Palladium-catalyzed denitrogenation/vinylation of benzotriazinones with vinylene carbonate

Jiang Nan*, Qiong Huang, Xinran Men, Shuai Yang, Jing Wang, Yangmin Ma

Key Laboratory of Chemical Additives for China National Light Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China

Xi'an Key Laboratory of Antiviral and Antimicrobial-Resistant Bacteria Therapeutics Research, Xi'an, 710021, China

Email: nanjiang@sust.edu.cn

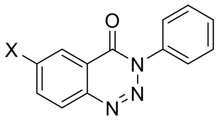
Electronic Supplementary Information

Table of Contents:

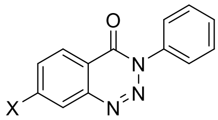
1. General information

All reagents were used from commercial received unless otherwise noted. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F_{254}); visualization of the developed chromatogram was performed by fluorescence. Flash Chromatography was performed with silica gel (300-400 mesh). Proton-1 nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker Ascend 400 (400 MHz) spectrometer, and chemical shifts are reported in delt a (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on a Bruker Ascend 400 spectrometer, chemical shifts are reported in ppm relative to the center line of a triplet at 77.0 ppm for $CDCl_3$. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) data were acquired at 376 MHz on a Bruker Ascend 400 spectrometer. Infrared spectra (IR) data were recorded on a TENSOR 27 FT-IR spectrometer and recorded in wave numbers (cm^{-1}). High resolution mass spectra were acquired on a Bruker Daltonics MicroTof-Q II mass spectrometer.

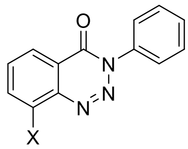
2. General procedure for the synthesis of starting materials



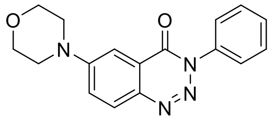
1a, X=H **1b,** X=Me **1c**, X=OMe **1e**, X=OPh **1f**, X=Ph **1g**, X=F **1h**, X=Cl **1i**, X=CF_3 **1j,** X=COOEt **1k**, X=Br **1l,** X=I **1m,**X=Bpin



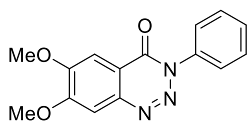
1n, X=OMe **1o**, X=Cl **1p,** X=Br **1q,** X=CF_3



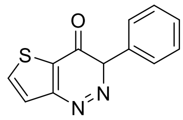
1r, X=Me **1s**, X=Br **1t**, X=NO_2



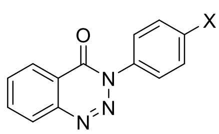
1d



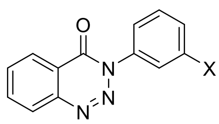
1u



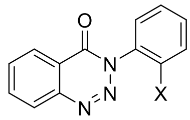
1v



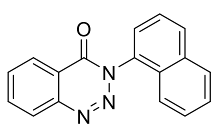
1a', X=Me **1b'**, X=OMe **1c',** X=SMe **1d'**, X=F **1e'**, X=Cl **1f'**, X=Br **1g'**, X=CF_3 **1h'**, X=I **1i'**, X=COOMe



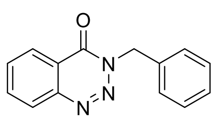
1j', X=Cl **1k'**, X=CN



1l', X=F 1**m'**, X=Me

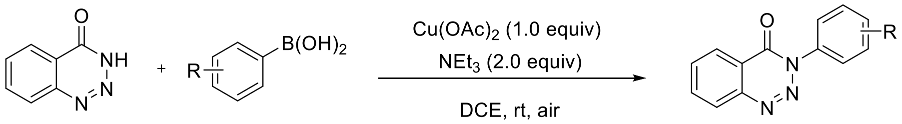


1n'



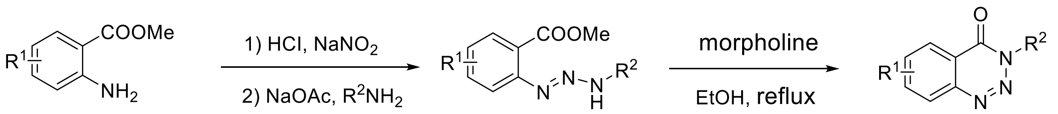
1o'

Method A: (1a, 1a', 1b', 1c', 1d', 1e', 1f', 1j', 1k', 1l', 1m', 1n', 1o'）[1-3]



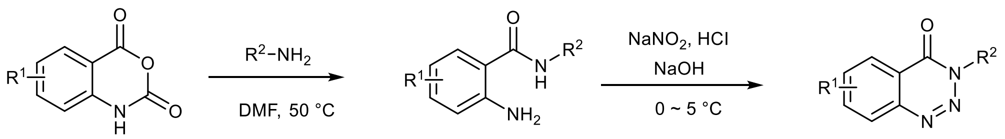
A mixture of the benzo[*d*][1,2,3]triazin-4(3*H*)-one (5.0 mmol), organoboronic acid (7.5 mmol), anhydrous $Cu(OAc)_2$ (5.0 mmol) and Et_3N (10.0 mmol) in DCE (30.0 mL) was stirred at room temperature (monitored by TLC). After finished, the reaction mixture was filtered through celite. The corresponding filtrate was collected, concentrated in vacuo. To obtained residue was finally purified by manual column chromatography on silica gel to afford the desired products.

Method B: (1b, 1c, 1d, 1e, 1f, 1h, 1i, 1j, 1k, 1l, 1m, 1n, 1o, 1p, 1q, 1r, 1s, 1t, 1u, 1v, 1g', 1h', 1i') [1-5]



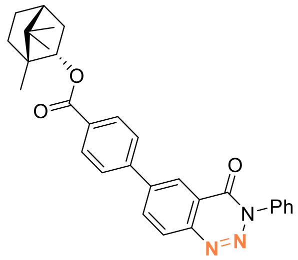
To a round bottom flask containing methyl anthranilate derivatives (10.0 mmol) were evacuated and purged with argon three times, and then HCl(aq) (16.0 mL, 2 M) was added, followed by being stirred at 0 °C for 5 min. A solution of $NaNO_2$ (11.7 mmol) in water (5.5 mL) were slowly added within 40 min to the system and then stirred at 0 °C for 30 min. Then, a solution of NaOAc (38.6 mmol) in water (12.5 mL) was slowly added within 20 min, followed by addition of corresponding anilines (15.2 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 3 h. The precipitate was collected by filtration, washed with cold water (25.0 ml). The above triazene and morpholine (30.0 mmol) was refluxed in ethanol (45.0 mL) until triazene was completely consumed. The reaction mixture was cooled to 0 °C for crystallization. The product was collected by filtration and washed with cold ethanol to give corresponding products. The residue was purified by manual column chromatography on silica gel to obtain the corresponding products.

Method C: (1g) [2]



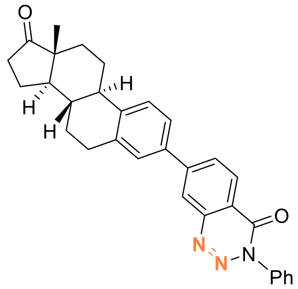
In a round bottom flask isotoic anhydride (10.0 mmol), aliphatic amine (11.1 mmol) and DMF (10.0 mL) were loaded and the be heated to 50 °C in an oil bath and stirred for 3 h. After completed, a solution of $NaNO_2$ (11.0 mmol) in 2 M aqueous HCl (20.0 mL) was added to the reaction mixture at 0 °C and stirred for 1 h. Then, 1 M aqueous NaOH solution was added slowly to adjust the pH to 12. The reaction mixture was vigorously stirred for 15 min and then reacidified to pH 2.0. After stirring for 30 min, the sturated NH_4Cl solution (3 × 20 mL) was added and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was purified by manual column chromatography on silica gel to obtain the corresponding products.

3. General procedure for the synthesis of bioactive molecules



(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl4-(4-oxo-3-phenyl-3,4-dihydrobenzo[*d*][1,2,3]triazin-6-yl)benzoate (1b'')

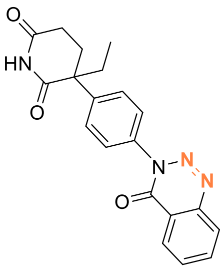
The reaction was performed following the general procedure method B. White solid ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 2.06 Hz, 1H), 8.31 (d, *J* = 8.45 Hz, 1H), 8.25 – 8.18 (m, 3H), 7.81 (d, *J* = 8.06 Hz, 2H), 7.67 (d, *J* = 7.68 Hz, 2H), 7.57 (t, *J* = 7.65 Hz, 2H), 7.53 – 7.47 (m, 1H), 5.16 (d, *J* = 9.91 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.21 – 2.10 (m, 1H), 1.87 – 1.79 (m, 1H), 1.76 (t, *J* = 4.51 Hz, 1H), 1.44 (t, *J* = 12.73 Hz, 1H), 1.39 – 1.29 (m, 1H), 1.19 – 1.13 (m, 1H), 0.99 (s, 3H), 0.94 (d, *J* = 3.97 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 155.5, 144.8, 143.3, 142.9, 139.0, 134.2, 131.5, 130.7, 130.6, 129.6, 129.4, 129.3, 127.8, 127.8, 126.3, 124.1, 121.1, 81.2, 49.4, 48.2, 45.3, 37.2, 28.4, 27.7, 20.0, 19.2, 13.9. IR: 3062, 3029, 1696, 1654, 1523, 1489, 1271, 749, 699 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{30}H_{30}N_3O_3$ $[M+H]^+$ 480.2282, found 480.2285.



7-((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl)-3-phenylbenzo[*d*][1,2,3]triazin-4(3*H*)-one (1c'')

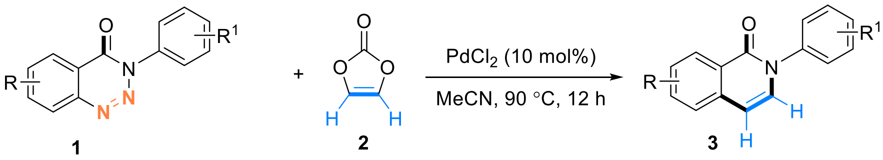
The reaction was performed following the general procedure method B. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.22, 1.90 Hz, 1H), 8.40 (d, *J* = 2.06 Hz, 1H), 8.07 (dt, *J* = 8.34, 1.99 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.60 – 7.53 (m, 3H), 7.50 (d, *J* = 5.09 Hz, 3H), 3.13 – 2.98 (m, 2H), 2.60 – 2.47 (m, 2H), 2.39 (d, *J* = 12.25 Hz, 1H), 2.25 – 2.15 (m, 1H), 2.15 – 2.07 (m, 2H), 2.02 (d, *J* = 11.49 Hz, 1H), 1.73 – 1.63 (m, 3H), 1.56 (d, *J* = 13.95 Hz, 3H), 0.95 (d, *J* = 1.91 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9, 155.5, 148.3, 144.6, 141.5, 139.1, 138.0, 136.3, 131.7, 129.4, 129.2, 128.4, 126.7, 126.5, 126.3, 126.3, 125.1, 119.0, 50.8, 48.3, 44.7, 38.4, 36.1, 31.9, 29.8, 26.7, 26.0, 21.9, 14.2. IR: 3064, 3041, 2985, 1734, 1694, 1552, 1269, 755, 694 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{31}H_{30}N_3O_2$ $[M+H]^+$ 476.2333, found 476.2328.

3-ethyl-3-(4-(4-oxobenzo[*d*][1,2,3]triazin-3(4*H*)-yl)phenyl)piperidine-2,6-dione(1e'')

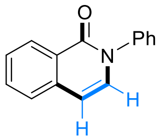


The reaction was performed following the general procedure method B. Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.86 Hz, 1H), 8.20 (d, *J* = 8.07 Hz, 1H), 7.98 (t, *J* = 7.71 Hz, 1H), 7.84 (t, *J* = 7.60 Hz, 1H), 7.70 (d, *J* = 8.33 Hz, 2H), 7.48 (d, *J* = 8.35 Hz, 2H), 2.64 (dt, *J* = 18.35, 3.62 Hz, 1H), 2.46 (ddt, *J* = 18.09, 7.17, 4.30 Hz, 2H), 2.28 (td, *J* = 14.12, 13.67, 4.41 Hz, 1H), 2.10 (dt, *J* = 14.62, 7.26 Hz, 1H), 1.97 (dt, *J* = 14.23, 7.36 Hz, 1H), 0.90 (t, *J* = 7.43 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 172.5, 155.4, 143.8, 139.9, 138.3, 135.5, 133.1, 128.8, 127.2, 126.6, 125.9, 120.5, 51.2, 33.2, 29.5, 27.2, 9.3. IR: 3058, 2012, 2867, 1695, 1653, 1518, 1473, 1268, 1194, 754, 669 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{20}H_{19}N_4O_3$ $[M+H]^+$ 363.1452, found 363.1446.

4. General procedure for the catalytic reaction

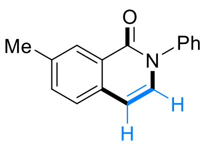


A pressure tube was charged with benzotriazinone **1** (0.2 mmol), vinylene carbonate **2** (0.6 mmol), $PdCl_2$ (10.0% mol) and CH_3CN (1.0 mL). The reaction mixture was stirred at 90 °C for 12 h under Ar atmosphere in an oil bath. After cooling to room temperature, all volatiles were removed under reduced pressure. The residue was purified by silica gel manual column chromatography to afford the product **3**.



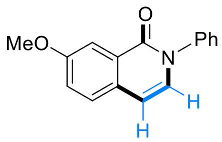
2-Phenyl-1(2*H*)-isoquinolinone (3a)[6]

White solid (34.1 mg, 77% yield). PE/DCM = 1:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.14, 1.37 Hz, 1H), 7.68 (t, *J* = 7.54 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.43 (t, 3H), 7.19 (d, *J* = 7.39 Hz, 1H), 6.57 (d, *J* = 7.40 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 141.3, 137.0, 132.5, 132.1, 129.2, 128.2, 128.0, 127.1, 126.8, 126.5, 125.9, 106.1. IR: 3065, 3021, 2986, 2910, 1657, 1645, 1501, 1282, 787, 688 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{12}NO$ $[M+H]^+$ 222.0913, found 222.0917.



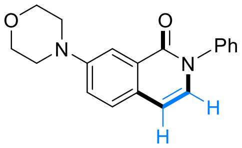
2-Phenyl-1(2*H*)-7-methylisoquinolinone (3b)

White solid (33.8 mg, 72% yield). PE/DCM =1:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.48 (dd, *J* = 7.49, 5.08 Hz, 4H), 7.45 – 7.38 (m, 3H), 7.12 (d, *J* = 7.38 Hz, 1H), 6.53 (d, *J* = 7.38 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 141.8, 137.5, 134.9, 134.3, 131.54, 129.5, 128.2, 128.1, 127.1, 126.7, 126.1, 106.3, 21.8. IR: 3068, 3023, 2986, 2912, 1657, 1630, 1616, 1335, 1283, 741, 691 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1061.



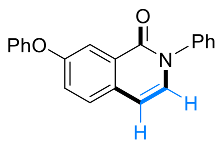
2-Phenyl-1(2*H*)-7-methoxyisoquinolinone (3c)

White solid (40.2 mg, 80% yield). PE/DCM = 1:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.71 Hz, 1H), 7.53 – 7.48 (m, 3H), 7.46 – 7.38 (m, 3H), 7.29 (dd, *J* = 8.65, 2.73 Hz, 1H), 7.08 (d, *J* = 7.36 Hz, 1H), 6.54 (d, *J* = 7.35 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 159.3, 141.8, 131.3, 130.2, 129.5, 128.3, 128.0, 127.8, 127.1, 123.3, 108.4, 106.3, 55.9. IR: 3065, 3002, 2913, 2942, 2856, 1655, 1607, 1280, 1219,833, 691 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$ 252.1019, found 252.1018.



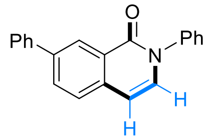
2-Phenyl-1(2*H*)-7-morpholinoisoquinolinone (3d)

White solid (39.7 mg, 65% yield). PE/DCM = 1:1, R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.49 (d, *J* = 8.74 Hz, 3H), 7.43 (d, *J* = 4.78 Hz, 3H), 7.35 (d, *J* = 8.62 Hz, 1H), 7.06 (dd, *J* = 7.35, 3.00 Hz, 1H), 6.51 (dd, *J* = 7.42, 2.98 Hz, 1H), 3.90 (q, *J* = 4.07 Hz, 4H), 3.29 (q, *J* = 4.02 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 150.1, 141.3, 129.7, 129.3, 128.9, 127.6, 127.2, 126.8, 126.5, 121.8, 111.5, 105.7, 66.4, 48.8. IR: 3059, 3040, 2986, 2913, 1665, 1654, 1601, 1273, 1046, 680 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{19}N_2O_2$ $[M+H]^+$ 307.1441, found 307.1435.



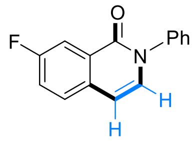
2-Phenyl-1(2*H*)-7-phenoxyisoquinolinone (3e)

White solid (40.1 mg, 64% yield). PE/DCM = 1:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.57 Hz, 1H), 7.56 (d, *J* = 8.61 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.44 – 7.39 (m, 4H), 7.38 – 7.34 (m, 2H), 7.13 (d, *J* = 7.51 Hz, 2H), 7.06 (d, *J* = 7.41 Hz, 2H), 6.57 (d, *J* = 7.41 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 156.5, 156.2, 141.0, 132.4, 130.6, 129.6, 128.9, 127.8, 127.6, 127.6, 126.5, 1244, 123.6, 118.9, 115.5, 105.5. IR: 3058, 3038, 2984, 2915, 1664, 1656, 1601, 1346, 1223, 838, 758, 690 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{21}H_{16}NO_2$ $[M+H]^+$ 314.1176, found 314.1173.



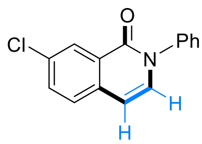
2-Phenyl-1(2*H*)-7-Phenylisoquinolinone (3f)

White solid (40.9 mg, 69% yield). PE/DCM = 2:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.94 (d, *J* = 9.92 Hz, 1H), 7.73 (d, *J* = 7.51 Hz, 2H), 7.64 (d, *J* = 8.22 Hz, 1H), 7.54 – 7.38 (m, 8H), 7.21 (d, *J* = 7.38 Hz, 1H), 6.61 (d, *J* = 7.39 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.76, 141.03, 139.68, 135.70, 131.84, 131.17, 128.97, 128.59, 127.78, 127.35, 126.86, 126.56, 126.52, 126.23, 125.94, 105.62. IR: 3063, 3005, 2968, 2913, 1663, 1630, 1652, 1524, 930, 761, 688 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1226, found 298.1220.



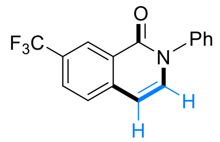
2-Phenyl-1(2*H*)-7-fluoroisoquinolinone (3g)

White solid (26.3 mg, 55 % yield). PE/DCM = 2:1, R_f = 0.28, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 11.58 Hz, 1H), 7.56 (dd, *J* = 8.60, 5.16 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.41 (dd, *J* = 12.31, 8.43 Hz, 4H), 7.16 (d, *J* = 7.42 Hz, 1H), 6.56 (d, *J* = 7.42 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ162.0 (d, *J* = 246.0Hz), 161.5, 141.4, 133.9, 131.8, 129.6, 128.6, 128.5, 128.4, 127.0,121.6 (d, *J* = 23.6 Hz), 113.7 (d, *J* = 22.7 Hz), 105.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -112.4. IR: 3065, 3041, 3020, 1653, 1625, 1605, 1591, 1502, 1325, 1286, 832, 757, 690 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}FNO$ $[M+H]^+$ 240.0819, found 240.0824.



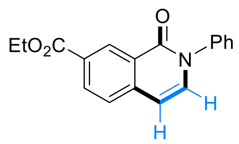
2-Phenyl-1(2*H*)-7-Chloroisoquinolinone (3h)

White solid (29.6 mg, 58% yield). PE/DCM= 2:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.62 (d, *J* = 9.66 Hz, 1H), 7.51 (t, *J* = 7.62 Hz, 3H), 7.43 (t, *J* = 6.80 Hz, 3H), 7.19 (d, *J* = 7.38 Hz, 1H), 6.54 (d, *J* = 7.41 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 140.7, 135.1, 132.8, 132.7, 132.2, 129.0, 128.0, 127.4, 127.4, 127.2, 126.4, 105.2. IR: 3068, 3048, 3021, 2916, 1653, 1502, 831, 689 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}ClNO$ $[M+H]^+$ 256.0524, found 256.0532.



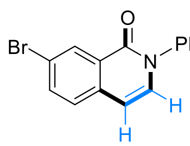
2-Phenyl-1(2*H*)-7-Trifluoroisoquinolinone (3i)

White solid (33.5 mg, 58% yield). PE/DCM = 1:1, R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.87 (d, *J* = 8.31 Hz, 1H), 7.68 (d, *J* = 8.30 Hz, 1H), 7.53 (t, *J* = 7.43 Hz, 2H), 7.44 (q, 3H), 7.30 (d, *J* = 7.42 Hz, 1H), 6.61 (d, *J* = 7.42 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 140.5, 139.2, 134.1, 129.1, 128.3(q, *J* =16.5 Hz), 128.1, 126.5, 126.4, 126.1, 125.7 (q, *J* = 12.4 Hz), 124.9, 122.3(q, *J* =280.3 Hz), 105.1. ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.3. IR: 3085, 3047, 3012, 2916, 1662, 1528, 1132, 798, 677 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{11}F_3NO$ $[M+H]^+$ 290.0787, found 290.0784.



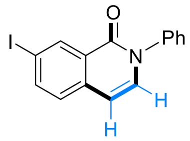
Ethyl 1-oxo-2-phenyl-1,2-dihydroisoquinoline-7-carboxylate (3j)

White solid (39.3 mg, 67% yield). PE/DCM = 1:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.39 Hz, 1H), 8.27 (s, 1H), 8.12 (d, *J* = 9.88 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.47 – 7.41 (m, 3H), 7.24 (d, *J* = 7.43 Hz, 1H), 6.64 (d, *J* = 7.43 Hz, 1H), 4.45 (q, *J* = 7.14 Hz, 2H), 1.45 (t, *J* = 7.14 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 161.2, 140.8, 136.5, 133.6, 132.7, 129.1, 129.0, 128.3, 128.0, 127.6, 126.8, 126.4, 105.9, 61.2, 14.0. IR: 3065, 3041, 3020, 1653, 1625, 1605, 1591, 1502, 1332, 1286, 832, 757, 690 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1125, found 294.1121.



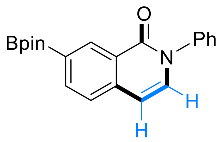
2-Phenyl-1(2*H*)-7--bromoisoquinolinone (3k)

White solid (38.3 mg, 64% yield). PE/DCM = 1:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 2.06 Hz, 1H), 7.76 (dd, *J* = 8.38, 2.09 Hz, 1H), 7.51 (t, *J* = 7.64 Hz, 2H), 7.43 (dd, *J* = 8.23, 6.42 Hz, 4H), 7.20 (d, *J* = 7.36 Hz, 1H), 6.53 (d, *J* = 7.37 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 141.4, 136.0, 133.0, 131.2, 129.7, 128.6, 128.3, 127.9, 127.0, 121.3, 105.9. IR: 3078, 3047, 2986, 2917, 1712, 1653, 1602, 1525, 1272, 792, 763, 684 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}BrNO$ $[M+H]^+$ 300.0019, found 300.0026.



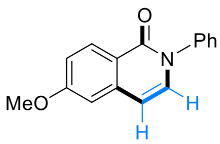
2-Phenyl-1(2*H*)-7-iodoisoquinolinone (3l)

White solid (43.7 mg, 63% yield). PE/DCM = 1:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 1.83 Hz, 1H), 7.94 (dd, *J* = 8.36, 1.88 Hz, 1H), 7.51 (t, *J* = 7.46 Hz, 2H), 7.42 (td, *J* = 8.25, 1.26 Hz, 3H), 7.30 (d, *J* = 8.34 Hz, 1H), 7.20 (d, *J* = 7.41 Hz, 1H), 6.51 (d, *J* = 7.41 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 140.9, 140.7, 136.8, 135.8, 132.6, 129.0, 128.0, 127.7, 127.3, 126.4, 105.3, 91.6. IR: 3083, 3045, 3012, 2918, 1667, 1651, 1526, 798, 762, 682 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}INO$ $[M+H]^+$ 347.9880, found 347.9881.



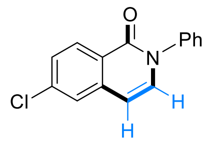
2-Phenyl-1(2*H*)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan) isoquinolinone (3m)

White solid (38.2 mg, 55% yield). PE/DCM = 1:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.9 (s, 1H), 8.1 (d, *J* = 7.84 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.5 – 7.4 (m, 3H), 7.2 (d, *J* = 7.40 Hz, 1H), 6.5 (d, *J* = 7.39 Hz, 1H), 1.36 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 141.4, 139.1, 138.0, 135.7, 133.2, 129.3, 128.0, 126.8, 125.8, 125.1, 106.1, 84.0, 24.9. IR: 3087, 3045, 2922, 2874, 1678, 1655, 1524, 1143, 806, 767, 670 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{21}H_{23}BNO_3$ $[M+H]^+$ 348.1766, found 348.1770.



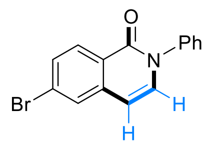
2-Phenyl-1(2*H*)-6-methoxyisoquinolinone (3n)

Yellow solid (39.7 mg, 79% yield). PE/DCM = 2:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.89 Hz, 1H), 7.49 (t, *J* = 7.65 Hz, 2H), 7.45 – 7.38 (m, 3H), 7.16 (d, *J* = 7.41 Hz, 1H), 7.08 (dd, *J* = 8.96, 2.43 Hz, 1H), 6.91 (d, *J* = 2.42 Hz, 1H), 6.48 (d, *J* = 7.42 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 161.4, 141.1, 138.8, 132.5, 130.0, 128.9, 127.6, 126.5, 120.0, 116.1, 106.2, 105.6, 55.2. IR: 3060, 3042, 3013, 2912, 1664, 1630, 1601, 1282, 1245, 690 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$ 252.1019, found 252.1015.



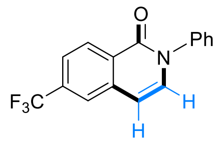
2-Phenyl-1(2*H*)-6-Chloroisoquinolinone (3o)

White solid (29.1 mg, 57% yield). PE/DCM = 2:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.61 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.43 (q, *J* = 7.51 Hz, 4H), 7.21 (d, *J* = 7.45 Hz, 1H), 6.48 (d, *J* = 7.43 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 141.3, 139.3, 138.6, 133.8, 130.4, 129.6, 128.5, 127.9, 127.0, 125.5, 125.2, 105.4. IR: 3082, 3042, 2986, 2867, 1657, 1623, 1514, 1283, 872, 772, 681 cm^{-1}. HRMS (ESI) m/z calcd for $C_{15}H_{11}ClNO$ $[M+H]^+$ 256.0524, found 256.0523.



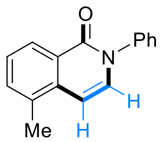
2-Phenyl-1(2*H*)-6--bromoisoquinolinone (3p)

Yellow solid (37.1 mg, 62% yield). PE/DCM = 2:1, R_f = 0.35)^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.60 Hz, 1H), 7.73 (s, 1H), 7.61 (d, *J* = 8.60 Hz, 1H), 7.51 (t, *J* = 7.67 Hz, 2H), 7.42 (d, *J* = 7.71 Hz, 3H), 7.21 (d, *J* = 7.43 Hz, 1H), 6.48 (d, *J* = 7.48 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 141.0, 138.5, 133.5, 130.4, 130.1, 129.3, 128.4, 128.3, 127.7, 126.7, 125.2, 105.0. IR: 3081, 3047, 2986, 2875, 1658, 1632, 1578, 1283, 872, 772, 681 cm^{-1}. HRMS (ESI) Calcd for $C_{15}H_{11}BrNO$ $[M+H]^+$ 300.0019, found 300.0013.



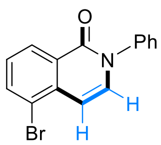
2-Phenyl-1(2*H*)-6 -Trifluoroisoquinolinone (3q)

White solid (29.5 mg, 51% yield). PE/DCM = 1:1, R_f = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.42 Hz, 1H), 7.84 (s, 1H), 7.72 (d, *J* = 8.50 Hz, 1H), 7.52 (d, *J* = 9.28 Hz, 2H), 7.45 (t, *J* = 8.06 Hz, 3H), 7.28 (d, *J* = 7.46 Hz, 1H), 6.63 (d, *J* = 7.44 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 161.2, 140.8, 137.0, 134.3 (q, *J* = 40.00 Hz), 133.6, 129.4, 129.4, 128.6, 128.4, 126.7, 123.6 (q, *J* =272.93 Hz), 123.3 (q, *J* =3.90 Hz), 123.1 (q, *J* = 3.07 Hz), 105.7. ^{19}F NMR (375 MHz, $CDCl_3$) δ -63.0. IR: 3085, 3045, 2968, 2875, 1668, 1654, 1518, 1129, 755, 694 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{11}F_3NO$ $[M+H]^+$ 290.0787, found 290.0780.



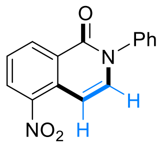
2-Phenyl-1(2*H*)-5-methylisoquinolinone (3r)

White solid (30.6 mg, 65% yield). PE/DCM = 1:1, R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.03 Hz, 1H), 7.51 (t, *J* = 7.50 Hz, 3H), 7.47 – 7.38 (m, 4H), 7.23 (d, *J* = 7.62 Hz, 1H), 6.70 (d, *J* = 7.65 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 141.0, 135.6, 133.0, 132.9, 131.4, 128.9, 127.7, 126.5, 126.5, 126.4, 125.9, 102.6, 18.7. IR: 3063, 3005, 2916, 2845, 1678, 1623, 1523, 1257, 776, 698 cm^{-1}. HRMS (ESI) mz/z Calcd for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1063.



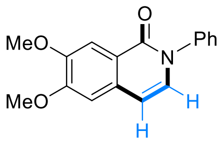
2-Phenyl-1(2*H*)-5-bromoisoquinolinone (3s)

Yellow solid (35.3 mg, 59% yield). PE/DCM = 1:1, R_f = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 9.03 Hz, 1H), 7.92 (dd, *J* = 7.71, 1.26 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.46 – 7.40 (m, 3H), 7.36 (t, *J* = 7.89 Hz, 1H), 7.28 (d, *J* = 7.72 Hz, 1H), 6.92 (d, *J* = 7.70 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 140.9, 136.4, 136.3, 133.3, 129.4, 128.3, 128.1, 127.9, 127.7, 126.7, 120.6, 104.8. IR: 3087, 3046, 2985, 2867, 1663, 1653, 1522, 758, 683 cm^{-1}. HRMS (ESI) Calcd for $C_{15}H_{11}BrNO$ [M+H]$^+$ 300.0019, found 300.0015.



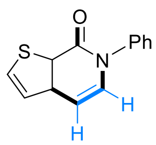
2-Phenyl-1(2*H*)-5-nitroisoquinolinone (3t)

White solid (31.9 mg, 60% yield). PE/DCM = 1:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.00 Hz, 1H), 7.69 (t, *J* = 7.46 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.47 (s, 1H), 7.41 (t, 2H), 7.35 (d, *J* = 7.42 Hz, 1H), 7.14 (d, *J* = 7.42 Hz, 1H), 6.58 (d, *J* = 7.42 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 141.9, 136.6, 134.4, 132.4, 131.2, 129.9, 128.0, 127.0, 126.1, 125.7, 124.9, 106.3. IR(neat): 3085, 3042, 2957, 2866, 1660, 1654, 1530, 1365, 1286, 873, 775, 684 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}N_2O_3$ [M+H]$^+$ 267.0764, found 267.0763.



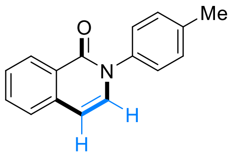
2-Phenyl-1(2*H*)-6,7-dimethoxyisoquinolinone (3u)

White solid (43.8 mg, 78% yield). PE/DCM = 1:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.49 (t, 2H), 7.45 – 7.38 (m, 3H), 7.11 (d, *J* = 7.35 Hz, 1H), 6.91 (s, 1H), 6.49 (d, *J* = 7.36 Hz, 1H), 4.00 (d, *J* = 3.45 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.00, 153.25, 149.10, 141.21, 132.21, 130.54, 128.85, 127.64, 126.53, 120.01, 107.79, 105.73, 105.50, 55.86, 55.80. IR: 3065, 3042, 2988, 2876, 1653, 1621, 1507, 1275, 1060, 867, 758, 690 cm^{-1}. HRMS (ESI) Calcd for $C_{17}H_{16}NO_3$ [M+H]$^+$ 282.1125, found 282.1120.



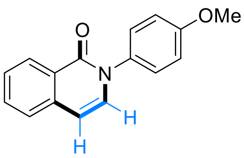
6-Phenyl-3a,7a-dihydrothieno[2,3-c]pyridin-7(6*H*)-one (3v)

White solid (28.6 mg, 63% yield). PE/DCM = 1:1, R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 5.16 Hz, 1H), 7.48 (t, 2H), 7.45 – 7.38 (m, 3H), 7.23 (t, 2H), 6.70 (d, *J* = 7.16 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 144.9, 140.4, 133.6, 133.2,130.4, 128.8, 127.8, 126.5, 123.9, 102.7. IR: 3082, 3041, 2985, 1653, 1624, 1507, 1390, 1276, 1132, 1060, 758, 690 cm^{-1}. HRMS (ESI) Calcd for $C_{13}H_{10}NOS$ $[M+H]^+$ 228.0478, found 228.0482.



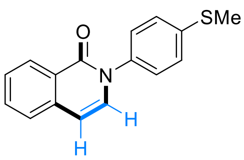
2-(4-Methylphenyl)-1(2*H*)-isoquinolinone (3a')

White solid (34.3 mg, 73% yield). PE/DCM = 2:1, R_f = 0.28. ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.07, 1.24 Hz, 1H), 7.67 (t, *J* = 7.55 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.31 (s, 4H), 7.17 (d, *J* = 7.39 Hz, 1H), 6.56 (d, *J* = 7.36 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 139.1, 138.3, 1374, 132.8, 132.6, 130.2, 128.6, 127.4, 126.9, 126.2, 106.4, 21.5. IR: 3063, 3042, 2943, 2896, 1665, 1654, 1518, 1281, 784, 732, 682 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1074.



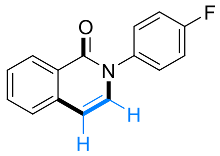
2-(4-Methoxyphenyl)-1(2*H*)-isoquinolinone (3b')

White solid (37.7 mg, 75% yield). PE/DCM = 1:1, R_f = 0.28. ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 8.09, 1.25 Hz, 1H), 7.66 (s, 1H), 7.56 – 7.47 (m, 2H), 7.38 – 7.30 (m, 2H), 7.16 (d, *J* = 7.40 Hz, 1H), 7.00 (d, *J* = 8.88 Hz, 2H), 6.54 (d, *J* = 7.36 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 158.7, 136.7, 133.9, 132.1, 132.1, 127.8, 127.5, 126.7, 126.1, 125.5, 114.1, 105.6, 55.2. IR: 3065, 3042, 3018, 2989, 1667, 1654, 1518, 1281, 784, 756, 682 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{14}NO_2$ $[M+H]^+$ 252.1019, found 252.1010



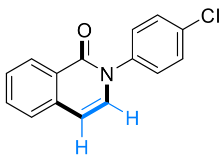
2-(4-(Methylthio)phenyl)-1(2*H*)-isoquinolinone(3c')

White solid (40.1mg, 75% yield). PE/DCM = 1:1, R_f = 0.35. ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.03 Hz, 1H), 7.70 (t, 1H), 7.57 (dd, *J* = 17.43, 7.48 Hz, 2H), 7.39 (s, 4H), 7.19 (d, *J* = 7.36 Hz, 1H), 6.60 (d, *J* = 7.38 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 138.4, 138.0, 136.6, 132.2, 131.7, 127.9, 126.8, 126.8, 126.7, 126.1, 125.6, 105.9, 15.5. IR: 3085，3048, 2987, 2854, 1689, 1653, 1649, 1547, 786, 683 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{14}NOS$ $[M+H]^+$ 268.0791, found 268.0792.



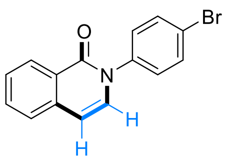
2-(4-Fluorophenyl)-1(2*H*)-isoquinolinone (3d')

White solid (32.9 mg, 69% yield). PE/DCM = 1:1, R_f = 0.32, ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.06 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.58 – 7.49 (m, 2H), 7.41 (dd, *J* = 8.92, 4.79 Hz, 2H), 7.21 – 7.09 (m, 3H), 6.57 (d, *J* = 7.40 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ162.3, 162.2(d, *J* = 246.3 Hz), 137.5, 137.3, 132.9, 132.2, 128.9(d, *J* = 8.6 Hz), 128.5, 127.5, 126.7, 126.3, 116.4 (d, *J* = 22.8Hz), 106.6. ^{19}F NMR (375 MHz, $CDCl_3$) δ -113.3. IR: 3068, 3041, 3012 2918, 1694, 1651, 1522, 1269, 791, 755, 698 cm^{-1}. HHRMS (ESI) m/z Calcd for $C_{15}H_{11}FNO$ $[M+H]^+$ 240.0819, found 240.0815.



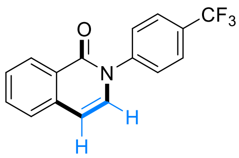
2-(4-Chlorophenyl)-1(2*H*)-isoquinolinone (3e')

White solid (34.7 mg, 68% yield). PE/DCM = 1:1, R_f = 0.35, ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 9.30 Hz, 1H), 7.68 (t, *J* = 7.53 Hz, 1H), 7.54 (dd, *J* = 15.72, 7.52 Hz, 2H), 7.47 (d, *J* = 8.70 Hz, 2H), 7.41 – 7.35 (m, 2H), 7.13 (d, *J* = 7.42 Hz, 1H), 6.58 (d, *J* = 7.41 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 140.0, 137.3, 134.1, 133.0, 131.9, 129.7, 128.5, 128.5, 127.6, 126.7, 126.3, 106.9. IR: 3069, 3043, 3019 2819, 1643, 1652, 1341, 820, 795, 677 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}ClNO$ $[M+H]^+$ 256.0524, found 256.0520.



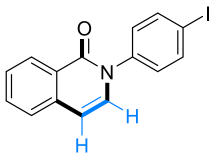
2-(4-Bromophenyl)-1(2*H*)-isoquinolinone (3f')

White solid (38.9 mg, 65% yield). PE/DCM = 1:1, R_f = 0.32, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, 1H), 7.68 (t, *J* = 8.06 Hz, 1H), 7.63 (d, *J* = 8.65 Hz, 2H), 7.54 (q, 2H), 7.33 (d, *J* = 8.65 Hz, 2H), 7.13 (d, *J* = 7.43 Hz, 1H), 6.58 (d, *J* = 7.43 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 140.6, 137.3, 133.0, 132.7, 131.9, 128.8, 128.6, 127.6, 126.7, 126.3, 122.2, 106.9. IR: 3061, 3045, 3012 2918, 1694, 1651, 1522, 1269, 791, 755, 698 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}BrNO$ $[M+H]^+$ 300.0019, found 300.0018.



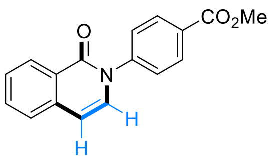
2-(4-Trifluorophenyl)-1(2*H*)-isoquinolinone (3g')

White solid (34.7 mg, 60% yield). PE/DCM = 1:1, R_f = 0.38, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.99 Hz, 1H), 7.78 (d, *J* = 8.26 Hz, 2H), 7.74 – 7.68 (m, 1H), 7.63 – 7.52 (m, 4H), 7.17 (d, *J* = 7.43 Hz, 1H), 6.62 (d, *J* = 7.45 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 144.2, 136.9, 132.9, 131.2, 130.1 (q, *J* = 32.9 Hz), 128.3, 127.5, 127.3, 126.4(4), 126.1, 123.8 (q, *J* = 270 Hz), 106.9. ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.6. IR: 3060, 3041, 3018, 2918, 1665, 1651, 1123, 792, 682 cm^{-1}. HRMS (ESI) m/z calcd for $C_{16}H_{11}F_3NO$ $[M+H]^+$ 290.0787, found 290.0785.



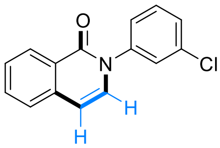
2-(4-Iodophenyl)-1(2*H*)-isoquinolinone (3h')

White solid (44.4 mg, 64% yield). PE/DCM = 1:1, R_f = 0.30, H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, *J* = 1.83 Hz, 1H), 7.94 (dd, *J* = 8.36, 1.88 Hz, 1H), 7.51 (t, *J* = 7.46 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.30 (d, *J* = 8.34 Hz, 1H), 7.20 (d, *J* = 7.41 Hz, 1H), 6.51 (d, *J* = 7.40 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 140.9, 140.7, 136.8, 135.8, 132.6, 129.0, 128.0, 127.7, 127.3, 126.4, 105.3, 91.6. IR: 3069, 3045, 3012, 2918, 1648, 1528, 1123, 789, 684 cm^{-1}.HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{11}INO$ $[M+H]^+$ 347.9880, found: 347.9888.



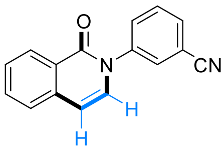
Methyl 4-(1-oxoisoquinolin-2(1*H*)-yl)benzoate(3i')

White solid (38.5 mg, 69% yield). PE/DCM = 1:1, R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.01 Hz, 1H), 8.18 (d, *J* = 8.44 Hz, 2H), 7.69 (t, *J* = 7.49 Hz, 1H), 7.54 (q, *J* = 7.55 Hz, 4H), 7.18 (d, *J* = 7.44 Hz, 1H), 6.60 (d, *J* = 7.44 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 161.4, 144.8, 136.6, 132.5, 131.0, 130.3, 129.2, 127.9, 127.1, 126.5, 126.1, 125.7, 106.5, 52.0. IR: 3068, 3040, 3019, 2926, 1655, 1527, 1225, 763, 676 cm^{-1}. HRMS (ESI) m/z calcd for $C_{17}H_{14}NO_3$ $[M+H]^+$ 280.0968, found 280.0960.



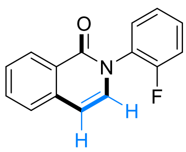
2-(3-Chlorophenyl)-1(2*H*)-isoquinolinone (3j')

White solid (31.6 mg, 62% yield). PE/DCM = 2:1, R_f = 0.28, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.06 Hz, 1H), 7.69 (t, *J* = 7.55 Hz, 1H), 7.55 (q, 2H), 7.49 – 7.37 (m, 3H), 7.34 (d, *J* = 5.75 Hz, 1H), 7.14 (d, *J* = 7.42 Hz, 1H), 6.58 (d, *J* = 7.44 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 142.5, 137.2, 135.0, 133.1, 131.8, 130.5, 128.6, 128.5, 127.6, 127.6,126.7, 126.3, 125.5, 106.9. IR: 3065, 3043, 3018, 2919, 1662, 1654, 762, 679 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}ClNO$ $[M+H]^+$ 256.0524, found 256.0519.



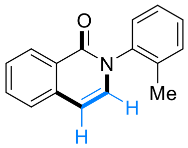
2-(3-Cyanophenyl)-1(2*H*)-isoquinolinone (3k')

White solid (29.7 mg, 60% yield). PE/DCM = 1:1, R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.01 Hz, 1H), 7.79 (s, 1H), 7.72 (q, 3H), 7.66 – 7.53 (m, 3H), 7.14 (d, *J* = 7.44 Hz, 1H), 6.63 (d, *J* = 7.45 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 142.2, 137.2, 133.4, 131.9, 131.2, 130.8, 130.5, 128.6, 127.9, 126.6, 126.5, 118.1, 113.8, 107.5. IR: 3052, 3041, 3012, 2918, 1657, 1648, 1135, 752, 679 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{11}N_2O$ $[M+H]^+$ 247.0866, found 247.0861.



