

Palladium-catalysed oxidative nucleophilic allylation between alkenes and activated ketimines

Yue Li,^a Peng Chen,^a Zhi-Chao Chen,^{*a} Wei Du,^a Qin Ouyang,^b Ying-Chun Chen^{*a,b}

^a Key Laboratory of Drug-Targeting and Drug Delivery System of the Ministry of Education and Sichuan Research Center for Drug Precision Industrial Technology, West China School of Pharmacy, Sichuan University, Chengdu 610041, China

^b College of Pharmacy, Third Military Medical University, Shapingba, Chongqing 400038, China

E-mail: chenzhichao@scu.edu.cn; ycchen@scu.edu.cn

Supplementary Information

1. General methods	S2
2. Screenings for the oxidative nucleophilic allylation.....	S4
3. Mechanism study for the umpolung allylation reactions	S7
4. General procedure for the oxidative nucleophilic allylation.....	S11
5. Screening conditions of asymmetric oxidative nucleophilic allylation.....	S32
6. Crystal data and structural refinement for racemic 7a and 7j.....	S34
7. NMR, HRMS spectra and HPLC chromatograms	S37

1. General methods

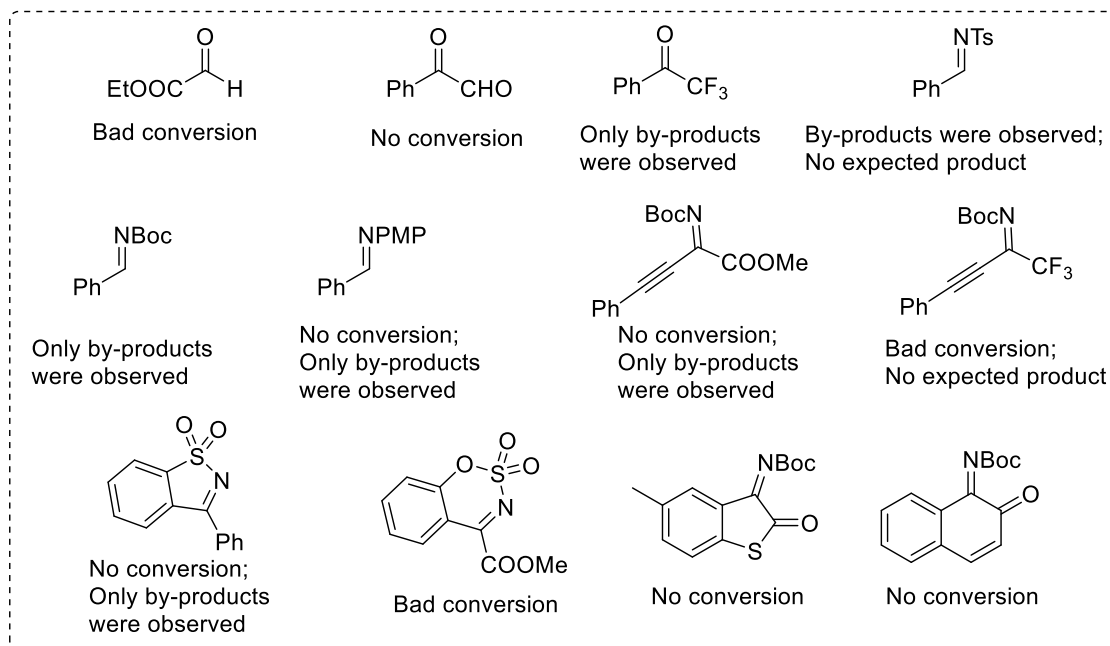
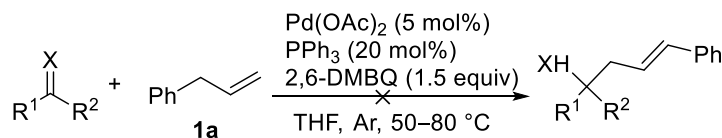
Unless otherwise noted, the reactions were carried out under ambient atmosphere; when the reactions required heating, the heat source was oil bath. ¹H NMR (400 MHz or 600 MHz), ¹³C NMR (100 MHz or 150 MHz) and ¹⁹F NMR (376 MHz) spectra were recorded on Varian INOVA–400/54, Agilent DD2–600/54 or Bruker Ascend™ 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl₃ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet doublet, td = triple doublet, dt = double triplet, brs = broad singlet, m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2, Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. X-ray diffraction experiments were carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre. In each case, enantiomeric excess was determined by HPLC analysis on a chiral stationary phase in comparison with the authentic racemate, using a Daicel Chiralpak IE Column (250 × 4.6 mm). UV detection was monitored at 254 nm. Column chromatography was performed on silica gel (200–300 mesh) eluting with redistilled EtOAc and petroleum ether (PE). TLC was performed on glass-backed silica plates. UV light (monitored at 254 nm), I₂ and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Alkenes **1**,¹ isatin-derived ketimines **2**, pyrazoledione-derived ketimines **4**, isoquinoline-1,3,4-trione-derived ketimines **6**,² allylic carbonates **8**,³ (allyl-1,1-*d*₂)benzene *d*-**1a**⁴ were prepared according to the literature procedures.

- (a) E. Alacid and C. Nájera, Palladium-Catalyzed Cross-Coupling Reactions of Potassium Alkenyltrifluoroborates with Organic Halides in Aqueous Media, *J. Org. Chem.*, 2009, **74**, 2321; (b) W. Yang, H. Chen, J. Li, C. Li, W. Wu and H. Jiang, Palladium-Catalyzed Aerobic Oxidative Double Allylic C–H Oxygenation of Alkenes: A Novel and Straightforward Route to α,β -Unsaturated Esters, *Chem. Commun.*, 2015, **51**, 9575; (c) X. Wang and Y. Wu, Direct Oxidative Isoperfluoropropylation of Terminal Alkenes via Hexafluoropropylene (HFP) and Silver Fluoride, *Chem. Commun.*, 2018, **54**, 1877; (d) V. Sabatino, J. G. Rebelein and T. R. Ward, “Close-to-Release”: Spontaneous Bioorthogonal Uncaging Resulting from Ring-Closing

- Metathesis, *J. Am. Chem. Soc.*, 2019, **141**, 17048; (e) S. Engl and O. Reiser, Copper Makes the Difference: Visible Light-Mediated Atom Transfer Radical Addition Reactions of Iodoform with Olefins, *ACS Catal.*, 2020, **10**, 9899; (f) W. Li, S. Yu, J. Li and Y. Zhao, Nickel-Catalyzed Allylmethylation of Alkynes with Allylic Alcohols and AlMe₃: Facile Access to Skipped Dienes and Trienes, *Angew. Chem., Int. Ed.*, 2020, **59**, 14404.
- 2 (a) J. Wang, Y. Liu, Y. Liu, Z. Wei, J. Cao, D. Liang, Y. Lin and H. Duan, L-*tert*-Leucine Derived Urea-Ammonium salts: Efficient Bifunctional Phase Transfer Catalysts for Highly Diastereo- and Enantioselective Aza-Henry Reaction of Isatin-Derived N-Boc Ketimines with α -Aryl Nitromethanes, *Tetrahedron*, 2019, **75**, 2883; (b) G.-Y. Ran, C. Chen, X.-X. Yang, Z. Zhao, W. Du and Y.-C. Chen, Cu(I)-Catalyzed Asymmetric α -Allenylation of Activated Ketimines with 3-Butynoates, *Org. Lett.*, 2020, **22**, 4732; (c) Y. You, W.-Y. Lu, K.-X. Xie, J.-Q. Zhao, Z.-H. Wang and W.-C. Yuan, Enantioselective Synthesis of Isoquinoline-1,3(2*H*,4*H*)-dione Derivatives via a Chiral Phosphoric Acid Catalyzed Aza-Friedel–Crafts Reaction, *Chem. Commun.*, 2019, **55**, 8478.
- 3 J. Štambaský, A. V. Malkov and P. Kočovský, Synthesis of Enantiopure 1-Arylprop-2-en-1-ols and Their *tert*-Butyl Carbonates, *J. Org. Chem.*, 2008, **73**, 9148.
- 4 Q. Wu, L. Wang, R. Jin, C. Kang, Z. Bian, Z. Du, X. Ma, H. Guo and L. Gao, Nickel-Catalyzed Allylic C(sp²)-H Activation: Stereoselective Allyl Isomerization and Regiospecific Allyl Arylation of Allylarenes, *Eur. J. Org. Chem.*, 2016, 5415.

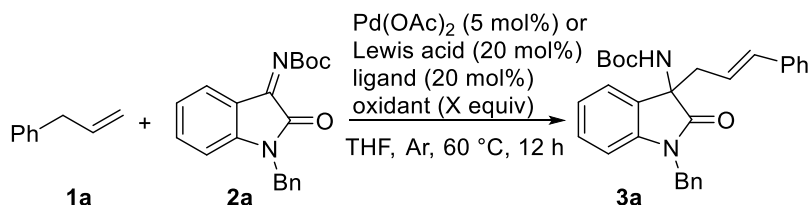
2. Screenings for the oxidative nucleophilic allylation

2.1 Unsuccessful exploration of allylbenzene **1a** and other electrophilic reagents



More electrophilic reagents were explored in the reactions with allylbenzene **1a** under similar catalytic conditions. Unfortunately, the reagents outlined in the above scheme did not react with allylbenzene **1a** or failed to give the desired allylation products.

2.2 Control experiments for the oxidative nucleophilic allylation of allylbenzene **1a** and isatin-derived ketimine **2a**

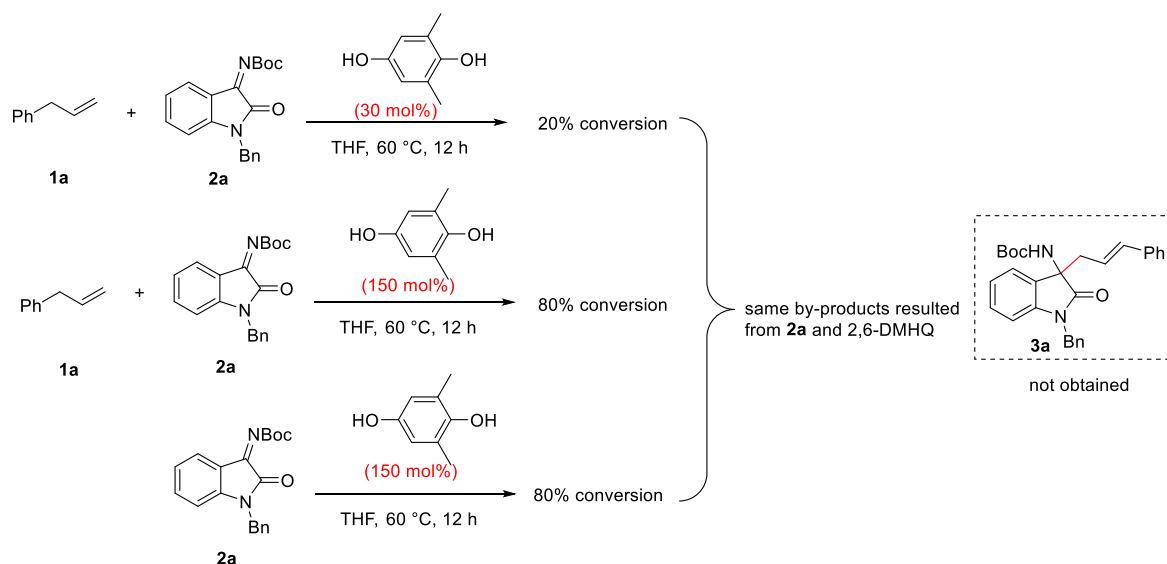


entry ^a	[Pd]	Lewis acid	base	ligand	oxidant	solvent	yield (%) ^b
1 ^c	Pd(OAc) ₂	/	/	PPh ₃	2,6-DMBQ	THF	40
2	Pd(OAc) ₂	/	/	PPh ₃	2,6-DMBQ	THF	52
3	/	/	/	PPh ₃	2,6-DMBQ	THF	NR
4	Pd(OAc) ₂	/	/	/	2,6-DMBQ	THF	NR

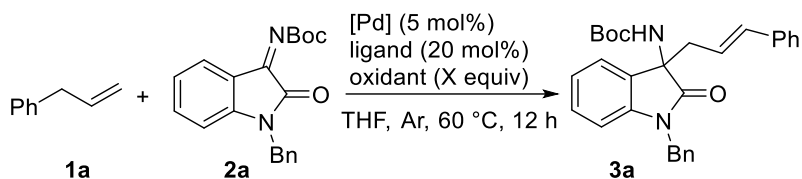
5	Pd(OAc) ₂	/	/	PPh ₃	/	THF	NR
6 ^d	Pd(OAc) ₂	/	/	PPh ₃	2,6-DMBQ	THF	NR
7	/	Sc(OTf) ₃	/	/	/	THF	NR
8	/	Zn(OAc) ₂	/	/	/	THF	NR
9	/	AlCl ₃	/	/	/	THF	NR
10	/	FeCl ₃	/	/	/	THF	NR
11 ^e	Pd(OAc) ₂	/	<i>t</i> -BuOK	PPh ₃	/	THF	NR
12 ^e	Pd(OAc) ₂	/	Cs ₂ CO ₃	PPh ₃	/	THF	NR
13 ^e	Pd(OAc) ₂	/	Et ₃ N	PPh ₃	/	THF	NR
14 ^e	Pd(OAc) ₂	/	NaHCO ₃	PPh ₃	/	THF	NR
15 ^e	Pd(OAc) ₂	/	/	PPh ₃	PhI(OAc) ₂	THF	NR
16 ^f	Pd(OAc) ₂	/	/	PPh ₃	/	THF	NR

^aUnless noted otherwise, reactions were performed with allylbenzene **1a** (0.25 mmol), isatin ketimine **2a** (0.1 mmol), [Pd] (5 mol%), ligand (20 mol%) and oxidant (0.15 mmol) in distilled THF (1.0 mL) at 60 °C for 12 h. ^bYield of the isolated **3a**. ^cAt 50 °C. ^dWith 2,6-DMBQ (10 mol%). ^eWith isoquinoline-1,3,4-trione-derived ketimine **6a**. ^fWith Pd(OAc)₂ (1.0 equiv) and PPh₃ (4.0 equiv). NR = No reaction.

Moreover, hydroquinone has been known as a viable catalyst for a carbonyl-ene reaction (*J. Am. Chem. Soc.*, **1960**, 82, 5411). Thus, control experiment between **1a** and **2a** in the presence of 2,6-dimethylhydroquinone were conducted, but only unwanted byproducts were observed, demonstrating that the current allylation of activated ketimine did not proceed through hydroquinone-catalyzed ene reaction.



2.3 Detailed screening conditions for the oxidative nucleophilic allylation of allylbenzene 1a and isatin-derived ketimine 2a



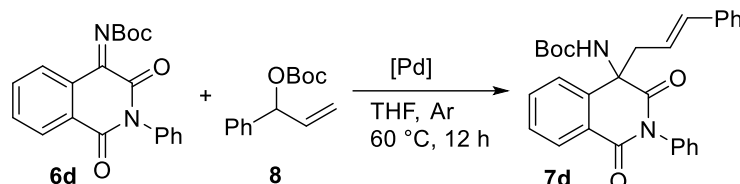
entry ^a	[Pd]	ligand	oxidant	X	additive	solvent	yield (%) ^b
1 ^c	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	/	THF	52
2 ^d	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	/	THF	44
3	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	/	THF	62
4	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	/	toluene	39
5	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	/	dioxane	42
6	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	/	MTBE	49
7	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	/	<i>n</i> Bu ₂ O	trace
8	Pd(OAc) ₂	(4-MeC ₆ H ₄) ₃ P	2,6-DMBQ	1.5	/	THF	53
9	Pd(OAc) ₂	(4-FC ₆ H ₄) ₃ P	2,6-DMBQ	1.5	/	THF	trace
10	Pd(OAc) ₂	PCy ₃	2,6-DMBQ	1.5	/	THF	NR
11	Pd(OAc) ₂	PBu ₃	2,6-DMBQ	1.5	/	THF	NR
12	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS	THF	trace
13	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/PhCO ₂ H	THF	50
14	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	68
15	Pd(OAc) ₂	PPh ₃	BQ	1.5	3 Å MS/H ₂ O	THF	bad conv.
16	Pd(OAc) ₂	PPh ₃	2,5-DMBQ	1.5	3 Å MS/H ₂ O	THF	66
17	Pd(OAc) ₂	PPh ₃	2,6-DTBQ	1.5	3 Å MS/H ₂ O	THF	trace
18	Pd(OAc) ₂	PPh ₃	phenyl- <i>p</i> -benzoquinone	1.5	3 Å MS/H ₂ O	THF	trace
19	Pd(OAc) ₂	PPh ₃	DDQ	1.5	3 Å MS/H ₂ O	THF	NR
20	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.0	3 Å MS/H ₂ O	THF	43
21	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.25	3 Å MS/H ₂ O	THF	50
22	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.75	3 Å MS/H ₂ O	THF	52
23 ^e	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	58
24 ^f	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	67
25 ^g	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	65
26	PdCl ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	NR
27	Pd(PPh ₃) ₄	/	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	trace
28	Pd ₂ (dba) ₃	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	trace
29	Pd(TFA) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	NR
30 ^h	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	no product
31 ⁱ	Pd(OAc) ₂	PPh ₃	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	no product

32 ^j	Pd(PPh ₃) ₄	/	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	51
33 ^k	Pd(PPh ₃) ₄	/	2,6-DMBQ	1.5	3 Å MS/H ₂ O	THF	49

^aUnless noted otherwise, reactions were performed with allylbenzene **1a** (0.25 mmol), isatin ketimine **2a** (0.1 mmol), [Pd] (5 mol%), ligand (20 mol%) and oxidant (0.15 mmol) in distilled THF (2.0 mL) at 60 °C for 12 h. For 3 Å MS (50 mg); H₂O (2 µL); PhCO₂H (20 mol%). ^bYield of the isolated **3a**. ^cIn THF (1.0 mL). ^dIn THF (0.4 mL). ^eWith allylbenzene **1a** (0.20 mmol). ^fWith allylbenzene **1a** (0.30 mmol). ^gWith PPh₃ (10 mol%). ^hWith *n*-Bu₄NBr (20 mol%). ⁱWith *n*-Bu₄NCl (20 mol%). ^jWith PhCO₂H (20 mol%). ^kWith HOAc (20 mol%). NR = No reaction.

3. Mechanism study for the umpolung allylation reactions

3.1 Reactions with allylic carbonate



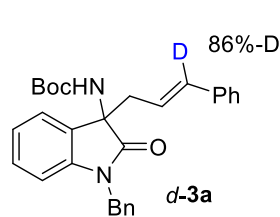
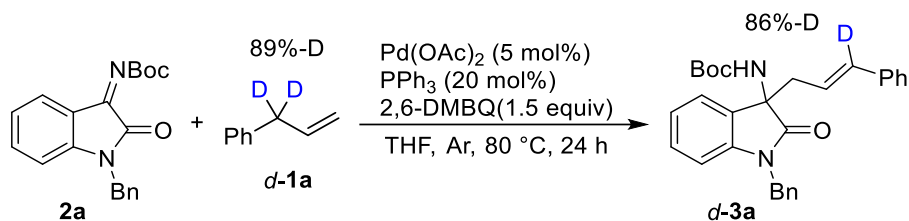
Procedure A: Pd(PPh₃)₄ (1.0 equiv) 63% yield
 Procedure B: Pd(OAc)₂ (1.0 equiv)/PPh₃ (4.0 equiv) 66% yield
 Procedure C: Pd(OAc)₂ (5 mol%)/PPh₃ (20 mol%) trace

Procedure A: *Tert*-butyl (1,3-dioxo-2-phenyl-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6d** (17.5 mg, 0.0499 mmol), Pd(PPh₃)₄ (57.8 mg, 0.0500 mmol, 1.0 equiv) and *tert*-butyl (1-phenylallyl) carbonate **8** (29.3 mg, 0.125 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (0.5 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7d**: 14.8 mg (0.0316 mmol), as a white solid, 63% yield.

Procedure B: *Tert*-butyl (1,3-dioxo-2-phenyl-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6d** (17.5 mg, 0.0499 mmol), Pd(OAc)₂ (11.2 mg, 0.0499 mmol, 1.0 equiv), PPh₃ (52.5 mg, 0.200 mmol, 4.0 equiv) and *tert*-butyl (1-phenylallyl) carbonate **8** (29.3 mg, 0.125 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (0.5 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the solvent was evaporated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7d**: 15.5 mg (0.0331 mmol), as a white solid, 66% yield.

Procedure C: *Tert*-butyl (1,3-dioxo-2-phenyl-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6d** (17.5 mg, 0.0499 mmol), Pd(OAc)₂ (0.6 mg, 0.0027 mmol, 5 mol%), PPh₃ (2.6 mg, 0.0099 mmol, 20 mol%) and *tert*-butyl (1-phenylallyl) carbonate **8** (29.3 mg, 0.125 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (0.5 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), only trace amount of product **7d** was generated.

3.2 Deuterium experiments

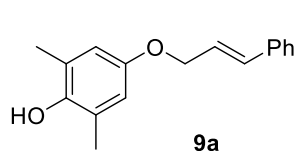
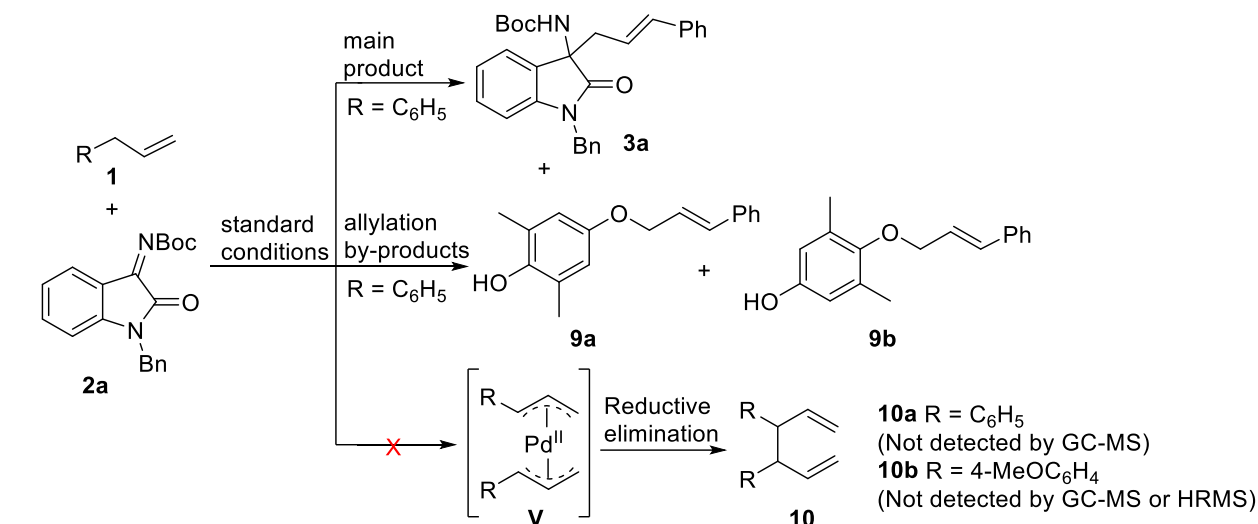


Synthesis of (*d*-3a): *Tert*-butyl (*E*)-(1-benzyl-2-oxoindolin-3-ylidene)carbamate **2a** (33.6 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and (allyl-1,1-*d*₂)benzene

***d*-1a** (35.6 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product ***d*-3a**: 28.8 mg (0.0632 mmol), as a white solid, 63% yield, D% = 86%; m.p. 157–159 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.49–6.92 (m, 13H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 15.6 Hz, 0.14H), 6.12–5.80 (m, 1H), 5.48–4.92 (m, 2H), 4.64 (s, 1H), 2.82 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H), 2.70 (dd, *J* = 13.2 Hz, 8.0 Hz, 1H), 1.26 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 176.7, 153.7, 142.5, 136.4, 135.7, 128.8, 128.7, 128.6, 127.8, 127.4, 127.2, 126.49, 126.47, 122.73, 122.65, 120.9, 109.3,

80.5, 61.5, 44.2, 41.6, 28.1; HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $[C_{29}H_{29}DN_2O_3 + Na]^+$ 478.2211; Found 478.2209.

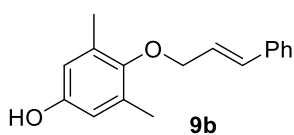
3.3 Characterisation of by-products in the oxidative nucleophilic allylation reaction



4-(Cinnamyloxy)-2,6-dimethylphenol (9a): *Tert*-butyl

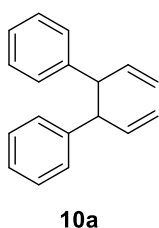
(1-benzyl-2-oxindolin-3-ylidene)carbamate **2a** (33.6 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 18:1) to give the **9a**:

11.2 mg (0.0440 mmol), as a white solid, consumed 18% of allylbenzene; m.p. 82–84 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.40 (d, $J = 7.2$ Hz, 2H), 7.32 (t, $J = 7.2$ Hz, 2H), 7.28–7.20 (m, 1H), 6.71 (d, $J = 16.0$ Hz, 1H), 6.61 (s, 2H), 6.48–6.30 (m, 1H), 4.61 (d, $J = 4.8$ Hz, 2H), 4.27 (s, 1H), 2.23 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 152.1, 146.4, 136.6, 132.6, 128.6, 127.8, 126.6, 125.0, 124.1, 114.9, 69.3, 16.3; HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $[C_{17}H_{18}O_2 + H]^+$ 255.1380; Found 255.1375.

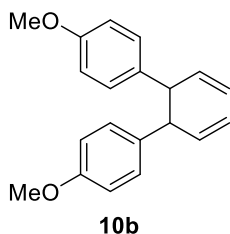


4-(Cinnamyloxy)-3,5-dimethylphenol (9b): *Tert*-butyl (1-benzyl-2-oxoindolin-3-ylidene)carbamate **2a** (33.6 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%),

2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 18:1) to give the **9b**: 12.0 mg (0.0472 mmol), as a white solid, consumed 19% of allylbenzene; m.p. 74–76 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.42 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.30–7.21 (m, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.49 (s, 2H), 6.48–6.41 (m, 1H), 4.57 (s, 1H), 4.42 (d, *J* = 5.6 Hz, 1H), 2.26 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 150.2, 148.7, 135.6, 131.4, 131.2, 127.6, 126.8, 125.5, 124.3, 114.0, 72.1, 15.5; HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₇H₁₈O₂ + H]⁺ 255.1380; Found 255.1373.



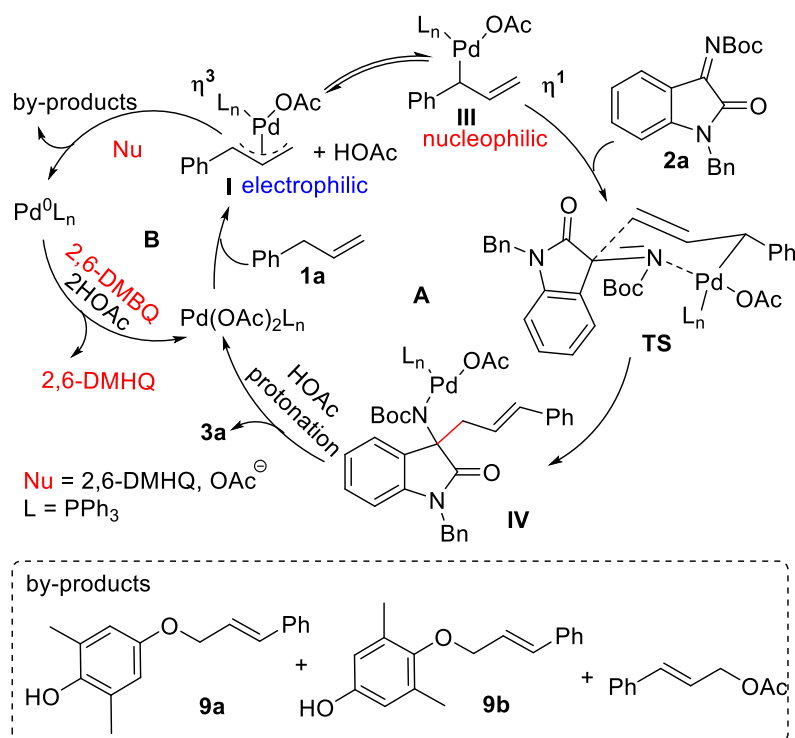
10a



10b

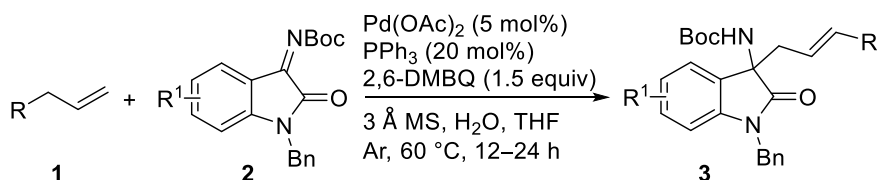
To further verifying whether the reaction involves the bisallylpalladium intermediate **V**, GC-MS and HRMS were used to monitor the formation of the reductive elimination product **10** of the η^3,η^3 -bisallylpalladium complex. However, the signal of the possible allyl-allyl cross-coupling product **10a** was not detected by GC-MS and **10b** was not detected by GC-MS or HRMS. As a result, the η^3,η^3 -bisallylpalladium species might not be formed in the current catalytic reaction, and the reaction might proceed via isomerisation to η^1 -allylpalladium species, as reported in the literature (*Chem. Commun.*, 2015, 51, 8027).

3.4 Plausible mechanism of oxidative nucleophilic allylation

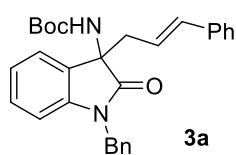


4. General procedure for the oxidative nucleophilic allylation

4.1 General procedure for the oxidative nucleophilic allylation of alkenes **1** and isatin-derived ketimines **2**

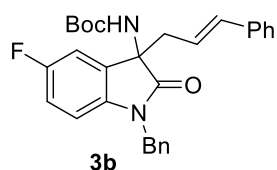


General procedure: Isatin-derived ketimine **2** (0.1 mmol), $\text{Pd}(\text{OAc})_2$ (0.005 mmol, 5 mol%), PPh_3 (0.02 mmol, 20 mol%), 2,6-DMBQ (0.15 mmol, 1.5 equiv), 3 Å MS (50 mg) and alkene **1** (0.25 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H_2O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The mixture was stirred at indicated temperature for 12–24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the product **3**.



Tert-butyl (1-benzyl-3-cinnamyl-2-oxoindolin-3-yl)carbamate (3a):

Tert-butyl (1-benzyl-2-oxoindolin-3-ylidene)carbamate 2a (33.6 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **3a**: 31.0 mg (0.0682 mmol), as a white solid, 68% yield; m.p. 158–160 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.36–7.20 (m, 8H), 7.21–7.13 (m, 2H), 7.13–7.02 (m, 3H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.12–5.79 (m, 1H), 5.42–5.05 (m, 2H), 4.63 (brs, 1H), 2.82 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H), 2.70 (dd, *J* = 13.2 Hz, 7.6 Hz, 1H), 1.26 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 176.7, 153.8, 142.5, 136.5, 135.9, 135.7, 130.4, 128.8, 128.7, 128.6, 127.8, 127.4, 127.2, 126.5, 122.73, 122.65, 121.0, 109.3, 80.5, 61.5, 44.2, 41.6, 28.1; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₂₉H₃₀N₂O₃ + Na]⁺ 477.2149; Found 477.2148.



Tert-butyl (1-benzyl-3-cinnamyl-5-fluoro-2-oxoindolin-3-yl)carbamate

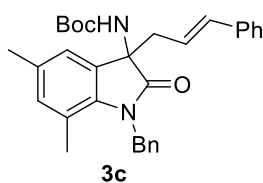
(3b): **Tert-butyl (1-benzyl-5-fluoro-2-oxoindolin-3-ylidene)carbamate 2b**

(35.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃

(5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5

equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture

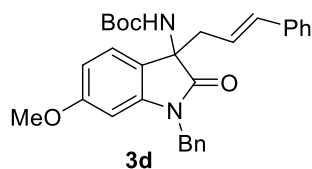
was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **3b**: 30.5 mg (0.0645 mmol), as a white solid, 65% yield; m.p. 134–136 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.36–7.21 (m, 7H), 7.20–7.02 (m, 4H), 6.86 (td, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.59–6.54 (m, 1H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.02–5.83 (m, 1H), 5.35–5.06 (m, 2H), 4.66 (s, 1H), 2.81 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H), 2.71 (dd, *J* = 13.2 Hz, 8.0 Hz, 1H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 176.5, 159.3 (¹*J*_{FC} = 241.2 Hz), 153.7, 138.4, 136.3 (³*J*_{FC} = 5.6 Hz), 135.4, 128.8, 128.7, 128.0, 127.5, 127.2, 126.5, 120.4, 115.0 (²*J*_{FC} = 23.6 Hz), 110.9 (²*J*_{FC} = 24.9 Hz), 109.9, 80.8, 61.8, 44.3, 41.5, 28.1; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –120.3; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₂₉H₂₉FN₂O₃ + Na]⁺ 495.2054; Found 495.2054.



Tert-butyl (1-benzyl-3-cinnamyl-5,7-dimethyl-2-oxoindolin-3-yl)

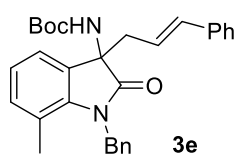
carbamate (3c): *Tert*-butyl (1-benzyl-5,7-dimethyl-2-oxoindolin-3-ylidene)-carbamate **2c** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150

mmol, 1.5 equiv), 3Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **3c**: 31.4 mg (0.0651 mmol), as a yellow solid, 65% yield; m.p. 193–195 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.36–7.23 (m, 5H), 7.24–7.17 (m, 2H), 7.18–7.05 (m, 3H), 7.00 (s, 1H), 6.77 (s, 1H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.18–5.96 (m, 1H), 5.36–5.13 (m, 2H), 5.04 (s, 1H), 2.78 (dd, *J* = 13.2 Hz, 6.8 Hz, 1H), 2.69 (dd, *J* = 13.2 Hz, 8.0 Hz, 1H), 2.29 (s, 3H), 2.16 (s, 3H), 1.30 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 177.6, 153.8, 138.0, 137.8, 136.6, 135.8, 133.3, 132.1, 131.4, 128.7, 128.6, 127.8, 126.9, 126.5, 125.6, 125.8, 121.4, 119.5, 80.4, 60.8, 45.4, 42.2, 28.1, 20.9, 18.6; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₁H₃₄N₂O₃ + Na]⁺ 505.2462; Found 505.2461.



Tert-butyl (1-benzyl-3-cinnamyl-6-methoxy-2-oxoindolin-3-yl)carbamate (3d):

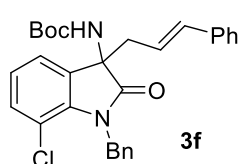
Tert-butyl (1-benzyl-6-methoxy-2-oxoindolin-3-ylidene) carbamate **2d** (36.6 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 6:1) to give the product **3d**: 32.3 mg (0.0667 mmol), as a white solid, 67% yield; m.p. 134–136 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.34–7.18 (m, 8H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.2 Hz, 2H), 6.58–6.53 (m, 1H), 6.51 (d, *J* = 15.2 Hz, 1H), 6.25 (d, *J* = 2.0 Hz, 1H), 6.06–5.86 (m, 1H), 5.41–5.09 (m, 2H), 4.60 (s, 1H), 3.71 (s, 3H), 2.80 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H), 2.68 (dd, *J* = 13.2 Hz, 8.4 Hz, 1H), 1.28 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 177.2, 160.4, 153.8, 143.8, 136.5, 135.8, 135.7, 128.7, 128.6, 127.8, 127.4, 127.2, 126.5, 123.5, 122.3, 121.3, 106.2, 97.5, 80.4, 61.2, 55.4, 44.2, 41.7, 28.2; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₀H₃₂N₂O₄ + Na]⁺ 507.2254; Found 507.2249.



Tert-butyl (1-benzyl-3-cinnamyl-7-methyl-2-oxoindolin-3-yl)carbamate

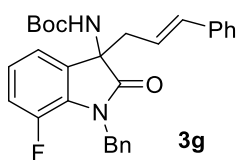
(3e): *Tert*-butyl (1-benzyl-7-methyl-2-oxoindolin-3-ylidene)carbamate **2e** (35.0 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The

combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **3e**: 30.2 mg (0.06444 mmol), as a white solid, 64% yield; m.p. 187–189 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43–7.06 (m, 11H), 7.05–6.92 (m, 2H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.24–5.94 (m, 1H), 5.39–5.18 (m, 1H), 5.05 (s, 1H), 2.80 (dd, *J* = 13.2 Hz, 6.8 Hz, 1H), 2.70 (dd, *J* = 13.2 Hz, 8.0 Hz, 1H), 2.22 (s, 3H), 1.29 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 177.7, 153.7, 140.5, 137.8, 136.5, 135.9, 132.8, 131.3, 128.7, 128.6, 127.8, 126.9, 126.5, 125.8, 122.7, 121.2, 120.7, 119.8, 80.4, 60.8, 45.4, 42.1, 28.1, 18.2; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₀H₃₂N₂O₃ + Na]⁺ 491.2305; Found 491.2305.



Tert-butyl (1-benzyl-7-chloro-3-cinnamyl-2-oxoindolin-3-yl)carbamate (3f):

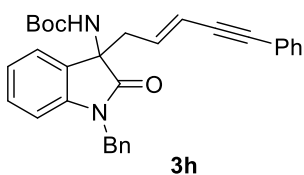
Tert-butyl (1-benzyl-7-chloro-2-oxoindolin-3-ylidene)carbamate 2f (37.1 mg, 0.100 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **3f**: 31.7 mg (0.0648 mmol), as a white solid, 65% yield; m.p. 161–164 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.37–7.23 (m, 7H), 7.23–7.09 (m, 5H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.14–5.90 (m, 1H), 5.51–5.08 (m, 3H), 2.77 (dd, *J* = 13.6 Hz, 7.2 Hz, 1H), 2.67 (dd, *J* = 13.2 Hz, 8.0 Hz, 1H), 1.29 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 177.3, 153.7, 138.6, 137.6, 136.4, 136.3, 133.6, 131.3, 128.6, 128.4, 128.0, 126.9, 126.51, 126.47, 123.5, 121.2, 120.4, 115.6, 80.8, 60.9, 45.2, 41.8, 28.1; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₂₉H₂₉³⁵ClN₂O₃ + Na]⁺ 511.1759; Found 511.1758; Calcd for [C₂₉H₂₉³⁷ClN₂O₃ + Na]⁺ 513.1729; Found 513.1743.



Tert-butyl (1-benzyl-3-cinnamyl-7-fluoro-2-oxoindolin-3-yl)carbamate (3g):

Tert-butyl (1-benzyl-7-fluoro-2-oxoindolin-3-ylidene)carbamate 2g (35.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020

mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **3g**: 28.2 mg (0.0597 mmol), as a white solid, 60% yield; m.p. 172–174 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.34 (d, *J* = 7.2 Hz, 2H), 7.31–7.19 (m, 5H), 7.19–7.11 (m, 3H), 7.08 (d, *J* = 6.8 Hz, 1H), 7.05–6.88 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.06–5.87 (m, 1H), 5.38–5.07 (m, 2H), 4.92 (s, 1H), 2.76 (dd, *J* = 13.6 Hz, 7.6 Hz, 1H), 2.65 (dd, *J* = 13.6 Hz, 8.0 Hz, 1H), 1.26 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 176.4, 153.7, 147.5 (¹*J*_{FC} = 244.5 Hz), 137.0, 136.3, 136.2, 129.0 (³*J*_{FC} = 8.8 Hz), 128.6, 128.5, 127.9, 127.4 (³*J*_{FC} = 8.8 Hz), 126.5, 123.33, 123.26, 120.4, 118.6 (⁴*J*_{FC} = 3.2 Hz), 117.0 (²*J*_{FC} = 19.7 Hz), 80.8, 61.5, 45.7, 45.6, 41.7, 28.0; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –133.8; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₂₉H₂₉FN₂O₃ + Na]⁺ 495.2054; Found 495.2055.



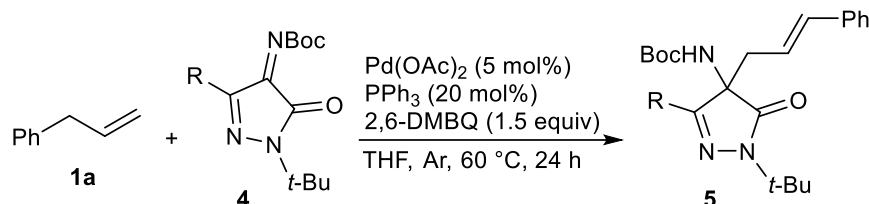
Tert-butyl (E)-(1-benzyl-2-oxo-3-(5-phenylpent-2-en-4-yn-1-yl)

indolin-3-yl)carbamate (3h): **Tert-butyl (1-benzyl-2-oxoindolin-3-ylidene) carbamate 2a** (33.6 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4

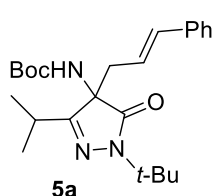
mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and pent-4-en-1-yn-1-ylbenzene **1b** (35.6 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then H₂O (2 μL) and distilled THF (2.0 mL) were added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 24 h. After completion (monitored by TLC),

the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **3h**: 20.2 mg (0.0422 mmol), as a yellow solid, 42% yield; m.p. 122–125 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.46–7.38 (m, 2H), 7.39–7.24 (m, 8H), 7.24–7.14 (m, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.08–5.93 (m, 1H), 5.85 (d, *J* = 15.8 Hz, 1H), 5.32–5.08 (m, 2H), 4.69 (s, 1H), 2.78 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H), 2.63 (dd, *J* = 13.2 Hz, 7.6 Hz, 1H), 1.26 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 176.4, 153.7, 142.4, 135.7, 134.7, 131.6, 130.1, 128.91, 128.85, 128.39, 128.37, 127.5, 127.3, 123.0, 122.9, 122.8, 116.0, 109.4, 90.1, 87.2, 80.6, 61.2, 44.2, 41.5, 28.1; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₁H₃₀N₂O₃ + Na]⁺ 501.2149; Found 501.2140.

4.2 General procedure for the oxidative nucleophilic allylation of alkenes **1** and pyrazoledione-derived ketimines **4**

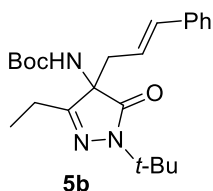


General procedure: Pyrazoledione-derived ketimine **4** (0.1 mmol), Pd(OAc)₂ (0.005 mmol, 5 mol%), PPh₃ (0.02 mmol, 20 mol%), 2,6-DMBQ (0.15 mmol, 1.5 equiv) and allylbenzene **1a** (0.25 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the product **5**.



Tert-butyl (1-(tert-butyl)-4-cinnamyl-3-isopropyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)carbamate (5a): *Tert*-butyl (1-(*tert*-butyl)-3-isopropyl-5-oxo-1,5-dihydro-4*H*-pyrazol-4-ylidene)carbamate **4a** (29.5 mg, 0.0999 mmol),

Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **5a**: 30.5 mg (0.0737 mmol), as a yellow solid, 74% yield; m.p. 129–132 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.31–7.28 (m, 4H), 7.27–7.19 (m, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.13–5.73 (m, 1H), 5.02 (s, 1H), 2.69–2.59 (m, 1H), 2.55 (d, *J* = 7.6 Hz, 2H), 1.44 (s, 9H), 1.40 (s, 9H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.9, 162.8, 153.6, 136.5, 135.7, 128.6, 127.8, 126.6, 120.1, 65.7, 57.5, 38.2, 28.2, 28.1, 20.8, 20.4; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₂₄H₃₅N₃O₃ + Na]⁺ 436.2571; Found 436.2571.

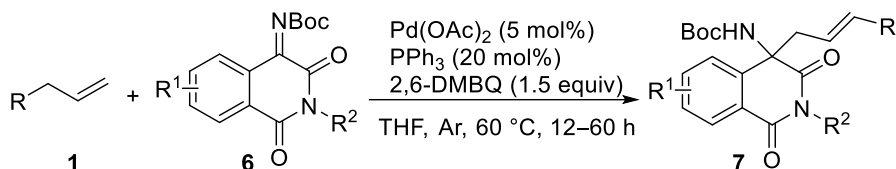


Tert-butyl (1-(tert-butyl)-4-cinnamyl-3-ethyl-5-oxo-4,5-dihydro-1H-pyrazol-4-yl)carbamate (5b): *Tert*-butyl (1-(*tert*-butyl)-3-ethyl-5-oxo-1,5-dihydro-4H-pyrazol-4-ylidene)carbamate **4b** (28.1 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4

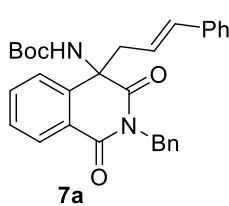
mg, 0.150 mmol, 1.5 equiv) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **5b**: 30.1 mg (0.0753 mmol), as a white solid, 75% yield; m.p. 112–115 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.52–7.09 (m, 5H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.06–5.83 (m, 1H), 5.08 (s, 1H), 2.59–2.44 (m, 2H), 2.39–2.28 (m, 2H), 1.46 (s, 9H), 1.39 (s, 9H), 1.23 (t, *J* = 7.6 Hz, 3H); ¹³C NMR

(100 MHz, CDCl₃): δ (ppm) 174.0, 160.6, 153.7, 136.5, 135.7, 128.6, 127.8, 126.4, 126.3, 120.0, 80.7, 65.6, 57.4, 38.3, 28.2, 28.1, 21.1, 9.5; HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $[C_{23}H_{33}N_3O_3 + Na]^+$ 422.2414; Found 422.2414.

4.3 General procedure for the oxidative nucleophilic allylation of alkenes **1** and isoquinoline-1,3,4-trione-derived ketimines **6**



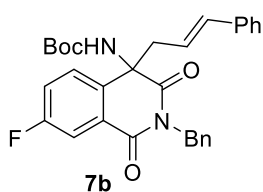
General procedure: Isoquinoline-1,3,4-trione-derived ketimine **6** (0.1 mmol), Pd(OAc)₂ (0.005 mmol, 5 mol%), PPh₃ (0.02 mmol, 20 mol%), 2,6-DMBQ (0.15 mmol, 1.5 equiv) and alkene **1** (0.25 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at indicated temperature for 12–60 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the product **7**.



