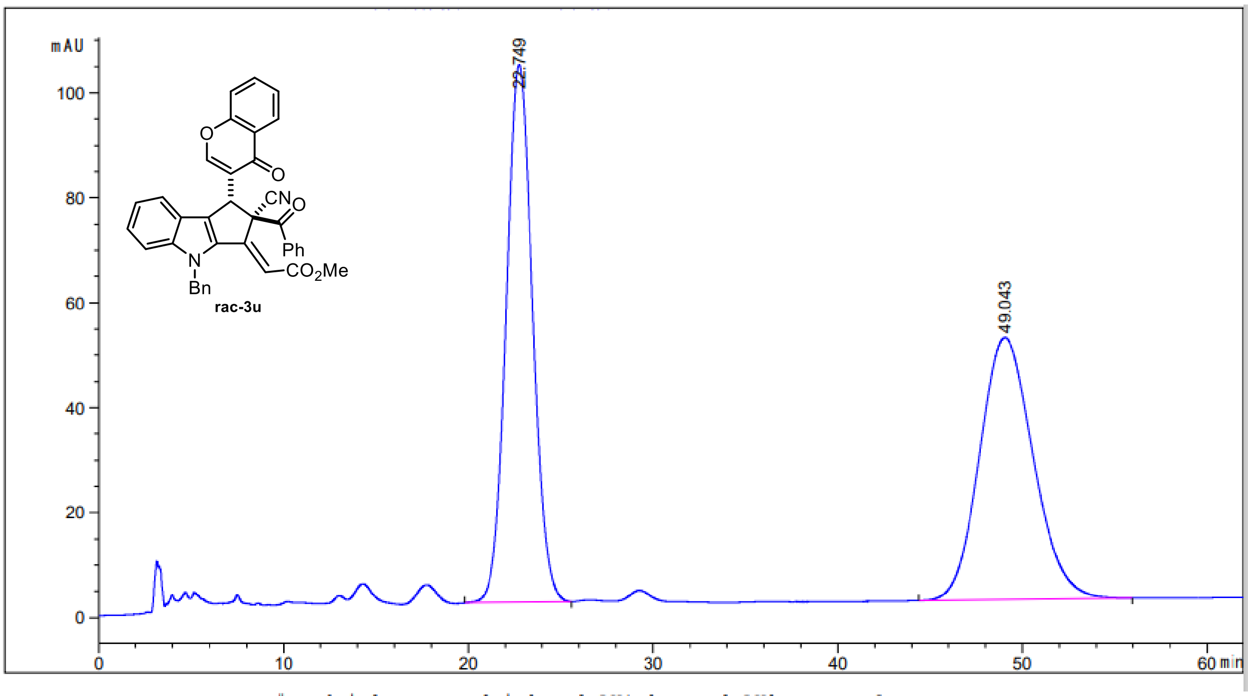
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.477	BBA	0.6183	8.04566e4	1870.48608	99.1371
2	24.292	BBA	0.9930	700.33234	10.18443	0.8629

Name	CYC-220406-39	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-39.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 10:58:13 AM (UTC+08:00)

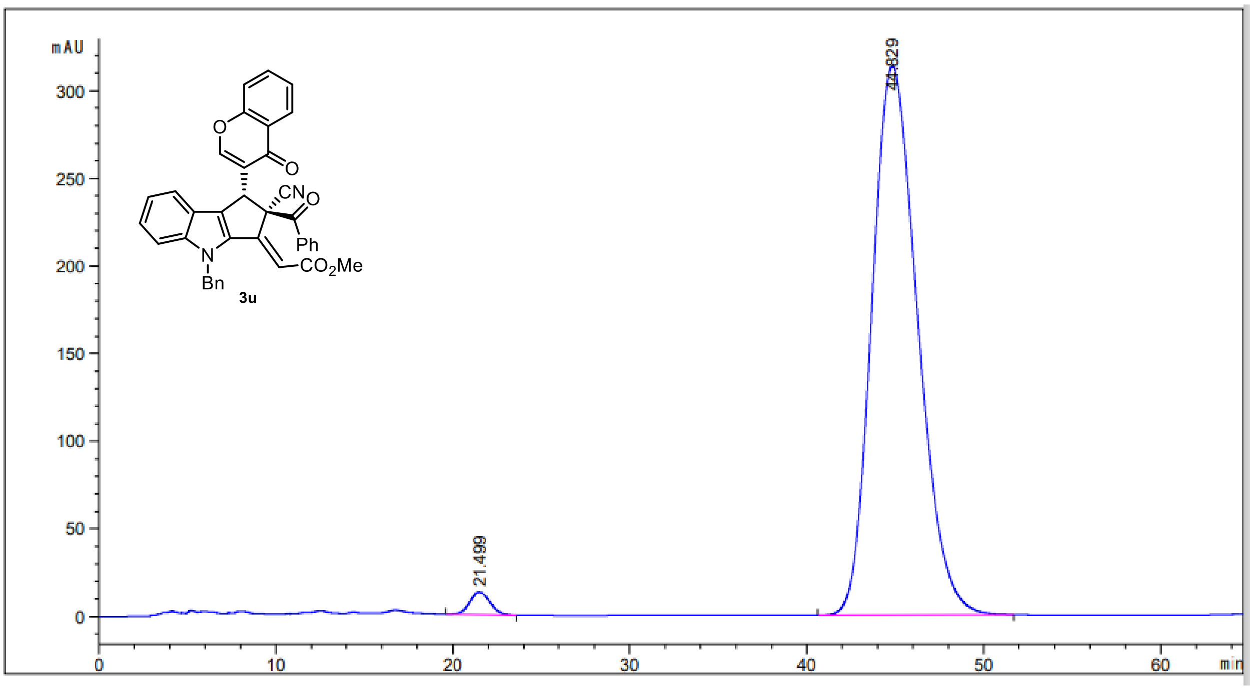



8.288
8.280
8.266
8.261
7.936
7.916
7.811
7.719
7.715
7.702
7.698
7.694
7.680
7.676
7.537
7.519
7.519
7.503
7.499
7.476
7.456
7.454
7.441
7.421
7.404
7.401
7.396
7.383
7.379
7.368
7.364
7.347
7.334
7.330
7.322
7.316
7.309
7.297
7.170
7.151
7.125
7.106
6.157
5.789
5.599
5.593
3.533
0.000
3u
^{1}H NMR (400 MHz, CDCl$_3$)
0.93
2.05
0.86
1.13
1.43
1.92
8.19
3.07
1.00
0.76
1.85
2.92
f1 (ppm)


188.744
176.011
165.393
156.850
156.354
145.946
145.451
140.251
136.087
134.041
133.971
133.174
129.251
129.158
128.974
128.238
128.090
126.454
126.379
125.821
125.572
123.693
121.805
121.573
121.341
120.696
118.282
117.368
110.956
110.013
77.318
77.000
76.682
69.241
42.292
3u
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

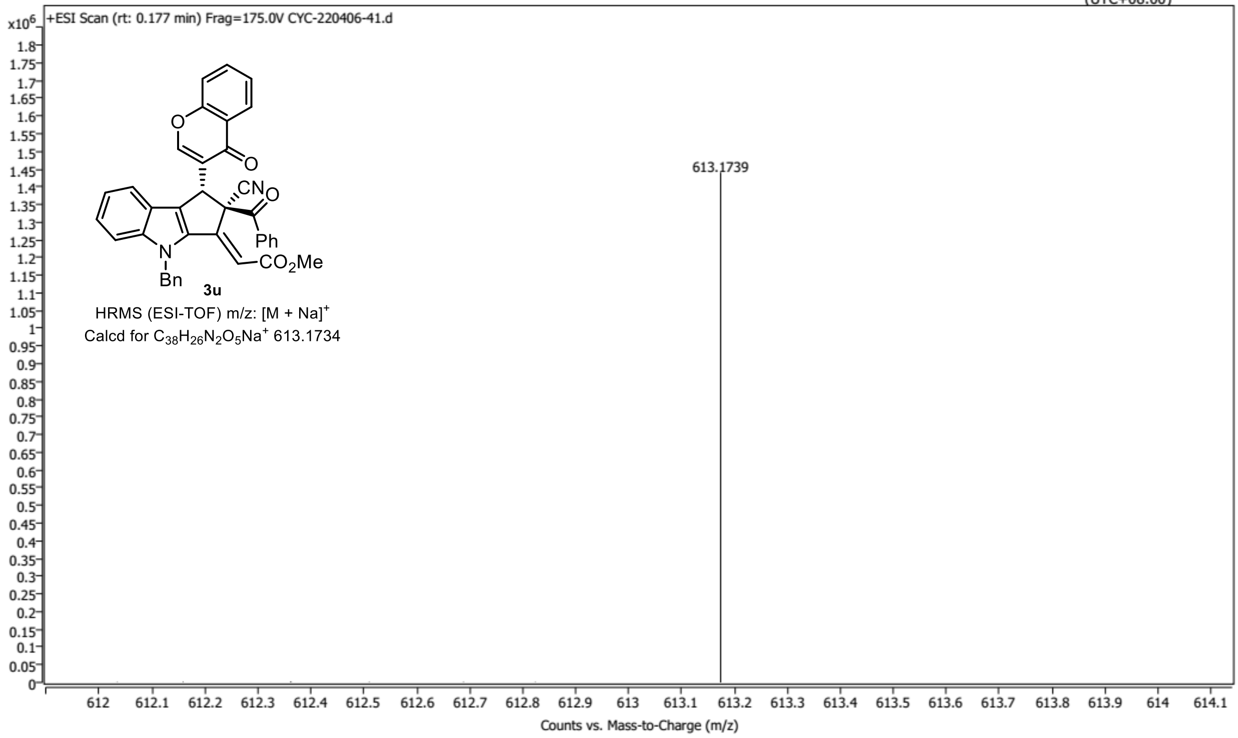


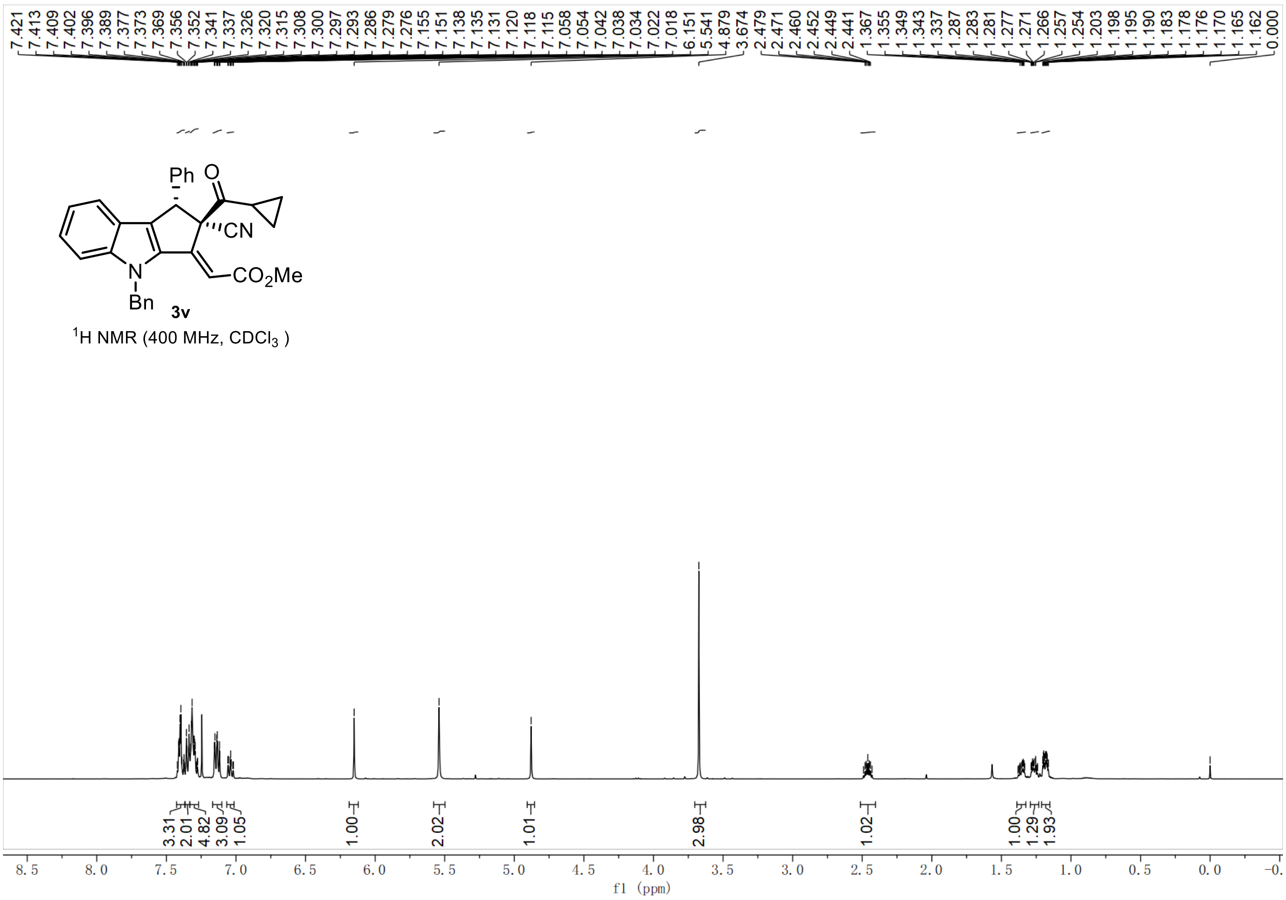
#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.749	BB	1.5409	1.01756e4	102.39329	50.2544
2	49.043	BB	2.8971	1.00726e4	49.95147	49.7456

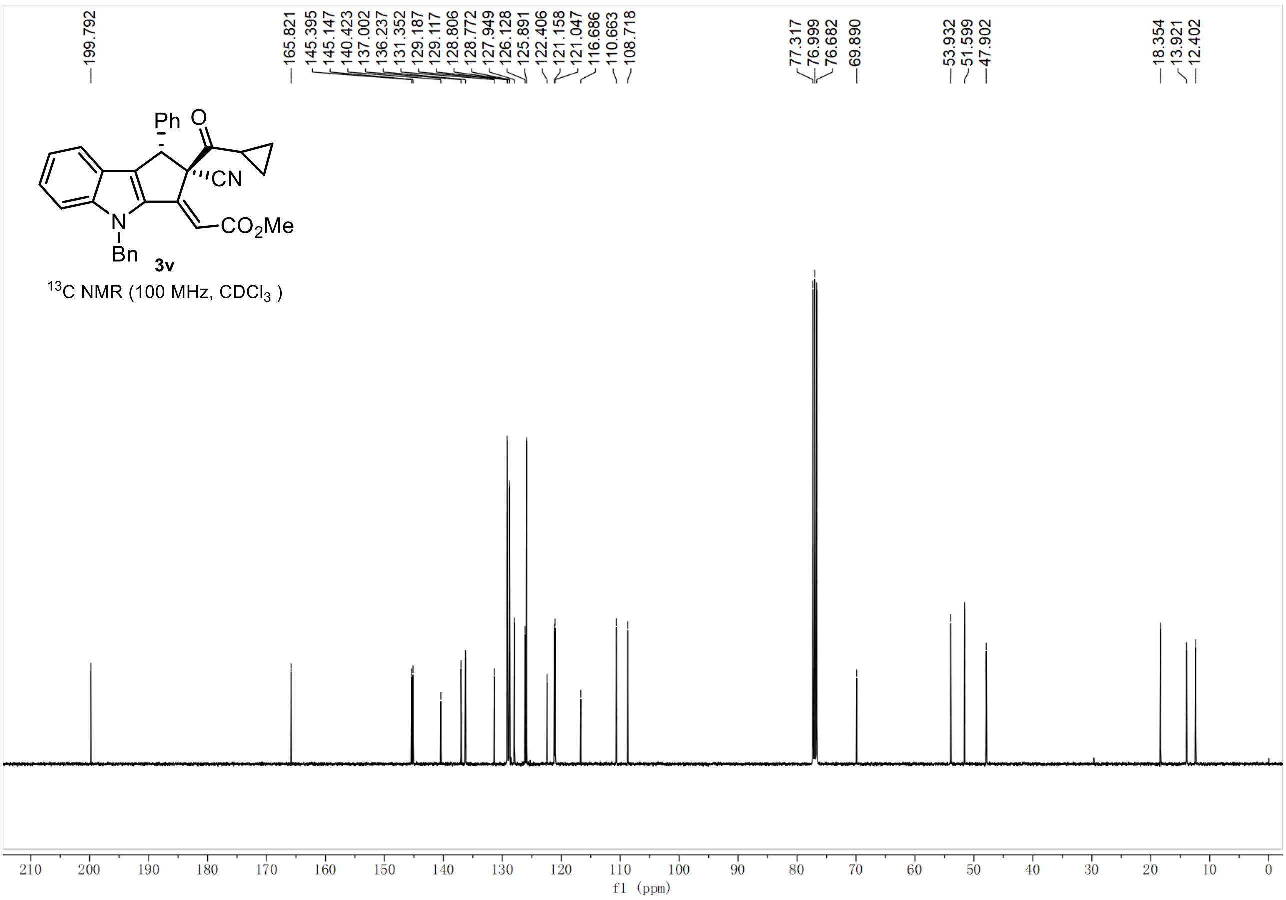


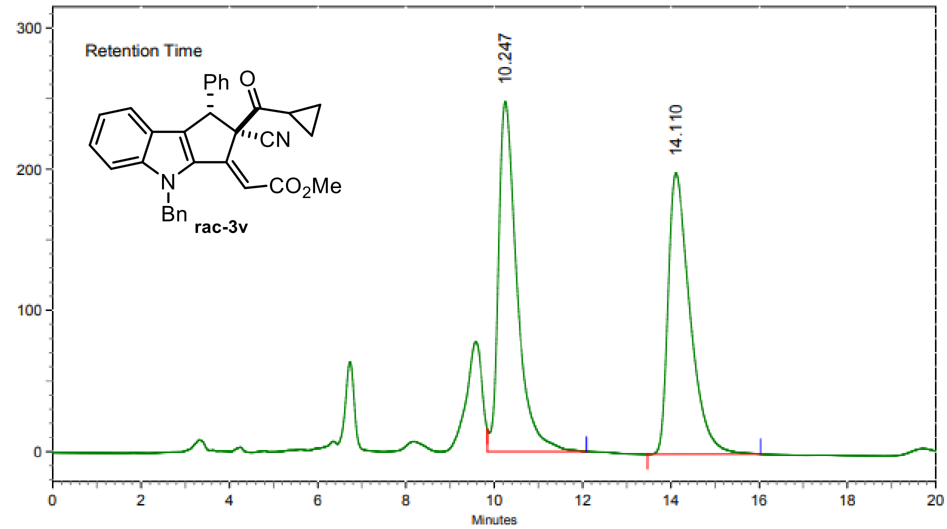
#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.499	BB	1.1485	1007.62488	12.90156	1.7624
2	44.829	BB	2.7559	5.61652e4	313.23096	98.2376

Name	CYC-220406-41	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-41.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:04:07 AM (UTC+08:00)



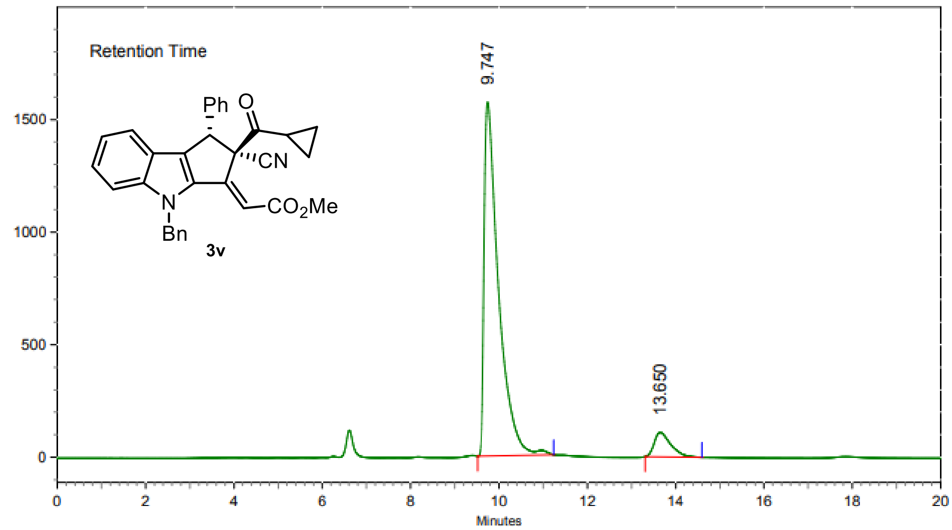

7.421 7.413 7.409 7.402 7.396 7.389 7.377 7.373 7.369 7.356 7.352 7.341 7.337 7.326 7.320 7.315 7.308 7.300 7.297 7.293 7.286 7.279 7.276 7.155 7.151 7.138 7.135 7.131 7.120 7.118 7.115 7.058 7.054 7.042 7.038 7.034 7.022 7.018 6.151 5.541 4.879 3.674 2.479 2.471 2.460 2.452 2.449 2.441 1.367 1.355 1.349 1.343 1.337 1.287 1.283 1.281 1.277 1.271 1.266 1.257 1.254 1.203 1.198 1.195 1.190 1.183 1.178 1.176 1.170 1.165 1.162 0.000
Ph
O
CN
N
Bn
CO_2Me
3v
^{1}H NMR (400 MHz, $CDCl_3$)
3.31 2.01 4.82 3.09 1.05 1.00 2.02 1.01 2.98 1.02 1.00 1.29 1.93
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


199.792
165.821 145.395 145.147 140.423 137.002 136.237 131.352 129.187 129.117 128.806 128.772 127.949 126.128 125.891 122.406 121.158 121.047 116.686 110.663 108.718
77.317 76.999 76.682 69.890
53.932 51.599 47.902
18.354 13.921 12.402
Ph
O
CN
N
Bn
CO_2Me
3v
^{13}C NMR (100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



AREA PERCENT REPORT

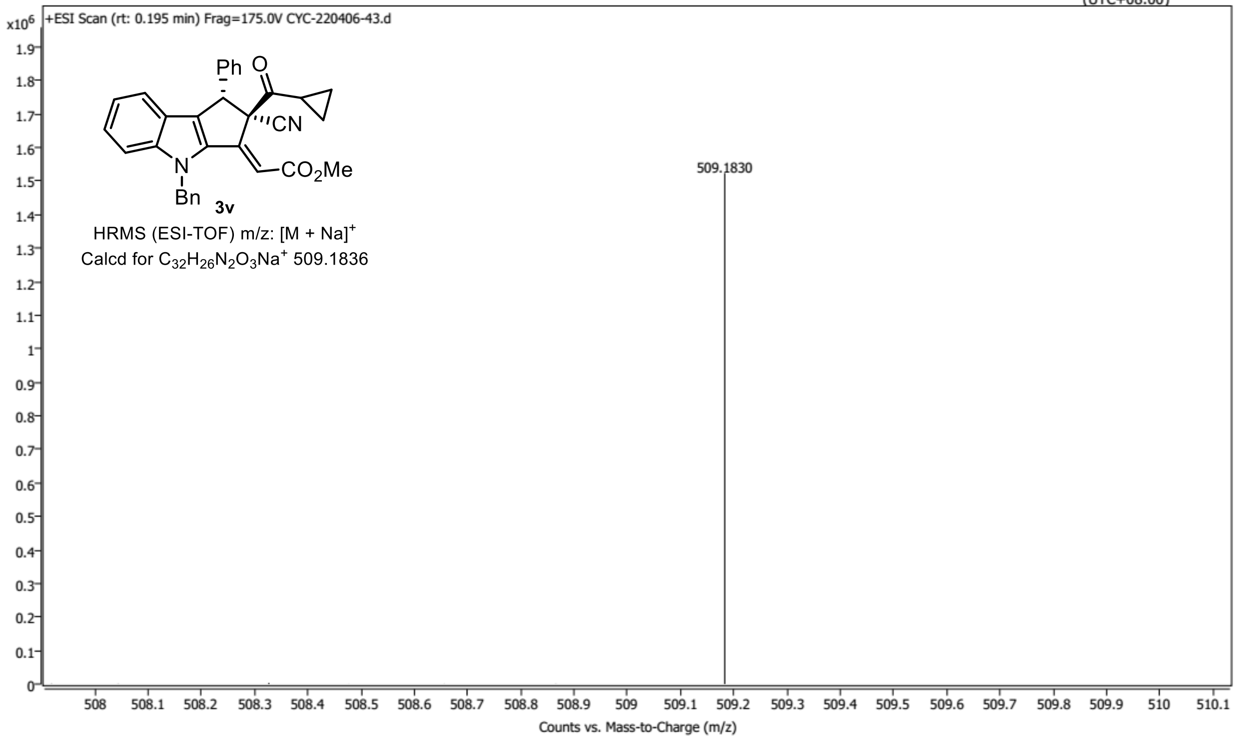
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.247	2.240	4154975	120554112	51.1625
2	14.110	2.560	3335470	115075891	48.8375



AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.747	1.720	26375701	593443940	92.6760
2	13.650	1.280	1810361	46898570	7.3240

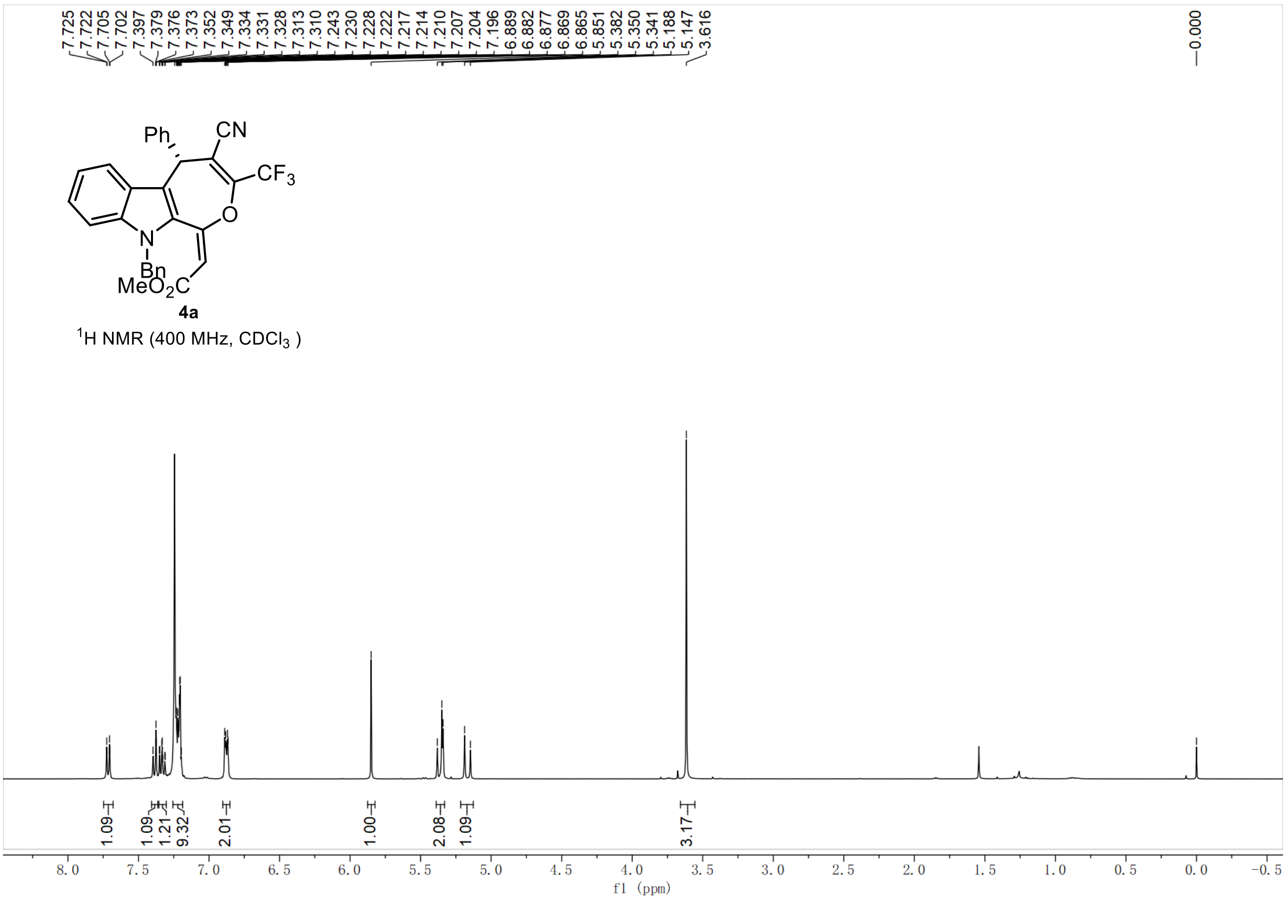
Name	CYC-220406-43	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-43.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:10:01 AM (UTC+08:00)

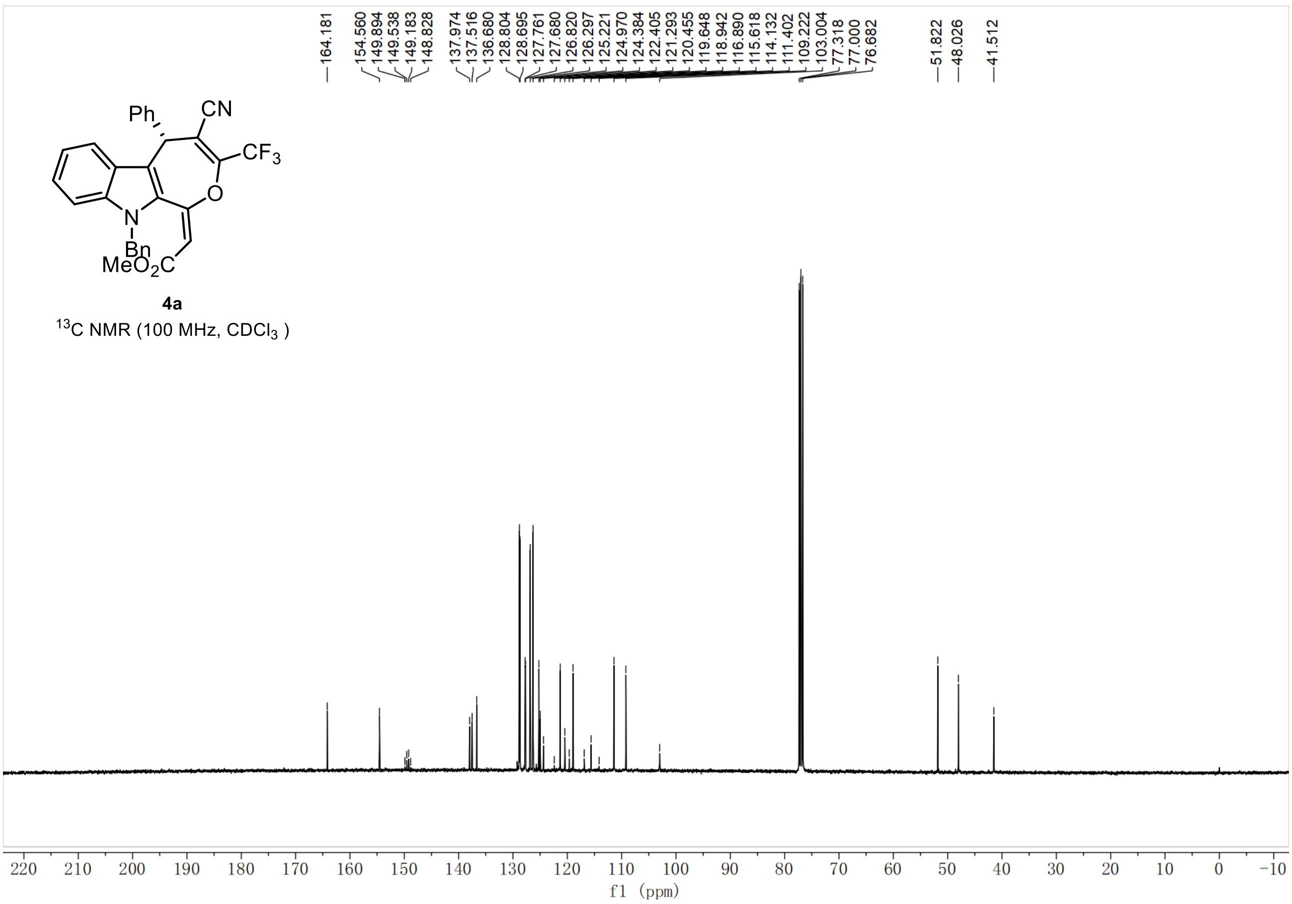


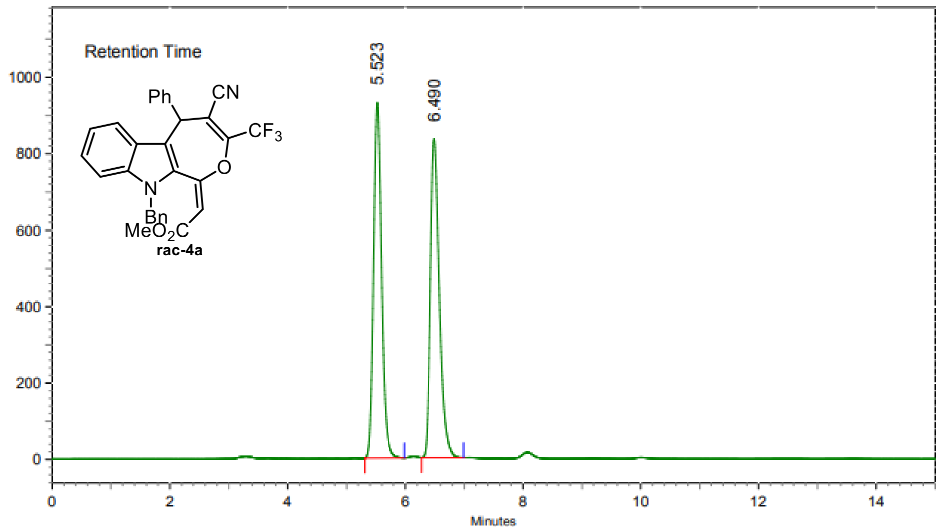
3v

HRMS (ESI-TOF) m/z: [M + Na]$^+$

Calcd for $C_{32}H_{26}N_2O_3Na^+$ 509.1836

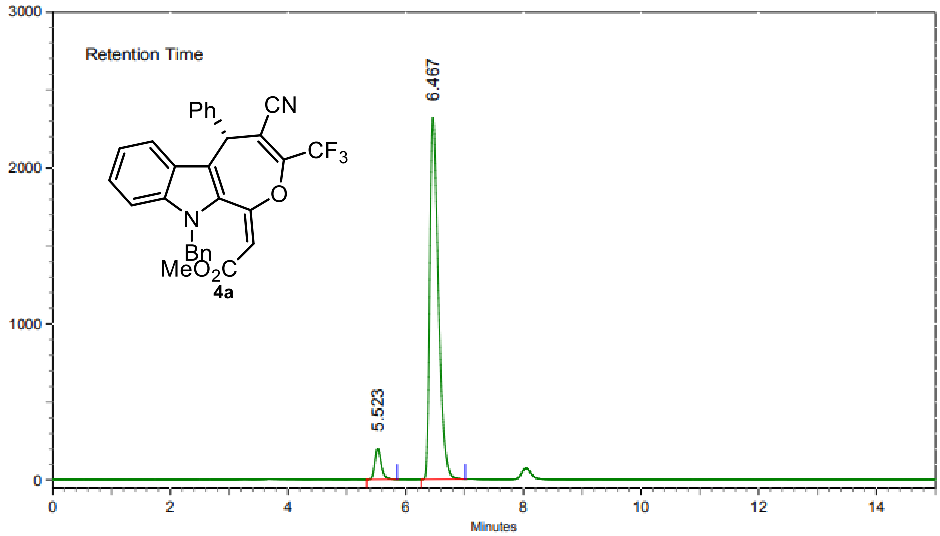

7.725
7.722
7.705
7.702
7.397
7.379
7.376
7.373
7.352
7.349
7.334
7.331
7.328
7.313
7.310
7.243
7.230
7.228
7.222
7.217
7.214
7.210
7.207
7.204
7.196
6.889
6.882
6.877
6.869
6.865
5.851
5.382
5.350
5.341
5.188
5.147
3.616
0.000
Ph
CN
CF3
O
N
Bn
MeO2C
4a
1H NMR (400 MHz, CDCl3)
1.09
1.09
1.21
9.32
2.01
1.00
2.08
1.09
3.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


164.181
154.560
149.894
149.538
149.183
148.828
137.974
137.516
136.680
128.804
128.695
127.761
127.680
126.820
126.297
125.221
124.970
124.384
122.405
121.293
120.455
119.648
118.942
116.890
115.618
114.132
111.402
109.222
103.004
77.318
77.000
76.682
51.822
48.026
41.512
Ph
CN
CF3
O
N
Bn
MeO2C
4a
13C NMR (100 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



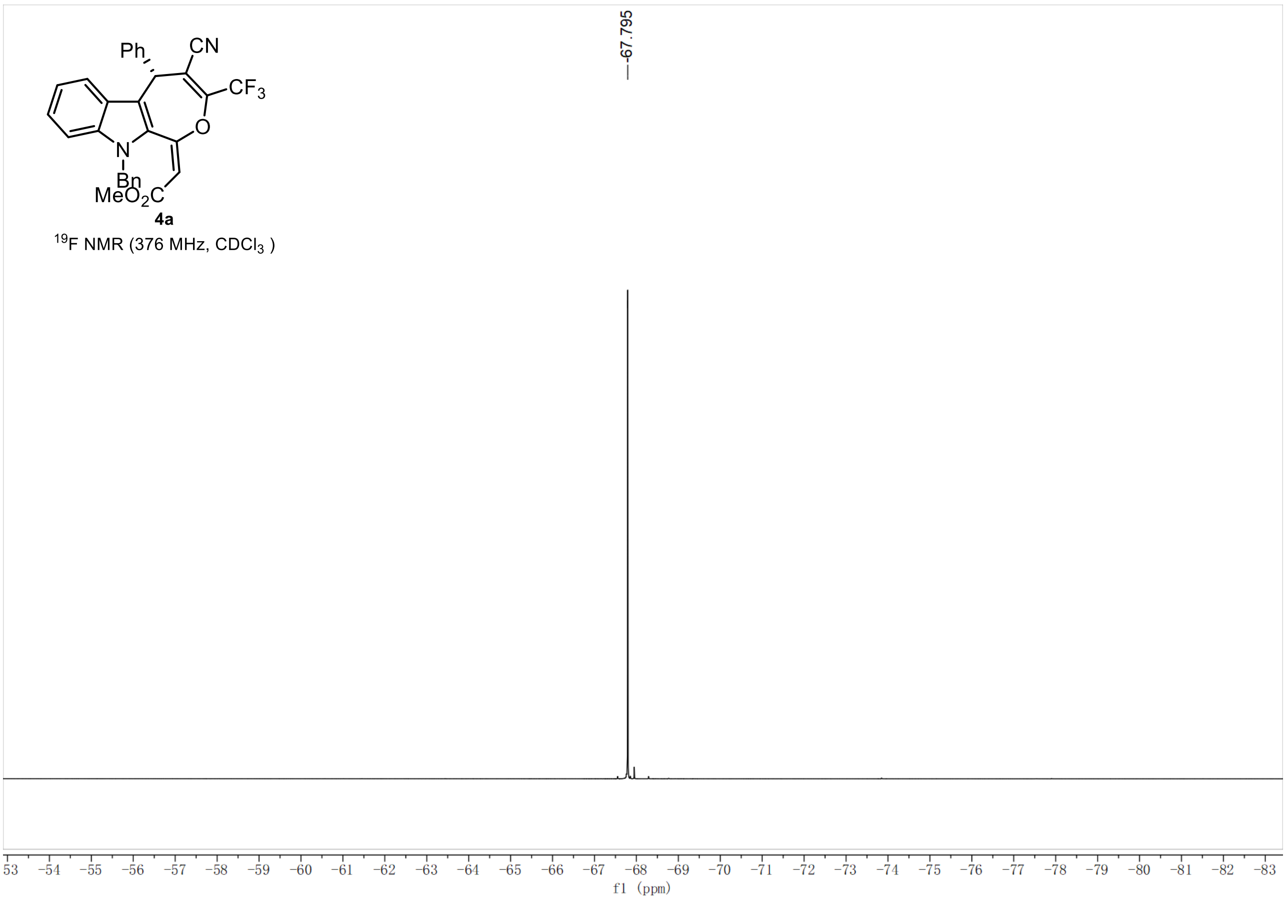
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.523	0.670	15600429	147327827	49.8698
2	6.490	0.713	13990158	148097265	50.1302

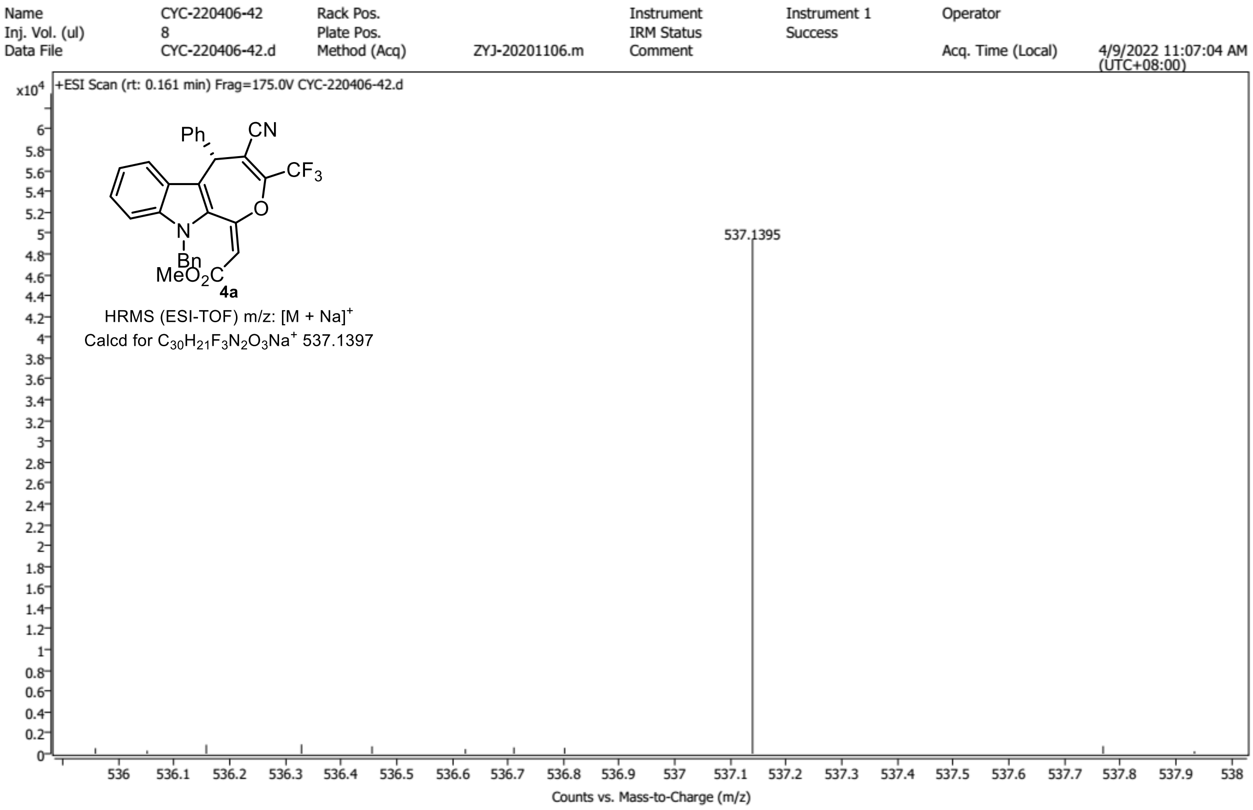


AREA PERCENT REPORT

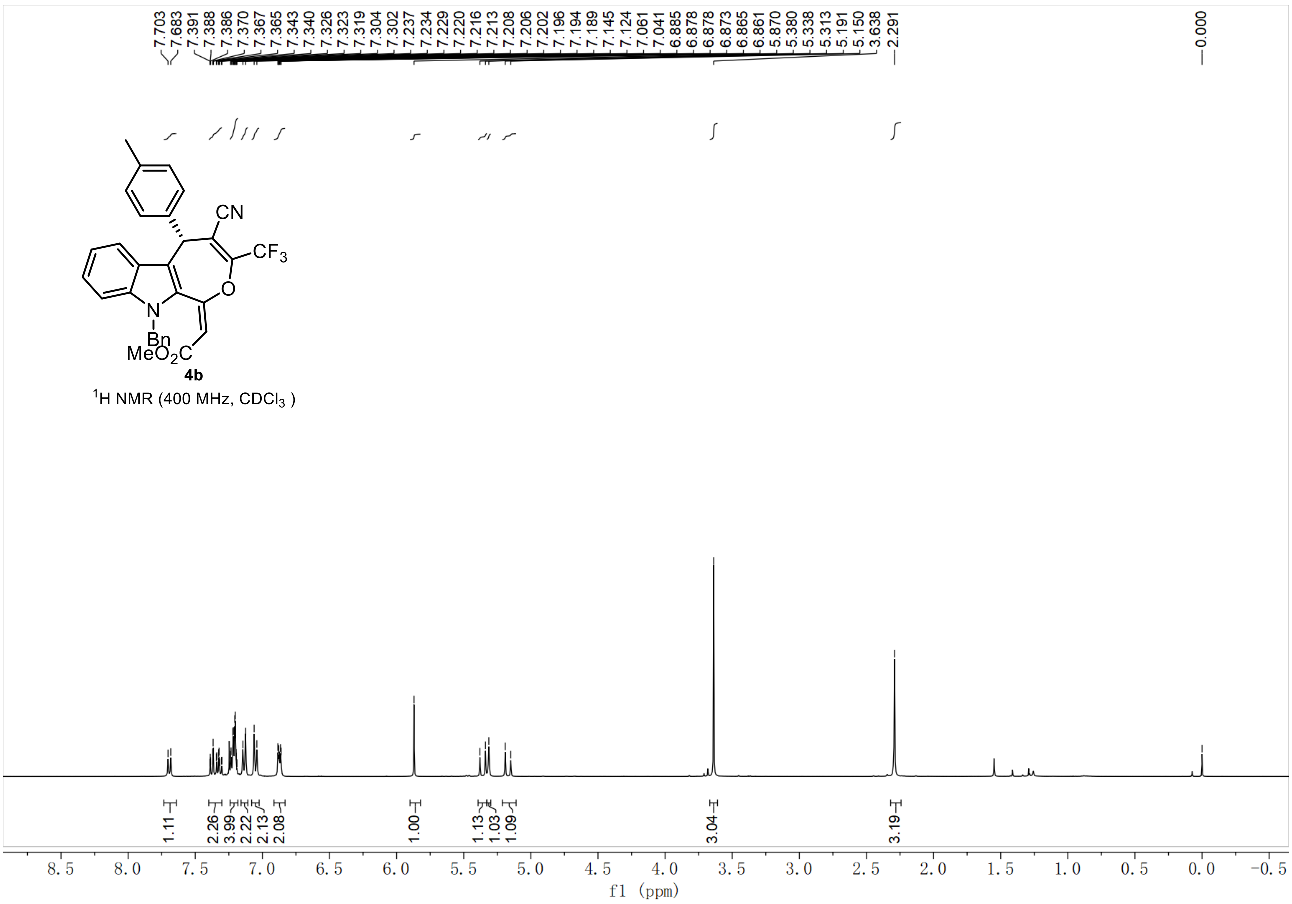
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.523	0.520	3349990	26433556	6.3092
2	6.467	0.747	38872533	392533493	93.6908

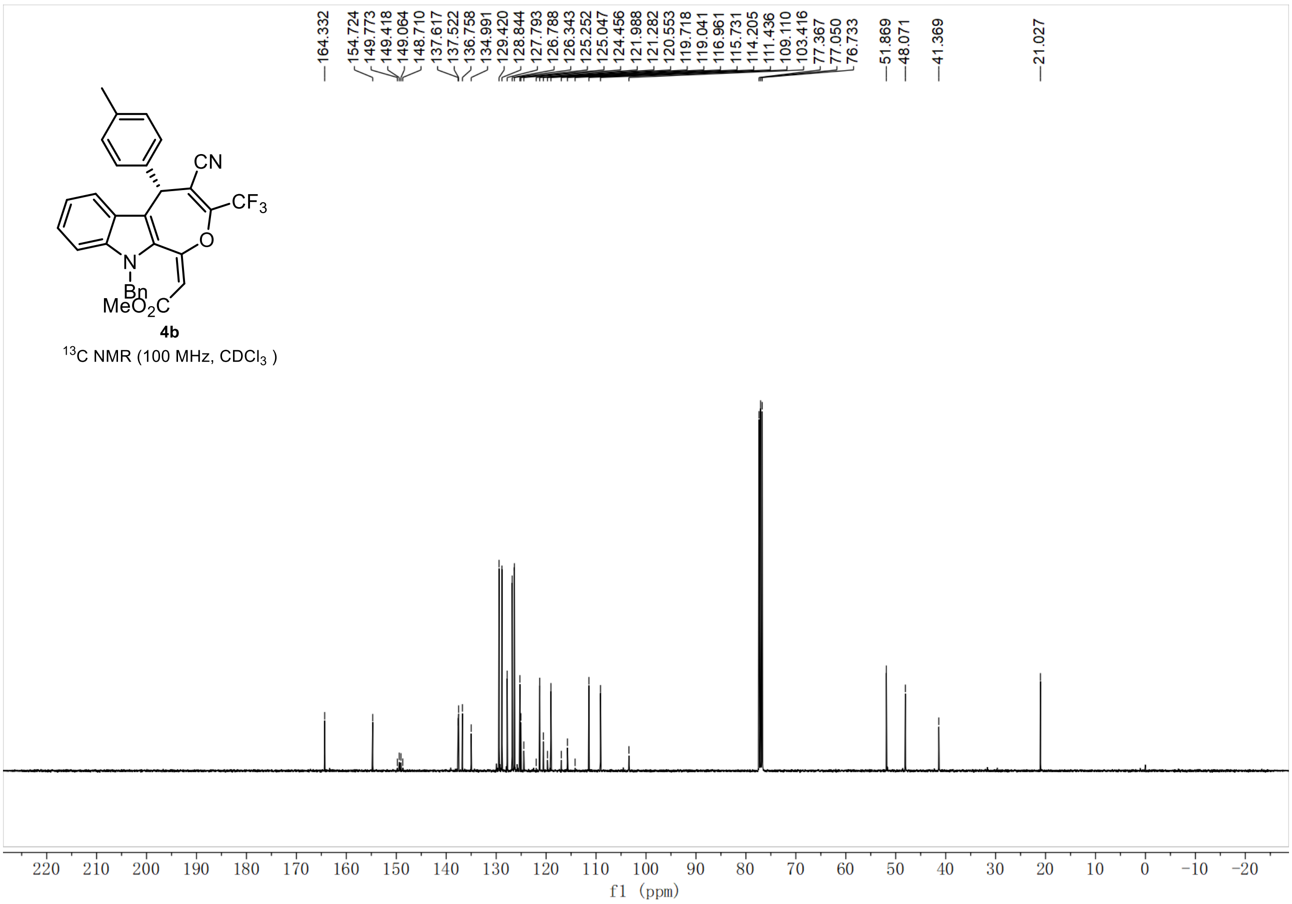


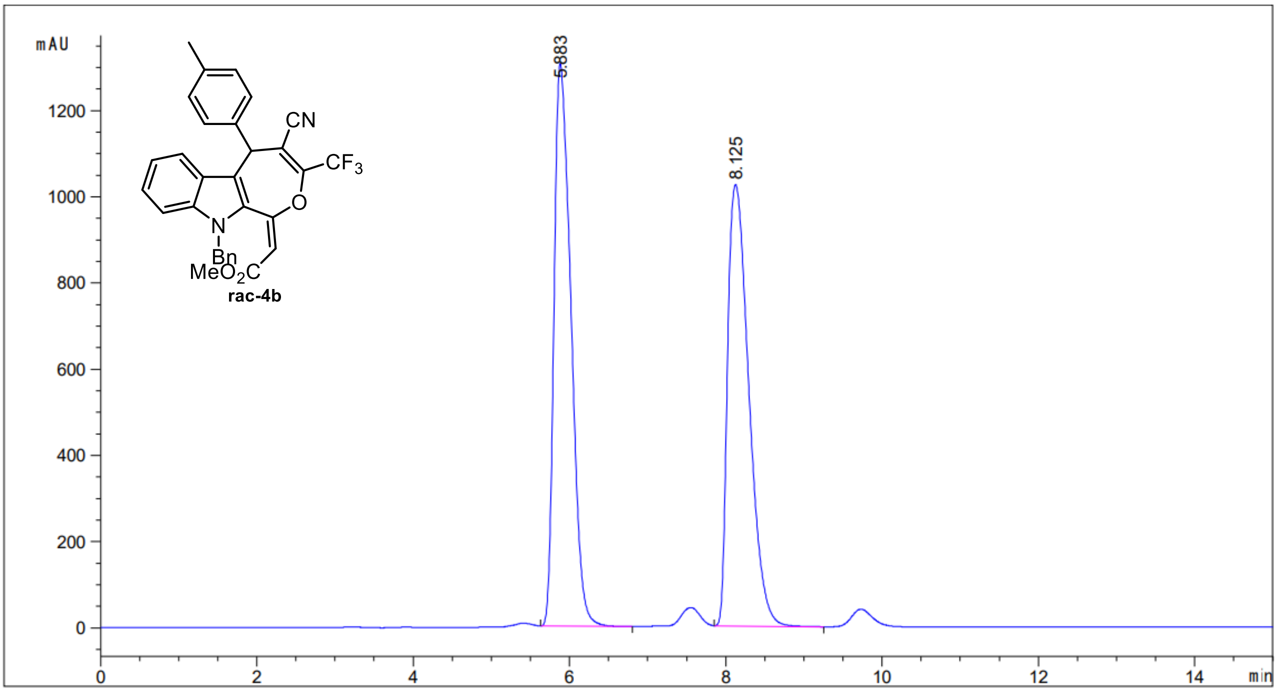
Ph
CN
CF_3
O
N
Bn
MeO_2C
4a
^{19}F NMR (376 MHz, $CDCl_3$)
-67.795
53 −54 −55 −56 −57 −58 −59 −60 −61 −62 −63 −64 −65 −66 −67 −68 −69 −70 −71 −72 −73 −74 −75 −76 −77 −78 −79 −80 −81 −82 −83
f1 (ppm)



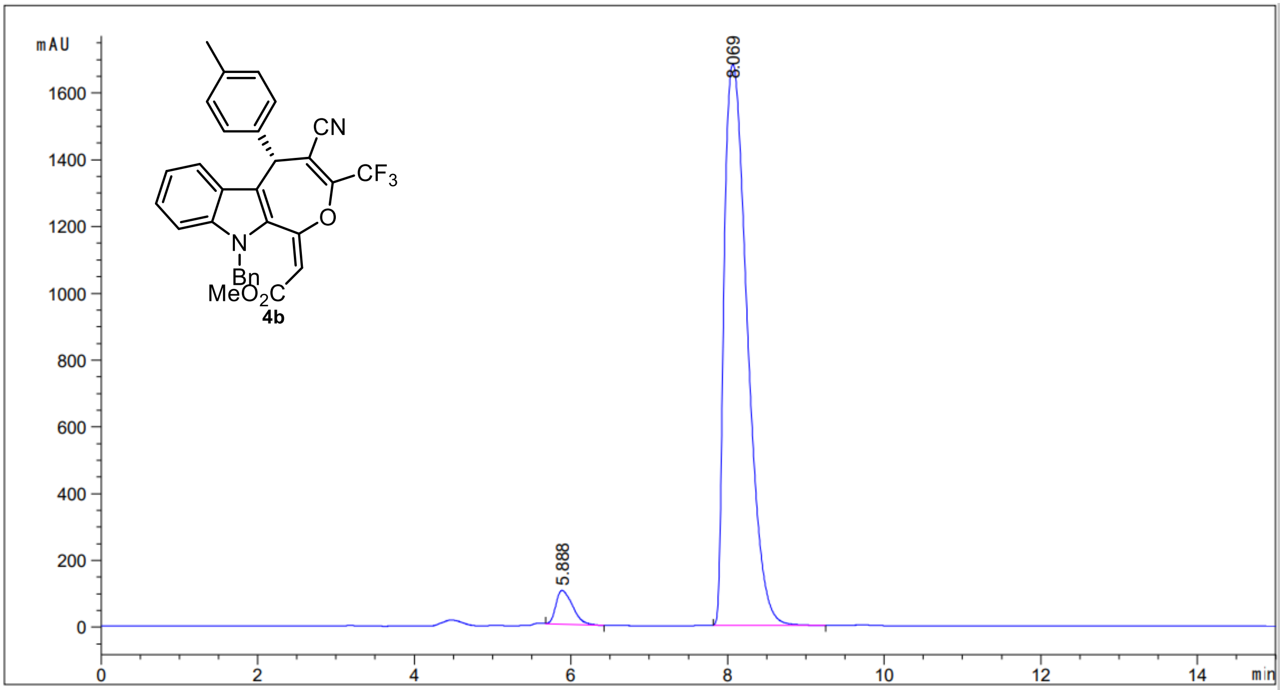
Name CYC-220406-42
Inj. Vol. (ul) 8
Data File CYC-220406-42.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument Instrument 1
IRM Status Success
Comment
Operator
Acq. Time (Local) 4/9/2022 11:07:04 AM (UTC+08:00)
+ESI Scan (rt: 0.161 min) Frag=175.0V CYC-220406-42.d
x10^4
Ph
CN
CF_3
O
N
Bn
MeO_2C
4a
HRMS (ESI-TOF) m/z: $[M + Na]^+$
Calcd for $C_{30}H_{21}F_3N_2O_3Na^+$ 537.1397
537.1395
Counts vs. Mass-to-Charge (m/z)


7.703
7.683
7.391
7.388
7.386
7.370
7.367
7.365
7.343
7.340
7.326
7.323
7.319
7.304
7.302
7.237
7.234
7.229
7.220
7.216
7.213
7.208
7.206
7.202
7.196
7.194
7.189
7.145
7.124
7.061
7.041
6.885
6.878
6.873
6.865
6.861
5.870
5.380
5.338
5.313
5.191
5.150
3.638
2.291
0.000
CN
CF_3
O
N
Bn
MeO_2C
4b
^1H NMR (400 MHz, $CDCl_3$)
1.11
2.26
3.99
2.22
2.13
2.08
1.00
1.13
1.03
1.09
3.04
3.19
f1 (ppm)

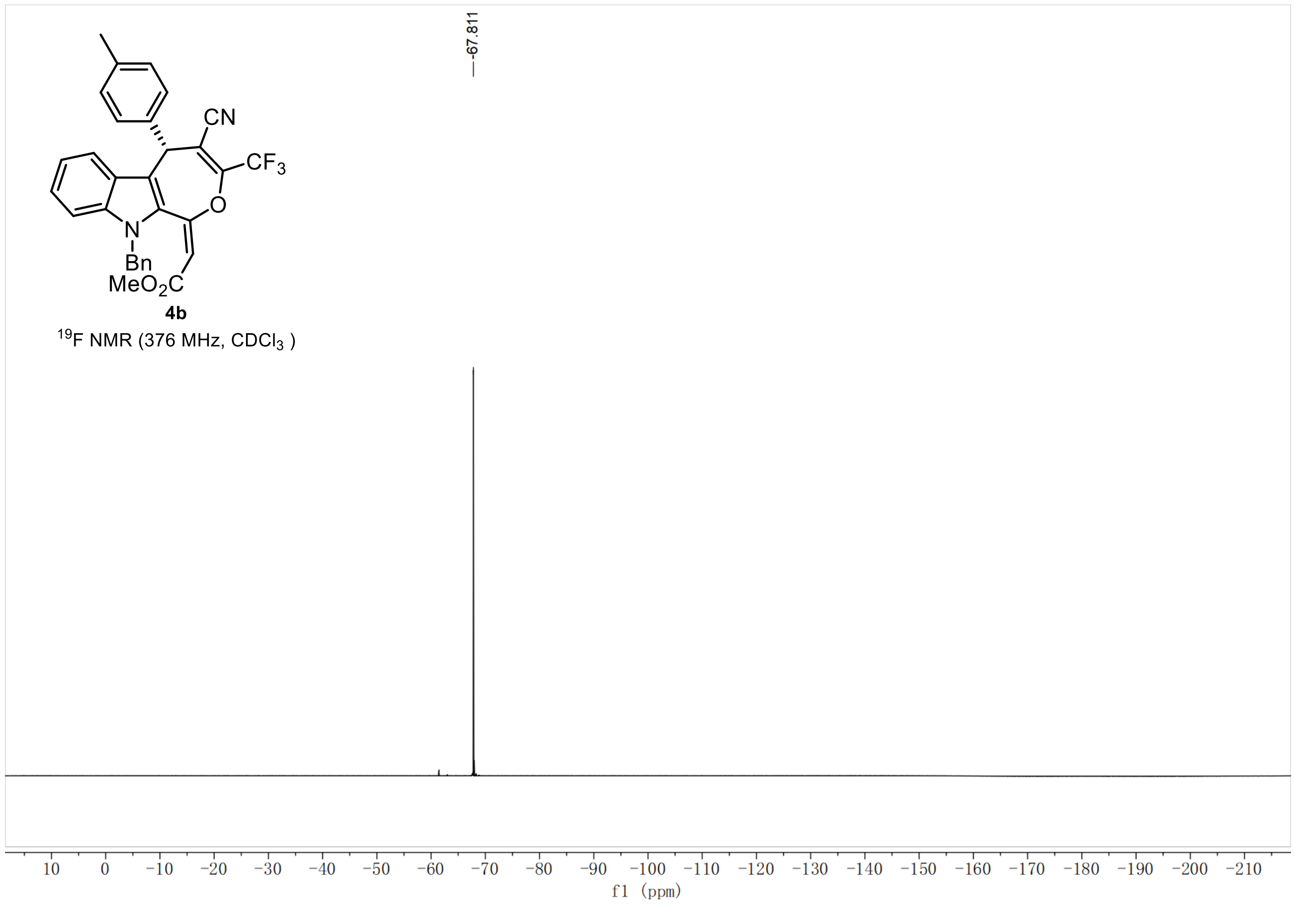

164.332
154.724
149.773
149.418
149.064
148.710
137.617
137.522
136.758
134.991
129.420
128.844
127.793
126.788
126.343
125.252
125.047
124.456
121.988
121.282
120.553
119.718
119.041
116.961
115.731
114.205
111.436
109.110
103.416
77.367
77.050
76.733
51.869
48.071
41.369
21.027
CN
CF_3
O
N
Bn
MeO_2C
4b
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



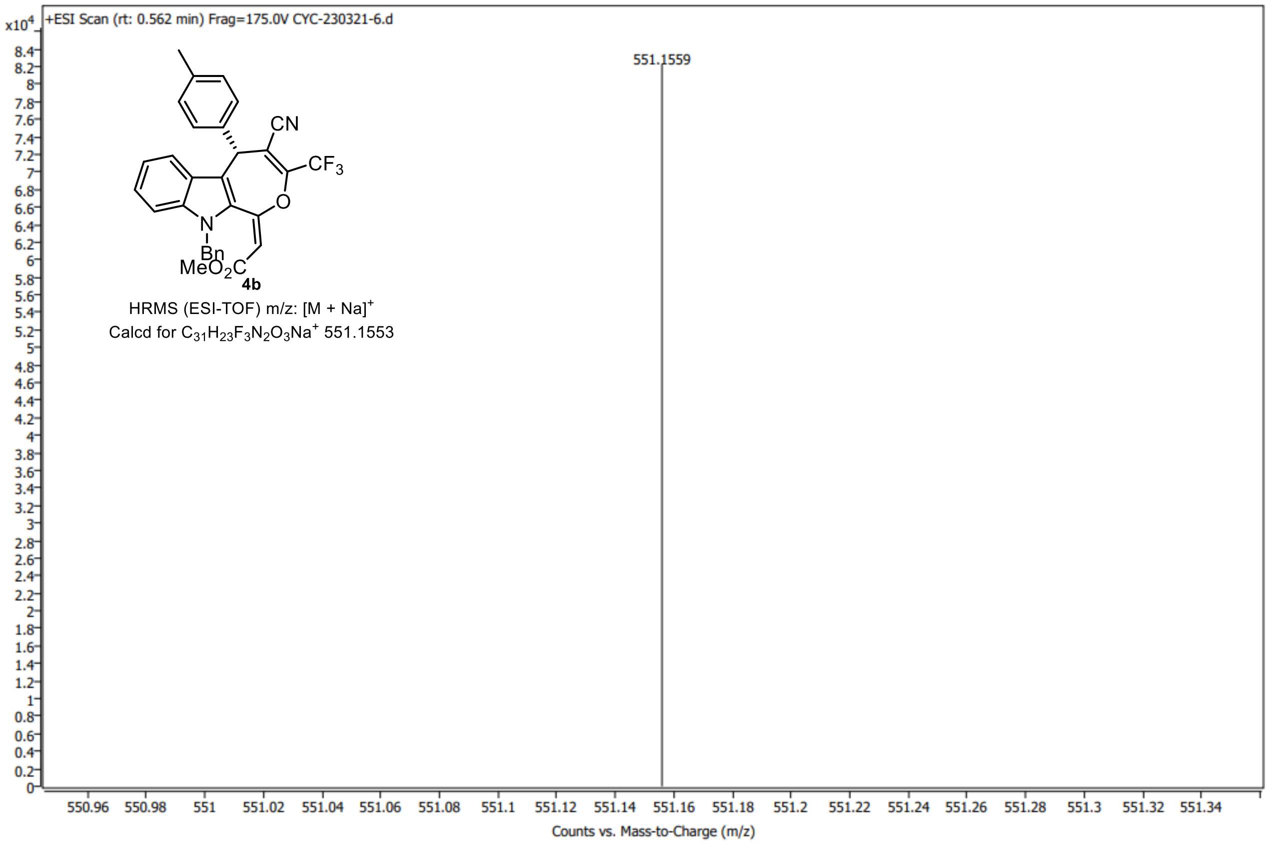
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.883	BB	0.2462	1.95629e4	1305.58386	50.4083
2	8.125	BBA	0.2965	1.92460e4	1023.95667	49.5917



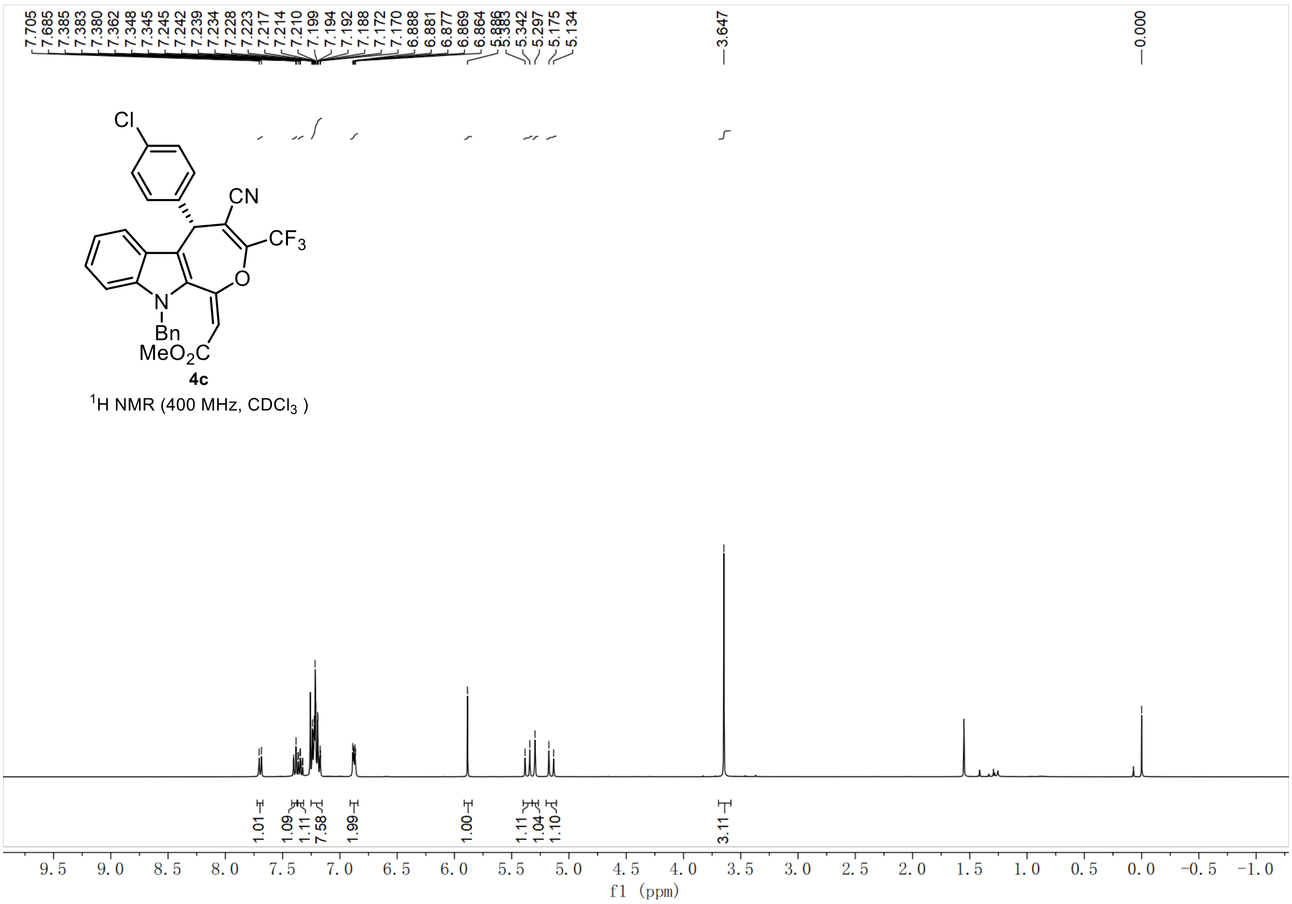
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.888	VB	0.2403	1493.01111	101.34855	4.1779
2	8.069	BBA	0.3234	3.42425e4	1682.23621	95.8221



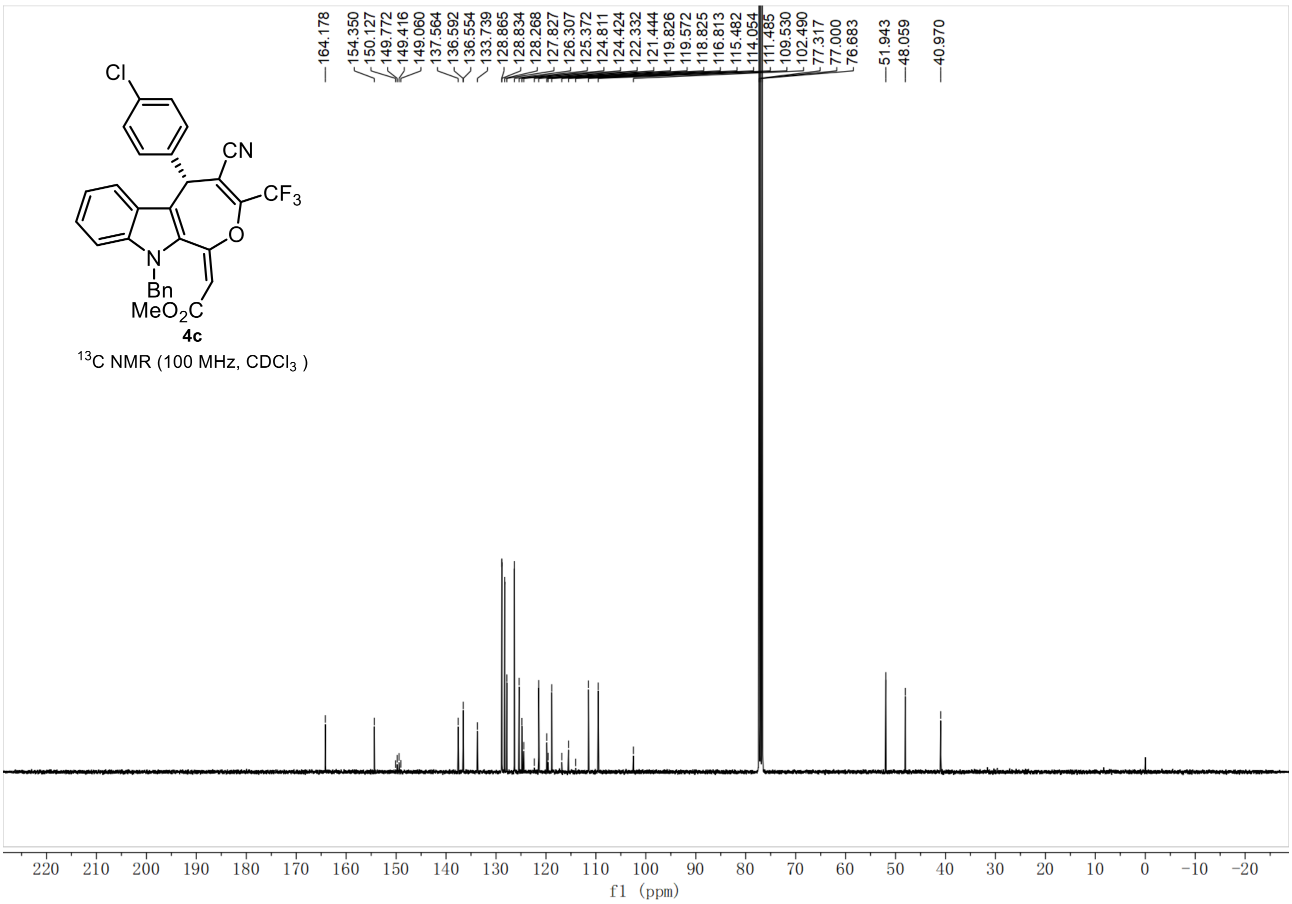
-67.811
CN
CF3
O
N
Bn
MeO2C
4b
19F NMR (376 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



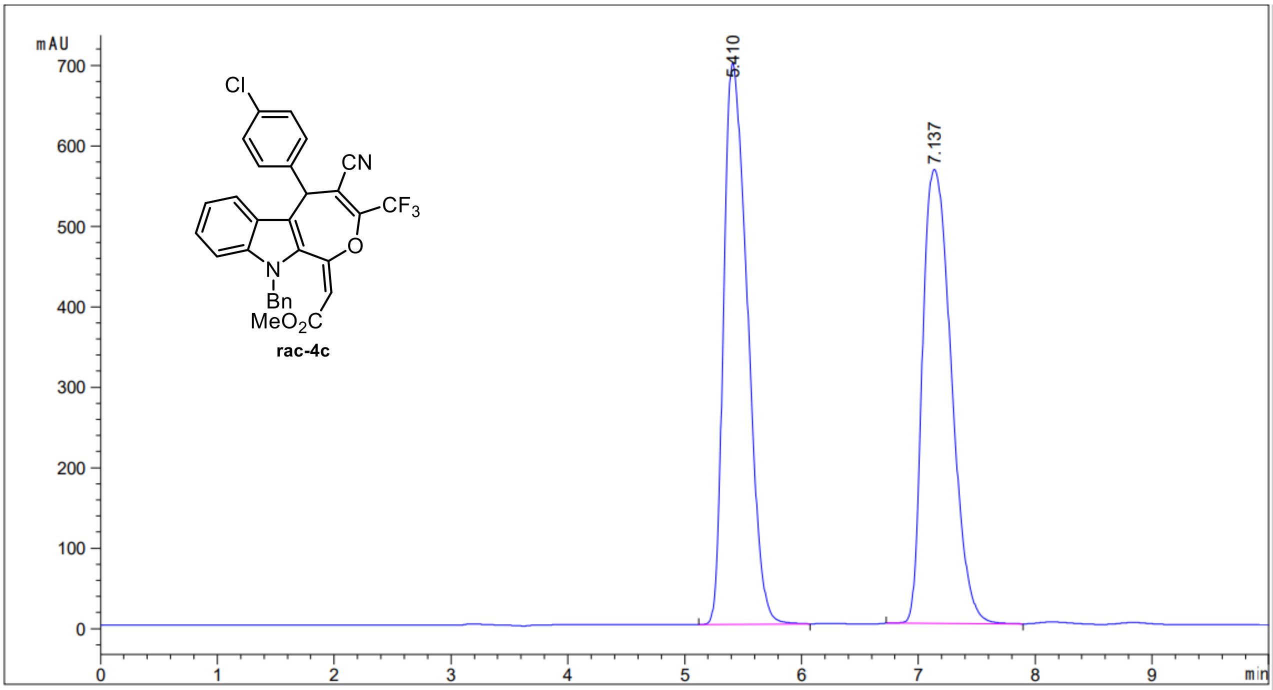
x10^4
+ESI Scan (rt: 0.562 min) Frag=175.0V CYC-230321-6.d
551.1559
CN
CF3
O
N
Bn
MeO2C
4b
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C31H23F3N2O3Na+ 551.1553
Counts vs. Mass-to-Charge (m/z)



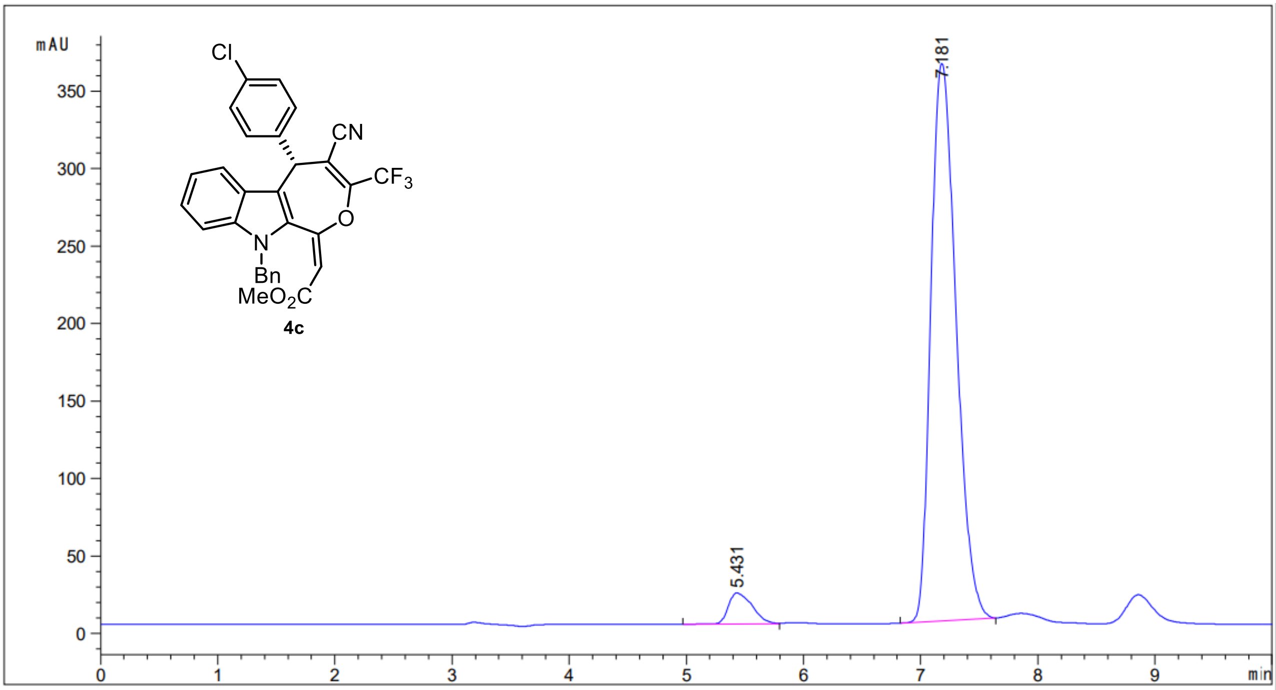
^{1}H NMR (400 MHz, $CDCl_3$)



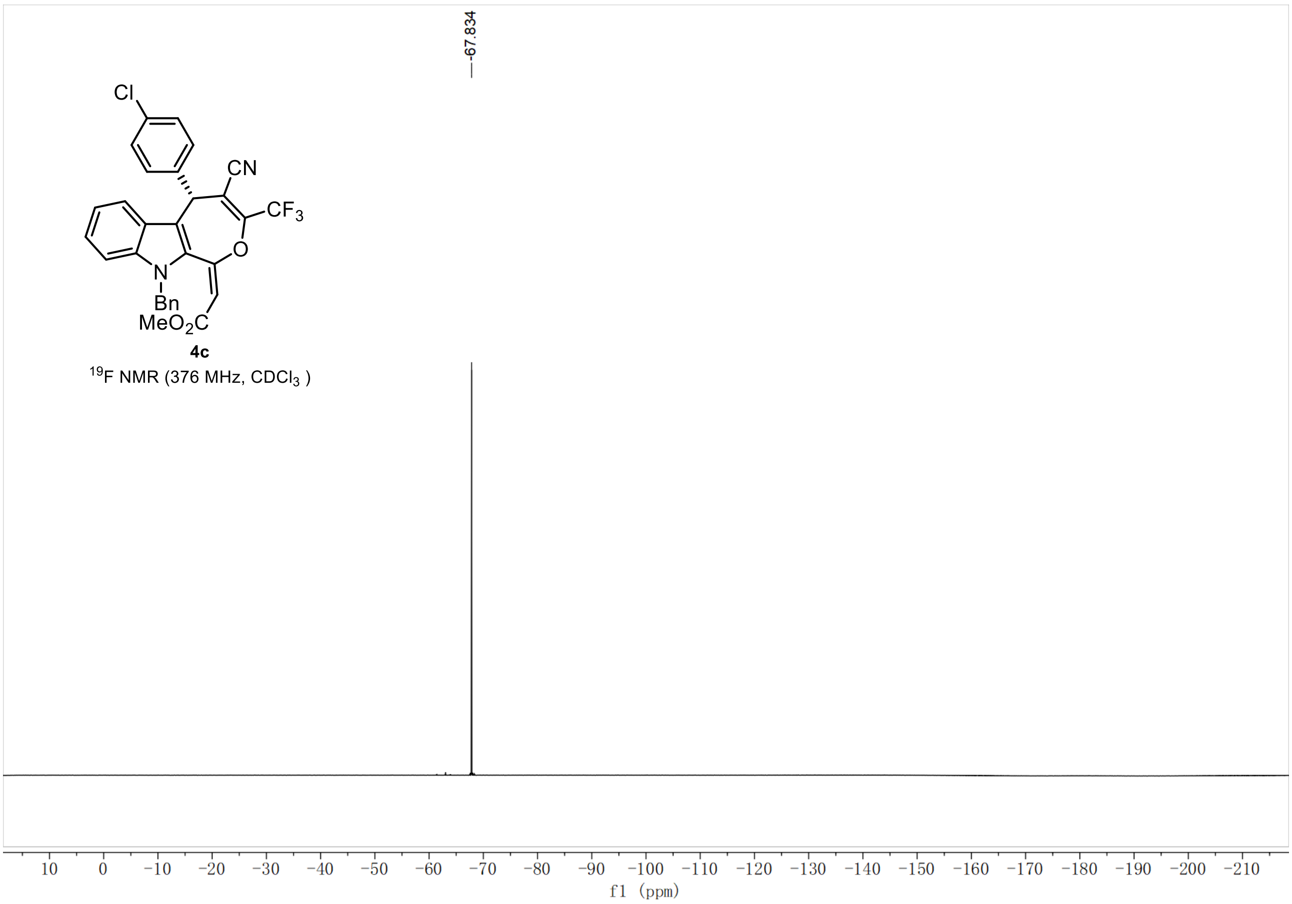
^{13}C NMR (100 MHz, $CDCl_3$)

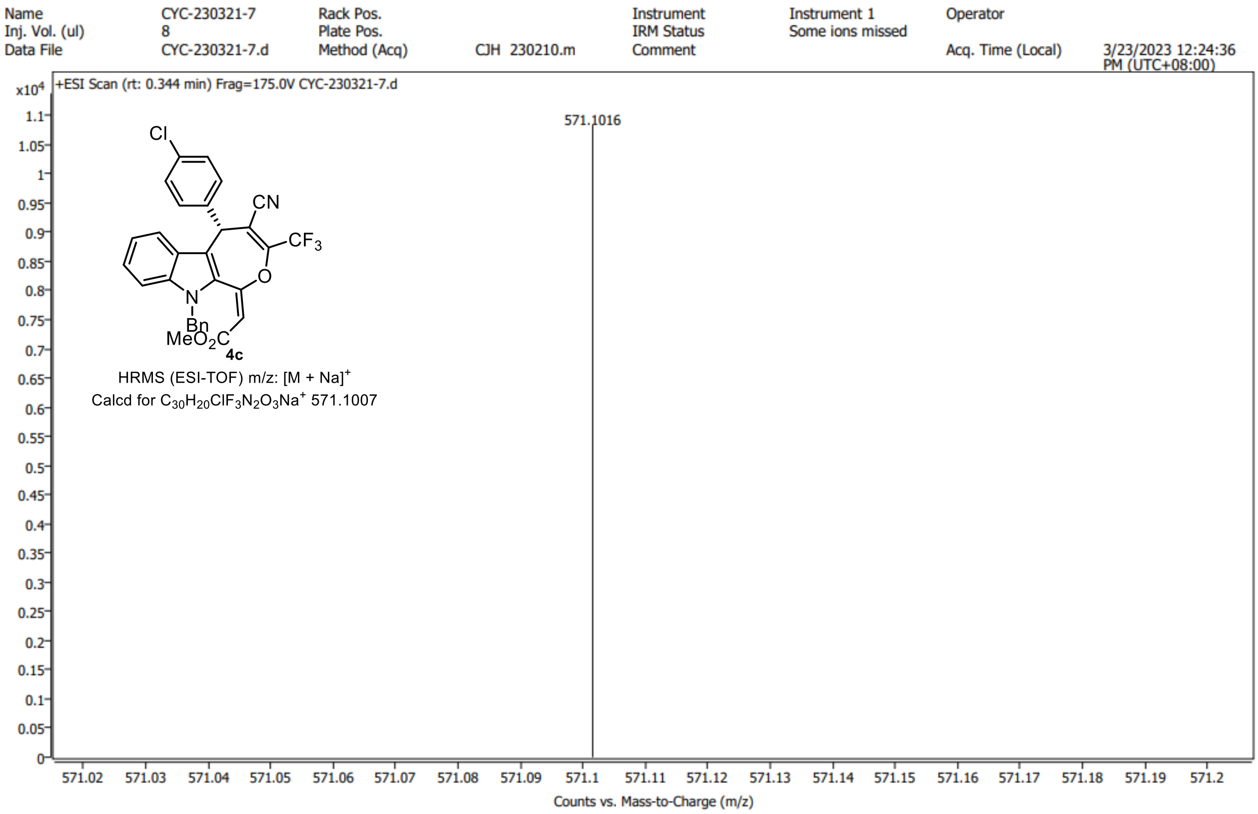


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.410	BBA	0.2324	9803.88086	697.57941	50.4515
2	7.137	BBA	0.2734	9628.40820	564.00427	49.5485

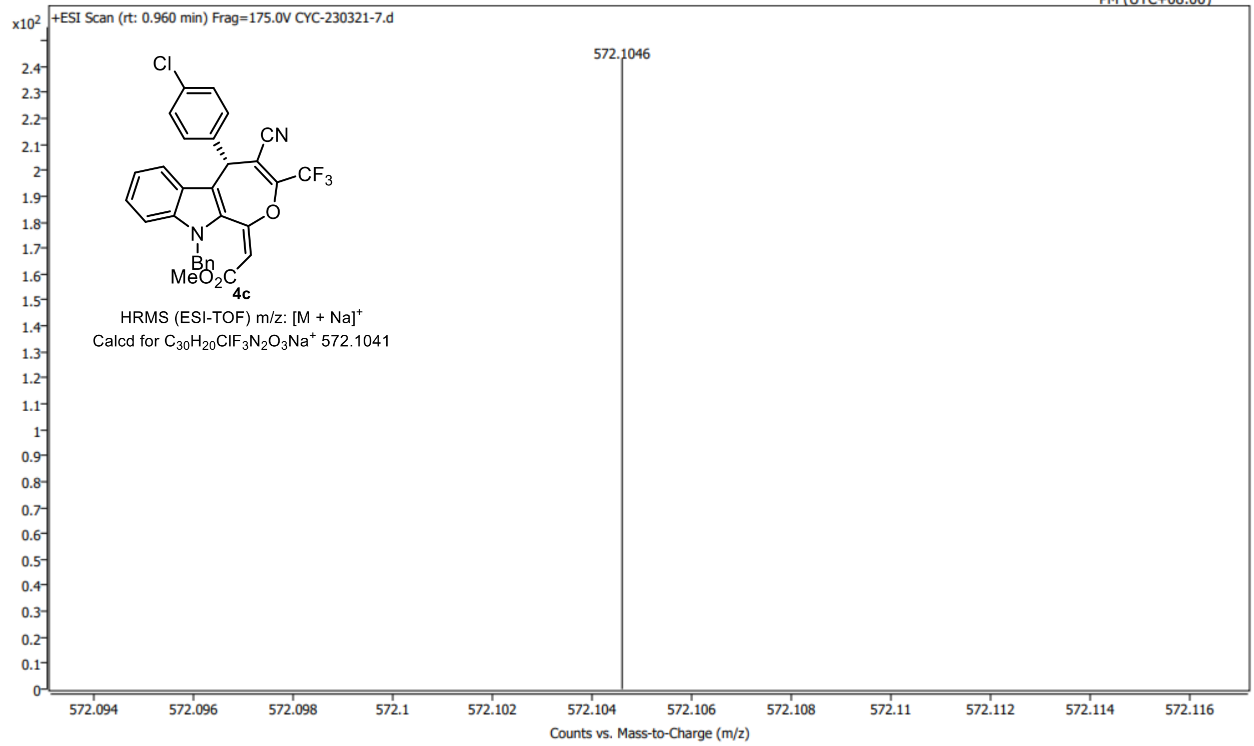


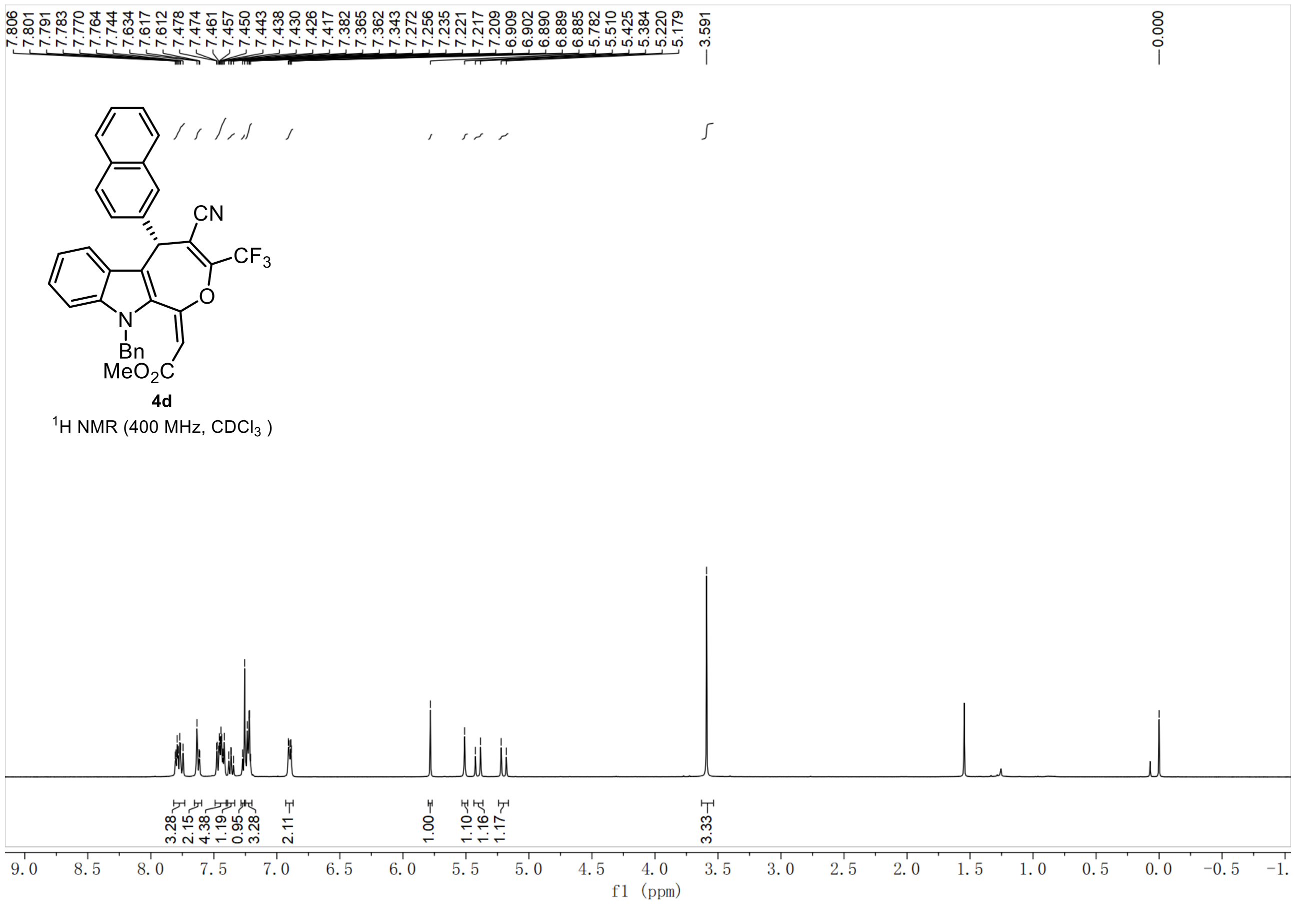
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.431	BV	0.2311	281.01428	19.98114	4.9671
2	7.181	BB	0.2356	5376.52393	359.63049	95.0329

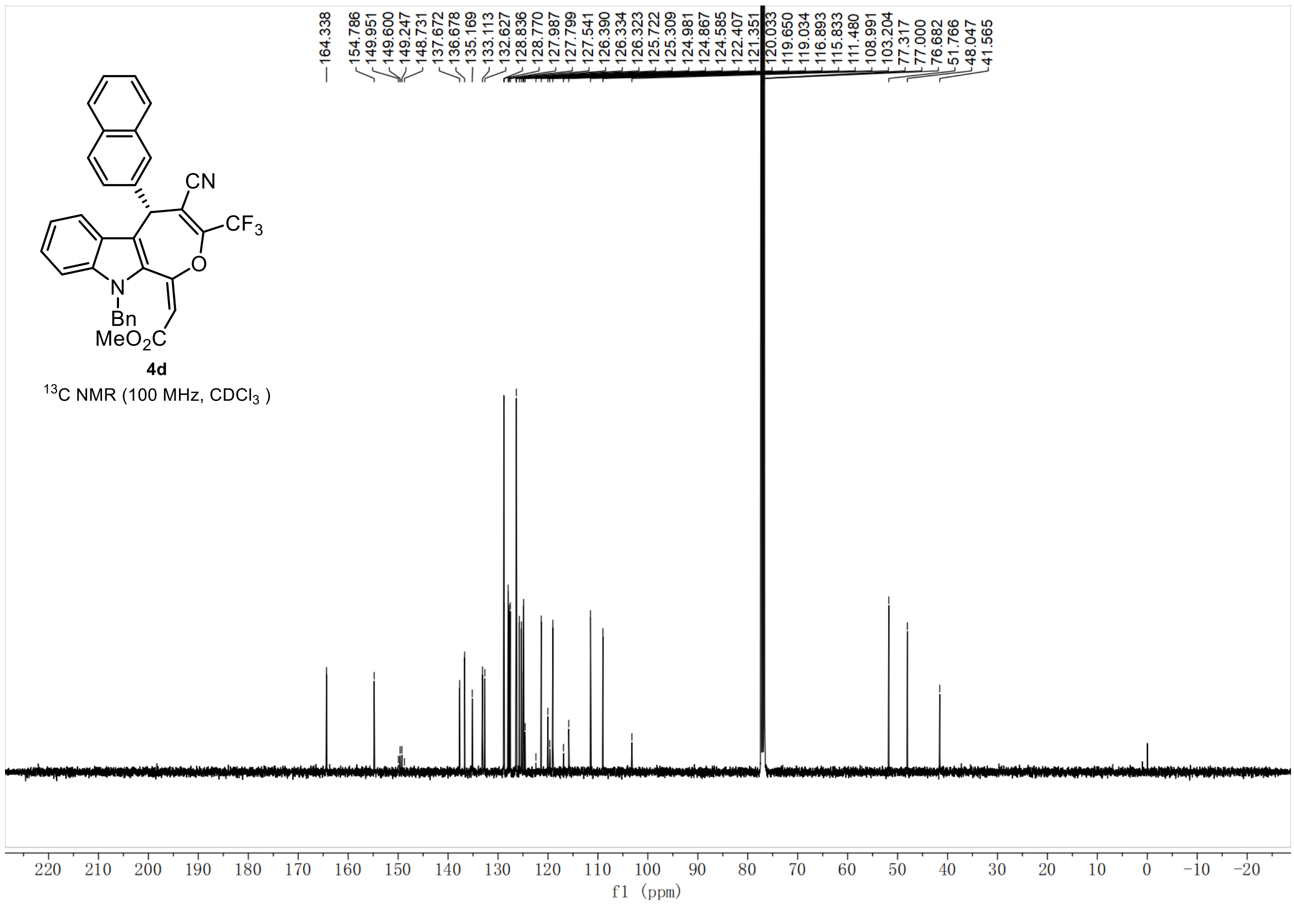

-67.834
Cl
CN
CF3
O
N
Bn
MeO2C
4c
19F NMR (376 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

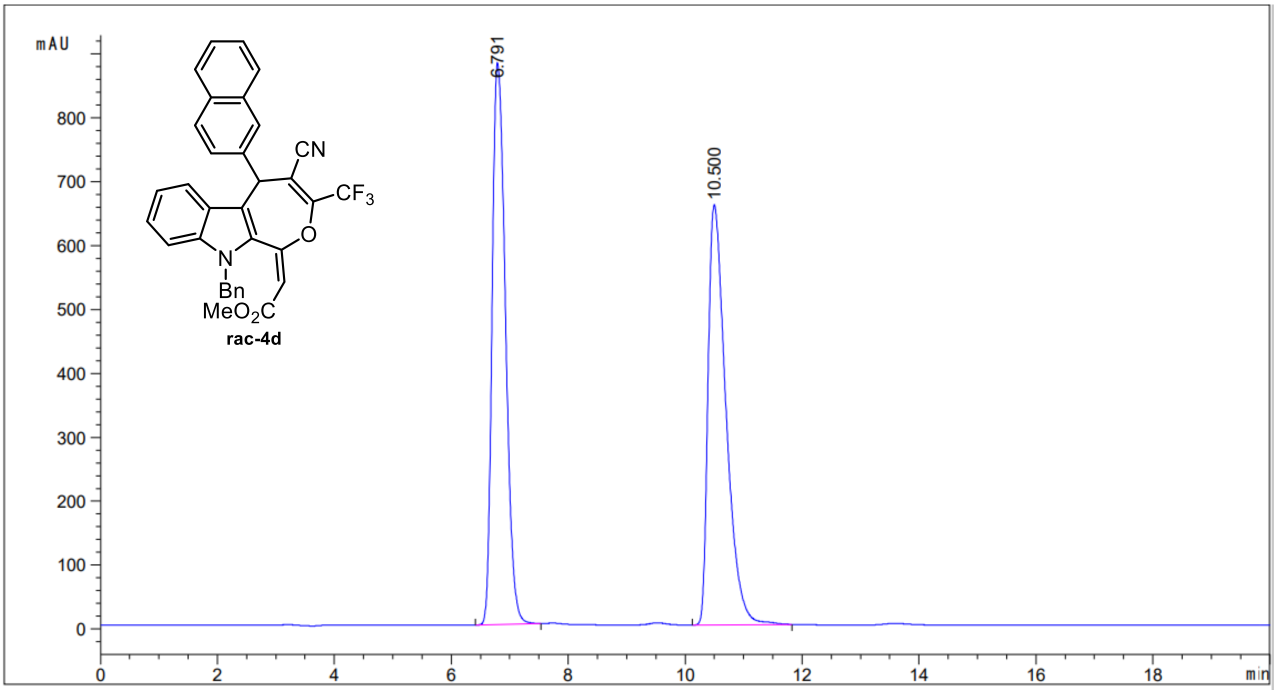

Name CYC-230321-7
Rack Pos.
Instrument Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status Some ions missed
Data File CYC-230321-7.d
Method (Acq) CJH 230210.m
Comment
Acq. Time (Local) 3/23/2023 12:24:36 PM (UTC+08:00)
x10^4 +ESI Scan (rt: 0.344 min) Frag=175.0V CYC-230321-7.d
571.1016
Cl
CN
CF3
O
N
Bn
MeO2C
4c
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C30H20ClF3N2O3Na+ 571.1007
Counts vs. Mass-to-Charge (m/z)

Name	CYC-230321-7	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-230321-7.d	Method (Acq)	CJH 230210.m	Comment		Acq. Time (Local)	3/23/2023 12:24:36 PM (UTC+08:00)

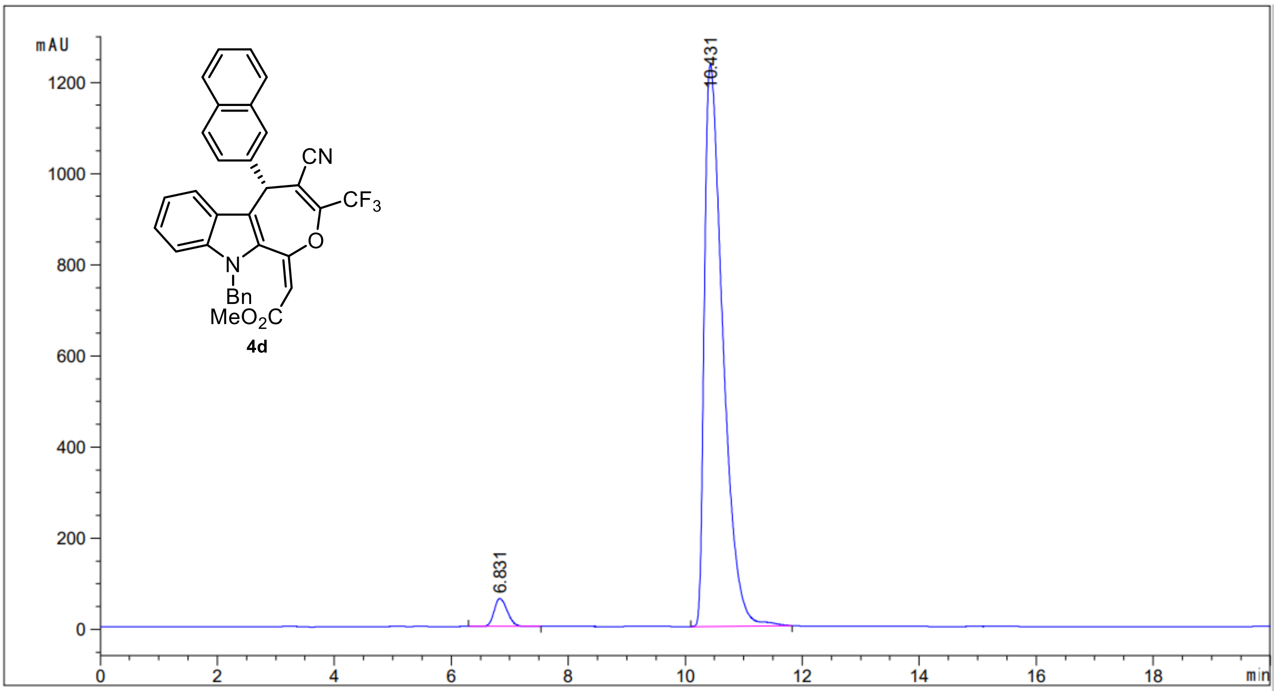




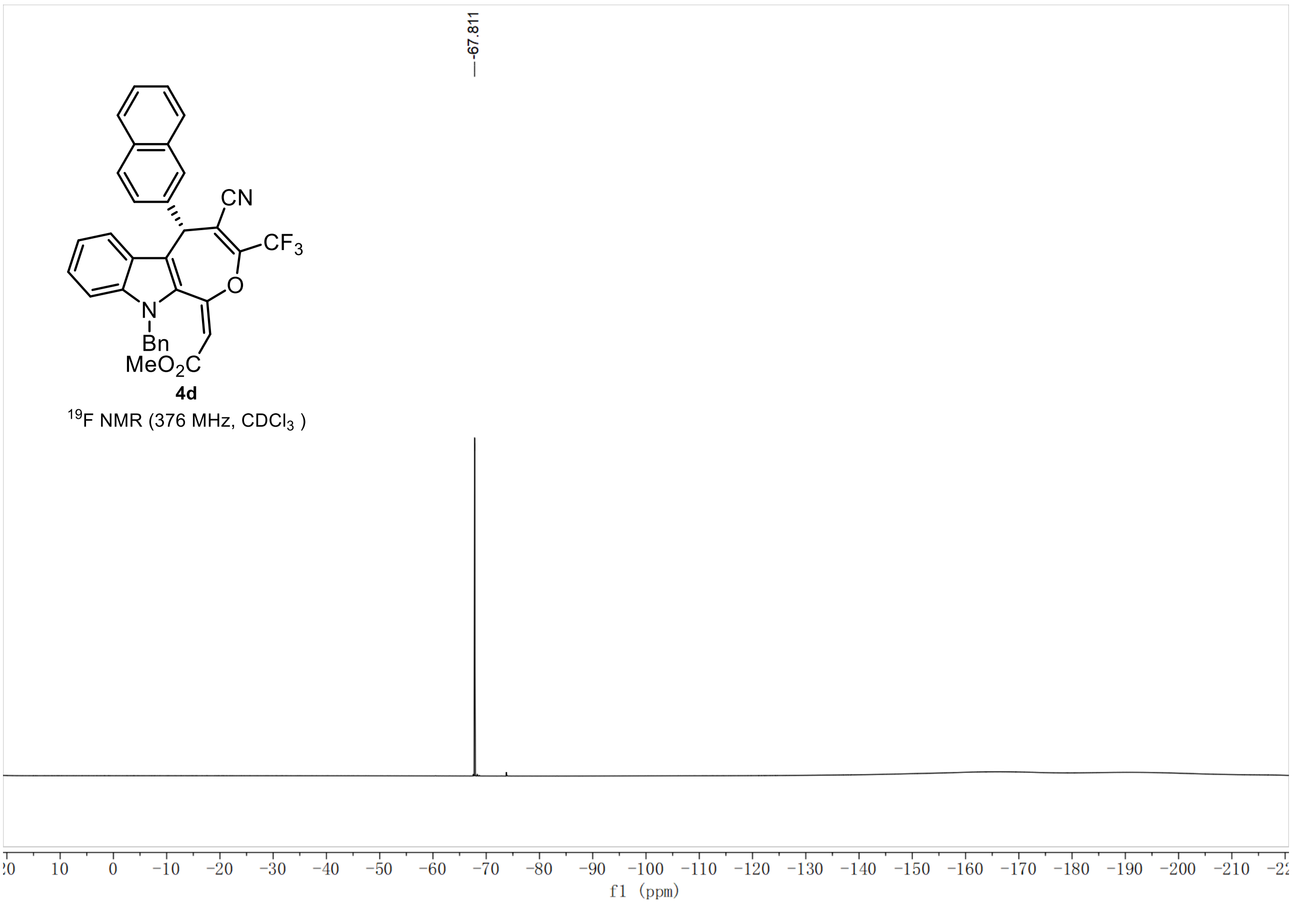




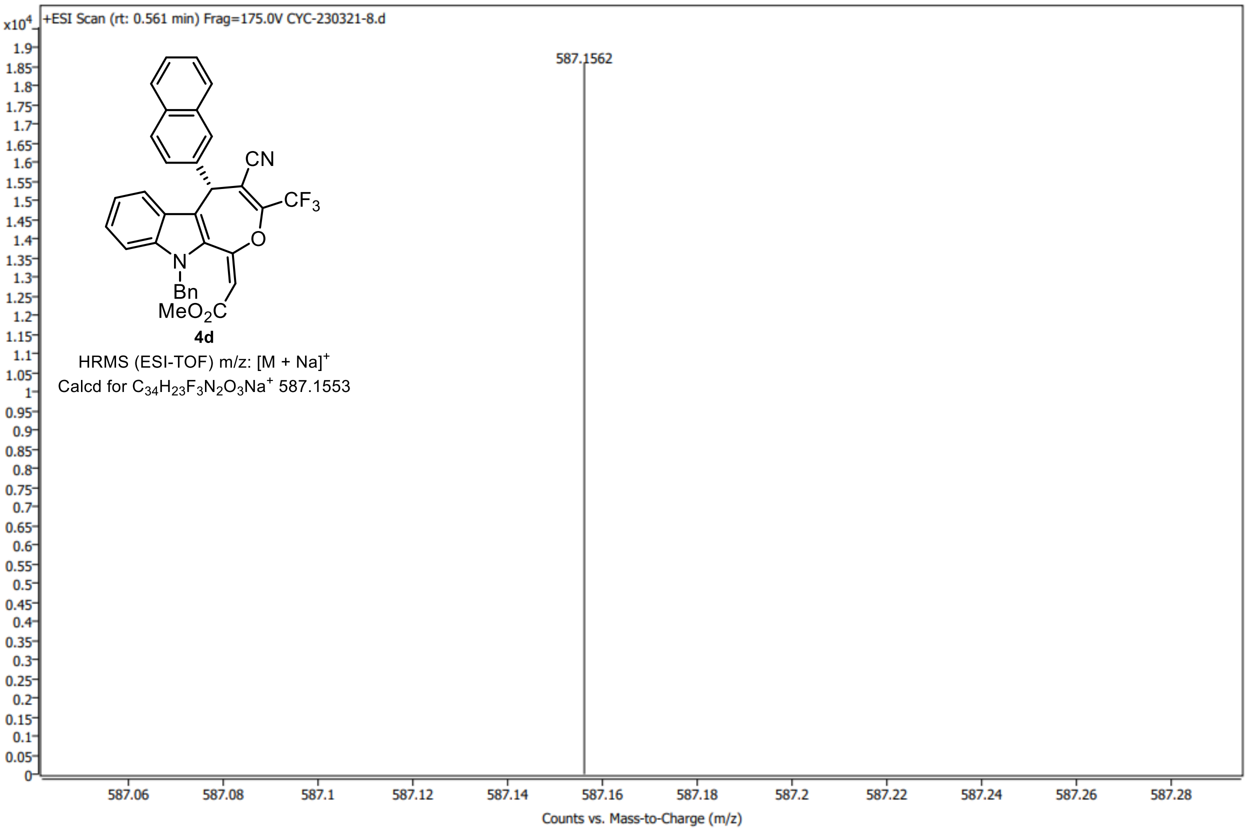
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.791	BBA	0.2537	1.39510e4	878.44855	49.9763
2	10.500	BBA	0.3250	1.39642e4	657.25604	50.0237



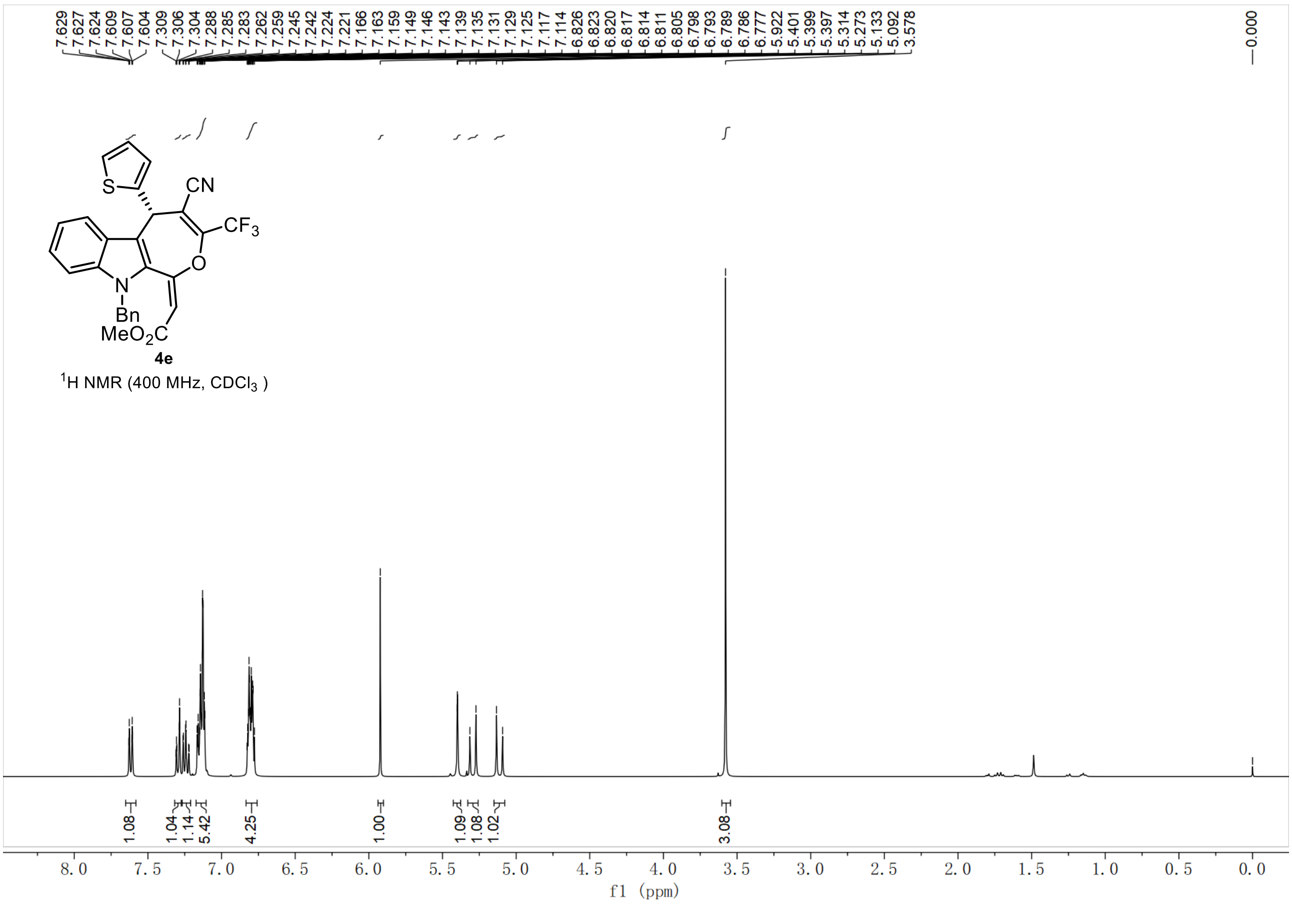
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.831	BBA	0.2460	952.53131	61.07289	3.3980
2	10.431	BBA	0.3348	2.70797e4	1233.45691	96.6020

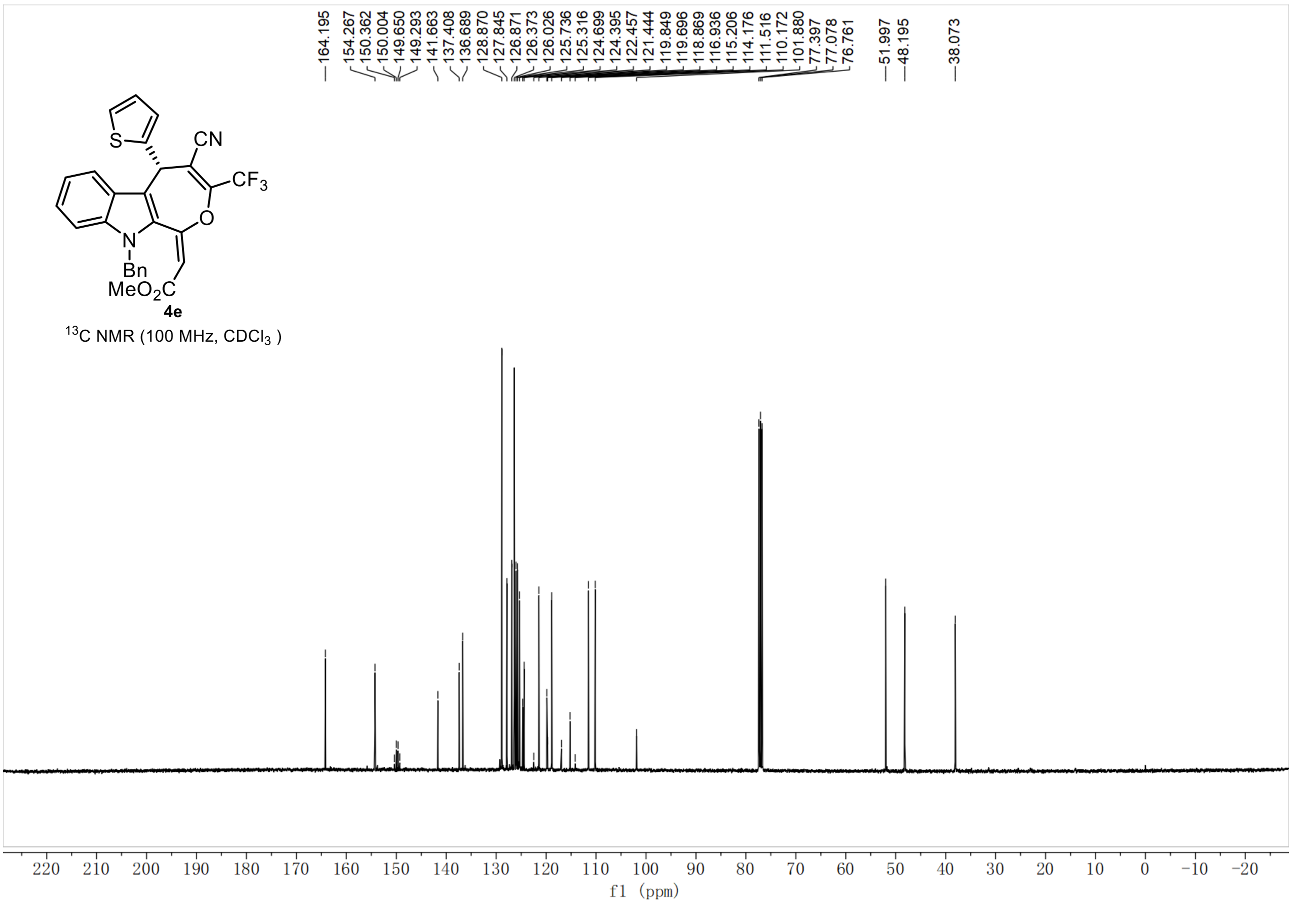


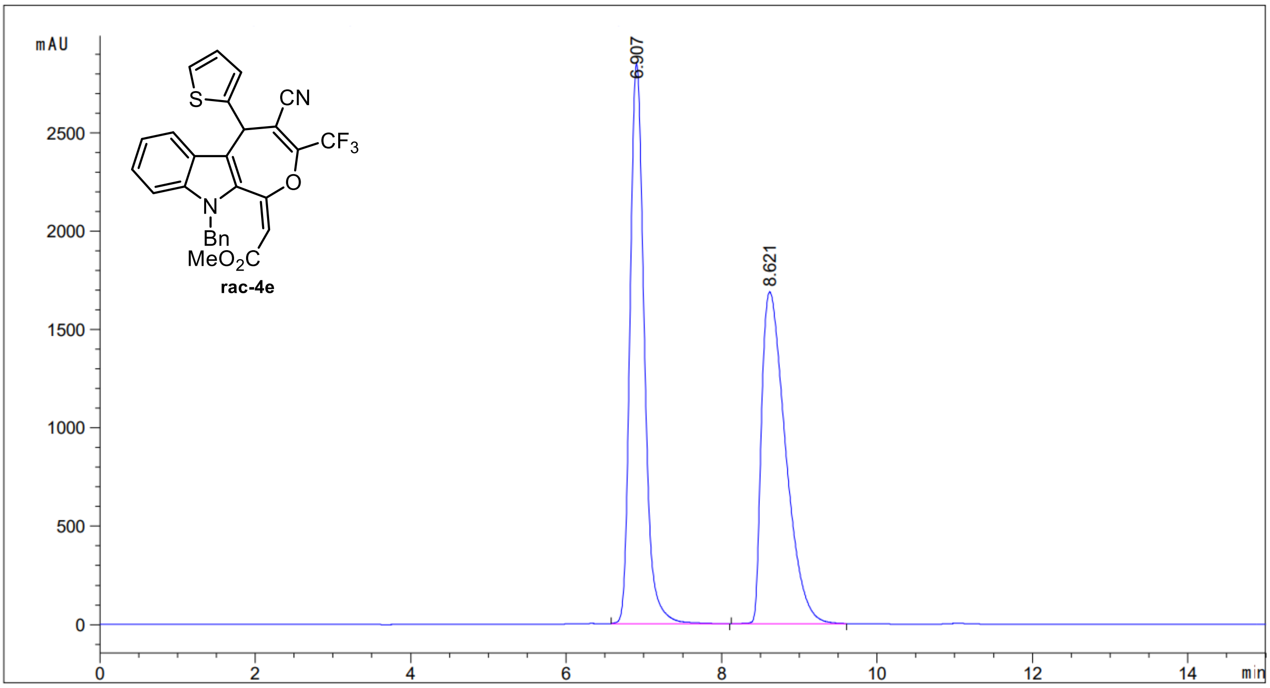
-67.811
CN
CF3
O
N
Bn
MeO2C
4d
19F NMR (376 MHz, CDCl3)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)



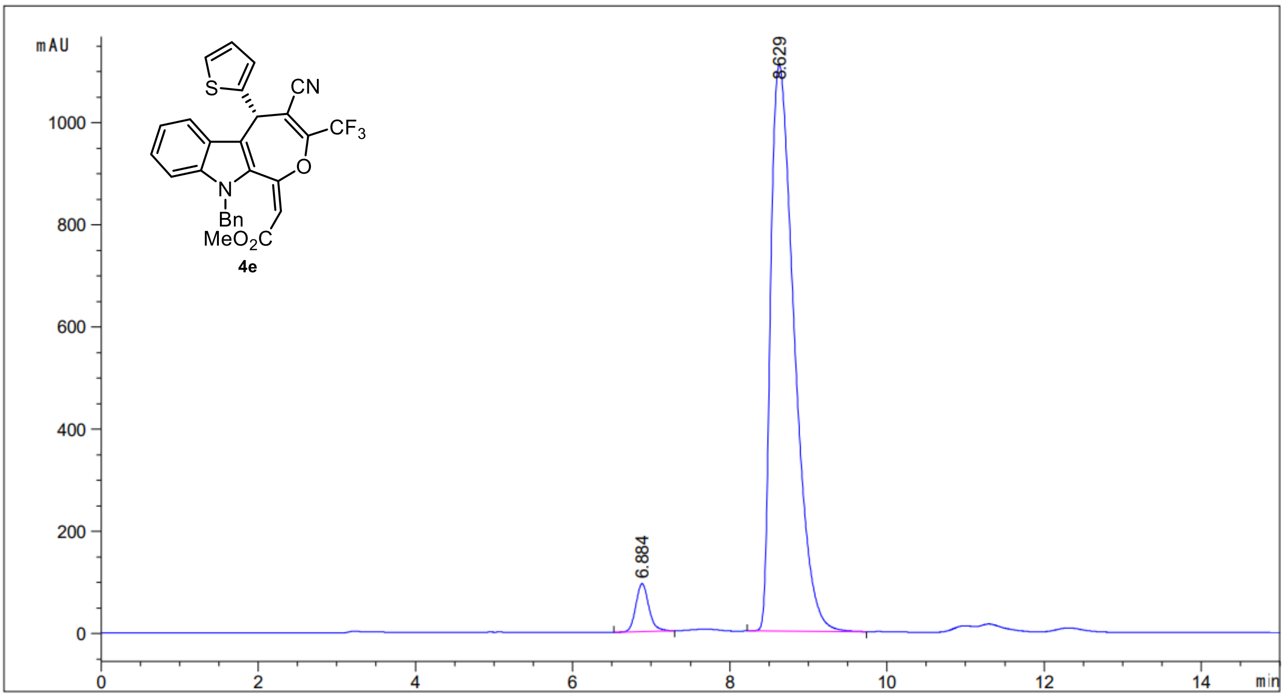
+ESI Scan (rt: 0.561 min) Frag=175.0V CYC-230321-8.d
x10^4
587.1562
CN
CF3
O
N
Bn
MeO2C
4d
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C34H23F3N2O3Na+ 587.1553
587.06
587.08
587.1
587.12
587.14
587.16
587.18
587.2
587.22
587.24
587.26
587.28
Counts vs. Mass-to-Charge (m/z)


7.629
7.627
7.624
7.609
7.607
7.604
7.309
7.306
7.304
7.288
7.285
7.283
7.262
7.259
7.245
7.242
7.224
7.221
7.166
7.163
7.159
7.149
7.146
7.143
7.139
7.135
7.131
7.129
7.125
7.117
7.114
6.826
6.823
6.820
6.817
6.814
6.811
6.805
6.798
6.793
6.789
6.786
6.777
5.922
5.401
5.399
5.397
5.314
5.273
5.133
5.092
3.578
0.000
CN
CF_3
S
O
N
Bn
MeO_2C
4e
^1H NMR (400 MHz, $CDCl_3$)
1.08
1.04
1.14
5.42
4.25
1.00
1.09
1.08
1.02
3.08
f1 (ppm)

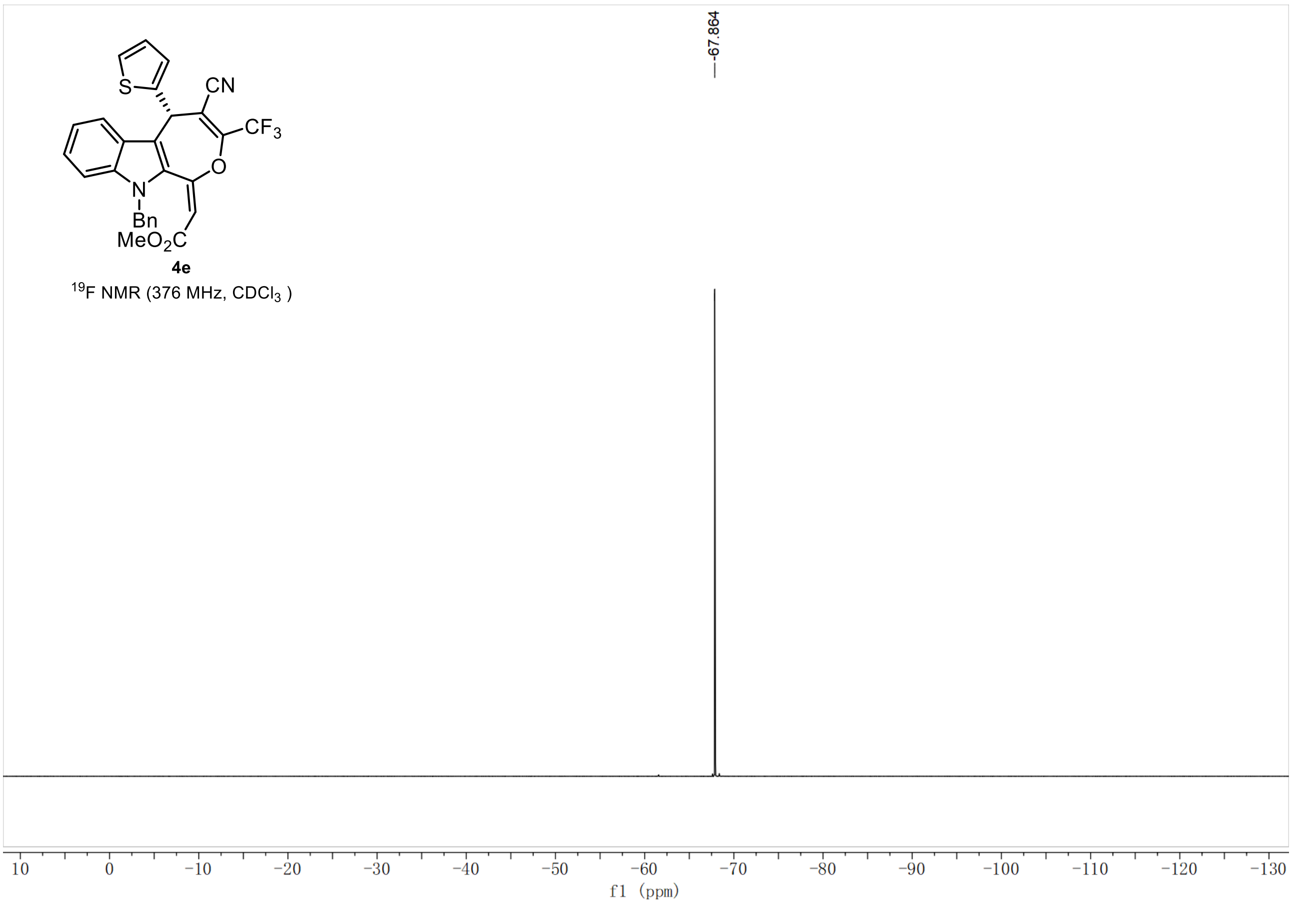

164.195
154.267
150.362
150.004
149.650
149.293
141.663
137.408
136.689
128.870
127.845
126.871
126.373
126.026
125.736
125.316
124.699
124.395
122.457
121.444
119.849
119.696
118.869
116.936
115.206
114.176
111.516
110.172
101.880
77.397
77.078
76.761
51.997
48.195
38.073
CN
CF_3
S
O
N
Bn
MeO_2C
4e
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



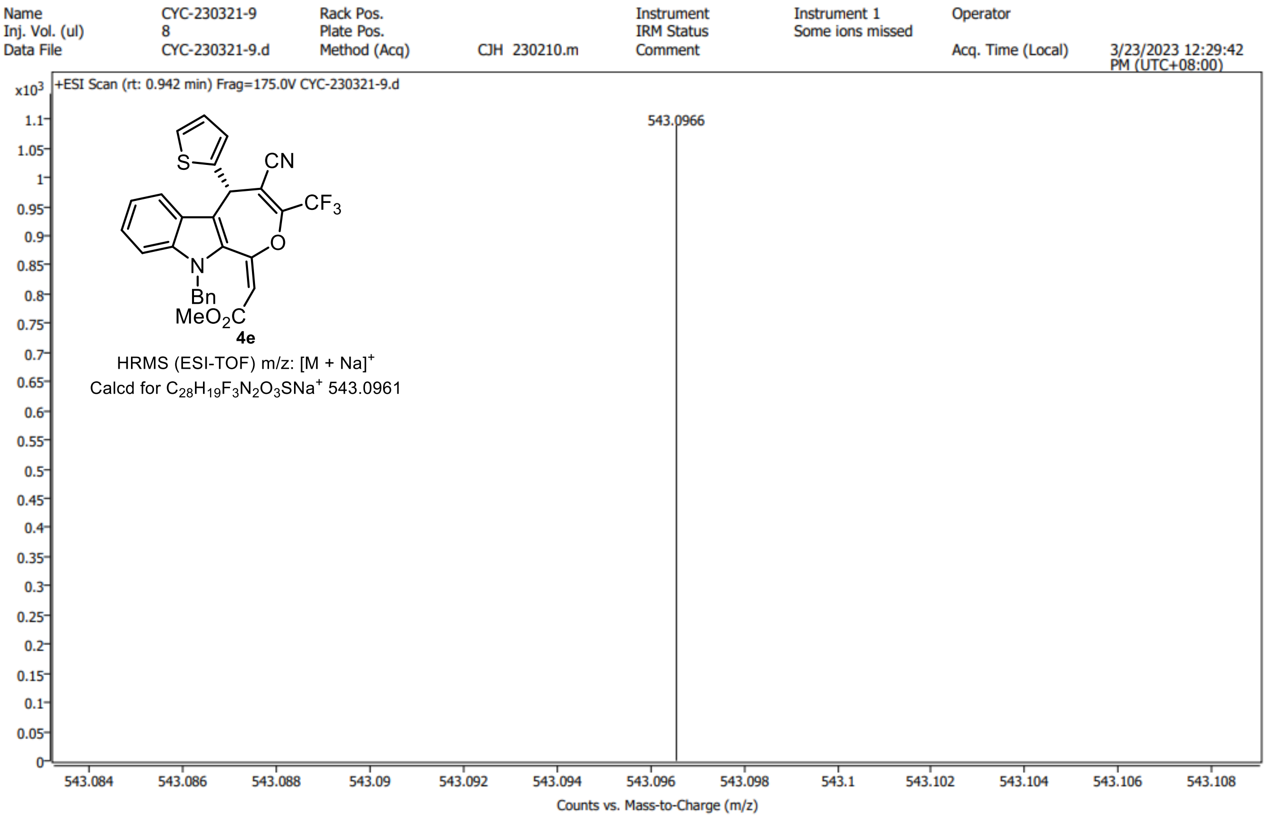
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.907	BB	0.1982	3.62914e4	2846.80493	50.0474
2	8.621	BBA	0.3351	3.62226e4	1686.12524	49.9526



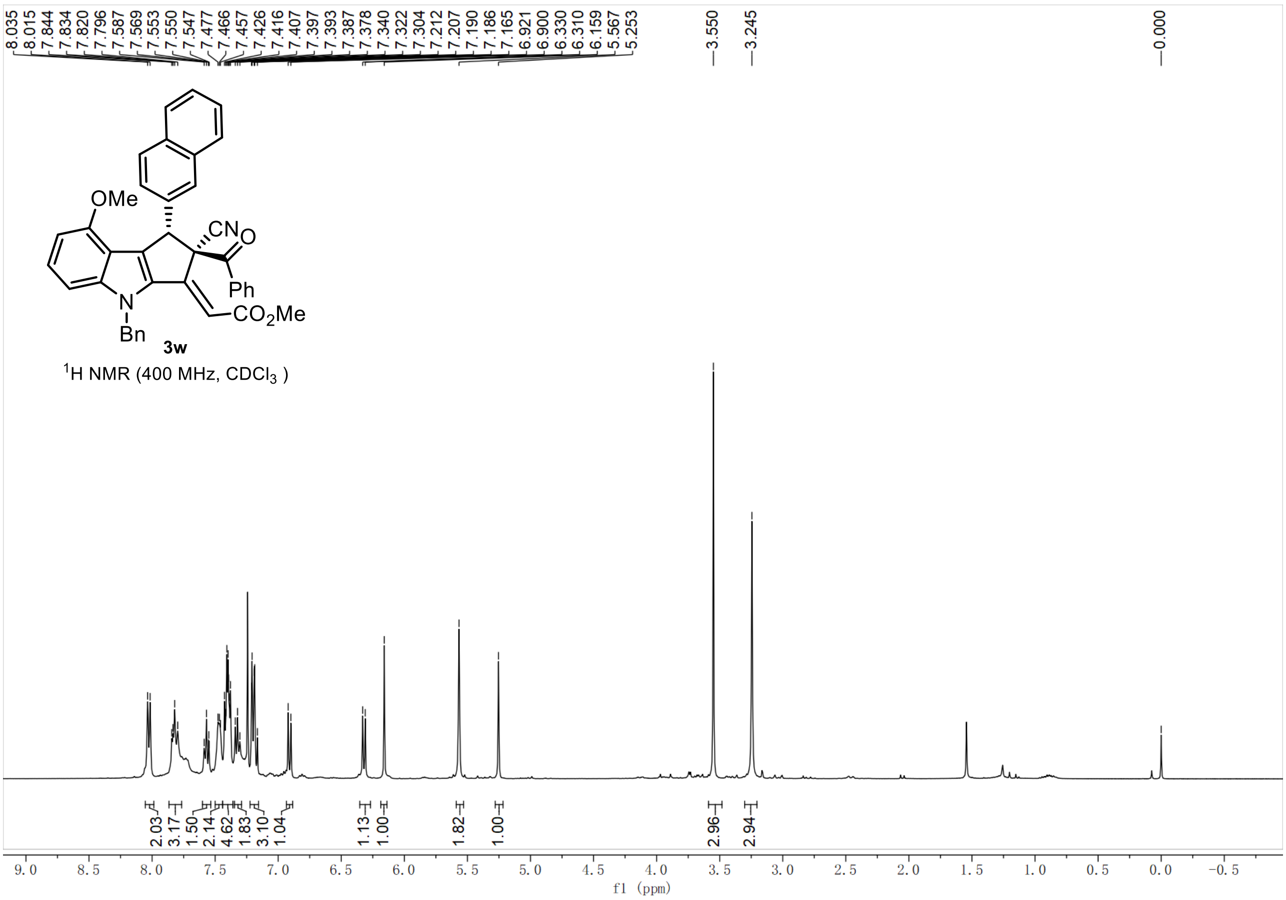
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.884	BB	0.1765	1081.65564	93.96207	4.4796
2	8.629	BB	0.3242	2.30647e4	1108.77832	95.5204

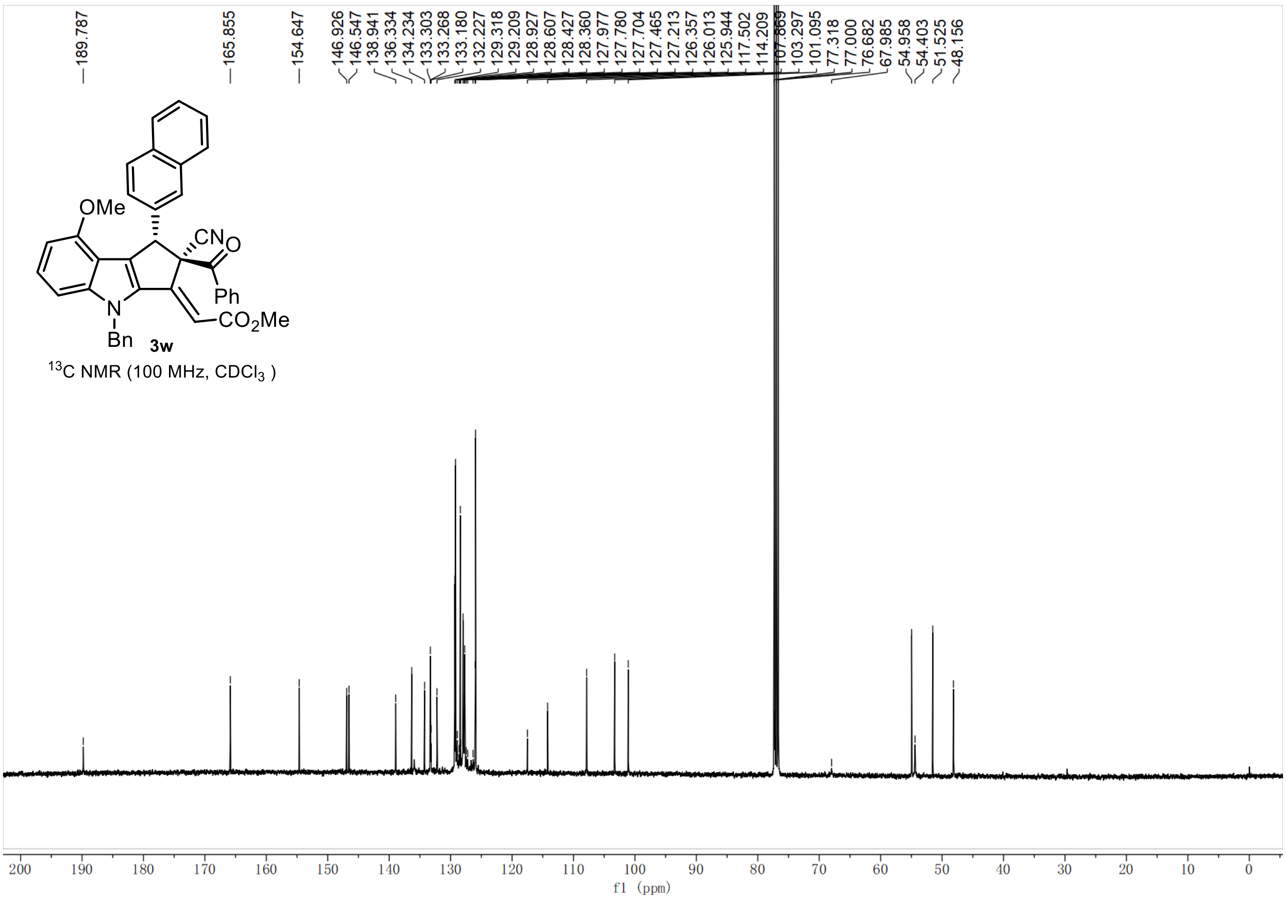


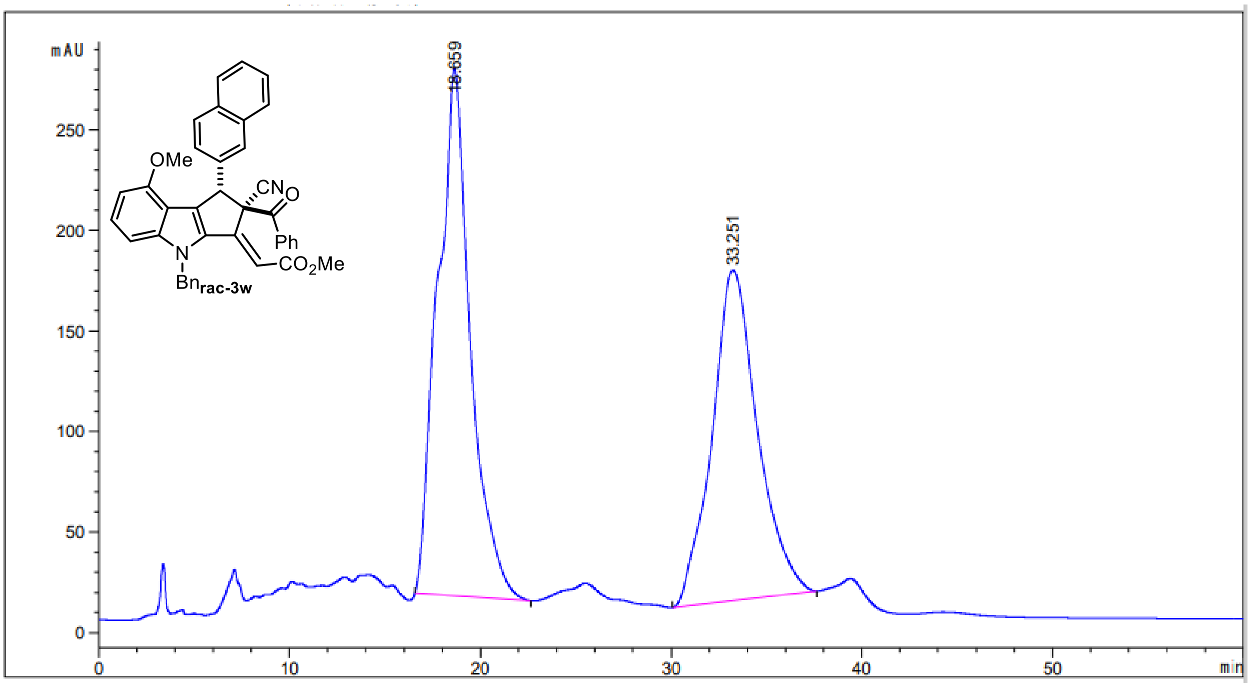
-67.864
CN
CF3
S
O
N
Bn
MeO2C
4e
19F NMR (376 MHz, CDCl3)
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
f1 (ppm)



