Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Intermolecular C−H silylation through cascade carbopalladation and vinylic to aryl 1,4-palladium migration

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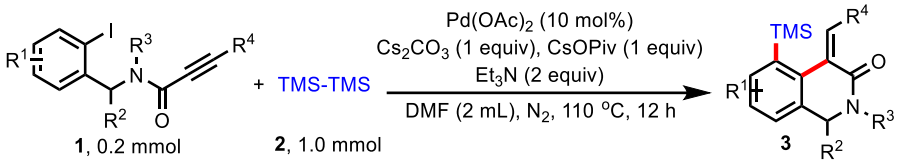
1. General Information:

$Pd(OAc)_2$ was purchased from Strem Chemicals. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX400 instrument (400 MHz) or Bruker DRX-600 instrument (600 MHz). High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. NMR spectra were recorded in $CDCl_3$. ^1H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

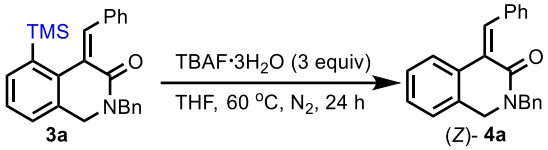
Alkyne-tethered aryl iodides were synthesized by following the reported procedures.[1]

2. General Procedure for the Synthesis of Exocyclic Alkene-Containing 5-Silylisoquinolines

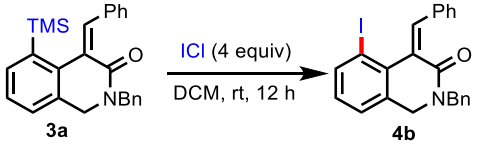


A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic stir bar was charged with $Pd(OAc)_2$ (0.02 mmol, 4.5 mg, 0.1 equiv), Cs_2CO_3 (0.2 mmol, 65.2 mg, 1.0 equiv), CsOPiv (0.2 mmol, 46.8 mg, 1.0 equiv), alkyne-tethered aryl iodides (0.2 mmol, 1.0 equiv), TMS-TMS (1.0 mmol, 205 μL, 5 equiv), Et_3N (0.4 mmol, 56 μL, 2 equiv) and DMF (2 mL). The reaction mixture was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (6 times). The reaction tube was put into an oil bath at room temperature and was then heated to 110 °C. The mixture was stirred at 110 °C for 12 hours. After being cooled down to room temperature, the reaction mixture was diluted with EtOAc (15 mL), washed with brine (3 times), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC with petroleum ether/ethyl acetate (using the indicated mobile phase) to afford **3.**

3. Procedure for the Transformation of the Arylsilane Product

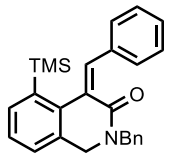


To a solution of arylsilane (**3a**) (39.7 mg, 0.1 mmol) in THF (1 mL) was added TBAF·$3H_2O$ (94.7 mg, 0.3 mmol) under N_2. The reaction was stirred at 60 °C (oil bath heating) for 24 h. Upon completion, the reaction mixture was diluted with EtOAc (15 mL) and washed with brine. The organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **4a** (19.5 mg, 60%) as a colorless oil.



To a solution of arylsilane (**3a**) (39.7 mg, 0.1 mmol) in DCM (1 mL) was added ICl (64.9 mg, 0.4 mmol). The reaction was stirred at room temperature for 12 h. Upon completion, the reaction mixture was diluted with EtOAc (15 mL) and washed with brine. The organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **4b** (37.4 mg, 83%) as a colorless oil.

4. Characterization of the Products



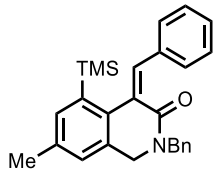
3a

(*Z*)-2-benzyl-4-benzylidene-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3a [2]**:** white solid, actual mass 72.3 mg, 91% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.7 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.19 (m, 9H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.70 (s, 1H), 4.74 (s, 2H), 4.23 (s, 2H), 0.39 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.5, 143.4, 136.8, 136.7, 136.6, 135.4, 134.8, 133.5, 133.4, 130.1, 128.6, 128.5, 128.1, 127.8, 127.4, 126.2, 125.0, 50.1, 49.6, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{26}H_{27}NNaOSi$ 420.1754, found 420.1736.



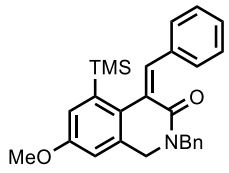
3b

(*Z*)-2-benzyl-4-benzylidene-7-methyl-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3b: colorless oil, actual mass 62.5 mg, 76% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.33 – 7.25 (m, 6H), 6.91 (s, 1H), 6.70 (s, 1H), 4.76 (s, 2H), 4.24 (s, 2H), 2.35 (s, 3H), 0.40 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.7, 140.7, 136.9, 136.7, 136.2, 136.2, 136.0, 135.1, 133.6, 133.3, 130.1, 128.7, 128.4, 128.2, 128.0, 127.4, 125.6, 50.2, 49.7, 21.2, 1.6.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{27}H_{29}NNaOSi$ 434.1911, found 434.1918.



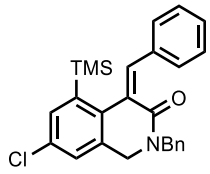
3c

(*Z*)-2-benzyl-4-benzylidene-7-methoxy-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3c: colorless oil, actual mass 56.4 mg, 66% yield, (eluent : petroleum ether/ethyl acetate = 5:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.34 – 7.15 (m, 8H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.52 – 6.48 (m, 2H), 6.36 – 6.35 (m, 1H), 4.82 (s, 2H), 4.29 (s, 2H), 3.67 (s, 3H), 0.16 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 167.9, 158.1, 152.2, 144.2, 138.4, 136.6, 134.6, 130.4, 128.7, 128.3, 127.9, 127.5, 127.2, 126.5, 125.6, 112.1, 109.9, 55.1, 50.1, 49.9, 1.1.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{27}H_{29}NNaO_2Si$ 450.1860, found 450.1845.



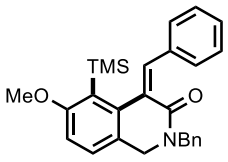
3d

(*Z*)-2-benzyl-4-benzylidene-7-chloro-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3d: colorless oil, actual mass 63.0 mg, 73% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.40 – 7.23 (m, 8H), 7.09 – 7.07 (m, 1H), 6.71 (s, 1H), 4.76 (s, 2H), 4.23 (s, 2H), 0.41 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 142.0, 139.6, 137.1, 136.6, 135.4, 135.1, 134.6, 132.7, 132.6, 130.2, 128.8, 128.8, 128.3, 127.9, 127.6, 125.0, 49.7, 49.7, 1.4.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{26}H_{26}ClNNaOSi$ 454.1364, found 454.1357.



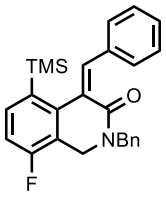
3f

(*Z*)-2-benzyl-4-benzylidene-6-methoxy-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3f: colorless oil, actual mass 18.8 mg, 22% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.27 (m, 8H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.49 (s, 1H), 4.82 (s, 2H), 4.28 (s, 2H), 3.83 (s, 3H), 0.37 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 165.5, 145.4, 137.8, 137.0, 135.0, 132.9, 130.2, 128.7, 128.5, 128.2, 128.0, 127.4, 126.4, 126.2, 124.5, 108.2, 55.3, 49.8, 49.7, 2.4.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{27}H_{29}NNaO_2Si$ 450.1860, found 450.1859.



3h

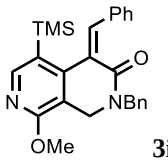
(*Z*)-2-benzyl-4-benzylidene-8-fluoro-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3h: colorless oil, actual mass 50.7 mg, 61% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.55 (m, 1H), 7.40 – 7.26 (m, 8H), 6.98 (t, *J* = 8.7 Hz, 1H), 6.75 (s, 1H), 4.78 (s, 2H), 4.36 (s, 2H), 0.39 (s, 9H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -120.36 (s).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 158.1 (d, *J* = 249.2 Hz), 146.3 (d, *J* = 3.2 Hz), 137.5, 137.2 (d, *J* = 7.8 Hz), 136.7, 134.6, 132.6 (d, *J* = 2.4 Hz), 132.2 (d, *J* = 4.3 Hz), 130.2, 128.8, 128.7, 128.3, 128.0, 127.6, 120.6 (d, *J* = 15.5 Hz), 113.1 (d, *J* = 19.4 Hz), 50.0, 43.4 (d, *J* = 4.2 Hz), 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{26}H_{26}FNNaOSi$ 438.1660, found 438.1664.



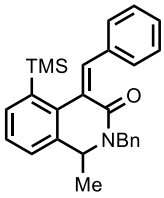
3i

(*Z*)-2-benzyl-4-benzylidene-8-methoxy-5-(trimethylsilyl)-1,4-dihydro-2,7-naphthyridin-3(2*H*)-one 3j: colorless oil, actual mass 42.8 mg, 50% yield, (eluent : petroleum ether/ethyl acetate = 2:1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.91 (s, 1H), 7.31 – 7.26 (m, 5H), 7.19 – 7.17 (m, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.07 – 7.06 (m, 2H), 5.29 (s, 2H), 4.33 (s, 2H), 4.01 (s, 3H), 0.32 (s, 9H).

^{13}C NMR (151 MHz, CDCl3) δ 163.9, 161.3, 152.5, 144.7, 139.9, 137.6, 135.7, 128.9, 128.5, 128.2, 128.0, 125.8, 123.1, 118.3, 105.5, 53.7, 53.7, 36.1, 1.8.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{26}H_{29}N_2O_2Si$ 429.1993, found 429.2003.



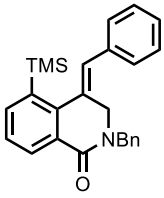
3j

(*Z*)-2-benzyl-4-benzylidene-1-methyl-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3j: colorless oil, actual mass 65.0 mg, 79% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.23 (m, 7H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.78 (s, 1H), 5.09 (d, *J* = 15.0 Hz, 1H), 4.47 (d, *J* = 15.0 Hz, 1H), 4.37 (q, *J* = 6.8 Hz, 1H), 1.36 (d, *J* = 6.8 Hz, 3H), 0.41 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.0, 142.1, 138.5, 137.4, 137.1, 136.9, 135.3, 135.1, 133.0, 130.0, 128.6, 128.4, 128.2, 128.0, 127.4, 126.4, 124.9, 57.4, 48.2, 21.5, 1.7.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{27}H_{29}NNaOSi$ 434.1911, found 434.1911.



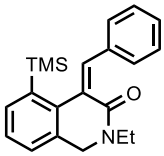
3k

(*Z*)-2-benzyl-4-benzylidene-5-(trimethylsilyl)-3,4-dihydroisoquinolin-1(2*H*)-one 3k: colorless oil, actual mass 58.0 mg, 73% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 8.24 – 8.23 (m, 1H), 7.81 – 7.79 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.24 – 7.20 (m, 5H), 7.09 – 7.08 (m, 2H), 6.77 (s, 1H), 4.74 (s, 2H), 4.29 (s, 2H), 0.32 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 163.6, 145.2, 139.8, 136.7, 136.7, 135.3, 133.3, 132.3, 129.2, 128.9, 128.8, 128.6, 128.5, 128.0, 127.7, 127.4, 127.3, 50.4, 46.9, 1.6.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{26}H_{27}NNaOSi$ 420.1754, found 420.1758.



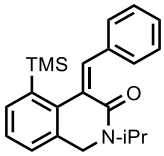
3l

(*Z*)-4-benzylidene-2-ethyl-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3l: colorless oil, actual mass 42.2 mg, 63% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.4 Hz, 2H), 7.62 – 7.60 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.21 (d, *J* = 7.1 Hz, 1H), 6.67 (s, 1H), 4.36 (s, 2H), 3.61 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.39 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.0, 143.8, 136.9, 136.3, 135.5, 135.0, 133.8, 133.8, 130.2, 128.5, 128.2, 126.2, 124.9, 50.2, 41.2, 13.1, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{21}H_{25}NNaOSi$ 358.1598, found 358.1588.



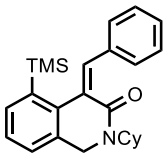
3m

(*Z*)-4-benzylidene-2-isopropyl-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 4m: colorless oil, actual mass 32.8 mg, 47% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.61 – 7.60 (m, 1H), 7.38 – 7.36 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 (d, *J* = 7.1 Hz, 1H), 6.65 (s, 1H), 4.99 – 4.95 (m, 1H), 4.23 (s, 2H), 1.18 (d, *J* = 6.8 Hz, 6H), 0.39 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 144.0, 136.7, 135.7, 135.4, 135.0, 134.2, 134.2, 130.0, 128.4, 128.2, 126.2, 124.9, 43.9, 43.4, 19.9, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{22}H_{27}NNaOSi$ 372.1754, found 372.1765.



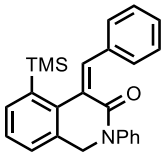
3n

(*Z*)-4-benzylidene-2-cyclohexyl-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 4n: colorless oil, actual mass 47.5 mg, 61% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 6.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 6.65 (s, 1H), 4.56 – 4.51 (m, 1H), 4.26 (s, 2H), 1.82 – 1.81 (m, 2H), 1.70 – 1.68 (m, 3H), 1.47 – 1.39 (m, 4H), 1.15 – 1.11 (m, 1H), 0.39 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 144.1, 136.1, 135.6, 135.4, 135.1, 134.3, 134.3, 130.0, 128.4, 128.2, 126.2, 124.8, 51.7, 45.0, 30.3, 25.6, 25.5, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{25}H_{31}NNaOSi$ 412.2067, found 412.2062.



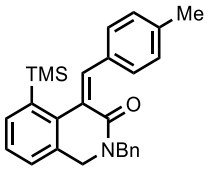
3o

(*Z*)-4-benzylidene-2-phenyl-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3o: colorless oil, actual mass 49.0 mg, 64% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.42 – 7.30 (m, 8H), 7.25 – 7.22 (m, 2H), 6.81 (s, 1H), 4.81 (s, 2H), 0.43 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 143.6, 141.8, 137.5, 137.3, 135.8, 134.7, 133.9, 133.8, 130.4, 128.9, 128.7, 128.3, 126.5, 126.1, 125.1, 125.0, 53.6, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{25}H_{25}NNaOSi$ 406.1598, found 406.1605.



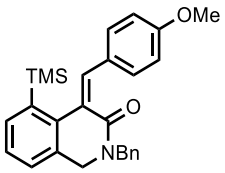
3q

(*Z*)-2-benzyl-4-(4-methylbenzylidene)-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3q: colorless oil, actual mass 55.9 mg, 68% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.60 – 7.59 (m, 1H), 7.32 – 7.18 (m, 8H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.69 (s, 1H), 4.78 (s, 2H), 4.26 (s, 2H), 2.37 (s, 3H), 0.40 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 143.8, 138.7, 136.9, 136.9, 136.8, 135.5, 133.5, 132.6, 132.1, 130.2, 129.0, 128.7, 127.9, 127.4, 126.1, 125.0, 50.2, 49.7, 21.4, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{27}H_{29}NNaOSi$ 434.1911, found 434.1922.



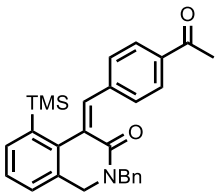
3r

(*Z*)-2-benzyl-4-(4-methoxybenzylidene)-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3r: colorless oil, actual mass 33.3 mg, 39% yield, (eluent : petroleum ether/ethyl acetate = 5:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.86 – 7.84 (m, 2H), 7.59 (d, *J* = 6.8 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.27 – 7.22 (m, 4H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.93 – 6.90 (m, 2H), 6.65 (s, 1H), 4.79 (s, 2H), 4.26 (s, 2H), 3.84 (s, 3H), 0.39 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.9, 160.0, 144.0, 137.0, 136.8, 135.5, 133.5, 132.1, 131.2, 128.7, 127.9, 127.6, 127.4, 126.0, 125.0, 113.7, 55.3, 50.3, 49.7, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{27}H_{29}NNaO_2Si$ 450.1860, found 450.1844.



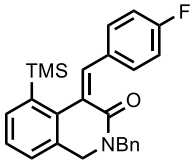
3s

(*Z*)-4-(4-acetylbenzylidene)-2-benzyl-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3s: colorless oil, actual mass 45.7 mg, 52% yield, (eluent : petroleum ether/ethyl acetate = 5:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.34 – 7.32 (m, 2H), 7.29 – 7.25 (m, 4H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.75 (s, 1H), 4.78 (s, 2H), 4.31 (s, 2H), 2.62 (s, 3H), 0.41 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 197.7, 166.2, 142.8, 139.7, 137.1, 136.7, 136.4, 135.7, 135.6, 135.2, 133.5, 130.1, 128.8, 128.2, 128.0, 127.6, 126.7, 125.2, 50.3, 49.8, 26.7, 1.6.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{28}H_{29}NNaO_2Si$ 462.1860, found 462.1837.



3t

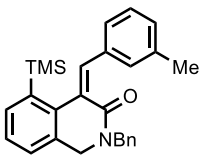
(*Z*)-2-benzyl-4-(4-fluorobenzylidene)-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3t: colorless oil, actual mass 78.1 mg, 94% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.89 – 7.77 (m, 2H), 7.64 – 7.57 (m, 1H), 7.33 – 7.23 (m, 6H), 7.12 – 7.03 (m, 3H), 6.67 (s, 1H), 4.77 (s, 2H), 4.28 (s, 2H), 0.39 (s, 9H).

^{19}**F NMR** (565 MHz, $CDCl_3$) δ -112.26 (s).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.5, 162.7 (d, *J* = 249.4 Hz), 143.4, 136.8 (d, *J* = 16.9 Hz), 135.6 (d, *J* = 9.0 Hz), 133.5, 133.1, 133.1, 132.2 (d, *J* = 8.2 Hz), 131.1 (d, *J* = 3.4 Hz), 128.7, 127.9, 127.5, 126.3, 125.1, 115.2 (d, *J* = 21.5 Hz), 50.3, 49.7, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{26}H_{26}FNNaOSi$ 438.1660, found 438.1679.



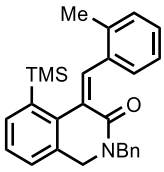
3u

(*Z*)-2-benzyl-4-(3-methylbenzylidene)-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3u: colorless oil, actual mass 52.6 mg, 64% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 3H), 7.33 – 7.23 (m, 7H), 7.15 – 7.09 (m, 2H), 6.69 (s, 1H), 4.78 (s, 2H), 4.28 (s, 2H), 2.38 (s, 3H), 0.41 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.7, 143.6, 137.7, 137.0, 136.8, 136.8, 135.5, 134.9, 133.6, 133.4, 130.6, 129.4, 128.7, 128.2, 128.0, 127.5, 127.2, 126.2, 125.0, 50.3, 49.8, 21.5, 1.5.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{27}H_{29}NNaOSi$ 434.1911, found 434.1914.



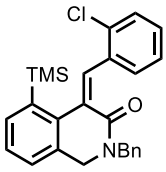
3v

(*Z*)-2-benzyl-4-(2-methylbenzylidene)-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3v: colorless oil, actual mass 77.3mg, 94% yield, (eluent : petroleum ether/ethyl acetate = 5:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 6.7 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.29 – 7.23 (m, 6H), 7.25 – 7.23 (m, 3H), 7.10 (d, *J* = 7.3 Hz, 1H), 6.85 (s, 1H), 4.67 (s, 2H), 4.26 (s, 2H), 2.27 (s, 3H), 0.42 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.4, 142.9, 137.0, 136.9, 136.3, 135.8, 135.5, 135.1, 134.7, 133.6, 130.8, 129.5, 128.6, 128.3, 128.0, 127.4, 126.3, 125.3, 125.2, 50.0, 49.6, 20.6, 1.7.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{27}H_{29}NNaOSi$ 434.1911, found 434.1910.



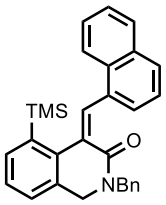
3w

(*Z*)-2-benzyl-4-(2-chlorobenzylidene)-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3w: colorless oil, actual mass 81.9 mg, 95% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.50 – 7.48 (m 1H), 7.42 – 7.36 (m, 6H), 7.31 – 7.30 (m, 2H), 7.20 (d, *J* = 7.3 Hz, 1H), 6.99 (s, 1H), 4.80 (s, 2H), 4.39 (s, 2H), 0.52 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.2, 142.4, 137.3, 136.7, 136.1, 135.6, 133.8, 133.8, 133.6, 133.1, 132.3, 129.4, 129.0, 128.7, 128.0, 127.5, 126.6, 126.2, 125.2, 50.1, 49.7, 1.6.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{26}H_{26}ClNNaOSi$ 454.1364, found 454.1360.



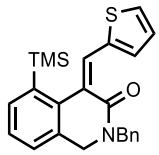
3x

(*Z*)-2-benzyl-4-(naphthalen-1-ylmethylene)-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3x: colorless oil, actual mass 86.9 mg, 96% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 8.26 (d, *J* = 7.1 Hz, 1H), 7.91 – 7.87 (m, 3H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.52 – 7.44 (m, 2H), 7.34 – 7.30 (m, 2H), 7.21 – 7.06 (m, 6H), 4.63 (s, 2H), 4.30 (s, 2H), 0.45 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.1, 142.8, 137.2, 136.7, 136.2, 135.6, 134.9, 133.6, 133.3, 132.0, 131.8, 129.1, 128.8, 128.7, 128.6, 127.8, 127.3, 126.5, 126.1, 125.5, 125.3, 125.3, 124.3, 50.1, 49.5, 1.8.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{30}H_{29}NNaOSi$ 470.1911, found 470.1914.



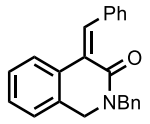
3y

(*Z*)-2-benzyl-4-(thiophen-2-ylmethylene)-5-(trimethylsilyl)-1,4-dihydroisoquinolin-3(2*H*)-one 3y: colorless oil, actual mass 28.2 mg, 35% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.6 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 5.1 Hz, 1H), 7.41 (d, *J* = 3.5 Hz, 1H), 7.33 – 7.23 (m, 6H), 7.09 – 7.06 (m, 2H), 6.98 (s, 1H), 4.81 (s, 2H), 4.25 (s, 2H), 0.38 (s, 9H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 166.4, 142.6, 137.8, 136.8, 136.8, 135.7, 133.7, 133.3, 130.7, 130.6, 128.7, 128.0, 127.5, 126.6, 126.2, 125.2, 50.1, 49.6, 1.4.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{24}H_{25}NNaOSSi$ 426.1318, found 426.1333.



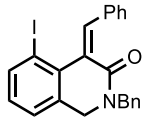
4a

(*Z*)-2-benzyl-4-benzylidene-1,4-dihydroisoquinolin-3(2*H*)-one 4a [3]: colorless oil, actual mass 19.5 mg, 60% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.24 (m, 10H), 7.16 (s, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 4.82 (s, 2H), 4.42 (s, 2H).

^{13}**C NMR** (151 MHz, $CDCl_3$) δ 164.8, 136.8, 136.7, 135.9, 135.7, 131.4, 130.1, 129.5, 128.7, 128.3, 128.1, 128.0, 127.9, 127.5, 127.4, 125.0, 123.7, 50.1, 49.9.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{23}H_{20}NO$ 326.1539, found 326.1526.



4b

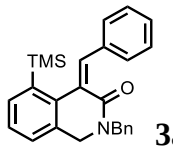
(*Z*)-2-benzyl-4-benzylidene-5-iodo-1,4-dihydroisoquinolin-3(2*H*)-one 4b: colorless oil, actual mass 37.4 mg, 83% yield, (eluent : petroleum ether/ethyl acetate = 10:1).