Tert-butyl (2-benzyl-4-cinnamyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7a): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ

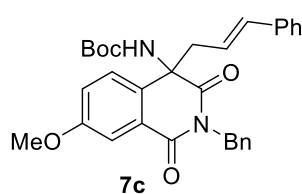
(20.4 mg, 0.150 mmol, 1.5 equiv) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the

product **7a**: 44.9 mg (0.0930 mmol), as a white solid, 93% yield; m.p. 139–141 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.21 (d, *J* = 7.6 Hz, 1H), 7.72–7.54 (m, 2H), 7.53–7.41 (m, 3H), 7.31–7.14 (m, 6H), 7.03 (d, *J* = 6.8 Hz, 2H), 6.16 (d, *J* = 15.6 Hz, 1H), 5.65 (s, 1H), 5.58–5.43 (m, 1H), 5.30–4.98 (m, 2H), 2.85–2.50 (m, 2H), 1.53–0.68 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.7, 163.7, 136.9, 136.5, 136.04, 134.00, 128.9, 128.5, 128.4, 128.04, 128.01, 127.5, 126.4, 125.1, 124.5, 119.7, 81.1, 61.7, 47.0, 44.0, 28.1; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₀H₃₀N₂O₄ + Na]⁺ 505.2098; Found 505.2102.



Tert-butyl (2-benzyl-4-cinnamyl-7-fluoro-1,3-dioxo-1,2,3,4-tetrahydro

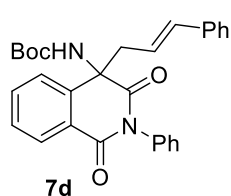
isoquinolin-4-yl)carbamate (7b): *Tert*-butyl (2-benzyl-7-fluoro-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6b** (38.2 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7b**: 44.0 mg (0.0879 mmol), as a white solid, 88% yield; m.p. 127–129 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.87 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 7.58 (dd, *J* = 8.8 Hz, 4.8 Hz, 1H), 7.49–7.41 (m, 1H), 7.35 (td, *J* = 8.0 Hz, 2.8 Hz, 1H), 7.30–7.15 (m, 6H), 7.11–7.00 (m, 2H), 6.16 (d, *J* = 15.6 Hz, 1H), 5.54 (s, 1H), 5.53–5.43 (m, 1H), 5.29–4.96 (m, 2H), 2.91–2.51 (m, 2H), 1.53–0.59 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.4, 162.7 (⁴*J*_{FC} = 2.6 Hz), 162.1 (¹*J*_{FC} = 248.3 Hz), 136.8, 136.6, 135.9, 129.0, 128.6, 128.4, 128.1, 127.6, 127.1 (³*J*_{FC} = 7.7 Hz), 127.0–126.6 (m), 126.4, 121.5 (²*J*_{FC} = 22.4 Hz), 119.3, 115.1 (²*J*_{FC} = 22.9 Hz), 81.3, 61.4, 47.0, 44.2, 28.0; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –112.9; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₀H₂₉FN₂O₄ + Na]⁺ 523.2004; Found 523.2004.



Tert-butyl (2-benzyl-4-cinnamyl-7-methoxy-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7c): *Tert*-butyl (2-benzyl-7-methoxy-

1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6c** (39.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg,

0.020 mmol, 20 mol %), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **7c**: 42.3 mg (0.0825 mmol), as a white solid, 83% yield; m.p. 106–108 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.67 (d, *J* = 2.4 Hz, 1H), 7.53–7.42 (m, 3H), 7.25–7.17 (m, 7H), 7.07–7.01 (m, 2H), 6.19 (d, *J* = 16.0 Hz, 1H), 5.66–5.43 (m, 2H), 5.27–5.01 (m, 2H), 3.87 (s, 3H), 2.84–2.48 (m, 2H), 1.50–0.74 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.8, 163.7, 159.2, 136.9, 136.3, 136.1, 134.1, 129.1, 128.5, 128.4, 128.0, 127.4, 126.4, 126.1, 126.0, 122.3, 119.8, 111.0, 81.0, 61.3, 55.6, 47.0, 44.1, 28.0; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₁H₃₂N₂O₅ + Na]⁺ 535.2203; Found 535.2199.

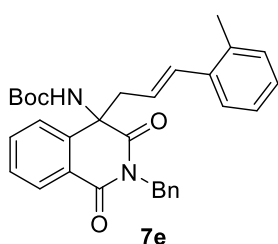


Tert-butyl (4-cinnamyl-1,3-dioxo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7d): *Tert*-butyl (1,3-dioxo-2-phenyl-2,3-dihydroisoquinolin-

4(1*H*)-ylidene)carbamate **6d** (35.0 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ

(20.4 mg, 0.150 mmol, 1.5 equiv) and allylbenzene **1a** (29.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture

was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7d**: 41.5 mg (0.0886 mmol), as a white solid, 89% yield; m.p. 195–197 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.26 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.78–7.64 (m, 2H), 7.56–7.48 (m, 1H), 7.47–7.35 (m, 3H), 7.32–7.19 (m, 5H), 7.09 (d, *J* = 6.0 Hz, 2H), 6.44 (d, *J* = 15.6 Hz, 1H), 5.83–5.59 (m, 2H), 2.91 (dd, *J* = 12.8 Hz, 8.8 Hz, 1H), 2.83 (dd, *J* = 12.8 Hz, 6.4 Hz, 1H), 1.53–0.95 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.4, 163.9, 136.8, 136.1, 135.3, 134.3, 129.2, 129.1, 128.8, 128.6, 128.5, 128.22, 128.20, 126.5, 125.4, 124.7, 119.8, 81.1, 62.1, 47.1, 28.1; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₂₉H₂₈N₂O₄ + Na]⁺ 491.1941; Found 491.1941.



Tert-butyl (*E*)-(2-benzyl-1,3-dioxo-4-(3-(*o*-tolyl)allyl)-1,2,3,4-tetrahydro

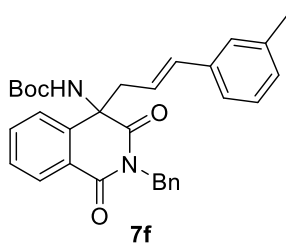
isoquinolin-4-yl)carbamate (7e): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydro

isoquinolin-4(*1H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol),

Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20

mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and

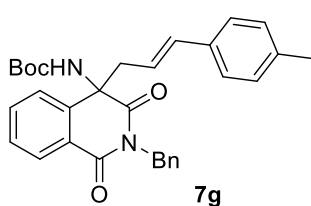
1-allyl-2-methylbenzene **1c** (33.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 9:1) to give the product **7e**: 46.2 mg (0.0930 mmol), as a yellow solid, 93% yield; m.p. 124–126 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.22 (d, *J* = 8.0 Hz, 1H), 7.71–7.55 (m, 2H), 7.51–7.35 (m, 3H), 7.22–6.86 (m, 7H), 6.34 (d, *J* = 15.6 Hz, 1H), 5.62 (s, 1H), 5.47–5.32 (m, 1H), 5.28–5.03 (m, 2H), 2.85–2.52 (m, 2H), 2.11 (s, 3H), 1.52–0.62 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.7, 163.7, 136.8, 135.27, 135.25, 134.6, 134.0, 130.2, 128.9, 128.3, 128.0, 127.9, 127.4, 126.2, 125.9, 125.2, 124.6, 121.0, 81.1, 61.7, 47.3, 44.0, 27.9, 19.6; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₁H₃₂N₂O₄ + Na]⁺ 519.2254; Found 519.2254.



Tert-butyl (E)-(2-benzyl-1,3-dioxo-4-(3-(*m*-tolyl)allyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7f): *Tert*-butyl (2-benzyl-1,3-dioxo-

2,3-dihydro isoquinolin-4(*1H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and

1-allyl-3-methylbenzene **1d** (33.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7f**: 46.8 mg (0.0942 mmol), as a white solid, 94% yield; m.p. 130–132 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.21 (dd, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.74–7.55 (m, 2H), 7.52–7.38 (m, 3H), 7.25–7.10 (m, 4H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.95–6.78 (m, 2H), 6.16 (d, *J* = 16.0 Hz, 1H), 5.56 (s, 1H), 5.55–5.46 (m, 1H), 5.29–5.04 (m, 2H), 2.90–2.53 (m, 2H), 2.30 (s, 3H), 1.55–0.54 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.6, 163.7, 138.1, 136.9, 136.6, 136.0, 133.9, 128.8, 128.43, 128.36, 128.0, 127.4, 127.2, 125.1, 124.5, 123.5, 119.4, 81.0, 61.7, 47.1, 44.0, 27.9, 21.3; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₁H₃₂N₂O₄ + Na]⁺ 519.2254; Found 519.2250.

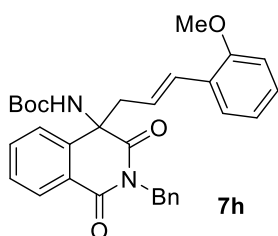


Tert-butyl (E)-(2-benzyl-1,3-dioxo-4-(3-(*p*-tolyl)allyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7g): *Tert*-butyl (2-benzyl-1,3-

dioxo-2,3-dihydroisoquinolin-4(*1H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg,

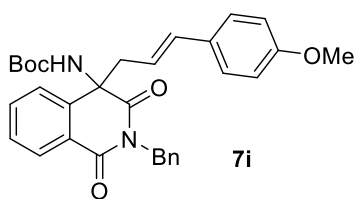
0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 1-allyl-4-methylbenzene **1e** (33.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was

stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7g**: 45.5 mg (0.0916 mmol), as a white solid, 92% yield; m.p. 103–106 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.20 (d, *J* = 7.2 Hz, 1H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.52–7.39 (m, 3H), 7.25–7.16 (m, 3H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 15.6 Hz, 1H), 5.54 (s, 1H), 5.52–5.39 (m, 1H), 5.32–5.01 (m, 2H), 2.86–2.51 (m, 2H), 2.31 (s, 3H), 1.51–0.58 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.6, 163.7, 137.9, 136.9, 136.4, 134.0, 133.3, 129.2, 129.0, 128.8, 128.4, 128.0, 127.5, 126.3, 125.1, 124.5, 118.5, 81.1, 61.8, 47.1, 44.0, 27.9, 21.2; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₁H₃₂N₂O₄ + Na]⁺ 519.2254; Found 519.2246.



Tert-butyl (E)-(2-benzyl-4-(3-(2-methoxyphenyl)allyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7h): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 1-allyl-2-methoxybenzene **1f** (37.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **7h**: 48.3 mg (0.0942 mmol), as a white solid, 94% yield; m.p. 157–160 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.22 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.51–7.39 (m, 3H), 7.23–7.13 (m, 4H), 7.03 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 5.62–5.49 (m, 2H), 5.28–5.09 (m, 2H), 3.75 (s, 3H), 2.90–2.52 (m, 2H), 1.52–0.57 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.7, 163.8, 156.6, 136.9, 133.9, 131.5, 129.0, 128.3, 127.9, 127.4, 127.2, 125.22, 125.15, 124.5, 120.6, 120.5, 110.7, 81.0,

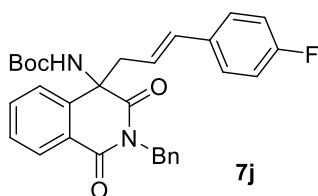
61.8, 55.3, 47.5, 44.0, 28.2; HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $[C_{31}H_{32}N_2O_5 + Na]^+$ 535.2203; Found 535.2195.



Tert-butyl (E)-(2-benzyl-4-(3-(4-methoxyphenyl)allyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7i): *Tert*-butyl

(2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5

mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 1-allyl-4-methoxybenzene **1g** (37.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **7i**: 38.3 mg (0.0747 mmol), as a white solid, 75% yield; m.p. 104–106 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.20 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.51–7.39 (m, 3H), 7.25–7.17 (m, 3H), 7.07–6.89 (m, 2H), 6.89–6.68 (m, 2H), 6.11 (d, *J* = 15.6 Hz, 1H), 5.59 (s, 1H), 5.44–5.31 (m, 1H), 5.25–5.08 (m, 2H), 3.79 (s, 3H), 2.86–2.40 (m, 2H), 1.51–0.62 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.7, 163.7, 159.5, 136.9, 135.9, 133.9, 128.8, 128.4, 128.0, 127.6, 127.4, 125.1, 124.5, 117.3, 113.9, 81.0, 61.8, 55.3, 47.1, 44.0, 27.9; HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $[C_{31}H_{32}N_2O_5 + Na]^+$ 535.2203; Found 535.2198.

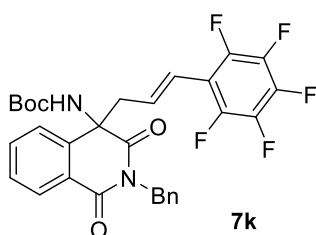


Tert-butyl (E)-(2-benzyl-4-(3-(4-fluorophenyl)allyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7j): *Tert*-butyl (2-benzyl-1,3-

dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg,

0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 1-allyl-4-fluorobenzene **1h** (34.0 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by

syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 36 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7j**: 45.6 mg (0.0911 mmol), as a white solid, 91% yield; m.p. 141–143 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.21 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.52–7.41 (m, 3H), 7.25–7.16 (m, 3H), 7.01–6.84 (m, 4H), 6.07 (d, *J* = 15.2 Hz, 1H), 5.73 (s, 1H), 5.50–5.30 (m, 1H), 5.33–5.02 (m, 2H), 2.94–2.43 (m, 2H), 1.61–0.57 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.6, 163.7, 162.5 (¹*J*_{FC} = 247.2 Hz), 136.9, 135.2, 134.0, 132.2 (⁴*J*_{FC} = 3.3 Hz), 128.9, 128.4, 128.1, 128.0, 127.9, 127.5, 125.2, 124.5, 119.4 (⁴*J*_{FC} = 2.2 Hz), 115.4 (²*J*_{FC} = 21.6 Hz), 81.1, 61.8, 46.9, 44.0, 27.9; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) –113.7; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₀H₂₉FN₂O₄ + Na]⁺ 523.2004; Found 523.2000.

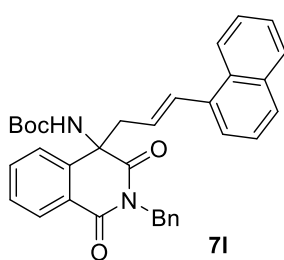


7k

Tert-butyl (E)-(2-benzyl-1,3-dioxo-4-(3-(perfluorophenyl)allyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7k): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150

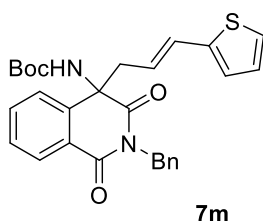
mmol, 1.5 equiv) and 1-allyl-2,3,4,5,6-pentafluorobenzene **1i** (52.0 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 48 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7k**: 50.0 mg (0.0873 mmol), as a white solid, 87% yield; m.p. 153–155 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.25 (d, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.56–7.40 (m, 3H), 7.20–6.98 (m, 3H), 5.98 (d, *J* = 16.4 Hz, 1H), 5.82–5.69 (m, 1H), 5.72

(s, 1H), 5.30–4.95 (m, 2H), 3.05–2.45 (m, 2H), 1.54–0.58 (brs, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 173.5, 163.5, 144.4 ($^1J_{\text{FC}} = 248.0$ Hz), 140.1 ($^1J_{\text{FC}} = 242.5$ Hz), 136.7, 136.6–135.9 (m), 130.1–129.4 (m), 128.9, 128.3, 128.1, 127.3, 125.2, 124.5, 120.2, 111.5–109.6 (m), 81.3, 61.3, 47.7, 43.9, 27.9; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) –142.7, –155.6, –162.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $[\text{C}_{30}\text{H}_{25}\text{F}_5\text{N}_2\text{O}_4 + \text{Na}]^+$ 595.1627; Found 595.1622.



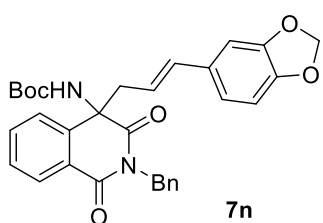
Tert-butyl (E)-(2-benzyl-4-(3-(naphthalen-1-yl)allyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7l): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $\text{Pd}(\text{OAc})_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and

1-allylnaphthalene **1j** (42.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7l**: 49.4 mg (0.0927 mmol), as a yellow solid, 93% yield; m.p. 197–199 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.23 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 7.6$ Hz, 1H), 7.77–7.60 (m, 4H), 7.52–7.39 (m, 5H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.20–6.99 (m, 4H), 6.85 (d, $J = 15.2$ Hz, 1H), 5.68 (s, 1H), 5.61–5.44 (m, 1H), 5.29–5.07 (m, 2H), 3.05–2.63 (m, 2H), 1.51–0.62 (brs, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 173.7, 163.7, 136.7, 134.1, 134.0, 133.7, 133.4, 130.8, 128.9, 128.5, 128.3, 128.1, 127.4, 126.0, 125.8, 125.6, 125.3, 124.6, 124.1, 123.5, 122.8, 81.1, 61.8, 47.3, 44.0, 27.9; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $[\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_4 + \text{Na}]^+$ 555.2254; Found 555.2254.



Tert-butyl (E)-(2-benzyl-1,3-dioxo-4-(3-(thiophen-2-yl)allyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7m): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $\text{Pd}(\text{OAc})_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020

mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 2-allylthiophene **1k** (31.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7m**: 41.5 mg (0.0849 mmol), as a white solid, 85% yield; m.p. 142–144 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.22 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.52–7.42 (m, 3H), 7.26–7.15 (m, 3H), 7.12 (d, *J* = 4.8 Hz, 1H), 6.90 (t, *J* = 3.6 Hz, 1H), 6.74 (d, *J* = 3.6 Hz, 1H), 6.30 (d, *J* = 15.2 Hz, 1H), 5.62 (s, 1H), 5.46–5.30 (m, 1H), 5.29–5.07 (m, 2H), 2.92–2.23 (m, 2H), 1.54–0.66 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.6, 163.6, 140.9, 136.8, 134.0, 129.3, 129.0, 128.4, 128.1, 127.4, 127.3, 126.1, 125.1, 124.8, 124.5, 119.2, 81.1, 61.7, 46.7, 44.0, 27.9; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₂₈H₂₈N₂O₄S + Na]⁺ 511.1662; Found 511.1664.

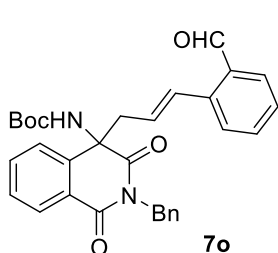


7n

Tert-butyl (E)-(4-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)-2-benzyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7n): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(*1H*)-ylidene) carbamate

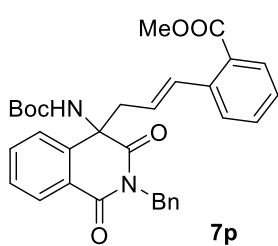
6a (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 5-allylbenzo[*d*][1,3]dioxole **1l** (40.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7n**: 34.6 mg (0.0657 mmol), as a yellow solid, 66% yield; m.p. 91–93 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm)

8.20 (d, $J = 7.6$ Hz, 1H), 7.65 (t, $J = 7.2$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.51–7.41 (m, 3H), 7.30–7.13 (m, 3H), 6.67 (d, $J = 8.0$ Hz, 1H), 6.53 (s, 1H), 6.48 (d, $J = 8.0$ Hz, 1H), 6.03 (d, $J = 15.6$ Hz, 1H), 5.93 (s, 2H), 5.54 (d, $J = 8.4$ Hz, 1H), 5.40–5.22 (m, 1H), 5.24–5.01 (m, 2H), 2.75–2.44 (m, 2H), 1.52–0.70 (brs, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 173.6, 163.7, 148.0, 147.6, 136.9, 136.0, 134.0, 130.5, 128.9, 128.4, 128.0, 127.5, 125.2, 124.4, 121.3, 117.6, 108.2, 105.6, 101.1, 81.1, 61.8, 47.0, 44.0, 28.0; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $[\text{C}_{31}\text{H}_{30}\text{N}_2\text{O}_6 + \text{Na}]^+$ 549.1996; Found 549.1994.



Tert-butyl (E)-(2-benzyl-4-(3-(2-formylphenyl)allyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7o): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $\text{Pd}(\text{OAc})_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and

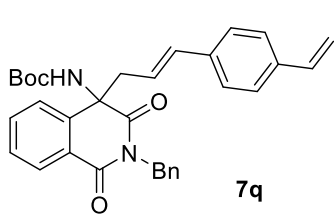
2-allylbenzaldehyde **1m** (36.5 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 6:1) to give the product **7o**: 49.2 mg (0.0964 mmol), as a white solid, 96% yield; m.p. 115–117 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.99 (s, 1H), 8.22 (d, $J = 8.0$ Hz, 1H), 7.72 (dd, $J = 7.2$ Hz, 0.8 Hz, 1H), 7.70–7.59 (m, 2H), 7.54–7.35 (m, 5H), 7.22–7.09 (m, 3H), 7.06–6.91 (m, 2H), 5.73 (s, 1H), 5.55–5.34 (m, 1H), 5.30–5.07 (m, 2H), 3.01–2.41 (m, 2H), 1.57–0.64 (brs, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 192.4, 173.4, 163.7, 138.4, 136.8, 134.2, 133.8, 133.4, 132.6, 132.3, 128.9, 128.3, 128.11, 128.05, 127.6, 127.5, 125.1, 124.8, 124.4, 81.1, 61.6, 47.0, 43.9, 27.9; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $[\text{C}_{31}\text{H}_{30}\text{N}_2\text{O}_5 + \text{Na}]^+$ 533.2047; Found 533.2040.



Methyl (E)-2-(3-(2-benzyl-4-((tert-butoxycarbonyl)amino)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)prop-1-en-1-yl)benzoate (7p):

Tert-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene) carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150

mmol, 1.5 equiv) and methyl 2-allylbenzoate **1n** (44.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 60 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5:1) to give the product **7p**: 52.8 mg (0.0977 mmol), as a white solid, 98% yield; m.p. 59–61 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.22 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.70–7.56 (m, 2H), 7.55–7.42 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24–7.11 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 16.4 Hz, 1H), 5.79 (s, 1H), 5.36 (s, 1H), 5.31–5.07 (m, 2H), 3.88 (s, 3H), 2.91–2.44 (m, 2H), 1.56–0.62 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.5, 167.4, 163.8, 138.5, 136.9, 136.1, 134.0, 132.4, 130.4, 129.0, 128.3, 128.1, 128.0, 127.8, 127.6, 127.5, 124.9, 124.5, 122.6, 80.9, 61.7, 52.1, 46.9, 44.0, 28.1; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₂H₃₂N₂O₆ + Na]⁺ 563.2153; Found 563.2151.

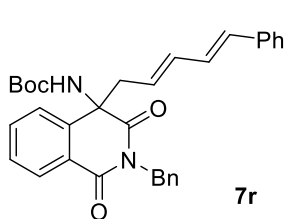


***Tert*-butyl (E)-(2-benzyl-1,3-dioxo-4-(3-(4-vinylphenyl)allyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7q):**

Tert-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃ (5.2

mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 1-allyl-4-vinylbenzene **1o** (36.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 48 h. After

completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **7q**: 39.3 mg (0.0773 mmol), as a white solid, 77% yield; m.p. 70–72 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.21 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.53–7.40 (m, 3H), 7.34–7.16 (m, 5H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.67 (dd, *J* = 17.6 Hz, 10.8 Hz, 1H), 6.14 (d, *J* = 16.0 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.56 (s, 1H), 5.55–5.43 (m, 1H), 5.28–5.19 (m, 2H), 5.14 (d, *J* = 13.6 Hz, 1H), 3.01–2.51 (m, 2H), 1.54–0.74 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.6, 163.7, 137.3, 136.9, 136.3, 136.1, 135.5, 134.0, 128.9, 128.4, 128.0, 127.5, 126.6, 126.4, 125.2, 124.5, 119.6, 114.1, 81.1, 61.8, 47.1, 44.0, 27.9; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for [C₃₂H₃₂N₂O₄ + Na]⁺ 531.2254; Found 531.2256.



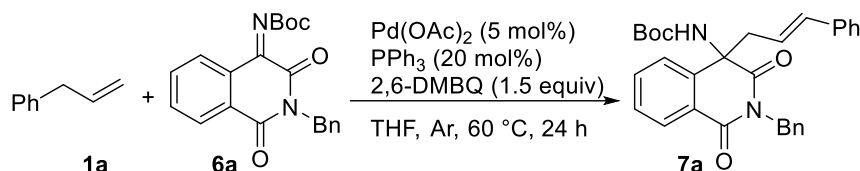
Tert-butyl (2-benzyl-1,3-dioxo-4-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7r): *Tert*-butyl

(2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), Pd(OAc)₂ (1.2 mg, 0.0053 mmol, 5 mol%), PPh₃

(5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and penta-1,4-dien-1-ylbenzene **1p** (36.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 60 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to give the product **7r**: 43.7 mg (0.0859 mmol), as a white solid, 86% yield; m.p. 75–78 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.22 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.54–7.40 (m, 3H), 7.38–7.02 (m, 8H), 6.46 (dd, *J* = 15.6 Hz, 10.4 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.13–5.88 (m, 1H), 5.74–5.49 (m, 1H), 5.36–5.00 (m, 3H), 2.85–2.42 (m, 2H), 1.52–0.62 (brs, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 173.6, 163.8, 136.9, 136.84, 136.78, 134.0, 133.4, 128.9, 128.7, 128.4,

128.0, 127.9, 127.5, 126.5, 125.1, 124.5, 123.3, 81.1, 61.7, 47.0, 44.0, 27.8; HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $[C_{32}H_{32}N_2O_4 + Na]^+$ 531.2254; Found 531.2257.

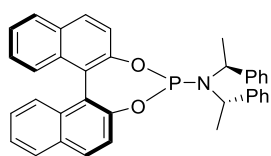
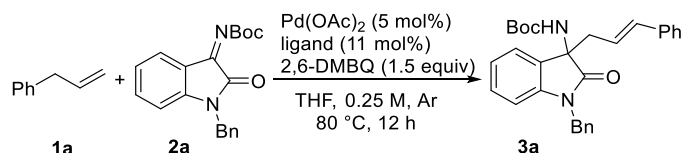
4.4 Oxidative nucleophilic allylation of isoquinoline-1,3,4-trione-derived ketimine **6a** on a 1.0 mmol scale



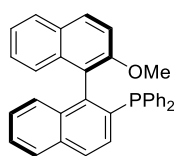
A mixture of *tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (364.4 mg, 1.000 mmol, 1.0 equiv), $Pd(OAc)_2$ (11.2 mg, 0.0499 mmol, 5 mol%), PPh_3 (52.5 mg, 0.200 mmol, 20 mol%), 2,6-DMBQ (204.2 mg, 1.500 mmol, 1.5 equiv) and allylbenzene **1a** (295.4 mg, 2.500 mmol, 2.5 equiv) were added to a 25 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (10 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 24 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 15:1) to give the product **7a**: 464.2 mg (0.9619 mmol), as a white solid, 96% yield.

5. Screening conditions of asymmetric oxidative nucleophilic allylation

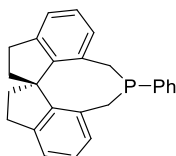
5.1 Screening conditions of asymmetric oxidative nucleophilic allylation of allylbenzene **1a** and isatin-derived ketimine **2a**



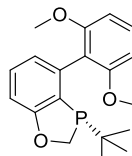
62% yield, 4% ee



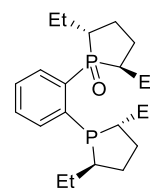
NR



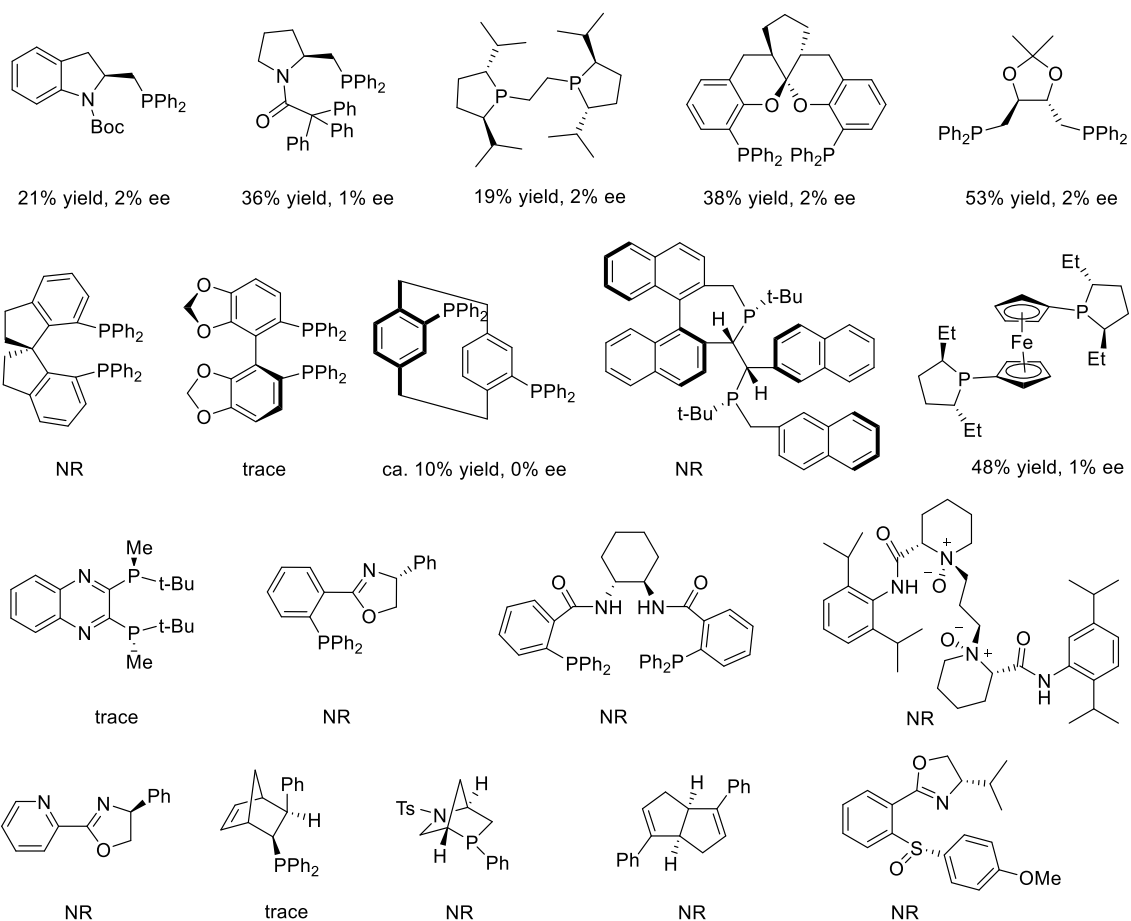
ca. 50% yield, 1% ee



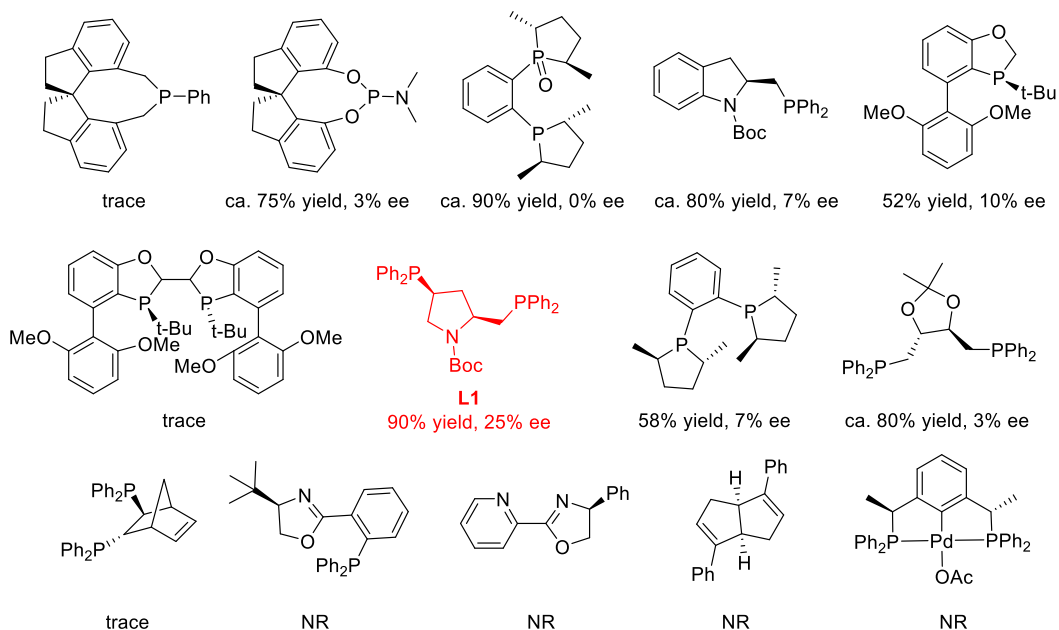
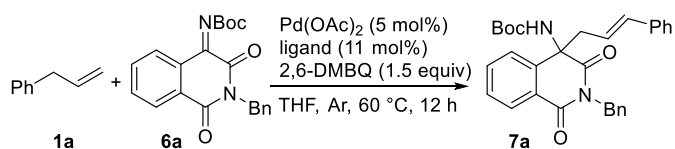
43% yield, 1% ee

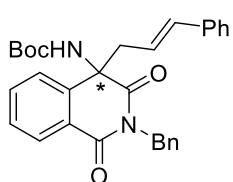


22% yield, 3% ee



5.2 Screening conditions of asymmetric oxidative nucleophilic allylation of allylbenzene **1a** and isoquinoline-1,3,4-trione-derived ketimine **6a**



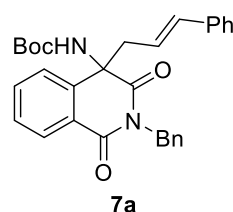
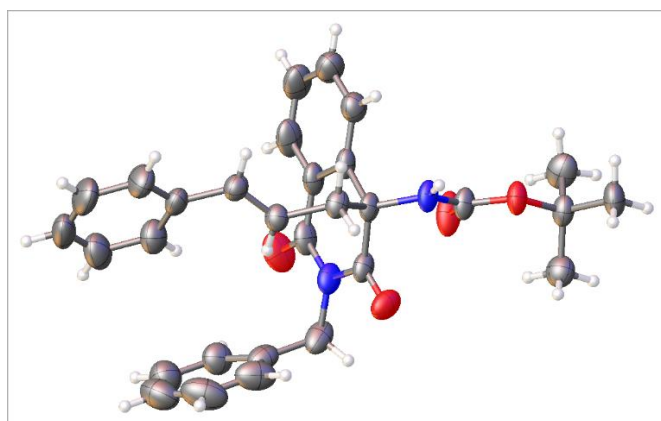


Synthesis of chiral 7a: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (18.2 mg, 0.0499 mmol), Pd(OAc)₂ (0.6 mg, 0.0027 mmol, 5 mol%), **L1** (3.0 mg, 0.0054 mmol, 11 mol%), 2,6-DMBQ (10.2 mg, 0.0749 mmol, 1.5 equiv) and allylbenzene **1a**

(14.8 mg, 0.125 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (0.5 mL) was added by syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 60 °C for 12 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product chiral **7a**: 21.7 mg (0.0450 mmol), as a white solid, 90% yield; 25% ee, determined by HPLC analysis [Daicel Chiralpak IE, *n*-hexane/*i*-PrOH = 60:40, 1.0 mL min⁻¹, λ = 254 nm]: t (minor) = 6.22 min, t (major) = 16.28 min.

7. Crystal data and structural refinement for racemic **7a** and **7j**

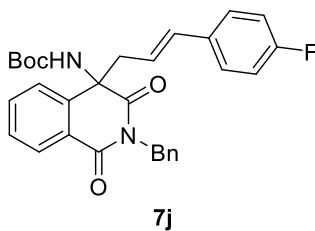
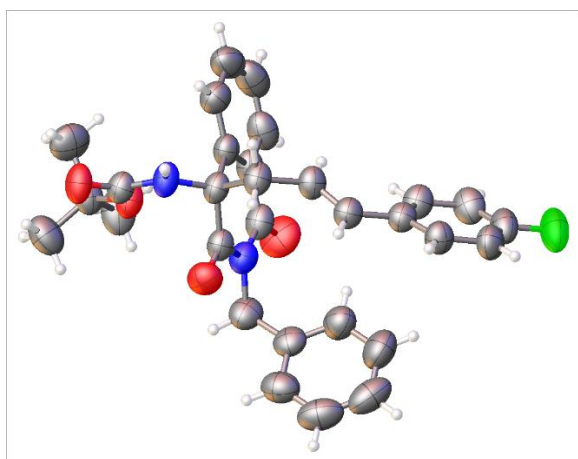
Procedure for the recrystallisation of 7a: To a 10 mL tube containing **7a** (80 mg) were added MeOH (4.0 mL) and CHCl₃ (0.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of **7a**. The data were collected by an Agilent Gemini equipped with a Cu radiation source (Kα = 1.54184 Å) at 296.1(5) K. CCDC 2057382 (**7a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



(ellipsoid contour probability 50%)

Identification code	7a
Empirical formula	C ₃₀ H ₃₀ N ₂ O ₄
Formula weight	482.56
Temperature/K	296.1(5)
Crystal system	monoclinic
Space group	I2/a
a/Å	16.9036(4)
b/Å	10.5122(3)
c/Å	29.9577(7)
α/°	90
β/°	101.225(2)
γ/°	90
Volume/Å ³	5221.4(2)
Z	8
ρ _{calc} /cm ³	1.228
μ/mm ⁻¹	0.656
F(000)	2048.0
Crystal size/mm ³	0.3 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.934 to 142.668
Index ranges	-20 ≤ h ≤ 20, -12 ≤ k ≤ 12, -36 ≤ l ≤ 28
Reflections collected	14234
Independent reflections	5001 [R _{int} = 0.0429, R _{sigma} = 0.0313]
Data/restraints/parameters	5001/0/328
Goodness-of-fit on F ²	1.055
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0634, wR ₂ = 0.1833
Final R indexes [all data]	R ₁ = 0.0716, wR ₂ = 0.1973
Largest diff. peak/hole / e Å ⁻³	0.27/-0.24

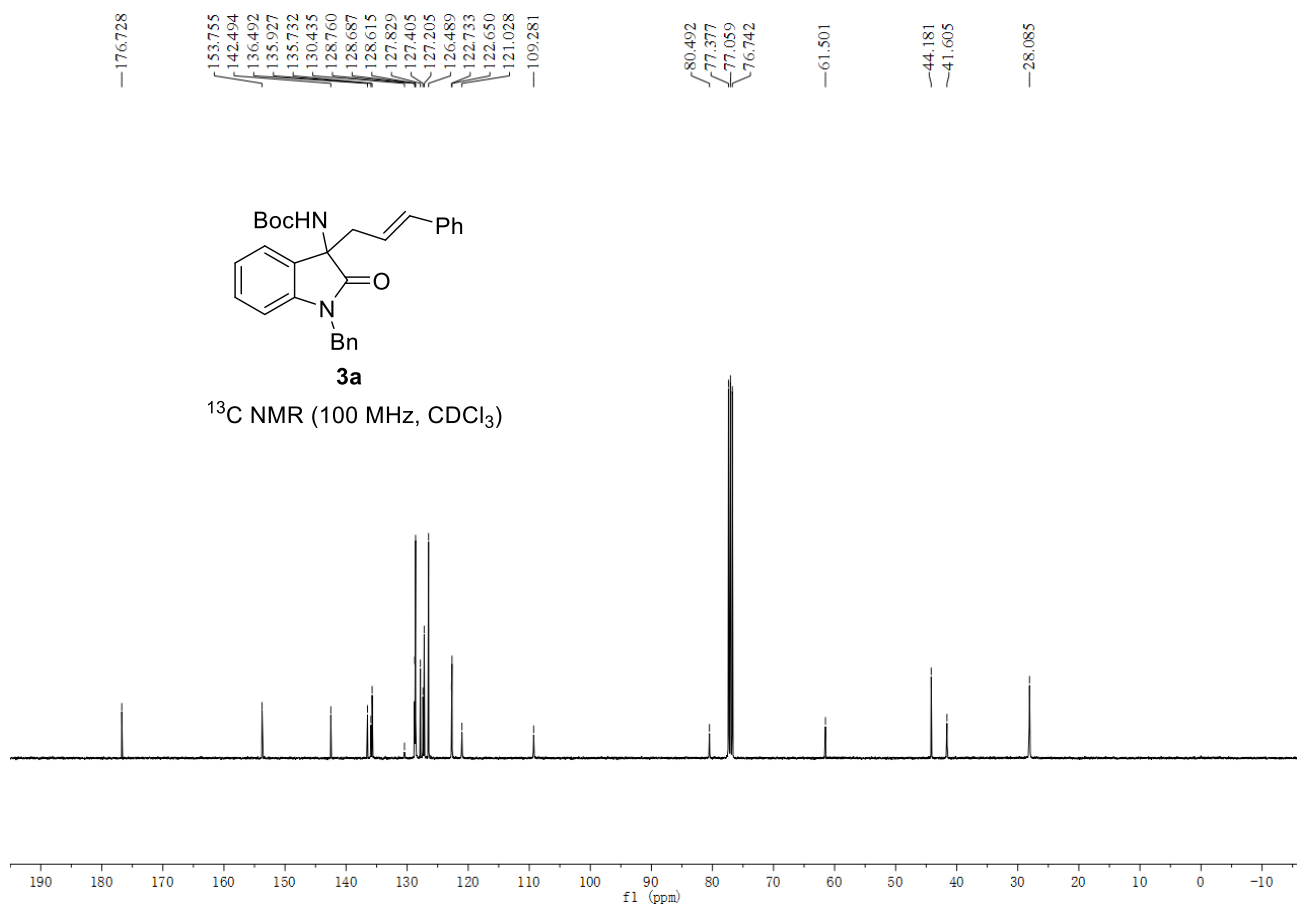
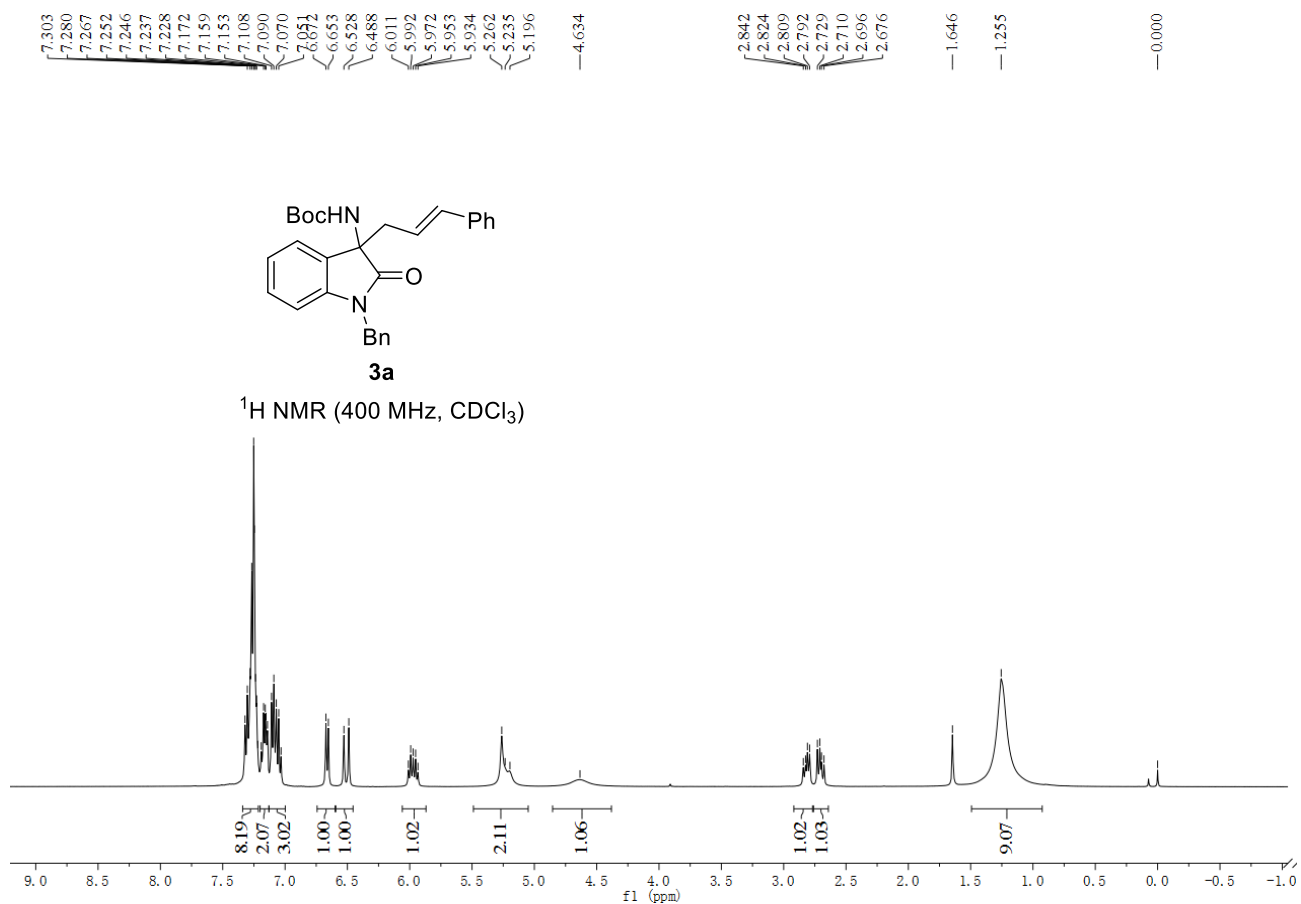
Procedure for the recrystallisation of 7j: To a 10 mL tube containing **7j** (52 mg) were added *n*-hexane (4.0 mL) and *i*-PrOH (0.5 mL). The mixture was heated until a clear solution was formed, which was kept aside at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of **7j**. The data were collected by an Agilent Gemini equipped with a Cu radiation source (Kα = 1.54184 Å) at 295.2(6) K. CCDC 2057383 (**7j**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

