Supporting Information

Palladium-Catalyzed C-H Dimethylamination of 1-Chloromethyl naphthalenes with *N*,*N*-Dimethylformamide as Dimethyl Amino Source

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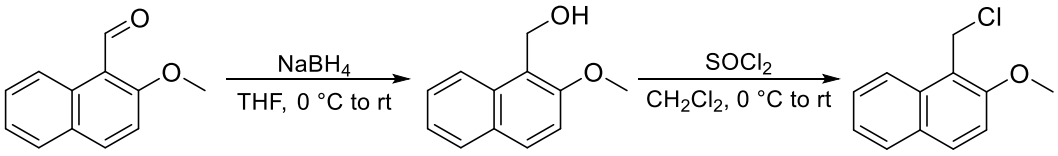
1. General Information

Unless otherwise noted, all reactions were carried out in oven-dried 25-mL Schlenk tubes under a nitrogen atmosphere and IKA plate was used as the heat source. Solvents were purified by standard techniques without special instructions. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AvanceII-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{19}F, 162 MHz for ^{31}P), Varian DLG400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) or Bruker Avance NEO 600M NMR Spectroscopy (600 MHz for ^{1}H, 150 MHz for ^{13}C); $CDCl_3$ and TMS were used as a solvent and an internal standard, respectively. The NMR yield was determined by ^{1}H NMR using CH_2Br_2 or 1,3,5-trimethoxybenzene as an internal standard. The chemical shifts are reported in ppm downfield (δ) from TMS, the coupling constants J are given in Hz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on either a Q-TOF mass spectrometry or a GC-TOF mass spectrometry. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light and iodoplatinate reagent. Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 mesh). Unless otherwise noted, starting materials are commercially available.

2. Synthesis of Starting Materials

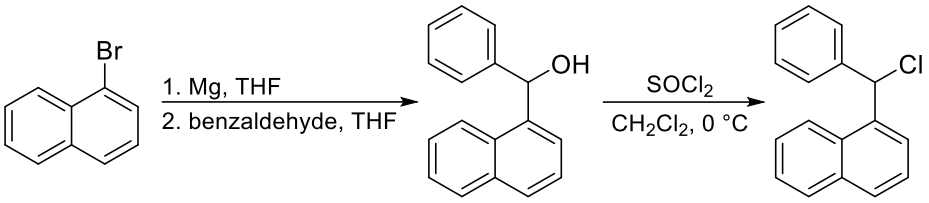
Representative procedure for synthesis of starting material 1p[1]:



To a solution of 2-methoxy-1-naphthaldehyde (0.93g, 5 mmol) in THF (20 mL) at 0 ℃, $NaBH_4$ (0.095 g, 2.5 mmol) was slowly added. The reaction mixture was slowly warmed to room temperature and stirred overnight. Then water (10 mL) was added slowly to quench the reaction. The product was extracted with ethyl ether (10 mL × 3), and the combined organic layers were washed with brine (10 mL × 3), dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue obtained was purified via silica gel chromatography (eluent: hexane/ethyl acetate = 10:1) to afford (2-methoxynaphthalen-1-yl)methanol as a yellow solid (0.87 g, 93% yield).

To a solution of the (2-methoxynaphthalen-1-yl)methanol (2 mmol) in CH_2Cl_2 (10 mL) at 0 ℃, $SOCl_2$ (2.0 equiv.) was slowly added. The reaction mixture was slowly warmed to room temperature and stirred overnight. After washed with the aqueous sodium bicarbonate, brine, the combined organic layers were dried over Na_2SO_4, filtrated, and then concentrated under vacuum to afford 1-(chloromethyl)-2-methoxynaphthalene (**1p**) (yellow solid, 0.40 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.6, 1.0 Hz, 1H), 7.85 (d, J = 9.1 Hz, 1H), 7.83–7.76 (m, 1H), 7.61–7.55 (m, 1H), 7.40–7.36 (m, 1H), 7.26 (d, J = 9.1 Hz, 1H), 5.18 (s, 2H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 132.5, 131.1, 129.1, 128.7, 127.4, 123.8, 122.7, 117.9, 113.0, 77.4, 77.1, 76.8, 56.7, 37.3.

