Supporting Information

C8-H Bond Activation Vs C2-H Bond Activation: From Naphthyl Amines to Lactams

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1. General

All reactions were carried out in oven-dried Schlenk tube under a mixed oxygen and carbon monoxide atmosphere with a balloon. Toluene and DMA were dried by molecular sieve. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. GC yields were recorded with a SHIMADZU GC-2014 gas chromatograph instrument with a FID detector and biphenyl was added as an internal standard. ^{1}H and ^{13}C NMR data were recorded with Bruker Advanced II (400 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform), respectively. High resolution massspectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion ($[M]^{+}$).

2. Preparation of *N, N*-disubstituted naphthylamines

Preparation of *N, N*-disubstituted naphthylamines employed the procedure of Zimmt [1]. General Procedure: A mixture of fresh naphthylamine (10.0 mmol), iodoalkane (42.0 mmol), and K_2CO_3(15.0 mmol) in DMF (13 mL) was refluxed at 65 ^{o}C for 25 h. Then we increase the temperature to 120 ^{o}C for 3 h. The suspension was filtered, and the resulting solid was washed with CH_2Cl_2. The filtered solution was extracted with water, and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel is conducted.

3. Preparation of *d_7-N, N*-dimethyl naphthylamines

Preparation of *N, N*-disubstituted naphthylamines employed the procedure of Miura[2]: NaNO3 (570 mg, 6.7 mmol) was dissolved in TFA (28 mL), and naphthalene-d8 (99% D, 1.0 g, 7.35 mmol) was added in several portions at room temperature under air. The mixture was stirred for 5 h at the same temperature, cooled to 0 °C with an ice water bath, and then neutralized with 6 M aq NaOH. The organic phase was extracted with diethyl ether and evaporated under reduced pressure. The crude *d_7*-1-nitronaphthalene obtained was used for the next step without further purification. To a mixture of the above d7-1-nitronaphthalene and concentrated aq HCl (ca. 11 M, 7.0 mL) in EtOH (15 mL), Sn powder (3.5 g, 29 mmol) was added in several portions, and the resulting mixture was stirred at room temperature under air. After 6 h, volatile materials were evaporated in vacuo, and residue was dissolved in water and diethyl ether. The mixture was neutralized with saturated aq K_2CO_3 and then filtered through a pad of Celite. The filtrate was extracted with ethyl acetate, concentrated under reduced pressure, and purified by column chromatography on silica gel with hexane/ethyl acetate (3/1, v/v) to afford *d_7*-1-naphthylamine. A mixture of fresh *d_7*-1-naphthylamine, iodoalkane (2.2 eq.), and K_2CO_3(2.2 eq.) in DMF was refluxed at 65 ^{o}C for 25 h. Then increase the temperature to 120 ^{o}C for 3 h. The suspension was filtered, and the resulting solid was washed with CH_2Cl_2. The filtered solution was extracted with water, and the organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by column chromatography on silica gel afforded *d_7-N, N*-

dimethyl naphthylamines.

4. Palladium / Copper-Catalyzed Oxidative C-H Activation/ N-Dealkylative Carbonylation of Tertiary 1-Naphthylamines

General Procedure: In an oven-dried Schlenk tube equipped with a stir-bar, $PdCl_2$ (3.6 mg, 10 mol%), $Cu(OAc)_2•H_2O$ (12.0 mg, 30 mol%) were combined. A balloon filled with CO and O_2 (the ratio is 2:1) was connected to the Schlenk tube via the side tube and purged for 3 times. Then DMA (0.2 mL) and toluene(1.0 mL) were added to the tube via a syringe. At last, naphthylamines (0.2 mmol), AcOH (4.8 mg, 40 mol%) was added to the tube. The Schlenk tube was heated at 110 ^oC for 24 hours and then cooled to room temperature. After the balloon gas was released carefully, the reaction was quenched by water and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with hexane, ethyl acetate.

Equivalent experiment: In an oven-dried Schlenk tube equipped with a stir-bar, $PdCl_2$ or $Pd(OAc)_2$ (0.4 mmol, 200 mol%) was added. A balloon filled with CO and O_2 (the ratio is 2:1) was connected to the Schlenk tube via the side tube and purged for 3 times. Then DMA (0.2 mL) and toluene(1.0 mL) were added to the tube via a syringe. At last, naphthylamines (0.2 mmol), AcOH (4.8 mg, 40 mol%) was added to the tube. The Schlenk tube was heated at 110 ^oC for 24 hours and then cooled to room temperature. After the balloon gas was released carefully, the reaction was quenched by water and extracted with CH_2Cl_2 three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by flash chromatography on silica gel with hexane, ethyl acetate.

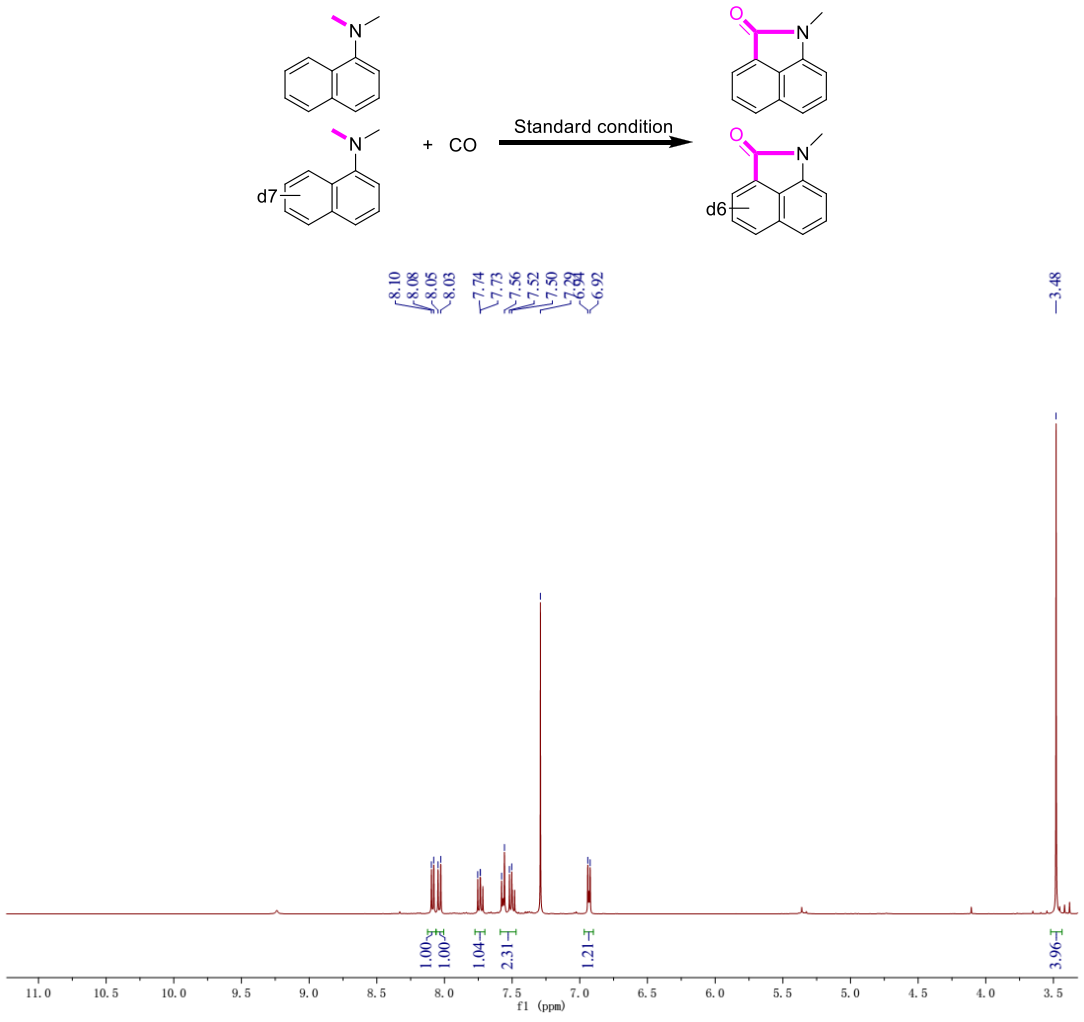
5. Palladium / copper-catalyzed oxidative intramolecular N-dealkylative carbonylation of 1a: effects of reaction parameters

Entry	Variation from "standard conditions"	Yield%[a]
1	none	70(71)
2	No $Cu(OAc)_2•H_2O$	0
3	No $PdCl_2$	0
4	$Pd(OAc)_2$ instead of $PdCl_2$	34
5	$PdCl_2(PPh_3)_2$ instead of $PdCl_2$	55

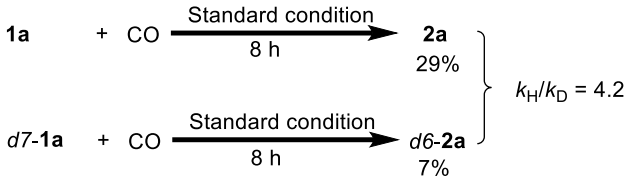
6	$Cu(OAc)_2$ instead of $Cu(OAc)_2 \cdot H_2O$	61
7	$Cu(OPiv)_2$ instead of $Cu(OAc)_2 \cdot H_2O$	53
8	CO/air = 3/ 1	21
9	1.0 mL toluene instead of mixed solvents	4
10	0.2 mL DMSO instead of DMA	20
11	0.2 mL DMF instead of DMA	60
12	90 °C instead of 110 °C	37
13	No AcOH	27

Standard reaction conditions : **1a** (0.2 mmol), $PdCl_2$ (10 mol%), $Cu(OAc)_2 \cdot H_2O$ (30 mol%), AcOH (40 mol%), CO/O_2 =2/1, toluene/DMA =1.0/0.2, 110 °C, 24 h. [a] The yields were determined by GC, and were calibrated using biphenyl as the internal standard.

6. Competing Kinetic Isotope Effect (KIE) Experiment



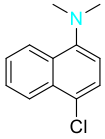
Note: The value of k_H/k_D was calculated from the ^1H NMR spectra above which should be the mixture of compound **2a** and d_6-**2a** (the KIE scheme). As a result, k_H/k_D = 3/(3.96-3) =3.1



Note: The value of k_H/k_D was calculated from GC yield. As a result, k_H/k_D = 4.2

7. Analytical Data of Substrates and Products

4-chloro-*N, N*-dimethylnaphthalen-1-amine

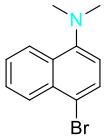


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.23 (m, 2H), 7.60-7.54 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 2.87 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.18, 131.58, 129.86, 126.78, 125.90, 125.83, 125.70, 124.84, 124.52, 114.05, 45.24.

HRMS (ESI) calcd for $C_{12}H_{12}ClN$ $[M]^+$: 205.0658; Found:205.0662.

4-bromo-*N, N*-dimethylnaphthalen-1-amine

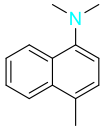


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.20 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60-7.51 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 2.88 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.87, 132.72, 130.02, 129.56, 127.54, 127.08, 125.85, 124.55, 116.35, 114.65, 45.19.

HRMS (ESI) calcd for $C_{12}H_{12}BrN$ $[M]^+$:249.0153; Found: 249.0150.

***N, N*, 4-trimethylnaphthalen-1-amine**

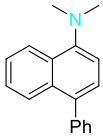


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.27 (m, 1H), 7.97-7.95 (m, 1H), 7.52-7.49 (m, 2H), 7.23 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 2.87 (s, 6H), 2.63 (d, *J* = 0.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.29, 133.58, 128.88, 128.86, 126.26, 125.57, 124.99, 124.57, 124.48, 113.73, 45.41, 19.13.

HRMS (ESI) calcd for $C_{13}H_{15}N$ $[M]^+$: 185.1204; Found: 185.1205.

_N_, _N_-dimethyl-4-phenylnaphthalen-1-amine

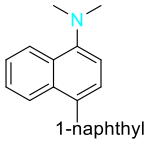


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31(d, *J* = 8.4Hz, 1H), 7.89(d, *J* = 8.4 Hz, 1H), 7.51-7.46 (m, 5H), 7.42-7.38 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 2.93 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.35, 141.00, 135.00, 132.74, 130.18, 128.84, 128.16, 126.85, 126.80, 126.46, 125.79, 125.00, 124.36, 113.52, 45.23.

HRMS (ESI) calcd for $C_{18}H_{17}N$ $[M]^+$: 247.1361; Found: 247.1356.

_N_, _N_ -dimethyl-1,1'-binaphthyl-4-amine

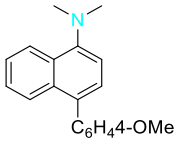


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.57-7.53 (m, 1H), 7.47-7.42 (m, 4H), 7.37 (dd, *J* = 8.0, 4.8 Hz, 2H), 7.28-7.22 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 2.97 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.64, 138.79, 134.03, 133.51, 133.13, 133.04, 128.68, 128.06, 128.01, 127.71, 127.61, 127.05, 126.72, 125.81, 125.70, 125.68, 125.38, 124.96, 124.26, 113.47, 45.31.

HRMS (ESI) calcd for $C_{22}H_{19}N$ $[M]^+$: 297.1517; Found: 297.1513.

4-(4-methoxyphenyl)-_N_, _N_-dimethylnaphthalen-1-amine



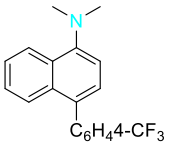
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.50-7.46 (m, 1H), 7.42-7.37 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.02-6.98 (m, 2H), 3,86 (s, 3H), 2.91 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.61, 150.07, 134.65, 133.33, 132.93, 131.16, 128.86, 126.74,

126.49, 125.69, 124.95, 124.31, 113.58, 113.55, 55.27, 45.23.

HRMS (ESI) calcd for $C_{19}H_{19}NO$ $[M]^+$:277.1467; Found:277.1465.

_N_, _N_-dimethyl-4-(4-(trifluoromethyl)phenyl)naphthalen-1-amine



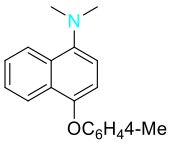
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.52-7.48 (m, 1H), 7.42-7.38 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 3.92 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.13, 144.82, 133.32, 132.46, 130.47, 129.00 (q, *J* = 32.3 Hz), 128.88, 127.04, 126.20, 125.93, 125.22, 125.14 (q, *J* = 1.6 Hz), 124.64, 124.44 (q, *J* = 272.7 Hz), 113.42, 45. 13.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.17.

HRMS (ESI) calcd for $C_{19}H_{16}F_3N$ $[M]^+$: 315.1235; Found: 315.1236.

_N_, _N_-dimethyl-4-(p-tolyloxy)naphthalen-1-amine

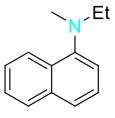


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 8.16-8.14 (m, 1H), 7.54-7.50 (m, 1H), 7.48-7.43 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.92-6.88 (m, 3H), 2.87 (s, 6H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.23, 148.57, 146.81, 132.00, 130.10, 129.98, 127.92, 125.84, 125.78, 124.10, 122.49, 117.76, 113.80, 113.70, 45.44, 20.64.

HRMS (ESI) calcd for $C_{19}H_{19}NO$ $[M]^+$: 277.1467; Found:277.1468.

_N_-ethyl-_N_-methylnaphthalen-1-amine



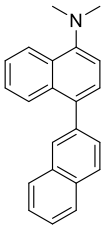
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23-8.21 (m, 1H), 7.82-7.80 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.49-7.42 (m, 2H), 7.40-7.36 (m, 1H), 7.08 (dd, *J* = 7.2, 0.8 Hz, 1H), 3.13 (q, *J* = 7.2 Hz, 2H), 2.85 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.26, 134.77, 129.48, 128.24, 125.63, 125.07, 123.98, 122.86,

115.30, 51.50, 41.22, 12.73.

HRMS (ESI) calcd for $C_{13}H_{15}N$ $[M]^+$: 185.1204; Found: 185.1209.

***N, N*-dimethyl-[1,2'-binaphthalen]-4-amine**

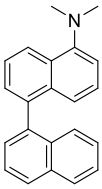


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.4 Hz, 1H), 7.93-7.85 (m, 4H), 7.63-7.48 (m, 6H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 2.93 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.08, 140.46, 138.80, 133.32, 133.05, 132.44, 129.19, 128.69, 128.59, 128.02, 127.68, 127.47, 127.17, 126.20, 125.93, 125.83, 124.63, 123.86, 121.01, 113.91, 45.35.

HRMS (ESI) calcd for $C_{22}H_{19}N$ $[M+H]^+$: 289.1590; Found: . 289.1591

***N, N*-dimethyl-[1,1'-binaphthalen]-5-amine**

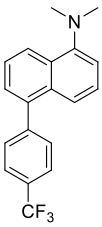


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.57-7.53 (m, 1H), 7.47-7.42 (m, 4H), 7.37-7.36 (m, 2H), 7.27-7.24 (m, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 2.97 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.57, 138.74, 133.97, 133.45, 133.08, 133.00, 128.60, 128.05, 128.00, 127.69, 127.60, 127.04, 126.69, 125.80, 125.70, 125.68, 125.38, 124.97, 124.23, 113.45, 45.30.

HRMS (ESI) calcd for $C_{22}H_{19}N$ $[M+H]^+$: 289.1590; Found: . 289.1591

***N, N*-dimethyl-5-(4-(trifluoromethyl)phenyl)naphthalen-1-amine**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 8.0

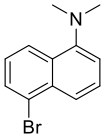
Hz, 2H),7.56-7.52 (m, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.39-7.33 (m, 2H), 7.12 (dd, *J* = 7.4 Hz,0.8 Hz 1H), 2.93 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.20, 144.97, 139.04, 132.56, 130.42, 129.16, 126.93, 126.18, 125.13, 125.09, 124.53, 124.50, 120.36, 114.11, 45.33.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.29.

HRMS (ESI) calcd for $C_{19}H_{16}F_3N$ $[M+H]^+$: 316.1308; Found: . 316.1308

5-bromo-*N, N*-dimethylnaphthalen-1-amine

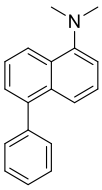


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.6 Hz 1H), 2.86 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.13, 133.17, 130.14, 129.87, 127.11, 125.24, 124.12, 123.11, 121.79, 114.81, 45.32.

HRMS (ESI) calcd for $C_{12}H_{12}BrN$ $[M+H]^+$: 250.0226; Found: . 250.0225

***N, N*-dimethyl-5-phenylnaphthalen-1-amine**

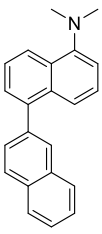


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 9.2 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.65-7.52 (m, 7H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 3.06 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.31, 140.96, 134.96, 132.71, 128.14, 126.82, 126.79, 126.44, 125.78, 124.99, 124.34, 45.19.

HRMS (ESI) calcd for $C_{18}H_{17}N$ $[M+H]^+$: 228.1434; Found: . 228.1434

***N, N*-dimethyl-[1,2'-binaphthalen]-5-amine**



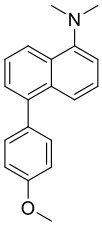
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.8 Hz, 1H), 7.94-7.85 (m, 5H), 7.62 (d, *J* = 8.4 Hz, 1H),

7.50-7.49 (m, 3H), 7.43-7.39 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 2.94 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.47, 138.55, 134.85, 133.41, 132.86, 132.35, 128.85, 128.72, 128.67, 127.96, 127.67, 127.50, 127.15, 126.52, 126.16, 125.89, 125.82, 125.07, 124.42, 113.55, 45.24.

HRMS (ESI) calcd for $C_{22}H_{19}N$ $[M+H]^+$: 298.1590; Found: . 298.1587.

5-(4-methoxyphenyl)-*N*, *N*-dimethylnaphthalen-1-amine

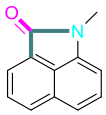


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.42-7.31 (m, 4H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 9.8 Hz, 2H), 3.88 (s, 3H), 2.91 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.75, 140.22, 133.60, 133.13, 131.14, 129.17, 126.87, 125.61, 124.64, 123.41, 121.05, 113.83, 113.54, 55.32, 45.36.

HRMS (ESI) calcd for $C_{19}H_{19}NO$ $[M+H]^+$: 278.1539; Found: . 278.1538.

1-methylbenzo[*cd*]indol-2(1*H*)-one

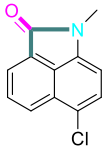


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.45 (dd, *J* = 8.4, 7.2 Hz, 1H), 6.88 (d, *J* = 6.8 Hz, 1H), 3.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.14, 139.96, 130.63, 128.87, 128.56, 128.42, 126.67, 125.00, 124.13, 120.24, 104.62, 26.28.

HRMS (ESI) calcd for $C_{12}H_9NO$ $[M]^+$: 183.0684; Found: 183.0687.

6-chloro-1-methylbenzo[*cd*]indol-2(1*H*)-one

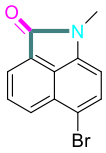


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.76 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 3.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.61, 138.93, 129.37, 128.03, 127.65, 127.27, 126.84, 125.83, 124.98, 124.88, 105.02, 26.31.

HRMS (ESI) calcd for $C_{12}H_8ClNO$ $[M]^+$: 217.0294; Found: 217.0297.

6-bromo-1-methylbenzo[*cd*]indol-2(1*H*)-one

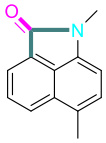


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 7.2 Hz, 1H), 7.75 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 3.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.51, 139.64, 131.13, 130.18, 129.64, 128.68, 126.88, 125.94, 125.04, 114.03, 105.69, 26.38.

HRMS (ESI) calcd for $C_{12}H_8BrNO$ $[M]^+$: 260.9789; Found: 260.9791.

1, 6-dimethylbenzo[*cd*]indol-2(1*H*)-one

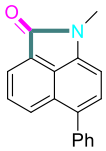


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 11.6, 7.6 Hz, 2H), 7.69 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.19 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 3.40 (s, 3H), 2.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.11, 138.13, 128.90, 128.66, 128.16, 128.09, 127.57, 126.99, 125.21, 123.81, 104.74, 26.20, 17.45.

HRMS (ESI) calcd for $C_{13}H_{11}NO$ $[M]^+$: 197.0841; Found: 197.0838.

1-methyl-6-phenylbenzo[*cd*]indol-2(1*H*)-one

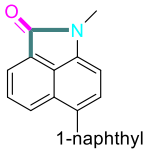


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 6.8 Hz, 1H), 7.67 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.55-7.48 (m, 4H), 7.45-7.42 (m, 2H), 6.94 (d, *J* = 7.2 Hz, 1H), 3.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.06, 139.23, 138.94, 134.11, 129.77, 129.67, 128.64, 128.48, 127.39, 127.25, 126.77, 125.13, 124.12, 104.75, 26.23.

HRMS (ESI) calcd for $C_{18}H_{13}NO$ $[M]^+$: 259.0997; Found: 259.0999.

1-methyl-6-(naphthalen-1-yl)benzo[*cd*]indol-2(1*H*)-one

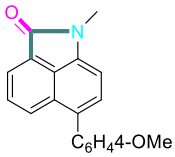


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.8 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.60-7.47 (m, 7H), 7.34-7.31 (m, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 3.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.27, 139.68, 136.56, 133.61, 132.79, 132.43, 130.19, 129.78, 128.96, 128.66, 128.25, 128.21, 128.11, 126.83, 126.23, 126.03, 125.86, 125.30, 125.06, 124.32, 104.65, 26.39.

HRMS (ESI) calcd for $C_{22}H_{15}NO$ $[M]^+$: 309.1154; Found: 309.1148.

6-(4-methoxyphenyl)-1-methylbenzo[*cd*]indol-2(1*H*)-one

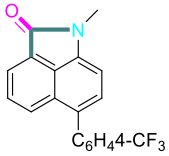


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 6.8 Hz, 1H), 7.65 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.46-7.43 (m, 2H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.05-7.02 (m, 2H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.06, 158.97, 138.87, 133.83, 131.38, 130.70, 129.82, 128.52, 128.12, 127.57, 126.80, 125.16, 124.04, 113.93, 104.81, 77.32, 77.00, 76.68, 55.28, 26.21.

HRMS (ESI) calcd for $C_{19}H_{15}NO_2$ $[M]^+$: 289.1103; Found: 289.1110.

1-methyl-6-(4-(trifluoromethyl)phenyl)benzo[*cd*]indol-2(1*H*)-one



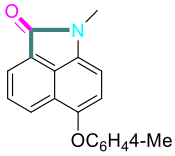
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.69-7.63 (m, 3H), 7.43 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 3.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.90, 142.64, 139.96, 132.40, 129.92, 129.65 (q, J = 32.3 Hz), 129.17, 128.99, 128.96, 127.04, 126.82, 125.43 (q, J = 3.7 Hz), 125.16, 124.31, 124.20 (q, J = 272.7 Hz), 104.57, 26.20.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.33.

HRMS (ESI) calcd for $C_{19}H_{12}F_3NO$ $[M]^+$: 327.0871; Found: 327.0866.

1-methyl-6-(p-tolyloxy)benzo[*cd*]indol-2(1*H*)-one

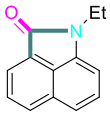


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 6.8 Hz, 1H), 7.64-7.60 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 3.39 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.88, 155.62, 149.10, 135.43, 132.60, 130.14, 128.24, 126.71, 126.45, 125.81, 124.56, 123.19, 117.97, 115.03, 104.79, 26.17, 20.53.

HRMS (ESI) calcd for $C_{19}H_{15}NO_2$ $[M]^+$: 289.1103; Found: 289.1104.

1-ethylbenzo[*cd*]indol-2(1*H*)-one

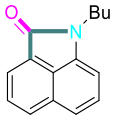


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.4, 6.8 Hz, 1H), 6.90 (d, *J* = 6.8 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.69, 139.06, 130.62, 129.03, 128.55, 128.40, 126.77, 125.10, 124.09, 120.09, 104.76, 34.89, 13.99.

HRMS (ESI) calcd for $C_{13}H_{11}NO$ $[M]^+$: 197.0841; Found: 197.0842.

1-butylbenzo[*cd*]indol-2(1*H*)-one

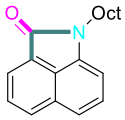


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.54-7.44 (m, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 3.93 (q, *J* = 7.2 Hz, 2H), 1.79-1.74 (m, 2H), 1.46-1.41 (m, 2H), 0.97 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.05, 139.58, 130.66, 129.04, 128.60, 128.44, 126.76, 125.09, 124.18, 120.10, 104.97, 40.02, 30.87, 20.21, 13.80.

HRMS (ESI) calcd for $C_{15}H_{15}NO$ $[M]^+$: 225.1154; Found: 225.1153.

1-octanoylbenzo[*cd*]indol-2(1*H*)-one

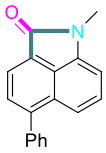


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.71 (dd, *J* = 8.0, 7.2 Hz, 1H), 7.55-7.49 (m 2H), 6.92 (d, *J* = 6.8 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 1.82-1.75 (m, 2H), 1.43-1.25 (m, 10H), 0.86 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.03, 139.60, 130.66, 129.05, 128.61, 128.45, 126.78, 125.10, 124.19, 120.09, 104.97, 40.32, 31.77, 29.30, 29.17, 28.81, 26.99, 22.61, 14.07.

HRMS (ESI) calcd for $C_{19}H_{23}NO$ $[M]^+$: 281.1780; Found: 281.1783.

1-methyl-5-phenylbenzo[*cd*]indol-2(1*H*)-one

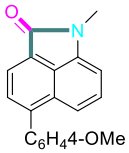


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.55-7.48 (m 4H), 7.44-7.42 (m, 2H), 6.93 (d, *J* = 6.8 Hz, 1H), 3.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.10, 138.95, 134.14, 129.81, 129.69, 128.66, 128.50, 127.40, 127.27, 126.79, 125.14, 124.16, 104.79, 26.26.

HRMS (ESI) calcd for $C_{18}H_{13}NO$ $[M+1]^+$: 260.1070; Found: 260.1069.

5-(4-methoxyphenyl)-1-methylbenzo[*cd*]indol-2(1*H*)-one

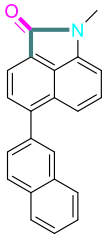


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.2 Hz, 1H), 7.64-7.59 (m, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 7.2 Hz, 1H), 3.89 (s, 3H), 3.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.93, 159.55, 144.18, 140.03, 131.16, 131.02, 128.95, 128.29, 127.20, 125.55, 125.16, 124.20, 119.34, 113.98, 104.52, 55.32, 26.29.

HRMS (ESI) calcd for $C_{19}H_{15}NO_2$ $[M]^+$: 289.1103; Found: 289.1106.

1-methyl-5-(naphthalen-2-yl)benzo[cd]indol-2(1*H*)-one

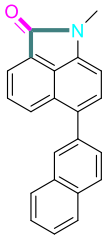


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 6.8 Hz, 1H), 7.98-7.91 (m, 4H), 7,.71-7.66 (m, 2H), 7.55-7.53 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 1H), 3.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.18, 139.44, 136.51, 134.13, 133.41, 132.48, 129.91, 128.90, 128.82, 128.47, 128.09, 128.00, 127.98, 127.68, 126.93, 126.41, 126.11, 125.32, 124.28, 104.85, 26.33.

HRMS (ESI) calcd for $C_{22}H_{15}NO$ $[M+1]^+$: 310.1226; Found: 310.1225.

1-methyl-6-(naphthalen-2-yl)benzo[*cd*]indol-2(1*H*)-one

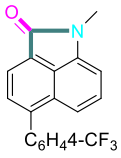


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 6.8 Hz, 1H), 8.03 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.94-7.91 (m, 2H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.57-7.62 (m, 2H), 7.47-7.42 (m, 1H), 6.61 (d, *J* = 6.8 Hz, 1H), 3.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.96, 144.42, 140.16, 136.28, 133.21, 132.76, 129.56, 129.05, 128.60, 128.20, 128.14, 127.73, 127.71, 127.40, 126.54, 126.52, 125.75, 125.59, 124.22, 119.37, 104.67, 26.37.

HRMS (ESI) calcd for $C_{22}H_{15}NO$ $[M+1]^+$: 310.1226; Found: 310.1224.

1-methyl-5-(4-(trifluoromethyl)phenyl)benzo[*cd*]indol-2(1*H*)-one



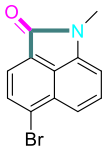
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.74-7.69 (m, 2H), 7.56-7.48 (m, 2H), 6.96 (d, *J* = 6.8 Hz, 1H), 3.50 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.76, 142.68, 140.25, 130.17, 129.39, 129.04, 127.04, 126.48, 125.55, 125.51, 125.48, 125.44, 124.12, 118.72, 104.88, 77.32, 77.00, 76.68, 26.40.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.43.

HRMS (ESI) calcd for $C_{19}H_{12}F_3NO$ $[M+1]^+$: 328.0944; Found: 328.0944.

5-bromo-1-methylbenzo[*cd*]indol-2(1*H*)-one

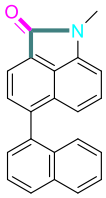


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.56-7.52 (m, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 3.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.47, 140.12, 132.08, 129.71, 129.19, 126.85, 126.12, 125.97, 124.86, 119.56, 105.45, 26.45.

HRMS (ESI) calcd for $C_{12}H_8BrNO$ $[M+1]^+$: 261.9862; Found: 261.9861.

1-methyl-5-(naphthalen-1-yl)benzo[*cd*]indol-2(1*H*)-one

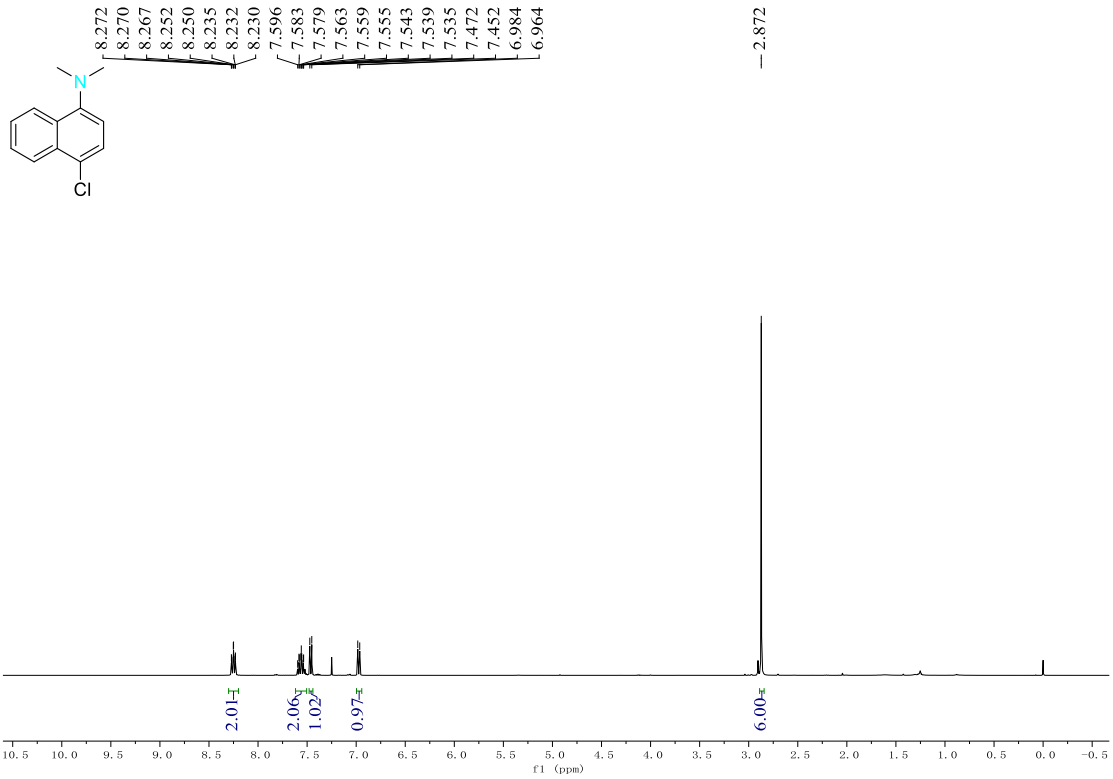


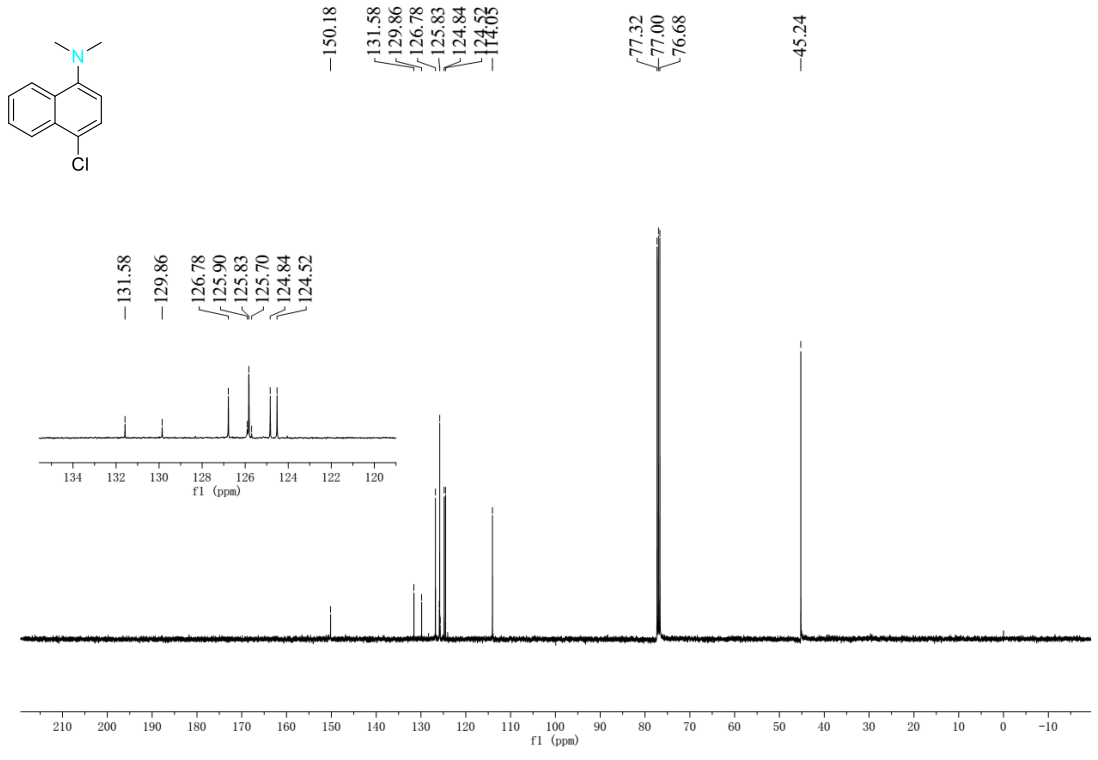
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.2 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.60-7.47 (m, 7H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 3.51 (s, 3H).

