Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Palladium-catalysed oxidative nucleophilic allylation between alkenes and activated ketimines

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Supplementary Information

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. ^{1}H NMR (400 MHz or 600 MHz), ^{13}C NMR (100 MHz or 150 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on Varian INOVA−400/54, Agilent DD2−600/54 or Bruker AscendTM 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, 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), I_2 and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. 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.

1 (*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 $AlMe_3$: Facile Access to Skipped Dienes and Trienes, *Angew. Chem., Int. Ed.*, 2020, **59**, 14404.

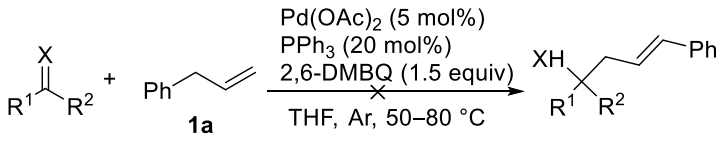
2 (*a*) J. Wang, Y. Liu, Y. Liu, Z. Wei, J. Cao, D. Liang, Y. Lin and H. Duan, L-*tert*-Leucine Derived Urea-Ammonium salts: Efficient Bifunctional Phase Transfer Catalysts for Highly Diastereo- and Enantioselective Aza-Henry Reaction of Isatin-Derived N-Boc Ketimines with *α*-Aryl Nitromethanes, *Tetrahedron*, 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.

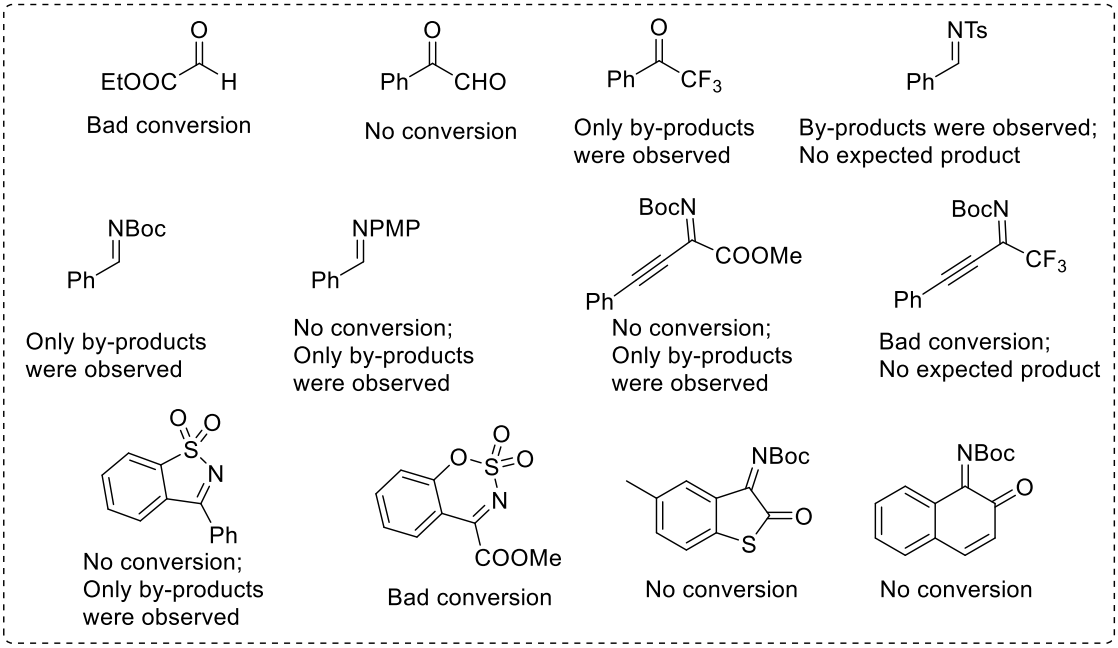
3 J. Štambaský, A. V. Malkov and P. Kočovský, Synthesis of Enantiopure 1-Arylprop-2-en-1-ols and Their *tert*-Butyl Carbonates, *J. Org. Chem.*, 2008, **73**, 9148.

4 Q. Wu, L. Wang, R. Jin, C. Kang, Z. Bian, Z. Du, X. Ma, H. Guo and L. Gao, Nickel-Catalyzed Allylic $C(sp^2)$–H Activation: Stereoselective Allyl Isomerization and Regiospecific Allyl Arylation of Allylarenes, *Eur. J. Org. Chem.*, 2016, 5415.

2. Screenings for the oxidative nucleophilic allylation

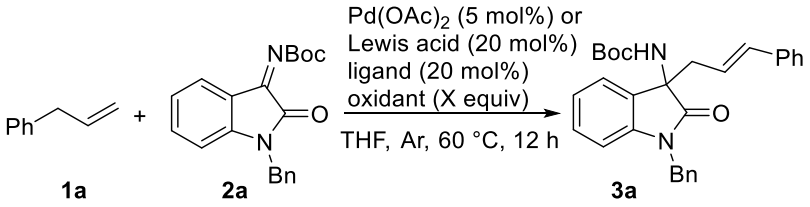
2.1 Unsuccessful exploration of allylbenzene 1a and other electrophilic reagents





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

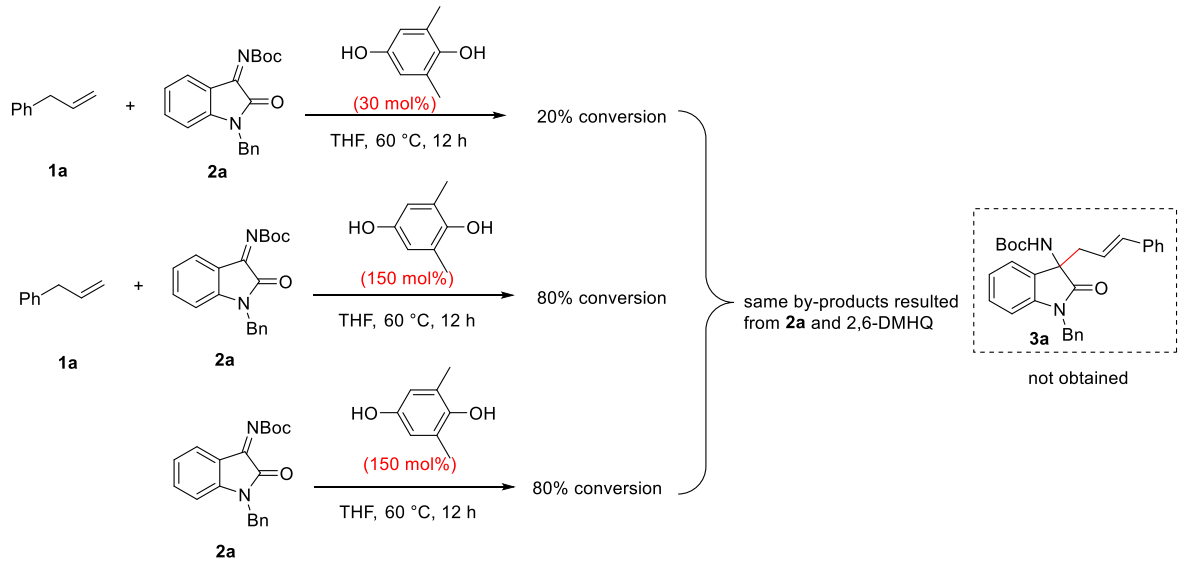


entry[a]	[Pd]	Lewis acid	base	ligand	oxidant	solvent	yield (%)[b]
1[c]	$Pd(OAc)_2$	/	/	PPh_3	2,6-DMBQ	THF	40
2	$Pd(OAc)_2$	/	/	PPh_3	2,6-DMBQ	THF	52
3	/	/	/	PPh_3	2,6-DMBQ	THF	NR
4	$Pd(OAc)_2$	/	/	/	2,6-DMBQ	THF	NR

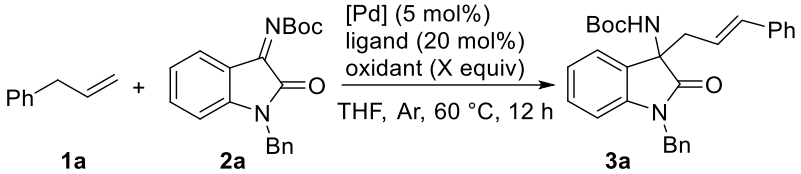
5	$Pd(OAc)_2$	/	/	PPh_3	/	THF	NR
6[d]	$Pd(OAc)_2$	/	/	PPh_3	2,6-DMBQ	THF	NR
7	/	$Sc(OTf)_3$		/	/	THF	NR
8	/	$Zn(OAc)_2$	/	/	/	THF	NR
9	/	$AlCl_3$	/	/	/	THF	NR
10	/	$FeCl_3$	/	/	/	THF	NR
11[e]	$Pd(OAc)_2$	/	*t*-BuOK	PPh_3	/	THF	NR
12[e]	$Pd(OAc)_2$	/	Cs_2CO_3	PPh_3	/	THF	NR
13[e]	$Pd(OAc)_2$	/	Et_3N	PPh_3	/	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

[a]Unless 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. [b]Yield of the isolated **3a**. [c]At 50 °C. [d]With 2,6-DMBQ (10 mol%). [e]With isoquinoline-1,3,4-trione-derived ketimine **6a**. [f]With $Pd(OAc)_2$ (1.0 equiv) and PPh_3 (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-dimethylhydroquinon were conducted, but only unwanted byproducts were observed, demonstrating that the current allylation of activated ketimine did not proceeded through hydroquinone-catalyzed ene reaction.



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



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

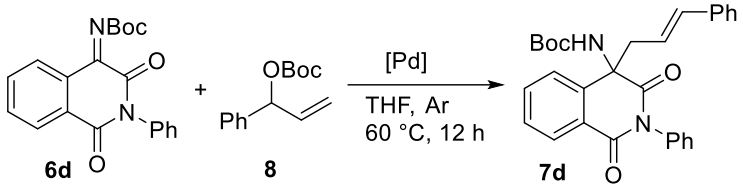
entry[a]	[Pd]	ligand	oxidant	X	additive	solvent	yield (%)[b]
1[c]	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	/	THF	52
2[d]	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	/	THF	44
3	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	/	THF	62
4	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	/	toluene	39
5	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	/	dioxane	42
6	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	/	MTBE	49
7	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	/	nBu$_2$O	trace
8	$Pd(OAc)_2$	$(4\text{-}MeC_6H_4)_3P$	2,6-DMBQ	1.5	/	THF	53
9	$Pd(OAc)_2$	$(4\text{-}FC_6H_4)_3P$	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/$PhCO_2H$	THF	50
14	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	68
15	$Pd(OAc)_2$	PPh_3	BQ	1.5	3 Å MS/H_2O	THF	bad conv.
16	$Pd(OAc)_2$	PPh_3	2,5-DMBQ	1.5	3 Å MS/H_2O	THF	66
17	$Pd(OAc)_2$	PPh_3	2,6-DTBQ	1.5	3 Å MS/H_2O	THF	trace
18	$Pd(OAc)_2$	PPh_3	phenyl-*p*-benzoquinone	1.5	3 Å MS/H_2O	THF	trace
19	$Pd(OAc)_2$	PPh_3	DDQ	1.5	3 Å MS/H_2O	THF	NR
20	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.0	3 Å MS/H_2O	THF	43
21	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.25	3 Å MS/H_2O	THF	50
22	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.75	3 Å MS/H_2O	THF	52
23[e]	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	58
24[f]	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	67
25[g]	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	3Å MS/H_2O	THF	65
26	$PdCl_2$	PPh_3	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	NR
27	$Pd(PPh_3)_4$	/	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	trace
28	$Pd_2(dba)_3$	PPh_3	2,6-DMBQ	1.5	3Å MS/H_2O	THF	trace
29	$Pd(TFA)_2$	PPh_3	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	NR
30[h]	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	no product
31[i]	$Pd(OAc)_2$	PPh_3	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	no product

32[j]	$Pd(PPh_3)_4$	/	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	51
33[k]	$Pd(PPh_3)_4$	/	2,6-DMBQ	1.5	3 Å MS/H_2O	THF	49

[a]Unless 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); H_2O (2 μL); $PhCO_2H$ (20 mol%). [b]Yield of the isolated **3a**. [c]In THF (1.0 mL). [d]In THF (0.4 mL). [e]With allylbenzene **1a** (0.20 mmol). [f]With allylbenzene **1a** (0.30 mmol). [g]With PPh_3 (10 mol%). [h]With *n*-Bu_4NBr (20 mol%). [i]With *n*-Bu_4NCl (20 mol%). [j]With $PhCO_2H$ (20 mol%). [k]With HOAc (20 mol%). NR = No reaction.

3. Mechanism study for the umpolung allylation reactions

3.1 Reactions with allylic carbonate



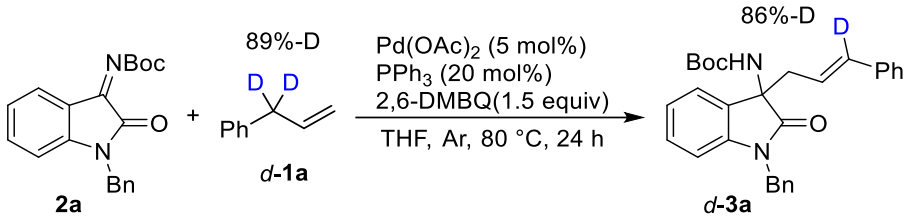
Procedure A: $Pd(PPh_3)_4$ (1.0 equiv)	63% yield
Procedure B: $Pd(OAc)_2$ (1.0 equiv)/PPh_3 (4.0 equiv)	66% yield
Procedure C: $Pd(OAc)_2$ (5 mol%)/PPh_3 (20 mol%)	trace

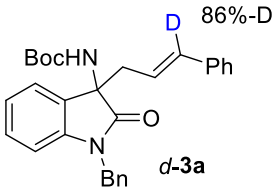
Procedure A: *Tert*-butyl (1,3-dioxo-2-phenyl-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6d** (17.5 mg, 0.0499 mmol), $Pd(PPh_3)_4$ (57.8 mg, 0.0500 mmol, 1.0 equiv) and *tert*-butyl (1-phenylallyl) carbonate **8** (29.3 mg, 0.125 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube 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), PPh_3 (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%), PPh_3 (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

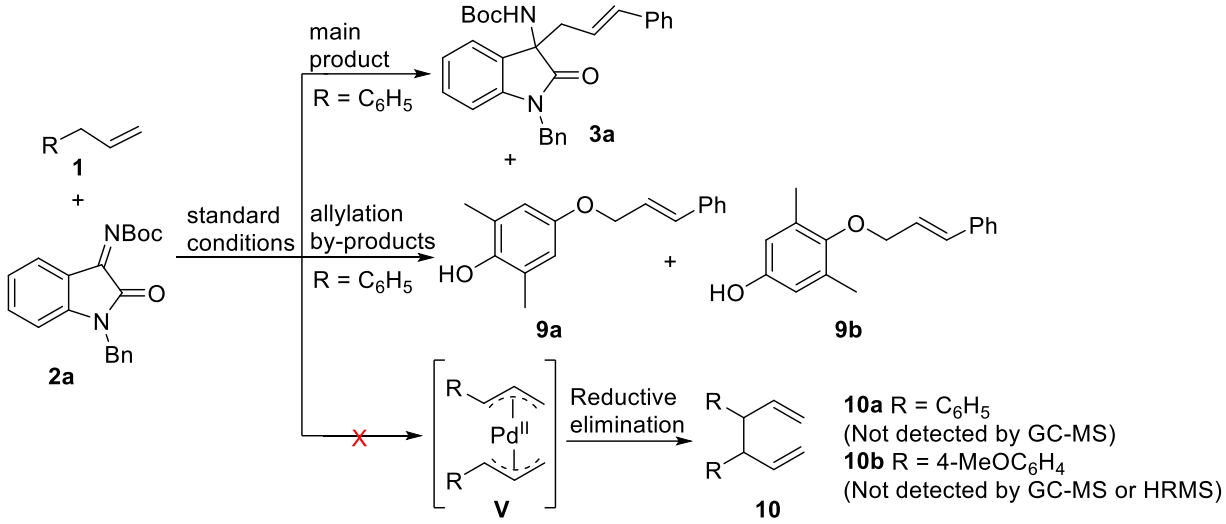


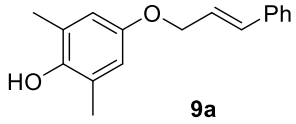


Synthesis of (*d*-3a): *Tert*-butyl (*E*)-(1-benzyl-2-oxoindolin-3-ylidene)carbamate **2a** (33.6 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and (allyl-1,1-d_2)benzene *d*-**1a** (35.6 mg, 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 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 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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,

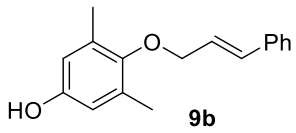
80.5, 61.5, 44.2, 41.6, 28.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{29}H_{29}DN_2O_3 + Na]^+$ 478.2211; Found 478.2209.

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



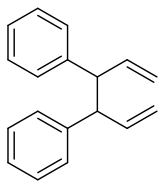


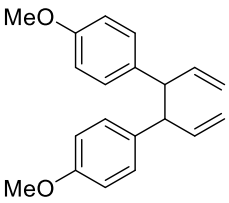
4-(Cinnamyloxy)-2,6-dimethylphenol (9a): *Tert*-butyl (1-benzyl-2-oxoindolin-3-ylidene)carbamate **2a** (33.6 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and allylbenzene **1a** (29.5 mg, 0.250 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 H_2O (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; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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.



9b

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%), PPh_3 (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 H_2O (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; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{17}H_{18}O_2 + H]^+$ 255.1380; Found 255.1373.

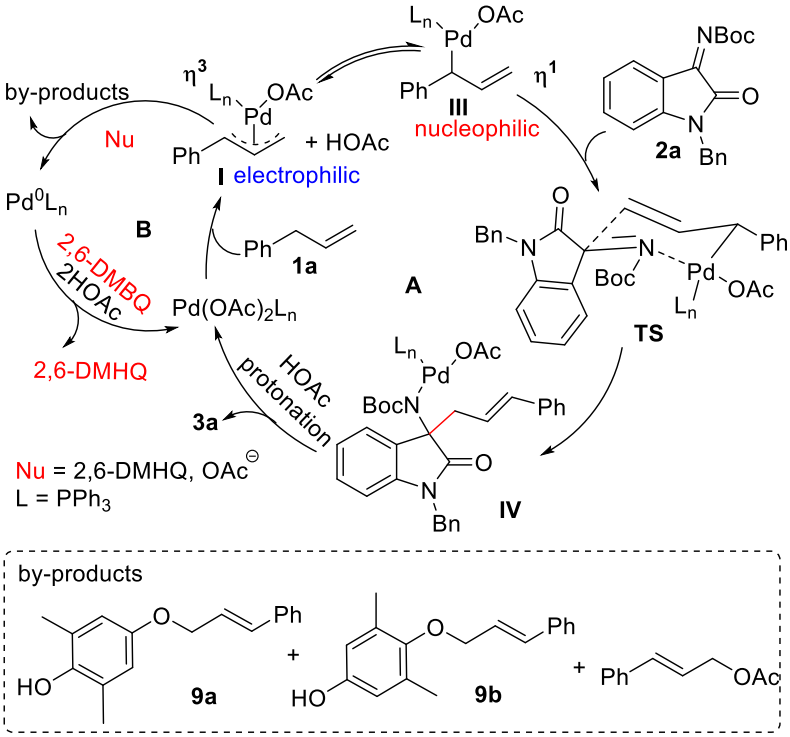

10a



10b

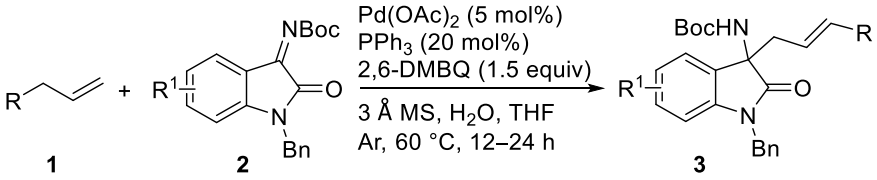
To further verifying whether the reaction involves the bisallylpalladium intermediate **V**, GC-MS and HRMS were used to monitor the formation of the reductive elimination product **10** of the η^3,η^3-bisallylpalladium complex. However, the signal of the possible allyl-allyl cross-coupling product **10a** 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

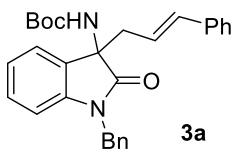


4. General procedure for the oxidative nucleophilic allylation

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

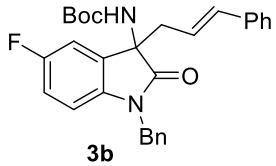


General procedure: Isatin-derived ketimine **2** (0.1 mmol), $Pd(OAc)_2$ (0.005 mmol, 5 mol%), PPh_3 (0.02 mmol, 20 mol%), 2,6-DMBQ (0.15 mmol, 1.5 equiv), 3 Å MS (50 mg) and alkene **1** (0.25 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times 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**.



3a

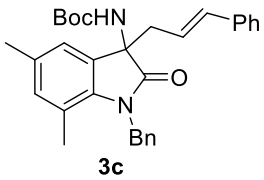
***Tert*-butyl (1-benzyl-3-cinnamyl-2-oxoindolin-3-yl)carbamate (3a)**: *Tert*-butyl (1-benzyl-2-oxoindolin-3-ylidene)carbamate **2a** (33.6 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 Å MS (50 mg) and 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 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 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{29}H_{30}N_2O_3 + Na]^+$ 477.2149; Found 477.2148.



3b

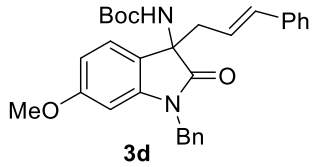
***Tert*-butyl (1-benzyl-3-cinnamyl-5-fluoro-2-oxoindolin-3-yl)carbamate (3b)**: *Tert*-butyl (1-benzyl-5-fluoro-2-oxoindolin-3-ylidene)carbamate **2b** (35.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 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 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 reaction mixture was stirred at 60 ℃ 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –120.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{29}H_{29}FN_2O_3 + Na]^+$ 495.2054; Found 495.2054.



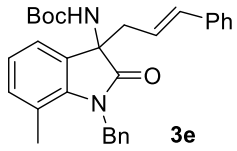
3c

***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%), PPh_3 (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 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 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{31}H_{34}N_2O_3 + Na]^+$ 505.2462; Found 505.2461.



3d

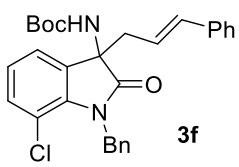
***Tert*-butyl (1-benzyl-3-cinnamyl-6-methoxy-2-oxoindolin-3-yl) carbamate (3d)**: *Tert*-butyl (1-benzyl-6-methoxy-2-oxoindolin-3-ylidene) carbamate **2d** (36.6 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 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 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 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{30}H_{32}N_2O_4 + Na]^+$ 507.2254; Found 507.2249.



3e

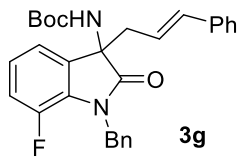
***Tert*-butyl (1-benzyl-3-cinnamyl-7-methyl-2-oxoindolin-3-yl)carbamate (3e)**: *Tert*-butyl (1-benzyl-7-methyl-2-oxoindolin-3-ylidene)carbamate **2e** (35.0 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv), 3 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 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 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{30}H_{32}N_2O_3 + Na]^+$ 491.2305; Found 491.2305.



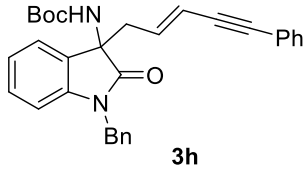
3f

***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%), PPh_3 (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 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 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{29}H_{29}{}^{35}ClN_2O_3 + Na]^+$ 511.1759; Found 511.1758; Calcd for $[C_{29}H_{29}{}^{37}ClN_2O_3 + Na]^+$ 513.1729; Found 513.1743.



3g

***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%), PPh_3 (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 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 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 176.4, 153.7, 147.5 ($^1J_{FC}$ = 244.5 Hz), 137.0, 136.3, 136.2, 129.0 ($^3J_{FC}$ = 8.8 Hz), 128.6, 128.5, 127.9, 127.4 ($^3J_{FC}$ = 8.8 Hz), 126.5, 123.33, 123.26, 120.4, 118.6 ($^4J_{FC}$ = 3.2 Hz), 117.0 ($^2J_{FC}$ = 19.7 Hz), 80.8, 61.5, 45.7, 45.6, 41.7, 28.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –133.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{29}H_{29}FN_2O_3 + Na]^+$ 495.2054; Found 495.2055.

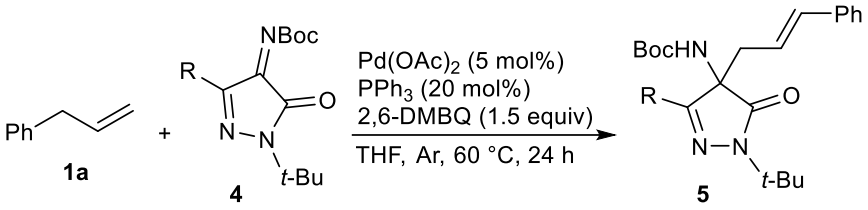


3h

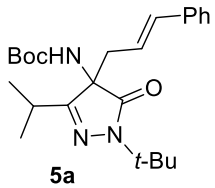
***Tert*-butyl (*E*)-(1-benzyl-2-oxo-3-(5-phenylpent-2-en-4-yn-1-yl) indolin-3-yl)carbamate (3h)**: *Tert*-butyl (1-benzyl-2-oxoindolin-3-ylidene) carbamate **2a** (33.6 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 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 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 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{31}H_{30}N_2O_3 + Na]^+$ 501.2149; Found 501.2140.

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

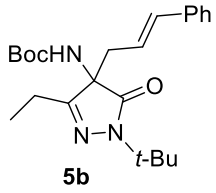


General procedure: Pyrazoledione-derived ketimine **4** (0.1 mmol), $Pd(OAc)_2$ (0.005 mmol, 5 mol%), PPh_3 (0.02 mmol, 20 mol%), 2,6-DMBQ (0.15 mmol, 1.5 equiv) and allylbenzene **1a** (0.25 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with 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-1*H*-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%), PPh_3 (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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{24}H_{35}N_3O_3 + Na]^+$ 436.2571; Found 436.2571.

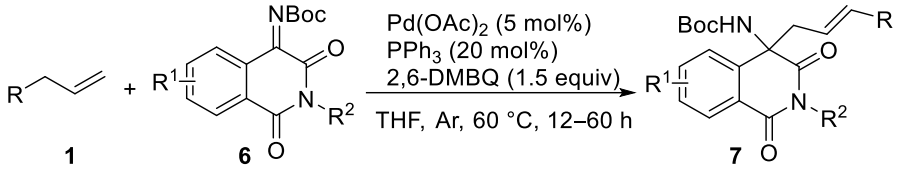


5b

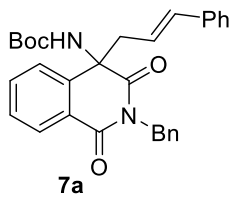
***Tert*-butyl (1-(*tert*-butyl)-4-cinnamyl-3-ethyl-5-oxo-4,5-dihydro-1*H*-pyrazol-4-yl)carbamate (5b)**: *Tert*-butyl (1-(*tert*-butyl)-3-ethyl-5-oxo-1,5-dihydro-4*H*-pyrazol-4-ylidene)carbamate **4b** (28.1 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR

(100 MHz, $CDCl_3$): 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

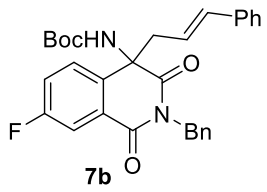


General procedure: Isoquinoline-1,3,4-trione-derived ketimine **6** (0.1 mmol), $Pd(OAc)_2$ (0.005 mmol, 5 mol%), PPh_3 (0.02 mmol, 20 mol%), 2,6-DMBQ (0.15 mmol, 1.5 equiv) and alkene **1** (0.25 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times 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**.



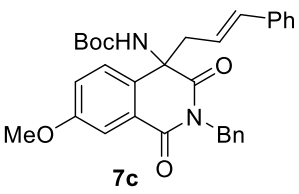
***Tert*-butyl (2-benzyl-4-cinnamyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7a)**: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{30}H_{30}N_2O_4 + Na]^+$ 505.2098; Found 505.2102.

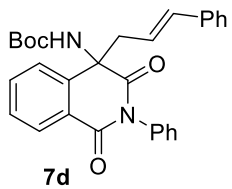


7b

***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%), PPh_3 (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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –112.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{30}H_{29}FN_2O_4 + Na]^+$ 523.2004; Found 523.2004.

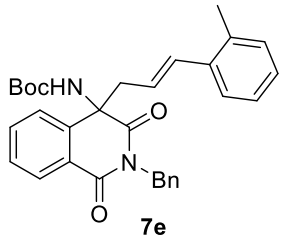


***Tert*-butyl (2-benzyl-4-cinnamyl-7-methoxy-1,3-dioxo-1,2,3,4- tetra-hydroisoquinolin-4-yl)carbamate (7c)**: *Tert*-butyl (2-benzyl-7-methoxy-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6c** (39.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{31}H_{32}N_2O_5 + Na]^+$ 535.2203; Found 535.2199.



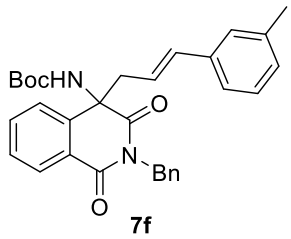
***Tert*-butyl (4-cinnamyl-1,3-dioxo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7d)**: *Tert*-butyl (1,3-dioxo-2-phenyl-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6d** (35.0 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{29}H_{28}N_2O_4 + Na]^+$ 491.1941; Found 491.1941.



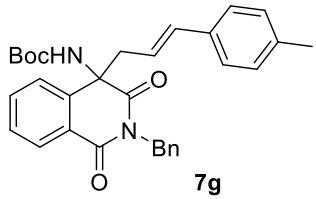
7e

***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(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (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-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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{31}H_{32}N_2O_4 + Na]^+$ 519.2254; Found 519.2254.



7f

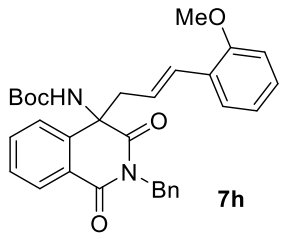
***Tert*-butyl (*E*)-(2-benzyl-1,3-dioxo-4-(3-(*m*-tolyl)allyl)-1,2,3,4- tetrahydroisoquinolin-4-yl)carbamate (7f)**: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydro isoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 1-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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{31}H_{32}N_2O_4 + Na]^+$ 519.2254; Found 519.2250.



7g

***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(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (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-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

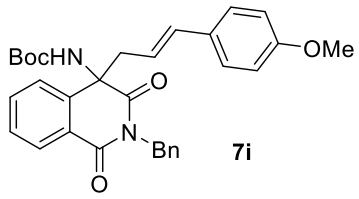
stirred vigorously for 30 min, then extracted with EtOAc. The combined organic phases were evaporated under vacuo. The crude reaction mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 8:1) to give the product **7g**: 45.5 mg (0.0916 mmol), as a white solid, 92% yield; m.p. 103–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{31}H_{32}N_2O_4 + Na]^+$ 519.2254; Found 519.2246.



7h

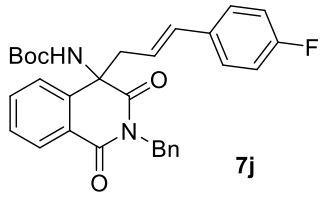
***Tert*-butyl (*E*)-(2-benzyl-4-(3-(2-methoxyphenyl)allyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7h)**: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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.



7i

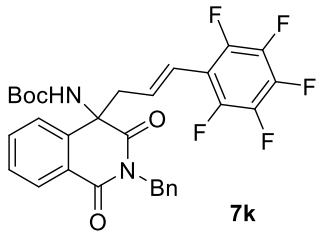
***Tert*-butyl (*E*)-(2-benzyl-4-(3-(4-methoxyphenyl)allyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7i)**: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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.



7j

***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%), PPh_3 (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

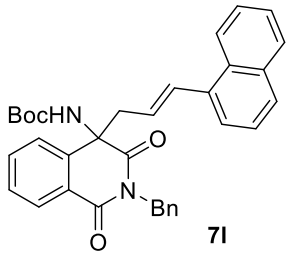
syringe, and the tube was evacuated and back-filled three times with argon again. The Schlenk tube was tightly capped. The reaction mixture was stirred at 80 °C for 36 h. After completion (monitored by TLC), the reaction was quenched by saturated sodium carbonate solution, and the mixture was stirred 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) −113.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $[C_{30}H_{29}FN_2O_4 + Na]^+$ 523.2004; Found 523.2000.



7k

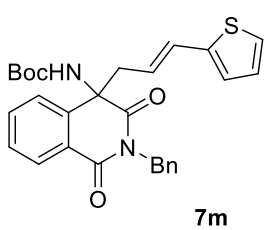
***Tert*-butyl (*E*)-(2-benzyl-1,3-dioxo-4-(3-(perfluorophenyl)allyl)-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7k)**: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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 ($^1J_{FC}$ = 248.0 Hz), 140.1 ($^1J_{FC}$ = 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: $[M + Na]^+$ Calcd for $[C_{30}H_{25}F_5N_2O_4 + Na]^+$ 595.1627; Found 595.1622.



7l

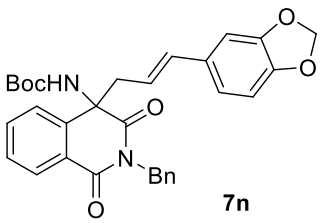
***Tert*-butyl (*E*)-(2-benzyl-4-(3-(naphthalen-1-yl)allyl)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7l)**: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 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; ^{1}H 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: $[M + Na]^+$ Calcd for $[C_{34}H_{32}N_2O_4 + Na]^+$ 555.2254; Found 555.2254.



7m

***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), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020

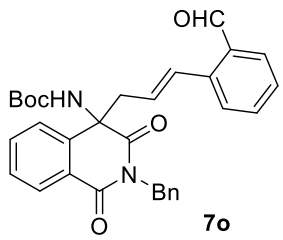
mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 2-allylthiophene **1k** (31.1 mg, 0.250 mmol, 2.5 equiv) were added to a 10 mL Schlenk tube, and the tube was evacuated and back-filled three times with argon. Then distilled THF (1.0 mL) was added by syringe, and the tube was evacuated and 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{28}H_{28}N_2O_4S + Na]^+$ 511.1662; Found 511.1664.



7n

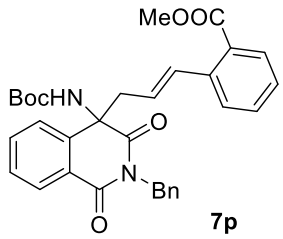
***Tert*-butyl (*E*)-(4-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)-2-benzyl-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)carbamate (7n)**: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene) carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 mg, 0.020 mmol, 20 mol%), 2,6-DMBQ (20.4 mg, 0.150 mmol, 1.5 equiv) and 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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: $[M + Na]^+$ Calcd for $[C_{31}H_{30}N_2O_6 + Na]^+$ 549.1996; Found 549.1994.



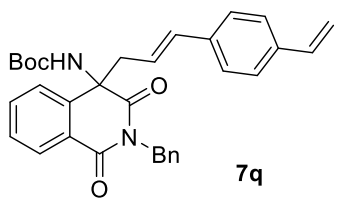
7o

***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), $Pd(OAc)_2$ (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; ^{1}H 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: $[M + Na]^+$ Calcd for $[C_{31}H_{30}N_2O_5 + Na]^+$ 533.2047; Found 533.2040.



7p

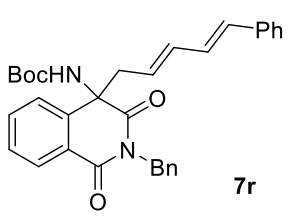
Methyl (*E*)-2-(3-(2-benzyl-4-((*tert*-butoxycarbonyl)amino)-1,3-dioxo-1,2,3,4-tetrahydroisoquinolin-4-yl)prop-1-en-1-yl)benzoate (7p): *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene) carbamate **6a** (36.4 mg, 0.0999 mmol), $Pd(OAc)_2$ (1.2 mg, 0.0053 mmol, 5 mol%), PPh_3 (5.2 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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{32}H_{32}N_2O_6 + Na]^+$ 563.2153; Found 563.2151.



7q

***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%), PPh_3 (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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $[C_{32}H_{32}N_2O_4 + Na]^+$ 531.2254; Found 531.2256.

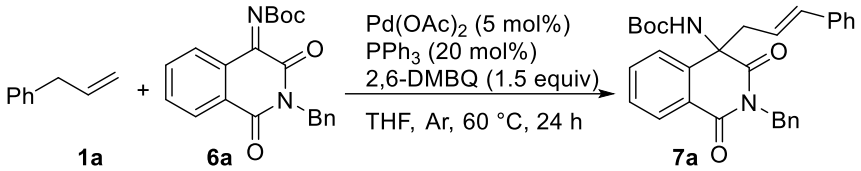


7r

***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%), PPh_3 (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; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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.

