Supporting Information

BCl_3 Catalyzed Z-Selective Intramolecular Chlorocarbamoylation of Alkynes/Allenes

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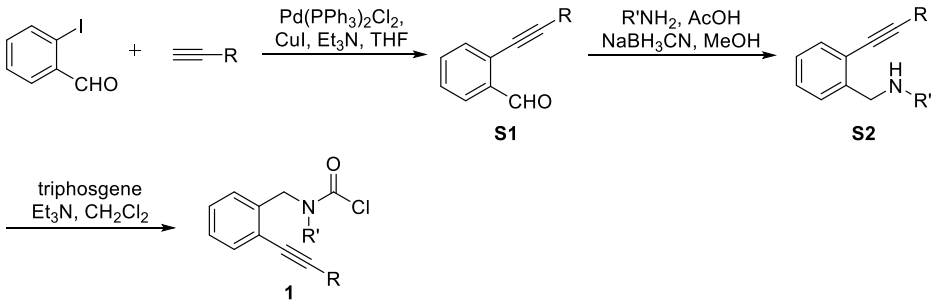
1. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed on silica gel GF254. Visualization was accomplished by irradiation with UV light at 254 nm or $KMnO_4$ stain solution. Column chromatography was performed on silica gel (200 - 300 mesh). ^1H NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz). Chemical shifts were reported in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (100 MHz) and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in parts per million (ppm) referenced to 77.16 ppm for $CDCl_3$. High resolution mass spectra (HRMS) were recorded on a waters LCT PremierxeTM (USA) (with Electron Spray Ionization as mass analyzer). Single-crystal experiments were recorded on Bruker Smart Apex II.

2. Synthesis of Substrates

2.1 General procedure for the synthesis of substrate 1

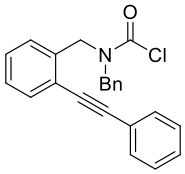


To a mixture of $Pd(PPh_3)_2Cl_2$ (5 mol %) and 2-iodobenzaldehyde (1 equiv) in THF (0.13−0.15 M) was added triethyl amine (3 equiv). After being stirred for 10 min at room temperature, terminal acetylene (1.5 equiv) and CuI (5 mol %) were added to the mixture. The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was quenched with saturated aq. NH_4Cl, extracted with EtOAc three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography.

Compound **S1** (1.1 equiv), AcOH (1.1 equiv), and $NaBH_3CN$ (1.1 equiv) were added to stirred

mixture of benzylamine (1 equiv) in MeOH (0.1 M). The mixture was stirred at room temperature for 12 h. The solution was then made alkaline with NaOH (1 N) and extracted with EtOAc. The organic layers were collected, dried over $MgSO_4$, and evaporated to dryness under reduced pressure to afford compound **S2**.

To a solution of **S2** (1 equiv) in CH_2Cl_2 was added Et_3N (2 equiv), followed by triphosgene (0.5 equiv). The resulting mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with H_2O, extracted with CH_2Cl_2 three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica gel column chromatography.



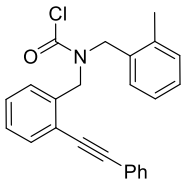
benzyl(2-(phenylethynyl)benzyl)carbamic chloride (1a)

Compound **1a** was prepared following the general procedure using 2-iodobenzaldehyde (1.8 g, 5.0 mmol) and was isolated as a pale yellow oil (1.3 g, 72% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.2 Hz, 1H), 7.31 – 7.11 (m, 13H), 4.85 (s, 1H), 4.76 (s, 1H), 4.56 (s, 1H), 4.43 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 135.8, 135.6, 134.3, 134.2, 131.6, 131.5, 130.6, 130.5, 127.9, 127.80, 127.76, 127.6, 127.50, 127.46, 127.3, 127.2, 127.1, 127.0, 126.83, 126.80, 126.1, 125.7, 122.1, 121.5, 121.4, 94.0, 93.4, 85.6, 85.3, 52.1, 50.7, 50.6, 48.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}ClNO$, 360.1155; found: 360.1159.



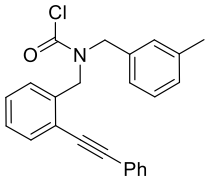
(2-methylbenzyl)(2-(phenylethynyl)benzyl)carbamic chloride (1b)

Compound **1b** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (670 mg, 60% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 1H), 7.36 – 6.93 (m, 12H), 4.82 (s, 1H), 4.80 (s, 1H), 4.56 (s, 1H), 4.51 (s, 1H), 2.09 (s, 1.5H), 1.97 (s, 1.5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.4, 136.0, 135.6, 135.5, 134.5, 132.0, 131.7, 131.6, 131.4, 130.4, 129.7, 128.0, 127.94, 127.87, 127.5, 127.4, 127.23, 127.16, 127.1, 126.9, 126.8, 126.7, 126.4, 125.5, 125.4, 125.3, 123.9, 122.2, 121.5, 121.4, 93.9, 93.2, 85.4, 85.0, 50.3, 49.9, 48.9, 48.4, 18.1, 17.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1321.



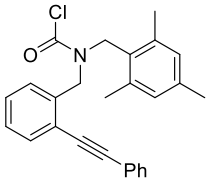
(3-methylbenzyl)(2-(phenylethynyl)benzyl)carbamic chloride (1c)

Compound **1c** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (650 mg, 58% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.34 (m, 1H), 7.33 – 7.07 (m, 8H), 7.06 – 6.99 (m, 1H), 6.99 – 6.84 (m, 3H), 4.82 (s, 1H), 4.74 (s, 1H), 4.50 (s, 1H), 4.36 (s, 1H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.74, 150.66, 138.7, 138.6, 137.1, 136.8, 135.33, 135.27, 132.7, 132.6, 131.69, 131.65, 129.4, 129.03, 128.96, 128.95, 128.85, 128.79, 128., 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.9, 126.8, 125.7, 124.2, 123.2, 122.7, 122.5, 95.1, 94.6, 86.8, 86.5, 53.2, 51.9, 51.7, 49.9, 21.4, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1309.



(2-(phenylethynyl)benzyl)(2,4,6-trimethylbenzyl)carbamic chloride (1d)

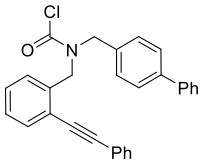
Compound **1d** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (660 mg, 55% yield) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.24 (m,

7H), 6.86 – 6.70 (m, 2H), 4.74 (s, 2H), 4.68 (s, 2H), 2.15 (s, 3H), 2.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 138.3, 138.1, 137.2, 132.5, 131.5, 129.7, 129.6, 128.9, 128.5, 128.3, 127.9, 127.5, 125.3, 122.7, 121.9, 95.0, 85.9, 49.5, 45.9, 20.8, 19.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClNO$, 402.1625; found:402.1629.



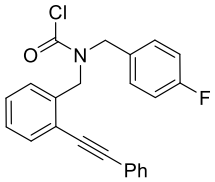
([1,1'-biphenyl]-4-ylmethyl)(2-(phenylethynyl)benzyl)carbamic chloride (1e)

Compound **1e** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (820 mg, 63% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.47 (m, 5H), 7.47 – 7.27 (m, 10H), 7.25 – 7.21 (m, 3H), 4.99 (s, 1H), 4.90 (s, 1H), 4.71 (s, 1H), 4.57 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 141.0, 140.8, 140.5, 140.4, 136.9, 136.6, 134.3, 134.2, 132.6, 132.5, 131.54, 131.51, 128.99, 128.98, 128.9, 128.79, 128.78, 128.6, 128.5, 128.4, 128.3, 127.9, 127.6, 127.50, 127.48, 127.4, 127.0, 126.8, 123.2, 122.6, 122.5, 95.0, 94.4, 86.7, 86.3, 52.8, 51.5, 51.4, 49.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{23}ClNO$, 436.1468; found: 436.1469.



(4-fluorobenzyl)(2-(phenylethynyl)benzyl)carbamic chloride (1f)

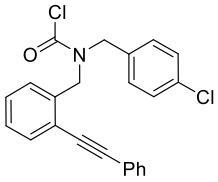
Compound **1f** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (635 mg, 56% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 12.2, 4.8 Hz, 1H), 7.42 – 7.29 (m, 8H), 7.28 – 7.19 (m, 2H), 6.93 (t, *J* = 8.6 Hz, 2H), 4.95 (s, 1H), 4.85 (s, 1H), 4.63 (s, 1H), 4.49 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.47 (dd, *J* = 246.7, 14.7 Hz), 150.7, 150.5, 136.8, 136.5, 132.7, 132.6, 131.5, 131.2 (d, *J* = 3.1 Hz), 131.0 (d, *J* = 3.1 Hz), 130.4, 130.4, 129.0, 128.9 (d, *J* = 5.7 Hz), 128.7 (d, *J* = 9.6 Hz), 128.44, 128.37, 128.2, 128.0, 126.9, 123.2, 122.5, 115.8 (d, *J* = 5.6 Hz),

115.6 (d, *J* = 5.6 Hz), 95.0, 94.4, 86.7, 86.3, 52.4, 51.5, 51.0, 49.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClFNO$, 378.1061; found: 378.1048.



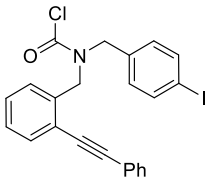
(4-chlorobenzyl)(2-(phenylethynyl)benzyl)carbamic chloride (1g)

Compound **1g** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (650 mg, 55% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 12.6, 4.9 Hz, 1H), 7.35 – 7.20 (m, 7H), 7.19 – 7.09 (m, 4H), 7.06 (d, *J* = 8.4 Hz, 1H), 4.85 (s, 1H), 4.76 (s, 1H), 4.54 (s, 1H), 4.39 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 150.6, 136.7, 136.4, 134.1, 133.9, 133.81, 133.78, 132.7, 132.6, 131.6, 129.9, 129.1, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 128.1, 127.0, 123.3, 122.6, 122.5, 95.1, 94.5, 86.7, 86.3, 52.4, 51.6, 51.0, 49.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}Cl_2NO$, 394.0765; found: 394.0768.



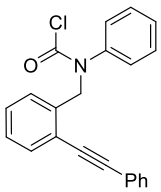
(4-iodobenzyl)(2-(phenylethynyl)benzyl)carbamic chloride (1h)

Compound **1h** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a yellow oil (725 mg, 50% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 9.5 Hz, 3H), 7.27 (ddd, *J* = 9.9, 8.2, 5.3 Hz, 7H), 7.14 (d, *J* = 3.6 Hz, 1H), 6.89 (dd, *J* = 19.4, 8.0 Hz, 2H), 4.84 (s, 1H), 4.75 (s, 1H), 4.50 (s, 1H), 4.36 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 149.5, 136.9, 135.6, 135.3, 133.9, 131.6, 131.5, 130.5, 129.3, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 127.2, 127.0, 126.0, 122.2, 121.6, 121.4, 94.0, 93.4, 92.7, 92.3, 85.6, 85.2, 51.5, 50.5, 50.0, 48.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClINO$, 486.0122; found: 486.0128.



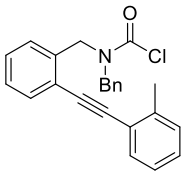
phenyl(2-(phenylethynyl)benzyl)carbamic chloride (1i)

Compound **1i** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (675 mg, 65% yield) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 3H), 7.27 – 7.18 (m, 4H), 7.14 (dd, *J* = 5.6, 3.7 Hz, 5H), 7.04 – 6.86 (m, 2H), 5.09 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 141.3, 136.9, 132.6, 131.7, 129.7, 129.3, 128.7, 128.6, 128.4, 128.1, 123.4, 122.9, 94.3, 86.7, 54.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}ClNO$, 346.0999; found: 346.1012.



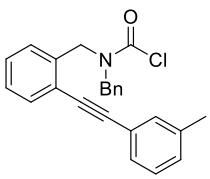
benzyl(2-(o-tolylethynyl)benzyl)carbamic chloride (1j)

Compound **1j** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (730 mg, 65% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.37 (m, 1H), 7.30 – 6.94 (m, 12H), 4.83 (s, 1H), 4.75 (s, 1H), 4.55 (s, 1H), 4.43 (s, 1H), 2.18 (s, 1.5H), 2.14 (s, 1.5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 149.5, 138.94, 138.91, 135.6, 135.4, 134.2, 134.1, 131.5, 131.4, 130.92, 130.89, 128.44, 128.36, 127.8, 127.7, 127.6, 127.5, 127.4, 127.1, 127.0, 126.9, 126.8, 126.7, 126.1, 125.2, 124.6, 124.5, 122.1, 121.45, 121.37, 93.1, 92.5, 89.4, 89.1, 52.3, 50.9, 50.6, 48.8, 19.7, 19.6.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1314.



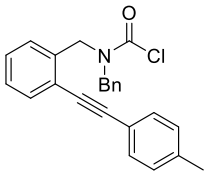
benzyl(2-(m-tolylethynyl)benzyl)carbamic chloride (1k)

Compound **1k** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (700 mg, 62% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 1H), 7.41 – 7.22 (m, 8H), 7.20 – 7.02 (m, 4H), 4.94 (s, 1H), 4.86 (s, 1H), 4.66 (s, 1H), 4.52 (s, 1H), 2.33 (s, 1.5H), 2.29 (s, 1.5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 138.1, 138.0, 137.0, 136.7, 135.44, 135.37, 132.7, 132.6, 132.2, 129.64, 129.56, 129.0, 128.91, 128.89, 128.84, 128.77, 128.7, 128.6, 128.35, 128.28, 128.2, 127.94, 127.92, 127.2, 126.8, 123.3, 122.6, 122.5, 95.3, 94.8, 86.4, 86.1, 53.2, 51.9, 51.7, 49.9, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1324.



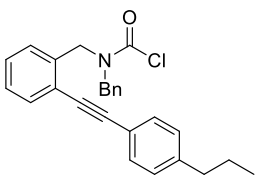
benzyl(2-(p-tolylethynyl)benzyl)carbamic chloride (1l)

Compound **1l** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (750 mg, 67% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 1H), 7.38 – 7.13 (m, 10H), 7.06 (dd, *J* = 11.2, 8.1 Hz, 2H), 4.91 (s, 1H), 4.83 (s, 1H), 4.61 (s, 1H), 4.48 (s, 1H), 2.30 (s, 1.5H), 2.30 (s, 1.5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 137.7, 137.6, 135.7, 135.4, 134.3, 134.2, 131.5, 131.4, 130.42, 130.37, 128.04, 127.97, 127.74, 127.70, 127.6, 127.4, 127.0, 126.9, 126.8, 126.7, 126.0, 125.7, 122.2, 121.6, 118.4, 94.2, 93.7, 85.0, 84.7, 52.0, 50.7, 50.5, 48.8, 20.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1318.



benzyl(2-((4-propylphenyl)ethynyl)benzyl)carbamic chloride (1m)

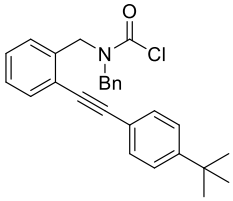
Compound **1m** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg,

3.0 mmol) and was isolated as a pale yellow oil (760 mg, 63% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 1H), 7.32 – 7.07 (m, 10H), 7.01 (dd, *J* = 12.3, 8.1 Hz, 2H), 4.85 (s, 1H), 4.76 (s, 1H), 4.57 (s, 1H), 4.43 (s, 1H), 2.55 – 2.42 (m, 2H), 1.62 – 1.45 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 149.6, 142.6, 142.5, 135.7, 135.5, 134.32, 134.25, 131.5, 131.4, 130.5, 130.4, 127.79, 127.76, 127.73, 127.68, 127.5, 127.4, 127.0, 126.8, 126.1, 125.6, 122.3, 121.6, 118.7, 94.3, 93.1, 85.1, 84.7, 52.1, 50.8, 50.6, 48.9, 36.9, 23.3, 12.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClNO$, 402.1625; found:402.1628.



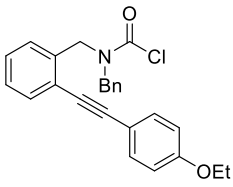
benzyl(2-((4-(tert-butyl)phenyl)ethynyl)benzyl)carbamic chloride (1n)

Compound **1n** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (685 mg, 55% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 1H), 7.32 – 7.05 (m, 12H), 4.84 (s, 1H), 4.75 (s, 1H), 4.56 (s, 1H), 4.42 (s, 1H), 1.21 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 150.8, 149.6, 149.5, 135.7, 135.5, 134.3, 134.2, 131.6, 131.5, 130.32, 130.28, 127.8, 127.75, 127.70, 127.66, 127.5, 127.0, 126.8, 126.1, 125.6, 124.3, 124.2, 122.3, 121.6, 118.5, 94.2, 93.7, 85.0, 84.7, 52.1, 50.8, 50.7, 48.9, 33.7, 30.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}ClNO$, 416.1781; found:416.1789.



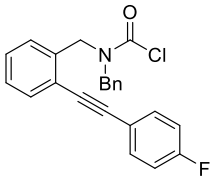
benzyl(2-((4-ethoxyphenyl)ethynyl)benzyl)carbamic chloride (1o)

Compound **1o** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (600 mg, 50% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 1H), 7.24 – 6.98 (m, 10H), 6.63 (dd, *J* = 10.9, 8.8 Hz, 2H), 4.77 (s, 1H), 4.68 (s, 1H), 4.47 (s, 1H), 4.34 (s, 1H), 3.81 (q, *J* = 6.8 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 159.3, 150.7, 150.6, 136.6, 136.4, 135.43, 135.37, 133.2, 133.1, 132.5, 132.4, 128.90, 128.86, 128.6, 128.13, 128.10, 127.90, 127.88, 127.2, 126.8, 123.6, 122.9, 114.6, 114.5, 95.3, 94.7, 85.5, 85.1, 63.6, 63.6, 53.1, 51.8, 51.7, 50.0, 14.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}ClNO_2$, 404.1417; found: 404.1429.



benzyl(2-((4-fluorophenyl)ethynyl)benzyl)carbamic chloride (1p)

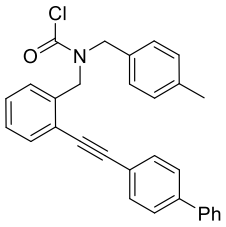
Compound **1p** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (655 mg, 58% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 6.9 Hz, 1H), 7.31 – 7.15 (m, 10H), 6.97 – 6.85 (m, 2H), 4.90 (s, 1H), 4.80 (s, 1H), 4.58 (s, 1H), 4.47 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (dd, *J* = 250.2, 4.9 Hz), 150.5, 137.0, 136.8, 135.5, 135.4, 133.8 (d, *J* = 7.9 Hz), 133.7 (d, *J* = 7.6 Hz), 132.8, 132.7, 129.2, 129.1, 129.02, 128.95, 128.5, 128.3 (d, *J* = 14.4 Hz), 128.0 (d, *J* = 11.7 Hz), 127.2, 123.1, 122.4, 118.92, 118.89, 115.9 (d, *J* = 9.0 Hz), 115.7 (d, *J* = 9.0 Hz), 94.1, 93.6, 86.7, 86.4, 53.0, 51.8, 51.8, 49.9.

^{19}F NMR (377 MHz, $CDCl_3$) δ -109.55, -109.72.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClFNO$, 378.1061; found: 378.1079.



(2-([1,1'-biphenyl]-4-ylethynyl)benzyl)(4-methylbenzyl)carbamic chloride (1q)

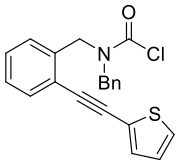
Compound **1q** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (860 mg, 64% yield, a mixture of two isomers 1：

1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.39 (m, 5H), 7.39 – 7.31 (m, 3H), 7.30 – 7.19 (m, 5H), 7.14 – 7.02 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 4.85 (s, 1H), 4.77 (s, 1H), 4.53 (s, 1H), 4.40 (s, 1H), 2.20 (s, 1.5H), 2.20 (s, 1.5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 141.4, 141.3, 140.31, 140.27, 137.9, 137.7, 137.0, 136.8, 132.7, 132.6, 132.4, 132.2, 132.13, 132.08, 129.60, 129.57, 129.0, 128.9, 128.7, 128.1, 127.9, 127.84, 127.80, 127.2, 127.1, 127.0, 126.8, 123.2, 122.5, 121.6, 95.0, 94.4, 87.5, 87.1, 52.9, 51.6, 51.5, 49.7, 21.22, 21.20.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{25}ClNO$, 450.1625; found: 450.1629.



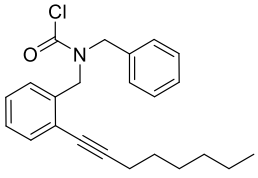
benzyl(2-(thiophen-2-ylethynyl)benzyl)carbamic chloride (1r)

Compound **1r** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (635 mg, 58% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 1H), 7.41 – 7.21 (m, 9H), 7.15 (dd, *J* = 22.8, 3.0 Hz, 1H), 7.03 – 6.95 (m, 1H), 4.91 (s, 1H), 4.81 (s, 1H), 4.66 (s, 1H), 4.52 (s, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 150.6, 136.8, 136.5, 135.3, 135.2, 132.6, 132.51, 132.45, 132.4, 129.1, 129.0, 128.94, 128.86, 128.8, 128.6, 128.2, 127.9, 127.84, 127.78, 127.3, 127.21, 127.17, 126.9, 122.8, 122.6, 122.1, 90.4, 90.0, 88.2, 87.7, 53.3, 51.9, 51.7, 50.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}ClNOS$, 366.0719; found: 366.0727.



benzyl(2-(oct-1-yn-1-yl)benzyl)carbamic chloride (1s)

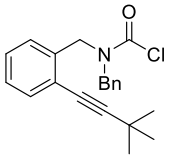
Compound **1s** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (630 mg, 57% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.08 (m, 9H), 4.75 (s, 1H), 4.67 (s, 1H), 4.53 (s, 1H), 4.40 (s,

1H), 2.24 (t, *J* = 7.1 Hz, 1H), 2.17 (t, *J* = 7.1 Hz, 1H), 1.45 – 1.30 (m, 2H), 1.29 – 1.11 (m, 6H), 0.79 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 150.5, 136.8, 136.5, 135.5, 132.6, 132.5, 128.79, 128.76, 128.5, 128.12, 128.08, 127.94, 127.88, 127.7, 127.1, 126.5, 124.0, 123.3, 96.6, 96.1, 78.0, 77.7, 53.1, 51.84, 51.78, 50.0, 31.3, 28.7, 28.6, 28.6, 22.6, 19.6, 19.5, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{27}ClNO$, 368.1781; found: 368.1779.



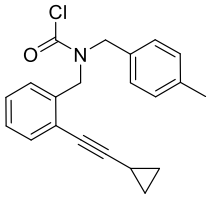
benzyl(2-(3,3-dimethylbut-1-yn-1-yl)benzyl)carbamic chloride (1t)

Compound **1t** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (610 mg, 60% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 9H), 4.84 (s, 1H), 4.78 (s, 1H), 4.62 (s, 1H), 4.49 (s, 1H), 1.22 (s, 4.5H), 1.16 (s, 4.5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 150.6, 136.4, 136.2, 135.4, 132.5, 132.4, 128.80, 128.75, 128.5, 128.1, 128.0, 127.81, 127.77, 127.6, 127.0, 126.1, 123.8, 123.1, 104.6, 104.0, 76.3, 76.1, 53.0, 51.7, 51.6, 50.0, 30.8, 30.7, 28.1, 28.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}ClNO$, 340.1468; found: 340.1476.



(2-(cyclopropylethynyl)benzyl)(4-methylbenzyl)carbamic chloride (1u)

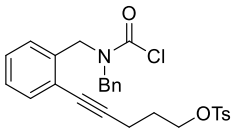
Compound **1u** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (600 mg, 60% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 1H), 7.30 – 7.19 (m, 3H), 7.19 – 7.10 (m, 4H), 4.79 (s, 1H), 4.70 (s, 1H), 4.56 (s, 1H), 4.43 (s, 1H), 2.35 (s, 1.5H), 2.34 (s, 1.5H), 1.45 – 1.29 (m, 1H), 0.91 – 0.75 (m, 2H), 0.74 – 0.59 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 150.1, 137.6, 137.4, 136.6, 136.4, 132.4, 132.3, 132.2,

132.1, 129.2, 129.1, 128.4, 128.3, 127.8, 127.7, 127.6, 127.4, 127.0, 126.3, 123.6, 122.9, 99.2, 98.7, 73.0, 72.7, 52.5, 51.3, 51.2, 49.6, 20.92, 20.88, 8.5, 8.4, 0.02, 0.00.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}ClNO$, 338.1312; found: 338.1315.



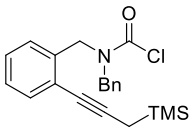
5-(2-((benzyl(chlorocarbonyl)amino)methyl)phenyl)pent-4-yn-1-yl 4-methylbenzenesulfonate (1v)

Compound **1v** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (965 mg, 65% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.69 (m, 2H), 7.38 – 7.27 (m, 8H), 7.25 – 7.18 (m, 3H), 4.77 (s, 1H), 4.66 (s, 1H), 4.58 (s, 1H), 4.47 (s, 1H), 4.07 (dt, *J* = 14.1, 6.0 Hz, 2H), 2.51 – 2.30 (m, 5H), 1.90 – 1.69 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 150.5, 144.8, 136.7, 136.5, 135.3, 132.9, 132.8, 132.6, 129.9, 128.8, 128.8, 128.6, 128.4, 128.4, 128.1, 128.0, 127.9, 127.7, 127.0, 126.7, 123.4, 122.6, 93.7, 93.2, 78.9, 78.7, 68.8, 68.8, 52.9, 51.7, 51.6, 49.8, 27.9, 27.7, 21.6, 15.9, 15.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}ClNO_4S$, 496.1349; found: 496.1371.



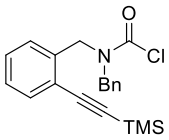
benzyl(2-(3-(trimethylsilyl)prop-1-yn-1-yl)benzyl)carbamic chloride (1w)

Compound **1w** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (655 mg, 59% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.10 (m, 9H), 4.75 (s, 1H), 4.68 (s, 1H), 4.58 (s, 1H), 4.46 (s, 1H), 1.59 (s, 1H), 1.53 (s, 1H), -0.00 (s, 4.5H), -0.02 (s, 4.5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152. 8, 152.4, 138.3, 138.1, 137.4, 134.5, 134.4, 130.7, 130.3, 130.0, 129.9, 129.8, 129.7, 129.55, 129.49, 129.1, 127.9, 126.5, 125.8, 96.9, 96.3, 55.1, 53.95, 53.86, 52.1, 10.2, 10.1, 0.00, -0.02.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{25}ClNOSi$, 370.1394; found: 370.1399.



benzyl(2-((trimethylsilyl)ethynyl)benzyl)carbamic chloride (1x)

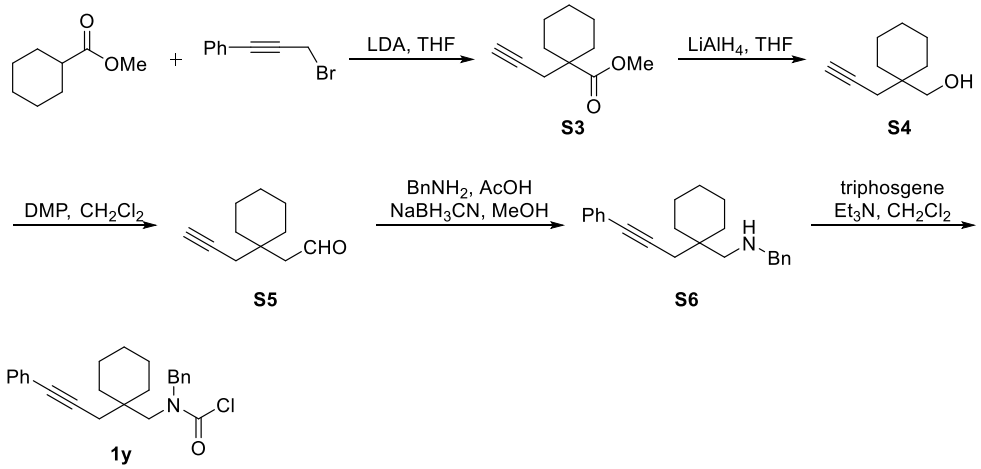
Compound **1x** was prepared following the general procedure using 2-iodobenzaldehyde (695 mg, 3.0 mmol) and was isolated as a pale yellow oil (480 mg, 45% yield, a mixture of two isomers 1：1) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 8.2 Hz, 1H), 7.25 – 6.95 (m, 8H), 4.69 (s, 1H), 4.62 (s, 1H), 4.46 (s, 1H), 4.31 (s, 1H), 0.00 (s, 4.5H), -0.05 (s, 4.5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 150.7, 137.4, 137.2, 135.5, 133.1, 133.0, 129.3, 129.0, 128.9, 128.7, 128.4, 128.3, 128.1, 128.2, 127.8, 127.2, 126.6, 123.0, 122.4, 102.2, 101.9, 100.7, 100.1, 53.4, 52.0, 51.8, 50.2, 0.0, -0.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{23}ClNOSi$, 356.1237; found: 356.1244.

2.2 Procedure for the synthesis of substrate 1y



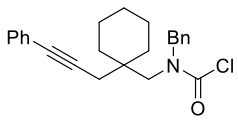
To a solution of methyl cyclohexanecarboxylate (1 equiv) in THF was added LDA (1.5 equiv) dropwise at -78℃, and the resulting mixture was stirred at -78℃. After 30 mins' stirring, (3-bromoprop-1-yn-1-yl)benzene (1.1 equiv) was added. The temperature was warmed to room temperature, and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with H_2O, extracted with EtOAc three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography.

To a cooled (0 ℃) solution of **S3** (1.0 equiv.) in THF was added $LiAlH_4$ (1.1 equiv.) portionwise, and the reaction mixture was kept stirring for 30 min at 0 ℃. The reaction mixture was carefully quenched with saturated aqueous $NaHSO_4$ solution at 0 ℃, and then extracted with EtOAc. The organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the crude product. The crude product was purified by column chromatography on silica gel.

To a solution of **S4** (1 equiv) in CH_2Cl_2 was added DMP (1.2 equiv) dropwise at room temperature, and the resulting mixture was stirred for 1 h. The reaction mixture was quenched with Saq. $Na_2S_2O_3$ and Saq. $NaHCO_3$, extracted with EtOAc three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography.

Compound **S5** (1.1 equiv), AcOH (1.1 equiv), and $NaBH_3CN$ (1.1 equiv) were added to stirred mixture of benzylamine (1 equiv) in MeOH (0.1 M). The mixture was stirred at room temperature for 12 h. The solution was then made alkaline with NaOH (1 N) and extracted with EtOAc. The organic layers were collected, dried over $MgSO_4$, and evaporated to dryness under reduced pressure to afford compound **S6**.

To a solution of **S6** (1 equiv) in CH_2Cl_2 was added Et_3N (2 equiv), followed by triphosgene (0.5 equiv). The resulting mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with H_2O, extracted with CH_2Cl_2 three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography. Compound **1y** was isolated as a yellow oil (400 mg, 35% yield) after silica gel column chromatography (Petroleum/EtOAc=20/1).



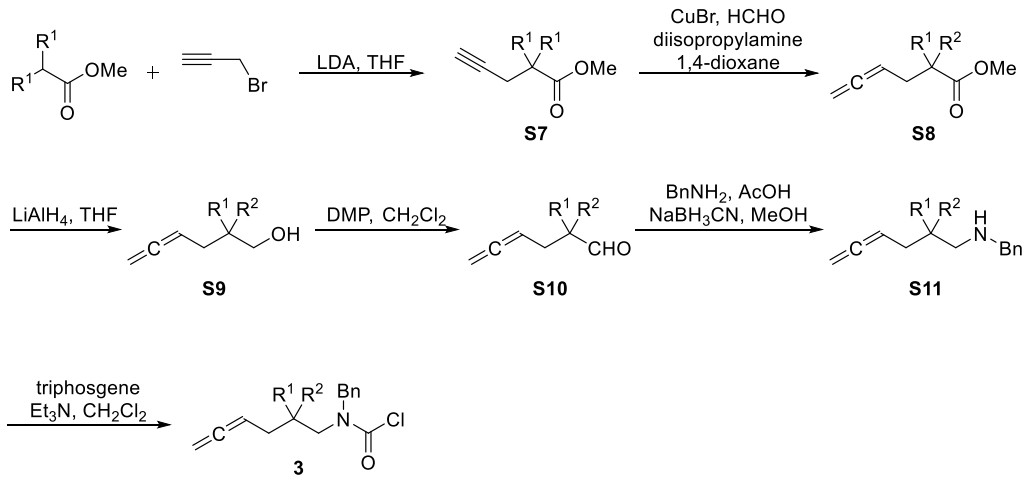
benzyl((1-(3-phenylprop-2-yn-1-yl)cyclohexyl)methyl)carbamic chloride (1y)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 10H), 4.86 (s, 2H), 3.38 (s, 2H), 2.49 (s, 2H), 1.57 – 1.45 (m, 6H), 1.42 – 1.36 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 135.0, 130.6, 127.8, 127.2, 126.81, 126.76, 125.8, 122.5, 85.9, 82.9, 55.5, 55.0, 38.9, 32.8, 24.8, 20.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{27}ClNO$, 380.1781; found: 380.1789.

2.3 General procedure for synthesis of substrate 3



To a solution of carboxymethyl ester (1 equiv) in THF was added LDA (1.5 equiv) dropwise at -78℃, and the resulting mixture was stirred at -78℃. After 30 mins' stirring, 3-bromoprop-1-yne (1.1 equiv) was added. The temperature was warmed to room temperature, and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with H_2O, extracted with EtOAc three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography.

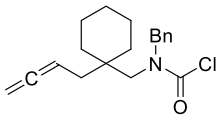
To a mixture of HCHO (2.0 equiv.) and CuBr (0.5 equiv.) was added 1,4-dioxane, diisopropylamine (2.0 equiv.) and **S7** (1.0 equiv.) under N_2 atmosphere. After completion of the reaction (monitored by TLC), the reaction was quenched with 1 M HCl solution and then extracted with EtOAc. The organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel.

To a cooled (0 ℃) solution of **S8** (1.0 equiv.) in THF was added $LiAlH_4$ (1.1 equiv.) portionwise, and the reaction mixture was kept stirring for 30 min at 0 ℃. The reaction mixture was carefully quenched with saturated aqueous $NaHSO_4$ solution at 0 ℃, and then extracted with EtOAc. The organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford the crude product. The crude product was purified by column chromatography on silica gel.

To a solution of **S9** (1 equiv) in CH_2Cl_2 was added DMP (1.2 equiv) dropwise at room temperature, and the resulting mixture was stirred for 1 h. The reaction mixture was quenched with Saq. $Na_2S_2O_3$ and Saq. $NaHCO_3$, extracted with EtOAc three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography.

Compound **S10** (1.1 equiv), AcOH (1.1 equiv), and $NaBH_3CN$ (1.1 equiv) were added to stirred mixture of benzylamine (1 equiv) in MeOH (0.1 M). The mixture was stirred at room temperature for 12 h. The solution was then made alkaline with NaOH (1 N) and extracted with EtOAc. The organic layers were collected, dried over $MgSO_4$, and evaporated to dryness under reduced pressure to afford compound **S11**.

To a solution of **S11** (1 equiv) in CH_2Cl_2 was added Et_3N (2 equiv), followed by triphosgene (0.5 equiv). The resulting mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with H_2O, extracted with CH_2Cl_2 three times, and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The crude mixture was purified by silica-gel column chromatography.



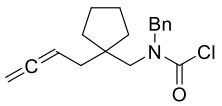
benzyl((1-(buta-2,3-dien-1-yl)cyclohexyl)methyl)carbamic chloride (3a)

Compound **3a** was prepared following the general procedure using methyl cyclohexanecarboxylate (710 mg, 5.0 mmol) and was isolated as a yellow oil (470 mg, 30% yield) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.25 (m, 3H), 7.20 (d, *J* = 7.3 Hz, 2H), 5.17 – 4.97 (m, 1H), 4.80 (s, 2H), 4.66 – 4.53 (m, 2H), 3.32 (s, 2H), 2.30 – 2.08 (m, 2H), 1.55 – 1.31 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 151.3, 136.0, 128.9, 127.8, 126.5, 85.2, 74.1, 57.0, 56.3, 39.9, 33.7, 25.8, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{25}ClNO$, 318.1625; found: 318.1635.



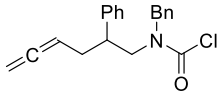
benzyl((1-(buta-2,3-dien-1-yl)cyclopentyl)methyl)carbamic chloride (3b)

Compound **3b** was prepared following the general procedure using methyl cyclopentanecarboxylate (640 mg, 5.0 mmol) and was isolated as a yellow oil (350 mg, 23% yield) after silica gel column chromatography (Petroleum/EtOAc=20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dq, *J* = 14.2, 7.1 Hz, 3H), 7.21 (d, *J* = 7.3 Hz, 2H), 5.10 (dt, *J* = 13.9, 6.9 Hz, 1H), 4.81 (s, 2H), 4.67 – 4.53 (m, 2H), 3.41 (s, 2H), 2.13 (dt, *J* = 7.7, 2.7 Hz, 2H), 1.73 – 1.46 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 151.4, 135.9, 128.9, 127.8, 126.5, 86.4, 74.3, 55.5, 55.1, 48.8, 36.3, 35.6, 23.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{23}ClNO$, 304.1468; found: 304.1456.



benzyl(2-phenylhexa-4,5-dien-1-yl)carbamic chloride (3c)

Compound **3c** was prepared following the general procedure using methyl benzoate (680 mg, 5.0 mmol) and was isolated as a yellow oil (350 mg, 22% yield) after silica gel column chromatography (Petroleum/EtOAc=20/1).

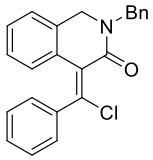
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 6H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 6.5 Hz, 2H), 4.87 – 4.72 (m, 1H), 4.58 – 4.37 (m, 3H), 3.81 – 3.59 (m, 2H), 3.49 (d, *J* = 15.0 Hz, 1H), 3.23 – 2.96 (m, 2H), 2.30 – 2.11 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 209.24, 209.18, 150.4, 149.8, 141.48, 141.46, 135.7, 135.5, 129.0, 128.94, 128.87, 128.12, 128.08, 127.5, 127.3, 127.1, 87.4, 87.3, 75.4, 75.3, 55.4, 54.9, 54.6, 52.9, 45.1, 43.7, 32.31, 32.29.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}ClNO$, 326.1312; found: 326.1322.

3. Typical Procedure for Chlorocarbamoylation

To a solution of **1** (0.2 mmol, 1.0 equiv) in dichloromethane (2 mL) was added BCl_3 (40𝓜L, 1M in CH_2Cl_2, 20%) at room temperature. The resulting mixture was stirred at room temperature for 30 min as monitored by TLC. Upon completion, the reaction mixture was quenched with water (2 mL) and extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by a short column chromatography on silica gel to afford chlorocarbamoylation products.



(Z)-2-benzyl-4-(chloro(phenyl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2a)

Compound **2a** was prepared according to the general procedure and was isolated as a yellow oil

(65 mg, 90% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

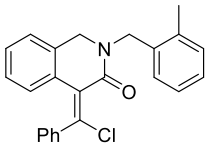
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.42 – 7.34 (m, 4H), 7.34 – 7.24 (m, 4H), 7.22 – 7.17 (m, 2H), 7.13 (d, *J* = 7.3 Hz, 1H), 4.64 (s, 2H), 4.35 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 139.5, 139.3, 136.8, 134.0, 132.5, 129.6, 129.2, 128.8, 128.73, 128.66, 128.2, 128.0, 127.9, 127.7, 127.0, 125.0, 50.5, 50.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{19}ClNO$, 360.1155; found: 360.1159.

Procedures of Synthesis of 2a in 2.0 mmol

To a solution of **1a** (720 mg, 2.0 mmol) in dichloromethane (20 mL) was added BCl_3 (400 *M*L, 1M in CH_2Cl_2, 20%) at room temperature. The resulting mixture was stirred at room temperature for 30 min as monitored by TLC. Upon completion, the reaction mixture was quenched with water (20 mL) and extracted with CH_2Cl_2 (30 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography to afford chlorocarbamoylation product **2a** as a yellow oil (620 mg, 86% yield).



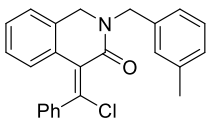
(Z)-4-(chloro(phenyl)methylene)-2-(2-methylbenzyl)-1,4-dihydroisoquinolin-3(2H)-one (2b)

Compound **2b** was prepared according to the general procedure and was isolated as a yellow oil (66 mg, 88% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.44 – 7.33 (m, 4H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.21 – 6.99 (m, 5H), 4.66 (s, 2H), 4.29 (s, 2H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 139.5, 139.3, 136.8, 134.2, 134.1, 132.6, 130.7, 129.6, 129.2, 128.74, 128.71, 128.6, 128.1, 128.0, 127.8, 127.0, 126.1, 125.0, 49.4, 48.2, 19.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1329.



(Z)-4-(chloro(phenyl)methylene)-2-(3-methylbenzyl)-1,4-dihydroisoquinolin-3(2H)-one (2c)

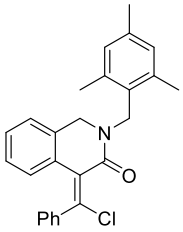
Compound **2c** was prepared according to the general procedure and was isolated as a yellow oil (65 mg, 87% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.28 (m, 4H),

7.22 (td, *J* = 7.5, 1.1 Hz, 1H), 7.16 – 7.05 (m, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.54 (s, 2H), 4.28 (s, 2H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 138.5, 138.2, 137.4, 135.6, 133.0, 131.5, 128.6, 128.2, 127.8, 127.7, 127.6, 127.5, 127.4, 127.0, 126.8, 125.9, 124.2, 123.9, 49.4, 49.0, 20.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1324.



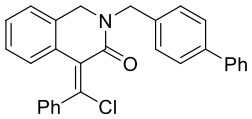
(Z)-4-(chloro(phenyl)methylene)-2-(2,4,6-trimethylbenzyl)-1,4-dihydroisoquinolin-3(2H)-one (2d)

Compound **2d** was prepared according to the general procedure and was isolated as a yellow oil (68 mg, 85% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.36 – 7.30 (m, 3H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.17 – 7.10 (m, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.78 (s, 2H), 4.60 (s, 2H), 3.95 (s, 2H), 2.20 (s, 3H), 2.09 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 138.4, 138.1, 137.1, 136.6, 133.4, 131.6, 128.8, 128.3, 128.1, 127.68, 127.66, 127.5, 126.9, 126.8, 125.9, 123.8, 45.9, 42.0, 19.9, 18.9.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClNO$, 402.1625; found: 402.1633.



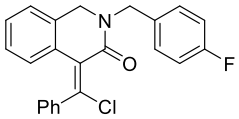
(Z)-2-([1,1'-biphenyl]-4-ylmethyl)-4-(chloro(phenyl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2e)

Compound **2e** was prepared according to the general procedure and was isolated as a yellow oil (75 mg, 86% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 1H), 7.63 – 7.51 (m, 4H), 7.50 – 7.26 (m, 12H), 7.18 (d, *J* = 7.4 Hz, 1H), 4.69 (s, 2H), 4.41 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 140.6, 139.5, 139.3, 135.8, 134.0, 132.5, 129.6, 129.3, 128.82, 128.76, 128.7, 128.6, 128.0, 127.9, 127.44, 127.41, 127.1, 127.0, 125.0, 50.18, 50.17.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{23}ClNO$, 436.1468; found: 436.1453.



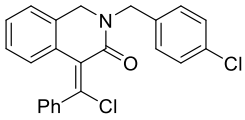
(Z)-4-(chloro(phenyl)methylene)-2-(4-fluorobenzyl)-1,4-dihydroisoquinolin-3(2H)-one (2f)

Compound **2f** was prepared according to the general procedure and was isolated as a yellow oil (60 mg, 79% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.35 (m, 6H), 7.29 (td, *J* = 7.5, 1.0 Hz, 1H), 7.21 – 7.12 (m, 3H), 6.99 (t, *J* = 8.7 Hz, 2H), 4.60 (s, 2H), 4.36 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 162.3 (d, *J* = 246.2 Hz), 139.5, 139.4, 133.9, 132.61, 132.58, 132.4, 129.8 (d, *J* = 8.0 Hz), 129.5, 129.3, 128.71, 128.68, 128.02, 127.97, 127.1, 124.9, 115.6 (d, *J* = 21.6 Hz), 50.1, 49.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClFNO$, 378.1061; found: 378.1059.



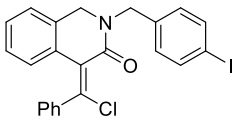
(Z)-4-(chloro(phenyl)methylene)-2-(4-chlorobenzyl)-1,4-dihydroisoquinolin-3(2H)-one (2g)

Compound **2g** was prepared according to the general procedure and was isolated as a yellow oil (70 mg, 89% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.35 (m, 6H), 7.33 – 7.26 (m, 3H), 7.14 (t, *J* = 8.4 Hz, 3H), 4.60 (s, 2H), 4.36 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 139.54, 139.46, 135.3, 133.8, 133.6, 132.4, 129.5, 129.4, 129.3, 128.9, 128.7, 128.02, 128.00, 127.1, 124.9, 50.1, 49.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}Cl_2NO$, 394.0765; found: 394.0782.



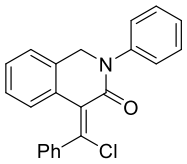
(Z)-4-(chloro(phenyl)methylene)-2-(4-iodobenzyl)-1,4-dihydroisoquinolin-3(2H)-one (2h)

Compound **2h** was prepared according to the general procedure and was isolated as a yellow oil (84 mg, 86% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.22 (m, 5H), 7.13 – 6.99 (m, 4H), 6.93 – 6.86 (m, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.76 (s, 2H), 4.34 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 138.6, 137.9, 137.0, 136.4, 133.3, 132.8, 129.9, 129.5, 129.2, 128.8, 128.4, 128.1, 127.4, 127.0, 125.0, 93.1, 49.9, 49.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClINO$, 486.0122; found: 486.0126.



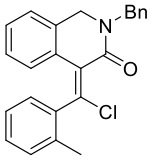
(Z)-4-(chloro(phenyl)methylene)-2-phenyl-1,4-dihydroisoquinolin-3(2H)-one (2i)

Compound **2i** was prepared according to the general procedure and was isolated as a yellow oil (62 mg, 90% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.3 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.44 (td, *J* = 7.7, 1.2 Hz, 1H), 7.41 – 7.28 (m, 6H), 7.29 – 7.22 (m, 3H), 7.22 – 7.15 (m, 1H), 4.86 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 141.9, 140.1, 139.1, 134.3, 132.7, 130.0, 129.3, 129.0, 128.9, 128.8, 128.1, 127.3, 126.4, 125.0, 53.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}ClNO$, 346.0999; found: 346.0982.



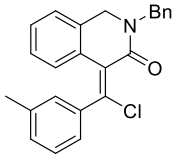
(Z)-2-benzyl-4-(chloro(o-tolyl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2j)

Compound **2j** was prepared according to the general procedure and was isolated as a yellow oil (62 mg, 83% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 6H), 7.21 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.12 – 7.07 (m, 1H), 7.07 – 6.98 (m, 2H), 6.90 – 6.82 (m, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 5.01 – 4.72 (m, 2H), 4.32 (dd, *J* = 34.7, 15.4 Hz, 2H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 138.1, 136.6, 136.1, 135.3, 133.0, 132.7, 130.5, 129.8, 129.6, 129.1, 128.8, 127.9, 127.62, 127.56, 127.3, 127.0, 126.2, 124.8, 50.1, 49.6, 19.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1328.