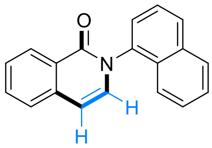
2-(2-Fluorophenyl)-1(2*H*)-isoquinolinone (3l')

White solid (30.1 mg, 63% yield). PE/DCM = 1:1, R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.99 Hz, 1H), 7.71 (t, *J* = 6.90 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.50 – 7.40 (m, 2H), 7.33 – 7.27 (m, 2H), 7.10 (d, *J* = 7.40 Hz, 1H), 6.60 (d, *J* = 7.42 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6,157.5(d, *J* = 250.6 Hz), 137.1, 132.7, 132.0, 130.2 (d, *J* = 7.8 Hz),129.1, 128.8 (d, *J* = 13.1 Hz), 128.3, 127.2, 126.4, 126.0, 124.7 (d, *J* = 3.8 Hz), 116.8 (d, *J* = 19.7 Hz), 106.4. ^{19}F NMR (375 MHz, $CDCl_3$) δ -120.3 (d, *J* = 10.69 Hz). IR: 3059, 3037, 3012, 2858, 1675, 1656, 1423, 756, 676 cm^{-1}. HRMS (ESI). m/z Calcd for $C_{15}H_{11}FNO$ $[M+H]^+$ 240.0819, found 240.0825.



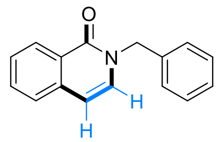
2-(2-Methylphenyl)-1(2*H*)-isoquinolinone (3m')

White solid (28.2 mg, 60% yield). PE/DCM = 2:1, R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.06 Hz, 1H), 7.69 (t, *J* = 7.55 Hz, 1H), 7.58 (d, *J* = 7.95 Hz, 1H), 7.53 (t, *J* = 7.64 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.25 (d, *J* = 7.85 Hz, 1H), 7.04 (d, *J* = 7.36 Hz, 1H), 6.58 (d, *J* = 7.38 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 140.2, 137.0, 135.1, 132.2, 131.8, 130.7, 128.5, 127.9, 127.2, 126.8, 126.7, 126.3, 125.6, 105.7, 17.4. IR: 3067, 3041, 2932, 2856, 1663, 1654, 1524, 1278, 758, 686 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1072.



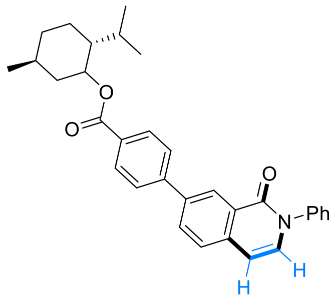
2-Naphthalen-1(2*H*)-isoquinolinone(3n')

White solid (36.3 mg, 67% yield). PE/DCM = 2:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.07 Hz, 1H), 7.99 (t, *J* = 8.13 Hz, 2H), 7.76 (t, 1H), 7.67 – 7.48 (m, 7H), 7.16 (d, *J* = 7.36 Hz, 1H), 6.66 (d, *J* = 7.36 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 137.7, 137.0, 134.1, 132.6, 132.3, 129.3, 128.9, 128.1, 128.0, 126.9, 126.8, 126.2,126.1, 125.7, 125.2, 125.1, 122.2, 105.7. IR: 3083, 3039, 3012, 2986, 1676, 1648, 1526, 1510, 1269, 754, 698 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{19}H_{14}NO$ $[M+H]^+$ 272.1070, found 272.1075.



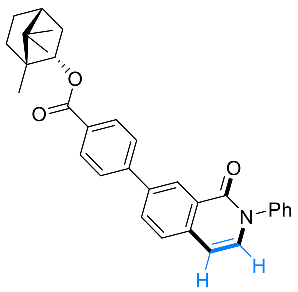
2-Benzyl-1(2*H*)-isoquinolinone (3o')

White solid (19.7mg, 42% yield). PE/DCM = 1:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.63 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.50 (t, *J* = 7.11 Hz, 2H), 7.33 (d, *J* = 3.98 Hz, 4H), 7.31 – 7.27 (m, 1H), 7.09 (d, *J* = 7.38 Hz, 1H), 6.49 (d, *J* = 7.39 Hz, 1H), 5.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ162.6, 137.3, 137.2, 132.5, 131.6, 129.1, 128.4, 128.2, 128.1, 127.2, 126.6, 126.2, 106.8, 52.0. IR: 3085，3041, 3012, 2918, 2876, 1706, 1662, 1518, 1272, 1181, 1107, 839, 756, 702 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{16}H_{14}NO$ $[M+H]^+$ 236.1070, found 236.1064.



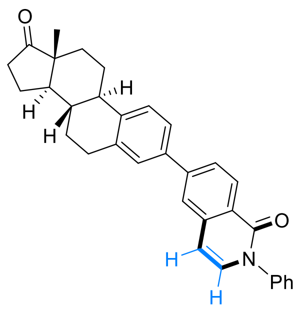
(2R,5S)-2-Isopropyl-5-methylcyclohexyl-4-(1-oxo-2-phenyl-1,2-dihydroisoquinolin-7-yl)benzoate (3a'')

White solid (71.8 mg, 75% yield). PE/DCM = 2:1, R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 1.91 Hz, 1H), 8.15 (d, *J* = 8.31 Hz, 2H), 7.95 (dd, *J* = 8.25, 2.01 Hz, 1H), 7.78 (d, *J* = 8.32 Hz, 2H), 7.65 (d, *J* = 8.26 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.45 (dt, *J* = 8.27, 2.94 Hz, 3H), 7.22 (d, *J* = 7.39 Hz, 1H), 6.61 (d, *J* = 7.40 Hz, 1H), 4.97 (td, *J* = 10.85, 4.39 Hz, 1H), 2.15 (d, *J* = 11.90 Hz, 1H), 2.00 (td, *J* = 6.91, 2.33 Hz, 1H), 1.82 – 1.67 (m, 3H), 1.58 (t, *J* = 10.14 Hz, 2H), 1.27 (d, *J* = 12.69 Hz, 1H), 1.16 – 1.11 (m, 1H), 0.94 (d, *J* = 6.30 Hz, 6H), 0.82 (d, *J* = 6.93 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 162.3,144.5,141.5, 139.0, 136.93, 132.9, 131.7, 130.5, 130.2, 129.6, 128.5, 127.3, 127.2, 127.1, 127.0, 126.9, 106.1, 75.2, 47.5, 41.3, 34.6, 31.7, 26.8, 23.9, 22.3, 21.1, 16.8. IR: 3335, 2955, 1706, 1662, 1519, 1272, 1182, 1108, 839, 756 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{32}H_{34}NO_3$ $[M+H]^+$ 480.2533, found 480.2534.



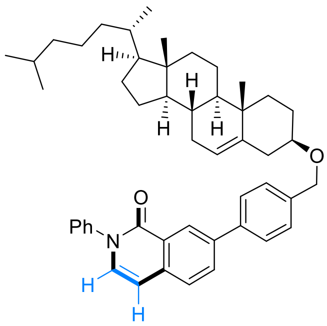
(1R,2S,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl-4-(1-oxo-2-phenyl-1,2-dihydroisoquinolin-7-yl)benzoate (3b'')

White solid (62.0 mg, 65% yield). PE/DCM = 2:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 1.95 Hz, 1H), 8.16 (d, *J* = 8.19 Hz, 2H), 7.96 (dd, *J* = 8.28, 2.00 Hz, 1H), 7.79 (d, *J* = 8.16 Hz, 2H), 7.67 (d, *J* = 8.14 Hz, 1H), 7.51 (d, *J* = 7.44 Hz, 2H), 7.45 (d, *J* = 7.92 Hz, 3H), 7.23 (d, *J* = 7.41 Hz, 1H), 6.62 (d, *J* = 7.40 Hz, 1H), 5.15 (d, *J* = 9.80 Hz, 1H), 2.55 – 2.42 (m, 1H), 2.22 – 2.11 (m, 1H), 1.82 (tt, *J* = 7.95, 3.98 Hz, 1H), 1.75 (t, *J* = 4.51 Hz, 1H), 1.48 – 1.39 (m, 1H), 1.36 – 1.31 (m, 1H), 1.18 – 1.11 (m, 1H), 0.98 (s, 3H), 0.93 (d, *J* = 3.42 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9,162.3,144.6, 141.6, 139.1, 137.0, 133.0, 131.7, 130.5, 130.3, 129.6, 129.4,128.5, 127.4, 127.2, 127.1, 127.1, 127.0, 106.1, 80.9, 49.43, 48.2, 45.3, 37.2, 28.4, 27.7, 20.1, 19.2, 14.0. IR: 3425, 2955, 1716, 1659, 1636, 1524, 1273, 1112, 756 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{32}H_{32}NO_3$ $[M+H]^+$ 478.2377, found 478.2375.



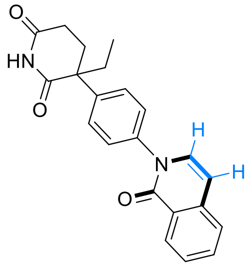
6-((8S,9R,13R,14R)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)-2-phenylisoquinolin-1(2*H*)-one (3c'')

White solid (64.3 mg, 68% yield). PE/DCM = 1:1, R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.55 Hz, 1H), 7.74 (d, *J* = 6.98 Hz, 2H), 7.54 – 7.48 (m, 3H), 7.47 – 7.41 (m, 5H), 7.21 (d, *J* = 7.45 Hz, 1H), 6.61 (d, *J* = 7.45 Hz, 1H), 3.03 (d, *J* = 13.86 Hz, 2H), 2.52 (dt, *J* = 19.32, 10.35 Hz, 2H), 2.38 (t, *J* = 11.11 Hz, 1H), 2.23 – 2.06 (m, 3H), 2.01 (d, *J* = 9.17 Hz, 1H), 1.66 (t, *J* = 12.19 Hz, 3H), 1.56 (t, *J* = 11.75 Hz, 3H), 0.94 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 220.4, 161.5, 144.7, 141.0, 139.7, 137.1, 136.8, 132.2, 128.9, 128.5, 127.7, 127.6, 126.5, 125.8, 125.7, 124.9, 124.4, 123.4, 106.0, 50.1, 47.6, 44.0, 37.8, 35.5, 31.2, 29.2, 26.1, 25.4, 21.2, 13.5. IR: 3043, 3012, 2954, 1678, 1657, 1521, 1436, 1269, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{33}H_{32}NO_2$ $[M+H]^+$ 474.2428, found 474.2425.



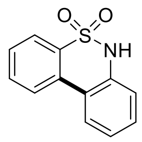
7-(4-((((3R,8R,9R,10S,13S,14R,17S)-10,13-Dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)methyl)phenyl)-2-phenylisoquinolin-1(2*H*)-one (3d'')

White solid (87.6 mg, 63% yield). PE/DCM = 1:1, R_f = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 1.87 Hz, 1H), 7.93 (dd, *J* = 8.26, 1.87 Hz, 1H), 7.69 (d, *J* = 7.94 Hz, 2H), 7.63 (d, *J* = 8.23 Hz, 1H), 7.52 (t, *J* = 7.65 Hz, 2H), 7.46 (dd, *J* = 7.95, 2.08 Hz, 5H), 7.20 (d, *J* = 7.39 Hz, 1H), 6.60 (d, *J* = 7.39 Hz, 1H), 5.37 (d, *J* = 5.03 Hz, 1H), 4.62 (s, 2H), 3.38 – 3.26 (m, 1H), 2.46 (dd, *J* = 15.37, 4.20 Hz, 1H), 2.31 (t, *J* = 12.43 Hz, 1H), 2.04 – 1.94 (m, 3H), 1.91 – 1.79 (m, 2H), 1.52 (dt, *J* = 17.63, 6.21 Hz, 8H), 1.34 (d, *J* = 7.89 Hz, 3H), 1.27 (d, *J* = 3.47 Hz, 2H), 1.15 – 1.05 (m, 6H), 1.03 (s, 3H), 1.01 – 0.94 (m, 2H), 0.91 (d, *J* = 6.53 Hz, 3H), 0.86 (dd, *J* = 6.59, 1.66 Hz, 6H), 0.68 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4,141.7, 141.2, 140.1,139.5,139.0, 136.3, 132.4, 131.8, 129.6, 128.5, 128.4, 127.5, 127.2, 127.2, 126.9, 126.5, 121.9, 106.3, 79.0,69.9, 57.1, 56.4, 50.5, 42.6, 40.1, 39.8, 39.5, 37.5, 37.2, 36.5, 36.1, 32.3, 32.2, 28.8, 28.5, 28.3, 24.6, 24.1, 23.1, 22.9, 21.4, 19.7, 19.0, 12.2. IR(neat): 3045, 2941, 2867, 1653, 1636, 1541, 1508, 1278, 1089, 752 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{49}H_{62}NO_2$ $[M+H]^+$ 696.4775, found 696.4773.



3-Ethyl-3-(4-(1-oxoisoquinolin-2(1*H*)-yl)phenyl)piperidine-2,6-dione(3e')

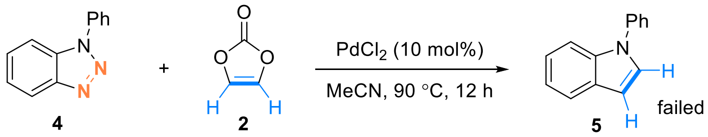
White solid (56.2 mg, 78% yield). PE/DCM = 1:1, R_f = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.00 Hz, 1H), 8.23 (s, 1H), 7.71 – 7.65 (m, 1H), 7.53 (dd, *J* = 16.63, 8.53 Hz, 2H), 7.47 (d, *J* = 8.49 Hz, 2H), 7.42 (d, *J* = 8.67 Hz, 2H), 7.17 (d, *J* = 7.41 Hz, 1H), 6.59 (d, *J* = 7.43 Hz, 1H), 2.69 – 2.61 (m, 1H), 2.54 – 2.39 (m, 2H), 2.33 – 2.23 (m, 1H), 2.11 (dt, *J* = 14.66, 7.28 Hz, 1H), 1.95 (dq, *J* = 14.53, 7.38 Hz, 1H), 0.91 (t, *J* = 7.38 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 175.10, 172.39, 162.22, 140.89, 138.97, 137.26, 133.00, 132.03, 128.54, 127.62, 127.59, 127.42, 126.71, 126.29, 106.88, 51.22, 33.23, 29.54, 27.17, 9.36. IR: 3063, 3012, 2985, 1670, 1636, 1541, 1269, 1195, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{22}H_{21}N_2O_3$ $[M+H]^+$ 361.1547, found 361.1545.



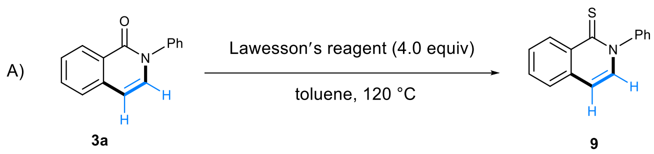
6*H*-dibenzo[c,e][1,2]thiazine 5,5-dioxide(8)

White solid (32.8mg, 71% yield). PE/DCM = 1:1, R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, *J* = 6.29 Hz, 3H), 7.72 (t, *J* = 7.79 Hz, 1H), 7.57 (t, *J* = 7.65 Hz, 1H), 7.42 (t, *J* = 7.73 Hz, 1H), 7.33 (d, *J* = 7.77 Hz, 1H), 7.24 (s, 1H), 7.14 (d, *J* = 7.96 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.2, 132.8, 132.7, 130.7, 128.6, 125.7,125.7, 125.5, 123.4, 122.4, 121.0. IR: 3219, 3021, 2914, 2876, 1745, 1693, 1522, 1269, 755 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{12}H_{10}NO_2S$ $[M+H]^+$ 232.0427, found 232.0427.

5. Further derivatives of method

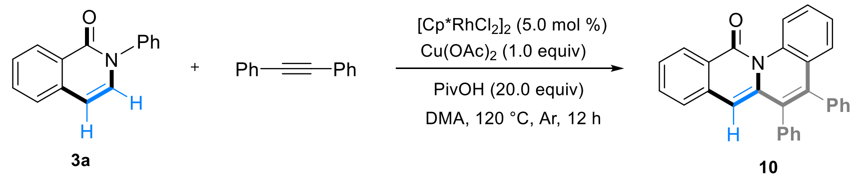


A pressure tube equipped with a stir bar was charged with **4**[7] (19.5 mg, 0.1 mmol), vinylene carbonate **2** (25.8 mg, 0.3 mmol), $PdCl_2$ (1.7 mg, 10.0 mol%) in CH_3CN (0.5 mL). The reaction mixture was stirred at 90 °C for 12 h under argon atmosphere in an oil bath. After cooling to room temperature, it was further detected by NMR spectroscopy and showed no product **5**.



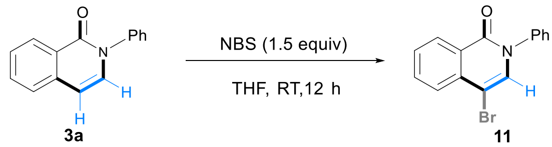
To a solution of 2-Phenyl-1(2*H*)-isoquinolinone **3a** (0.2 mmol, 44.6 mg, 1.0 equiv.) in toluene (6.0 mL) was added Lawesson's reagent (0.8 mmol, 32.3 mg, 4.0 equiv.). The reaction was stirred at 120 °C for 12 h. The reaction mixture was filtered through a pad of celite and washed with DCM. The combined organic layer was concentrated in vacuo. The crude product was purified by manual column chromatography on silica gel to give **9** as a yellow solid (29.9 mg, 63% yield). R_f = 0.4 (PE: EA = 10:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 8.30 Hz, 1H), 7.72 (t, *J* = 7.54 Hz, 1H), 7.65 – 7.53 (m, 4H), 7.49 (d, *J* = 7.28 Hz, 1H), 7.39 (dd, *J* = 16.90, 7.28 Hz, 3H), 6.94 (d, *J* = 7.07 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 146.0, 134.0, 133.2, 132.4, 132.3, 132.1, 129.3, 128.5, 128.4, 126.7, 126.4, 111.2. IR: 3063, 3042, 2986, 1725, 1694, 1653, 1528, 1269, 755, 687 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{12}NS$ $[M+H]^+$ 238.0685, found 238.0684.

B)



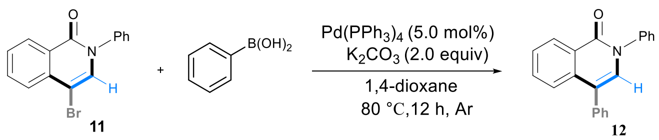
To a solution of 2-Phenyl-1(2*H*)-isoquinolinone **3a** (0.2 mmol, 44.6 mg) was added 1,2-diphenylethyne (53.5 mg, 0.3 mmol), $[Cp^*RhCl_2]_2$ (6.2 mg, 5.0 mol%), $Cu(OAc)_2$（36.4 mg, 0.2 mmol), PivOH (408.5 mg, 40.0 mmol) and DMA (1.0 mL) under Ar . The tube was sealed with a Teflon-coated cap and the reaction solution was heated at 120 °C for 12 h. The reaction mixture was filtered through a pad of celite and washed with DCM. The combined organic layer was concentrated in vacuo. The crude product was purified by manual column chromatography on silica gel to give **10** as a yellow solid (32.6 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, *J* = 8.70 Hz, 1H), 8.58 (d, *J* = 8.14 Hz, 1H), 7.62 (s, 1H), 7.49 (dt, *J* = 15.44, 8.06 Hz, 2H), 7.39 (d, *J* = 7.95 Hz, 1H), 7.23 (q, *J* = 5.30, 4.83 Hz, 7H), 7.11 (dd, *J* = 17.31, 7.44 Hz, 5H), 6.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 138.1, 137.5, 137.1, 136.9, 135.2, 135.0, 134.2, 132.4, 130.5, 130.2, 128.4, 128.2, 127.9, 127.6, 127.3, 127.1, 127.0, 126.8, 126.3, 125.8, 125.4, 124.3, 121.6, 105.5. IR: 3063, 3014, 2918, 1723, 1646, 1522, 1498, 1268, 755, 698 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{29}H_{20}NO$ $[M+H]^+$ 398.1539, found 398.1538.

C)

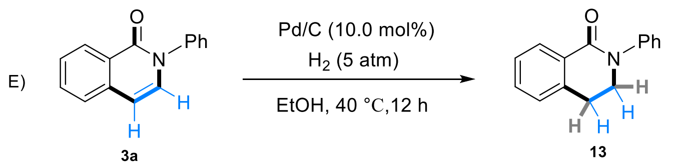


Isoquinolone **3a** (44.6 mg, 0.2 mmol) was placed in a single-necked round-bottomed flask fitted with a stirring bar. THF (1.0 mL) was added via a syringe under argon. *N*-Bromosuccinimide (53.5 mg, 0.3 mmol) was added under argon atmosphere. The reaction mixture was allowed to stir at room temperature for 12 h. The solvent was removed under reduced pressure. The residue was purified by manual column chromatography on silica gel to provide 4-bromoisoquinolone **11** as a white solid (55.0 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 9.35 Hz, 1H), 7.87 (d, *J* = 1.16 Hz, 1H), 7.80 (t, 1H), 7.60 (t, *J* = 8.19 Hz, 1H), 7.51 (t, 3H), 7.44 (q, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 140.8, 135.8, 133.6, 132.9, 129.7, 129.0, 128.8, 128.5, 127.0, 126.2, 100.6. IR: 3065, 2916, 2845, 1672, 1661, 1518, 1270, 755, 691 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{11}BrNO$ $[M+H]^+$ 300.0019, found 300.0022.

D)

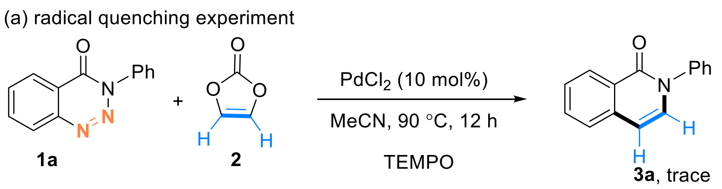


To a 10.0 mL round bottom flask charged with $[Pd(PPh_3)_4]$ (11.6 mg, 5.0 mol%) under argon was added brominated isoquinolinone **11** (59.8 mg, 0.2 mmol) and arylboronic acid (36.6 mg, 1.5 equiv) with 3 mL of 1,4-dioxane (1.0 mL). K_2CO_3 (55.3 mg, 2.0 equiv) was then added to this solution. The mixture was heated in an oil bath at 80 °C under argon for12 h. The reaction mixture was diluted with 15 mL of H_2O at room temperature and extracted with ethyl acetate (10.0 mL×3). The combined organic layers were dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by manual column chromatography on silica gel to give **12** as white solid (50.5 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 8.03, 1.36 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.59 – 7.53 (m, 1H), 7.51 – 7.40 (m, 10H), 7.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 140.9, 136.1, 135.8, 132.2, 130.8, 129.6, 129.0, 128.3, 127.8, 127.4, 126.9, 126.5, 126.0, 124.4, 119.4. IR: 3065, 3006, 2916, 2873, 1658, 1516, 1270, 756, 693 cm^{-1}. HRMS (ESI): m/z calcd for $C_{21}H_{16}NO$ $[M+H]^+$ 298.1226, found 298.1229.

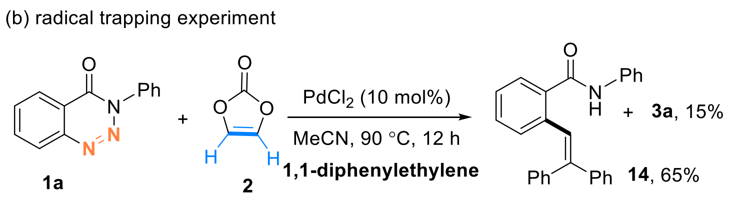


An autoclave equipped with a stir bar was charged with Pd/C (2.1 mg, 10.0 mol%), isoquinolone **3a** (44.2 mg, 0.2 mmol) in EtOH (1.0 mL), The reaction mixture was stirred under H_2 atmosphere (5 atm) at 40 °C for 12 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtered with celite and washed with EtOAc. The solvent was removed under reduced pressure. Then the residue was purified by manual column chromatography on silica gel to afford the desired product **13**. White solid (22.3 mg, 50% yield). PE/DCM = 1:1, R_f = 0.3.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.80, 1.40 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.42 – 7.35 (m, 5H), 7.24 (d, *J* = 8.23 Hz, 2H), 3.99 (t, *J* = 6.46 Hz, 2H), 3.14 (t, *J* = 6.45 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.18, 143.08, 138.27, 132.01, 129.69, 128.90, 128.73, 127.18, 126.91, 126.24, 125.30, 49.41, 28.62. IR: 3051, 3018, 2986, 1654, 1516, 1410, 1267, 754, 692 cm^{-1}. HRMS (ESI) m/z Calcd for $C_{15}H_{14}NO$ $[M+H]^+$ 224.1070, found 224.1067.

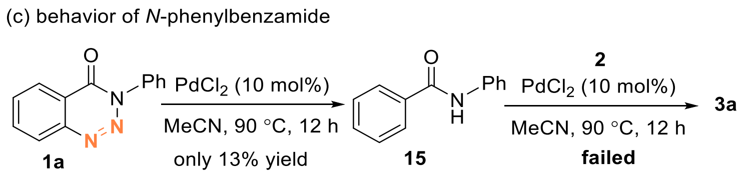
6. Mechanistic studies



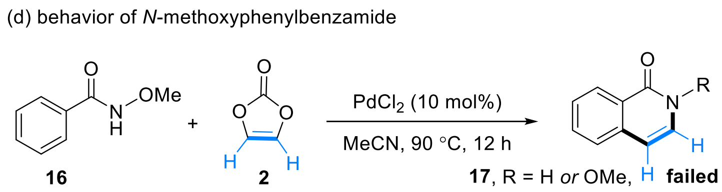
A pressure tube equipped with a stir bar was charged with **1a** (22.3 mg, 0.1 mmol), vinylene carbonate **2** (25.8 mg, 0.3 mmol), $PdCl_2$ (1.7 mg, 10.0 mol%), and TEMPO (31.2 mg, 0.2 mmol) in CH_3CN (0.5 mL). The reaction mixture was stirred at 90 °C for 12 h under argon atmosphere in an oil bath. After cooling to room temperature, it was further detected by NMR spectroscopy and showed trace product **3a**.



A pressure tube equipped with a stir bar was charged with **1a** (22.3 mg, 0.1 mmol), vinylene carbonate **2** (25.8 mg, 0.3 mmol), $PdCl_2$ (1.7 mg, 10 mol%), and ethene-1,1-diyldibenzene (36.1 mg, 0.2 mmol) in CH_3CN (0.5 mL). The reaction mixture was stirred at 90 °C for 12 h under argon atmosphere in an oil bath. After cooling to room temperature, it was filtered through a short pad of silica gel. The resulting residue was further purified by manual column chromatography on silica gel to give **14** (24.3 mg, 65% yield) and **3a** (3.3 mg, 15% yield).



A round bottom flask equipped with a stir bar was charged with the **1a** (223.3 mg, 1.0 mmol), $PdCl_2$ (17.0 mg, 10 mol%) and CH_3CN (3.0 mL) were loaded and the be heated to 90 °C in an oil bath and stirred for 12 h. After cooling to room temperature, it was filtered through a short pad of silica gel. The resulting residue was further purified by column chromatography (PE:EA = 5:1 as the eluent) to give **15** (25.6 mg, 15% yield). A pressure tube equipped with a stir bar was charged with **1a** (19.7 mg, 0.1 mmol), vinylene carbonate **2** (25.8 mg, 0.3 mmol), and $PdCl_2$ (1.7 mg, 10.0 mol%) in CH_3CN (0.5 mL). The reaction mixture was stirred at 90 °C for 12 h under argon atmosphere in an oil bath. After cooling to room temperature, it was further detected by NMR spectroscopy and showed no product **3a**.



A pressure tube equipped with a stir bar was charged with **16**[8] (15.1 mg, 0.1 mmol), vinylene carbonate **2** (25.8 mg, 0.3 mmol), and $PdCl_2$ (1.7 mg, 10.0 mol%) in CH_3CN (0.5 mL). The reaction mixture was stirred at 90 °C for 12 h under argon atmosphere in an oil bath. After cooling to room temperature, it was further detected by NMR spectroscopy and showed no product **17**.

7. References

(1) Vijaykumar, H.; Nitinkumar, U.; Murakami, M.; Cheng, C. H. *Adv. Synth. Catal.* **2017**, *2*, 284.

(2) Li, J.; Zheng, Y.; Huang, M.; Li, W. *Org. Lett*. **2020**, *22*, 5020.

(3) Chen, F.; Hu, S.; Li, S.; Tang, G.; Zhao, Y. *Green Chem*. **2021**, *23*, 296.

(4) Madasamy, K.; Balakrishnan, M. H.; Korivi, R.; Mannathan, S. *J. Org. Chem.* **2022**, *87*, 8752.

(5) Wang, F.; Tong, Y.; Zou, G. *Org. Lett*. **2022**, *24*, 5741.

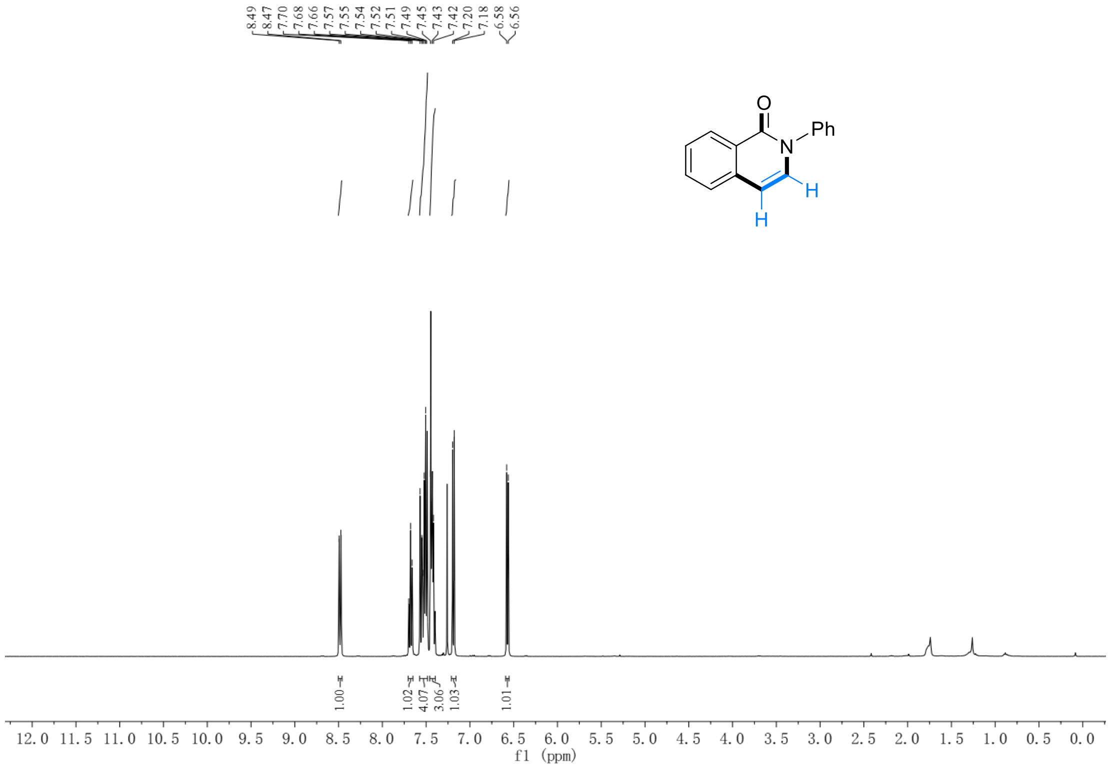
(6) Lee, J.; Oh, K.; Kim, H. Y. *Org. Lett.* **2020**, *22*, 474.

(7) Nasrollahzadeh, M.; Sajadi, S, M., Maham. M. *RSC Adv.***,** **2015**, *5*, 40628.

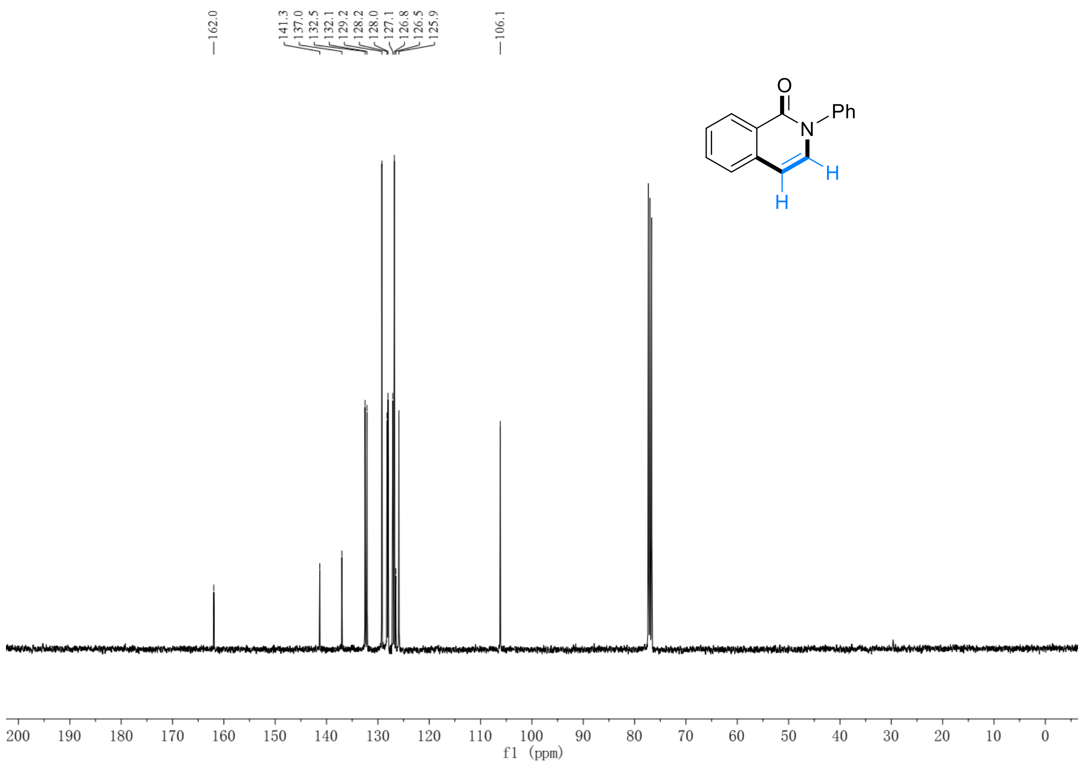
(8) Liu, P.; He, Z, T.; Tian, p.; Lin, G, Q.; Yuki, F. *J. Am. Chem. Soc.* **2014**, *136*, 15607.

8. NMR spectra

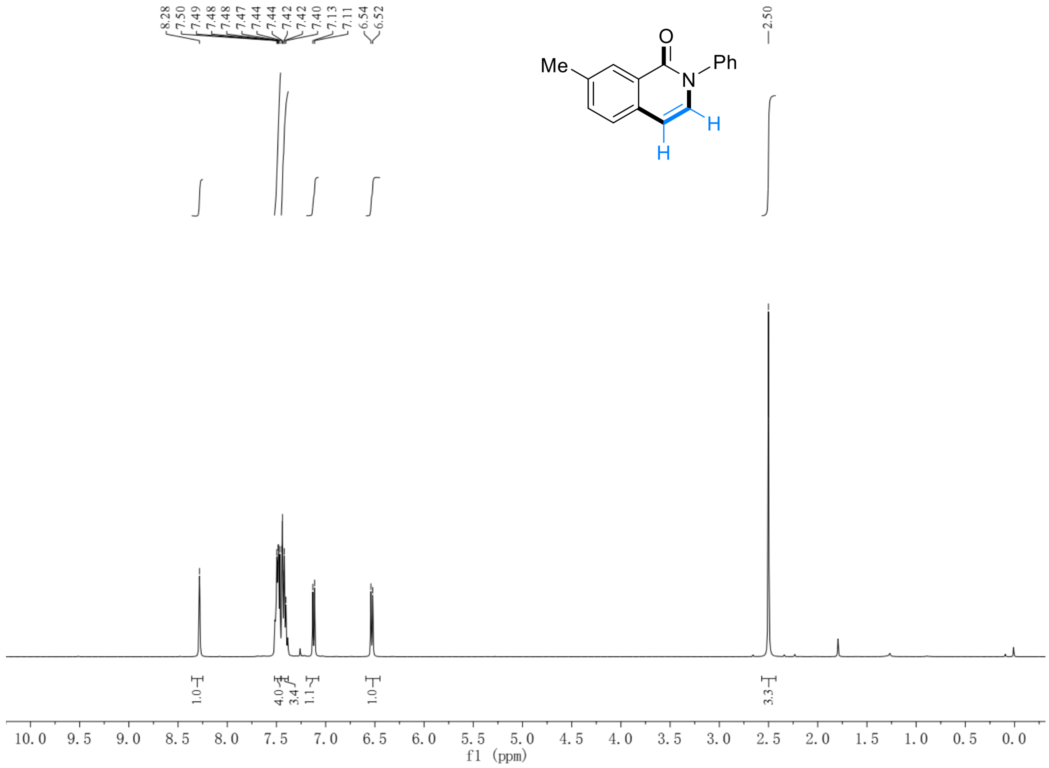
^{1}H NMR of **3a** (400 MHz, $CDCl_3$)



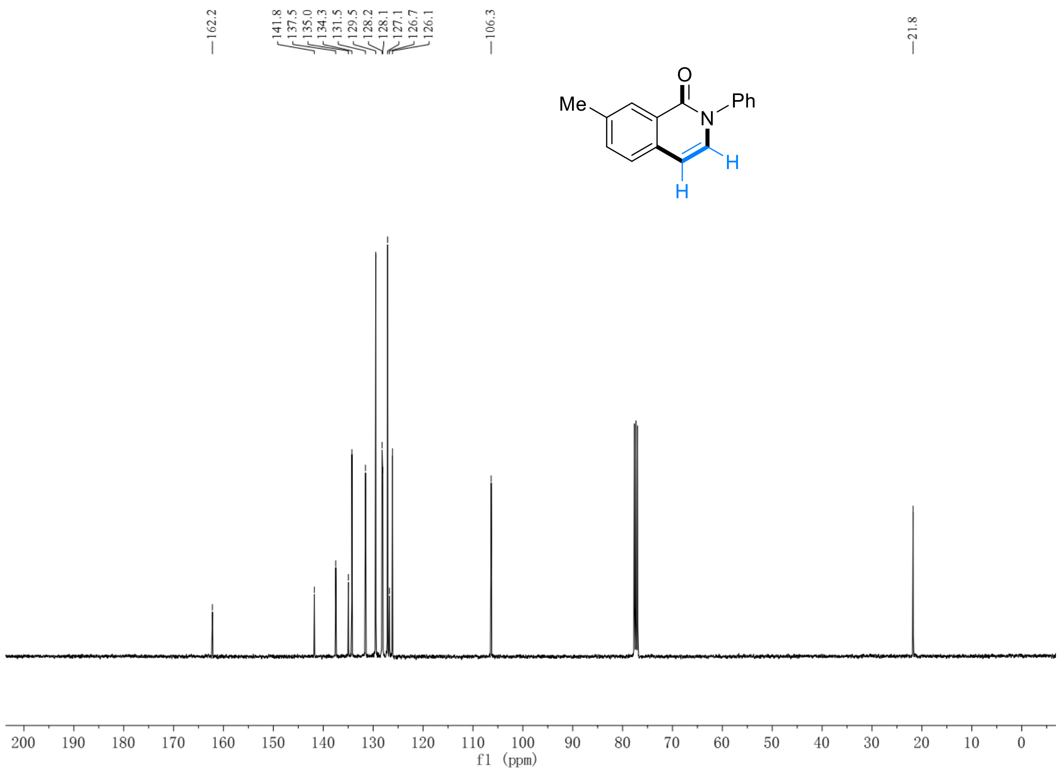
^{13}C NMR of **3a** (100 MHz, $CDCl_3$)



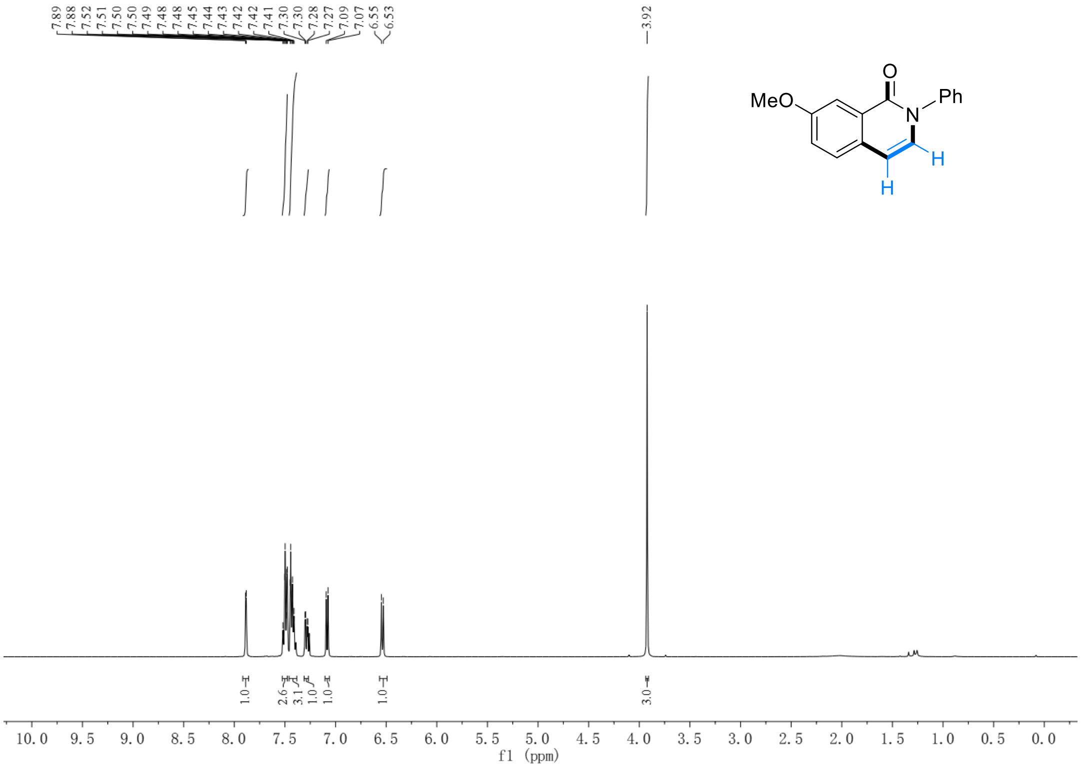
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



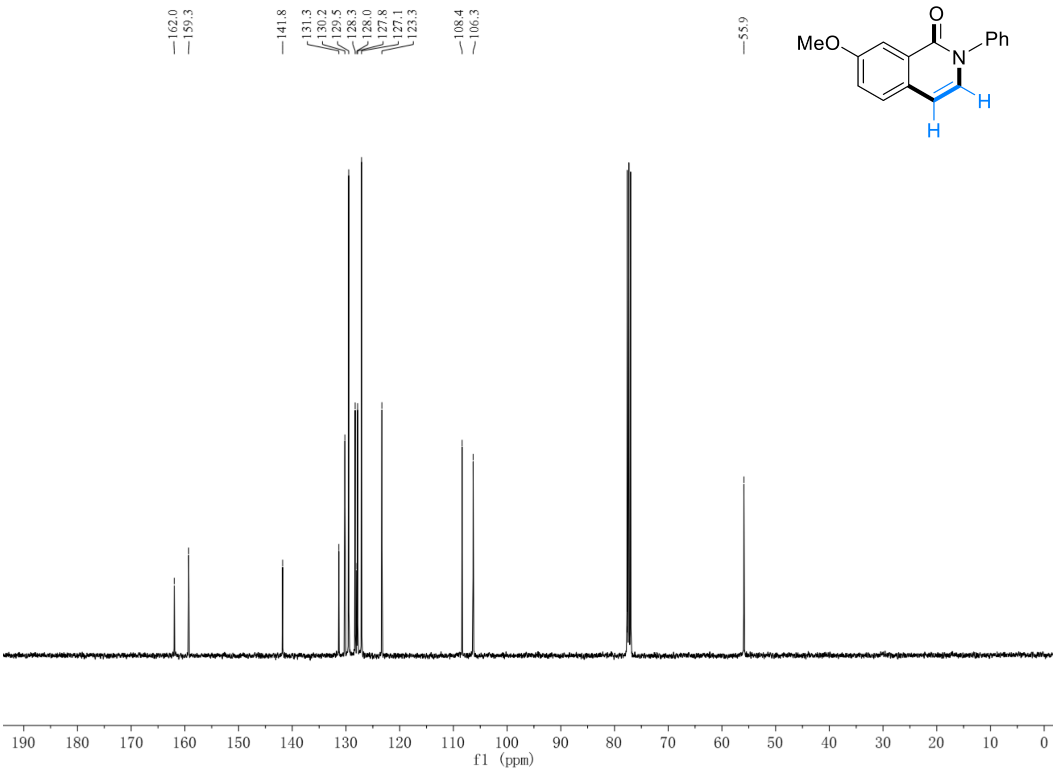
^{13}C NMR of **3b** (100 MHz, $CDCl_3$)