Representative procedure for synthesis of starting materials 1a-1f, 1i-1m, 1r[2] :



To an oven-dried 50-mL round-bottom flask containing benzaldehyde (1.06g, 10.0 mmol) in THF (10 mL), (naphthalen-1-yl)magnesium bromide in THF (20 mL) prepared from 1-bromonaphthalene (2.07g, 10.0 mmol) and magnesium powder (Mg, 0.26g, 11.0 mmol) was added dropwise at 0 ℃ under a N_2 atmosphere. The resulting mixture was stirred overnight at room temperature, and then the saturated NH_4Cl aqueous solution (10 mL) was added to quench the reaction. And then the resulting mixture was extracted with ethyl ether (10 mL × 3). The combined organic layers were washed with brine (10 mL × 3), dried over Na_2SO_4 and filtrated. The solvent was removed by evaporation under vacuum to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 10:1) to afford naphthalen-1-yl(phenyl)methanol (1.89 g, 75% yield) as a white solid.

To a solution of naphthalen-1-yl(phenyl)methanol (1.17 g, 5 mmol) in dichloromethane (CH_2Cl_2, 25 mL) at 0 ℃, $SOCl_2$ (2 equiv.) was slowly added. The resulting mixture was stirred overnight at room temperature, and then the aqueous sodium bicarbonate (25 mL) was added to quench the reaction for neutralize excess of $SOCl_2$. The resulting mixture was washed with dichloromethane (10 mL × 3), the combined organic layers were washed with brine (10 mL × 3) and dried over Na_2SO_4. The solvent was removed under reduced pressure to give 1-(chloro(phenyl)methyl) naphthalene (**1a**) as a yellowish solid (1.21 g, 96% yield), which was used without further purification in the amination reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.05 (m, 1H), 7.92–7.86 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.54–7.42 (m, 5H), 7.39–7.28 (m, 3H), 6.89 (s, 1H).

1-(chloro(*p*-tolyl)methyl)naphthalene (1b)[1], yellowish solid (1.21 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10–8.03 (m, 1H), 7.91–7.85 (m, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 1H), 7.54–7.42 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.87 (s, 1H), 2.34 (s, 3H).

1-(chloro(*o*-tolyl)methyl)naphthalene (1c), yellowish solid (1.24 g, 92% yield). mp 58-60 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.56–7.45 (m, 4H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.25–7.18 (m, 3H), 7.06 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 135.7, 135.5, 133.9, 130.7, 130.6, 129.2, 129.0, 128.5, 128.3, 126.8, 126.5, 126.4, 125.9, 125.4, 123.1, 77.4, 77.1, 76.8, 58.7, 19.3. IR (KBr) 3052, 2956, 2924, 2853, 1742, 1666, 1510, 1488, 1383, 1461, 1261, 1091, 800, 779, 736 cm^{-1}; HRMS (EI) calcd for C18H15Cl: 266.0862 [M]+; found: 266.0856.

1-(chloro(3,4-dimethylphenyl)methyl)naphthalene (1d), yellowish solid (1.34 g, 92% yield). mp 62-64 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.04 (m, 1H), 7.91–7.85 (m, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.53–7.43 (m, 3H), 7.24 (d, *J* = 2.1 Hz, 1H), 7.17 (dd, *J* =

7.8, 2.1 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.85 (s, 1H), 2.24 (d, *J* = 2.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 136.9, 136.7, 136.2, 133.9, 130.5, 129.8, 129.2, 129.1, 128.9, 126.8, 126.5, 125.8, 125.5, 125.3, 123.8, 77.4, 77.1, 76.8, 61.9, 19.9, 19.5. IR (KBr) 3048, 2922, 2853, 1733, 1645, 1600, 1508, 1454, 1383, 1258, 1061, 1020, 826, 781, 740 cm^{-1}; HRMS (EI) calcd for C19H17Cl: 280.1019 [M]+; found: 280.1011.