(Z)-2-benzyl-4-(chloro(m-tolyl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2k)

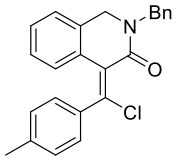
Compound **2k** was prepared according to the general procedure and was isolated as a yellow oil (60 mg, 80% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.34 – 7.19 (m, 10H),

7.15 (d, *J* = 7.5 Hz, 1H), 4.65 (s, 2H), 4.35 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 139.58, 139.55, 137.7, 136.9, 134.0, 132.5, 130.1, 129.4, 129.2, 128.7, 128.6, 128.1, 128.0, 127.9, 127.7, 127.0, 125.8, 124.9, 50.4, 50.1, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1314.



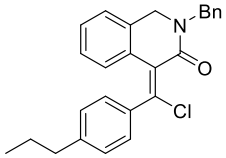
(Z)-2-benzyl-4-(chloro(p-tolyl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2l)

Compound **2l** was prepared according to the general procedure and was isolated as a yellow oil (68 mg, 91% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 5H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.10 – 6.99 (m, 4H), 6.93 – 6.85 (m, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 4.82 (s, 2H), 4.33 (s, 2H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 139.3, 137.0, 136.7, 135.8, 133.6, 133.1, 129.5, 129.1, 128.79, 128.76, 127.99, 127.95, 127.6, 127.3, 126.9, 125.0, 50.2, 49.8, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{21}ClNO$, 374.1312; found: 374.1326.



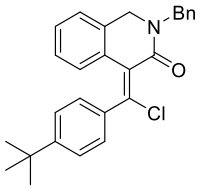
(Z)-2-benzyl-4-(chloro(4-propylphenyl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2m)

Compound **2m** was prepared according to the general procedure and was isolated as a yellow oil (71 mg, 88% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.00 (m, 4H), 6.92 – 6.84 (m, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 4.83 (s, 2H), 4.33 (s, 2H), 2.60 – 2.49 (m, 2H), 1.65 – 1.57 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 144.0, 137.2, 136.7, 136.0, 133.5, 133.1, 129.5, 128.81, 128.77, 128.4, 127.9, 127.6, 127.2, 126.8, 124.9, 50.2, 49.8, 37.7, 24.2, 13.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}ClNO$, 402.1625; found: 402.1641.



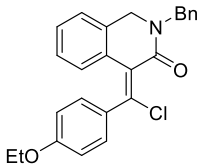
(Z)-2-benzyl-4-((4-(tert-butyl)phenyl)chloromethylene)-1,4-dihydroisoquinolin-3(2H)-one (2n)

Compound **2n** was prepared according to the general procedure and was isolated as a yellow oil (65 mg, 78% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 7.24 (t, *J* = 2.0 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.10 – 7.02 (m, 2H), 6.92 – 6.85 (m, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 4.83 (s, 2H), 4.34 (s, 2H), 1.28 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 152.5, 137.1, 136.7, 135.7, 133.5, 133.1, 129.3, 128.82, 128.78, 128.0, 127.6, 127.2, 126.9, 125.2, 124.9, 50.2, 49.8, 34.7, 31.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}ClNO$, 416.1781; found: 416.1778.



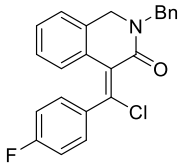
(Z)-2-benzyl-4-(chloro(4-ethoxyphenyl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2o)

Compound **2o** was prepared according to the general procedure and was isolated as a yellow oil (74 mg, 92% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.34 – 7.22 (m, 6H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.93 – 6.81 (m, 2H), 4.66 (s, 2H), 4.36 (s, 2H), 4.07 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 159.7, 139.5, 136.8, 134.0, 132.9, 131.4, 130.4, 128.8, 128.7, 128.2, 127.69, 127.66, 126.9, 124.8, 113.8, 63.5, 50.5, 50.1, 14.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{23}ClNO_2$, 404.1417; found: 404.1412.



(Z)-2-benzyl-4-(chloro(4-fluorophenyl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2p)

Compound **2p** was prepared according to the general procedure and was isolated as a white solid (68 mg, 90% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

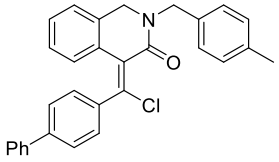
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.47 – 7.35 (m, 3H), 7.34 – 7.26 (m, 4H),

7.23 – 7.12 (m, 3H), 7.11 – 7.02 (m, 2H), 4.65 (s, 2H), 4.37 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.0 (d, *J* = 249.5 Hz), 138.1, 136.6, 135.5 (d, *J* = 3.5 Hz), 133.9, 132.3, 130.8 (d, *J* = 8.5 Hz), 129.8, 128.7, 128.6, 128.1, 128.0, 127.0, 124.9, 115.1 (d, *J* = 21.9 Hz), 50.5, 50.1.

^{19}F NMR (377 MHz, $CDCl_3$) δ -111.45.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{18}ClFNO$, 378.1061; found: 378.1077.



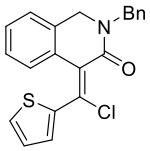
(Z)-4-([1,1'-biphenyl]-4-ylchloromethylene)-2-(4-methylbenzyl)-1,4-dihydroisoquinolin-3(2H)-one (2q)

Compound **2q** was prepared according to the general procedure and was isolated as a yellow oil (93 mg, 93% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.29 (m, 3H), 7.22 – 7.02 (m, 6H), 6.95 – 6.86 (m, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 4.80 (s, 2H), 4.34 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 141.8, 140.0, 137.6, 137.3, 136.4, 133.7, 133.6, 132.9, 130.1, 129.5, 128.9, 128.8, 128.4, 128.0, 127.8, 127.4, 127.05, 127.02, 126.9, 125.1, 50.0, 49.7, 21.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{25}ClNO$, 450.1625; found: 450.1630.



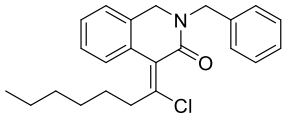
(Z)-2-benzyl-4-(chloro(thiophen-2-yl)methylene)-1,4-dihydroisoquinolin-3(2H)-one (2r)

Compound **2r** was prepared according to the general procedure and was isolated as a yellow oil (62 mg, 85% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 6H), 7.20 – 7.13 (m, 1H), 7.13 – 7.01 (m, 4H), 6.87 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.81 (s, 2H), 4.32 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 140.5, 136.5, 134.0, 132.9, 130.4, 129.2, 128.8, 128.7, 128.5, 128.4, 127.9, 127.8, 127.6, 127.1, 126.8, 125.2, 50.2, 49.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}ClNOS$, 366.0719; found: 366.0717.



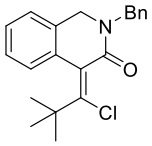
(Z)-2-benzyl-4-(1-chloroheptylidene)-1,4-dihydroisoquinolin-3(2H)-one (2s)

Compound **2s** was prepared according to the general procedure and was isolated as a yellow oil (66 mg, 90% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.4 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.32 – 7.26 (m, 3H), 7.22 – 7.19 (m, 3H), 6.91 (d, *J* = 7.1 Hz, 1H), 4.97 (d, *J* = 14.9 Hz, 1H), 4.38 (d, *J* = 14.6 Hz, 1H), 4.29 (d, *J* = 14.9 Hz, 1H), 3.85 (d, *J* = 14.6 Hz, 1H), 3.02 – 2.81 (m, 2H), 1.76 – 1.58 (m, 2H), 1.49 – 1.28 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 138.2, 136.92, 136.85, 136.4, 134.3, 129.3, 129.1, 128.7, 128.21, 128.18, 127.6, 126.4, 49.71, 49.70, 33.7, 31.7, 29.4, 28.6, 22.6, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{27}ClNO$, 368.1781; found: 368.1773.



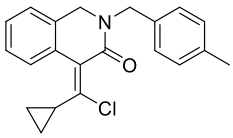
(Z)-2-benzyl-4-(1-chloro-2,2-dimethylpropylidene)-1,4-dihydroisoquinolin-3(2H)-one (2t)

Compound **2t** was prepared according to the general procedure and was isolated as a yellow oil (69 mg, 86% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.25 (m, 4H), 7.25 – 7.14 (m, 3H), 6.97 (d, *J* = 7.3 Hz, 1H), 5.03 (d, *J* = 15.0 Hz, 1H), 4.38 (d, *J* = 14.6 Hz, 1H), 3.92 (d, *J* = 15.0 Hz, 1H), 3.76 (d, *J* = 14.6 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 145.3, 137.7, 137.4, 137.0, 130.2, 130.1, 128.70, 128.65, 128.3, 128.2, 127.6, 126.4, 49.8, 47.8, 37.2, 29.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{23}ClNO$, 340.1468; found: 340.1476.



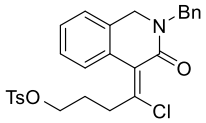
(Z)-4-(chloro(cyclopropyl)methylene)-2-(4-methylbenzyl)-1,4-dihydroisoquinolin-3(2H)-one (2u)

Compound **2u** was prepared according to the general procedure and was isolated as a yellow oil (55 mg, 81% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 5.30 – 5.11 (m, 1H), 4.78 – 4.59 (m, 2H), 4.41 (d, *J* = 16.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 3.65 – 3.51 (m, 1H), 3.37 – 3.24 (m, 1H), 2.86 – 2.72 (m, 1H), 2.47 – 2.36 (m, 1H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 151.6, 137.2, 133.7, 131.4, 130.6, 129.4, 128.1, 127.5, 127.4, 127.2, 125.3, 124.5, 57.4, 49.7, 49.6, 32.0, 31.7, 21.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}ClNO$, 338.1312; found: 338.1326.



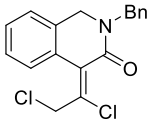
(Z)-4-(2-benzyl-3-oxo-2,3-dihydroisoquinolin-4(1H)-ylidene)-4-chlorobutyl 4-methylbenzene sulfonate (2v)

Compound **2v** was prepared according to the general procedure and was isolated as a yellow oil (77 mg, 78% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.22 – 7.13 (m, 6H), 7.05 (td, *J* = 7.7, 1.1 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 4.91 (d, *J* = 14.8 Hz, 1H), 4.48 (d, *J* = 14.6 Hz, 1H), 4.36 (d, *J* = 14.9 Hz, 1H), 3.92 (d, *J* = 14.7 Hz, 1H), 3.64 – 3.48 (m, 2H), 2.91 – 2.81 (m, 1H), 2.80 – 2.66 (m, 1H), 2.40 (s, 3H), 2.15 – 1.99 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 146.9, 145.4, 137.2, 136.7, 133.6, 132.3, 131.6, 129.7, 129.5, 128.7, 128.2, 128.0, 127.72, 127.65, 127.6, 126.5, 50.1, 49.7, 44.7, 32.0, 27.7, 21.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}ClNO_4S$, 496.1349; found: 496.1350.



(Z)-2-benzyl-4-(1,2-dichloroethylidene)-1,4-dihydroisoquinolin-3(2H)-one (2w)

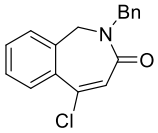
Compound **2w** was prepared according to the general procedure and was isolated as a yellow oil (47 mg, 71% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 2H), 7.32 – 7.29 (m, 1H), 7.29 – 7.28 (m, 1H), 7.26 – 7.24 (m, 2H), 7.24 – 7.21 (m, 2H), 6.95 (d, *J* = 7.4 Hz, 1H), 4.73 (s, 2H), 4.70 (s, 2H), 4.17 (s,

2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 136.9, 136.5, 135.8, 134.7, 134.4, 129.5, 129.4, 128.7, 128.3, 128.2, 127.6, 127.2, 50.5, 50.1, 47.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}Cl_2NO$, 332.0609; found: 332.0618.



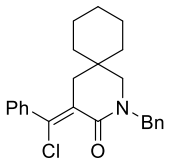
2-benzyl-5-chloro-1,2-dihydro-3H-benzo[c]azepin-3-one (2x)

Compound **2x** was prepared according to the general procedure and was isolated as a white solid (50 mg, 88% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.41 (td, *J* = 7.8, 1.1 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.24 – 7.19 (m, 2H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.83 (s, 1H), 4.65 (s, 2H), 4.21 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 141.1, 136.6, 136.5, 134.7, 130.4, 128.8, 128.7, 128.5, 128.3, 127.7, 127.3, 125.9, 50.2, 50.1.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{15}ClNO$, 284.0842; found: 284.0844.



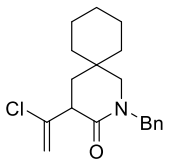
(Z)-2-benzyl-4-(chloro(phenyl)methylene)-2-azaspiro[5.5]undecan-3-one (2y)

Compound **2y** was prepared according to the general procedure and was isolated as a yellow oil (69 mg, 91% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 5H), 7.31 – 7.18 (m, 5H), 4.52 (s, 2H), 3.07 (s, 2H), 2.70 (s, 2H), 1.55 – 1.39 (m, 5H), 1.38 – 1.20 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 142.6, 140.5, 137.3, 128.6, 128.4, 128.1, 127.9, 127.45, 127.40, 56.6, 50.6, 40.0, 35.0, 33.8, 26.1, 21.7.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{27}ClNO$, 380.1781; found: 380.1788.



2-benzyl-4-(1-chlorovinyl)-2-azaspiro[5.5]undecan-3-one (4a)

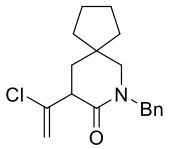
Compound **4a** was prepared according to the general procedure and was isolated as a yellow oil

(58 mg, 91% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.19 (m, 5H), 5.37 (dd, *J* = 9.8, 1.1 Hz, 2H), 4.68 (d, *J* = 14.5 Hz, 1H), 4.54 (d, *J* = 14.5 Hz, 1H), 3.60 – 3.38 (m, 1H), 3.02 (s, 2H), 1.96 – 1.84 (m, 2H), 1.49 – 1.10 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 141.4, 137.1, 128.6, 128.3, 127.5, 115.9, 56.4, 51.0, 48.6, 37.3, 32.3, 31.7, 26.2, 21.6, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{25}ClNO$, 318.1625; found: 318.1633.



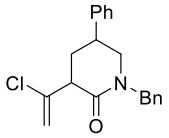
7-benzyl-9-(1-chlorovinyl)-7-azaspiro[4.5]decan-8-one (4b)

Compound **4b** was prepared according to the general procedure and was isolated as a yellow oil (56 mg, 92% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 5.39 (d, *J* = 1.3 Hz, 1H), 5.36 (s, 1H), 4.61 (q, *J* = 14.5 Hz, 2H), 3.52 (dd, *J* = 11.9, 6.8 Hz, 1H), 3.18 (d, *J* = 12.1 Hz, 1H), 2.84 (dd, *J* = 12.1, 2.8 Hz, 1H), 2.26 – 2.12 (m, 1H), 1.81 – 1.74 (m, 1H), 1.72 – 1.62 (m, 2H), 1.60 – 1.53 (m, 2H), 1.48 – 1.37 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 141.2, 136.9, 128.6, 128.3, 127.5, 116.0, 57.0, 51.0, 50.1, 41.1, 38.9, 37.9, 34.4, 24.8, 24.0.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{23}ClNO$, 304.1468; found: 304.1464.



1-benzyl-3-(1-chlorovinyl)-5-phenylpiperidin-2-one (4c)

Compound **4c** was prepared according to the general procedure and was isolated as a yellow oil (58 mg, 89% yield) after silica gel column chromatography (Petroleum/EtOAc=10/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.41 – 6.80 (m, 7H), 6.79 – 6.58 (m, 2H), 5.62 (s, 1H), 5.31 (s, 1H), 4.58 (d, *J* = 15.1 Hz, 1H), 4.28 (d, *J* = 15.1 Hz, 1H), 3.64 – 3.48 (m, 2H), 3.17 – 3.01 (m, 2H), 2.25 – 2.12 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 141.6, 138.0, 136.6, 132.8, 128.7, 128.6, 128.4, 127.4,

127.2, 127.0, 124.2, 111.2, 55.7, 49.5, 46.8, 34.0, 28.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}ClNO$, 326.1312; found: 326.1324.

4. Calculation results

Computation Details

All the geometrical structures were optimized at the ωB97X-D level with integral equation formalism model by the Gaussian 09 package[1-3]. The 6-31+G* basis set was used for all atoms. Frequency analyses were done at the same level. For all the reactants, products and mediums, there are no imaginary frequencies. While, for transition states, there are only one imaginary frequency. All positive frequencies that are less than 100 cm^{-1} are set to 100 cm^{-1} for thermodynamics calculations[4]. The single point energies were revised at the M06-2X/6-311++G(2df,2p) level with SMD solvation model[5-6]. Relative energies include electronic energies and thermal corrections to Gibbs free energies.

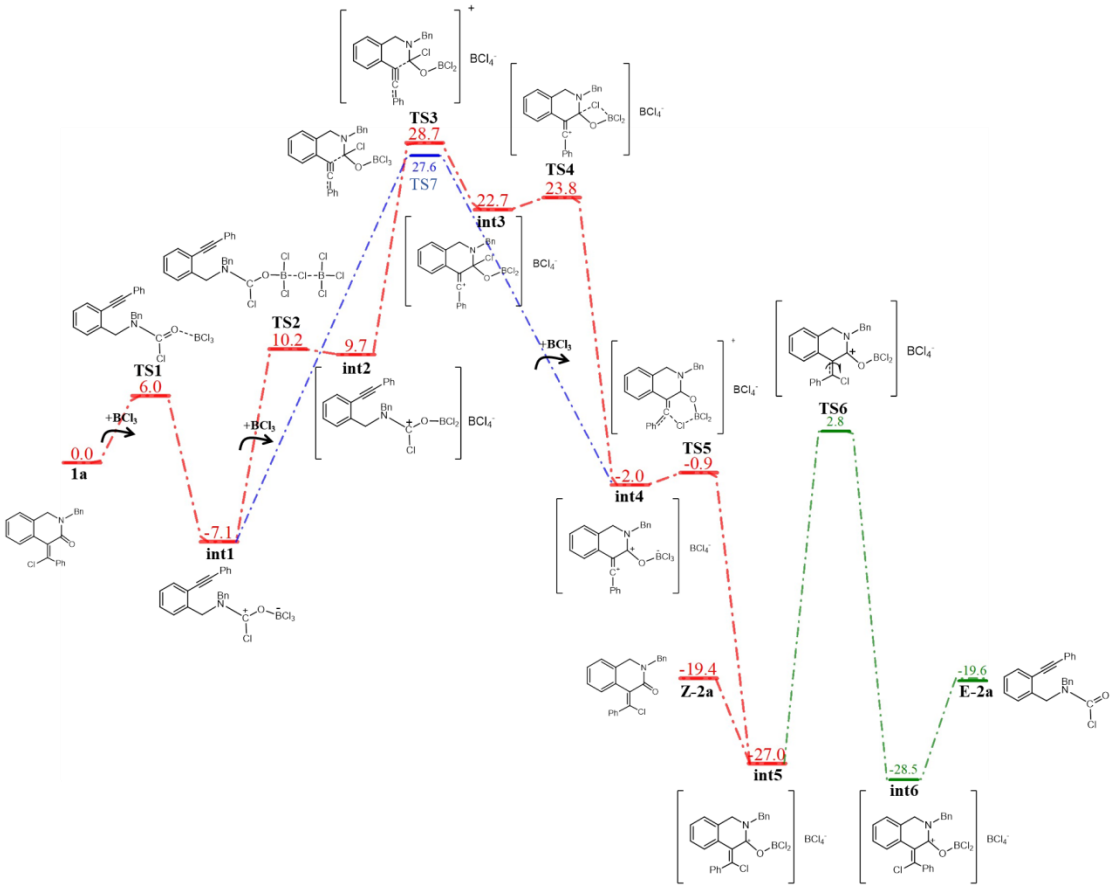


Figure S1. Simplified potential energy surface for reactant **1a**. The unit of relative energy is kcal/mol.

5. References

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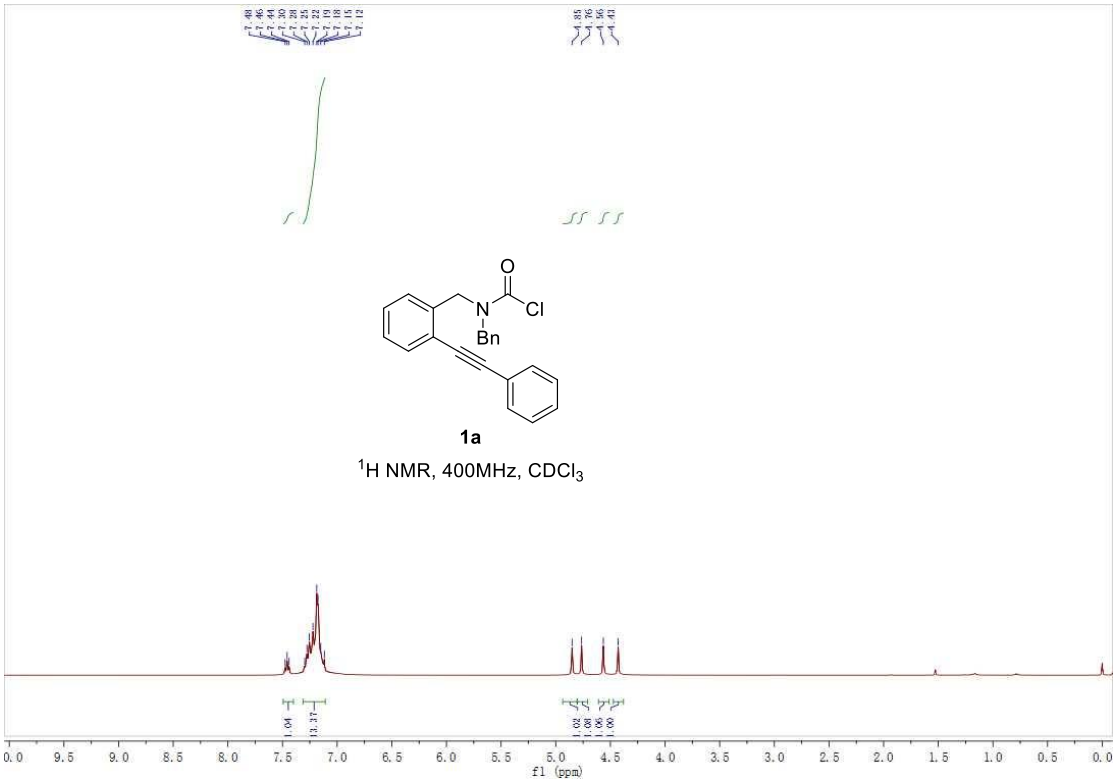
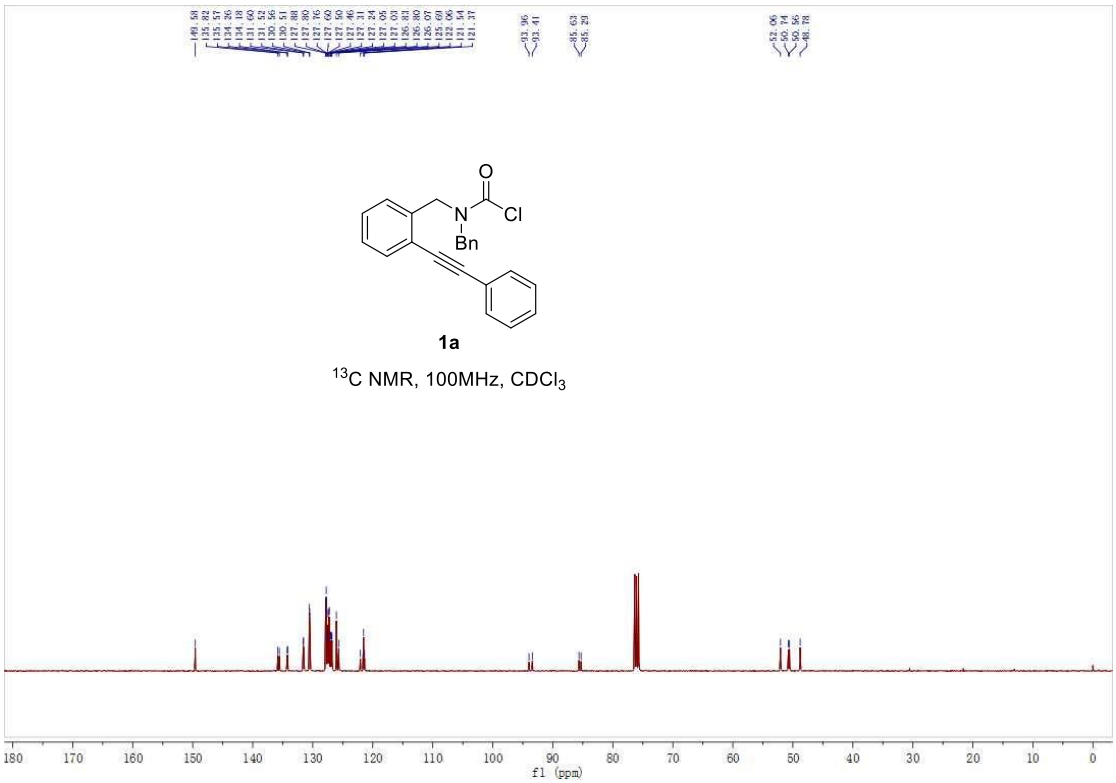
6. Copies of NMR Spectra



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



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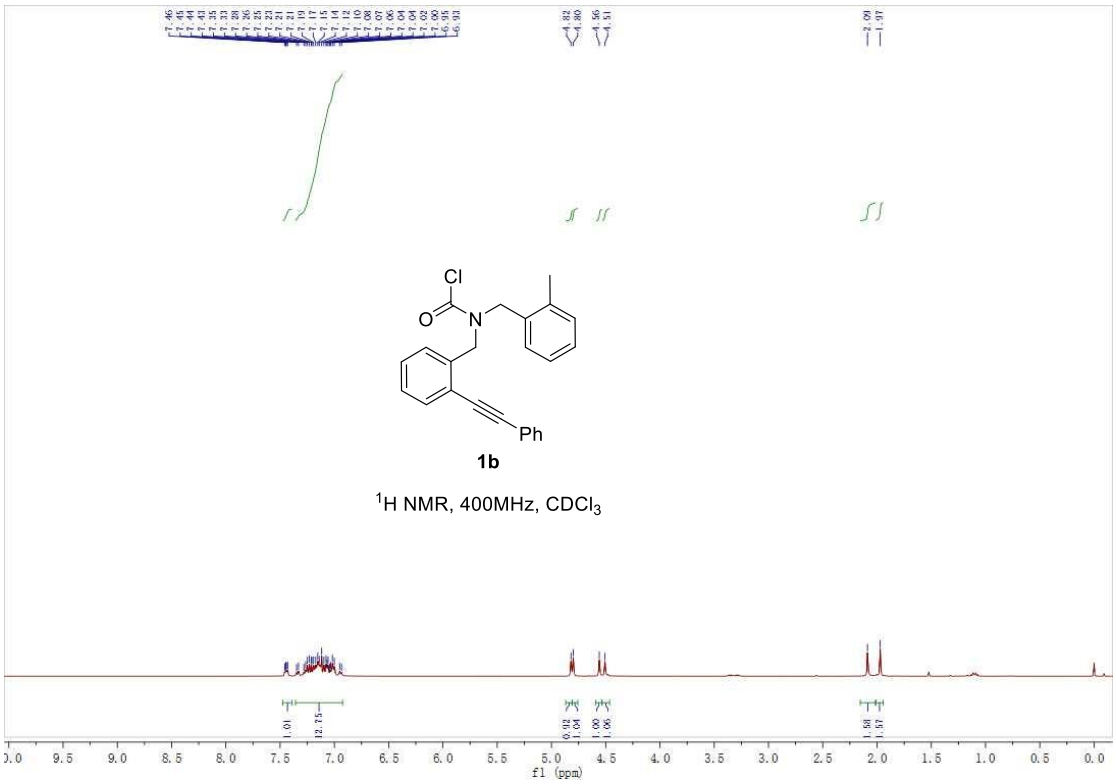

1b

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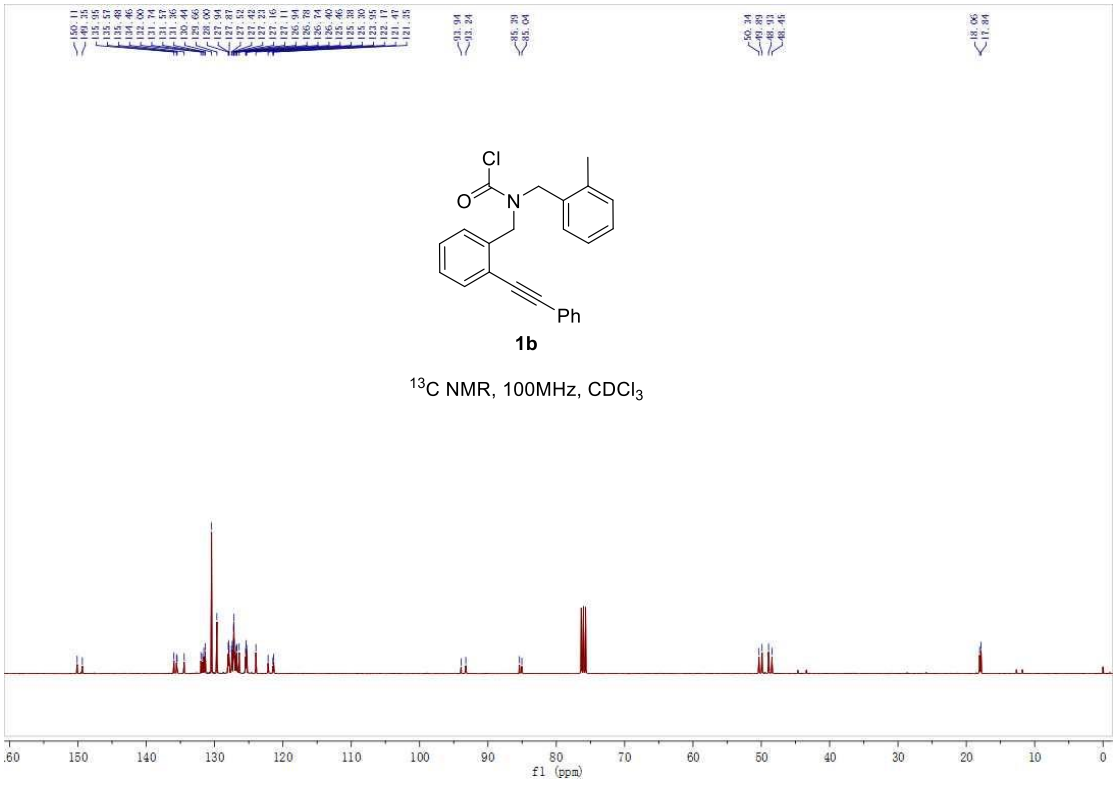

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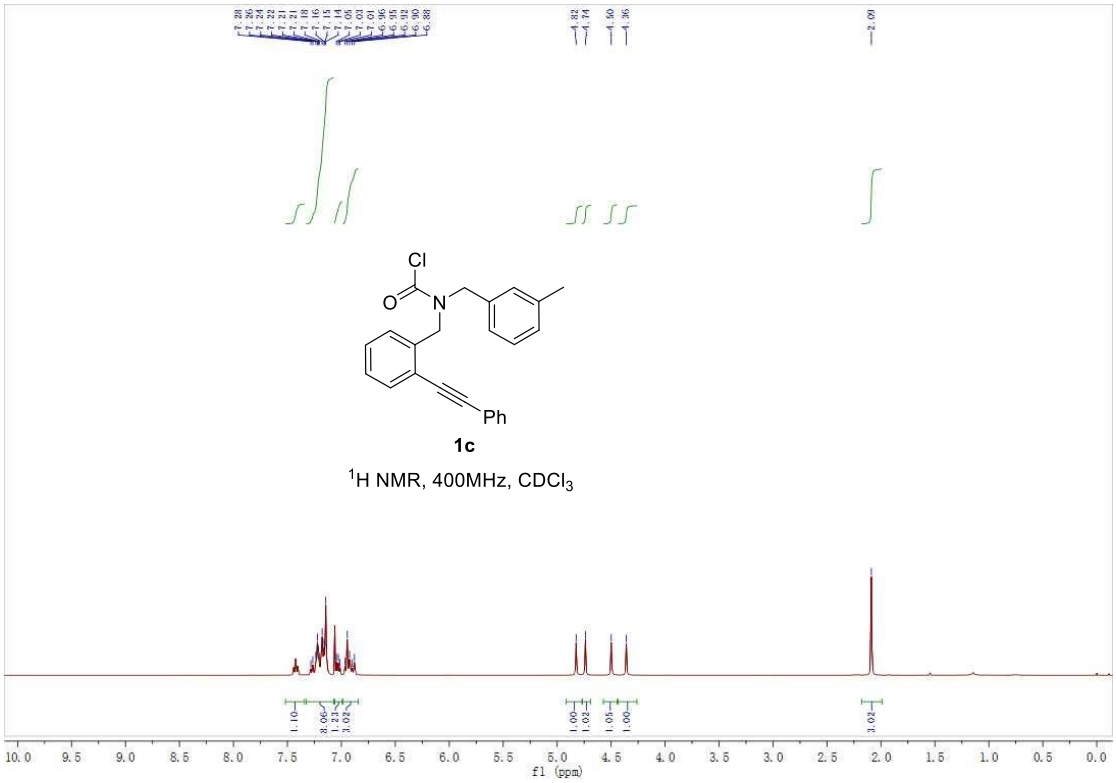

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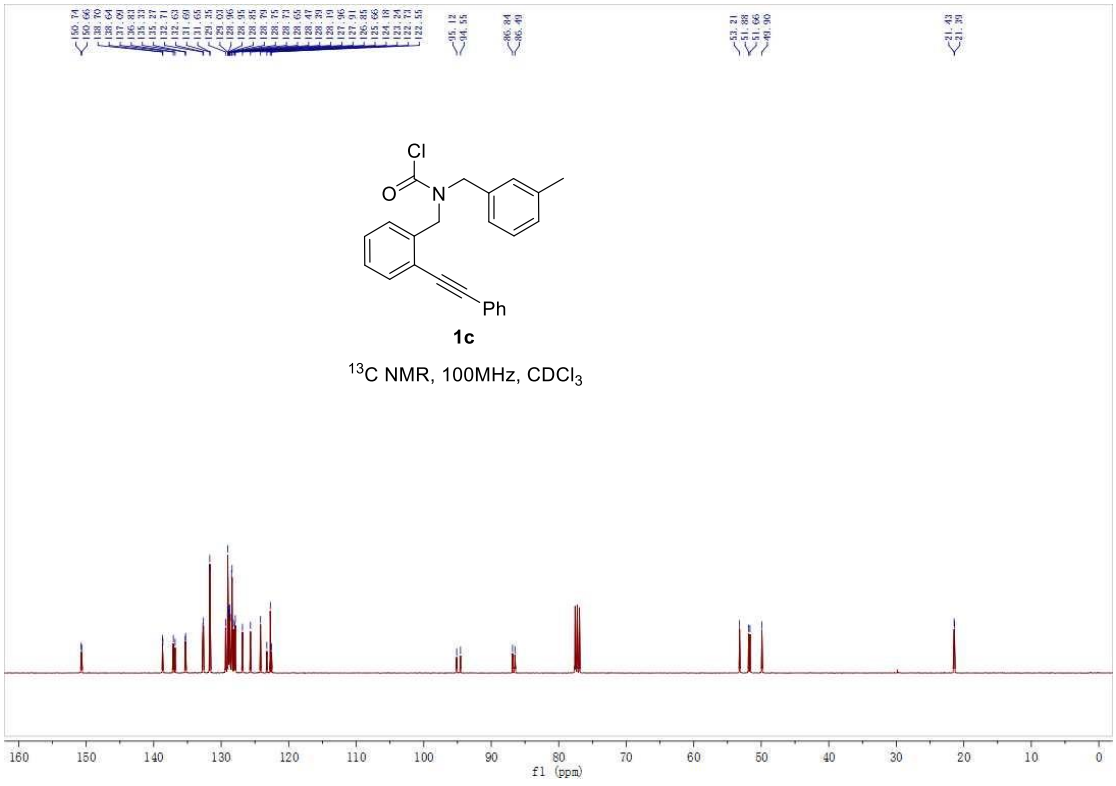

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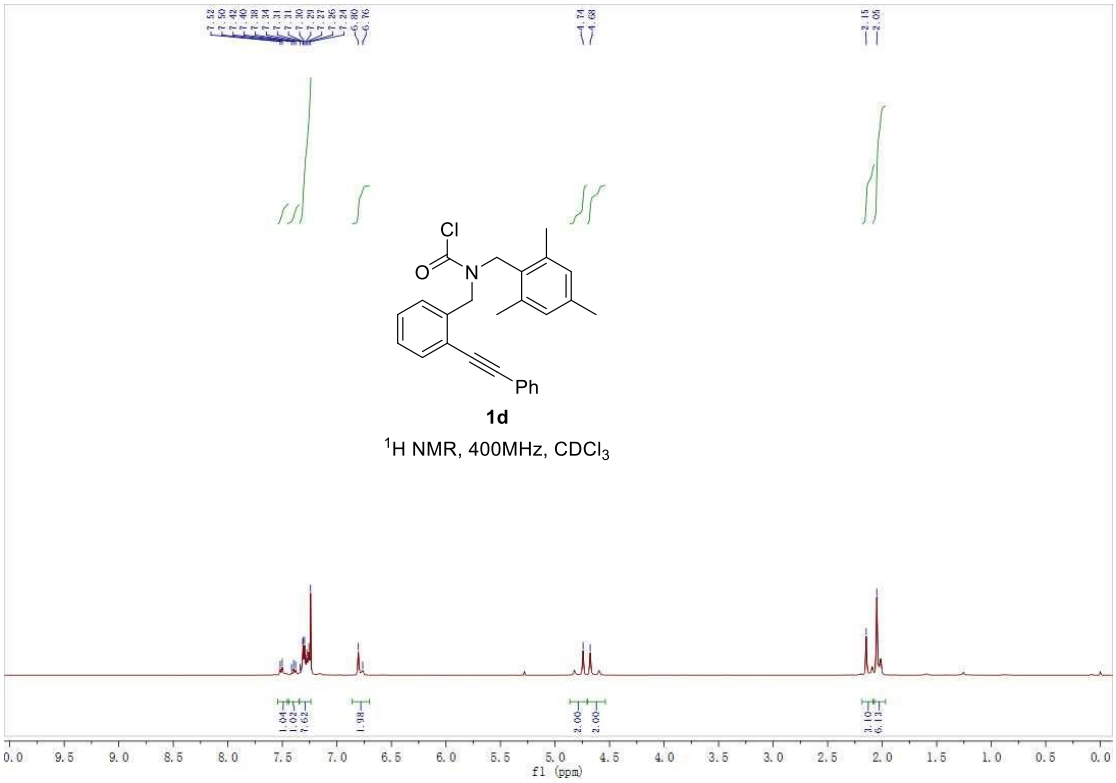

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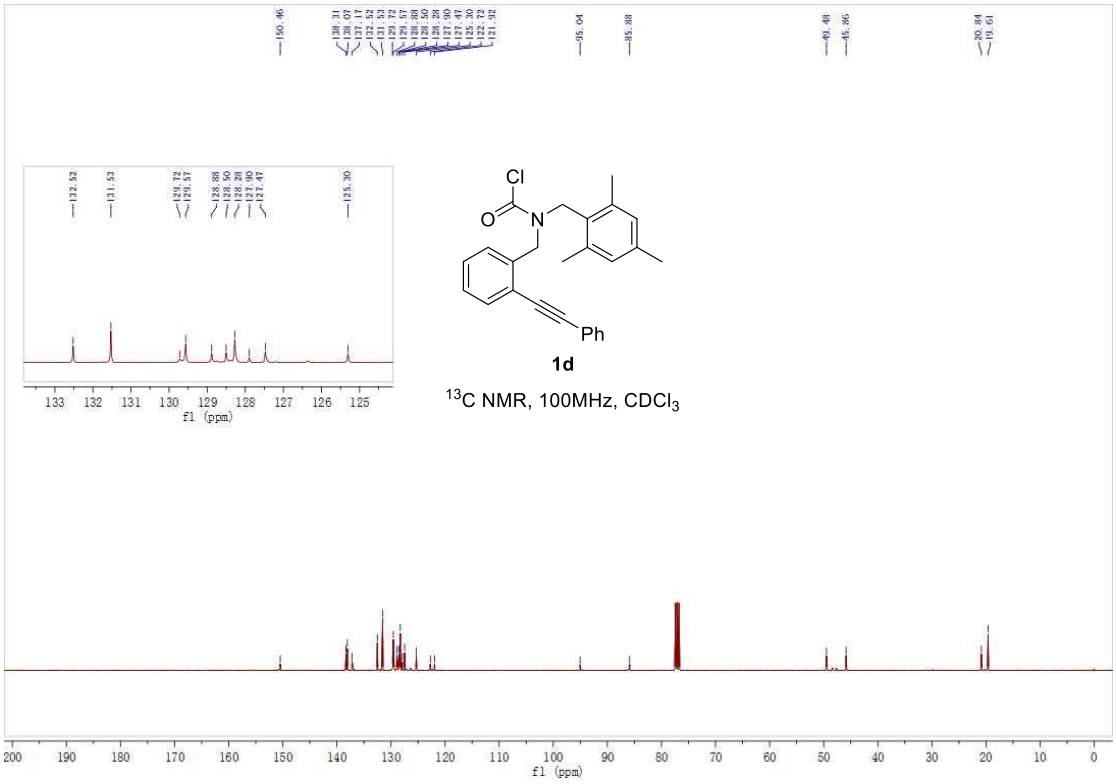

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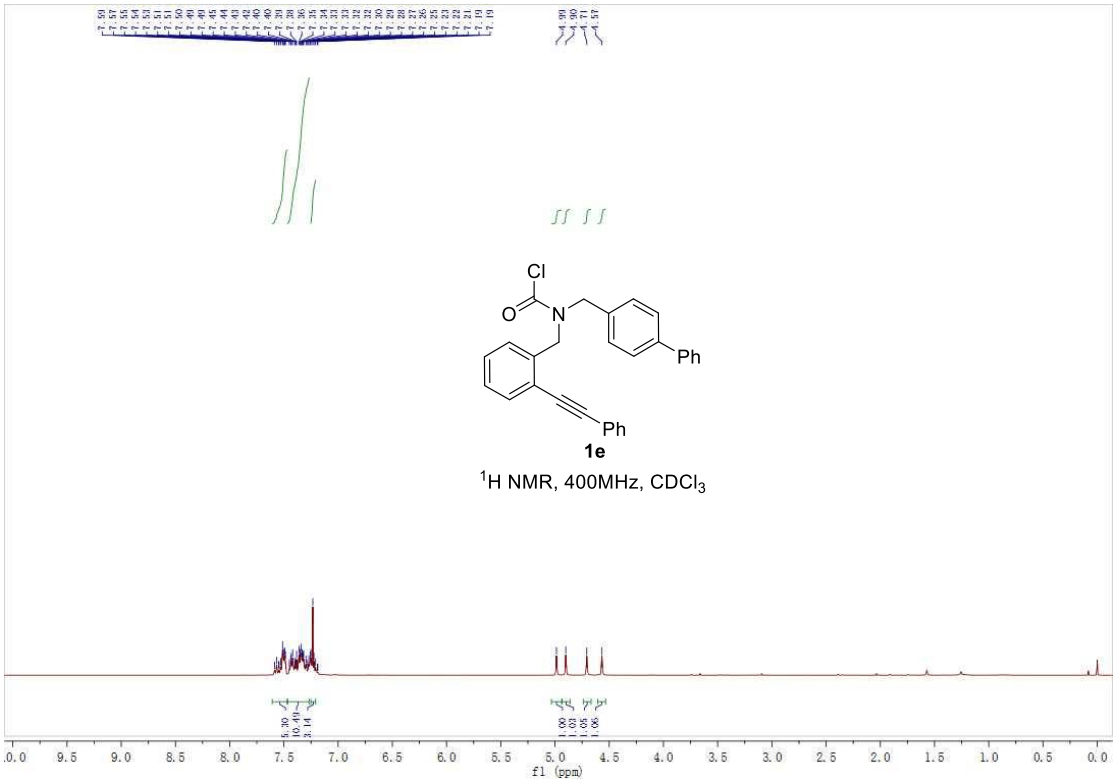

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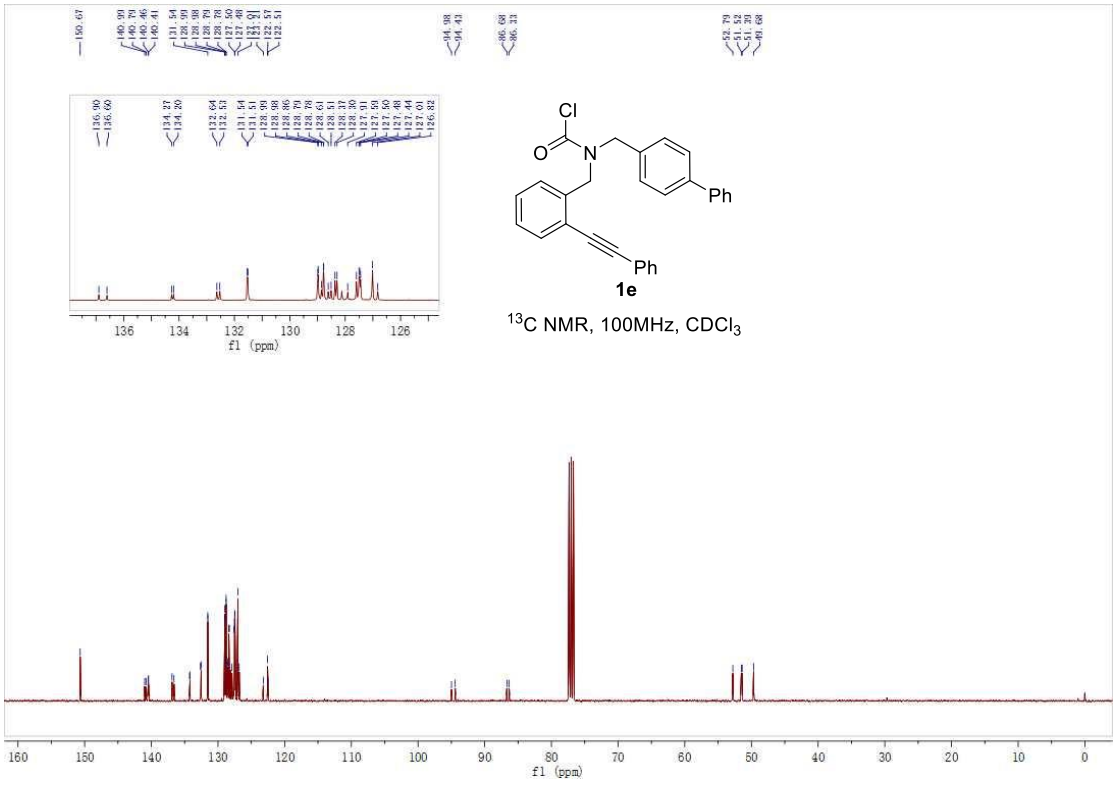