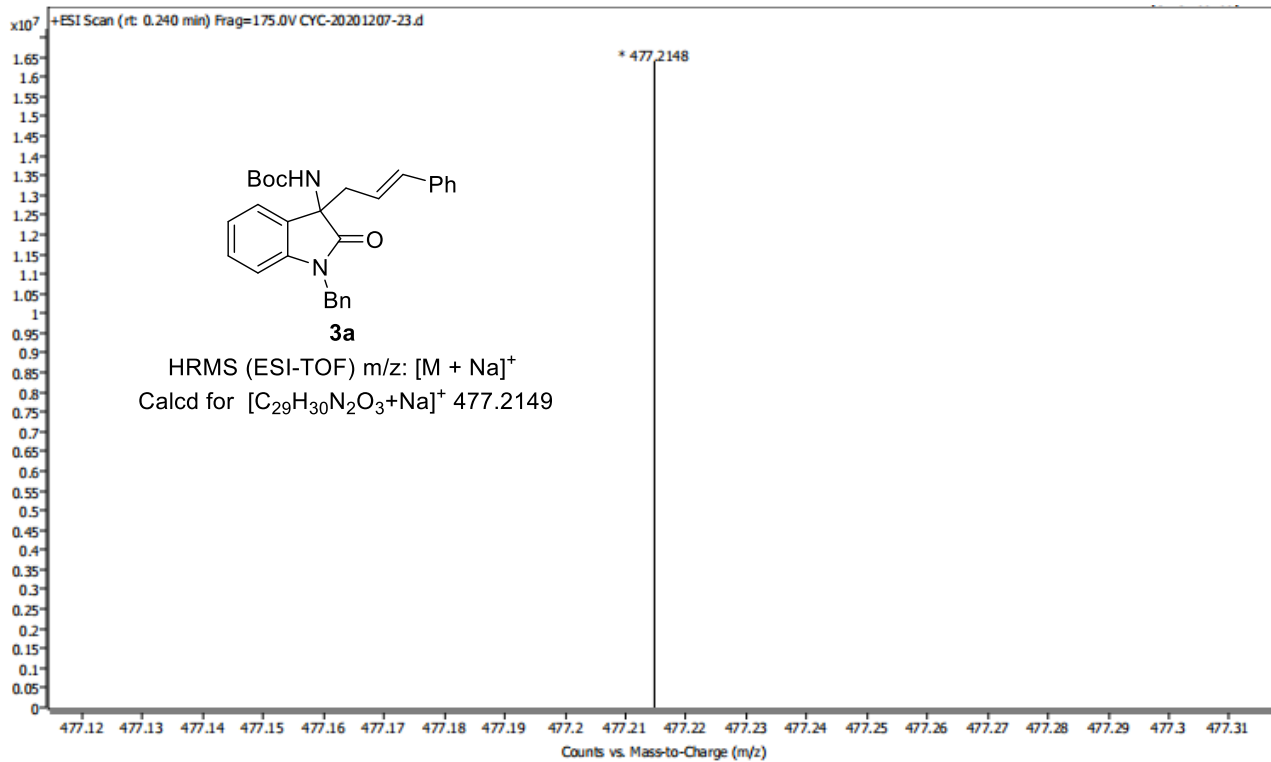


(ellipsoid contour probability 50%)

Identification code	7j
Empirical formula	$C_{30}H_{29}FN_2O_4$
Formula weight	500.55
Temperature/K	295.2(6)
Crystal system	triclinic
Space group	P-1
a/Å	10.1910(8)
b/Å	10.8141(7)
c/Å	12.7446(8)
$\alpha/^\circ$	102.470(6)
$\beta/^\circ$	92.057(6)
$\gamma/^\circ$	102.338(6)
Volume/Å ³	1334.77(17)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.245
μ/mm^{-1}	0.716
F(000)	528.0
Crystal size/mm ³	0.5 × 0.3 × 0.05
Radiation	CuK α ($\lambda = 1.54184$)
2 θ range for data collection/ $^\circ$	7.13 to 171.374
Index ranges	$-12 \leq h \leq 11, -13 \leq k \leq 11, -15 \leq l \leq 14$
Reflections collected	13682
Independent reflections	5224 [$R_{\text{int}} = 0.0537, R_{\text{sigma}} = 0.0491$]
Data/restraints/parameters	5224/0/337
Goodness-of-fit on F^2	1.051
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0633, wR_2 = 0.1687$
Final R indexes [all data]	$R_1 = 0.0948, wR_2 = 0.2071$
Largest diff. peak/hole / e Å ⁻³	0.21/−0.28

8. NMR, HRMS spectra and HPLC chromatograms



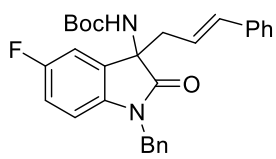


7.298
7.293
7.287
7.275
7.258
7.250
7.231
7.169
7.152
7.115
7.096
7.089
7.082
7.071
7.063
6.574
6.564
6.531
6.492
5.954
5.935
5.915
5.896
5.242
5.191
5.157
5.151
4.663

2.830
2.812
2.797
2.780
2.740
2.720
2.687

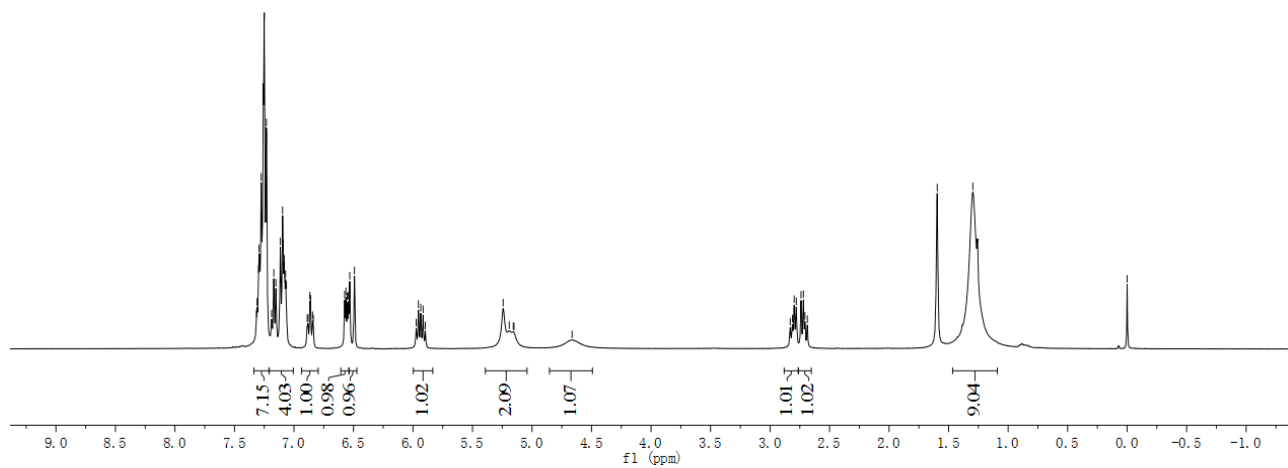
1.596
1.296

0.000



3b

¹H NMR (400 MHz, CDCl₃)



176.516

160.526
158.129
153.684

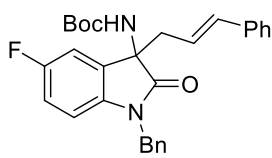
138.380
136.319
136.264
135.381
128.749
128.655
127.522
127.152
126.505
120.411
115.091
114.857
111.033
110.785
109.915

80.768
77.358
77.041
76.724

61.747

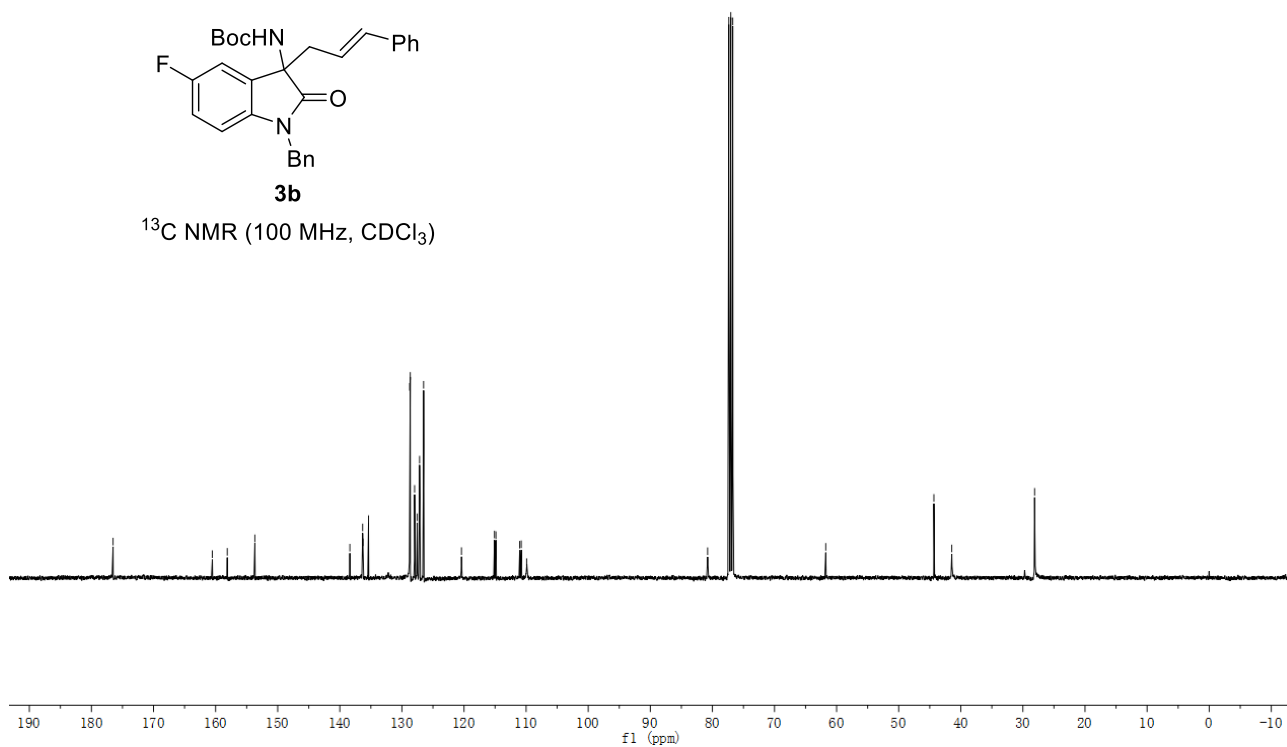
44.330
41.456

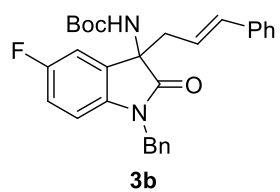
28.115



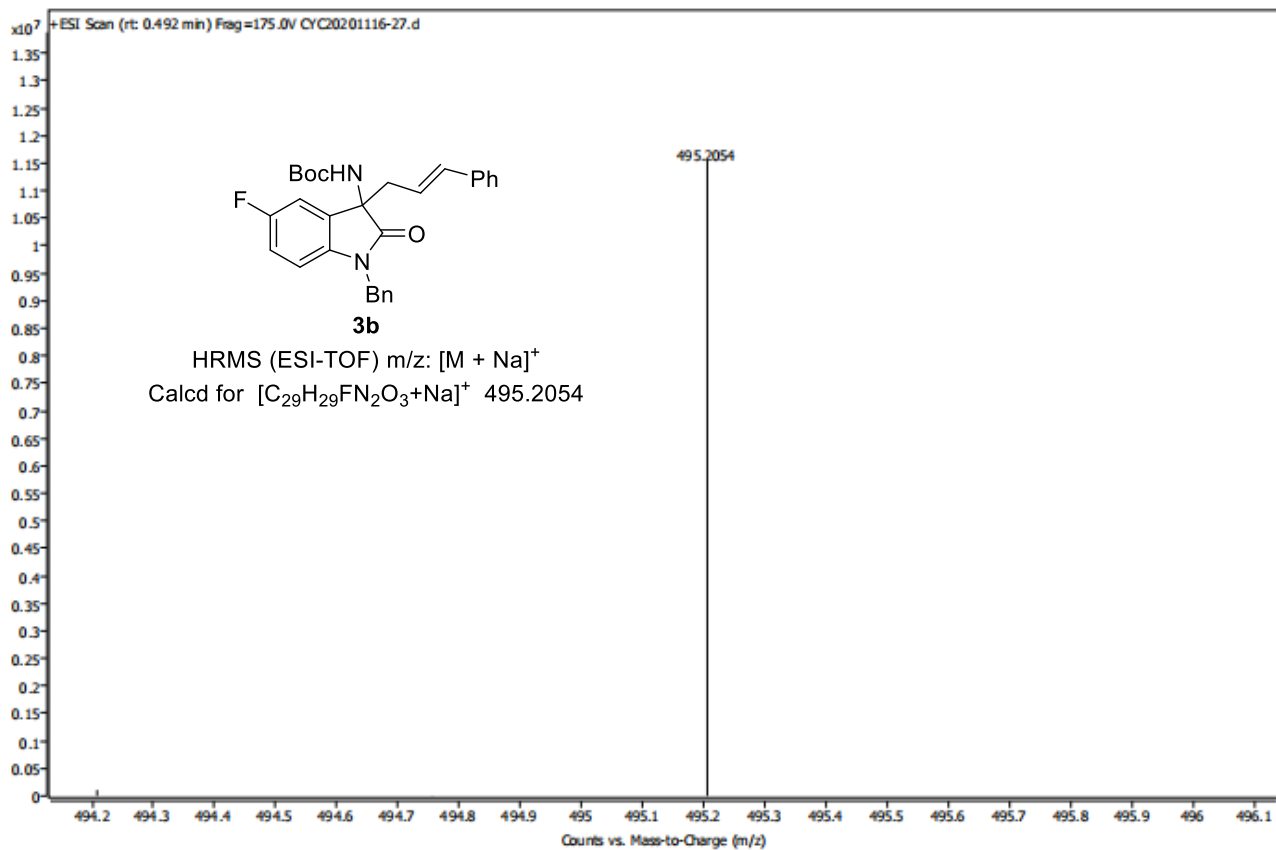
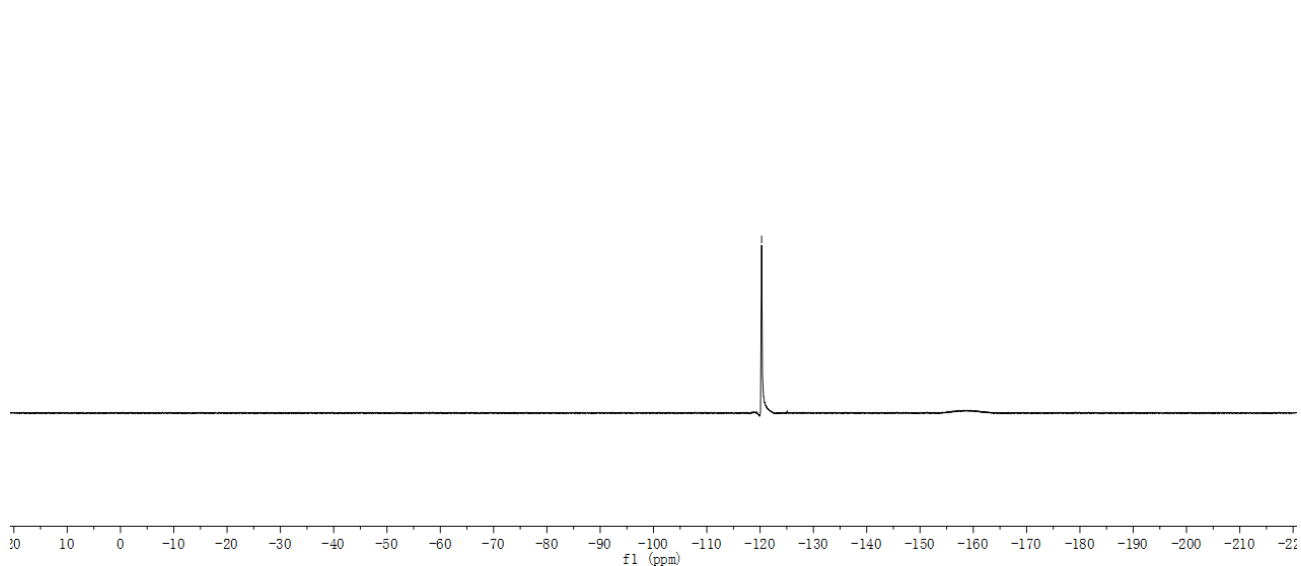
3b

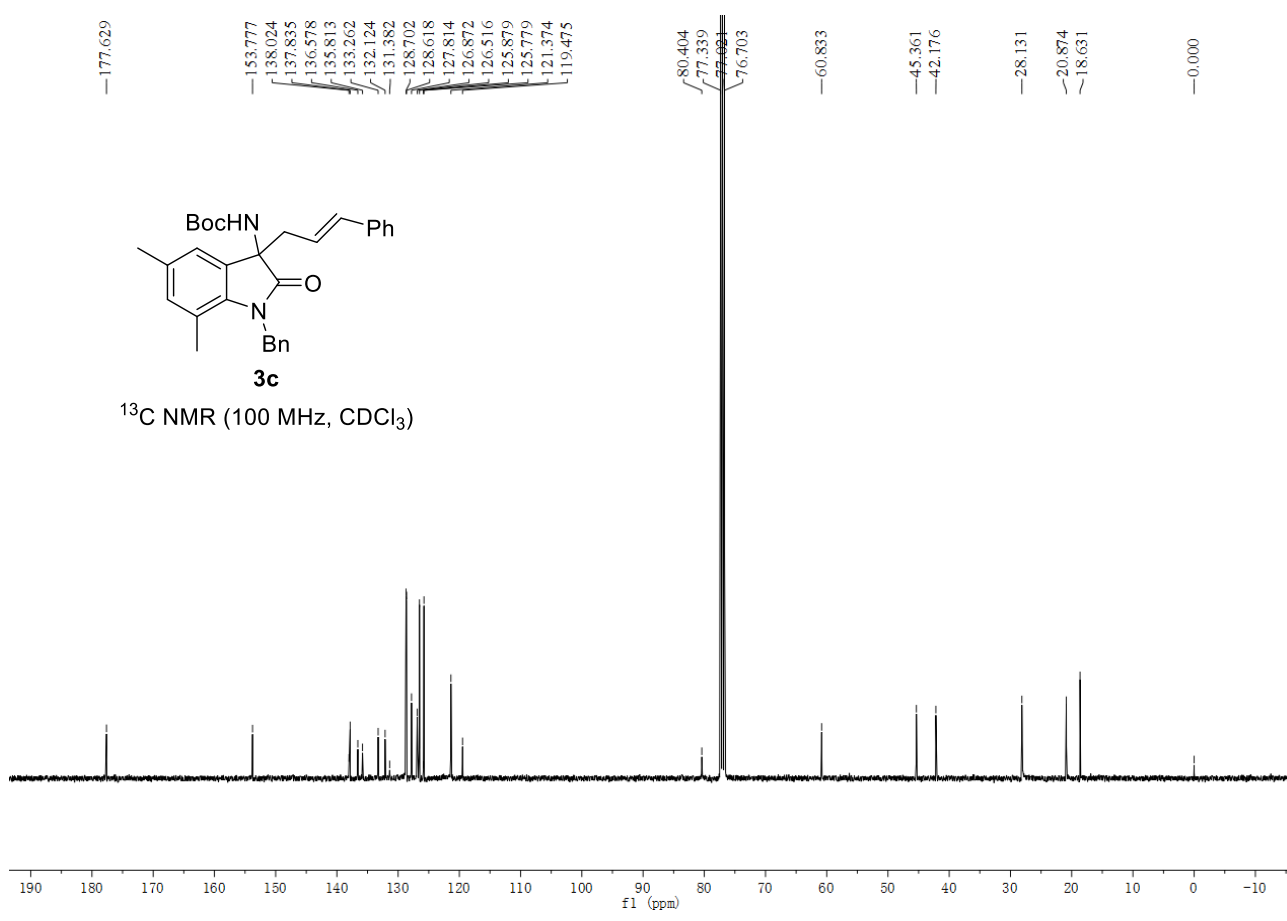
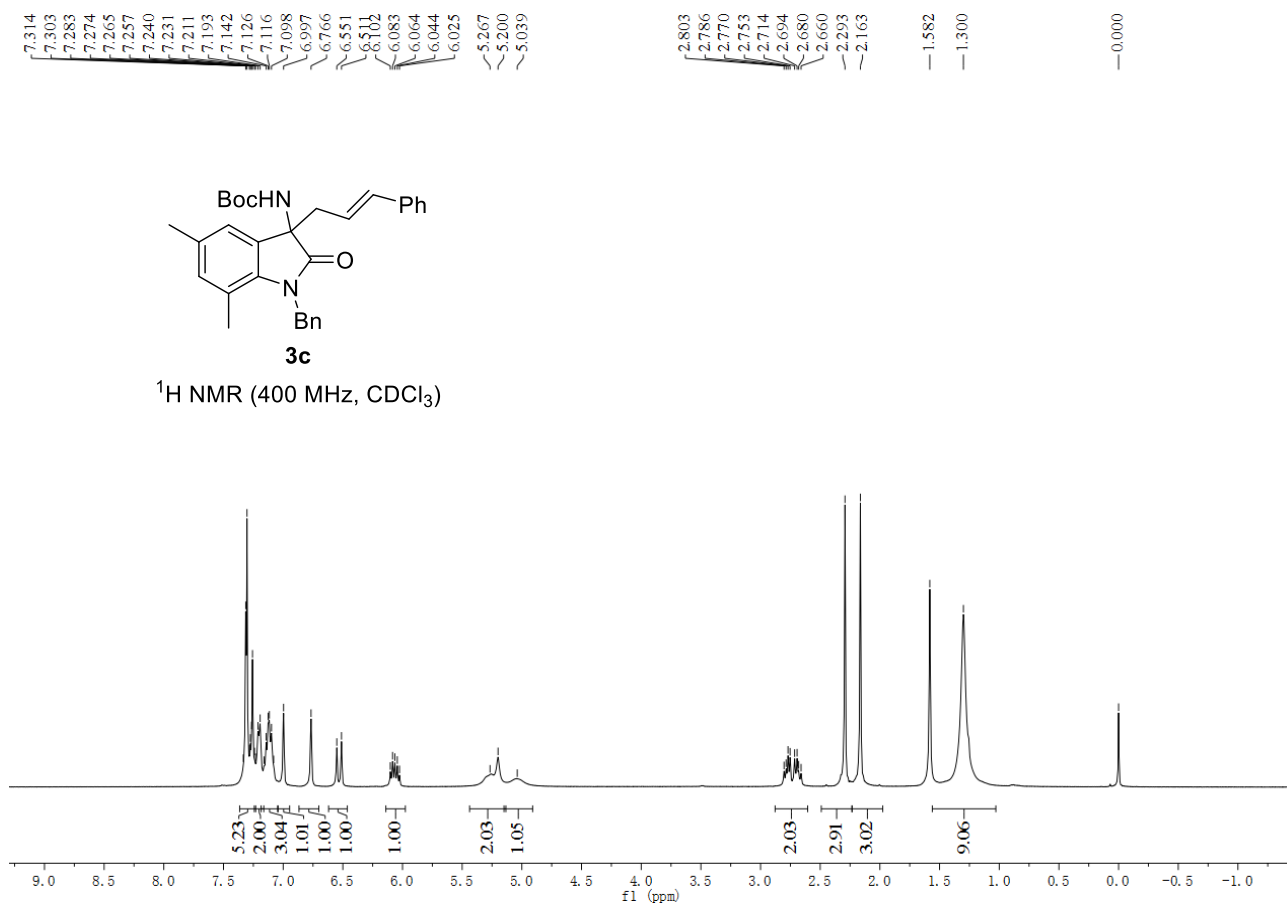
¹³C NMR (100 MHz, CDCl₃)

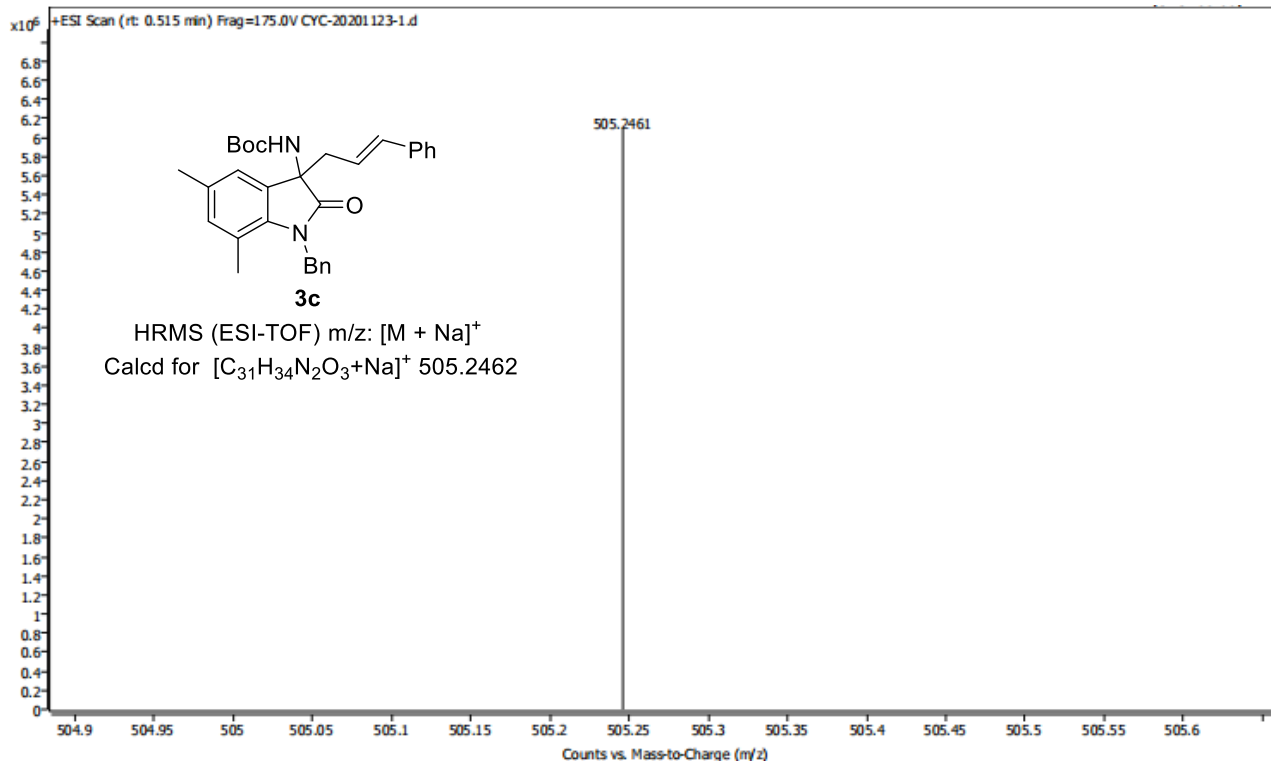


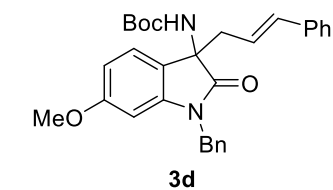
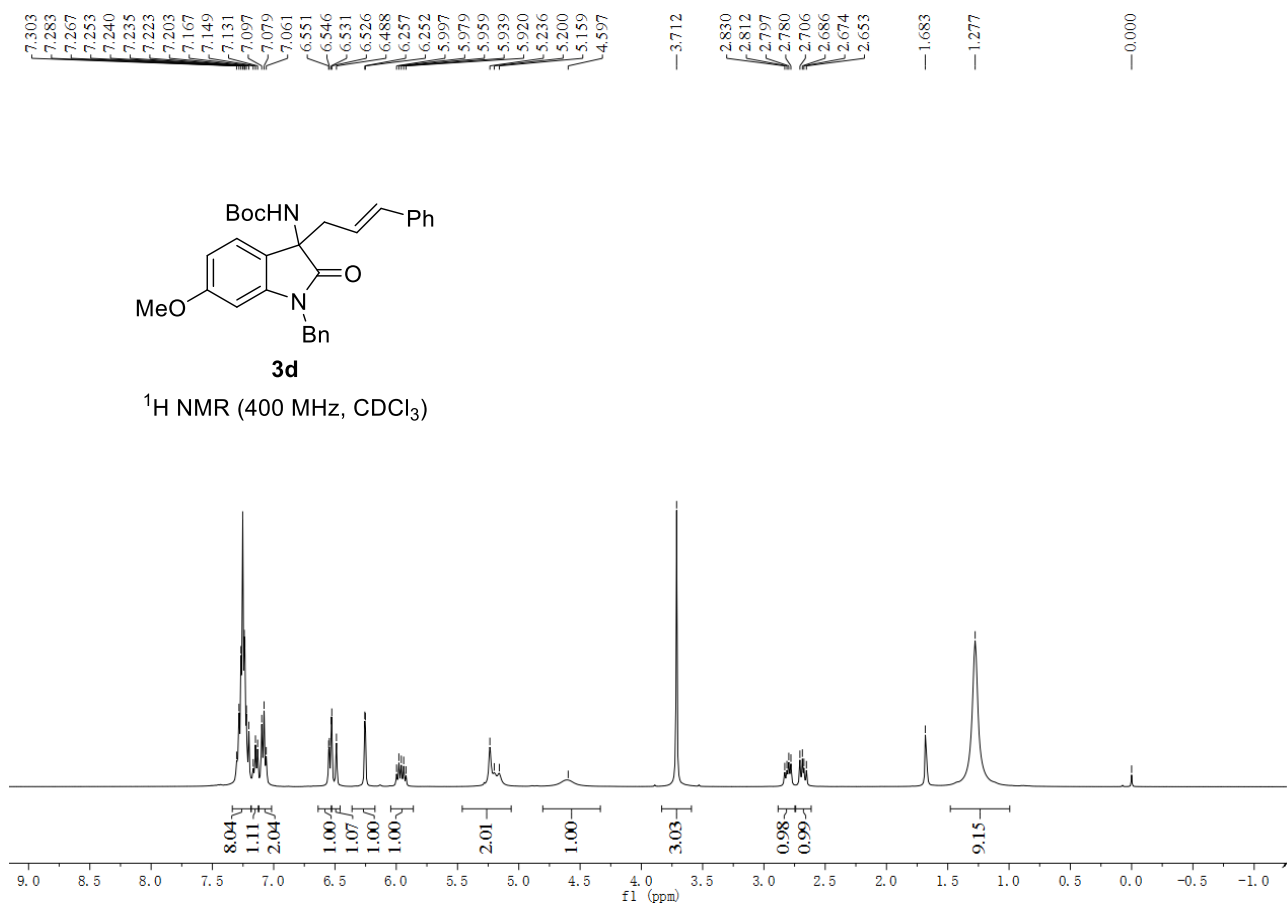


^{19}F NMR (376 MHz, CDCl_3)

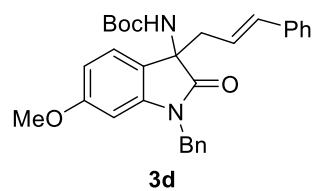
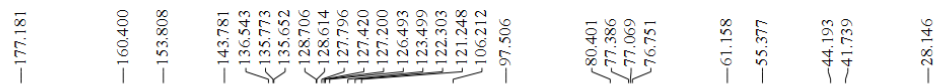




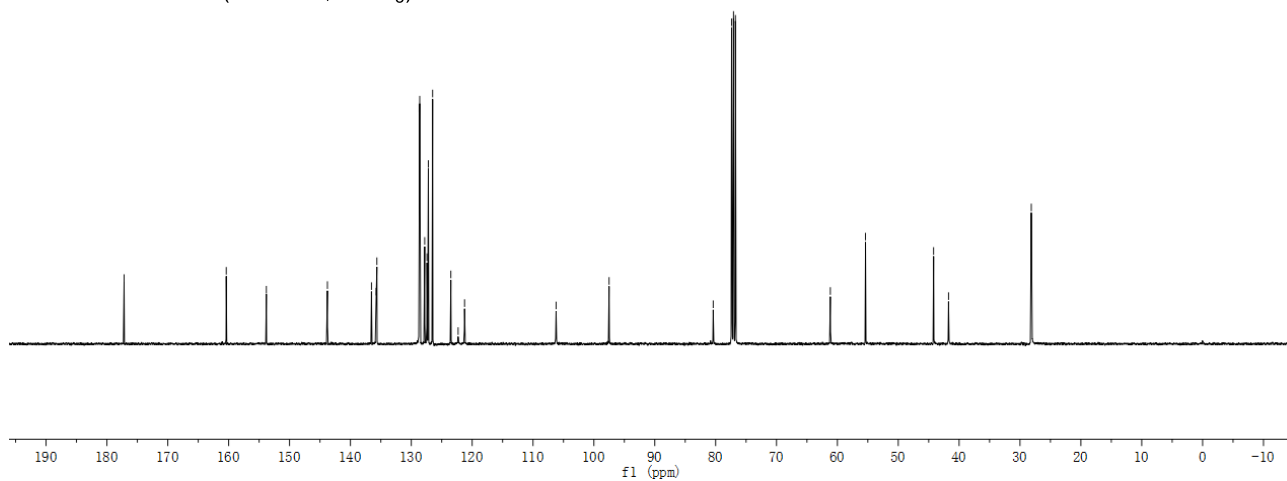


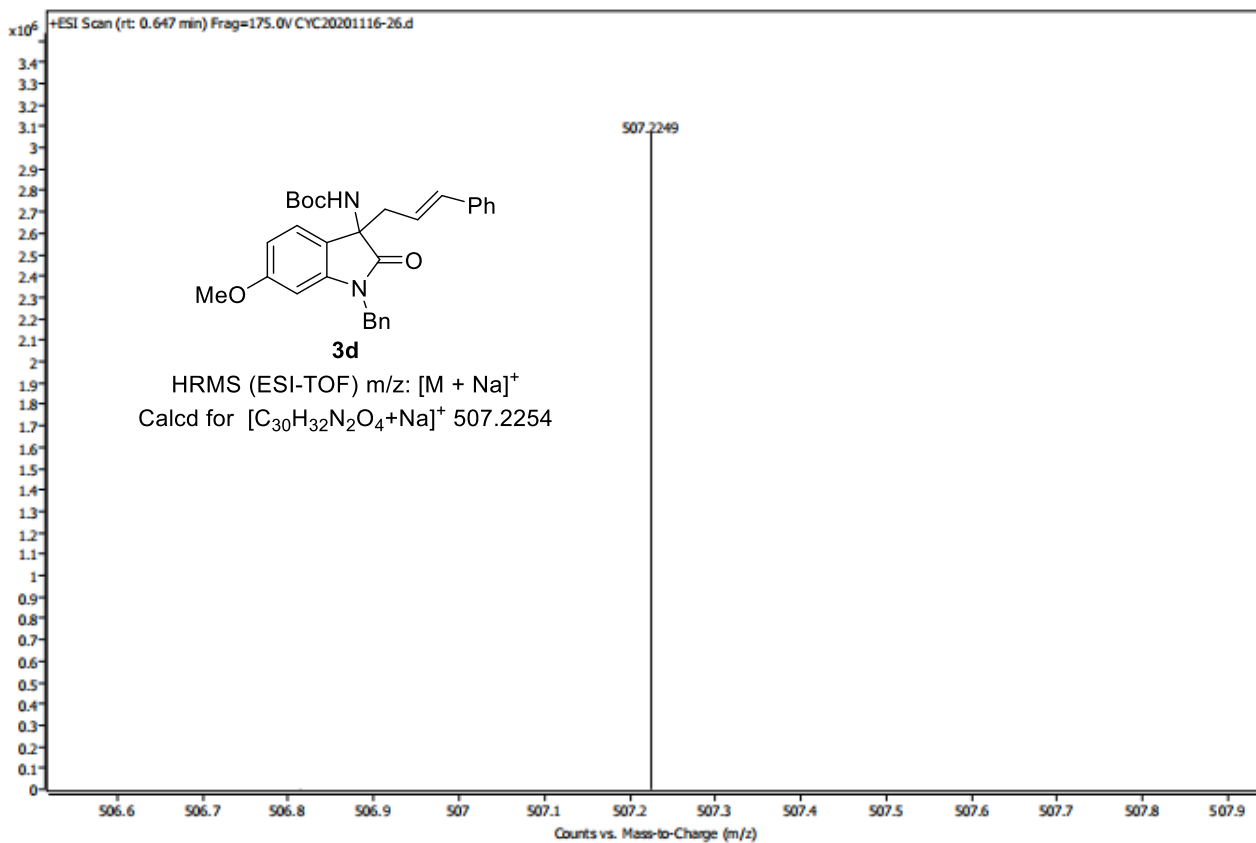


¹H NMR (400 MHz, CDCl₃)

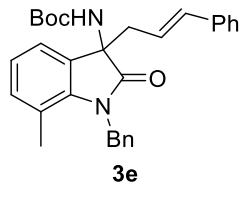


¹³C NMR (100 MHz, CDCl₃)

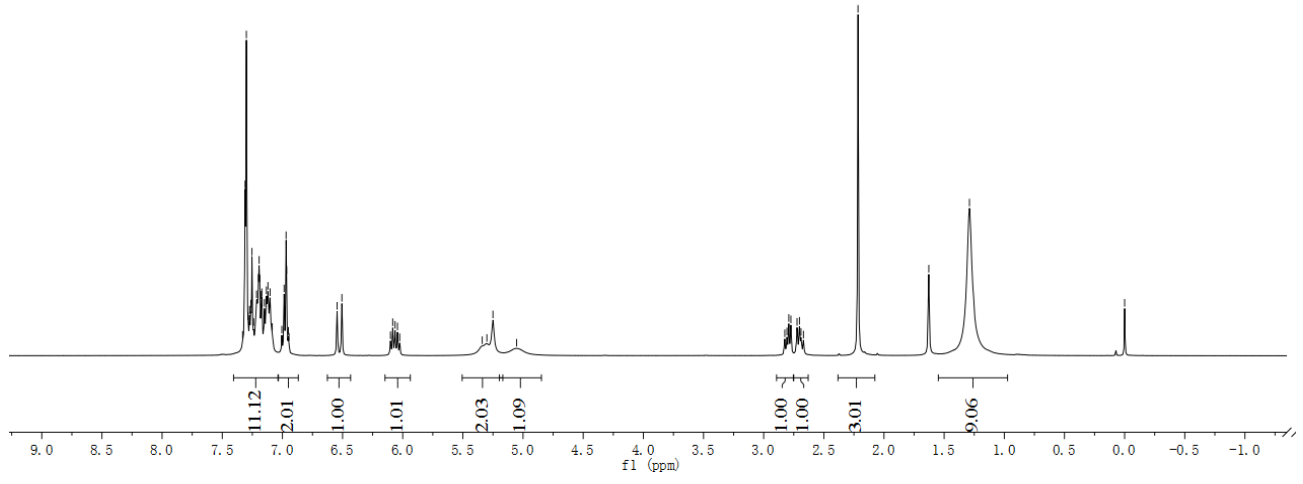




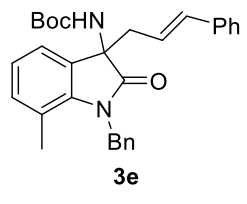
7.331
7.310
7.300
7.284
7.273
7.265
7.262
7.253
7.240
7.215
7.199
7.193
7.188
7.176
7.171
7.150
7.137
7.133
7.120
7.102
7.084
7.005
6.986
6.969
6.965
6.951
6.945
6.545
6.506
6.102
6.083
6.064
6.044
5.250
2.824
2.807
2.791
2.774
2.723
2.703
2.690
2.669
2.616
1.628
1.290
0.000



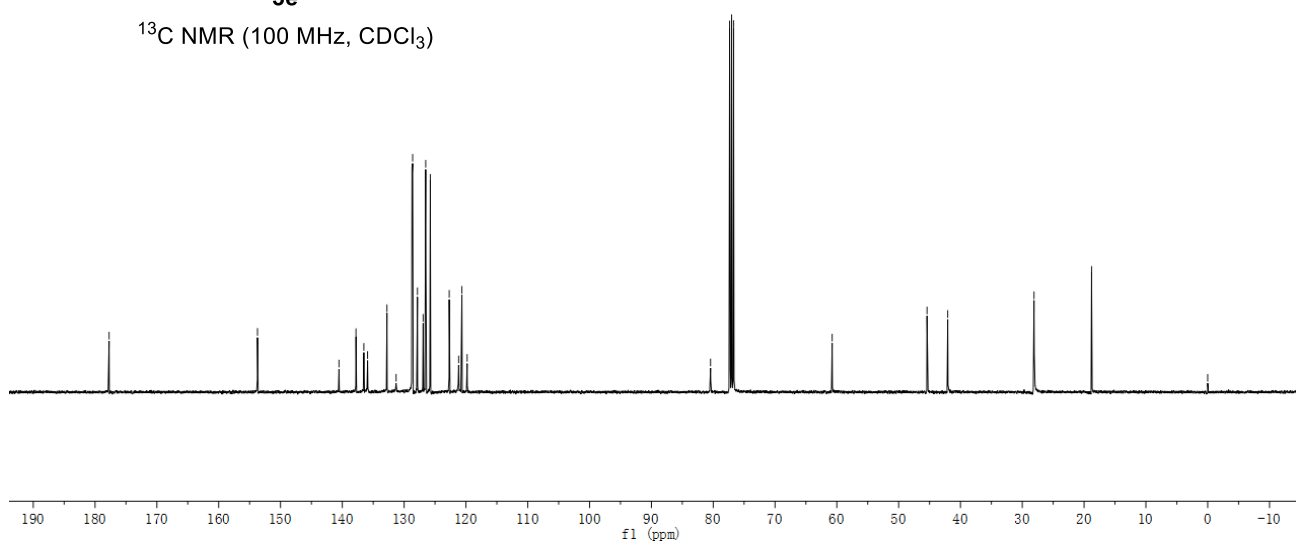
¹H NMR (400 MHz, CDCl₃)

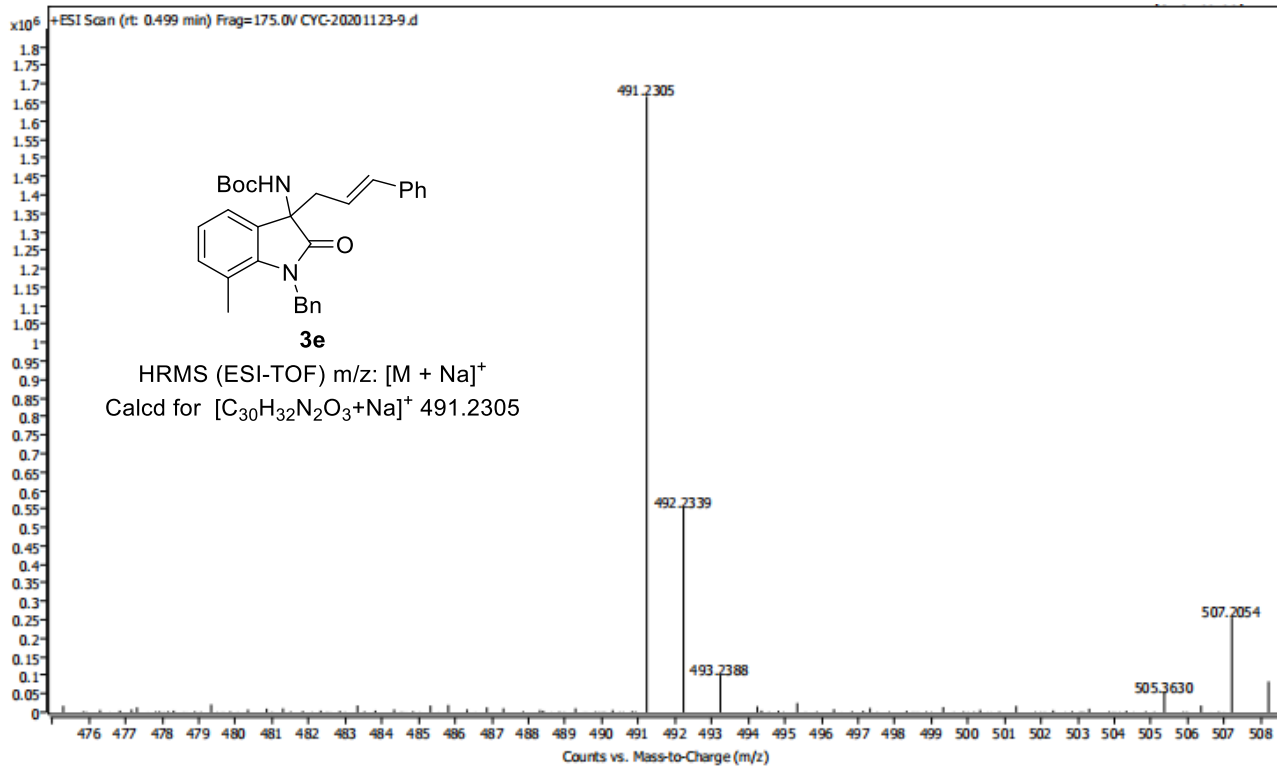


177.728
153.722
140.537
137.789
136.514
135.910
132.778
131.297
128.726
128.620
127.842
126.924
126.506
125.765
122.703
121.182
120.656
119.804
80.427
77.343
77.026
76.708
60.755
45.406
42.057
28.100
18.789
0.000



¹³C NMR (100 MHz, CDCl₃)



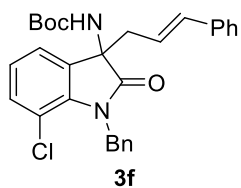


7.311
7.307
7.293
7.285
7.277
7.267
7.259
7.255
7.221
7.203
7.162
7.145
7.139
7.122
6.991
6.482
6.030
6.032
6.012
5.992
5.974
5.402
5.362
5.339
5.284