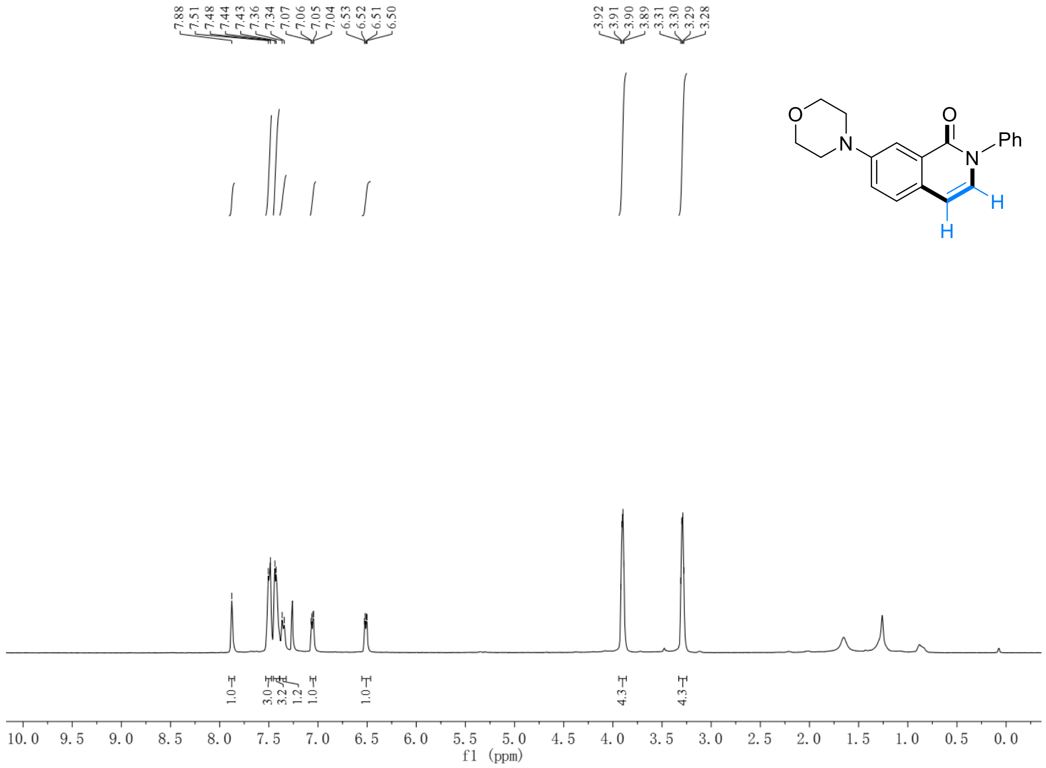
[1]H NMR of **3c** (400 MHz, $CDCl_3$)



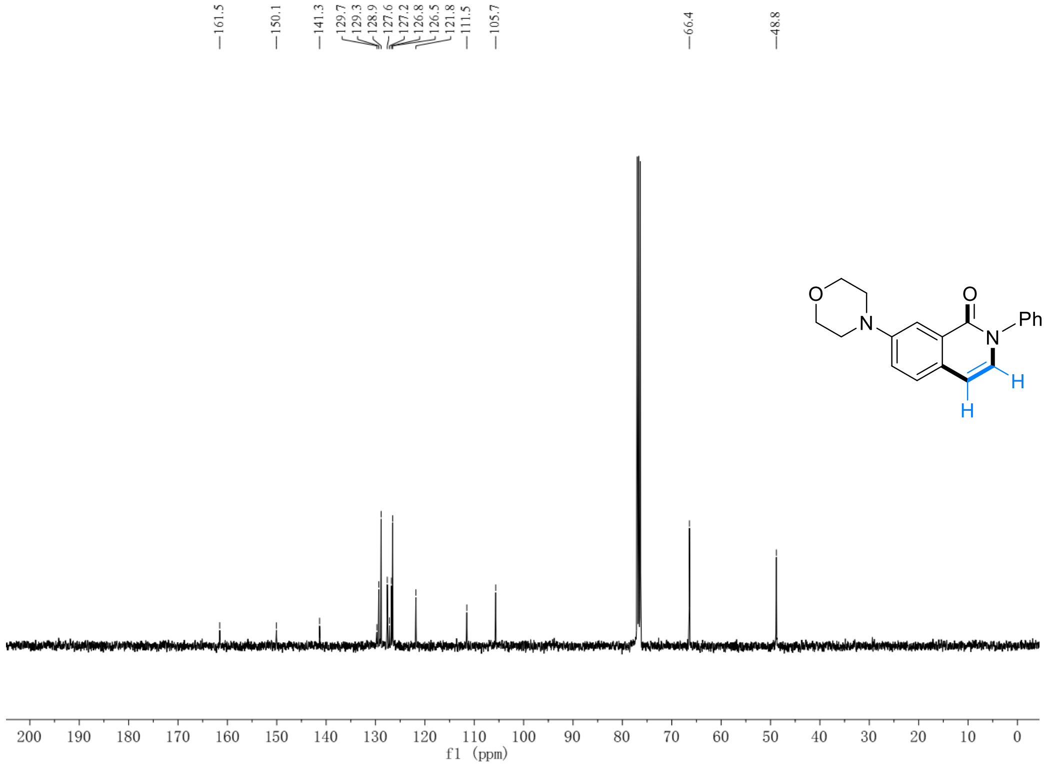
[13]C NMR of **3c** (100 MHz, $CDCl_3$)



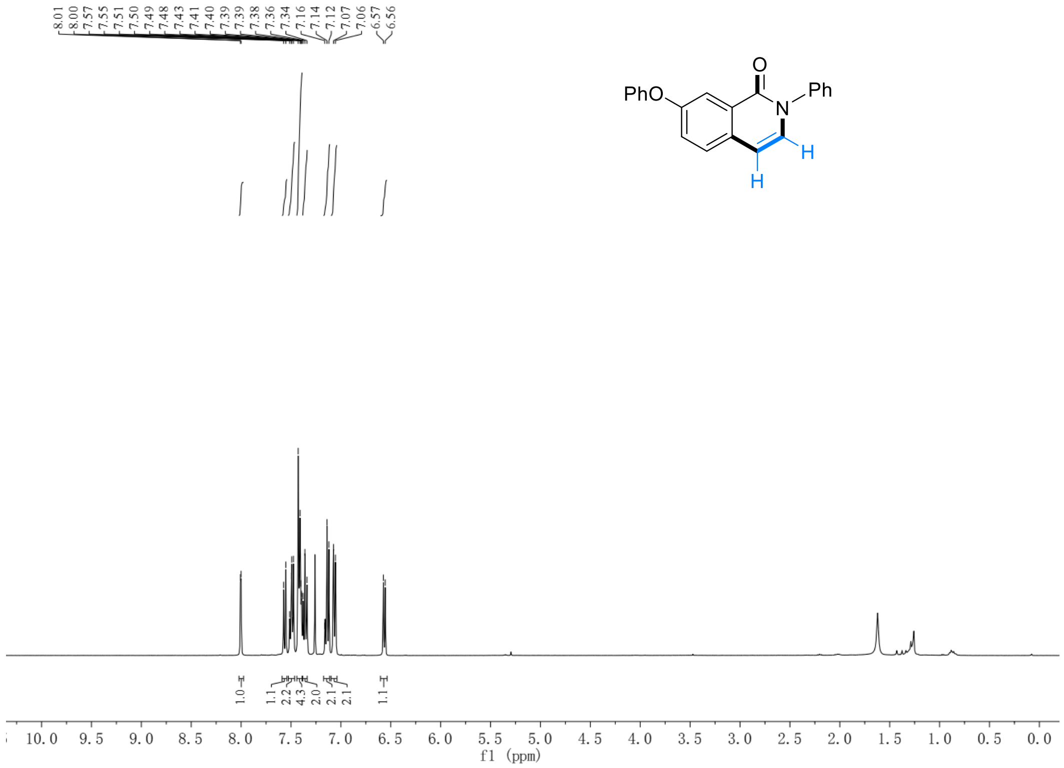
^{1}H NMR of **3d** (400 MHz, $CDCl_3$)



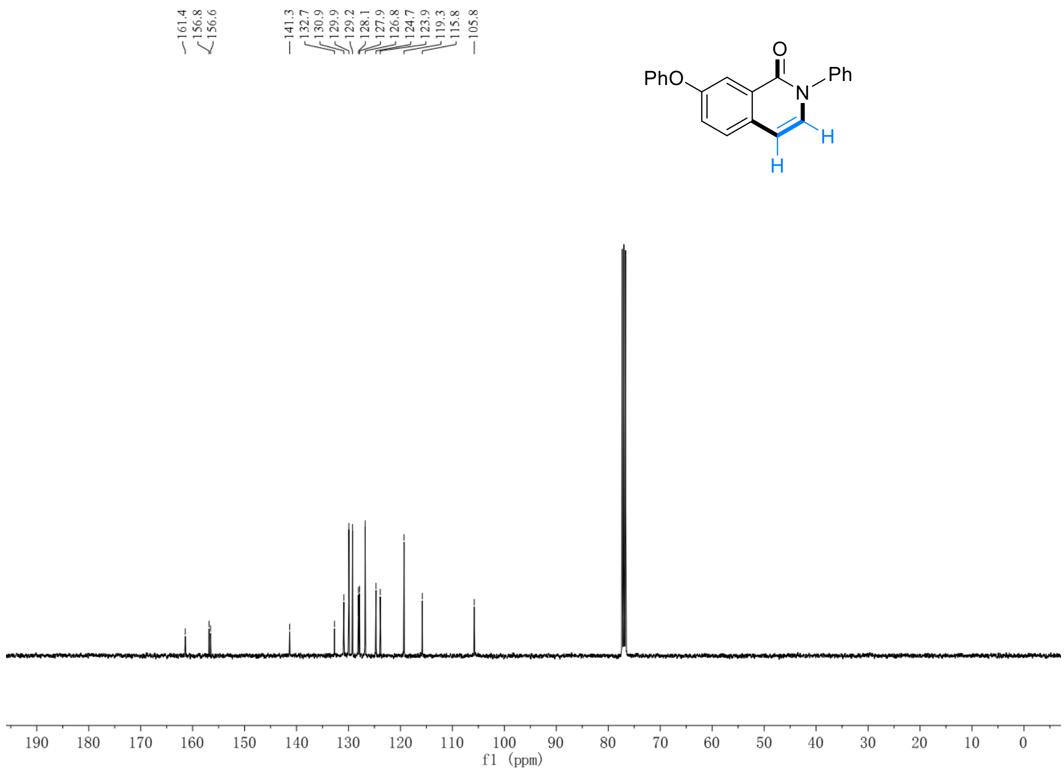
^{13}C NMR of **3d** (100 MHz, $CDCl_3$)



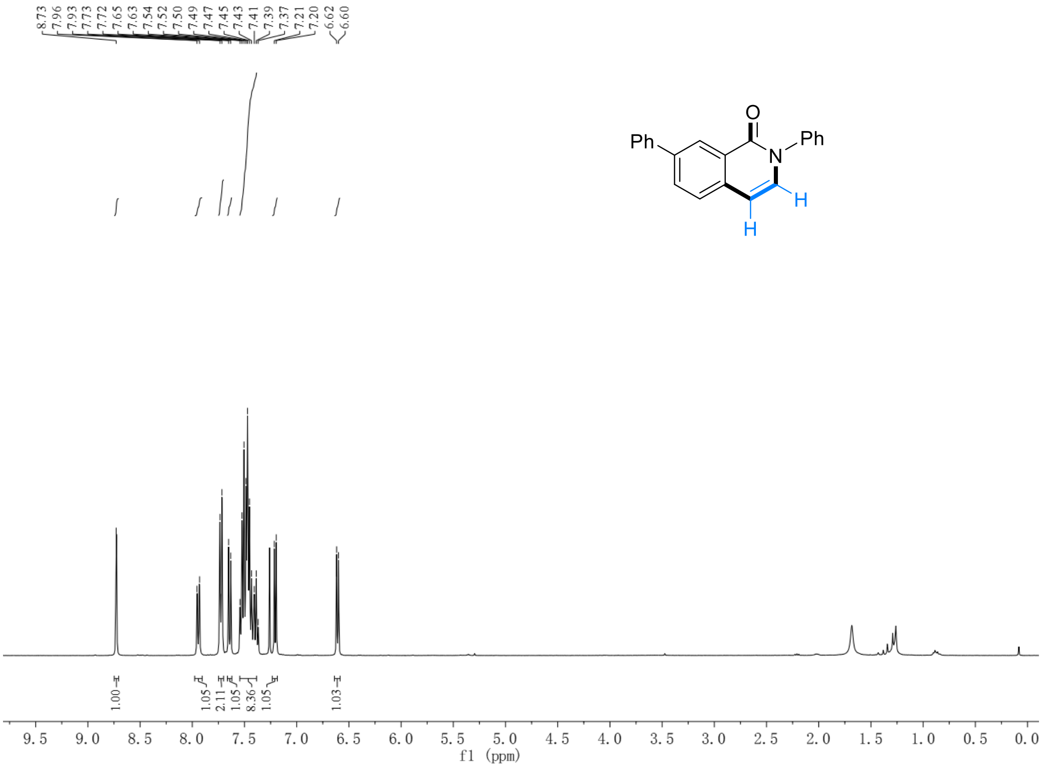
^{1}H NMR of **3e** (400 MHz, $CDCl_3$)



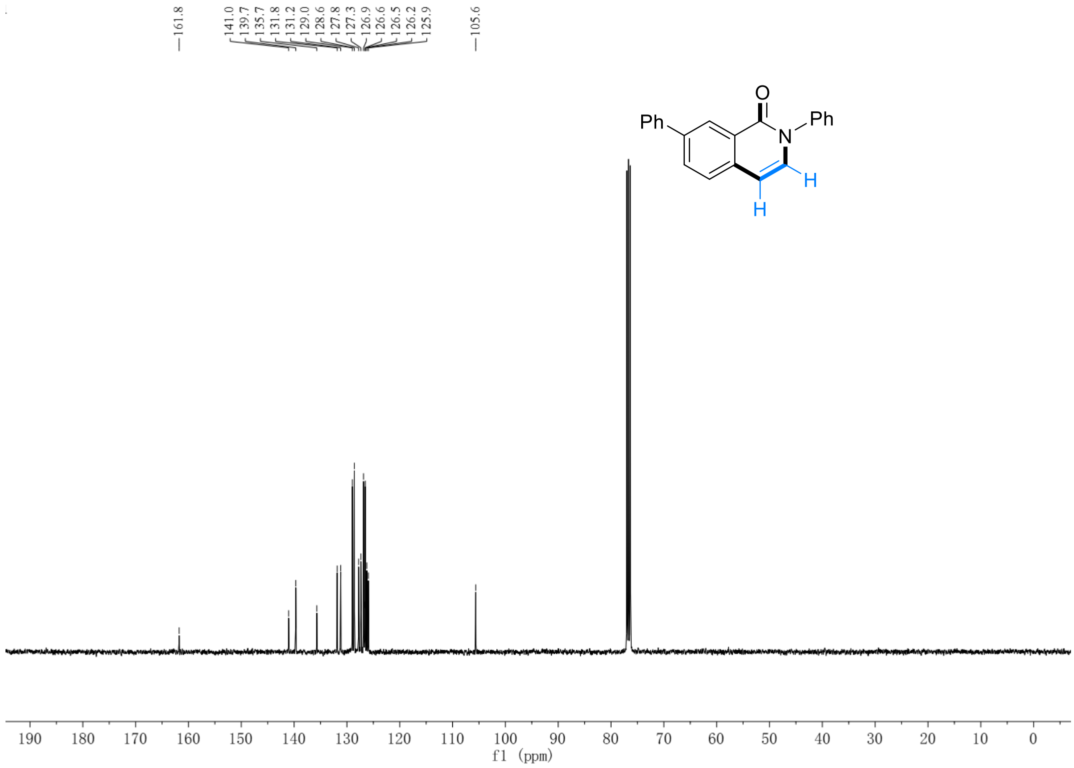
^{13}C NMR of **3e** (100 MHz, $CDCl_3$)



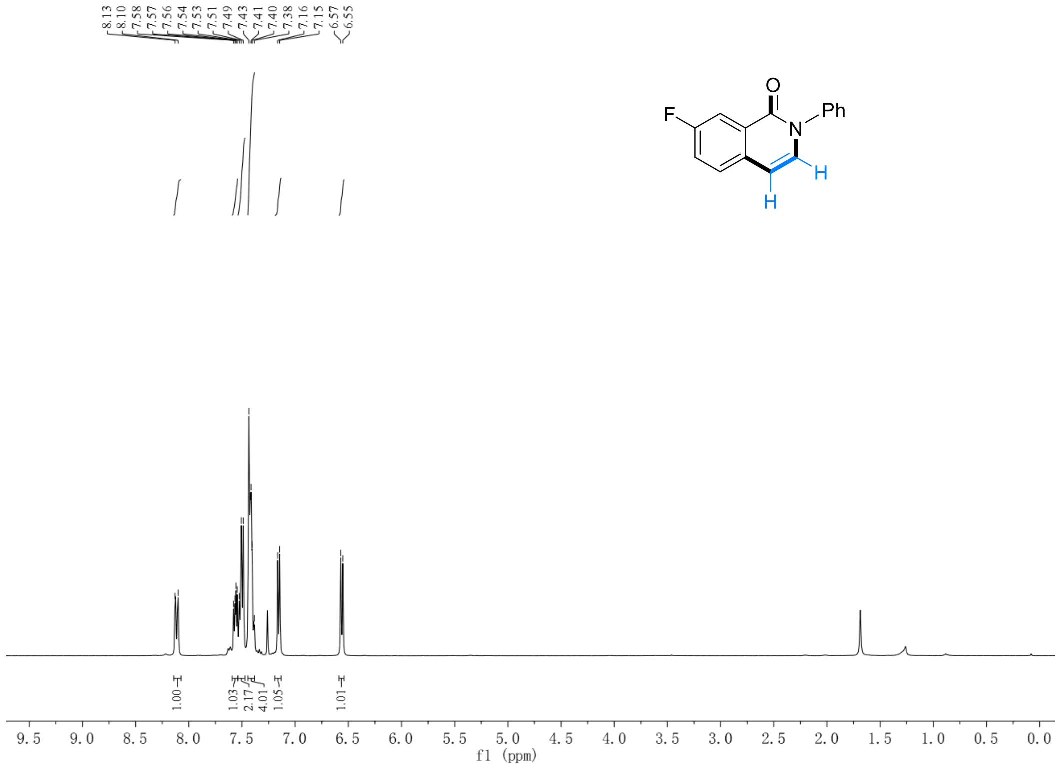
[1]H NMR of **3f** (400 MHz, $CDCl_3$)



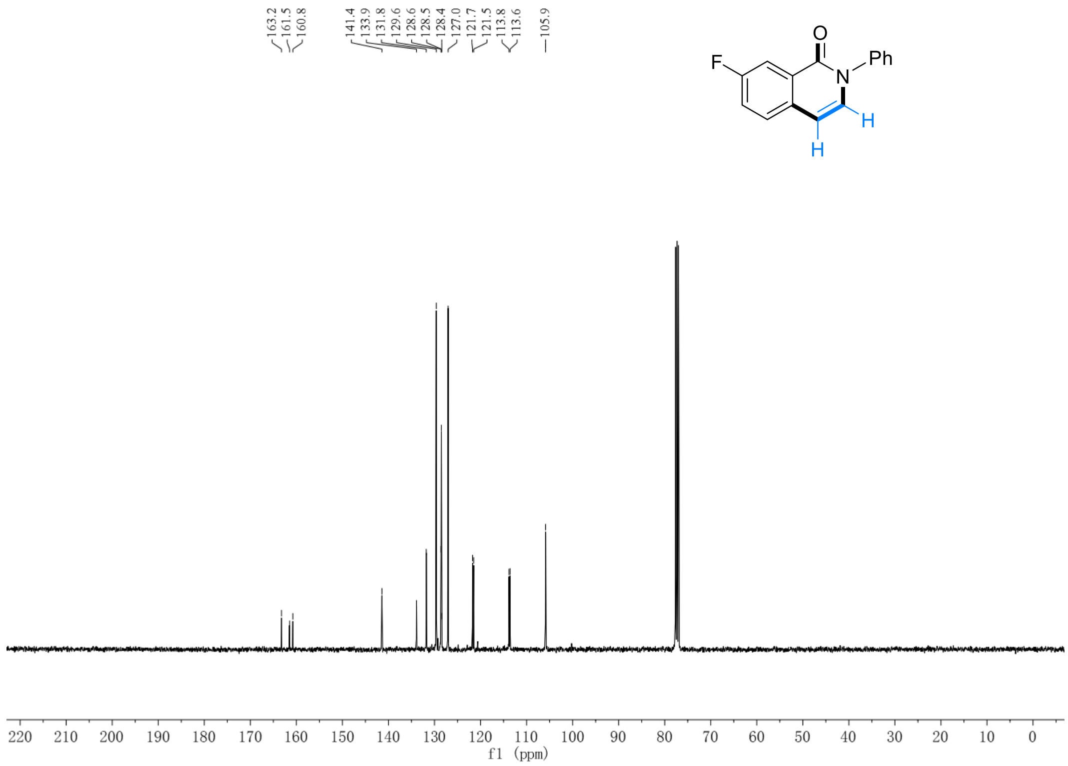
[13]C NMR of **3f** (100 MHz, $CDCl_3$)



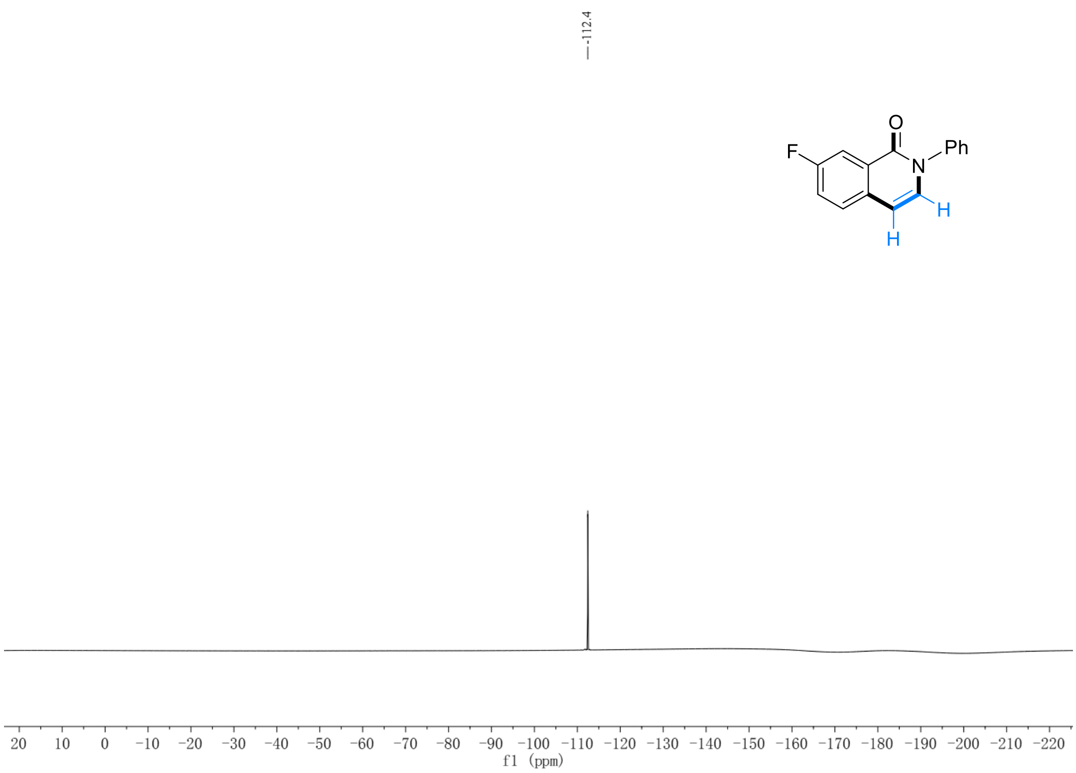
[1]H NMR of **3g** (400 MHz, $CDCl_3$)



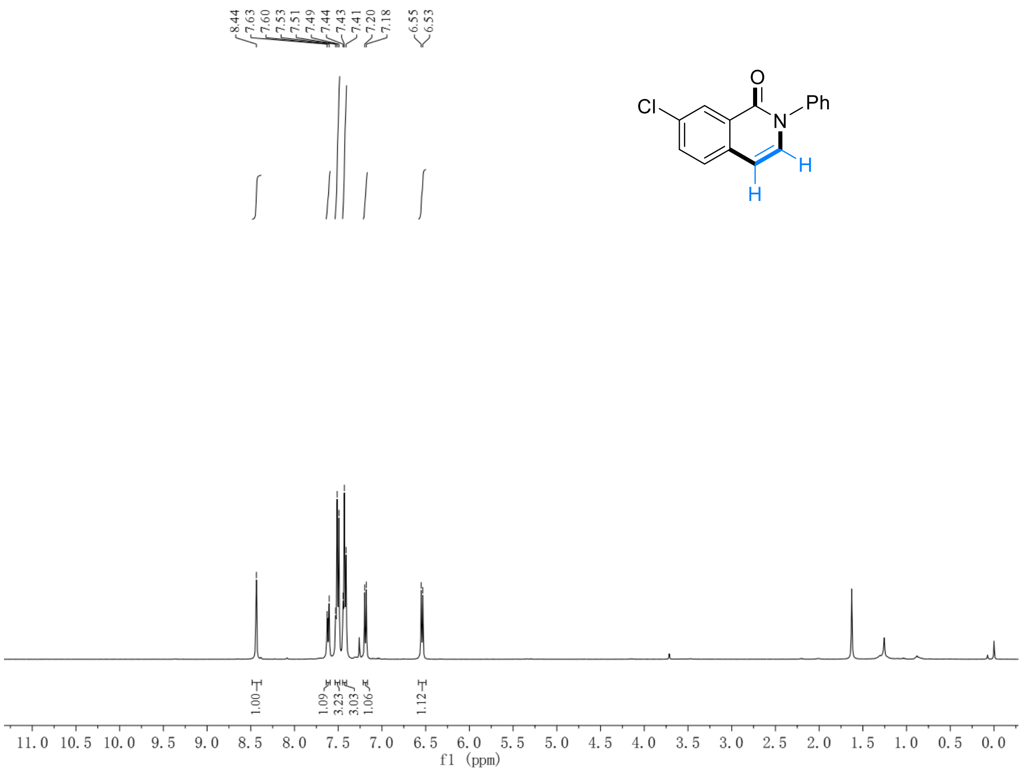
[13]C NMR of **3g** (100 MHz, $CDCl_3$)



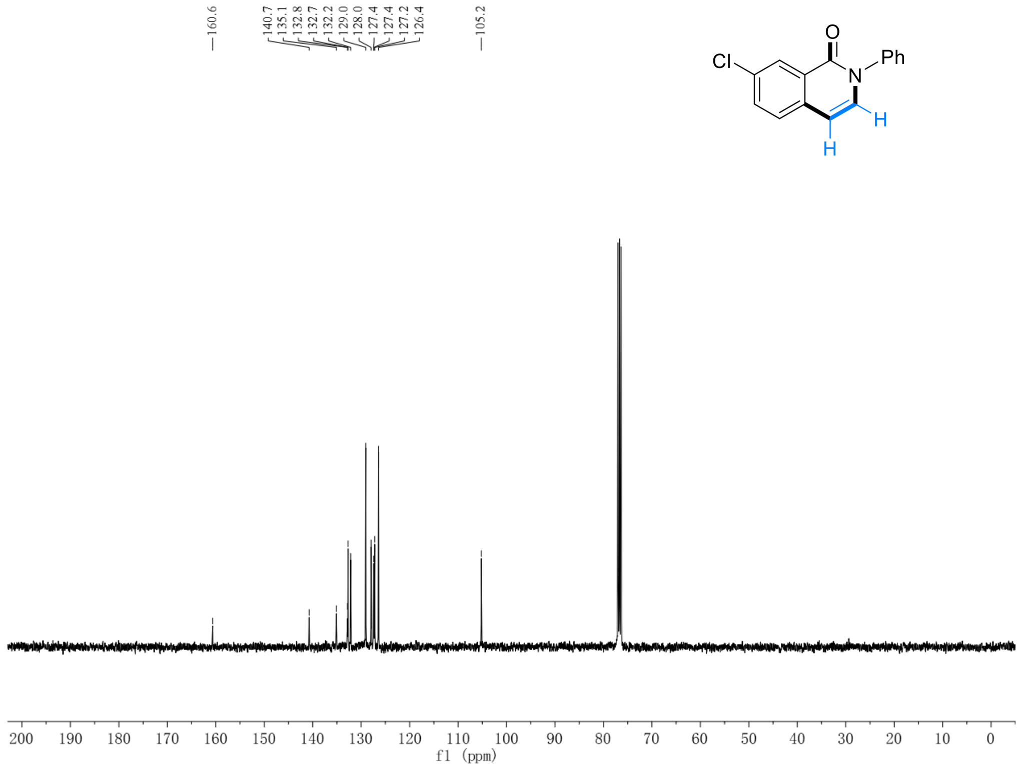
^{19}F NMR of **3g** (375 MHz, $CDCl_3$)



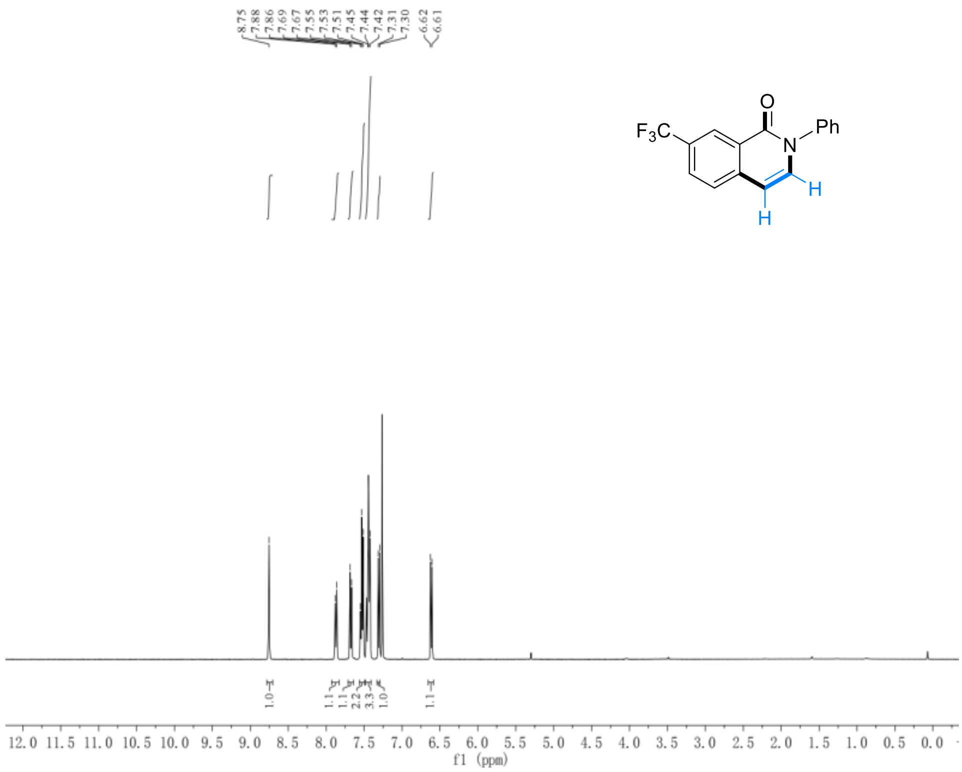
^{1}H NMR of **3h** (400 MHz, $CDCl_3$)



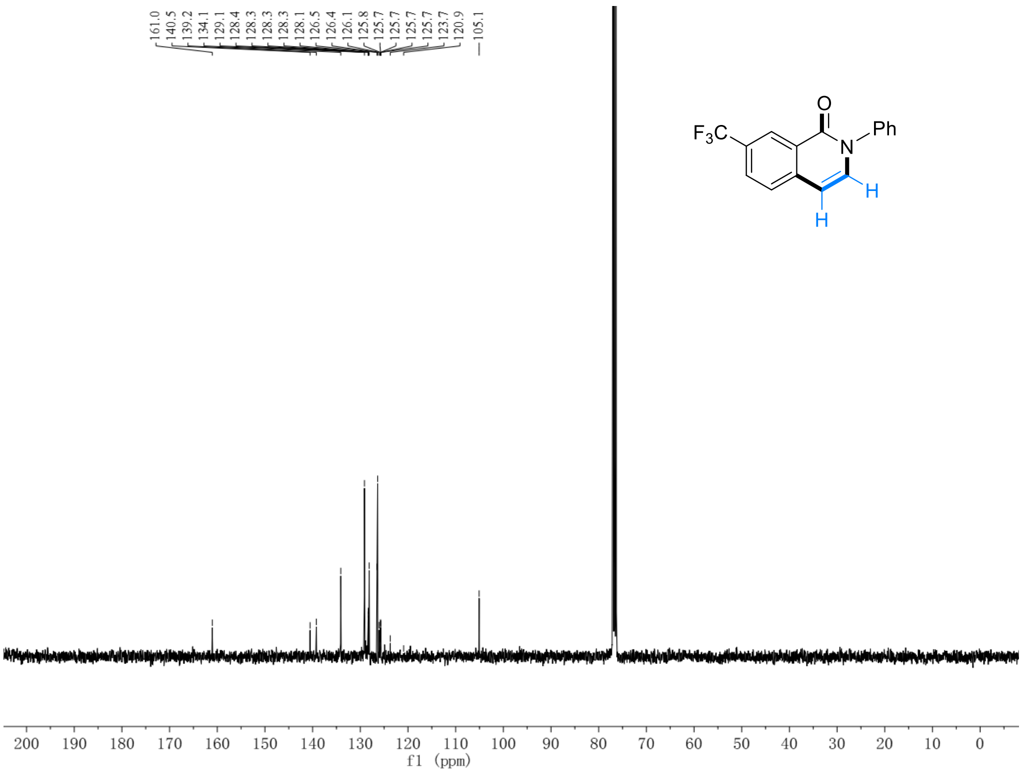
^{13}C NMR of **3h** (100 MHz, $CDCl_3$)



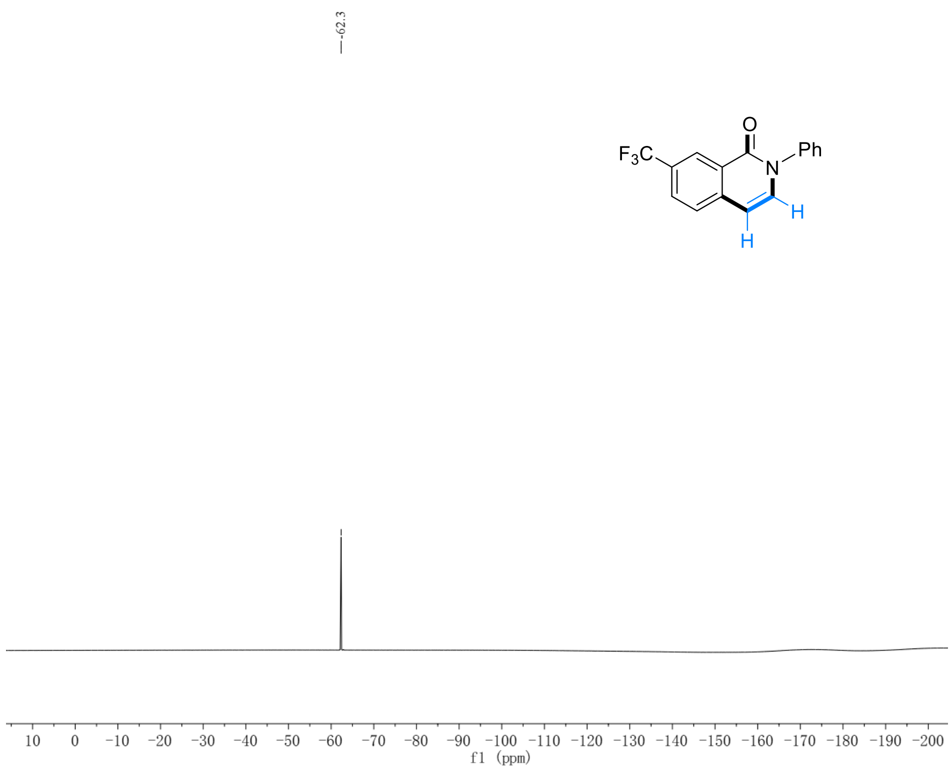
^{1}H NMR of **3i** (400 MHz, $CDCl_3$)



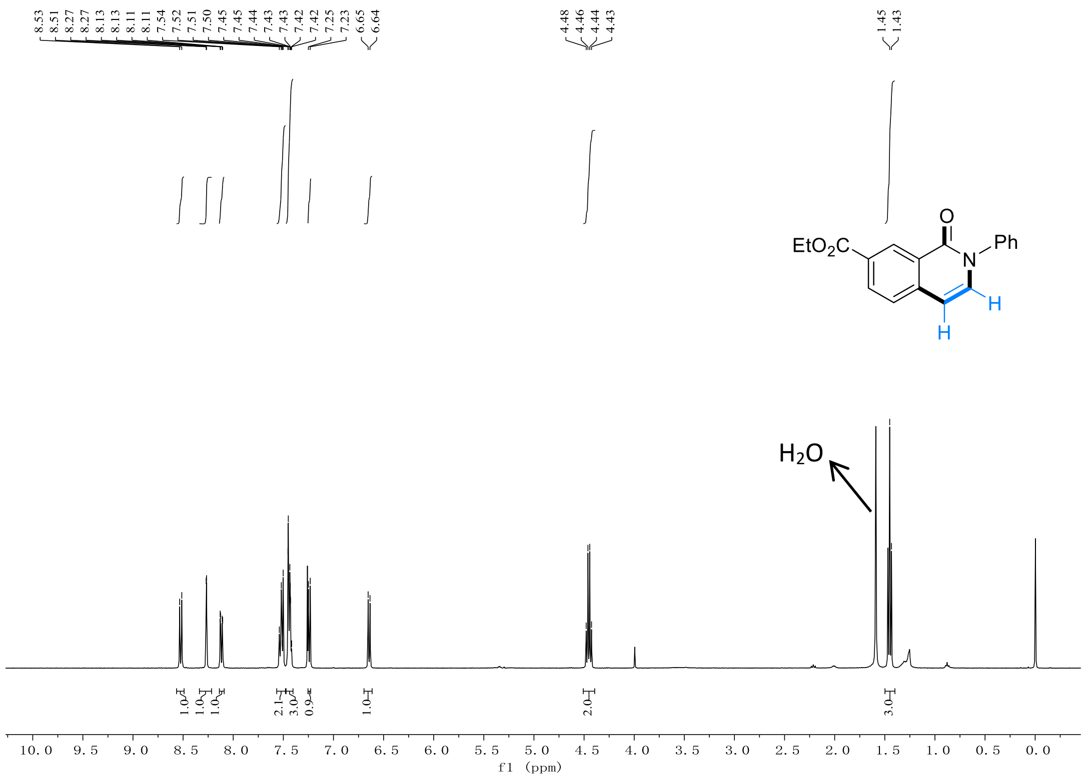
^{13}C NMR of **3i** (100 MHz, $CDCl_3$)



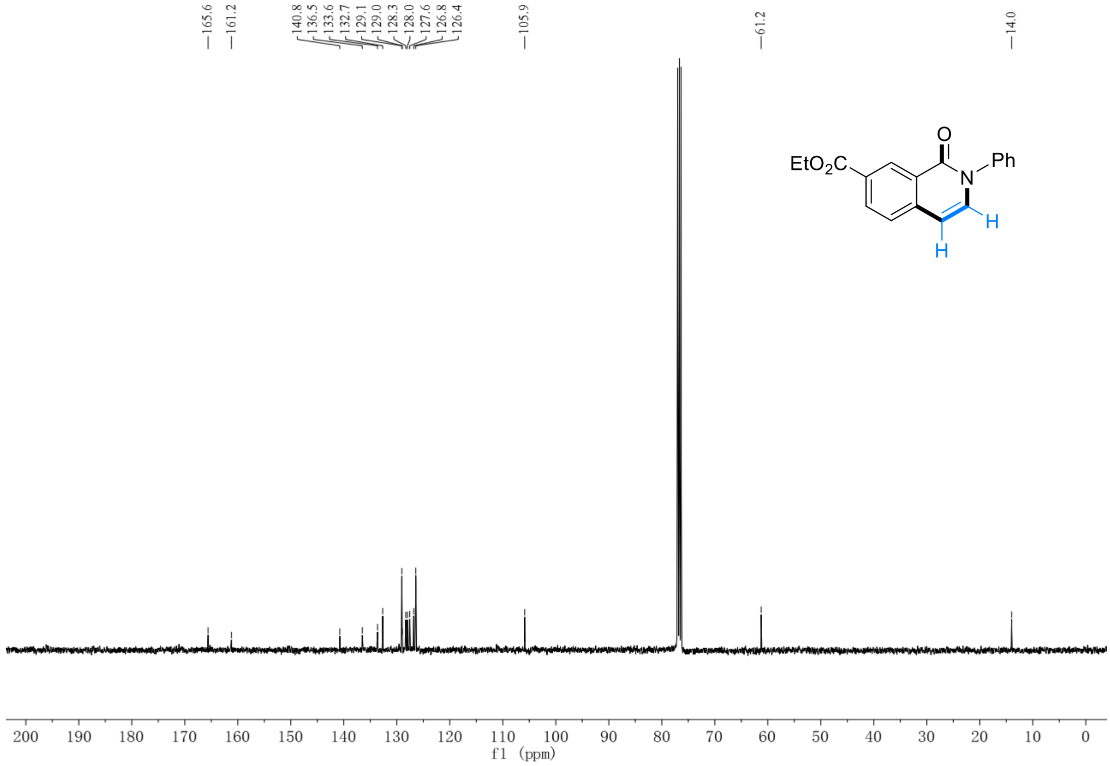
^{19}F NMR of **3i** (375 MHz, $CDCl_3$)



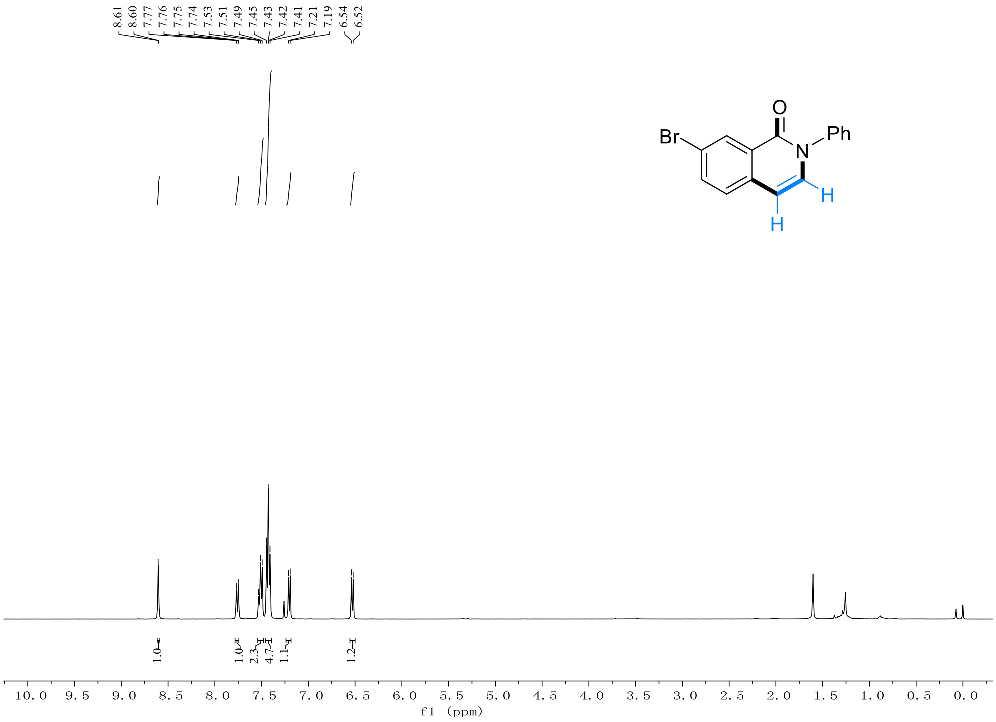
^{1}H NMR of **3j** (400 MHz, $CDCl_3$)



