Electronic Supplementary Material (ESI) for ChemComm.

Palladium-catalyzed asymmetric [4+2] annulation of vinyl benzoxazinanone with pyrazolone 4,5-diones to access spirobenzoxazine frameworks

Supporting Information

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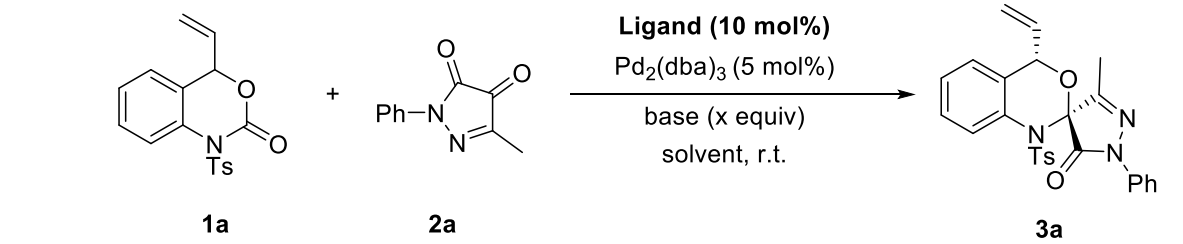
1. General information

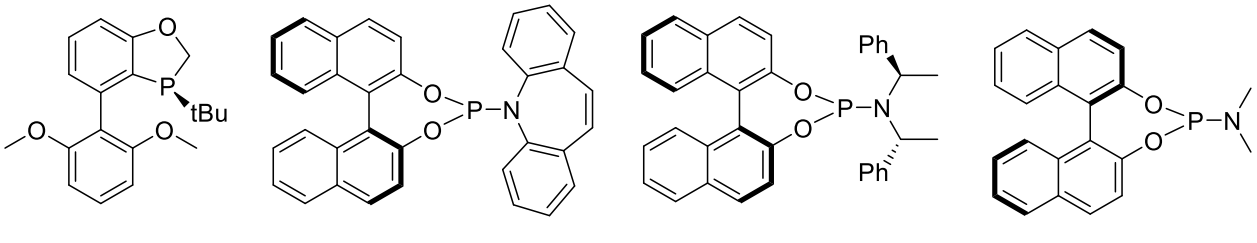
High Performance Liquid Chromatography (HPLC) was analyzed by chiral column in comparison with authentic racemates, using a Daicel Chiralpak ID Column (250 × 4.6 mm), Daicel Chiralpak IB Column (250 × 4.6 mm), Daicel Chiralpak IA Column (250 × 4.6 mm) UV detection was performed at 220 nm or 254 nm. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or DMSO-d_6 on Bruker 600 or 700 MHz NMR instrument (at 600, or 700 MHz for ^1H, and at 150, or 175 for ^{13}C). Protonchemical shifts are reported in parts per million (δ scale). The ^1H NMR chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as standard. The ^{13}C NMR chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.00 ppm, DMSO-d_6: δ = 39.52 ppm). Data are reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s) (Hz), integration]. High-resolution mass spectra (HRMS) were obtained using Agilent P/N G1969-90010. High-resolution mass spectra were reported for the molecular ion $[M+H]^+$ or $[M+Na]^+$. X-ray diffraction experiment was carried out on on Agilent Gemini or Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre. UV detection was performed at 254 nm. Column UV detection was performed at 254 nm. Column chromatography was performed on silica gel (200–300 mesh) using an eluent of ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates; products were visualized using UV light. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at 25 ℃. All reagents and solvents were obtained from commercial sources andused without further purification. Oil baths were used as the heat source. Melting points were recorded on BUCHI Melting Point M-565 instrument. Vinyl benzoxazinanone **1**[1] and Pyrazolone 4,5-Diones **2**[2] were prepared according to the literature procedures.

2. Screening of catalysts and condition optimization

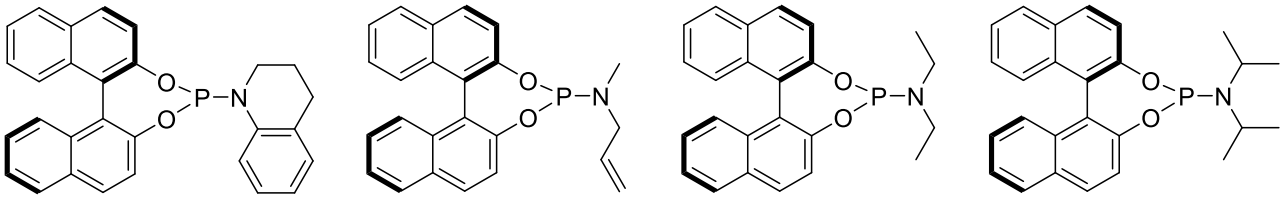
2.1 Condition optimization for catalytic asymmetric [4+2] cycloaddition[a]



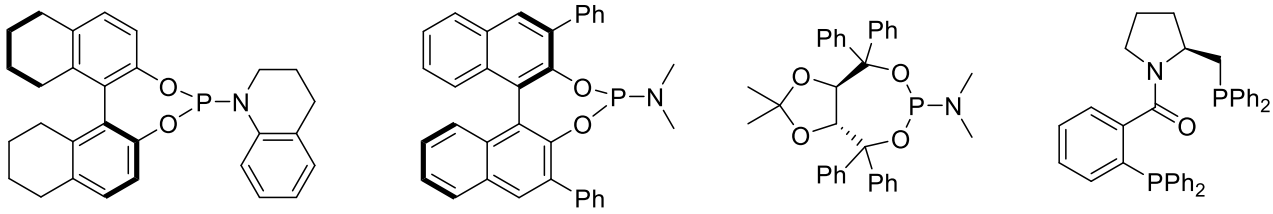
1a **2a** **3a**



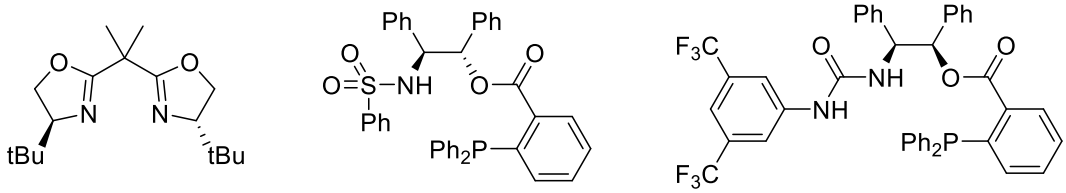
L1 **L2** **L3** **L4**



L5 **L6** **L7** **L8**



L9 **L10** **L11** **L12**



L13 **L14** **L15**

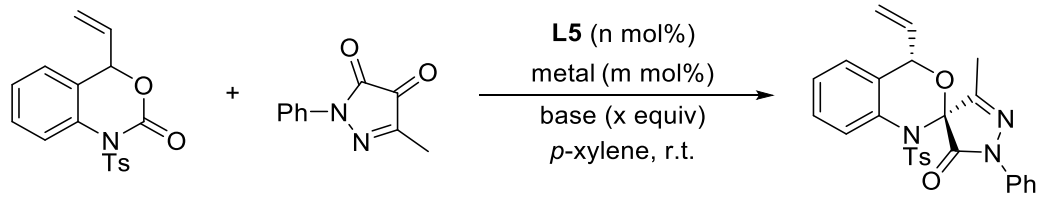
entry	lig.	1a:2a	base	x	solvent	Yield (%)[b]	dr[c]	ee(%)[d]
1	**L1**	1:1.2	-	-	Toluene	N.R.	-	-

2	**L2**	1:1.2	-	-	Toluene	9	>19:1	36
3	**L3**	1:1.2	-	-	Toluene	11	>19:1	20
4	**L4**	1:1.2	-	-	Toluene	41	>19:1	60
5	**L5**	1:1.2	-	-	Toluene	11	>19:1	90
6	**L6**	1:1.2	-	-	Toluene	61	>19:1	4
7	**L7**	1:1.2	-	-	Toluene	10	>19:1	80
8	**L8**	1:1.2	-	-	Toluene	25	>19:1	88
9	**L9**	1:1.2	-	-	Toluene	10	>19:1	64
10	**L10**	1:1.2	-	-	Toluene	N.R.	-	-
11	**L11**	1:1.2	-	-	Toluene	N.R.	-	-
12	**L12**	1:1.2	-	-	Toluene	N.R.	-	-
13	**L13**	1:1.2	-	-	Toluene	N.R.	-	-
14	**L14**	1:1.2	-	-	Toluene	N.R.	-	-
15	**L15**	1:1.2	-	-	Toluene	N.R.	-	-
16	**L5**	1:1.2	-	-	MeCN	74	>19:1	74
17	**L5**	1:1.2	-	-	THF	23	>19:1	90
18	**L5**	1:1.2	-	-	DCM	18	>19:1	90
19	**L5**	1:1.2	-	-	Toluene	11	>19:1	90
20	**L5**	1:1.2	-	-	DCE	26	>19:1	86
21	**L5**	1:1.2	-	-	CCl_4	-	-	-
22	**L5**	1:1.2	-	-	*m*-xylene	14	>19:1	90
23	**L5**	1:1.2	-	-	*p*-xylene	20	>19:1	92
24	**L5**	1:1.2	PhCOOH	1.0	*p*-xylene	N.R.	-	-

25	**L5**	1:1.2	K_2CO_3	1.0	*p*-xylene	32	>19:1	92
26	**L5**	1:1.2	Cs_2CO_3	1.0	*p*-xylene	51	>19:1	92
27	**L5**	1:1.2	tBuOK	1.0	*p*-xylene	N.R.	-	-
28	**L5**	1:1.2	TEA	1.0	*p*-xylene	41	>19:1	92
29	**L5**	1.5:1	Cs_2CO_3	1.0	*p*-xylene	62	>19:1	92
30	**L5**	2.0:1	Cs_2CO_3	1.0	*p*-xylene	53	>19:1	92
31	**L5**	1:1.5	Cs_2CO_3	1.0	*p*-xylene	64	>19:1	92
32	**L5**	1:1.5	Cs_2CO_3	0.1	*p*-xylene	37	>19:1	92
33	**L5**	1:1.5	Cs_2CO_3	0.3	*p*-xylene	64	>19:1	92
34	**L5**	1:1.5	Cs_2CO_3	0.5	*p*-xylene	66	>19:1	92
35	**L5**	1:1.2	Cs_2CO_3	0.5	*p*-xylene	58	>19:1	92
36	**L5**	1.5:1	Cs_2CO_3	0.5	*p*-xylene	53	>19:1	92
37[e]	**L5**	1:1.5	Cs_2CO_3	0.5	*p*-xylene	35	>19:1	76
38[f]	**L5**	1:1.5	Cs_2CO_3	0.5	*p*-xylene	22	>19:1	64

[a]Unless otherwise noted. The reaction was carried out in solvent (1.0 mL) at room temperature for 12 h. [b]Isolated yield. [c]Determined by ^{1}H NMR. [d]Determined by HPLC analysis. [e]At 40 °C. [f]At 60 °C

2.2 Screening of the Ratio of matel and Ligand[a]



1a **2a** **3a**

entry	metal	m/n	x	Yield(%)[b]	dr[c]	ee(%)[d]
1	$Pd_2(dba)_3$	5/10	0.5	64	>19:1	92
2	$Pd_2(dba)_3$•$CHCl_3$	5/10	0.5	66	>19:1	92

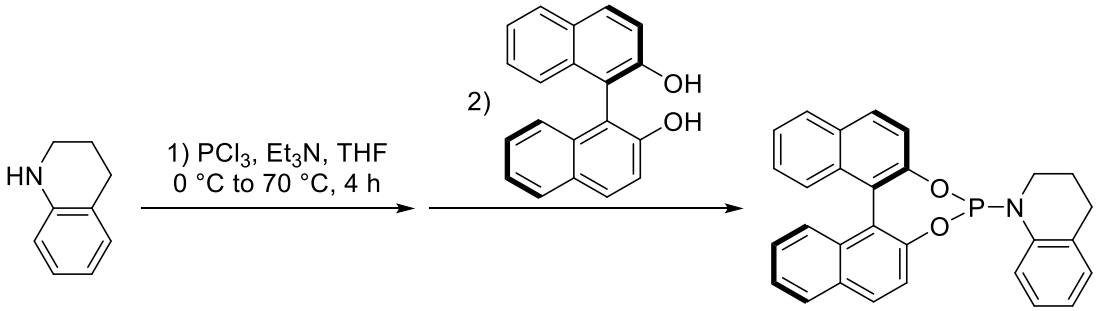
3	$Pd(PPh_3)_4$	5/10	0.5	28	>19:1	54
4	$Pd(PPh_3)Cl_2$	5/10	0.5	38	>19:1	66
5	$Pd(OAc)_2$	5/10	0.5	27	>19:1	24
6	$Pd_2(dba)_3$	10/20	0.5	76	>19:1	92
7	$Pd_2(dba)_3$	5/15	0.5	73	>19:1	92
8	$Pd_2(dba)_3$	2.5/7.5	0.5	59	>19:1	92
9	$Pd_2(dba)_3•CHCl_3$	2.5/7.5	0.5	56	>19:1	92
10	$Pd_2(dba)_3$	5/20	0.5	72	>19:1	92
11	$Pd_2(dba)_3$	2.5/10	0.5	65	>19:1	92
12	$Pd_2(dba)_3•CHCl_3$	2.5/10	0.5	67	>19:1	92
13	$Pd_2(dba)_3•CHCl_3$	2.5/10	0.75	76	>19:1	92
14	$Pd_2(dba)_3•CHCl_3$	2.5/10	1.0	69	>19:1	92
15	$Pd_2(dba)_3•CHCl_3$	2.5/10	1.5	68	>19:1	92
16	$Pd_2(dba)_3•CHCl_3$	2.5/5	0.75	44	>19:1	92
17	$Pd_2(dba)_3•CHCl_3$	2.5/10	-	23	>19:1	92

[a]Unless otherwise noted, reactions were carried out with **1a** (0.1 mmol), **2a** (0.15 mmol), chiral ligands **L5** and Cs_2CO_3 (x equiv) in *p*-xylene (1.0 mL) at room temperature for 12 h. [b]Isolated yield. [c]Determined by ^1H NMR. [d]Determined by HPLC analysis.

3. Preparation of Phosphoramidite ligands

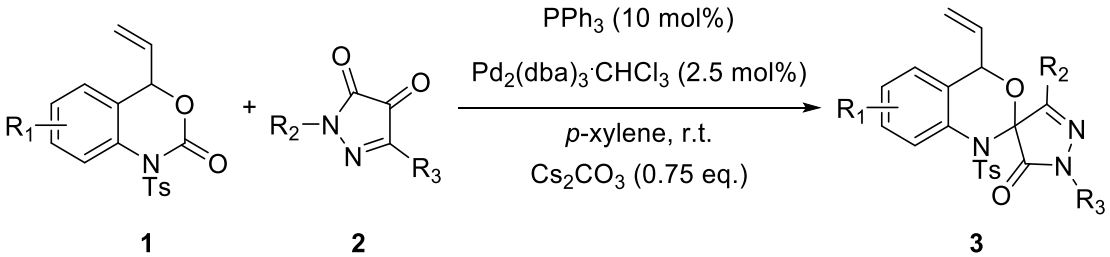
Preparation of Phosphoramidite ligands **L4-L9**[3-4] ware accomplished according to the reported procedures.

[**(*R*)-L5** as a representative example]



A flame-dried Schlenk tube was equipped with vacuum/argon stopcock and a magnetic stirring bar. The Schlenk tube was charged with PCl_3 (0.3 mL, 3.0 mmol, 1.0 equiv.), anhydrous Et_3N (2.1 mL, 15.0 mmol, 5.0 equiv.) DMAP (0.02 mmol, 0.05 equiv.) and THF (4 mL), and then cooled down to 0 °C. Another flame-dried tube was charged with 1,2,3,4-tetrahydroquinoline (3.0 mmol, 1.0 equiv.) and THF (5 mL). This mixture was added dropwise to the above mentioned PCl_3 solution at 0 °C. After the addition was complete, the reaction mixture was heated at 70 °C for 4h, and then was cooled down to 0 °C. To this Schlenk tube at 0°C was slowly added a solution of (*R*)-1,1-Bi(2-Naphthol) (3.0 mmol) in THF (5 mL). The resulting mixture was stirred at room temperature overnight and monitored by TLC (petroleum ether/ethyl acetate). After completion of the reaction, the reaction filtered through celite. The organic phase was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200/1 to v/v) to give the final products (***R***)-**L5** (807.4 mg, 60% yield) as a white solid.

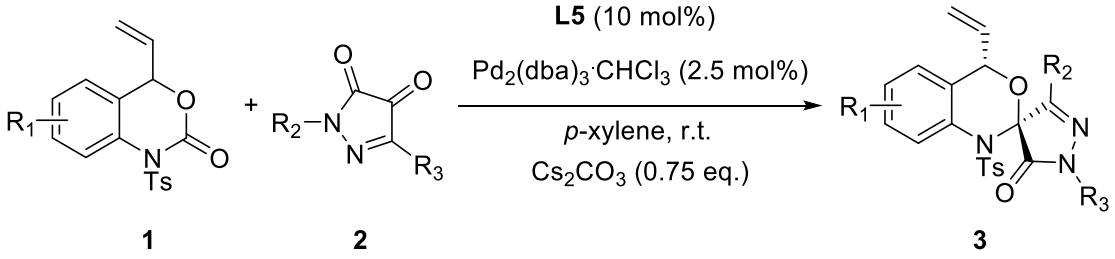
4. General procedure for synthesis of Compound (±) 3



To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.0025 mmol) and PPh_3 (0.0100

mmol), then 1 mL *p*-xylene was added under Ar atmosphere. This solution was stirred at room temperature for 0.5 h. Then vinyl benzoxazinanone **1** (0.1000 mmol), pyrazolone 4,5-diones **2** (0.1500 mmol) and Cs_2CO_3 (0.0750 mmol) were added subsequently. The reaction mixture was stirred at room temperature for 12 h and monitored by TLC (petroleum ether/ethyl acetate). After completion of the reaction, the reaction mixture was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200/1 to v/v) to give the final products (±) **3**.

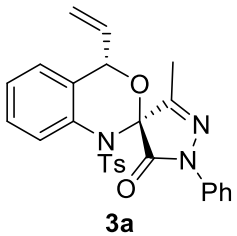
5. General procedure for synthesis of Compound 3



1 **2** **3**

To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.0025 mmol) and **L5** (0.0100 mmol), then 1 mL *p*-xylene was added under Ar atmosphere. This solution was stirred at room temperature for 0.5 h. Then vinyl benzoxazinanone (0.1000 mmol) **1**, Pyrazolone 4,5-Diones **2** (0.1500 mmol) and Cs_2CO_3 (0.0750 mmol) were added subsequently. The reaction mixture was stirred at room temperature for 12 h and monitored by TLC (petroleum ether/ethyl acetate). After completion of the reaction, the reaction mixture was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200/1 to v/v) to give the final products **3**.

(2*S*,4*S*)-3'-methyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3a)

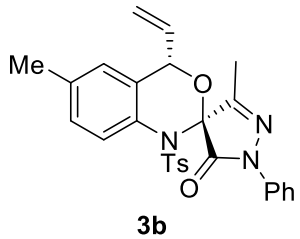


3a

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3a** as a white solid in 76% yield (35.9 mg), m.p. 180–182 °C; $[\alpha]_D^{25}$ = +54.19 (c = 0.387, CH_2Cl_2); >19:1 *dr*; 92% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol =90/10, 1 mL/min), t_R = 7.67 min (minor), t_R = 8.54 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93–7.92 (m, 2H), 7.85–7.82 (m, 3H), 7.38–7.35 (m, 2H), 7.18–7.15 (m, 2H), 7.14–7.13 (m, 2H), 6.99–6.95 (m, 2H), 5.93 (d, *J* = 7.8 Hz, 1H), 5.88–5.82 (m, 1H), 5.49 (s, 1H), 5.47 (d, *J* = 4.2 Hz, 1H), 2.26

(s, 3H), 2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 157.3, 144.9, 138.0, 134.2, 133.0, 132.2, 130.8, 129.5, 129.2, 128.9, 128.8, 125.4, 124.3, 123.9, 122.4, 119.4, 87.6, 71.6, 21.6, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{27}NNaO_4^+$ 496.1301, found 496.1305.

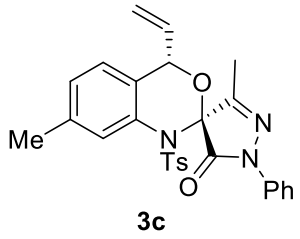
(2*S*,4*S*)-3',6-dimethyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3b)



3b

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3b** as a white solid in 68% yield (34.5 mg), m.p. 178–180 °C; $[\alpha]_D^{25}$ = +73.84 (*c* = 0.05, CH_2Cl_2); >19:1 *dr*; 80% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 8.87 min (minor), t_R = 10.31 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.91–7.90 (m, 2H), 7.83–7.82 (m, 2H), 7.72, (d, *J* = 8.4 Hz, 1H), 7.36–7.34 (m, 2H), 7.14–7.12 (m, 3H), 6.97 (d, *J* = 6.3 Hz, 1H), 6.77 (s, 1H), 5.88 (d, *J* = 8.4 Hz, 1H), 5.86–5.81 (m, 1H), 5.47 (d, *J* = 2.1 Hz, 1H), 2.26 (s, 3H), 2.17 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.8, 157.4, 144.8, 134.4, 133.7, 132.3, 130.9, 130.4, 129.5, 129.3, 129.2, 128.9, 125.4, 124.9, 122.2, 119.5, 119.4, 87.5, 71.7, 21.6, 20.9, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{25}N_3NaO_4S^+$ 510.1458, found 510.1467.

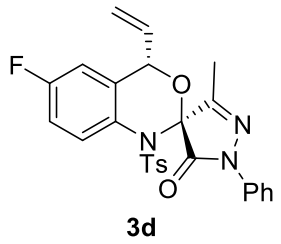
(2*S*,4*S*)-3',7-dimethyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3c)



3c

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3c** as a white solid in 71% yield (34.5 mg), m.p. 124–126 °C; $[\alpha]_D^{25}$ = +118.15 (*c* = 0.24, CH_2Cl_2); >19:1 *dr*; 94% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 11.29 min (minor), t_R = 12.68 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2H), 7.84–7.83 (m, 2H), 7.64 (s, 1H), 7.37–7.35 (m, 2H), 7.15–7.13 (m, 3H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 7.0 Hz, 1H), 5.89 (d, *J* = 7.7 Hz, 1H), 5.85–5.80 (m, 1H), 5.46 (d, *J* = 3.6 Hz, 1H), 5.44 (s, 1H), 2.27 (s, 3H), 2.23 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.8, 157.3, 144.9, 138.8, 138.0, 134.2, 132.8, 132.4, 129.5, 129.2, 128.9, 127.9, 125.4, 124.4, 124.0, 122.1, 120.1, 119.4, 87.5, 71.5, 21.63, 21.61, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{25}N_3NaO_4S^+$ 510.1458, found 510.1460.

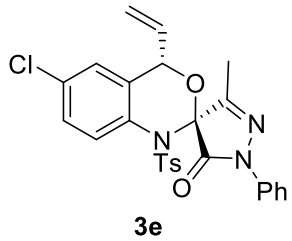
(2*S*,4*S*)-6-fluoro-3'-methyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3d)



3d

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3d** as a white solid in 73% yield (36.0 mg); m.p. 172–174 °C; $[\alpha]_D^{25}$ = +93.26 (*c* = 0.09, CH_2Cl_2); >19:1 *dr*; 92% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 10.91 min (minor), t_R = 13.00 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.90–7.89 (m, 2H), 7.83–7.81 (m, 3H), 7.37–7.35 (m, 2H), 7.16–7.14 (m, 3H), 6.87 (td, *J* = 8.4, 2.8 Hz, 1H), 6.87 (dd, *J* = 8.4, 3.5 Hz, 1H), 5.88 (d, *J* = 7.7 Hz, 1H), 5.83–5.78 (m, 1H), 5.50–5.46 (m, 2H), 2.27 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 159.0 (d, $^1J_{CF}$ = 245.0 Hz), 157.0, 145.1, 137.9, 134.0, 133.4 (d, $^3J_{CF}$ = 7.0 Hz), 131.5, 129.6, 129.1, 129.0 (d, $^4J_{CF}$ = 3.5 Hz), 128.9, 125.5, 122.9, 121.4 (d, $^3J_{CF}$ = 8.8 Hz), 119.4, 115.4 (d, $^2J_{CF}$ = 22.8 Hz), 112.0 (d, $^2J_{CF}$ = 24.5 Hz), 87.4, 71.3, 21.6, 12.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}FN_3NaO_4S^+$ 514.1207, found 514.1198.

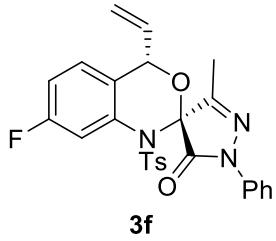
(2*S*,4*S*)-6-chloro-3'-methyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3e)



3e

The residue was purified by a silica gel flash chrom atography (PE/EA = 200/1) giving the product **3e** as a white solid in 63% yield (33.0 mg), m.p. 175–177 °C; $[\alpha]_D^{25}$ = +84.77 (*c* = 0.07, CH_2Cl_2); >19:1 *dr*; 82% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 8.90 min (minor), t_R = 10.39 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92–7.91 (m, 2H), 7.83–7.82 (m, 2H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.38–7.35 (m, 2H), 7.16–7.12 (m, 4H), 6.96 (d, *J* = 3.0 Hz, 1H), 5.90 (d, *J* = 7.8 Hz, 1H), 5.84–5.78 (m, 1H), 5.52–5.47 (m, 2H), 2.29 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 157.0, 145.3, 137.8, 133.8, 132.5, 131.6, 131.5, 129.7, 129.5, 129.2, 128.9, 128.8, 125.5, 124.7, 123.0, 120.7, 119.4, 87.5, 71.2, 21.7, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}ClN_3NaO_4S^+$ 530.0912, found 530.0918.

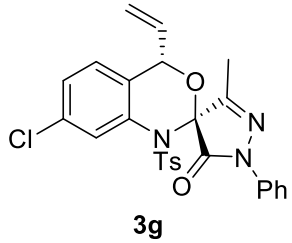
(2*S*,4*S*)-7-fluoro-3'-methyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3f)



3f

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3f** as a white solid in 62% yield (30.7 mg), m.p. 153–155 °C; $[\alpha]_D^{25}$ = +95.21 (*c* = 0.07, CH_2Cl_2); >19:1 *dr*; 92% *ee*, determined by HPLC on a Chiralpak IB column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 5.71 min (minor), t_R = 6.34 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.95–7.94 (m, 2H), 7.83–7.82 (m, 2H),7.59 (dd, *J* = 10.5, 2.1 Hz, 1H), 7.38–7.35 (m, 2H), 7.18–7.14 (m, 3H), 6.94–6.92 (m, 1H), 6.65 (td, *J* = 8.4, 2.8 Hz, 1H), 5.89 (d, *J* = 8.4 Hz, 1H), 5.84–5.79 (m, 1H), 5.49–5.46 (m, 2H), 2.28 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.5, 162.6 (d, $^1J_{CF}$ = 245.0 Hz), 157.1, 145.3, 137.9, 134.2 (d, $^3J_{CF}$ = 12.3 Hz), 133.7, 132.0, 129.7, 129.3, 128.9 126.3 (d, $^4J_{CF}$ = 1.8 Hz), 125.6 (d, $^3J_{CF}$ = 10.5 Hz), 125.5, 122.6, 119.4, 110.4 (d, $^2J_{CF}$ = 21.0 Hz), 107.4 (d, $^2J_{CF}$ = 26.3 Hz), 87.5, 71.3, 21.7, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}FN_3NaO_4S^+$ 514.1207, found 514.1214.

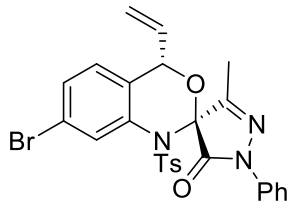
(2*S*,4*S*)-7-chloro-3'-methyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3g)



3g

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3g** as a white solid in 55% yield (27.8 mg), m.p. 161–163 °C; $[\alpha]_D^{25}$ = +79.43 (*c* = 0.04, CH_2Cl_2); >19:1 *dr*; 96% *ee*, determined by HPLC on a Chiralpak IA column at 254 nm (*n*-hexane/2-propanol = 95/5, 1 mL/min), t_R = 8.67 min (minor), t_R = 11.76 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.94–7.93 (m, 2H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.84–7.82 (m, 2H), 7.38–7.36 (m, 2H), 7.18–7.16 (m, 3H), 6.94–6.92 (m, 1H), 6.90–6.89 (m, 1H), 5.89 (d, *J* = 7.7 Hz, 1H), 5.82–5.77 (m, 1H), 5.49 (d, *J* = 4.9 Hz, 1H), 5.48–5.46 (m, 1H), 2.29 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.5, 157.0, 145.4, 137.9, 134.5, 134.0, 133.6, 131.8, 129.7, 129.3, 128.94, 128.90, 125.5, 125.4, 123.8, 122.8, 119.5, 119.4, 87.6, 71.2, 21.7, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}ClN_3NaO_4S^+$ 530.0912, found 530.0921.

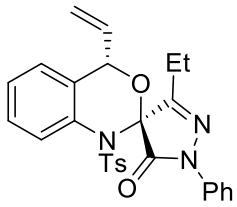
(2*S*,4*S*)-7-bromo-3'-methyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3h)



3h

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3h** as a white solid in 72% yield (40.0 mg), m.p. 142–144 °C; $[\alpha]_D^{25}$ = +113.19 (*c* = 0.17, CH_2Cl_2); >19:1 *dr*; 96% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 6.10 min (minor), t_R = 6.79 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.94–7.93 (m, 2H), 7.84–7.82 (m, 2H), 7.38–7.35 (m, 2H), 7.19–7.15 (m, 3H), 7.08 (dd, *J* = 1.8, 8.4 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 5.87 (d, *J* = 8.4 Hz, 1H), 5.82–5.76 (m, 1H), 5.49 (d, *J* = 4.2 Hz, 1H), 5.47 (d, *J* = 12.6 Hz, 1H), 2.29 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 157.0, 145.4, 137.9, 134.1, 133.6, 131.7, 129.7,129.39, 129.36, 128.9, 126.7, 125.7, 125.5, 122.8, 122.3, 122.2, 119.4, 87.6, 71.2, 21.7, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}BrN_3NaO_4S^+$ 574.0407, found 574.0403.

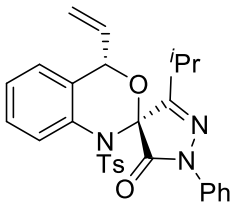
(2*S*,4*S*)-3'-ethyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3i)



3i

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3i** as a white solid in 72% yield (35.1 mg), m.p. 164–166 °C; $[\alpha]_D^{25}$ = +90.37 (*c* = 0.054, CH_2Cl_2); >19:1 *dr*; 92% *ee*, determined by HPLC on a Chiralpak IA column at 254 nm (*n*-hexane/2-propanol = 95/5, 1 mL/min), t_R = 7.87 min (minor), t_R = 11.30 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2H), 7.87–7.85 (m, 2H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.37–7.35 (m, 2H), 7.18–7.14 (m, 2H), 7.13–7.11 (m, 2H), 6.98–6.94 (m, 2H), 5.92 (d, *J* = 7.8 Hz, 1H), 5.87–5.81 (m, 1H), 5.47 (s, 1H), 5.45 (d, *J* = 3.6 Hz, 1H), 2.63–2.57 (m, 1H), 2.42–2.36 (m, 1H), 2.25 (s, 3H), 1.22 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.9, 161.0, 144.9, 138.1, 134.3, 133.1, 132.2, 131.0, 129.5, 129.2, 128.9, 128.8, 125.3, 124.2, 123.9, 122.3, 119.6, 119.4, 87.8, 71.5, 21.6, 20.2, 9.1. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{25}N_3NaO_4S^+$ 510.1458, found 510.1463.

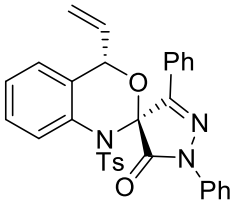
(2*S*,4*S*)-3'-isopropyl-1'-phenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3j)



3j

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3j** as a white solid in 65% yield (32.8 mg), m.p. 195–197 °C; $[\alpha]_D^{25}$ = +132.78 (*c* = 0.07, CH_2Cl_2); >19:1 *dr*; 80% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 8.24 min (minor), t_R = 9.60 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.91–7.90 (m, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.86–7.85 (m, 2H), 7.37–7.35 (m, 2H), 7.20–7.18 (m, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.12–7.11 (m, 2H), 6.98–6.97 (m, 2H), 5.93 (d, *J* = 7.7 Hz, 1H), 5.87–5.82 (m, 1H), 5.46 (s, 1H), 5.44 (d, *J* = 6.3 Hz, 1H), 2.86–2.80 (m, 1H), 2.26 (s, 3H), 1.34 (d, *J* = 7.0 Hz, 1H), 1.07 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 163.5, 144.8, 138.1, 134.5, 133.2, 132.3, 131.3, 129.5, 129.1, 128.8, 128.4, 125.3, 124.2, 124.0, 122.0, 119.9, 119.4, 88.5, 71.2, 27.9, 21.6, 20.7, 19.8. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{27}N_3NaO_4S^+$ 524.1614, found 524.1623.

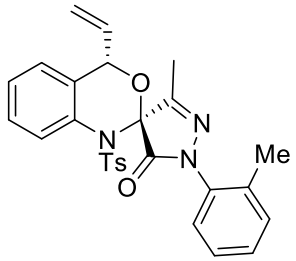
(2*S*,4*S*)-1',3'-diphenyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3k)



3k

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3k** as a white solid in 63% yield (33.7 mg), m.p. 195–197 °C; $[\alpha]_D^{25}$ = +132.78 (*c* = 0.07, CH_2Cl_2); >19:1 *dr*; 82% *ee*, determined by HPLC on a Chiralpak ID column at 220 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 8.61 min (minor), t_R = 10.03 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.97–7.95 (m, 2H), 7.90–7.89 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.68–7.67 (m, 2H), 7.42–7.40 (m, 2H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.20–7.17 (m, 2H), 7.12–7.10 (m, 2H), 7.05 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.0 Hz, 1H), 6.15 (d, *J* = 7.7 Hz, 1H), 5.90–5.85 (m, 1H), 5.51–5.47 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.8, 154.5, 144.8, 138.0, 134.5, 133.4, 132.4, 130.7, 130.3, 129.5, 129.2, 129.0, 128.9, 128.53, 128.52, 127.2, 125.7, 124.5, 123.9, 122.4, 119.7, 119.6, 88.1, 71.6, 21.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{25}N_3NaO_4S^+$ 558.1458, found 558.1456.

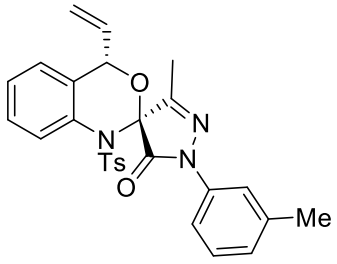
(2*S*,4*S*)-3'-methyl-1'-(*o*-tolyl)-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3l)



3l

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3l** as a white solid in 73% yield (35.8 mg), m.p. 173–175 °C; $[\alpha]_D^{25}$ = +119.07 (*c* = 0.11, CH_2Cl_2); >19:1 *dr*; 96% *ee*, determined by HPLC on a Chiralpak IB column at 220 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 6.21 min (minor), t_R = 6.95 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.40–7.36 (m, 1H), 7.24–7.20 (m, 3H), 7.17–7.14 (m, 1H), 7.11–7.09 (m, 2H), 6.99–6.94 (m, 2H), 5.95 (d, *J* = 7.8 Hz, 1H), 5.91–5.85 (m, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 5.48–5.47 (m, 1H), 2.32 (s, 3H), 2.24 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4, 157.2, 144.9, 135.6, 134.1, 133.1, 132.4, 130.6, 129.5, 129.4, 128.8, 128.6, 126.7, 126.5, 124.2, 123.7, 122.3, 119.3, 87.1, 71.3, 21.6, 18.0, 12.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{25}N_3NaO_4S^+$ 510.1458, found 510.1460.

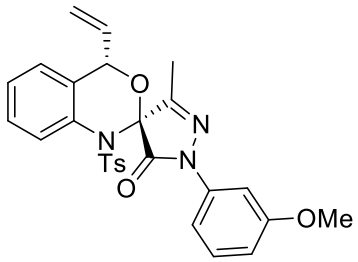
(2*S*,4*S*)-3'-methyl-1'-(*m*-tolyl)-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3m)



3m

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3m** as a white solid in 72% yield (35.1 mg), m.p. 117–119 °C; $[\alpha]_D^{25}$ = +72.14 (*c* = 0.10, CH_2Cl_2); >19:1 *dr*; 86% *ee*, determined by HPLC on a Chiralpak IA column at 254 nm (*n*-hexane/2-propanol = 95/5, 1 mL/min), t_R = 7.68 min (minor), t_R = 8.48 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94–7.93 (m, 2H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.65 (s, 1H), 7.63 (d, *J* = 6.0 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.19–7.15 (m, 1H), 7.14–7.12 (m, 2H), 6.98–6.95 (m, 3H), 5.93 (d, *J* = 7.8 Hz, 1H), 5.87–5.82 (m, 1H), 5.49 (s, 1H), 5.47 (d, *J* = 3.6 Hz, 1H), 2.34 (s, 3H), 2.26 (s, 3H), .2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 157.2, 144.9, 138.8, 137.8, 134.1, 133.0, 132.2, 130.8, 129.5, 129.2, 128.8, 128.7, 126.3, 124.3, 123.8, 122.4, 120.0, 119.4, 116.7, 87.6, 71.5, 21.6, 21.6, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{25}N_3NaO_4S^+$ 510.1458, found 510.1462.

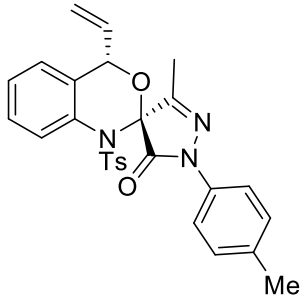
(2*S*,4*S*)-1'-(3-methoxyphenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3n)



3n

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3n** as a white solid in 75% yield (37.5 mg), m.p. 122–124 °C; $[\alpha]_D^{25}$ = +173.70 (*c* = 0.07, CH_2Cl_2); >19:1 *dr*; 92% *ee*, determined by HPLC on a Chiralpak ID column at 220 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 15.31 min (minor), t_R = 29.64 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93–7.91 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.48–7.46 (m, 1H), 7.45–7.44 (m, 1H), 7.25 (t, *J* = 8.4 Hz, 1H), 7.19–7.15 (m, 1H), 7.13–7.12 (m, 2H), 6.99–6.94 (m, 2H), 6.71–6.70 (m, 1H), 5.92 (d, *J* = 7.8 Hz, 1H), 5.87–5.81 (m, 1H), 5.49 (d, *J* = 1.8 Hz, 1H), 5.46 (d, *J* = 3.6 Hz, 1H), 3.78 (s, 3H), 2.26 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 160.1, 157.2, 145.0, 139.1, 134.1, 133.0, 132.2, 130.8, 129.6, 129.5, 129.2, 128.8, 124.3, 123.9, 122.4, 119.4, 111.6, 111.5, 104.8, 87.6, 71.6, 55.4, 21.6, 12.4. HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{25}N_3NaO_5S^+$ 526.1407, found 526.1411.

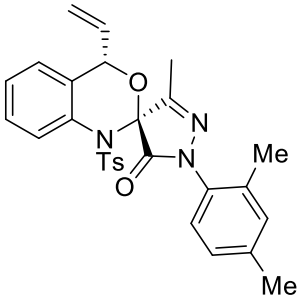
(2*S*,4*S*)-3'-methyl-1'-(*p*-tolyl)-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3o)



3o

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3o** as a white solid in 75% yield (36.3 mg), m.p. 170–172 °C; $[\alpha]_D^{25}$ = +76.70 (*c* = 0.06, CH_2Cl_2); >19:1 *dr*; 86% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 85/15, 1 mL/min), t_R = 10.24 min (minor), t_R = 11.68 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.93–7.92 (m, 2H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.70–7.68 (m, 2H), 7.18–7.16 (m, 3H), 7.13–7.12 (m, 2H), 6.99–6.95 (m, 2H), 5.94 (d, *J* = 8.4 Hz, 1H), 5.87–5.82 (m, 1H), 5.49 (s, 1H), 5.47–5.46 (m, 1H), 2.29 (s, 3H), 2.26 (s, 3H), .2.12 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.6, 157.1, 144.9, 135.5, 135.2, 134.2, 133.1, 132.2, 130.9, 129.5, 129.4, 129.2, 128.8, 124.3, 123.8, 122.3, 119.6, 119.5, 87.6, 71.5, 21.6, 21.0, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{25}N_3NaO_4S^+$ 510.1458, found 510.1459.

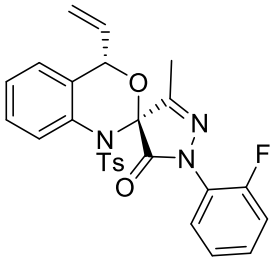
(2*S*,4*S*)-1'-(2,4-dimethylphenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro [benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3p)



3p

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3p** as a white solid in 73% yield (36.5 mg), m.p. 161–163 °C; $[\alpha]_D^{25}$ = +108.43 (*c* = 0.056, CH_2Cl_2); >19:1 *dr*; 96% *ee*, determined by HPLC on a Chiralpak IB column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 6.47 min (minor), t_R = 7.42 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.17–7.14 (m, 1H), 7.10–7.09 (m, 2H), 7.04, (s, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.98–6.93 (m, 2H), 5.94 (d, *J* = 7.8 Hz, 1H), 5.91–5.85 (m, 1H), 5.49 (d, *J* = 2.4 Hz, 1H), 5.47 (d, *J* = 2.4 Hz, 1H), 2.27 (s, 6H), 2.24 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 157.0, 144.9, 138.5, 135.3, 134.2, 133.1, 133.0, 132.4, 131.6, 130.6, 129.5, 129.4, 128.7, 127.3, 126.3, 124.2, 123.7, 122.2, 119.3, 87.1, 71.2, 21.6, 21.2, 17.9, 12.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{27}N_3NaO_4S^+$ 524.1614, found 524.1619.

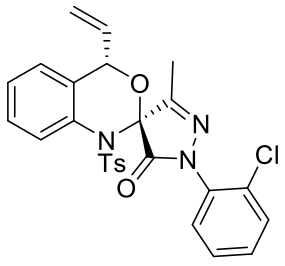
(2*S*,4*S*)-1'-(2-fluorophenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3q)



3q

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3q** as a white solid in 62% yield (30.6 mg), m.p. 184–186 °C; $[\alpha]_D^{25}$ = +79.55 (*c* = 0.04, CH_2Cl_2); >19:1 *dr*; 92% *ee*, determined by HPLC on a Chiralpak IB column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 10.79 min (minor), t_R = 12.23 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94–7.93 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.54–7.51 (m, 1H), 7.28–7.25 (m, 1H), 7.18–7.14 (m, 3H), 7.12–7.10 (m, 2H), 6.99–6.95 (m, 2H), 5.91–5.84 (m, 2H), 5.51 (d, *J* = 4.2 Hz, 1H), 5.49–5.48 (m, 1H), 2.25 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 157.8, 156.7 (d, $^1J_{CF}$ = 252.0 Hz), 145.0, 134.1, 133.0, 132.1, 130.7, 129.6, 129.3(d, $^3J_{CF}$ = 7.5 Hz), 129.3, 128.8, 126.8, 124.9 (d, $^2J_{CF}$ = 12.0 Hz), 124.5 (d, $^3J_{CF}$ = 4.5 Hz), 124.3, 123.8, 122.5, 119.3, 116.7 (d, $^2J_{CF}$ = 19.5 Hz), 86.8, 71.6, 21.6, 12.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}FN_3NaO_4S^+$ 514.1207, found 514.1215.

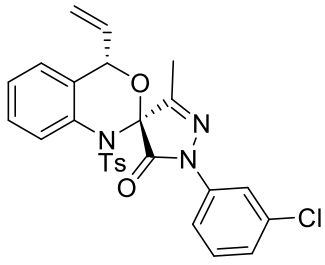
(2*S*,4*S*)-1'-(2-chlorophenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3r)



3r

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3r** as a white solid in 66% yield (33.4 mg), m.p. 180–182 °C; $[\alpha]_D^{25}$ = +127.31 (*c* = 0.13, CH_2Cl_2); >19:1 *dr*; 94% *ee*, determined by HPLC on a Chiralpak IB column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 7.08 min (minor), t_R = 9.25 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.95–7.93 (m, 2H), 7.80 (d, *J* = 7.0 Hz, 1H), 7.51 (dd, *J* = 1.4, 7.7 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.30–7.24 (m, 2H), 7.16–7.14 (m, 1H), 7.10–7.09 (m, 2H), 6.98 (d, *J* = 5.6 Hz, 1H), 6.96–6.94 (m, 1H), 5.92–5.86 (m, 2H), 5.51–5.48 (m, 2H), 2.23 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 169.2, 157.6, 145.0, 134.6, 134.0, 133.1, 132.2, 131.8, 130.6, 130.3, 129.7, 129.6, 129.4, 128.8, 128.3, 127.7, 124.3, 123.8, 122.4, 119.2, 87.0, 71.1, 21.6, 12.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}ClN_3NaO_4S^+$ 530.0912, found 530.0913.

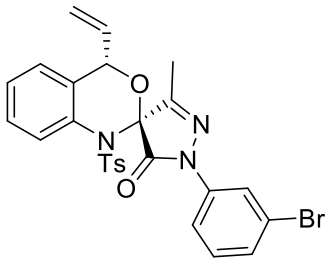
(2*S*,4*S*)-1'-(3-chlorophenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3s)



3s

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3s** as a white solid in 73% yield (37.2 mg), m.p. 126–128 °C; $[\alpha]_D^{25}$ = +123.73 (*c* = 0.06, CH_2Cl_2); >19:1 *dr*; 96% *ee*, determined by HPLC on a Chiralpak IA column at 254 nm (*n*-hexane/2-propanol = 95/5, 1 mL/min), t_R = 7.67 min (minor), t_R = 8.36 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94–7.94 (m, 1H), 7.91–7.90 (m, 2H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.79–7.77 (m, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.19–7.16 (m, 1H), 7.15–7.14 (m, 2H), 7.12–7.10 (m, 1H), 6.99–6.96 (m, 2H), 5.89 (d, *J* = 8.4 Hz, 1H), 5.87–5.81 (m, 1H), 5.50 (s, 1H), 5.48–5.47 (m, 1H), 2.27 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 157.6, 145.1, 139.0, 134.6, 134.0, 132.9, 132.1, 130.8, 129.9, 129.6, 129.2, 128.9, 125.2, 124.3, 124.0, 122.5, 119.4, 119.1, 116.9, 87.5, 71.7, 21.7, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}ClN_3NaO_4S^+$ 530.0912, found 530.0914.

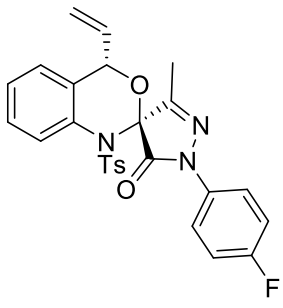
(2*S*,4*S*)-1'-(3-bromophenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3t)



3t

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3t** as a white solid in 68% yield (37.8 mg), m.p. 121–123 °C; $[\alpha]_D^{25}$ = +89.60 (*c* = 0.08, CH_2Cl_2); >19:1 *dr*; 90% *ee*, determined by HPLC on a Chiralpak IA column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 6.82 min (minor), t_R = 7.66 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09–8.08 (m, 1H), 7.91–7.90 (m, 2H), 7.84–7.81 (m, 2H), 7.27–7.26 (m, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.18–7.16 (m, 1H), 7.15–7.14 (m, 2H), 6.99–6.96 (m, 2H), 5.89 (d, *J* = 7.8 Hz, 1H), 5.87–5.81 (m, 1H), 5.50 (s, 1H), 5.48–5.47 (m, 1H), 2.27 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 157.7, 145.1, 139.1, 134.0, 132.9, 132.1, 130.8, 130.2, 129.6, 129.2, 128.9, 128.1, 124.3, 124.0, 122.6, 122.5, 121.9, 119.8, 118.0, 87.5, 71.7, 21.7, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}BrN_3NaO_4S^+$ 574.0407, found 574.0405.

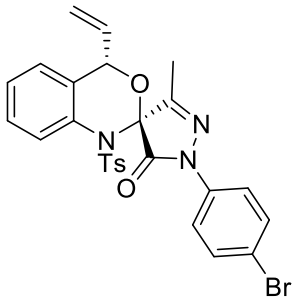
(2*S*,4*S*)-1'-(4-fluorophenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5' (1'*H*)-one (3u)



3u

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3u** as a white solid in 64% yield (31.2 mg), m.p. 181–183 °C; $[\alpha]_D^{25}$ = +156.23 (*c* = 0.11, CH_2Cl_2); >19:1 *dr*; 80% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 6.89 min (minor), t_R = 7.85 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92–7.91 (m, 2H), 7.82–7.79 (m, 3H), 7.19–7.16 (m, 1H), 7.14–7.13 (m, 2H), 7.06–7.03 (m, 2H), 6.99–6.95 (m, 2H), 5.91 (d, *J* = 7.8 Hz, 1H), 5.88–5.82 (m, 1H), 5.50 (s, 1H), 5.48–5.47 (m, 1H), 2.26 (s, 3H), .2.12 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7, 160.2 (d, $^1J_{CF}$ = 243.0 Hz), 157.4, 145.0, 134.09, 134.07, 133.0, 132.1, 130.8, 129.6, 129.2, 128.9, 124.3, 123.9, 122.4, 121.3 (d, $^3J_{CF}$ = 7.5 Hz), 119.4, 115.6 (d, $^2J_{CF}$ = 22.5 Hz), 87.5, 71.6, 21.6, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}FN_3NaO_4S^+$ 514.1207, found 514.1216.