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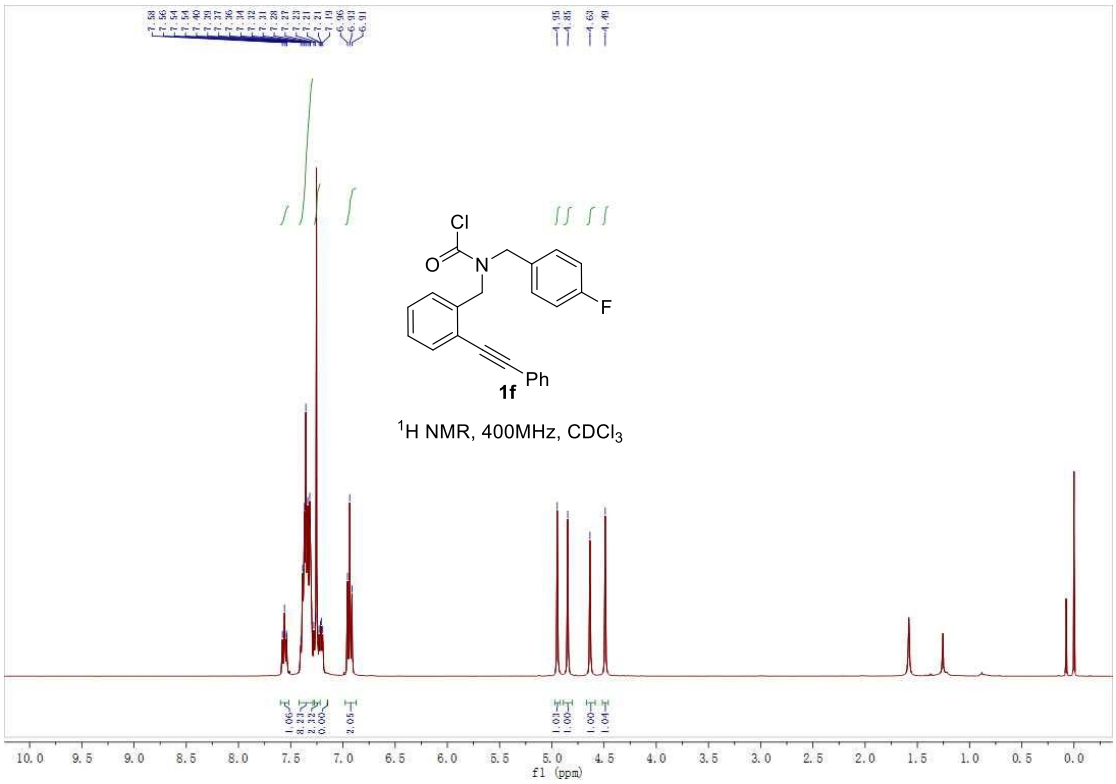

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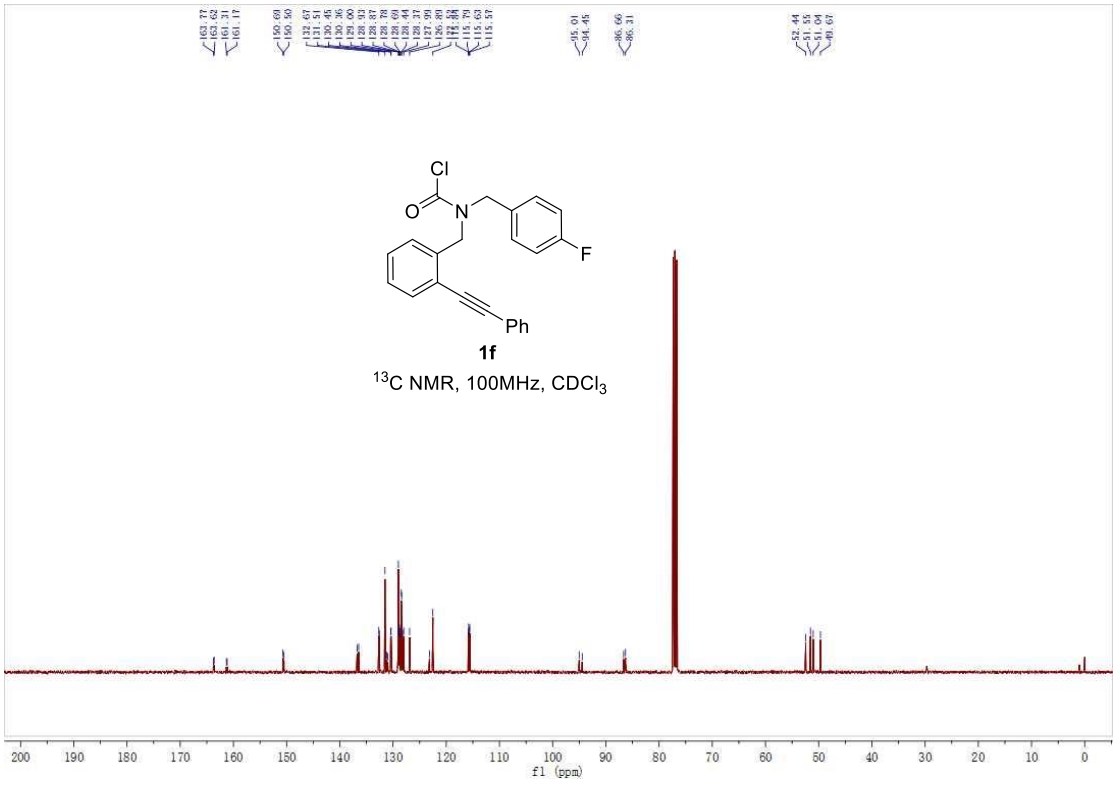

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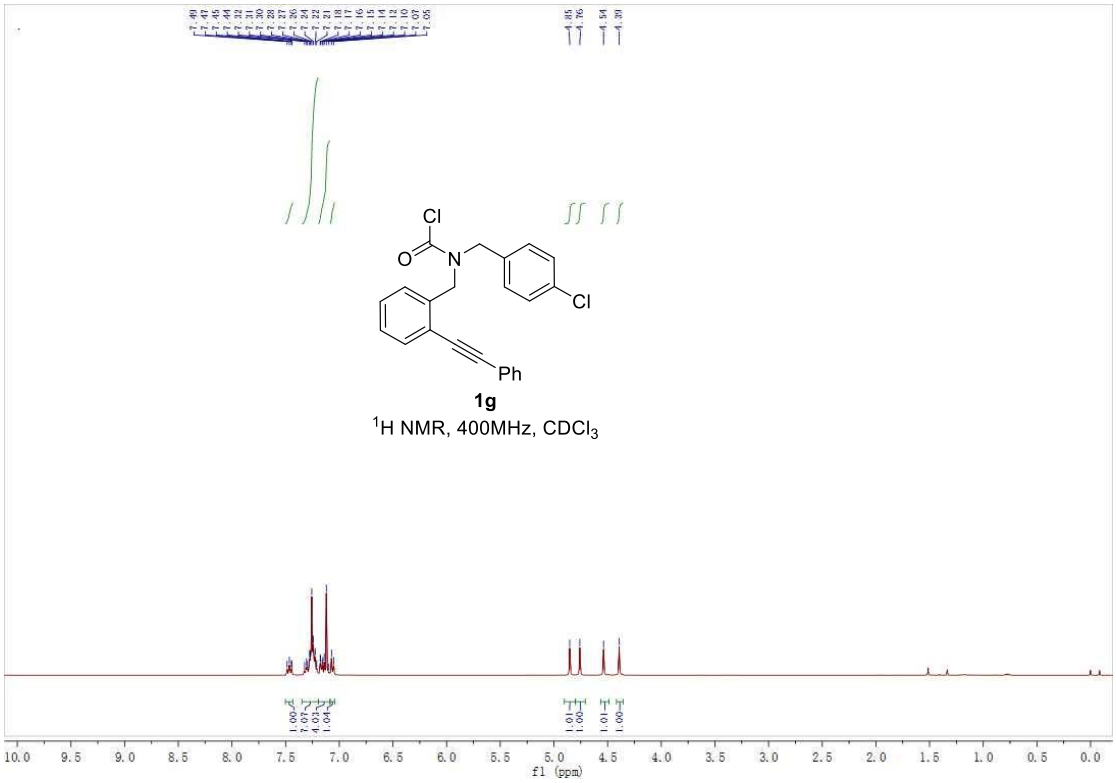

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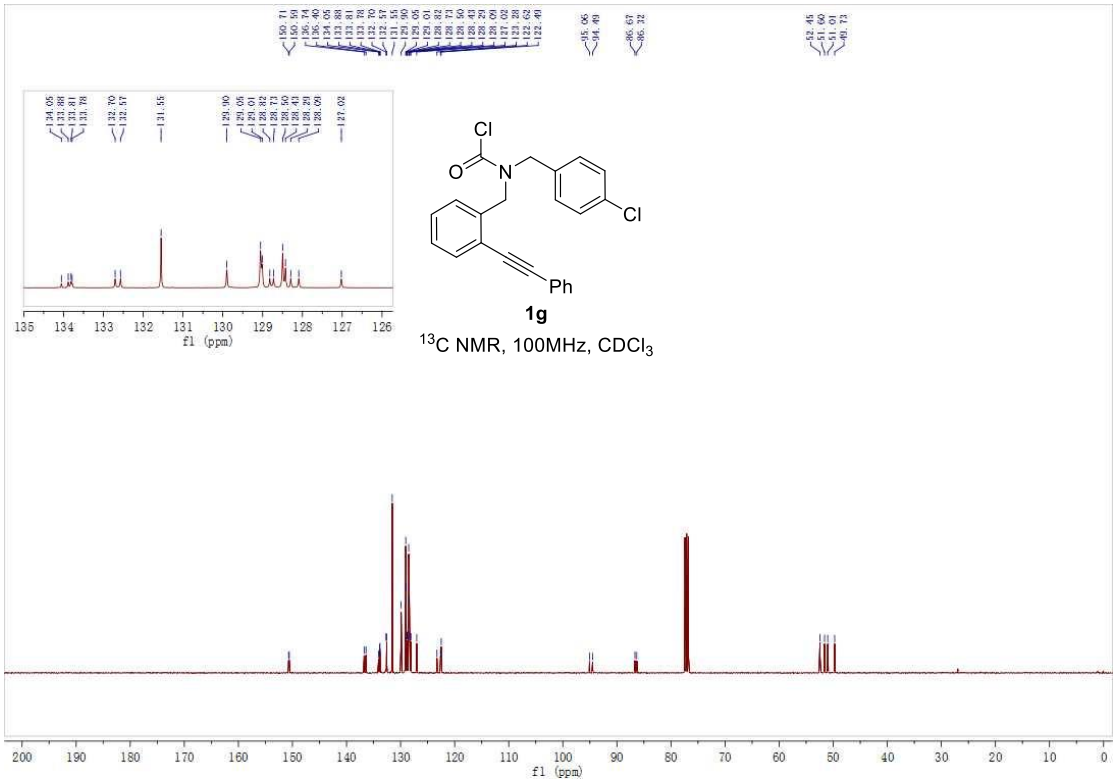

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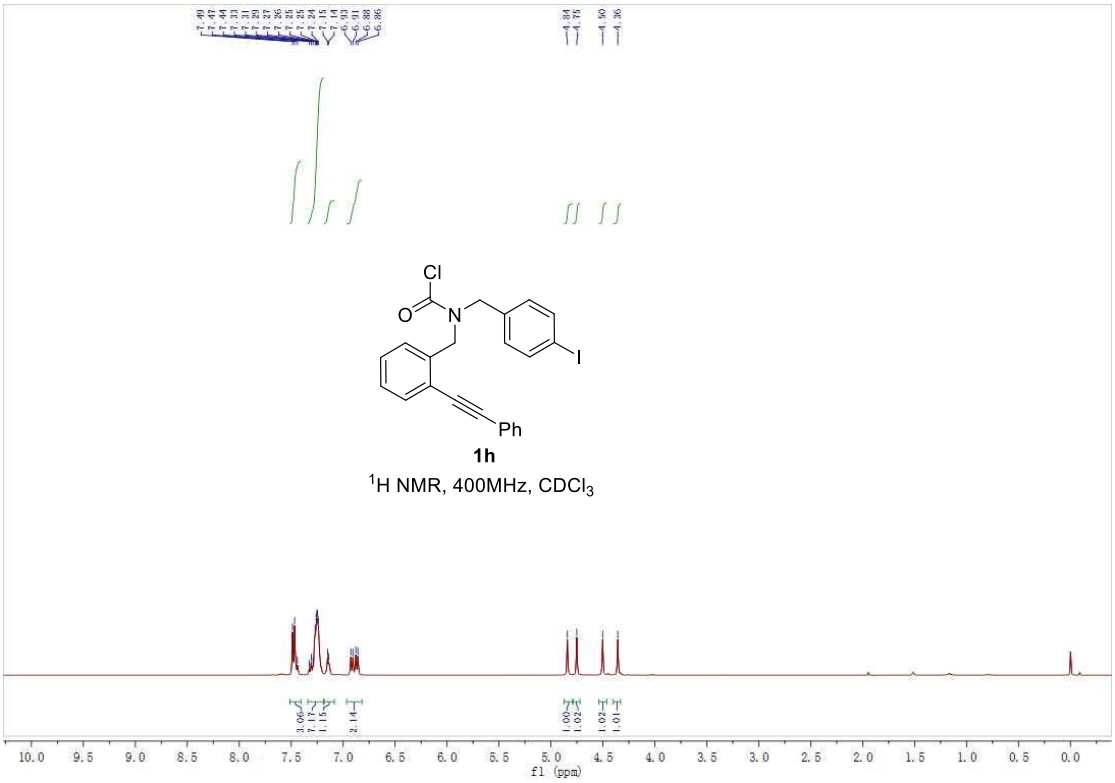

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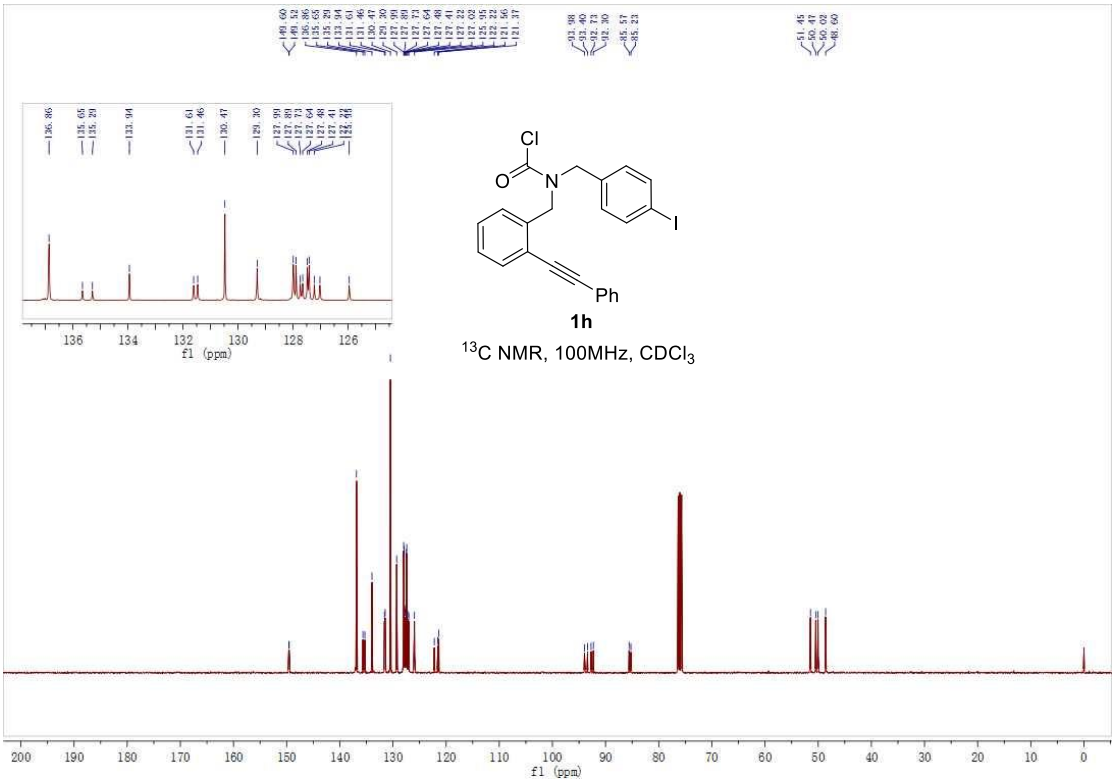

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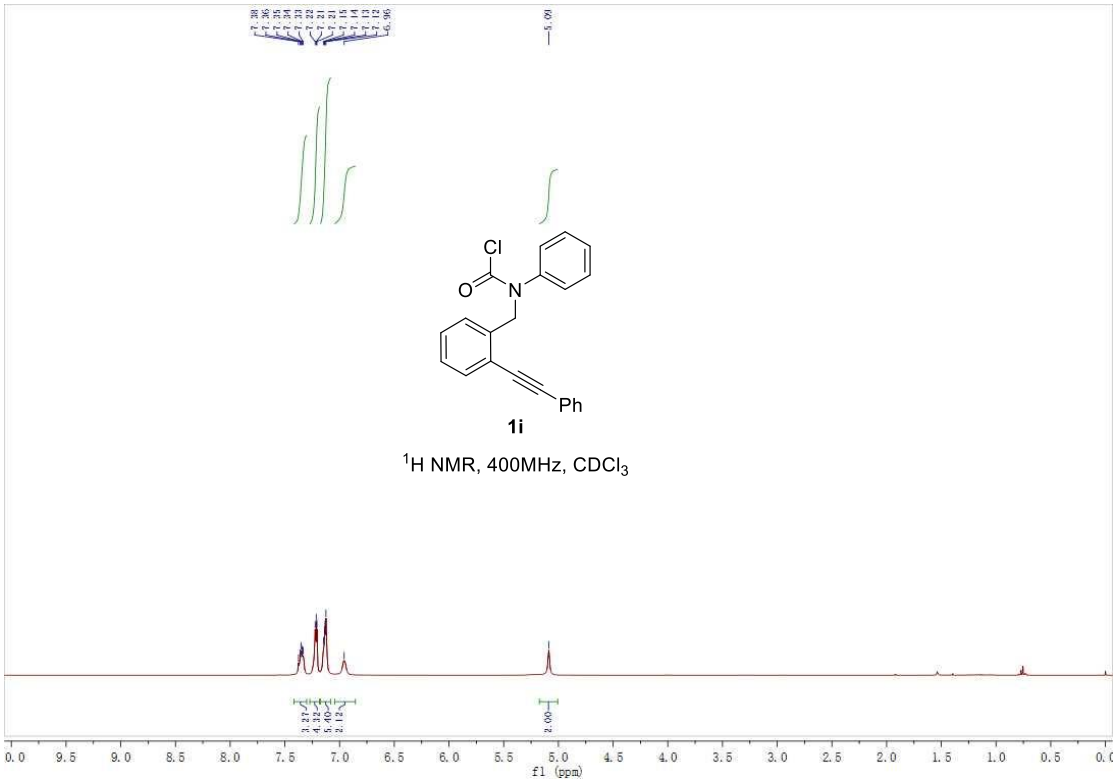

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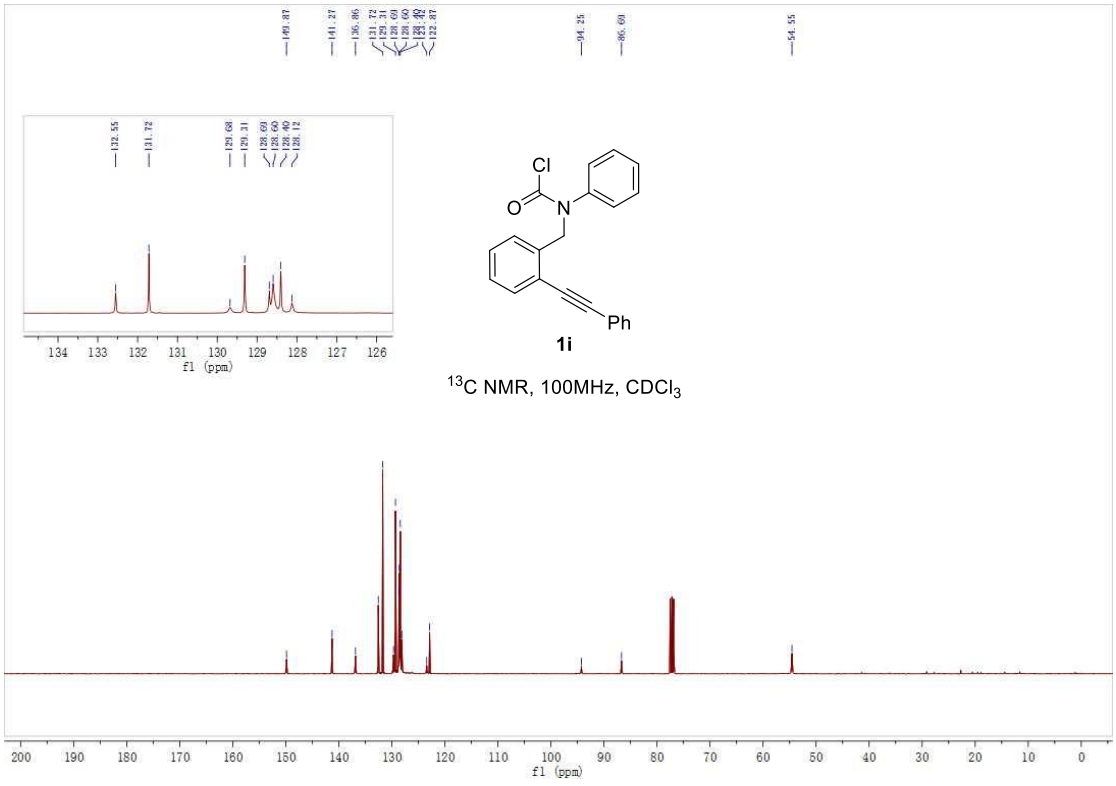

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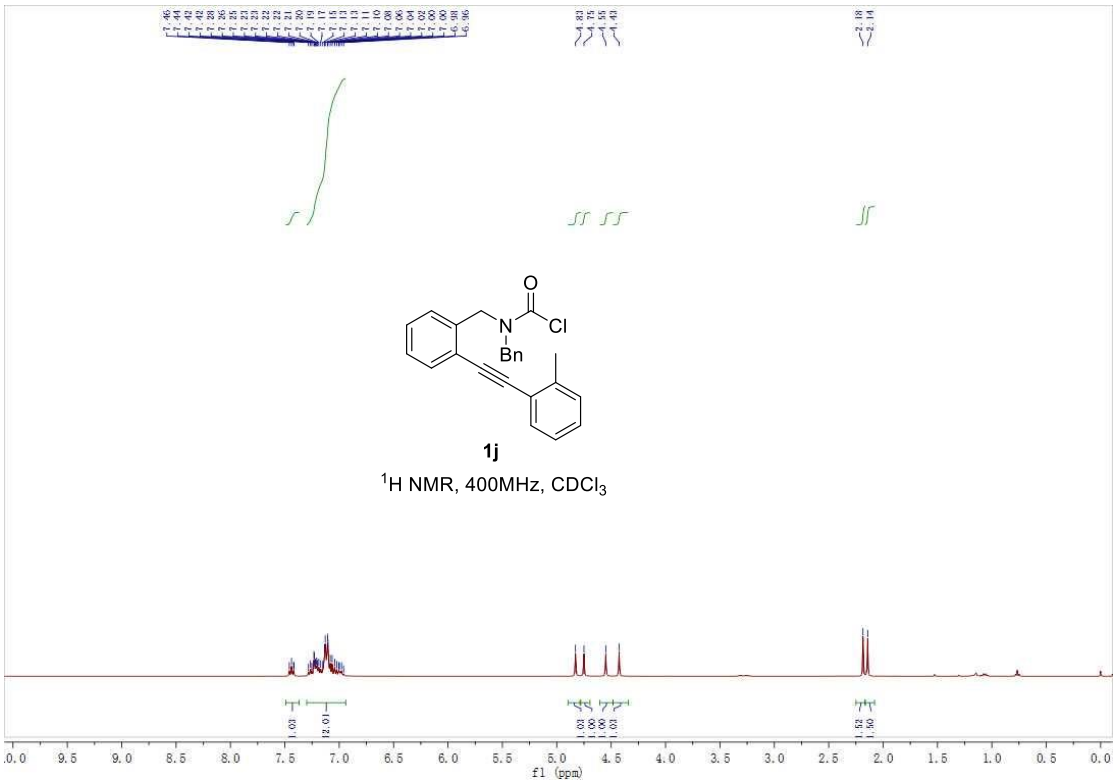

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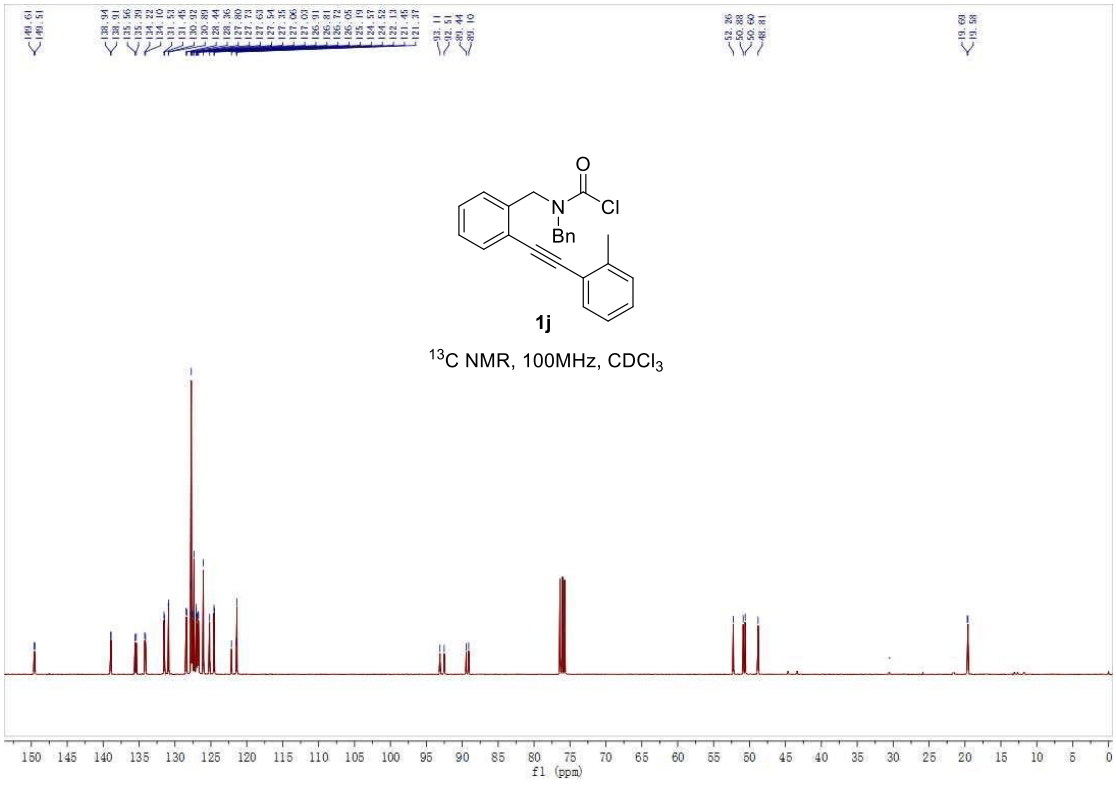

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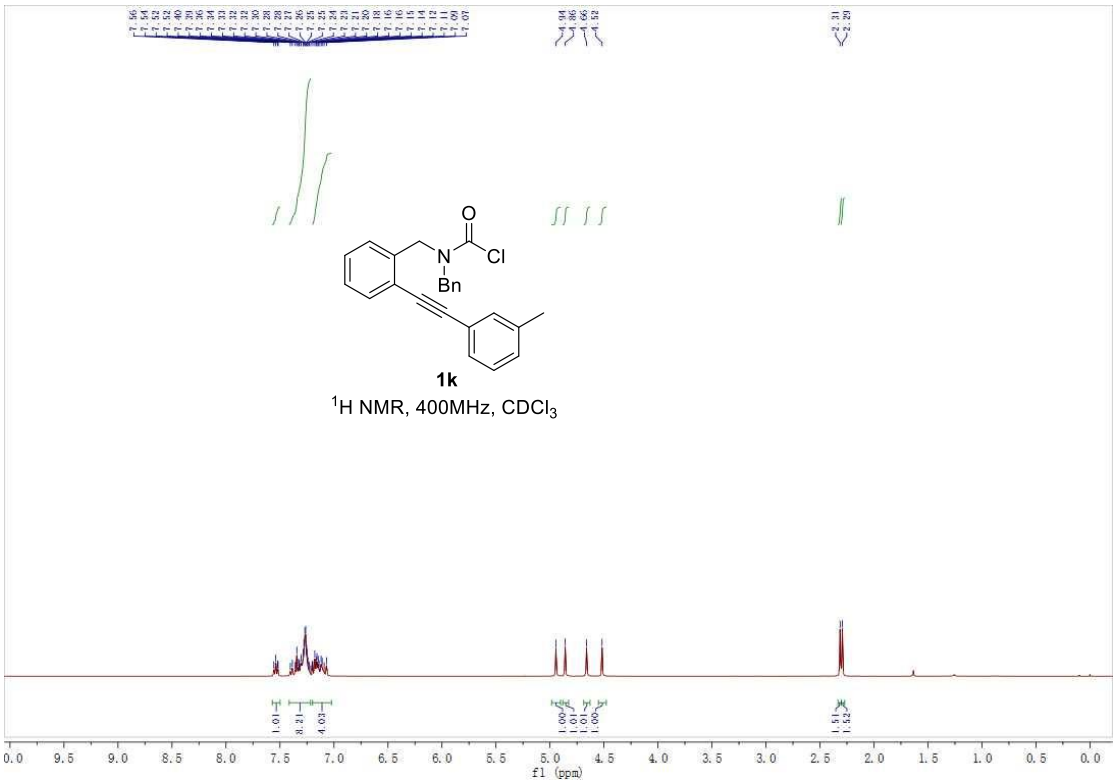

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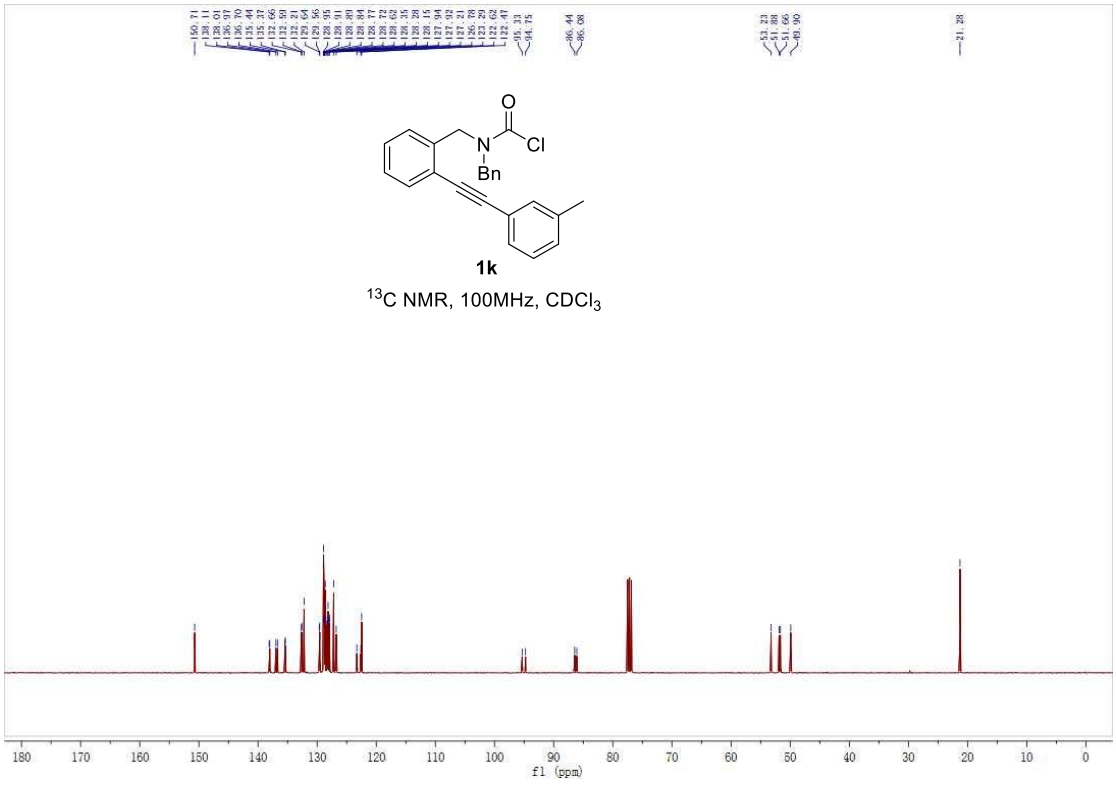

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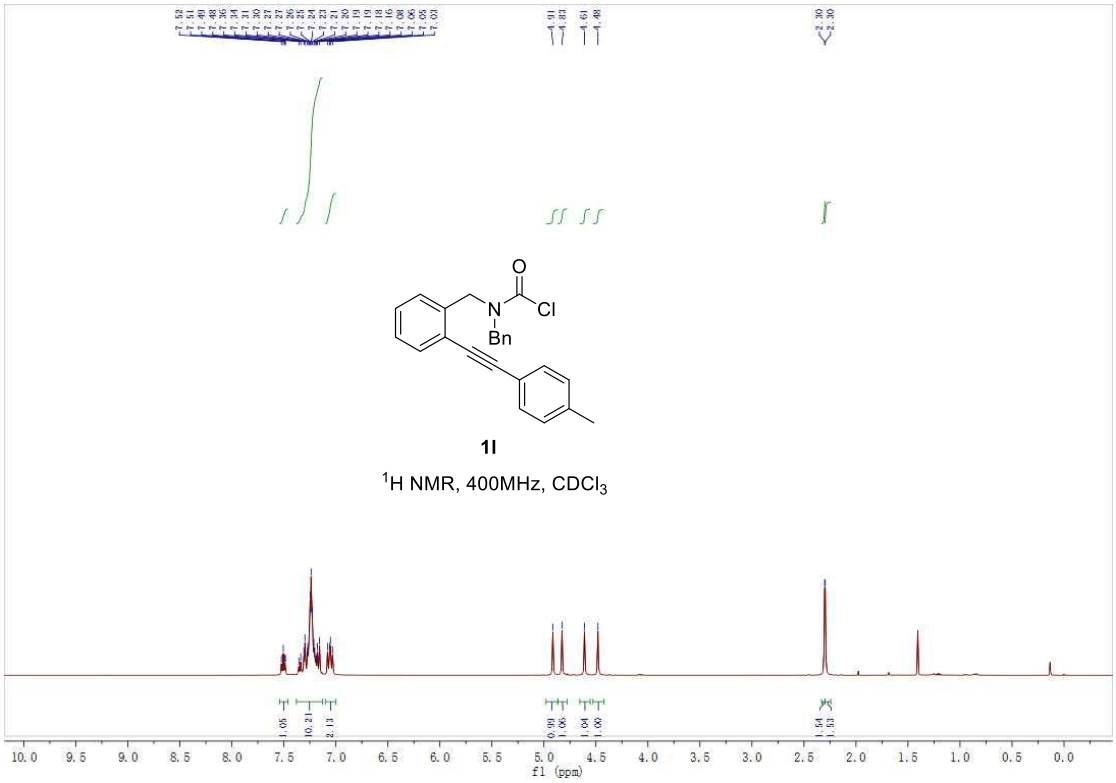

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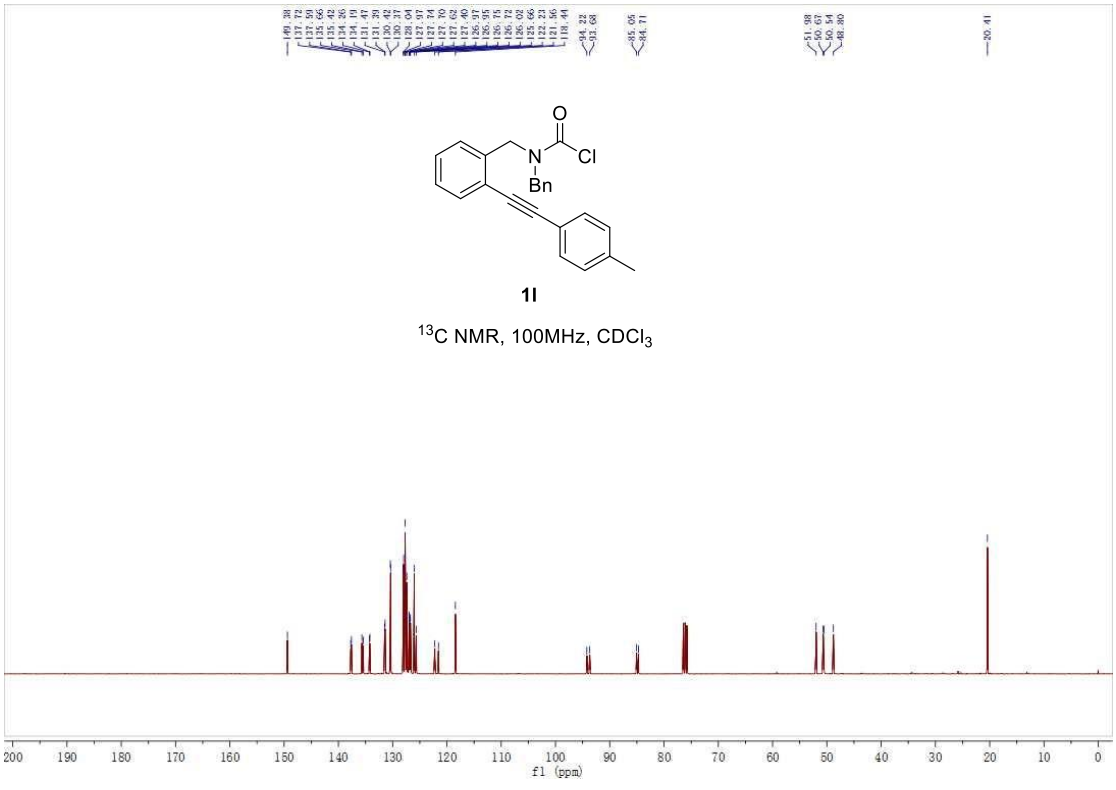

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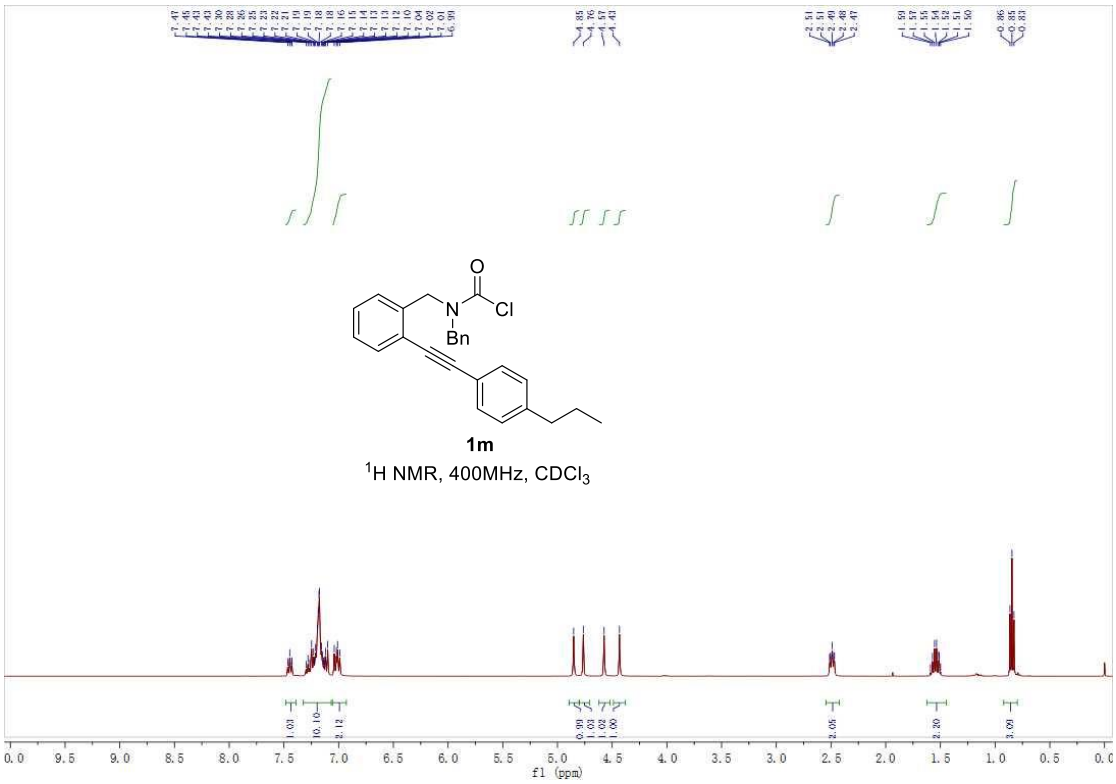

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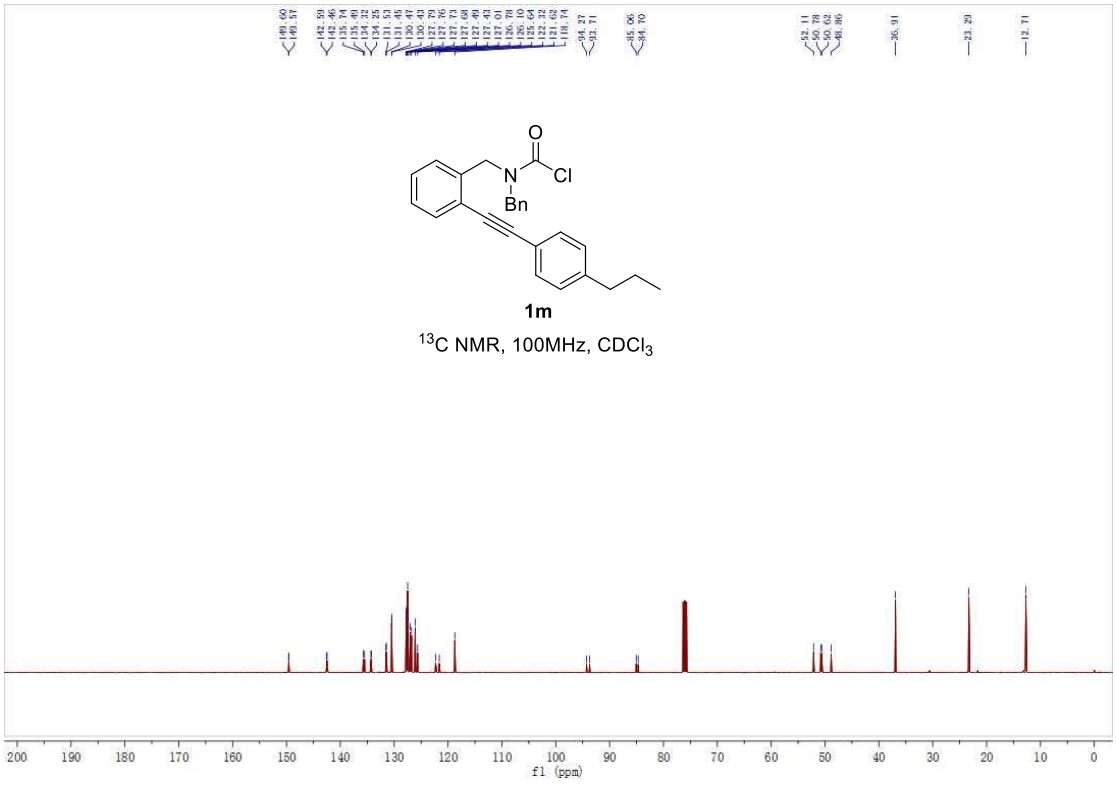

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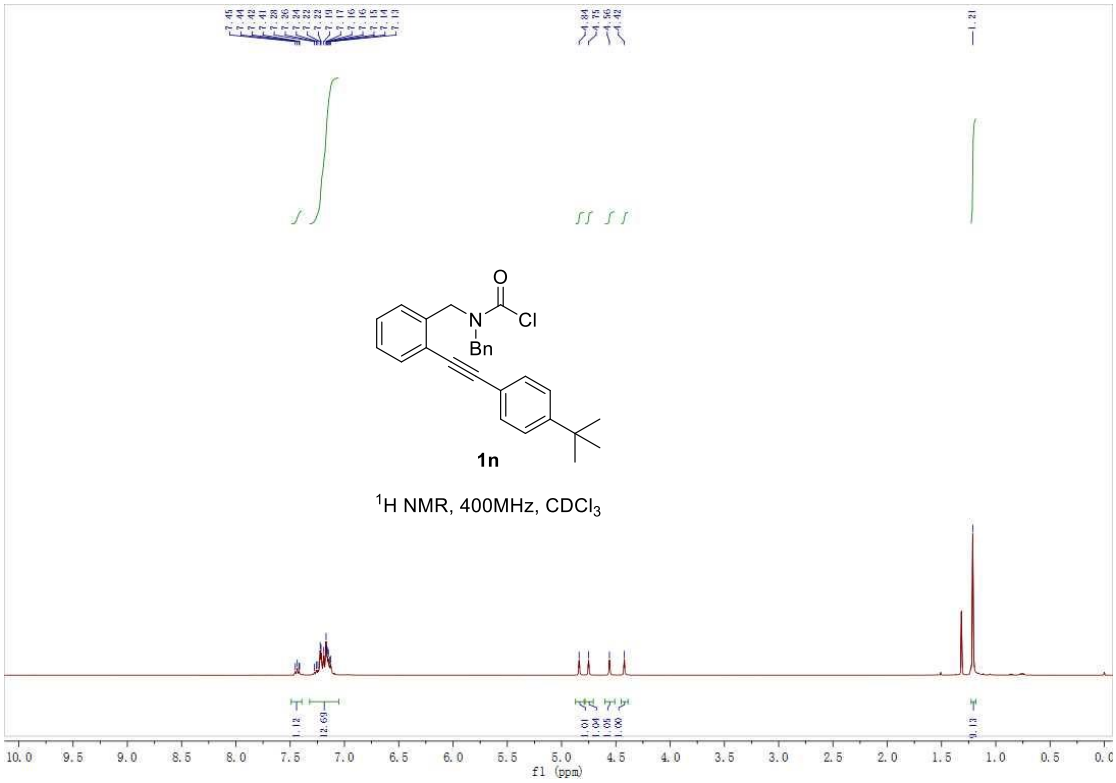