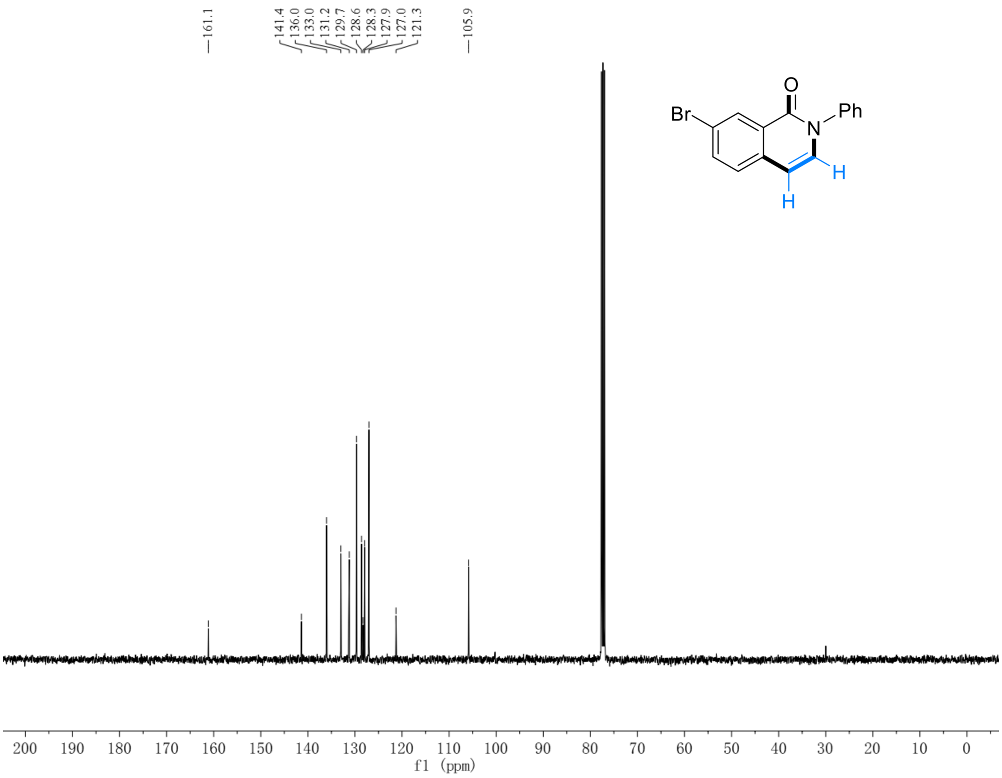
^{13}C NMR of **3j** (100 MHz, $CDCl_3$)



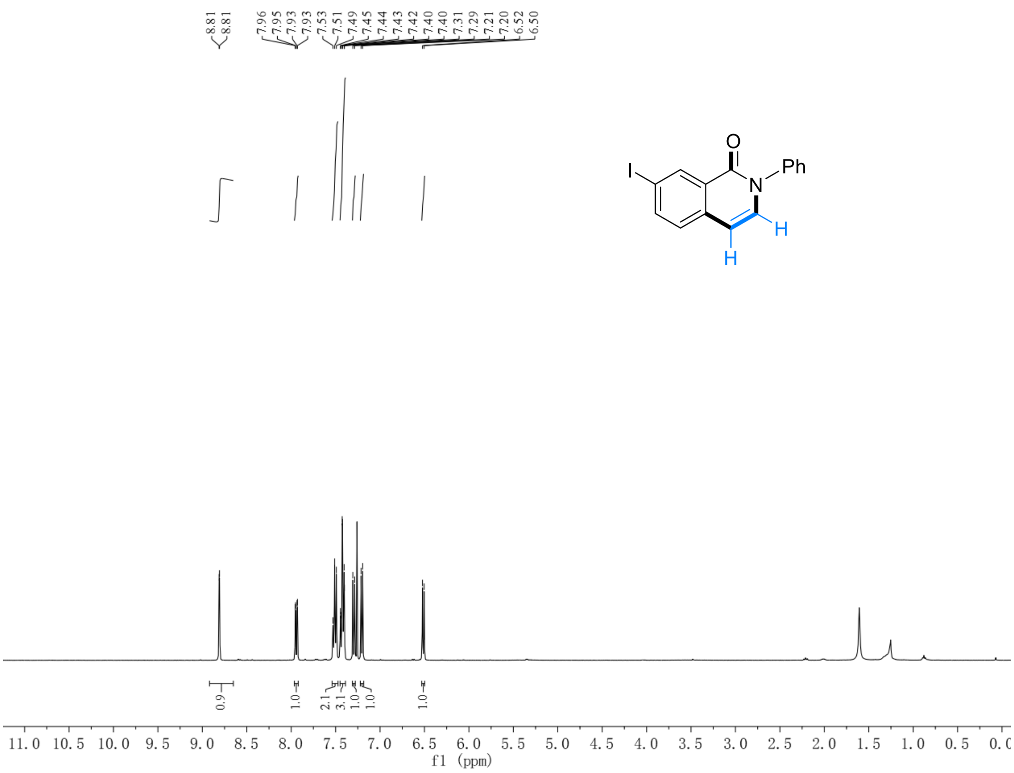
^{1}H NMR of **3k** (400 MHz, $CDCl_3$)



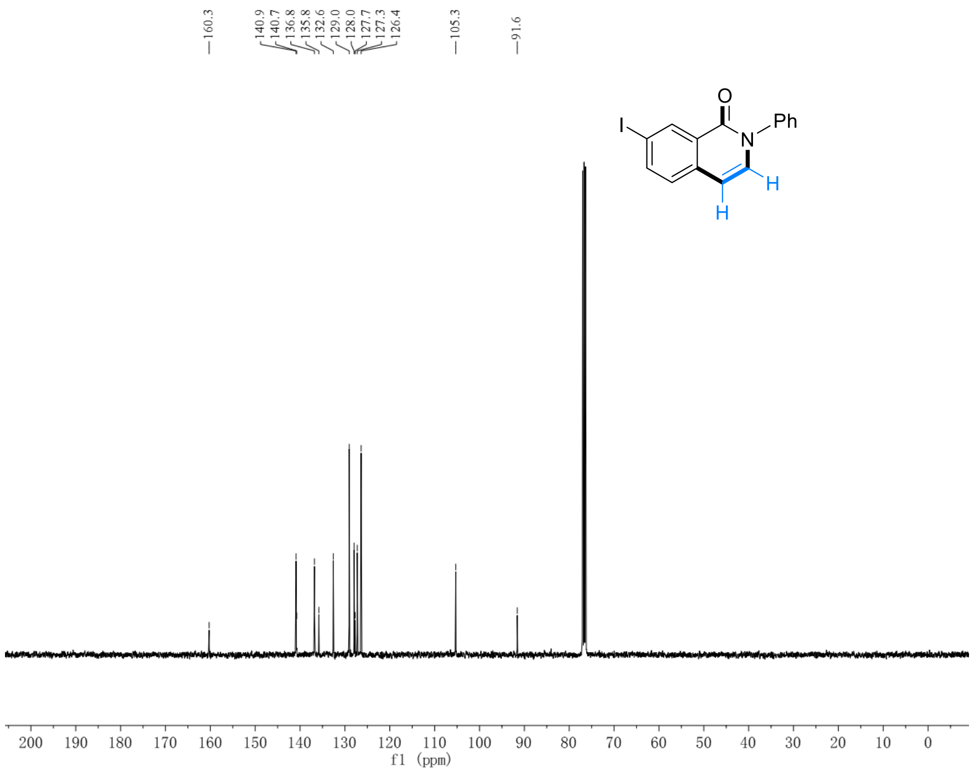
^{13}C NMR of **3k** (100 MHz, $CDCl_3$)



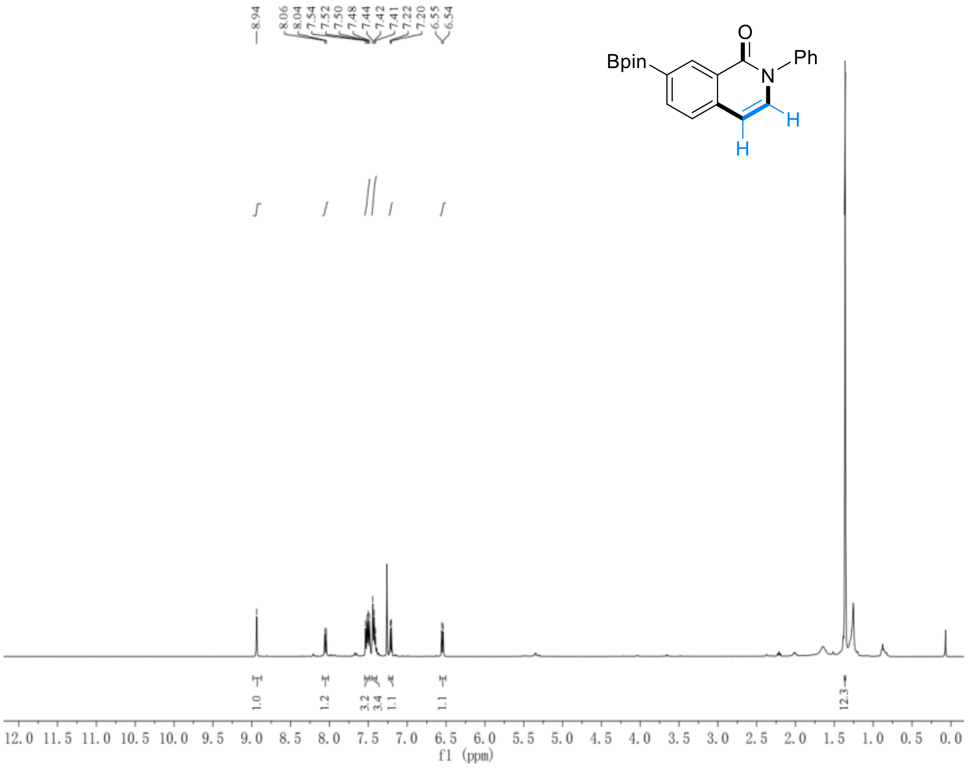
^{1}H NMR of **3l** (400 MHz, $CDCl_3$)



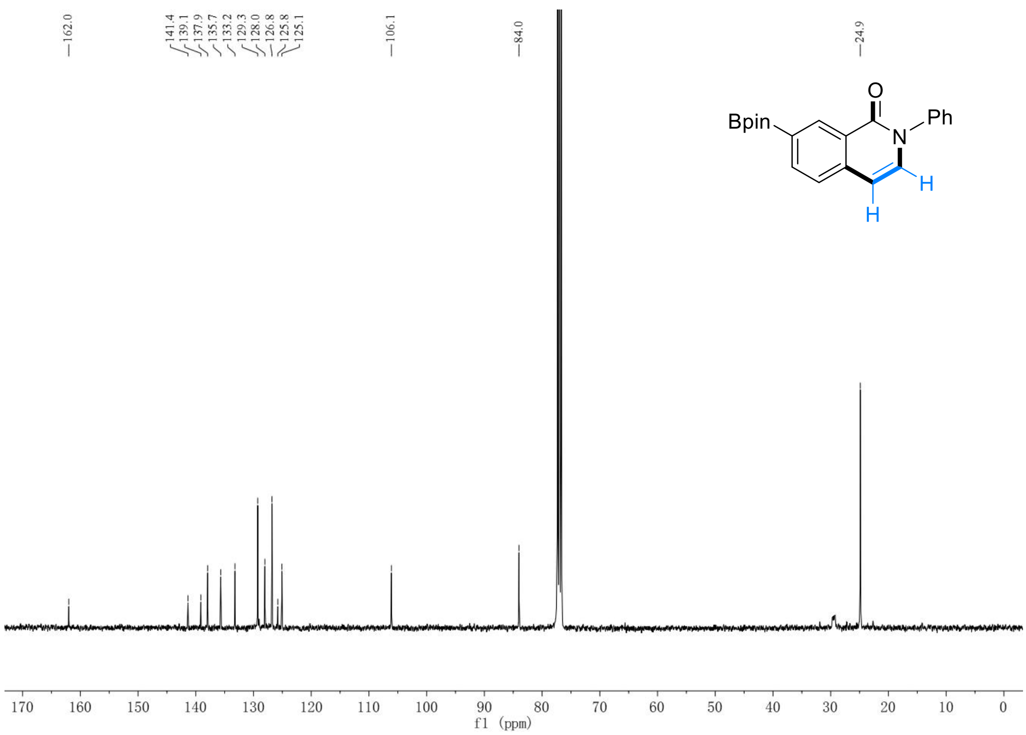
^{13}C NMR of **3l** (100 MHz, $CDCl_3$)



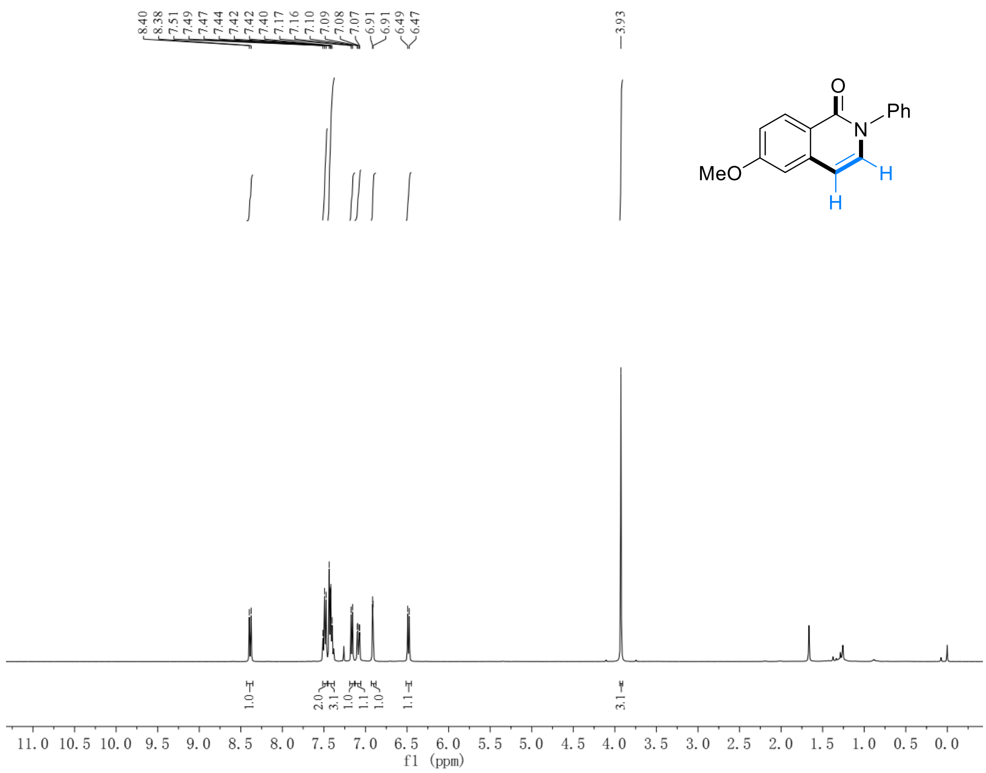
^{1}H NMR of **3m** (400 MHz, $CDCl_3$)



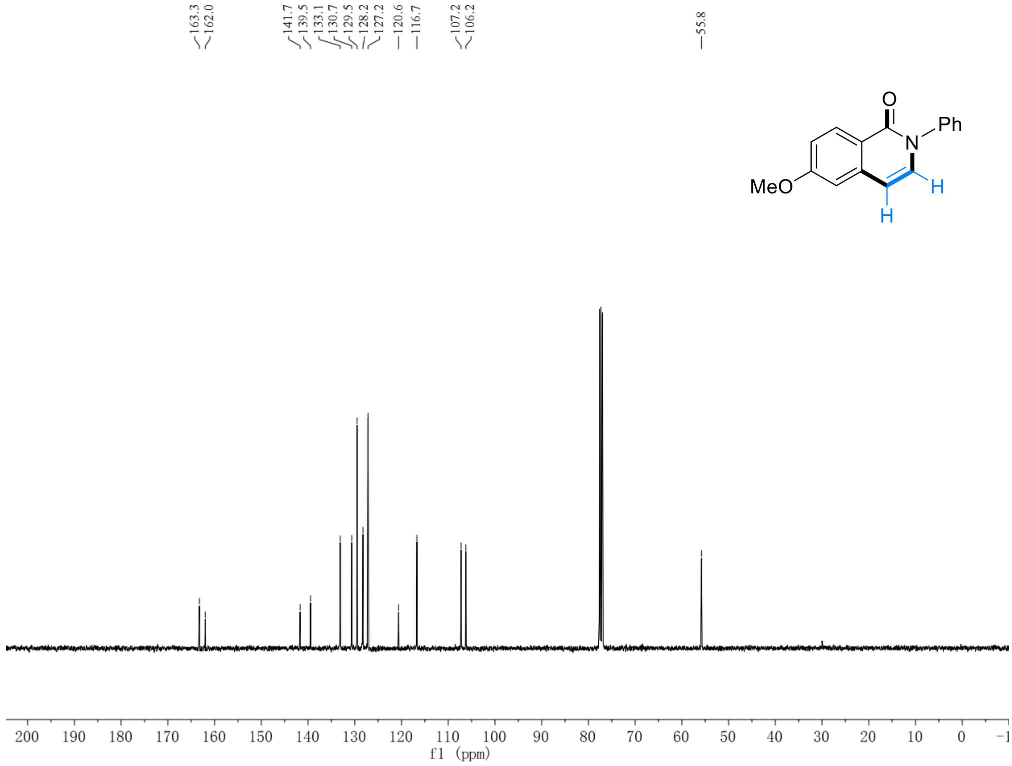
^{13}C NMR of **3m** (100 MHz, $CDCl_3$)



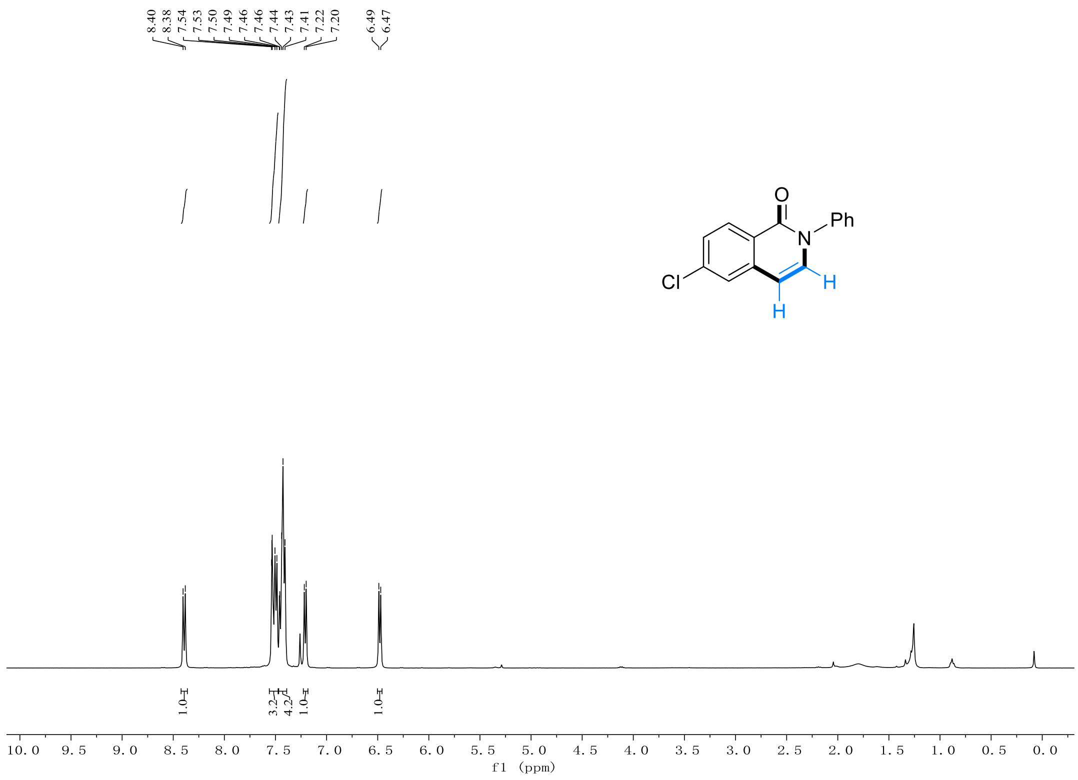
[1]H NMR of **3n** (400 MHz, $CDCl_3$)



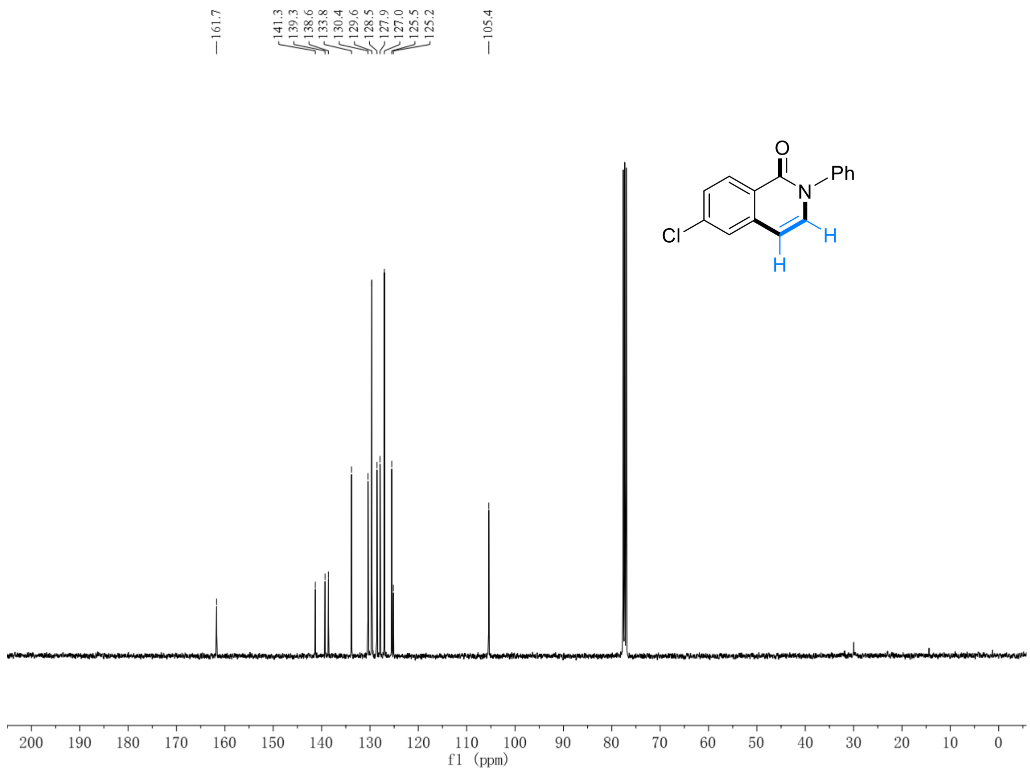
[13]C NMR of **3n** (100 MHz, $CDCl_3$)



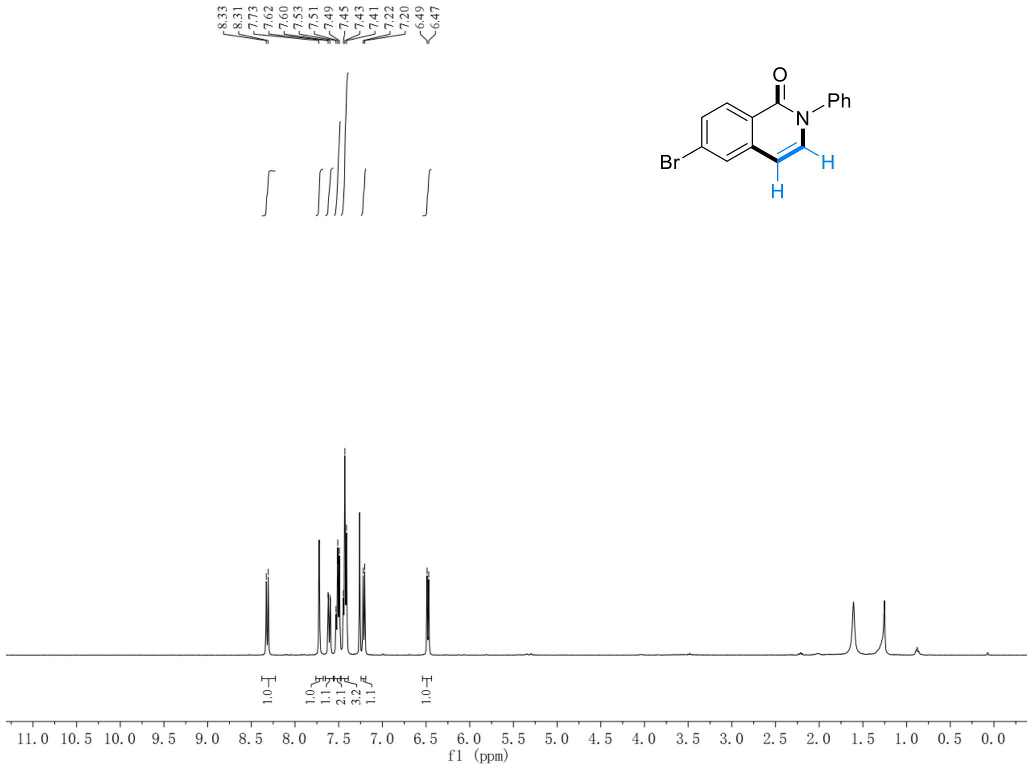
[1]H NMR of **3o** (400 MHz, $CDCl_3$)



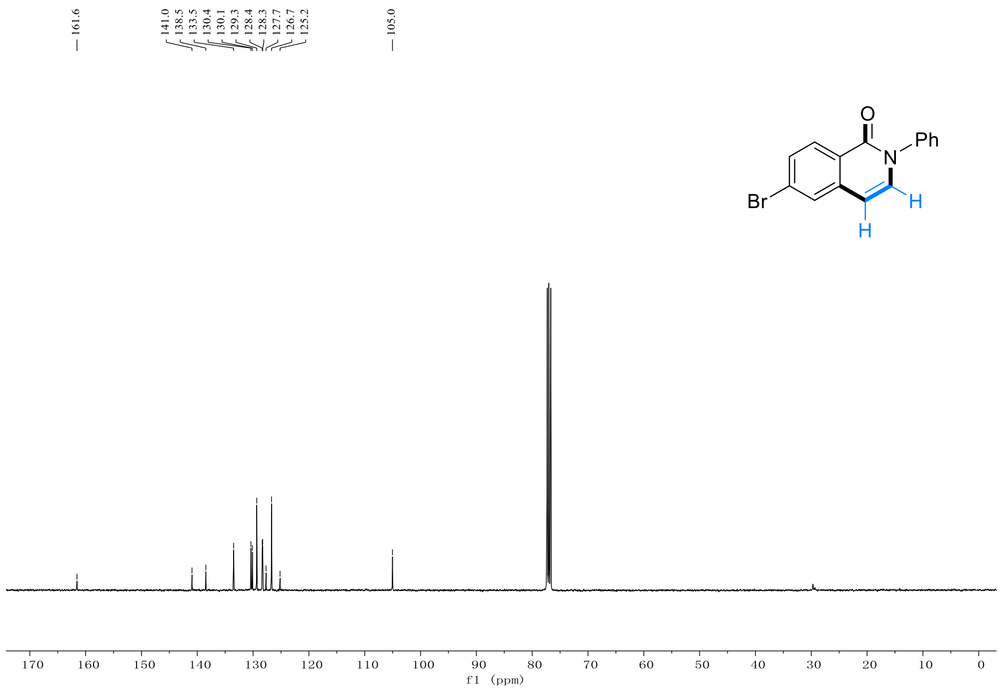
[13]C NMR of **3o** (100 MHz, $CDCl_3$)



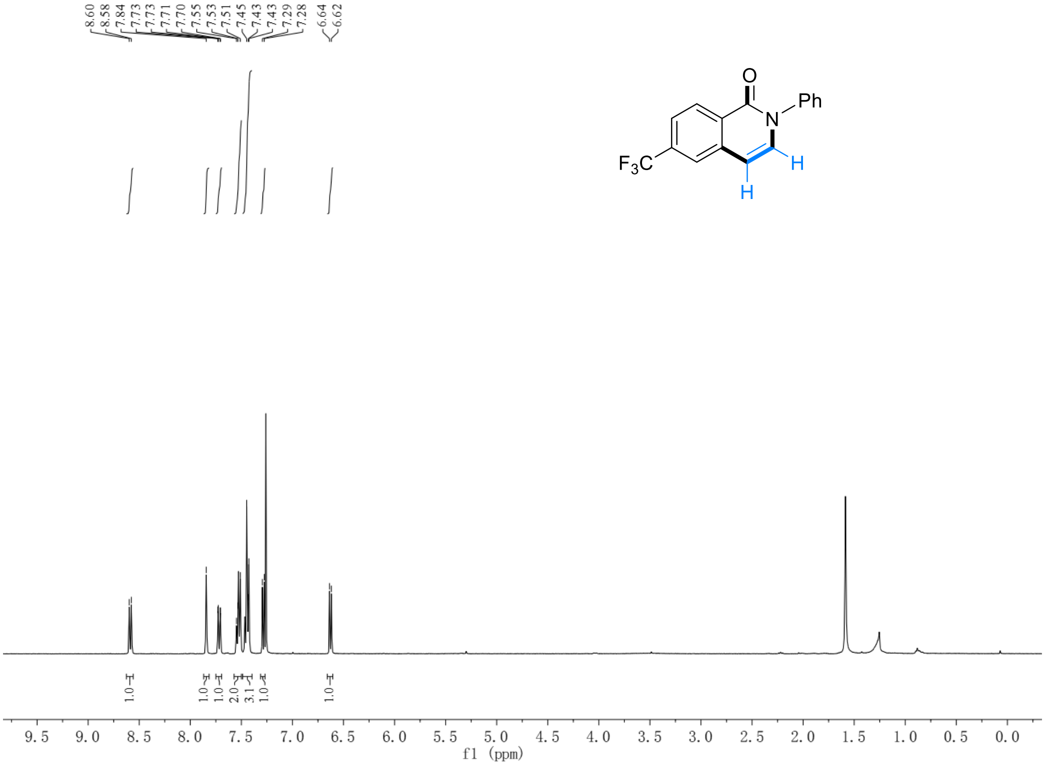
^{1}H NMR of **3p** (400 MHz, $CDCl_3$)



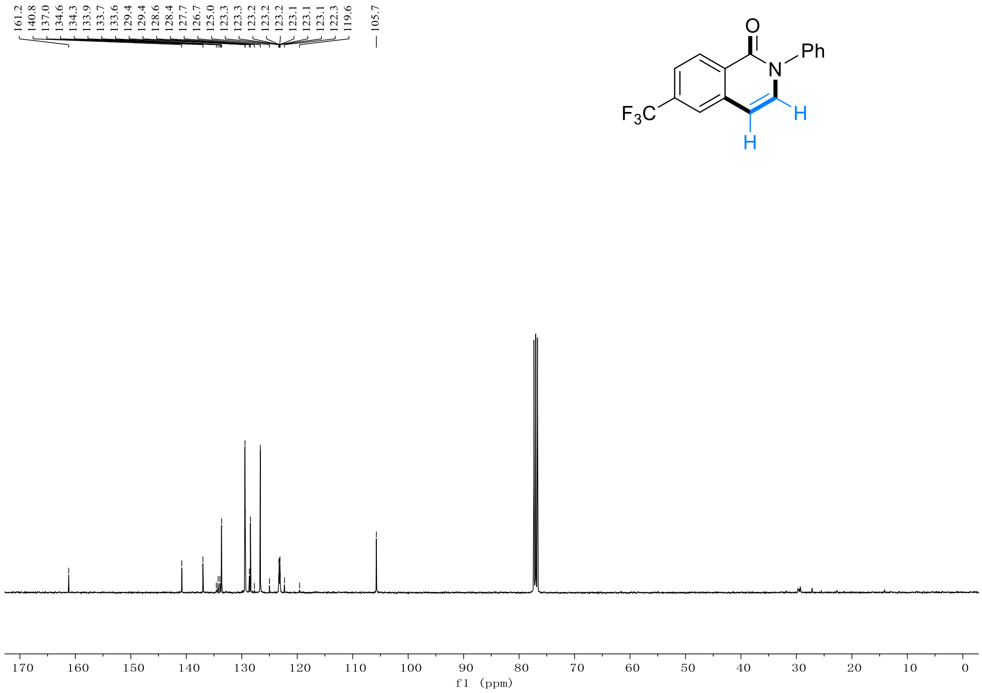
^{13}C NMR of **3p** (100 MHz, $CDCl_3$)



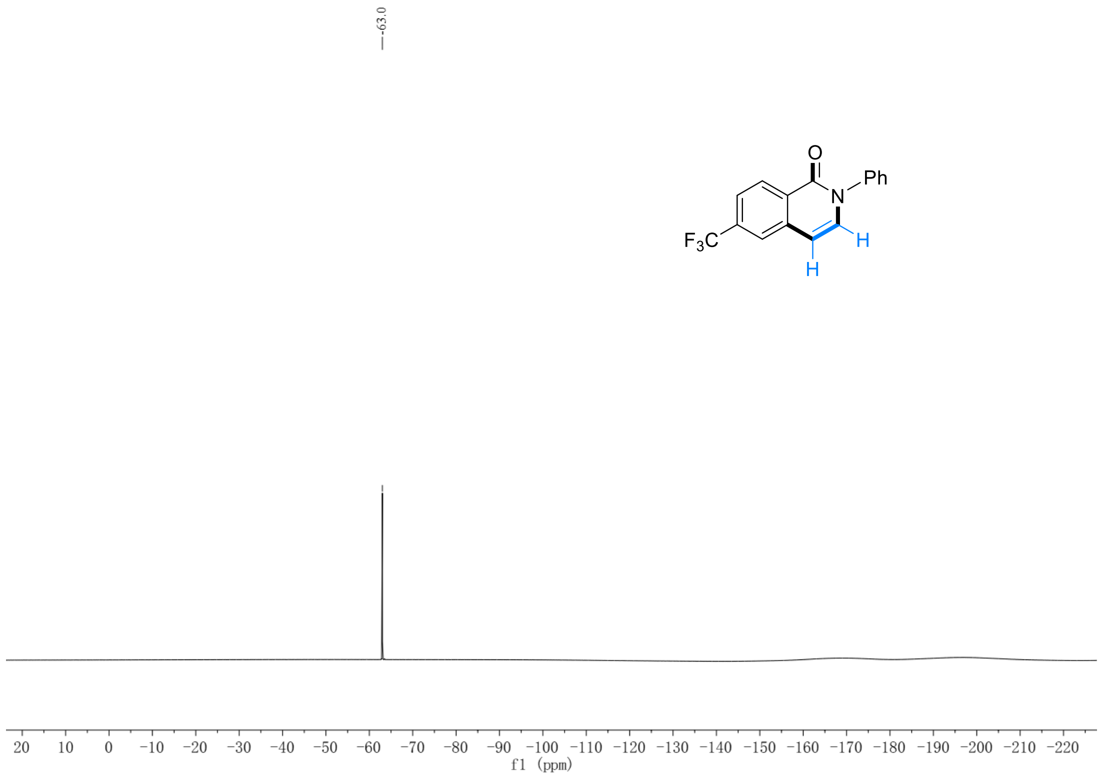
[1]H NMR of **3q** (400 MHz, $CDCl_3$)



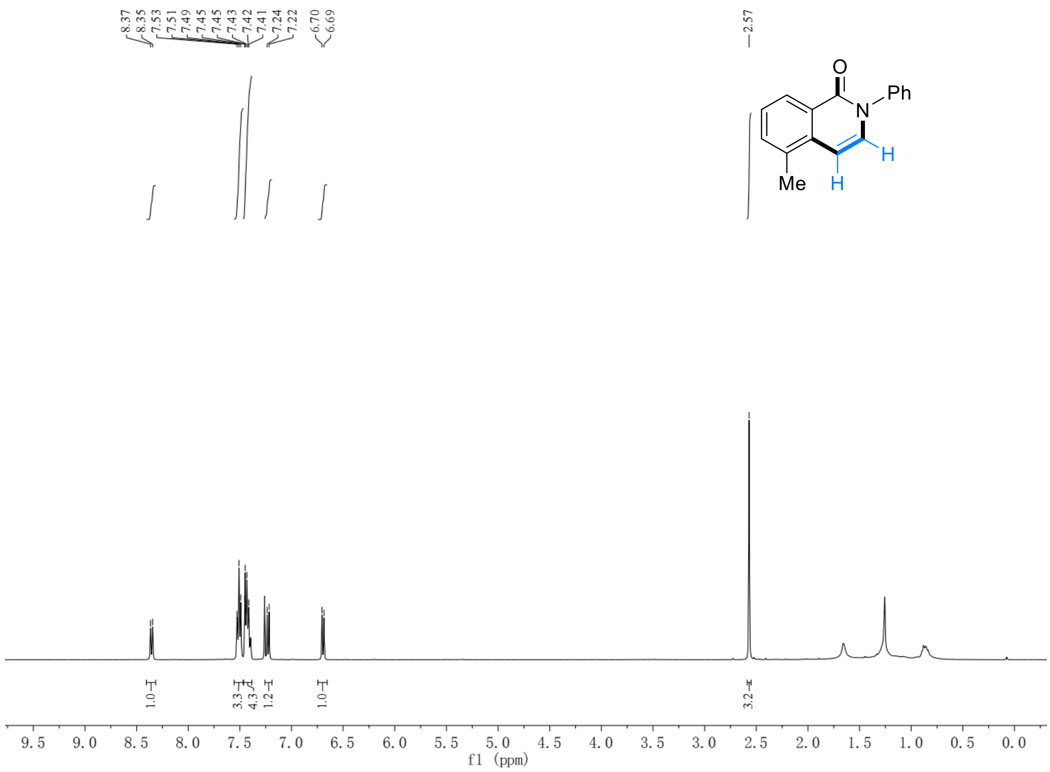
[13]C NMR of **3q** (100 MHz, $CDCl_3$)



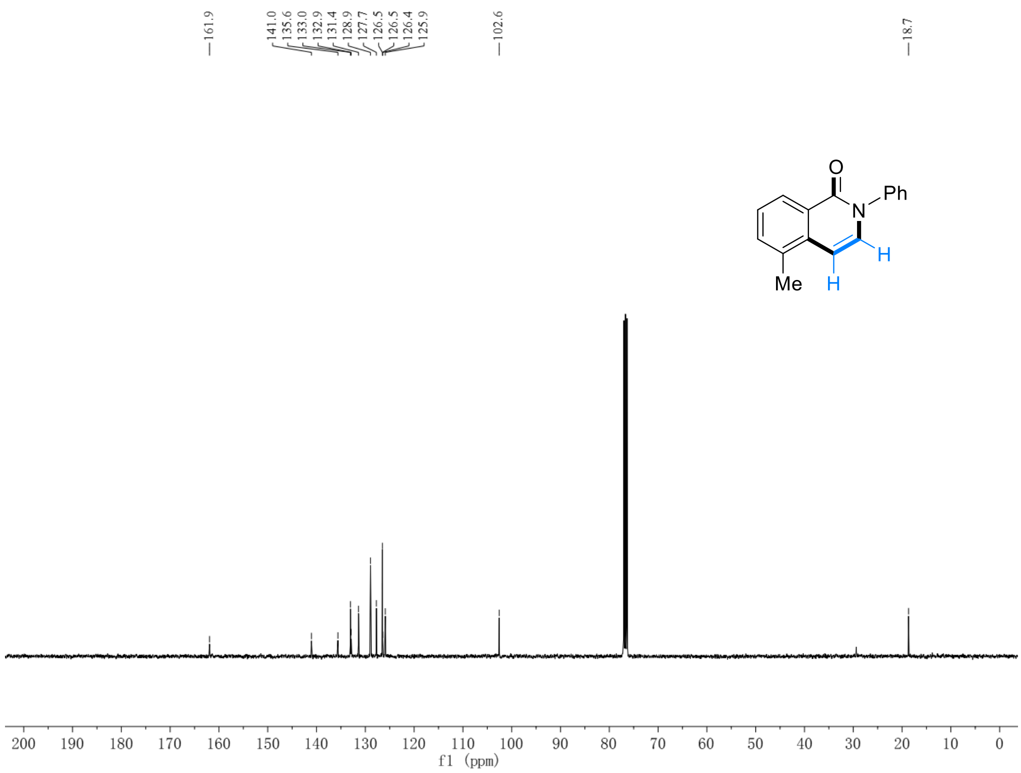
[19]F NMR of **3q** (375 MHz, $CDCl_3$)



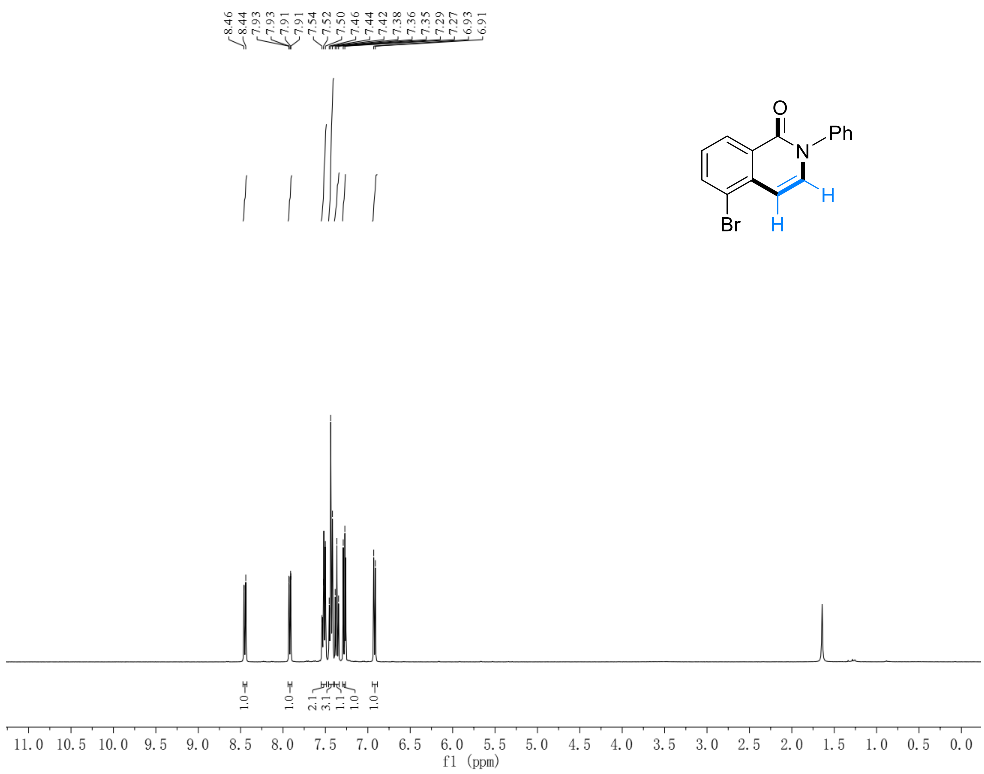
[1]H NMR of **3r** (400 MHz, $CDCl_3$)



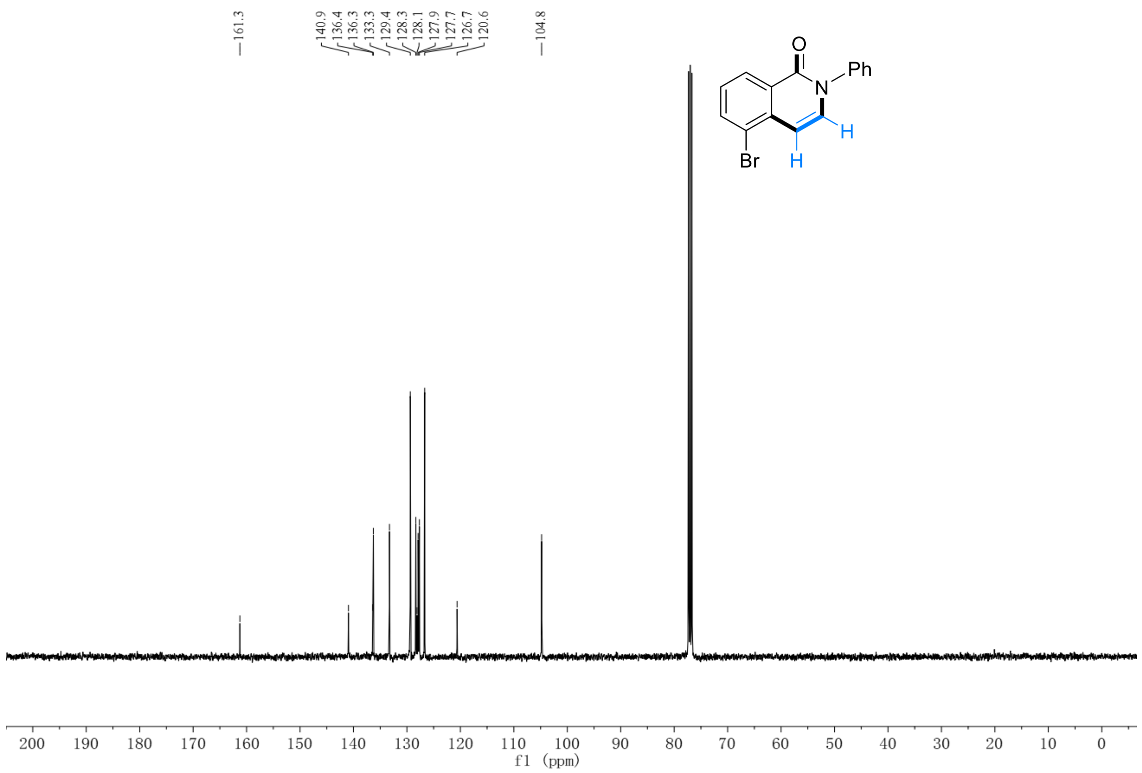
^{13}C NMR of **3r** (100 MHz, $CDCl_3$)