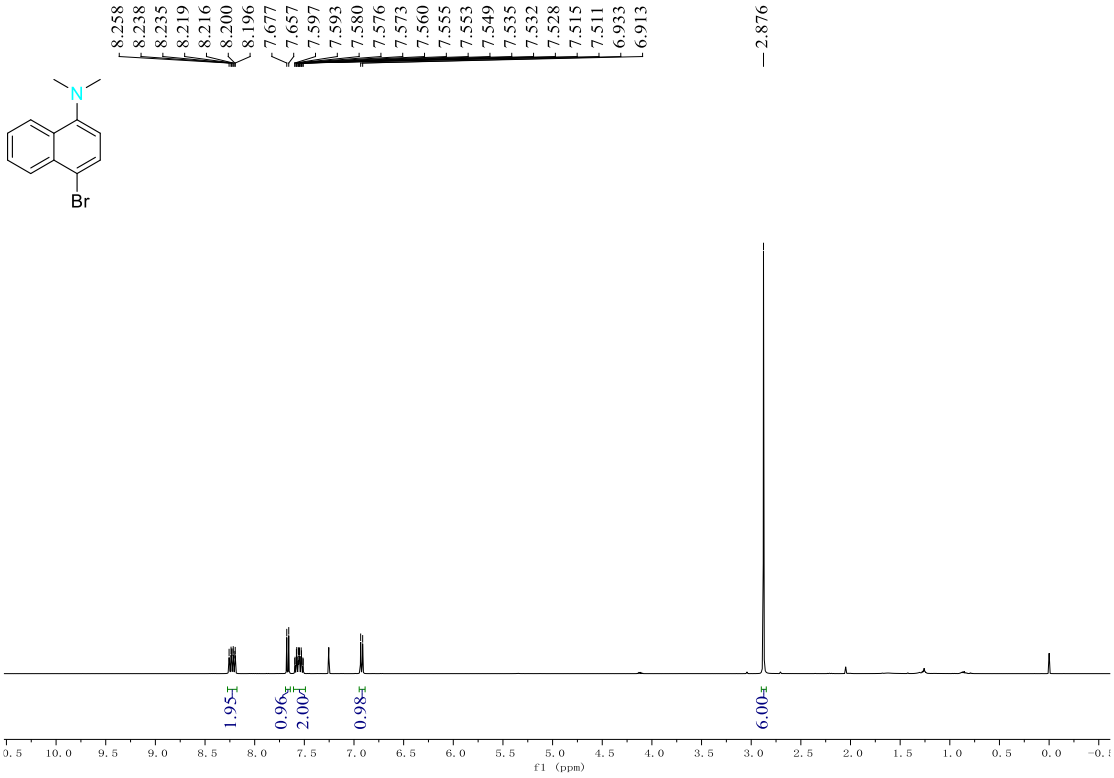
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.24, 139.62, 136.52, 133.57, 132.74, 132.38, 130.16, 129.76, 128.91, 128.64, 128.23, 128.19, 128.09, 126.79, 126.21, 126.01, 125.84, 125.29, 125.01, 124.30, 104.65, 26.37.

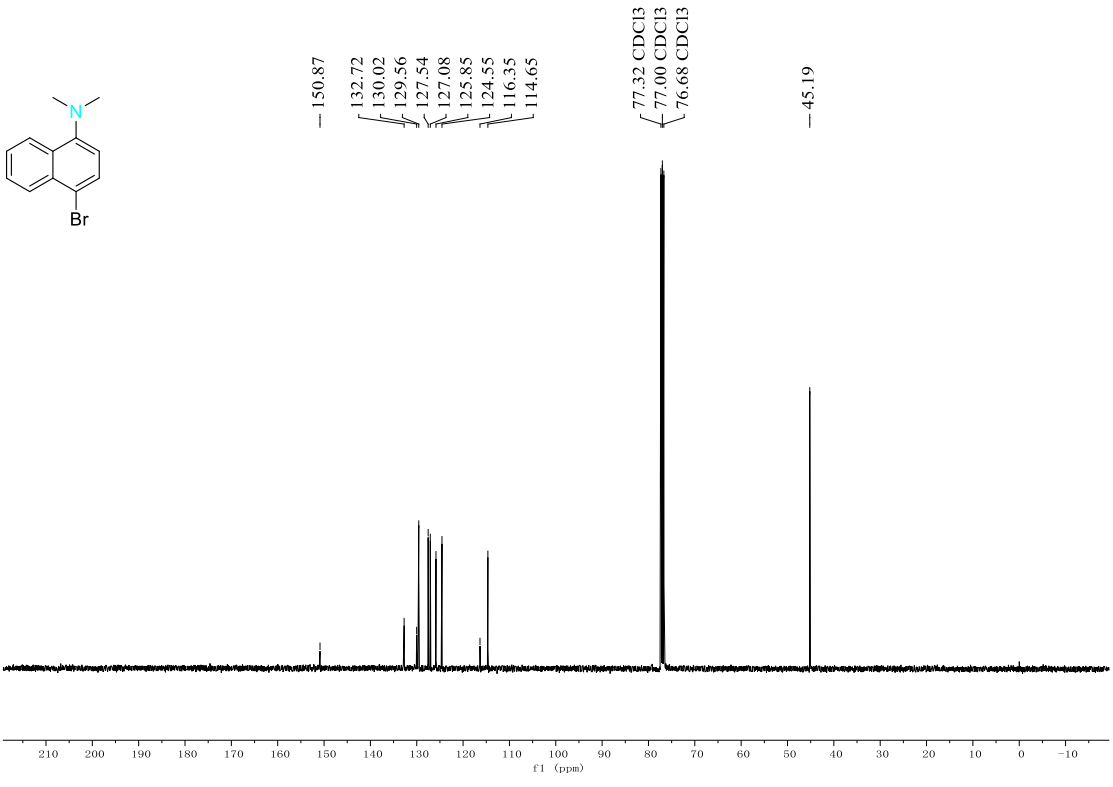
HRMS (ESI) calcd for $C_{22}H_{15}NO$ $[M+1]^+$: 310.1226; Found: 310.1227.

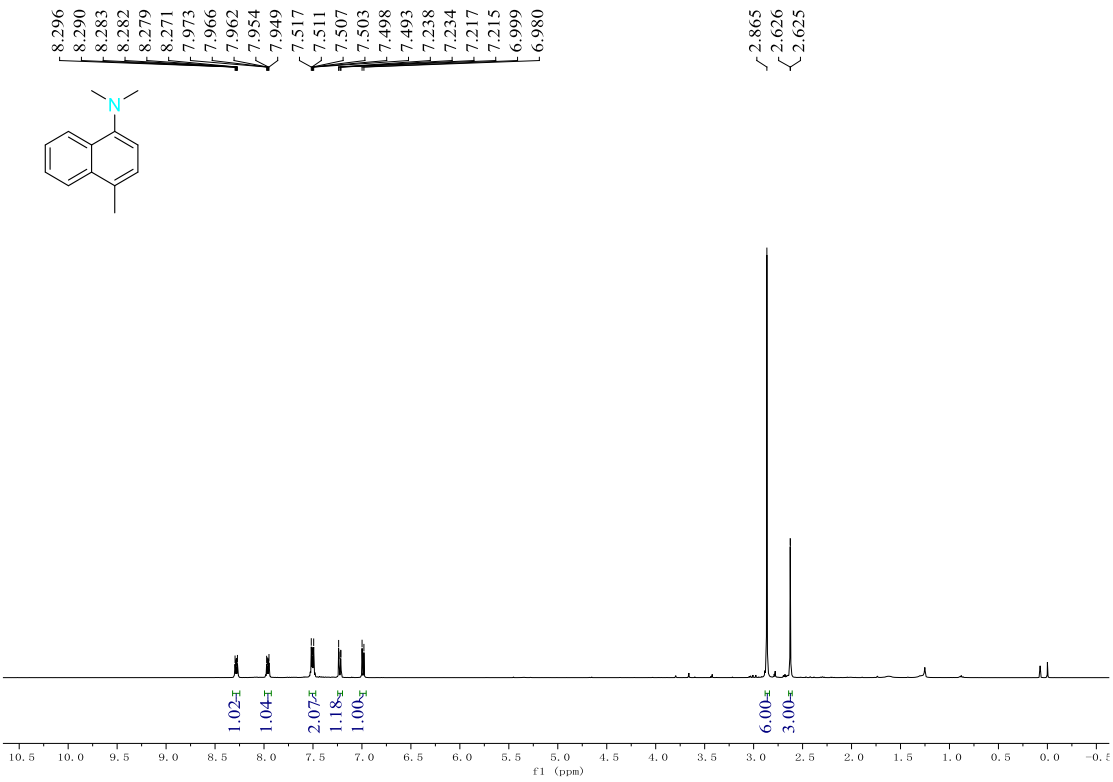
8. NMR Spectra of Substrates andProducts

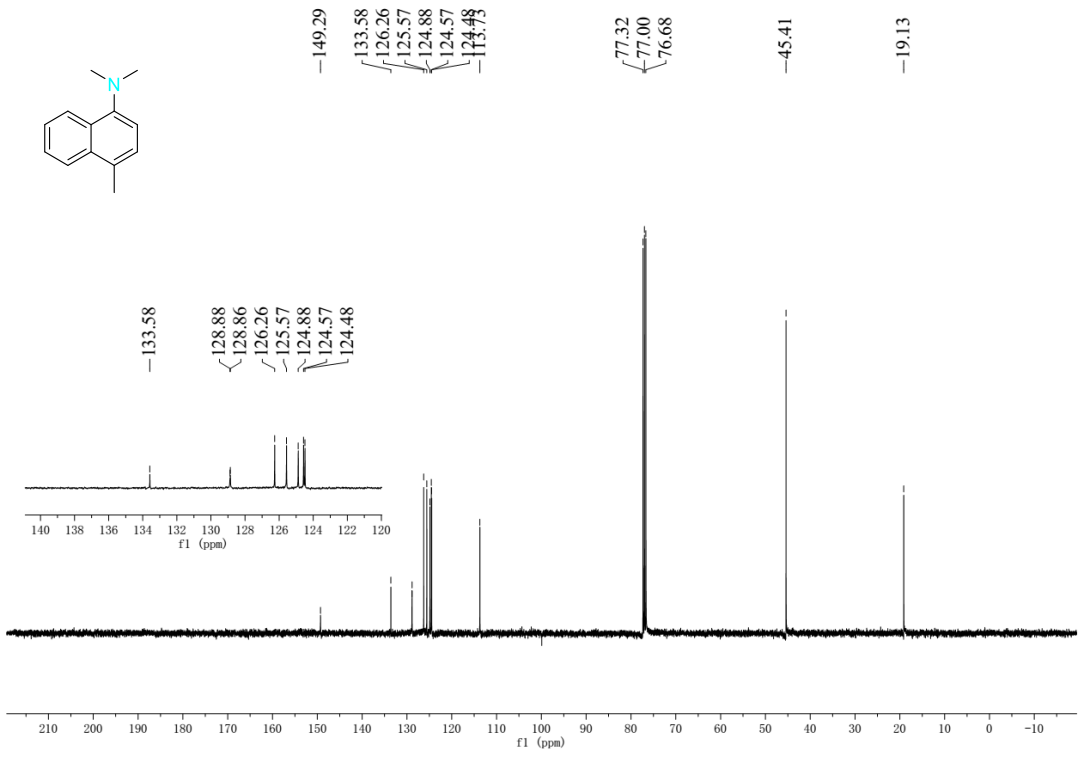


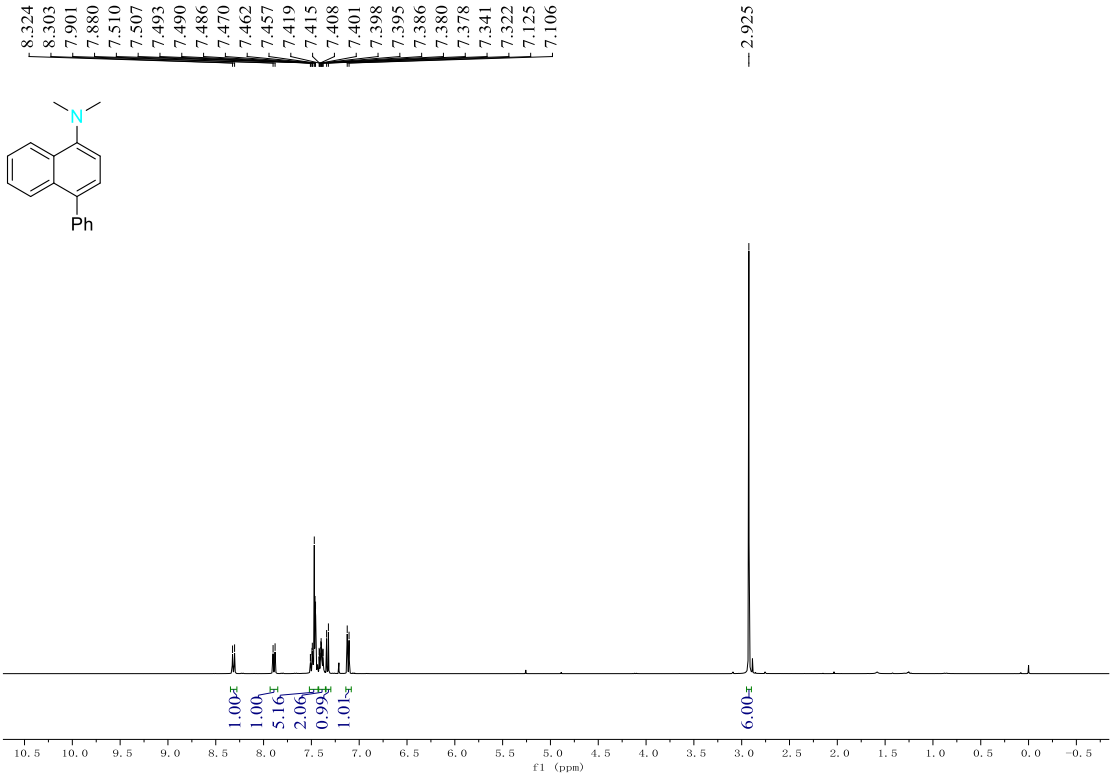


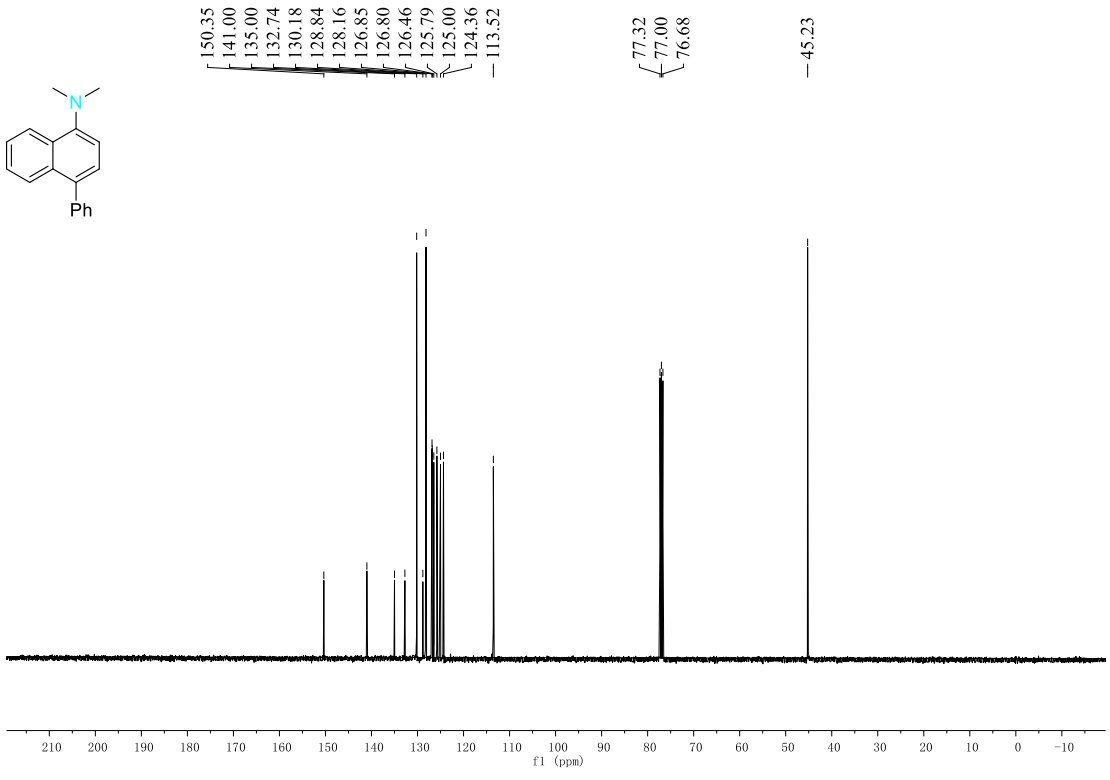

8.258
8.238
8.235
8.219
8.216
8.200
8.196
7.677
7.657
7.597
7.593
7.580
7.576
7.573
7.560
7.555
7.553
7.549
7.535
7.532
7.528
7.515
7.511
6.933
6.913
2.876
N
Br
1.95
0.96
2.00
0.98
6.00
f1 (ppm)

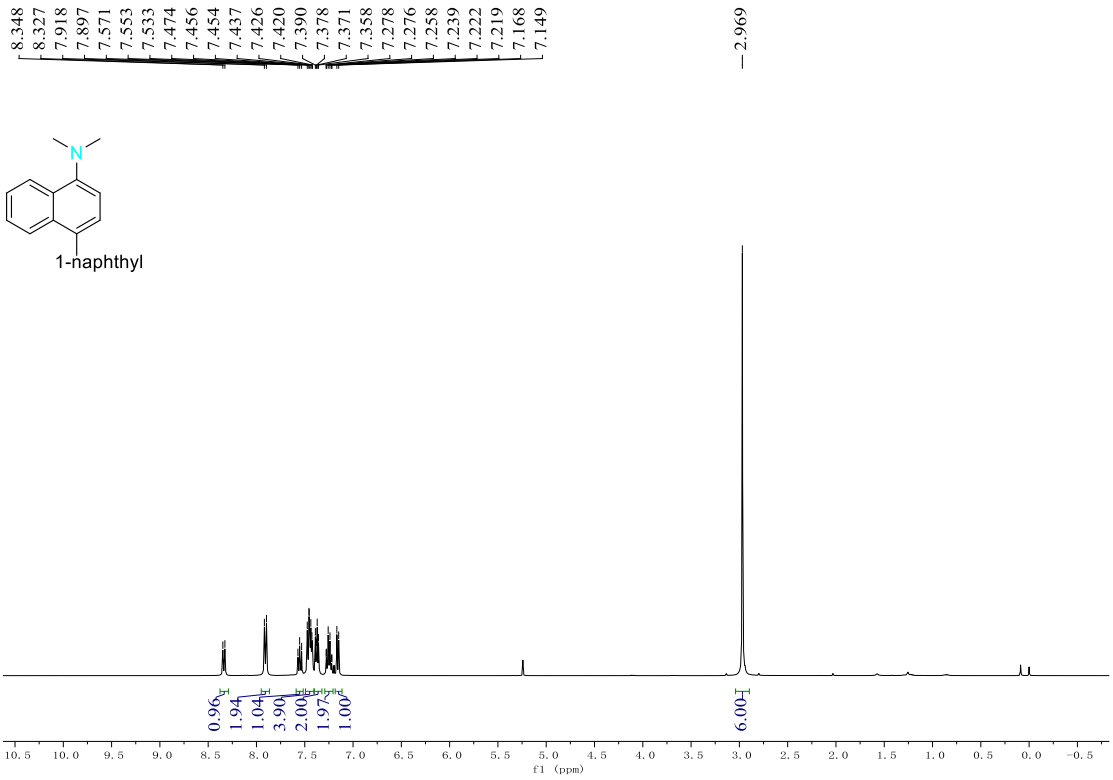

150.87
132.72
130.02
129.56
127.54
127.08
125.85
124.55
116.35
114.65
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
45.19
N
Br
f1 (ppm)


8.296
8.290
8.283
8.282
8.279
8.271
7.973
7.966
7.962
7.954
7.949
7.517
7.511
7.507
7.503
7.498
7.493
7.238
7.234
7.217
7.215
6.999
6.980
2.865
2.626
2.625
N
1.02
1.04
2.07
1.18
1.00
6.00
3.00
f1 (ppm)


149.29
133.58
126.26
125.57
124.88
124.57
124.48
113.73
77.32
77.00
76.68
45.41
19.13
N
133.58
128.88
128.86
126.26
125.57
124.88
124.57
124.48
f1 (ppm)


8.324
8.303
7.901
7.880
7.510
7.507
7.493
7.490
7.486
7.470
7.462
7.457
7.419
7.415
7.408
7.401
7.398
7.395
7.386
7.380
7.378
7.341
7.322
7.125
7.106
2.925
N
Ph
1.00
1.00
5.16
2.06
0.99
1.01
6.00
f1 (ppm)


150.35
141.00
135.00
132.74
130.18
128.84
128.16
126.85
126.80
126.46
125.79
125.00
124.36
113.52
77.32
77.00
76.68
45.23
N
Ph
f1 (ppm)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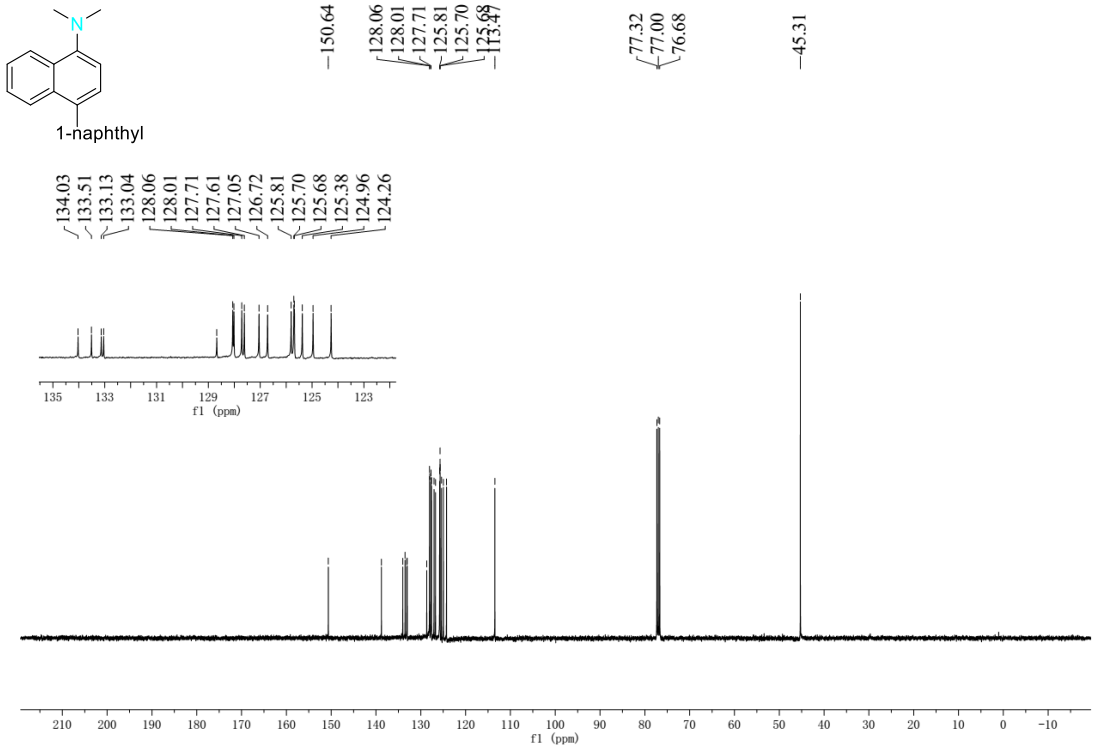
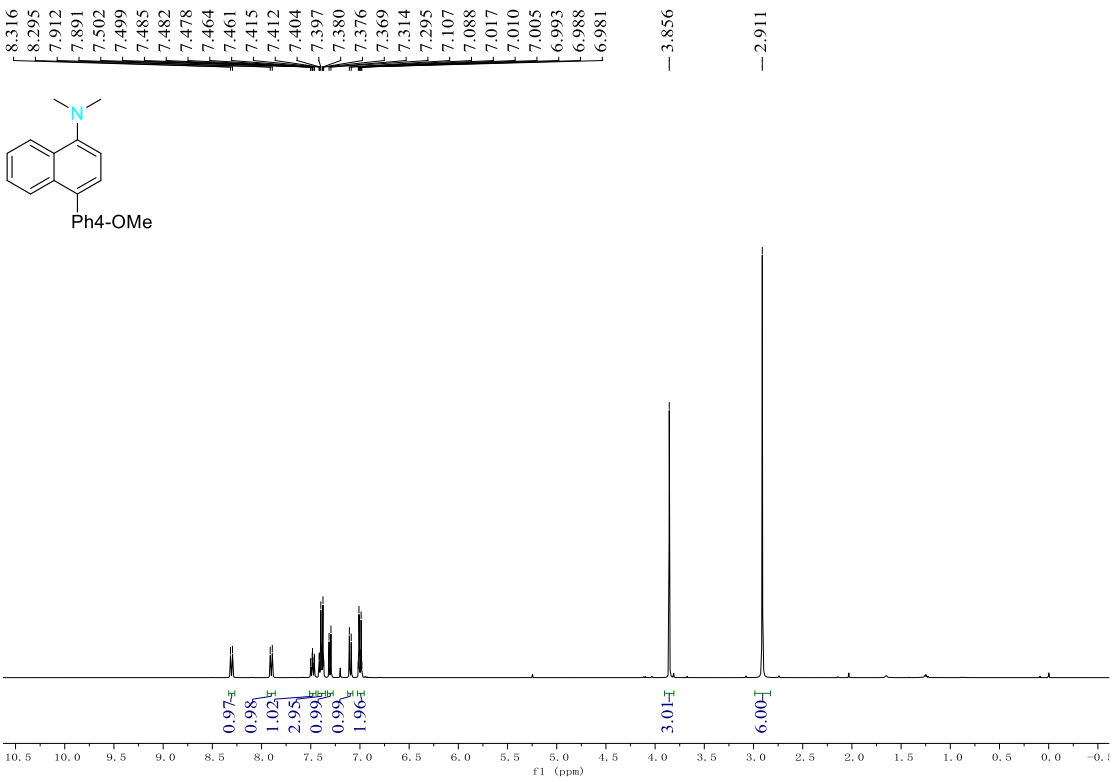
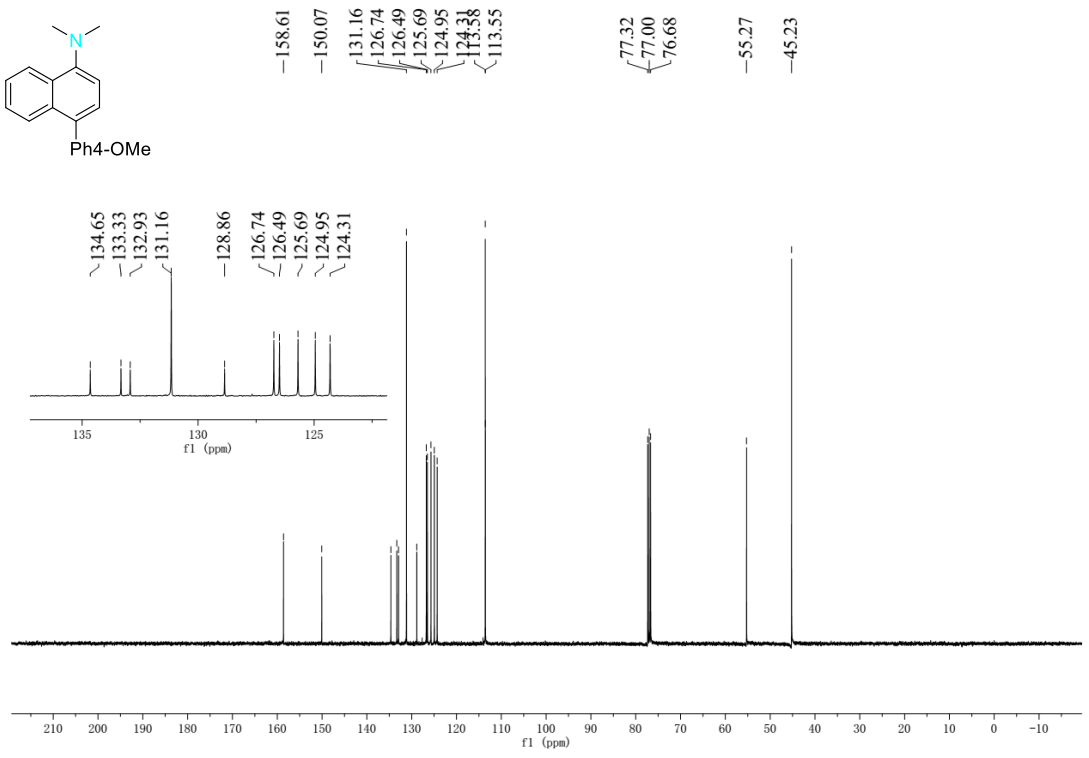
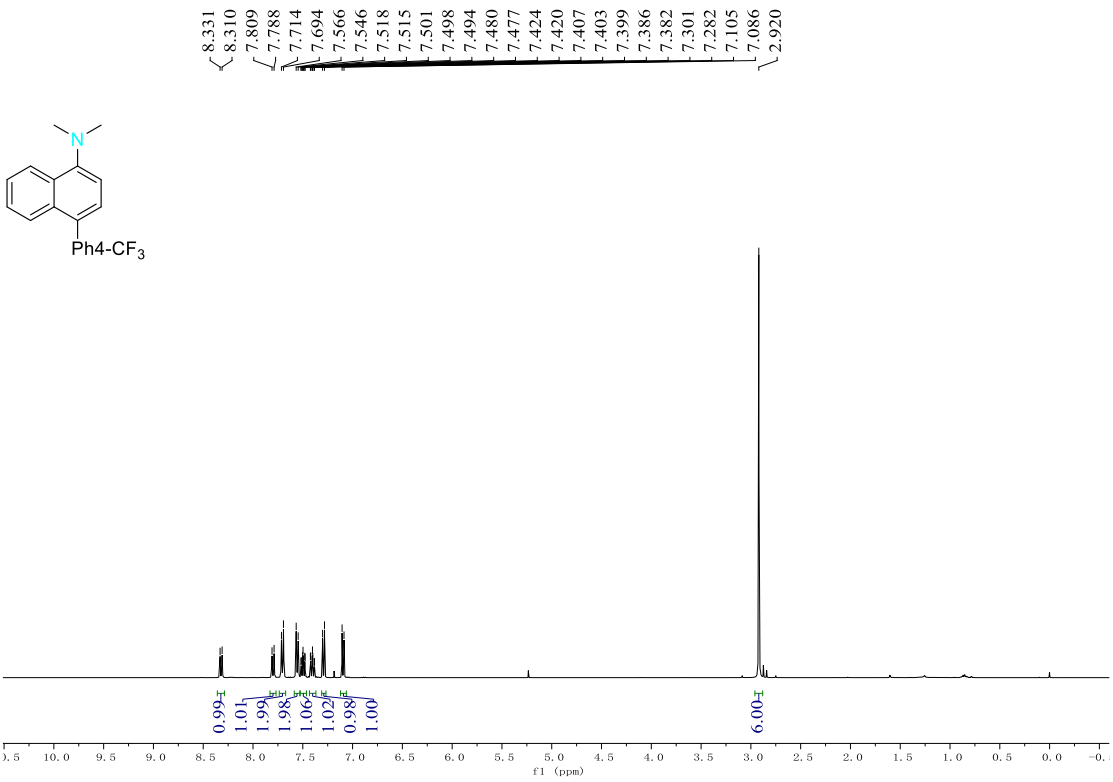
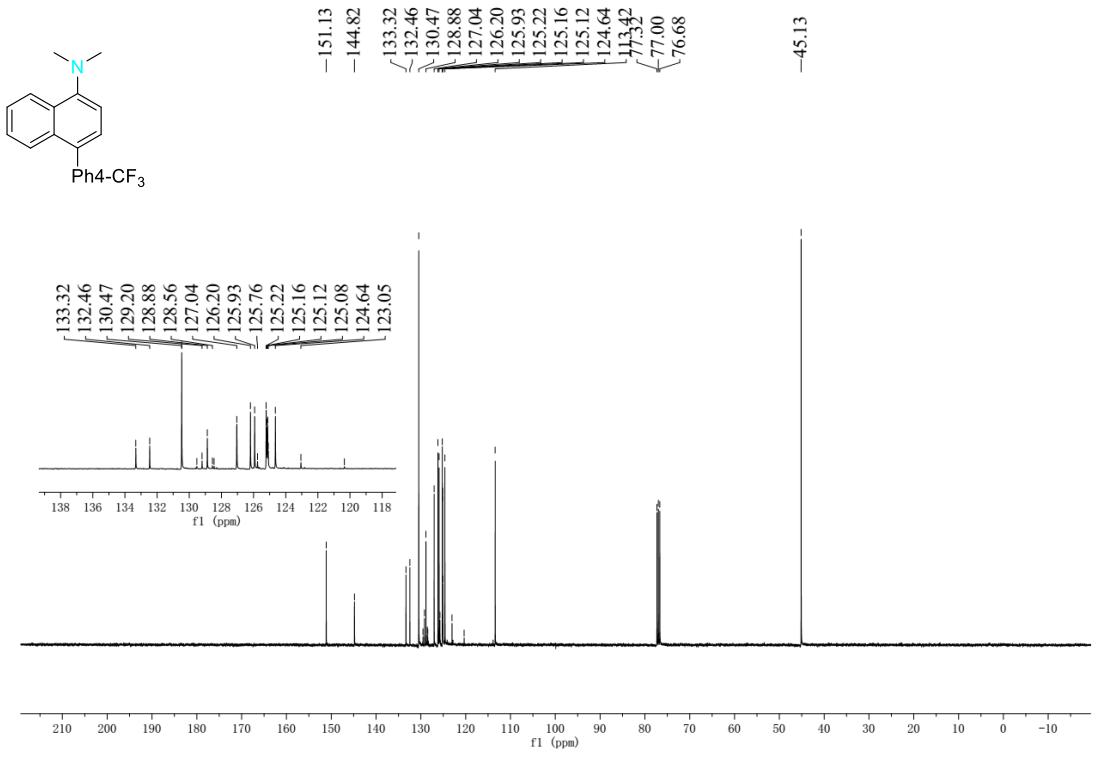
8.327
7.918
7.897
7.571
7.553
7.533
7.474
7.456
7.454
7.437
7.426
7.420
7.390
7.378
7.371
7.358
7.278
7.276
7.258
7.239
7.222
7.219
7.168
7.149
2.969
N
1-naphthyl
0.96
1.94
1.04
3.90
2.00
1.97
1.00
6.00
f1 (ppm)