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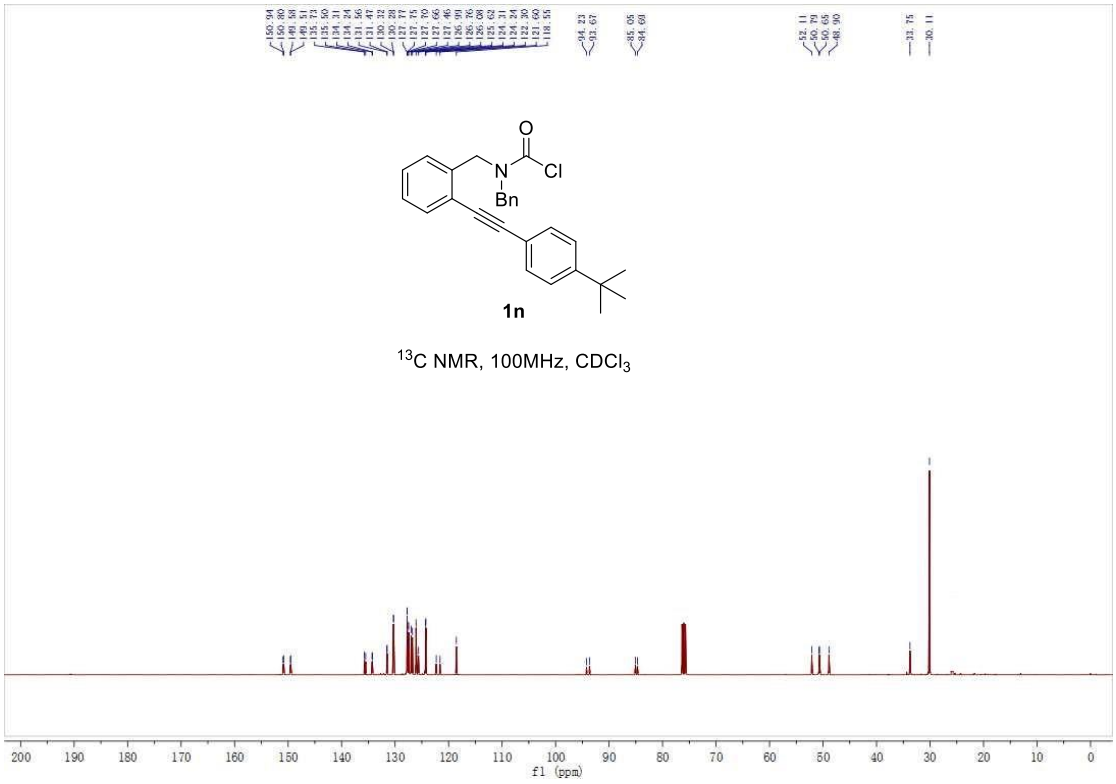

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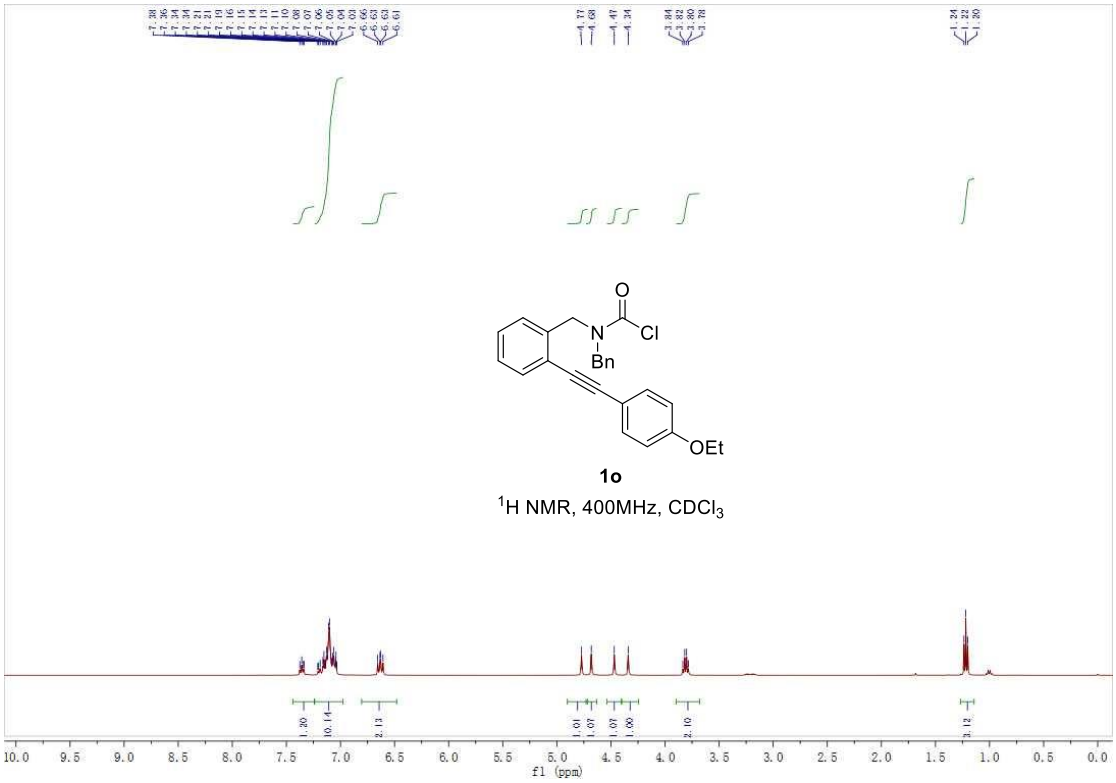

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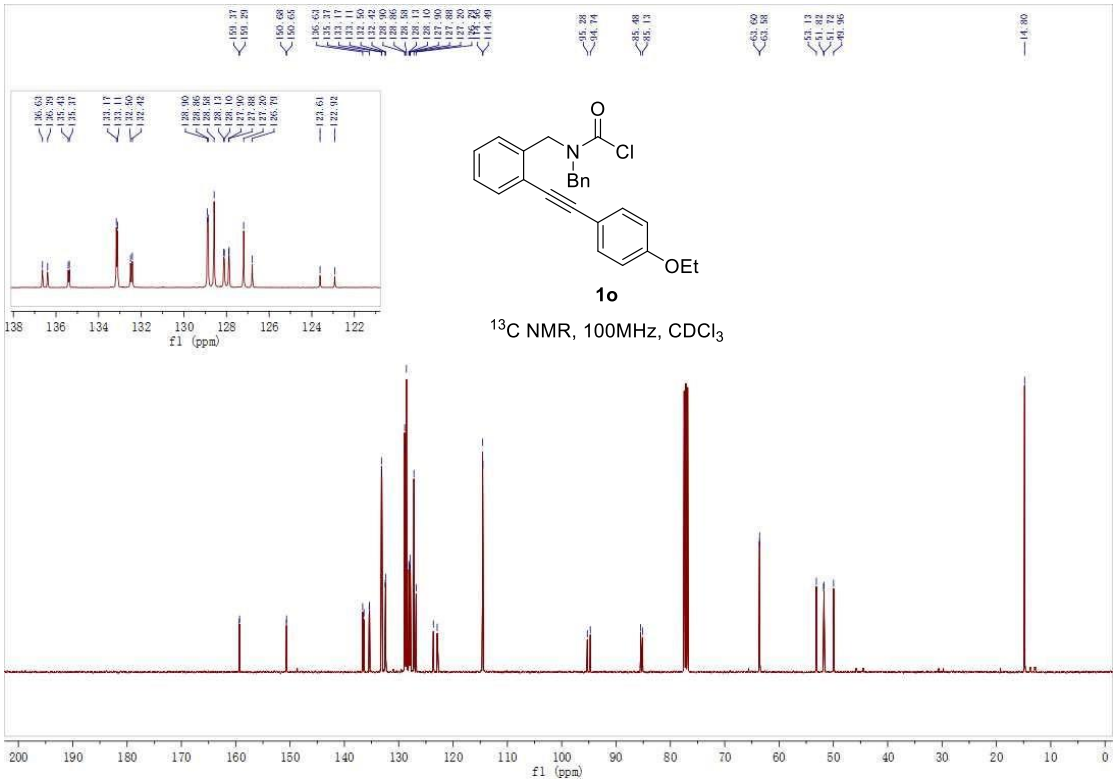

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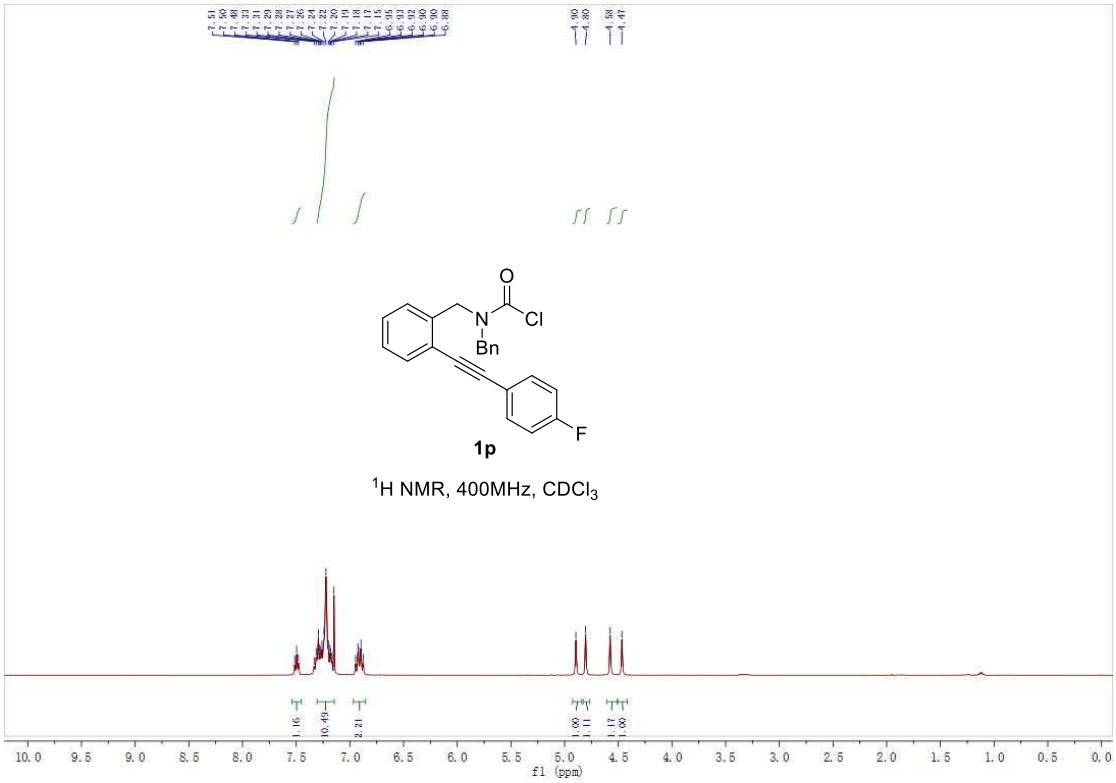

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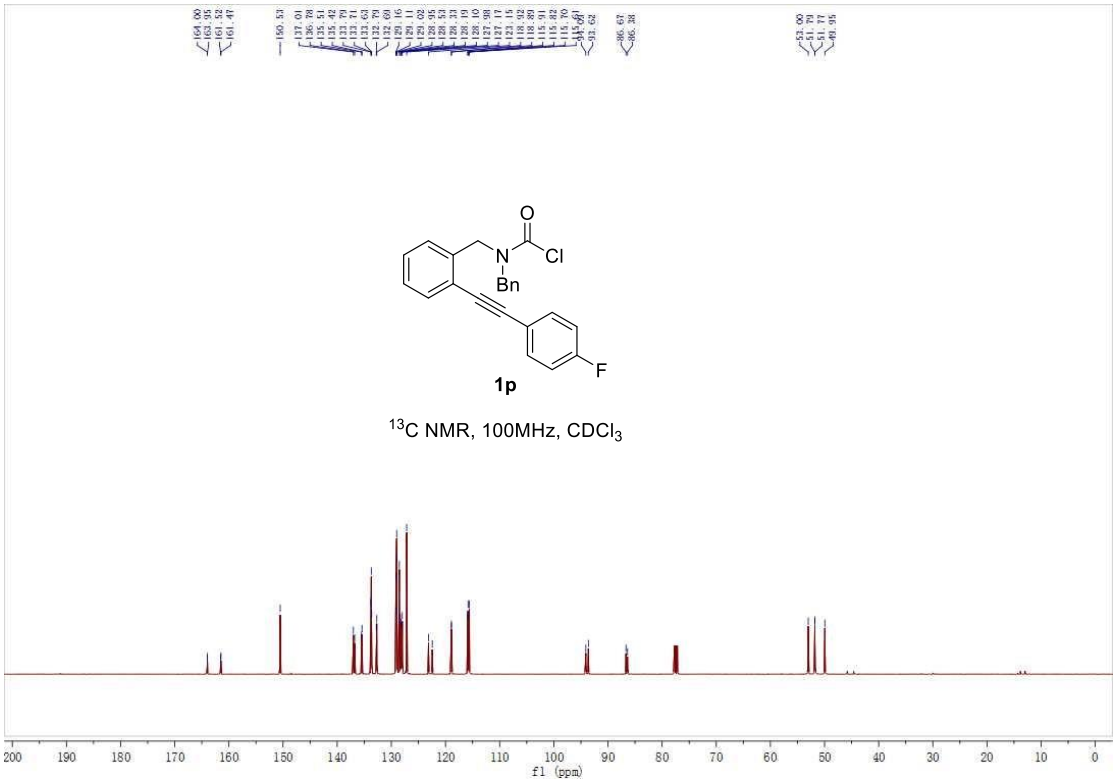

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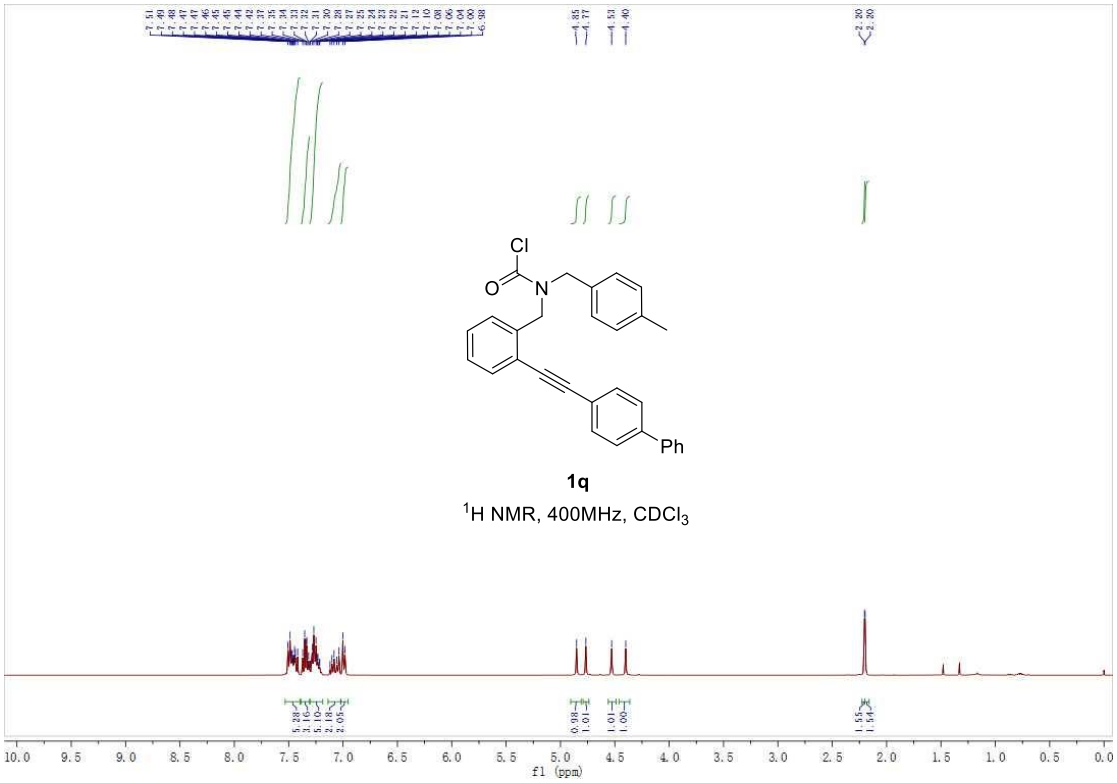

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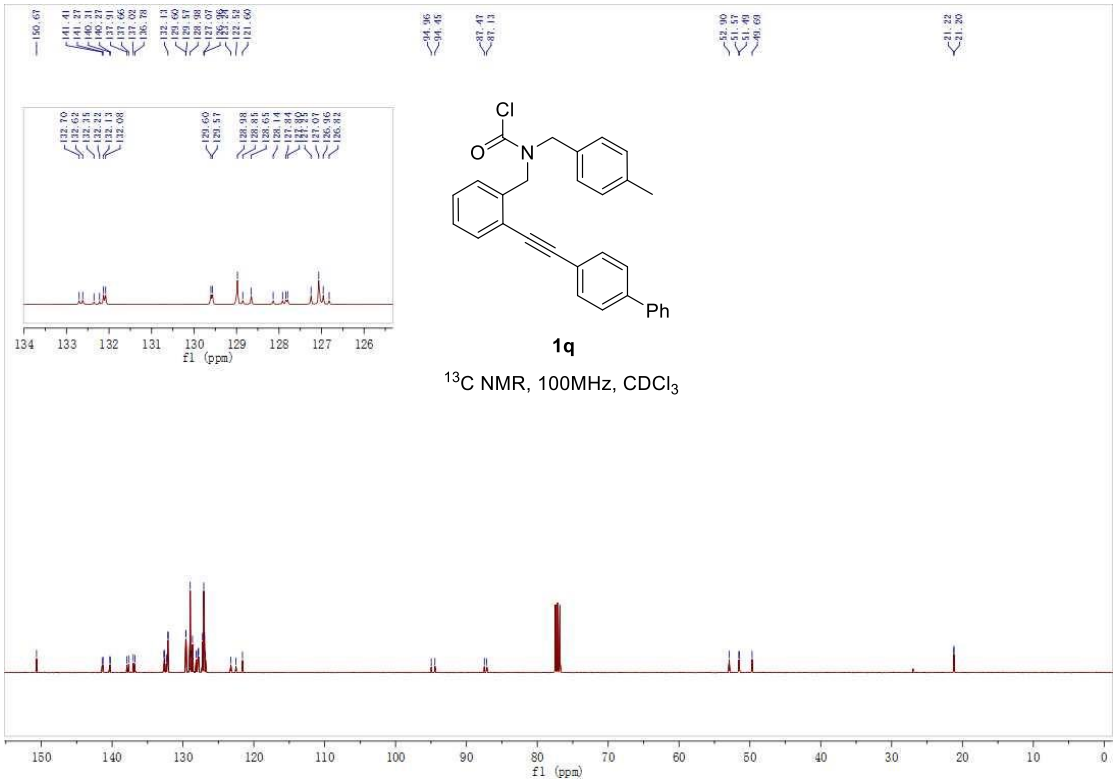

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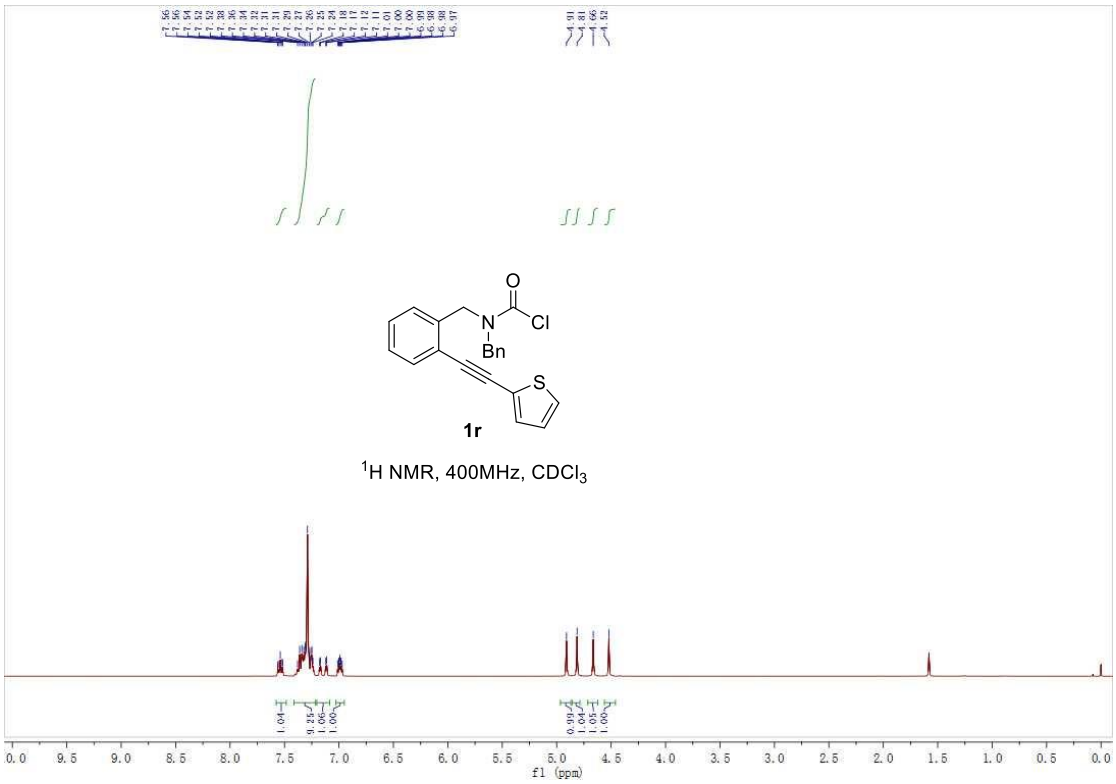

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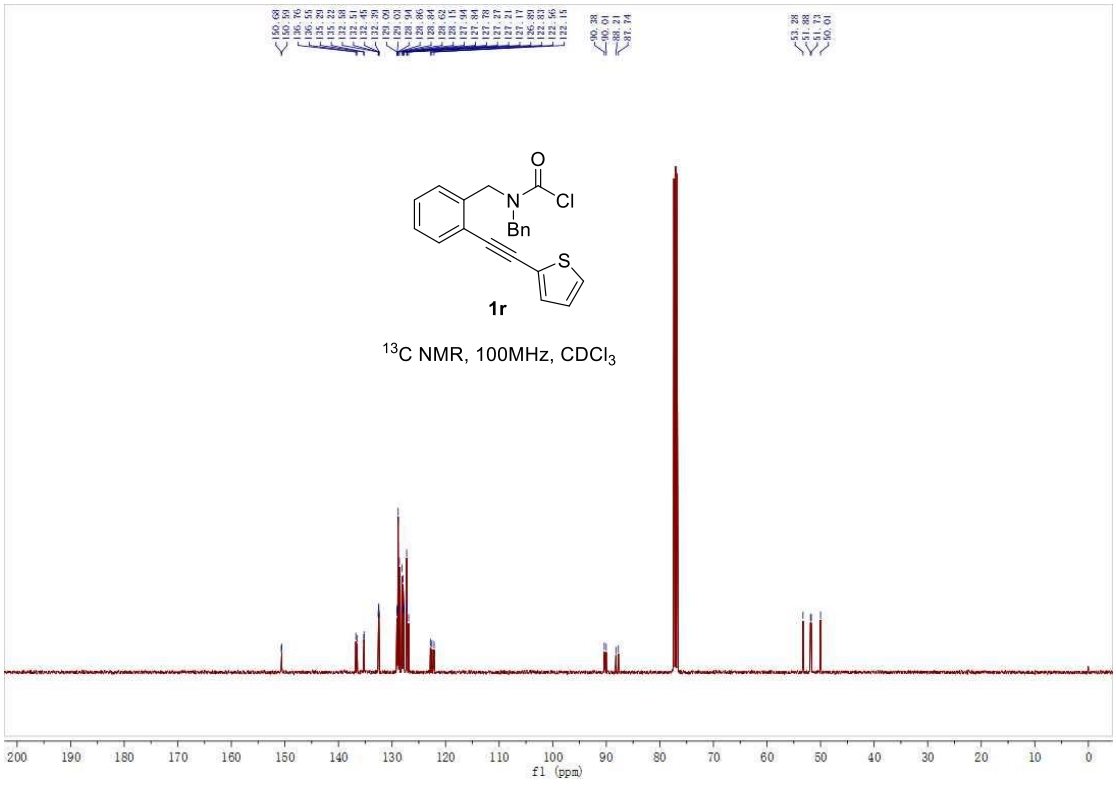

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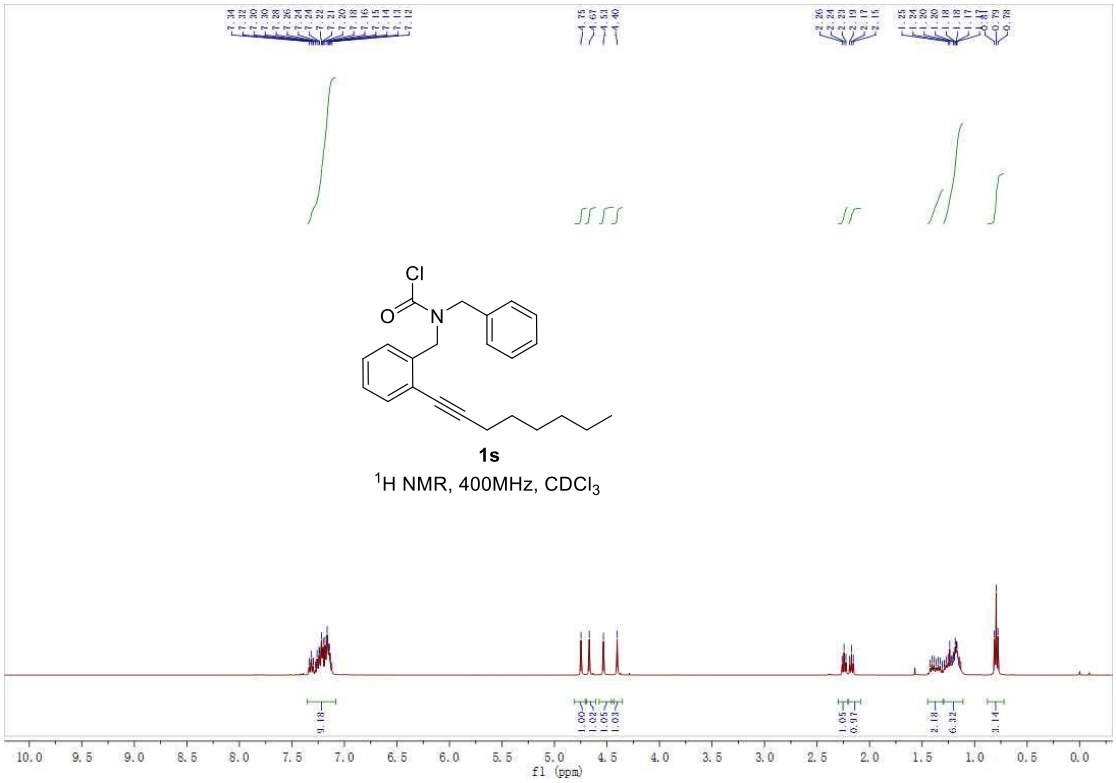

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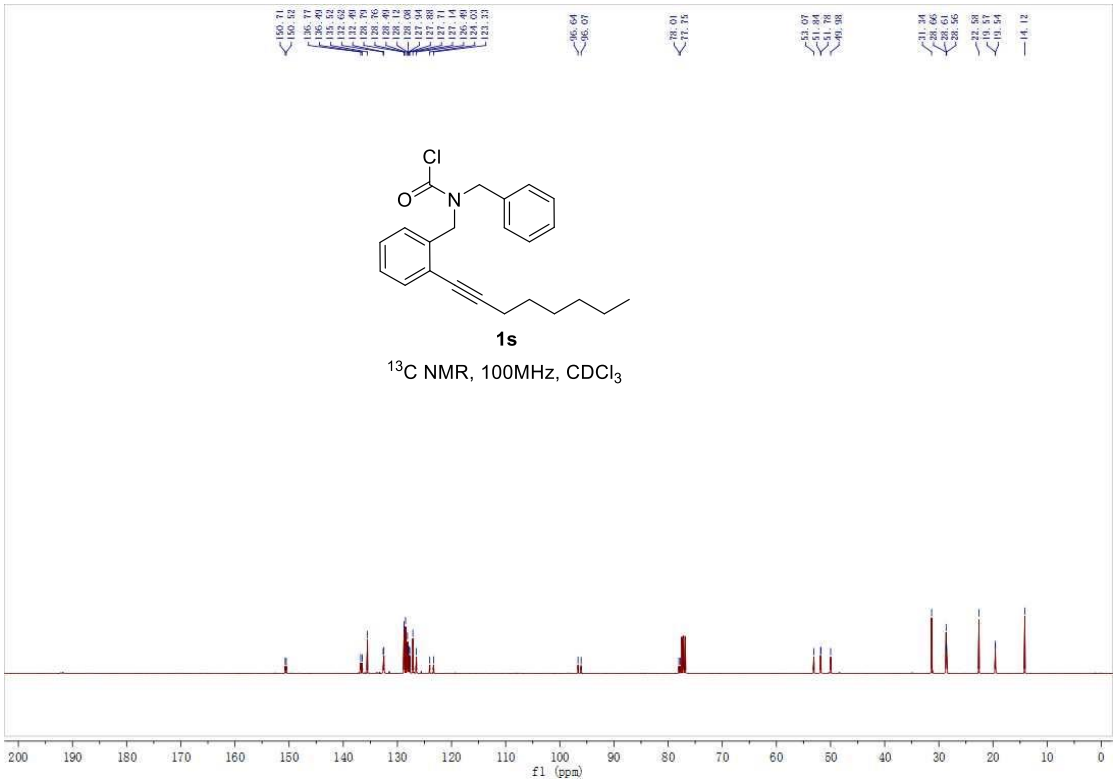

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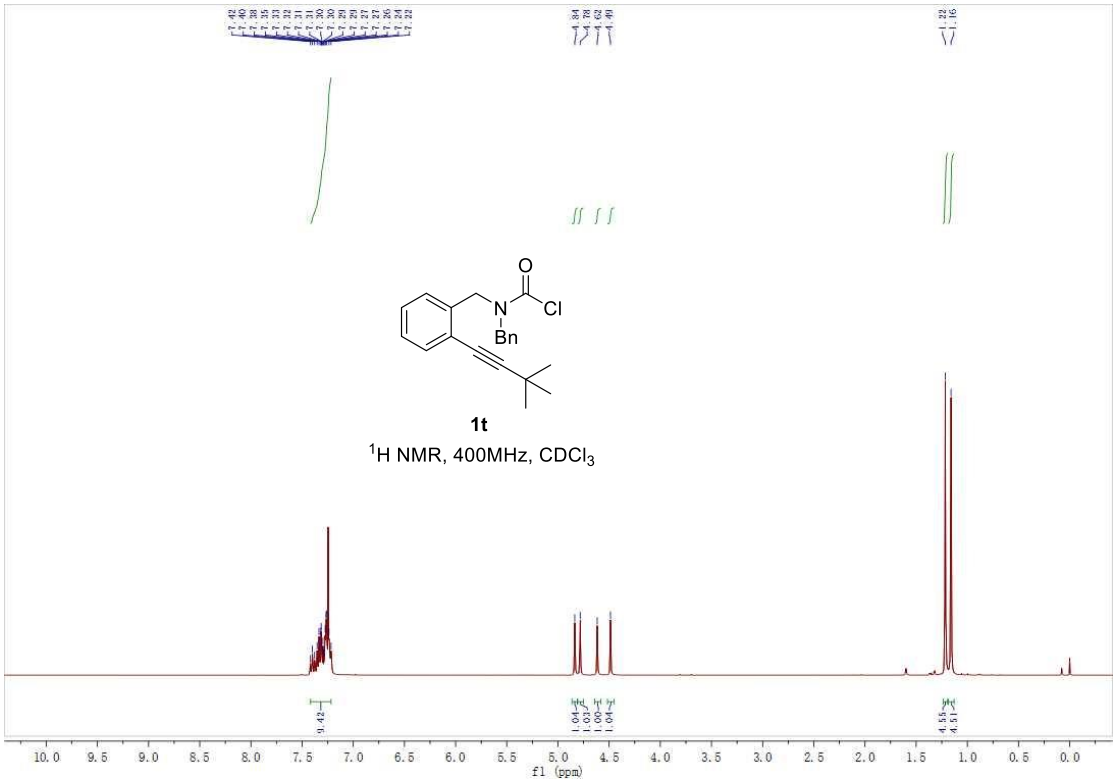

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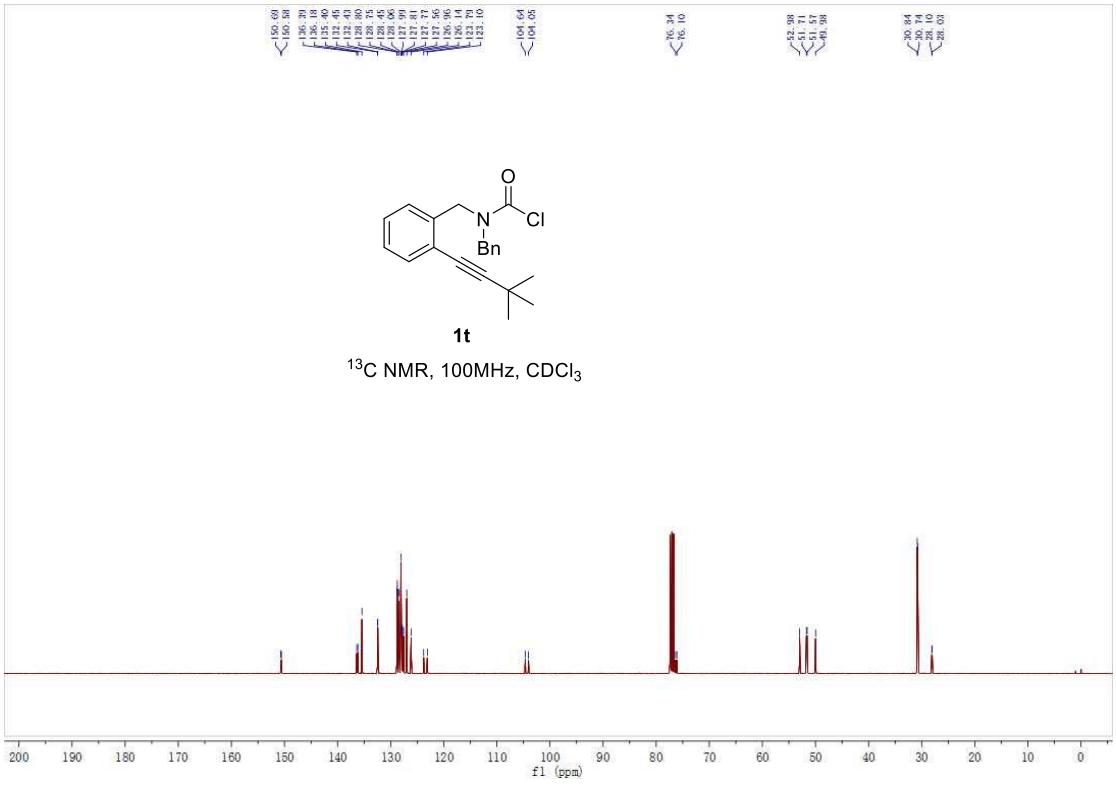

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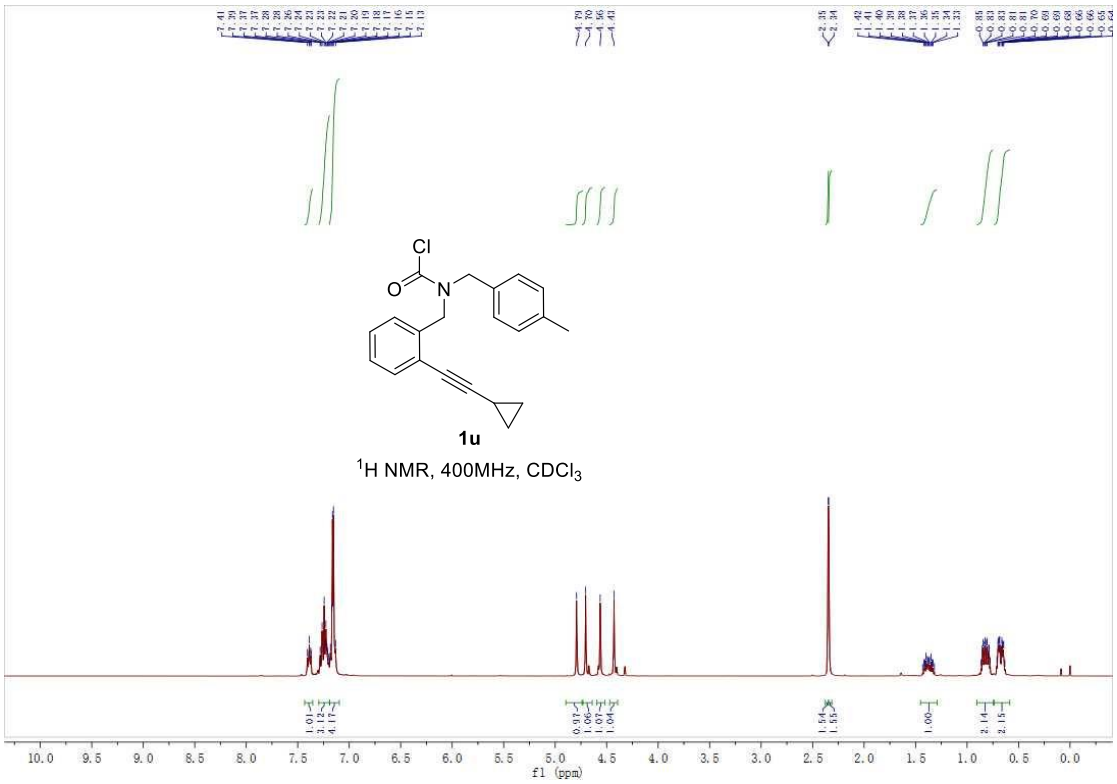
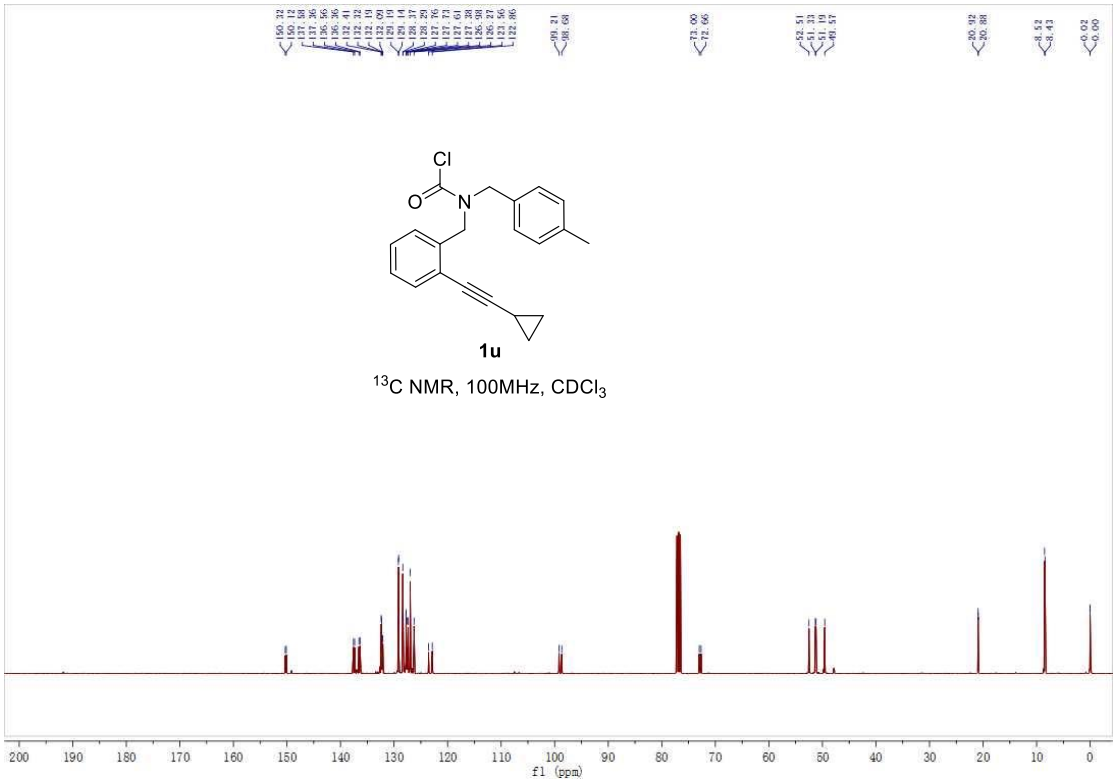
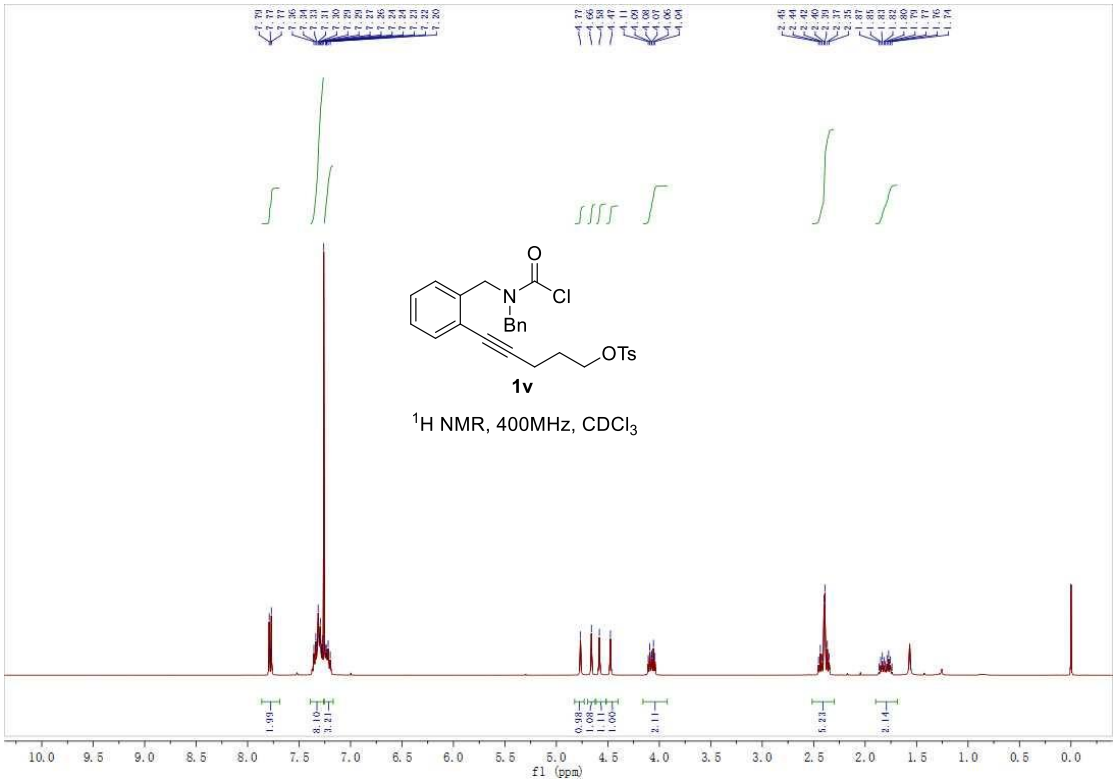
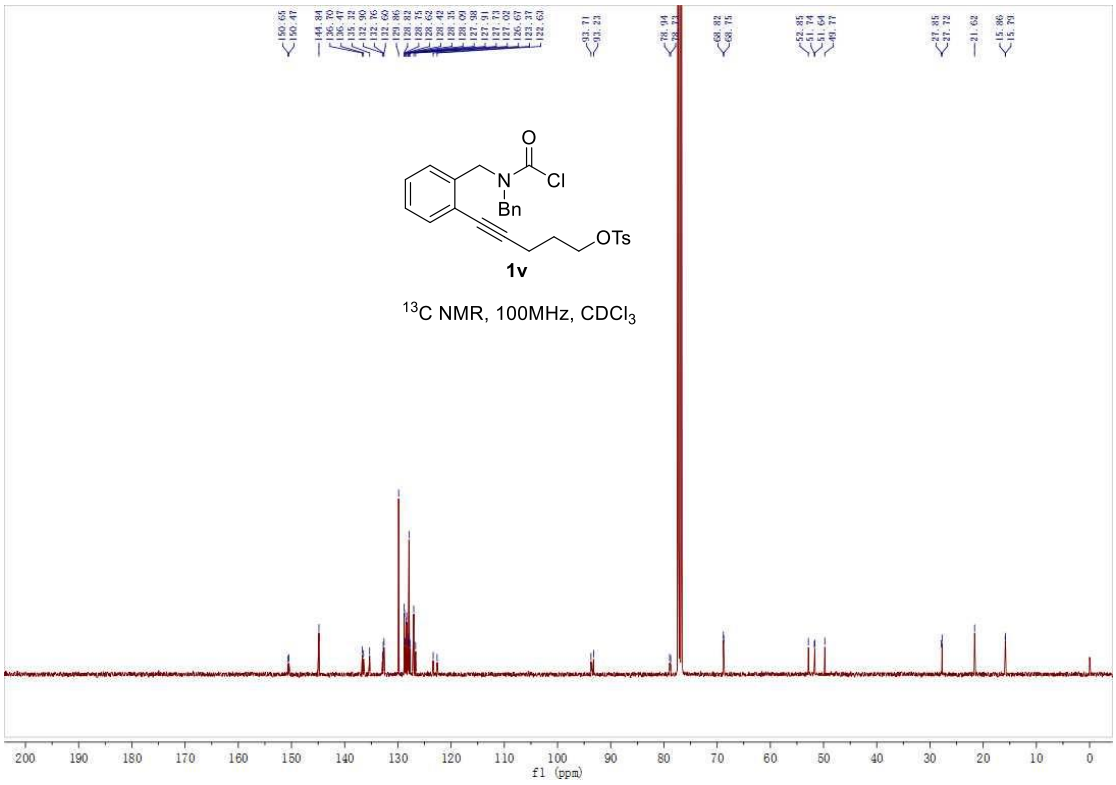

Cl
O
N
1u
1H NMR, 400MHz, CDCl3
f1 (ppm)

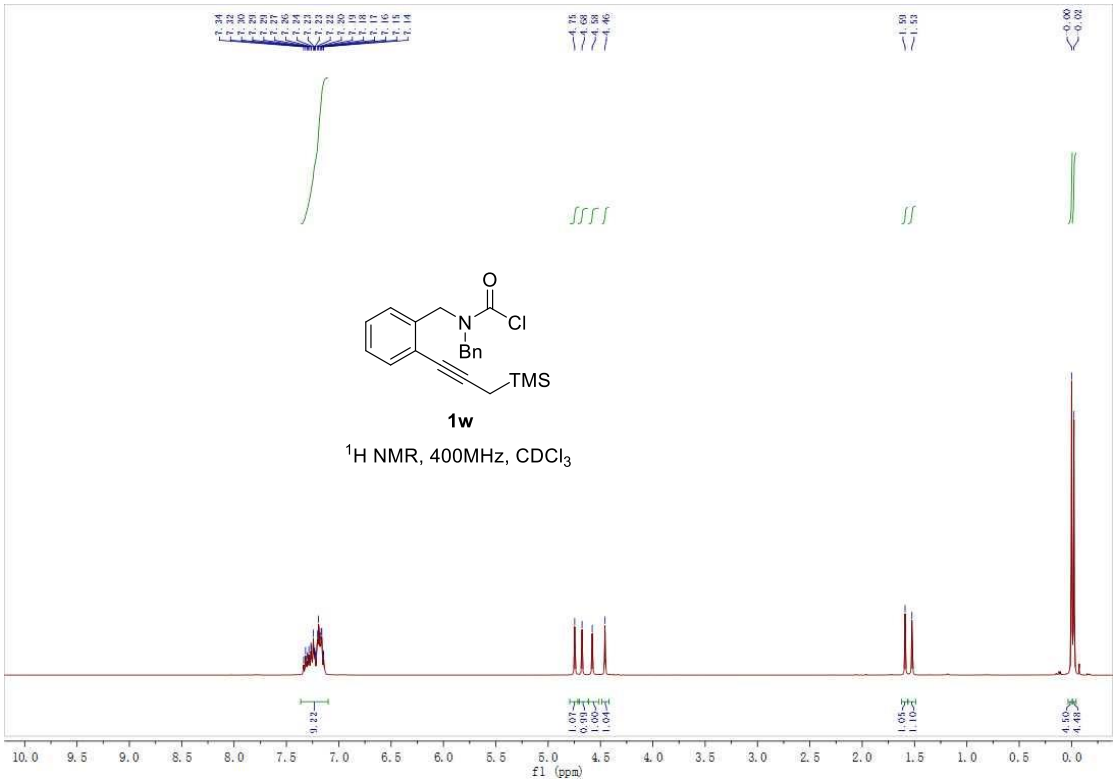

Cl
O
N
1u
13C NMR, 100MHz, CDCl3
f1 (ppm)