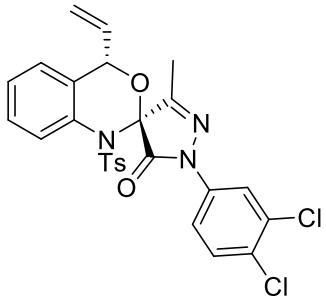
(2*S*,4*S*)-1'-(4-bromophenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3v)



3v

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3v** as a white solid in 72% yield (40.0 mg), m.p. 177–179 °C; $[\alpha]_D^{25}$ = +168.89 (c = 0.12, CH2Cl2); >19:1 *dr*; 90% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 8.95 min (minor), t_R = 11.23 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.90–7.89 (m, 2H), 7.82 (d, *J* = 9.1 Hz, 1H), 7.77–7.75 (m, 2H), 7.47–7.45 (m, 2H), 7.18–7.16 (m, 1H), 7.14–7.12 (m, 2H), 6.98–6.95 (m, 2H), 5.89 (d, *J* = 7.7 Hz, 1H), 5.87–5.82 (m, 1H), 5.49 (s, 1H), 5.47–5.46 (m, 1H), 2.26 (s, 3H), .2.12 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.7, 157.6, 145.1, 137.1, 134.1, 132.9, 132.1, 131.9, 130.8, 129.6, 129.2, 128.9, 124.3, 124.0, 122.5, 120.7, 119.5, 118.2, 87.5, 71.7, 21.6, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{22}BrN_3NaO_4S^+$ 574.0407, found 574.0408.

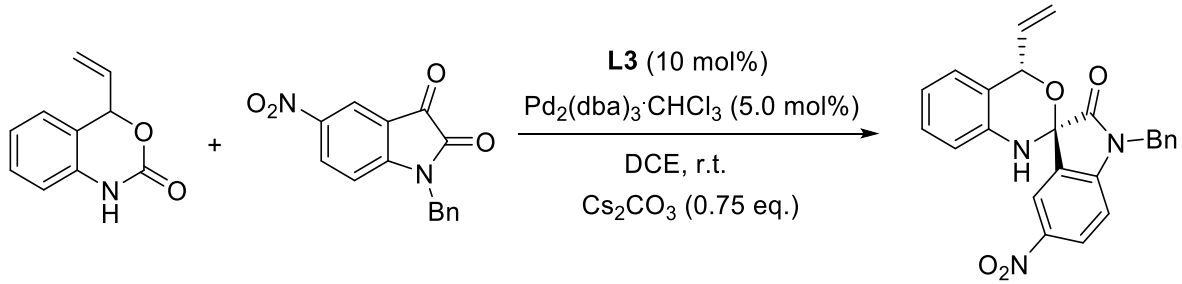
(2*S*,4*S*)-1'-(3,4-dichlorophenyl)-3'-methyl-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3] oxazine-2,4'-pyrazol]-5'(1'*H*)-one (3w)



3w

The residue was purified by a silica gel flash chromatography (PE/EA = 200/1) giving the product **3w** as a white solid in 74% yield (39.9 mg), m.p. 169–171 °C; $[\alpha]_D^{25}$ = +144.27 (*c* = 0.14, CH_2Cl_2); >19:1 *dr*; 88% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 7.73 min (minor), t_R = 8.93 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.4 Hz, 1H), 7.90–7.88 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.76 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.41 (d, *J* = 9.0 Hz, 1H), 7.18–7.16 (m, 1H), 7.16–7.14 (m, 2H), 6.99–6.96 (m, 2H), 5.87–5.81 (m, 2H), 5.50–5.46 (m, 2H), 2.27 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.8, 157.9, 145.2, 137.3, 133.9, 132.84, 132.78, 132.0, 130.7, 130.5, 129.6, 129.1, 129.0, 128.5, 124.3, 124.1, 122.6, 120.5, 119.4, 118.0, 87.4, 71.8, 21.7, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{21}Cl_2N_3NaO_4S^+$ 564.0522, found 564.0524.

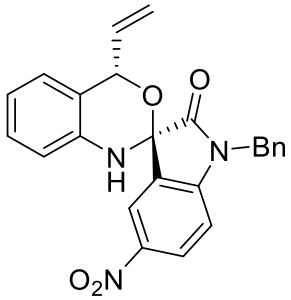
6. More Substrate Explorations



1b **4a** **5a**, 68%, 6:1 *dr*, 42% *ee*

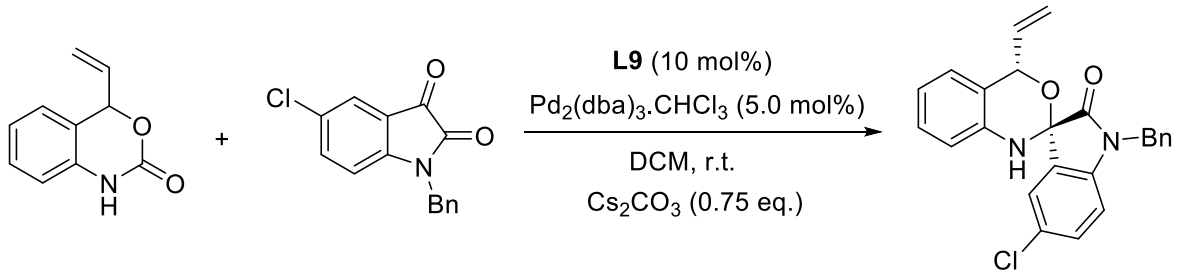
To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.0050 mmol) and **L3** (0.0100 mmol), then 1 mL DCE was added under Ar atmosphere. This solution was stirred at room temperature for 0.5 h. Then vinyl benzoxazinanone **1b** (0.1000 mmol), 1-benzyl-5-nitroindoline-2,3-dione **4a** (0.1500 mmol) and Cs_2CO_3 (0.0750 mmol) were added subsequently. The reaction mixture was stirred at room temperature for 12 h and monitored by TLC (petroleum ether/ethyl acetate). After completion of the reaction, the reaction mixture was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 12/1 to v/v) to give the final products **5a** (28.2 mg, 68% yield, 6:1 *dr*, 42% *ee*) as a white solid.

(2*R*,4*S*)-1'-benzyl-5'-nitro-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,3'-indolin]-2'-one (5a)



5a

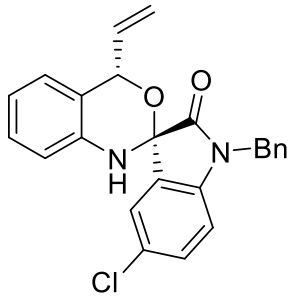
The residue was purified by a silica gel flash chromatography (PE/EA = 12/1) giving the product **5a** as a white solid in 68% yield (28.2 mg), m.p. 173–175 °C; $[\alpha]_D^{25}$ = +98.55 (*c* = 0.17, CH_2Cl_2); 6:1 *dr*; 42% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 80/20, 1 mL/min), t_R = 13.79 min (minor), t_R = 9.95 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.4 Hz, 1H), 8.23 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.36–7.34 (m, 2H), 7.32–7.28 (m, 3H), 7.17 (t, *J* = 6.0 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.07 (d, *J* = 7.8 Hz, 1H), 6.01–5.95 (m, 1H), 5.57 (d, *J* = 16.8 Hz, 1H), 5.48 (dd, *J* = 9.6, 1.2 Hz, 1H), 4.94 (d, *J* = 15.6 Hz, 1H), 4.85 (d, *J* = 15.6 Hz, 1H), 4.49 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1, 148.6, 143.8, 137.7, 136.1, 134.3, 129.2, 128.30, 128.28, 128.12, 128.10, 127.4, 125.9, 122.3, 120.9, 120.9, 120.3, 115.9, 109.3, 81.2, 75.3, 43.9. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{19}N_3NaO_4^+$ 436.1268, found 436.1277.



1b **4b** **5b**, 52%, 5:1 *dr*, 49% *ee*

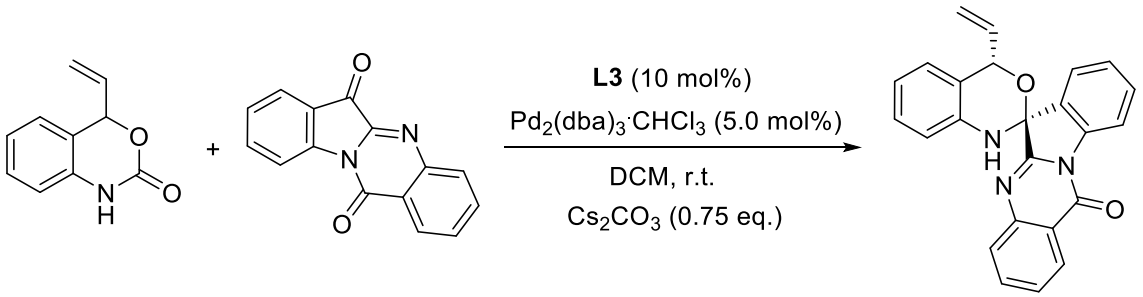
To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.0050 mmol) and **L9** (0.0100 mmol), then 1 mL DCM was added under Ar atmosphere. This solution was stirred at room temperature for 0.5 h. Then vinyl benzoxazinanone (0.1000 mmol) **1b**, 1-benzyl-5-chloroindoline-2,3-dione (0.1500 mmol) and Cs_2CO_3 (0.0750 mmol) were added subsequently. The reaction mixture was stirred at room temperature for 12 h and monitored by TLC (petroleum ether/ethyl acetate). After completion of the reaction, the reaction mixture was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to v/v) to give the final products **5b** (21.1 mg, 52% yield, 5:1 *dr*, 49% *ee*) as a white solid.

(2*S*,4*S*)-1'-benzyl-5'-chloro-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,3'-indolin]-2'-one (5b)



5b

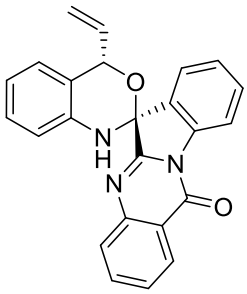
The residue was purified by a silica gel flash chromatography (PE/EA = 20/1) giving the product **5b** as a white solid in 52% yield (21.1 mg), m.p. 162–165 °C; $[\alpha]_D^{25}$ = +105.42 (*c* = 0.21, CH_2Cl_2); 5:1 *dr*; 49% *ee*, determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 80/20, 1 mL/min), t_R = 8.47 min (minor), t_R = 10.22 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.4 Hz, 1H), 7.34–7.32 (m, 2H), 7.29–7.28 (m, 3H), 7.22 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.11 (d, *J* = 8.4 Hz, 1H), 6.00–5.94 (m, 1H), 5.57 (d, *J* = 17.4 Hz, 1H), 5.46 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 4.78 (d, *J* = 15.6 Hz, 1H), 4.44 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 141.5, 138.2, 136.4, 135.0, 131.1, 128.9, 128.80, 128.79, 128.1, 127.9, 127.4, 125.9, 125.3, 122.4, 120.7, 119.8, 115.6, 110.6, 81.7, 75.1, 43.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{19}ClN_2NaO_2^+$ 425.1027, found 425.1033.



1b **6** **7**, 36%, >19:1 *dr*, 90% *ee*

To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.0050 mmol) and **L3** (0.0100 mmol), then 1 mL DCM was added under Ar atmosphere. This solution was stirred at room temperature for 0.5 h. Then vinyl benzoxazinanone (0.1000 mmol) **1b**, indolo[2,1-*b*]quinazoline-6,12-dione (0.1500 mmol) and Cs_2CO_3 (0.0750 mmol) were added subsequently. The reaction mixture was stirred at room temperature for 12 h and monitored by TLC (petroleum ether/ethyl acetate). After completion of the reaction, the reaction mixture was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1 to v/v) to give the final products **7** (13.7 mg, 36% yield, >19:1 *dr*, 90% *ee*) as a white solid.

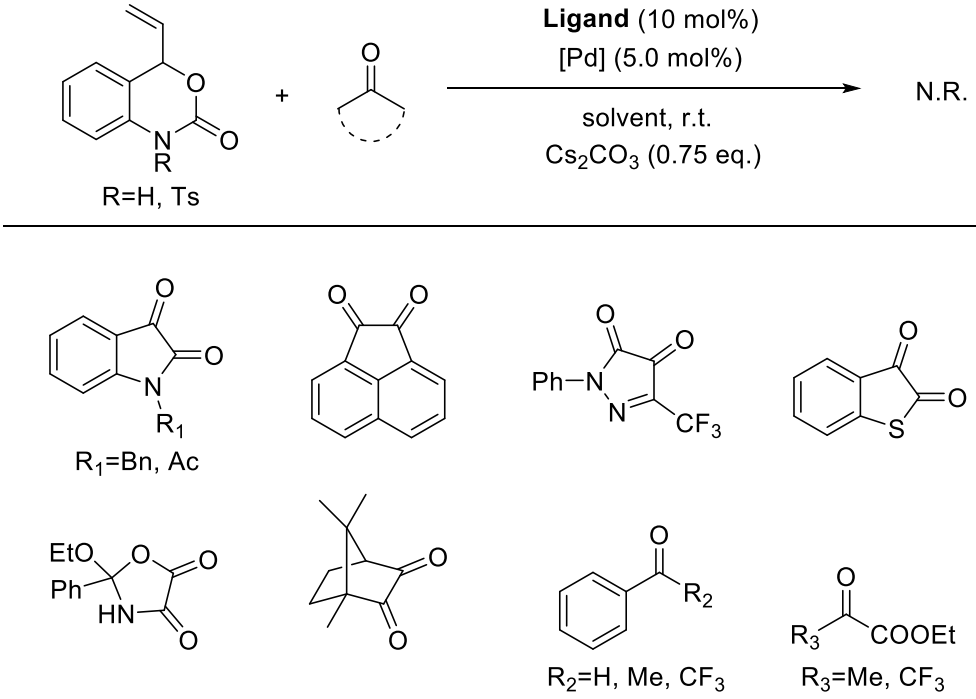
(2*S*,4*S*)-4-vinyl-1,4-dihydro-12'H-spiro[benzo[*d*][1,3]oxazine-2,6'-indolo[2,1-*b*]quinazolin]-12'-one (7)



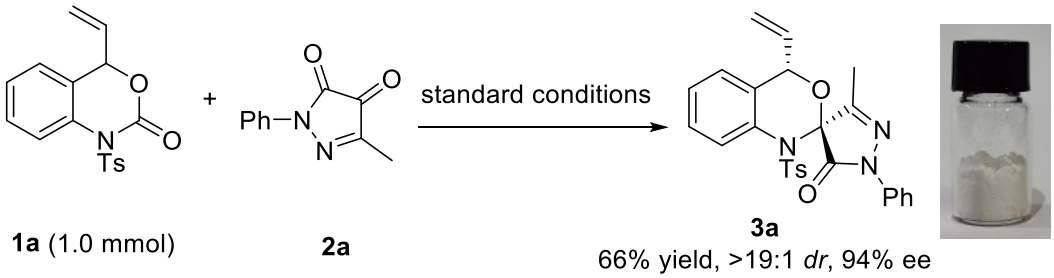
7

The residue was purified by a silica gel flash chromatography (PE/EA = 30/1) giving the product **7** as a white solid in 36% yield (13.7 mg), m.p. 170–172 °C; $[\alpha]_D^{25}$ = +124.78 (*c* = 0.12, CH_2Cl_2); >19:1 *dr*; 90% *ee*; determined by HPLC on a Chiralpak IA column at 254 nm (*n*-hexane/2-propanol = 80/20, 1 mL/min), t_R = 16.46 min (minor), t_R = 9.08 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.8 Hz, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 7.73–7.70 (m, 1H), 7.68–7.66 (m, 2H), 7.58–7.55 (m, 1H), 7.53–7.51 (m, 1H), 7.39–7.37 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 1H), 6.93–6.91 (m, 3H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.33 (d, *J* = 7.8 Hz, 1H), 6.06–6.00 (m, 1H), 5.52 (d, *J* = 16.8 Hz, 1H), 5.45 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.64 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 156.8, 147.1, 138.8, 136.1, 134.3, 132.1, 130.1, 128.7, 128.2, 127.6, 127.2, 126.8, 125.6, 124.7, 122.6, 122.2, 120.6, 119.4, 117.22, 117.21, 115.1, 84.8, 74.6. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{17}N_3NaO_2^+$ 402.1213, found 402.1210.

As outline in the following scheme, other types of carbonyl compound were explored in the reaction with vinyl benzoxazinanone **1a** or **1b** in different conditions, unfortunally, the expected products were not obtained.



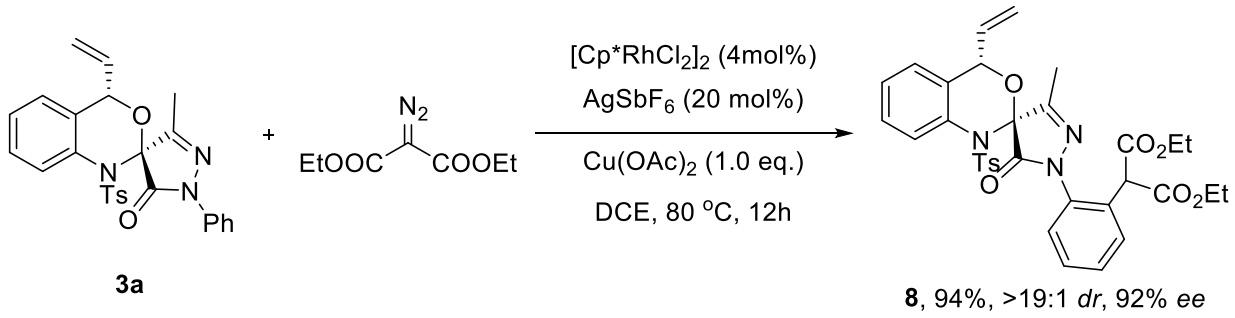
7. The scale-up reaction



To a dry flask filled with nitrogen were added $Pd_2(dba)_3$•$CHCl_3$ (0.0250 mmol) and **L5** (0.1000 mmol), then 1 mL *p*-xylene was added under Ar atmosphere. This solution was stirred at room temperature for 0.5 h. Then vinyl benzoxazinanone (1.0000 mmol) **1a**, Pyrazolone 4,5-Diones **2a** (1.5000 mmol) and Cs_2CO_3 (0.7500 mmol) were added subsequently. The reaction mixture was stirred at room temperature for 12 h and monitored by TLC (petroleum ether/ethyl acetate). After completion of the reaction, the reaction mixture was concentrated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200/1 to v/v) to give the final products **3a** (332.5 mg, 66% yield, >19:1 *dr*, 94% *ee*) as a white solid.

8. Synthetic transformations of 3a

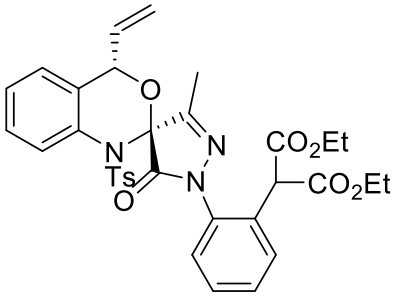
8.1 Procedure for synthesis of compound 8



3a **8**, 94%, >19:1 *dr*, 92% *ee*

3a (47.4 mg, 0.1000 mmol), diazo compound (27.9 mg, 0.1500 mmol), $[Cp^*RhCl_2]_2$ (2.5 mg, 0.0040 mmol), $AgSbF_6$ (6.9 mg, 0.0200 mmol) and $Cu(OAc)_2$ (18.2 mg, 0.1000 mmol) were dissolved in DCE (1.0 mL) under Ar atmosphere. The mixture was stirred at 80 °C for 12h and monitored by TLC (petroleum ether/ethyl acetate). After that the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1 to v/v) to give the final products **8** (59,4 mg, 94% yield, >19:1 *dr*, 92% *ee*) as a white solid.

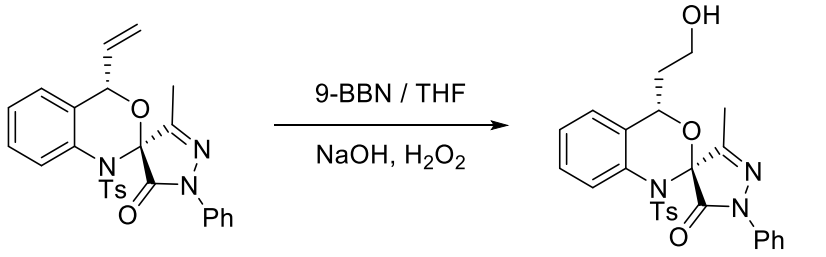
diethyl 2-(2-((2*S*,4*S*)-3'-methyl-5'-oxo-1-tosyl-4-vinyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-1'(5'*H*)-yl)phenyl)malonate (8).



8

The residue was purified by a silica gel flash chromatography (PE/EA = 15/1) giving the product **8** as a white solid in 94% yield (59.4 mg), m.p. 168–170 °C; $[\alpha]_D^{25}$ = +114.55 (*c* = 0.09, CH_2Cl_2); >19:1 *dr*; 92% *ee*; determined by HPLC on a Chiralpak IA column at 254 nm (*n*-hexane/2-propanol = 90/10, 1 mL/min), t_R = 16.10 min (minor), t_R = 21.81 min (major); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92–7.91 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.56–7.54 (m, 1H), 7.47–7.46 (m, 1H), 7.38–7.32 (m, 2H), 7.18–7.15 (m, 1H), 7.11–7.10 (m, 2H), 6.99–6.94 (m, 2H), 5.90–5.84 (m, 2H), 5.53–5.49 (m, 2H), 5.01 (s, 1H), 4.18–4.09 (m, 4H), 2.25 (s, 3H), 2.10 (s, 3H), 1.19 (t, *J* = 6.6 Hz 3H), 1.14 (t, *J* = 7.2 Hz 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 168.4, 168.3, 157.5, 145.0, 135.8, 134.0, 133.0, 132.2, 130.7, 130.13, 130.08, 129.5, 129.4, 128.9, 128.8, 128.5, 126.2, 124.3, 123.8, 122.4 ,119.3, 86.9, 71.4, 61.8, 61.7, 53.0, 21.6, 14.1, 14.0, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{33}H_{33}N_3NaO_8S^+$ 654.1881, found 654.1879.

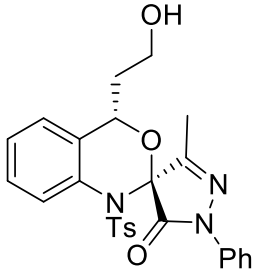
8.2 Procedure for synthesis of compound 9



3a **9**, 82%, >19:1 *dr*, 90% *ee*

To 3 ml of 9-BBN (0.5 M in THF) solution at 0 °C under Ar atmosphere, a solution of the cycloaddition product **3a** (0.2 M in THF, 0.1 mmol, 47.4 mg) was added dropwise. This mixture was stirred at room temperature for 36 h. After that, this mixture quenched with 2.0 mL of 2 N aqueous NaOH solution and 0.60 mL of 30% aqueous H_2O_2 solution. After stirring for 30 min, the aqueous layer was extracted with EtOAc (10 mL × 2). The organic layer was dried over Na_2SO_4, concentrated, and purified by column chromatography eluting with petroleum ether/ethyl acetate (2:1) to provide the product **9** (40.1 mg 82% yield, >19:1 *dr*, 90% *ee*) as a white solid.

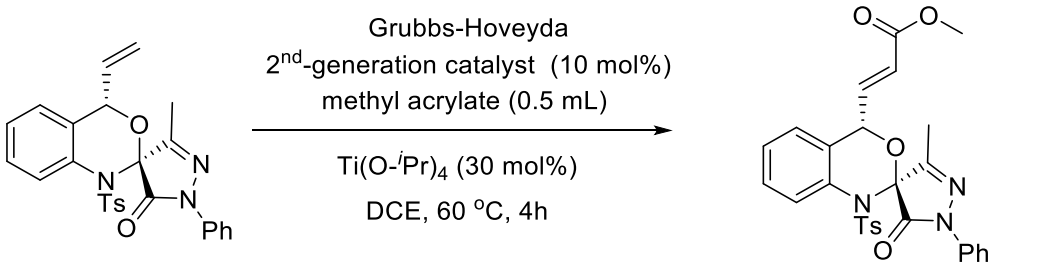
(2*S*,4*S*)-4-(2-hydroxyethyl)-3'-methyl-1'-phenyl-1-tosyl-1,4-dihydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-5'(1'*H*)-one (9).



9

The residue was purified by a silica gel flash chromatography (PE/EA = 2/1) giving the product **9** as a white solid in 82% yield (40.1 mg), m.p. 187–189 °C; $[\alpha]_D^{25}$ = +110.60 (*c* = 0.08, CH_2Cl_2); >19:1 *dr*; 90% *ee*; determined by HPLC on a Chiralpak ID column at 220 nm (*n*-hexane/2-propanol = 80/20, 1 mL/min), t_R = 9.56 min (minor), t_R = 10.50 min (major); ^{1}H NMR (700 MHz, DMSO-d_6) δ 7.97–7.96 (m, 2H), 7.83–7.82 (m, 3H), 7.52–7.50 (m, 2H), 7.38–7.37 (m, 2H), 7.32 (t, *J* = 8.4 Hz, 1H), 7.30–7.28 (m, 2H), 7.13 (t, *J* = 7.7 Hz, 1H), 5.59 (dd, *J* = 9.8, 3.5 Hz, 1H), 4.61–4.60 (m, 1H), 3.60–3.56 (m, 1H), 3.54–3.50 (m, 1H), 2.43–2.38 (m, 1H), 2.32 (s, 3H), 2.08 (s, 3H), 1.80–1.75 (m, 1H). ^{13}C NMR (175 MHz, DMSO-d_6) δ 168.7, 157.6, 146.0, 137.9, 133.8, 133.0, 131.9, 130.4, 129.6, 129.3, 129.1, 126.0, 124.9, 124.1, 119.3, 119.2, 87.6, 67.7, 57.2, 33.8, 21.5, 12.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{25}N_3NaO_5S^+$ 514.1407, found 514.1411.

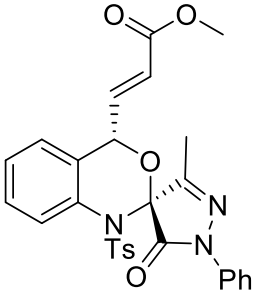
8.3 Procedure for synthesis of compound 10



3a **10**, 63%, >19:1 *dr*, 90% *ee*

To a solution of **3a** (47.4 mg, 0.1000 mmol) and methyl acrylate (0.5 mL) in 1,2-dichloroethane (1.0 mL), Titanium (IV) isopropoxide (9.54 mg, 0.0300 mmol) was added under Ar atmosphere. This mixture was stirred at room temperature for 15 min. After that, Hoveyda-Grubbs catalyst (7.0 mg, 0.0100 mmol) was added into the system and stirring at 60 °C for 4h and monitored by TLC (petroleum ether/ethyl acetate). After completion of the reaction, the solvent and remaining methylacrylate were removed in vacuo and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1 to v/v) to give the final products **10** (33.4 mg, 63% yield, >19:1 *dr*, 90% *ee*) as a white solid.

methyl (*E*)-3-((2*S*,4*S*)-3'-methyl-5'-oxo-1'-phenyl-1-tosyl-1,1',4,5'-tetrahydrospiro[benzo[*d*][1,3]oxazine-2,4'-pyrazol]-4-yl)acrylate (10).

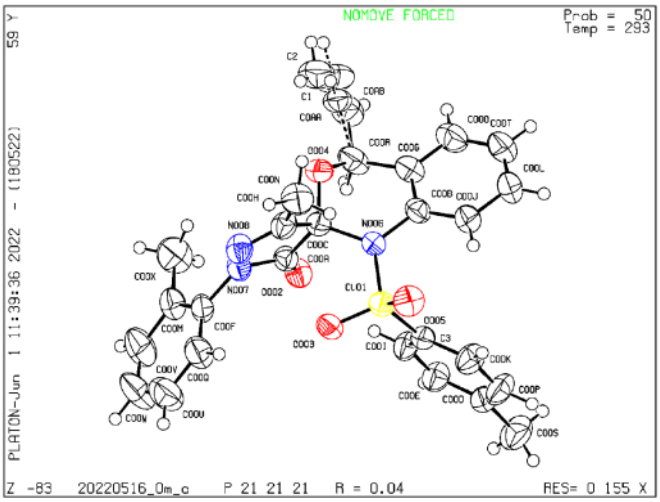


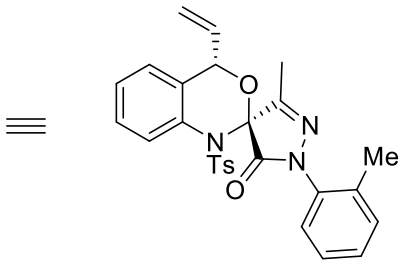
10

The residue was purified by a silica gel flash chromatography (PE/EA = 20/1) giving the product **10** as a white solid in 63% yield (33.5 mg), m.p. 160–162 °C; $[\alpha]_D^{25}$ = +62.11 (*c* = 0.07, CH_2Cl_2); >19:1 *dr*; 90% *ee*; determined by HPLC on a Chiralpak ID column at 254 nm (*n*-hexane/2-propanol = 70/30, 1 mL/min), t_R = 10.77 min (minor), t_R = 13.93 min (major); ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.91–7.90 (m, 2H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.83–7.82 (m, 2H), 7.37–7.35 (m, 2H), 7.21 (d, *J* = 6.3 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.14–7.13 (m, 2H), 7.02 (dd, *J* = 6.3, 15.4 Hz, 1H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 4.9.Hz, 1H), 6.16–6.14 (m, 1H), 6.12 (d, *J* = 6.3 Hz, 1H), 3.70 (s, 3H), 2.26 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.5, 165.9, 157.0, 145.1, 140.2, 137.8, 134.0, 132.9, 129.8, 129.6, 129.3, 129.2, 128.9, 125.6, 125.3, 124.2, 124.1, 119.9, 119.4, 87.4, 68.9, 52.0, 21.6, 12.4. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{25}N_3NaO_6S^+$ 554.1356, found 554.1351.

9. X-ray Crystal Structures of 3l

To a 5 mL tube containing **3l** (20 mg) was added propan-2-ol (4 mL). A clear solution was obtained through ultrasound treatment and was kept at room temperature and **3l** crystals were obtained after the solvent evaporated, which were characterized by single crystal X-ray diffraction. X-ray diffraction experiment was carried out on an Agilent D8 QUEST and the data obtained were deposited at the Cambridge Crystallographic Data Centre. The crystal structure was solved by Olex2 with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. CCDC 2189303 (**3l**) contains the supplementary crystallographic data for this paper. X-ray crystal structure of **3l** with the ellipsoid contour at 50% probability levels.





3l, CCDC 2189303

Identification code	20220516_0m_a
Empirical formula	$C_{27}H_{25}N_3O_4S$
Formula weight	487.56
Temperature/K	293.15
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.0617(4)
b/Å	10.9968(5)
c/Å	27.6122(12)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	2447.9(2)
Z	4
ρ_{calc}g/cm^3	1.323
μ/mm^{-1}	1.495
F(000)	1024.0
Crystal size/mm^3	0.23 x 0.15 x 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.402 to 136.984
Index ranges	$-9 \leq h \leq 9$, $-13 \leq k \leq 12$, $-33 \leq l \leq 33$
Reflections collected	21413
Independent reflections	4512 [R_{int} = 0.0515, R_{sigma} = 0.0375]
Data/restraints/parameters	4512/0/339
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.0926
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.0983
Largest diff. peak and hole / e Å^{-3}	0.18/-0.31
Flack parameter	0.006(11)

10. References

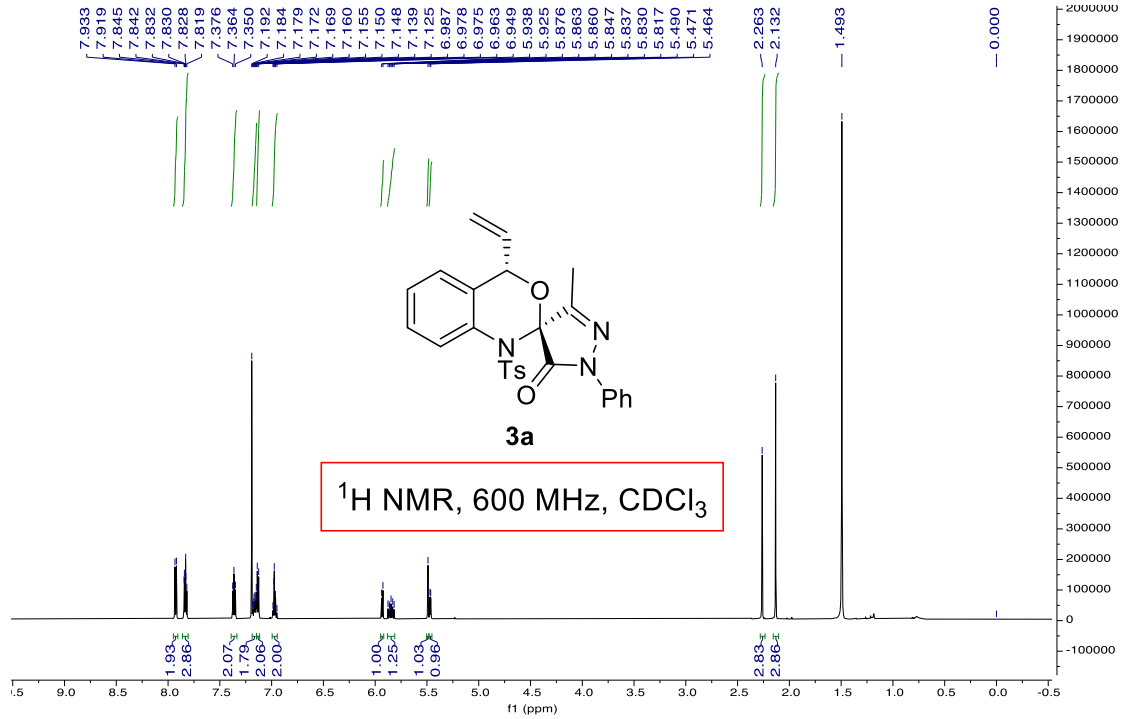
[1] G. J. Mei, C. Y. Bian, G. H. Li, S. L. Xu, W. Q. Zheng and F. Shi, *Org. Lett.,* 2017, **19**, 3219-3222.

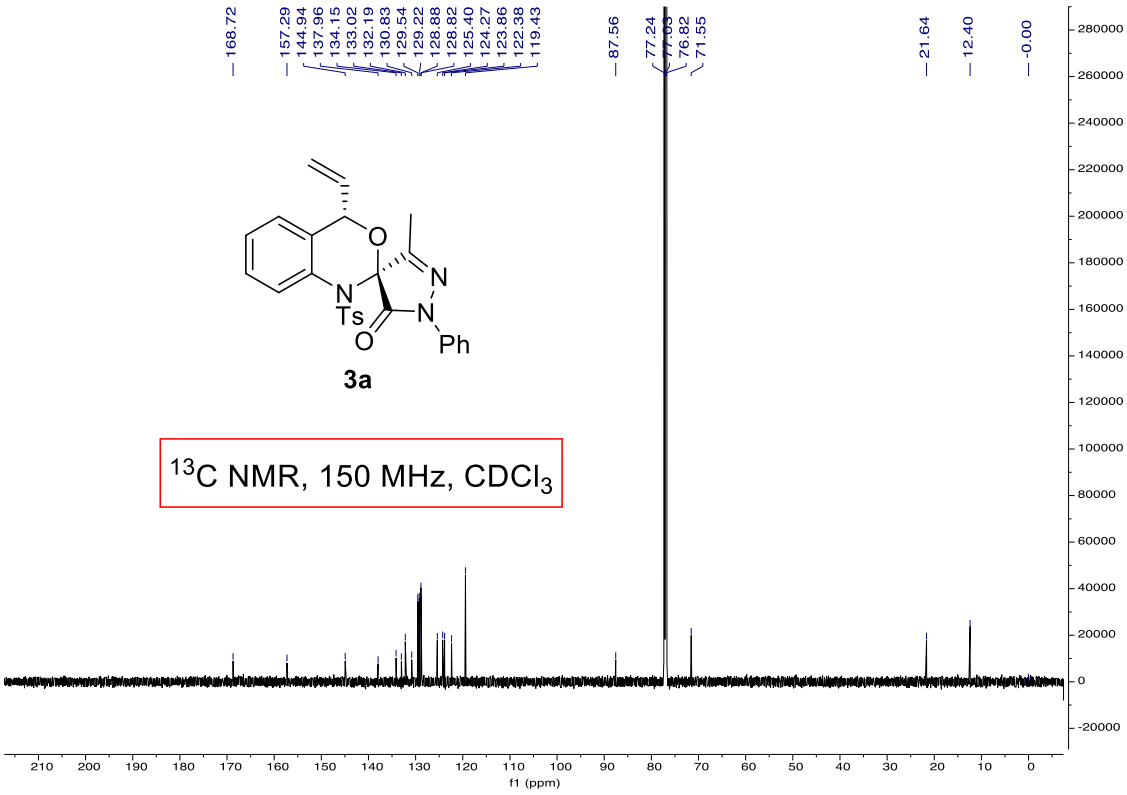
[2] U. Kaya, P. Chauhan, S. Mahajan, K. Deckers, A. Valkonen, K. Rissanen and D. Enders, *Angew. Chem., Int. Ed.,* 2017, **56**, 15358-15362.

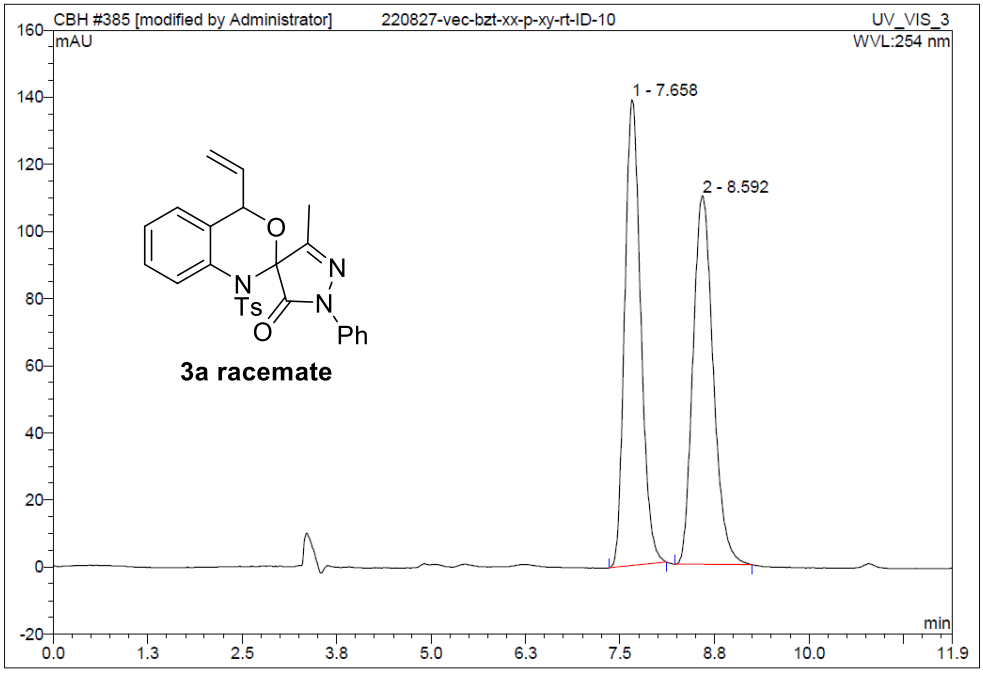
[3] W. B. Liu, C. Zheng, C. X. Zhuo, L. X. Dai and S. L. You, *J. Am. Chem. Soc*., 2012, **134**, 4812-4821.

[4] Z. Y. Dai, P. S. Wang and L. Z. Gong, *Chem. Commun.,* 2021, **57**, 6748-6751.

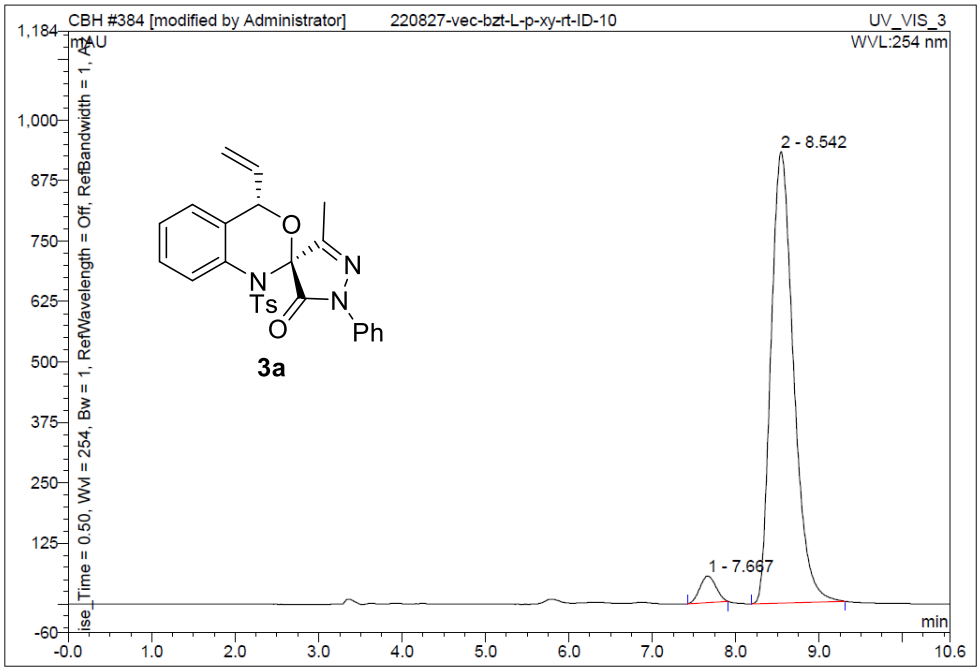
11. NMR and HPLC Spectra



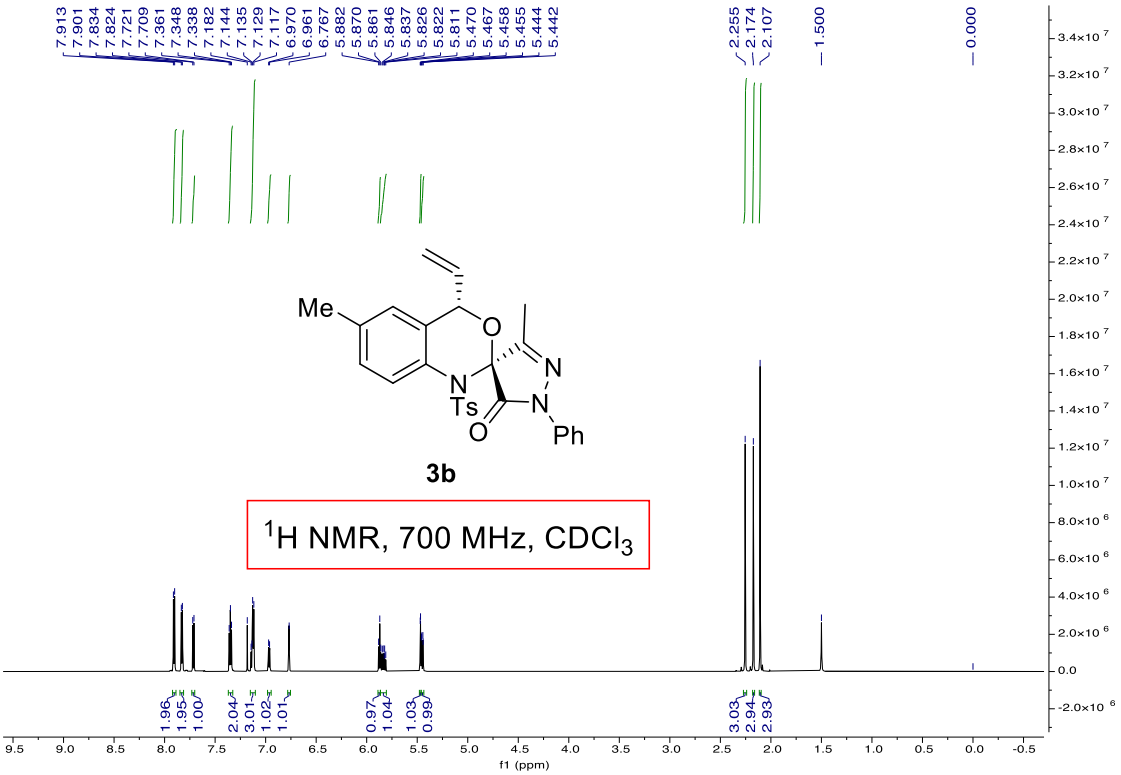


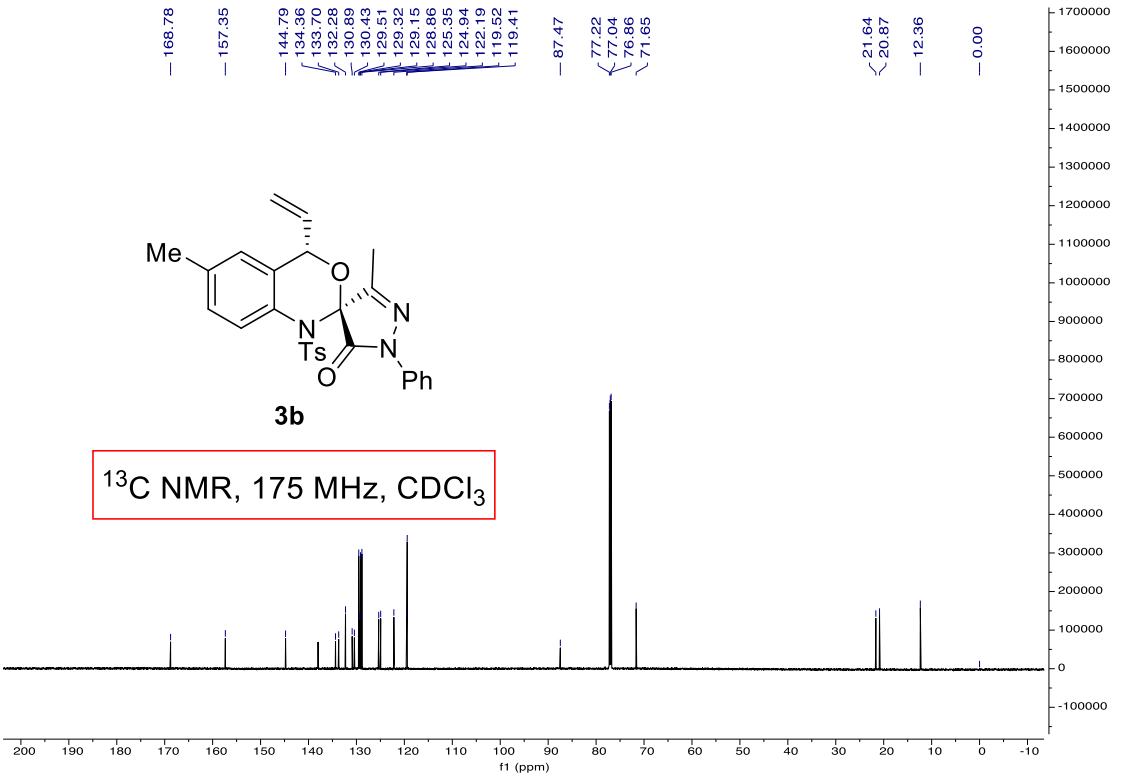


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.66	n.a.	138.781	34.028	49.98	n.a.	BMB*
2	8.59	n.a.	109.925	34.053	50.02	n.a.	BMB*
Total:			248.706	68.081	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.67	n.a.	54.899	12.230	4.02	n.a.	BMB*
2	8.54	n.a.	932.914	292.340	95.98	n.a.	BMB*
Total:			987.813	304.570	100.00	0.000	