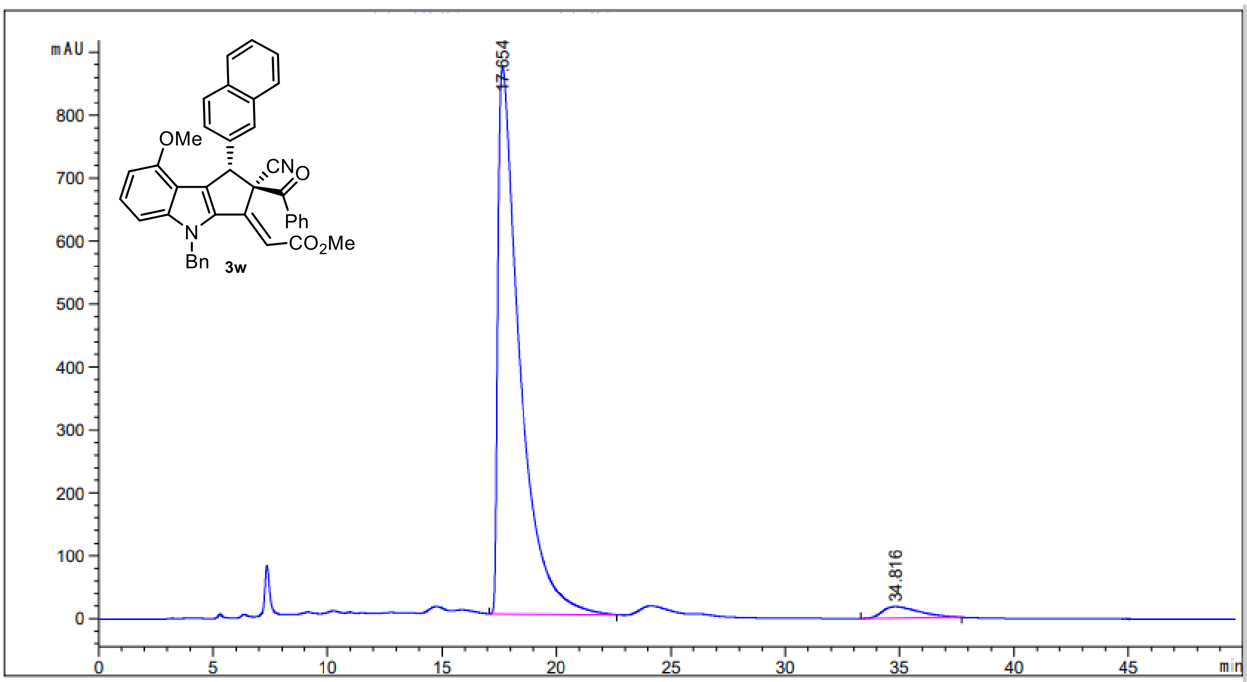
Name CYC-230321-9
Inj. Vol. (ul) 8
Data File CYC-230321-9.d
Rack Pos.
Plate Pos.
Method (Acq) CJH 230210.m
Instrument Instrument 1
IRM Status Some ions missed
Comment
Operator
Acq. Time (Local) 3/23/2023 12:29:42 PM (UTC+08:00)
+ESI Scan (rt: 0.942 min) Frag=175.0V CYC-230321-9.d
x10^3
543.0966
4e
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C28H19F3N2O3SNa+ 543.0961
Counts vs. Mass-to-Charge (m/z)





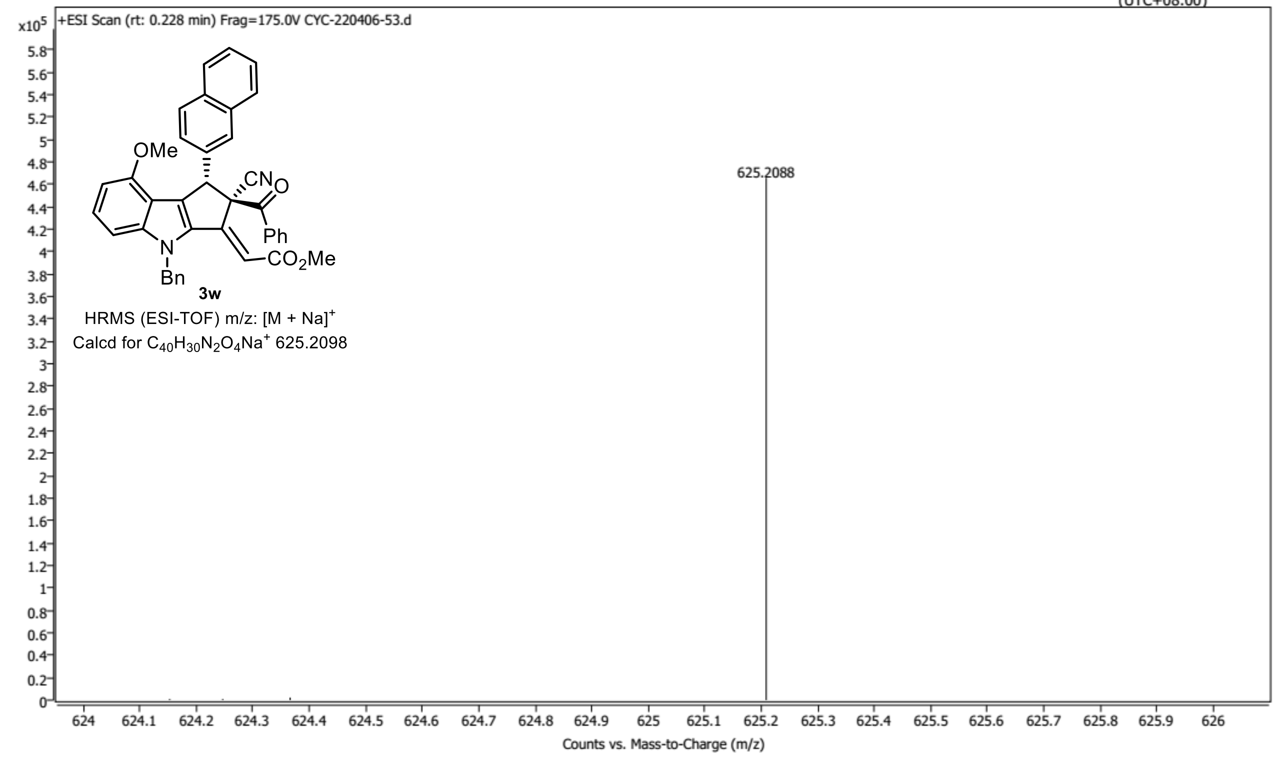


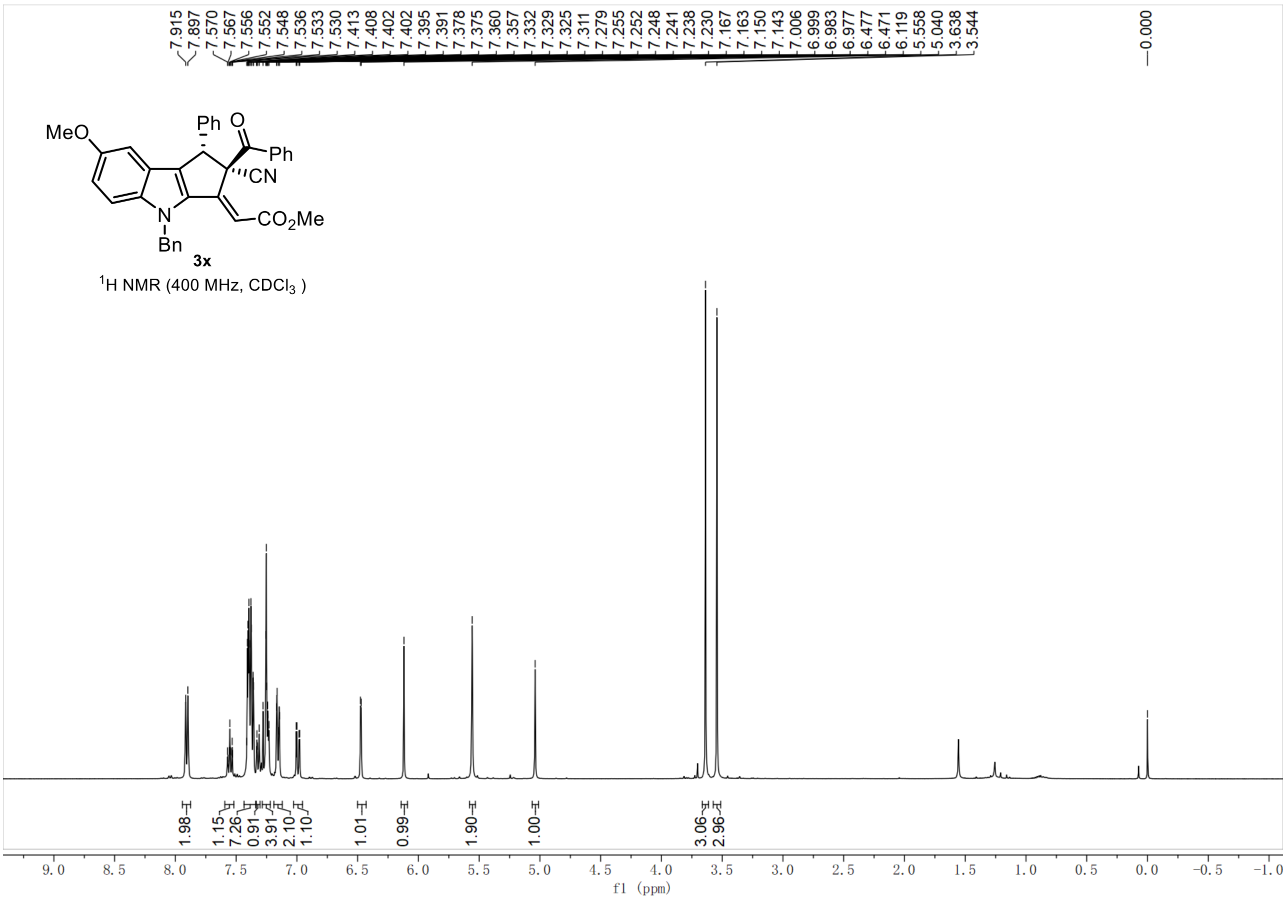
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.659	BBA	1.6107	3.14459e4	262.12656	53.5540
2	33.251	BB	2.3815	2.72722e4	164.23045	46.4460

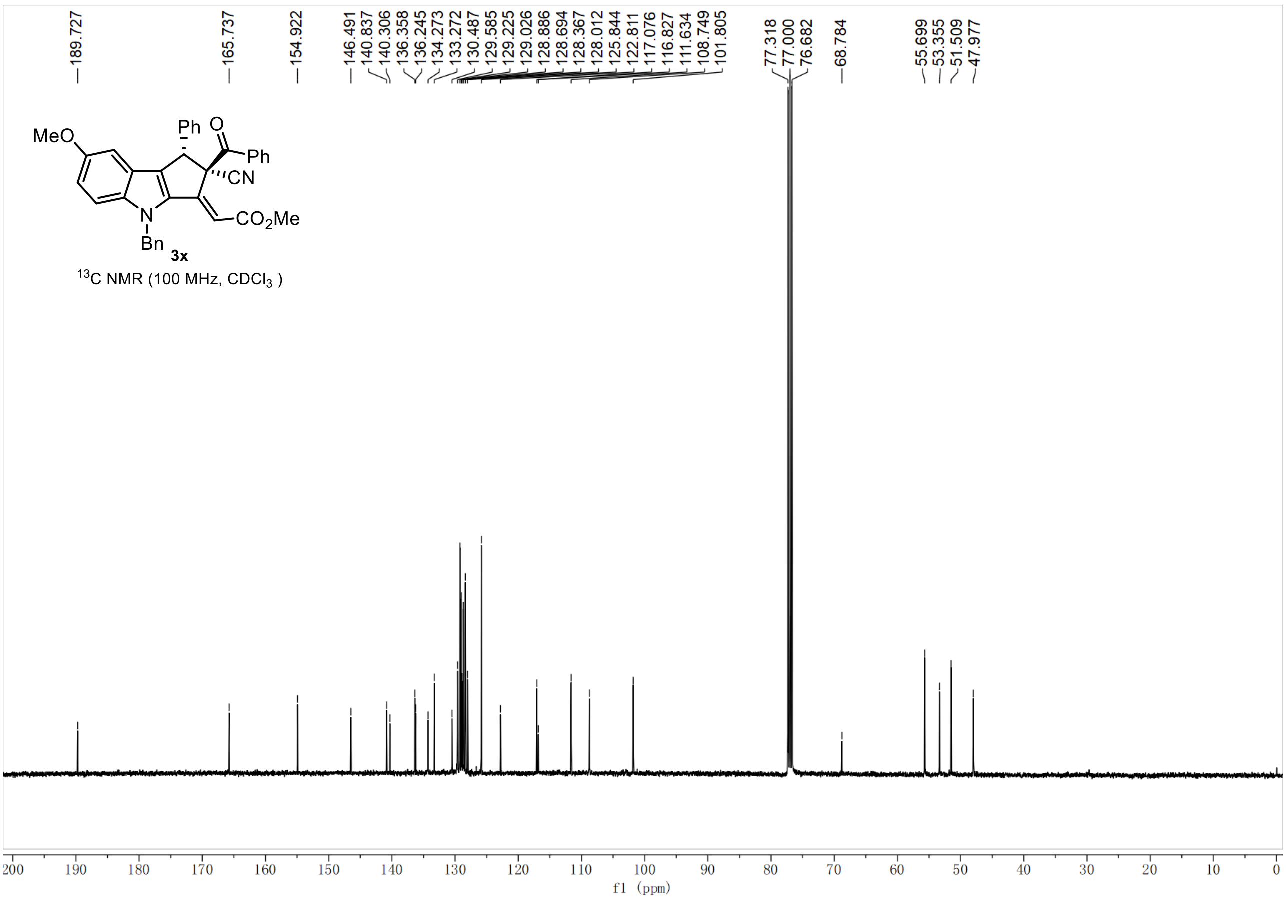


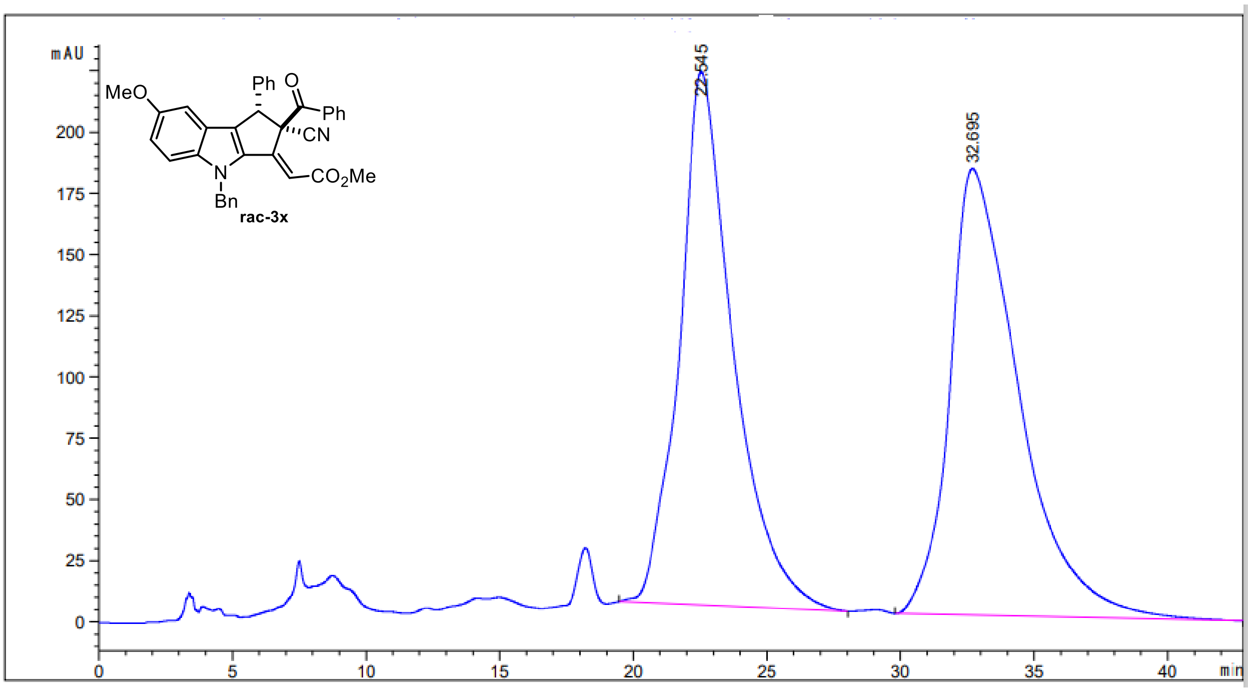
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.654	BBA	0.9437	5.73497e4	868.43475	96.6236
2	34.816	BBA	1.5441	2003.99097	17.87139	3.3764

Name	CYC-220406-53	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-53.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:42:00 AM (UTC+08:00)

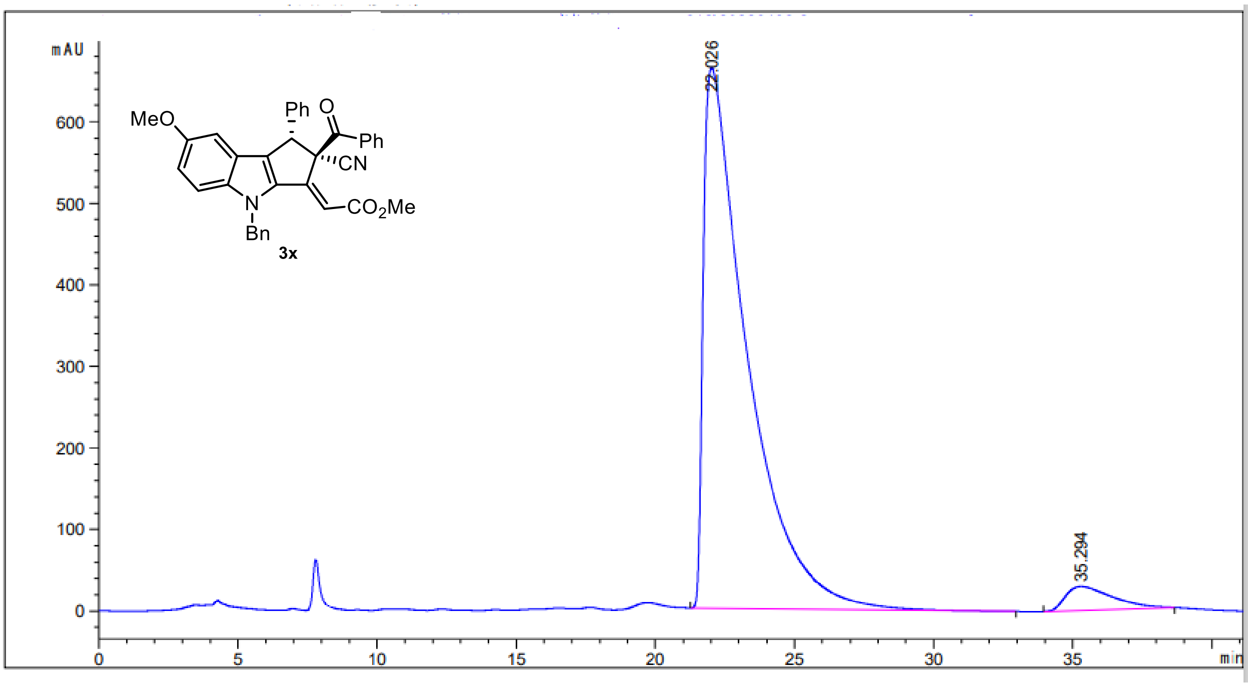






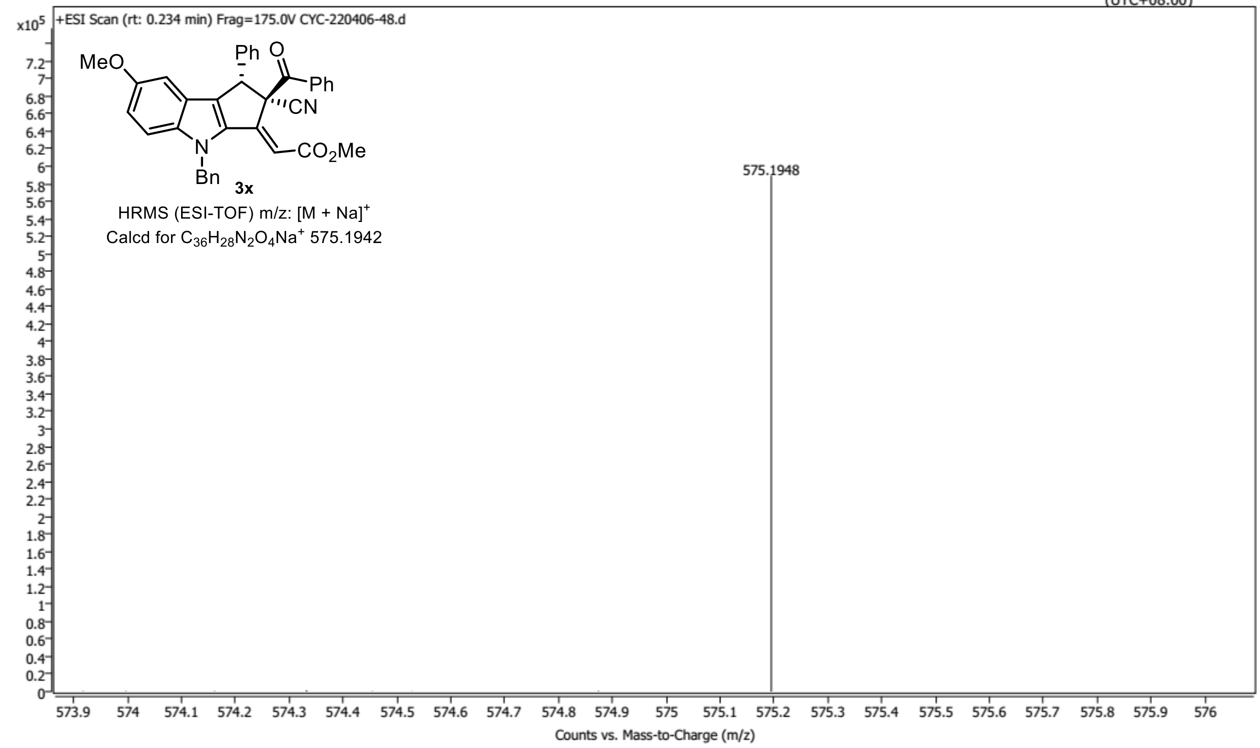


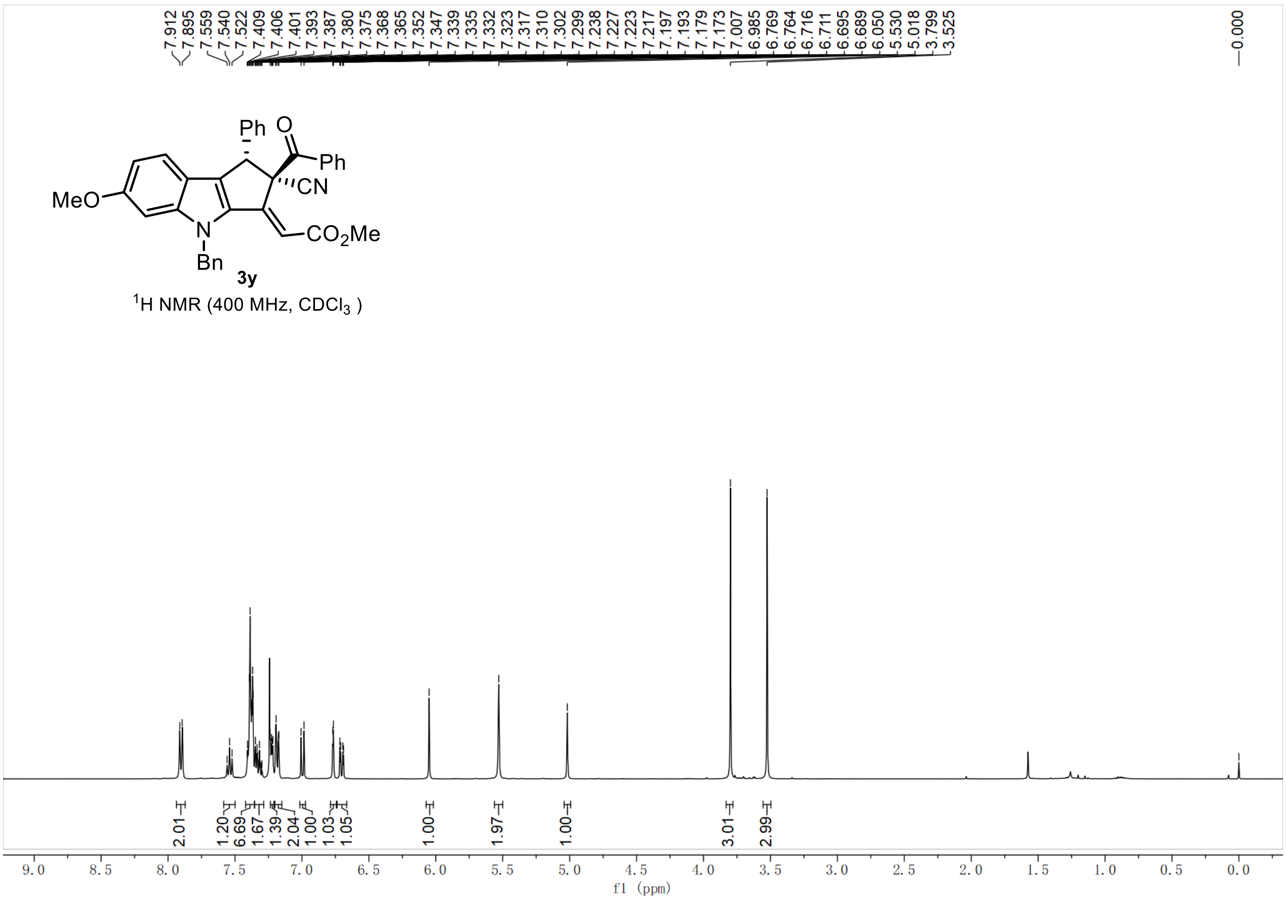
#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.545	BB	1.9922	3.04902e4	217.69656	48.1512
2	32.695	BBA	2.7024	3.28316e4	182.42897	51.8488



#	[min]		[min]	[mAU*s]	[mAU]	%
1	22.026	BB	1.5326	7.26656e4	662.73047	95.5206
2	35.294	BBA	1.7566	3407.63232	29.09478	4.4794

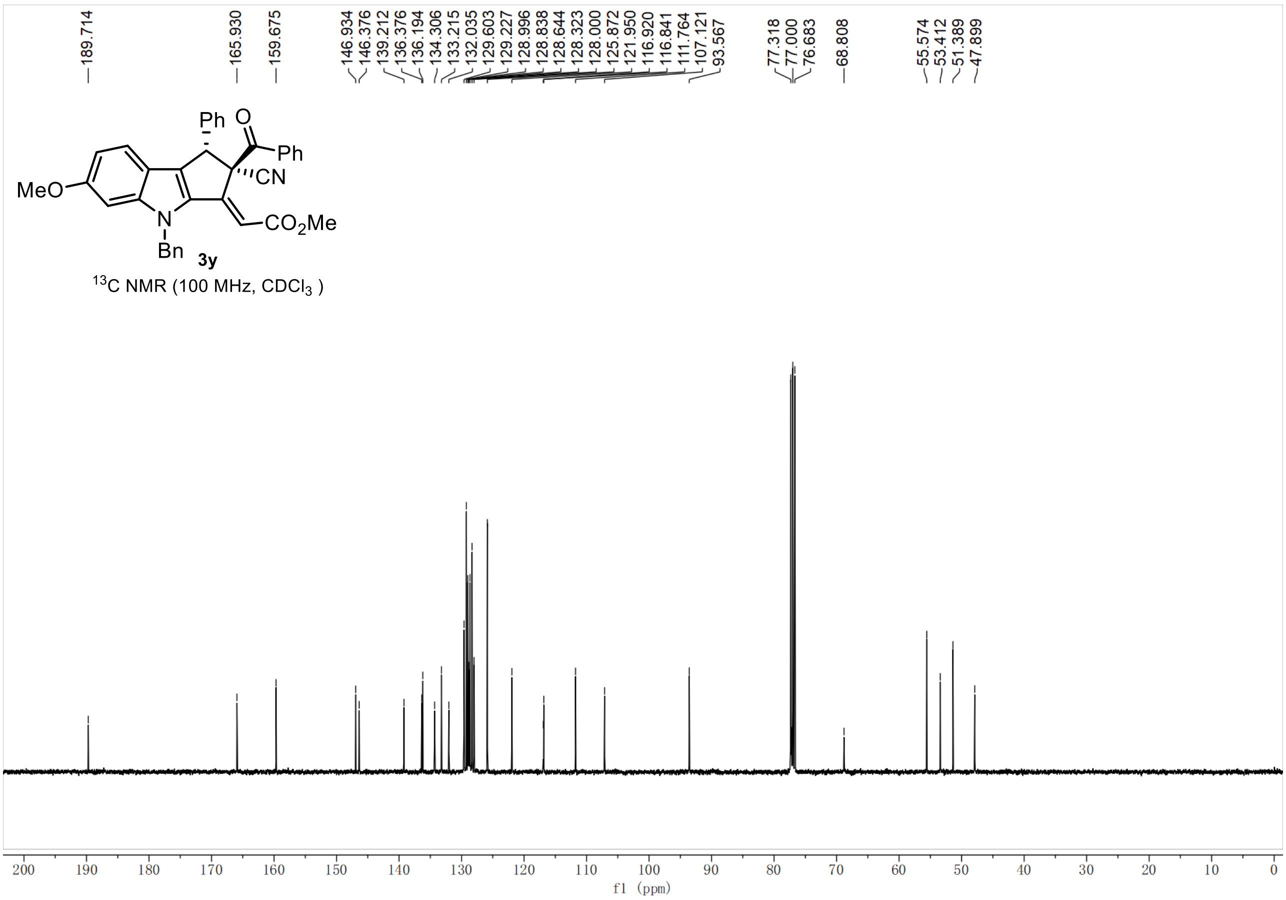
Name	CYC-220406-48	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-48.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:24:46 AM (UTC+08:00)





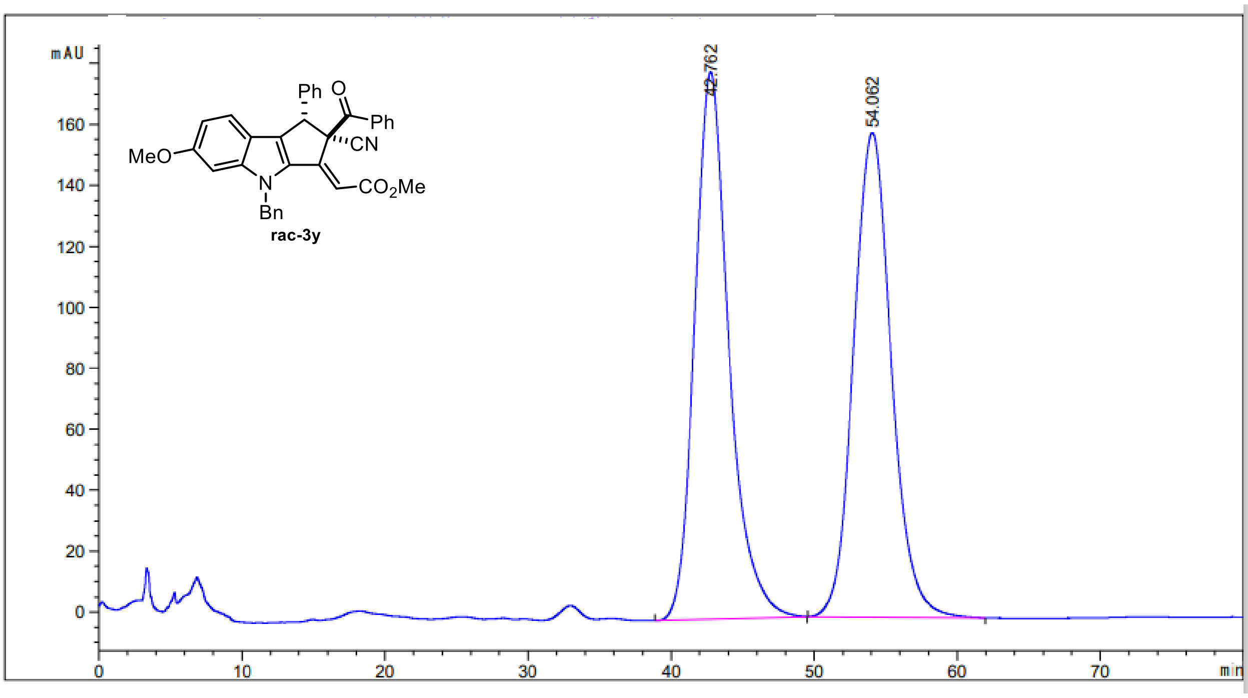
3y

^{1}H NMR (400 MHz, $CDCl_3$)

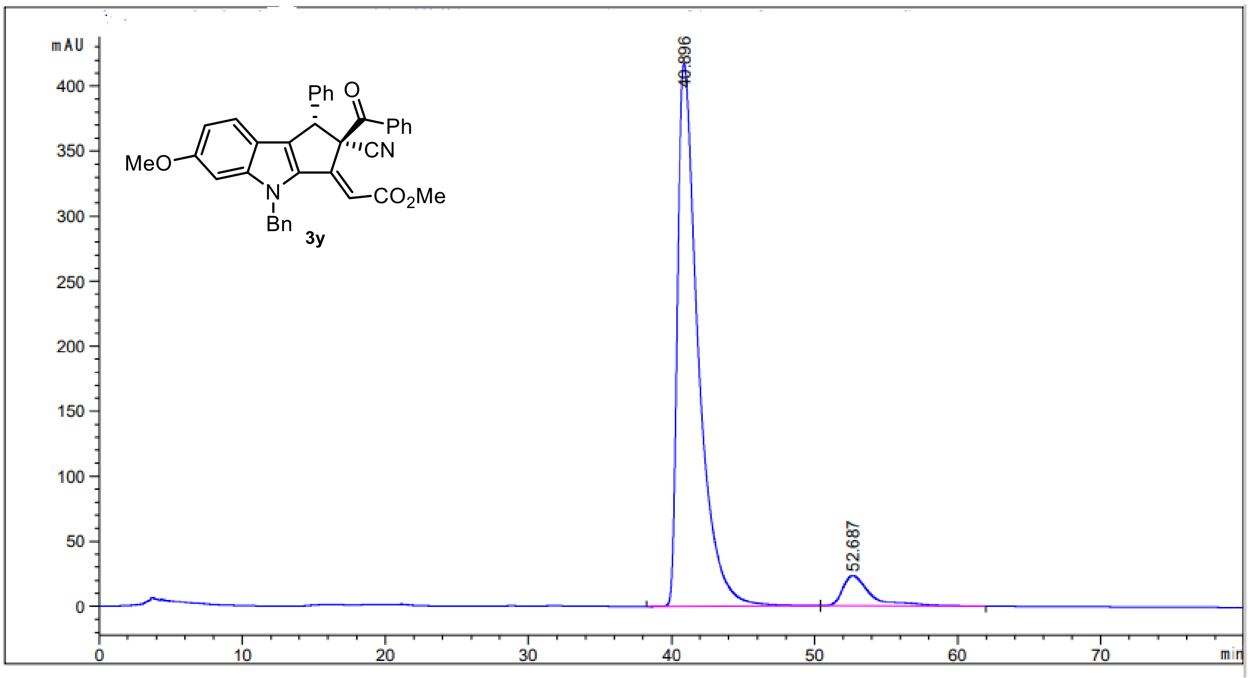


3y

^{13}C NMR (100 MHz, $CDCl_3$)

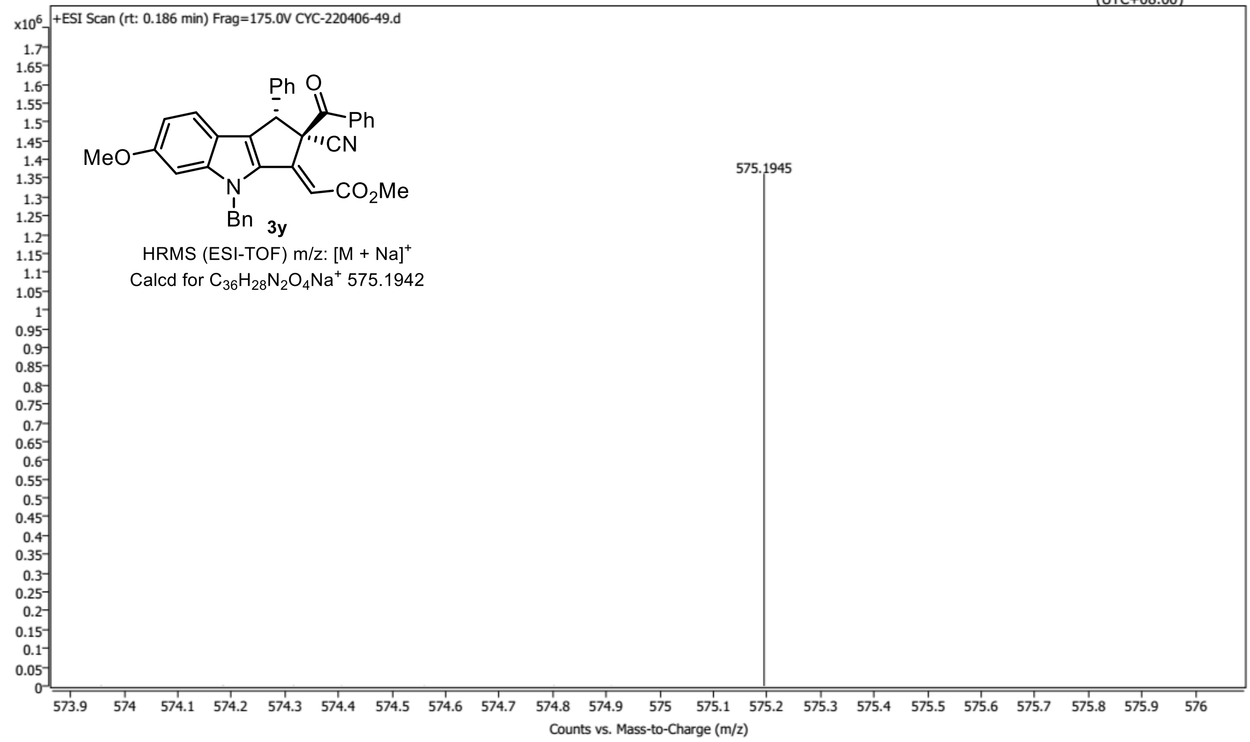


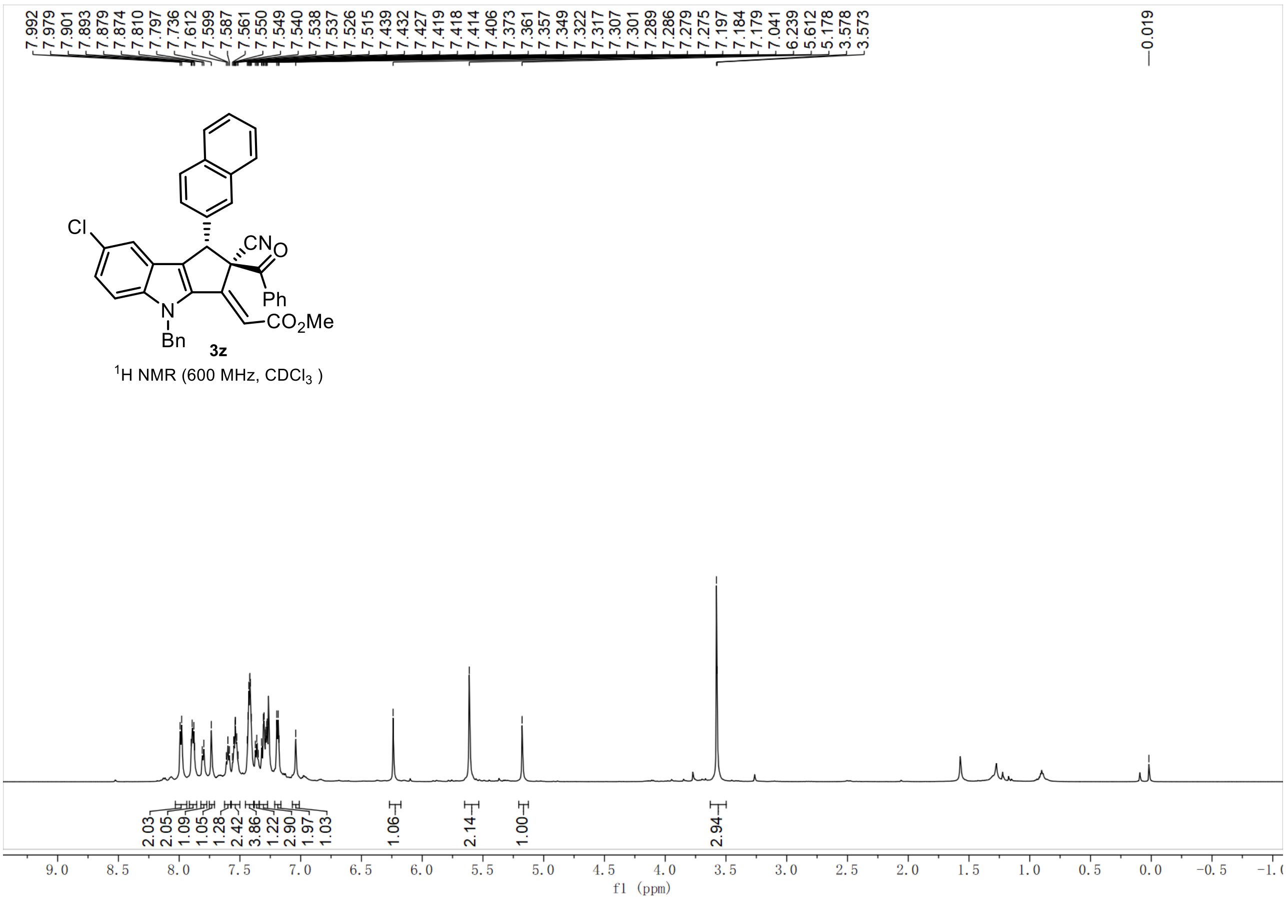
#	[min]		[min]	[mAU*s]	[mAU]	%
1	42.762	BB	2.5239	2.97878e4	179.53484	50.5523
2	54.062	BBA	2.8670	2.91369e4	158.92183	49.4477



#	[min]		[min]	[mAU*s]	[mAU]	%
1	40.896	BB	1.4904	4.20676e4	417.38489	92.9689
2	52.687	BBA	2.0008	3181.49878	23.34082	7.0311

Name	CYC-220406-49	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-49.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:27:44 AM (UTC+08:00)




7.992
7.979
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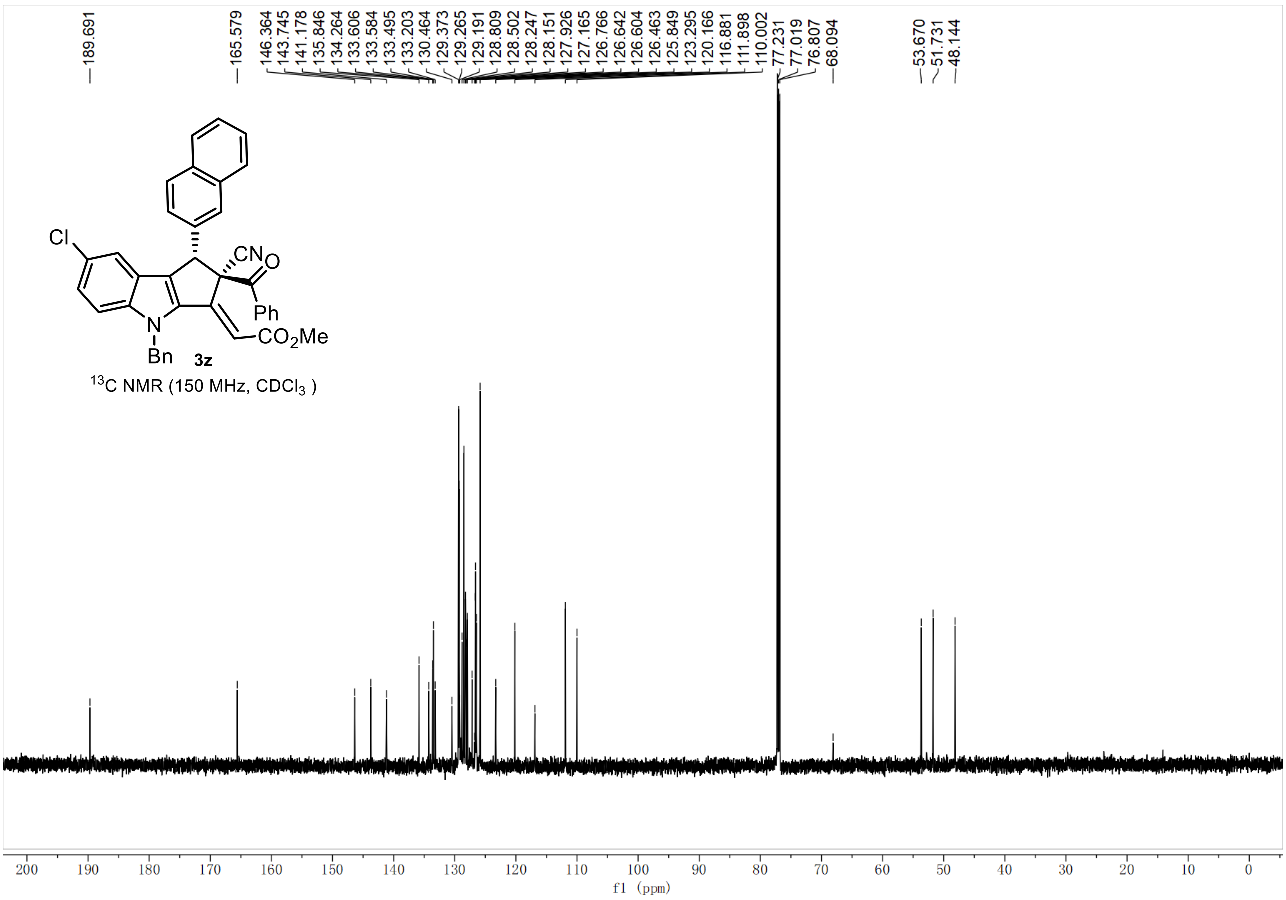
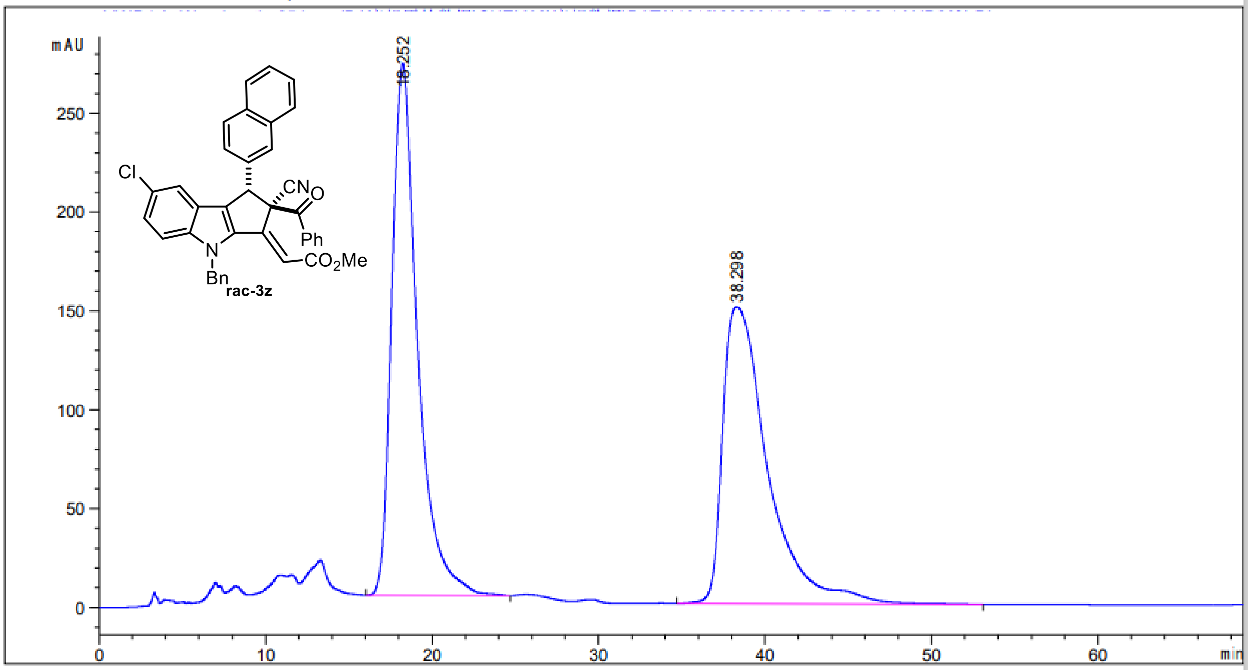
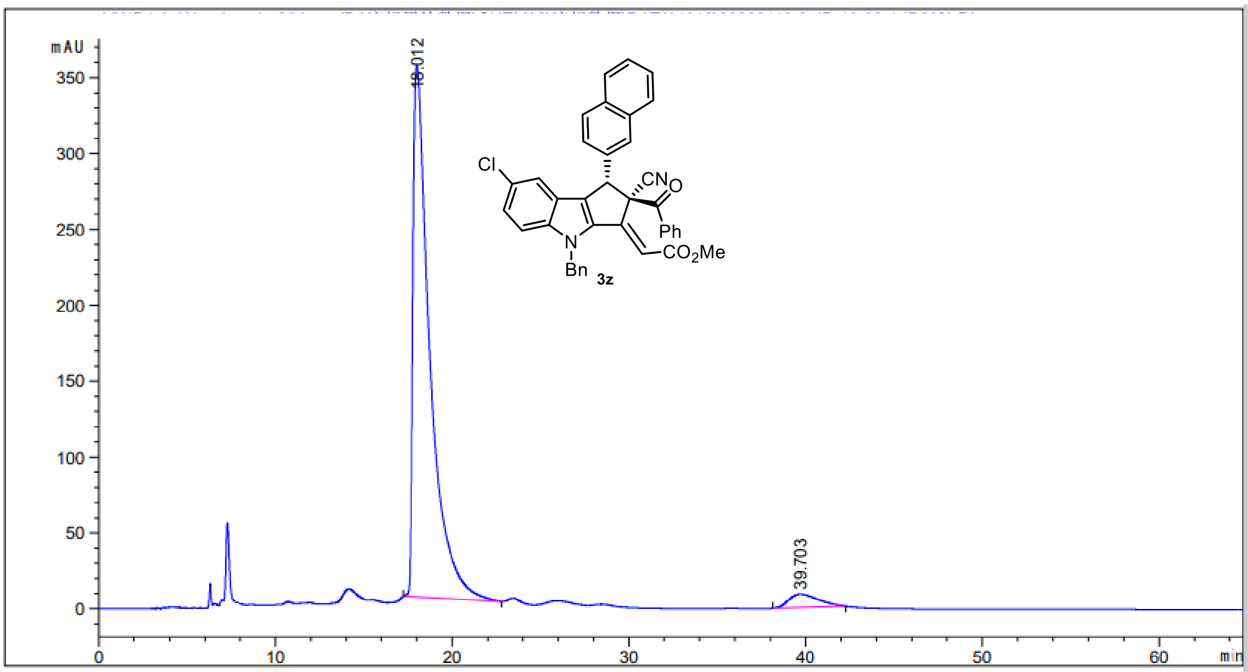
7.893
7.879
7.874
7.810
7.797
7.736
7.612
7.599
7.587
7.561
7.550
7.549
7.540
7.538
7.537
7.526
7.515
7.439
7.432
7.427
7.419
7.418
7.414
7.406
7.373
7.361
7.357
7.349
7.322
7.317
7.307
7.301
7.289
7.286
7.279
7.275
7.197
7.184
7.179
7.041
6.239
5.612
5.178
3.578
3.573
0.019
Cl
CN
O
Ph
N
CO2Me
Bn
3z
1H NMR (600 MHz, CDCl3)
2.03
2.05
1.09
1.05
1.28
2.42
3.86
1.22
2.90
1.97
1.03
1.06
2.14
1.00
2.94
f1 (ppm)


189.691
165.579
146.364
143.745
141.178
135.846
134.264
133.606
133.584
133.495
133.203
130.464
129.373
129.265
129.191
128.809
128.502
128.247
128.151
127.926
127.165
126.766
126.642
126.604
126.463
125.849
123.295
120.166
116.881
111.898
110.002
77.231
77.019
76.807
68.094
53.670
51.731
48.144
Cl
CN
O
Ph
N
CO2Me
Bn
3z
13C NMR (150 MHz, CDCl3)
f1 (ppm)

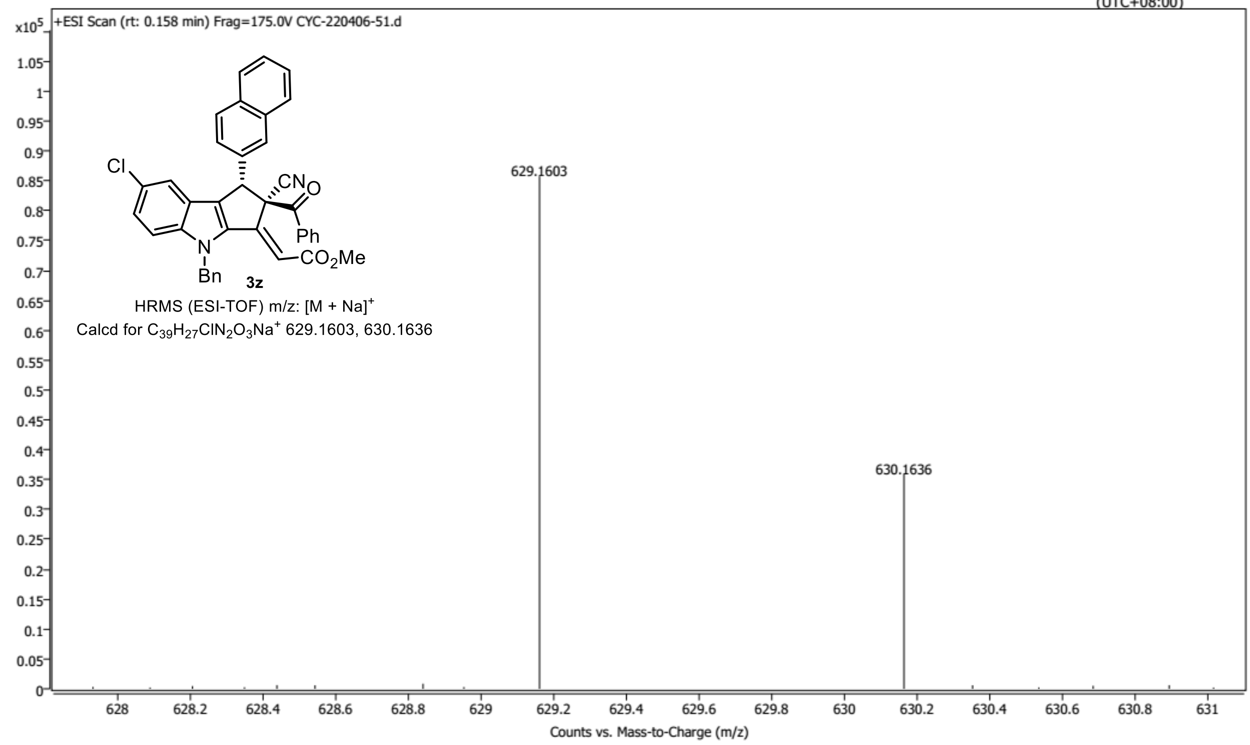


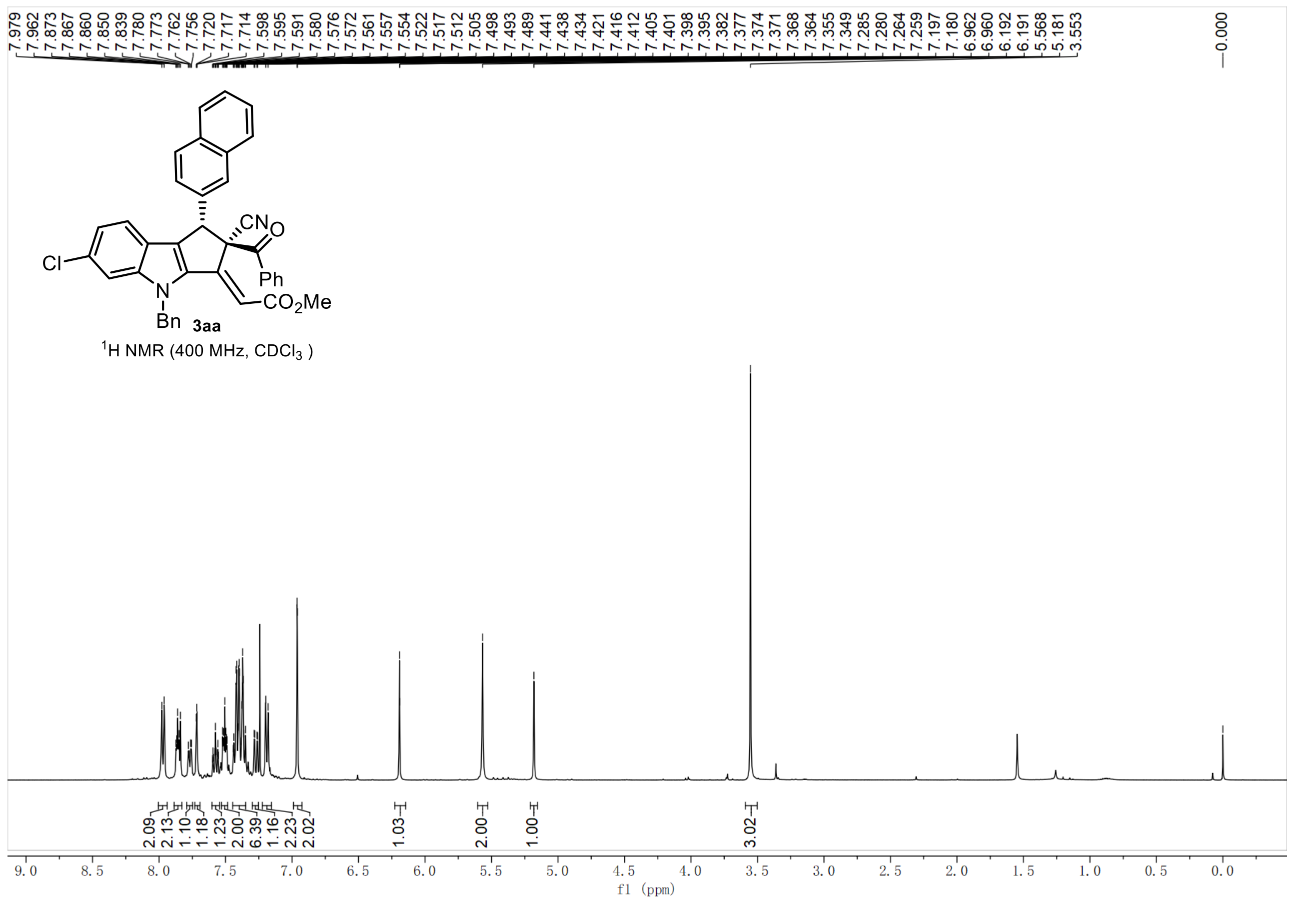
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.252	BB	1.6271	2.91339e4	269.09268	50.6993
2	38.298	BB	2.8329	2.83301e4	150.16870	49.3007

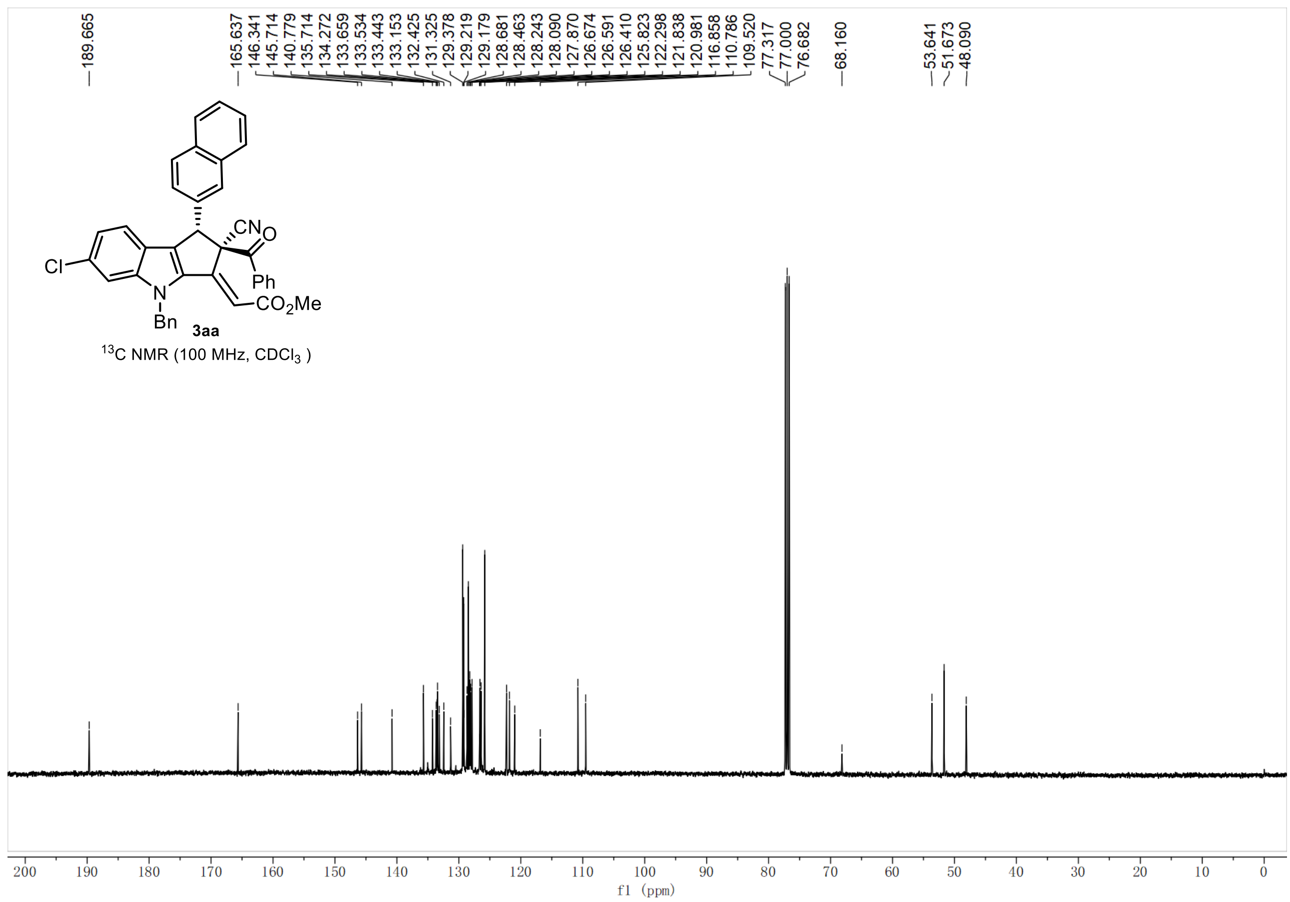


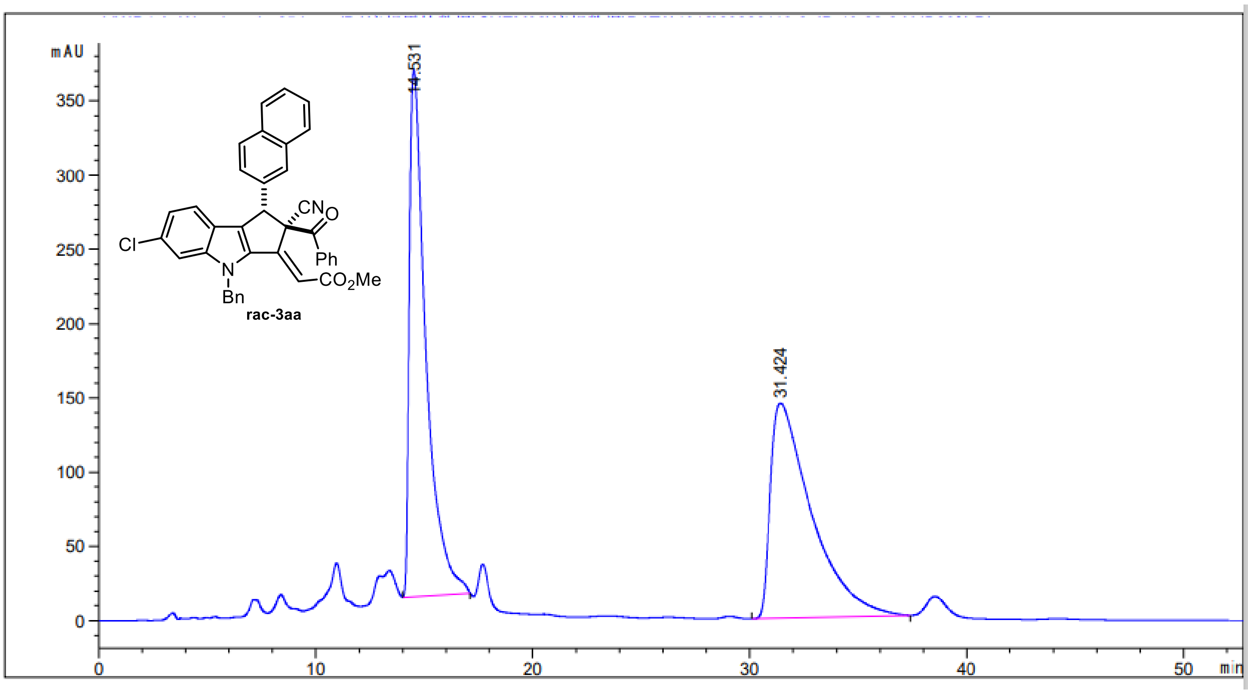
#	[min]		[min]	[mAU*s]	[mAU]	%
1	18.012	BB	0.9560	2.31965e4	350.28351	95.8037
2	39.703	BBA	1.4130	1016.02179	8.65627	4.1963

Name	CYC-220406-51	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-51.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:33:38 AM (UTC+08:00)

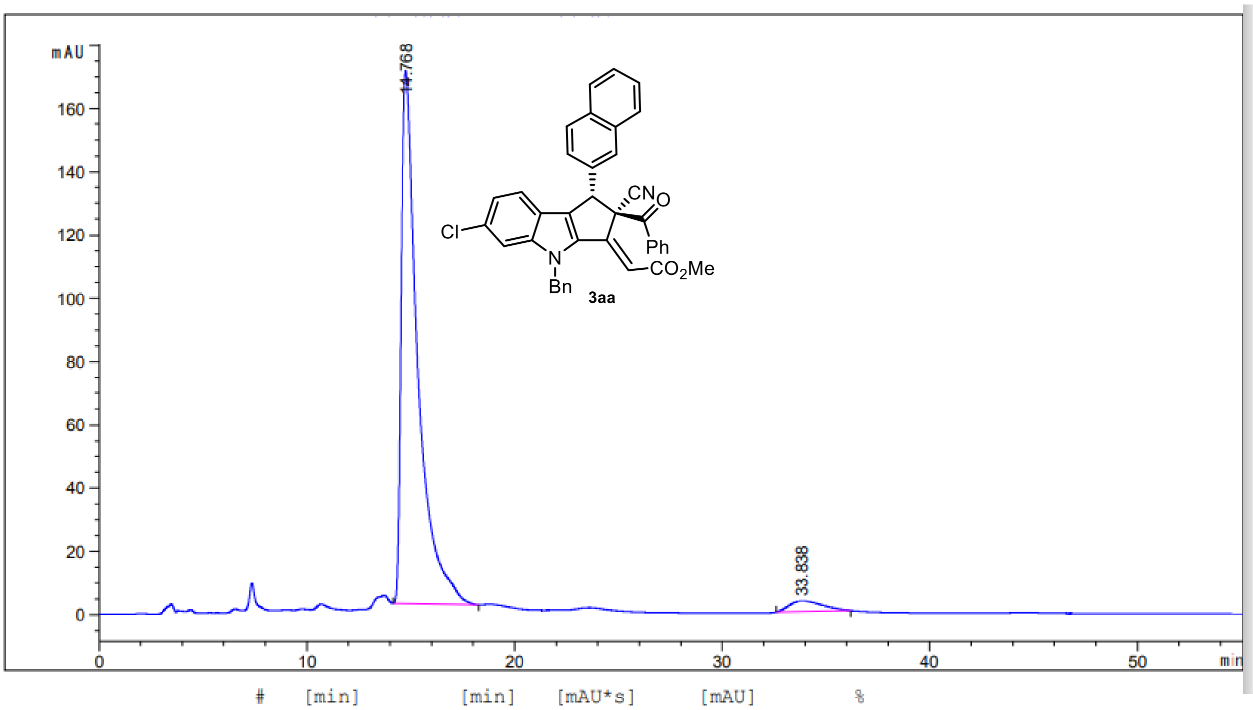






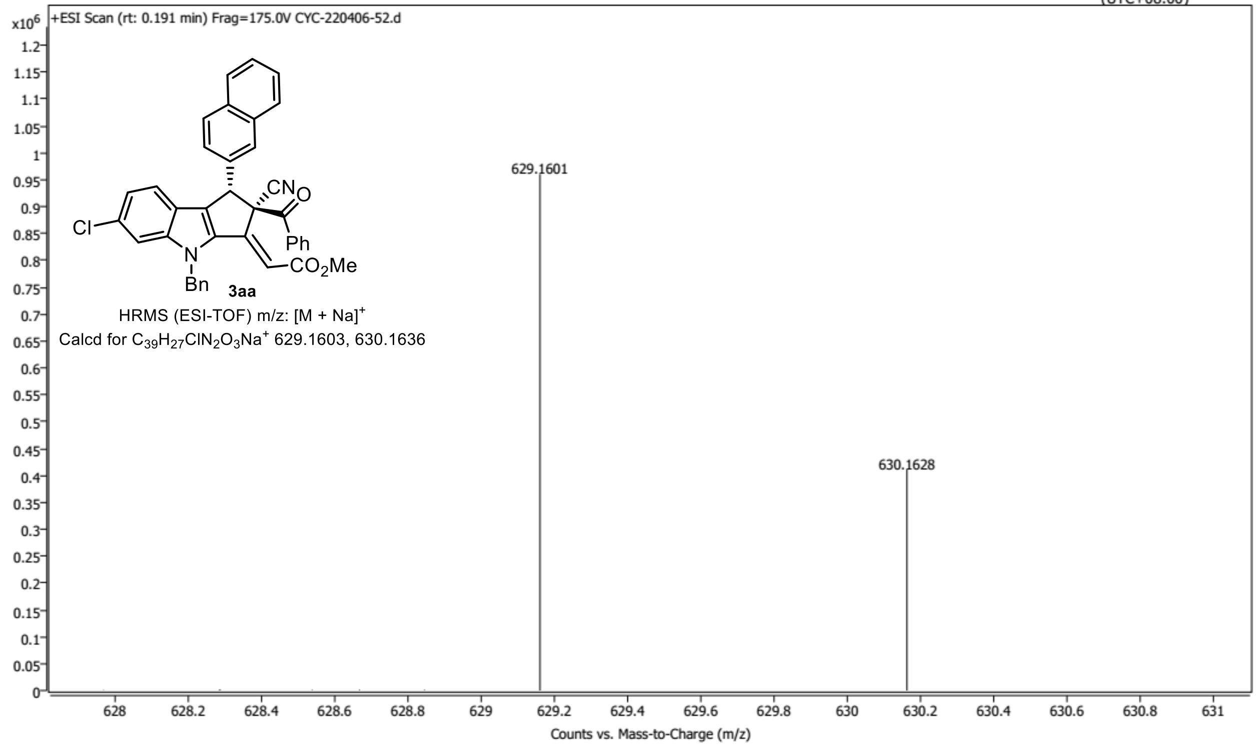


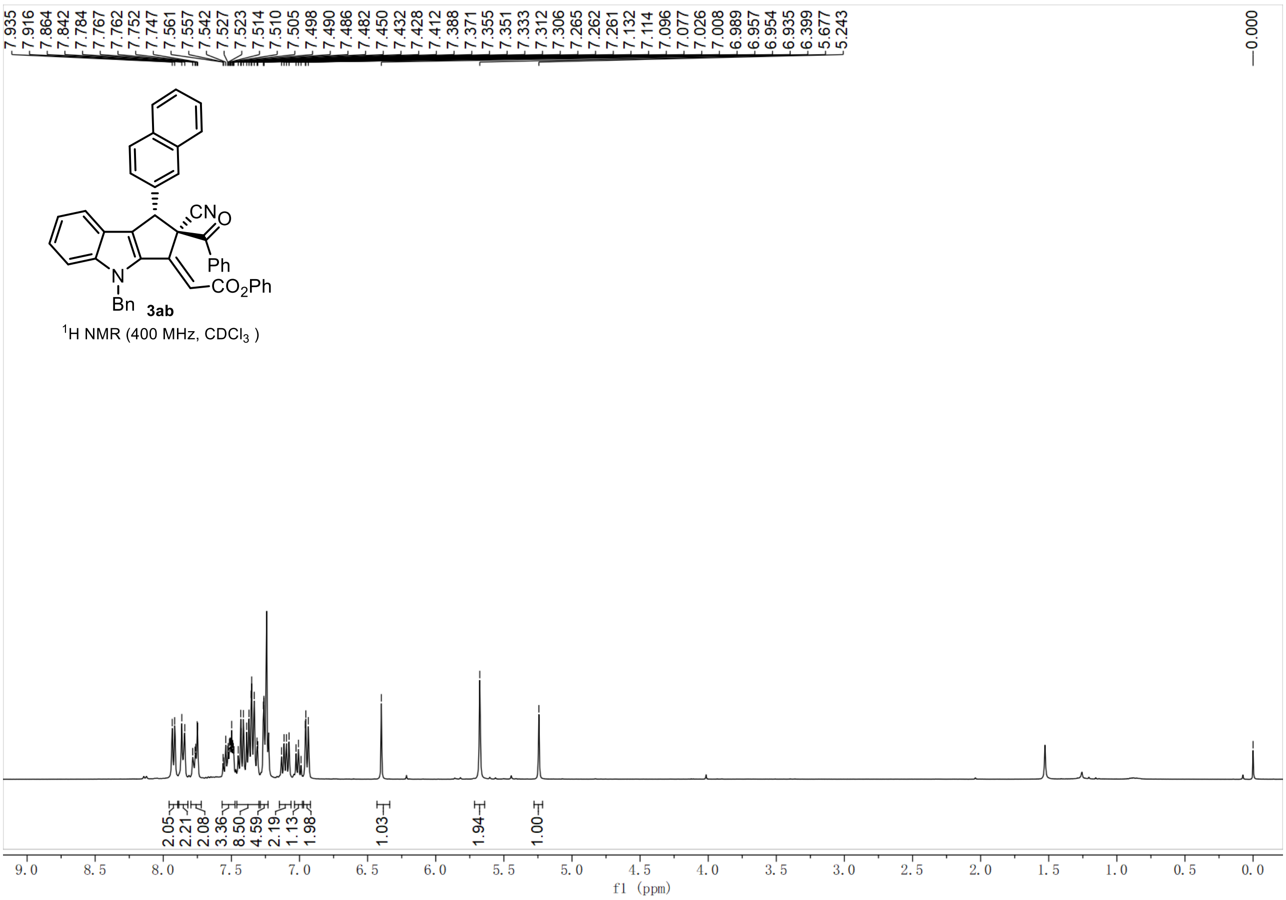
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.531	BBA	0.7769	1.88728e4	354.49387	49.7494
2	31.424	BBA	1.8202	1.90629e4	144.90726	50.2506



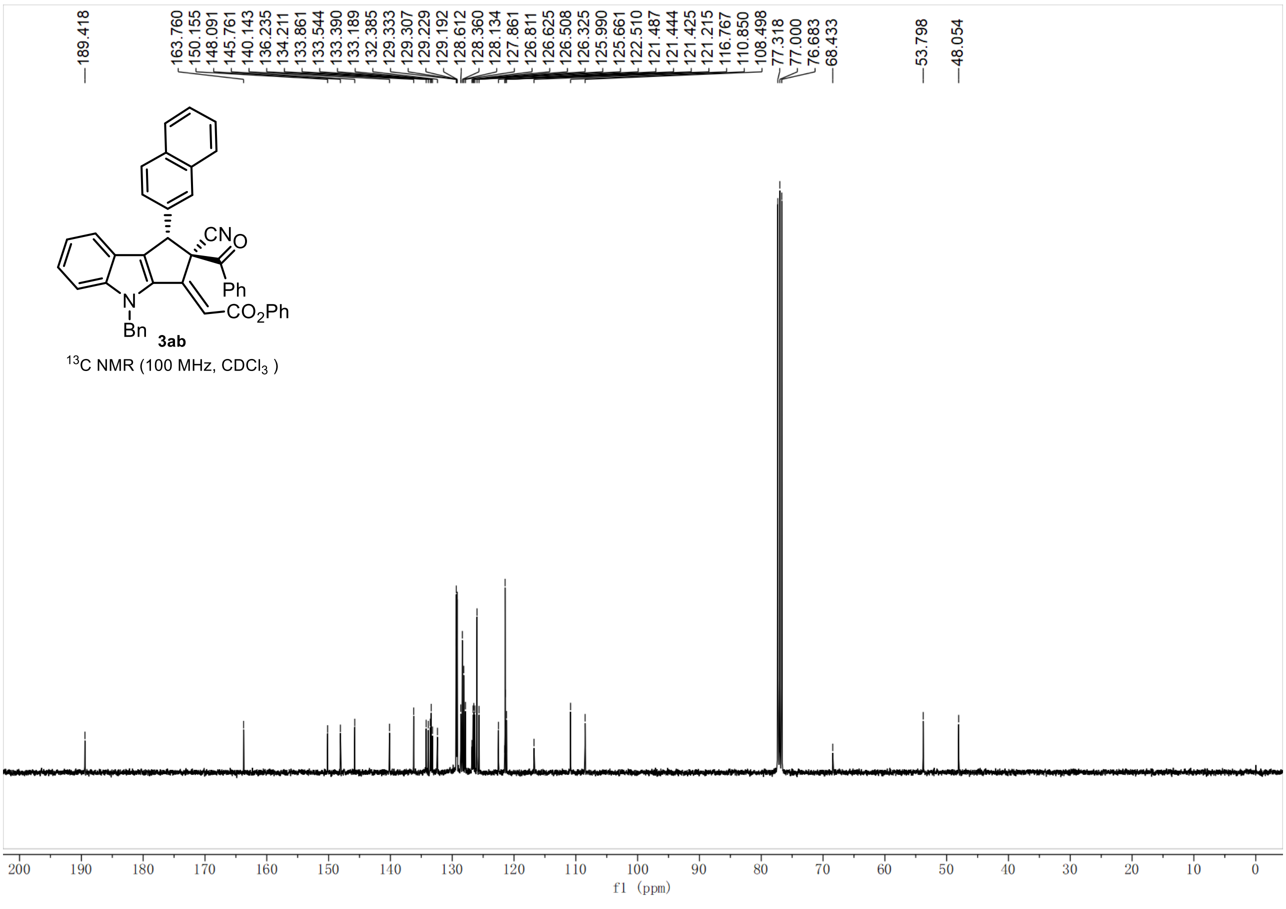
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.768	BB	0.8164	9497.54297	168.47437	96.2453
2	33.838	BBA	1.2818	370.52020	3.41913	3.7547

Name	CYC-220406-52	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-52.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:36:35 AM (UTC+08:00)

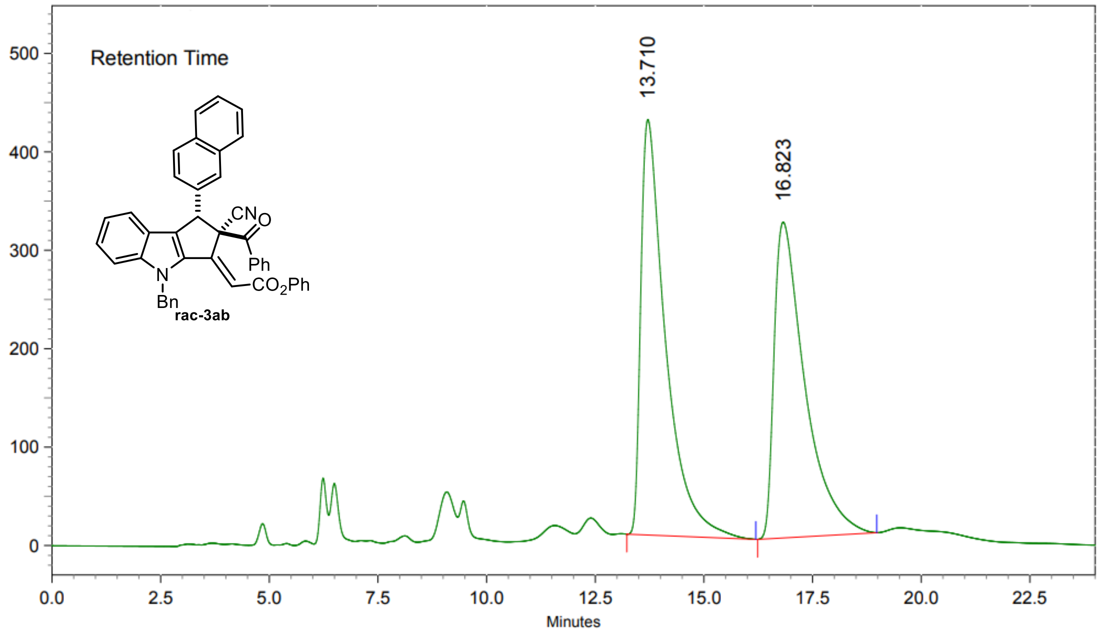




7.935
7.916
7.864
7.842
7.784
7.767
7.762
7.752
7.747
7.561
7.557
7.542
7.527
7.523
7.514
7.510
7.505
7.498
7.490
7.486
7.482
7.450
7.432
7.428
7.412
7.388
7.371
7.355
7.351
7.333
7.312
7.306
7.265
7.262
7.261
7.132
7.114
7.096
7.077
7.026
7.008
6.989
6.957
6.954
6.935
6.399
5.677
5.243
0.000
CN
O
Ph
N
Bn
CO_2Ph
3ab
^{1}H NMR (400 MHz, $CDCl_3$)
2.05
2.21
2.08
3.36
8.50
4.59
2.19
1.13
1.98
1.03
1.94
1.00
f1 (ppm)

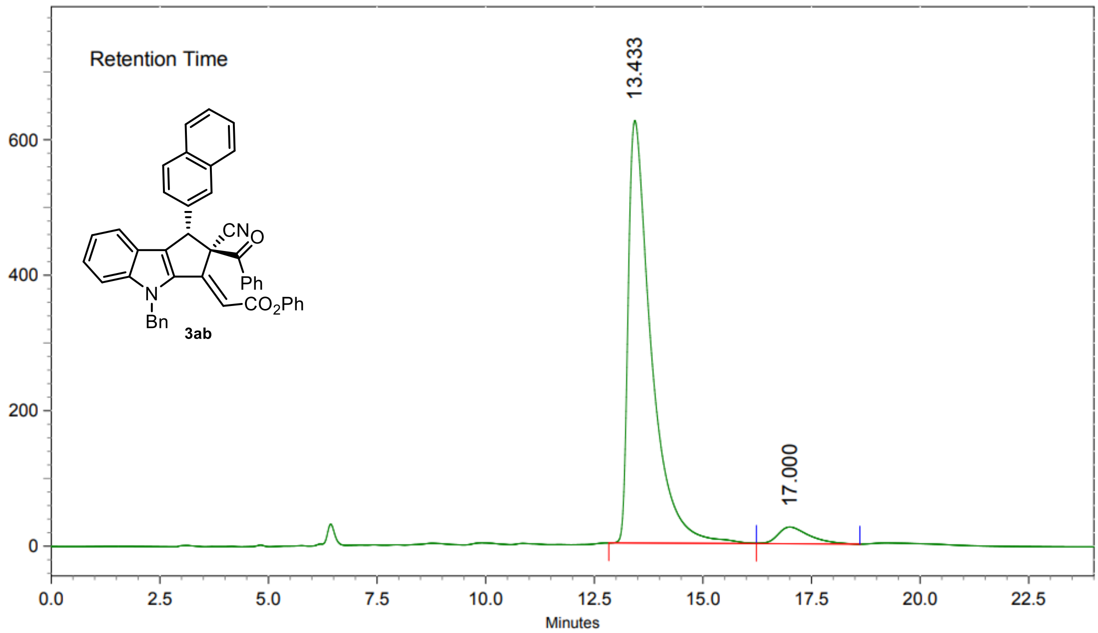


189.418
163.760
150.155
148.091
145.761
140.143
136.235
134.211
133.861
133.544
133.390
133.189
132.385
129.333
129.307
129.229
129.192
128.612
128.360
128.134
127.861
126.811
126.625
126.508
126.325
125.990
125.661
122.510
121.487
121.444
121.425
121.215
116.767
110.850
108.498
77.318
77.000
76.683
68.433
53.798
48.054
CN
O
Ph
N
Bn
CO_2Ph
3ab
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)



AREA PERCENT REPORT

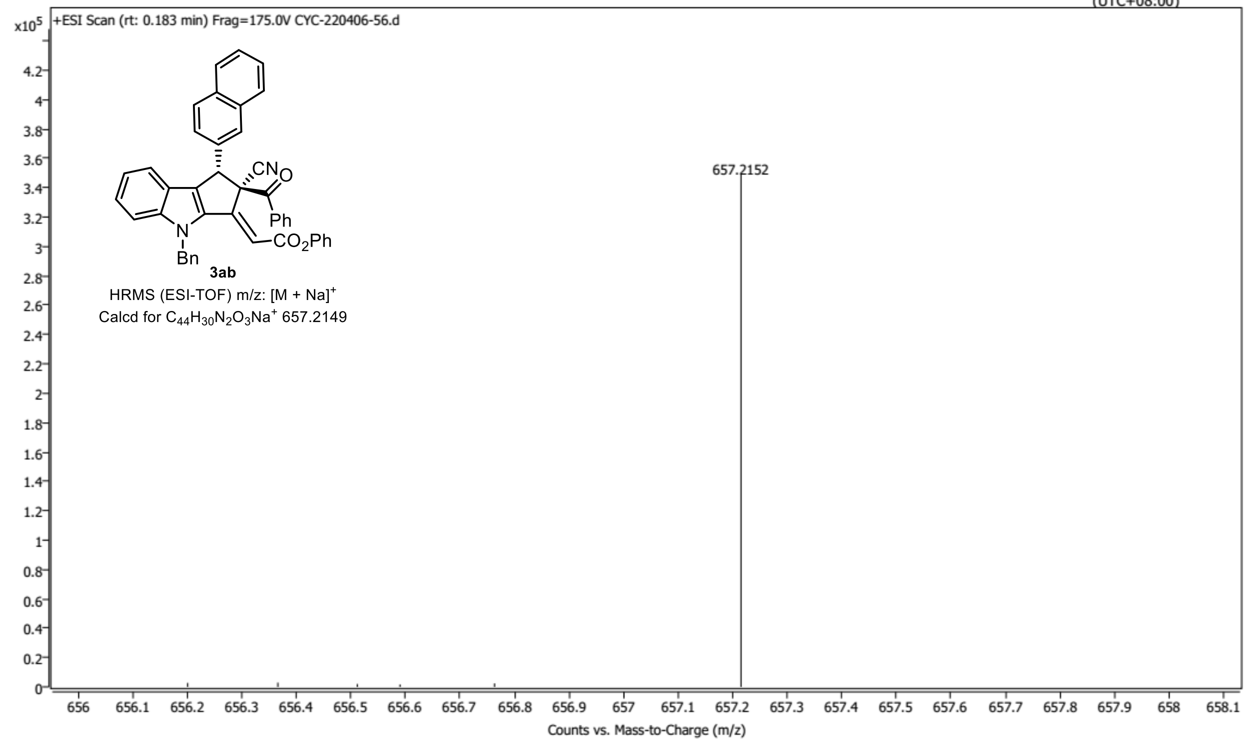
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.710	2.967	7082341	280591765	51.4656
2	16.823	2.740	5383467	264610468	48.5344

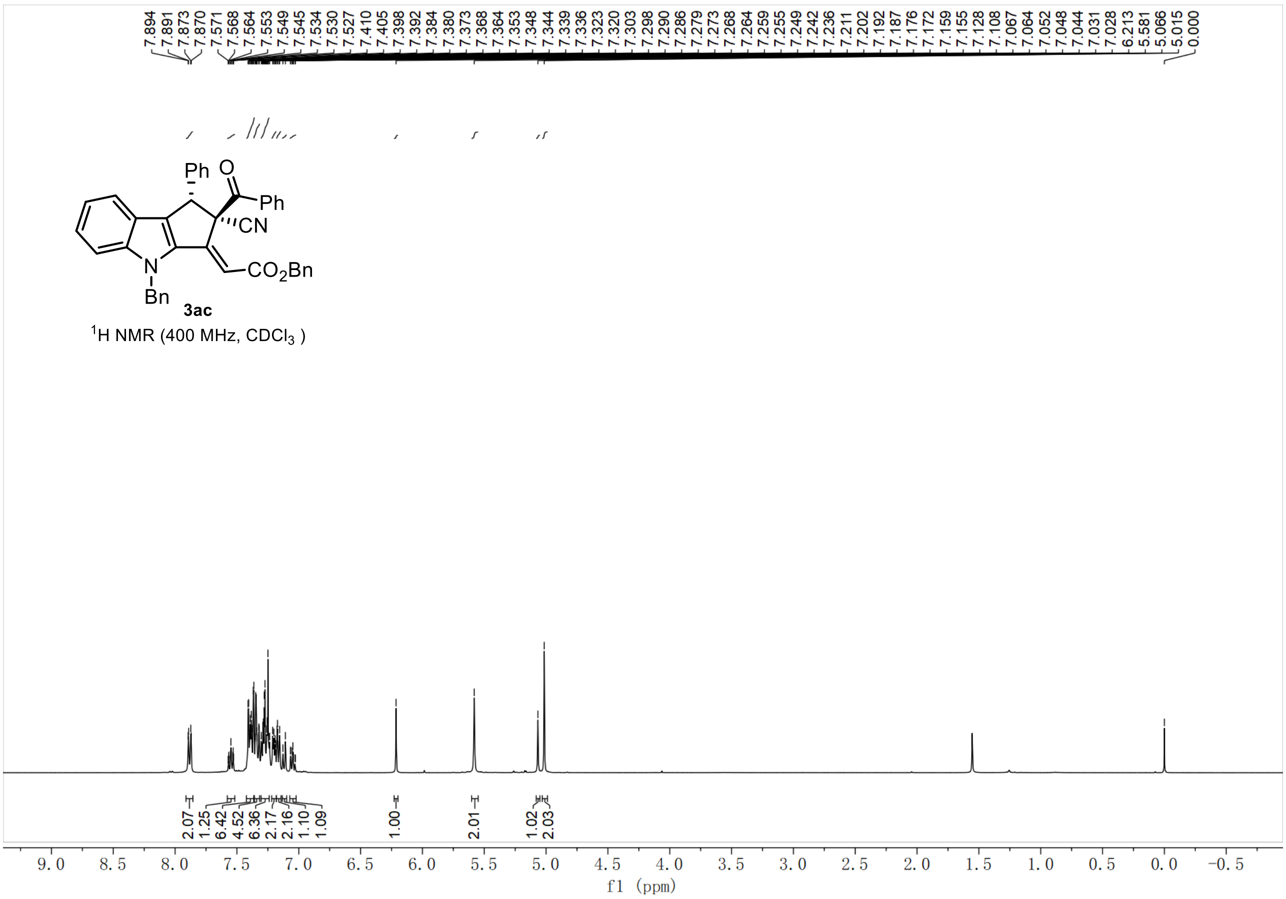


AREA PERCENT REPORT

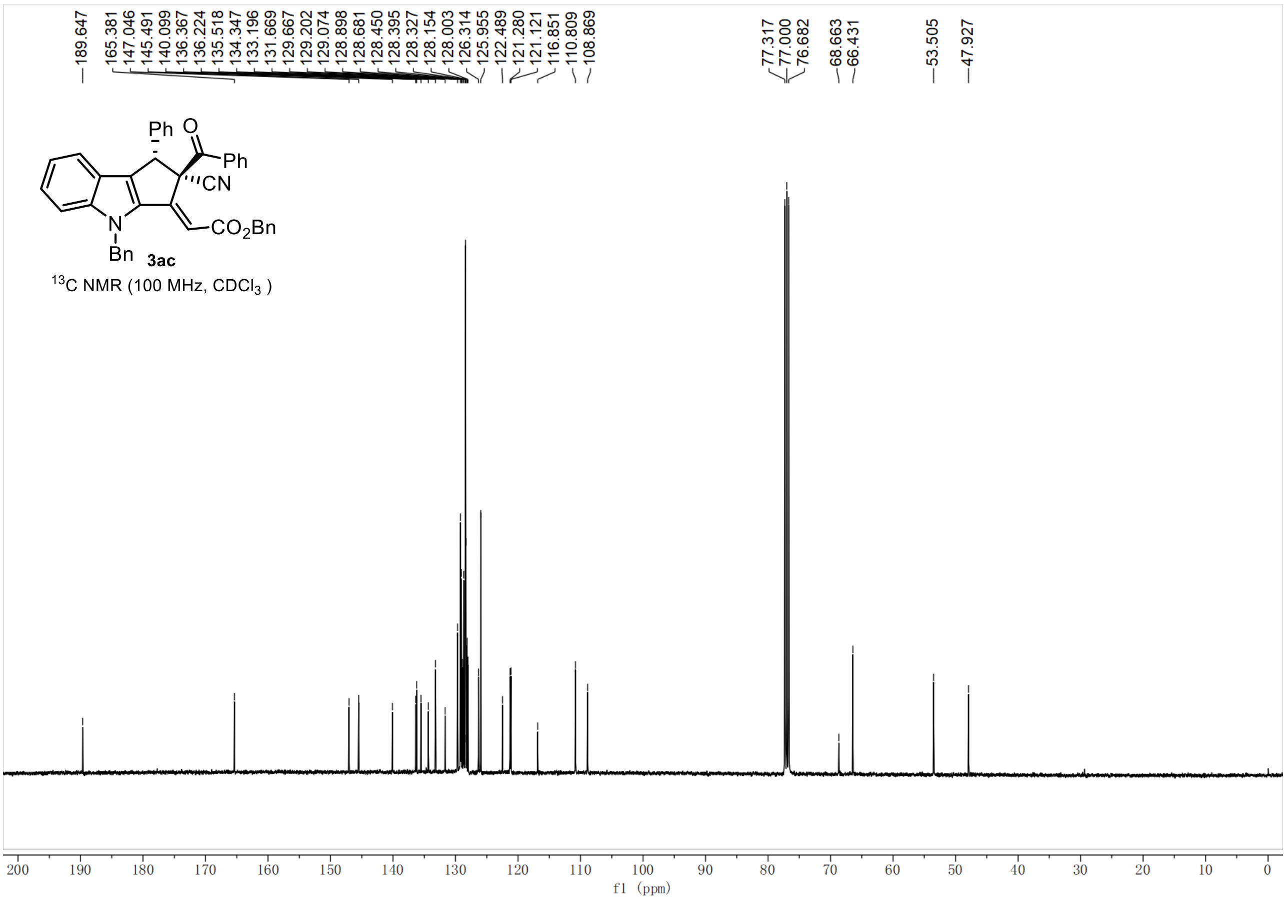
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.433	3.397	10462208	382501506	94.8707
2	17.000	2.383	413924	20680376	5.1293

Name	CYC-220406-56	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-56.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:51:01 AM (UTC+08:00)

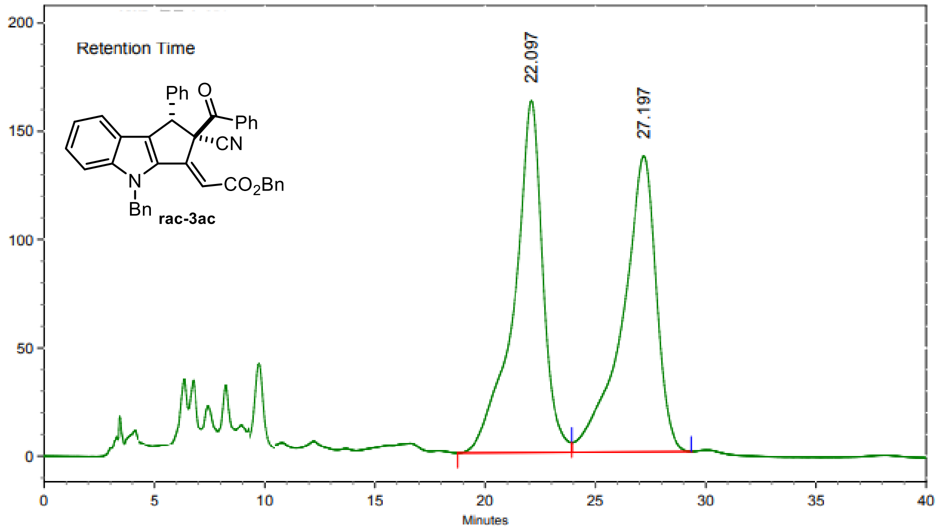




7.894 7.891 7.873 7.870 7.571 7.568 7.564 7.553 7.549 7.545 7.534 7.530 7.527 7.410 7.405 7.398 7.392 7.384 7.380 7.373 7.368 7.364 7.353 7.348 7.344 7.339 7.336 7.323 7.320 7.303 7.298 7.290 7.286 7.279 7.273 7.268 7.264 7.259 7.255 7.249 7.242 7.236 7.211 7.202 7.192 7.187 7.176 7.172 7.159 7.155 7.128 7.108 7.067 7.064 7.052 7.048 7.044 7.031 7.028 6.213 5.581 5.066 5.015 0.000
Ph
O
Ph
CN
N
CO2Bn
Bn
3ac
1H NMR (400 MHz, CDCl3)
2.07 1.25 6.42 4.52 6.36 2.17 2.16 1.10 1.09 1.00 2.01 1.02 2.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

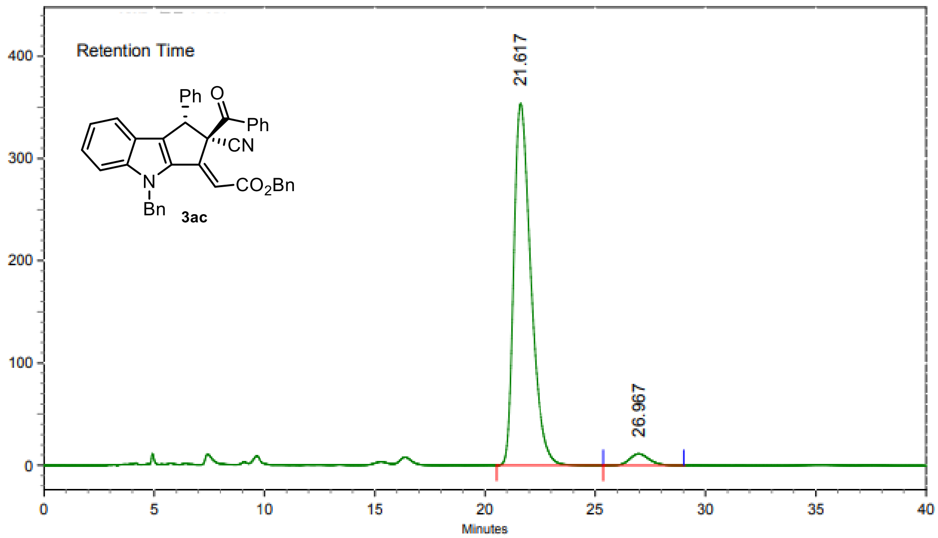


189.647 165.381 147.046 145.491 140.099 136.367 136.224 135.518 134.347 133.196 131.669 129.667 129.202 129.074 128.898 128.681 128.450 128.395 128.327 128.154 128.003 126.314 125.955 122.489 121.280 121.121 116.851 110.809 108.869 77.317 77.000 76.682 68.663 66.431 53.505 47.927
Ph
O
Ph
CN
N
CO2Bn
Bn
3ac
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



AREA PERCENT REPORT

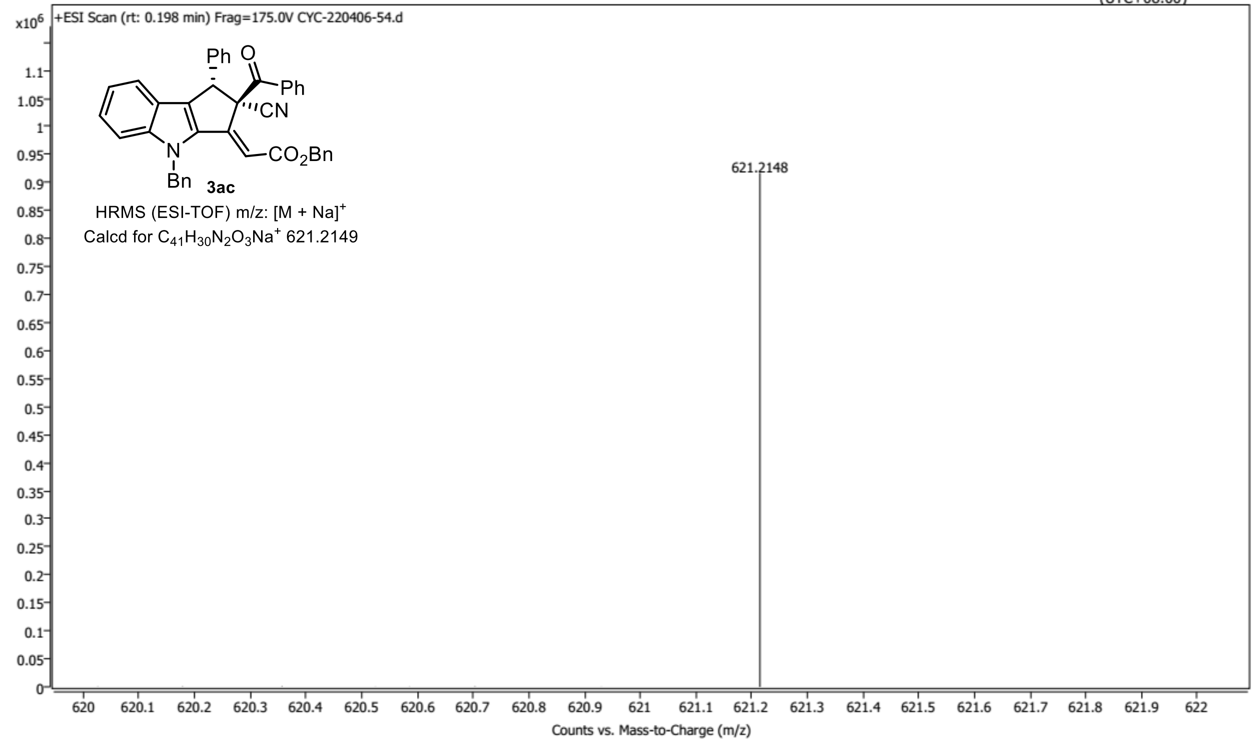
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	22.097	5.177	2726183	247420821	50.1825
2	27.197	5.413	2293385	245621075	49.8175

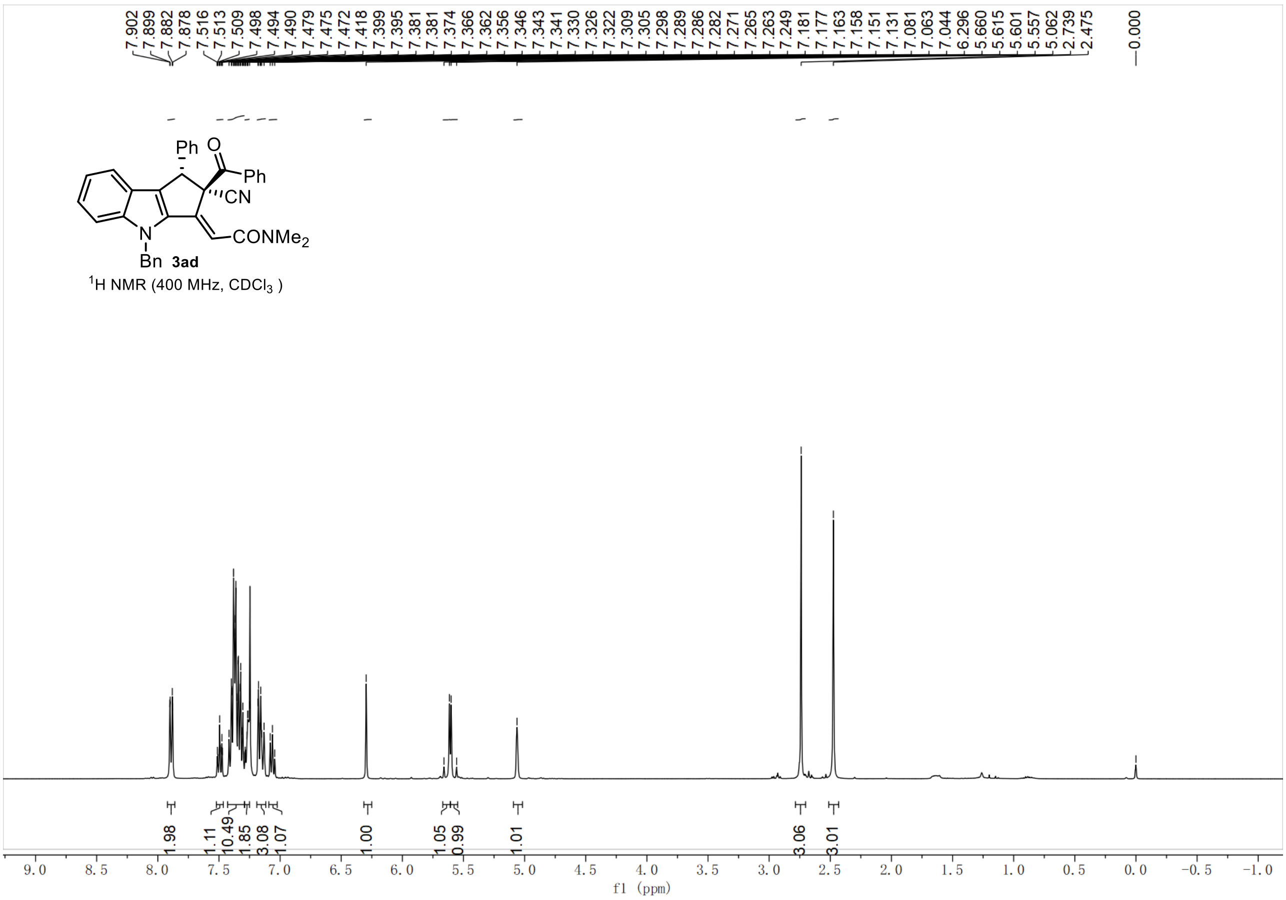


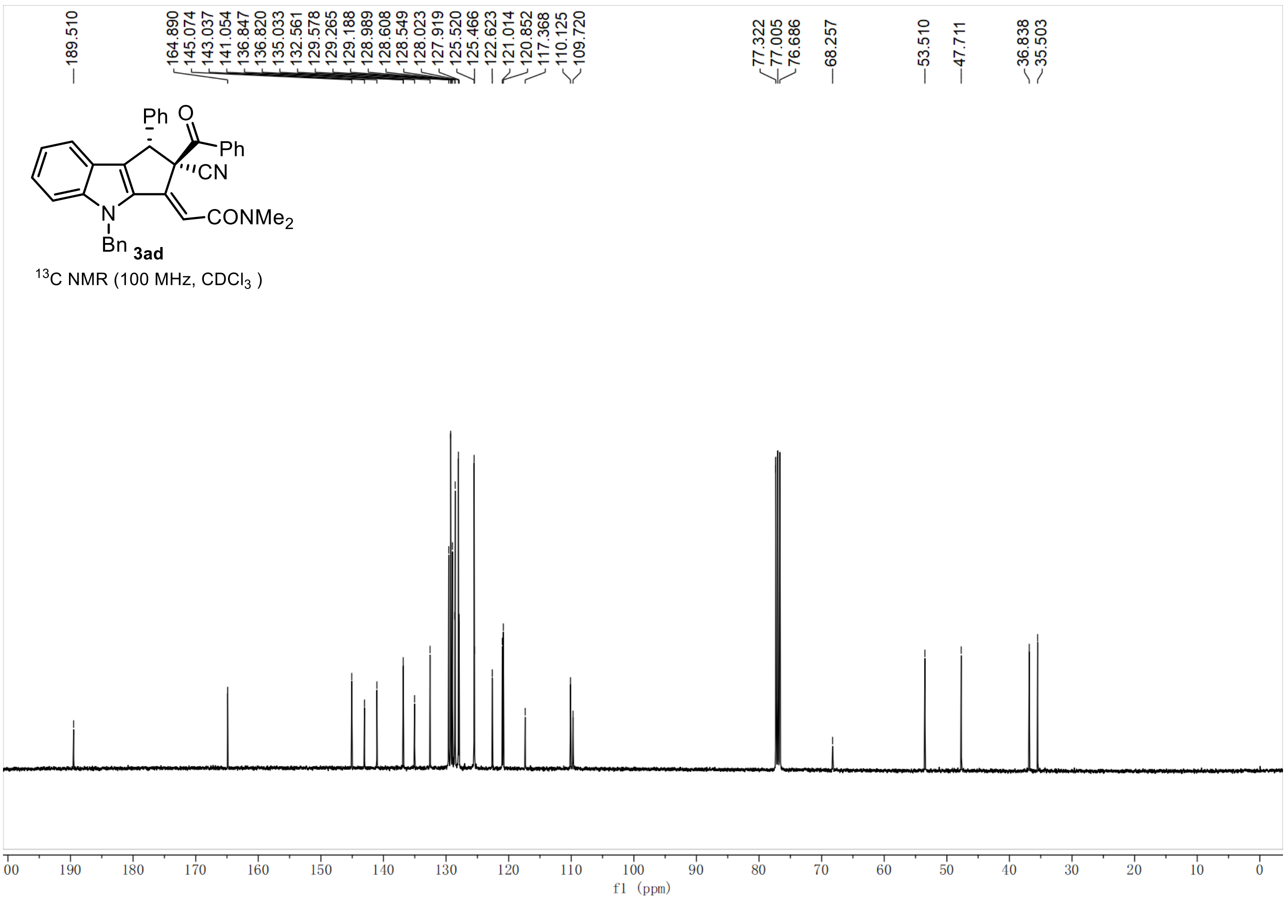
AREA PERCENT REPORT

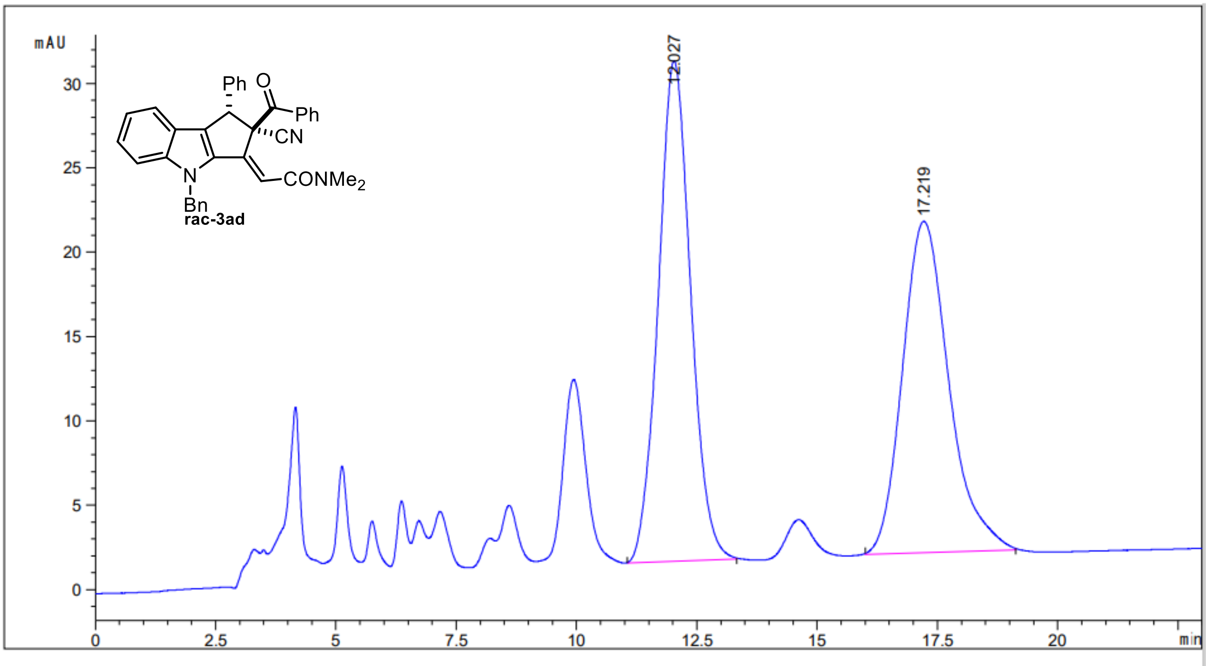
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	21.617	4.837	5933354	316584930	96.5171
2	26.967	3.653	187267	11424122	3.4829

Name	CYC-220406-54	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-54.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:45:07 AM (UTC+08:00)

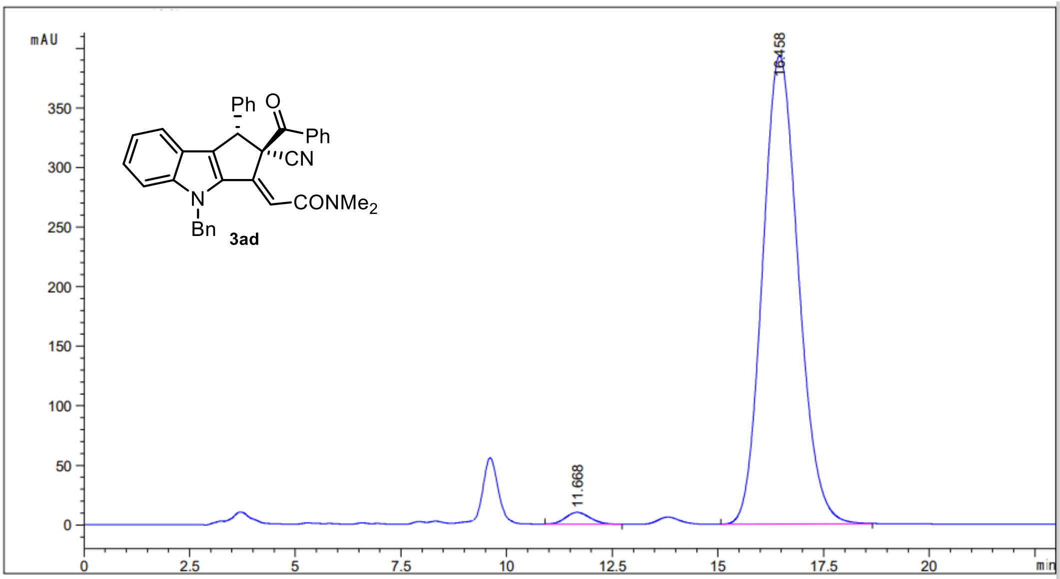



7.902 7.899 7.882 7.878 7.516 7.513 7.509 7.498 7.494 7.490 7.479 7.475 7.472 7.418 7.399 7.395 7.381 7.381 7.374 7.366 7.362 7.356 7.346 7.343 7.341 7.330 7.326 7.322 7.309 7.305 7.298 7.289 7.286 7.282 7.271 7.265 7.263 7.249 7.181 7.177 7.163 7.158 7.151 7.131 7.081 7.063 7.044 6.296 5.660 5.615 5.601 5.557 5.062 2.739 2.475
0.000
Ph
O
Ph
CN
CONMe2
N
Bn
3ad
1H NMR (400 MHz, CDCl3)
1.98 1.11 10.49 1.85 3.08 1.07 1.00 1.05 0.99 1.01 3.06 3.01
f1 (ppm)


189.510
164.890 145.074 143.037 141.054 136.847 136.820 135.033 132.561 129.578 129.265 129.188 128.989 128.608 128.549 128.023 127.919 125.520 125.466 122.623 121.014 120.852 117.368 110.125 109.720
77.322 77.005 76.686
68.257
53.510
47.711
36.838 35.503
Ph
O
Ph
CN
CONMe2
N
Bn
3ad
13C NMR (100 MHz, CDCl3)
f1 (ppm)

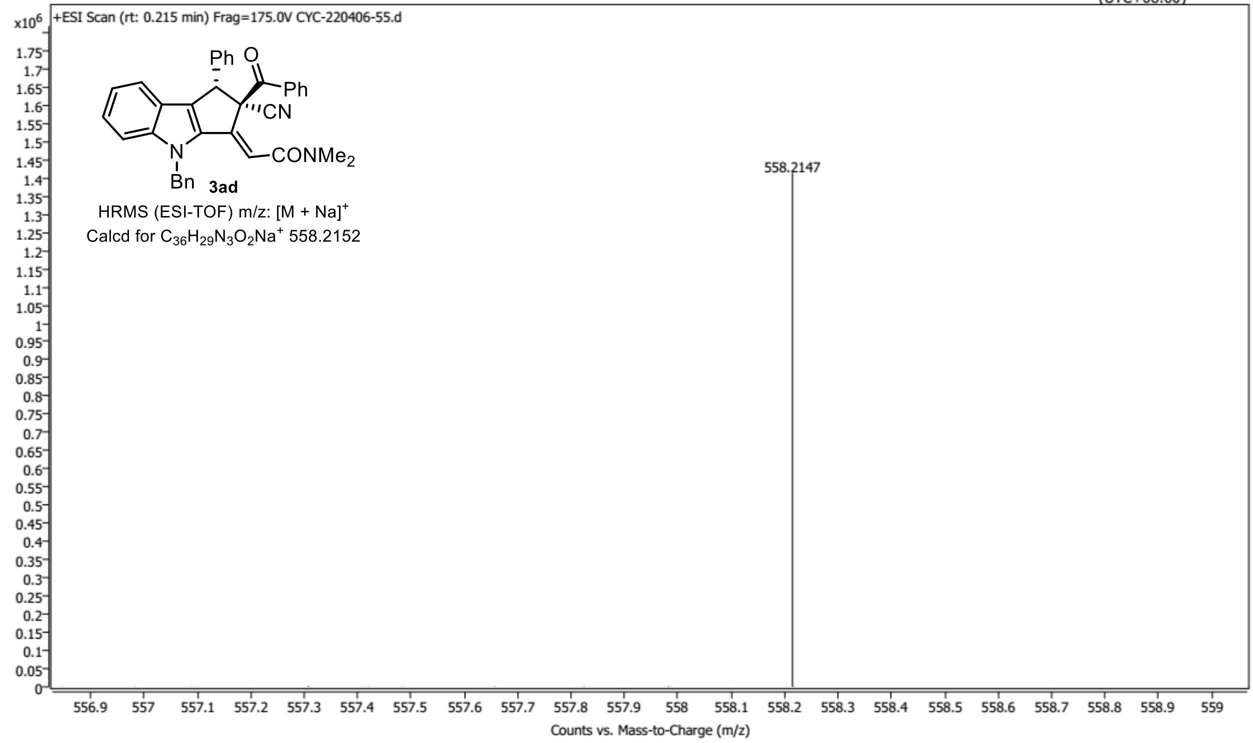


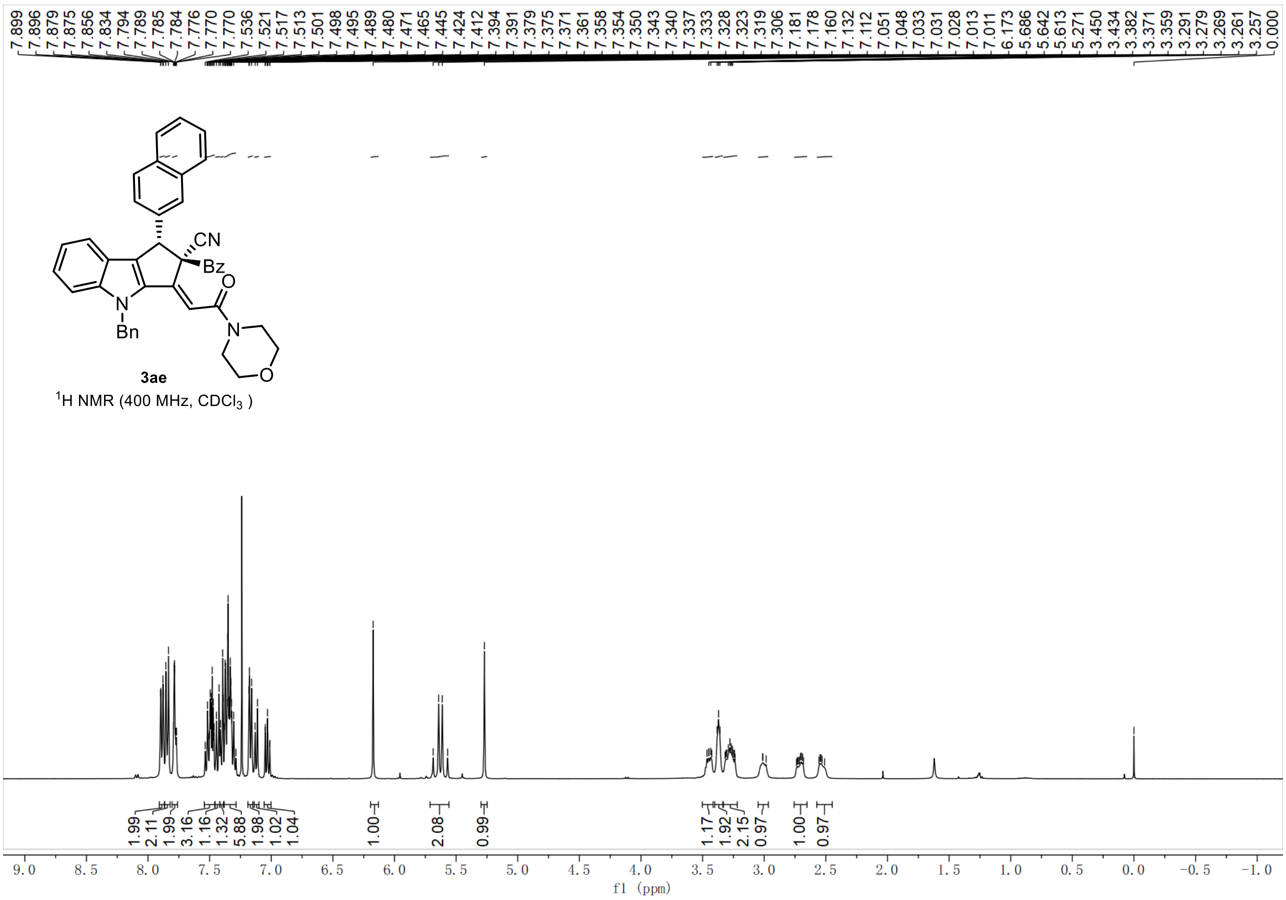
#	[min]		[min]	mAU *s	[mAU]	%
1	12.027	BB	0.7112	1385.19910	29.64283	51.2419
2	17.219	BB	0.9910	1318.05688	19.64542	48.7581

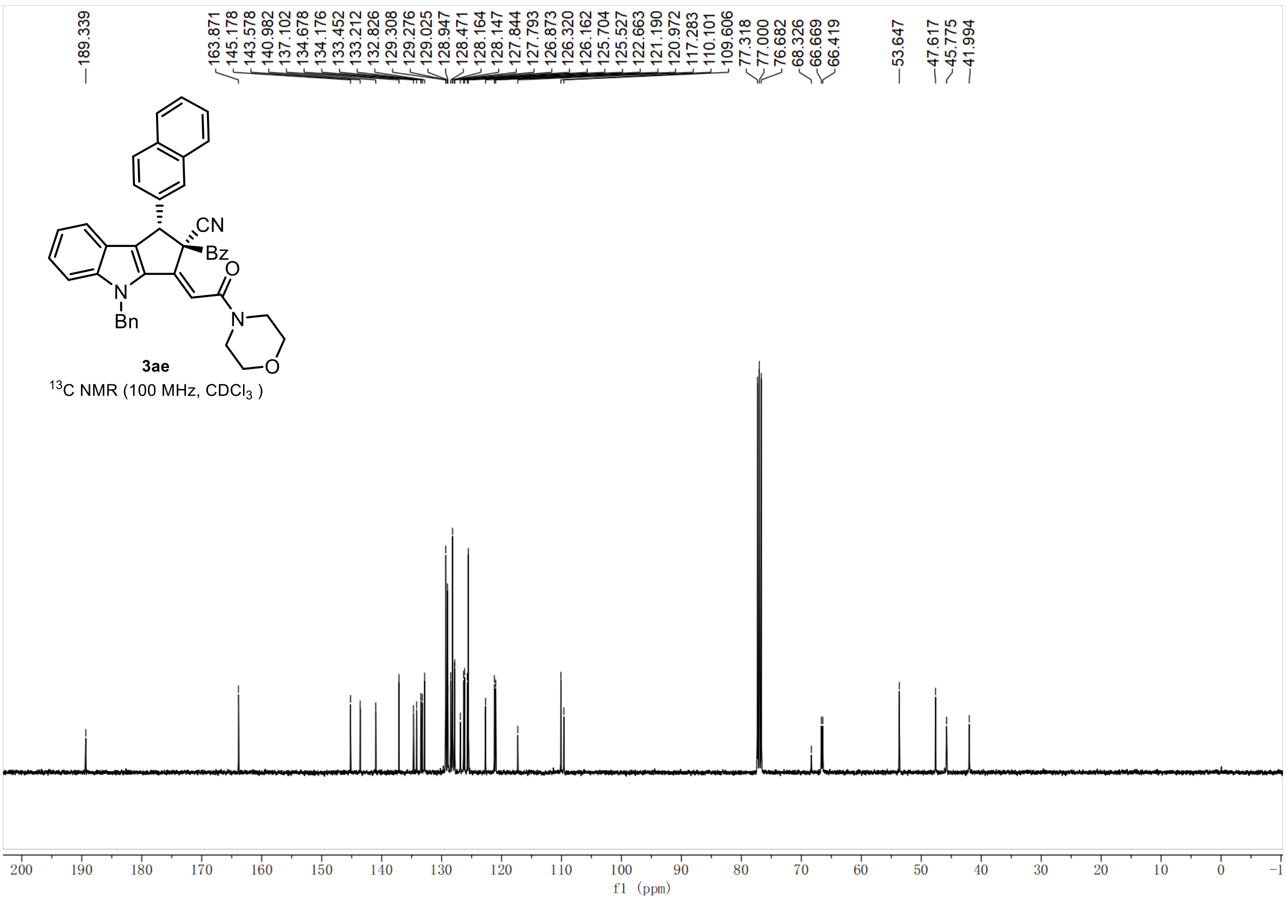


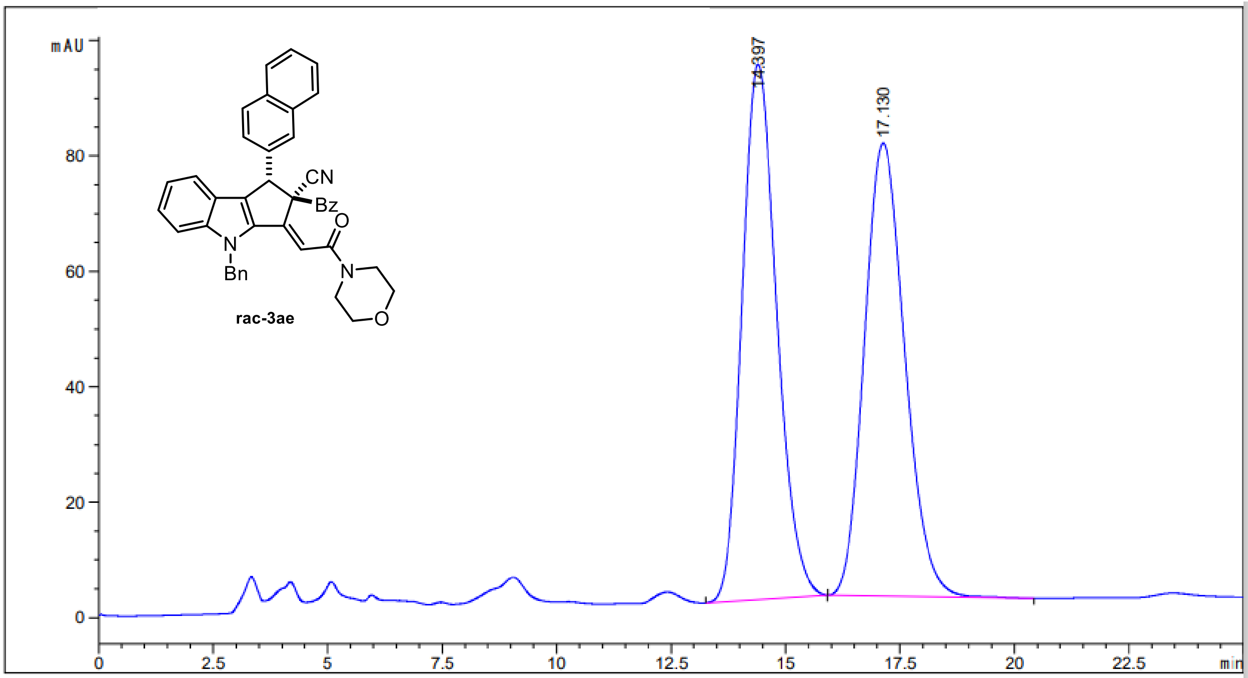
#	[min]		[min]	mAU *s	[mAU]	%
1	11.668	BB	0.6204	396.85764	9.87316	1.6882
2	16.458	BB	0.9133	2.31102e4	392.94519	98.3118

Name	CYC-220406-55	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-55.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:48:04 AM (UTC+08:00)

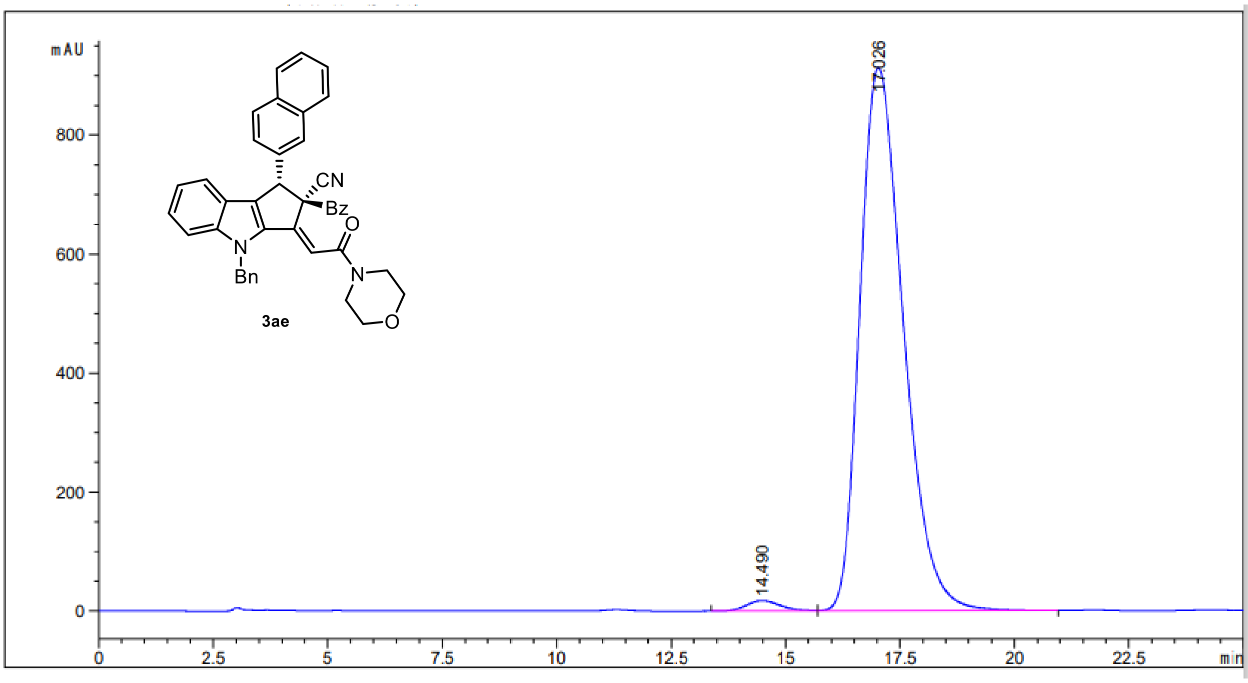



7.899 7.896 7.879 7.875 7.856 7.834 7.794 7.789 7.785 7.784 7.776 7.770 7.770 7.536 7.521 7.517 7.513 7.501 7.498 7.495 7.489 7.480 7.471 7.465 7.445 7.424 7.412 7.394 7.391 7.379 7.375 7.371 7.361 7.358 7.354 7.350 7.343 7.340 7.337 7.333 7.328 7.323 7.319 7.306 7.181 7.178 7.160 7.132 7.112 7.051 7.048 7.033 7.031 7.028 7.013 7.011 6.173 5.686 5.642 5.613 5.271 3.450 3.434 3.382 3.371 3.359 3.291 3.279 3.269 3.261 3.257 0.000
CN
Bz
O
N
Bn
N
O
3ae
1H NMR (400 MHz, CDCl3)
1.99 2.11 1.99 3.16 1.16 1.32 5.88 1.98 1.02 1.04 1.00 2.08 0.99 1.17 1.92 2.15 0.97 1.00 0.97
f1 (ppm)


189.339
163.871 145.178 143.578 140.982 137.102 134.678 134.176 133.452 133.212 132.826 129.308 129.276 129.025 128.947 128.471 128.164 128.147 127.844 127.793 126.873 126.320 126.162 125.704 125.527 122.663 121.190 120.972 117.283 110.101 109.606 77.318 77.000 76.682 68.326 66.669 66.419
53.647
47.617 45.775 41.994
CN
Bz
O
N
Bn
N
O
3ae
13C NMR (100 MHz, CDCl3)
f1 (ppm)

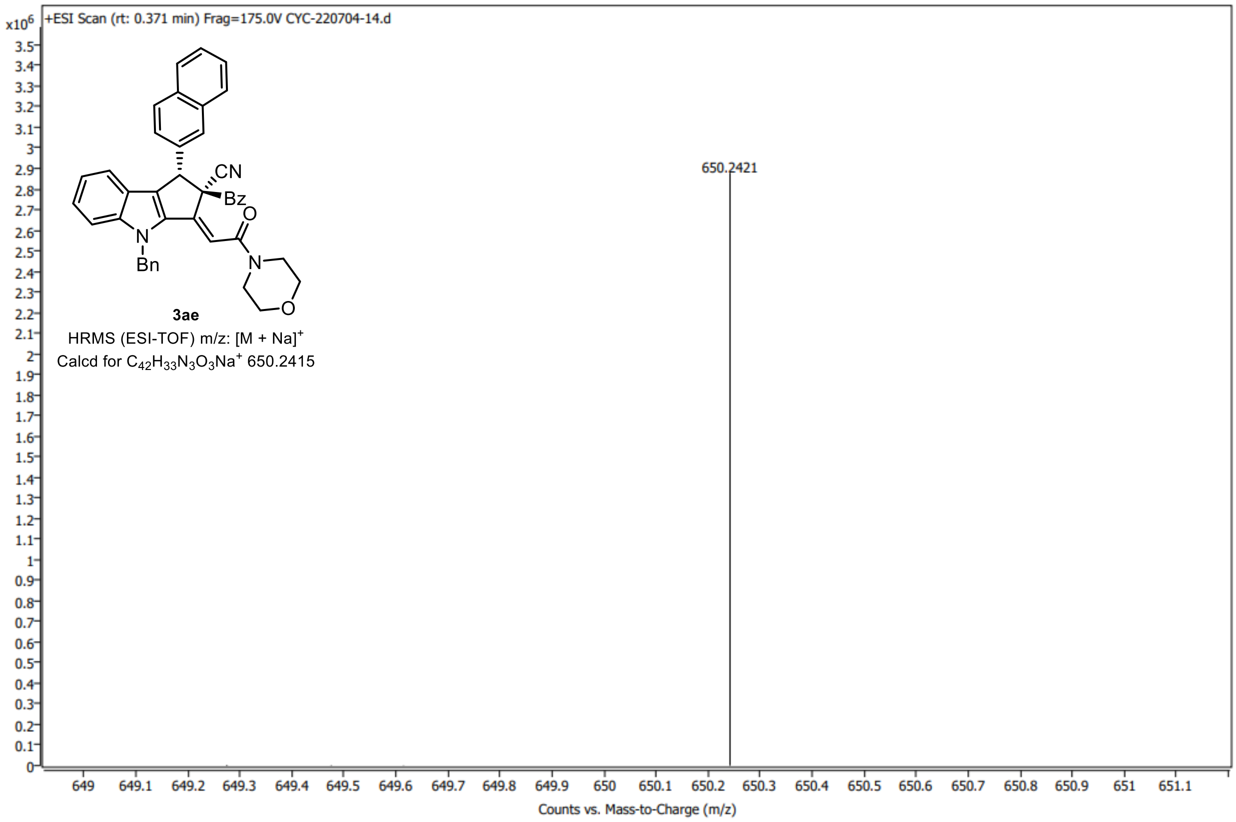


#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.397	BB	0.8171	4889.56006	92.80397	50.3535
2	17.130	BB	0.9563	4820.90869	78.54870	49.6465



#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.490	BV	0.8138	945.61395	17.87238	1.5463
2	17.026	VB	1.0198	6.02094e4	913.04218	98.4537