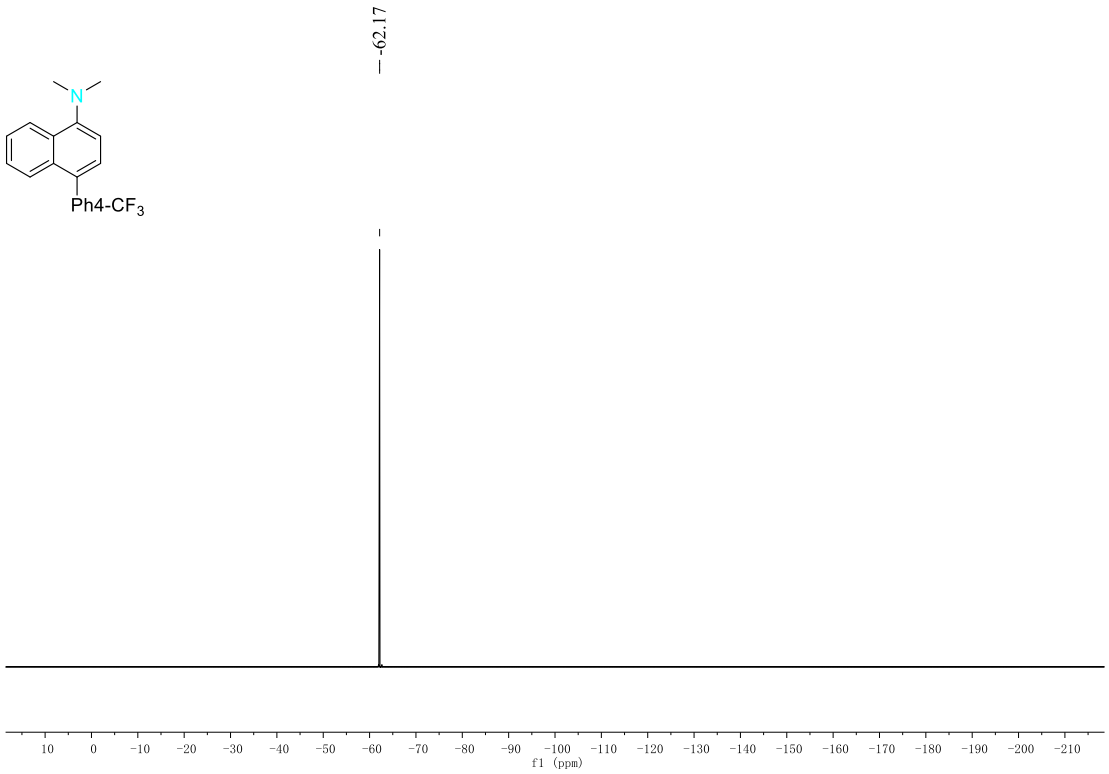

N
1-naphthyl
150.64
128.06
128.01
127.71
125.81
125.70
113.47
77.32
77.00
76.68
45.31
134.03
133.51
133.13
133.04
128.06
128.01
127.71
127.61
127.05
126.72
125.81
125.70
125.68
125.38
124.96
124.26
f1 (ppm)
f1 (ppm)

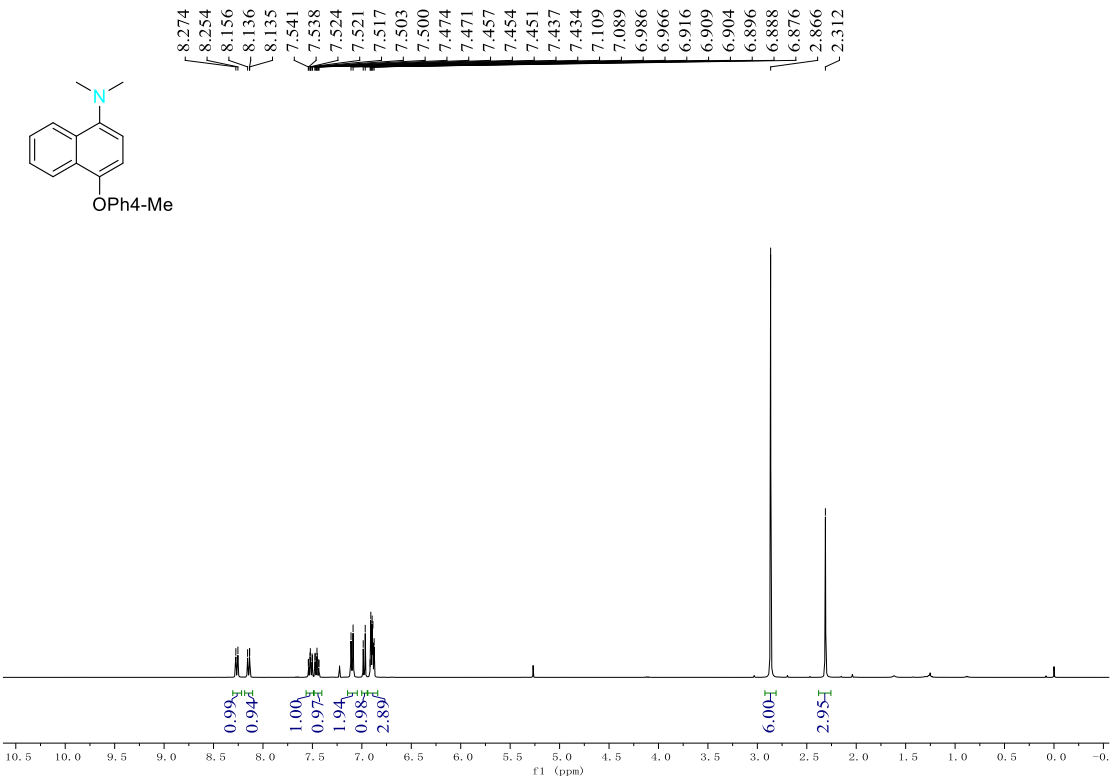

8.316
8.295
7.912
7.891
7.502
7.499
7.485
7.482
7.478
7.464
7.461
7.415
7.412
7.404
7.397
7.380
7.376
7.369
7.314
7.295
7.107
7.088
7.017
7.010
7.005
6.993
6.988
6.981
3.856
2.911
N
Ph4-OMe
0.97
0.98
1.02
2.95
0.99
0.99
1.96
3.01
6.00
f1 (ppm)

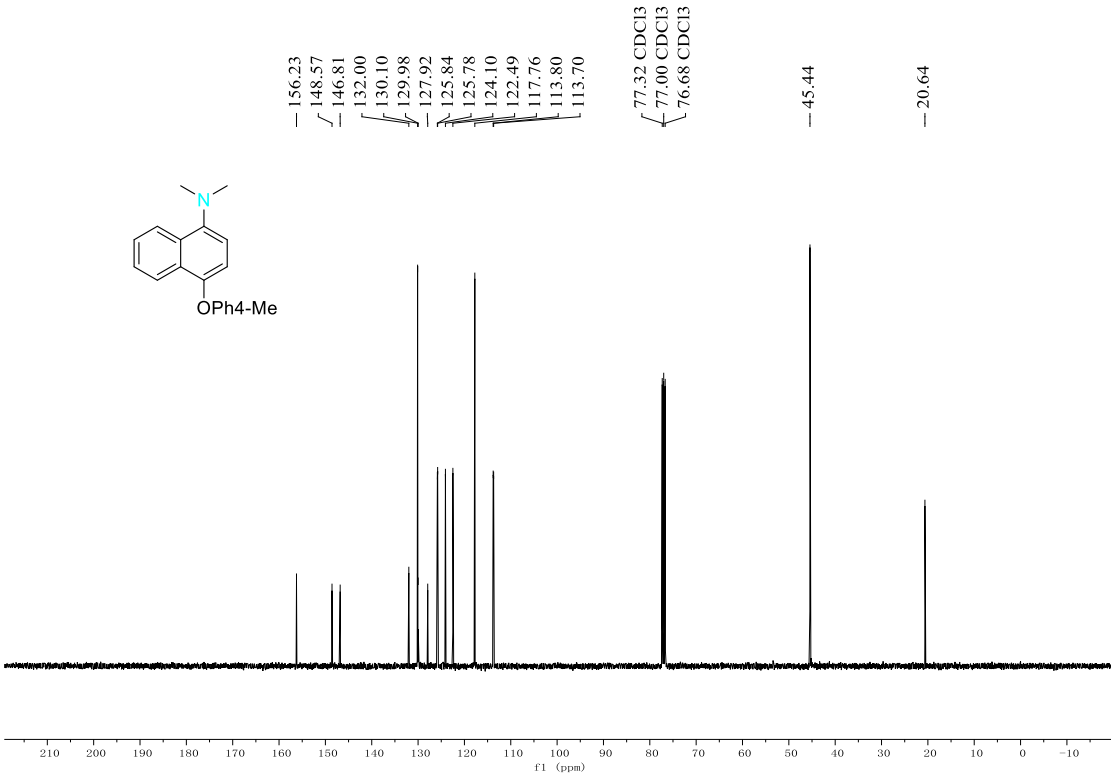

158.61
150.07
131.16
126.74
126.49
125.69
124.95
124.31
113.55
77.32
77.00
76.68
55.27
45.23
N
Ph4-OMe
134.65
133.33
132.93
131.16
128.86
126.74
126.49
125.69
124.95
124.31
f1 (ppm)

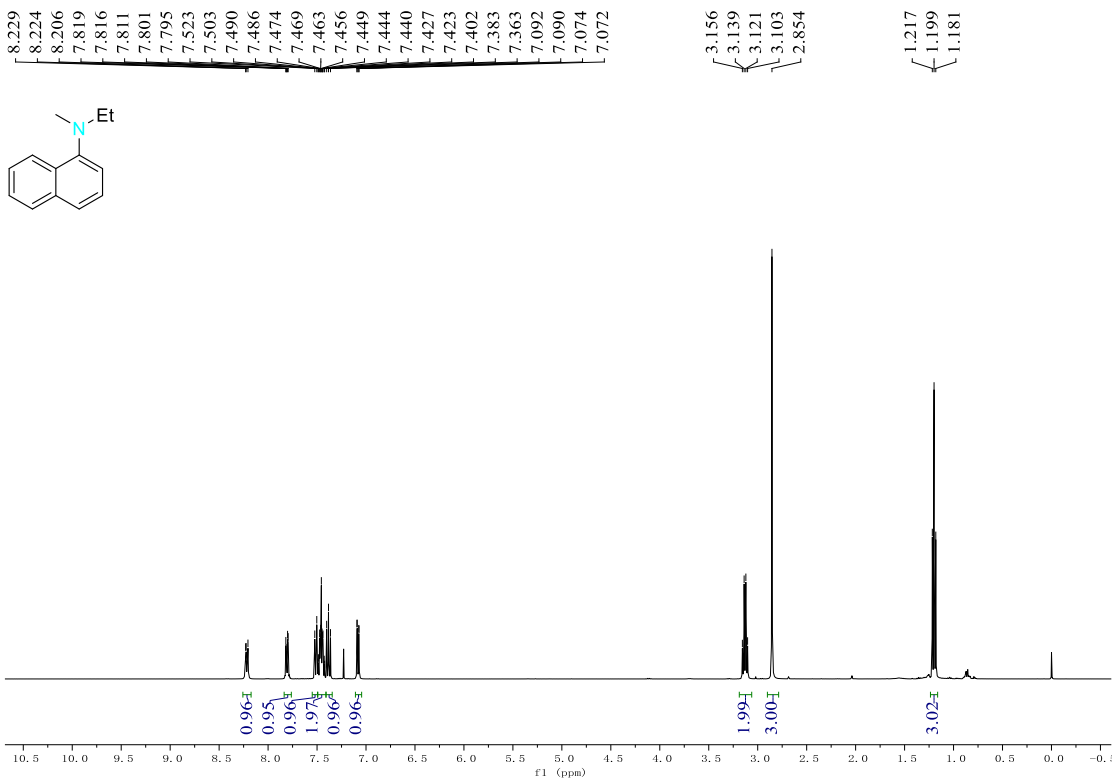

8.331
8.310
7.809
7.788
7.714
7.694
7.566
7.546
7.518
7.515
7.501
7.498
7.494
7.480
7.477
7.424
7.420
7.407
7.403
7.399
7.386
7.382
7.301
7.282
7.105
7.086
2.920
N
Ph4-CF3
0.99
1.01
1.99
1.98
1.06
1.02
0.98
1.00
6.00
f1 (ppm)

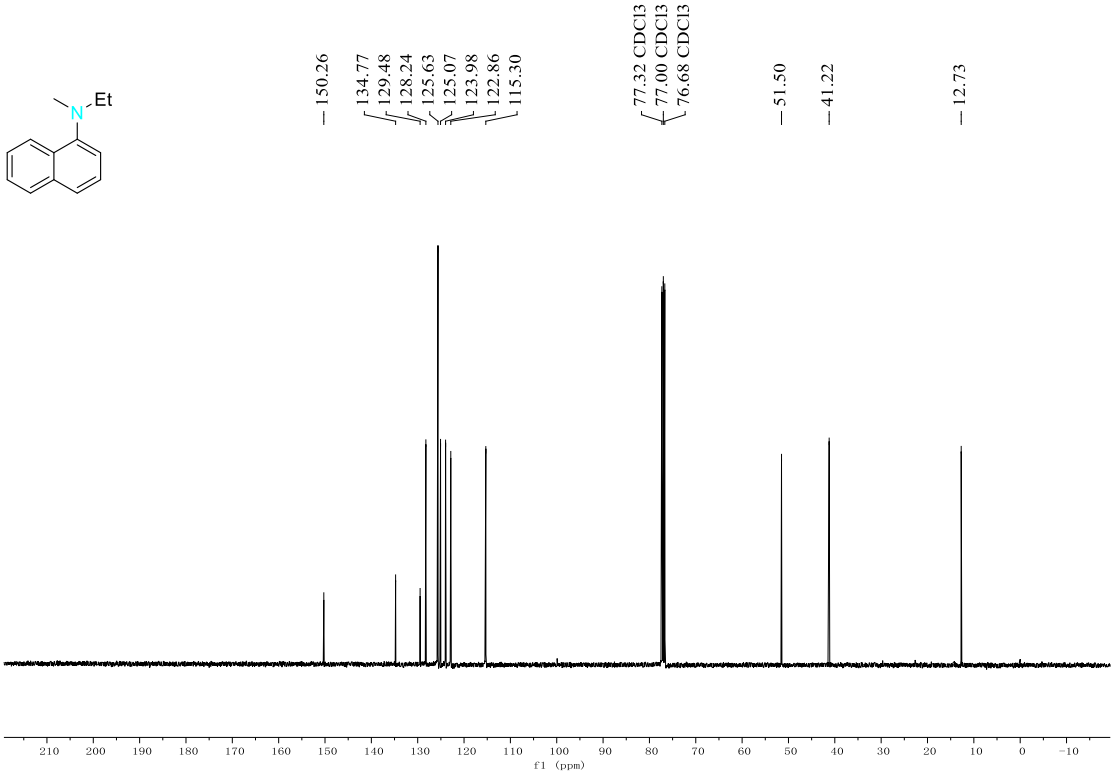

151.13
144.82
133.32
132.46
130.47
128.88
127.04
126.20
125.93
125.22
125.16
125.12
124.64
113.42
77.32
77.00
76.68
45.13
N
Ph4-CF3
133.32
132.46
130.47
129.20
128.88
128.56
127.04
126.20
125.93
125.76
125.22
125.16
125.12
125.08
124.64
123.05
f1 (ppm)
f1 (ppm)

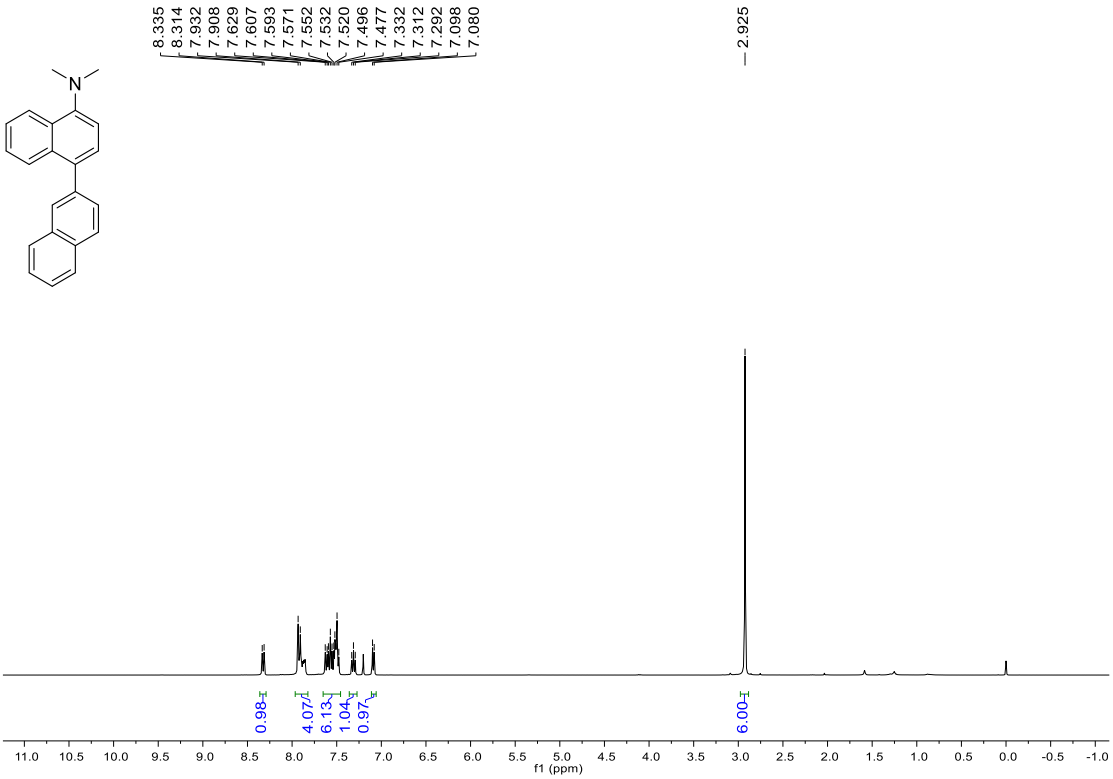

-62.17
Ph4-CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

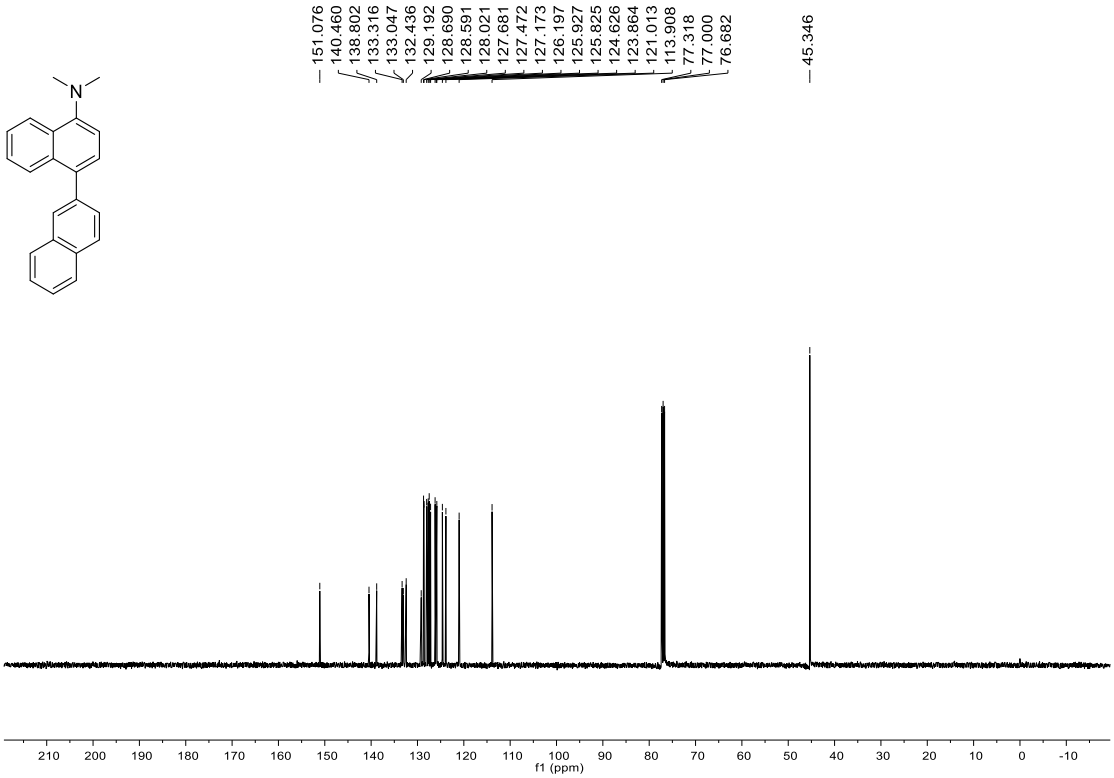

8.274
8.254
8.156
8.136
8.135
7.541
7.538
7.524
7.521
7.517
7.503
7.500
7.474
7.471
7.457
7.454
7.451
7.437
7.434
7.109
7.089
6.986
6.966
6.916
6.909
6.904
6.896
6.888
6.876
2.866
2.312
OPh4-Me
0.99
0.94
1.00
0.97
1.94
0.98
2.89
6.00
2.95
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

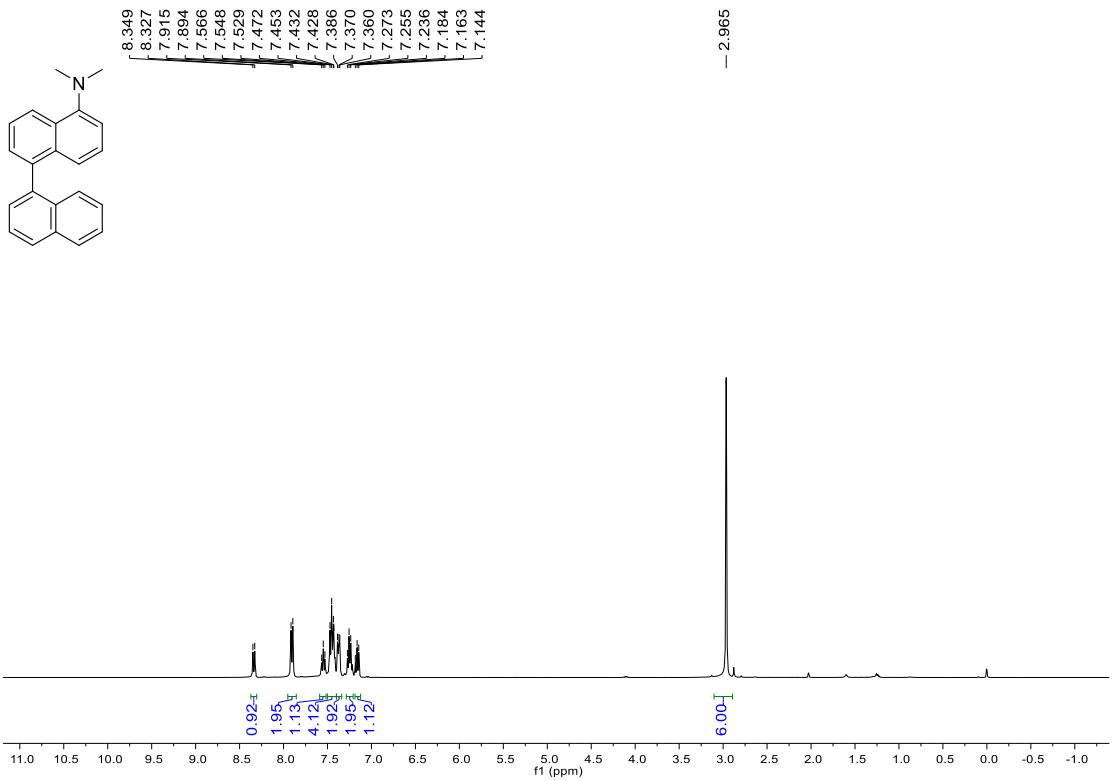

156.23
148.57
146.81
132.00
130.10
129.98
127.92
125.84
125.78
124.10
122.49
117.76
113.80
113.70
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
45.44
20.64
N
OPh4-Me
f1 (ppm)

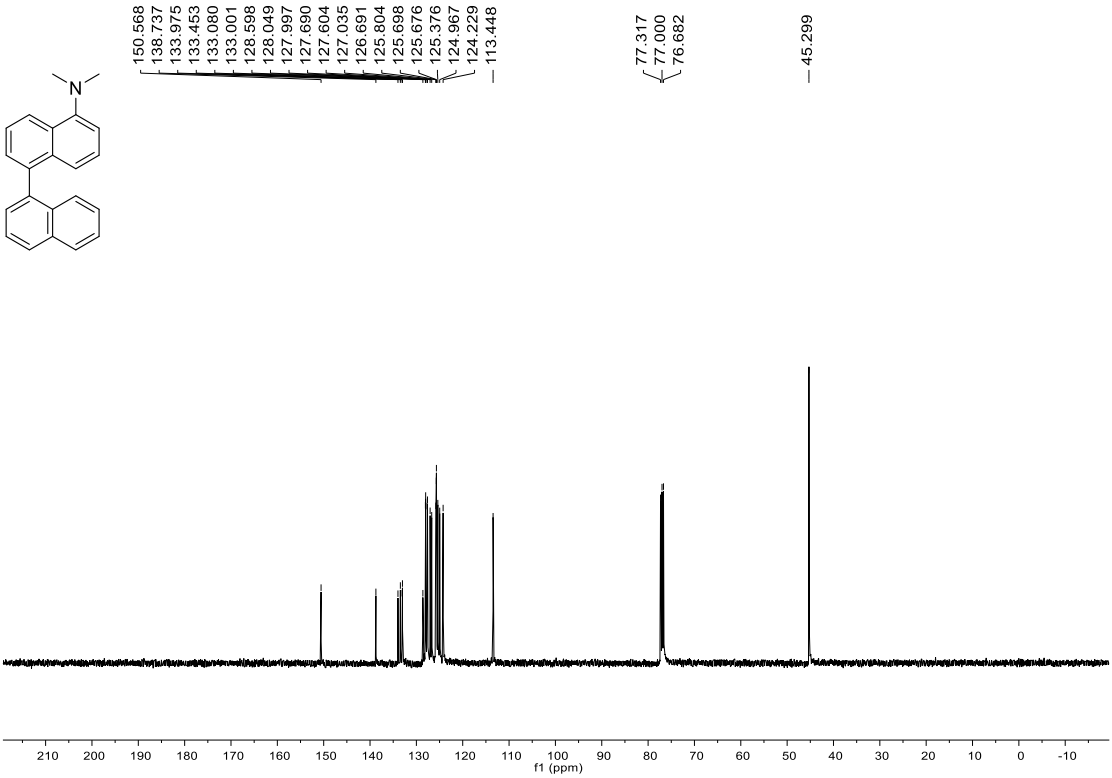

8.229
8.224
8.206
7.819
7.816
7.811
7.801
7.795
7.523
7.503
7.490
7.486
7.474
7.469
7.463
7.456
7.449
7.444
7.440
7.427
7.423
7.402
7.383
7.363
7.092
7.090
7.074
7.072
3.156
3.139
3.121
3.103
2.854
1.217
1.199
1.181
N
Et
0.96
0.95
0.96
1.97
0.96
0.96
1.99
3.00
3.02
f1 (ppm)


N
Et
150.26
134.77
129.48
128.24
125.63
125.07
123.98
122.86
115.30
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
51.50
41.22
12.73
f1 (ppm)


N
8.335
8.314
7.932
7.908
7.629
7.607
7.593
7.571
7.552
7.532
7.520
7.496
7.477
7.332
7.312
7.292
7.098
7.080
2.925
0.98
4.07
6.13
1.04
0.97
6.00
f1 (ppm)


151.076
140.460
138.802
133.316
133.047
132.436
129.192
128.690
128.591
128.021
127.681
127.472
127.173
126.197
125.927
125.825
124.626
123.864
121.013
113.908
77.318
77.000
76.682
45.346
N
f1 (ppm)


8.349
8.327
7.915
7.894
7.566
7.548
7.529
7.472
7.453
7.432
7.428
7.386
7.370
7.360
7.273
7.255
7.236
7.184
7.163
7.144
2.965
N
0.92
1.95
1.13
4.12
1.92
1.95
1.12
6.00
f1 (ppm)


150.568
138.737
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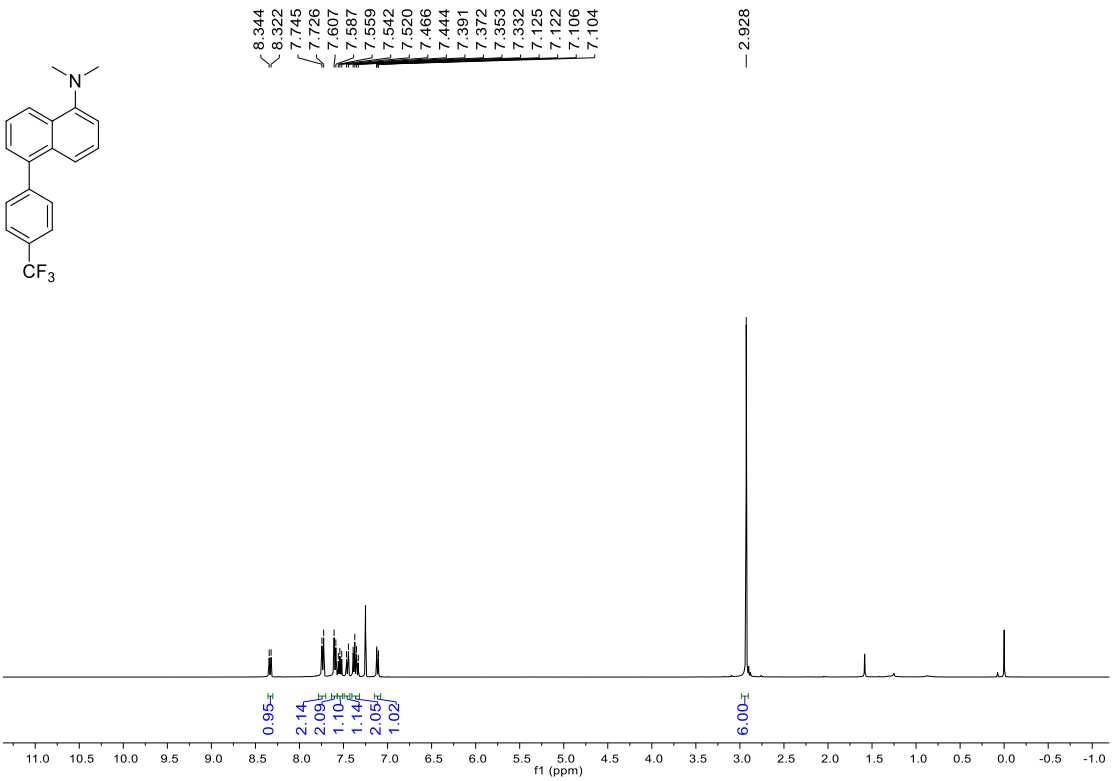
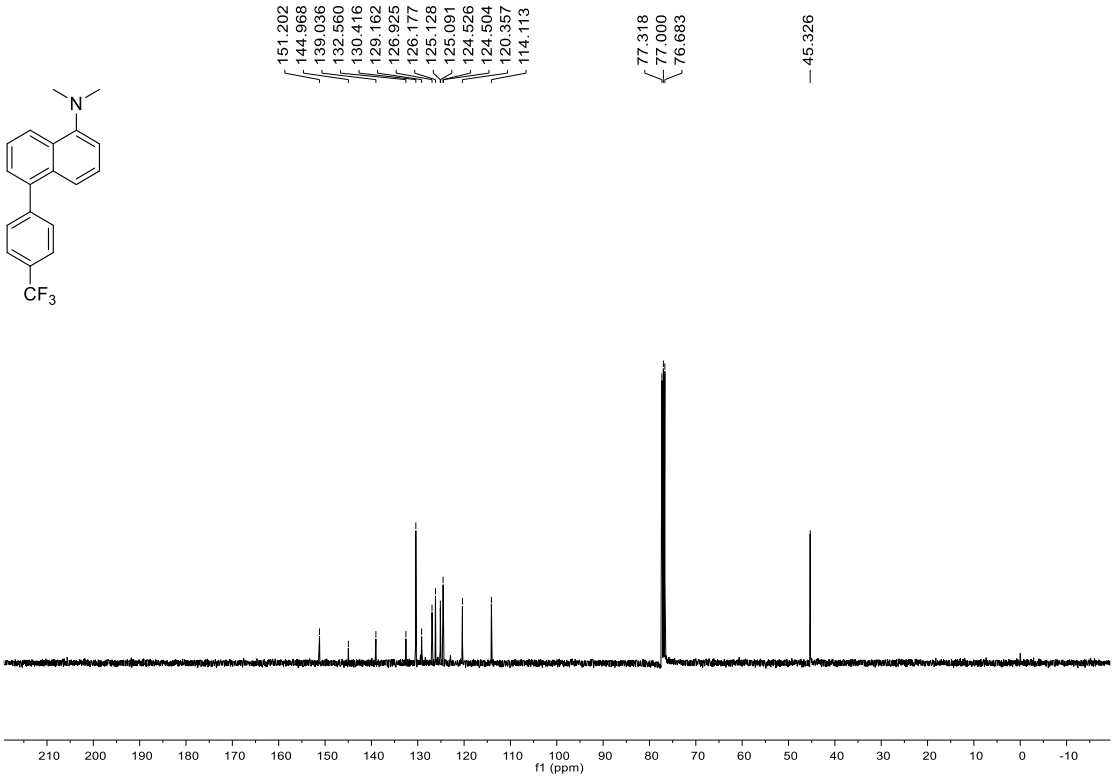
133.453
133.080
133.001
128.598
128.049
127.997
127.690
127.604
127.035
126.691
125.804
125.698
125.676
125.376
124.967
124.229
113.448
77.317
77.000
76.682
45.299
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.344
8.322
7.745
7.726
7.607
7.587
7.559
7.542
7.520
7.466
7.444
7.391
7.372
7.353
7.332
7.125
7.122
7.106
7.104
2.928
N
CF3
0.95
2.14
2.09
1.10
1.14
2.05
1.02
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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139.036
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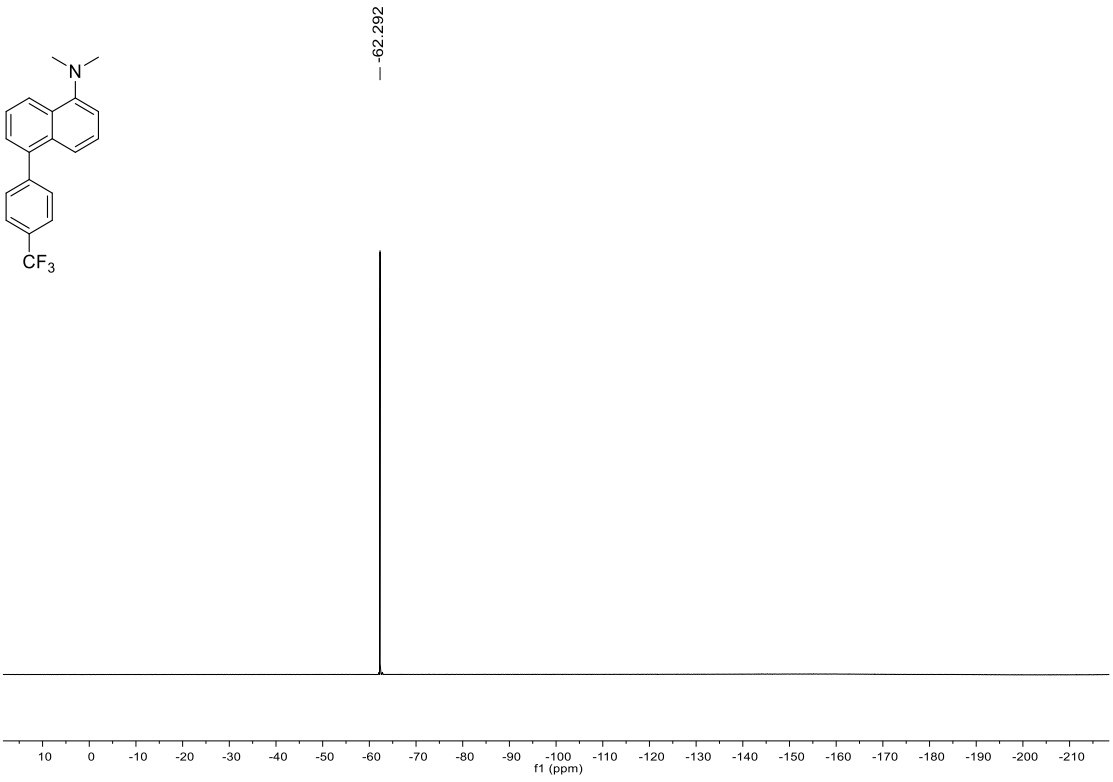
130.416
129.162
126.925
126.177
125.128
125.091
124.526
124.504
120.357
114.113
77.318
77.000
76.683
45.326
N
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.292
N
CF3
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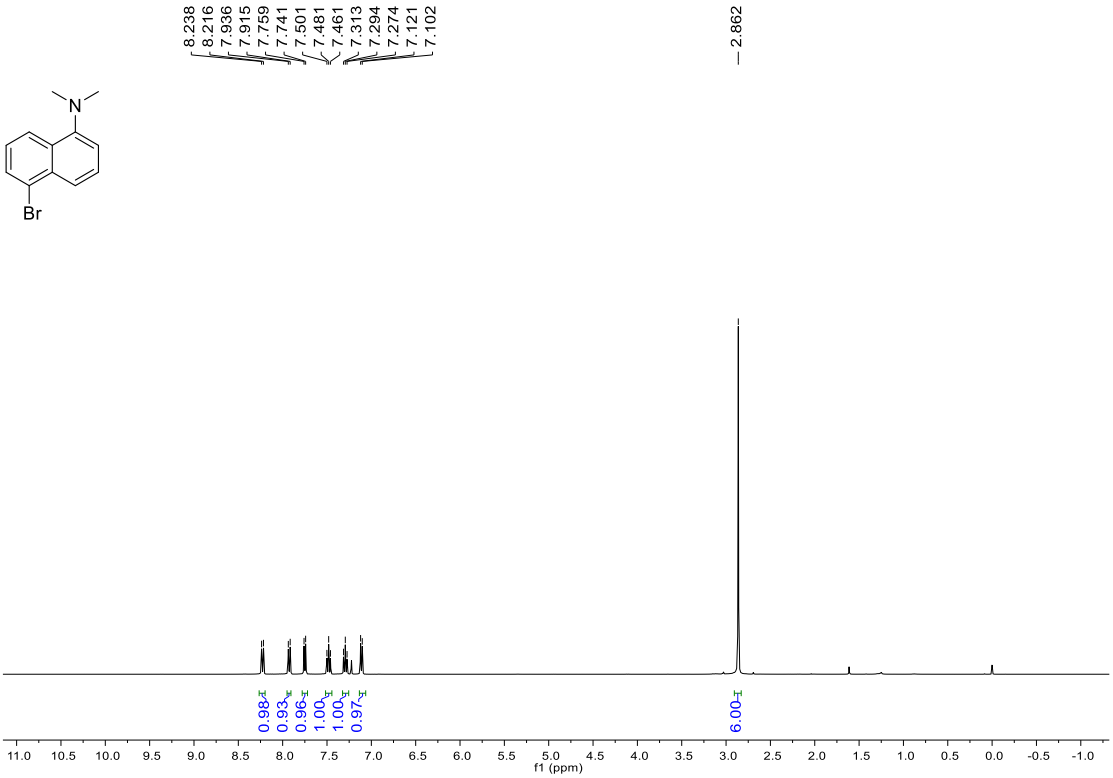
f1 (ppm)