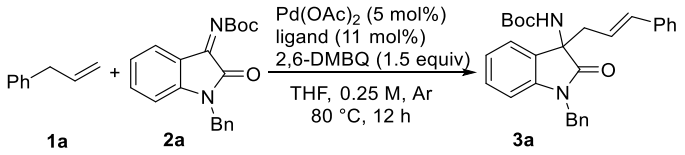
4.4 Oxidative nucleophilic allylation of isoquinoline-1,3,4-trione-derived ketimine 6a on a 1.0 mmol scale

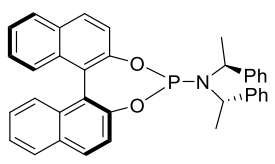


A mixture of *tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (364.4 mg, 1.000 mmol, 1.0 equiv), $Pd(OAc)_2$ (11.2 mg, 0.0499 mmol, 5 mol%), PPh_3 (52.5 mg, 0.200 mmol, 20 mol%), 2,6-DMBQ (204.2 mg, 1.500 mmol, 1.5 equiv) and allylbenzene **1a** (295.4 mg, 2.500 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.

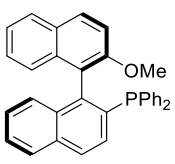
5. Screening conditions of asymmetric oxidative nucleophilic allylation

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

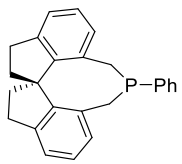




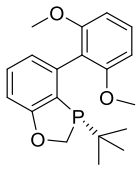
62% yield, 4% ee



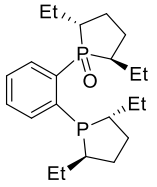
NR



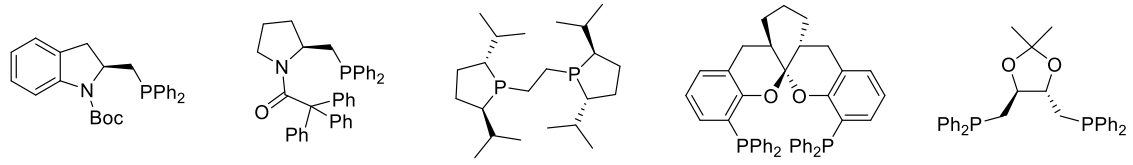
ca. 50% yield, 1% ee



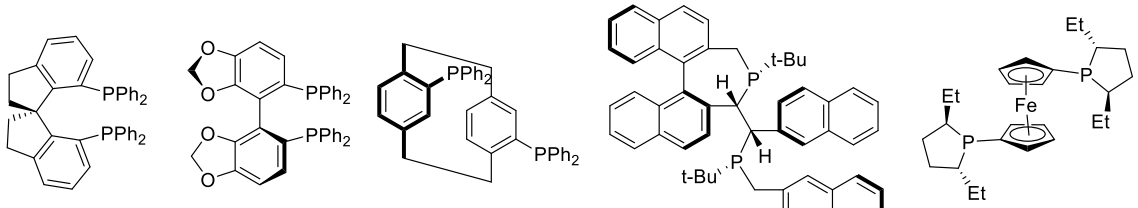
43% yield, 1% ee



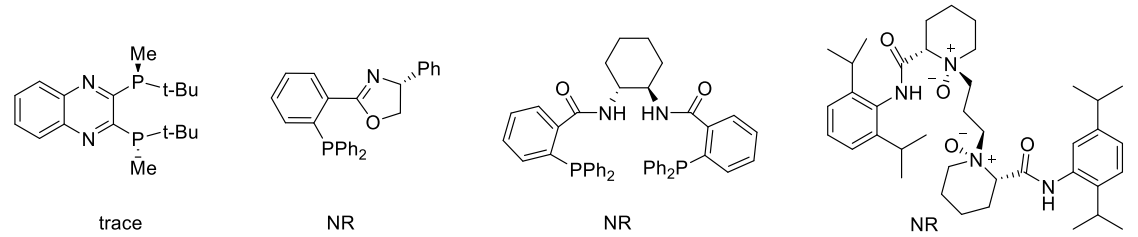
22% yield, 3% ee



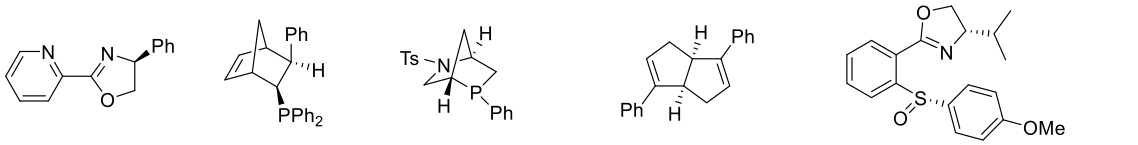
21% yield, 2% ee | 36% yield, 1% ee | 19% yield, 2% ee | 38% yield, 2% ee | 53% yield, 2% ee



NR | trace | ca. 10% yield, 0% ee | NR | 48% yield, 1% ee

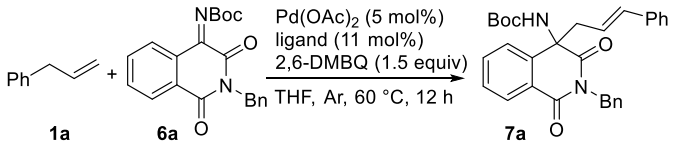


trace | NR | NR | NR

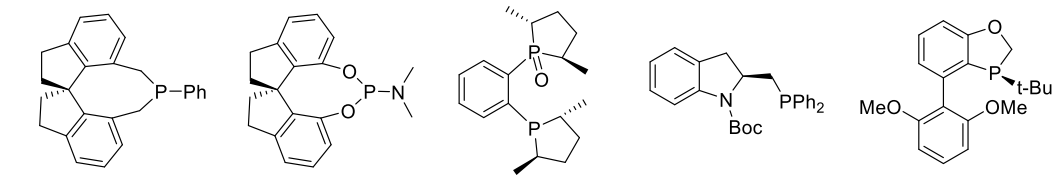


NR | trace | NR | NR | NR

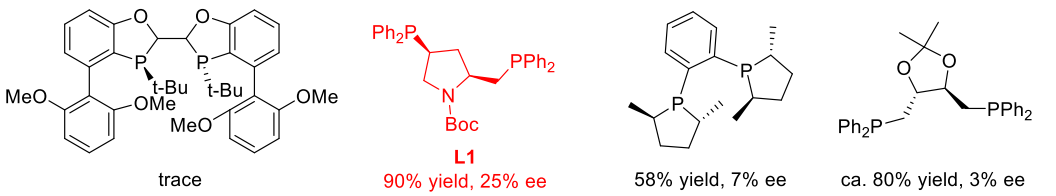
5.2 Screening conditions of asymmetric oxidative nucleophilic allylation of allylbenzene 1a and and isoquinoline-1,3,4-trione-derived ketimine 6a



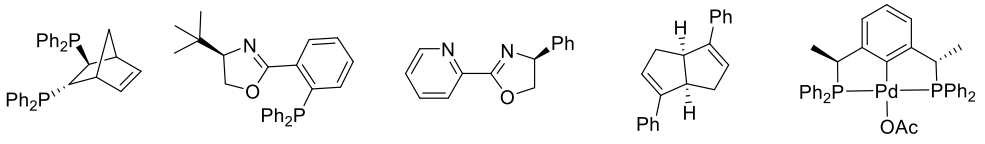
1a | 6a | 7a



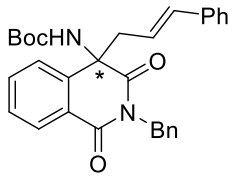
trace | ca. 75% yield, 3% ee | ca. 90% yield, 0% ee | ca. 80% yield, 7% ee | 52% yield, 10% ee



trace | **L1** 90% yield, 25% ee | 58% yield, 7% ee | ca. 80% yield, 3% ee



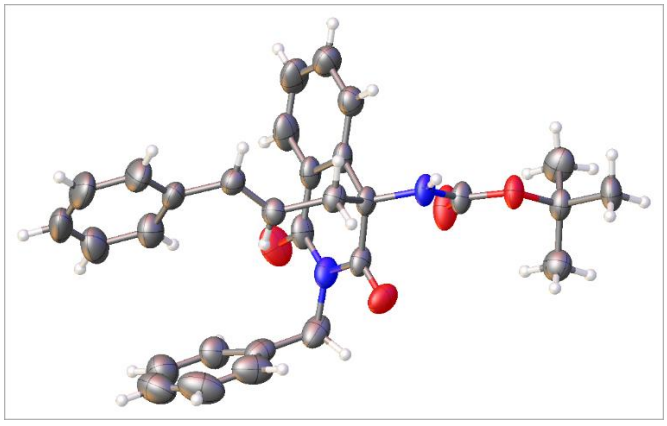
trace | NR | NR | NR | NR



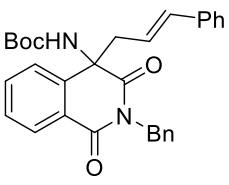
Synthesis of chiral 7a: *Tert*-butyl (2-benzyl-1,3-dioxo-2,3-dihydroisoquinolin-4(1*H*)-ylidene)carbamate **6a** (18.2 mg, 0.0499 mmol), $Pd(OAc)_2$ (0.6 mg, 0.0027 mmol, 5 mol%), **L1** (3.0 mg, 0.0054 mmol, 11 mol%), 2,6-DMBQ (10.2 mg, 0.0749 mmol, 1.5 equiv) and allylbenzene **1a** (14.8 mg, 0.125 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 $CHCl_3$ (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.



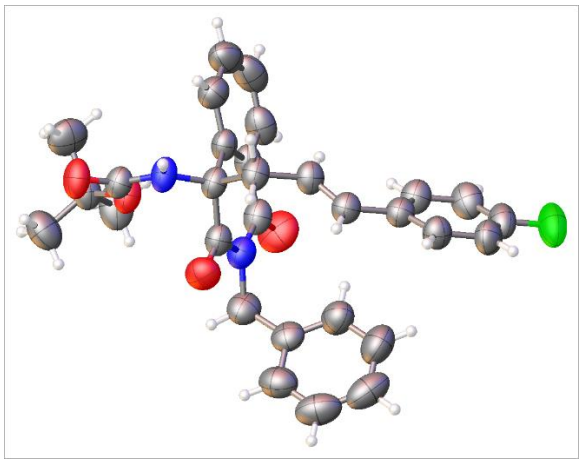
(ellipsoid contour probability 50%)

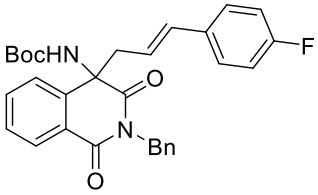


7a

Identification code	**7a**
Empirical formula	$C_{30}H_{30}N_2O_4$
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}g/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	$-20 \leq h \leq 20$, $-12 \leq k \leq 12$, $-36 \leq l \leq 28$
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.



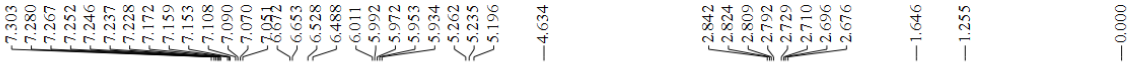


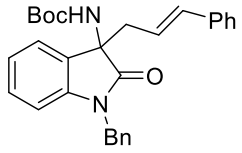
7j

(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)
α/°	102.470(6)
β/°	92.057(6)
γ/°	102.338(6)
Volume/Å^3	1334.77(17)
Z	2
ρ_{calc}g/cm^3	1.245
μ/mm^{-1}	0.716
F(000)	528.0
Crystal size/mm^3	0.5 × 0.3 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.13 to 171.374
Index ranges	$-12 \le h \le 11$, $-13 \le k \le 11$, $-15 \le l \le 14$
Reflections collected	13682
Independent reflections	5224 [R_{int} = 0.0537, R_{sigma} = 0.0491]
Data/restraints/parameters	5224/0/337
Goodness–of–fit on F^2	1.051
Final R indexes [I>=2σ (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

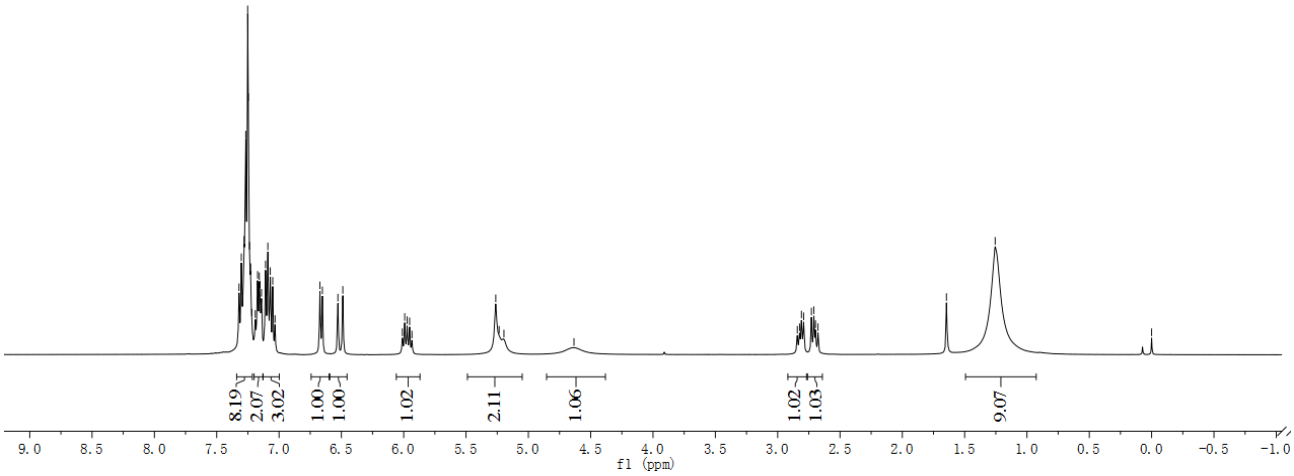
8. NMR, HRMS spectra and HPLC chromatograms

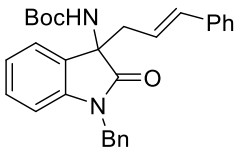




3a

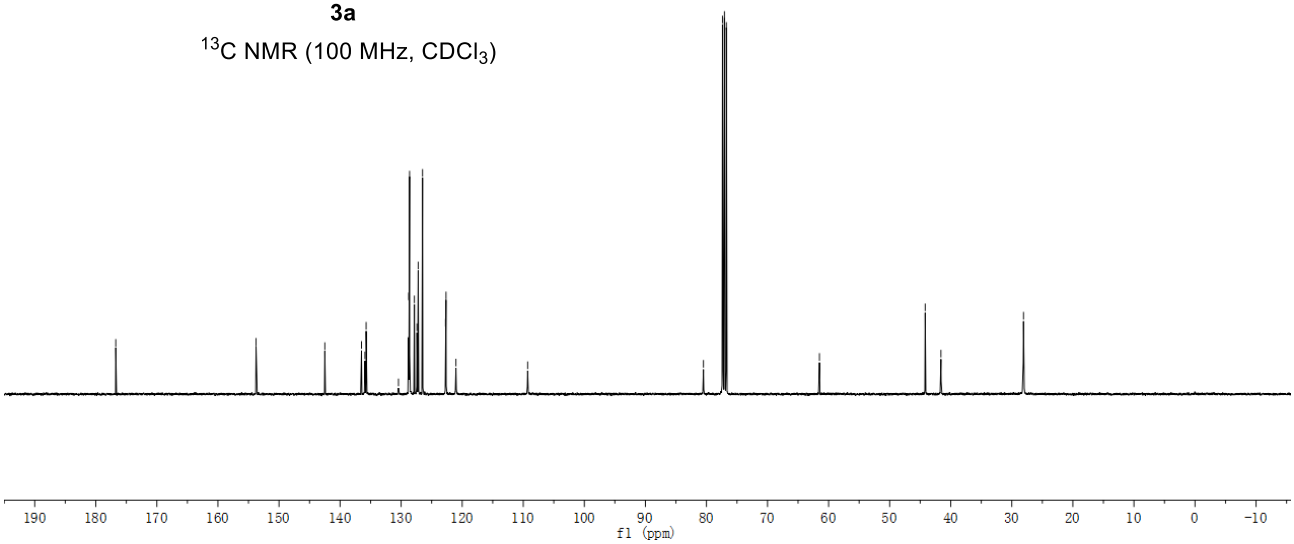
^{1}H NMR (400 MHz, $CDCl_3$)

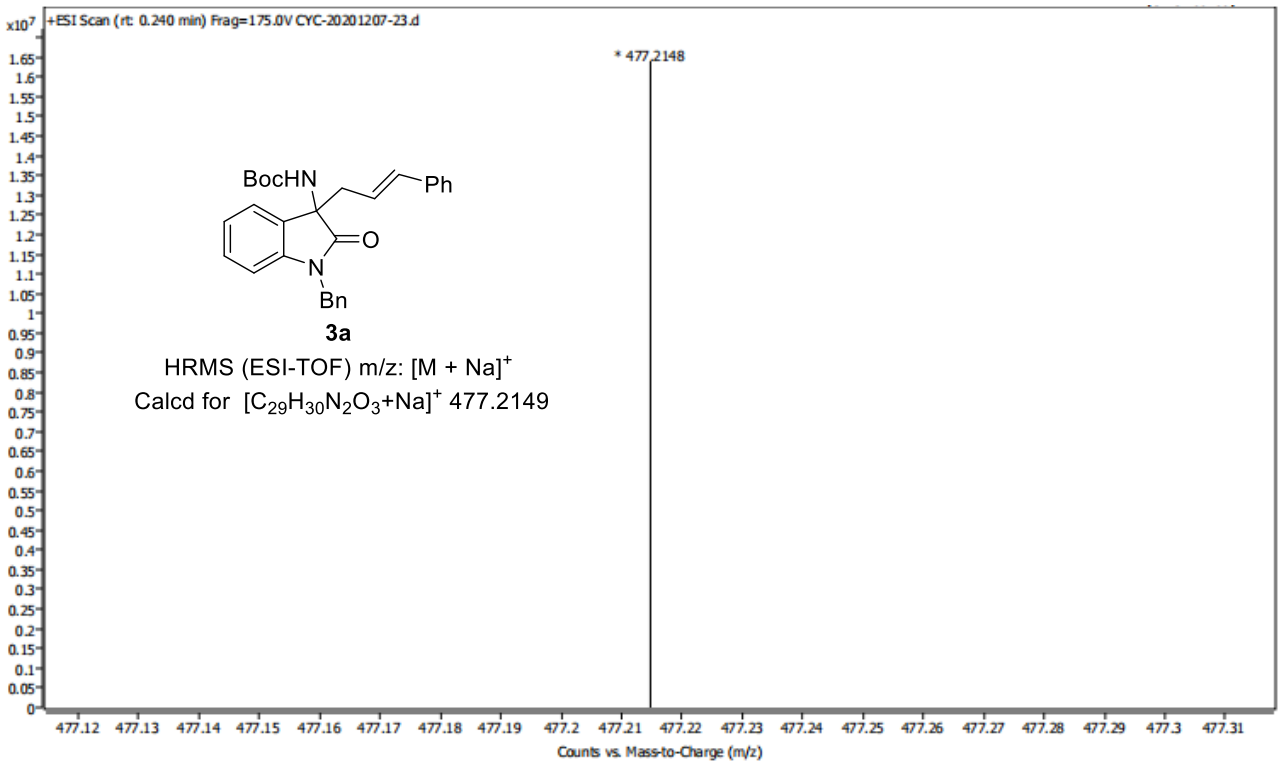




3a

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

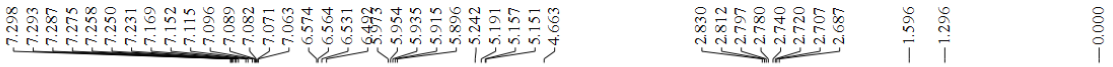


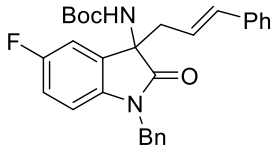


3a

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

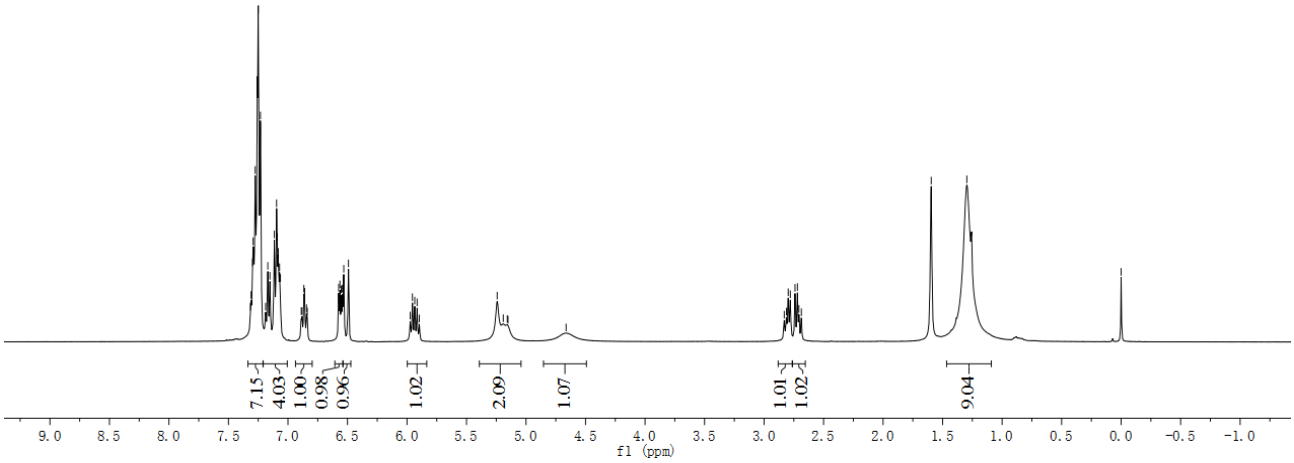
Calcd for $[C_{29}H_{30}N_2O_3+Na]^+$ 477.2149

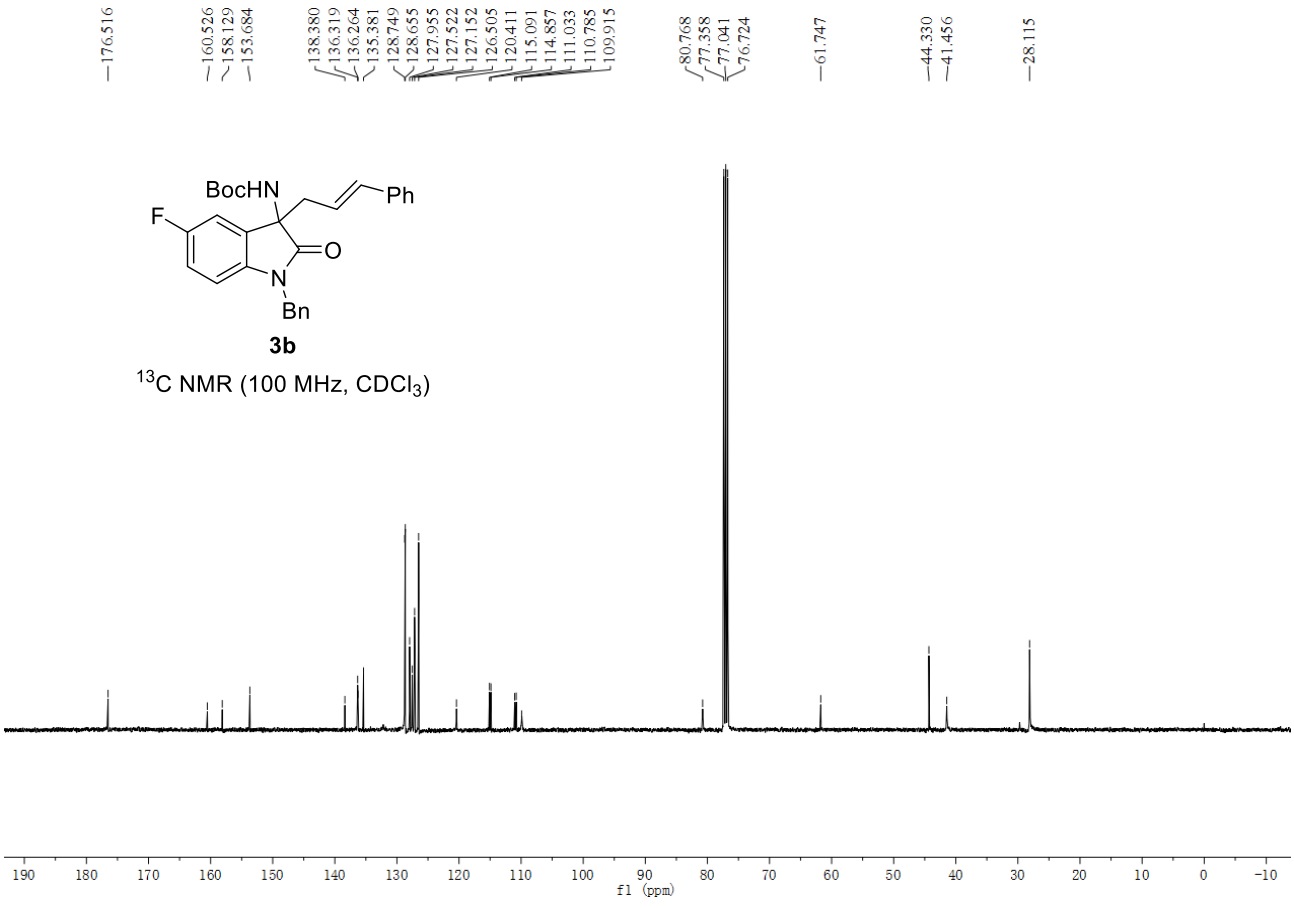




3b

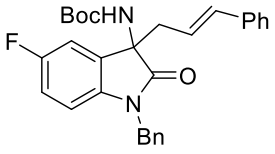
^{1}H NMR (400 MHz, $CDCl_3$)





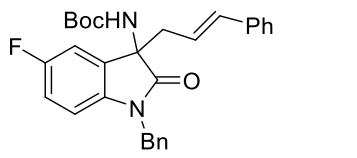
3b

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



3b

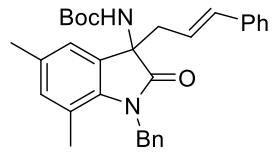
^{19}F NMR (376 MHz, $CDCl_3$)



3b

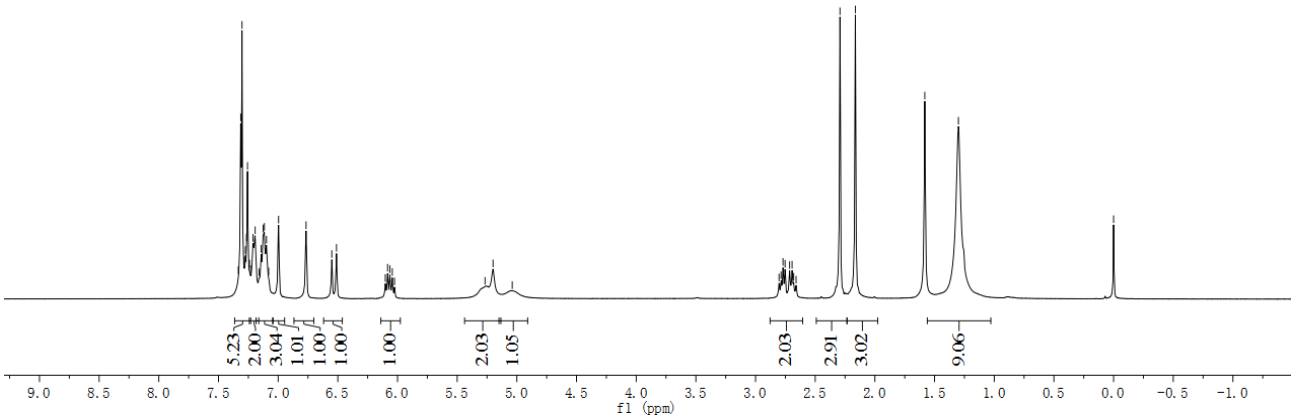
HRMS (ESI-TOF) m/z: $[M + Na]^+$

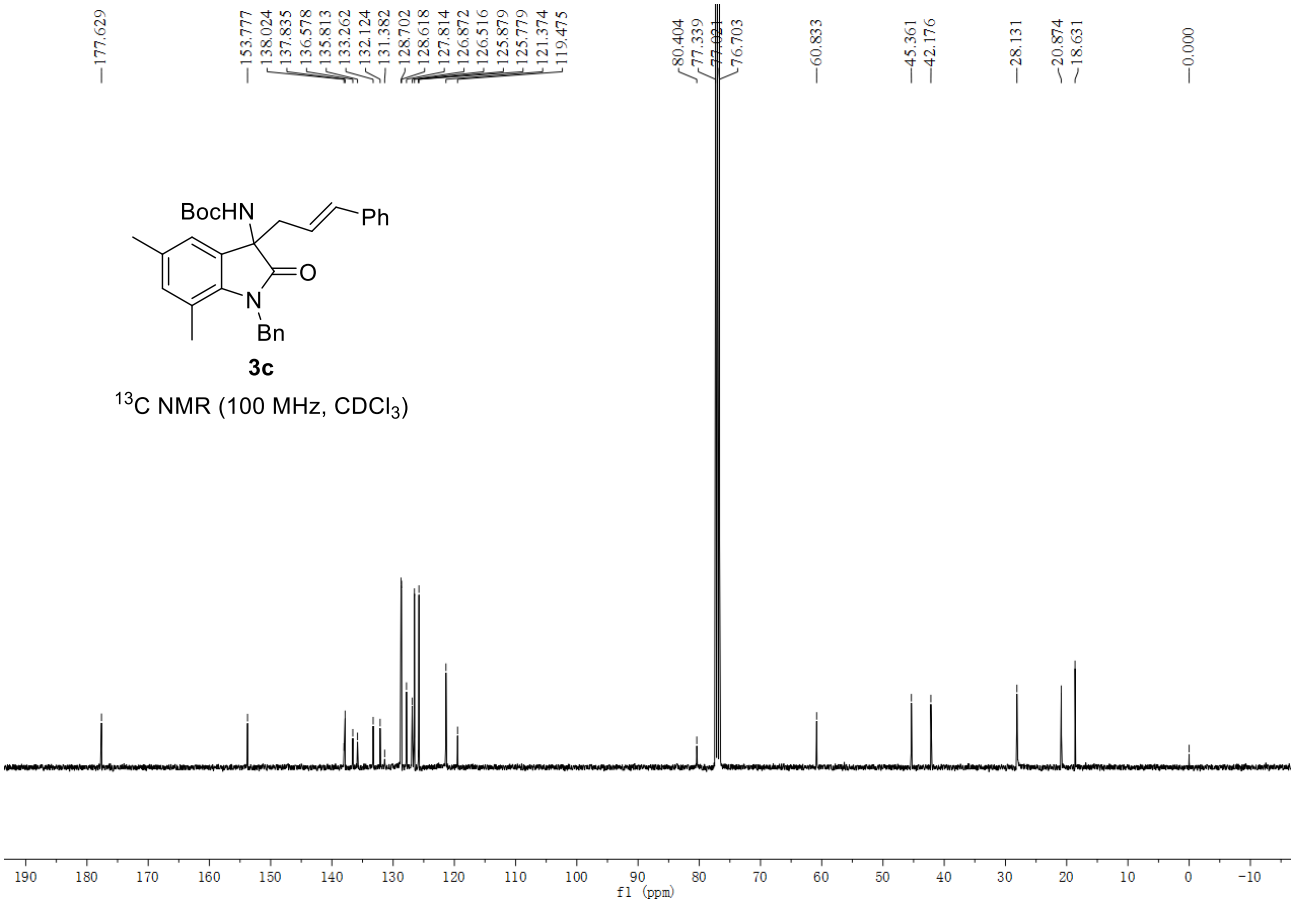
Calcd for $[C_{29}H_{29}FN_2O_3+Na]^+$ 495.2054



3c

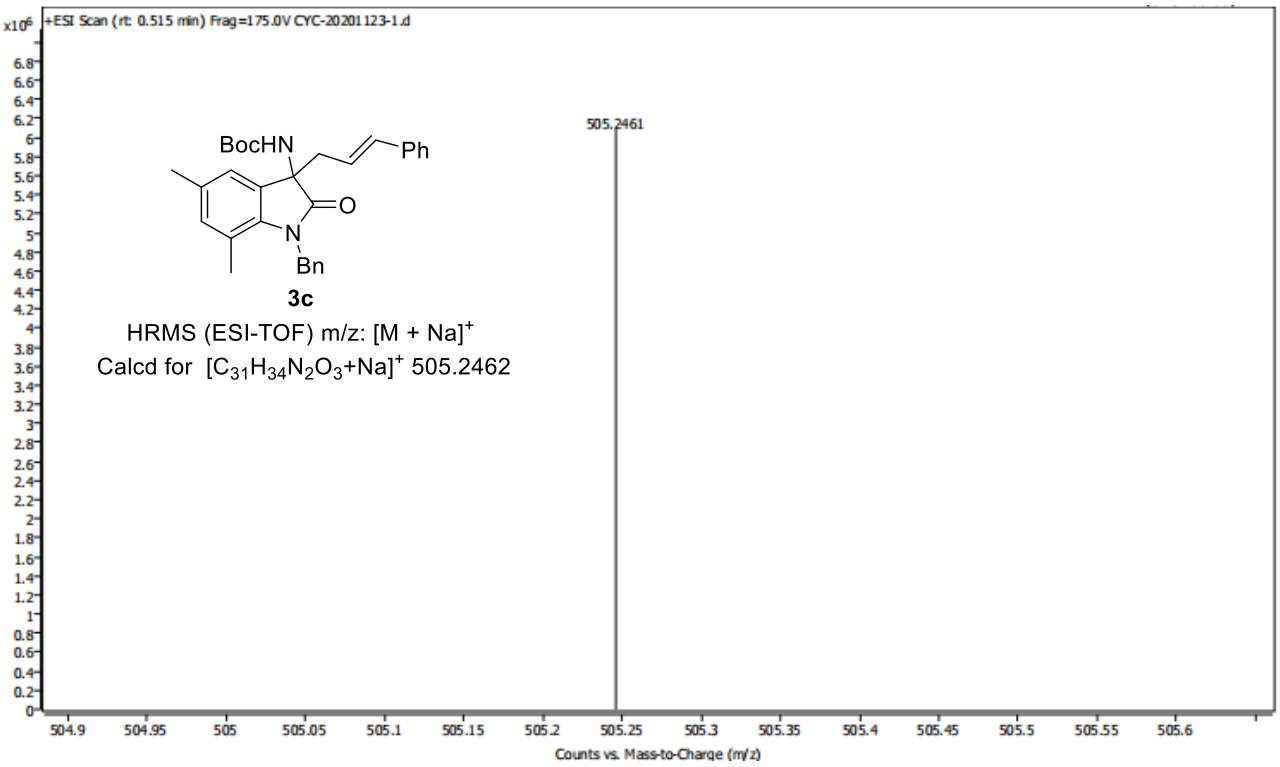
^{1}H NMR (400 MHz, $CDCl_3$)





3c

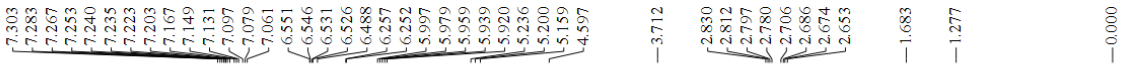
^{13}C NMR (100 MHz, $CDCl_3$)

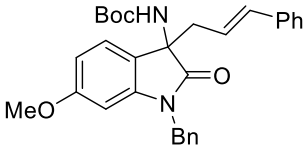


3c

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

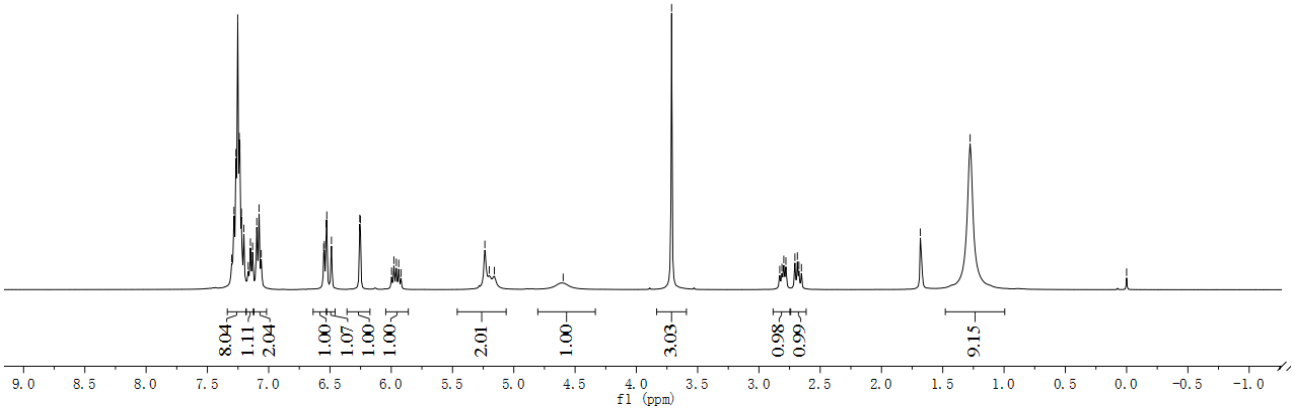
Calcd for $[C_{31}H_{34}N_2O_3+Na]^+$ 505.2462