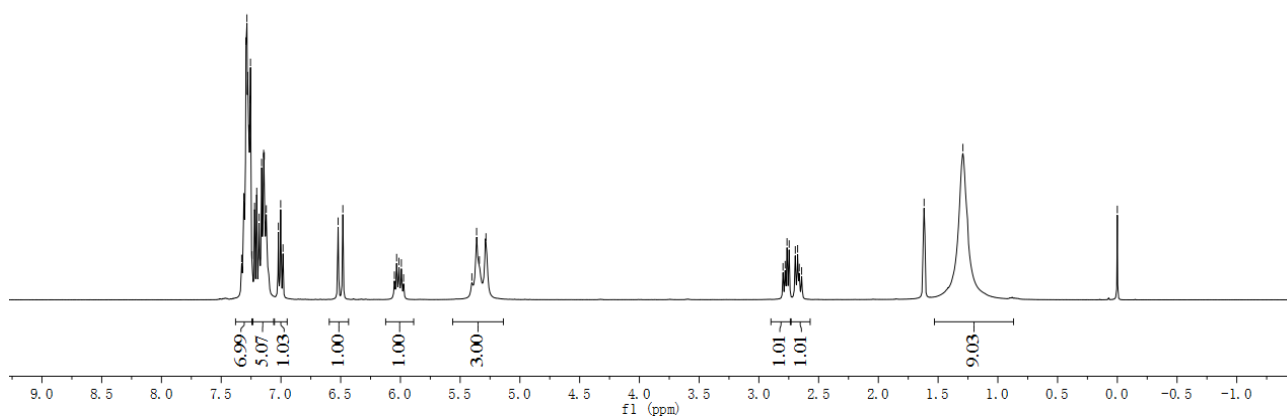
2.798
2.780
2.764
2.746
2.695
2.675
2.662
2.642

— 1.617
— 1.292

— 0.000



¹H NMR (400 MHz, CDCl₃)



— 177.319

153.647
138.583
137.634
136.363
136.282
133.583
131.338
128.643
128.438
127.980
126.894
126.515
126.473
123.516
121.229
120.394
115.567

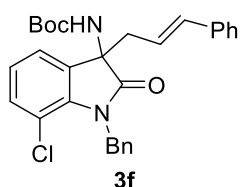
80.825
77.342
77.024
76.706

— 60.930

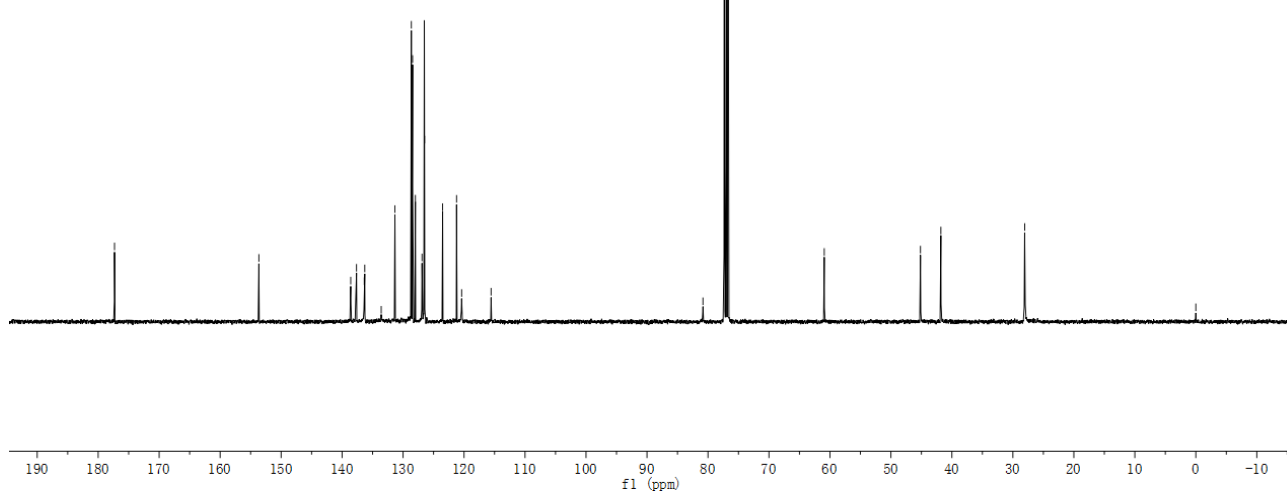
— 45.156
— 41.808

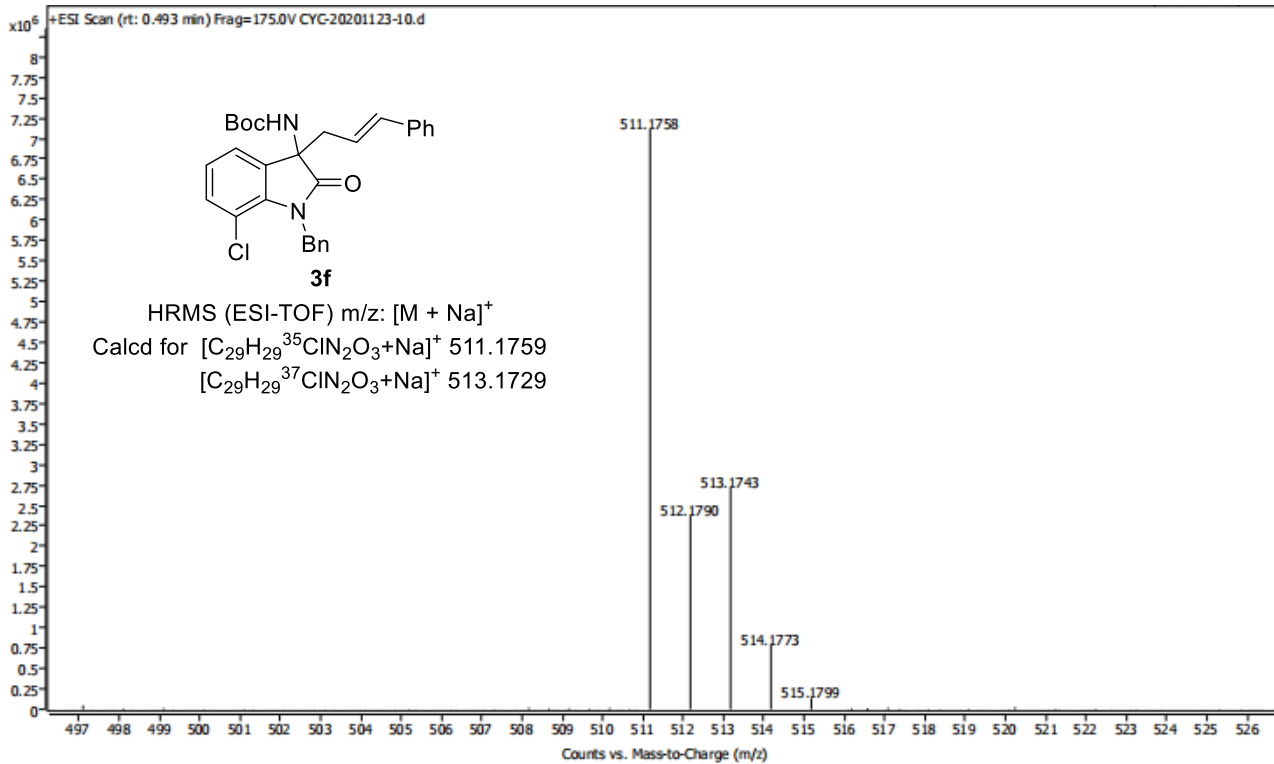
— 28.065

— 0.000



¹³C NMR (100 MHz, CDCl₃)

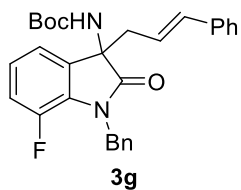




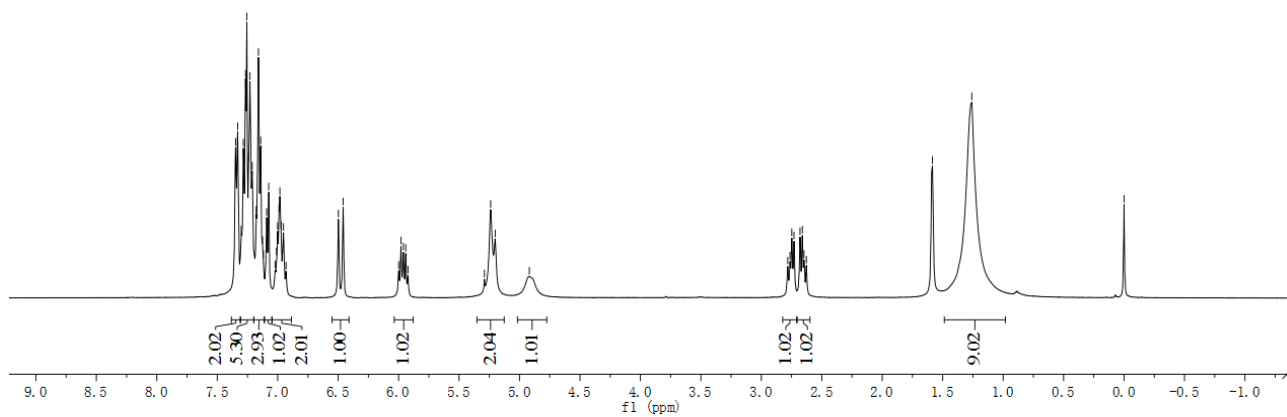
7.349
7.331
7.284
7.266
7.255
7.241
7.229
7.210
7.177
7.159
7.141
7.092
7.075
6.989
6.858
6.458
5.999
5.980
5.961
5.941
5.922
5.290
5.238
5.201
4.919

2.782
2.763
2.748
2.730
2.680
2.661
2.647
2.627

1.585
1.260
0.000



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



176.444

153.664
148.741
146.311

137.037
136.299
136.232

129.044
128.957
128.608
128.481
127.916
127.426
127.338
126.463
123.327
123.264
120.435
118.573
118.541
117.091
116.895

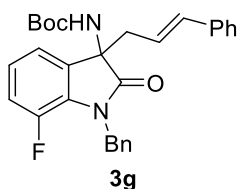
80.762
77.339
77.023
76.706

61.474

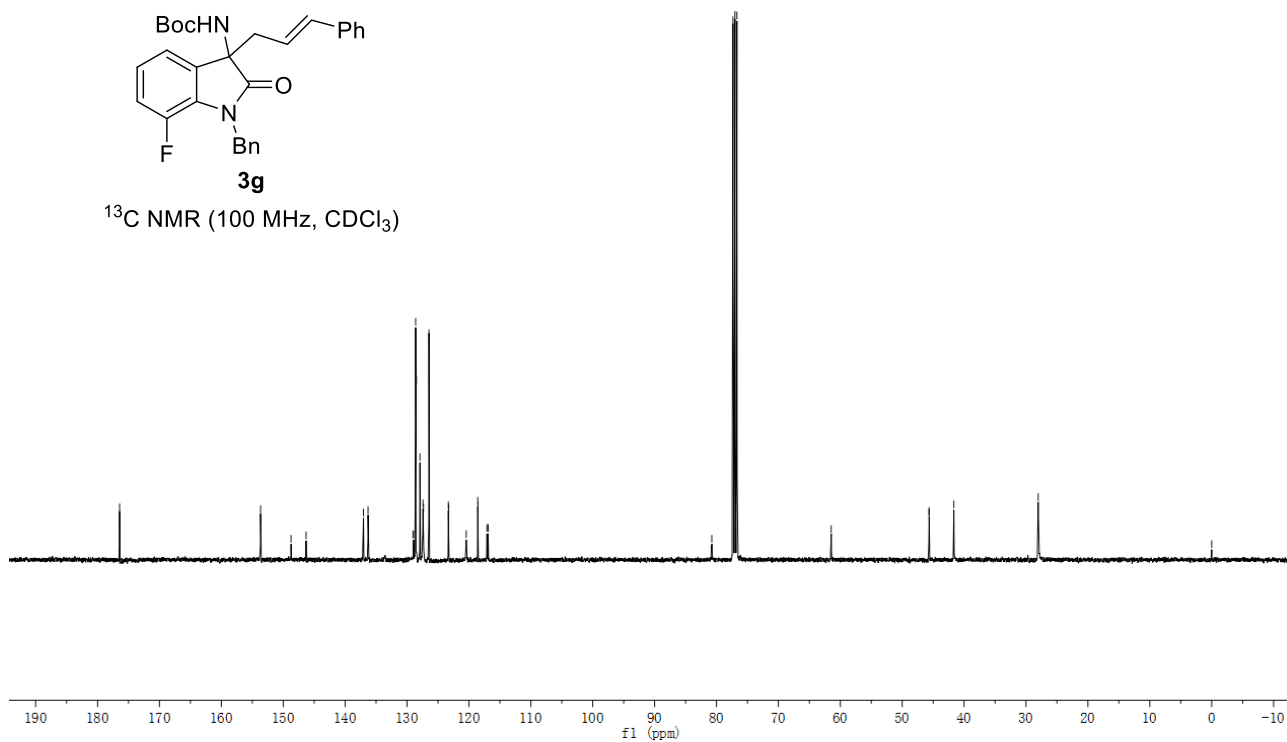
45.690
45.643
41.658

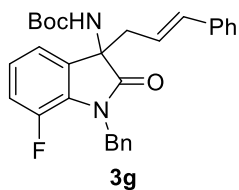
28.031

0.000



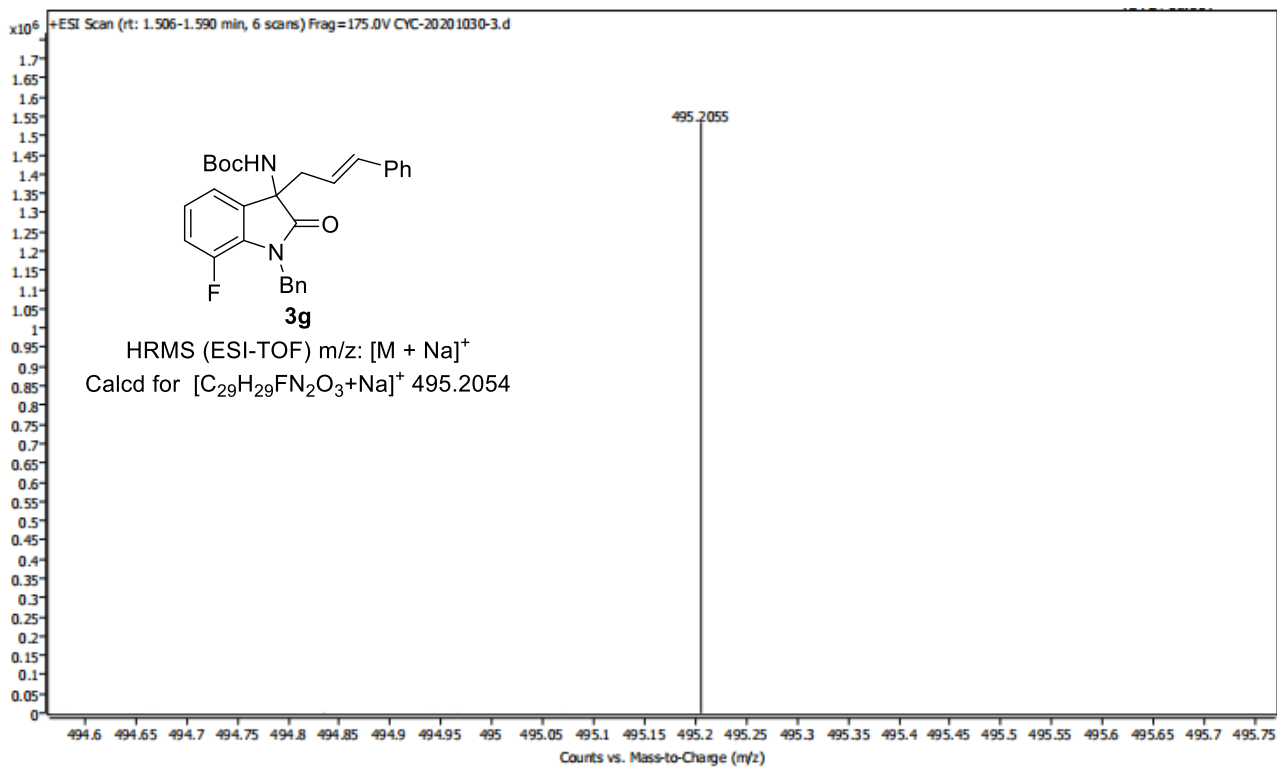
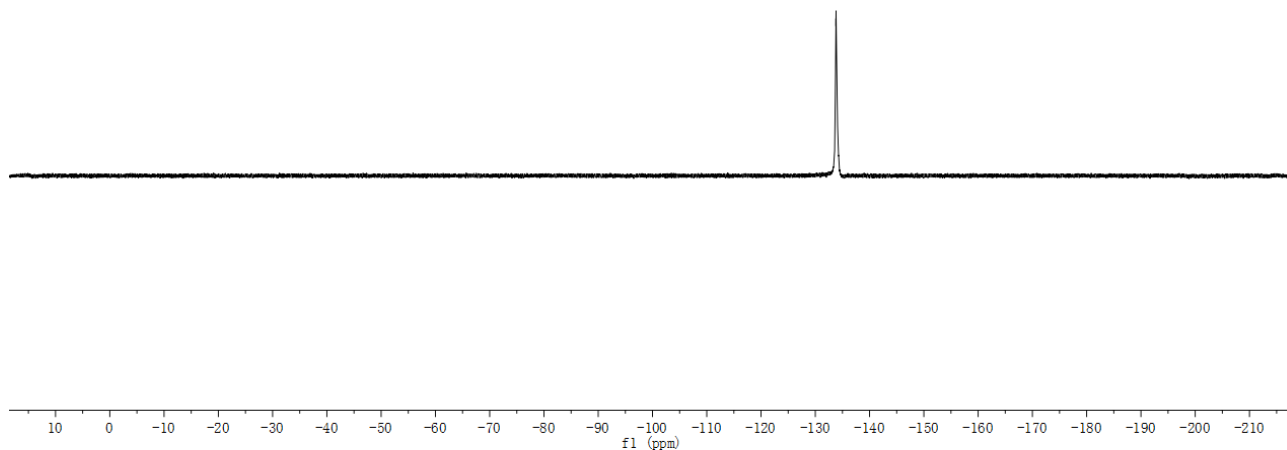
$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

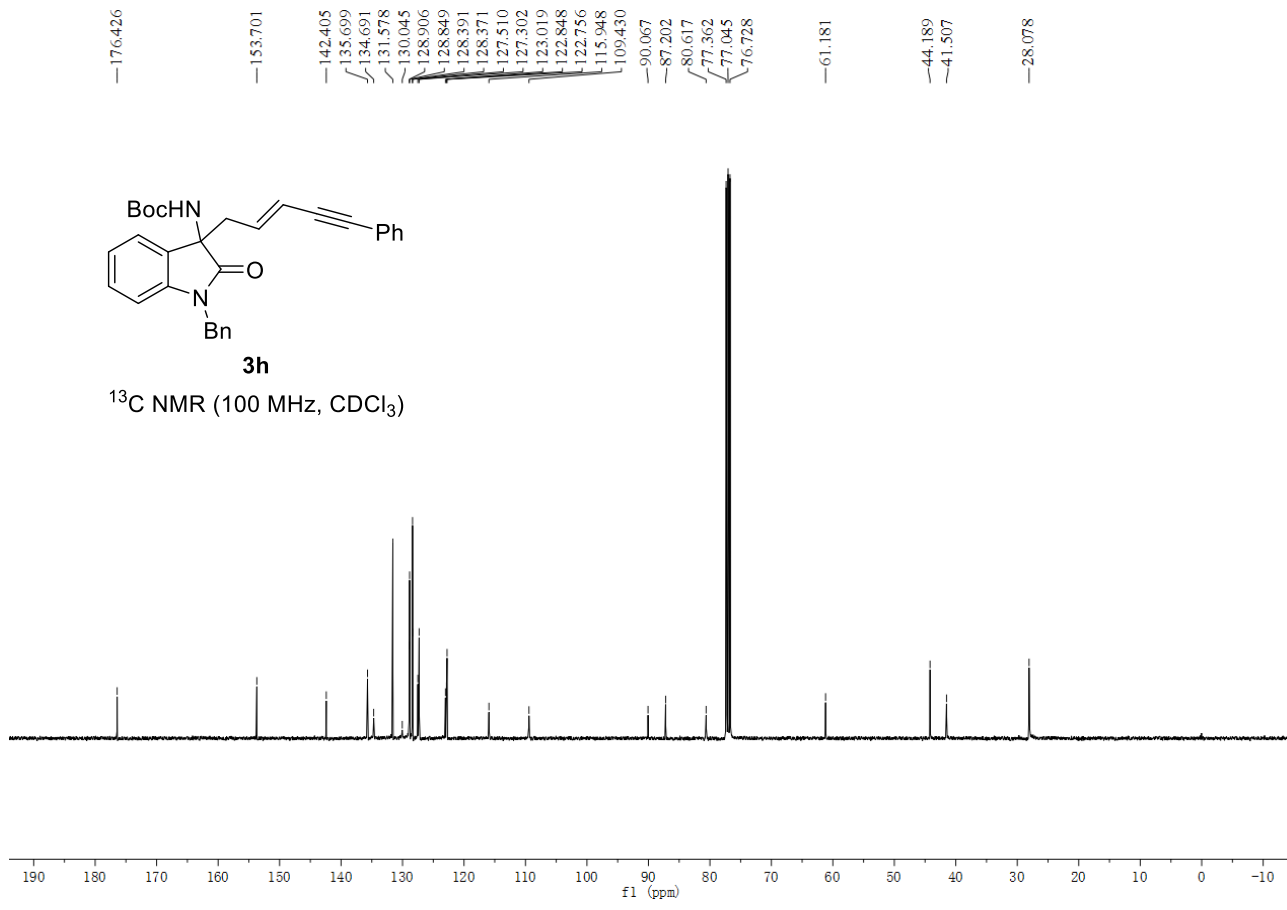
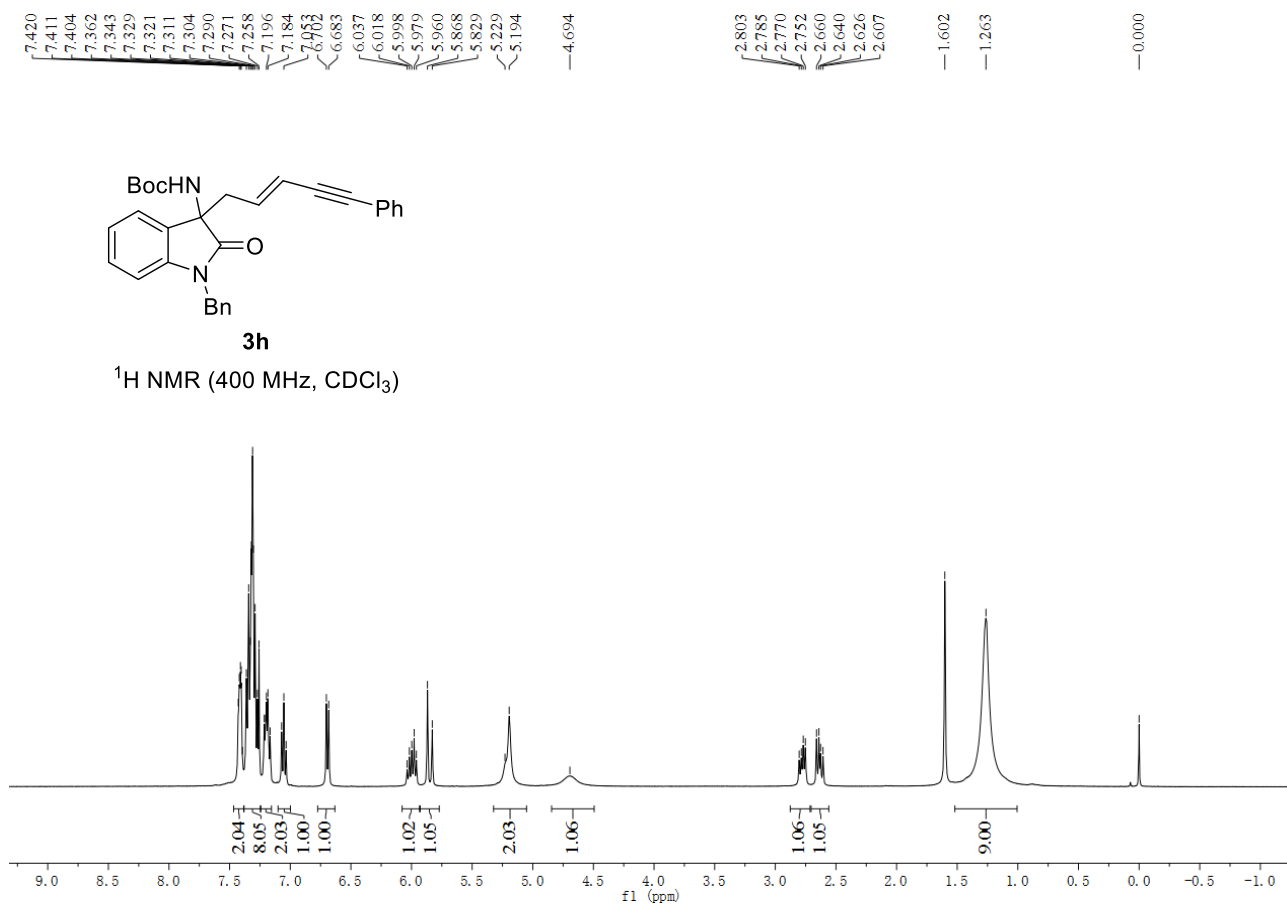


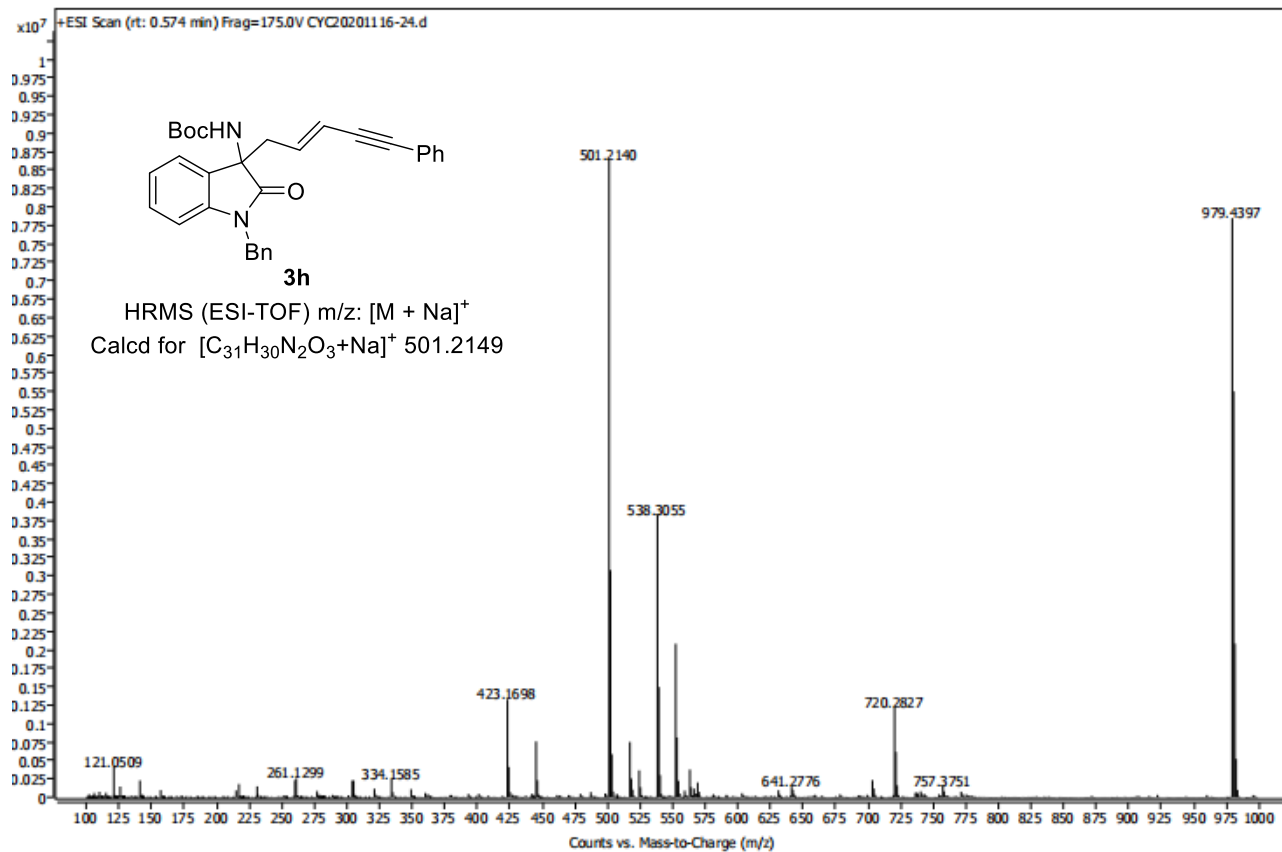


^{19}F NMR (376 MHz, CDCl_3)

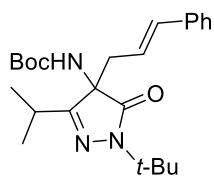
—133.780





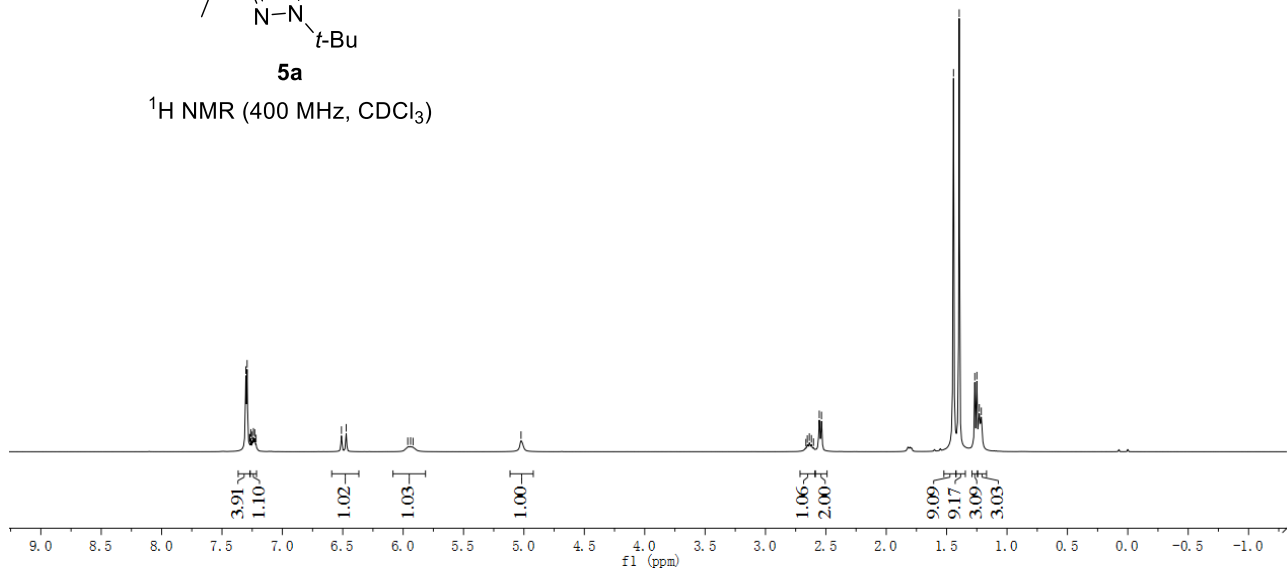


7.303
7.292
7.272
7.270
7.261
7.250
7.240
7.229
7.218
6.511
6.472
5.962
5.938
5.918
5.024
2.665
2.654
2.637
2.620
2.602
2.555
2.536
1.443
1.396
1.267
1.250
1.230
1.213

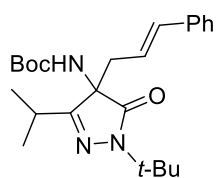


5a

¹H NMR (400 MHz, CDCl₃)

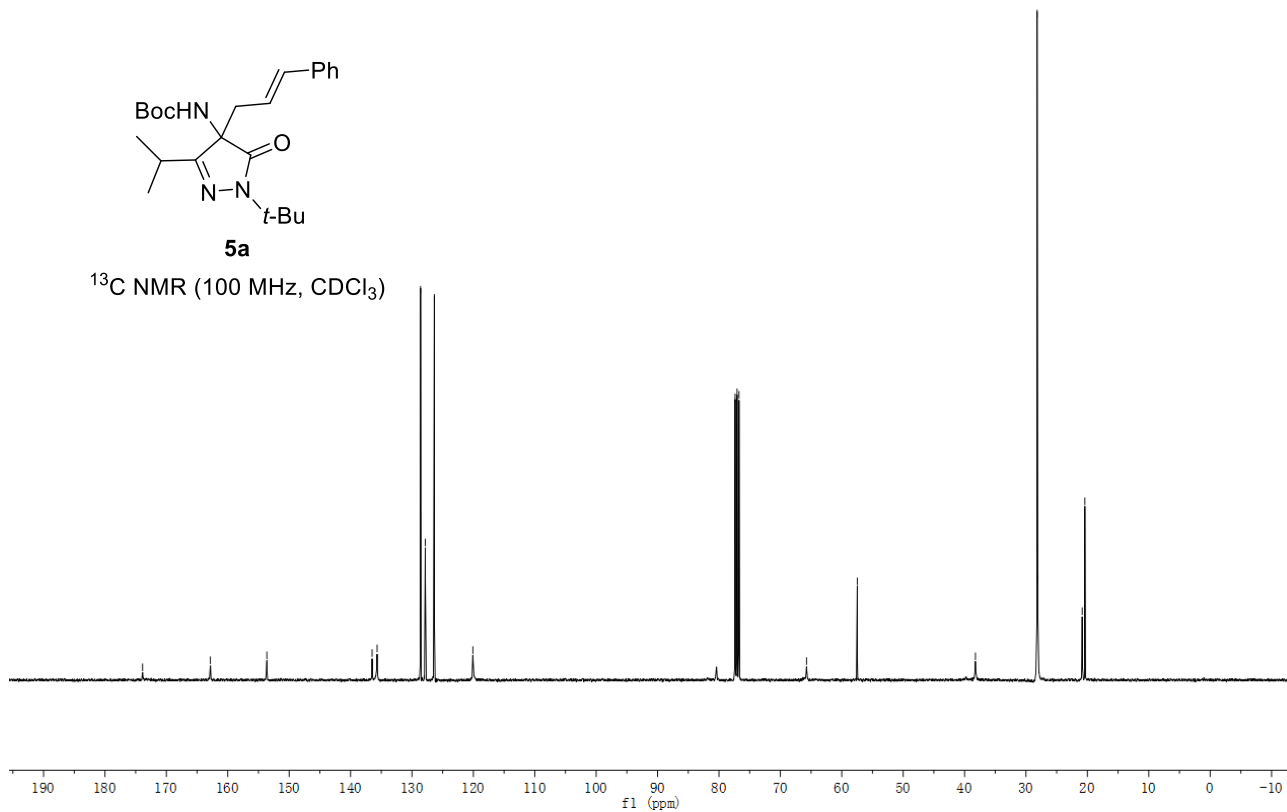


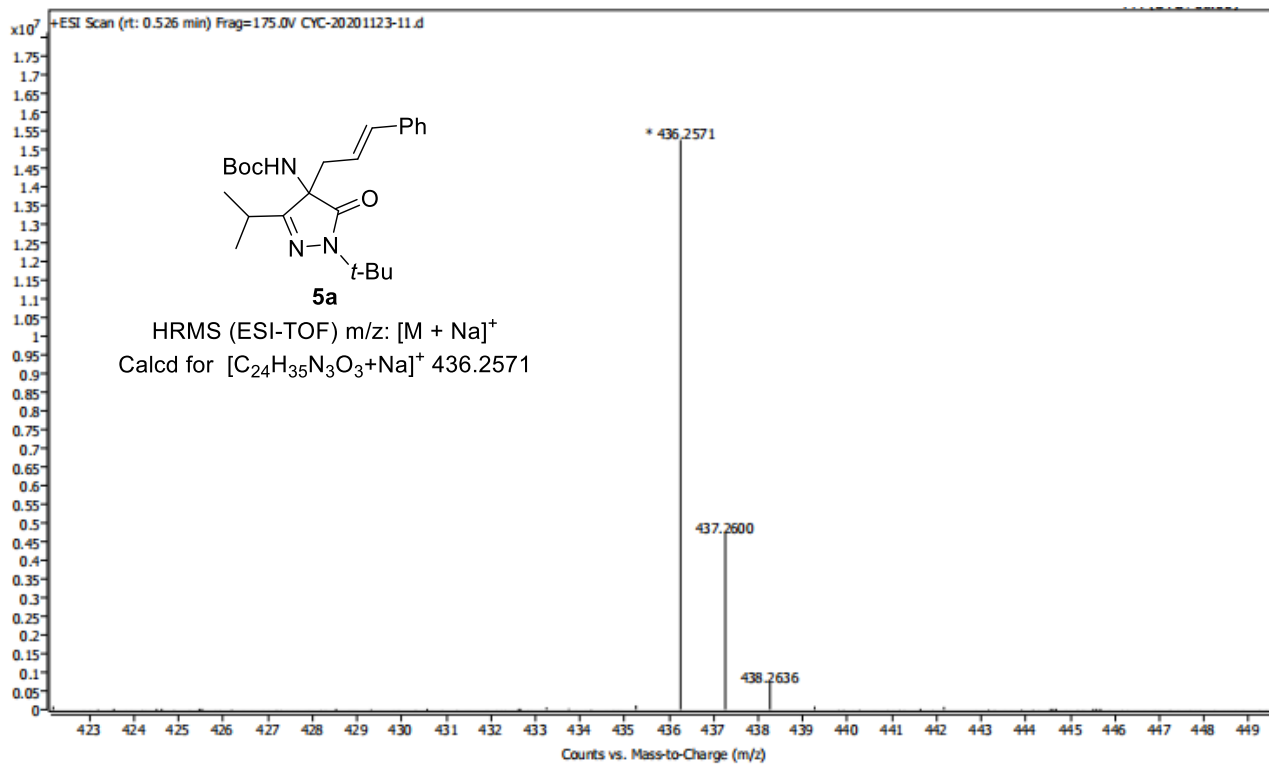
173.872
162.828
153.632
136.495
135.677
128.599
127.829
126.353
120.078
77.374
77.057
76.740
65.741
57.470
38.230
28.191
28.097
20.842
20.409



5a

¹³C NMR (100 MHz, CDCl₃)

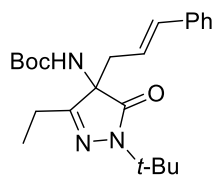




7.329
7.322
7.309
7.302
7.294
7.279
7.274
7.262
7.252
7.238
7.231
7.222
7.216
7.209
6.509
6.470
5.997
5.978
5.959
5.939
5.920

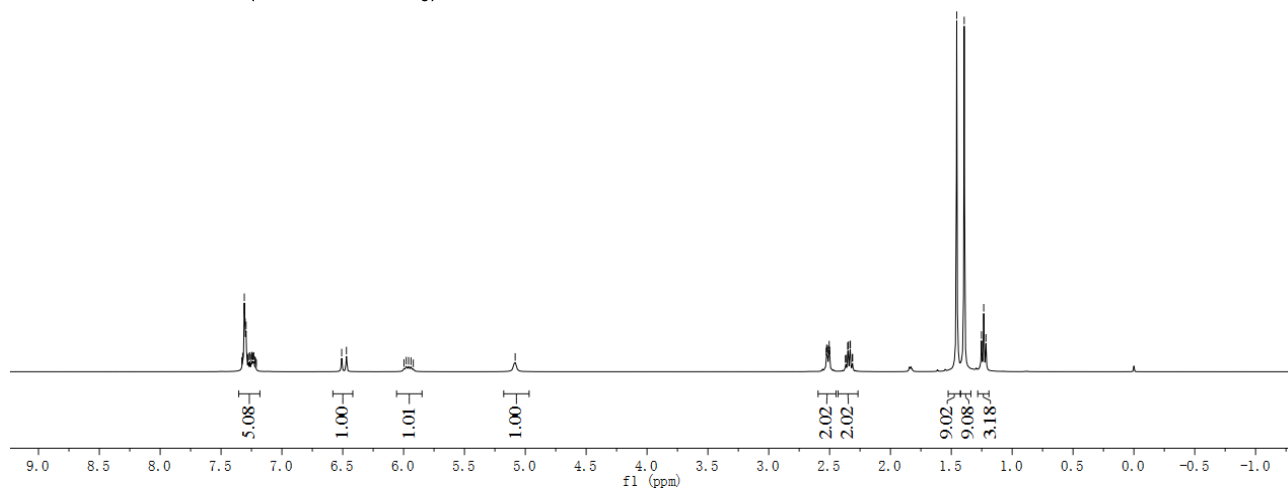
— 5.083

2.527
2.524
2.520
2.516
2.507
2.503
2.499
2.370
2.366
2.351
2.348
2.333
2.329
2.314
2.311
1.456
1.394
1.252
1.234
1.215



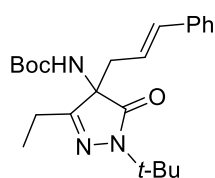
5b

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



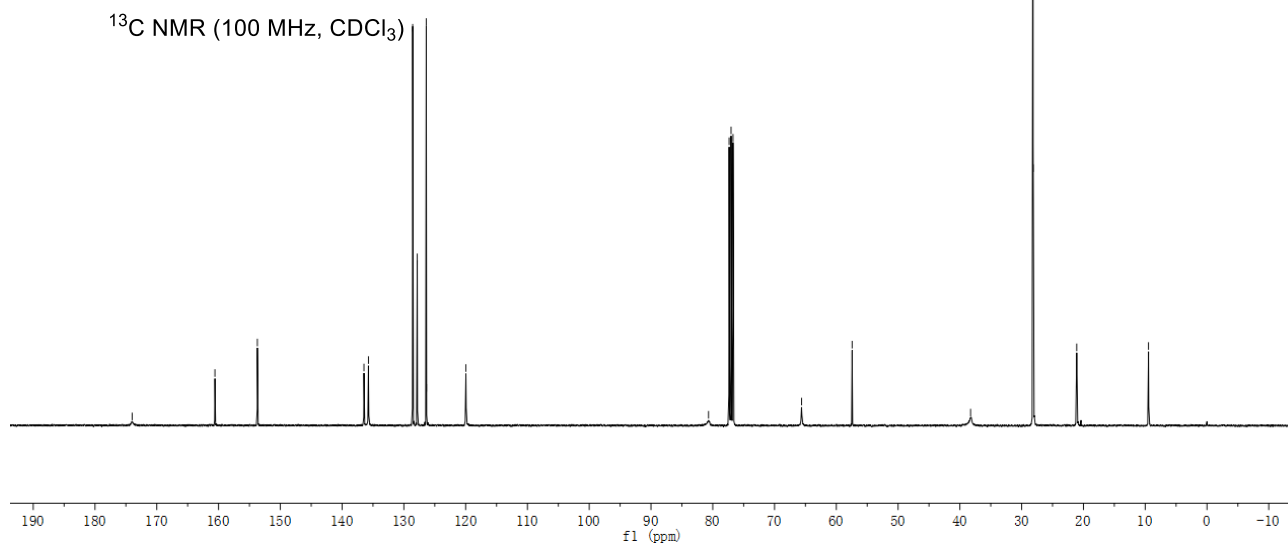
173.980
160.585
153.718
136.461
135.739
128.575
127.835
126.378
126.341
119.962

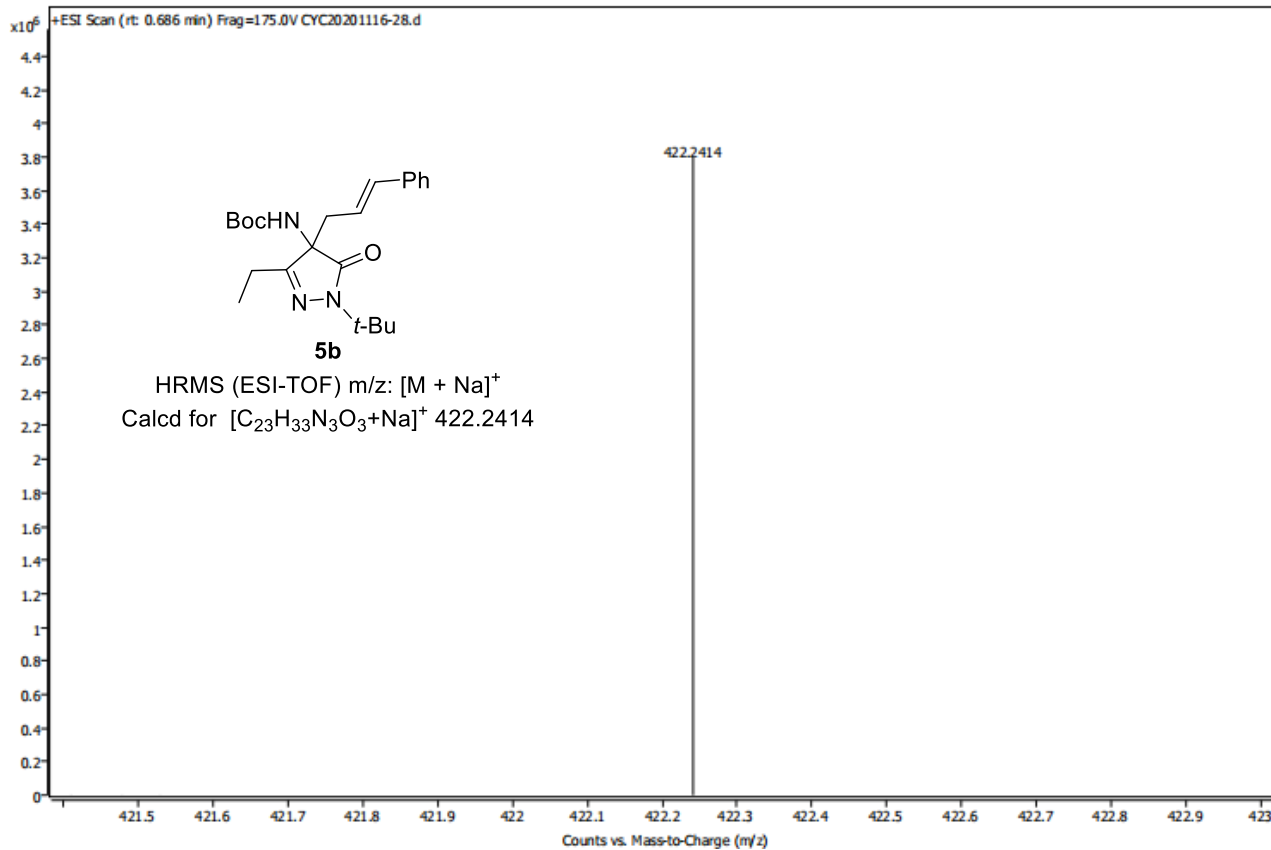
80.685
77.356
77.038
76.721
65.628
57.441
38.264
28.168
28.135
21.081
9.463