8.238
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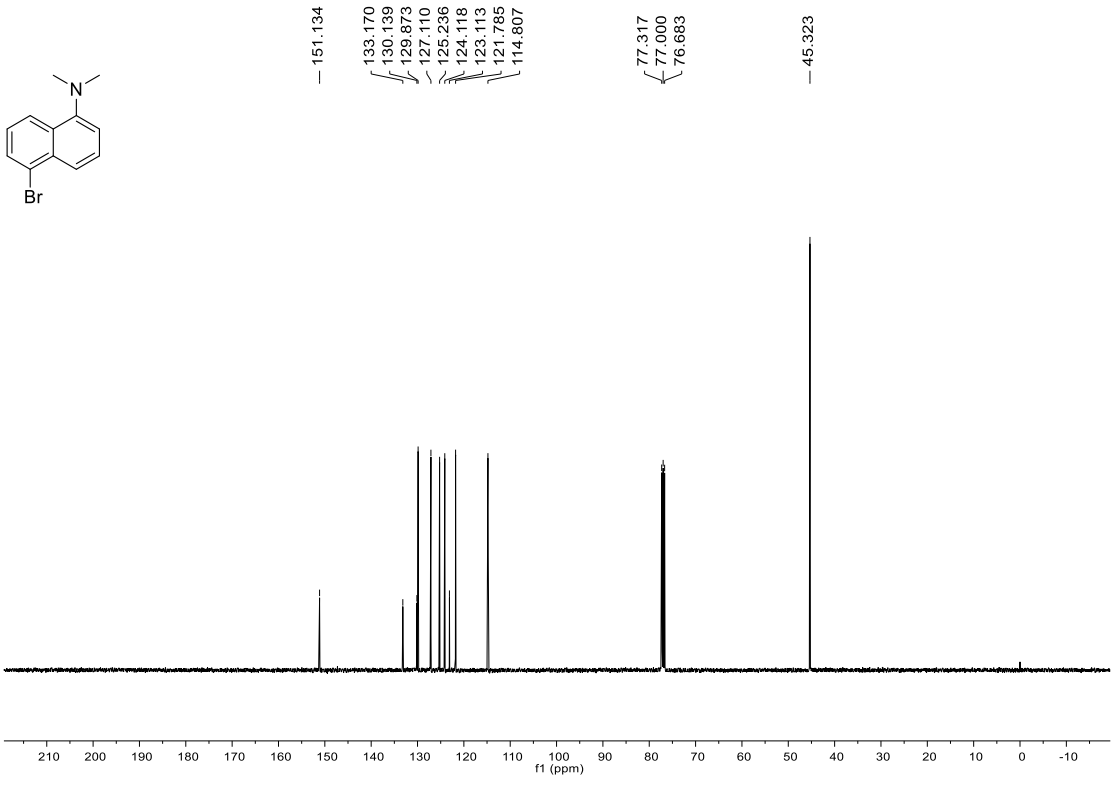
7.759
7.741
7.501
7.481
7.461
7.313
7.294
7.274
7.121
7.102
2.862
N
Br
0.98
0.93
0.96
1.00
1.00
0.97
6.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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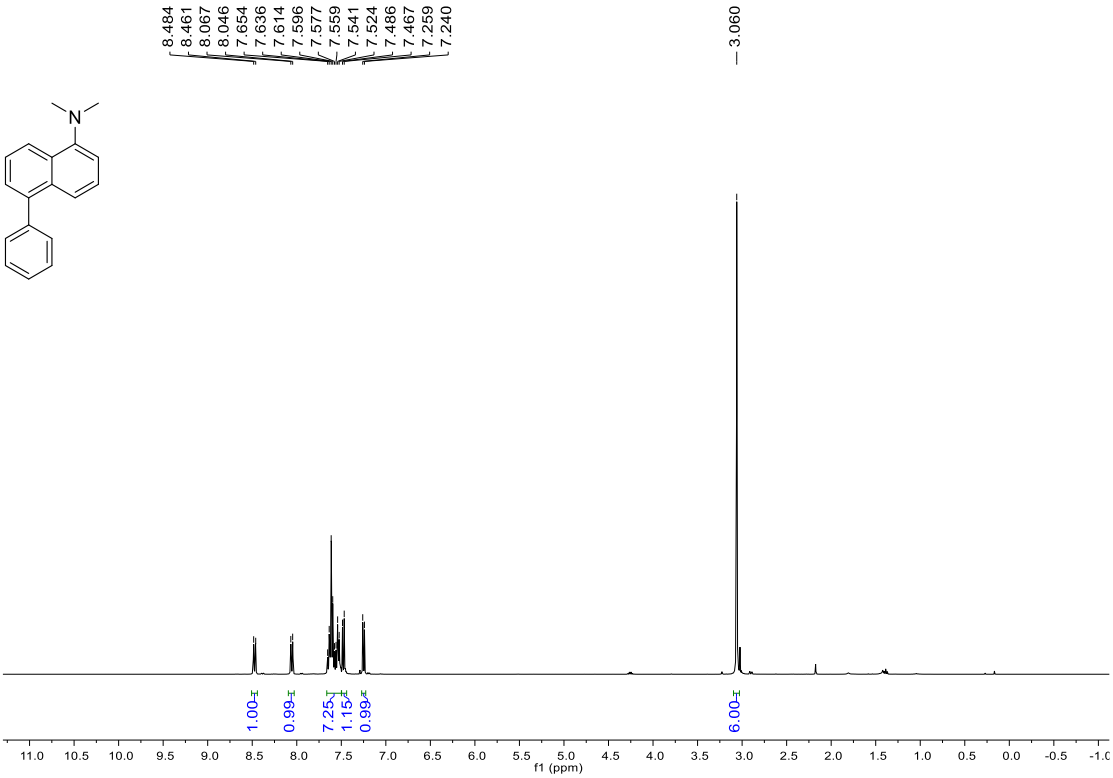
133.170
130.139
129.873
127.110
125.236
124.118
123.113
121.785
114.807
77.317
77.000
76.683
45.323
N
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.541
7.524
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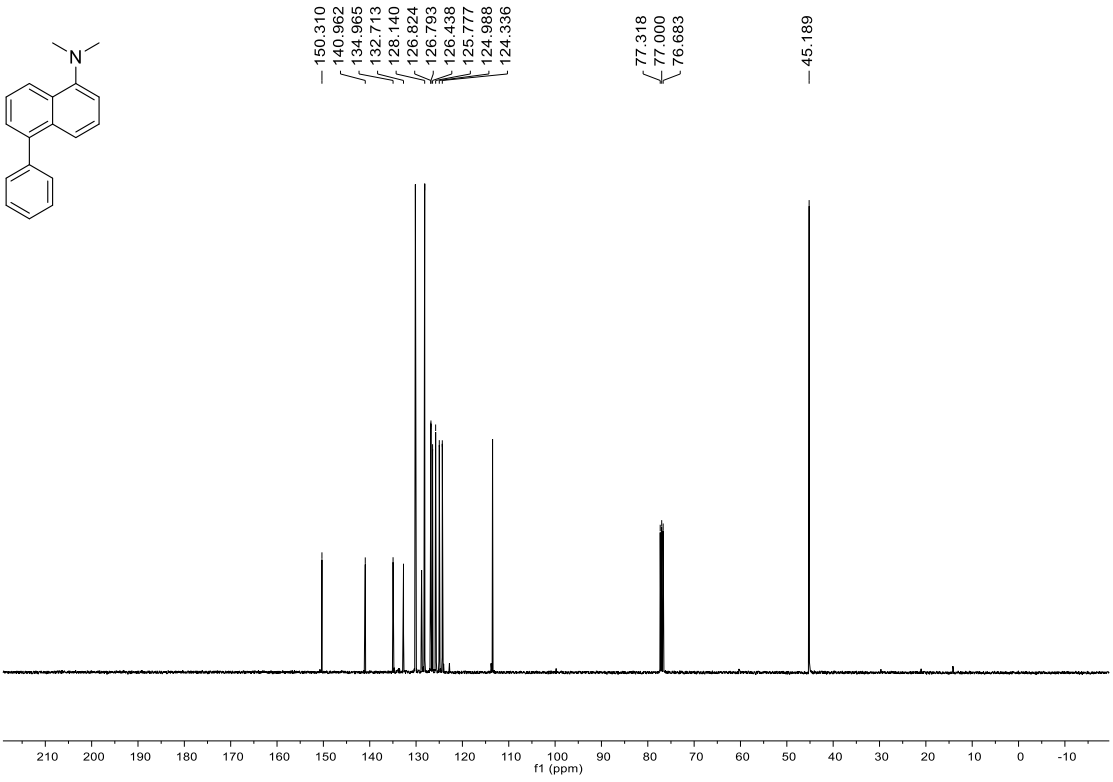
3.060
1.00
0.99
7.25
1.15
0.99
6.00
f1 (ppm)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132.713
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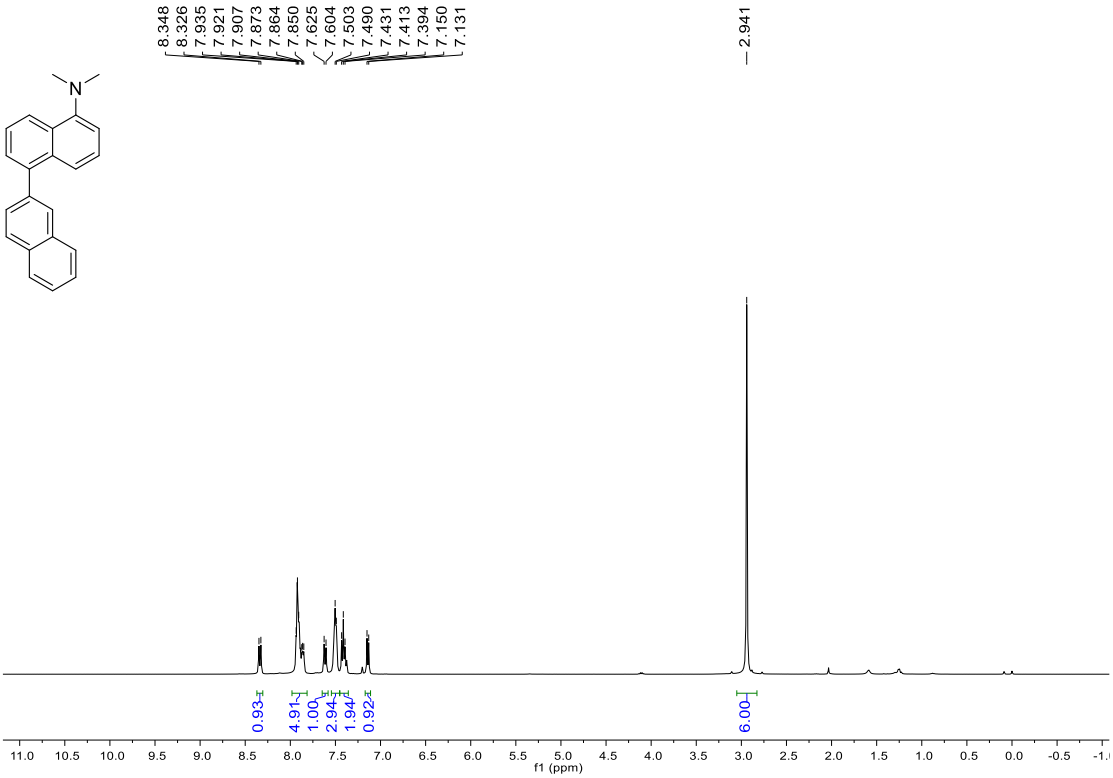
125.777
124.988
124.336
77.318
77.000
76.683
45.189
f1 (ppm)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7.907
7.873
7.864
7.850
7.625
7.604
7.503
7.490
7.431
7.413
7.394
7.150
7.131
2.941
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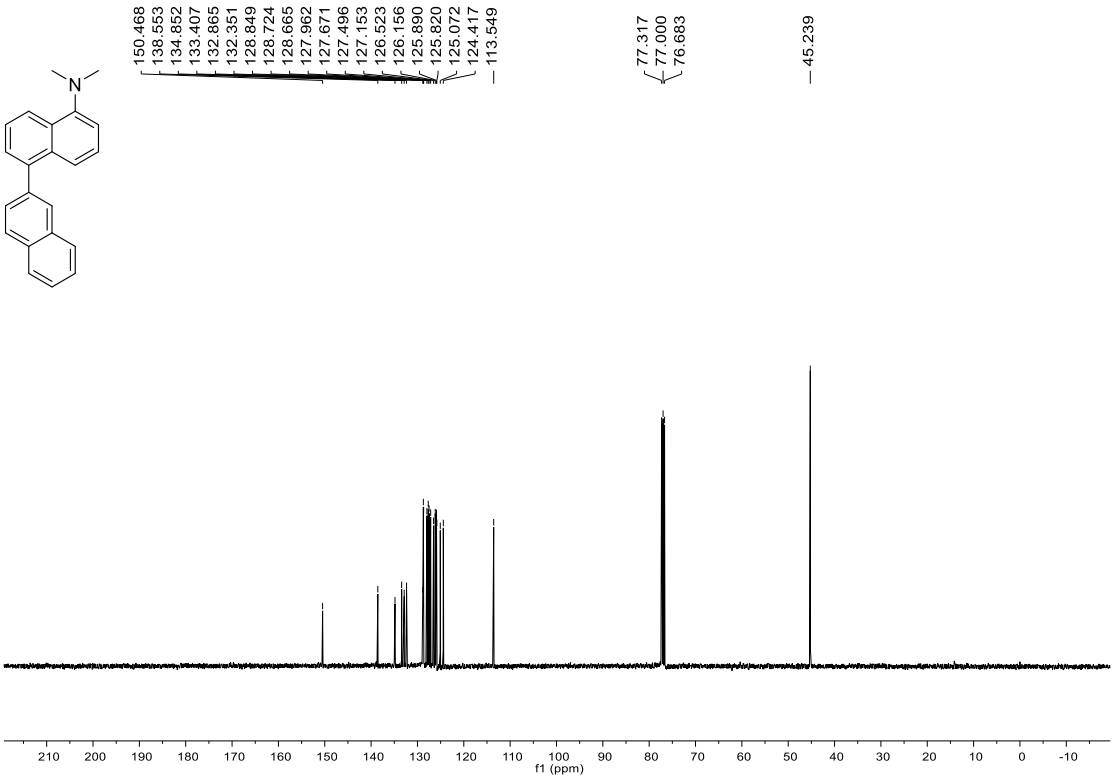
4.91
1.00
2.94
1.94
0.92
6.00
f1 (ppm)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127.153
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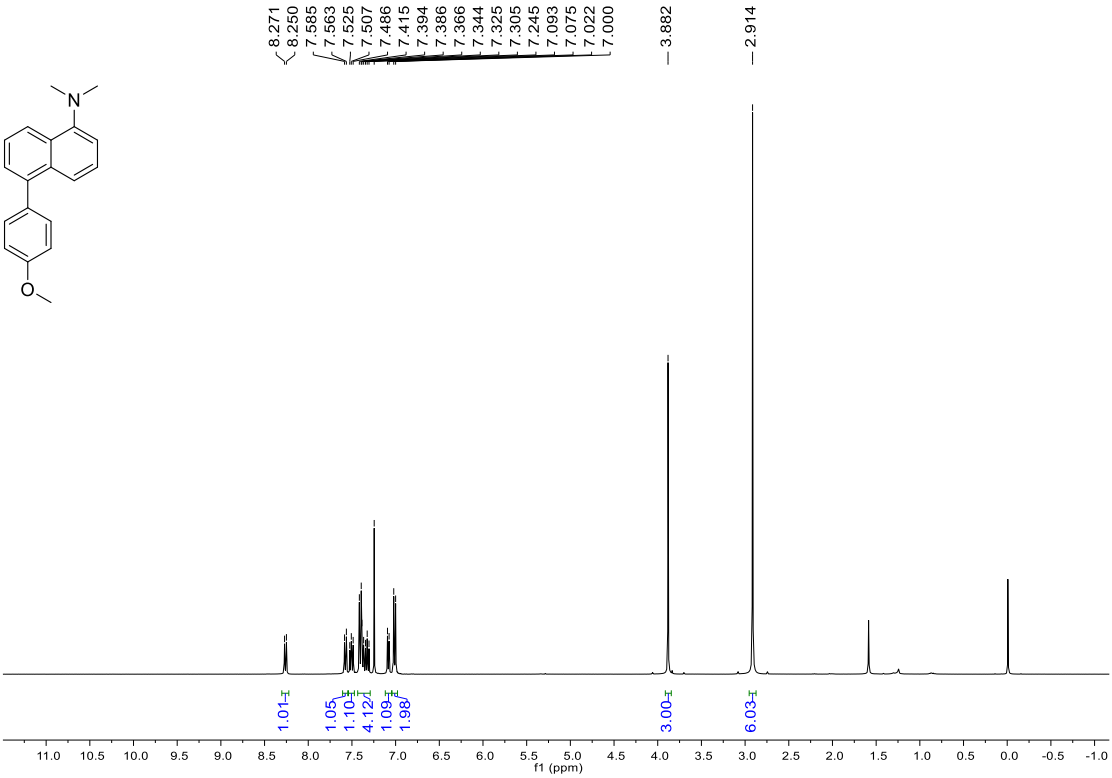
125.072
124.417
113.549
77.317
77.000
76.683
45.239
f1 (ppm)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7.563
7.525
7.507
7.486
7.415
7.394
7.386
7.366
7.344
7.325
7.305
7.245
7.093
7.075
7.022
7.000
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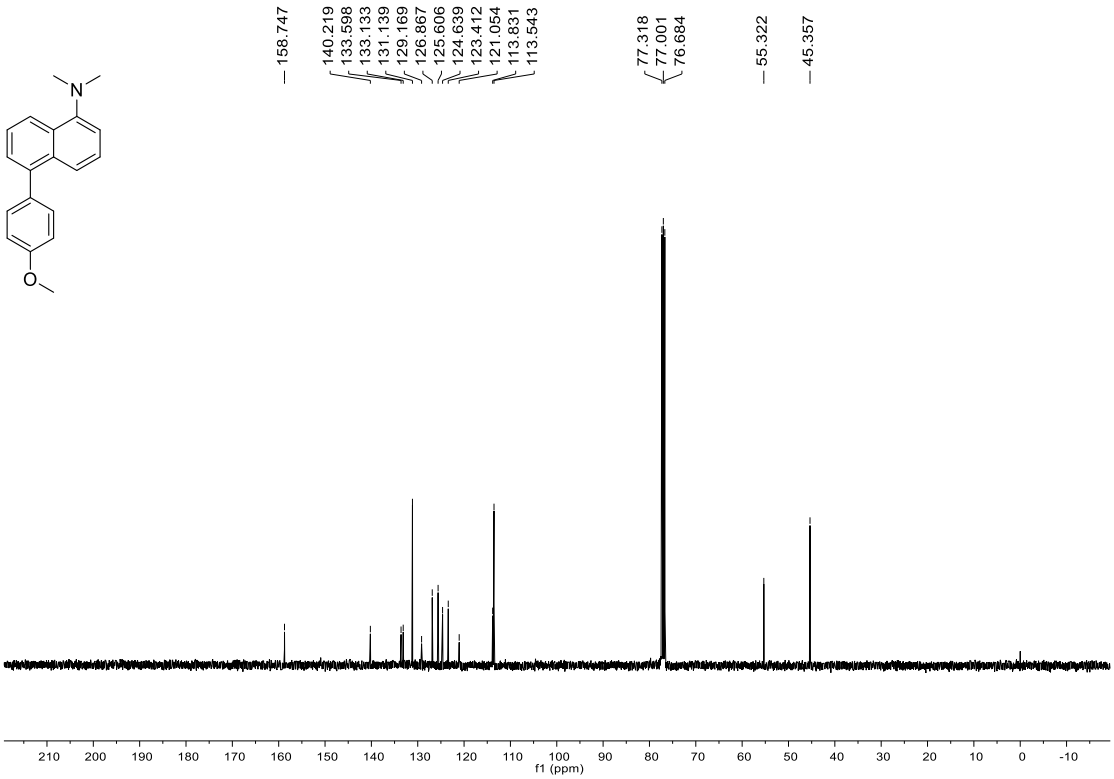
1.05
1.10
4.12
1.09
1.98
3.00
6.03
f1 (ppm)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140.219
133.598
133.133
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129.169
126.867
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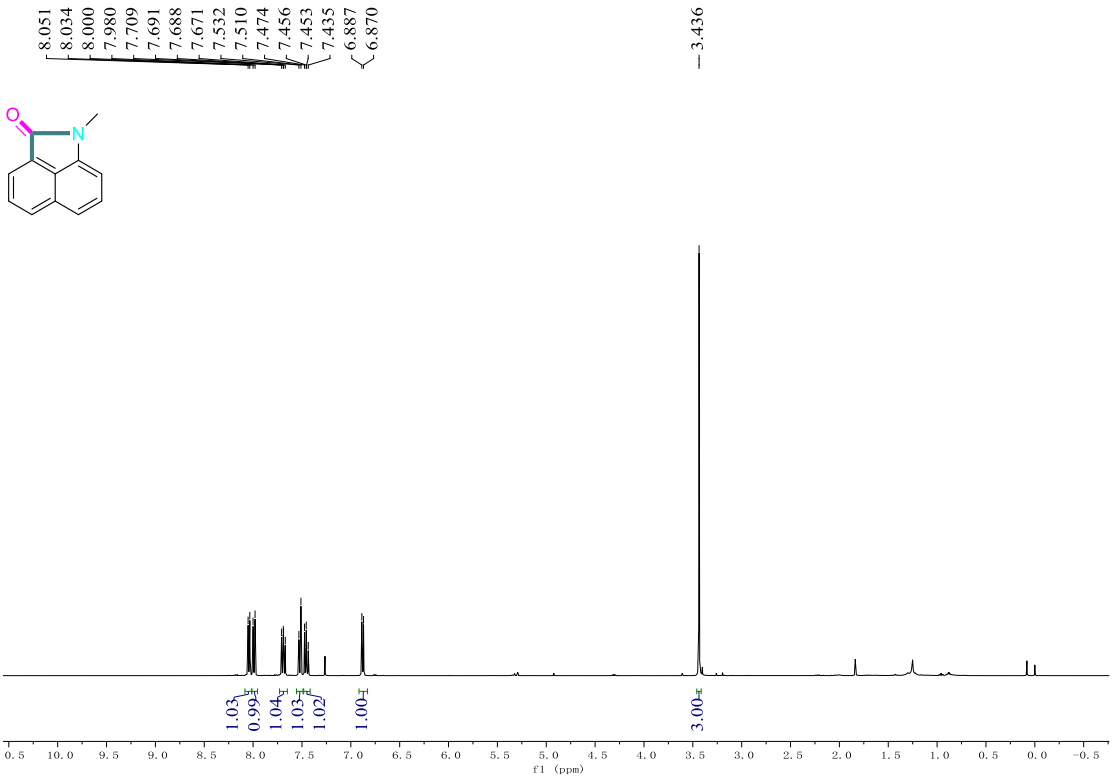
113.543
77.318
77.001
76.684
55.322
45.357
f1 (ppm)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8.034
8.000
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7.709
7.691
7.688
7.671
7.532
7.510
7.474
7.456
7.453
7.435
6.887
6.870
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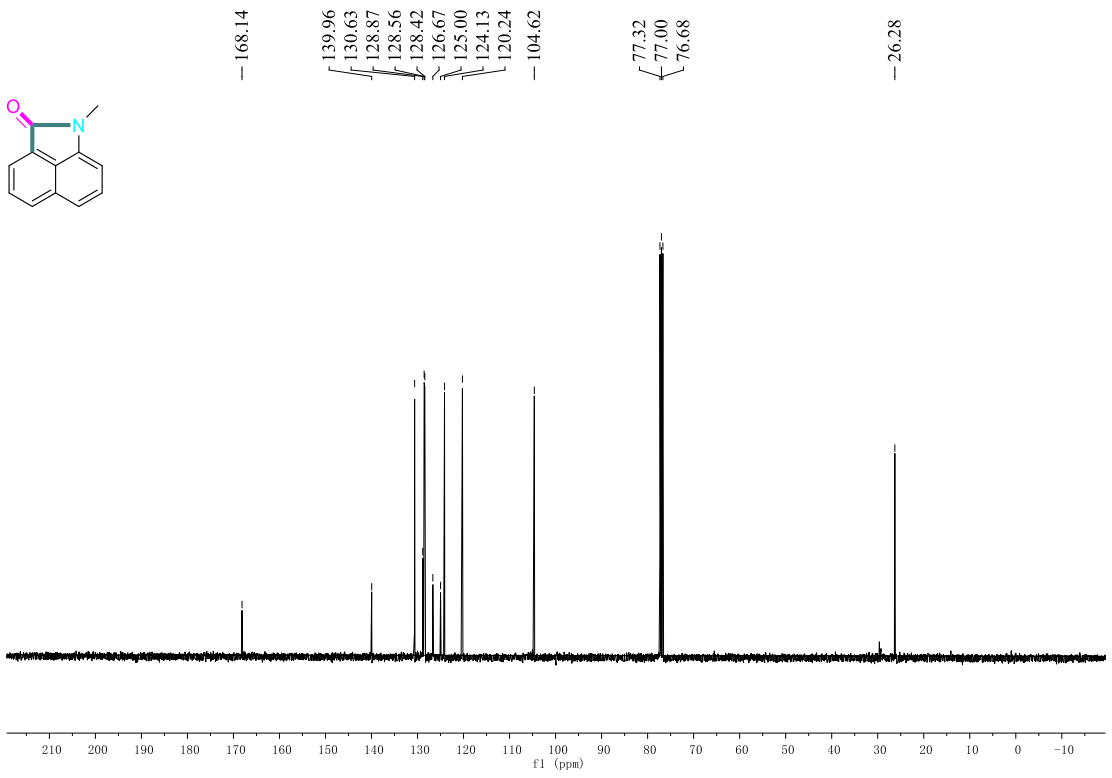
O
N
1.03
0.99
1.04
1.03
1.02
1.00
3.00
f1 (ppm)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130.63
128.87
128.56
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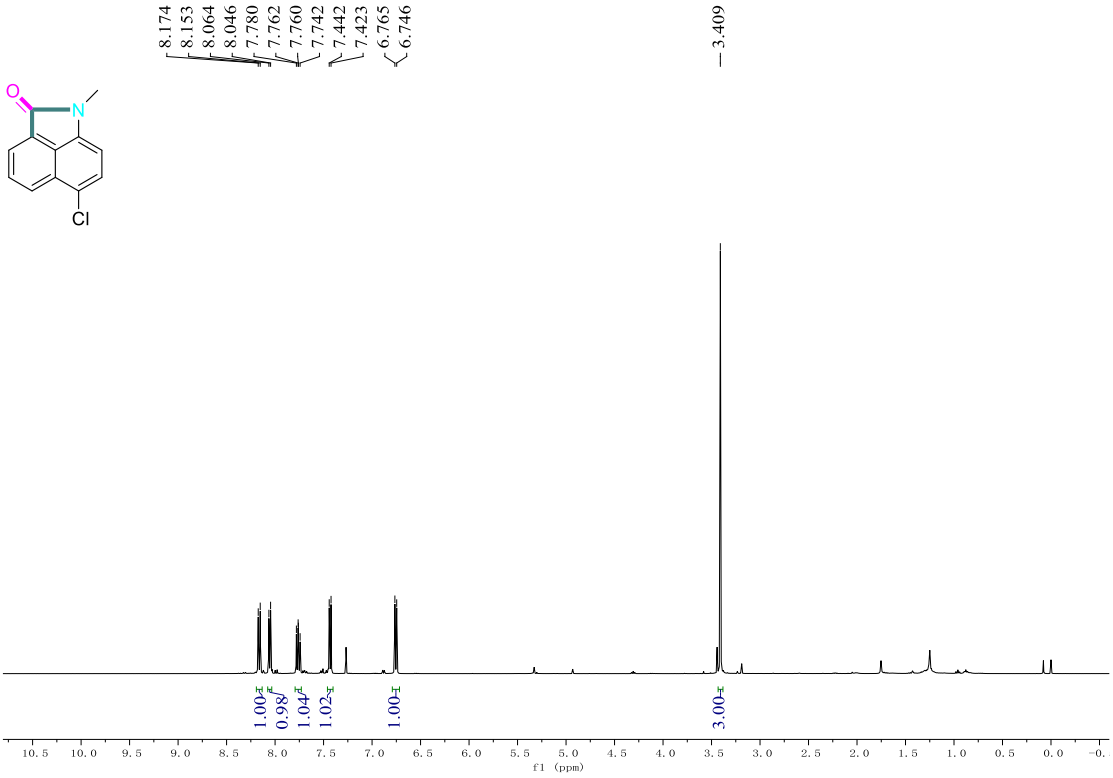
126.67
125.00
124.13
120.24
104.62
77.32
77.00
76.68
26.28
O
N
f1 (ppm)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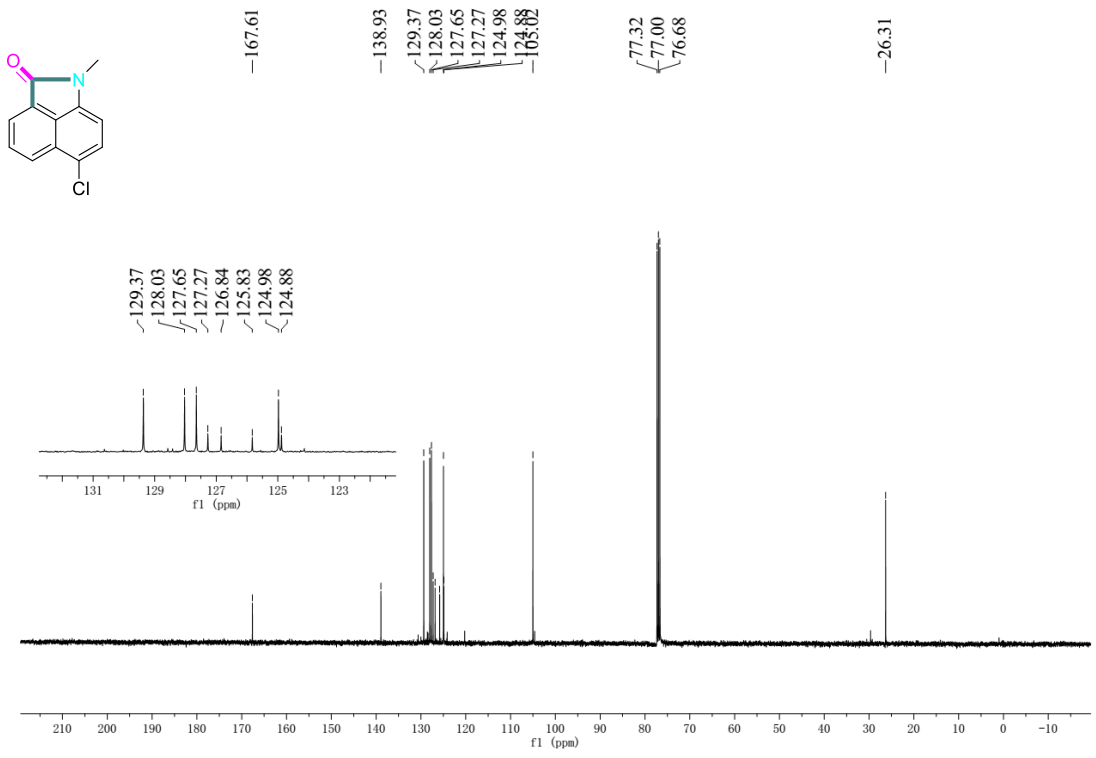
8.153
8.064
8.046
7.780
7.762
7.760
7.742
7.442
7.423
6.765
6.746
3.409
O
N
Cl
1.00
0.98
1.04
1.02
1.00
3.00
f1 (ppm)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127.65
127.27
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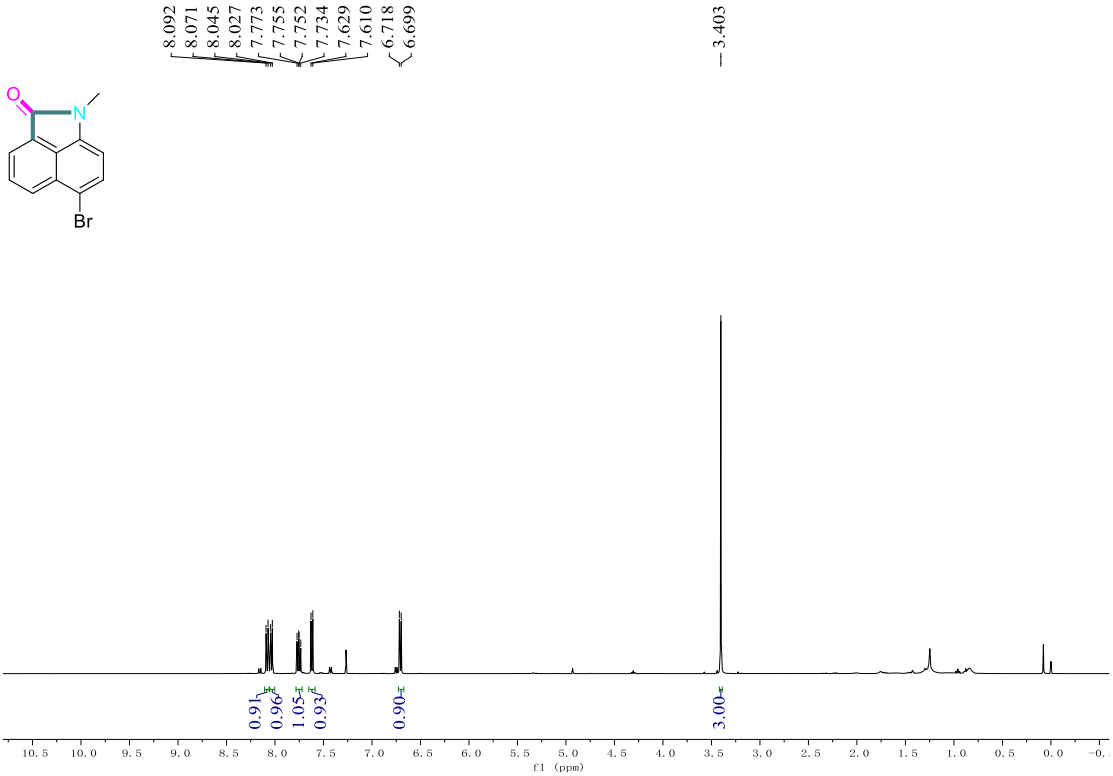
124.88
105.02
77.32
77.00
76.68
26.31
O
N
Cl
129.37
128.03
127.65
127.27
126.84
125.83
124.98
124.88
f1 (ppm)
f1 (ppm)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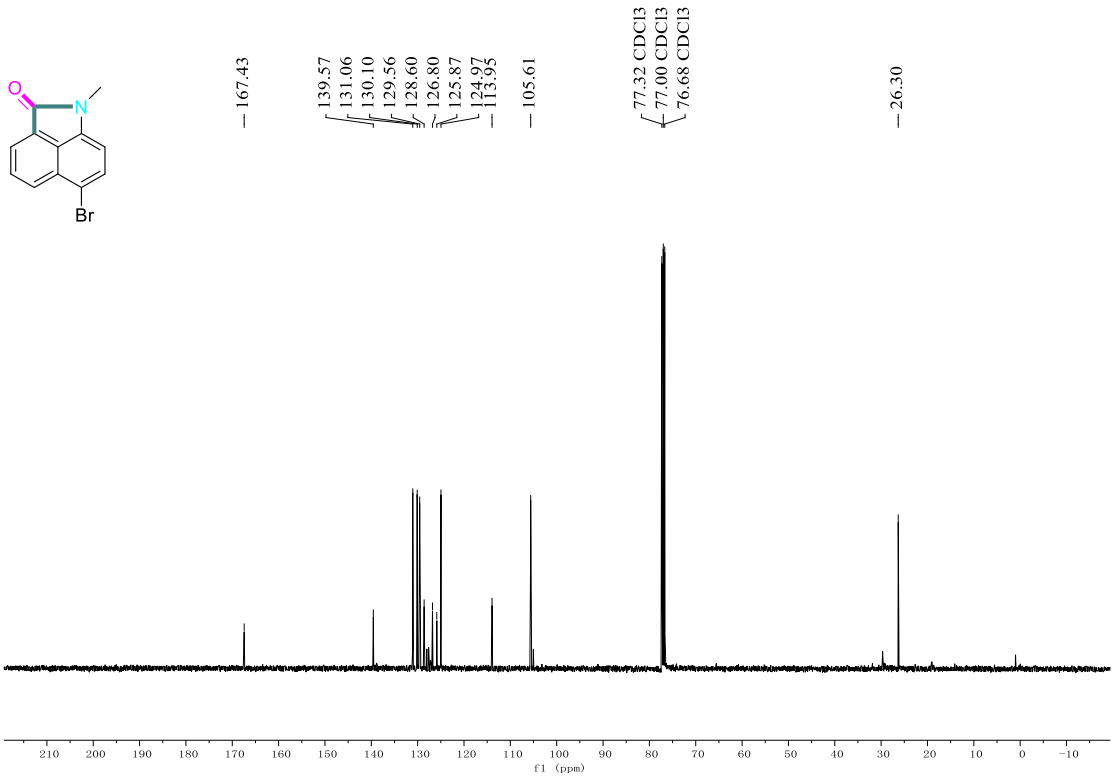
8.045
8.027
7.773
7.755
7.752
7.734
7.629
7.610
6.718
6.699
3.403
O
N
Br
0.91
0.96
1.05
0.93
0.90
3.00
f1 (ppm)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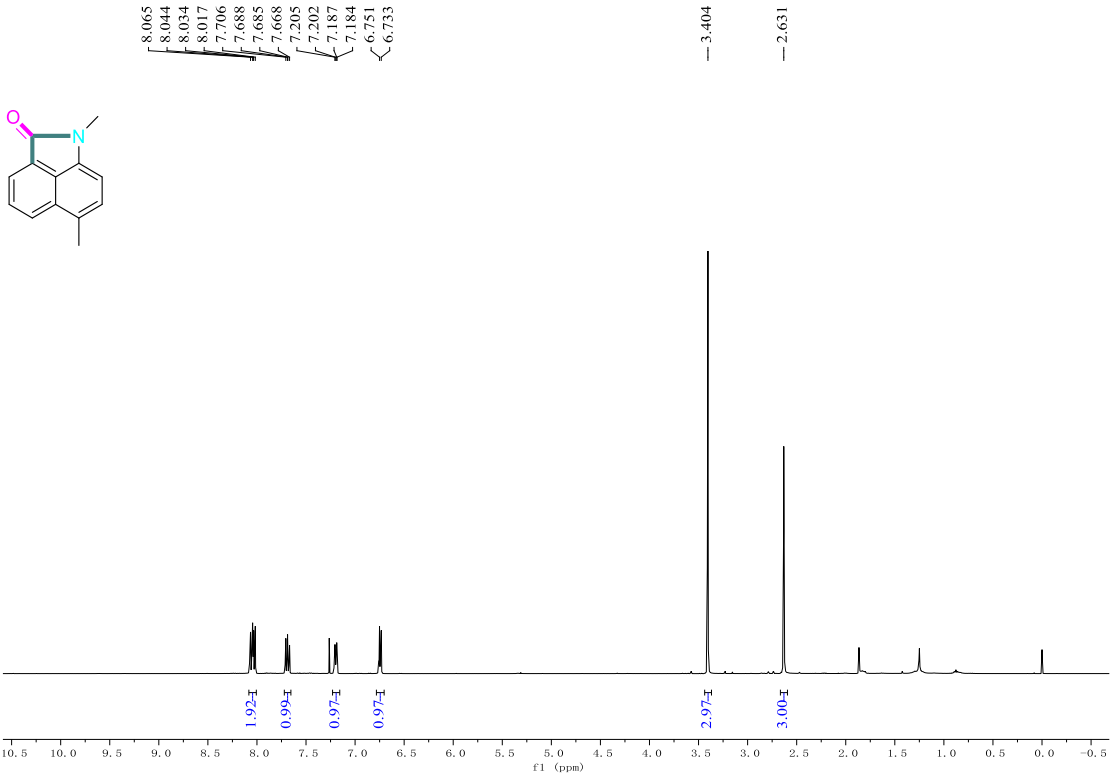
139.57
131.06
130.10
129.56
128.60
126.80
125.87
124.97
113.95
105.61
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
26.30
O
N
Br
f1 (ppm)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8.044
8.034
8.017
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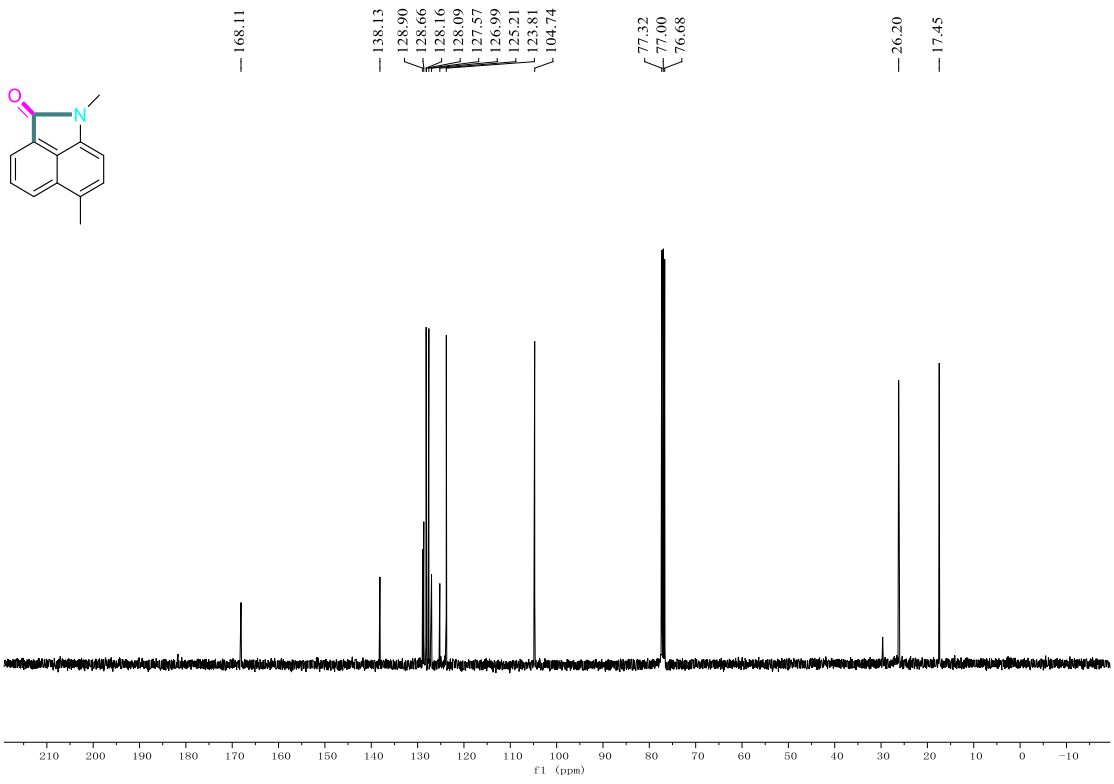
7.688
7.685
7.668
7.205
7.202
7.187
7.184
6.751
6.733
3.404
2.631
1.92
0.99
0.97
0.97
2.97
3.00
f1 (ppm)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128.16
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127.57
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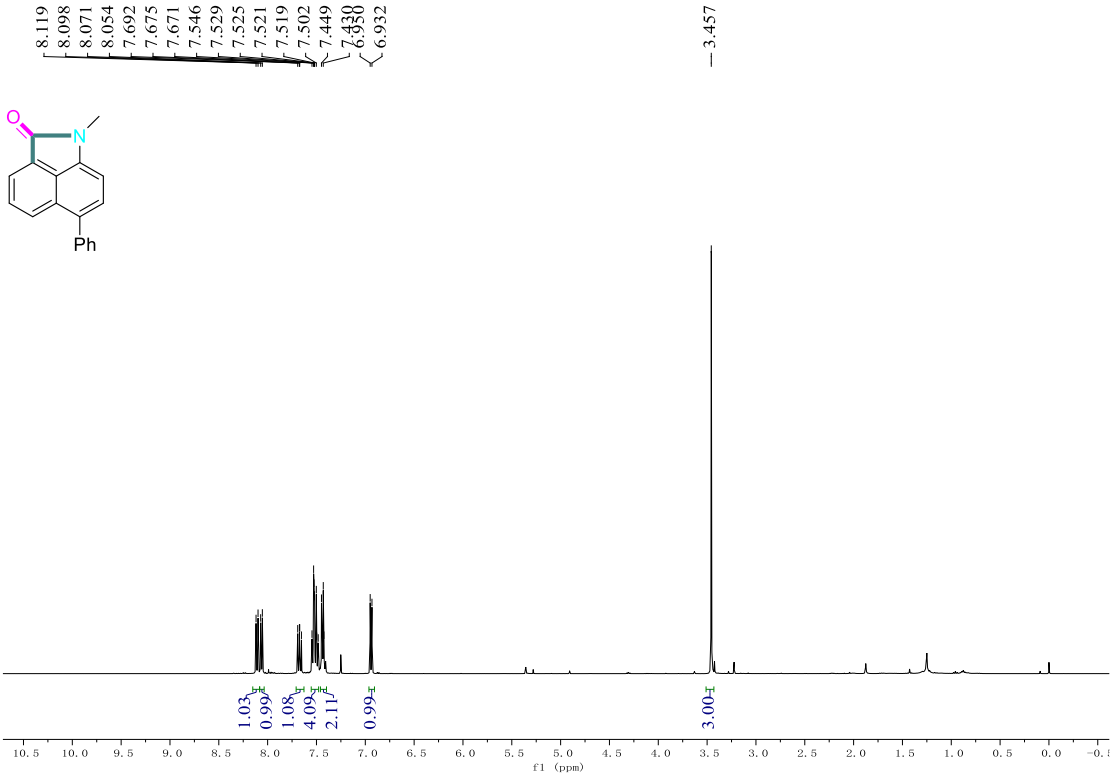
125.21
123.81
104.74
77.32
77.00
76.68
26.20
17.45
f1 (ppm)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8.054
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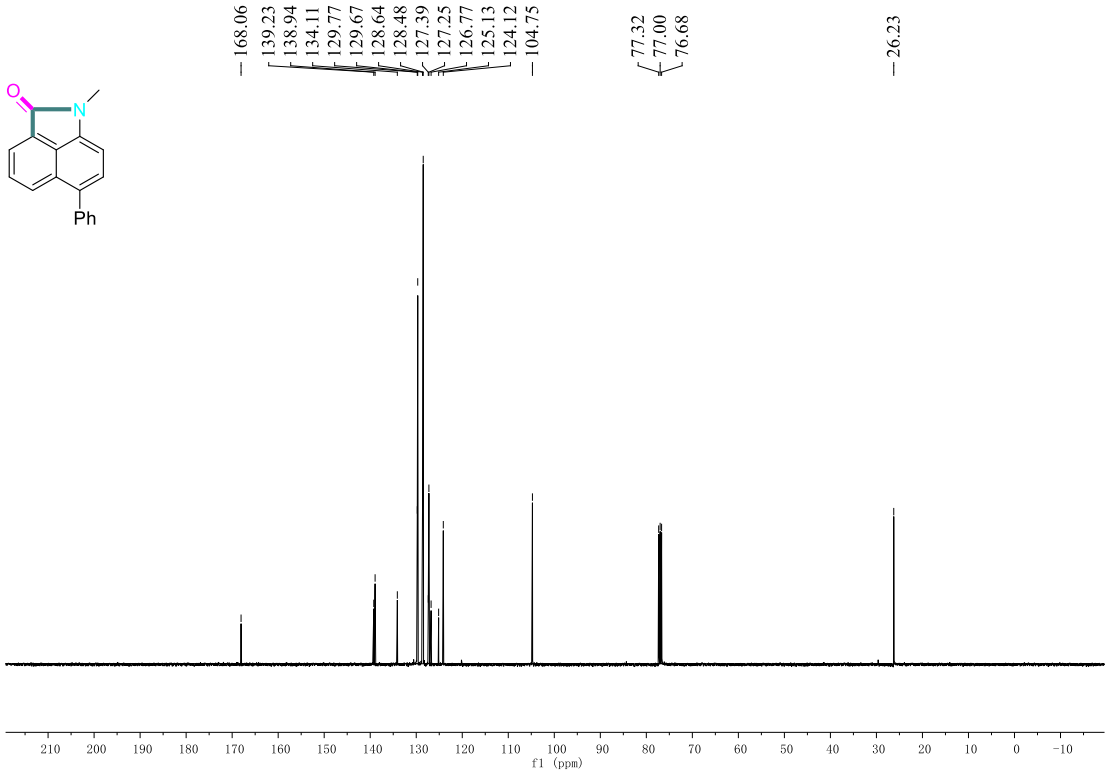
7.675
7.671
7.546
7.529
7.525
7.521
7.519
7.502
7.449
7.430
6.950
6.932
3.457
O
N
Ph
1.03
0.99
1.08
4.09
2.11
0.99
3.00
f1 (ppm)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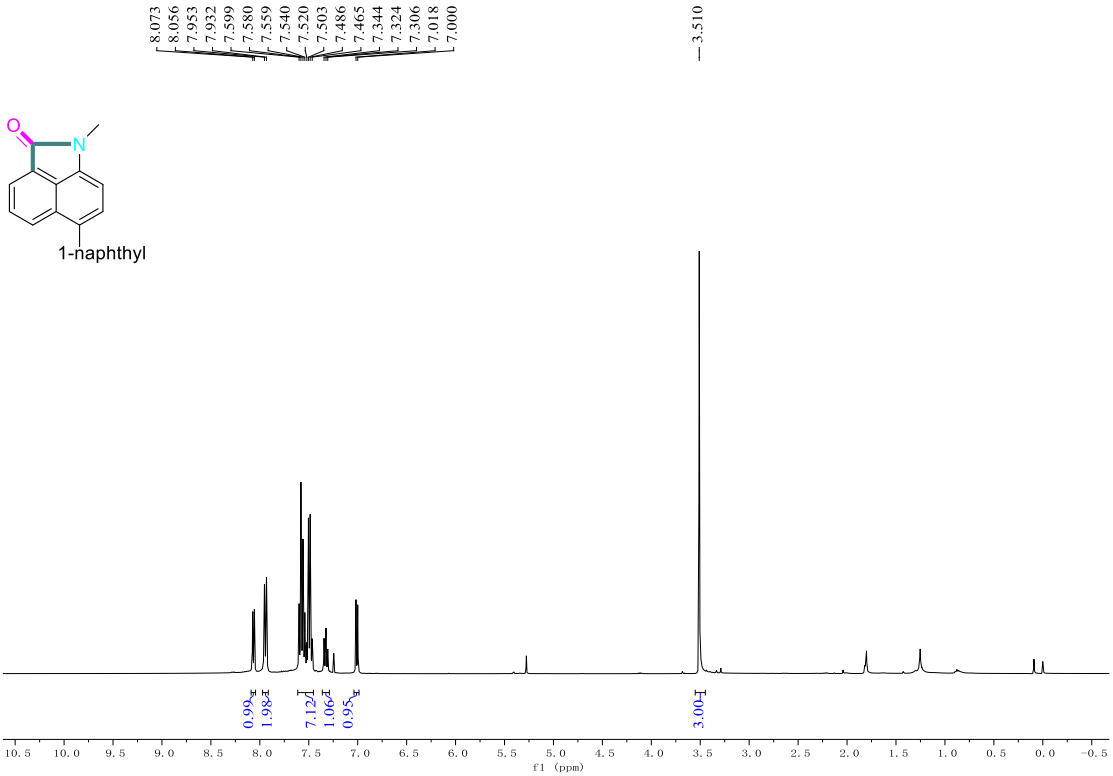
77.32
77.00
76.68
26.23
O
N
Ph
f1 (ppm)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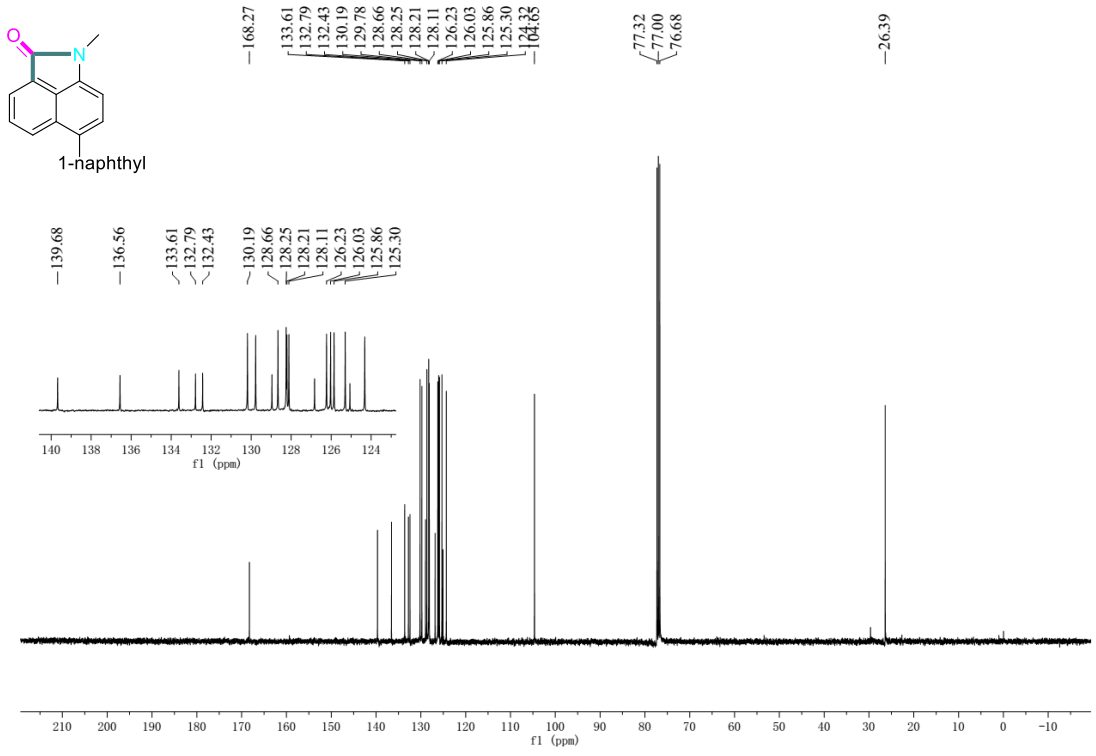
7.503
7.486
7.465
7.344
7.324
7.306
7.018
7.000
3.510
1-naphthyl
0.99
1.98
7.12
1.06
0.95
3.00
f1 (ppm)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128.21
128.11
126.23
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1-naphthyl
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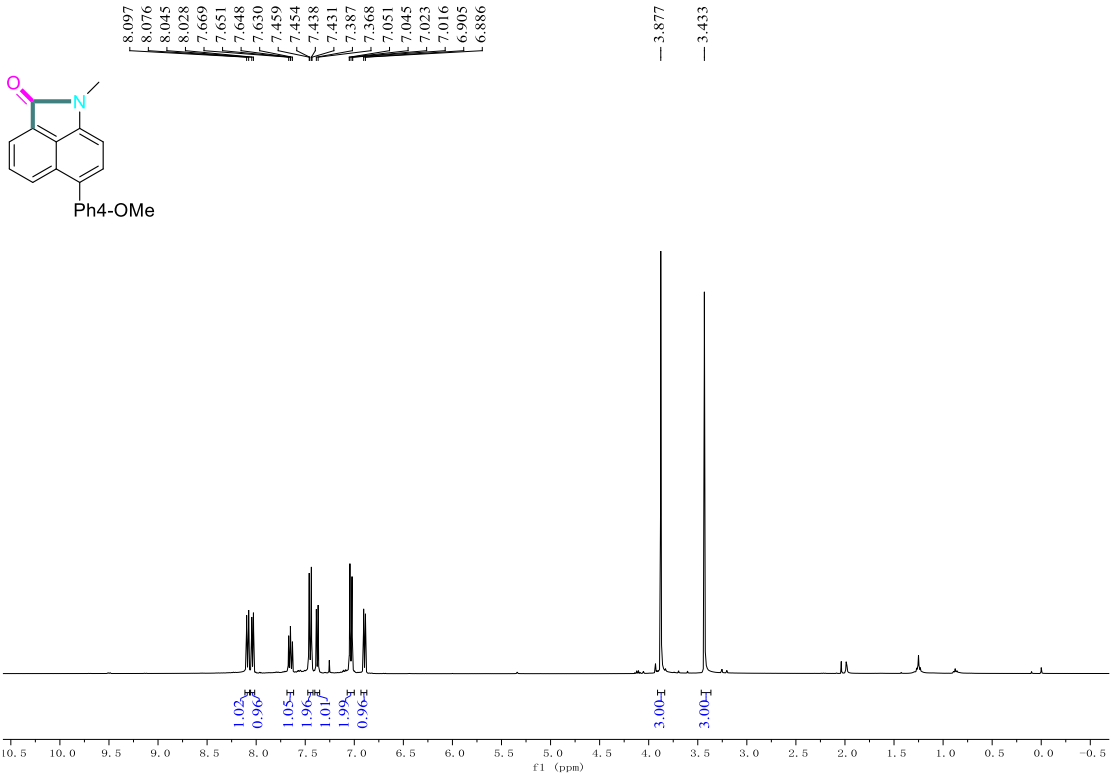
136.56
f1 (ppm)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7.630
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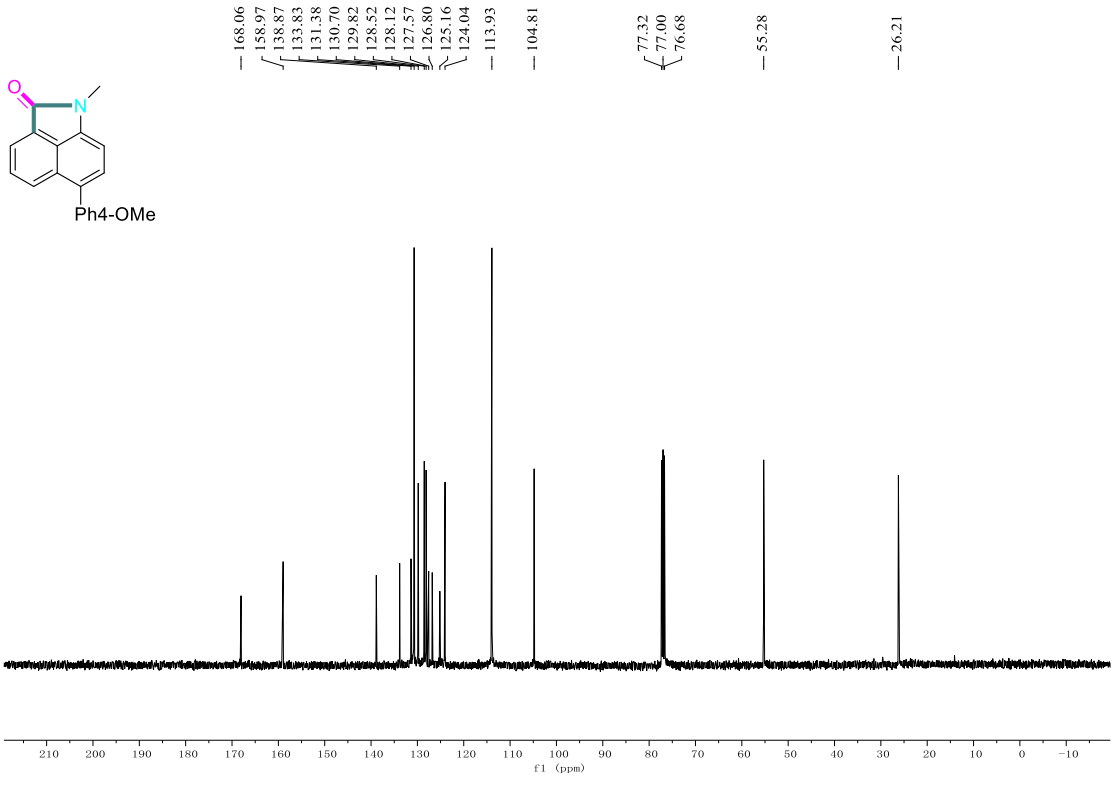
7.454
7.438
7.431
7.387
7.368
7.051
7.045
7.023
7.016
6.905
6.886
3.877
3.433
Ph4-OMe
1.02
0.96
1.05
1.96
1.01
1.99
0.96
3.00
3.00
f1 (ppm)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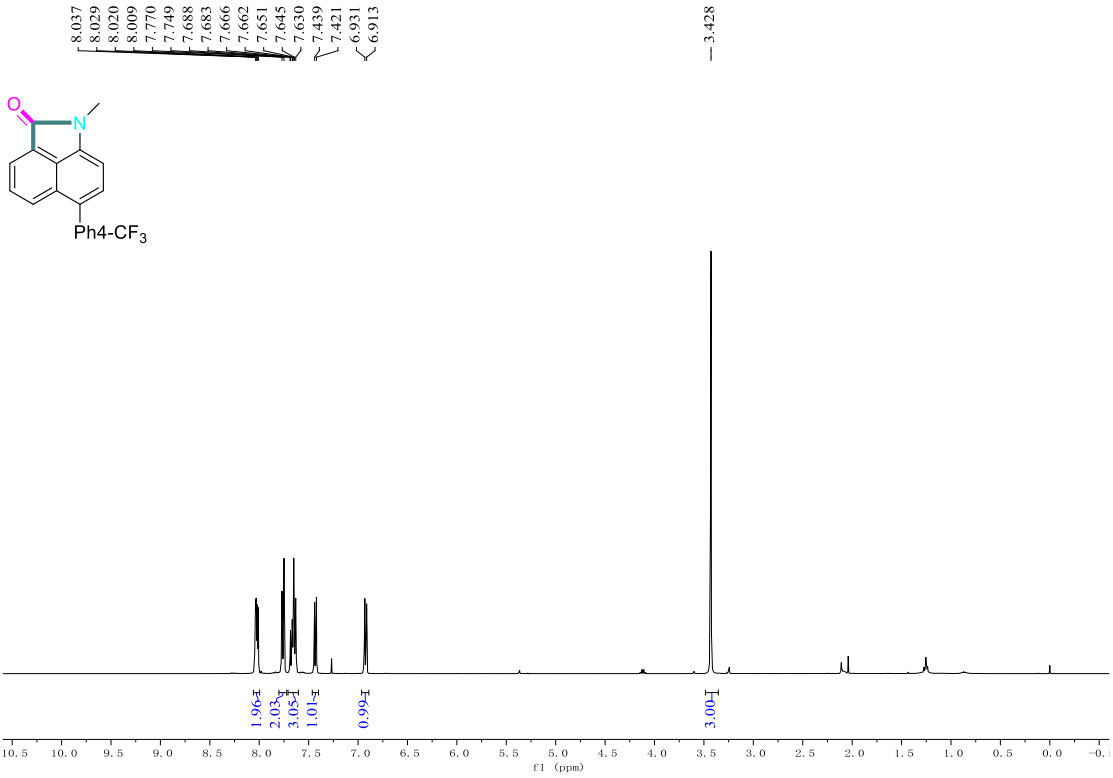
77.00
76.68
55.28
26.21
Ph4-OMe
f1 (ppm)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7.630
7.439
7.421
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3.428
Ph4-CF3
1.96
2.03
3.05
1.01
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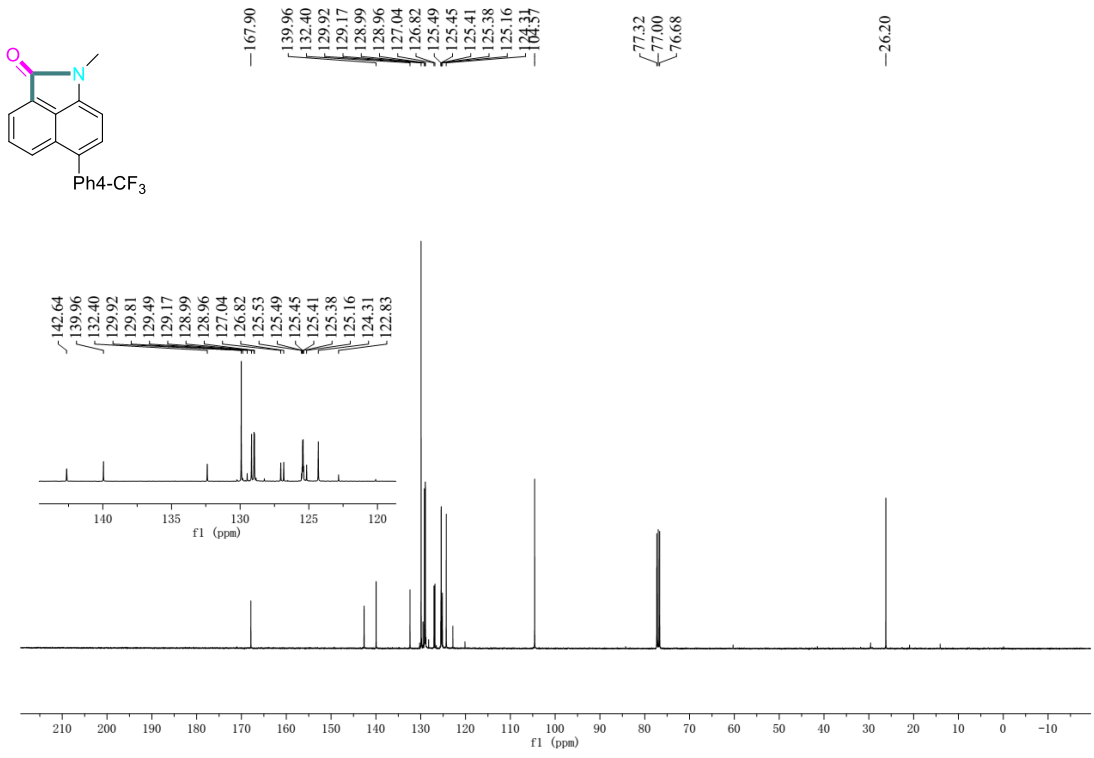
3.00
f1 (ppm)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125.45
125.41
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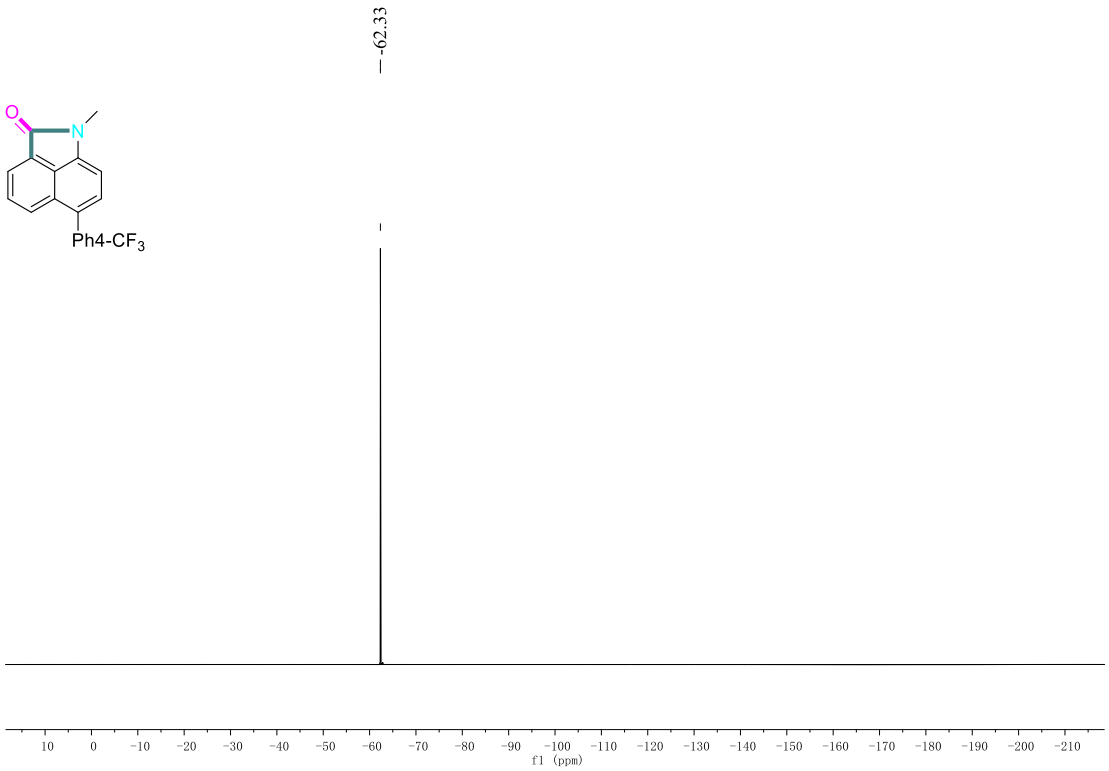
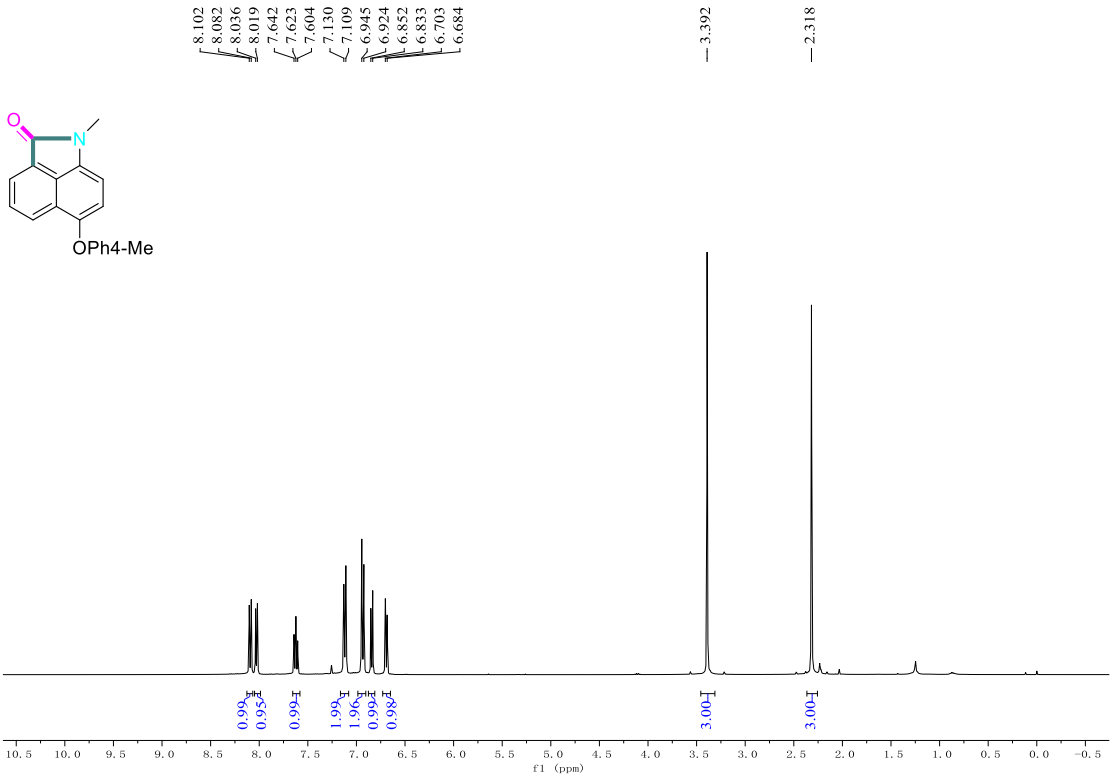
124.31
122.83
77.32
77.00
76.68
26.20
Ph4-CF3
142.64
f1 (ppm)