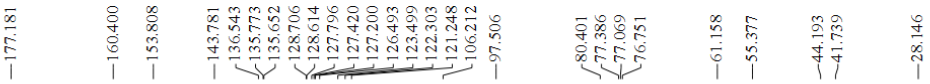


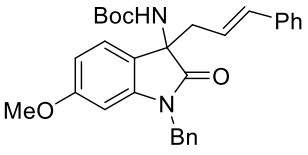


3d

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

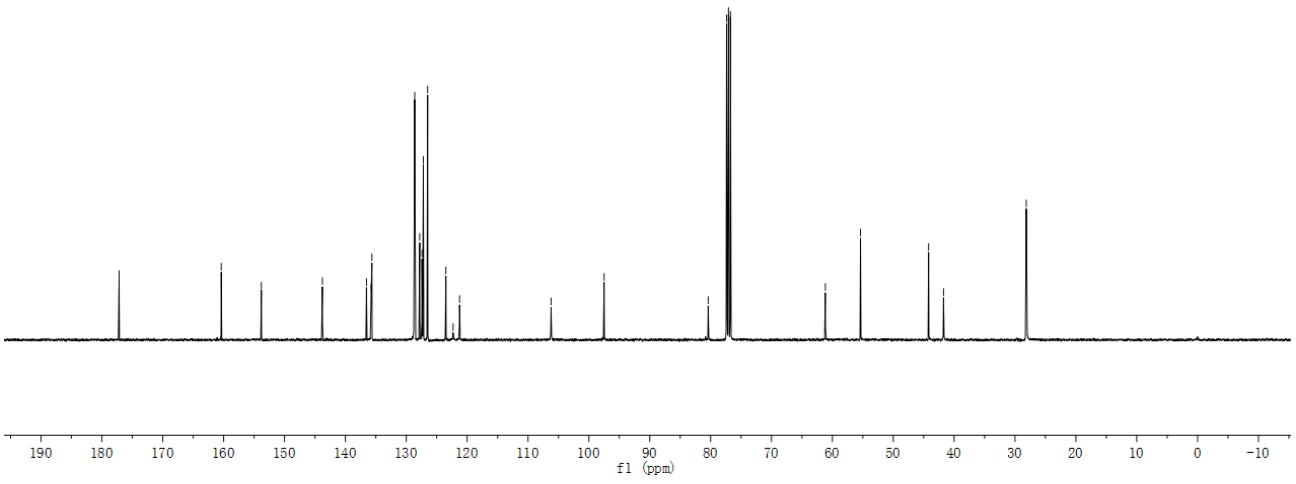


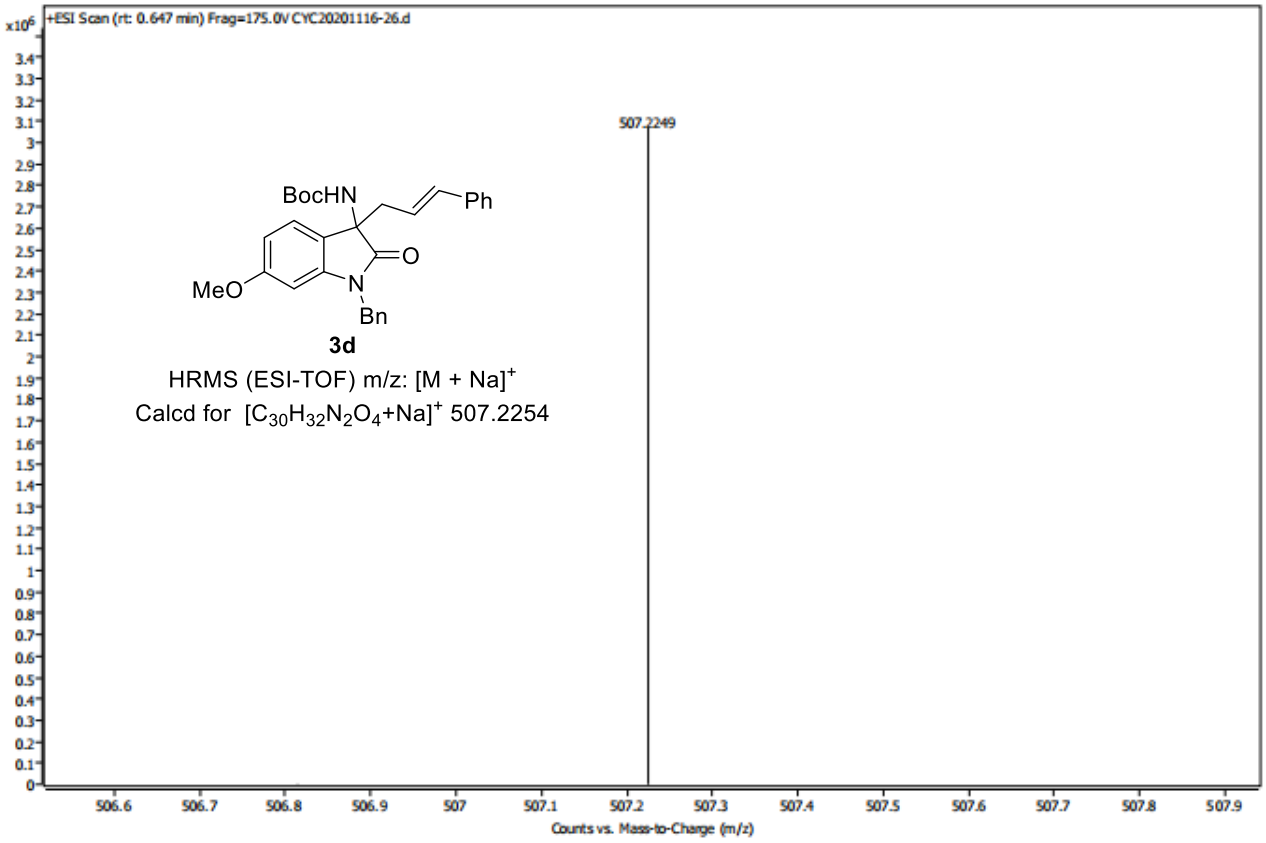




3d

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

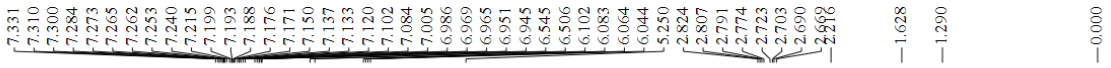


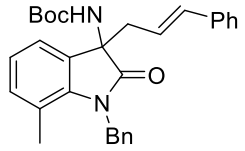


3d

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

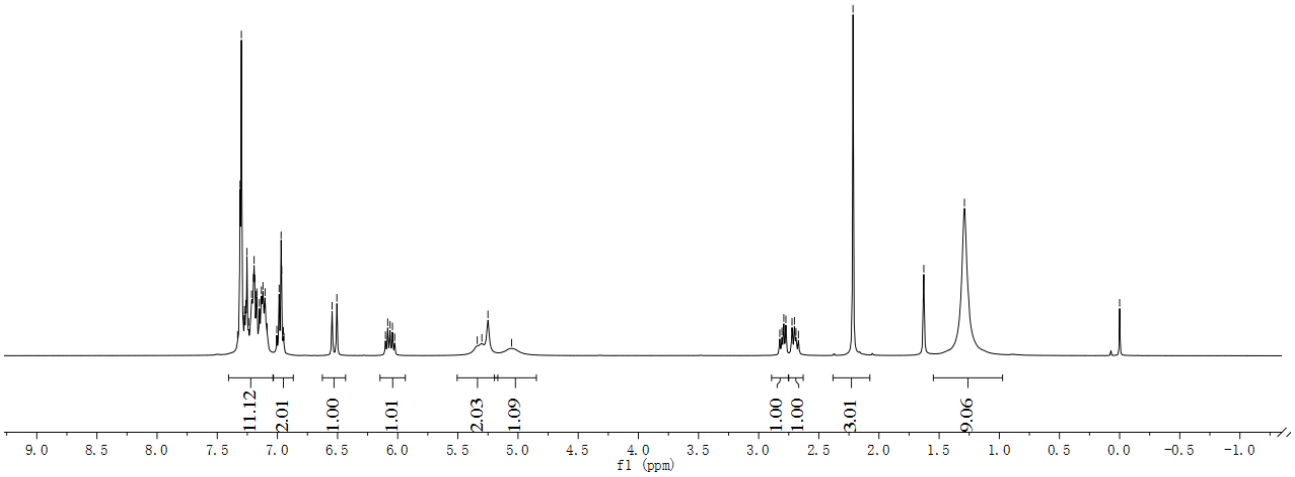
Calcd for $[C_{30}H_{32}N_2O_4+Na]^+$ 507.2254

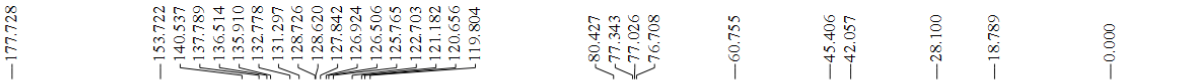


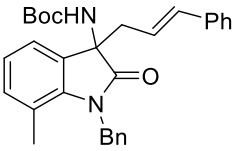


3e

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

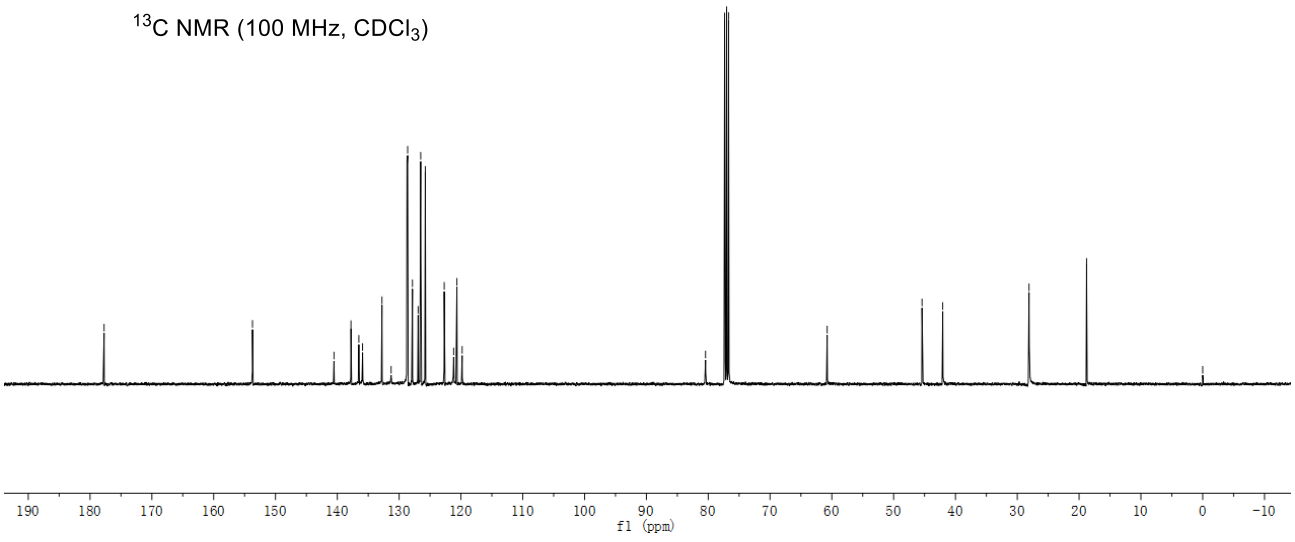


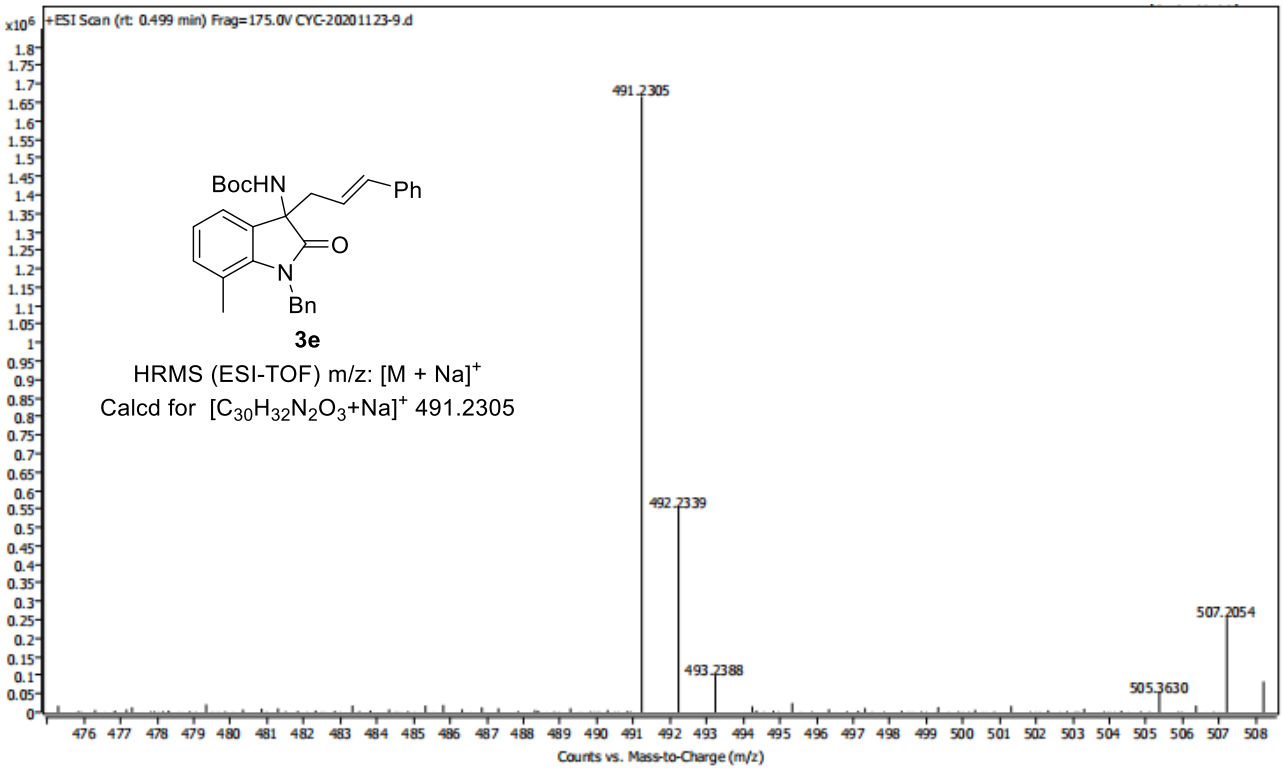




3e

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

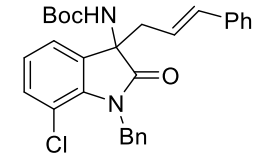




3e

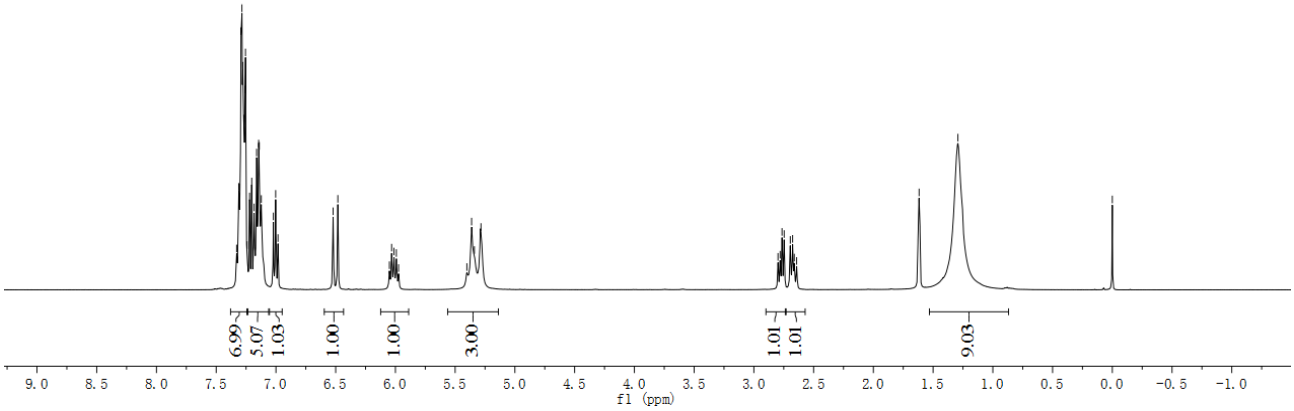
HRMS (ESI-TOF) m/z: $[M + Na]^+$

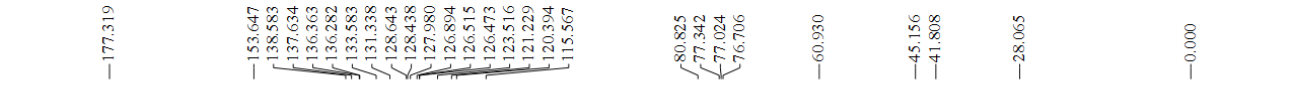
Calcd for $[C_{30}H_{32}N_2O_3+Na]^+$ 491.2305

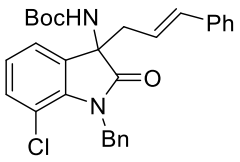


3f

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

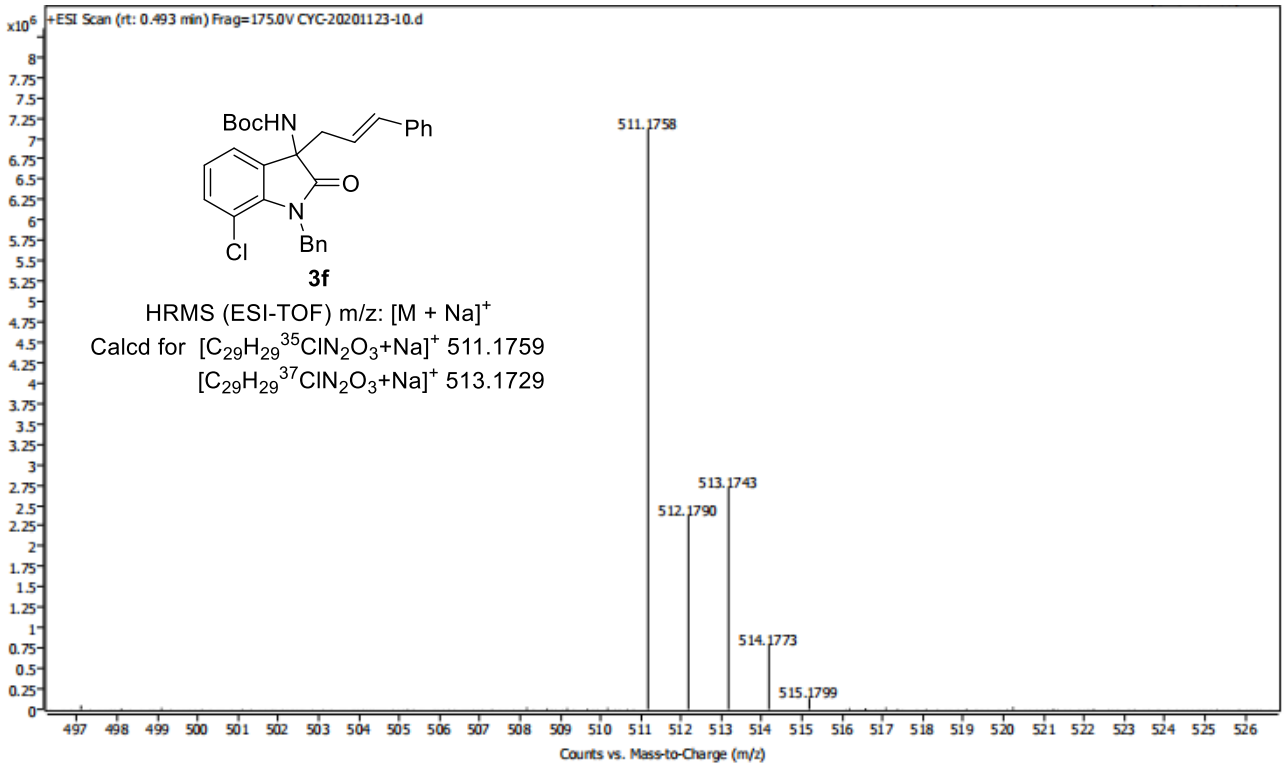






3f

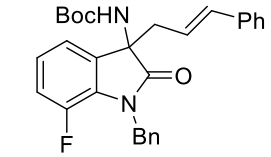
^{13}C NMR (100 MHz, $CDCl_3$)



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

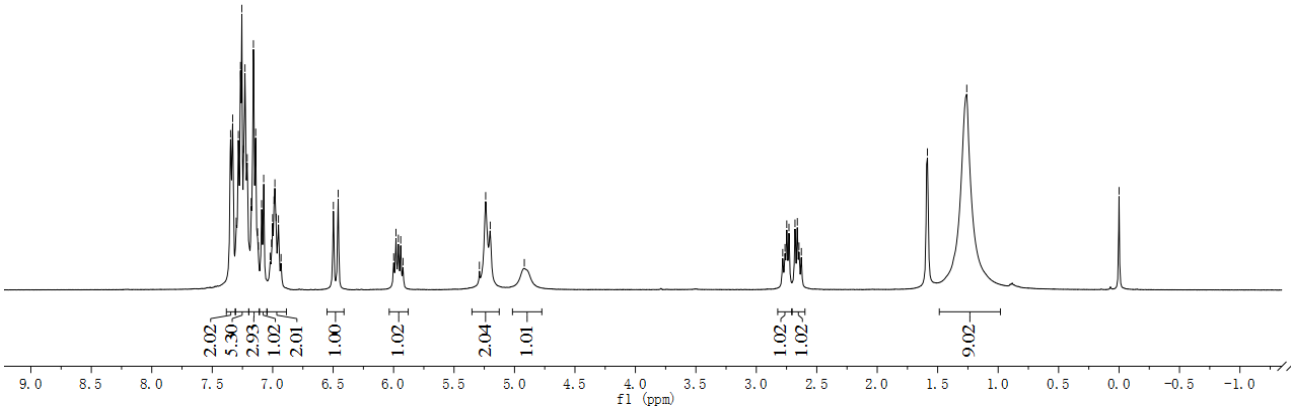
Calcd for $[C_{29}H_{29}{}^{35}ClN_2O_3+Na]^+$ 511.1759

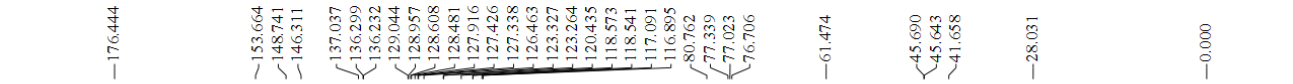
$[C_{29}H_{29}{}^{37}ClN_2O_3+Na]^+$ 513.1729

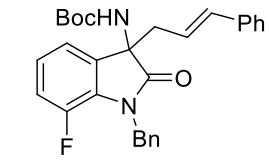


3g

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

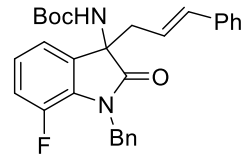






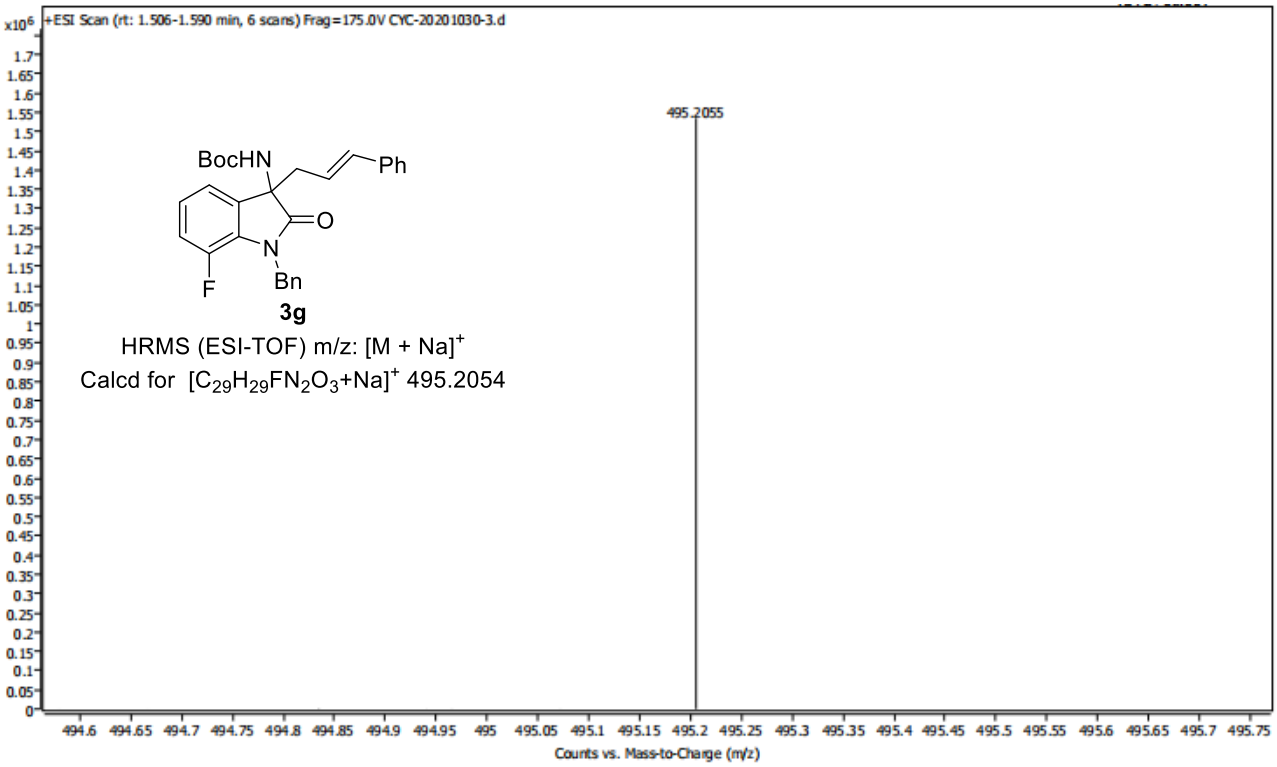
3g

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



3g

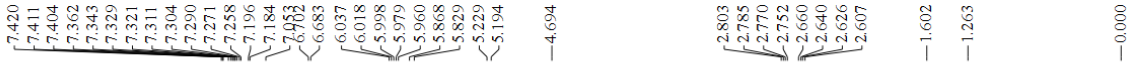
^{19}F NMR (376 MHz, $CDCl_3$)

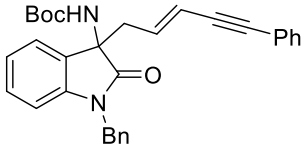


3g

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

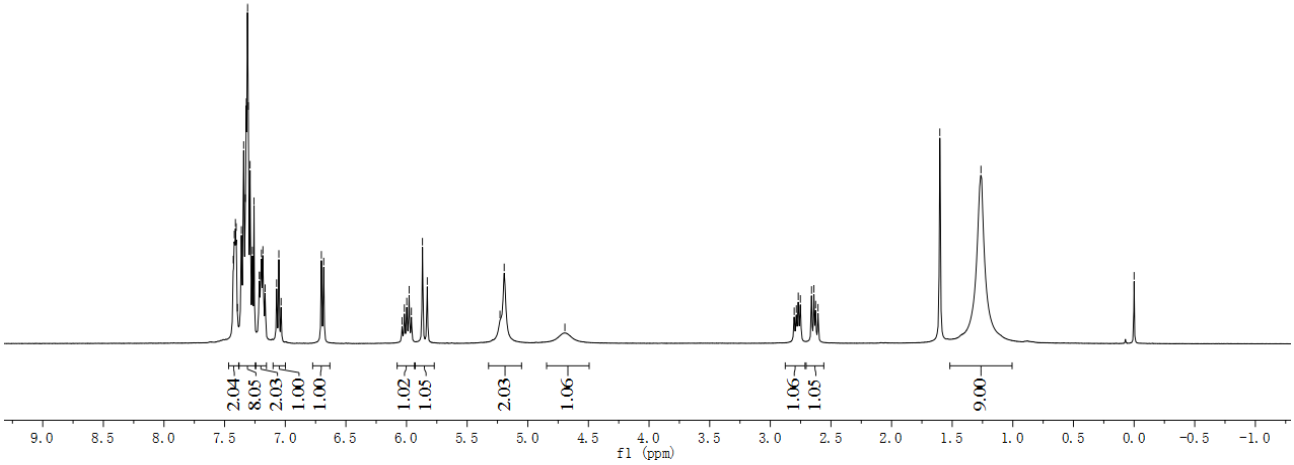
Calcd for $[C_{29}H_{29}FN_2O_3+Na]^+$ 495.2054