7.913
7.901
7.834
7.824
7.721
7.709
7.361
7.348
7.338
7.182
7.144
7.135
7.129
7.117
6.970
6.961
6.767
5.882
5.870
5.861
5.846
5.837
5.826
5.822
5.811
5.470
5.467
5.458
5.455
5.444
5.442
2.255
2.174
2.107
1.500
0.000
Me
O
N
Ts
O
N
N
Ph
3b
1H NMR, 700 MHz, CDCl3
1.96
1.95
1.00
2.04
3.01
1.02
1.01
0.97
1.04
1.03
0.99
3.03
2.94
2.93
f1 (ppm)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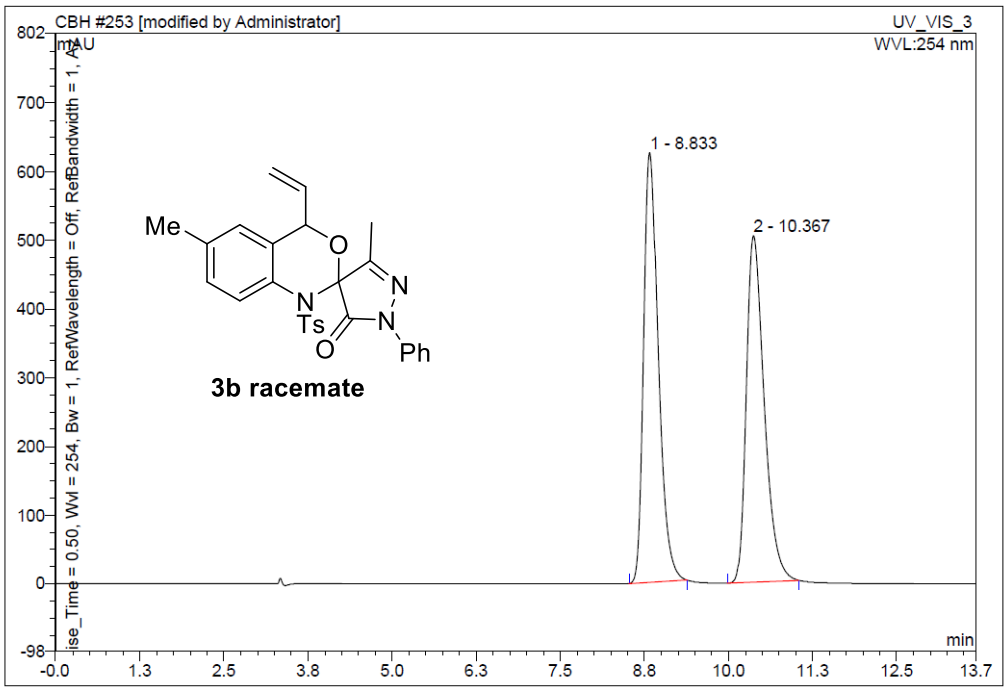
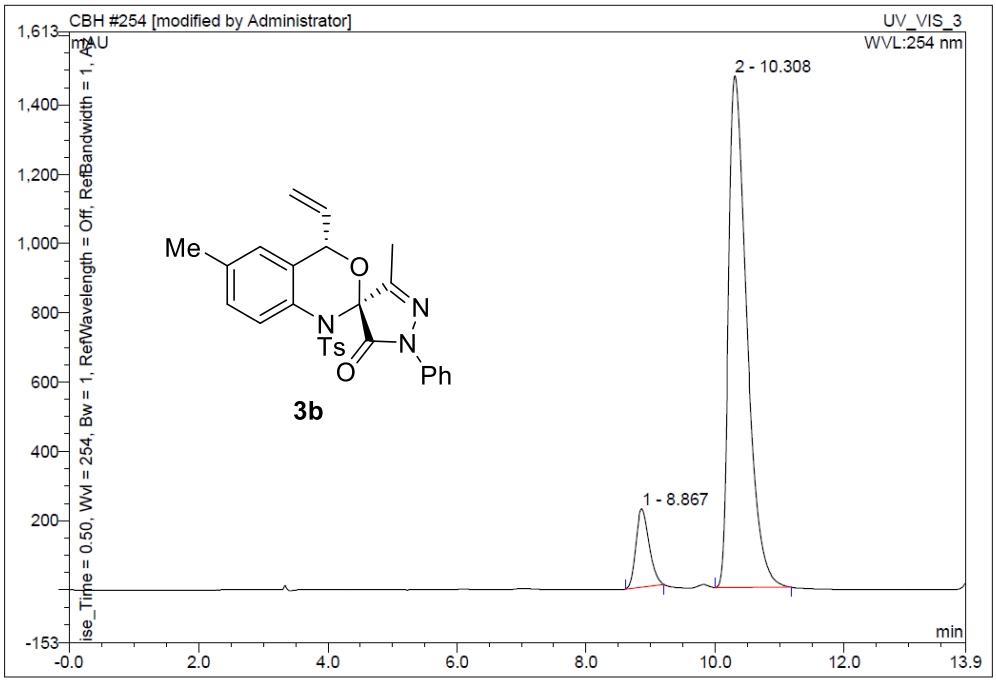
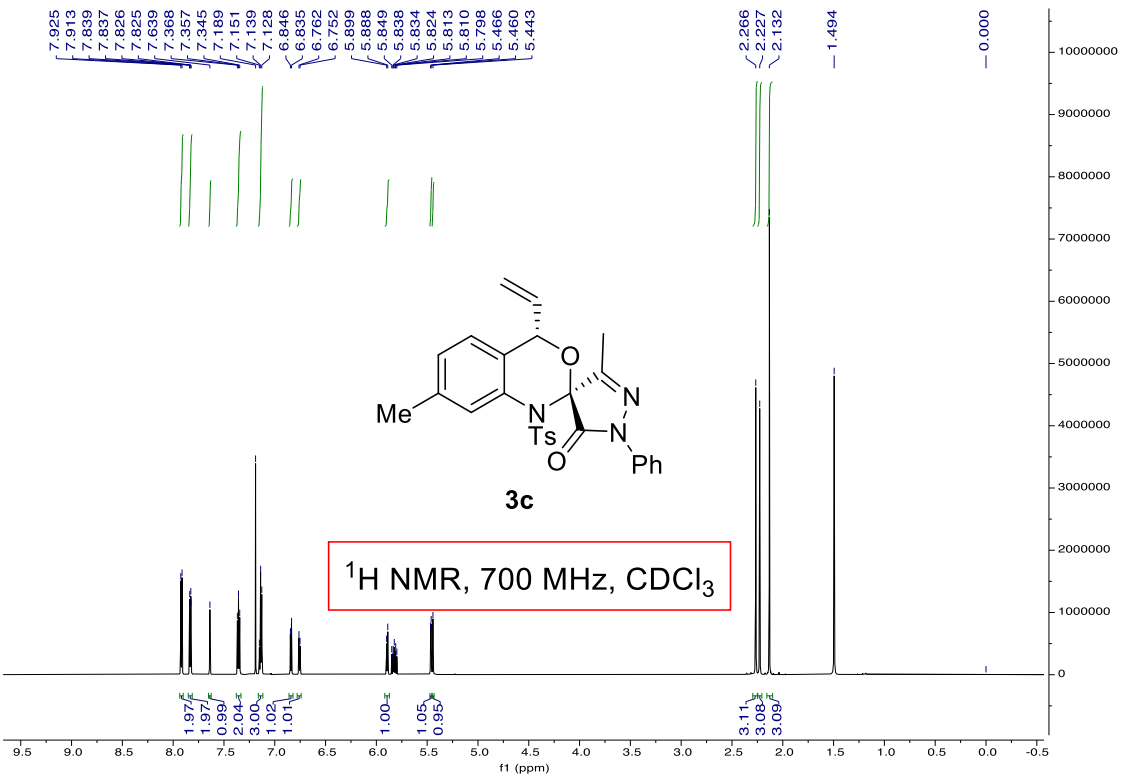
157.35
144.79
134.36
133.70
132.28
130.89
130.43
129.51
129.32
129.15
128.86
125.35
124.94
122.19
119.52
119.41
87.47
77.22
77.04
76.86
71.65
21.64
20.87
12.36
0.00
Me
O
N
Ts
O
N
N
Ph
3b
13C NMR, 175 MHz, CDCl3
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.83	n.a.	625.264	156.363	50.08	n.a.	BMB*
2	10.37	n.a.	504.064	155.894	49.92	n.a.	BMB*
Total:			1129.328	312.257	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.87	n.a.	225.714	53.524	9.96	n.a.	BMB*
2	10.31	n.a.	1478.174	483.950	90.04	n.a.	BMB*
Total:			1703.888	537.474	100.00	0.000	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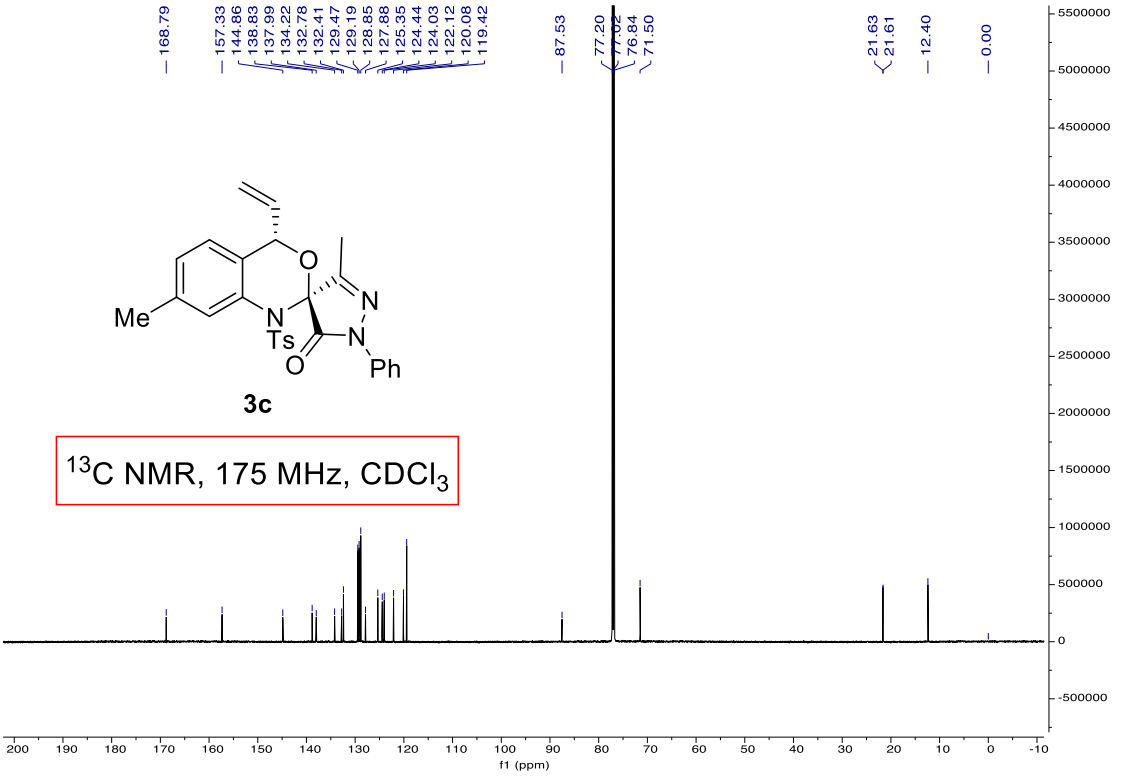
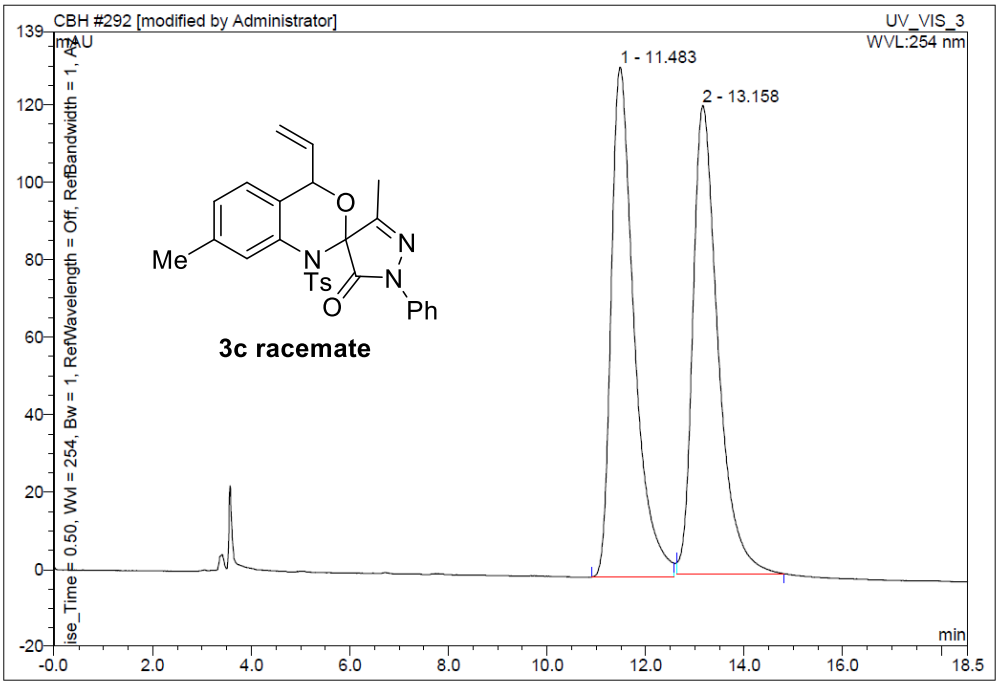
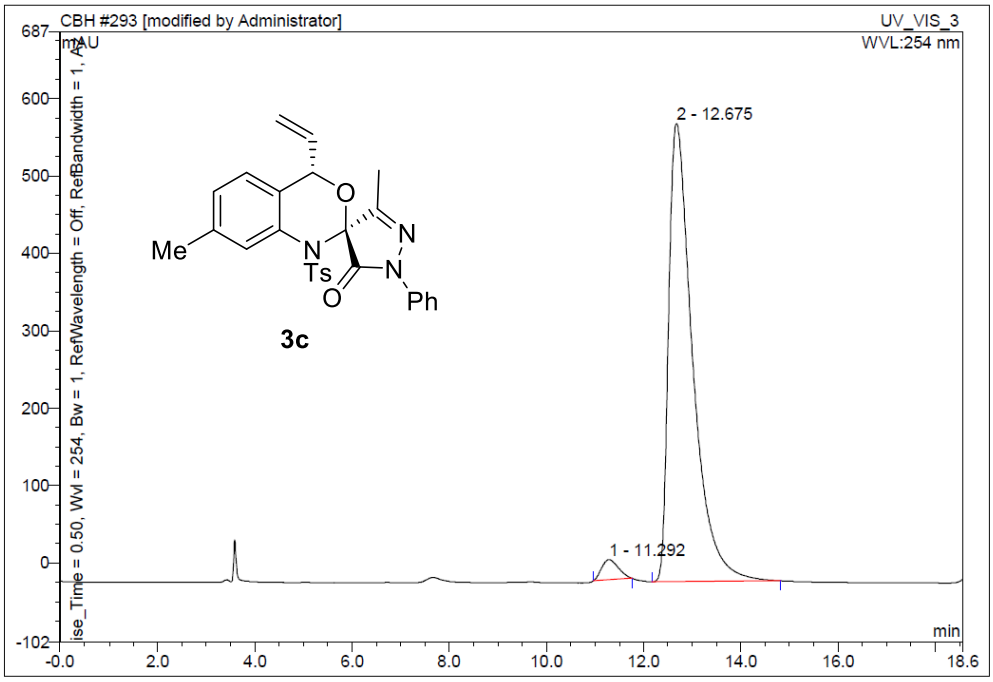
7.913
7.839
7.837
7.826
7.825
7.639
7.368
7.357
7.345
7.189
7.151
7.139
7.128
6.846
6.835
6.762
6.752
5.899
5.888
5.849
5.838
5.834
5.824
5.813
5.810
5.798
5.466
5.460
5.443
2.266
2.227
2.132
1.494
0.000
Me
N
Ts
O
O
N
N
Ph
3c
1H NMR, 700 MHz, CDCl3
1.97
1.97
0.99
2.04
3.00
1.02
1.01
1.00
1.05
0.95
3.11
3.08
3.09
f1 (ppm)

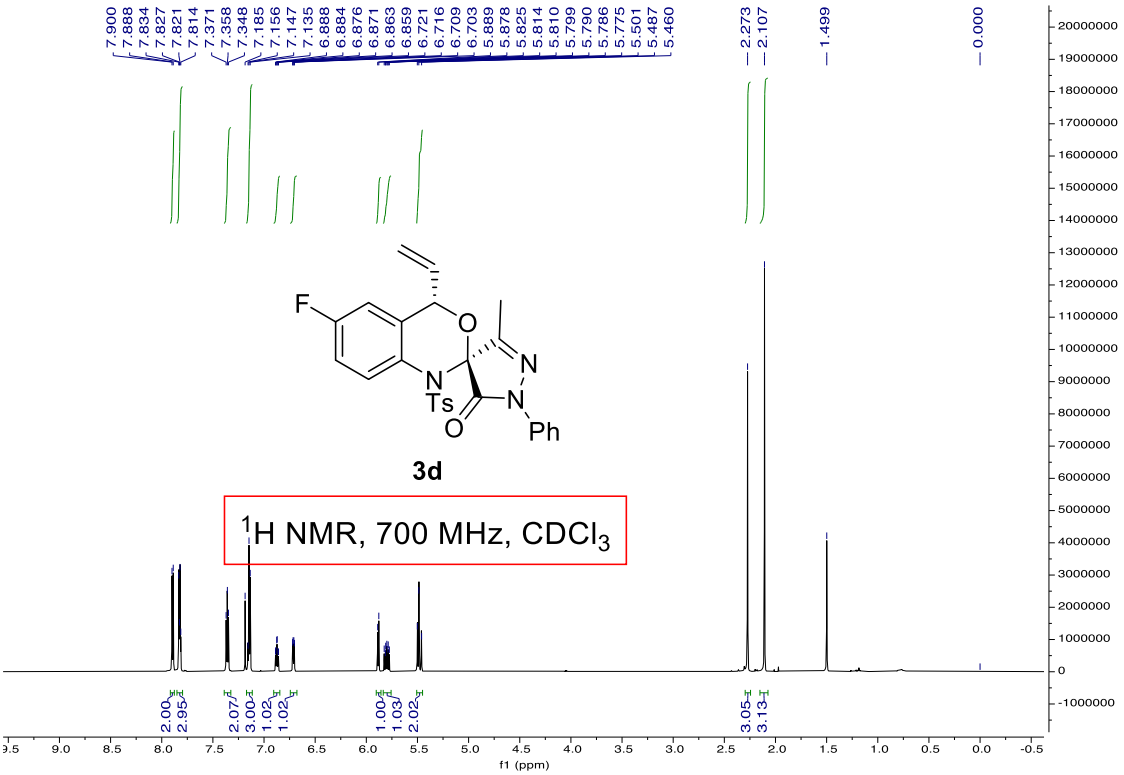

168.79
157.33
144.86
138.83
137.99
134.22
132.78
132.41
129.47
129.19
128.85
127.88
125.35
124.44
124.03
122.12
120.08
119.42
87.53
77.20
77.02
76.84
71.50
21.63
21.61
12.40
0.00
Me
N
Ts
O
O
N
N
Ph
3c
13C NMR, 175 MHz, CDCl3
f1 (ppm)

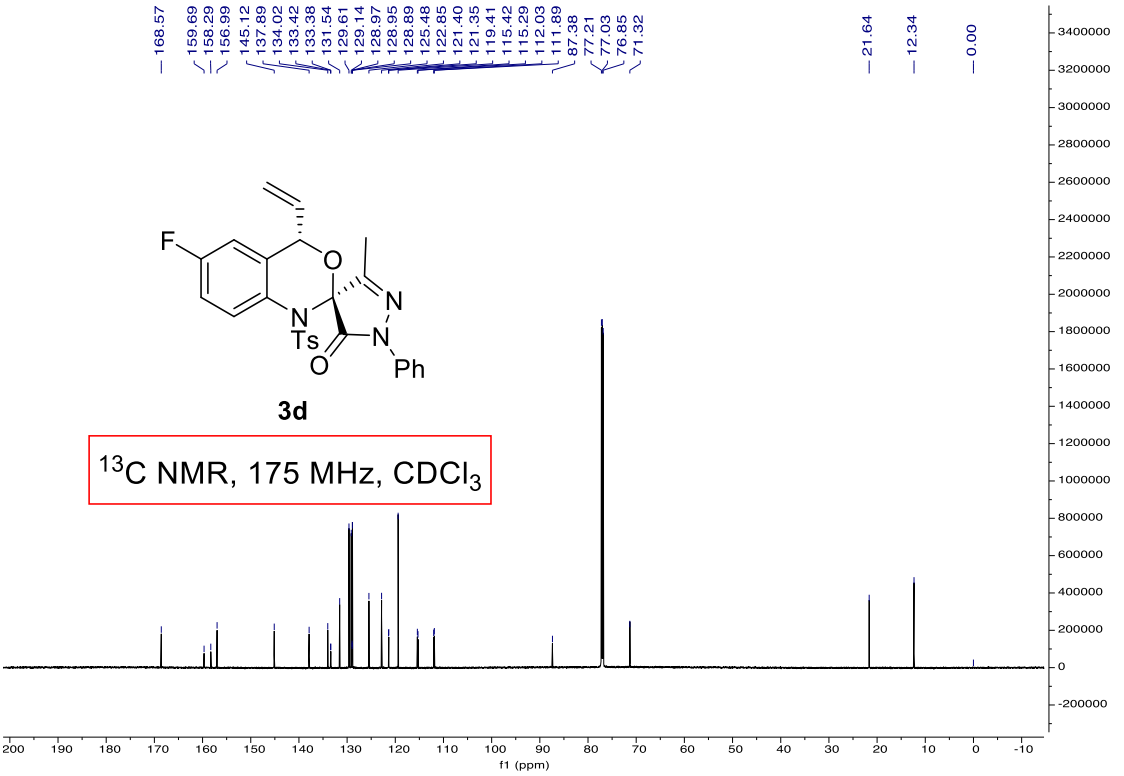


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.48	n.a.	131.563	71.222	50.02	n.a.	BM *
2	13.16	n.a.	120.832	71.164	49.98	n.a.	MB*
Total:			252.395	142.386	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	11.29	n.a.	25.975	10.443	3.00	n.a.	BMB*
2	12.68	n.a.	591.739	337.414	97.00	n.a.	BMB*
Total:			617.714	347.857	100.00	0.000	


7.900
7.888
7.834
7.827
7.821
7.814
7.371
7.358
7.348
7.185
7.156
7.147
7.135
6.888
6.884
6.876
6.871
6.863
6.859
6.721
6.716
6.709
6.703
5.889
5.878
5.825
5.814
5.810
5.799
5.790
5.786
5.775
5.501
5.487
5.460
2.273
2.107
1.499
0.000
F
O
N
Ts
O
N
N
Ph
3d
1H NMR, 700 MHz, CDCl3
2.00
2.95
2.07
3.00
1.02
1.02
1.00
1.03
2.02
3.05
3.13
f1 (ppm)


168.57
159.69
158.29
156.99
145.12
137.89
134.02
133.42
133.38
131.54
129.61
129.14
128.97
128.95
128.89
125.48
122.85
121.40
121.35
119.41
115.42
115.29
112.03
111.89
87.38
77.21
77.03
76.85
71.32
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Ts
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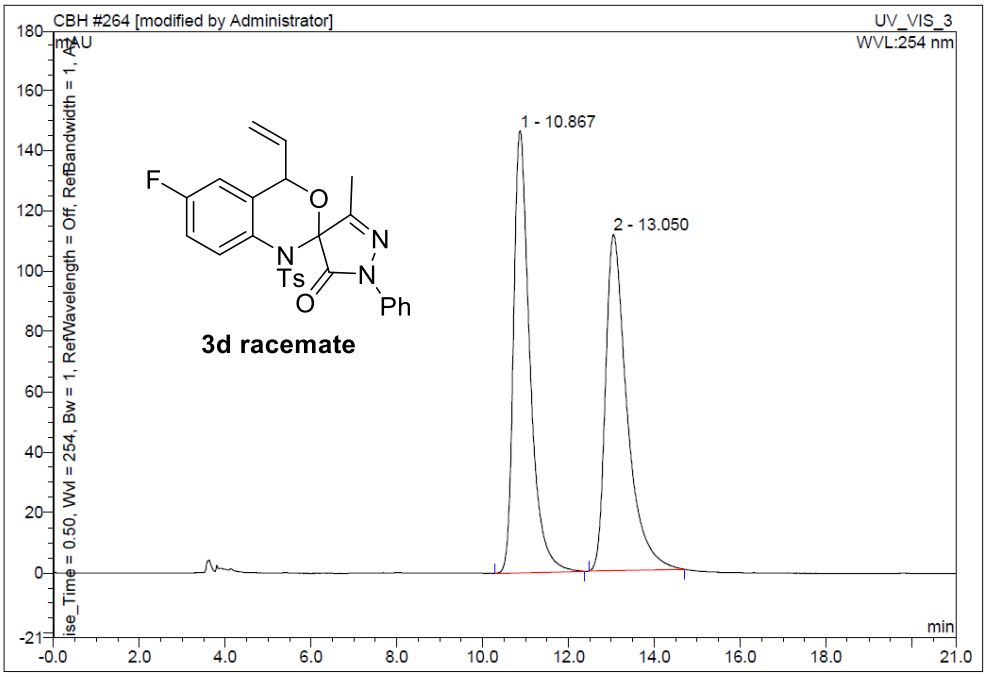
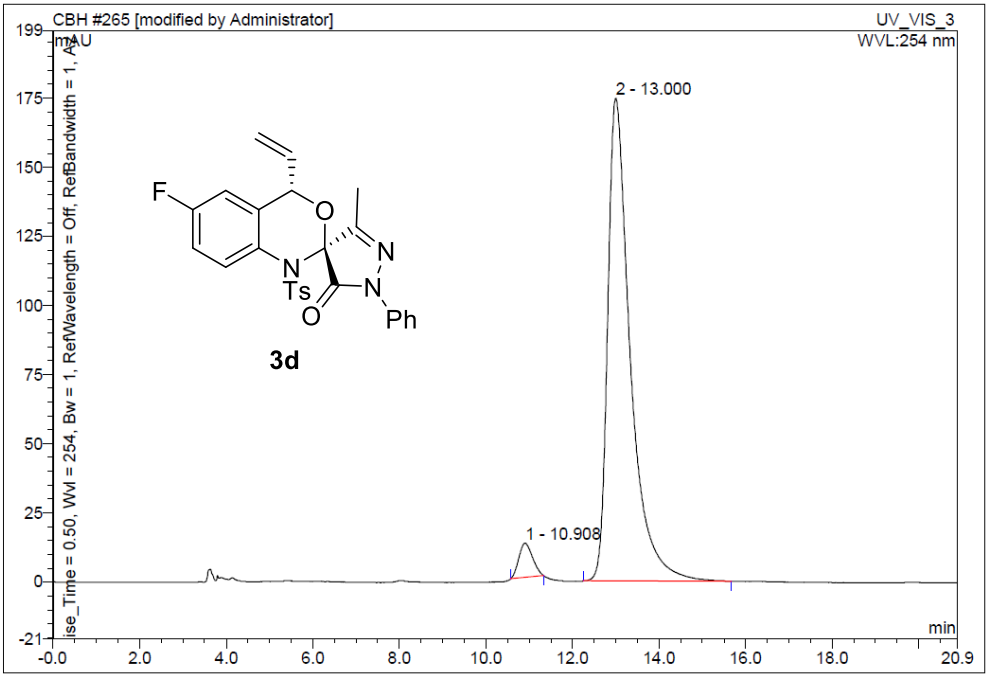
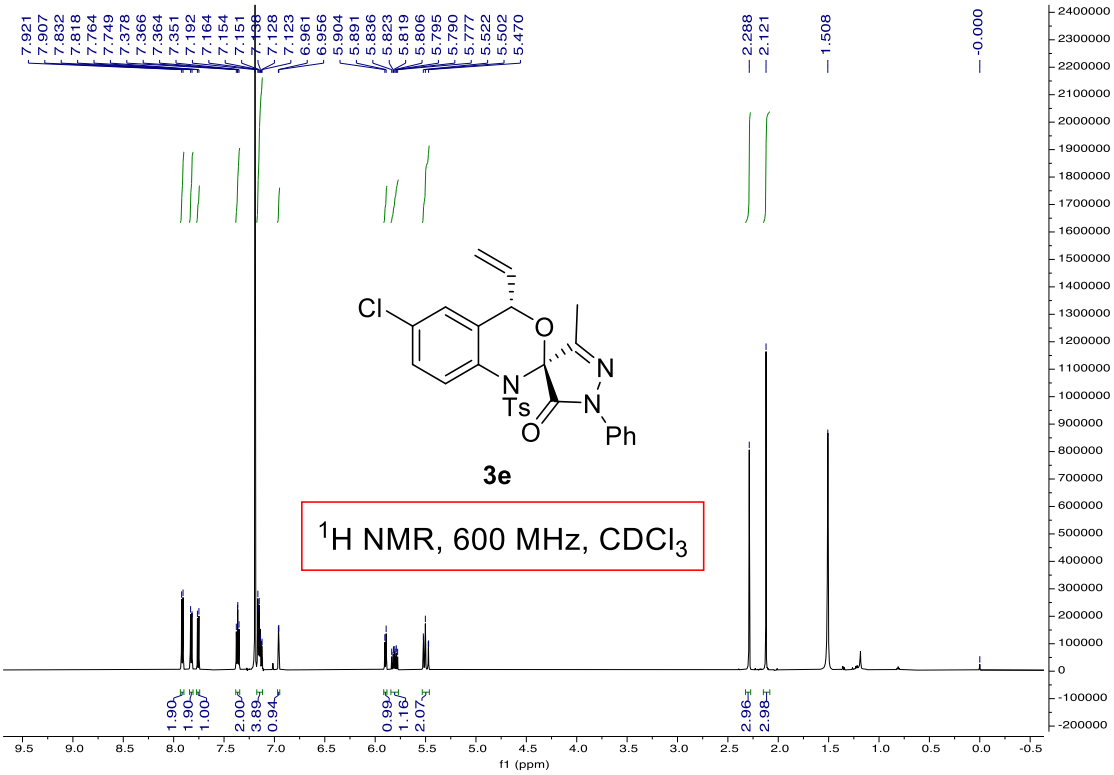
N
Ph
3d
13C NMR, 175 MHz, CDCl3
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.87	n.a.	146.615	64.555	49.95	n.a.	BMB*
2	13.05	n.a.	111.333	64.696	50.05	n.a.	BMB*
Total:			257.948	129.251	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.91	n.a.	12.390	4.549	4.15	n.a.	BMB*
2	13.00	n.a.	174.595	105.176	95.85	n.a.	BMB*
Total:			186.985	109.726	100.00	0.000	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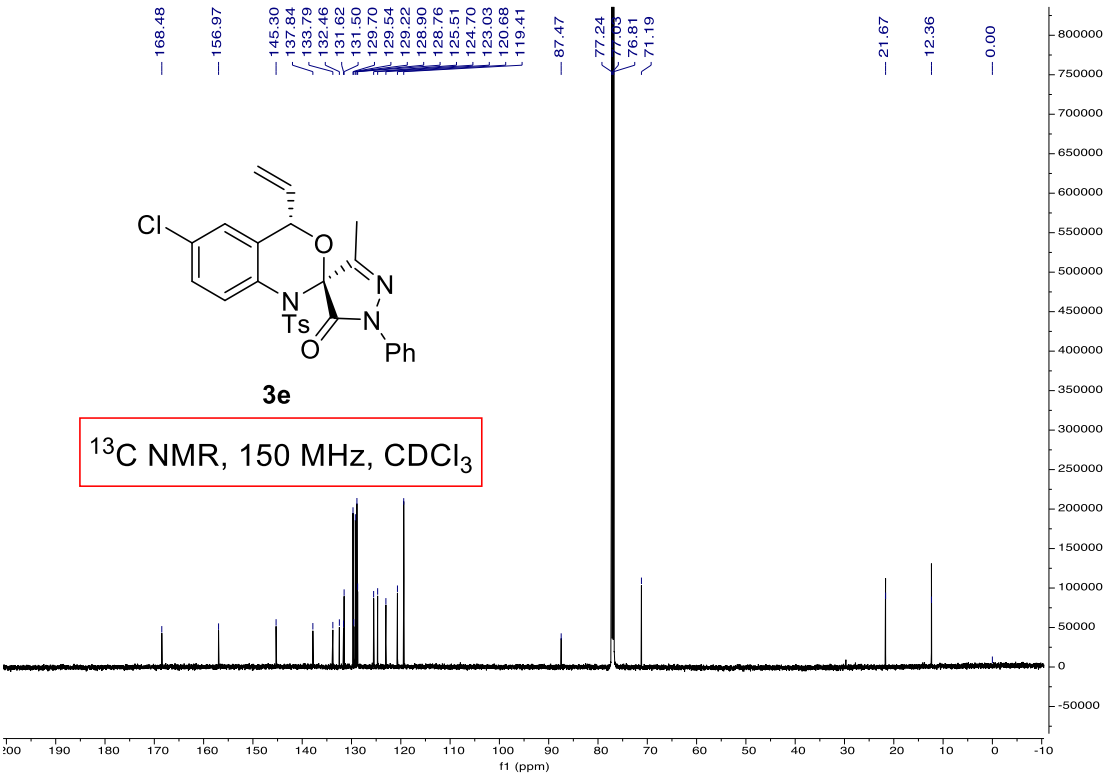
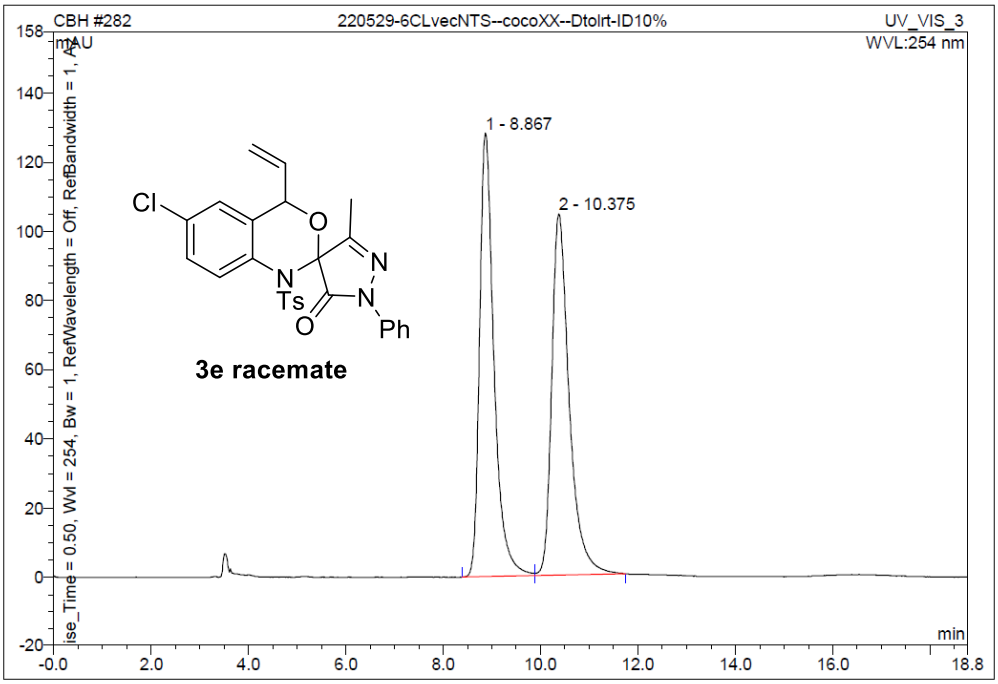
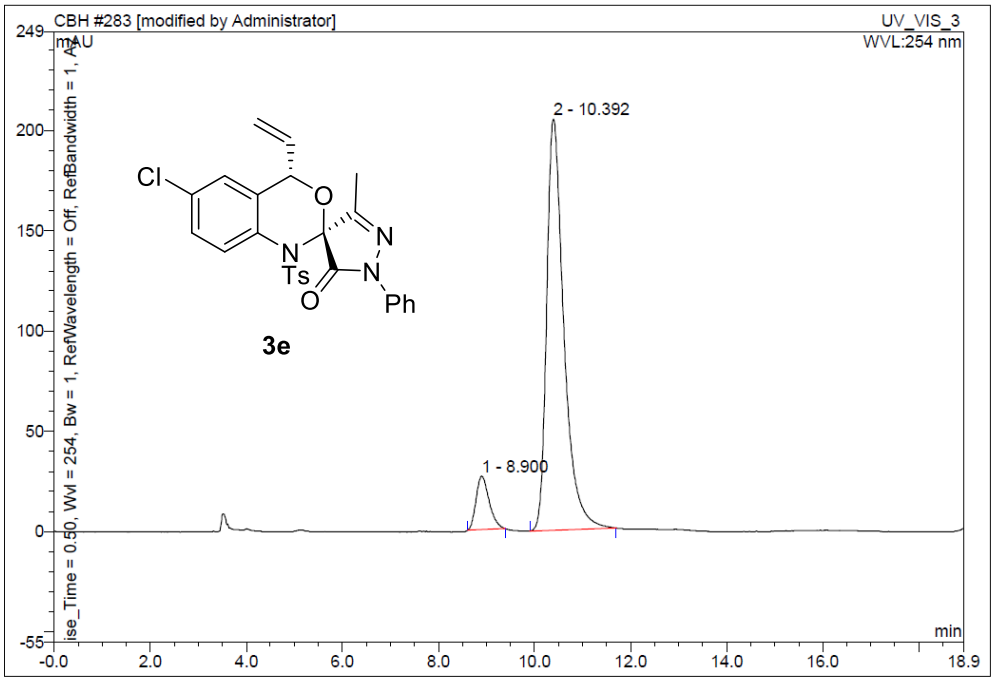
7.907
7.832
7.818
7.764
7.749
7.378
7.366
7.364
7.351
7.192
7.164
7.154
7.151
7.128
7.123
6.961
6.956
5.904
5.891
5.836
5.823
5.819
5.806
5.795
5.790
5.777
5.522
5.502
5.470
2.288
2.121
1.508
-0.000
Cl
O
N
N
Ts
O
N
Ph
3e
1H NMR, 600 MHz, CDCl3
1.90
1.90
1.00
2.00
3.89
0.94
0.99
1.16
2.07
2.96
2.98
f1 (ppm)

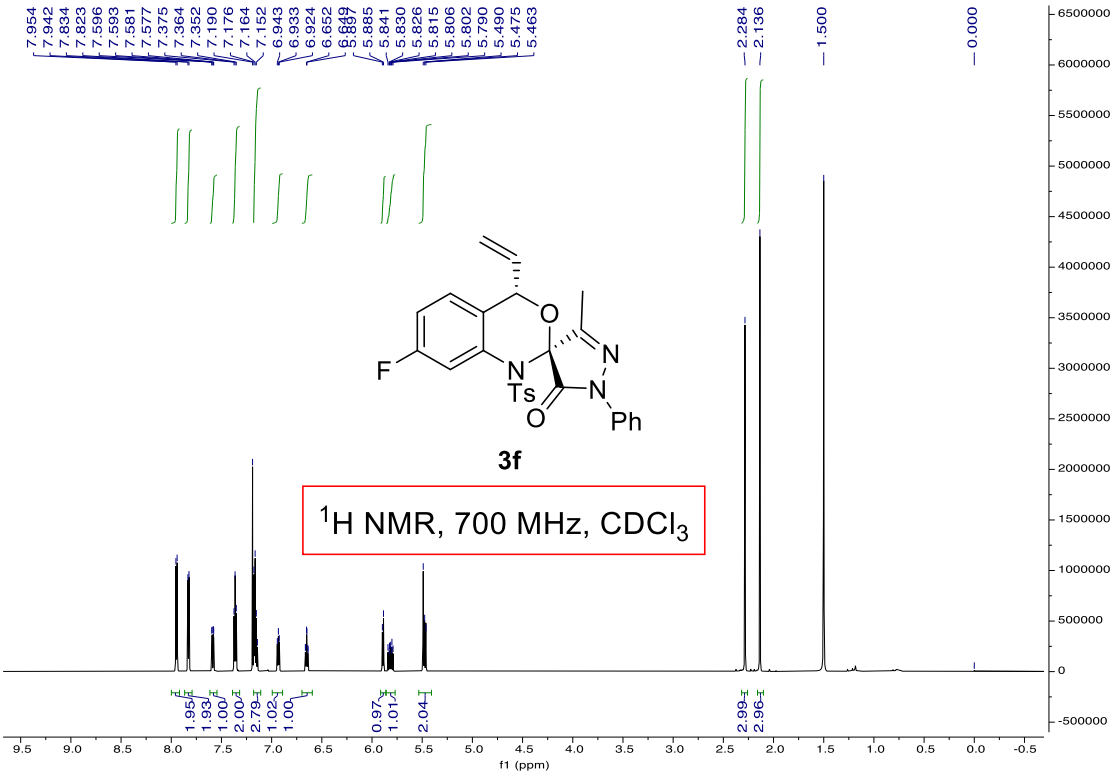

168.48
156.97
145.30
137.84
133.79
132.46
131.62
131.50
129.70
129.54
129.22
128.90
128.76
125.51
124.70
123.03
120.68
119.41
87.47
77.24
76.81
71.19
21.67
12.36
0.00
Cl
O
N
N
Ts
O
N
Ph
3e
13C NMR, 150 MHz, CDCl3
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.87	n.a.	128.337	43.838	50.20	n.a.	BM
2	10.38	n.a.	104.472	43.489	49.80	n.a.	MB
Total:			232.809	87.327	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.90	n.a.	26.726	8.405	9.01	n.a.	BMB*
2	10.39	n.a.	204.958	84.889	90.99	n.a.	BMB*
Total:			231.684	93.294	100.00	0.000	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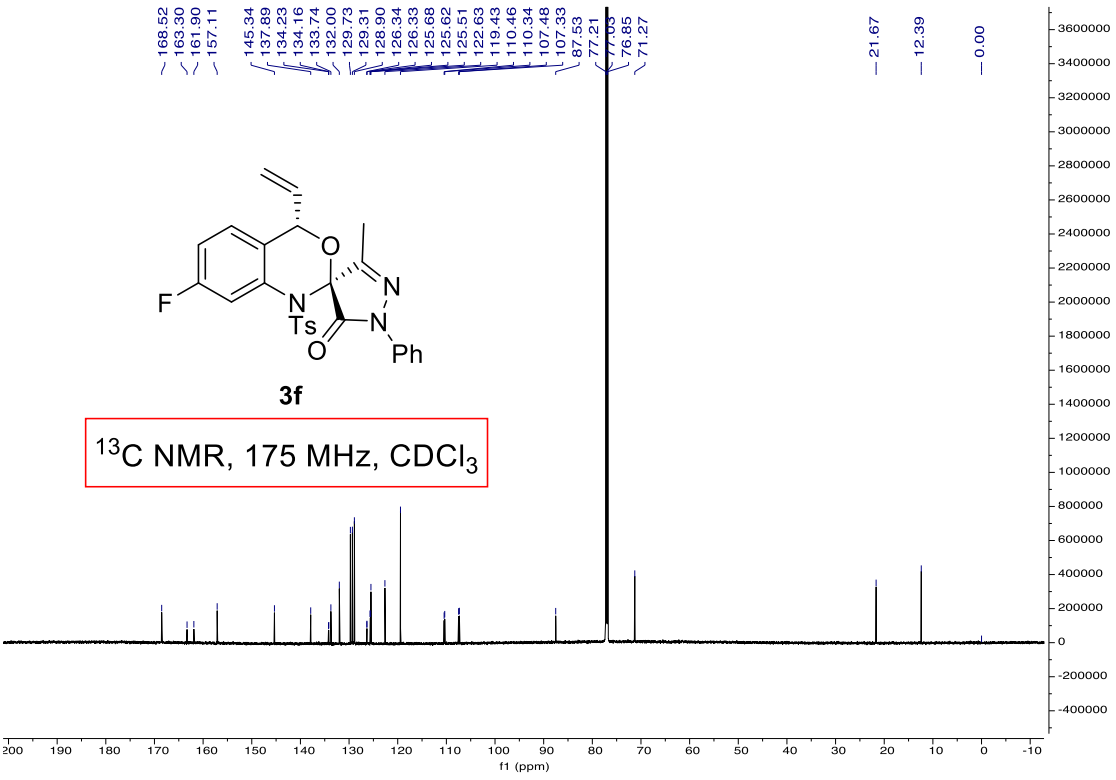
7.942
7.834
7.823
7.596
7.593
7.581
7.577
7.375
7.364
7.352
7.190
7.176
7.164
7.152
6.943
6.933
6.924
6.652
5.885
5.841
5.830
5.826
5.815
5.806
5.802
5.790
5.490
5.475
5.463
2.284
2.136
1.500
0.000
F
O
N
N
Ts
O
N
Ph
3f
1H NMR, 700 MHz, CDCl3
1.95
1.93
1.00
2.00
2.79
1.02
1.00
0.97
1.01
2.04
2.99
2.96
f1 (ppm)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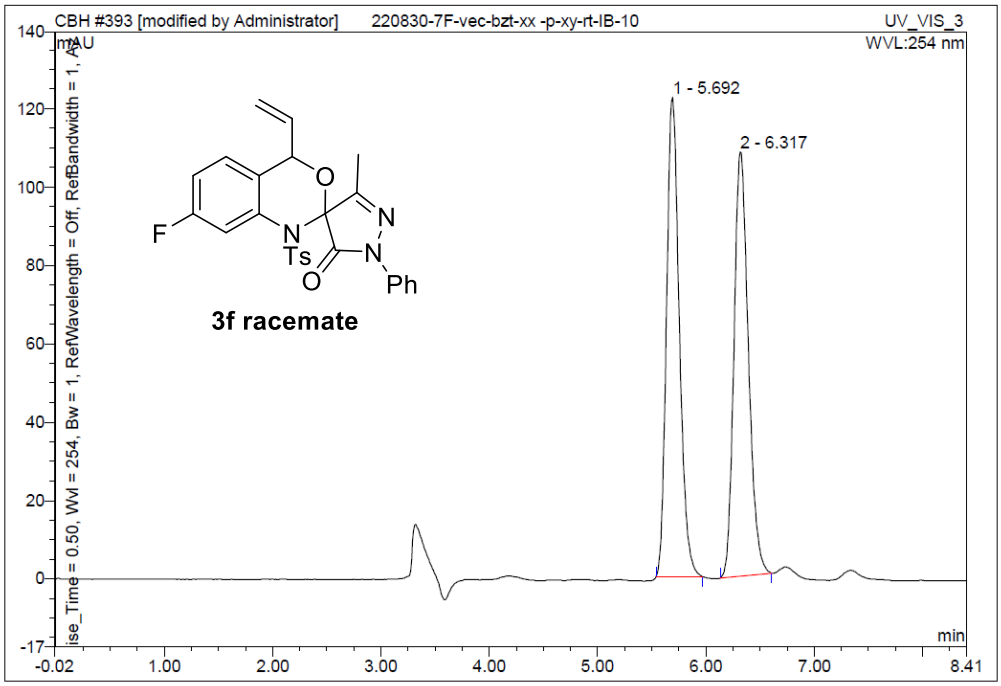
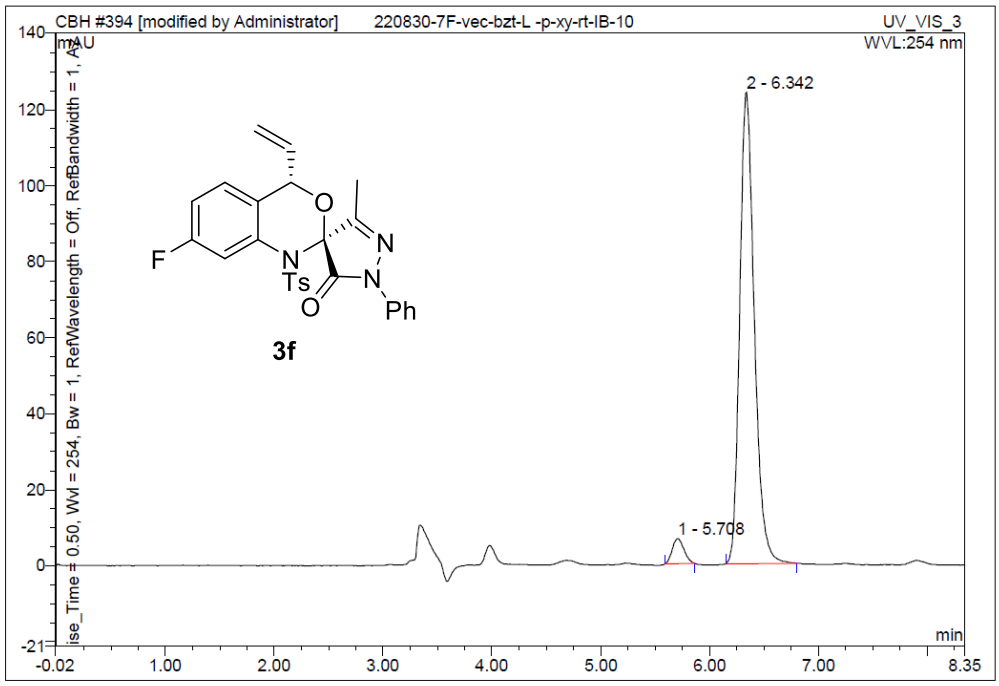
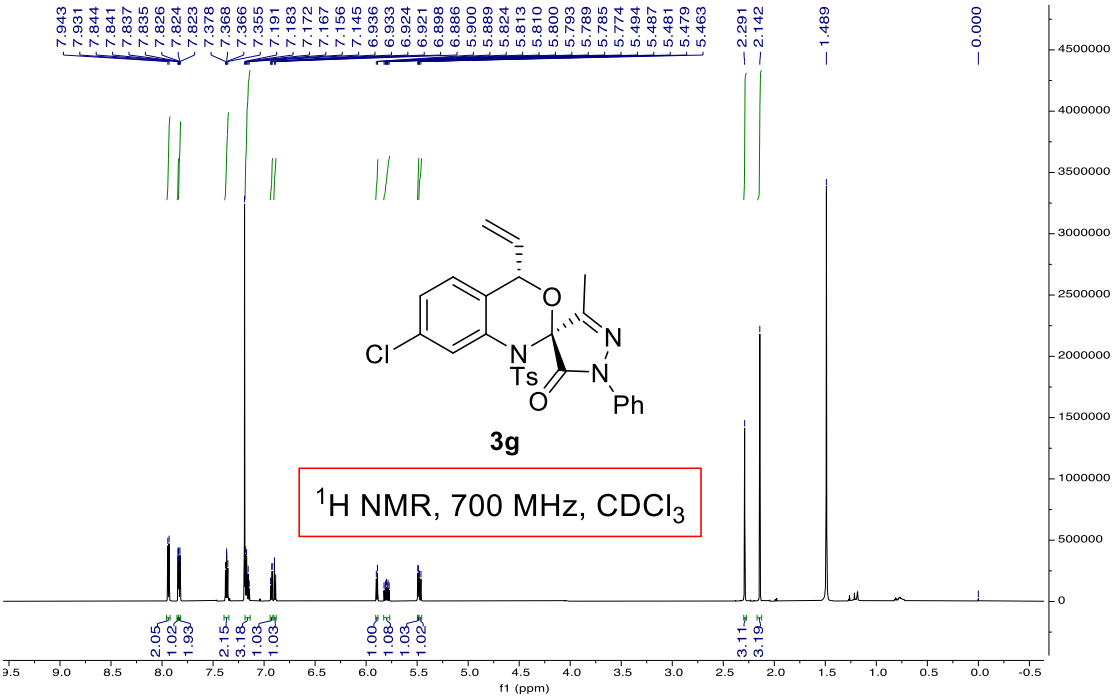
163.30
161.90
157.11
145.34
137.89
134.23
134.16
133.74
132.00
129.73
129.31
128.90
126.34
126.33
125.68
125.62
125.51
122.63
119.43
110.46
110.34
107.48
107.33
87.53
77.21
77.03
76.85
71.27
21.67
12.39
0.00
F
O
N
N
Ts
O
N
Ph
3f
13C NMR, 175 MHz, CDCl3
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.69	n.a.	122.307	16.748	50.15	n.a.	BMB*
2	6.32	n.a.	108.289	16.650	49.85	n.a.	BMB*
Total:			230.596	33.398	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	5.71	n.a.	6.619	0.823	4.11	n.a.	BMB*
2	6.34	n.a.	124.129	19.172	95.89	n.a.	BMB*
Total:			130.748	19.995	100.00	0.000	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7.841
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7.826
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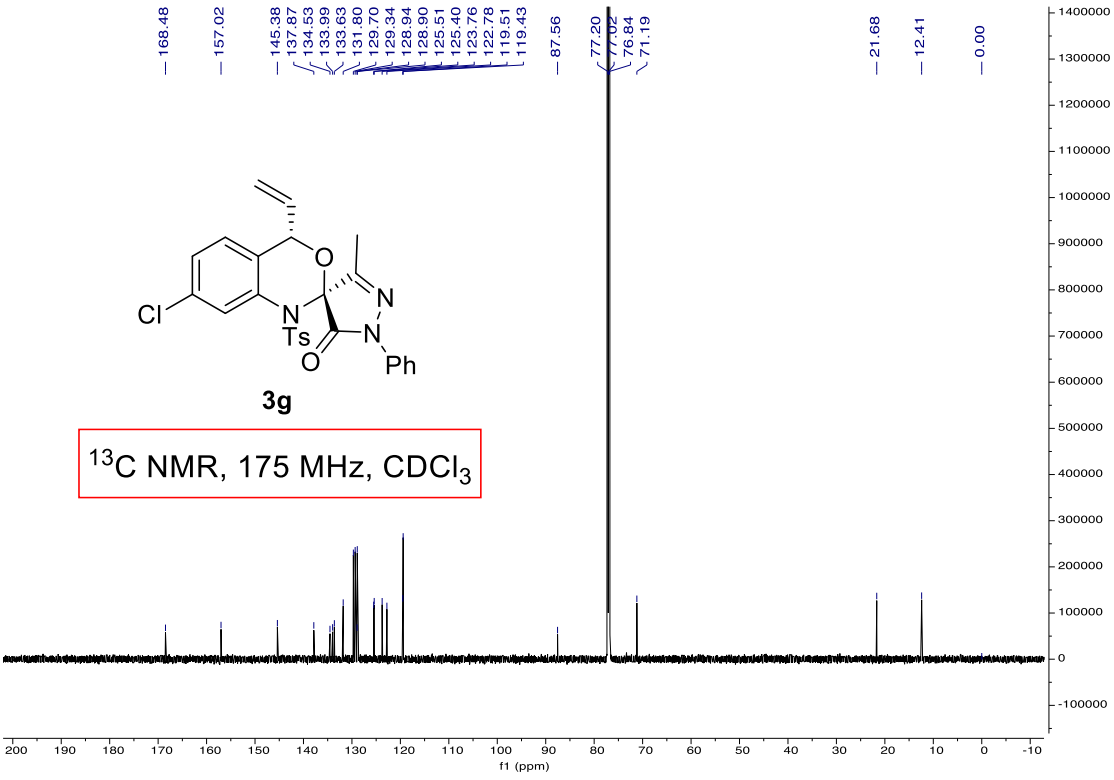
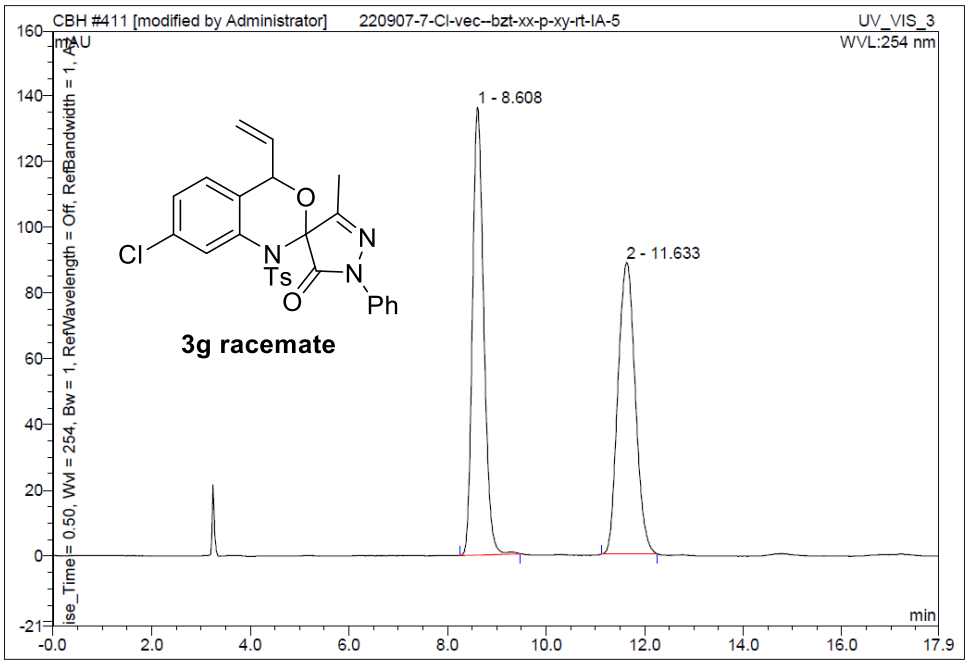
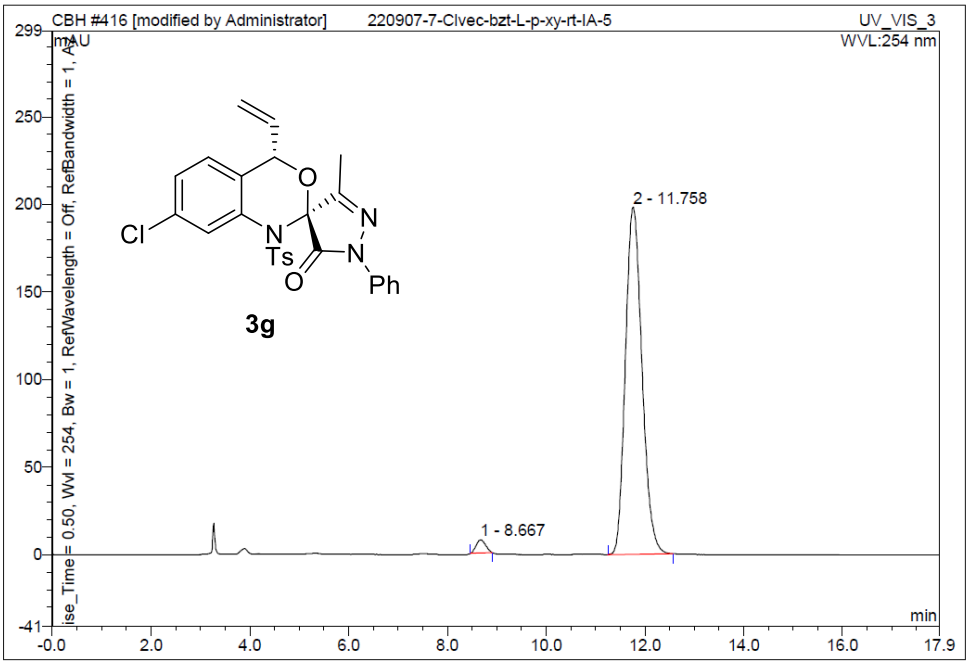
7.823
7.378
7.368
7.366
7.355
7.191
7.183
7.172
7.167
7.156
7.145
6.936
6.933
6.924
6.921
6.898
6.886
5.900
5.889
5.824
5.813
5.810
5.800
5.793
5.789
5.785
5.774
5.494
5.487
5.481
5.479
5.463
2.291
2.142
1.489
0.000
Cl
N
O
Ts
O
N
N
Ph
3g
^{1}H NMR, 700 MHz, CDCl$_3$
2.05
1.02
1.93
2.15
3.18
1.03
1.03
1.00
1.08
1.03
1.02
3.11
3.19
f1 (ppm)