-62.33
Ph4-CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.130
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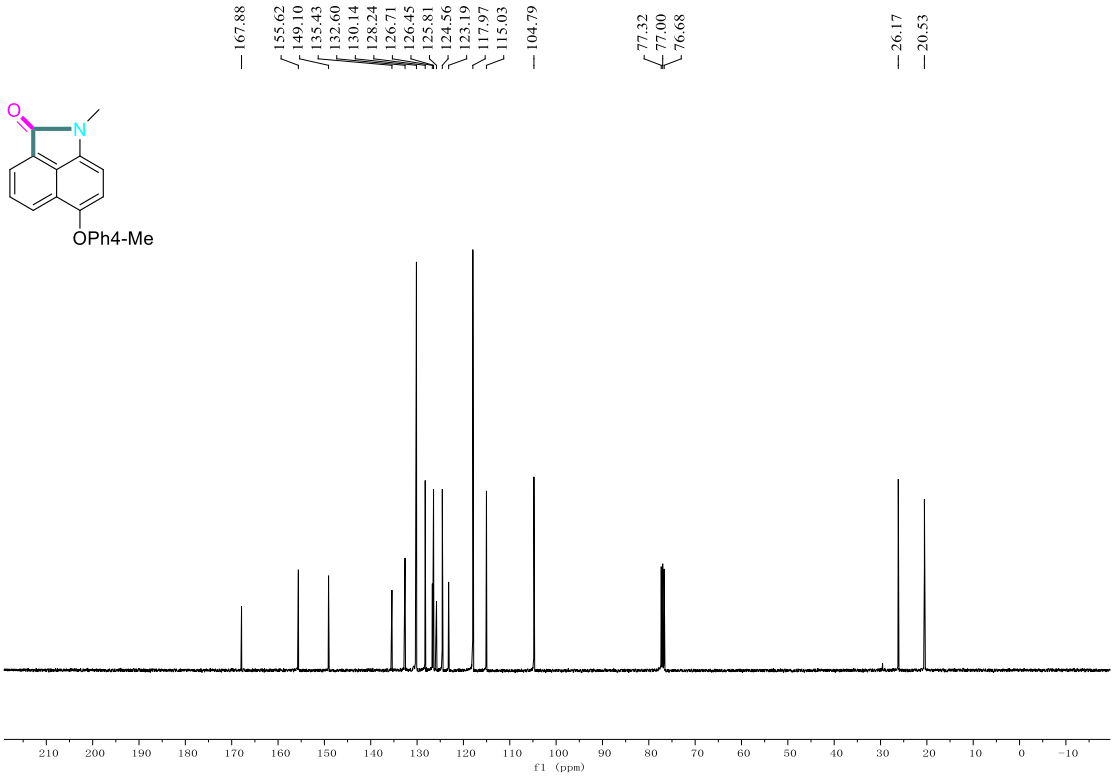
6.924
6.852
6.833
6.703
6.684
3.392
2.318
OPh4-Me
0.99
0.95
0.99
1.99
1.96
0.99
0.98
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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124.56
123.19
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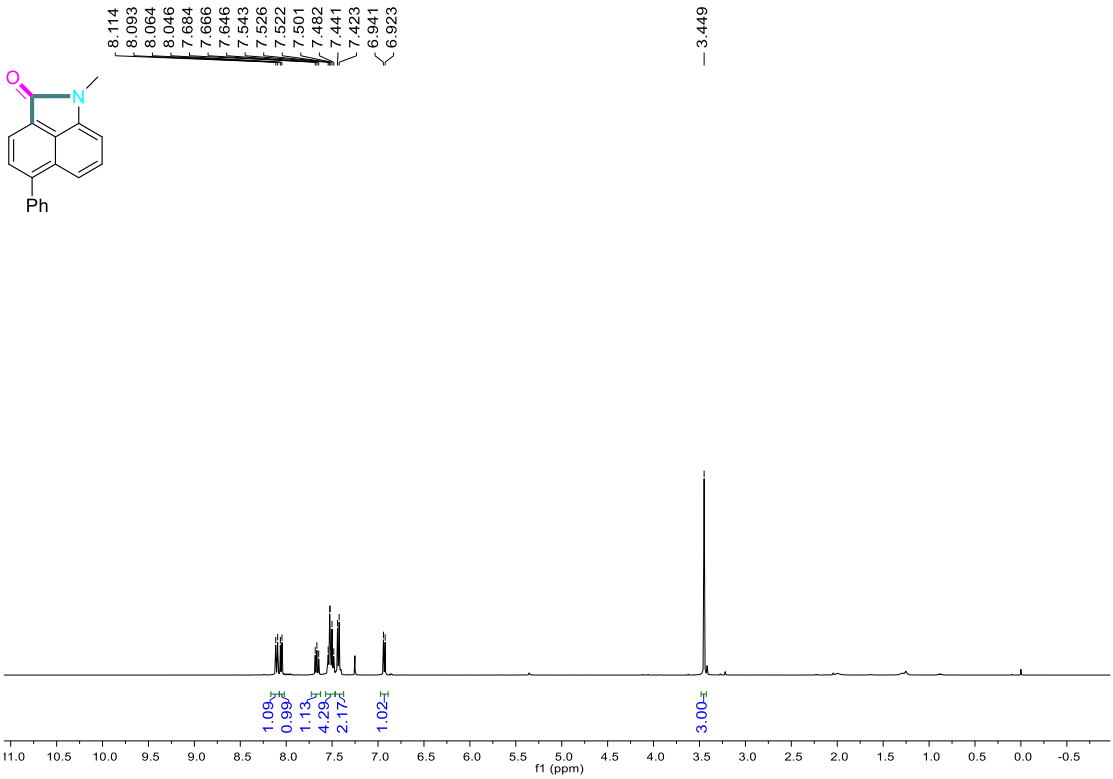
77.32
77.00
76.68
26.17
20.53
O
N
OPh4-Me
f1 (ppm)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7.501
7.482
7.441
7.423
6.941
6.923
3.449
O
N
Ph
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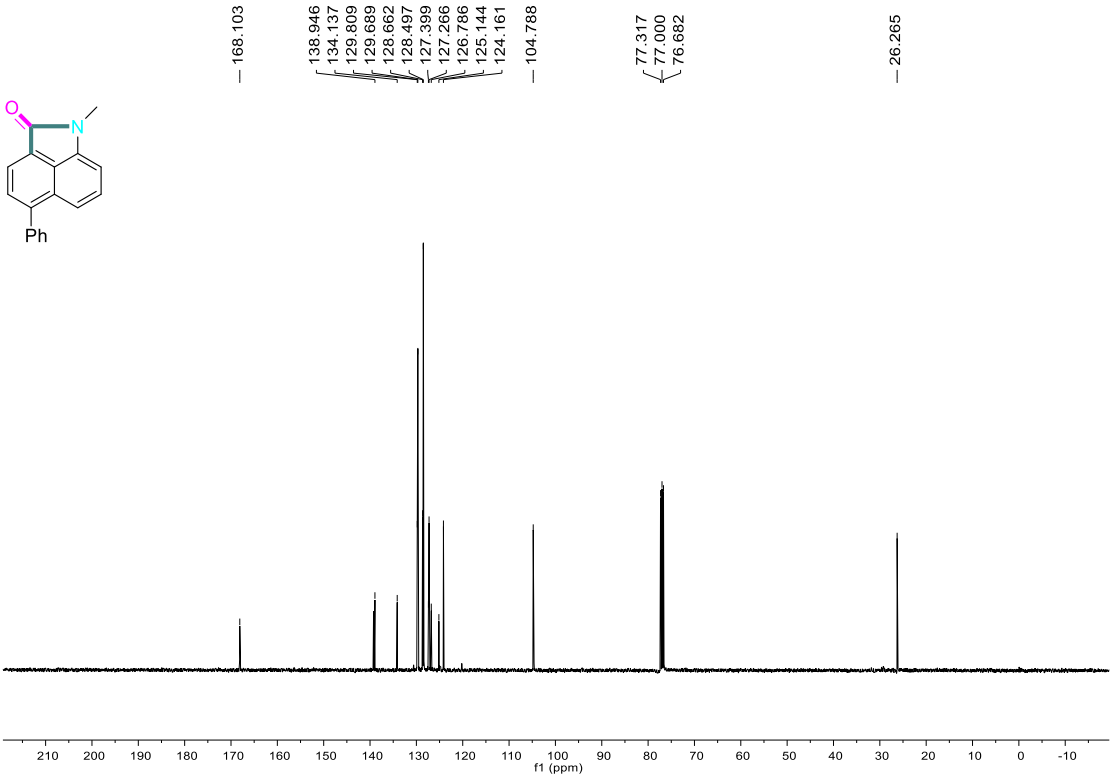
1.13
4.29
2.17
1.02
3.00
f1 (ppm)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77.000
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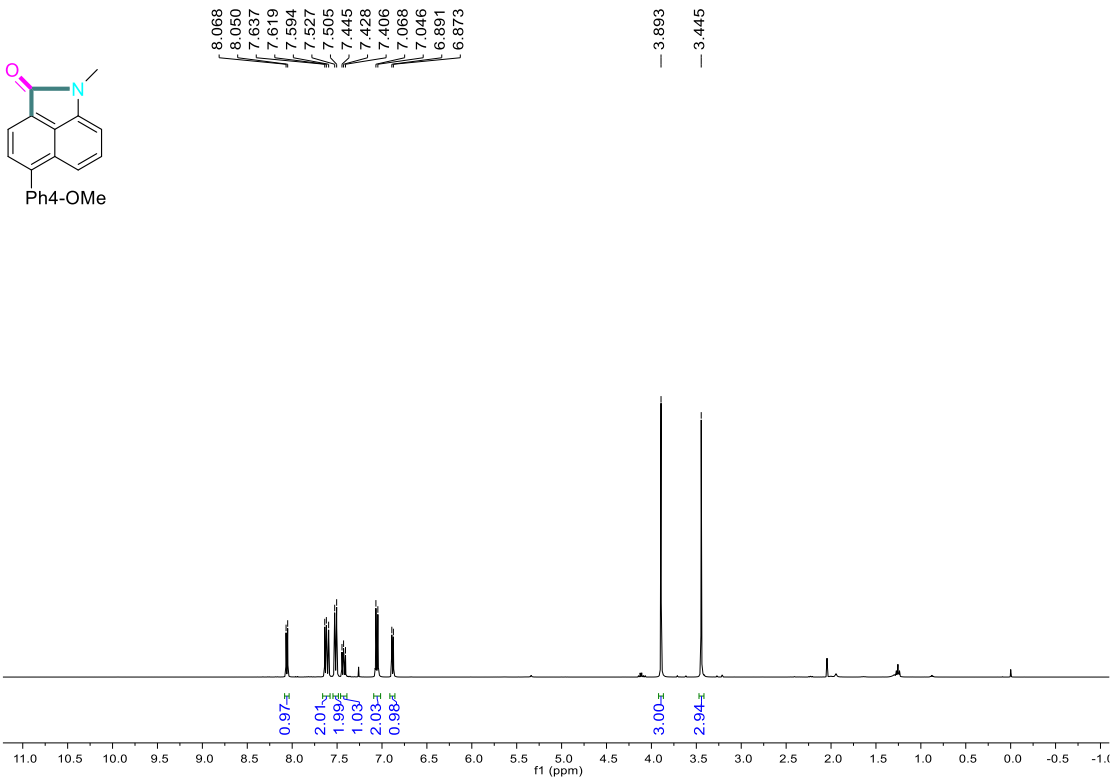
26.265
O
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.505
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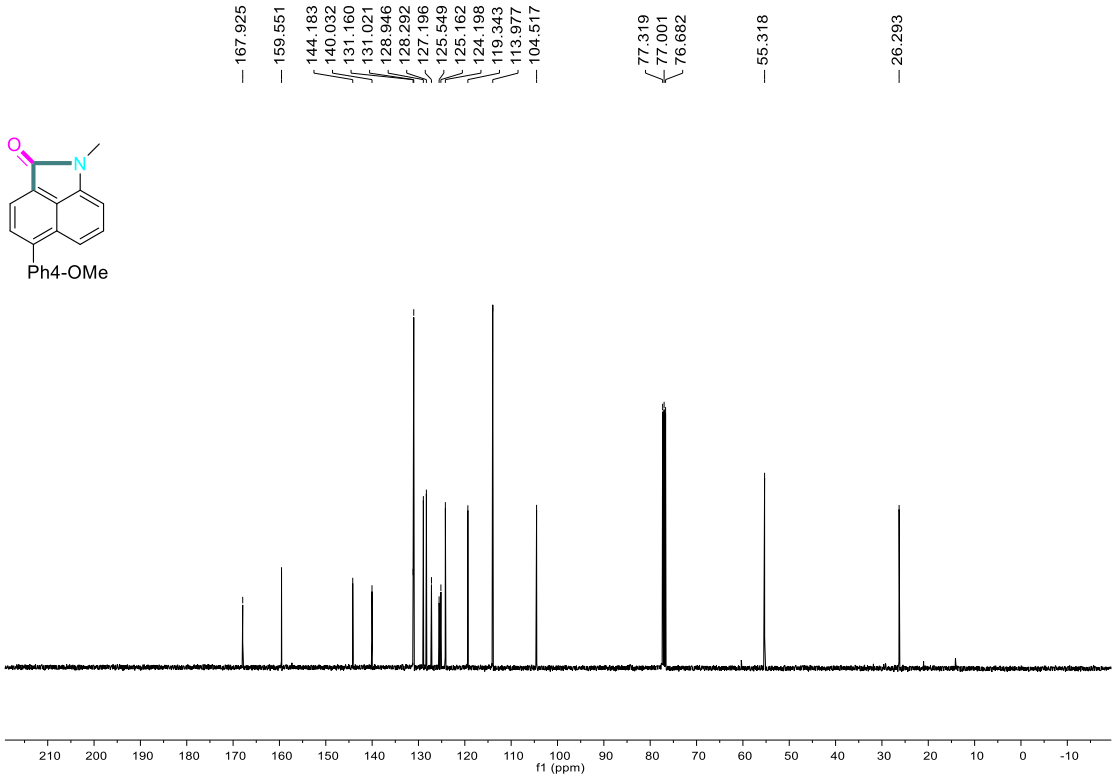
7.068
7.046
6.891
6.873
3.893
3.445
O
N
Ph4-OMe
0.97
2.01
1.99
1.03
2.03
0.98
3.00
2.94
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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125.162
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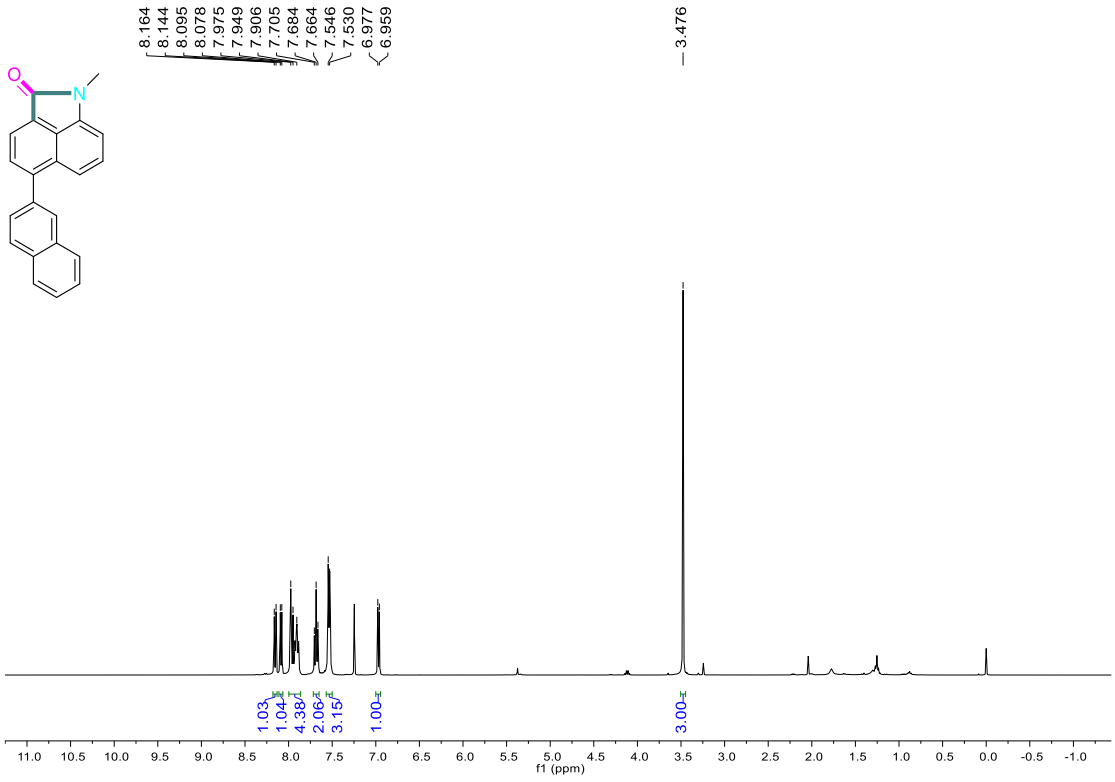
104.517
77.319
77.001
76.682
55.318
26.293
Ph4-OMe
f1 (ppm)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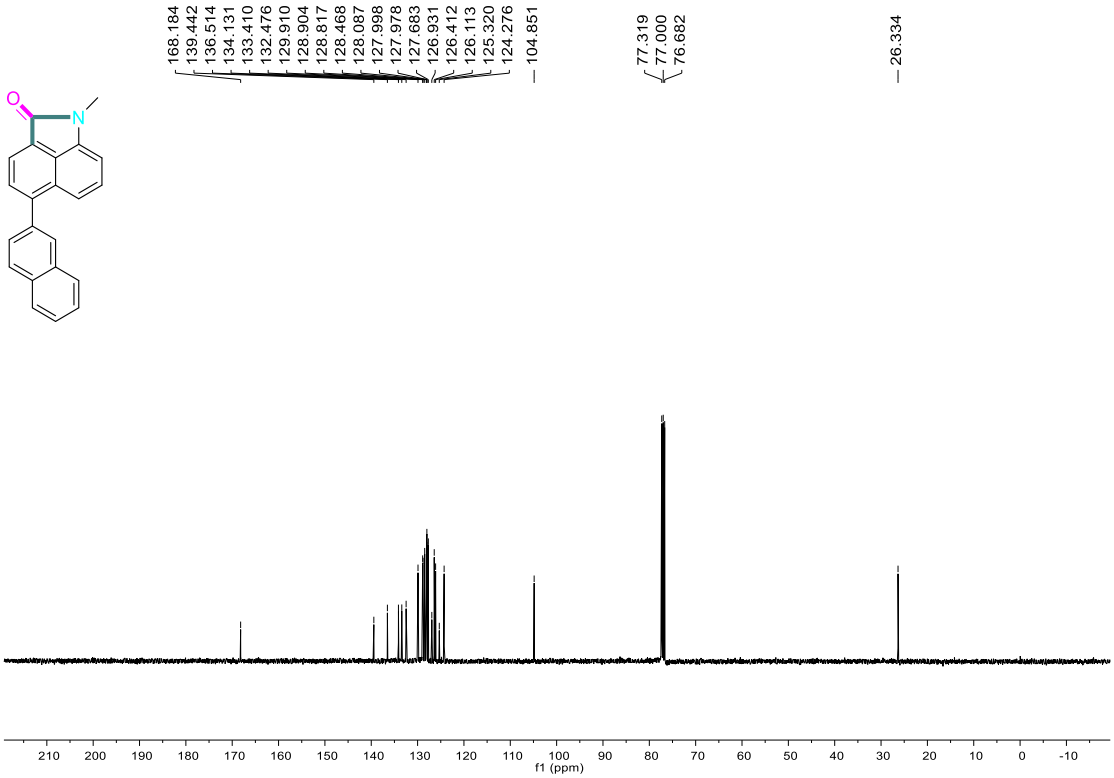
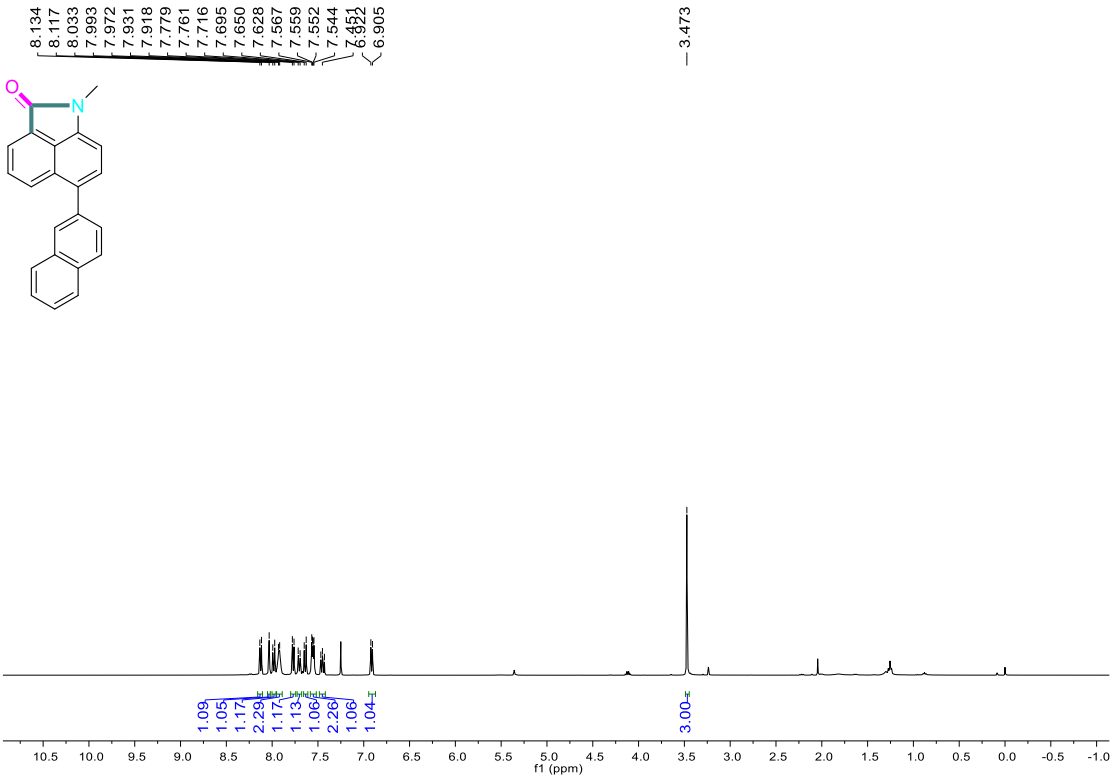
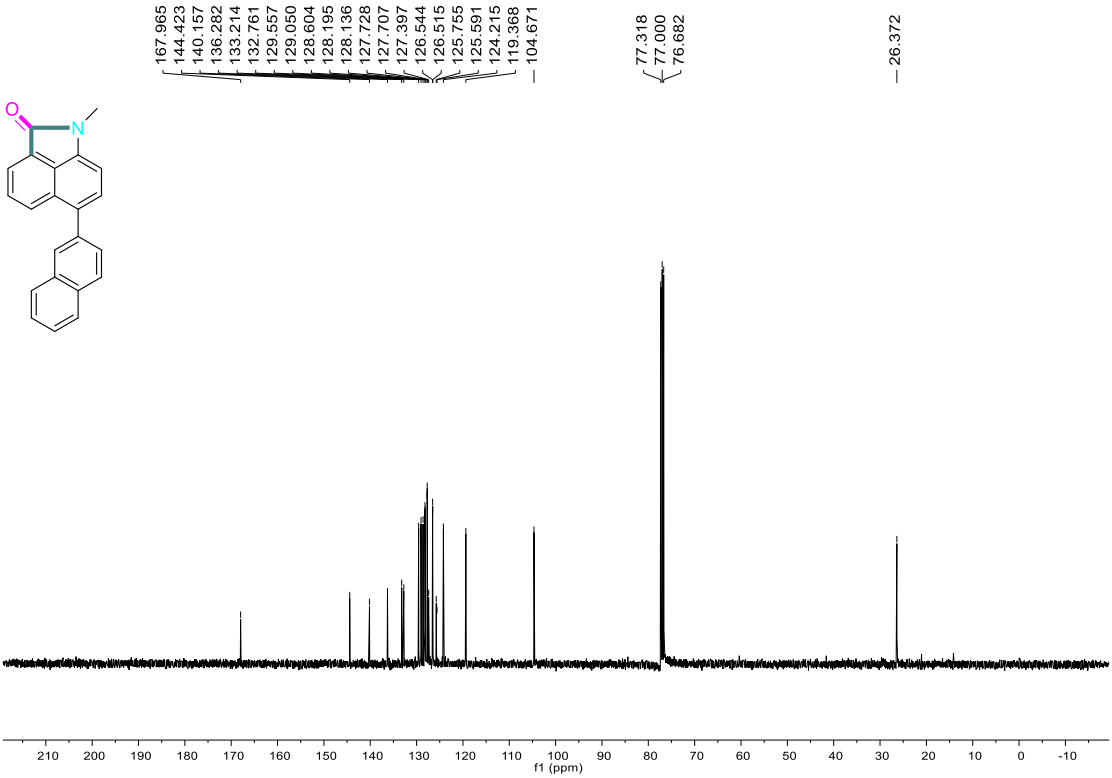
8.144
8.095
8.078
7.975
7.949
7.906
7.705
7.684
7.664
7.546
7.530
6.977
6.959
3.476
1.03
1.04
4.38
2.06
3.15
1.00
3.00
f1 (ppm)