5b

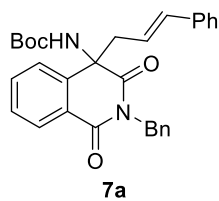
$^{13}\text{C NMR}$ (100 MHz, CDCl_3)



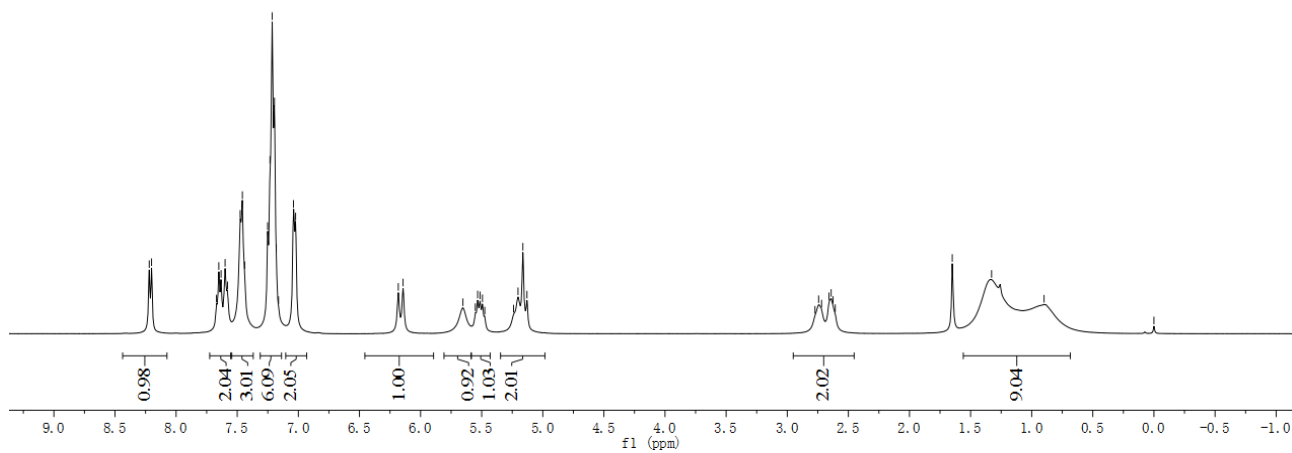


8.220
8.201
7.670
7.651
7.632
7.599
7.579
7.476
7.458
7.439
7.251
7.232
7.214
7.195
7.180
7.162
7.039
7.022
6.182
6.143
5.653
5.552
5.533
5.513
5.494
5.475
5.239
5.203
5.163
5.129

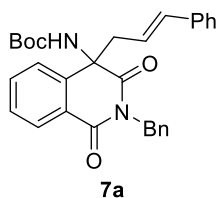
2.773
2.743
2.719
2.658
2.641
2.625
2.607
— 1.650
— 1.328
— 0.899
— 0.000



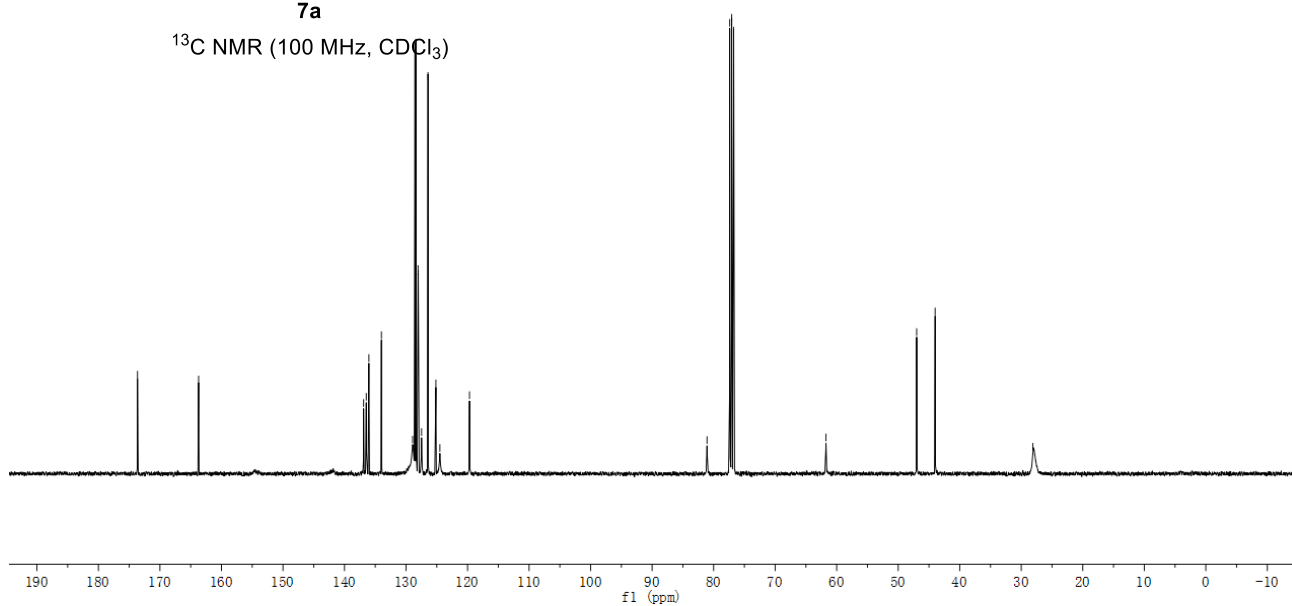
¹H NMR (400 MHz, CDCl₃)

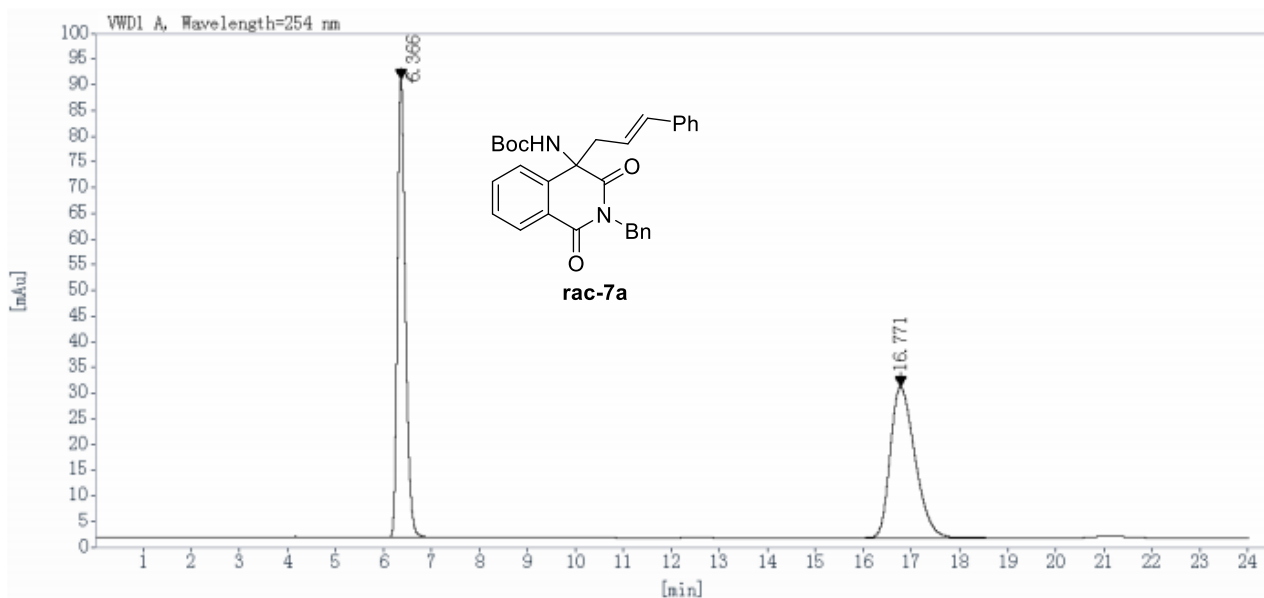


173.645
163.713
136.893
136.461
136.036
134.002
128.927
128.542
128.387
128.041
128.006
127.475
126.427
125.143
124.498
119.684
81.072
77.385
77.067
76.750
61.738
46.999
43.996
28.109

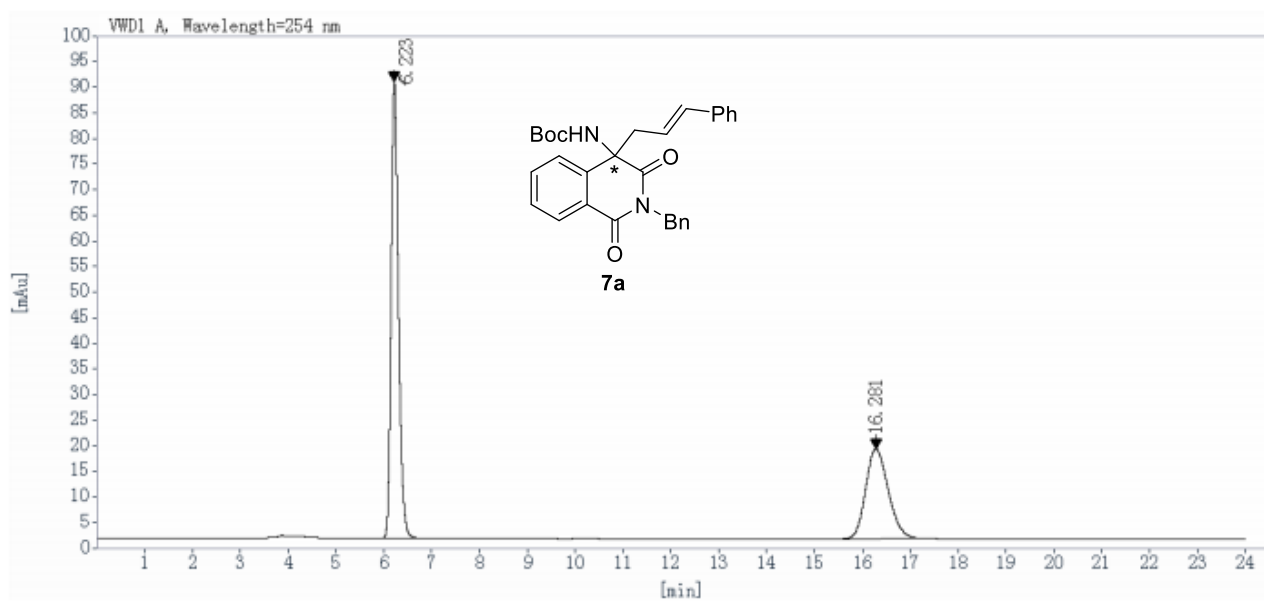


¹³C NMR (100 MHz, CDCl₃)

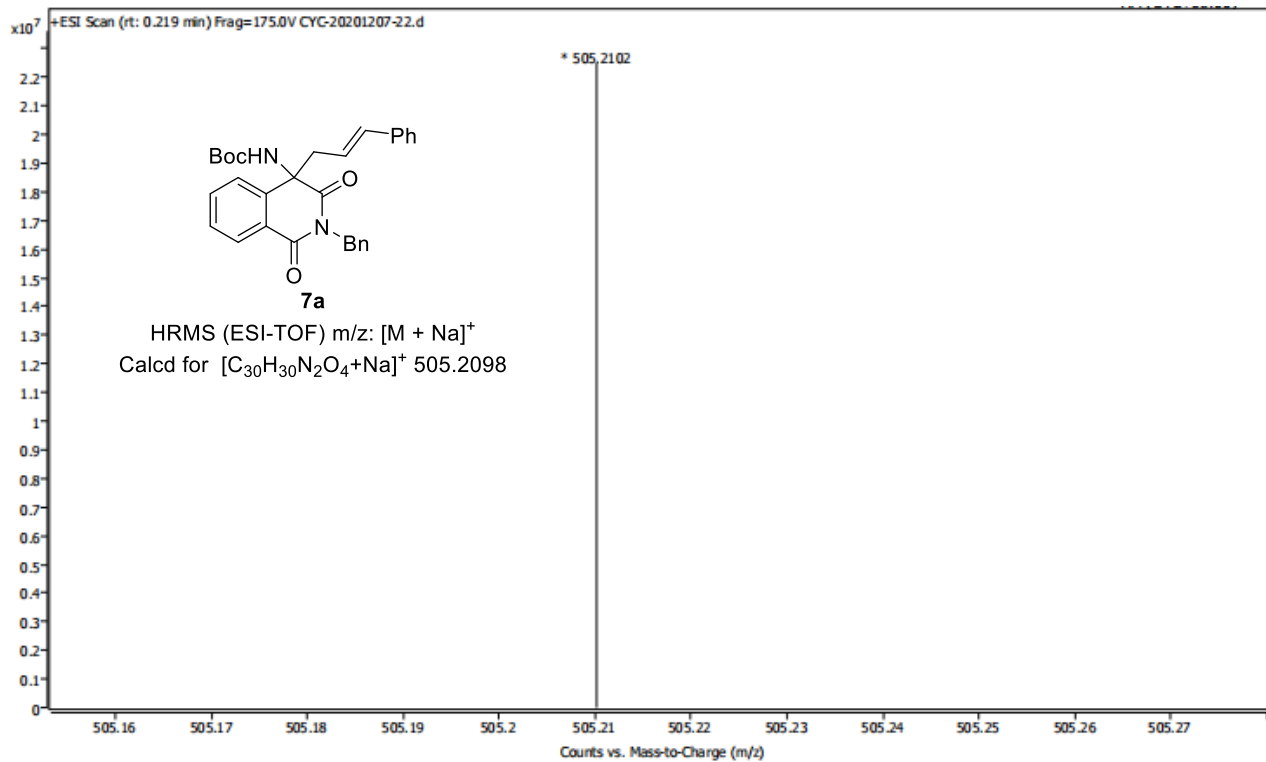




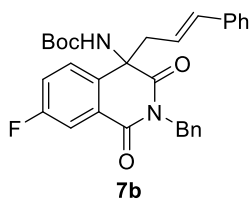
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.366	BB	0.18	2541.4800	29407.3379	49.5486
16.771	BBA	0.56	834.9534	29943.1660	50.4514
Totals:				59350.5039	100.0000



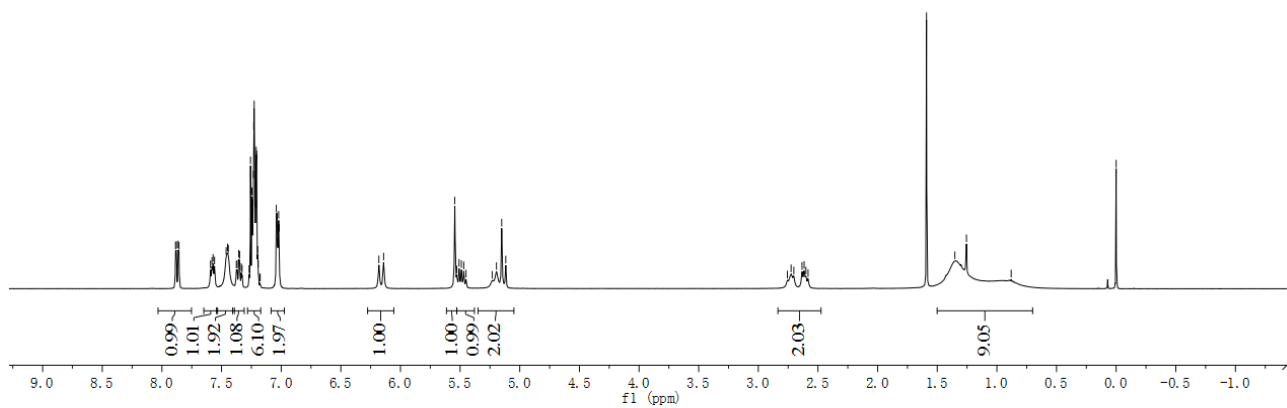
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.223	BV R	0.16	1554.8115	16612.5664	62.4217
16.281	BBA	0.51	305.9828	10000.8613	37.5783
Totals:				26613.4277	100.0000



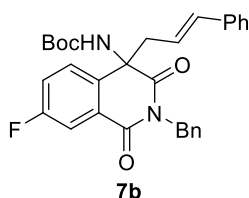
7.886
7.879
7.864
7.857
7.593
7.581
7.571
7.559
7.462
7.450
7.443
7.376
7.369
7.356
7.349
7.335
7.328
7.268
7.264
7.257
7.246
7.242
7.237
7.233
7.226
7.221
7.214
7.209
7.206
7.197
7.192
7.180
7.176
7.041
7.035
7.030
7.027
7.021
7.017
6.181
6.142
5.545
5.529
5.509
5.489
5.469
5.450
5.231
5.195
5.151
5.117
2.756
2.725
2.702
2.633
2.616
2.601
2.583
1.590
1.352
1.255
0.880
0.000



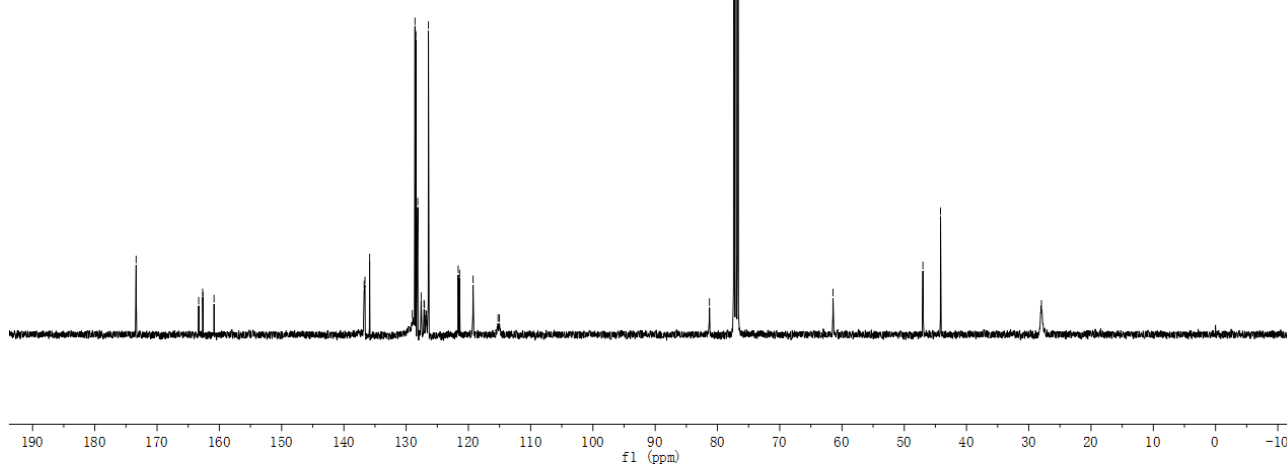
$^1\text{H NMR}$ (400 MHz, CDCl_3)



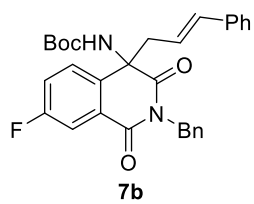
173.369
163.320
162.673
162.647
160.852
136.748
136.612
135.861
129.012
128.579
128.430
128.131
127.588
127.135
127.059
126.895
126.822
126.742
126.670
126.422
121.633
121.410
119.250
115.244
115.016
81.296
77.353
77.353
77.035
76.718
61.437
47.001
44.169
27.970



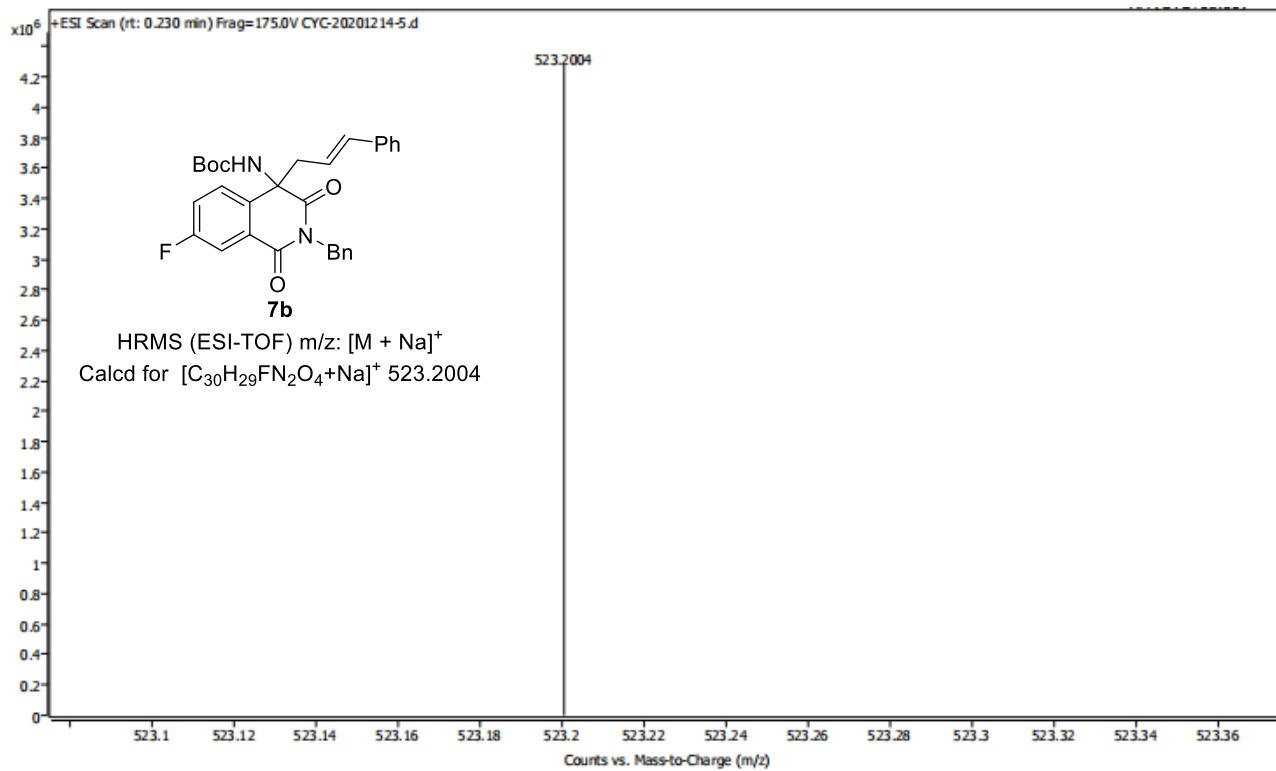
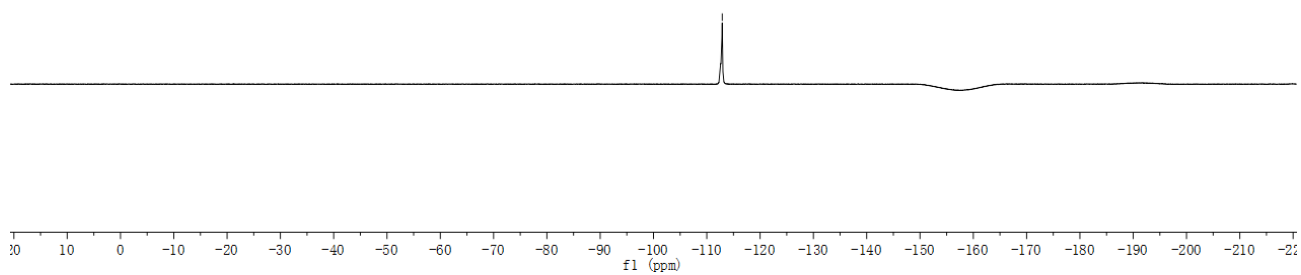
$^{13}\text{C NMR}$ (100 MHz, CDCl_3)



—112.897



¹⁹F NMR (376 MHz, CDCl₃)



7.672
7.666
7.484
7.463
7.257
7.240
7.235
7.227
7.221
7.212
7.201
7.196
7.191
7.054
7.048
7.034
6.889
6.167
5.562
5.543
5.532
5.524
5.504
5.485
5.232
5.195
5.157
5.123

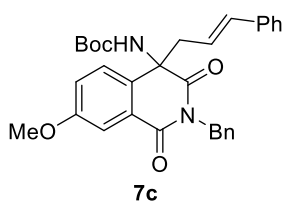
—3.871

2.760
2.739
2.727
2.707
2.642
2.625
2.610
2.592

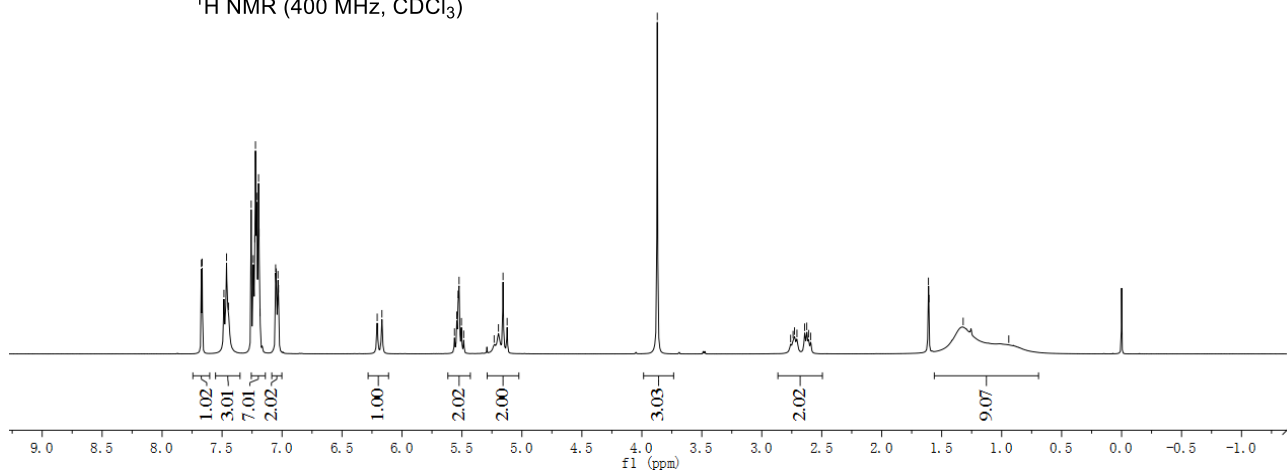
1.611
1.606

1.321

—0.941



¹H NMR (400 MHz, CDCl₃)



173.813
163.661
159.186
136.853
136.331
136.056
134.058
129.121
128.513
128.359
127.951
127.426
126.401
126.122
125.996
122.264
119.788
110.985

80.968
77.348
77.031
76.713

61.263

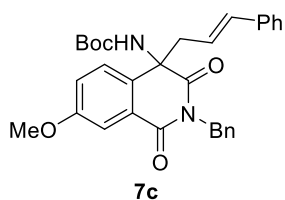
55.616

47.036

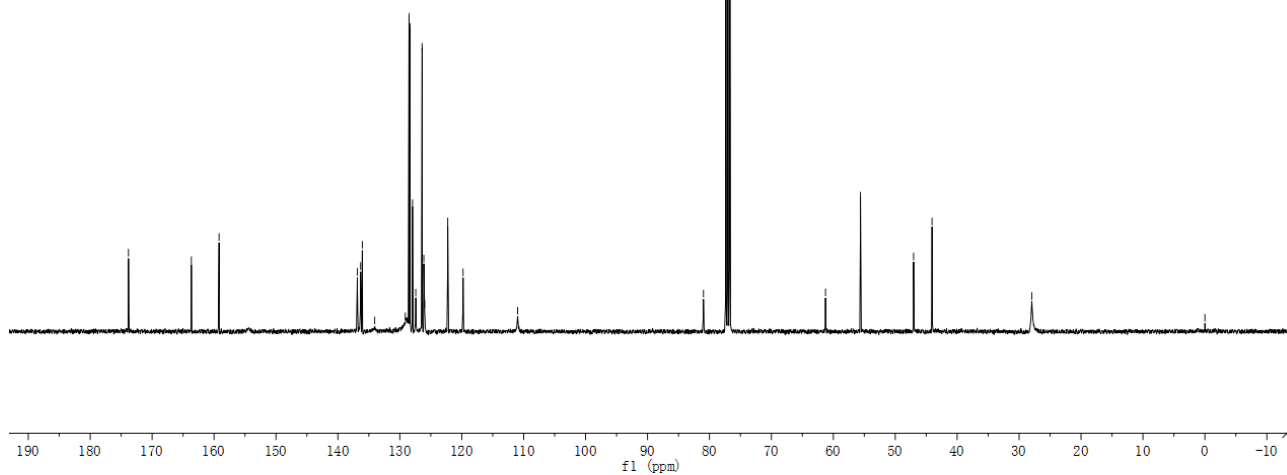
44.060

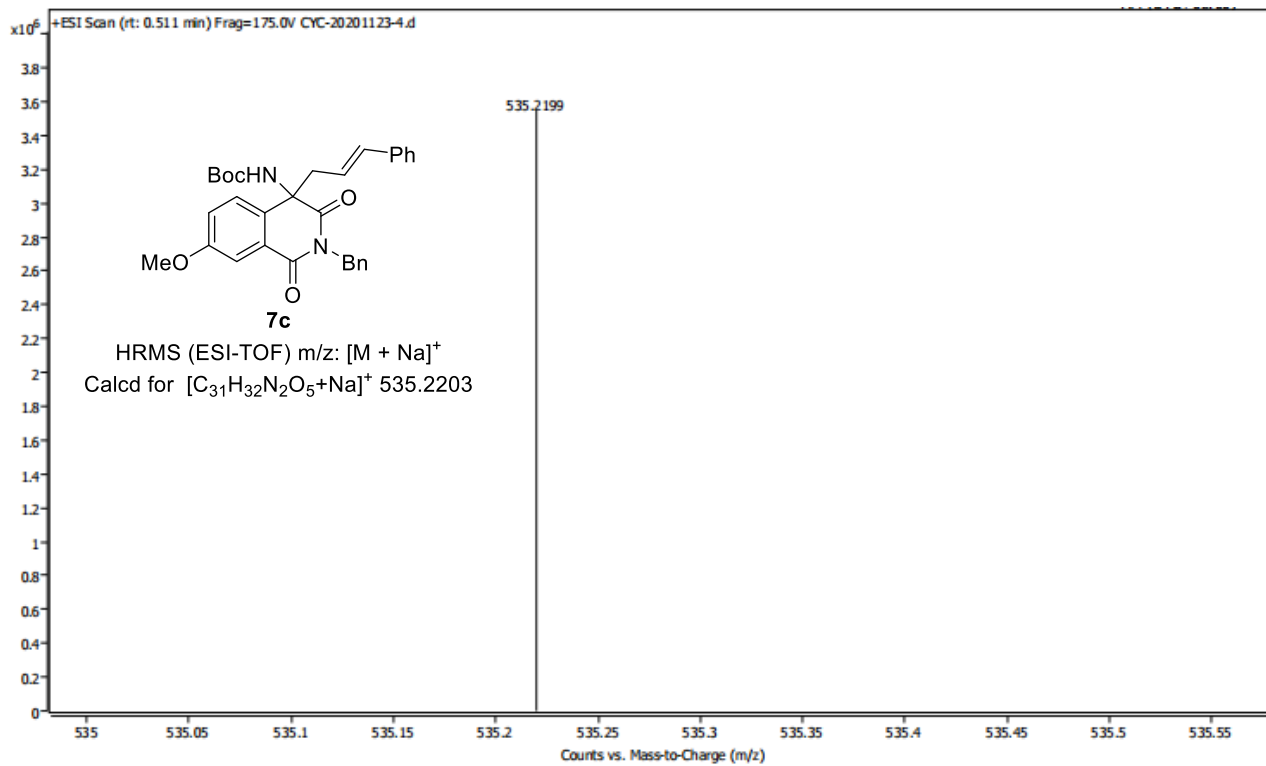
27.946

—0.000

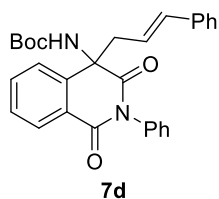


¹³C NMR (100 MHz, CDCl₃)

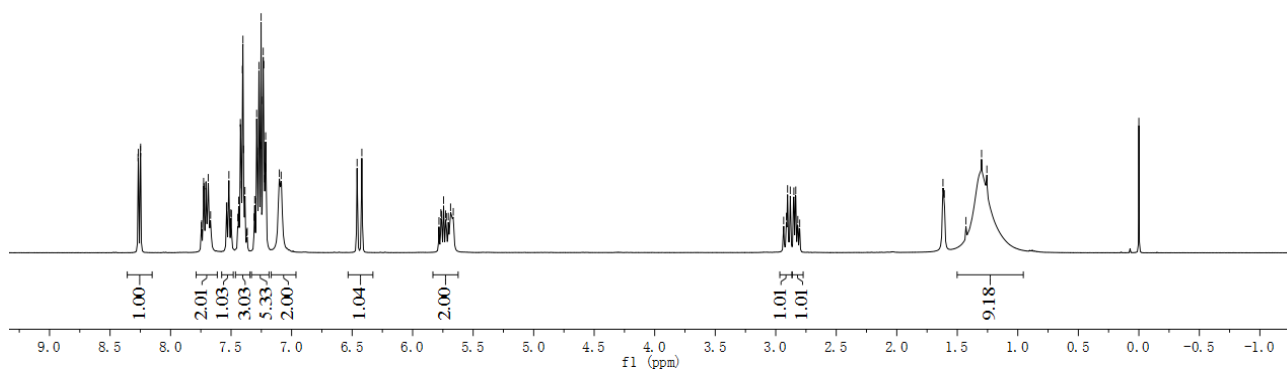




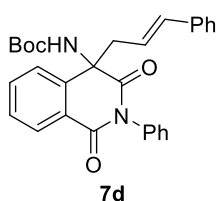
8.269
8.267
8.249
8.247
7.727
7.724
7.709
7.706
7.689
7.669
7.538
7.535
7.518
7.501
7.498
7.444
7.437
7.423
7.420
7.414
7.406
7.402
7.397
7.385
7.310
7.305
7.301
7.294
7.289
7.284
7.270
7.260
7.256
7.252
7.239
7.235
7.230
7.224
7.220
7.215
7.211
7.101
7.086
6.459
6.420
5.767
5.760
5.744
5.727
5.721
5.705
5.687
5.664
2.935
2.912
2.902
2.880
2.850
2.834
2.818
1.618
1.607
1.299
1.256
-0.000



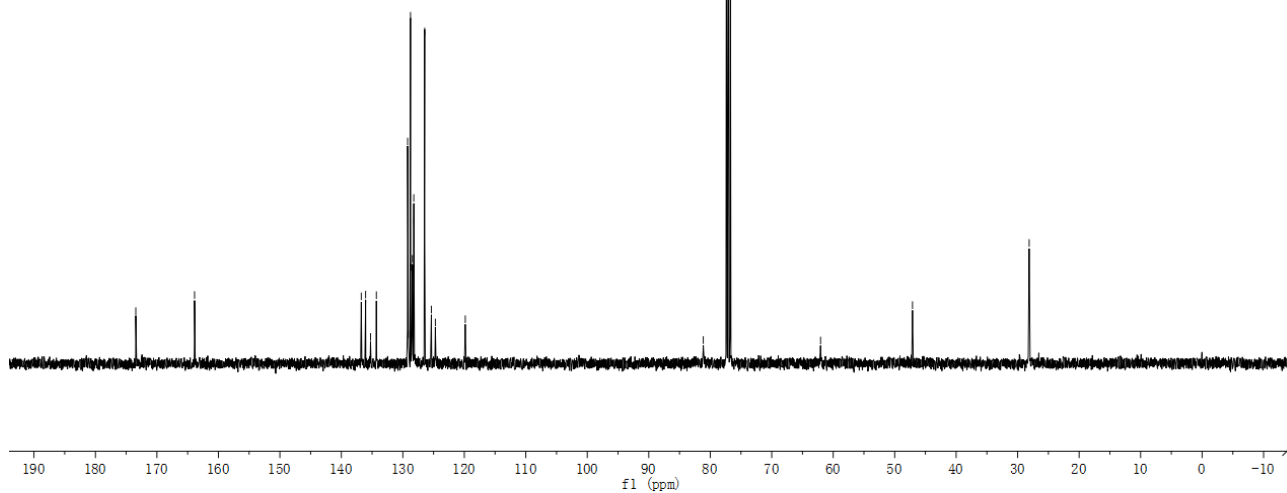
$^1\text{H NMR}$ (400 MHz, CDCl_3)

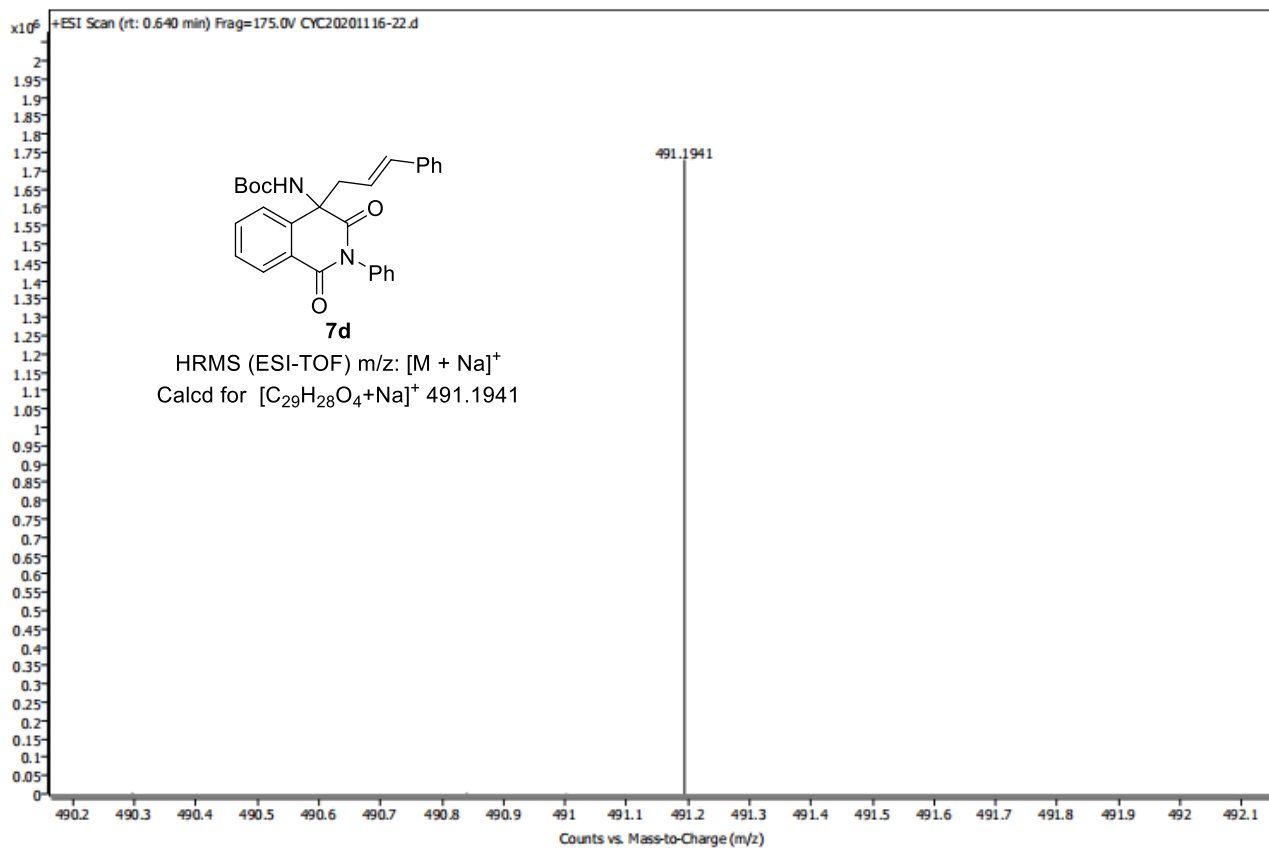


173.437
163.879
136.763
135.247
134.305
129.222
129.114
128.754
128.611
128.451
128.219
128.196
126.449
125.362
124.711
119.843
81.131
77.370
77.053
76.735
62.055
47.101
28.127

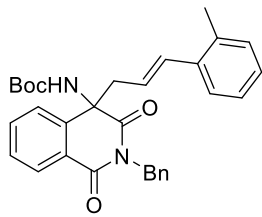


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)



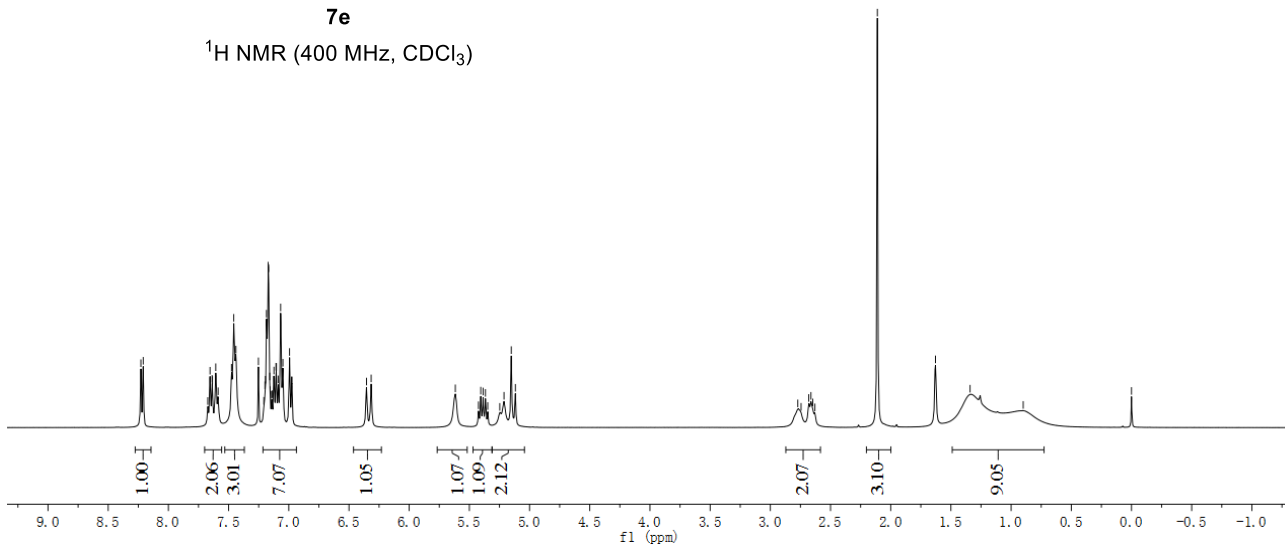


8.229
8.209
7.673
7.654
7.637
7.634
7.607
7.587
7.476
7.457
7.439
7.252
7.207
7.198
7.194
7.185
7.172
7.167
7.158
7.154
7.143
7.139
7.123
7.107
7.103
7.088
7.067
7.049
6.994
6.977
6.973
6.955
6.316
5.617
5.424
5.405
5.386
5.366
5.347
5.247
5.212
5.152
5.118
2.772
2.745
2.681
2.662
2.648
2.630
2.111
1.628
1.341
1.0899
0.000

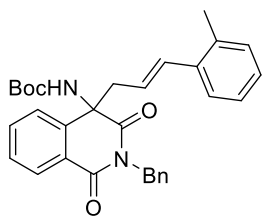


7e

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

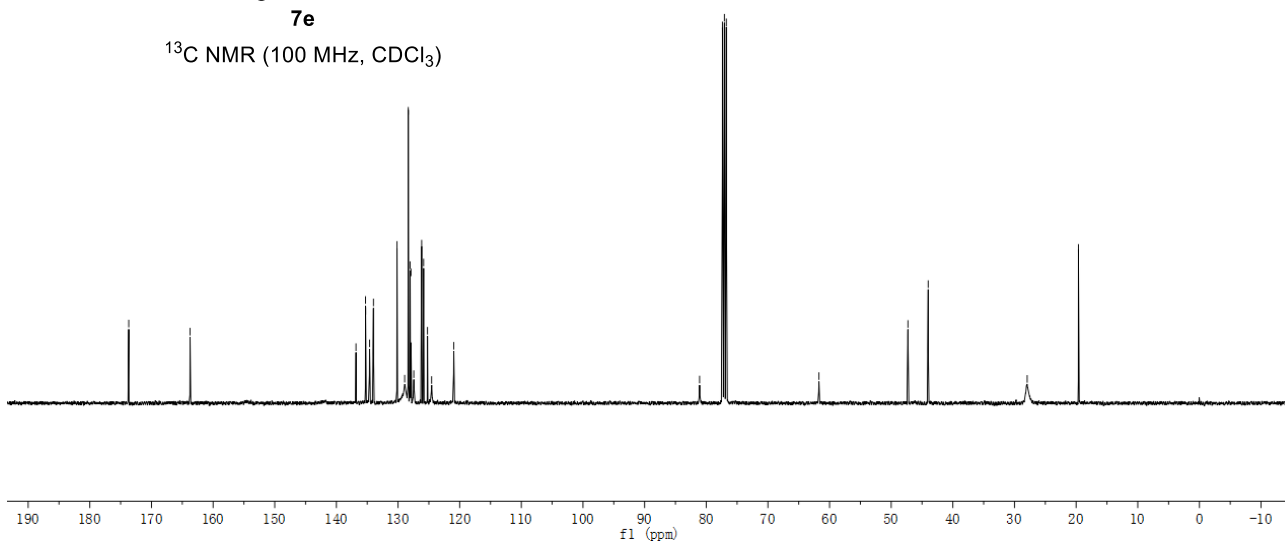


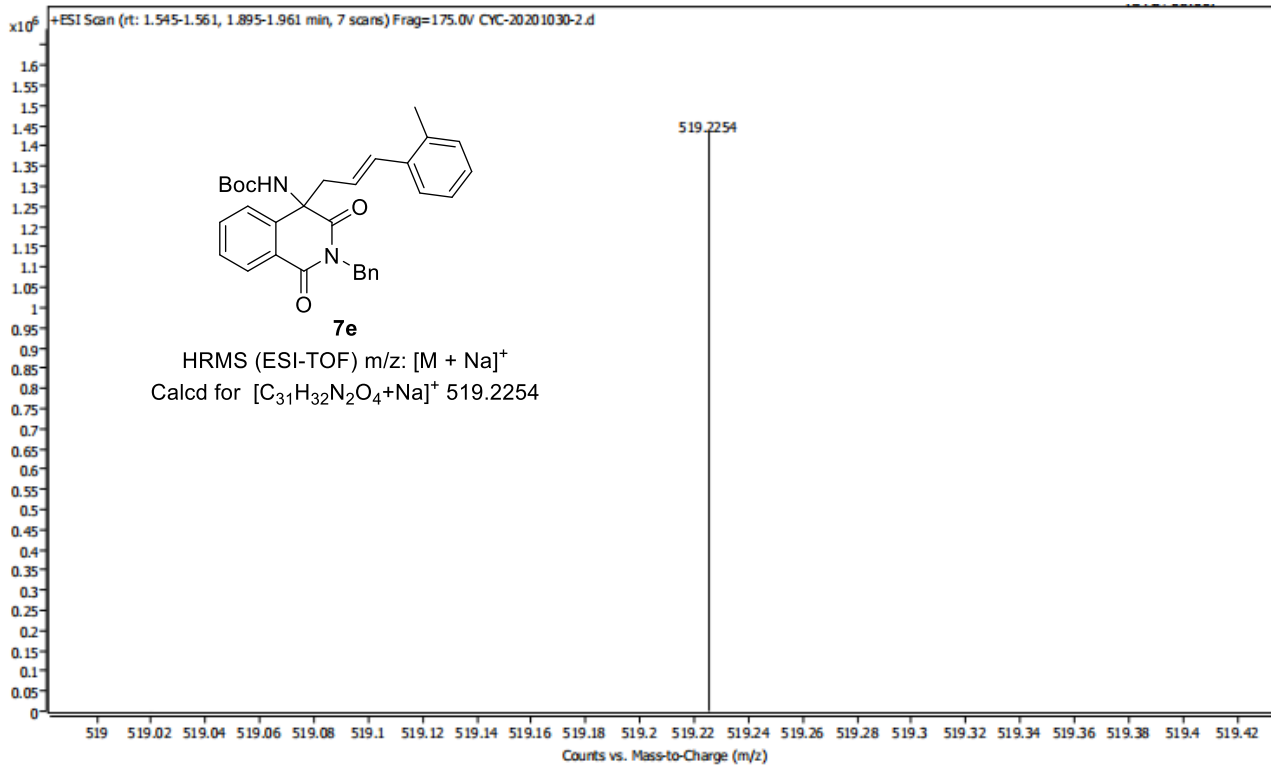
173.684
163.736
136.820
135.274
135.251
134.618
133.990
130.166
128.925
128.341
128.033
127.902
127.442
126.164
125.849
125.223
124.550
120.962
81.081
77.378
77.061
76.744
61.723
47.284
44.000
27.941
19.628