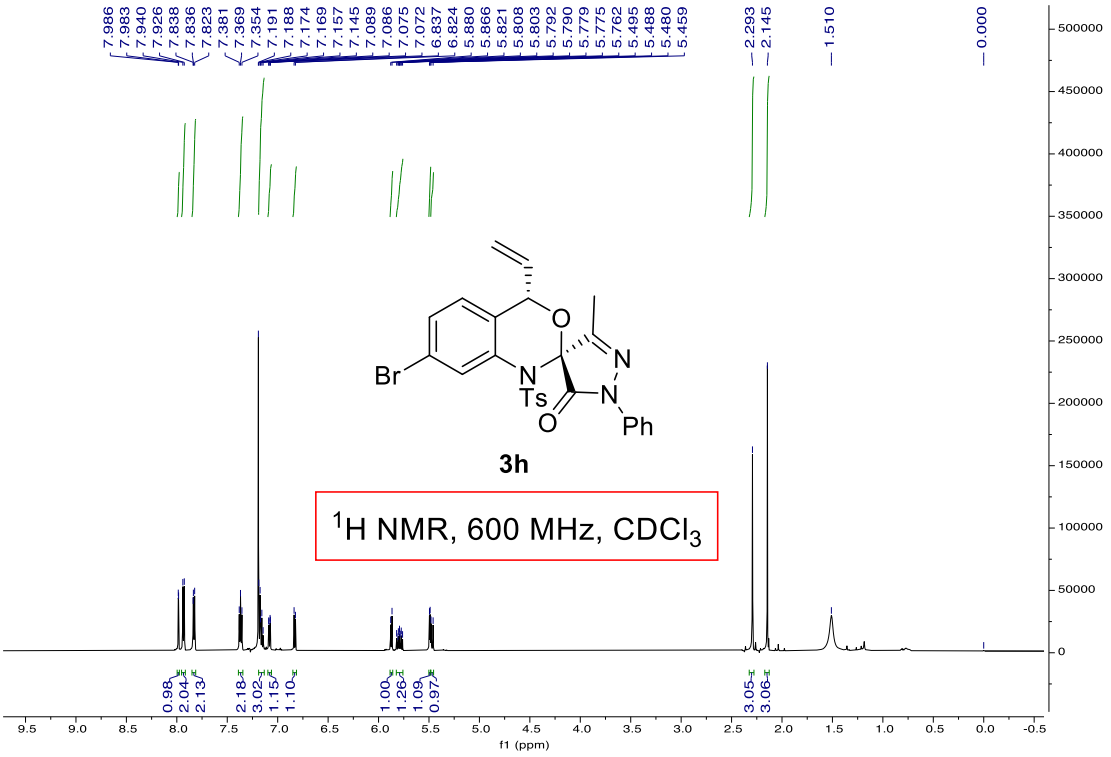

168.48
157.02
145.38
137.87
134.53
133.99
133.63
131.80
129.70
129.34
128.94
128.90
125.51
125.40
123.76
122.78
119.51
119.43
87.56
77.20
77.02
76.84
71.19
21.68
12.41
0.00
Cl
N
O
Ts
O
N
N
Ph
3g
^{13}C NMR, 175 MHz, CDCl$_3$
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.61	n.a.	136.121	36.128	50.02	n.a.	BMB*
2	11.63	n.a.	88.635	36.103	49.98	n.a.	BMB*
Total:			224.755	72.231	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.67	n.a.	7.449	1.656	2.11	n.a.	BMB*
2	11.76	n.a.	198.149	76.964	97.89	n.a.	BMB*
Total:			205.598	78.620	100.00	0.000	


7.986
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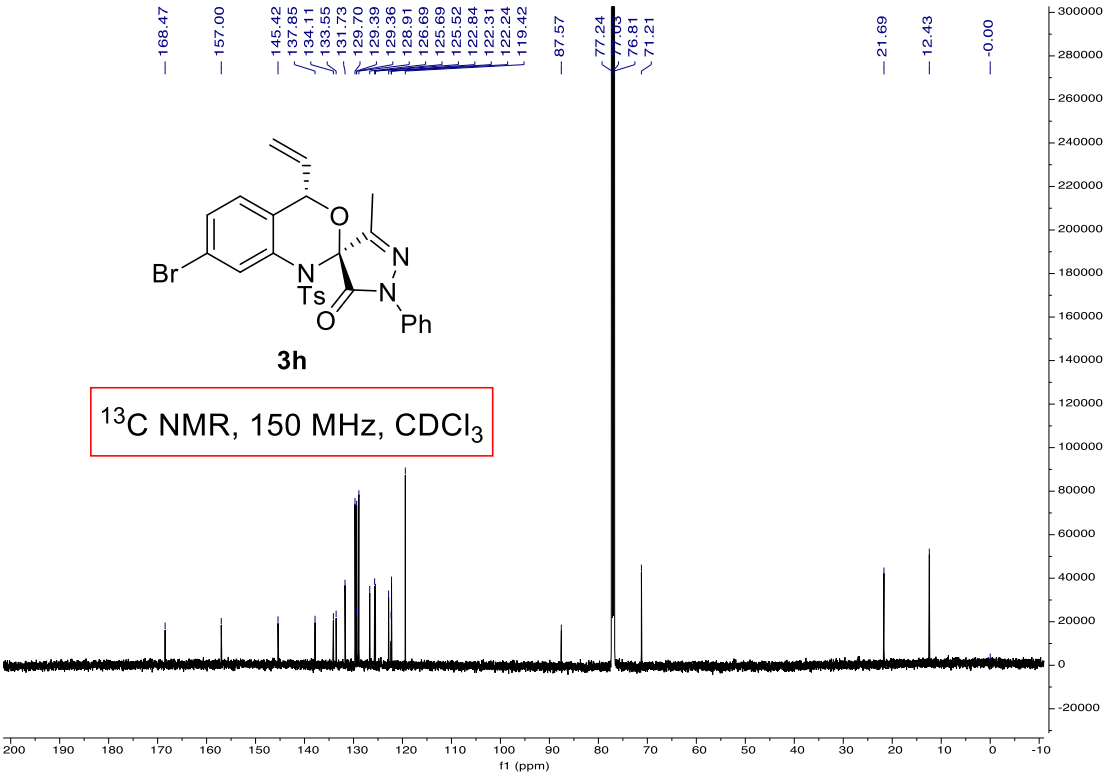
7.940
7.926
7.838
7.836
7.823
7.381
7.369
7.354
7.191
7.188
7.174
7.169
7.157
7.145
7.089
7.086
7.075
7.072
6.837
6.824
5.880
5.866
5.821
5.808
5.803
5.792
5.790
5.779
5.775
5.762
5.495
5.488
5.480
5.459
2.293
2.145
1.510
0.000
Br
N
Ts
O
N
N
Ph
O
3h
1H NMR, 600 MHz, CDCl3
0.98
2.04
2.13
2.18
3.02
1.15
1.10
1.00
1.26
1.09
0.97
3.05
3.06
f1 (ppm)


168.47
157.00
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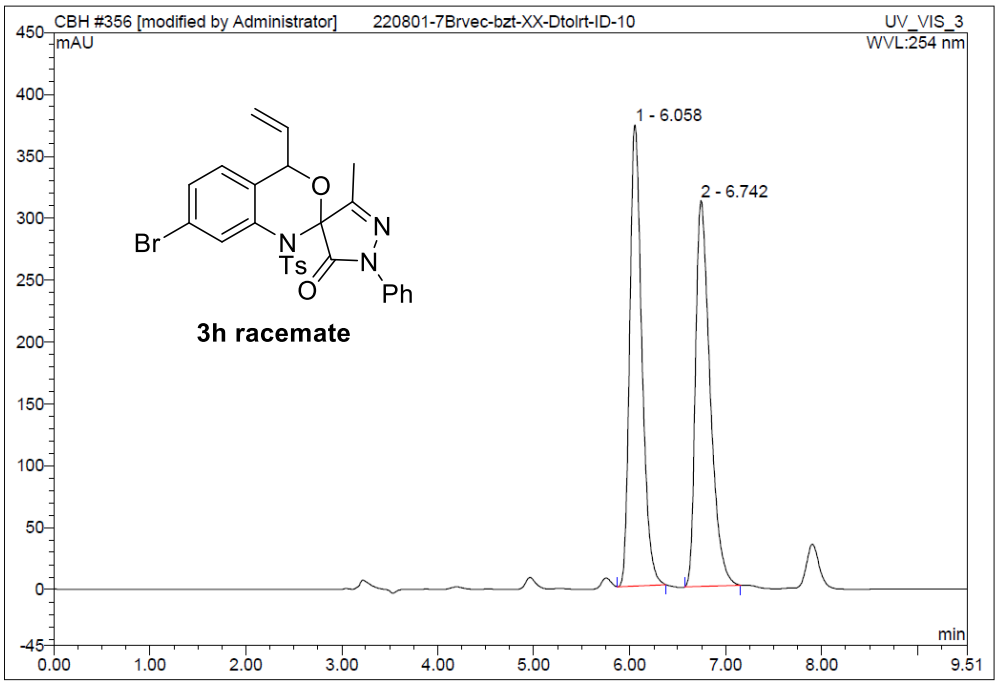
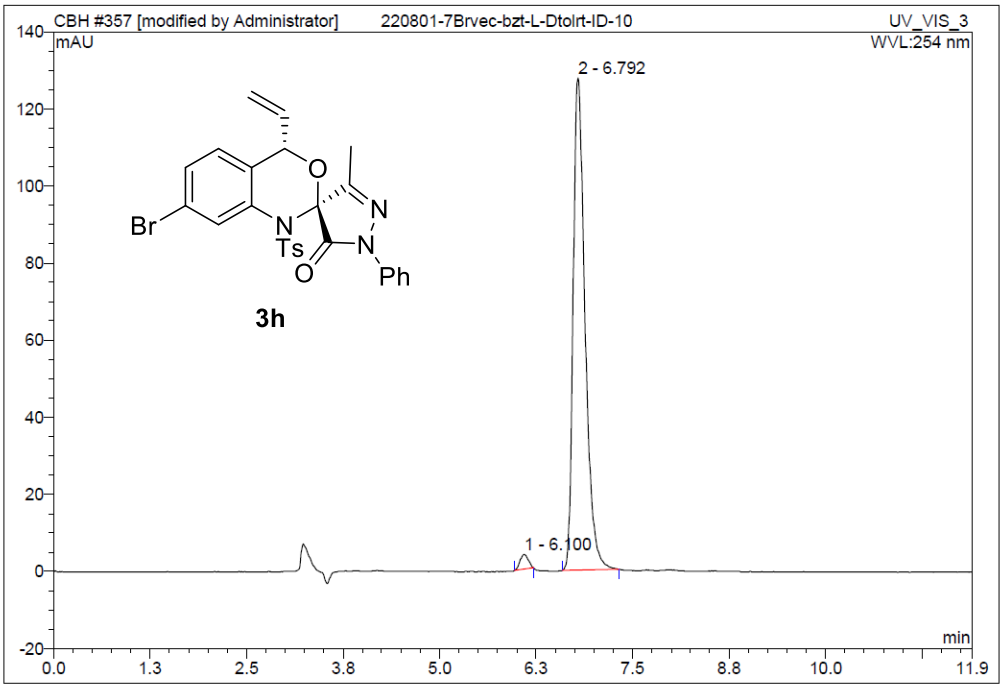
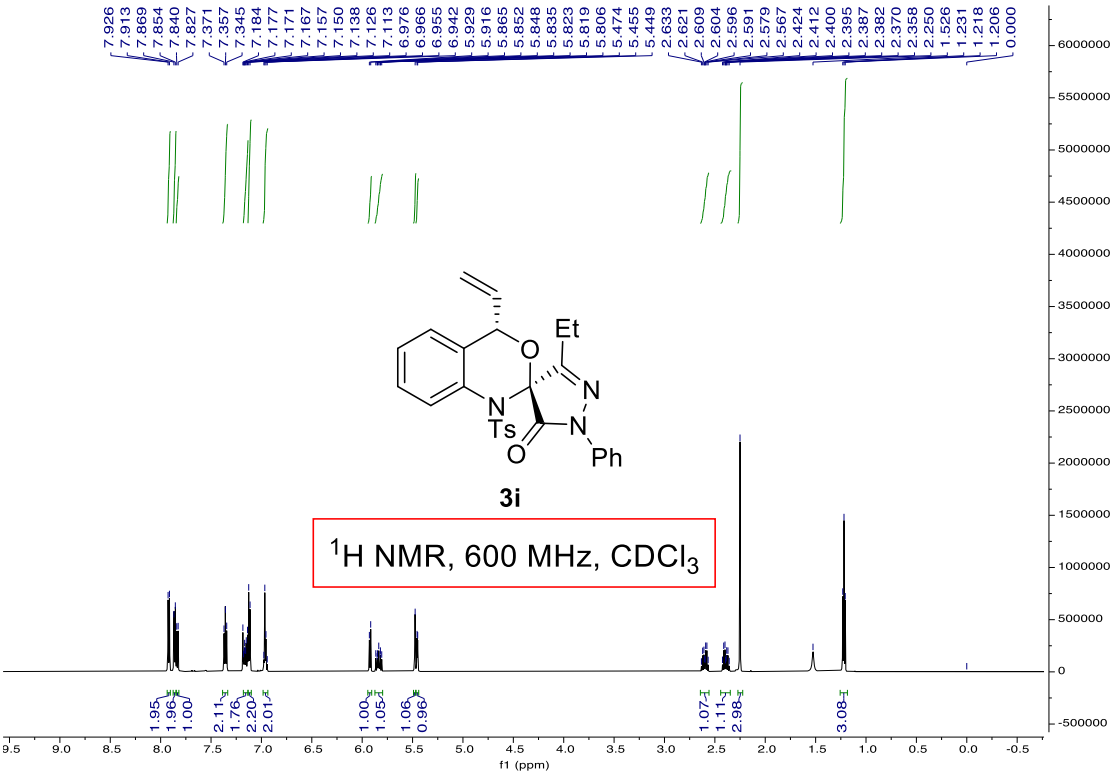
137.85
134.11
133.55
131.73
129.70
129.39
129.36
128.91
126.69
125.69
125.52
122.84
122.31
122.24
119.42
87.57
77.24
77.03
76.81
71.21
21.69
12.43
-0.00
Br
N
Ts
O
N
N
Ph
O
3h
13C NMR, 150 MHz, CDCl3
f1 (ppm)

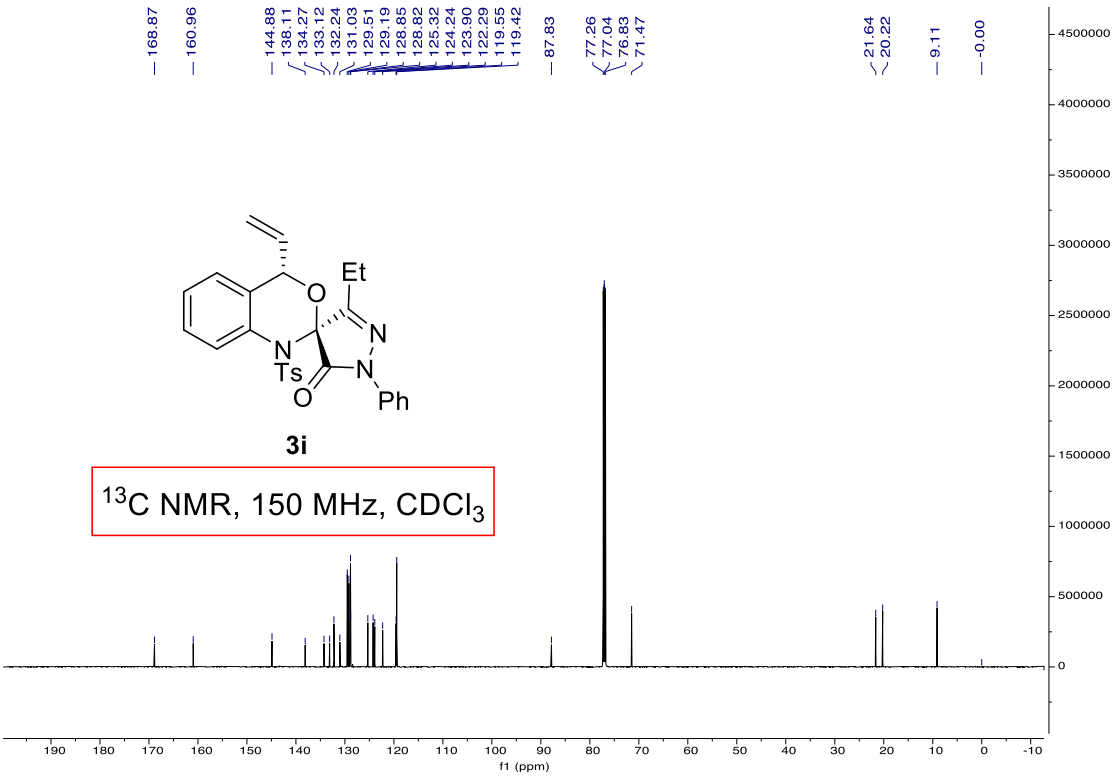


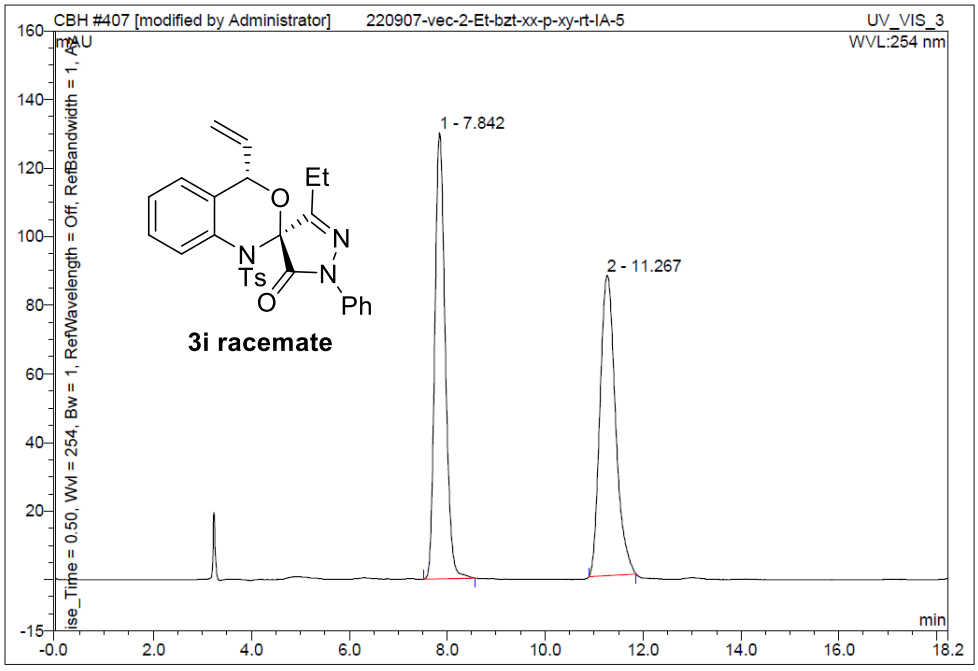
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.06	n.a.	372.150	54.833	50.05	n.a.	BMB*
2	6.74	n.a.	311.441	54.722	49.95	n.a.	BMB*
Total:			683.591	109.555	100.00	0.000	



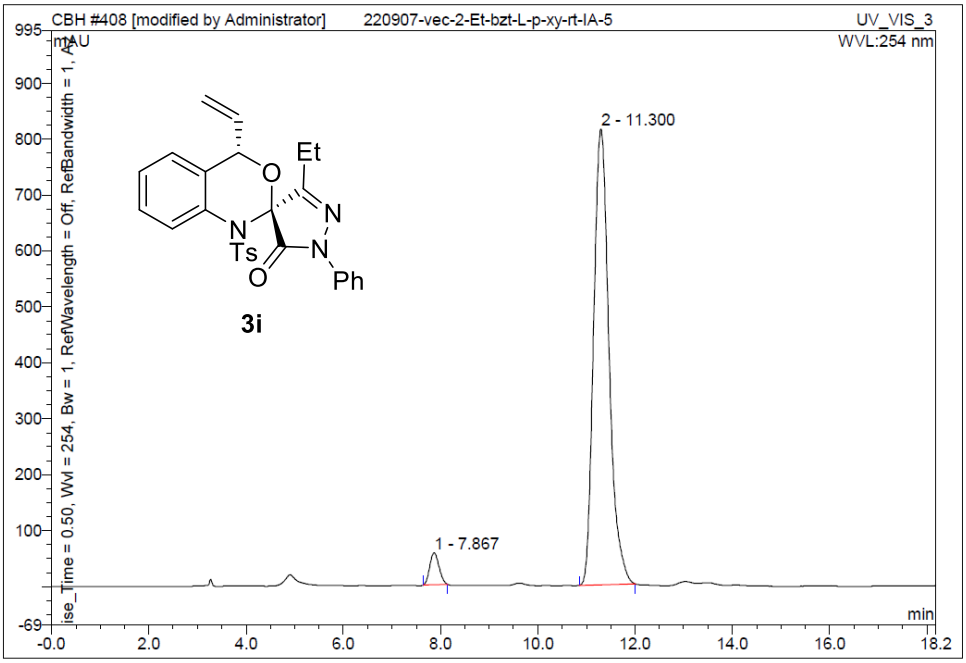
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.10	n.a.	3.778	0.470	2.03	n.a.	BMB*
2	6.79	n.a.	127.661	22.725	97.97	n.a.	BMB*
Total:			131.440	23.195	100.00	0.000	


Et
O
N
N
Ts
O
N
Ph
3i
^{1}H NMR, 600 MHz, $CDCl_3$
f1 (ppm)

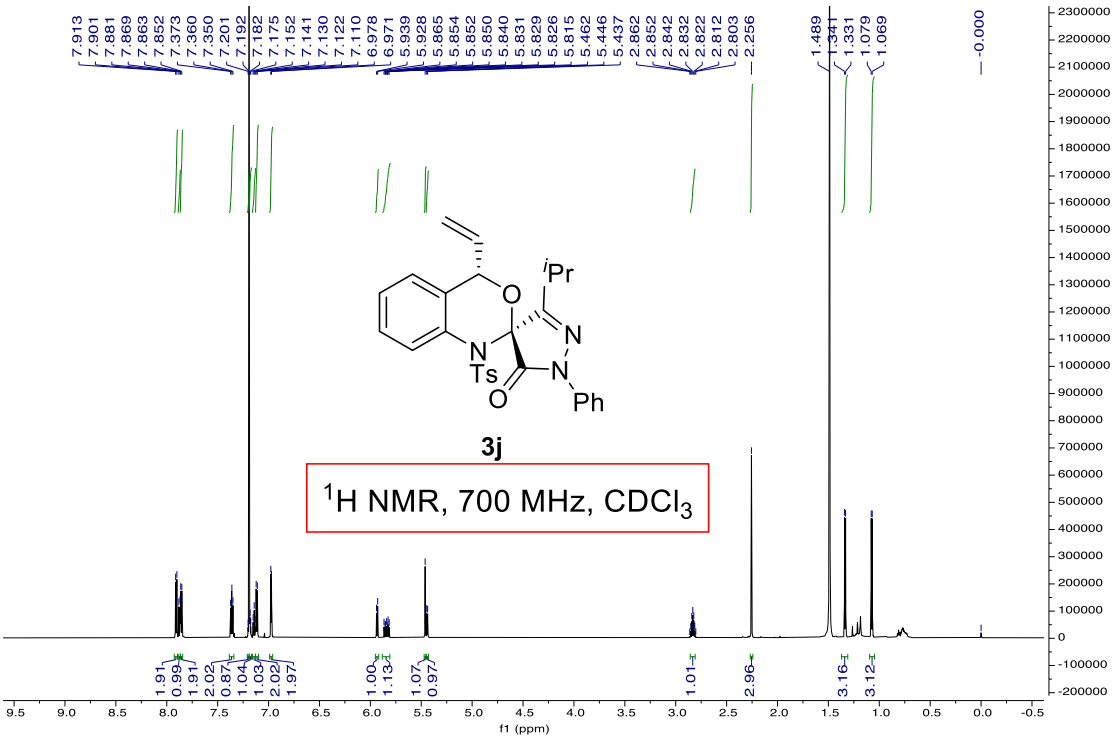

Et
O
N
N
Ts
O
N
Ph
3i
^{13}C NMR, 150 MHz, $CDCl_3$
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.84	n.a.	129.976	32.060	49.98	n.a.	BMB*
2	11.27	n.a.	87.580	32.081	50.02	n.a.	BMB*
Total:			217.556	64.141	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.87	n.a.	56.831	12.593	4.05	n.a.	BMB*
2	11.30	n.a.	814.655	298.498	95.95	n.a.	BMB*
Total:			871.486	311.091	100.00	0.000	


7.913
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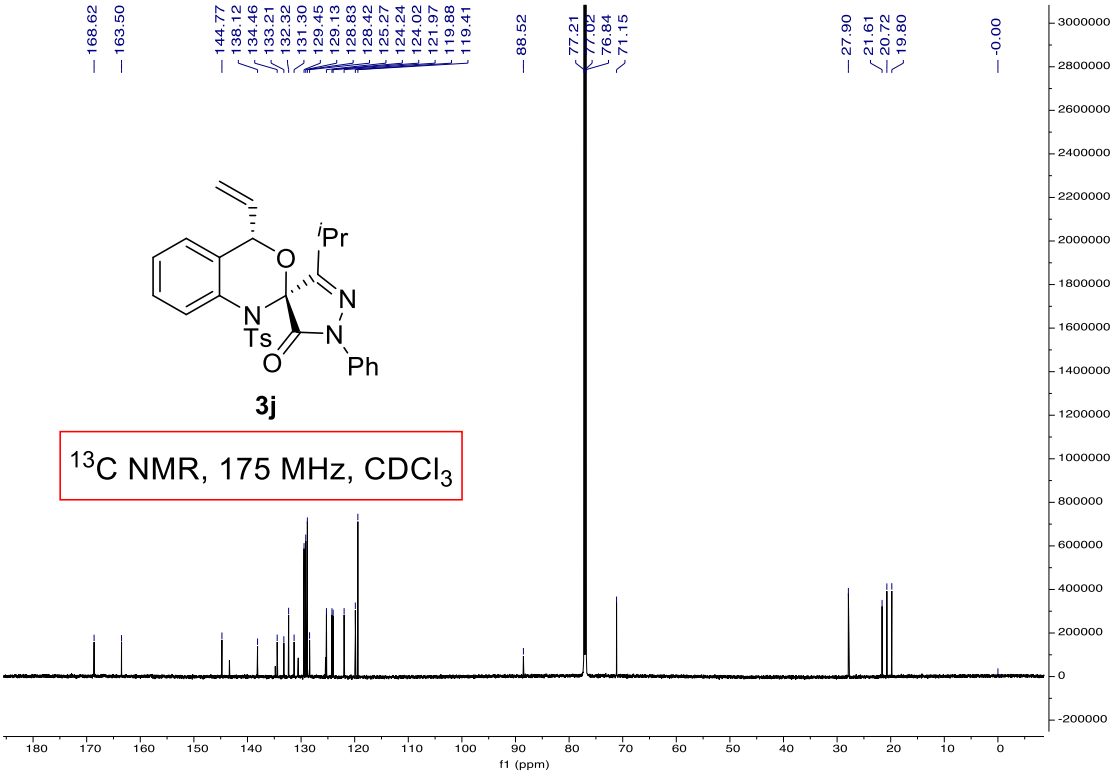
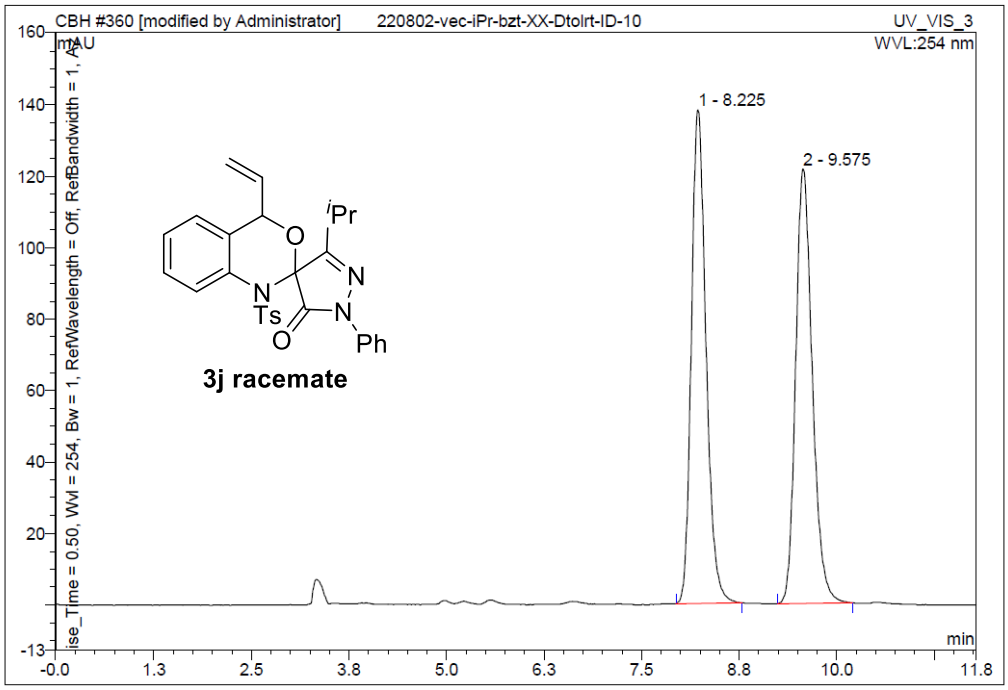
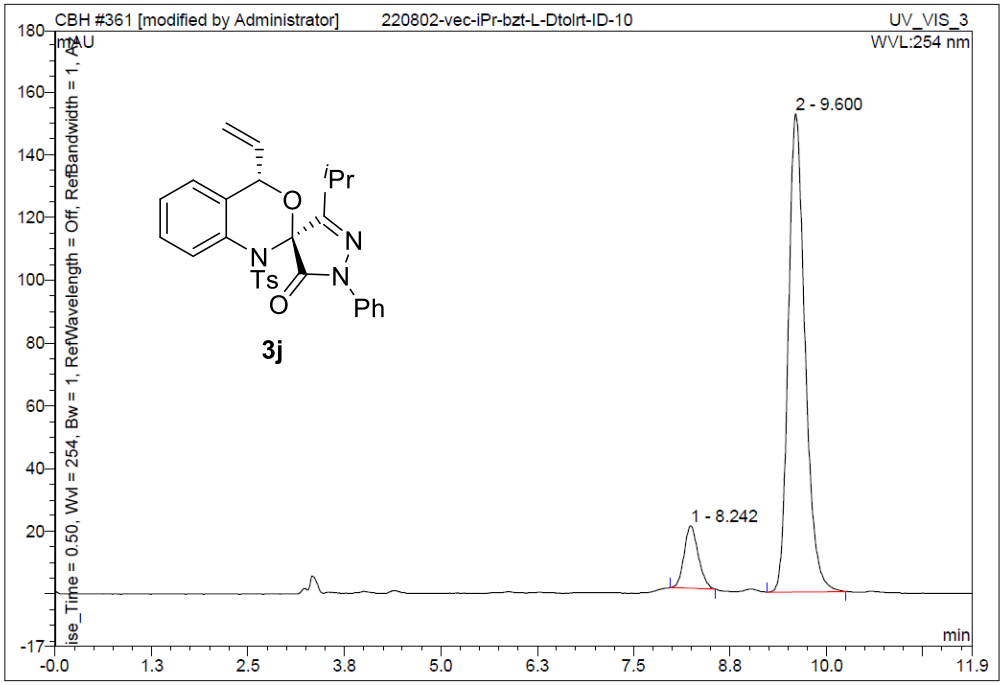
7.881
7.869
7.863
7.852
7.373
7.360
7.350
7.201
7.192
7.182
7.175
7.152
7.141
7.130
7.122
7.110
6.978
6.971
5.939
5.928
5.865
5.854
5.852
5.850
5.840
5.831
5.829
5.826
5.815
5.462
5.446
5.437
2.862
2.852
2.842
2.832
2.822
2.812
2.803
2.256
1.489
1.341
1.331
1.079
1.069
-0.000
iPr
O
N
N
Ts
N
Ph
O
3j
1H NMR, 700 MHz, CDCl3
1.91
0.99
1.91
2.02
0.87
1.04
1.03
2.02
1.97
1.00
1.13
1.07
0.97
1.01
2.96
3.16
3.12
f1 (ppm)

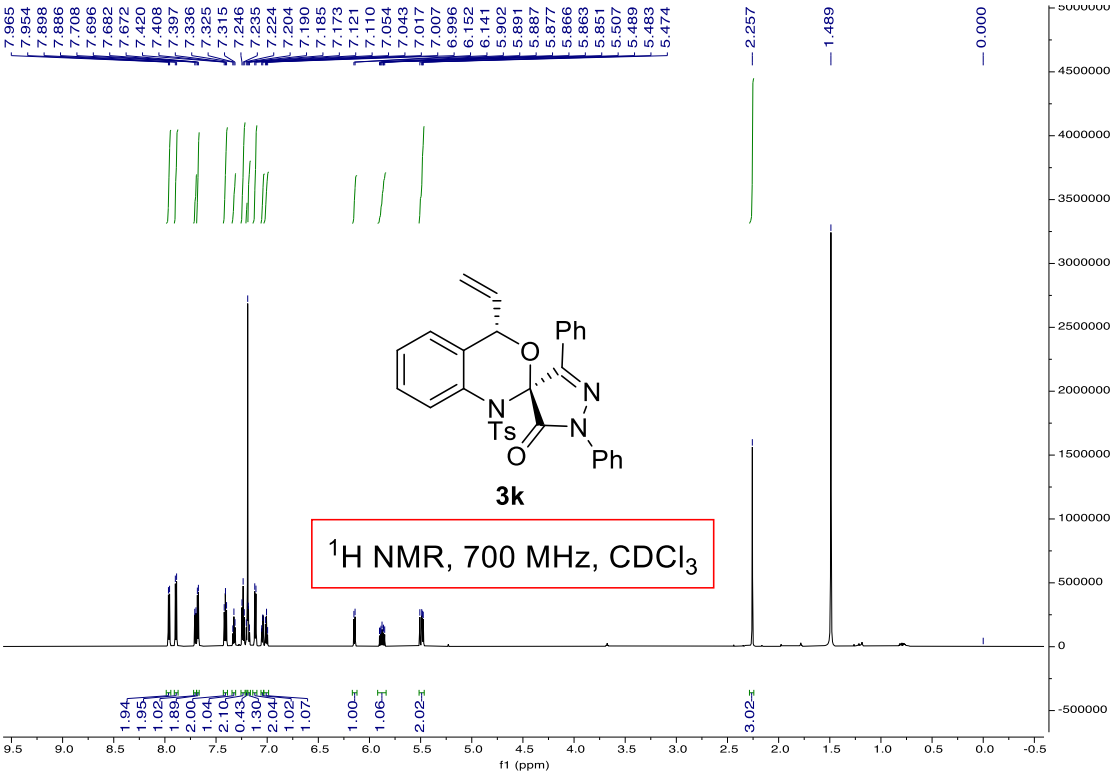

168.62
163.50
144.77
138.12
134.46
133.21
132.32
131.30
129.45
129.13
128.83
128.42
125.27
124.24
124.02
121.97
119.88
119.41
88.52
77.21
77.02
76.84
71.15
27.90
21.61
20.72
19.80
-0.00
iPr
O
N
N
Ts
N
Ph
O
3j
13C NMR, 175 MHz, CDCl3
f1 (ppm)

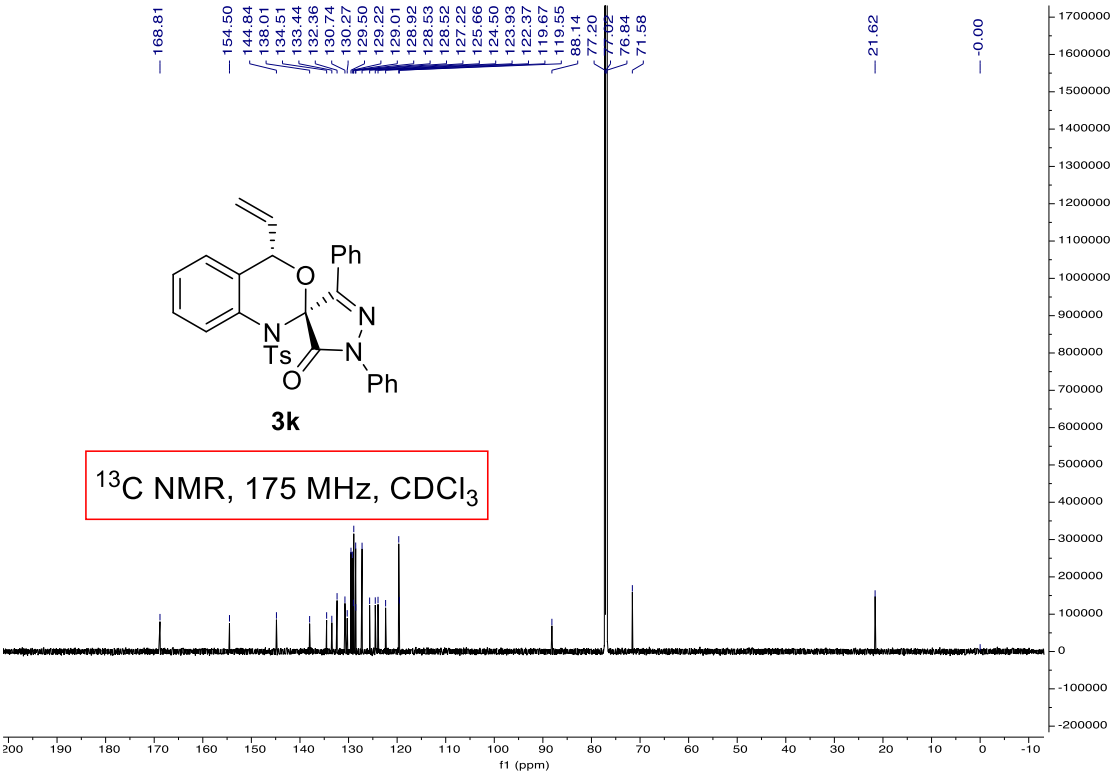


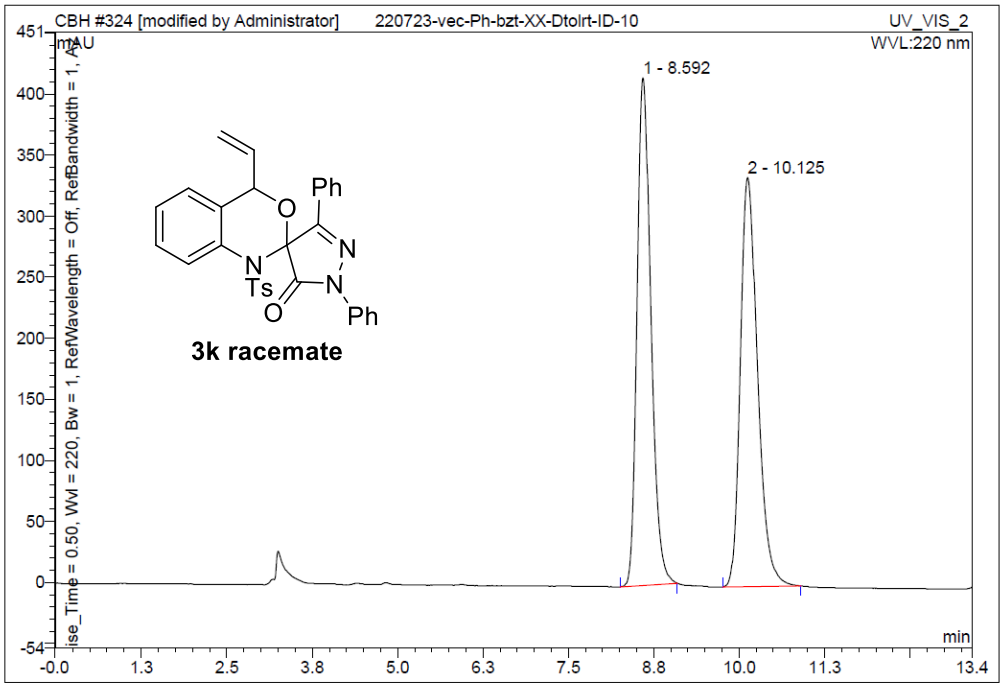
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.23	n.a.	138.237	30.083	50.04	n.a.	BMB*
2	9.58	n.a.	121.557	30.033	49.96	n.a.	BMB*
Total:			259.794	60.116	100.00	0.000	