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

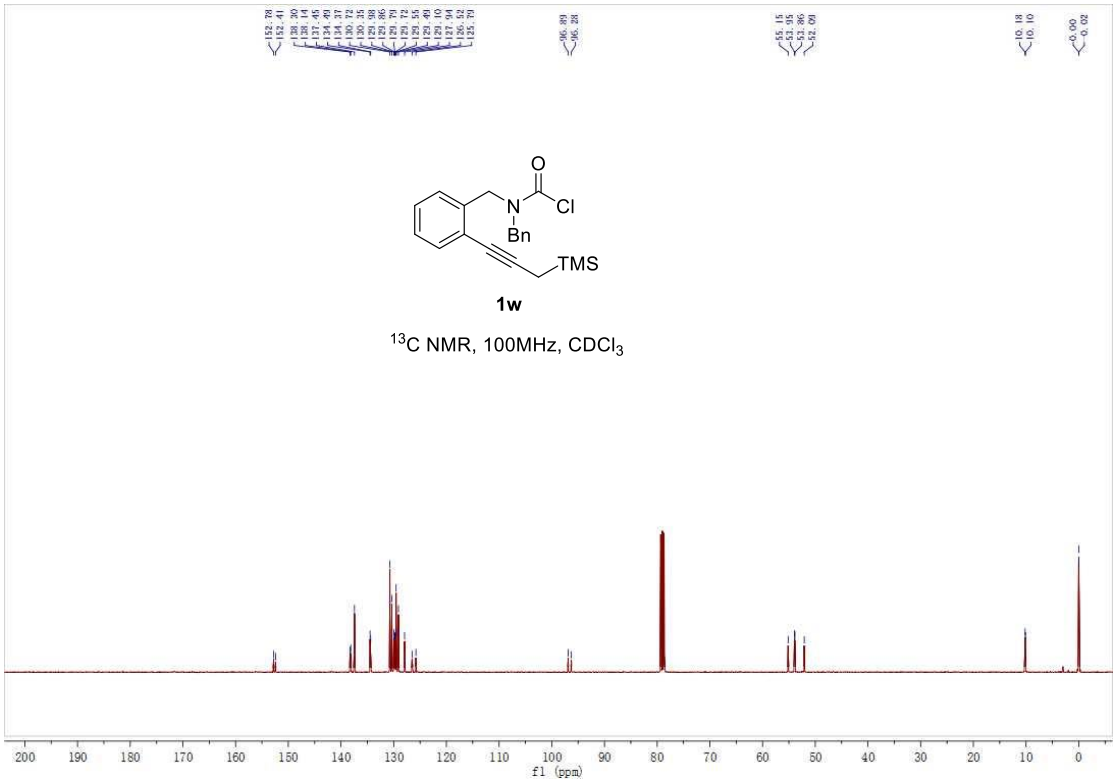


^{13}C NMR, 100MHz, $CDCl_3$



1w

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



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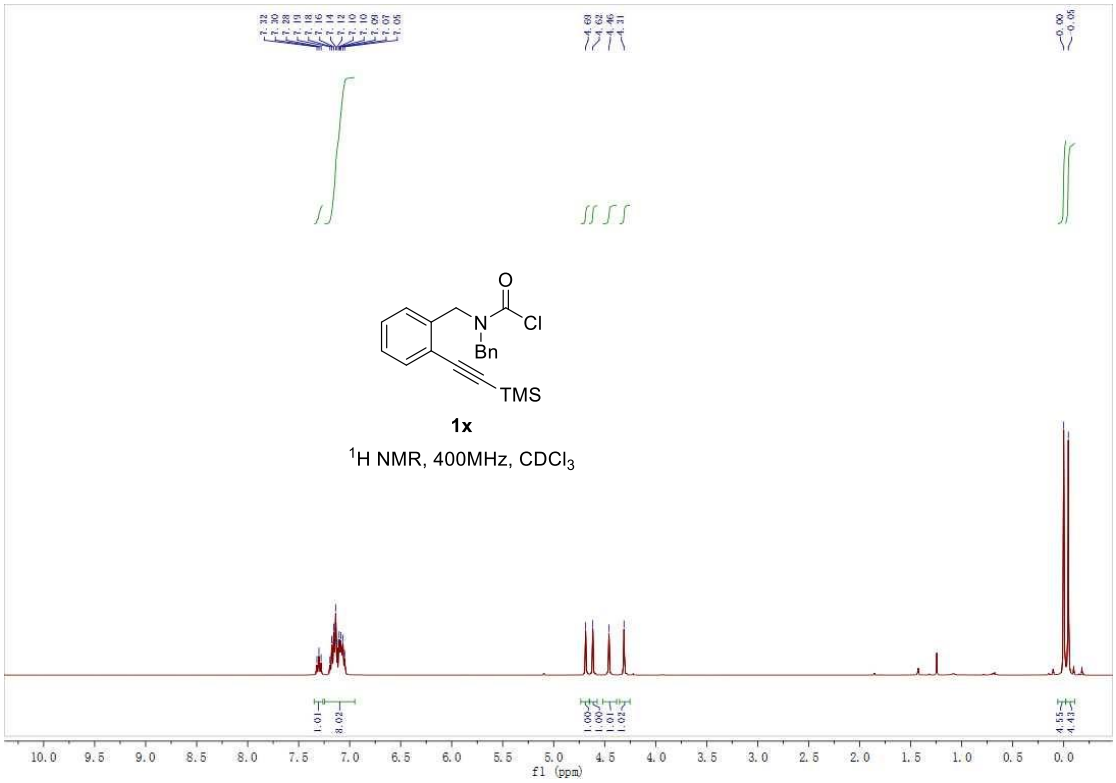
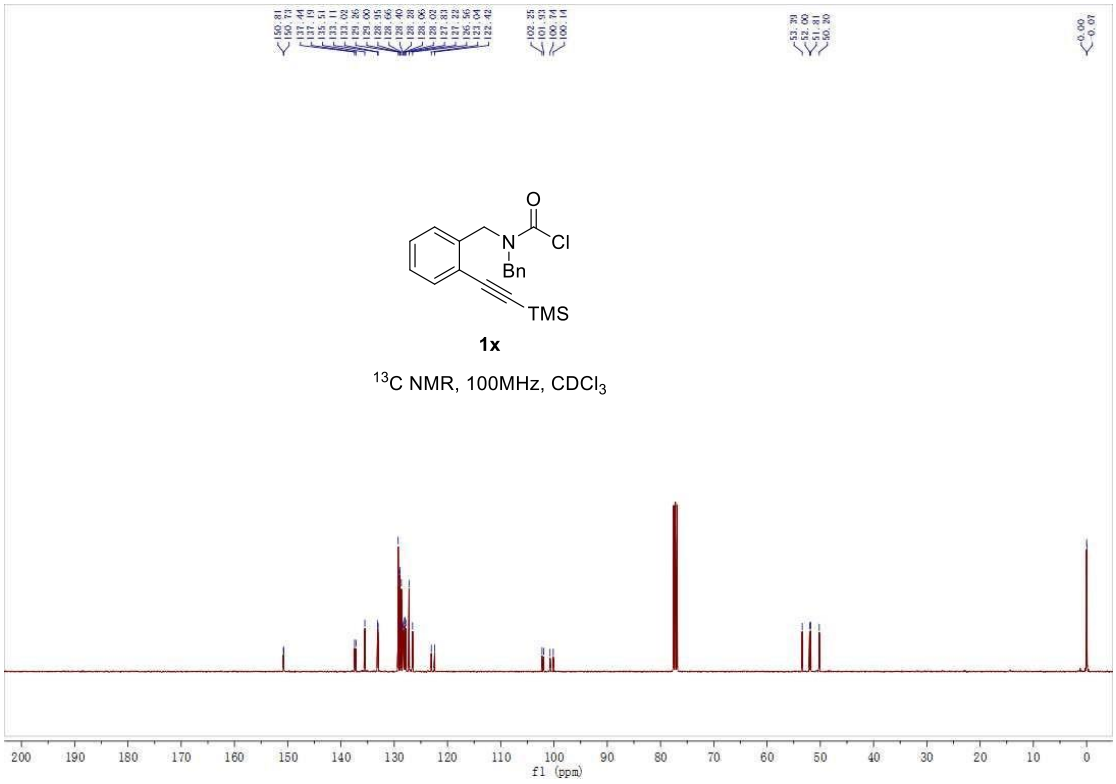
^{13}C NMR, 100MHz, $CDCl_3$



1x

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



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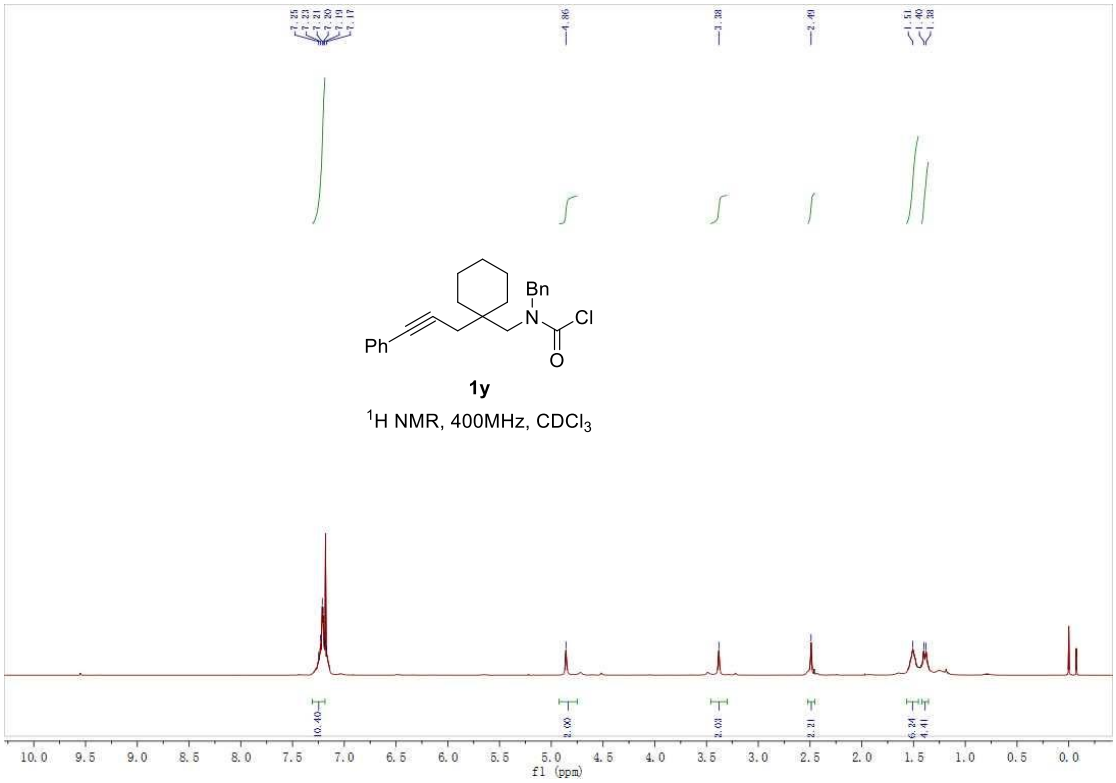
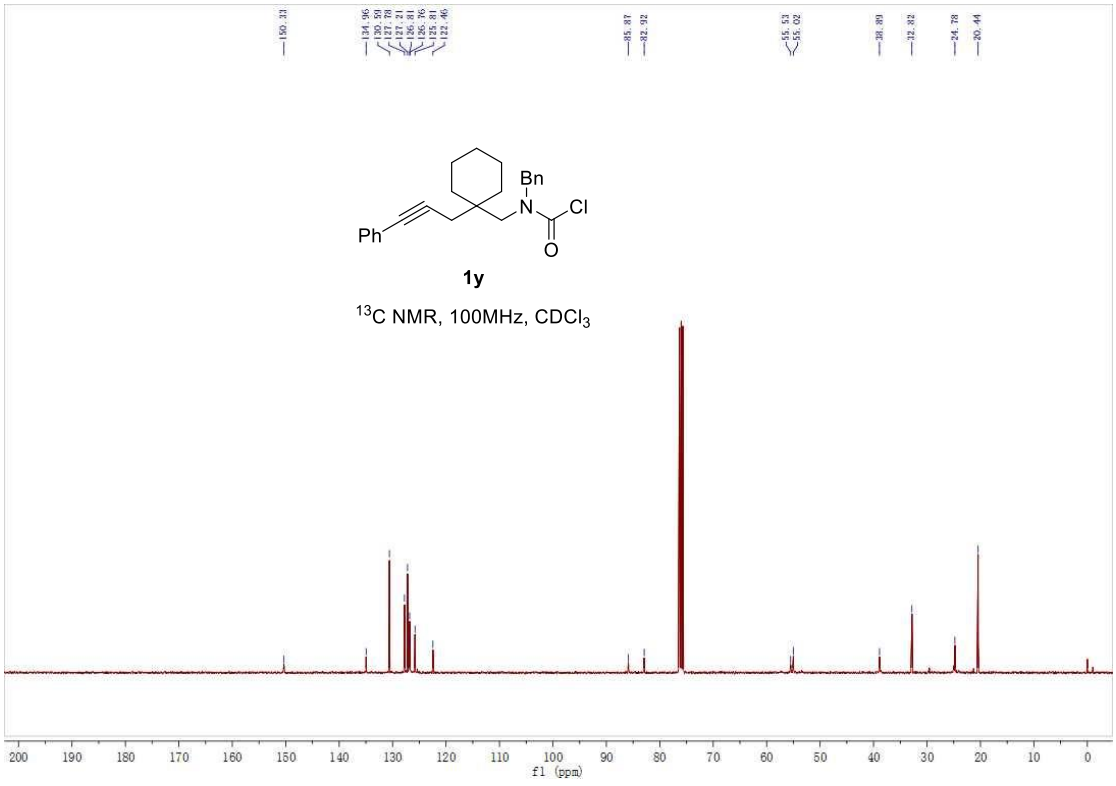
^{13}C NMR, 100MHz, $CDCl_3$



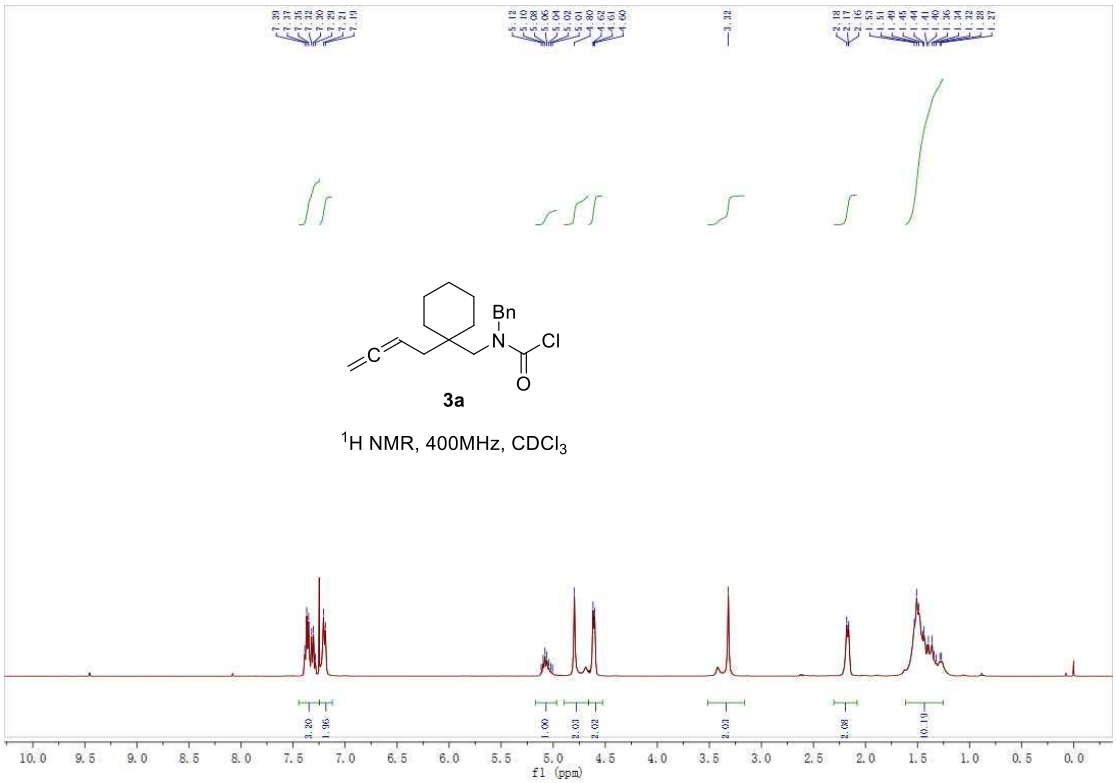
1y

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



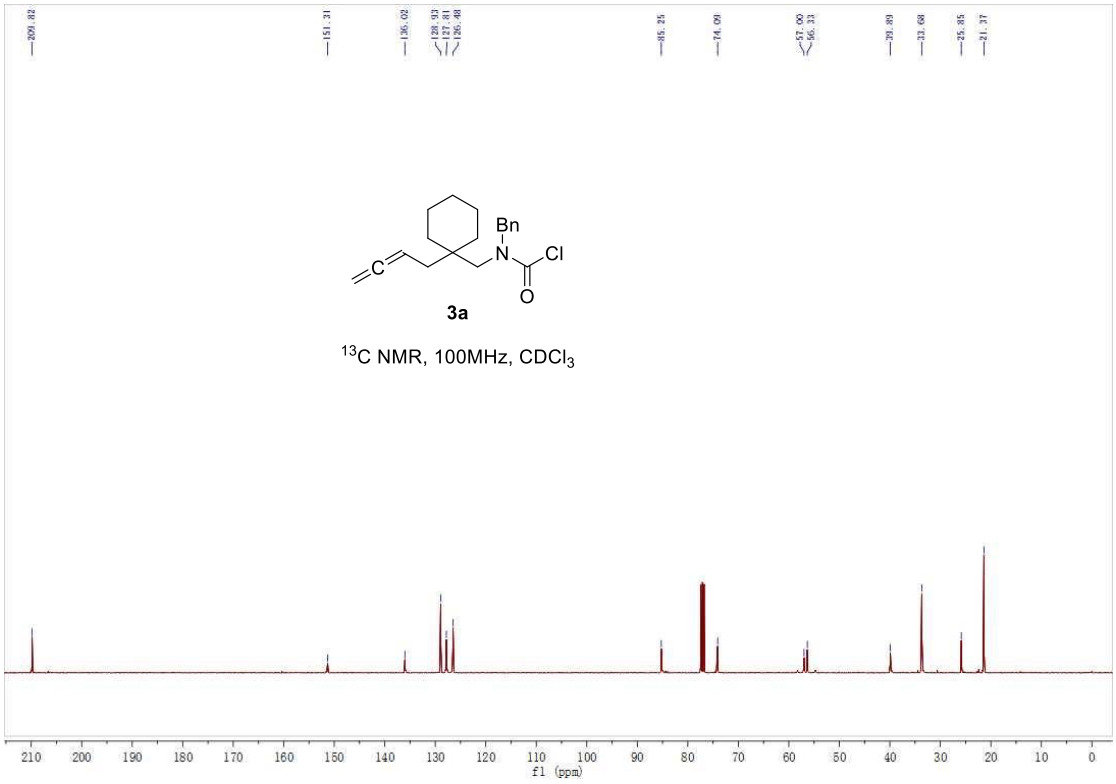
1y

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



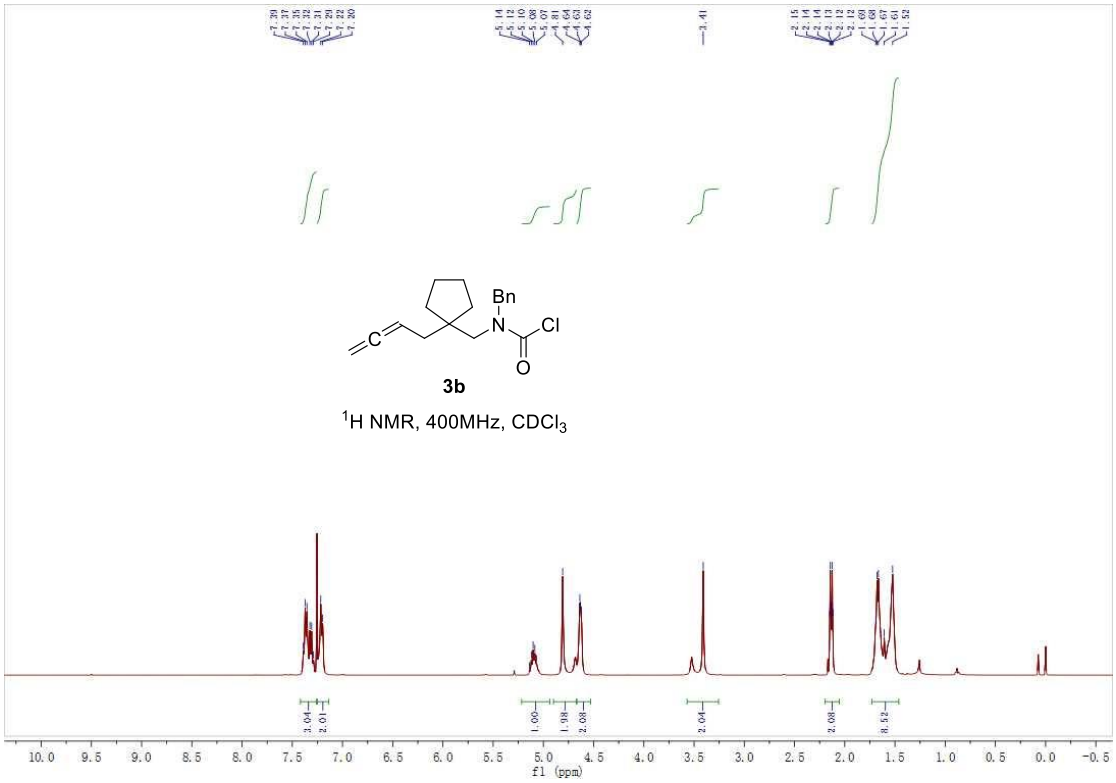
3a

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



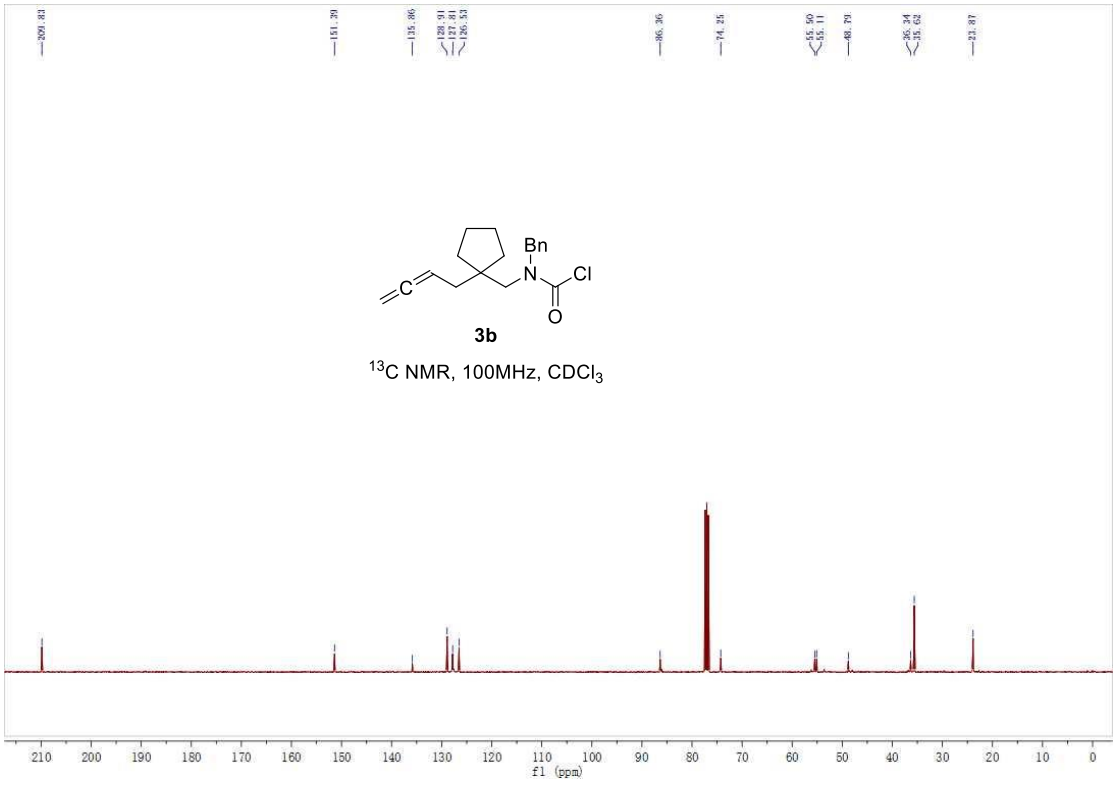
3a

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



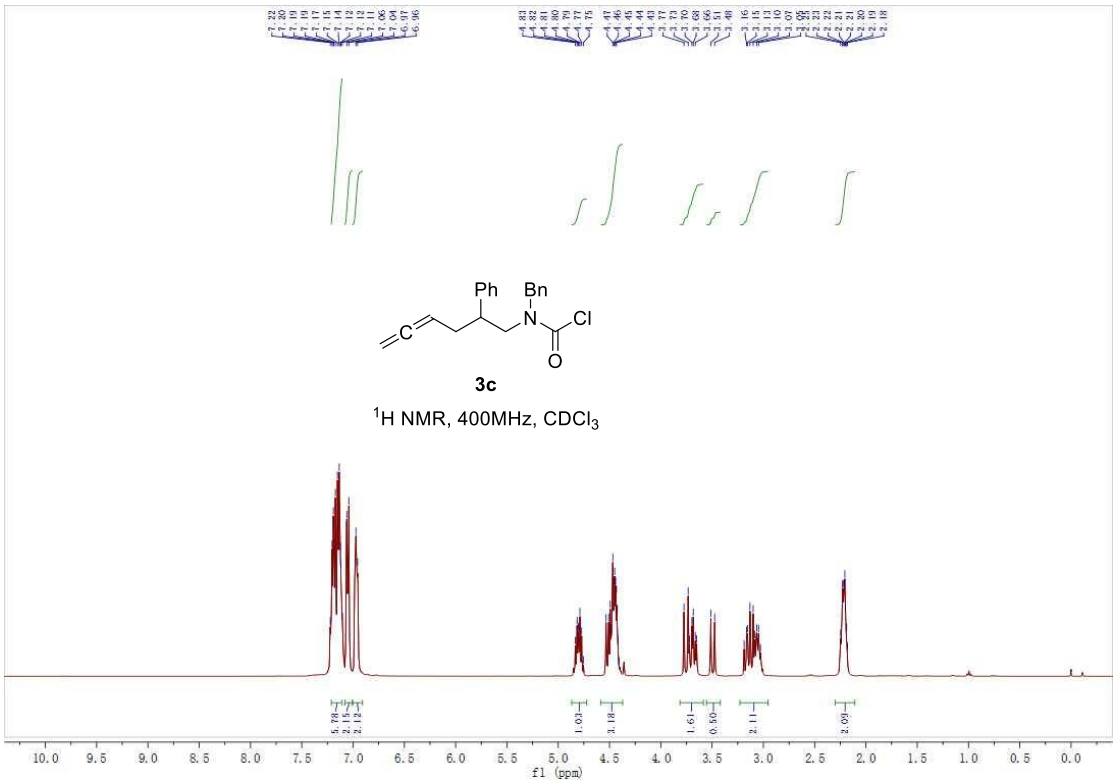
3b

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



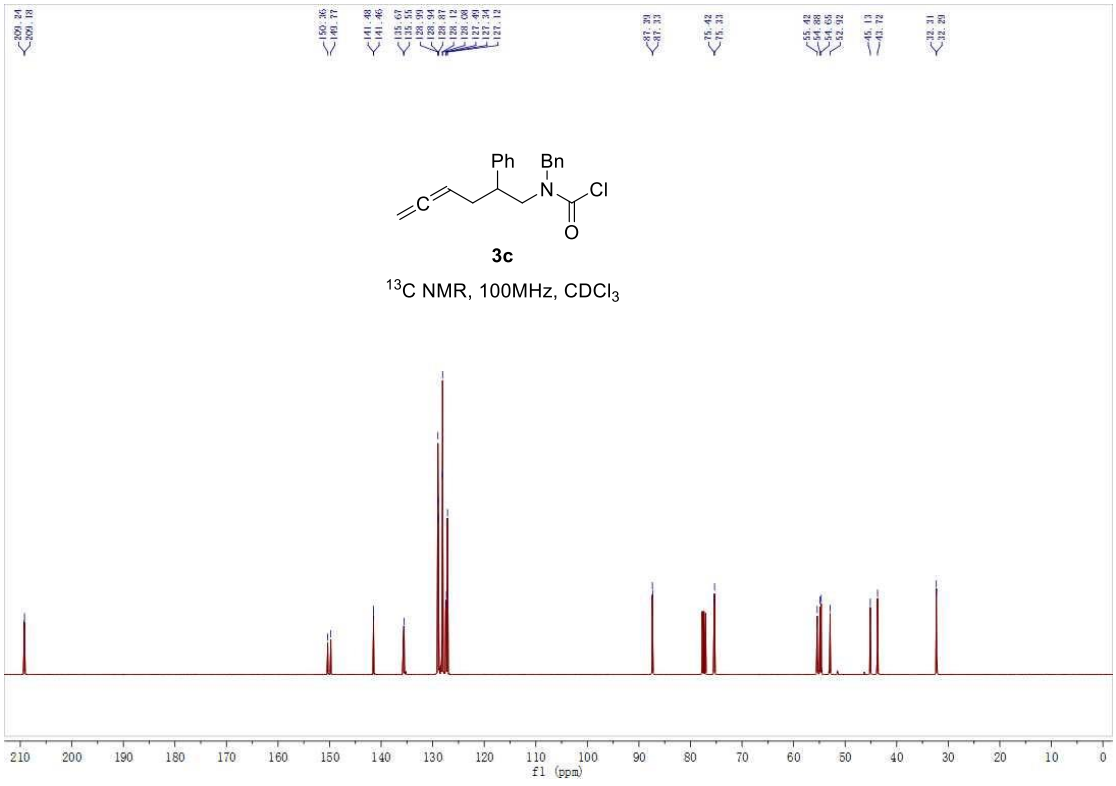
3b

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



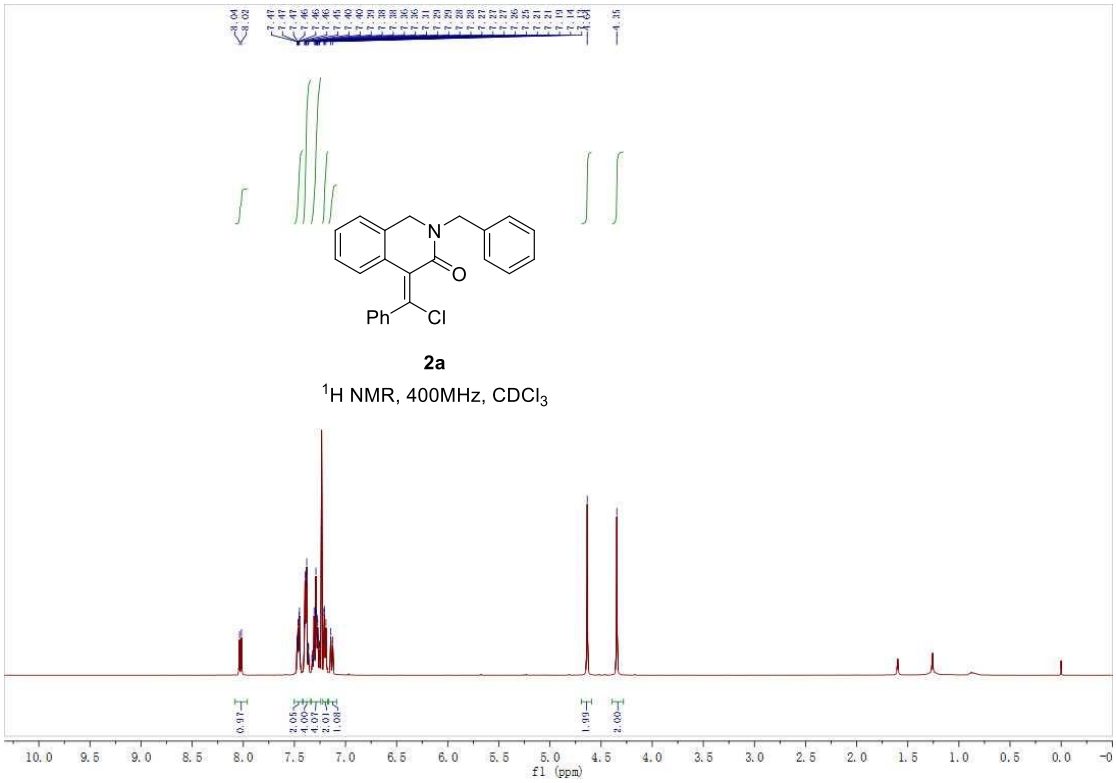
3c

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



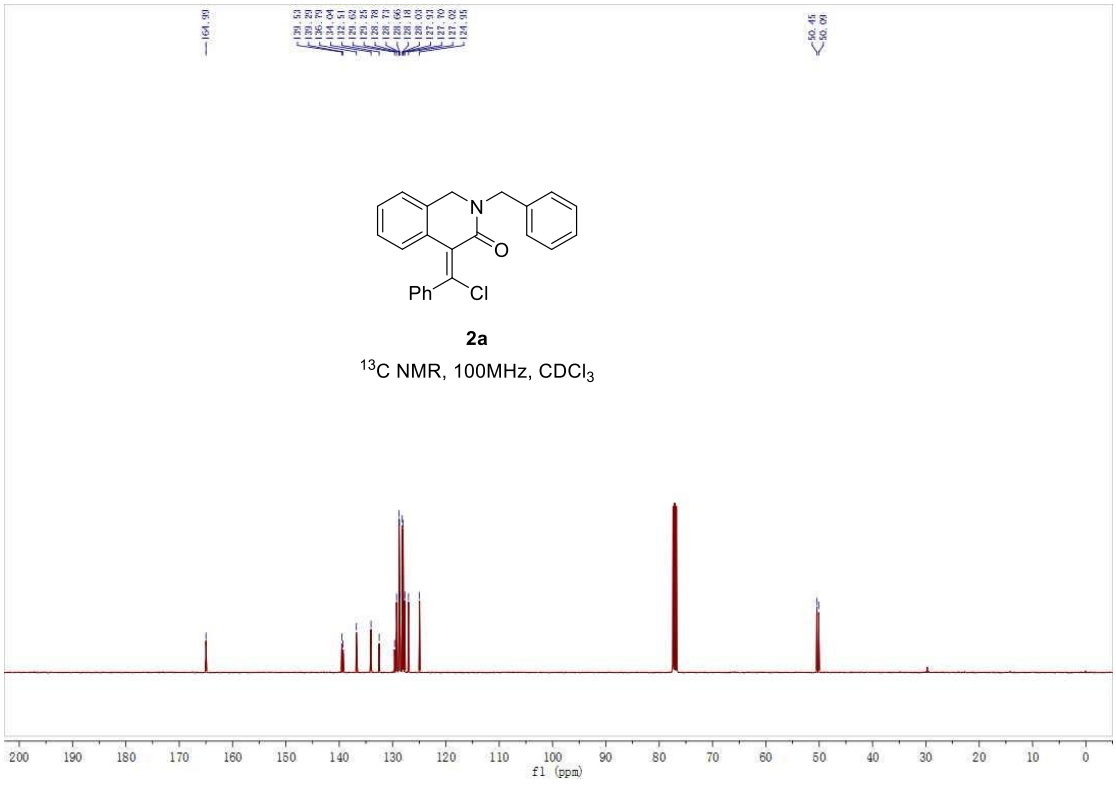
3c

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



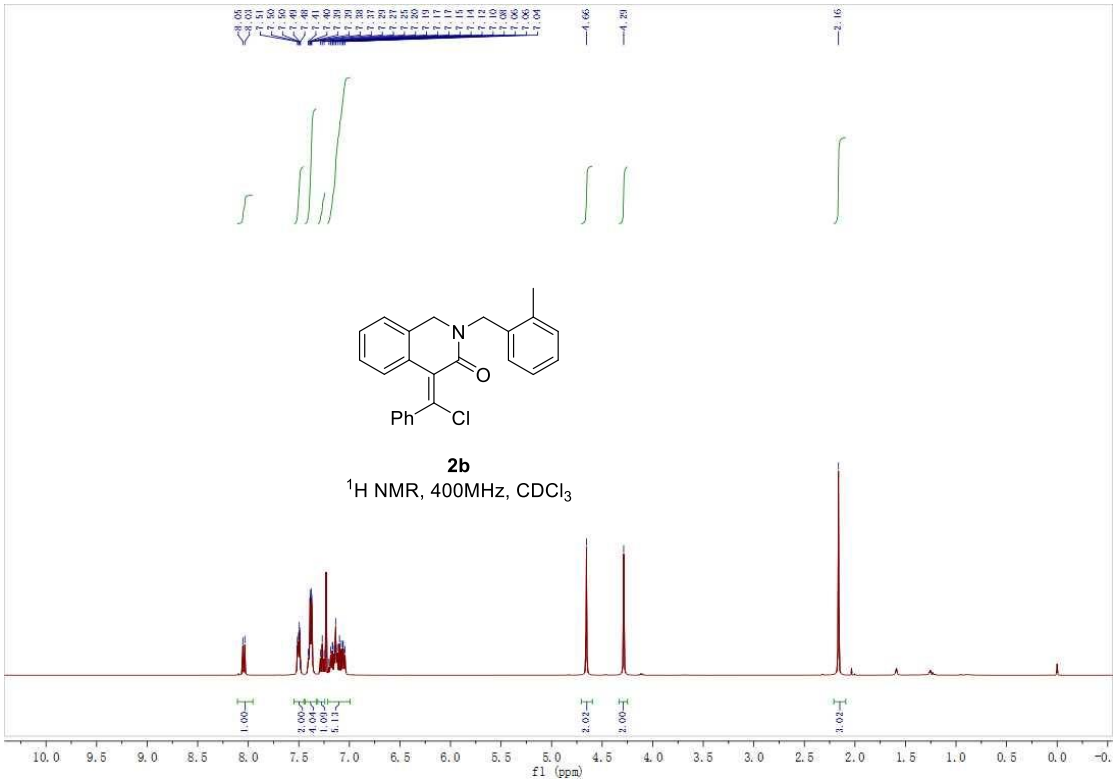
2a

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



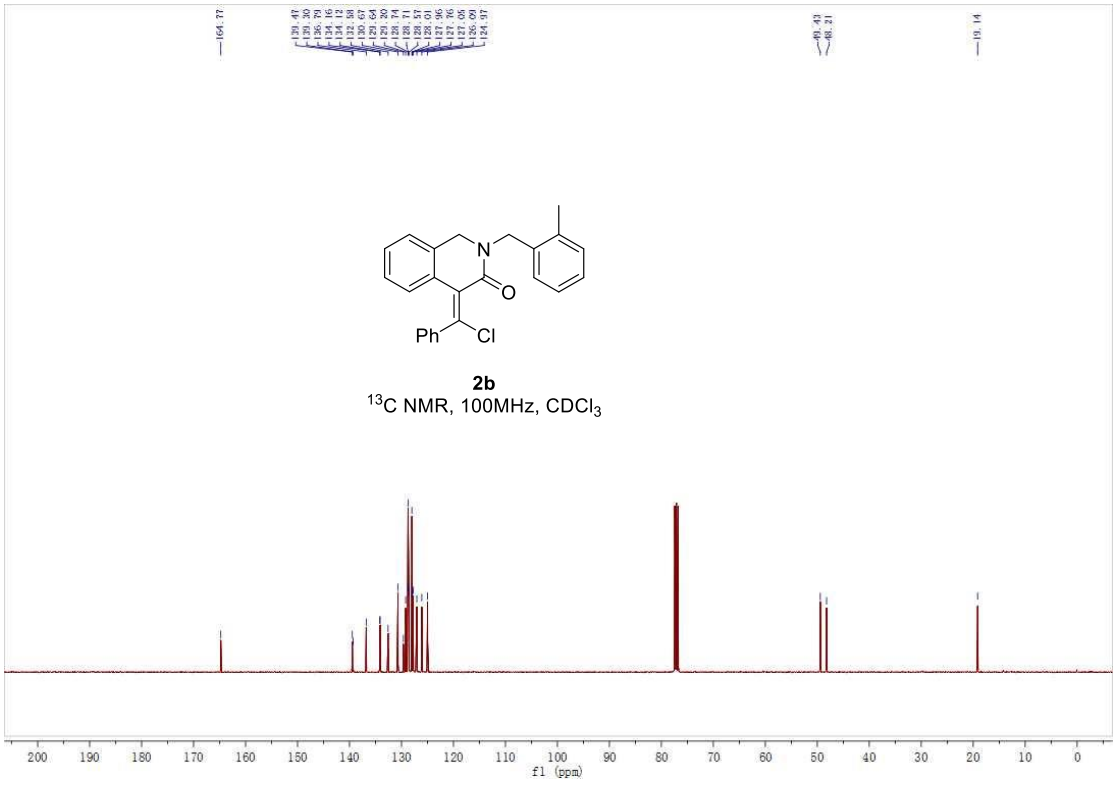
2a

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



2b

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



2b

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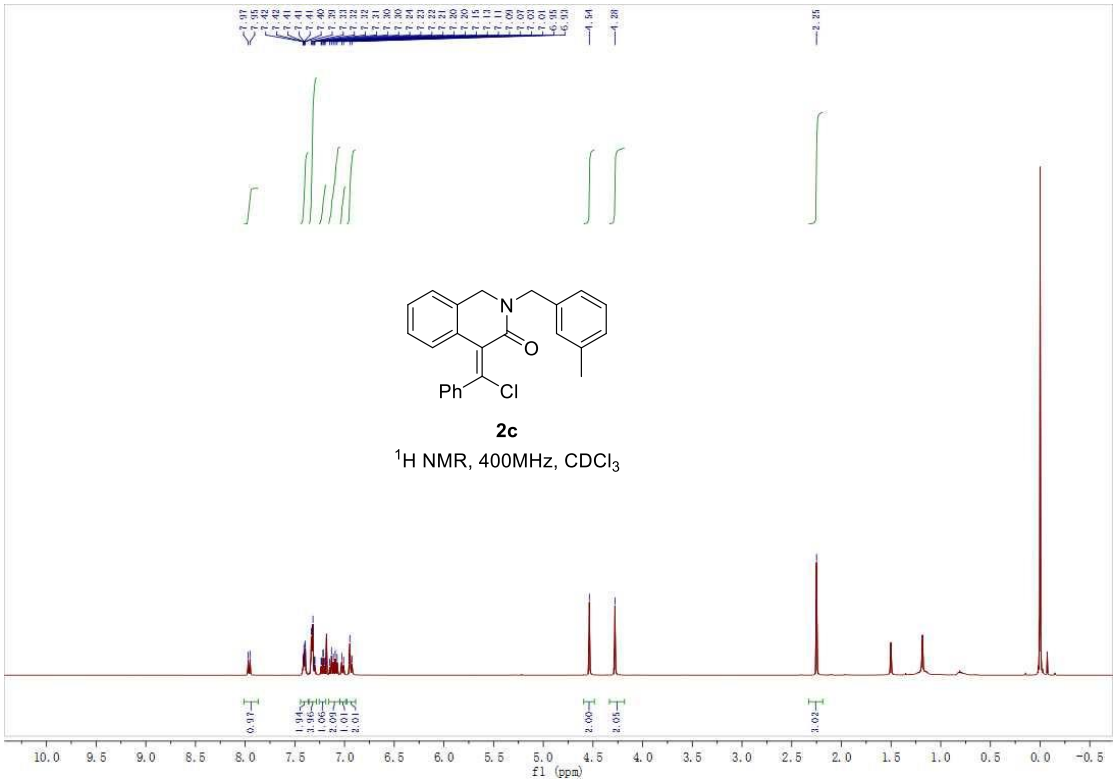
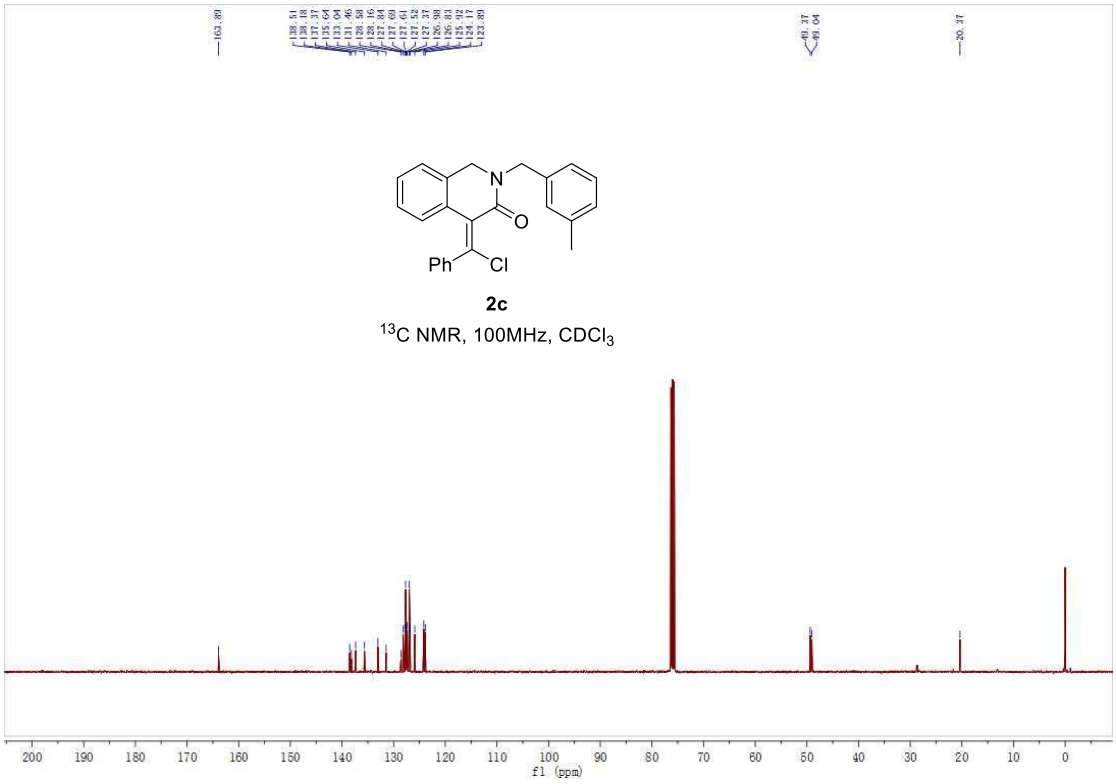