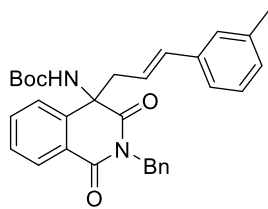
7e

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



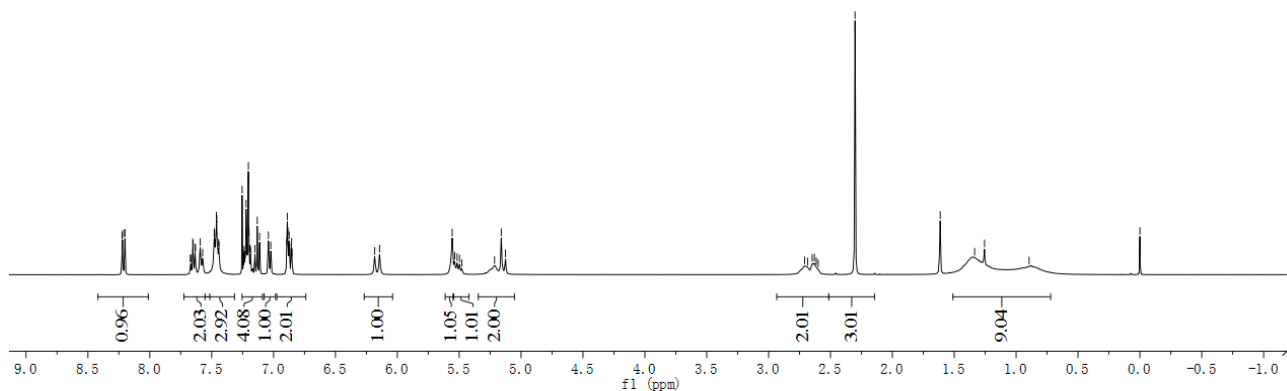


8.223
8.221
8.204
8.201
7.672
7.669
7.653
7.649
7.635
7.631
7.593
7.573
7.479
7.478
7.462
7.459
7.444
7.441
7.254
7.244
7.240
7.237
7.233
7.230
7.222
7.218
7.214
7.208
7.203
7.198
7.195
7.188
7.186
7.151
7.132
7.113
7.041
7.023
6.894
6.889
6.884
6.874
6.869
6.858
6.854
6.850
6.183
6.143
5.557
5.536
5.517
5.214
5.497
5.160
5.126
2.709
2.648
2.630
2.302
1.613
1.335
1.255
0.895
0.000

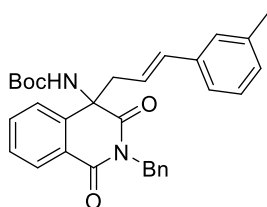


7f

¹H NMR (400 MHz, CDCl₃)

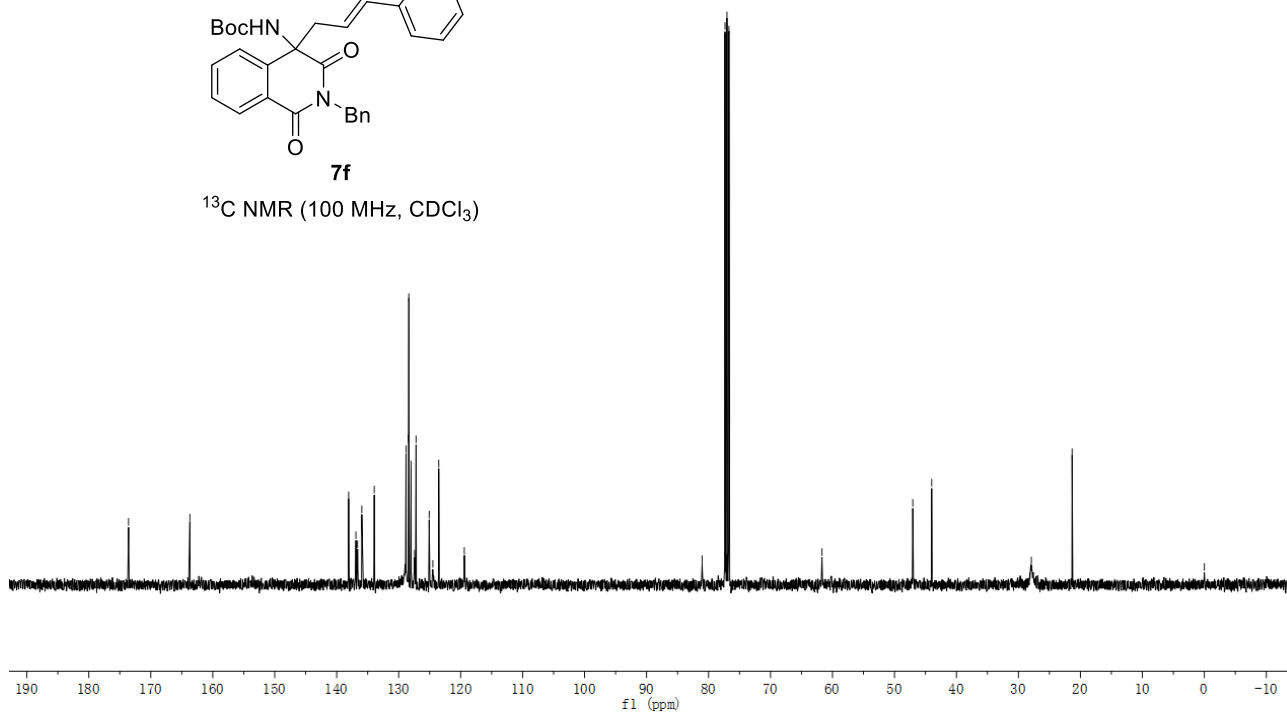


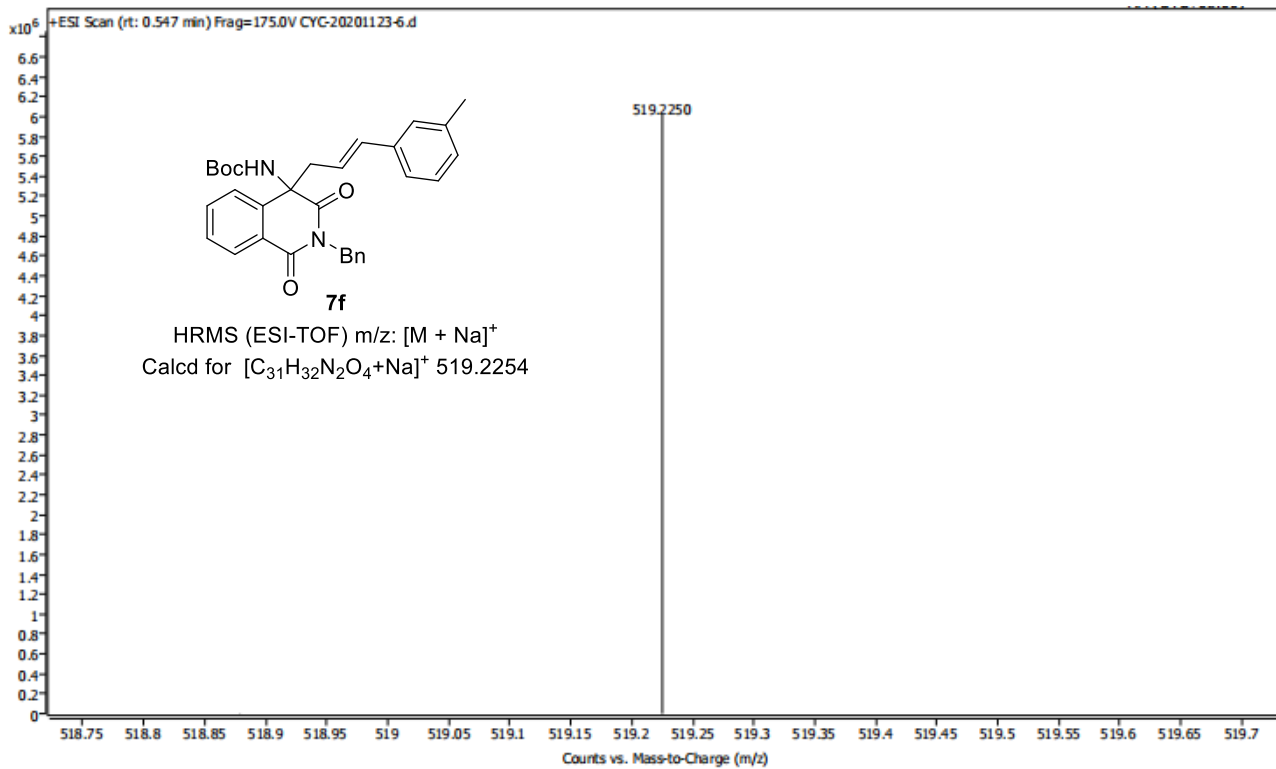
173.586
163.691
138.074
136.897
136.631
135.951
133.941
128.819
128.432
128.361
127.996
127.426
127.194
125.077
124.489
123.533
119.410
81.039
77.345
77.028
76.710
61.698
47.046
43.995
27.912
21.335
0.000



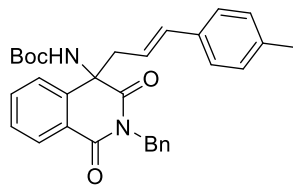
7f

¹³C NMR (100 MHz, CDCl₃)



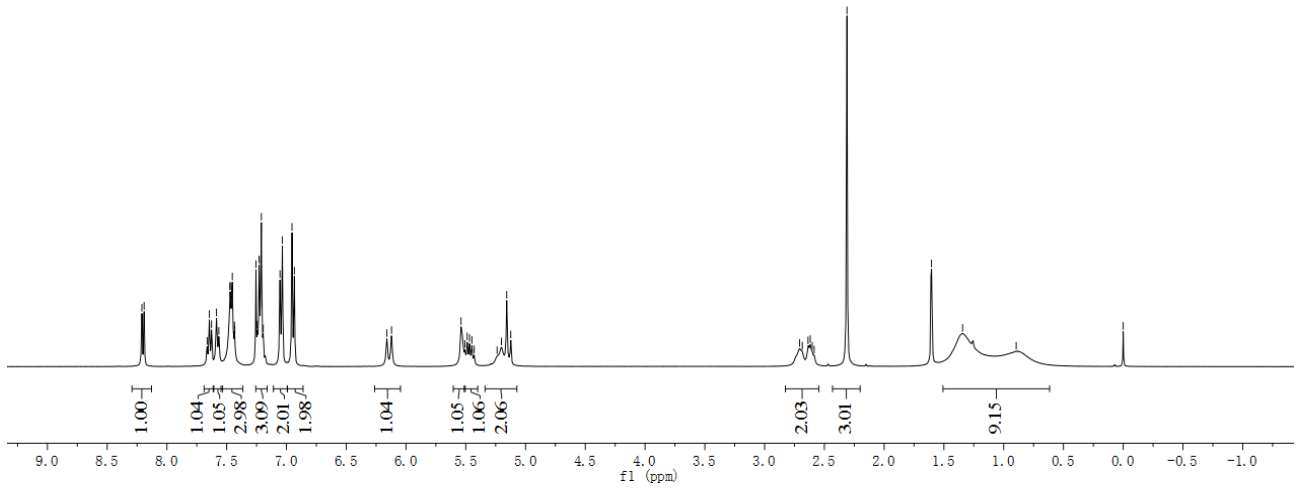


8.209
8.191
7.663
7.645
7.627
7.585
7.566
7.472
7.471
7.453
7.435
7.432
7.255
7.244
7.229
7.215
7.210
7.204
7.194
7.054
7.035
6.954
6.934
6.160
6.121
5.540
5.507
5.488
5.468
5.449
5.430
5.202
5.238
5.157
5.123
2.707
2.685
2.636
2.618
2.602
2.585
2.311
1.604
1.344
-0.895
-0.000

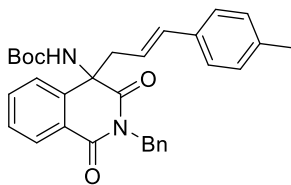


7g

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

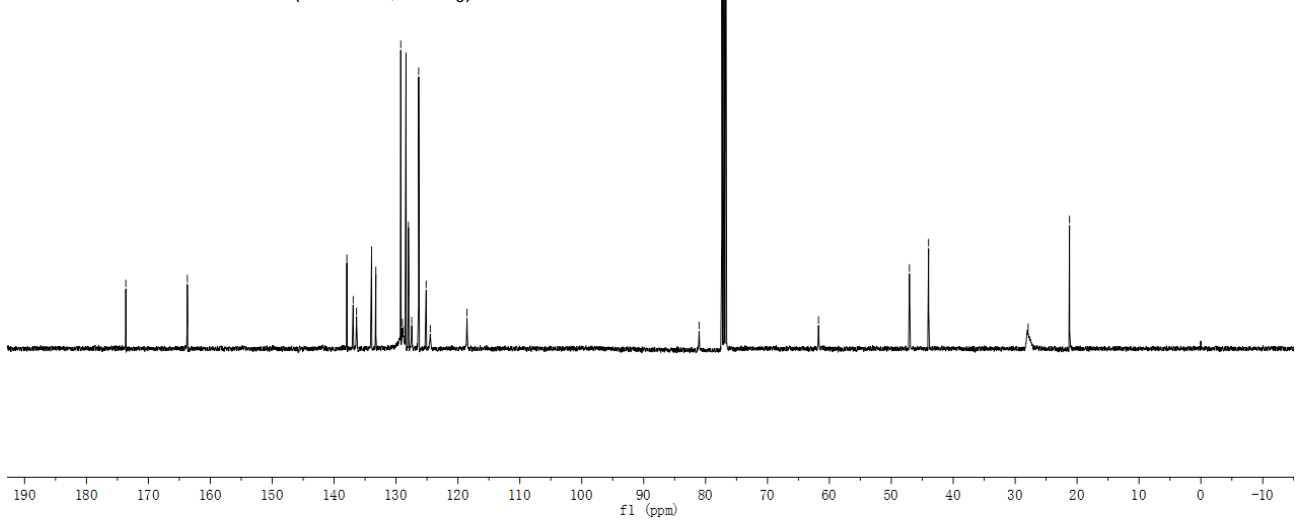


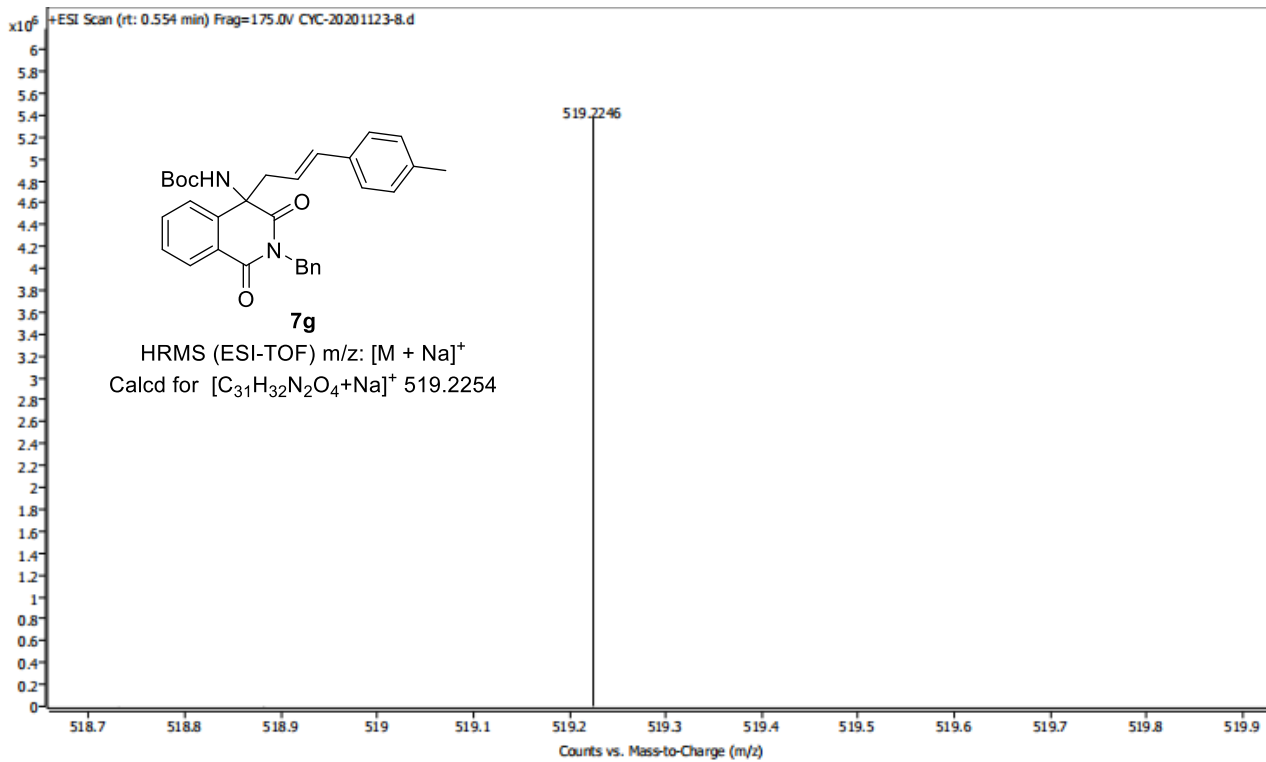
173.640
163.704
137.942
136.923
136.379
133.948
133.256
129.236
128.965
128.809
128.387
127.996
127.461
126.344
125.126
124.467
118.537
81.047
77.365
77.046
76.729
61.763
47.079
43.985
27.907
21.225



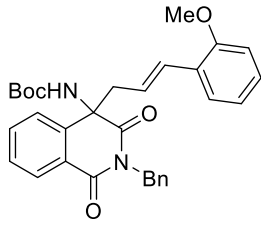
7g

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



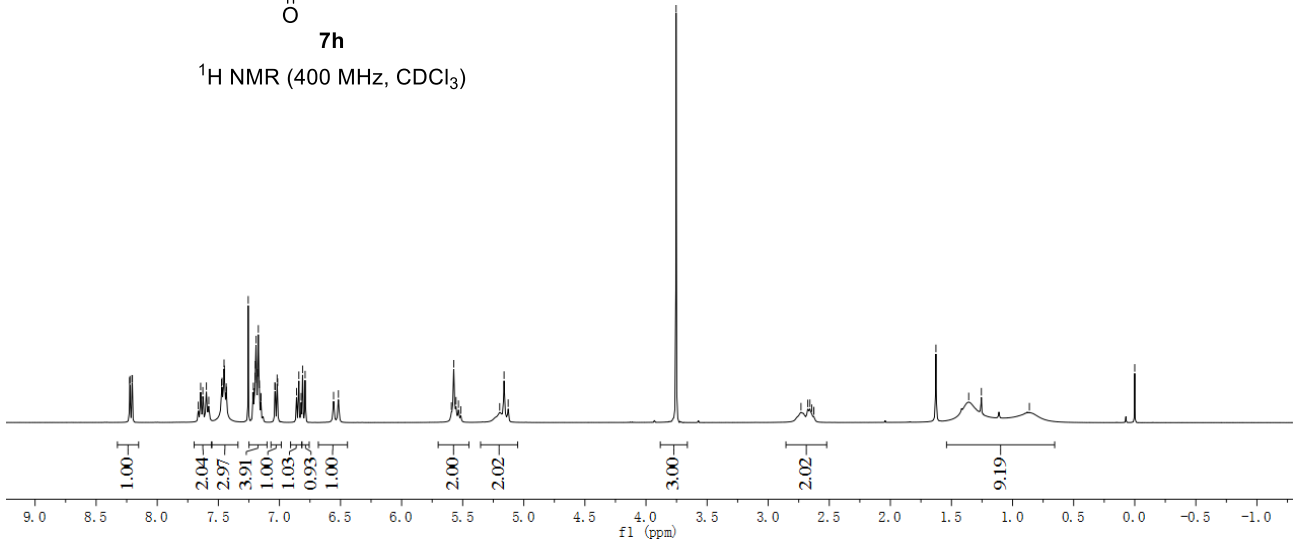


8.227
8.223
8.207
8.203
7.664
7.645
7.627
7.598
7.578
7.473
7.470
7.453
7.451
7.436
7.432
7.255
7.218
7.213
7.207
7.200
7.196
7.191
7.186
7.179
7.173
7.164
7.153
7.151
7.038
7.034
7.019
7.014
6.860
6.841
6.822
6.810
6.790
6.557
6.517
5.593
5.573
5.555
5.535
5.516
5.197
5.162
5.128
3.753
2.731
2.676
2.658
2.643
2.627
2.626
1.627
1.359
1.255
0.862
0.000

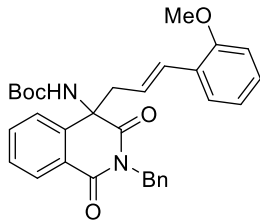


7h

¹H NMR (400 MHz, CDCl₃)

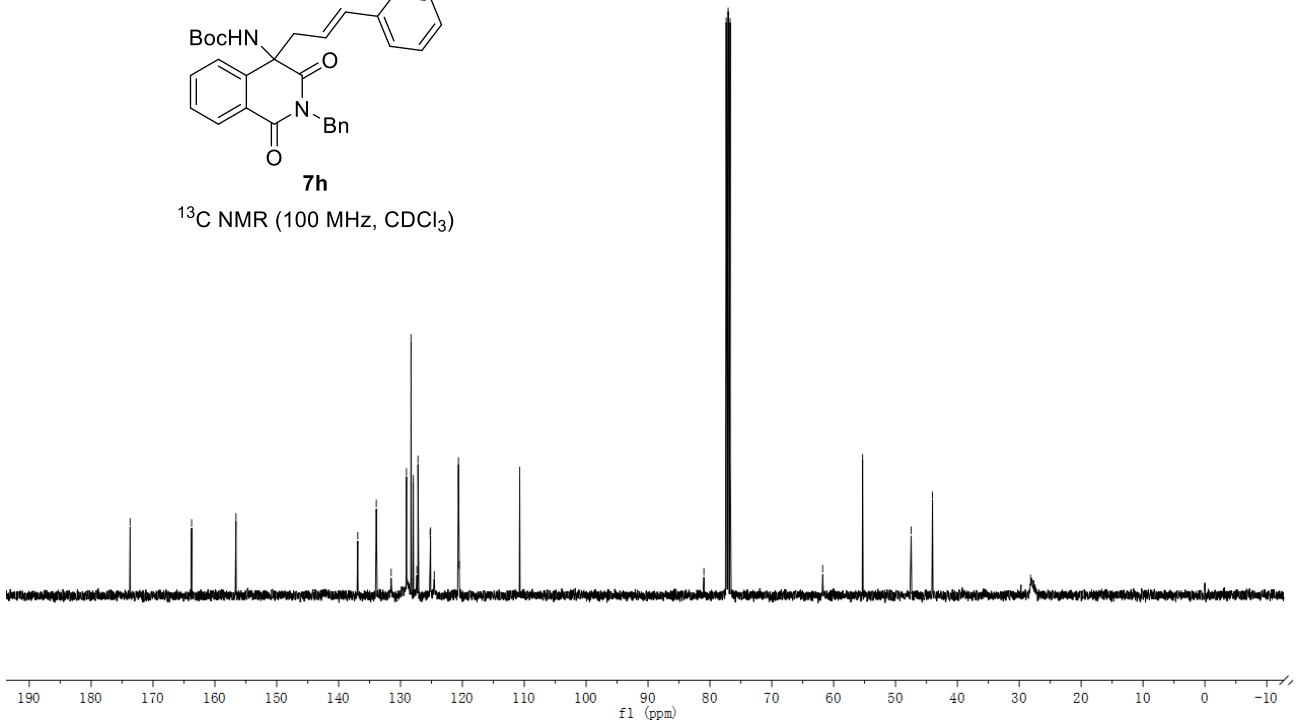


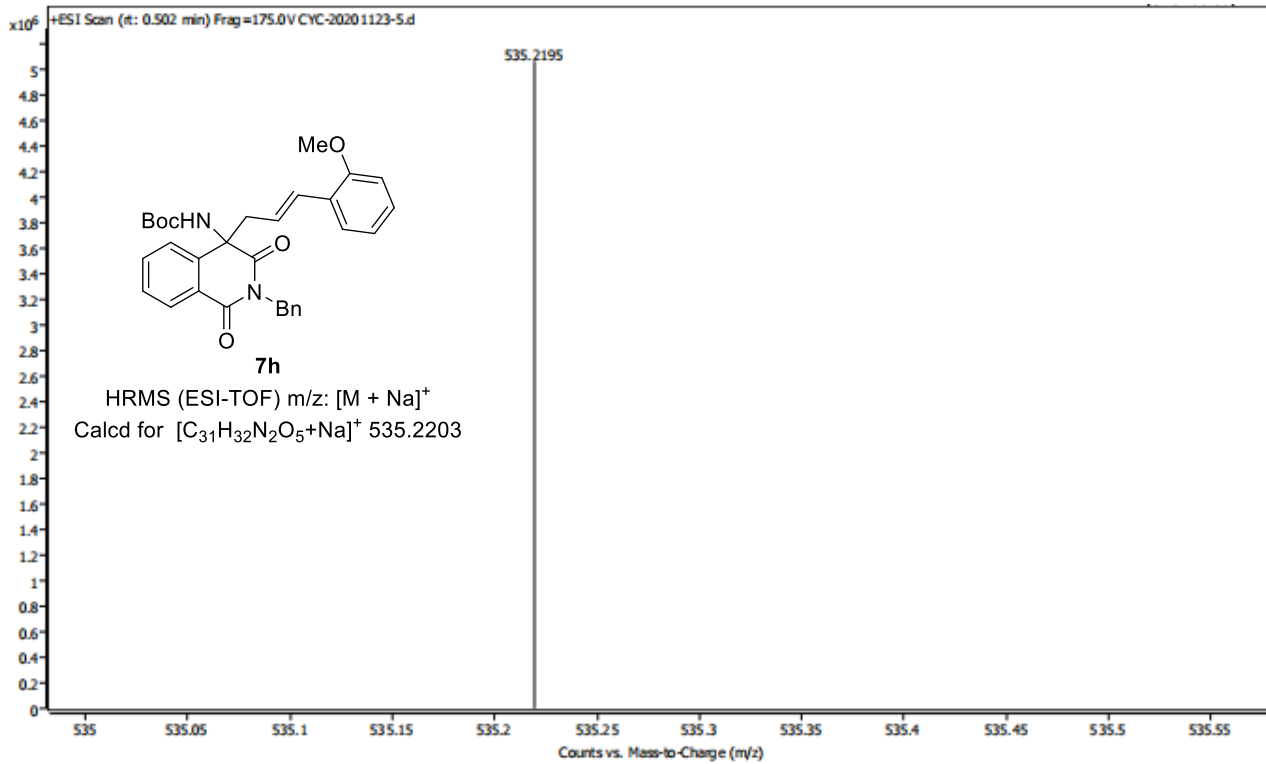
173.698
163.762
156.593
136.911
133.913
131.516
129.035
128.301
127.931
127.361
127.176
125.218
125.145
124.538
120.636
120.514
110.739
80.969
77.364
77.046
76.729
61.766
55.317
47.473
44.024
28.168

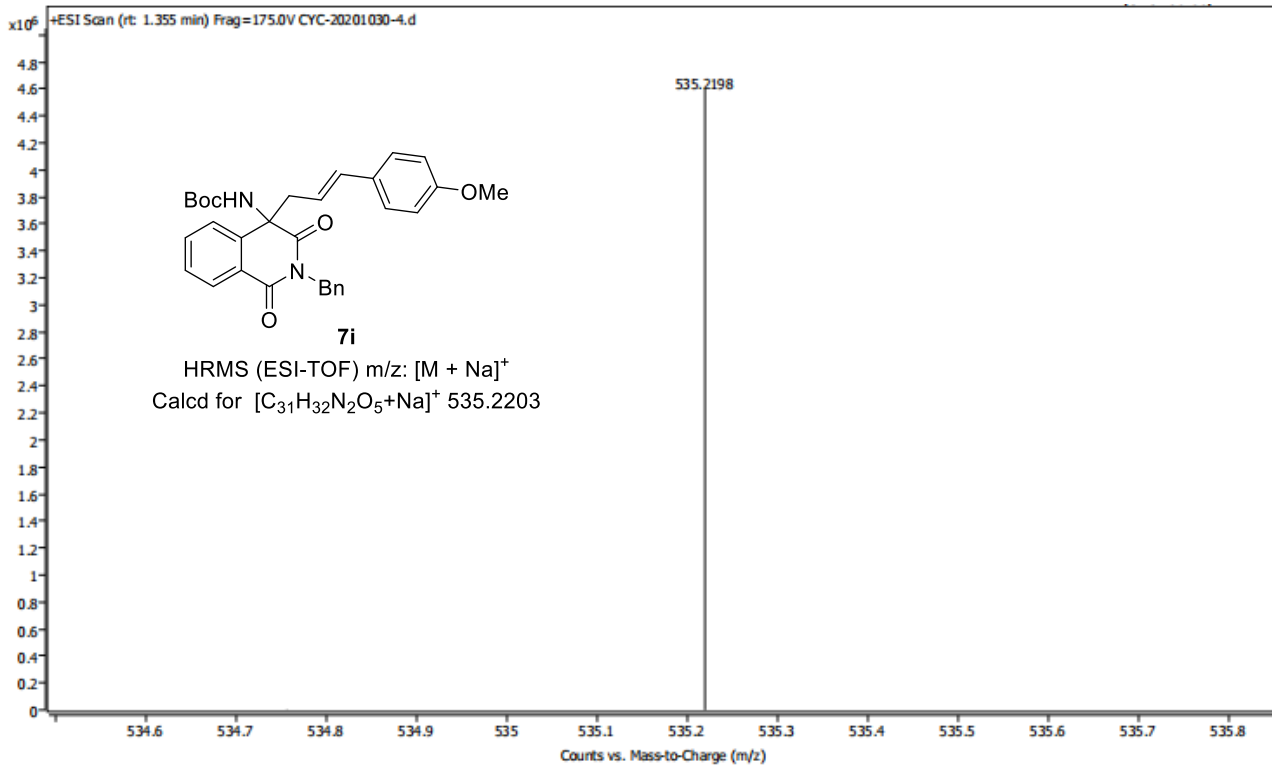


7h

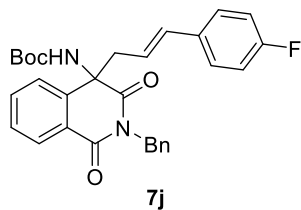
¹³C NMR (100 MHz, CDCl₃)



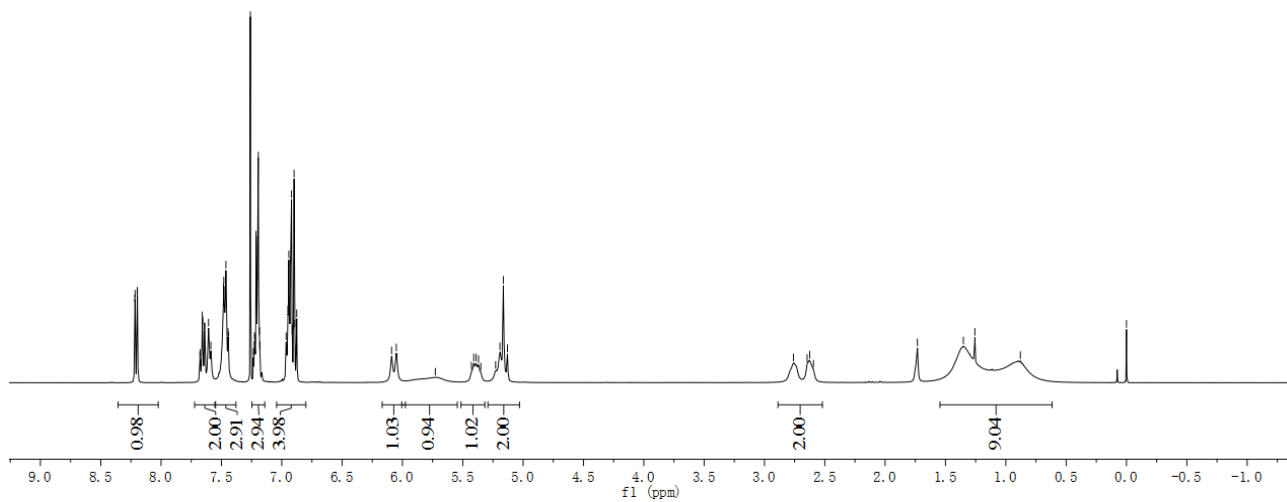




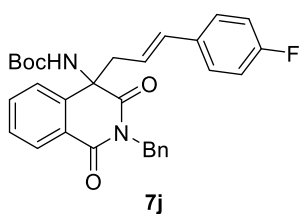
8.218
8.216
8.198
8.196
7.679
7.675
7.659
7.655
7.641
7.638
7.607
7.587
7.483
7.480
7.463
7.445
7.442
7.260
7.235
7.231
7.226
7.221
7.213
7.210
7.203
7.197
7.194
7.185
7.180
7.180
6.964
6.958
6.949
6.941
6.927
6.919
6.913
6.903
6.898
6.892
6.881
6.876
6.089
6.051
5.428
5.409
5.390
5.370
5.350
5.228
5.192
5.164
5.130
5.130
2.760
2.646
2.625
2.594
1.733
1.352
1.256
0.879



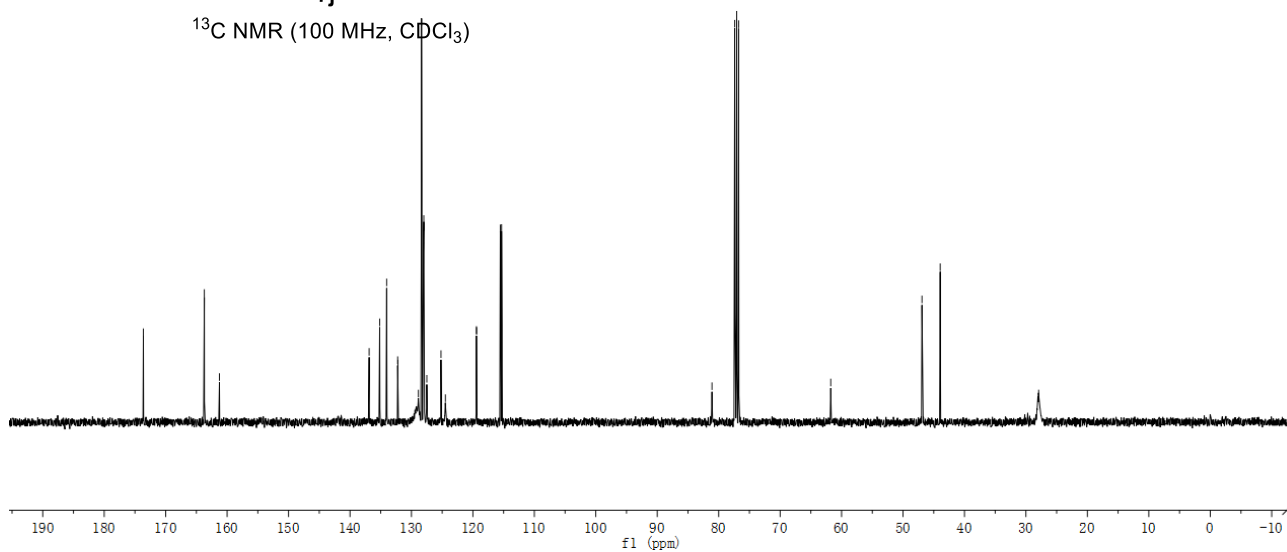
¹H NMR (400 MHz, CDCl₃)

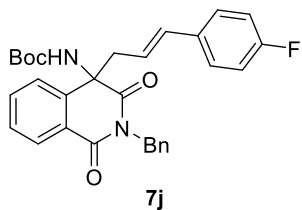


173.629
163.706
161.249
136.887
135.171
134.037
132.241
132.208
128.868
128.365
128.049
127.988
127.908
127.497
125.193
124.478
119.423
119.401
115.539
115.324
81.092
77.388
77.070
76.752
61.763
46.918
43.952
27.927



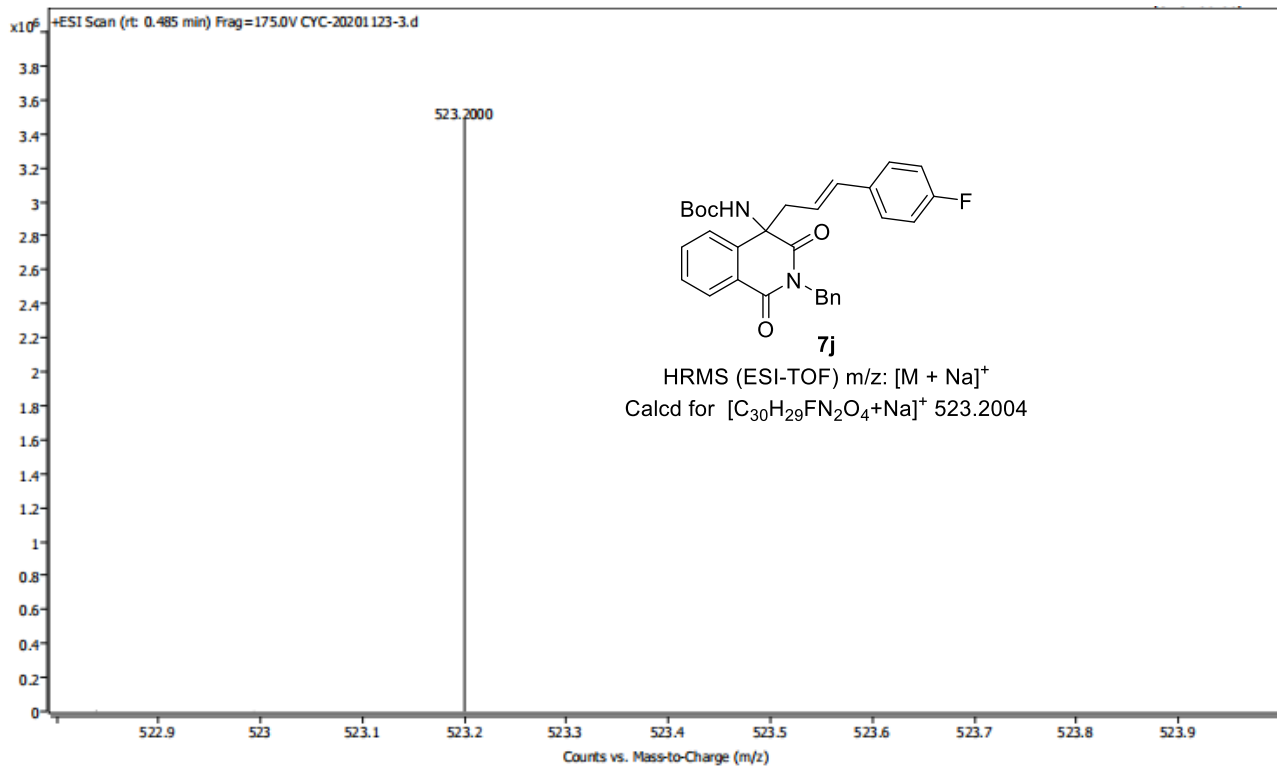
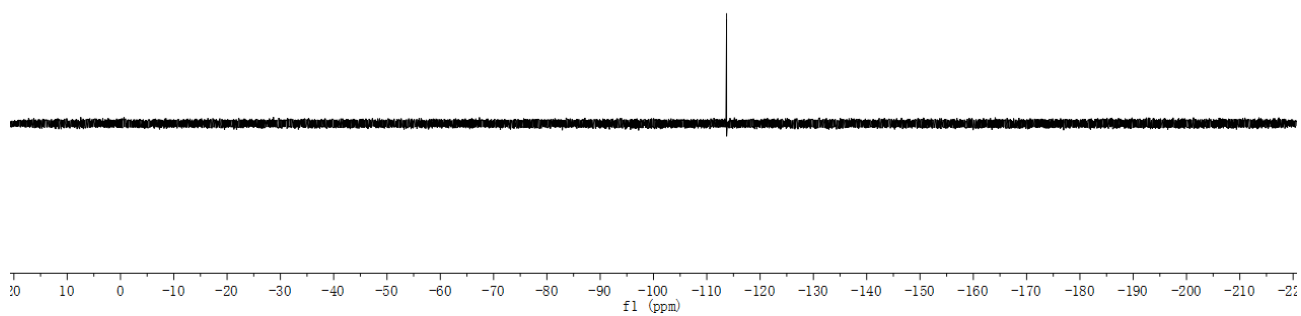
¹³C NMR (100 MHz, CDCl₃)





^{19}F NMR (376 MHz, CDCl_3)

---113.709



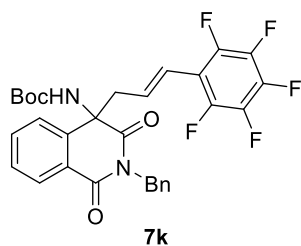
8.258
8.239
7.696
7.678
7.659
7.613
7.594
7.512
7.492
7.473
7.262
7.172
7.154
7.135
7.114
7.096
7.077
6.004
5.963
5.795
5.778
5.774
5.756
5.737
5.733
5.717
5.228
5.194
5.145
5.111

2.821
2.796
2.725
2.708
2.692
2.675

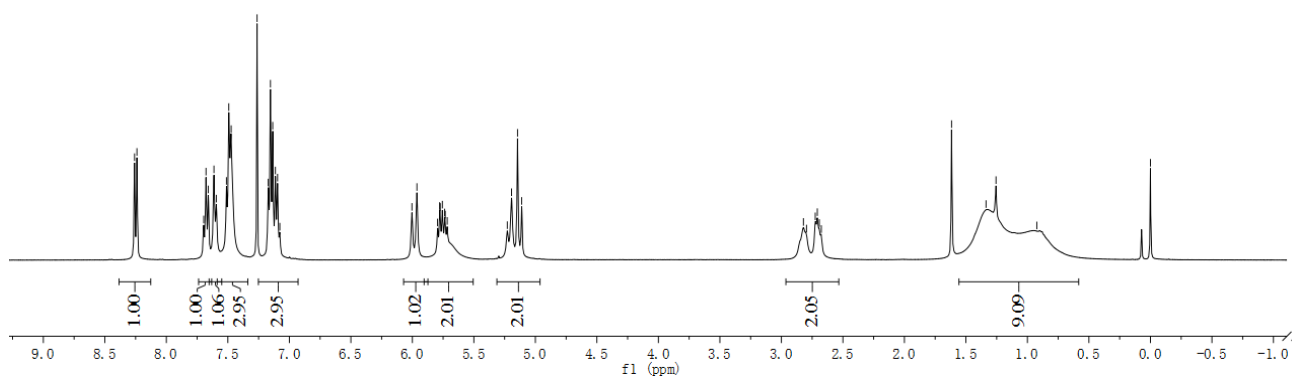
1.617
1.336
1.255

0.924

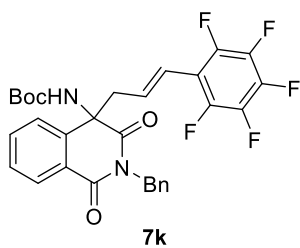
0.000



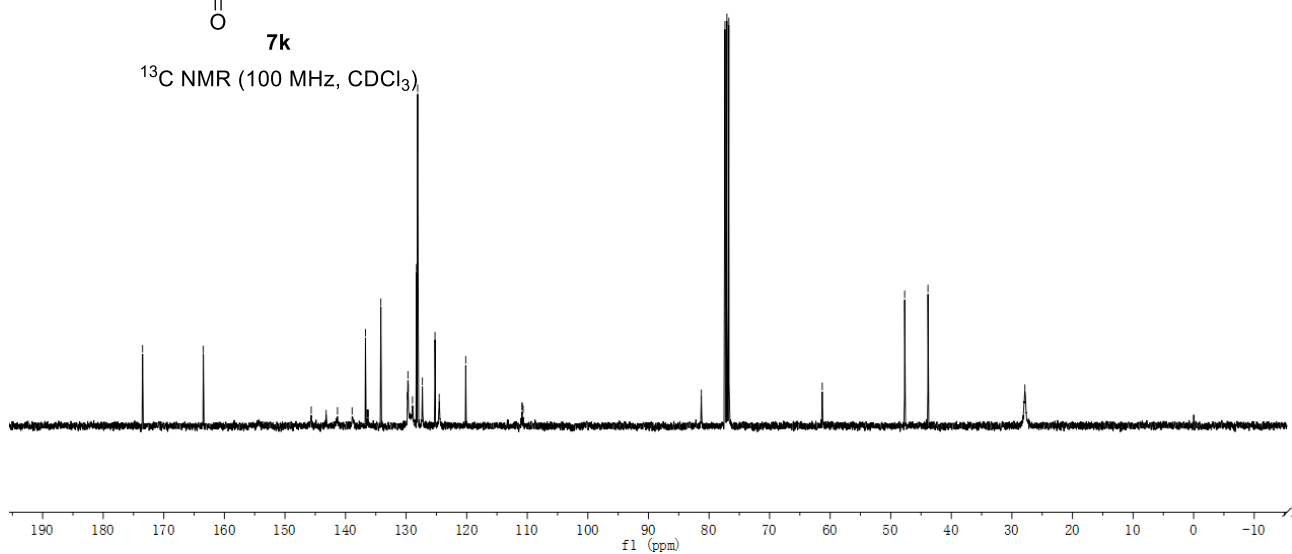
$^1\text{H NMR}$ (400 MHz, CDCl_3)