168.184
139.442
136.514
134.131
133.410
132.476
129.910
128.904
128.817
128.468
128.087
127.998
127.978
127.683
126.931
126.412
126.113
125.320
124.276
104.851
77.319
77.000
76.682
26.334
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.134
8.117
8.033
7.993
7.972
7.931
7.918
7.779
7.761
7.716
7.695
7.650
7.628
7.567
7.559
7.552
7.544
7.451
6.905
3.473
O
N
1.09
1.05
1.17
2.29
1.17
1.13
1.06
2.26
1.06
1.04
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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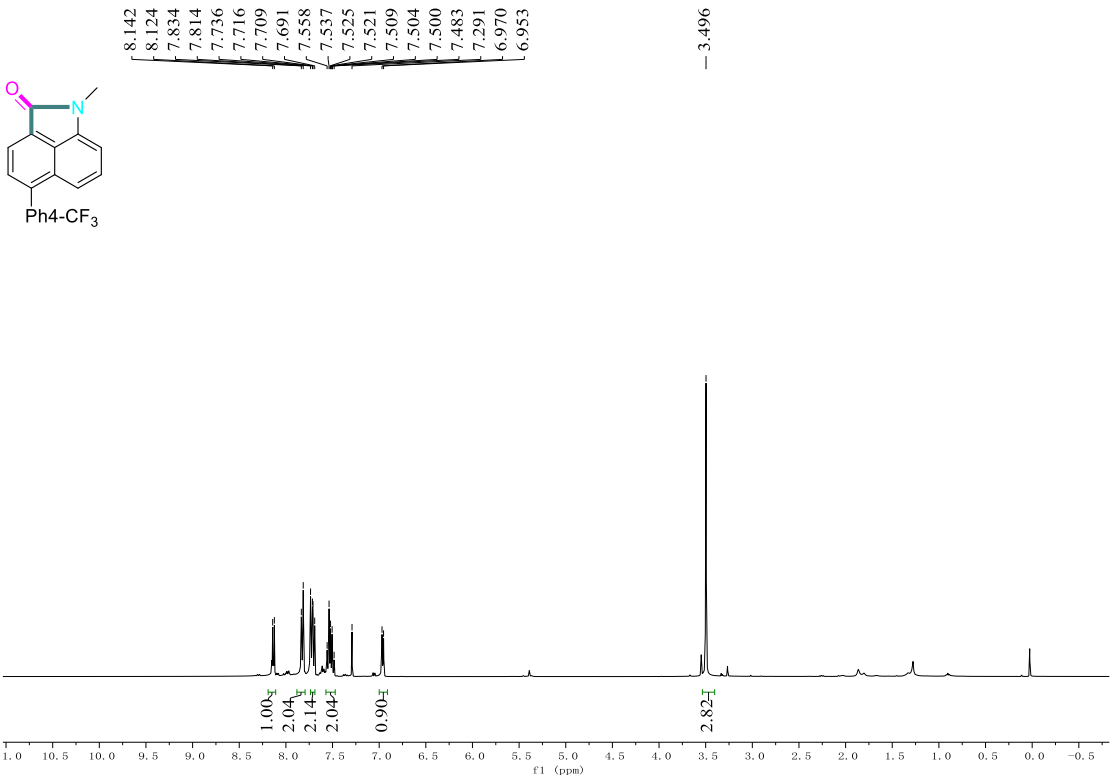
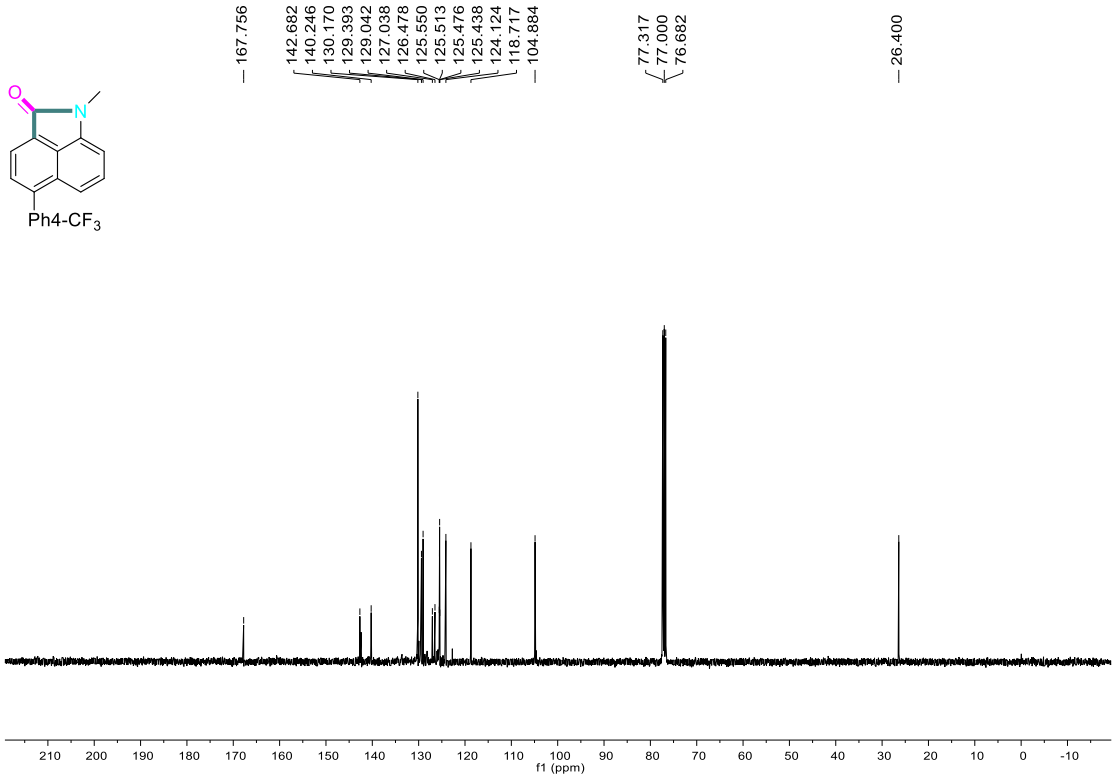
144.423
140.157
136.282
133.214
132.761
129.557
129.050
128.604
128.195
128.136
127.728
127.707
127.397
126.544
126.515
125.755
125.591
124.215
119.368
104.671
77.318
77.000
76.682
26.372
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.142
8.124
7.834
7.814
7.736
7.716
7.709
7.691
7.558
7.537
7.525
7.521
7.509
7.504
7.500
7.483
7.291
6.970
6.953
3.496
O
N
Ph4-CF3
1.00
2.04
2.14
2.04
0.90
2.82
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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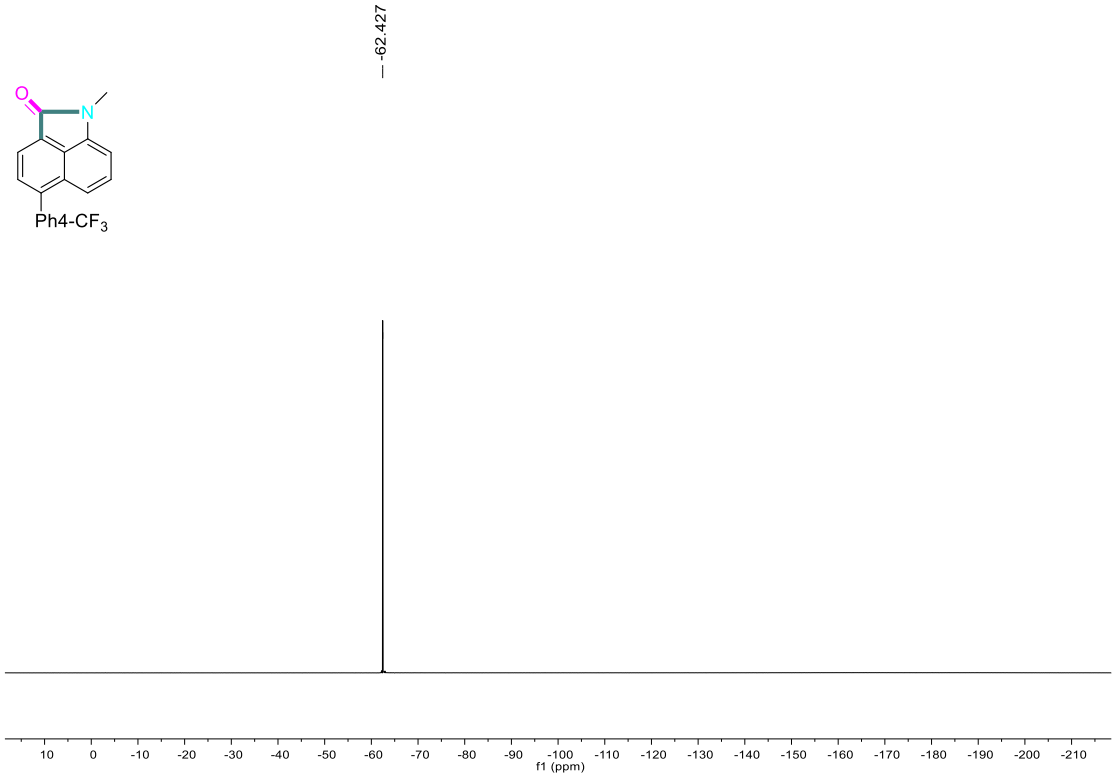
142.682
140.246
130.170
129.393
129.042
127.038
126.478
125.550
125.513
125.476
125.438
124.124
118.717
104.884
77.317
77.000
76.682
26.400
O
N
Ph4-CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.427
O
N
Ph4-CF3
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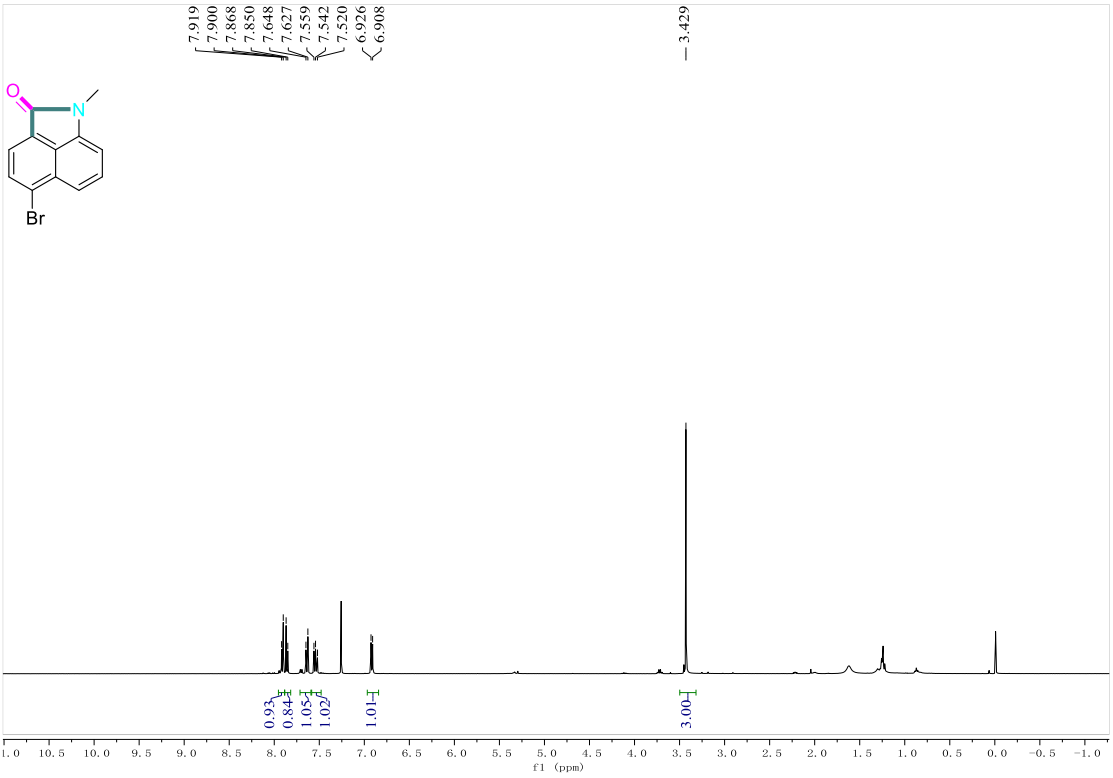
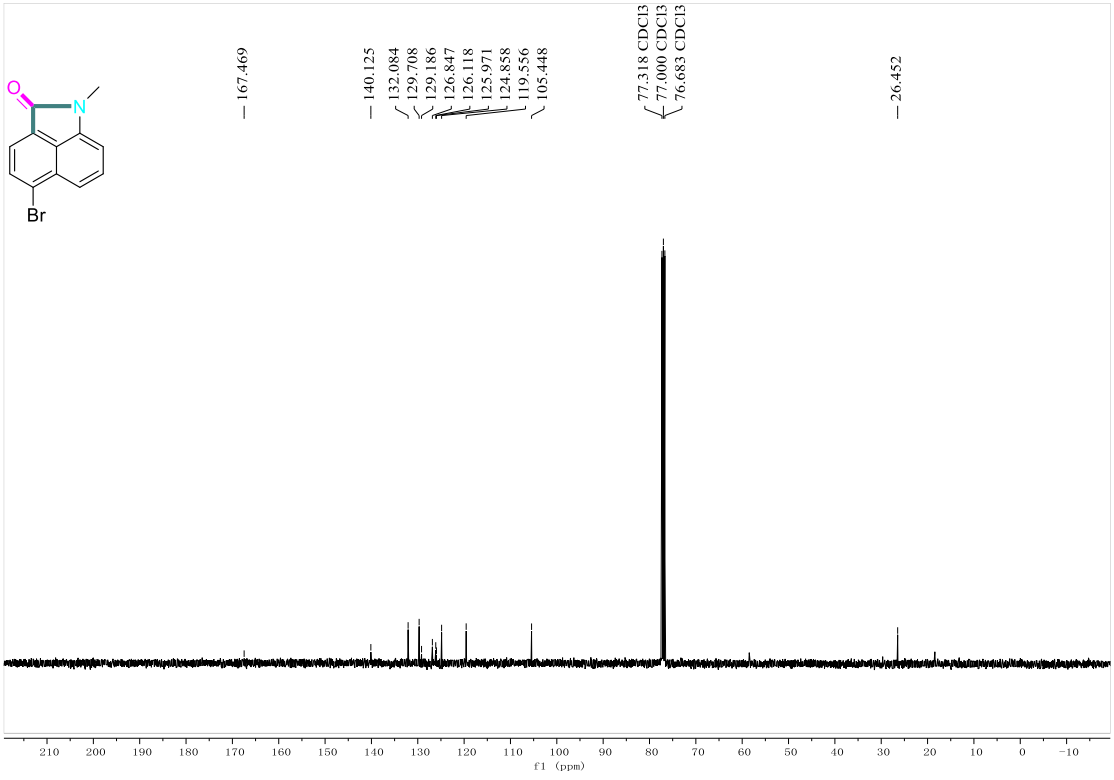
f1 (ppm)