User Spectrum Plot Report



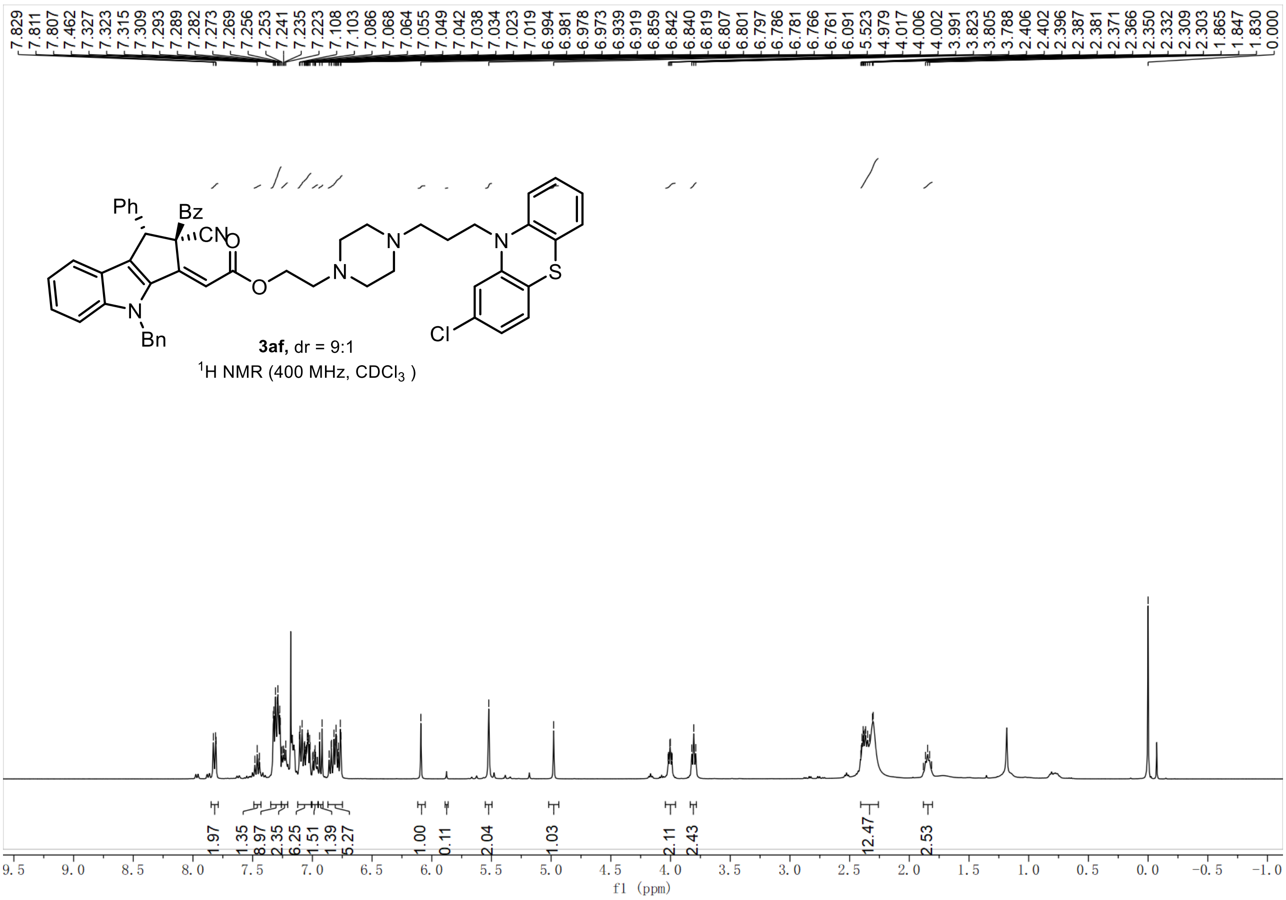
3ae

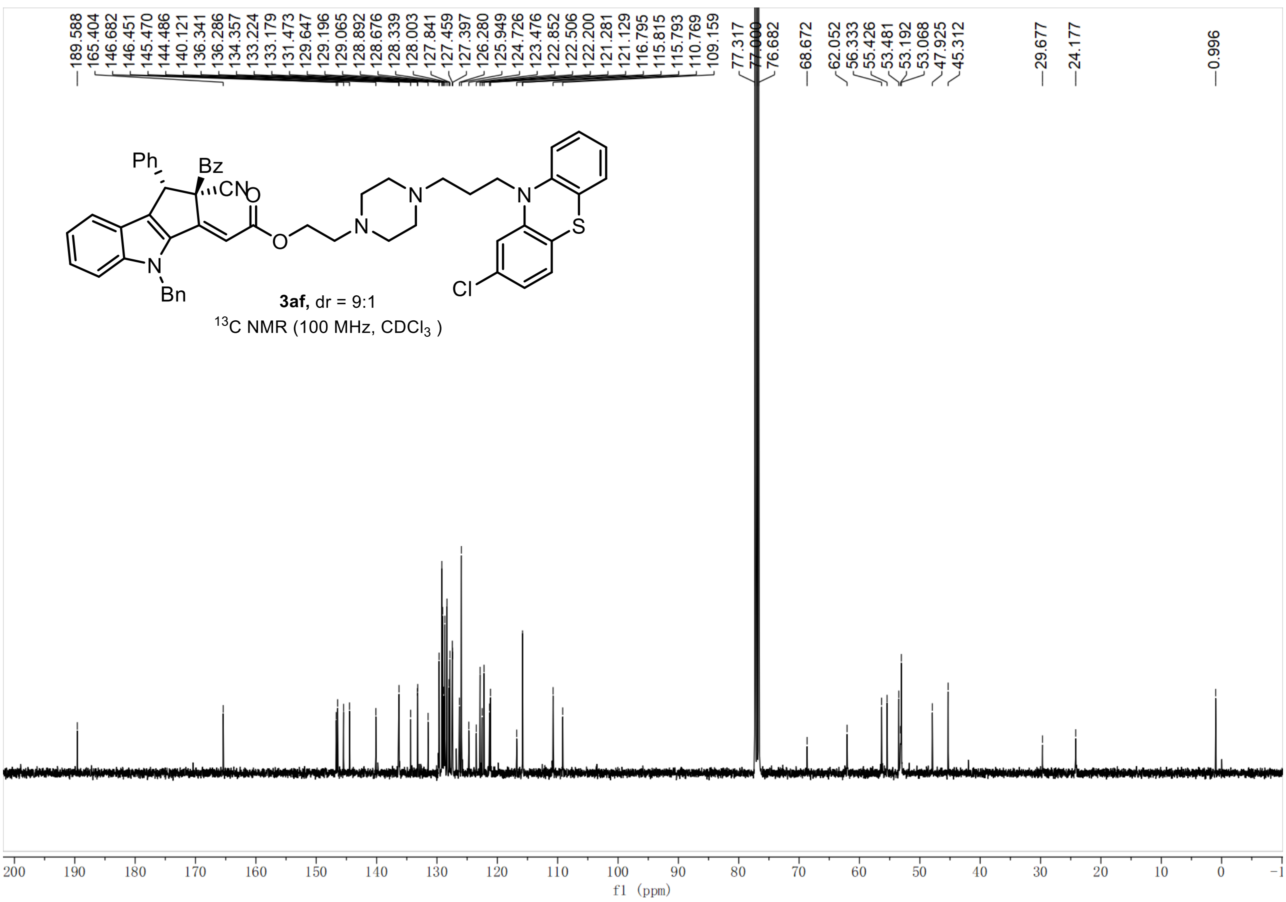
HRMS (ESI-TOF) m/z: $[M + Na]^+$

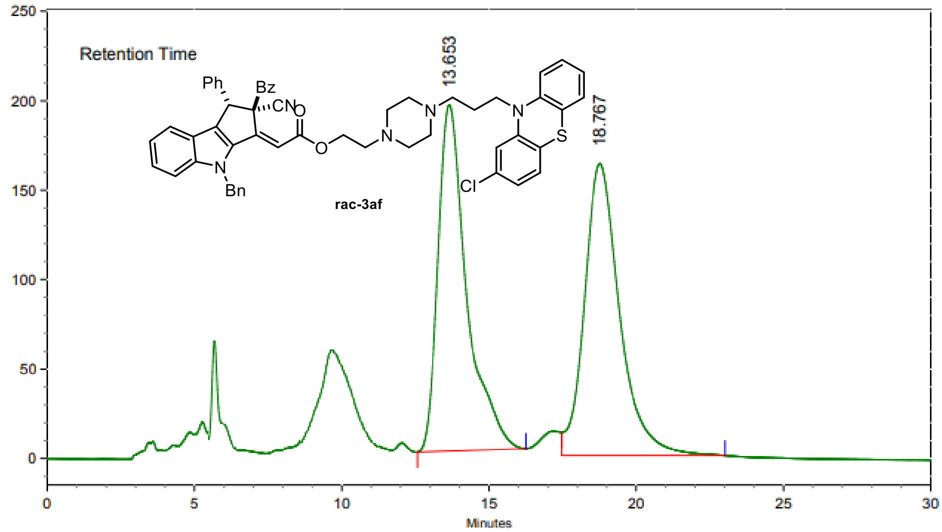
Calcd for $C_{42}H_{33}N_3O_3Na^+$ 650.2415

Page 1 of 1

Generated at 4:54 PM on 7/6/2022

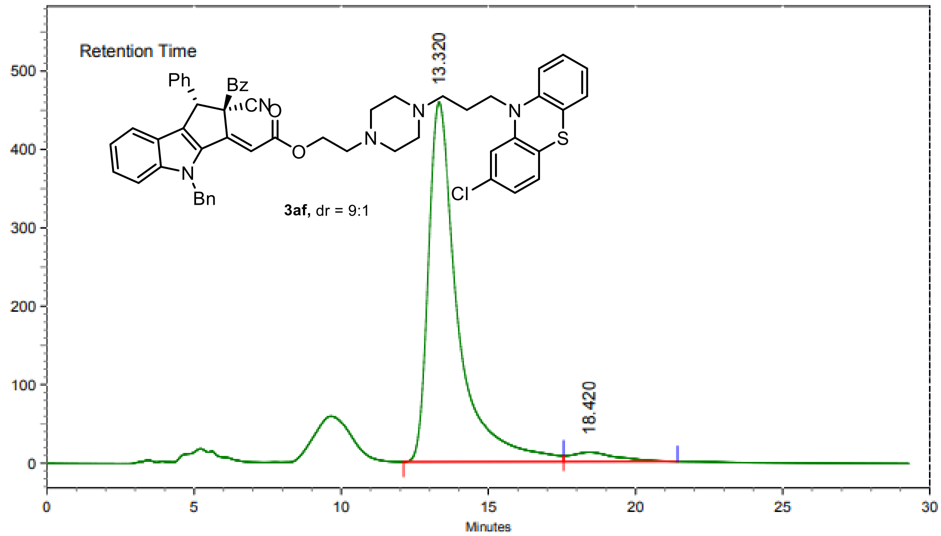

7.829 7.811 7.807 7.462 7.327 7.323 7.315 7.309 7.293 7.289 7.282 7.273 7.269 7.256 7.253 7.241 7.235 7.223 7.108 7.103 7.086 7.068 7.064 7.055 7.049 7.042 7.038 7.034 7.023 7.019 6.994 6.981 6.978 6.973 6.939 6.919 6.859 6.842 6.840 6.819 6.807 6.801 6.797 6.786 6.781 6.766 6.761 6.091 5.523 4.979 4.017 4.006 4.002 3.991 3.823 3.805 3.788 2.406 2.402 2.396 2.387 2.381 2.371 2.366 2.350 2.332 2.309 2.303 1.865 1.847 1.830 0.000
Ph
Bz
CN
O
O
N
N
N
S
N
Bn
Cl
3af, dr = 9:1
^{1}H NMR (400 MHz, $CDCl_3$)
1.97 1.35 8.97 2.35 6.25 1.51 1.39 5.27 1.00 0.11 2.04 1.03 2.11 2.43 12.47 2.53
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


189.588 165.404 146.682 146.451 145.470 144.486 140.121 136.341 136.286 134.357 133.224 133.179 131.473 129.647 129.196 129.065 128.892 128.676 128.339 128.003 127.841 127.459 127.397 126.280 125.949 124.726 123.476 122.852 122.506 122.200 121.281 121.129 116.795 115.815 115.793 110.769 109.159 77.317 77.000 76.682 68.672 62.052 56.333 55.426 53.481 53.192 53.068 47.925 45.312 29.677 24.177 0.996
Ph
Bz
CN
O
O
N
N
N
S
N
Bn
Cl
3af, dr = 9:1
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



AREA PERCENT REPORT

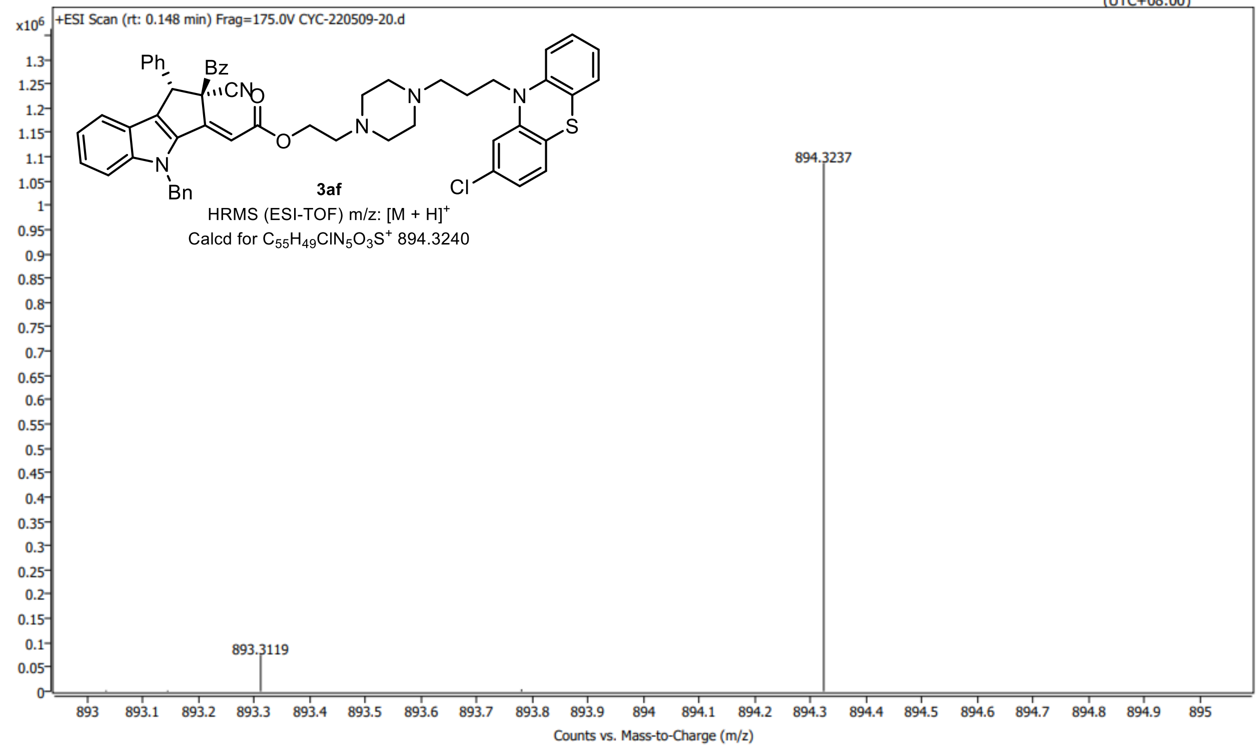
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.653	3.690	3247868	219235294	49.0299
2	18.767	5.547	2735948	227910397	50.9701

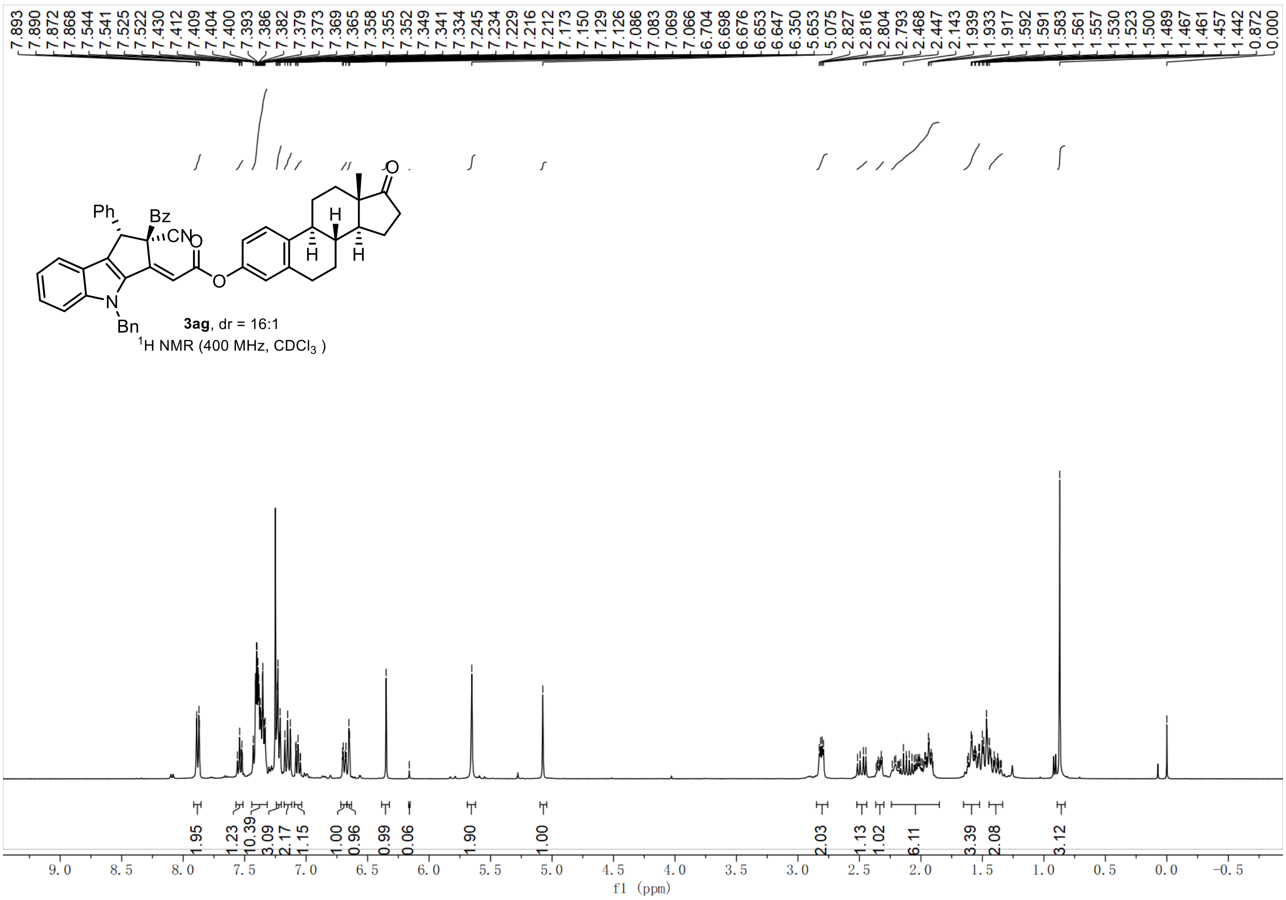


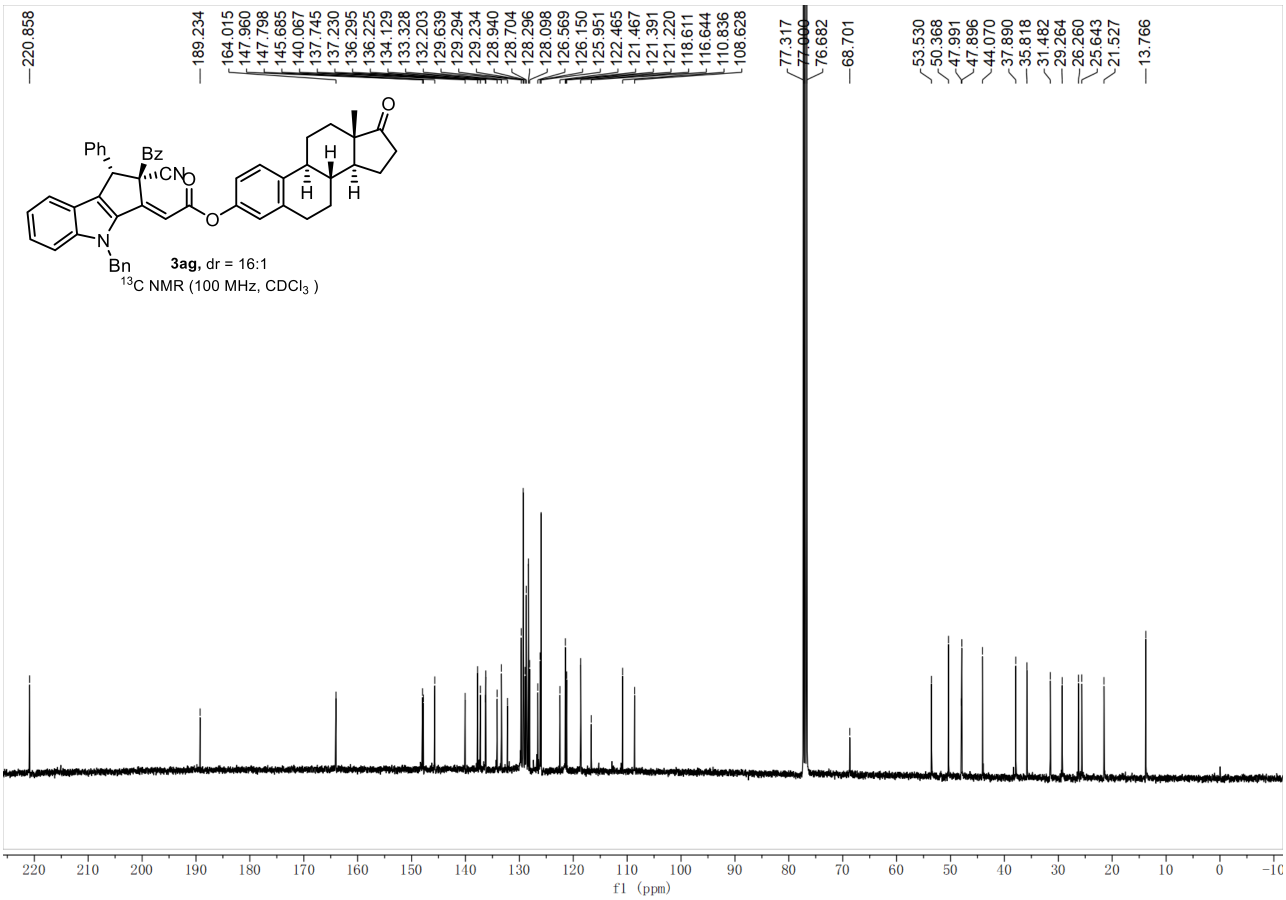
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.320	5.437	7686765	533953003	96.1849
2	18.420	3.873	198602	21178873	3.8151

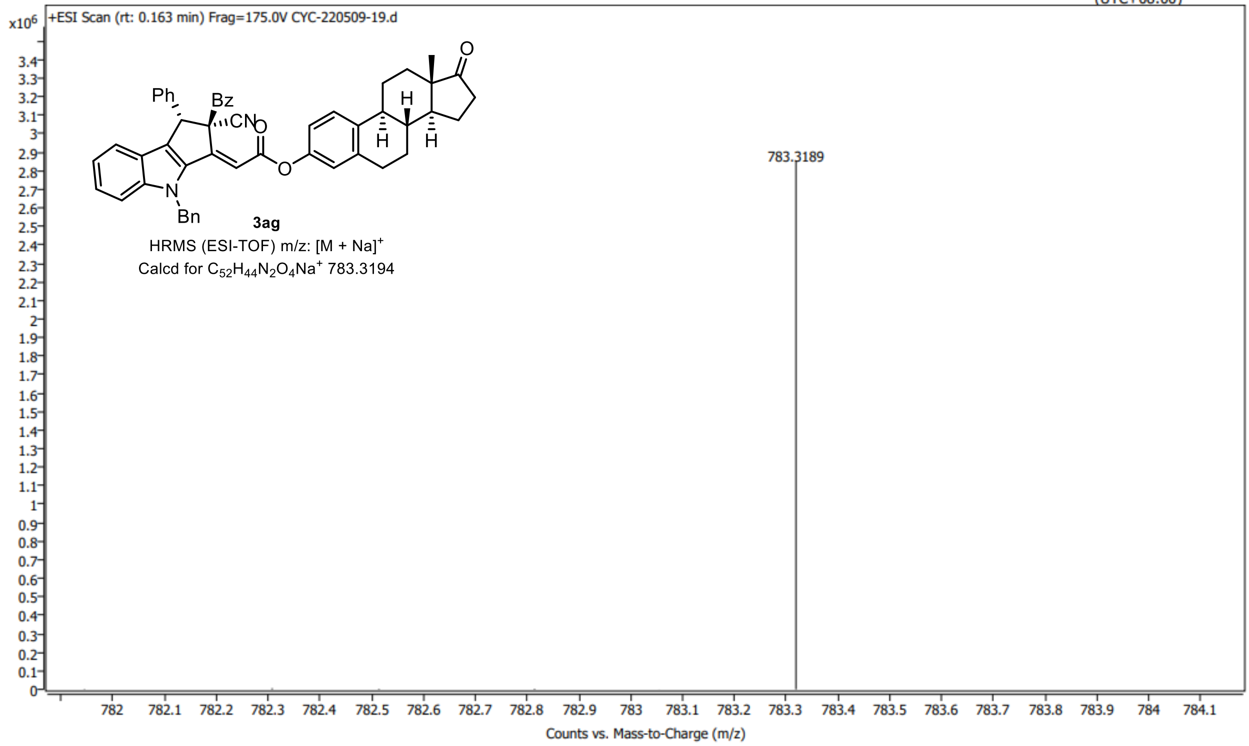
Name	CYC-220509-20	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220509-20.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	5/11/2022 5:06:42 PM (UTC+08:00)

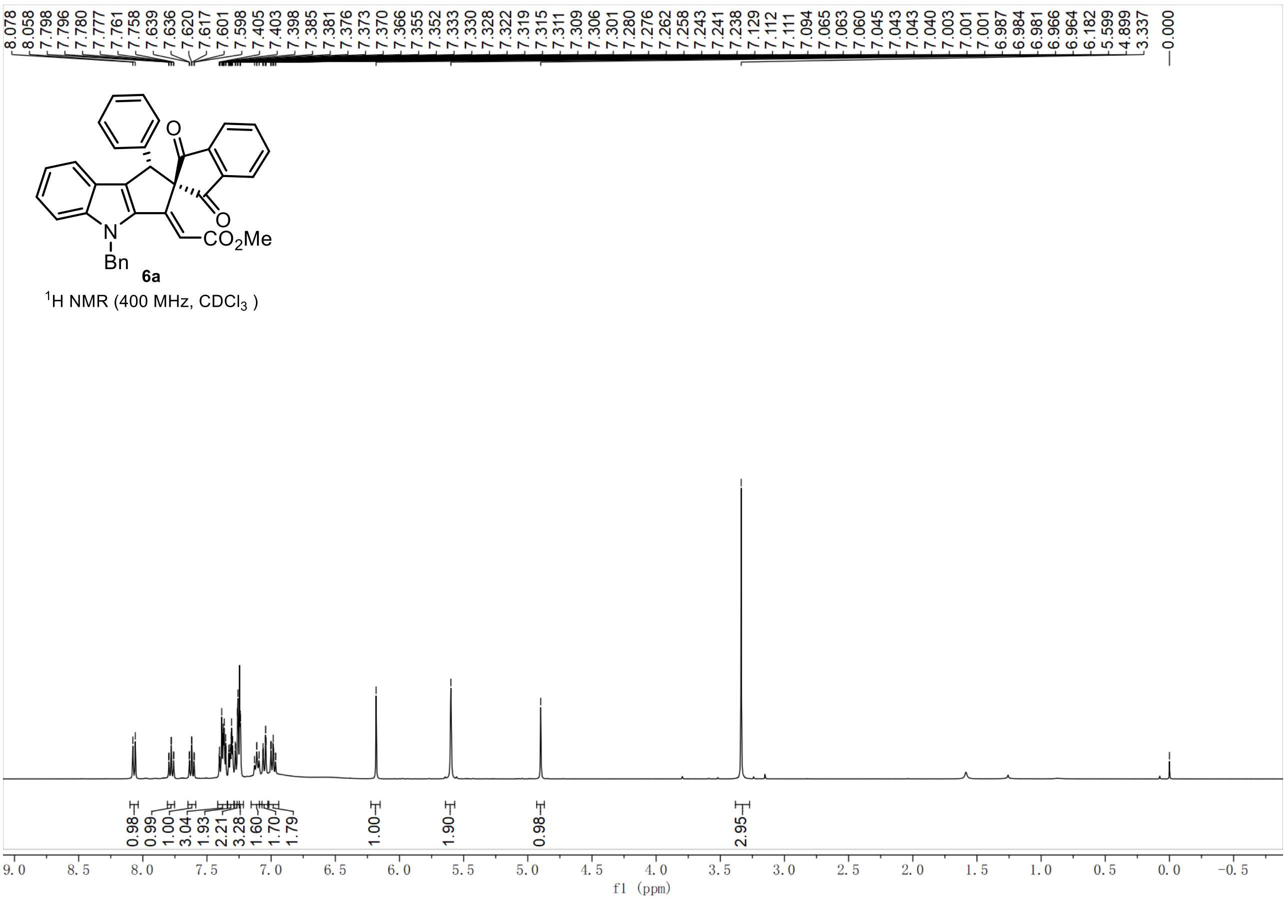


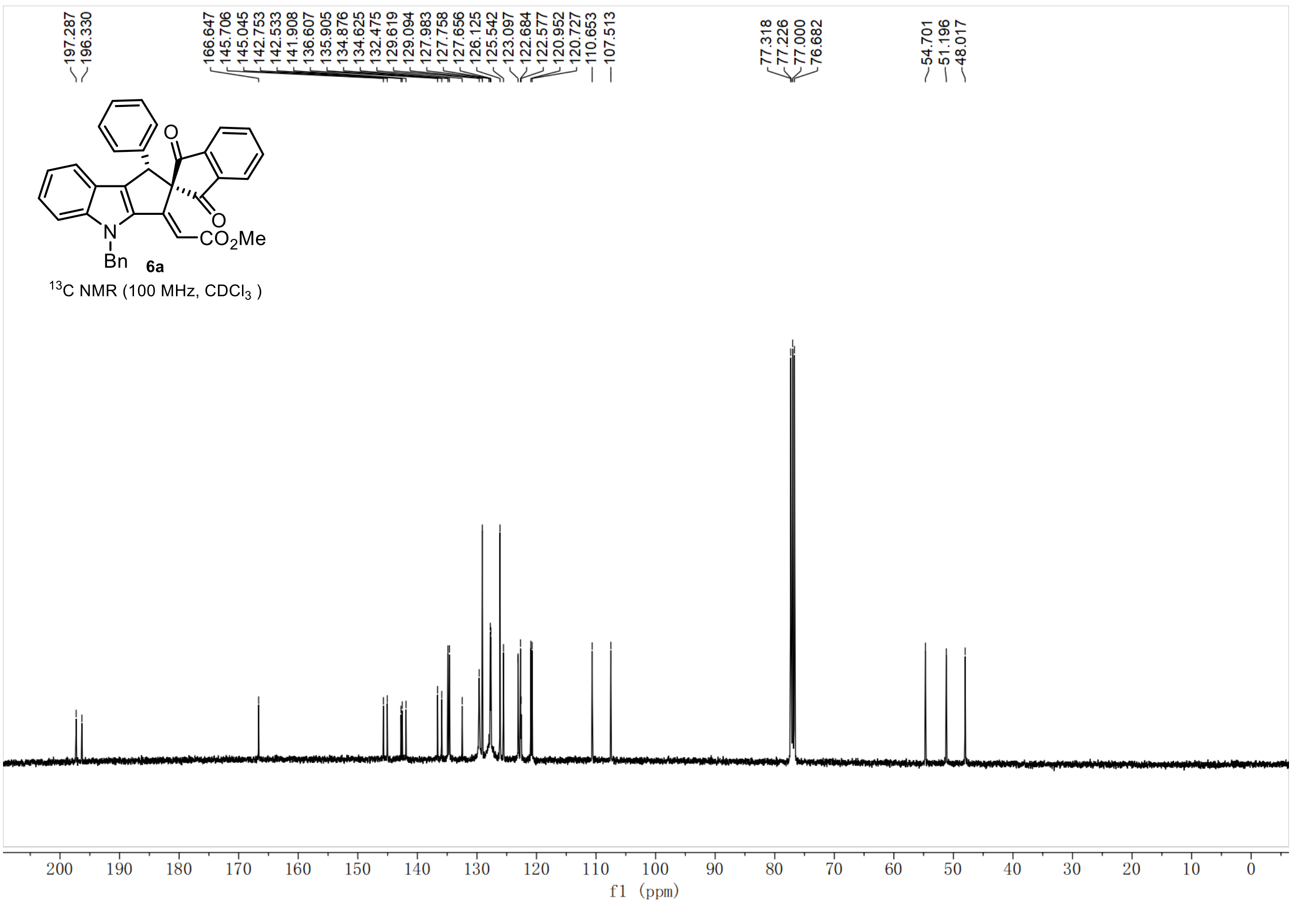

7.893 7.890 7.872 7.868 7.544 7.541 7.525 7.522 7.430 7.412 7.409 7.404 7.400 7.393 7.386 7.382 7.379 7.373 7.369 7.365 7.358 7.355 7.352 7.349 7.341 7.334 7.245 7.234 7.229 7.216 7.212 7.173 7.150 7.129 7.126 7.086 7.083 7.069 7.066 6.704 6.698 6.676 6.653 6.647 6.350 5.653 5.075 2.827 2.816 2.804 2.793 2.468 2.447 2.143 1.939 1.933 1.917 1.592 1.591 1.583 1.561 1.557 1.530 1.523 1.500 1.489 1.467 1.461 1.457 1.442 0.872 0.000
Ph
Bz
CN
O
N
Bn
O
H
H
H
O
3ag, dr = 16:1
1H NMR (400 MHz, CDCl3)
1.95 1.23 10.39 3.09 2.17 1.15 1.00 0.96 0.99 0.06 1.90 1.00 2.03 1.13 1.02 6.11 3.39 2.08 3.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

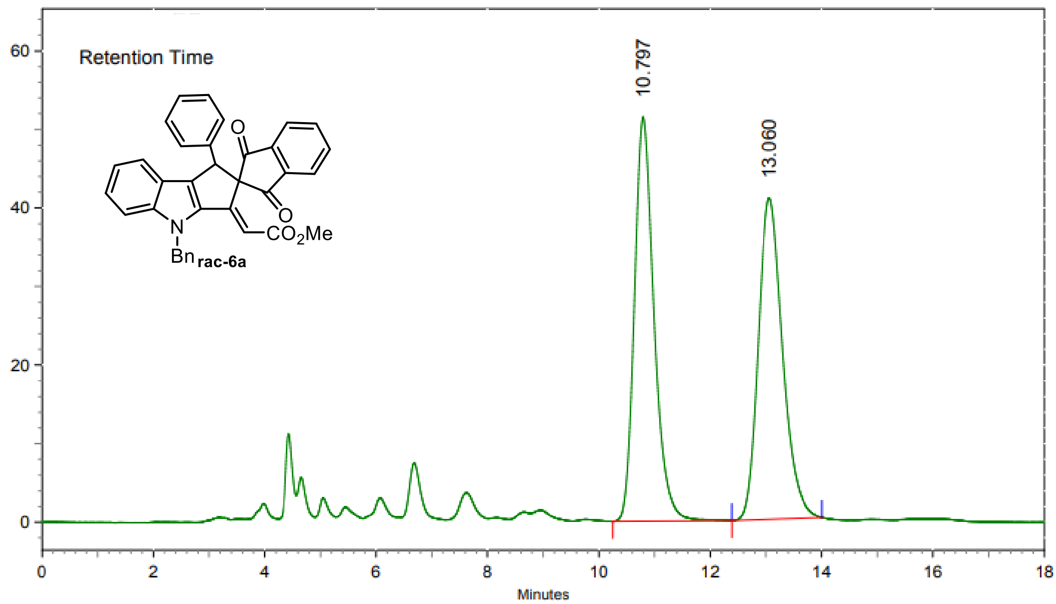

220.858 189.234 164.015 147.960 147.798 145.685 140.067 137.745 137.230 136.295 136.225 134.129 133.328 132.203 129.639 129.294 129.234 128.940 128.704 128.296 128.098 126.569 126.150 125.951 122.465 121.467 121.391 121.220 118.611 116.644 110.836 108.628 77.317 77.000 76.682 68.701 53.530 50.368 47.991 47.896 44.070 37.890 35.818 31.482 29.264 26.260 25.643 21.527 13.766
Ph
Bz
CN
O
N
Bn
O
H
H
H
O
3ag, dr = 16:1
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Name	CYC-220509-19	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220509-19.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	5/11/2022 5:03:45 PM (UTC+08:00)




8.078
8.058
7.798
7.796
7.780
7.777
7.761
7.758
7.639
7.636
7.620
7.617
7.601
7.598
7.405
7.403
7.398
7.385
7.381
7.376
7.373
7.370
7.366
7.355
7.352
7.333
7.330
7.328
7.322
7.319
7.315
7.311
7.309
7.306
7.301
7.280
7.276
7.262
7.258
7.243
7.241
7.238
7.129
7.112
7.111
7.094
7.065
7.063
7.060
7.045
7.043
7.043
7.040
7.003
7.001
7.001
6.987
6.984
6.981
6.966
6.964
6.182
5.599
4.899
3.337
0.000
O
O
N
Bn
CO2Me
6a
1H NMR (400 MHz, CDCl3)
0.98
0.99
1.00
3.04
1.93
2.21
3.28
1.60
1.70
1.79
1.00
1.90
0.98
2.95
f1 (ppm)


197.287
196.330
166.647
145.706
145.045
142.753
142.533
141.908
136.607
135.905
134.876
134.625
132.475
129.619
129.094
127.983
127.758
127.656
126.125
125.542
123.097
122.684
122.577
120.952
120.727
110.653
107.513
77.318
77.226
77.000
76.682
54.701
51.196
48.017
O
O
N
Bn
CO2Me
6a
13C NMR (100 MHz, CDCl3)
f1 (ppm)



AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
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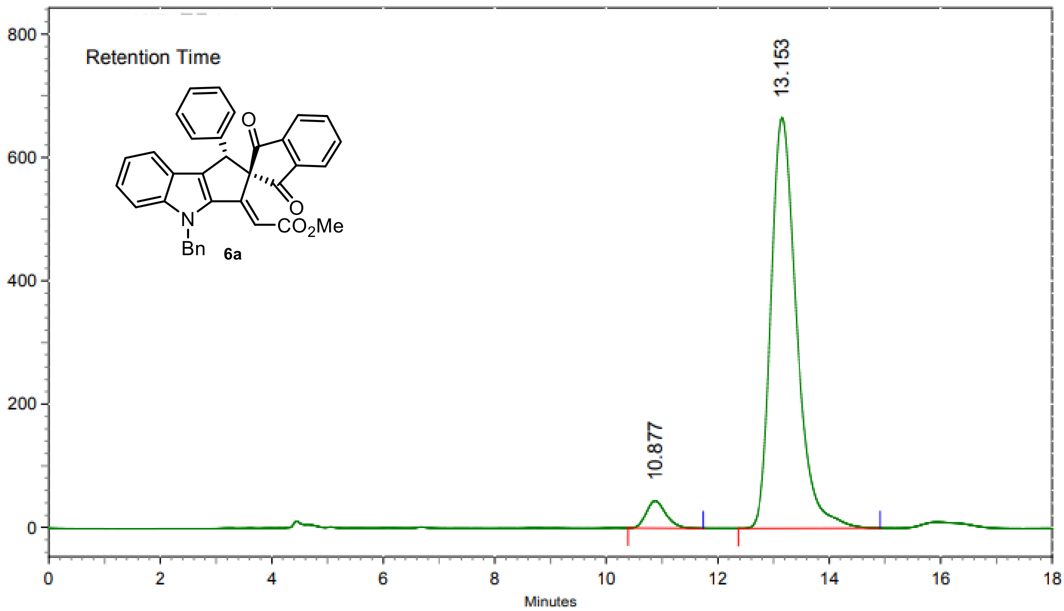
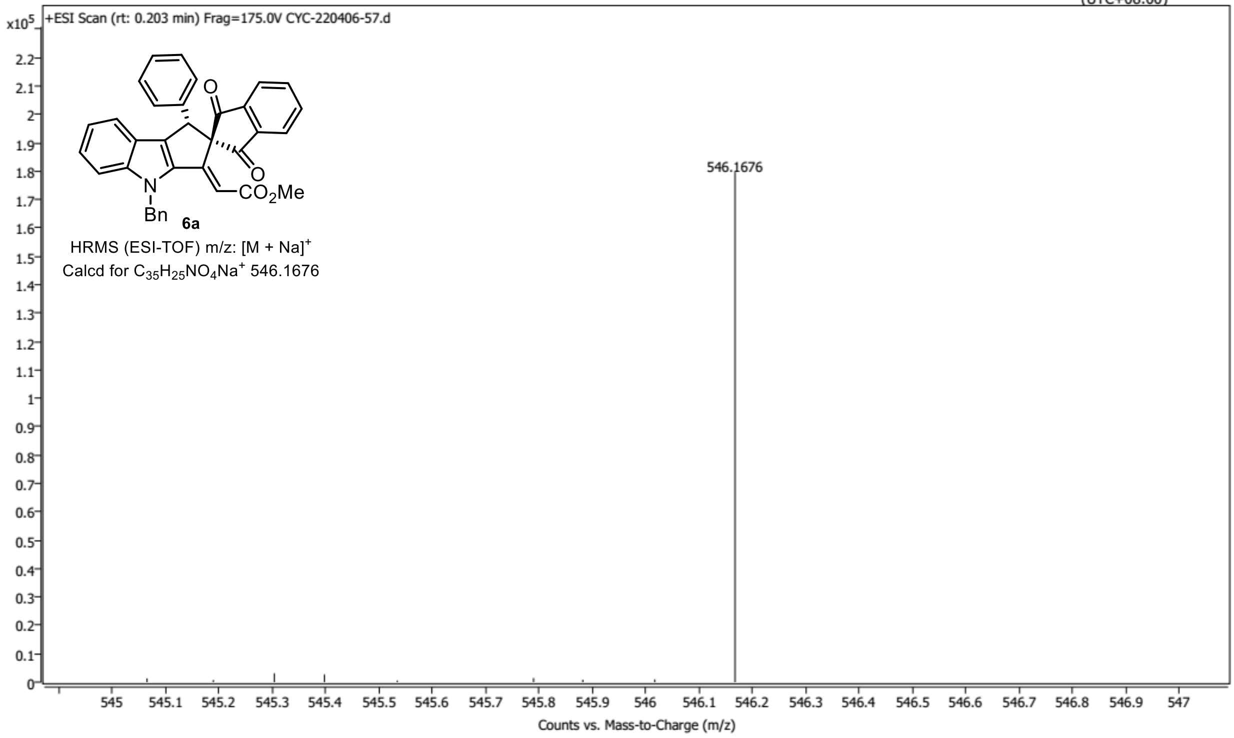
2	13.060	1.613	686538	20787199	49.4079

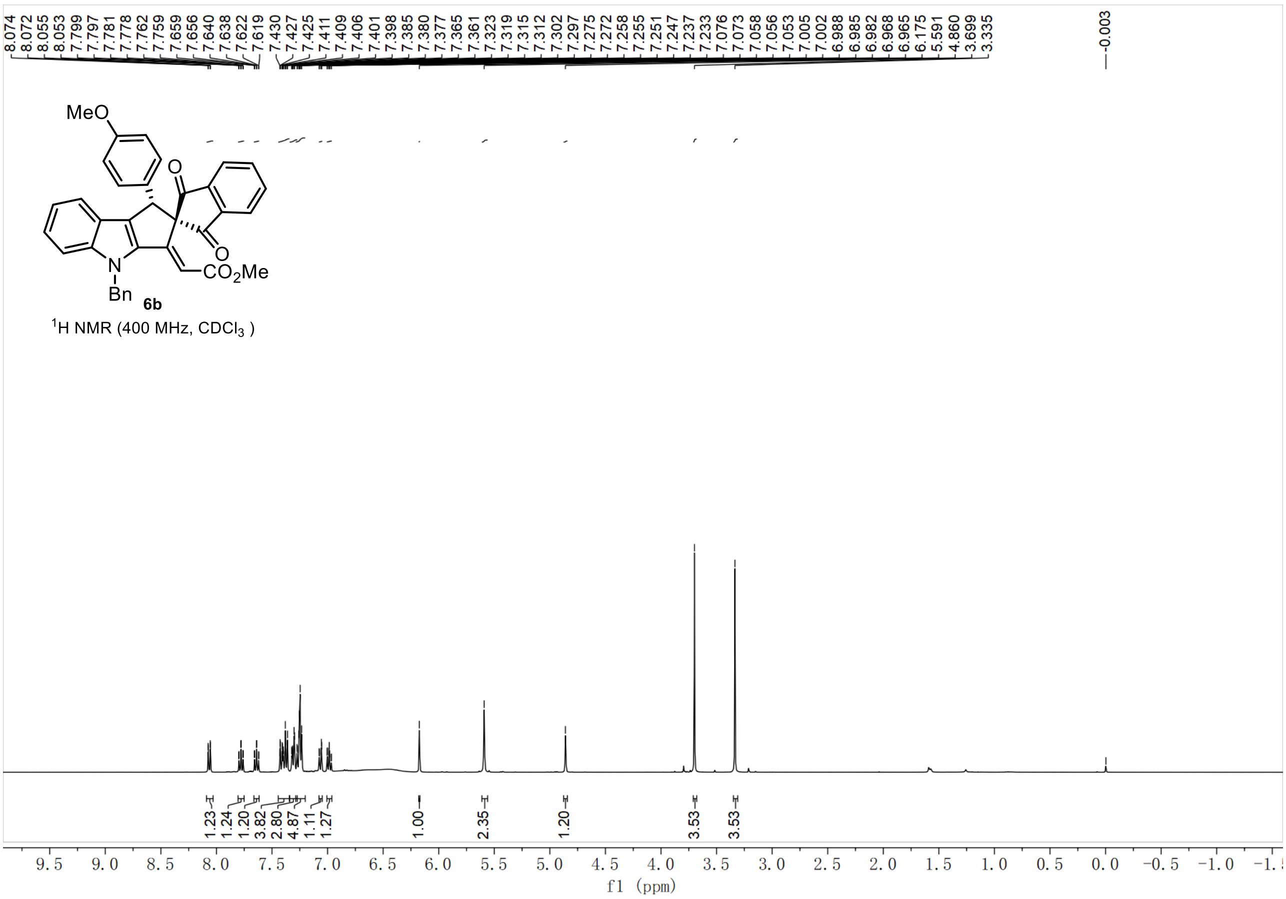


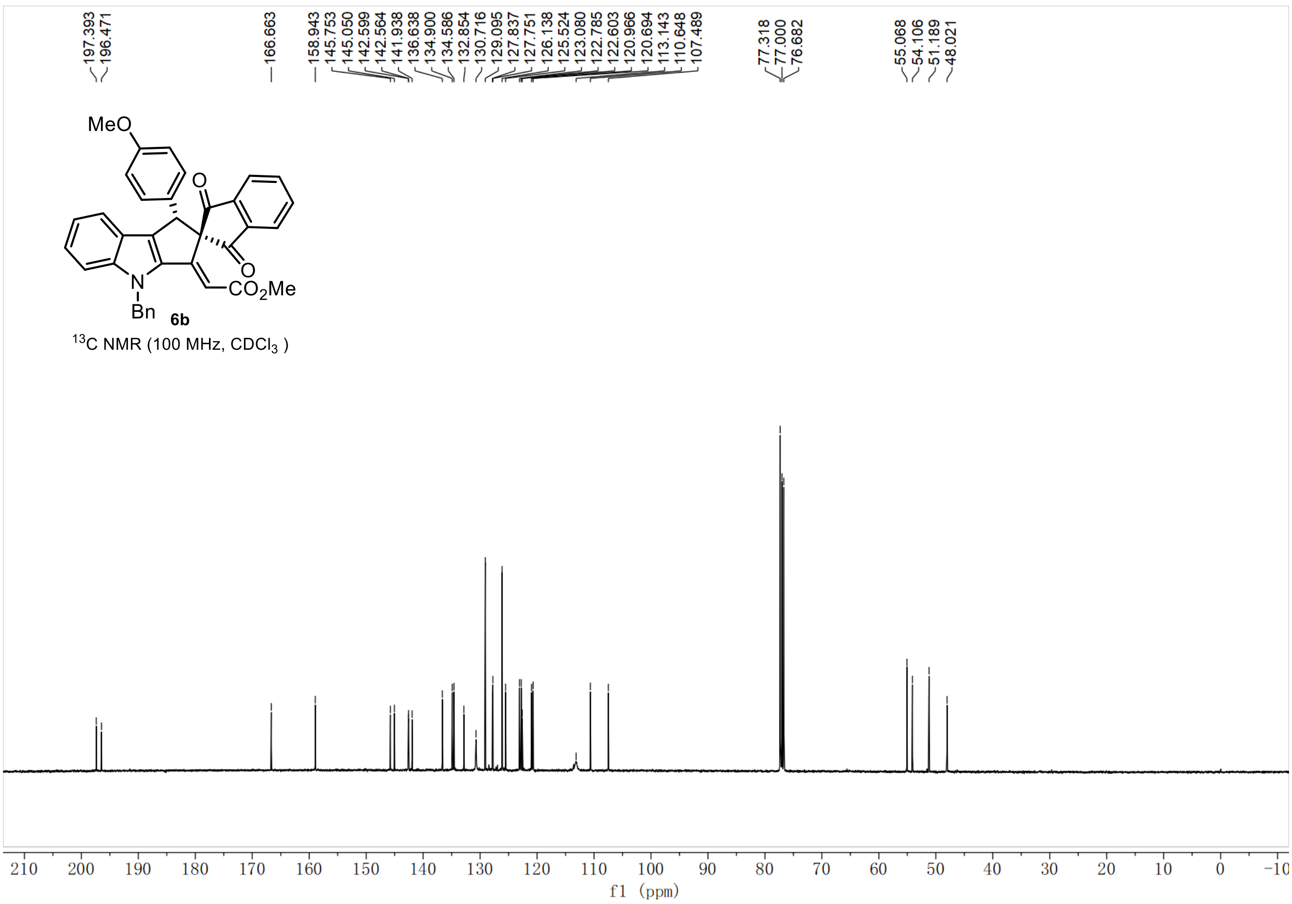
AREA PERCENT REPORT

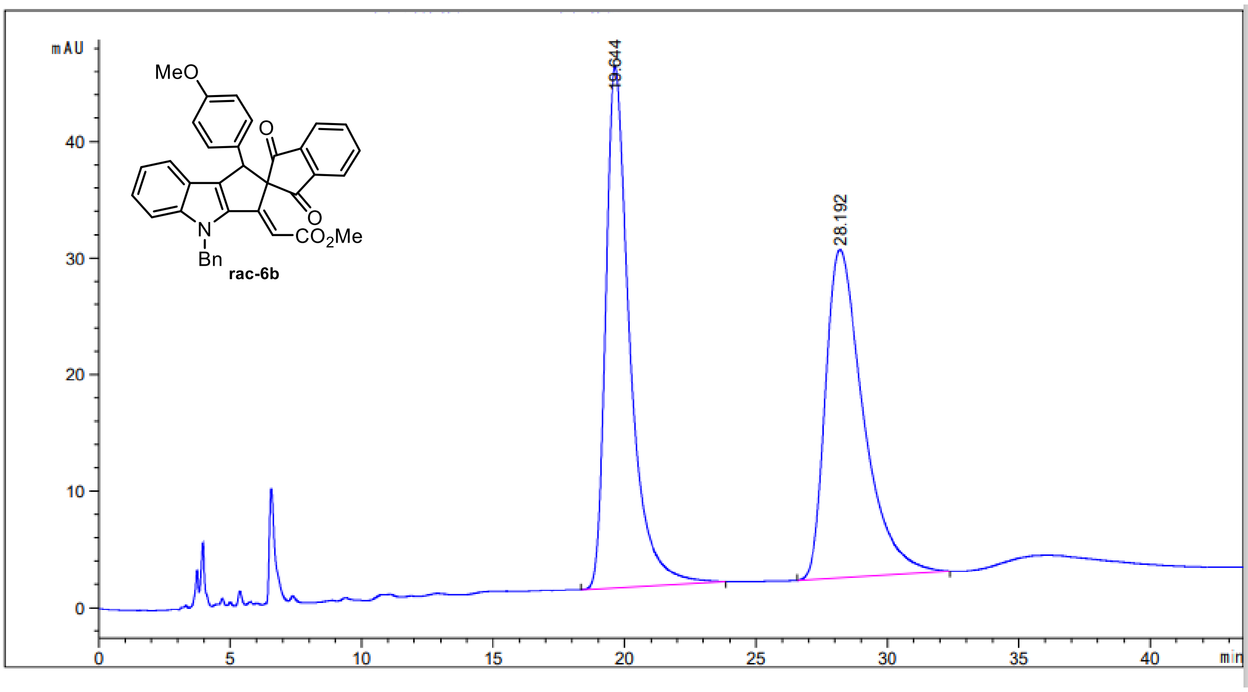
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.877	1.350	746160	18234744	4.8699
2	13.153	2.543	11176580	356199763	95.1301

Name	CYC-220406-57	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-57.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:53:58 AM (UTC+08:00)

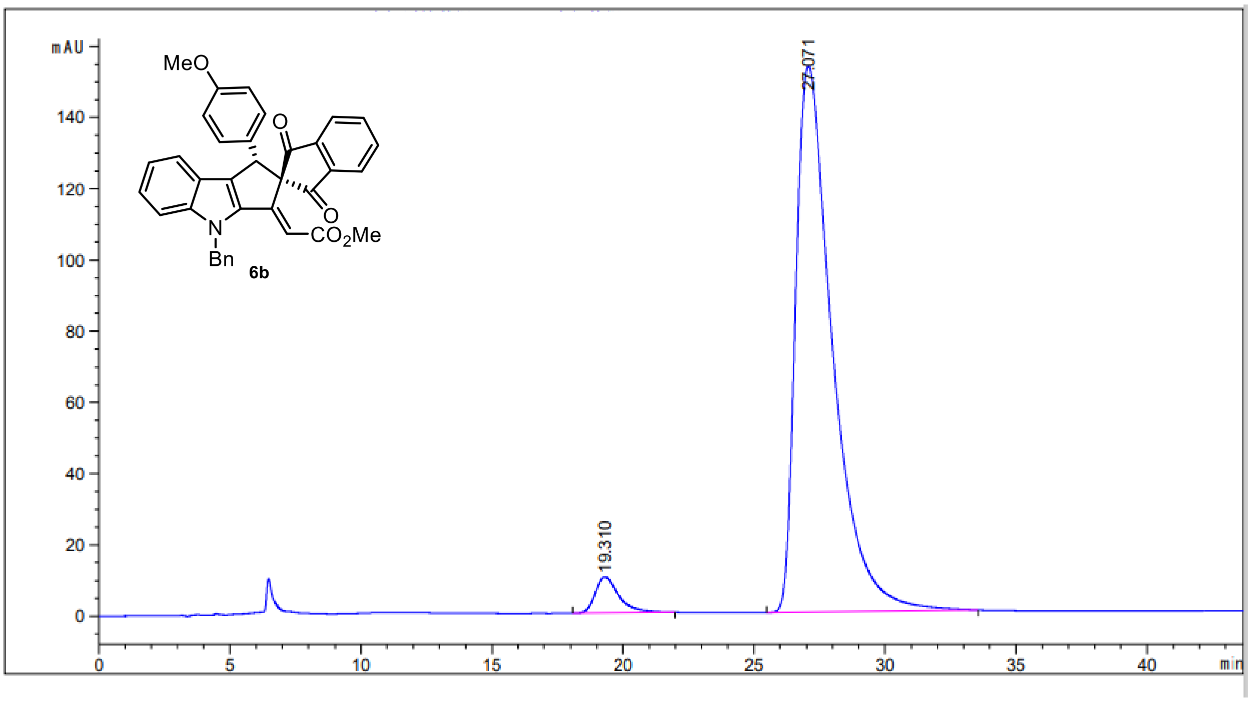






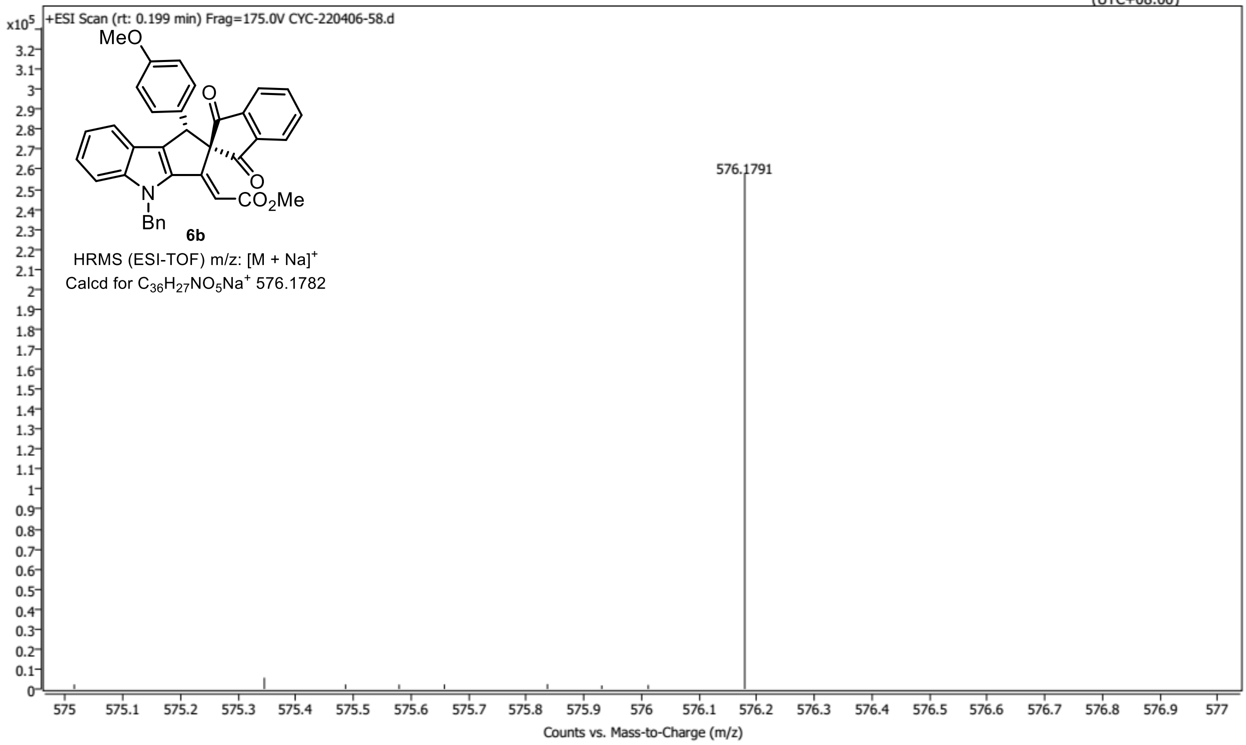


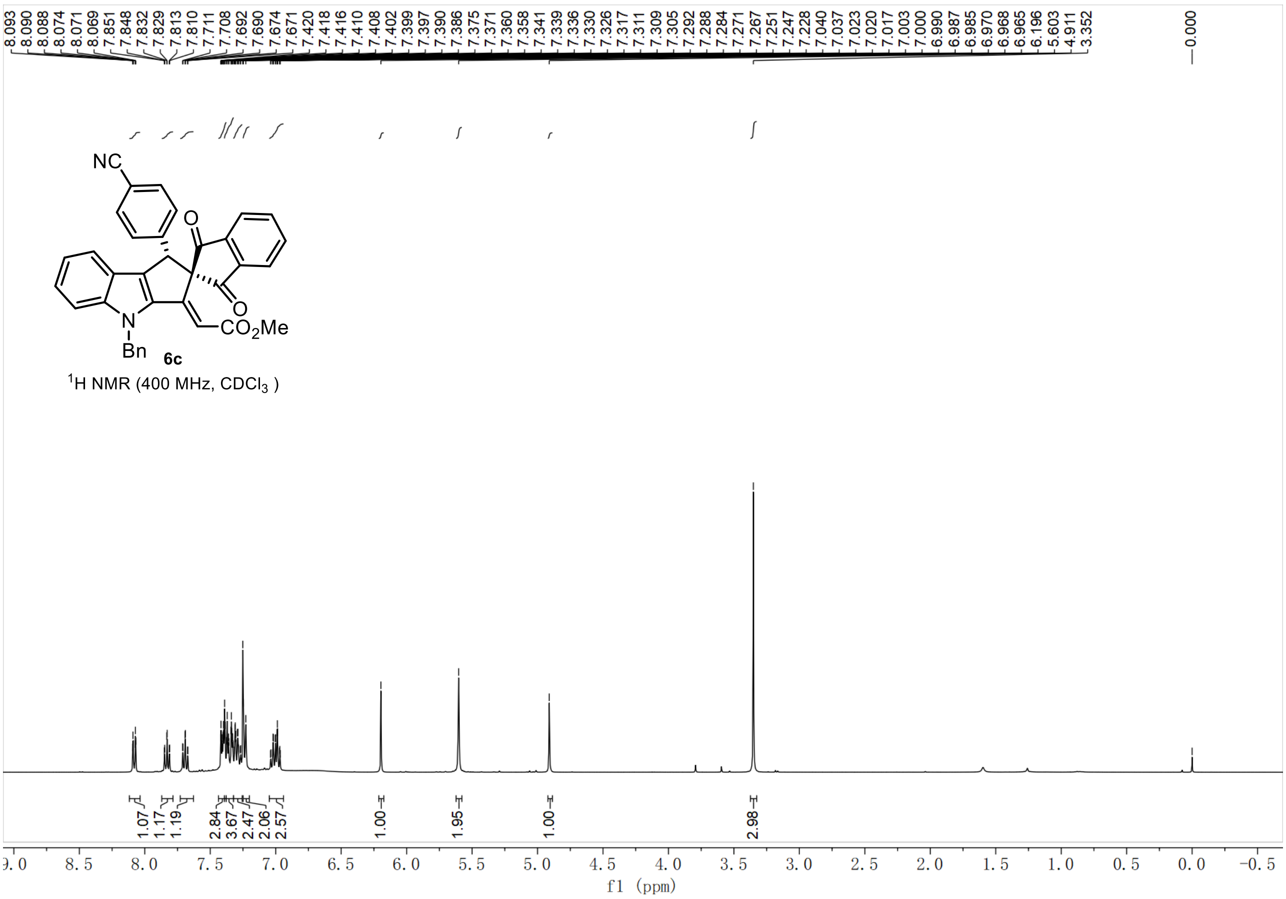
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.644	BB	0.9560	2860.42334	44.71669	50.3412
2	28.192	BB	1.4642	2821.64746	28.16907	49.6588



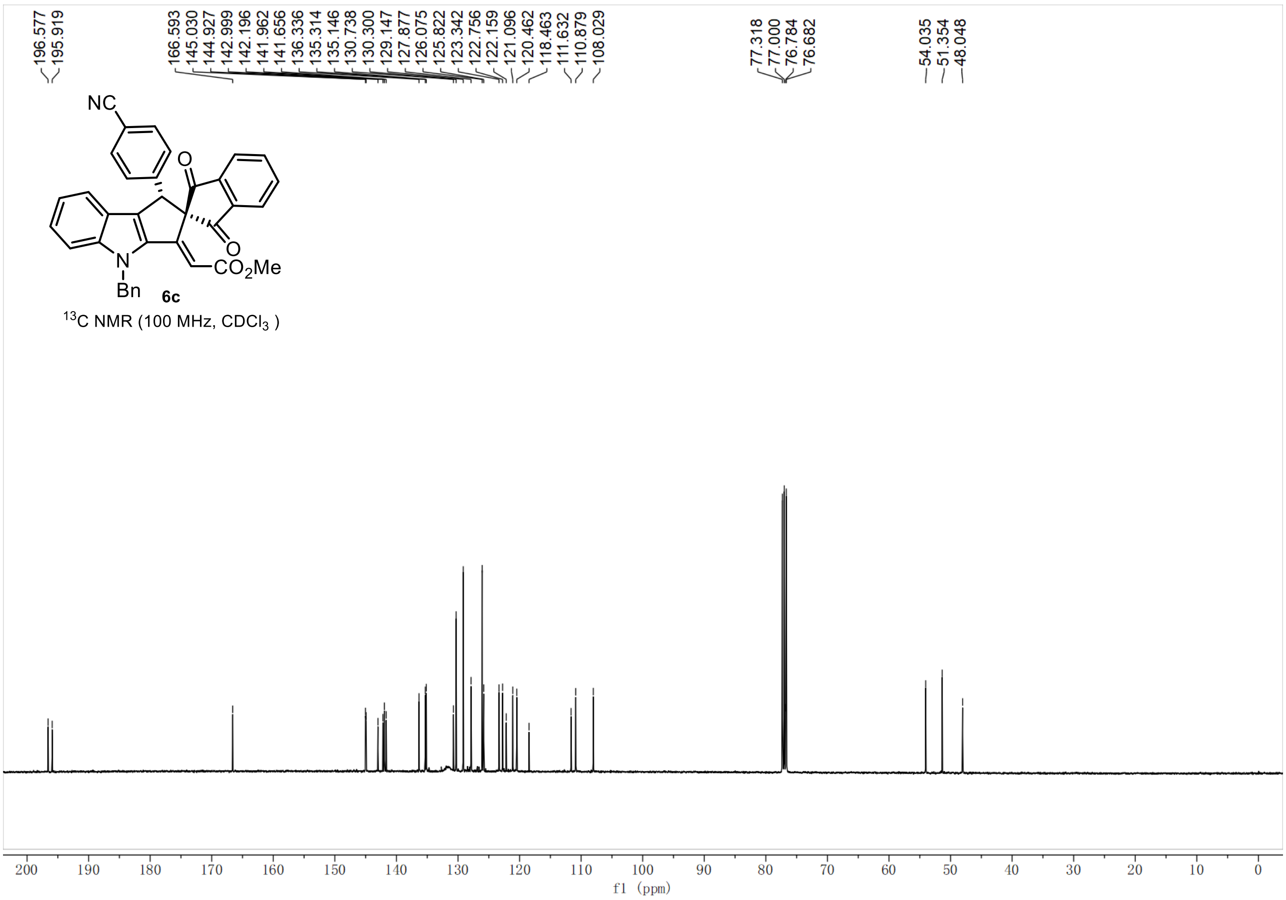
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.310	BB	0.9240	631.48846	10.10697	4.0553
2	27.071	BBA	1.4501	1.49403e4	153.30089	95.9447

Name	CYC-220406-58	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-220406-58.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:56:54 AM (UTC+08:00)

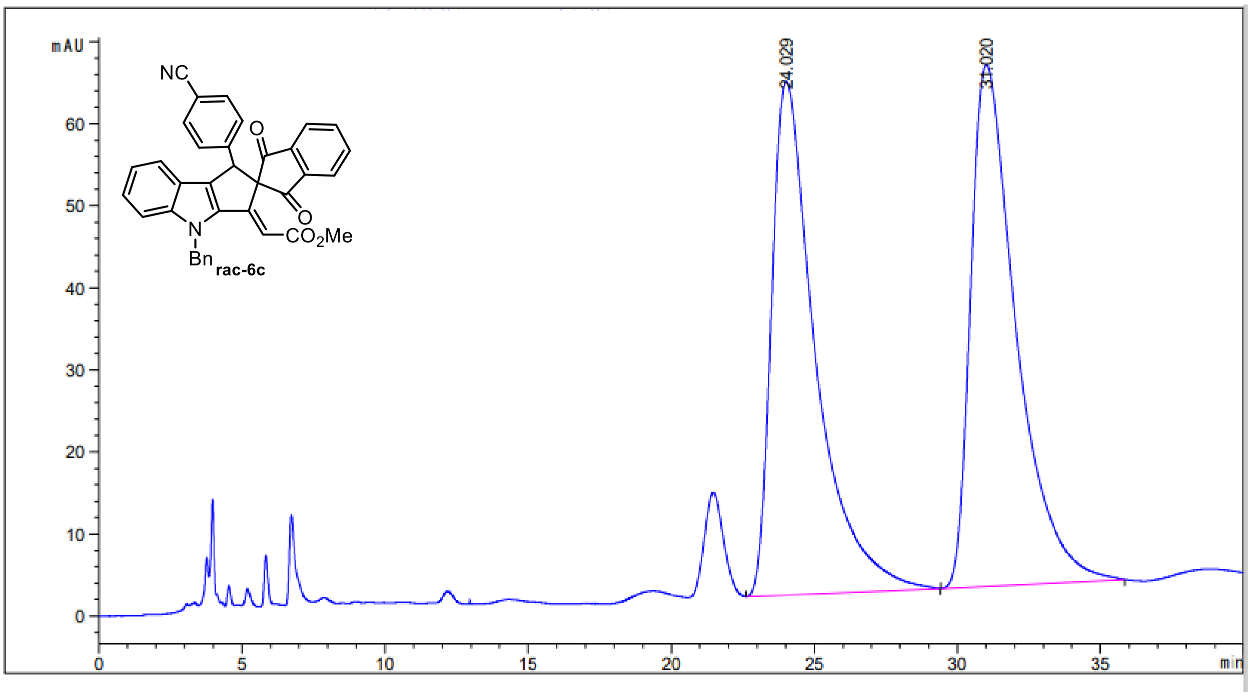




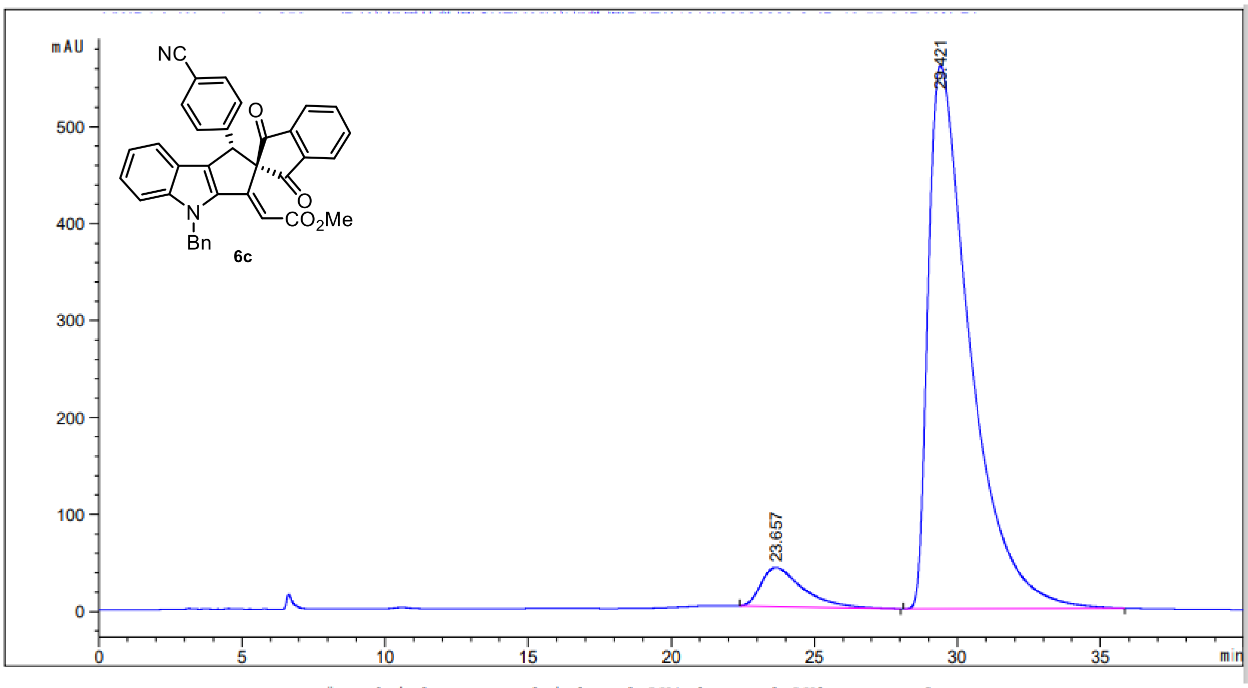
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

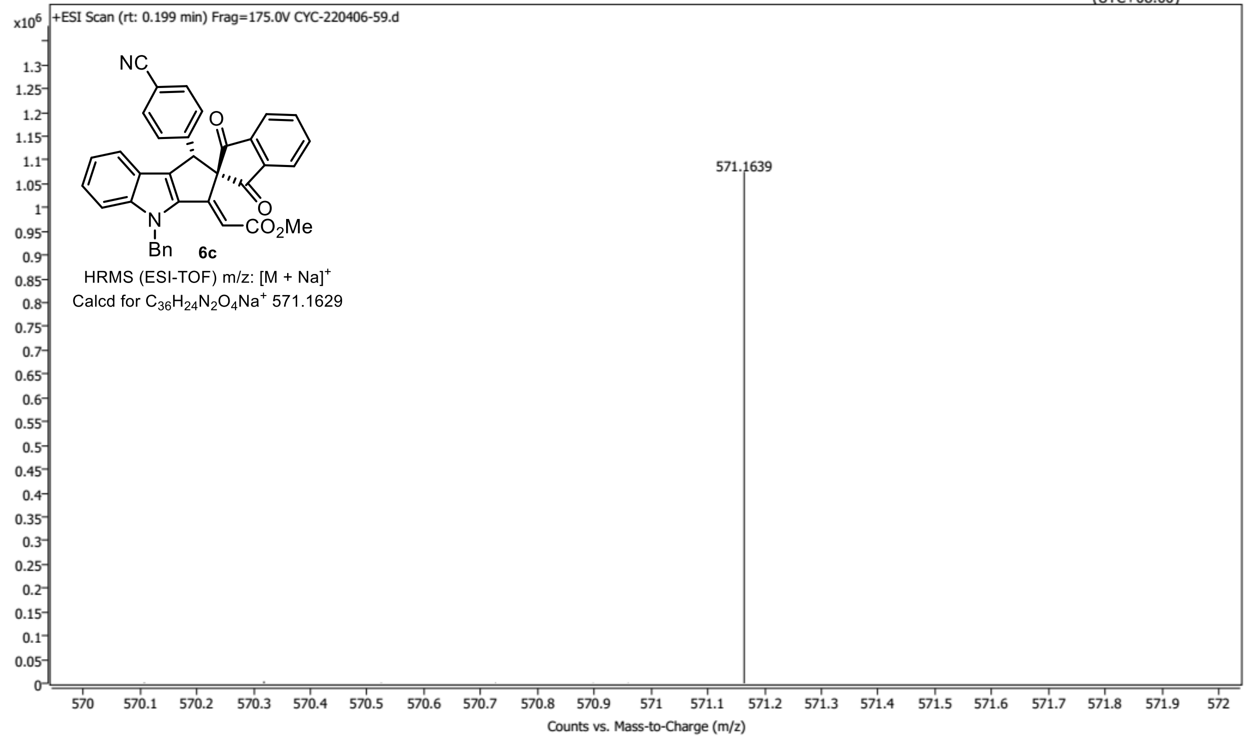


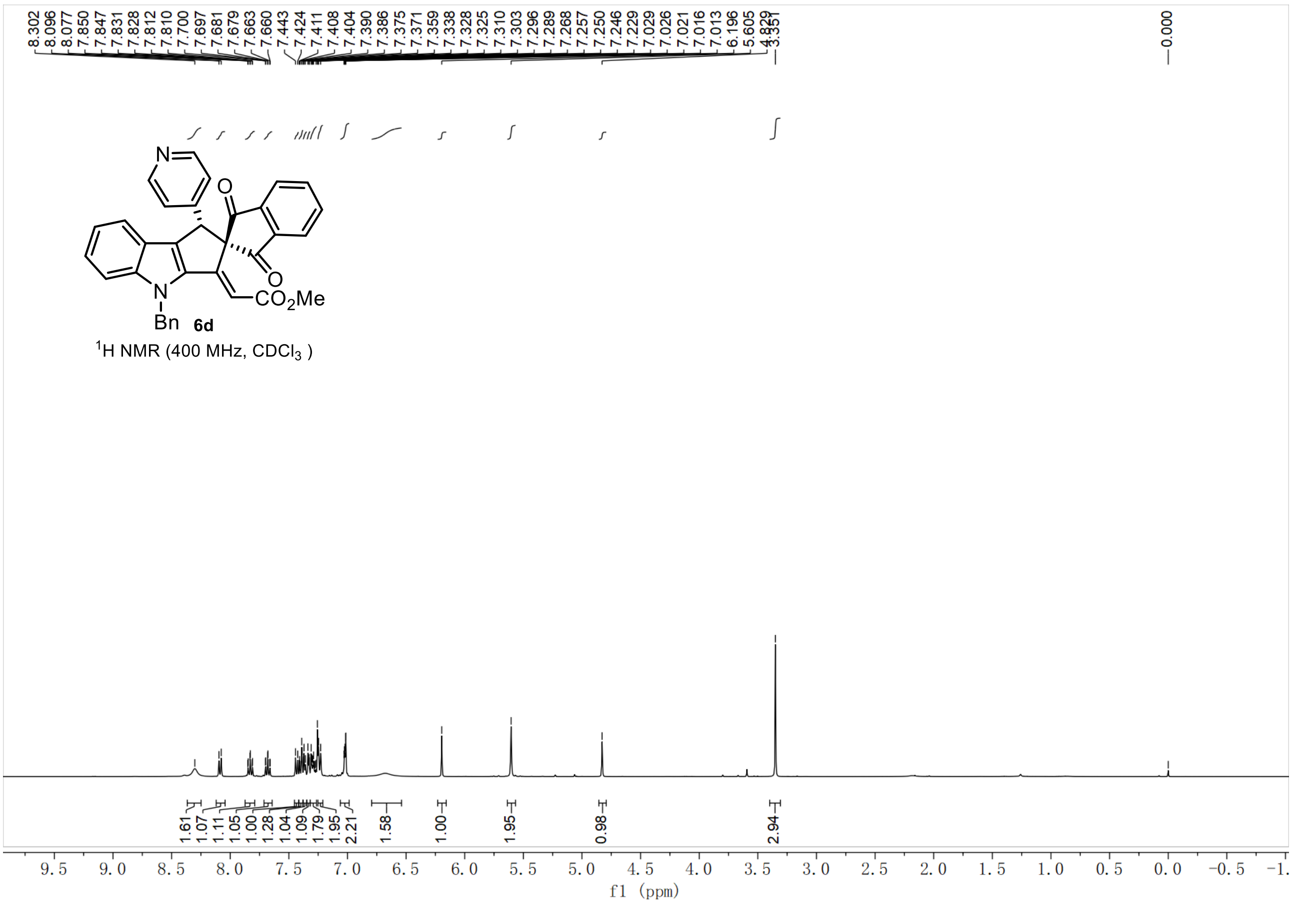
#	[min]		[min]	[mAU*s]	[mAU]	%
1	24.029	BB	1.5350	6700.97998	62.55965	48.8262
2	31.020	BBA	1.6250	7023.17822	63.51157	51.1738



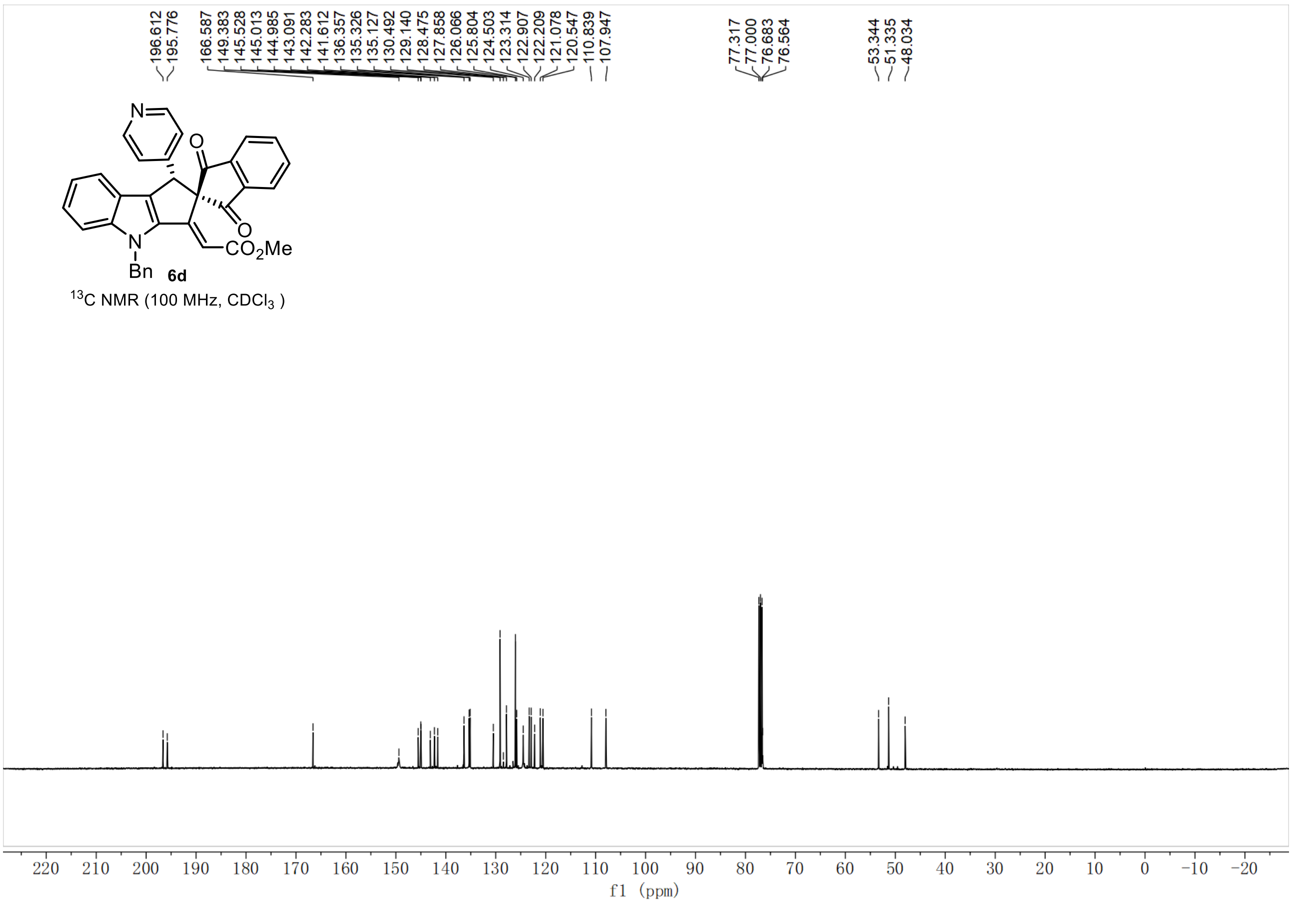
#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.657	BB	1.4589	4039.04761	40.20602	6.6009
2	29.421	BBA	1.5086	5.71504e4	559.73596	93.3991

Name	CYC-220406-59	Rack Pos.		Instrument	Instrument 1	Operator		
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed			
Data File	CYC-220406-59.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 11:59:51 AM (UTC+08:00)	

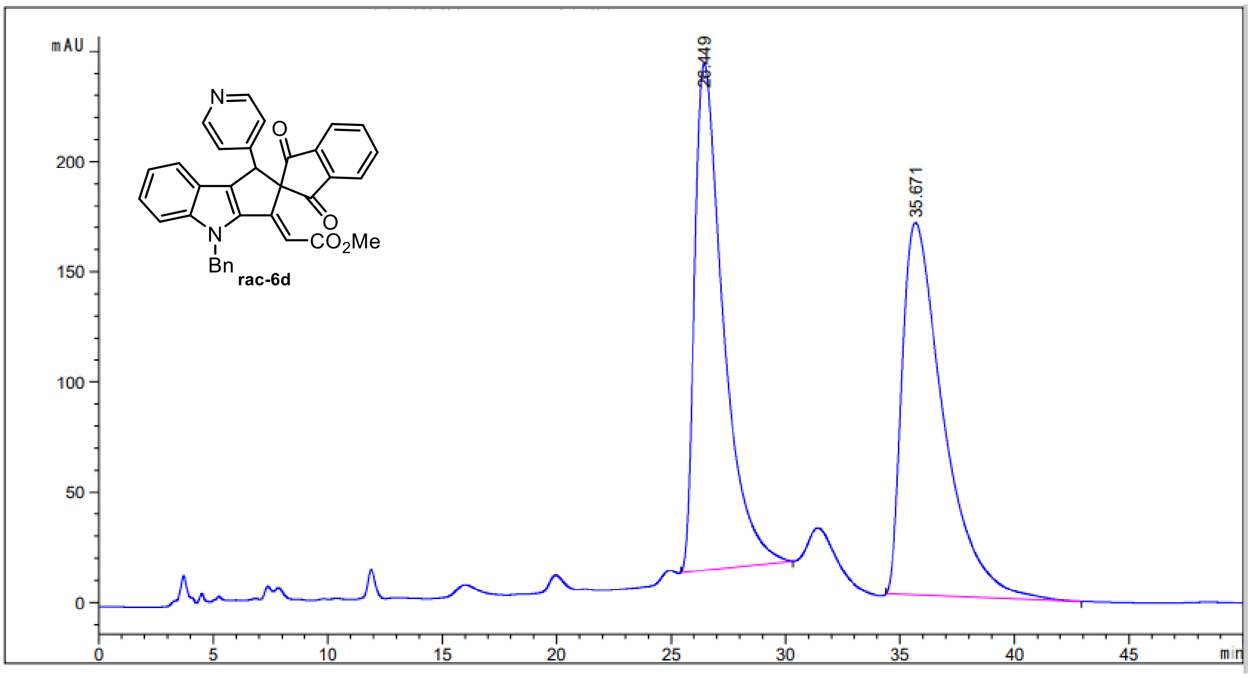




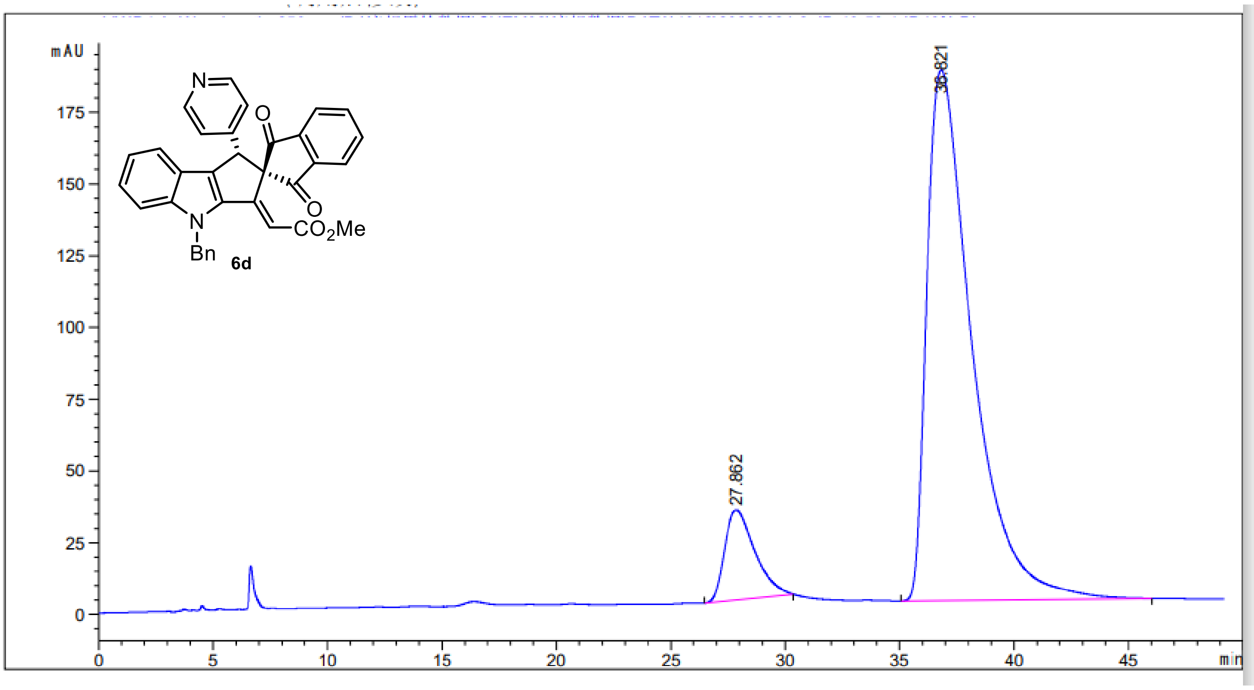
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

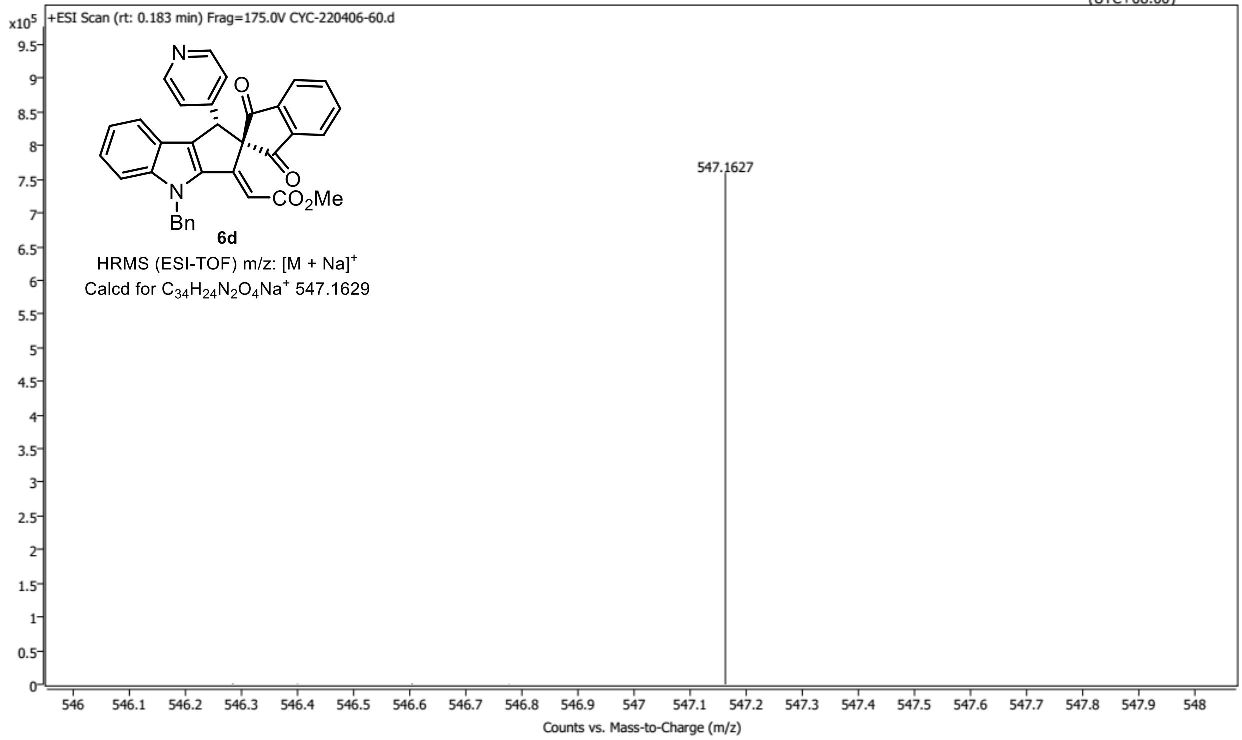


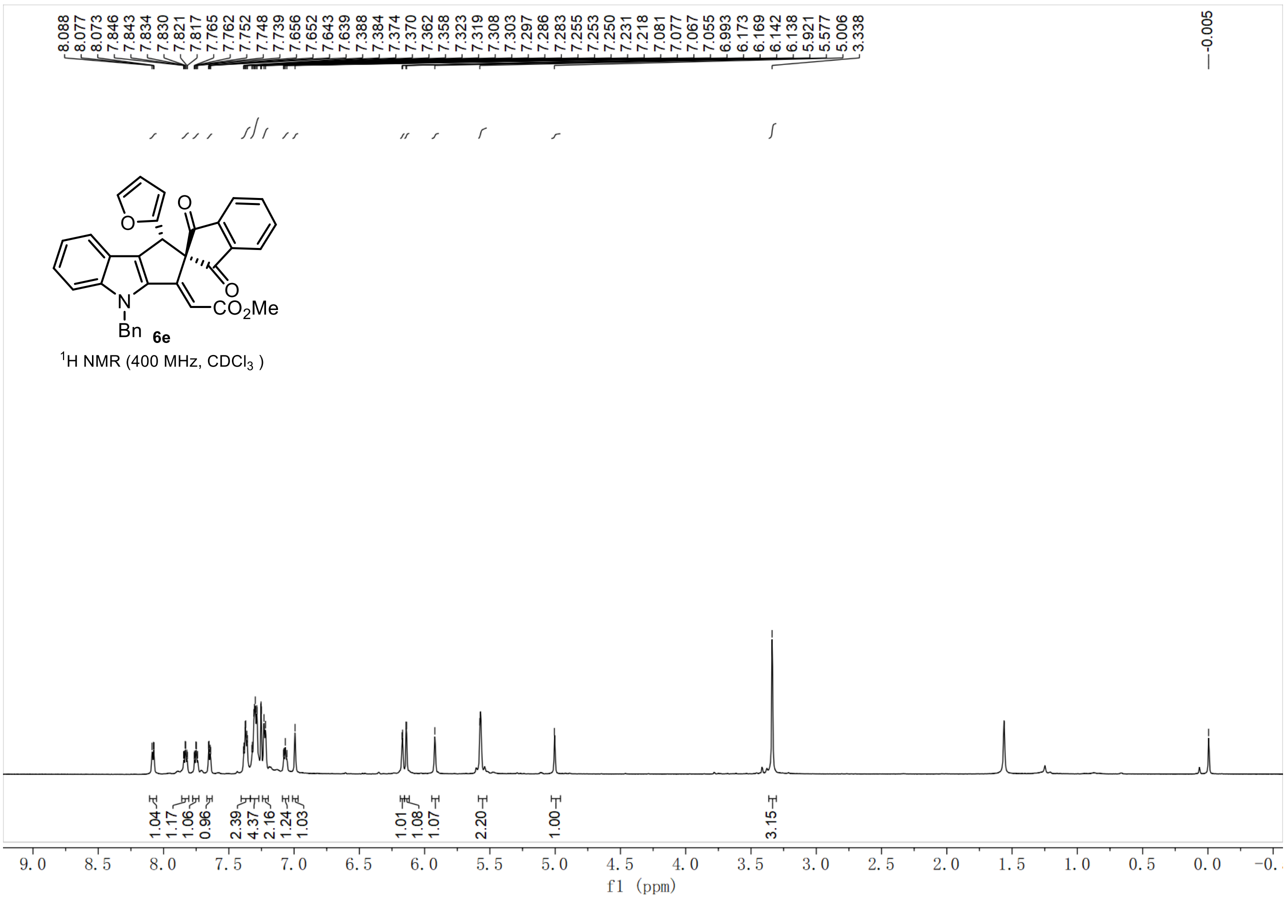
#	[min]		[min]	[mAU*s]	[mAU]	%
1	26.449	BBA	1.2984	1.99618e4	229.88953	48.6621
2	35.671	BB	1.8539	2.10594e4	168.86966	51.3379

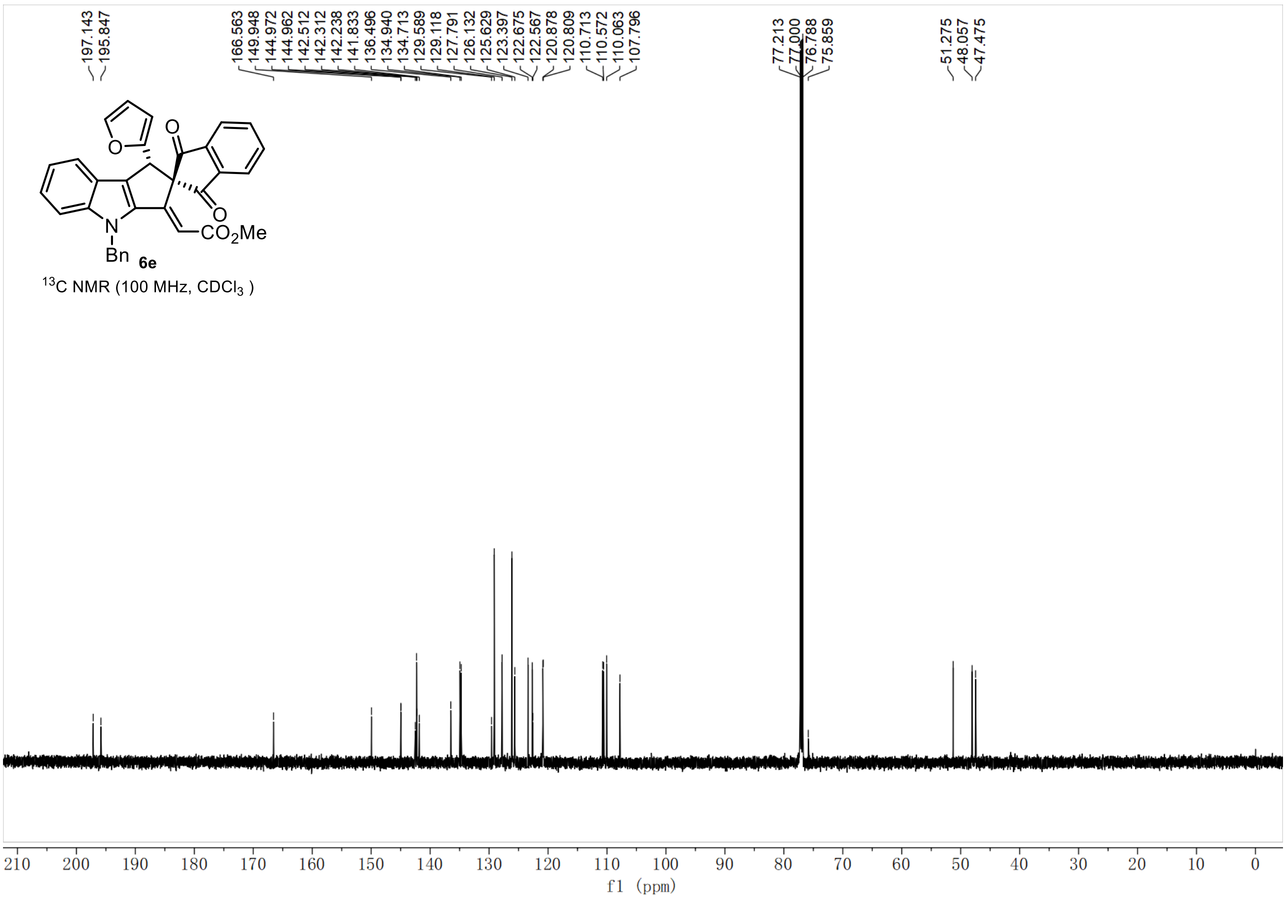


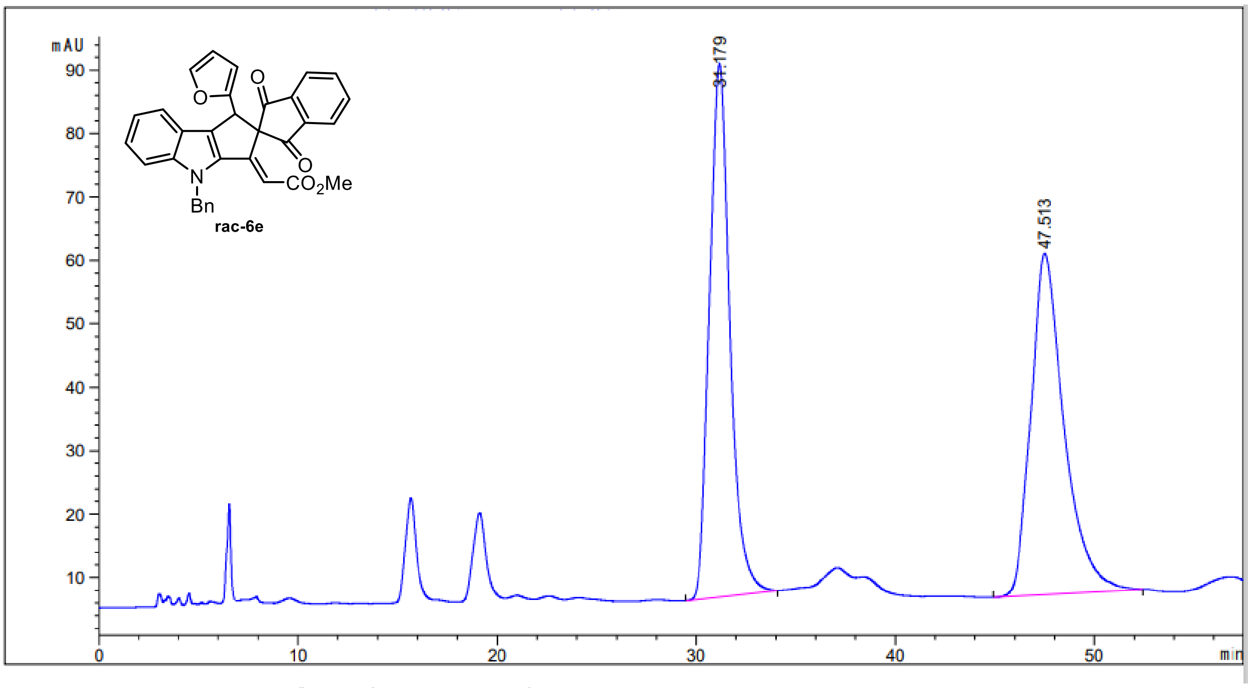
#	[min]		[min]	[mAU*s]	[mAU]	%
1	27.862	BBA	1.3312	2871.55713	31.42143	10.1418
2	36.821	BB	2.0229	2.54427e4	184.93391	89.8582

Name	CYC-220406-60	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-60.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 12:02:48 PM (UTC+08:00)

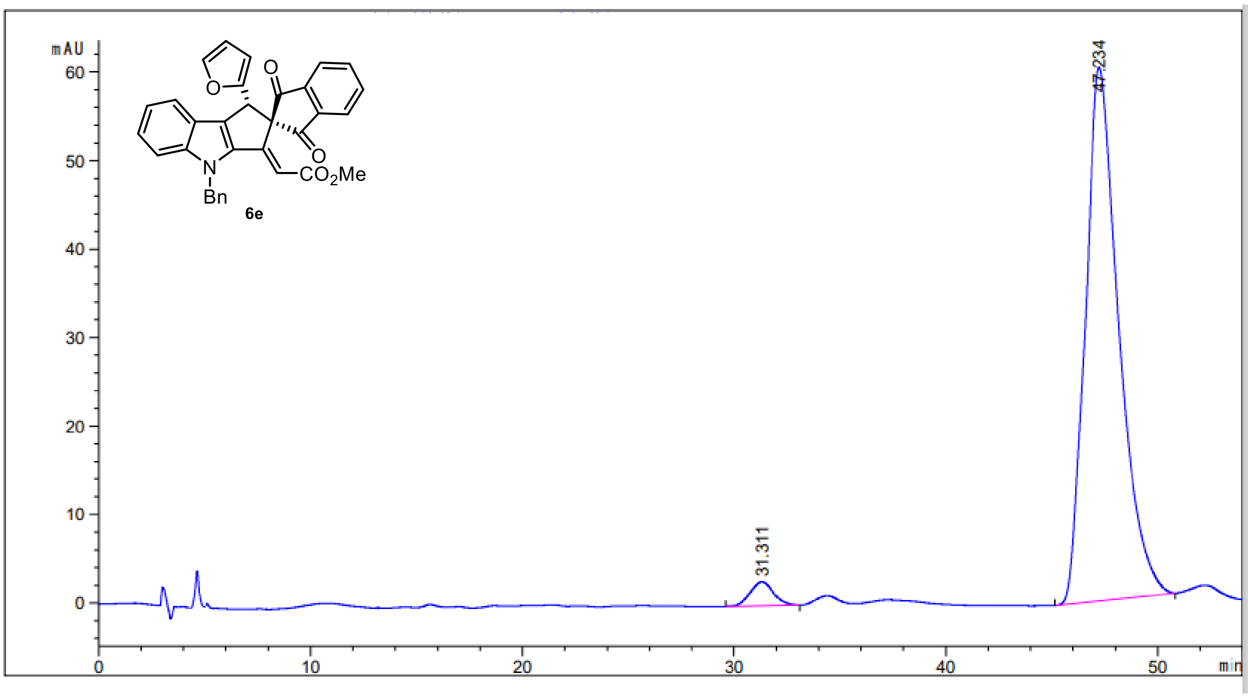



8.088
8.077
8.073
7.846
7.843
7.834
7.830
7.821
7.817
7.765
7.762
7.752
7.748
7.739
7.656
7.652
7.643
7.639
7.388
7.384
7.374
7.370
7.362
7.358
7.323
7.319
7.308
7.303
7.297
7.286
7.283
7.255
7.253
7.250
7.231
7.218
7.081
7.077
7.067
7.055
6.993
6.173
6.169
6.142
6.138
5.921
5.577
5.006
3.338
-0.005
O
O
O
N
Bn
CO_2Me
6e
^{1}H NMR (400 MHz, $CDCl_3$)
1.04
1.17
1.06
0.96
2.39
4.37
2.16
1.24
1.03
1.01
1.08
1.07
2.20
1.00
3.15
f1 (ppm)


197.143
195.847
166.563
149.948
144.972
144.962
142.512
142.312
142.238
141.833
136.496
134.940
134.713
129.589
129.118
127.791
126.132
125.629
123.397
122.675
122.567
120.878
120.809
110.713
110.572
110.063
107.796
77.213
77.000
76.788
75.859
51.275
48.057
47.475
O
O
O
N
Bn
CO_2Me
6e
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

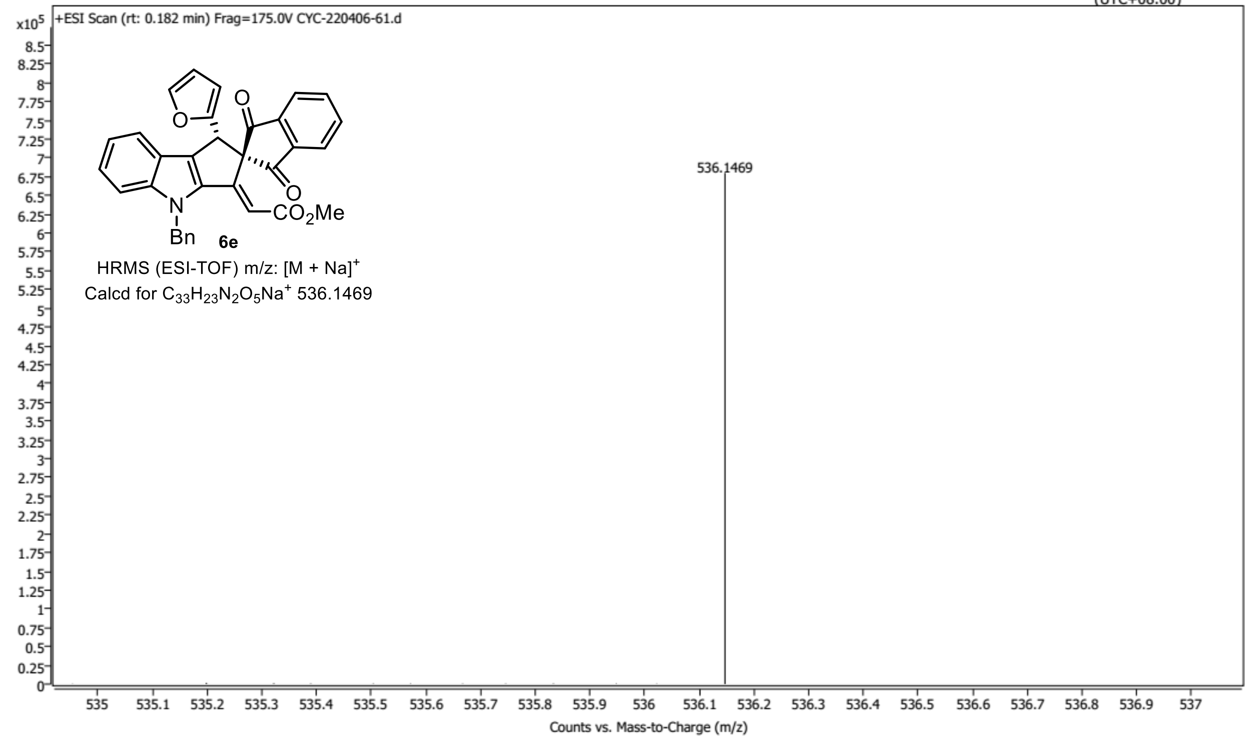


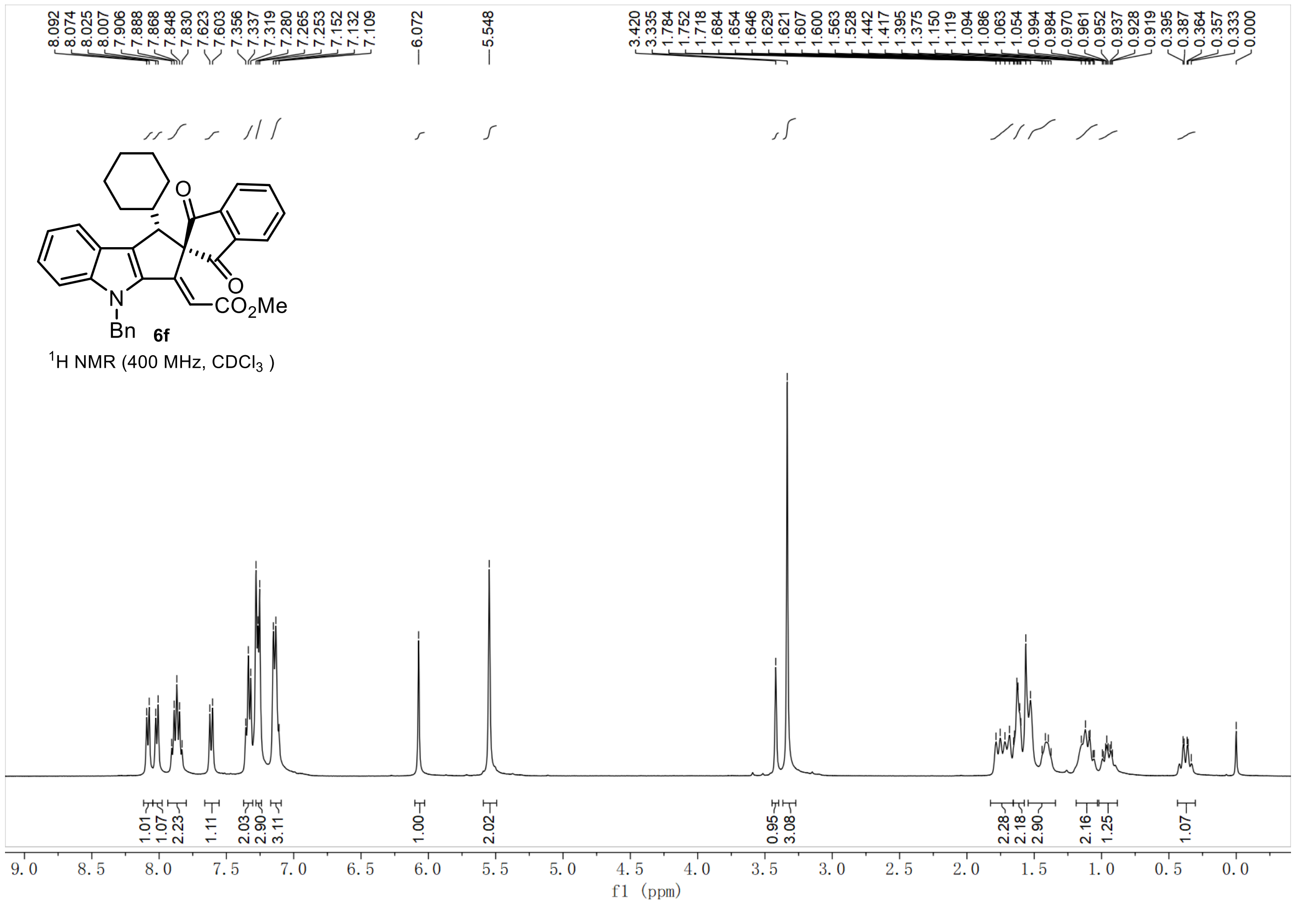
#	[min]		[min]	[mAU*s]	[mAU]	%
1	31.179	BB	1.0493	5963.98877	84.03705	48.9144
2	47.513	BB	1.6479	6228.72021	53.79495	51.0856



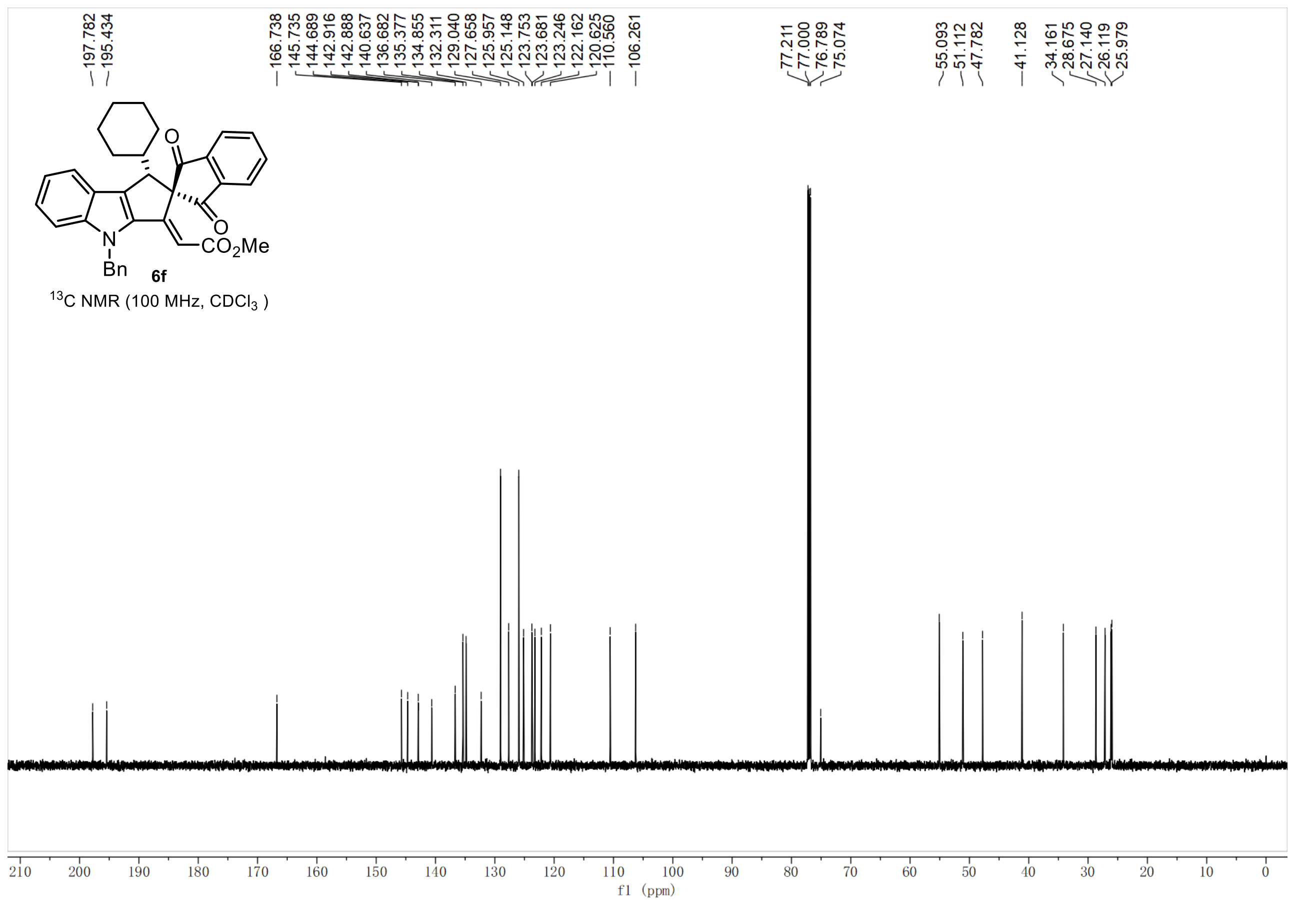
#	[min]		[min]	[mAU*s]	[mAU]	%
1	31.311	BB	1.0779	207.99541	2.73079	3.0605
2	47.234	BB	1.5773	6588.11279	60.30794	96.9395

Name	CYC-220406-61	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-61.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 12:05:45 PM (UTC+08:00)

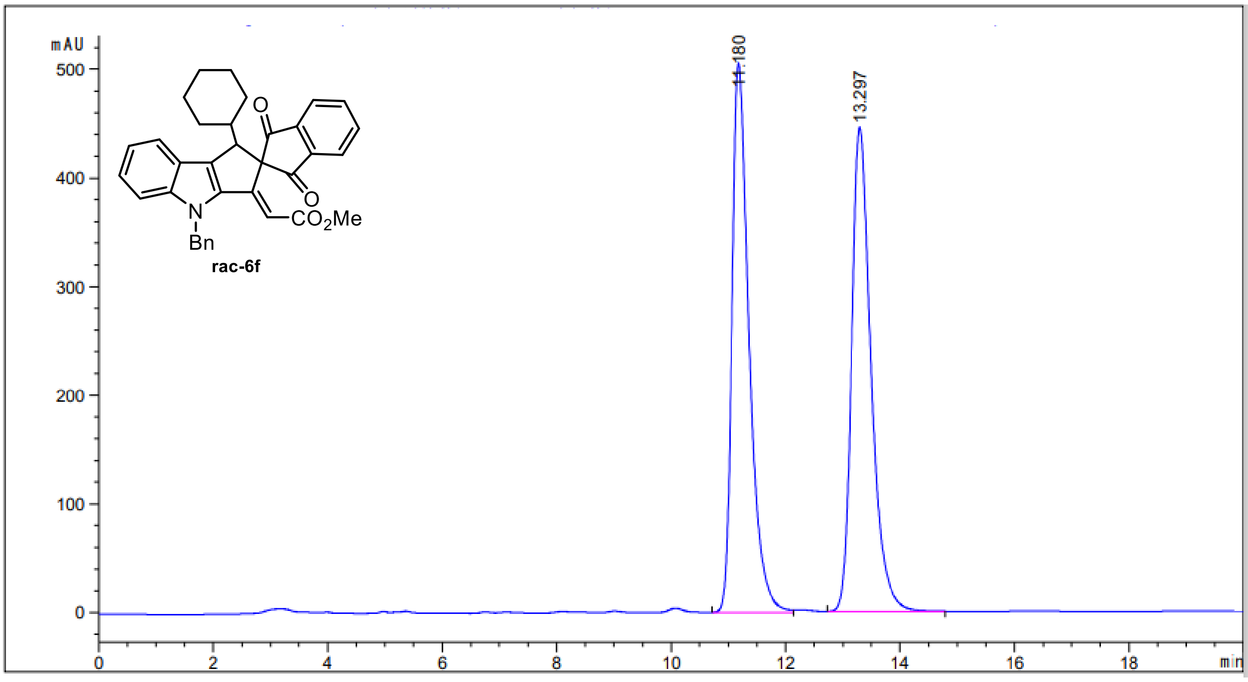




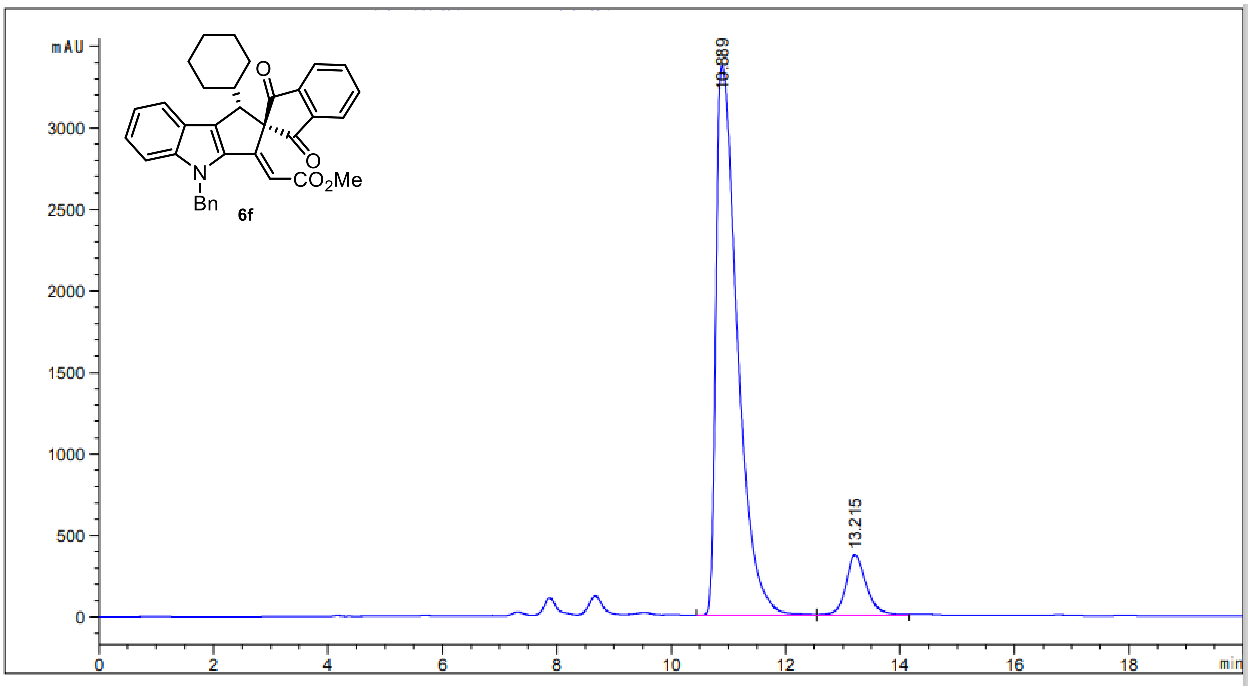
6f
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)



6f
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

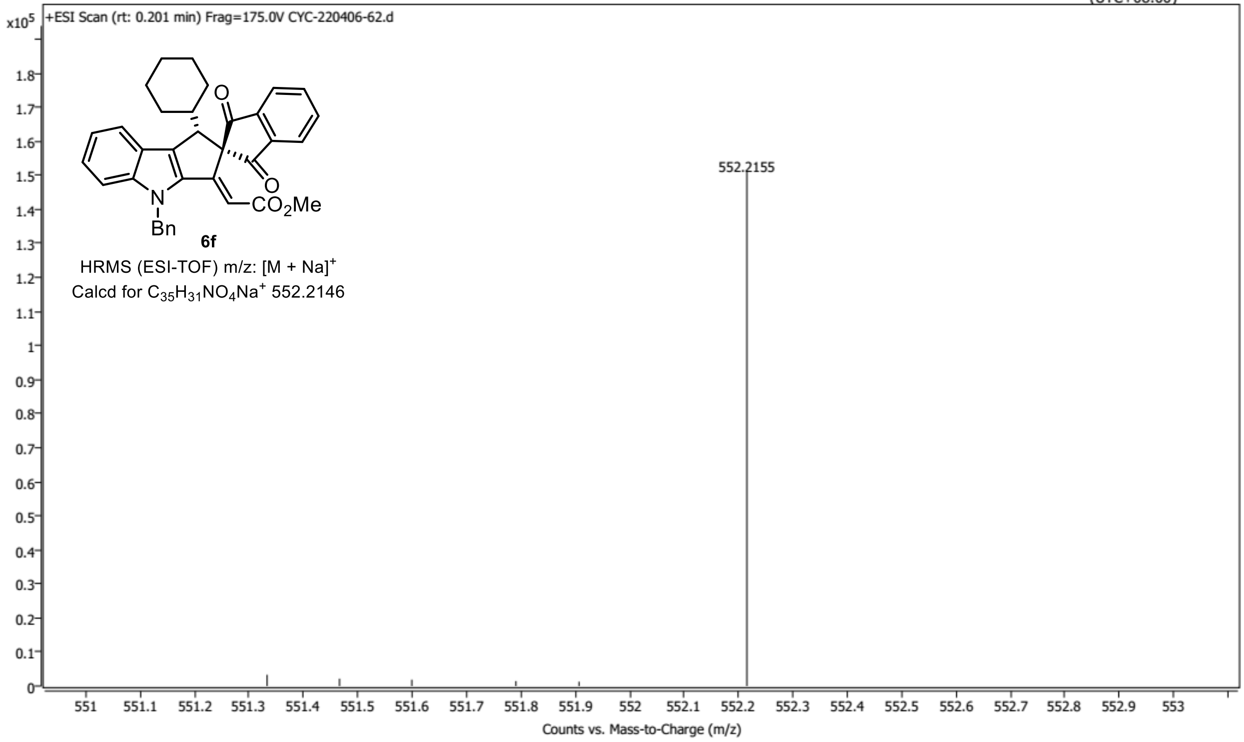


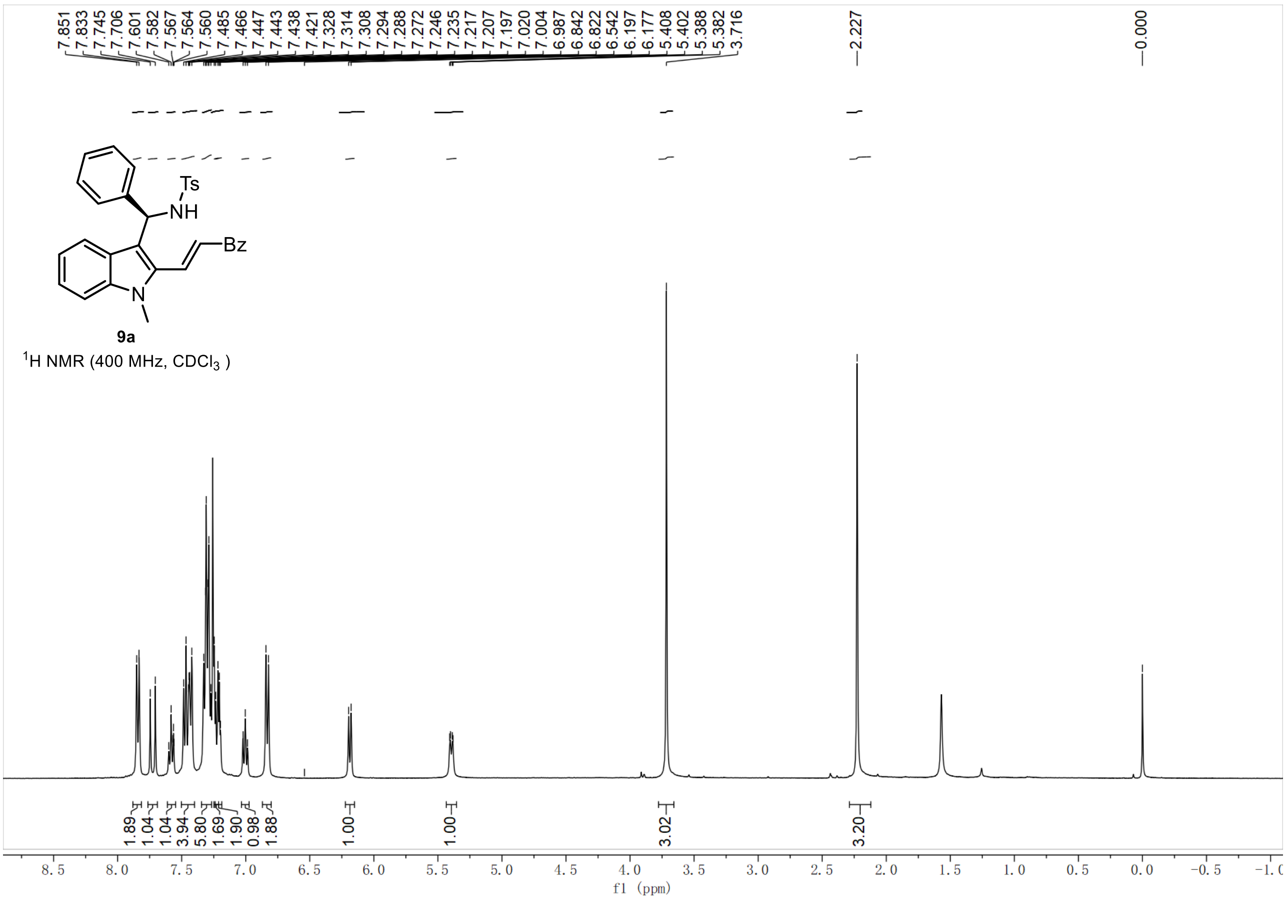
#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.180	BBA	0.3118	1.04887e4	505.81995	49.9451
2	13.297	BB	0.3566	1.05117e4	445.79291	50.0549

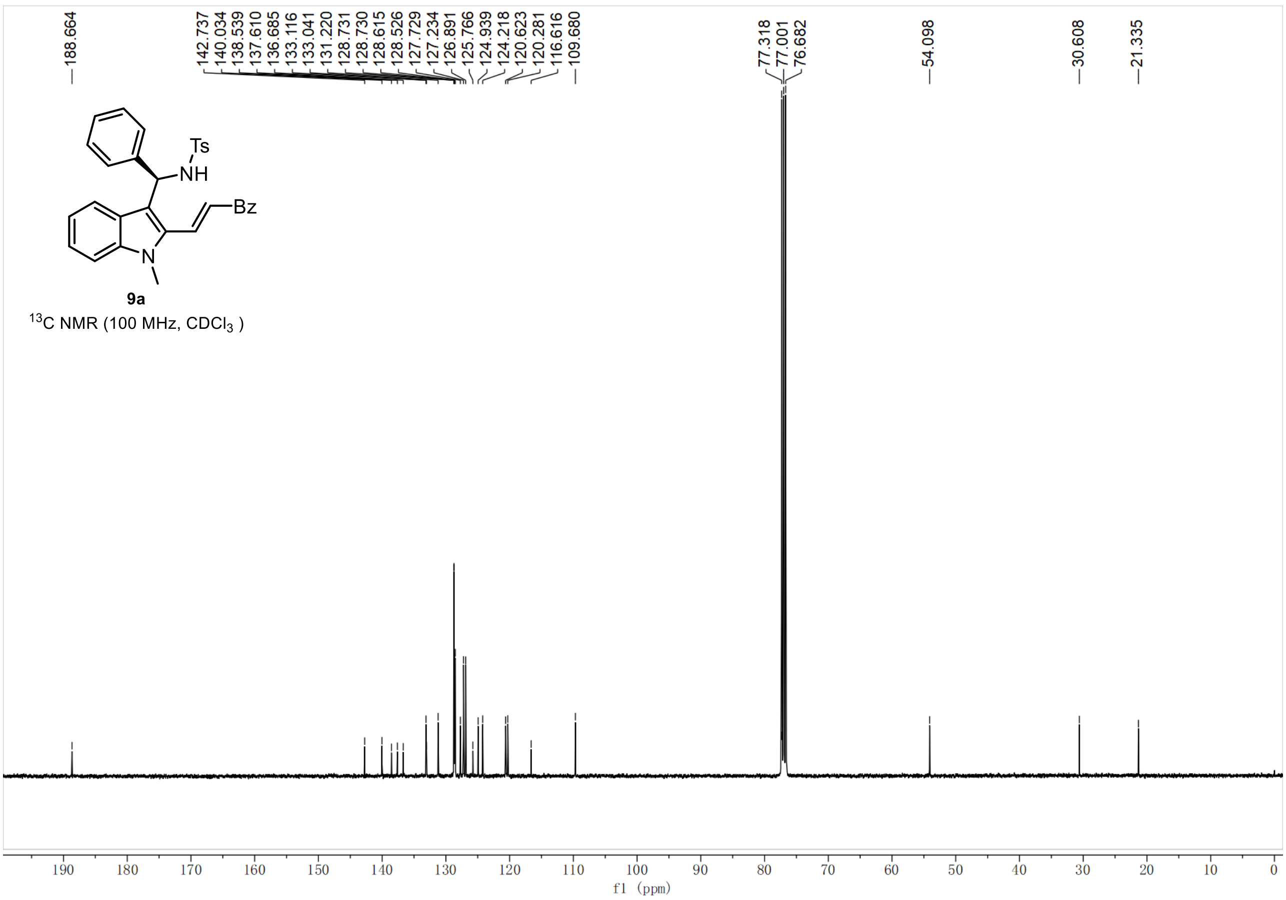


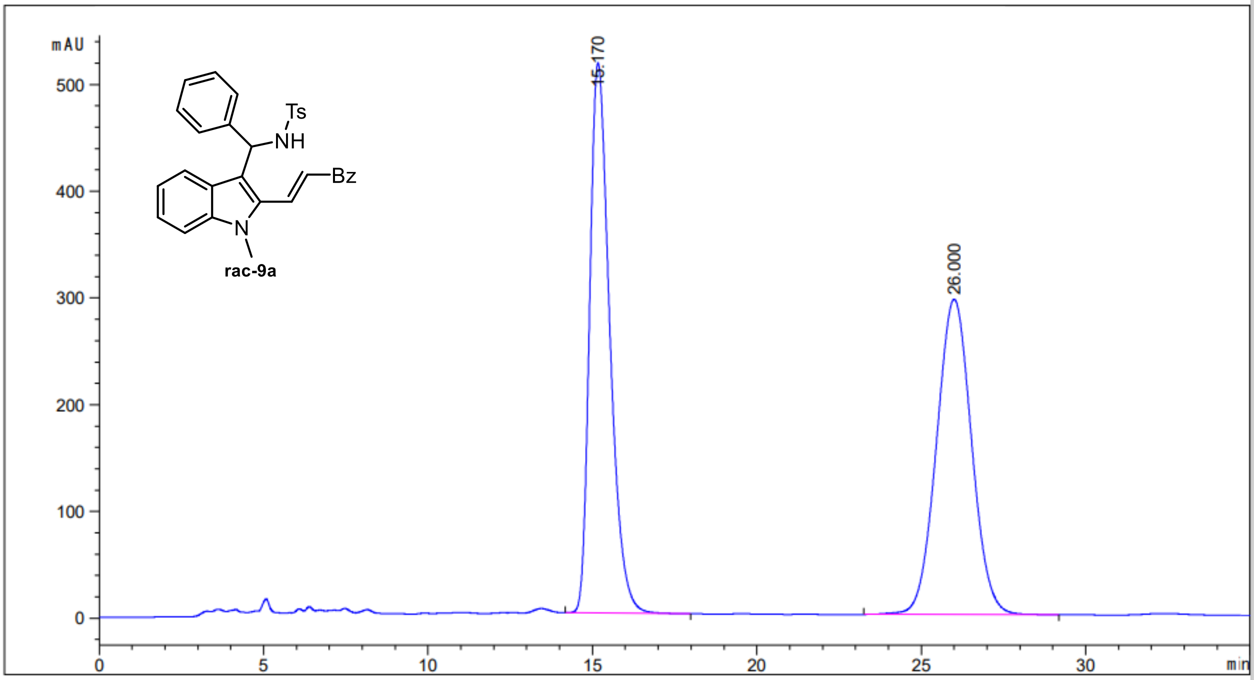
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.889	BV	0.3966	8.81260e4	3372.20557	90.3338
2	13.215	VV	0.3798	9429.94727	372.52789	9.6662

Name	CYC-220406-62	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Some ions missed		
Data File	CYC-220406-62.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	4/9/2022 12:08:42 PM (UTC+08:00)

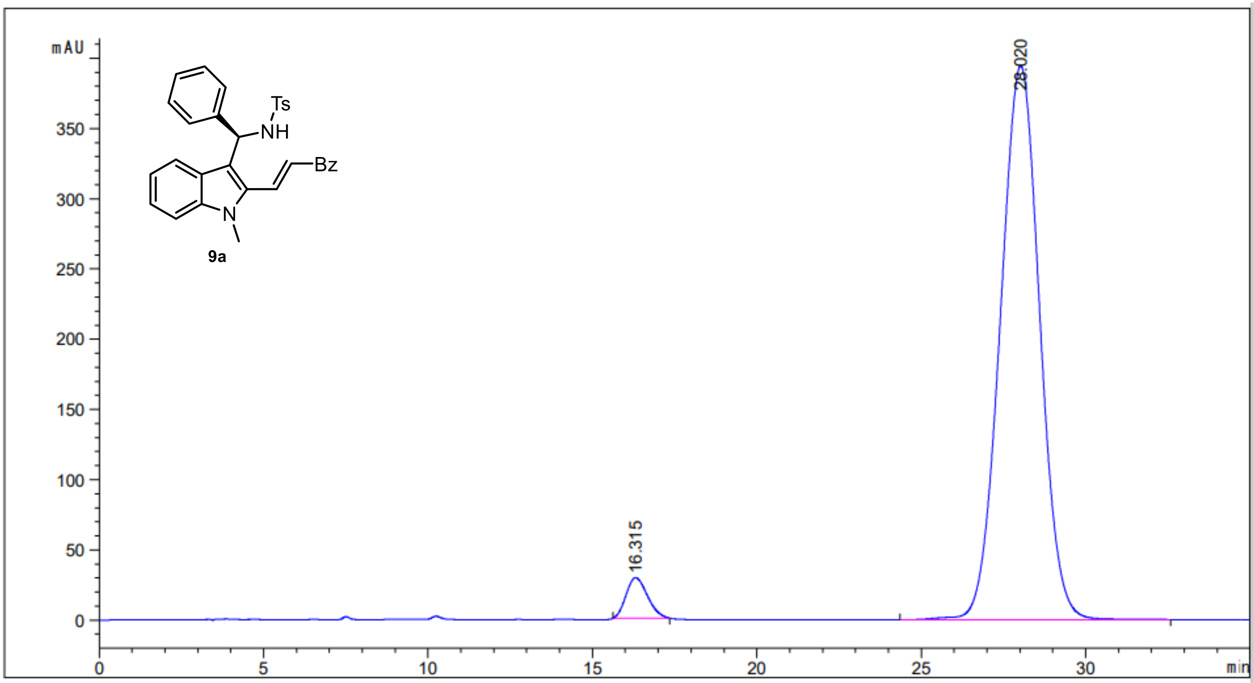



7.851
7.833
7.745
7.706
7.601
7.582
7.567
7.564
7.560
7.485
7.466
7.447
7.443
7.438
7.421
7.328
7.314
7.308
7.294
7.288
7.272
7.246
7.235
7.217
7.207
7.197
7.020
7.004
6.987
6.842
6.822
6.542
6.197
6.177
5.408
5.402
5.388
5.382
3.716
2.227
0.000
Ts
NH
Bz
N
9a
^{1}H NMR (400 MHz, $CDCl_3$)
1.89
1.04
1.04
3.94
5.80
1.69
1.90
0.98
1.88
1.00
1.00
3.02
3.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

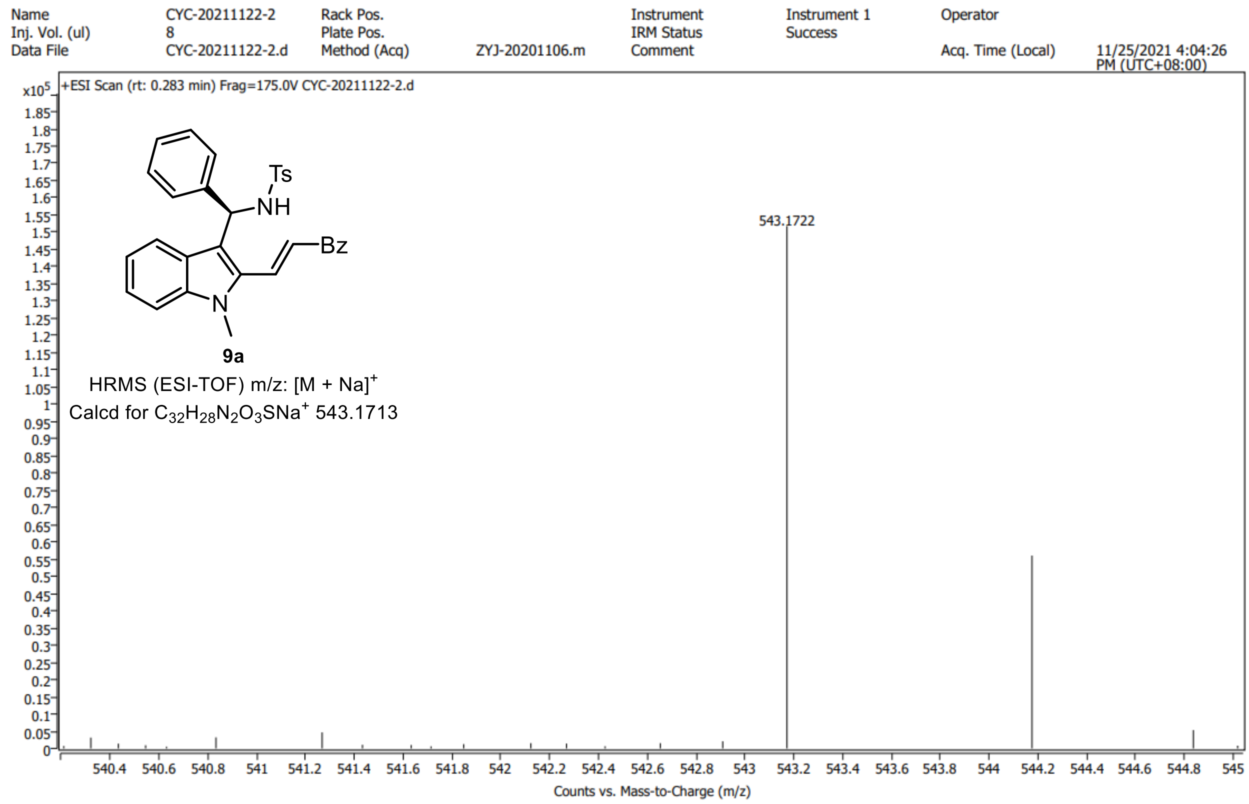

188.664
142.737
140.034
138.539
137.610
136.685
133.116
133.041
131.220
128.731
128.730
128.615
128.526
127.729
127.234
126.891
125.766
124.939
124.218
120.623
120.281
116.616
109.680
77.318
77.001
76.682
54.098
30.608
21.335
Ts
NH
Bz
N
9a
^{13}C NMR (100 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