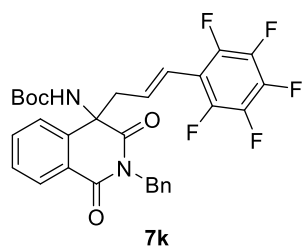


173.504
163.478
145.667
143.202
141.324
138.914
136.711
136.454
136.410
136.346
136.280
136.253
134.171
129.785
129.700
129.631
128.949
128.290
128.093
127.314
125.232
124.534
120.158
110.866
110.823
110.682
81.265
77.362
77.044
76.726
61.305
47.703
43.857
27.862



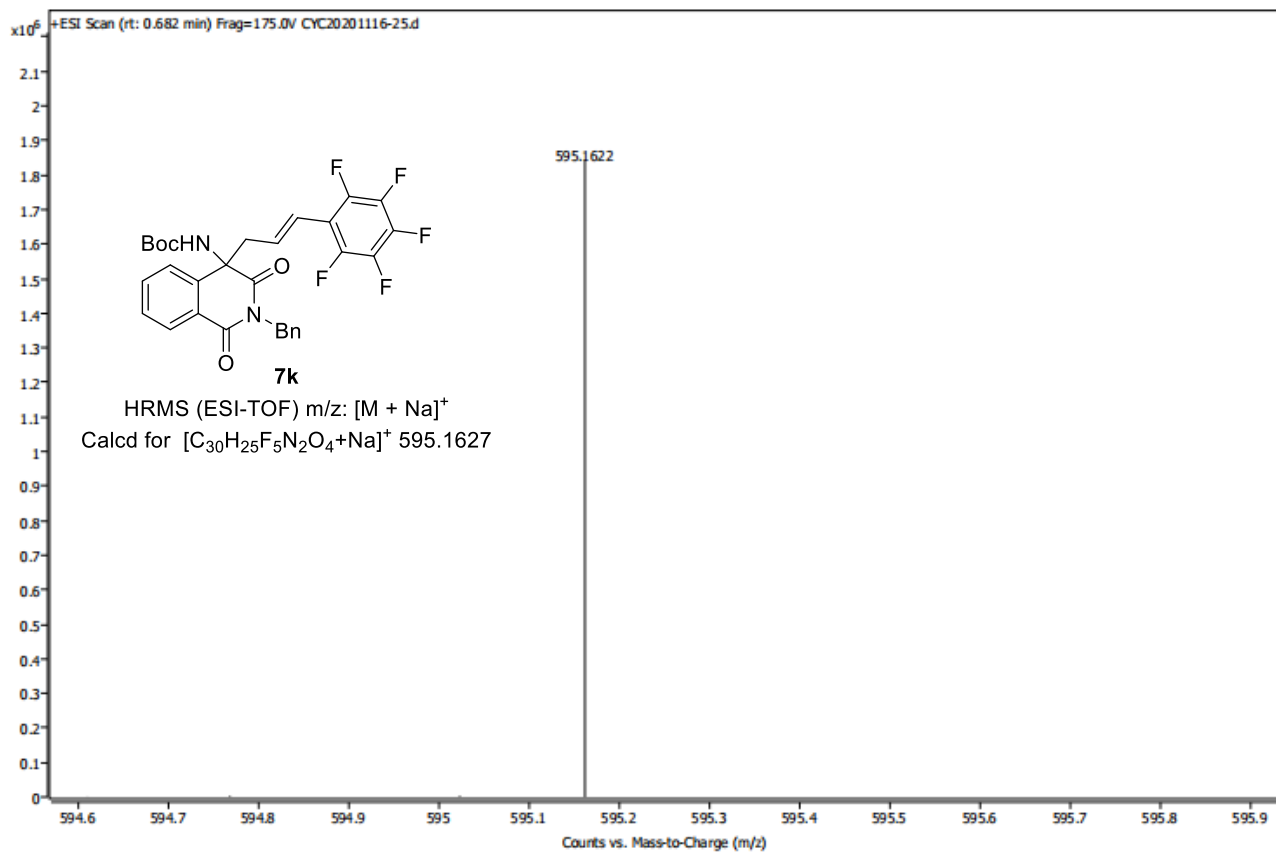
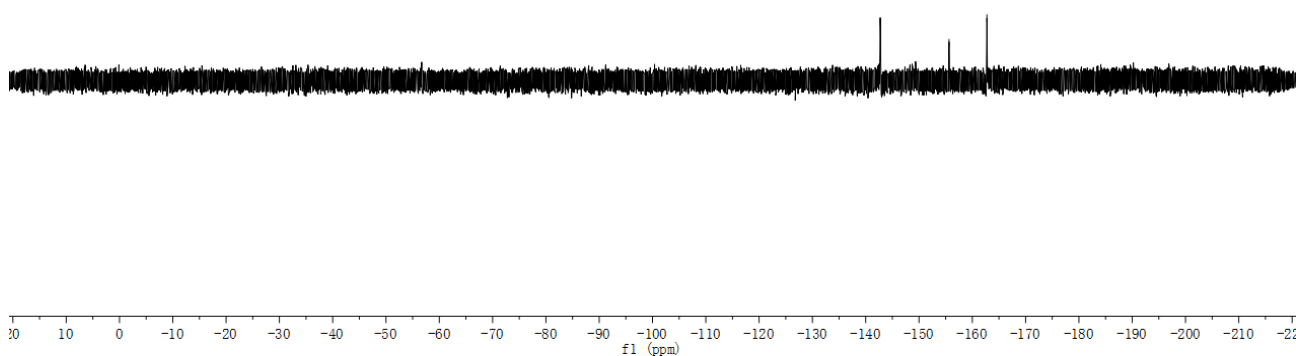
$^{13}\text{C NMR}$ (100 MHz, CDCl_3)



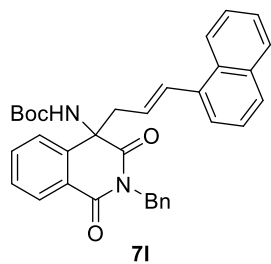


^{19}F NMR (376 MHz, CDCl_3)

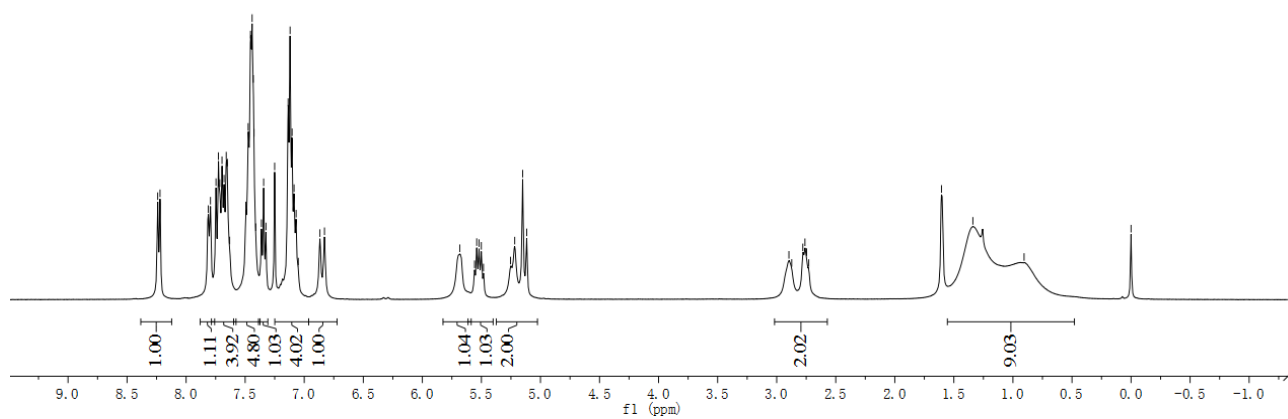
— -142.730
 — -155.635
 — -162.742



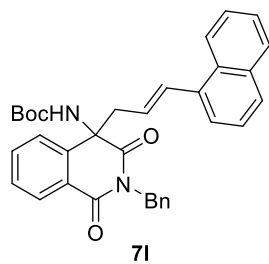
8.241
8.221
7.813
7.794
7.747
7.726
7.715
7.696
7.679
7.660
7.651
7.631
7.494
7.474
7.455
7.441
7.432
7.425
7.410
7.363
7.344
7.324
7.250
7.136
7.120
7.103
7.086
7.069
7.050
7.050
6.867
6.829
5.683
5.558
5.540
5.520
5.501
5.482
5.253
5.218
5.151
5.116
2.897
2.873
2.779
2.761
2.747
2.728
1.605
1.339
0.905
0.000



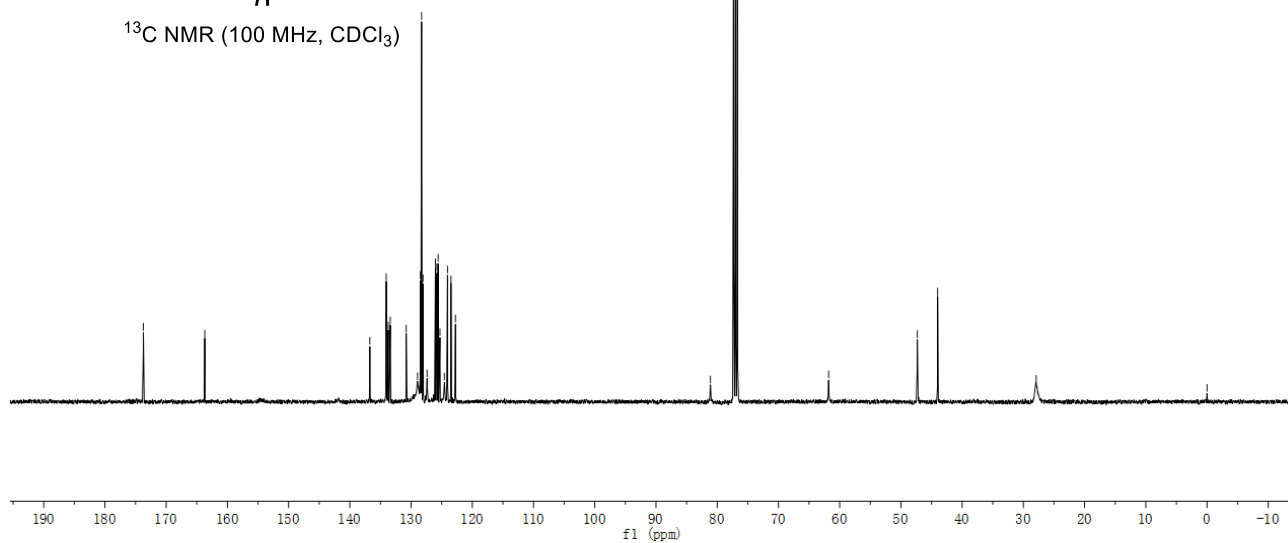
¹H NMR (400 MHz, CDCl₃)

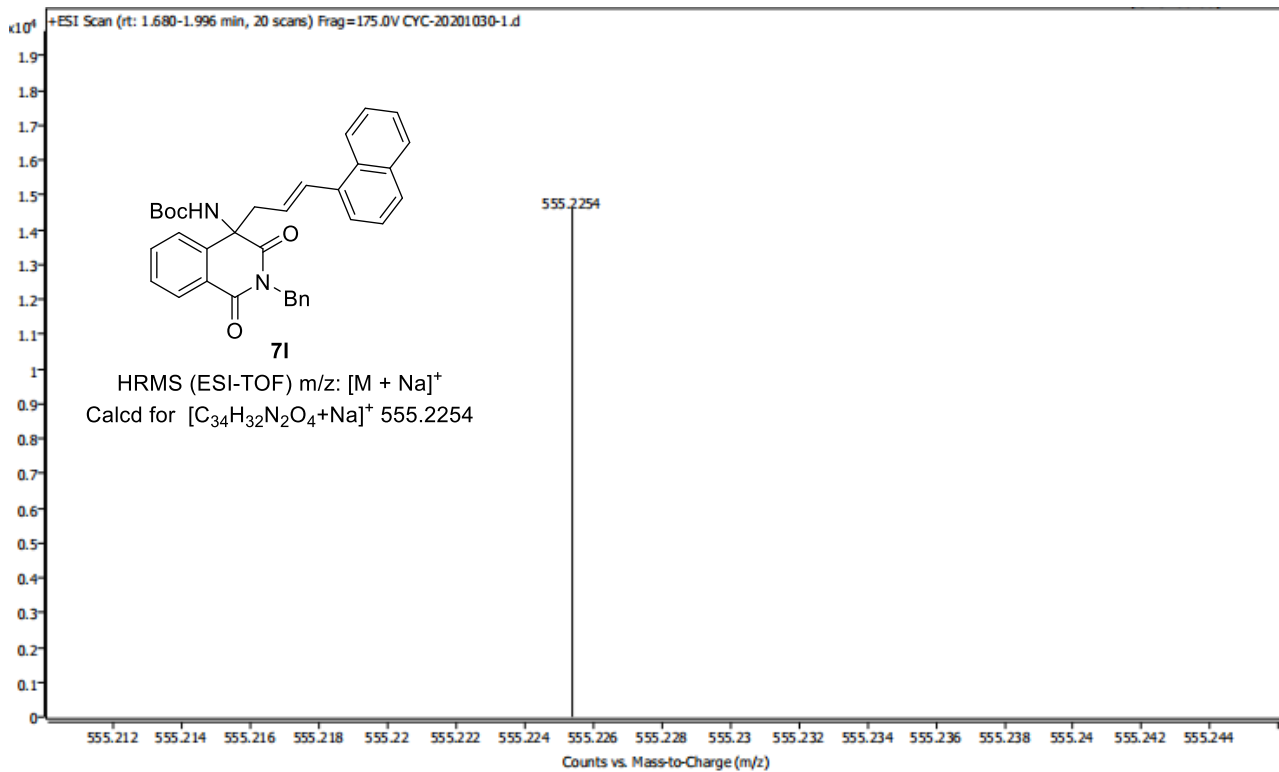


173.720
163.694
136.732
134.060
134.037
133.728
133.398
130.796
128.941
128.477
128.285
128.052
127.391
126.025
125.785
125.578
125.283
124.559
124.050
123.482
122.749
81.108
77.341
77.023
76.706
61.801
47.321
44.000
27.901
0.000



¹³C NMR (100 MHz, CDCl₃)



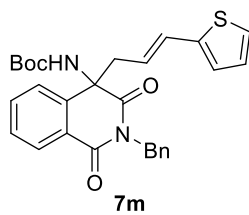


8.227
8.208
7.671
7.652
7.633
7.582
7.562
7.484
7.465
7.446
7.257
7.242
7.226
7.206
7.187
7.169
7.122
7.110
6.909
6.899
6.887
6.749
6.740
6.319
6.281
5.618
5.418
5.399
5.380
5.360
5.341
5.242
5.206
5.149
5.116

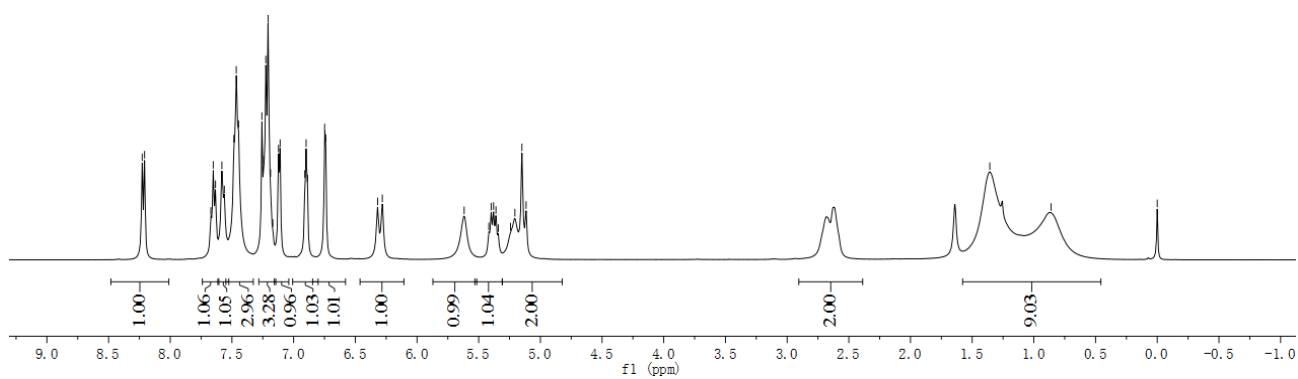
1.357

0.861

0.000



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



173.585
163.624
140.905
136.814
133.962
129.281
128.956
128.360
128.054
127.419
127.313
126.116
125.068
124.843
124.505
119.168

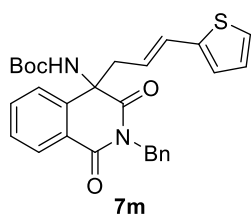
81.081
77.349
77.031
76.714

61.701

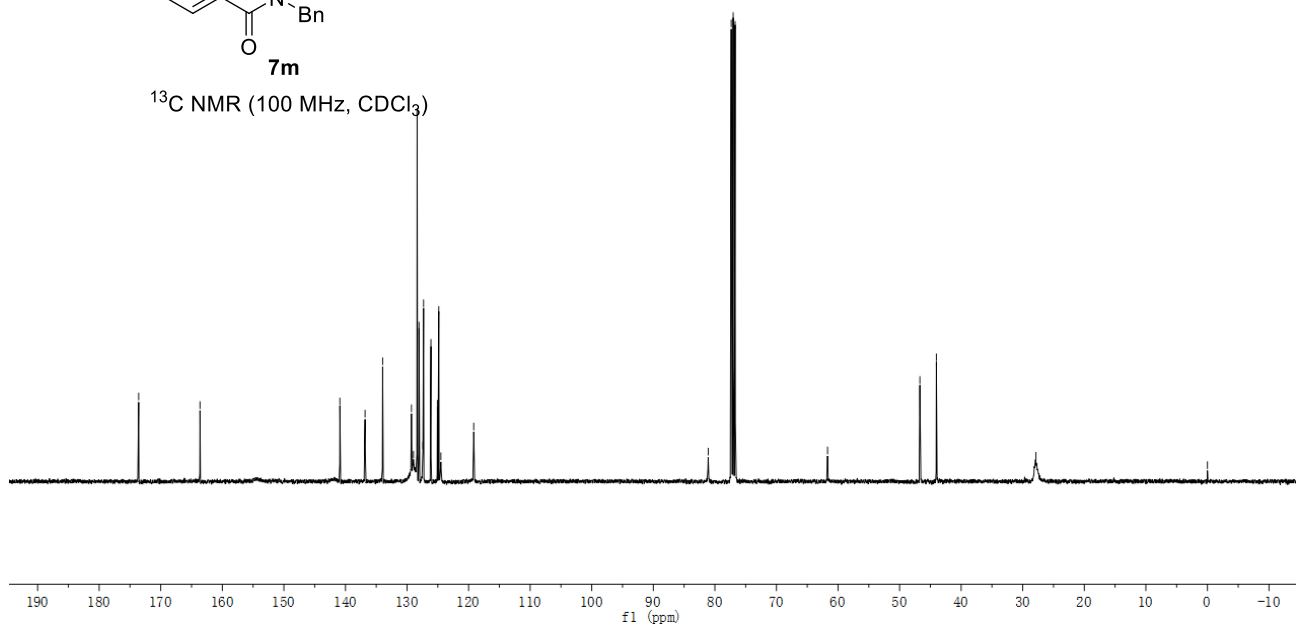
46.704
44.026

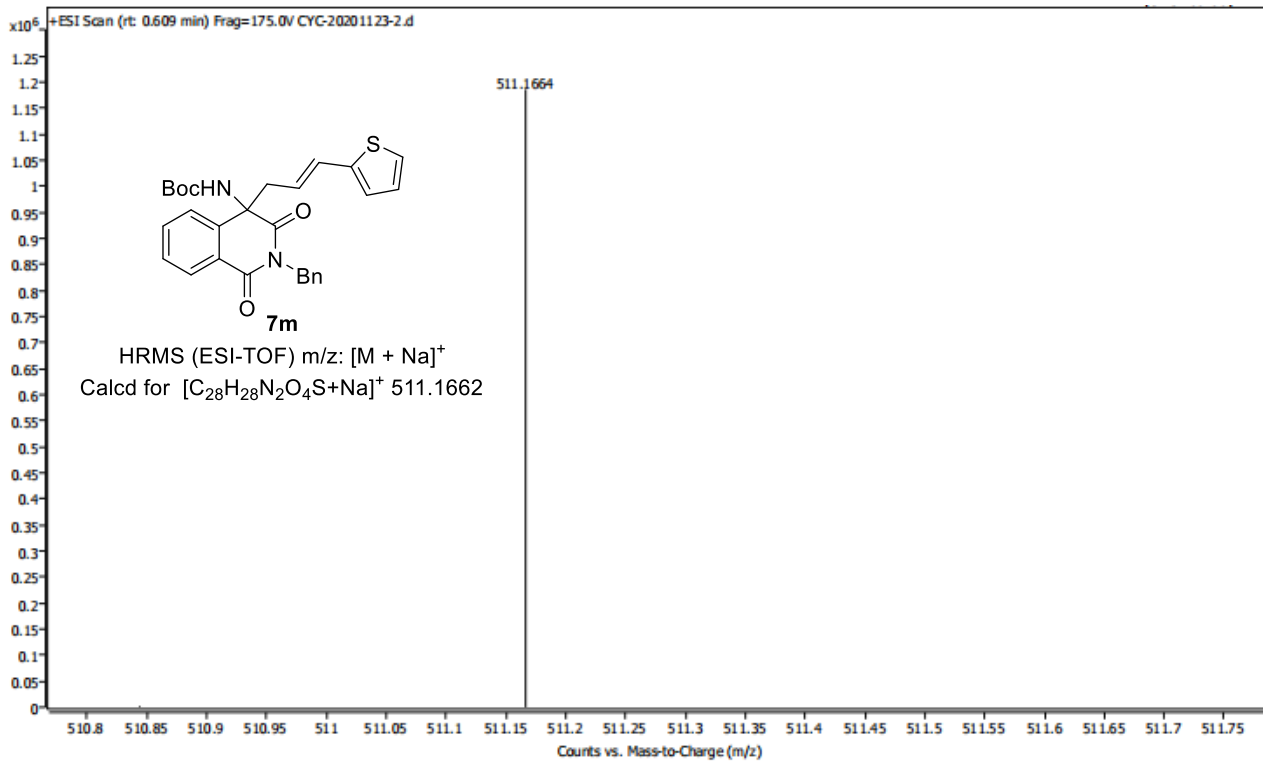
27.855

0.000

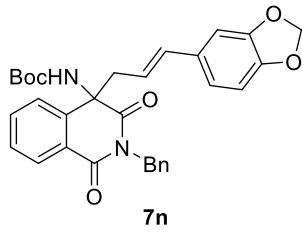


$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

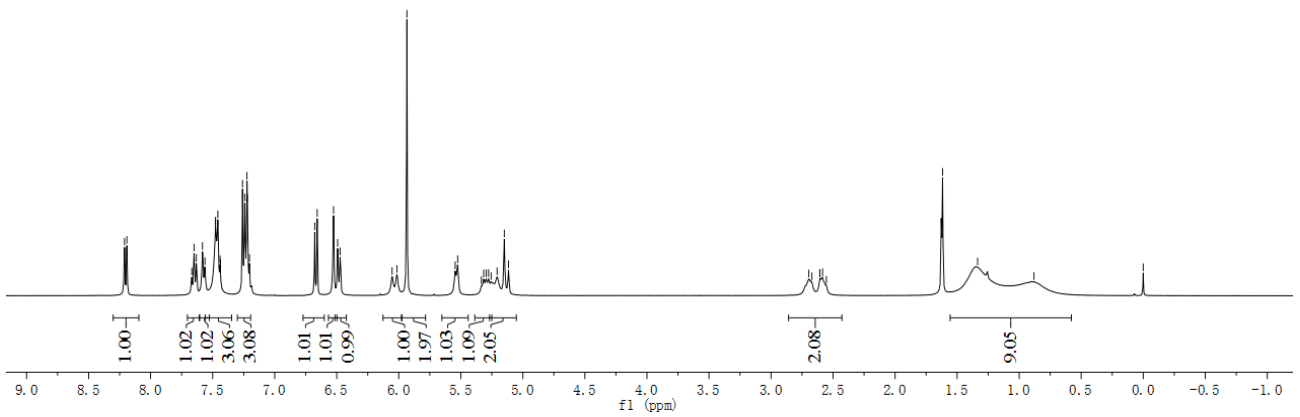




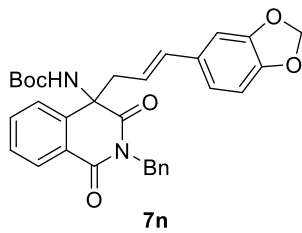
8.211
8.192
7.668
7.650
7.632
7.582
7.562
7.478
7.477
7.458
7.440
7.437
7.259
7.242
7.224
7.220
7.216
7.204
6.678
6.658
6.526
6.493
6.473
6.054
6.015
5.934
5.546
5.525
5.334
5.316
5.296
5.277
5.256
5.208
5.150
5.115
2.695
2.670
2.607
2.606
2.584
2.554
1.617
1.335
0.881
0.000



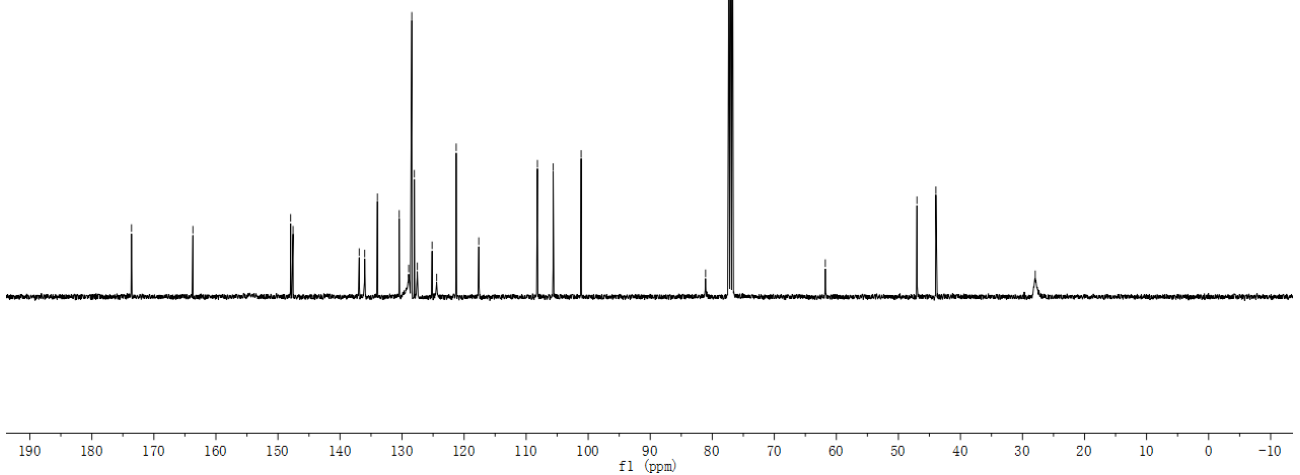
¹H NMR (400 MHz, CDCl₃)

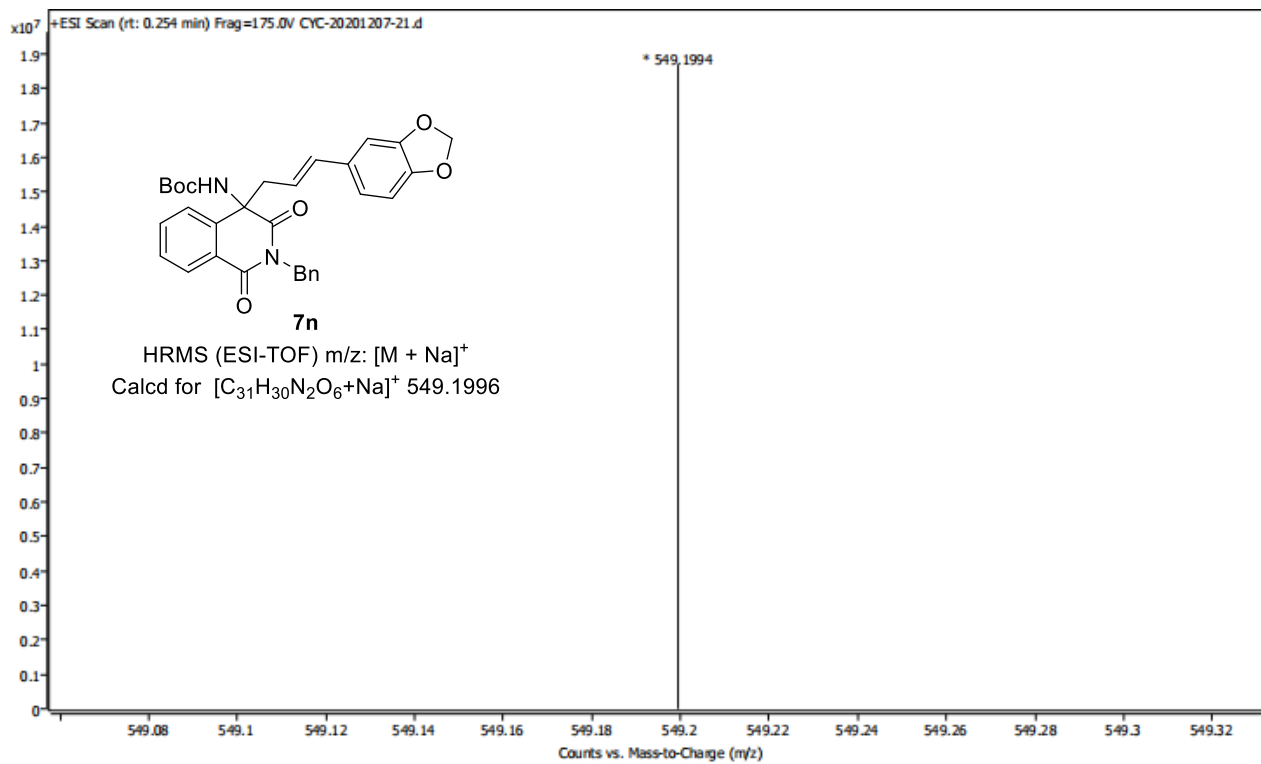


173.602
163.708
147.953
147.565
136.900
136.021
133.976
130.458
128.928
128.425
128.013
127.530
125.153
124.422
121.275
117.632
108.183
105.637
101.139
81.071
77.365
77.048
76.731
61.783
47.006
43.960
27.948



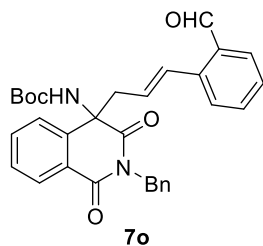
¹³C NMR (100 MHz, CDCl₃)



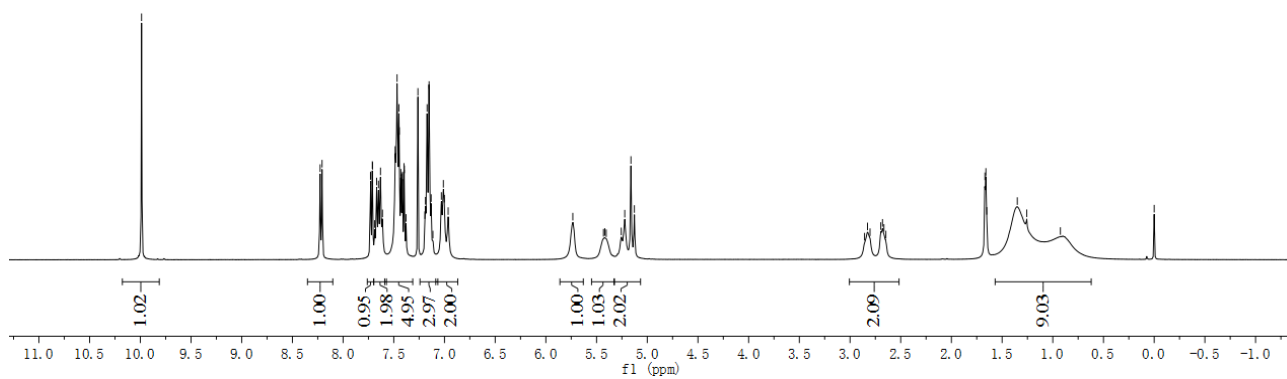


9.988

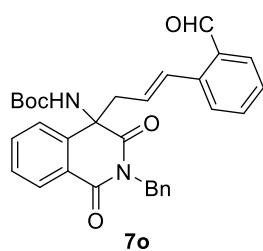
8.227
8.207
7.730
7.728
7.712
7.709
7.688
7.669
7.651
7.631
7.612
7.486
7.467
7.449
7.445
7.431
7.426
7.418
7.414
7.399
7.395
7.379
7.262
7.193
7.187
7.171
7.152
7.132
7.031
7.011
7.001
6.964
5.734
5.419
5.257
5.222
5.161
5.127
2.803
2.696
2.679
2.665
1.670
1.660
1.651
1.350
1.257
0.925
0 nms



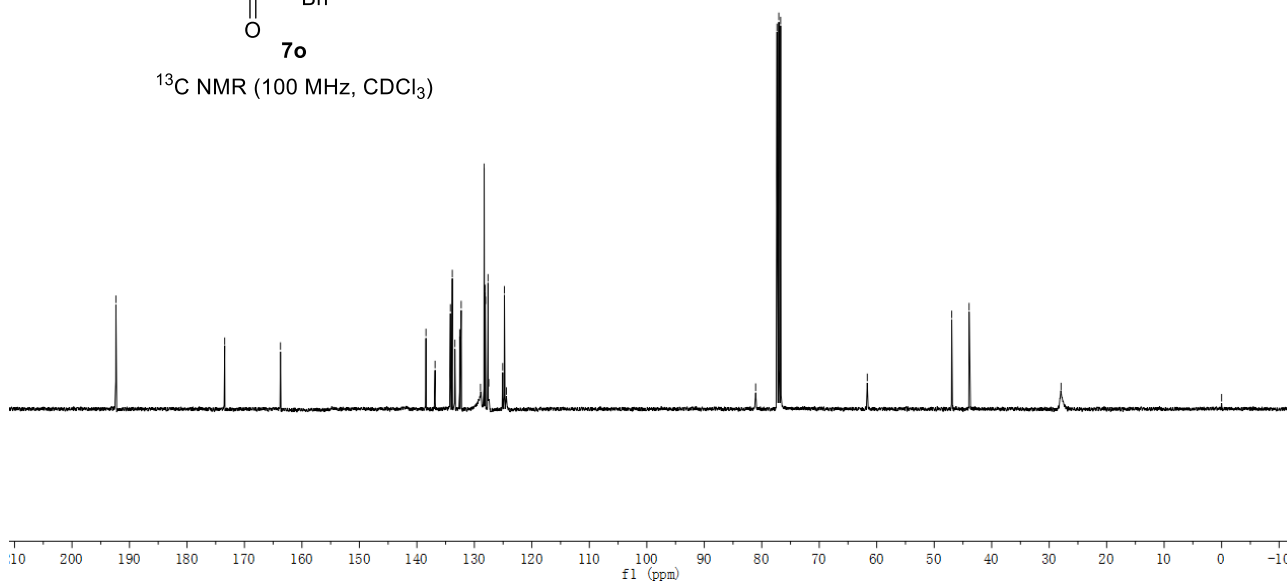
¹H NMR (400 MHz, CDCl₃)

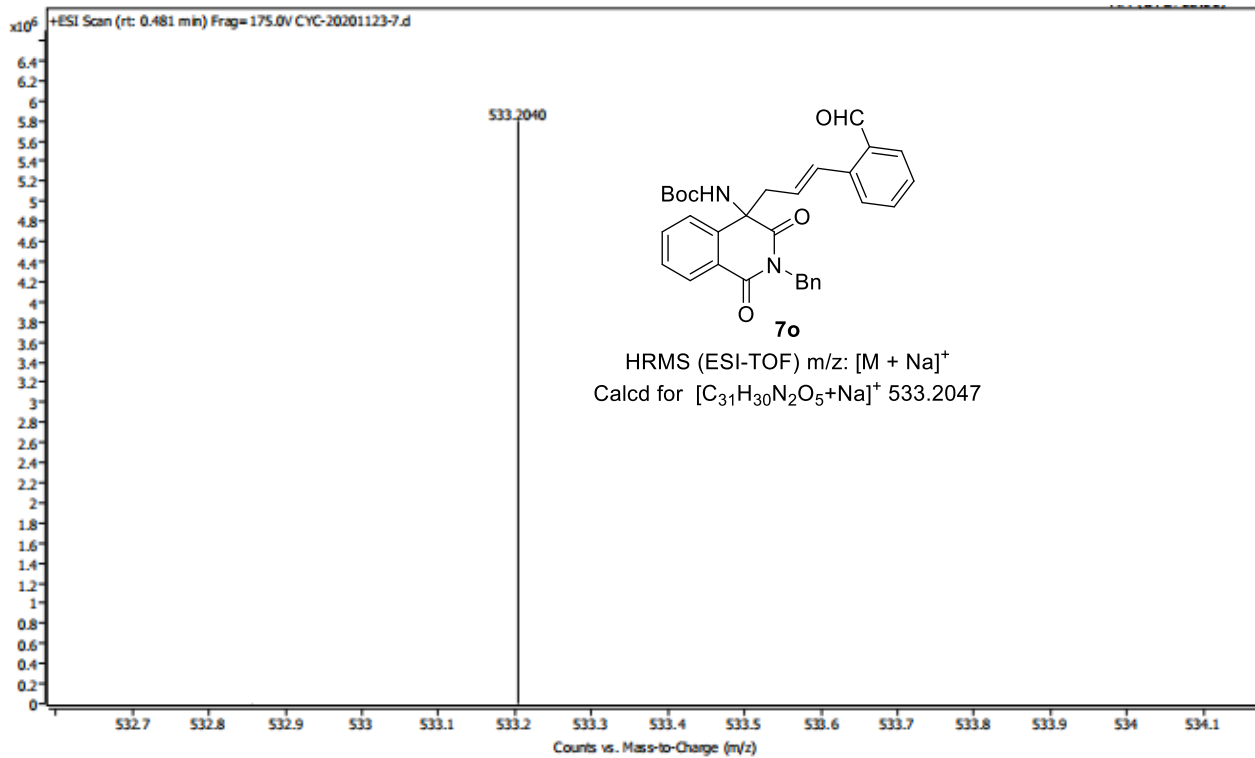


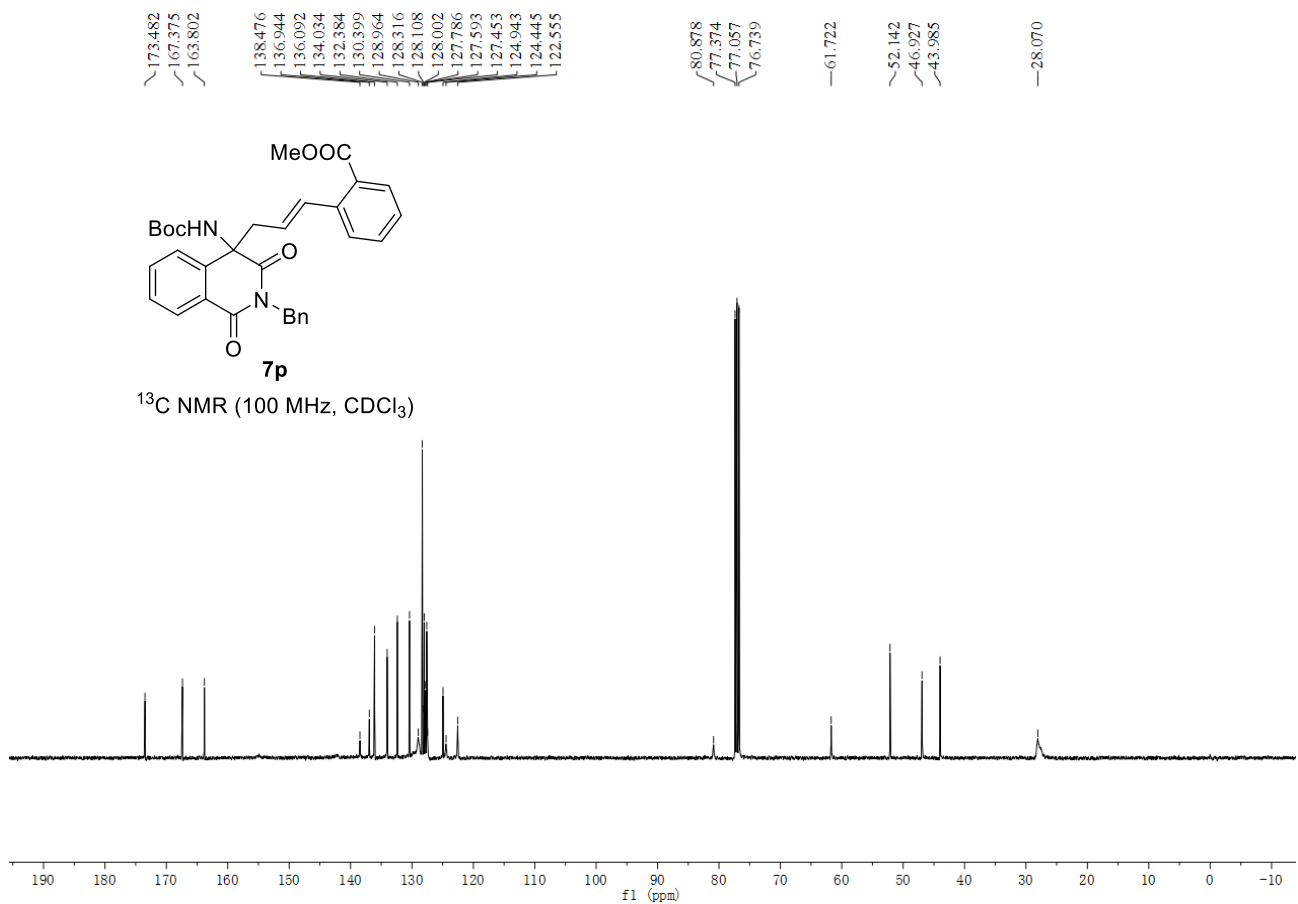
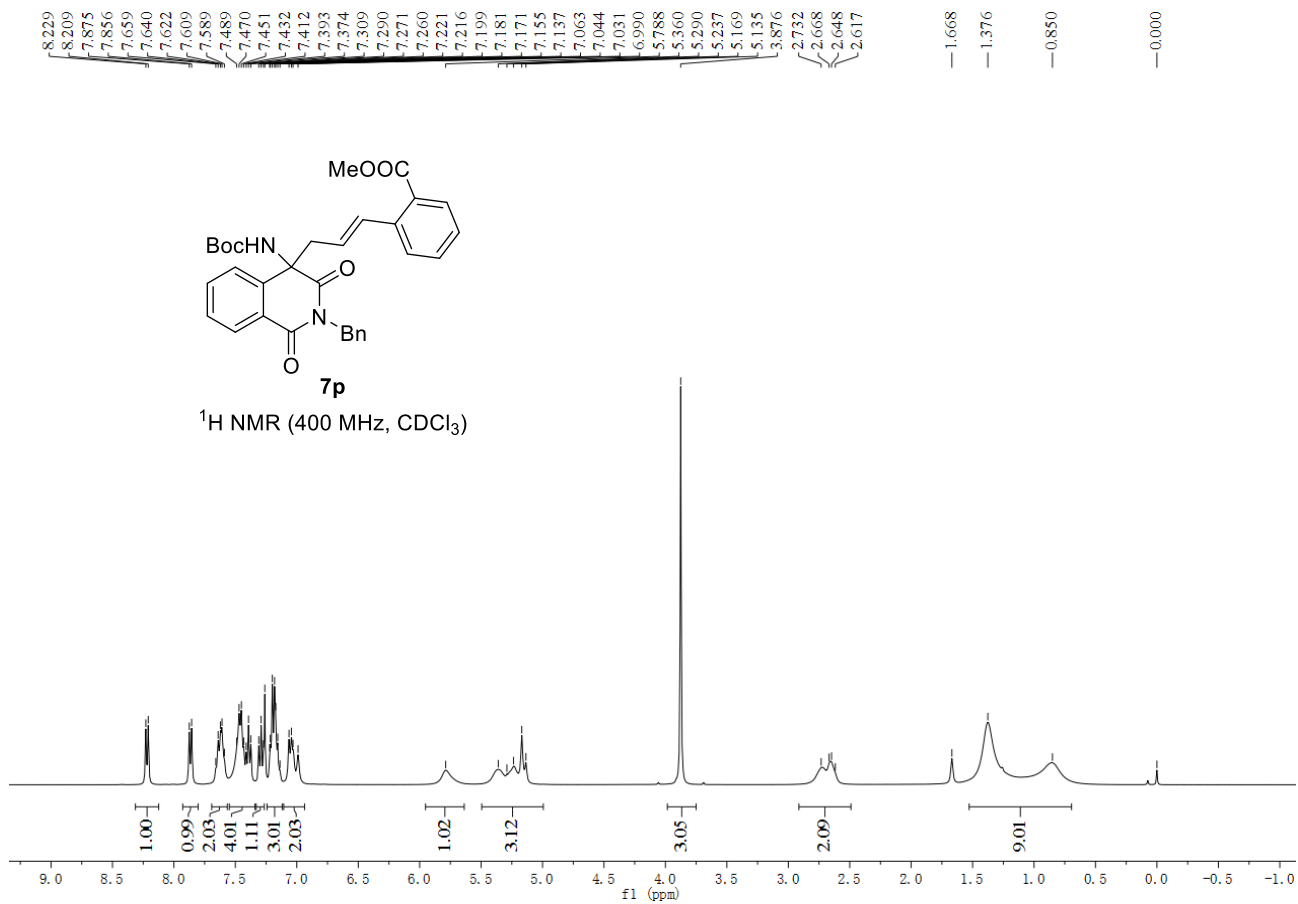
192.357
173.436
163.727
138.416
136.832
134.168
133.839
133.387
132.551
132.291
128.934
128.292
128.112
128.052
127.623
127.496
125.069
124.770
124.425
81.064
77.352
77.034
76.716
61.642
46.954
43.933
27.928
0.000