7.919
7.900
7.868
7.850
7.648
7.627
7.559
7.542
7.520
6.926
6.908
3.429
O
N
Br
0.93
0.84
1.05
1.02
1.01
3.00
f1 (ppm)


167.469
140.125
132.084
129.708
129.186
126.847
126.118
125.971
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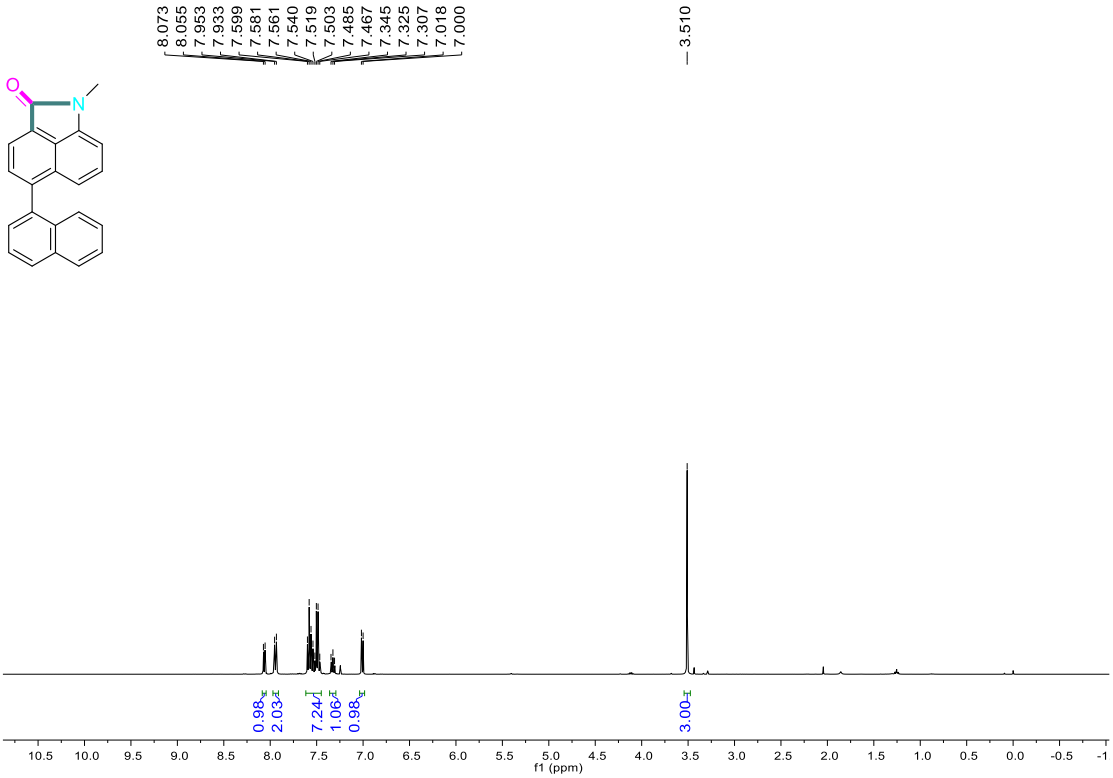
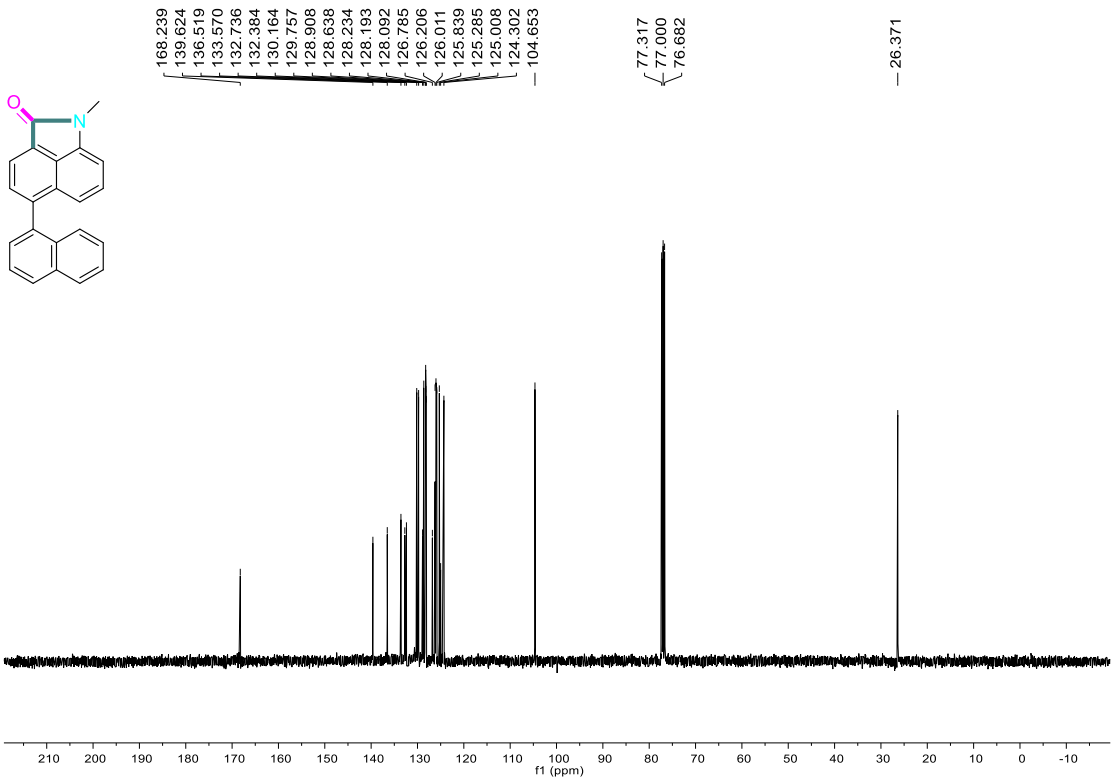
119.556
105.448
77.318 CDCl3
77.000 CDCl3
76.683 CDCl3
26.452
O
N
Br
f1 (ppm)


8.073
8.055
7.953
7.933
7.599
7.581
7.561
7.540
7.519
7.503
7.485
7.467
7.345
7.325
7.307
7.018
7.000
3.510
O
N
0.98
2.03
7.24
1.06
0.98
3.00
f1 (ppm)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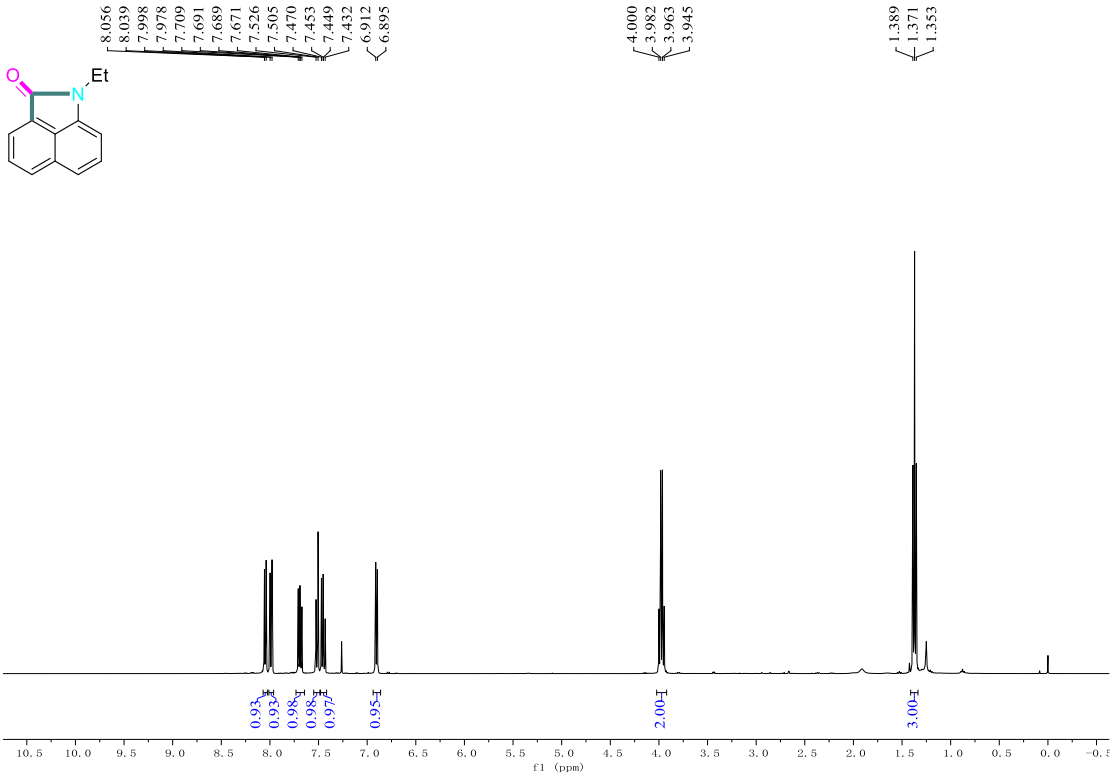
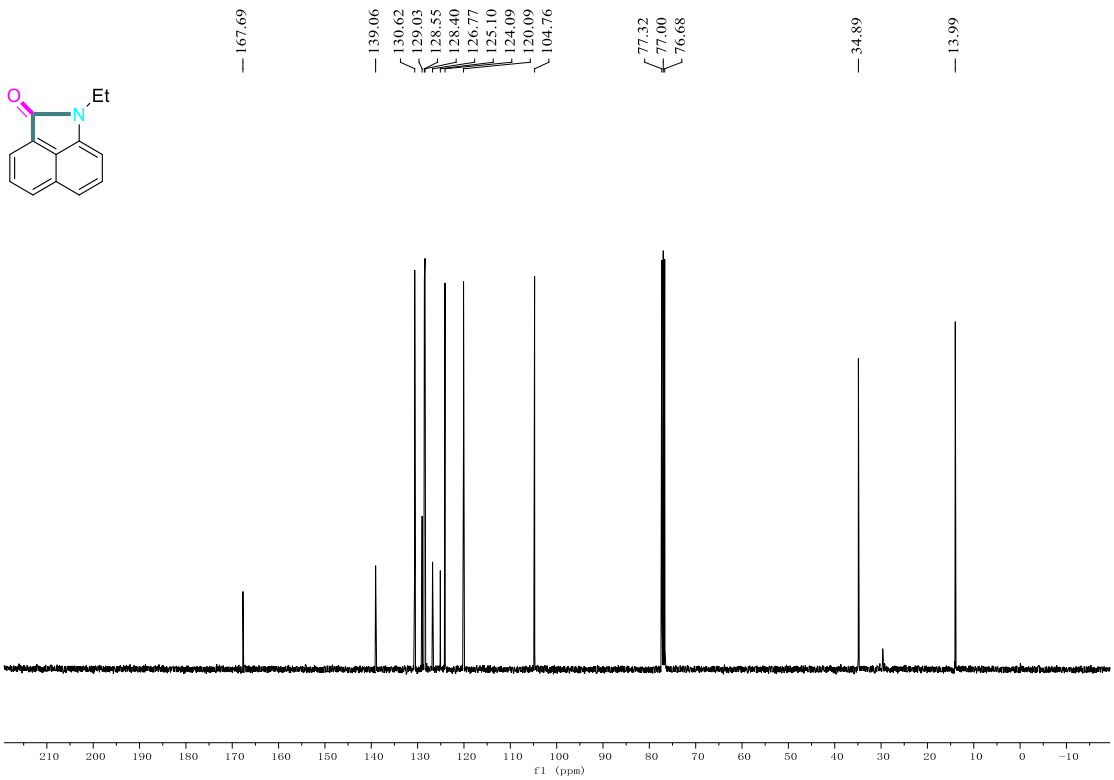
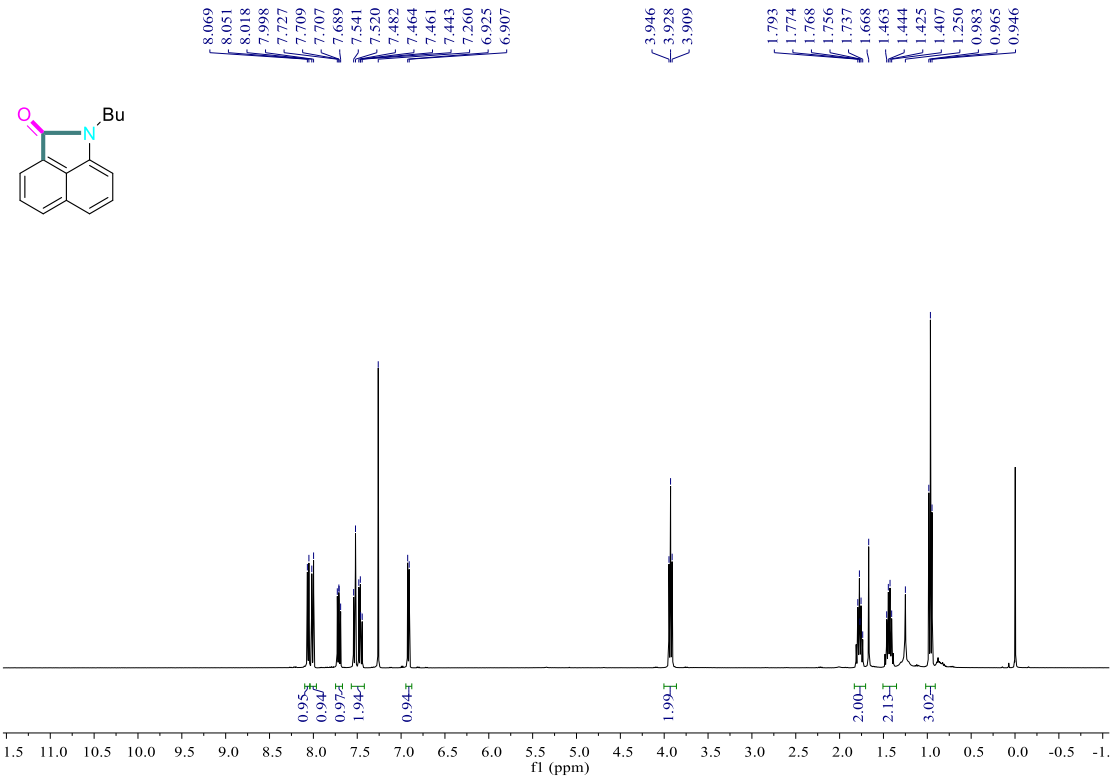
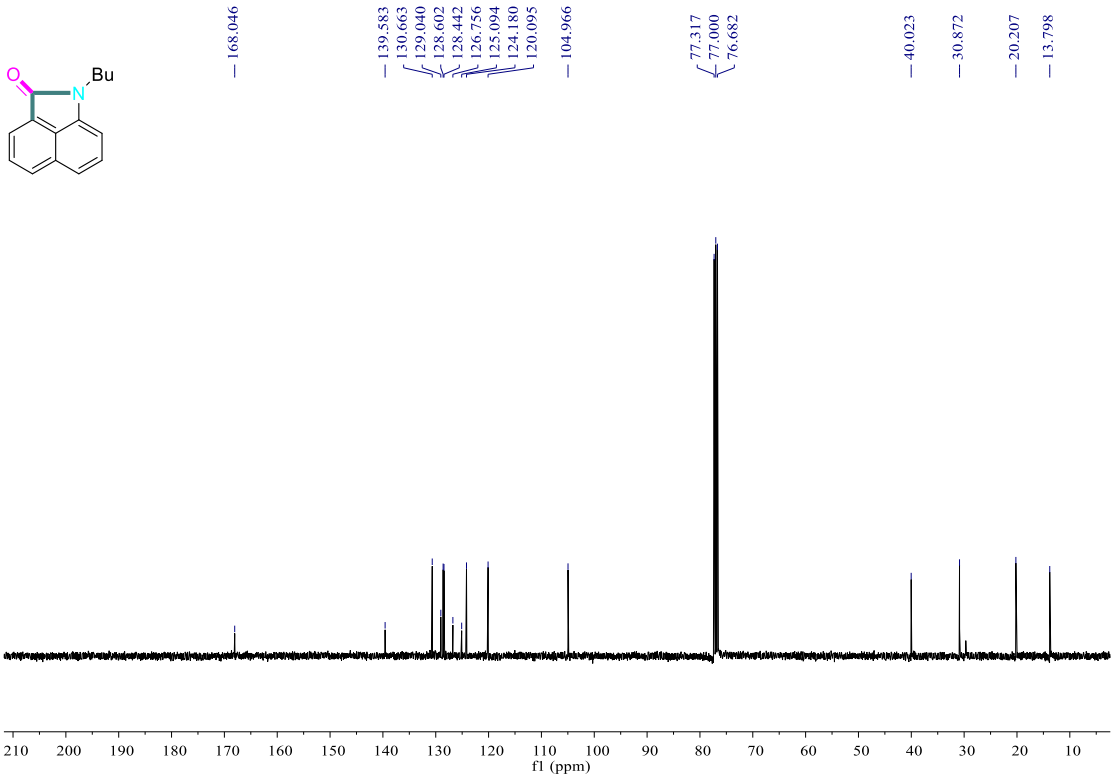
136.519
133.570
132.736
132.384
130.164
129.757
128.908
128.638
128.234
128.193
128.092
126.785
126.206
126.011
125.839
125.285
125.008
124.302
104.653
77.317
77.000
76.682
26.371
O
N
f1 (ppm)


8.056
8.039
7.998
7.978
7.709
7.691
7.689
7.671
7.526
7.505
7.470
7.453
7.449
7.432
6.912
6.895
4.000
3.982
3.963
3.945
1.389
1.371
1.353
O
N
Et
0.93
0.93
0.98
0.98
0.97
0.95
2.00
3.00
f1 (ppm)


167.69
139.06
130.62
129.03
128.55
128.40
126.77
125.10
124.09
120.09
104.76
77.32
77.00
76.68
34.89
13.99
O
N
Et
f1 (ppm)


8.069
8.051
8.018
7.998
7.727
7.709
7.707
7.689
7.541
7.520
7.482
7.464
7.461
7.443
7.260
6.925
6.907
3.946
3.928
3.909
1.793
1.774
1.768
1.756
1.737
1.668
1.463
1.444
1.425
1.407
1.250
0.983
0.965
0.946
O
N
Bu
0.95
0.94
0.97
1.94
0.94
1.99
2.00
2.13
3.02
f1 (ppm)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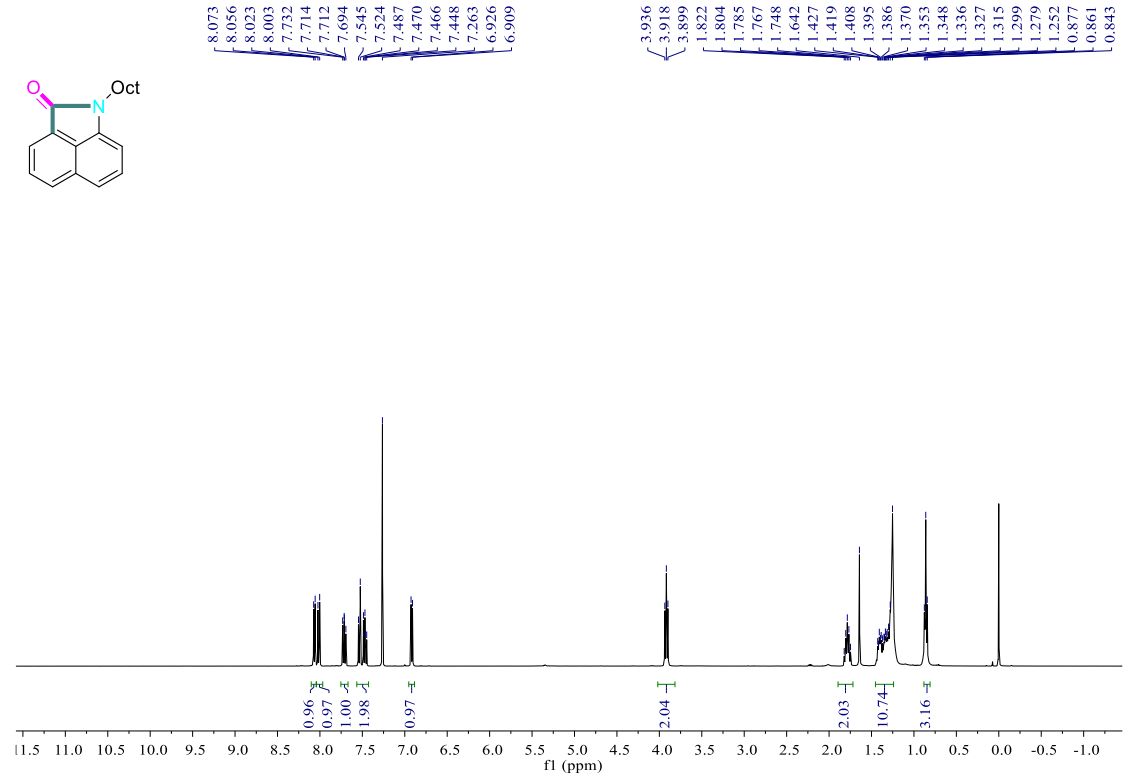
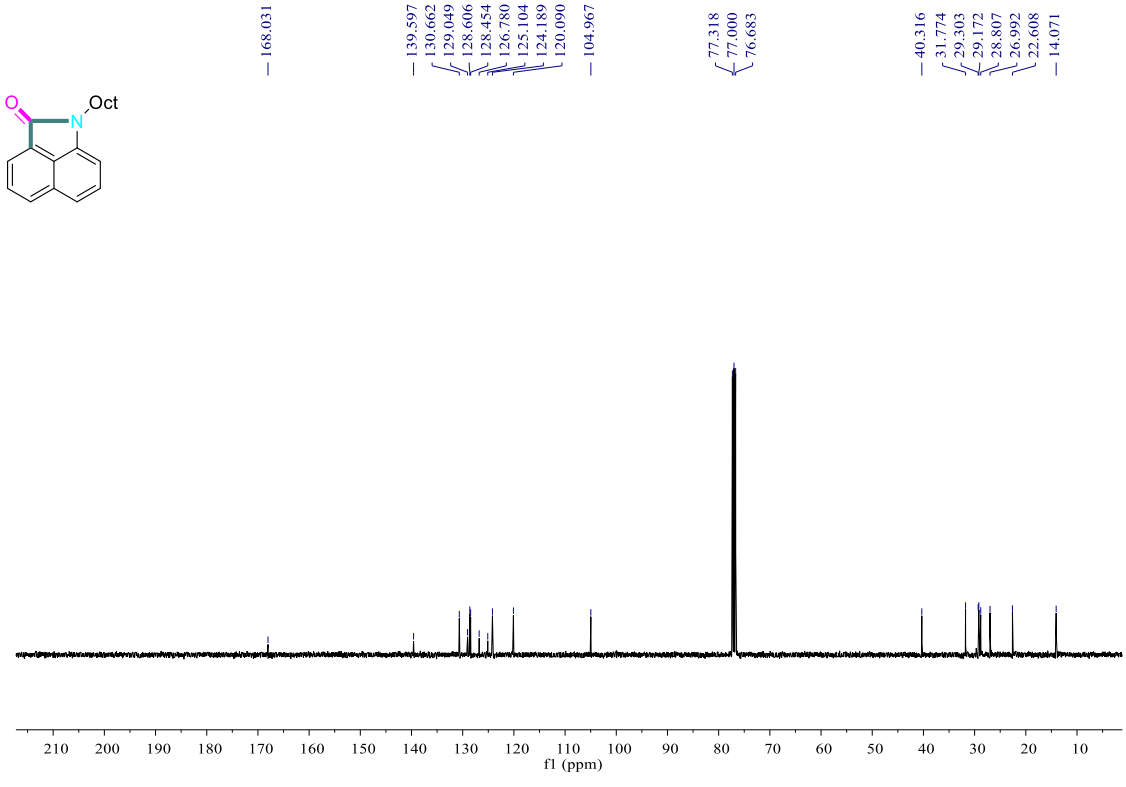
130.663
129.040
128.602
128.442
126.756
125.094
124.180
120.095
104.966
77.317
77.000
76.682
40.023
30.872
20.207
13.798
O
N
Bu
f1 (ppm)


8.073
8.056
8.023
8.003
7.732
7.714
7.712
7.694
7.545
7.524
7.487
7.470
7.466
7.448
7.263
6.926
6.909
3.936
3.918
3.899
1.822
1.804
1.785
1.767
1.748
1.642
1.427
1.419
1.408
1.395
1.386
1.370
1.353
1.348
1.336
1.327
1.315
1.299
1.279
1.252
0.877
0.861
0.843
O
N
Oct
0.96
0.97
1.00
1.98
0.97
2.04
2.03
10.74
3.16
f1 (ppm)


168.031
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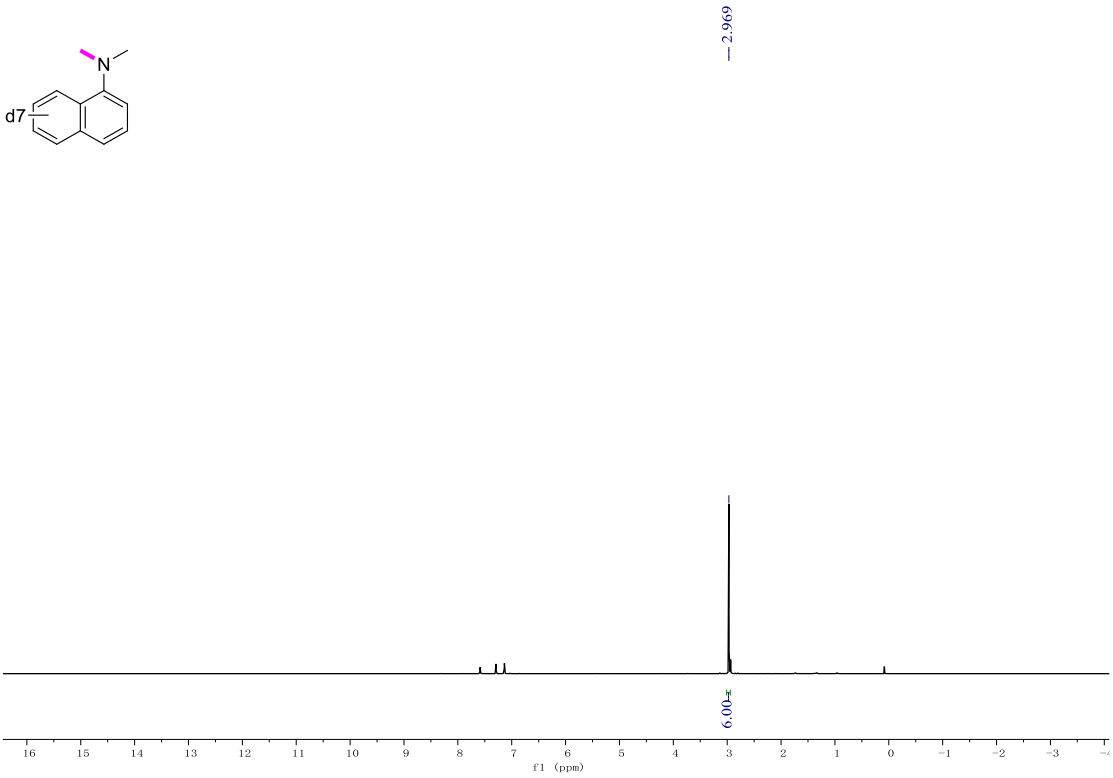
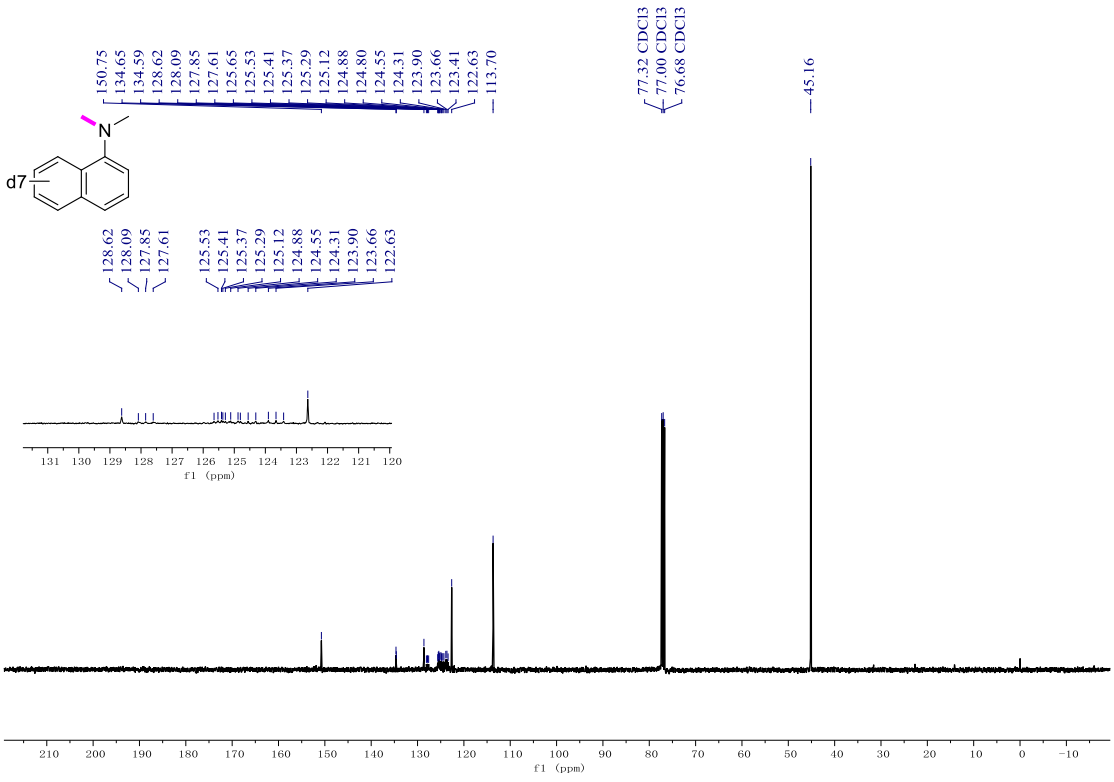
129.049
128.606
128.454
126.780
125.104
124.189
120.090
104.967
77.318
77.000
76.683
40.316
31.774
29.303
29.172
28.807
26.992
22.608
14.071
O
N
Oct
f1 (ppm)


d7
N
2.969
6.00
f1 (ppm)


150.75
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134.59
128.62
128.09
127.85
127.61
125.65
125.53
125.41
125.37
125.29
125.12
124.88
124.80
124.55
124.31
123.90
123.66
123.41
122.63
113.70
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
45.16
d7
N
f1 (ppm)

9. Computational Details

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. DFT method B3-LYP[1] with a standard 6-31G(d) basis set (SDD basis set for Pd) was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies. M11-L functional,[2] recently proposed by Truhlar group, which could give more accurate energy information, is used to calculate single point energies. Solvent effects were considered by single point calculations on the gas-phase stationary points with a SMD continuum solvation model.[3] The larger basis set 6-311+G(d) (SDD basis set for Pd) is used in the solvation single point calculations. The energies given in this work are the M11-L calculated Gibbs free energies in n,n-diMethylacetamide (DMA) solvent.