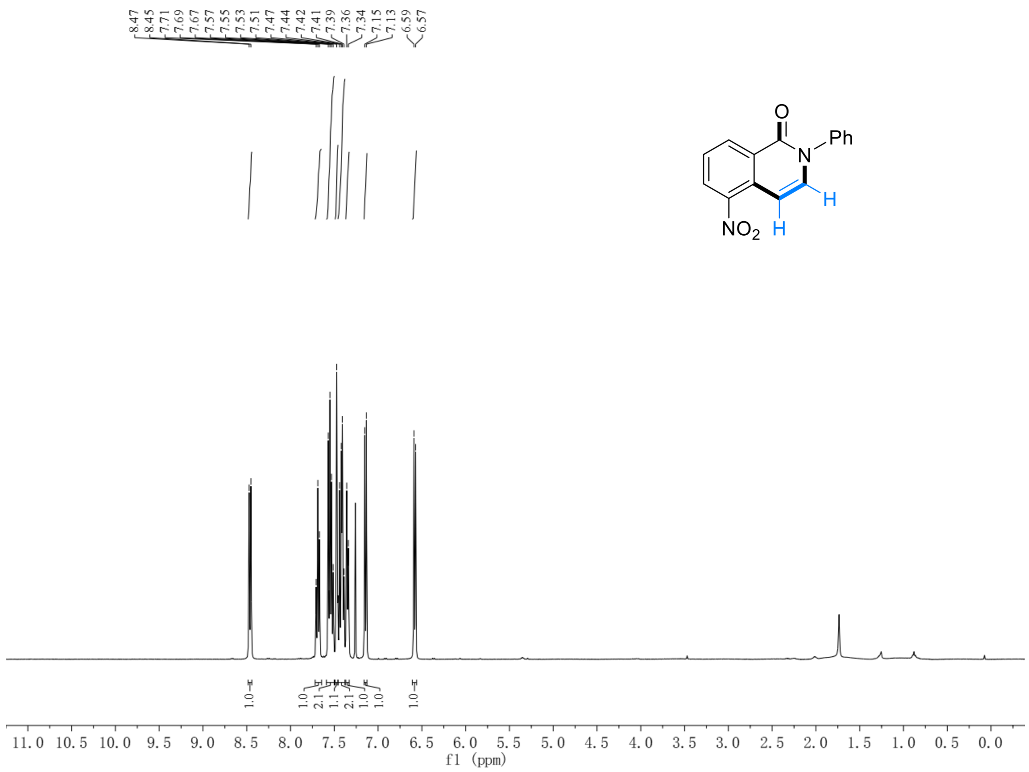
^{1}H NMR of **3s** (400 MHz, $CDCl_3$)



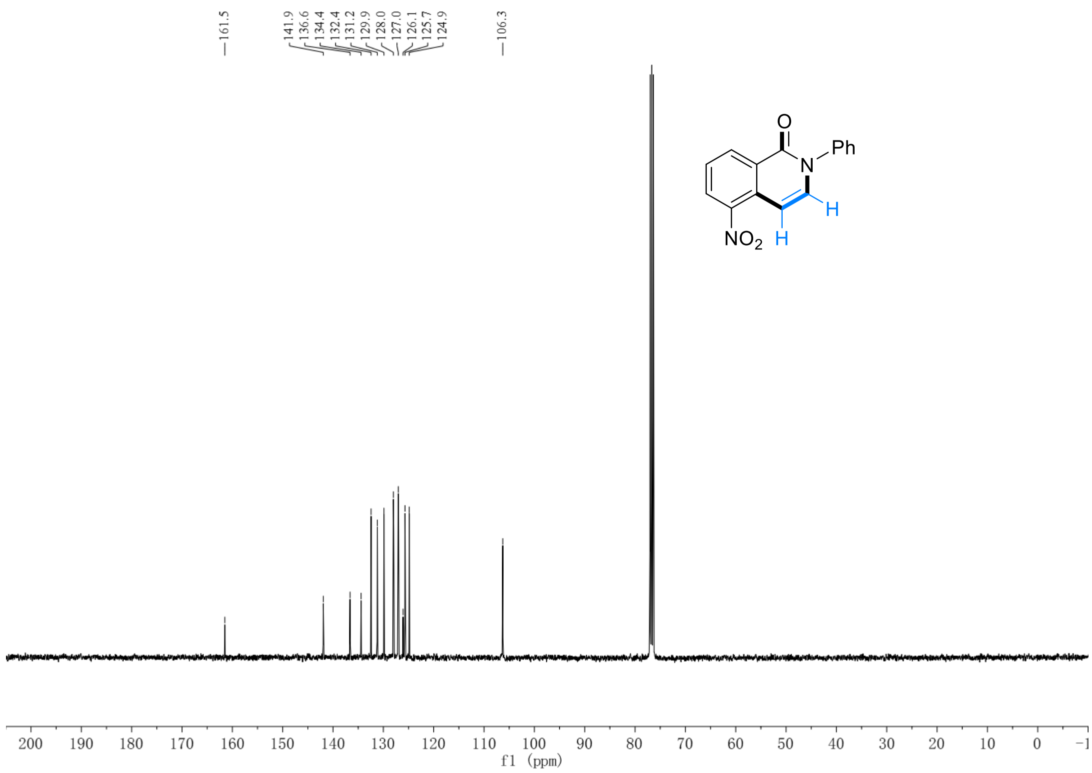
^{13}C NMR of **3s** (100 MHz, $CDCl_3$)



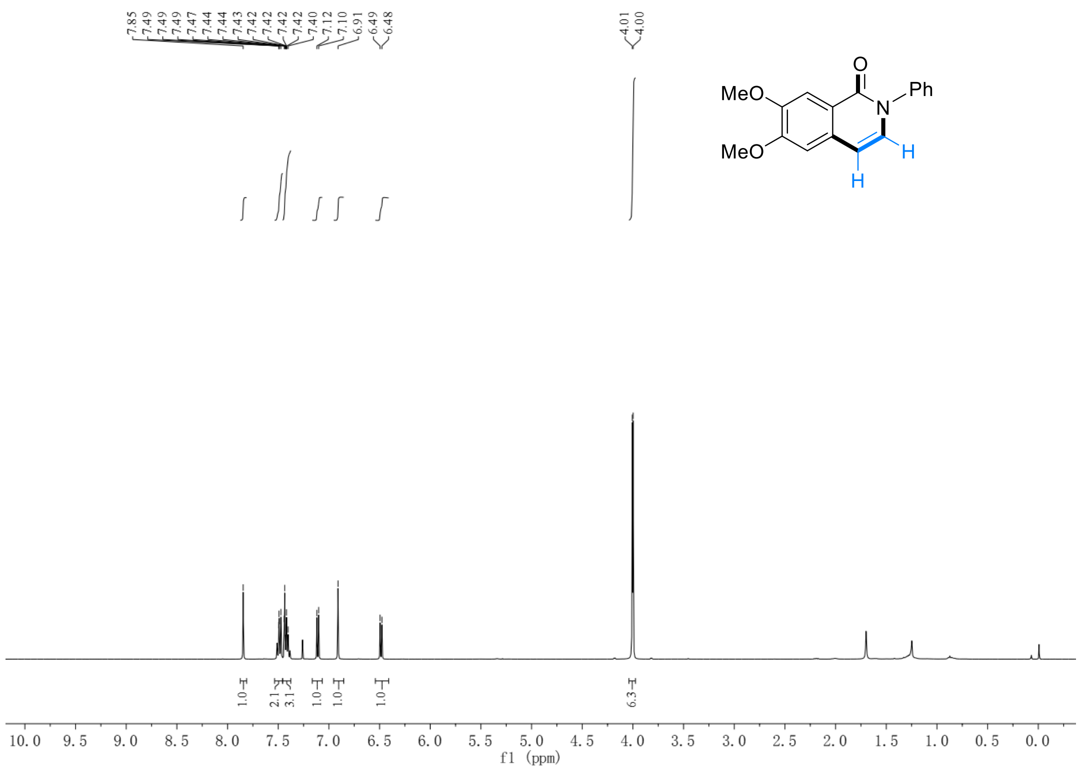
^{1}H NMR of **3t** (400 MHz, $CDCl_3$)



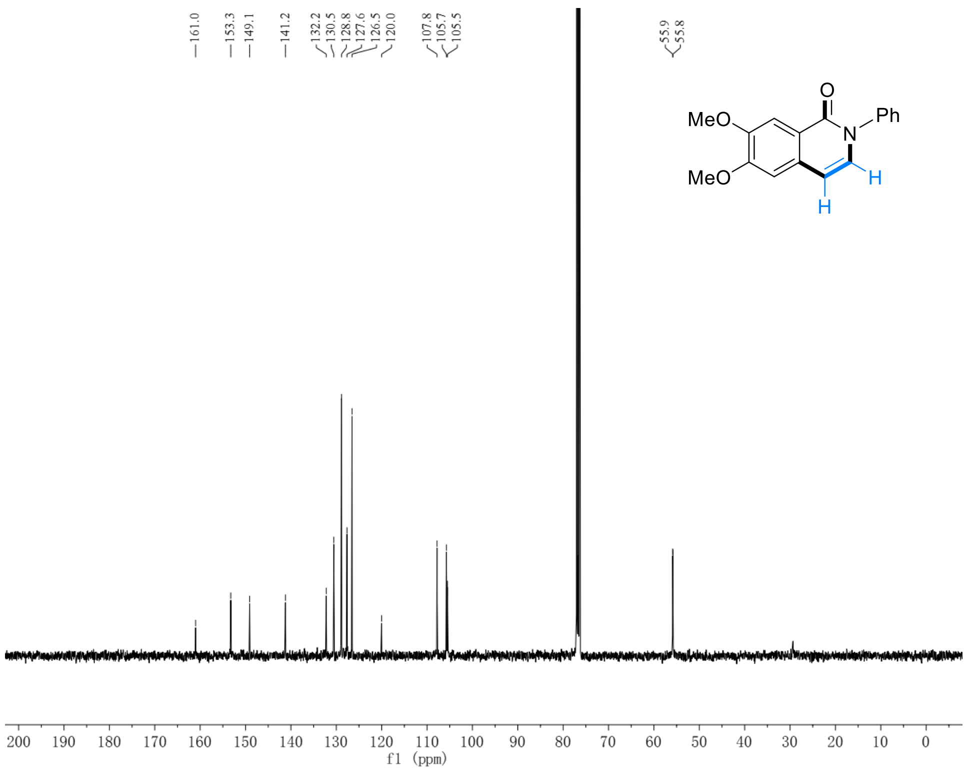
[13]C NMR of **3t** (100 MHz, $CDCl_3$)



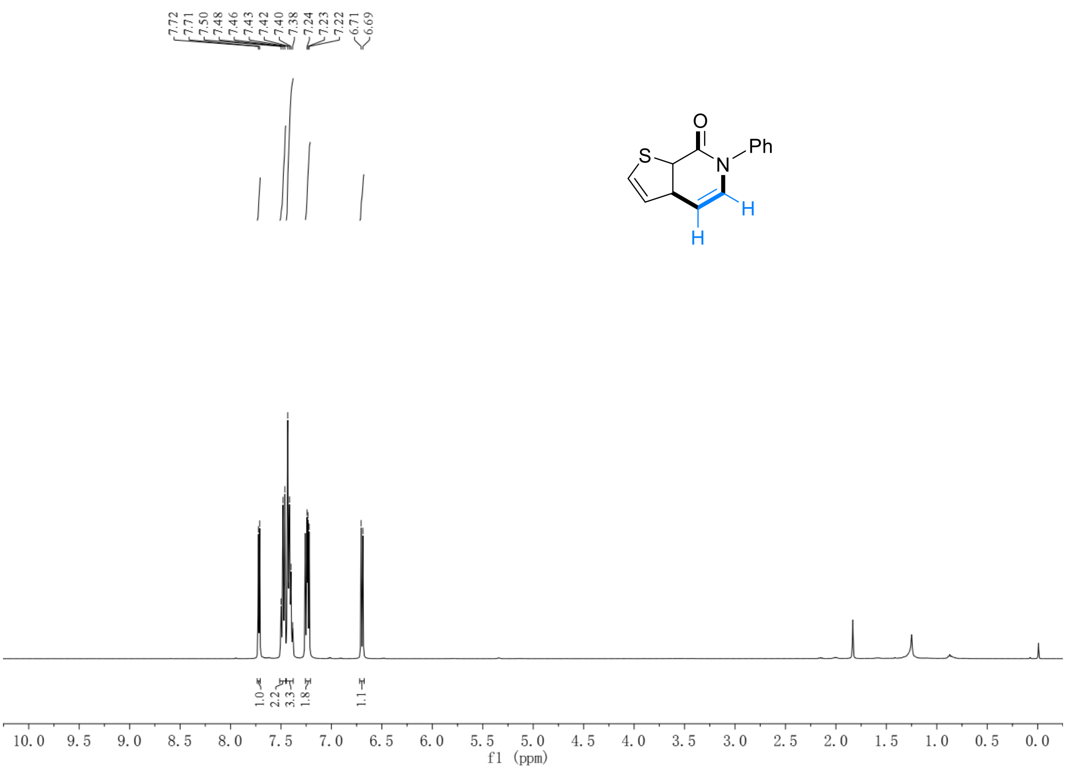
[1]H NMR of **3u** (400 MHz, $CDCl_3$)



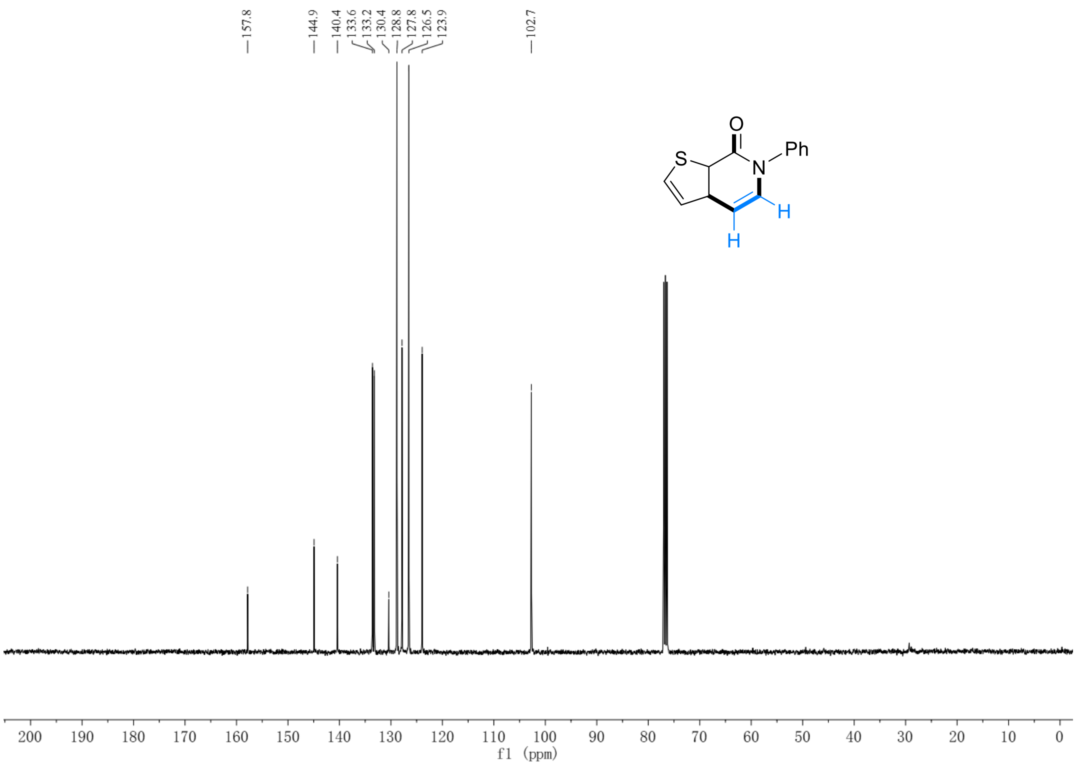
^{13}C NMR of **3u** (100 MHz, $CDCl_3$)



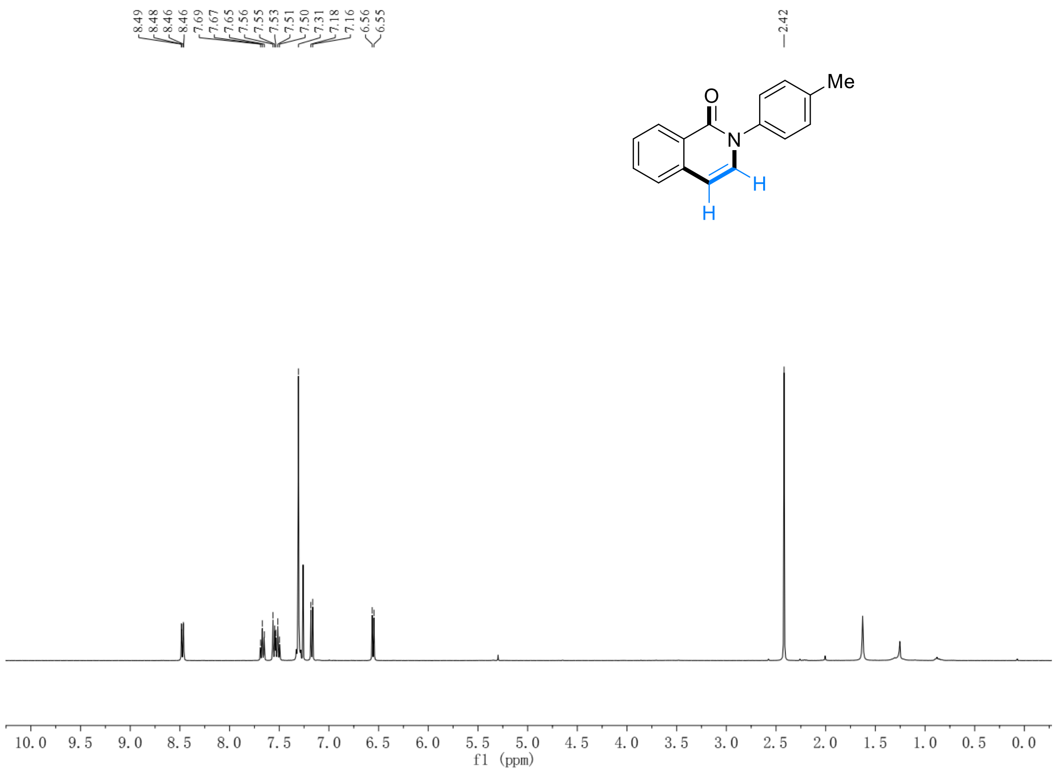
^{1}H NMR of **3v** (400 MHz, $CDCl_3$)



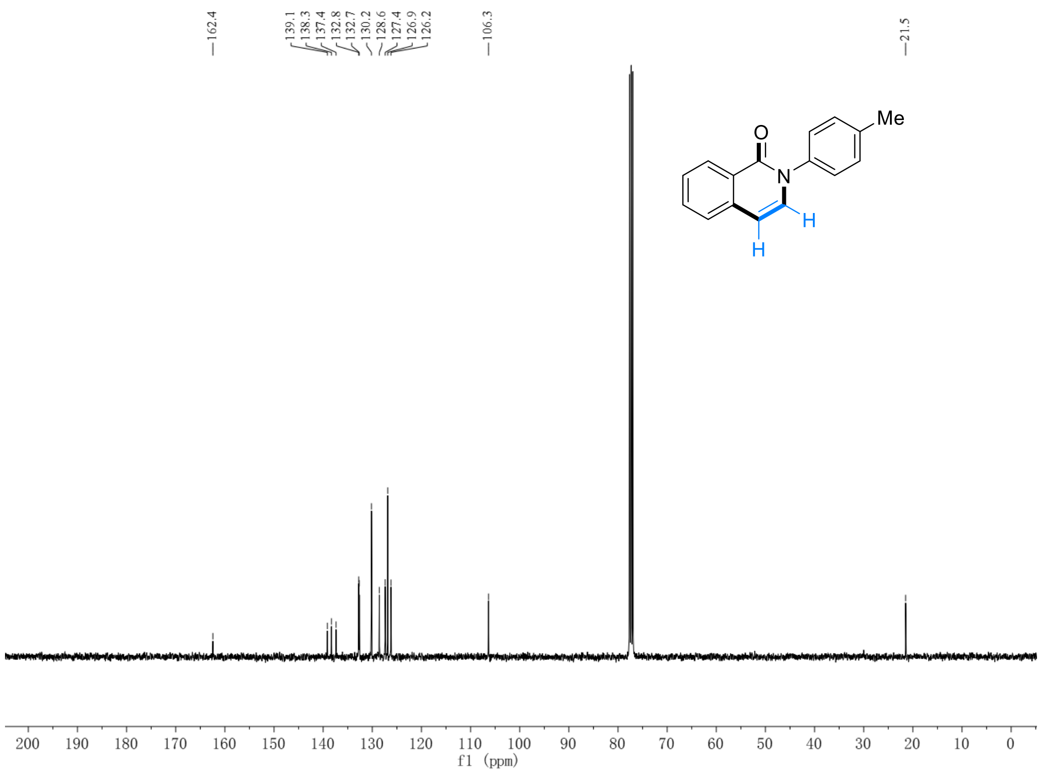
^{13}C NMR of **3v** (100 MHz, $CDCl_3$)



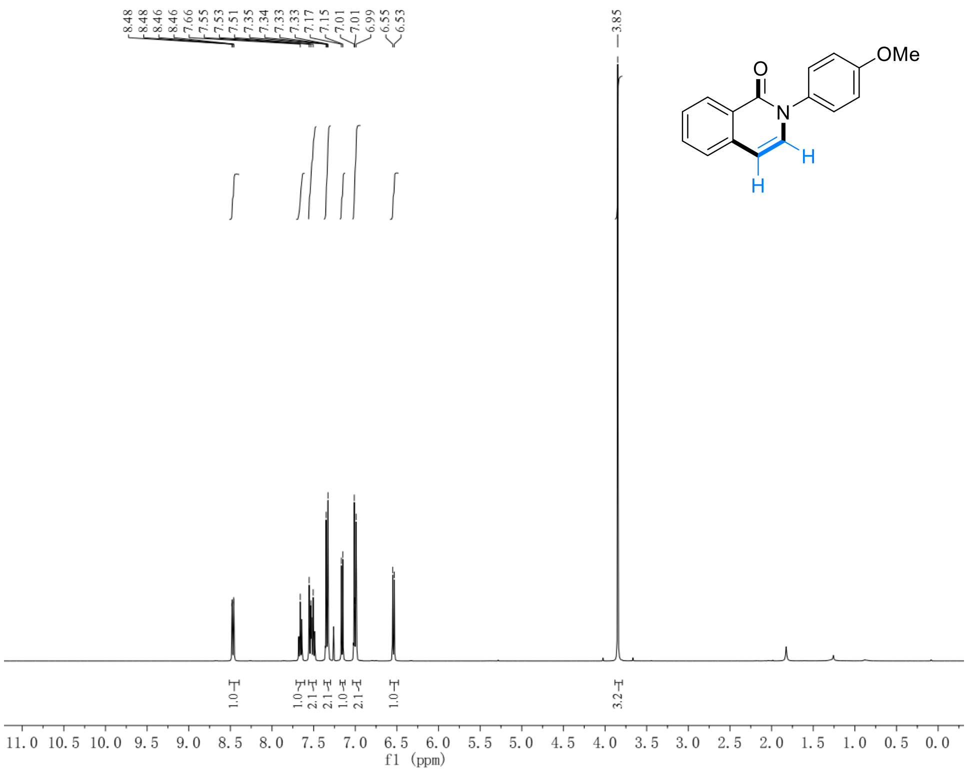
^{1}H NMR of **3a'** (400 MHz, $CDCl_3$)



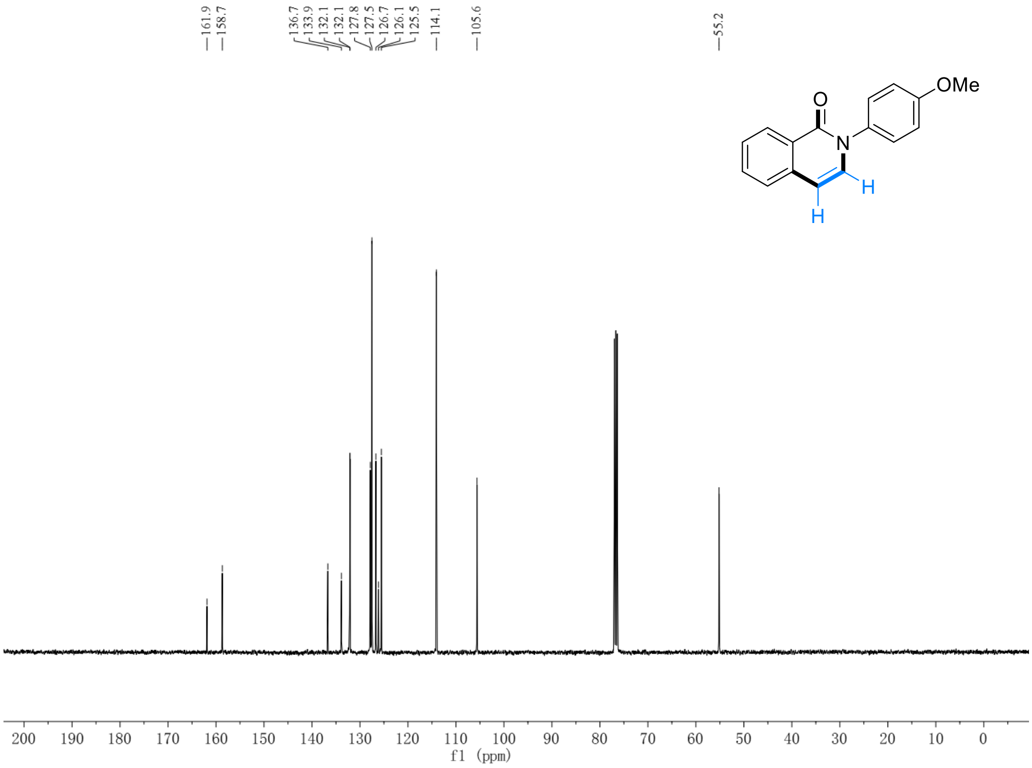
^{13}C NMR of **3a'** (100 MHz, $CDCl_3$)



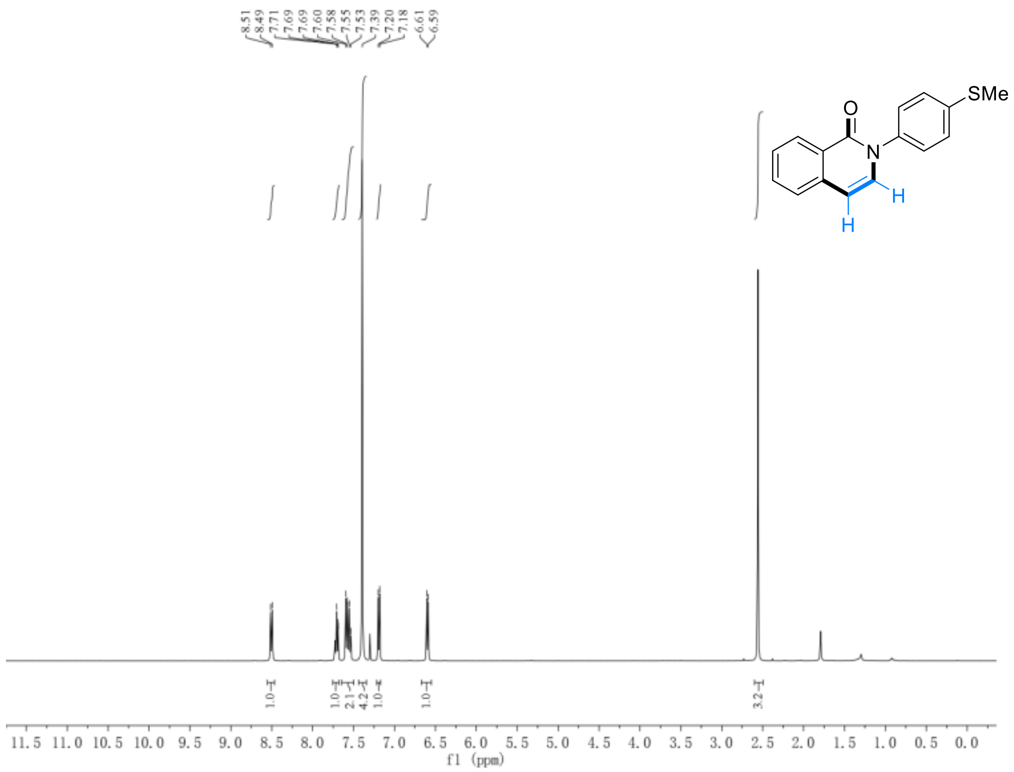
^{1}H NMR of **3b'** (400 MHz, $CDCl_3$)



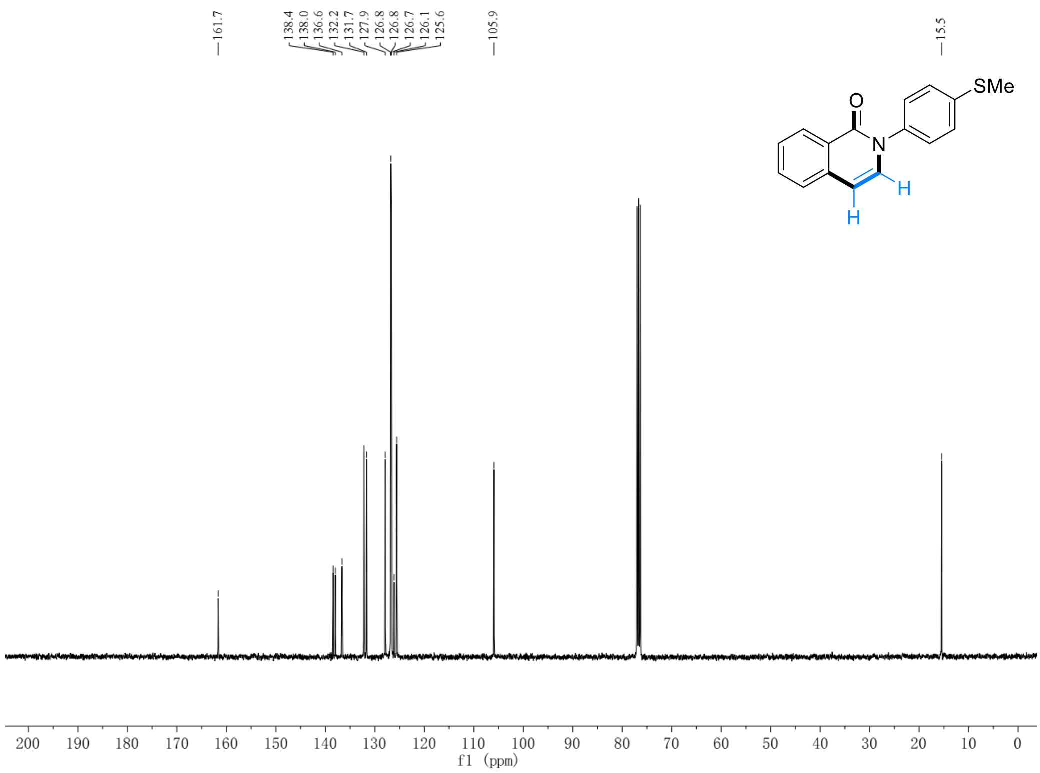
^{13}C NMR of **3b'** (100 MHz, $CDCl_3$)



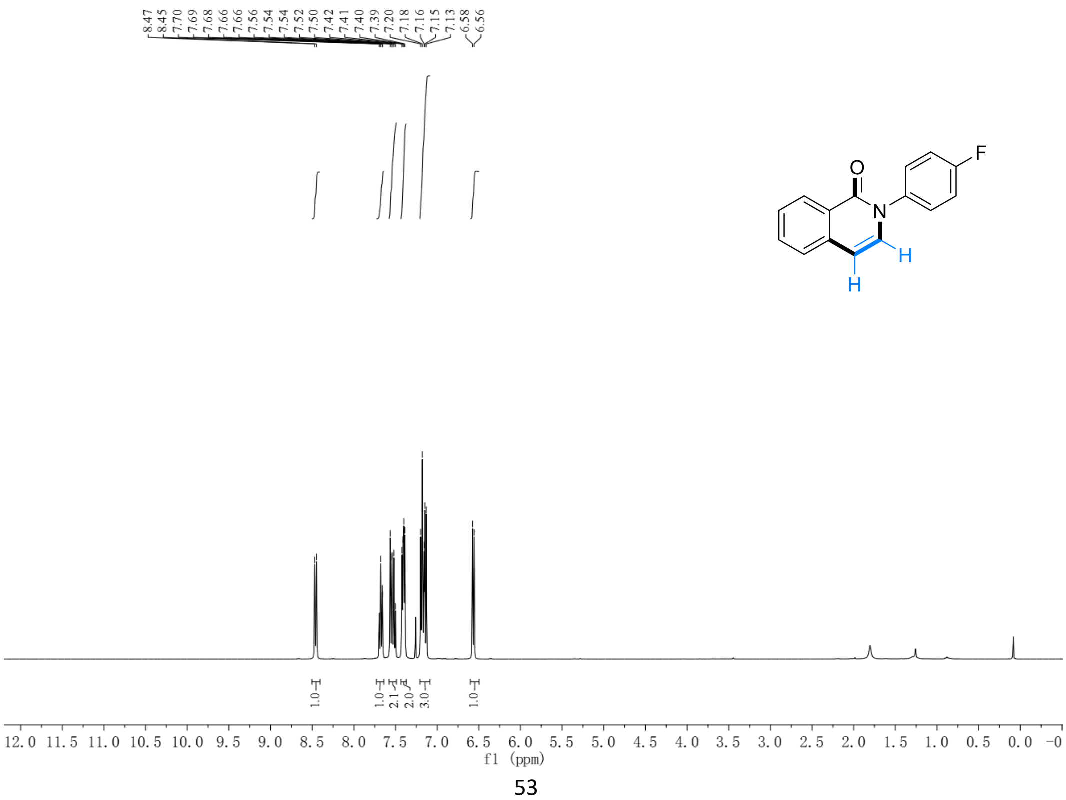
^{1}H NMR of **3c'** (400 MHz, $CDCl_3$)



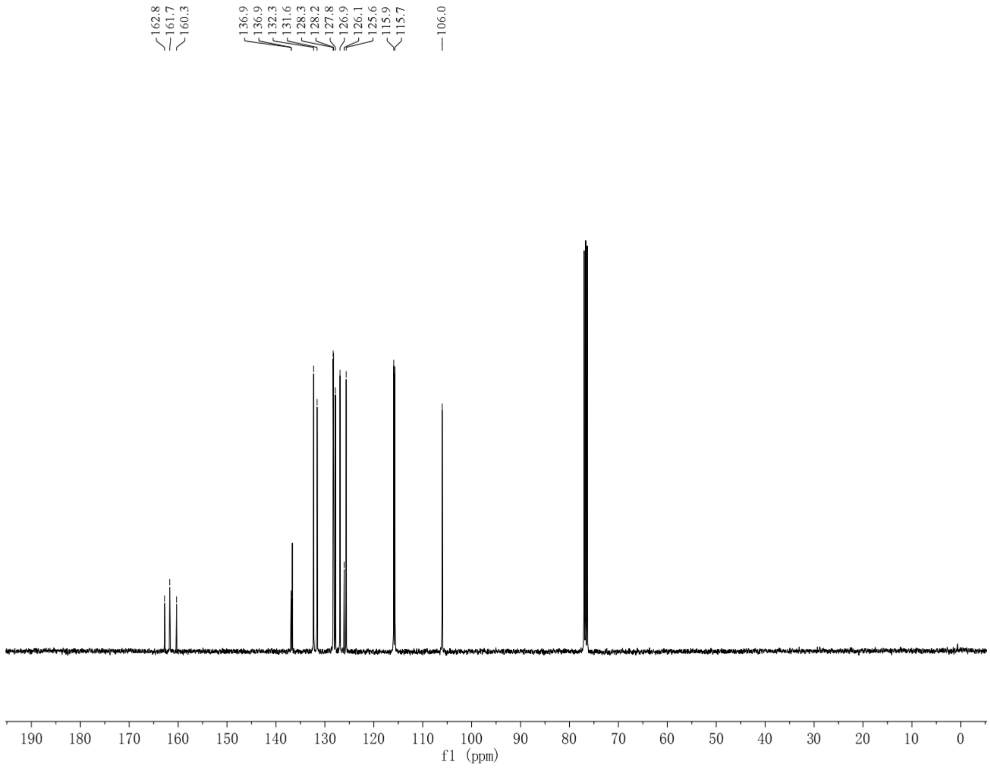
^{13}C NMR of **3c'** (100 MHz, CDCl$_3$)



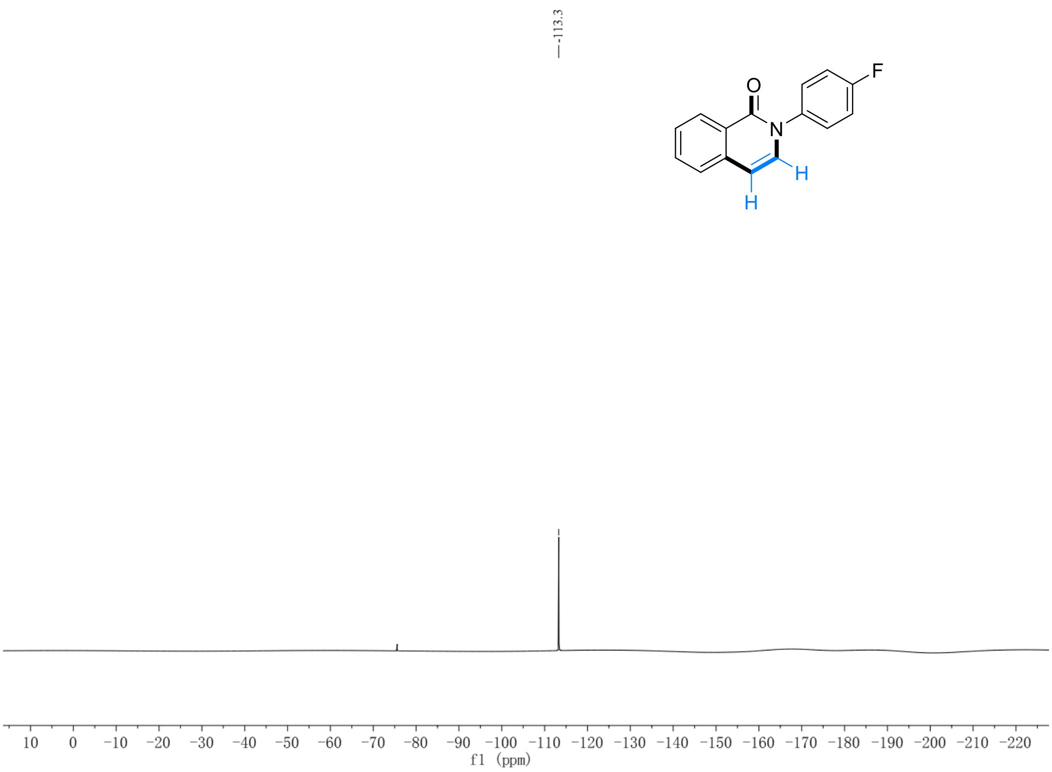
^{1}H NMR of **3d'** (400 MHz, CDCl$_3$)



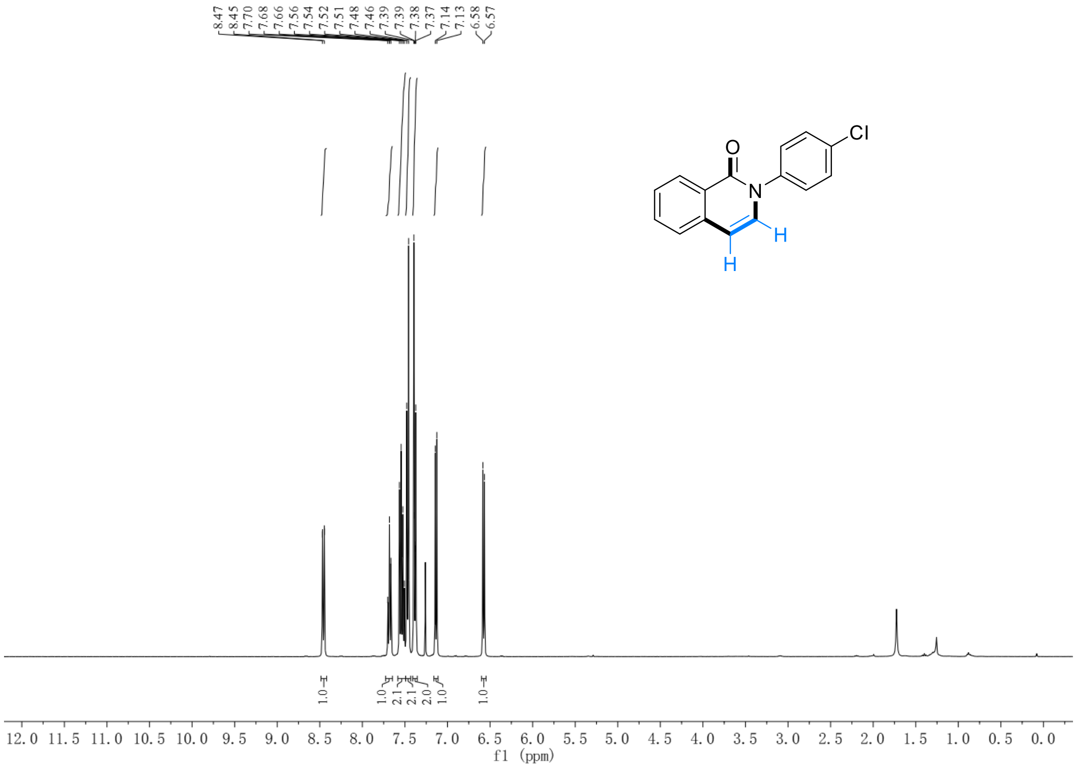
^{13}C NMR of **3d'** (100 MHz, $CDCl_3$)



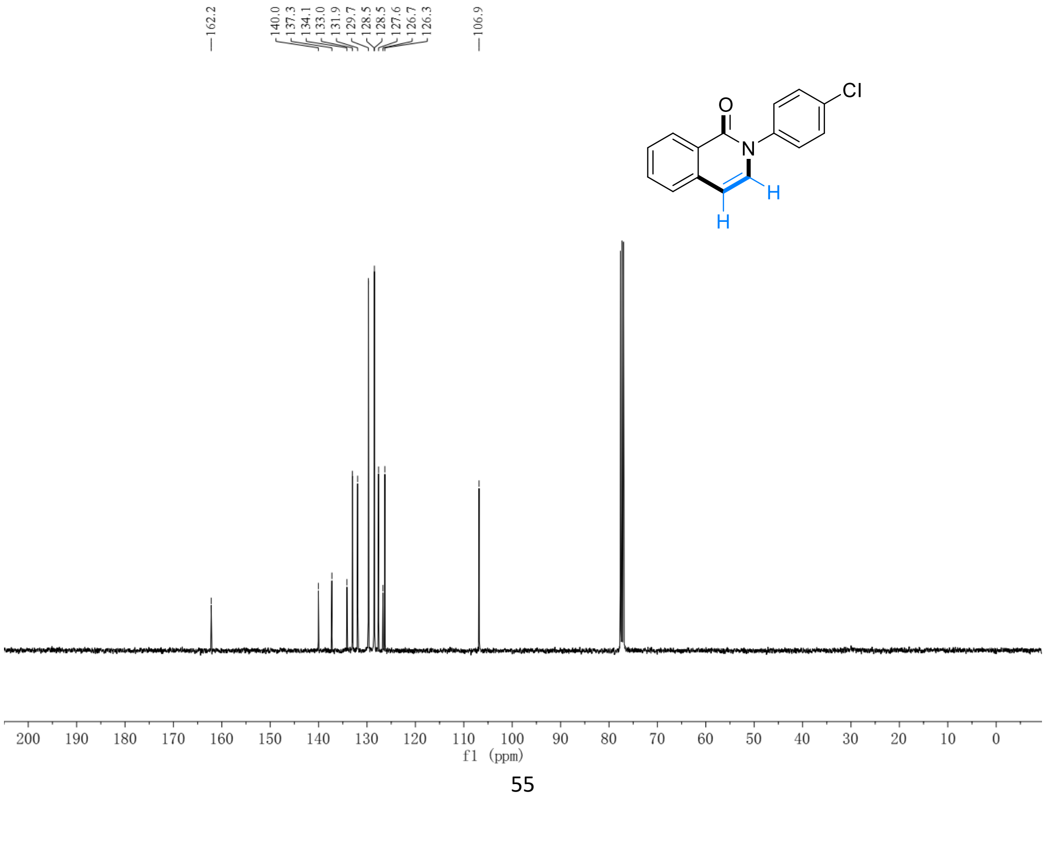
^{19}F NMR of **3d'** (375 MHz, $CDCl_3$)