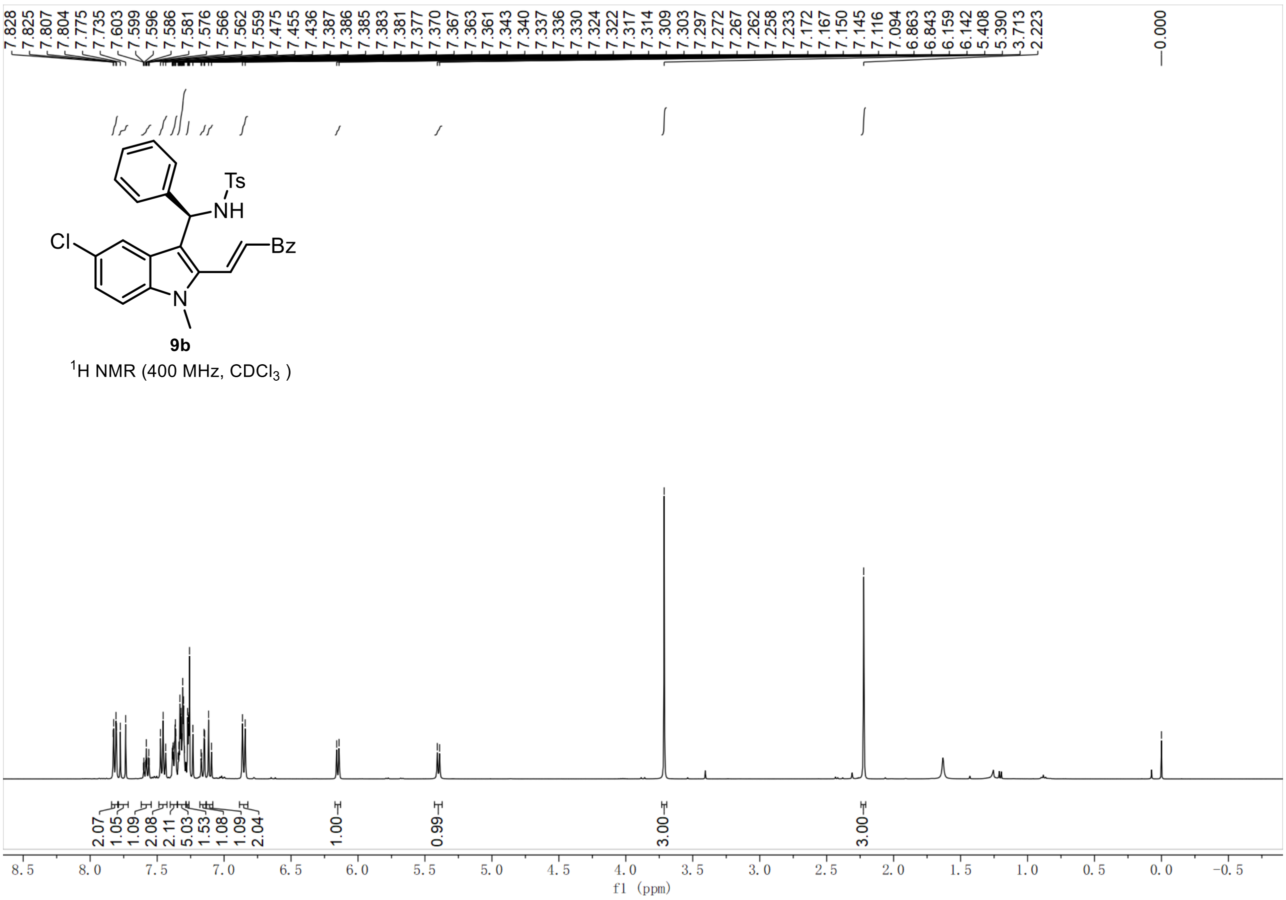


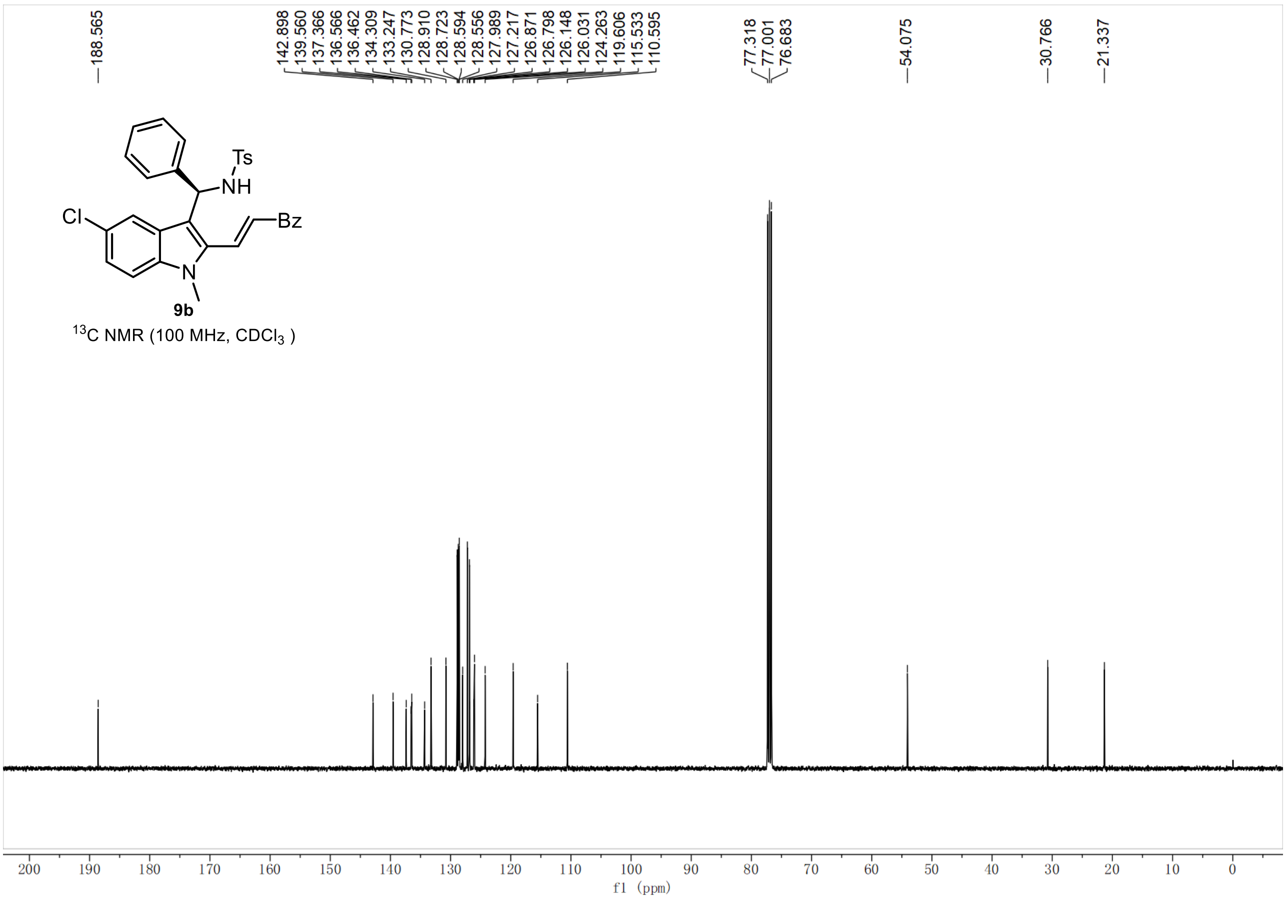
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.170	BB	0.6499	2.18285e4	515.45807	49.9173
2	26.000	BBA	1.1533	2.19008e4	295.38242	50.0827

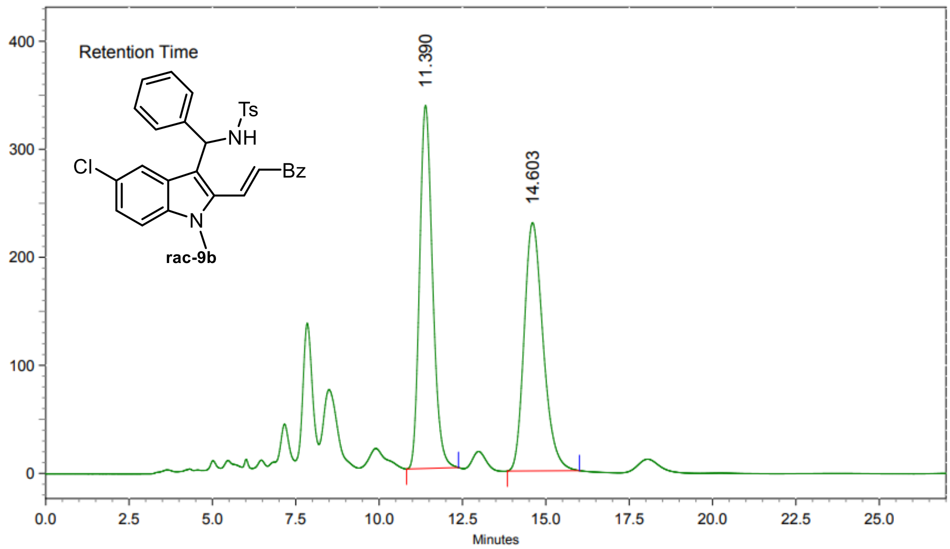


#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.315	BBA	0.7081	1307.49438	28.91422	3.8330
2	28.020	BB	1.2968	3.28044e4	394.28125	96.1670


Name CYC-20211122-2
Inj. Vol. (ul) 8
Data File CYC-20211122-2.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument Instrument 1
IRM Status Success
Comment
Operator
Acq. Time (Local) 11/25/2021 4:04:26 PM (UTC+08:00)
+ESI Scan (rt: 0.283 min) Frag=175.0V CYC-20211122-2.d
x10^5
Ts
NH
Bz
N
9a
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C32H28N2O3SNa+ 543.1713
543.1722
Counts vs. Mass-to-Charge (m/z)

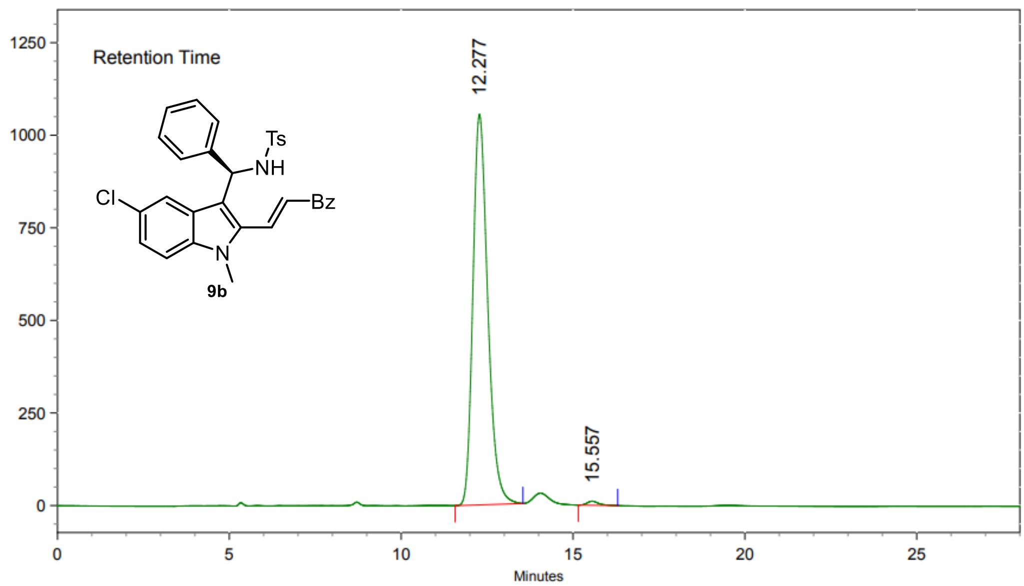






AREA PERCENT REPORT

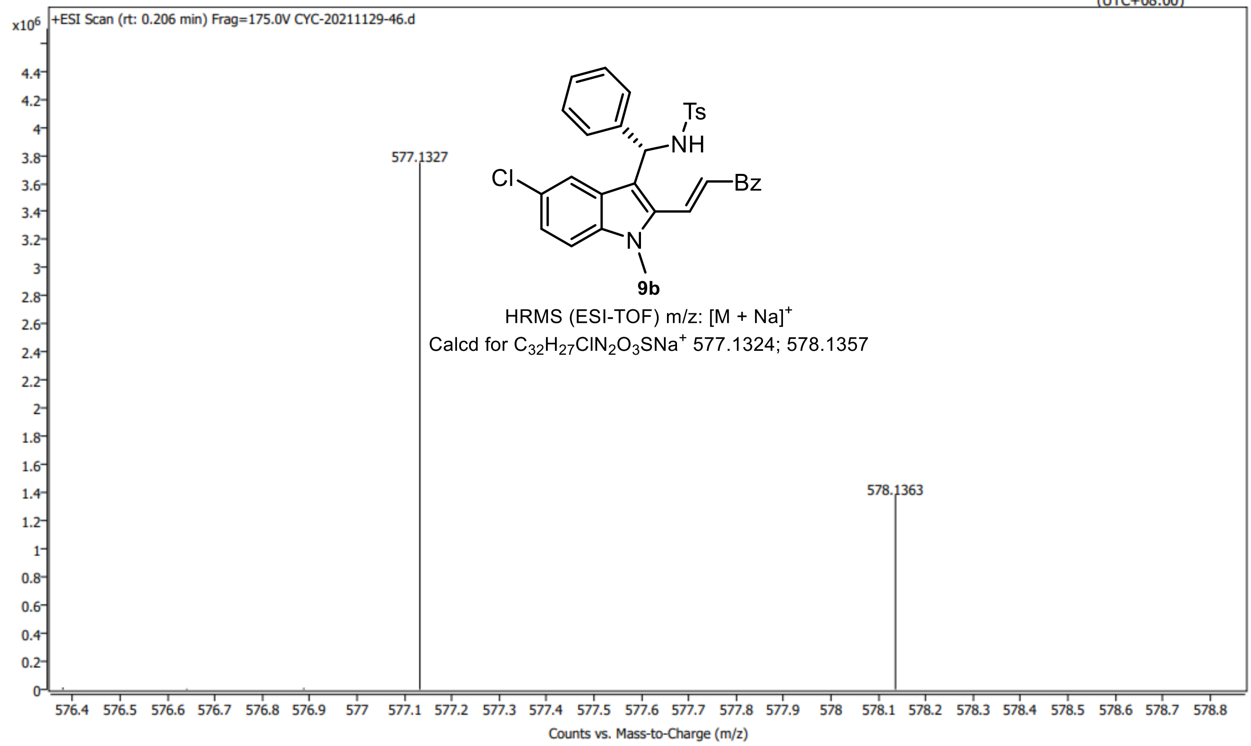
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	11.390	1.557	5639066	152337813	50.0221
2	14.603	2.160	3856711	152202933	49.9779

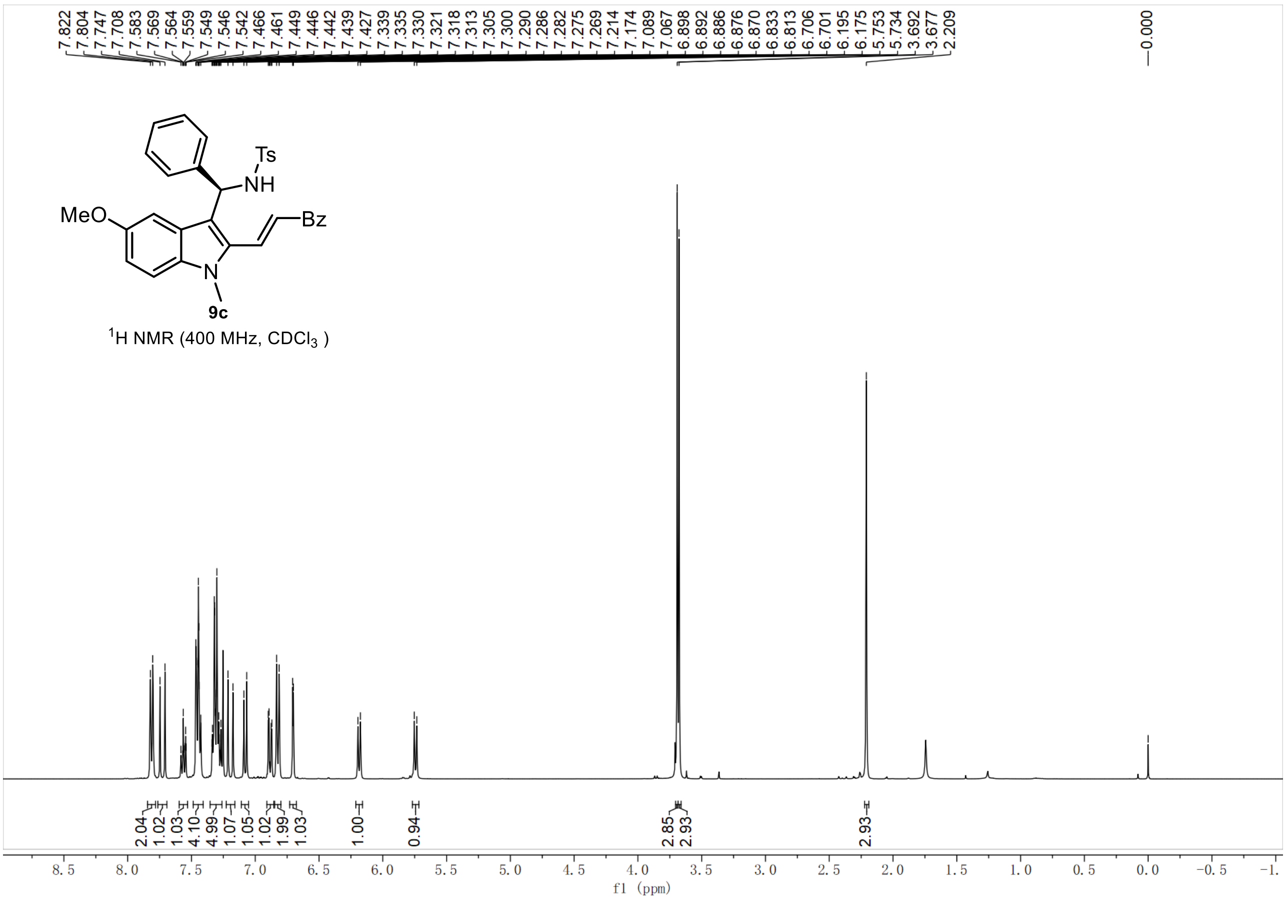


AREA PERCENT REPORT

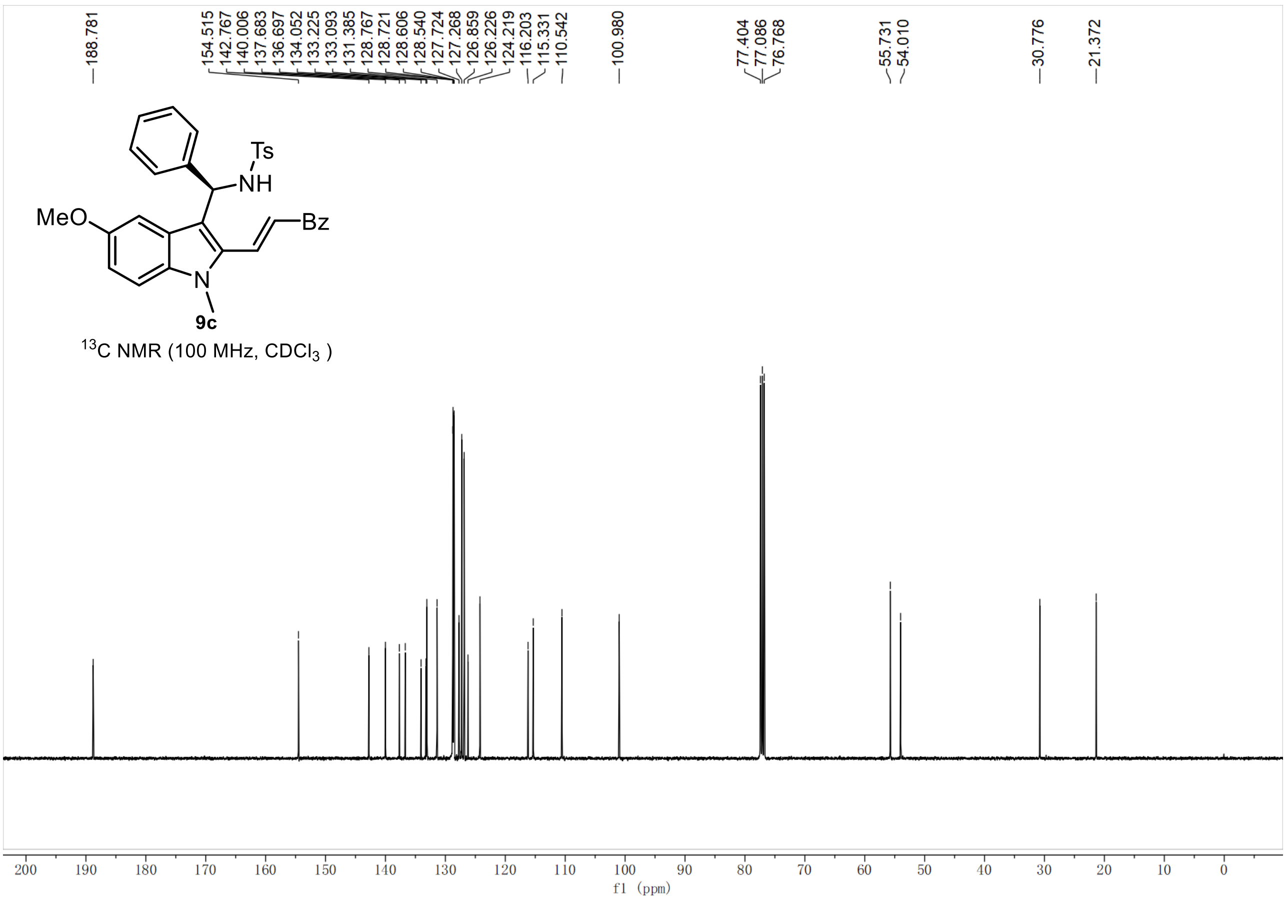
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	12.277	1.973	17699235	530018258	99.1872
2	15.557	1.147	185379	4343132	0.8128

Name	CYC-20211129-46	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-46.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 5:54:58 PM (UTC+08:00)

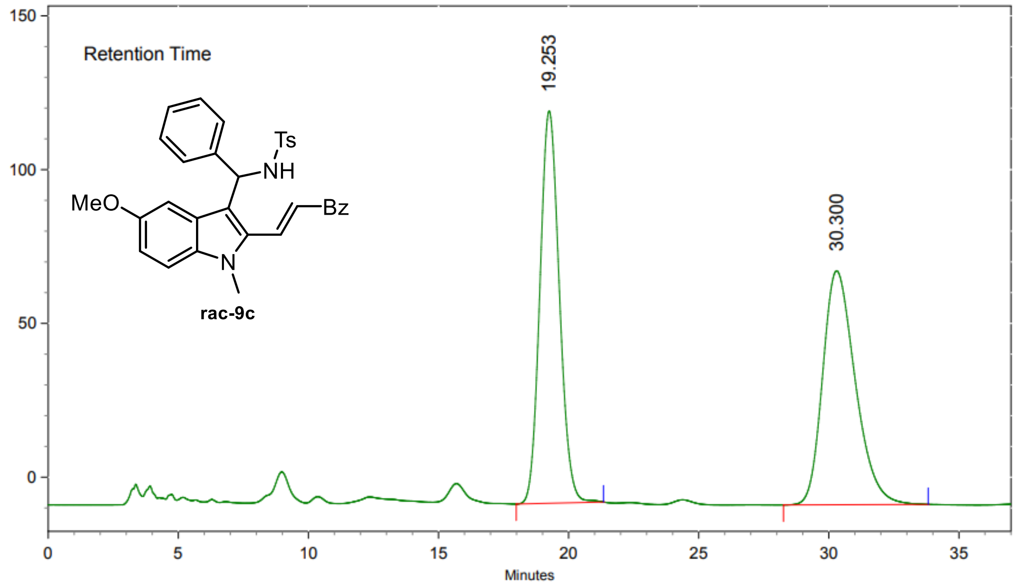




7.822 7.804 7.747 7.708 7.583 7.569 7.564 7.559 7.549 7.546 7.542 7.466 7.461 7.449 7.446 7.442 7.439 7.427 7.339 7.335 7.330 7.321 7.318 7.313 7.305 7.300 7.290 7.286 7.282 7.275 7.269 7.214 7.174 7.089 7.067 6.898 6.892 6.886 6.876 6.870 6.833 6.813 6.706 6.701 6.195 6.175 5.753 5.734 3.692 3.677 2.209
0.000
Ts
NH
MeO
Bz
N
9c
^{1}H NMR (400 MHz, $CDCl_3$)
2.04 1.02 1.03 4.10 4.99 1.07 1.05 1.02 1.99 1.03 1.00 0.94 2.85 2.93 2.93
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

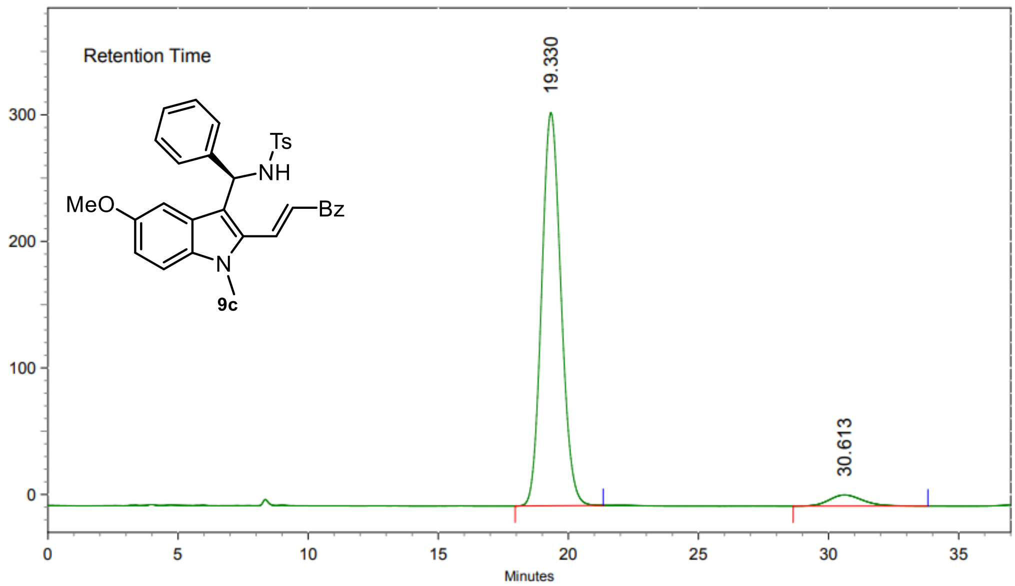


188.781
154.515 142.767 140.006 137.683 136.697 134.052 133.225 133.093 131.385 128.767 128.721 128.606 128.540 127.724 127.268 126.859 126.226 124.219 116.203 115.331 110.542
100.980
77.404 77.086 76.768
55.731 54.010
30.776
21.372
Ts
NH
MeO
Bz
N
9c
^{13}C NMR (100 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



AREA PERCENT REPORT

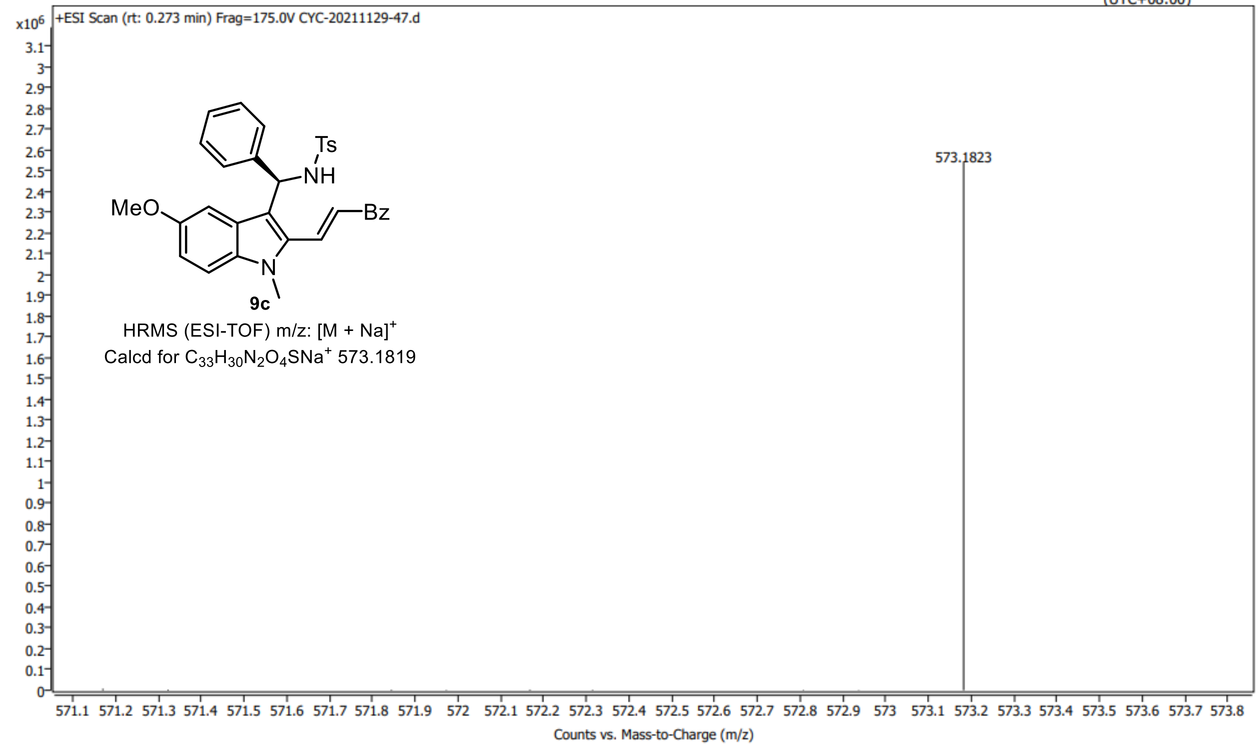
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	19.253	3.350	2139544	110998462	49.9433
2	30.300	5.563	1276119	111250474	50.0567

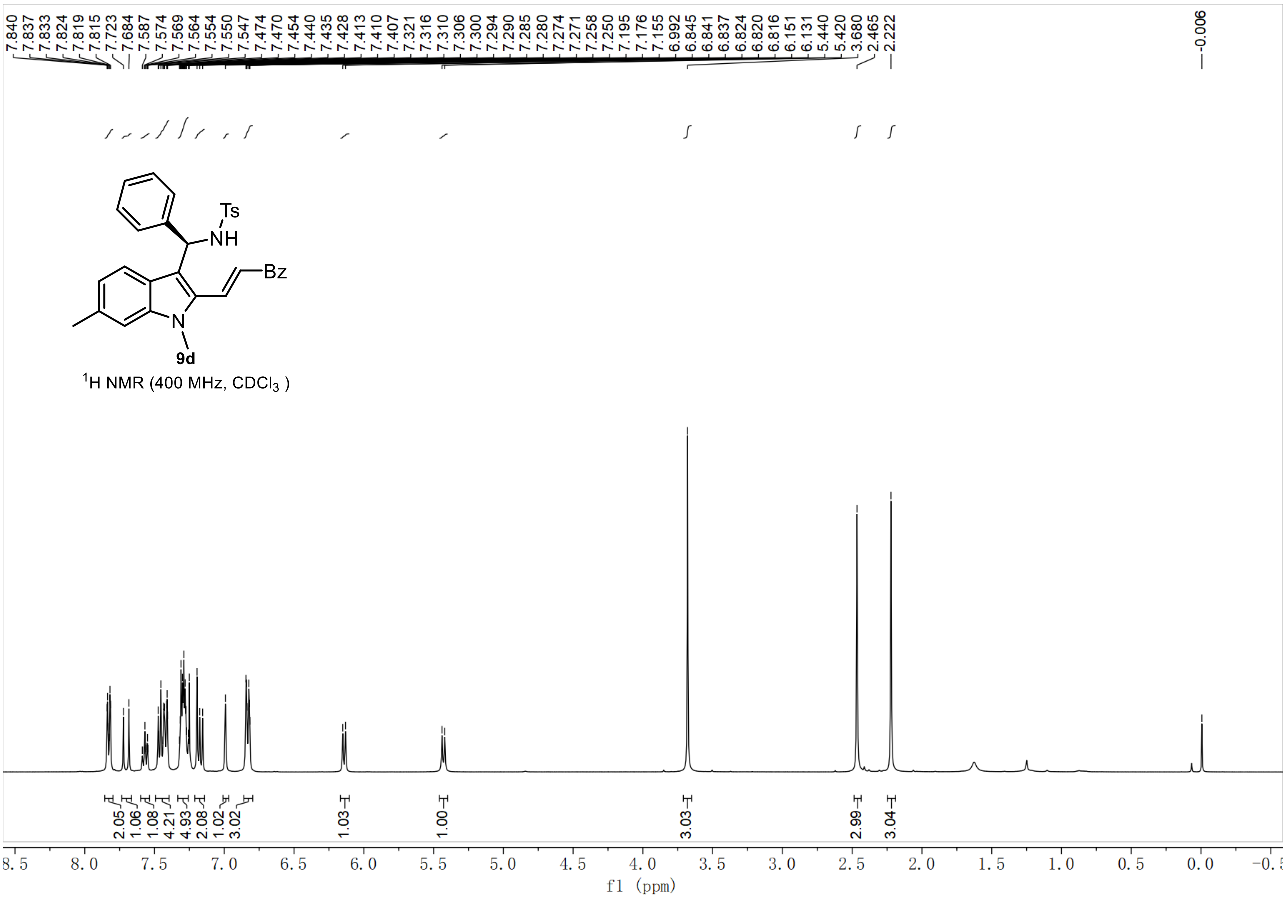


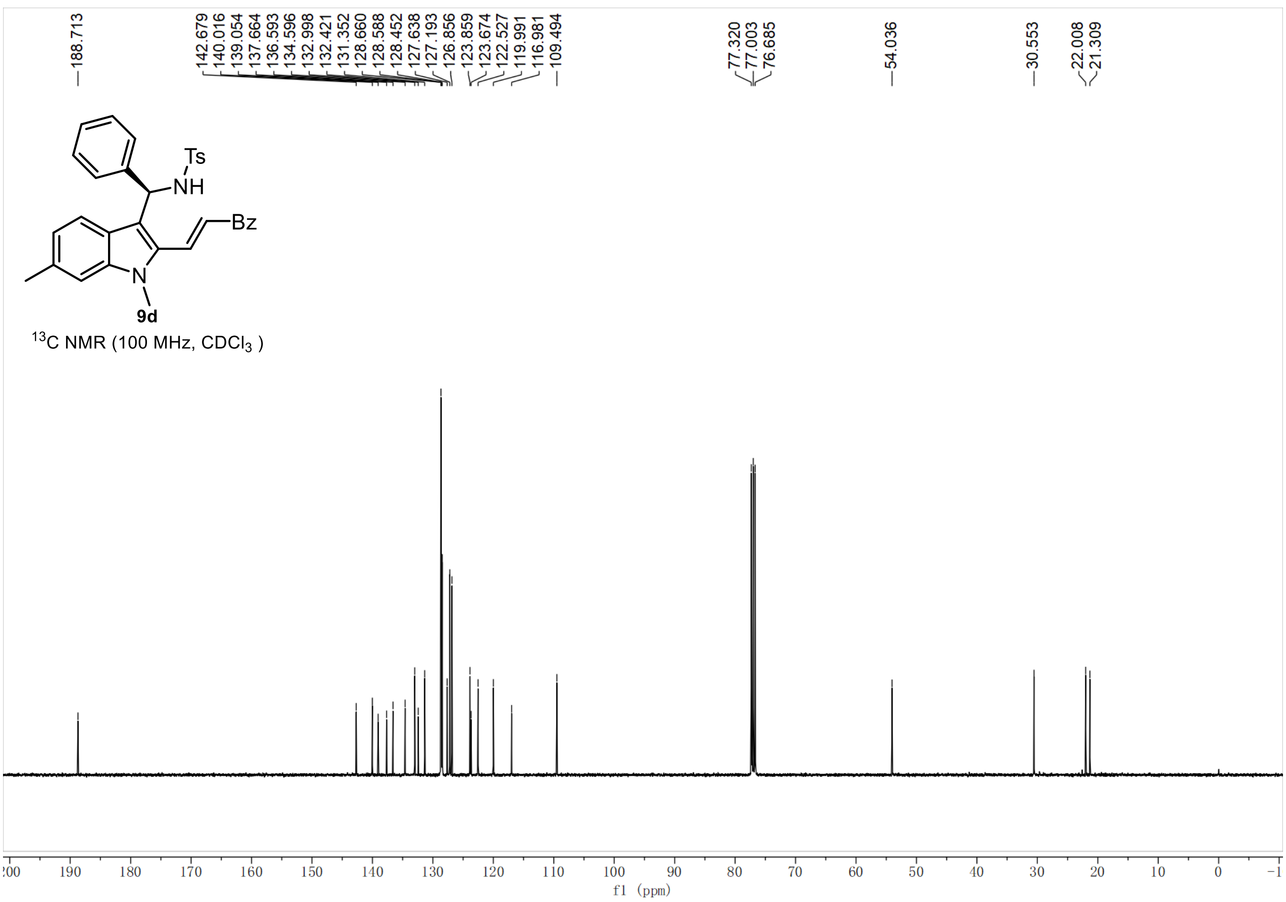
AREA PERCENT REPORT

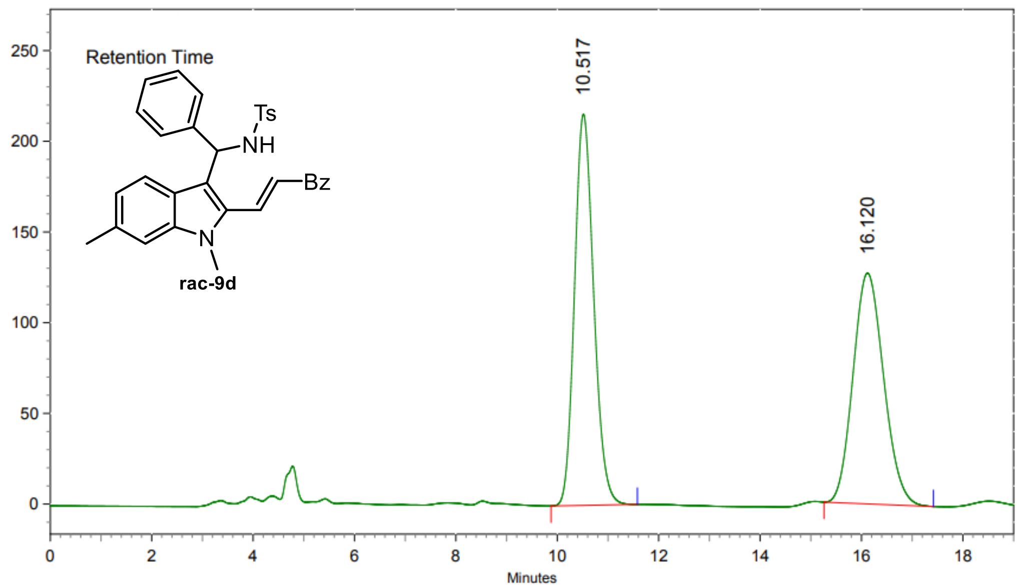
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	19.330	3.383	5209470	268629475	95.3700
2	30.613	5.180	146489	13041364	4.6300

Name	CYC-20211129-47	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-47.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 5:57:55 PM (UTC+08:00)



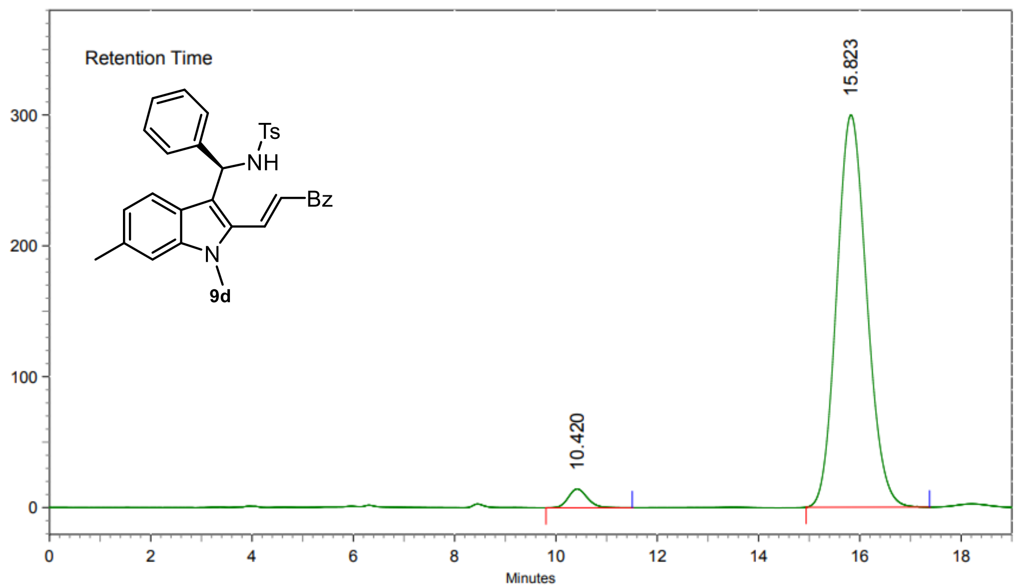

9d
^{1}H NMR (400 MHz, CDCl$_3$)


9d
^{13}C NMR (100 MHz, CDCl$_3$)



AREA PERCENT REPORT

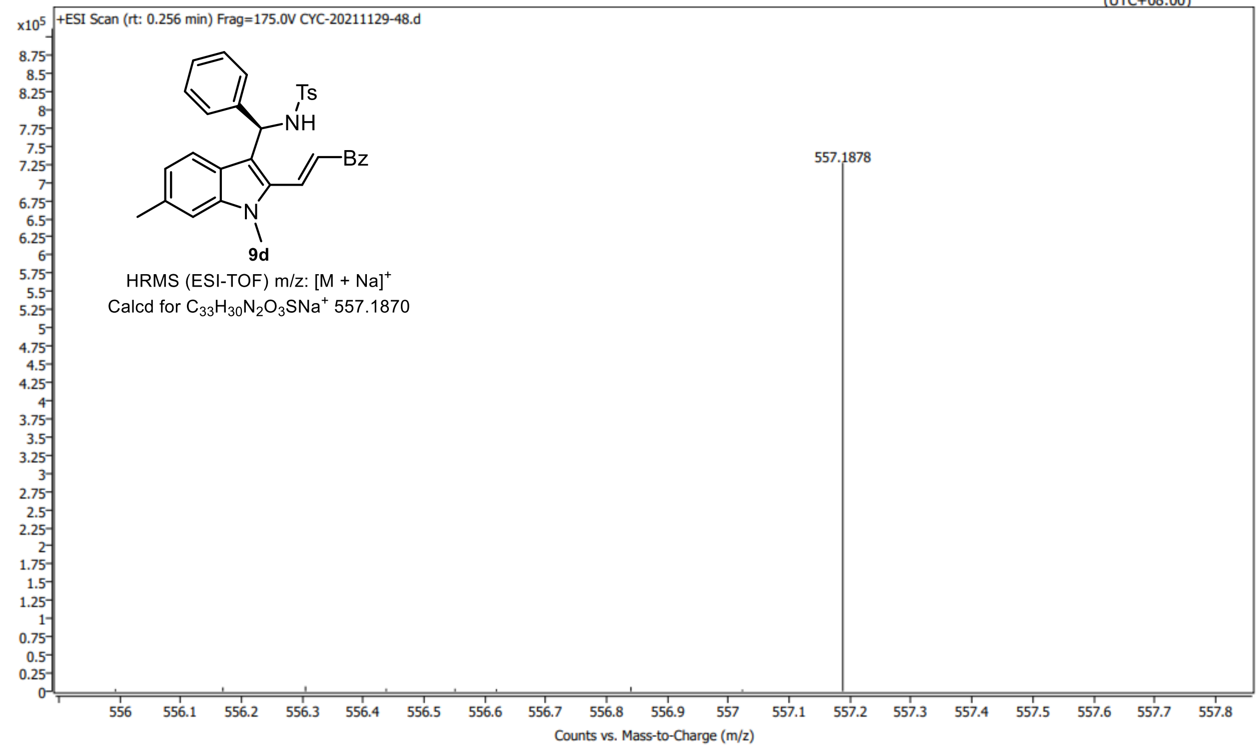
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.517	1.703	3617658	95289523	51.5117
2	16.120	2.160	2134571	89696755	48.4883

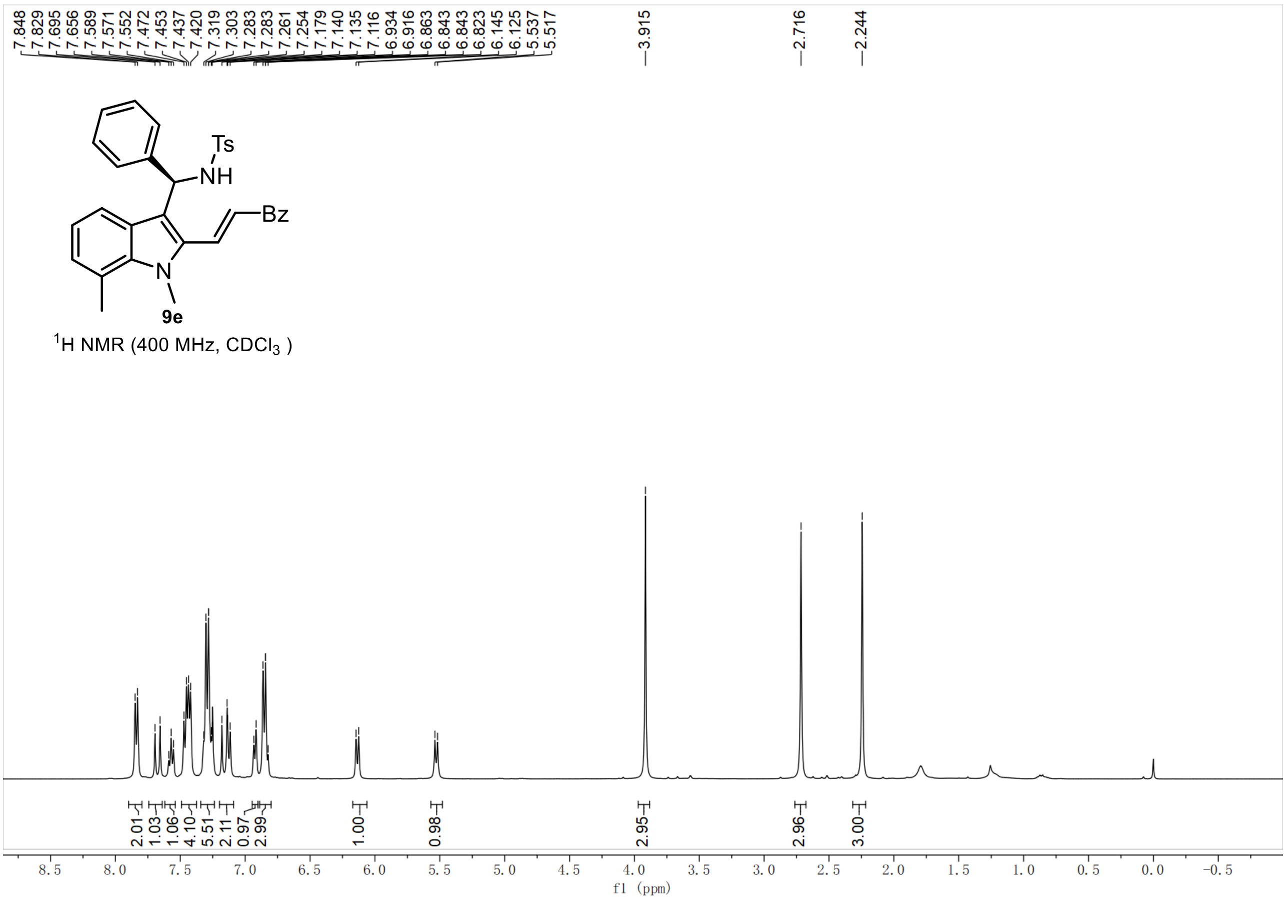


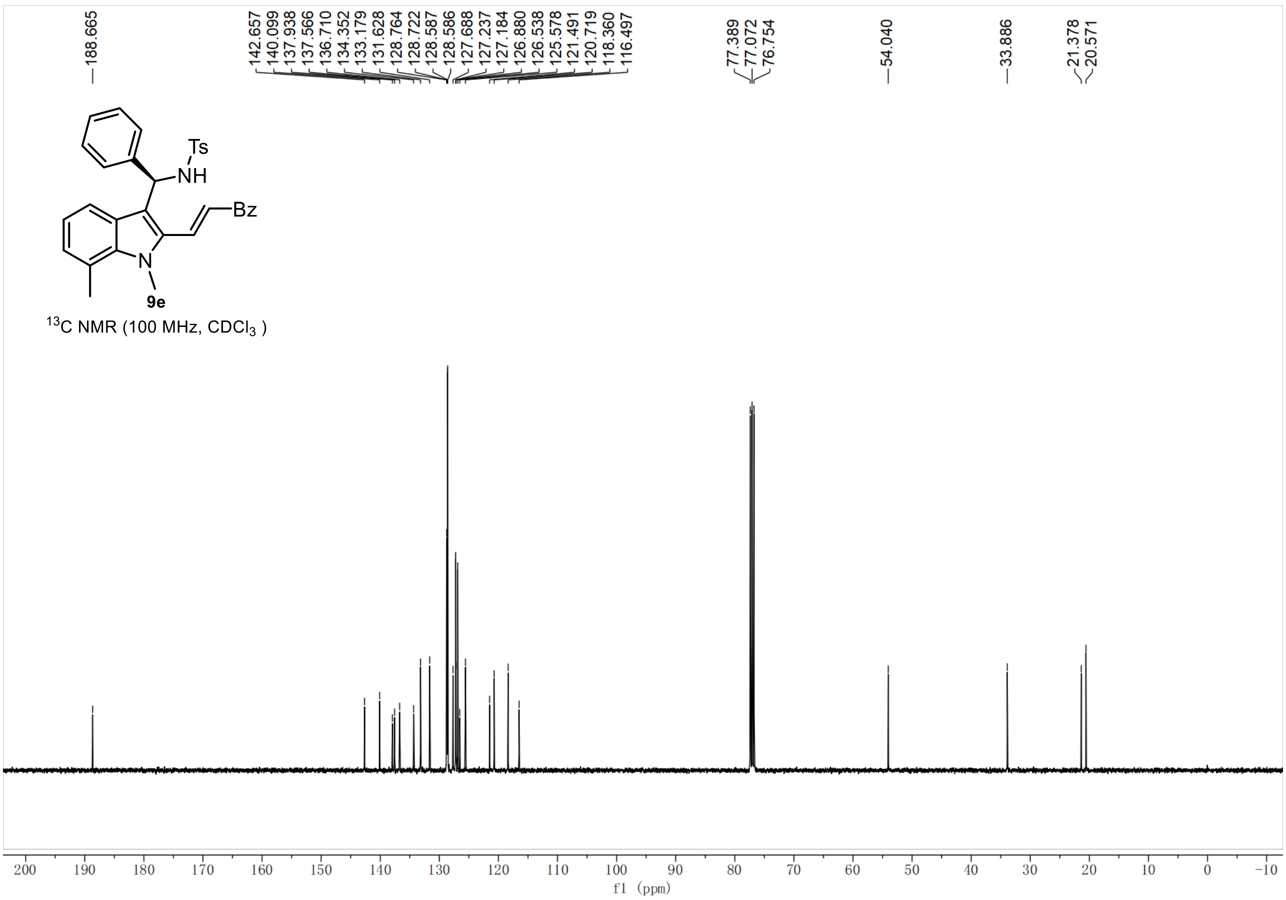
AREA PERCENT REPORT

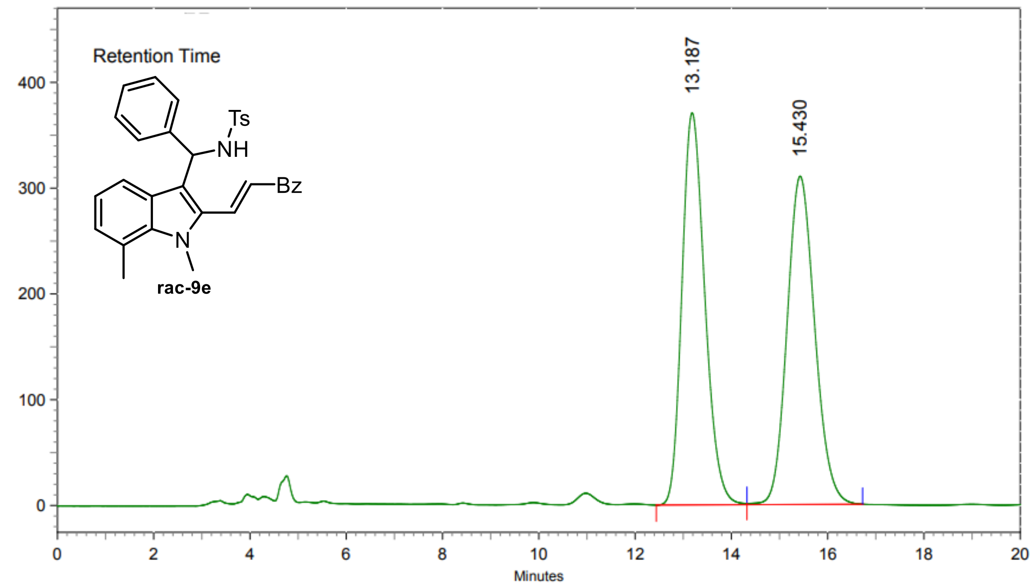
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.420	1.703	241044	6302803	2.9518
2	15.823	2.437	5028017	207223010	97.0482

Name	CYC-20211129-48	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-48.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:00:52 PM (UTC+08:00)



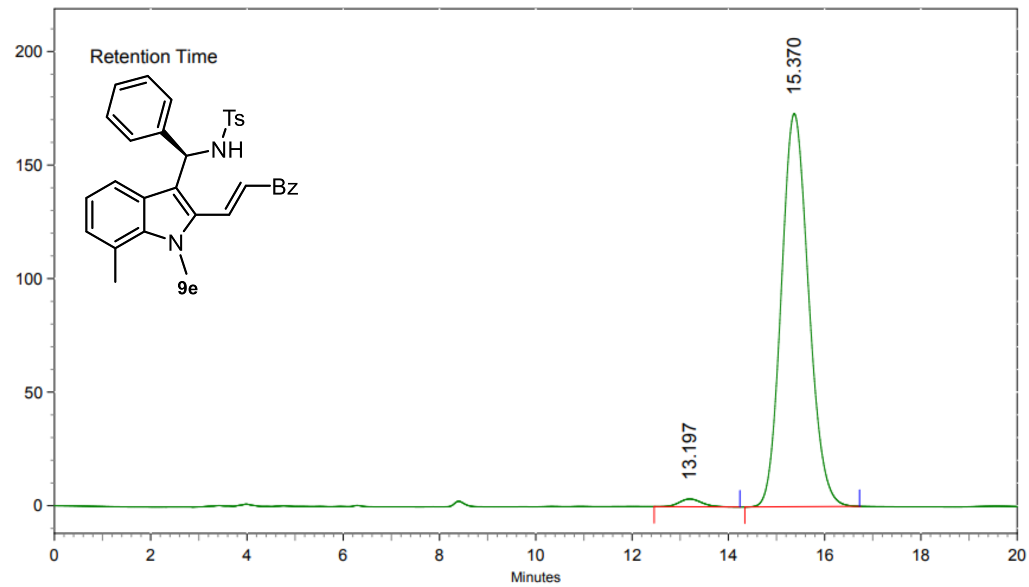

7.848
7.829
7.695
7.656
7.589
7.571
7.552
7.472
7.453
7.437
7.420
7.319
7.303
7.283
7.283
7.261
7.254
7.179
7.140
7.135
7.116
6.934
6.916
6.863
6.843
6.843
6.823
6.145
6.125
5.537
5.517
3.915
2.716
2.244
Ts
NH
Bz
N
9e
1H NMR (400 MHz, CDCl3)
2.01
1.03
1.06
4.10
5.51
2.11
0.97
2.99
1.00
0.98
2.95
2.96
3.00
f1 (ppm)


188.665
142.657
140.099
137.938
137.566
136.710
134.352
133.179
131.628
128.764
128.722
128.587
128.586
127.688
127.237
127.184
126.880
126.538
125.578
121.491
120.719
118.360
116.497
77.389
77.072
76.754
54.040
33.886
21.378
20.571
Ts
NH
Bz
N
9e
13C NMR (100 MHz, CDCl3)
f1 (ppm)



AREA PERCENT REPORT

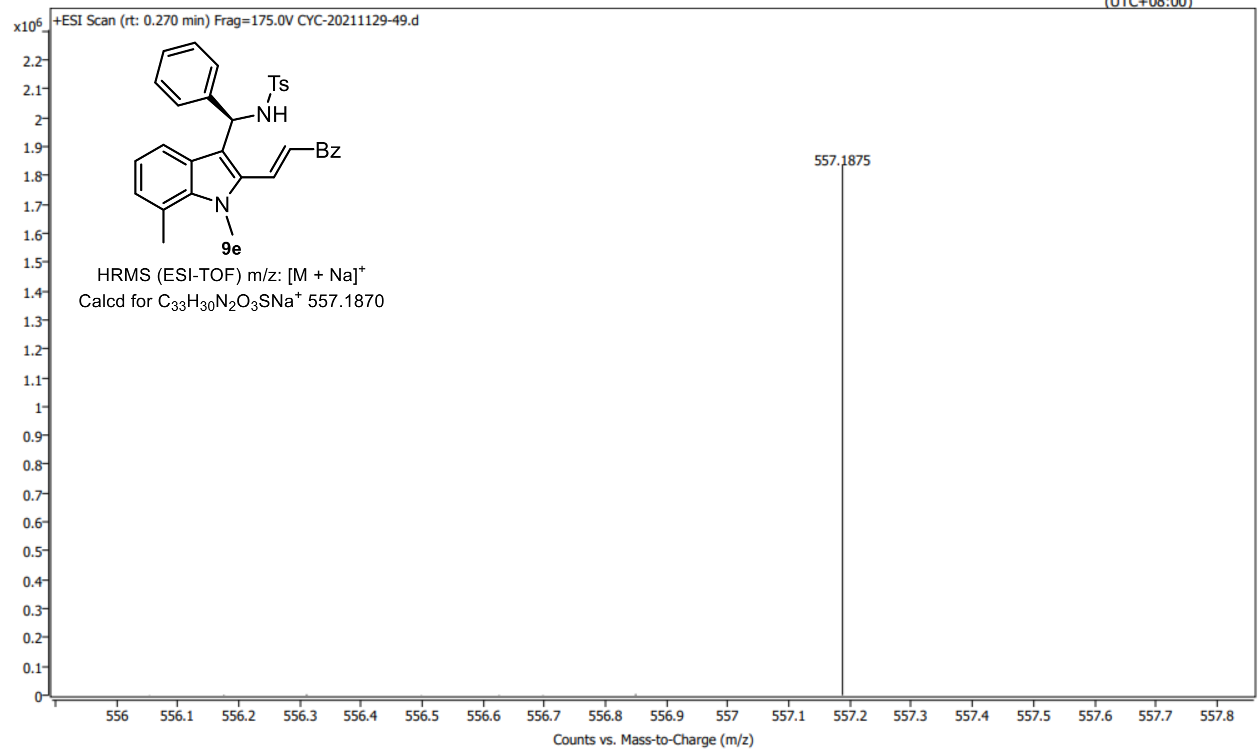
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.187	1.883	6217001	205089247	49.5989
2	15.430	2.403	5206164	208405889	50.4011

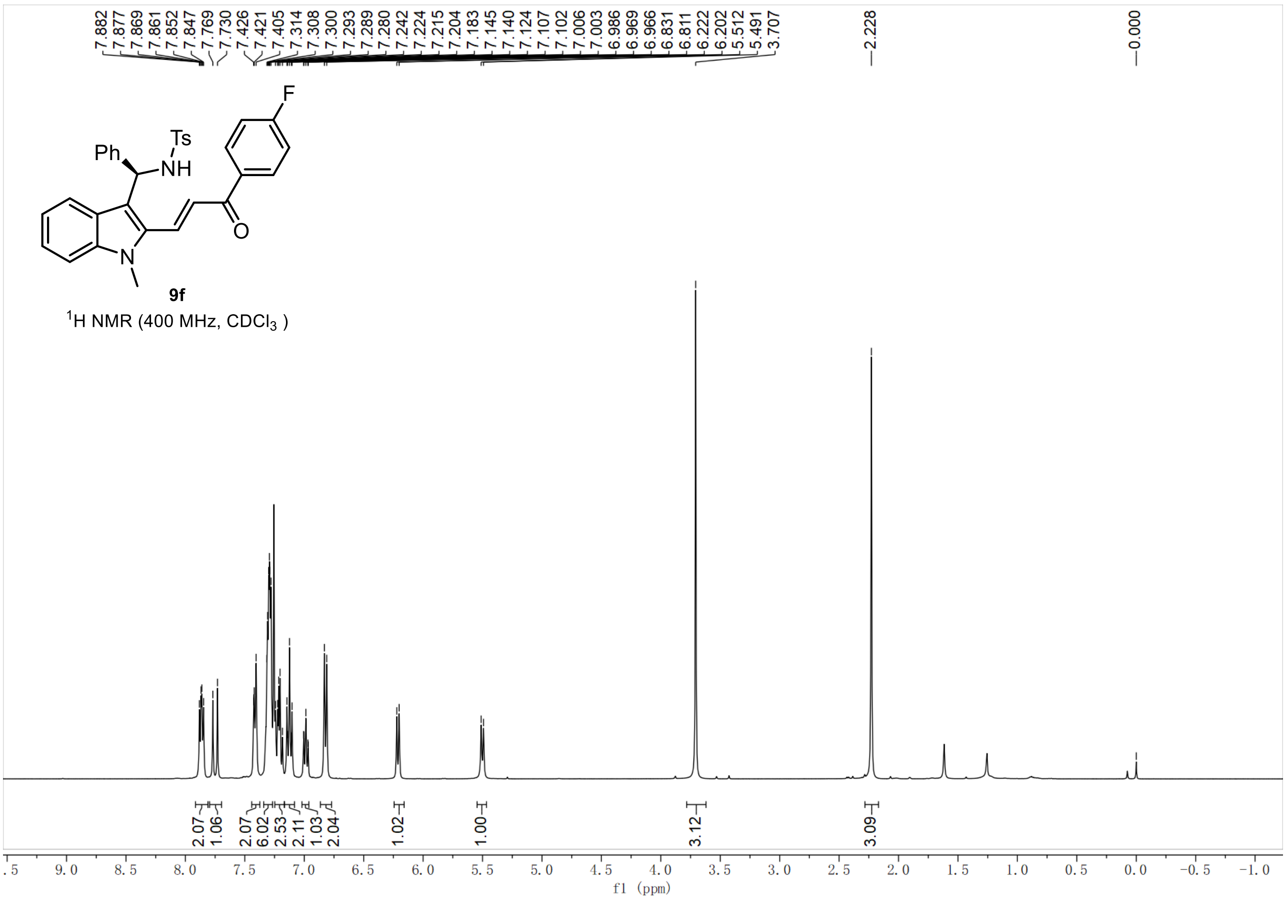


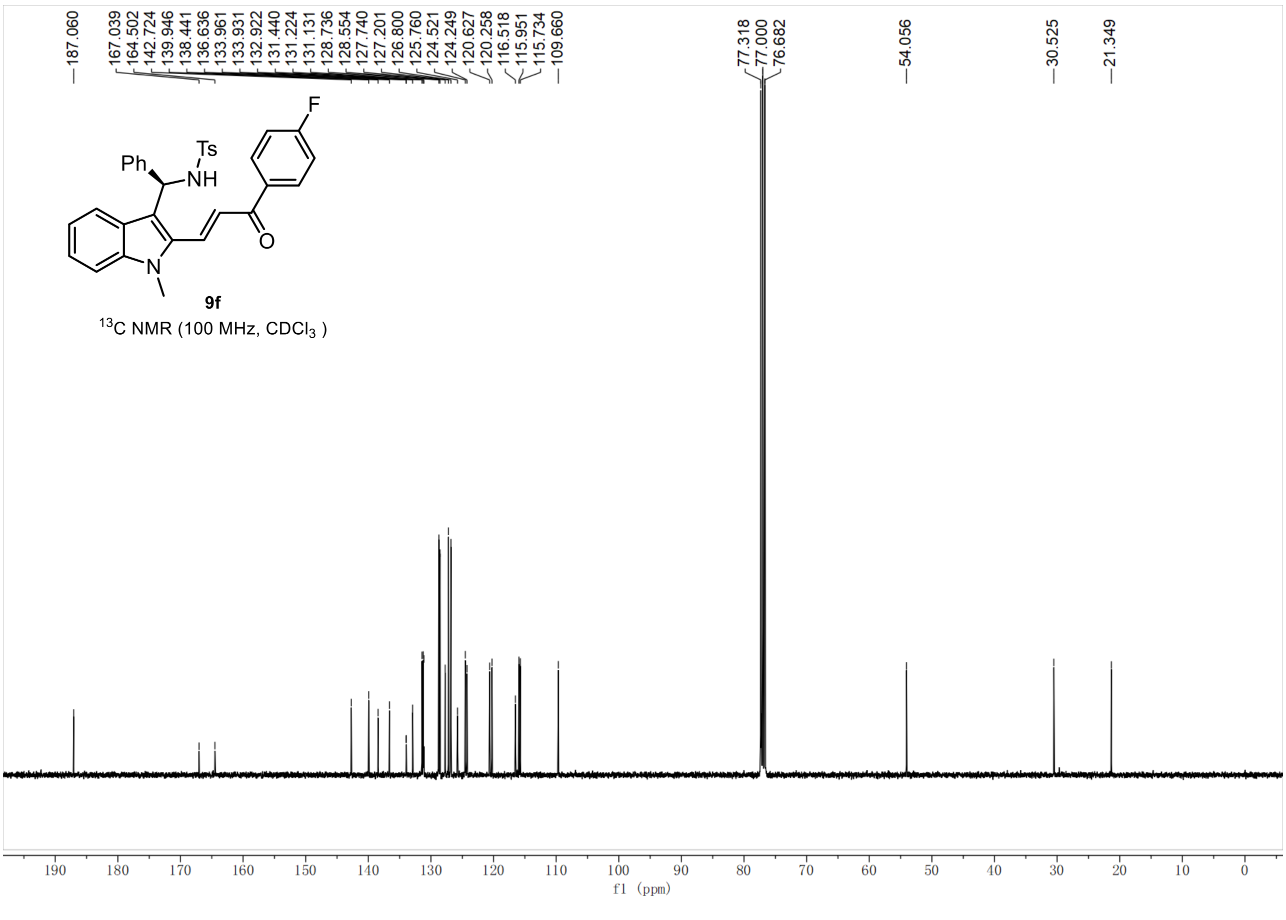
AREA PERCENT REPORT

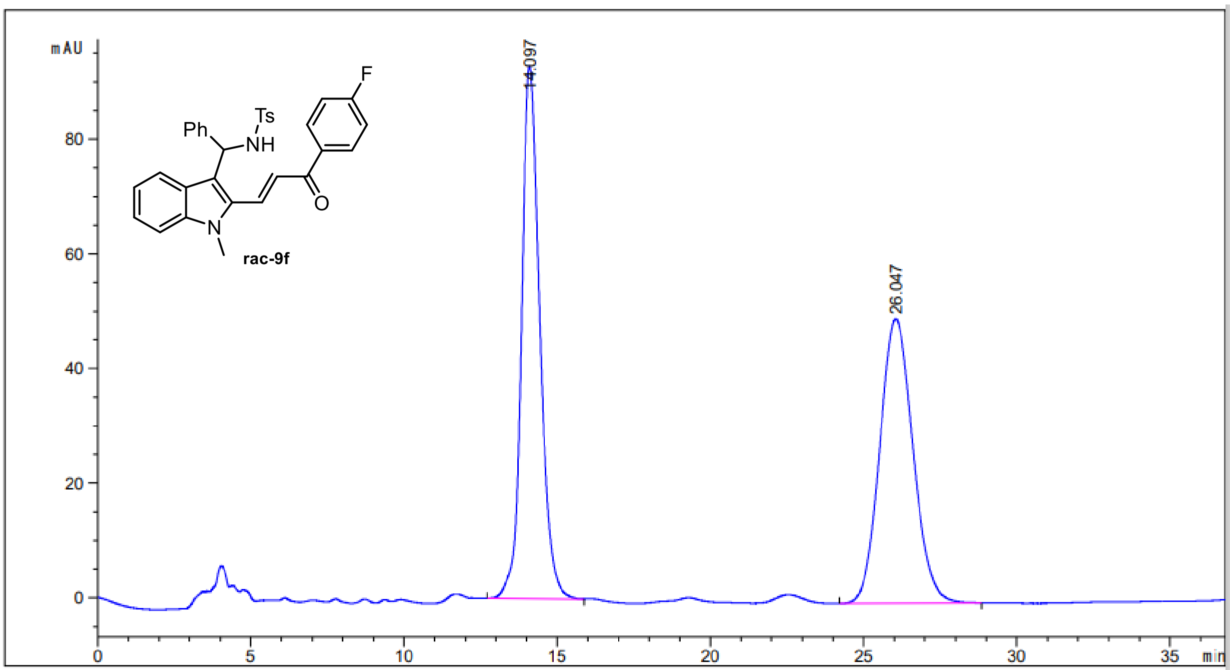
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.197	1.780	57651	1878293	1.6145
2	15.370	2.383	2904245	114463831	98.3855

Name	CYC-20211129-49	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-49.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:03:49 PM (UTC+08:00)

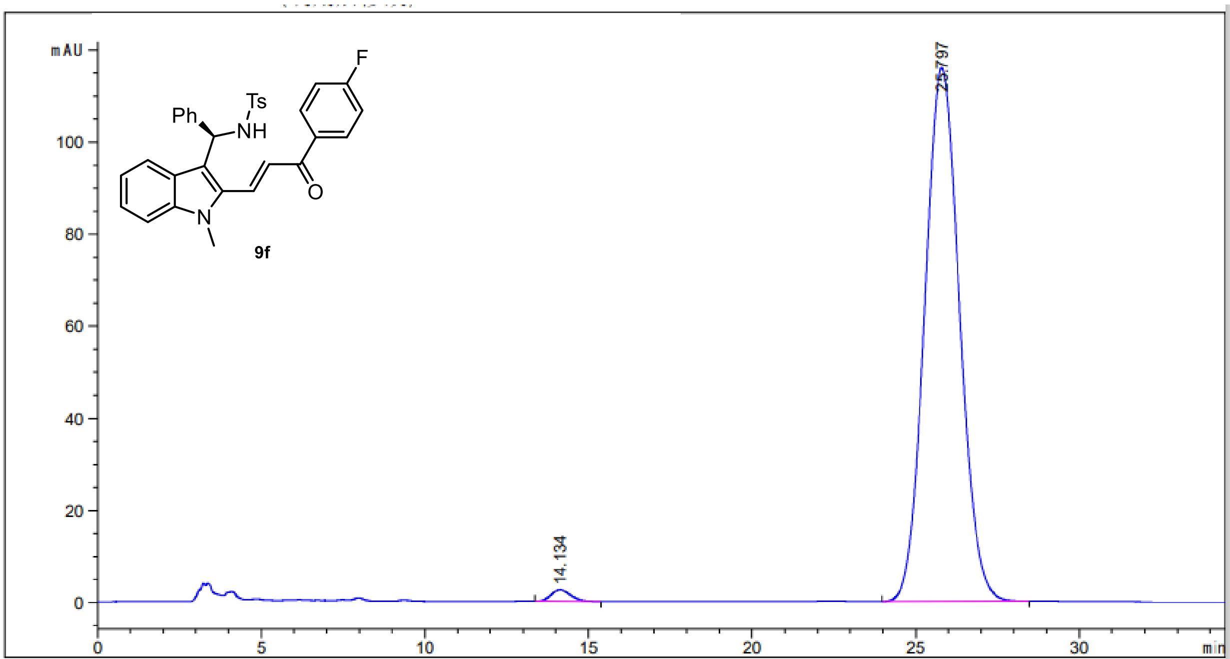



7.882 7.877 7.869 7.861 7.852 7.847 7.769 7.730 7.426 7.421 7.405 7.314 7.308 7.300 7.293 7.289 7.280 7.242 7.224 7.215 7.204 7.183 7.145 7.140 7.124 7.107 7.102 7.006 7.003 6.986 6.969 6.966 6.831 6.811 6.222 6.202 5.512 5.491 3.707
2.228
0.000
F
Ph
Ts
NH
O
N
9f
^{1}H NMR (400 MHz, $CDCl_3$)
2.07 1.06 2.07 6.02 2.53 2.11 1.03 2.04 1.02 1.00 3.12 3.09
f1 (ppm)

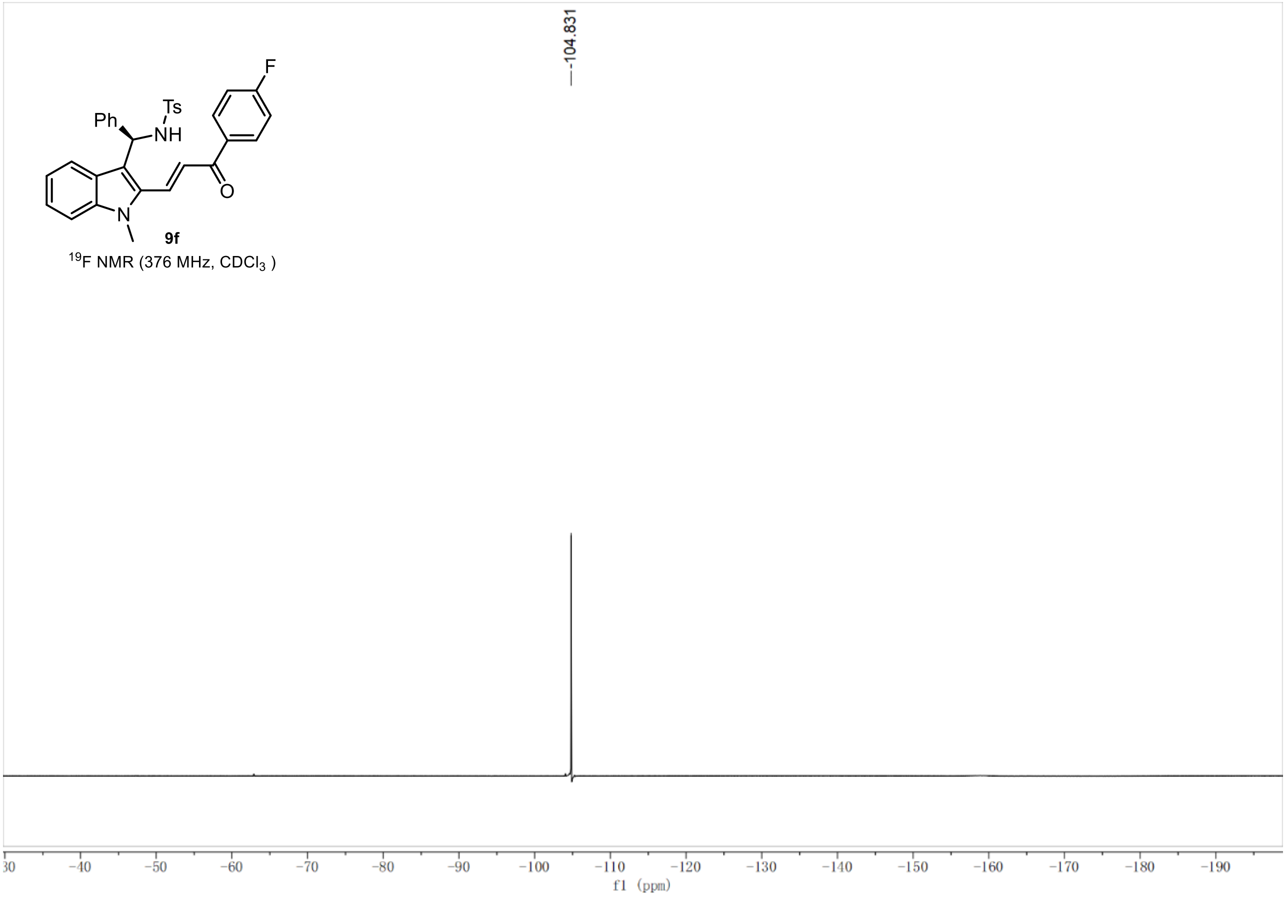

187.060
167.039 164.502 142.724 139.946 138.441 136.636 133.961 133.931 132.922 131.440 131.224 131.131 128.736 128.554 127.740 127.201 126.800 125.760 124.521 124.249 120.627 120.258 116.518 115.951 115.734 109.660
77.318 77.000 76.682
54.056
30.525
21.349
F
Ph
Ts
NH
O
N
9f
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

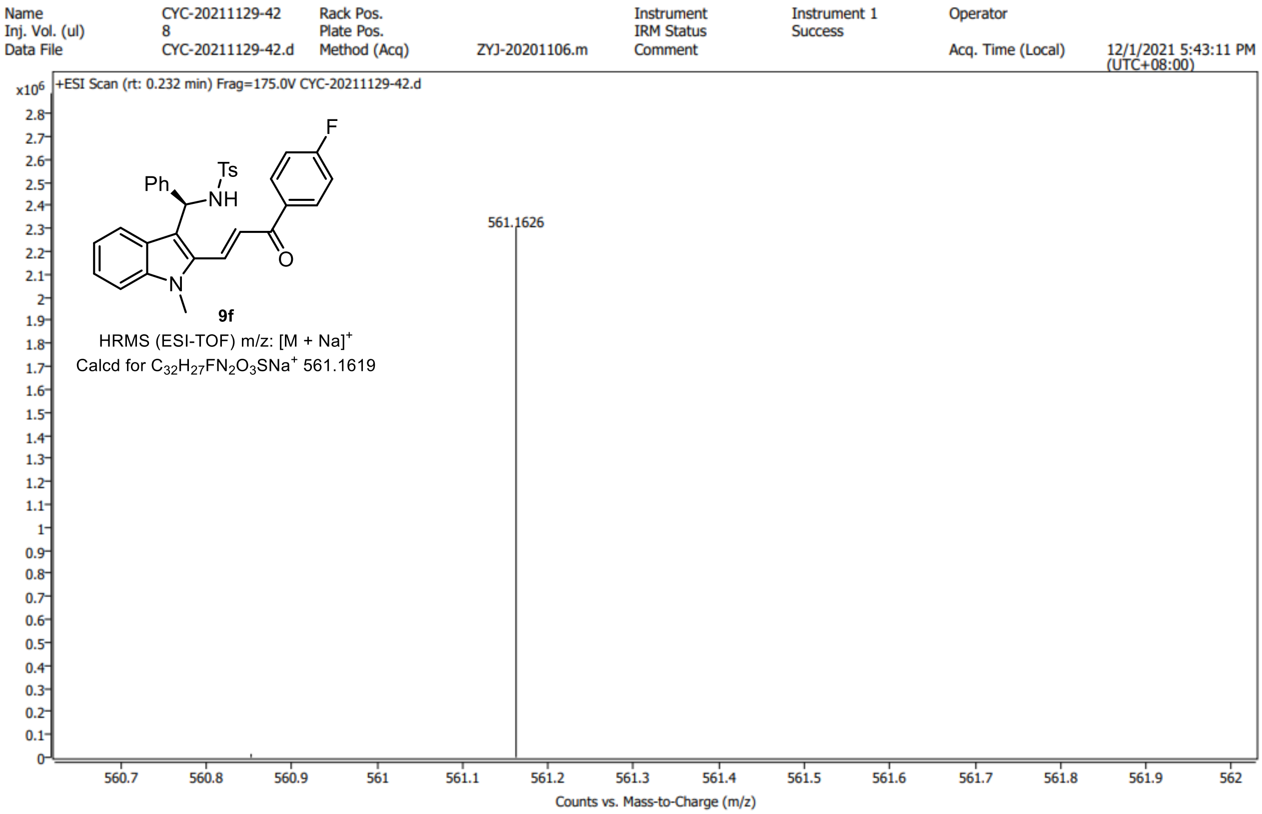


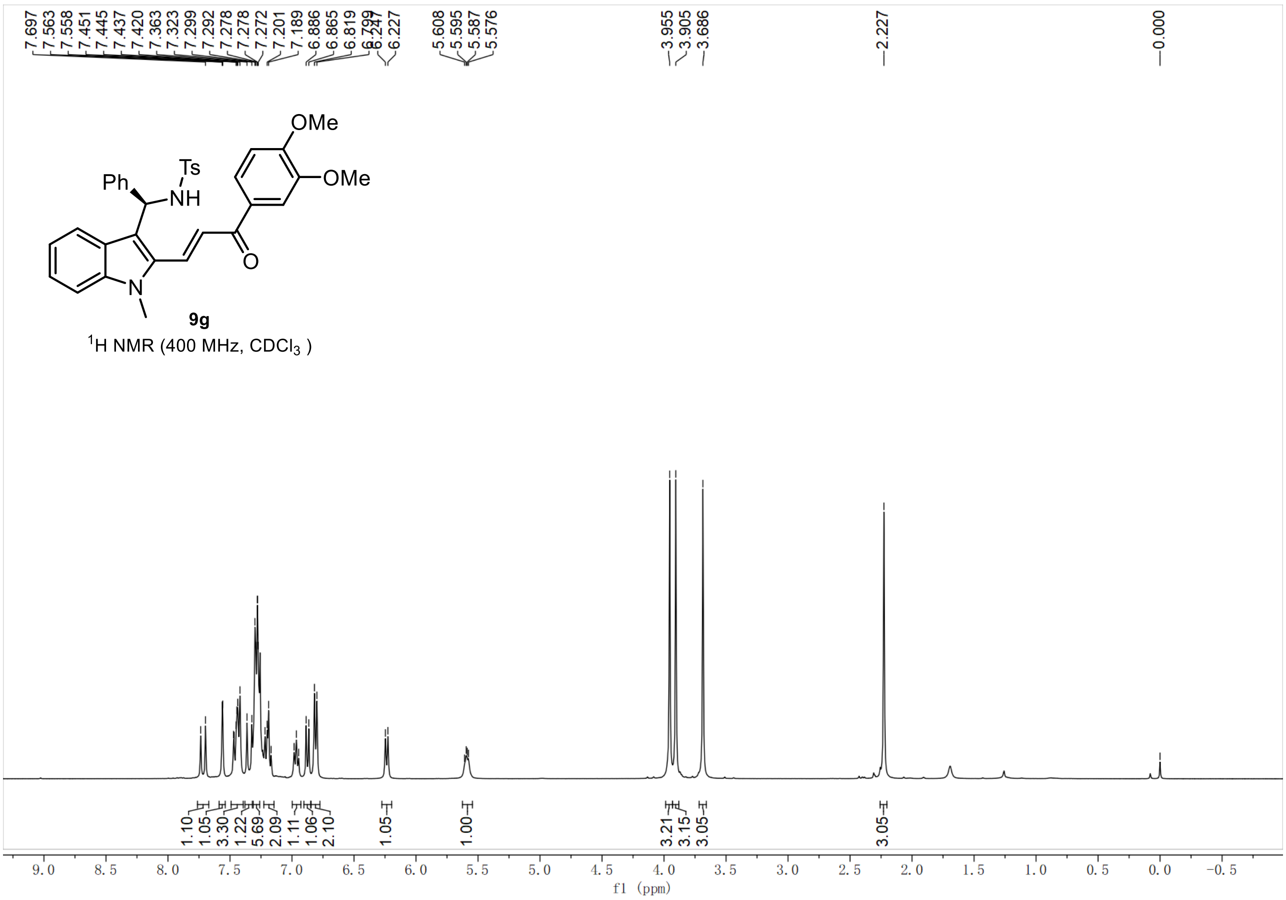
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.097	BB	0.6307	3837.86670	92.86835	50.6715
2	26.047	BB	1.1595	3736.15186	49.61930	49.3285



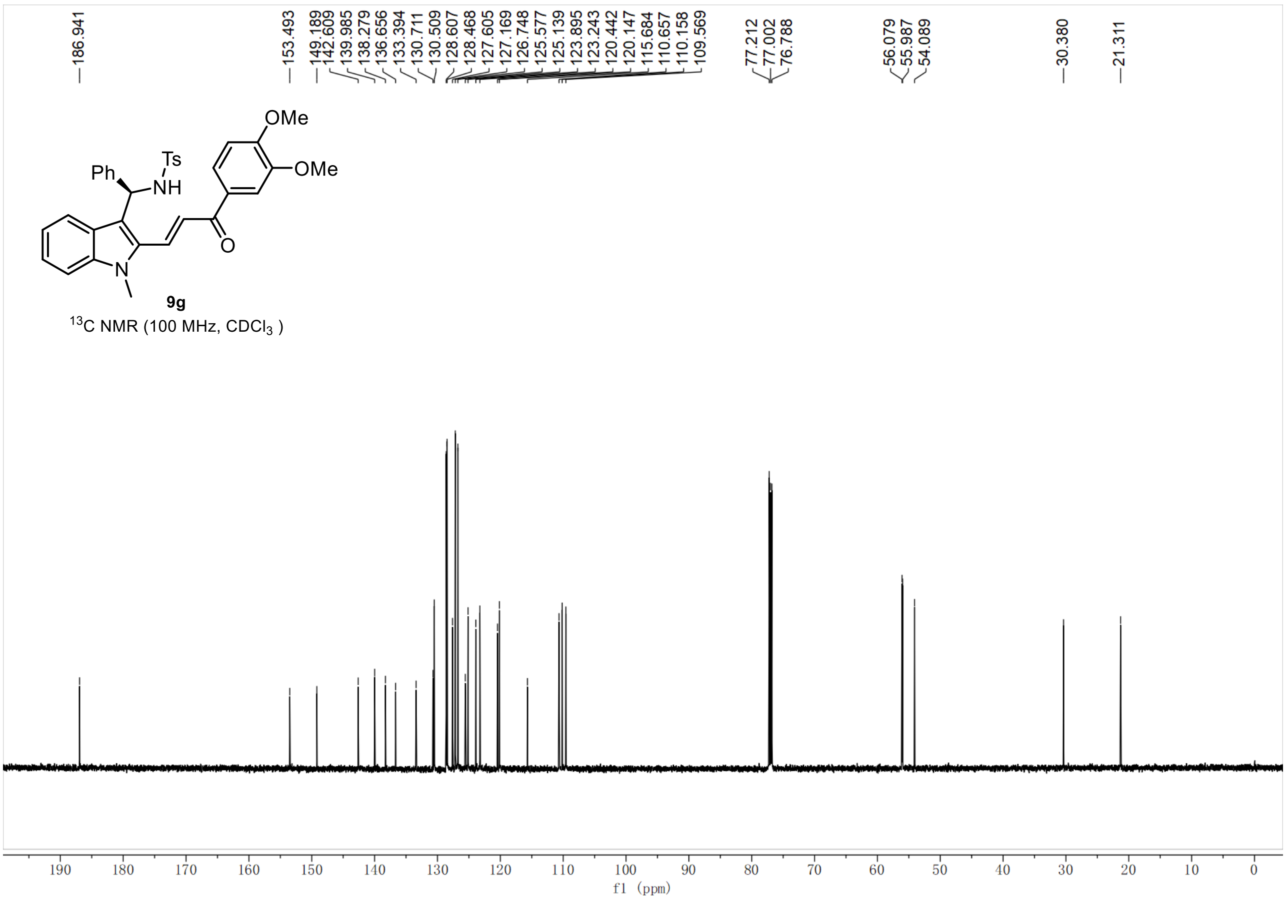
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.134	BB	0.5884	103.50513	2.53538	1.1951
2	25.797	BB	1.1544	8557.31055	115.85522	98.8049


-104.831
Ph
Ts
NH
F
O
N
9f
^{19}F NMR (376 MHz, $CDCl_3$)
f1 (ppm)

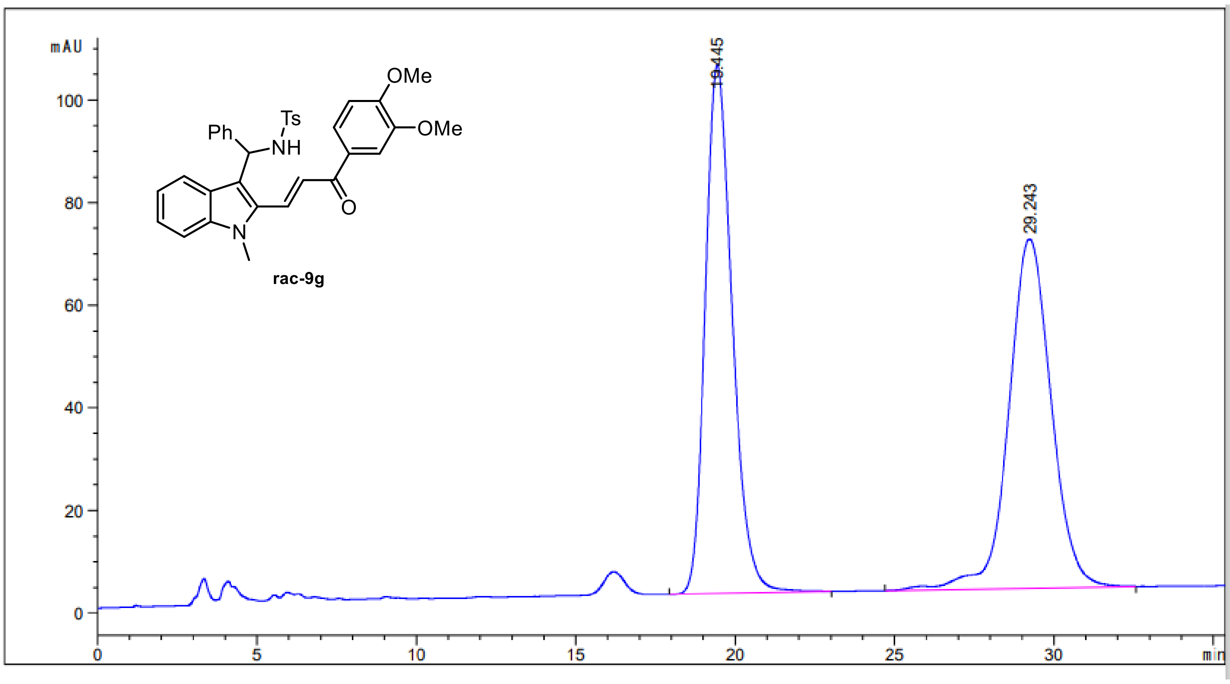

Name CYC-20211129-42
Inj. Vol. (ul) 8
Data File CYC-20211129-42.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument Instrument 1
IRM Status Success
Comment
Operator
Acq. Time (Local) 12/1/2021 5:43:11 PM (UTC+08:00)
+ESI Scan (rt: 0.232 min) Frag=175.0V CYC-20211129-42.d
561.1626
9f
HRMS (ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{32}H_{27}FN_2O_3SNa^+$ 561.1619
Counts vs. Mass-to-Charge (m/z)



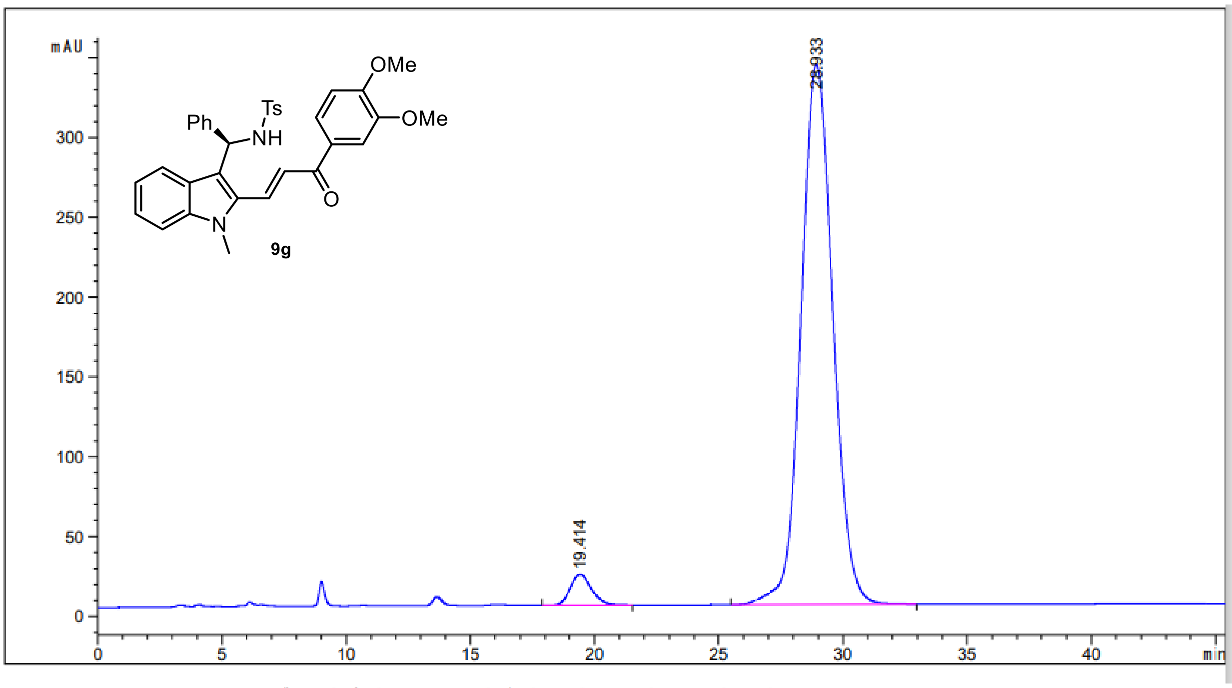
OMe
OMe
Ph
Ts
NH
N
O
9g
[1]H NMR (400 MHz, CDCl3)
f1 (ppm)



OMe
OMe
Ph
Ts
NH
N
O
9g
[13]C NMR (100 MHz, CDCl3)
f1 (ppm)

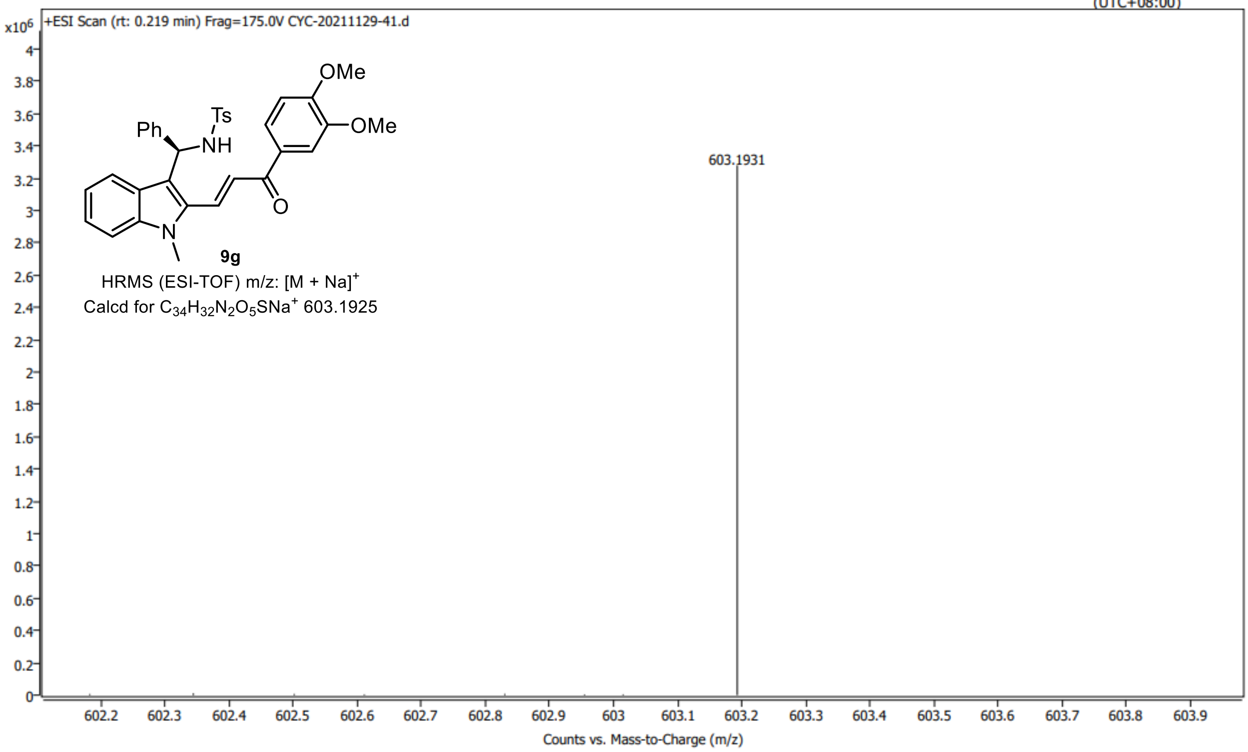


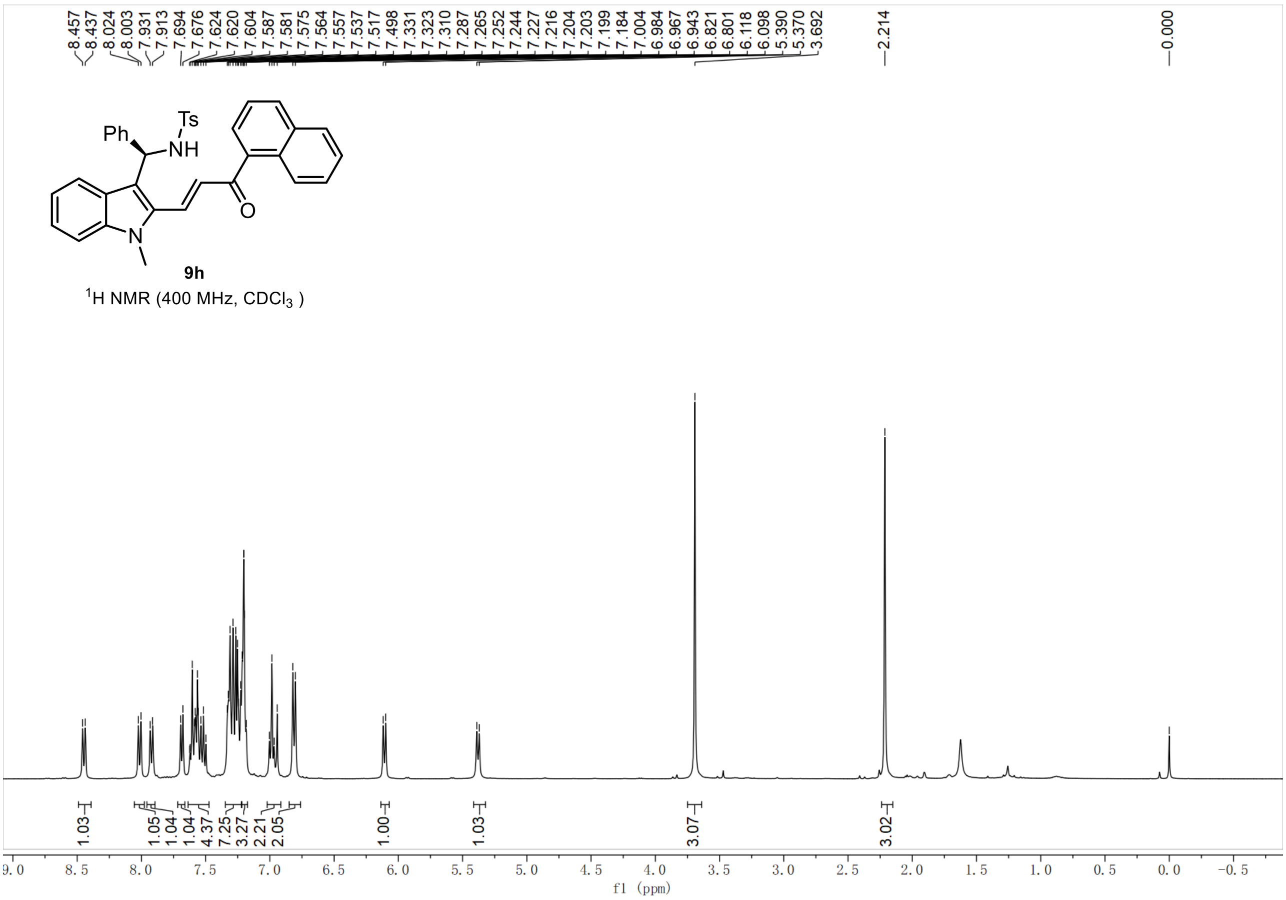
#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.445	BB	0.9056	6057.05322	103.04829	48.9834
2	29.243	BB	1.4177	6308.47754	68.06034	51.0166



#	[min]		[min]	[mAU*s]	[mAU]	%
1	19.414	BB	0.8950	1140.88245	19.25821	3.6408
2	28.933	BB	1.3824	3.01951e4	338.17093	96.3592

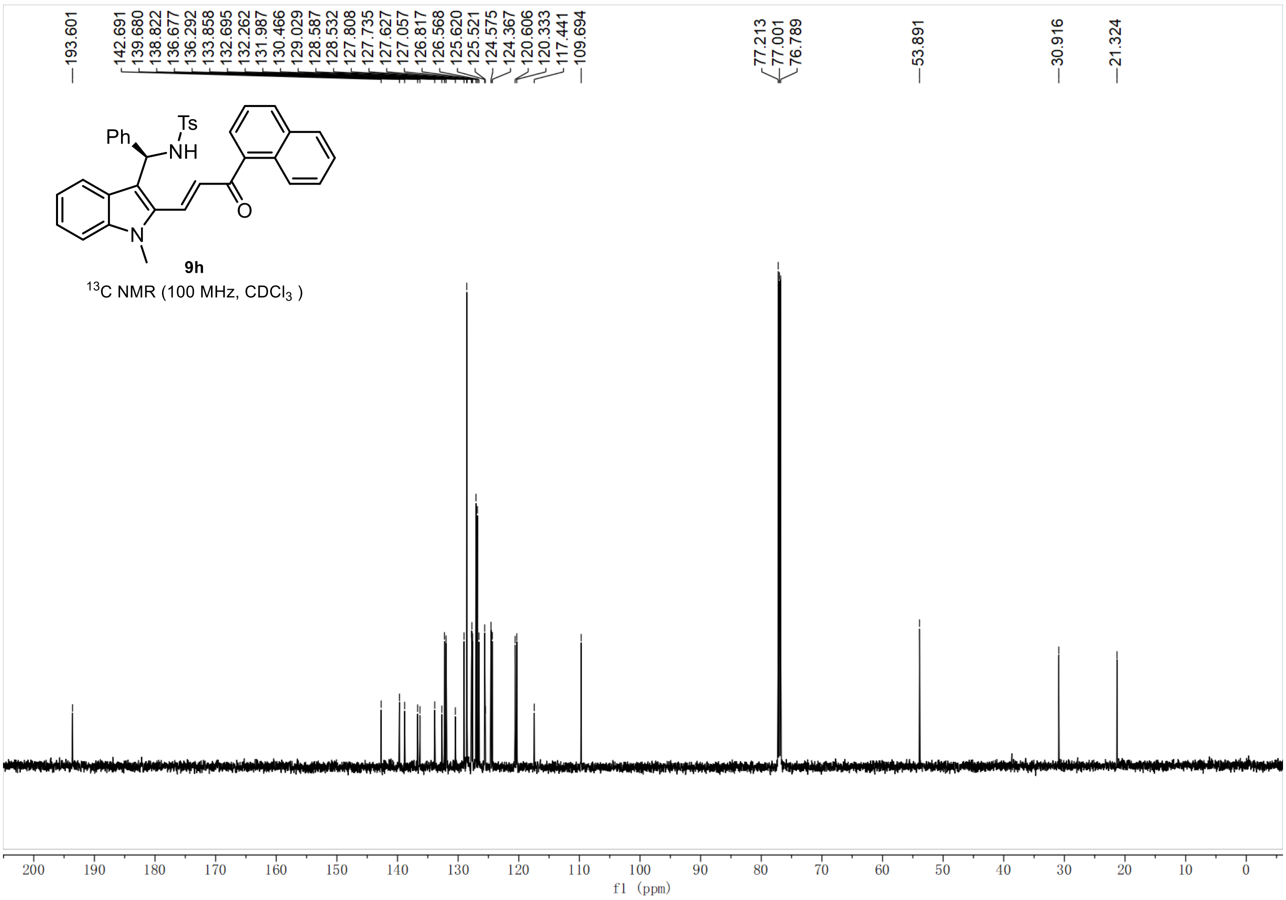
Name	CYC-20211129-41	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-41.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 5:39:58 PM (UTC+08:00)





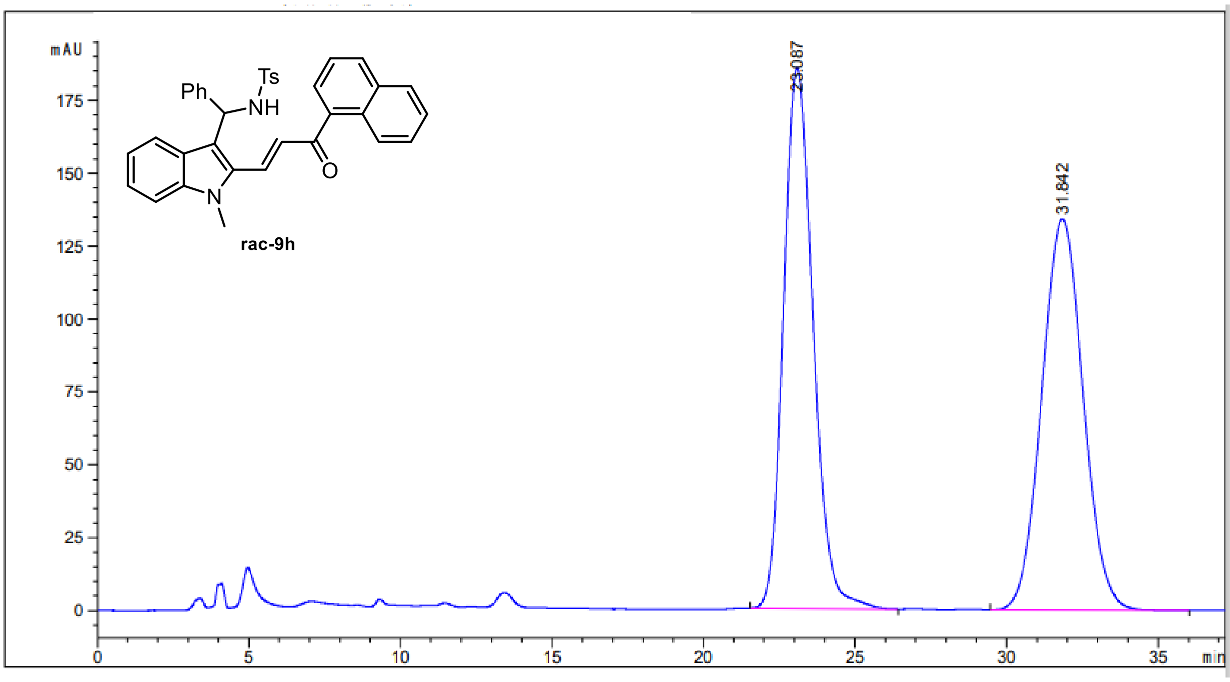
9h

[1]H NMR (400 MHz, $CDCl_3$)

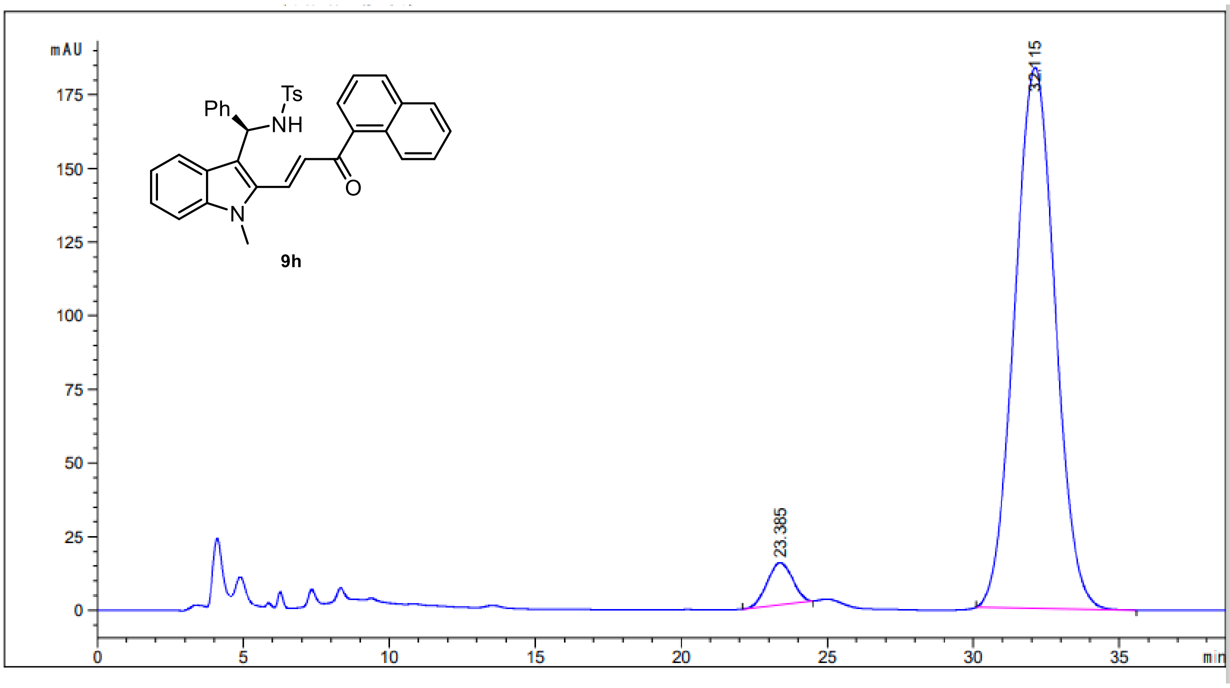


9h

[13]C NMR (100 MHz, $CDCl_3$)

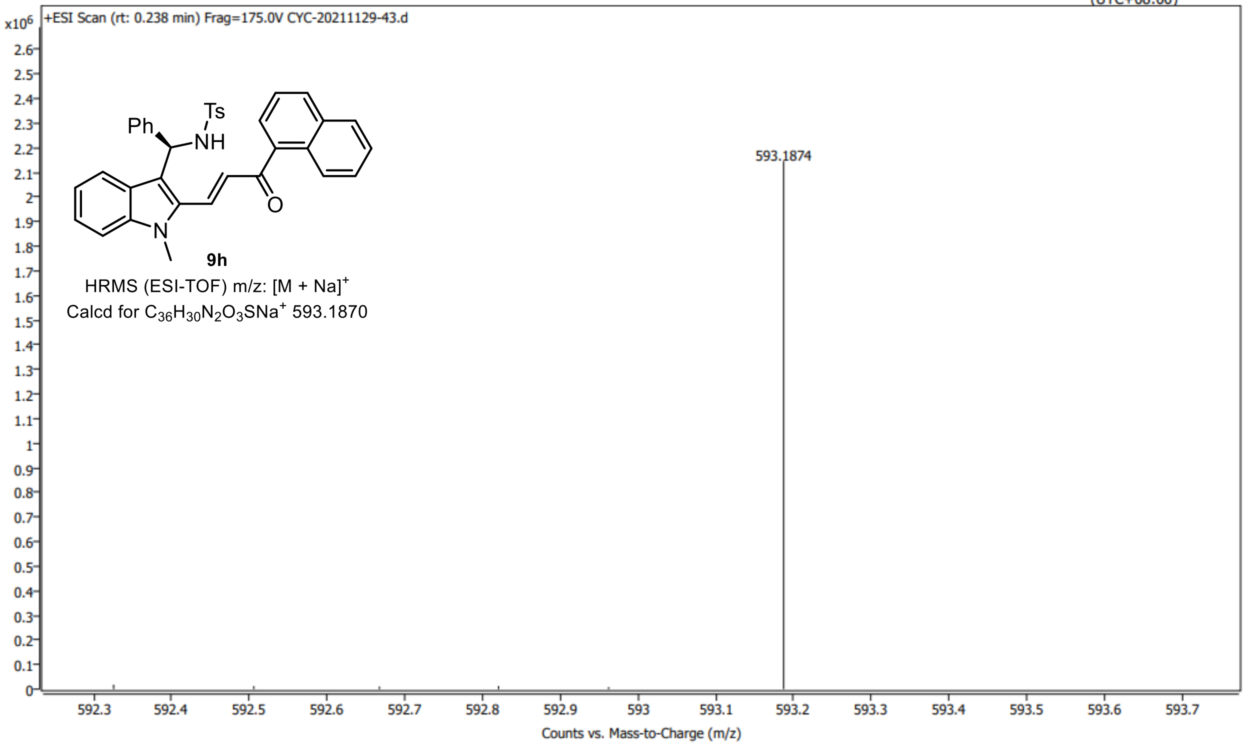


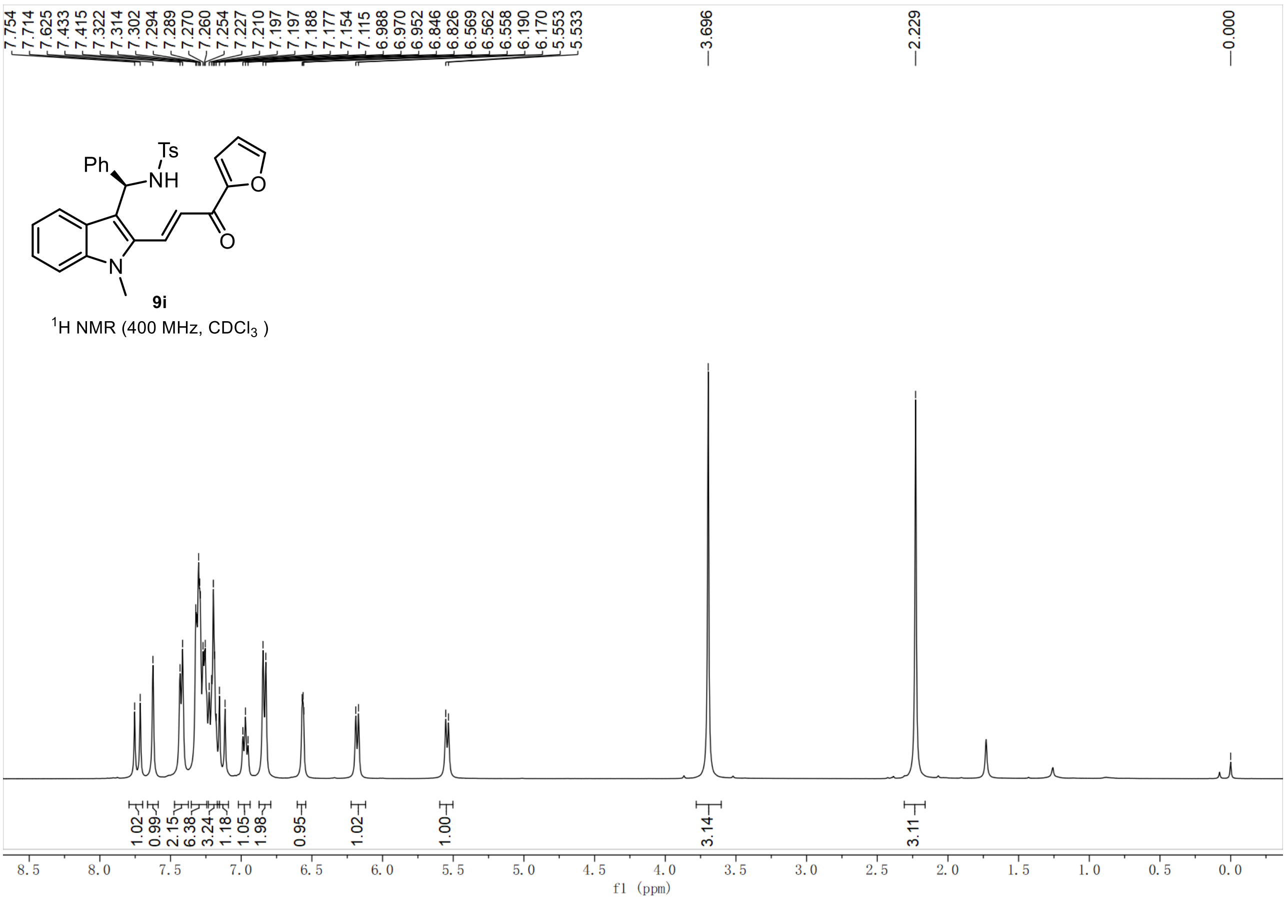
#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.087	BB	1.0482	1.25178e4	185.43149	49.6461
2	31.842	BB	1.4730	1.26963e4	134.09778	50.3539

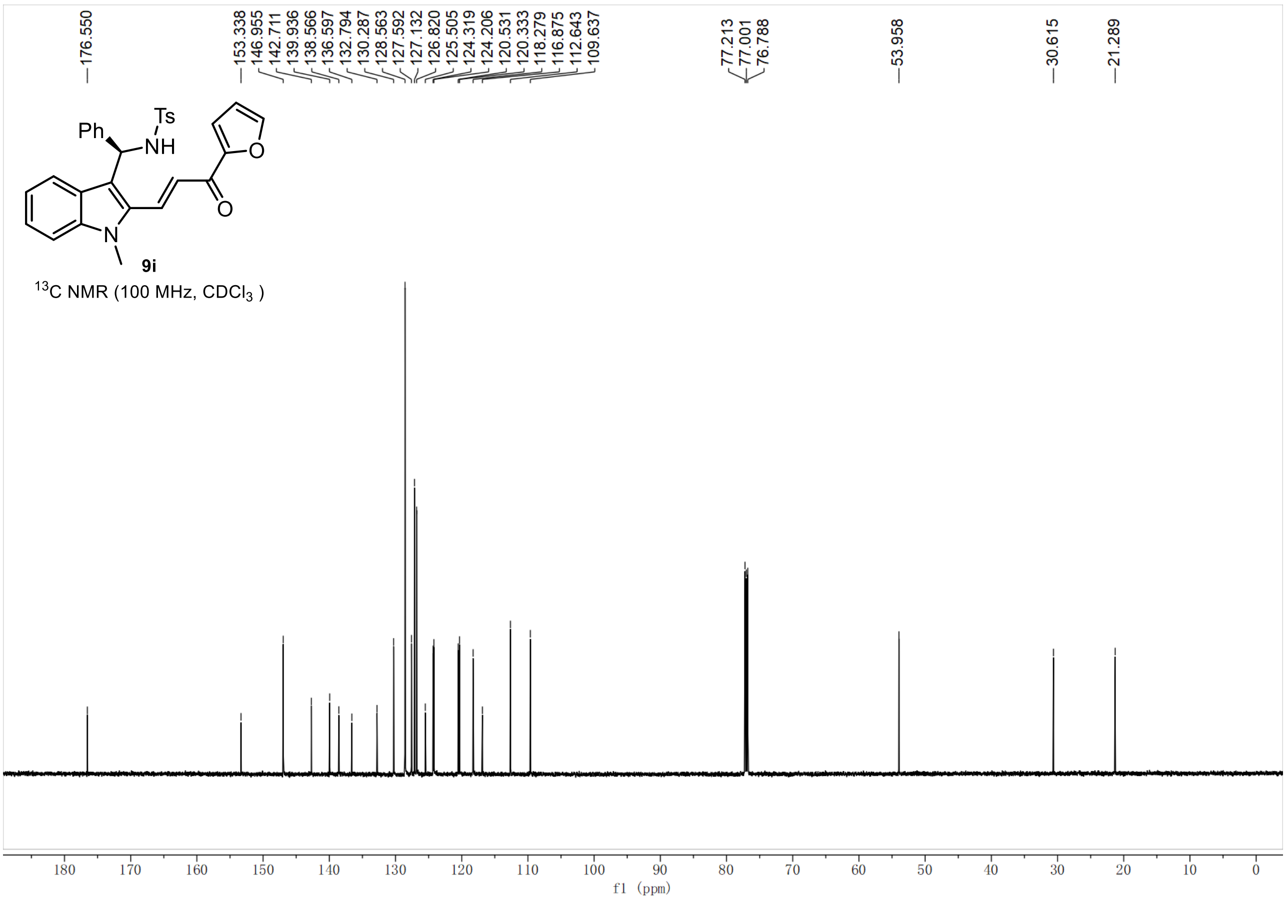


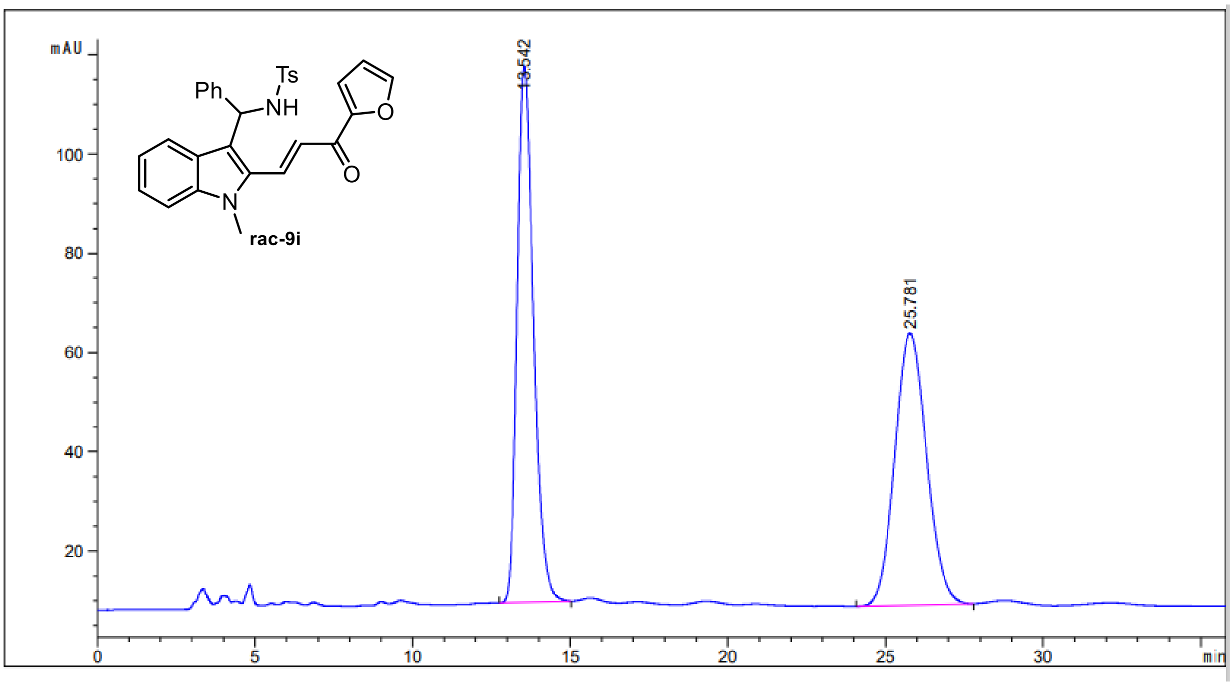
#	[min]		[min]	[mAU*s]	[mAU]	%
1	23.385	BB	0.9409	858.65027	14.23808	4.6249
2	32.115	BB	1.4287	1.77073e4	183.49400	95.3751

Name	CYC-20211129-43	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-43.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 5:46:08 PM (UTC+08:00)

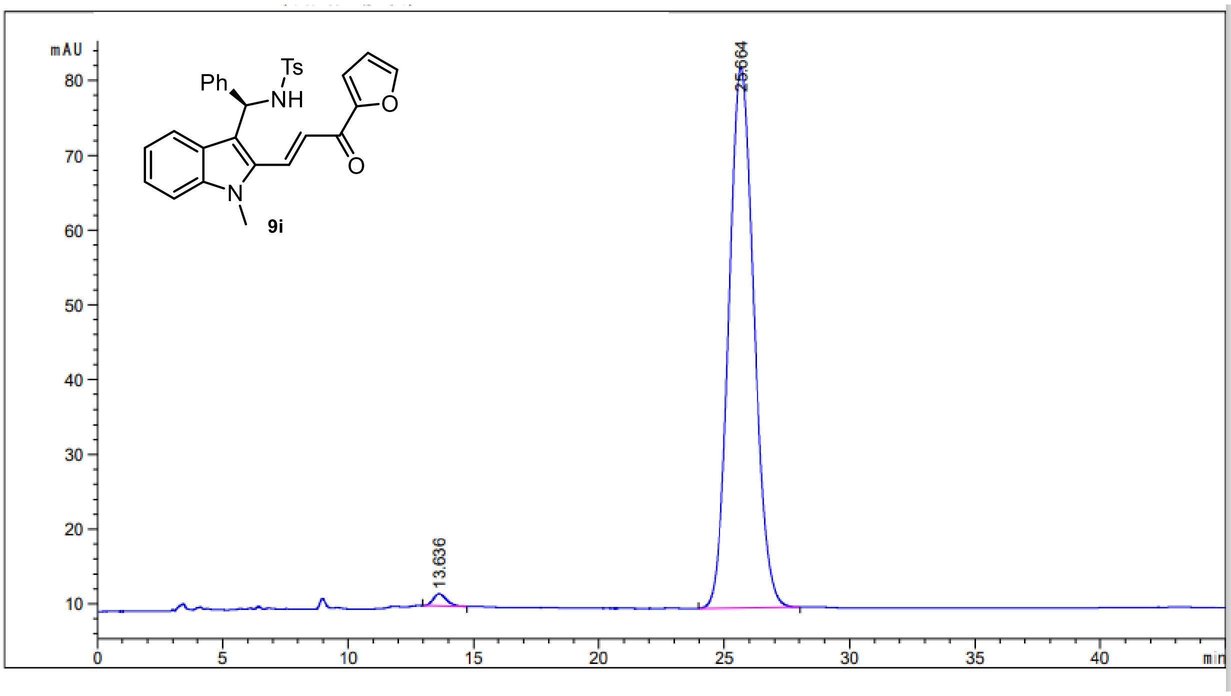



7.754
7.714
7.625
7.433
7.415
7.322
7.314
7.302
7.294
7.289
7.270
7.260
7.254
7.227
7.210
7.197
7.197
7.188
7.177
7.154
7.115
6.988
6.970
6.952
6.846
6.826
6.569
6.562
6.558
6.190
6.170
5.553
5.533
3.696
2.229
0.000
Ph
Ts
NH
O
O
N
9i
^{1}H NMR (400 MHz, CDCl$_3$)
1.02
0.99
2.15
6.38
3.24
1.18
1.05
1.98
0.95
1.02
1.00
3.14
3.11
f1 (ppm)


176.550
153.338
146.955
142.711
139.936
138.566
136.597
132.794
130.287
128.563
127.592
127.132
126.820
125.505
124.319
124.206
120.531
120.333
118.279
116.875
112.643
109.637
77.213
77.001
76.788
53.958
30.615
21.289
Ph
Ts
NH
O
O
N
9i
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

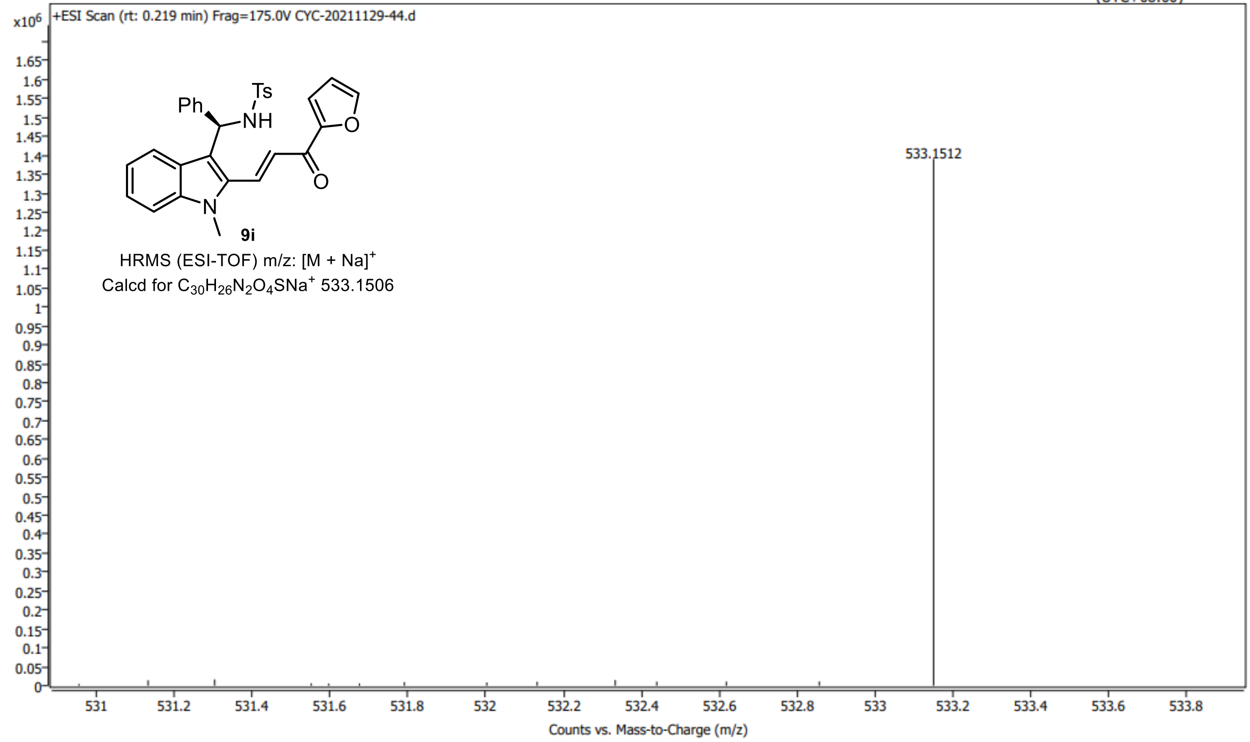


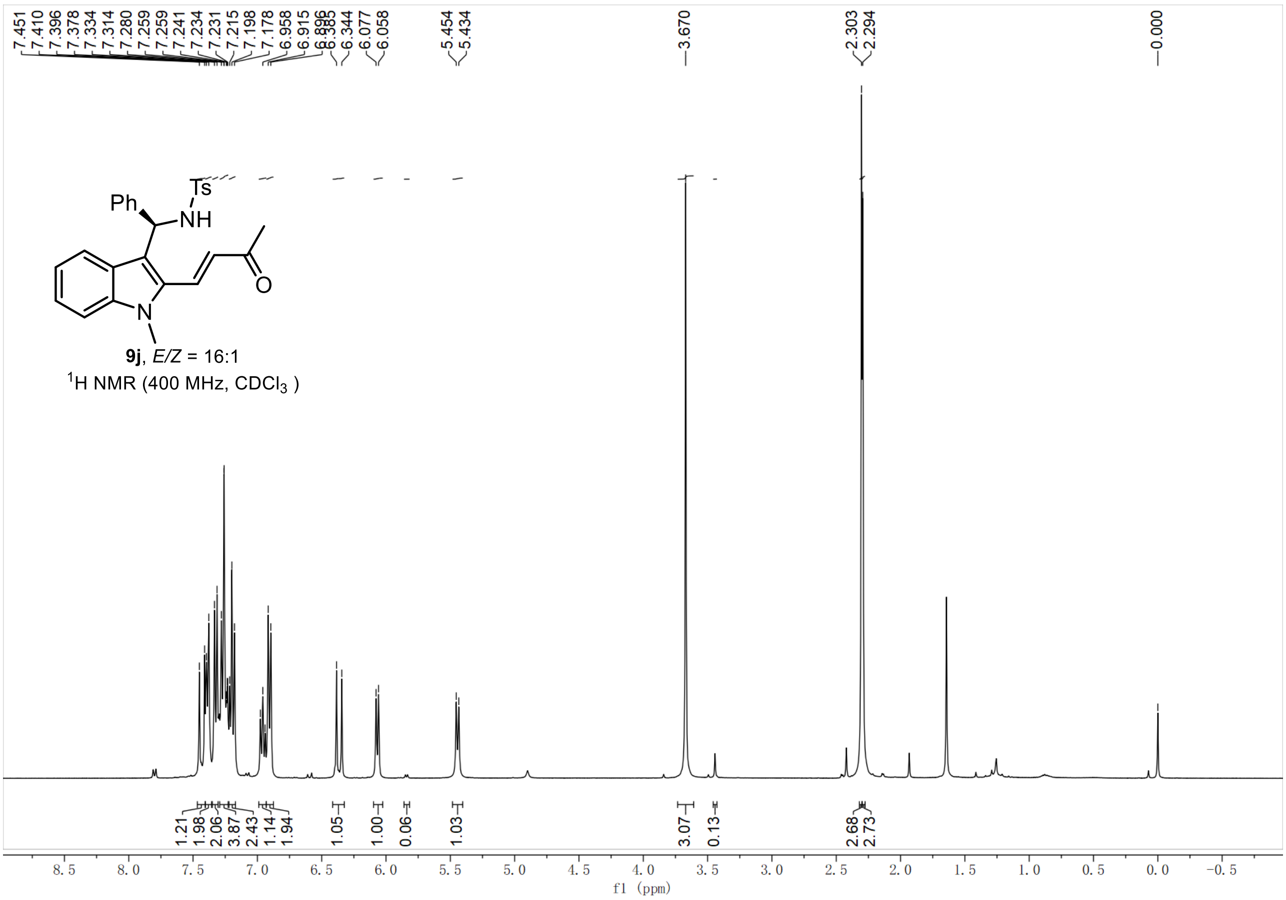
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.542	BB	0.5564	3898.24414	108.02244	50.3727
2	25.781	BB	1.0918	3840.55884	54.77457	49.6273

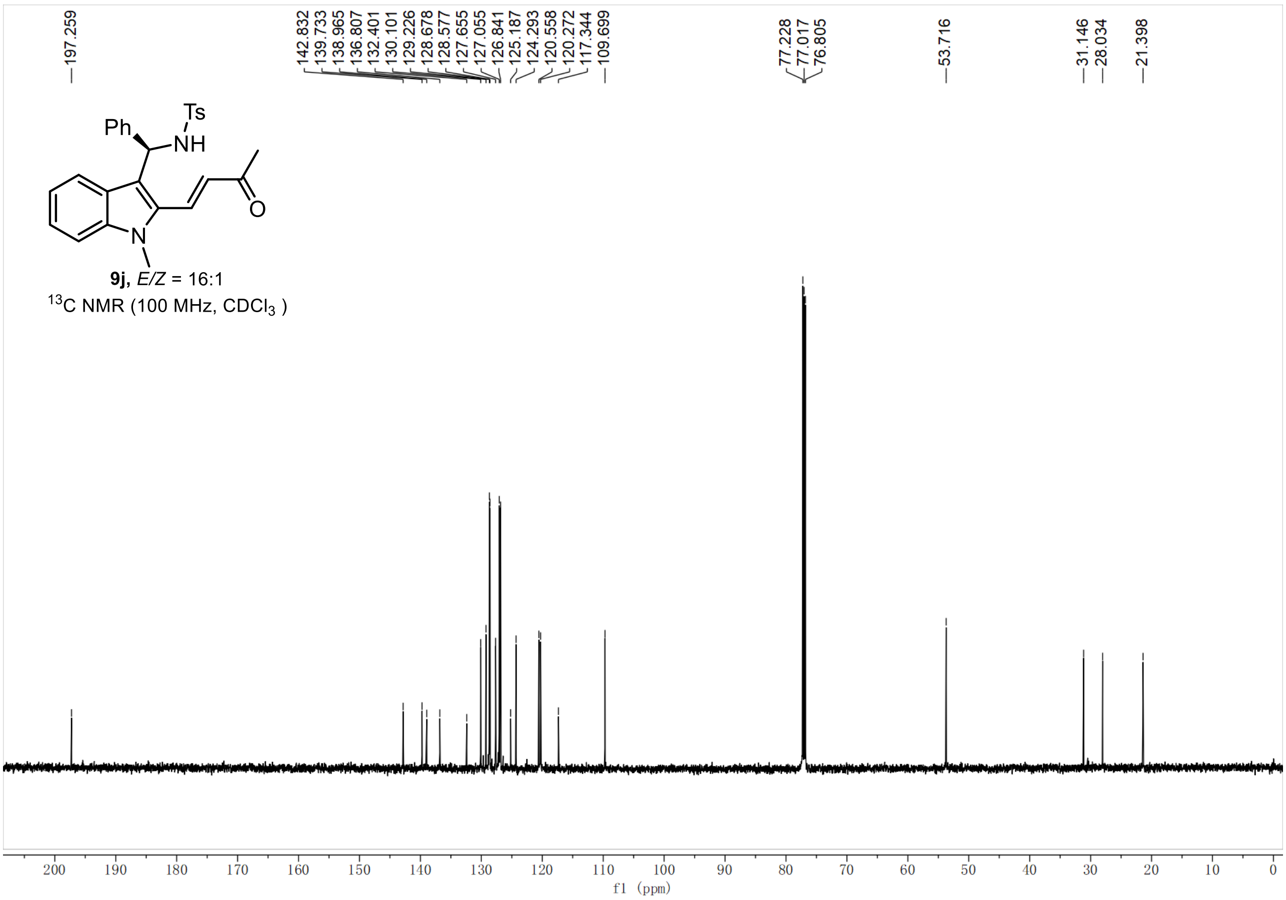


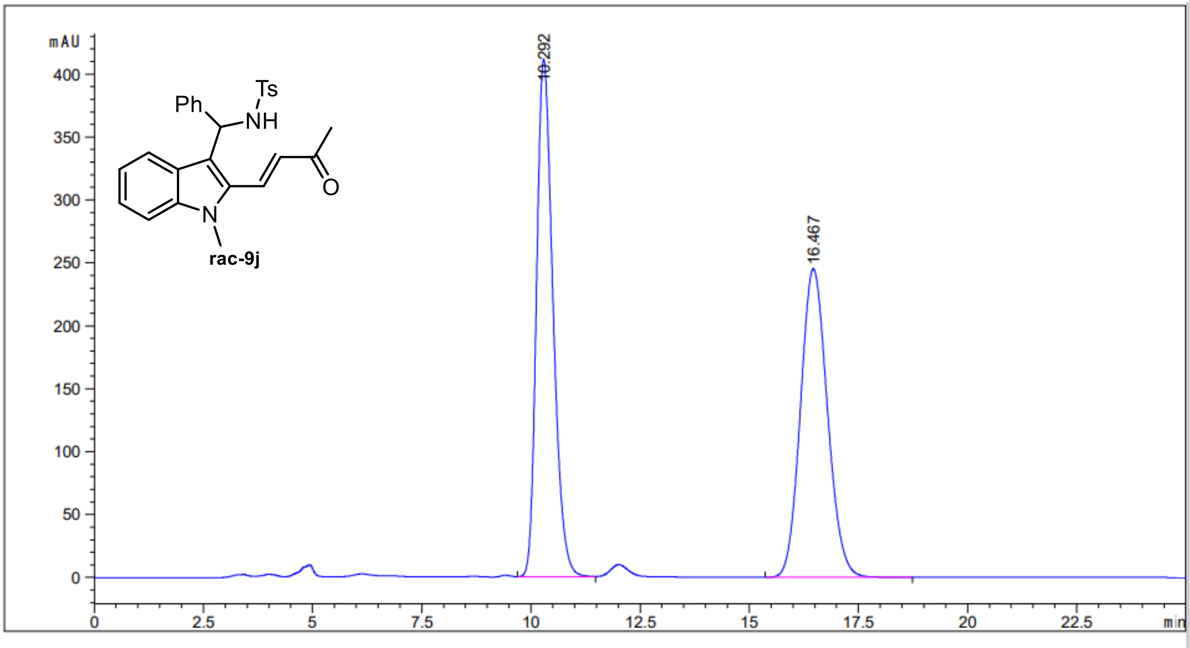
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.636	BB	0.5217	58.91714	1.62634	1.1582
2	25.664	BB	1.0815	5027.89990	72.22445	98.8418

Name	CYC-20211129-44	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-44.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 5:49:05 PM (UTC+08:00)

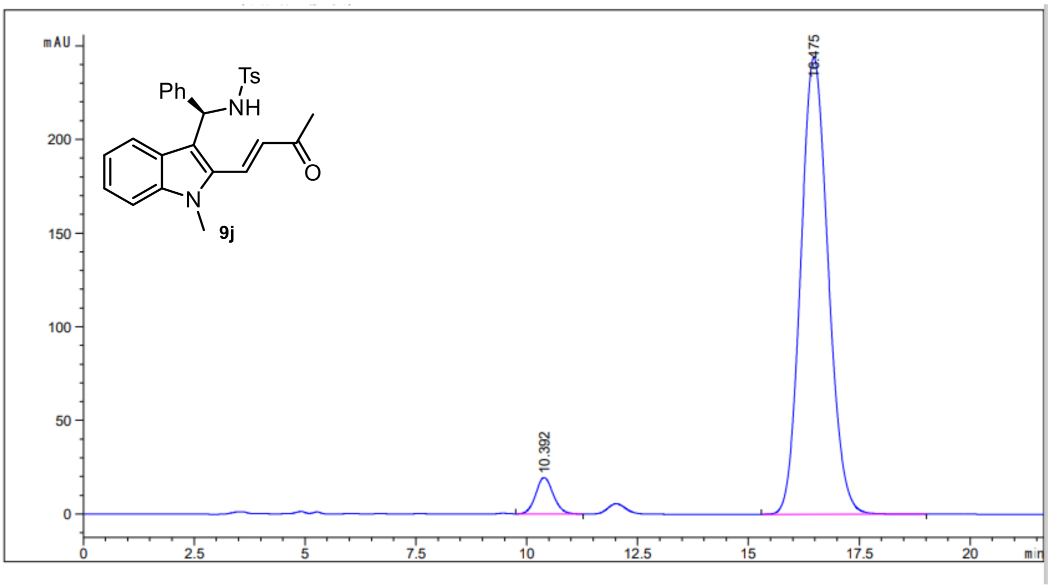



7.451
7.410
7.396
7.378
7.334
7.314
7.280
7.259
7.259
7.241
7.234
7.231
7.215
7.198
7.178
6.958
6.915
6.896
6.385
6.344
6.077
6.058
5.454
5.434
3.670
2.303
2.294
0.000
Ph
Ts
NH
O
N
9j, E/Z = 16:1
1H NMR (400 MHz, CDCl3)
1.21
1.98
2.06
3.87
2.43
1.14
1.94
1.05
1.00
0.06
1.03
3.07
0.13
2.68
2.73
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


197.259
142.832
139.733
138.965
136.807
132.401
130.101
129.226
128.678
128.577
127.655
127.055
126.841
125.187
124.293
120.558
120.272
117.344
109.699
77.228
77.017
76.805
53.716
31.146
28.034
21.398
Ph
Ts
NH
O
N
9j, E/Z = 16:1
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