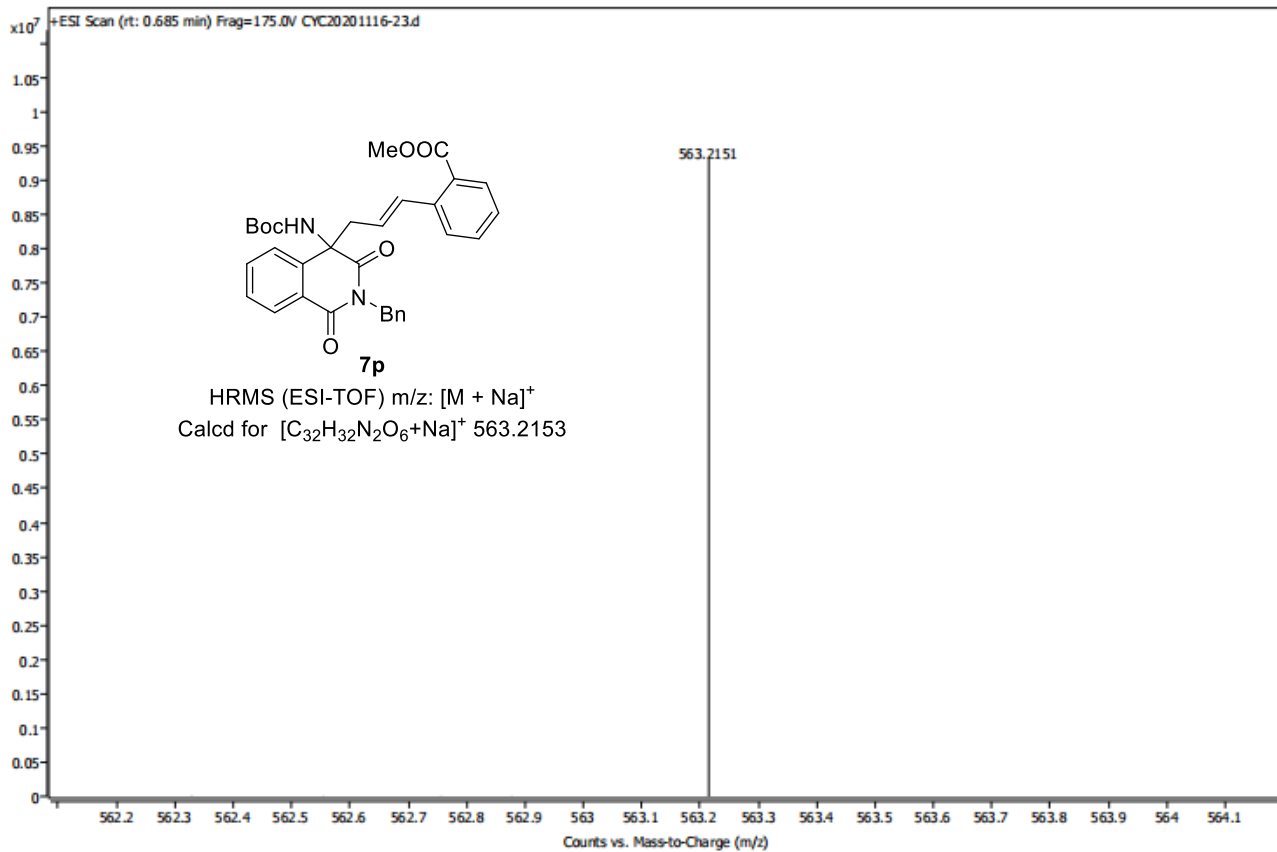


¹³C NMR (100 MHz, CDCl₃)

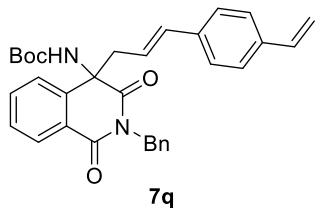




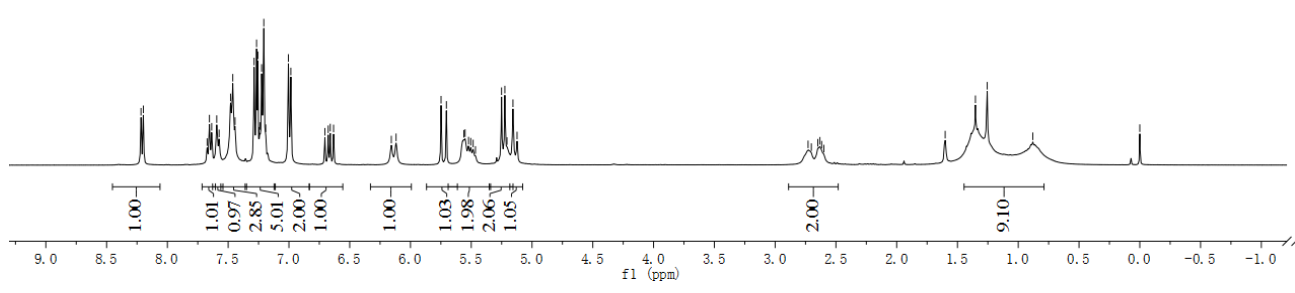




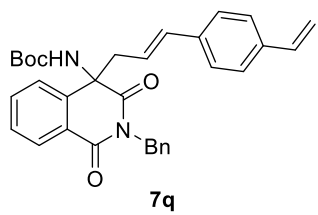
8.217
8.198
7.673
7.654
7.635
7.594
7.574
7.480
7.462
7.443
7.286
7.266
7.256
7.247
7.239
7.225
7.207
7.191
7.004
6.984
6.704
6.677
6.660
6.633
6.158
6.118
5.749
5.705
5.561
5.550
5.522
5.504
5.484
5.465
5.251
5.224
5.206
5.157
5.123
2.729
2.702
2.649
2.631
2.617
2.599
1.601
1.352
1.255
0.880
0.000



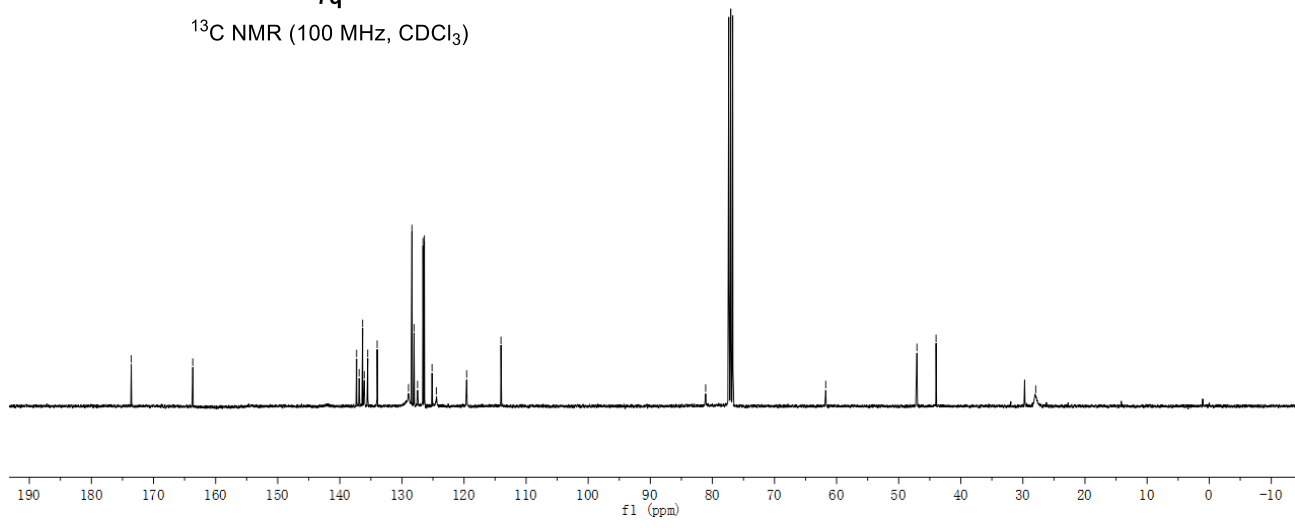
¹H NMR (400 MHz, CDCl₃)

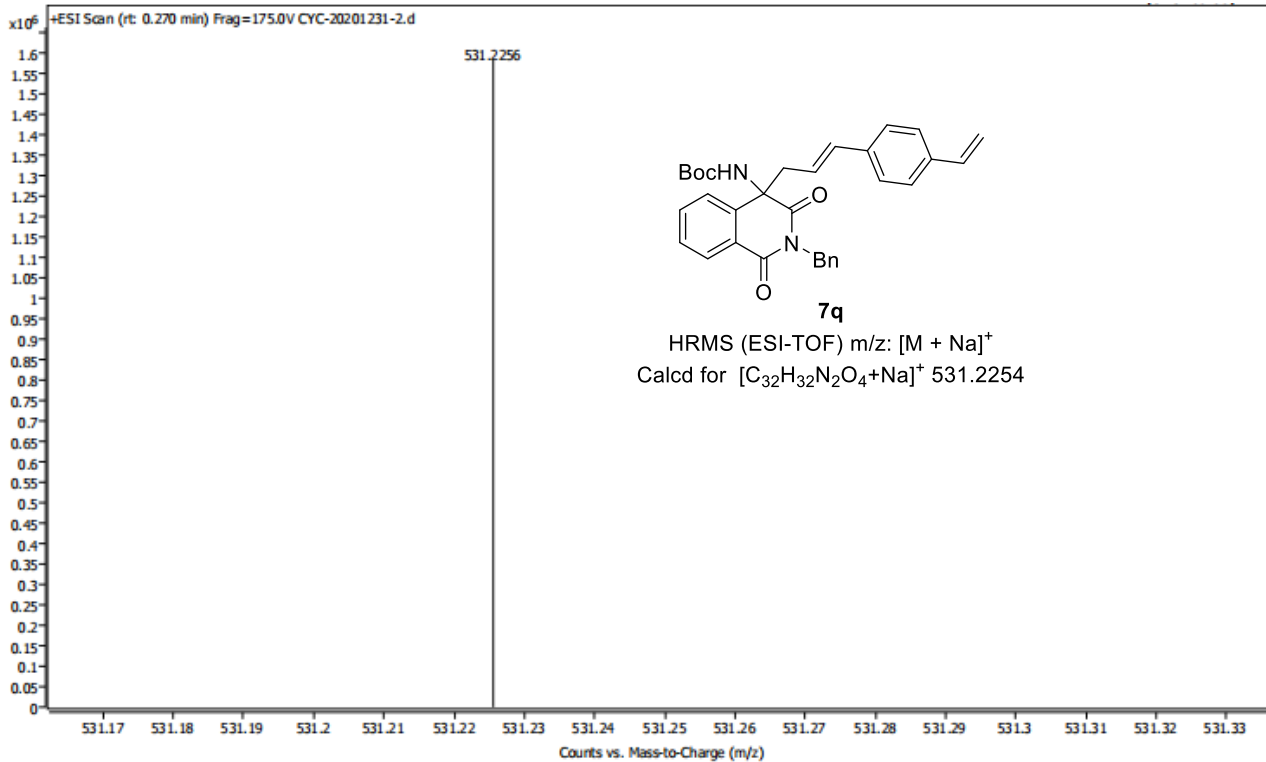


173.586
163.677
137.301
136.893
136.328
136.071
135.503
133.988
128.943
128.387
128.041
127.481
126.606
126.380
125.145
124.451
119.574
114.048
81.090
61.752
47.067
43.984
27.934

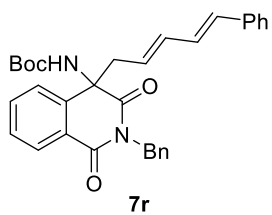


¹³C NMR (100 MHz, CDCl₃)

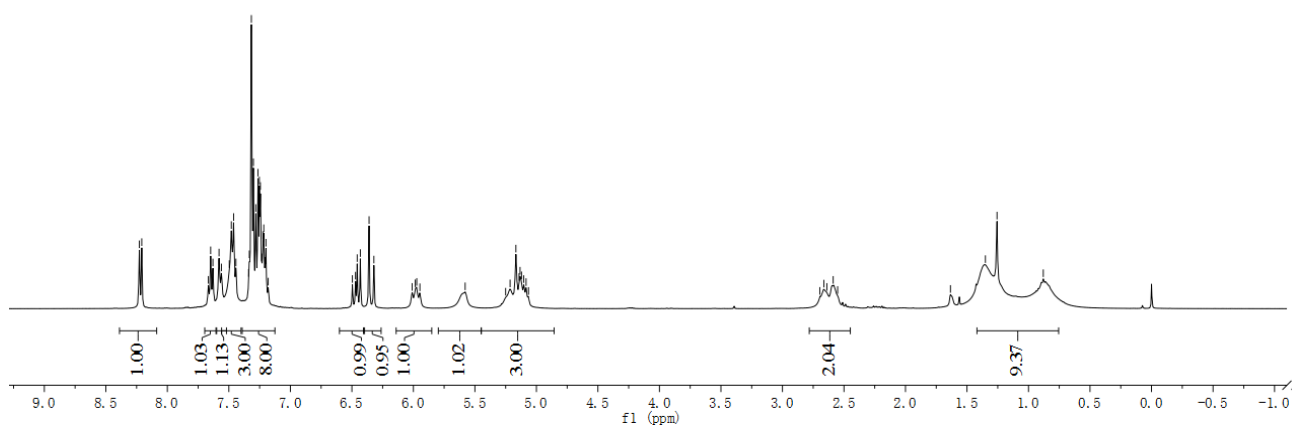




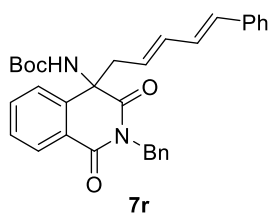
8.227
8.208
7.667
7.648
7.630
7.580
7.561
7.497
7.480
7.461
7.442
7.340
7.333
7.317
7.301
7.281
7.263
7.252
7.244
7.231
7.223
7.216
7.206
7.199
7.180
6.496
6.471
6.457
6.431
6.360
6.321
6.010
5.985
5.973
5.947
5.579
5.250
5.214
5.167
5.141
5.133
5.121
5.103
5.084
5.064
2.696
2.663
2.639
2.588
2.551
1.634
1.350
1.256
0.880



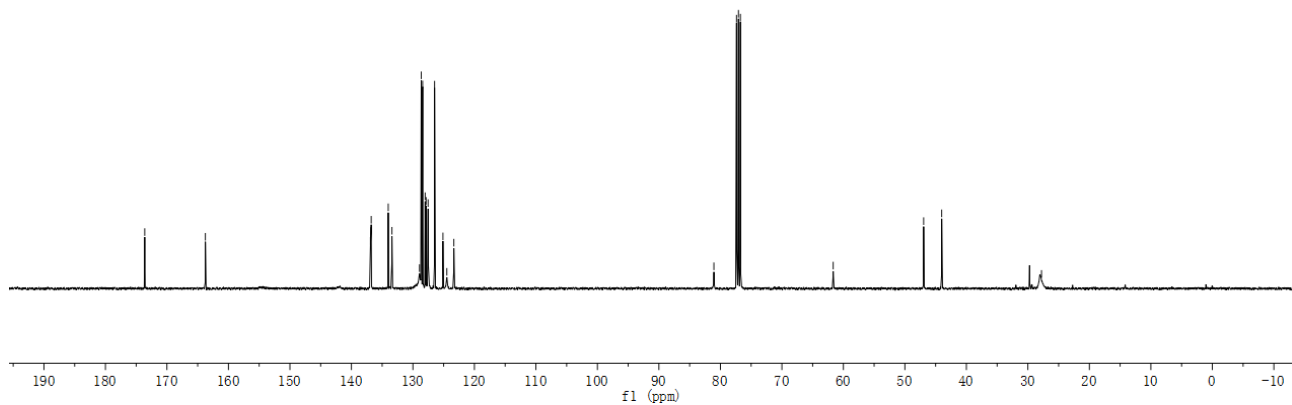
¹H NMR (400 MHz, CDCl₃)

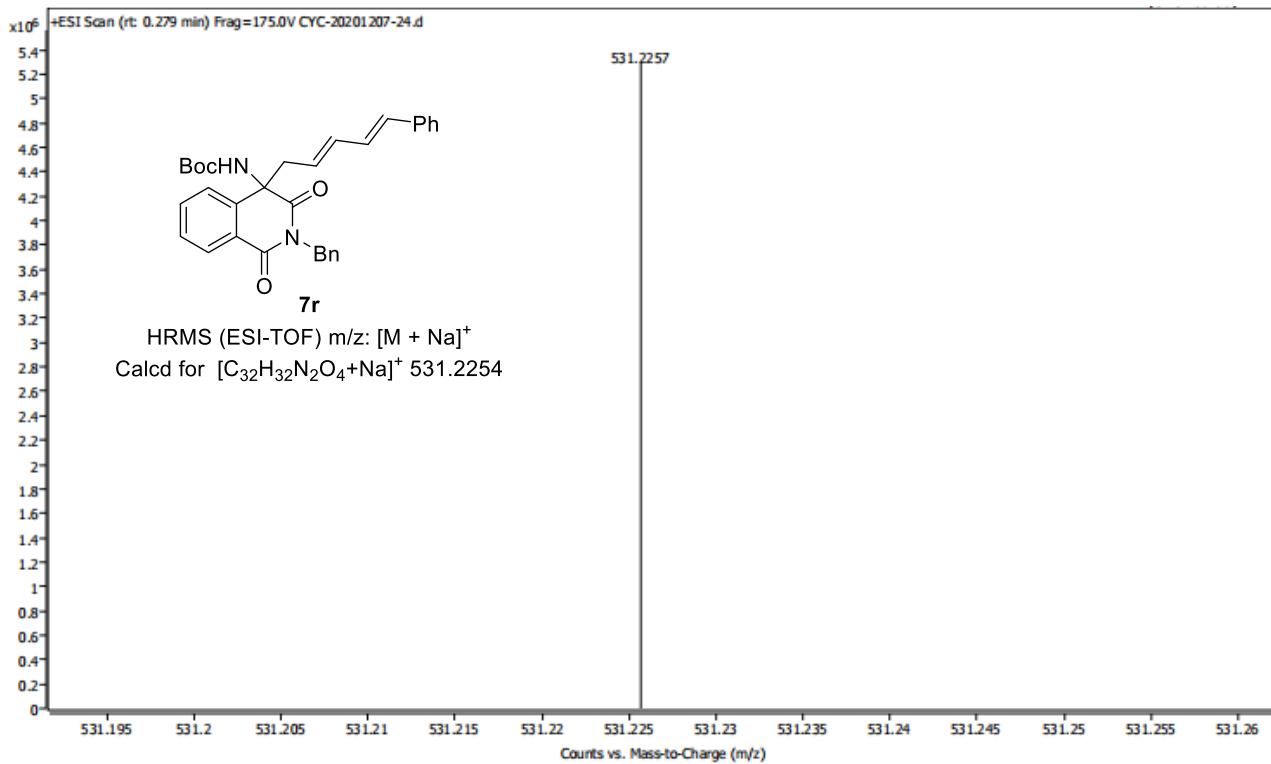


173.606
163.747
136.909
136.838
136.784
134.010
133.408
128.927
128.646
128.412
128.010
127.857
127.530
126.473
125.113
124.481
123.341
81.056
77.382
77.064
76.747
61.657
46.948
44.013
27.783

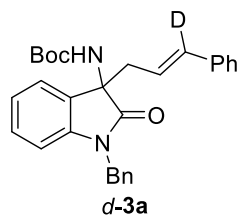


¹³C NMR (100 MHz, CDCl₃)

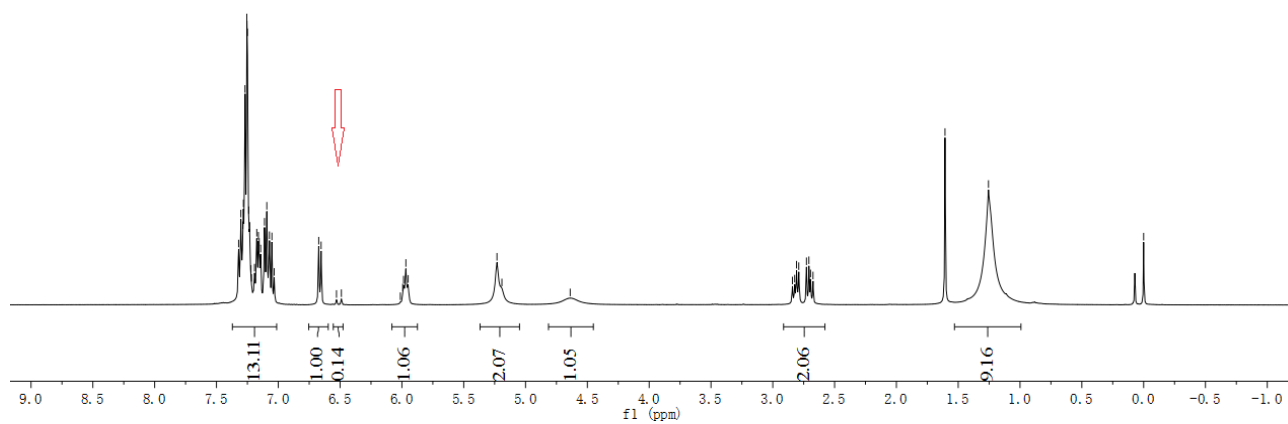




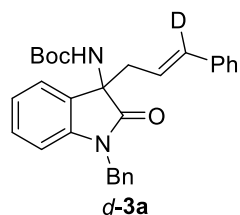
7.303
7.287
7.282
7.269
7.255
7.250
7.239
7.231
7.174
7.161
7.112
7.093
7.072
7.052
6.673
6.654
6.529
6.490
6.013
5.994
5.987
5.968
5.949
5.231
5.191
— 4.639
2.841
2.823
2.808
2.790
2.728
2.708
2.694
2.674
— 1.607
— 1.255
— 0.000



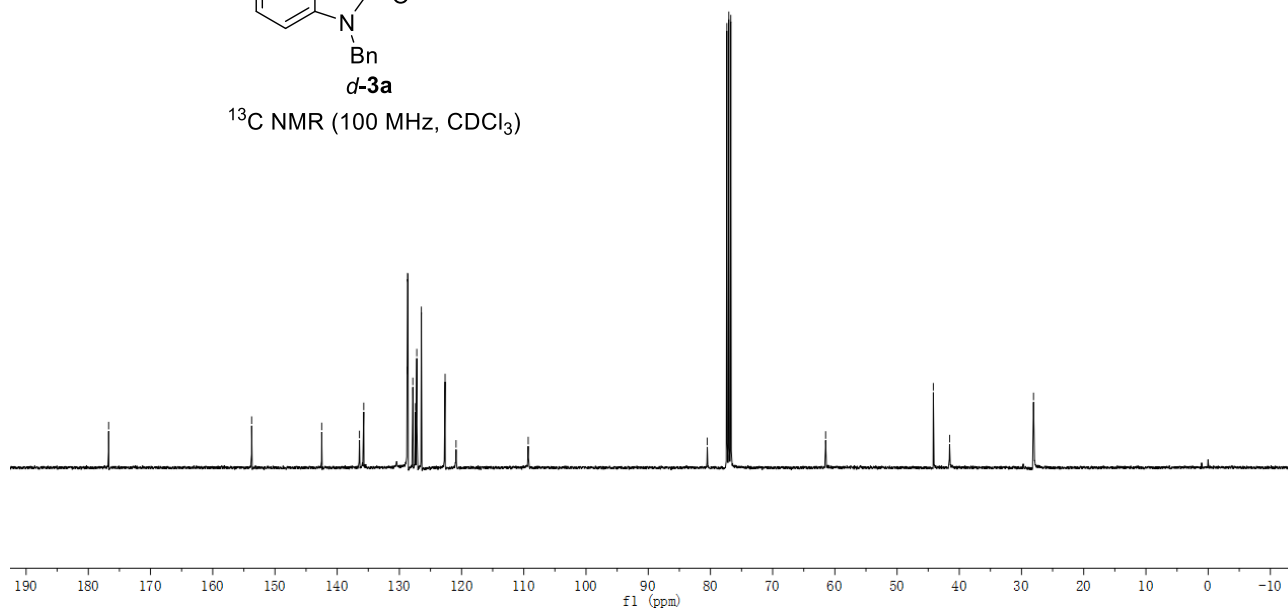
¹H NMR (400 MHz, CDCl₃)

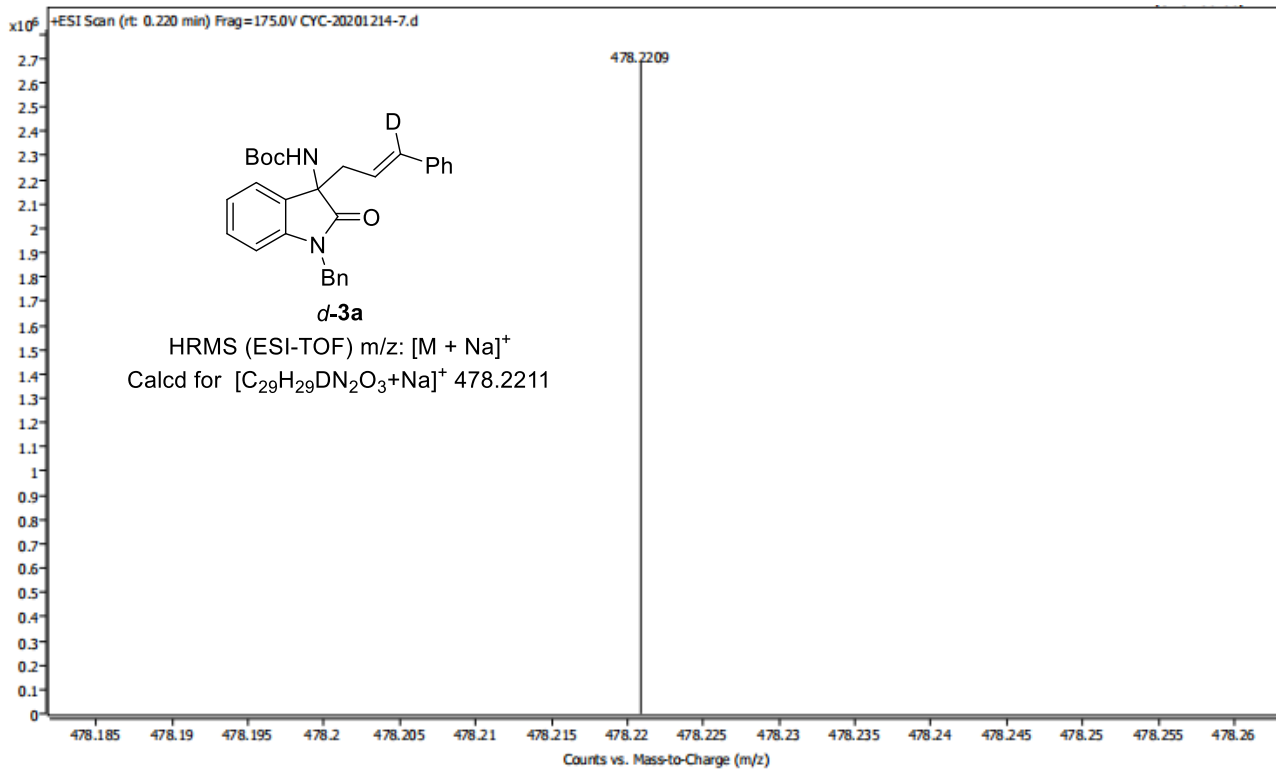


— 176.733
— 153.744
— 142.484
136.414
135.722
128.764
128.686
128.619
127.837
127.407
127.200
126.489
126.467
122.725
122.651
120.889
109.293
80.507
77.363
77.046
76.728
— 61.483
— 44.173
— 41.559
— 28.072



¹³C NMR (100 MHz, CDCl₃)



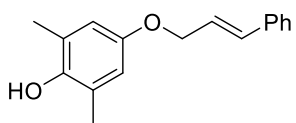


7.414
7.396
7.339
7.321
7.302
7.268
7.264
7.261
7.251
7.246
7.240
7.228
6.725
6.685
6.613
6.436
6.421
6.407
6.396
6.381
6.367

4.620
4.608
4.270

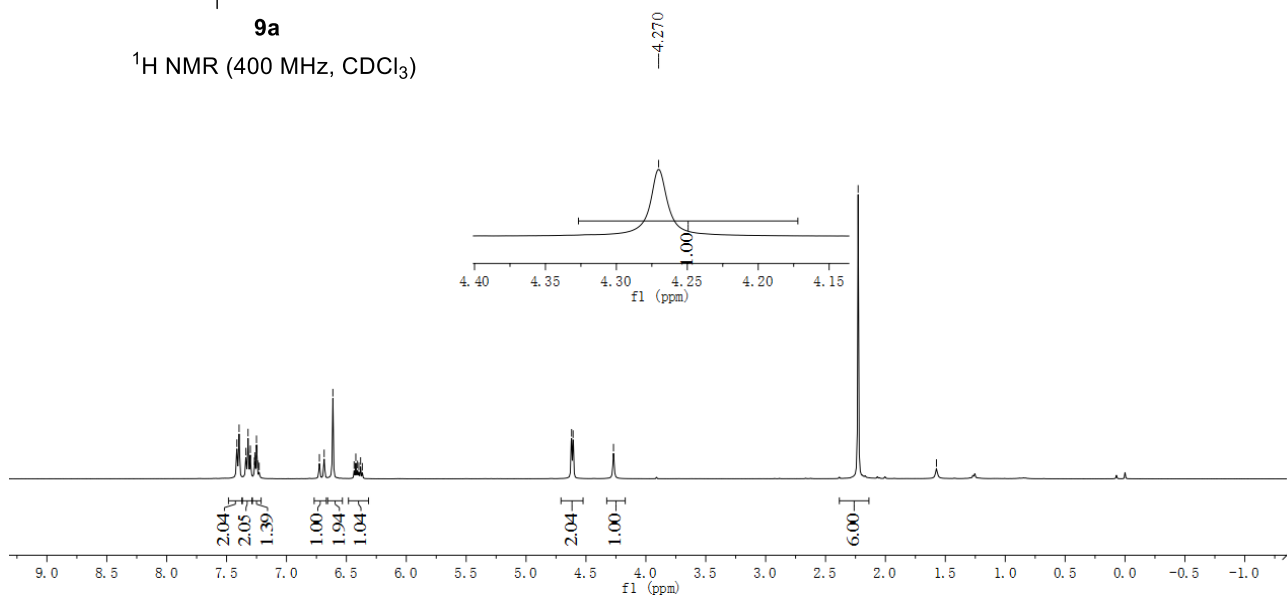
2.228

1.574



9a

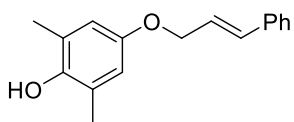
^1H NMR (400 MHz, CDCl_3)



6.609

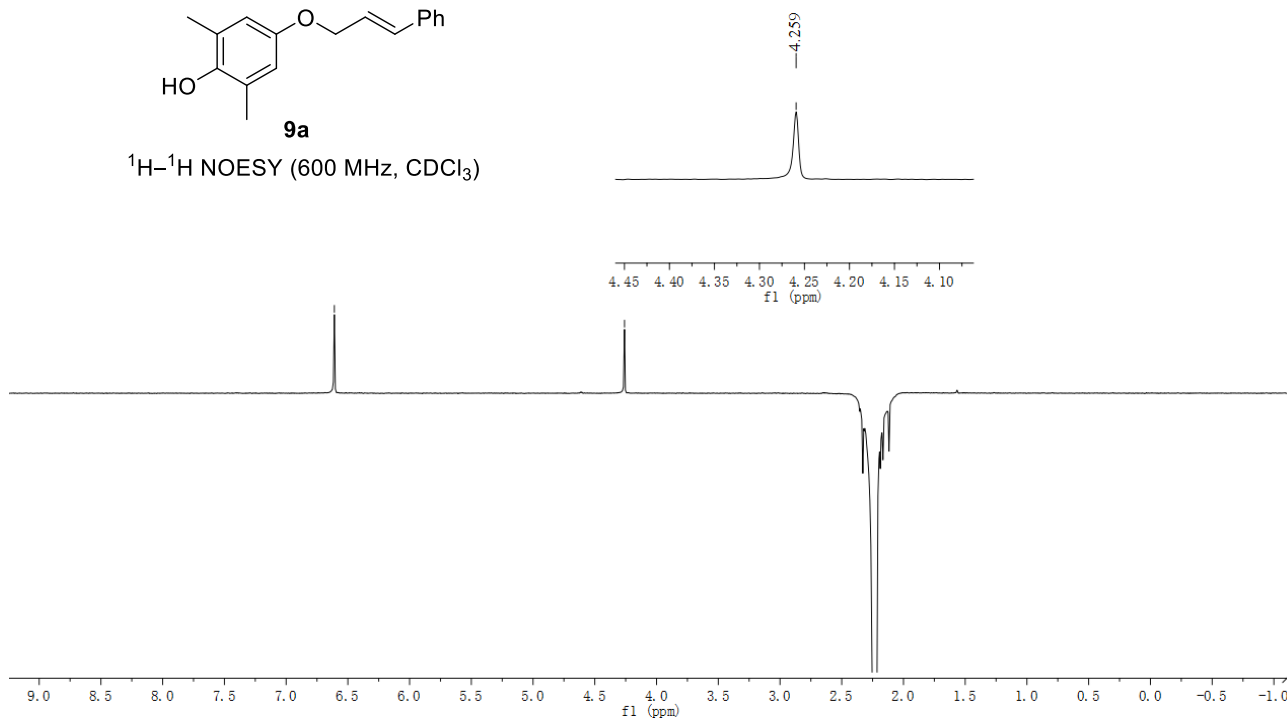
4.259

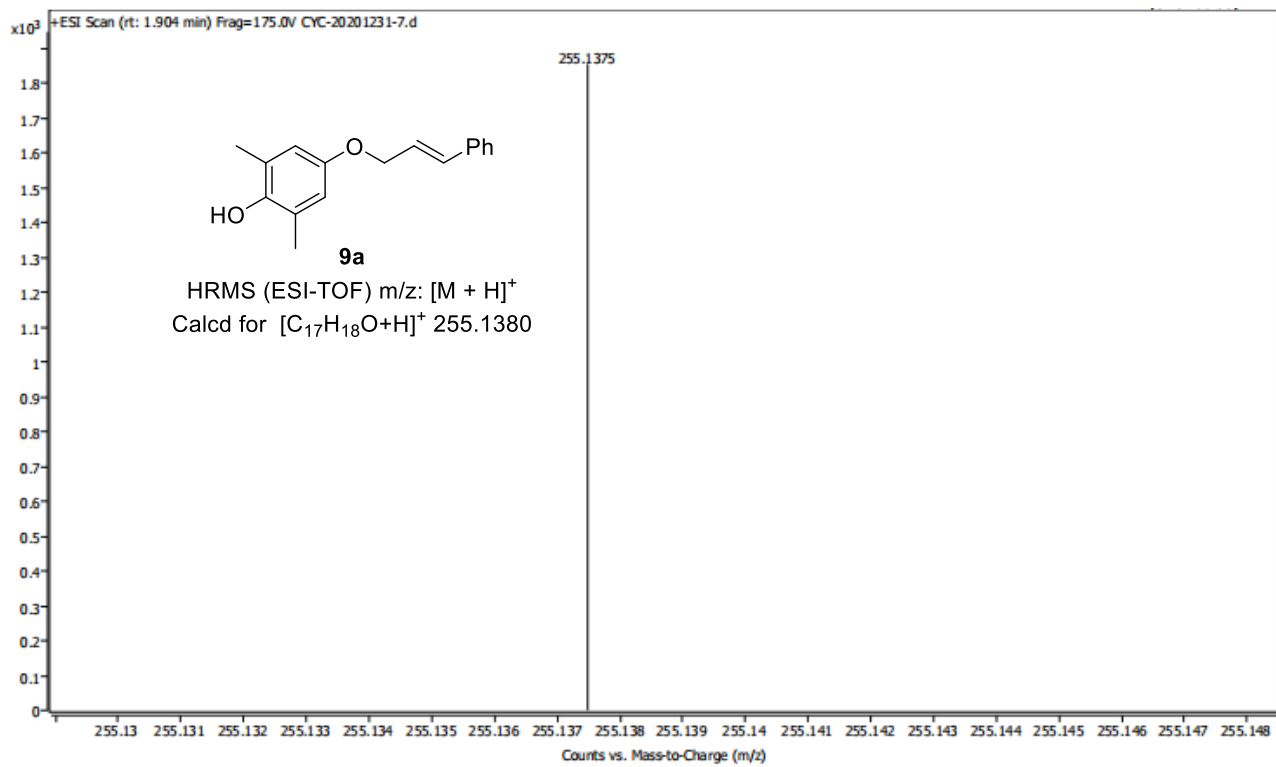
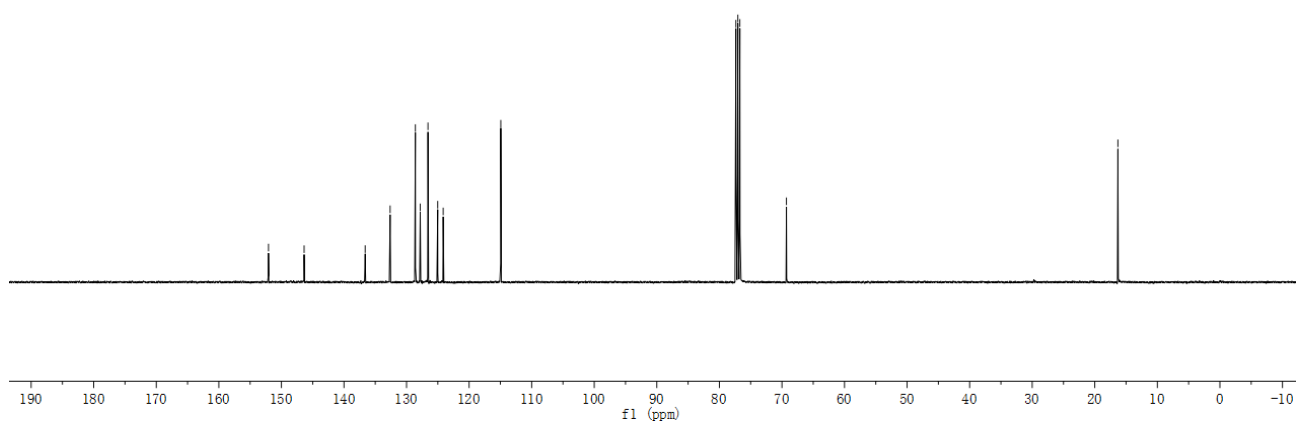
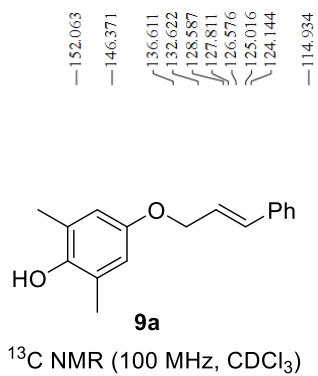
2.225



9a

^1H - ^1H NOESY (600 MHz, CDCl_3)

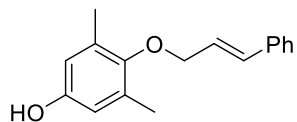




7.431
7.412
7.351
7.333
7.314
7.277
7.274
7.270
7.260
7.253
7.237
6.738
6.698
6.490
6.476
6.461
6.451
6.436
6.421

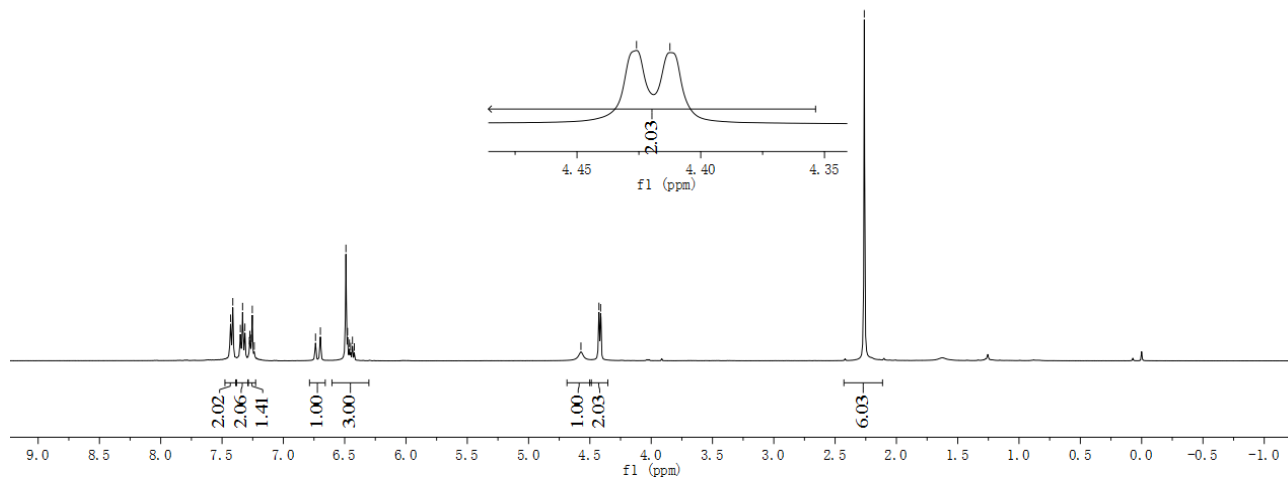
4.573
4.426
4.412

2.262



9b

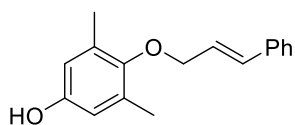
^1H NMR (400 MHz, CDCl_3)



6.484

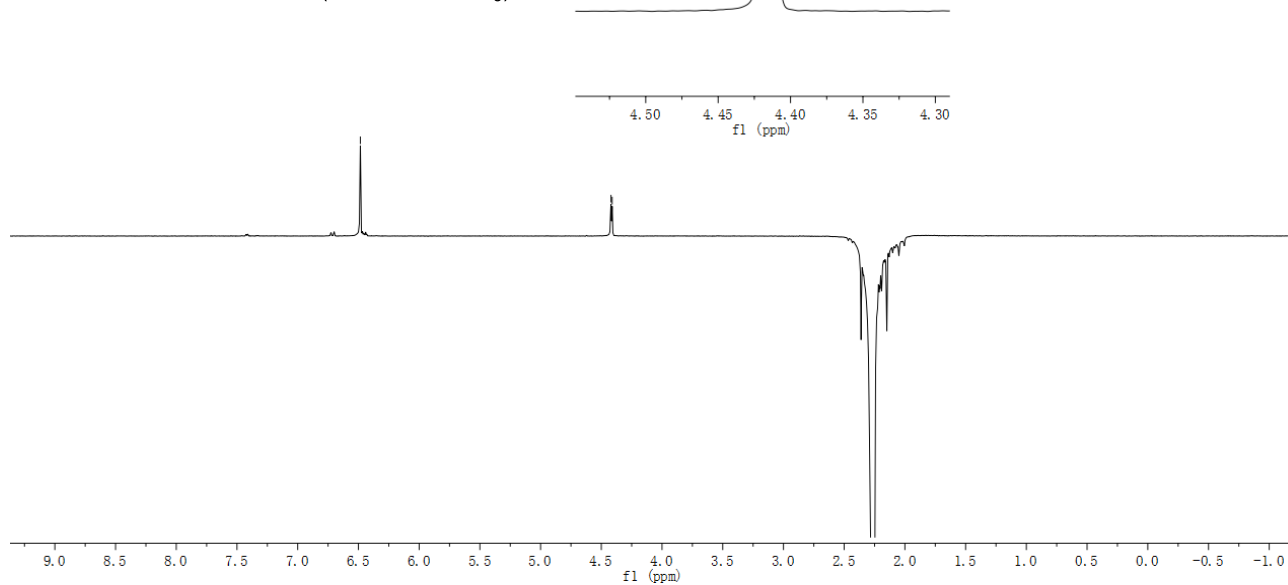
4.420
4.410

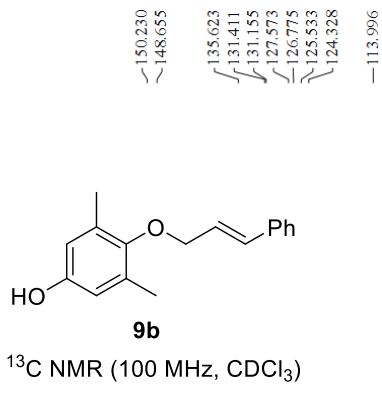
2.257



9b

^1H - ^1H NOESY (600 MHz, CDCl_3)





150.230
 148.655
 135.623
 131.411
 131.155
 127.573
 126.775
 125.533
 124.328
 113.996

76.311
 75.994
 75.677
 72.139

15.526

-0.000