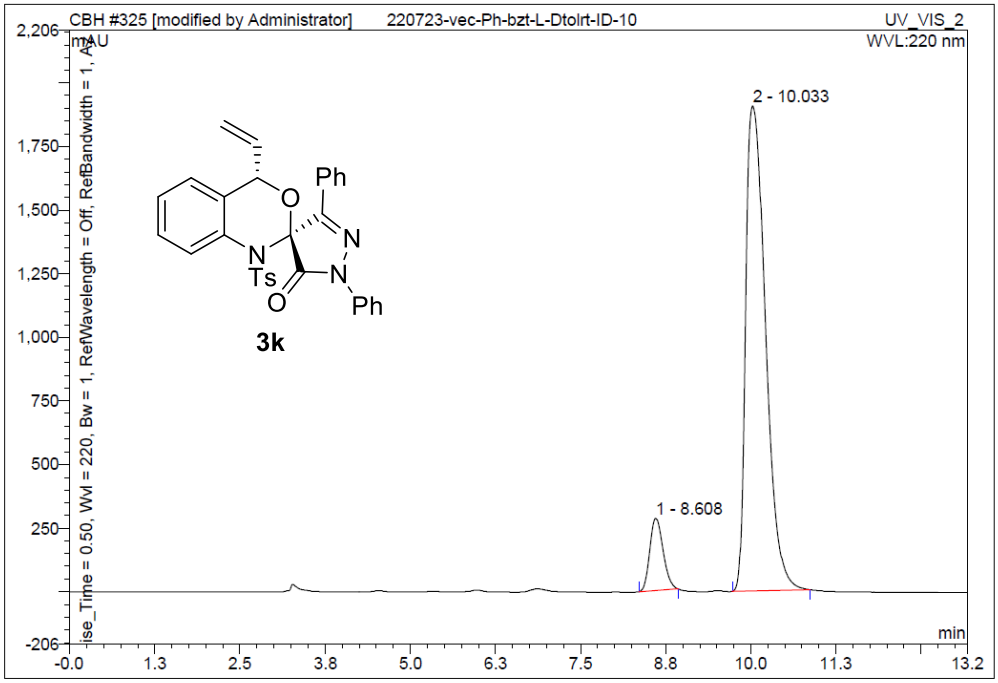
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.24	n.a.	19.896	4.247	9.98	n.a.	BMB*
2	9.60	n.a.	152.466	38.304	90.02	n.a.	BMB*
Total:			172.362	42.552	100.00	0.000	


Ph
O
N
N
Ts
O
N
Ph
3k
^{1}H NMR, 700 MHz, $CDCl_3$

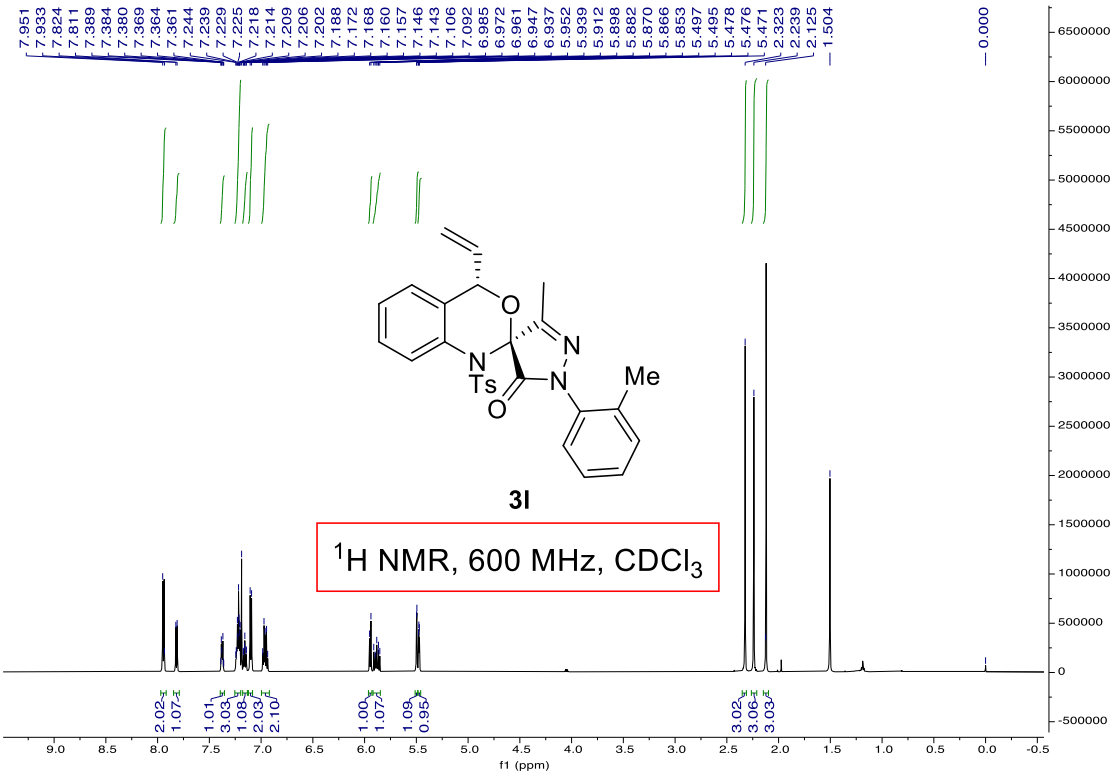

Ph
O
N
N
Ts
O
N
Ph
3k
^{13}C NMR, 175 MHz, $CDCl_3$



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.59	n.a.	415.963	97.935	49.90	n.a.	BMB*
2	10.13	n.a.	335.058	98.325	50.10	n.a.	BMB*
Total:			751.021	196.260	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.61	n.a.	283.928	63.857	9.02	n.a.	BMB*
2	10.03	n.a.	1906.471	644.352	90.98	n.a.	BMB*
Total:			2190.399	708.209	100.00	0.000	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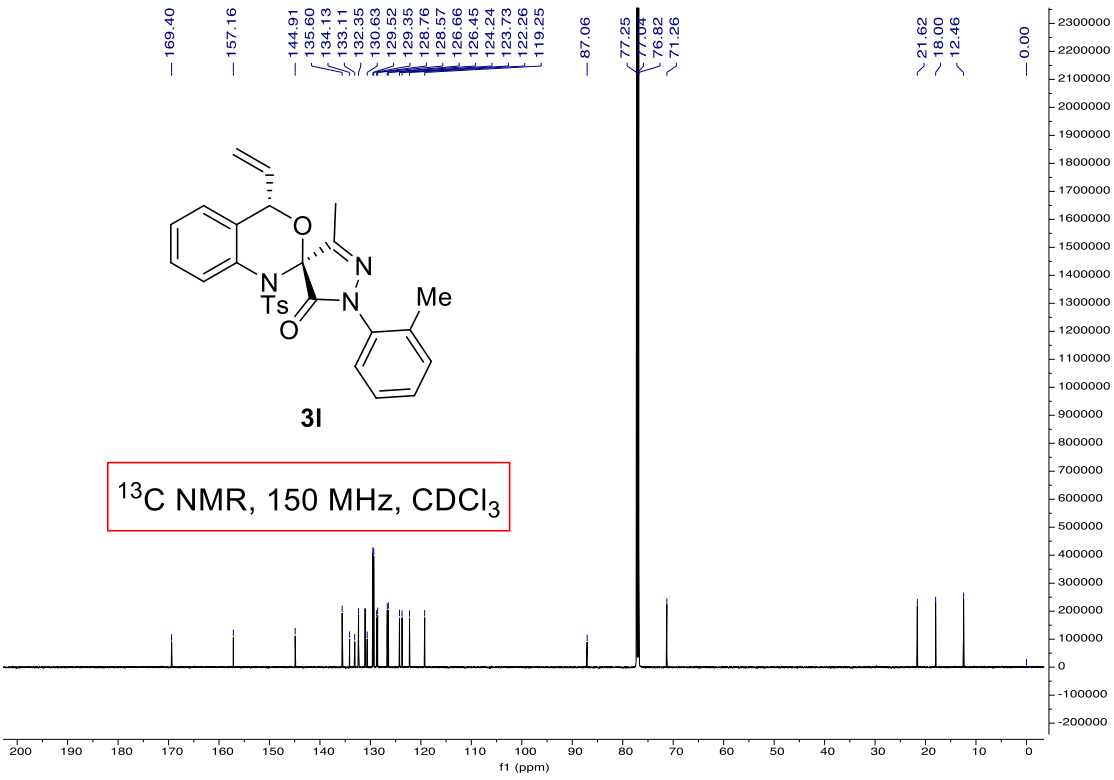
7.824
7.811
7.389
7.384
7.380
7.369
7.364
7.361
7.244
7.239
7.229
7.225
7.218
7.214
7.209
7.206
7.202
7.188
7.172
7.168
7.160
7.157
7.146
7.143
7.106
7.092
6.985
6.972
6.961
6.947
6.937
6.952
5.939
5.912
5.898
5.882
5.870
5.866
5.853
5.497
5.495
5.478
5.476
5.471
2.323
2.239
2.125
1.504
0.000
O
N
N
Ts
O
N
Me
3l
1H NMR, 600 MHz, CDCl3
2.02
1.07
1.01
3.03
1.08
2.03
2.10
1.00
1.07
1.09
0.95
3.02
3.06
3.03
f1 (ppm)


169.40
157.16
144.91
135.60
134.13
133.11
132.35
130.63
129.52
129.35
128.76
128.57
126.66
126.45
124.24
123.73
122.26
119.25
87.06
77.25
77.04
76.82
71.26
21.62
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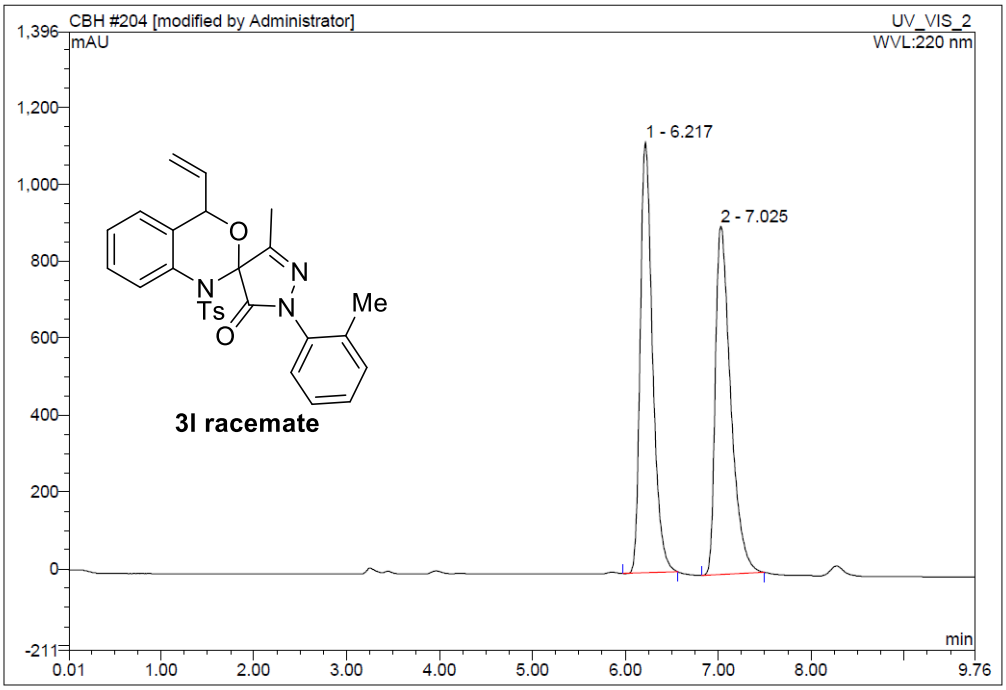
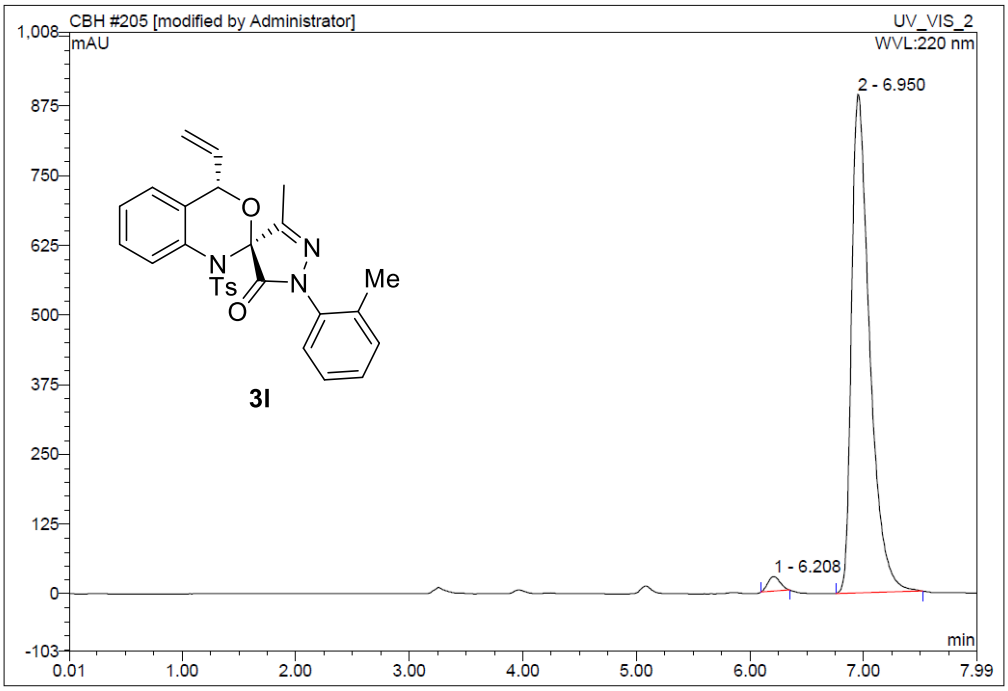
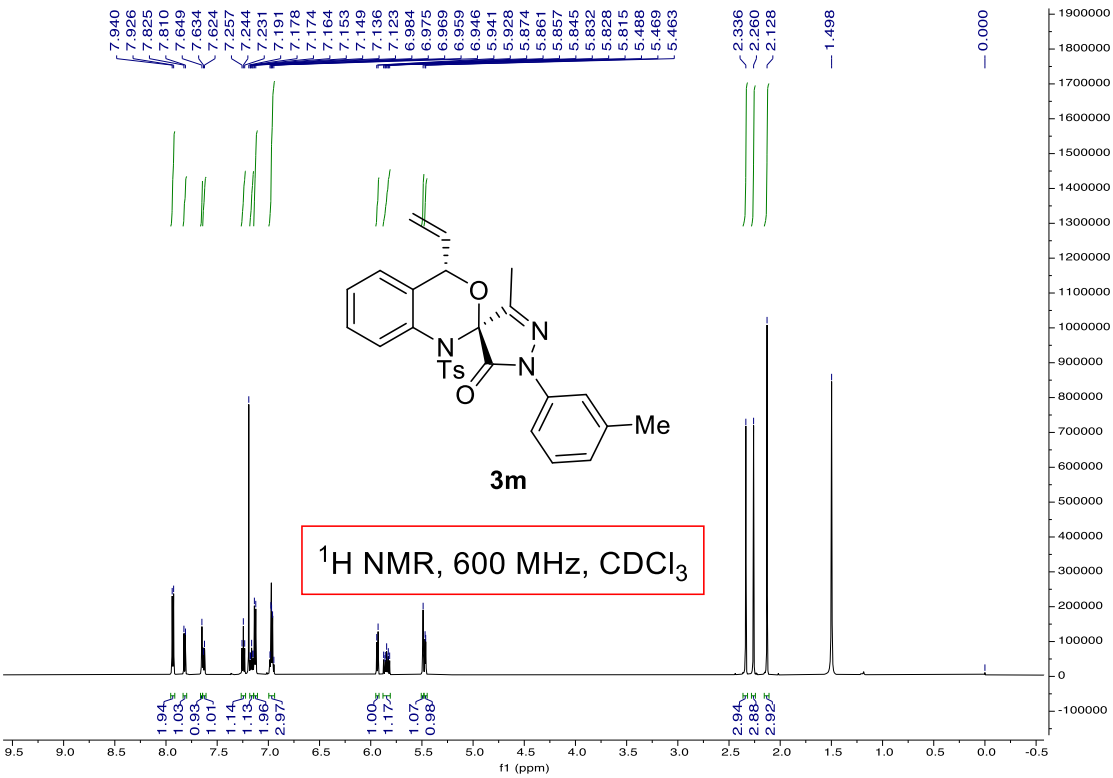
N
Me
3l
13C NMR, 150 MHz, CDCl3
f1 (ppm)

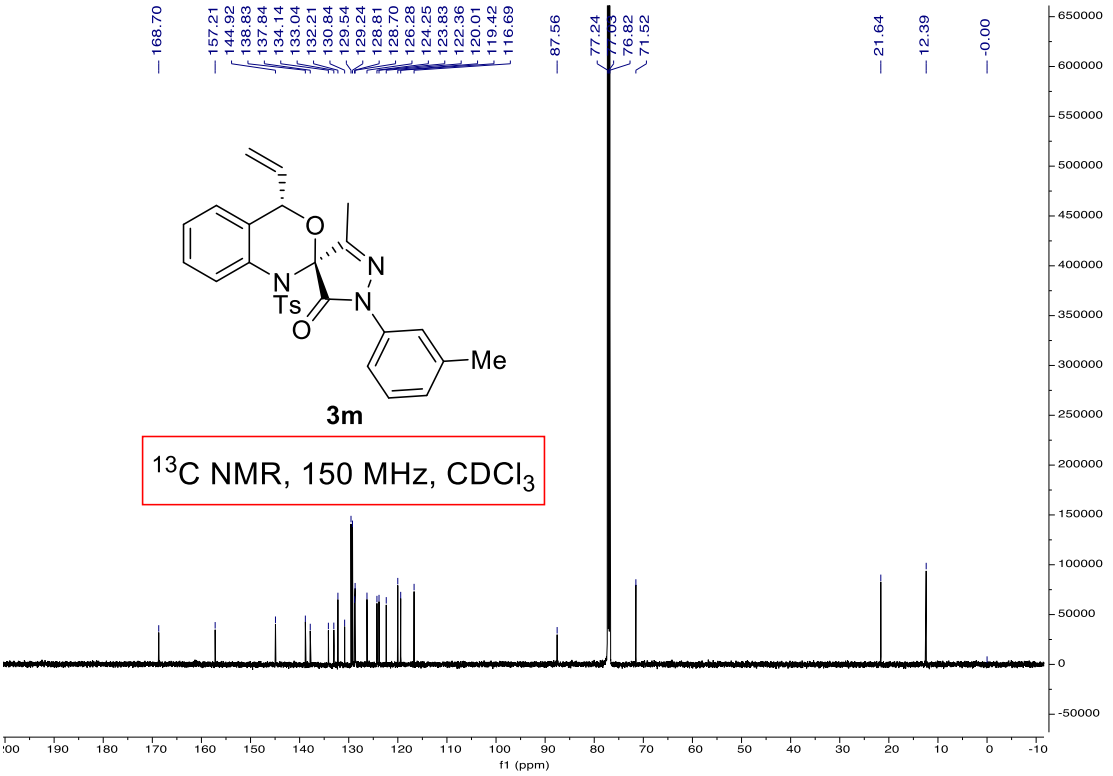


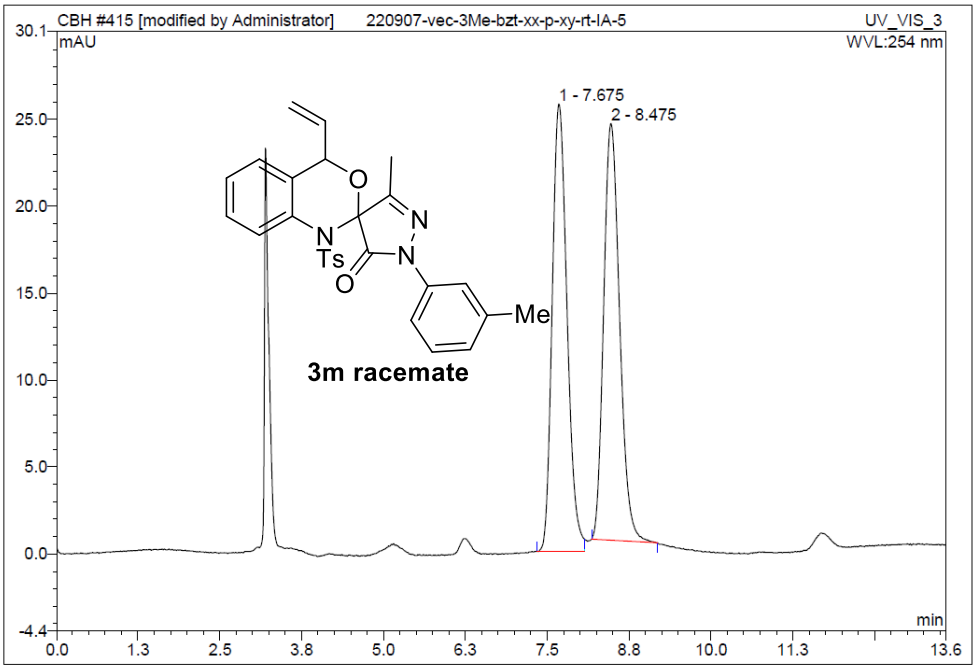
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.22	n.a.	1120.479	171.483	49.80	n.a.	BMB*
2	7.03	n.a.	905.427	172.887	50.20	n.a.	BMB*
Total:			2025.906	344.370	100.00	0.000	



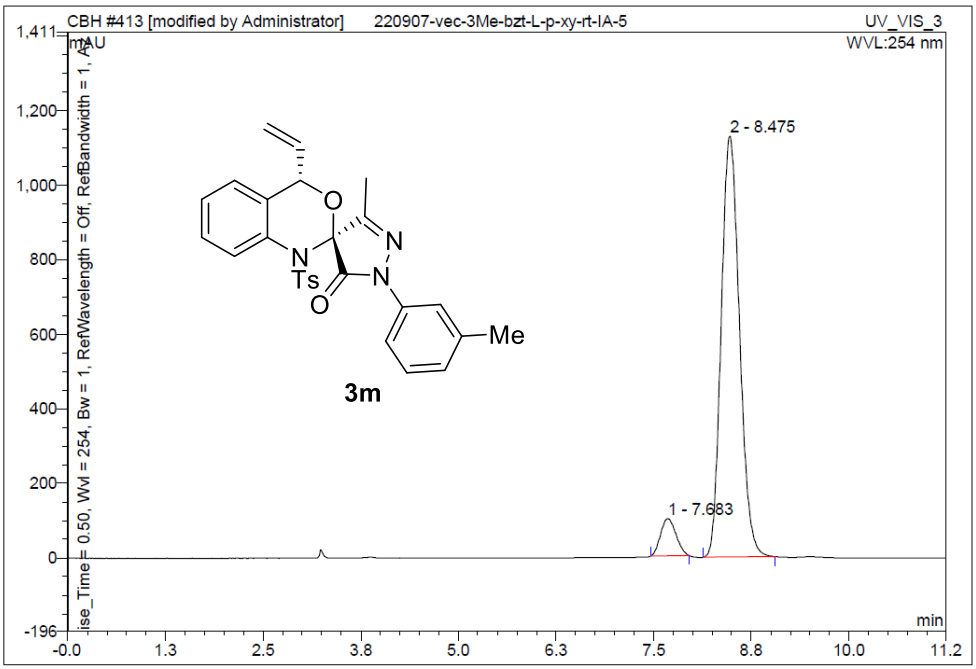
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.21	n.a.	26.371	3.257	1.93	n.a.	BMB*
2	6.95	n.a.	894.042	165.388	98.07	n.a.	BMB*
Total:			920.413	168.645	100.00	0.000	


3m
^{1}H NMR, 600 MHz, $CDCl_3$
f1 (ppm)

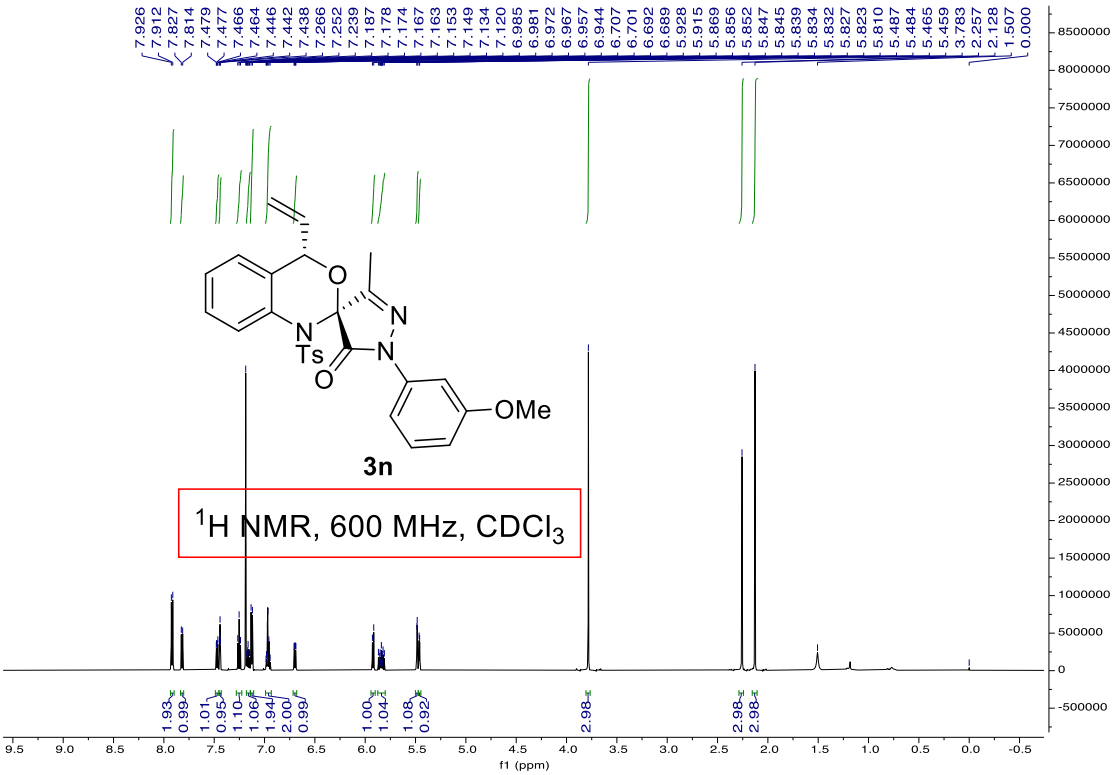

3m
^{13}C NMR, 150 MHz, $CDCl_3$
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.68	n.a.	25.718	6.803	49.94	n.a.	BM *
2	8.48	n.a.	23.962	6.820	50.06	n.a.	BMB*
Total:			49.680	13.624	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.68	n.a.	99.124	22.670	6.90	n.a.	BMB*
2	8.48	n.a.	1128.064	305.851	93.10	n.a.	BMB*
Total:			1227.188	328.521	100.00	0.000	


7.926
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7.479
7.477
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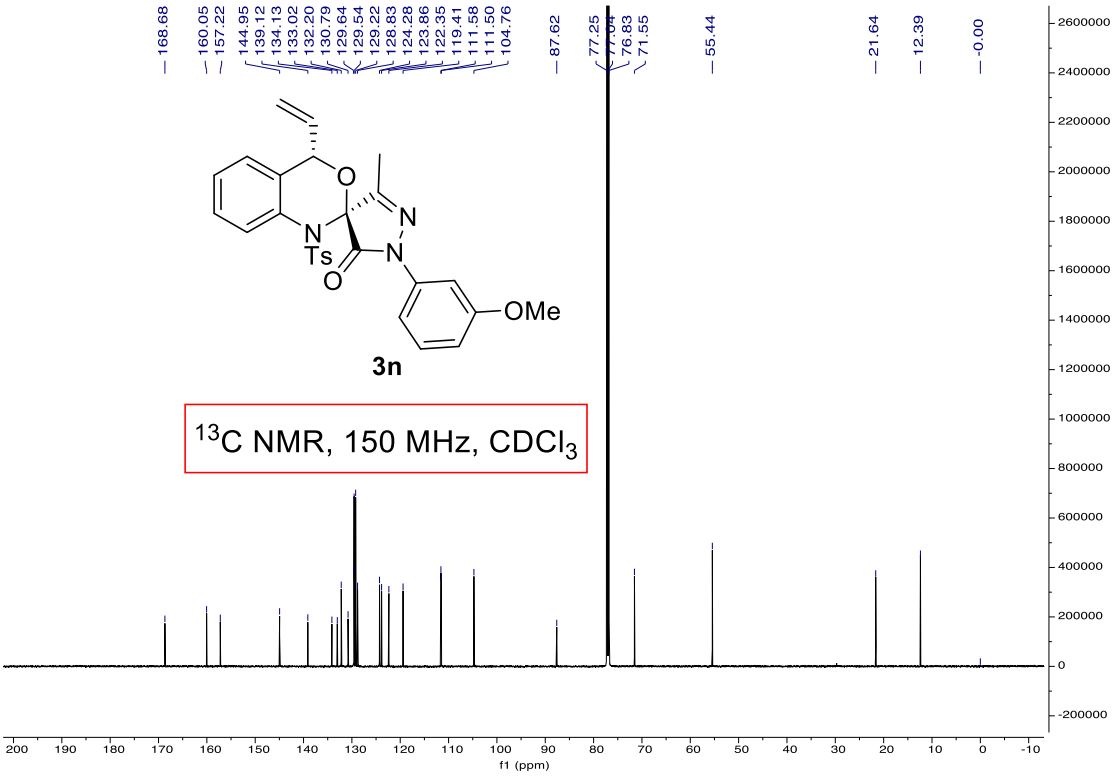
7.464
7.446
7.442
7.438
7.266
7.252
7.239
7.187
7.178
7.174
7.167
7.163
7.153
7.149
7.134
7.120
6.985
6.981
6.972
6.967
6.957
6.944
6.707
6.701
6.692
6.689
5.928
5.915
5.869
5.856
5.852
5.847
5.845
5.839
5.834
5.832
5.827
5.823
5.810
5.487
5.484
5.465
5.459
3.783
2.257
2.128
1.507
0.000
O
N
N
Ts
O
N
OMe
3n
1H NMR, 600 MHz, CDCl3
1.93
0.99
1.01
0.95
1.10
1.06
1.94
2.00
0.99
1.00
1.04
1.08
0.92
2.98
2.98
2.98
f1 (ppm)


168.68
160.05
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144.95
139.12
134.13
133.02
132.20
130.79
129.64
129.54
129.22
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123.86
122.35
119.41
111.58
111.50
104.76
87.62
77.25
77.04
76.83
71.55
55.44
21.64
12.39
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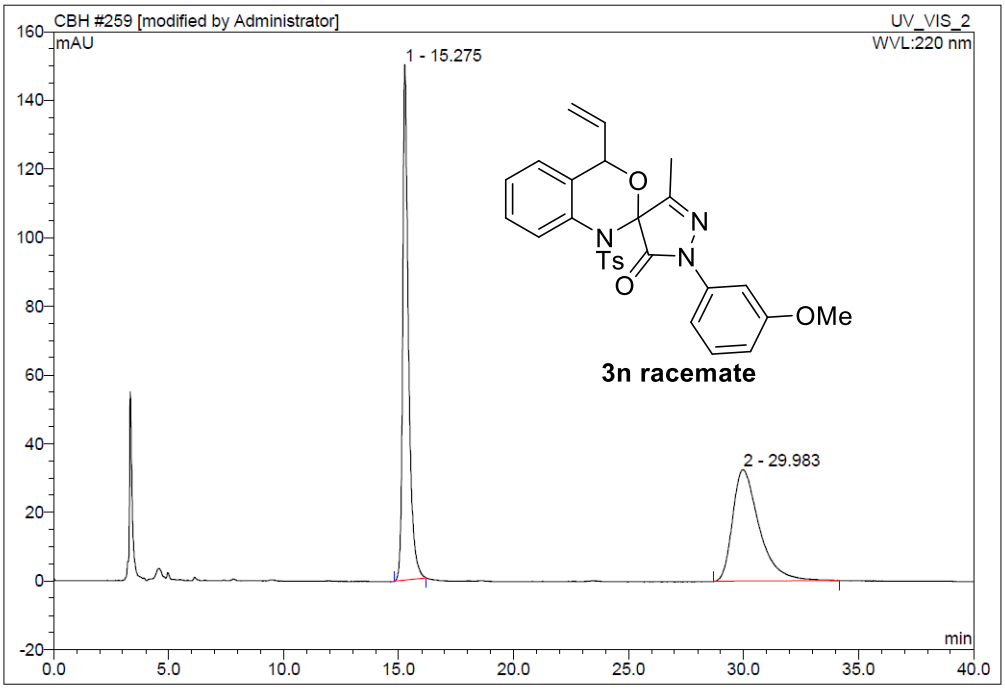
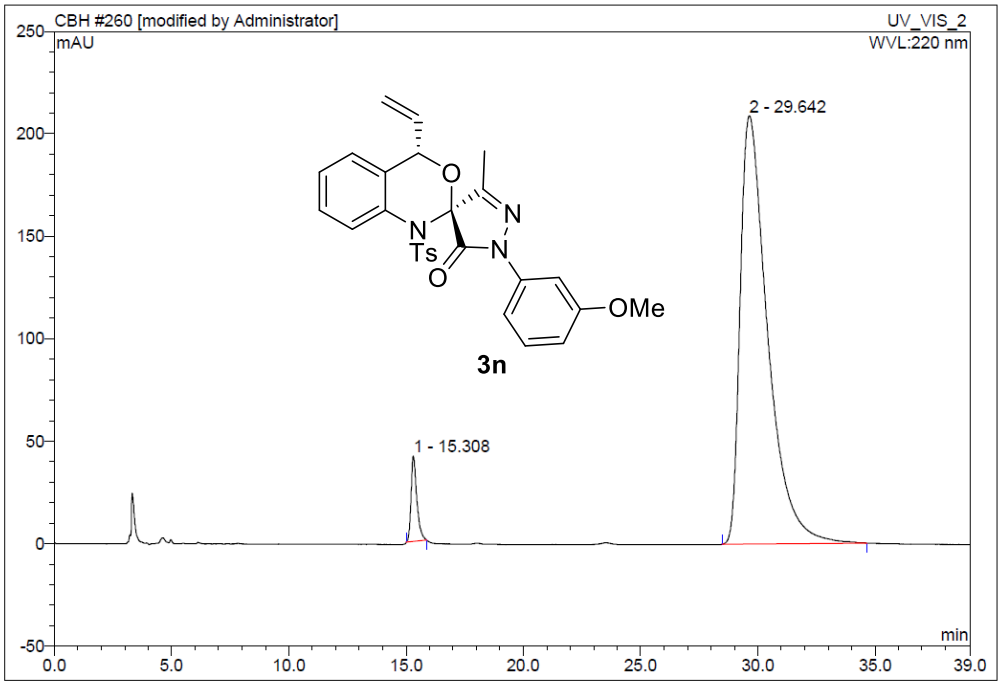
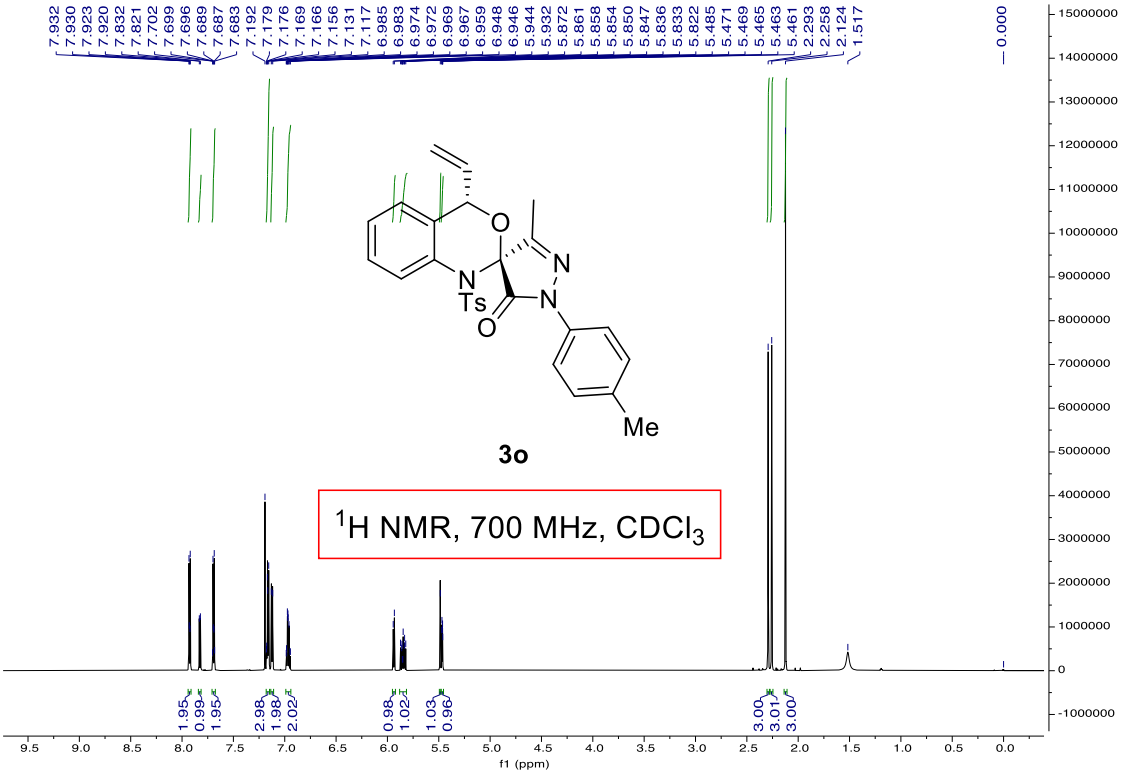
O
N
N
Ts
O
N
OMe
3n
13C NMR, 150 MHz, CDCl3
f1 (ppm)

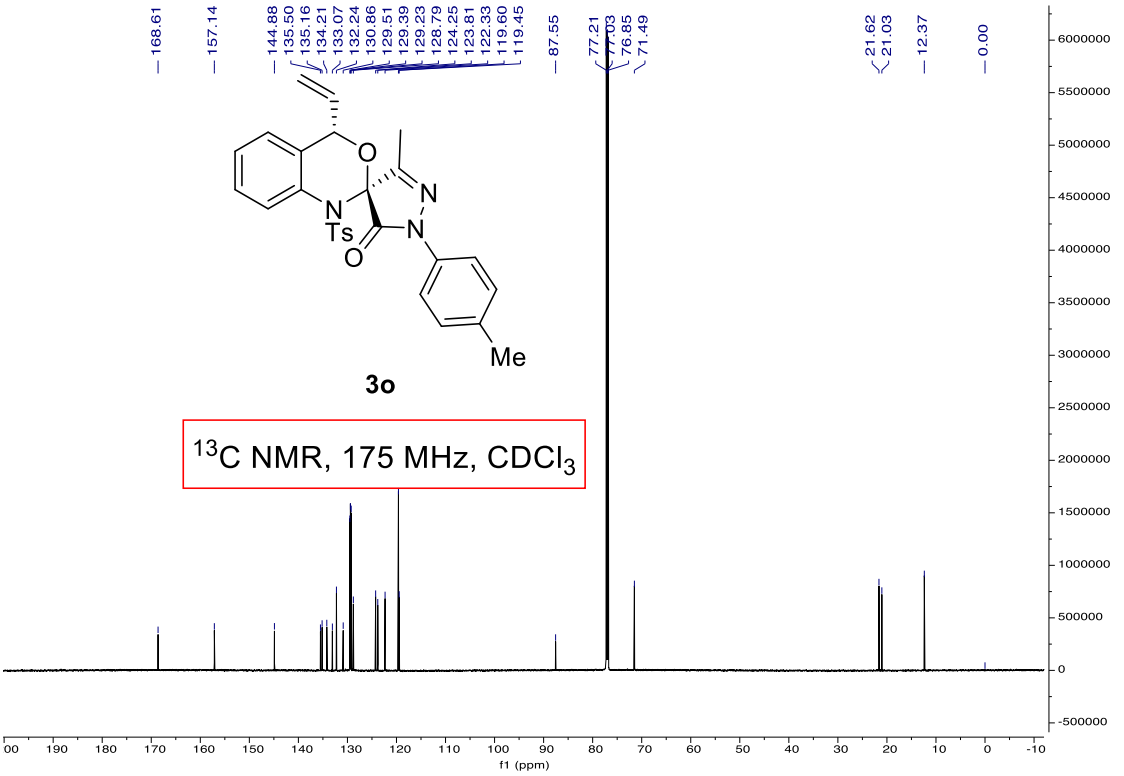


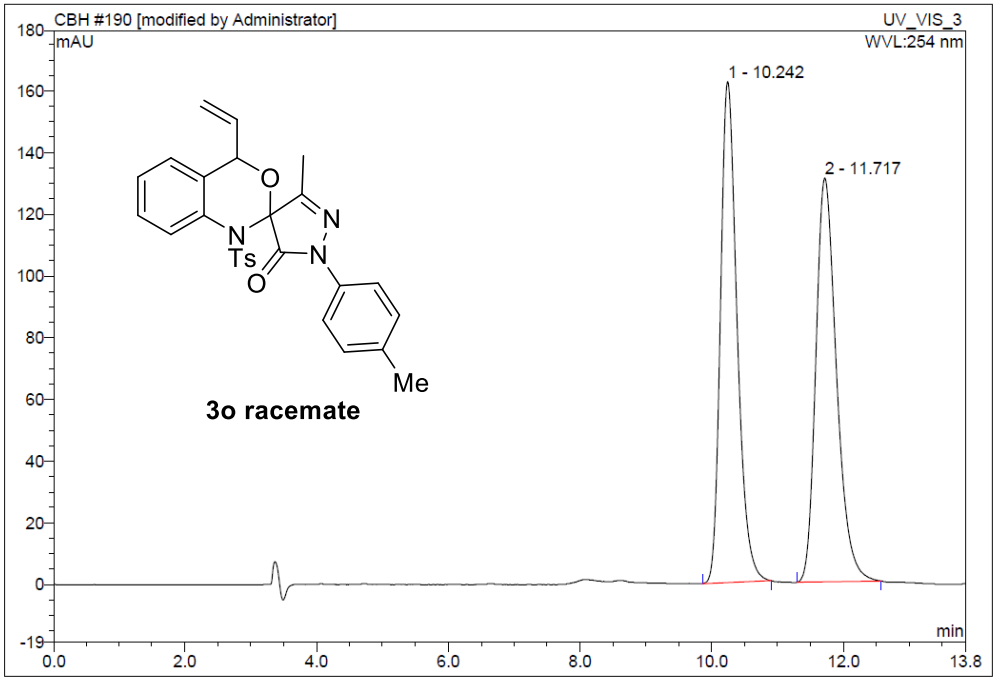
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.28	n.a.	150.204	43.597	49.96	n.a.	BMB*
2	29.98	n.a.	32.484	43.659	50.04	n.a.	BMB*
Total:			182.689	87.257	100.00	0.000	



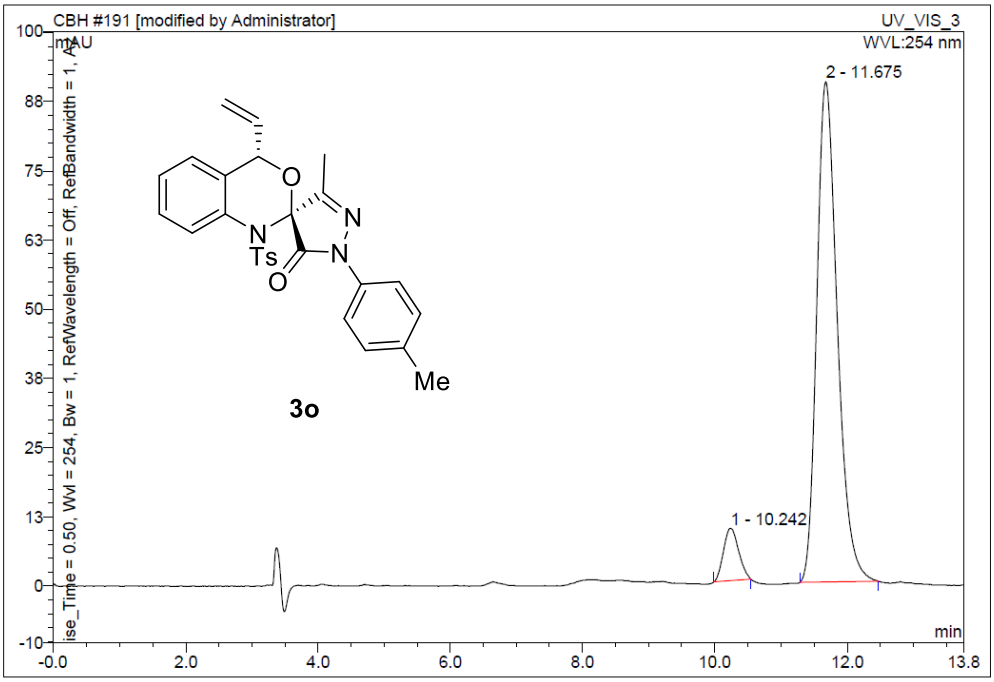
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.31	n.a.	41.754	11.915	4.03	n.a.	BMB*
2	29.64	n.a.	209.119	283.639	95.97	n.a.	BMB*
Total:			250.872	295.554	100.00	0.000	


7.932
7.930
7.923
7.920
7.832
7.821
7.702
7.699
7.696
7.689
7.687
7.683
7.192
7.179
7.176
7.169
7.166
7.156
7.131
7.117
6.985
6.983
6.974
6.972
6.969
6.967
6.959
6.948
6.946
5.944
5.932
5.872
5.861
5.858
5.854
5.850
5.847
5.836
5.833
5.822
5.485
5.471
5.469
5.465
5.463
5.461
2.293
2.258
2.124
1.517
0.000
O
N
N
Ts
O
N
Me
3o
^{1}H NMR, 700 MHz, $CDCl_3$
1.95
0.99
1.95
2.98
1.98
2.02
0.98
1.02
1.03
0.96
3.00
3.01
3.00
f1 (ppm)