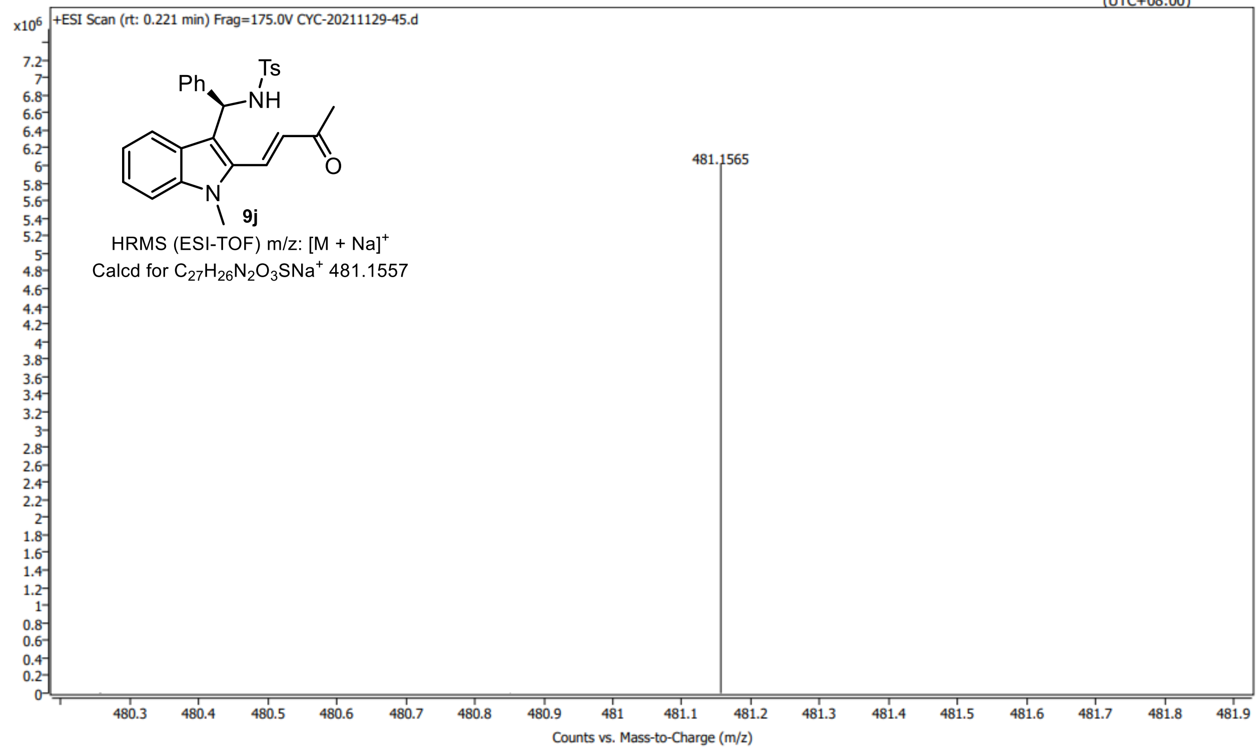


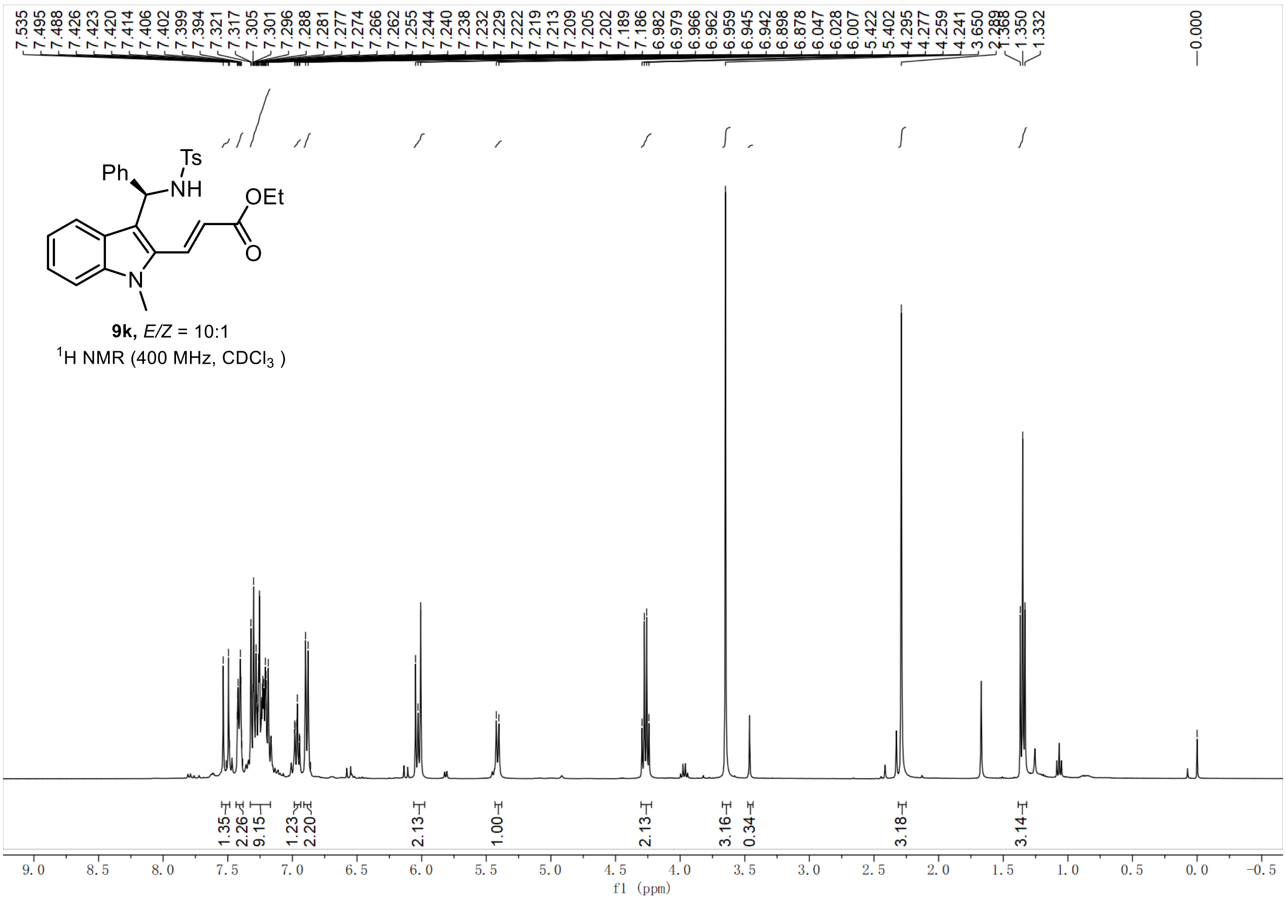
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.292	VB	0.4027	1.07586e4	411.27167	50.5925
2	16.467	BB	0.6676	1.05066e4	245.09351	49.4075

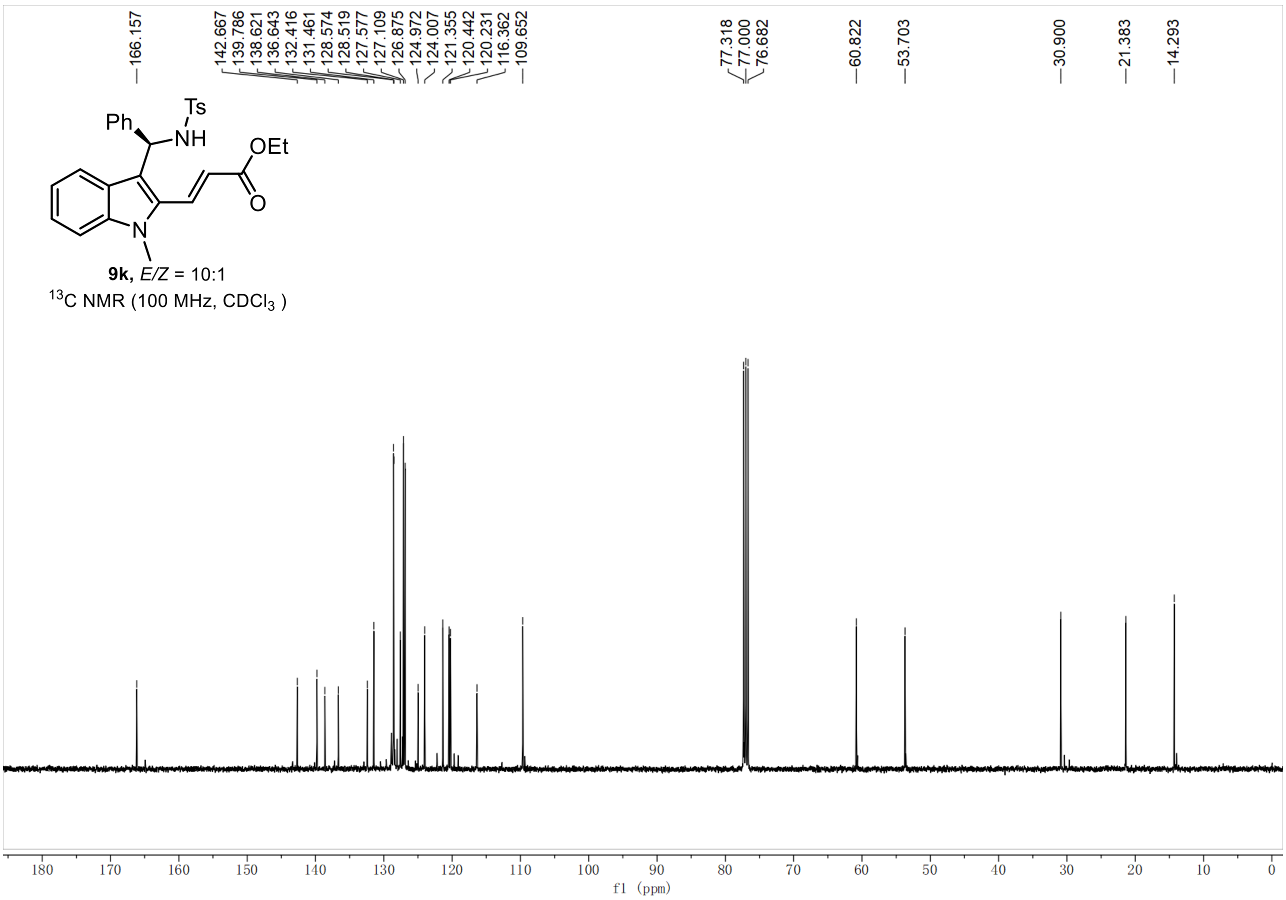


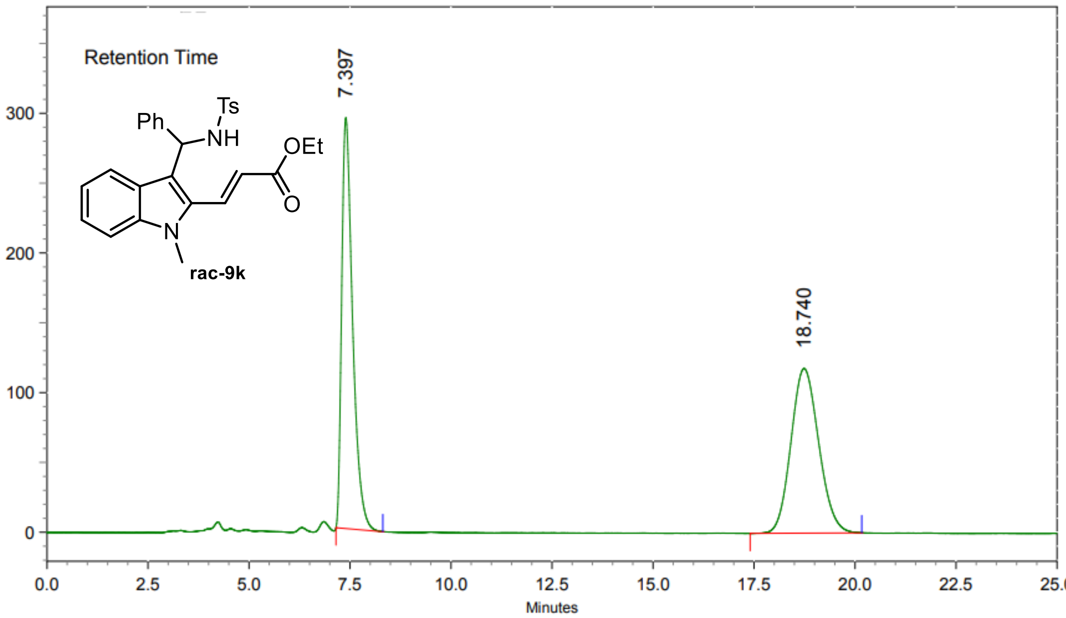
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.392	BBA	0.4227	533.86273	19.41428	4.8499
2	16.475	BB	0.6683	1.04738e4	243.95703	95.1501

Name	CYC-20211129-45	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-45.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 5:52:02 PM (UTC+08:00)



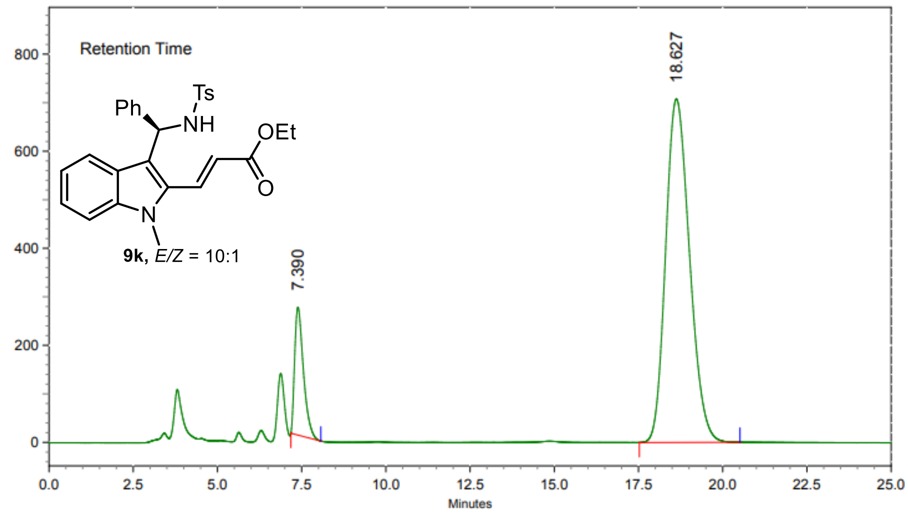

7.535
7.495
7.488
7.426
7.423
7.420
7.414
7.406
7.402
7.399
7.394
7.321
7.317
7.305
7.301
7.296
7.288
7.281
7.277
7.274
7.266
7.262
7.255
7.244
7.240
7.238
7.232
7.229
7.222
7.219
7.213
7.209
7.205
7.202
7.189
7.186
6.982
6.979
6.966
6.962
6.959
6.945
6.942
6.898
6.878
6.047
6.028
6.007
5.422
5.402
4.295
4.277
4.259
4.241
3.650
2.289
1.368
1.350
1.332
0.000
Ph
Ts
NH
OEt
O
N
9k, E/Z = 10:1
1H NMR (400 MHz, CDCl3)
1.35
2.26
9.15
1.23
2.20
2.13
1.00
2.13
3.16
0.34
3.18
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


166.157
142.667
139.786
138.621
136.643
132.416
131.461
128.574
128.519
127.577
127.109
126.875
124.972
124.007
121.355
120.442
120.231
116.362
109.652
77.318
77.000
76.682
60.822
53.703
30.900
21.383
14.293
Ph
Ts
NH
OEt
O
N
9k, E/Z = 10:1
13C NMR (100 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



AREA PERCENT REPORT

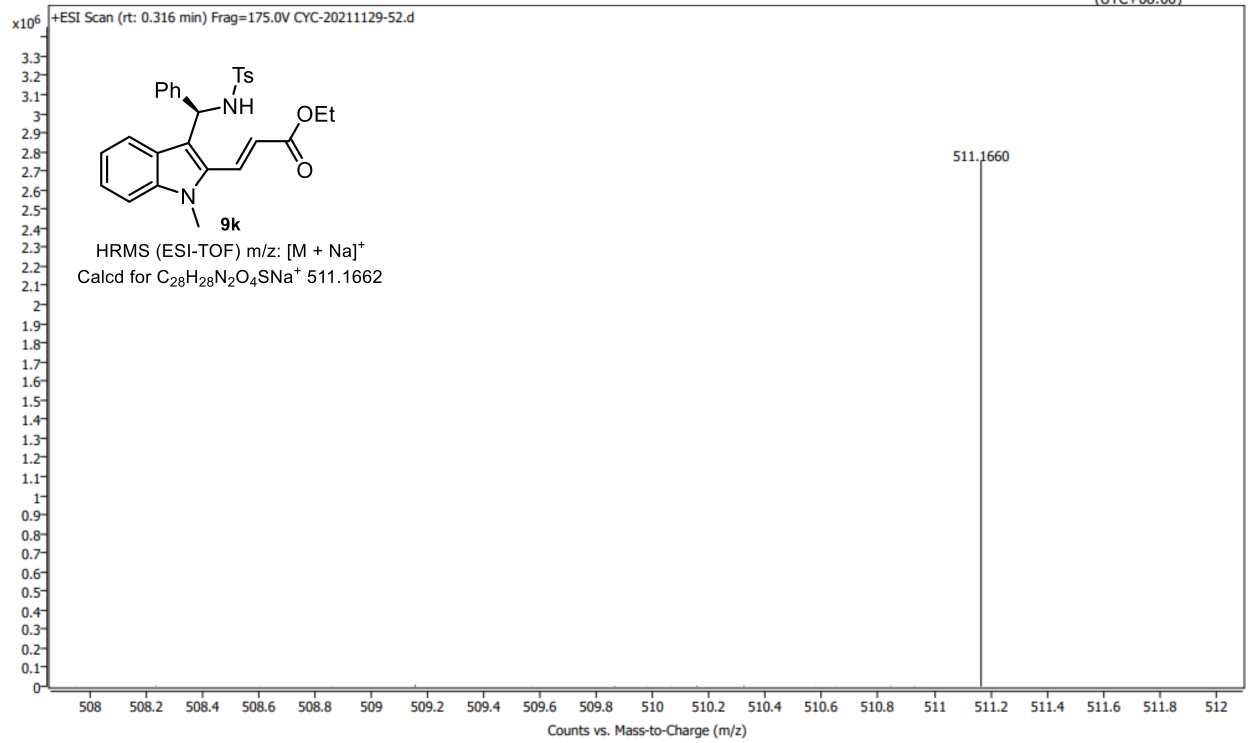
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.397	1.160	4936632	92519742	49.4281
2	18.740	2.763	1977249	94660544	50.5719

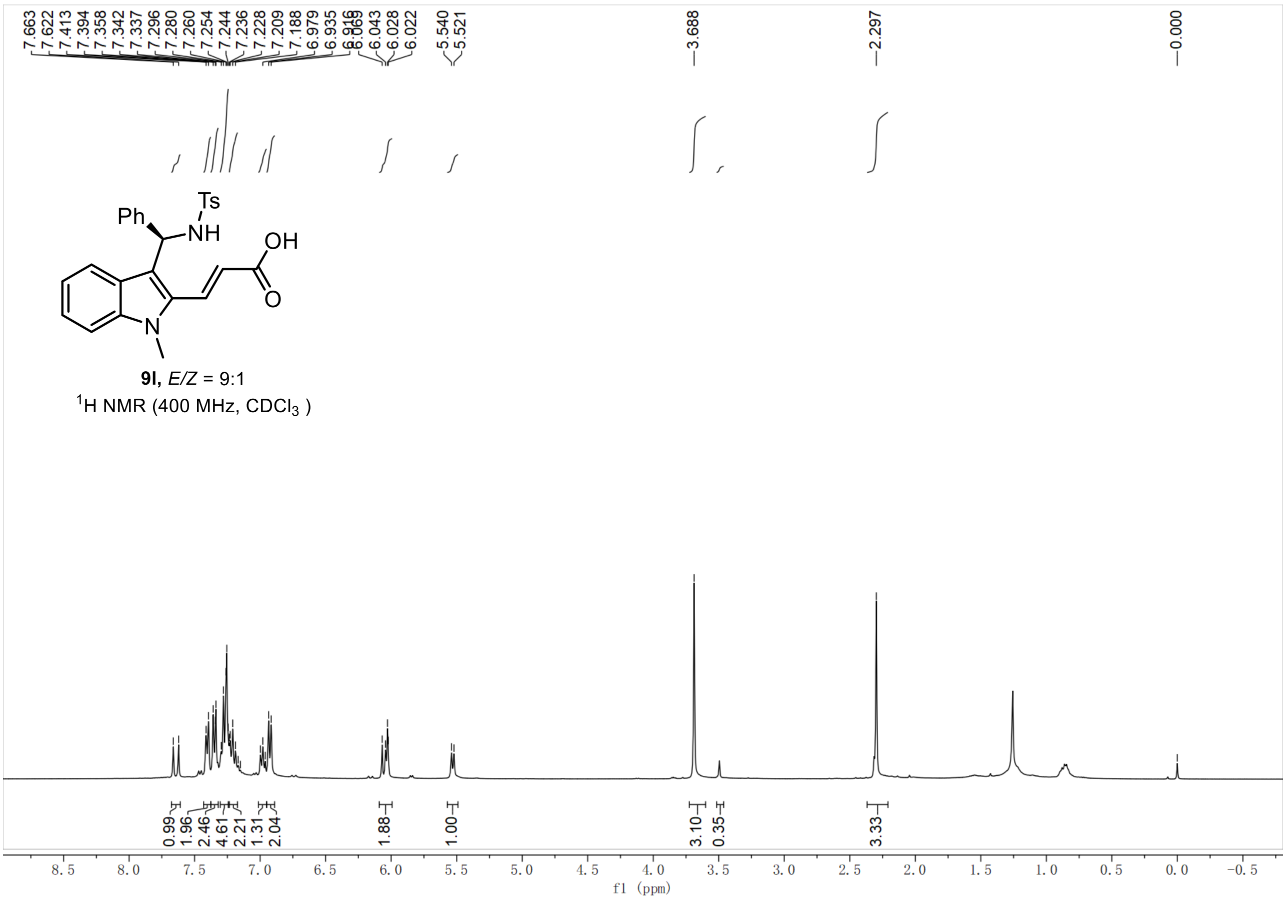


AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.390	0.890	4420301	80351244	12.0741
2	18.627	2.987	11874025	585132245	87.9259

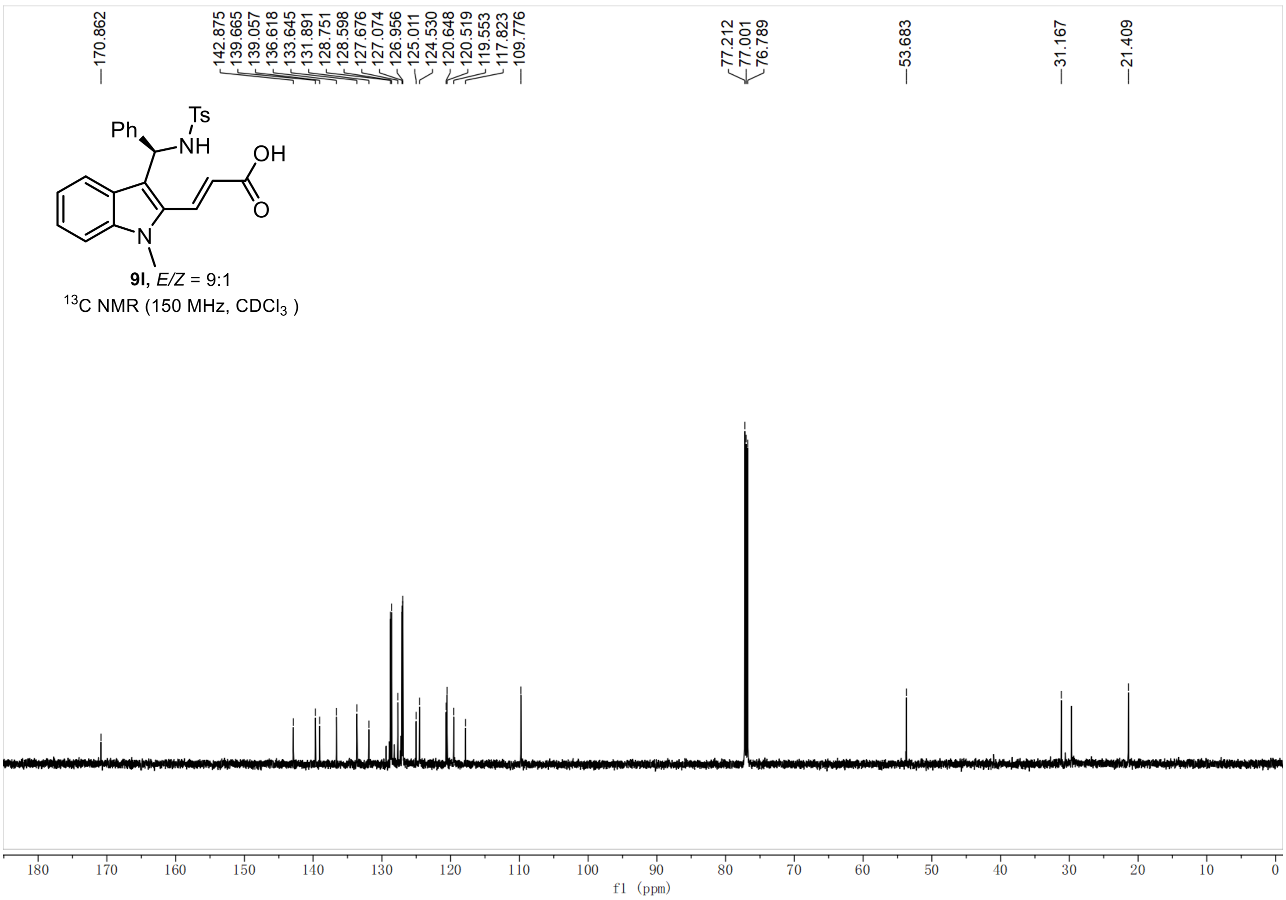
Name	CYC-20211129-52	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-52.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:12:56 PM (UTC+08:00)





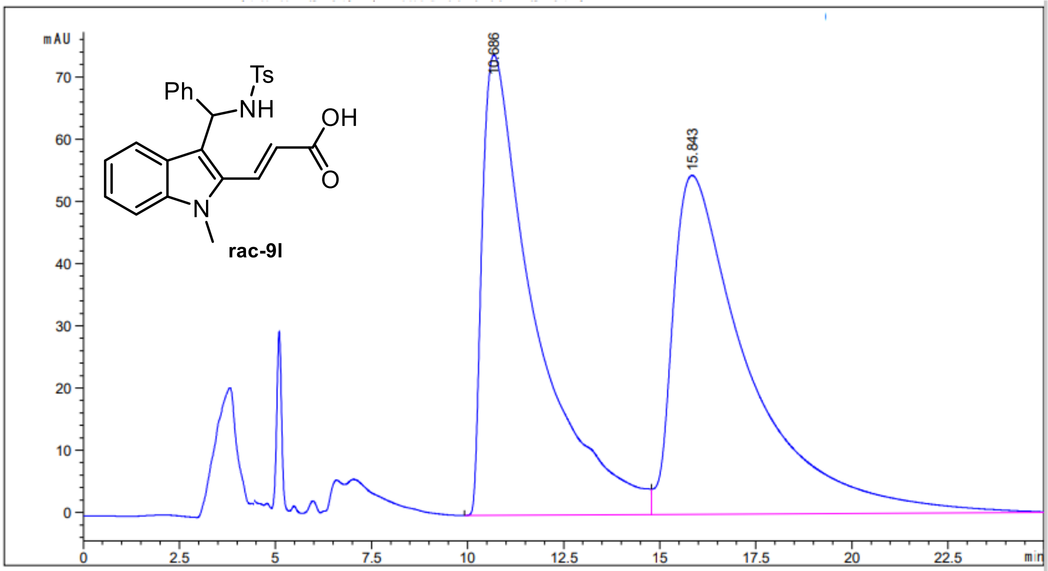
9l, *E/Z* = 9:1

^{1}H NMR (400 MHz, $CDCl_3$)

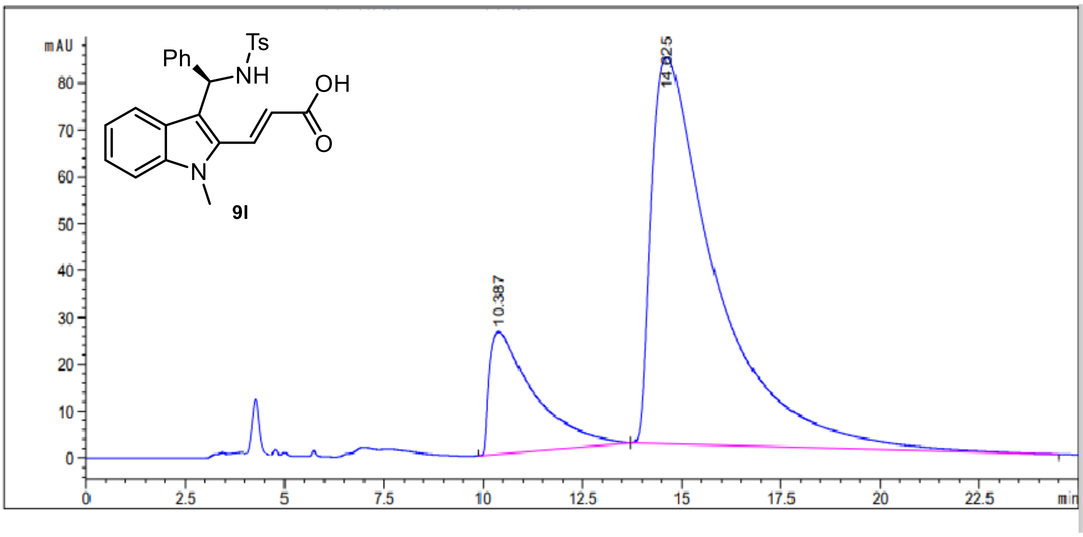


9l, *E/Z* = 9:1

^{13}C NMR (150 MHz, $CDCl_3$)

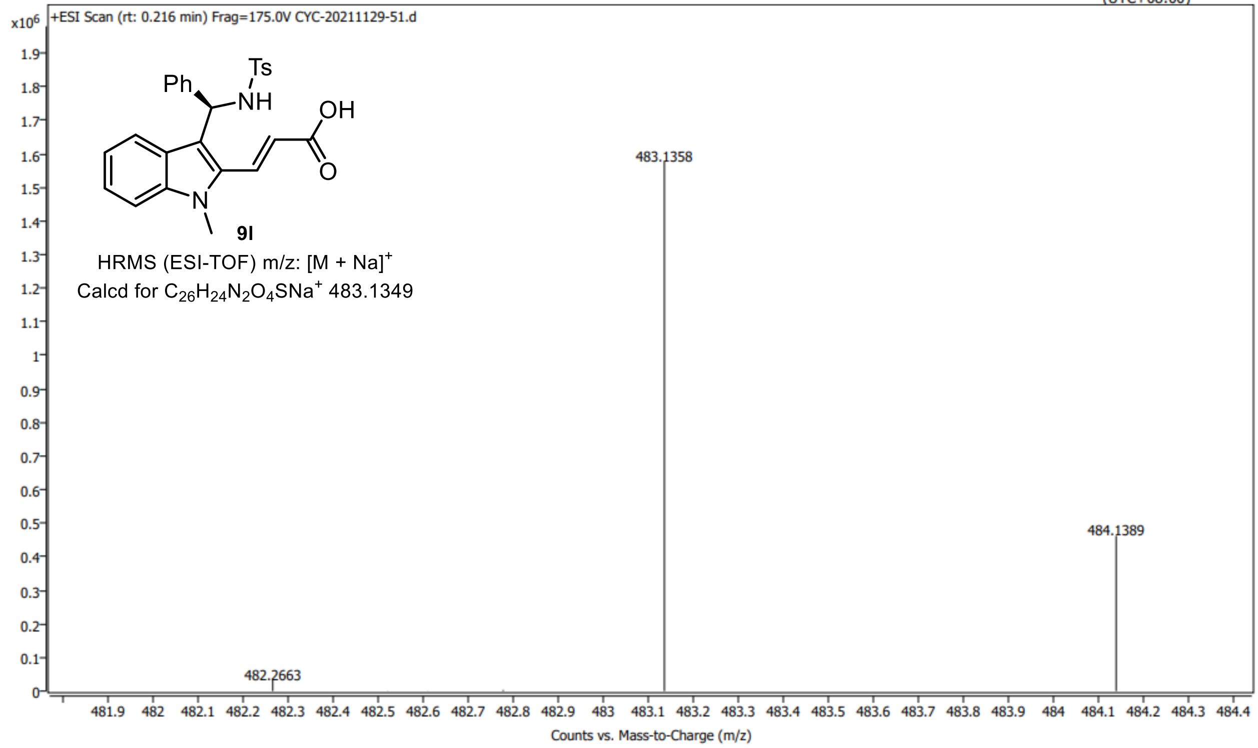


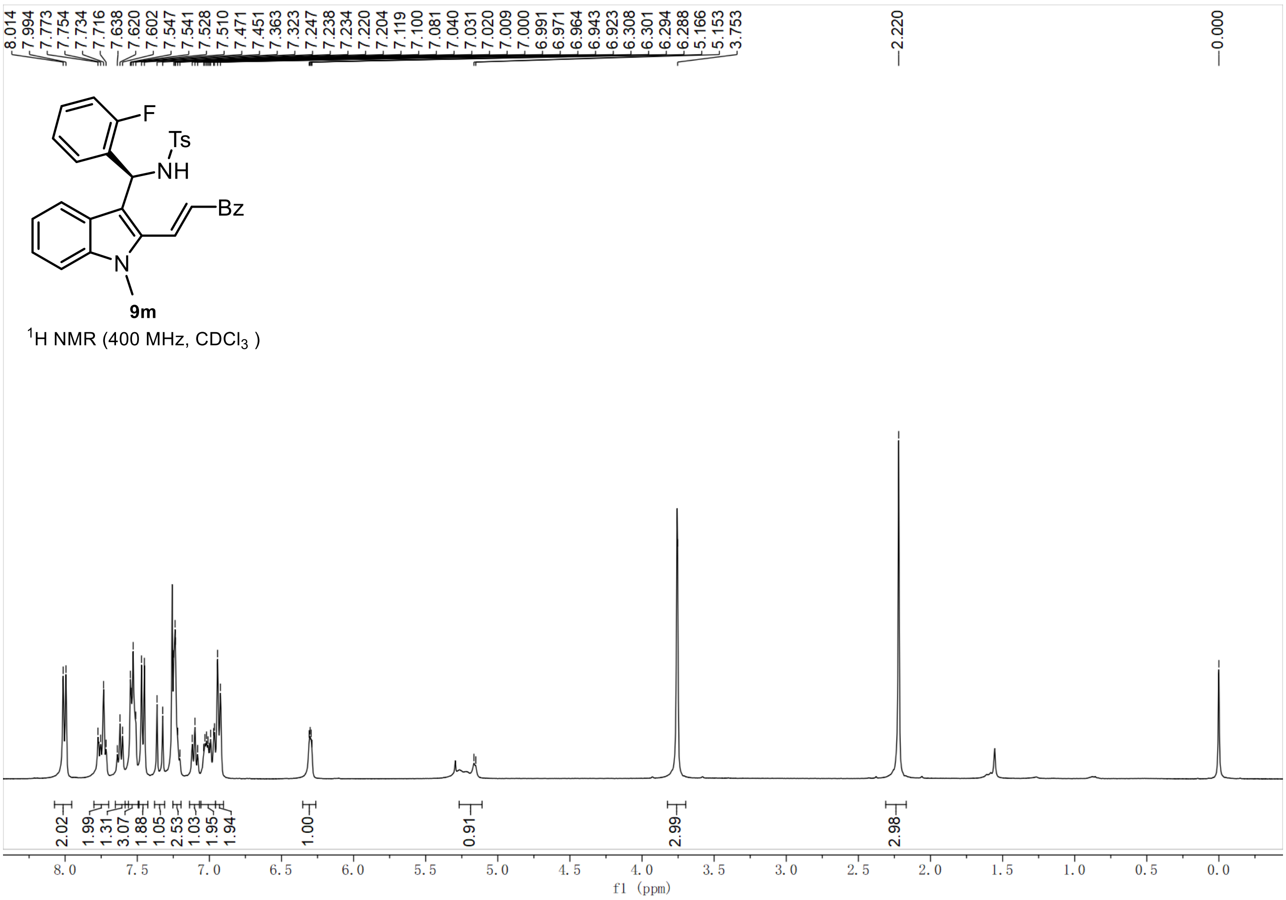
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.686	BV	1.3441	7067.25732	74.01096	48.5016
2	15.843	VBA	1.9038	7503.93066	54.48624	51.4984

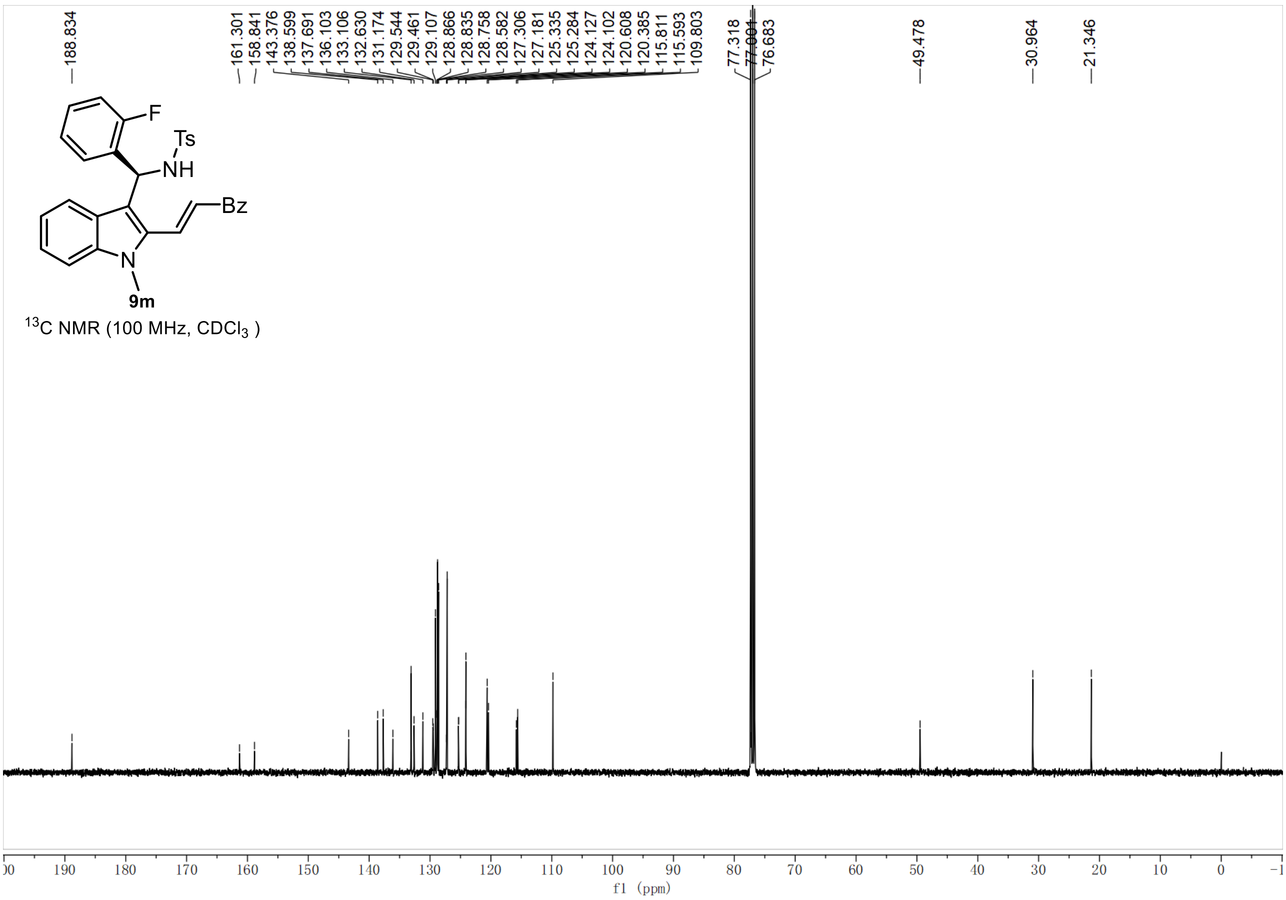


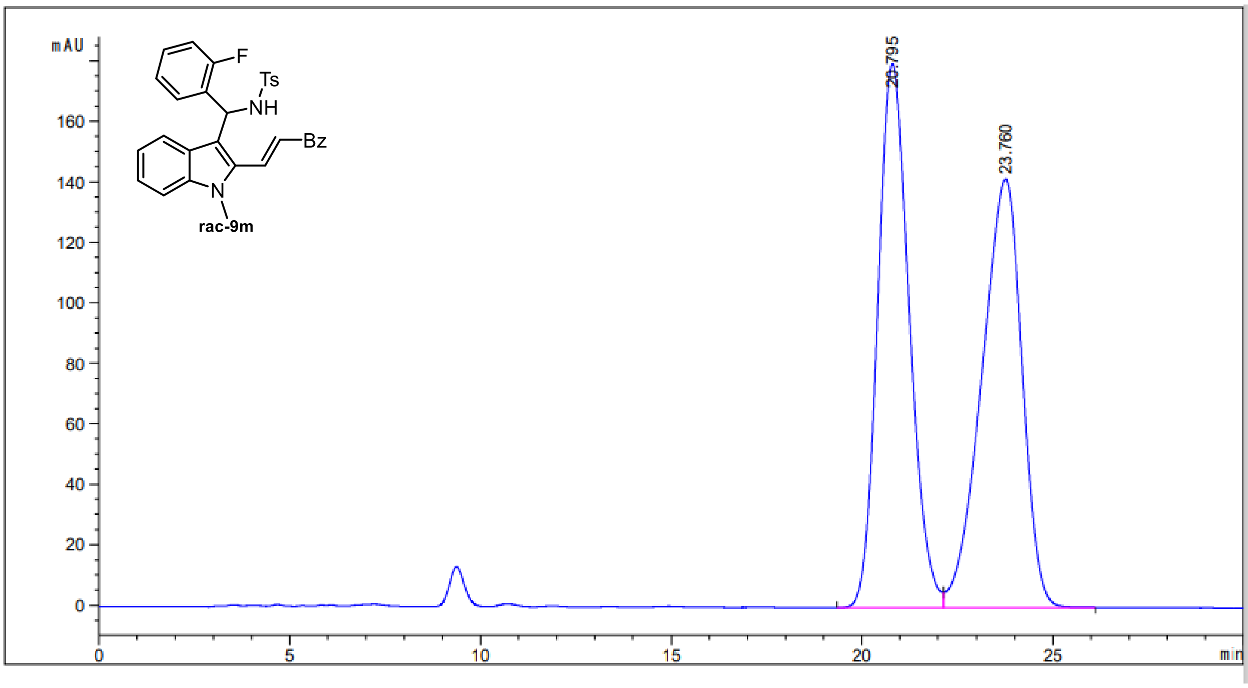
#	[min]		[min]	[mAU*s]	[mAU]	%
1	10.387	BB	1.0978	2069.87354	26.12100	18.1252
2	14.625	BB	1.5990	9350.00781	82.58299	81.8748

Name	CYC-20211129-51	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-51.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:09:59 PM (UTC+08:00)

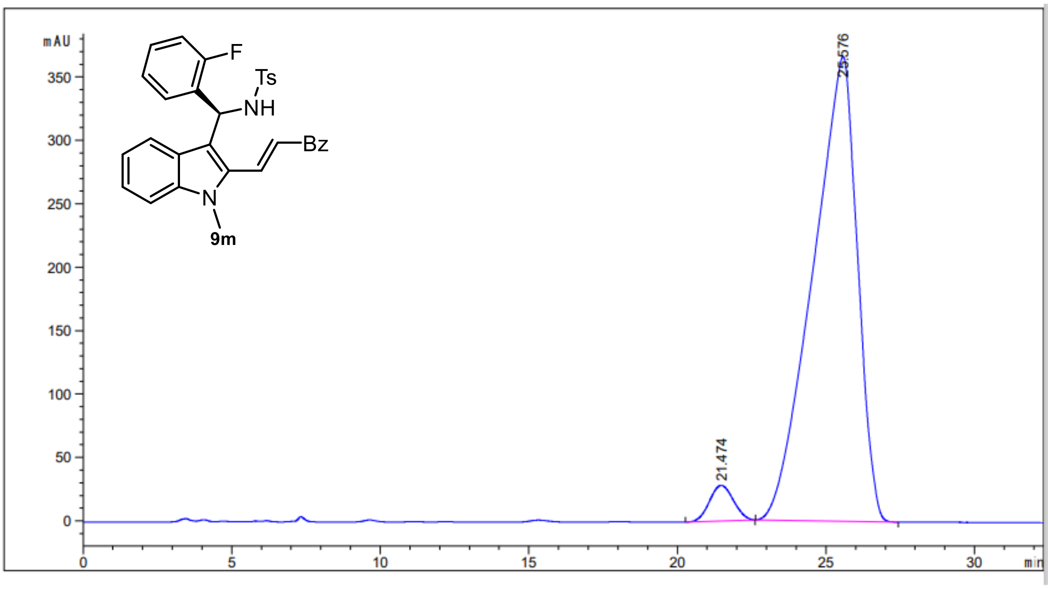



8.014 7.994 7.773 7.754 7.734 7.716 7.638 7.620 7.602 7.547 7.541 7.528 7.510 7.471 7.451 7.363 7.323 7.247 7.238 7.234 7.220 7.204 7.119 7.100 7.081 7.040 7.031 7.020 7.009 7.000 6.991 6.971 6.964 6.943 6.923 6.308 6.301 6.294 6.288 5.166 5.153 3.753
2.220
0.000
F
Ts
NH
Bz
N
9m
1H NMR (400 MHz, CDCl3)
2.02 1.99 1.31 3.07 1.88 1.05 2.53 1.03 1.95 1.94 1.00 0.91 2.99 2.98
f1 (ppm)

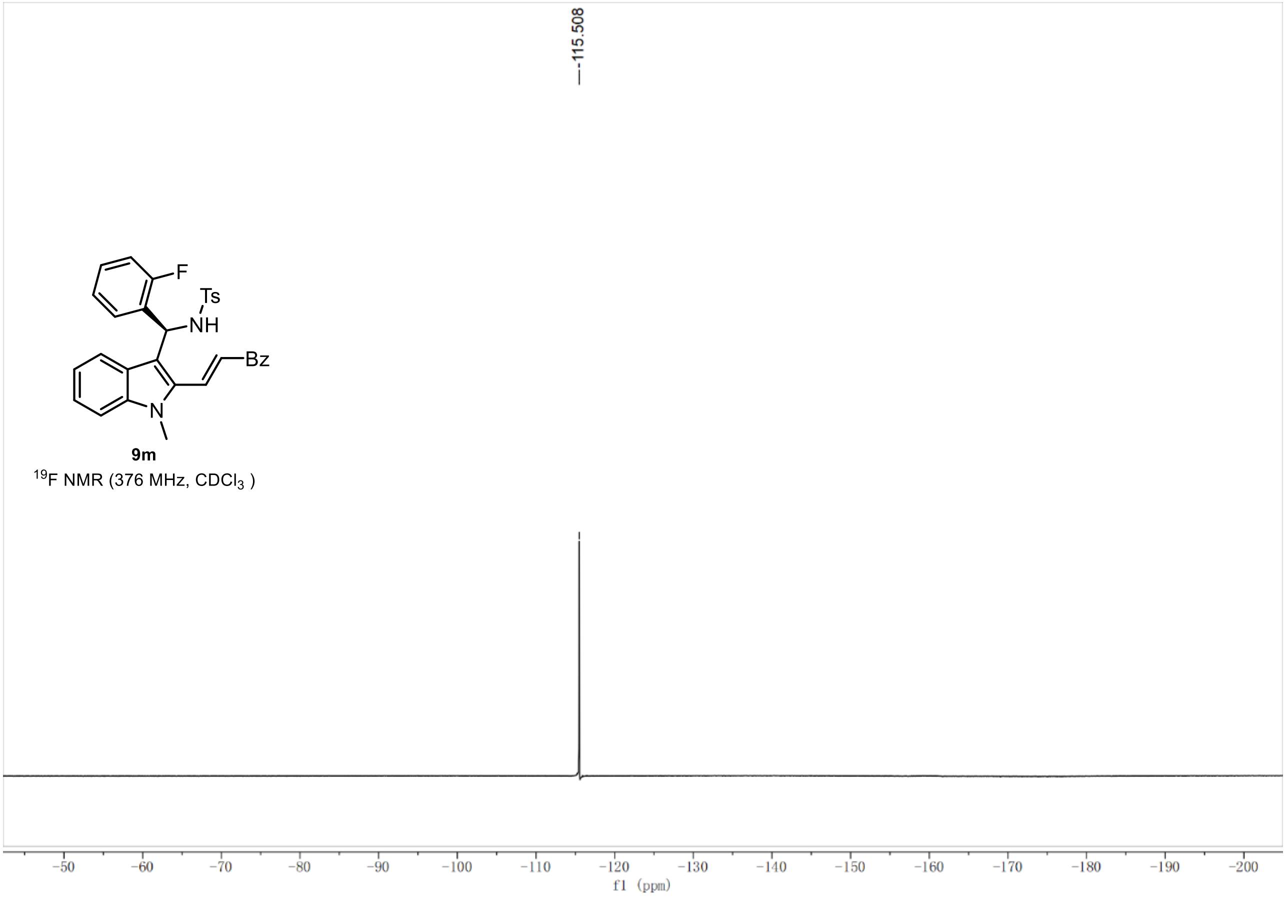

188.834
161.301 158.841 143.376 138.599 137.691 136.103 133.106 132.630 131.174 129.544 129.461 129.107 128.866 128.835 128.758 128.582 127.306 127.181 125.335 125.284 124.127 124.102 120.608 120.385 115.811 115.593 109.803
77.318 77.001 76.683
49.478
30.964
21.346
F
Ts
NH
Bz
N
9m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

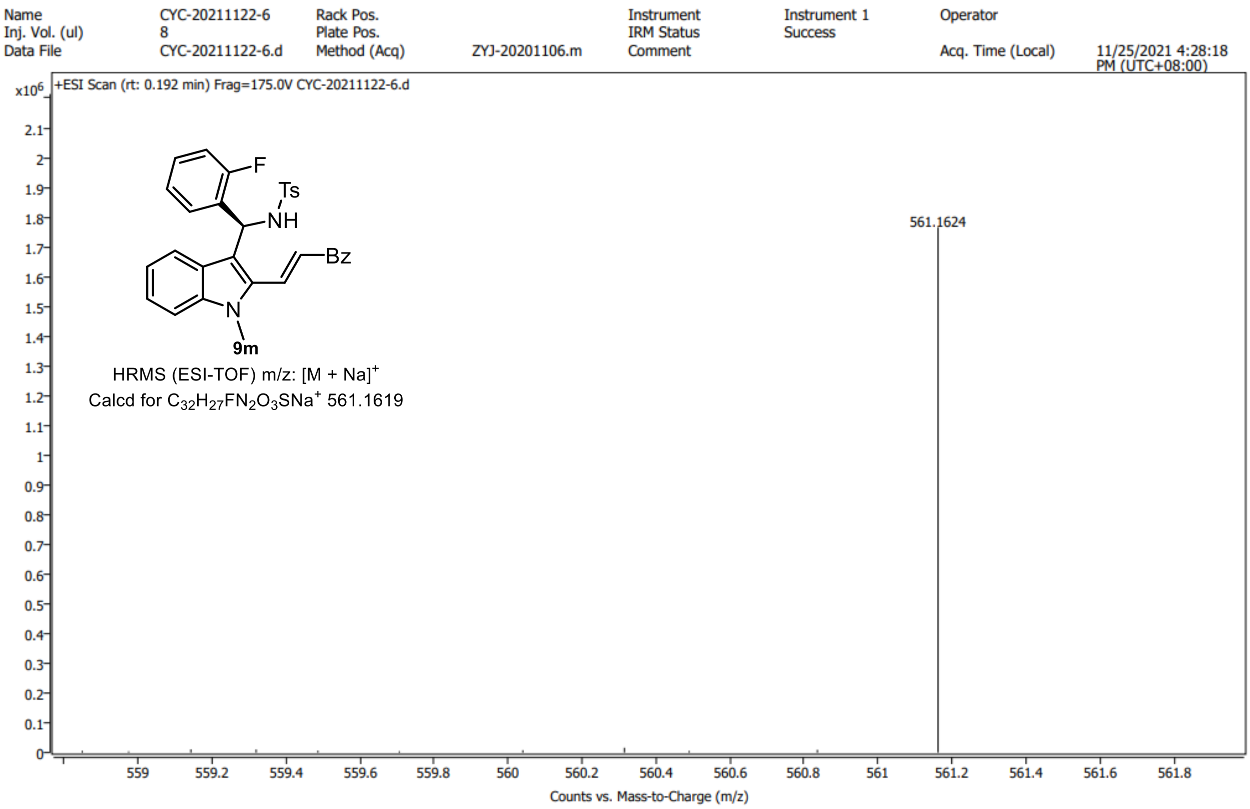


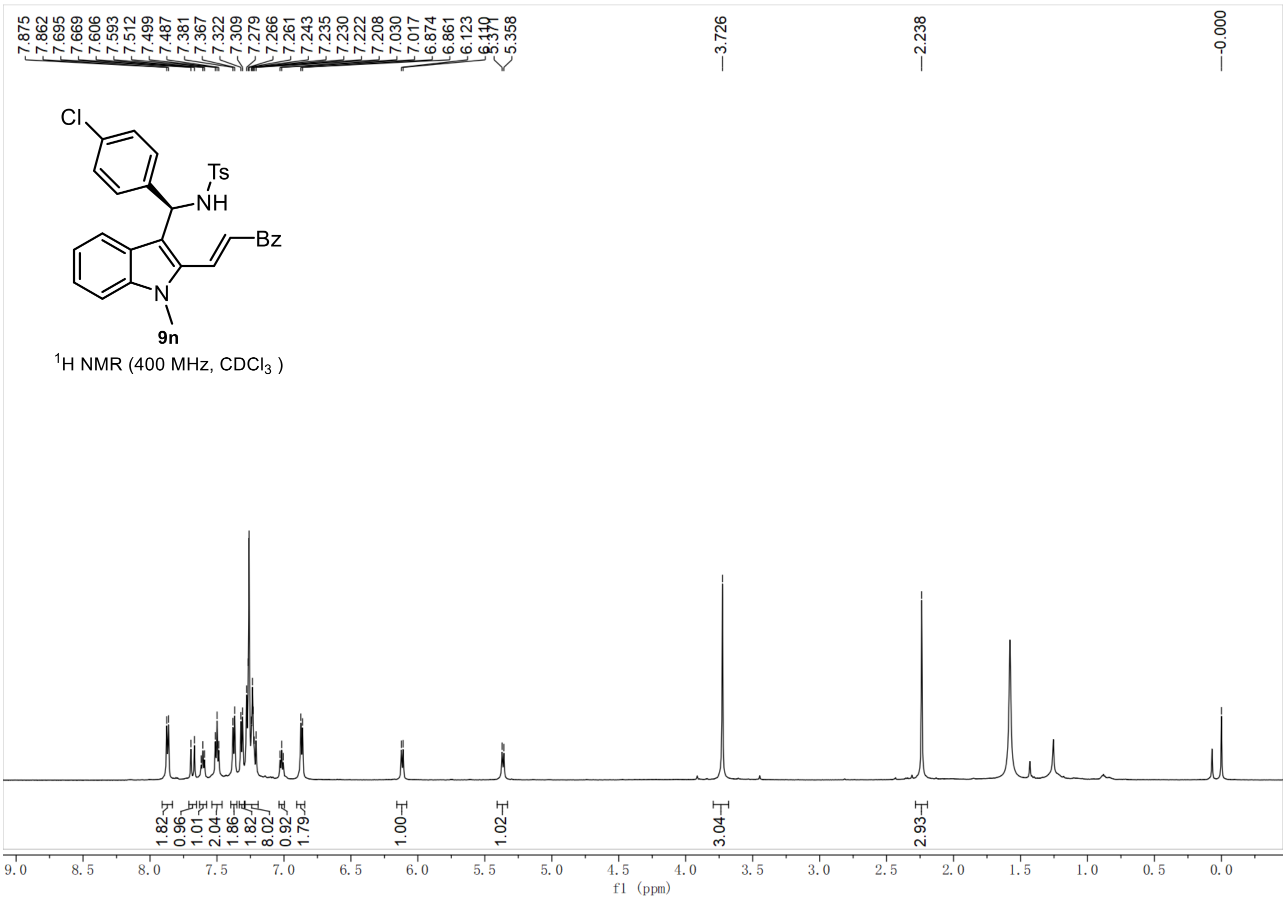
#	[min]		[min]	[mAU*s]	[mAU]	%
1	20.795	BV	0.8973	1.03498e4	179.77708	49.8935
2	23.760	VBA	1.1228	1.03939e4	141.60875	50.1065

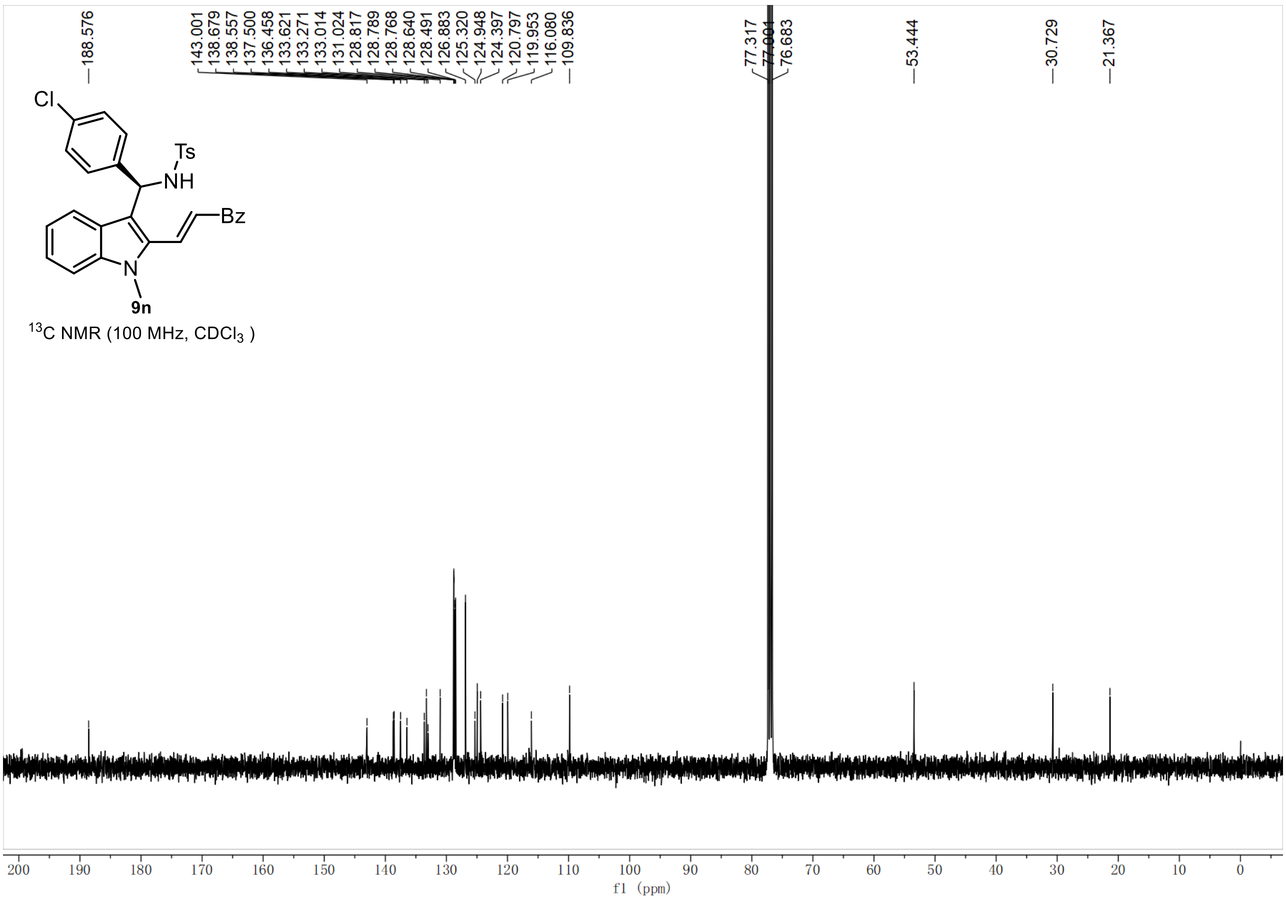


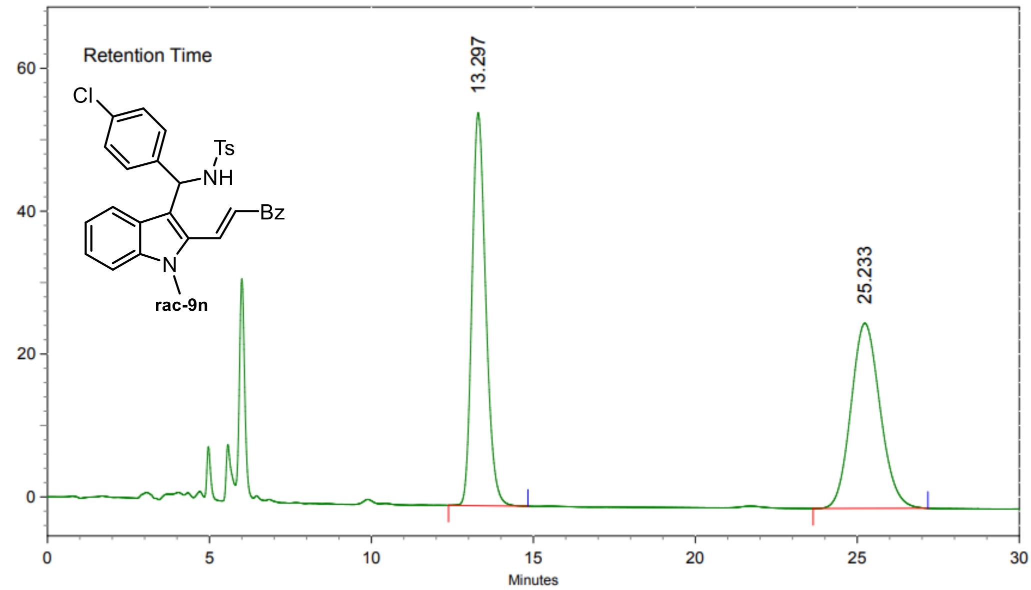
#	[min]		[min]	[mAU*s]	[mAU]	%
1	21.474	BB	0.8831	1579.38049	28.15120	3.9808
2	25.576	BB	1.4125	3.80957e4	366.39322	96.0192


-115.508
F
Ts
NH
Bz
N
9m
19F NMR (376 MHz, CDCl3)
−50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200
f1 (ppm)


Name CYC-20211122-6
Rack Pos.
Instrument Instrument 1
Operator
Inj. Vol. (ul) 8
Plate Pos.
IRM Status Success
Data File CYC-20211122-6.d
Method (Acq) ZYJ-20201106.m
Comment
Acq. Time (Local) 11/25/2021 4:28:18 PM (UTC+08:00)
x10^6
+ESI Scan (rt: 0.192 min) Frag=175.0V CYC-20211122-6.d
561.1624
F
Ts
NH
Bz
N
9m
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C32H27FN2O3SNa+ 561.1619
Counts vs. Mass-to-Charge (m/z)

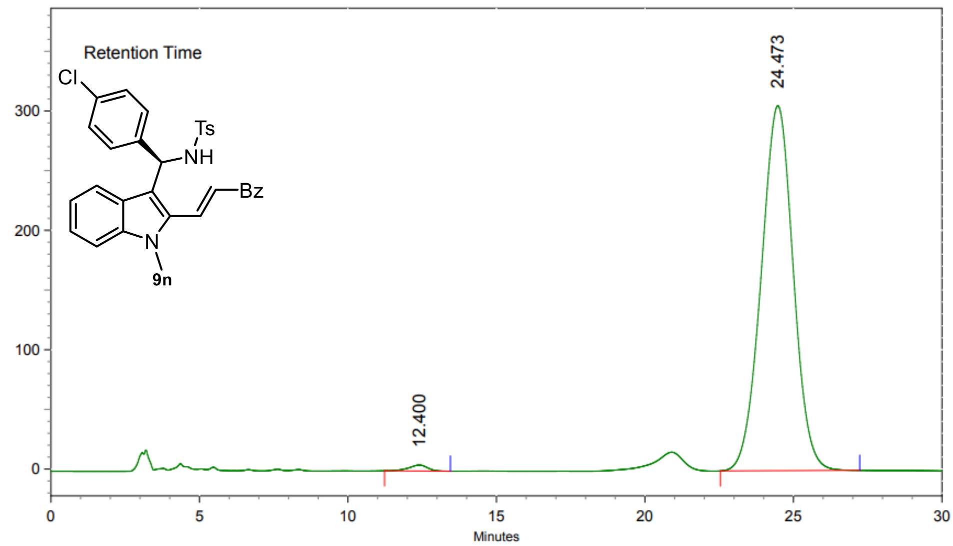

7.875 7.862 7.695 7.669 7.606 7.593 7.512 7.499 7.487 7.381 7.367 7.322 7.309 7.279 7.266 7.261 7.243 7.235 7.230 7.222 7.208 7.030 7.017 6.874 6.861 6.123 6.110 5.371 5.358
3.726
2.238
-0.000
Cl
Ts
NH
Bz
N
9n
1H NMR (400 MHz, CDCl3)
1.82 0.96 1.01 2.04 1.86 1.82 8.02 0.92 1.79
1.00
1.02
3.04
2.93
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


188.576
143.001 138.679 138.557 137.500 136.458 133.621 133.271 133.014 131.024 128.817 128.789 128.768 128.640 128.491 126.883 125.320 124.948 124.397 120.797 119.953 116.080 109.836
77.317 77.001 76.683
53.444
30.729
21.367
Cl
Ts
NH
Bz
N
9n
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



AREA PERCENT REPORT

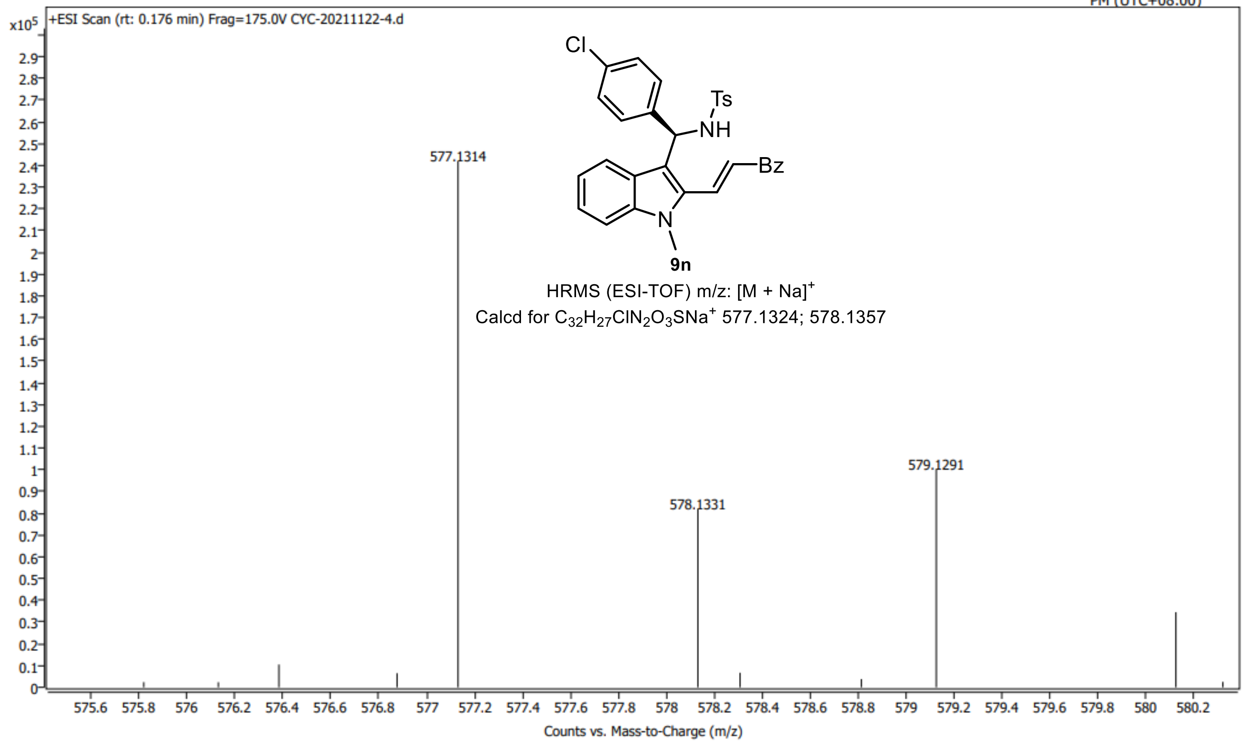
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.297	2.453	922603	27319036	50.0964
2	25.233	3.543	434887	27213883	49.9036

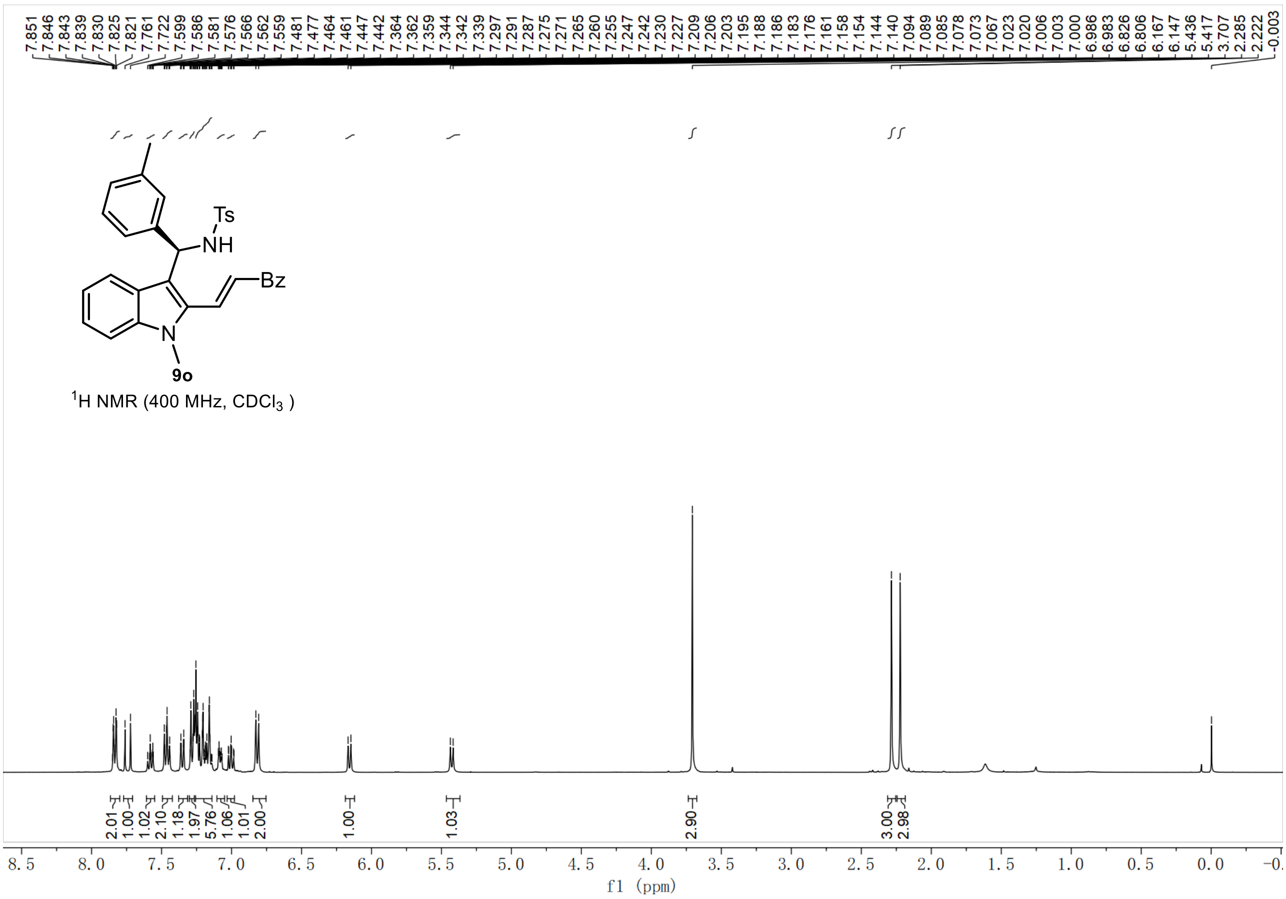


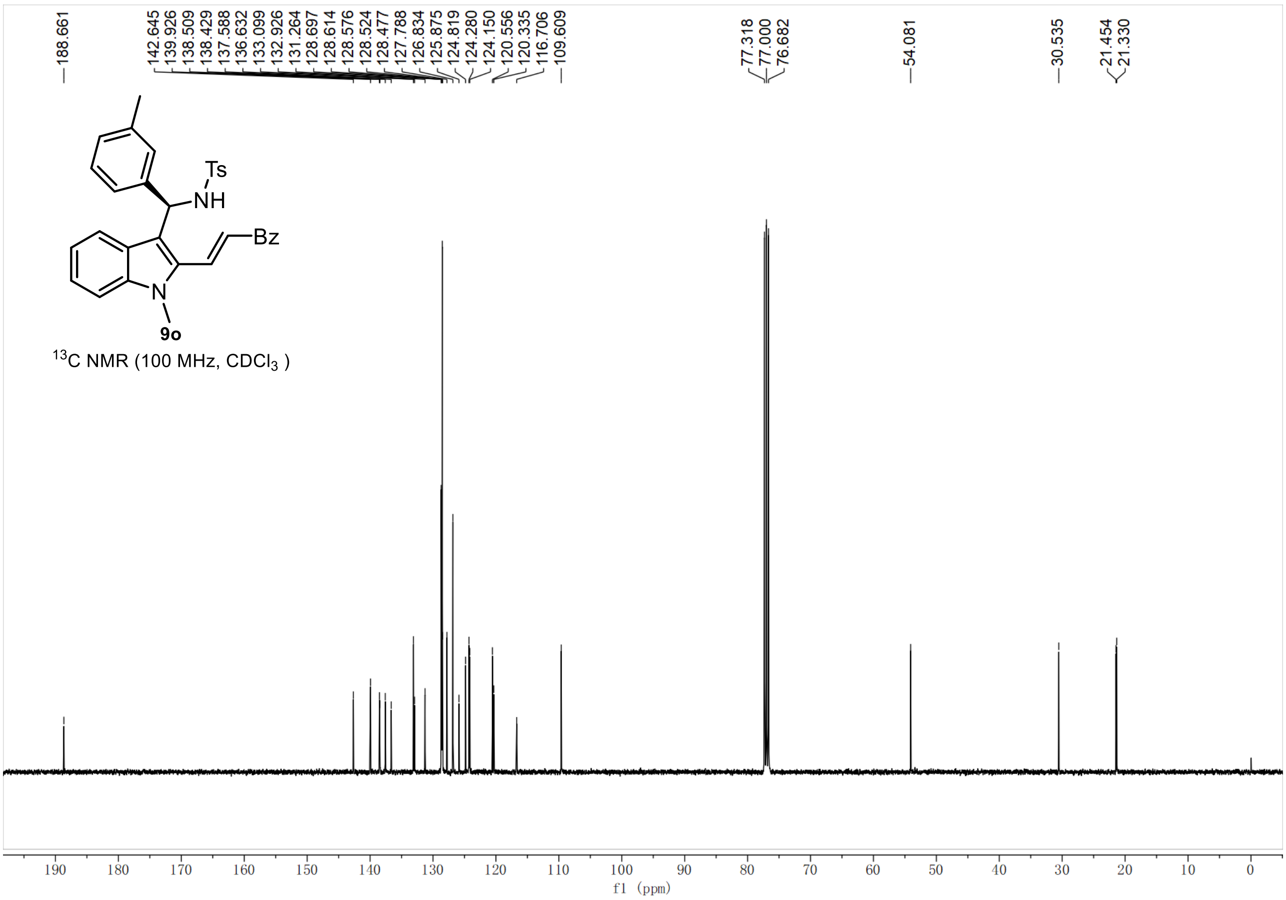
AREA PERCENT REPORT

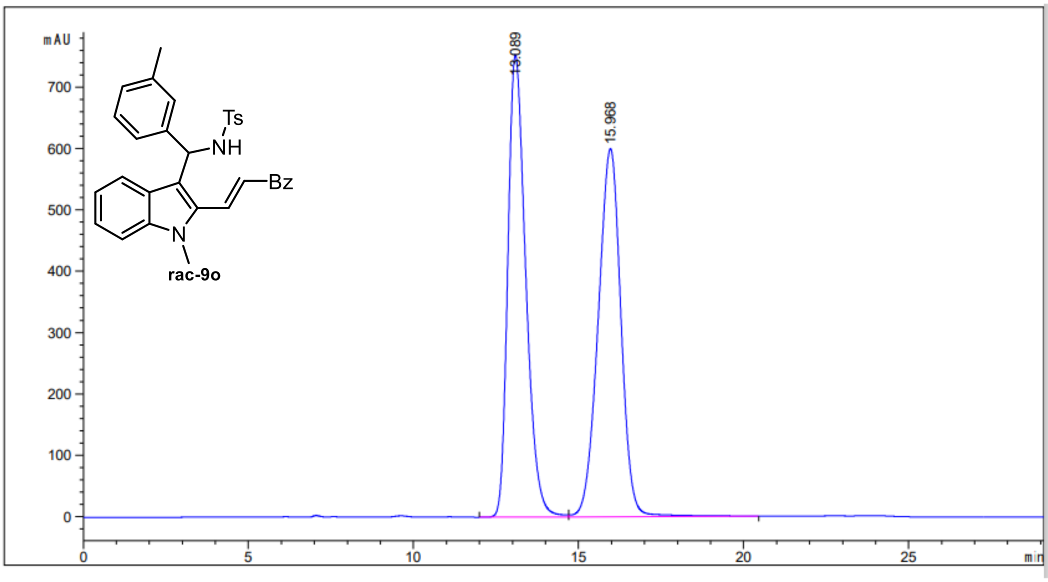
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	12.400	2.217	83826	3716754	0.9574
2	24.473	4.693	5129430	384479094	99.0426

Name	CYC-20211122-4	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-4.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 4:18:25 PM (UTC+08:00)

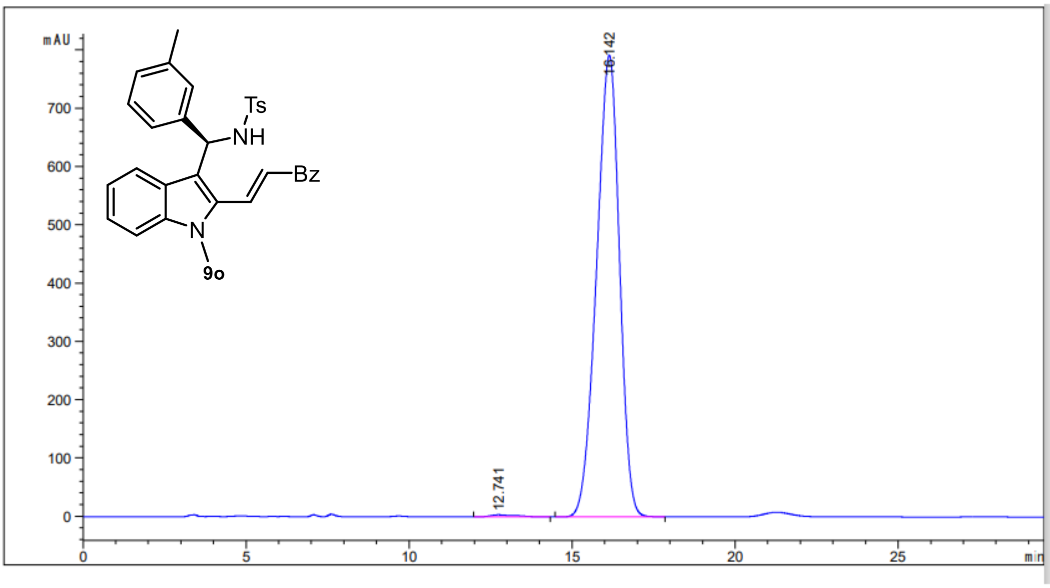



7.851 7.846 7.843 7.839 7.830 7.825 7.821 7.761 7.722 7.599 7.586 7.581 7.576 7.566 7.562 7.559 7.481 7.477 7.464 7.461 7.447 7.442 7.364 7.362 7.359 7.344 7.342 7.339 7.297 7.291 7.287 7.275 7.271 7.265 7.260 7.255 7.247 7.242 7.230 7.227 7.209 7.206 7.203 7.195 7.188 7.186 7.183 7.176 7.161 7.158 7.154 7.144 7.140 7.094 7.089 7.085 7.078 7.073 7.067 7.023 7.020 7.006 7.003 7.000 6.986 6.983 6.826 6.806 6.167 6.147 5.436 5.417 3.707 2.285 2.222 -0.003
Ts
NH
Bz
N
9o
1H NMR (400 MHz, CDCl3)
2.01 1.00 1.02 2.10 1.18 1.97 5.76 1.06 1.01 2.00 1.00 1.03 2.90 3.00 2.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


188.661
142.645 139.926 138.509 138.429 137.588 136.632 133.099 132.926 131.264 128.697 128.614 128.576 128.524 128.477 127.788 126.834 125.875 124.819 124.280 124.150 120.556 120.335 116.706 109.609
77.318 77.000 76.682
54.081
30.535
21.454 21.330
Ts
NH
Bz
N
9o
13C NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

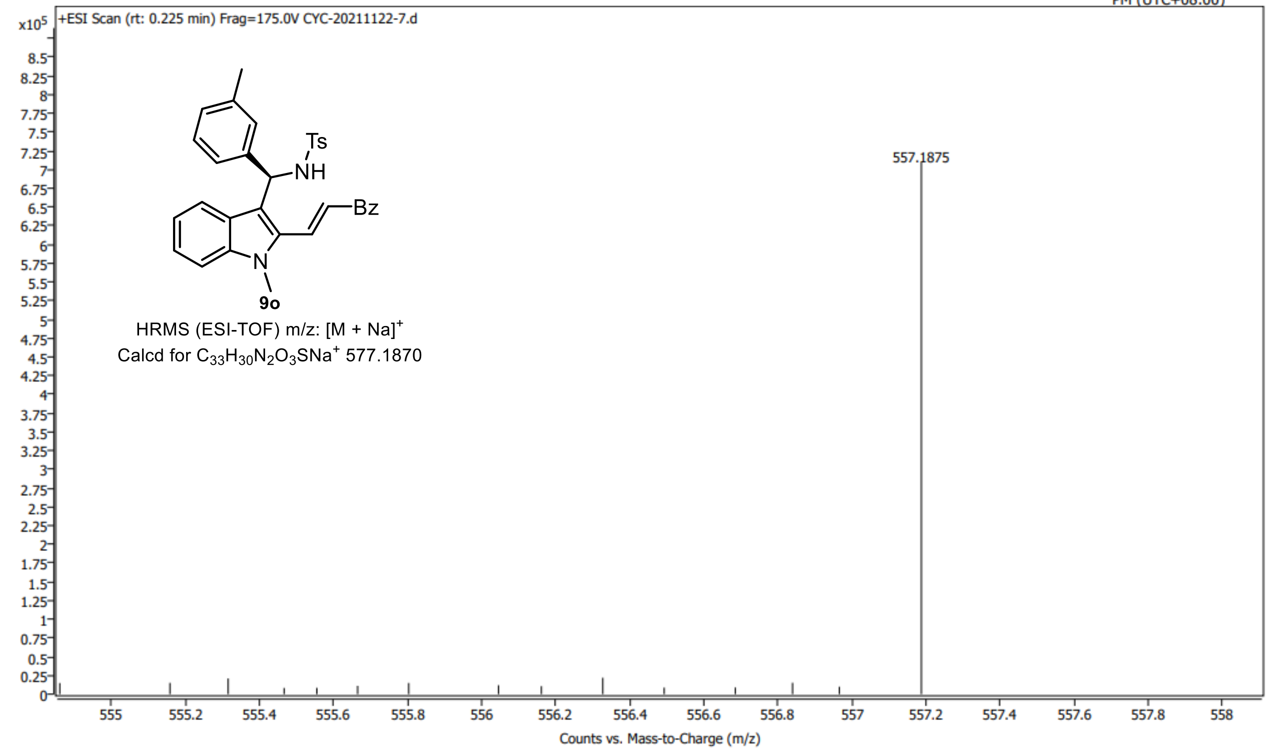


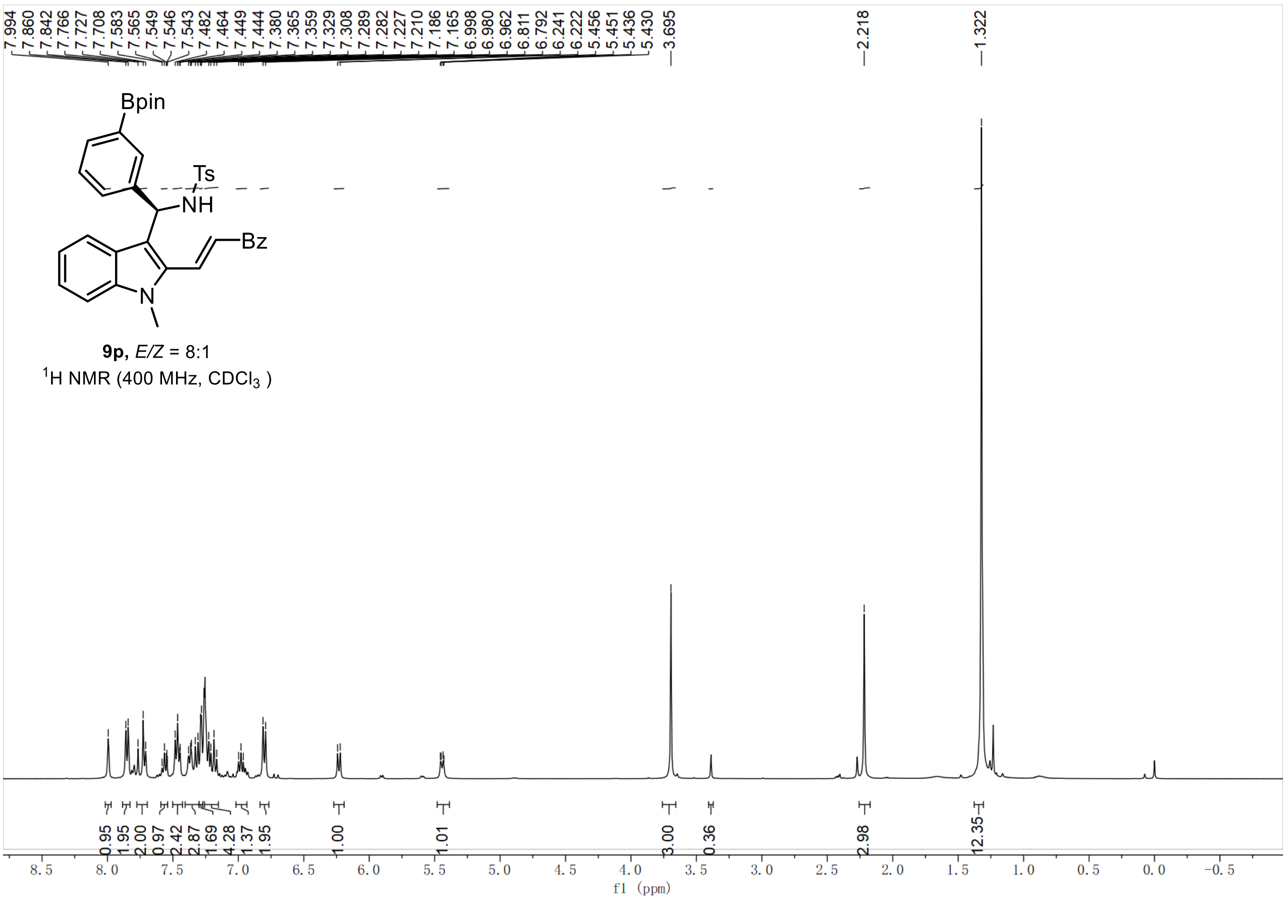
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.089	BV	0.5807	2.83891e4	753.72095	49.6213
2	15.968	VB	0.7404	2.88224e4	600.61591	50.3787



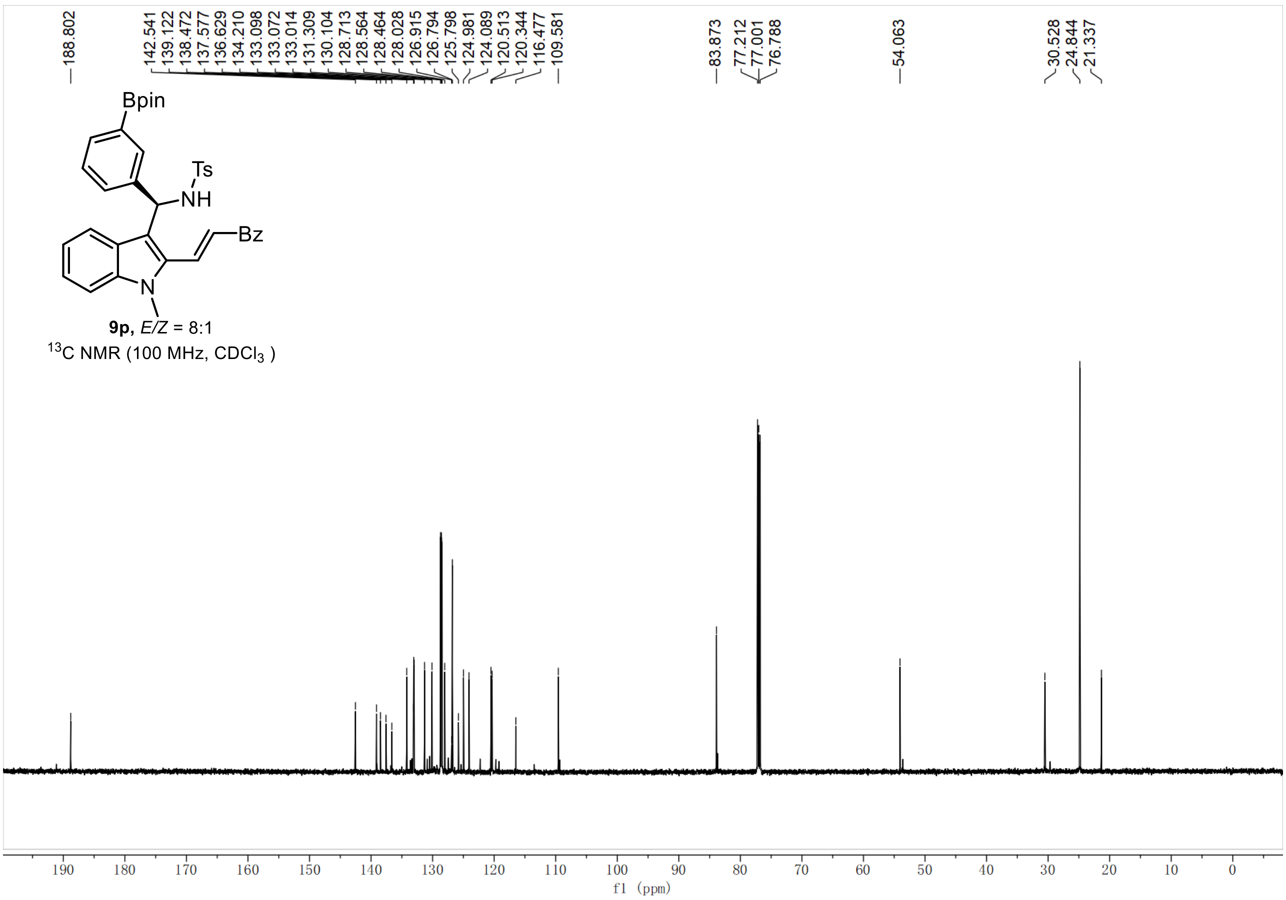
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.741	BB	0.7331	204.36742	3.63517	0.5264
2	16.142	BB	0.7538	3.86200e4	792.07098	99.4736

Name	CYC-20211122-7	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-7.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 4:44:08 PM (UTC+08:00)

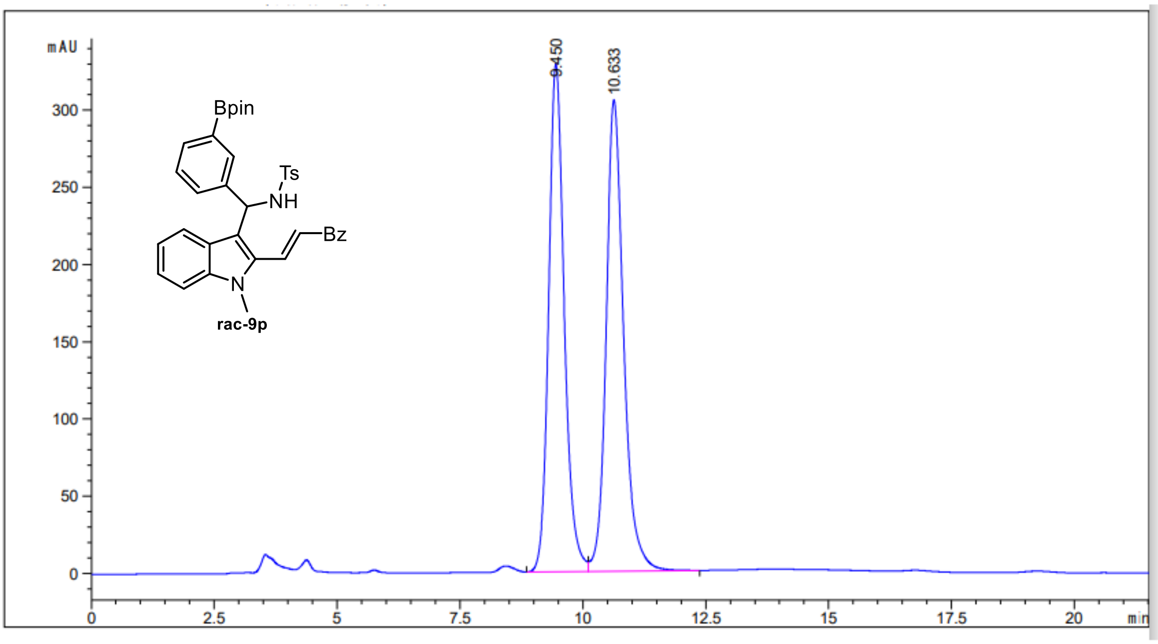




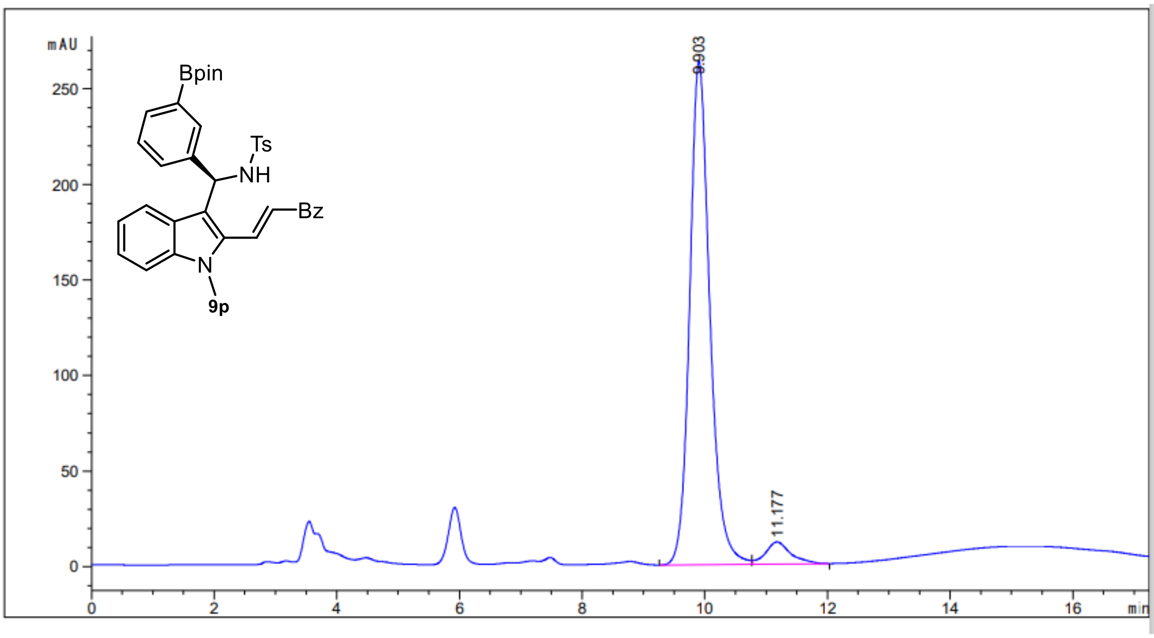
9p, *E/Z* = 8:1
^{1}H NMR (400 MHz, $CDCl_3$)



9p, *E/Z* = 8:1
^{13}C NMR (100 MHz, $CDCl_3$)

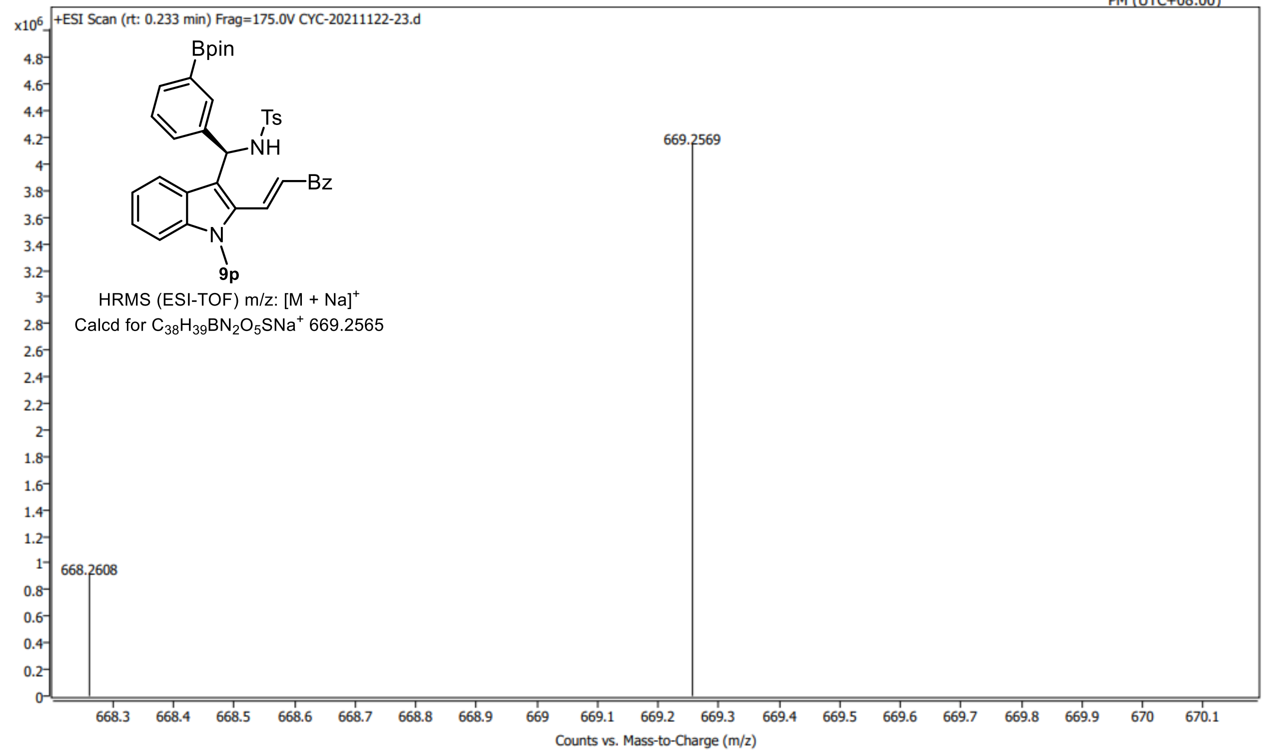


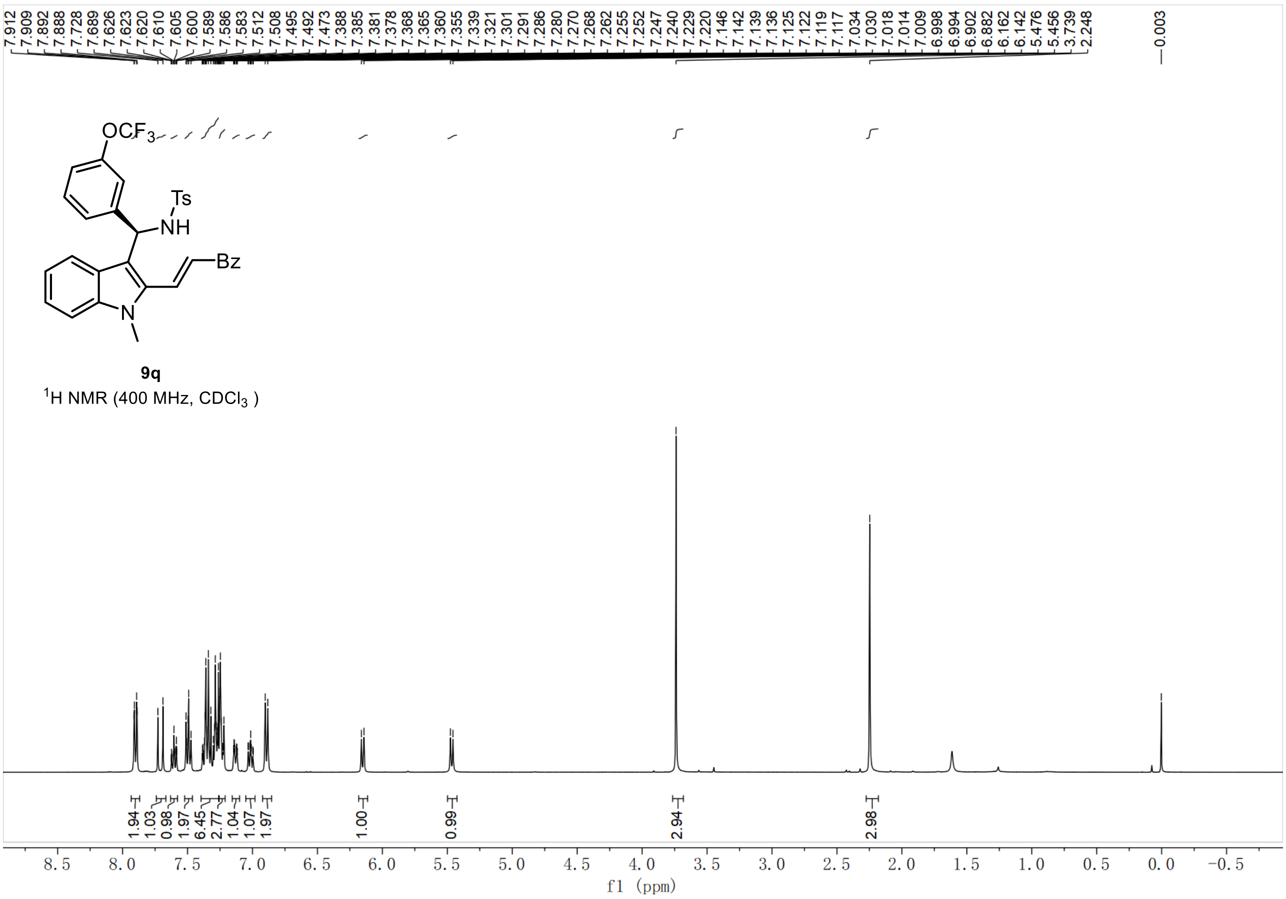
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.450	BV	0.3342	7248.03320	329.00491	48.9734
2	10.633	VB	0.3731	7551.90332	305.28229	51.0266

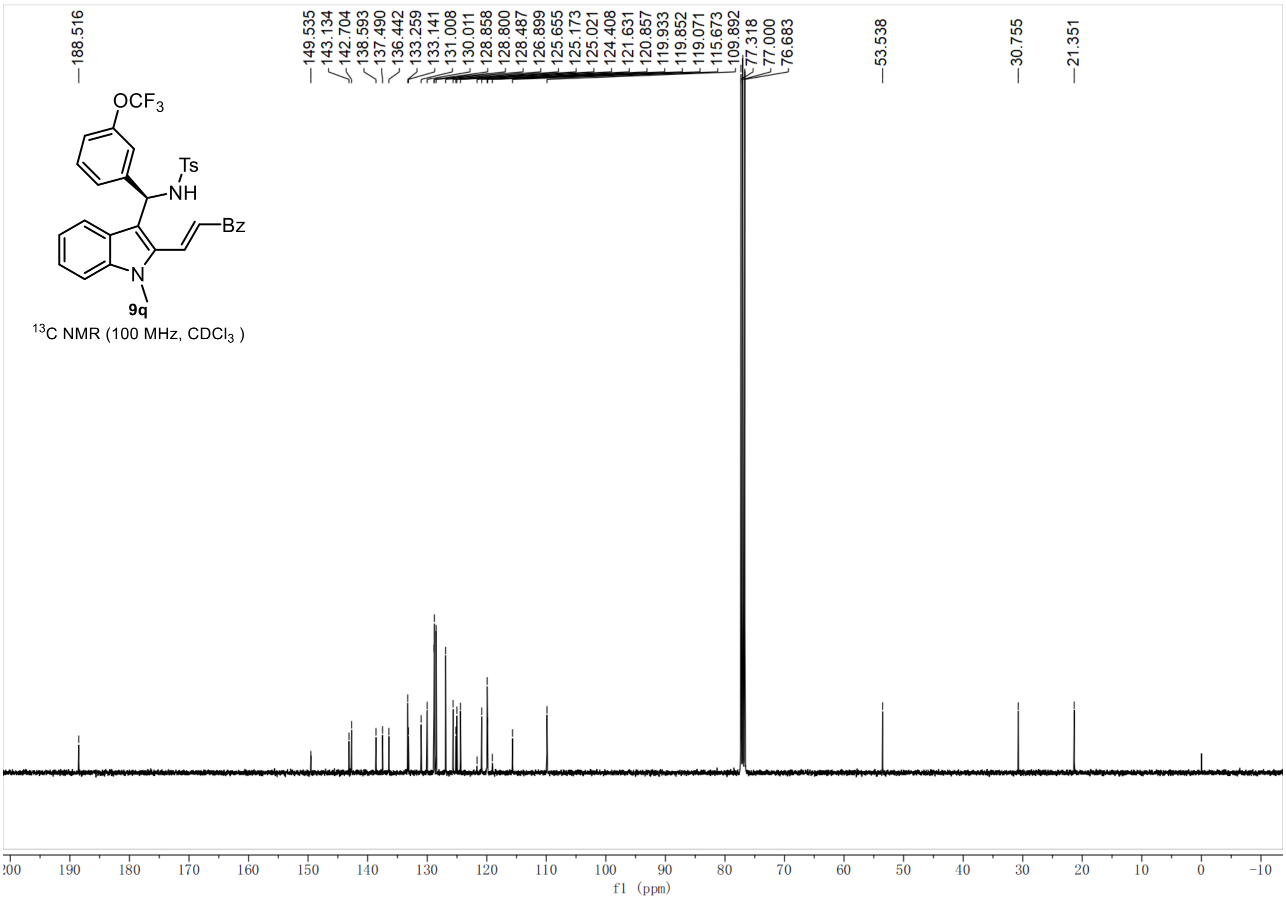


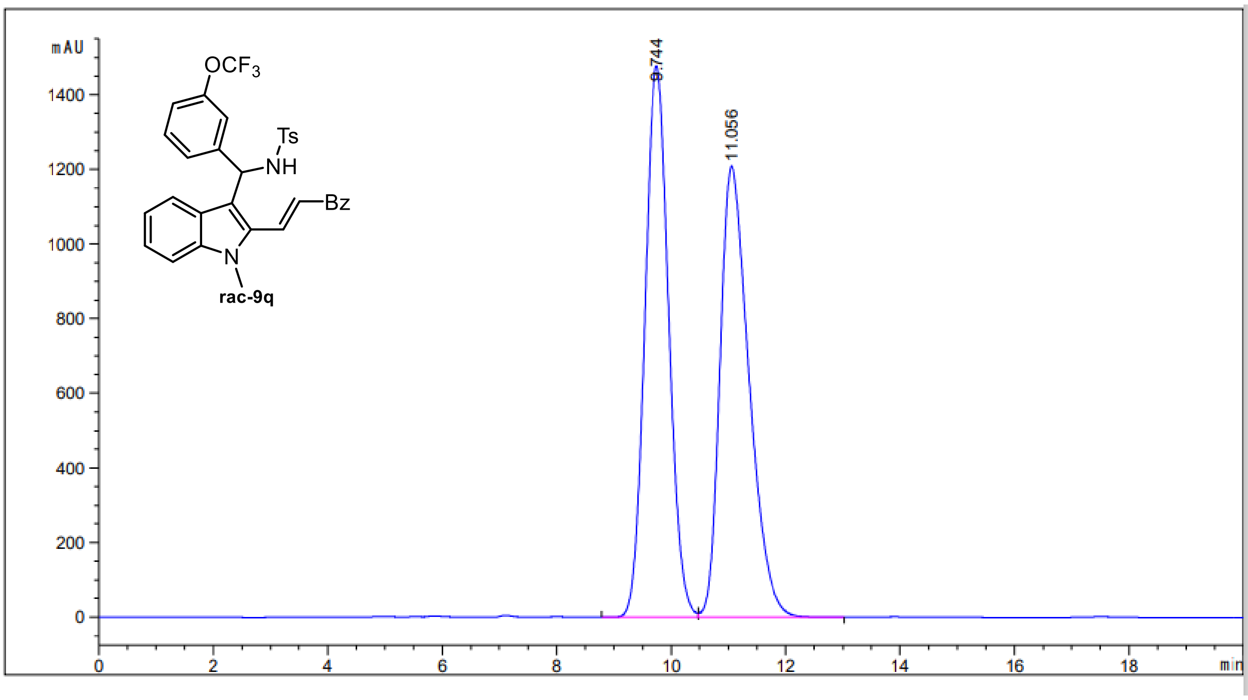
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.903	BV	0.3446	6006.89209	263.43942	94.7943
2	11.177	VB	0.4205	329.87622	11.55410	5.2057

Name	CYC-20211122-23	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-23.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 5:31:41 PM (UTC+08:00)

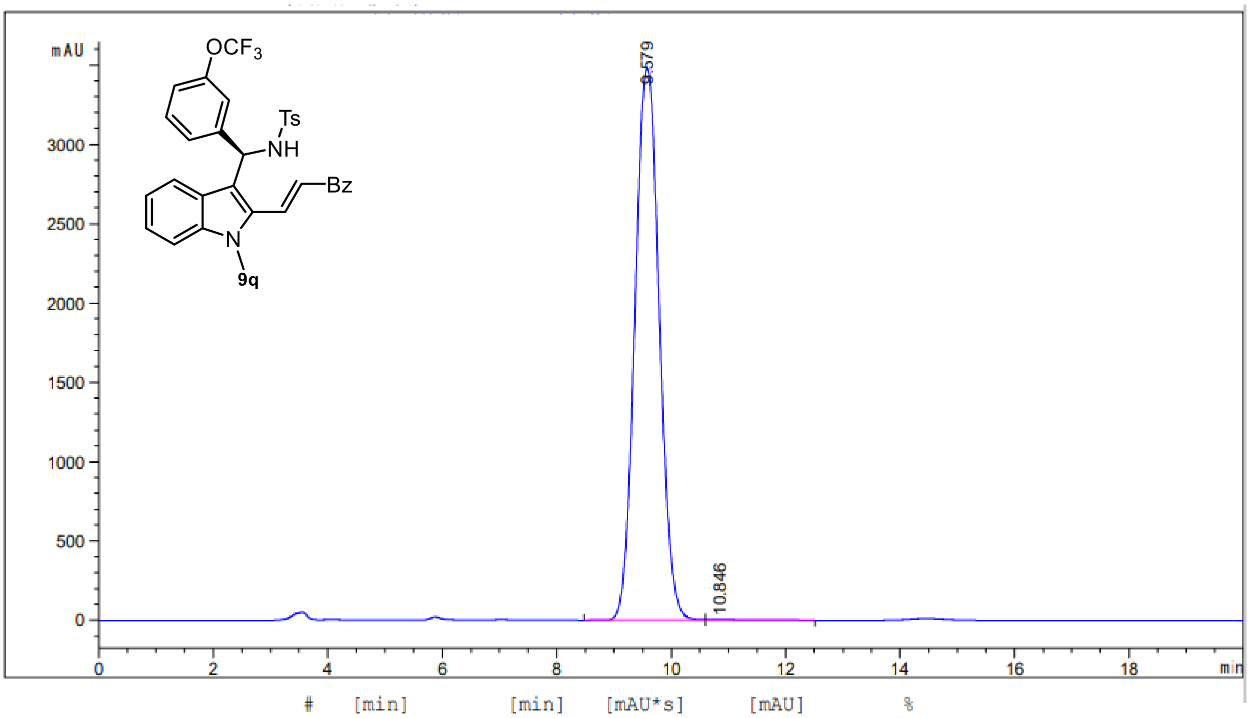




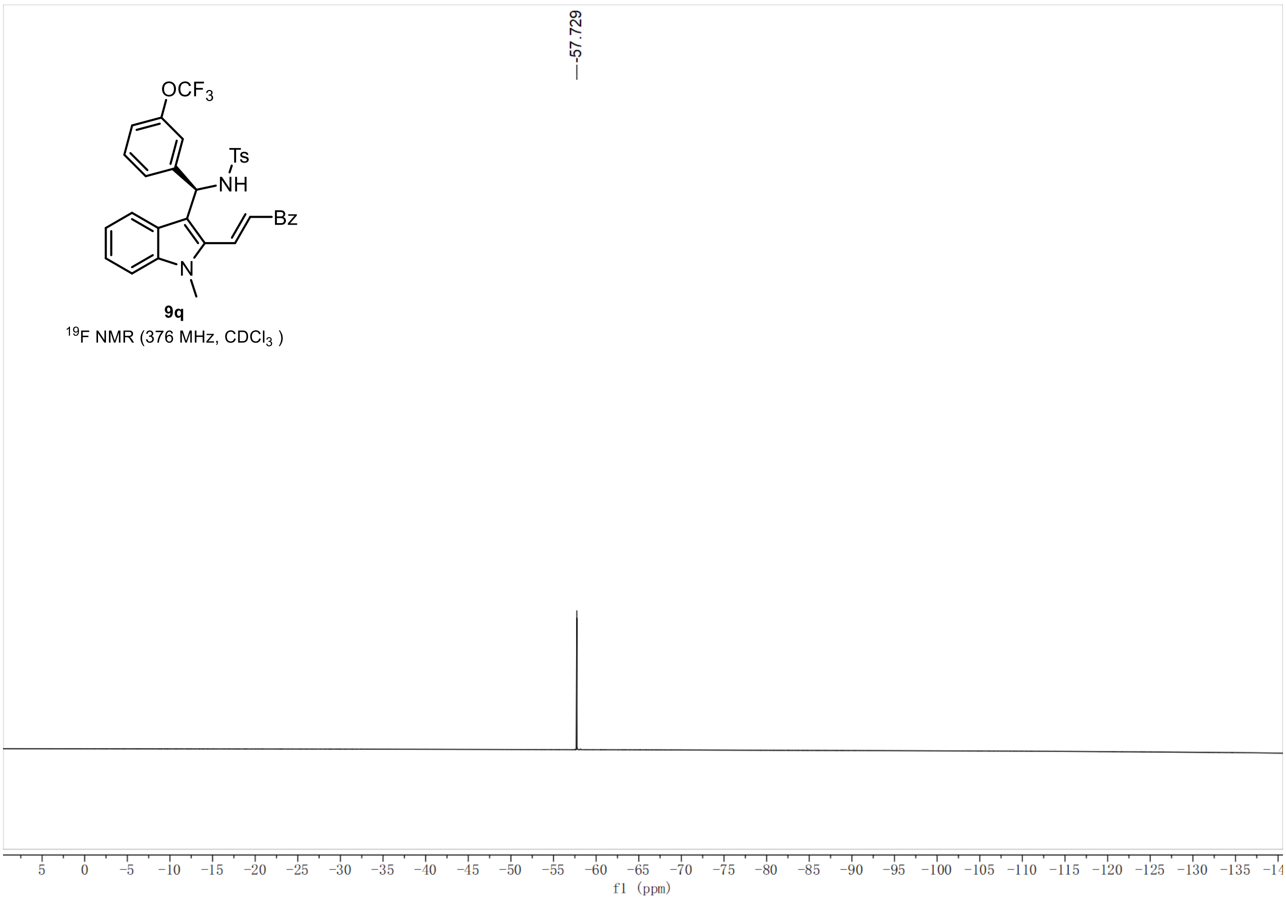


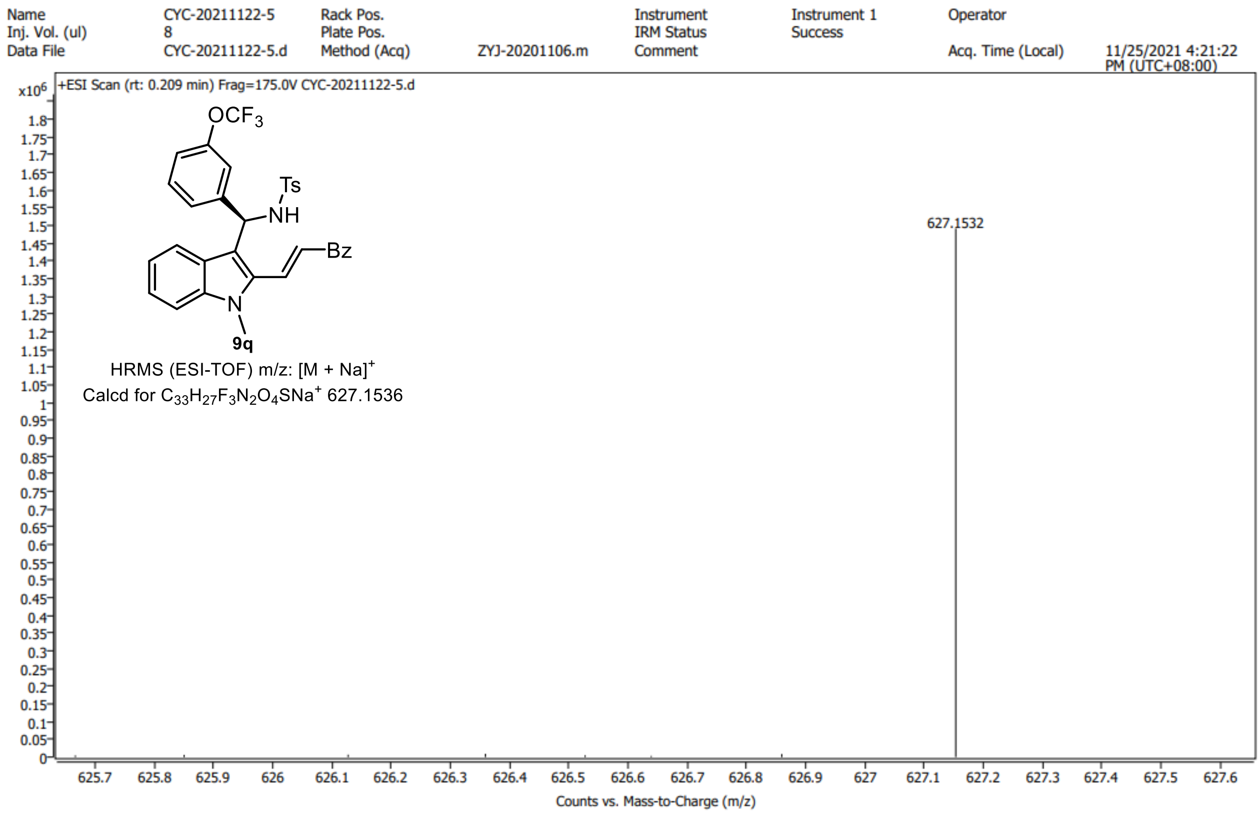


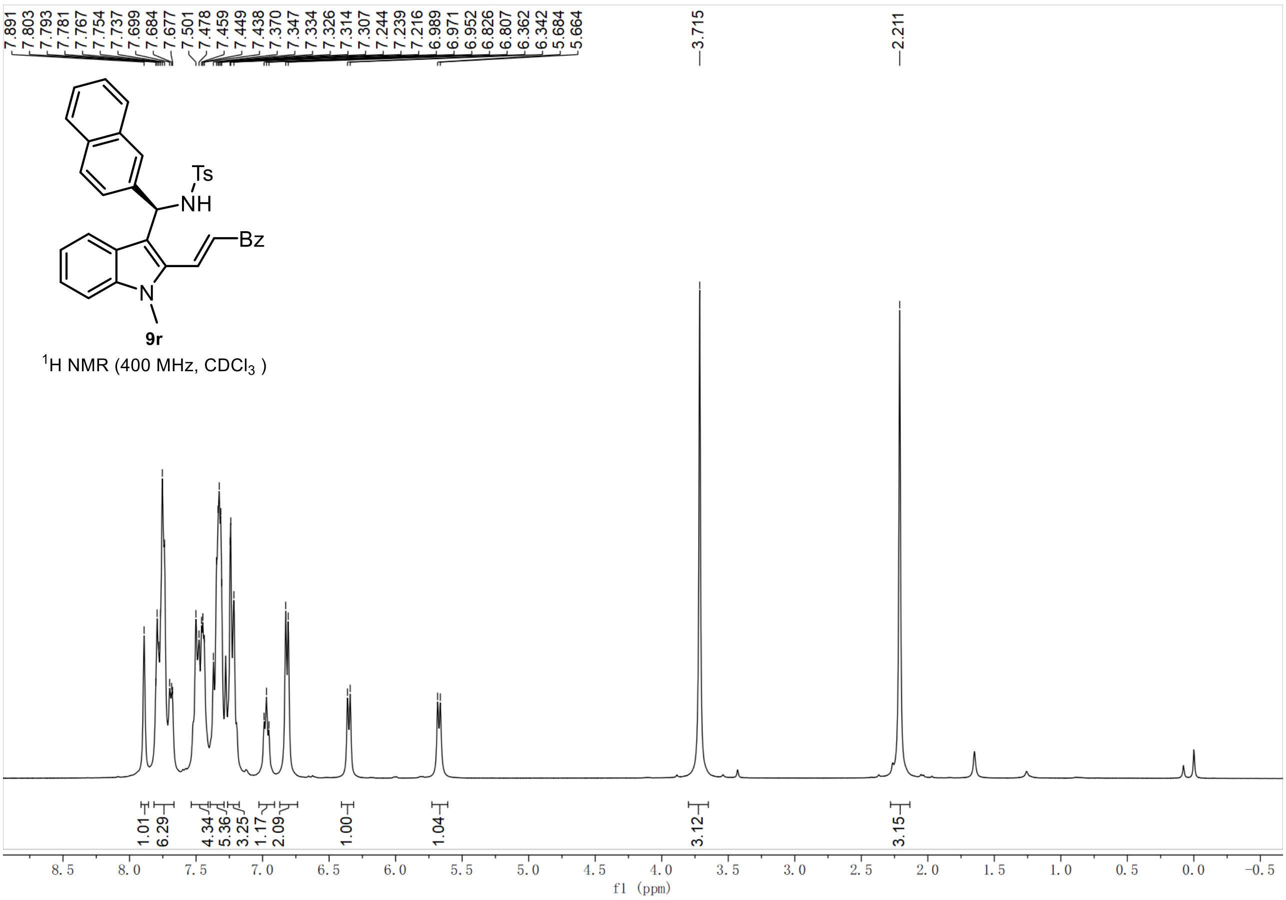
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.744	BV	0.4509	4.27206e4	1477.50684	49.9751
2	11.056	VBA	0.5437	4.27632e4	1208.91479	50.0249

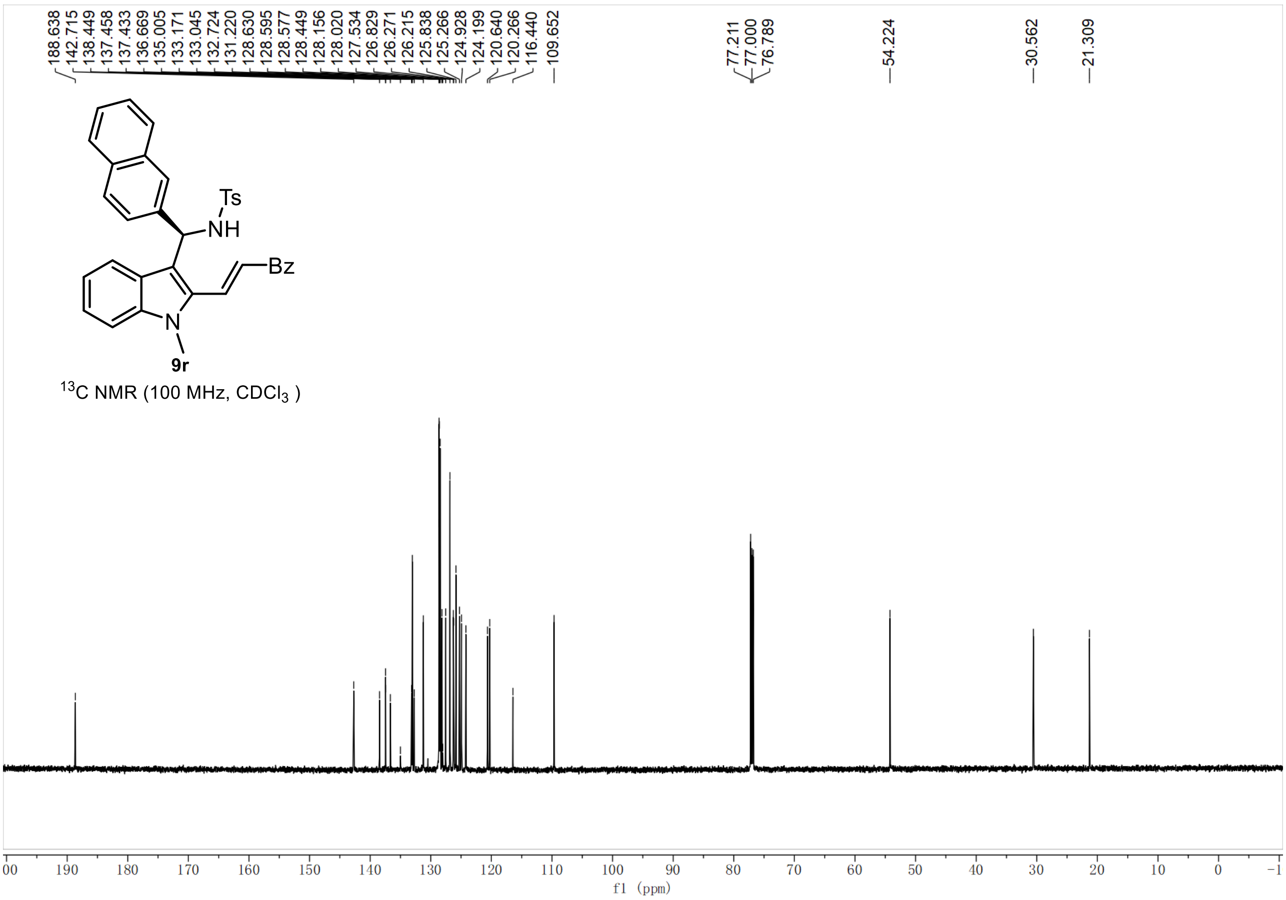


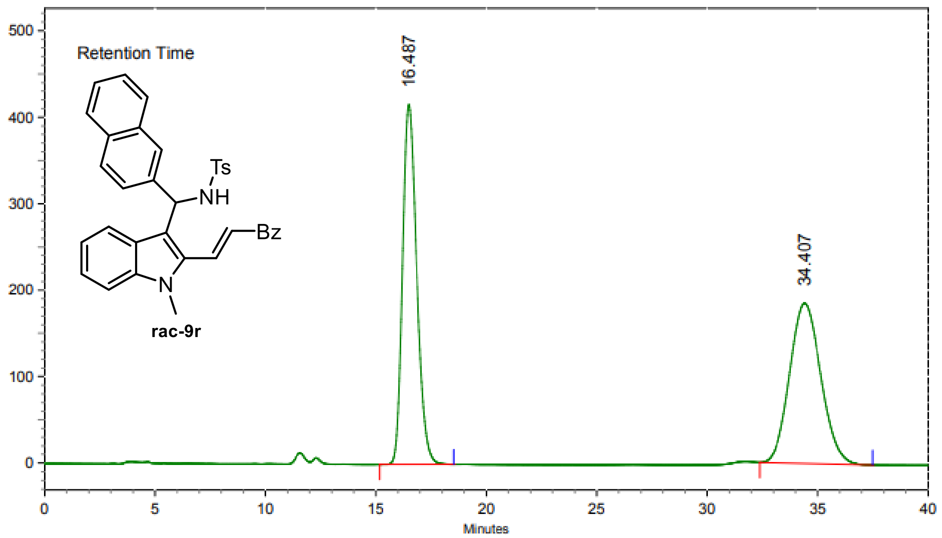
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9.579	BV	0.4667	1.03429e5	3474.81714	99.8132
2	10.846	VB	0.5508	193.61464	5.04878	0.1868


-57.729
OCF3
Ts
NH
Bz
N
9q
19F NMR (376 MHz, CDCl3)
f1 (ppm)


Name CYC-20211122-5
Inj. Vol. (ul) 8
Data File CYC-20211122-5.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument Instrument 1
IRM Status Success
Comment
Operator
Acq. Time (Local) 11/25/2021 4:21:22 PM (UTC+08:00)
+ESI Scan (rt: 0.209 min) Frag=175.0V CYC-20211122-5.d
OCF3
Ts
NH
Bz
N
9q
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C33H27F3N2O4SNa+ 627.1536
627.1532
Counts vs. Mass-to-Charge (m/z)

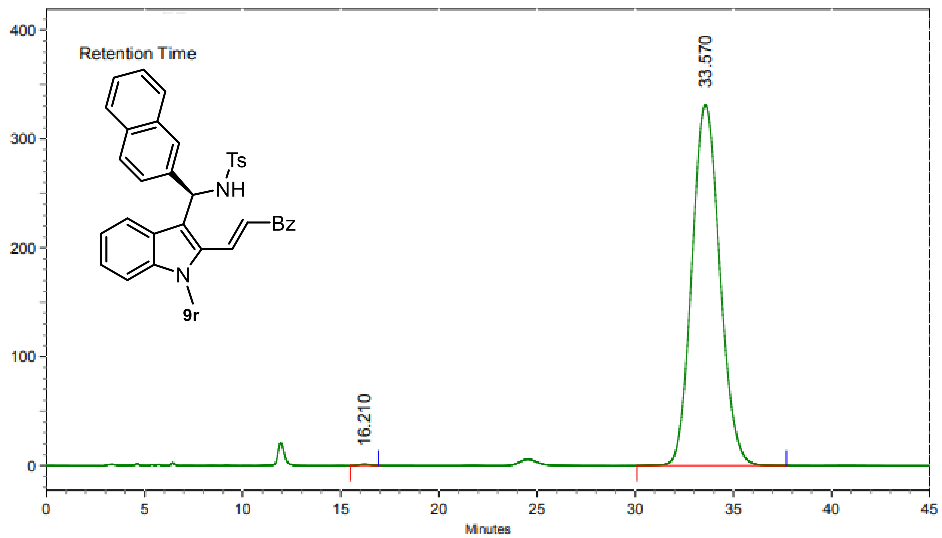

9r
^{1}H NMR (400 MHz, CDCl$_3$)


9r
^{13}C NMR (100 MHz, CDCl$_3$)



AREA PERCENT REPORT

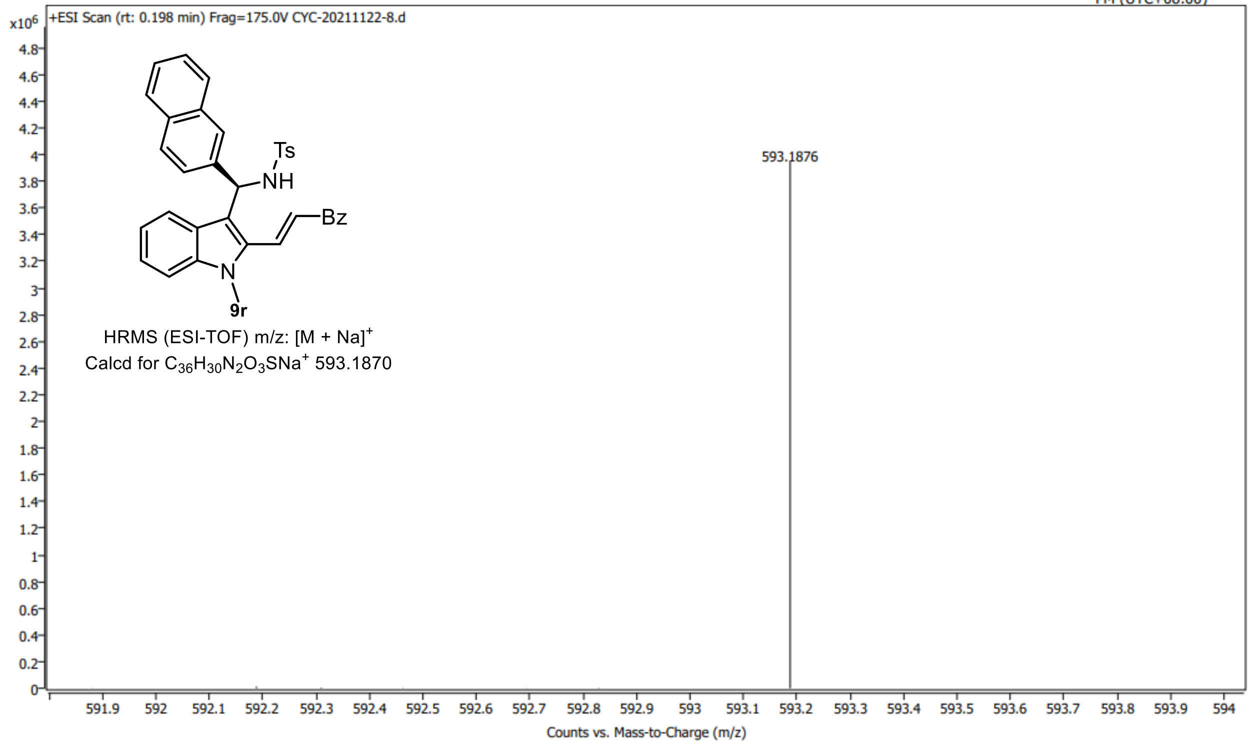
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	16.487	3.333	6979236	312816302	50.5441
2	34.407	5.113	3108400	306080935	49.4559

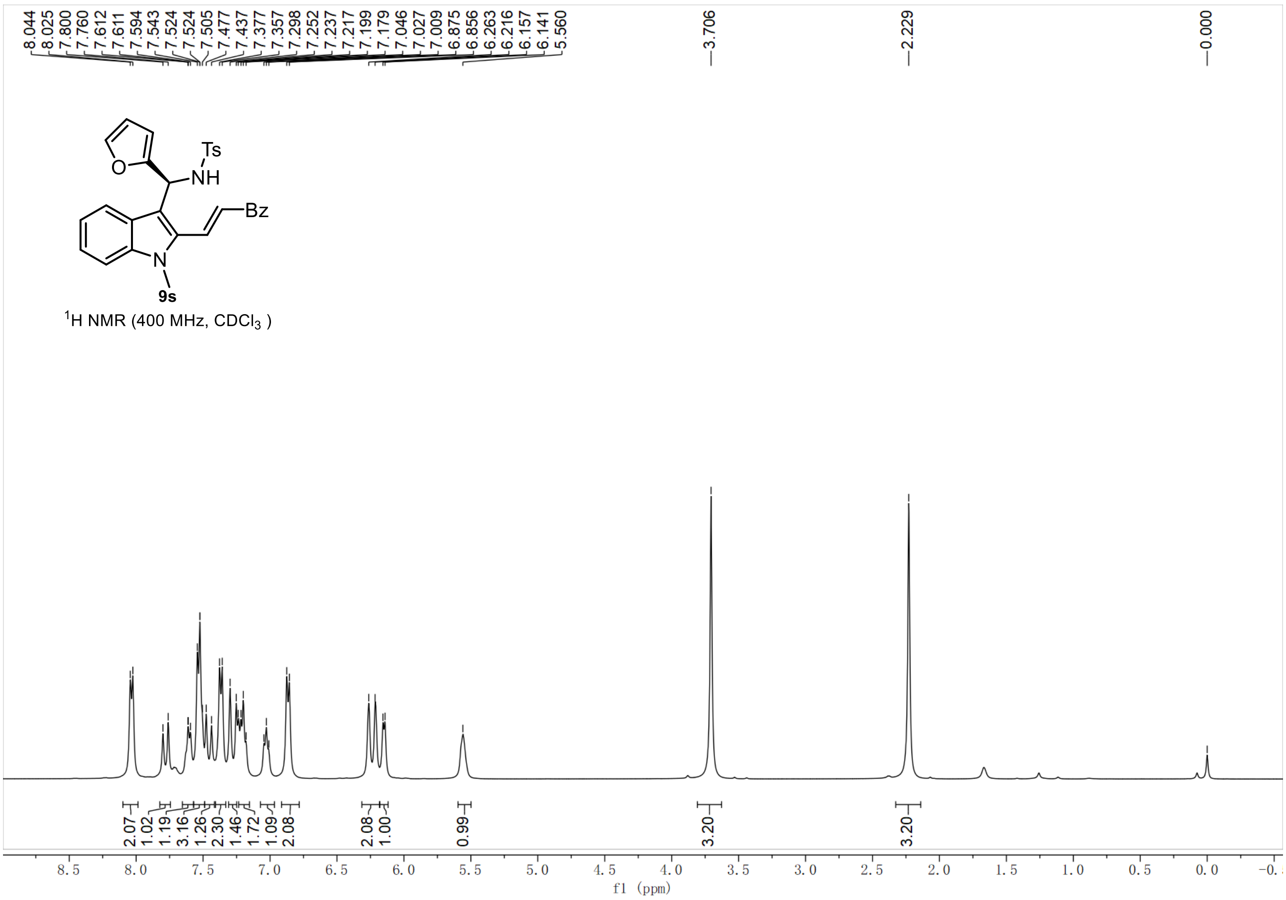


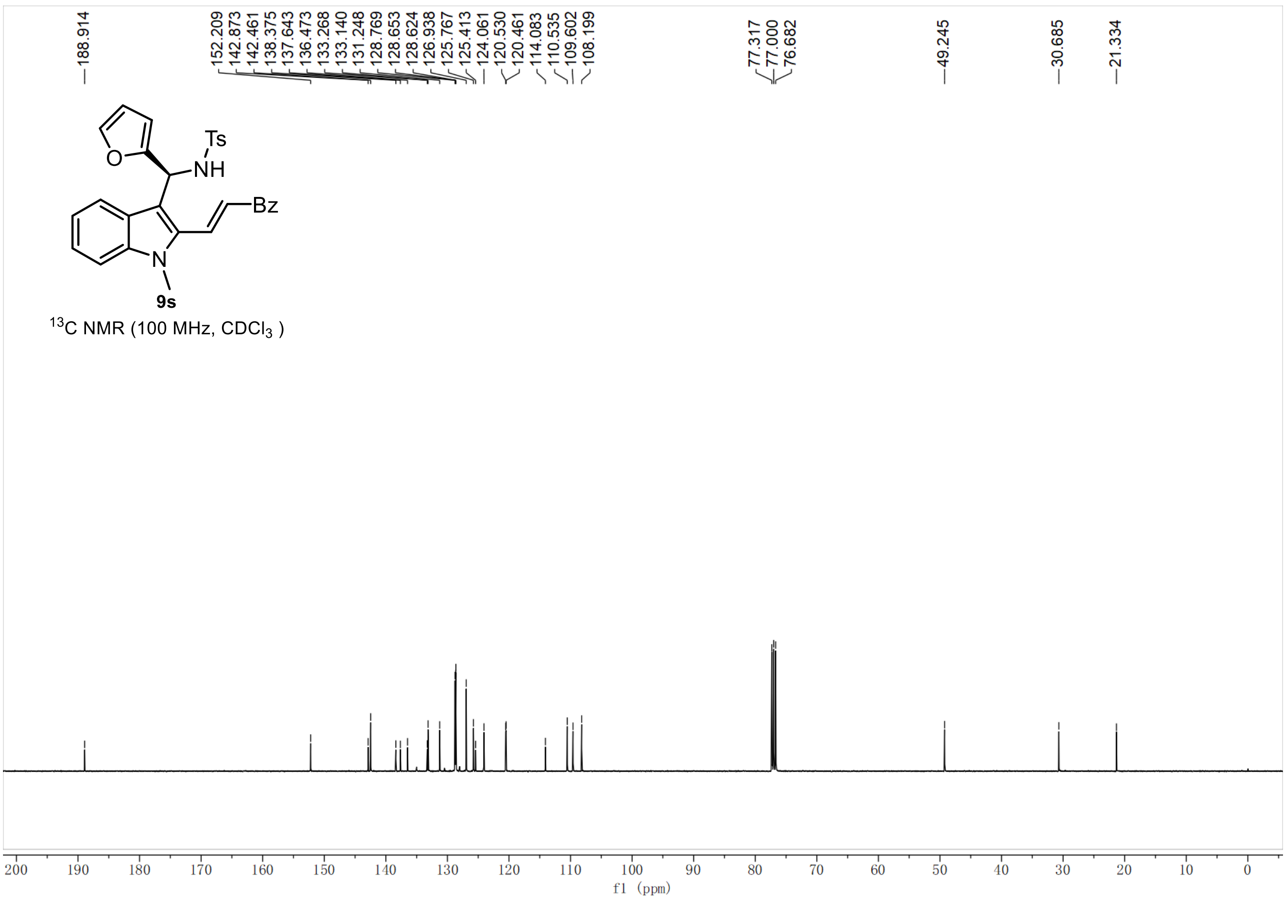
AREA PERCENT REPORT

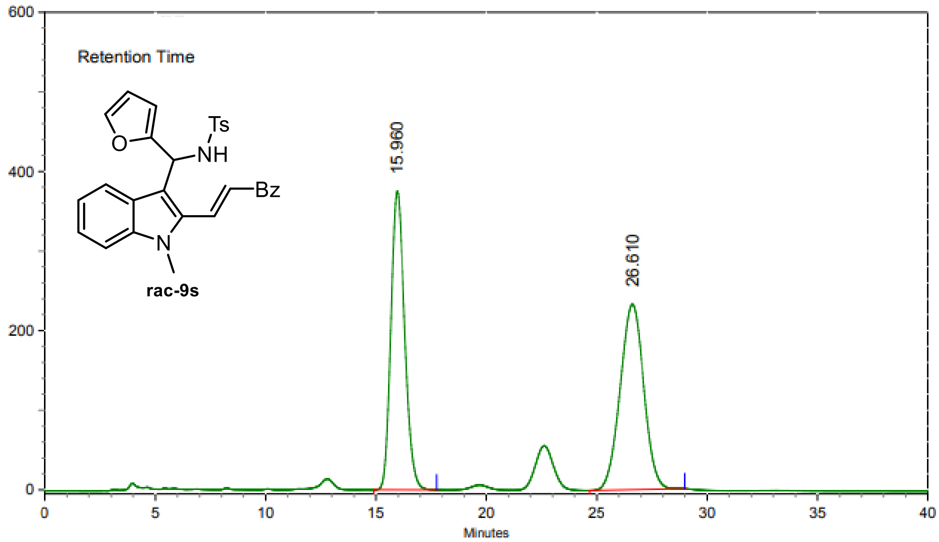
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	16.210	1.440	20984	850281	0.1545
2	33.570	7.627	5557583	549577262	99.8455