1-(chloro(4-fluorophenyl)methyl)naphthalene (1e)[1], yellowish solid (1.22 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.93 (m, 1H), 7.81–7.77 (m, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.45–7.29 (m, 5H), 6.92 (t, *J* = 8.6 Hz, 2H), 6.77 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, J_{CF} = 247.5 Hz), 136.5 (d, J_{CF} = 3.3 Hz), 134.0, 134.2, 130.5, 120.0 (d, J_{CF} = 8.3 Hz), 129.6, 129.2, 126.9, 126.8, 126.1, 125.4, 123.8, 115.7 (d, J_{CF} = 21.7 Hz), 77.6, 77.3, 77.0, 61.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.42.

1-(chloro(4-chlorophenyl)methyl)naphthalene (1f), yellowish solid (1.32 g, 91 % yield). mp 66-68 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.96 (m, 1H), 7.92–7.87 (m, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.55–7.43 (m, 3H), 7.43–7.36 (m, 2H), 7.35–7.27 (m, 2H), 6.83 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 135.6, 134.1, 130.4, 129.6, 129.5, 129.1, 128.8, 126.9, 126.7, 126.1, 125.3, 123.7, 77.5, 77.2, 76.8, 61.1. IR (KBr) 3058, 2925, 2856, 1597, 1510, 1490, 1397, 1091, 1014, 821, 797, 777, 741 cm^{-1}; HRMS (EI) calcd for C17H12Cl2: 286.0316 [M]+; found: 286.0309.

1-(1-chloroethyl)naphthalene (1i)[1], yellow oil (1.88 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 1H), 7.93–7.85 (m, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.71 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.60–7.56 (m, 1H), 7.54–7.44 (m, 2H), 5.90 (q, *J* = 6.8 Hz, 1H), 2.06 (d, *J* = 6.8 Hz, 3H).

1-(1-chloropropyl)naphthalene (1j)[3], yellow oil (1.87g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.61–7.41 (m, 3H), 5.61 (t, *J* = 6.8 Hz, 1H), 2.45–2.21 (m, *J* = 7.0 Hz, 2H), 1.11 (t, *J* = 7.3 Hz, 3H).

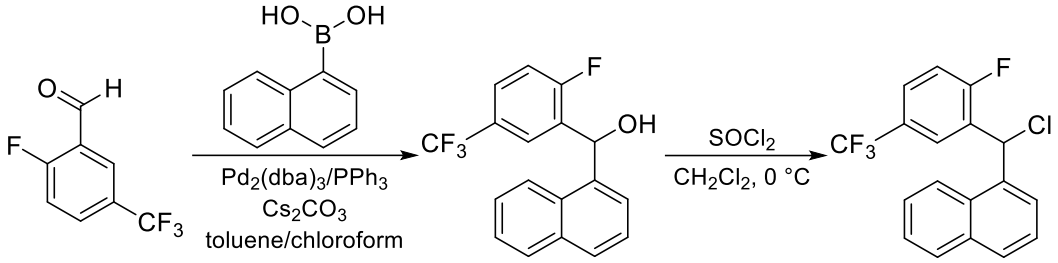
1-(1-chloro-2-methylpropyl)naphthalene (1k)[1], yellow oil (1.97 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 7.3 Hz, 1H), 7.59–7.44 (m, 3H), 5.49 (d, *J* = 7.4 Hz, 1H), 2.59–2.50 (m, 1H), 1.18 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H).

1-(1-chlorobutyl)naphthalene (1l)[1], yellow oil (2.04 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.52–7.46 (m, 2H), 5.70 (dd, *J* = 8.6, 5.6 Hz, 1H), 2.39–2.19 (m, 2H), 1.72–1.59 (m, 1H), 1.57–1.42 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

1-(1-chloropentyl)naphthalene (1m)[3], yellow oil (2.21 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.63–7.54 (m, 1H), 7.52–7.46 (m, 2H), 5.69 (t, *J* = 7.0 Hz, 1H), 2.34–2.27 (m, 2H), 1.61–1.59 (m, 1H), 1.47–1.33 (m, 3H), 0.92 (t, *J* = 7.0 Hz, 3H).