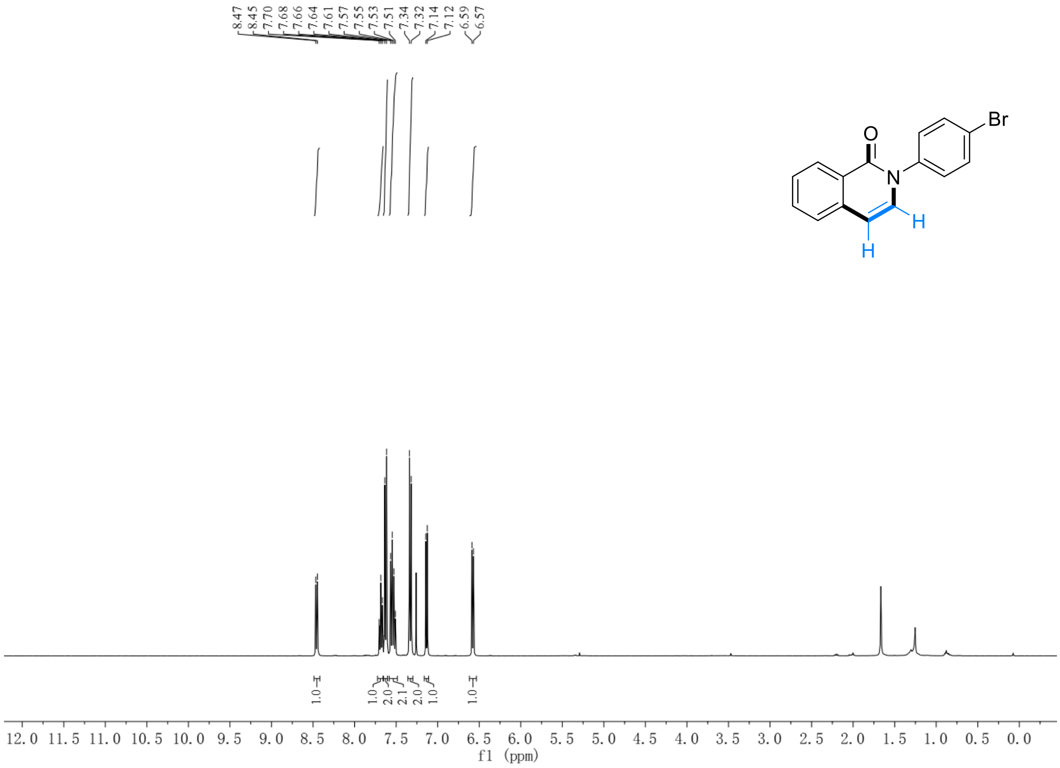
[1]H NMR of **3e'** (400 MHz, $CDCl_3$)



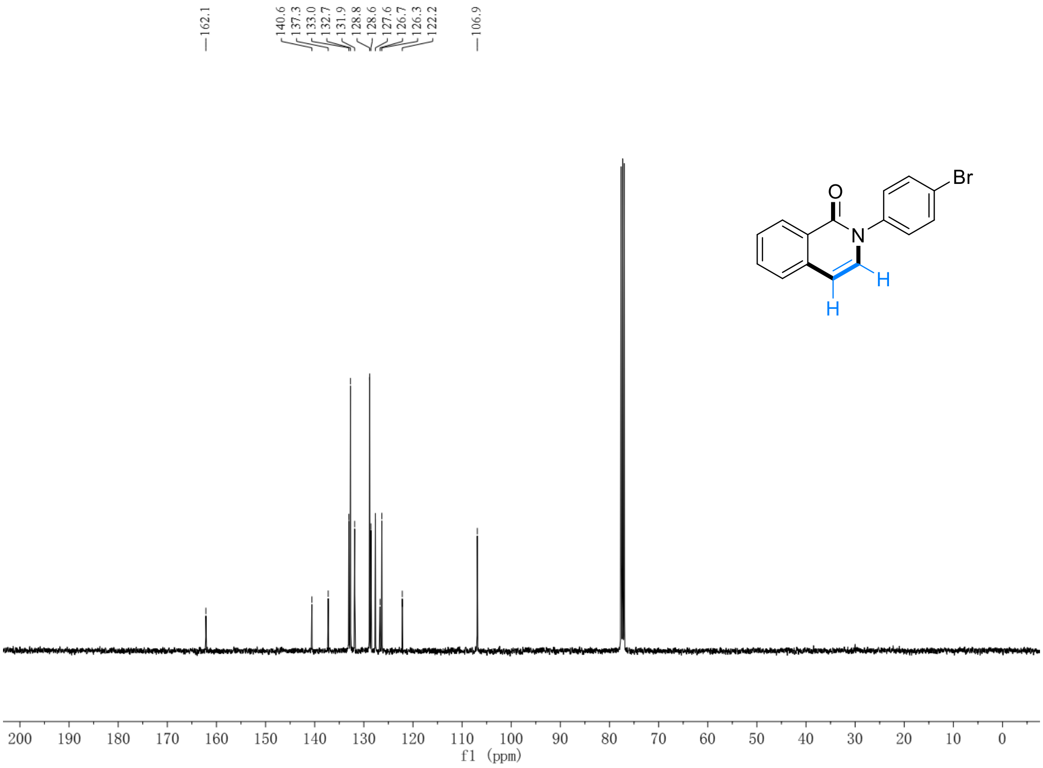
[13]C NMR of **3e'** (100 MHz, $CDCl_3$)



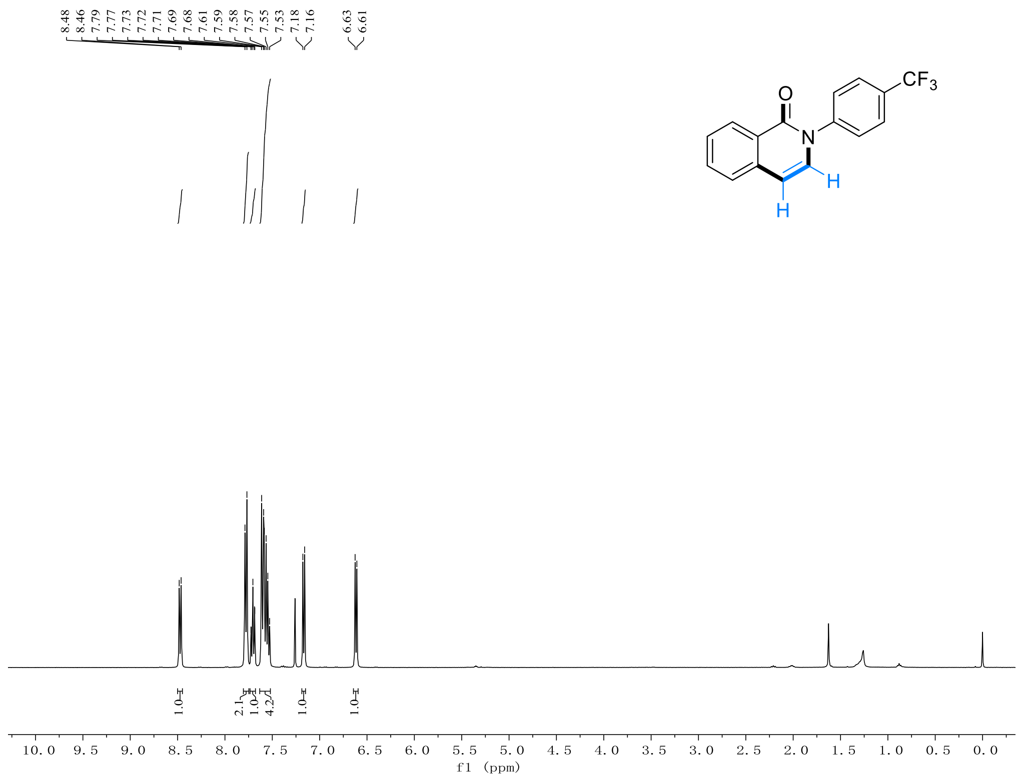
[1]H NMR of **3f'** (400 MHz, $CDCl_3$)



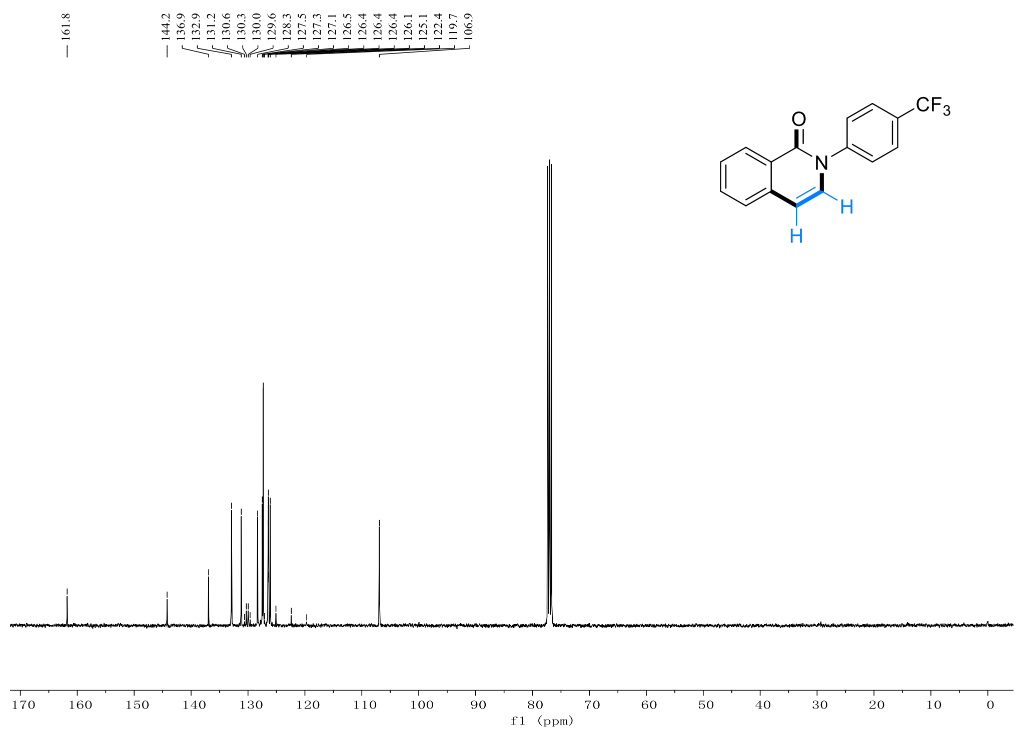
[13]C NMR of **3f'** (100 MHz, $CDCl_3$)



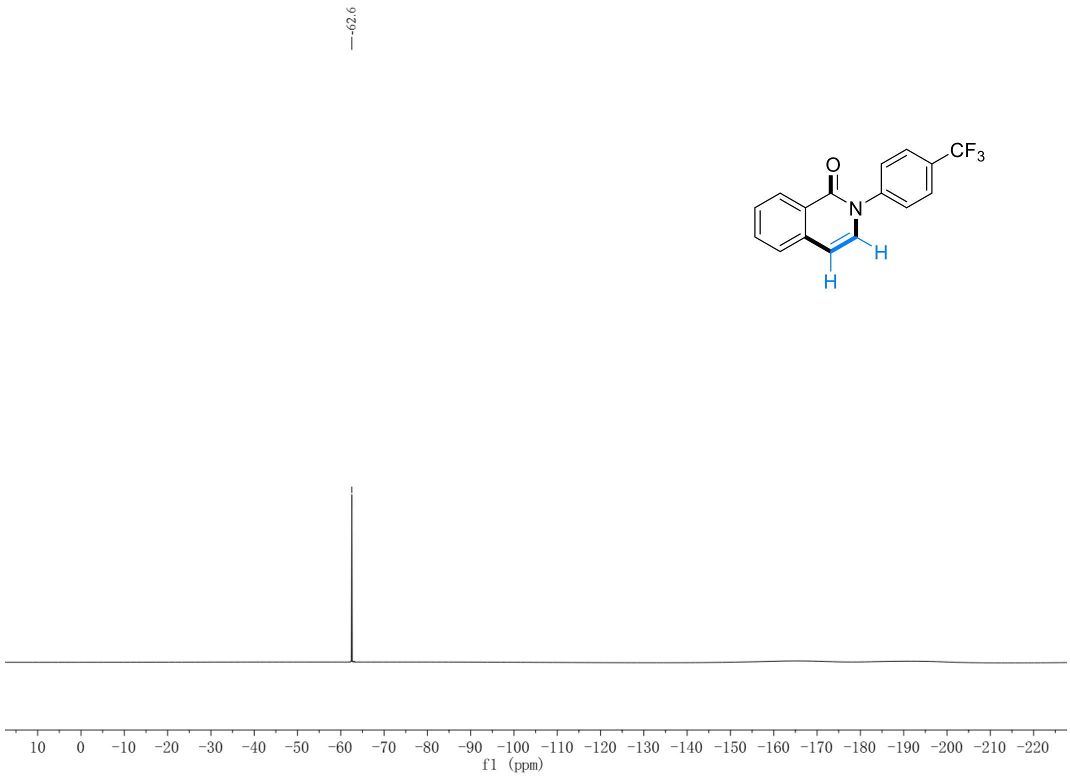
[1]H NMR of **3g'** (400 MHz, $CDCl_3$)



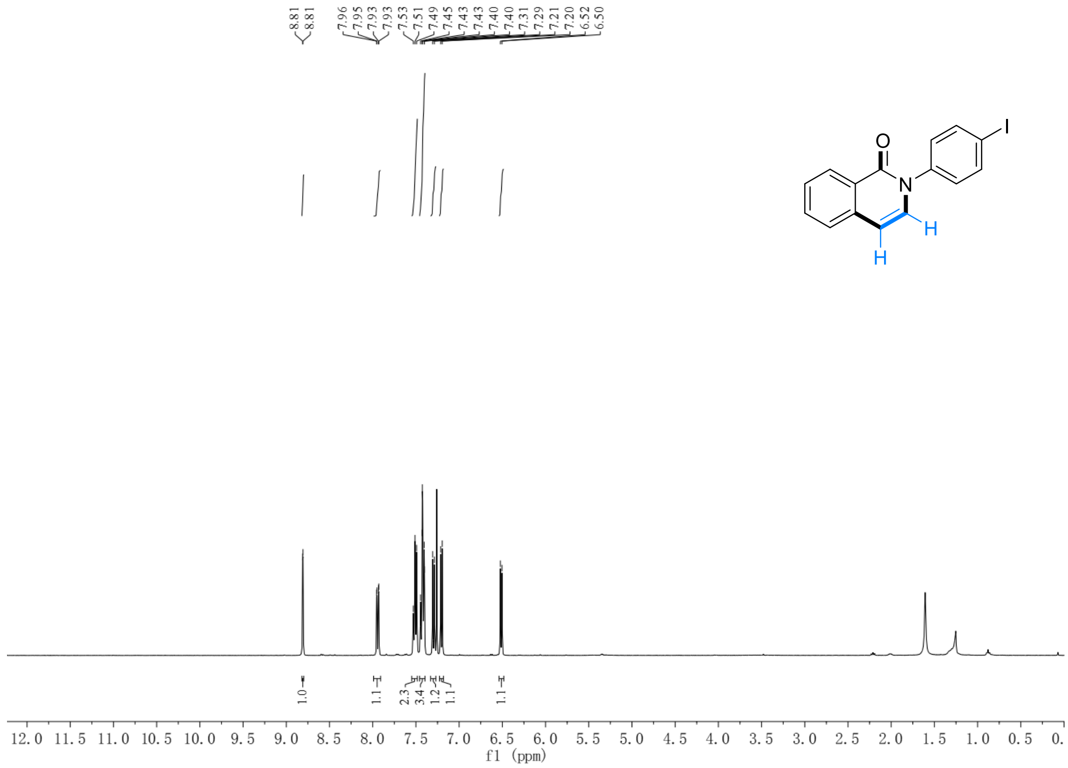
[13]C NMR of **3g'** (100 MHz, $CDCl_3$)



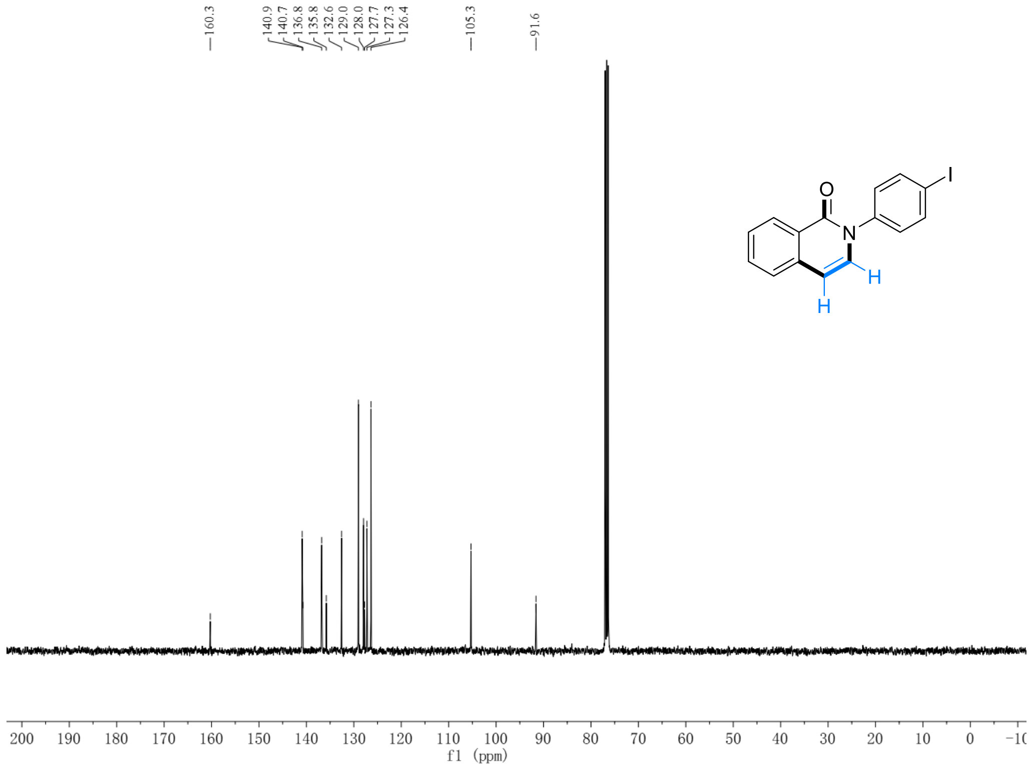
^{19}F NMR of **3g'** (375 MHz, $CDCl_3$)



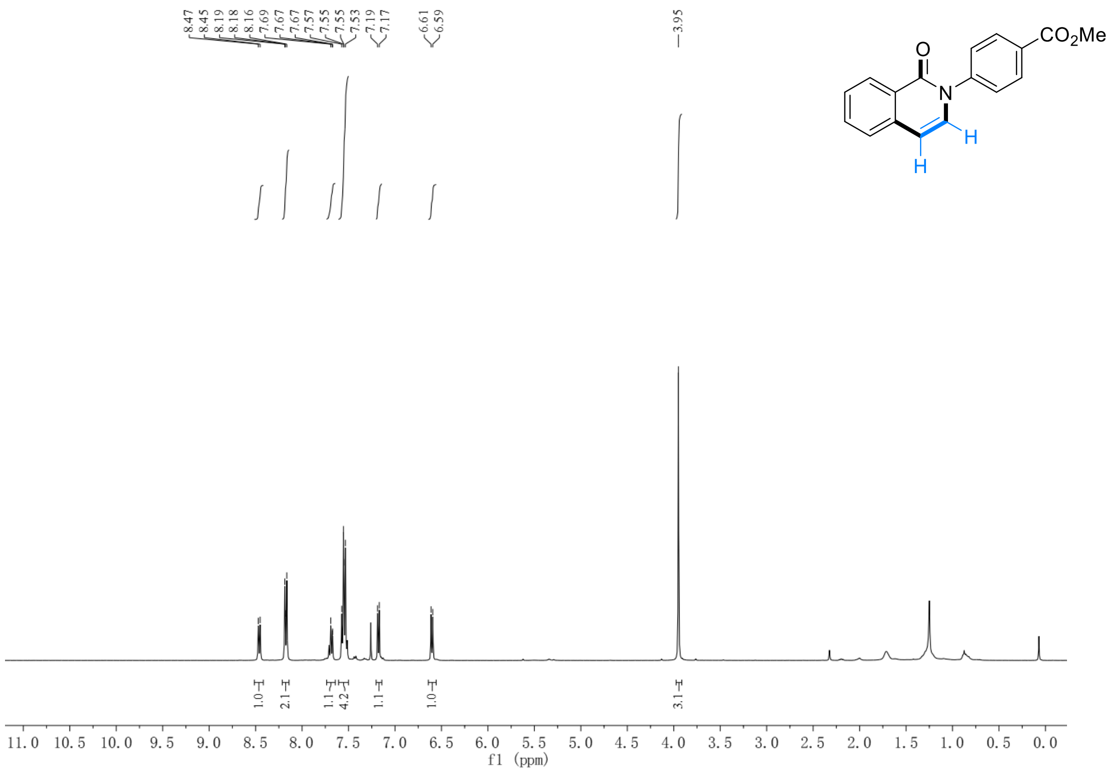
^{1}H NMR of **3h'** (400 MHz, $CDCl_3$)



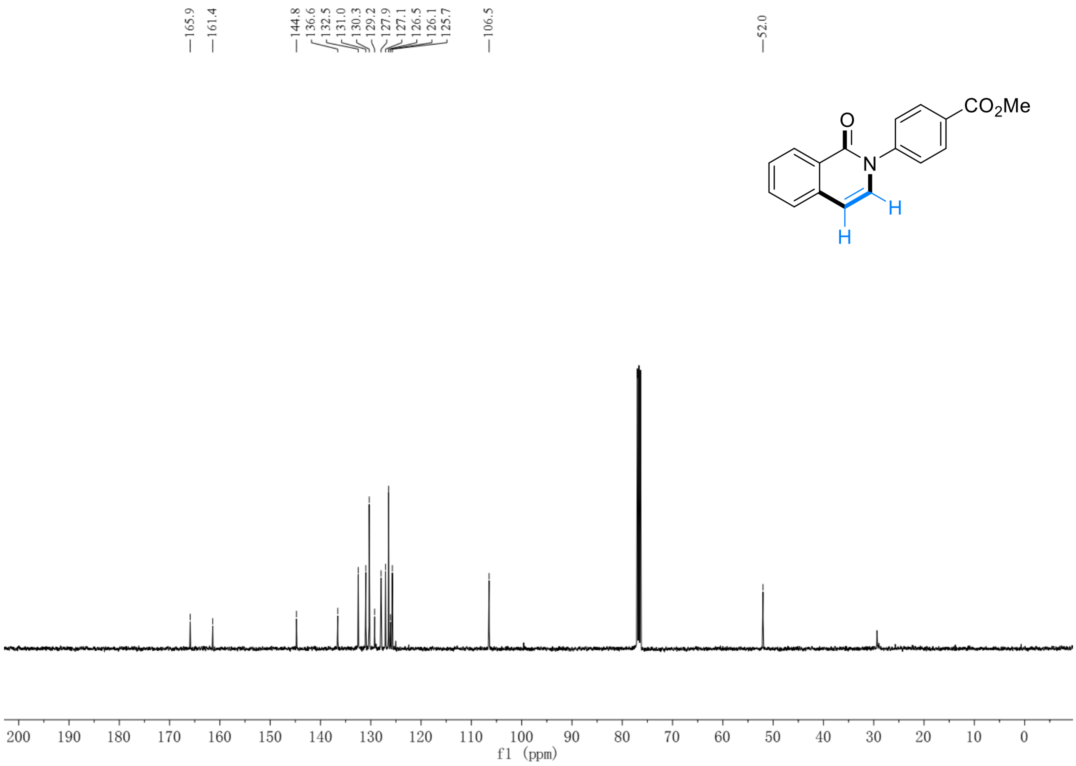
^{13}C NMR of **3h '** (100 MHz, $CDCl_3$)



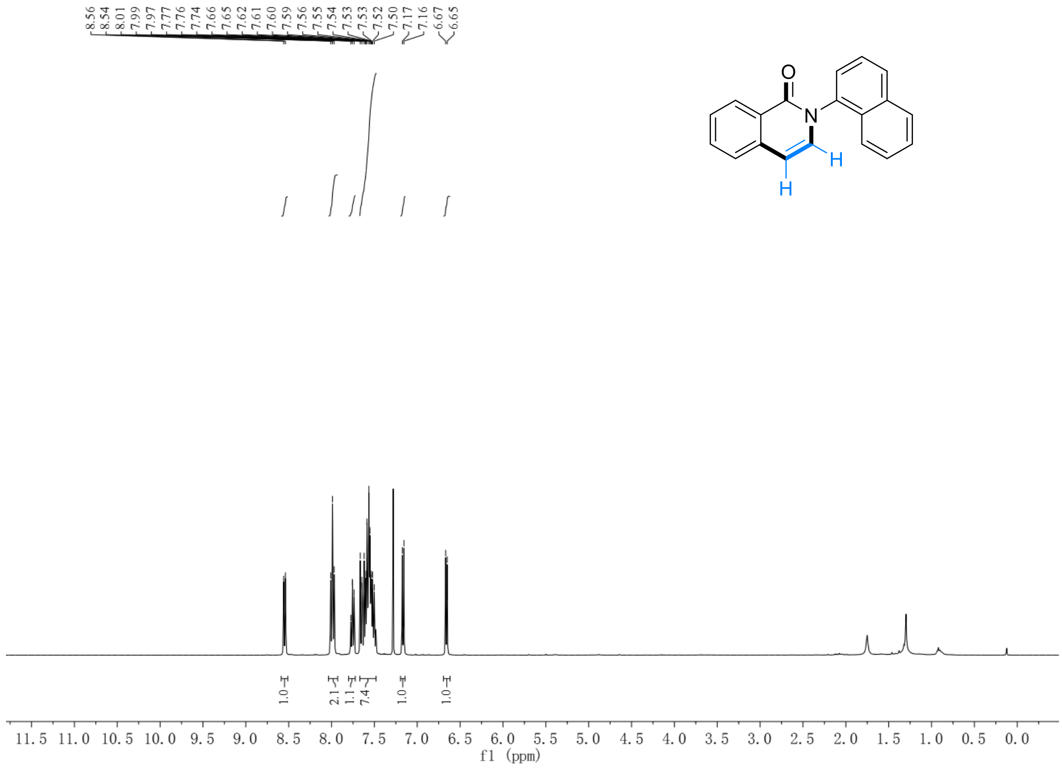
^{1}H NMR of **3i'** (400 MHz, $CDCl_3$)



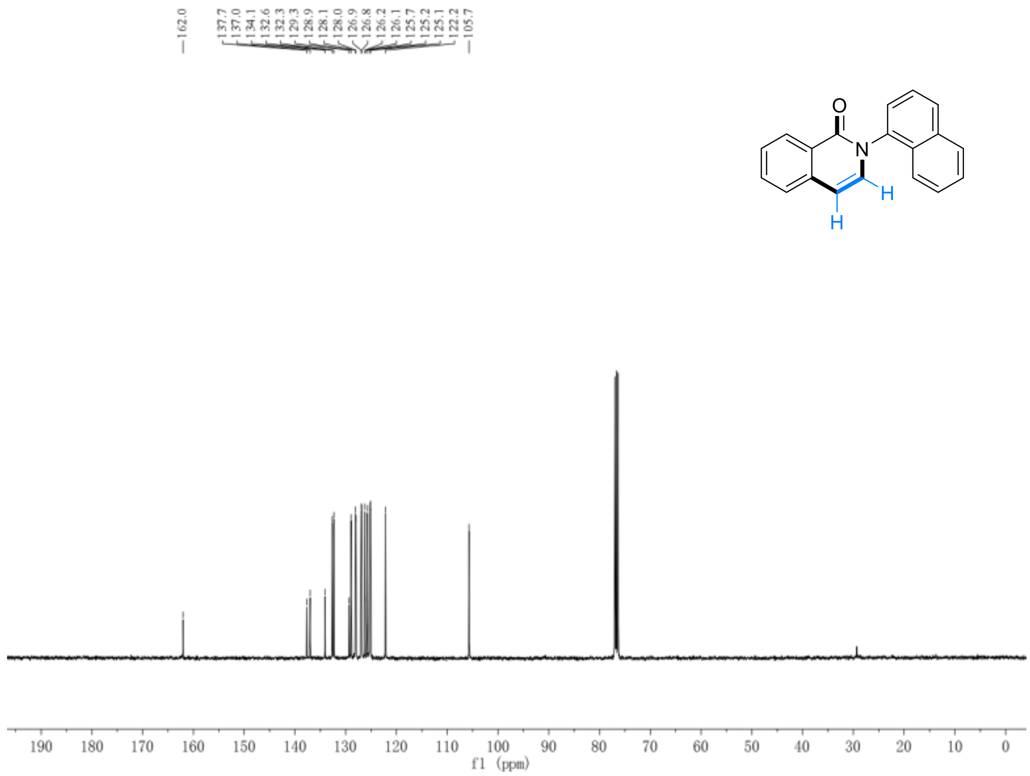
^{13}C NMR of **3i'** (100 MHz, $CDCl_3$)



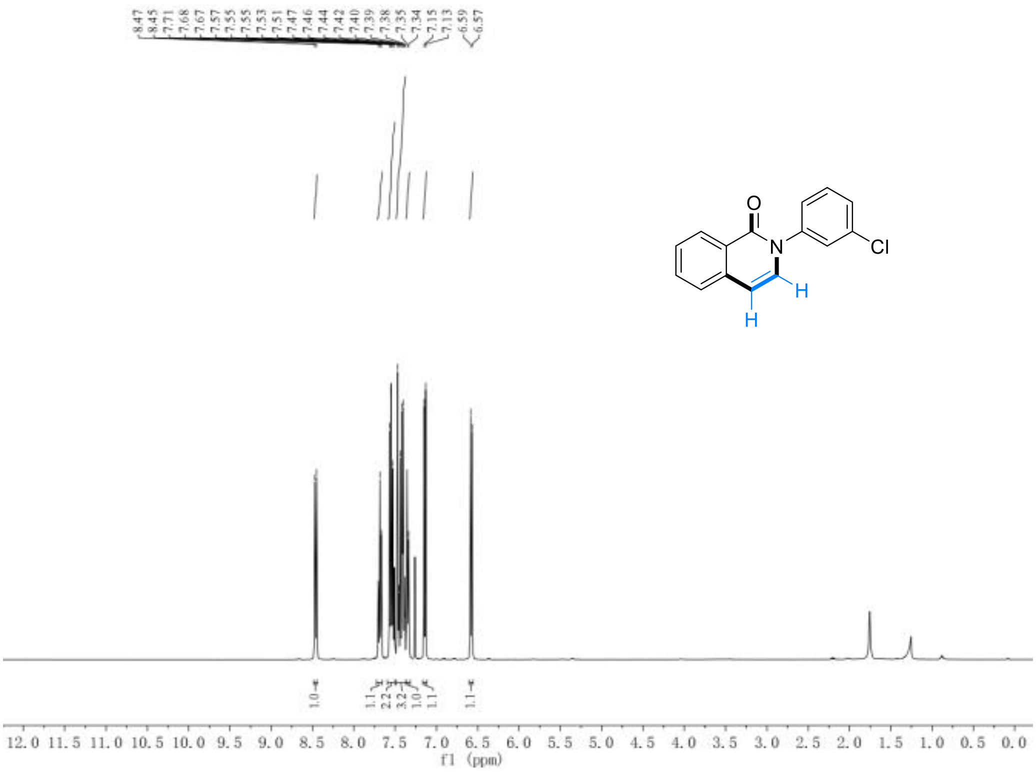
^{1}H NMR of **3j'** (400 MHz, $CDCl_3$)



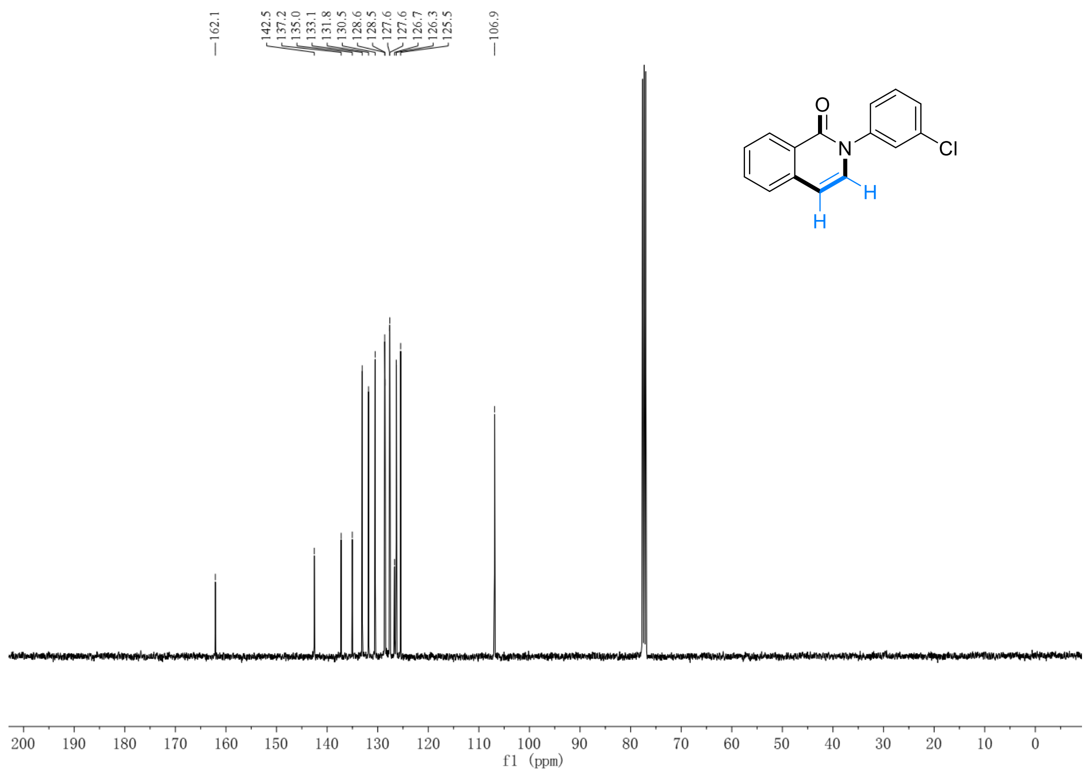
^{13}C NMR of **3j'** (100 MHz, $CDCl_3$)



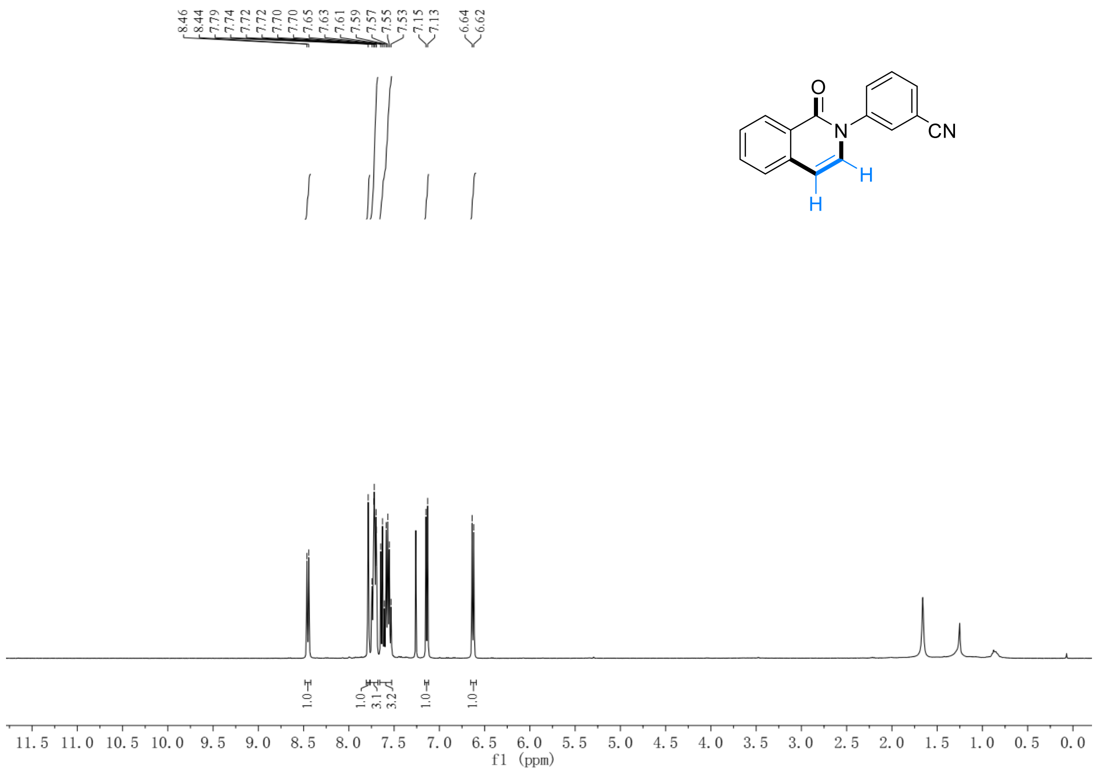
^{1}H NMR of **3k'** (400 MHz, $CDCl_3$)



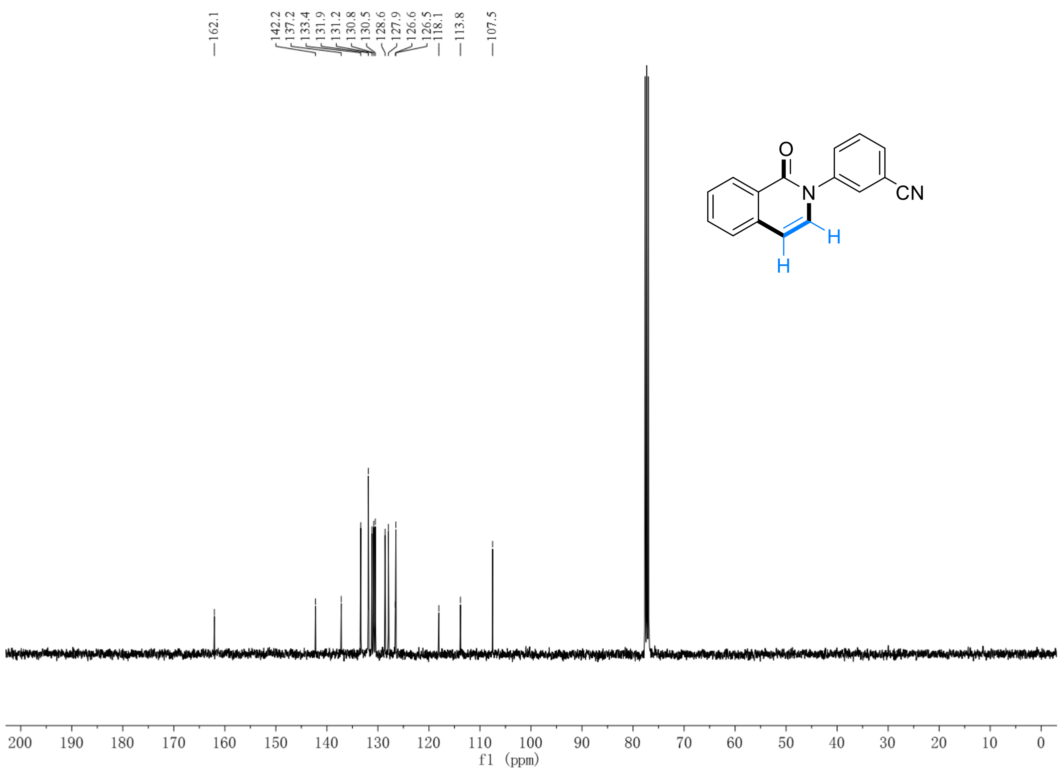
^{13}C NMR of **3k'** (100 MHz, $CDCl_3$)



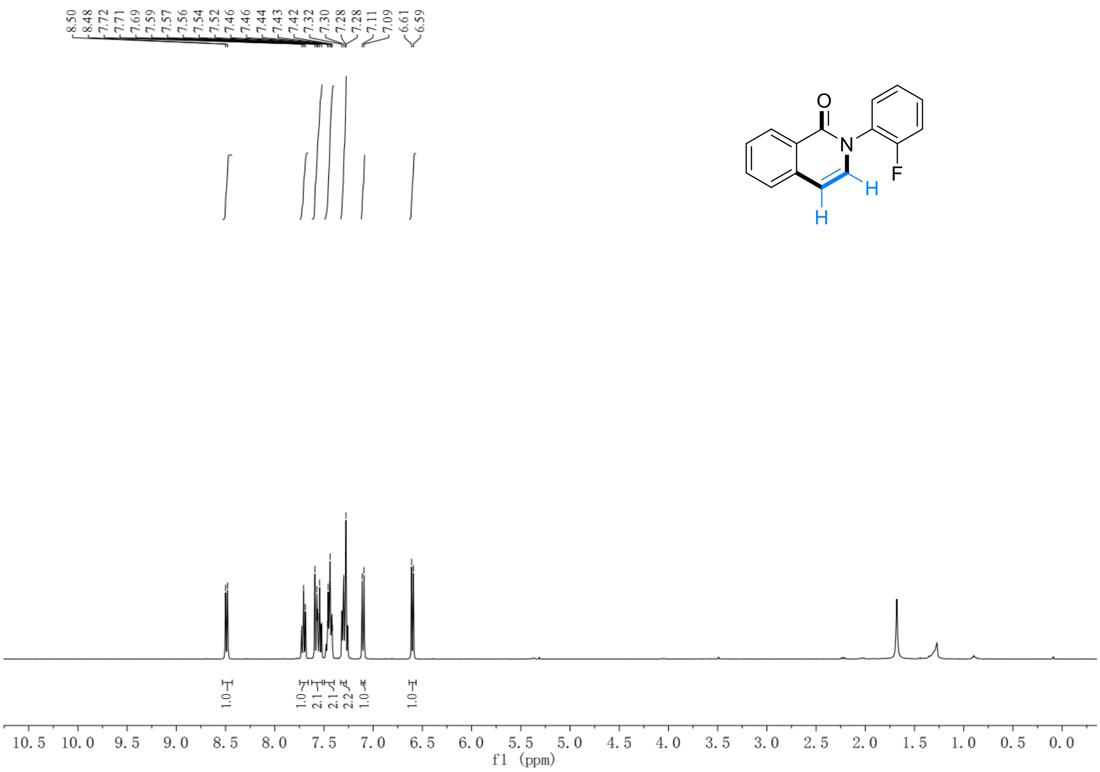
^{1}H NMR of **3l'** (400 MHz, $CDCl_3$)



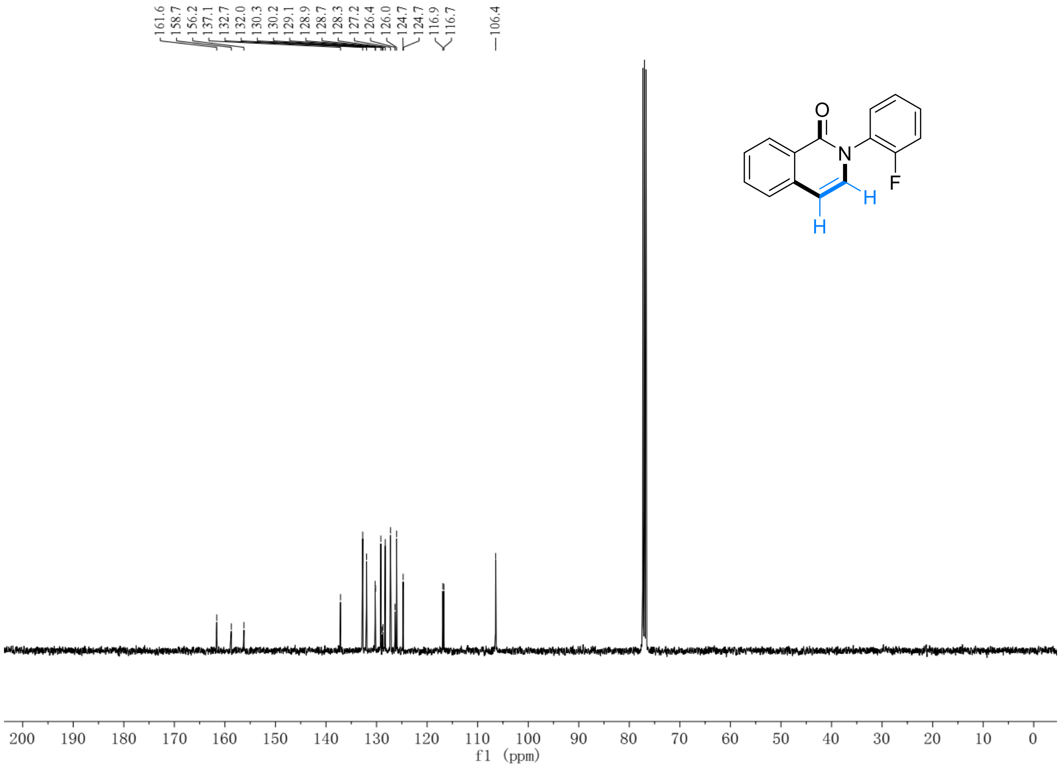
^{13}C NMR of **3l'** (100 MHz, $CDCl_3$)