Name	CYC-20211122-8	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-8.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 4:47:23 PM (UTC+08:00)



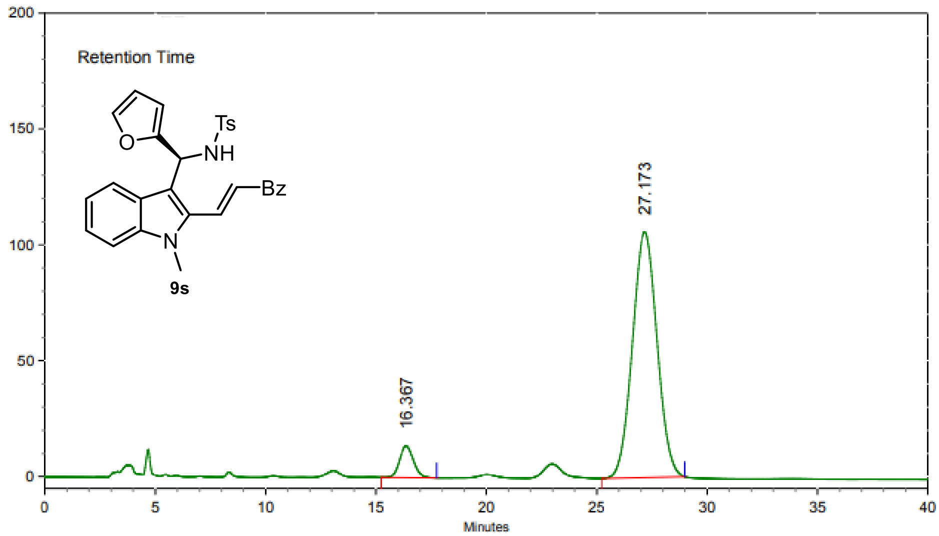

8.044
8.025
7.800
7.760
7.612
7.611
7.594
7.543
7.524
7.524
7.505
7.477
7.437
7.377
7.357
7.298
7.252
7.237
7.217
7.199
7.179
7.046
7.027
7.009
6.875
6.856
6.263
6.216
6.157
6.141
5.560
3.706
2.229
0.000
Ts
NH
O
Bz
N
9s
^{1}H NMR (400 MHz, CDCl$_3$)
2.07
1.02
1.19
3.16
1.26
2.30
1.46
1.72
1.09
2.08
2.08
1.00
0.99
3.20
3.20
f1 (ppm)


188.914
152.209
142.873
142.461
138.375
137.643
136.473
133.268
133.140
131.248
128.769
128.653
128.624
126.938
125.767
125.413
124.061
120.530
120.461
114.083
110.535
109.602
108.199
77.317
77.000
76.682
49.245
30.685
21.334
Ts
NH
O
Bz
N
9s
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



AREA PERCENT REPORT

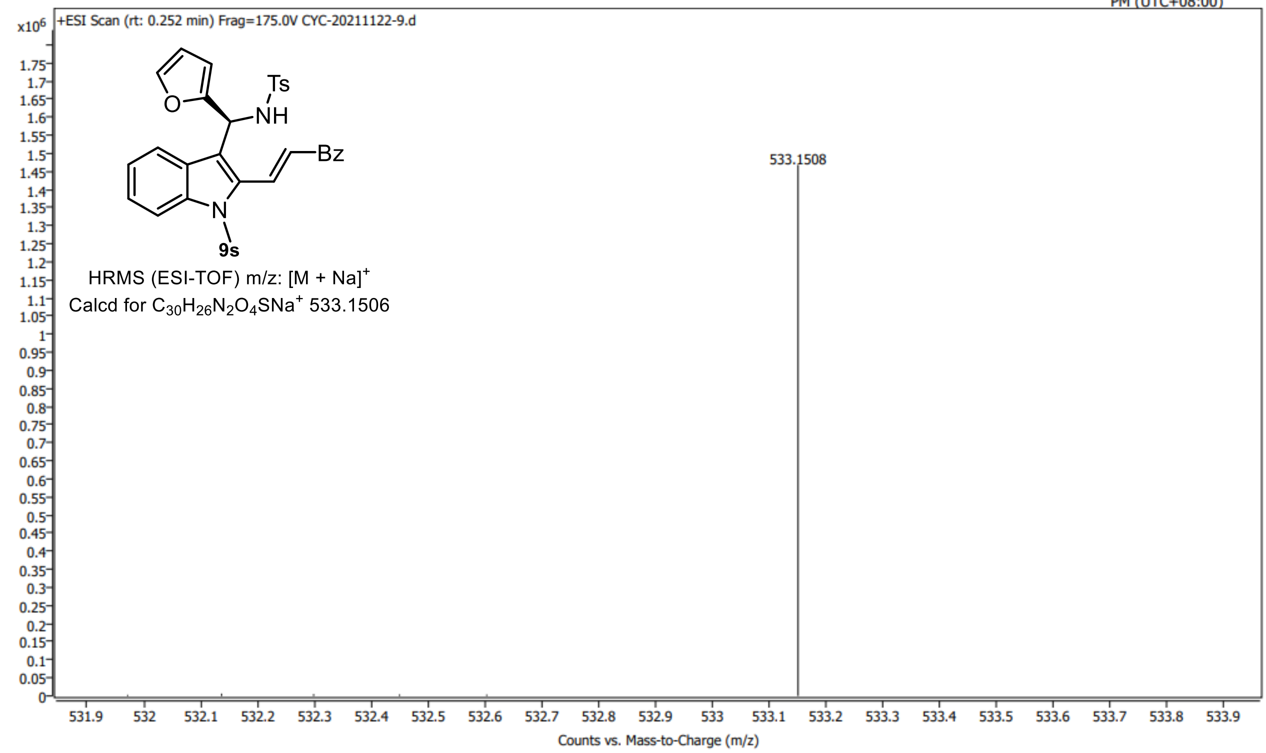
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	15.960	2.837	6290548	274844169	48.5817
2	26.610	4.320	3902253	290892002	51.4183

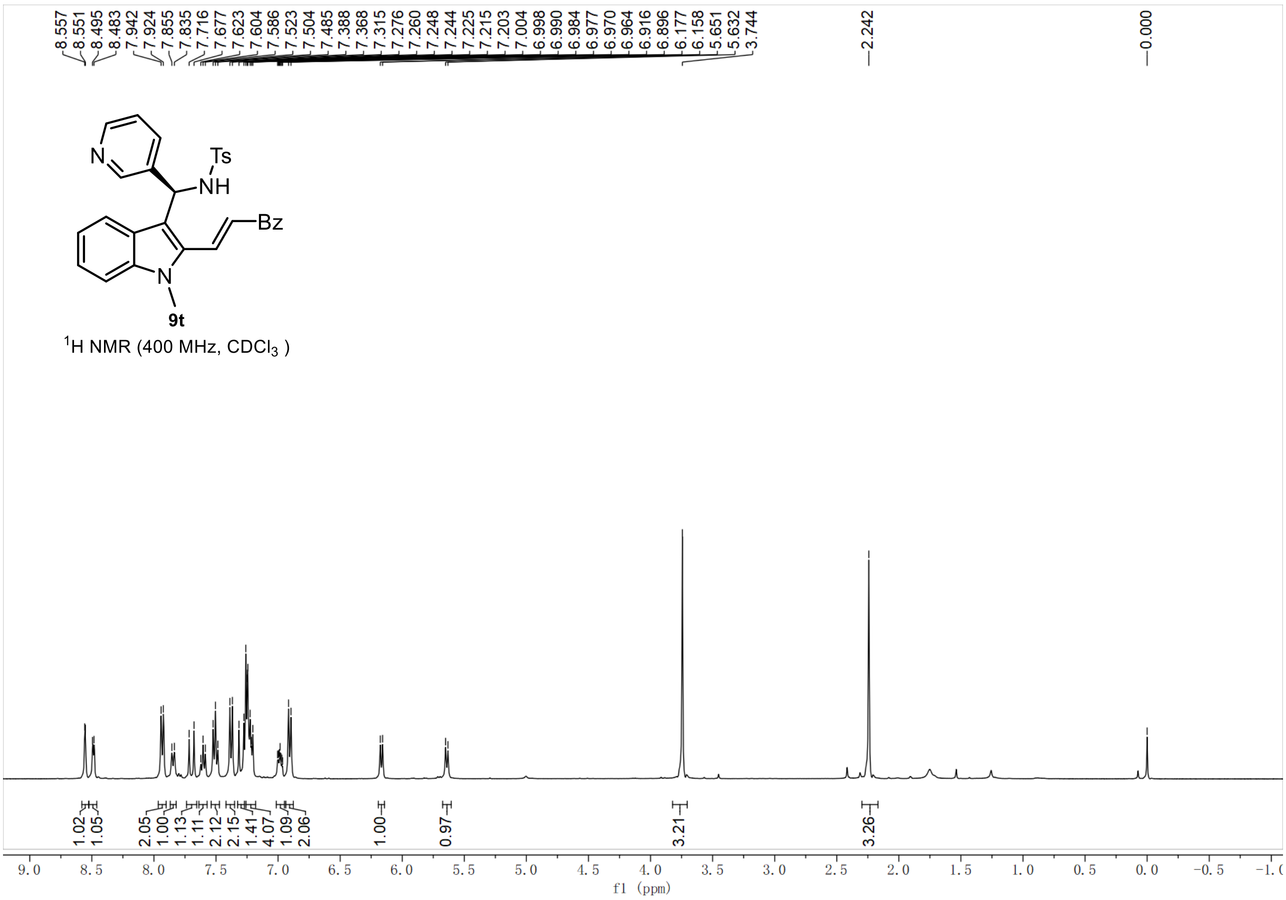


AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	16.367	2.507	230225	10180317	6.8558
2	27.173	3.767	1779123	138311245	93.1442

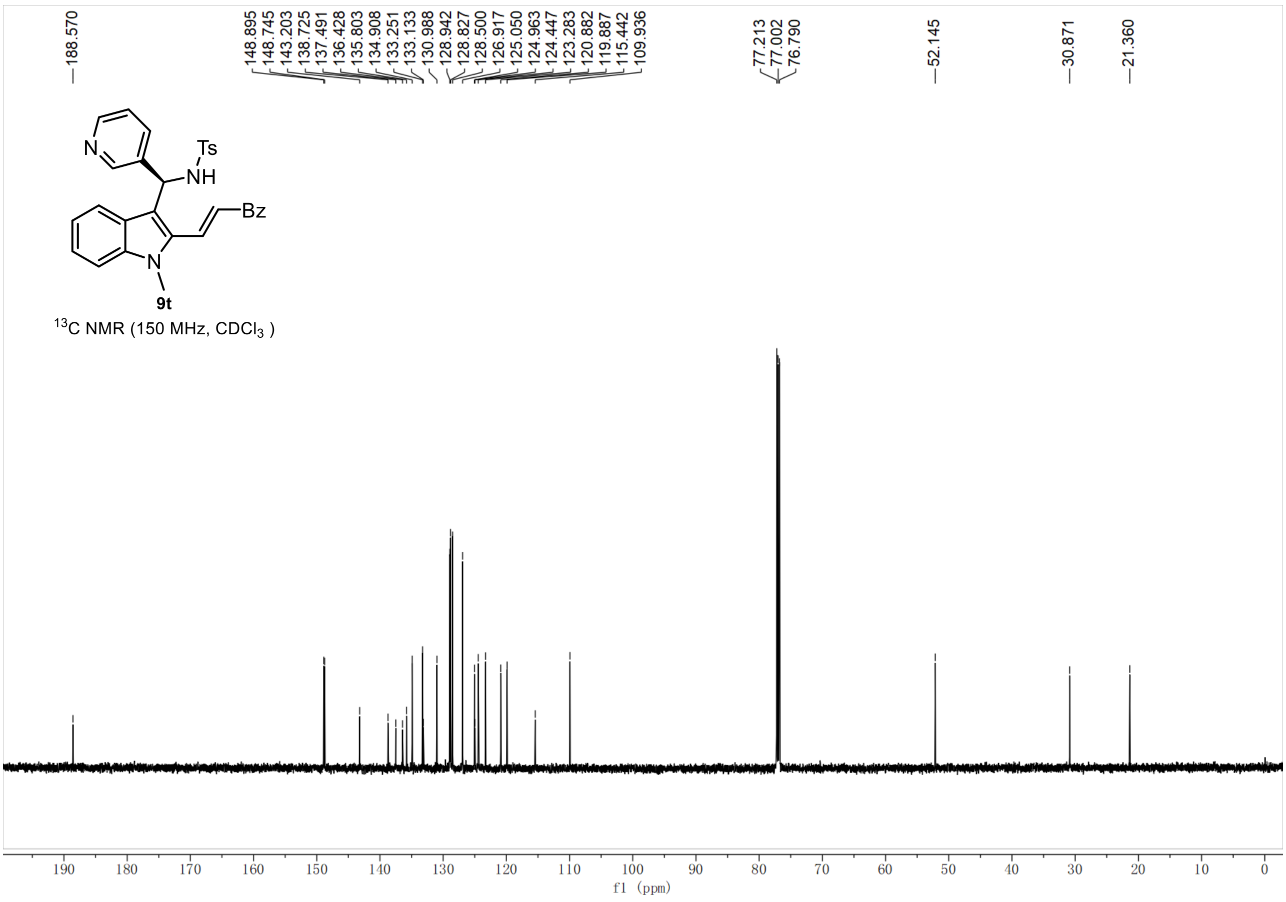
Name	CYC-20211122-9	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-9.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 4:50:22 PM (UTC+08:00)





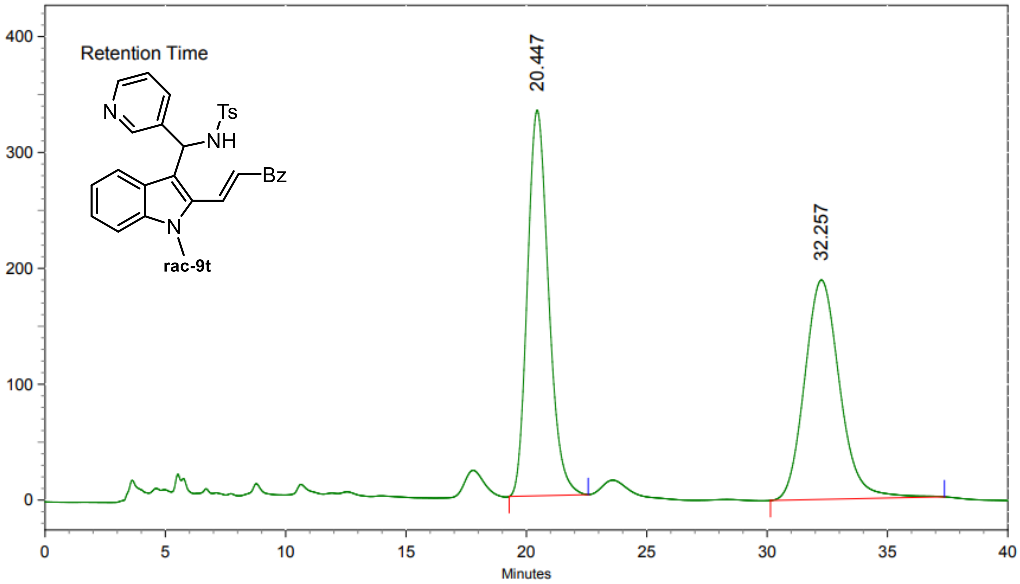
9t

^{1}H NMR (400 MHz, $CDCl_3$)



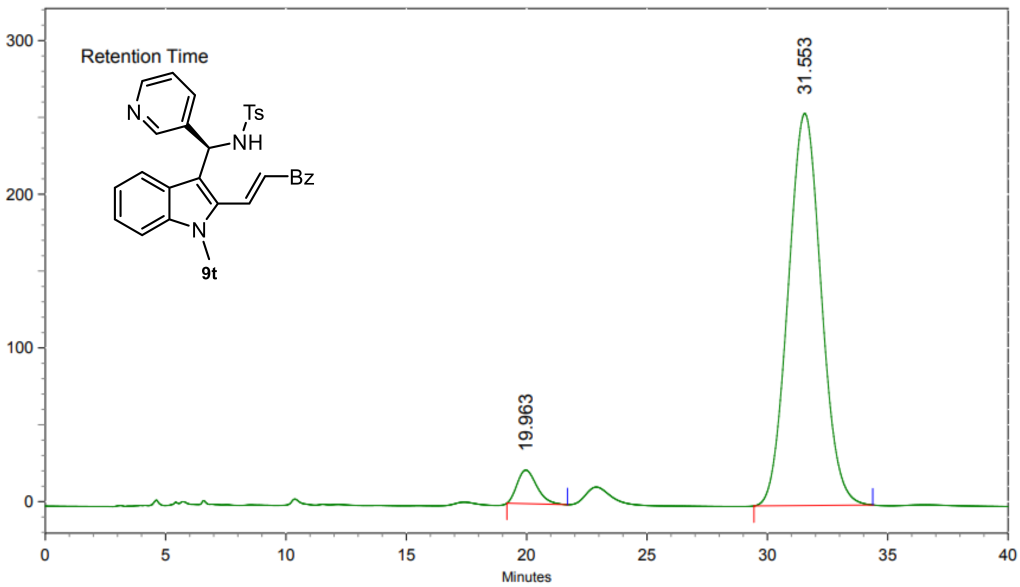
9t

^{13}C NMR (150 MHz, $CDCl_3$)



AREA PERCENT REPORT

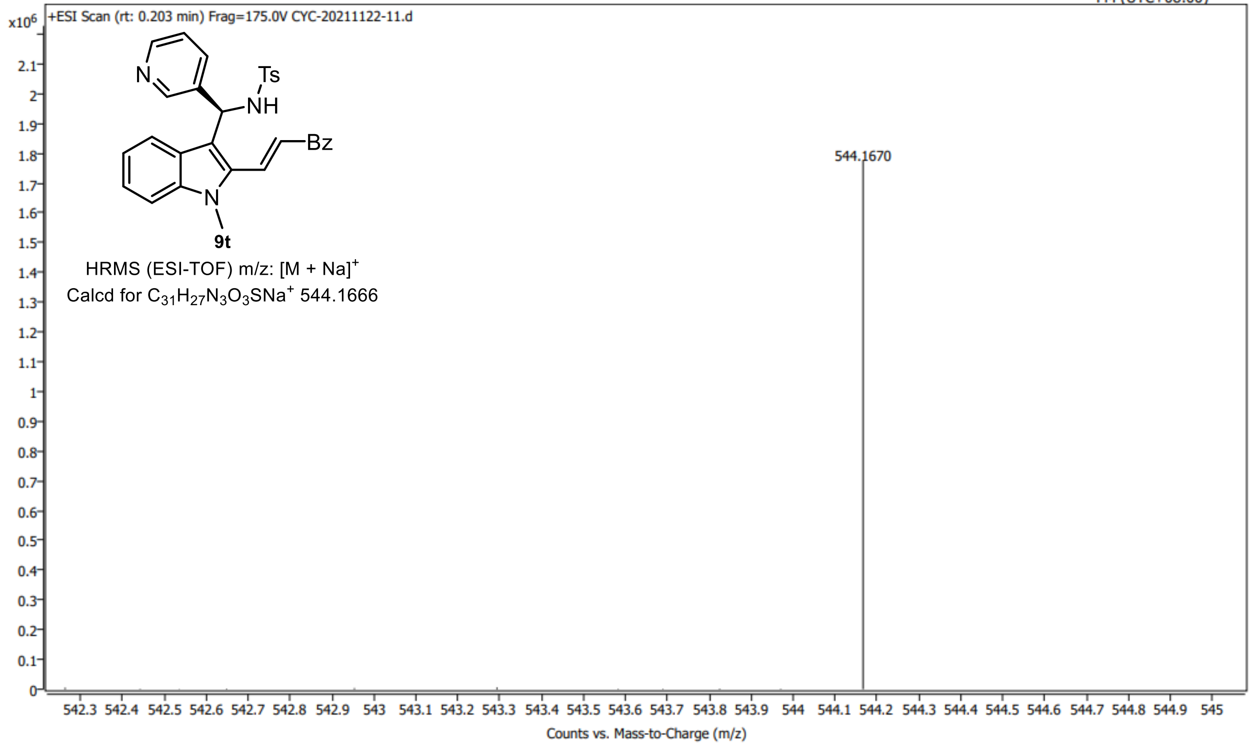
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	20.447	3.280	5582775	340881714	51.4650
2	32.257	7.227	3177083	321474059	48.5350

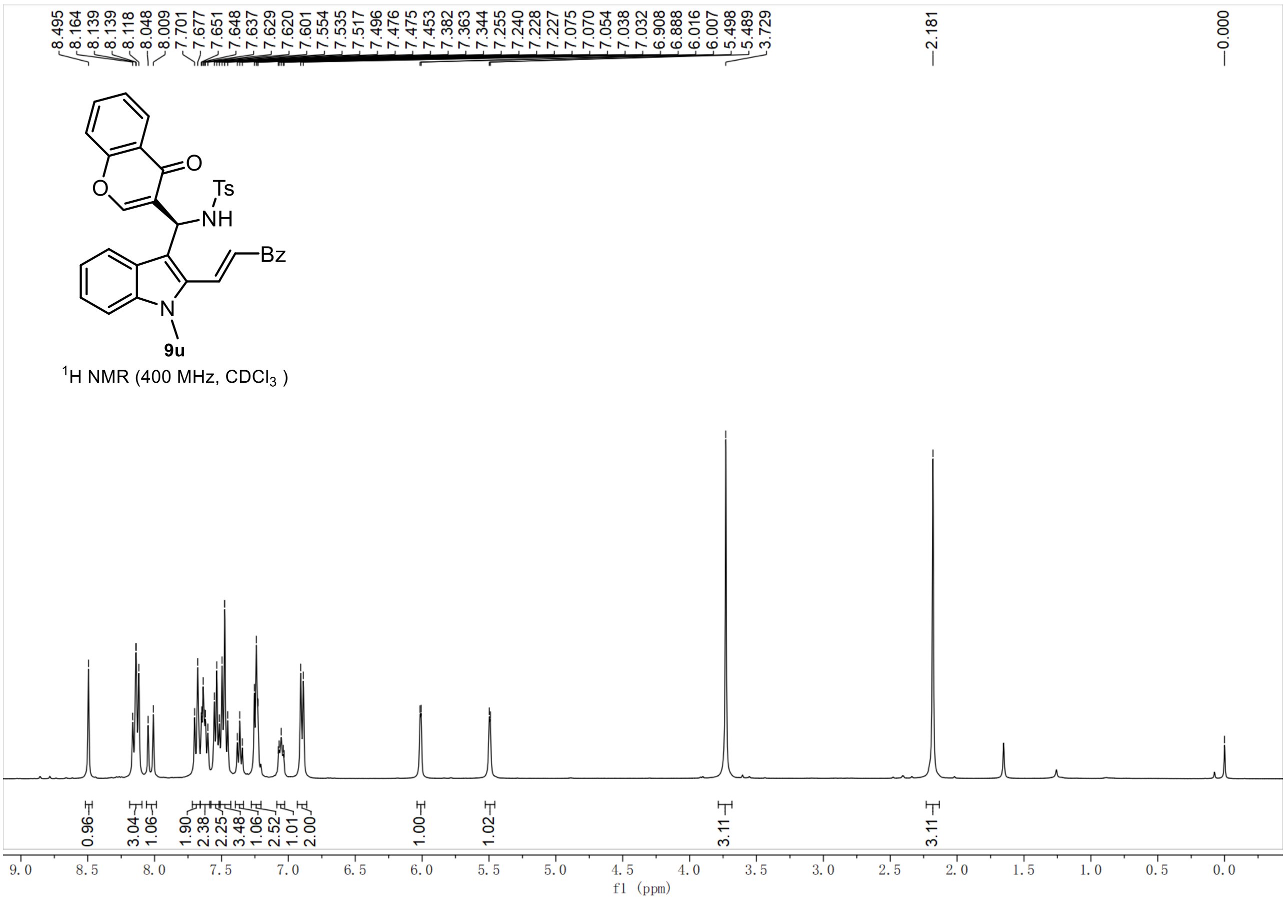


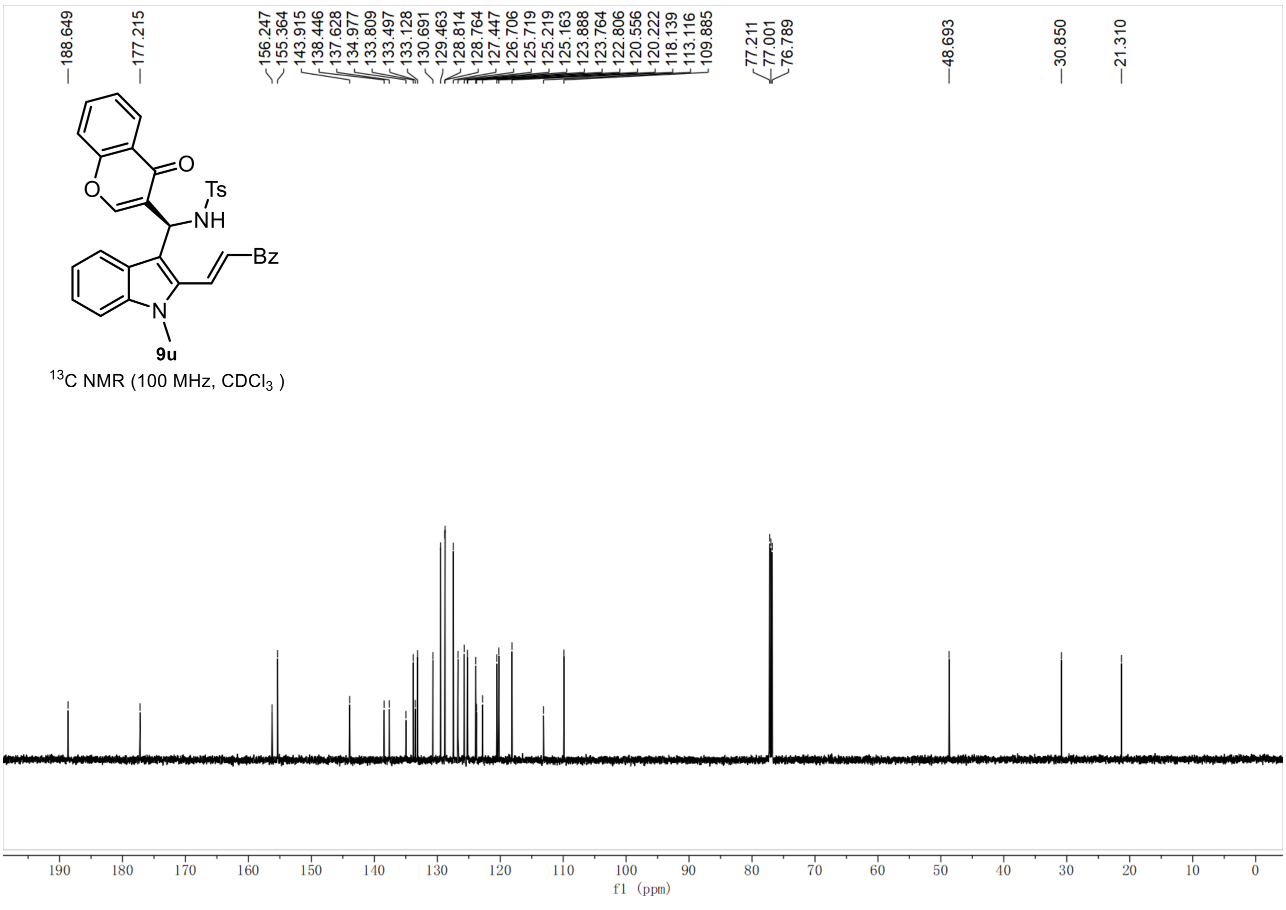
AREA PERCENT REPORT

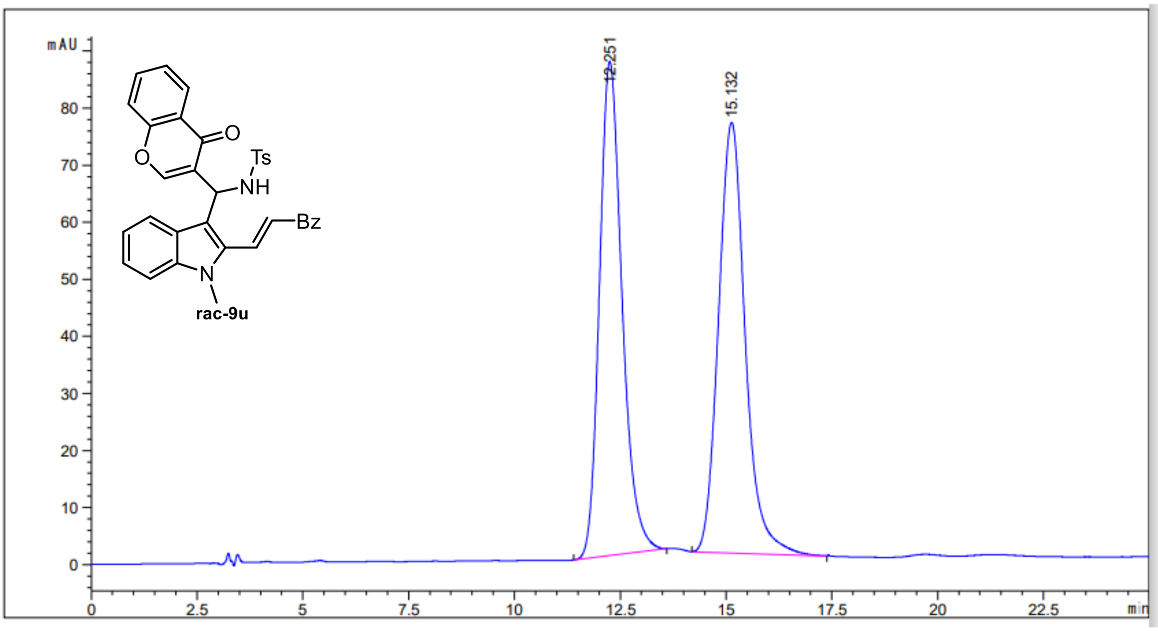
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	19.963	2.517	366335	20766529	4.8474
2	31.553	4.933	4280988	407636260	95.1526

Name	CYC-20211122-11	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-11.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 4:56:16 PM (UTC+08:00)

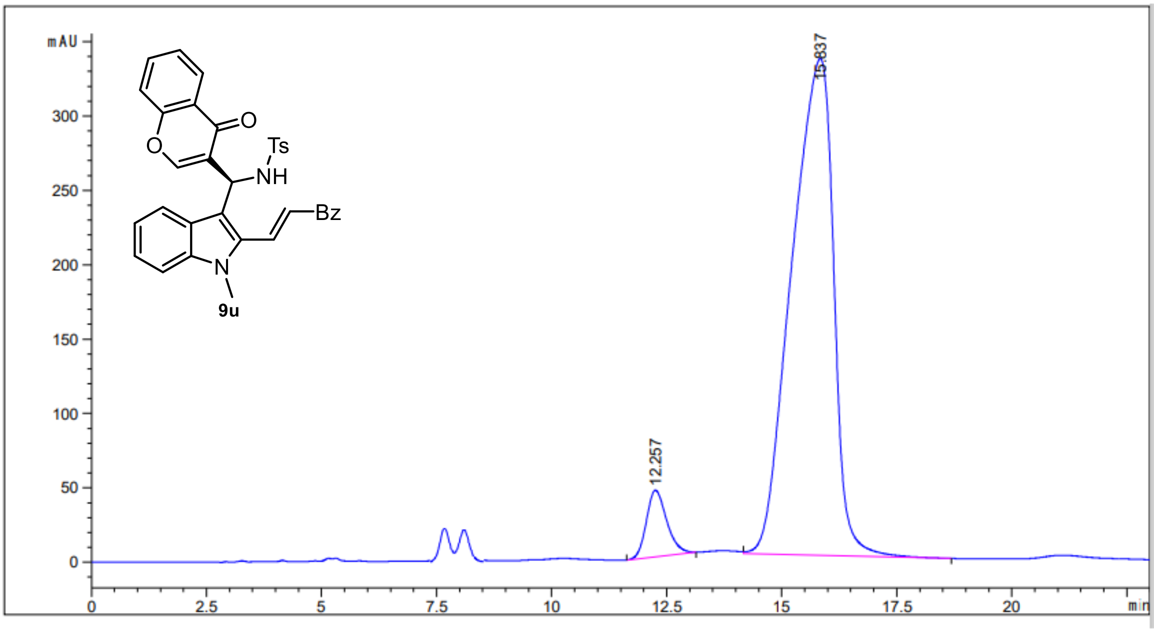



9u
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


9u
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

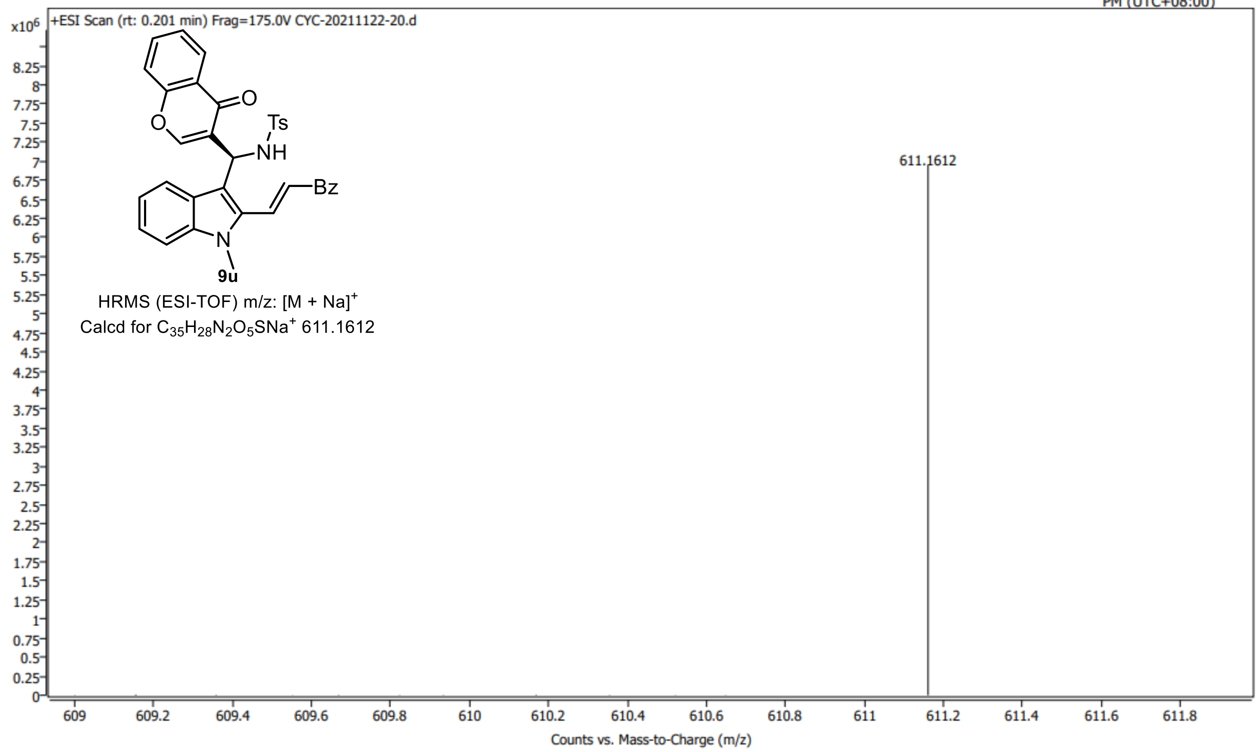


#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.251	BB	0.5695	3211.00171	86.58423	49.2991
2	15.132	BB	0.6721	3302.30249	75.47702	50.7009



#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.257	BB	0.4699	1372.73193	44.75978	6.1124
2	15.837	VB	1.0700	2.10853e4	333.96313	93.8876

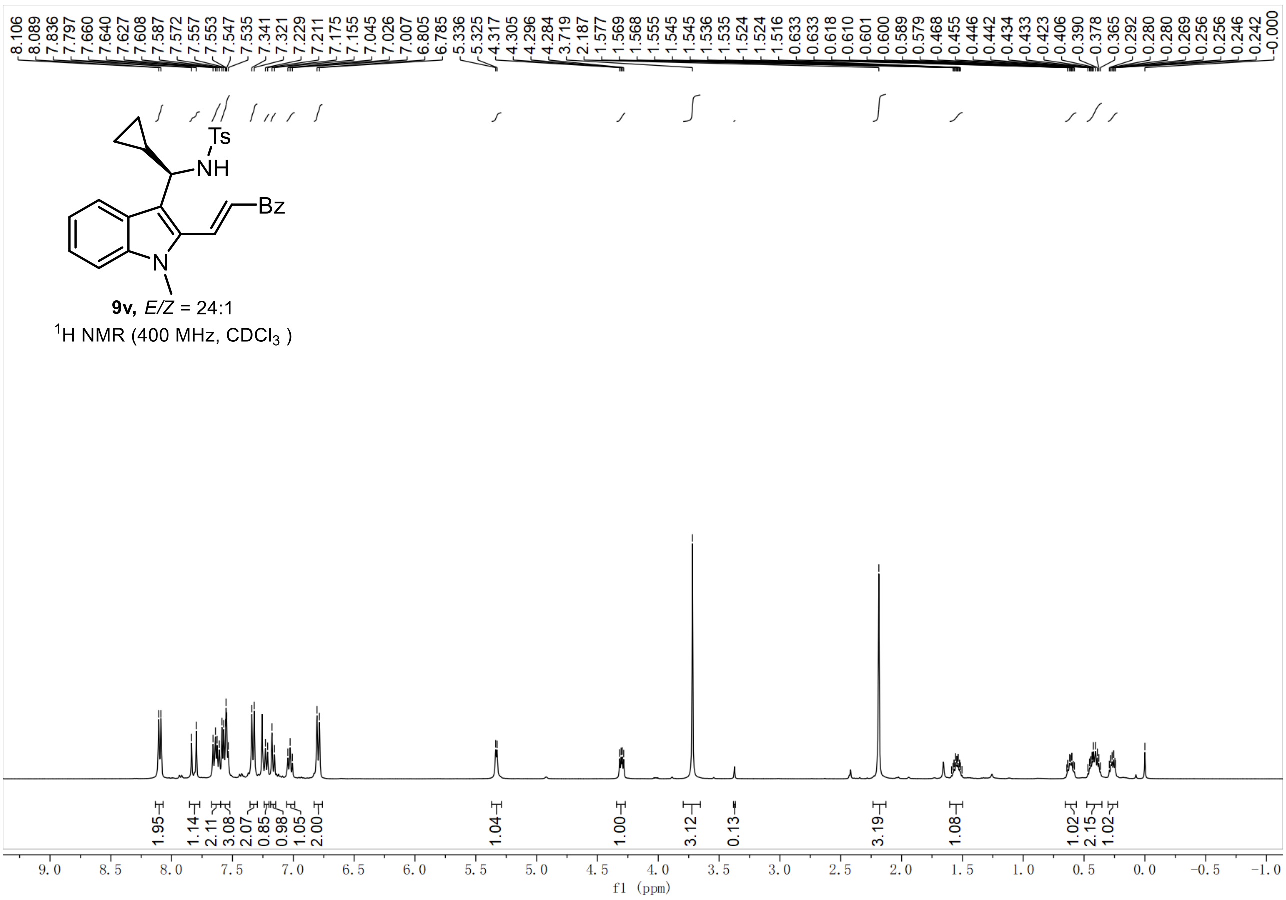
Name	CYC-20211122-20	Rack Pos.		Instrument	Instrument 1	Operator		
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success			
Data File	CYC-20211122-20.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 5:22:50 PM (UTC+08:00)	

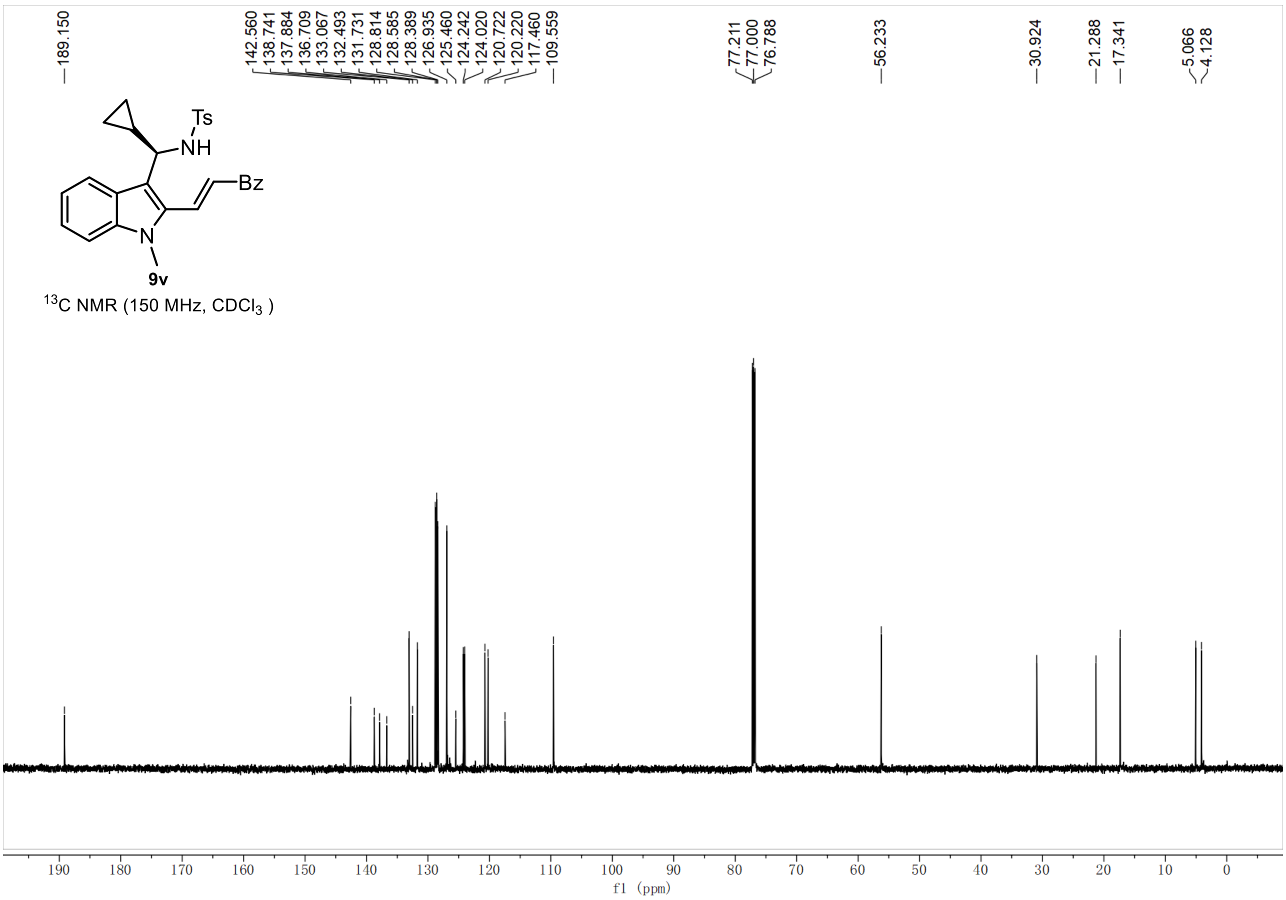


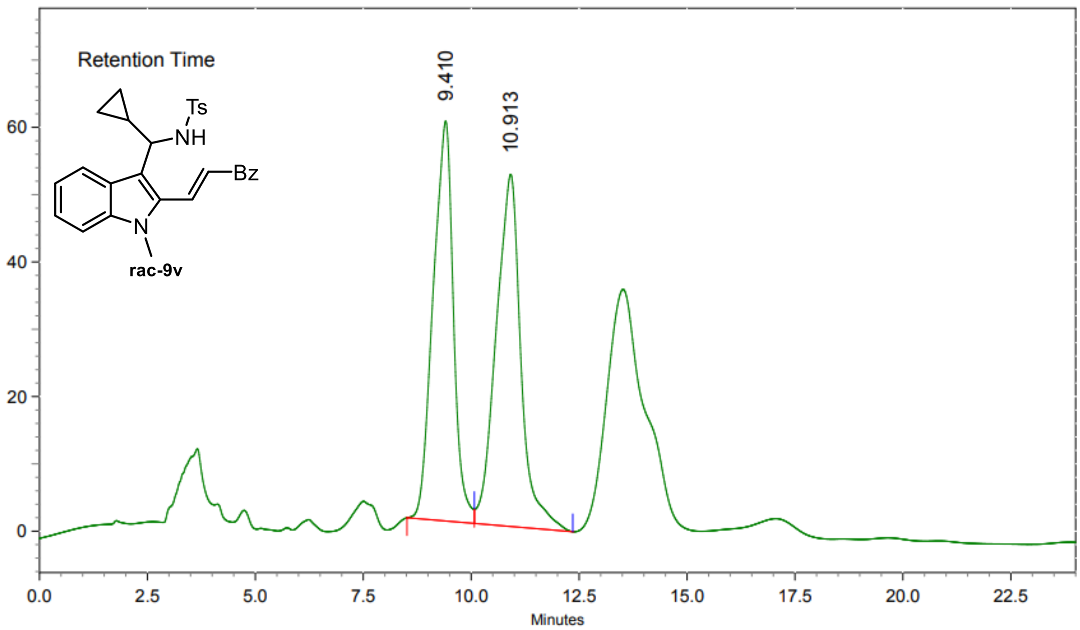
9u

HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{35}H_{28}N_2O_5SNa^+$ 611.1612

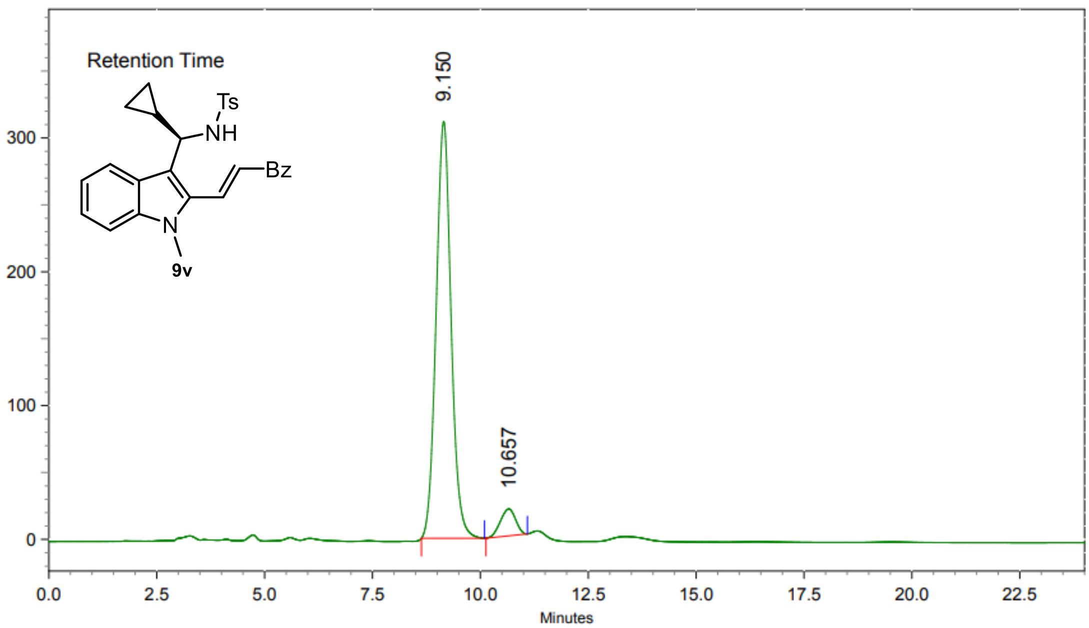

9v, E/Z = 24:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)


9v
13C NMR (150 MHz, CDCl3)
f1 (ppm)



AREA PERCENT REPORT

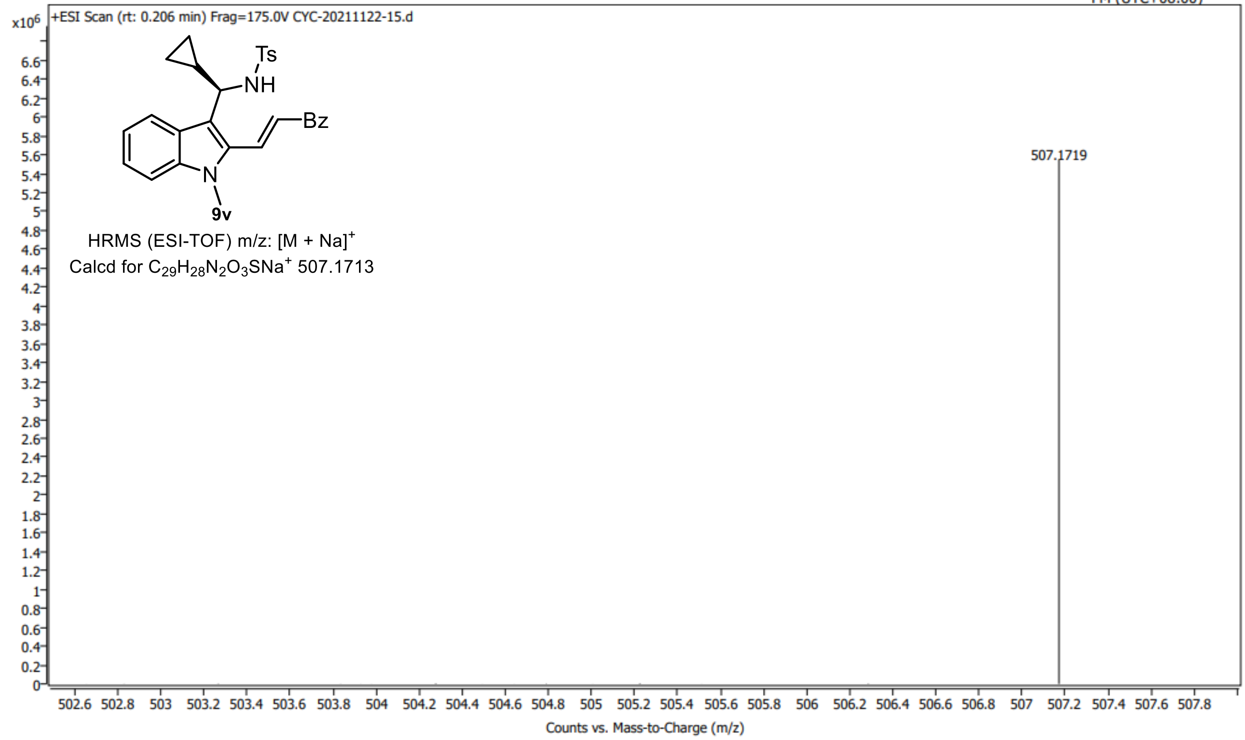
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.410	1.560	996789	32491910	48.1116
2	10.913	2.280	877866	35042593	51.8884

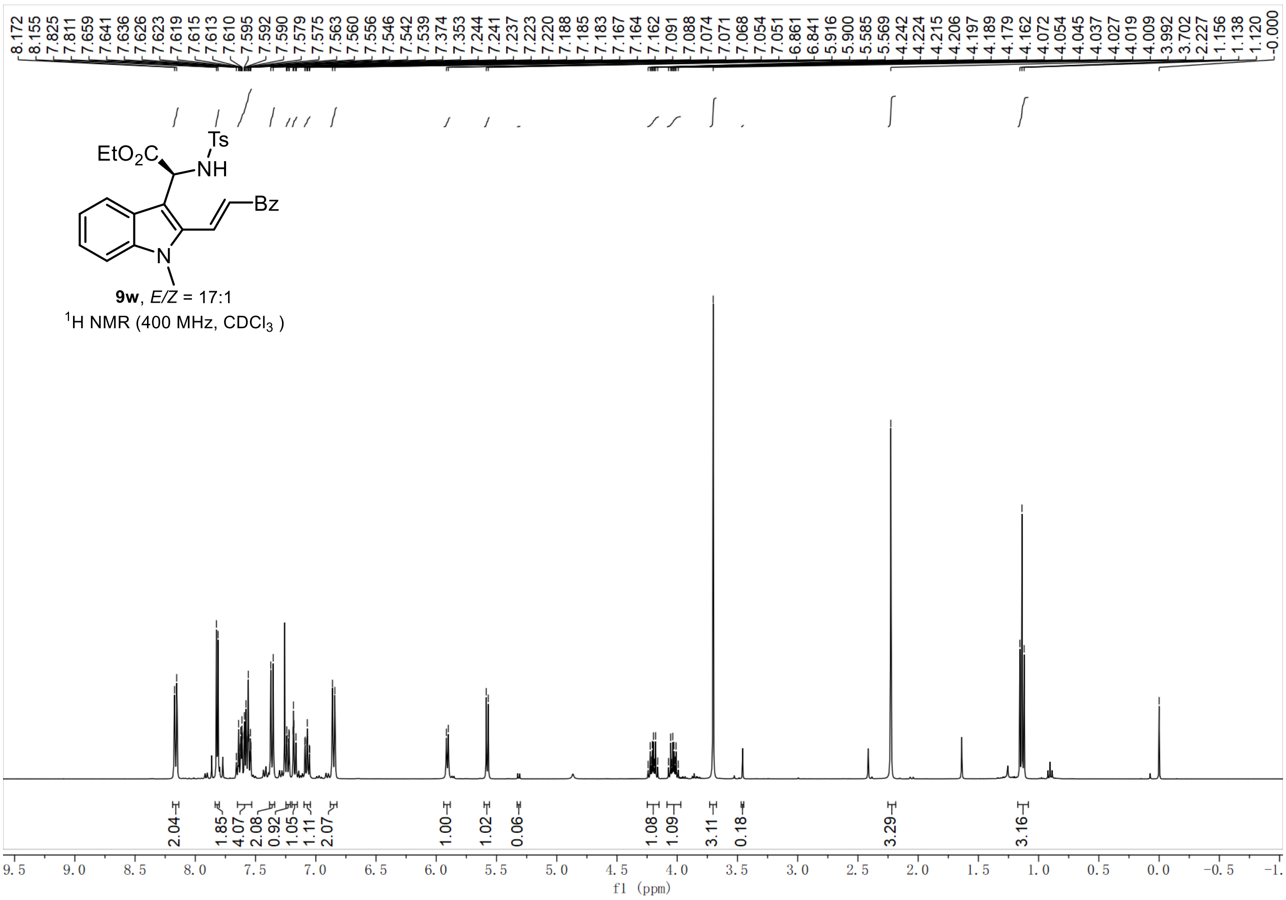


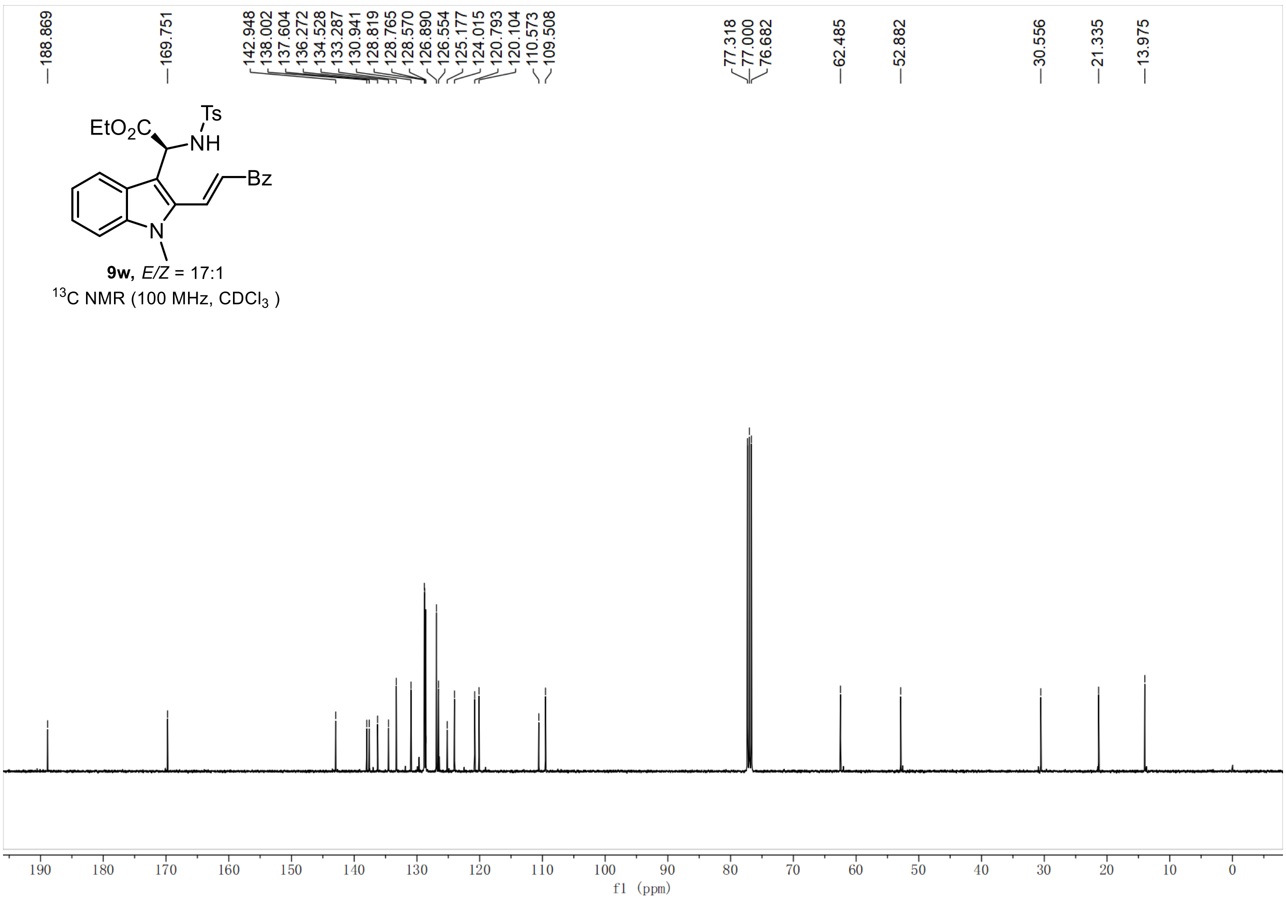
AREA PERCENT REPORT

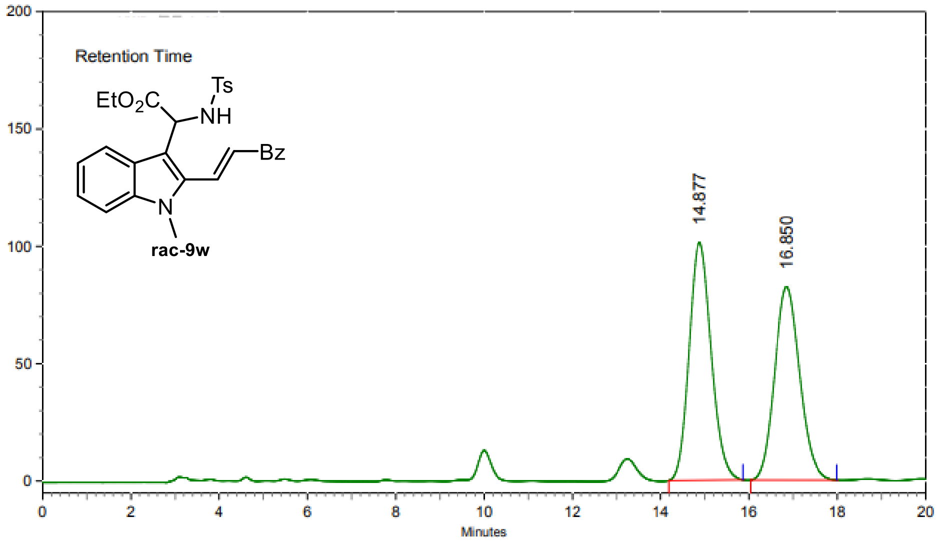
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.150	1.463	5224330	125892065	93.8284
2	10.657	0.960	337253	8280647	6.1716

Name	CYC-20211122-15	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-15.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 5:08:04 PM (UTC+08:00)



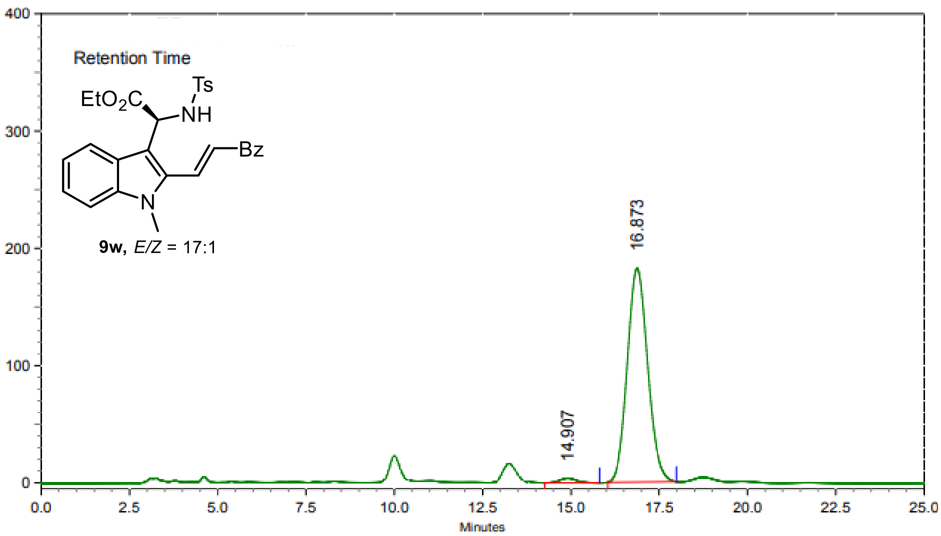

EtO2C
Ts
NH
Bz
N
9w, E/Z = 17:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)


EtO2C
Ts
NH
Bz
N
9w, E/Z = 17:1
13C NMR (100 MHz, CDCl3)
f1 (ppm)



AREA PERCENT REPORT

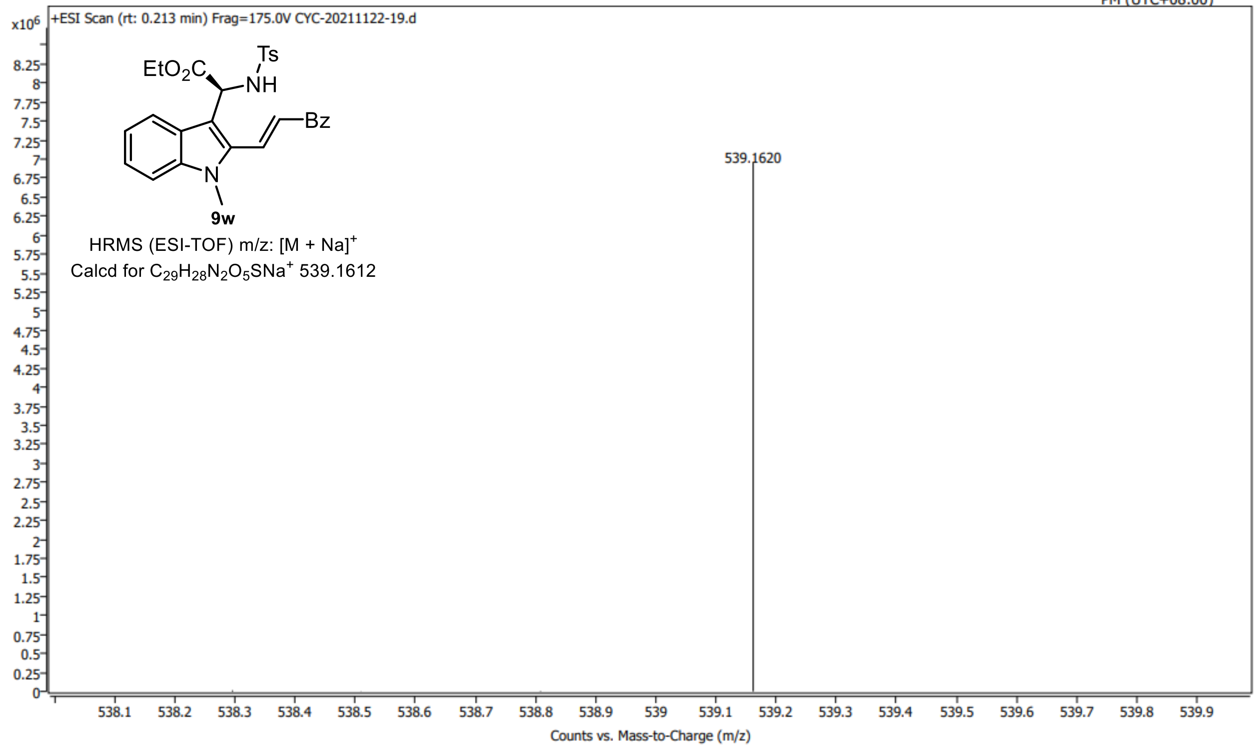
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	14.877	1.680	1699988	59201541	51.9062
2	16.850	1.947	1383275	54853235	48.0938

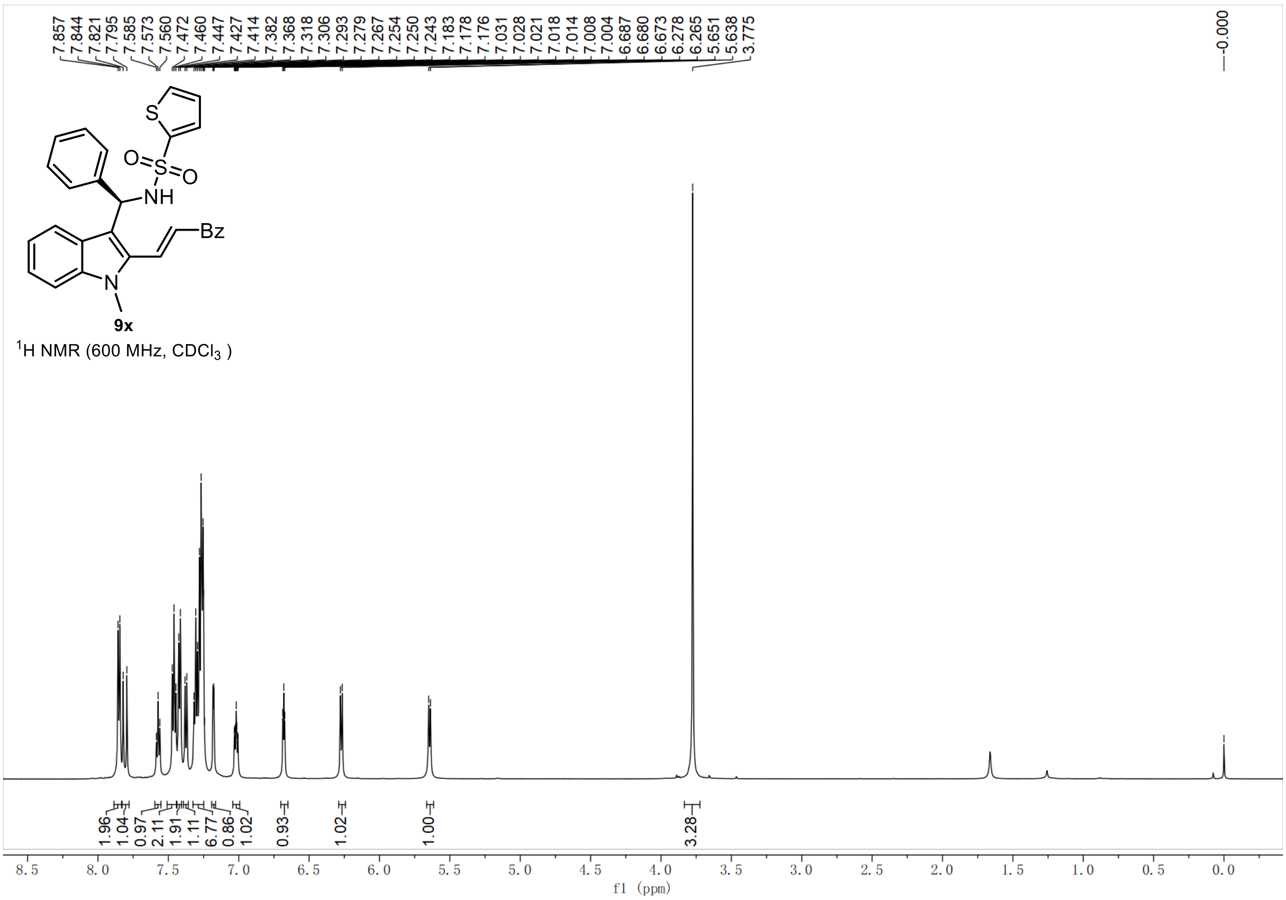


AREA PERCENT REPORT

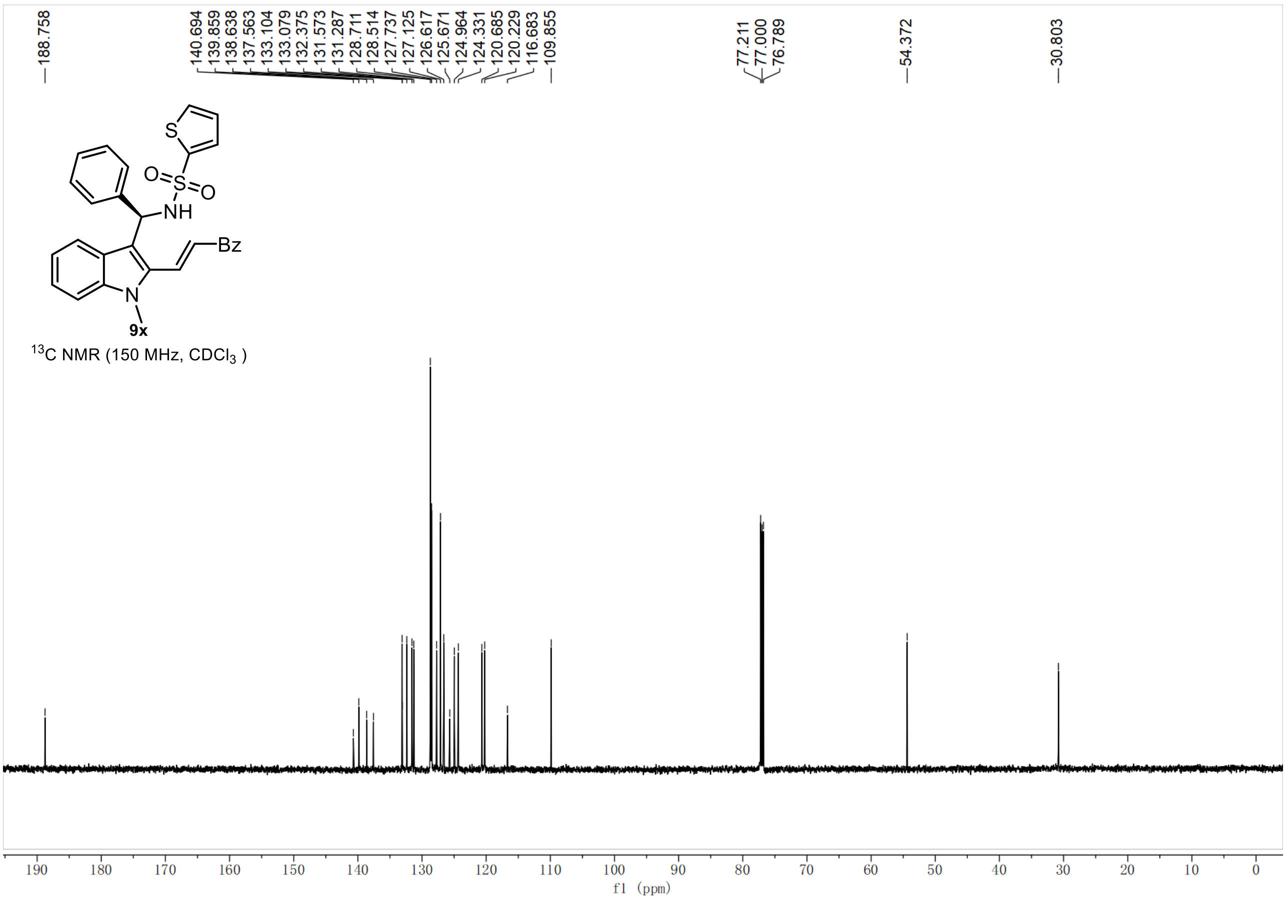
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	14.907	1.550	62750	2128894	1.7129
2	16.873	1.947	3058157	122154159	98.2871

Name	CYC-20211122-19	Rack Pos.		Instrument	Instrument 1	Operator		
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success			
Data File	CYC-20211122-19.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 5:19:53 PM (UTC+08:00)	

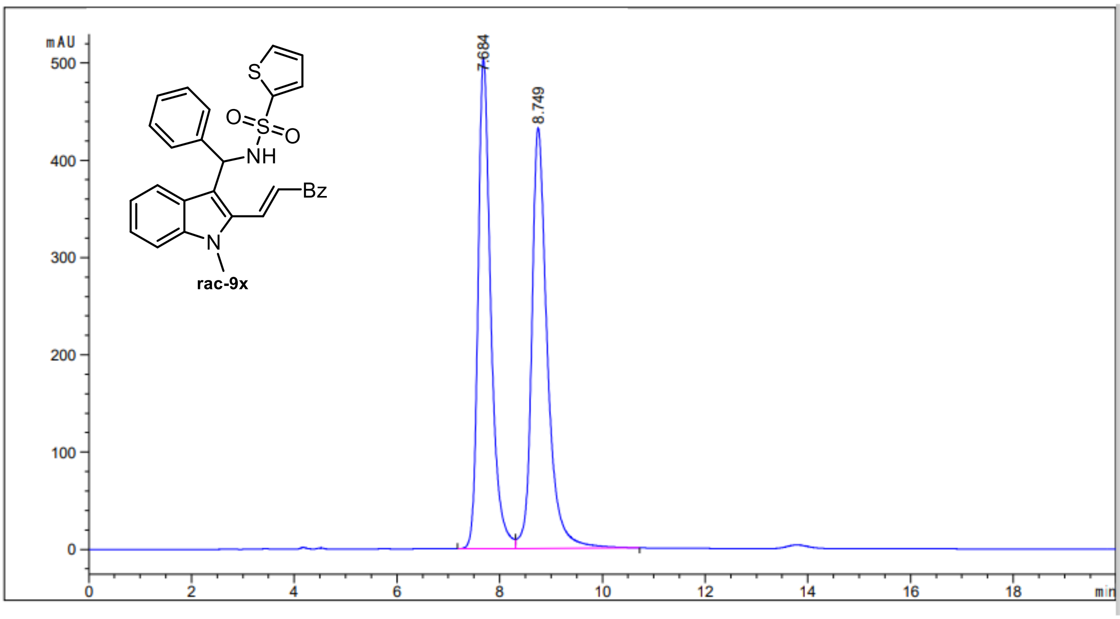




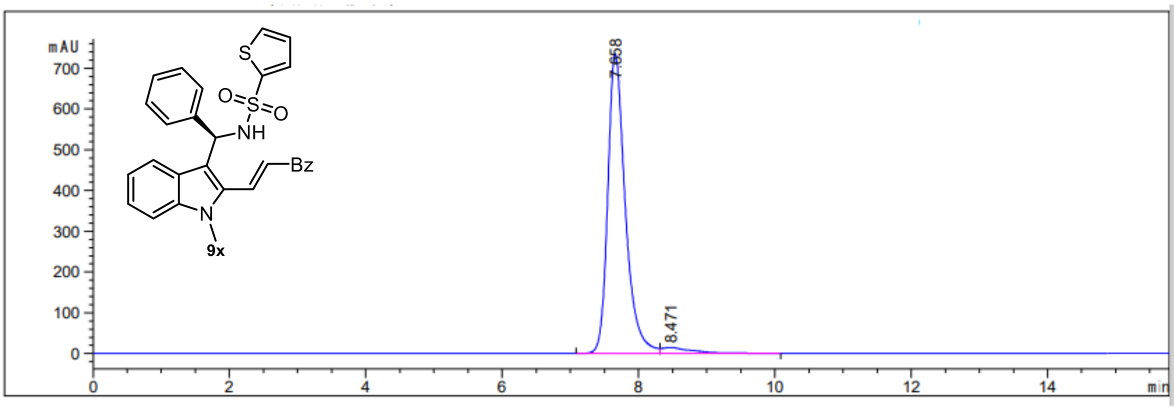
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

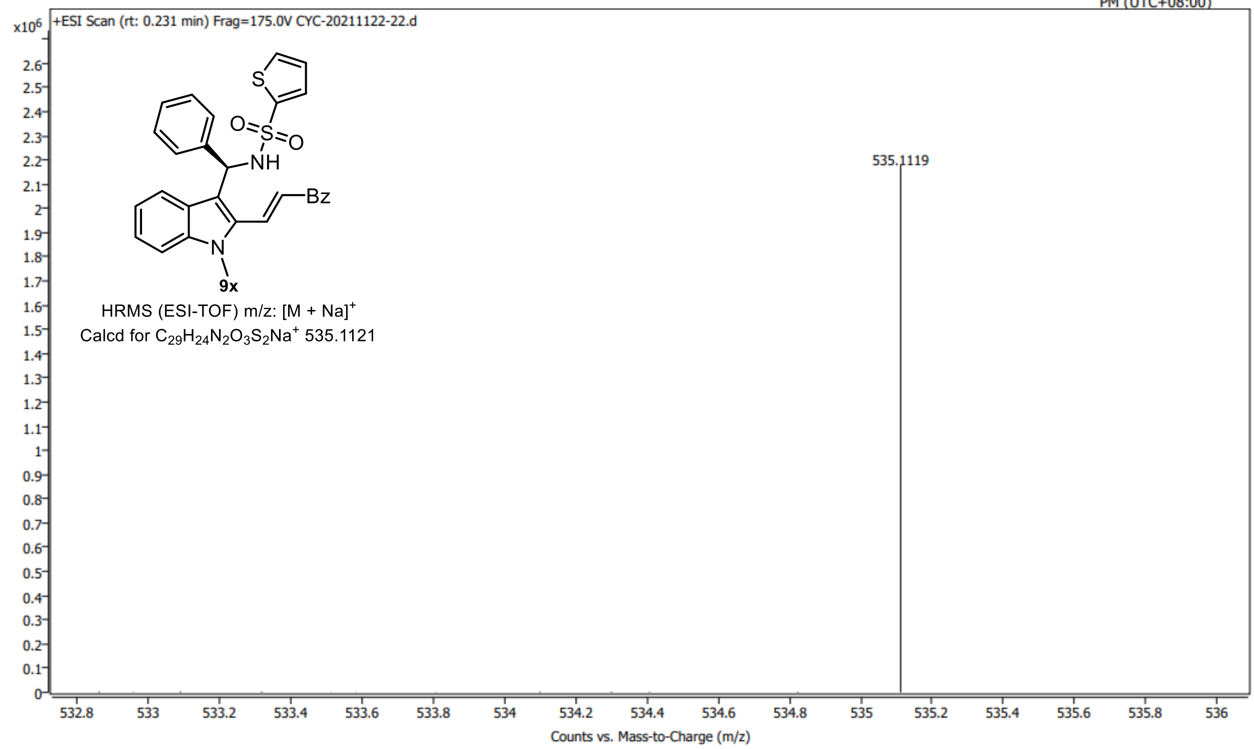


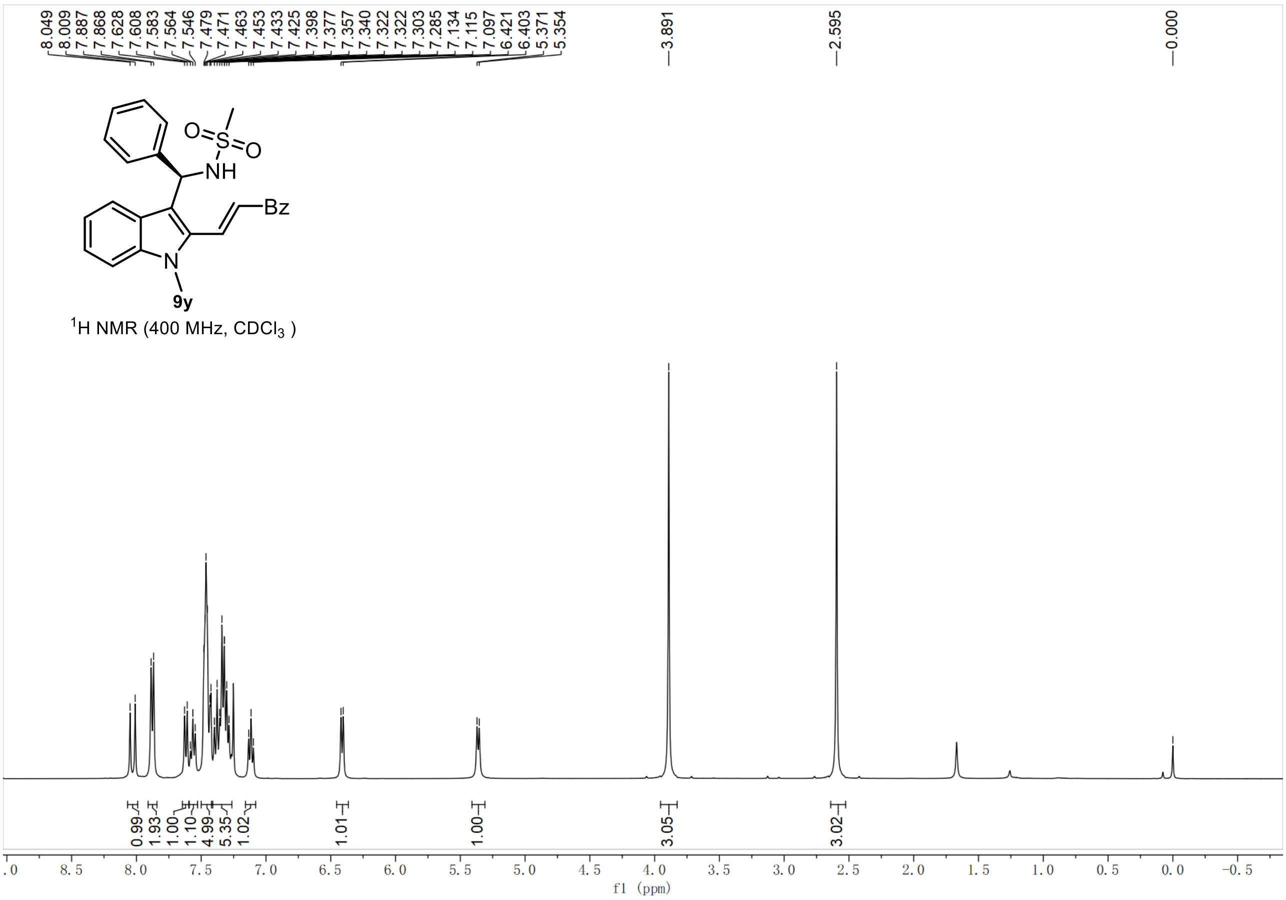
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.684	BV	0.2592	8683.84863	504.04816	48.8358
2	8.749	VBA	0.3141	9097.86035	432.13358	51.1642

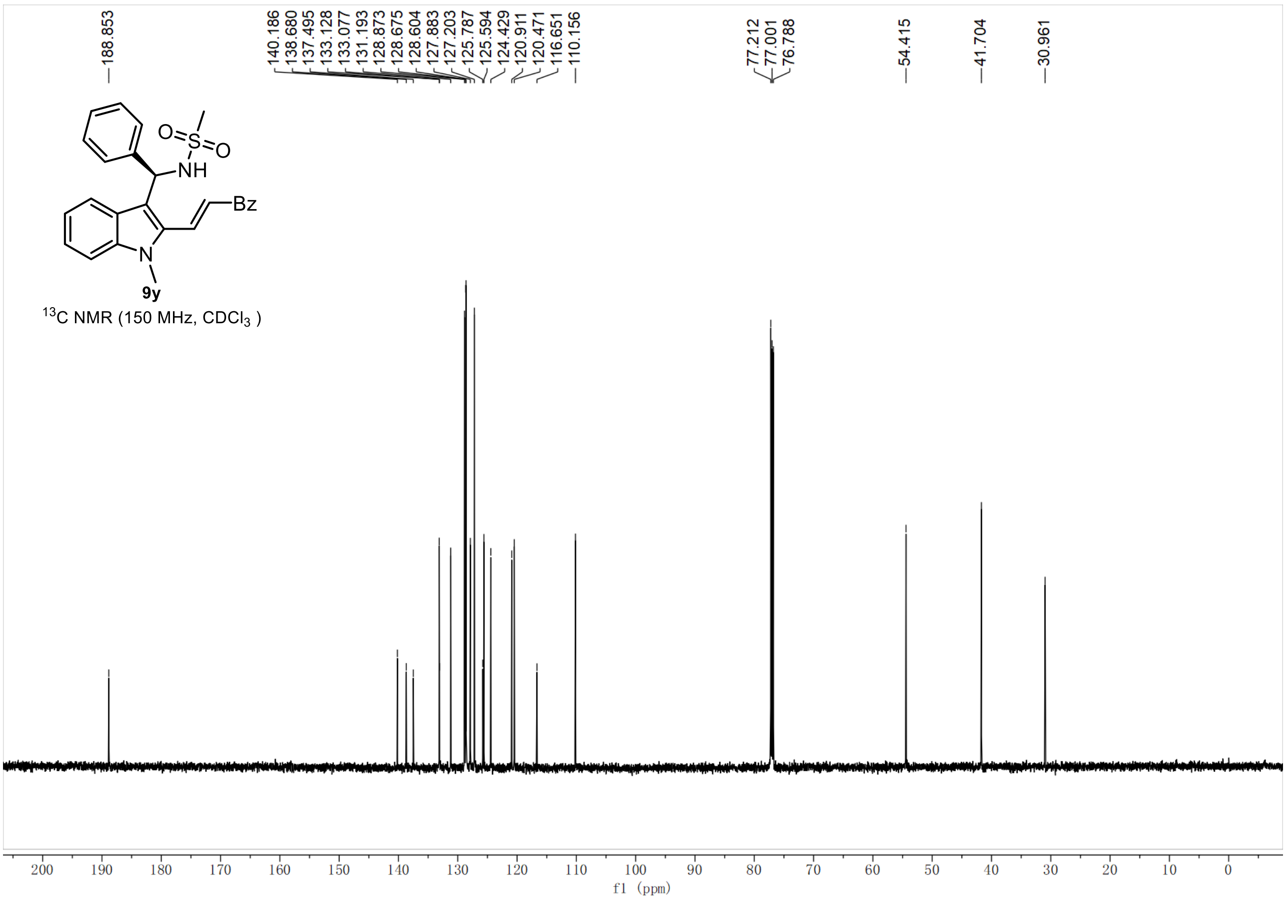


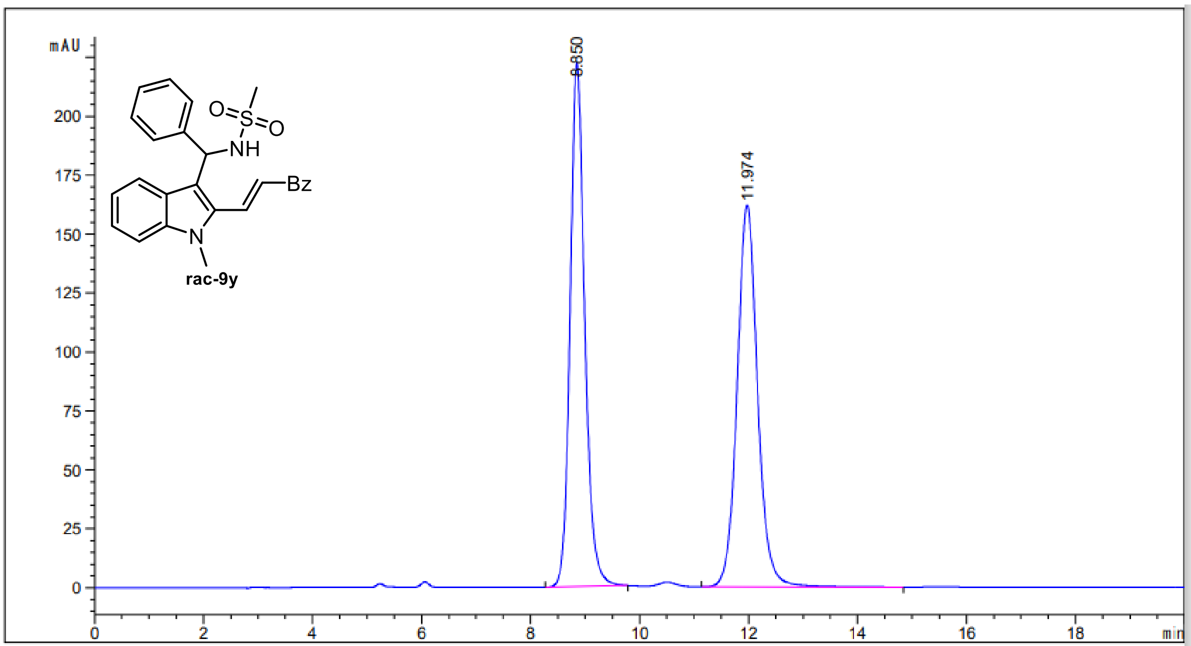
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.658	BV	0.2677	1.31134e4	735.52069	96.7122
2	8.471	VB	0.4113	445.80045	14.67216	3.2878

Name	CYC-20211122-22	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-22.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 5:28:44 PM (UTC+08:00)

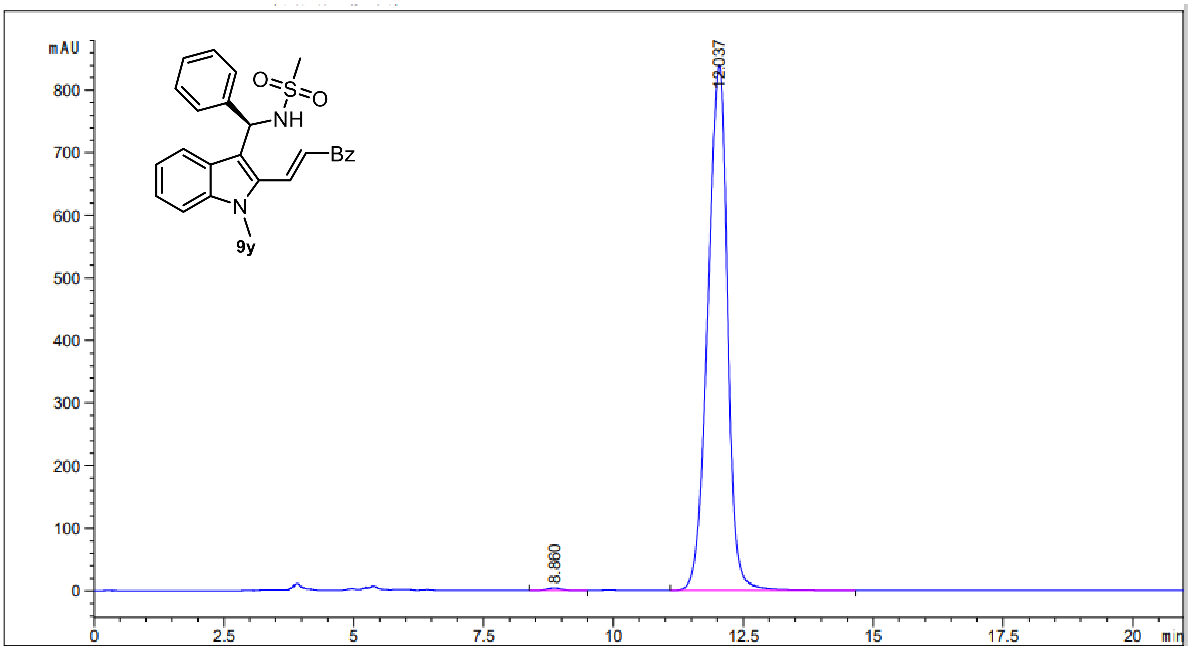



8.049
8.009
7.887
7.868
7.628
7.608
7.583
7.564
7.546
7.479
7.471
7.463
7.453
7.433
7.425
7.398
7.377
7.357
7.340
7.322
7.303
7.285
7.134
7.115
7.097
6.421
6.403
5.371
5.354
3.891
2.595
0.000
NH
Bz
N
9y
^{1}H NMR (400 MHz, $CDCl_3$)
0.99
1.93
1.00
1.10
4.99
5.35
1.02
1.01
1.00
3.05
3.02
f1 (ppm)


188.853
140.186
138.680
137.495
133.128
133.077
131.193
128.873
128.675
128.604
127.883
127.203
125.787
125.594
124.429
120.911
120.471
116.651
110.156
77.212
77.001
76.788
54.415
41.704
30.961
NH
Bz
N
9y
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)

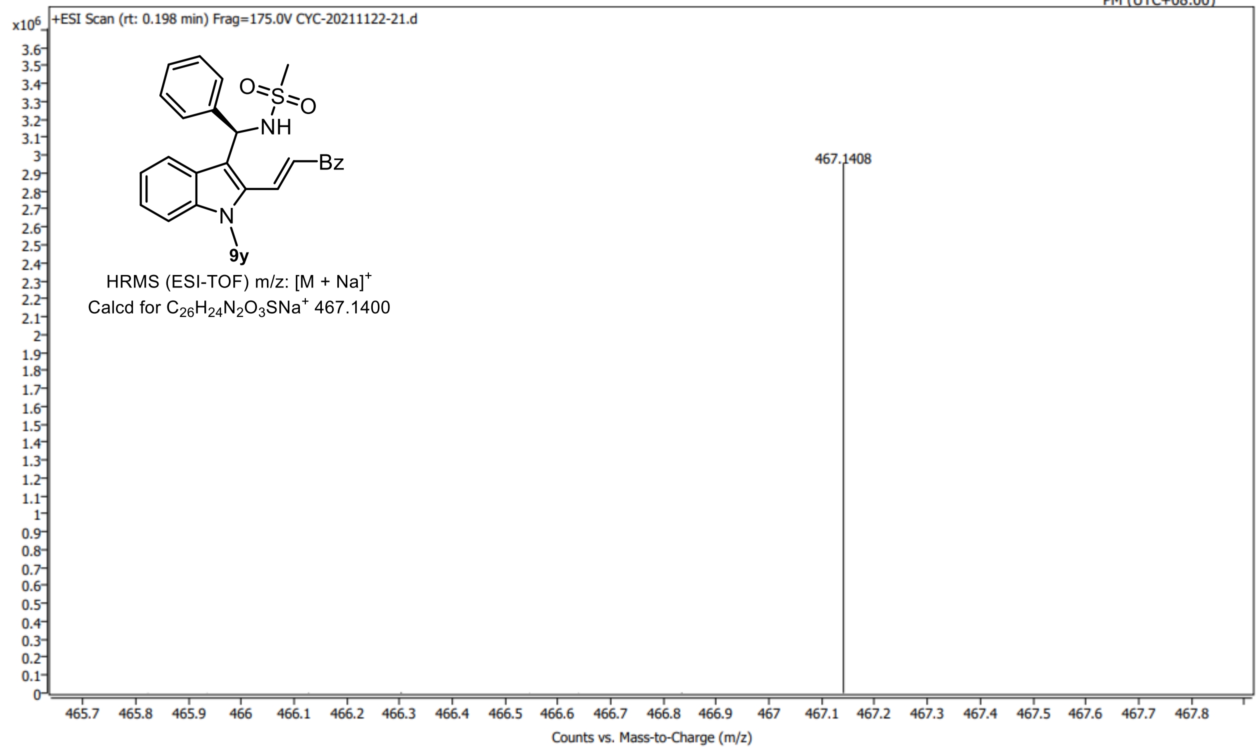


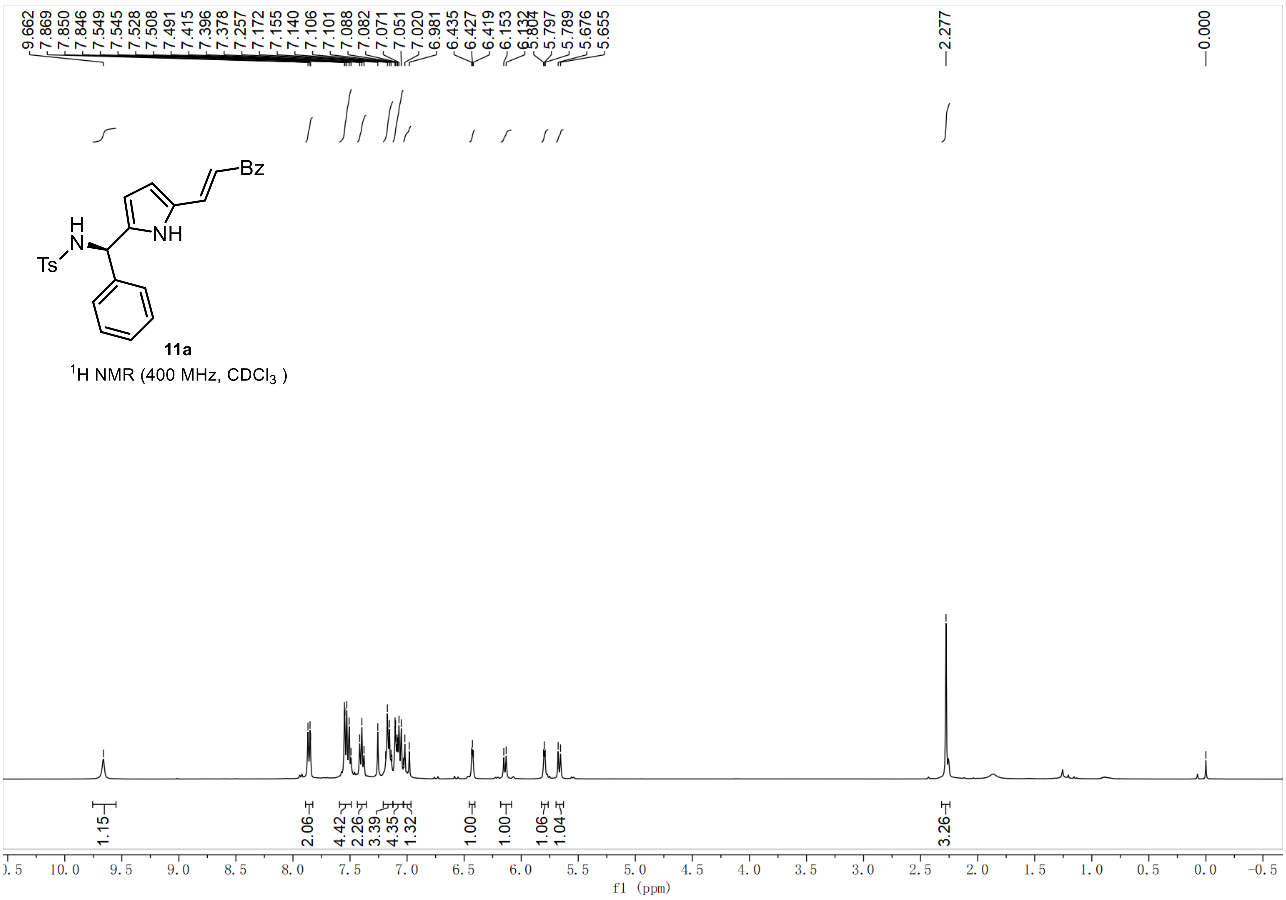
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.850	BBA	0.2829	4140.24658	222.21770	49.4794
2	11.974	BB	0.3979	4227.36621	161.87129	50.5206



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.860	BB	0.2910	83.94486	4.37178	0.3756
2	12.037	BB	0.4114	2.22635e4	839.33252	99.6244

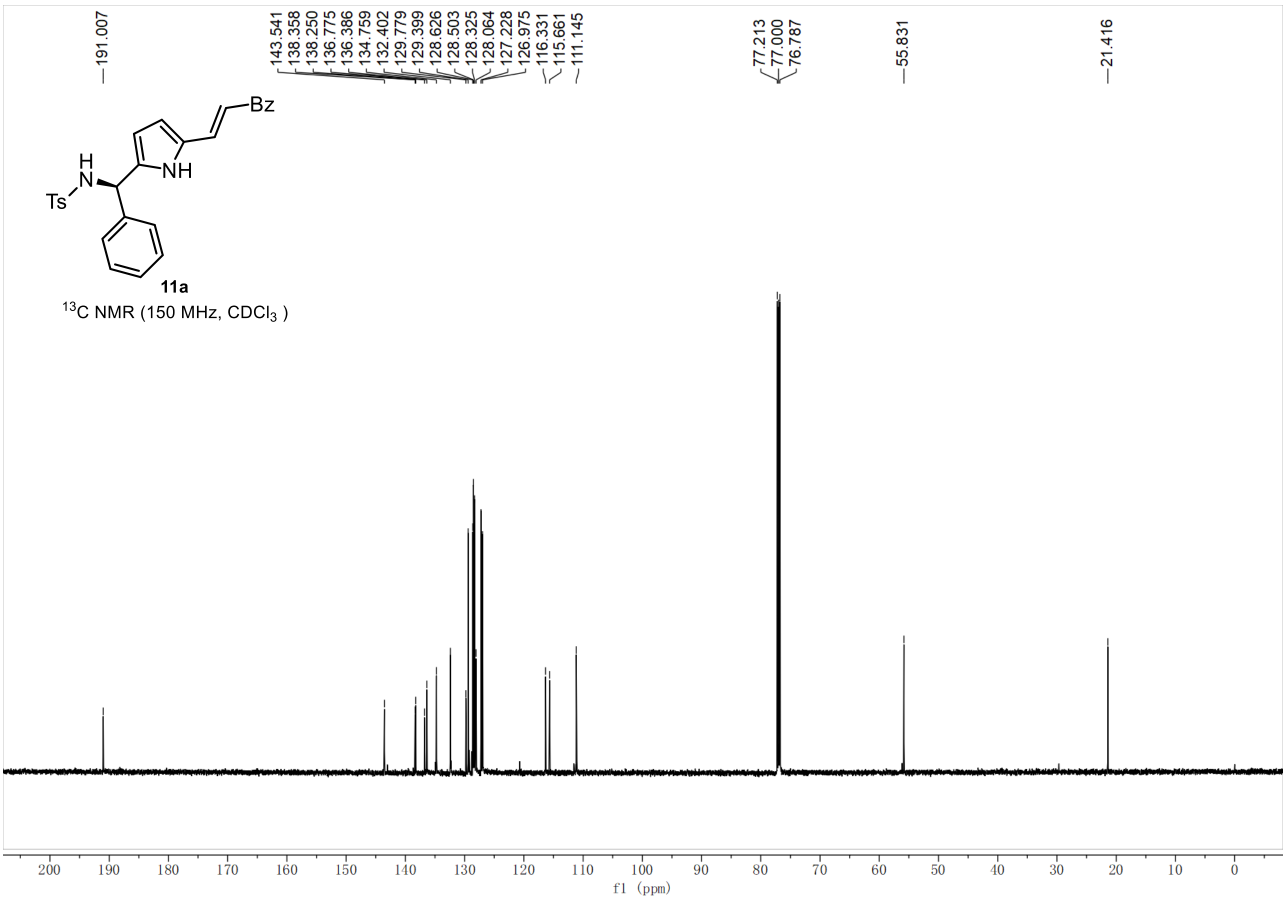
Name	CYC-20211122-21	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211122-21.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	11/25/2021 5:25:47 PM (UTC+08:00)





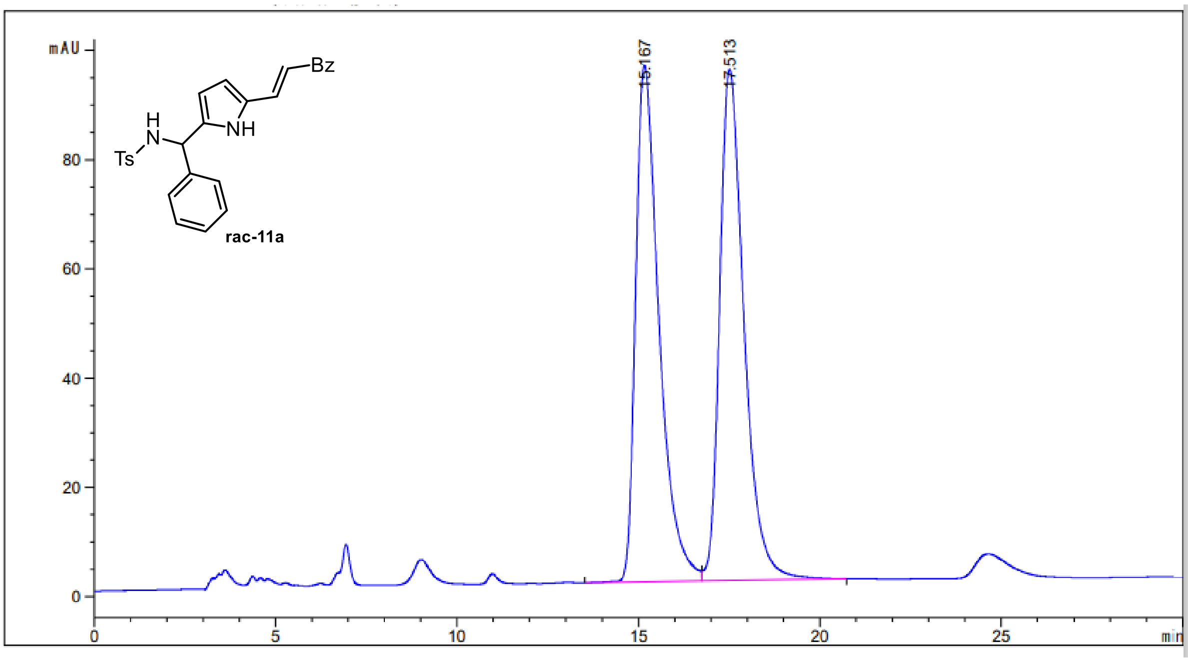
11a

^{1}H NMR (400 MHz, $CDCl_3$)

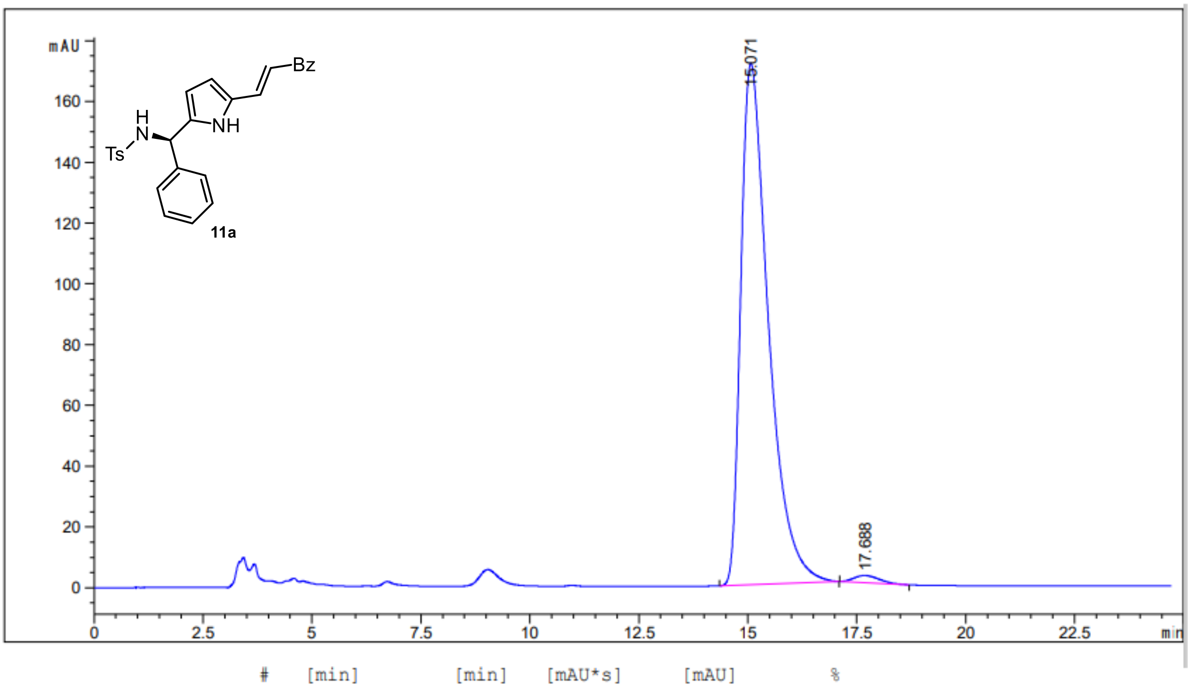


11a

^{13}C NMR (150 MHz, $CDCl_3$)

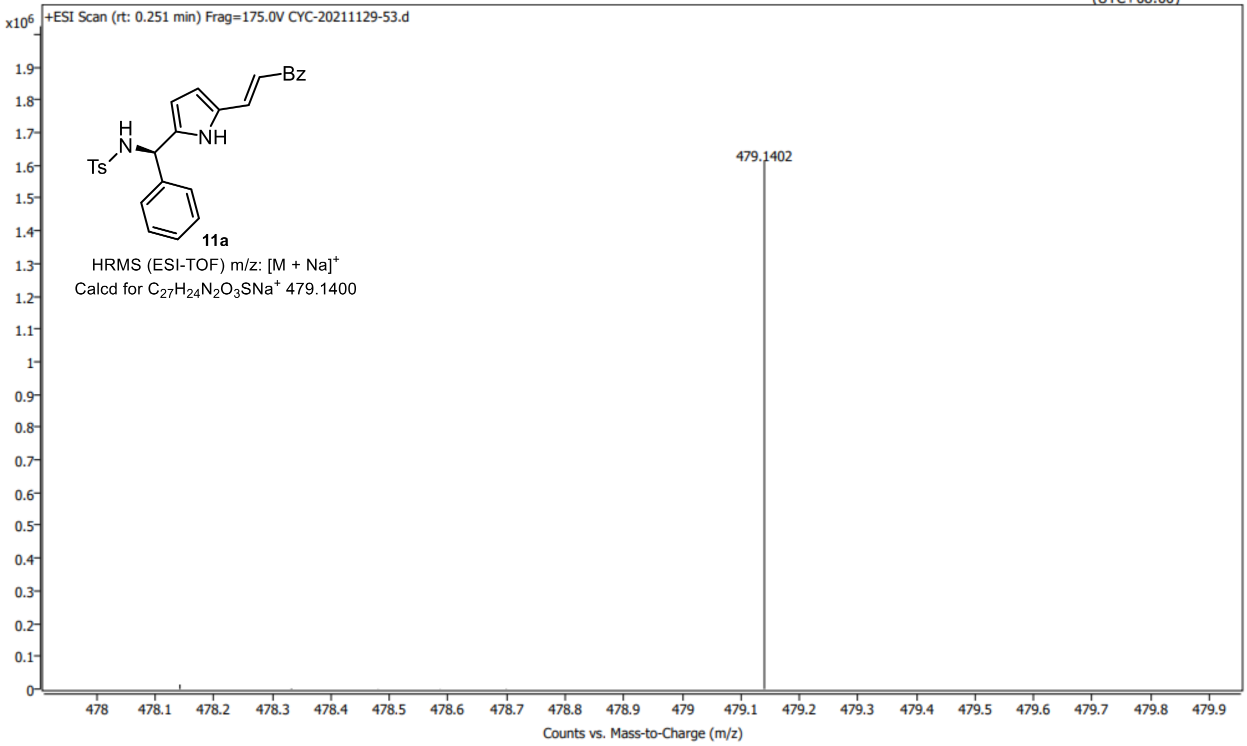


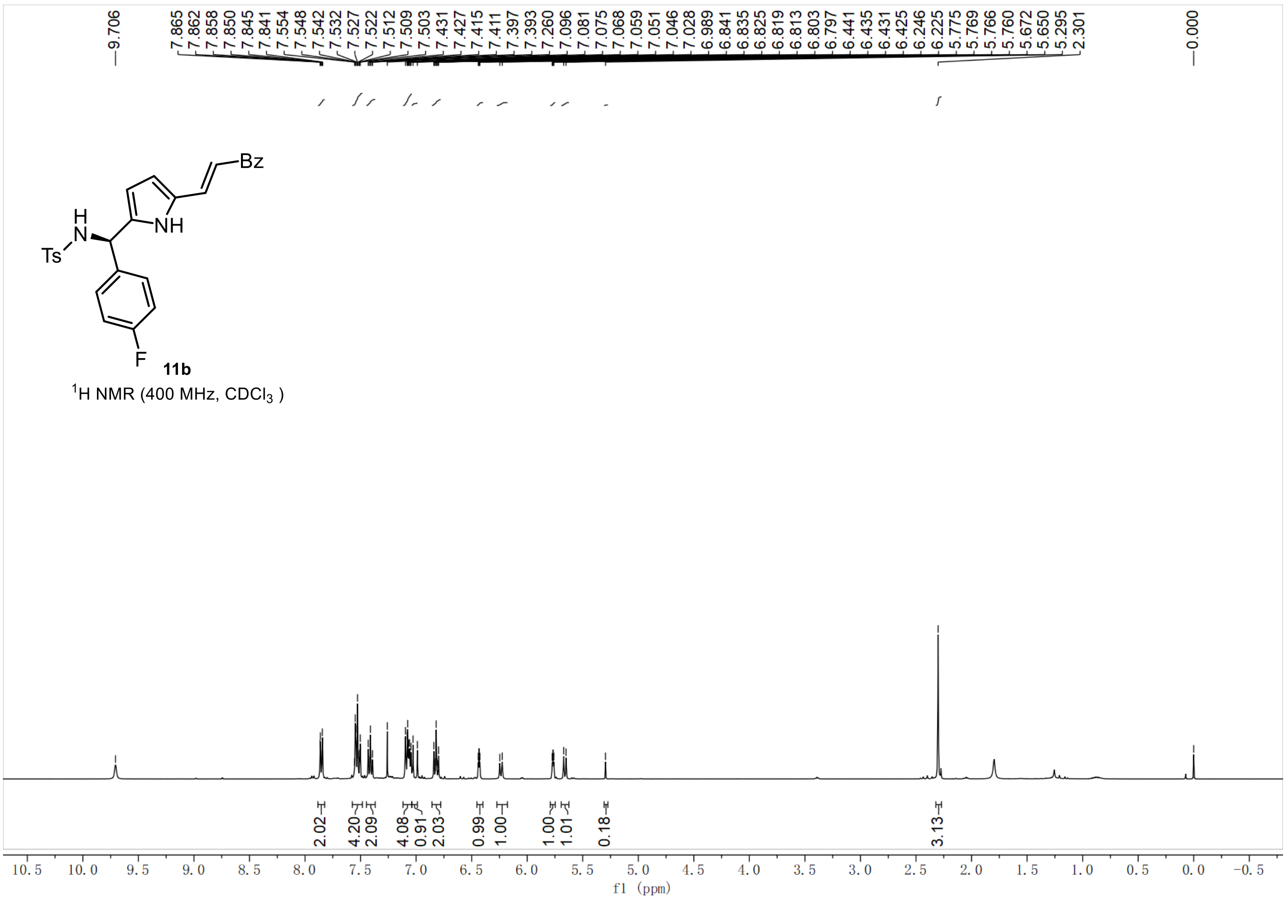
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.167	BV	0.6820	4254.12012	94.57399	49.2873
2	17.513	VB	0.7111	4377.14258	93.67582	50.7127

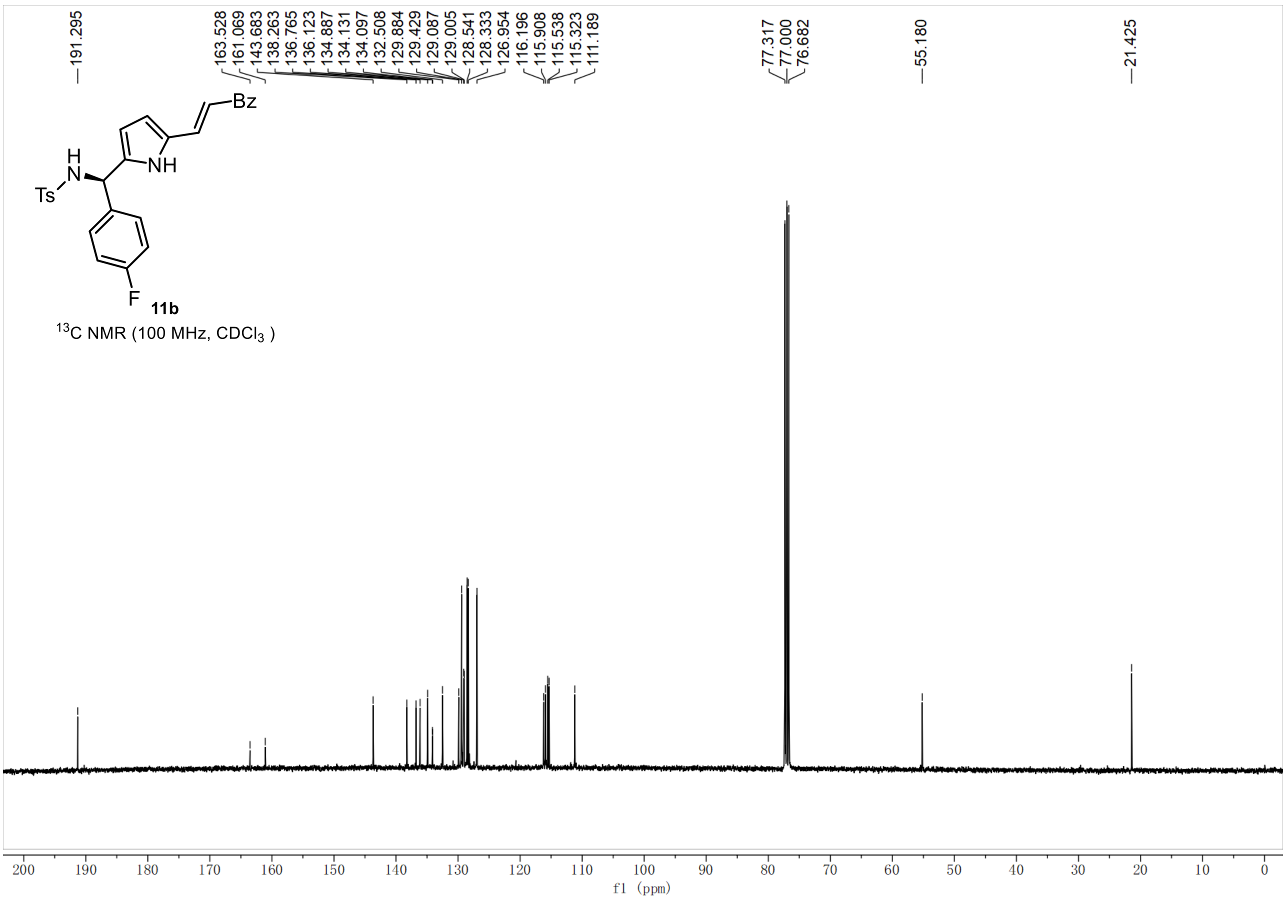


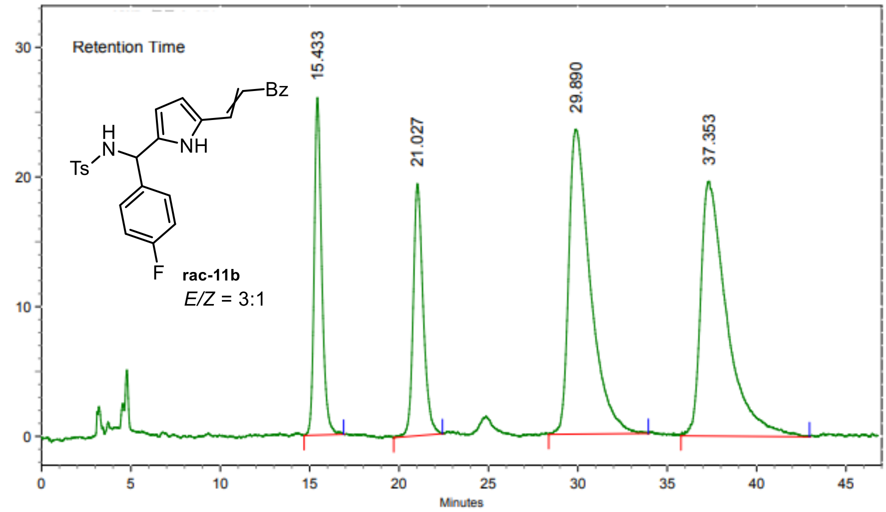
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.071	BB	0.6659	7563.99414	171.51733	98.7498
2	17.688	BB	0.5725	95.76326	2.37399	1.2502

Name	CYC-20211129-53	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-53.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:15:53 PM (UTC+08:00)



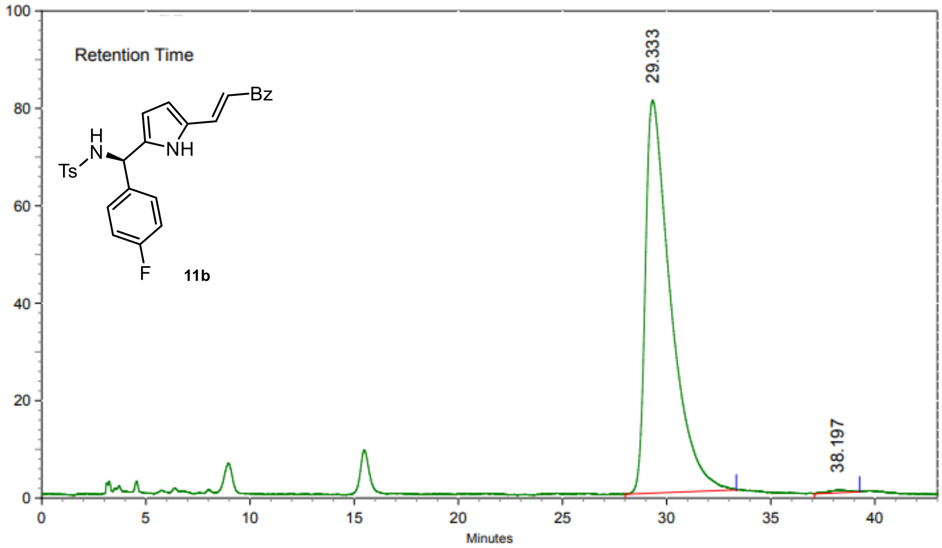

9.706
7.865 7.862 7.858 7.850 7.845 7.841 7.554 7.548 7.542 7.532 7.527 7.522 7.512 7.509 7.503 7.431 7.427 7.415 7.411 7.397 7.393 7.260 7.096 7.081 7.075 7.068 7.059 7.051 7.046 7.028 6.989 6.841 6.835 6.825 6.819 6.813 6.803 6.797 6.441 6.435 6.431 6.425 6.246 6.225 5.775 5.769 5.766 5.760 5.672 5.650 5.295 2.301
0.000
Bz
H
N
NH
Ts
F
11b
1H NMR (400 MHz, CDCl3)
2.02 4.20 2.09 4.08 0.91 2.03 0.99 1.00 1.00 1.01 0.18 3.13
f1 (ppm)


191.295
163.528 161.069 143.683 138.263 136.765 136.123 134.887 134.131 134.097 132.508 129.884 129.429 129.087 129.005 128.541 128.333 126.954 116.196 115.908 115.538 115.323 111.189
77.317 77.000 76.682
55.180
21.425
Bz
H
N
NH
Ts
F
11b
13C NMR (100 MHz, CDCl3)
f1 (ppm)



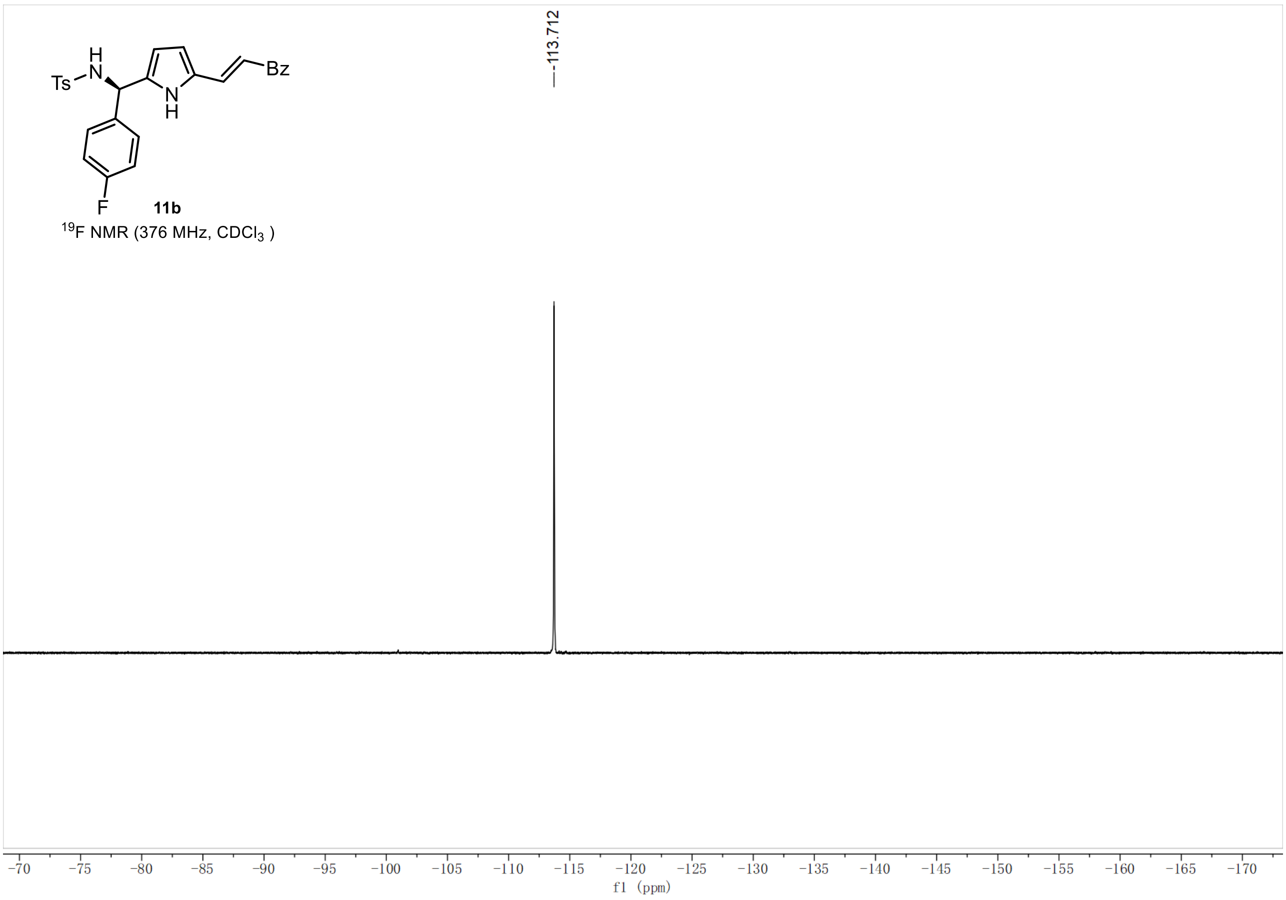
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	15.433	2.210	436644	12770825	13.8708
2	21.027	2.723	326034	12600103	13.6854
3	29.890	5.573	394524	33193753	36.0527
4	37.353	7.190	329626	33505312	36.3911

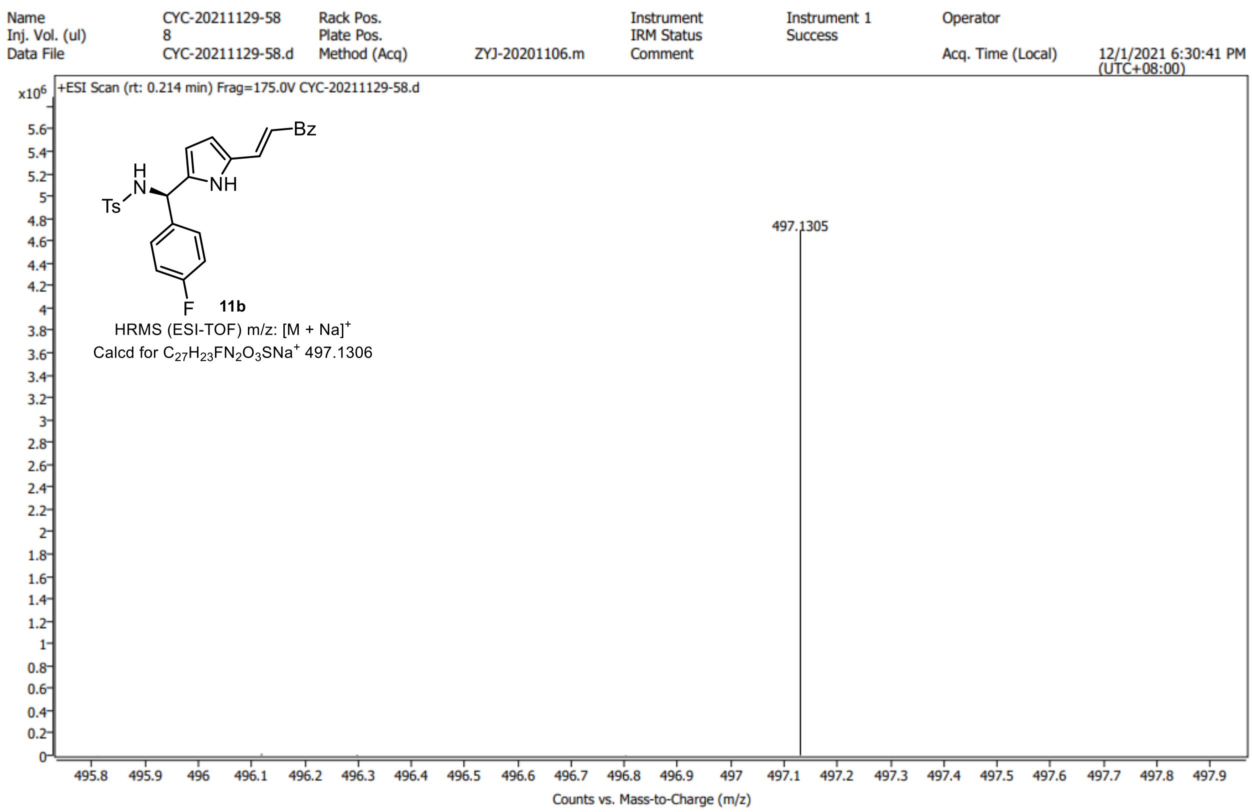


AREA PERCENT REPORT

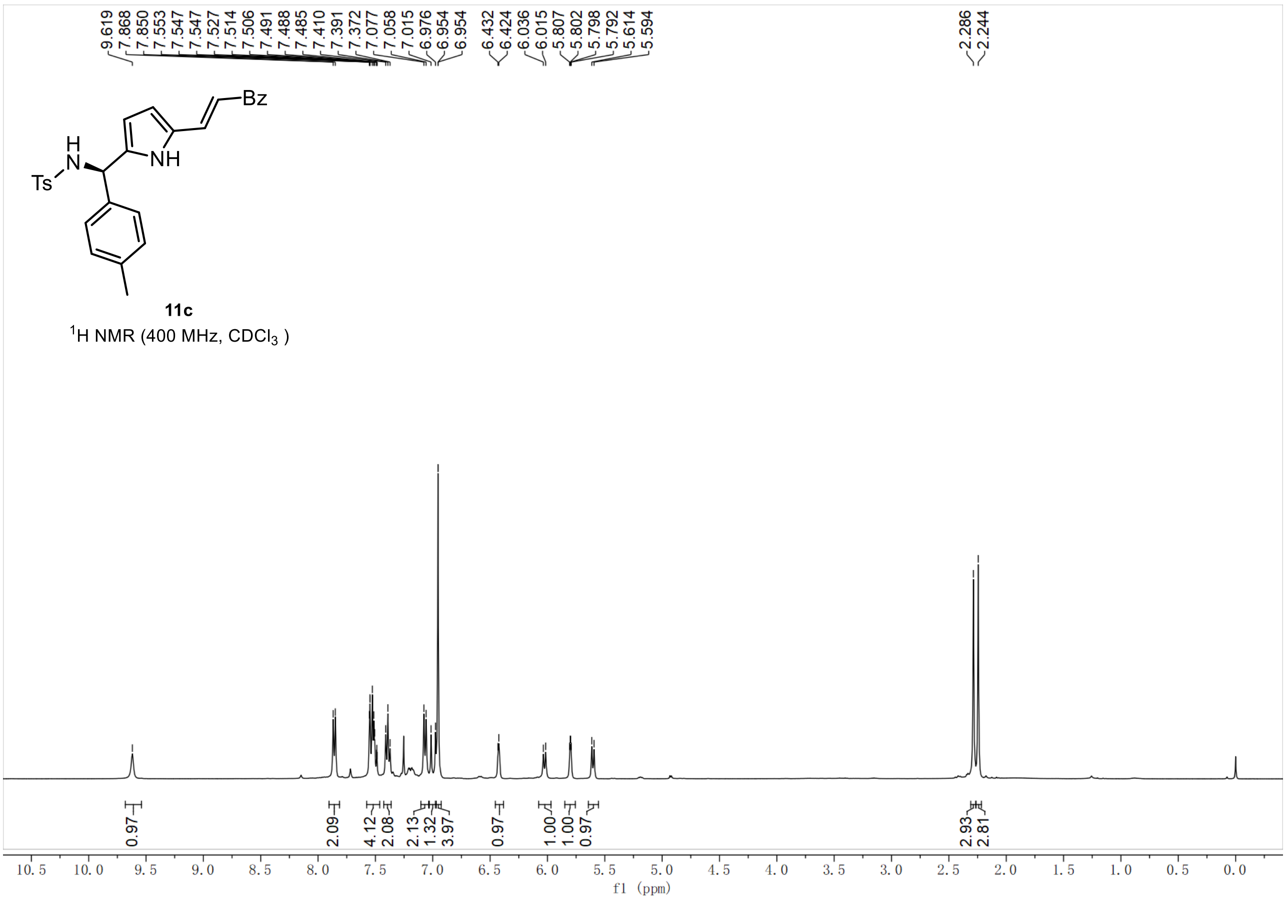
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	29.333	5.333	1352577	114406982	99.4295
2	38.197	2.163	10474	656434	0.5705

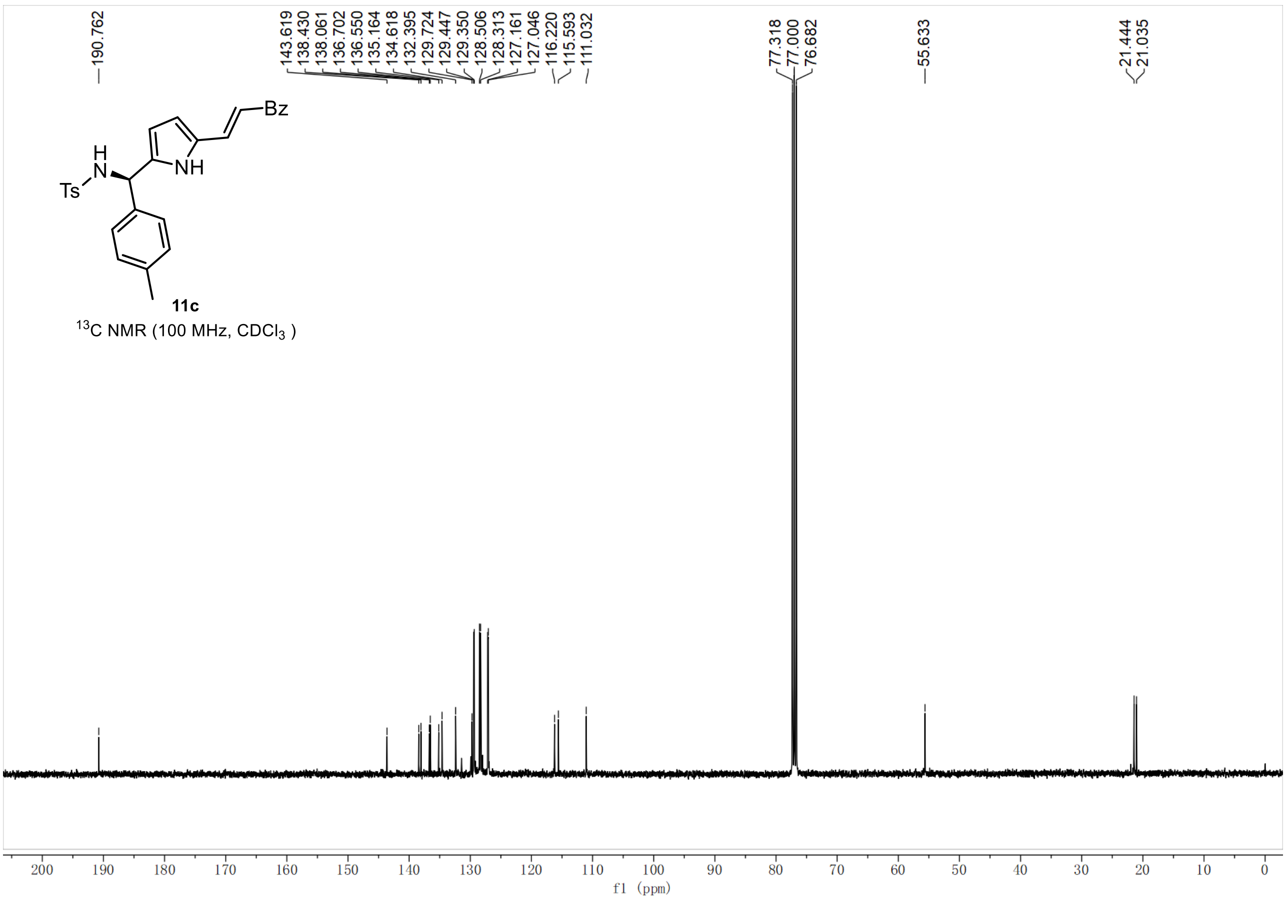


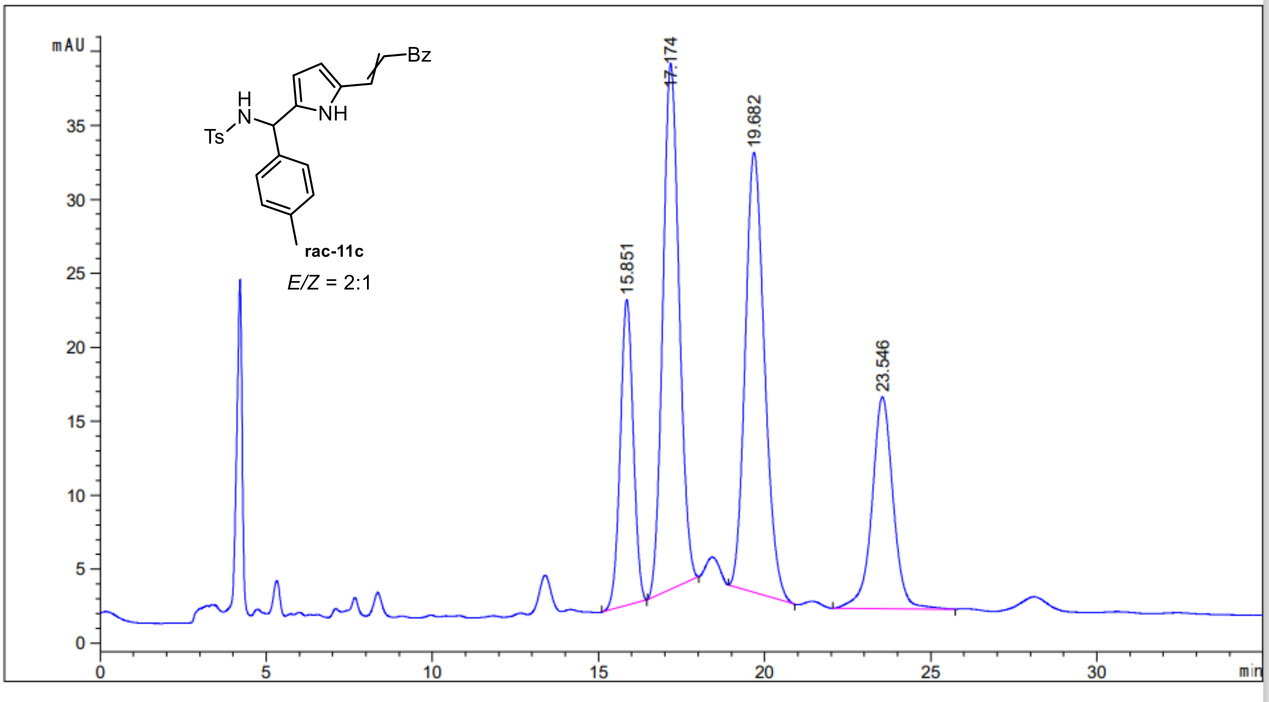
Ts
N
H
NH
Bz
F
11b
^{19}F NMR (376 MHz, $CDCl_3$)
-113.712
−70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170
f1 (ppm)