2c

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



2c

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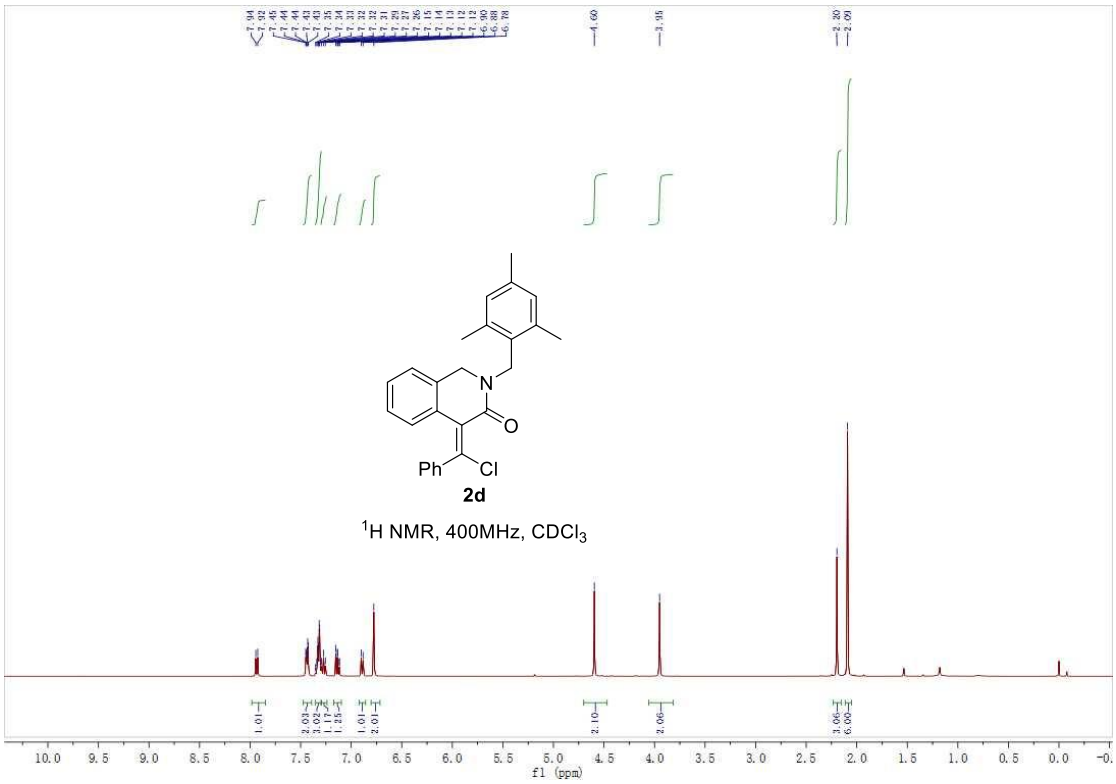
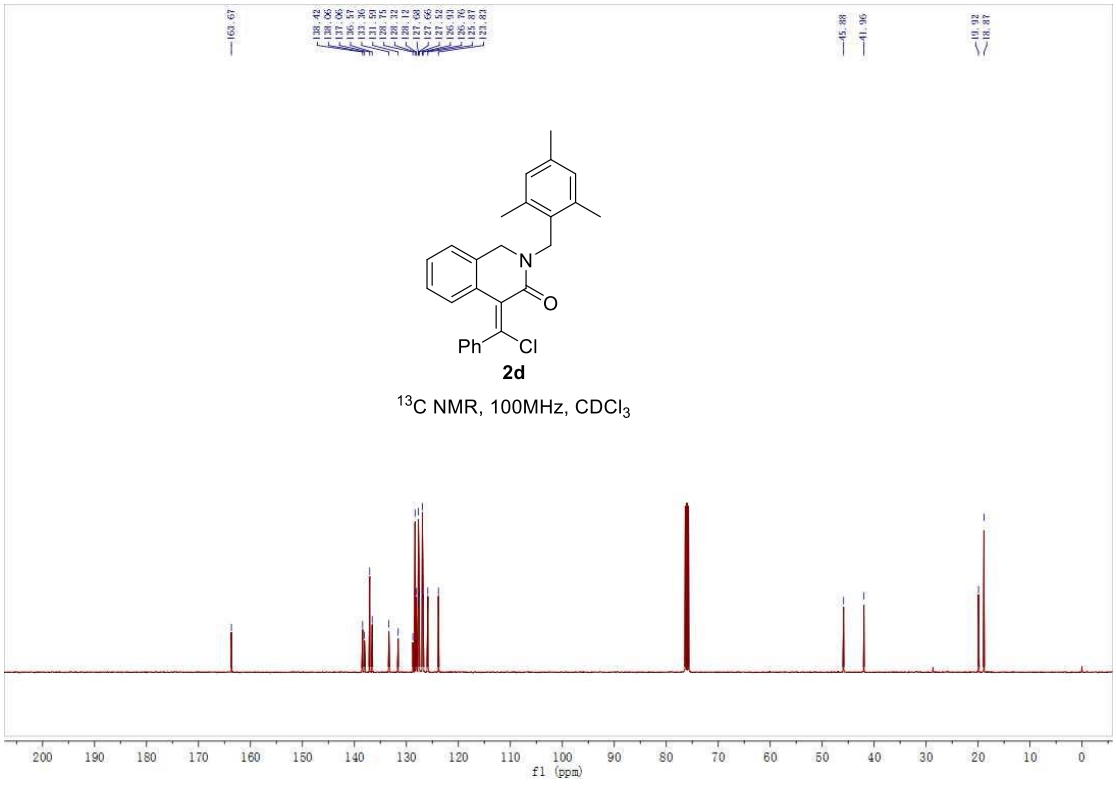


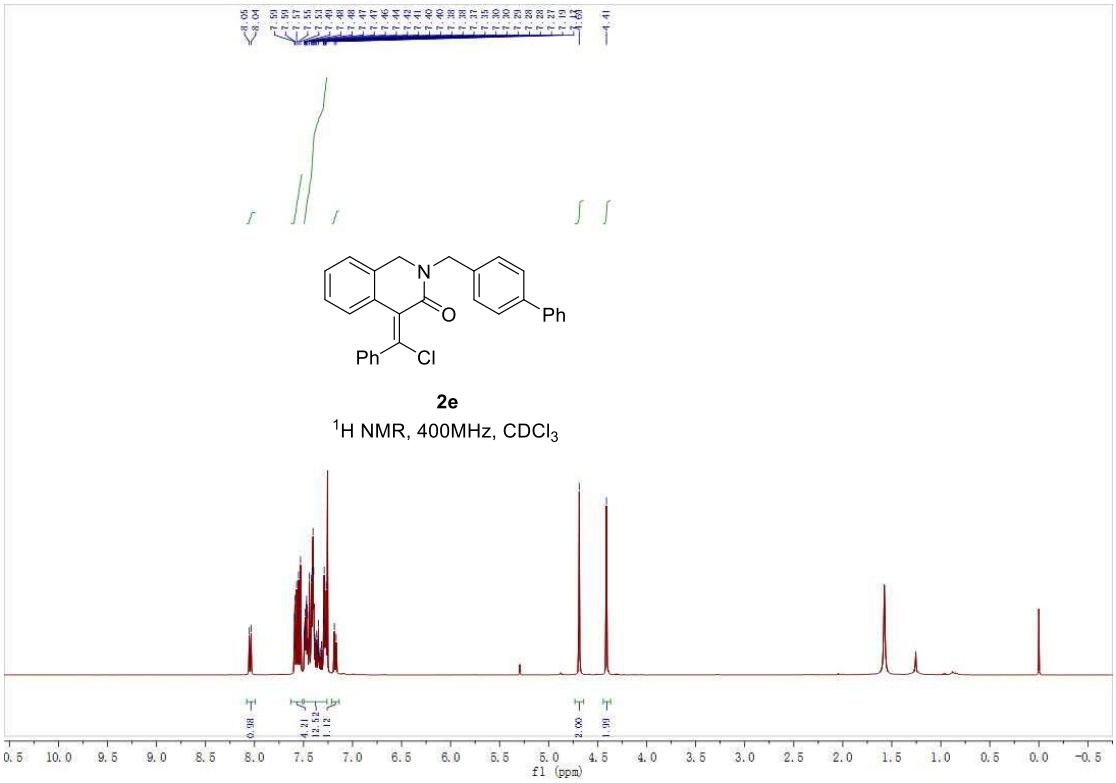
2d

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



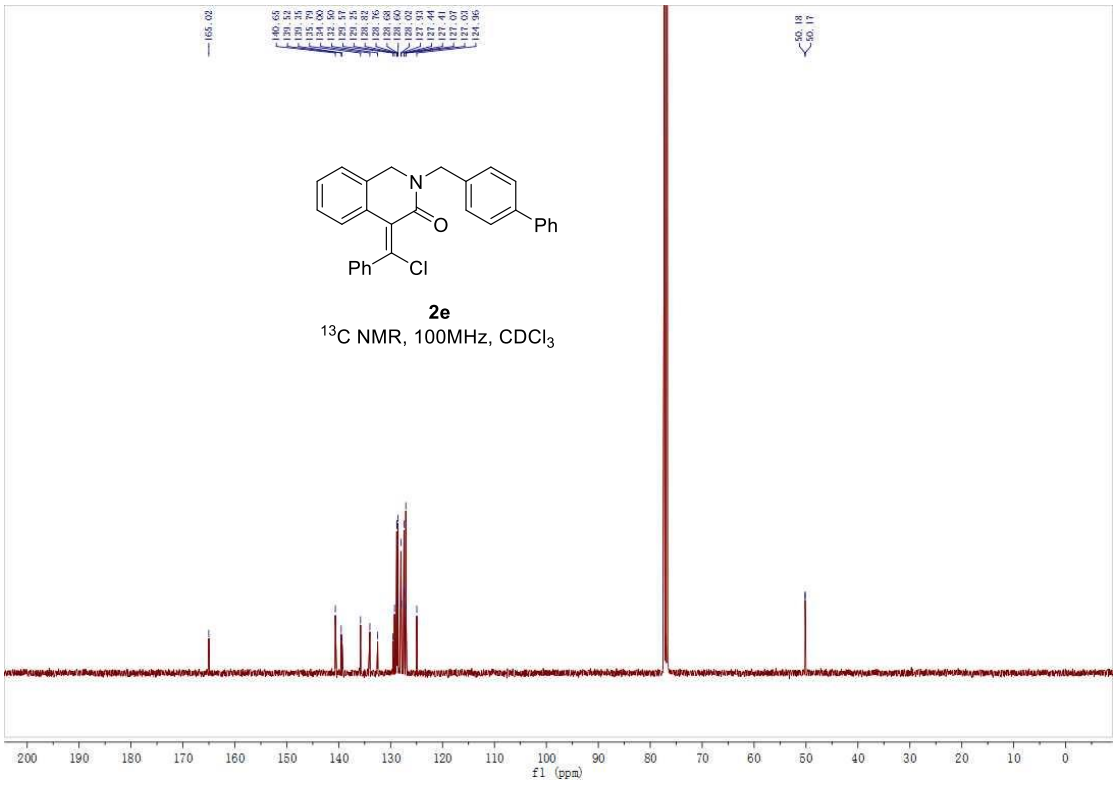
2d

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



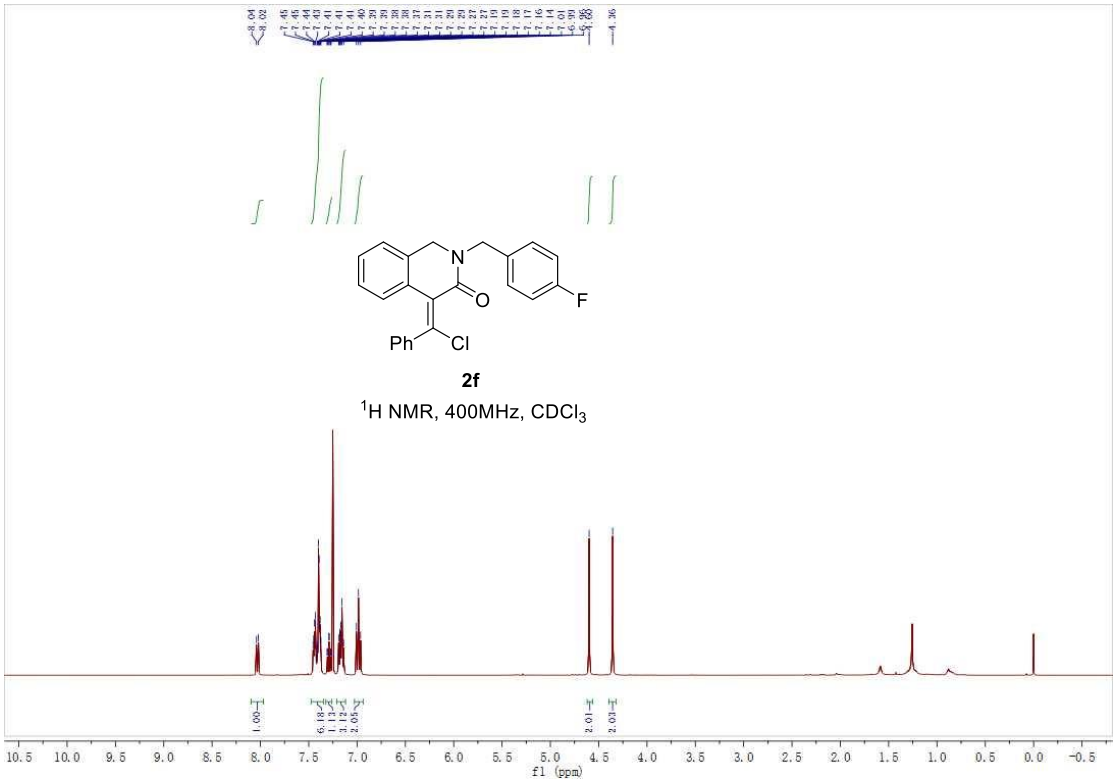
2e

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



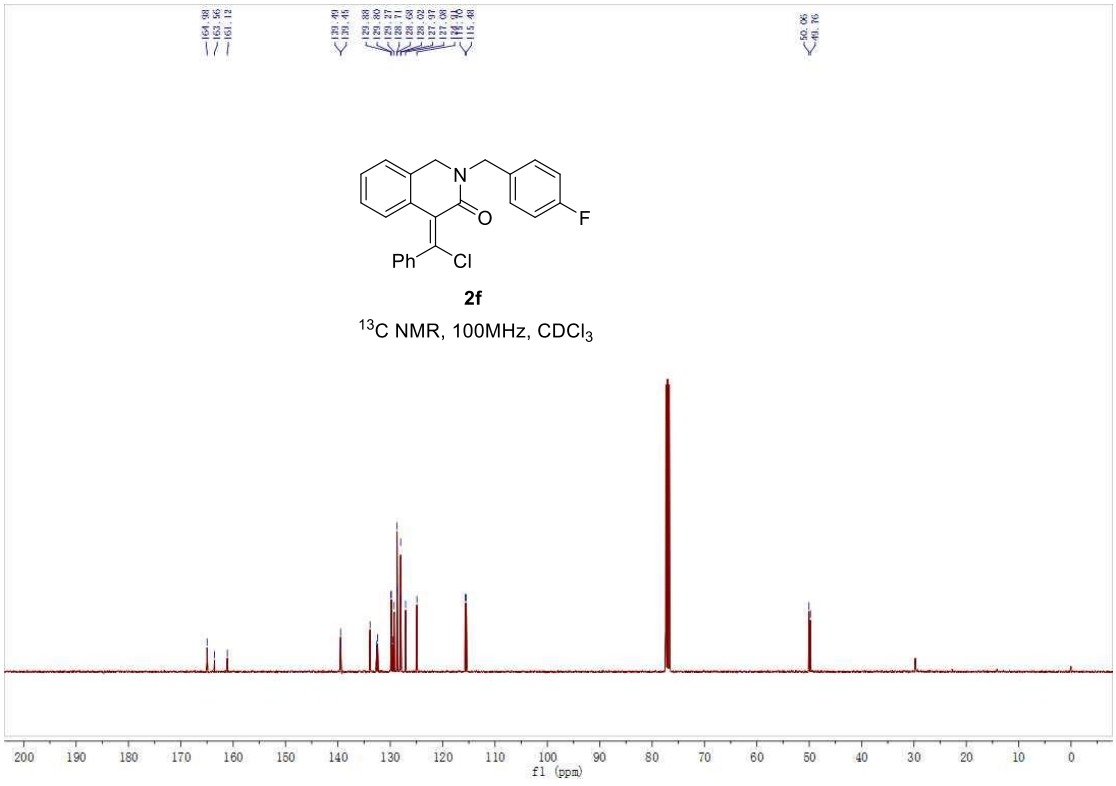
2e

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



2f

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



2f

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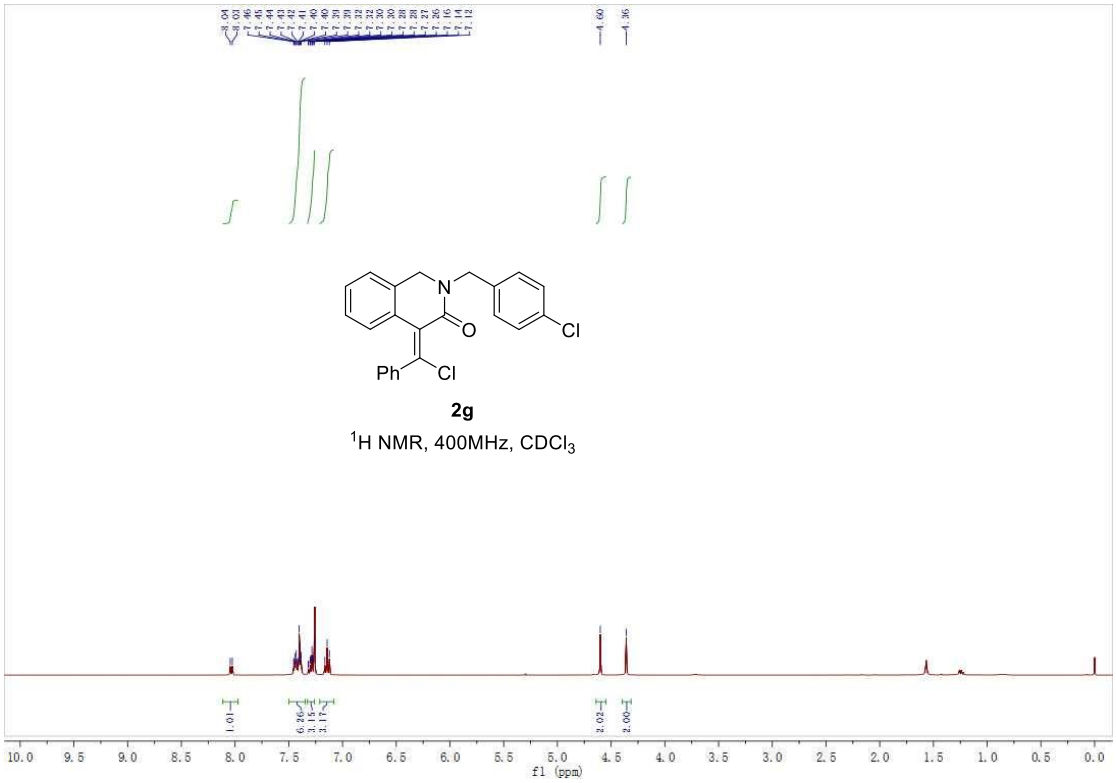
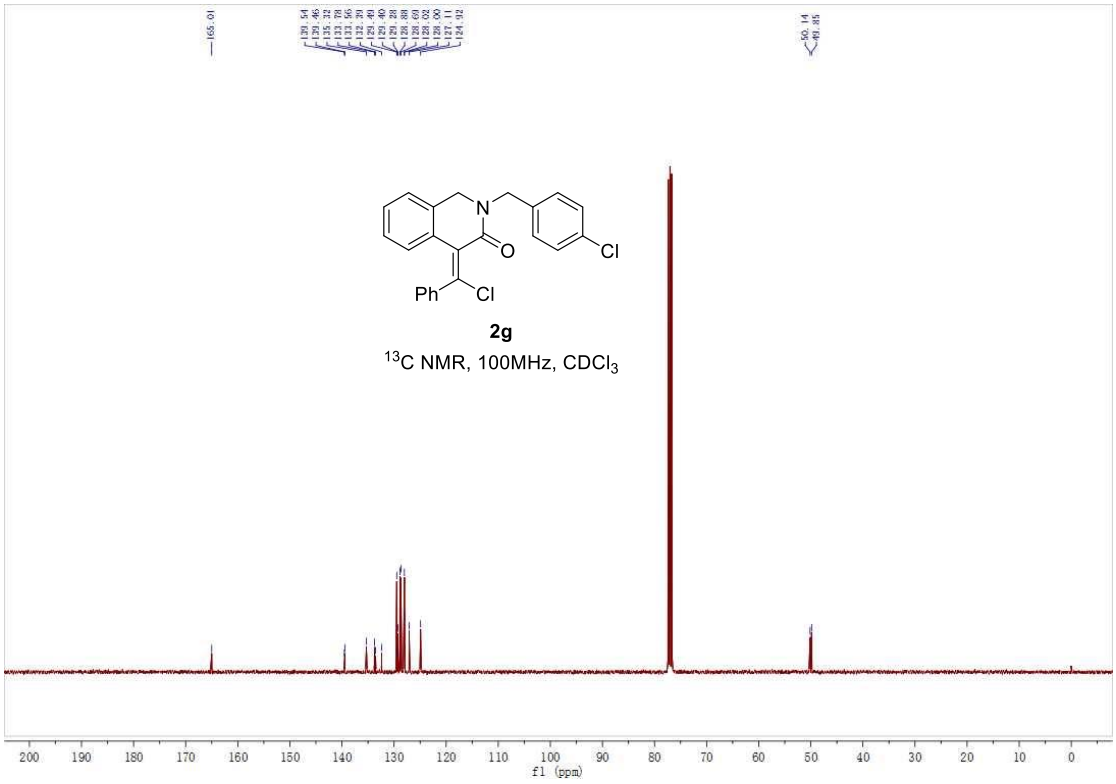


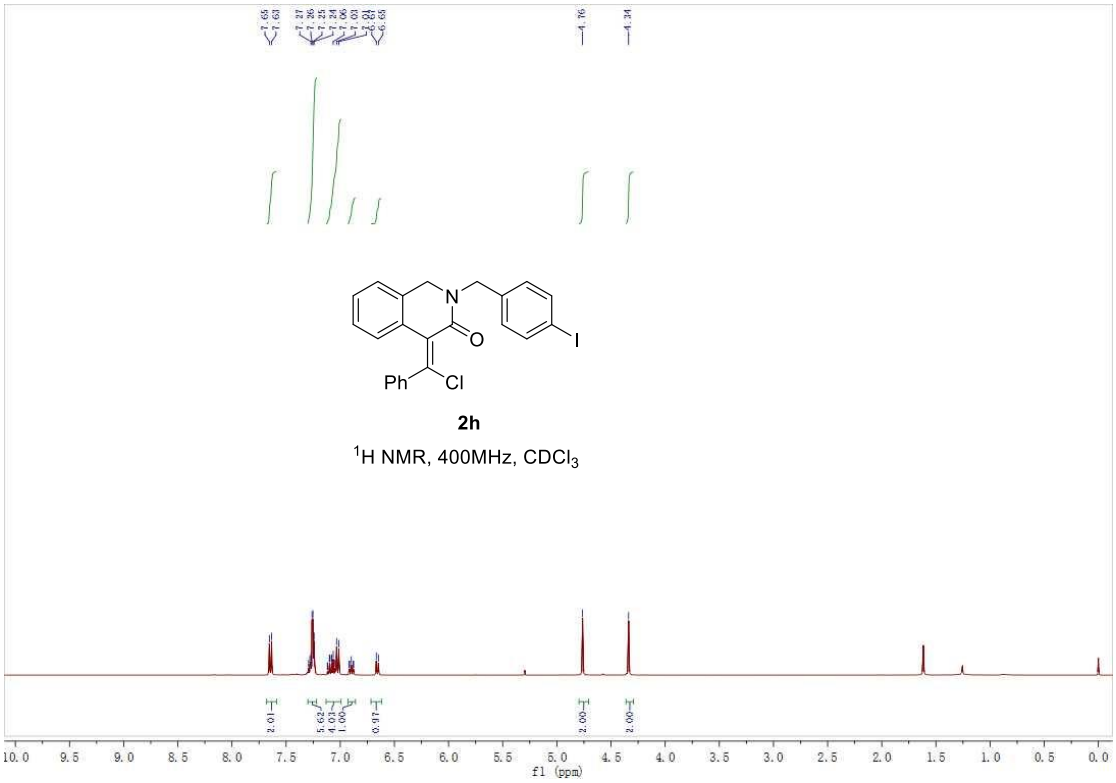
2g

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



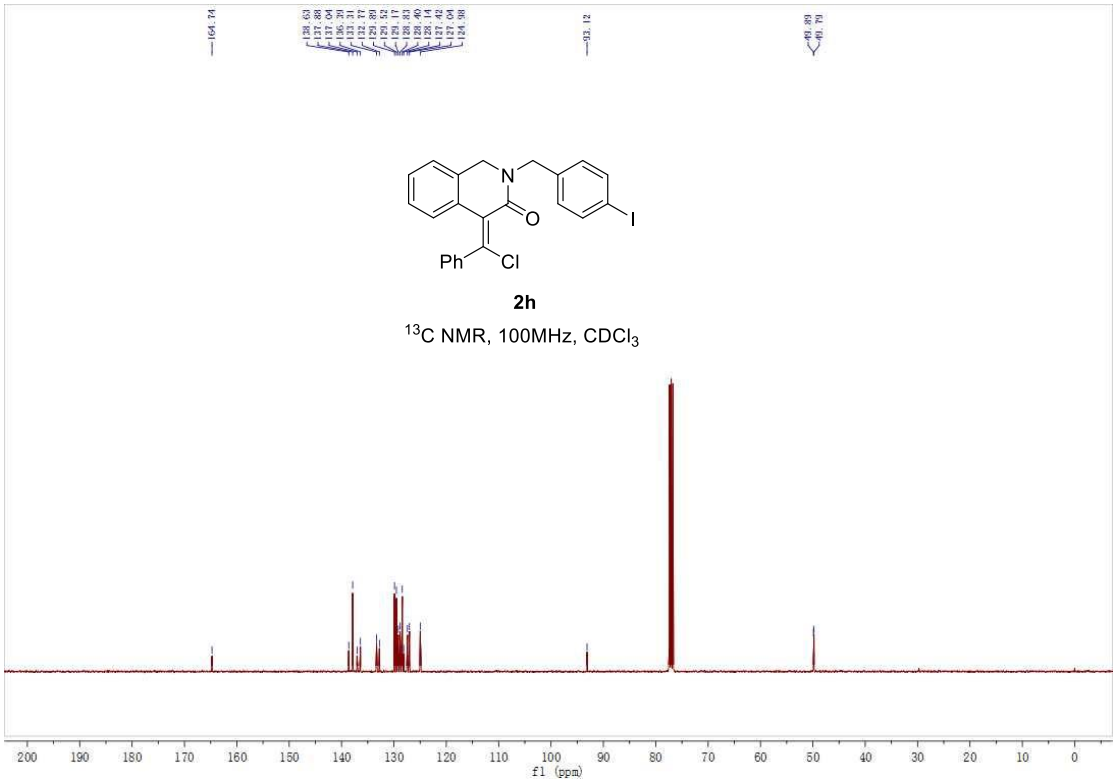
2g

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



2h

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



2h

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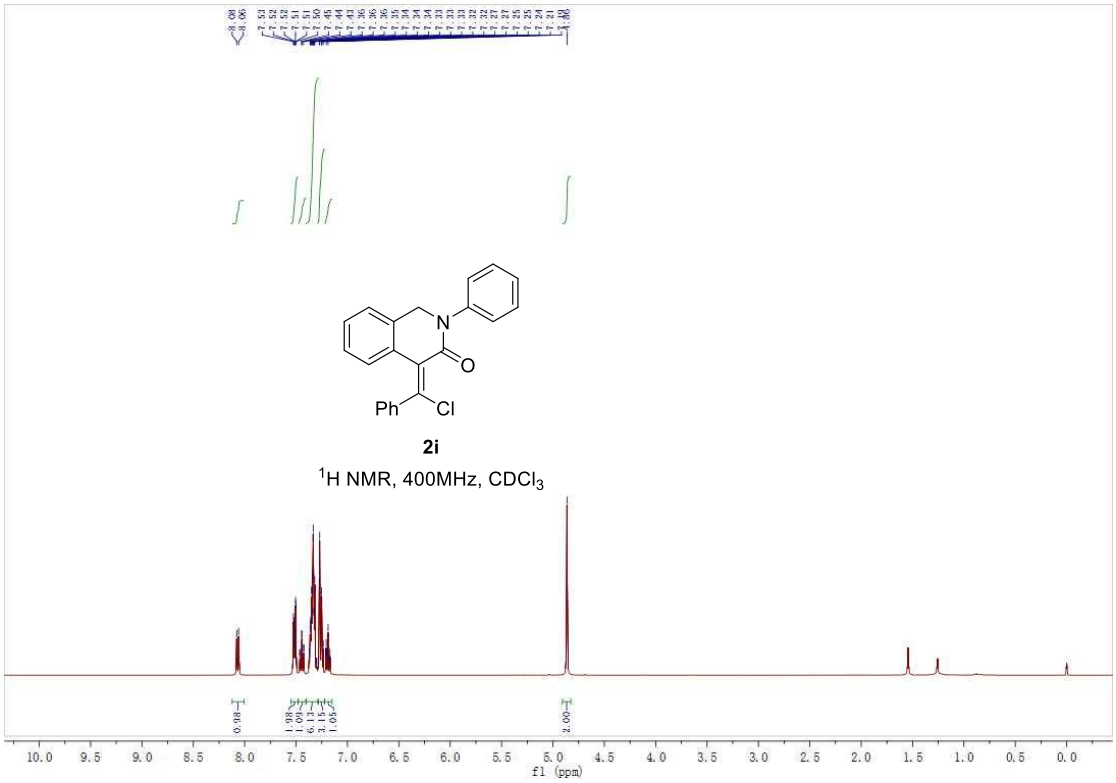

2i

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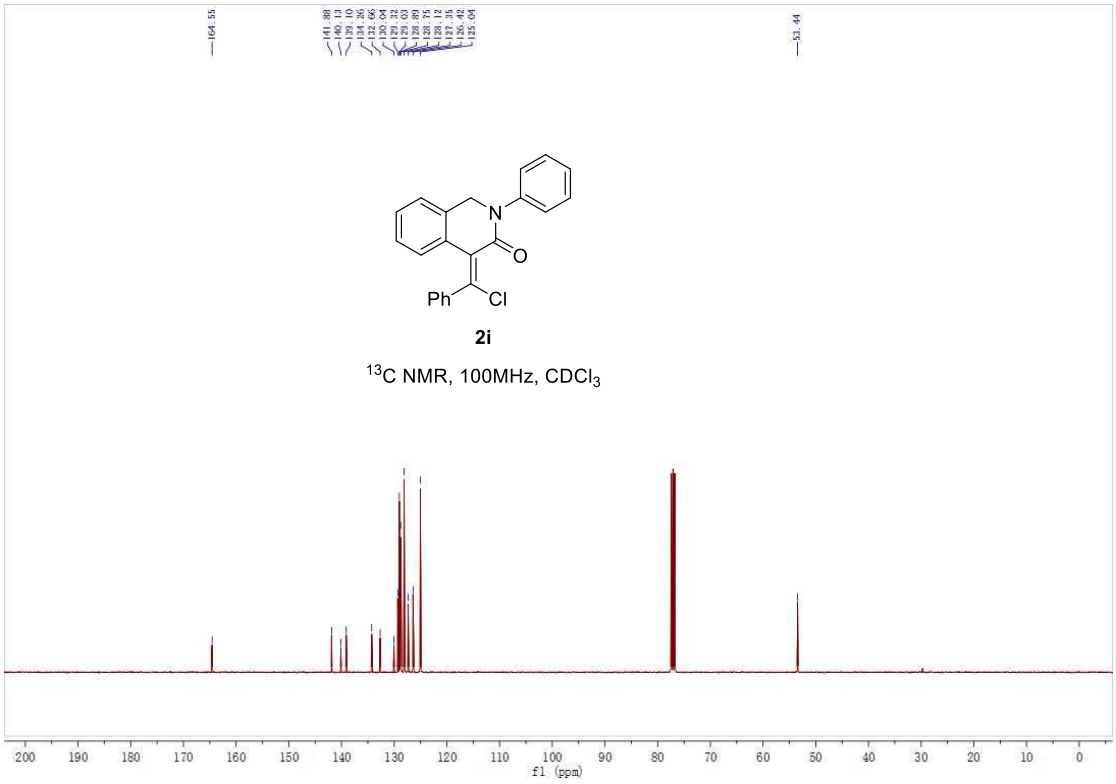

2i

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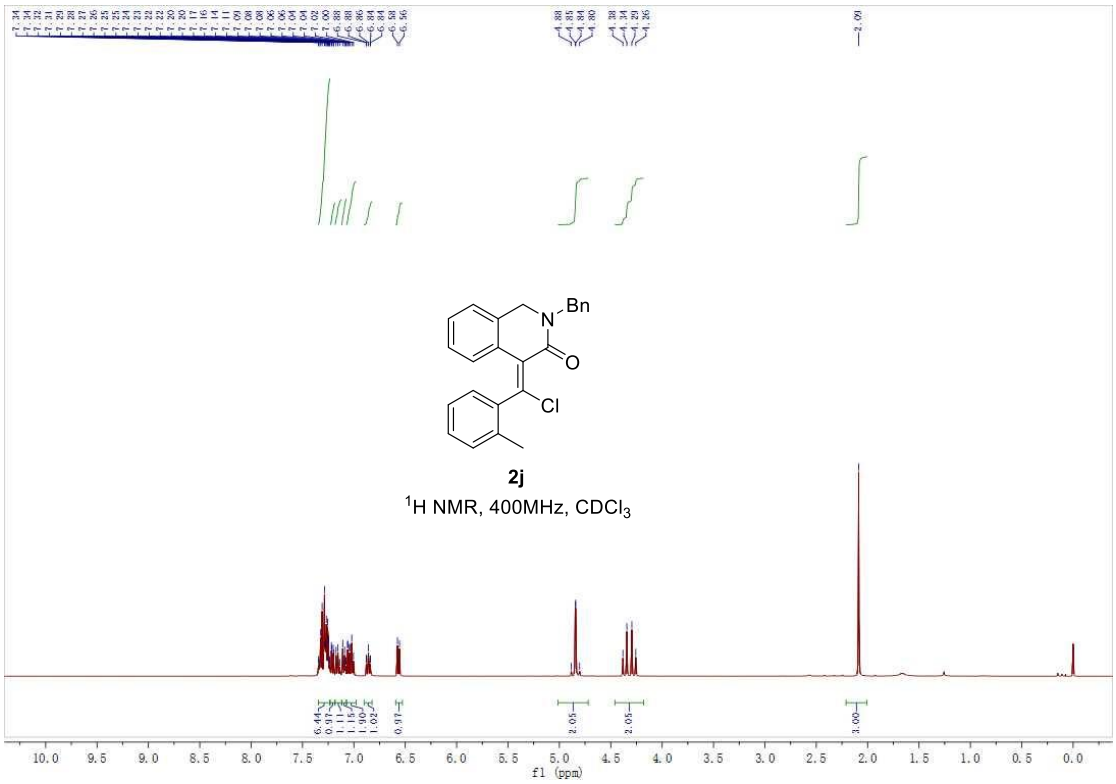
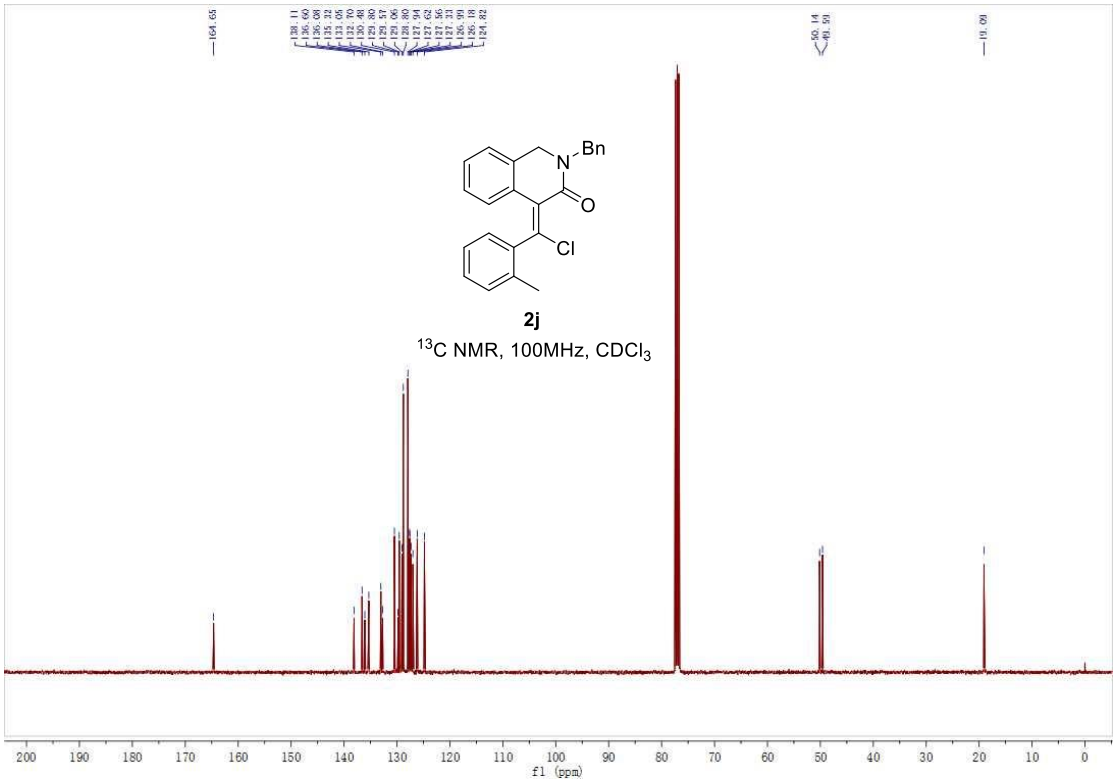


2j

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



2j

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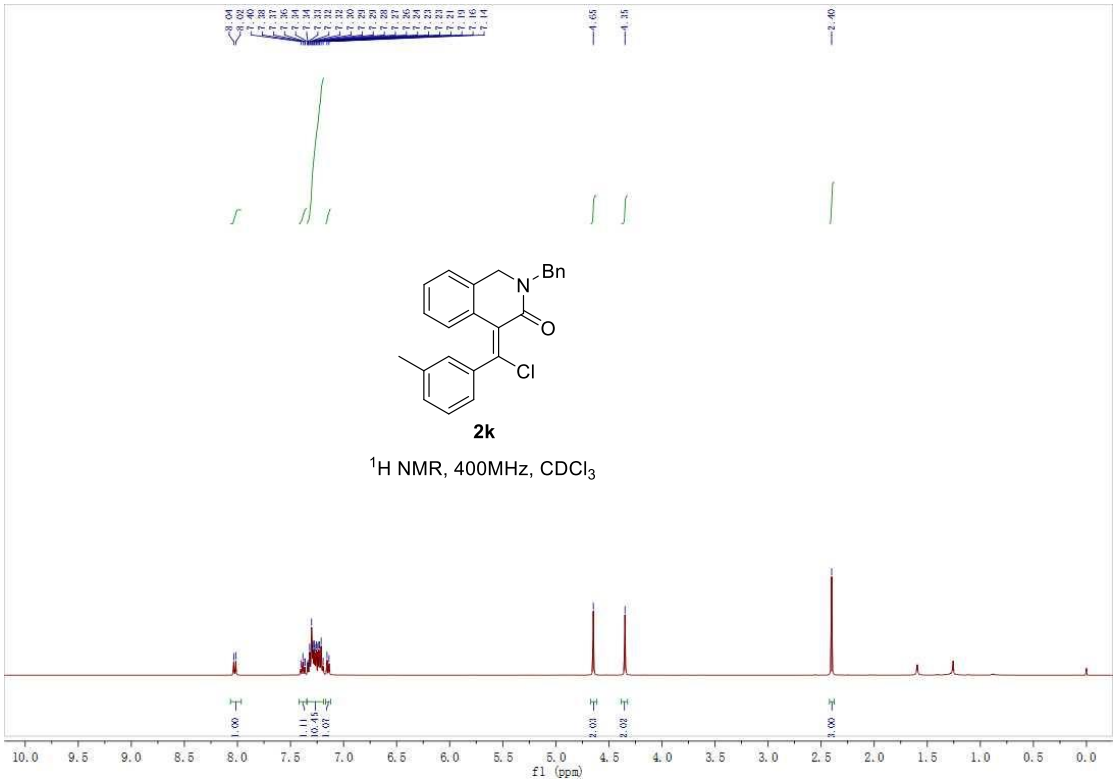
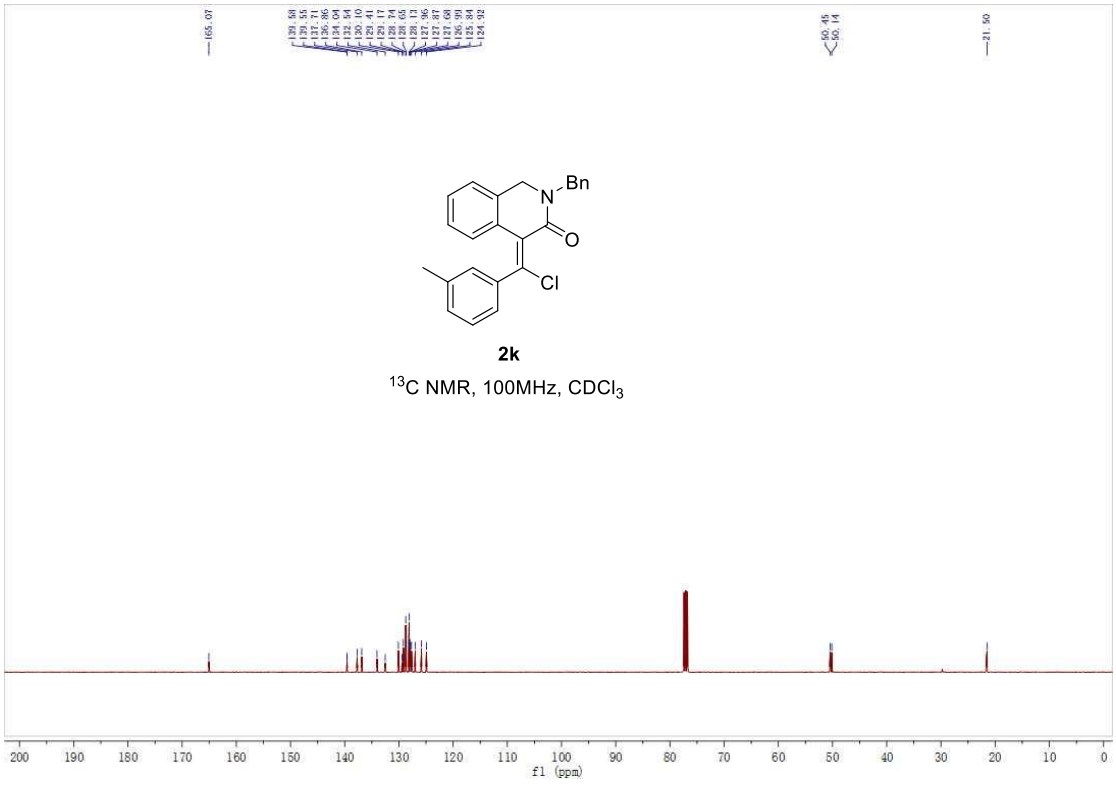