^{1}**H NMR** (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.41 – 7.24 (m, 9H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.88 (t, *J* = 7.7 Hz, 1H), 4.78 (s, 2H), 4.27 (s, 2H).

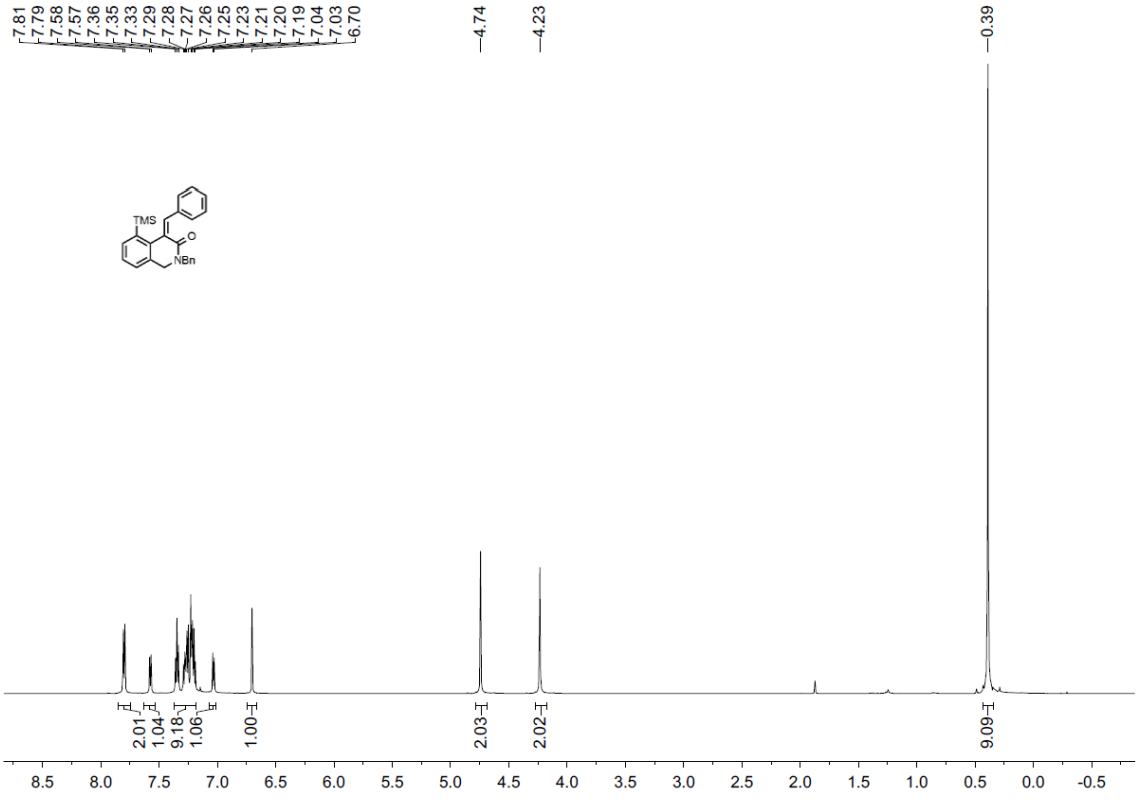
^{13}**C NMR** (151 MHz, $CDCl_3$) δ 165.7, 140.5, 139.0, 138.7, 136.6, 134.4, 134.3, 131.2, 130.1, 128.9, 128.7, 128.4, 128.1, 127.9, 127.6, 125.1, 93.7, 50.2, 49.7.

HRMS (ESI) m/z calcd for molecular formula $[M + Na]^+$ $C_{23}H_{18}INNaO$ 474.0325, found 474.0346.

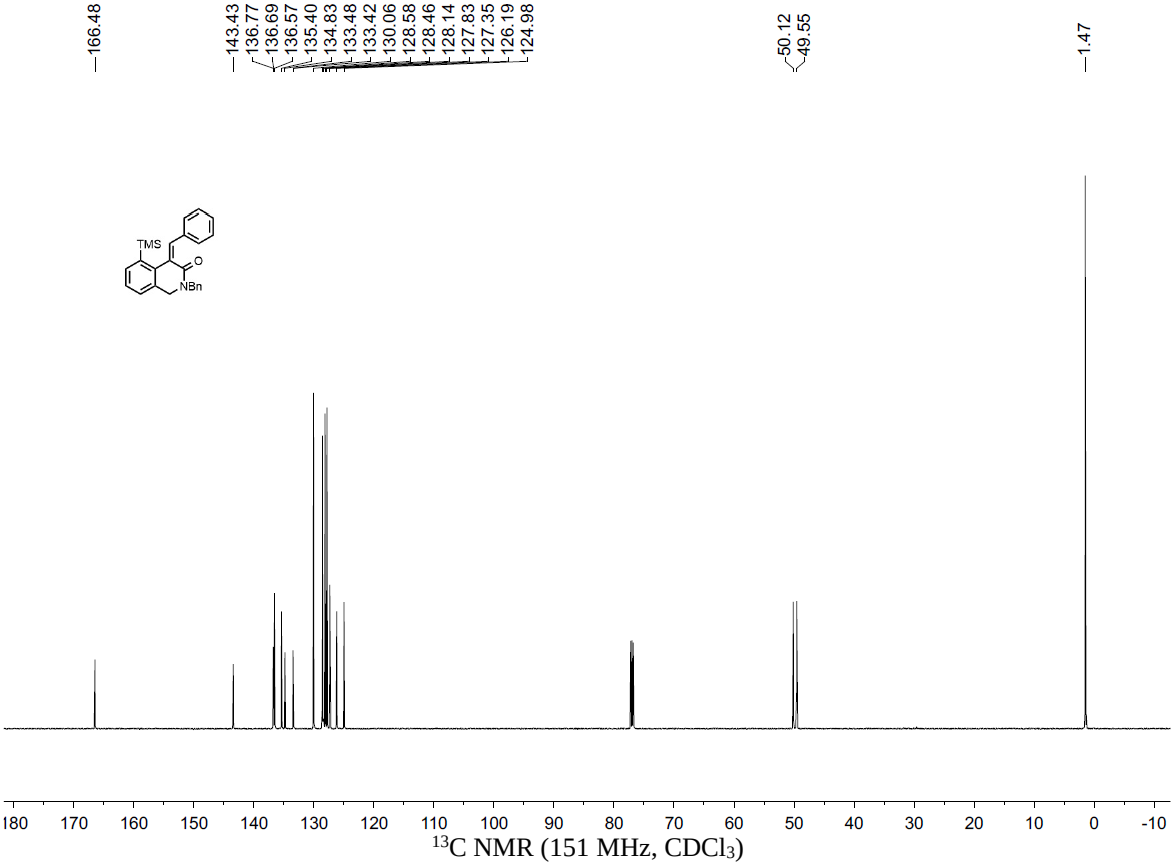
5. NMR Spectra



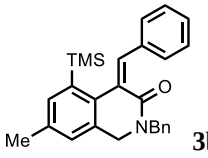
3a



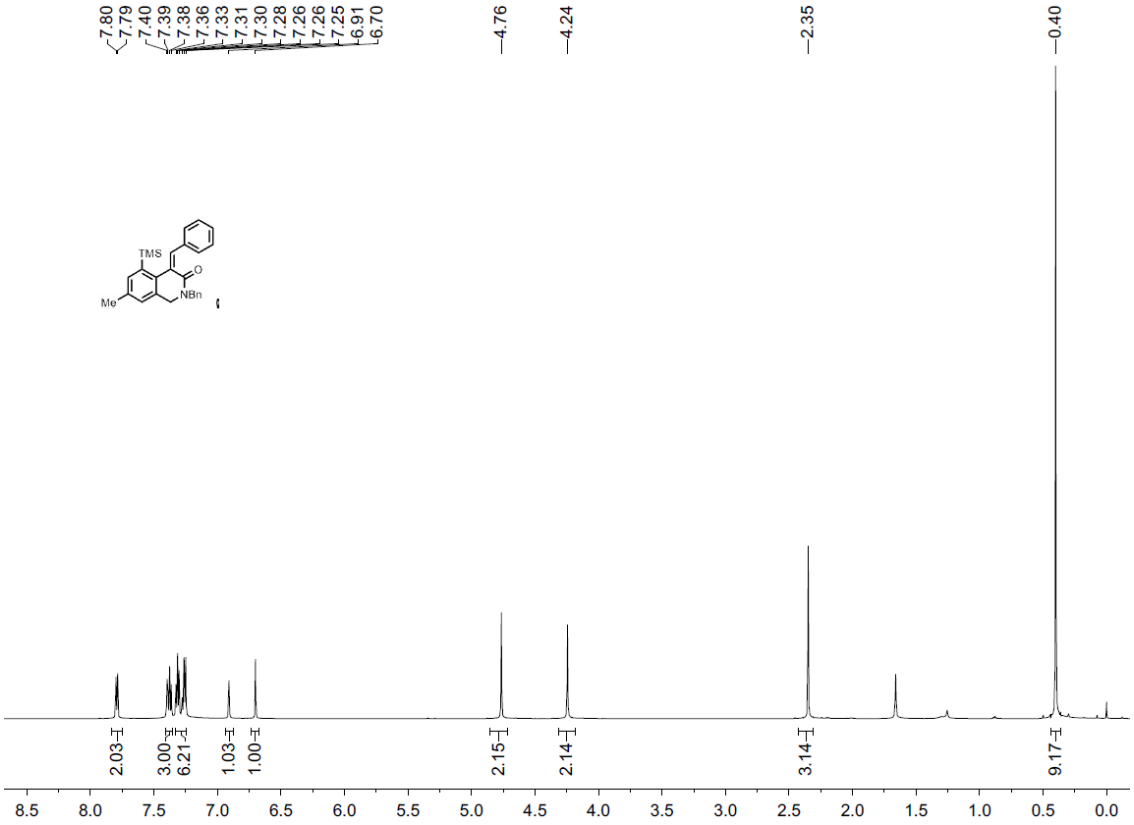
^{1}H NMR (600 MHz, $CDCl_3$)



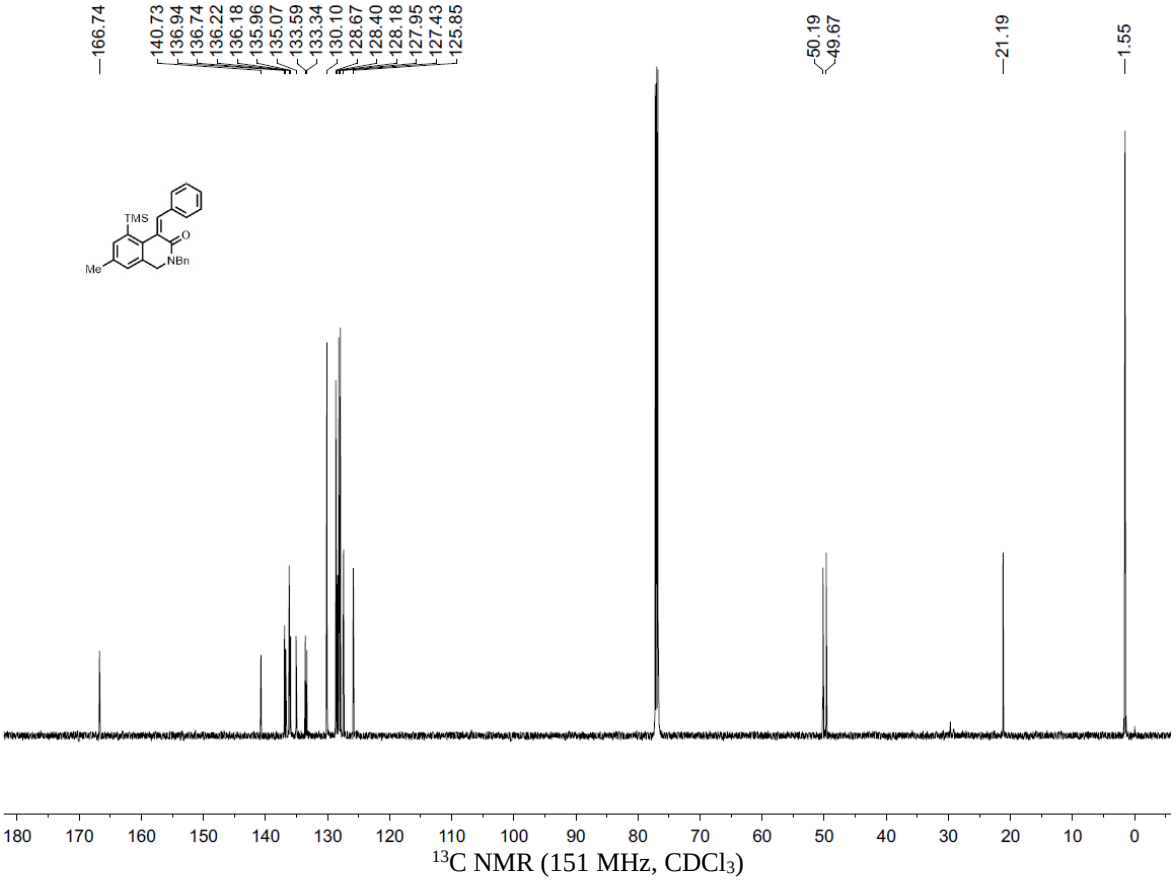
^{13}C NMR (151 MHz, $CDCl_3$)



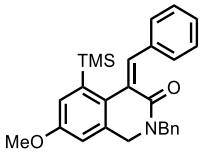
3b



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



^{13}C NMR (151 MHz, $CDCl_3$)



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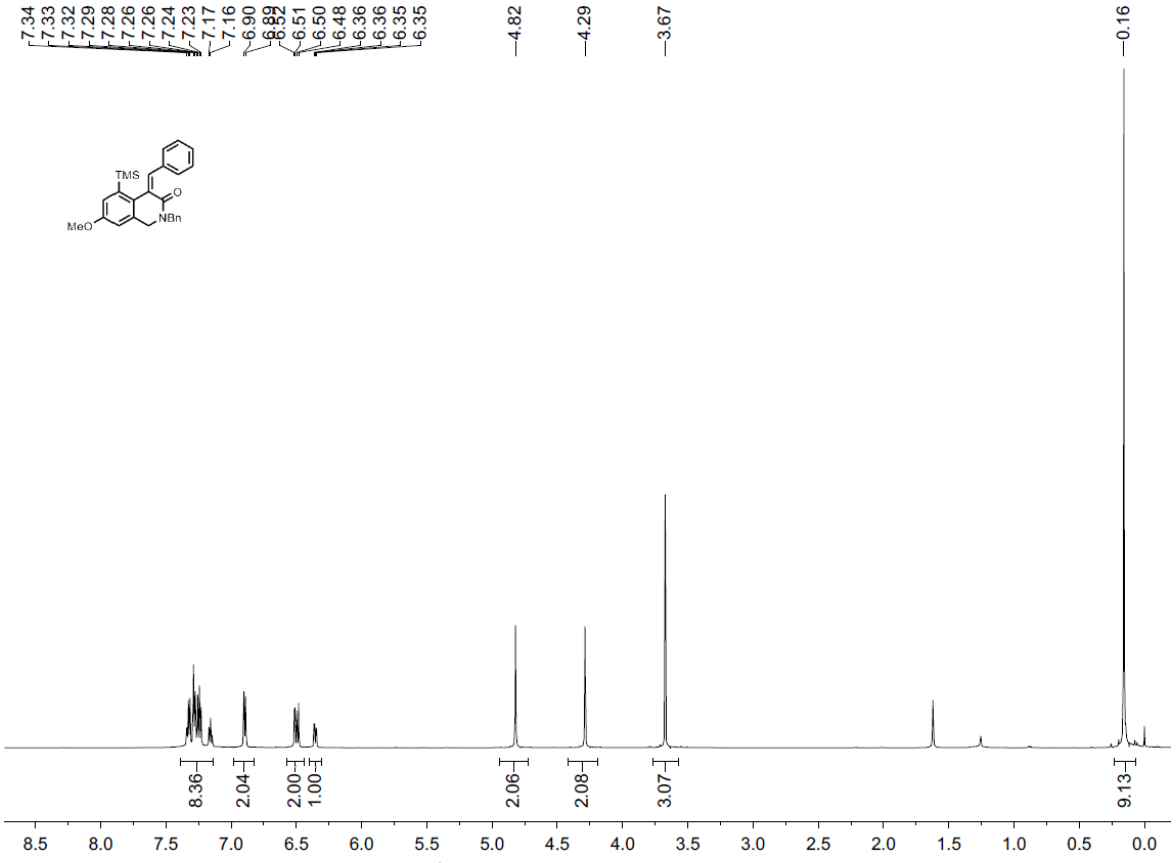
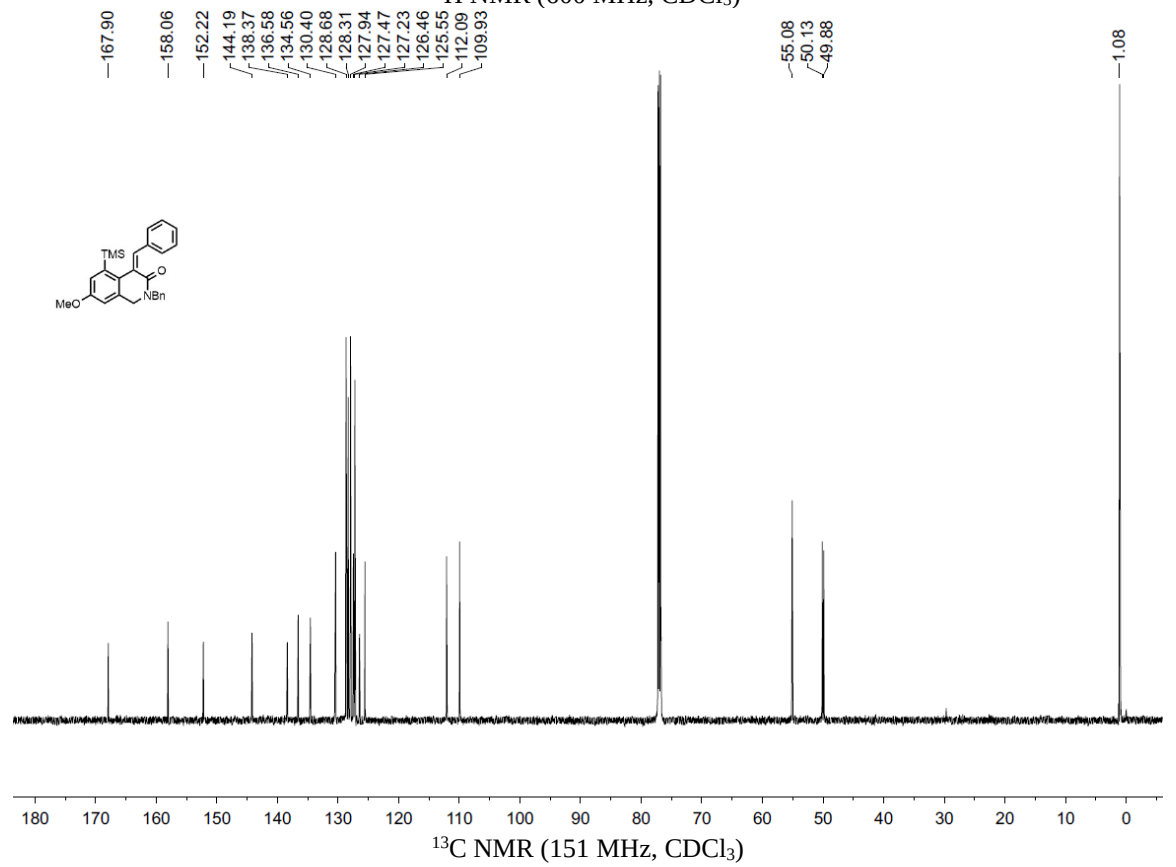
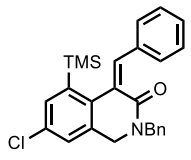


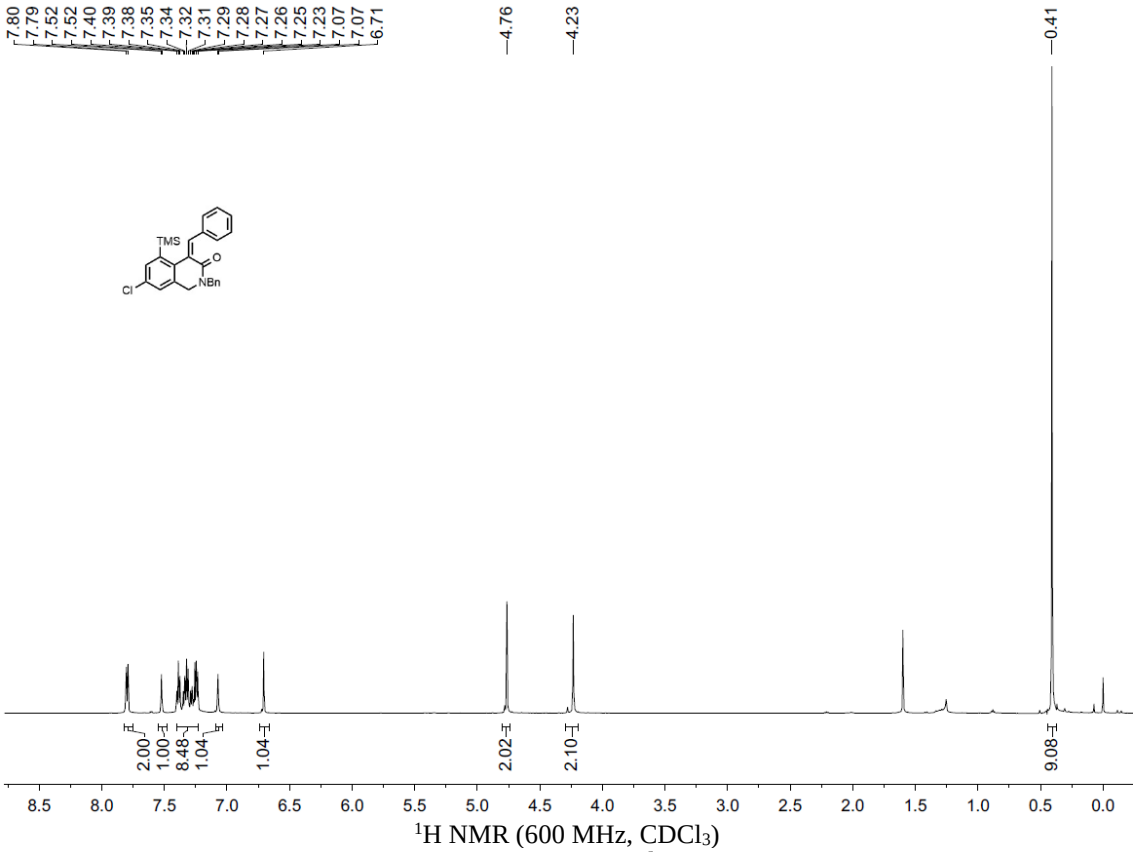
^{1}H NMR (600 MHz, $CDCl_3$)