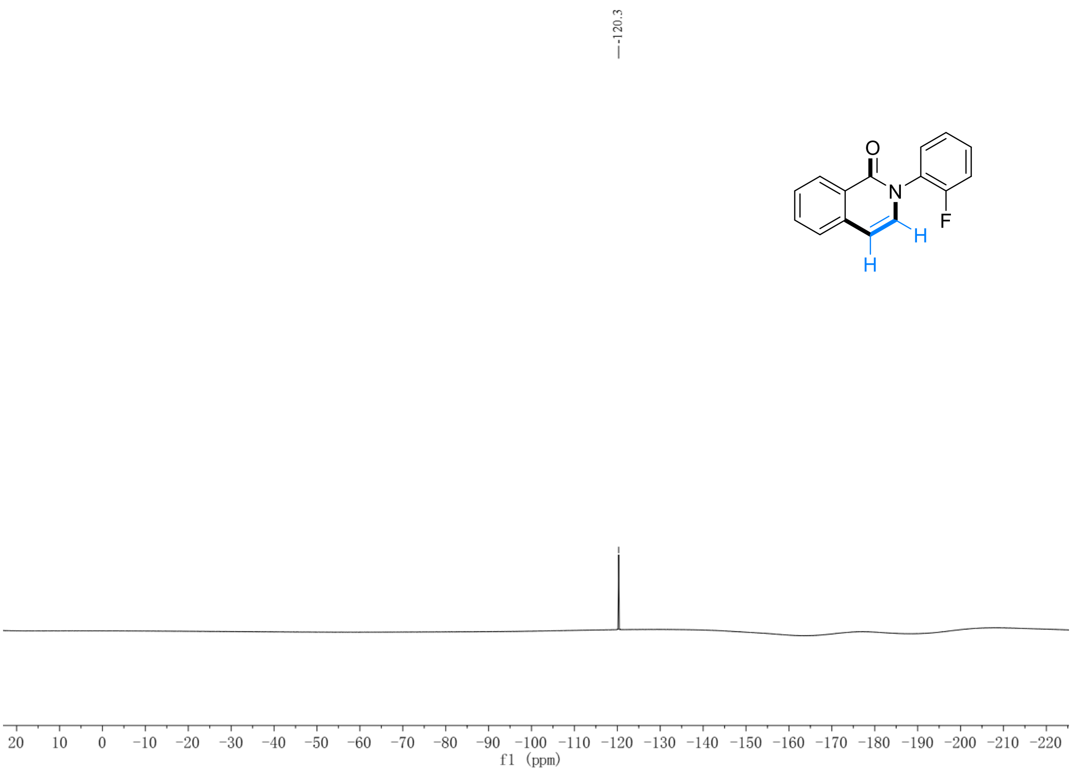
^{1}H NMR of **3m'** (400 MHz, $CDCl_3$)



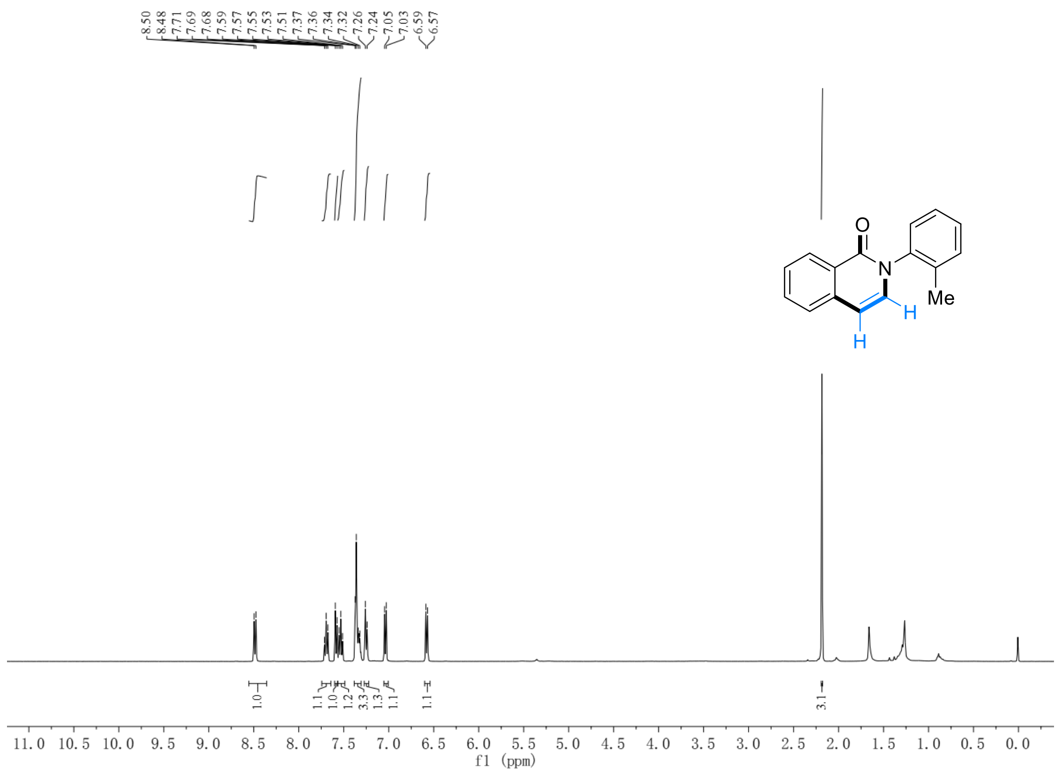
^{13}C NMR of **3m'** (100 MHz, $CDCl_3$)



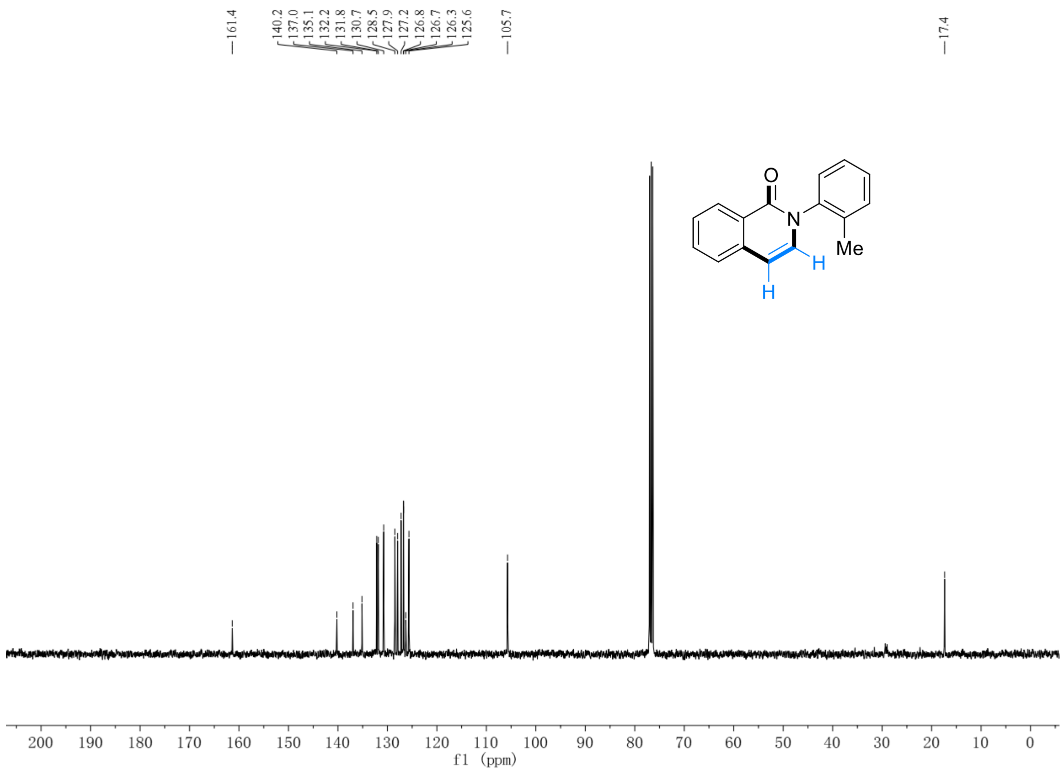
^{19}F NMR of **3m'** (375 MHz, $CDCl_3$)



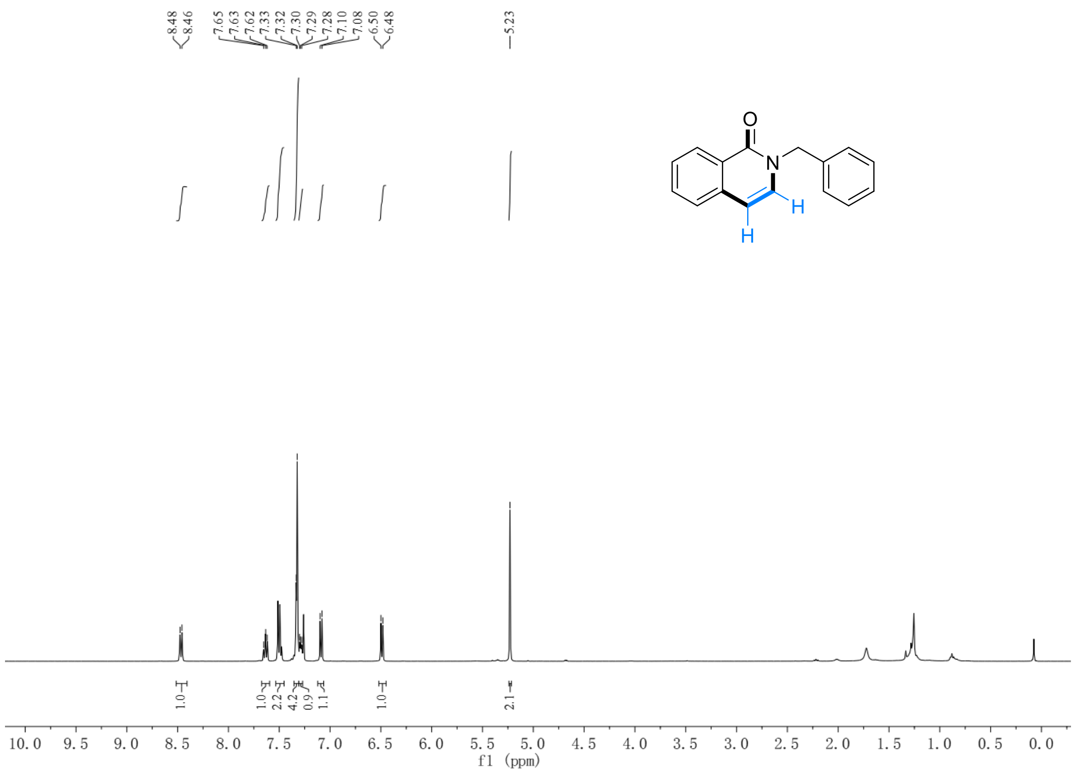
^{1}H NMR of **3n'** (400 MHz, $CDCl_3$)



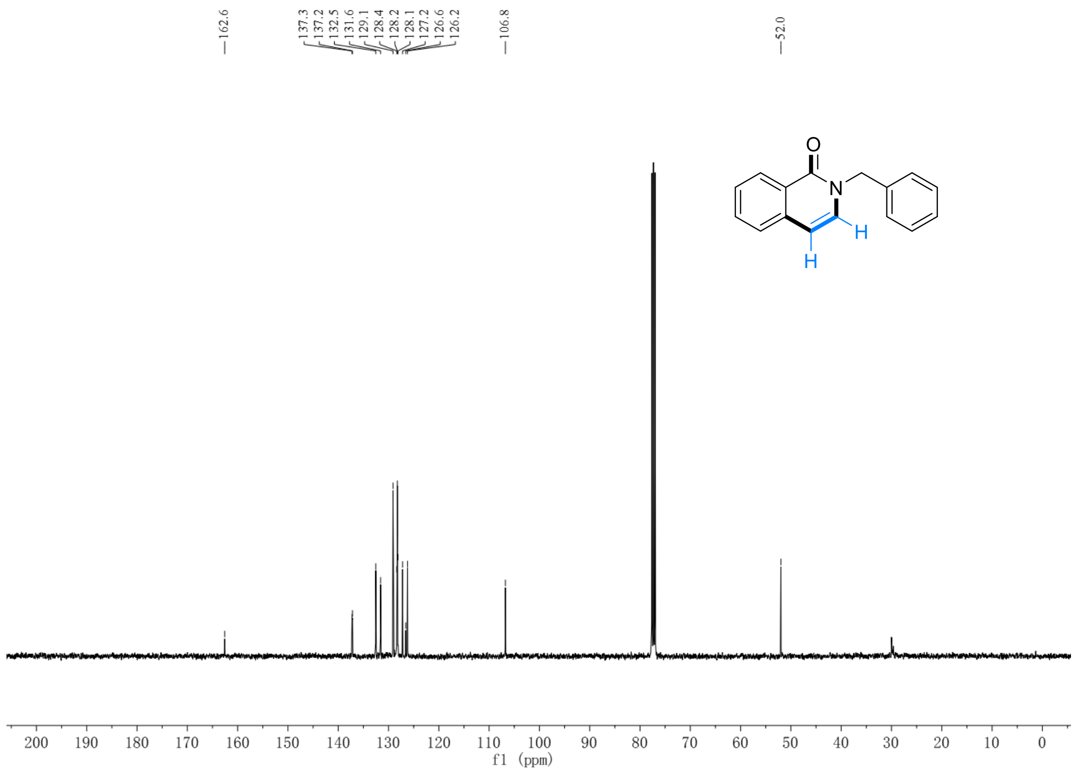
^{13}C NMR of **3n'** (100 MHz, $CDCl_3$)



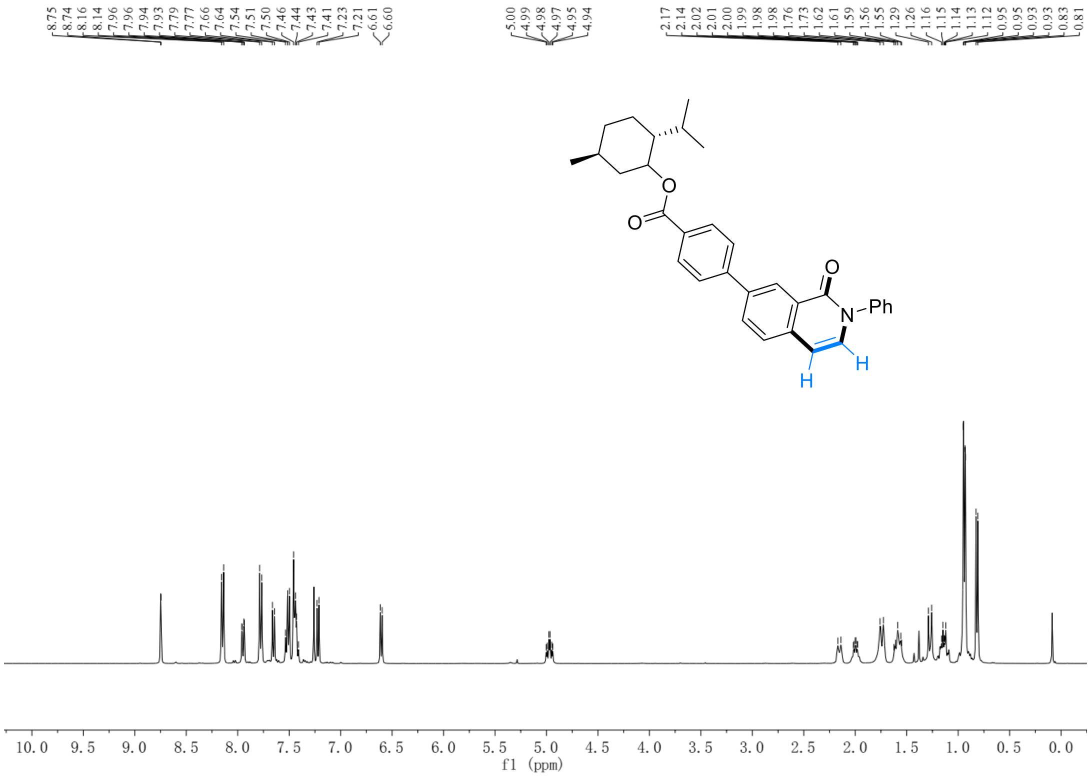
^{1}H NMR of **3o'** (400 MHz, $CDCl_3$)



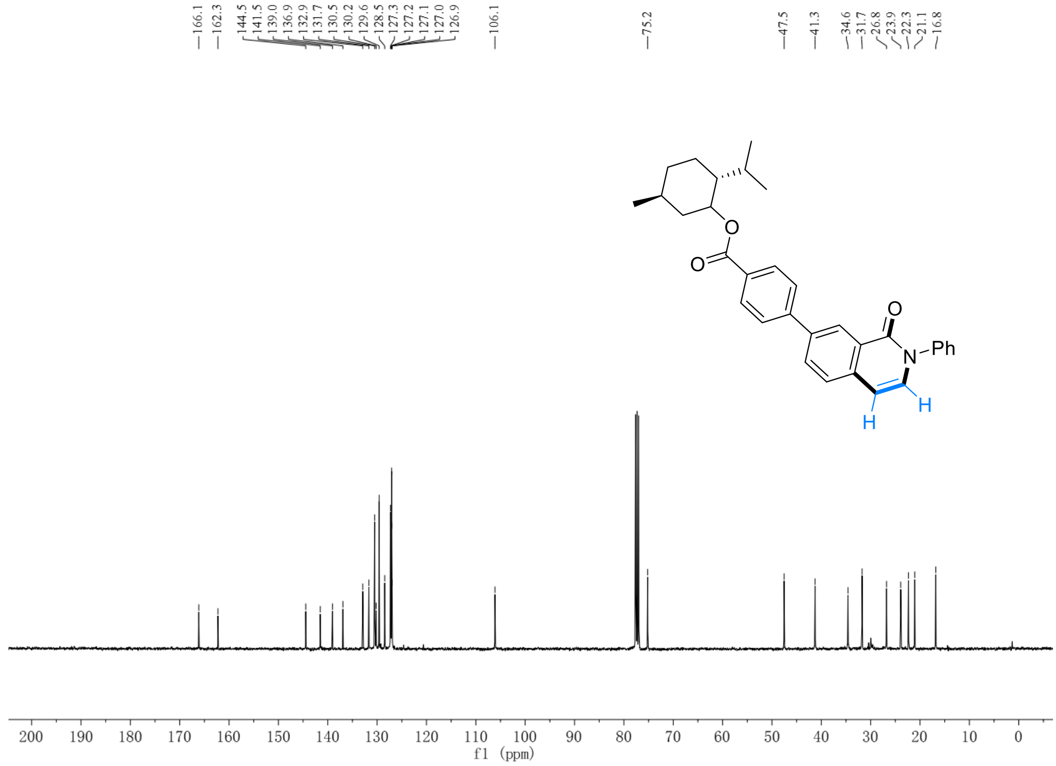
^{13}C NMR of **3o'** (100 MHz, $CDCl_3$)



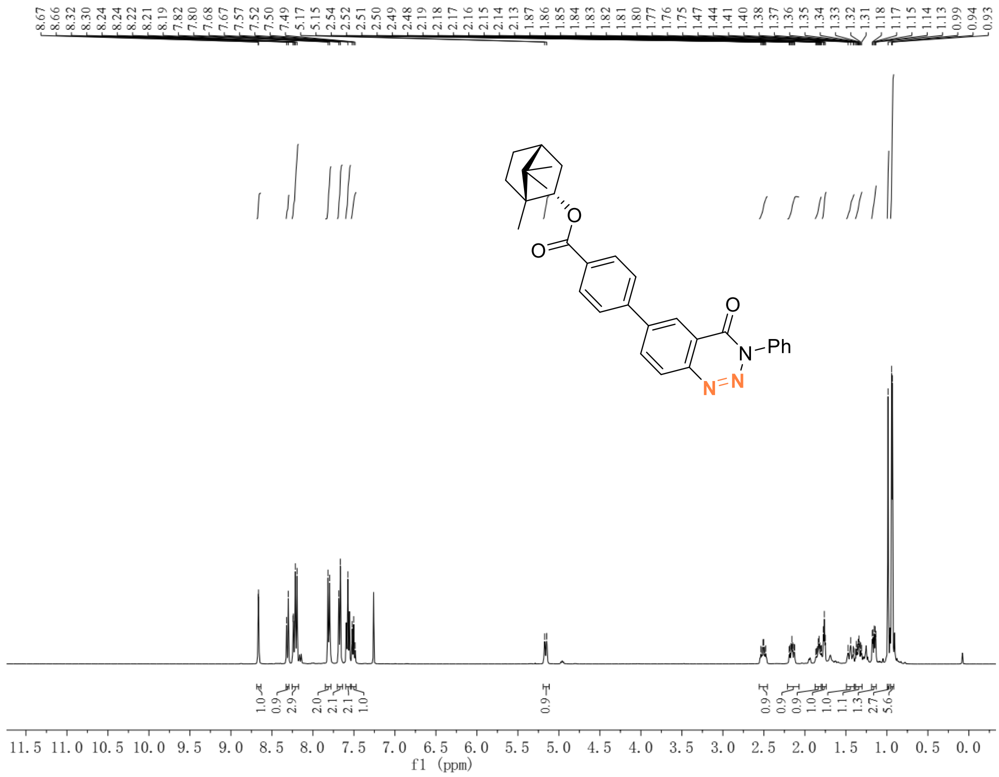
^{1}H NMR of **3a''** (400 MHz, $CDCl_3$)



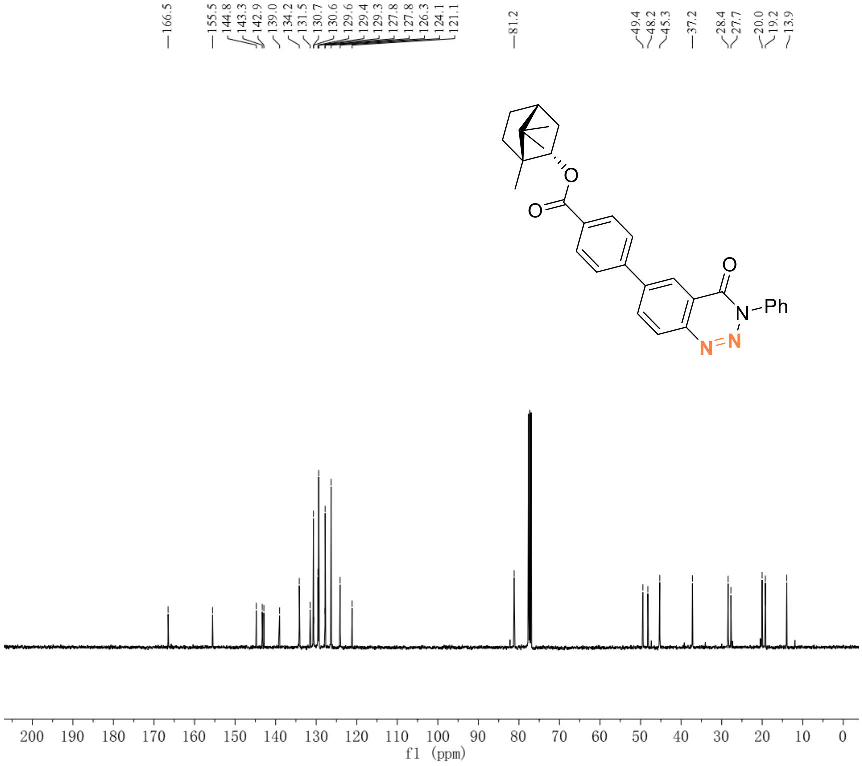
^{13}C NMR of **3a''** (100 MHz, $CDCl_3$)



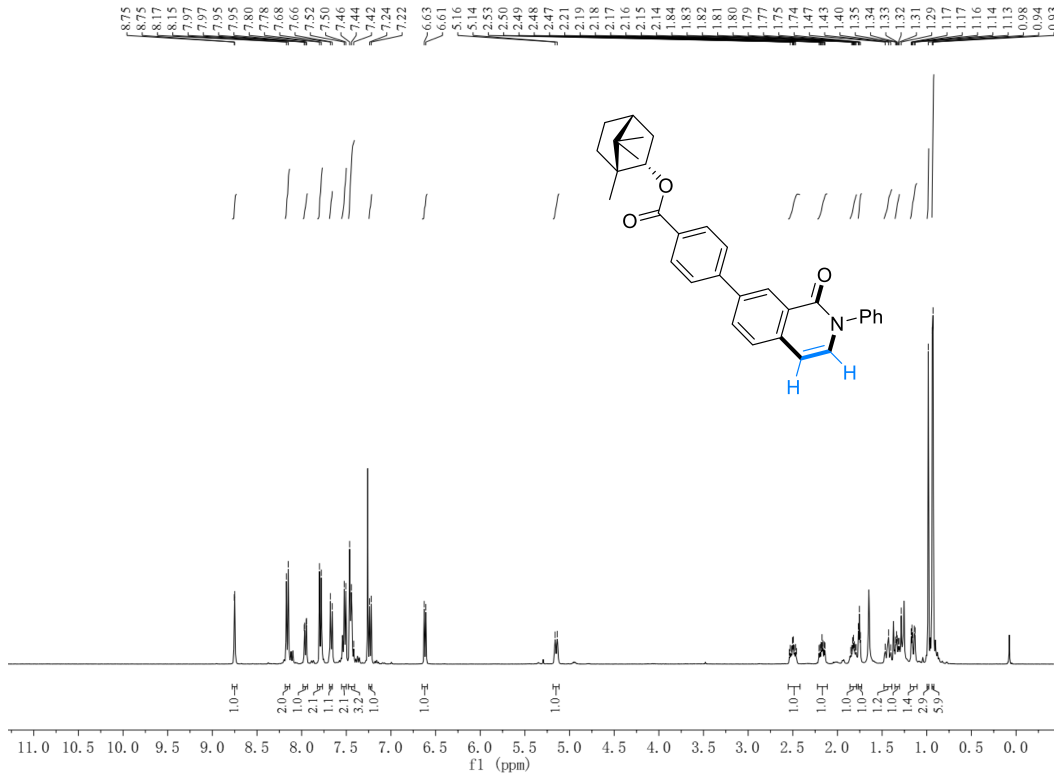
^{1}H NMR of **1b''** (400 MHz, $CDCl_3$)



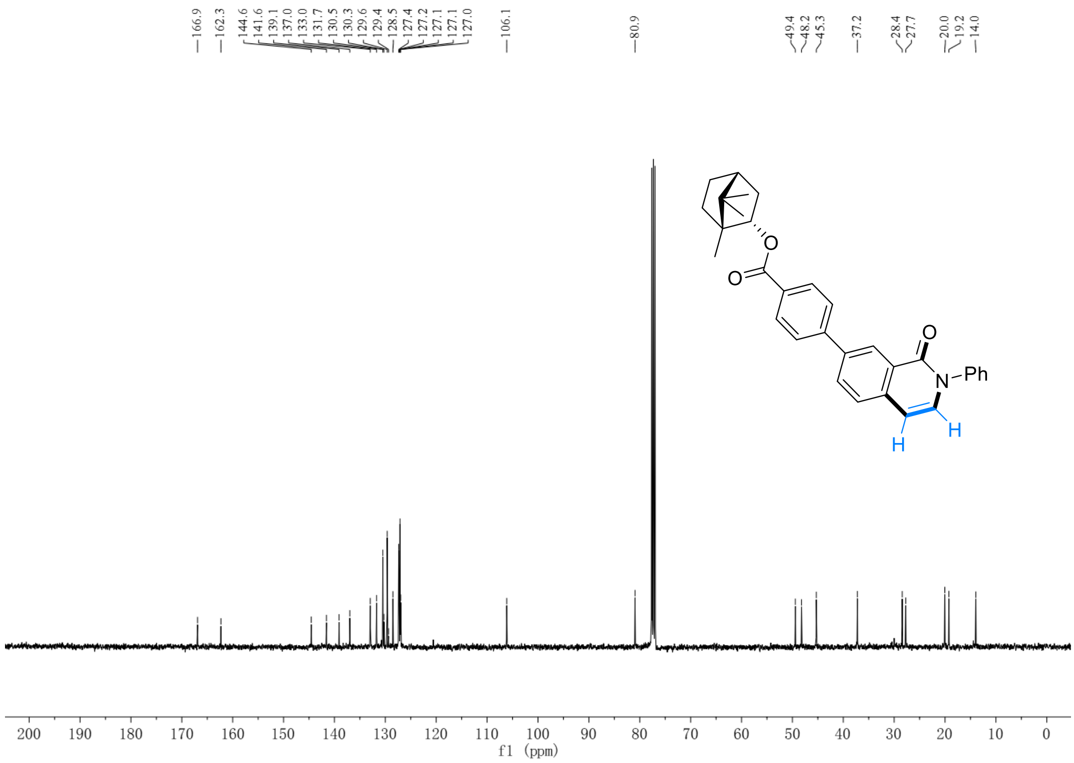
^{13}C NMR of **1b''** (100 MHz, $CDCl_3$)



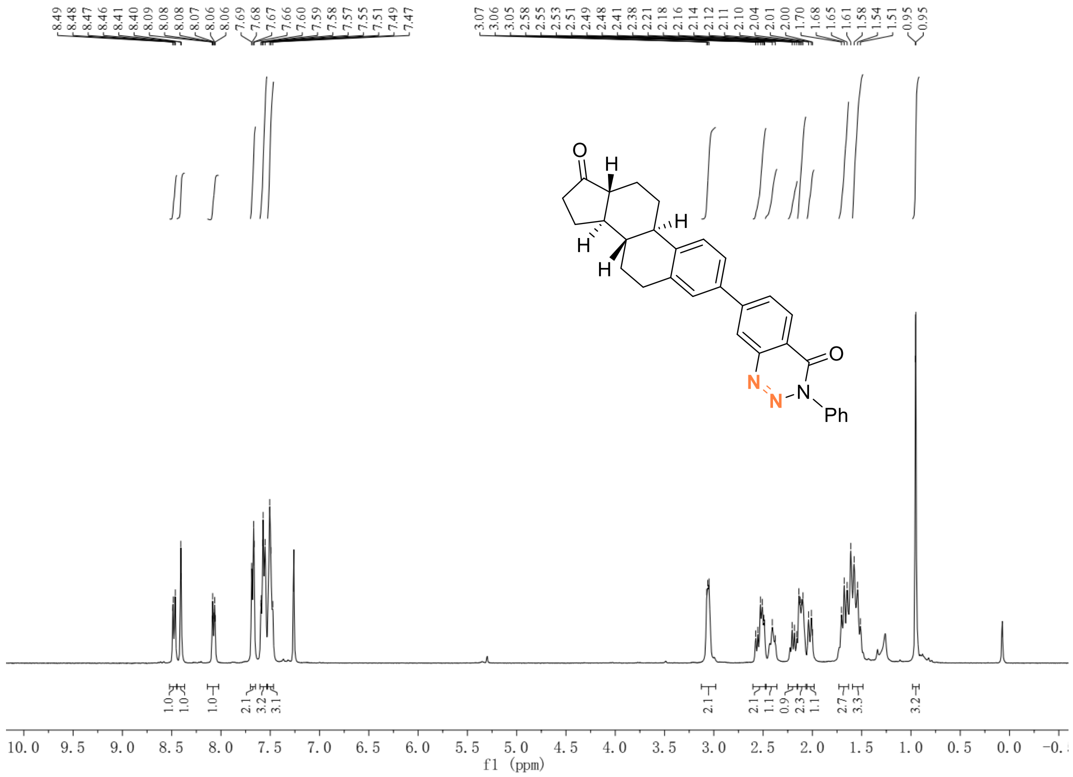
^{1}H NMR of **3b''** (400 MHz, $CDCl_3$)



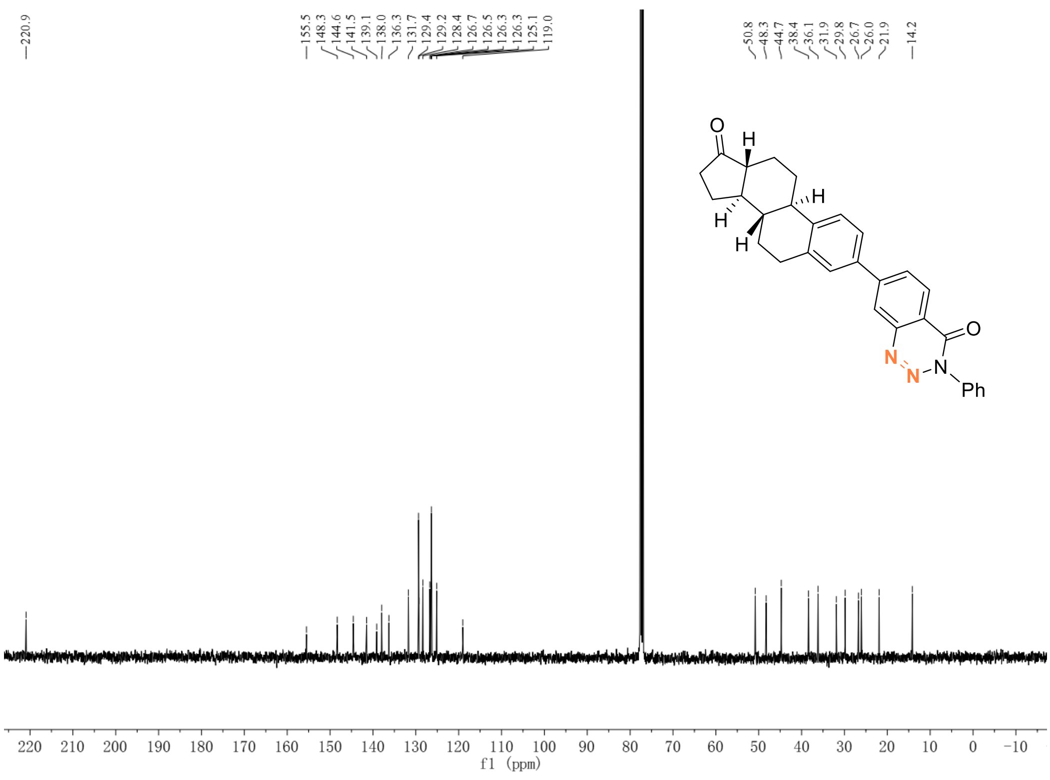
^{13}C NMR of **3b''** (100 MHz, $CDCl_3$)



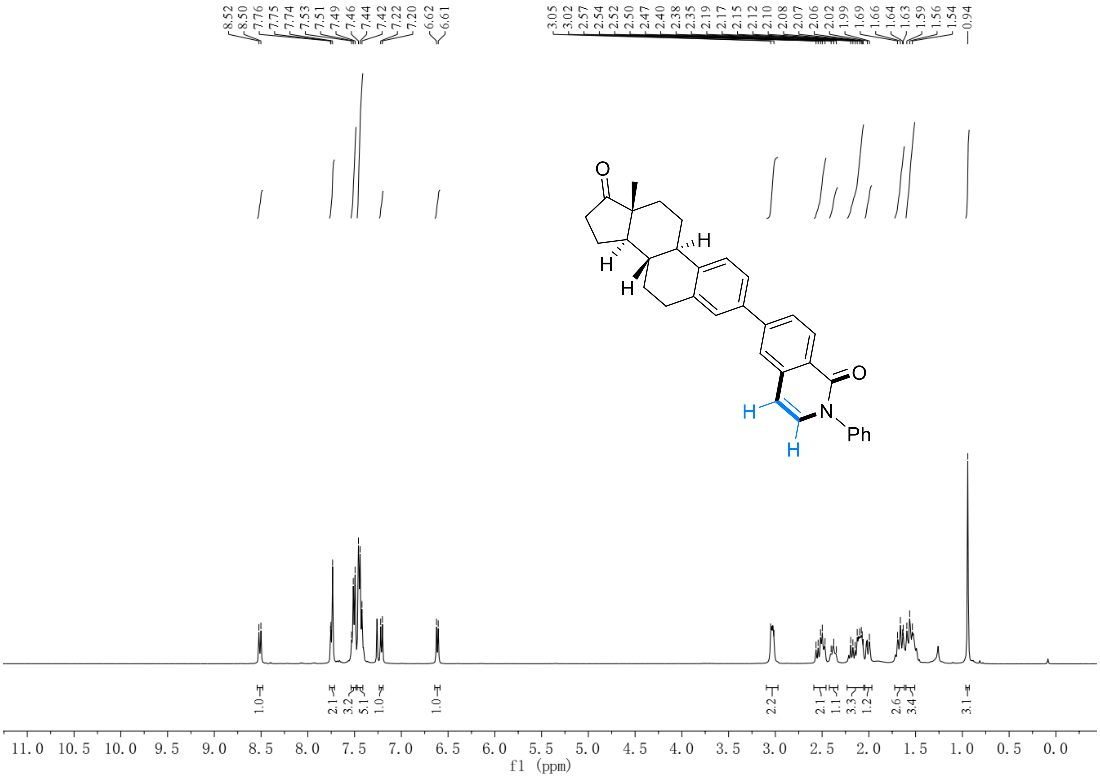
^{1}H NMR of **1c''** (400 MHz, $CDCl_3$)



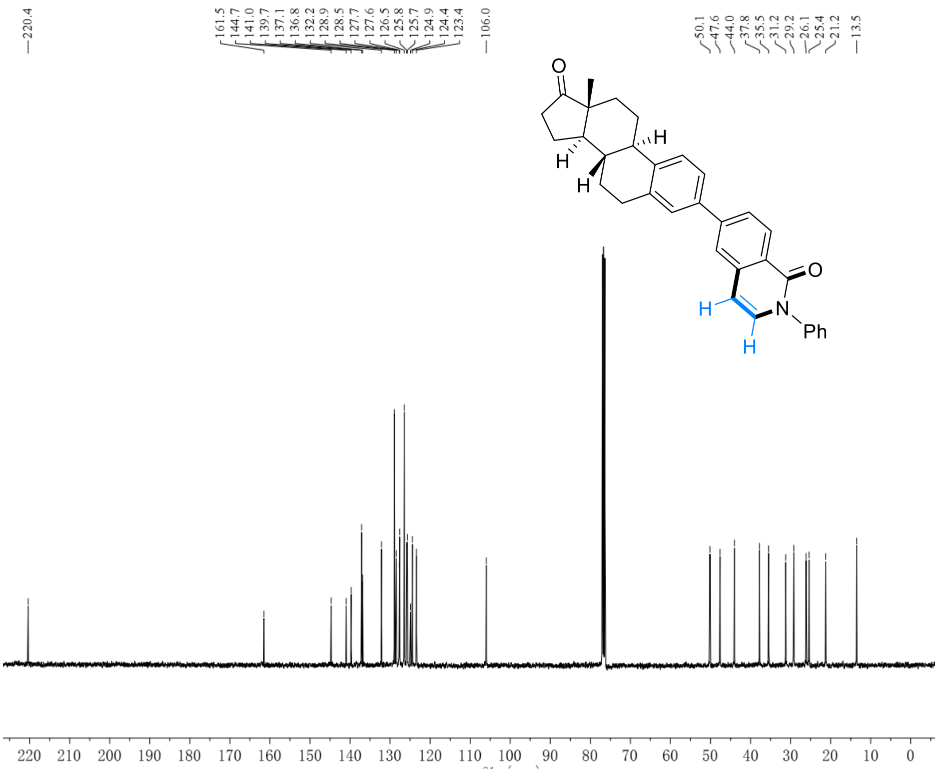
^{13}C NMR of **1c''** (100 MHz, $CDCl_3$)



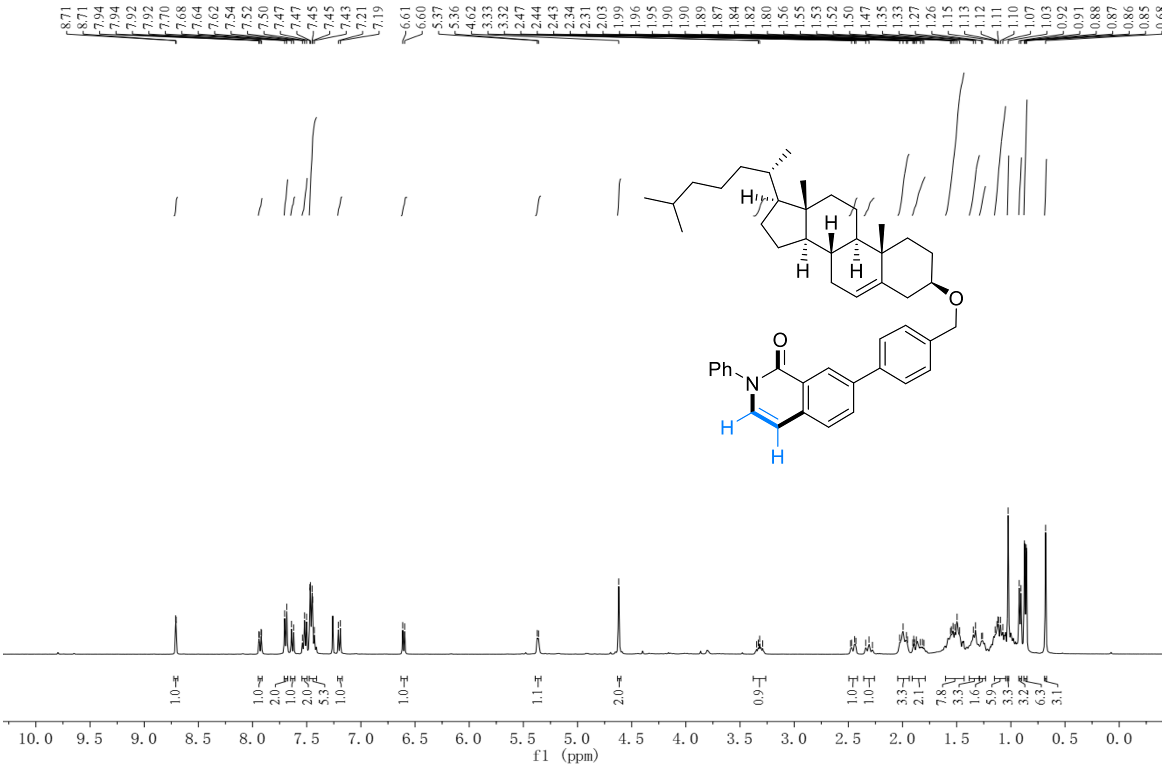
[1]H NMR of **3c''** (400 MHz, $CDCl_3$)



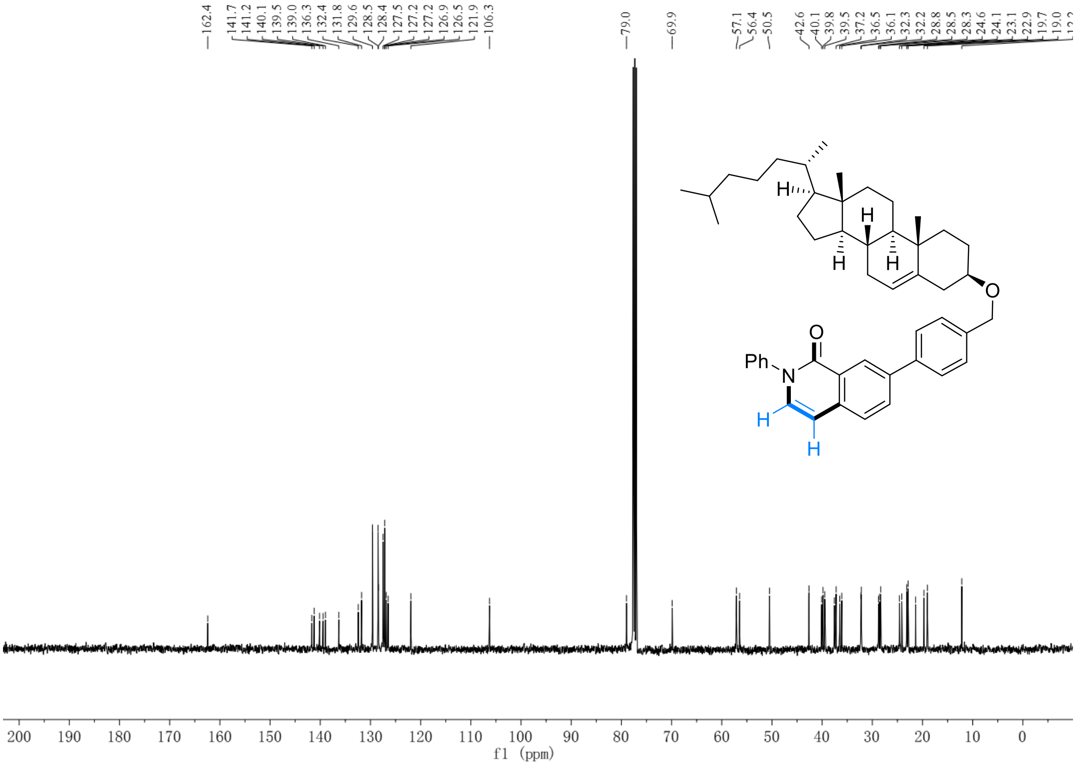
[13]C NMR of **3c''** (100 MHz, $CDCl_3$)