1-(chloro(phenyl)methyl)-4-methylnaphthalene (1r)[4], yellow oil (1.31 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.00 (m, 1H), 8.00–7.94 (m, 1H), 7.48–7.43 (m, 2H), 7.42–7.36 (m, 3H), 7.30–7.20 (m, 4H), 6.80 (s, 1H), 2.62 (s, 3H).

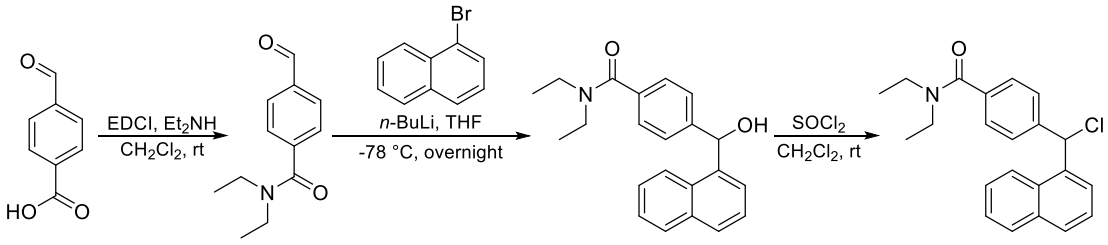
Representative procedure for synthesis of starting materials 1g:



$Pd_2(dba)_3$ (0.025 mmol, 5 mol%) and triphenylphosphine (0.05 mmol, 5 mol%), 1-naphthyl boronic acid (2.0 mmol), 2-fluoro-5-(trifluoromethyl)benzaldehyde (1.0 mmol), and Cs_2CO_3 (1.0 mmol) were dissolved in toluene (2 mL) and chloroform (0.01 mL). After the mixture was stirred at 80 ℃ for 24 h, then the product was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layers were washed with brine (10 mL × 3), dried over Na_2SO_4 and filtrated. The solvent was removed by evaporation under vacuum to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 20:1) to afford (2-fluoro-5-(trifluoromethyl)phenyl)(naphthalen-1-yl)methanol (0.28 g, 91% yield) as a white solid.

To a solution of (2-fluoro-5-(trifluoromethyl)phenyl)(naphthalen-1-yl)methanol (0.28 g, 0.91 mmol) in dichloromethane (CH_2Cl_2, 5 mL) at 0 ℃, $SOCl_2$ (2 equiv.) was slowly added. The resulting mixture was stirred overnight at room temperature, and then the aqueous sodium bicarbonate (10 mL) was added to quench the reaction for neutralize excess of $SOCl_2$. The resulting mixture was washed with dichloromethane (5 mL × 3), the combined organic layers were washed with brine (5 mL × 3) and dried over Na_2SO_4. The solvent was removed under reduced pressure to give 1-(chloro(2-fluoro-5-(trifluoromethyl)phenyl)methyl)naphthalene (**1g**) as a yellow oil (0.27 g, 88% yield), which was used without further purification in the amination reaction. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 1H), 7.80–7.78 (m, 1H), 7.75–7.69 (m, 2H), 7.44–7.40 (m, 3H), 7.38–7.35 (m, 1H), 7.33–7.29 (m, 1H), 7.07 (s, 1H), 7.03–6.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, J_{CF} = 257.8 Hz), 134.3, 134.0, 130.3, 129.8, 129.3, 129.2, 127.6 (qd, J_{CF} = 4.2 Hz), 127.5 (d, J_{CF} = 3.7 Hz), 127.1 (d, J_{CF} = 3.6 Hz), 127.0, 126.1 (d, J_{CF} = 7.1 Hz), 125.3, 122.3 (q, J_{CF} = 272.4 Hz, CF_3), 122.8, 116.5, 116.3, 77.4, 77.1, 76.8, 53.3 (d, J_{CF} = 5.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.88, -110.86. IR (neat) 2831, 2787, 1587, 1504, 1455, 1392, 1330, 1164, 1125, 1015, 896, 825, 763 cm^{-1}; HRMS (EI) calcd for C18H11ClF4: 338.0485 [M]+; found: 338.0478.