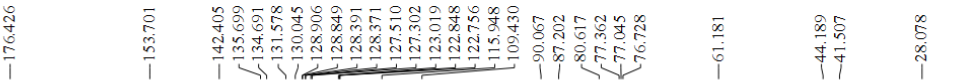


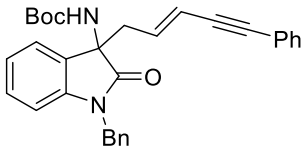


3h

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

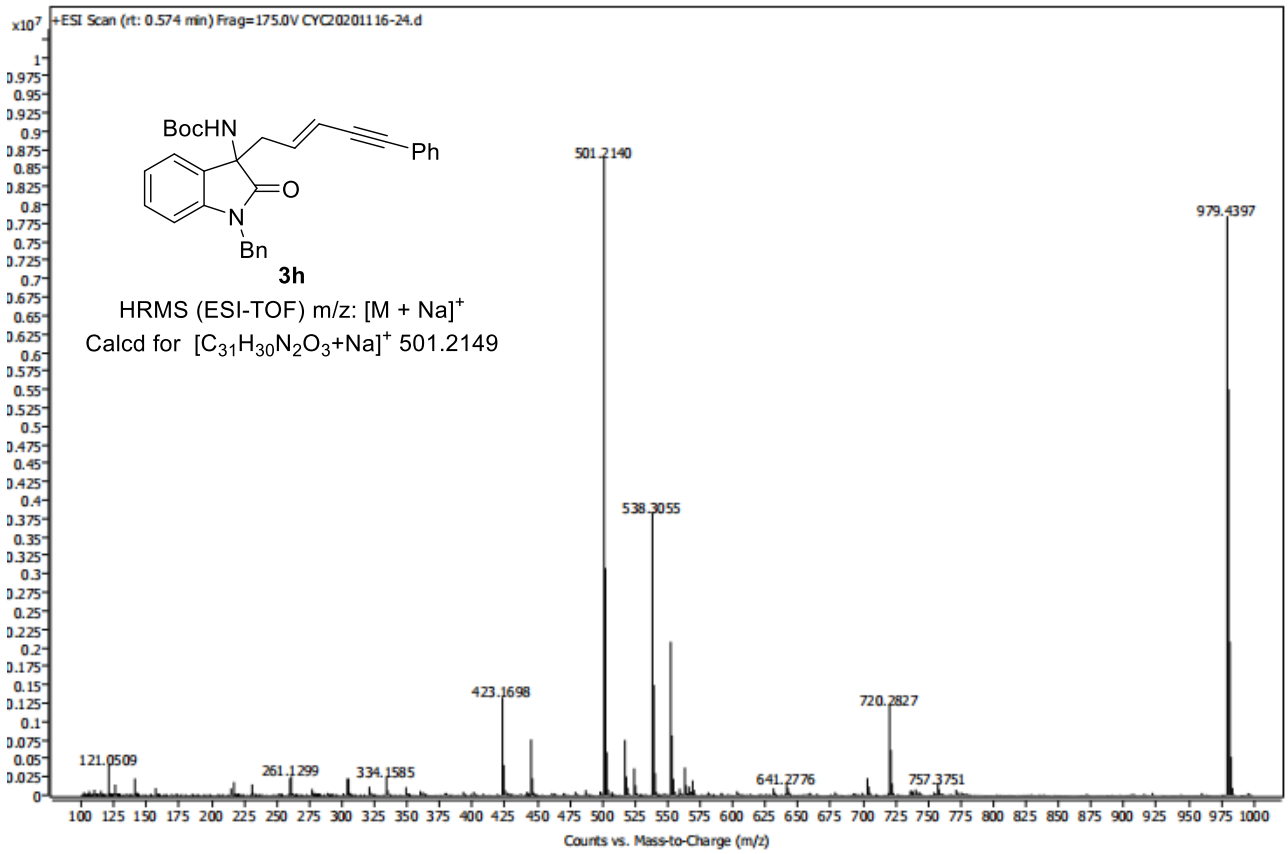


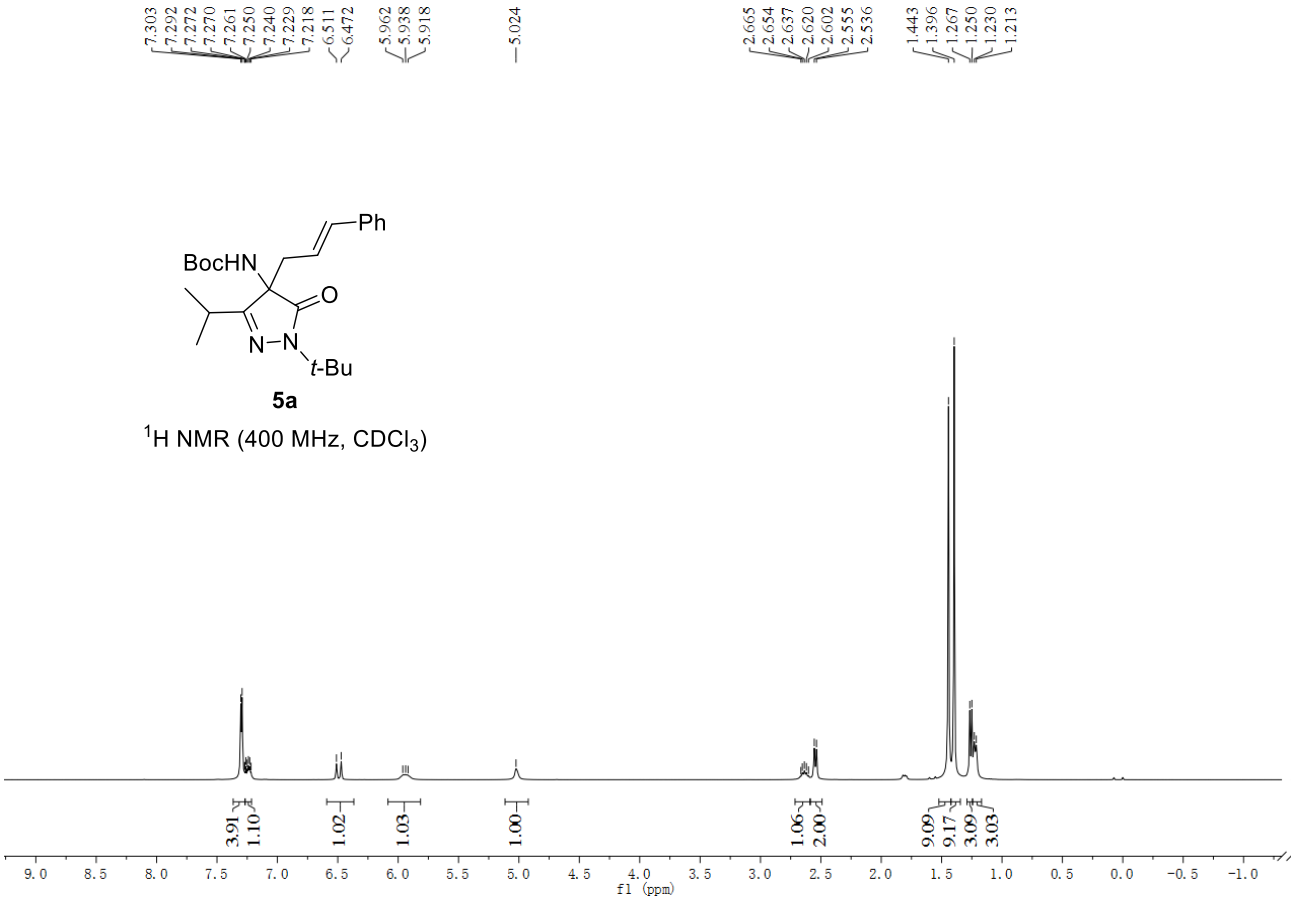


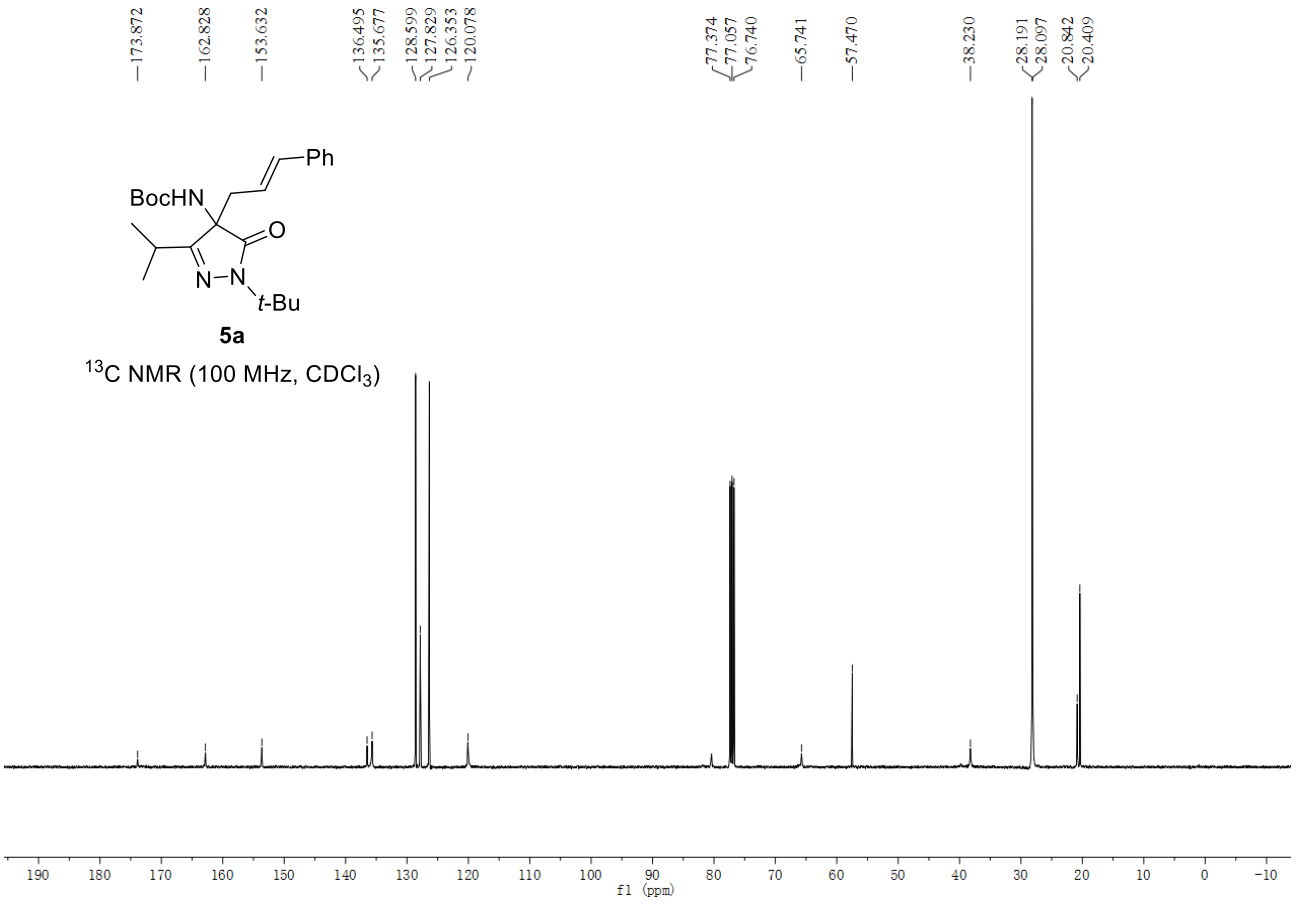


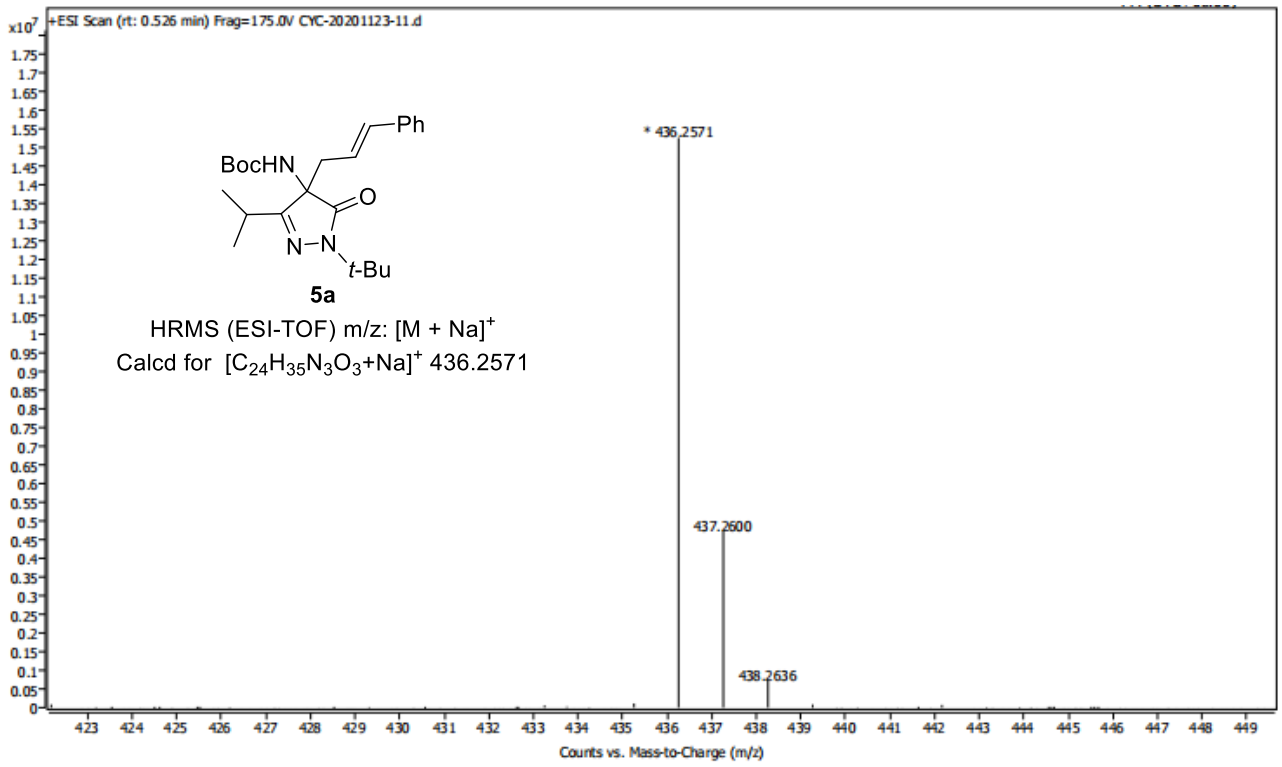
3h

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


+ESI Scan (rt: 0.574 min) Frag=175.0V CYC20201116-24.d
x10^7
BocHN
Ph
O
N
Bn
3h
HRMS (ESI-TOF) m/z: [M + Na]+
Calcd for [C31H30N2O3+Na]+ 501.2149
501.2140
979.4397
538.3055
423.1698
720.2827
121.0509
261.1299
334.1585
641.2776
757.3751
Counts vs. Mass-to-Charge (m/z)


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
Ph
BocHN
O
N–N
t-Bu
5a
1H NMR (400 MHz, CDCl3)
3.91
1.10
1.02
1.03
1.00
1.06
2.00
9.09
9.17
3.09
3.03
f1 (ppm)

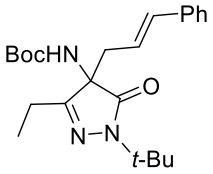

173.872
162.828
153.632
136.495
135.677
128.599
127.829
126.353
120.078
77.374
77.057
76.740
65.741
57.470
38.230
28.191
28.097
20.842
20.409
Ph
BocHN
O
N–N
t-Bu
5a
13C NMR (100 MHz, CDCl3)
f1 (ppm)



5a

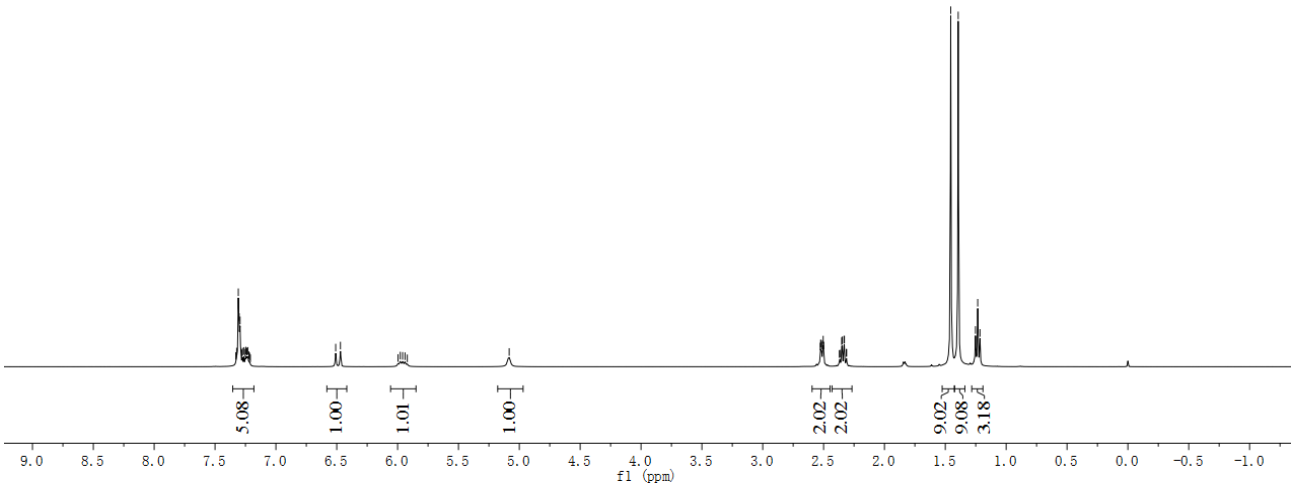
HRMS (ESI-TOF) m/z: $[M + Na]^+$

Calcd for $[C_{24}H_{35}N_3O_3+Na]^+$ 436.2571



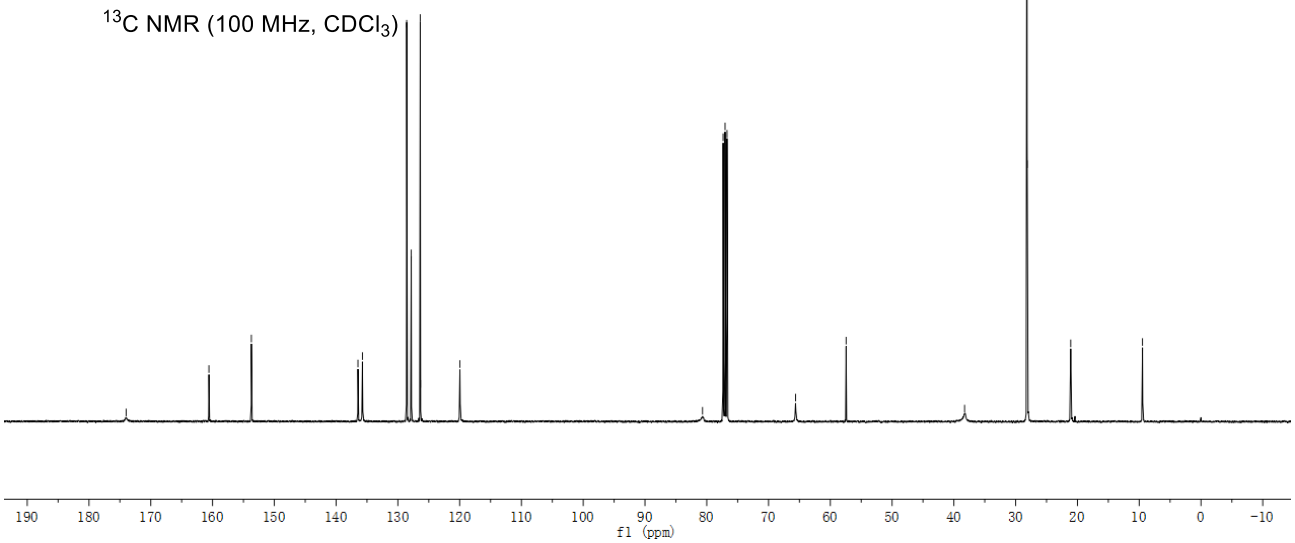
5b

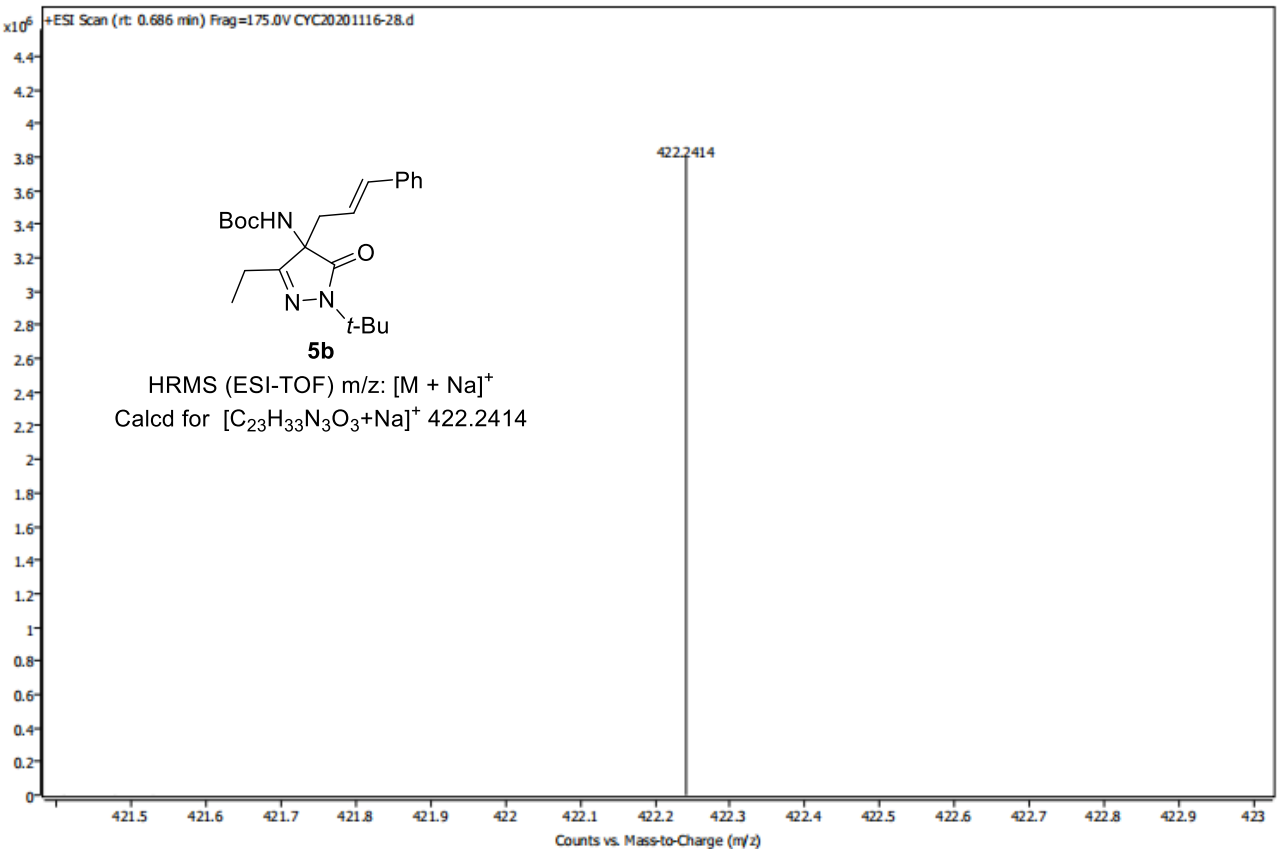
^{1}H NMR (400 MHz, $CDCl_3$)



5b

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

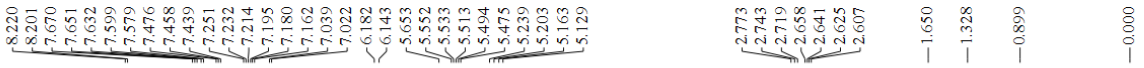


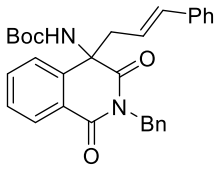


5b

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

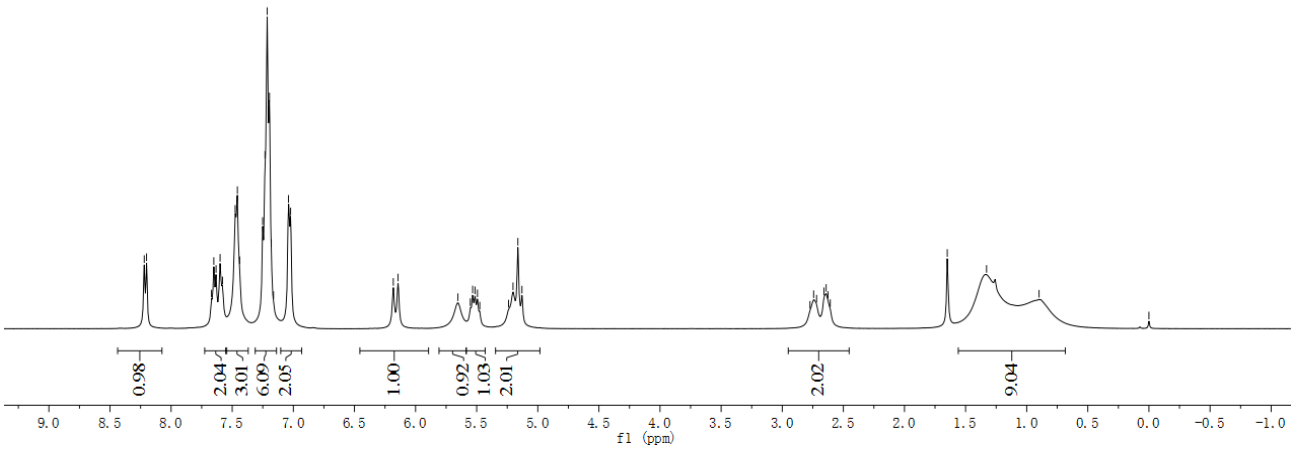
Calcd for $[C_{23}H_{33}N_3O_3+Na]^+$ 422.2414

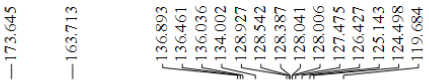


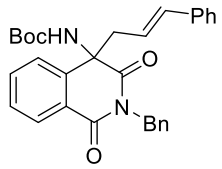


7a

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

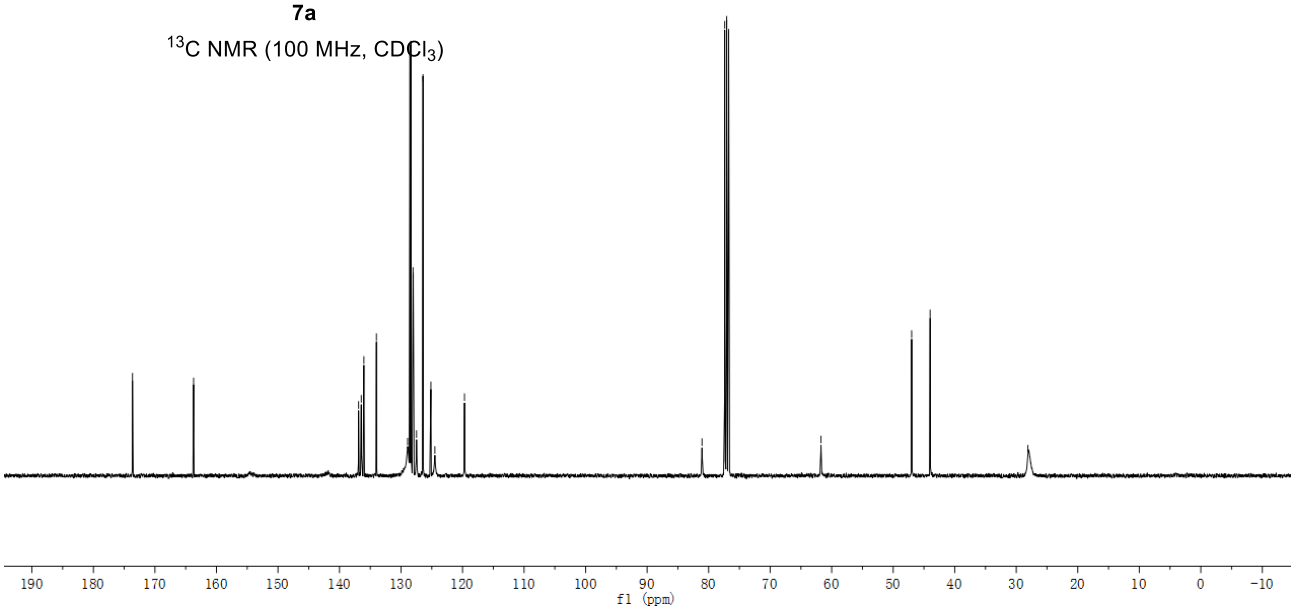


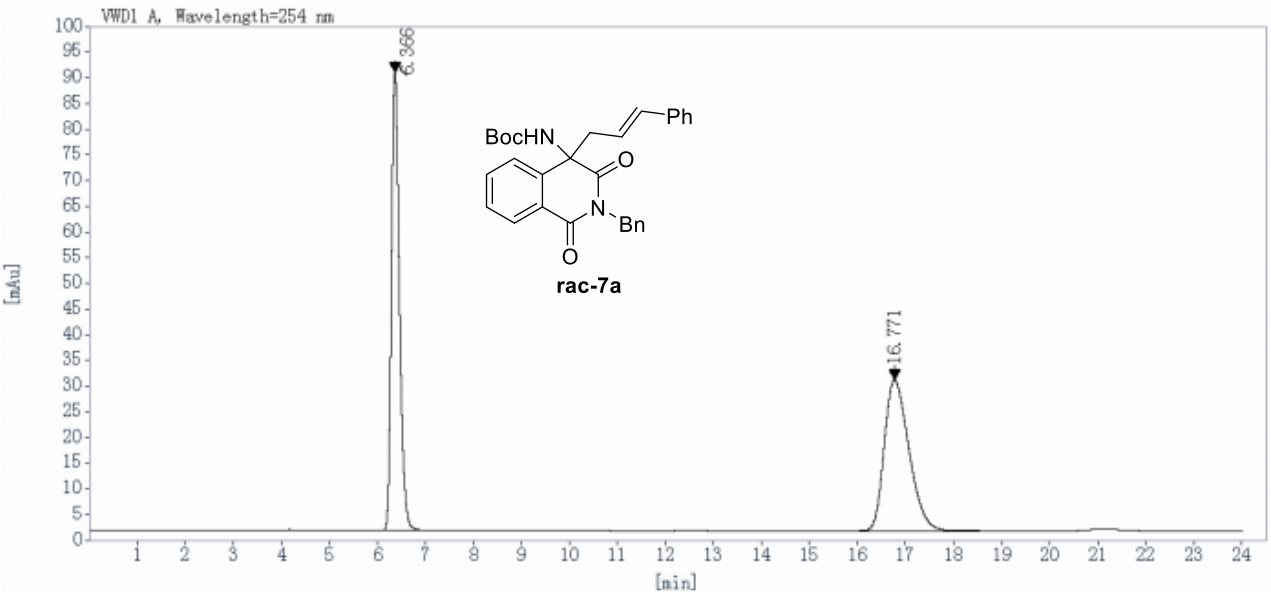




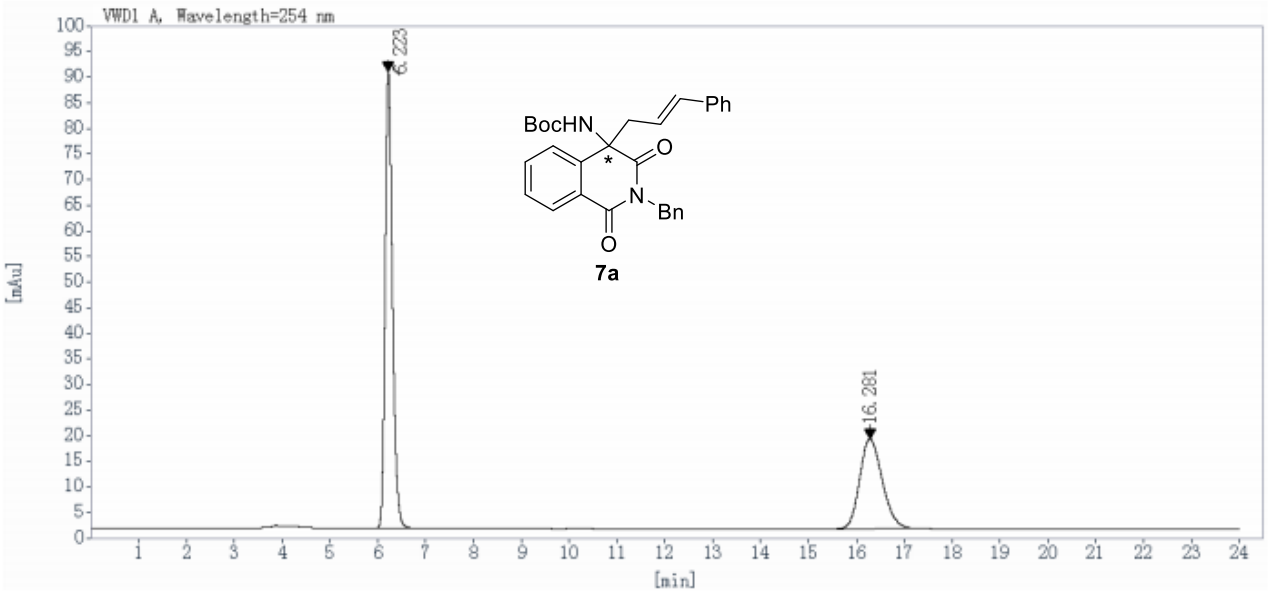
7a

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

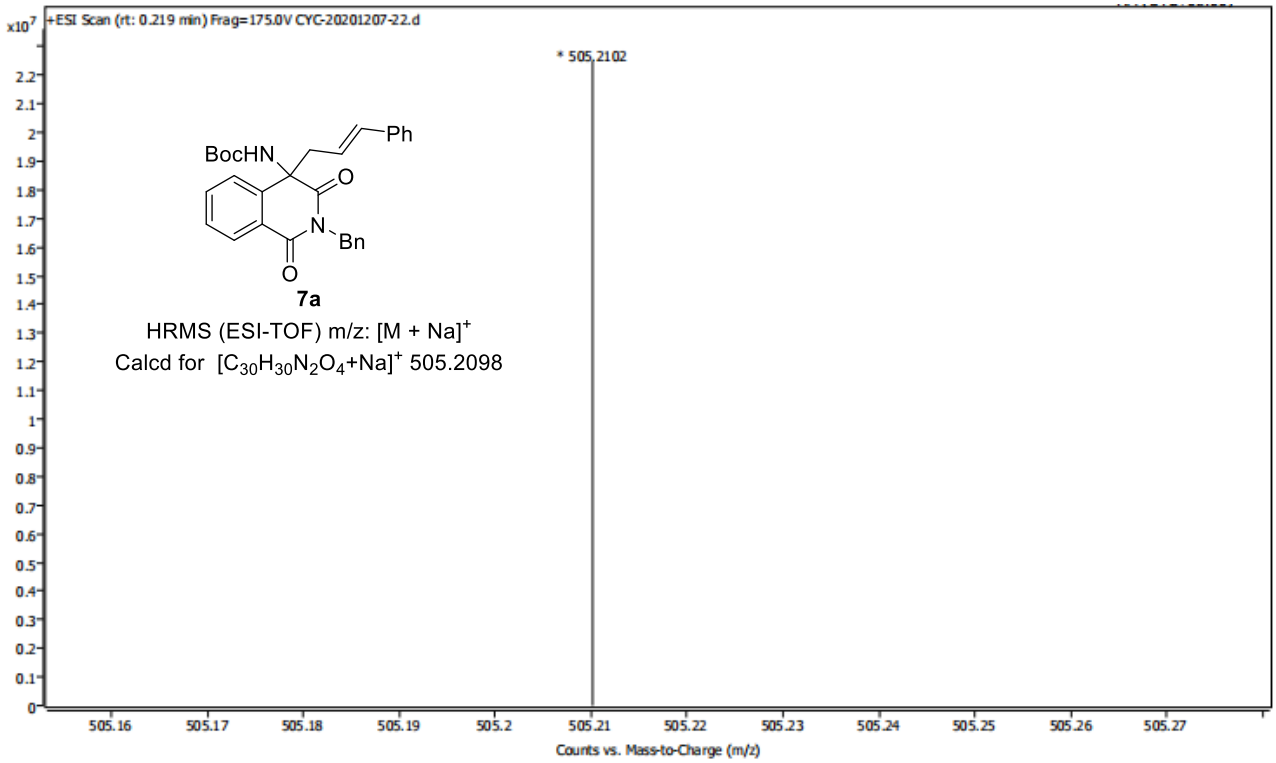




Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.366	BB	0.18	2541.4800	29407.3379	49.5486
16.771	BBA	0.56	834.9534	29943.1660	50.4514
			Totals:	59350.5039	100.0000



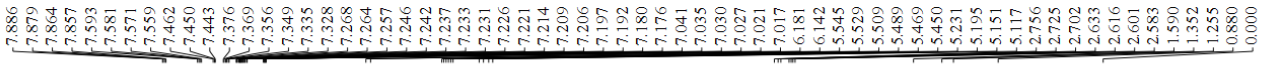
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
6.223	BV R	0.16	1554.8115	16612.5664	62.4217
16.281	BBA	0.51	305.9828	10000.8613	37.5783
			Totals:	26613.4277	100.0000

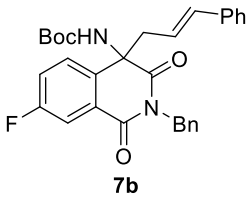


7a

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

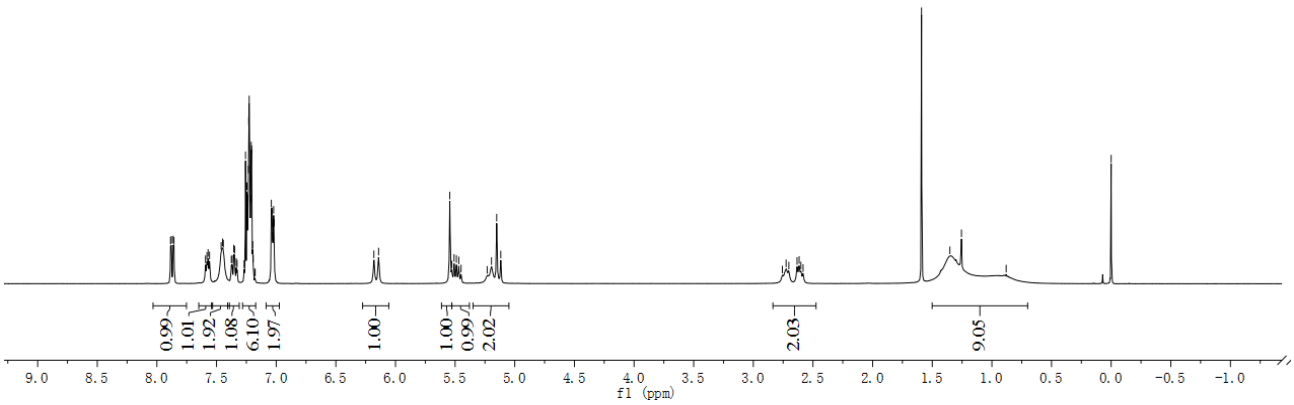
Calcd for $[C_{30}H_{30}N_2O_4+Na]^+$ 505.2098

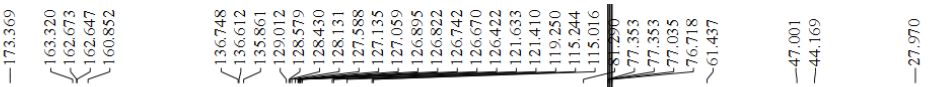


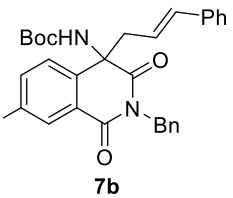


7b

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

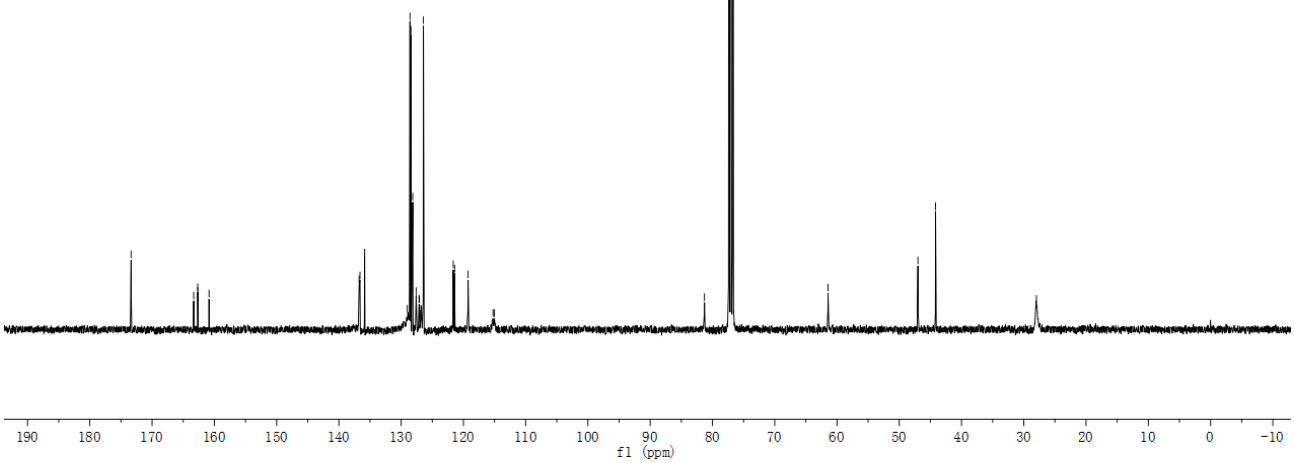


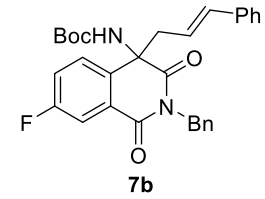




7b

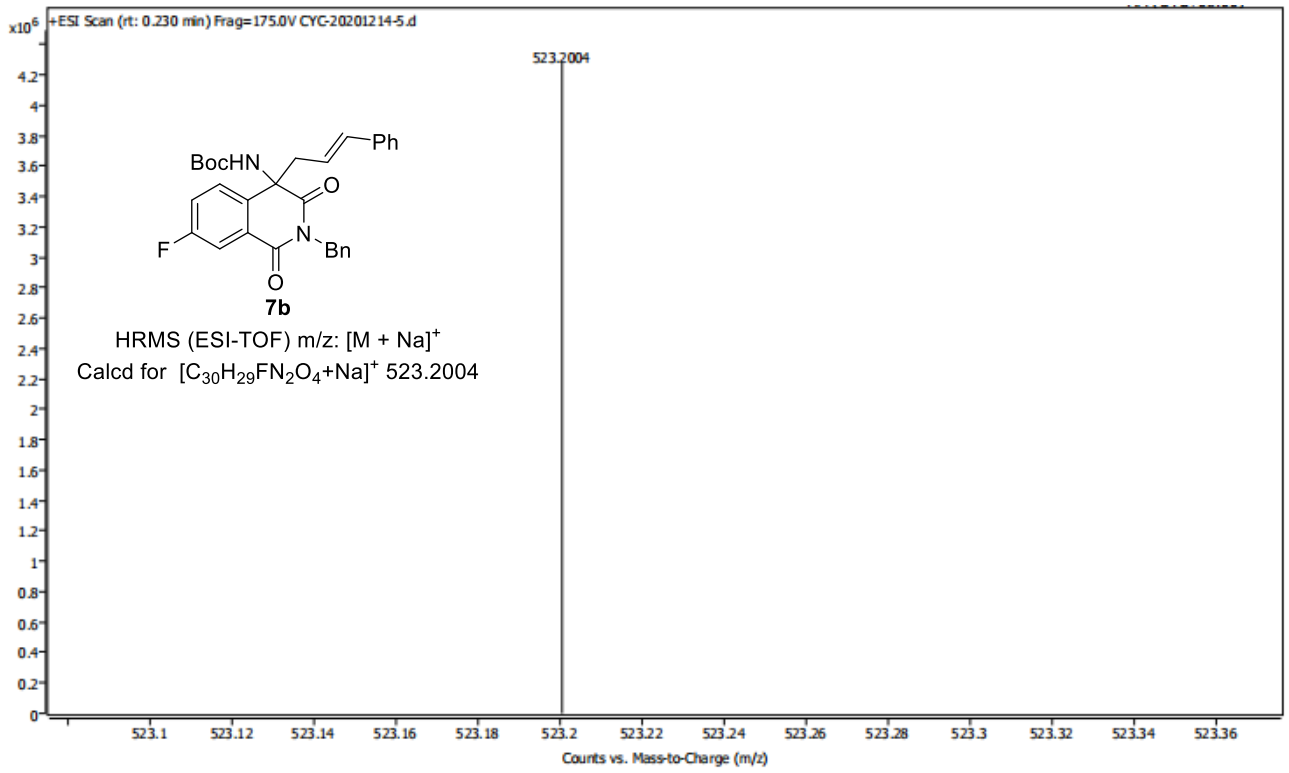
^{13}C NMR (100 MHz, $CDCl_3$)





7b

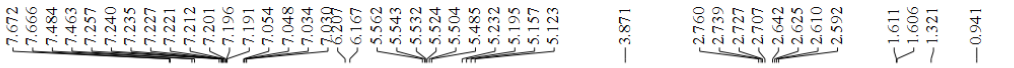
^{19}F NMR (376 MHz, $CDCl_3$)