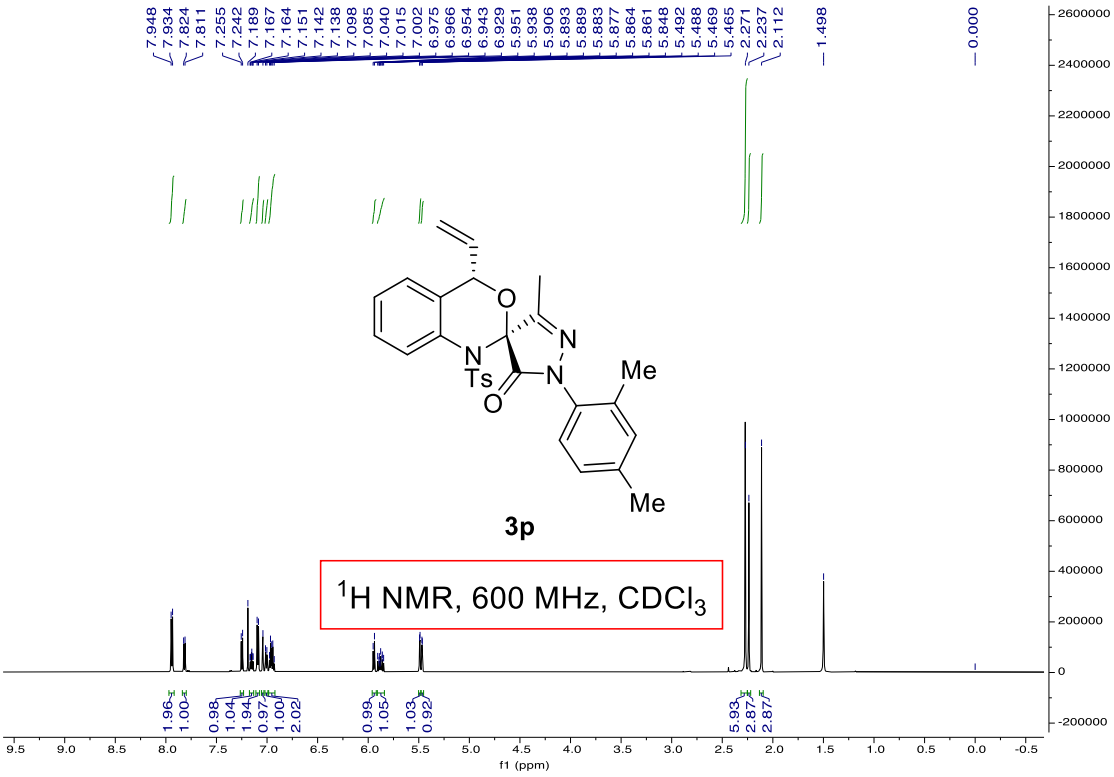

168.61
157.14
144.88
135.50
135.16
134.21
133.07
132.24
130.86
129.51
129.39
129.23
128.79
124.25
123.81
122.33
119.60
119.45
87.55
77.21
77.03
76.85
71.49
21.62
21.03
12.37
0.00
O
N
N
Ts
O
N
Me
3o
^{13}C NMR, 175 MHz, $CDCl_3$
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.24	n.a.	162.305	47.132	49.92	n.a.	BMB*
2	11.72	n.a.	130.784	47.277	50.08	n.a.	BMB*
Total:			293.089	94.410	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.24	n.a.	9.456	2.489	7.11	n.a.	BMB*
2	11.68	n.a.	90.454	32.540	92.89	n.a.	BMB*
Total:			99.910	35.029	100.00	0.000	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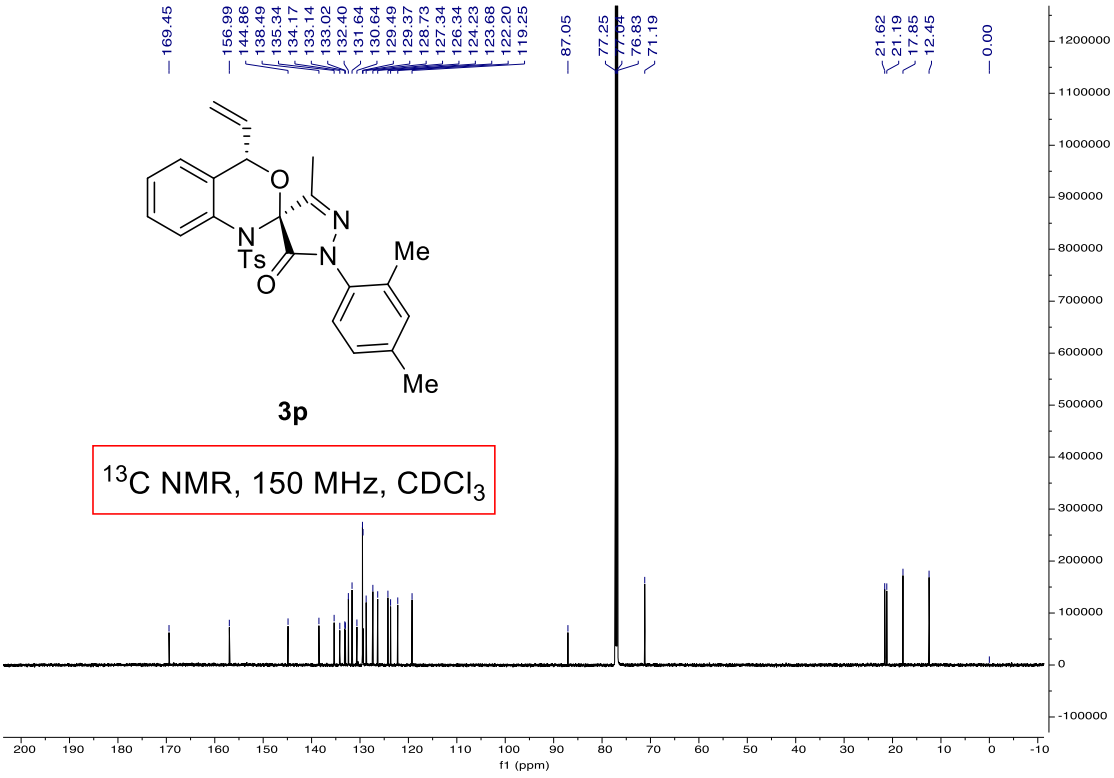
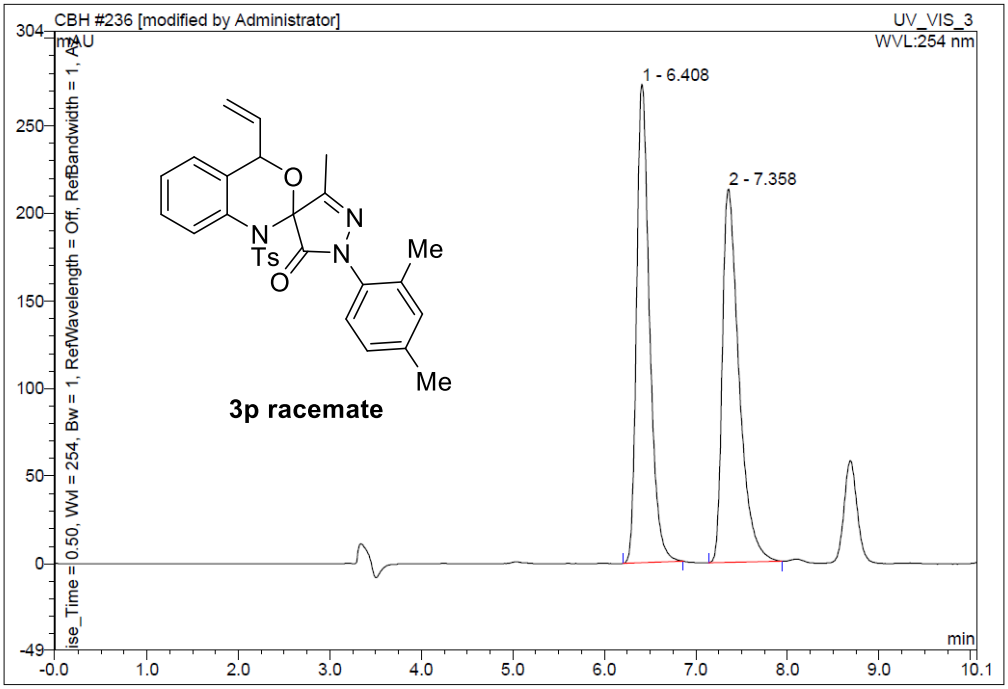
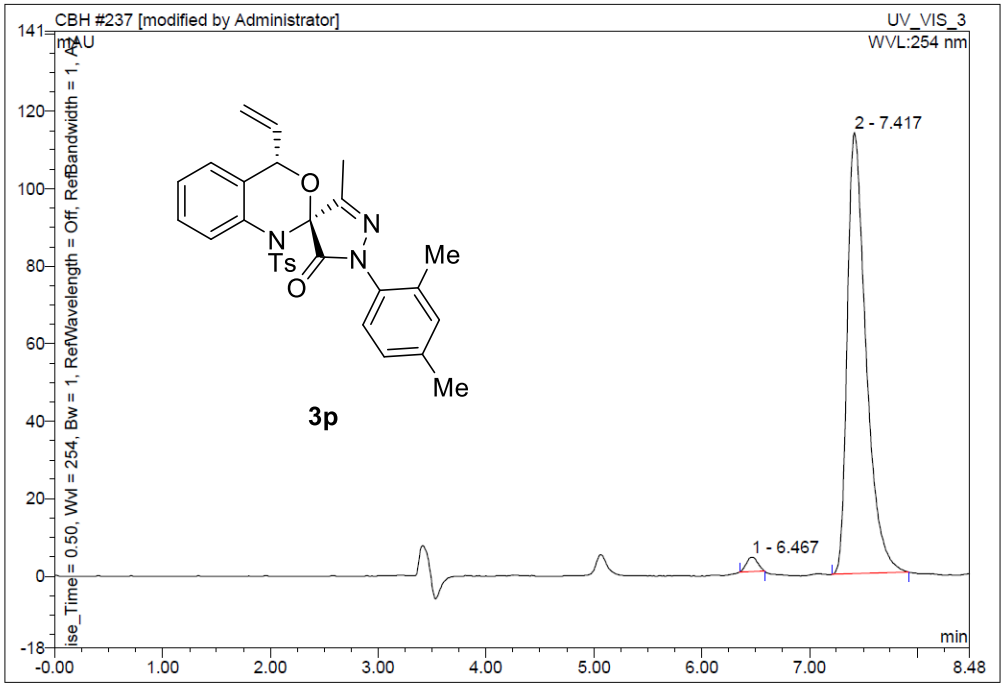
7.934
7.824
7.811
7.255
7.242
7.189
7.167
7.164
7.151
7.142
7.138
7.098
7.085
7.040
7.015
7.002
6.975
6.966
6.954
6.943
6.929
5.951
5.938
5.906
5.893
5.889
5.883
5.877
5.864
5.861
5.848
5.492
5.488
5.469
5.465
2.271
2.237
2.112
1.498
0.000
O
N
N
Ts
O
N
Me
Me
3p
1H NMR, 600 MHz, CDCl3
1.96
1.00
0.98
1.04
1.94
0.97
1.00
2.02
0.99
1.05
1.03
0.92
5.93
2.87
2.87
f1 (ppm)

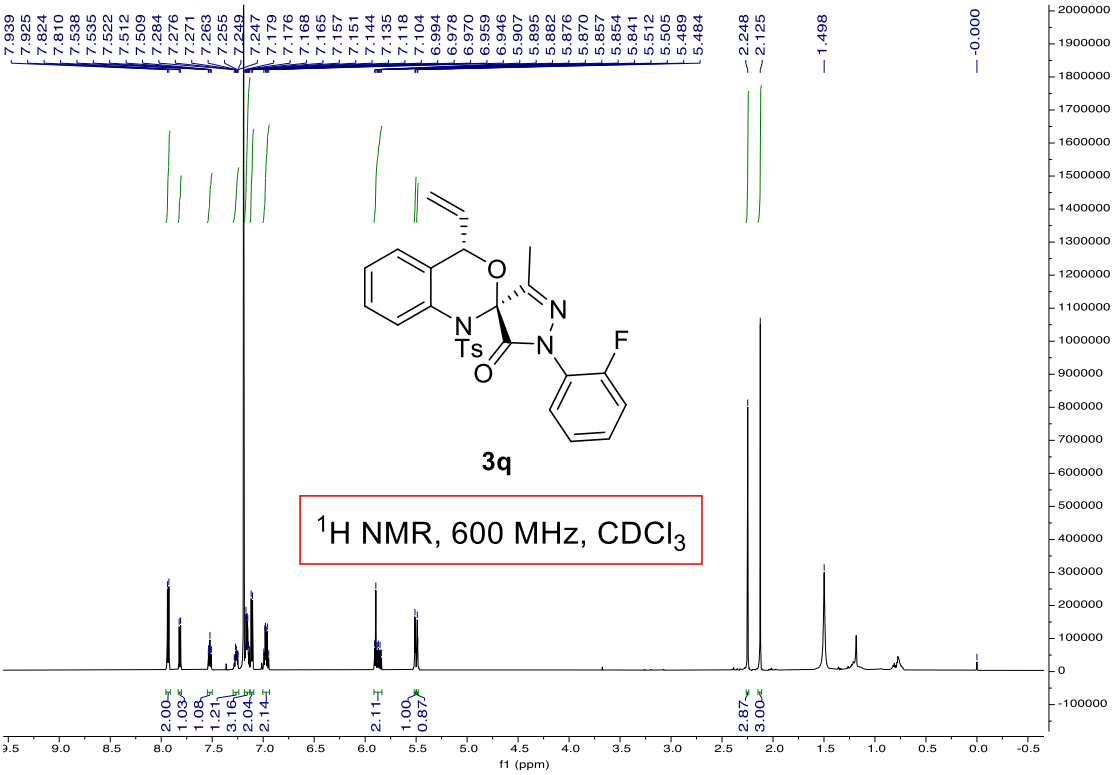

169.45
156.99
144.86
138.49
135.34
134.17
133.14
133.02
132.40
131.64
130.64
129.49
129.37
128.73
127.34
126.34
124.23
123.68
122.20
119.25
87.05
77.25
77.04
76.83
71.19
21.62
21.19
17.85
12.45
0.00
O
N
N
Ts
O
N
Me
Me
3p
13C NMR, 150 MHz, CDCl3
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.41	n.a.	273.028	44.852	49.92	n.a.	BMB*
2	7.36	n.a.	213.085	45.002	50.08	n.a.	BMB*
Total:			486.113	89.854	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.47	n.a.	3.752	0.460	1.97	n.a.	BMB*
2	7.42	n.a.	113.851	22.903	98.03	n.a.	BMB*
Total:			117.603	23.363	100.00	0.000	


7.939
7.925
7.824
7.810
7.538
7.535
7.522
7.512
7.509
7.284
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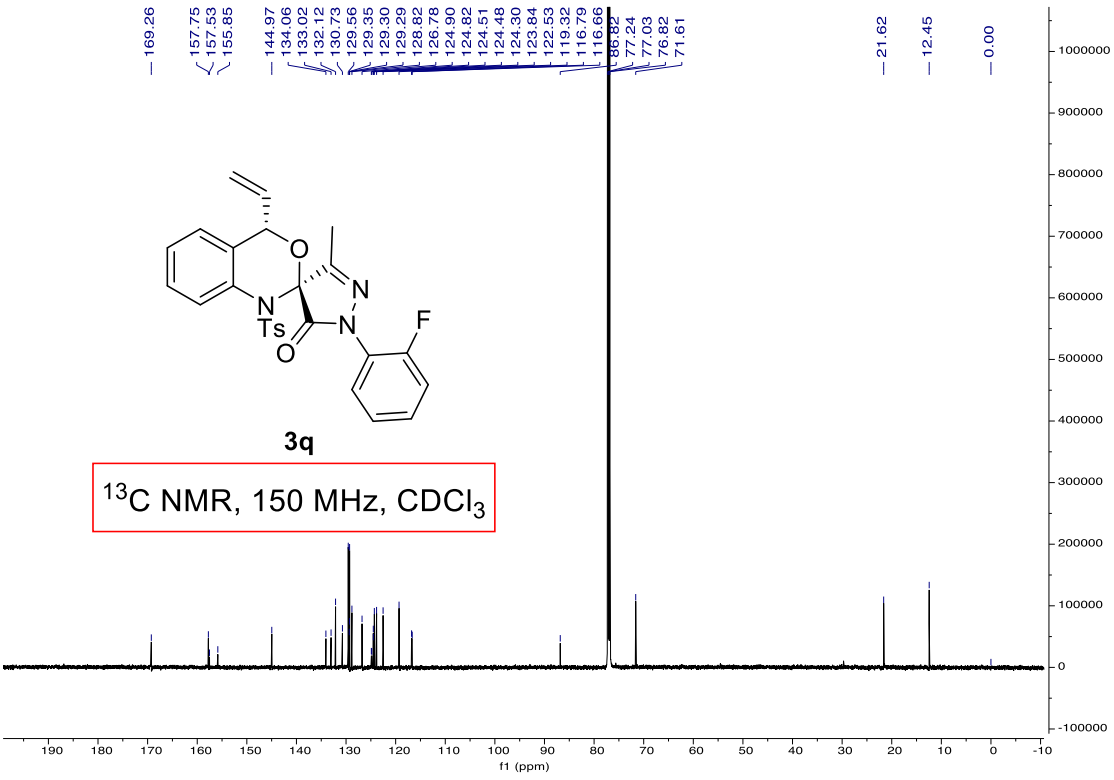
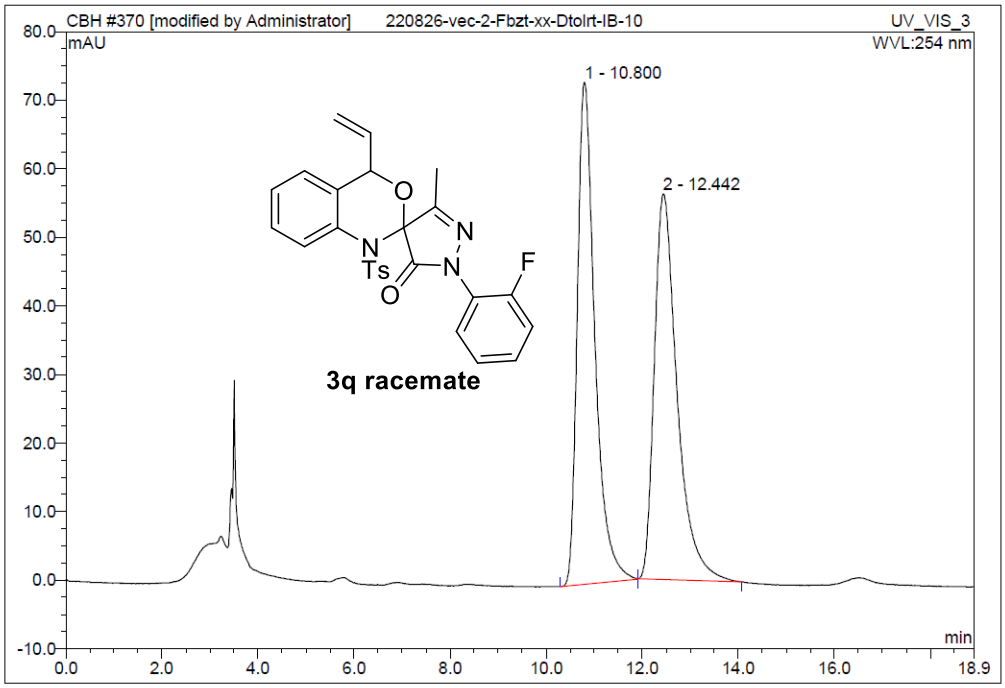
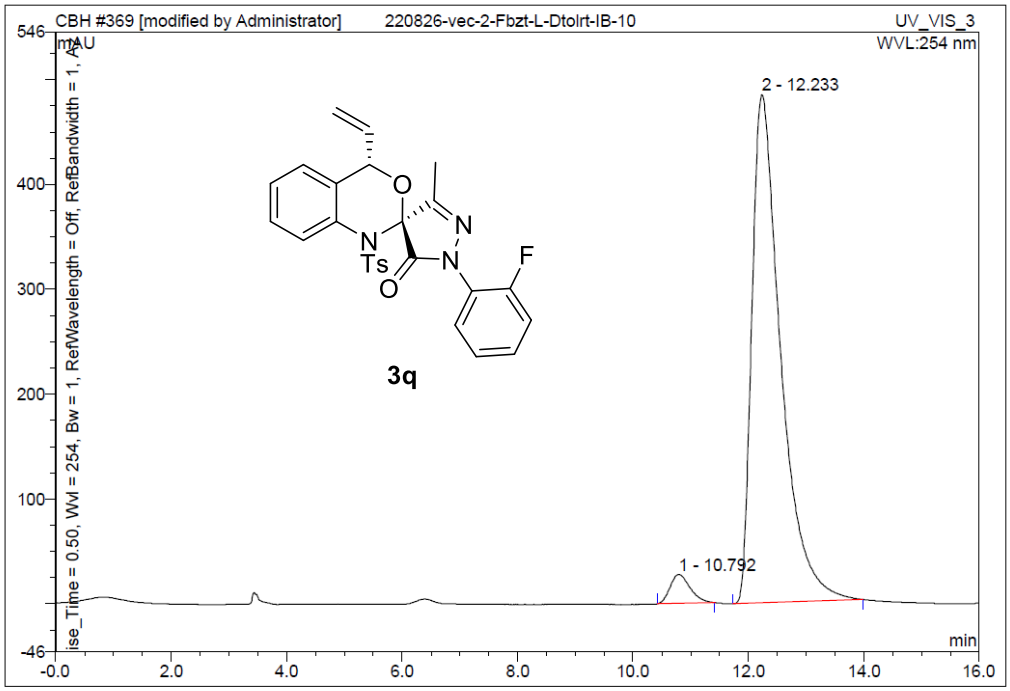
7.271
7.263
7.255
7.249
7.247
7.179
7.176
7.168
7.165
7.157
7.151
7.144
7.135
7.118
7.104
6.994
6.978
6.970
6.959
6.946
5.907
5.895
5.882
5.876
5.870
5.857
5.854
5.841
5.512
5.505
5.489
5.484
2.248
2.125
1.498
-0.000
O
N
N
Ts
O
N
F
3q
1H NMR, 600 MHz, CDCl3
2.00
1.03
1.08
1.21
3.16
2.04
2.14
2.11
1.00
0.87
2.87
3.00
f1 (ppm)

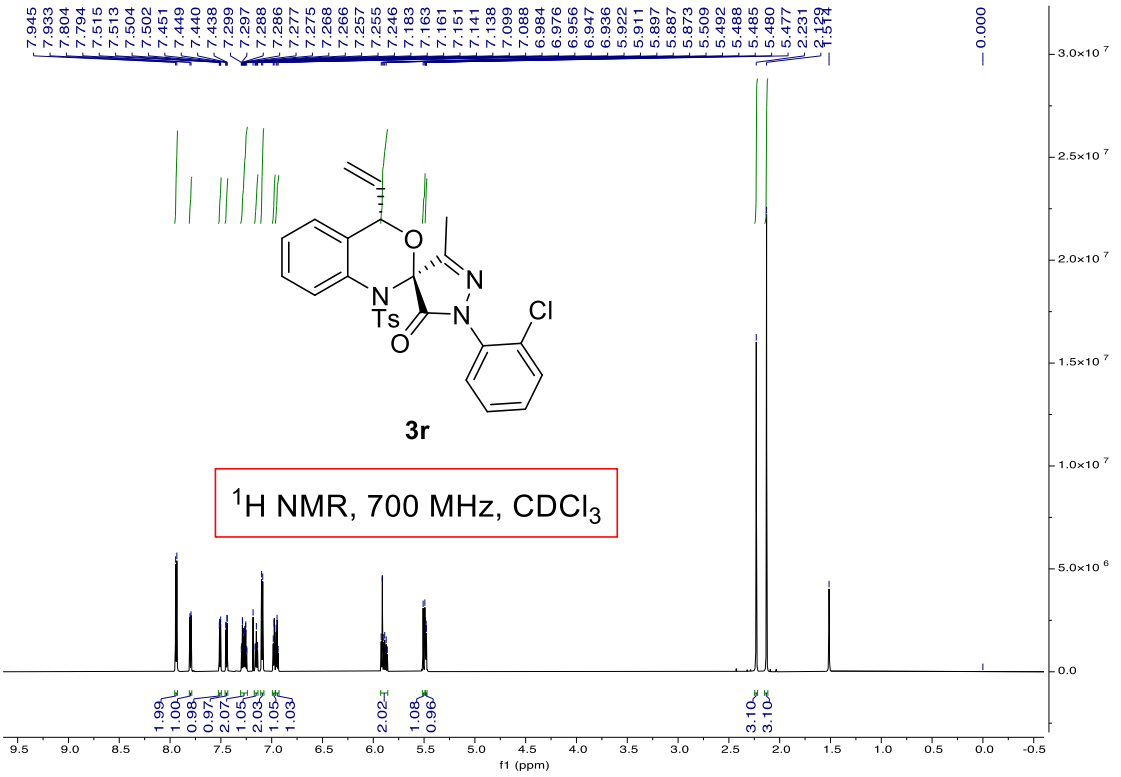

169.26
157.75
157.53
155.85
144.97
134.06
133.02
132.12
130.73
129.56
129.35
129.30
129.29
128.82
126.78
124.90
124.82
124.51
124.48
124.30
123.84
122.53
119.32
116.79
116.66
86.82
77.24
77.03
76.82
71.61
21.62
12.45
0.00
O
N
N
Ts
O
N
F
3q
13C NMR, 150 MHz, CDCl3
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.80	n.a.	73.269	30.954	50.04	n.a.	BMB*
2	12.44	n.a.	56.306	30.906	49.96	n.a.	BMB*
Total:			129.574	61.860	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.79	n.a.	27.564	11.086	3.81	n.a.	BMB*
2	12.23	n.a.	484.922	279.819	96.19	n.a.	BMB*
Total:			512.486	290.905	100.00	0.000	


7.945
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7.804
7.794
7.515
7.513
7.504
7.502
7.451
7.449
7.440
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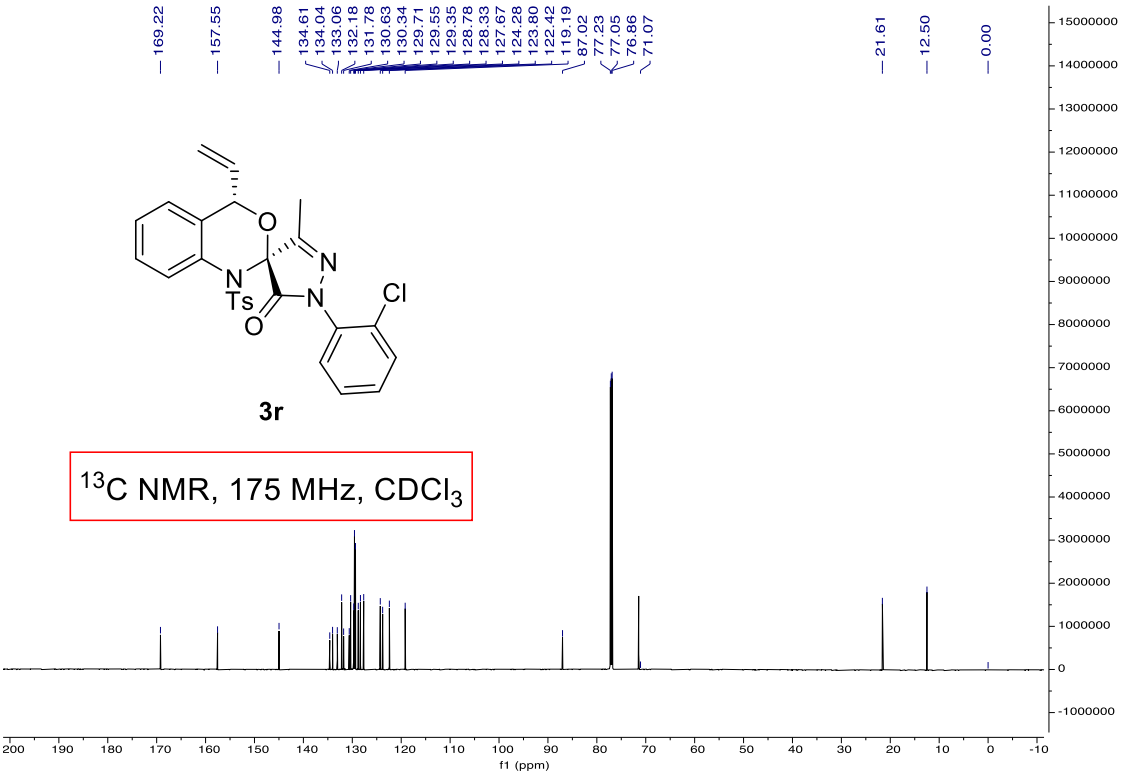
7.297
7.288
7.286
7.277
7.275
7.268
7.266
7.257
7.255
7.246
7.183
7.163
7.161
7.151
7.141
7.138
7.099
7.088
6.984
6.976
6.956
6.947
6.936
5.922
5.911
5.897
5.887
5.873
5.509
5.492
5.488
5.485
5.480
5.477
2.231
1.514
0.000
O
N
Ts
O
N
N
Cl
3r
1H NMR, 700 MHz, CDCl3
1.99
1.00
0.98
0.97
2.07
1.05
2.03
1.05
1.03
2.02
1.08
0.96
3.10
3.10
f1 (ppm)


169.22
157.55
144.98
134.61
134.04
133.06
132.18
131.78
130.63
130.34
129.71
129.55
129.35
128.78
128.33
127.67
124.28
123.80
122.42
119.19
87.02
77.23
77.05
76.86
71.07
21.61
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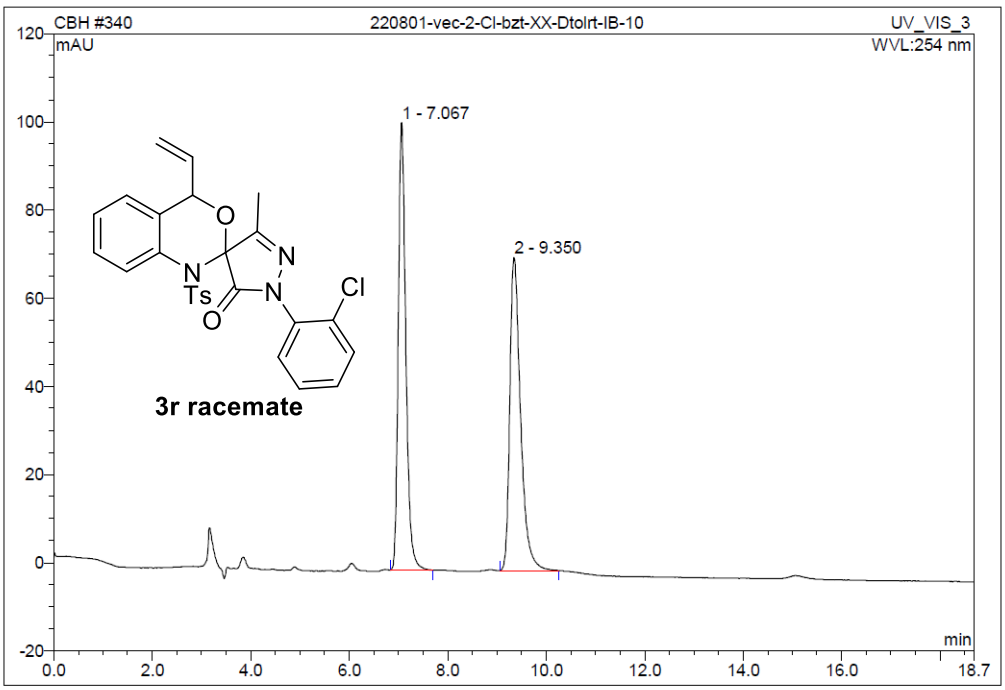
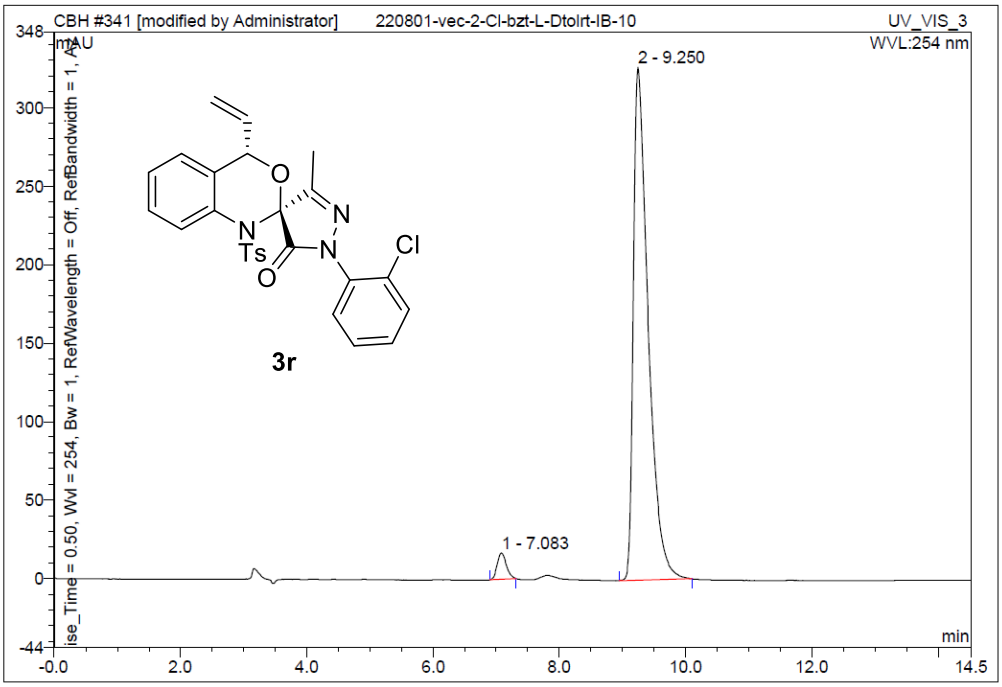
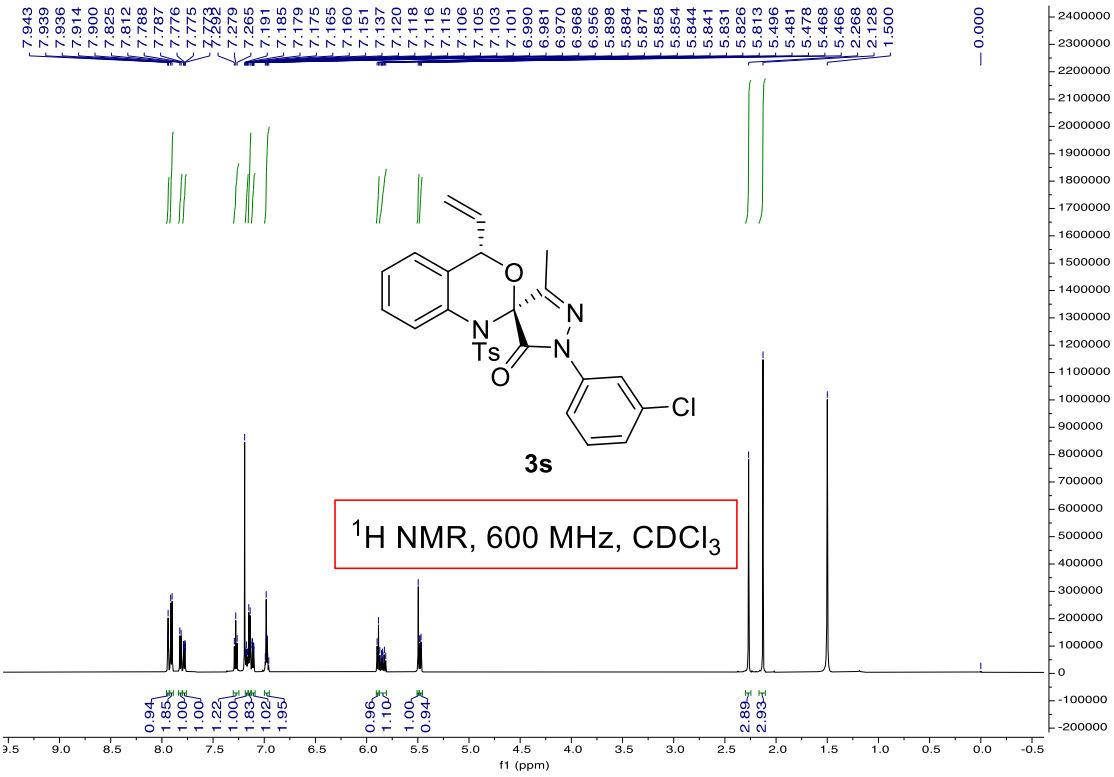
Ts
O
N
N
Cl
3r
13C NMR, 175 MHz, CDCl3
f1 (ppm)

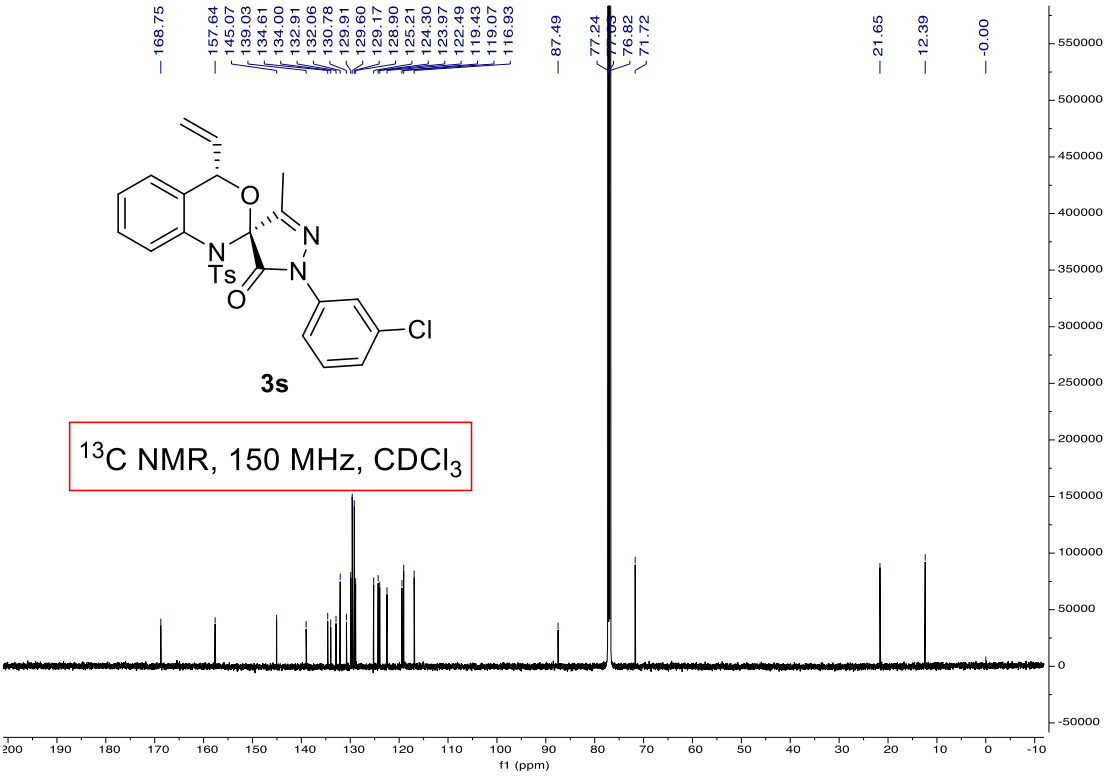


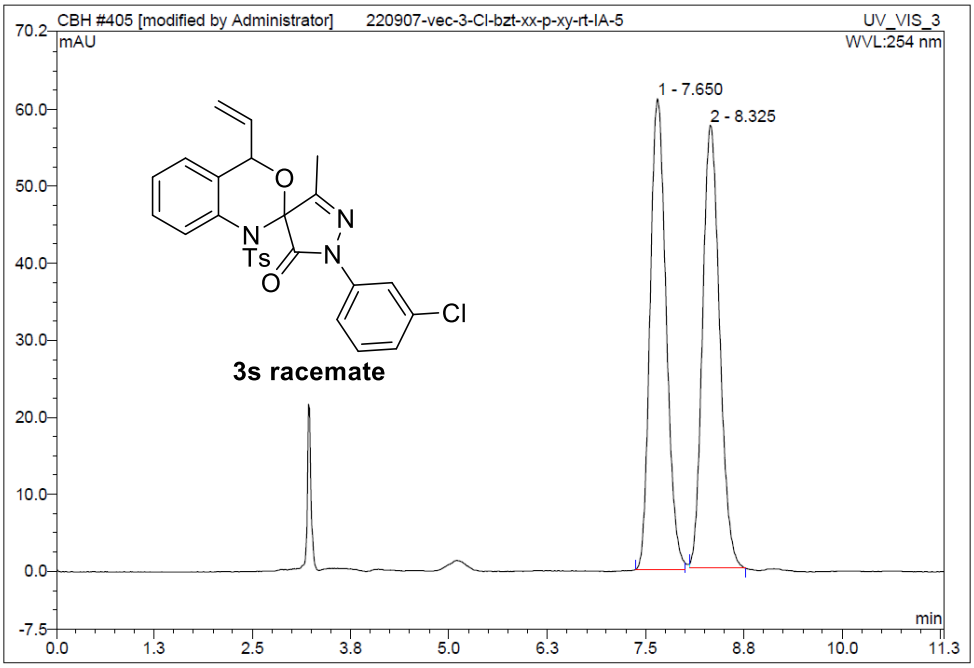
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.07	n.a.	101.523	17.908	49.90	n.a.	BMB
2	9.35	n.a.	71.022	17.980	50.10	n.a.	BMB
Total:			172.544	35.888	100.00	0.000	



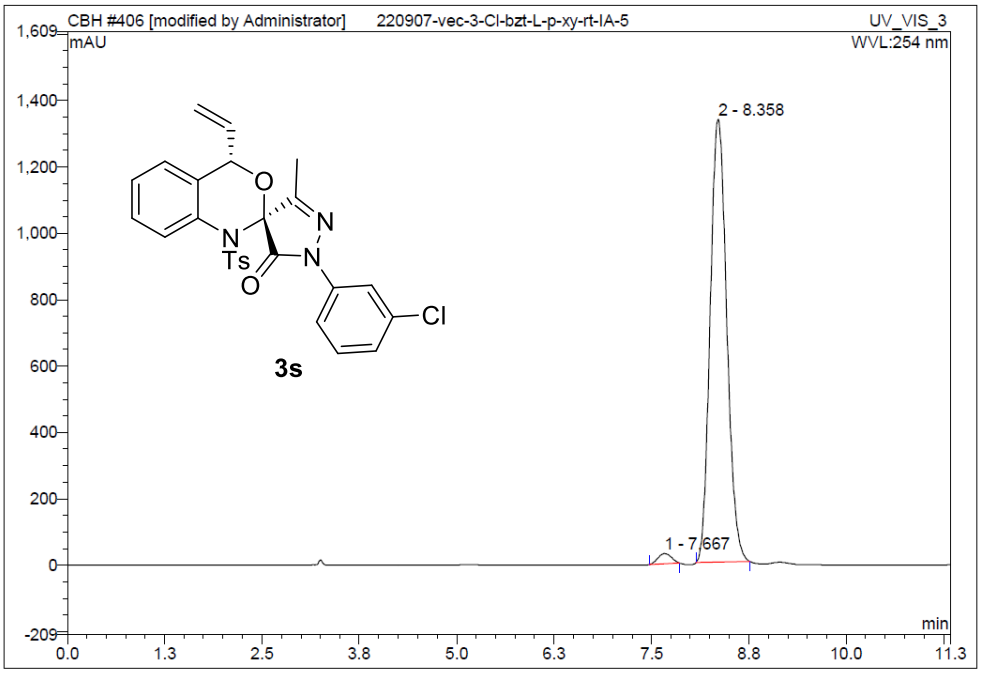
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.08	n.a.	16.741	2.814	3.08	n.a.	BMB*
2	9.25	n.a.	326.786	88.587	96.92	n.a.	BMB*
Total:			343.527	91.401	100.00	0.000	


3s
^{1}H NMR, 600 MHz, CDCl$_3$
f1 (ppm)

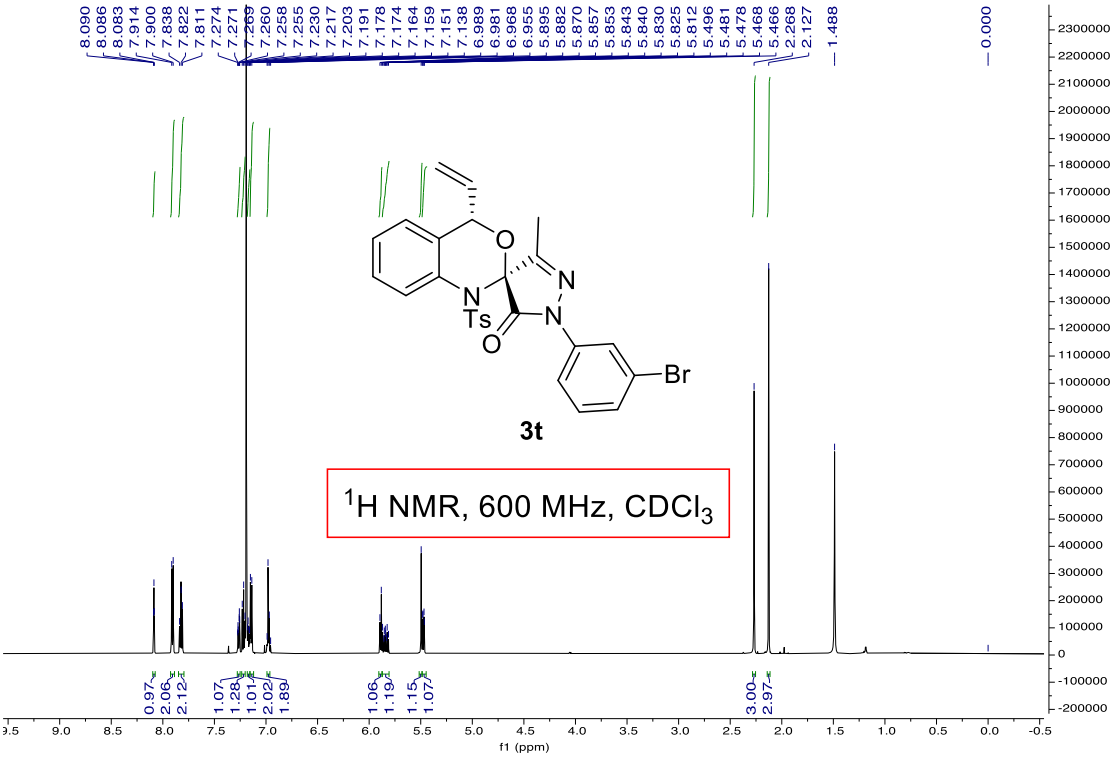

3s
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.65	n.a.	61.138	14.520	50.05	n.a.	BM *
2	8.33	n.a.	57.493	14.491	49.95	n.a.	MB*
Total:			118.632	29.010	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.67	n.a.	31.090	6.184	1.85	n.a.	BMB*
2	8.36	n.a.	1334.098	328.990	98.15	n.a.	BMB*
Total:			1365.188	335.174	100.00	0.000	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8.086
8.083
7.914
7.900
7.838
7.822
7.811
7.274
7.271
7.269
7.260
7.258
7.255
7.230
7.217
7.203
7.191
7.178
7.174
7.164
7.159
7.151
7.138
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6.981
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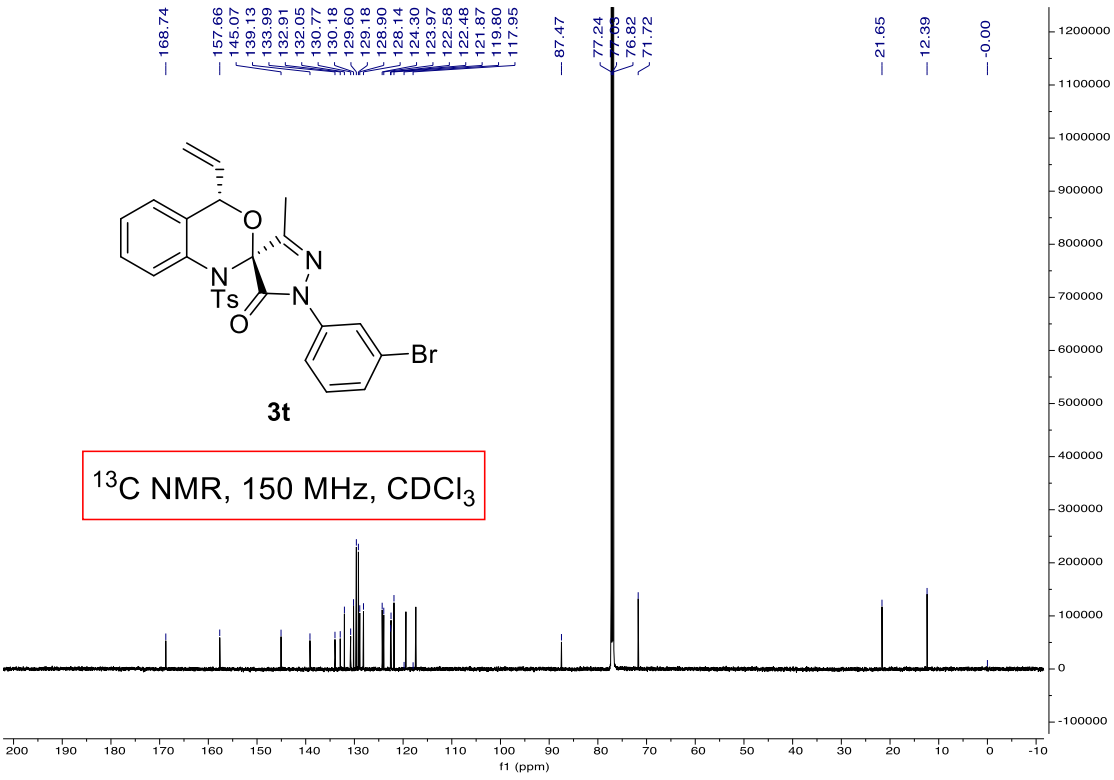
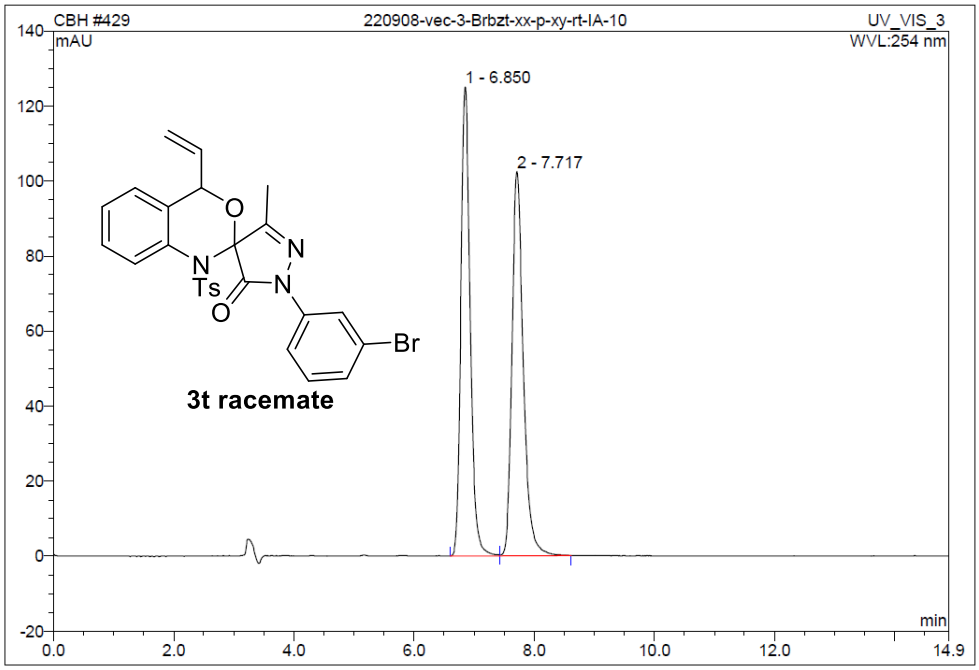
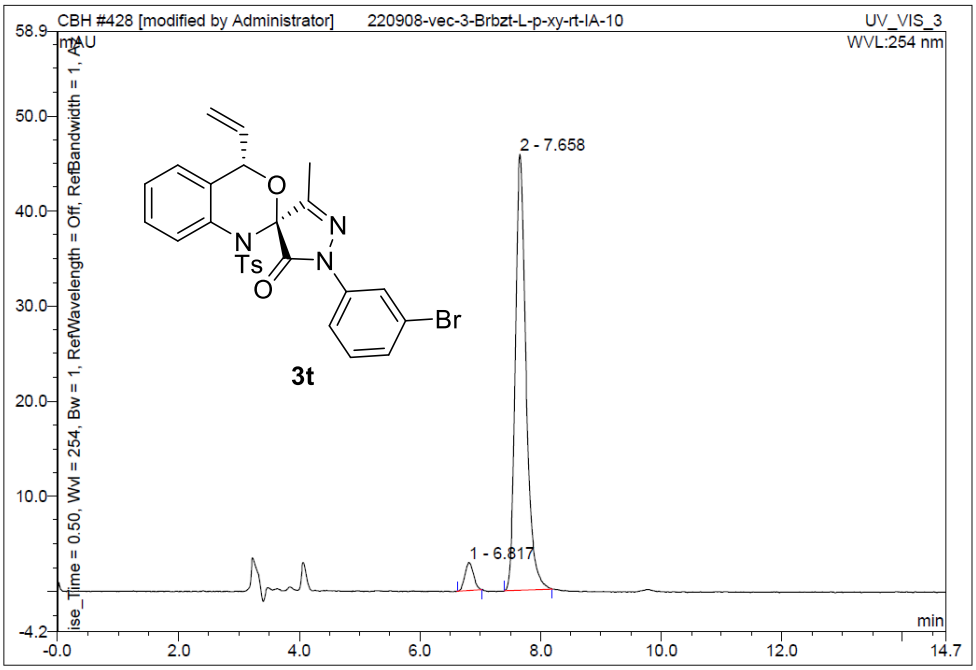
6.955
5.895
5.882
5.870
5.857
5.853
5.843
5.840
5.830
5.825
5.812
5.496
5.481
5.478
5.468
5.466
2.268
2.127
1.488
0.000
0.97
2.06
2.12
1.07
1.28
1.01
2.02
1.89
1.06
1.19
1.15
1.07
3.00
2.97
f1 (ppm)
Ts
Br
3t
^{1}H NMR, 600 MHz, CDCl$_3$