Representative procedure for synthesis of starting materials 1h:



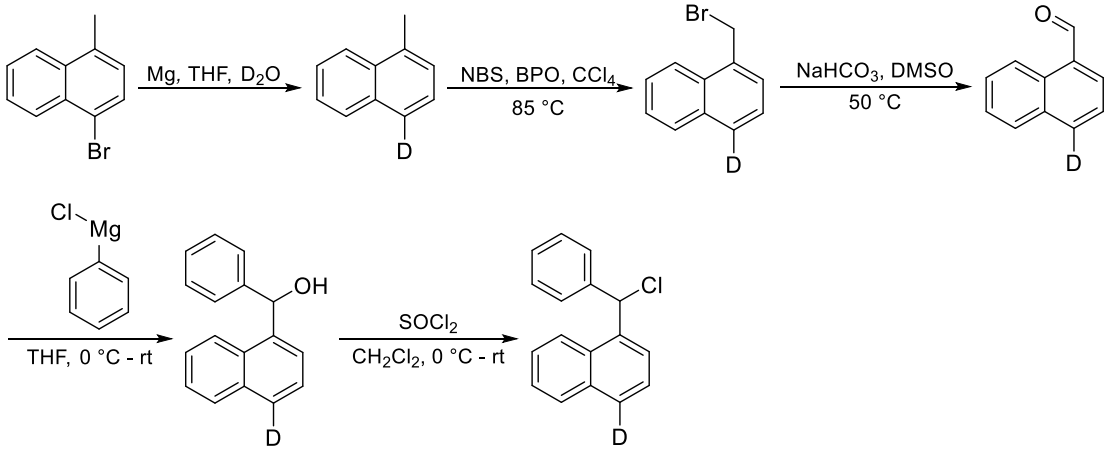
1-(3-Dimethylaminopropyl)-3-ethylcarbodimide hydrochloride (8.45 g, 44 mmol) was added

portionwise to a cold solution (0 ℃) of 4-formylbenzoic acid (6.02 g, 40 mmol), diethylamine (2.93 g, 40 mmol), and triethylamine (6 mL) in 100 mL of anhydrous CH_2Cl_2. The mixture was stirred at 0 ℃ for 30 min and warmed to the room temperature under N_2. After 4 h, the reaction was quenched by the addition of 60 mL of saturated aqueous $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organics were washed successively with water, aqueous hydrochloric acid (5%), water, and brine, then dried over Na_2SO_4, and concentrated. The residue obtained was purified via silica gel chromatography (eluent: hexane/ethyl acetate = 5:1) to afford *N*,*N*-diethyl-4-formylbenzamide as a yellow oil (0.82 g, 10% yield).

1-bromonaphthalene (0.39 mL, 3.0 mmol) was dissolved in THF (10 mL) and cooled to -78 ℃. *n*-BuLi (1.2 mL, 2.5 M in *n*-hexane, 3.0 mmol) was added dropwise. After 30 min *N*,*N*-diethyl-4-formylbenzamide (0.60 g, 3.0 mmol) was added dissolved in THF (2 mL). The solution was stirred 1 h, then NH_4Cl (aq) was added. After aqueous workup and chromatography on silica (eluent: hexane/ethyl acetate = 2:1) of *N*,*N*-diethyl-4-(hydroxy(naphthalen-1-yl)methyl)benzamide was obtained as a yellow solid (0.58 g, 58% yield).