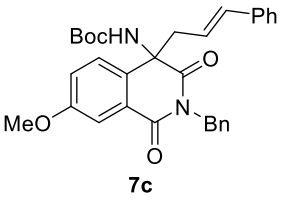


7b

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

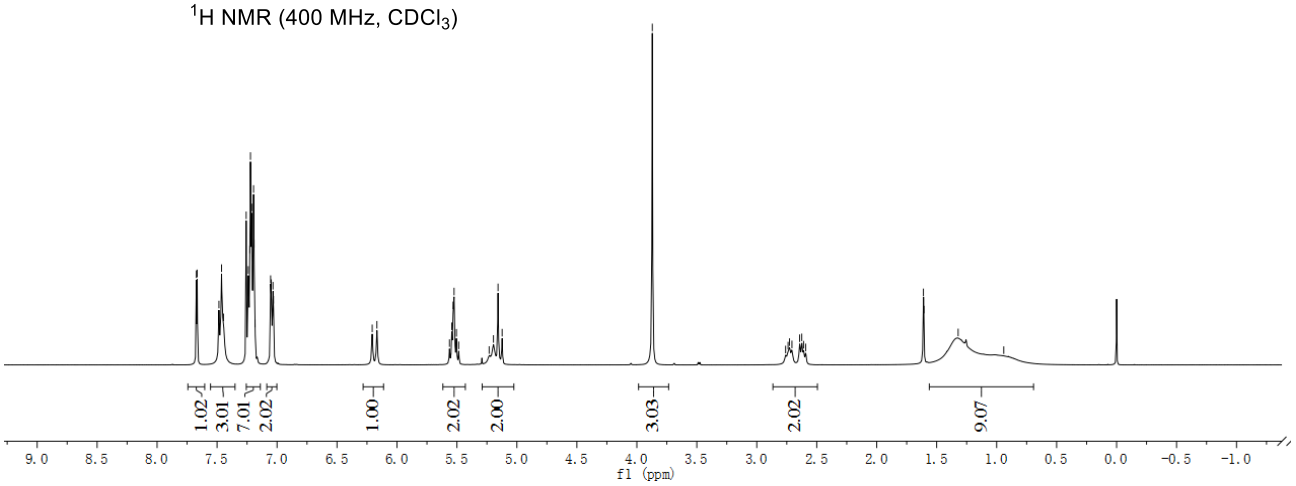
Calcd for $[C_{30}H_{29}FN_2O_4+Na]^+$ 523.2004

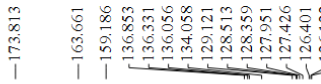


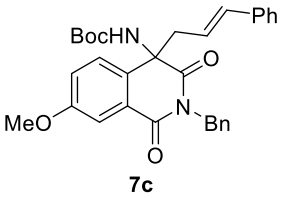


7c

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

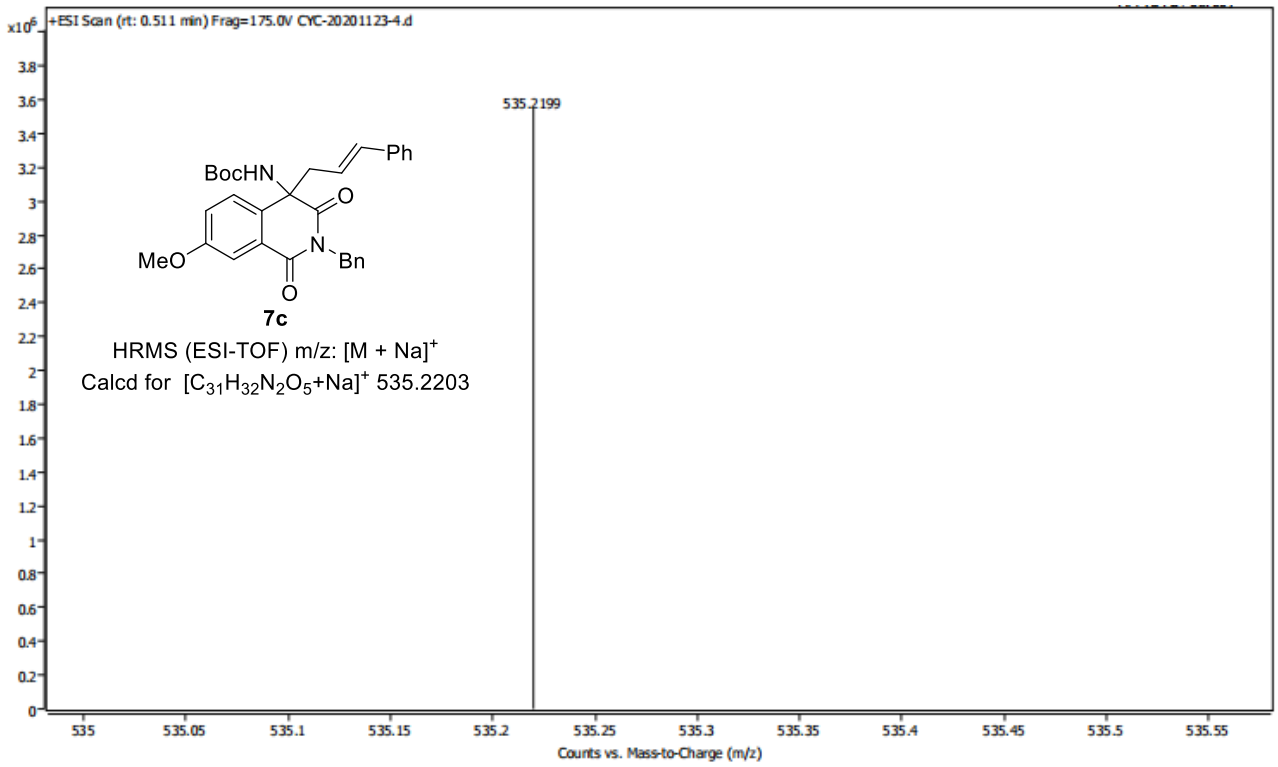






7c

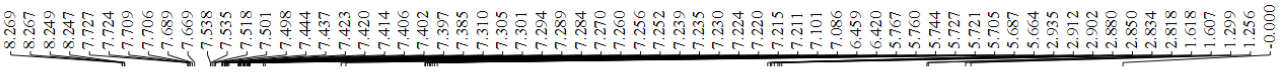
^{13}C NMR (100 MHz, $CDCl_3$)

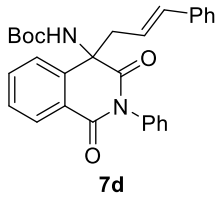


7c

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

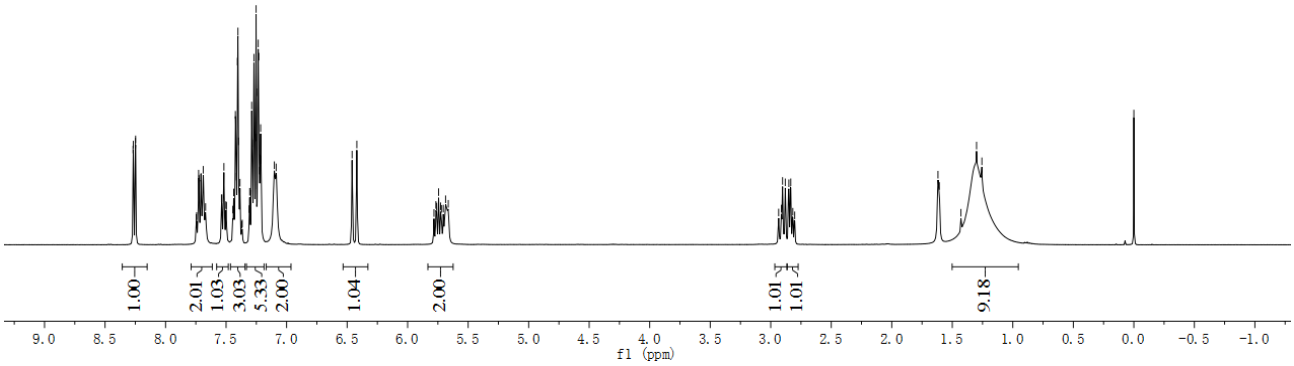
Calcd for $[C_{31}H_{32}N_2O_5+Na]^+$ 535.2203

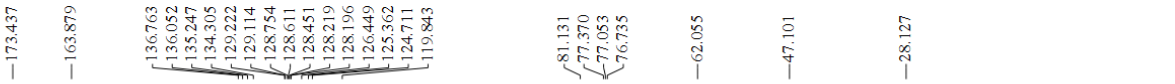


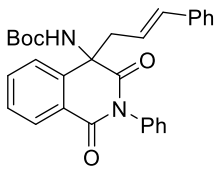


7d

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

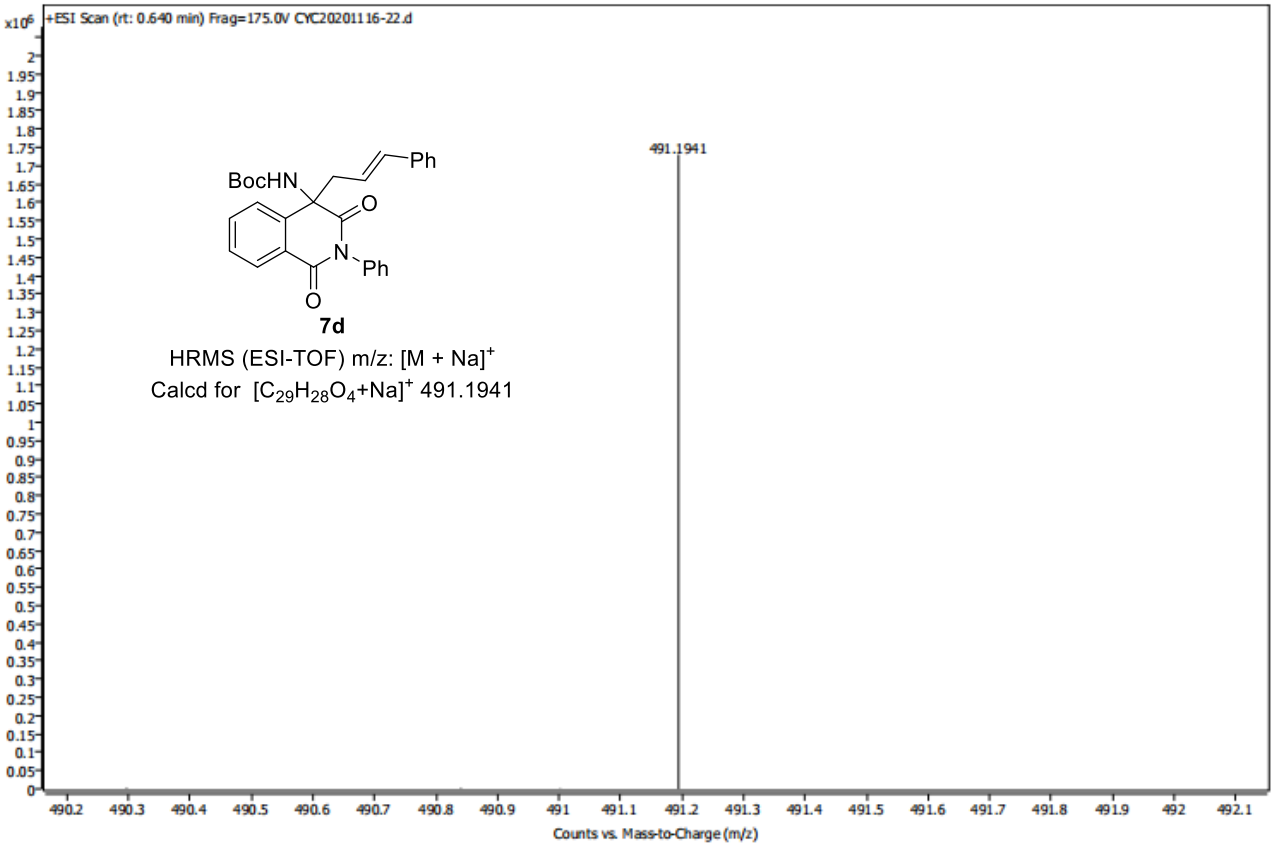






7d

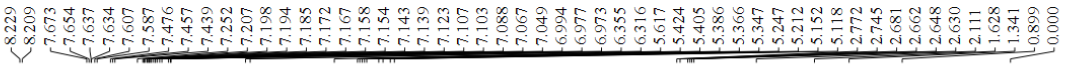
^{13}C NMR (100 MHz, $CDCl_3$)

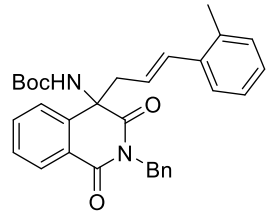


7d

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

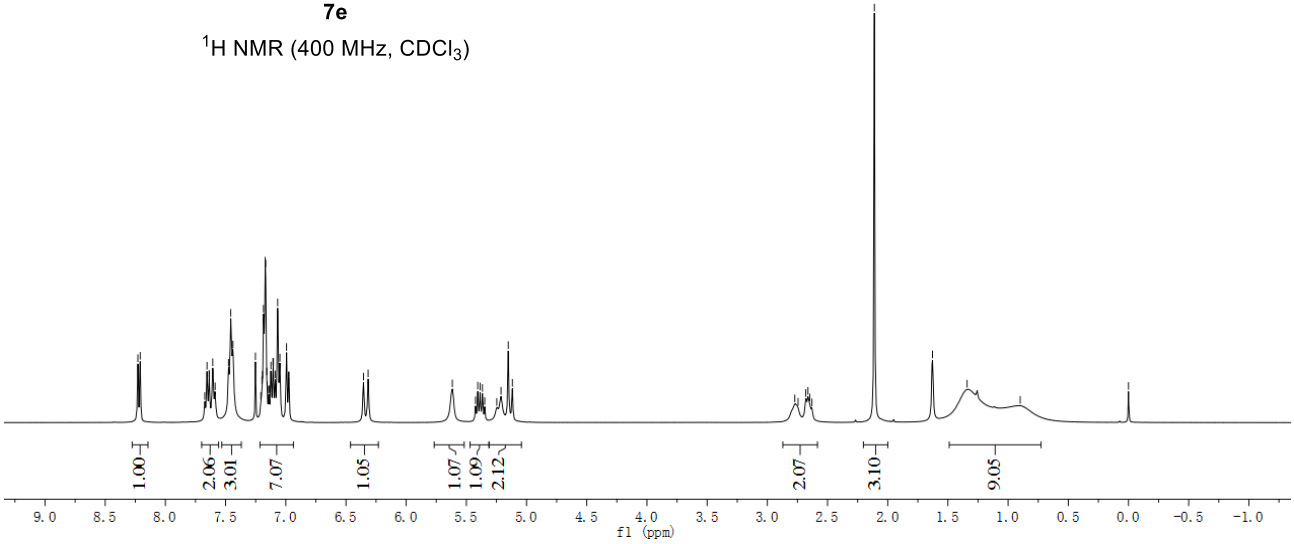
Calcd for $[C_{29}H_{28}O_4+Na]^+$ 491.1941

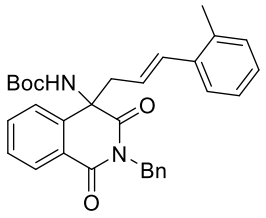




7e

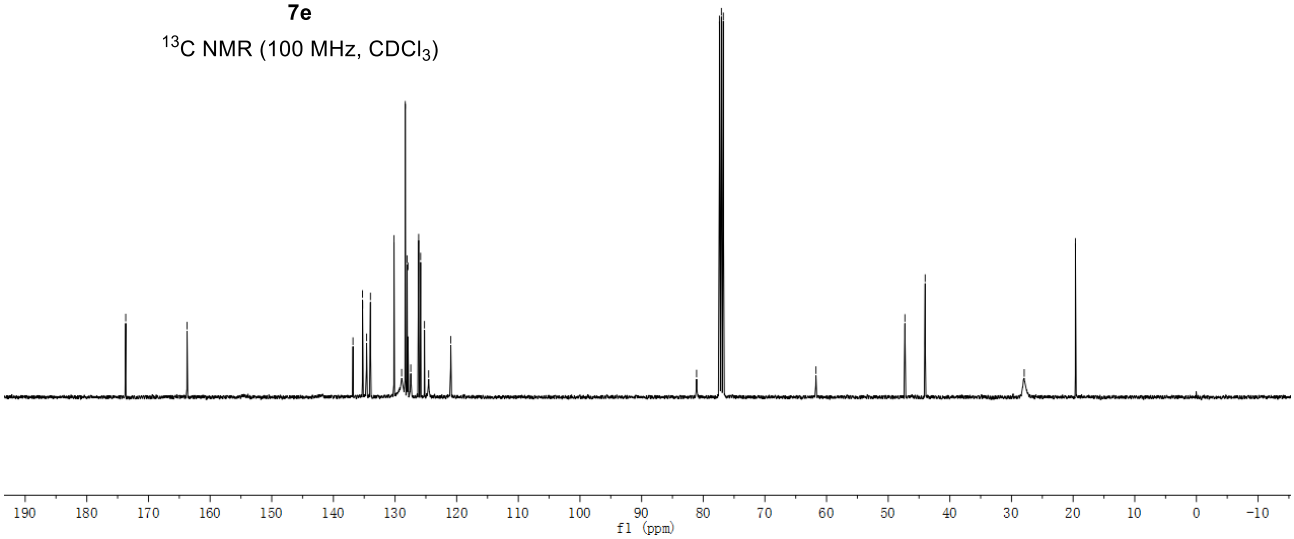
^{1}H NMR (400 MHz, $CDCl_3$)

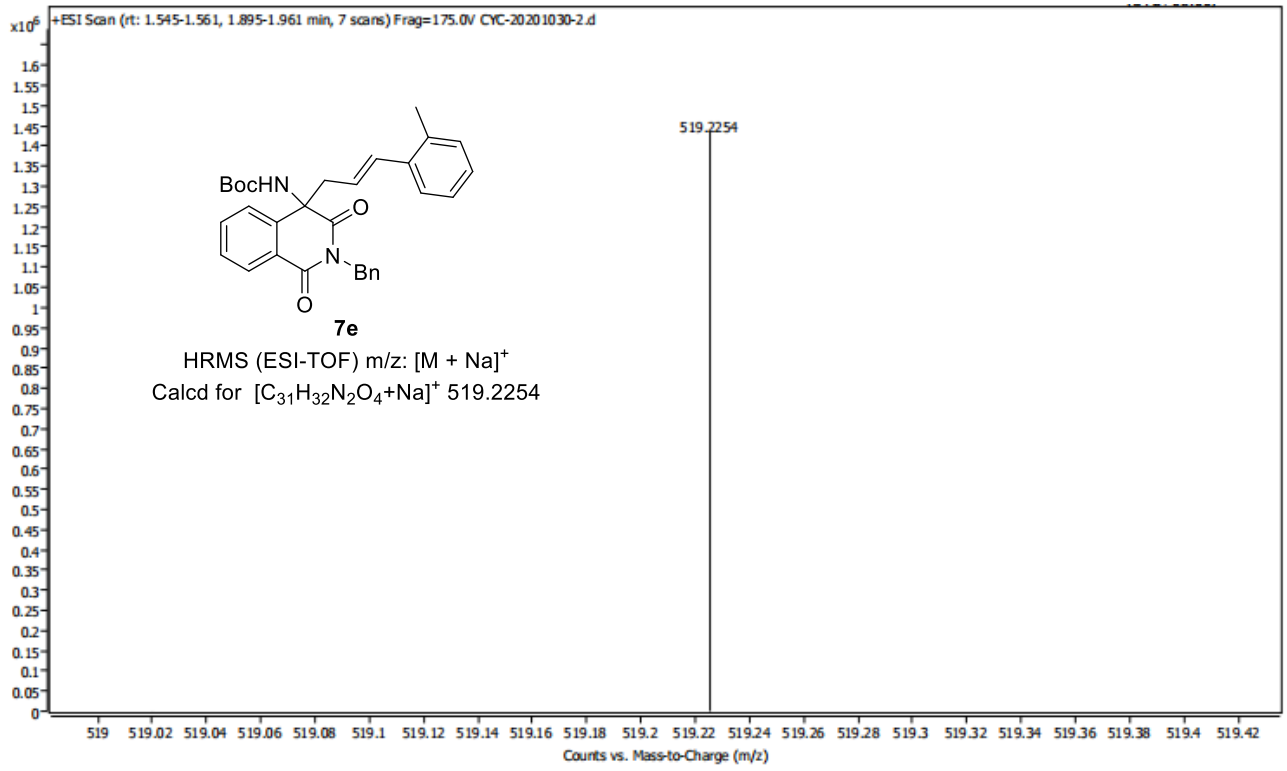




7e

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

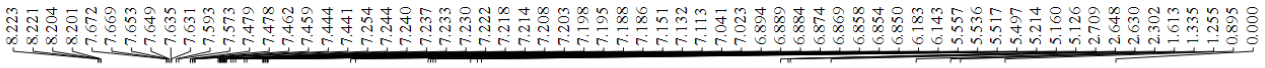


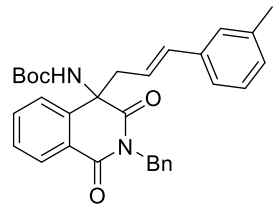


7e

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

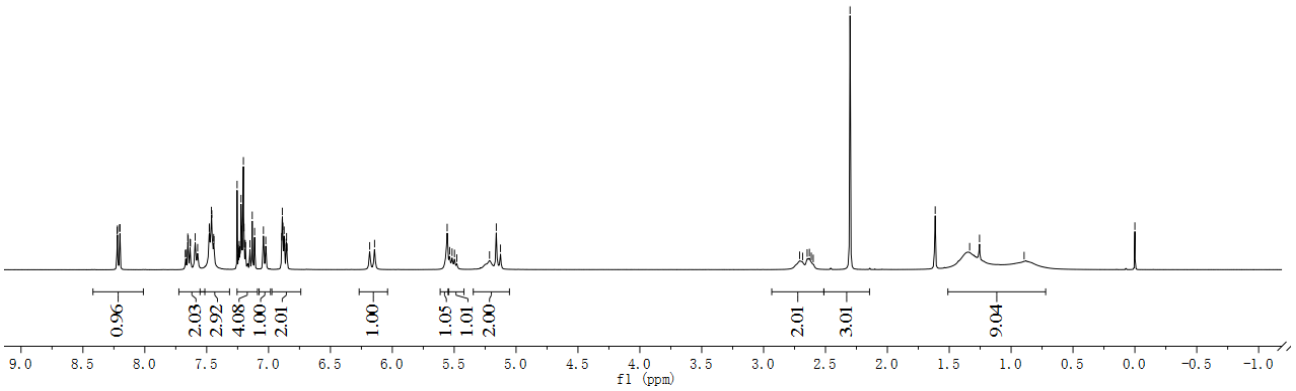
Calcd for $[C_{31}H_{32}N_2O_4+Na]^+$ 519.2254

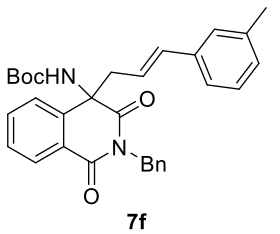




7f

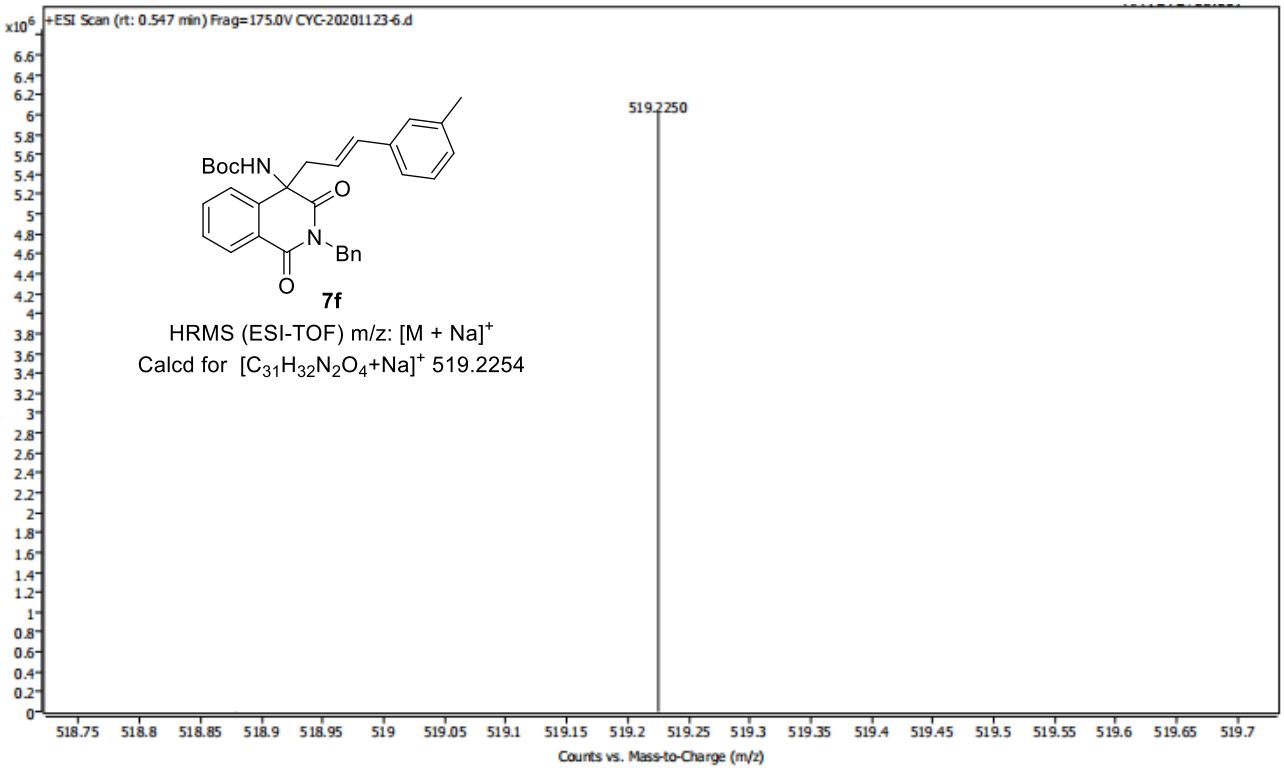
^{1}H NMR (400 MHz, $CDCl_3$)





7f

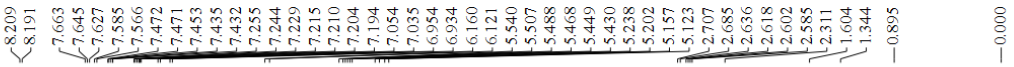
^{13}C NMR (100 MHz, $CDCl_3$)

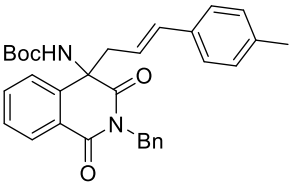


7f

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

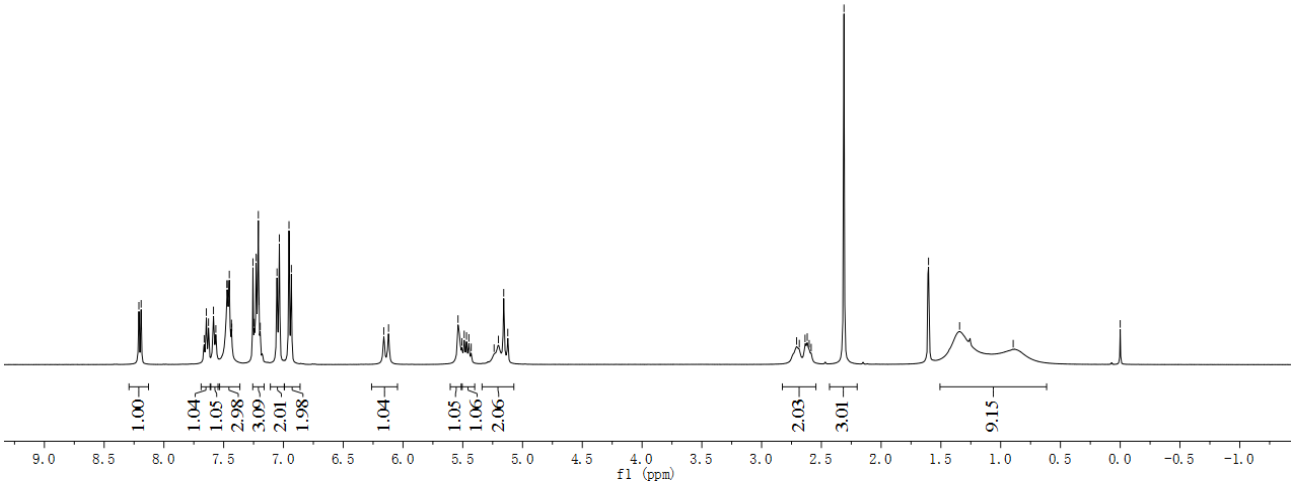
Calcd for $[C_{31}H_{32}N_2O_4+Na]^+$ 519.2254

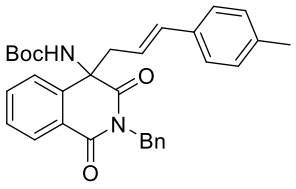




7g

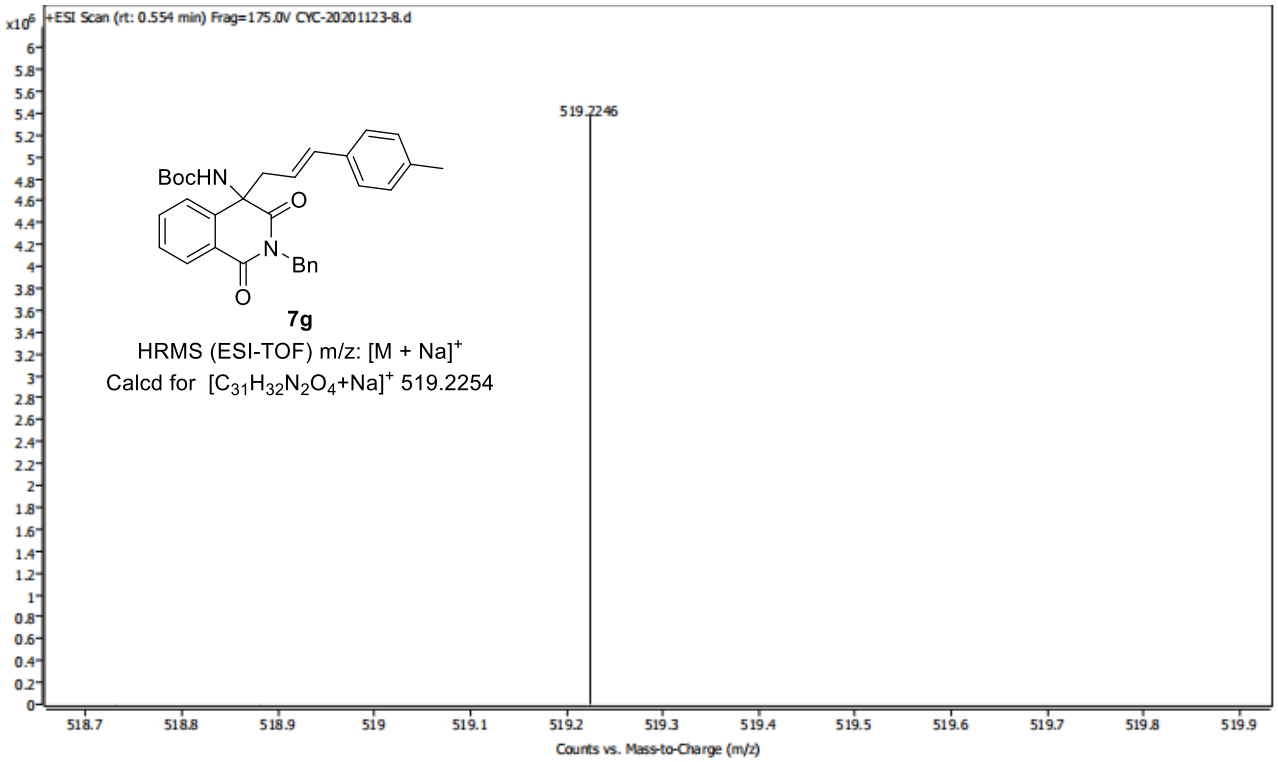
^{1}H NMR (400 MHz, $CDCl_3$)





7g

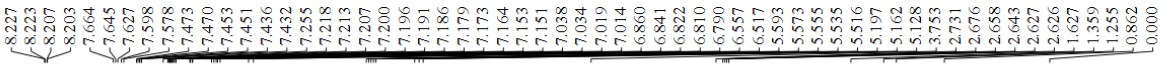
^{13}C NMR (100 MHz, $CDCl_3$)

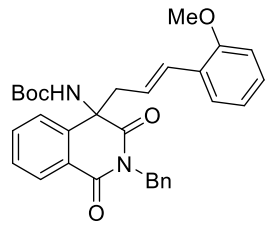


7g

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

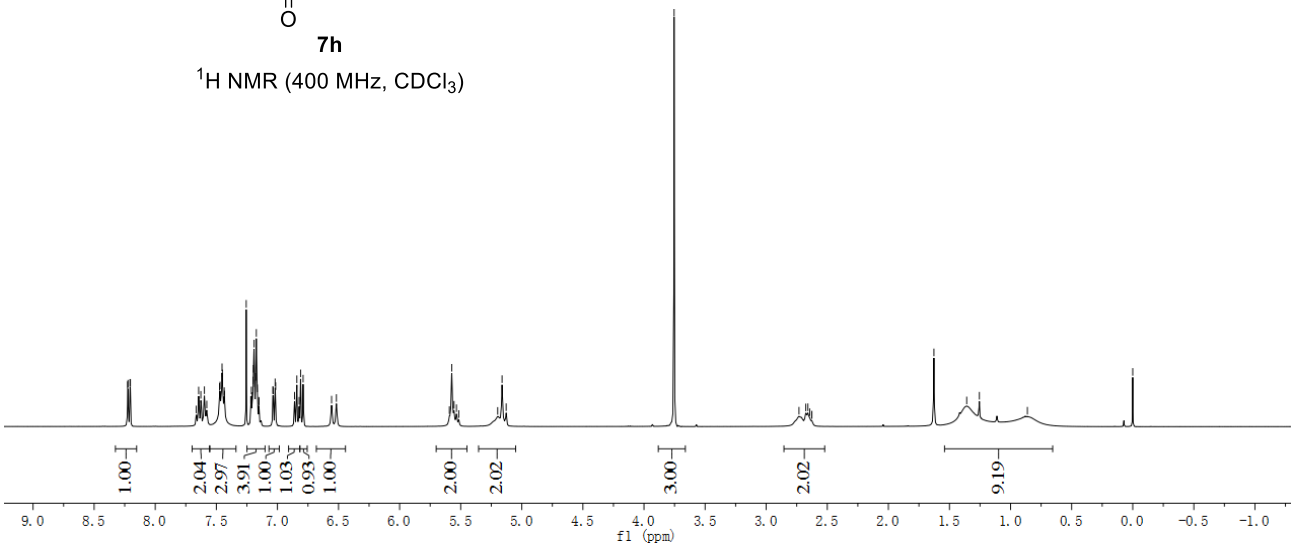
Calcd for $[C_{31}H_{32}N_2O_4+Na]^+$ 519.2254

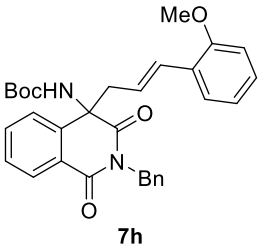




7h

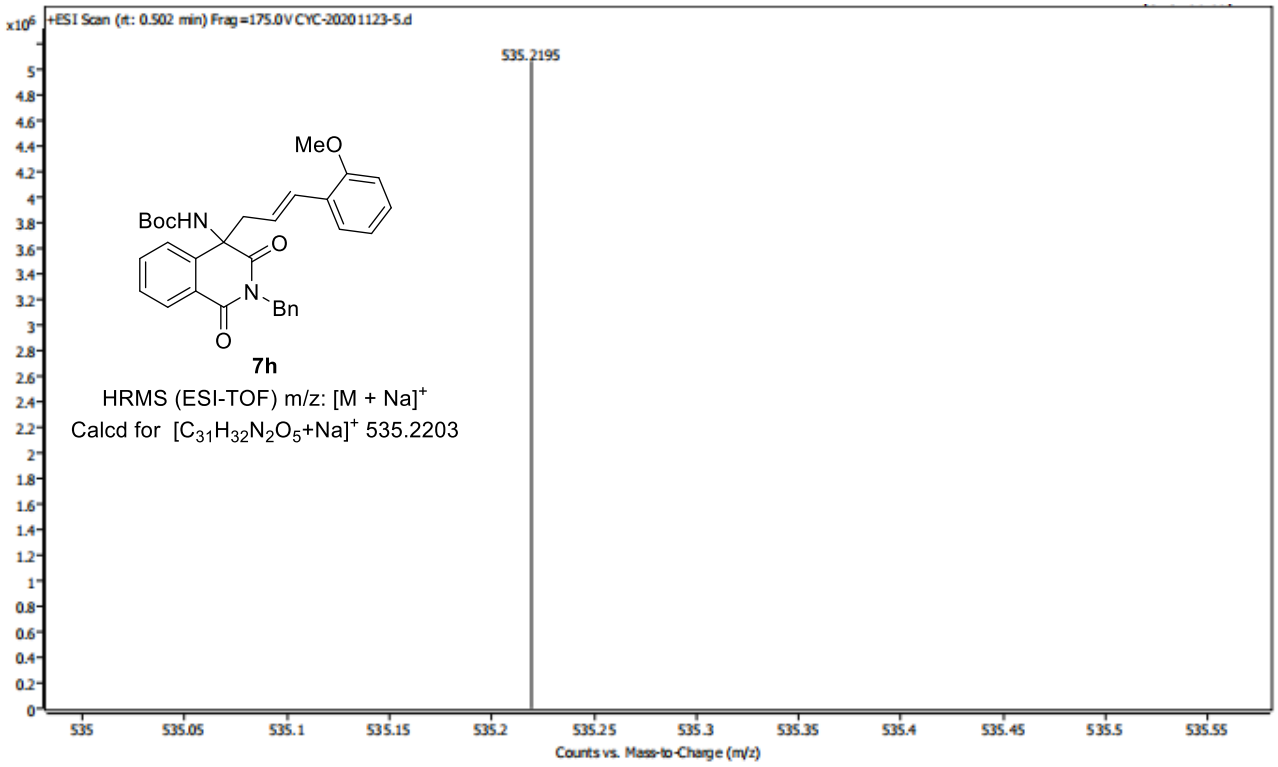
^{1}H NMR (400 MHz, $CDCl_3$)