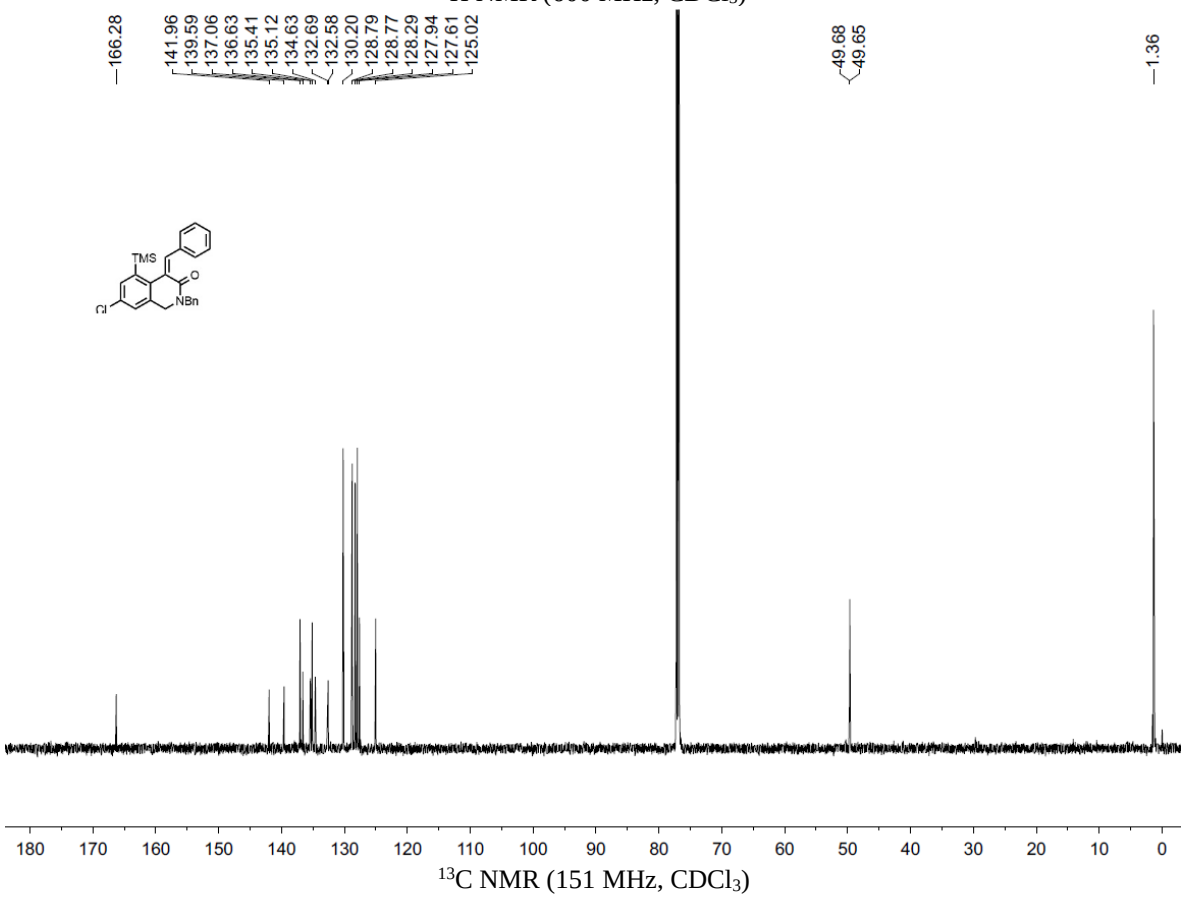
^{13}C NMR (151 MHz, $CDCl_3$)



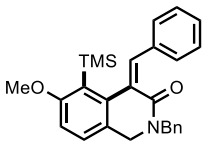
3d



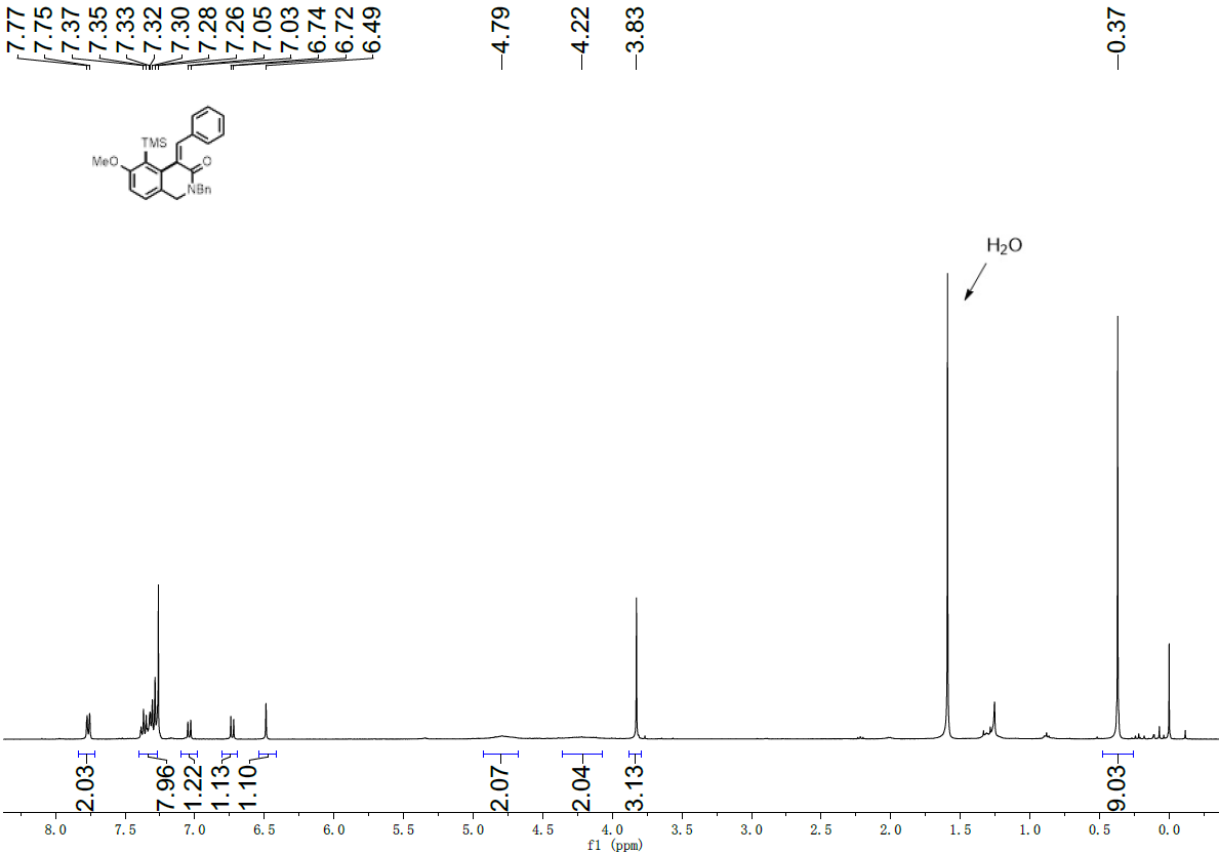
^{1}H NMR (600 MHz, $CDCl_3$)



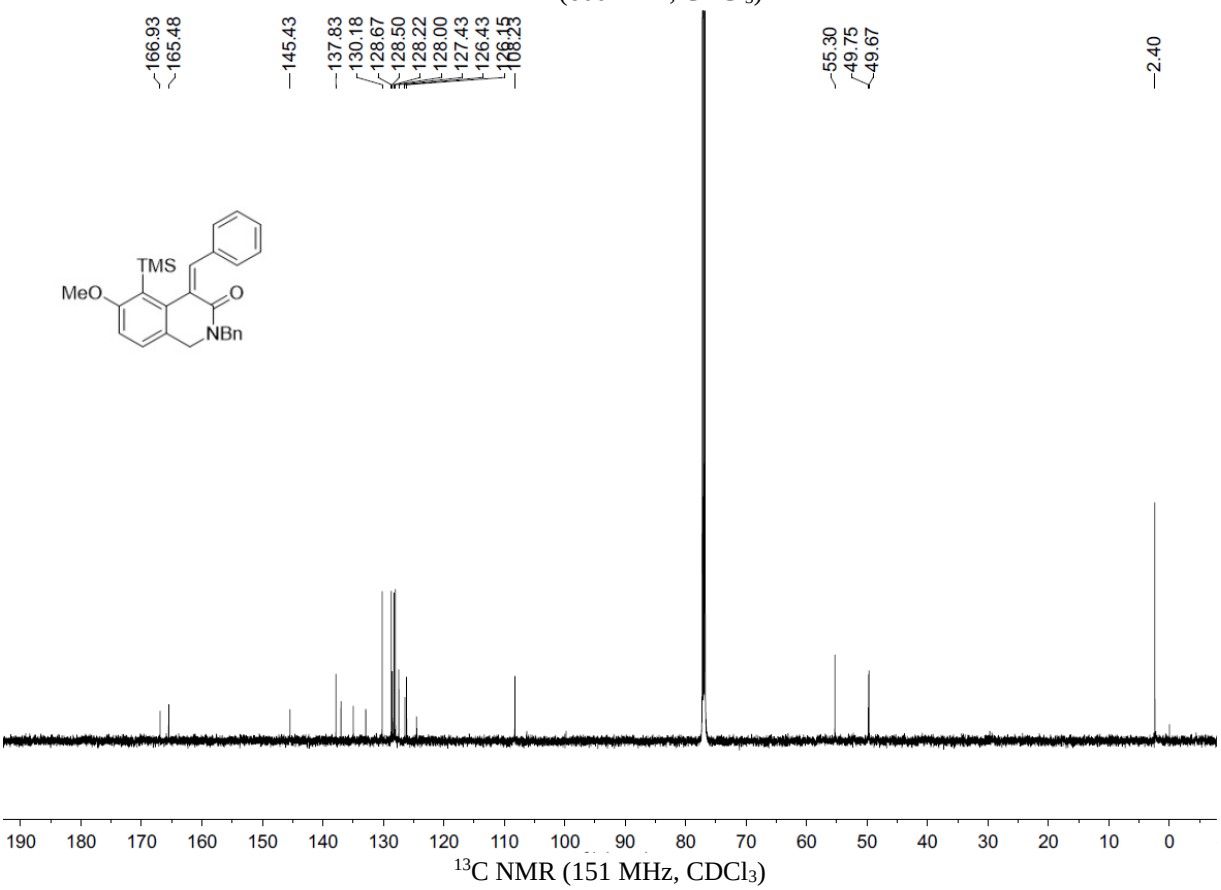
^{13}C NMR (151 MHz, $CDCl_3$)



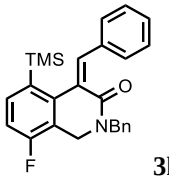
3f



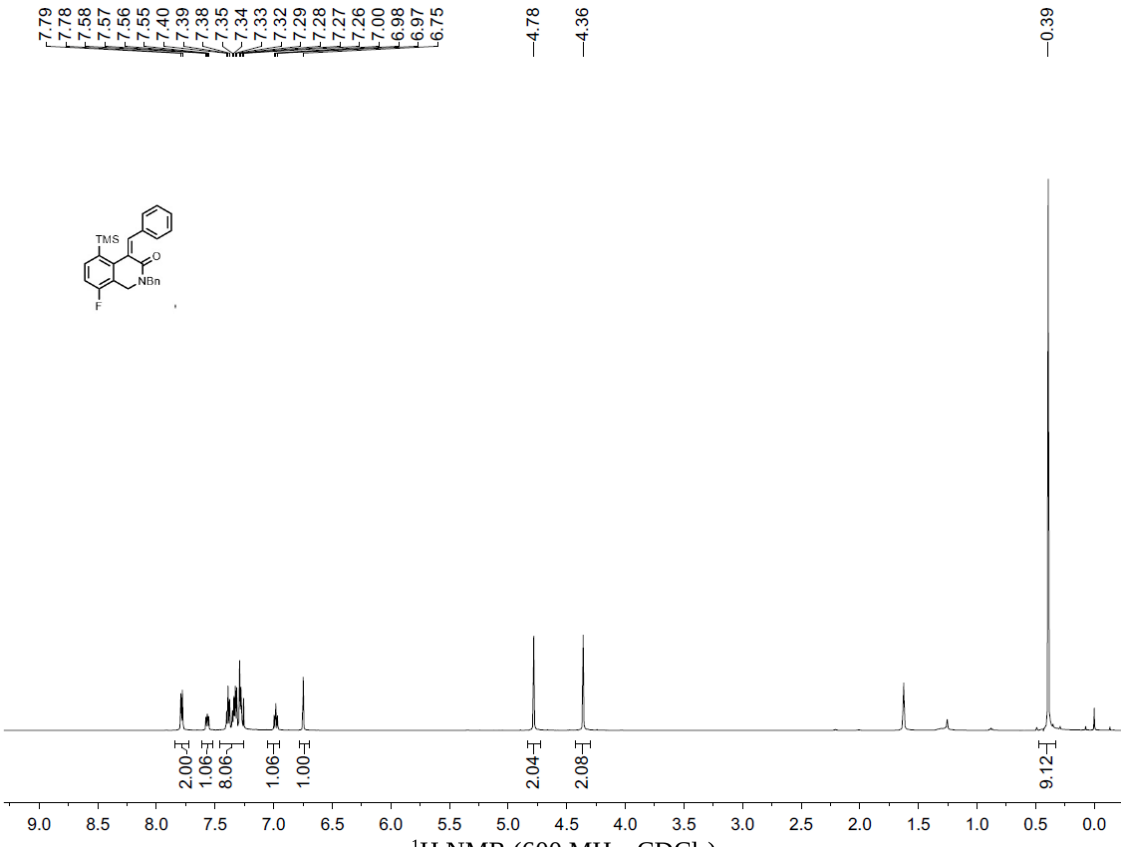
^{1}H NMR (600 MHz, $CDCl_3$)



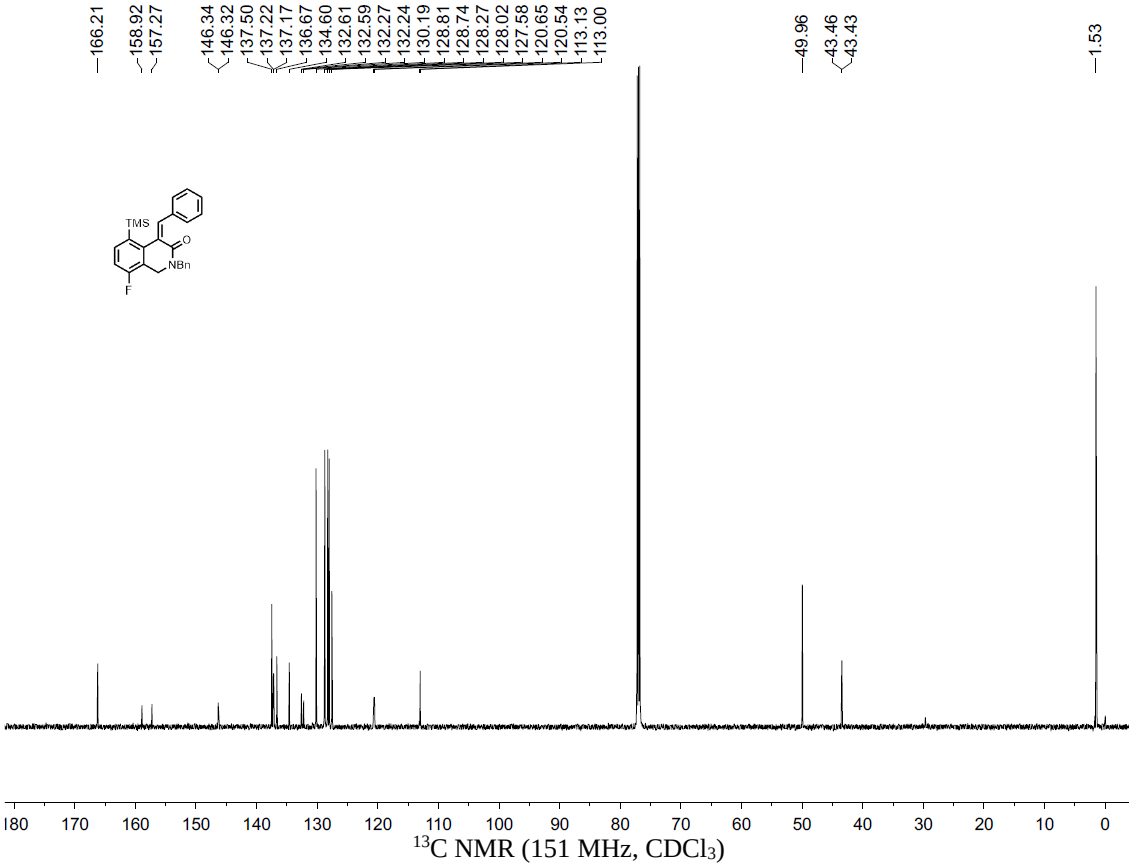
^{13}C NMR (151 MHz, $CDCl_3$)



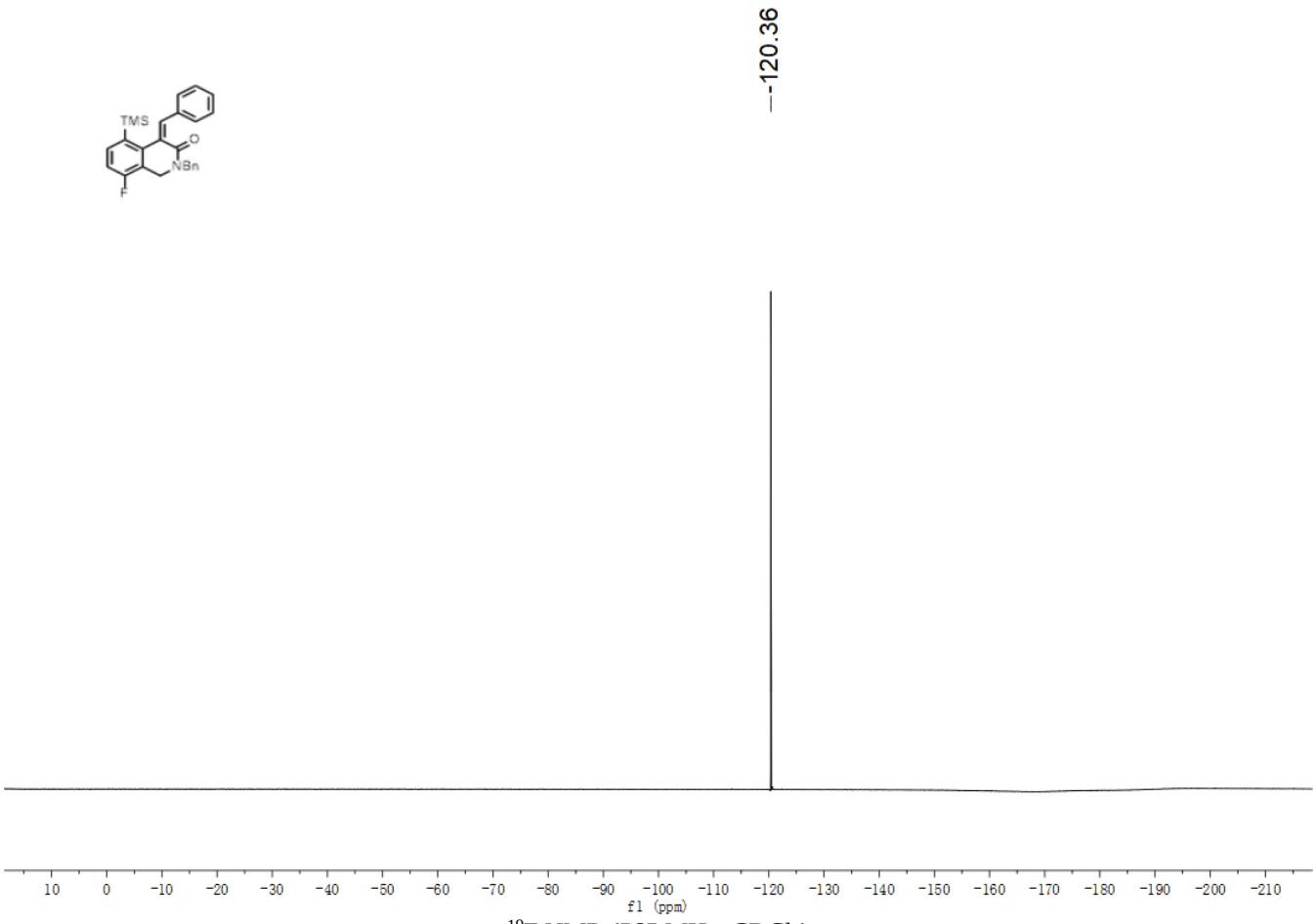
3h



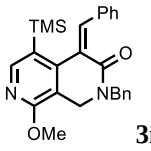
^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)



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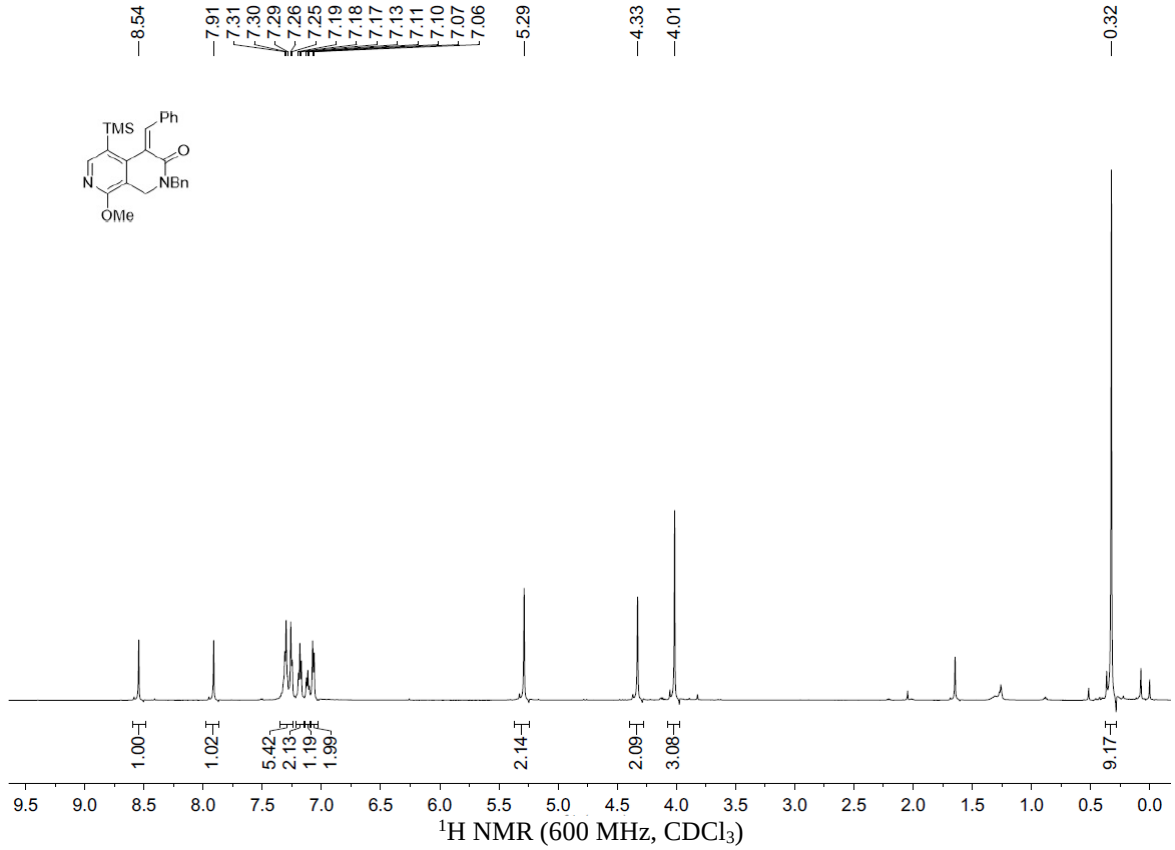
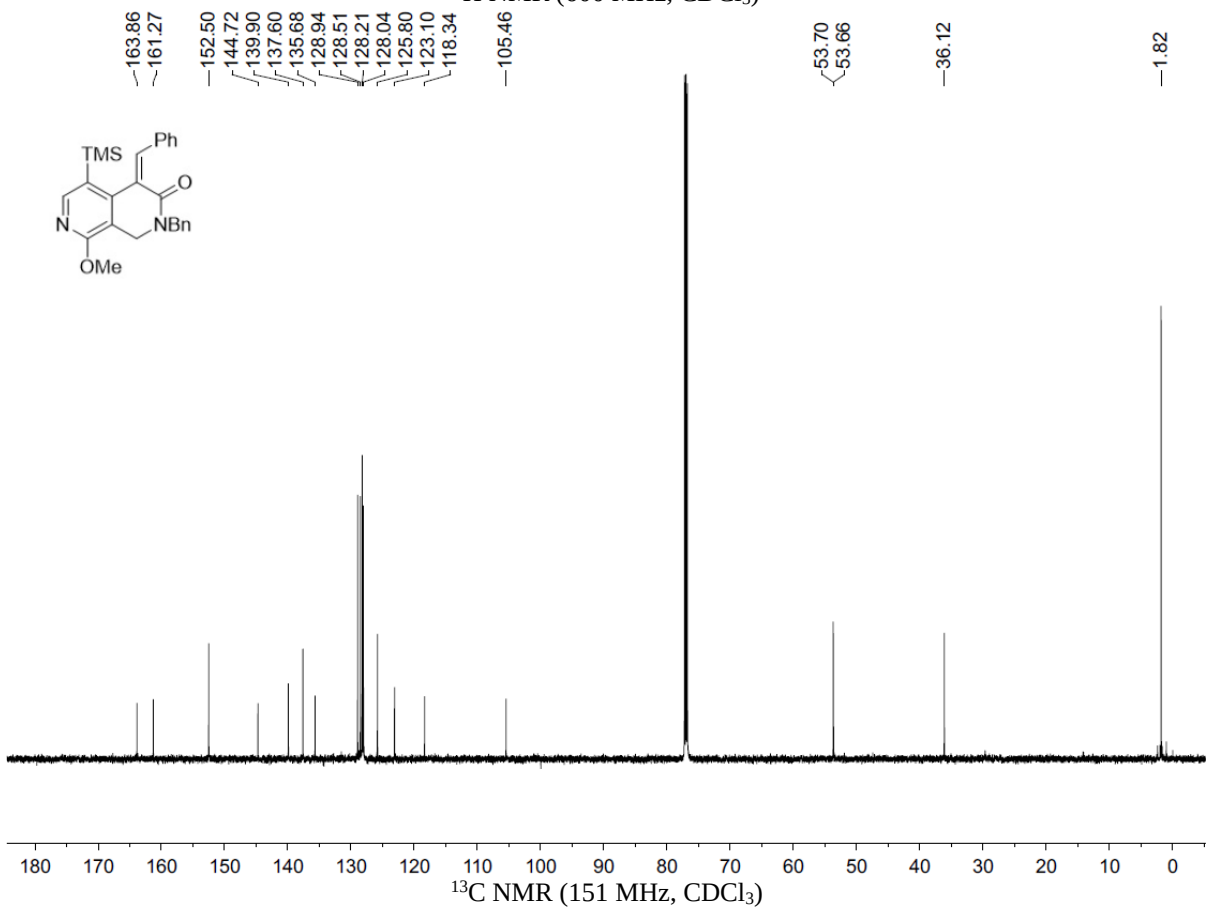
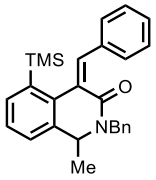