N,*N*-diethyl-4-(hydroxy(naphthalen-1-yl)methyl)benzamide (0.58 g, 1.75 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and $SOCl_2$ (0.15 mL, 1.93 mmol) was added. The solution was stirred at 25 ℃ for 1 h and the solvent was evaporated in vacuo. 4-(chloro(naphthalen-1-yl)methyl)-*N*,*N*-diethylbenzamide (**1h**) (yellowish oil, 0.58 g, 95% yield) was obtained and used in the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.94 (m, 1H), 7.85–7.74 (m, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.45–7.40 (m, 4H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.81 (s, 1H), 3.33 (bs, s, 4H), 1.10 (bs, s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 141.4, 137.0, 135.7, 134.0, 130.4, 129.5, 129.0, 128.1, 127.0, 126.7, 126.6, 126.0, 125.2, 123.7, 77.4, 77.1, 76.8, 61.3, 43.3, 14.1. IR (neat) 3050, 2972, 2873, 1628, 1509, 1458, 1381, 1287, 1159, 1071, 947, 825, 800, 736 cm^{-1}; HRMS (ESI) calcd for C22H22ClNNaO: 374.1288 [M+Na]+; found: 374.1282.

Representative procedure for synthesis of starting materials 1a-d_1:



To a mixture of magnesium ribbon (0.28 g, 11 mmol) in dry THF (30 mL), 1-bromo-4-methylnaphthalene (2.21 g, 10 mmol) was added dropwise keeping reflux under a N_2 atmosphere. After the reaction temperature downed to room temperature, the resulting mixture was stirred for another 1 h, and then D_2O (0.3 mL) was added to quench the reaction at 0 ℃. The resulting

mixture was stirred overnight at room temperature, then solvents were removed under vacuum, and the residue obtained was then extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with brine (30 mL), dried over Na_2SO_4. The crude product was then purified via silica gel chromatography (eluent: hexane) to afford 1-methylnaphthalene-4-*d* as a colorless oil (1.17 g, 82% yield).

1-Methylnaphthalene-4-*d* (1.17 g, 8.2 mmol) and N-bromosuccinimide (NBS) (1.60 g, 9.0 mmol) were dissolved in CCl_4 (50 mL).The mixture was stirred at 85 ℃, benzoyl peroxide (BPO) (0.024 g, 0.10 mmol) was added into the mixture immediately when the solution was refluxed. After the resulting mixture was stirred under reflux for 12 h, the mixture was allowed to cool to room temperature, then the mixture was transferred to ice-salt bath, solid was obtained after filtration. The crude product was then purified via silica gel chromatography (eluent: hexane) to afford 1-(bromomethyl)naphthalene-4-*d* as a colorless oil (1.09 g, 60% yield).

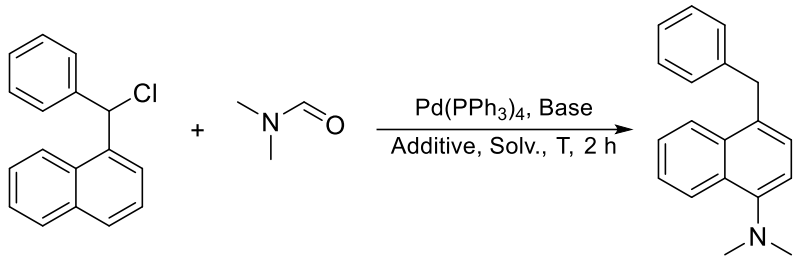
A suspension of 1-(bromomethyl)naphthalene-4-*d* (1.09 g, 4.9 mmol), $NaHCO_3$ (0.8233 g, 9.8 mmol) in DMSO (20 mL) was heated to 95 ℃ for 3 h. Then the mixture was cooled to room temperature. The mixture was quenched with H_2O (50 mL). Then the mixture was washed by ethyl acetate (50 mL × 3). And the combined organic layers were washed with brine (50 mL × 3), dried over anhydrous Na_2SO_4 and purified via silica gel chromatography (hexane/ethyl acetate = 20:1) to afford 1-naphthaldehyde-4-*d* as a colorless oil (0.32 g, 42% yield).

To an oven-dried 25-mL round-bottom flask containing 1-naphthaldehyde-4-*d* (0.32g, 2.0 mmol) in THF (5 mL), Phenylmagnesium chloride (1.5 mL, 2.0 M in THF, 3.0mmol) was added dropwise at 0 ℃ under a N_2 atmosphere. The resulting mixture was stirred overnight at room temperature, and then the saturated NH_4Cl aqueous solution (5 mL) was added to quench the reaction. And then the resulting mixture was extracted with ethyl ether (5 mL × 3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtrated. The solvent was removed by evaporation under vacuum to afford a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 10:1) to afford (naphthalen-1-yl-4-*d*)(phenyl)methanol as a white solid (0.35 g, 74% yield).