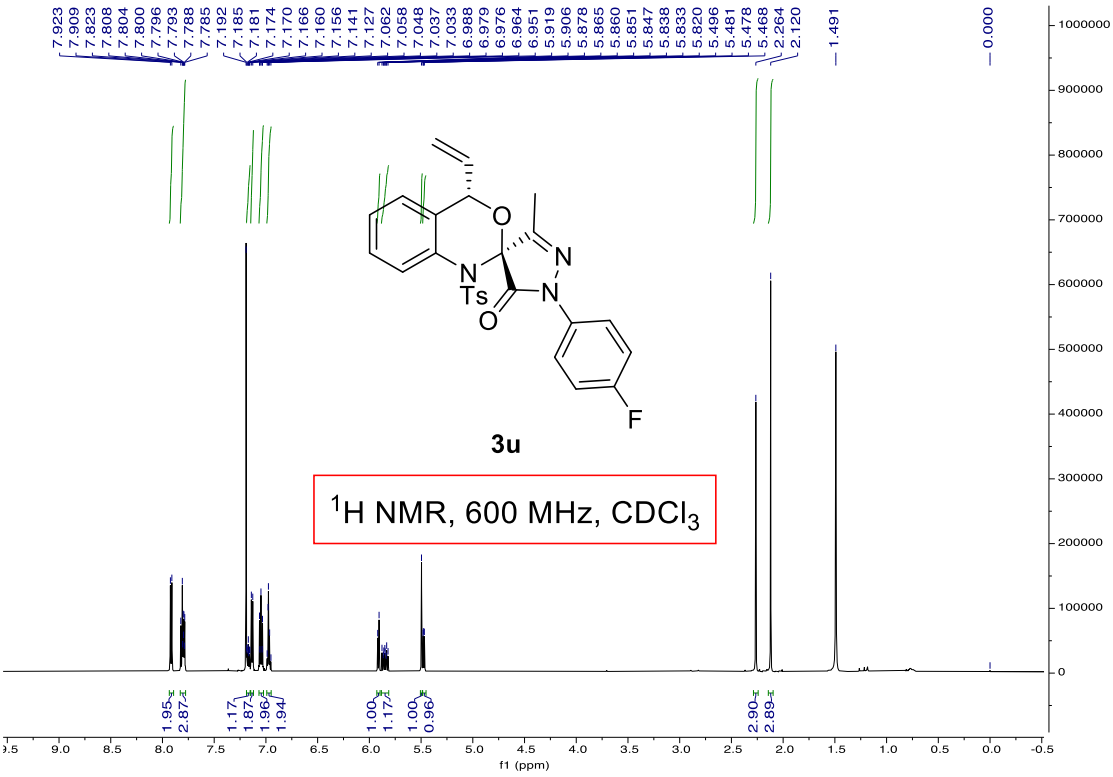

168.74
157.66
145.07
139.13
133.99
132.91
132.05
130.77
130.18
129.60
129.18
128.90
128.14
124.30
123.97
122.58
122.48
121.87
119.80
117.95
87.47
77.24
77.03
76.82
71.72
21.65
12.39
-0.00
f1 (ppm)
Ts
Br
3t
^{13}C NMR, 150 MHz, CDCl$_3$



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.85	n.a.	124.960	22.407	50.02	n.a.	BM
2	7.72	n.a.	102.356	22.388	49.98	n.a.	MB
Total:			227.316	44.795	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.82	n.a.	2.961	0.491	4.96	n.a.	BMB*
2	7.66	n.a.	45.853	9.404	95.04	n.a.	BMB*
Total:			48.814	9.894	100.00	0.000	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7.823
7.808
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7.800
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7.793
7.788
7.785
7.192
7.185
7.181
7.174
7.170
7.166
7.160
7.156
7.141
7.127
7.062
7.058
7.048
7.037
7.033
6.988
6.979
6.976
6.964
6.951
5.919
5.906
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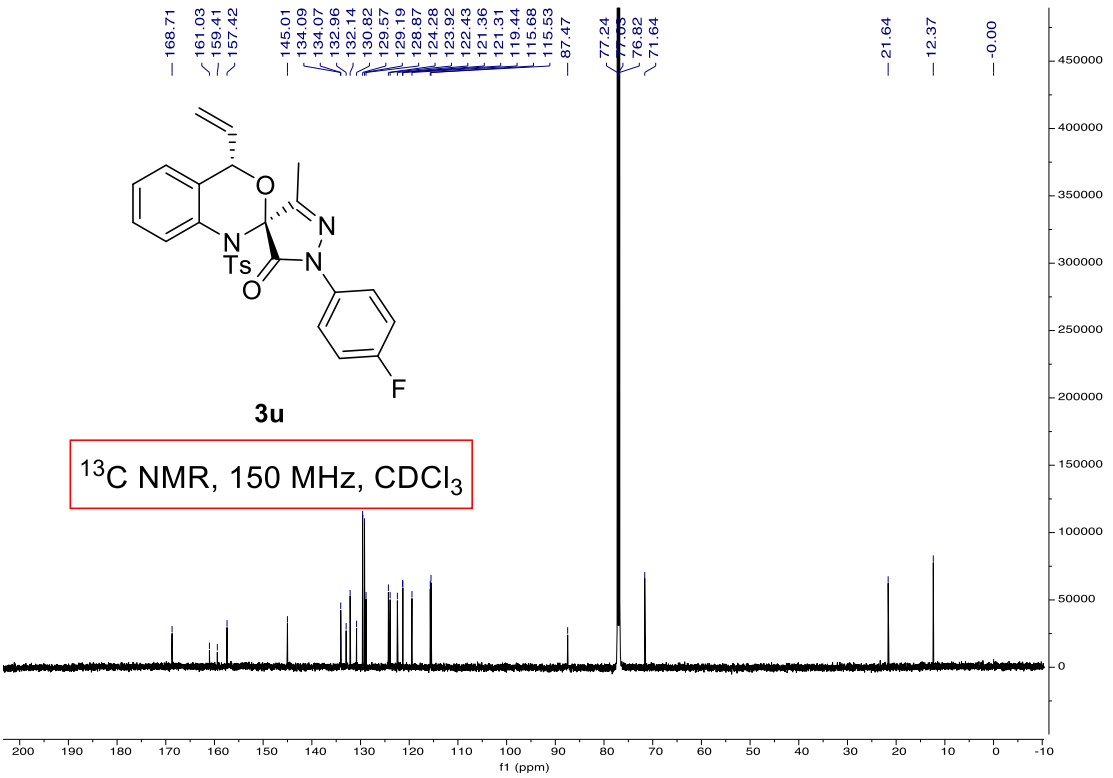
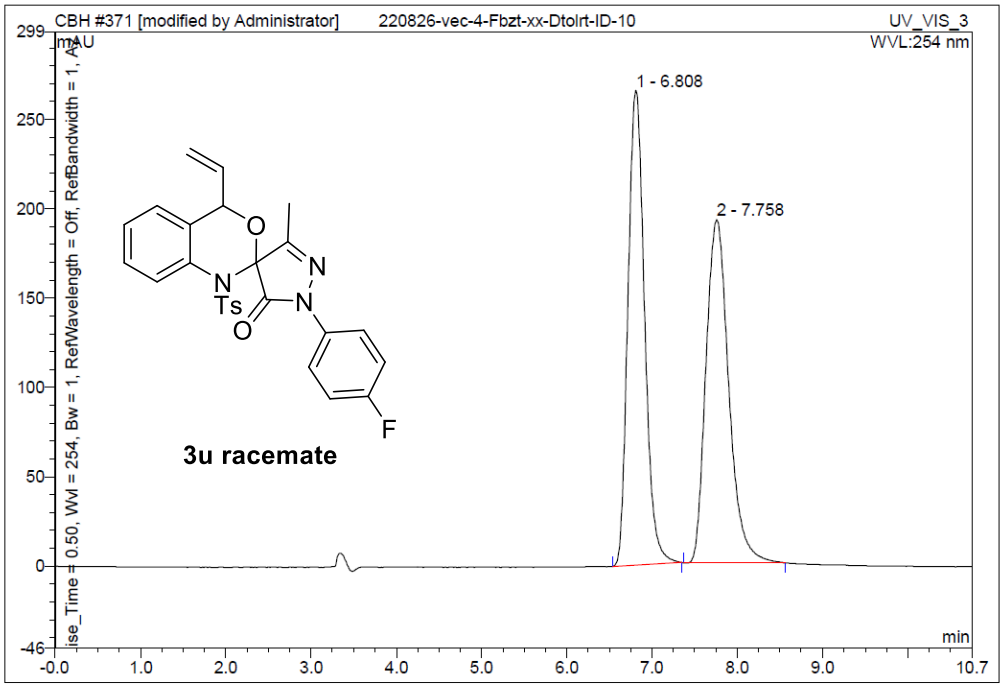
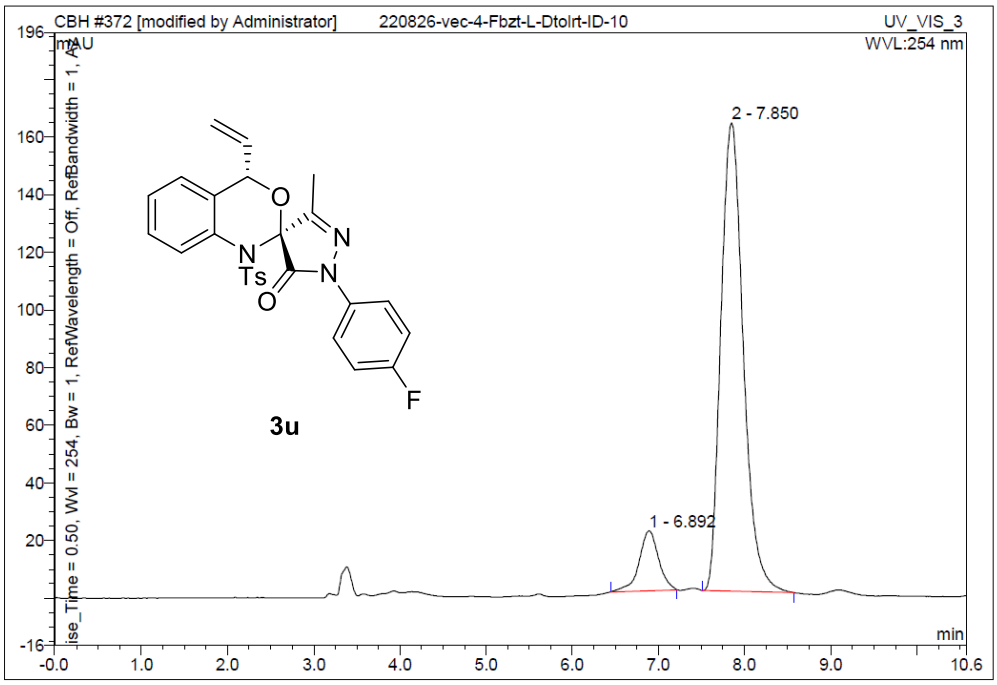
5.851
5.847
5.838
5.833
5.820
5.496
5.481
5.478
5.468
2.264
2.120
1.491
0.000
O
N
Ts
O
N
N
F
3u
^{1}H NMR, 600 MHz, CDCl$_3$
1.95
2.87
1.17
1.87
1.96
1.94
1.00
1.17
1.00
0.96
2.90
2.89
f1 (ppm)

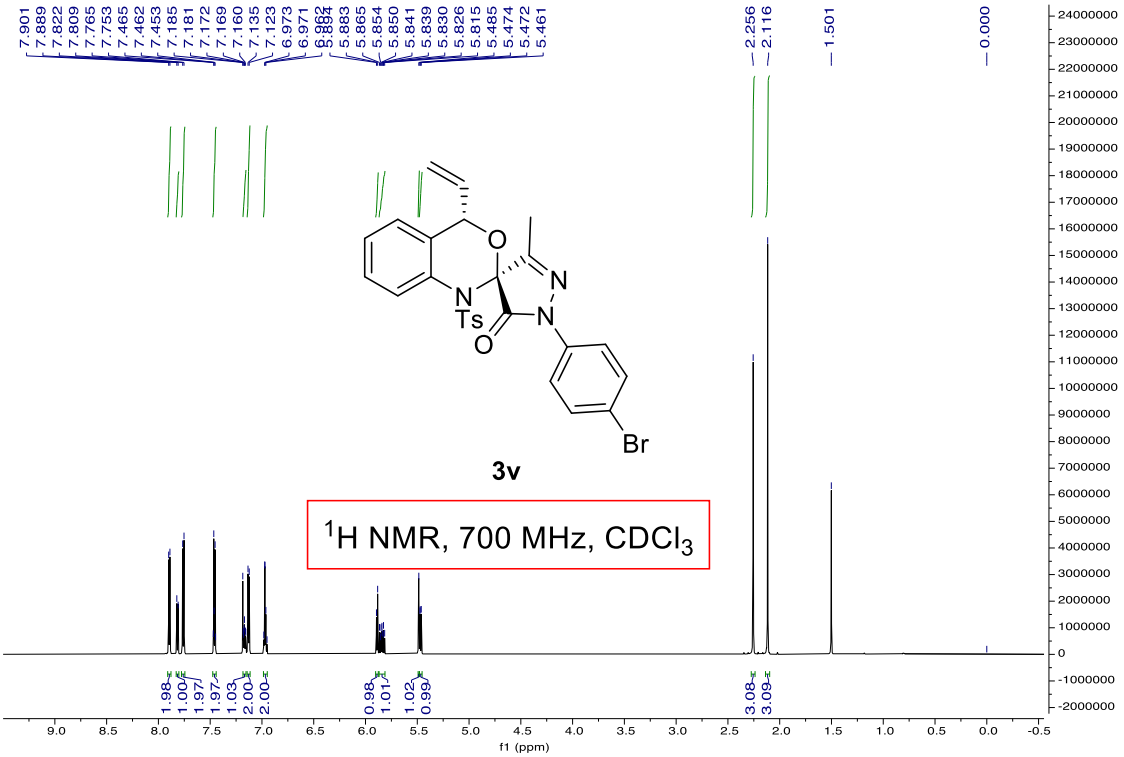

168.71
161.03
159.41
157.42
145.01
134.09
134.07
132.96
132.14
130.82
129.57
129.19
128.87
124.28
123.92
122.43
121.36
121.31
119.44
115.68
115.53
87.47
77.24
77.03
76.82
71.64
21.64
12.37
-0.00
O
N
Ts
O
N
N
F
3u
^{13}C NMR, 150 MHz, CDCl$_3$
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.81	n.a.	265.585	59.824	50.18	n.a.	BMB*
2	7.76	n.a.	192.002	59.406	49.82	n.a.	BMB*
Total:			457.587	119.231	100.00	0.000	

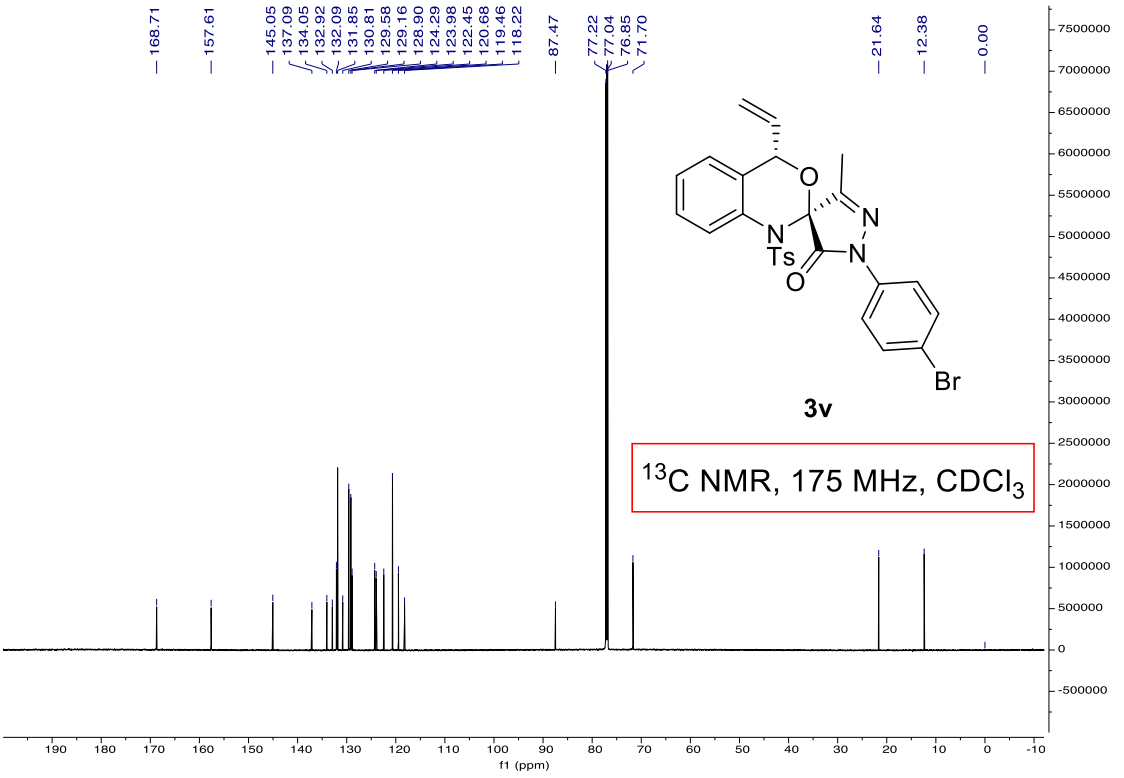


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.89	n.a.	20.702	5.411	9.97	n.a.	BMB*
2	7.85	n.a.	162.424	48.855	90.03	n.a.	BMB*
Total:			183.126	54.267	100.00	0.000	



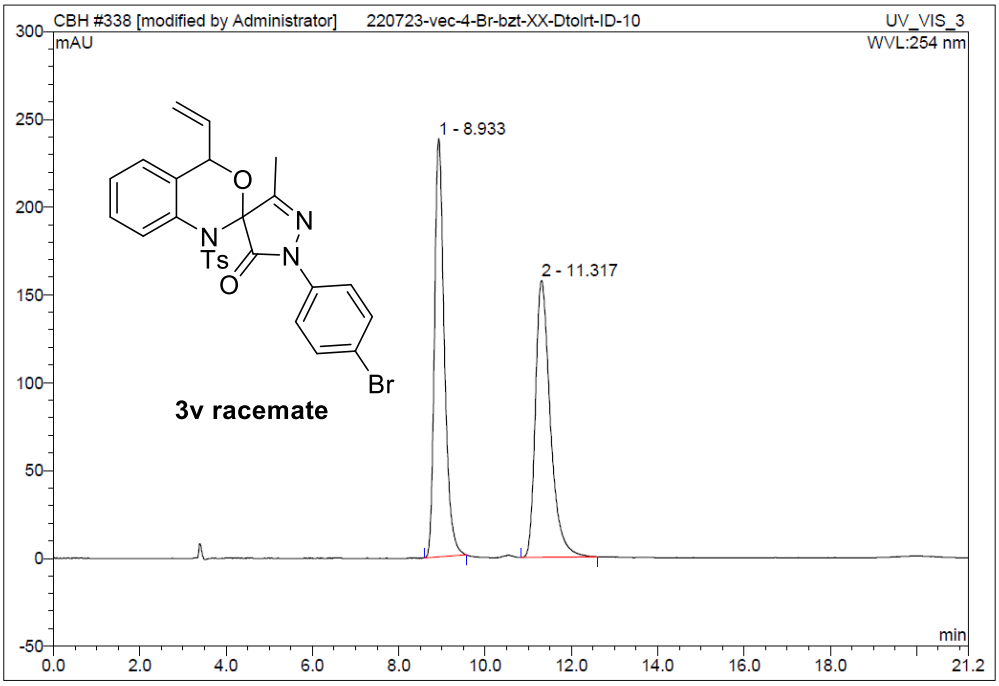
3v

^{1}H NMR, 700 MHz, $CDCl_3$

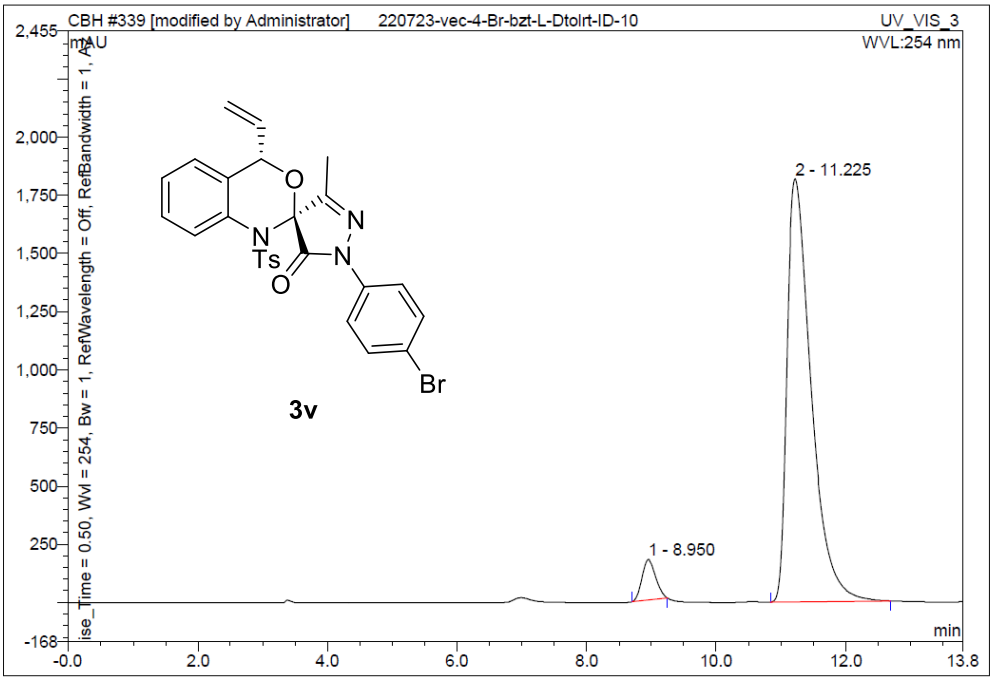


3v

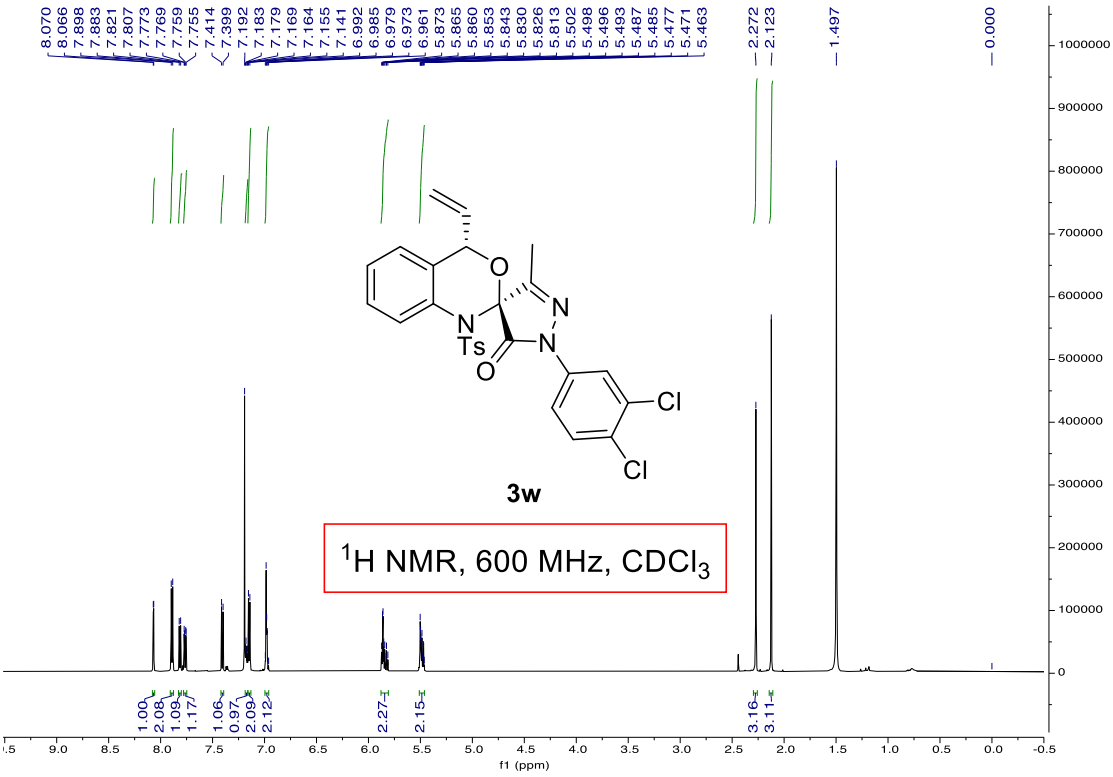
^{13}C NMR, 175 MHz, $CDCl_3$

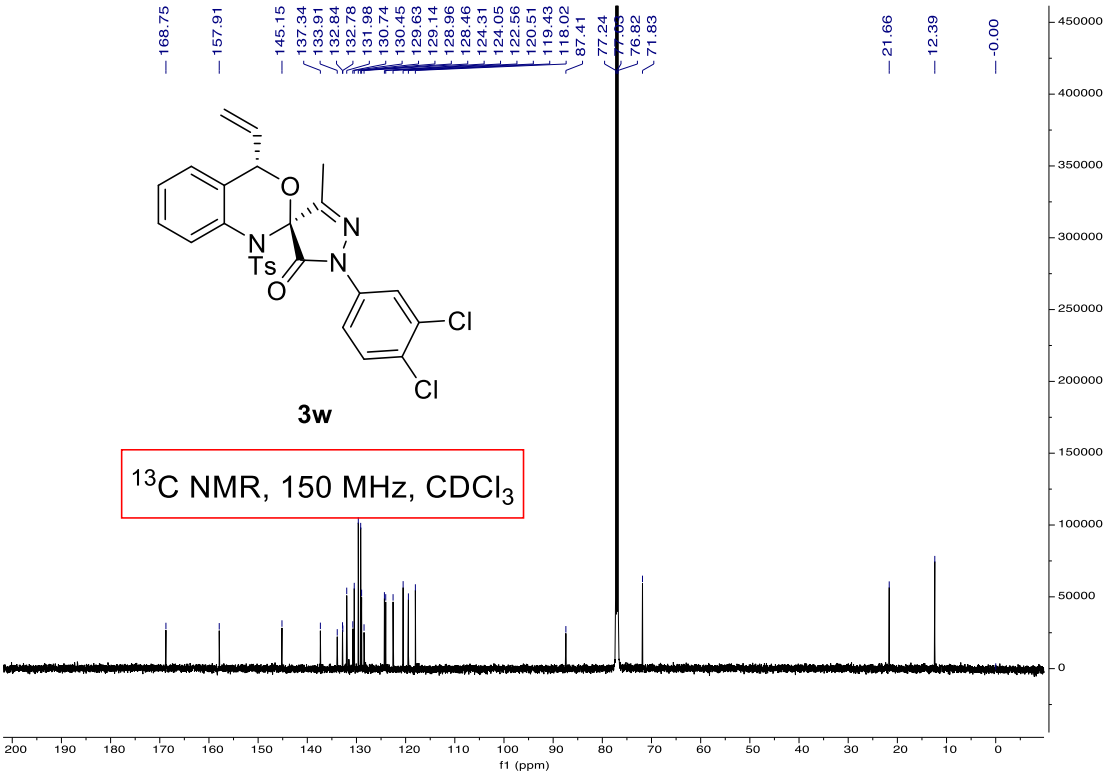


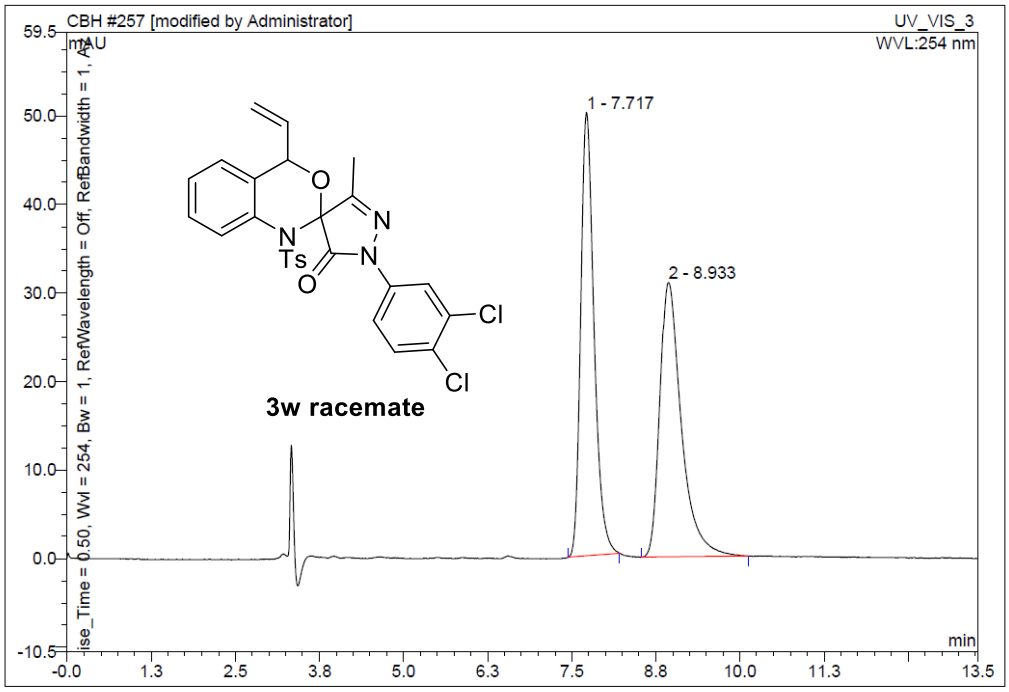
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.93	n.a.	238.405	63.103	49.97	n.a.	BMB*
2	11.32	n.a.	157.886	63.176	50.03	n.a.	BMB
Total:			396.290	126.279	100.00	0.000	



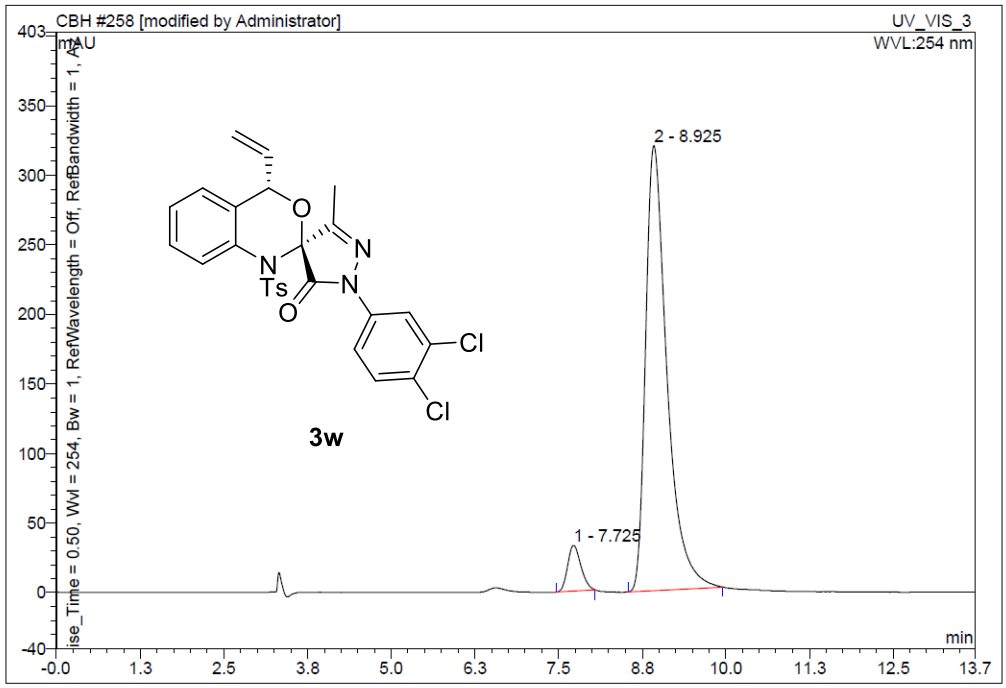
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.95	n.a.	173.697	42.603	5.15	n.a.	BMB*
2	11.23	n.a.	1817.360	784.408	94.85	n.a.	BMB*
Total:			1991.057	827.011	100.00	0.000	


8.070
8.066
7.898
7.883
7.821
7.807
7.773
7.769
7.759
7.755
7.414
7.399
7.192
7.183
7.179
7.169
7.164
7.155
7.141
6.992
6.985
6.979
6.973
6.961
5.873
5.865
5.860
5.853
5.843
5.830
5.826
5.813
5.502
5.498
5.496
5.493
5.487
5.485
5.477
5.471
5.463
2.272
2.123
1.497
0.000
O
N
Ts
O
N
N
Cl
Cl
3w
1H NMR, 600 MHz, CDCl3
1.00
2.08
1.09
1.17
1.06
0.97
2.09
2.12
2.27
2.15
3.16
3.11
f1 (ppm)

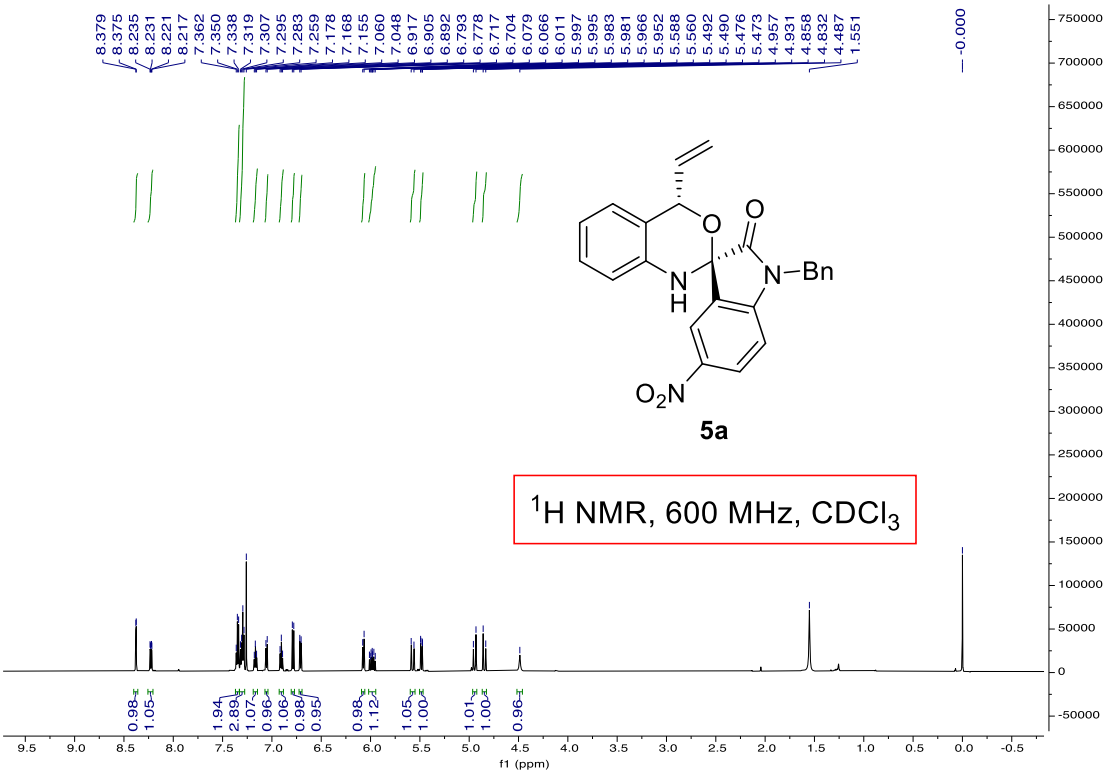

168.75
157.91
145.15
137.34
133.91
132.84
132.78
131.98
130.74
130.45
129.63
129.14
128.96
128.46
124.31
124.05
122.56
120.51
119.43
118.02
87.41
77.24
77.03
76.82
71.83
21.66
12.39
-0.00
O
N
Ts
O
N
N
Cl
Cl
3w
13C NMR, 150 MHz, CDCl3
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.72	n.a.	50.087	11.531	50.26	n.a.	BMB*
2	8.93	n.a.	31.010	11.412	49.74	n.a.	BMB*
Total:			81.098	22.944	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.73	n.a.	32.981	7.609	6.03	n.a.	BMB*
2	8.93	n.a.	319.916	118.526	93.97	n.a.	BMB*
Total:			352.897	126.136	100.00	0.000	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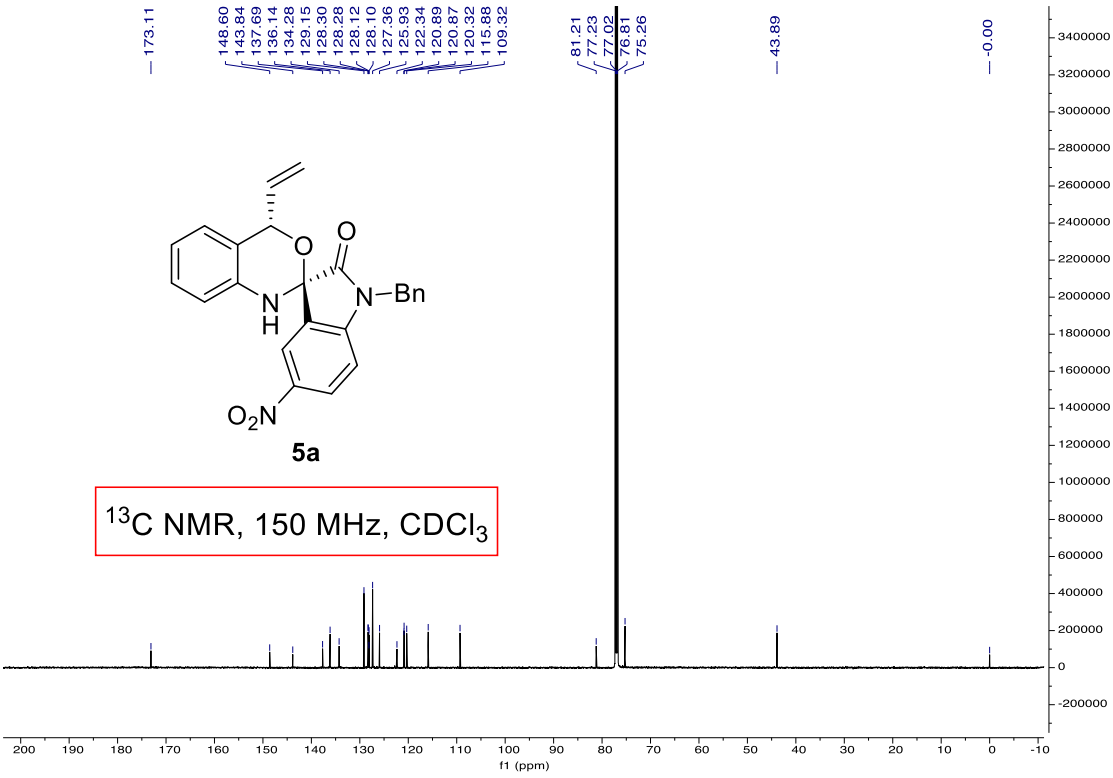
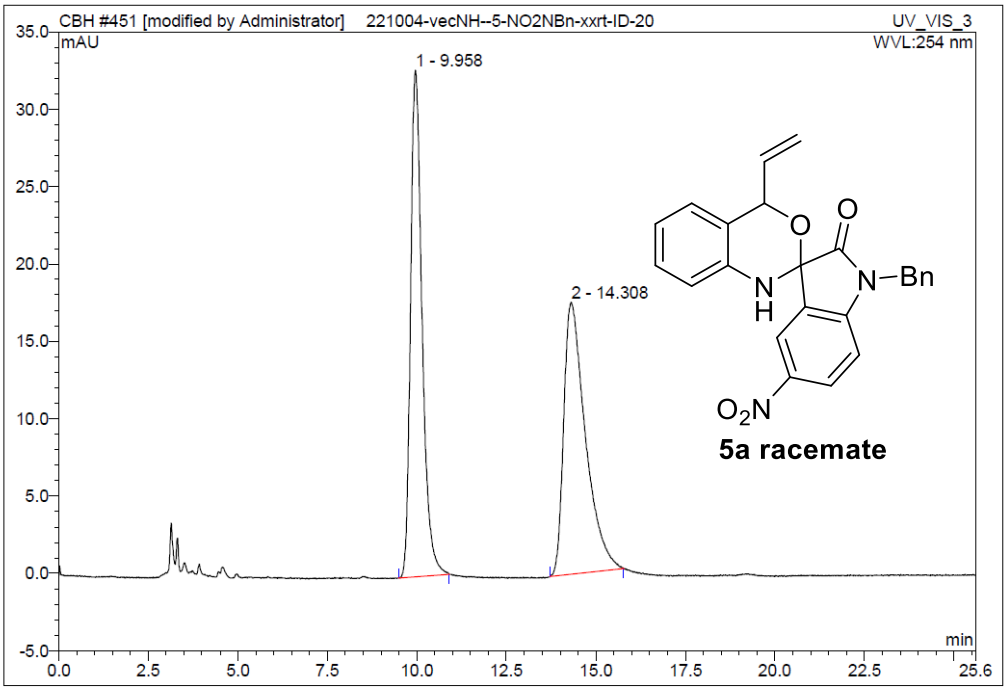
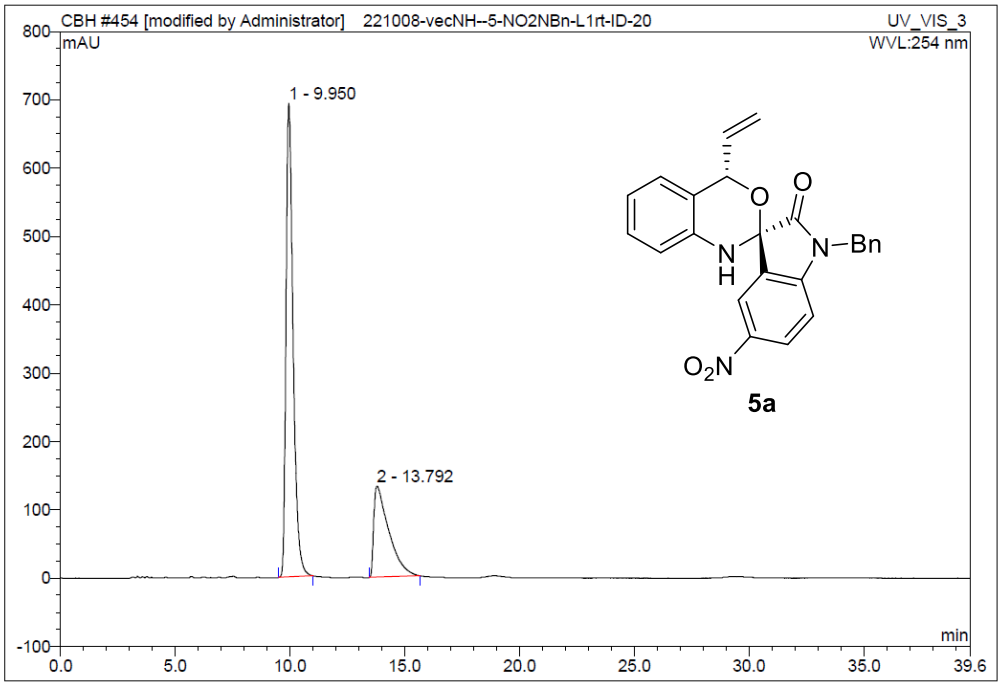
8.235
8.231
8.221
8.217
7.362
7.350
7.338
7.319
7.307
7.295
7.283
7.259
7.178
7.168
7.155
7.060
7.048
6.917
6.905
6.892
6.793
6.778
6.717
6.704
6.079
6.066
6.011
5.997
5.995
5.983
5.981
5.966
5.952
5.588
5.560
5.492
5.490
5.476
5.473
4.957
4.931
4.858
4.832
4.487
1.551
-0.000
O
O
N
H
N–Bn
O2N
5a
1H NMR, 600 MHz, CDCl3
0.98
1.05
1.94
2.89
1.07
0.96
1.06
0.98
0.95
0.98
1.12
1.05
1.00
1.01
1.00
0.96
f1 (ppm)

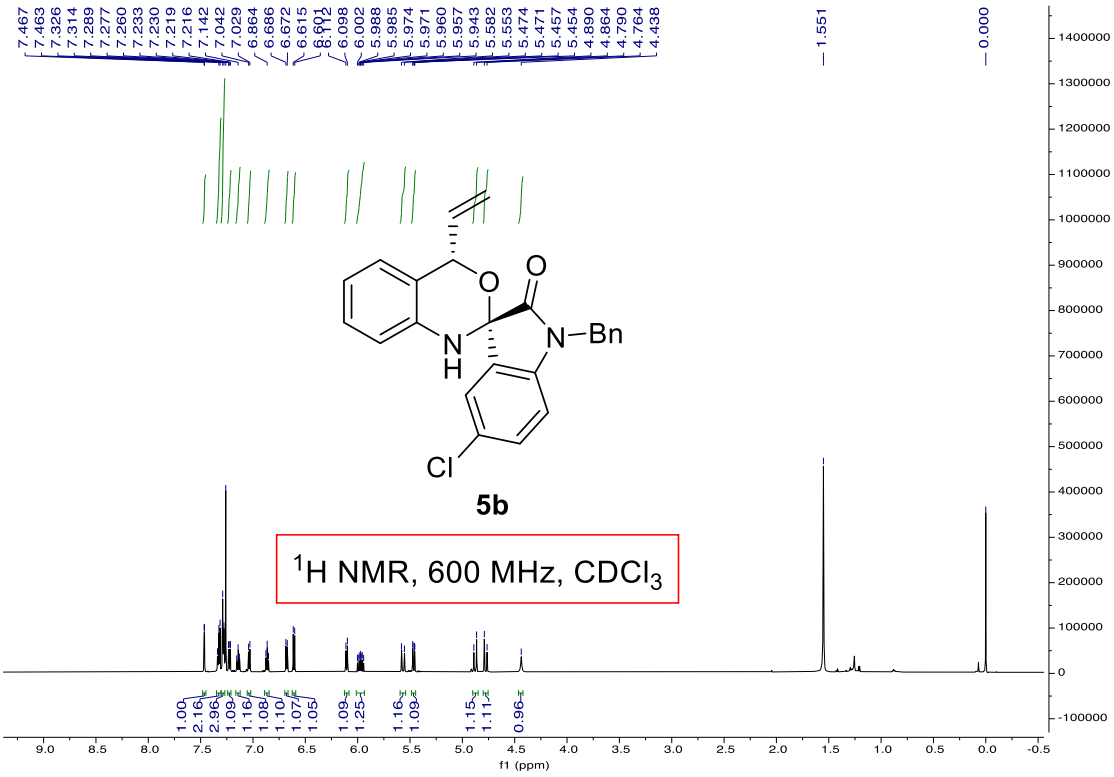

173.11
148.60
143.84
137.69
136.14
134.28
129.15
128.30
128.28
128.12
128.10
127.36
125.93
122.34
120.89
120.87
120.32
115.88
109.32
81.21
77.23
77.02
76.81
75.26
43.89
-0.00
O
O
N
H
N–Bn
O2N
5a
13C NMR, 150 MHz, CDCl3
f1 (ppm)