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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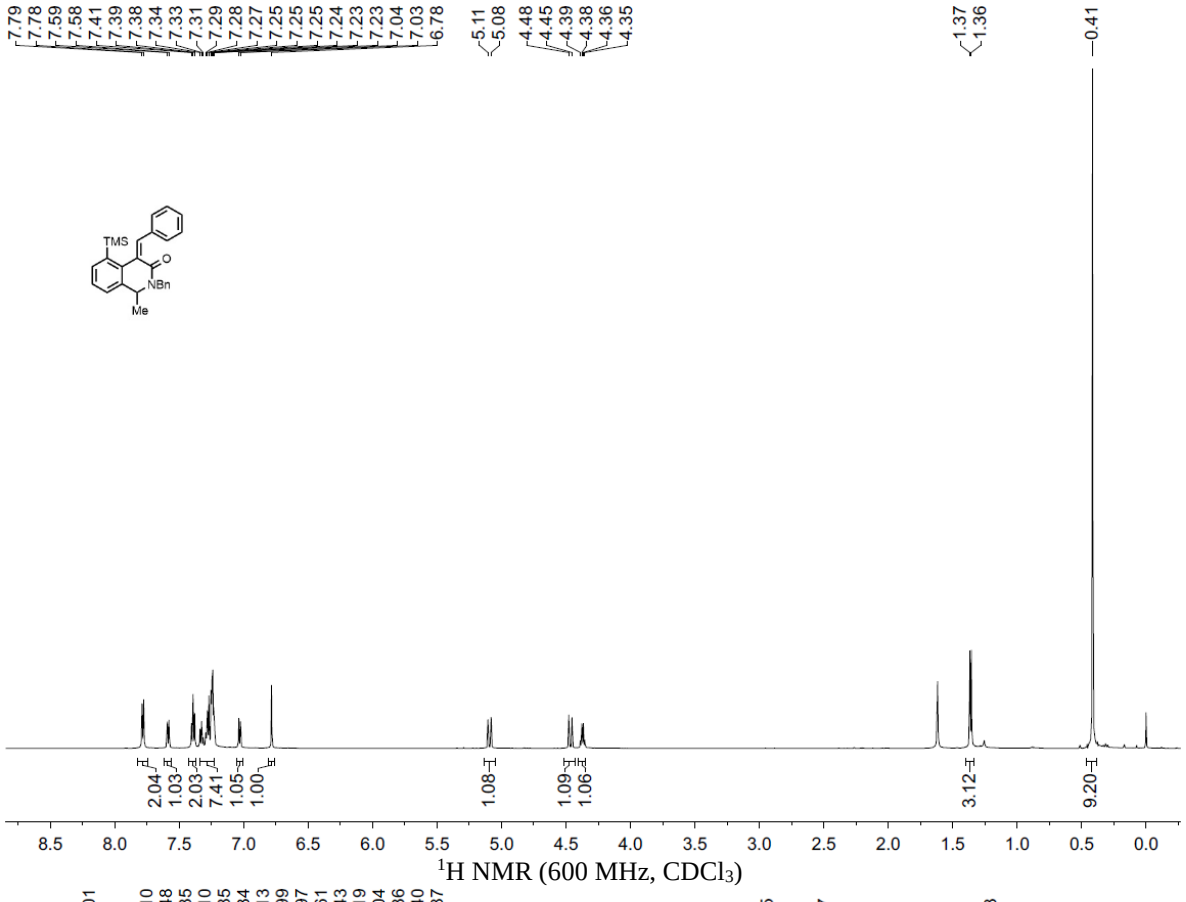
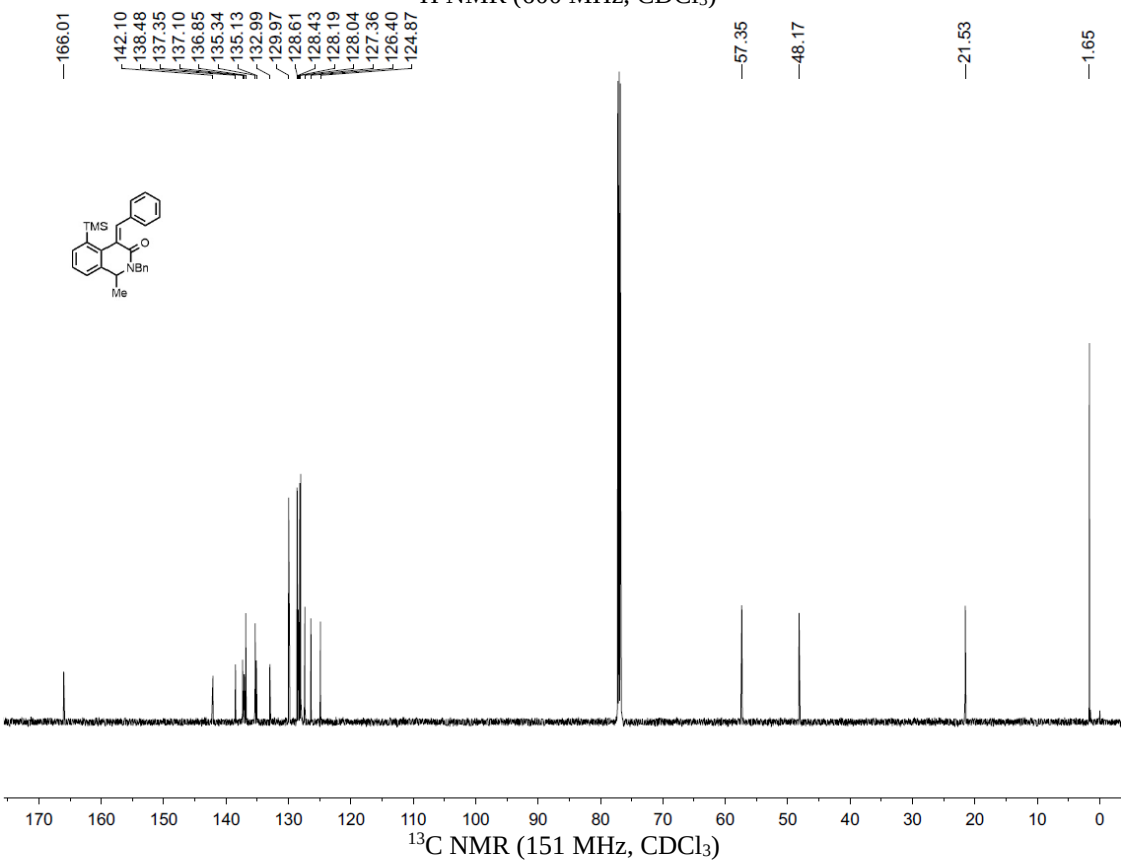
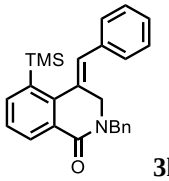


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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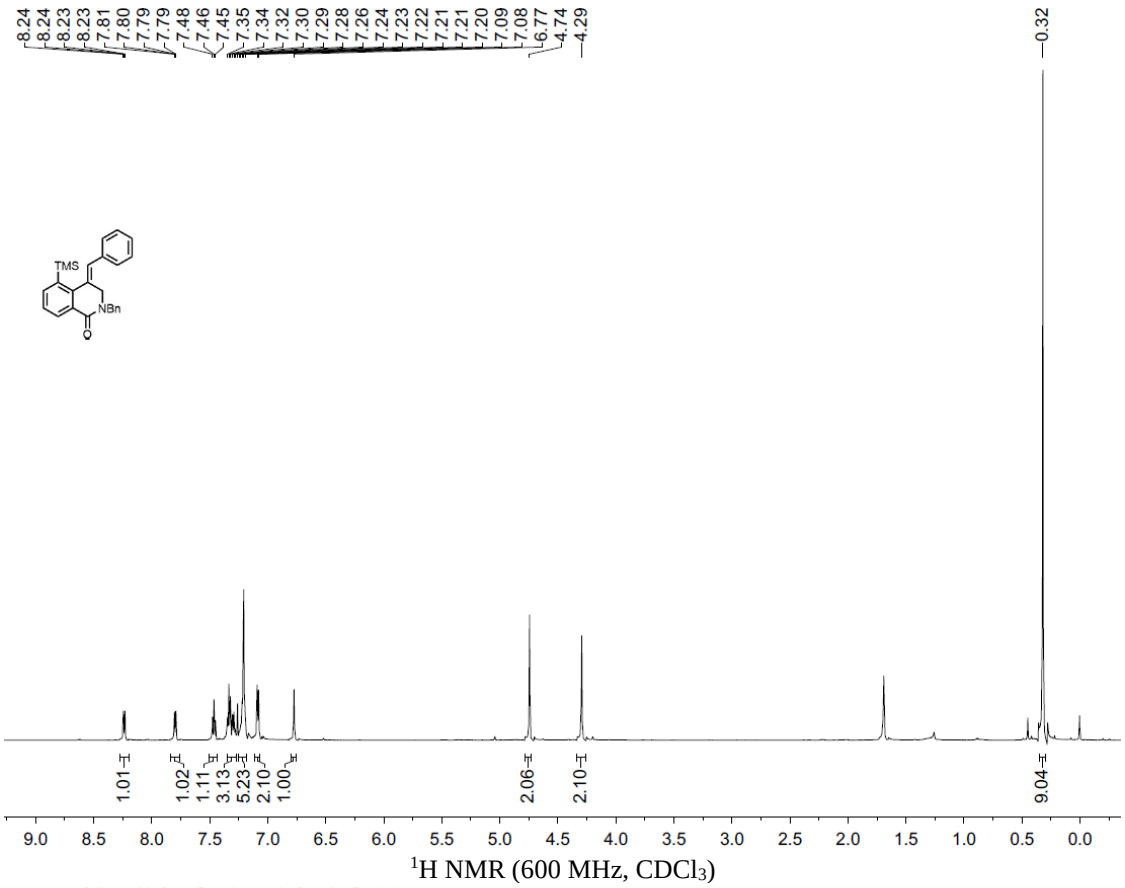
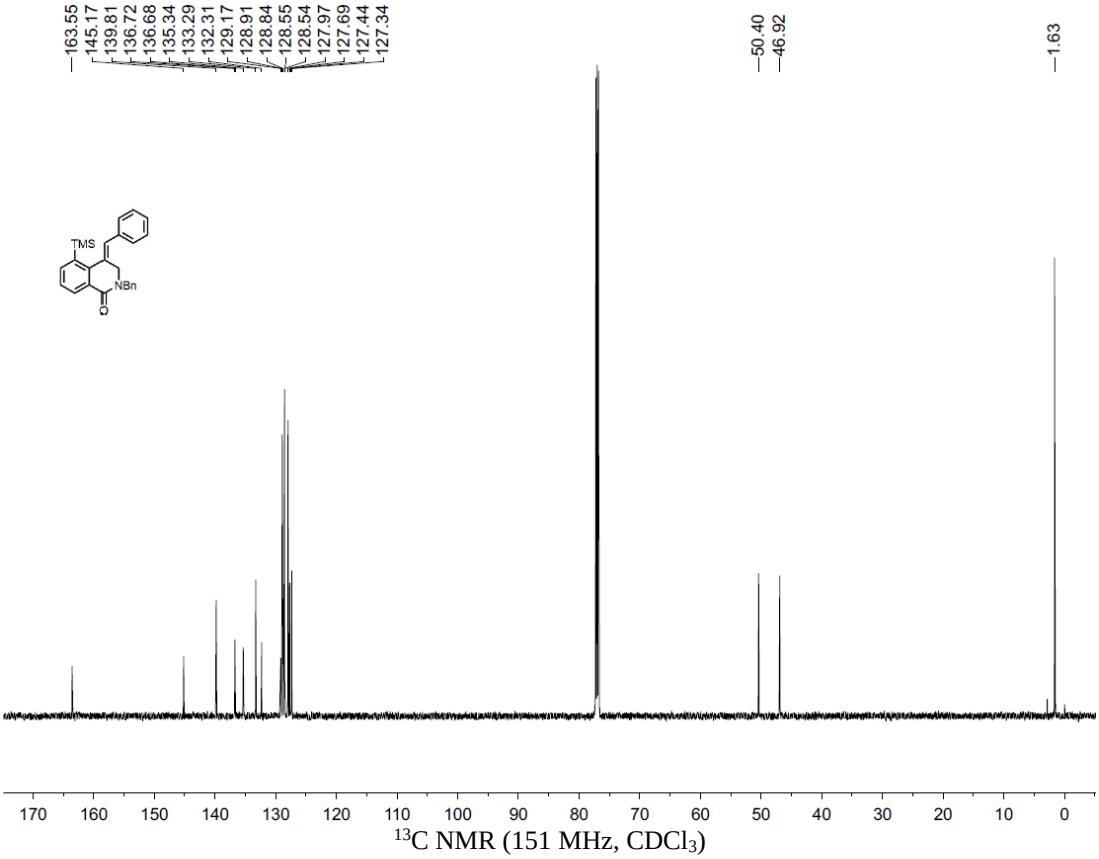


^{1}H NMR (600 MHz, $CDCl_3$)



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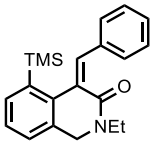

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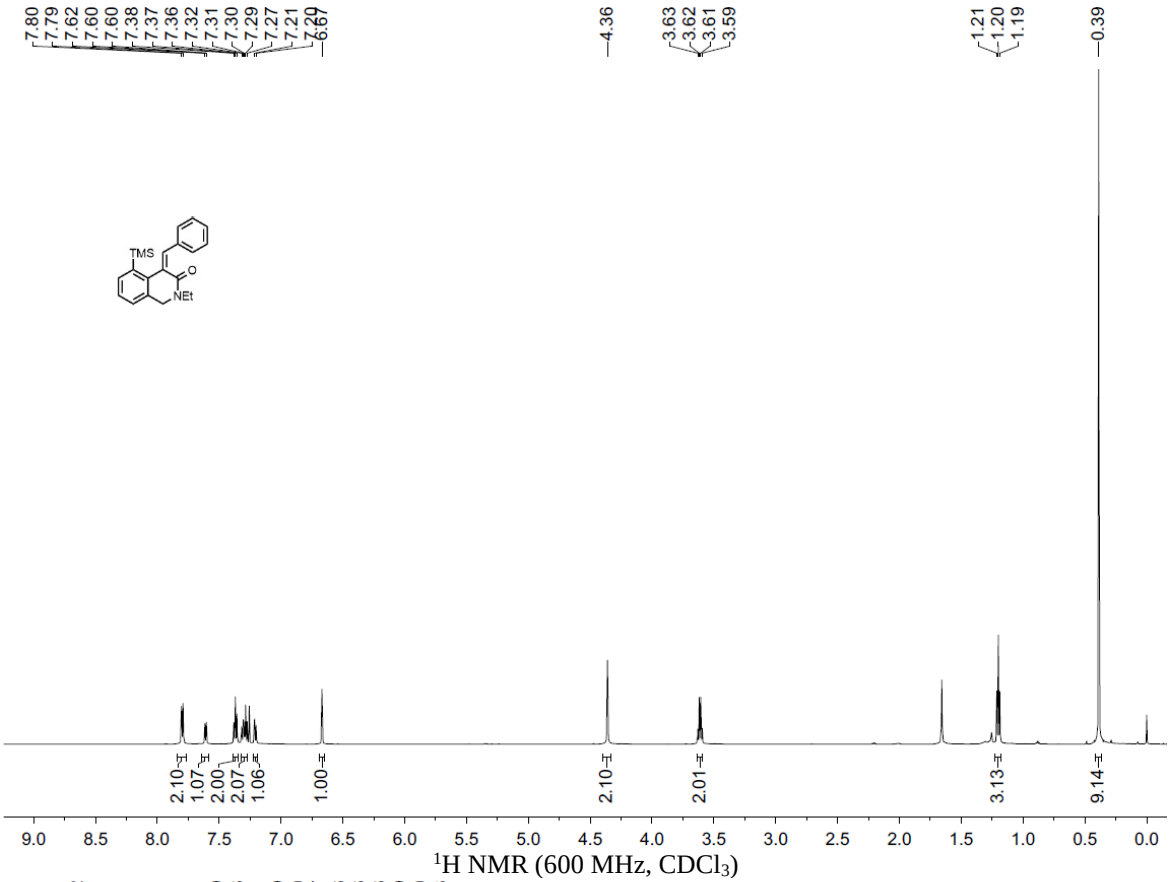

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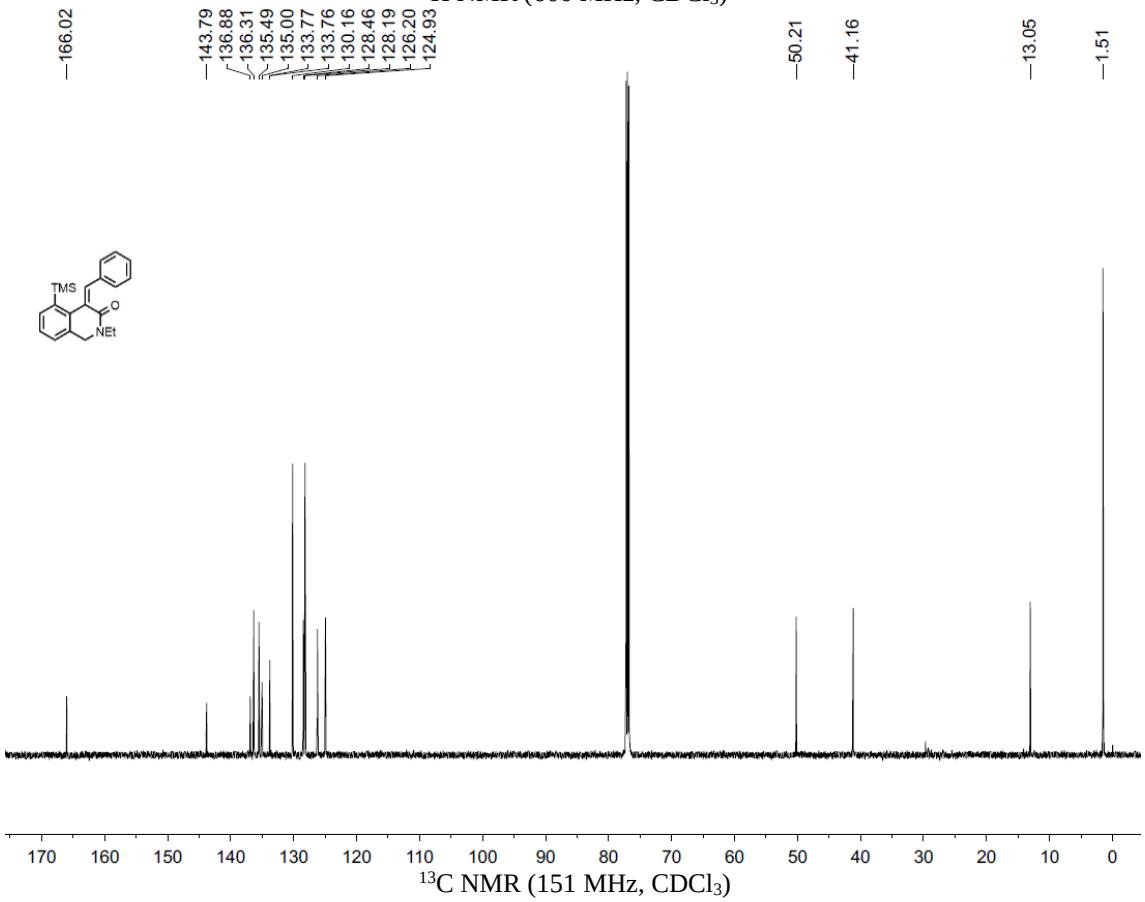
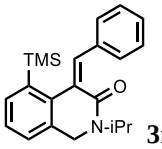


^{13}C NMR (151 MHz, $CDCl_3$)