To a solution of (naphthalen-1-yl-4-*d*)(phenyl)methanol (0.35 g, 1.5 mmol) in dichloromethane (CH_2Cl_2, 10 mL) at 0 ℃, $SOCl_2$ (2 equiv.) was slowly added. The resulting mixture was stirred overnight at room temperature, and then the aqueous sodium bicarbonate (10 mL) was added to quench the reaction for neutralize excess of $SOCl_2$. The resulting mixture was washed with dilute aqueous sodium bicarbonate (5 mL × 3), the combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure to give 1-(chloro(phenyl)methyl) naphthalene-4-*d* (**1a**-d_1) as a yellowish oil (0.35 g, 92% yield, 88% D). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–8.01 (m, 1H), 7.85–7.80 (m, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.48–7.37 (m, 5H), 7.34–7.21 (m, 3H), 6.85 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.6, 136.2, 134.0, 130.6, 129.0, 128.7, 128.2, 128.1, 127.0, 126.7, 126.0, 125.2, 123.9, 77.5, 77.2, 76.9, 61.9. IR (neat) 3059, 2925, 2849, 1592, 1494, 1452, 1386, 1251, 1030, 822, 766, 712, 798 cm^{-1}; HRMS (EI) calcd for C17H12DCl: 253.0769 [M]+; found: 253.0762.

3. Optimization of Reaction Conditions (Method A)

Table S1 Optimization of the reaction conditions for the dimethylamination of 1-(chloro(phenyl)-methyl)naphthalene with DMF



1a **2a**

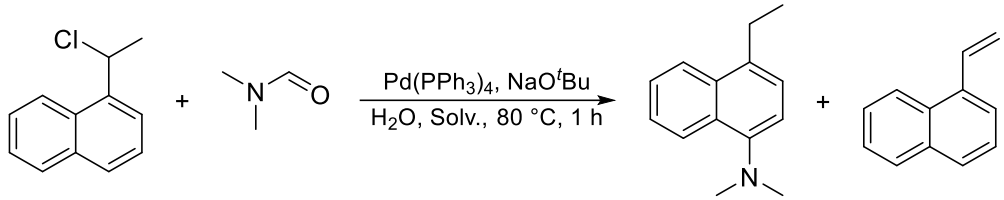
Entry[a]	The radio of **1a** to **DMF**	Base/X equiv.	Additive /X μL	Solv.	T (℃)	**2a** yield (%)[b]
1	1:1	Cs_2CO_3 /4	None	THF	60	ND[c]
2	1:1	Na_2CO_3/4	None	THF	60	ND[c]
3	1:1	K_3PO_4/4	None	THF	60	ND[c]
4	1:1	NaH/4	None	THF	60	ND[c]
5	1:1	LiO^{t}Bu/4	None	THF	60	ND[c]
6	1:1	KO^{t}Bu/4	None	THF	60	15
7	1:1	NaO^{t}Bu/4	None	THF	60	35
8	1:1	NaO^{t}Bu/4	None	2-MeTHF	60	39
9	1:1	NaO^{t}Bu/4	None	DMF	60	23
10	1:1	NaO^{t}Bu/4	None	1,4-dioxane	60	12
11	1:1	NaO^{t}Bu/4	None	DME	60	29
12	1:1	NaO^{t}Bu/4	None	toluene	60	9
13	1:1	NaO^{t}Bu/4	None	acetone	60	trace[d]
14	1:2	NaO^{t}Bu/4	None	2-MeTHF	60	42
15	1:3	NaO^{t}Bu/4	None	2-MeTHF	60	45
16	1:4	NaO^{t}Bu/4	None	2-MeTHF	60	39
17	1:3	NaO^{t}Bu/4	None	2-MeTHF	40	17
18	1:3	NaO^{t}Bu/4	None	2-MeTHF	80	48
19	1:3	NaO^{t}Bu/4	None	2-MeTHF	100	34
20	1:3	NaO^{t}Bu/4	H_2O/2	2-MeTHF	80	86
21	1:3	**NaO^{t}Bu/4**	**H_2O/5**	2-MeTHF	**80**	**97(95)**
22	1:3	NaO^{t}Bu/4	H_2O/10	2-MeTHF	80	88
23	1:3	NaO^{t}Bu/4	H_2O/20	2-MeTHF	80	75
24	1:3	NaO^{t}Bu/4	H_2O/60	2-MeTHF	80	62
25	1:3	NaO^{t}Bu/1	H_2O/5	2-MeTHF	80	47
26	1:3	NaO^{t}Bu/2	H_2O/5	2-MeTHF	80	71
27	1:3	NaO^{t}Bu/3	H_2O/5	2-MeTHF	80	65
28	1:3		H_2O/5	2-MeTHF	80	NR[e]
29	1:3	NaO^{t}Bu/4	H_2O/5	2-MeTHF	80	NR[e,f]