1. (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.
2. (a) Zhao, Y.; Ng, H. T.; Peverati, R.; Truhlar, D. G. *J. Chem. Theory Comput.* **2012**, *8*, 2824−2834. (b) Peverati, R.; Truhlar, D. G. *J. Phys. Chem. Lett.* **2012**, *3*, 117−124. (c) Peverati, R.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11363−11370.
3. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.

10. Absolute Calculation Energies, Enthalpies, and Free Energies

Geometry	$E_{(elec\text{-}B3LYP)}$[1]	$G_{(corr\text{-}B3LYP)}$[2]	$H_{(corr\text{-}B3LYP)}$[3]	$E_{(solv,\ M11\text{-}L)}$[4]	IF[5]
1	-949.7076287	0.192841	0.260542	-949.921136	
2-ts	-949.6872659	0.191839	0.260594	-949.896435	-276.59
3	-949.7148190	0.193452	0.263562	-949.9291438	
4-ts	-949.6721718	0.192997	0.257526	-949.8915669	-1000.47
4b-ts	-949.6720064	0.191941	0.257118	-949.8933924	-934.14
5	-949.7126389	0.196292	0.263782	-949.9333623	
5b	-949.706077	0.19457	0.26348	-949.9317052	
6-ts	-949.6893270	0.195639	0.261555	-949.906837	-301.26
6b-ts	-949.6522238	0.19284	0.260712	-949.87756	-171.58
7	-949.7214374	0.193956	0.264095	-949.942671	

8	-949.6550575	0.191513	0.262587	-949.8780452	
9-ts	-949.6639016	0.188482	0.255423	-949.8743806	-1294.31
10	-949.6885556	0.191124	0.261225	-949.9105457	
11-ts	-949.6208186	0.1933	0.26029	-949.8382375	-246.07
12-ts	-949.6297969	0.189961	0.259491	-949.870072	-353.57
13	-949.6832857	0.194355	0.261621	-949.9251033	
14-ts	-949.6691858	0.192852	0.261239	-949.9130887	-171.78

[1]The electronic energy calculated by B3LYP in gas phase. [2]The thermal correction to Gibbs free energy calculated by B3LYP in gas phase. [3]The thermal correction to enthalpy calculated by B3LYP in gas phase. [4]The electronic energy calculated by M11-L in n,n-DiMethylAcetamide (DMA) solvent. [5]The B3LYP calculated imaginary frequencies for the transition states.

11. Optimized geometries for all the compounds and transition states

1

C	2.98239900	3.02089100	-0.29888800
C	3.78701500	1.90733600	-0.39413400
C	3.30144600	0.61889600	-0.04280600
C	1.94294100	0.48003800	0.39175900
C	1.15252600	1.65203500	0.51565500
C	1.65765000	2.89142800	0.17565200
H	5.17503800	-0.40507100	-0.41743500
H	3.36843200	4.00004200	-0.56904900
H	4.81604600	1.99811400	-0.73398700
C	4.14408400	-0.52459800	-0.09432400
C	1.43478200	-0.83994400	0.71104500
H	0.14759000	1.56881300	0.91490500
H	1.03627200	3.77574500	0.28885300
C	2.31611700	-1.92163900	0.66430400
C	3.66158500	-1.75986900	0.27559100
H	1.96670600	-2.91628100	0.91666900
H	4.31244600	-2.62994900	0.25151900
N	0.09827900	-0.95363000	1.09809600
C	-0.30361800	-2.21876600	1.71025700
H	-1.34650100	-2.14100000	2.02891200

H	-0.20129400	-3.10086800	1.05794800
H	0.30768000	-2.38968600	2.60711500
Pd	-1.33876500	-0.40364900	-0.24409100
O	-2.68559300	0.52262100	1.16896300
O	-3.16132900	0.51649100	-0.97660900
C	-3.47367600	0.84575900	0.21683000
C	-4.74492700	1.59959300	0.49278300
H	-5.39283400	0.99828300	1.13979500
H	-4.51368300	2.52478900	1.03071200
H	-5.26529100	1.82917100	-0.43869400
C	-0.54100900	-1.20489400	-1.75439000
O	-0.08048700	-1.68241700	-2.68632300

2-ts

C	2.72038900	3.25444500	-0.13499200
C	3.59719200	2.24375000	-0.45699200
C	3.24132000	0.87893100	-0.28083400
C	1.93300400	0.55693500	0.21765800
C	1.06454200	1.62610700	0.56914700
C	1.44778100	2.93938300	0.39554500
H	5.15204900	0.09787400	-0.93433600
H	3.00810300	4.29322300	-0.27266900
H	4.58624200	2.47451700	-0.84585200
C	4.16317700	-0.16290900	-0.56554500
C	1.57665000	-0.82952300	0.36704900
H	0.09523900	1.40759800	1.00043800
H	0.76766100	3.73810600	0.67864000
C	2.51779800	-1.81045600	0.08485800
C	3.81264700	-1.47848600	-0.36747200
H	2.24937000	-2.85629400	0.19389300
H	4.52202200	-2.27411200	-0.57815100
N	0.27831800	-1.19443700	0.81421600
C	0.17181800	-2.16975200	1.90297400
H	-0.86757200	-2.23168400	2.23513300
H	0.50351000	-3.18054100	1.62055200
H	0.77949800	-1.82961200	2.75013700
Pd	-1.46932100	-0.50185500	-0.07532200
O	-2.44843600	1.24827400	0.77798100
O	-3.25235300	0.16347400	-0.95130500
C	-3.34551900	1.13406100	-0.11679400
C	-4.47335500	2.12003400	-0.23024000
H	-5.36317600	1.63579600	-0.63940900
H	-4.68843300	2.56208900	0.74520800
H	-4.17554700	2.92269700	-0.91546300

C	-0.62826900	-2.04496900	-0.72240700
O	-0.26464400	-3.01906900	-1.23224600

3

C	4.10148100	1.35632600	1.80332300
C	3.96712700	1.75709700	0.49339000
C	3.07683400	1.08703700	-0.38811300
C	2.31991300	-0.02603800	0.10712300
C	2.47188400	-0.40911600	1.46694100
C	3.34260900	0.26644700	2.29369000
H	3.48735800	2.34579700	-2.09967300
H	4.78422900	1.87905800	2.46719900
H	4.53909600	2.59979100	0.11289300
C	2.91153100	1.49739200	-1.73846200
C	1.43704400	-0.68840200	-0.79759500
H	1.88097300	-1.23284800	1.85484900
H	3.44444800	-0.03508200	3.33245100
C	1.29805000	-0.26575200	-2.10086800
C	2.03736100	0.84295800	-2.57499000
H	0.61228800	-0.78963400	-2.76016800
H	1.91056100	1.16832400	-3.60310600
N	0.70634100	-1.84817100	-0.34968200
C	1.38091000	-3.15759400	-0.38239900
H	0.75164100	-3.88858000	0.12670700
H	1.54557100	-3.47275800	-1.41832800
H	2.34635800	-3.08144300	0.12464800
Pd	-2.00711900	-0.51786900	0.19286200
O	-1.76562600	1.52360700	-0.17147400
O	-3.75004900	0.83510000	0.48399100
C	-2.98917600	1.78179900	0.13586500
C	-3.46808600	3.20911600	0.06890000
H	-2.86840100	3.83060300	0.74221800
H	-3.32984100	3.59742800	-0.94559000
H	-4.52128500	3.26947800	0.34880500
C	-0.58160000	-1.75465500	-0.02172700
O	-1.36372300	-2.66003800	0.32532500

4-ts

C	4.20980700	0.60759500	0.70190800
C	3.65903200	1.78954400	0.27807300
C	2.28702700	1.83992900	-0.07685200
C	1.43956000	0.68133600	0.04579700
C	2.08576600	-0.56822800	0.36490700
C	3.43352100	-0.56632400	0.71263800

H	2.42148000	3.90401500	-0.68467000
H	5.25586800	0.55086100	0.98807700
H	4.25579200	2.69420200	0.20208500
C	1.75086000	3.05395000	-0.58499300
C	0.02515300	0.86104900	-0.18419500
H	3.93080300	-1.49262600	0.96502200
C	-0.42640500	2.07261000	-0.72896000
C	0.43008400	3.16255000	-0.95398800
H	-1.49133800	2.18861200	-0.90312300
H	0.03990600	4.09048700	-1.36163400
N	1.43363000	-1.82958900	0.27459800
C	2.14358000	-3.04570600	0.69971400
H	1.44137000	-3.87426700	0.63116900
H	3.00316500	-3.25201700	0.05252000
H	2.48319300	-2.93536400	1.73303100
C	0.23721500	-2.01979600	-0.35304500
O	-0.25895900	-3.11673100	-0.61796700
Pd	-1.18433700	-0.78342000	-0.59476400
O	-3.10565500	0.18167300	-0.29157600
O	-2.09205100	0.94766500	1.57100100
C	-3.12146500	0.73633300	0.85895300
C	-4.47288800	1.14950600	1.41080100
H	-4.97332200	0.26199300	1.81596900
H	-4.35927000	1.88321800	2.21091900
H	-5.10235800	1.54579400	0.60966000
H	-0.89297400	0.65260800	0.74172400

4b-ts

C	-0.18237300	-1.56711800	-0.97250000
C	-1.45052700	-2.02587400	-1.17060100
C	-2.55657700	-1.36748700	-0.54812500
C	-2.37112300	-0.13531000	0.17293400
C	-1.04864800	0.44985600	0.13776700
C	0.06955400	-0.37659600	-0.20222200
H	-3.98015800	-2.85998100	-1.17081700
H	0.67481000	-2.13641700	-1.31875800
H	-1.63370900	-2.94089400	-1.72679600
C	-3.85052900	-1.93908900	-0.60840600
C	-3.49133300	0.40614100	0.86208700
C	-4.73162400	-0.19847200	0.81008200
C	-4.92057400	-1.36896900	0.04897700
H	-5.56095800	0.22895700	1.36588900
H	-5.90228300	-1.83154800	-0.00210600
N	-0.76711300	1.78672800	0.30586000

C	-1.69488400	2.85030400	0.69429100
H	-1.19104100	3.79277500	0.48164800
H	-2.61532500	2.78764600	0.10904700
H	-1.93027100	2.80951800	1.76240600
C	0.54874900	2.17586700	-0.11339000
O	0.87854500	3.34547200	-0.15598700
Pd	1.77939000	0.72190200	-0.45300900
O	3.21100100	-0.87001400	-0.26853900
C	2.94195800	-1.64350600	0.71011100
C	4.02717100	-2.61249300	1.14084900
H	4.76734200	-2.06812600	1.73919500
H	3.61122100	-3.41959400	1.74638100
H	4.54229200	-3.01348600	0.26397900
O	1.84949300	-1.65158400	1.35862900
H	0.86234800	-0.81755600	0.71656800
H	-3.37414800	1.27958000	1.48678800

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C	4.30181600	0.82665600	-0.63763400
C	3.64774000	1.99538000	-0.34732600
C	2.27432400	1.97122800	0.00895300
C	1.54404800	0.72655500	0.05897500
C	2.28093800	-0.48785800	-0.21418400
C	3.62350600	-0.40651600	-0.56312200
H	2.18986300	4.11009600	0.28726000
H	5.35191300	0.83219300	-0.91641000
H	4.16355400	2.95141900	-0.38222800
C	1.61517200	3.18799900	0.32672400
C	0.15481200	0.77981600	0.38343700
H	4.18777900	-1.30238700	-0.78195100
C	-0.44052500	1.99321700	0.70335700
C	0.28895400	3.20265300	0.68347100
H	-1.49058600	2.02277400	0.98257800
H	-0.20563300	4.13624600	0.94030700
N	1.70116500	-1.78094500	-0.11688900
C	2.54797600	-2.96553500	-0.31222300
H	1.92616000	-3.84117000	-0.13790300
H	2.94176700	-2.99856200	-1.33348600
H	3.38184700	-2.95976600	0.39640800
C	0.38619600	-2.01829800	0.15648200
O	-0.11667000	-3.14336000	0.23895600
Pd	-1.05544000	-0.79233800	0.42505600
O	-3.16655800	0.03465400	0.47255400
C	-3.61094600	0.51456400	-0.57338700

C	-5.02397200	0.99883200	-0.72612800
H	-5.56880000	0.85314800	0.20648500
H	-5.02215100	2.05890700	-1.00030400
H	-5.51472700	0.45238100	-1.53816300
O	-2.87656000	0.65334600	-1.67135500
H	-1.96084300	0.32961100	-1.46255800

5b

C	-0.18300100	-1.64694000	-0.68008900
C	-1.40008100	-2.29716500	-0.68268400
C	-2.57819500	-1.61287300	-0.30127700
C	-2.52895300	-0.21508100	0.06255800
C	-1.25889400	0.44523200	-0.03313700
C	-0.10729500	-0.28241900	-0.34382100
H	-3.83414000	-3.35169900	-0.54303100
H	0.71922000	-2.18692200	-0.95732400
H	-1.46645500	-3.34661000	-0.95891500
C	-3.82103100	-2.30440300	-0.25018500
C	-3.74489500	0.37878900	0.51982100
C	-4.92385800	-0.32985400	0.57186700
C	-4.97277500	-1.68490400	0.16869300
H	-5.82461100	0.15876800	0.93368100
H	-5.91127800	-2.23112200	0.20563400
N	-1.01586500	1.83112400	0.16981200
C	-2.00103000	2.90968100	0.23932400
H	-1.46662100	3.84153600	0.05290300
H	-2.77213700	2.77605400	-0.52399200
H	-2.46917000	2.97319300	1.22744500
C	0.31743700	2.17619300	0.04382000
O	0.76393600	3.30967100	0.12090100
Pd	1.59985100	0.75852300	-0.30991300
O	3.42220800	-0.54892500	-0.46244900
C	3.61277100	-1.38434200	0.42580700
C	4.82018700	-2.27500600	0.47551900
H	5.35927800	-2.11224500	1.41454800
H	4.50533600	-3.32353300	0.45750300
H	5.47158800	-2.06389200	-0.37231600
H	-3.75445800	1.40268600	0.86162200
O	2.76160400	-1.57940000	1.42566800
H	1.99703600	-0.95832200	1.29927900

6-ts

C	-4.12723000	1.39036500	-0.93165200
C	-4.32560300	0.04920400	-0.68224100

C	-3.26028800	-0.74011100	-0.15844700
C	-2.00421300	-0.11552600	0.02994100
C	-1.84394700	1.28173200	-0.16322600
C	-2.89131800	2.03604500	-0.65001800
H	-4.31398200	-2.61583500	0.12861900
H	-4.94468900	1.99034100	-1.32223100
H	-5.29625700	-0.40744600	-0.85696600
C	-3.36724100	-2.09568400	0.25379600
C	-0.87383300	-0.79653000	0.53486600
H	-2.80024300	3.10770900	-0.79383200
C	-1.04252500	-2.09404500	1.01348700
C	-2.29617200	-2.73807400	0.85037300
H	-0.22222600	-2.63332300	1.47872000
H	-2.40939800	-3.76381800	1.19239700
N	-0.61459500	1.75418600	0.31596400
C	-0.42933600	3.16449500	0.63416100
H	0.54079500	3.27639200	1.11681300
H	-0.45575300	3.76650600	-0.28050700
H	-1.21259900	3.51842000	1.31604800
C	0.27207700	0.79499600	0.82117700
O	1.11456500	1.09136700	1.68496700
Pd	0.95750400	-0.62520600	-0.42631000
O	3.05157900	-0.45492400	-1.03737900
C	3.91687200	-0.01315700	-0.26947000
C	5.37764700	-0.02721000	-0.63551200
H	5.51433200	-0.49716900	-1.60953700
H	5.76140900	0.99821600	-0.65735600
H	5.94433800	-0.57005000	0.12791200
O	3.68532000	0.50862400	0.91763100
H	2.71018100	0.57071900	1.15327200

6b-ts

C	1.08150500	-1.65532800	1.14474400
C	2.43193400	-1.89819000	0.95196500
C	3.28231200	-0.95404900	0.30785000
C	2.76965100	0.31633600	-0.15748800
C	1.39009100	0.50364900	0.03445700
C	0.56004400	-0.44559300	0.63579300
H	5.07010300	-2.16283200	0.46507700
H	0.45422900	-2.36855700	1.66952800
H	2.87303100	-2.82523600	1.30887700
C	4.66859300	-1.21194000	0.12349100
C	3.64876100	1.25498400	-0.76669100
C	4.98192300	0.95795200	-0.92536500

C	5.49380900	-0.28610300	-0.47421500
H	5.64755500	1.67326500	-1.39985600
H	6.54954600	-0.50777800	-0.60522500
N	0.47072500	1.58442400	-0.10044700
C	0.78805300	2.95069300	0.30208400
H	-0.15559100	3.46818800	0.48726700
H	1.39539400	2.99382800	1.21963600
H	1.31753200	3.46949500	-0.50198500
C	-0.51741500	0.82632400	0.69737500
O	-1.29937700	1.33338000	1.50213000
Pd	-1.33946500	-0.69327600	-0.40226300
O	-3.46402700	-0.59980900	-0.90609100
C	-4.28199300	0.01393700	-0.21085600
C	-5.75276700	0.01606000	-0.53180300
H	-6.32411500	-0.31565800	0.34089200
H	-6.07504700	1.03688600	-0.76369000
H	-5.94920100	-0.63686100	-1.38228400
H	3.25069600	2.20082800	-1.12052800
O	-3.98578100	0.72595400	0.86053000
H	-3.00735200	0.76554700	1.04889400

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C	1.84920200	-2.87932900	0.04623600
C	3.22939400	-2.70860300	0.09116500
C	3.80090700	-1.40555700	0.09277800
C	2.87286000	-0.35827000	0.04751100
C	1.48024000	-0.51566500	0.00113800
C	0.94126200	-1.78854600	-0.00111800
H	5.95553300	-1.77214800	0.16928900
H	1.44654100	-3.88832900	0.04585800
H	3.87665100	-3.58166400	0.12468500
C	5.17486800	-1.01744300	0.13325500
C	3.21227300	1.01097400	0.04086100
H	-0.13508700	-1.94506700	-0.03816900
C	4.53869000	1.37676700	0.07988400
C	5.50688000	0.32560600	0.12589600
H	4.86199900	2.41303500	0.07662700
H	6.55589500	0.60716500	0.15660500
C	0.91964900	0.85567900	-0.03407100
N	2.00801100	1.73108500	-0.00933000
O	-0.25514500	1.25331700	-0.07251900
C	1.88237200	3.17507900	-0.03569500
H	0.82012200	3.41661800	-0.09275800
H	2.30526600	3.61878300	0.87296000

H	2.39546400	3.59171500	-0.90989800
Pd	-2.03358100	0.16026700	-0.23771500
O	-3.90197700	-0.83517500	-0.36916700
C	-4.85171000	-0.28246300	0.19814000
C	-6.24326400	-0.84526000	0.19860200
H	-6.26508100	-1.78457000	-0.35449600
H	-6.57651300	-1.00918700	1.22871600
H	-6.93278200	-0.12707500	-0.25744600
O	-4.71399300	0.85879100	0.85570100
H	-3.73215500	1.09755500	0.75860700

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C	2.83879600	-2.29741400	-0.37372700
C	4.16335600	-1.87690700	-0.38012300
C	4.53142000	-0.50939900	-0.21430400
C	3.53344700	0.52857900	-0.03557100
C	2.22195500	0.04517500	-0.03670600
C	1.88961900	-1.29220100	-0.18120400
H	6.66132900	-0.86827600	-0.35540000
H	2.57337900	-3.34271000	-0.49313200
H	4.95952200	-2.60424700	-0.51250500
C	5.89624500	-0.10707600	-0.22436800
C	3.93215400	1.88608700	0.11394400
C	5.26503900	2.22009700	0.09390700
C	6.25266700	1.21381200	-0.07468800
H	5.56914000	3.25682300	0.20574700
H	7.30216800	1.49480100	-0.08657500
N	0.84896800	0.50738300	-0.00186800
C	0.27041600	1.52157700	0.86836200
H	-0.81597000	1.36834400	0.87217900
H	0.64787100	1.44894000	1.89928400
H	0.48379000	2.51935900	0.47367200
C	0.45895500	-0.86994700	-0.03813400
O	-0.62952600	-1.40815000	0.05983900
Pd	-2.55628300	-0.62454000	0.33628600
O	-4.54511800	0.09862900	0.52066400
C	-4.96467400	0.79703800	-0.40909000
C	-6.35198300	1.36895100	-0.44040500
H	-6.30233800	2.45932100	-0.52717600
H	-6.88547000	0.99502800	-1.32065000
H	-6.88964900	1.08993800	0.46602200
H	3.17117700	2.65064700	0.24026300
O	-4.21589800	1.09721100	-1.46003900
H	-3.32882500	0.63746000	-1.28885200

9-ts

C	-4.21061800	0.86796900	0.46599500
C	-4.19201300	-0.45978800	0.09347500
C	-2.94453900	-1.10181200	-0.13048700
C	-1.73595200	-0.38074400	0.10497800
C	-1.77792600	1.01678900	0.41288600
C	-3.02572000	1.62227800	0.59947800
H	-3.75455600	-2.97201600	-0.85456400
H	-5.16284800	1.36899800	0.62321000
H	-5.11448200	-1.00746800	-0.07778200
C	-2.84032400	-2.41269200	-0.66826700
C	-0.46125300	-1.00318400	-0.10333700
H	-3.09950200	2.67951600	0.82531900
C	-0.42536200	-2.26126100	-0.71003800
C	-1.61611000	-2.96222000	-0.99290400
H	0.52785600	-2.75188600	-0.88329100
H	-1.56242100	-3.95485500	-1.43183900
N	-0.55858300	1.65983500	0.47855300
C	-0.57385200	3.10886100	0.57195800
H	0.44452700	3.49180100	0.65853500
H	-1.06487600	3.59734600	-0.28673400
H	-1.10747800	3.42055200	1.48164800
Pd	0.99344800	0.57096300	-0.21748000
C	2.15832500	2.05093700	-0.71056700
O	2.84136900	2.88442600	-1.08934400
O	2.61309200	-0.79143700	-0.34606600
O	1.60393700	-1.73525300	1.42892900
C	2.59288500	-1.59760800	0.64451200
C	3.83411600	-2.42223400	0.90195000
H	4.45855200	-2.47182400	0.00843400
H	4.40796800	-1.94679400	1.70601600
H	3.55639500	-3.42396300	1.23806700
H	0.52521600	-1.16616900	0.82124800

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C	-4.34458400	0.61852500	0.41984300
C	-4.21500500	-0.73696600	0.19050700
C	-2.92337200	-1.28260900	-0.05040600
C	-1.80281300	-0.40841500	-0.00801600
C	-1.94848300	0.98838800	0.24212500
C	-3.23602800	1.49733900	0.43285200
H	-3.51619600	-3.33511400	-0.42369600
H	-5.33436700	1.03905700	0.58404300

H	-5.08760900	-1.38383100	0.15787400
C	-2.67857600	-2.64207000	-0.38597500
C	-0.48864500	-0.86623700	-0.28711500
H	-3.40281100	2.55650400	0.59520800
C	-0.29599900	-2.19182500	-0.64449200
C	-1.40476200	-3.07813200	-0.68839100
H	0.68718600	-2.57515200	-0.90574300
H	-1.23946400	-4.11707000	-0.96462100
N	-0.76756900	1.69783800	0.27169000
C	-0.84764400	3.14601400	0.30088200
H	0.15096400	3.58197200	0.36910900
H	-1.34785600	3.56906700	-0.58674500
H	-1.40379500	3.48395400	1.18883500
Pd	0.87681300	0.63228300	-0.22351600
C	2.16579200	2.18301600	-0.33958800
O	2.92033500	3.03116700	-0.46847500
O	2.59418700	-0.70611500	-0.42732100
C	2.87790300	-1.51068900	0.46976100
C	4.15499100	-2.29864800	0.46900200
H	4.79936500	-1.96484400	-0.34409500
H	4.66297900	-2.18287300	1.43137800
H	3.92343900	-3.36245600	0.34708400
O	2.09061300	-1.76197100	1.50088800
H	1.23005200	-1.28991500	1.36461300

11-ts

C	-1.59384300	3.32853900	0.42786800
C	-2.75587800	2.75918700	-0.03489000
C	-2.83730700	1.35343100	-0.22782200
C	-1.68598100	0.54697600	0.07704100
C	-0.44946500	1.14352800	0.53431500
C	-0.45739300	2.52215100	0.69995400
H	-4.87521700	1.38180400	-0.95415800
H	-1.53879500	4.40451300	0.58068300
H	-3.62666000	3.36993800	-0.26208100
C	-4.02359900	0.74652400	-0.72099000
C	-1.83323400	-0.86781900	-0.10831500
H	0.43759500	3.02730700	1.06241900
C	-2.99133900	-1.43301800	-0.60122500
C	-4.09891500	-0.61334800	-0.91438200
H	-3.05912900	-2.50688200	-0.74578500
H	-5.00557700	-1.06782200	-1.30348500
N	-0.74607300	-1.76191800	0.30167900
C	-1.08388900	-2.86889000	1.21974900

H	-0.16224500	-3.32119200	1.59000400
H	-1.64985600	-2.46592100	2.06194200
H	-1.67798300	-3.63533000	0.70794000
Pd	1.00844200	-0.47013500	0.52152800
C	0.41929600	-1.95456500	-0.51094100
O	0.68376000	-2.58909100	-1.48871200
O	3.13967200	-0.28611000	0.08108000
C	3.50560500	0.77466800	-0.44613800
C	4.93554200	1.02631200	-0.82897000
H	5.55686300	0.18526600	-0.52138300
H	5.00280600	1.16172100	-1.91376000
H	5.28726100	1.95100100	-0.36067100
O	2.68680100	1.77194000	-0.72064400
H	1.76564600	1.51925900	-0.40901400

12-ts

C	-2.85244500	-2.34504200	-1.15035800
C	-3.70095200	-1.26967800	-0.99838800
C	-3.26393800	-0.03333900	-0.44188800
C	-1.89320400	0.08777800	-0.03010700
C	-1.08664000	-1.10703400	-0.03490100
C	-1.54183600	-2.28424200	-0.63613500
H	-5.16003300	0.99073800	-0.66779500
H	-3.20761300	-3.26750200	-1.60125200
H	-4.73274700	-1.34153500	-1.33494700
C	-4.12286600	1.08850600	-0.36037900
C	-1.33362100	1.39971000	0.24459400
H	-0.93459800	-3.18293800	-0.59986100
C	-2.25023000	2.46986700	0.35736400
C	-3.61172600	2.29931800	0.07331200
H	-1.88944700	3.45847600	0.61645900
H	-4.27079500	3.16156500	0.15087600
N	0.02054100	1.51573700	0.33857100
C	0.55919300	2.80908900	0.70275100
H	0.31130400	3.59317600	-0.03531500
H	0.19319100	3.16377300	1.68147900
H	1.65024700	2.74388800	0.76527100
Pd	0.92024900	-0.41844600	0.16589000
C	-0.00806300	-1.63331700	1.22284200
O	-0.17711500	-2.13722300	2.26793600
O	3.16821900	-0.42911600	0.20313400
C	3.92871200	0.17272200	-0.55197200
C	3.51326300	0.96904700	-1.75325000
H	2.53732600	1.42691400	-1.56845100

H	4.25930300	1.72592400	-2.00245500
H	3.41056300	0.28807900	-2.60714300
O	5.25027500	0.13604700	-0.35718900
H	5.41312500	-0.42017100	0.43027200

13

C	1.66125100	1.24414500	-0.00035900
C	2.57816700	2.31686000	-0.00008500
C	2.21246900	-0.10501300	-0.00003800
C	1.43173100	-1.30586000	-0.00053400
C	2.04181000	-2.56320600	-0.00019400
H	1.40372400	-3.43989400	-0.00061200
C	3.43524600	-2.69614600	0.00066500
C	4.21397300	-1.56008900	0.00111100
C	3.64622700	-0.26010600	0.00073900
C	4.51092600	0.86504000	0.00109700
C	3.96714300	2.12791400	0.00063200
H	4.61355500	3.00285300	0.00085000
H	5.58545900	0.70709900	0.00167100
H	3.88918500	-3.68322700	0.00094700
H	5.29878600	-1.64014400	0.00174600
H	2.20319300	3.33226200	-0.00039500
N	0.32299700	1.46926500	-0.00096800
C	-0.15442200	2.84015900	-0.00133400
H	0.17444100	3.40025700	0.88997500
H	0.17520900	3.39999900	-0.89251500
H	-1.25154900	2.84820300	-0.00182400
C	-0.04753100	-1.38413400	-0.00138900
O	-0.69658600	-2.40569100	-0.00260700
Pd	-1.18849300	0.18495500	-0.00025400
O	-3.18756500	-0.78867300	0.00110500
C	-4.24185000	-0.17751100	0.00123500
C	-5.59133200	-0.84844400	0.00216500
H	-6.16462500	-0.55446000	0.88960900
H	-6.16529400	-0.55566000	-0.88524600
H	-5.45589700	-1.92986600	0.00283900
O	-4.21213200	1.17085800	0.00012600
H	-5.10908300	1.54617600	0.00017600

14-ts

C	-1.71840700	-1.15658500	-0.05599800
C	-2.57377900	-2.03968300	-0.70204800
C	-2.05835700	0.23510400	-0.06936500
C	-1.26115400	1.07714900	0.73490700

C	-1.53552600	2.43074900	0.81994900
H	-0.93246900	3.07562400	1.45245400
C	-2.61789700	2.95579700	0.07560100
C	-3.41940500	2.13507000	-0.69867800
C	-3.17566100	0.73696400	-0.77871400
C	-3.99892000	-0.19667800	-1.47278800
C	-3.70110200	-1.54206700	-1.40740200
H	-4.34350500	-2.25529000	-1.91880900
H	-4.86810400	0.15548000	-2.02179900
H	-2.83207200	4.01987200	0.13105700
H	-4.26158300	2.55574100	-1.24355600
H	-2.37443600	-3.10713000	-0.69302000
N	-0.57910800	-1.44531800	0.67264300
C	-0.43858800	-2.73314900	1.32638200
H	-1.39740000	-3.05743000	1.75830900
H	-0.08453800	-3.52310200	0.64528100
H	0.28927400	-2.64008400	2.13879900
C	-0.14909100	0.40533100	1.46311500
O	0.22385200	0.56230000	2.59849700
Pd	1.14040700	-0.41048300	0.13546500
O	2.87691900	0.82292700	-0.26279100
C	3.91913900	0.47364700	-0.79303300
C	5.08873500	1.40274900	-0.99934000
H	5.97552100	1.02086300	-0.47944300
H	5.32953700	1.48465000	-2.06602600
H	4.84120500	2.38981600	-0.60915200
O	4.04608000	-0.79518300	-1.21929300
H	4.91887700	-0.94633000	-1.62079000

12. References

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