7h

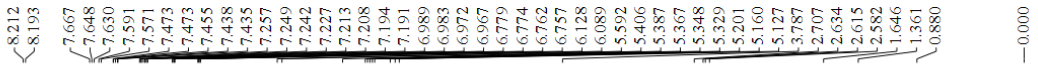
^{13}C NMR (100 MHz, $CDCl_3$)

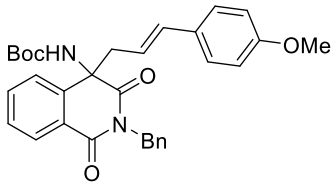


7h

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

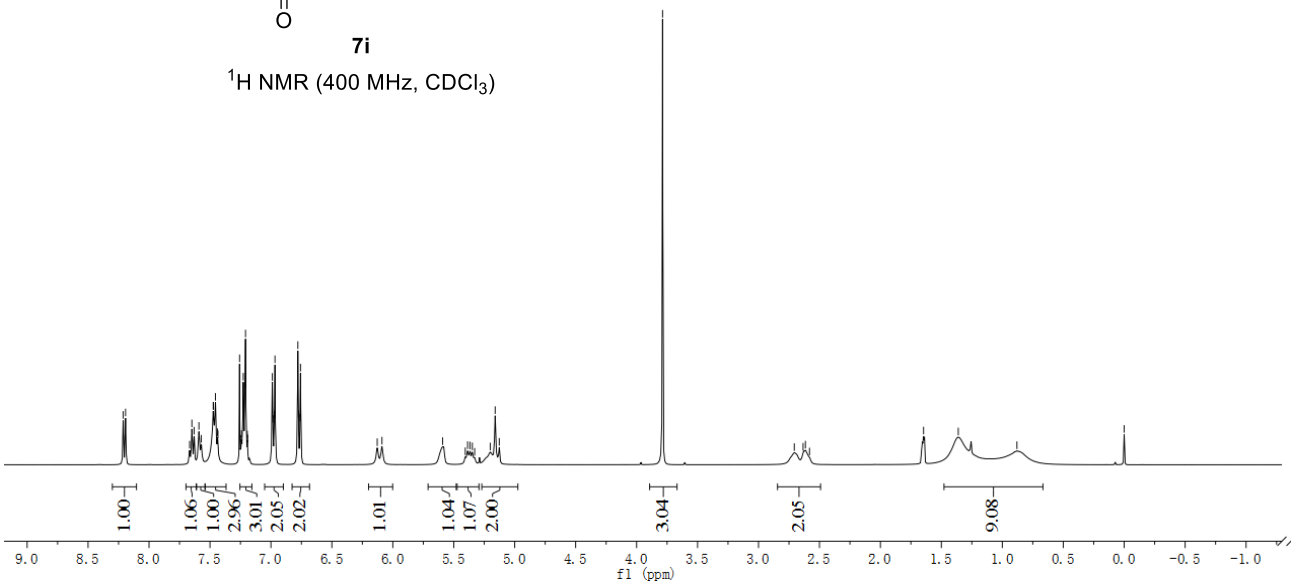
Calcd for $[C_{31}H_{32}N_2O_5+Na]^+$ 535.2203

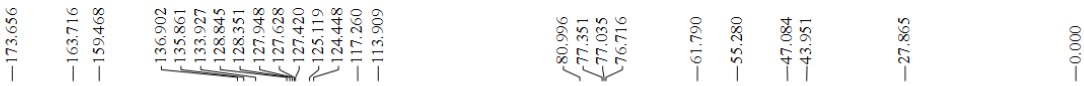


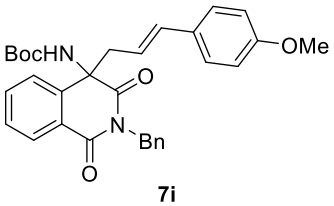


7i

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

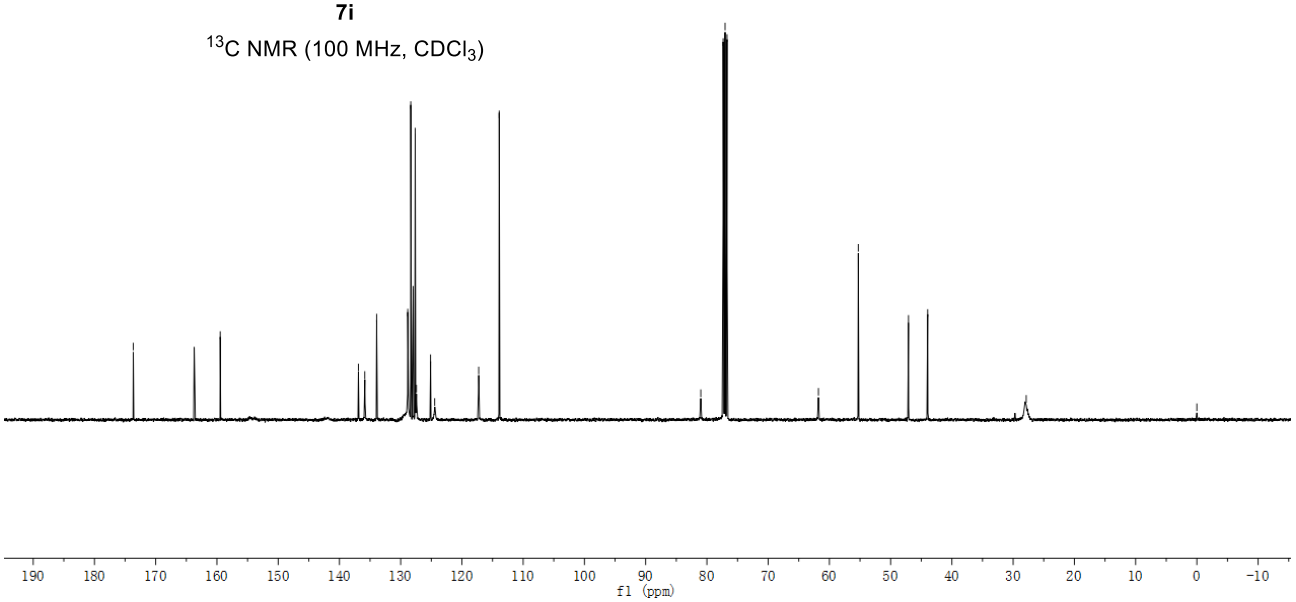


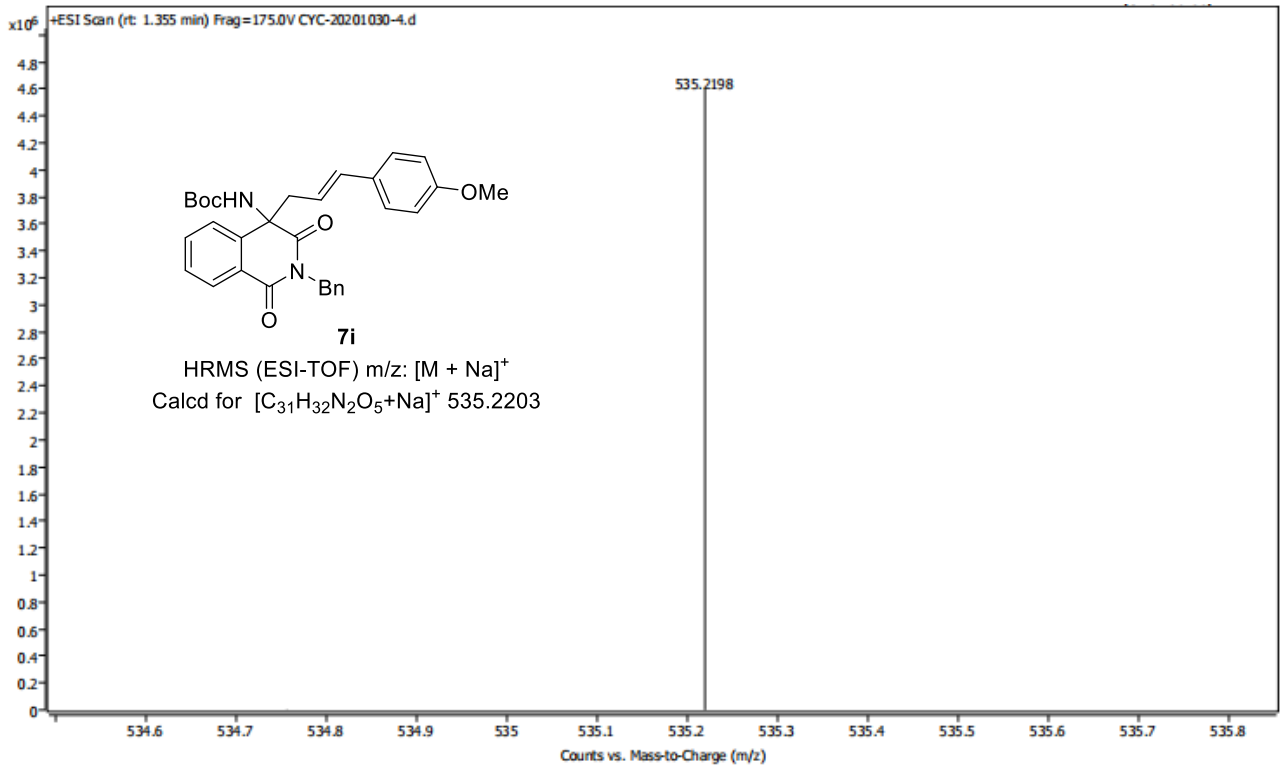




7i

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

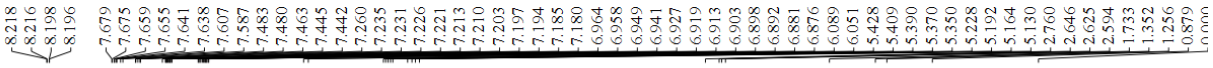


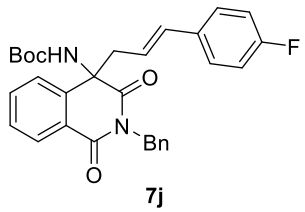


7i

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

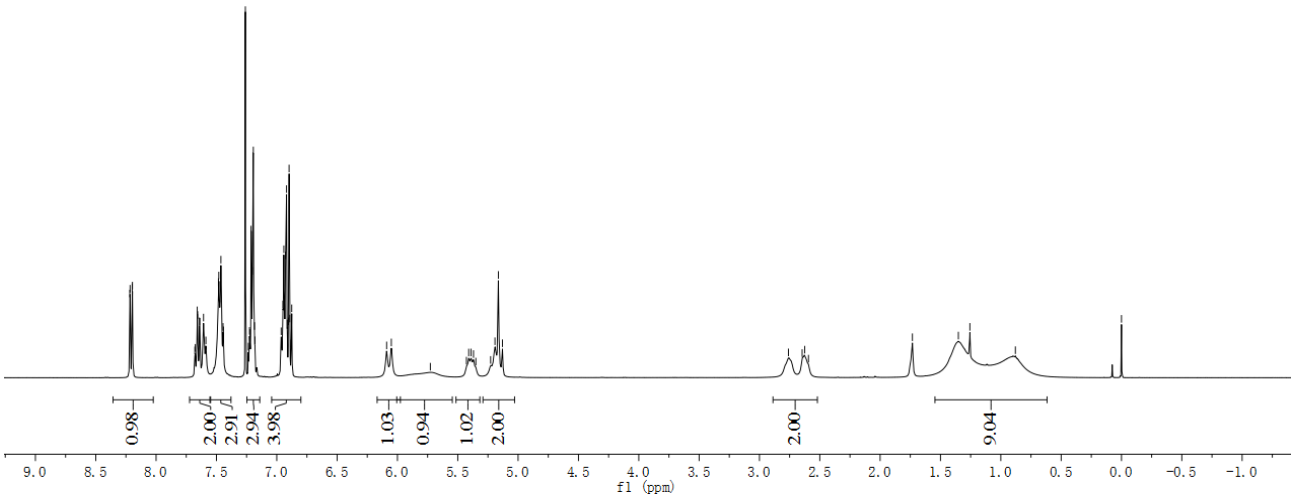
Calcd for $[C_{31}H_{32}N_2O_5+Na]^+$ 535.2203

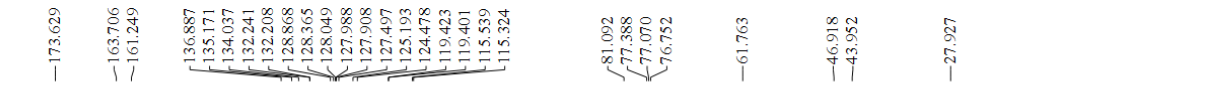


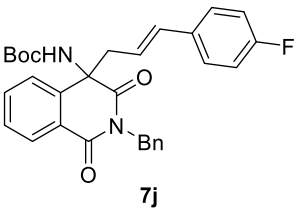


7j

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

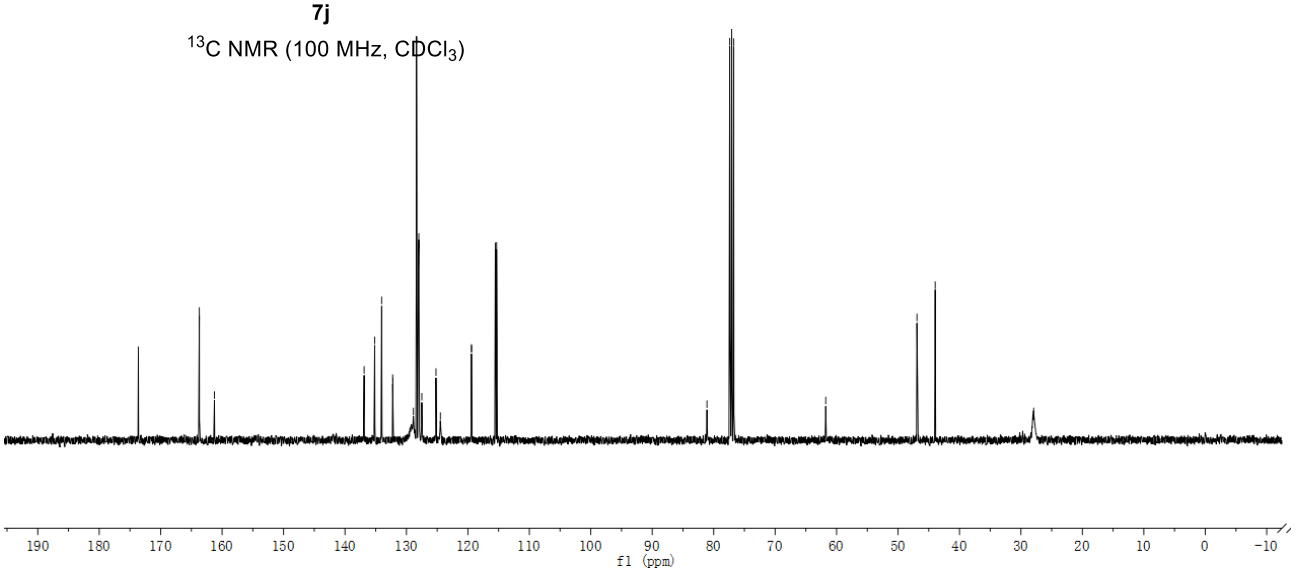


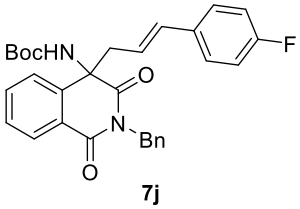




7j

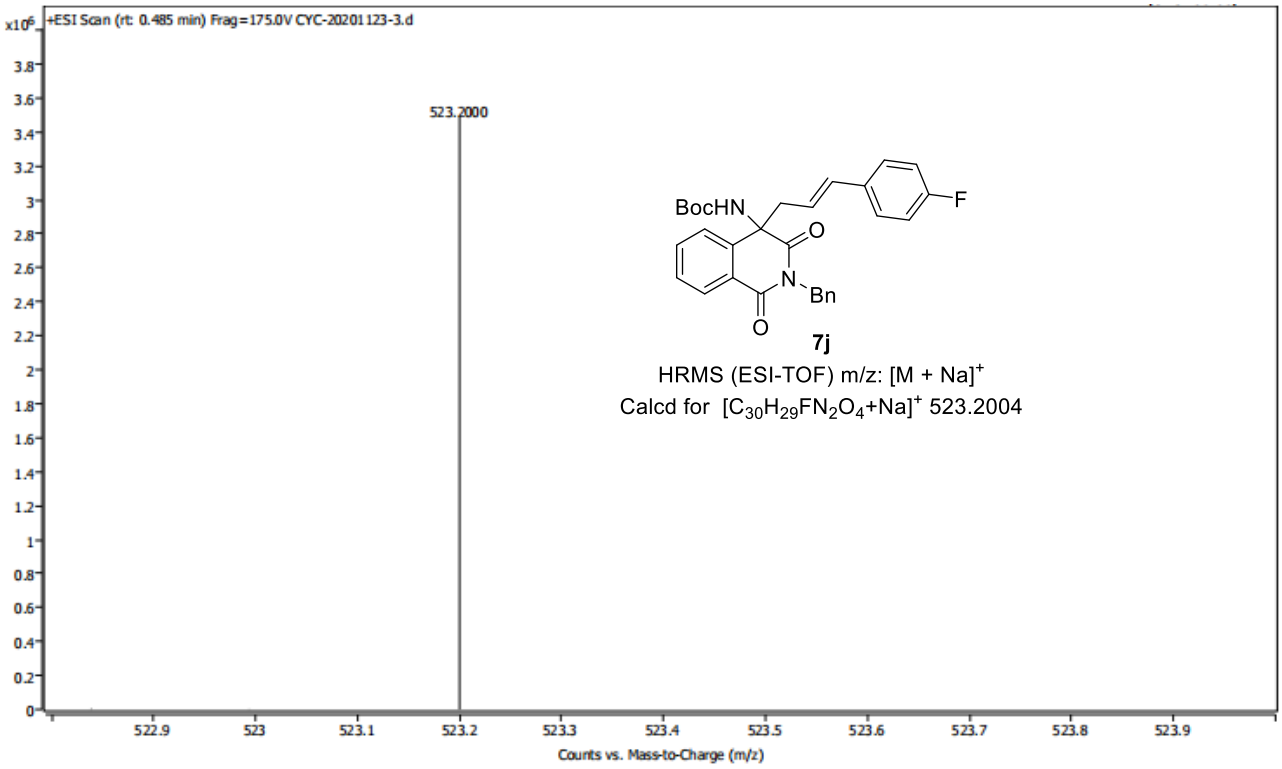
^{13}C NMR (100 MHz, $CDCl_3$)





7j

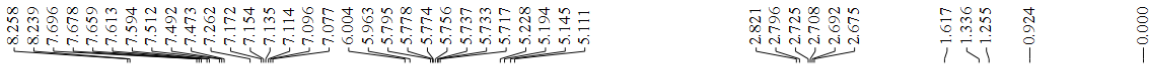
^{19}F NMR (376 MHz, $CDCl_3$)

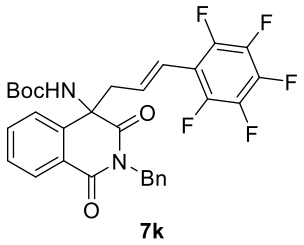


7j

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

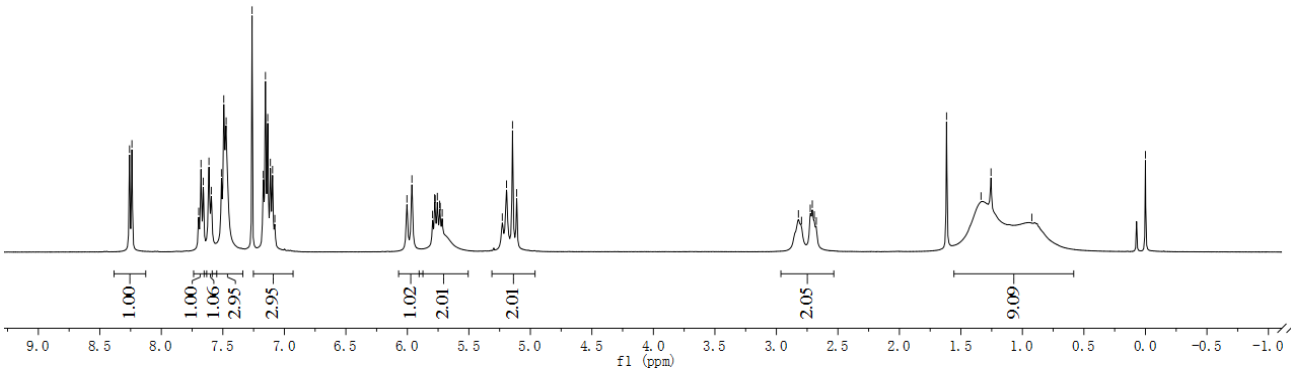
Calcd for $[C_{30}H_{29}FN_2O_4+Na]^+$ 523.2004

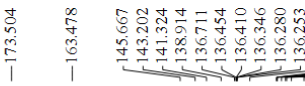


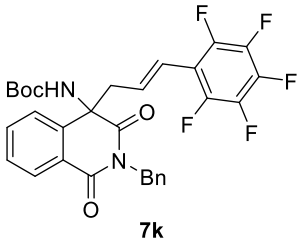


7k

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

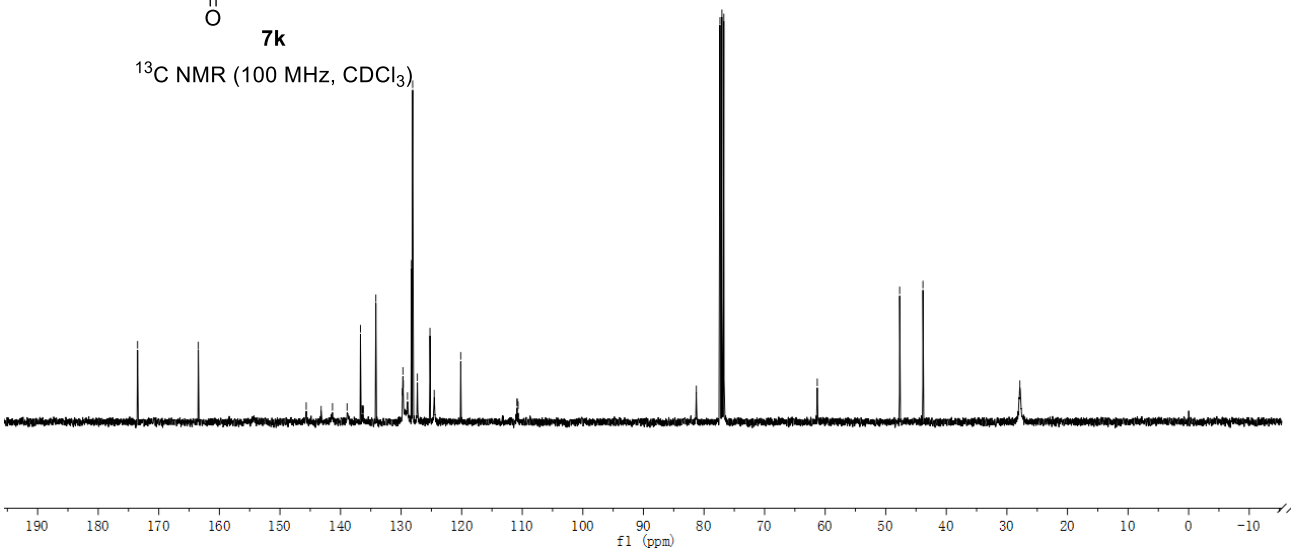


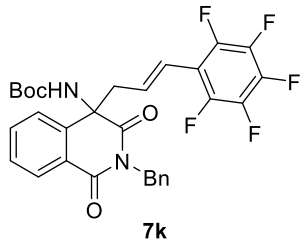




7k

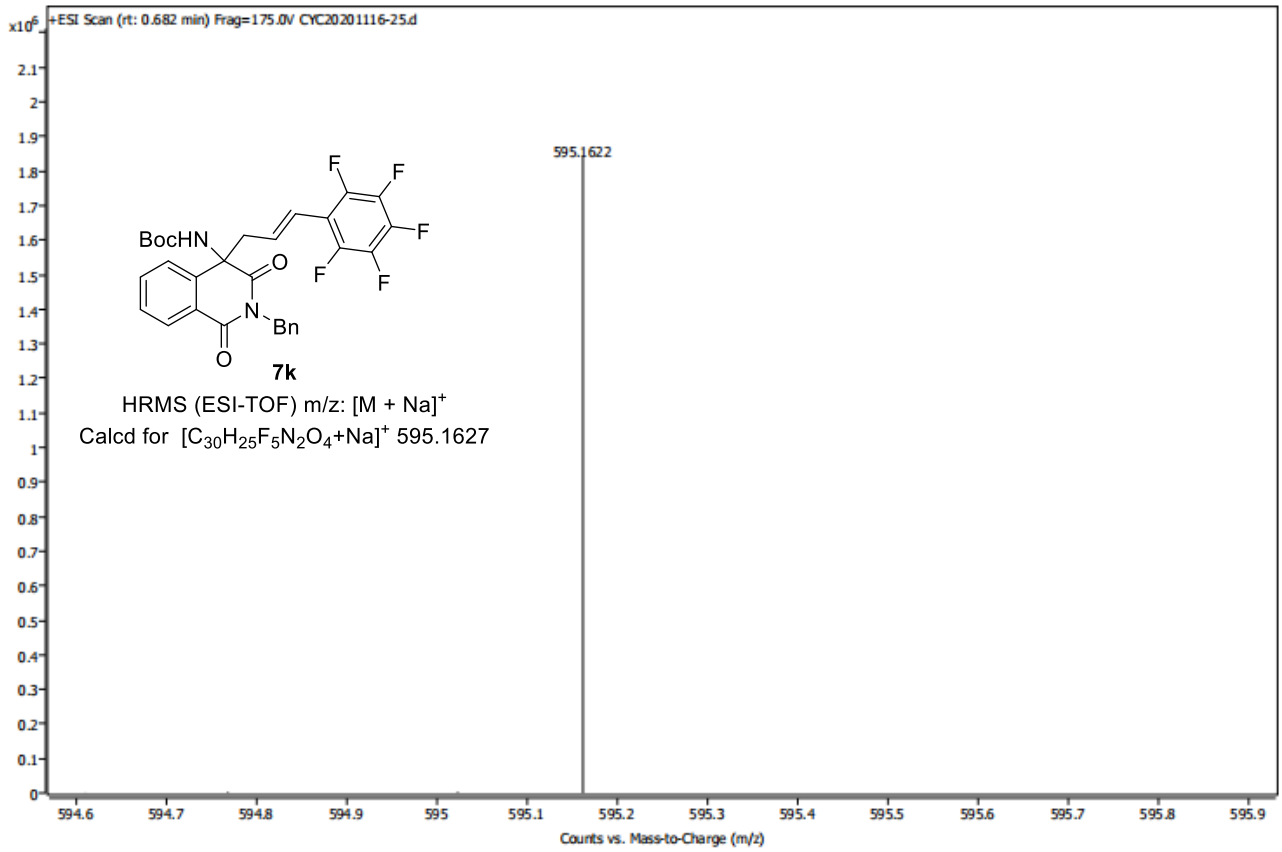
^{13}C NMR (100 MHz, $CDCl_3$)





7k

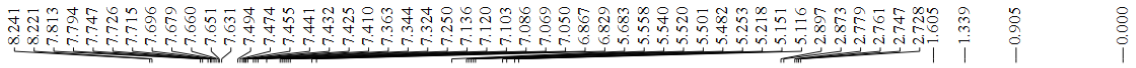
^{19}F NMR (376 MHz, $CDCl_3$)

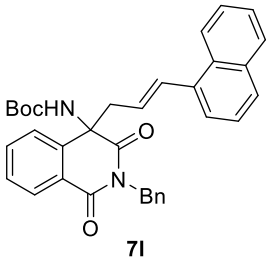


7k

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

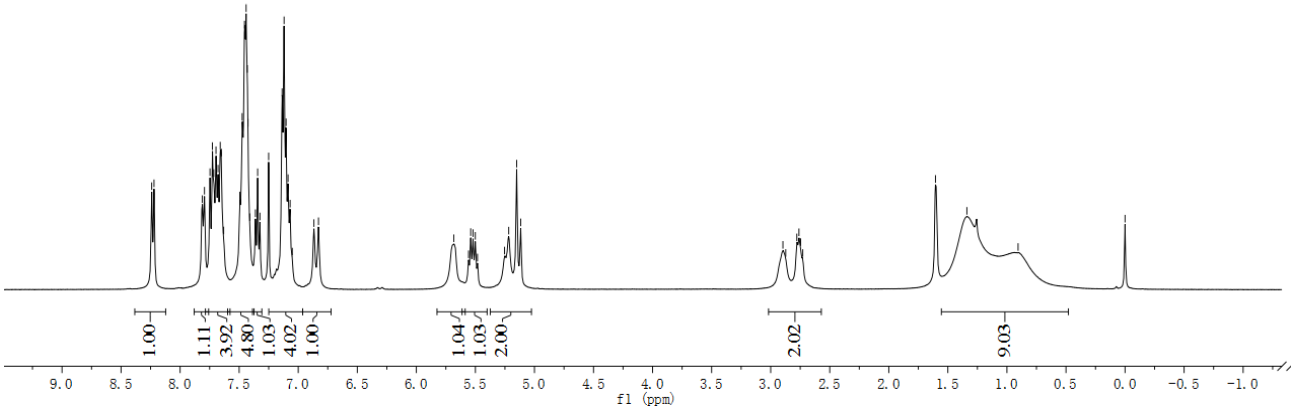
Calcd for $[C_{30}H_{25}F_5N_2O_4+Na]^+$ 595.1627

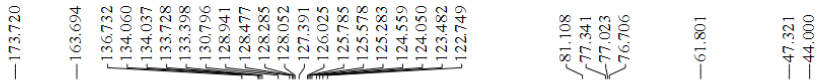


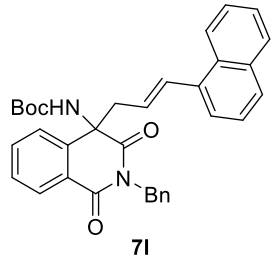


7l

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

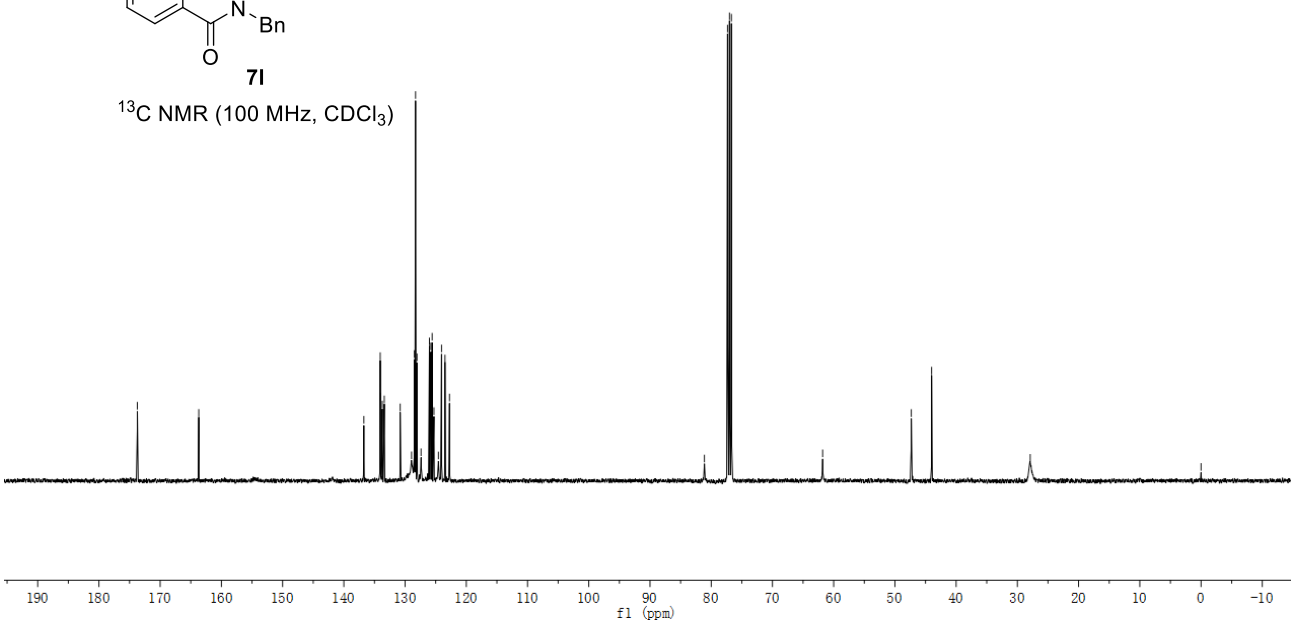


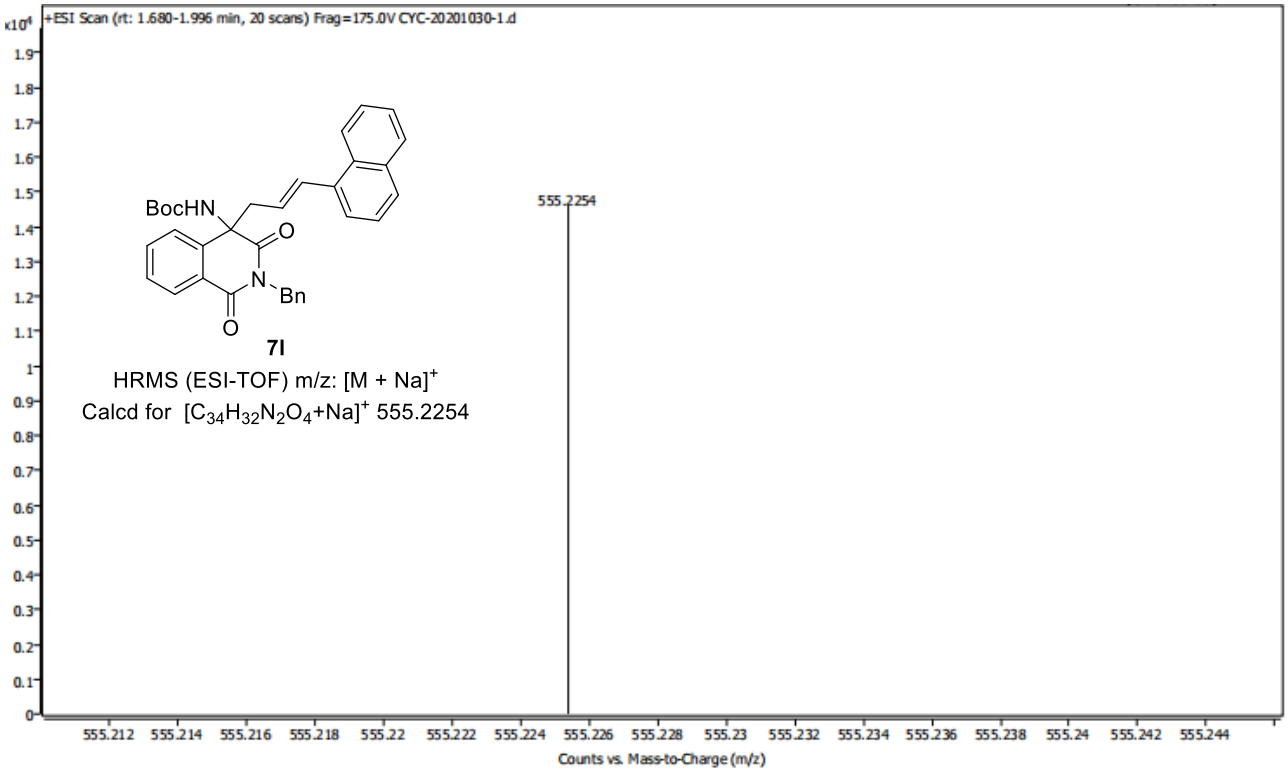




7l

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

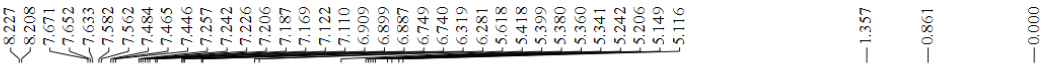


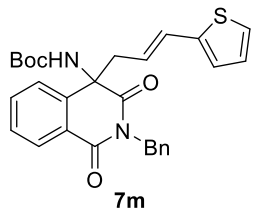


7l

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

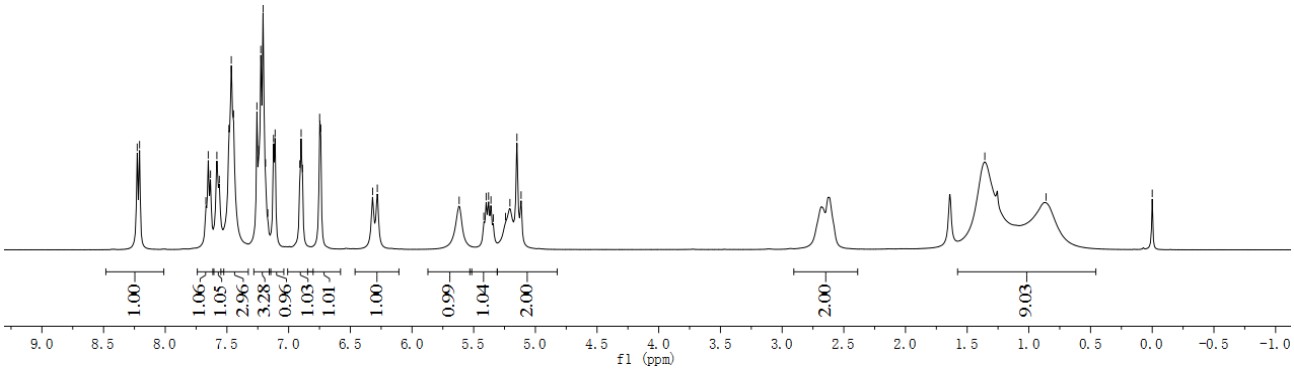
Calcd for $[C_{34}H_{32}N_2O_4+Na]^+$ 555.2254