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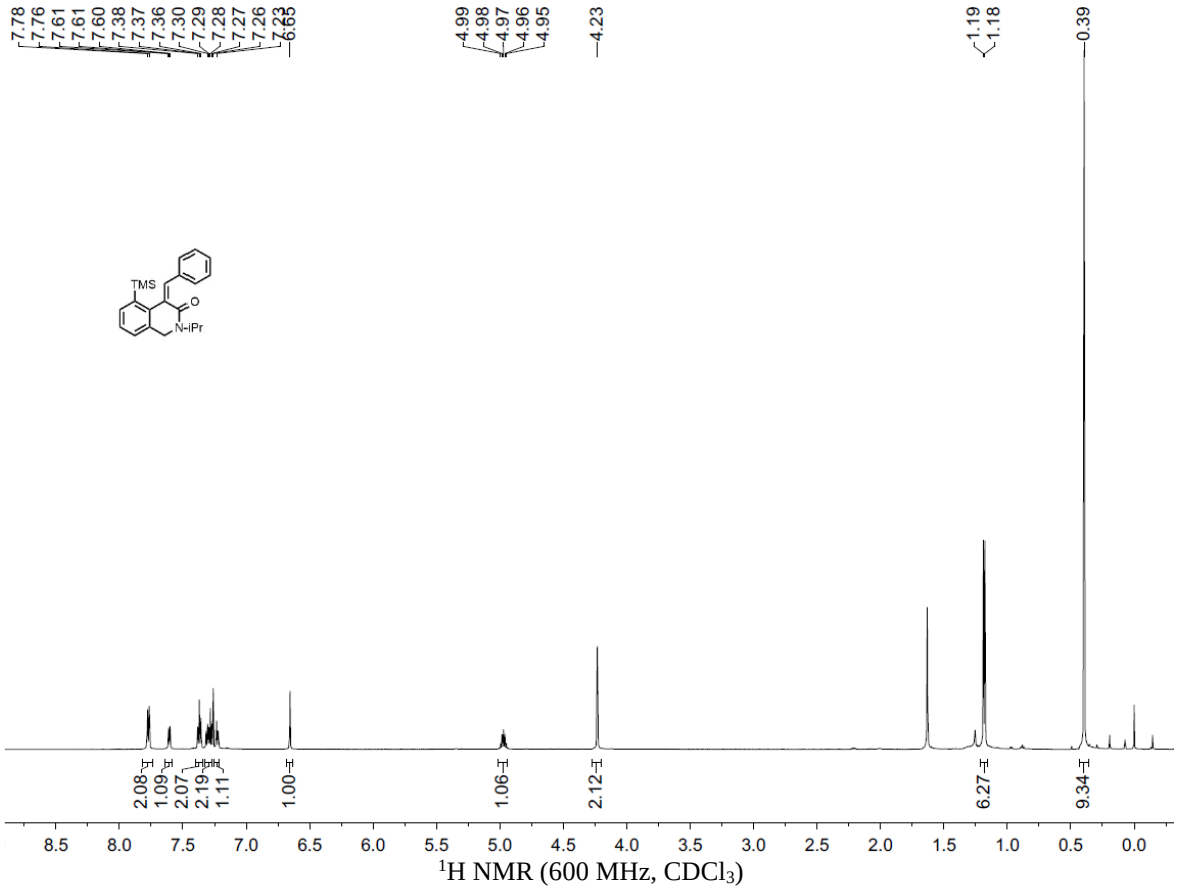
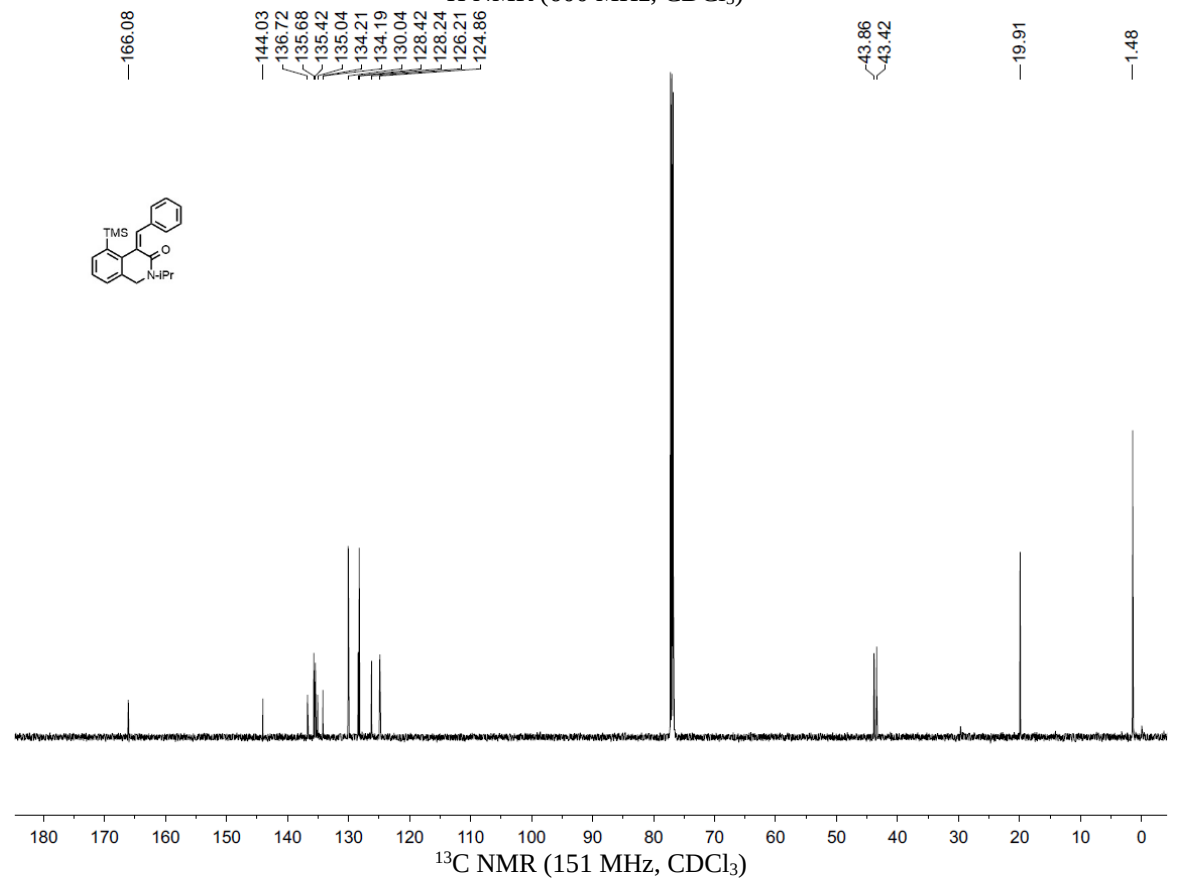
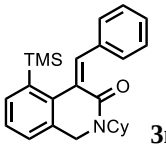


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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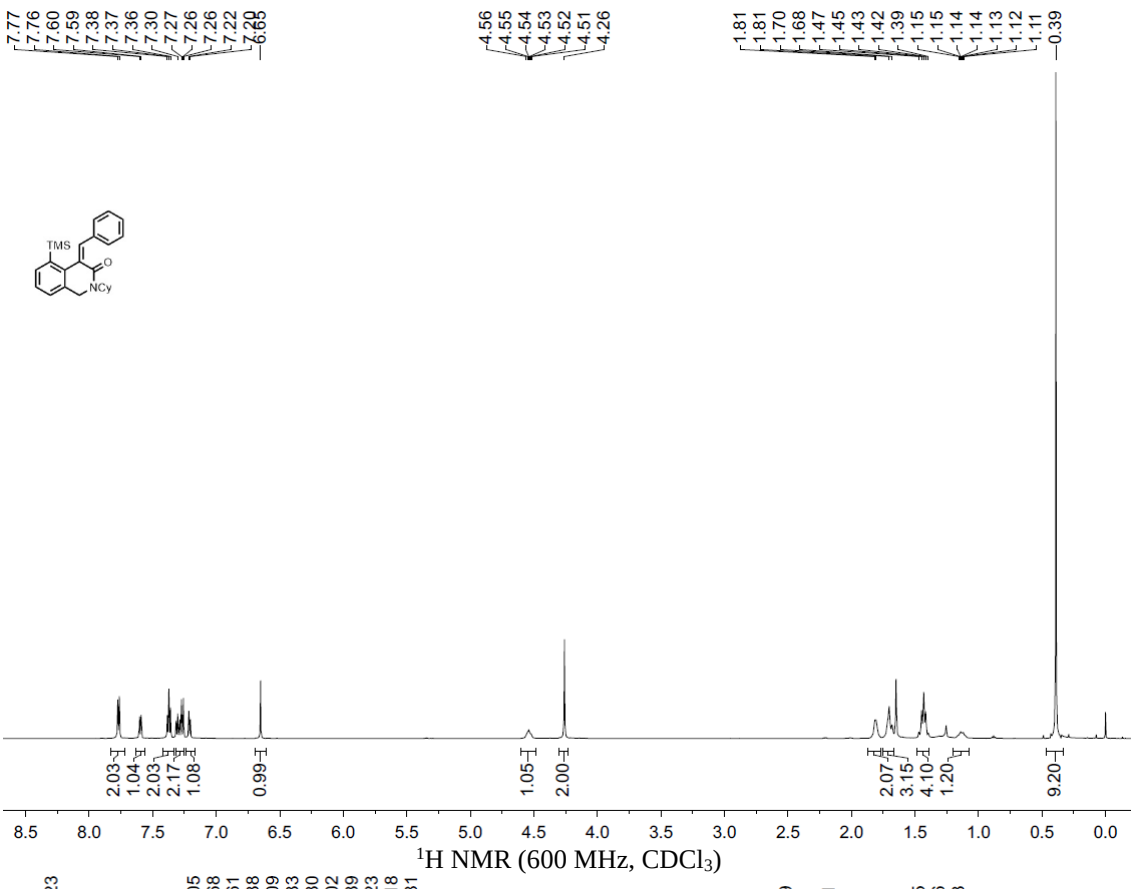

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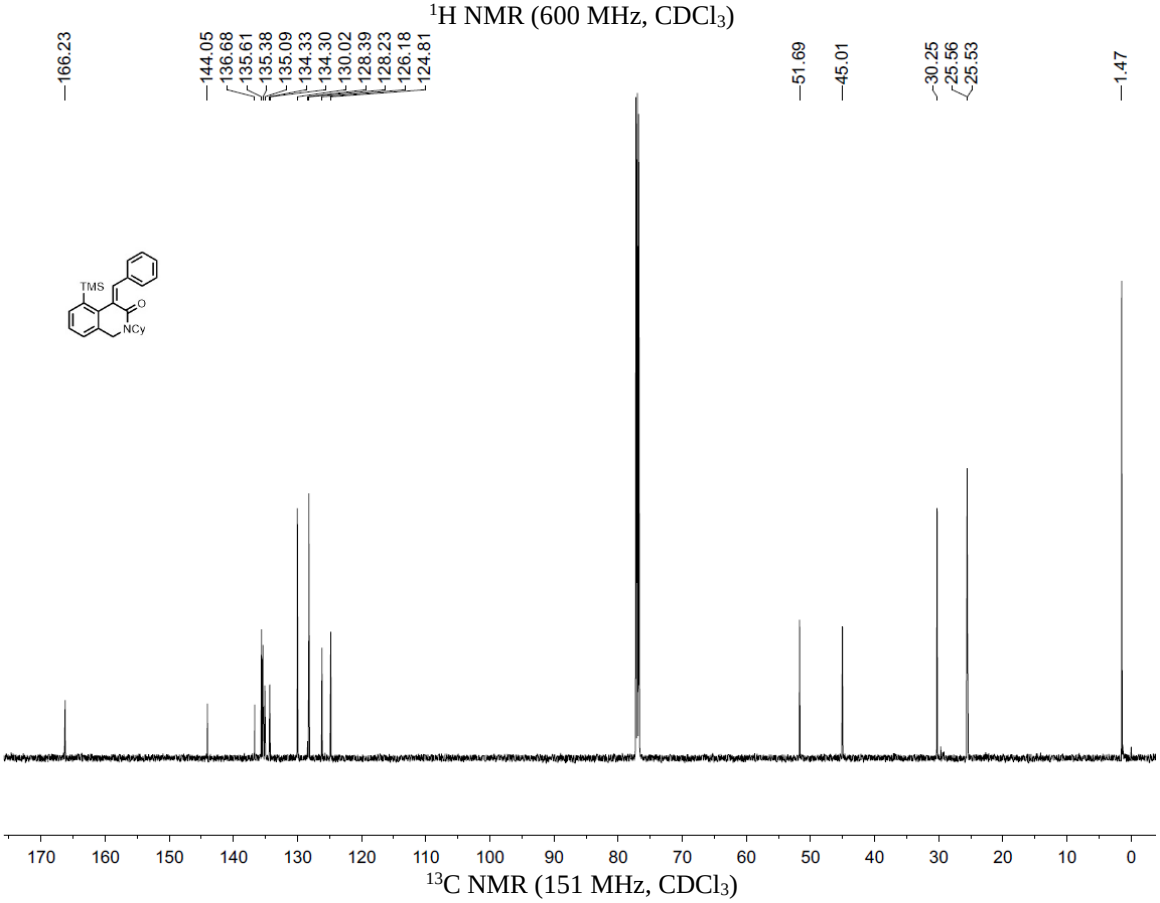

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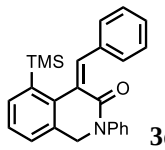

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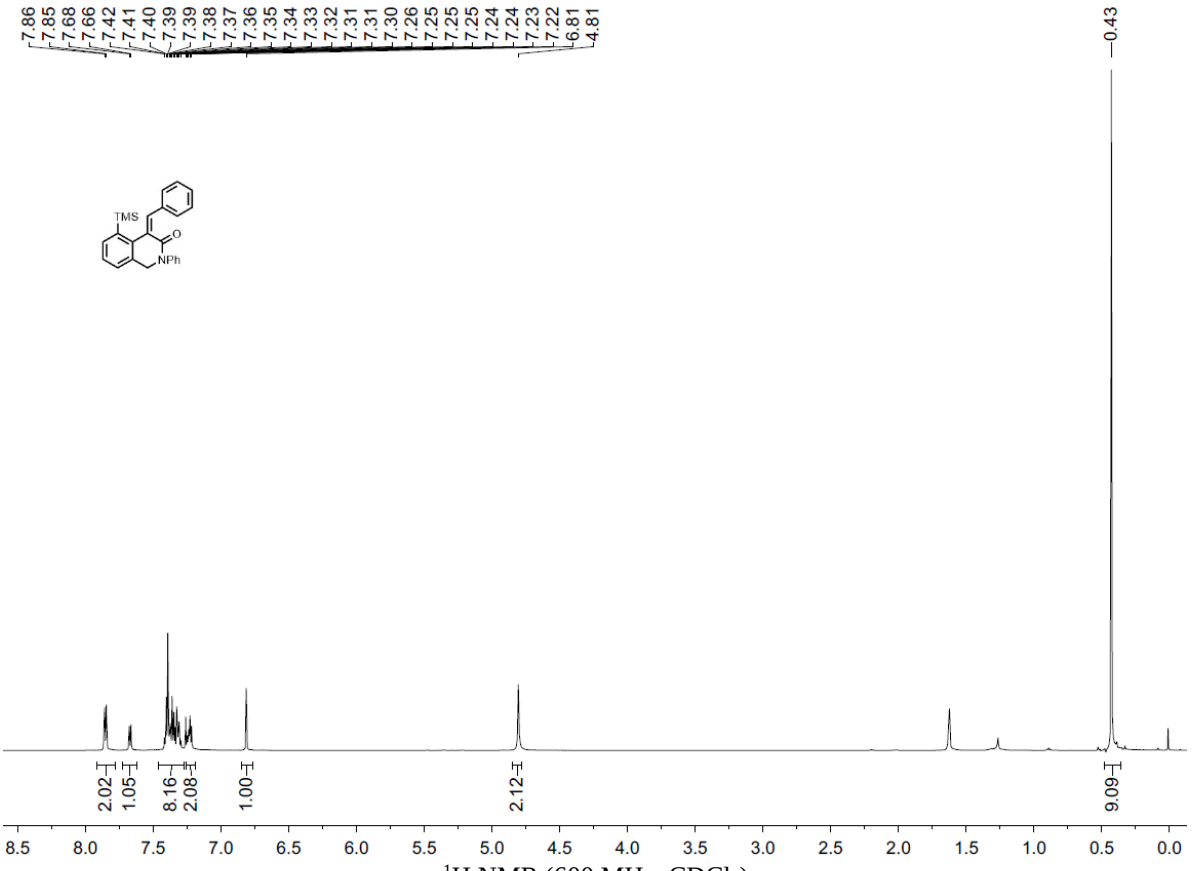

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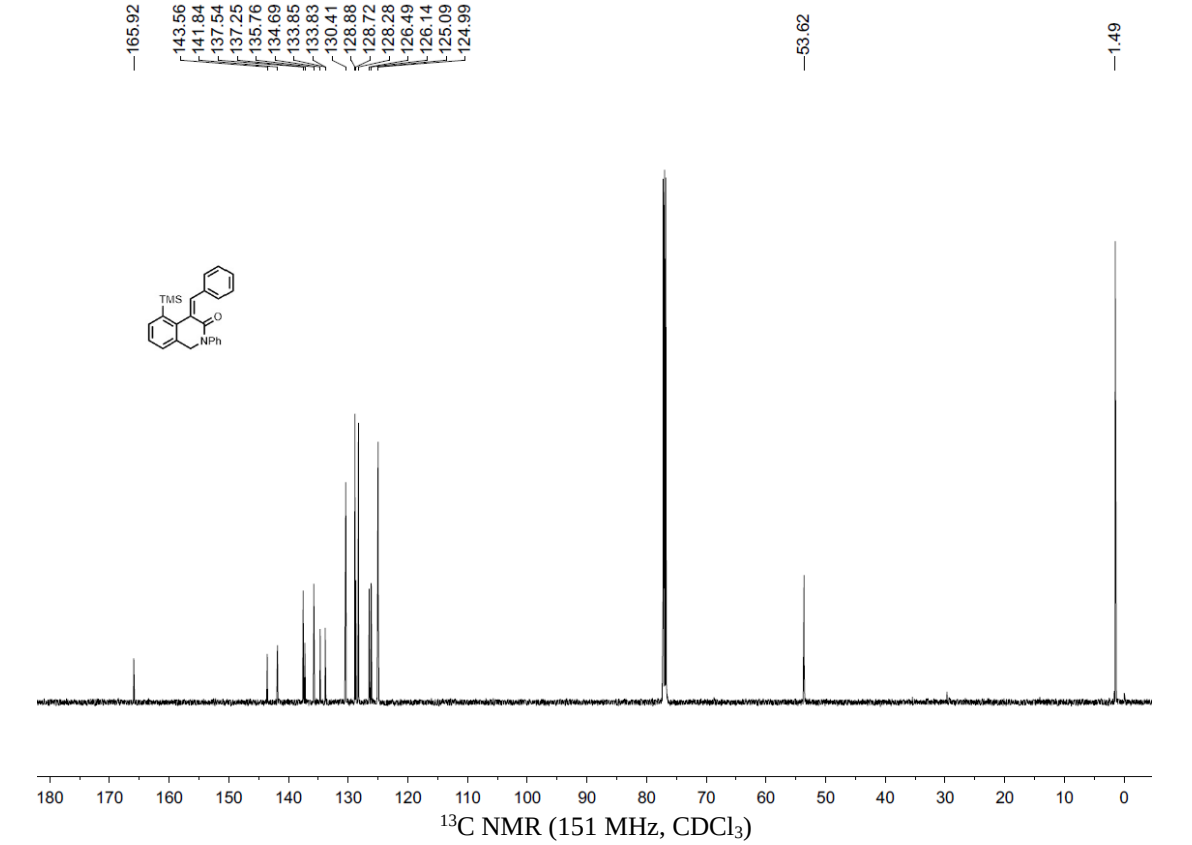

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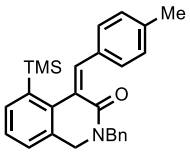

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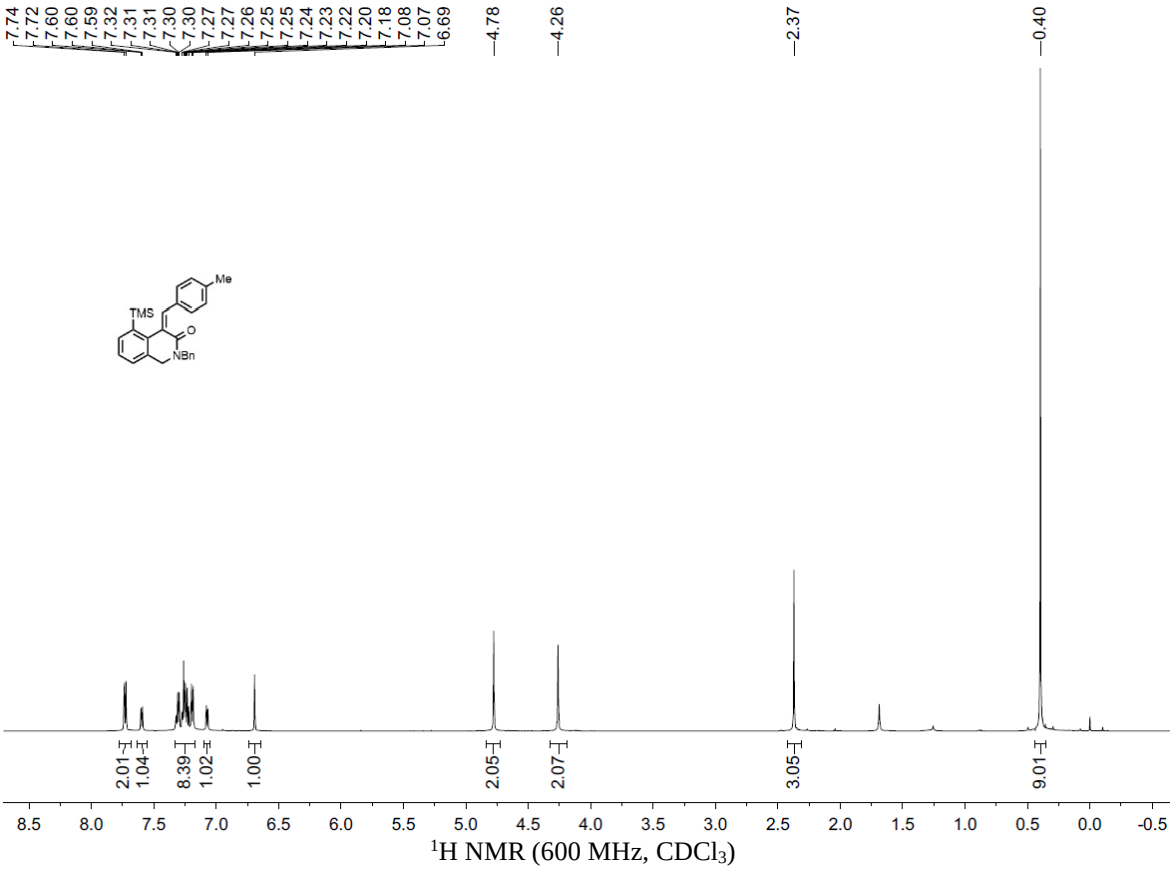
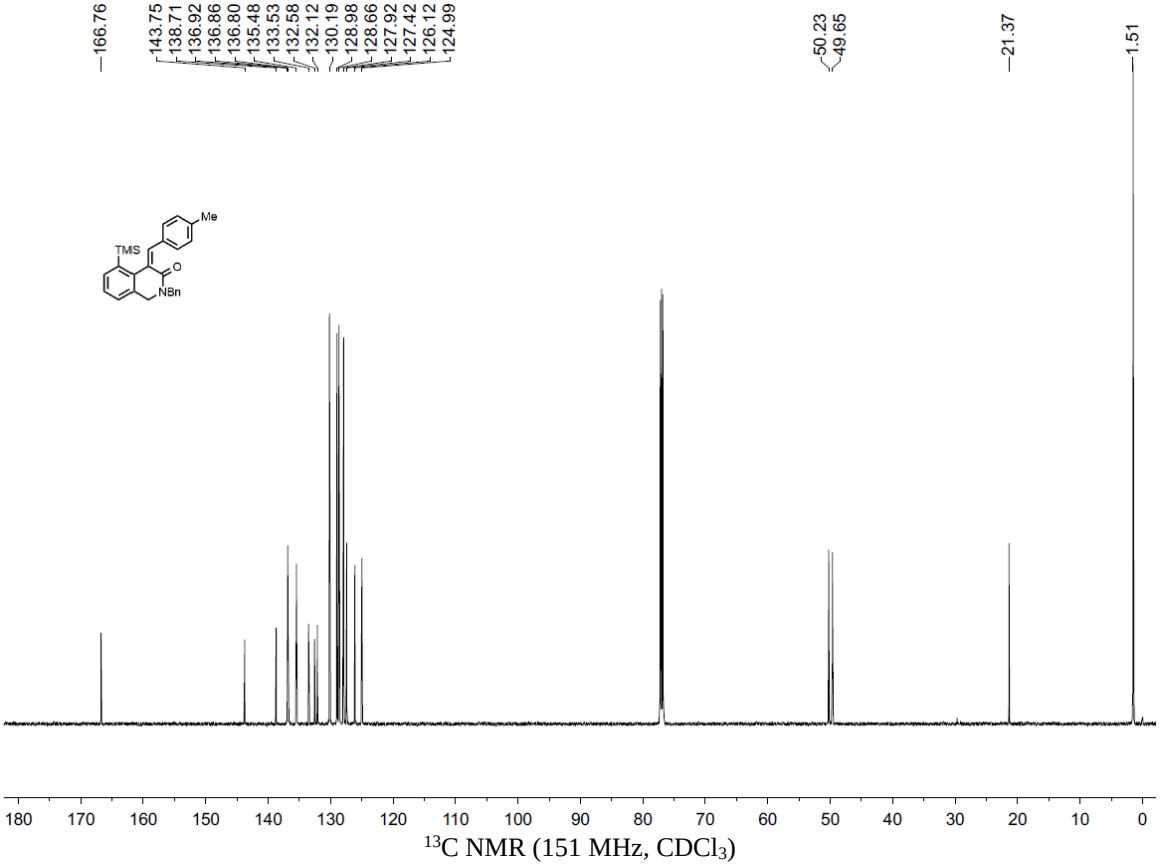
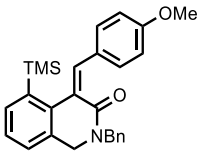