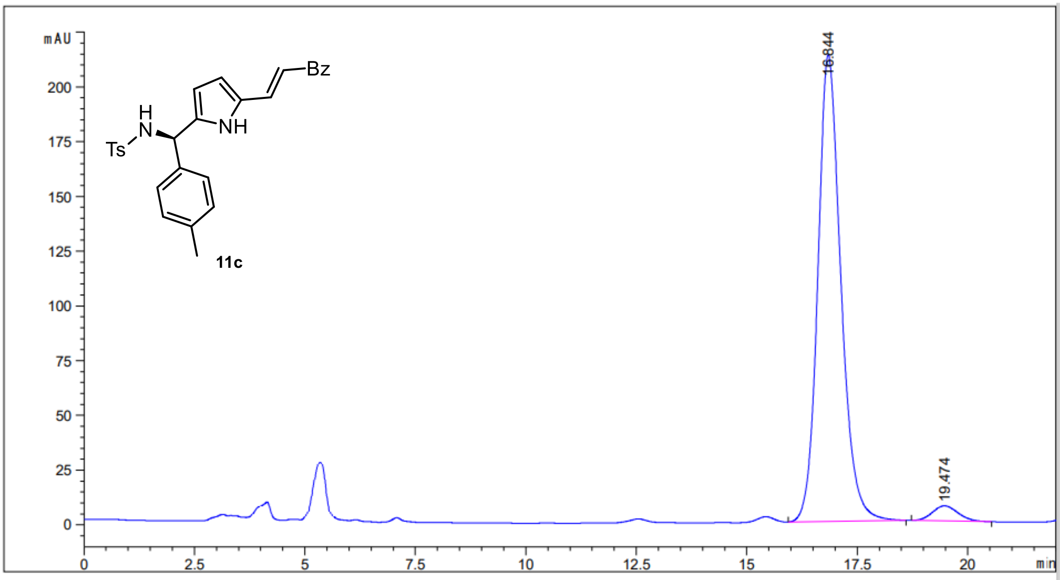
Name CYC-20211129-58
Inj. Vol. (ul) 8
Data File CYC-20211129-58.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument Instrument 1
IRM Status Success
Comment
Operator
Acq. Time (Local) 12/1/2021 6:30:41 PM (UTC+08:00)
+ESI Scan (rt: 0.214 min) Frag=175.0V CYC-20211129-58.d
x10^6
11b
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for $C_{27}H_{23}FN_2O_3SNa^+$ 497.1306
497.1305
Counts vs. Mass-to-Charge (m/z)


9.619
7.868
7.850
7.553
7.547
7.527
7.514
7.506
7.491
7.488
7.485
7.410
7.391
7.372
7.077
7.058
7.015
6.976
6.954
6.954
6.432
6.424
6.036
6.015
5.807
5.802
5.798
5.792
5.614
5.594
2.286
2.244
Bz
H
N
Ts
NH
11c
1H NMR (400 MHz, CDCl3)
0.97
2.09
4.12
2.08
2.13
1.32
3.97
0.97
1.00
1.00
0.97
2.93
2.81
f1 (ppm)


190.762
143.619
138.430
138.061
136.702
136.550
135.164
134.618
132.395
129.724
129.447
129.350
128.506
128.313
127.161
127.046
116.220
115.593
111.032
77.318
77.000
76.682
55.633
21.444
21.035
Bz
H
N
Ts
NH
11c
13C NMR (100 MHz, CDCl3)
f1 (ppm)

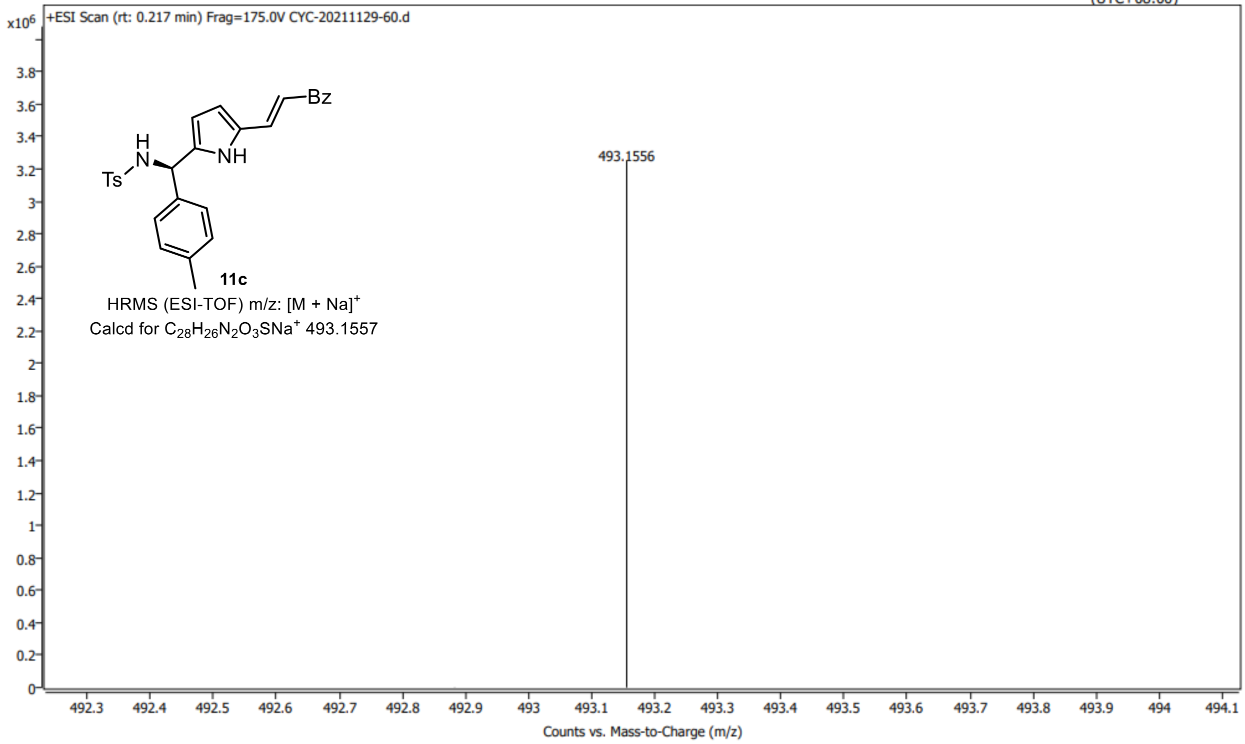


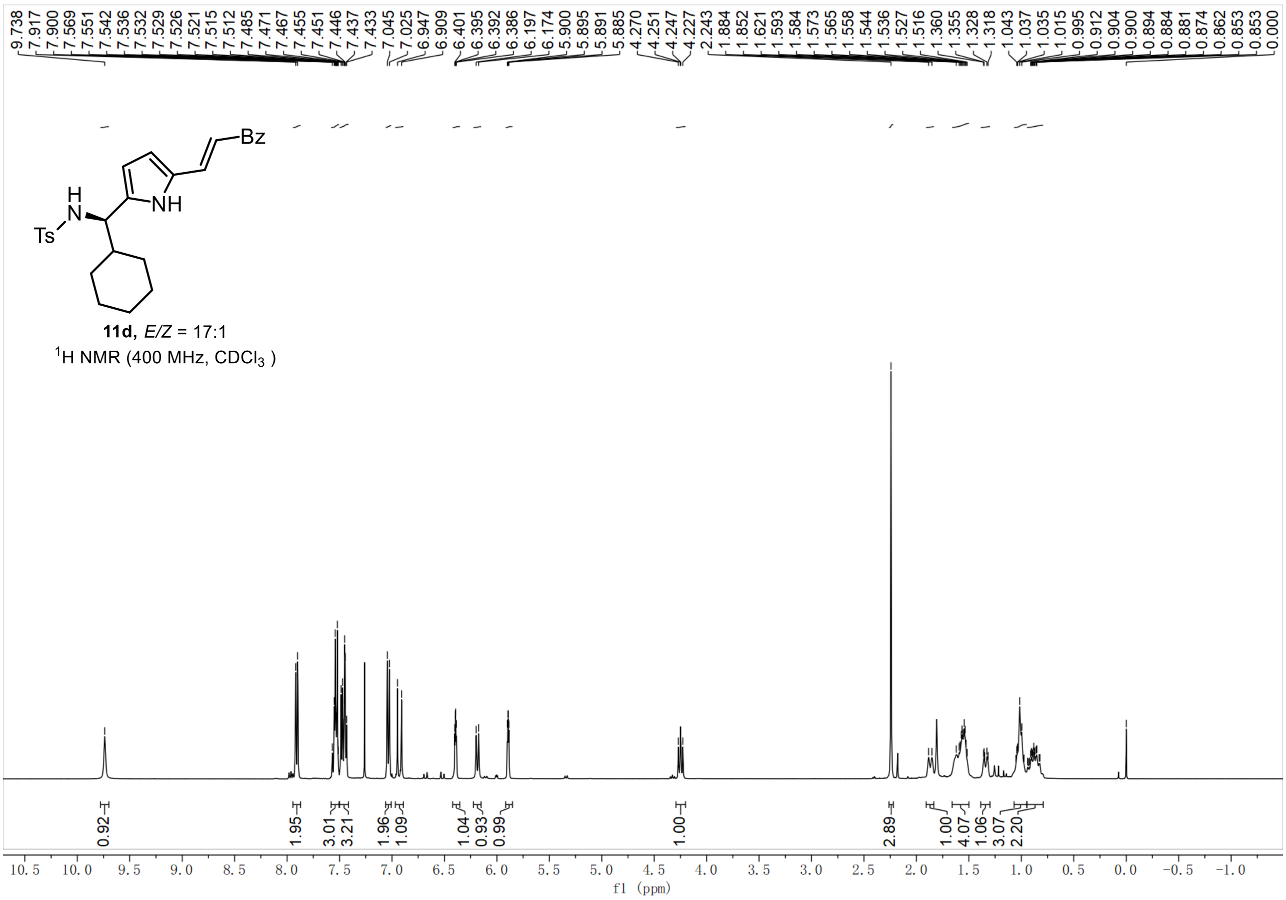
#	[min]		[min]	[mAU*s]	[mAU]	%
1	15.851	BB	0.4177	562.23639	20.67464	15.5810
2	17.174	BBA	0.5294	1213.41089	35.53400	33.6268
3	19.682	BB	0.6158	1199.03784	29.75334	33.2285
4	23.546	BB	0.6689	633.77832	14.32913	17.5637

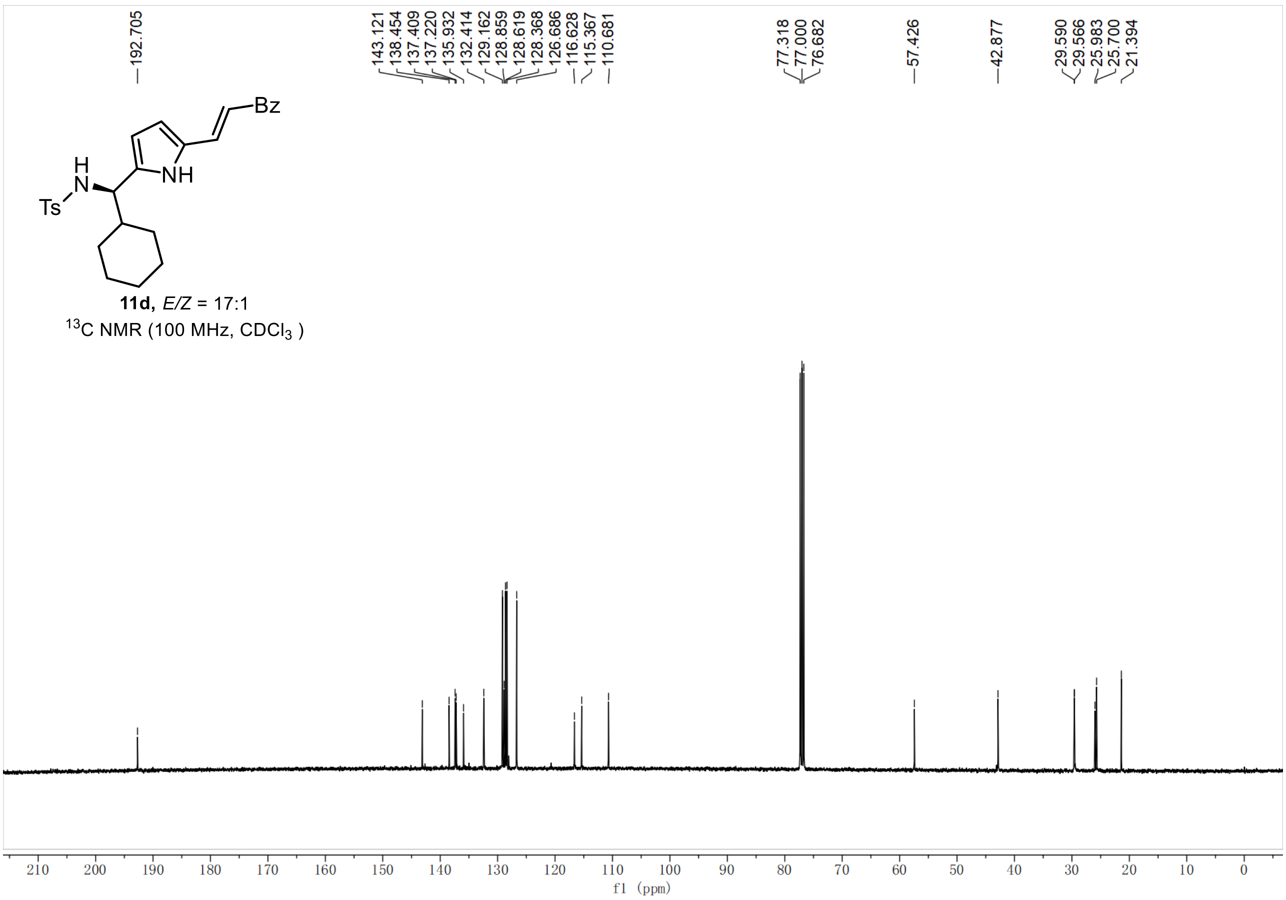


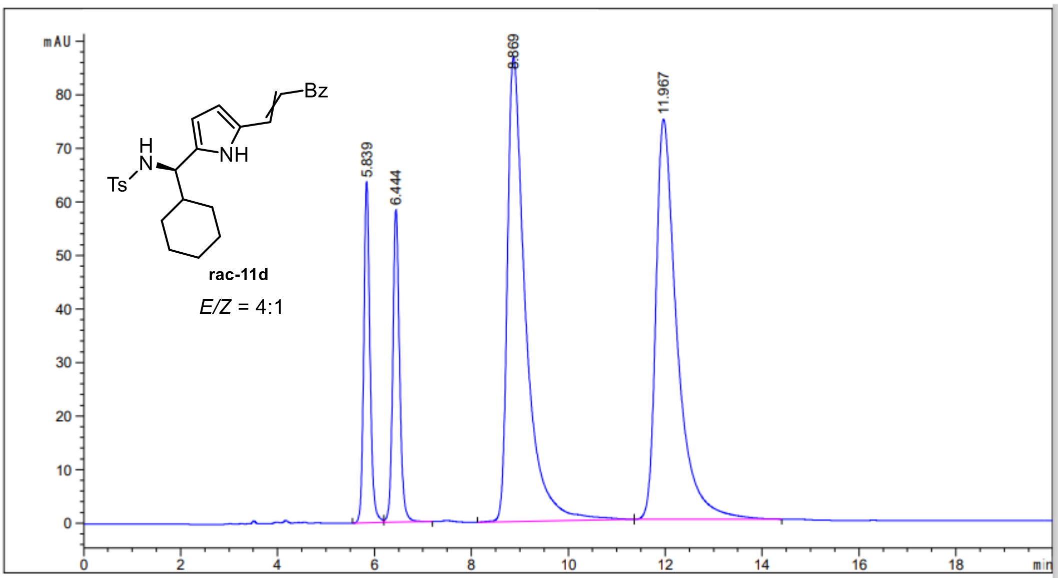
#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.844	BB	0.5492	7718.96436	213.11310	96.4754
2	19.474	BB	0.6251	281.99893	6.94596	3.5246

Name	CYC-20211129-60	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-60.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:36:35 PM (UTC+08:00)

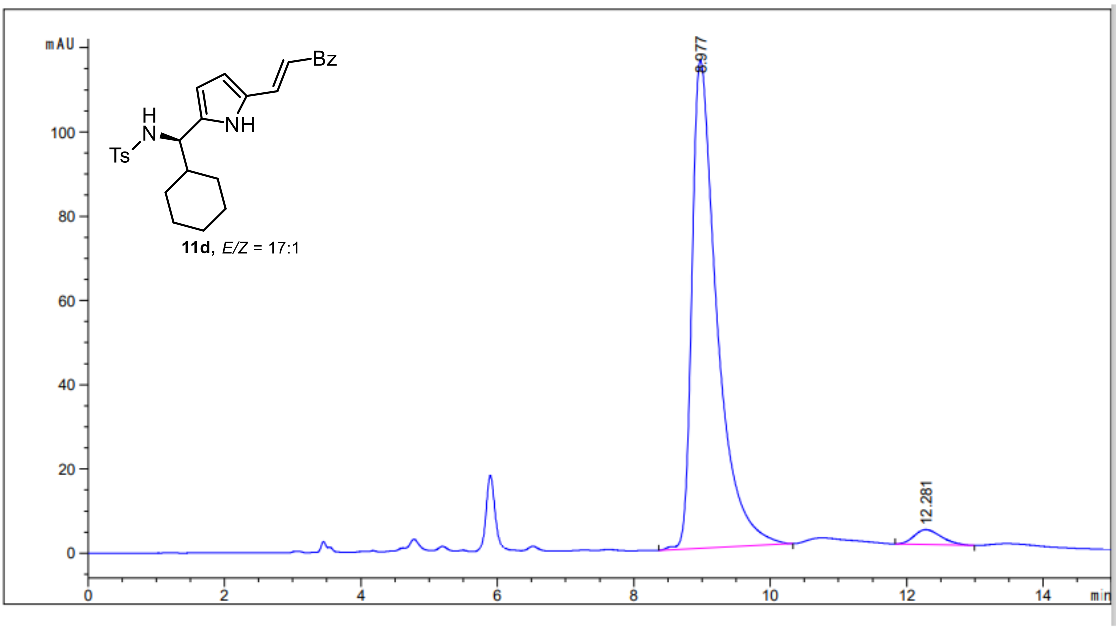



Bz
H
N
NH
Ts
11d, E/Z = 17:1
1H NMR (400 MHz, CDCl3)
f1 (ppm)


Bz
H
N
NH
Ts
11d, E/Z = 17:1
13C NMR (100 MHz, CDCl3)
f1 (ppm)

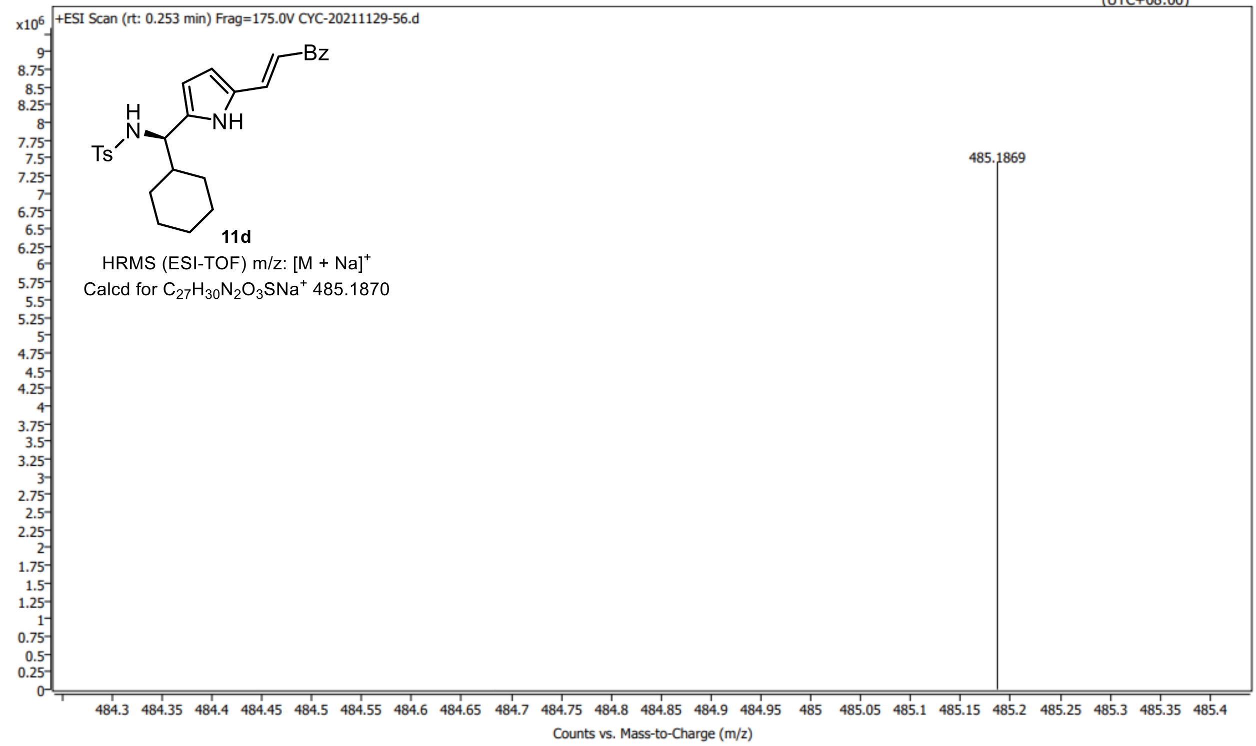


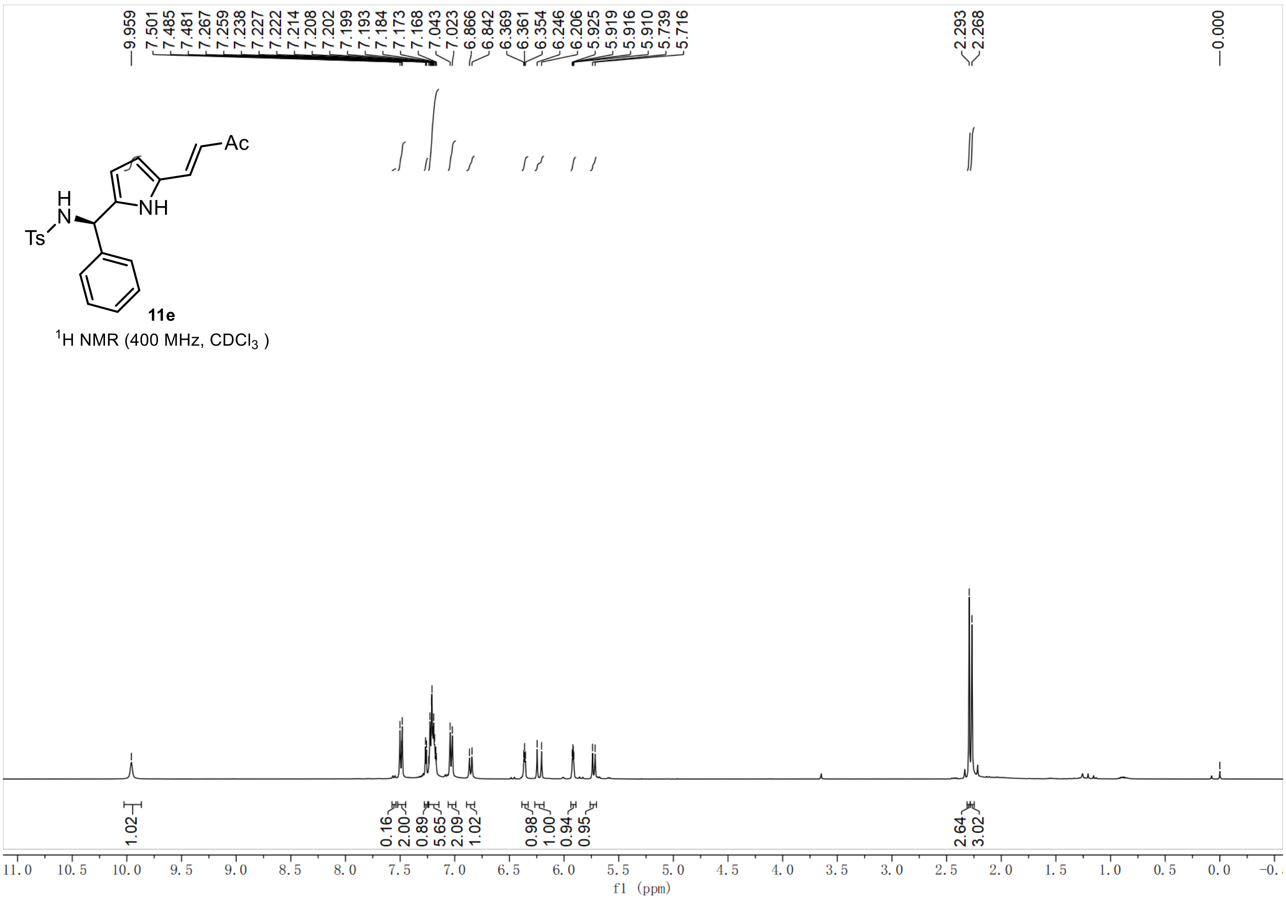
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.839	BV	0.1341	565.35107	63.68229	9.9761
2	6.444	VB	0.1487	569.52203	58.40378	10.0497
3	8.869	BB	0.3824	2271.32837	86.81559	40.0794
4	11.967	BB	0.4461	2260.86426	74.74084	39.8948



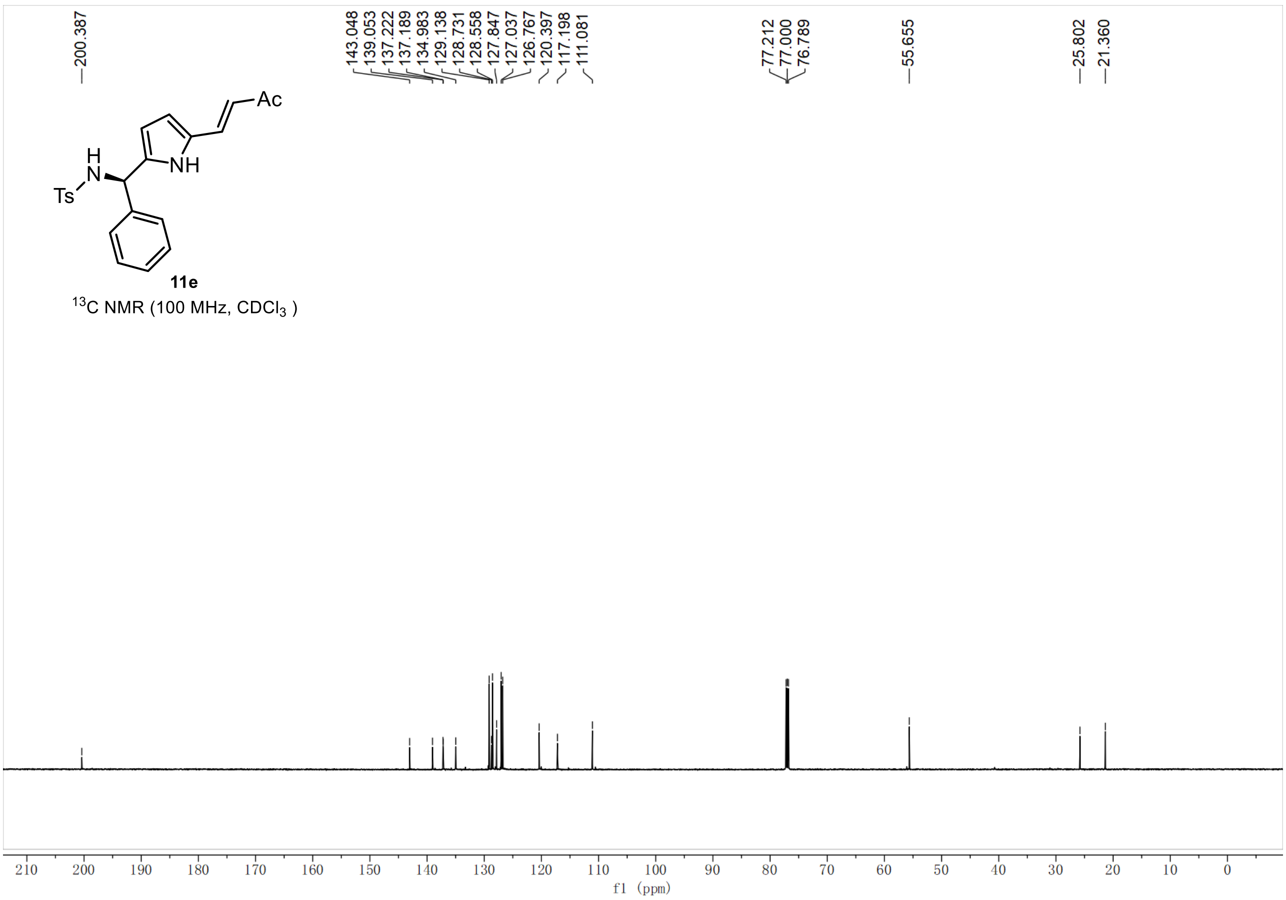
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.977	BB	0.3742	2949.18115	115.84160	96.7727
2	12.281	BB	0.4181	98.35177	3.54715	3.2273

Name	CYC-20211129-56	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-56.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:24:48 PM (UTC+08:00)

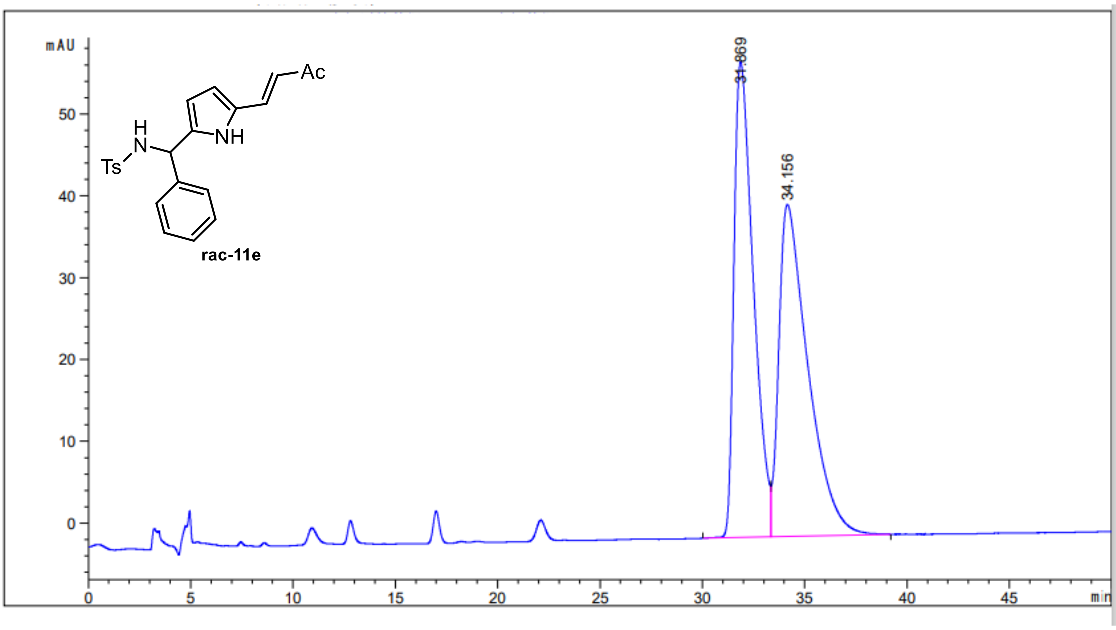




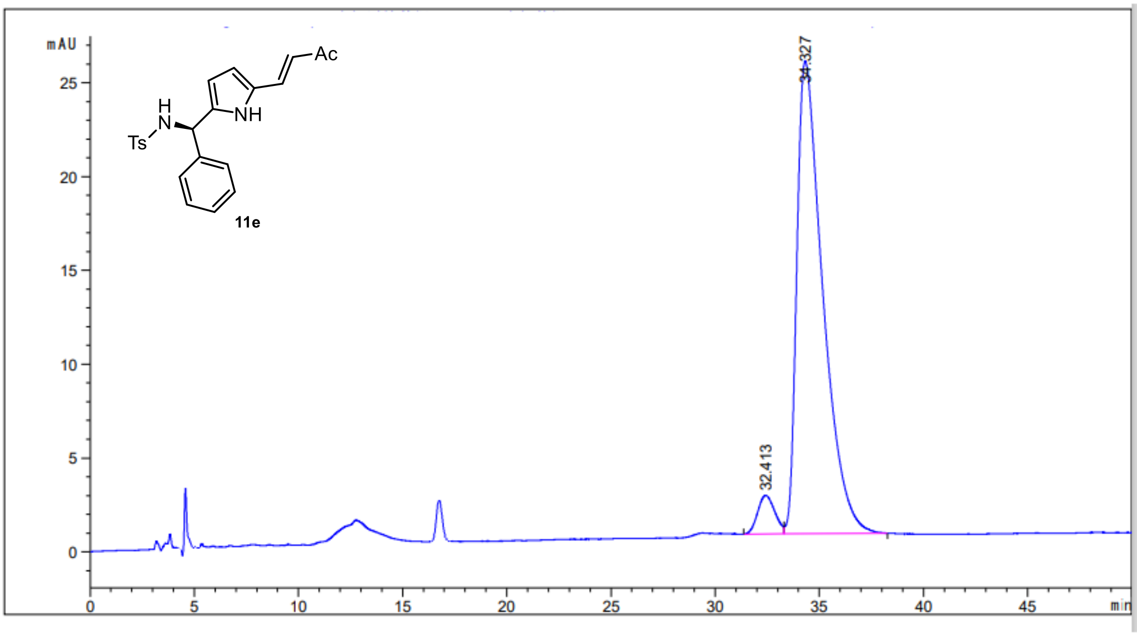
11e
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)



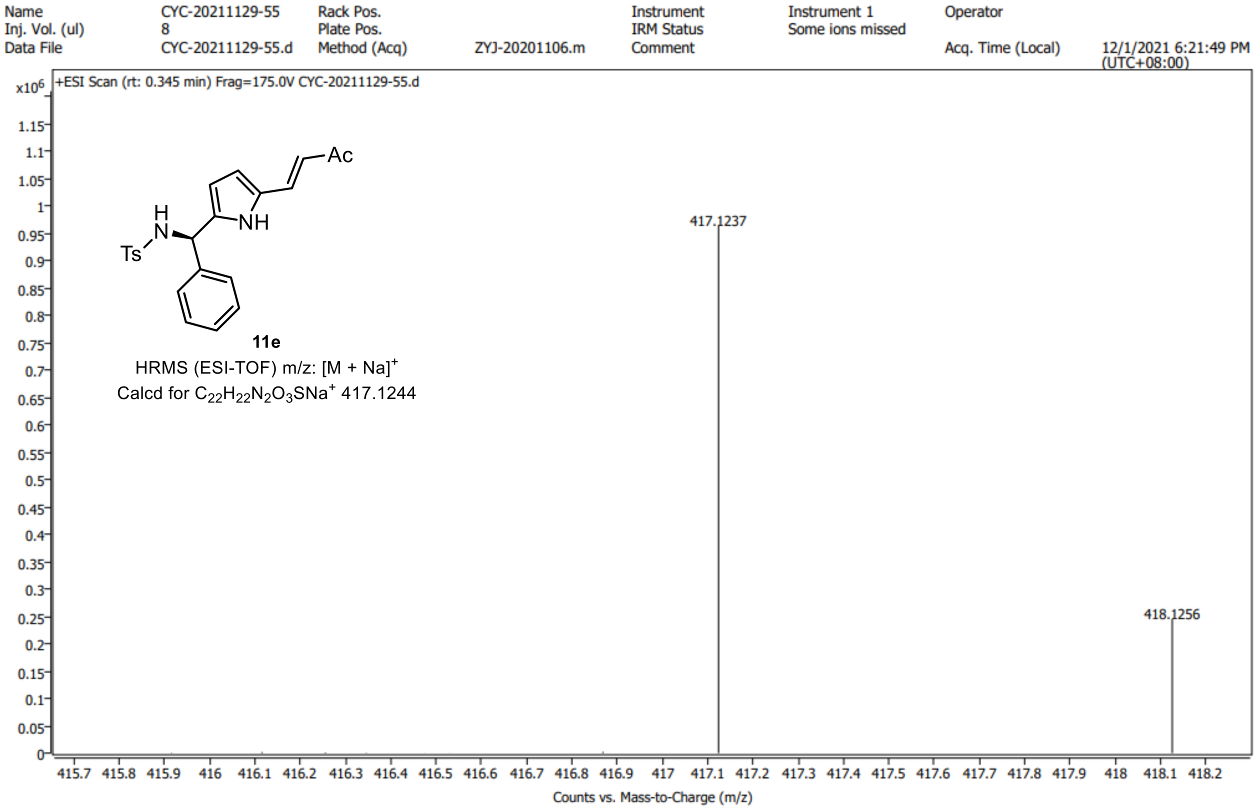
11e
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

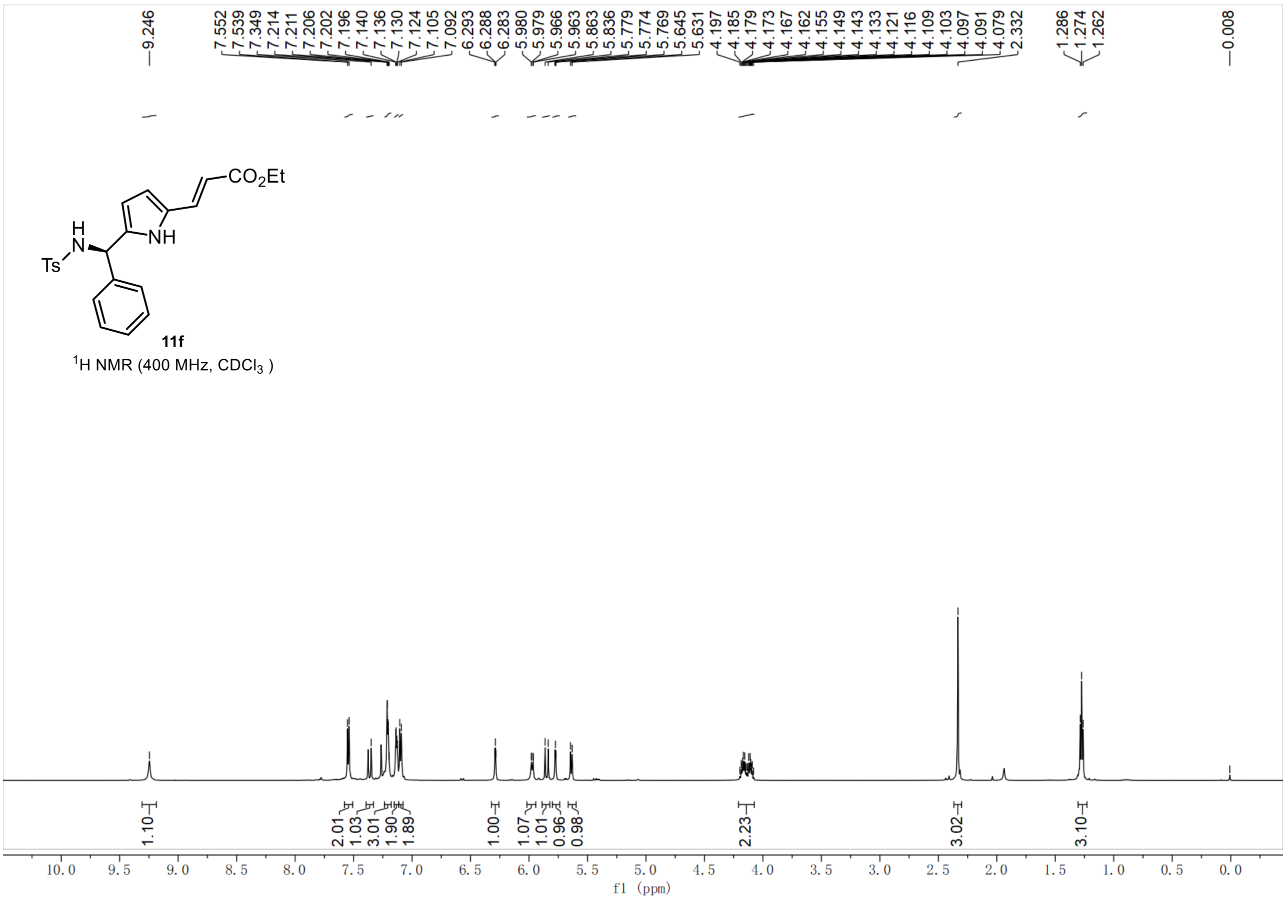


#	[min]		[min]	[mAU*s]	[mAU]	%
1	31.869	BV	0.9920	3823.67993	58.10288	48.7311
2	34.156	VB	1.4276	4022.80835	40.57302	51.2689

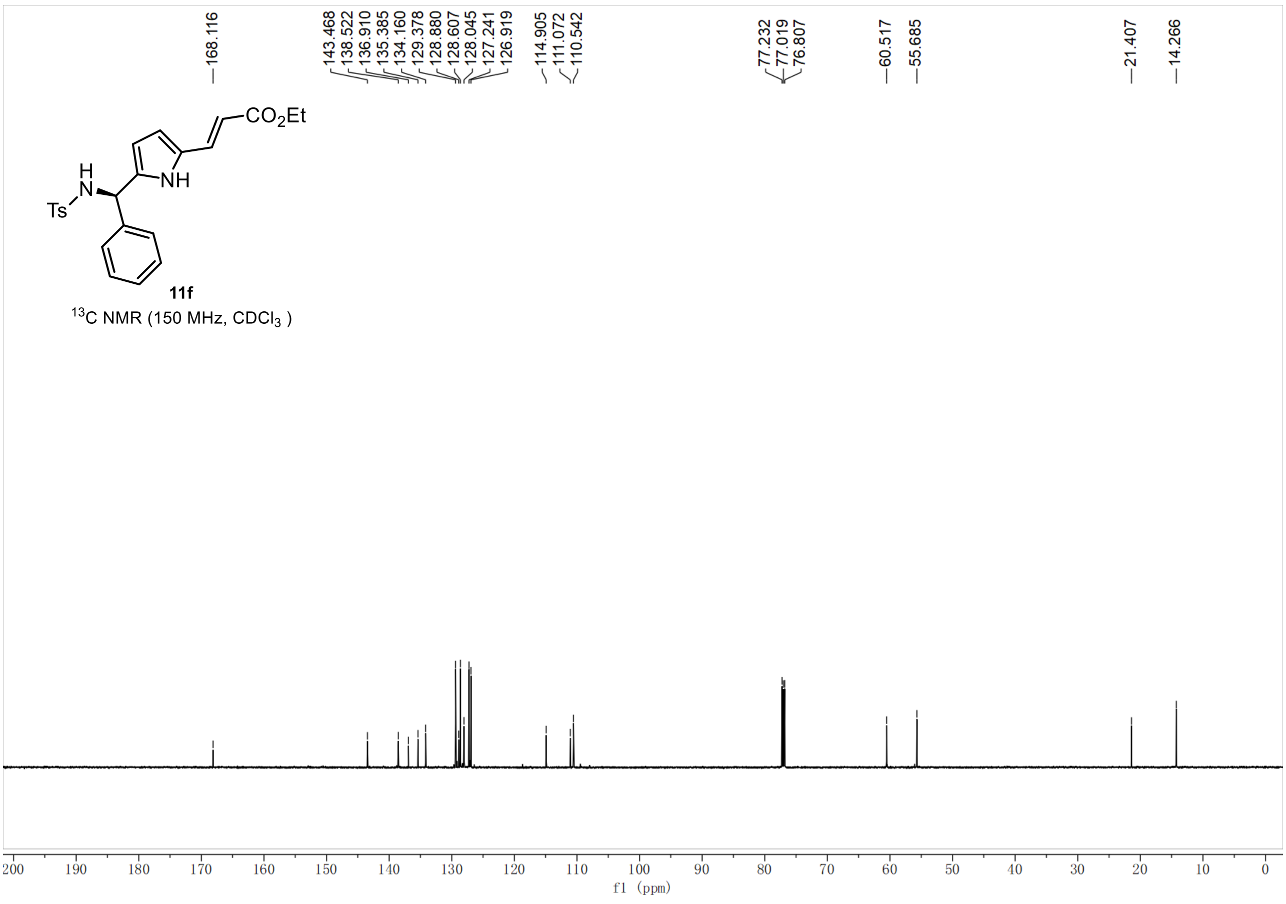


#	[min]		[min]	[mAU*s]	[mAU]	%
1	32.413	BV	0.7532	118.07346	2.05979	5.1363
2	34.327	VB	1.2716	2180.74023	25.20245	94.8637

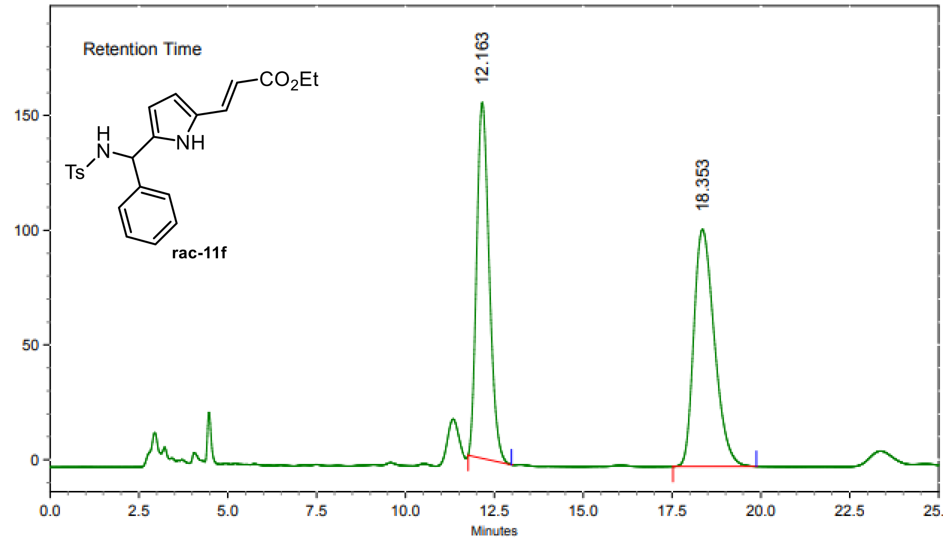

Name CYC-20211129-55
Inj. Vol. (ul) 8
Data File CYC-20211129-55.d
Rack Pos.
Plate Pos.
Method (Acq) ZYJ-20201106.m
Instrument Instrument 1
IRM Status Some ions missed
Comment
Operator
Acq. Time (Local) 12/1/2021 6:21:49 PM (UTC+08:00)
+ESI Scan (rt: 0.345 min) Frag=175.0V CYC-20211129-55.d
x10^6
417.1237
418.1256
Ac
NH
H
N
Ts
11e
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C22H22N2O3SNa+ 417.1244
Counts vs. Mass-to-Charge (m/z)



11f
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

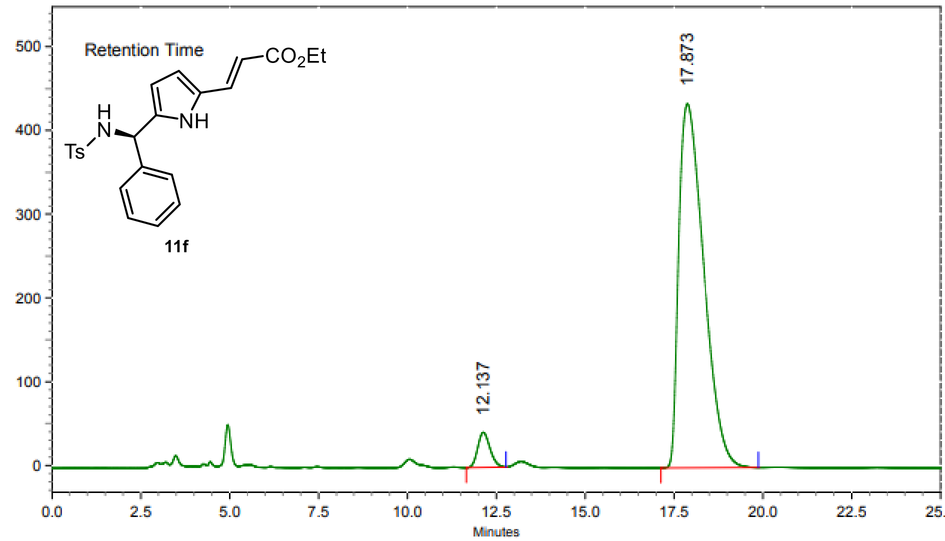


11f
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)



AREA PERCENT REPORT

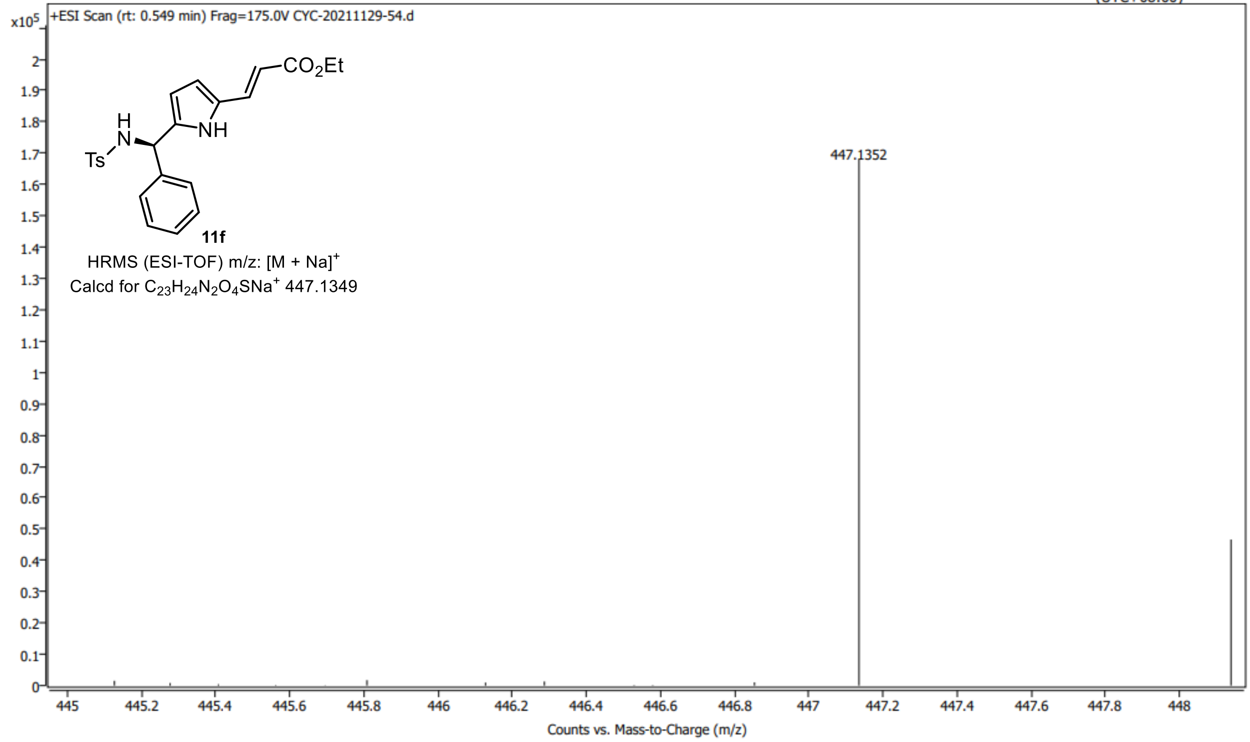
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	12.163	1.213	2600395	63666453	47.8414
2	18.353	2.347	1732438	69411745	52.1586

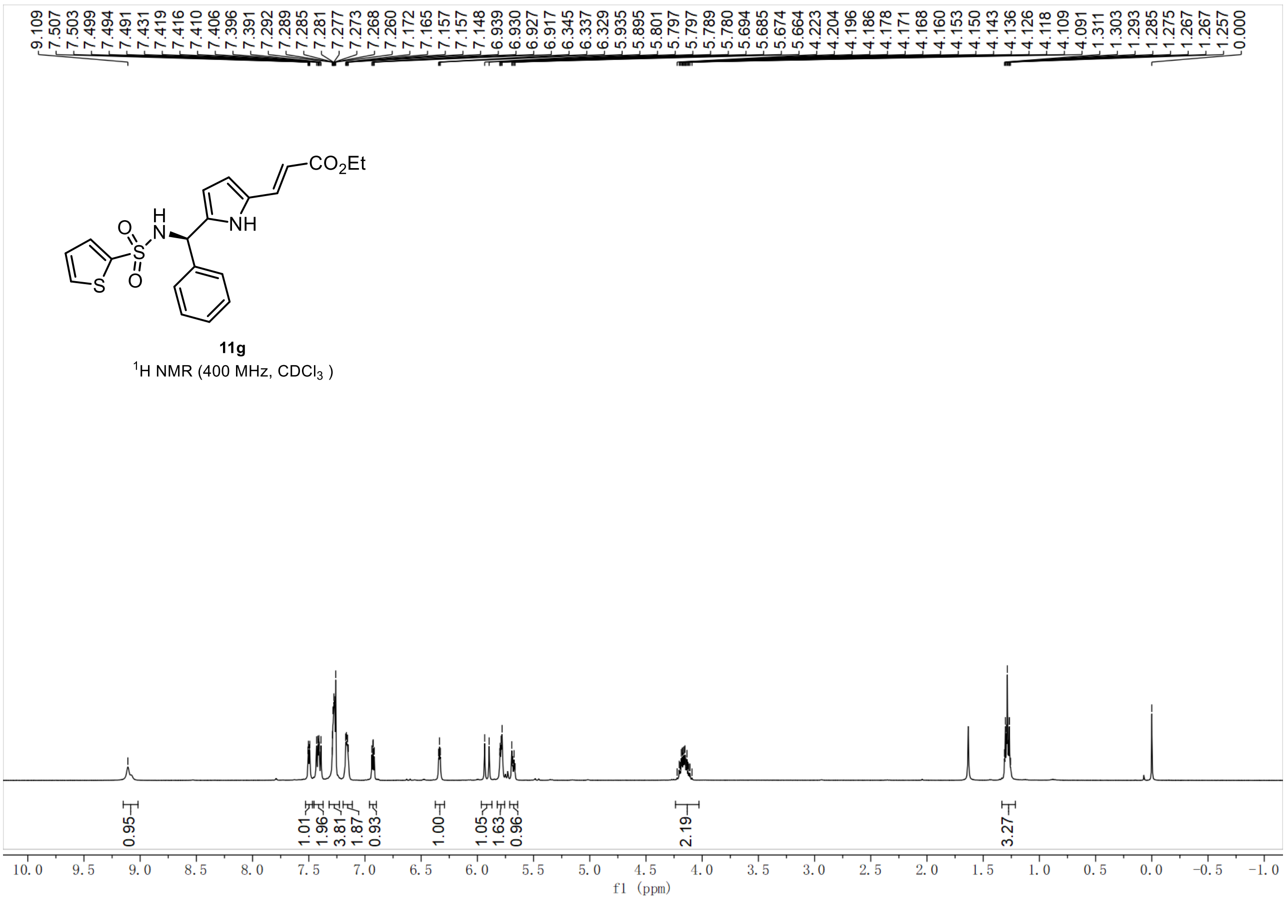


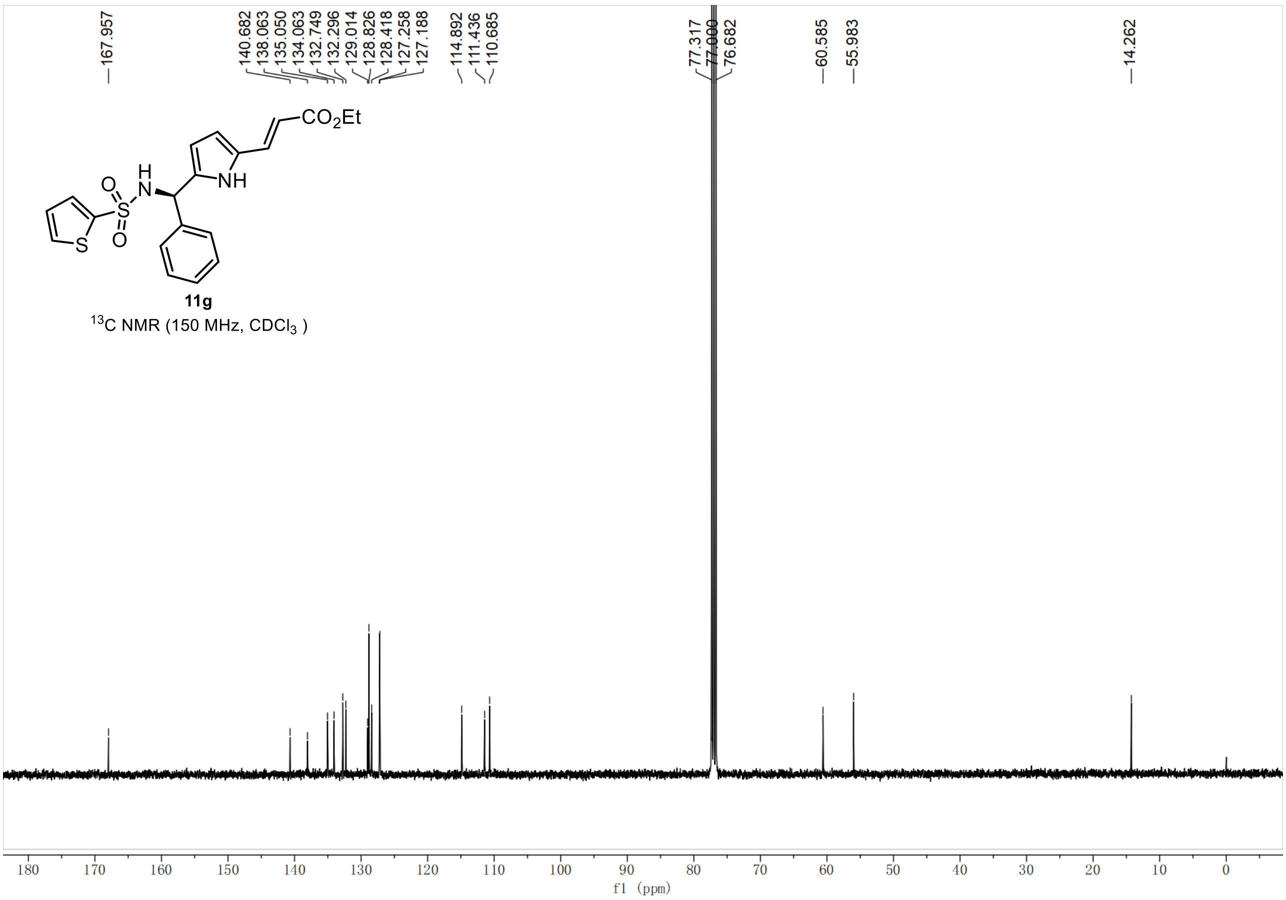
AREA PERCENT REPORT

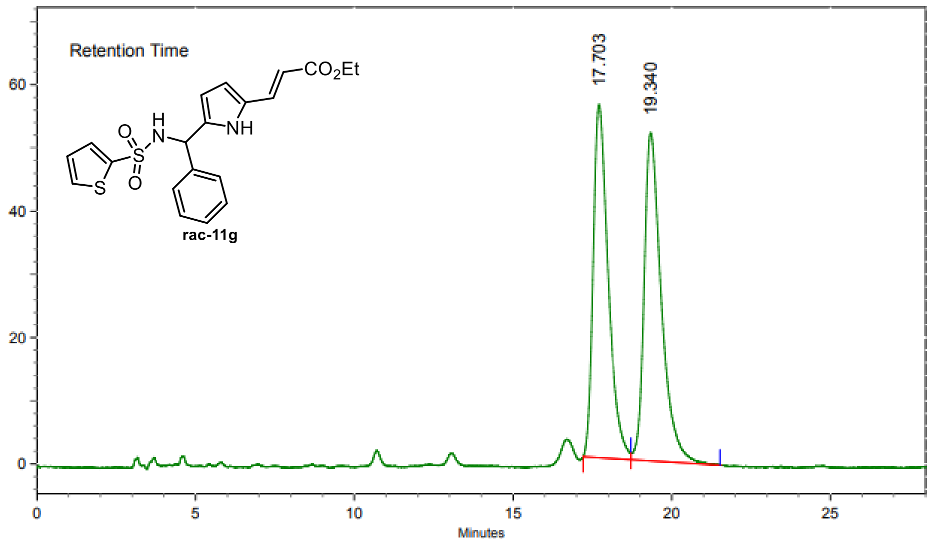
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	12.137	1.110	698028	16745391	4.4855
2	17.873	2.740	7293626	356577069	95.5145

Name	CYC-20211129-54	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-54.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:18:50 PM (UTC+08:00)



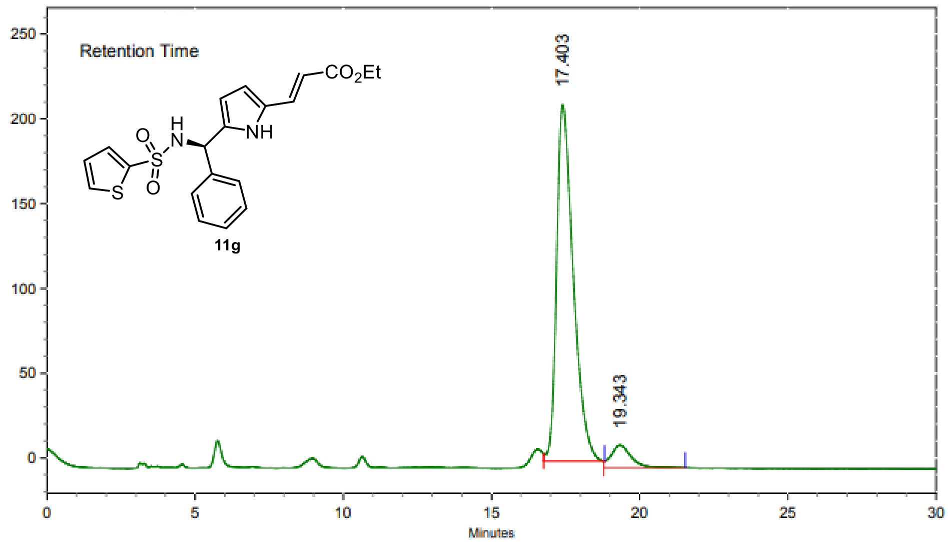

9.109
7.507
7.503
7.499
7.494
7.491
7.431
7.419
7.416
7.410
7.406
7.396
7.391
7.292
7.289
7.285
7.281
7.277
7.273
7.268
7.260
7.172
7.165
7.157
7.157
7.148
6.939
6.930
6.927
6.917
6.345
6.337
6.329
5.935
5.895
5.801
5.797
5.789
5.780
5.694
5.685
5.674
5.664
4.223
4.204
4.196
4.186
4.178
4.171
4.168
4.160
4.153
4.150
4.143
4.136
4.126
4.118
4.109
4.091
1.311
1.303
1.293
1.285
1.275
1.267
1.267
1.257
0.000
CO2Et
H
N
O
S
O
S
NH
11g
1H NMR (400 MHz, CDCl3)
0.95
1.01
1.96
3.81
1.87
0.93
1.00
1.05
1.63
0.96
2.19
3.27
f1 (ppm)


167.957
140.682
138.063
135.050
134.063
132.749
132.296
129.014
128.826
128.418
127.258
127.188
114.892
111.436
110.685
77.317
77.000
76.682
60.585
55.983
14.262
CO2Et
H
N
O
S
O
S
NH
11g
13C NMR (150 MHz, CDCl3)
f1 (ppm)



AREA PERCENT REPORT

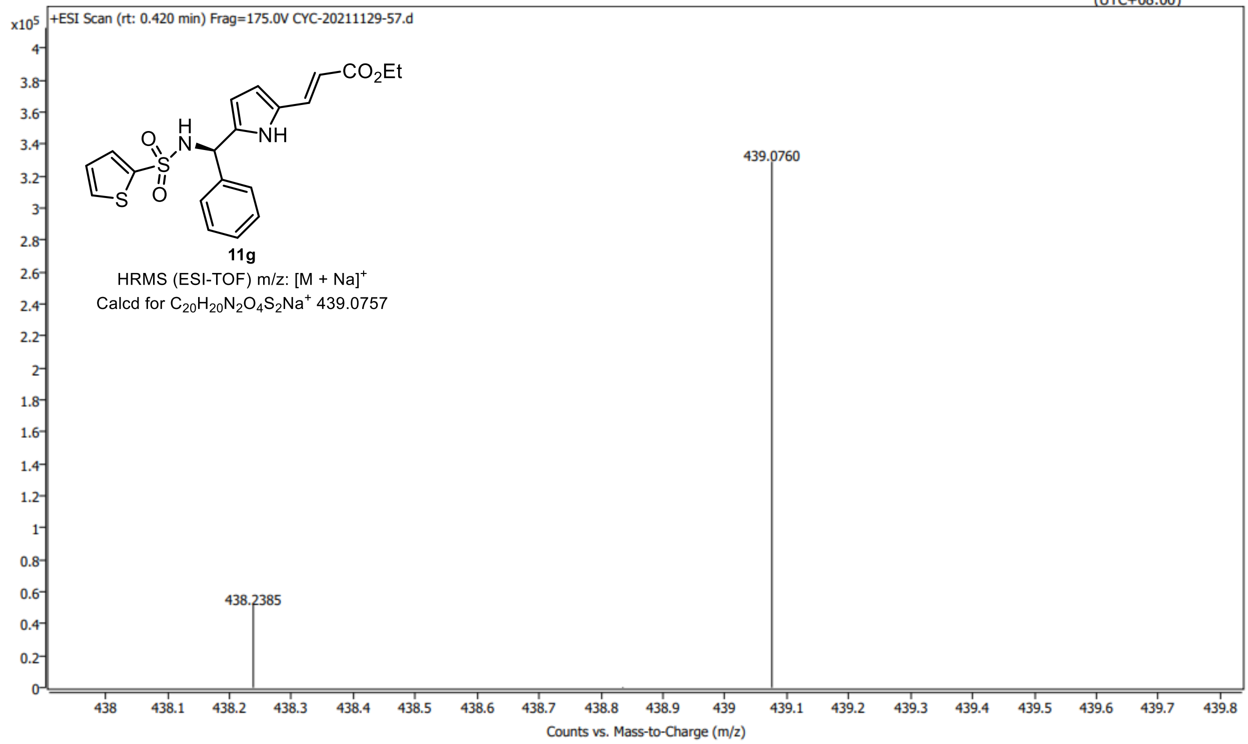
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	17.703	1.510	937768	30939886	48.6280
2	19.340	2.810	870344	32685829	51.3720

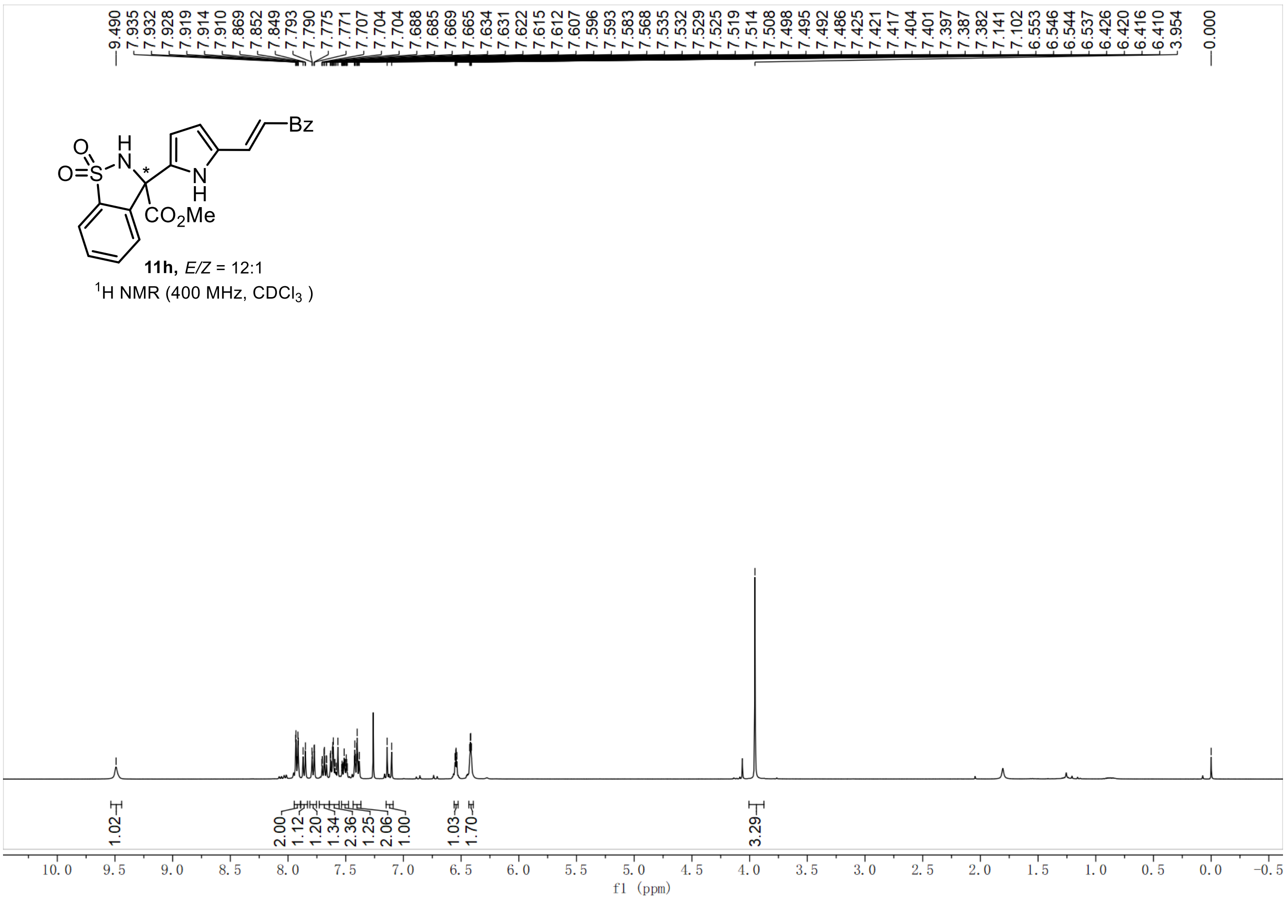


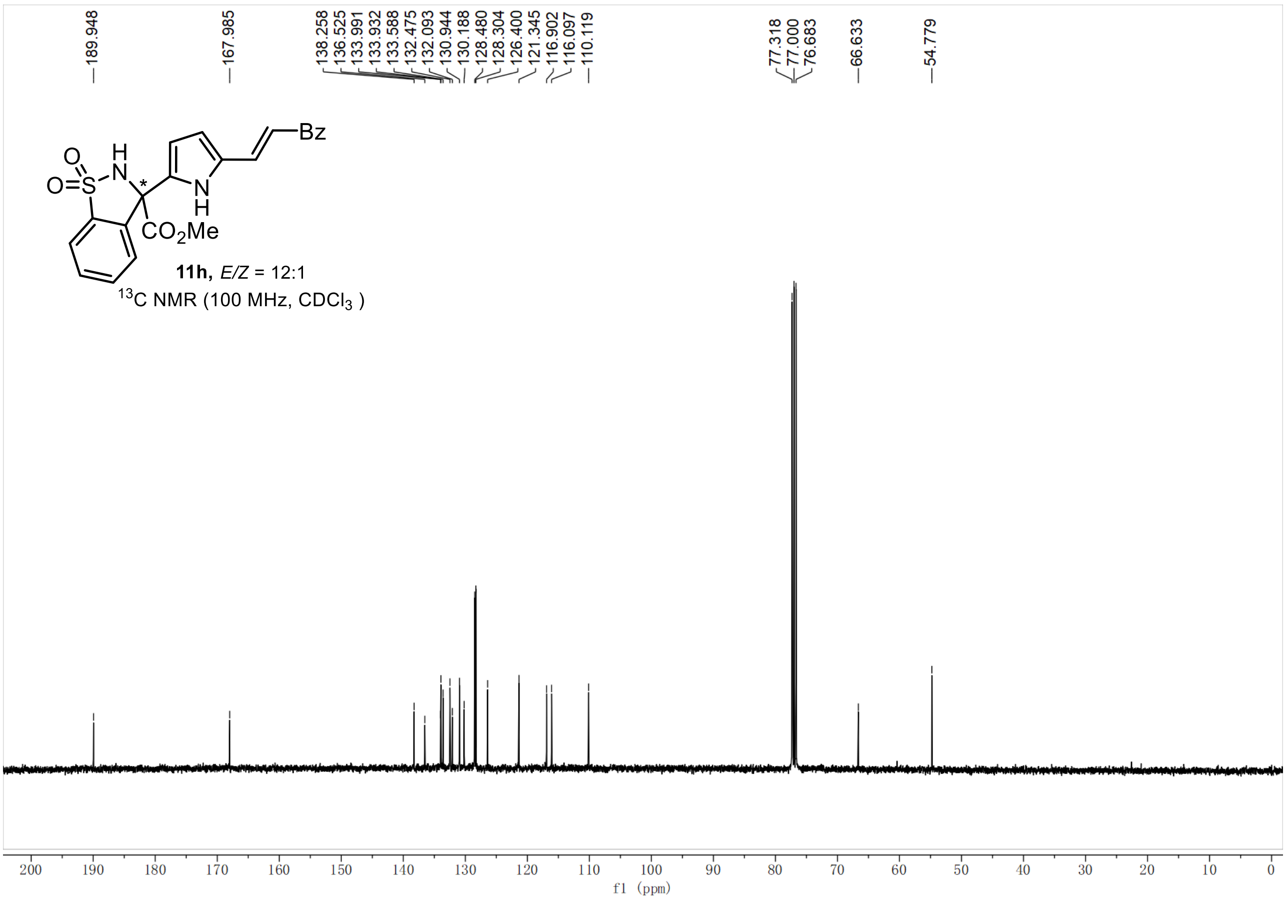
AREA PERCENT REPORT

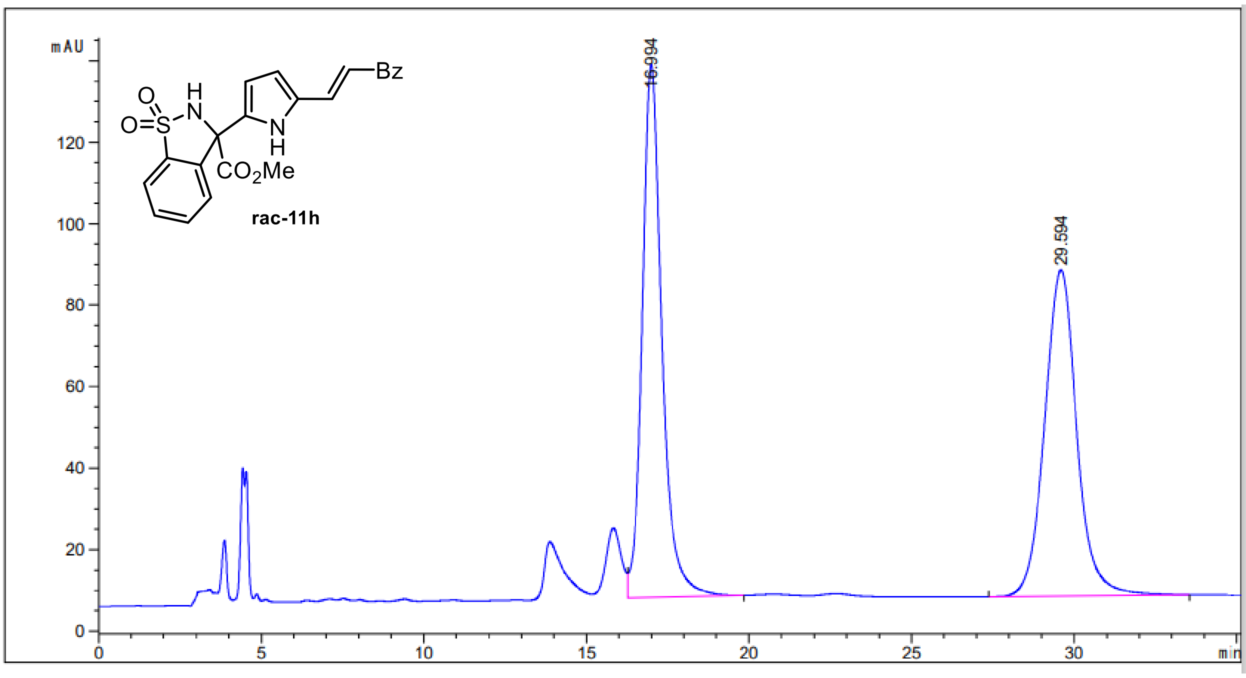
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	17.403	2.058	3525321	136808681	92.8331
2	19.343	2.733	223303	10561952	7.1669

Name CYC-20211129-57 Rack Pos. Instrument Instrument 1 Operator
Inj. Vol. (ul) 8 Plate Pos. IRM Status Some ions missed
Data File CYC-20211129-57.d Method (Acq) ZYJ-20201106.m Comment Acq. Time (Local) 12/1/2021 6:27:45 PM (UTC+08:00)

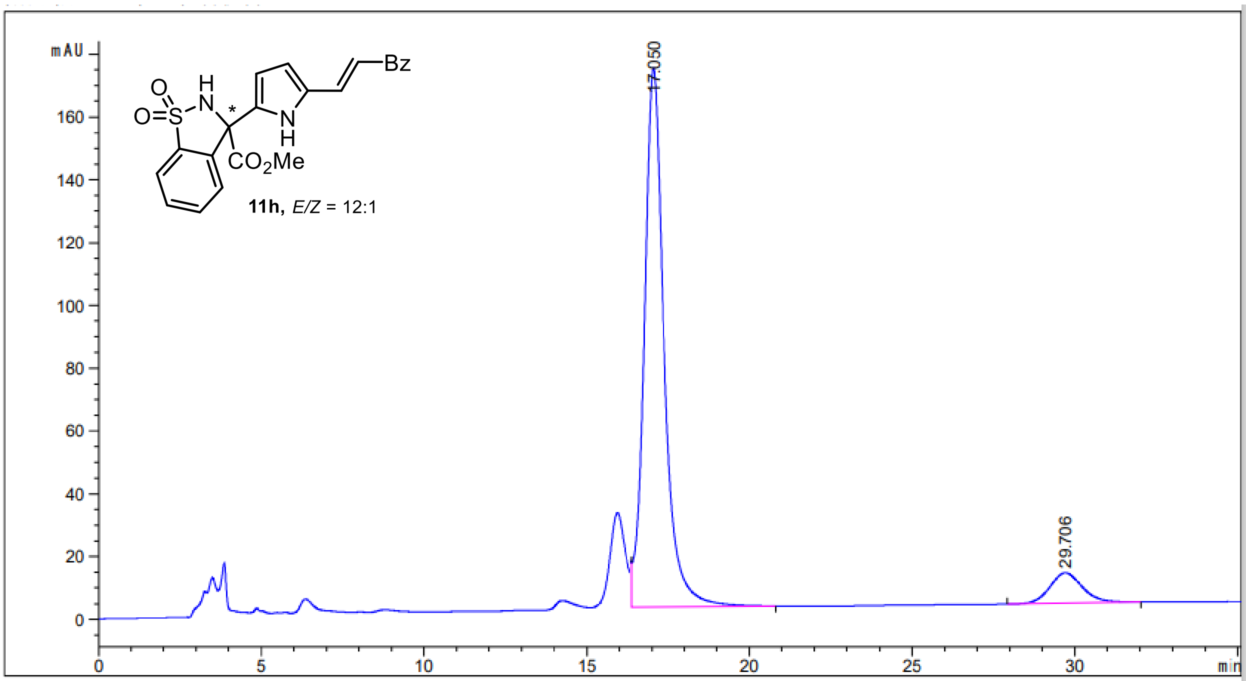



11h, E/Z = 12:1
¹H NMR (400 MHz, CDCl₃)
f1 (ppm)


11h, E/Z = 12:1
¹³C NMR (100 MHz, CDCl₃)
f1 (ppm)

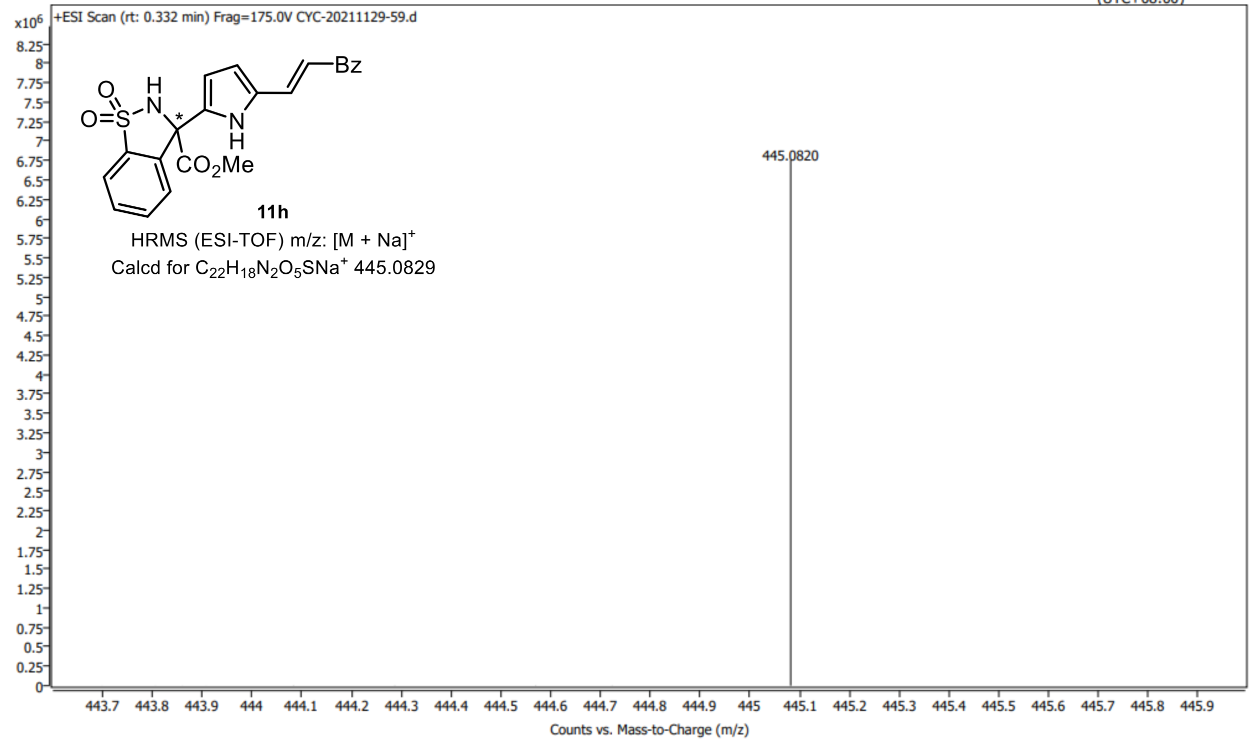


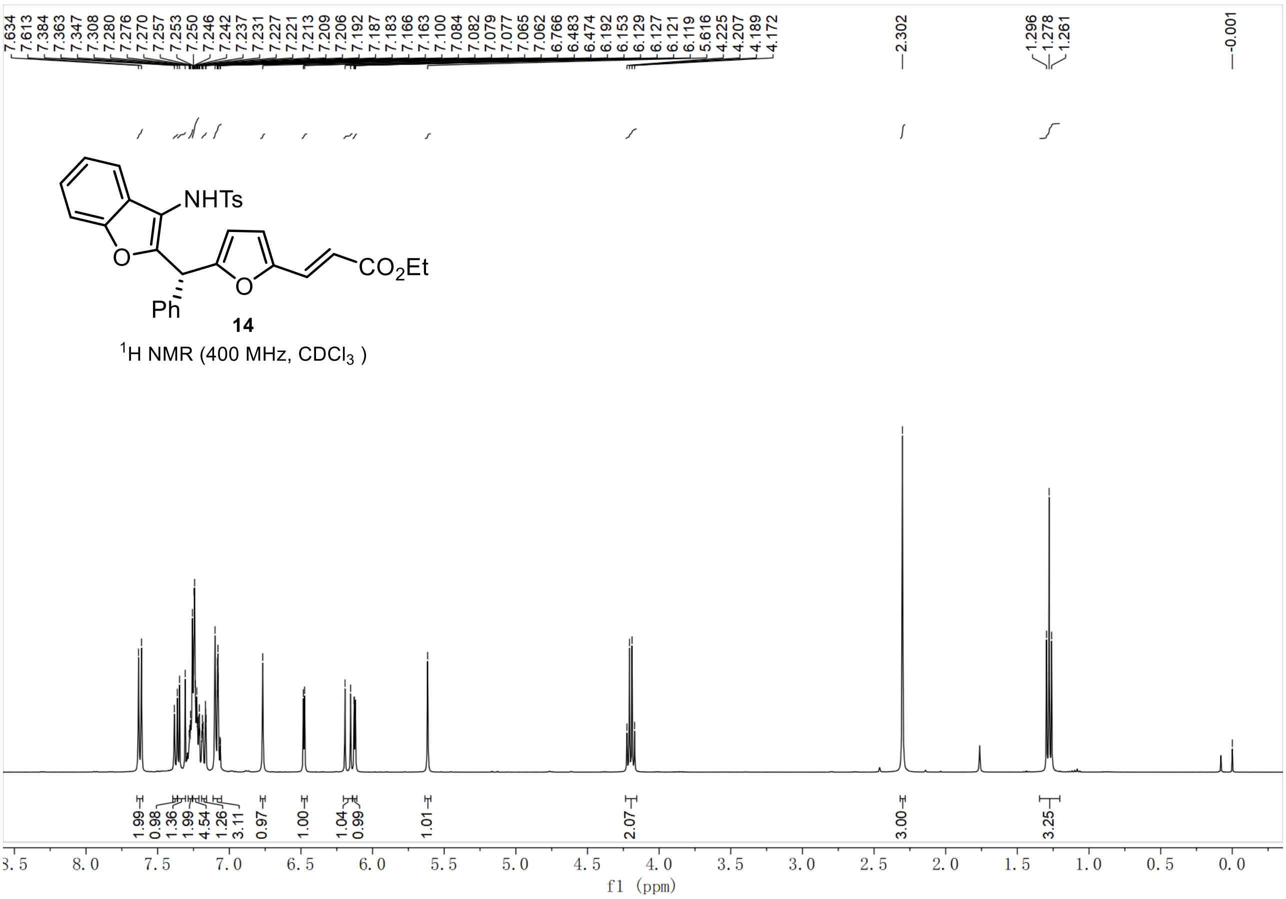
#	[min]		[min]	[mAU*s]	[mAU]	%
1	16.994	VB	0.6286	5481.13477	130.80486	49.8597
2	29.594	BB	1.0496	5511.98486	80.02951	50.1403

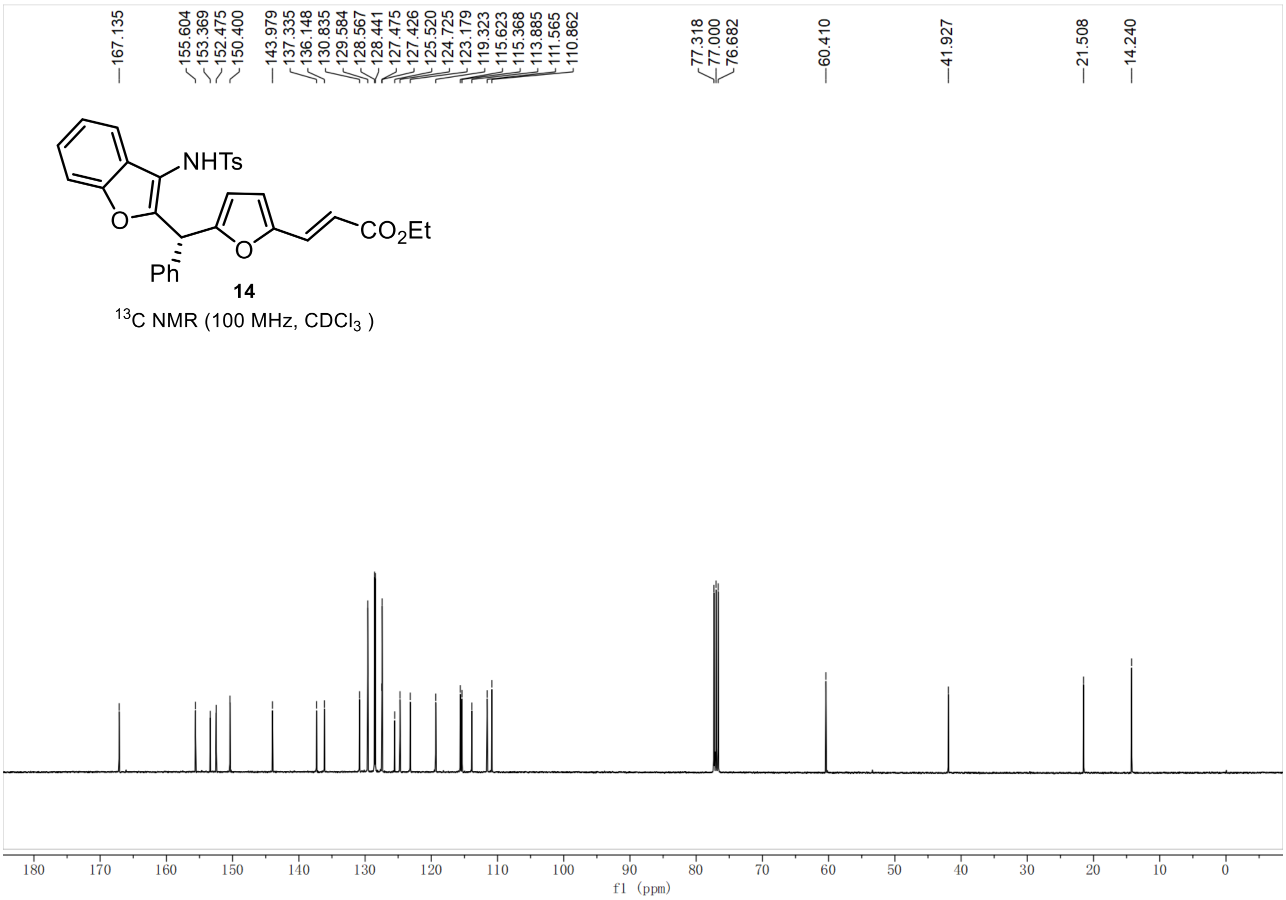


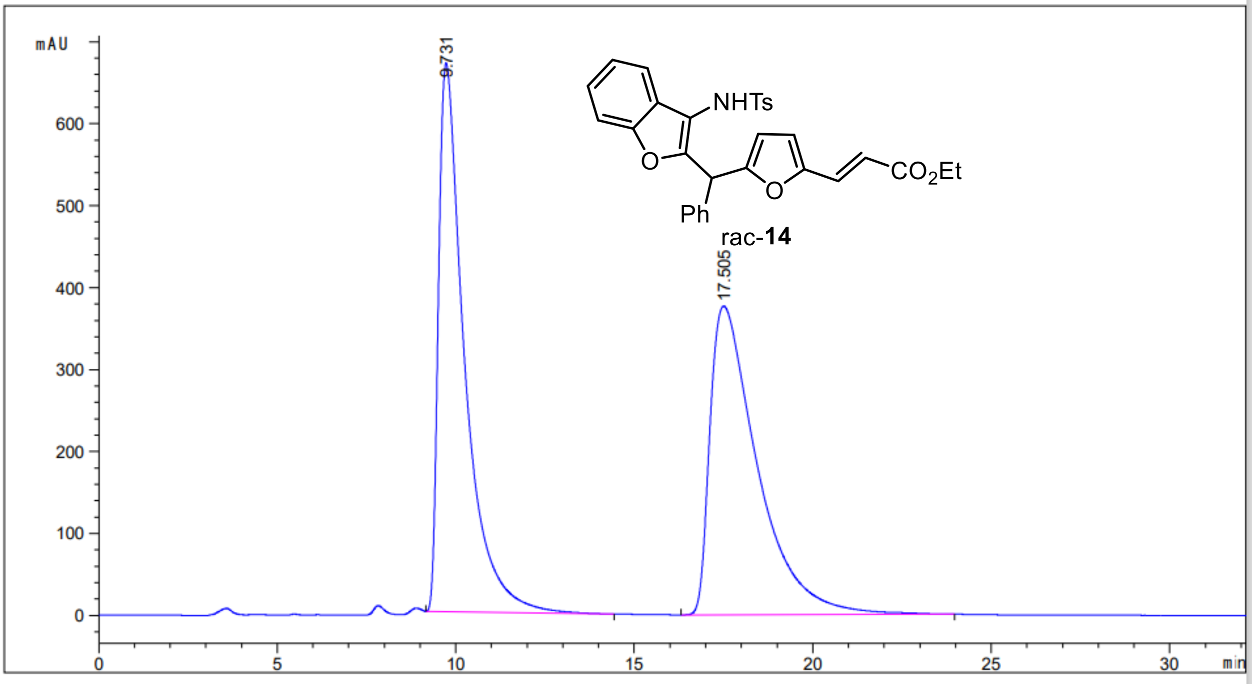
#	[min]		[min]	[mAU*s]	[mAU]	%
1	17.050	VB	0.6324	7263.78516	171.52957	91.4431
2	29.706	BB	1.0178	679.71722	9.75972	8.5569

Name	CYC-20211129-59	Rack Pos.		Instrument	Instrument 1	Operator	
Inj. Vol. (ul)	8	Plate Pos.		IRM Status	Success		
Data File	CYC-20211129-59.d	Method (Acq)	ZYJ-20201106.m	Comment		Acq. Time (Local)	12/1/2021 6:33:38 PM (UTC+08:00)

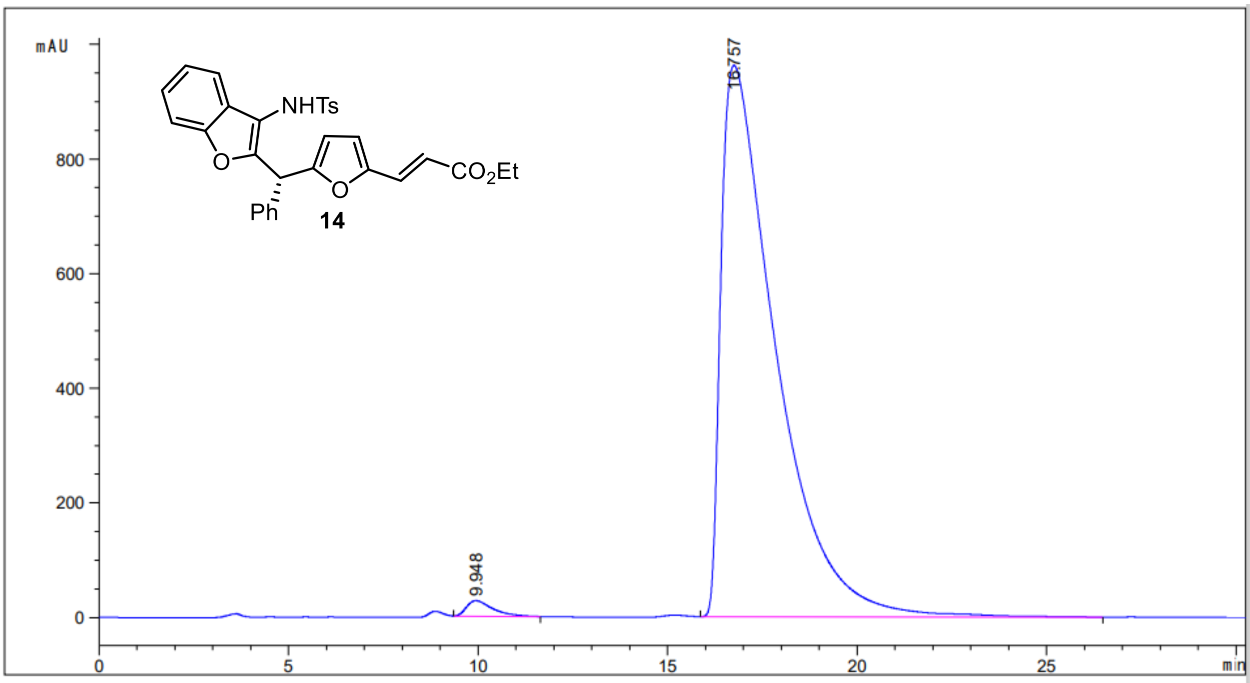



7.634 7.613 7.384 7.363 7.347 7.308 7.280 7.276 7.270 7.257 7.253 7.250 7.246 7.242 7.237 7.231 7.227 7.221 7.213 7.209 7.206 7.192 7.187 7.183 7.166 7.163 7.100 7.084 7.082 7.079 7.077 7.065 7.062 6.766 6.483 6.474 6.192 6.153 6.129 6.127 6.121 6.119 5.616 4.225 4.207 4.189 4.172
2.302
1.296 1.278 1.261
-0.001
NHTs
O
O
CO2Et
Ph
14
1H NMR (400 MHz, CDCl3)
1.99 0.98 1.36 1.99 4.54 1.26 3.11 0.97 1.00 1.04 0.99 1.01 2.07 3.00 3.25
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

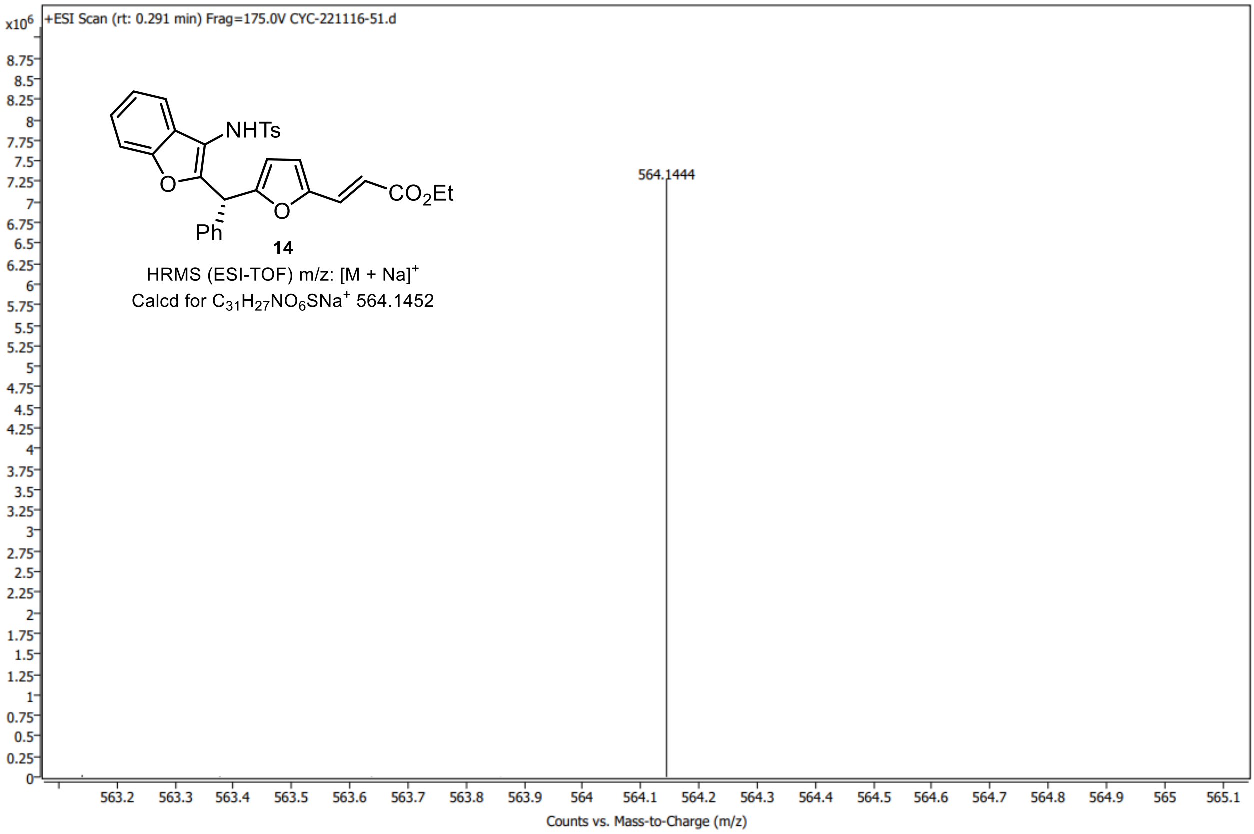

167.135
155.604 153.369 152.475 150.400
143.979 137.335 136.148 130.835 129.584 128.567 128.441 127.475 127.426 125.520 124.725 123.179 119.323 115.623 115.368 113.885 111.565 110.862
77.318 77.000 76.682
60.410
41.927
21.508
14.240
NHTs
O
O
CO2Et
Ph
14
13C NMR (100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

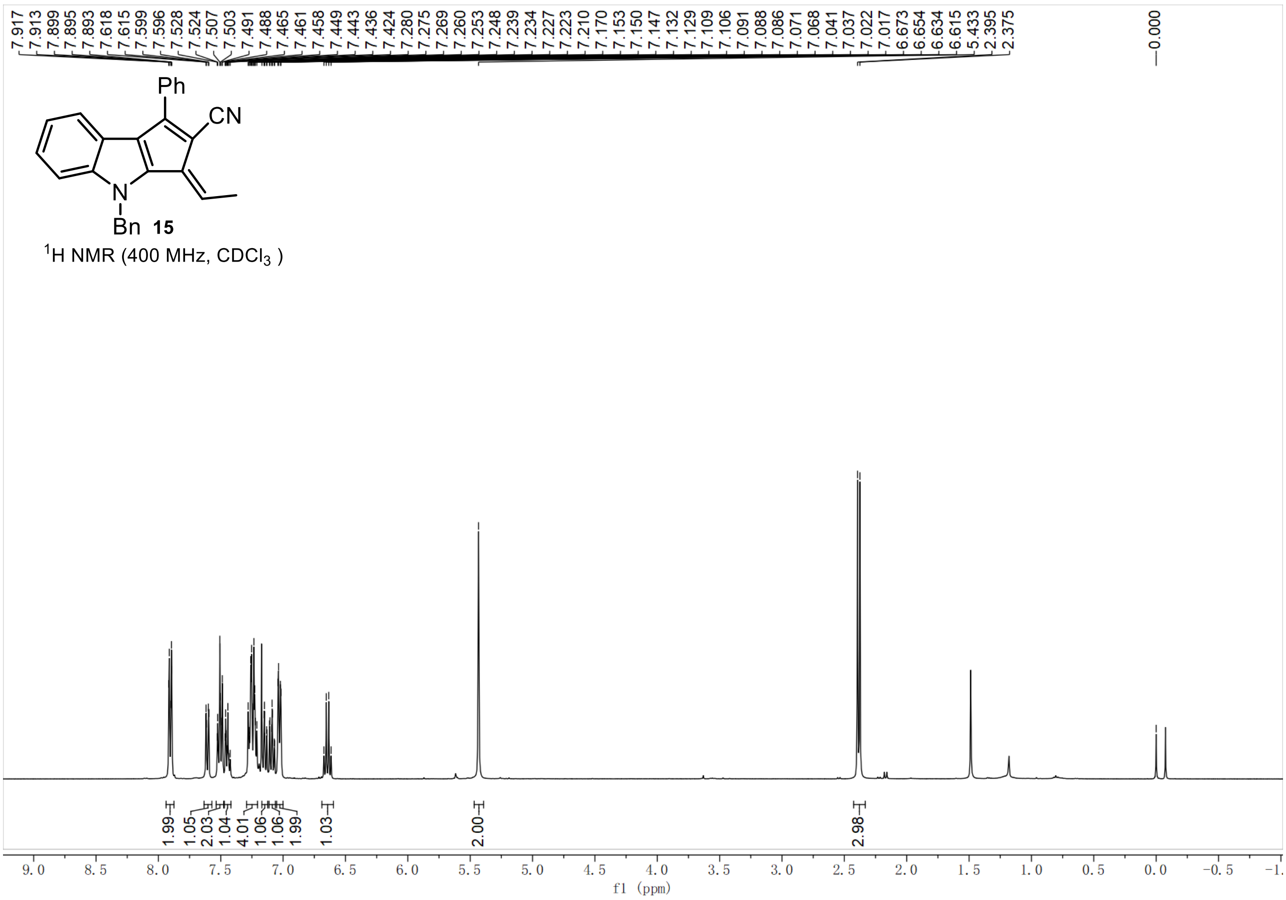


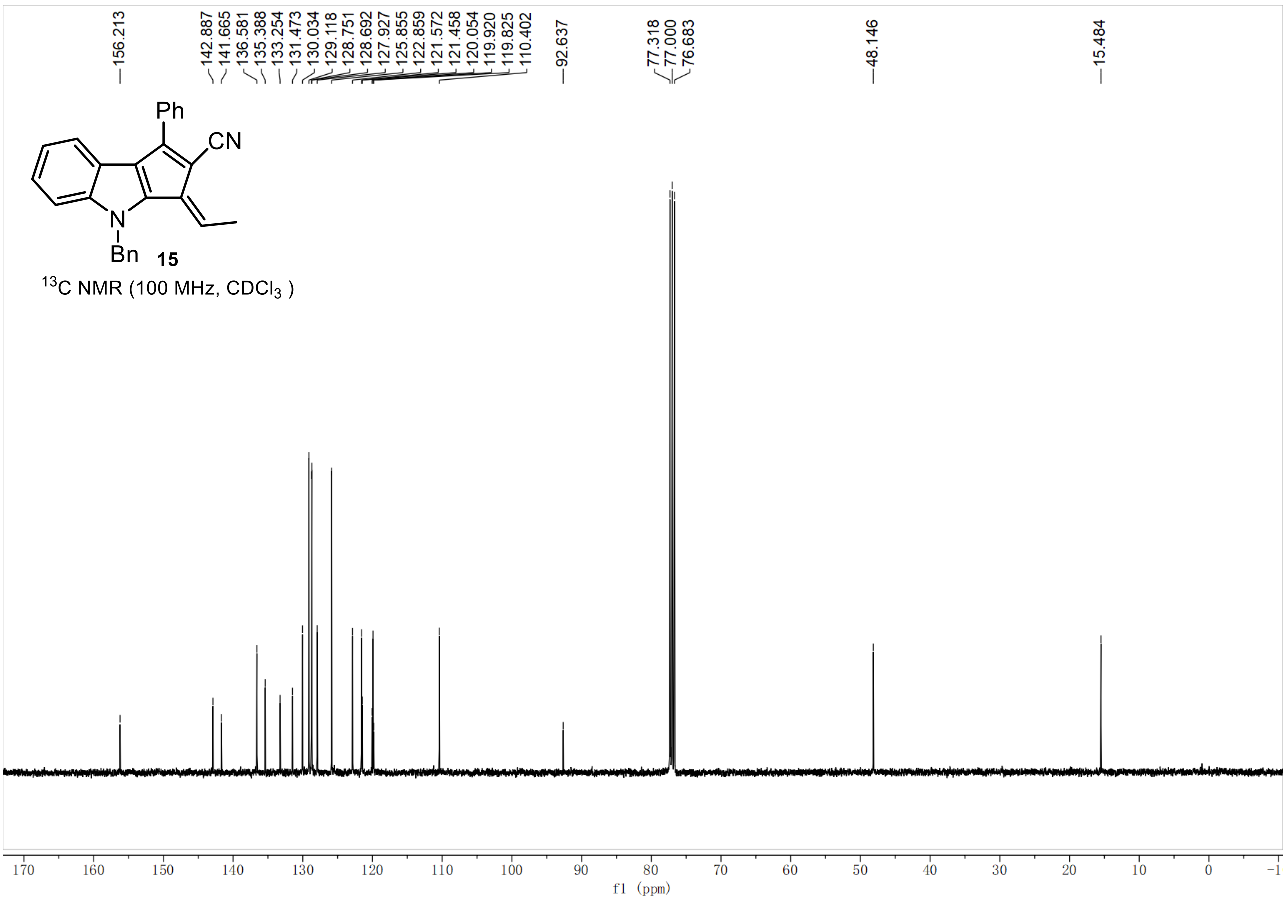
#	[min]		[min]	mAU *s	[mAU]	%
1	9.731	BB	0.7475	3.41244e4	669.52655	49.4824
2	17.505	BB	1.3689	3.48383e4	376.62680	50.5176

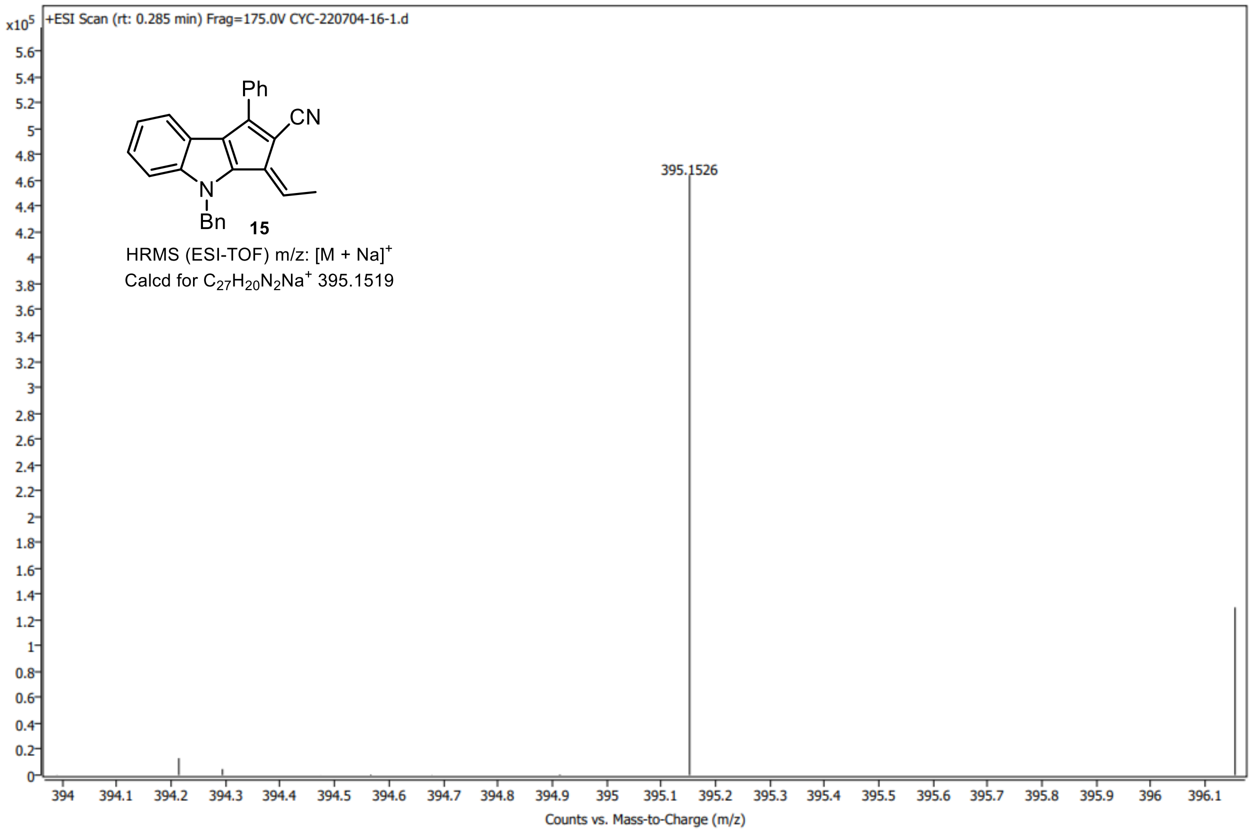


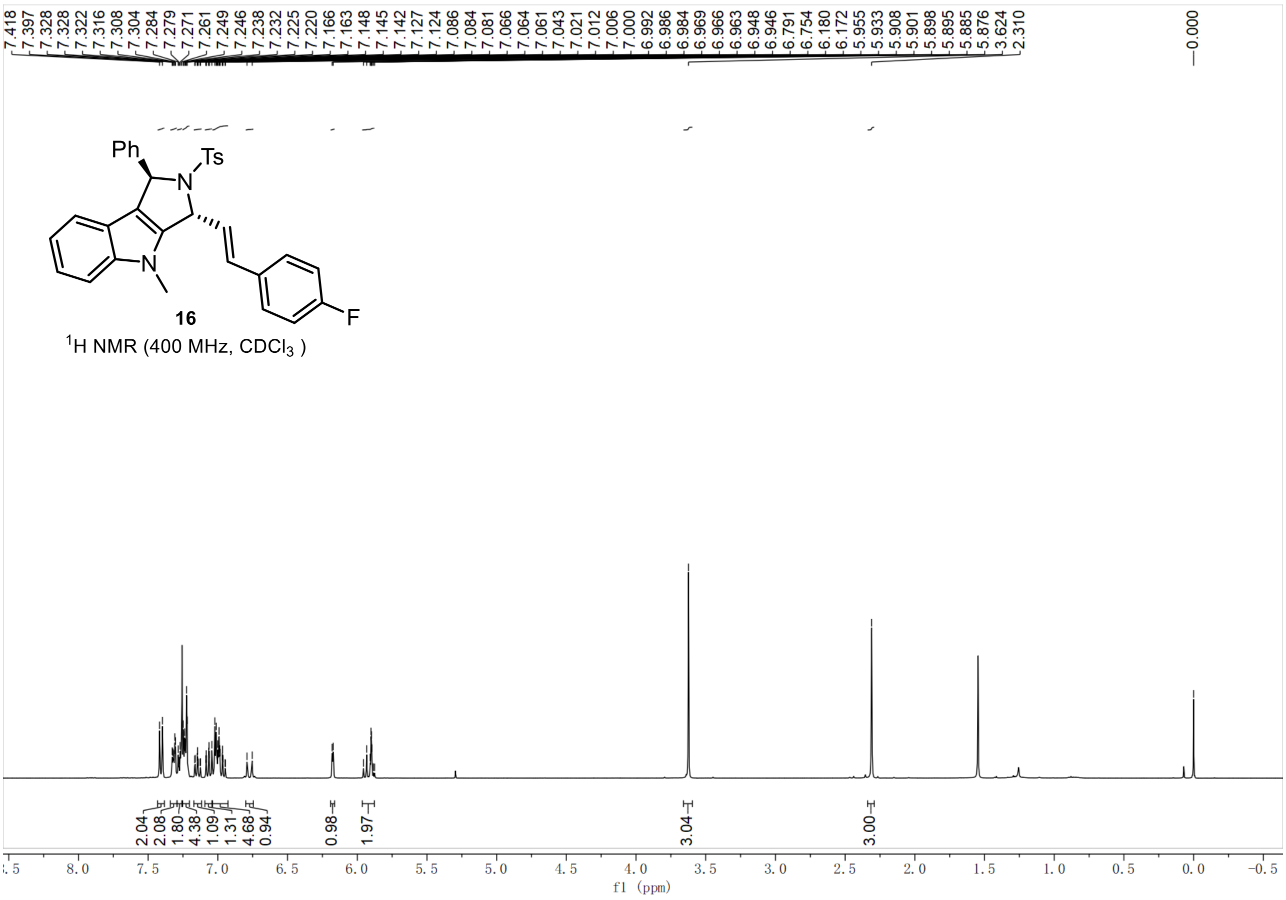
#	[min]		[min]	mAU *s	[mAU]	%
1	9.948	BBA	0.7228	1303.33203	27.02454	1.3264
2	16.757	BB	1.4699	9.69607e4	962.11920	98.6736


+ESI Scan (rt: 0.291 min) Frag=175.0V CYC-221116-51.d
x10^6
NHTs
CO2Et
Ph
14
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C31H27NO6SNa+ 564.1452
564.1444
Counts vs. Mass-to-Charge (m/z)


7.917
7.913
7.899
7.895
7.893
7.618
7.615
7.599
7.596
7.528
7.524
7.507
7.503
7.491
7.488
7.465
7.461
7.458
7.449
7.443
7.436
7.424
7.280
7.275
7.269
7.260
7.253
7.248
7.239
7.234
7.227
7.223
7.210
7.170
7.153
7.150
7.147
7.132
7.129
7.109
7.106
7.091
7.088
7.086
7.071
7.068
7.041
7.037
7.022
7.017
6.673
6.654
6.634
6.615
5.433
2.395
2.375
0.000
Ph
CN
N
Bn
15
1H NMR (400 MHz, CDCl3)
1.99
1.05
2.03
1.04
4.01
1.06
1.06
1.99
1.03
2.00
2.98
f1 (ppm)

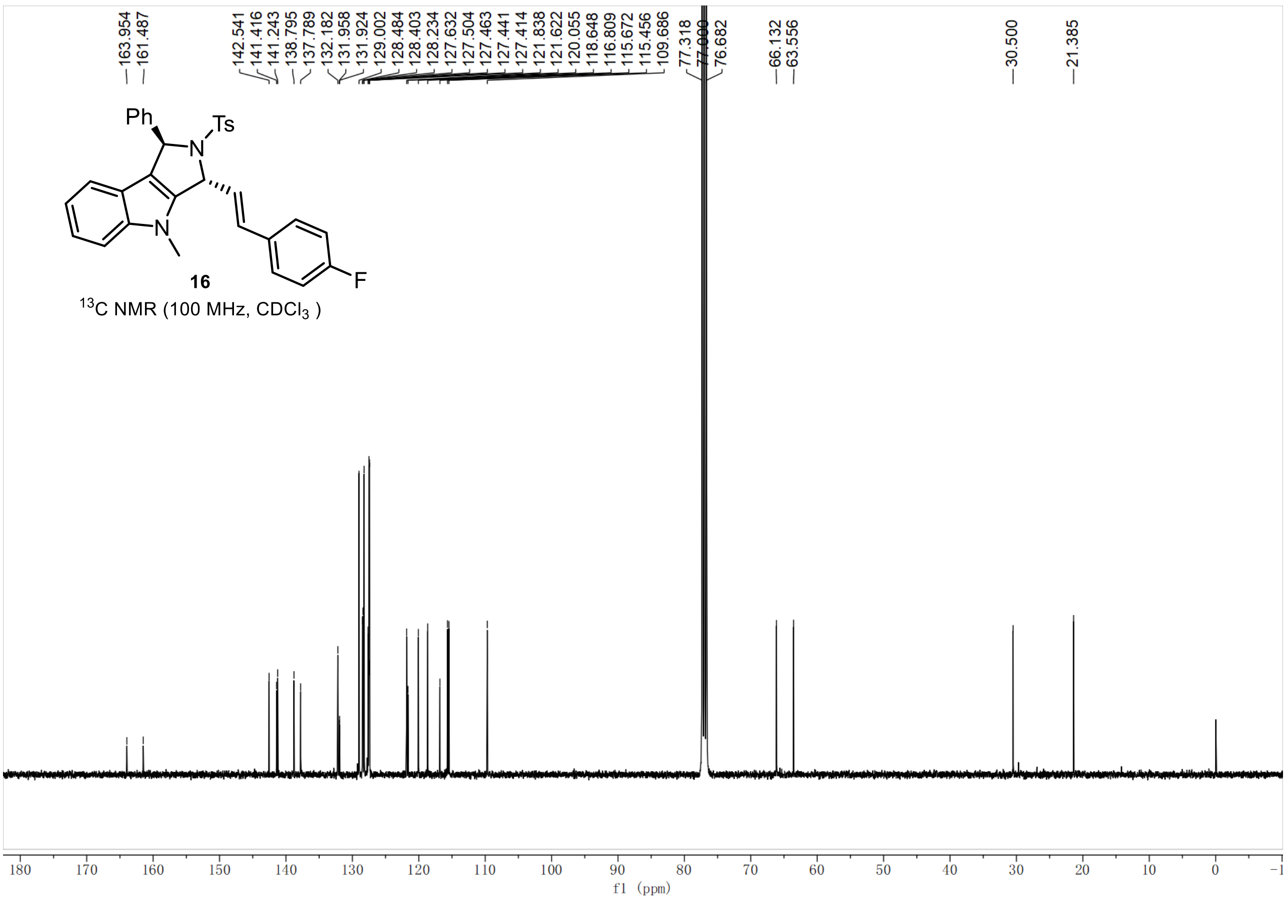

156.213
142.887
141.665
136.581
135.388
133.254
131.473
130.034
129.118
128.751
128.692
127.927
125.855
122.859
121.572
121.458
120.054
119.920
119.825
110.402
92.637
77.318
77.000
76.683
48.146
15.484
Ph
CN
N
Bn
15
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.285 min) Frag=175.0V CYC-220704-16-1.d
x10^5
Ph
CN
N
Bn
15
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C27H20N2Na+ 395.1519
395.1526
Counts vs. Mass-to-Charge (m/z)



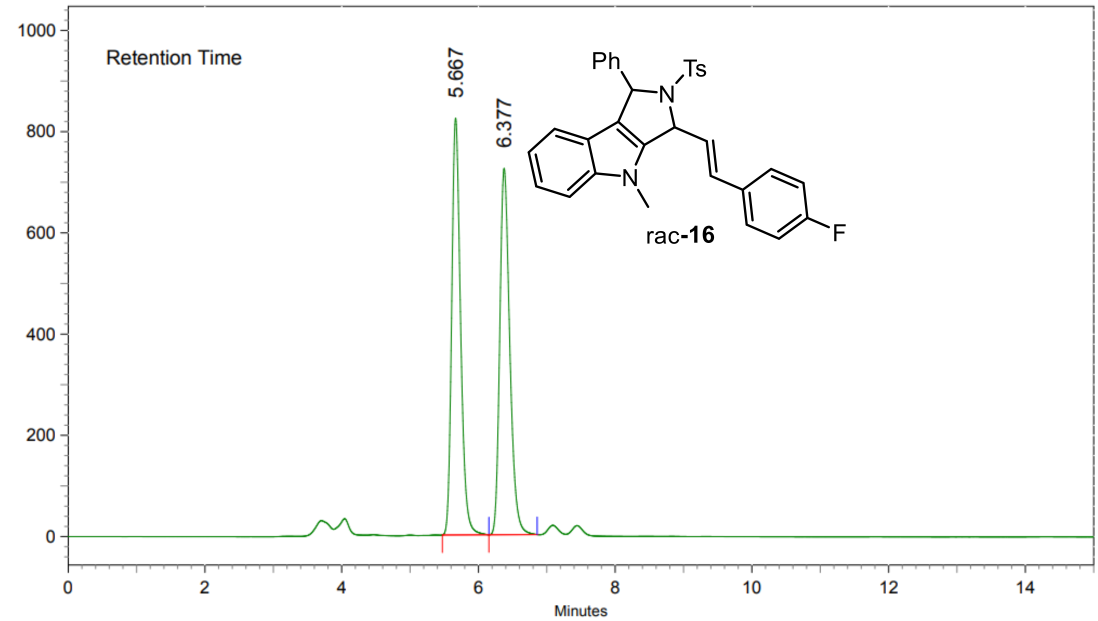
16

^{1}H NMR (400 MHz, $CDCl_3$)



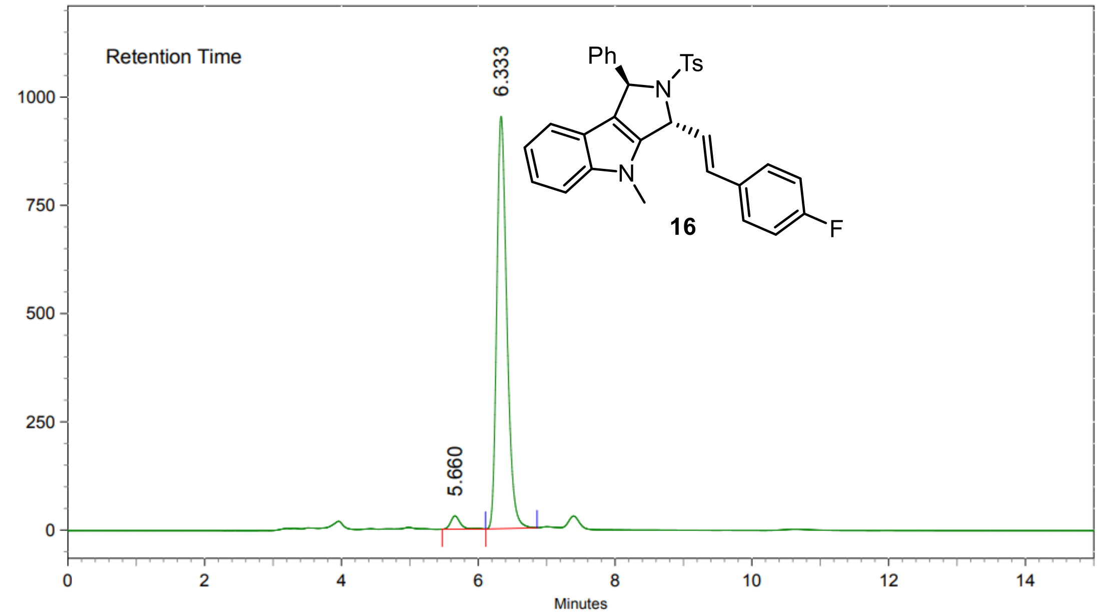
16

^{13}C NMR (100 MHz, $CDCl_3$)



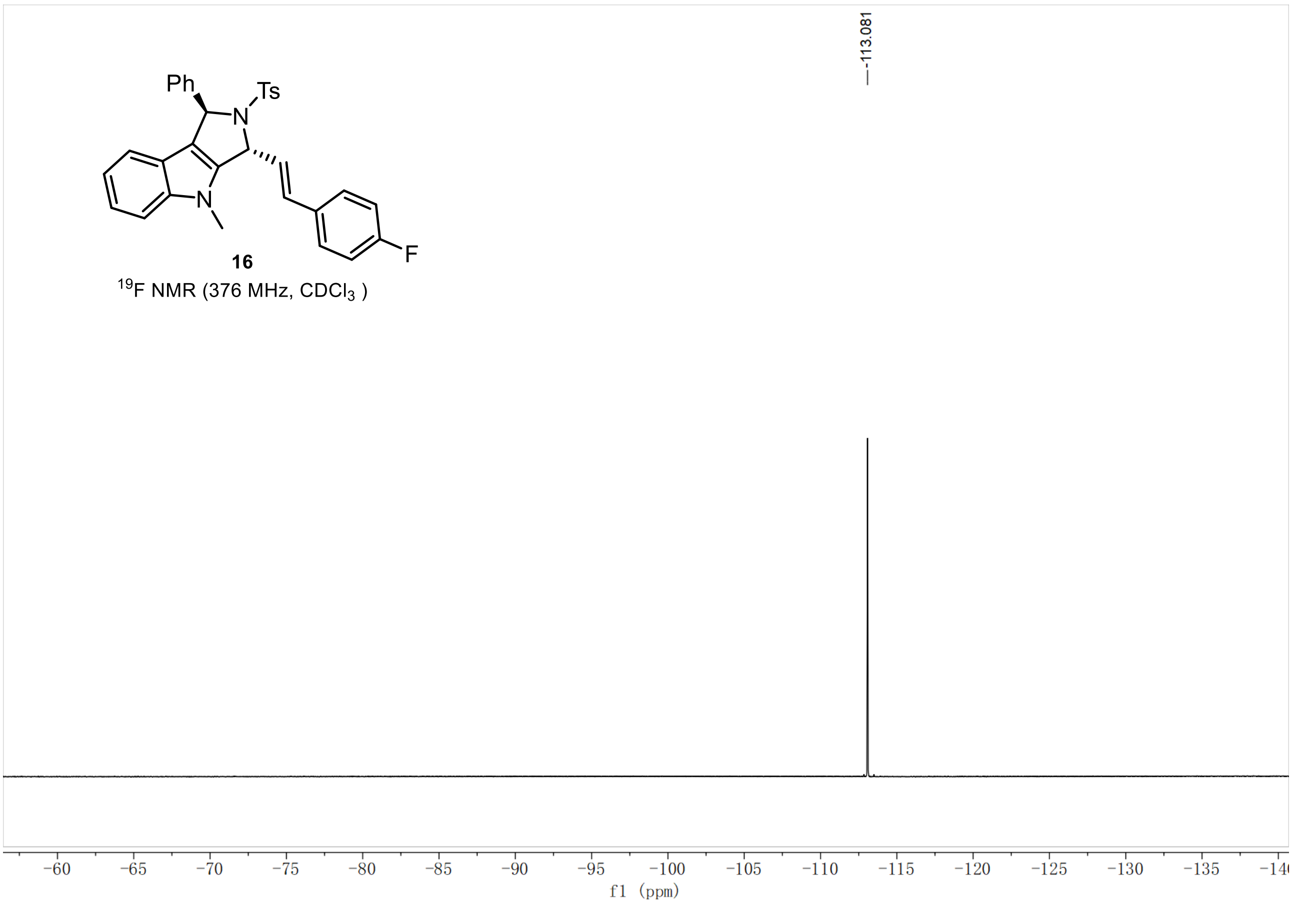
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.667	0.680	13816775	124349448	50.1392
2	6.377	0.707	12141863	123659064	49.8608

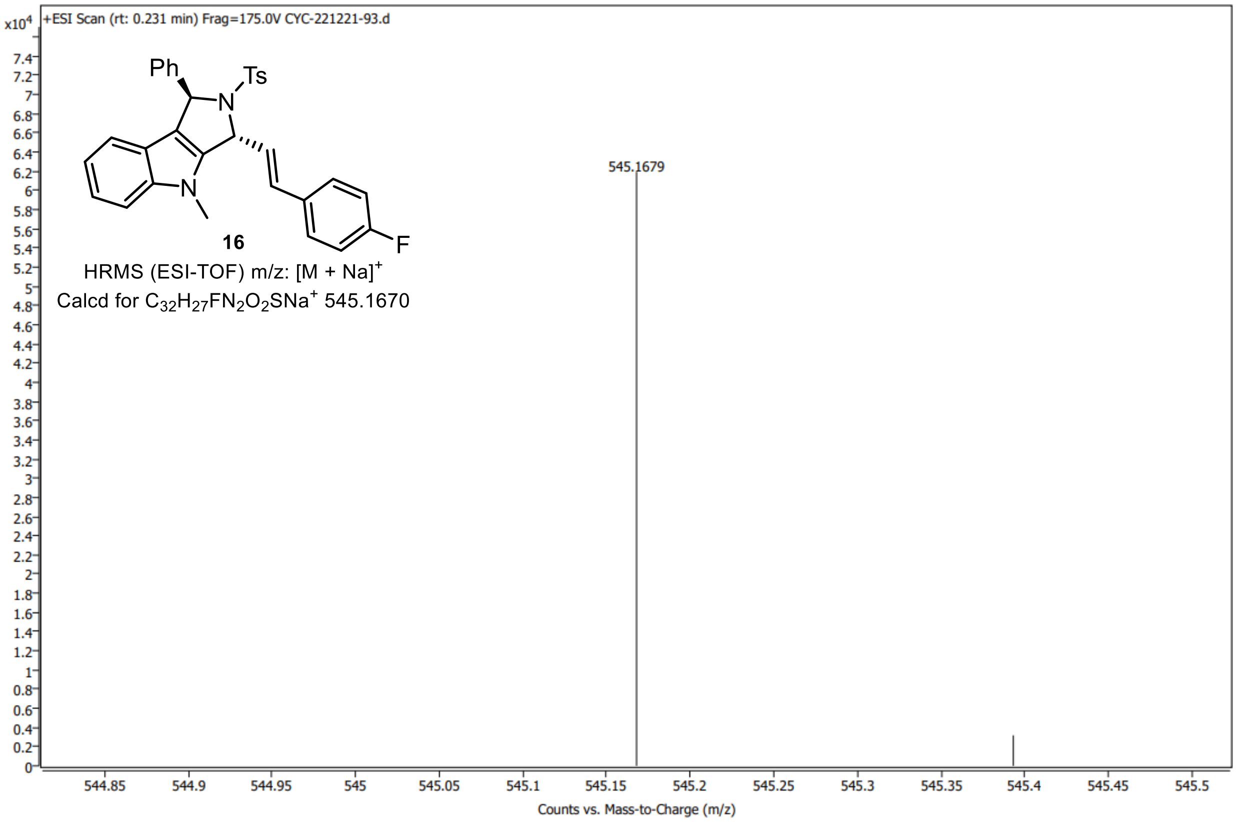


AREA PERCENT REPORT

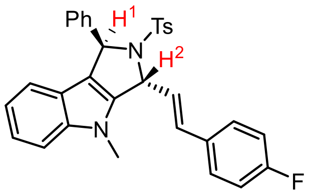
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.660	0.633	511382	5037454	2.9866
2	6.333	0.750	15979081	163631377	97.0134



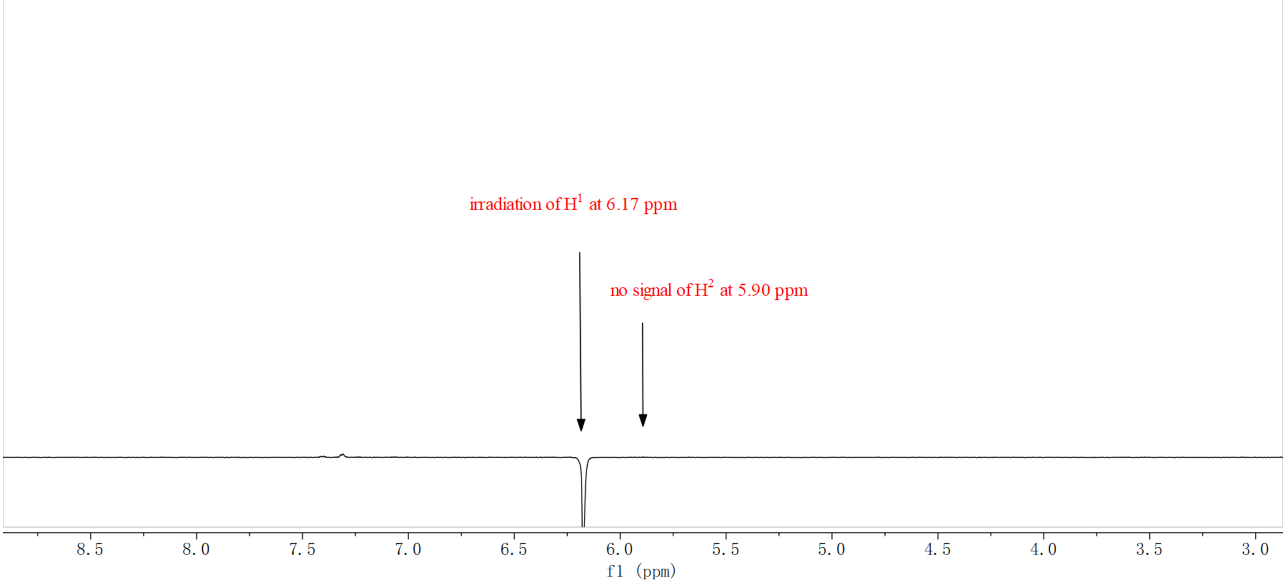
—113.081
Ph
N
Ts
N
F
16
^{19}F NMR (376 MHz, $CDCl_3$)
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
−135
f1 (ppm)

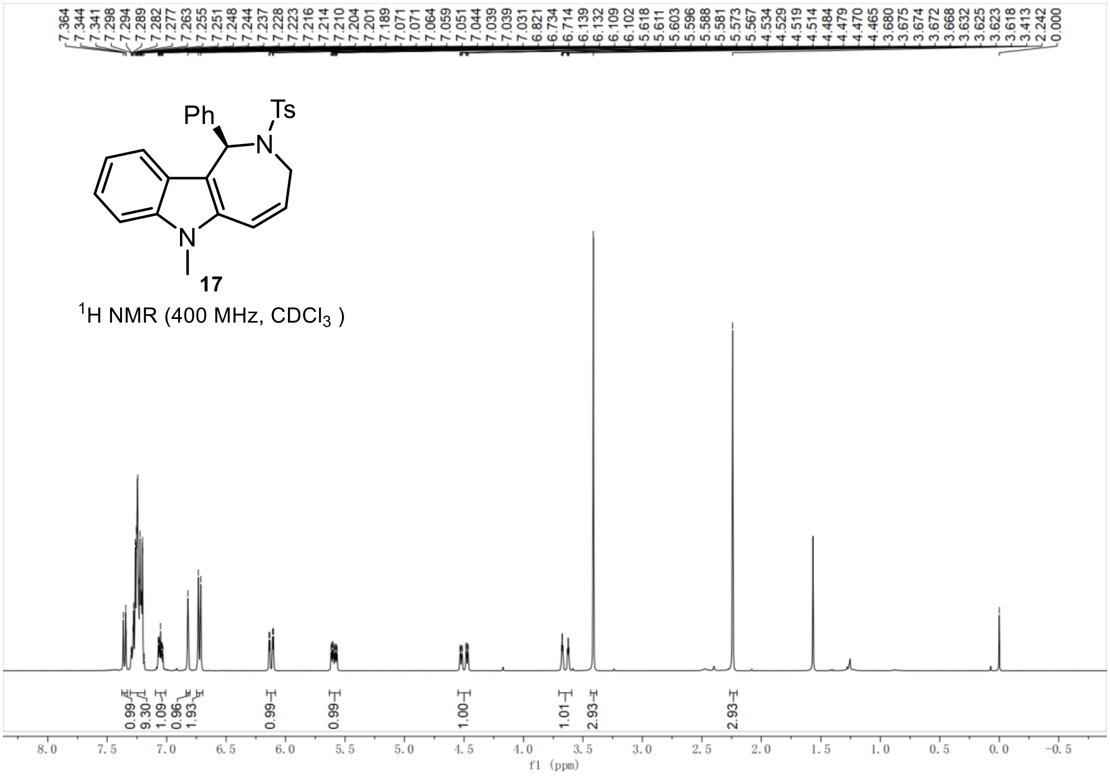


x10^4
+ESI Scan (rt: 0.231 min) Frag=175.0V CYC-221221-93.d
Ph
N
Ts
N
F
16
HRMS (ESI-TOF) m/z: [M + Na]$^+$
Calcd for $C_{32}H_{27}FN_2O_2SNa^+$ 545.1670
545.1679
544.85
544.9
544.95
545
545.05
545.1
545.15
545.2
545.25
545.3
545.35
545.4
545.45
545.5
Counts vs. Mass-to-Charge (m/z)

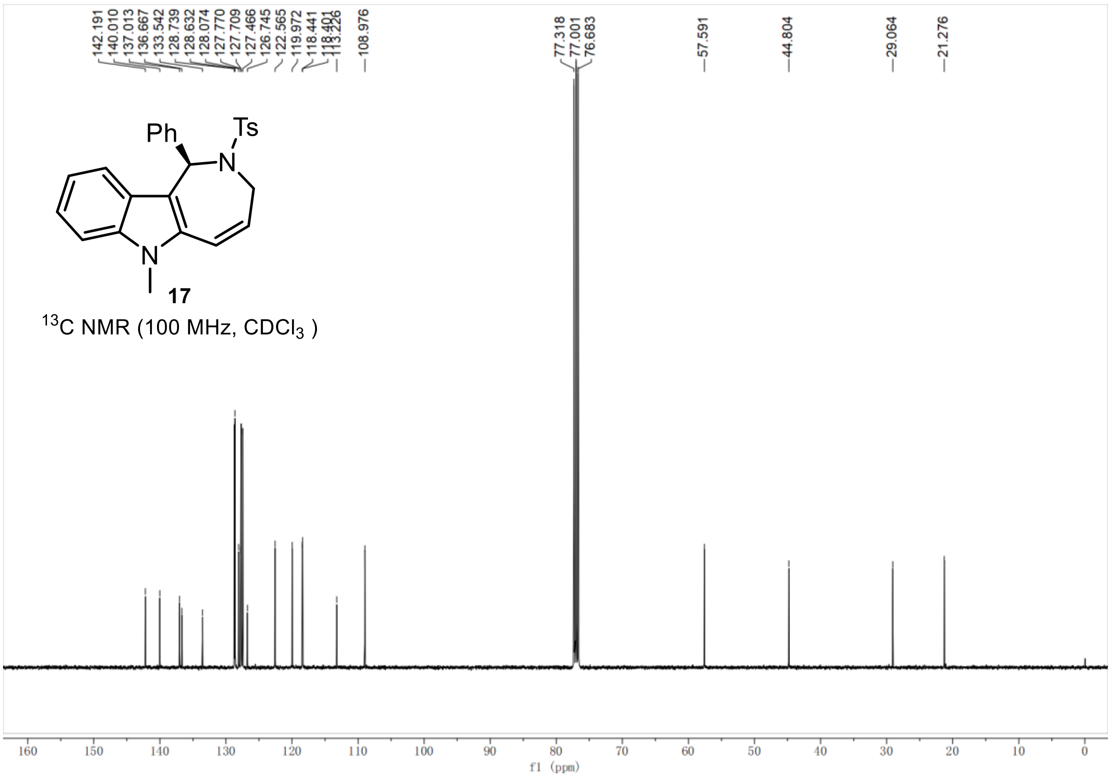


16, **NOEDS, 6.17 ppm**
NOEDS NMR (600 MHz, CDCl3)