2k

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



2k

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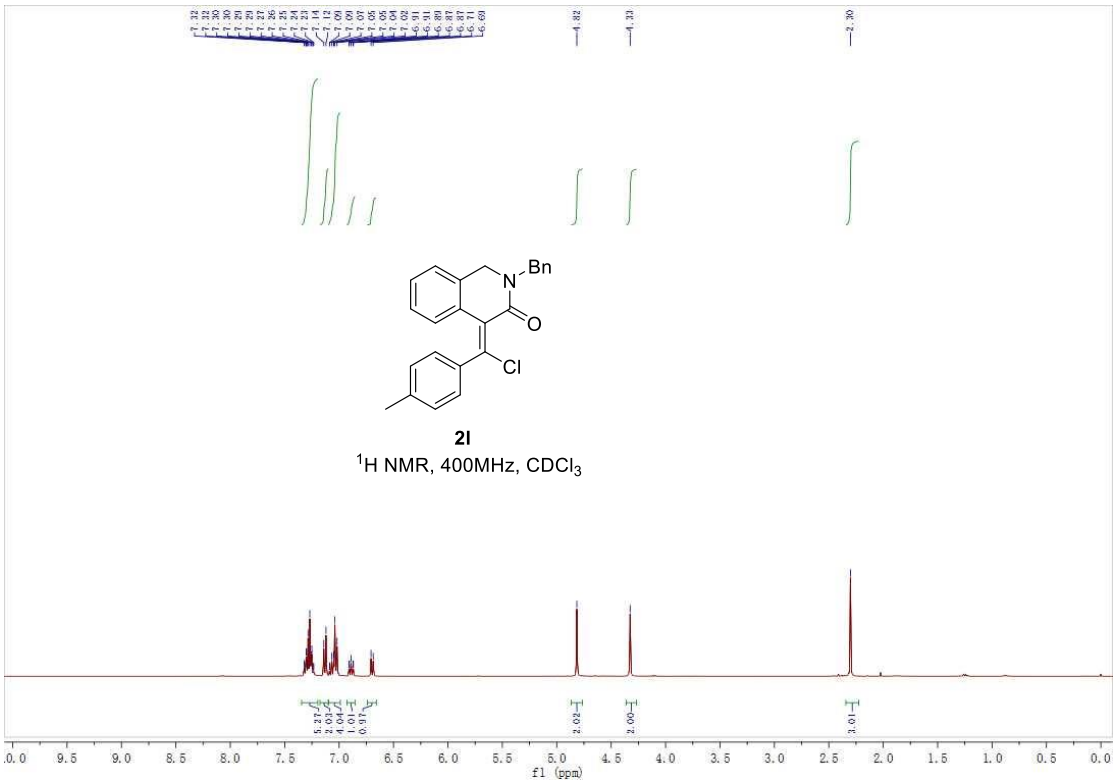
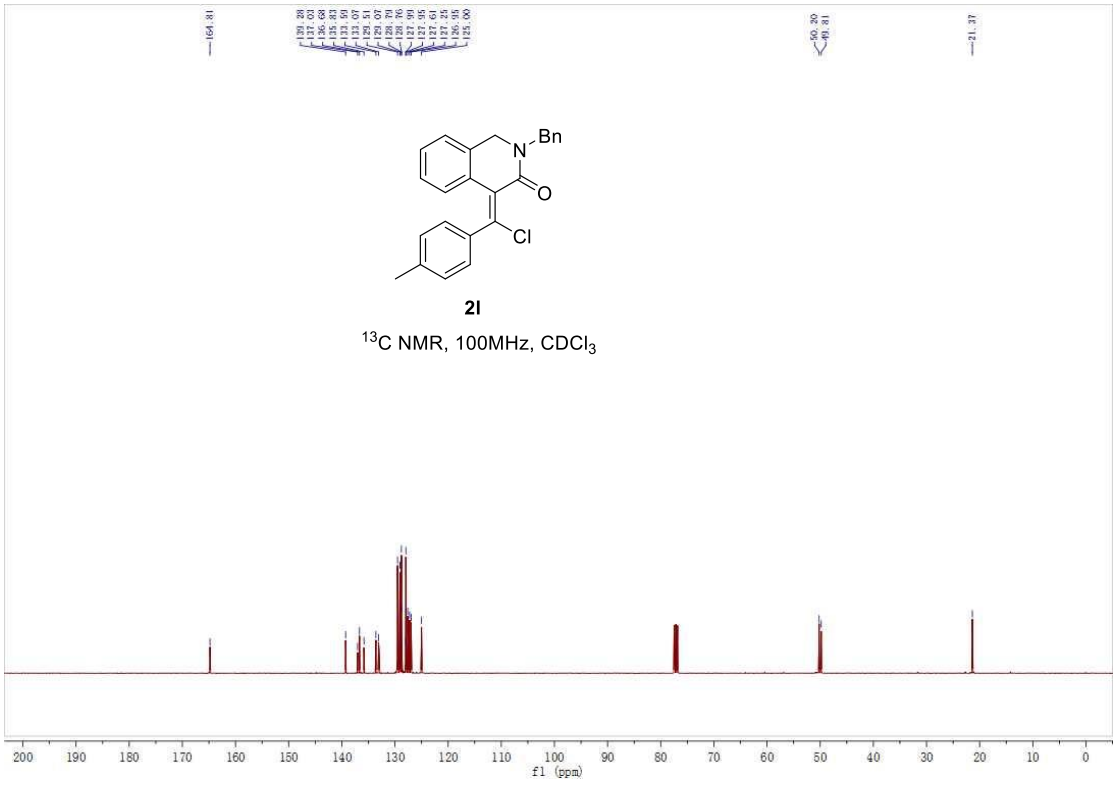


2l

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



2l

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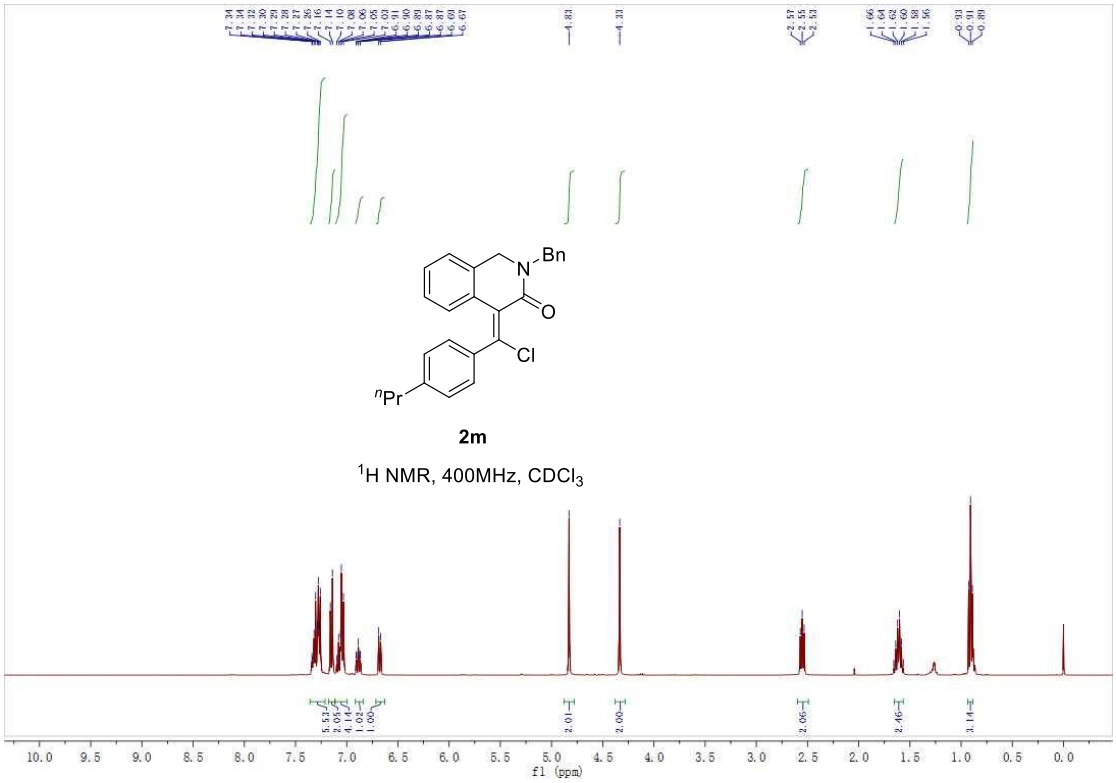

2m

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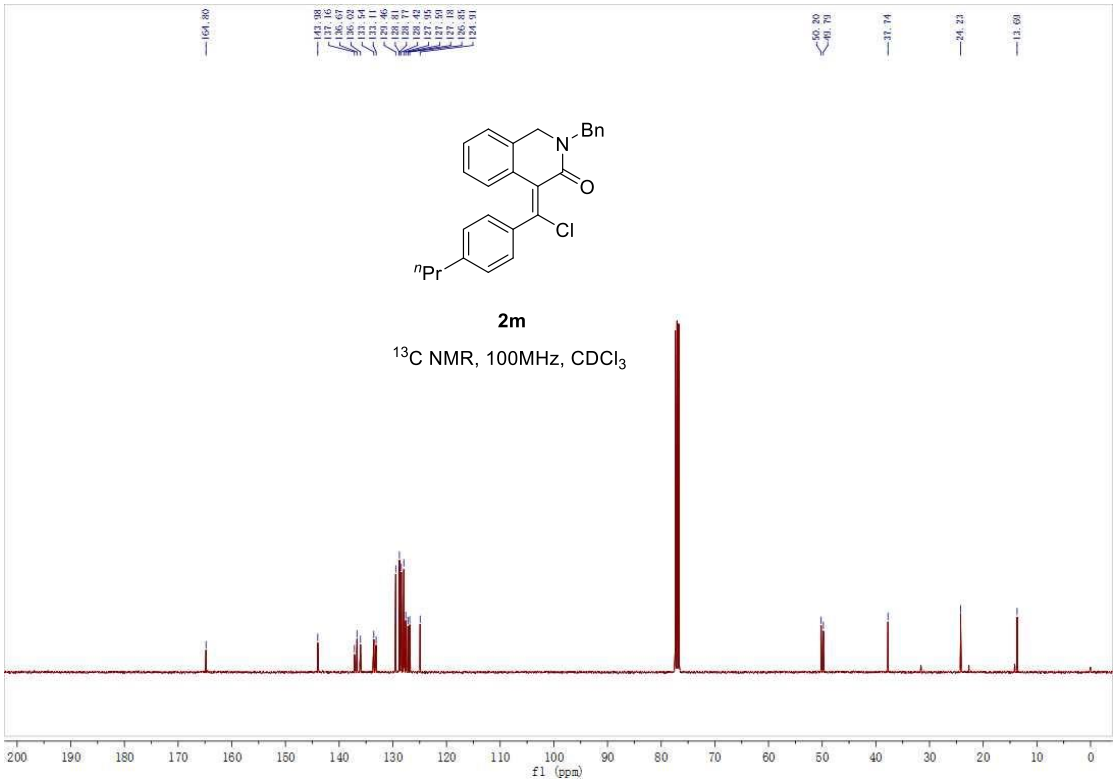
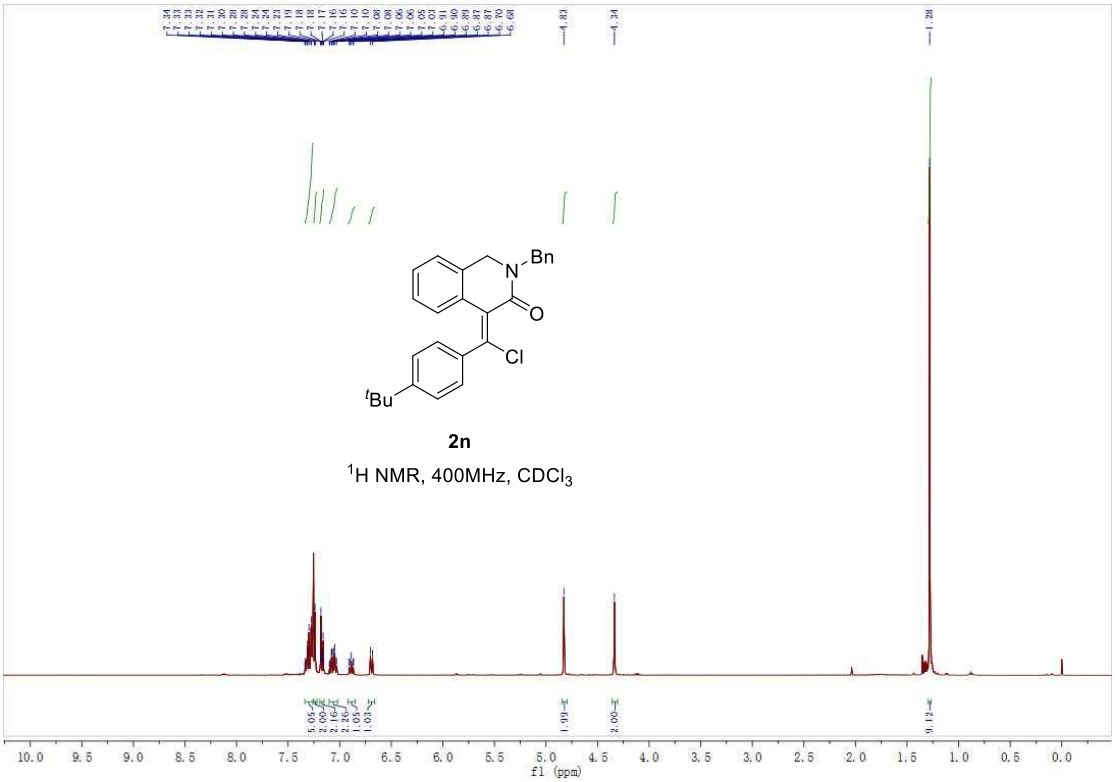


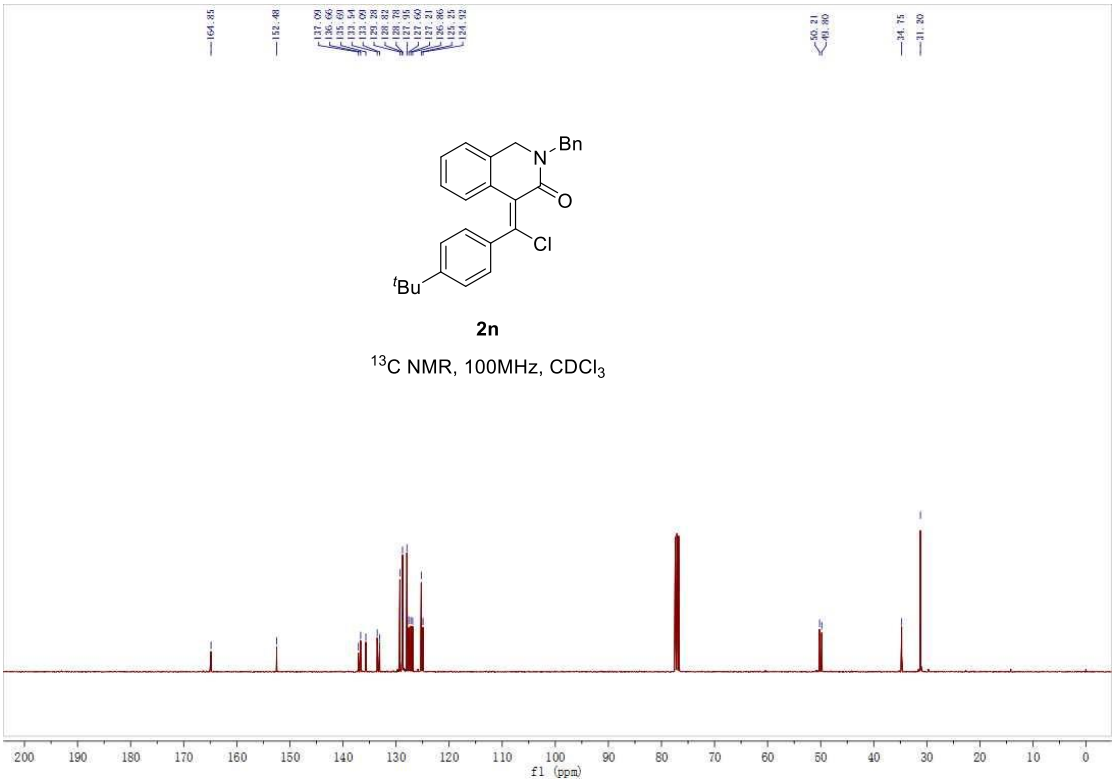
2m

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



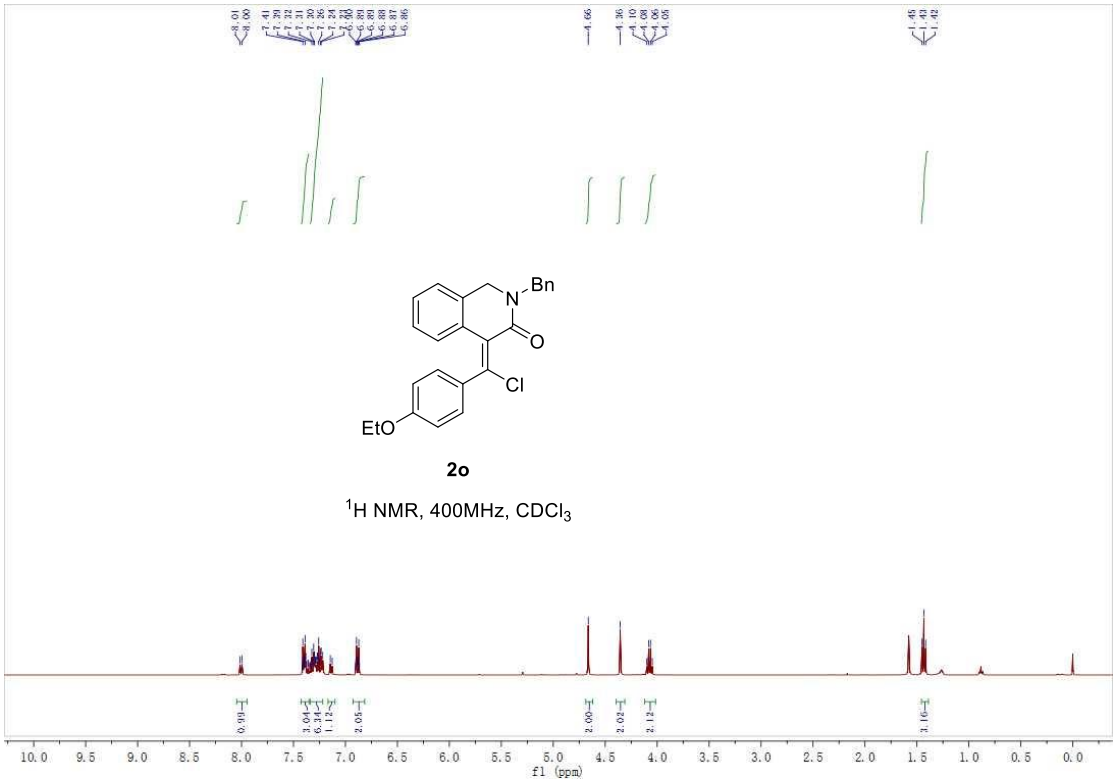
2n

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



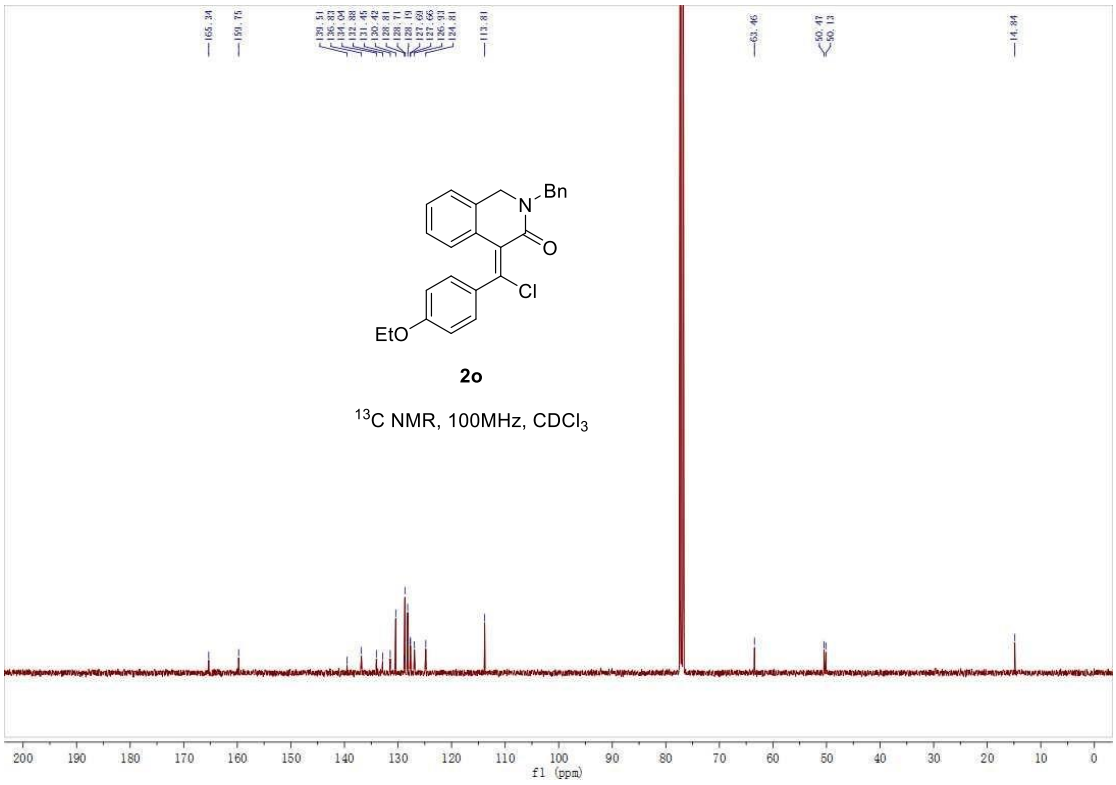
2n

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



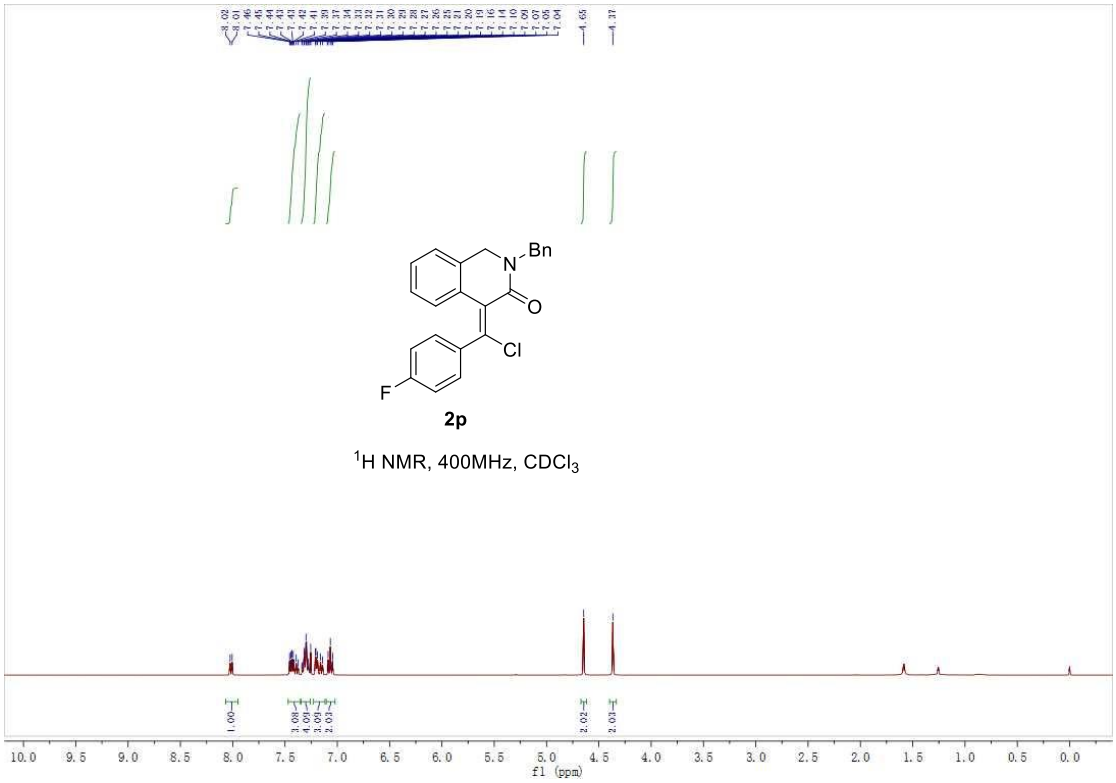
2o

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



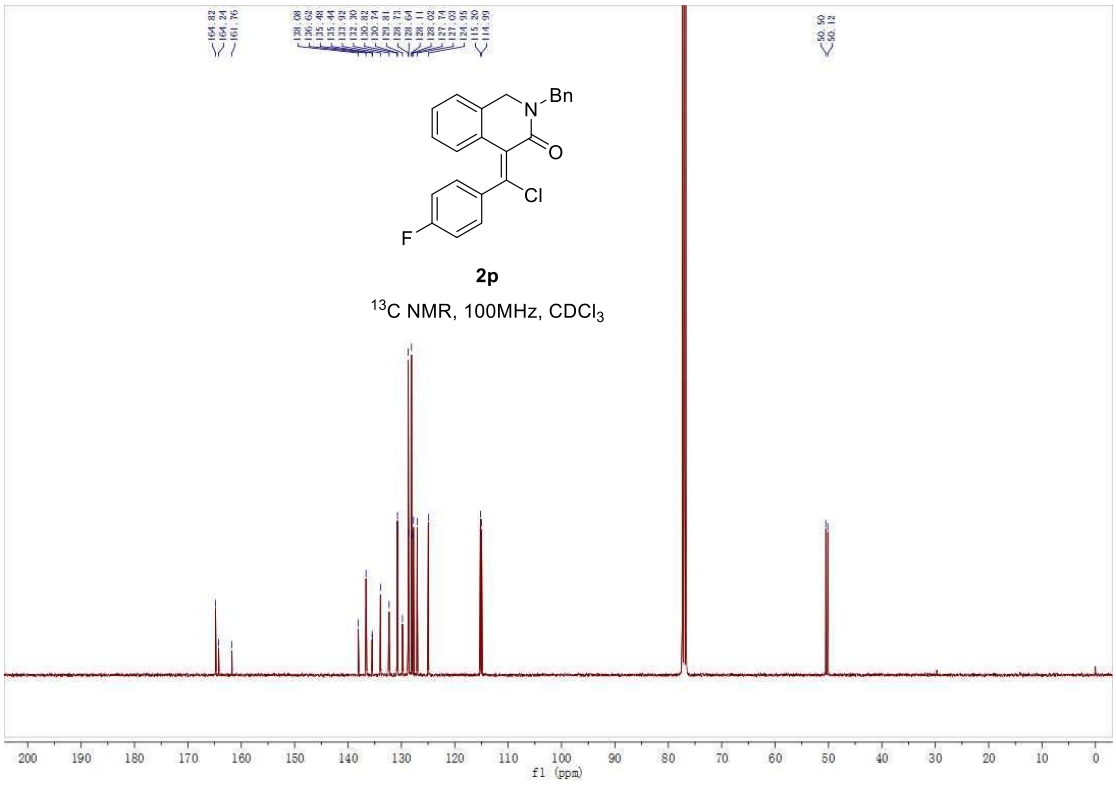
2o

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



2p

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



2p

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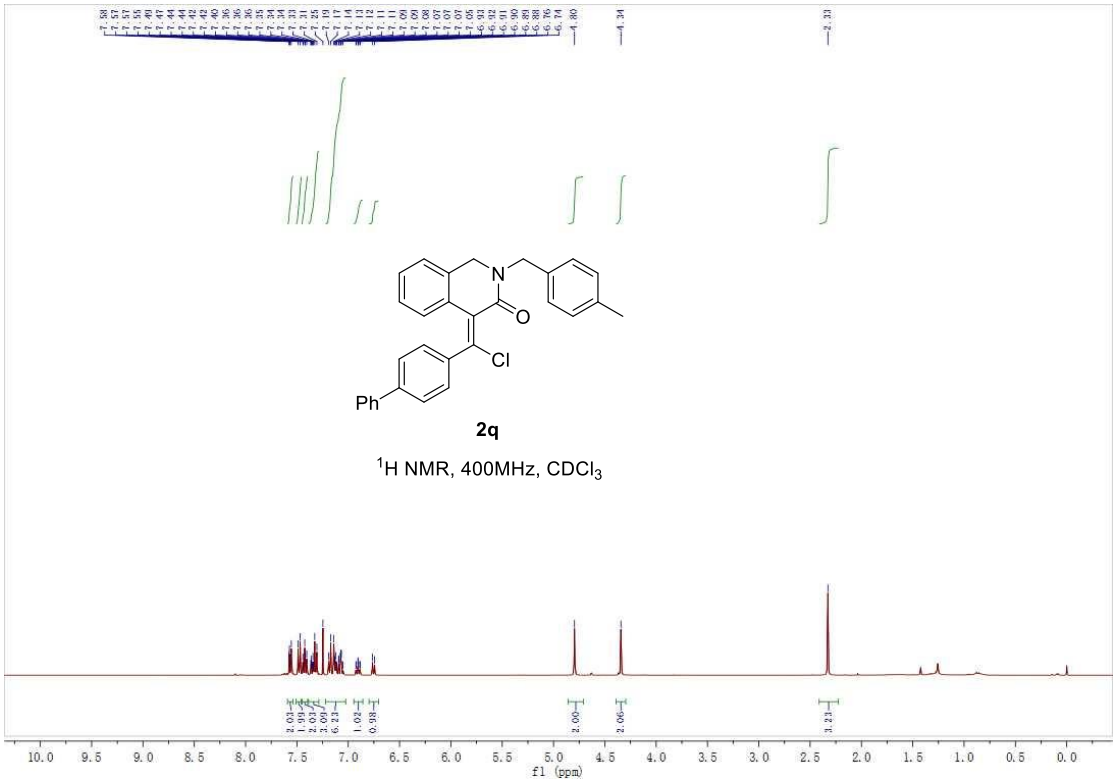

2q

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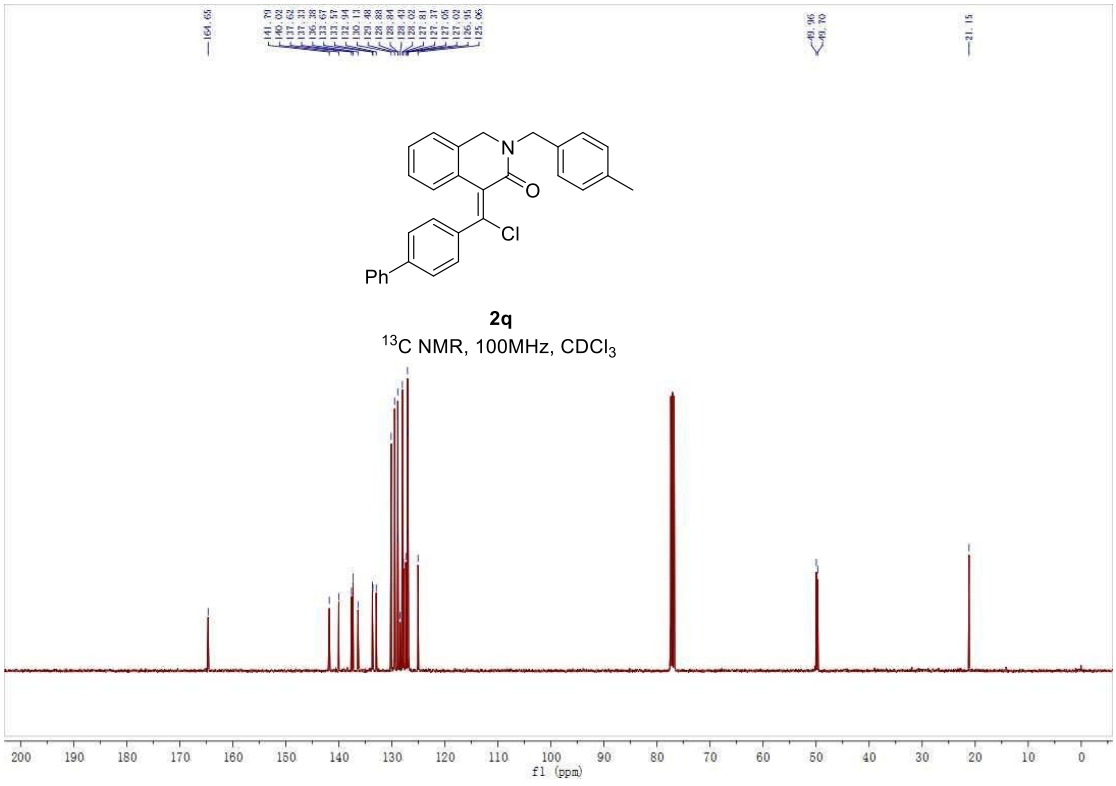

2q

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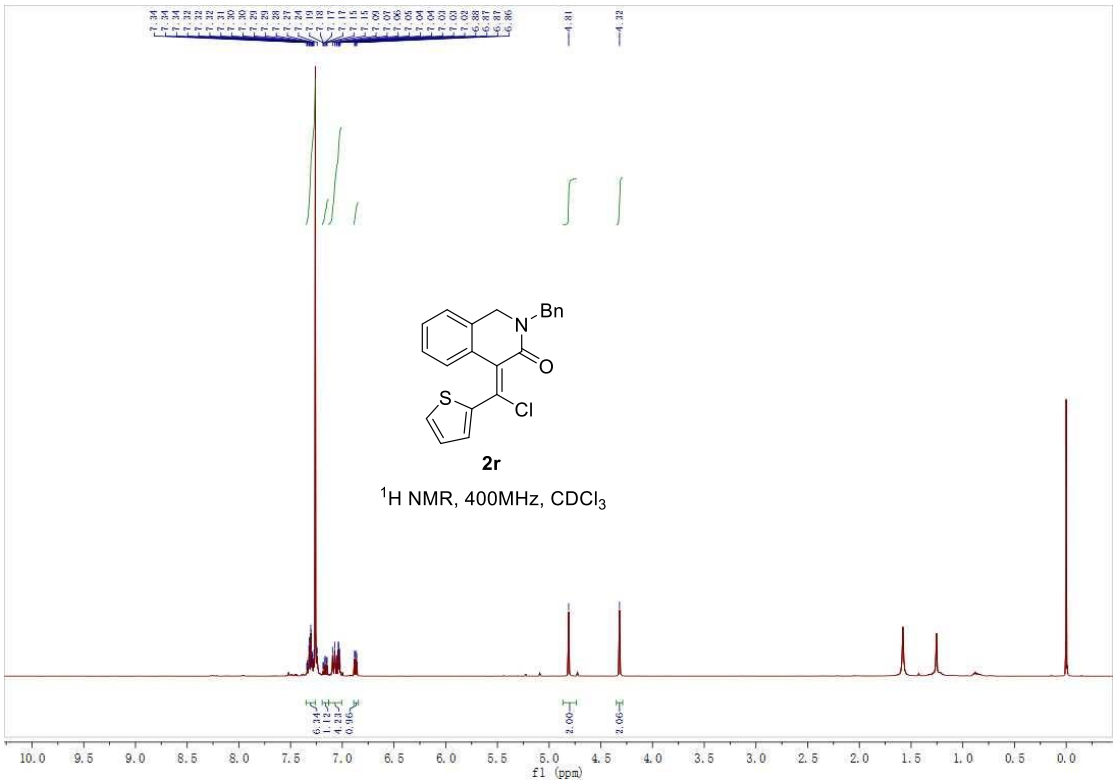

2r

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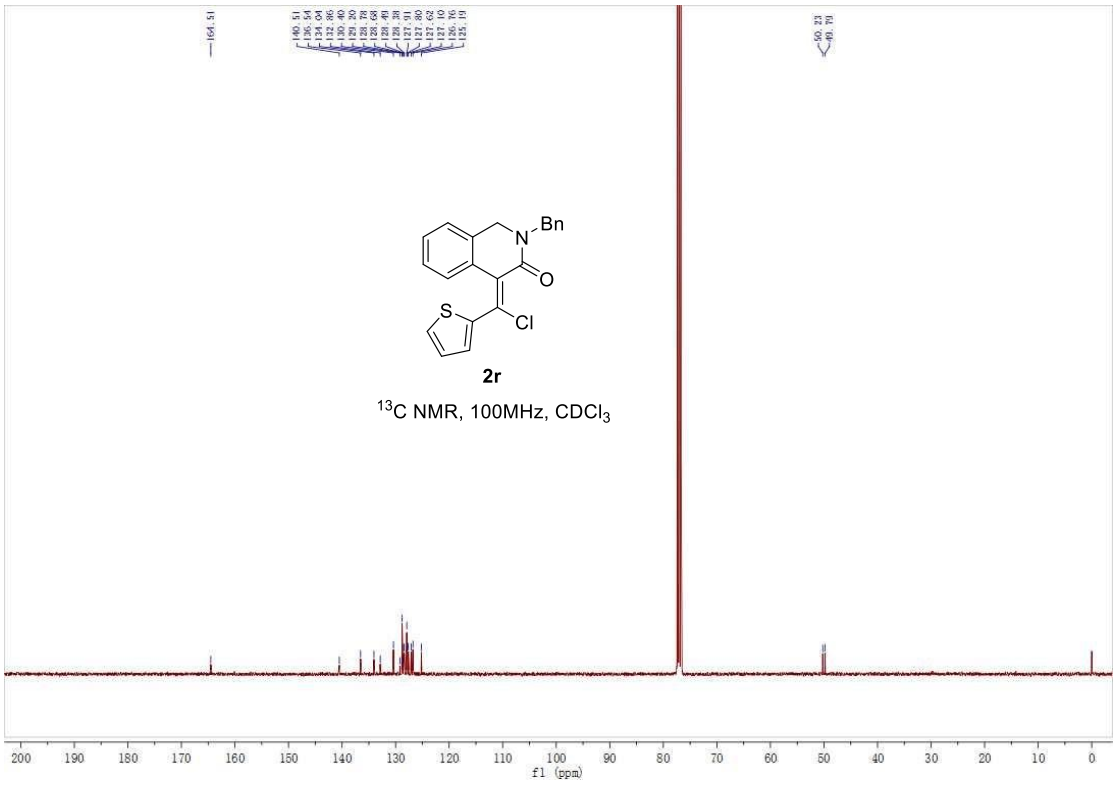

2r

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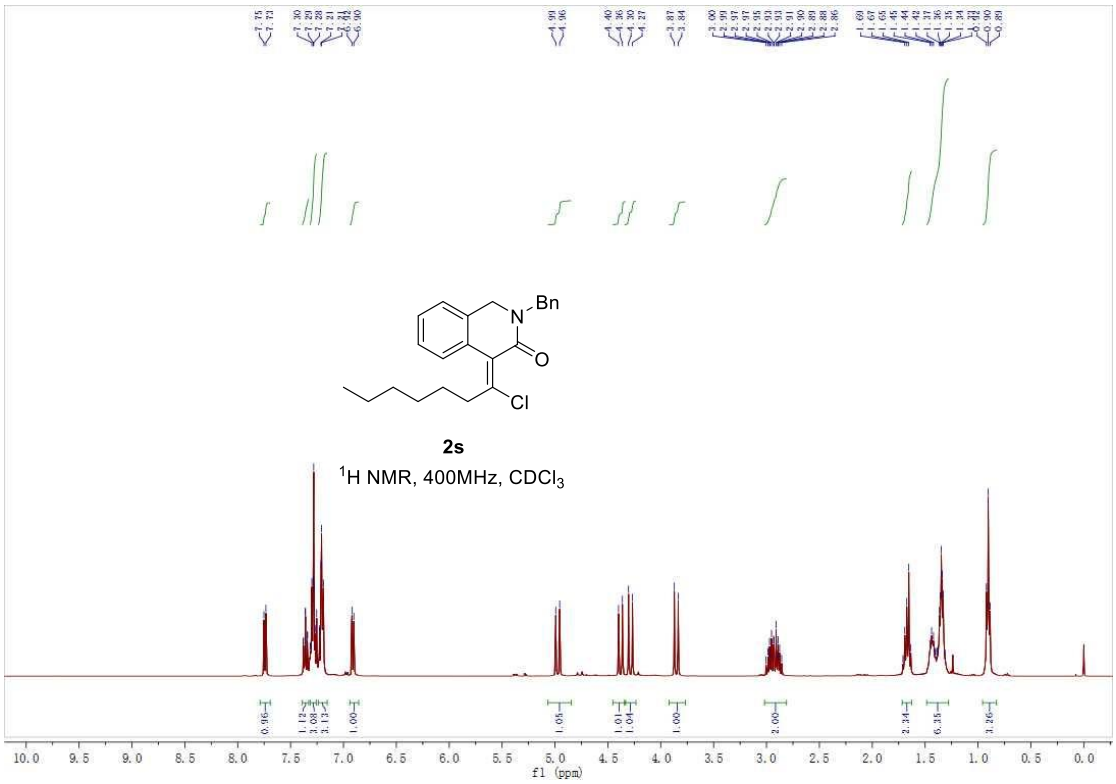

2s

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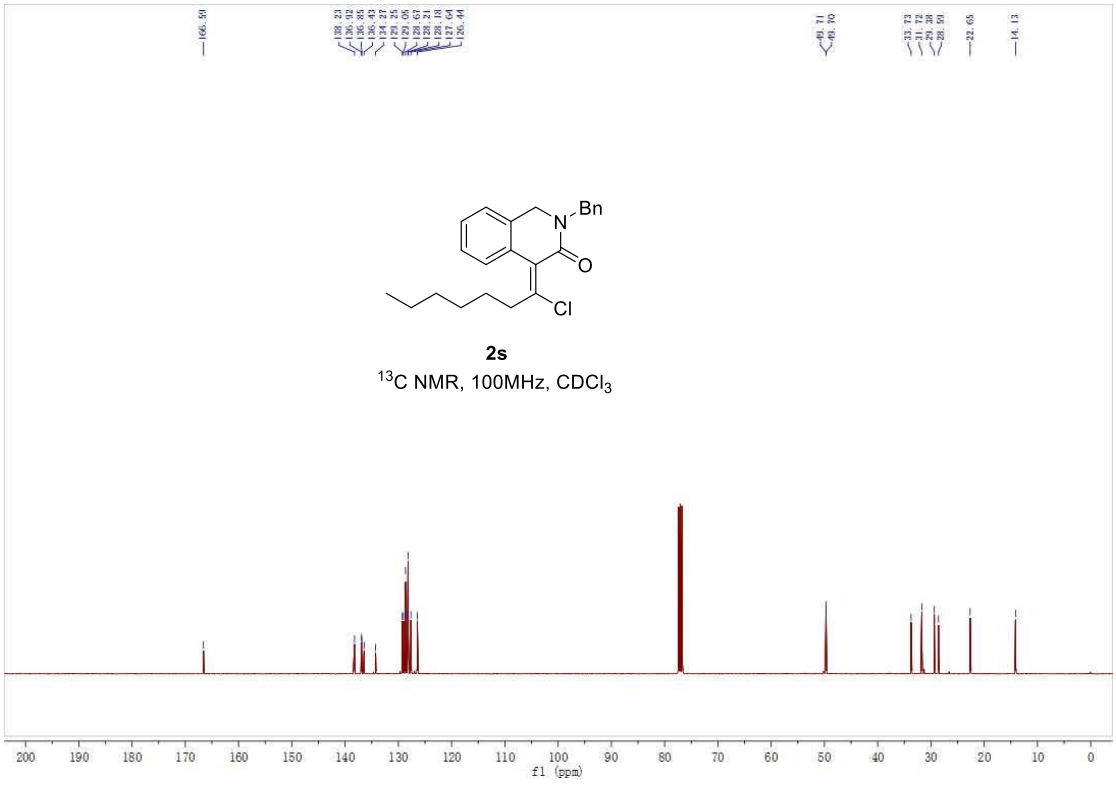
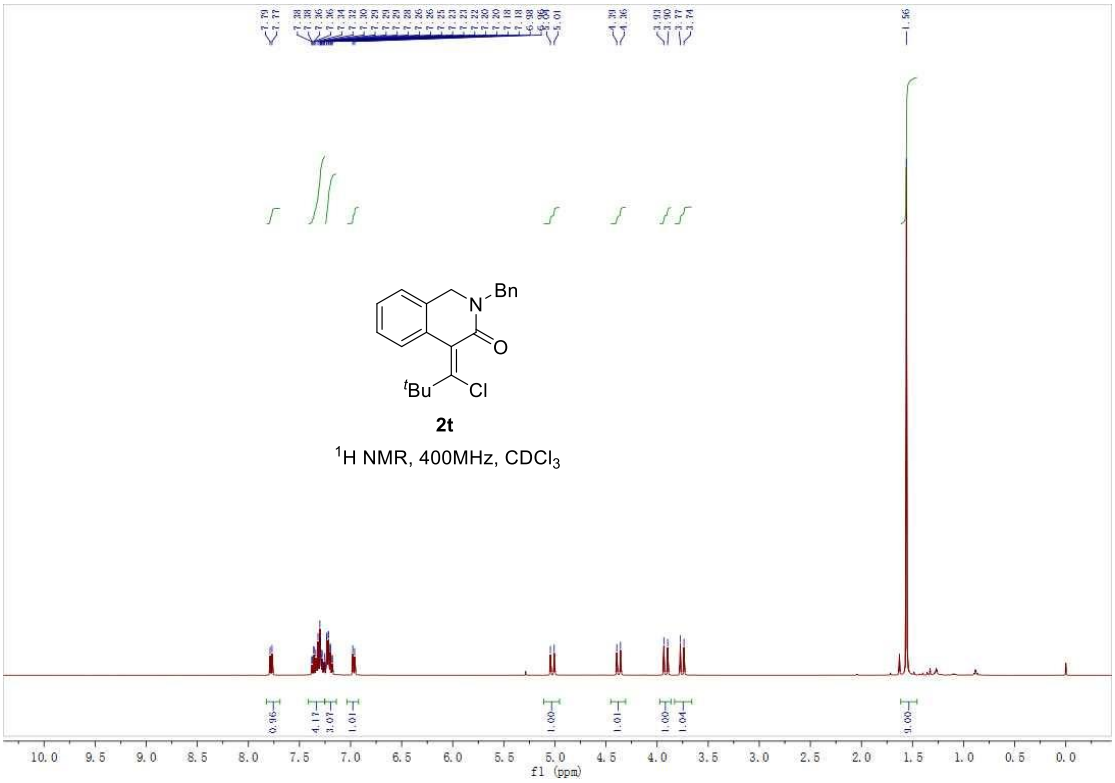