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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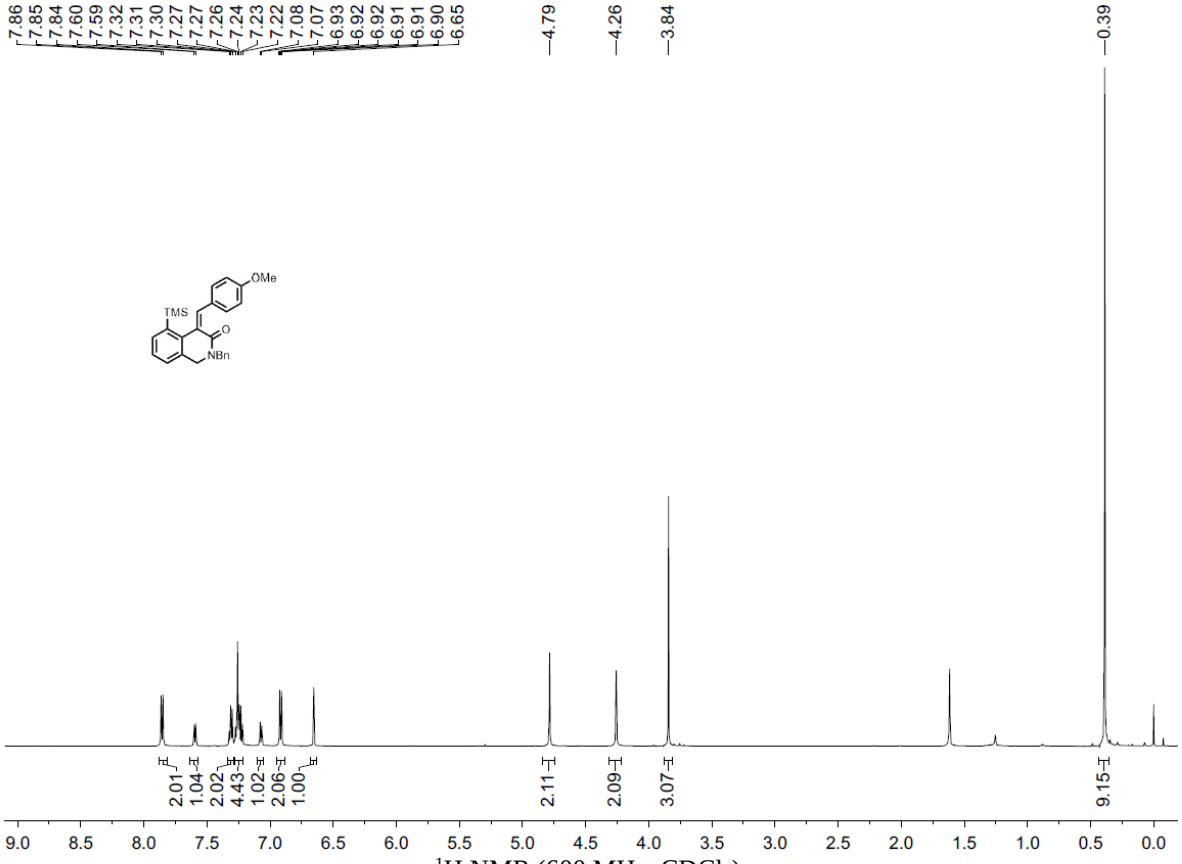
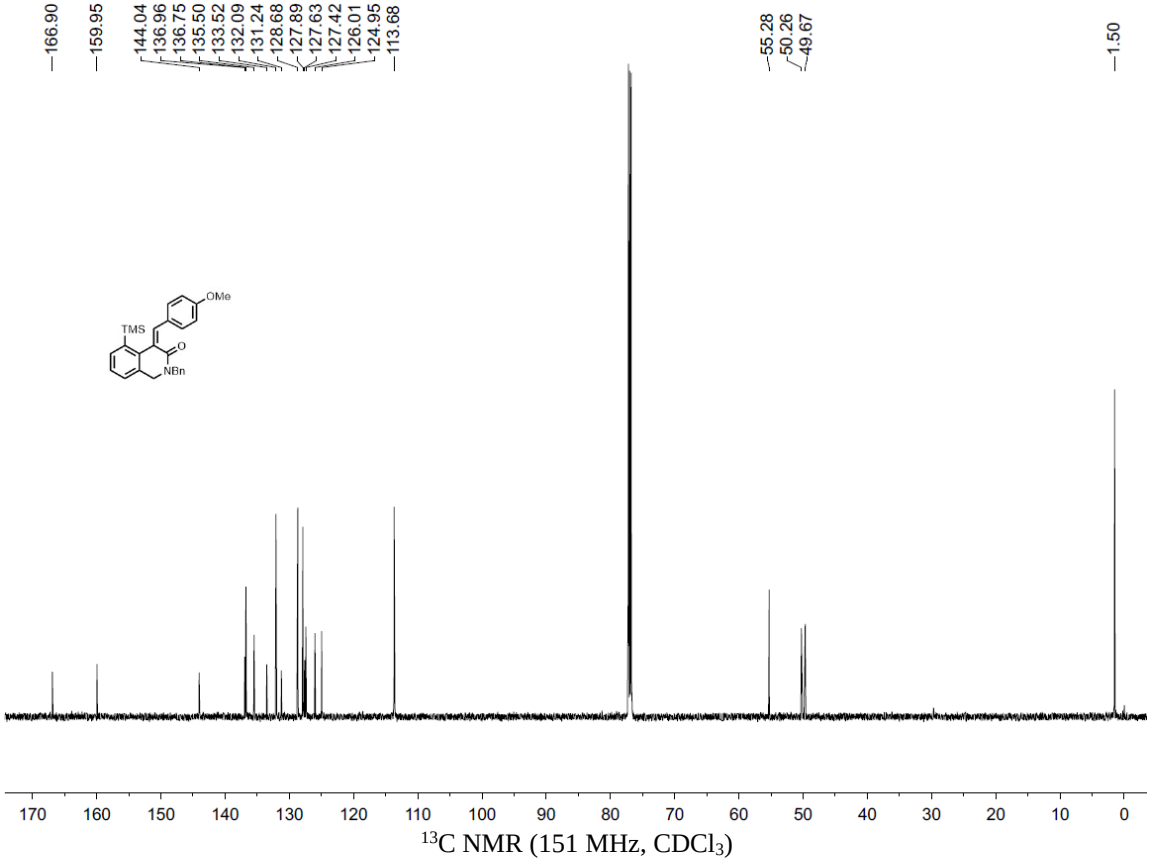
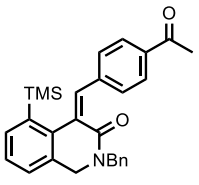


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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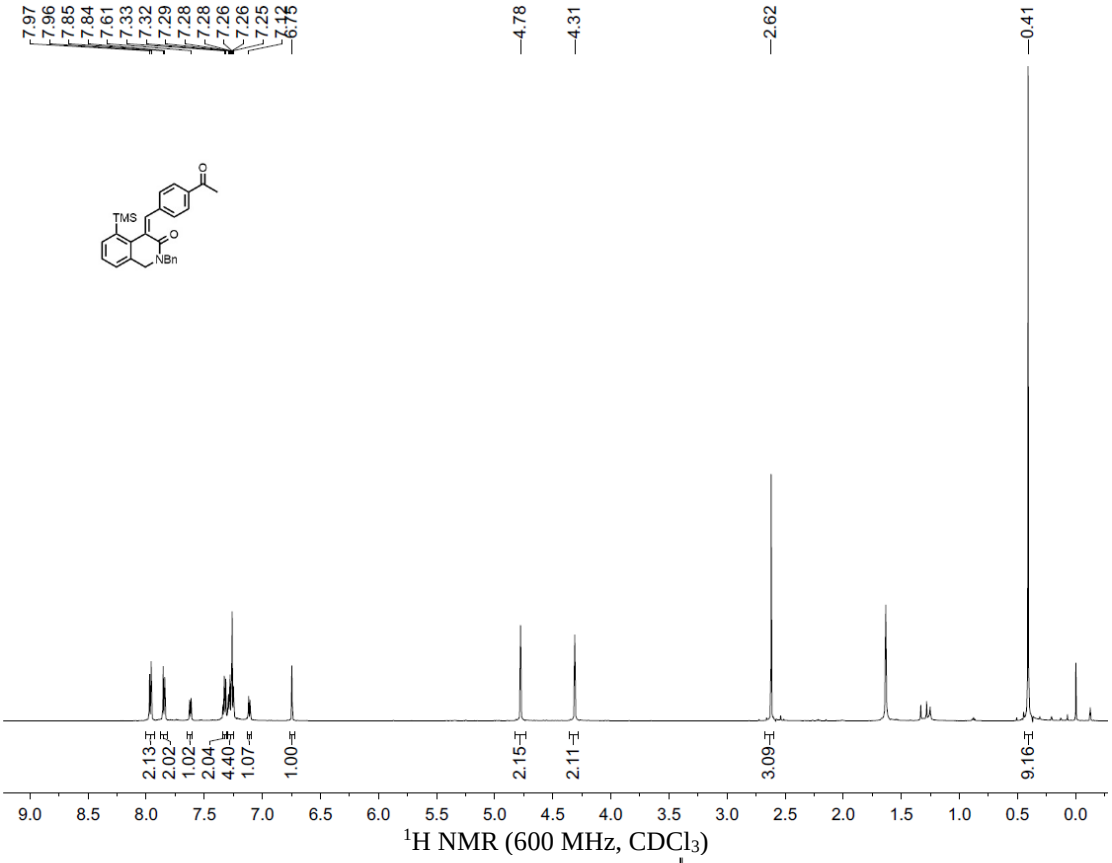
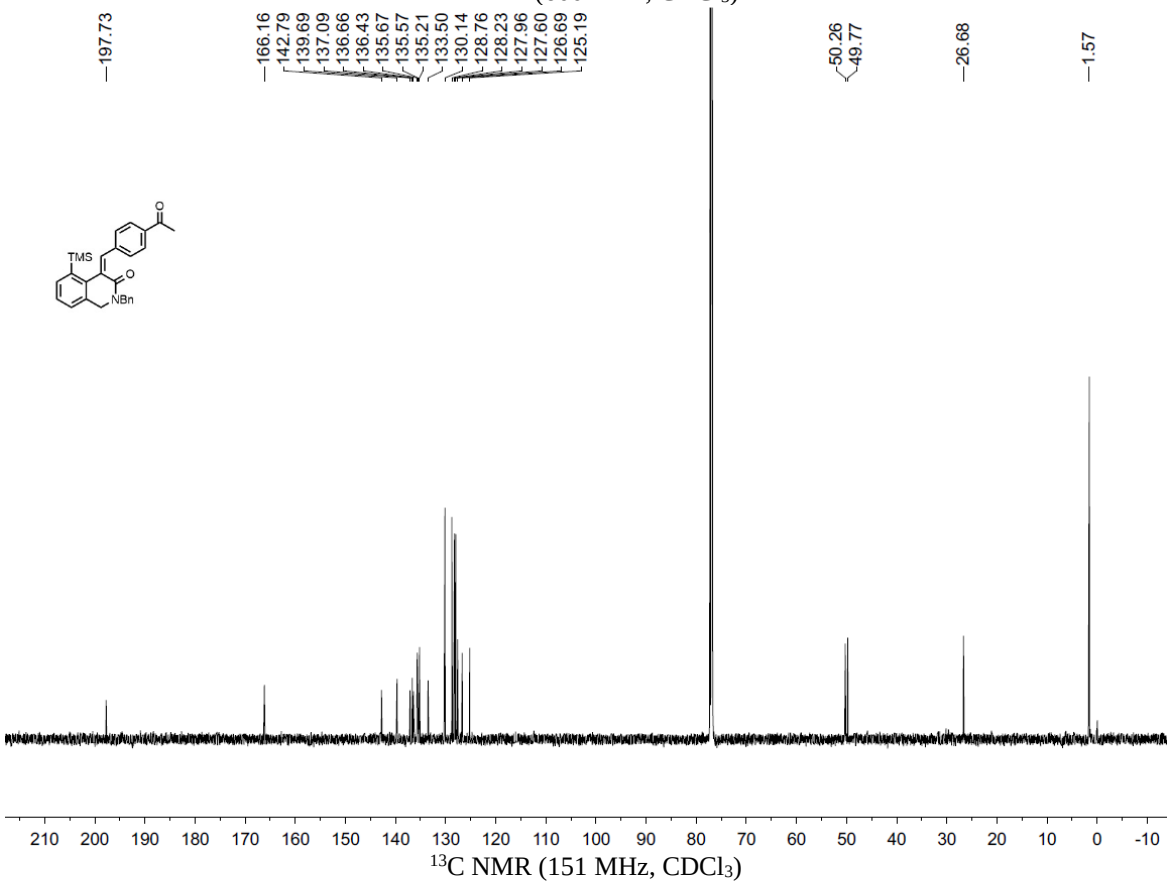
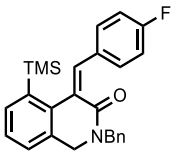


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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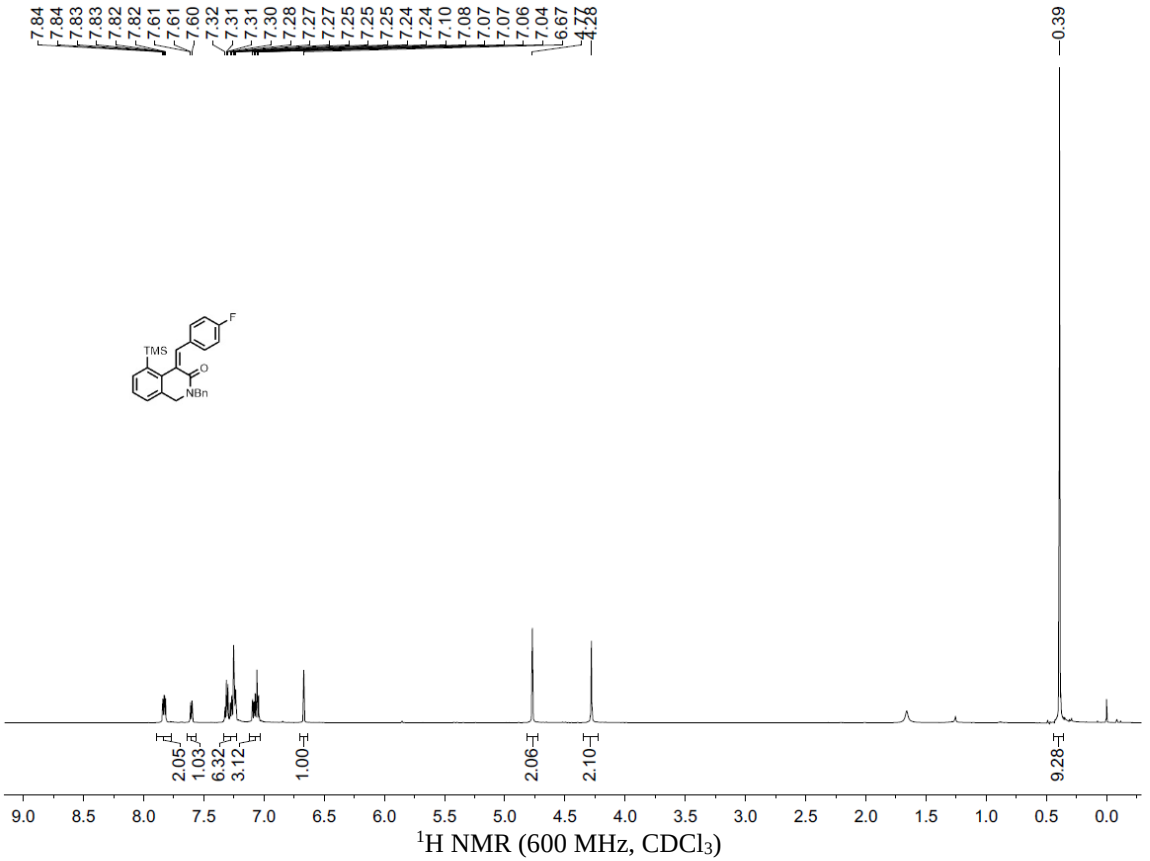
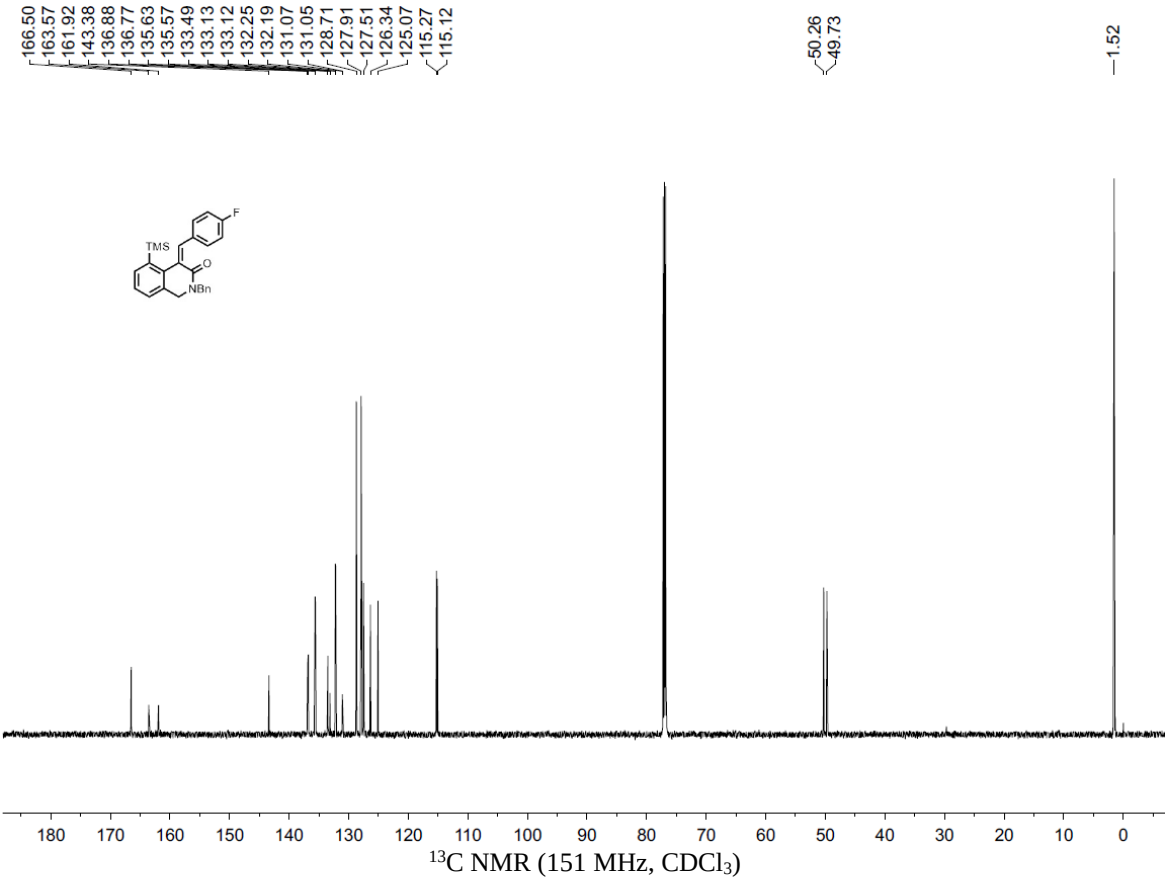


^{1}H NMR (600 MHz, $CDCl_3$)