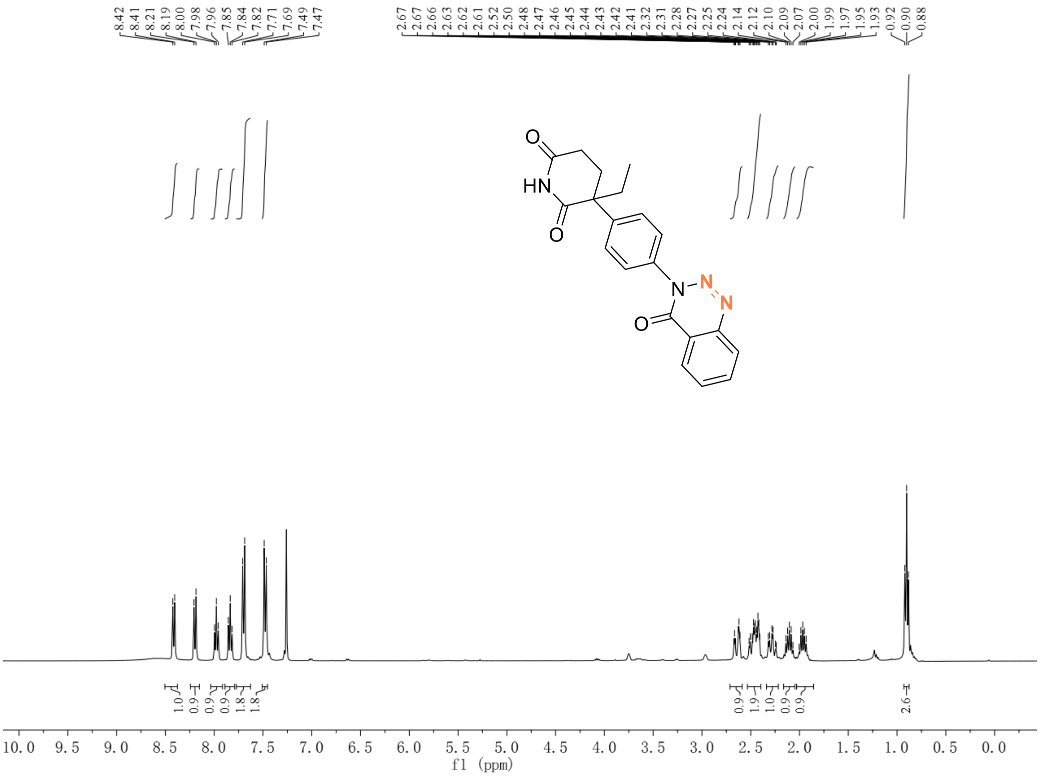
^{1}H NMR of **3d''** (400 MHz, $CDCl_3$)



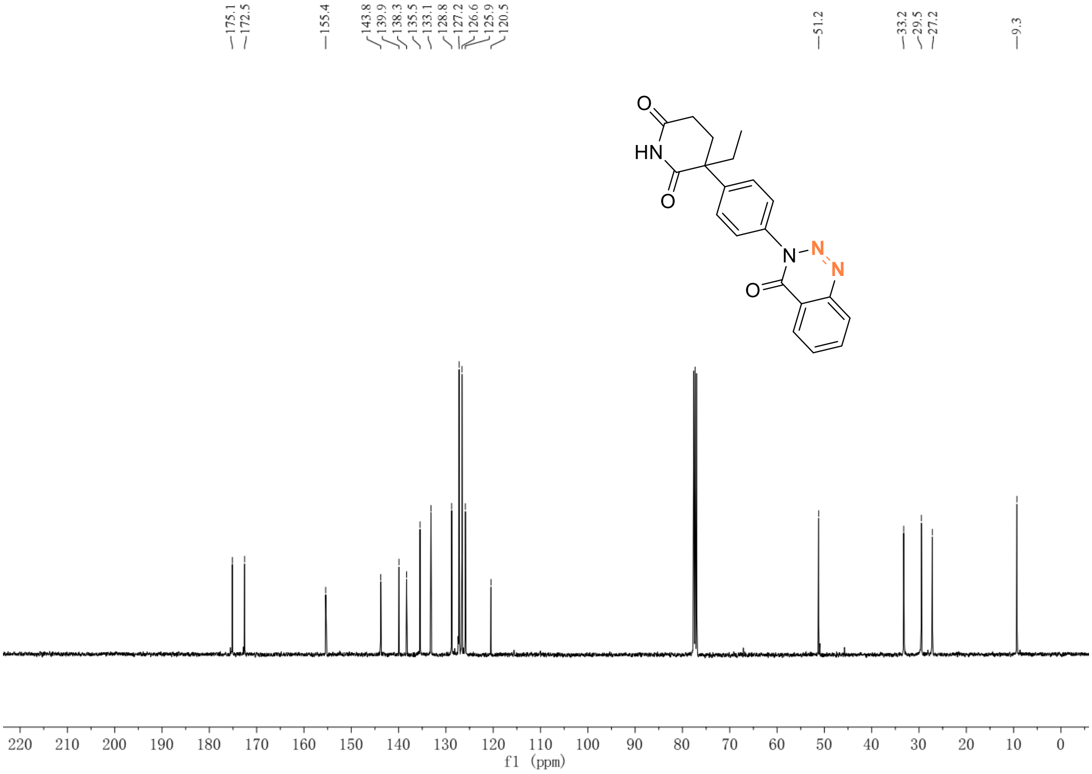
^{13}C NMR of **3d''** (100 MHz, $CDCl_3$)



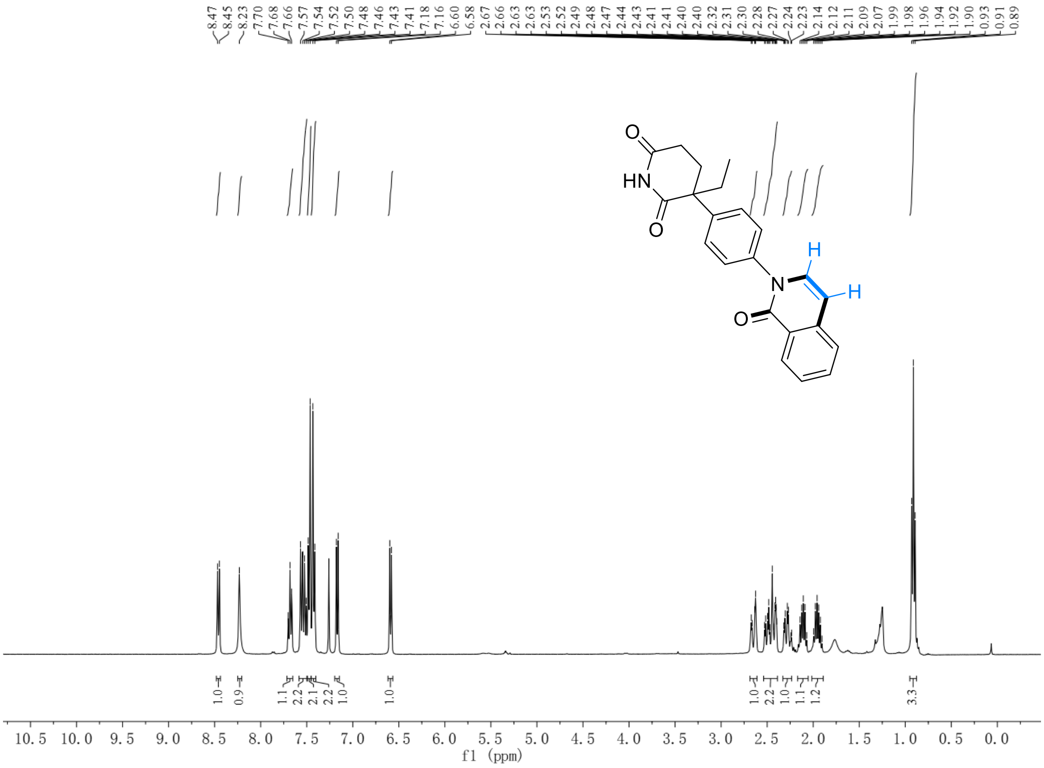
[1]H NMR of **1e''** (400 MHz, $CDCl_3$)



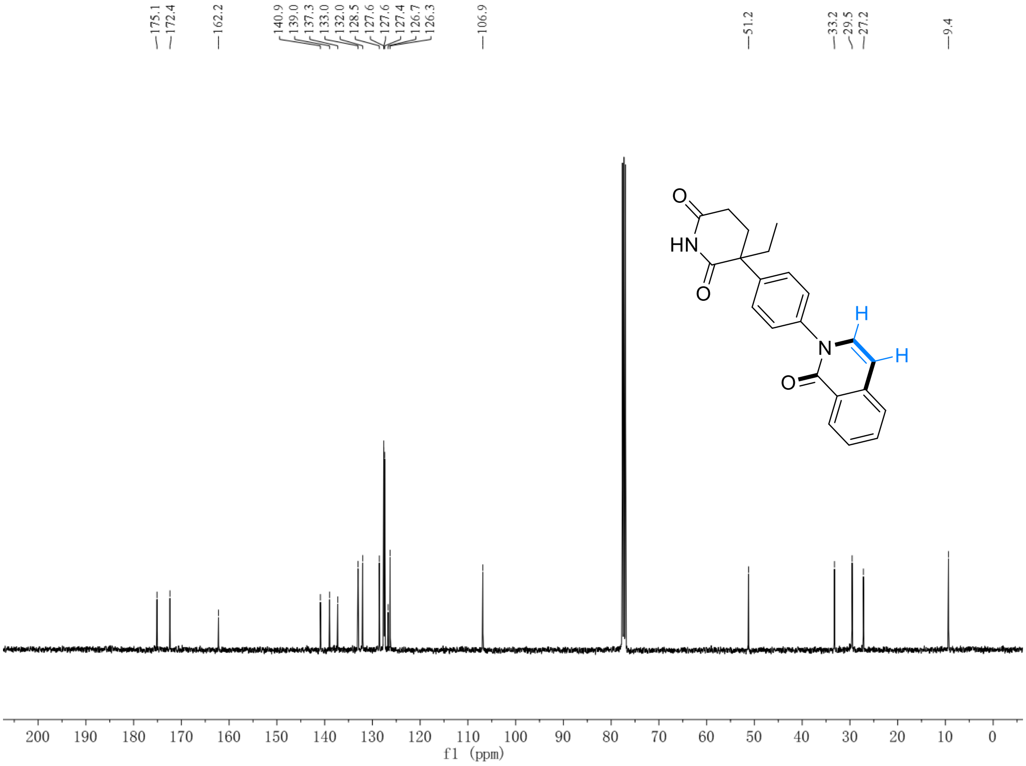
[13]C NMR of **1e''** (100 MHz, $CDCl_3$)



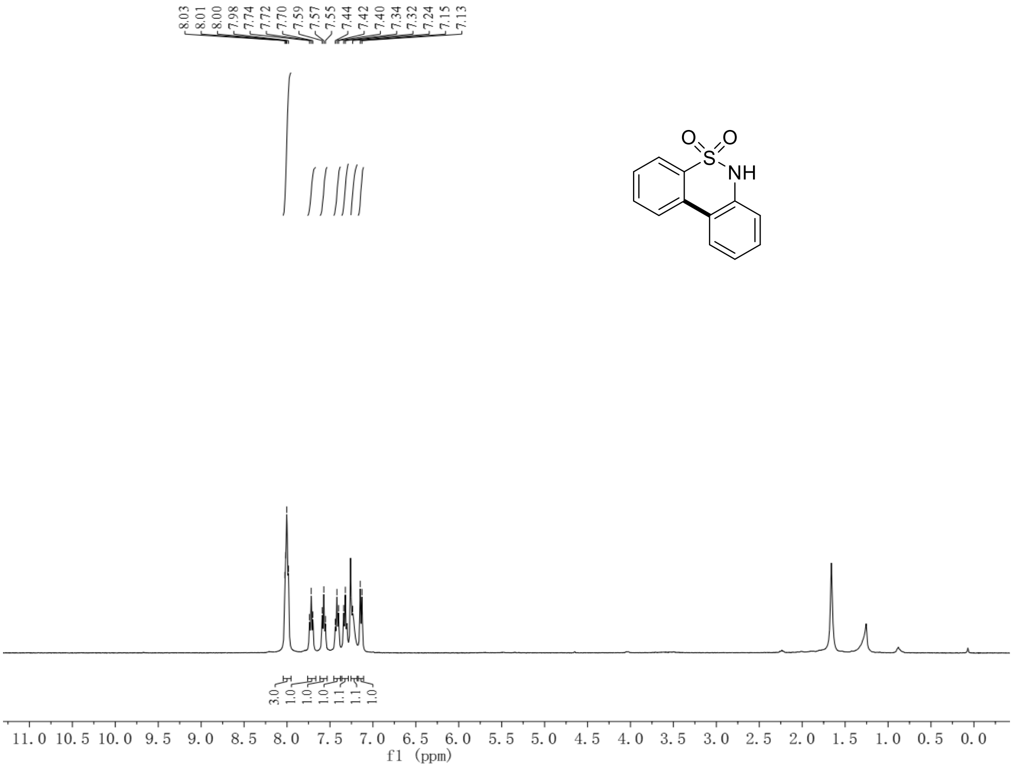
^{1}H NMR of **3e''** (400 MHz, $CDCl_3$)



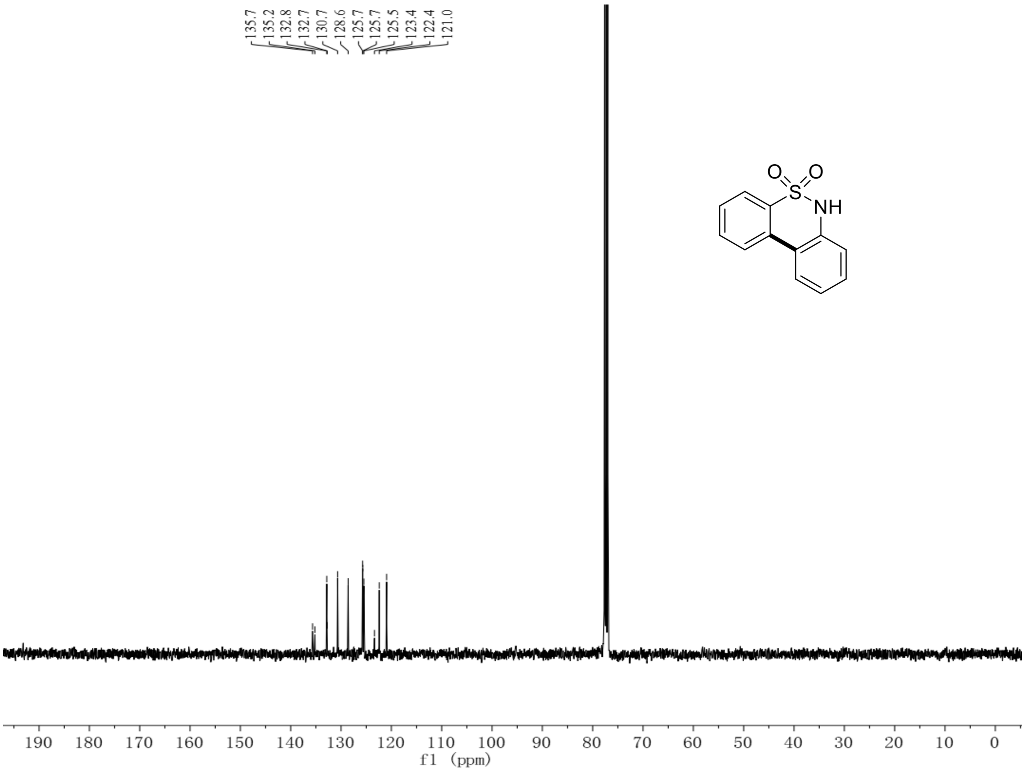
^{13}C NMR of **3e''** (100 MHz, $CDCl_3$)



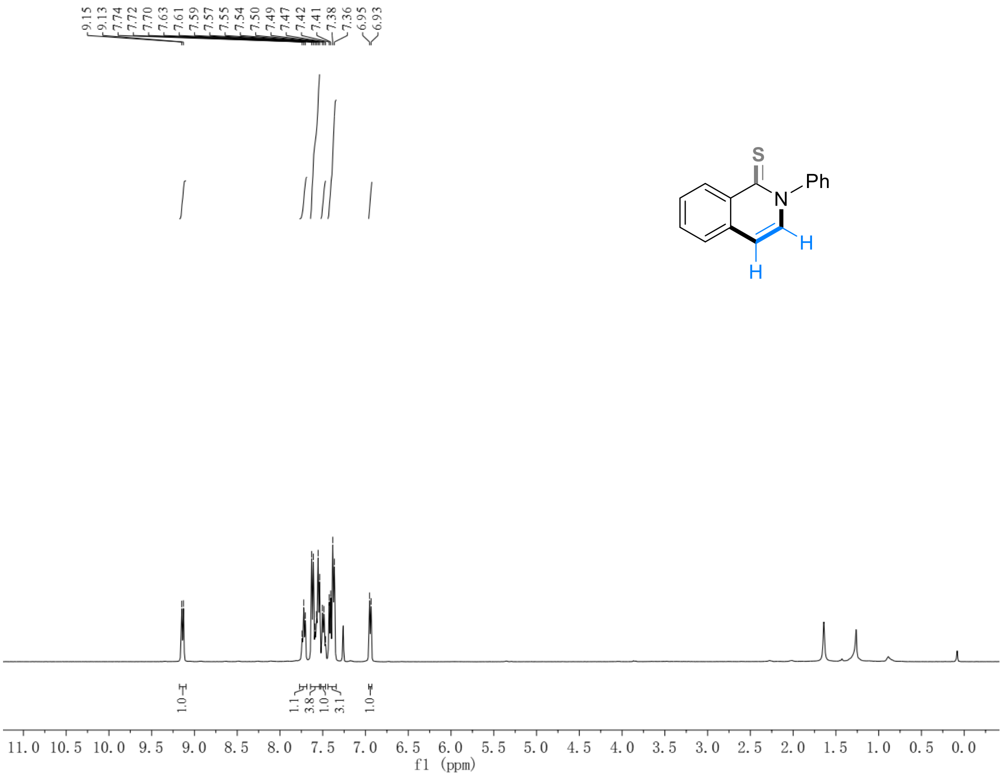
¹H NMR of **8** (400 MHz, $CDCl_3$)



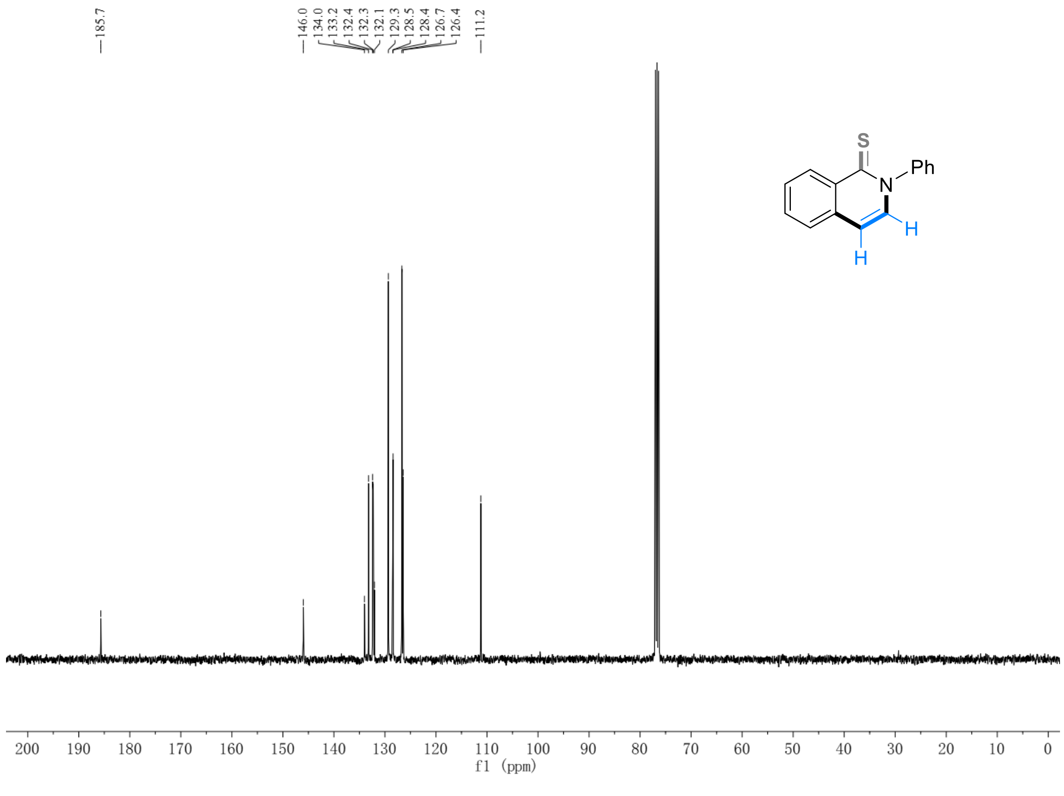
¹³C NMR of **8** (100 MHz, $CDCl_3$)



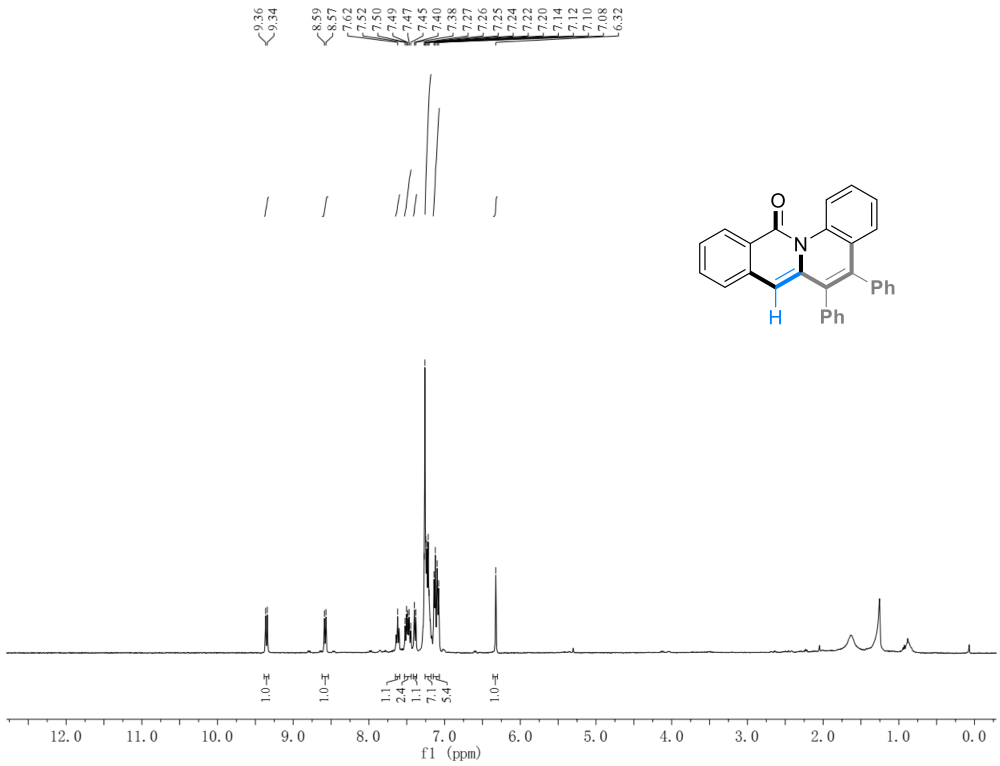
[1]H NMR of **9** (400 MHz, $CDCl_3$)



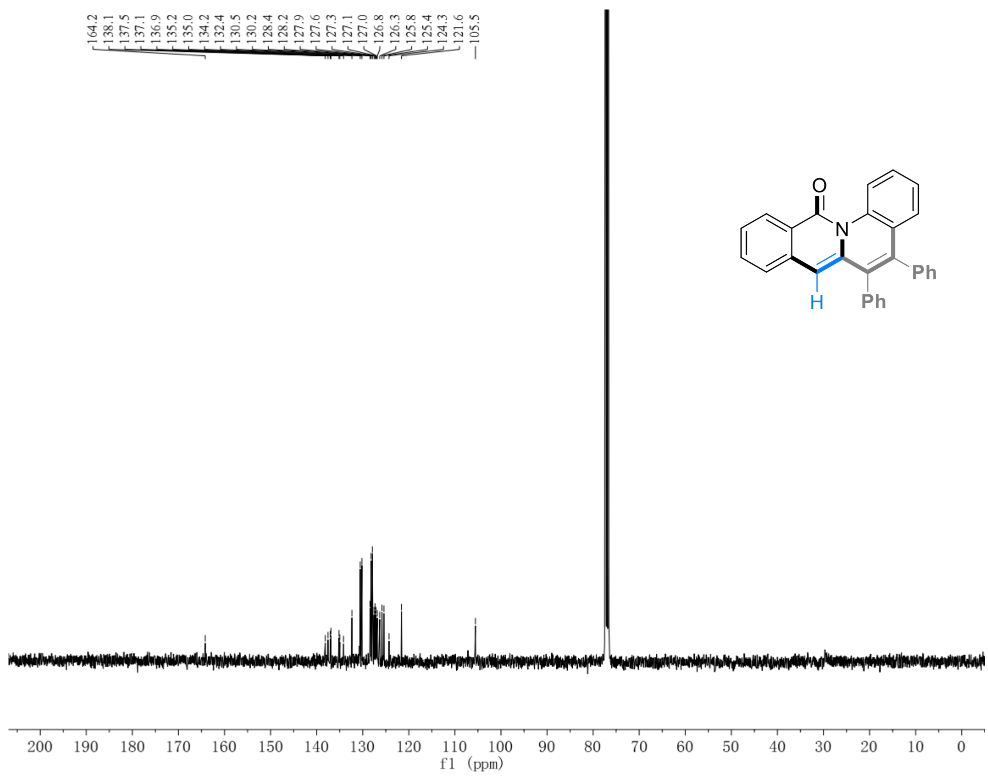
[13]C NMR of **9** (100 MHz, $CDCl_3$)



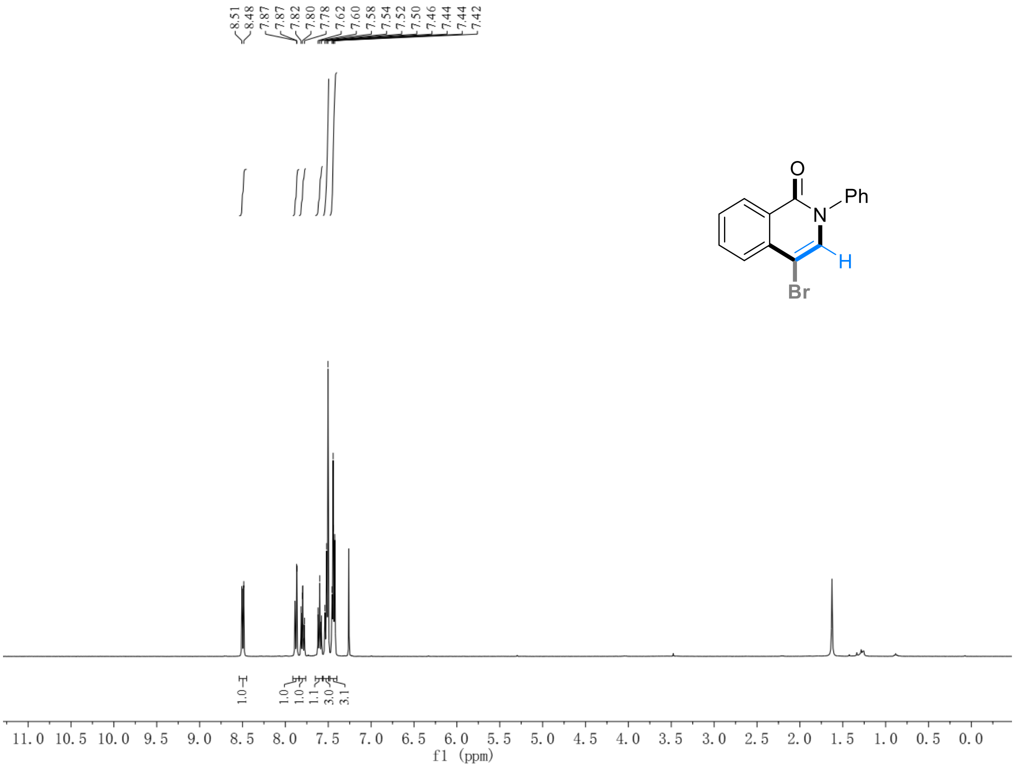
[1]H NMR of **10** (400 MHz, $CDCl_3$)



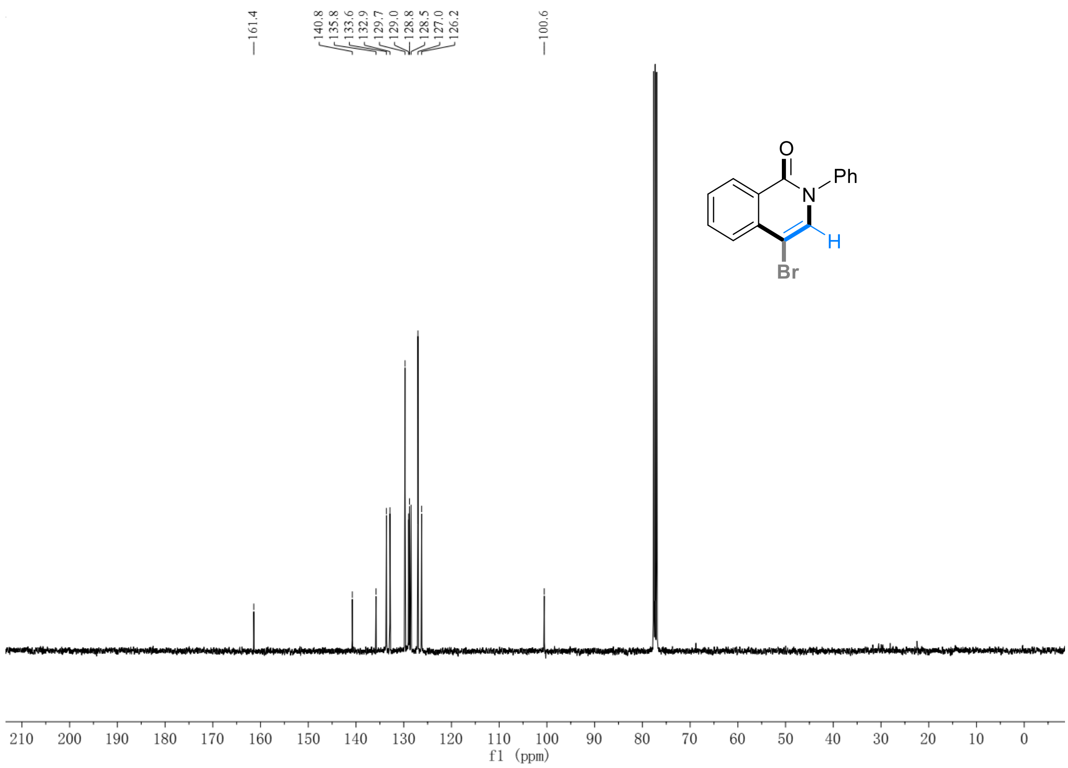
[13]C NMR of **10** (100 MHz, $CDCl_3$)



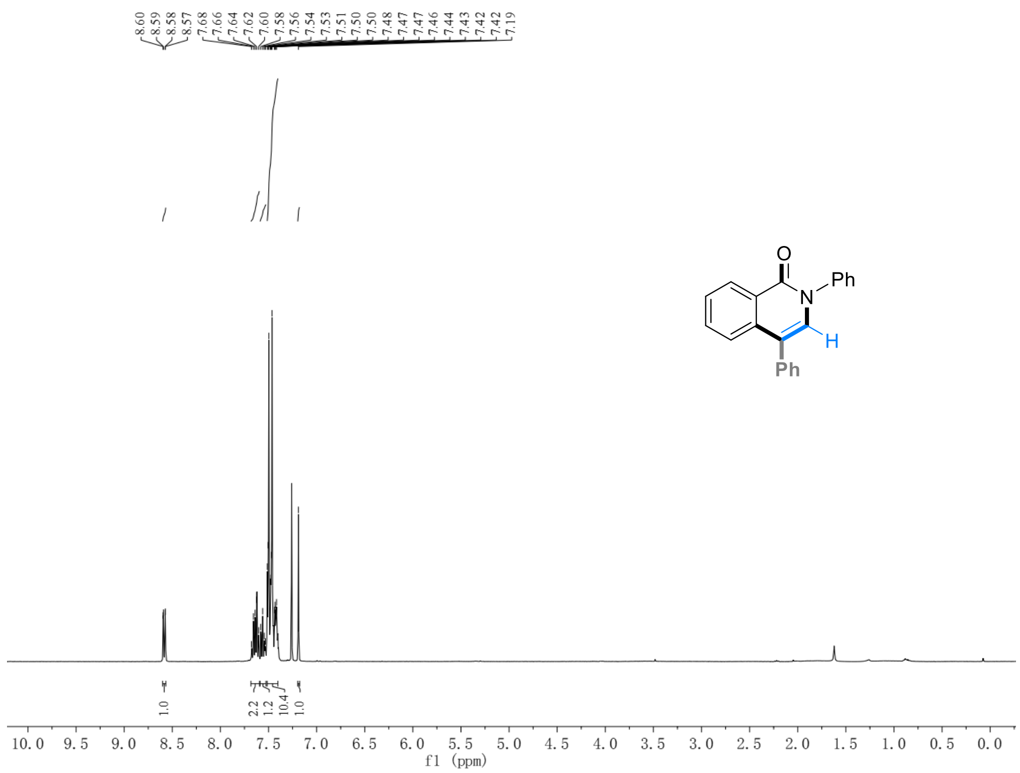
^{1}H NMR of **11** (400 MHz, $CDCl_3$)



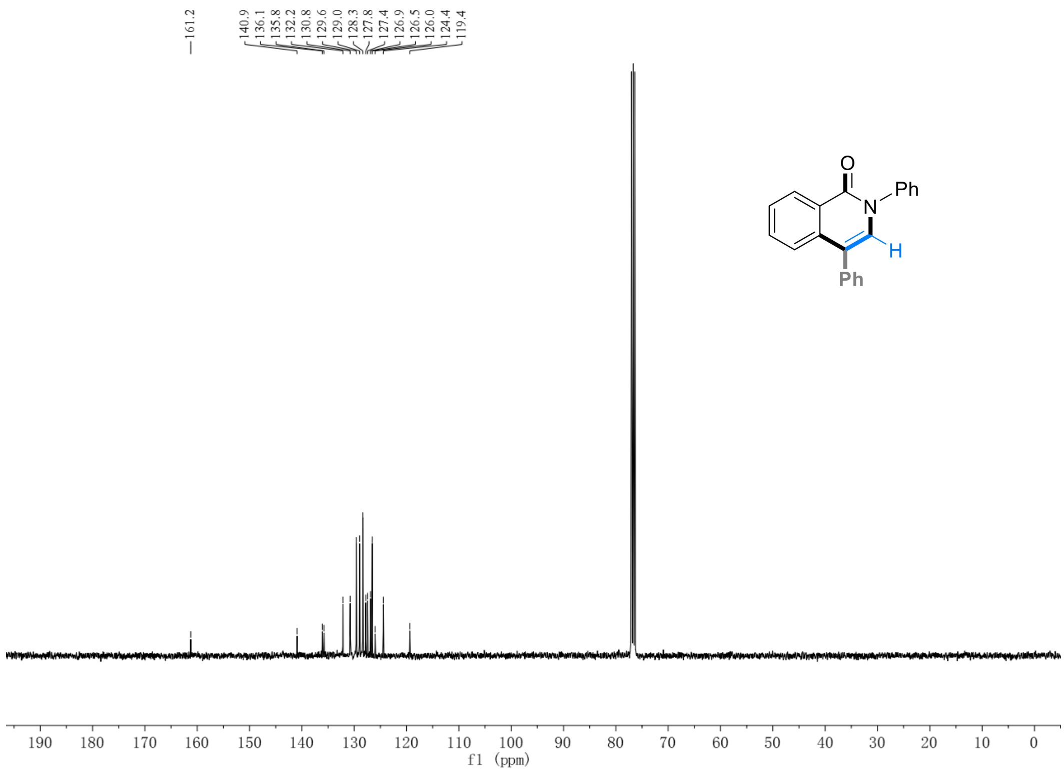
^{13}C NMR of **11** (100 MHz, $CDCl_3$)



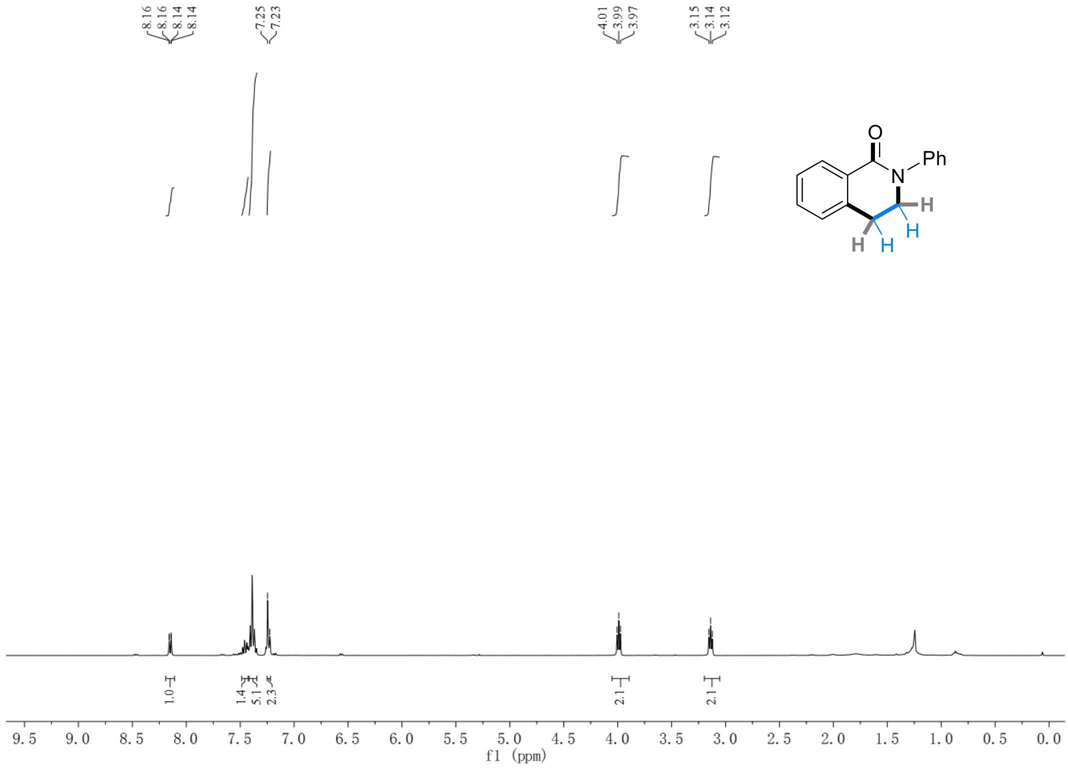
^{1}H NMR of **12** (400 MHz, $CDCl_3$)



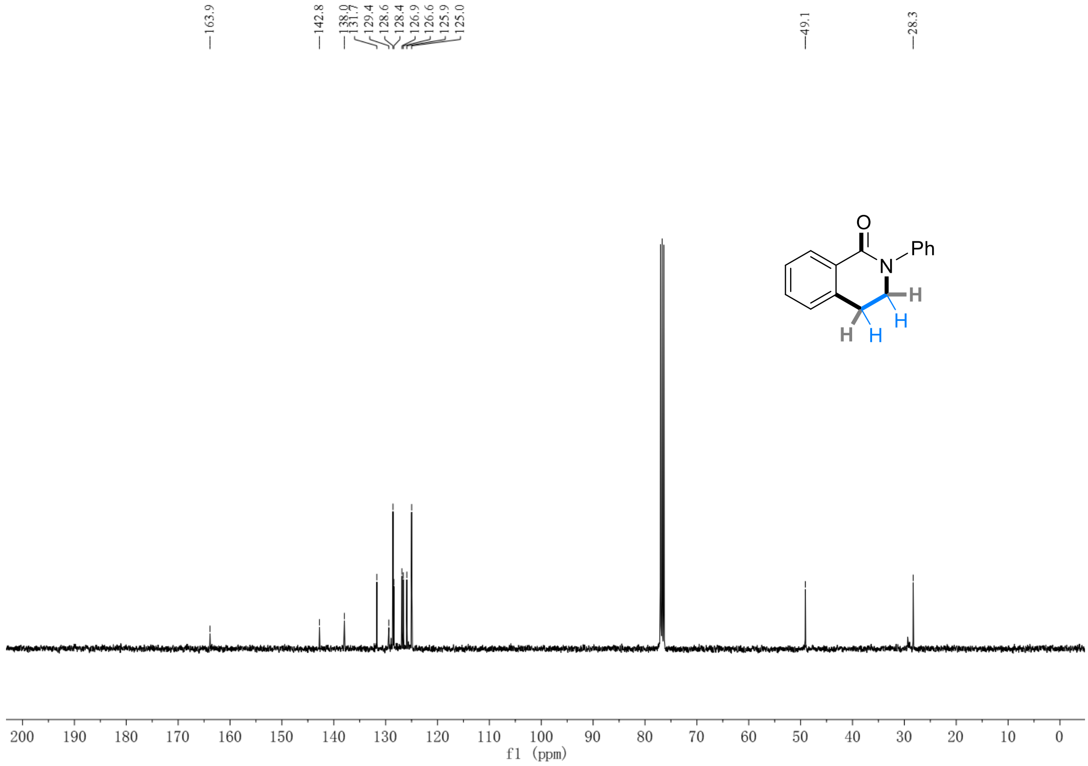
^{13}C NMR of **12** (100 MHz, $CDCl_3$)



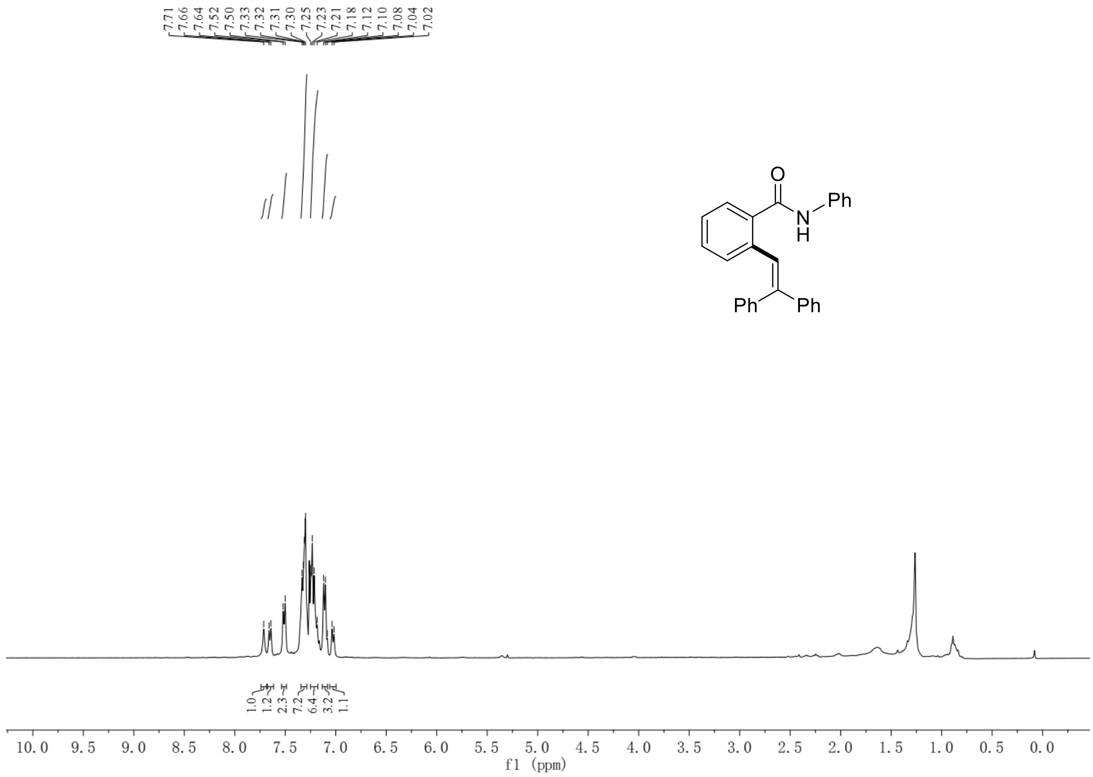
[1]H NMR of **13** (400 MHz, $CDCl_3$)



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



[1]H NMR of **14** (400 MHz, $CDCl_3$)



[13]C NMR of **14** (100 MHz, $CDCl_3$)