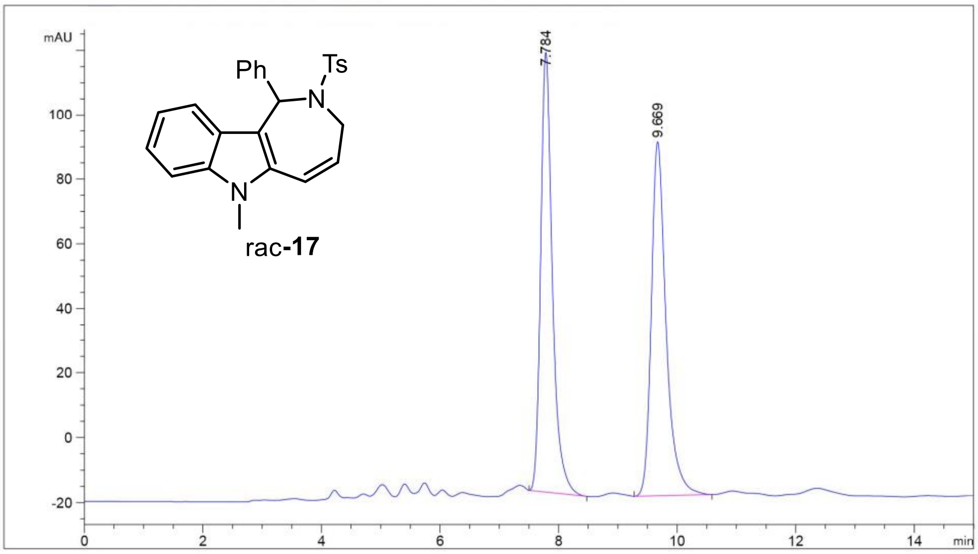




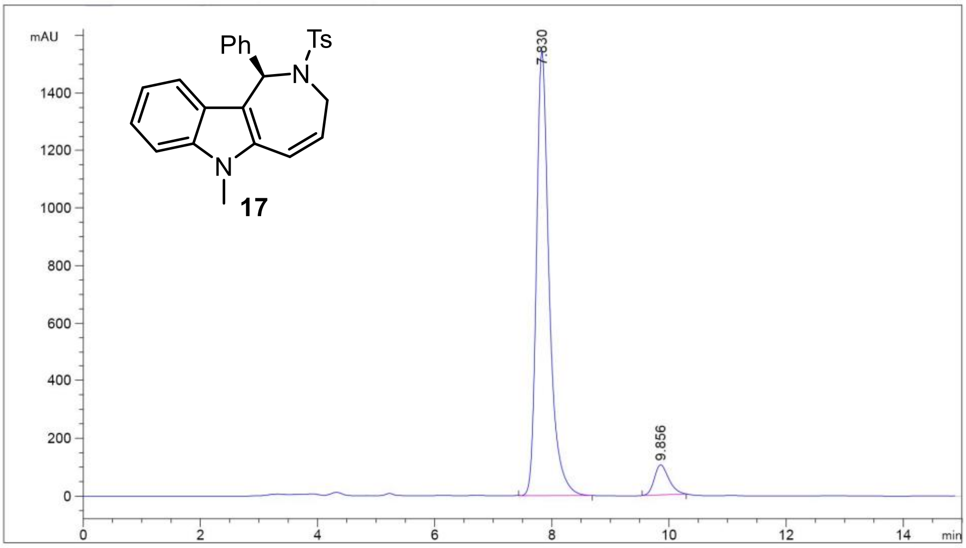
7.364 7.344 7.341 7.298 7.294 7.289 7.282 7.277 7.263 7.255 7.251 7.248 7.244 7.237 7.228 7.223 7.216 7.214 7.210 7.204 7.201 7.189 7.071 7.071 7.064 7.059 7.051 7.044 7.039 7.039 7.031 6.821 6.734 6.714 6.139 6.132 6.109 6.102 5.618 5.611 5.603 5.596 5.588 5.581 5.573 5.567 4.534 4.529 4.519 4.514 4.484 4.479 4.470 4.465 3.680 3.675 3.674 3.672 3.668 3.632 3.625 3.623 3.618 3.413 2.242 0.000
Ph
Ts
N
N
17
^{1}H NMR (400 MHz, CDCl$_3$)
0.99 9.30 1.09 0.96 1.93 0.99 0.99 1.00 1.01 2.93 2.93
f1 (ppm)



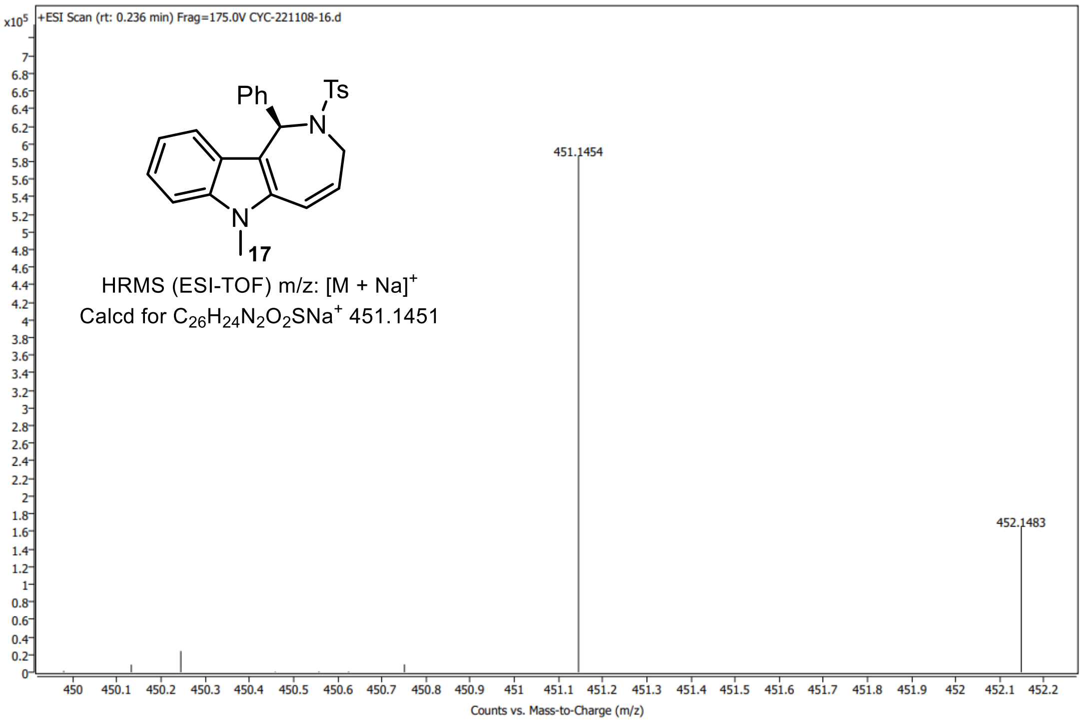
142.191 140.010 137.013 136.667 133.542 128.739 128.632 128.074 127.770 127.709 127.466 126.745 122.565 119.972 118.441 113.401 113.226 108.976
77.318 77.001 76.683
57.591
44.804
29.064
21.276
Ph
Ts
N
N
17
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

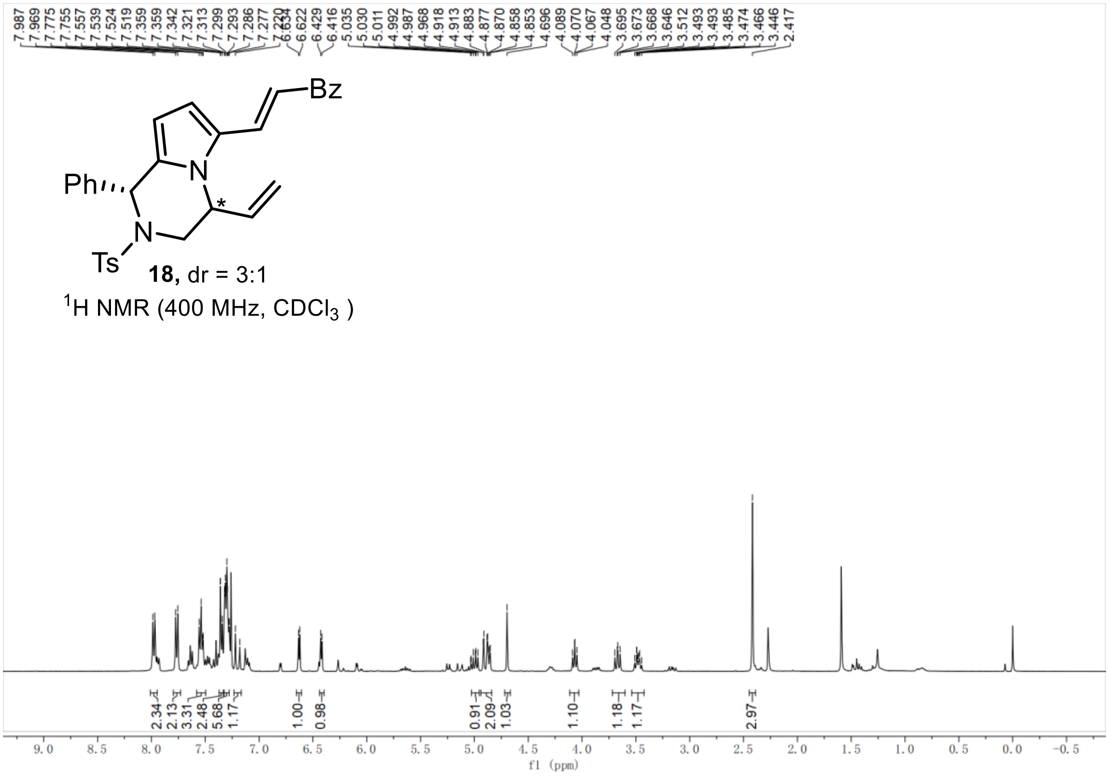


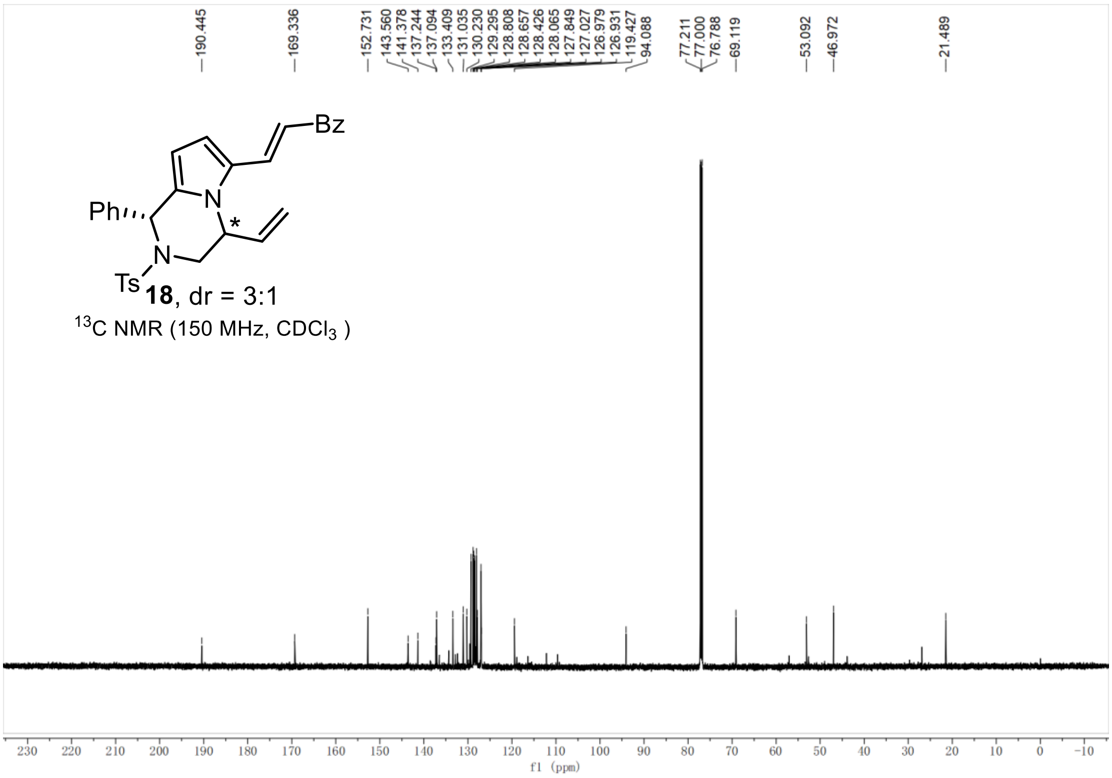
#	[min]		[min]	[mAU*s]	[mAU]	%
1	7.784	BB	0.2059	1859.19116	136.14977	49.5583
2	9.669	BBA	0.2585	1892.33118	109.43252	50.4417

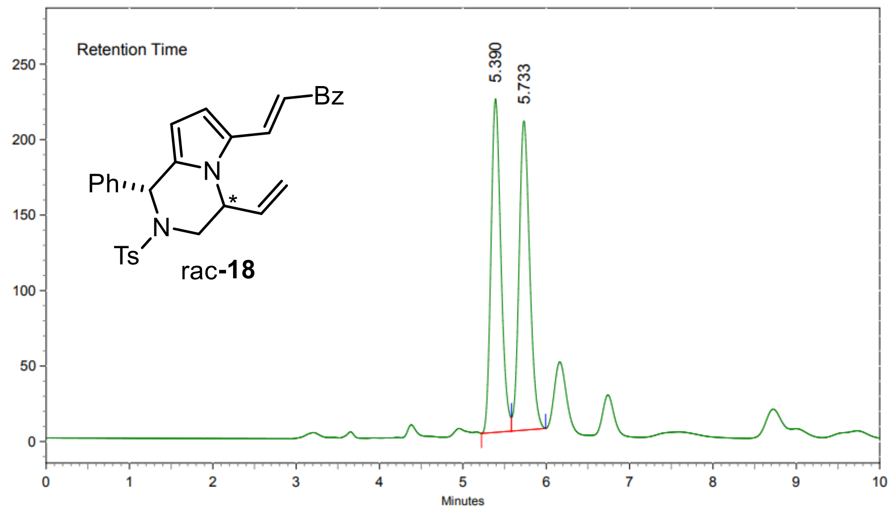


#	[min]		[min]	mAU *s	[mAU]	%
1	7.830	VBA	0.2273	2.33143e4	1542.44690	92.9078
2	9.856	BBA	0.2616	1779.71838	103.58669	7.0922


+ESI Scan (rt: 0.236 min) Frag=175.0V CYC-221108-16.d
x10^5
Ph
Ts
N
N
17
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C26H24N2O2SNa+ 451.1451
451.1454
452.1483
Counts vs. Mass-to-Charge (m/z)

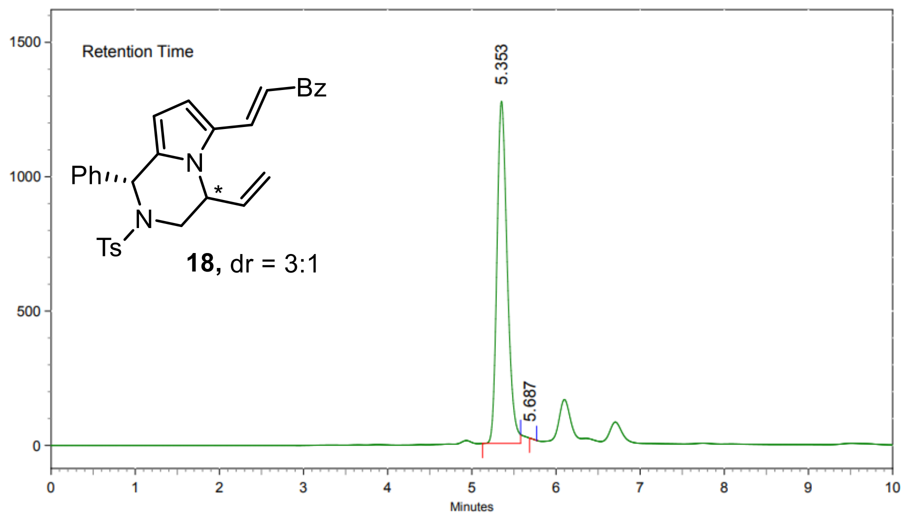






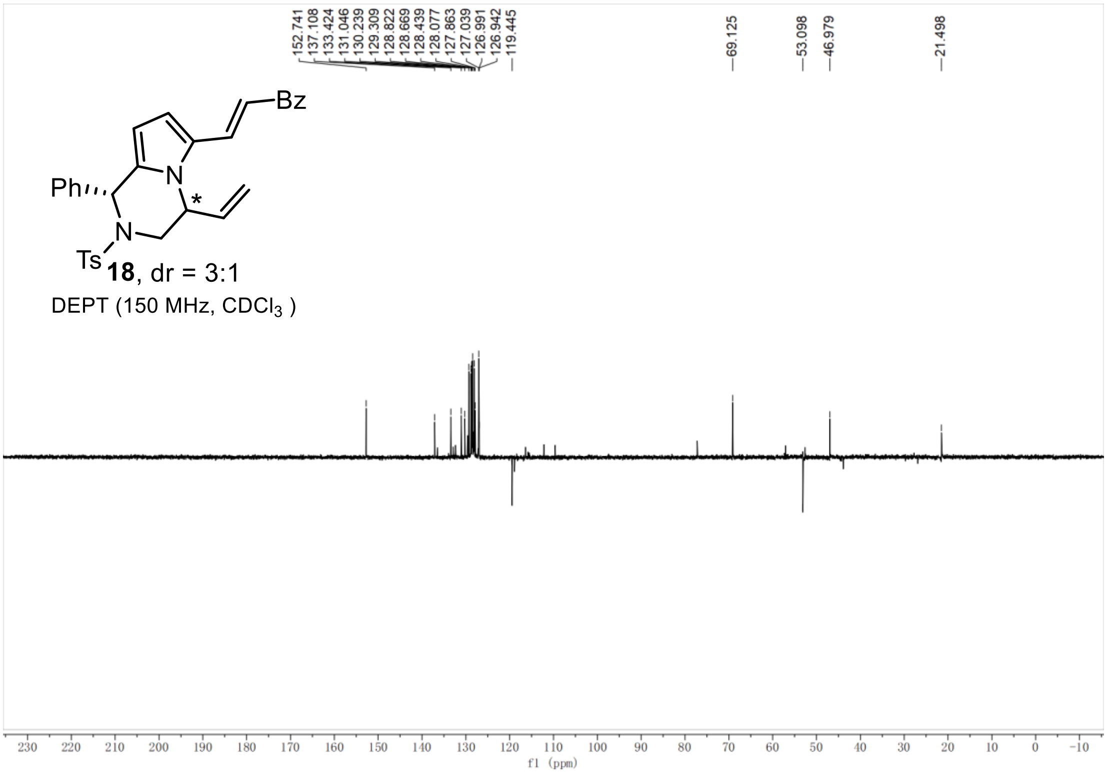
AREA PERCENT REPORT

Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.390	0.360	3705253	30571708	50.0149
2	5.733	0.410	3435941	30553461	49.9851

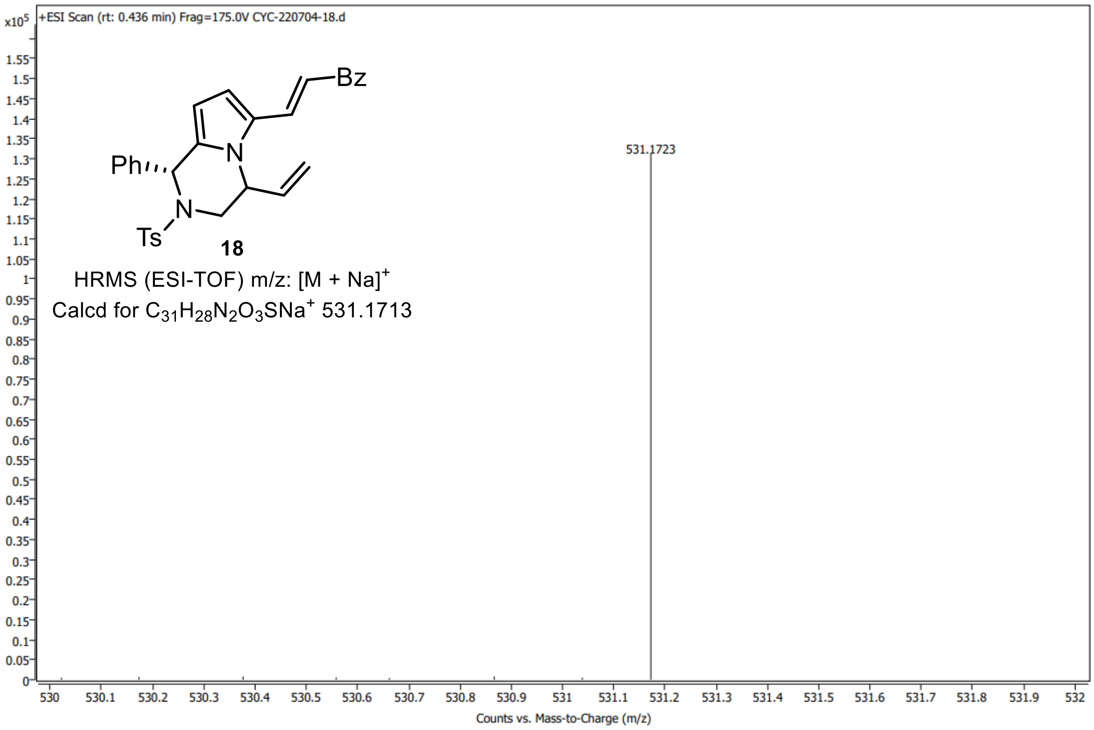


AREA PERCENT REPORT

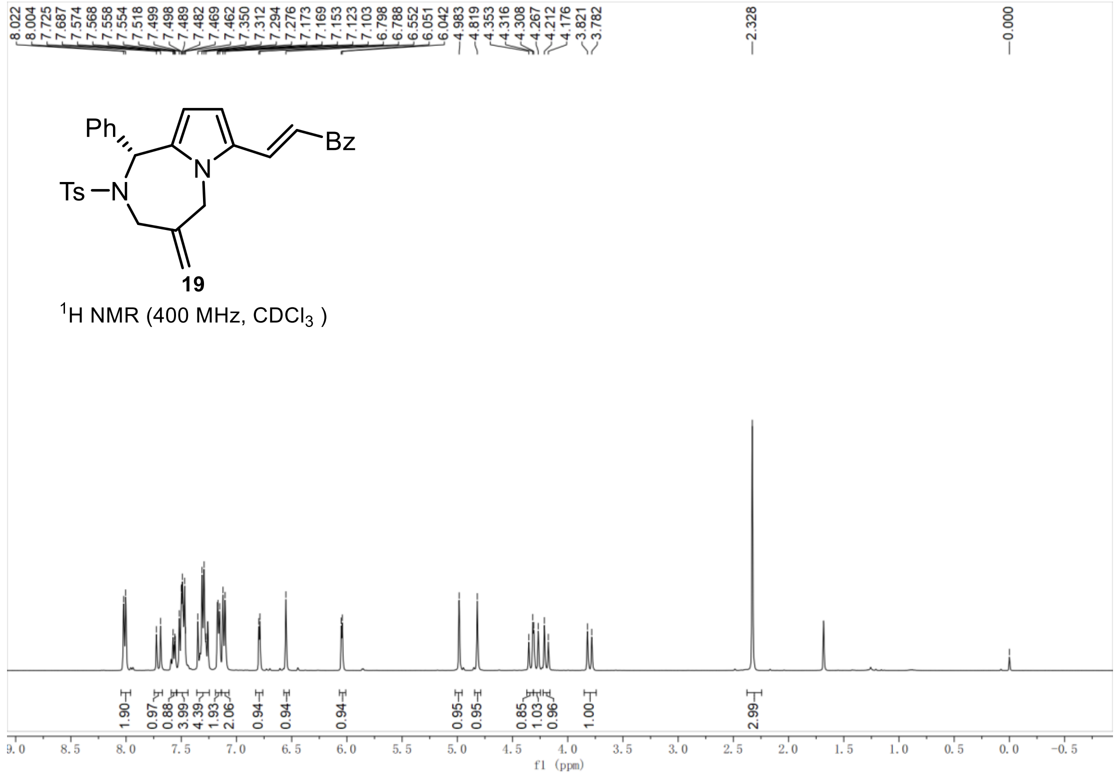
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.353	0.453	21355708	181135446	99.9939
2	5.687	0.083	0	11068	0.0061



152.741
137.108
133.424
131.046
130.239
129.309
128.822
128.669
128.439
128.077
127.863
127.039
126.991
126.942
119.445
69.125
53.098
46.979
21.498
Bz
Ph
N
N
Ts
18, dr = 3:1
DEPT (150 MHz, CDCl3)
f1 (ppm)

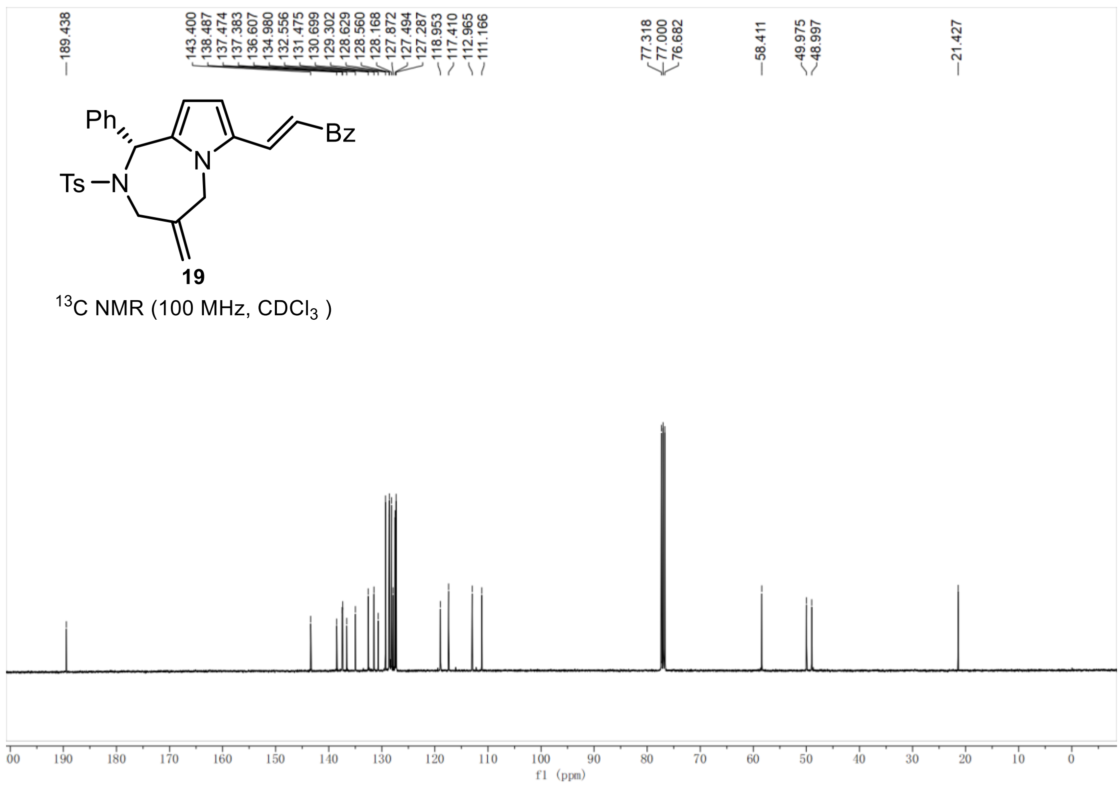


+ESI Scan (rt: 0.436 min) Frag=175.0V CYC-220704-18.d
531.1723
Bz
Ph
N
N
Ts
18
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C31H28N2O3SNa+ 531.1713
Counts vs. Mass-to-Charge (m/z)



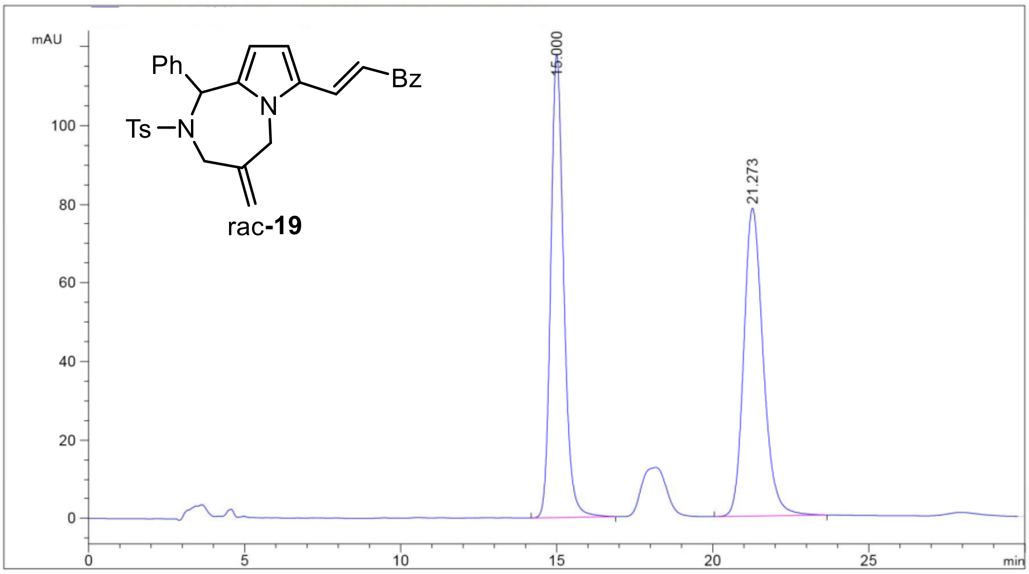
19

^{1}H NMR (400 MHz, $CDCl_3$)

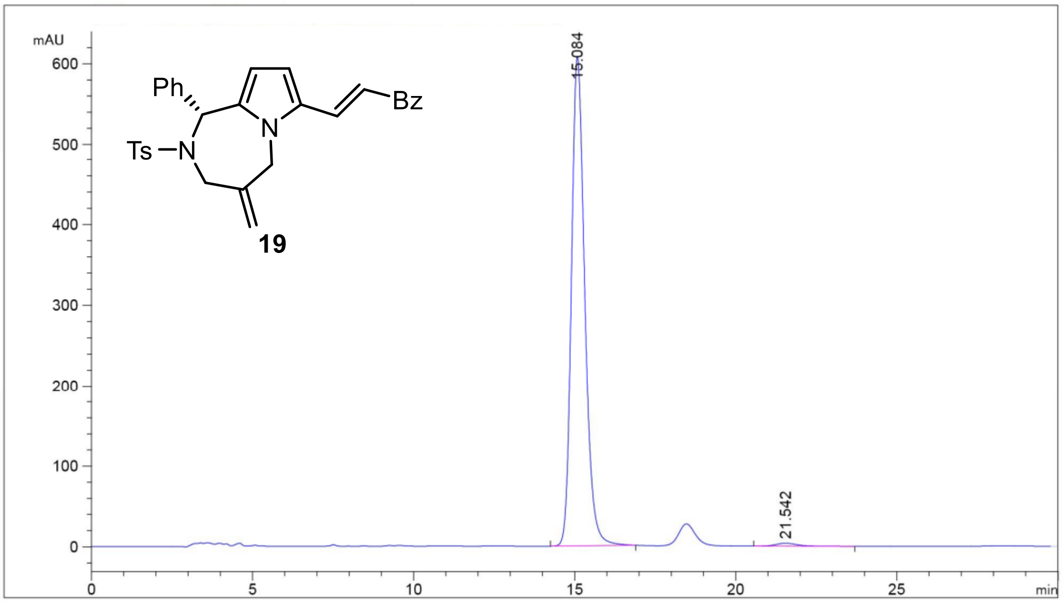


19

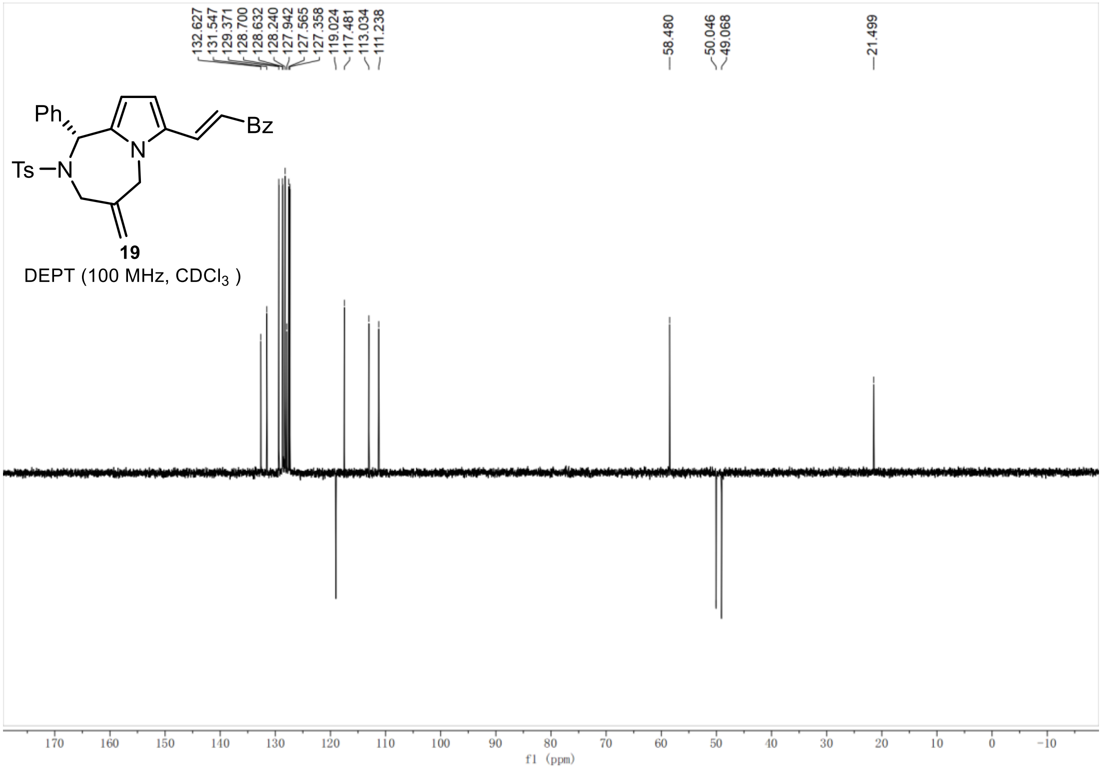
^{13}C NMR (100 MHz, $CDCl_3$)

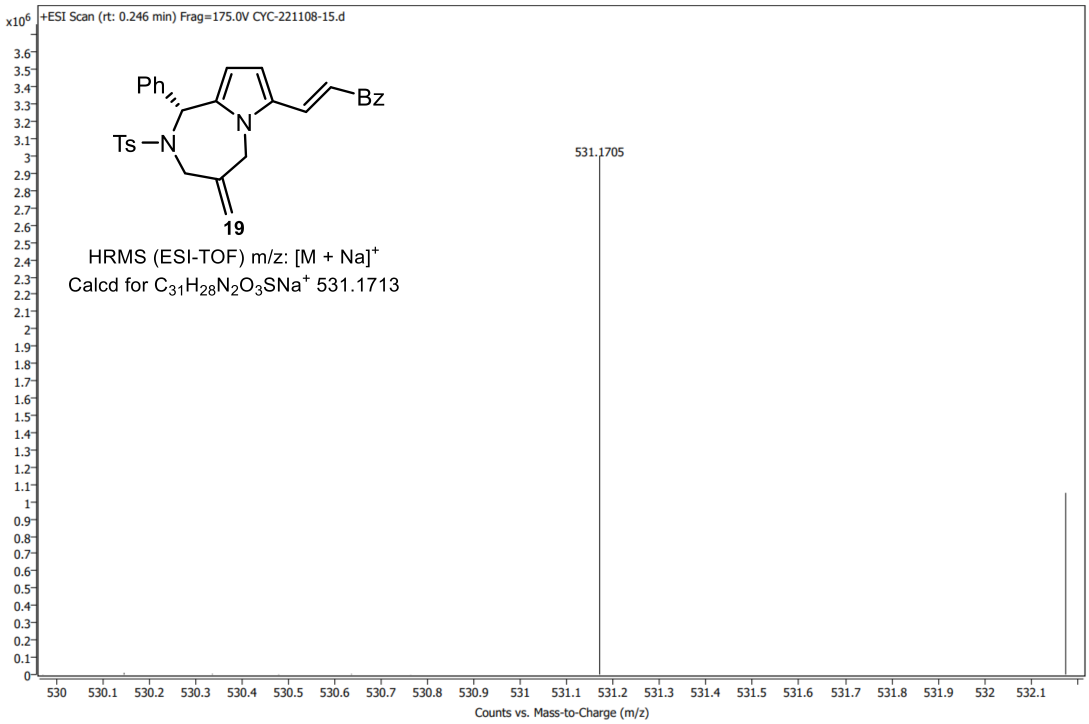


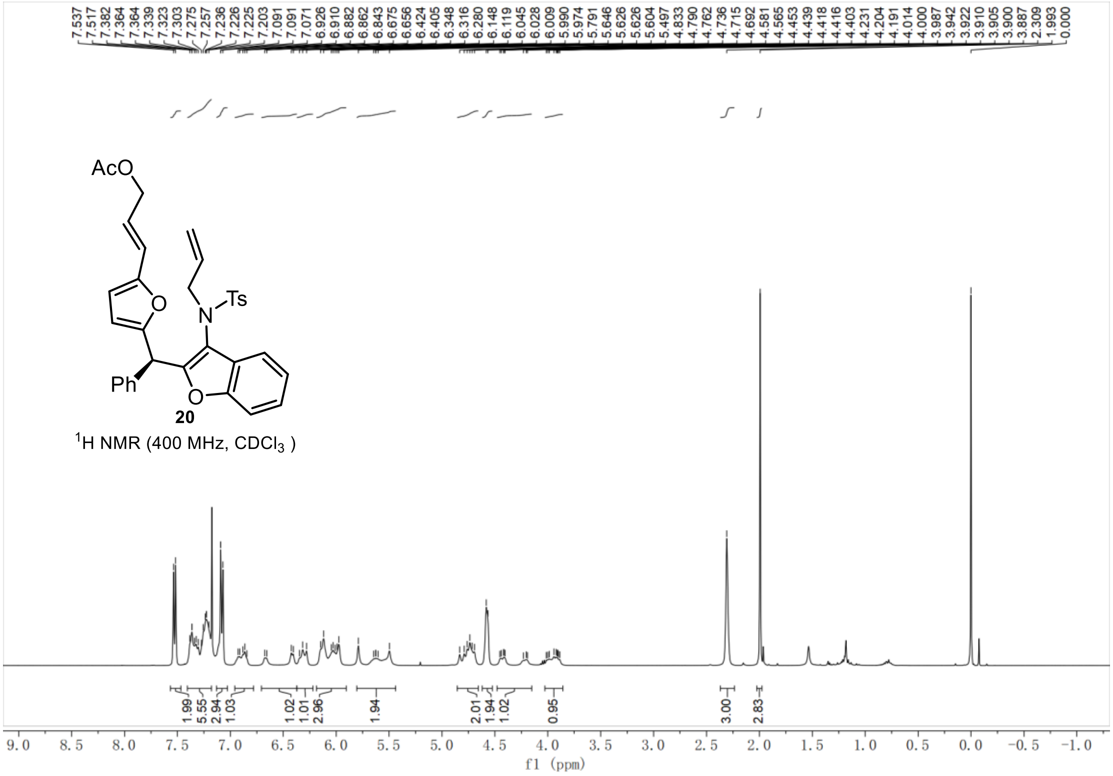
#	[min]		[min]	mAU *s	[mAU]	%
1	15.000	BBA	0.4415	3401.80054	117.89696	49.9901
2	21.273	BB	0.6625	3403.14160	78.58511	50.0099

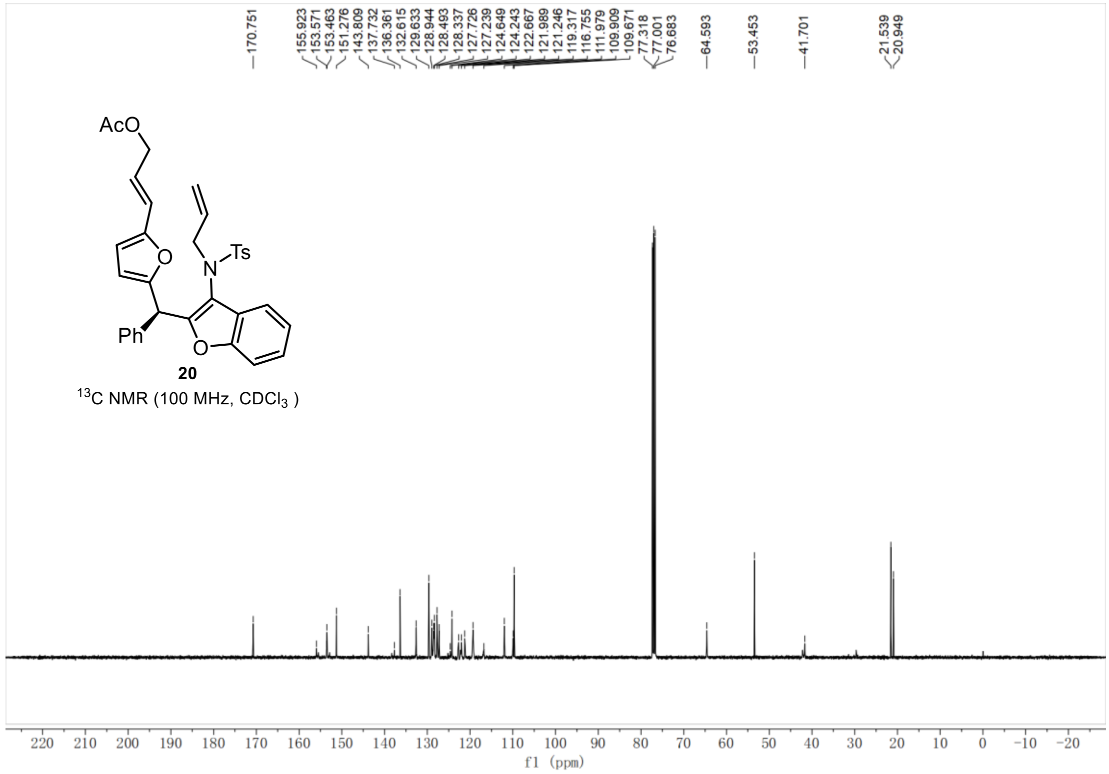


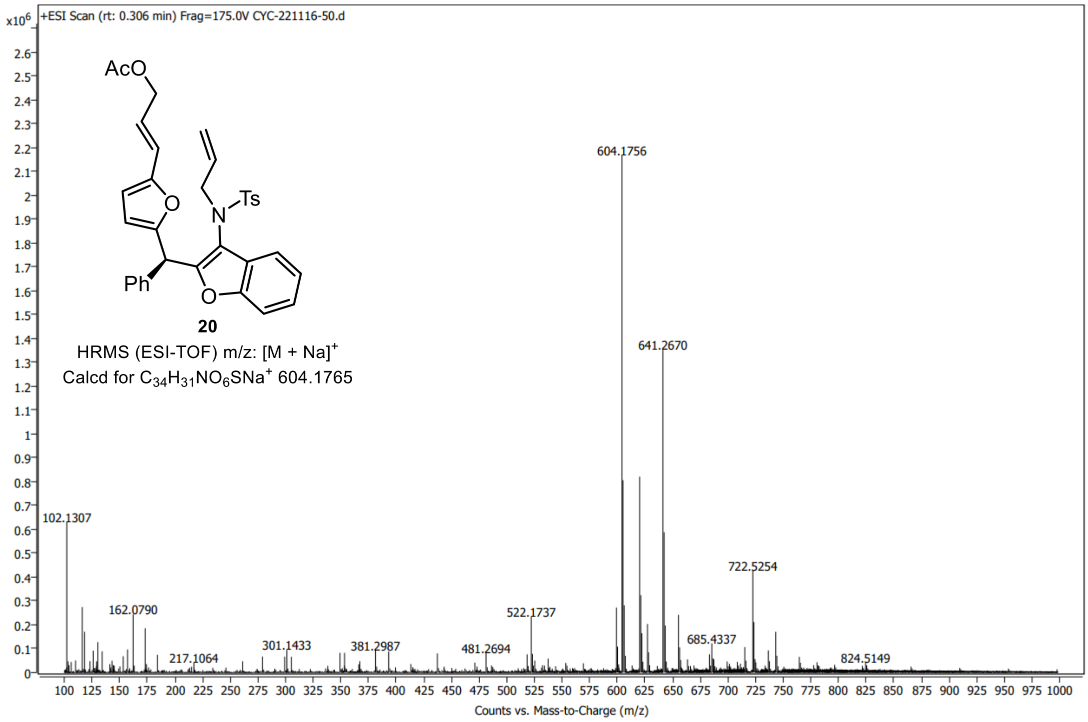
#	[min]		[min]	mAU *s	[mAU]	%
1	15.084	BBA	0.4401	1.74824e4	608.33490	99.0550
2	21.542	BB	0.6556	166.78807	3.63901	0.9450


132.627
131.547
129.371
128.700
128.632
128.240
127.942
127.565
127.358
119.024
117.481
113.034
111.238
58.480
50.046
49.068
21.499
Ph
Bz
Ts
N
N
19
DEPT (100 MHz, $CDCl_3$)
f1 (ppm)

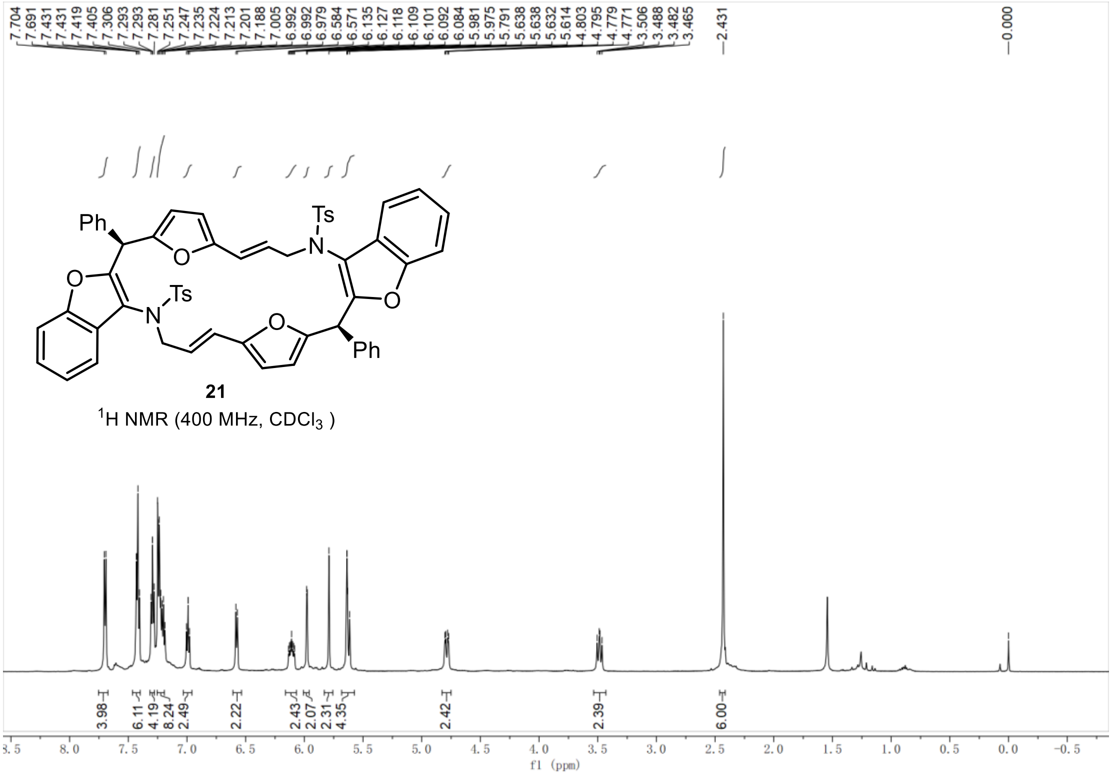

+ESI Scan (rt: 0.246 min) Frag=175.0V CYC-221108-15.d
x10^6
531.1705
Ph
Bz
Ts
N
N
19
HRMS (ESI-TOF) m/z: $[M + Na]^+$
Calcd for $C_{31}H_{28}N_2O_3SNa^+$ 531.1713
Counts vs. Mass-to-Charge (m/z)


AcO
N
Ts
O
Ph
O
20
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)


AcO
N
Ts
O
Ph
O
20
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)

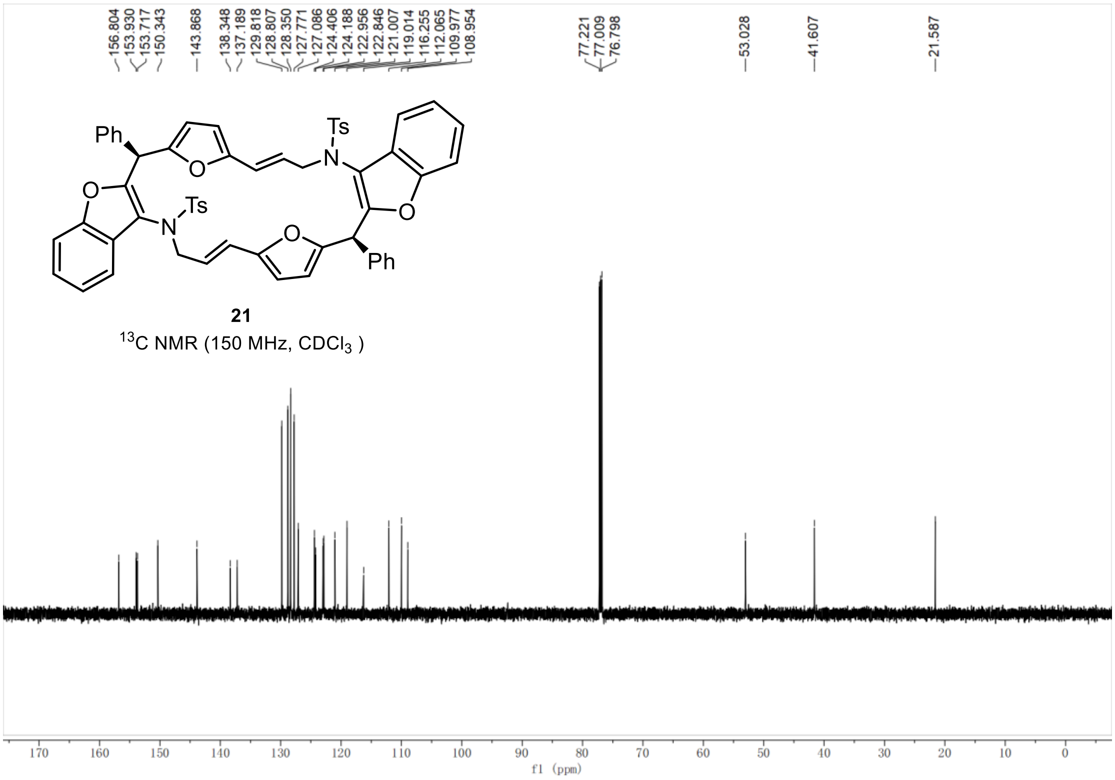


Page 1 of 1 Generated at 7:49 PM on 11/18/2022



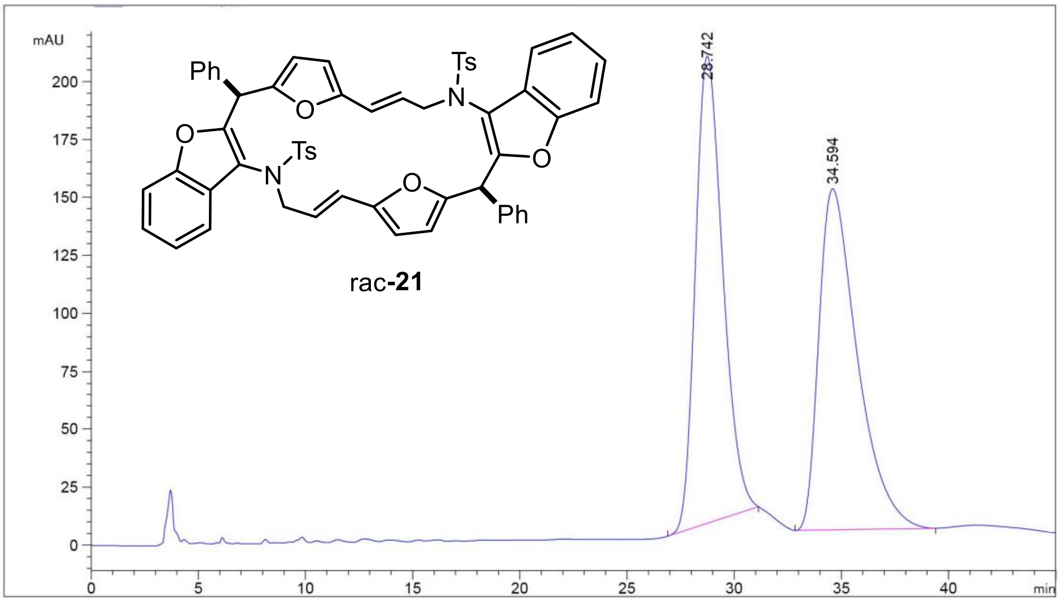
21

^{1}H NMR (400 MHz, $CDCl_3$)

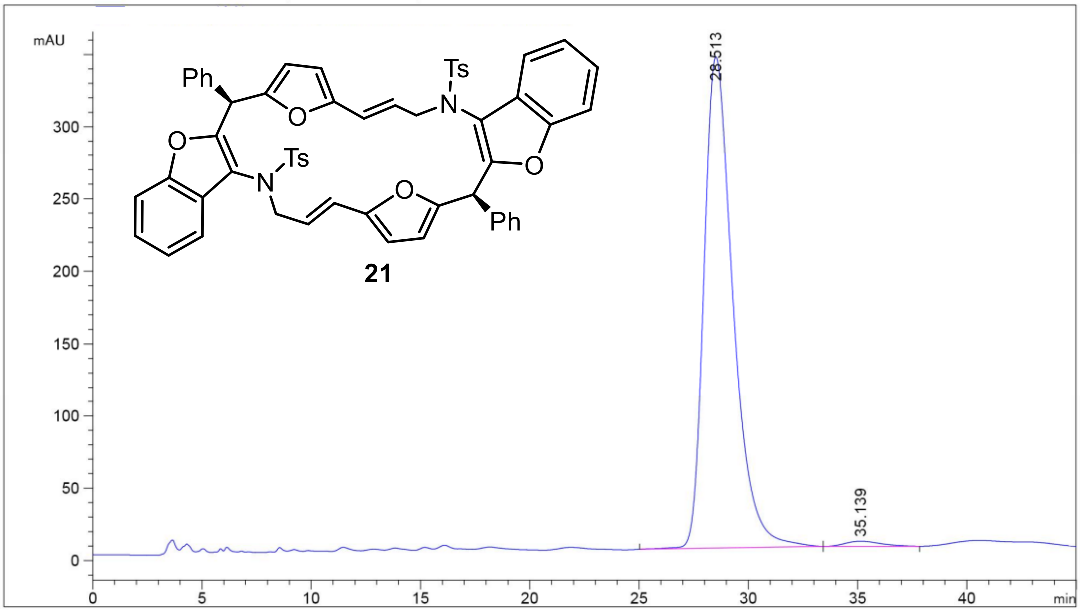


21

^{13}C NMR (150 MHz, $CDCl_3$)



#	[min]		[min]	mAU *s	[mAU]	%
1	28.742	BBA	1.3556	1.78390e4	201.59328	49.3382
2	34.594	BB	1.8529	1.83176e4	146.98248	50.6618



#	[min]		[min]	mAU *s	[mAU]	%
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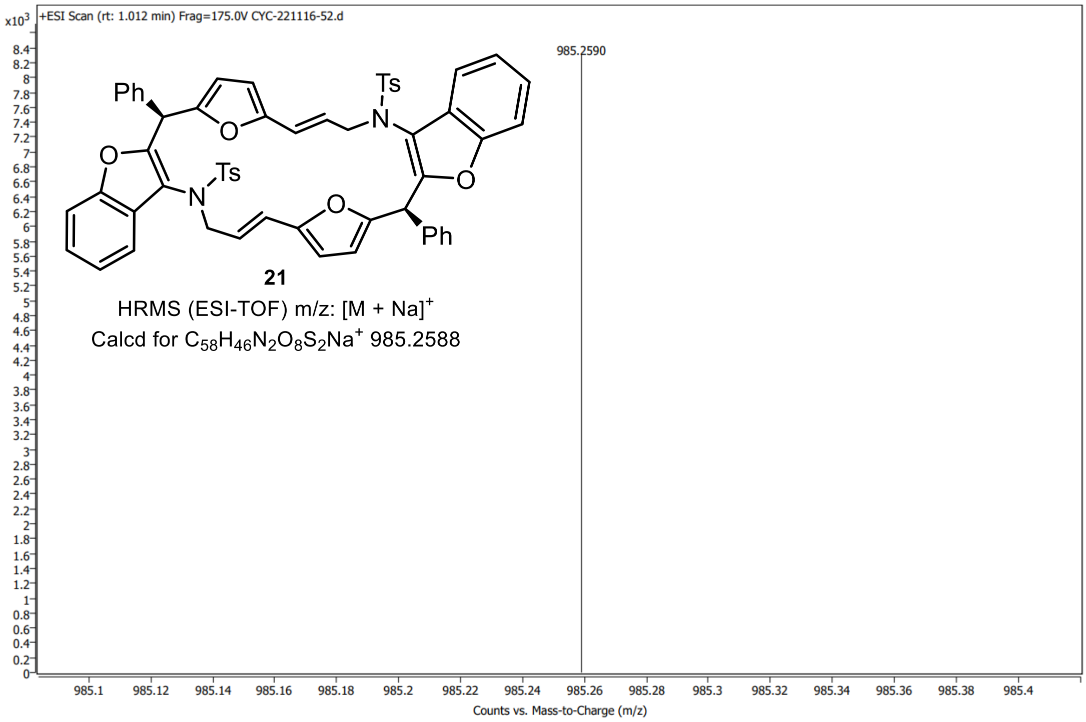
2	35.139	BB	1.3174	400.49359	3.57047	1.2589


+ESI Scan (rt: 1.012 min) Frag=175.0V CYC-221116-52.d
x10^3
985.2590
21
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for C58H46N2O8S2Na+ 985.2588
Counts vs. Mass-to-Charge (m/z)

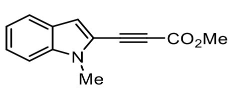
19. Computational details

1) Absolute Calculation Energies, Enthalpies, and Free Energies

Geometry	$E_{(\text{elec-B3})}$[1]	$G_{(\text{corr-B3})}$[2]	$H_{(\text{corr-B3})}$[3]	$E_{(\text{solv, M06})}$[4]	IF[5]
(*R*,*S*)-TS	-4224.837456	1.057278	1.253668	-4223.320381	*326.35i*
(*R*,*R*)-TS	-4224.833453	1.056277	1.253795	-4223.317726	*313.95i*
(*S*,*R*)-TS	-4224.819943	1.055002	1.253119	-4223.313514	*227.69i*
(*S*,*S*)-TS	-4224.815116	1.055172	1.253309	-4223.310020	*269.03i*
(*R*,*S*)-TS-II	-4224.822610	1.054981	1.253520	-4223.303477	*341.04i*
(*R*,*S*)-TS2	-4224.836034	1.055585	1.251349	-4223.323011	218.11*i*
I	-3478.600656	0.850089	1.012213	-3477.407463	-
(*R*,*S*)-II	-4224.839988	1.059184	1.255204	-4223.328724	-
(*S*)-III	-4224.867259	1.058267	1.255826	-4223.356108	-
2a	-746.260011	0.180539	0.240081	-745.918135	-
(*S*,*R*)-3b-(*E*)	-1684.500785	0.452774	0.556429	-1683.772500	-
(*S*,*R*)-3b-(*Z*)	-1684.492408	0.451968	0.556531	-1683.761263	-
(*S*,*S*)-3b-(*E*)	-1684.495472	0.453354	0.556316	-1683.769379	-
(*S*)-4a-(*E*)	-1790.450200	0.379823	0.479381	-1789.827674	-
(*S*)-4a-(*Z*)	-1790.448115	0.379014	0.479535	-1789.826573	-

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M06 in 1,4-Dioxane solvent. [5]The B3LYP calculated imaginary frequencies for the transition states.

2) Geometries for All Optimized Structures



C	-4.85066500	-0.67407700	-0.00001300
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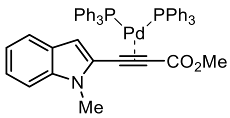
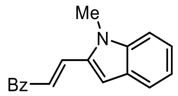
C	-3.44450300	1.32628400	0.00005200
C	-2.32717400	0.47816900	0.00003700
C	-2.45800500	-0.94290800	-0.00000400
C	-3.74720300	-1.51224600	-0.00002500
N	-0.98851000	0.79083400	0.00004500
C	-0.25916800	-0.40538100	0.00000000
C	-1.13888700	-1.47707800	0.00001400
C	-0.43724700	2.13231600	-0.00009700
C	1.14628300	-0.42362000	-0.00002200
C	2.36322500	-0.42533200	-0.00002700

C	3.79930500	-0.51669000	-0.00001200
O	4.42542000	-1.55813000	-0.00001000
O	4.36430900	0.71345500	0.00001700
C	5.80138700	0.71563400	0.00003700
H	-5.85048100	-1.09887800	-0.00003400
H	-5.58490300	1.36095200	0.00003300
H	-3.33649100	2.40682500	0.00009000
H	-3.86917700	-2.59204700	-0.00003400
H	-0.84575100	-2.51738300	0.00001300
H	-0.75767300	2.68330500	-0.89181500
H	-0.75810700	2.68363800	0.89125900
H	0.65165200	2.06496300	0.00019400
H	6.08858700	1.76748400	0.00002100
H	6.18722200	0.21077700	0.88983000
H	6.18724600	0.21074200	-0.88972600



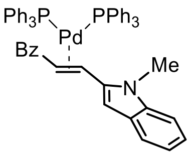
C	-7.74531400	0.34814600	0.37927500
C	-7.81619300	1.69973100	-0.02150300
C	-6.66687500	2.45734800	-0.21808700
C	-5.42987500	1.83191400	-0.00828100
C	-5.33805500	0.47024300	0.40385700
C	-6.52068000	-0.26909100	0.59303800
N	-4.15033600	2.32906400	-0.13510600
C	-3.23768700	1.31618000	0.20935100
C	-3.95009300	0.17347500	0.52869900
C	-3.82602000	3.69099600	-0.50824300
C	-1.82103600	1.53389200	0.21473300
C	-0.86701000	2.39695100	0.22406600
C	-0.46182400	3.78441000	0.37334400
O	-0.19525900	4.33832800	1.42438600
O	-0.39792400	4.41774800	-0.83033200
C	0.02622800	5.78943000	-0.77674400
H	-8.66514800	-0.21228800	0.52419200
H	-8.78865100	2.16020100	-0.17499500
H	-6.73446200	3.49986900	-0.51525000
H	-6.47083000	-1.30964500	0.90402500
H	-3.51163500	-0.77013700	0.81519500
H	-4.58317700	4.06288900	-1.20434800
H	-3.79328200	4.35699200	0.36437800
H	-2.85710600	3.71894000	-1.00777600
H	-0.01466100	6.14557100	-1.80706400
H	-0.64120700	6.37745000	-0.14035600
H	1.04536000	5.85867200	-0.38816900
Pd	0.02868900	0.52794000	0.14339500
P	-0.40991000	-1.82034300	-0.02219200
P	2.40934600	0.73196500	0.05543200
C	0.88722400	-3.03707400	-0.55992100
C	0.93878500	-3.51776100	-1.87718800
C	1.88175700	-3.45186300	0.34277700
C	1.94781200	-4.39676000	-2.27664500
H	0.18437900	-3.21438600	-2.59553800
C	2.88419600	-4.33628200	-0.05571300
H	1.87110300	-3.09447300	1.36727700
C	2.92009400	-4.81409800	-1.36755700
H	1.96576400	-4.75999100	-3.30088000
H	3.63610000	-4.65243200	0.66286300
H	3.69910200	-5.50587200	-1.67728300
C	-1.77012100	-2.17378300	-1.23187600
C	-2.59629200	-3.30546500	-1.15660200
C	-1.95699400	-1.27017100	-2.28895300
C	-3.58415900	-3.52676700	-2.11713000
H	-2.48135200	-4.01228900	-0.34121700
C	-2.93622500	-1.49953700	-3.25732400
H	-1.34295400	-0.37483500	-2.33733600
C	-3.75374400	-2.62716100	-3.17191500
H	-4.22333600	-4.40245900	-2.03928100
H	-3.06966300	-0.78754100	-4.06741200
H	-4.52559700	-2.80003200	-3.91713300

C	-0.99650700	-2.55996800	1.57357400
C	-1.46563200	-1.69061700	2.57198500
C	-0.99741100	-3.94226900	1.83048200
C	-1.94173800	-2.18979800	3.78674100
H	-1.45472500	-0.61897400	2.39204500
C	-1.47115900	-4.43932500	3.04533100
H	-0.61156500	-4.63307000	1.08705800
C	-1.94713400	-3.56460100	4.02527100
H	-2.30377000	-1.50083400	4.54508600
H	-1.46485500	-5.51095600	3.22716300
H	-2.31409400	-3.95367200	4.97138700
C	3.08753200	-0.01803500	-1.49184500
C	2.50659200	0.40362800	-2.70236600
C	4.09861300	-0.98647600	-1.53279800
C	2.94807300	-0.10917200	-3.92110800
H	1.70504500	1.13849800	-2.68576200
C	4.52998500	-1.50979000	-2.75513900
H	4.54637900	-1.34637600	-0.61312800
C	3.96366200	-1.06901000	-3.95066800
H	2.49425700	0.23555700	-4.84668600
H	5.31080000	-2.26560700	-2.76736500
H	4.30441100	-1.47455300	-4.89969100
C	3.36311600	-0.01363400	1.45727000
C	4.75887900	0.10682900	1.56967900
C	2.65755000	-0.65396700	2.48589700
C	5.43163400	-0.43133600	2.66647600
H	5.32036000	0.63611900	0.80497800
C	3.33017600	-1.18506500	3.58998800
H	1.57489200	-0.72162300	2.42406300
C	4.71852100	-1.08092900	3.67823500
H	6.51177300	-0.33325300	2.73769100
H	2.76615300	-1.67225500	4.38102600
H	5.24360400	-1.49175800	4.53658400
C	3.15979400	2.42982700	0.03901300
C	4.10736600	2.85361100	-0.90497200
C	2.77564800	3.31653200	1.05761900
C	4.66009400	4.13473100	-0.82780000
H	4.41858300	2.18719700	-1.70276200
C	3.33408300	4.59258400	1.13689600
H	2.02499900	3.01921100	1.78331100
C	4.27908400	5.00566200	0.19398000
H	5.39292300	4.44776400	-1.56730700
H	3.01777700	5.26417700	1.93007400
H	4.71255700	6.00069200	0.25368900



C	5.51990800	-1.72125200	-0.09706700
C	5.91519800	-0.36622800	-0.01510800
C	4.98270900	0.66061900	0.04374300
C	3.62397100	0.31081500	0.02119400
C	3.20616600	-1.05224300	-0.06421200
C	4.18009200	-2.07036700	-0.12228800
N	2.49437600	1.09957700	0.06991200
C	1.36428300	0.27456100	0.00854100
C	1.78631600	-1.04579900	-0.07067400
C	2.47568500	2.54997500	0.14389900
C	0.03532300	0.82678100	0.02769000
C	-1.12807800	0.13590200	-0.01420700
C	-2.41393900	0.86567300	-0.00435000
C	-6.18397900	-1.22365200	0.00673700
C	-5.01156800	-1.94346400	0.24304100
C	-3.77713700	-1.29288700	0.23823700
C	-3.70049200	0.08904900	0.00278500
C	-4.88900800	0.80360600	-0.22218900
C	-6.11939900	0.15387900	-0.22566300
O	-2.44461800	2.09776900	-0.01508900
H	6.28164700	-2.49451200	-0.14165000
H	6.97373100	-0.12170000	0.00053900
H	5.30734900	1.69517700	0.10176800

H	3.87771300	-3.11229500	-0.18679500
H	1.13645100	-1.90829300	-0.12791700
H	3.49290200	2.91024000	0.30040600
H	2.08804000	2.99451600	-0.77998000
H	1.86251700	2.89027400	0.98426600
H	-0.06580700	1.90898800	0.07654200
H	-1.12660600	-0.94673900	-0.07573200
H	-7.14426200	-1.73267900	0.00629200
H	-5.05689300	-3.01241200	0.43308800
H	-2.88096700	-1.87063000	0.43902800
H	-4.81578100	1.87265500	-0.39165800
H	-7.03003200	0.71841100	-0.40752400



C	4.66167800	-4.35282100	2.96269900
C	5.59248200	-4.14237700	1.92415000
C	5.20033600	-3.60411400	0.70167400
C	3.85021400	-3.27198700	0.53857400
C	2.89099300	-3.49176200	1.57007800
C	3.31972300	-4.03460400	2.79603600
N	3.19406600	-2.71395000	-0.54462600
C	1.83316600	-2.59988400	-0.23959400
C	1.63259200	-3.06470600	1.05287900
C	3.82141200	-2.48426100	-1.83403000
C	0.86867800	-2.03662900	-1.17963500
C	-0.52169900	-2.28643200	-1.07849500
C	-1.36027300	-2.05306300	-2.27109400
C	-5.31174000	-3.74525300	-2.67665600
C	-4.63030700	-3.90248600	-1.46908000
C	-3.35505600	-3.35953400	-1.30442000
C	-2.74430200	-2.64631100	-2.34727700
C	-3.44396500	-2.49018000	-3.55631600
C	-4.71395500	-3.03438500	-3.72192100
O	-0.93946300	-1.40841400	-3.24261500
H	5.00196100	-4.77592400	3.90421900
H	6.63483900	-4.40802200	2.07851900
H	5.92407700	-3.45305500	-0.09385100
H	2.60621800	-4.20729800	3.59811200
H	0.68388000	-3.06604800	1.57143100
H	4.84889200	-2.14587200	-1.67793100
H	3.83901300	-3.39772900	-2.44329600
H	3.29700600	-1.70175200	-2.38113400
H	1.23159900	-1.75914600	-2.16271300
H	-0.88814100	-2.95801700	-0.31076800
H	-6.30316900	-4.17287600	-2.80351700
H	-5.09054800	-4.44444500	-0.64779900
H	-2.85425300	-3.48563300	-0.35153400
H	-2.95947300	-1.93967900	-4.35552700
H	-5.23907600	-2.90789600	-4.66530200
Pd	-0.07767400	-0.26442900	-0.25158300
P	-1.91287900	0.47299500	1.07507300
P	1.52826100	1.45443700	-0.68073700
C	-1.52320600	1.12864300	2.76780000
C	-2.50627400	1.28654200	3.76117600
C	-0.19306000	1.43780800	3.08717800
C	-2.16930000	1.77283200	5.02443900
H	-3.53647800	1.01288700	3.55229800
C	0.14573300	1.92135000	4.35391800
H	0.58426700	1.28002600	2.34668500
C	-0.84236000	2.09551300	5.32275400
H	-2.94209800	1.89082700	5.77970400

H	1.18390900	2.14952200	4.57960800
H	-0.58107700	2.46815000	6.30973400
C	-3.17644800	-0.80825900	1.53304100
C	-4.53836000	-0.70781000	1.22061300
C	-2.72772500	-1.94063400	2.23612100
C	-5.43196000	-1.71076400	1.61024500
H	-4.90845500	0.15411700	0.67491700
C	-3.62001000	-2.93577600	2.63140700
H	-1.67259400	-2.03618200	2.48271800
C	-4.97893500	-2.82278800	2.31918500
H	-6.48516300	-1.61614400	1.35884500
H	-3.25613100	-3.79916200	3.18265900
H	-5.67629300	-3.59751800	2.62698300
C	-2.92655800	1.78757100	0.25766200
C	-3.04839500	1.71248000	-1.14091000
C	-3.55934100	2.84100200	0.93435200
C	-3.80260500	2.65500300	-1.84049900
H	-2.53974700	0.91920900	-1.68309600
C	-4.30336100	3.79061300	0.23042300
H	-3.46702100	2.93119900	2.01173500
C	-4.43078000	3.69785200	-1.15653700
H	-3.88726300	2.57965100	-2.92122000
H	-4.78357300	4.60362800	0.76921300
H	-5.01021900	4.43801700	-1.70211800
C	2.84067500	1.67753000	0.60742700
C	3.22177800	0.55116600	1.35627400
C	3.47017600	2.90633700	0.86453100
C	4.21977900	0.64751500	2.32800500
H	2.72887400	-0.40191500	1.18612000
C	4.46174700	3.00258100	1.84326500
H	3.18308100	3.79038200	0.30324600
C	4.84040800	1.87410400	2.57446800
H	4.50385300	-0.23701800	2.89145800
H	4.93847900	3.96094400	2.03316200
H	5.61286900	1.95196200	3.33520100
C	0.91481100	3.18755200	-0.94076600
C	1.14317600	3.90814300	-2.12277700
C	0.16785700	3.79782400	0.08158100
C	0.63924200	5.20269800	-2.27655000
H	1.71658100	3.46355000	-2.92875900
C	-0.32460500	5.09302200	-0.06873500
H	-0.02957500	3.26079400	1.00412000
C	-0.09301300	5.80007800	-1.25122000
H	0.82541000	5.74270300	-3.20142300
H	-0.89971800	5.54468800	0.73496300
H	-0.48370300	6.80704600	-1.37195600
C	2.50286700	1.16207600	-2.23123600
C	3.86615600	1.47349900	-2.35271100
C	1.83153700	0.60932000	-3.33660100
C	4.54368900	1.23852100	-3.55165100
H	4.40413100	1.89774700	-1.51083400
C	2.51007700	0.38693400	-4.53723000
H	0.78578200	0.32266800	-3.25562100
C	3.86759000	0.69829800	-4.64756500
H	5.60075400	1.48086400	-3.62765600
H	1.97551200	-0.04381800	-5.37962300
H	4.39640500	0.51624600	-5.57961100

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C	-3.50881400	-5.76381000	-2.78380100
C	-3.16783100	-6.03820200	-1.31323300

C	-3.71192800	-4.92188400	-0.41325200
C	-3.19639800	-3.53199300	-0.83770300
C	-3.51315400	-3.24877800	-2.32030700
C	-2.99599900	-4.38511000	-3.22134000
N	-3.78386400	-2.48849100	0.00234300
N	-2.95018200	-1.98645700	-2.80214000
C	-3.22847700	-2.15492100	1.19468900
O	-2.23020400	-2.71949500	1.65628100
C	-3.54397300	-0.78025100	-2.64889000
O	-4.56059400	-0.59002600	-1.96604800
H	-4.38533400	-1.80656900	-0.46332300
H	-2.00484600	-1.99584100	-3.18909800
C	-5.46039000	0.68099200	3.54279600
C	-4.07724100	0.83355700	3.42119500
C	-3.30442400	-0.05102300	2.65683600
C	-3.97030300	-1.10243400	1.98007800
C	-5.35895200	-1.23999200	2.10146900
C	-6.10655900	-0.35892900	2.88218400
H	-6.02547200	1.38221100	4.15088700
H	-3.59994400	1.66483900	3.92602400
P	-1.48335400	0.23641100	2.39663500
H	-5.84993600	-2.06120400	1.58839800
H	-7.18188500	-0.48696500	2.96862700
C	-2.12986800	2.32399000	-5.27363800
C	-2.02547000	2.51456300	-3.89491300
C	-2.43762000	1.53310700	-2.97782100
C	-2.95516000	0.32437100	-3.49514400
C	-3.03702600	0.13388900	-4.88219300
C	-2.63658900	1.12663900	-5.77402700
H	-1.81107900	3.11338100	-5.94907800
H	-1.61167300	3.44657400	-3.52948700
P	-2.19080900	1.82676900	-1.14639200
H	-3.43112600	-0.80570700	-5.25787500
H	-2.71945000	0.96296900	-6.84493500
H	-4.59921600	-5.80867700	-2.91923700
H	-3.08101800	-6.53782100	-3.43254700
H	-2.07613200	-6.10554200	-1.19786100
H	-3.57541100	-7.00679000	-0.99906000
H	-3.43277000	-5.08790700	0.63268000
H	-4.81066700	-4.91420600	-0.45546100
H	-2.10801300	-3.50261500	-0.70284000
H	-4.60365400	-3.16947700	-2.42660300
H	-3.28556100	-4.17321900	-4.25755900
H	-1.89634400	-4.38039200	-3.19425200
C	-6.23150600	3.67842100	0.27208500
C	-6.15536100	3.08036700	-0.98564200
C	-4.95680200	2.51789700	-1.42991600
C	-3.81521700	2.54186200	-0.61616300
C	-3.90545900	3.13443800	0.65478300
C	-5.10089900	3.70412000	1.09136900
H	-7.16422200	4.12044100	0.61263500
H	-7.02983100	3.05023000	-1.63028200
H	-4.92128300	2.04878000	-2.40495800
H	-3.03584100	3.16924700	1.30344500
H	-5.14687500	4.16683400	2.07370000
C	0.69563500	5.50208300	-1.13948000
C	1.19629800	4.19845800	-1.12305200
C	0.31444200	3.11552100	-1.12798800
C	-1.07742600	3.31567000	-1.14724000
C	-1.56719500	4.63278700	-1.16771000
C	-0.68519400	5.71593800	-1.16407400
H	1.37727800	6.34885300	-1.13086100
H	2.26265700	3.99506600	-1.08672800
H	0.72742300	2.11271200	-1.10189300
H	-2.63654000	4.81662700	-1.18372200
H	-1.08125300	6.72831600	-1.17858100
C	0.72098200	-2.43886700	5.51095100
C	1.42487800	-1.56121700	4.68310200
C	0.74162900	-0.79403700	3.73888000
C	-0.65208100	-0.89224000	3.60929100

C	-1.34978600	-1.77641000	4.44191100
C	-0.66547900	-2.54344000	5.38727300
H	1.25100100	-3.03683600	6.24770000
H	2.50444400	-1.47610800	4.76483100
H	1.29928100	-0.10957100	3.10468600
H	-2.42506800	-1.87600800	4.34934400
H	-1.22085600	-3.22469200	6.02698800
C	-0.44008500	4.27185600	4.50573600
C	-0.90226100	3.19378100	5.26738100
C	-1.22943200	1.98773000	4.64969900
C	-1.11951300	1.84358500	3.25391200
C	-0.63643400	2.92536400	2.50572600
C	-0.30109300	4.13325400	3.12573000
H	-0.17713300	5.20811100	4.99093700
H	-0.99575500	3.28852600	6.34608900
H	-1.55688300	1.14903400	5.25726300
H	-0.50066600	2.82011100	1.43537400
H	0.07622200	4.95467900	2.52314200
Pd	-0.91750100	0.15207500	0.05165100
C	5.51218300	-2.41709700	3.22756100
C	4.77883800	-3.60469300	3.38099300
C	3.57757700	-3.80409800	2.69886300
C	3.14040400	-2.77490600	1.86702300
C	3.87403200	-1.58451400	1.67732700
C	5.07044600	-1.40200300	2.37594700
N	1.95769300	-2.68741600	1.11529800
C	1.92850000	-1.50454100	0.45375300
C	3.16541300	-0.77908300	0.67410300
C	0.92161700	-3.70984500	1.07343600
C	0.83840600	-1.03633800	-0.31541600
C	0.31433300	-0.65073700	-1.41789600
C	0.41839300	-0.71345000	-2.86834300
O	-0.18186000	-1.50309800	-3.58773500
O	1.24680000	0.22893900	-3.35230300
C	1.37081600	0.29051700	-4.78711900
H	6.44323300	-2.28951600	3.77210600
H	5.15000100	-4.38296500	4.04185100
H	3.01216800	-4.72226300	2.82060600
H	5.65505600	-0.49722700	2.24585200
H	3.08889900	0.30554100	0.74126300
H	1.14510300	-4.45334000	0.29975900
H	0.87218100	-4.20064700	2.04748100
H	-0.04653300	-3.24312500	0.88320000
H	2.06440500	1.10942100	-4.97557300
H	1.77111300	-0.64923200	-5.17590600
H	0.39829300	0.49161300	-5.24168100
C	4.12381200	-0.68726800	-0.97292700
C	5.21250900	0.25605000	-0.78814800
C	4.83648700	1.64545500	-0.65709900
O	3.62693600	1.96452800	-0.55214400
C	4.36015500	-2.07762900	-1.47908700
C	5.29715700	-2.96683800	-0.92483900
C	5.45695500	-4.24977100	-1.44981700
C	4.68964300	-4.67534000	-2.53579500
C	3.75691300	-3.80286600	-3.09909800
C	3.59548200	-2.52180900	-2.57177600
C	6.54593100	-0.17594200	-0.58953900
N	7.64486800	-0.54106000	-0.42013100
C	5.86161300	2.74542900	-0.60742000
C	5.55561200	3.88815400	0.14936700
C	6.44060400	4.96210600	0.20826900
C	7.63945600	4.92012000	-0.50933700
C	7.94409700	3.79766000	-1.28122600
C	7.06444000	2.71492900	-1.32839700
H	3.30682600	-0.19914800	-1.50053400
H	5.90956400	-2.65907600	-0.08711400
H	6.19091200	-4.91760800	-1.00663900
H	4.82113700	-5.67497700	-2.94205500
H	3.15649600	-4.11477200	-3.94998300
H	2.88045100	-1.84226700	-3.02464100

H	4.61399400	3.91285200	0.68872100
H	6.19626700	5.83355900	0.81085600
H	8.33029800	5.75858000	-0.46868300
H	8.86954500	3.76187600	-1.85000100
H	7.31352600	1.85124500	-1.93442300

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C	0.38940800	6.24071600	-2.24605900
C	0.58595900	5.24081700	-3.39302000
C	-0.60697600	4.28134200	-3.48693700
C	-0.85731700	3.53893500	-2.15897800
C	-1.03973400	4.53082400	-0.99236700
C	0.14265500	5.51427900	-0.91695500
N	-2.03507700	2.67531900	-2.26722100
N	-1.17687500	3.87586900	0.30896100
C	-1.93911800	1.43176800	-2.79705000
O	-0.88513200	0.96530600	-3.24506400
C	-2.34122700	3.39343300	0.79630100
O	-3.39407800	3.32217000	0.14429500
H	-2.82368100	2.89126000	-1.65394400
H	-0.33052900	3.66513400	0.84456100
C	-5.61445700	-0.71797400	-3.41131300
C	-4.52494900	-1.37628800	-2.83542200
C	-3.31683500	-0.71314100	-2.58117900
C	-3.22994700	0.66134000	-2.91196900
C	-4.33347500	1.31569300	-3.47284400
C	-5.52329400	0.63387700	-3.72751300
H	-6.53222700	-1.26732800	-3.60353200
H	-4.62913400	-2.42277100	-2.57384200
P	-1.91839900	-1.55791200	-1.68391000
H	-4.24309400	2.36665100	-3.73017900
H	-6.36590300	1.15707400	-4.17078100
C	-2.40115400	2.69306800	5.04266500
C	-2.65723600	1.62459400	4.18183700
C	-2.62222900	1.77582800	2.78567700
C	-2.31281300	3.05240600	2.26730800
C	-2.04212700	4.11530600	3.13969200
C	-2.08915900	3.94638700	4.52176100
H	-2.44572400	2.53777400	6.11731200
H	-2.88588700	0.65670700	4.61110500
P	-2.87911200	0.28961200	1.68350700
H	-1.79534600	5.08561600	2.71950600
H	-1.88192300	4.78515500	5.18044700
H	-0.46791400	6.89115900	-2.47307300
H	1.26300100	6.89672300	-2.14930600
H	1.50801000	4.66623300	-3.22242700
H	0.71883300	5.76933800	-4.34492500
H	-0.45172100	3.53645300	-4.27452000
H	-1.51514400	4.84321800	-3.74919400
H	0.00954900	2.90386700	-1.93963100
H	-1.96868100	5.09174300	-1.16372600
H	-0.04769900	6.23258900	-0.11061200
H	1.04632500	4.95520200	-0.63355300
C	-7.42598800	0.40199500	0.64736000
C	-6.85020400	1.47678700	1.32512700
C	-5.48947800	1.46776200	1.63752300
C	-4.68248700	0.38136200	1.27036300
C	-5.26866700	-0.68993000	0.57690600
C	-6.63018100	-0.68302300	0.27475300
H	-8.48631900	0.41013400	0.40878900
H	-7.45872000	2.32935600	1.61480800
H	-5.05875000	2.31516100	2.15600500
H	-4.66655000	-1.54363400	0.28288100
H	-7.06582700	-1.52485600	-0.25655100
C	-2.65722400	-3.19560300	4.79665100
C	-1.50009300	-2.67389000	4.21286200
C	-1.58928100	-1.63592500	3.28473900
C	-2.83767600	-1.09515100	2.92793400
C	-3.99252400	-1.62060600	3.52834900
C	-3.90164600	-2.66519500	4.45246000
H	-2.58894100	-4.00871900	5.51447600

H	-0.52550400	-3.07912900	4.47175700
H	-0.68517700	-1.24452200	2.82787900
H	-4.96747800	-1.21796700	3.27571600
H	-4.80764400	-3.06072300	4.90431800
C	0.94384700	-3.19661700	-4.97374500
C	1.19247500	-3.42764200	-3.61894800
C	0.33608000	-2.89795200	-2.65321500
C	-0.77876400	-2.13253800	-3.02650800
C	-1.01819400	-1.90230000	-4.38718700
C	-0.16123100	-2.43335900	-5.35363800
H	1.61064300	-3.60659000	-5.72768800
H	2.05662400	-4.00894500	-3.31104100
H	0.53717300	-3.08607300	-1.60158700
H	-1.86549900	-1.30052100	-4.69531200
H	-0.35926800	-2.24537900	-6.40585300
C	-3.57751600	-5.73690800	-0.40165600
C	-3.39537900	-5.45188600	-1.75843400
C	-2.90897500	-4.20689600	-2.15501400
C	-2.61048200	-3.21549700	-1.20171600
C	-2.78063200	-3.52185400	0.15508400
C	-3.26398800	-4.77182600	0.55418800
H	-3.94993600	-6.71074000	-0.09482400
H	-3.62240400	-6.20452000	-2.50898800
H	-2.74727700	-4.00913600	-3.21056300
H	-2.51755900	-2.78654200	0.90680800
H	-3.38455100	-4.98443900	1.61286700
Pd	-1.06900900	-0.22020400	0.14372400
C	5.25192200	-3.70090100	-2.29989300
C	5.18551300	-2.74973400	-3.32749900
C	4.38104600	-1.61413200	-3.21208500
C	3.65340700	-1.46786500	-2.03387800
C	3.74302000	-2.38653900	-0.97019100
C	4.53983500	-3.52213600	-1.11087100
N	2.68942900	-0.49483900	-1.69551100
C	2.19142800	-0.74655400	-0.46909800
C	2.94537000	-1.83863800	0.14166300
C	2.32450300	0.65126600	-2.51584500
C	1.07139300	-0.10336700	0.11546700
C	0.59064500	0.60999100	1.06578400
C	1.00883600	1.56621100	2.08573300
O	0.87546800	2.77841100	2.01804700
O	1.53437600	0.95323600	3.16625200
C	2.04392500	1.83616100	4.18485400
H	5.87845400	-4.57938600	-2.42311900
H	5.76551900	-2.89766600	-4.23387900
H	4.32692100	-0.88818500	-4.01629700
H	4.61087100	-4.24973900	-0.30860200
H	2.39239400	-2.50133800	0.79935000
H	2.61221200	0.45509700	-3.54913700
H	1.24337900	0.80251100	-2.48209000
H	2.84318900	1.54080400	-2.14307500
H	2.43295100	1.18092100	4.96442600
H	2.84047000	2.45859100	3.77074100
H	1.24375900	2.47051500	4.57393600
C	4.07773200	-1.02172700	1.40960700
C	5.12064400	-0.19422700	0.81903700
C	4.75593600	1.16670100	0.50791600
O	3.55889800	1.53551300	0.59308200
C	4.38384000	-2.14134800	2.36861900
C	5.43257300	-3.06491200	2.22284400
C	5.62419500	-4.07656400	3.16680000
C	4.77799400	-4.19256700	4.27047900
C	3.73151800	-3.28133600	4.42792600
C	3.53760300	-2.27224200	3.48566900
C	6.37367800	-0.73404200	0.44547100
N	7.40256800	-1.19948900	0.13702800
C	5.76739800	2.19572600	0.06677300
C	5.29081400	3.28831900	-0.67678900
C	6.14945200	4.30186200	-1.09468800
C	7.50413600	4.25460300	-0.75428500

C	7.98488500	3.19009600	0.00938100
C	7.12607500	2.16783400	0.41740600
H	3.32400800	-0.36730900	1.83914900
H	6.11460800	-2.98765200	1.38593900
H	6.44756600	-4.77435600	3.03725200
H	4.93490200	-4.98078200	5.00225900
H	3.06936000	-3.35210400	5.28759700
H	2.72471700	-1.56082200	3.61467900
H	4.23025500	3.33021300	-0.90237800
H	5.76307300	5.13329900	-1.67946200
H	8.17737200	5.04565200	-1.07524500
H	9.03338300	3.15245300	0.29327600
H	7.52049800	1.35528800	1.01507500

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C	1.01226800	-5.04832600	4.65364200
C	2.02789300	-5.41186900	3.56346100
C	2.87163800	-4.18915400	3.18597800
C	2.00916200	-2.99478200	2.72575000
C	0.93795700	-2.64009100	3.78122700
C	0.12687700	-3.87678700	4.20936200
N	2.86090100	-1.83210700	2.47685400
N	-0.00203500	-1.61174400	3.32441600
C	3.54823000	-1.68978800	1.31140700
O	3.48444700	-2.49760200	0.38253400
C	0.23191900	-0.27153400	3.37705600
O	1.32564400	0.20252500	3.70239000
H	2.69570400	-1.00493300	3.05101700
H	-0.89013500	-1.91803600	2.94860100
C	6.59476800	1.35406400	1.27499200
C	5.71173500	1.26696500	0.19637900
C	4.66831400	0.32912500	0.16977800
C	4.52421400	-0.53587900	1.28072800
C	5.40520000	-0.42606500	2.36583800
C	6.43856500	0.50950500	2.36999100
H	7.39765100	2.08626700	1.25280800
H	5.83640400	1.95477700	-0.63135200
P	3.42402600	0.33921700	-1.22251900
H	5.28421500	-1.10366400	3.20524900
H	7.11385800	0.57096100	3.21879100
C	-3.24878000	2.16595700	2.71827300
C	-2.09280700	2.41672900	1.97335800
C	-0.92882500	1.65388500	2.14095700
C	-0.96357100	0.59067100	3.07688400
C	-2.12819300	0.34567200	3.81626300
C	-3.26785400	1.13330800	3.64974600
H	-4.13123900	2.77502200	2.54634600
H	-2.12343800	3.20047500	1.22821500
P	0.56219100	1.98673900	1.06548700
H	-2.13155900	-0.46114500	4.54407200
H	-4.15934200	0.93001300	4.23598200
H	1.54741400	-4.77328100	5.57370200
H	0.38119200	-5.90954500	4.90456500
H	1.49692400	-5.78545800	2.67544900
H	2.67834800	-6.22709000	3.90243200
H	3.57626700	-4.42835500	2.38305300
H	3.46713200	-3.87176100	4.05404500
H	1.50792000	-3.26217600	1.78676100
H	1.45194300	-2.22814500	4.66005100
H	-0.56429900	-3.58501500	5.00936600
H	-0.49534500	-4.20201200	3.36119500
C	3.45960500	4.36274700	3.83886600
C	2.13861200	4.15509500	4.24126700
C	1.26398700	3.42565900	3.43569100
C	1.69887700	2.89061600	2.21382600
C	3.02543800	3.10544100	1.81902600
C	3.90016200	3.83720000	2.62391900
H	4.14001900	4.92938500	4.46918000
H	1.78594800	4.55919700	5.18663000
H	0.24194900	3.27081700	3.76411100
H	3.38311400	2.70268700	0.87879700

H	4.92676600	3.98570400	2.30107800	C	-5.64964400	-2.60638700	2.18079900
C	-0.90275500	5.37543100	-1.79360300	C	-4.99323500	-3.84324800	2.25581200
C	-1.21519300	4.03788400	-2.04394600	C	-3.74668300	-4.03493200	1.65442600
C	-0.77309200	3.04034900	-1.17480800	C	-3.19053800	-2.94446900	0.98803500
C	-0.02741800	3.36619800	-0.02992300	C	-3.83769600	-1.69892200	0.88817800
C	0.27115100	4.71594000	0.22038500	C	-5.08203500	-1.52802000	1.49565000
C	-0.16000300	5.71135400	-0.65938500	N	-1.94890600	-2.85022400	0.33274500
H	-1.24157000	6.15221400	-2.47420100	C	-1.77631000	-1.58412100	-0.15106500
H	-1.80998700	3.76314300	-2.90970000	C	-3.00356900	-0.82123900	0.04314300
H	-1.03445800	2.00787300	-1.37659800	C	-1.09247500	-3.99865200	0.07836200
H	0.84241700	4.99483300	1.09889900	C	-0.56436900	-1.16479600	-0.73989200
H	0.08162700	6.75071800	-0.45199900	C	0.38227600	-1.38806700	-1.58255700
C	5.10238000	-2.62620600	-4.40299600	C	0.65688600	-2.16500000	-2.79557300
C	4.05816100	-1.75018300	-4.70988700	O	0.51447800	-1.75094700	-3.92956900
C	3.55142500	-0.89376000	-3.73149100	O	1.07461600	-3.41201000	-2.49231300
C	4.08552100	-0.89849200	-2.43268700	C	1.36585900	-4.26048400	-3.61778500
C	5.12565500	-1.78728000	-2.12989100	H	-6.61952300	-2.48737600	2.65490800
C	5.62924400	-2.64453500	-3.11061000	H	-5.46046000	-4.66863800	2.78538400
H	5.50224300	-3.28915100	-5.16607300	H	-3.24627400	-4.99711500	1.70127000
H	3.63432700	-1.72798300	-5.71024000	H	-5.60161300	-0.57865300	1.42892400
H	2.73945400	-0.22000600	-3.98671800	H	-2.89551100	0.23491400	0.28893000
H	5.53644400	-1.82161800	-1.12874600	H	-0.96789000	-4.57587400	0.99936600
H	6.43847800	-3.32568900	-2.86045100	H	-1.54674000	-4.63950600	-0.68570400
C	4.35321100	4.26976900	-3.57279600	H	-0.11977800	-3.66038200	-0.27581700
C	5.23549500	3.18843600	-3.65875100	H	1.69876400	-5.20469200	-3.18613000
C	4.97061200	2.00960100	-2.96317200	H	0.46797800	-4.40853700	-4.22395700
C	3.82163600	1.89482000	-2.15752200	H	2.15516500	-3.81931800	-4.22934600
C	2.94053000	2.98149000	-2.09126900	C	-3.76764700	-0.55240200	-1.59185500
C	3.20423900	4.16266100	-2.79094000	C	-4.99690200	0.22293800	-1.39223800
H	4.55828300	5.18491200	-4.12203900	C	-4.80653500	1.58810100	-0.97692700
H	6.12773400	3.25970800	-4.27535100	O	-3.63886000	2.02145000	-0.80152300
H	5.65543900	1.17209100	-3.05423500	C	-3.78404800	-1.83705200	-2.37220200
H	2.03236400	2.90270000	-1.50671200	C	-4.64421700	-2.91207800	-2.08996900
H	2.50062900	4.98762800	-2.72565800	C	-4.58369700	-4.08719500	-2.84133300
Pd	1.14164900	0.14520300	-0.45956500	C	-3.66716000	-4.21488700	-3.88736900

C	-2.80766300	-3.15399500	-4.17951800
C	-2.86595400	-1.98082600	-3.42629000
C	-6.26377100	-0.36739600	-1.59502900
N	-7.30633600	-0.87207900	-1.76739400
C	-5.93735700	2.55775000	-0.73092900
C	-5.62488600	3.92448800	-0.84625300
C	-6.58492200	4.90370600	-0.60628100
C	-7.87819700	4.53756300	-0.22229700
C	-8.19601900	3.18634500	-0.08352000
C	-7.23791600	2.20217300	-0.33784800
H	-2.98723300	0.11095400	-1.96368700
H	-5.37317900	-2.83112500	-1.29296600
H	-5.26502000	-4.90222200	-2.61097600
H	-3.62950900	-5.12979100	-4.47355000
H	-2.08978700	-3.22921700	-4.99189000
H	-2.18653300	-1.16674100	-3.66215000
H	-4.61155900	4.19478900	-1.12343000
H	-6.32519700	5.95402000	-0.71505100
H	-8.62980300	5.29952300	-0.03106600
H	-9.19603100	2.89011100	0.22292400
H	-7.51481000	1.16148900	-0.22765100

(*S*,*S*)-TS

C	0.98547800	0.83928700	6.47817500
C	0.34597000	2.14461800	5.98875800
C	-0.94759100	1.85355000	5.21992300
C	-0.72525800	0.89697500	4.02960300
C	-0.02960800	-0.40589900	4.48325000
C	1.23862100	-0.11995600	5.30809100
N	-2.00696500	0.57684000	3.40137900
N	0.34422600	-1.27806400	3.36333500
C	-2.59276000	1.42086400	2.50893100
O	-2.09278300	2.49261300	2.16123800
C	-0.49781200	-2.13785700	2.73293200
O	-1.71006300	-2.19499400	2.96684400
H	-2.28536900	-0.40449200	3.39244800
H	1.30330500	-1.23939600	3.03949900
C	-6.65671300	0.45859000	1.45142100
C	-5.76467800	0.83827400	0.44621600
C	-4.42031000	1.12859600	0.72186800
C	-3.97803800	1.01389600	2.06224300
C	-4.88003700	0.61934000	3.06048700
C	-6.21423900	0.34375500	2.76555700
H	-7.69342000	0.25231900	1.19853900
H	-6.12844900	0.89784000	-0.57248600
P	-3.22504300	1.50845600	-0.66224300
H	-4.52662200	0.55131800	4.08457200
H	-6.89668200	0.04681900	3.55700100
C	1.46873200	-4.95137700	0.14185600
C	0.43966100	-4.15751700	-0.37156800
C	-0.24048800	-3.22002900	0.42155400
C	0.17208200	-3.07996000	1.76836900
C	1.20336200	-3.88087500	2.27621700
C	1.84661900	-4.82374000	1.47484400
H	1.97554300	-5.65569400	-0.51104700
H	0.17106400	-4.27323100	-1.41404400
P	-1.57471700	-2.14295400	-0.33064100
H	1.49542500	-3.76687400	3.31626600
H	2.63900800	-5.44063000	1.88881100
H	0.31918200	0.35888300	7.20903600
H	1.93023700	1.03709100	6.99885700
H	1.05313300	2.67913000	5.33728400
H	0.13842300	2.81095800	6.83467100
H	-1.39458800	2.77563200	4.83484400
H	-1.68311000	1.39702100	5.89782700
H	-0.09136900	1.39733400	3.28607500
H	-0.74013800	-0.97192100	5.10090200
H	1.64656800	-1.07251500	5.66762900
H	2.00204700	0.31479400	4.64571300
C	-5.54802700	-4.27625400	0.86508700
C	-4.32952900	-4.84799000	1.23422000

C	-3.12745500	-4.22069100	0.90282100
C	-3.12706300	-3.00867500	0.19724900
C	-4.35688200	-2.44042200	-0.16484500
C	-5.55784700	-3.07014100	0.16288800
H	-6.48280600	-4.76603000	1.12498800
H	-4.31037700	-5.78493900	1.78477400
H	-2.19114100	-4.67723900	1.20268700
H	-4.38244100	-1.50387200	-0.71070600
H	-6.49940600	-2.61105600	-0.12533200
C	-1.28861000	-3.30604700	-4.85410500
C	-0.58506000	-2.21008000	-4.34899000
C	-0.68044000	-1.87938600	-2.99561400
C	-1.47892200	-2.64047900	-2.12356400
C	-2.18311700	-3.73826600	-2.64416400
C	-2.08763500	-4.06747500	-3.99848500
H	-1.21938900	-3.56097900	-5.90829400
H	0.02896900	-1.60135900	-5.00718900
H	-0.15216900	-1.00839400	-2.61714800
H	-2.81008600	-4.33862900	-1.99295800
H	-2.64124300	-4.92001300	-4.38336600
C	-3.23146700	6.15598200	-1.05505500
C	-2.69059100	5.34531600	-2.05563000
C	-2.67844700	3.95793200	-1.90597200
C	-3.21044600	3.36087800	-0.75111900
C	-3.74852400	4.18089900	0.24941100
C	-3.75794300	5.56899600	0.09608500
H	-3.24411100	7.23649100	-1.17306300
H	-2.28117000	5.78802400	-2.96004000
H	-2.24992000	3.34464600	-2.69151200
H	-4.14949600	3.74238400	1.15430400
H	-4.18024200	6.19017900	0.88176100
C	-5.61446300	0.60617500	-4.57792200
C	-5.96332600	1.71128700	-3.79549400
C	-5.26142500	1.99140500	-2.62394600
C	-4.20433100	1.16175400	-2.20424500
C	-3.85666600	0.06748900	-3.00639600
C	-4.55712100	-0.21197900	-4.18356100
H	-6.15794800	0.39469400	-5.49505100
H	-6.77760200	2.36221000	-4.10311600
H	-5.52896400	2.86565900	-2.03830500
H	-3.02018400	-0.55948400	-2.72214300
H	-4.26247800	-1.06337700	-4.79080500
Pd	-1.15535800	0.27518300	-0.40438400
C	5.34856200	-2.00601700	2.84238300
C	5.42037600	-0.73970800	3.43650700
C	4.64185600	0.32270100	2.96863300
C	3.79940100	0.06380400	1.88888700
C	3.73792800	-1.19066800	1.25333600
C	4.51744800	-2.23806500	1.74160500
N	2.85432000	0.91530200	1.28627900
C	2.17727300	0.24799200	0.31146400
C	2.83938700	-1.03897700	0.08545200
C	2.67822700	2.30639500	1.66988500
C	0.97611000	0.72225800	-0.25614900
C	0.29186700	1.67518200	-0.77231900
C	0.46587900	2.90516400	-1.55303500
O	0.21635700	3.00545300	-2.73666900
O	0.93249600	3.91659100	-0.79002100
C	1.19211100	5.14239300	-1.49743500
H	5.96018500	-2.81461800	3.23177800
H	6.09097000	-0.57668100	4.27522700
H	4.70209800	1.30522500	3.42567300
H	4.48176200	-3.21487900	1.27175300
H	2.19387900	-1.86242300	-0.20014900
H	2.48094900	2.37420000	2.74535500
H	3.58918900	2.86584100	1.43381800
H	1.84801400	2.73648000	1.11392400
H	1.53854700	5.84507700	-0.73869400
H	1.96184100	4.97987100	-2.25597300
H	0.27784700	5.50920300	-1.96898000

C	3.84592600	-0.83117200	-1.44245400
C	4.92156800	0.15092600	-1.30022000
C	4.54561900	1.52892400	-1.49332100
O	3.33786900	1.83417000	-1.63658800
C	4.11332700	-2.24046200	-1.91127300
C	5.19518000	-3.03596900	-1.49685400
C	5.34831000	-4.33746500	-1.98109500
C	4.43085300	-4.87615300	-2.88491700
C	3.35168000	-4.09669300	-3.30730800
C	3.19838200	-2.79862200	-2.82187400
C	6.20560900	-0.20983700	-0.83291600
N	7.26253100	-0.52343200	-0.43785400
C	5.55336000	2.65036800	-1.49581400
C	5.09746700	3.92319200	-1.11376700
C	5.95421700	5.02150000	-1.11540300
C	7.28176500	4.87089900	-1.52564100
C	7.73859700	3.61694000	-1.93436600
C	6.88382900	2.51316100	-1.91871800
H	3.06746300	-0.38184500	-2.05793700
H	5.93437300	-2.63801100	-0.81387700
H	6.20033000	-4.92815100	-1.65397000
H	4.56135200	-5.88658000	-3.26408200
H	2.63203700	-4.49263300	-4.01960600
H	2.35566500	-2.20080600	-3.16000300
H	4.05519100	4.02751400	-0.83038300
H	5.58688700	5.99709300	-0.80567600
H	7.95247600	5.72647400	-1.53395400
H	8.76499100	3.49388800	-2.27006700
H	7.25640100	1.54975900	-2.24549500

(*R*,*S*)-TS-II

C	0.15236700	6.58576200	-1.84730900
C	-0.84500500	6.07253500	-2.89232500
C	-1.92385300	5.21551400	-2.22185700
C	-1.33237600	4.02626000	-1.43489000
C	-0.27321900	4.50374100	-0.41562700
C	0.77771400	5.41869500	-1.07409700
N	-2.40191500	3.32838300	-0.71638500
N	0.43948800	3.40343200	0.24812500
C	-3.31470800	2.55510400	-1.34675300
O	-3.33266700	2.34876300	-2.56260600
C	-0.02032800	2.74983000	1.33718700
O	-1.18005800	2.86890000	1.76915100
H	-2.29692700	3.24419700	0.29760000
H	1.36215500	3.16750600	-0.13070800
C	-6.74294400	1.36233600	0.98217100
C	-5.90216600	0.37206400	0.47069800
C	-4.74523000	0.69423100	-0.25718900
C	-4.44191200	2.05938900	-0.46060900
C	-5.28230100	3.04395100	0.07545600
C	-6.42977100	2.70558800	0.79146100
H	-7.63615900	1.07677800	1.53170400
H	-6.15253000	-0.66683700	0.65081900
P	-3.55538600	-0.63306200	-0.78745100
H	-5.03009600	4.08788400	-0.08611300
H	-7.06976100	3.48583700	1.19414800
C	2.87119500	0.55999800	3.66084900
C	1.59901500	0.01596700	3.46267700
C	0.63118100	0.66547600	2.68152000
C	0.97907100	1.90587400	2.08599700
C	2.26074100	2.43537300	2.28827300
C	3.20877300	1.77222800	3.06756000
H	3.59200800	0.02617000	4.27409000
H	1.36577100	-0.93600000	3.92431700
P	-0.99713900	-0.18545000	2.34097500
H	2.51527900	3.38616100	1.83308100
H	4.19775900	2.20116800	3.19814400
H	-0.36670900	7.26065700	-1.15061400
H	0.94636900	7.17544300	-2.32192600
H	-0.31090500	5.47622500	-3.64629000
H	-1.31115600	6.90964500	-3.42692600

H	-2.63084300	4.81914300	-2.95690900
H	-2.50002000	5.83769700	-1.52127000
H	-0.86243900	3.32608300	-2.13785500
H	-0.80079700	5.06408700	0.36928600
H	1.45390100	5.78843700	-0.29380800
H	1.39469800	4.81654200	-1.75212900
C	-4.08181400	1.72444000	5.25836200
C	-2.72042300	1.98284000	5.43394400
C	-1.78254800	1.43827300	4.55654700
C	-2.19482600	0.62522200	3.49082500
C	-3.56208500	0.37286900	3.32106800
C	-4.50015200	0.91805500	4.19946800
H	-4.81117100	2.15358000	5.94039400
H	-2.38610300	2.61536700	6.25220300
H	-0.72877000	1.65606200	4.69617300
H	-3.90236800	-0.24668900	2.49801600
H	-5.55708300	0.71939300	4.04539900
C	-0.39039600	-4.36735300	4.35616600
C	-0.00306100	-4.14309000	3.03318200
C	-0.19944200	-2.89074900	2.44997300
C	-0.76896700	-1.83367100	3.18010900
C	-1.15331100	-2.07266400	4.50962200
C	-0.96807400	-3.32985200	5.08991400
H	-0.24375900	-5.34338300	4.81104700
H	0.45178900	-4.94145100	2.45284300
H	0.08702500	-2.72747800	1.41593700
H	-1.59845100	-1.27682300	5.09709800
H	-1.27451300	-3.49483500	6.11961600
C	-4.49140200	-1.55011700	-5.26121500
C	-3.55193800	-2.29949200	-4.54824400
C	-3.27366500	-1.98483200	-3.21808400
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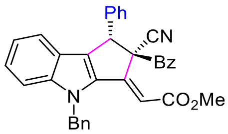

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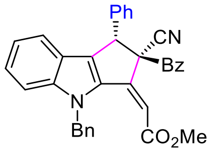

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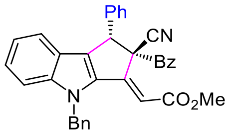

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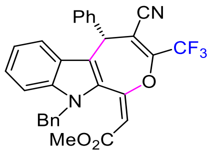

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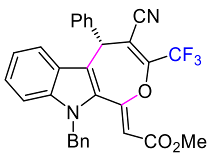
H	4.91308800	-2.25214900	-0.26611400
H	6.03426500	-2.31892500	-2.47351100
H	5.20737100	-0.88745300	-4.33362000
H	3.25969600	0.61443300	-3.95943900
H	2.15033000	0.68882600	-1.75795700
H	3.25992000	-1.44412500	1.19723300
H	2.95198700	0.26235500	0.95027800
H	3.36734900	1.86472300	6.00551000
H	2.27587900	0.44774200	5.85329200
H	3.83363500	0.45534000	4.99620000



C	-1.92399100	-0.78912100	-0.30532200
C	-2.45536400	3.97593300	-1.01876100
C	-1.21401300	4.59206100	-1.28488400
C	-0.04763700	3.84670100	-1.35804500
C	-0.14386400	2.46176200	-1.16016200
C	-1.37988200	1.82030000	-0.84952800
C	-2.55057100	2.61109700	-0.80325600
N	0.85492600	1.51046700	-1.23259700
C	0.27588800	0.27033600	-0.95756200
C	-1.08179200	0.42433000	-0.68918800
C	-1.28740200	-1.37704900	0.98129800
C	-0.05995000	-1.92336400	0.87037600
O	0.57672100	-2.05411000	-0.32755300
C	0.96830400	-0.99886900	-1.13143800
C	1.88737200	-1.24807300	-2.09763600
C	-3.43597800	-0.61830800	-0.25833300

C	-4.09433700	0.16292300	0.70306700
C	-5.48578900	0.26941400	0.70095000
C	-6.24364500	-0.39773100	-0.26356500
C	-5.60057400	-1.17589900	-1.22630600
C	-4.20936100	-1.28595000	-1.21766400
C	2.74226200	2.45542400	0.12749800
C	3.32190100	3.72836800	0.15235800
C	3.77402300	4.28446400	1.35129900
C	3.64708100	3.56961000	2.54211900
C	3.07441700	2.29476900	2.52631300
C	2.62869000	1.73948000	1.32759100
C	2.28559300	1.84625700	-1.18863200
C	-1.95995200	-1.30518300	2.23793500
N	-2.55038000	-1.21771500	3.23676600
C	0.80740200	-2.52568800	1.95581800
F	0.22004300	-2.53768000	3.15806000
F	1.94991800	-1.80362700	2.05611600
F	1.15233500	-3.78502200	1.64114600
C	2.69615200	-2.45297500	-2.34797700
O	3.42187800	-2.55259500	-3.32264000
O	2.58351300	-3.41595700	-1.40691800
C	3.38875100	-4.58168100	-1.63057800
H	-1.73399700	-1.55547000	-1.06788200
H	-3.35451300	4.58455500	-0.98455400
H	-1.17201500	5.66590800	-1.44375900
H	0.90422300	4.32152500	-1.56798200
H	-3.51527900	2.16049500	-0.61249900
H	2.05514600	-0.47353600	-2.83511800
H	-3.52604100	0.69560700	1.45756800
H	-5.97612500	0.87444600	1.45842300
H	-7.32690800	-0.31373700	-0.26151500
H	-6.17809700	-1.70170900	-1.98159200
H	-3.71704700	-1.89967500	-1.96865800
H	3.42709600	4.28907200	-0.77424900
H	4.22102600	5.27492000	1.35260300
H	3.99464600	3.99973800	3.47740000
H	2.98003500	1.72852300	3.44885000
H	2.19987000	0.74089100	1.32990800
H	2.49717100	2.53282400	-2.01520200
H	2.84090600	0.92902700	-1.38604200
H	3.18288900	-5.23962200	-0.78568300
H	3.11544100	-5.06594300	-2.57227600
H	4.44977500	-4.31888900	-1.66466300

(*R*,*S*)-TS2

C	-4.43250400	-5.63234000	1.97463800
C	-3.86499900	-4.95313400	3.22777200
C	-4.11806200	-3.44103500	3.18663700
C	-3.54144000	-2.79098300	1.91254600
C	-4.08969400	-3.47504900	0.64368000
C	-3.86460500	-4.99732600	0.69824300
N	-3.84843500	-1.35980400	1.88437900
N	-3.49469100	-2.96673600	-0.59339700
C	-3.07351300	-0.46975200	2.55217400
O	-2.09346000	-0.80526800	3.22718100
C	-3.92711800	-1.85903600	-1.23917000
O	-4.77939000	-1.08277600	-0.78401200
H	-4.44242800	-1.02755000	1.12253300
H	-2.63909300	-3.40847800	-0.93488300
C	-4.51936100	3.57519400	2.77527800
C	-3.18153500	3.34884700	2.44298400

C	-2.66011100	2.05299800	2.32120200	C	-5.86105200	3.68579000	-1.68852800
C	-3.54178800	0.96318100	2.52902900	C	-5.97984500	2.47169900	-2.36527900
C	-4.88556600	1.20162100	2.84446200	C	-4.89559300	1.59488000	-2.43821800
C	-5.37895300	2.49955200	2.97270100	C	-3.67552800	1.92174500	-1.82997100
H	-4.88236700	4.59508800	2.87035700	C	-3.56793800	3.14204100	-1.14361200
H	-2.54087400	4.20395800	2.26473600	C	-4.65017800	4.01895600	-1.07815500
P	-0.91840500	1.77914800	1.70852400	H	-6.70589900	4.36748700	-1.63569700
H	-5.54142000	0.35252500	3.01101500	H	-6.91892800	2.20050700	-2.84036800
H	-6.42285600	2.66261800	3.22541900	H	-5.00933700	0.65251900	-2.95956800
C	-2.67713600	-1.48320300	-5.33902400	H	-2.63216200	3.42017200	-0.66935900
C	-2.36052100	-0.46009800	-4.44347500	H	-4.54559700	4.96090200	-0.54669500
C	-2.71096400	-0.53101600	-3.08529000	C	0.75225600	3.30847400	-4.57927600
C	-3.38817700	-1.68865300	-2.63901000	C	1.22540000	2.29429700	-3.74402400
C	-3.68418700	-2.71965700	-3.54172400	C	0.33369300	1.56179500	-2.95829500
C	-3.34162900	-2.62153400	-4.88912400	C	-1.04493500	1.83308000	-2.99475200
H	-2.39888000	-1.38428600	-6.38481800	C	-1.50947700	2.85511300	-3.83926800
H	-1.82869400	0.40756400	-4.81435500	C	-0.61610500	3.58562100	-4.62567100
P	-2.18166700	0.83163200	-1.91914300	H	1.44654400	3.88371500	-5.18596700
H	-4.20058900	-3.60206700	-3.17593700	H	2.28870700	2.08070200	-3.68498400
H	-3.59161300	-3.42623900	-5.57497900	H	0.71605200	0.79217300	-2.29455800
H	-5.52815000	-5.53829900	1.97412900	H	-2.56929200	3.08457200	-3.88233700
H	-4.21073200	-6.70644400	1.98073000	H	-0.99183000	4.37467800	-5.27195500
H	-2.78359400	-5.14427000	3.28890600	C	1.82024000	1.17133900	5.42666300
H	-4.30992500	-5.38409900	4.13292100	C	2.35516600	1.30568400	4.14231800
H	-3.67610600	-2.94423000	4.05661900	C	1.51023300	1.47163800	3.04431200
H	-5.19962700	-3.24545900	3.21866300	C	0.11569400	1.50087100	3.21975800
H	-2.45016000	-2.90337800	1.92209400	C	-0.41398100	1.37042500	4.50913800
H	-5.16686700	-3.26903900	0.58324300	C	0.43631000	1.20757200	5.60618300
H	-4.31165000	-5.45153400	-0.19410400	H	2.47957200	1.04452100	6.28140200
H	-2.78365200	-5.19349100	0.64349100	H	3.43059900	1.28112000	3.99108300

H	1.94425700	1.59468700	2.05434300
H	-1.48691600	1.37965300	4.65916700
H	0.01187300	1.10975400	6.60226400
C	0.72352400	6.00722700	0.60039300
C	0.41975200	5.70864900	1.93258000
C	-0.07874800	4.45260600	2.27314900
C	-0.30263800	3.47730800	1.28277300
C	0.02402900	3.78344400	-0.04371500
C	0.53202800	5.04061500	-0.38480800
H	1.12302500	6.98343700	0.33870600
H	0.58427400	6.45089500	2.70932600
H	-0.28135300	4.22403900	3.31549100
H	-0.09019400	3.02968100	-0.81271100
H	0.78950800	5.24861500	-1.41936900
Pd	-0.83402300	0.11417000	-0.04346800
C	5.88493900	-1.95757400	3.35591400
C	5.00960000	-2.36961300	4.37362300
C	3.63102300	-2.39844600	4.16518200
C	3.17281600	-1.99997700	2.90980800
C	4.03019600	-1.57254200	1.87819900
C	5.40934100	-1.55232600	2.10762600
N	1.84903800	-1.95987900	2.43680100
C	1.82894500	-1.55508800	1.15123500
C	3.18086600	-1.18702000	0.72525700
C	0.69454500	-2.29384000	3.26126000
C	0.65583100	-1.36485200	0.37524300
C	0.00492700	-1.66294200	-0.69037600
C	-0.11983400	-2.68140000	-1.72711100
O	-0.84535600	-3.66612900	-1.65425000
O	0.63940400	-2.40267100	-2.79618200
C	0.59944100	-3.36727800	-3.86700400
H	6.95515900	-1.95594200	3.54189200
H	5.40971600	-2.67582200	5.33602000
H	2.95034000	-2.72020700	4.94671900
H	6.09598400	-1.24196600	1.32782400
H	3.11628900	0.01839700	0.64794300
H	0.66102000	-3.37553500	3.43410700
H	0.77778700	-1.77339400	4.21845300
H	-0.22105000	-1.96005400	2.77618000
H	1.24058000	-2.95394600	-4.64471200
H	0.99246000	-4.32607100	-3.52213300
H	-0.42398600	-3.48790300	-4.22822300
C	3.62340600	-1.33644300	-0.76076300
C	4.76248900	-0.34416600	-1.02819800
C	4.50151600	0.98869900	-0.68869800
O	3.38447900	1.28717200	-0.09695000
C	3.85636500	-2.75840500	-1.25796700
C	3.77478200	-3.88876000	-0.43782900
C	3.93650900	-5.17459600	-0.96406700
C	4.18961200	-5.35258000	-2.32275200
C	4.27855000	-4.23163600	-3.15367900
C	4.11036200	-2.95334500	-2.62623900
C	6.03185300	-0.81434300	-1.43006900
N	7.07612800	-1.23295100	-1.75404300
C	5.44769900	2.12483400	-0.92034600
C	5.36207800	3.23914100	-0.06838600
C	6.19816300	4.33912800	-0.24547600
C	7.12522100	4.35463300	-1.29102500
C	7.20452900	3.26203100	-2.15663400
C	6.37278600	2.15637000	-1.97628900

H	2.75654600	-0.95572700	-1.31924100
H	3.59482500	-3.77633100	0.62610800
H	3.87105300	-6.03525600	-0.30315400
H	4.32413300	-6.35097900	-2.73082000
H	4.48632100	-4.35323100	-4.21390700
H	4.18368800	-2.08793000	-3.27912900
H	4.62638300	3.22347600	0.72834600
H	6.12501600	5.18739100	0.43094400
H	7.77707900	5.21319900	-1.43259100
H	7.91485100	3.26860100	-2.97945400
H	6.44465600	1.31928800	-2.66080500

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C	-0.22425400	5.87159200	3.25051400
C	-1.32052100	4.93448900	3.77377900
C	-0.76687800	3.52147700	3.99478600
C	-0.12914400	2.94342700	2.71522100
C	0.96683600	3.88212600	2.17089600
C	0.42096100	5.30879200	1.97684800
N	0.42863200	1.61457400	2.97404800
N	1.54525700	3.43523200	0.90247800
C	-0.37014400	0.51864400	2.95155000
O	-1.59052800	0.57854600	2.76947600
C	2.55222100	2.53771300	0.81017700
O	2.99424200	1.88921600	1.77010900
H	1.43602200	1.50102800	2.84747800
H	1.10478300	3.73396600	0.02883200
C	1.34828100	-3.23665300	4.14875400
C	0.58711400	-3.17526000	2.97842100
C	0.04079800	-1.96909400	2.51888000
C	0.29112200	-0.79723700	3.27434000
C	1.07184100	-0.86565400	4.43430400
C	1.59960500	-2.07847900	4.87756300
H	1.74664900	-4.19223900	4.47960900
H	0.42834100	-4.08636200	2.41329400
P	-0.83511900	-1.86487600	0.87379100
H	1.24433200	0.04327700	5.00298200
H	2.19661600	-2.11319100	5.78462300
C	4.69376600	2.47201200	-2.91921300
C	4.07091600	1.30257900	-2.47923700
C	3.32346800	1.26535800	-1.29056500
C	3.21327300	2.45918600	-0.54441700
C	3.82541000	3.63355400	-1.00301200
C	4.56926600	3.64708100	-2.18126100
H	5.27279800	2.45734700	-3.83887300
H	4.17075200	0.40476900	-3.07732200
P	2.42032200	-0.29603900	-0.79538900
H	3.71844100	4.54173600	-0.41740100
H	5.04473500	4.56523300	-2.51526100
H	0.54616100	5.99885300	4.02500200
H	-0.63078000	6.86982800	3.04660300
H	-2.14594300	4.89650800	3.04806500
H	-1.74375700	5.32324900	4.70813800
H	-1.55568900	2.83744400	4.32375500
H	-0.00419900	3.54130100	4.78681300
H	-0.90885700	2.83874600	1.95047000
H	1.78840000	3.90416500	2.89973400
H	1.23864900	5.95553300	1.63658500
H	-0.32429100	5.29138000	1.16802000
C	5.40271100	-2.49259200	2.04232400
C	5.70405500	-1.20487500	1.59809700

C	4.82505700	-0.52603600	0.75200100
C	3.62617500	-1.12599500	0.34119300
C	3.32572600	-2.41716700	0.80456300
C	4.20984400	-3.09759000	1.64155400
H	6.09010800	-3.02003800	2.69860800
H	6.62667500	-0.72169600	1.90899300
H	5.07144900	0.47653600	0.42438900
H	2.40323600	-2.90274900	0.50192300
H	3.96092100	-4.09806500	1.98481100
C	2.76723100	-2.79166300	-4.73938200
C	1.75220600	-1.84710300	-4.56700300
C	1.66686000	-1.11561000	-3.38196300
C	2.60157000	-1.30950900	-2.34863200
C	3.62260600	-2.25397500	-2.53693600
C	3.70125100	-2.99156200	-3.72170600
H	2.82935100	-3.36657800	-5.65966900
H	1.01863200	-1.68300300	-5.35195300
H	0.86721600	-0.39216000	-3.25355600
H	4.35974800	-2.41945300	-1.75861600
H	4.49765600	-3.72079300	-3.84676200
C	-5.38779200	-2.26543100	1.77183400
C	-4.91808700	-2.11526900	0.46492900
C	-3.55076400	-1.96928700	0.22622200
C	-2.63624800	-1.97343500	1.29044400
C	-3.11555800	-2.12135500	2.59849700
C	-4.48381400	-2.26766100	2.83596300
H	-6.45272800	-2.37665000	1.95909400
H	-5.61348400	-2.09725600	-0.36907300
H	-3.19796200	-1.84332400	-0.79385500
H	-2.42495400	-2.10963000	3.43423500

H	-4.84174700	-2.37936500	3.85640800
C	-0.31395200	-6.09805800	-1.04491200
C	-1.12974800	-5.94565200	0.08032900
C	-1.29051200	-4.69050800	0.66625000
C	-0.62575400	-3.56471100	0.14606500
C	0.17430900	-3.72953000	-0.99240900
C	0.33351100	-4.98677900	-1.58302300
H	-0.19586700	-7.07625100	-1.50384400
H	-1.65015700	-6.80425100	0.49690400
H	-1.94614400	-4.58282300	1.52527300
H	0.66041700	-2.86634700	-1.43215300
H	0.95746400	-5.08620900	-2.46704300
Pd	0.00076800	-0.06618900	-0.48608500
C	-7.40267700	0.62526200	-3.00870300
C	-7.60730000	0.98686500	-1.65950100
C	-6.53578200	1.20466900	-0.79995000
C	-5.24345500	1.04781100	-1.31824800
C	-5.01511600	0.69138800	-2.68054300
C	-6.12191100	0.47698900	-3.52393400
N	-4.02100600	1.19008600	-0.69713400
C	-3.01883000	0.96090800	-1.63750900
C	-3.60057800	0.64595200	-2.85649700
C	-3.83625300	1.60542200	0.68110000
C	-1.61274300	1.02998000	-1.35380000
C	-0.49707400	1.57234400	-1.67520500
C	0.10033000	2.71032800	-2.34246700
O	0.46363200	3.74800700	-1.79726000
O	0.24213300	2.50700600	-3.67007700
C	0.85916600	3.58134600	-4.40026200
H	-8.26385800	0.46395000	-3.65189200

H	-8.62148200	1.09928300	-1.28534200
H	-6.69887300	1.48591600	0.23615200
H	-5.97248200	0.20245100	-4.56529700
H	-3.05356200	0.40751600	-3.75809700
H	-4.02375700	2.68145800	0.79730500
H	-4.52503300	1.05165200	1.32523400
H	-2.82398600	1.37399300	1.00951500
H	0.88236700	3.24726000	-5.43804800
H	0.27078100	4.49791800	-4.30636600
H	1.87196800	3.76174400	-4.03092500

(*S*,*R*)-II

C	-3.73453100	-6.02115500	-1.91108000
C	-3.36048900	-6.10522700	-0.42541900
C	-3.85300300	-4.86383400	0.32865900
C	-3.31549400	-3.55867300	-0.29168500
C	-3.66509500	-3.46792900	-1.79104400
C	-3.20033400	-4.72851200	-2.54287700
N	-3.85373300	-2.39504400	0.41311000
N	-3.08263200	-2.29712500	-2.44972700
C	-3.24881800	-1.90868500	1.52548300
O	-2.24410500	-2.42547000	2.02841400
C	-3.63777000	-1.06353100	-2.44140500
O	-4.62885000	-0.75523900	-1.76386000
H	-4.45470000	-1.76901400	-0.12610200
H	-2.15579400	-2.39162400	-2.86799000
C	-5.32741600	1.30213000	3.50027300
C	-3.94386100	1.38752700	3.32872700
C	-3.21918200	0.37662400	2.68300500
C	-3.93614200	-0.73491200	2.17507700
C	-5.32472500	-0.80556300	2.34523900
C	-6.02319800	0.20206600	3.00942000
H	-5.85385900	2.10232600	4.01327800
H	-3.42855500	2.26581600	3.69790300
P	-1.39711700	0.56345200	2.35021500
H	-5.85470800	-1.67333200	1.96485200
H	-7.09922700	0.12484100	3.13709900
C	-2.23744000	1.62213100	-5.49966300
C	-2.05658900	1.98149000	-4.16329500
C	-2.46145600	1.14560700	-3.10870400
C	-3.04696000	-0.09687800	-3.44201100
C	-3.20423200	-0.45845300	-4.78820400
C	-2.81370000	0.39455200	-5.81811300
H	-1.92220700	2.30422200	-6.28467700
H	-1.58808000	2.93237200	-3.94119700
P	-2.12202800	1.67580000	-1.34568200
H	-3.65069000	-1.42052800	-5.02150100
H	-2.95665700	0.09961400	-6.85395900
H	-4.82893800	-6.05381600	-2.01352100
H	-3.34312100	-6.88659300	-2.45932200
H	-2.26802000	-6.18654500	-0.32791600
H	-3.78269000	-7.01128800	0.02588200
H	-3.55003400	-4.89579800	1.38073300
H	-4.95193900	-4.83151300	0.31179600
H	-2.22346300	-3.54120000	-0.18817800
H	-4.75575100	-3.37254800	-1.88188300
H	-3.51303900	-4.64986900	-3.59095600
H	-2.10061800	-4.75073000	-2.54295400
C	-6.03617200	3.84608800	-0.02667100
C	-6.05014300	3.03718200	-1.16265700
C	-4.89198900	2.37315000	-1.57308700
C	-3.70073000	2.50680100	-0.84581900
C	-3.69949300	3.31407600	0.30463900
C	-4.85525700	3.98249500	0.70620000
H	-6.93752500	4.36678900	0.28593300
H	-6.96384500	2.92042500	-1.73938300
H	-4.92774000	1.74042400	-2.45036100
H	-2.78910500	3.44112400	0.88160800
H	-4.83005400	4.61111500	1.59244700

C	0.83861900	5.24369100	-1.90475200
C	1.31496100	3.95444000	-1.66028700
C	0.41339100	2.89863800	-1.50280700
C	-0.97328700	3.11565100	-1.57847100
C	-1.43914400	4.41931200	-1.82641000
C	-0.53786800	5.47269600	-1.99075400
H	1.53576000	6.06922900	-2.02374500
H	2.37482500	3.73987900	-1.56028600
H	0.81297300	1.91040300	-1.30053300
H	-2.50478500	4.61520200	-1.88839000
H	-0.91474400	6.47452600	-2.18117400
C	0.81941500	-1.72674400	5.75005600
C	1.52120100	-0.97056500	4.80805100
C	0.83316500	-0.32180400	3.78208100
C	-0.56363400	-0.41719300	3.68461300
C	-1.25931600	-1.17867400	4.63205200
C	-0.56994000	-1.82818900	5.65843200
H	1.35296700	-2.23108600	6.55140800
H	2.60239100	-0.88760100	4.86639700
H	1.38867400	0.27328200	3.06121800
H	-2.33686200	-1.27413800	4.56718000
H	-1.12373300	-2.41386200	6.38780200
C	-0.13291000	4.79087200	3.87782100
C	-0.65200600	3.85687900	4.78033800
C	-1.04784500	2.59674300	4.33539700
C	-0.95264600	2.25465400	2.97319200
C	-0.41196000	3.19250600	2.08383100
C	-0.00625700	4.45386300	2.53137700
H	0.18446200	5.76904000	4.22920200
H	-0.73542900	4.10570900	5.83502500
H	-1.41693900	1.86988800	5.05324800
H	-0.28482700	2.93344800	1.03912400
H	0.41658700	5.15950600	1.82196300
Pd	-0.87836700	0.12795000	0.02477200
C	5.56796400	-2.17774600	3.33709300
C	4.76429400	-3.25073100	3.74524400
C	3.52078600	-3.48441900	3.15219000
C	3.12699900	-2.60709500	2.14607400
C	3.92716700	-1.54284500	1.70103300
C	5.15826400	-1.31576500	2.31334100
N	1.91143600	-2.58914400	1.42523700
C	1.91245400	-1.58114100	0.53829700
C	3.22084300	-0.86141600	0.57195800
C	0.81665400	-3.52414400	1.65275600
C	0.82225700	-1.19685200	-0.25760700
C	0.25599000	-0.89844500	-1.36735100
C	0.29181400	-1.14245100	-2.80638400
O	-0.33239500	-2.02197800	-3.38574000
O	1.07545700	-0.25757700	-3.44186900
C	1.14220800	-0.38074600	-4.87736000
H	6.52990900	-2.01690000	3.81485700
H	5.10896900	-3.91182900	4.53528400
H	2.89493800	-4.31112000	3.47144900
H	5.79766100	-0.50343000	1.98581600
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H	1.00357100	-4.46135900	1.11673300
H	0.73982300	-3.72258600	2.72369600
H	-0.12262400	-3.07804800	1.32401200
H	1.81269000	0.41601500	-5.19745900
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H	0.14921600	-0.25356500	-5.31313600
C	3.98090100	-0.86397400	-0.88363100
C	5.11889900	0.11958100	-0.85076700
C	4.73894200	1.48734800	-0.75375800
O	3.51940300	1.80595800	-0.60937800
C	4.26756500	-2.26287200	-1.40249900
C	5.16973200	-3.15190300	-0.79499700
C	5.37221500	-4.43161100	-1.31461900
C	4.68368000	-4.85432800	-2.45289500
C	3.79420700	-3.97886500	-3.07635100

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C	6.45356500	-0.32300600	-0.75148600
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C	5.43670200	3.77555700	-0.05874600
C	6.30329700	4.86655600	-0.05930700
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C	7.79828800	3.66933400	-1.52851800
C	6.93562300	2.57170400	-1.51803300
H	3.20973300	-0.41415400	-1.51456400
H	5.73530900	-2.84304700	0.07479000
H	6.08143600	-5.09689100	-0.82885500
H	4.84664700	-5.85116100	-2.85481200
H	3.25754200	-4.28646100	-3.97058500
H	2.91601900	-2.01620000	-3.05505200
H	4.50337900	3.80541500	0.49457900
H	6.05377500	5.75737000	0.51270400
H	8.16660900	5.66825500	-0.80244700
H	8.71356700	3.62573400	-2.11348600
H	7.18837900	1.68941900	-2.09484600

(*S*)-III

C	-3.87441100	-6.00832600	1.81594800
C	-3.45179500	-5.28021600	3.09864100
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C	-3.30503200	-3.08586800	1.80844200
C	-3.71640800	-3.81437700	0.51284400
C	-3.32076400	-5.30111500	0.57141800
N	-3.75750500	-1.69333100	1.76967400
N	-3.13681800	-3.22912800	-0.69749800
C	-3.11243100	-0.74255600	2.48856500
O	-2.16134900	-0.99376000	3.23635100
C	-3.67719000	-2.17856000	-1.35498700
O	-4.62898400	-1.50955900	-0.92582600
H	-4.33708800	-1.41463900	0.97557100
H	-2.22808000	-3.56698000	-1.02255400
C	-4.82280600	3.19611000	2.66168100
C	-3.45762200	3.05507200	2.39909500
C	-2.85735000	1.79382700	2.28176900
C	-3.68188300	0.65135300	2.42887100
C	-5.05283100	0.80336000	2.66824600
C	-5.62786500	2.06849100	2.78794000
H	-5.24986100	4.19087400	2.75798900
H	-2.85830100	3.94924200	2.27431100
P	-1.06984200	1.62138000	1.76813400
H	-5.66480600	-0.08589700	2.78615900
H	-6.69215200	2.16636800	2.98281000
C	-2.33644200	-1.62169800	-5.40421300
C	-2.15508700	-0.58515600	-4.48651000
C	-2.54272600	-0.71138500	-3.14241600
C	-3.11799900	-1.93590700	-2.73561700
C	-3.28103000	-2.97679800	-3.65955000
C	-2.90145200	-2.82611200	-4.99181600
H	-2.03341700	-1.48024000	-6.43827300
H	-1.70196800	0.33707800	-4.82906900
P	-2.18989800	0.66982500	-1.93190200
H	-3.71825600	-3.91167900	-3.32190300
H	-3.04518300	-3.64167900	-5.69514300
H	-4.97228400	-6.03993000	1.76002800
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H	-3.89095600	-5.76669700	3.97818900
H	-3.52908300	-3.27058200	3.94162600
H	-4.96727300	-3.73121900	3.02709000

H	-2.20976900	-3.08197900	1.87326500
H	-4.80691200	-3.73332700	0.40879400
H	-3.66908200	-5.79505000	-0.34361700
H	-2.22309200	-5.37229900	0.56985300
C	-6.15651300	3.11730300	-1.75576900
C	-6.12149400	1.92696800	-2.48267700
C	-4.95068500	1.16837200	-2.53924200
C	-3.79687600	1.59010200	-1.86370900
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C	-5.01297700	3.54444200	-1.07806900
H	-7.06851800	3.70722800	-1.71566700
H	-7.00727500	1.58256400	-3.00997100
H	-4.94436000	0.24287700	-3.10172400
H	-2.96330800	3.13301100	-0.59849900
H	-5.02850000	4.46750500	-0.50518000
C	0.47270200	3.50504900	-4.52896900
C	1.04257900	2.49203200	-3.75502300
C	0.23024900	1.65522500	-2.98817800
C	-1.16543900	1.81665900	-2.98074800
C	-1.72761800	2.83628400	-3.76650500
C	-0.91368400	3.67308400	-4.53341800
H	1.10466300	4.16121600	-5.12165500
H	2.12055100	2.35993400	-3.73149400
H	0.68392900	0.88286700	-2.37593200
H	-2.80261900	2.98120500	-3.78076800
H	-1.36658600	4.45814200	-5.13351800
C	1.42491500	1.21957500	5.68277000
C	2.04368200	1.27396700	4.43123900
C	1.26999800	1.36947700	3.27425100
C	-0.13083000	1.41206500	3.35155100
C	-0.74334700	1.35608800	4.60975700
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H	2.02592700	1.14392600	6.58517800
H	3.12613000	1.23108400	4.35263600
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H	-1.82420200	1.37083800	4.68809200
H	-0.45728800	1.21742100	6.73753900
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C	-0.38001900	4.33321300	2.39009600
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H	0.64553900	6.97520500	0.50143400
H	0.16002500	6.36017900	2.86410200
H	-0.56634900	4.07319100	3.42785600
H	-0.33419700	2.97768600	-0.72484300
H	0.40146900	5.25942600	-1.29185400
Pd	-0.76619800	0.02878600	-0.02641400
C	5.99593000	-2.11358300	3.42839000
C	5.09165000	-2.34721700	4.48606400
C	3.71817100	-2.28432700	4.28476100
C	3.26520800	-1.97191800	2.99575200
C	4.15905600	-1.74059200	1.91227500
C	5.54722700	-1.81472400	2.14897000
N	1.97393500	-1.84323400	2.53448500
C	2.01598100	-1.56659800	1.17250600
C	3.34874500	-1.49425800	0.75075300
C	0.78949400	-2.13512000	3.32172200
C	0.84493300	-1.32852600	0.37139500

C	0.27491500	-1.61225600	-0.74625400
C	0.26272700	-2.61369400	-1.79969500
O	-0.46237300	-3.60155800	-1.82900700
O	1.15511000	-2.33680900	-2.76922100
C	1.24544500	-3.30039900	-3.83632800
H	7.06407700	-2.17191400	3.61860500
H	5.47539300	-2.58278900	5.47522300
H	3.02238400	-2.46789200	5.09763300
H	6.25794900	-1.64487600	1.34702900
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H	0.70451900	-3.21392200	3.50914500
H	0.84270400	-1.60913300	4.27855800
H	-0.10108600	-1.78775100	2.80246700
H	2.06298900	-2.95135300	-4.46600000
H	1.47212200	-4.29077400	-3.43519300
H	0.30607200	-3.33403800	-4.39382200
C	3.79415400	-1.17451800	-0.66052500
C	4.64293700	0.11547900	-0.71601400
C	4.04821600	1.34564300	-0.64721800
O	2.70982200	1.46727700	-0.43573100
C	4.43671000	-2.33596800	-1.43265100
C	4.60530800	-3.60916000	-0.88057600
C	5.13907900	-4.65299700	-1.64295700
C	5.51058400	-4.44053200	-2.96951200
C	5.34235600	-3.17245300	-3.53318800
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C	6.05854000	-0.01053000	-0.77067500
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C	4.69095400	2.67143300	-0.78614000
C	4.12892300	3.77386300	-0.11567500
C	4.69944200	5.03925300	-0.23151300
C	5.83156500	5.23069000	-1.02652700
C	6.38517400	4.14687200	-1.71121800
C	5.81945500	2.87836100	-1.59832700
H	2.88046300	-0.95354900	-1.22821800
H	4.32095300	-3.78893600	0.15036900
H	5.26603600	-5.63350000	-1.19114900
H	5.92992400	-5.25133700	-3.55944900
H	5.63123000	-2.99051700	-4.56539900
H	4.68107300	-1.15145600	-3.21834300
H	3.24549900	3.63080400	0.49574400
H	4.25624400	5.87650200	0.30083200
H	6.27651200	6.21818900	-1.11635100
H	7.25814000	4.28761400	-2.34247700
H	6.25428400	2.05229800	-2.14801300

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C	-1.25879500	-0.77239200	0.04486000
C	-0.07234400	-0.13198500	-0.16494300
C	1.17776700	-0.99020300	-0.11966700
O	1.06210300	-2.20694200	-0.20326000
C	-2.64004600	-0.31664600	0.05783100
C	-3.06584100	1.00832600	-0.18425500
C	-4.41881500	1.32985800	-0.14561400
C	-5.37629600	0.34907500	0.13244400
C	-4.97398700	-0.96657500	0.37404000
C	-3.62248000	-1.29284400	0.33700800
C	0.01984800	1.25392200	-0.49232900
N	0.09131300	2.38141800	-0.77911000
C	2.53220400	-0.37412600	0.02027100
C	3.62344600	-1.10609700	-0.47958400

C	4.91963000	-0.61905200	-0.34766600	H	-5.71133000	-1.73435700	0.59007000
C	5.14606000	0.59456600	0.30959900	H	-3.30849400	-2.31653000	0.52436900
C	4.07147900	1.31587400	0.83206700	H	3.43016400	-2.05498600	-0.96880900
C	2.76851700	0.83974700	0.68433900	H	5.75478600	-1.18492000	-0.75104700
H	-1.13022500	-1.83620700	0.23692600	H	6.15863900	0.97428500	0.41693300
H	-2.34379700	1.78452700	-0.40332900	H	4.24472300	2.25208200	1.35489900
H	-4.72934700	2.35348200	-0.33468700	H	1.94743600	1.40928200	1.10407500
H	-6.43064900	0.61027300	0.16003400				

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