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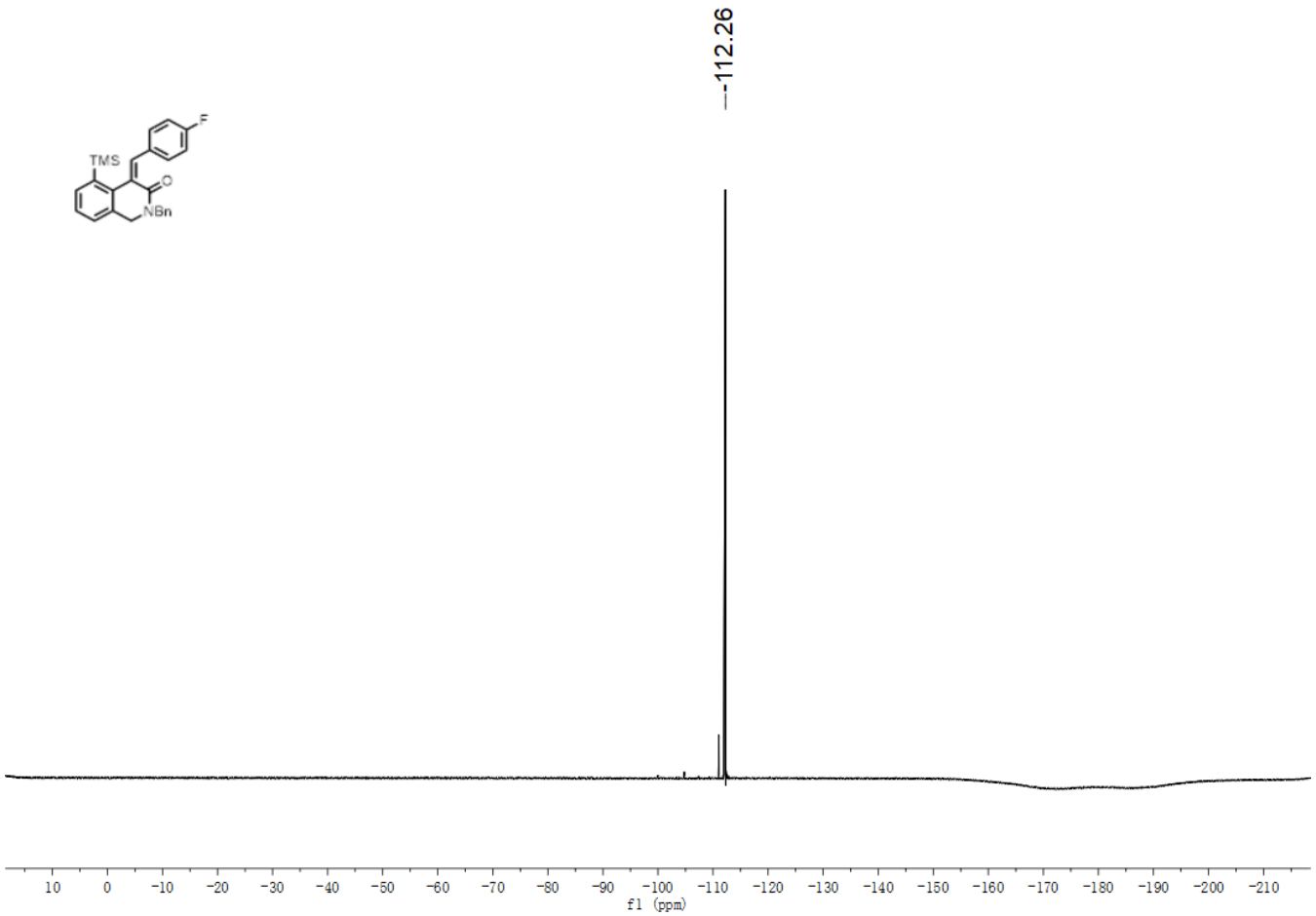
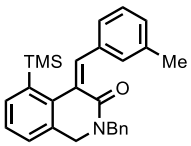


^{19}F NMR (565 MHz, $CDCl_3$)



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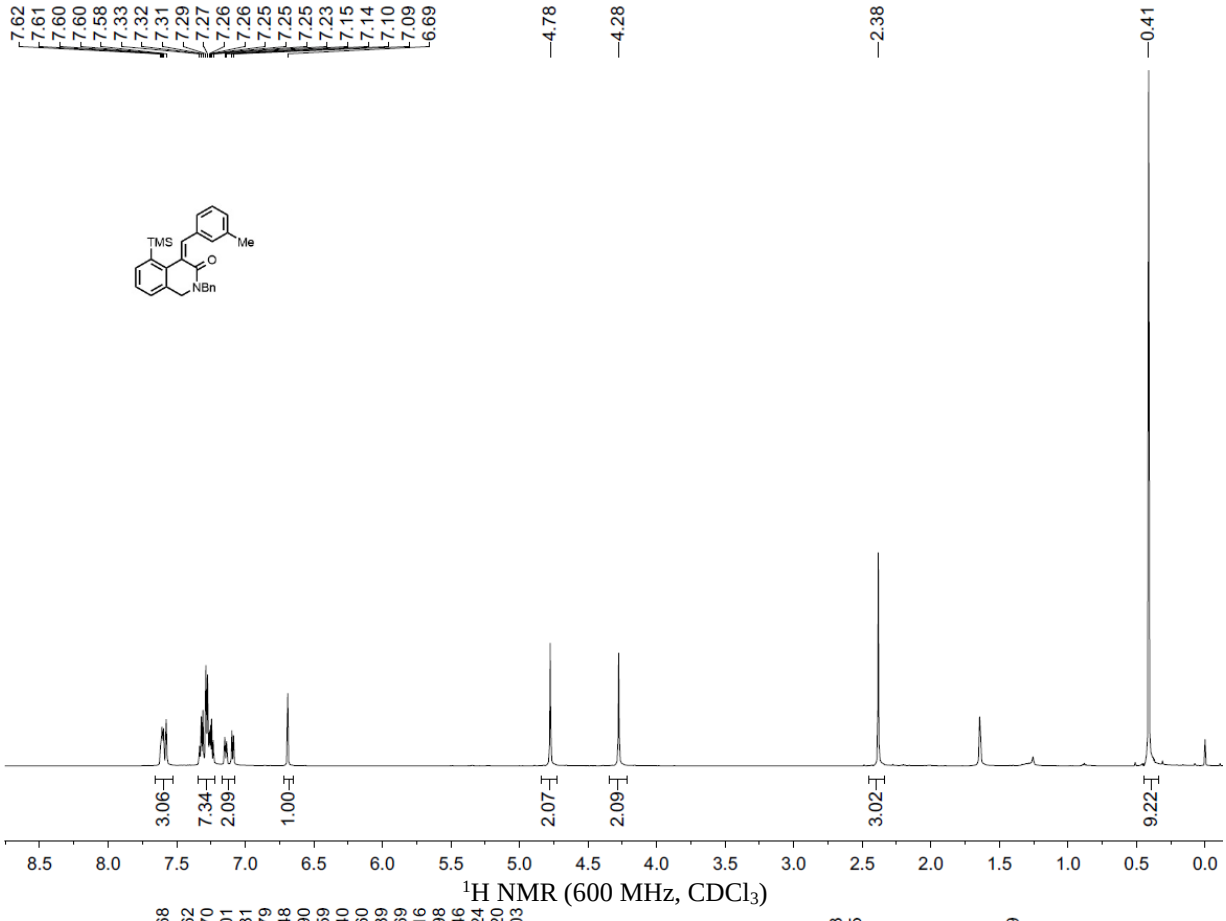
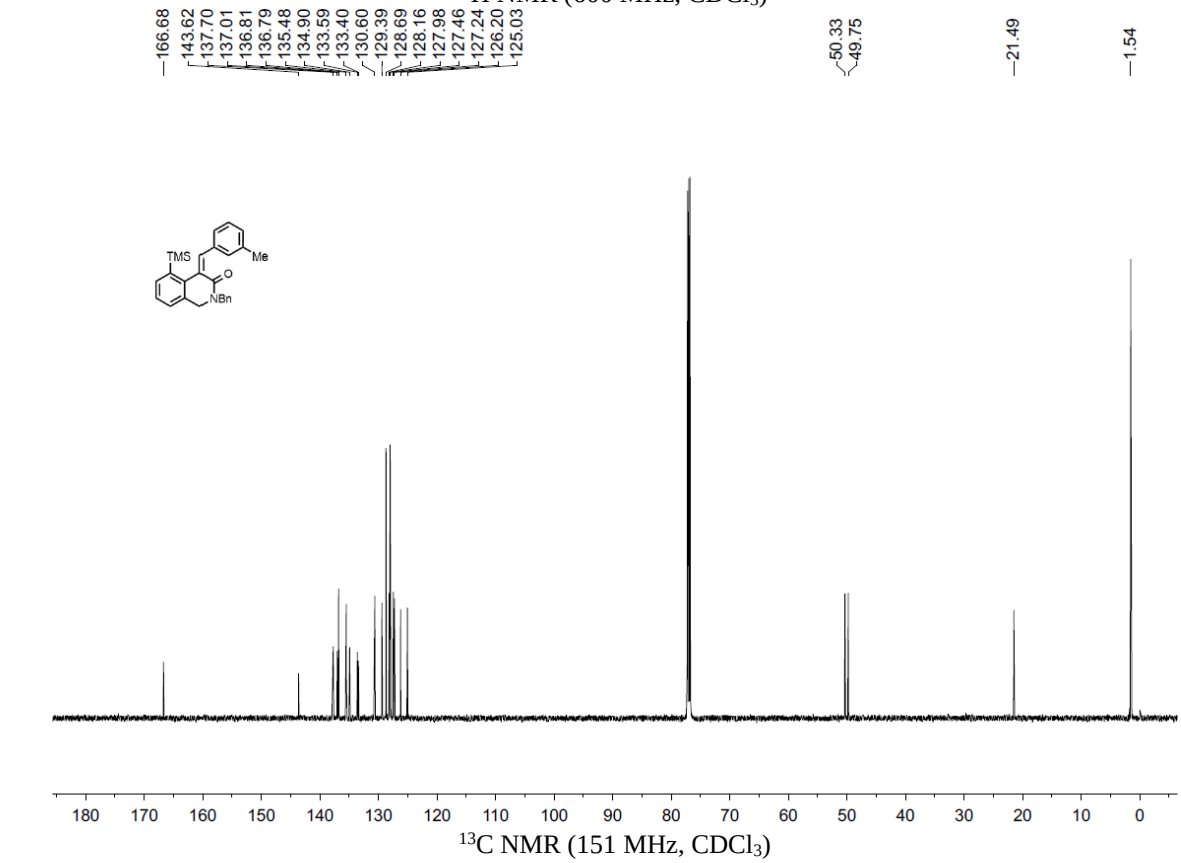
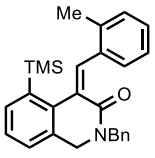


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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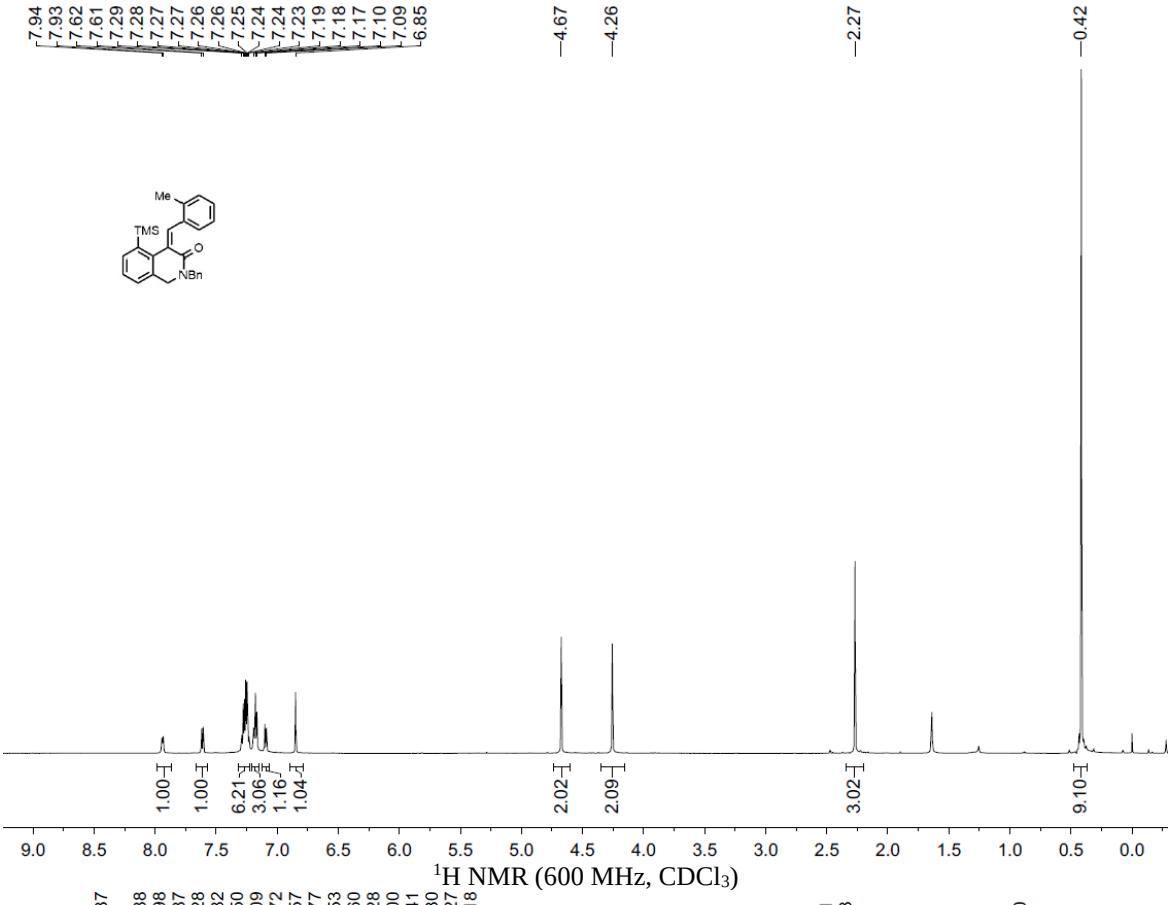
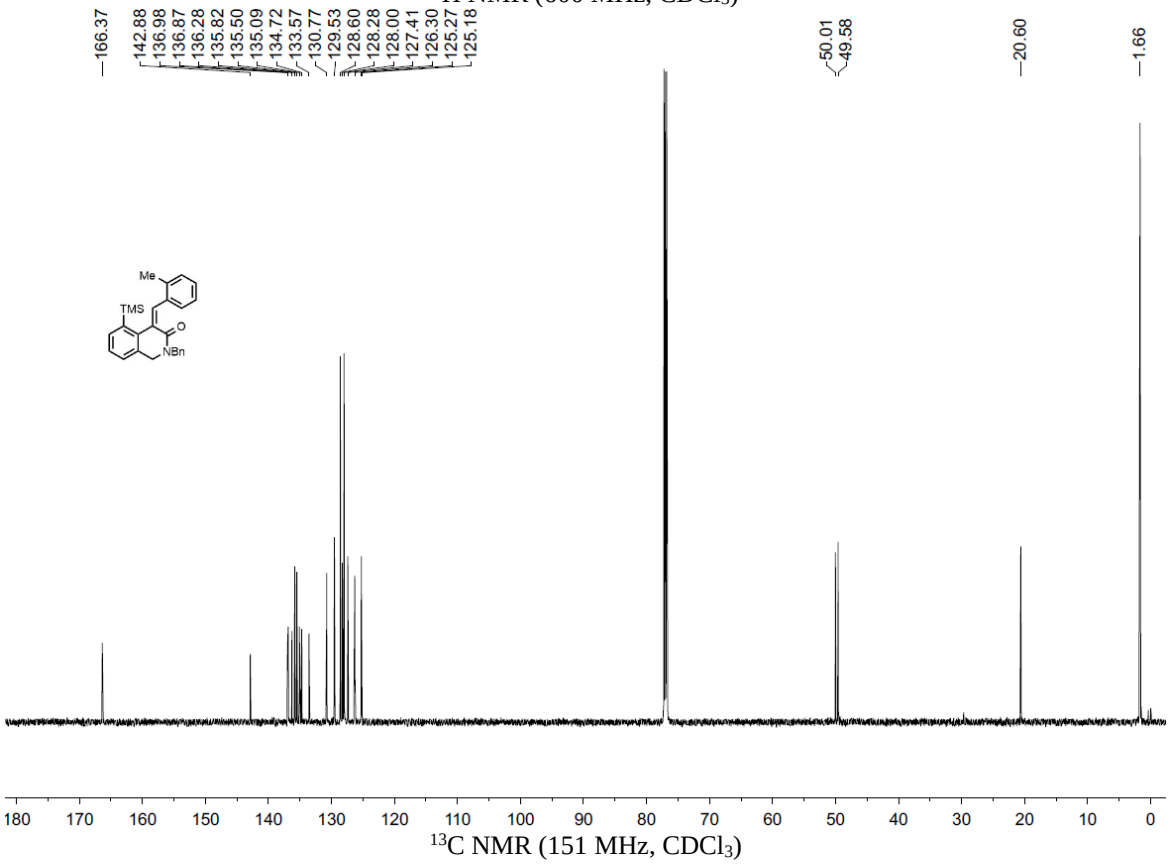
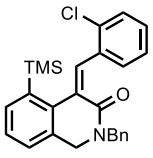


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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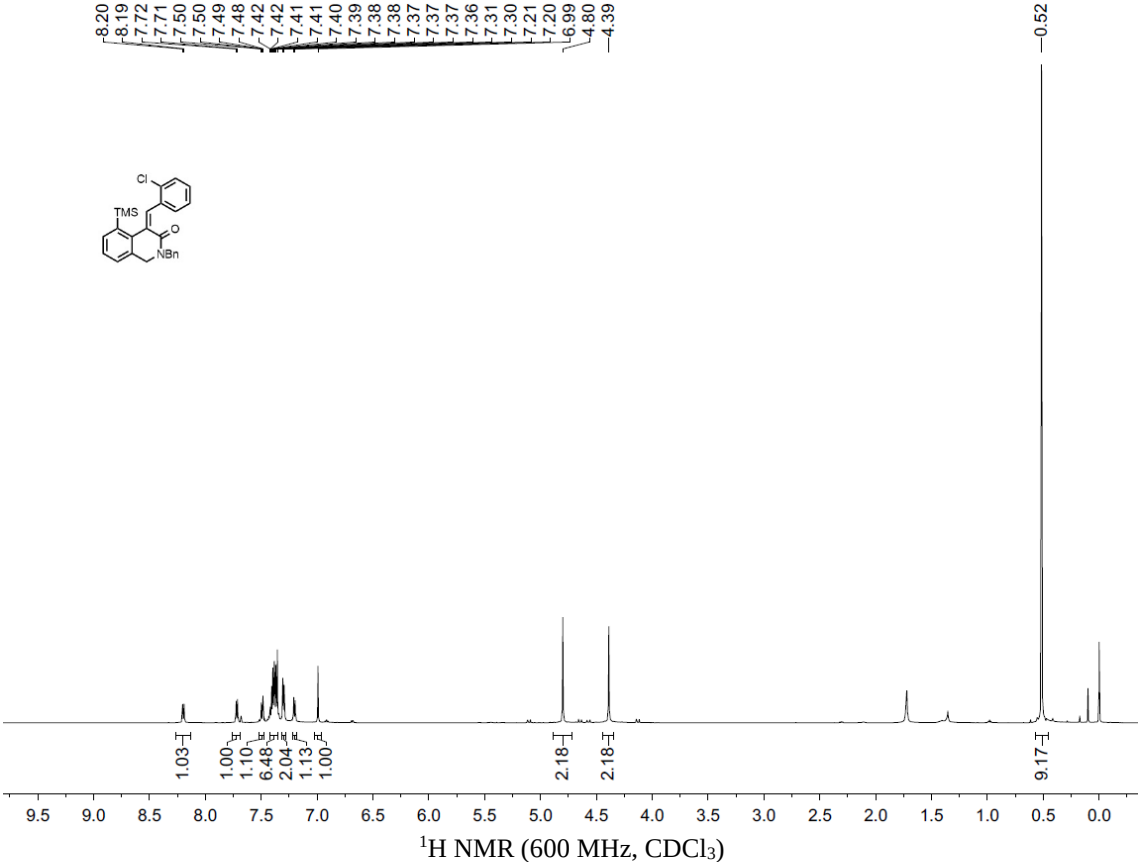
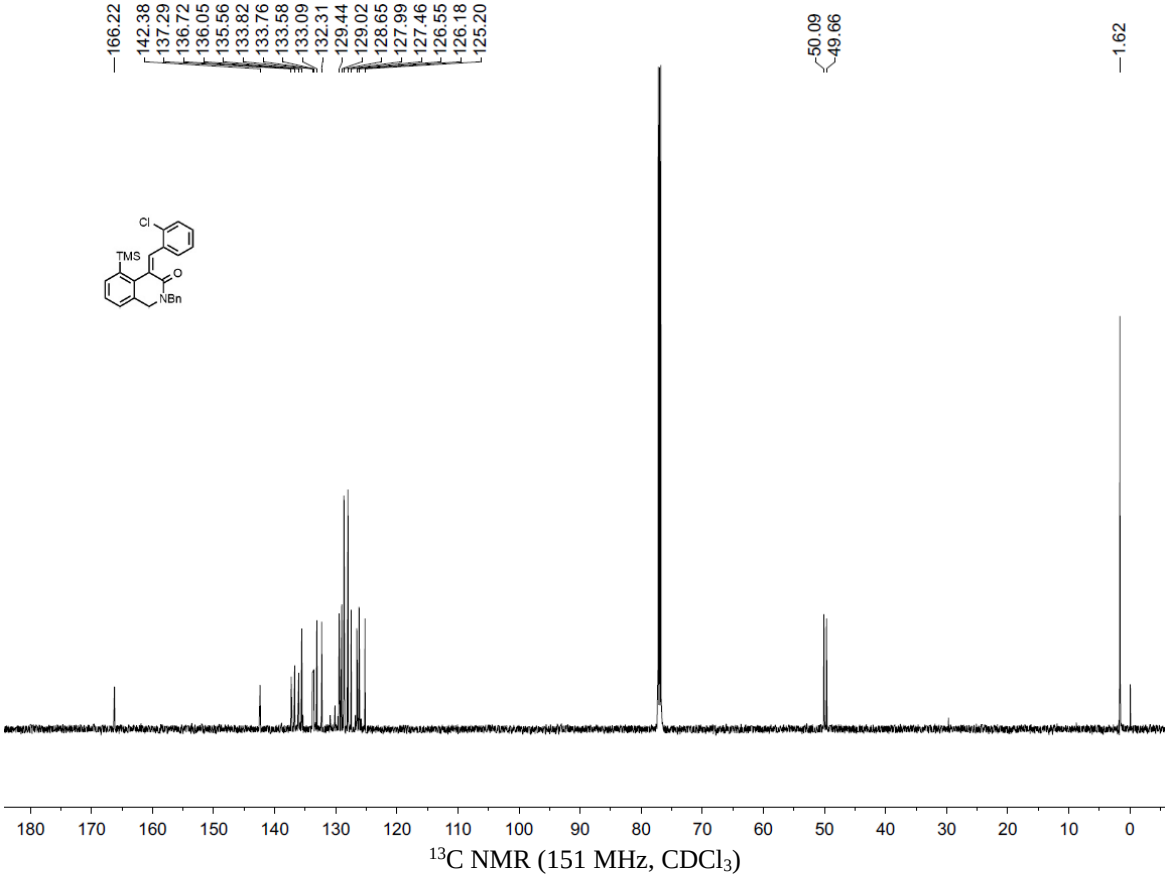
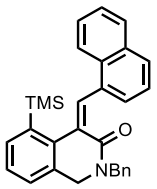