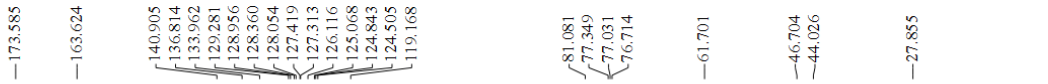


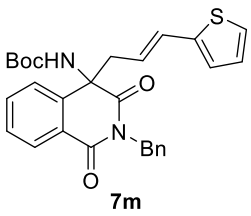


7m

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

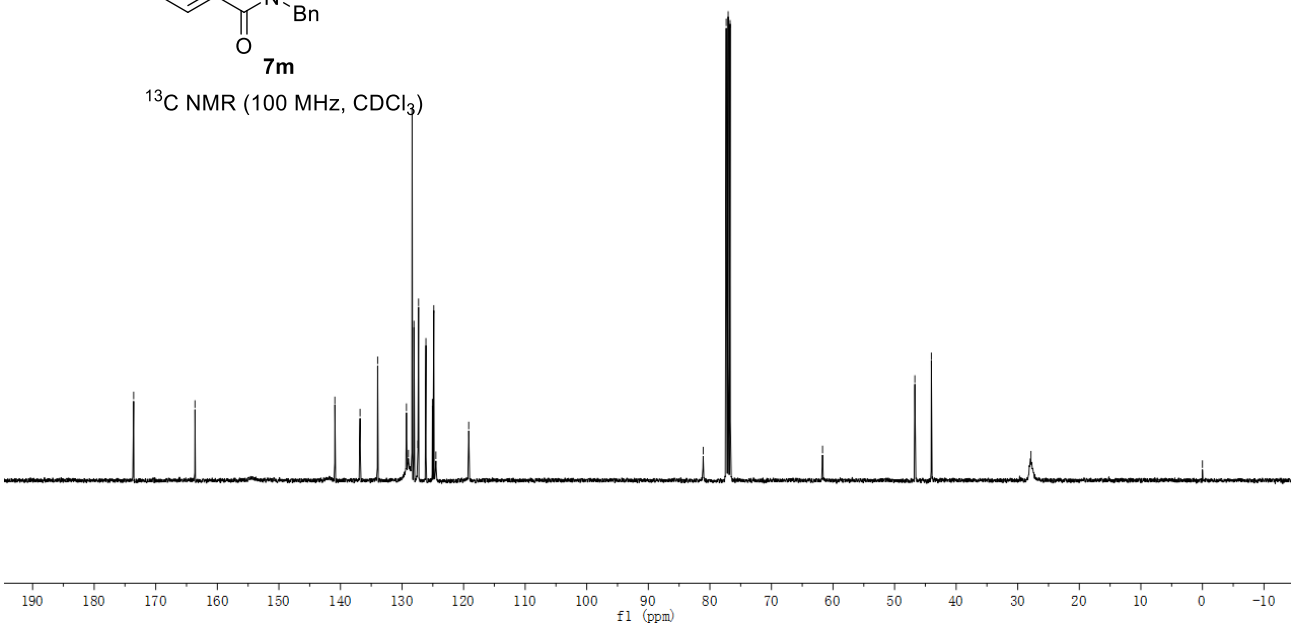


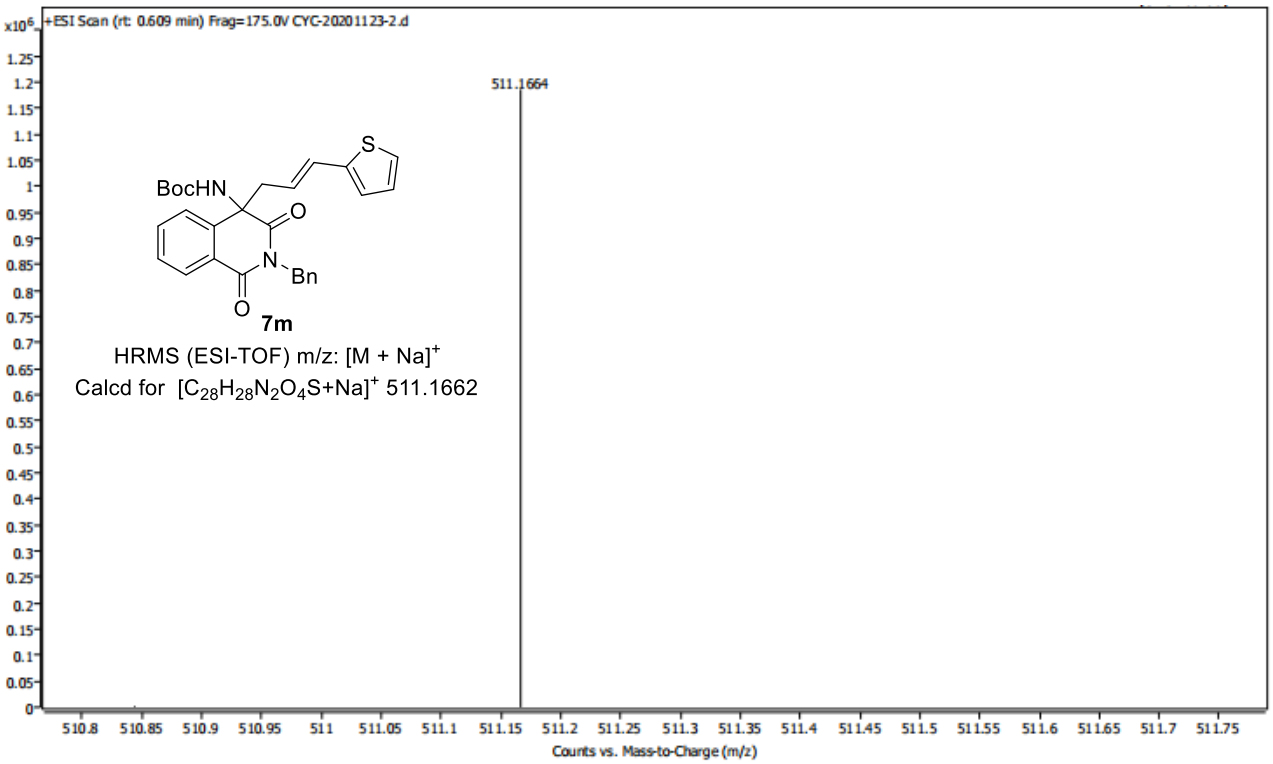




7m

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

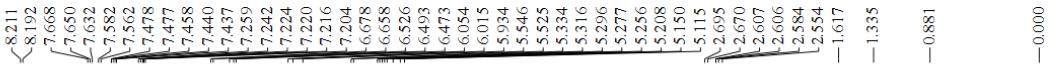


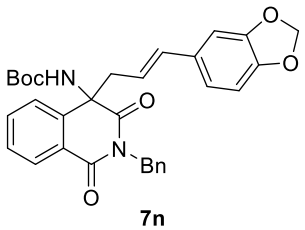


7m

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

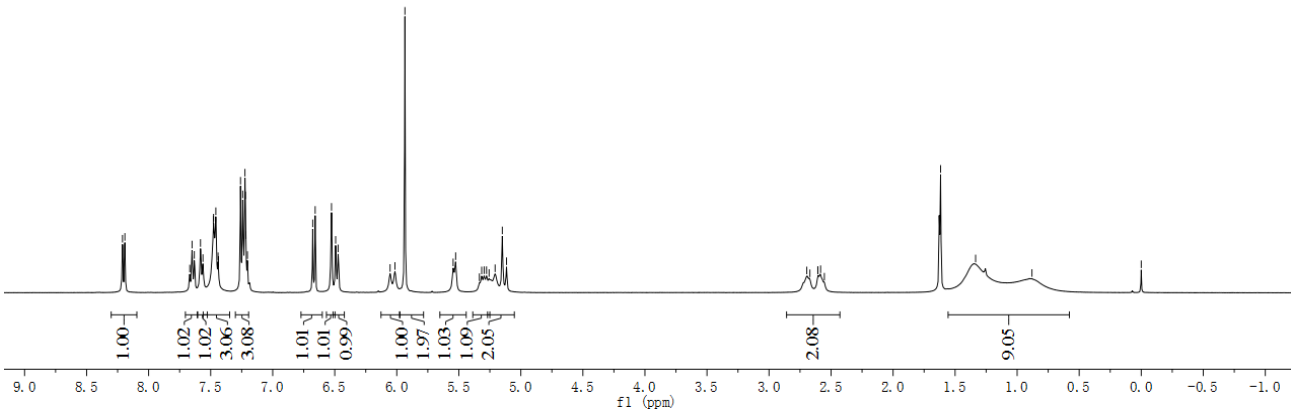
Calcd for $[C_{28}H_{28}N_2O_4S+Na]^+$ 511.1662

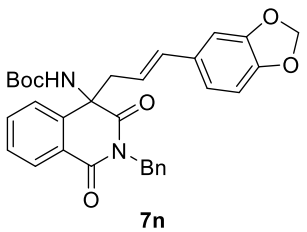




7n

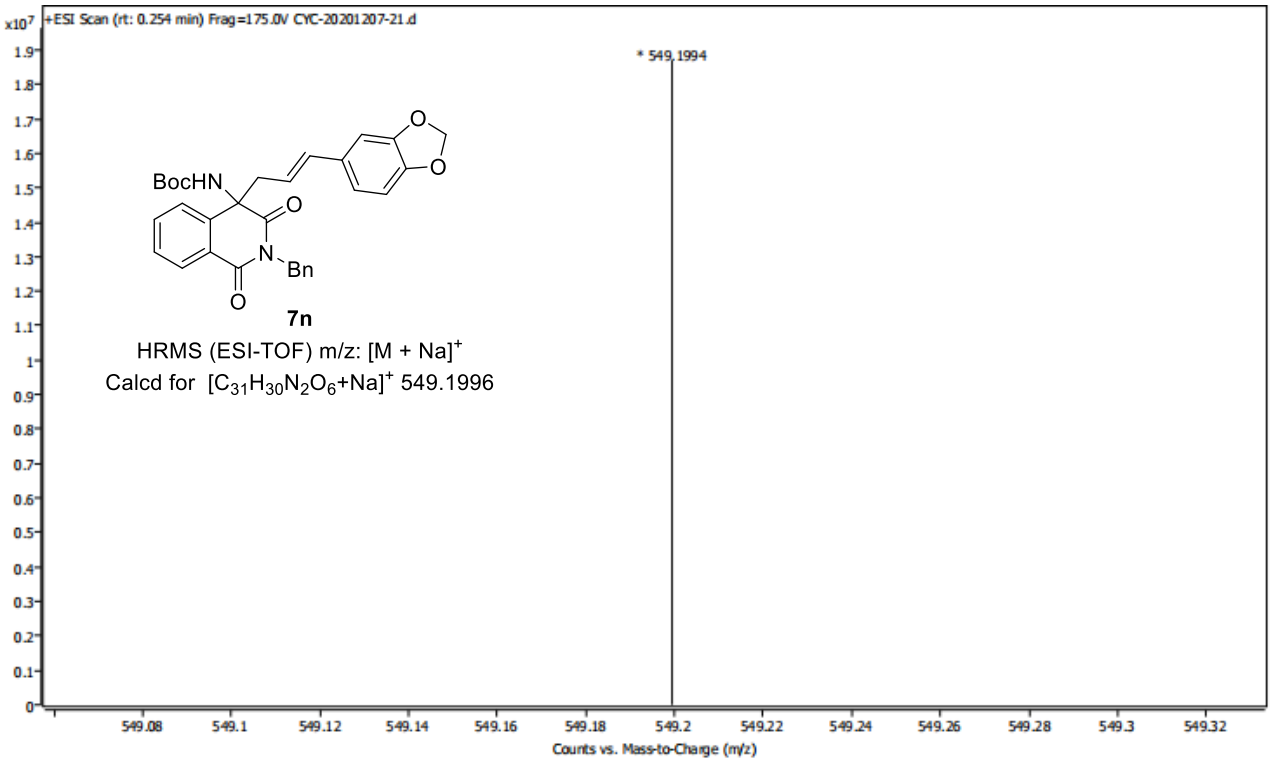
^{1}H NMR (400 MHz, $CDCl_3$)





7n

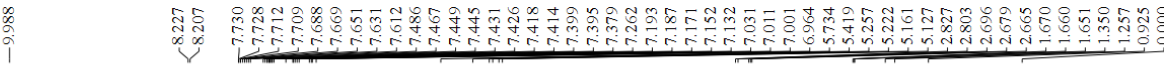
^{13}C NMR (100 MHz, $CDCl_3$)

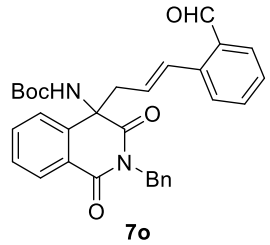


7n

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

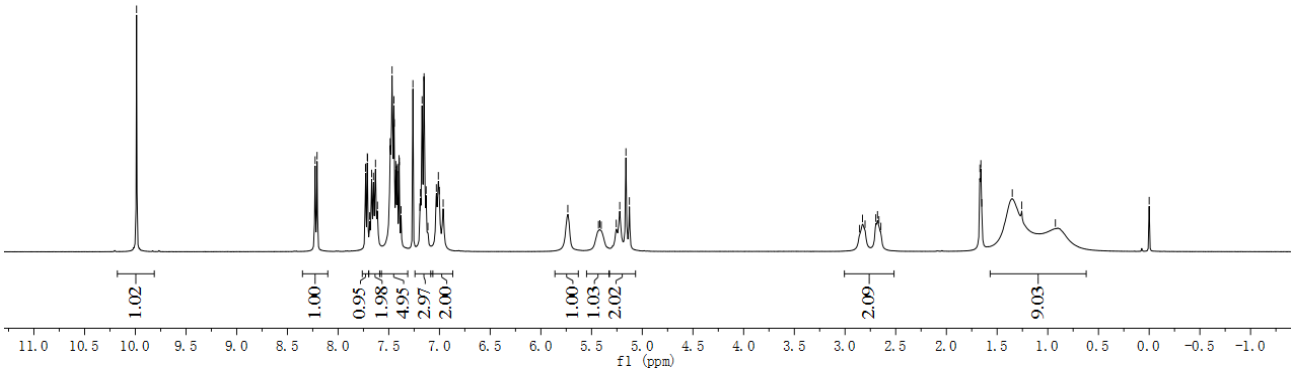
Calcd for $[C_{31}H_{30}N_2O_6+Na]^+$ 549.1996

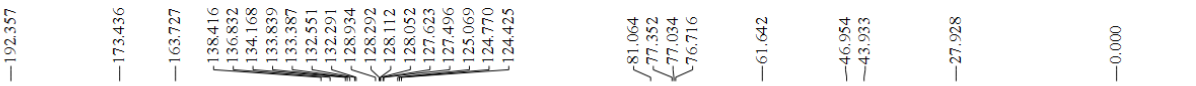


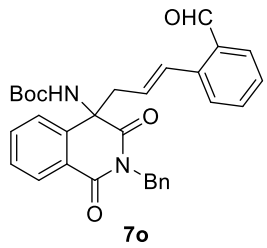


7o

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

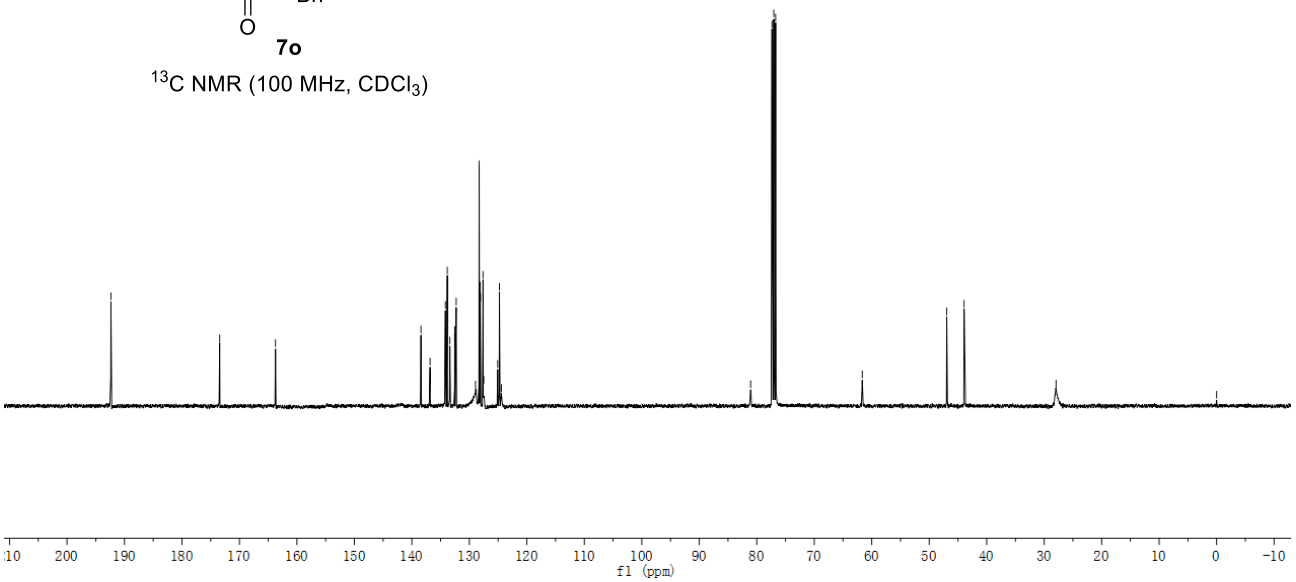


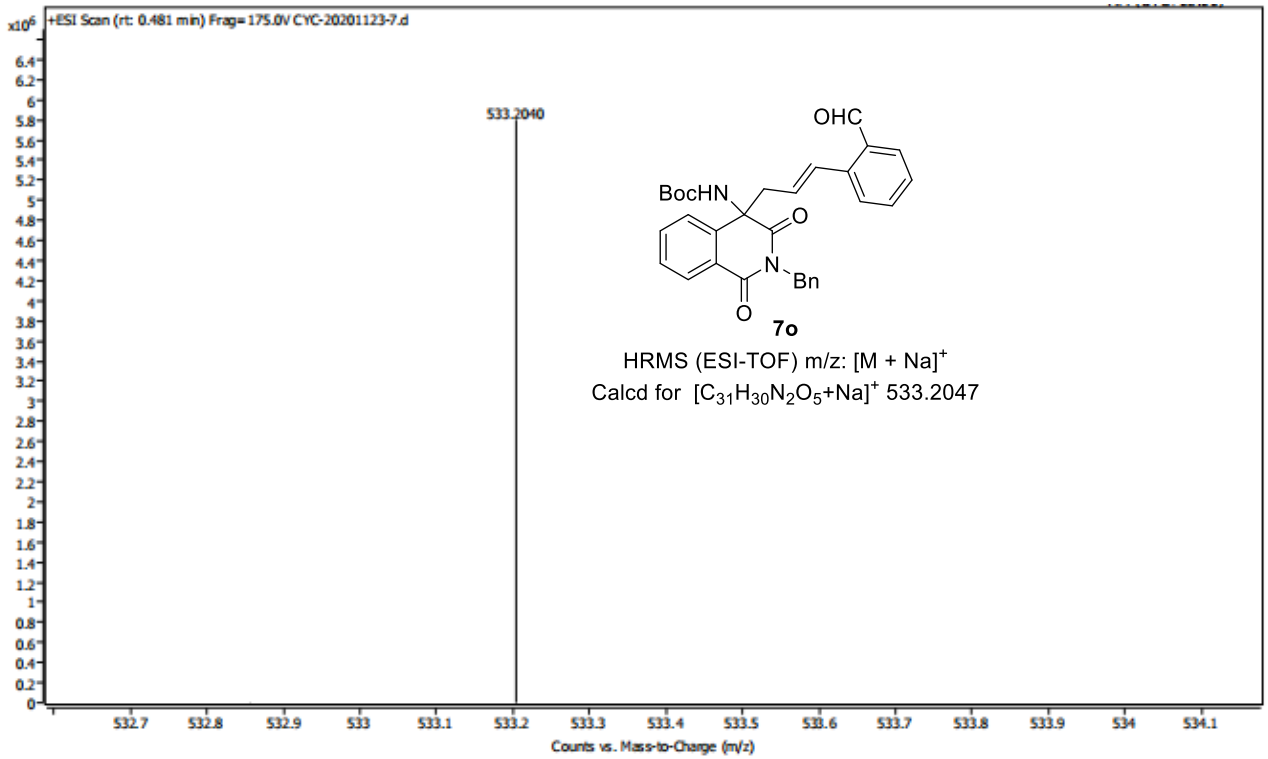




7o

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

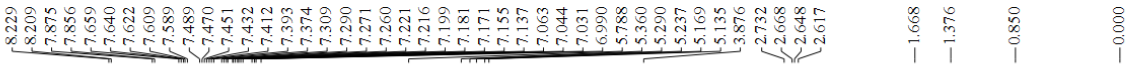


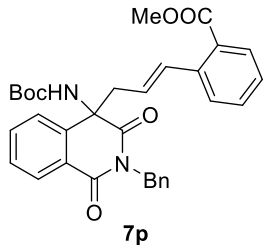


7o

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

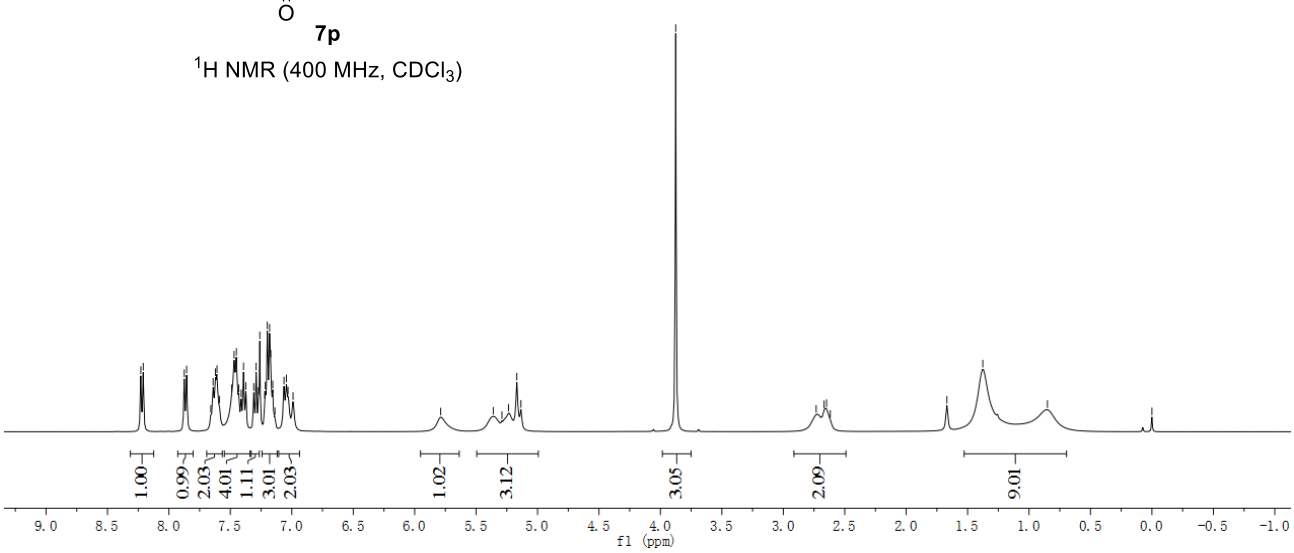
Calcd for $[C_{31}H_{30}N_2O_5+Na]^+$ 533.2047

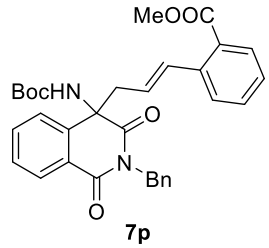




7p

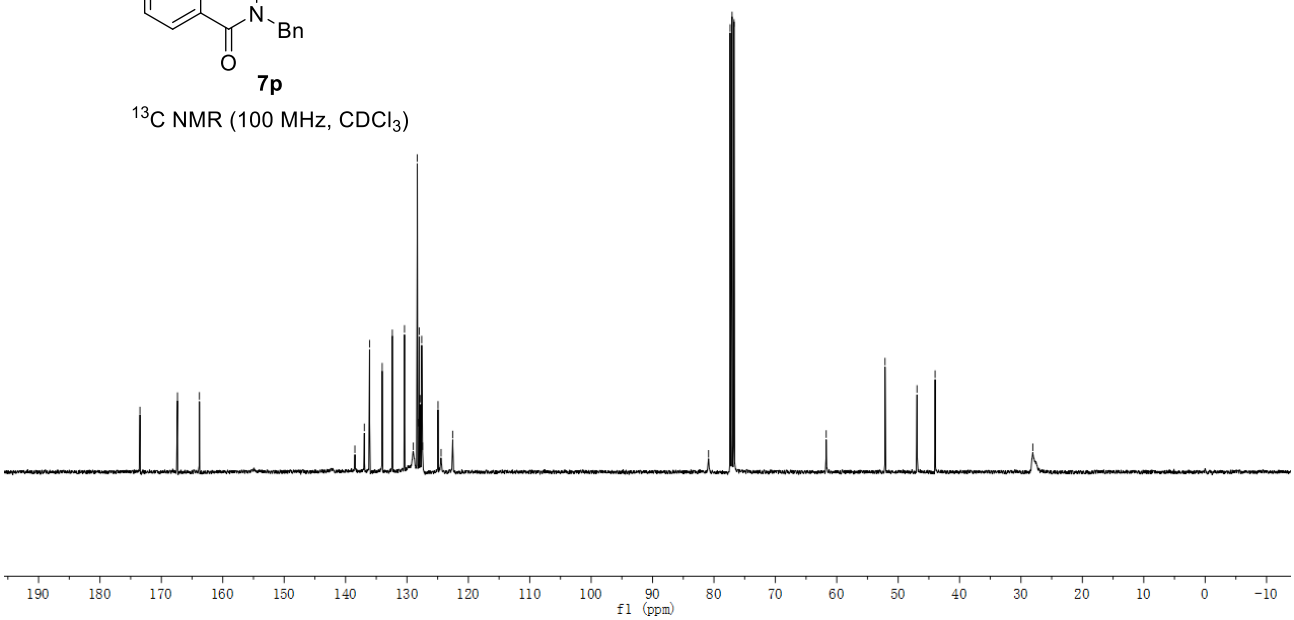
^{1}H NMR (400 MHz, $CDCl_3$)

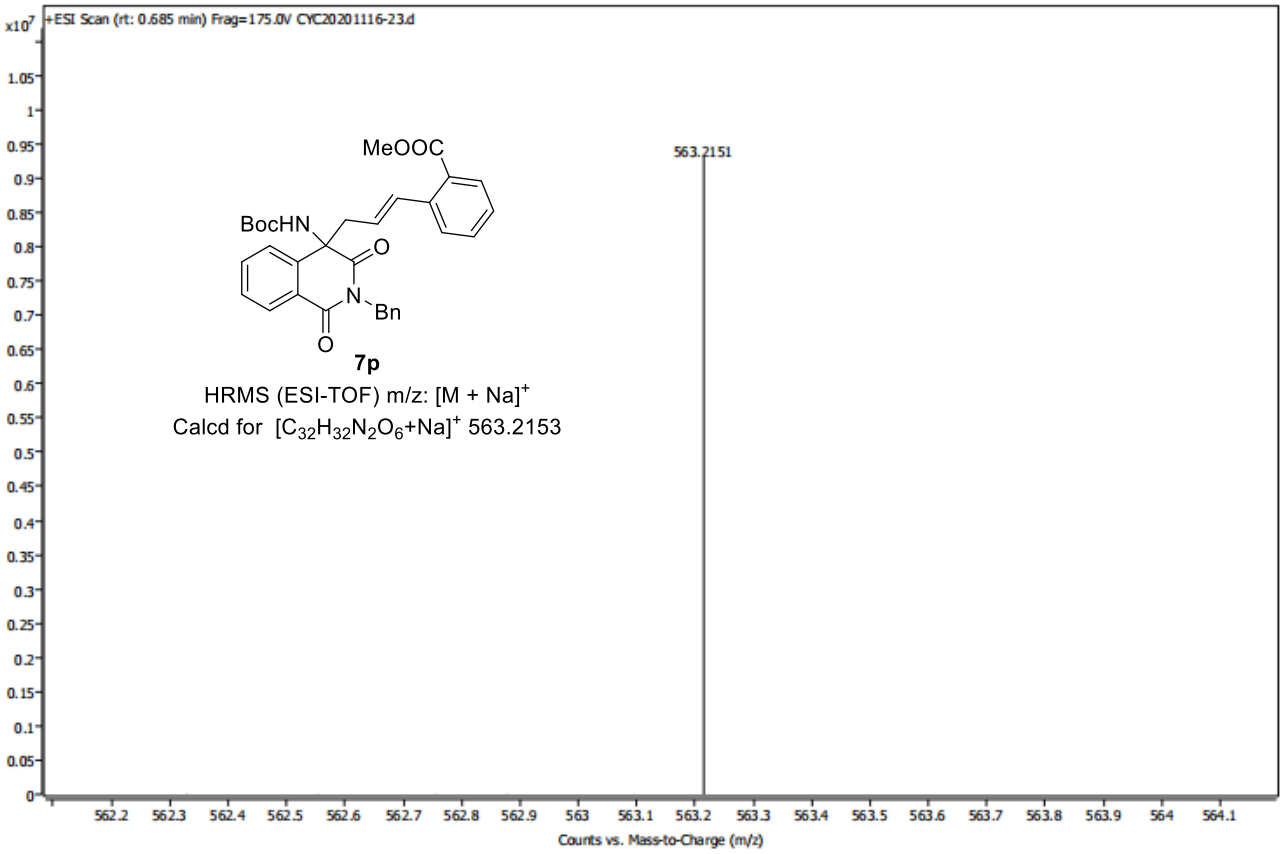




7p

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

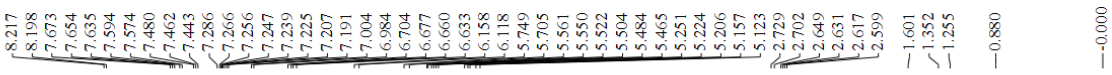


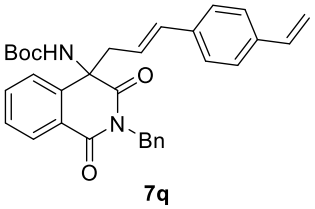


7p

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

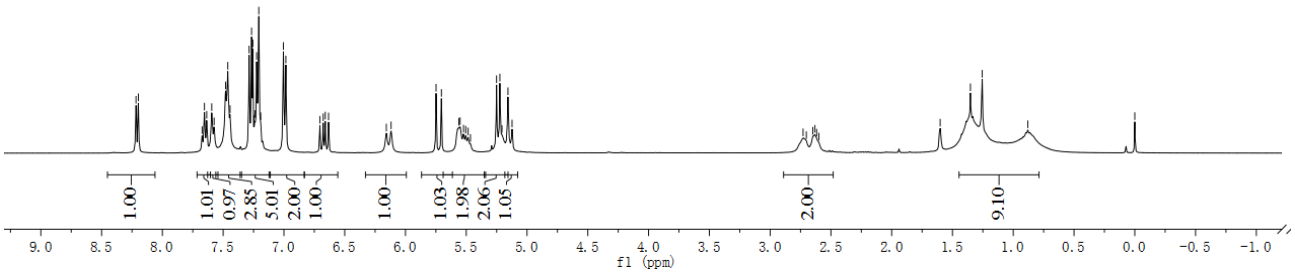
Calcd for $[C_{32}H_{32}N_2O_6+Na]^+$ 563.2153

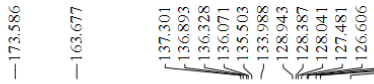


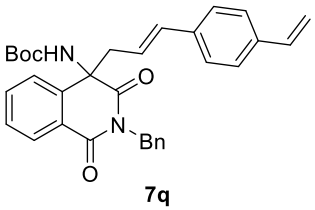


7q

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

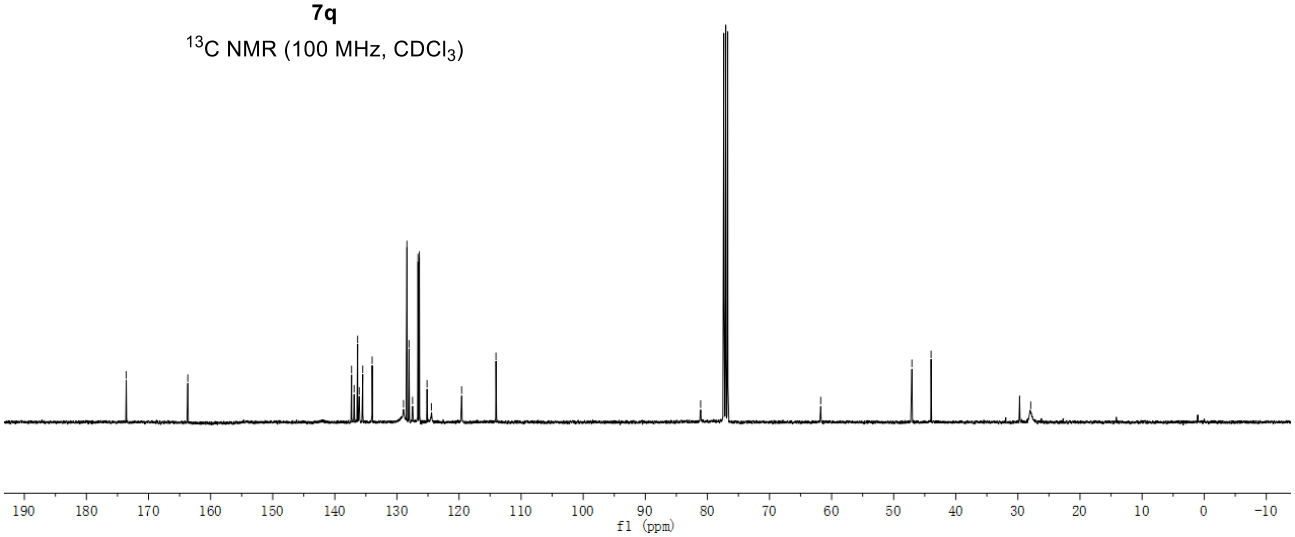


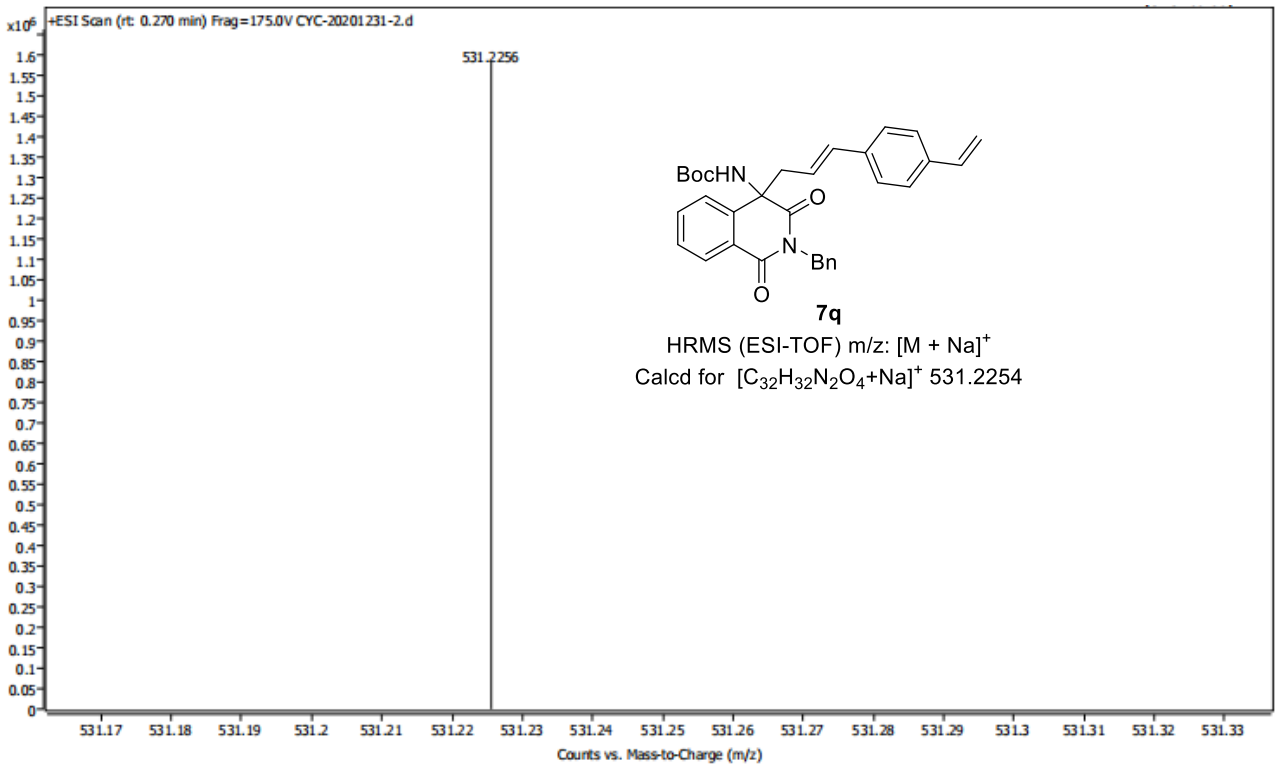




7q

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

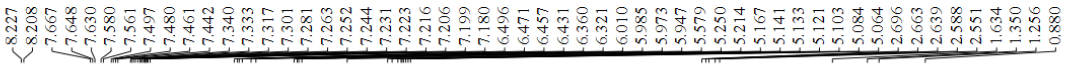


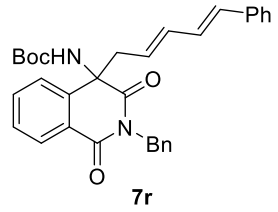


7q

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

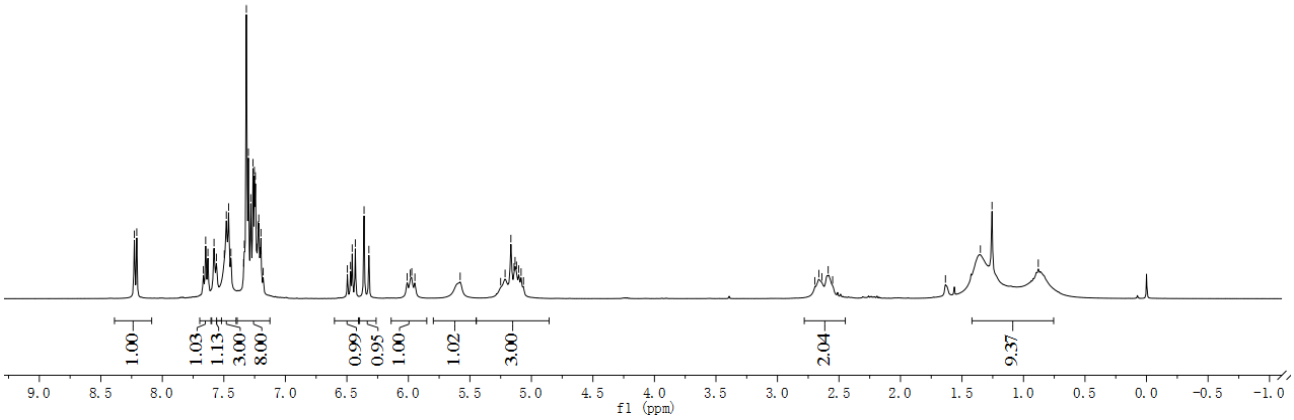
Calcd for $[C_{32}H_{32}N_2O_4+Na]^+$ 531.2254