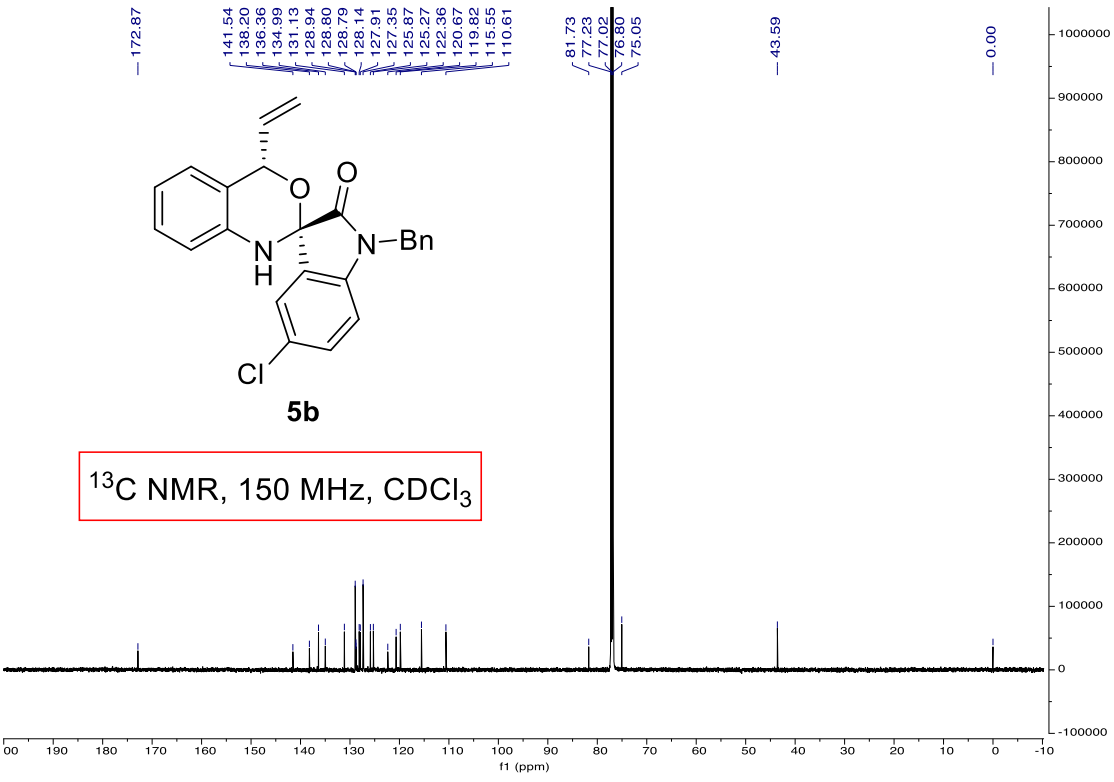


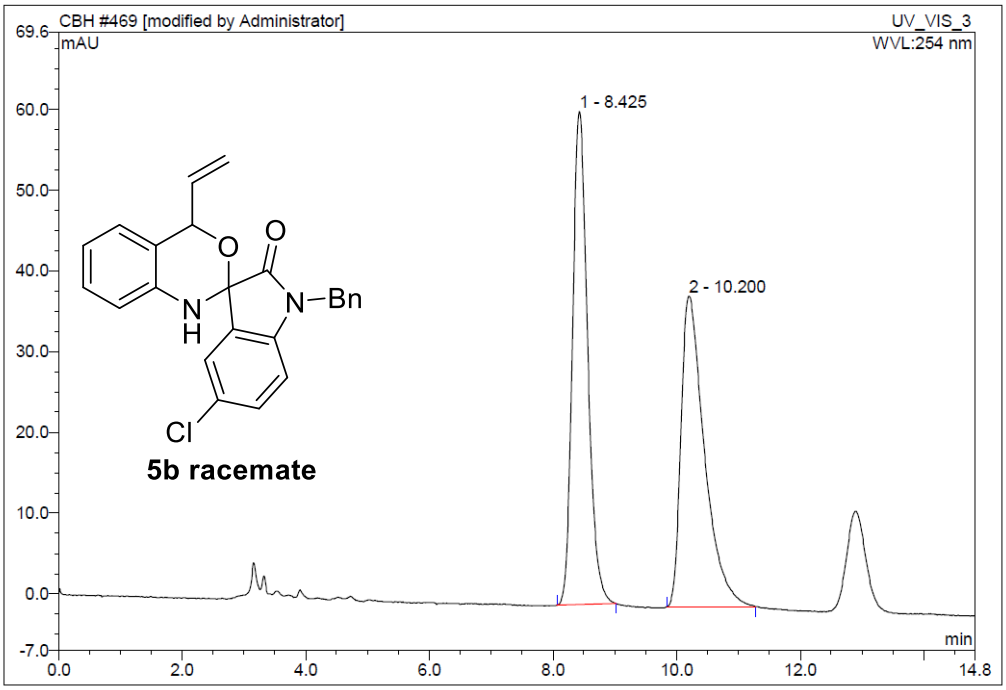
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.96	n.a.	32.731	12.180	49.69	n.a.	BMB*
2	14.31	n.a.	17.573	12.333	50.31	n.a.	BMB*
Total:			50.304	24.513	100.00	0.000	



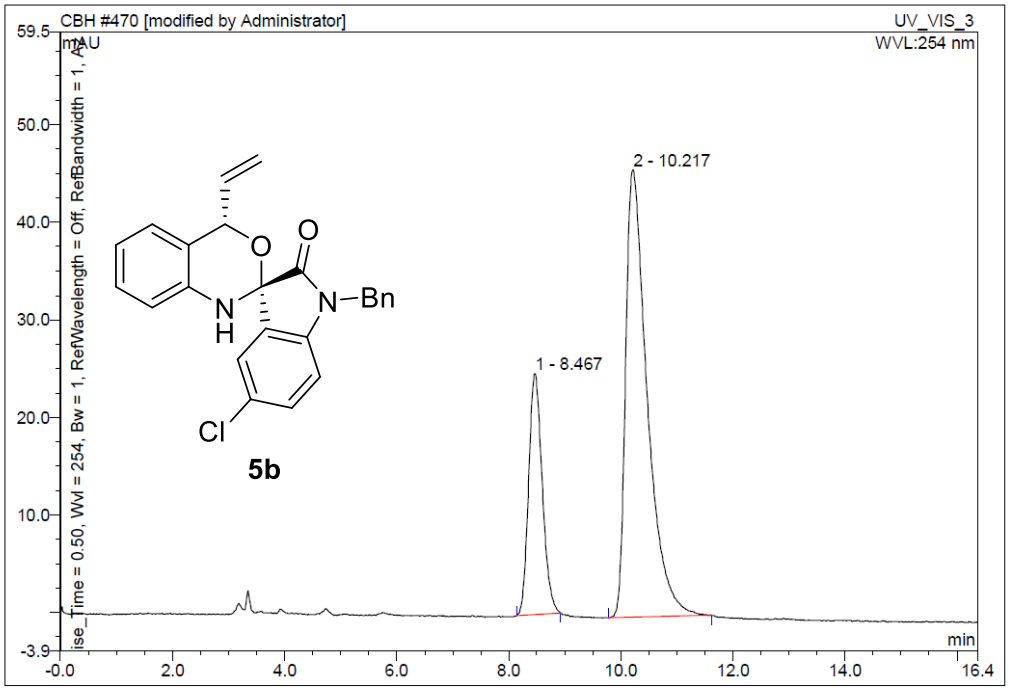
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.95	n.a.	693.224	248.332	71.02	n.a.	BMB*
2	13.79	n.a.	133.405	101.350	28.98	n.a.	BMB*
Total:			826.629	349.681	100.00	0.000	


7.467
7.463
7.326
7.314
7.289
7.277
7.260
7.233
7.230
7.219
7.216
7.142
7.042
7.029
6.864
6.686
6.672
6.615
6.601
6.112
6.098
6.002
5.988
5.985
5.974
5.971
5.960
5.957
5.943
5.582
5.553
5.474
5.471
5.457
5.454
4.890
4.864
4.790
4.764
4.438
1.551
0.000
O
O
N
H
N–Bn
Cl
5b
1H NMR, 600 MHz, CDCl3
1.00
2.16
2.96
1.09
1.16
1.08
1.10
1.07
1.05
1.09
1.25
1.16
1.09
1.15
1.11
0.96
f1 (ppm)

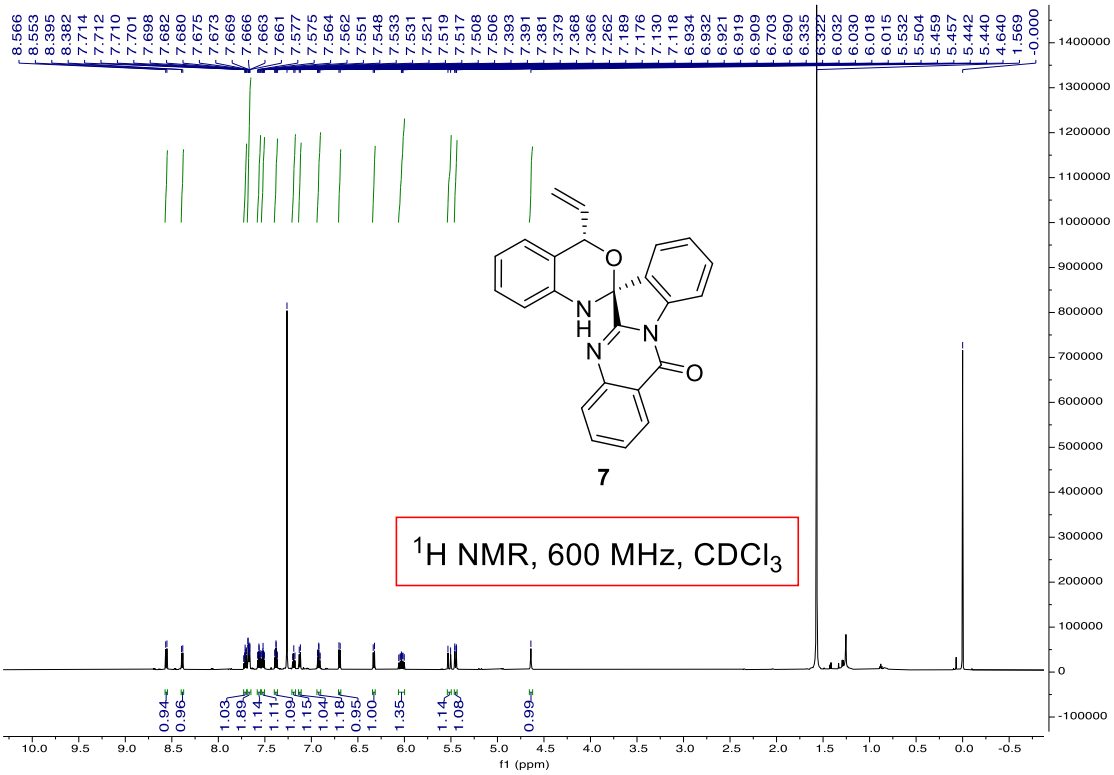

172.87
141.54
138.20
136.36
134.99
131.13
128.94
128.80
128.79
128.14
127.91
127.35
125.87
125.27
122.36
120.67
119.82
115.55
110.61
81.73
77.23
77.02
76.80
75.05
43.59
0.00
O
O
N
H
N–Bn
Cl
5b
13C NMR, 150 MHz, CDCl3
f1 (ppm)

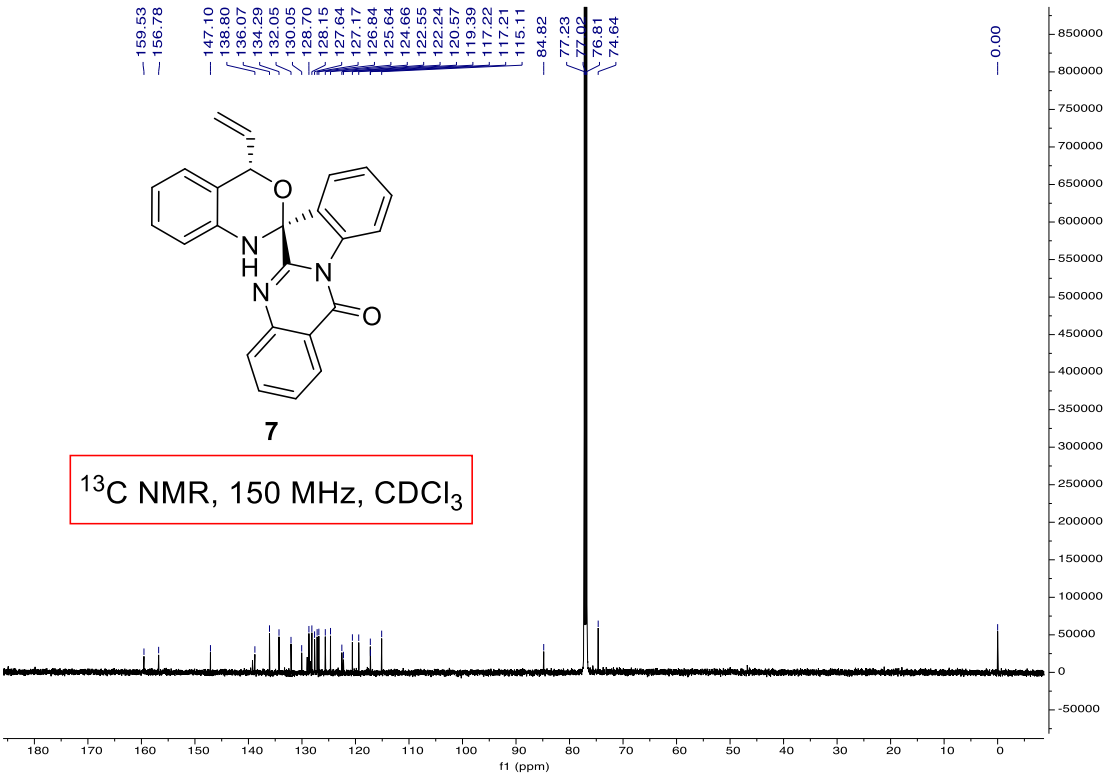


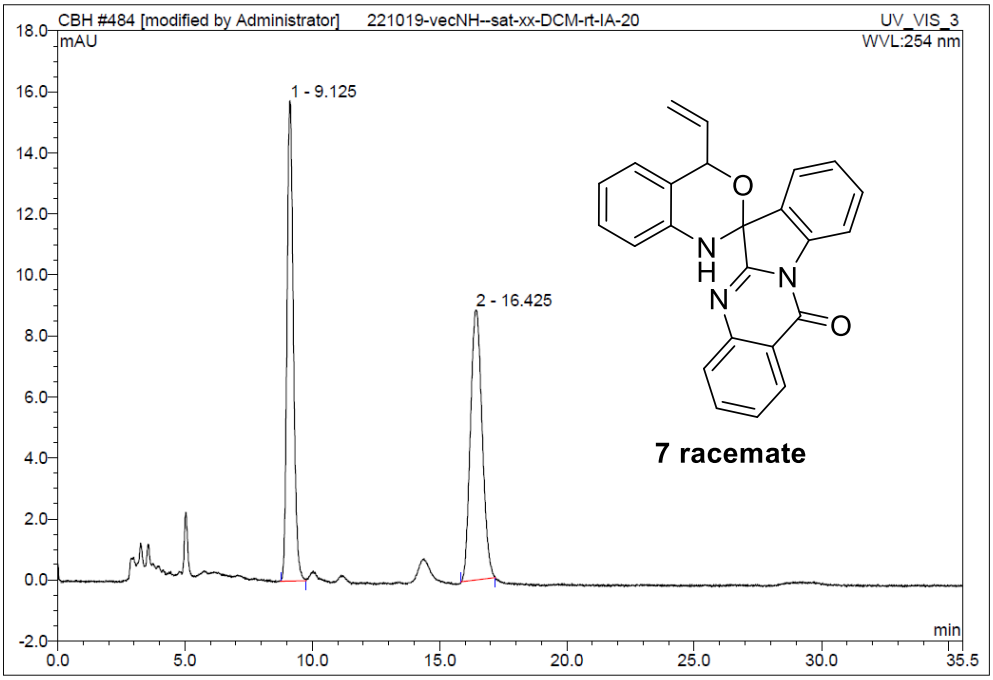
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.43	n.a.	61.041	17.280	50.60	n.a.	BMB*
2	10.20	n.a.	38.453	16.867	49.40	n.a.	BMB*
Total:			99.494	34.147	100.00	0.000	



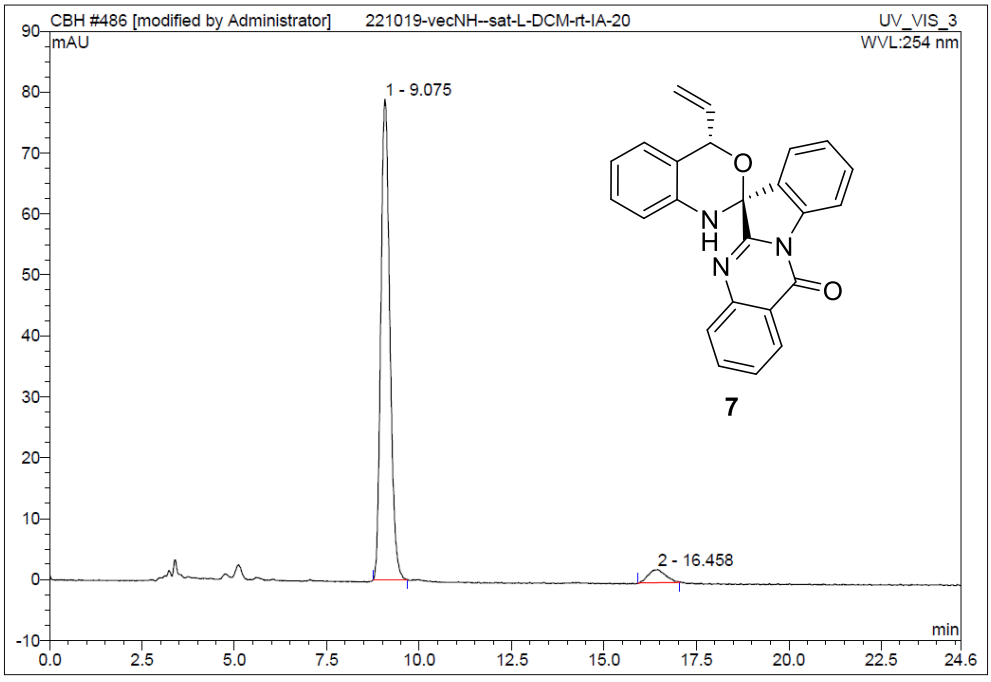
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	8.47	n.a.	24.668	6.929	25.40	n.a.	BMB*
2	10.22	n.a.	45.827	20.349	74.60	n.a.	BMB*
Total:			70.495	27.278	100.00	0.000	


7
^{1}H NMR, 600 MHz, $CDCl_3$
f1 (ppm)

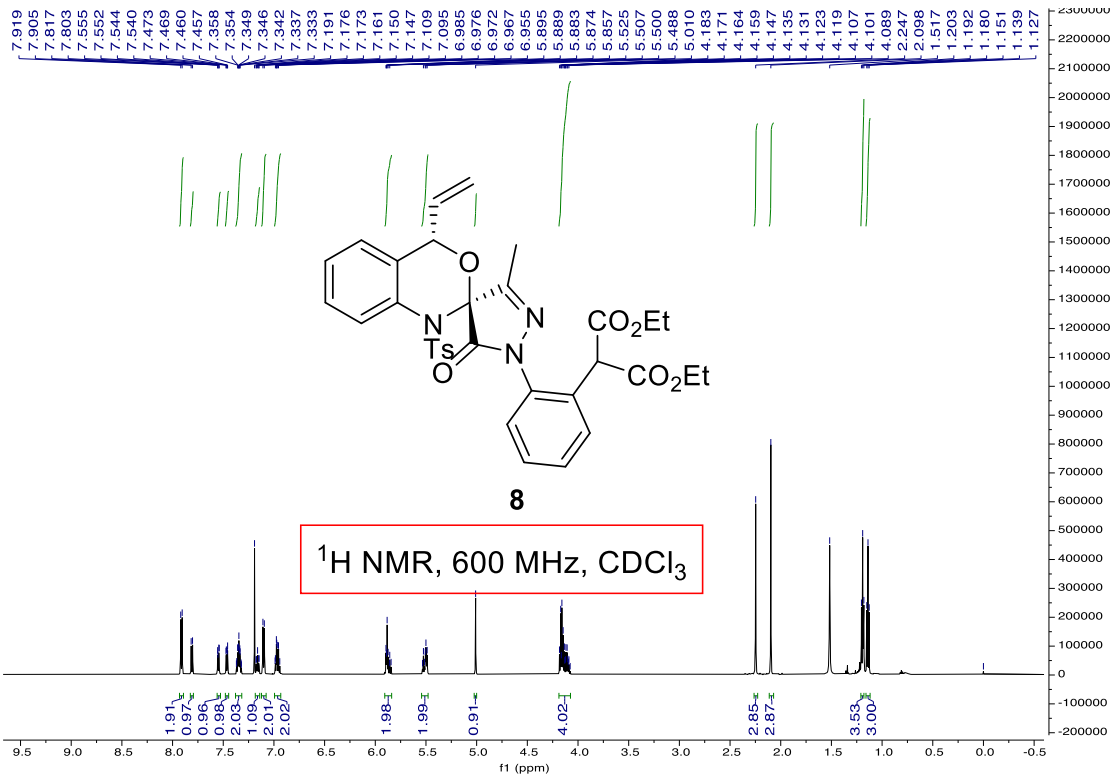

7
^{13}C NMR, 150 MHz, $CDCl_3$
f1 (ppm)

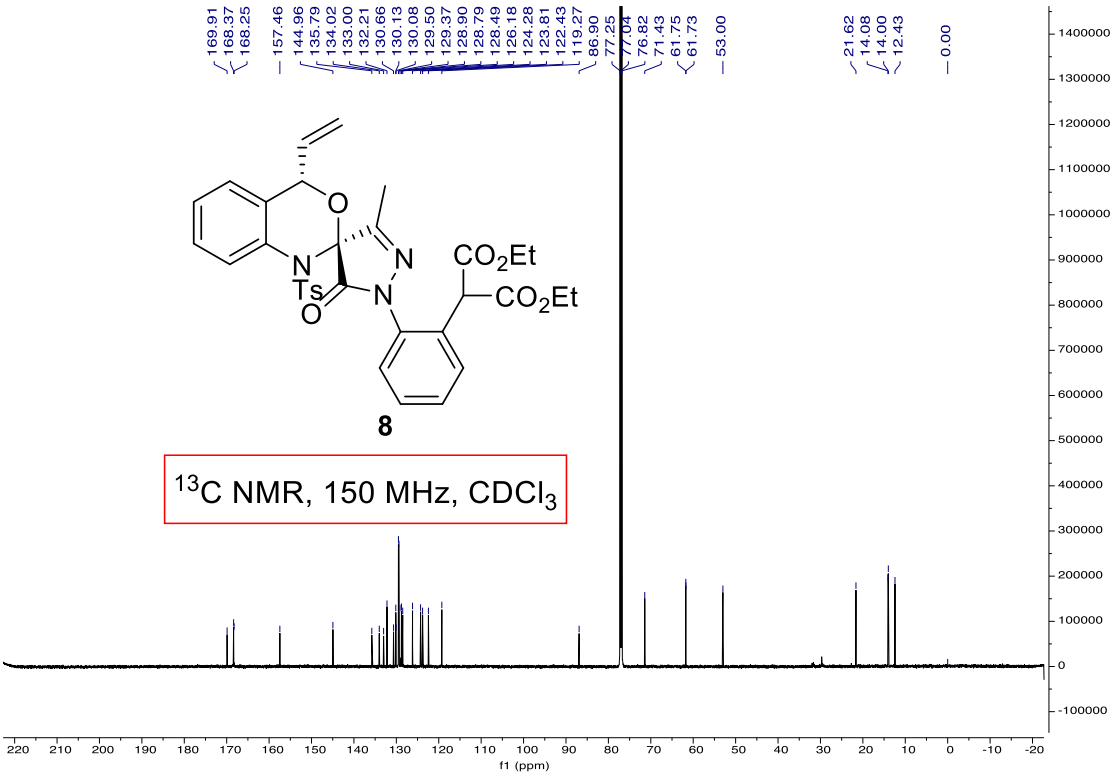


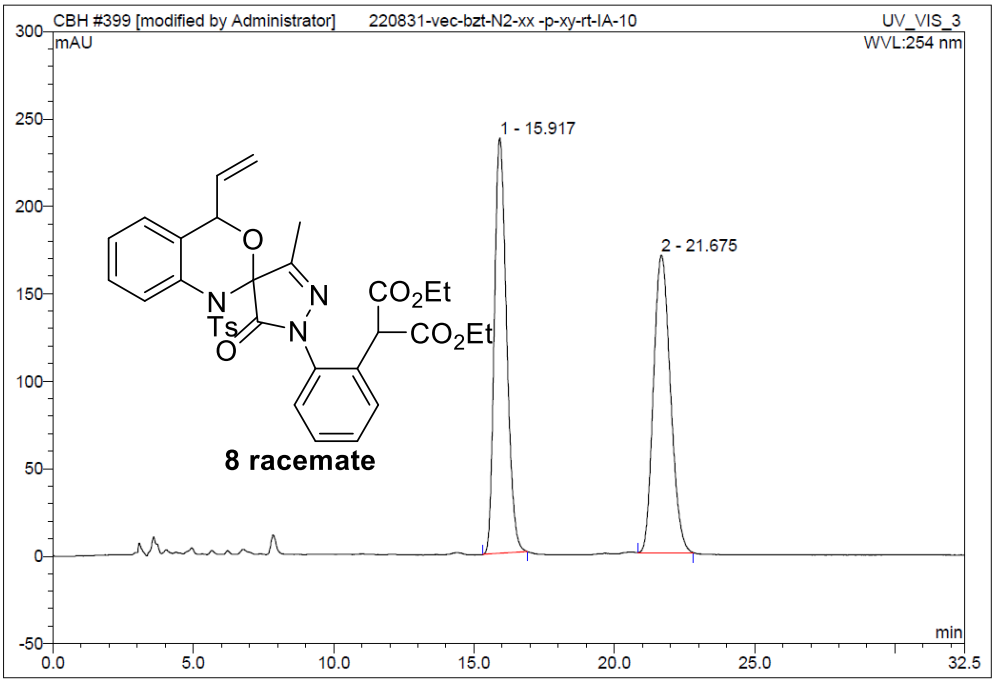
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.13	n.a.	15.755	4.578	49.30	n.a.	BMB
2	16.43	n.a.	8.858	4.709	50.70	n.a.	BMB*
Total:			24.613	9.287	100.00	0.000	



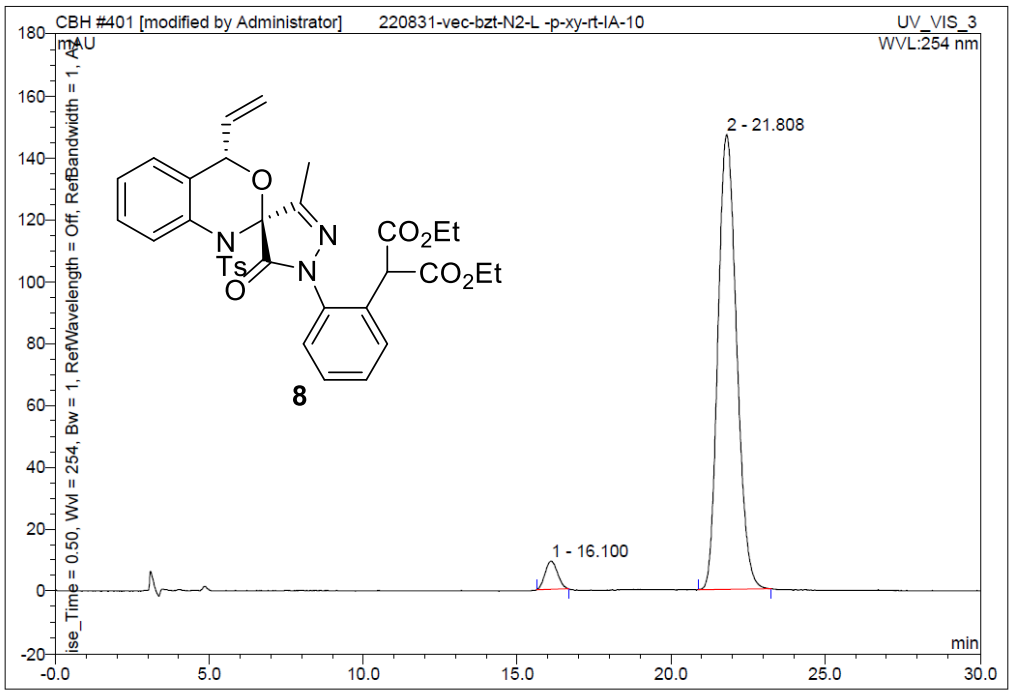
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.08	n.a.	78.867	22.329	95.10	n.a.	BMB*
2	16.46	n.a.	2.162	1.150	4.90	n.a.	BMB*
Total:			81.028	23.479	100.00	0.000	


8
^{1}H NMR, 600 MHz, $CDCl_3$
f1 (ppm)

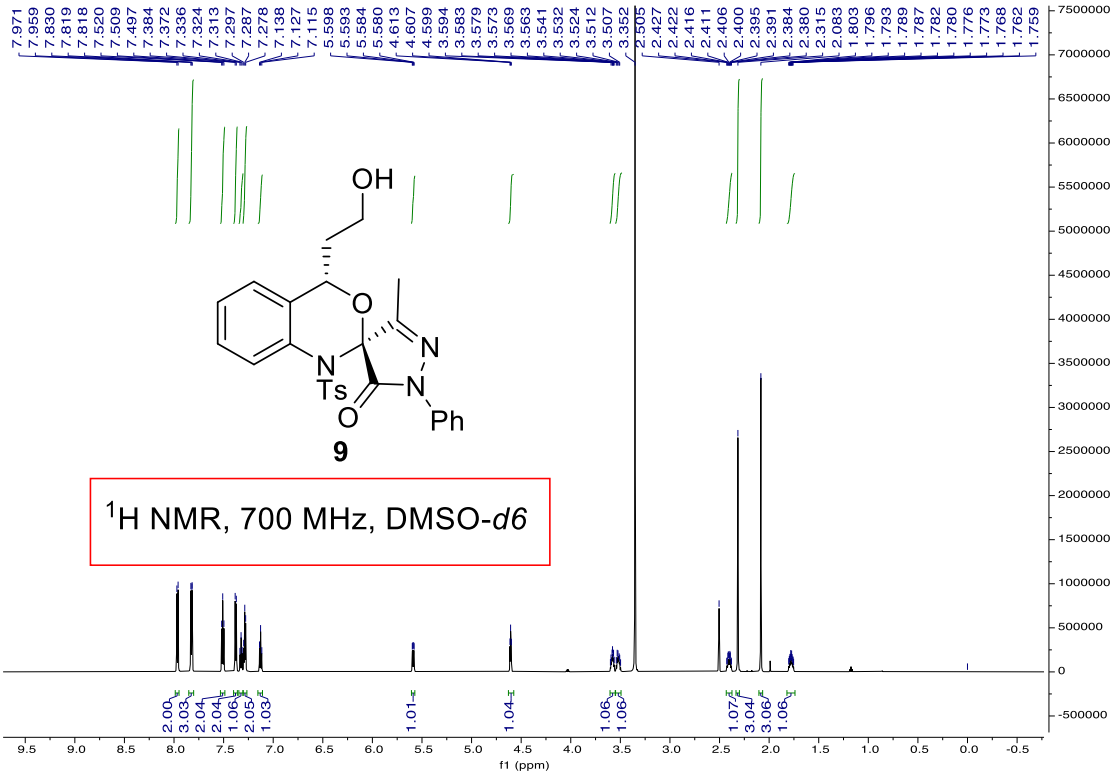

8
^{13}C NMR, 150 MHz, $CDCl_3$
f1 (ppm)

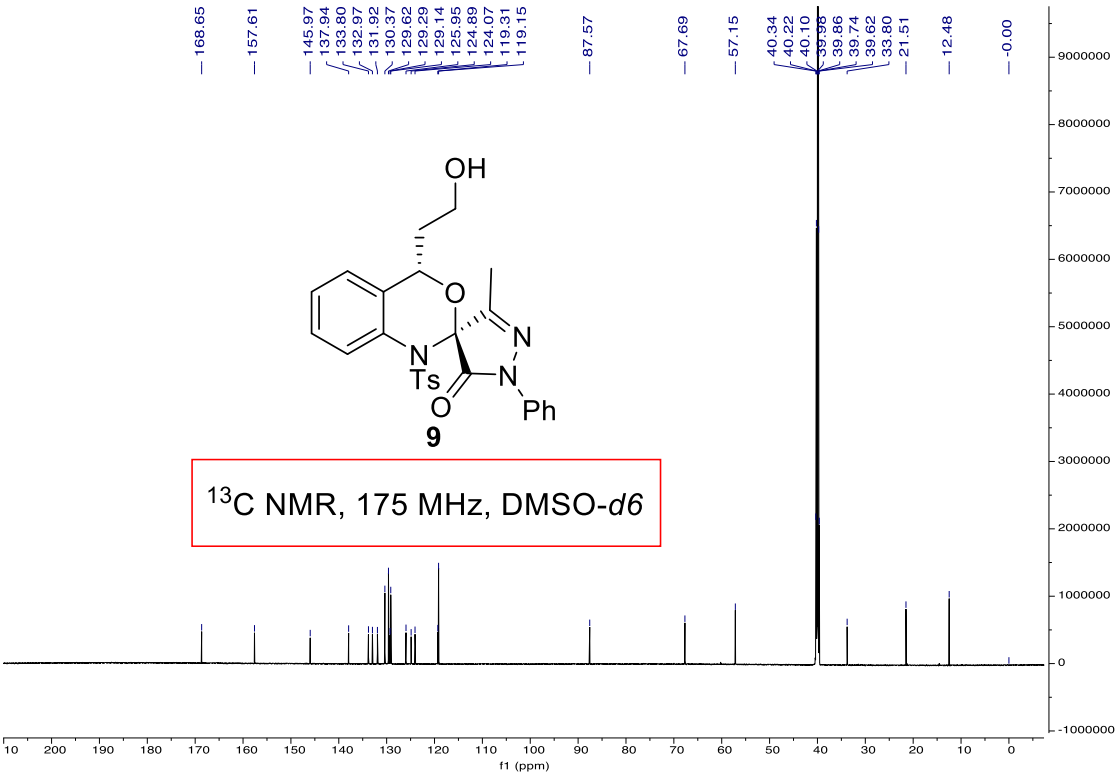


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.92	n.a.	237.452	119.585	50.11	n.a.	BMB*
2	21.68	n.a.	170.068	119.068	49.89	n.a.	BMB*
Total:			407.519	238.653	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	16.10	n.a.	9.136	4.275	3.98	n.a.	BMB*
2	21.81	n.a.	147.174	103.265	96.02	n.a.	BMB*
Total:			156.310	107.540	100.00	0.000	


OH
O
N
N
Ts
O
N
N
Ph
9
^{1}H NMR, 700 MHz, DMSO-*d6*
f1 (ppm)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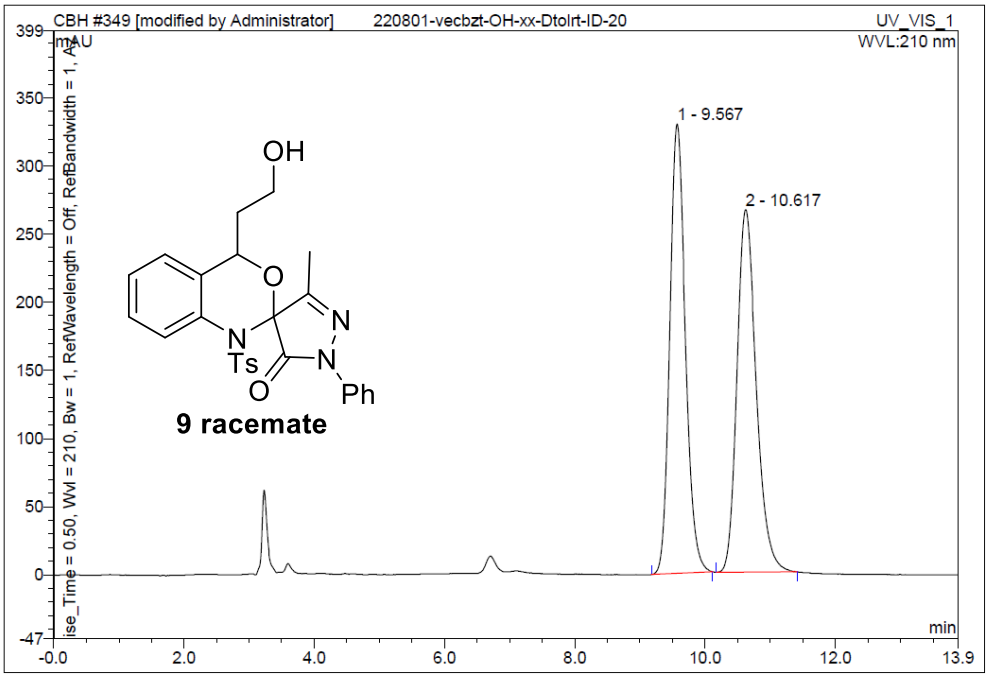
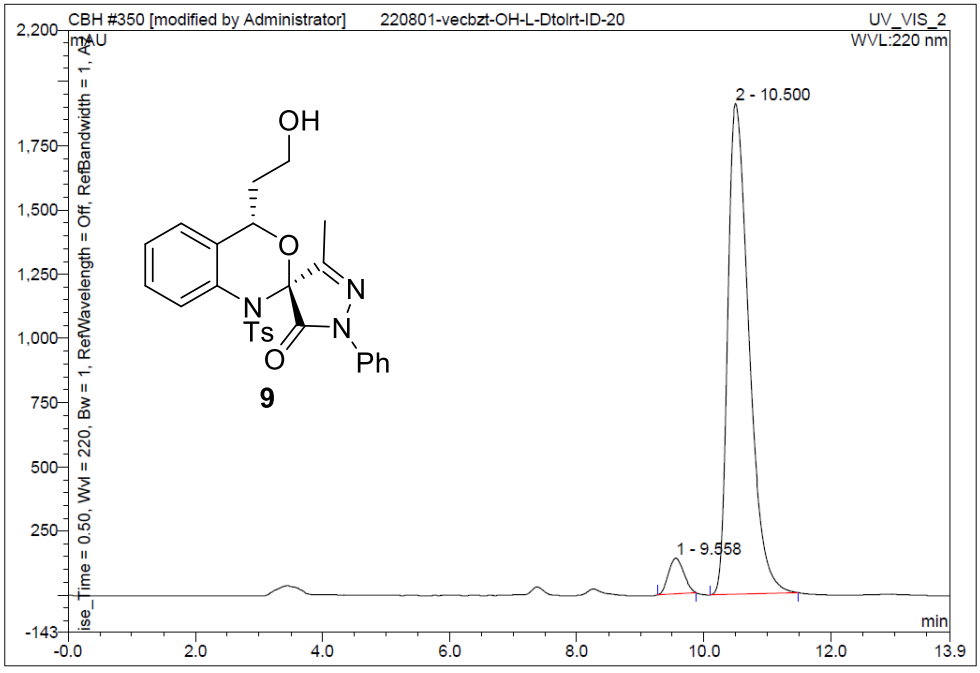
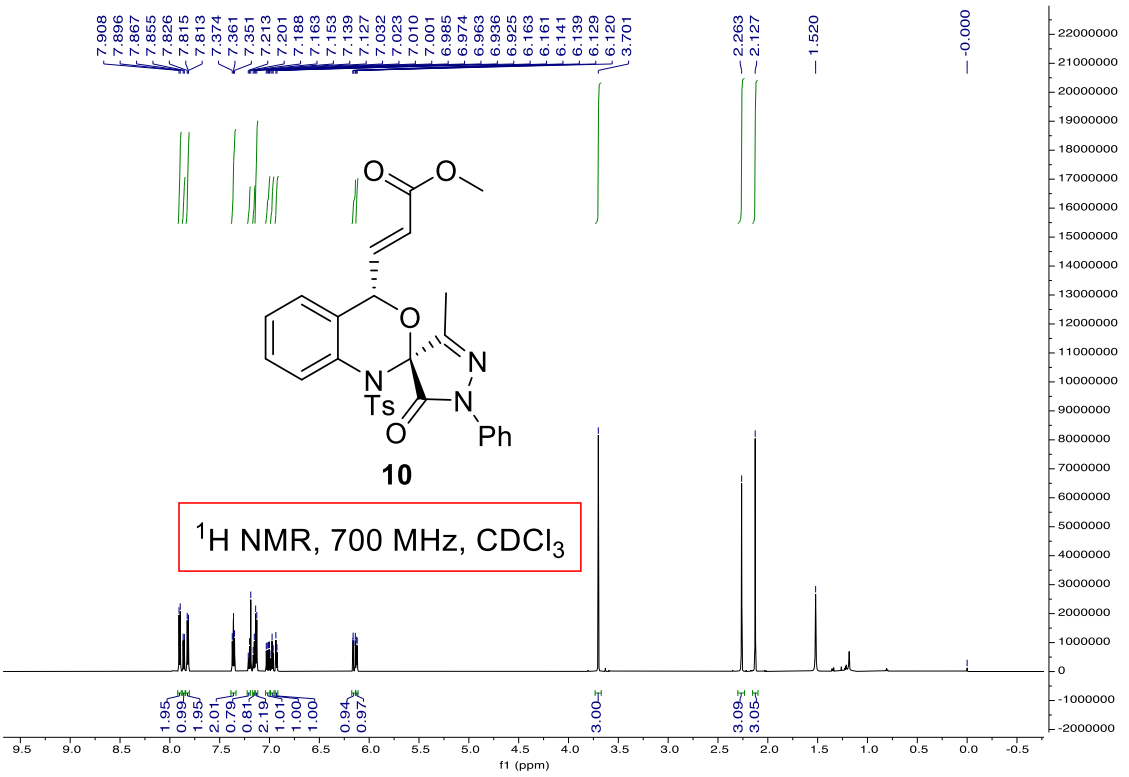
N
Ts
O
N
N
Ph
9
^{13}C NMR, 175 MHz, DMSO-*d6*
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.57	n.a.	329.975	92.325	50.14	n.a.	BMB*
2	10.62	n.a.	265.996	91.793	49.86	n.a.	BMB*
Total:			595.970	184.119	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.56	n.a.	137.972	38.173	4.92	n.a.	BMB*
2	10.50	n.a.	1910.176	738.277	95.08	n.a.	BMB*
Total:			2048.148	776.450	100.00	0.000	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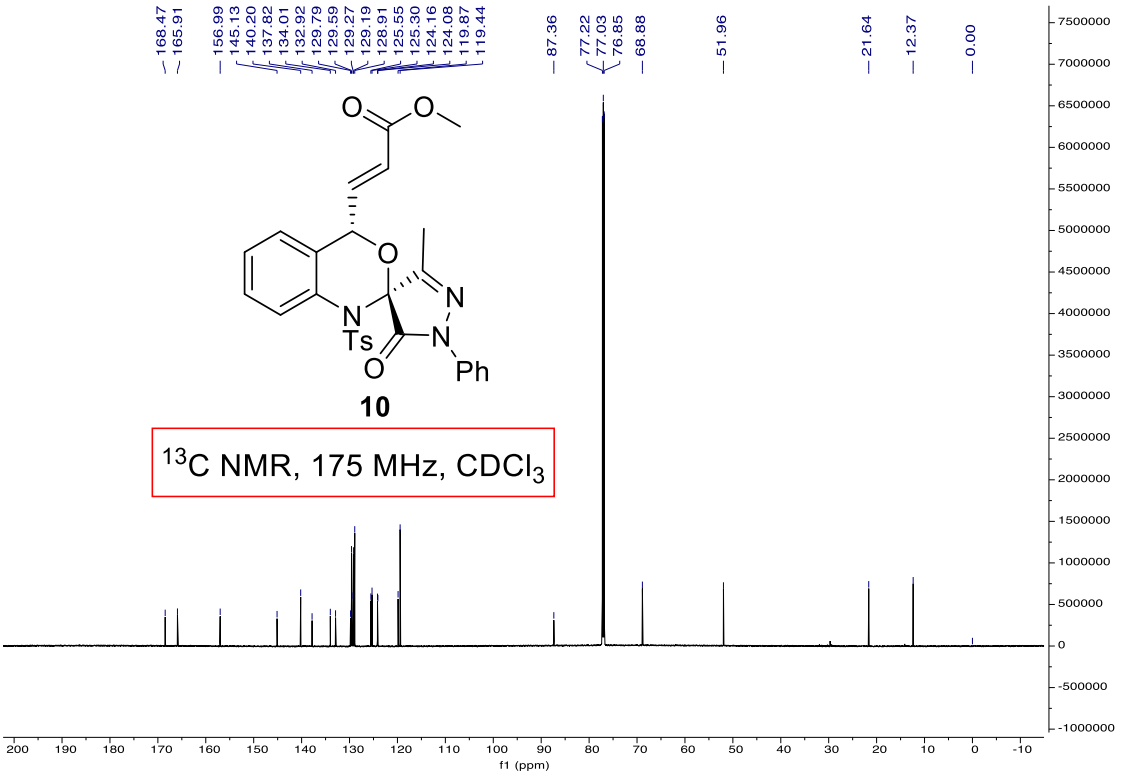
7.361
7.351
7.213
7.201
7.188
7.163
7.153
7.139
7.127
7.032
7.023
7.010
7.001
6.985
6.974
6.963
6.936
6.925
6.163
6.161
6.141
6.139
6.129
6.120
3.701
2.263
2.127
1.520
-0.000
O
O
O
N
N
Ts
O
N
Ph
10
1H NMR, 700 MHz, CDCl3
1.95
0.99
1.95
2.01
0.79
0.81
2.19
1.01
1.00
1.00
0.94
0.97
3.00
3.09
3.05
f1 (ppm)


168.47
165.91
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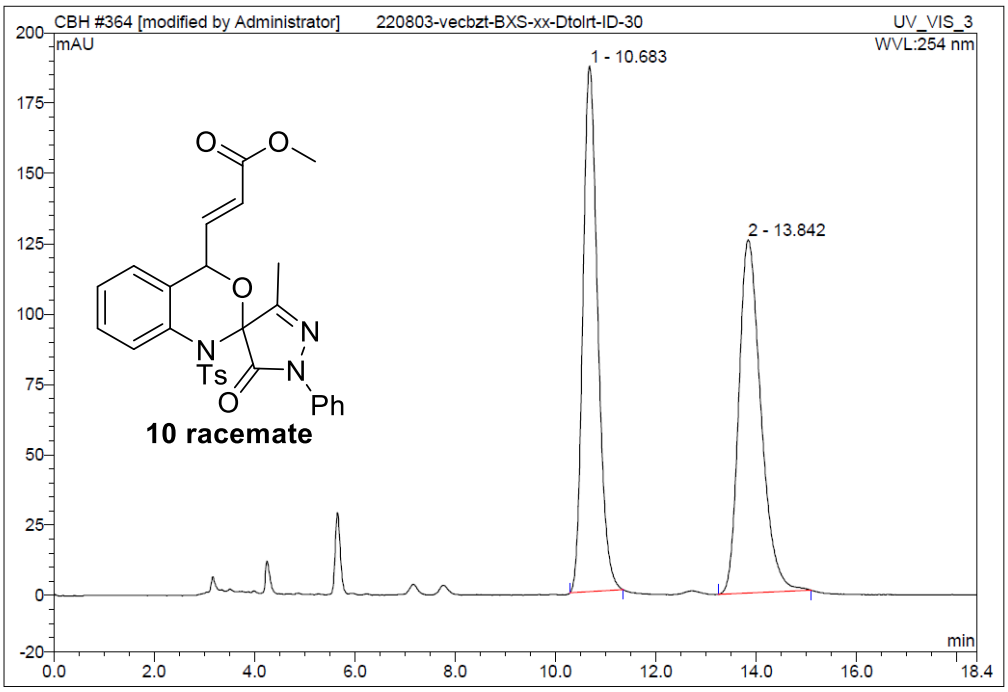
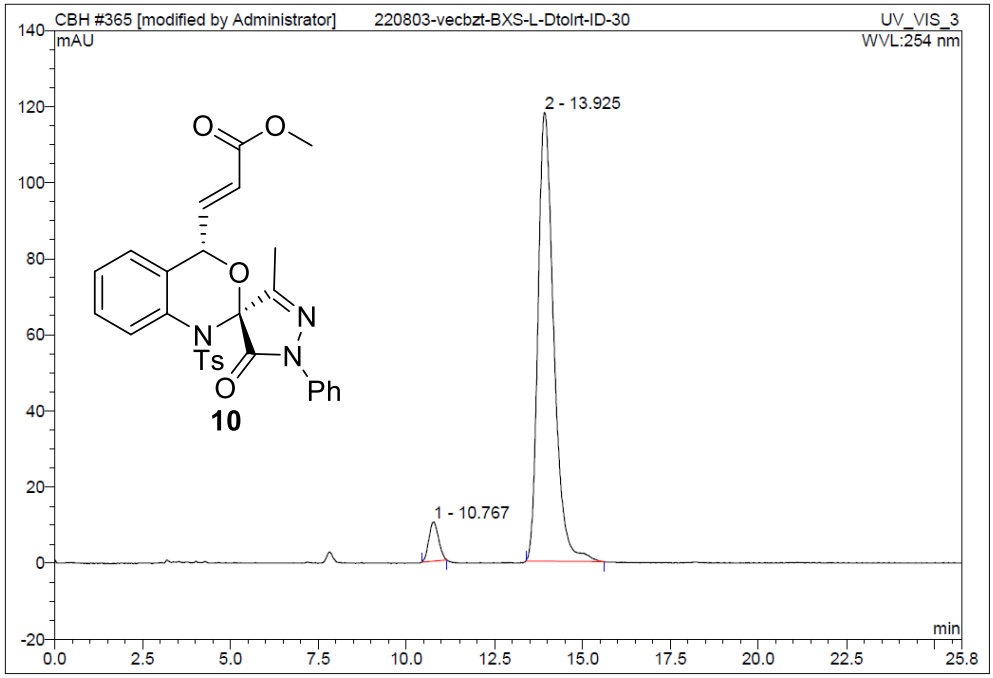
140.20
137.82
134.01
132.92
129.79
129.59
129.27
129.19
128.91
125.55
125.30
124.16
124.08
119.87
119.44
87.36
77.22
77.03
76.85
68.88
51.96
21.64
12.37
0.00
O
O
O
N
N
Ts
O
N
Ph
10
13C NMR, 175 MHz, CDCl3
f1 (ppm)



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.68	n.a.	186.933	63.883	49.92	n.a.	BMB*
2	13.84	n.a.	125.557	64.097	50.08	n.a.	BMB*
Total:			312.491	127.980	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.77	n.a.	10.202	3.266	5.07	n.a.	BMB*
2	13.93	n.a.	117.931	61.174	94.93	n.a.	BMB*
Total:			128.133	64.440	100.00	0.000	