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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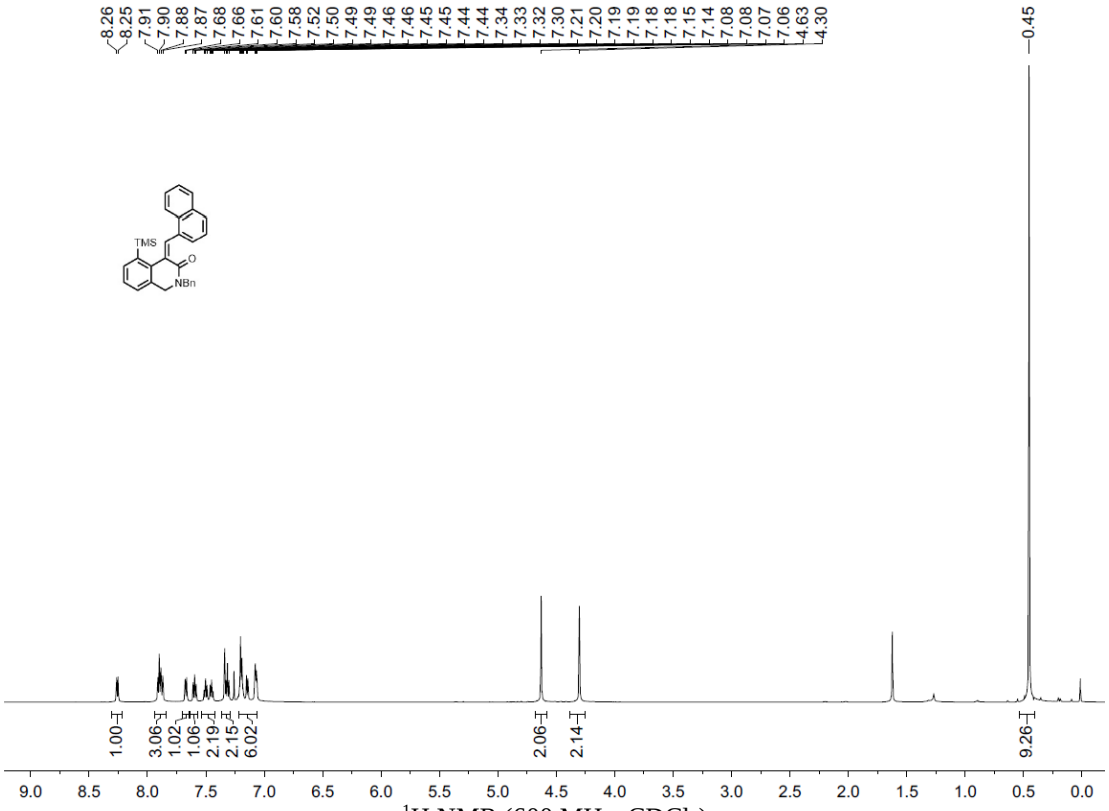
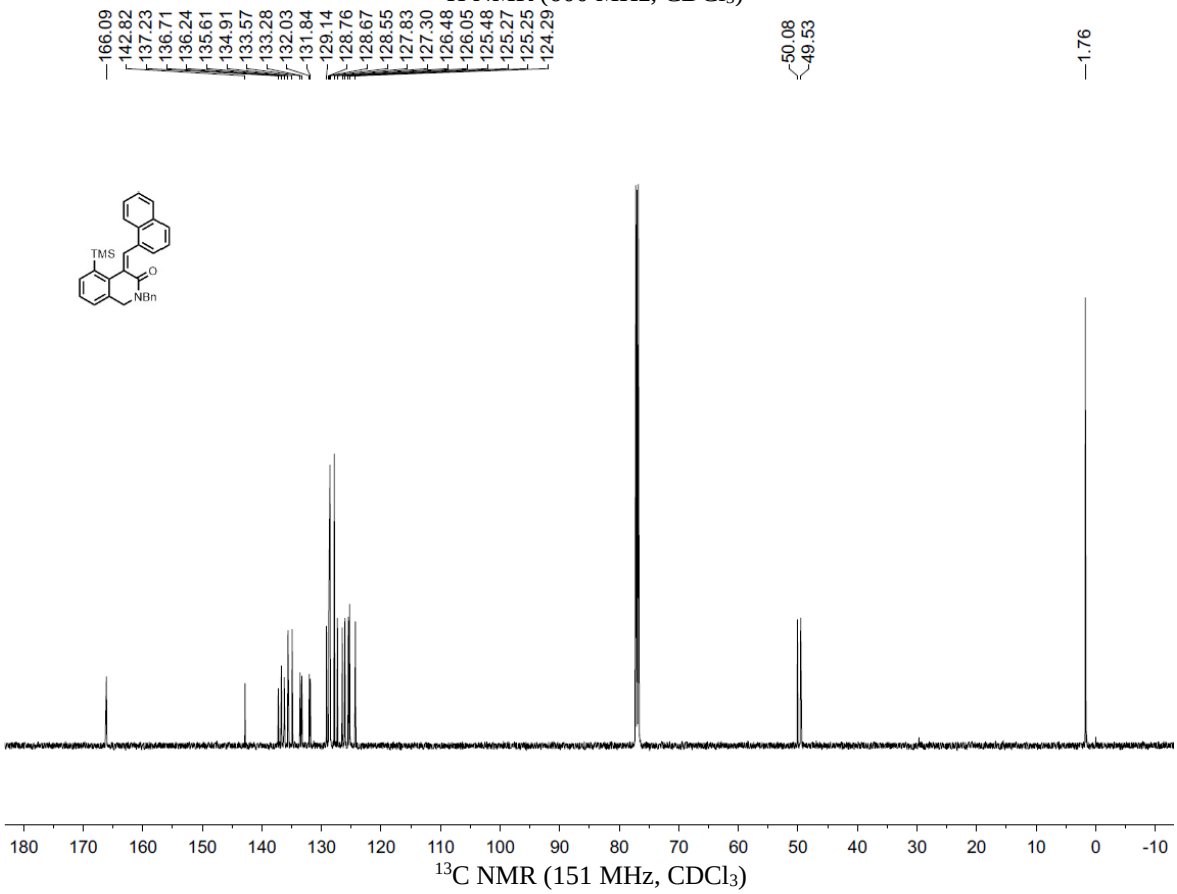
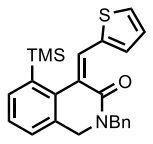


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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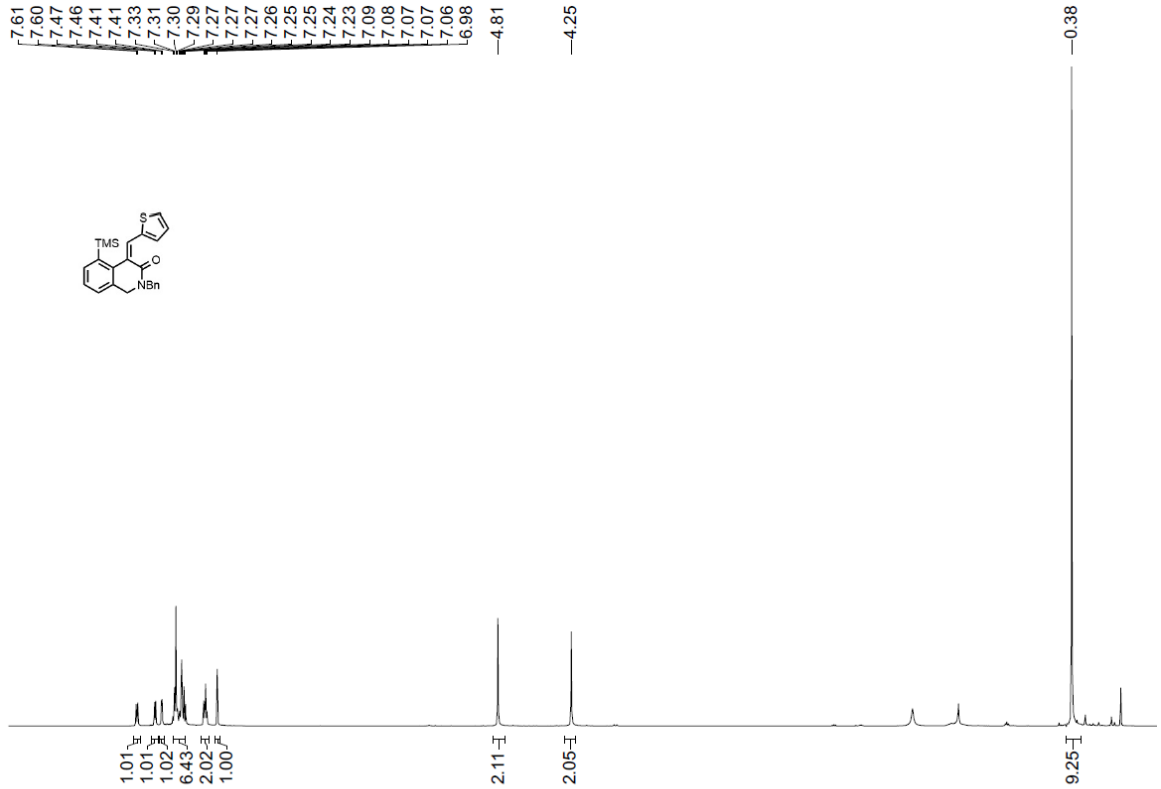
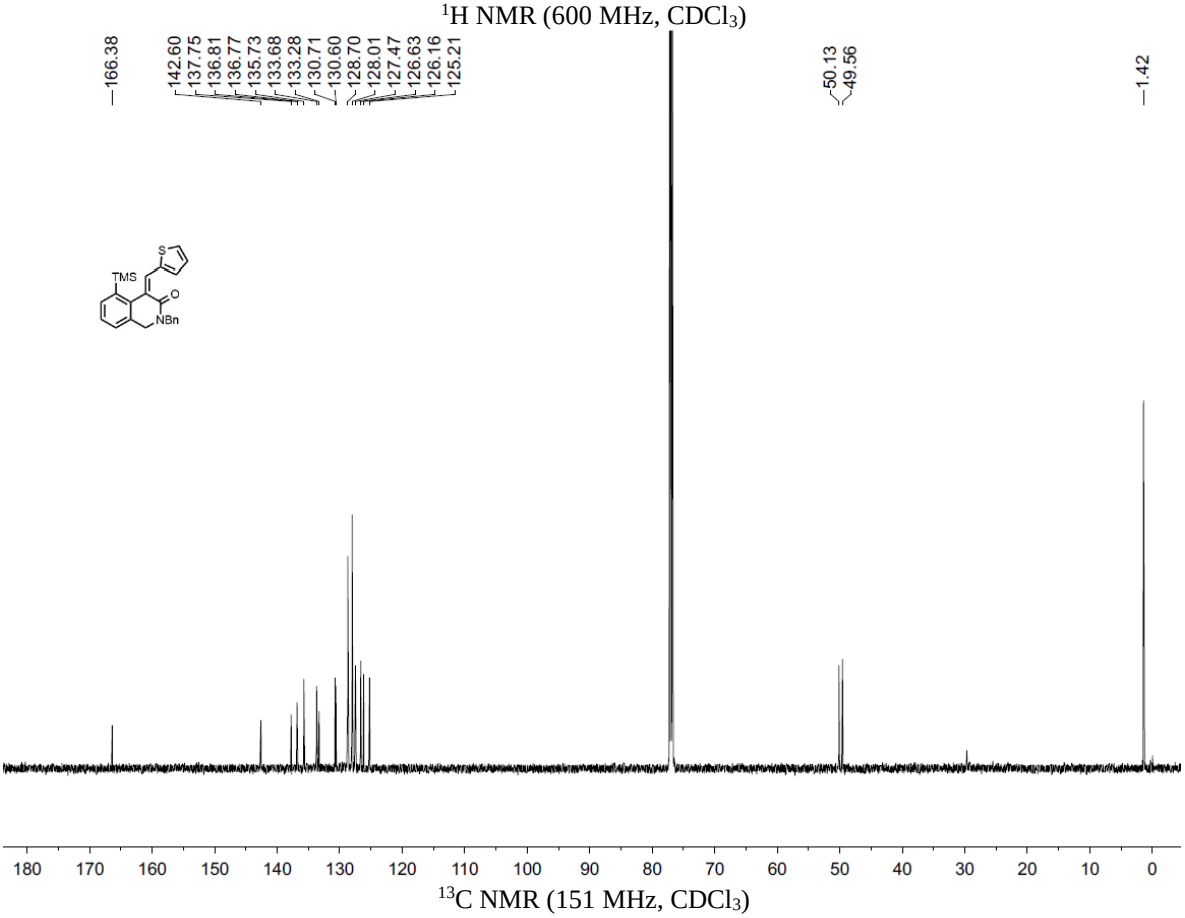
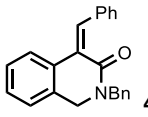


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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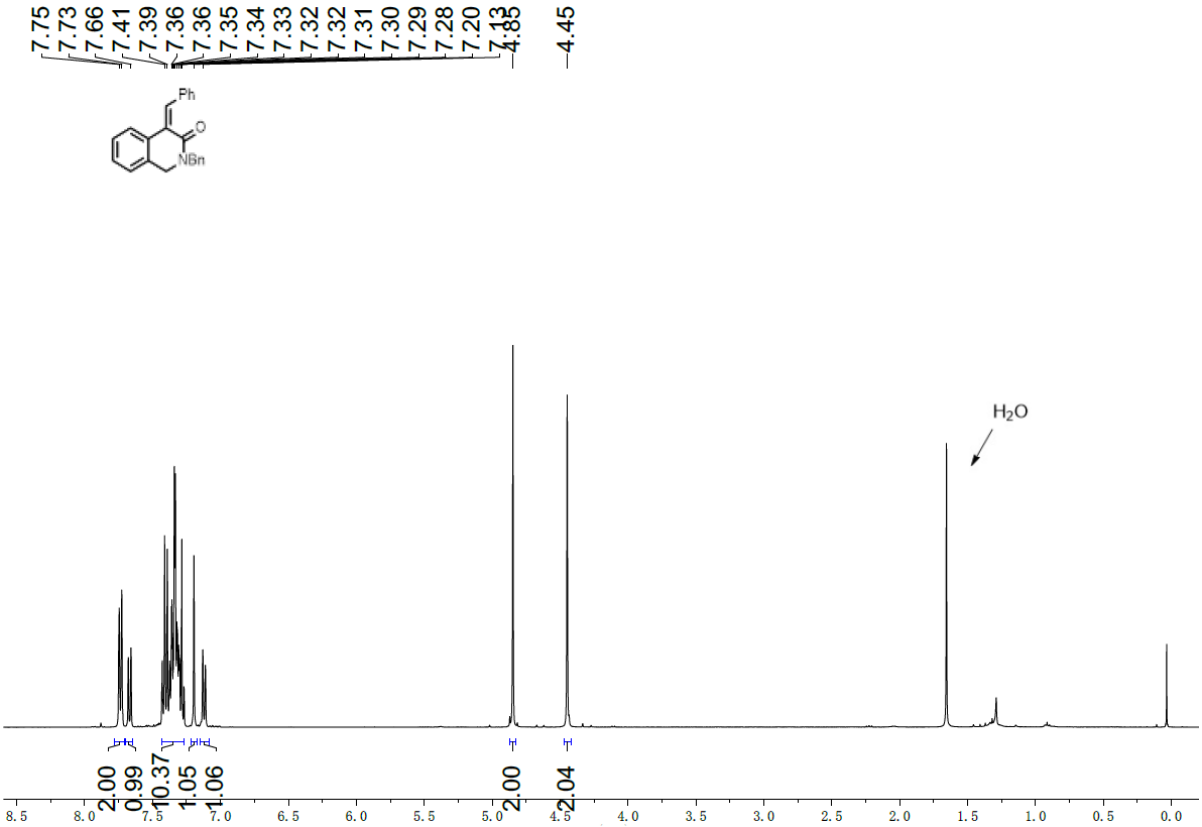
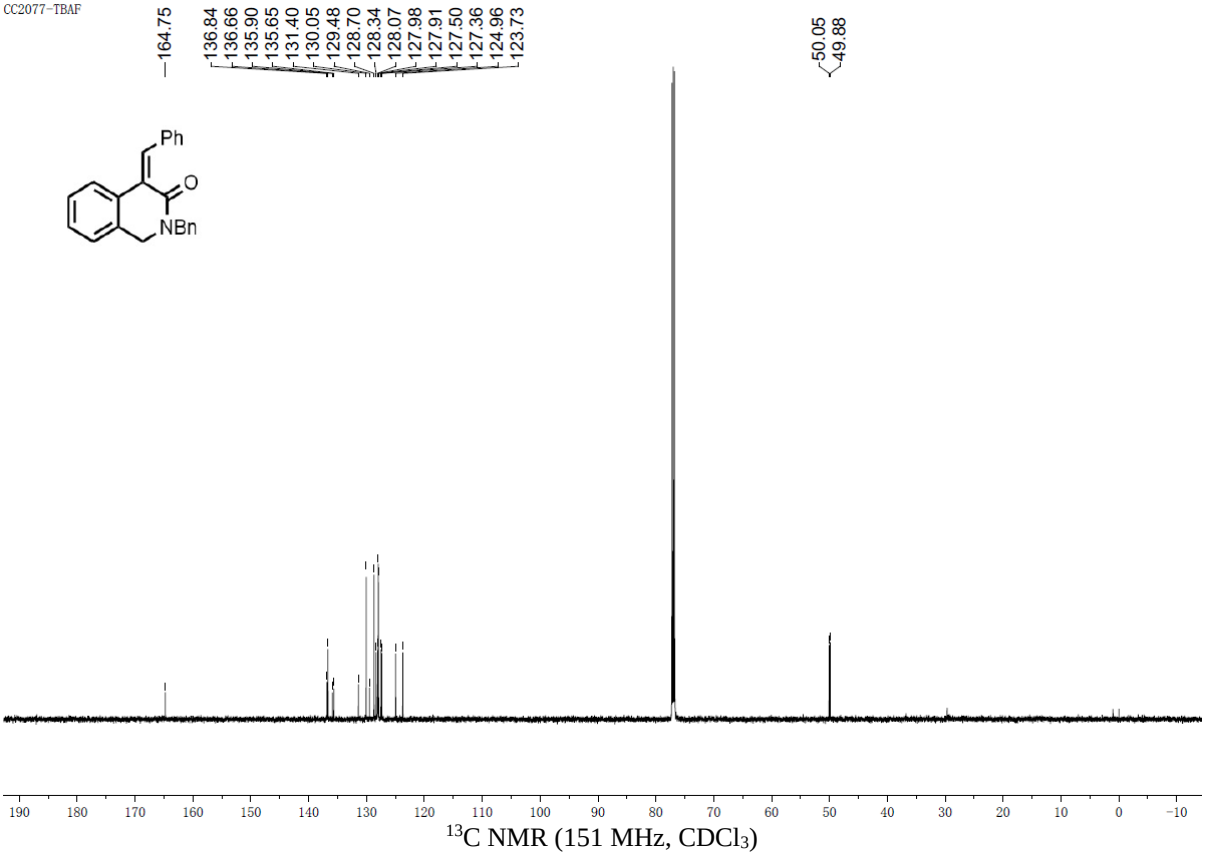
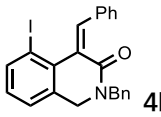


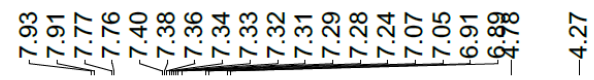
^{1}H NMR (600 MHz, $CDCl_3$)

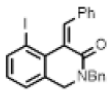


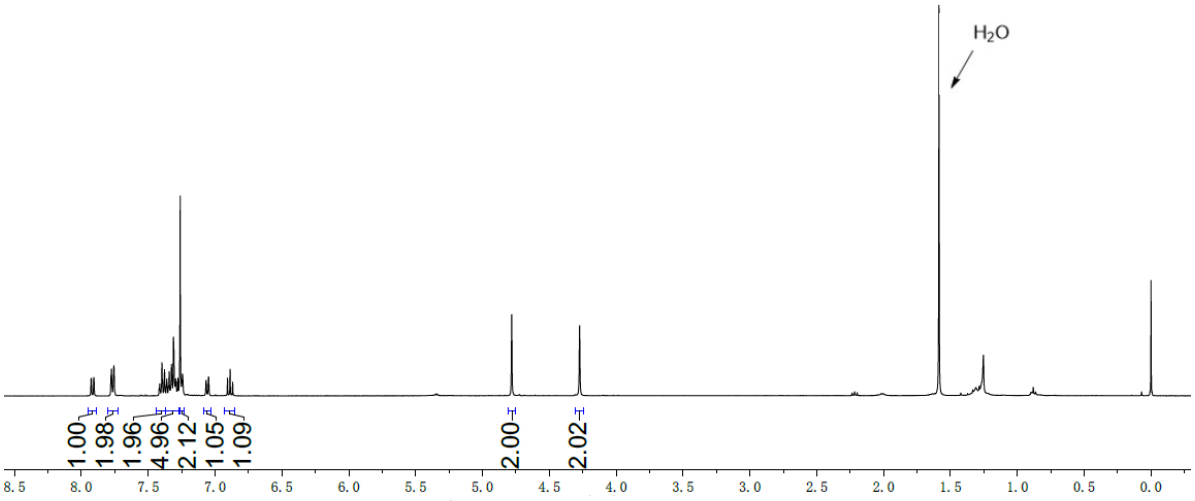
^{13}C NMR (151 MHz, $CDCl_3$)



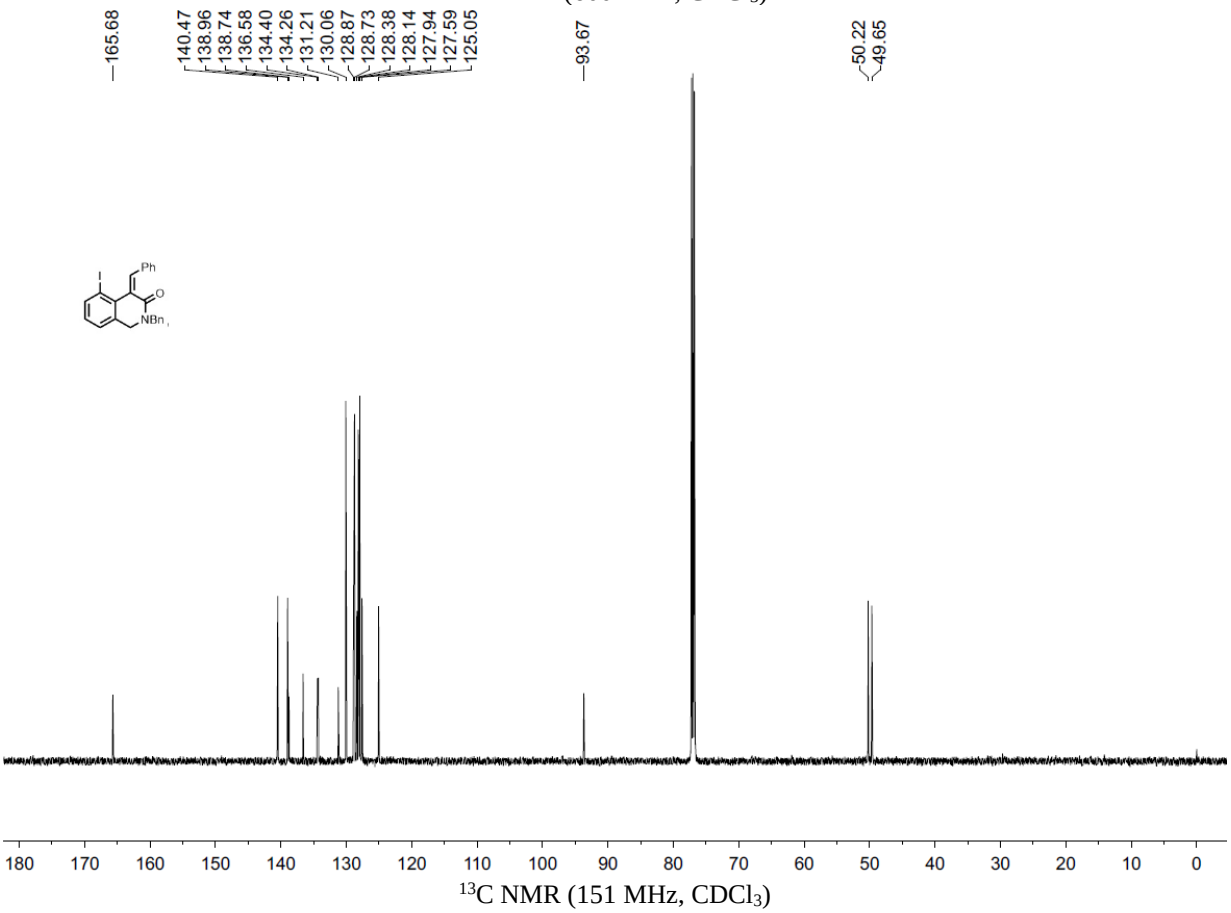
4b







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



^{13}C NMR (151 MHz, $CDCl_3$)

6. References

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[3] T. Ma, W. T. Chen, G. L. Zhang, Y. P. Yu, *J. Comb. Chem*., 2010, **12**, 488-490.