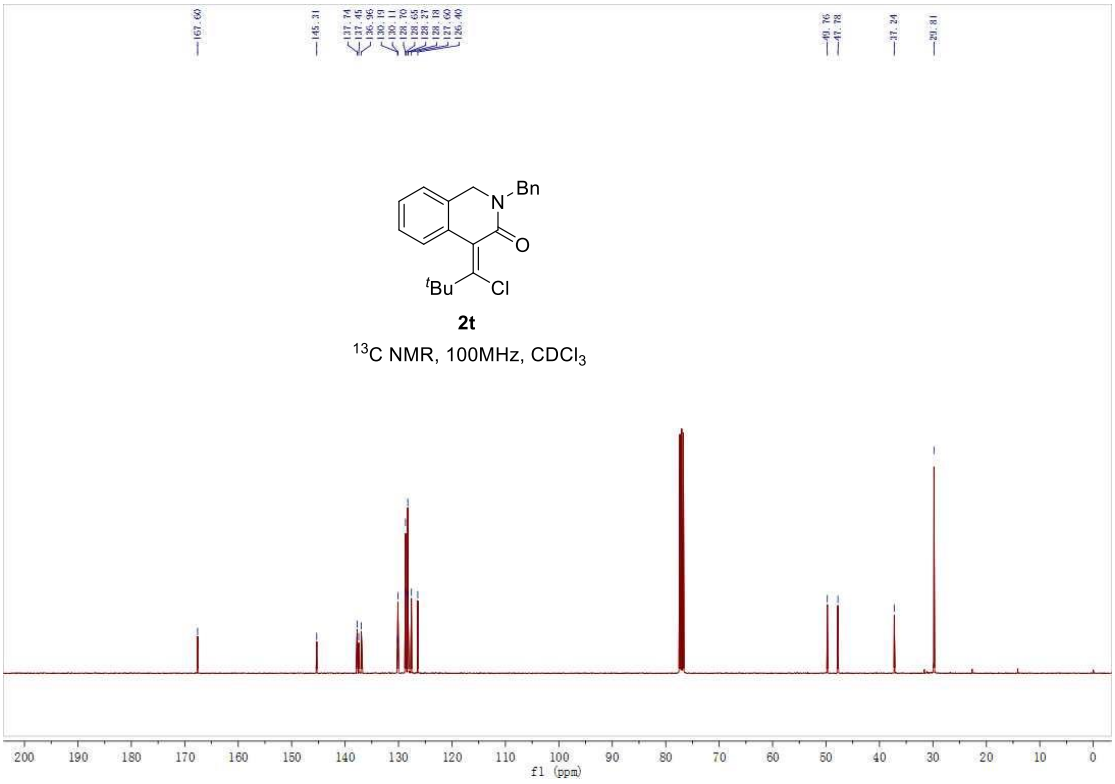
2s

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



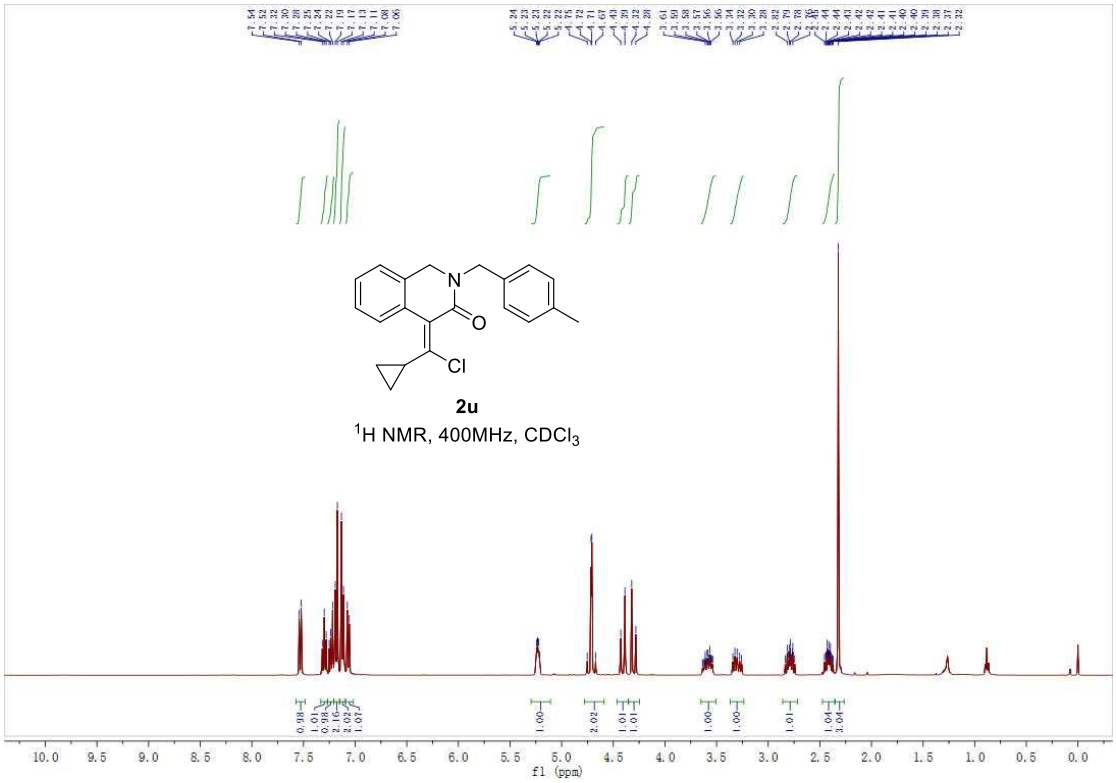
2t

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



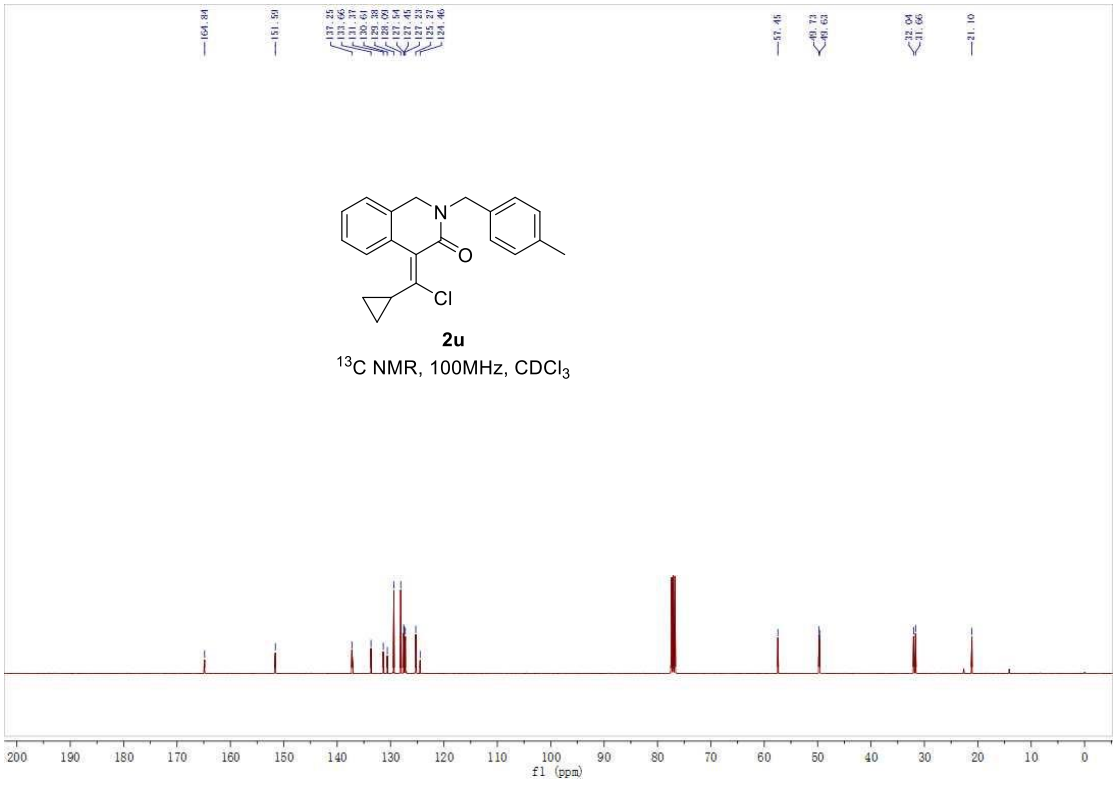
2t

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



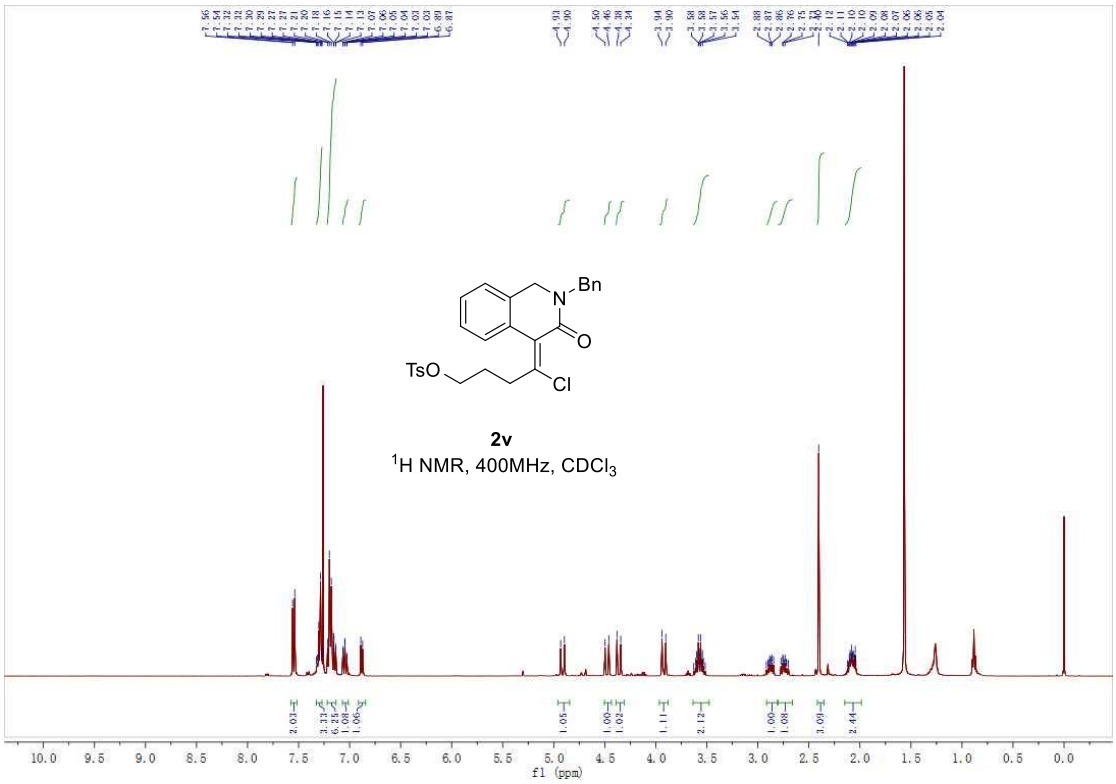
2u

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



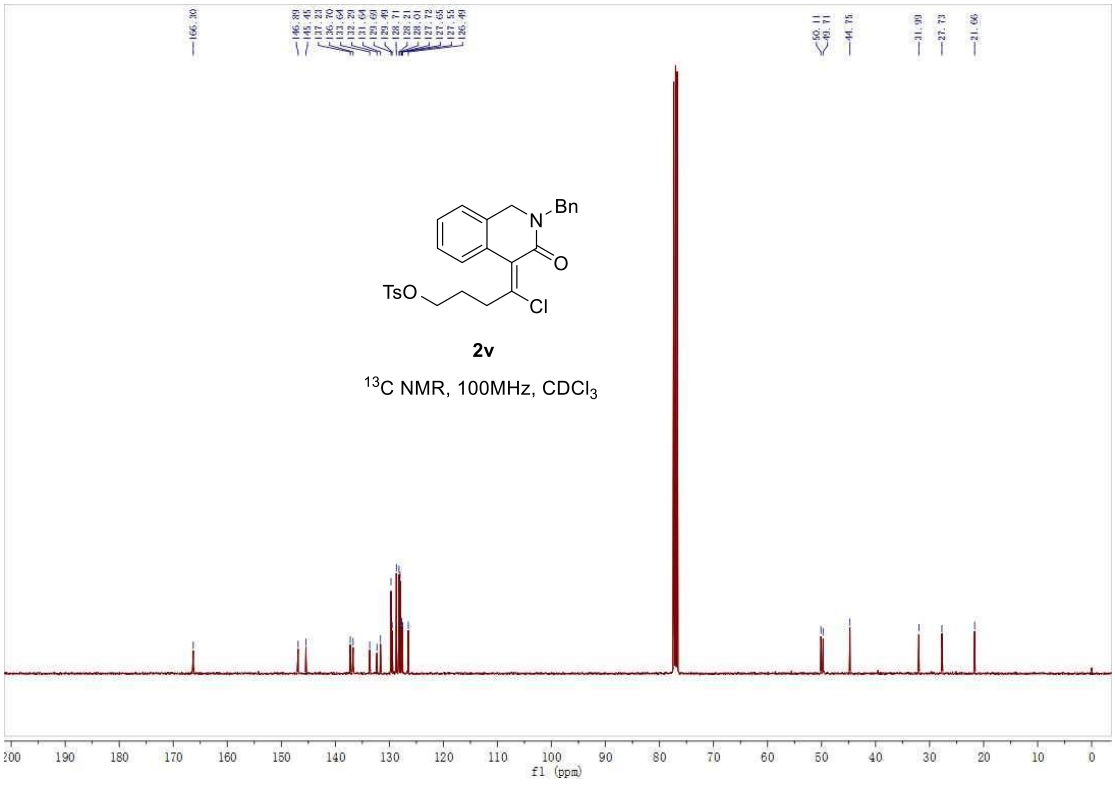
2u

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



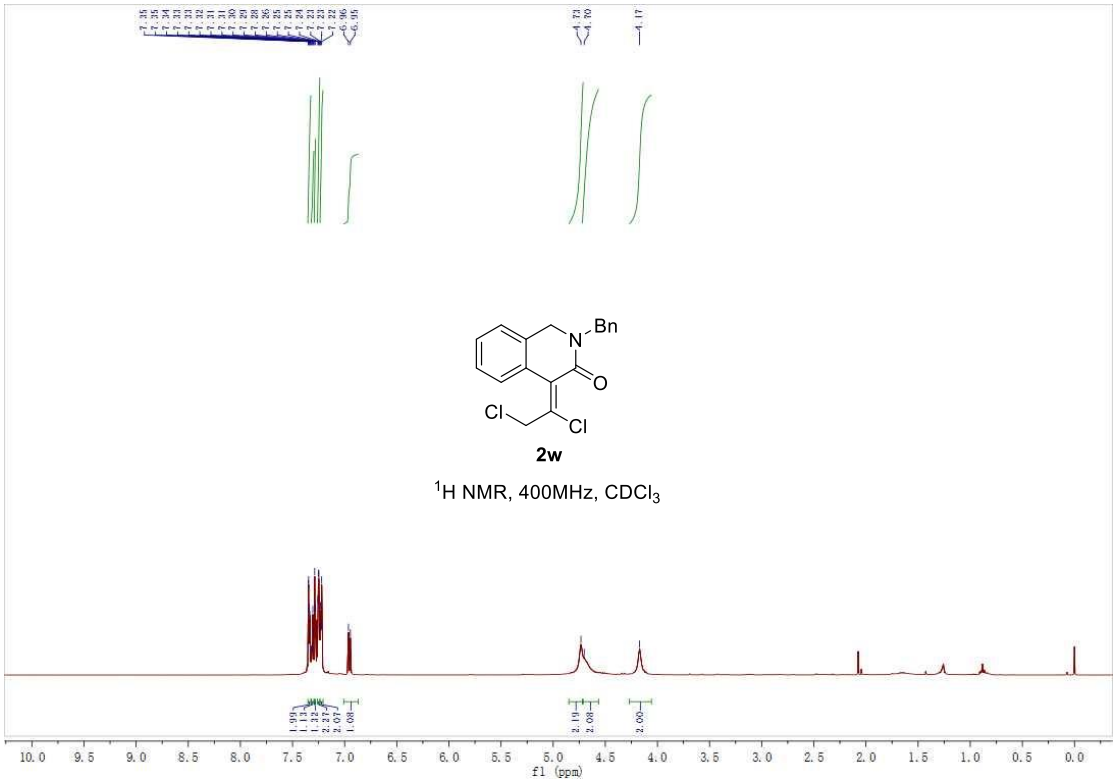
2v

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



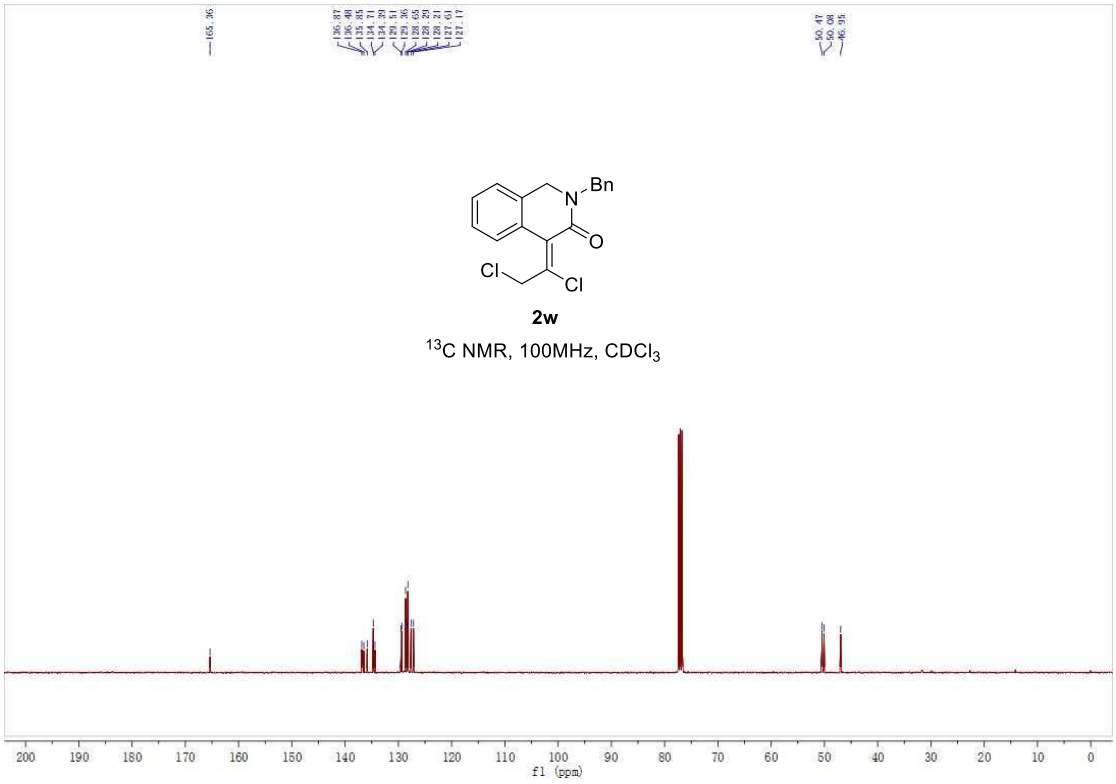
2v

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



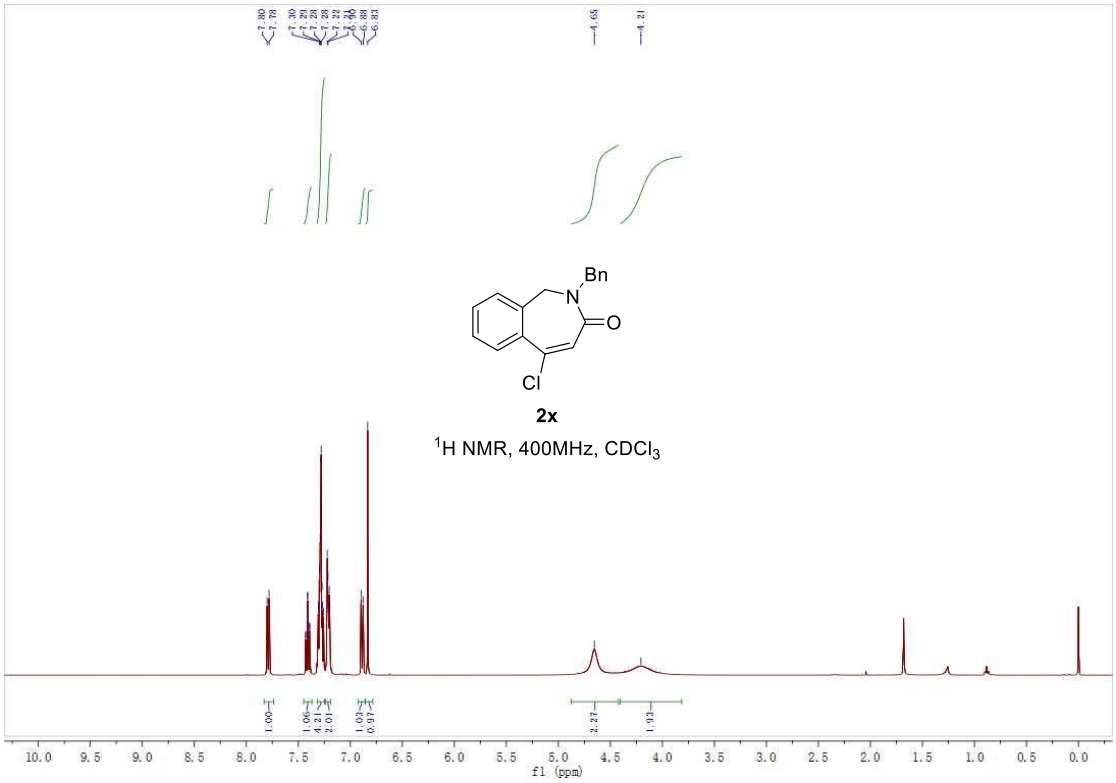
2w

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



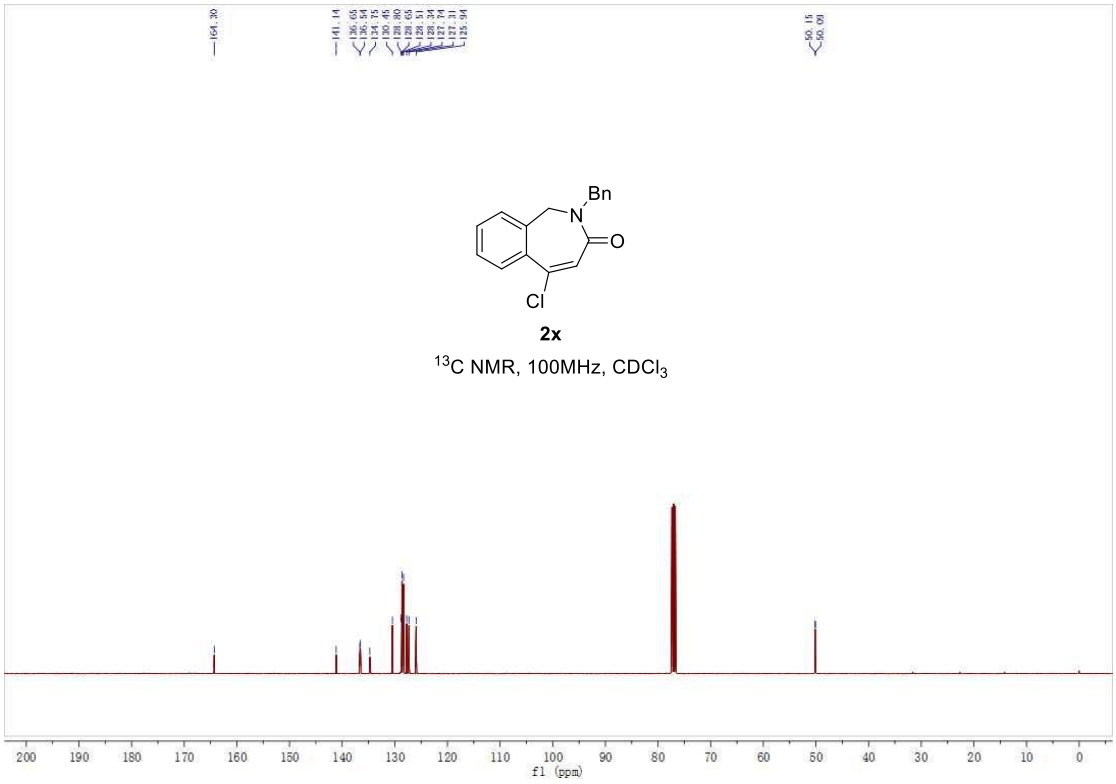
2w

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



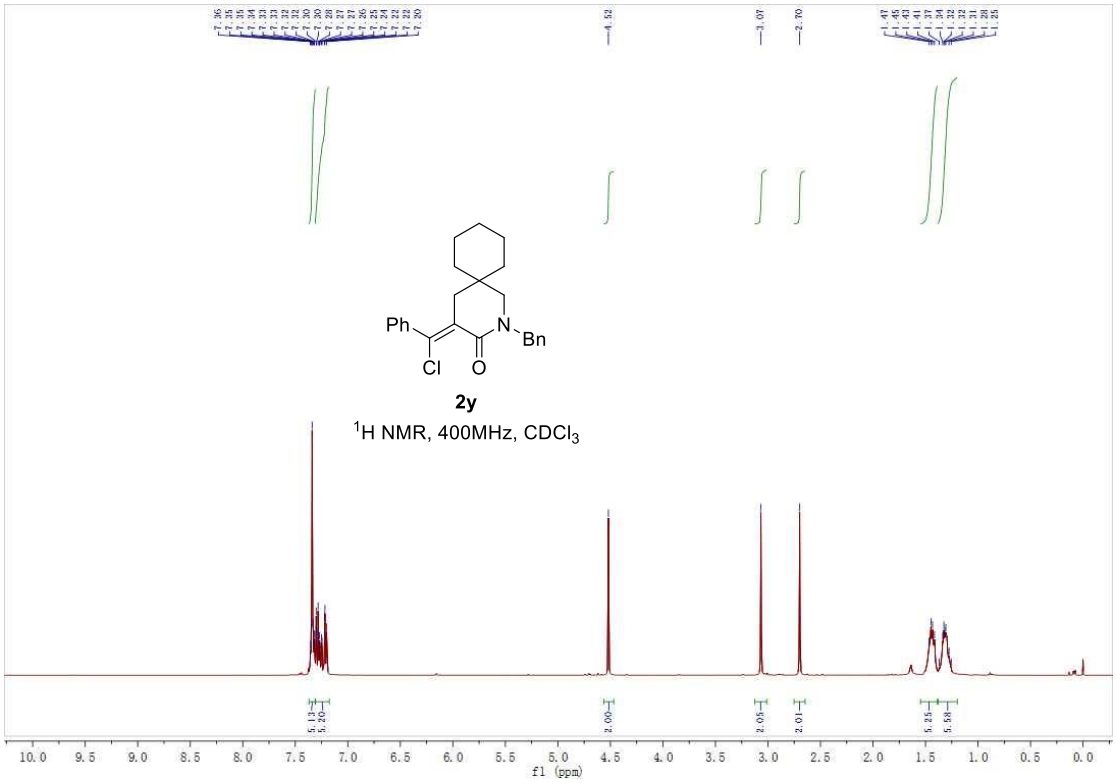
2x

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



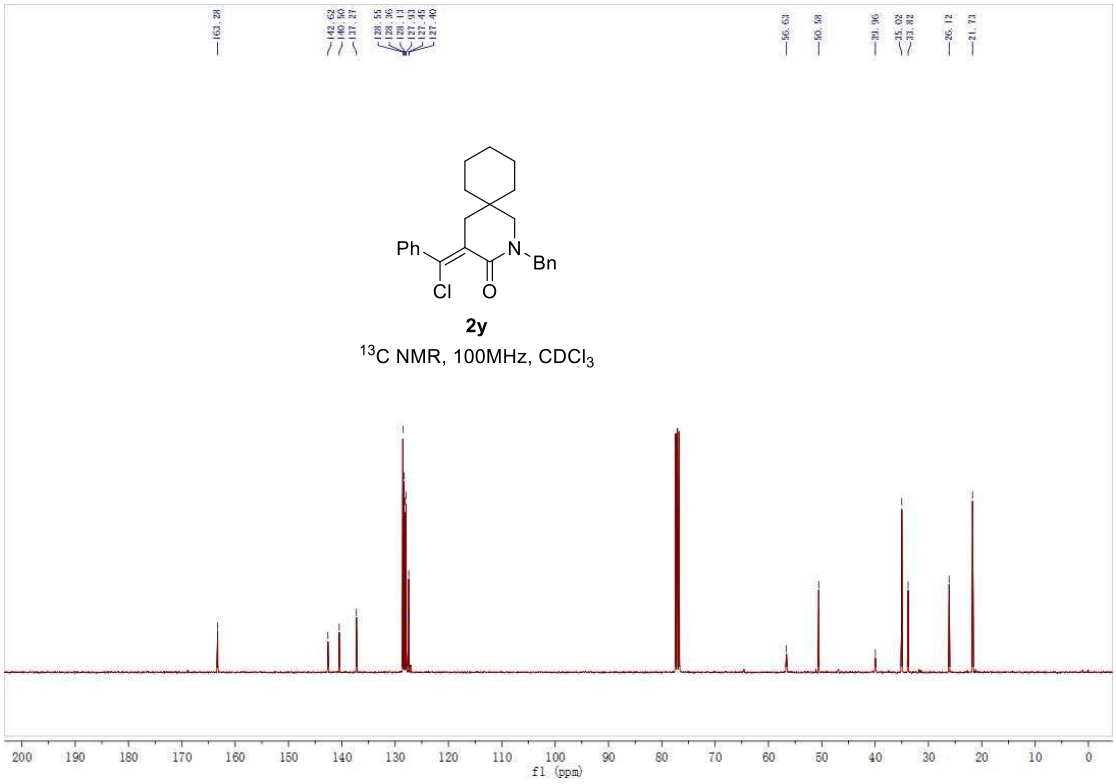
2x

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



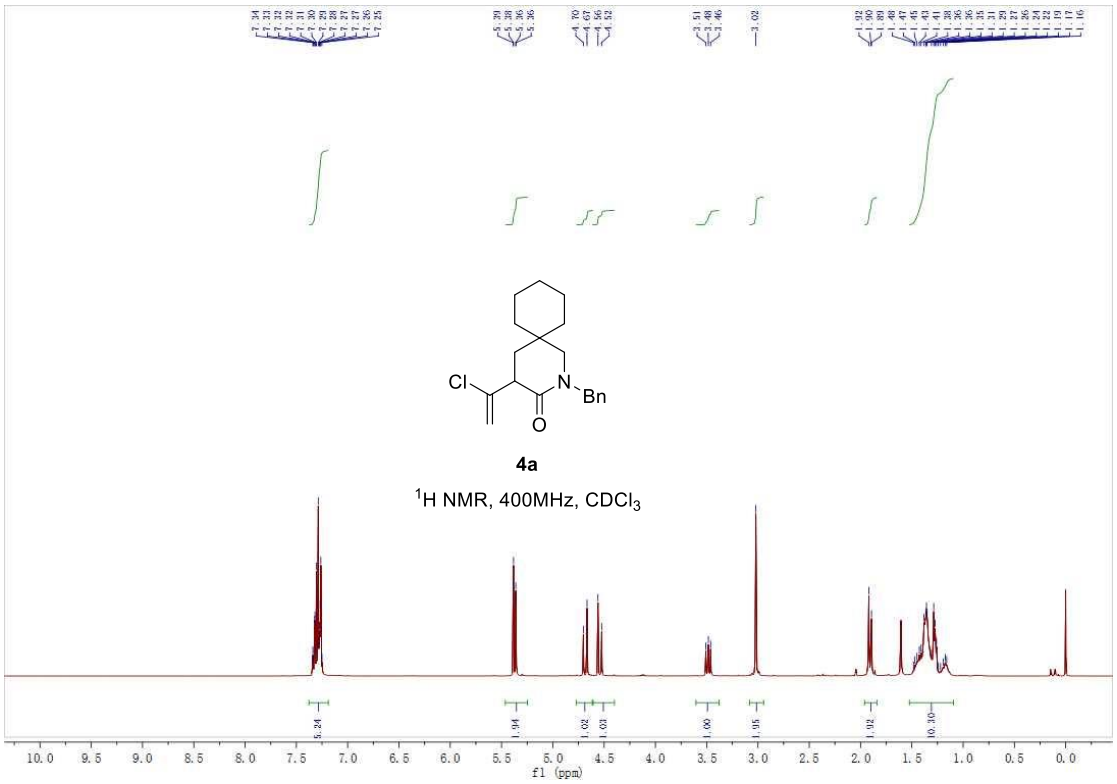
2y

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



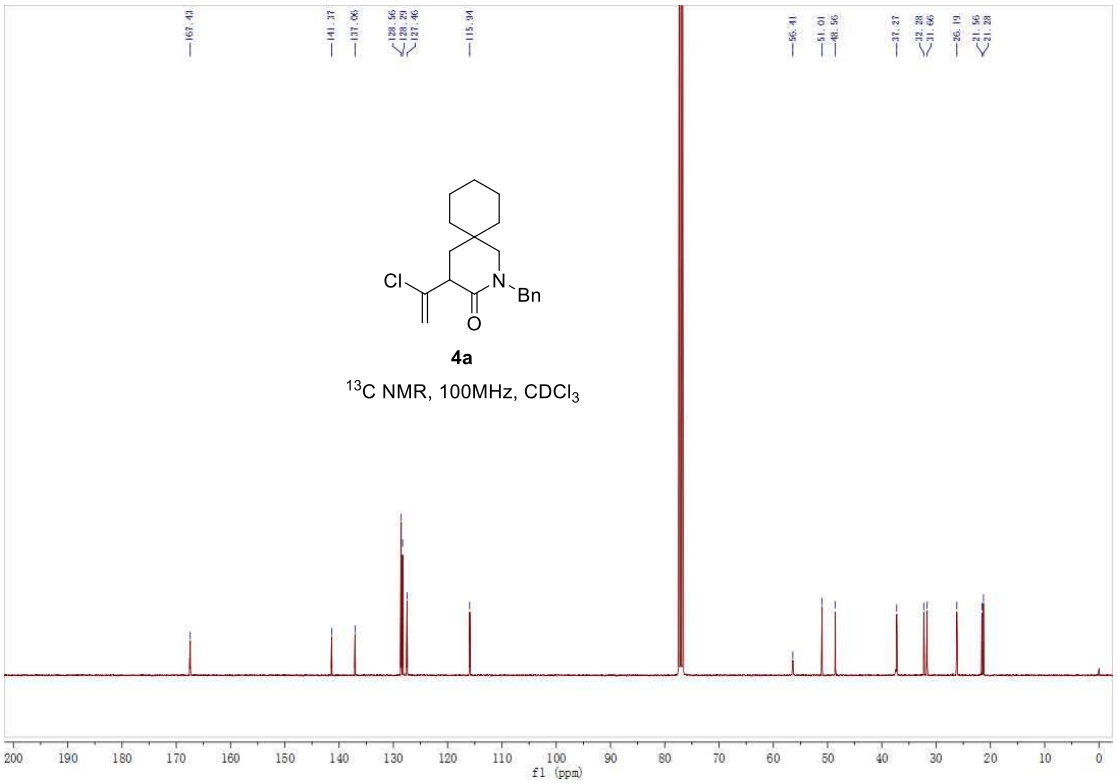
2y

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



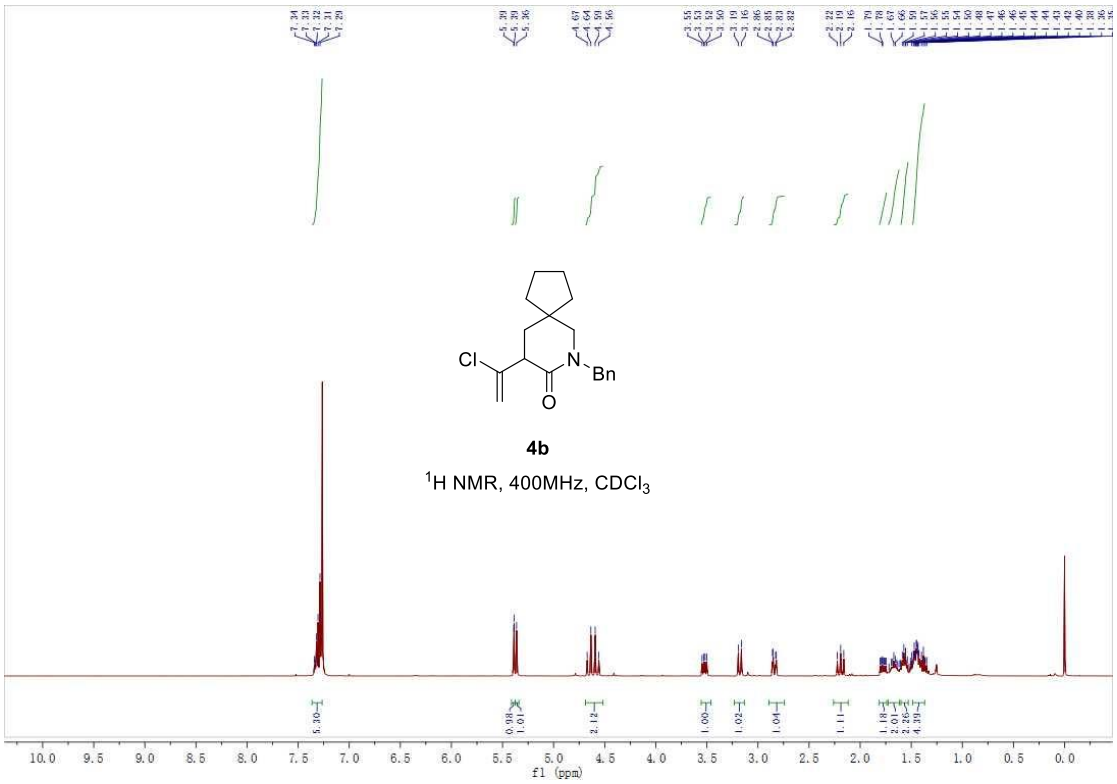
4a

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



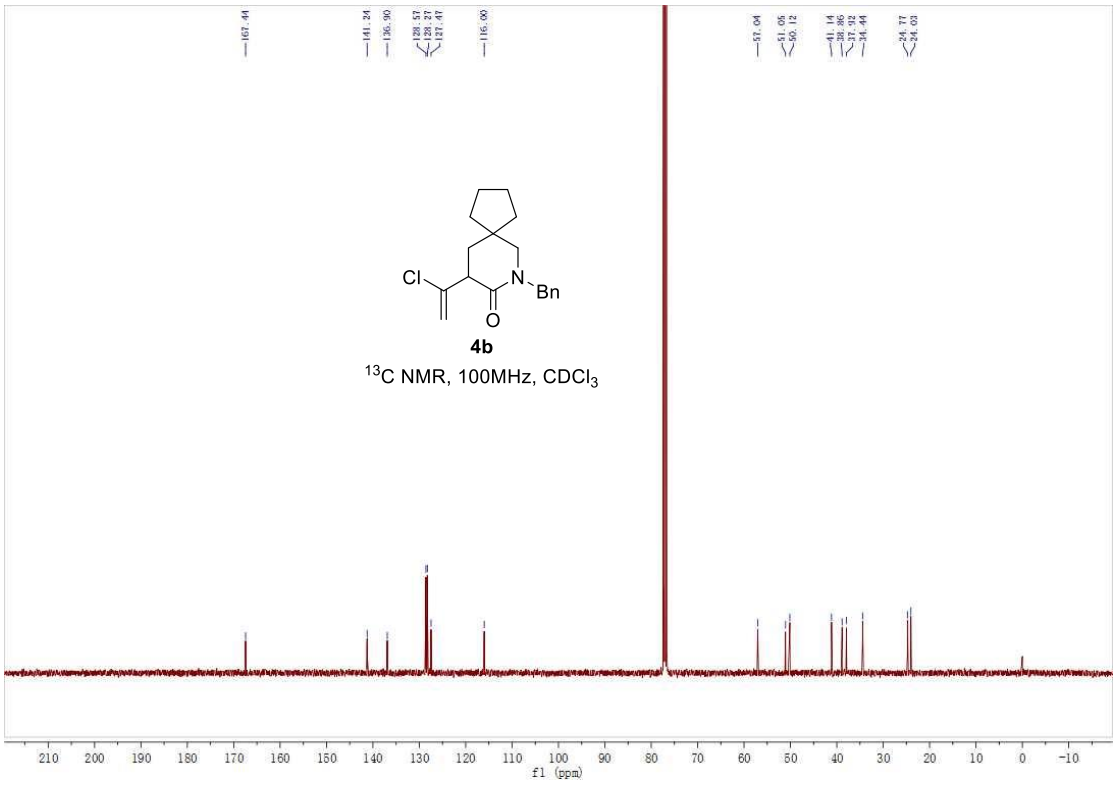
4a

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



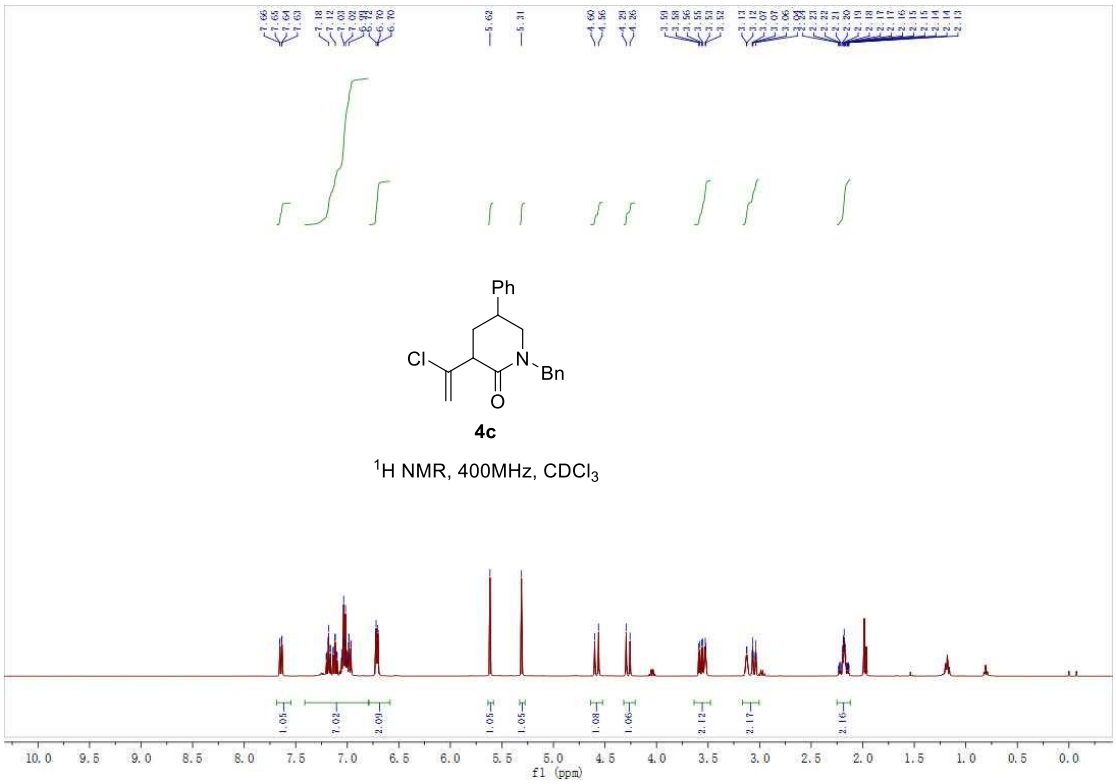
4b

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



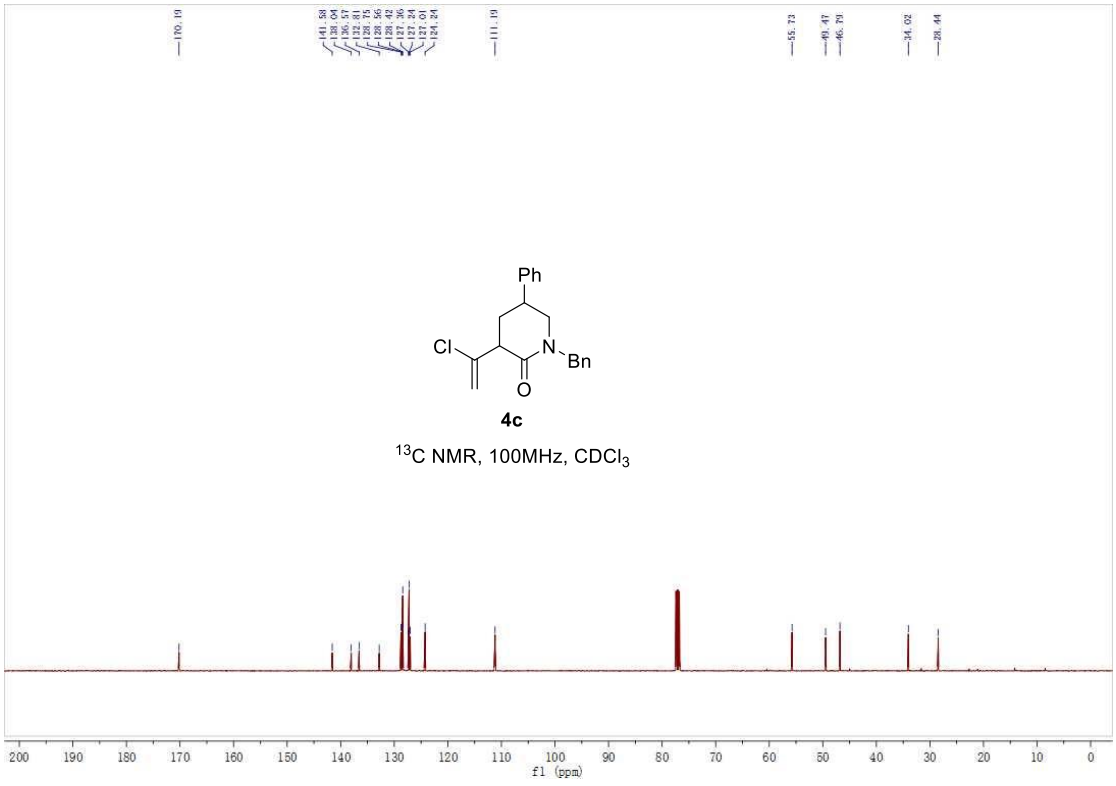
4b

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



4c

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



4c

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

7. X-ray Crystal Structure and Date of 2p

To get a high quality crystal for X-ray analysis, compound **2p** was dissolved in ethyl acetate and hexane, and was allowed to crystalize via careful evaporation of the solvent. (CCDC: 2361520).

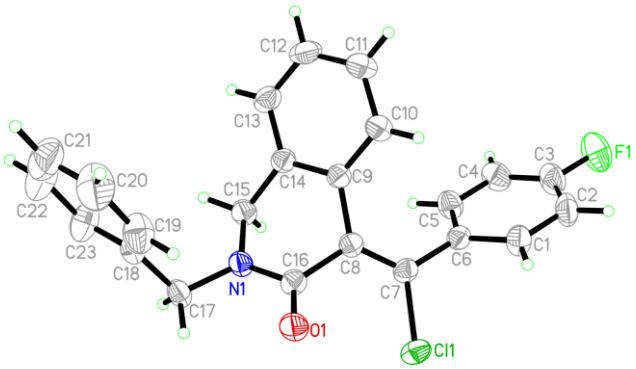


Figure S2. ORTEP drawings of **2p** at 30% displacement ellipsoid probability (the hydrogen atoms are omitted for clarity).

Table S1. Crystal data and structure refinement for **2p**.

Empirical formula	$C_{23}H_{17}ClFNO$
Formula weight	377.83
Temperature	273(2)
Wavelength	0.71073
Unit cell dimensions	a=14.9521(12)
	b=6.7931(5)
	c=18.8317(16)
	α =90
	β =95.218(5)
	γ = 90
Volume	1904.8(3)
Z, Calculated density	4, 1.317
Absorption coefficient	0.222
F(000)	784
Theta range for data collection	2.172-28.338

Limiting indices	-19 < h < 19, -8 < k < 7, -24 < l< 25
Reflections collected / unique	12683/4306
Completeness to theta = 28.51	0.967
Refinement method	none
Data / restraints / parameters	12683/4306/244
Goodness-of-fit on F^2	1.004
Final R indices [I>2sigma(I)]	0.0640
R indices (all data)	0.2036
Largest diff. peak and hole	0.223/-0.227

8. X-ray Crystal Structure and Date of 2x

To get a high quality crystal for X-ray analysis, compound **2x** was dissolved in ethyl acetate and hexane, and was allowed to crystalize via careful evaporation of the solvent. (CCDC: 2361518).

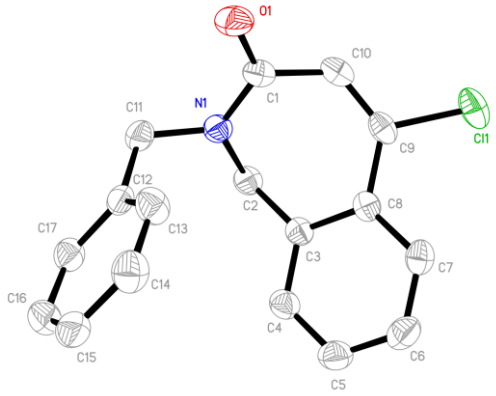


Figure S3. ORTEP drawings of **2x** at 30% displacement ellipsoid probability (the hydrogen atoms are omitted for clarity).

Table S2. Crystal data and structure refinement for **2x**.

Empirical formula	$C_{17}H_{14}ClNO$
Formula weight	283.74
Temperature	273(2)
Wavelength	0.71073

Unit cell dimensions	a=9.6809(3)
	b=6.2345(2)
	c=23.1731(8)
	α =90
	β =93.7841(14)
	γ = 90
Volume	1395.58(8)
Z, Calculated density	4
Absorption coefficient	0.222
F(000)	592
Theta range for data collection	2.23-28.15
Limiting indices	-12 < h < 12, -8 < k < 8, -30 < l< 30
Reflections collected / unique	3470/2767
Completeness to theta = 28.51	0.967
Refinement method	none
Data / restraints / parameters	3470/2767/181
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	0.0439
R indices (all data)	0.1302
Largest diff. peak and hole	0.201/-0.342