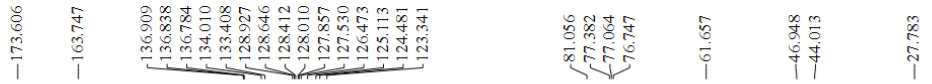


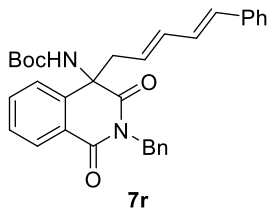


7r

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

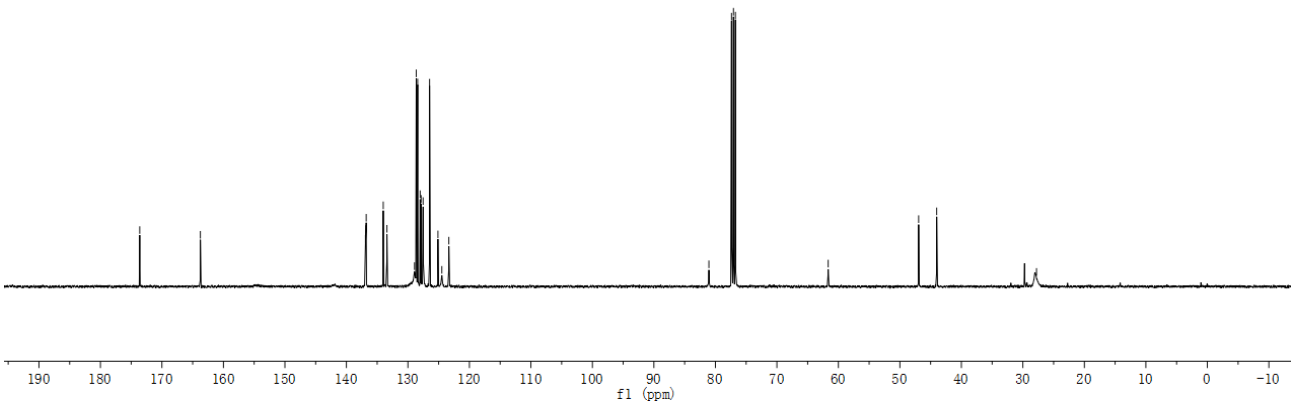


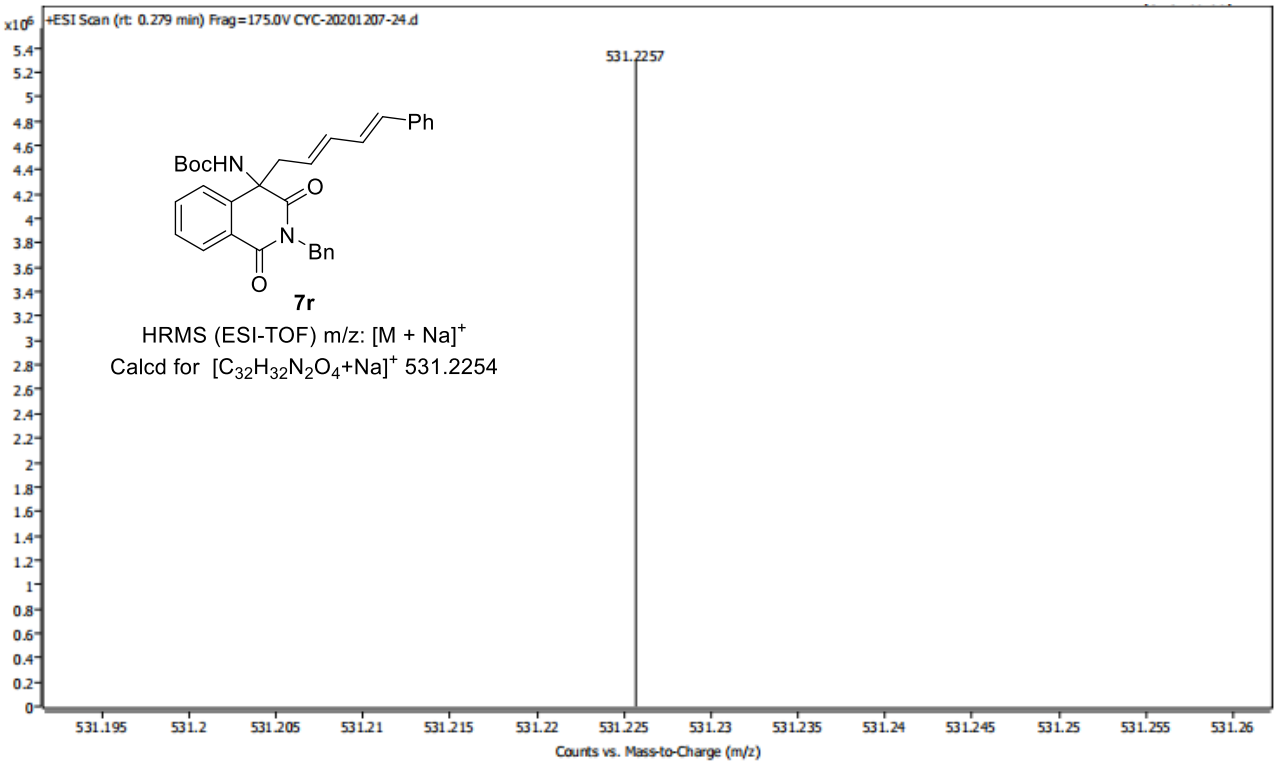




7r

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

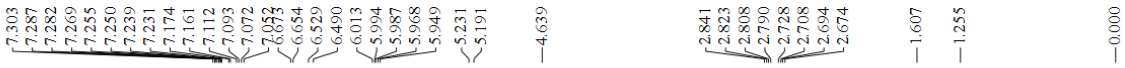


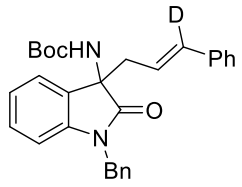


7r

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

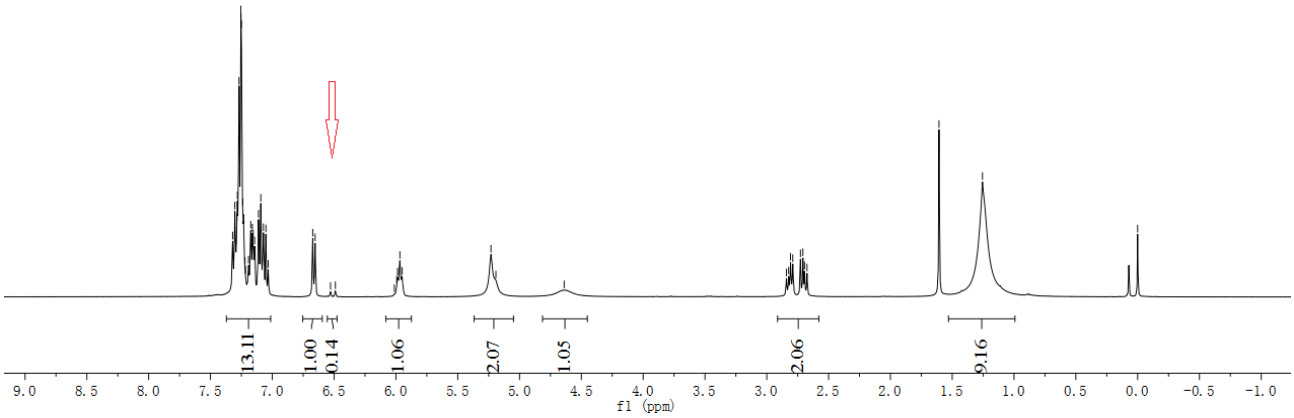
Calcd for $[C_{32}H_{32}N_2O_4+Na]^+$ 531.2254

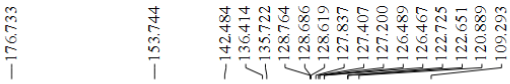


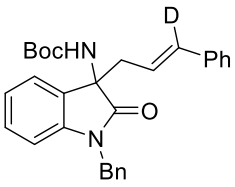


d-**3a**

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

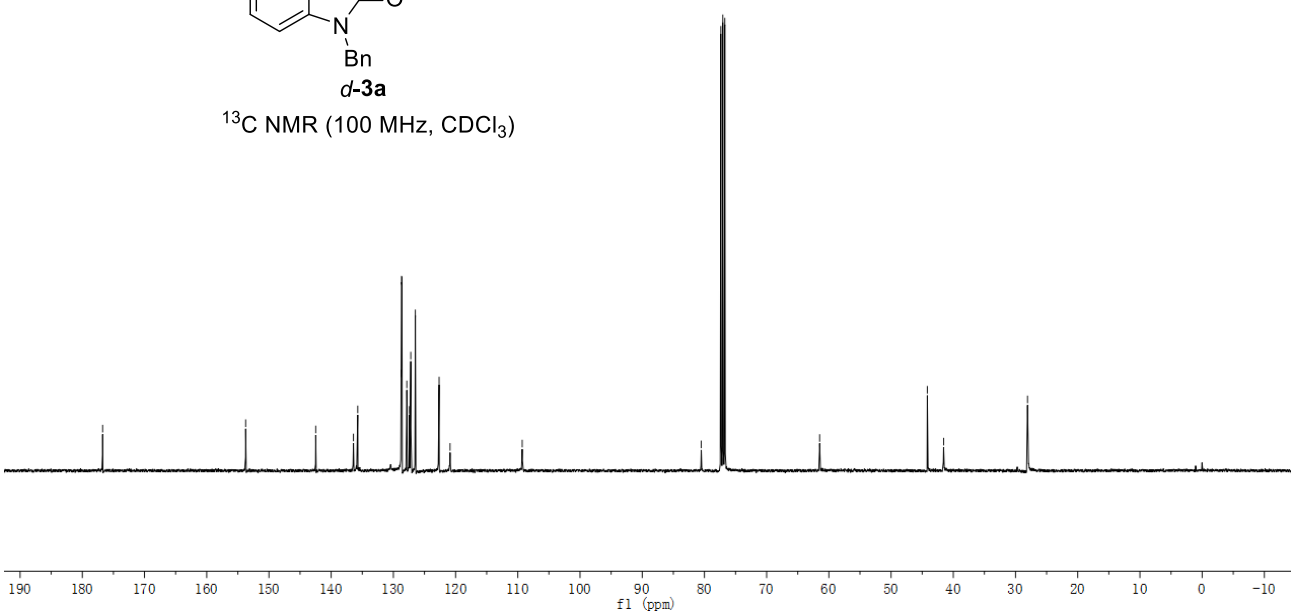


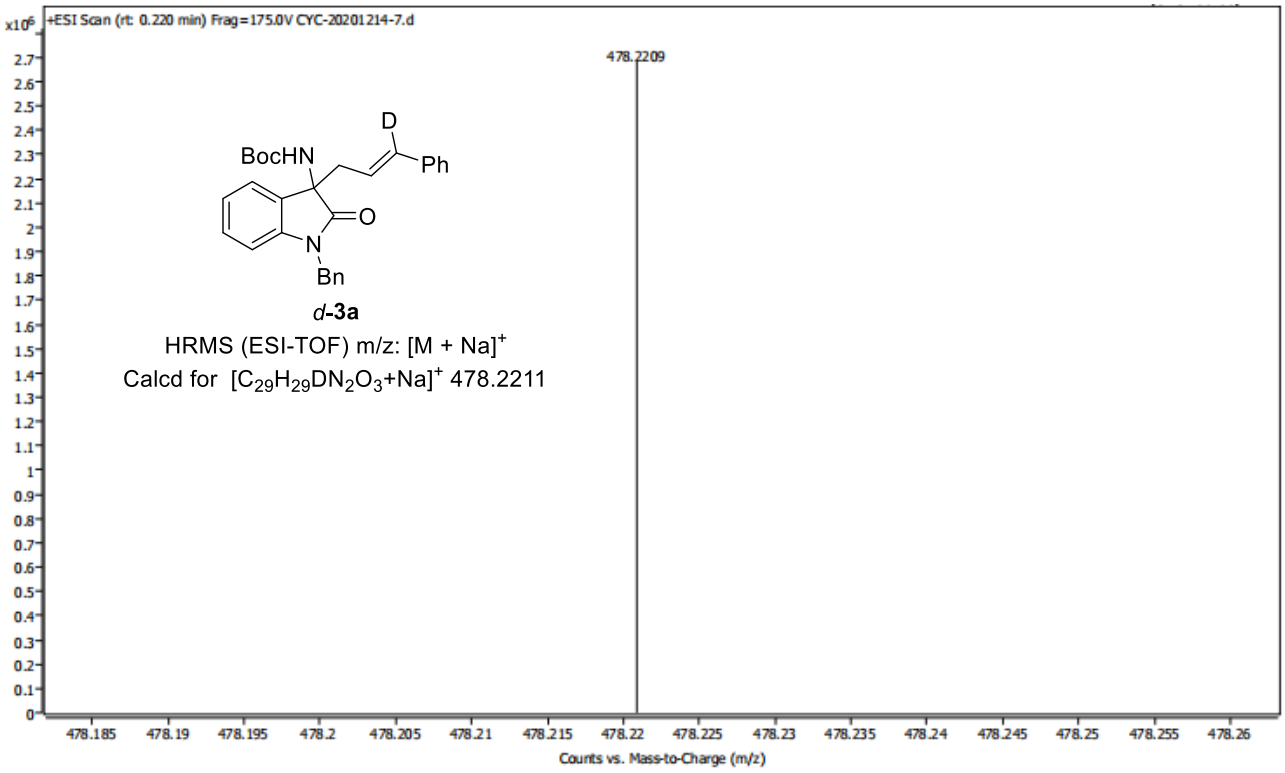




d-**3a**

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

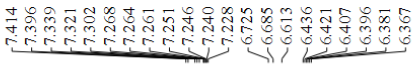


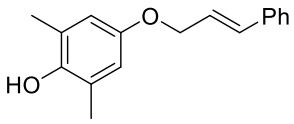


d-**3a**

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

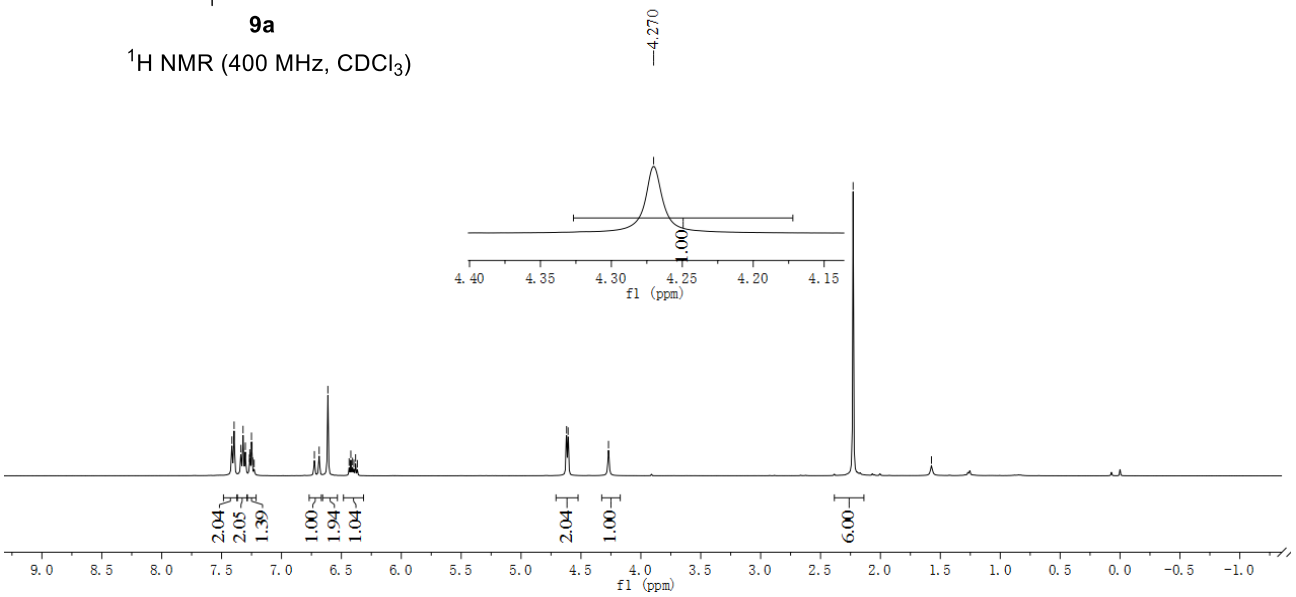
Calcd for $[C_{29}H_{29}DN_2O_3+Na]^+$ 478.2211

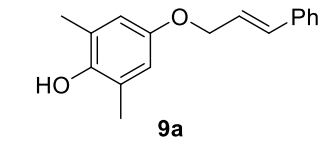




9a

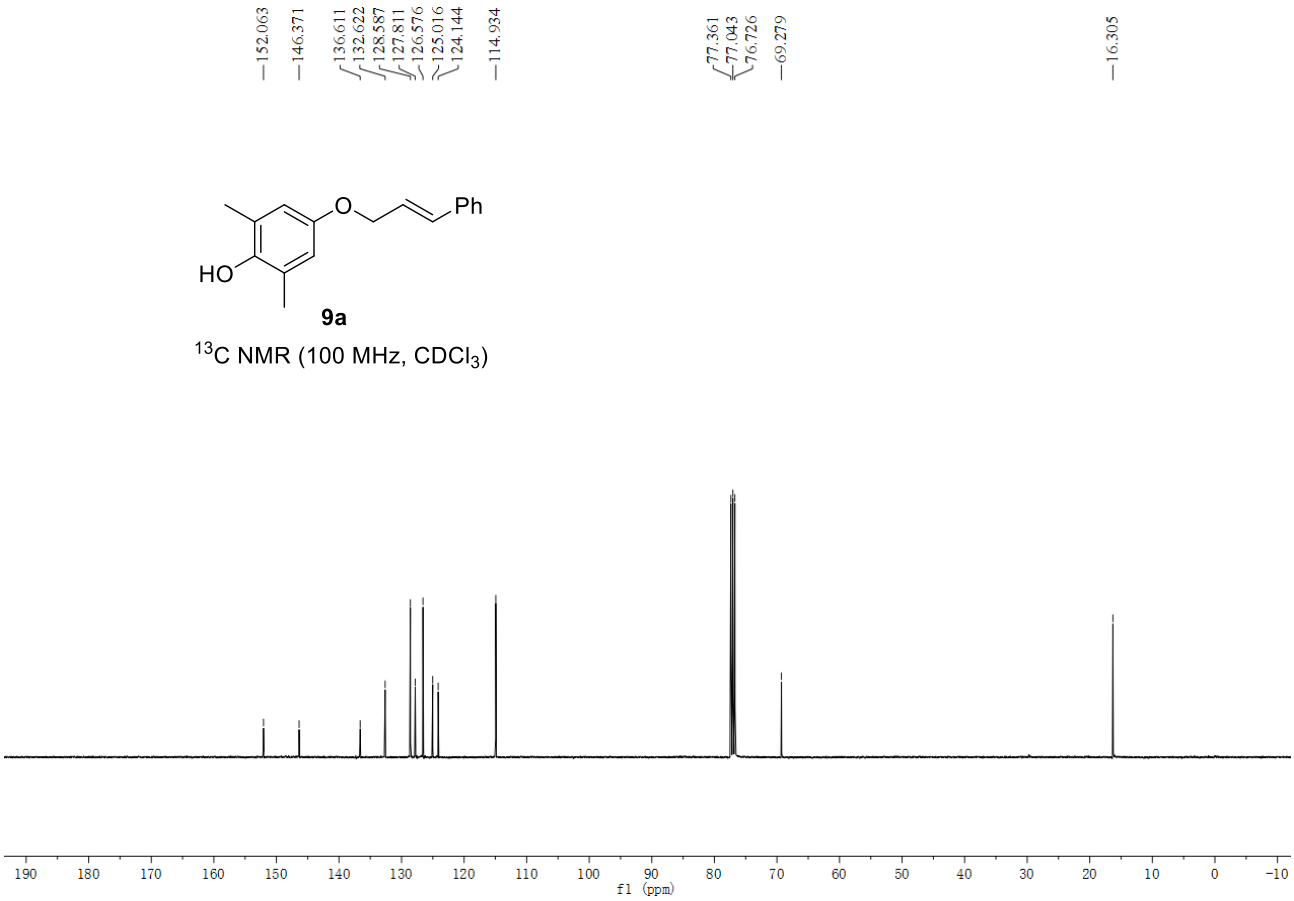
^{1}H NMR (400 MHz, $CDCl_3$)





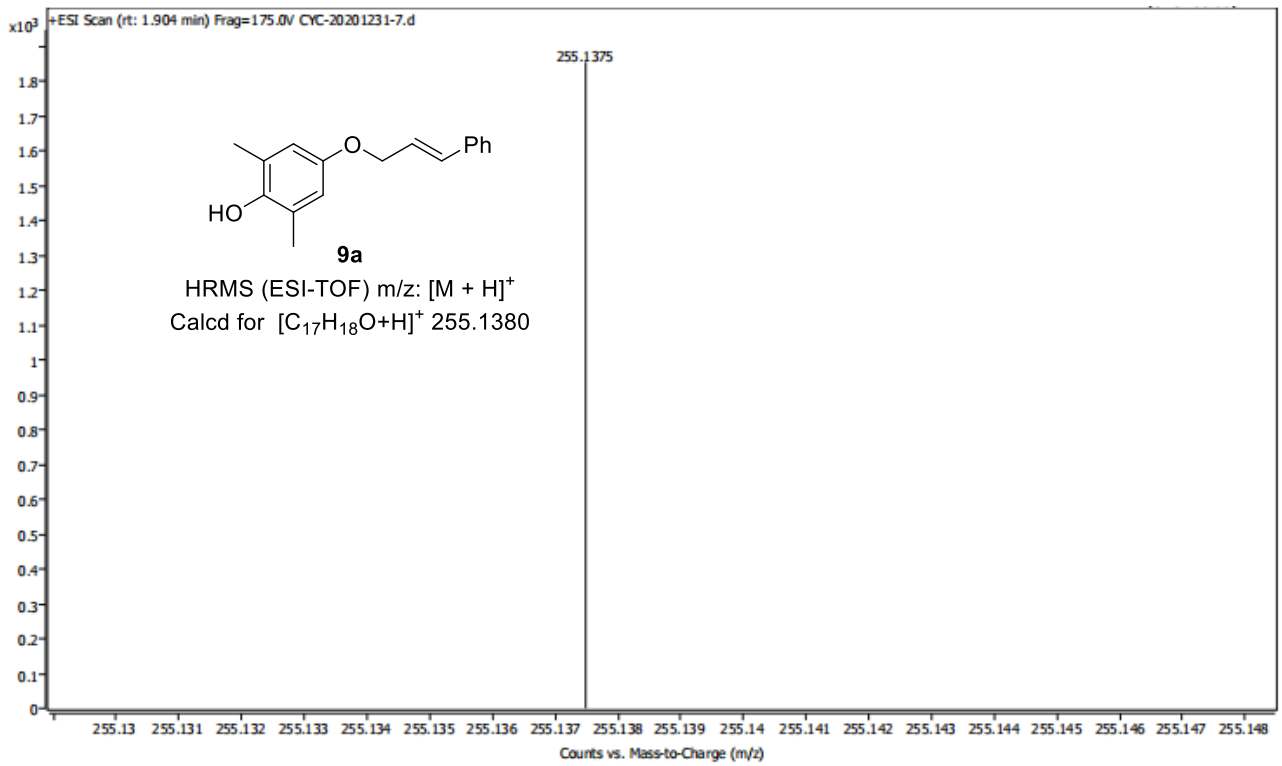
9a

^{1}H–^{1}H NOESY (600 MHz, $CDCl_3$)



9a

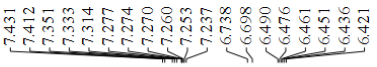
^{13}C NMR (100 MHz, $CDCl_3$)

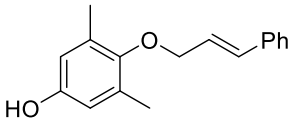


9a

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

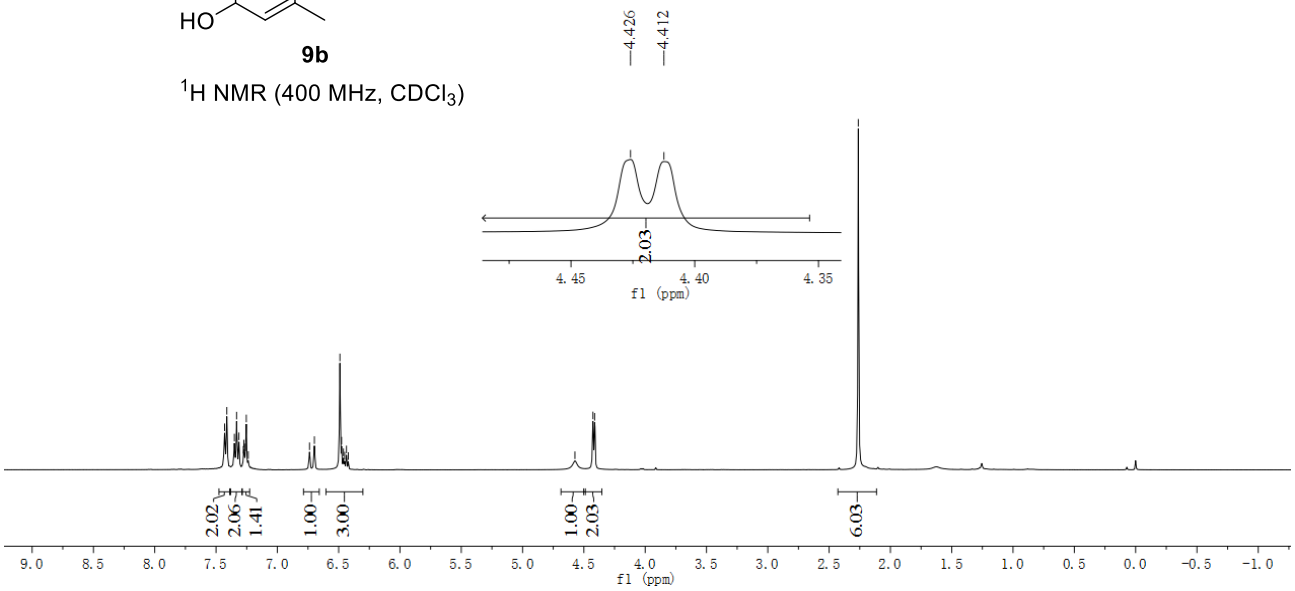
Calcd for $[C_{17}H_{18}O+H]^+$ 255.1380

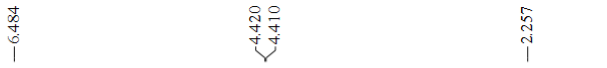


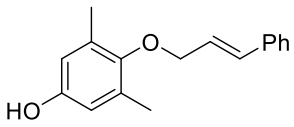


9b

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

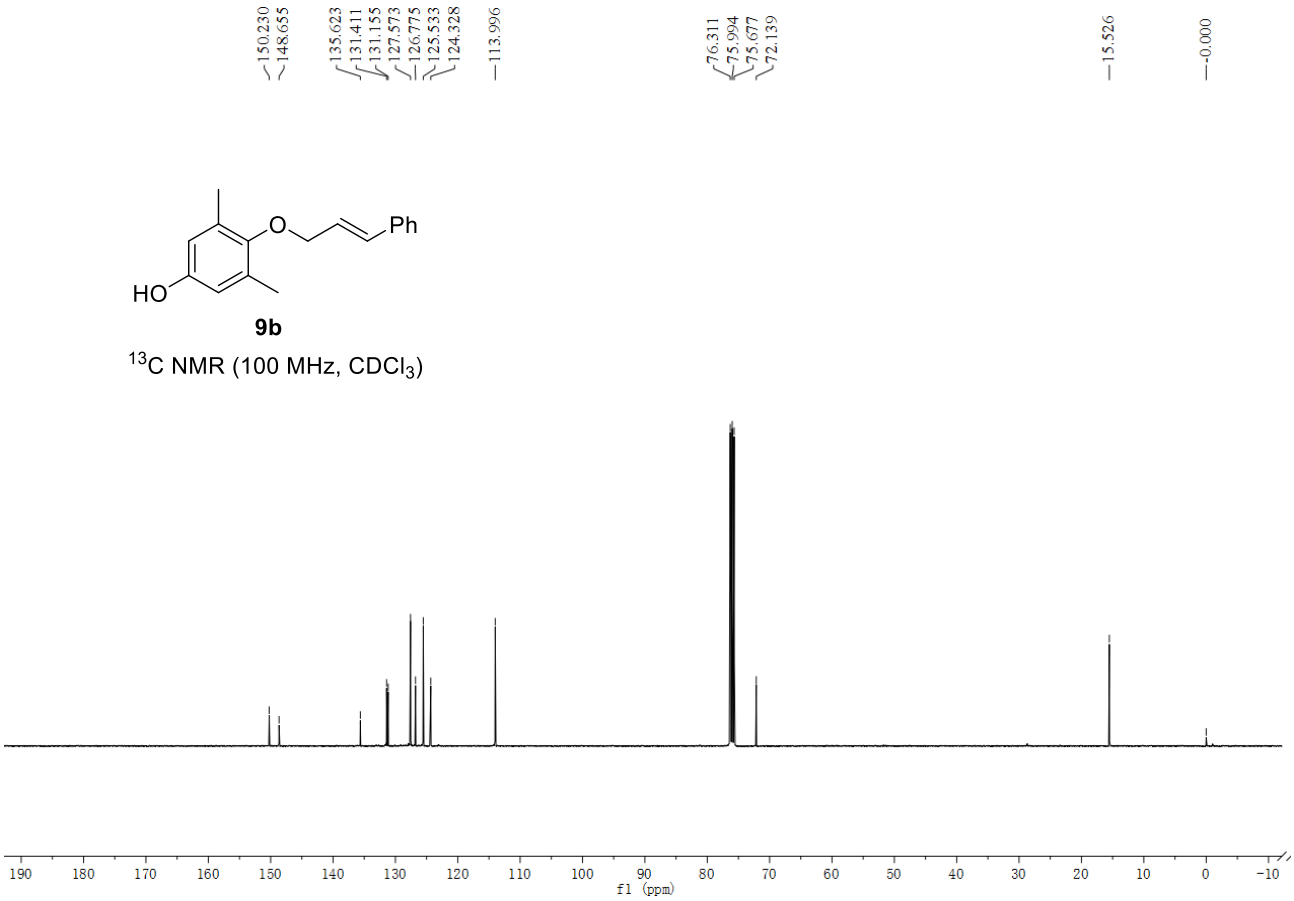






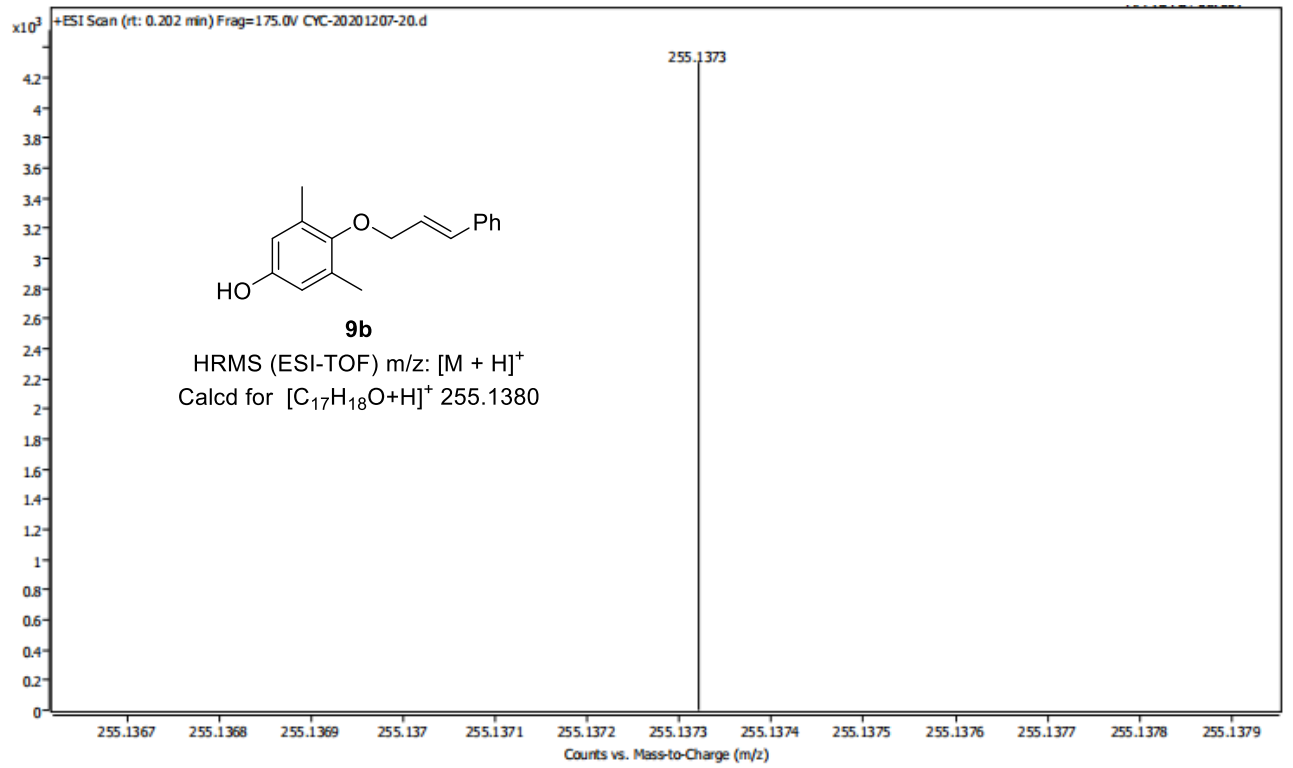
9b

^{1}H–^{1}H NOESY (600 MHz, $CDCl_3$)



9b

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



9b

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

Calcd for $[C_{17}H_{18}O+H]^+$ 255.1380