[a]Reaction conditions: 1-(α-chlorobenzyl) naphthalene (**1a**, 0.3 mmol), DMF (X equiv.), $Pd(PPh_3)_4$ (5 mol%), base (X equiv.) and H_2O (X μL), in solvent (3 mL) at T ℃ under N_2 atmosphere, 2 h. [b]Yields determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield is given in parentheses. [c]Not detected; **1a** was decomposed. [d]Trace amount of product **2a** was observed; starting material **1a** was

decomposed. [e]No reaction; **1a** was recovered. [f]No catalyst was added.

4. Optimization of Reaction Conditions (method B)

Table S2 Optimization of the reaction conditions for the dimethylamination of 1-(1-chloroethyl) naphthalene with DMF



1i **2i** **2ib**

Entry[a]	Base	Additive	Solv.	T (°C)	**2i** yield (%)[b]	**2ib** yield (%)[b]
1	NaO^{t}Bu	H_2O	2-MeTHF	80	15	75
2	NaO^{t}Bu	H_2O	THF	80	12	78
3[c]	NaO^{t}Bu	H_2O	CH_3CN	80	trace	70
4	NaO^{t}Bu	H_2O	DME	80	4	87
5	**NaO^{t}Bu**	**H_2O**	**DMF**	**80**	**46(44)**	**18**
6	NaO^{t}Bu	H_2O	DMSO	80	6	64

[a]Reaction conditions: 1-(1-chloroethyl)naphthalene (**1i**, 0.3 mmol), DMF (3 equiv.), $Pd(PPh_3)_4$ (5 mol%), NaO^{t}Bu (4 equiv.) and H_2O (5 μL), in solvent (3 mL) at 80 °C under N_2 atmosphere, 1 h. [b]^{1}H NMR yields using CH_2Br_2 as an internal standard. Isolated yield is given in parentheses. [c]Trace amount of product **2i** was observed; starting material **1i** was decomposed.

5. General Procedure for Remote dimethylamination

Method A:

Representative Procedure for Obtaining Products 2a-2h, 2n-2r:

An oven-dried 25-mL Schlenk tube was charged with a mixture of 1-(chloro(phenyl)methyl)naphthalene (**1a**, 0.3 mmol, 1.0 equiv.), DMF (69.24 μL, 0.9 mmol, 3.0 equiv.), $Pd(PPh_3)_4$ (0.0173 g, 5 mol%), NaO^{t}Bu (0.1152 g, 1.2 mmol, 4.0 equiv.), H_2O (5.0 μL) and dry 2-MeTHF (3.0 mL). The reaction mixture was stirred for a certain period under a N_2 atmosphere. After cooled to room temperature, the solvent was removed in *vacuo*. The residue obtained was purified via silica gel chromatography (eluent: hexane/ethyl acetate = 100:1) to afford 4-benzyl-*N*,*N*-dimethylnaphthalen-1-amine (**2a**) in 95% yield (74.8 mg) as a yellowish solid.

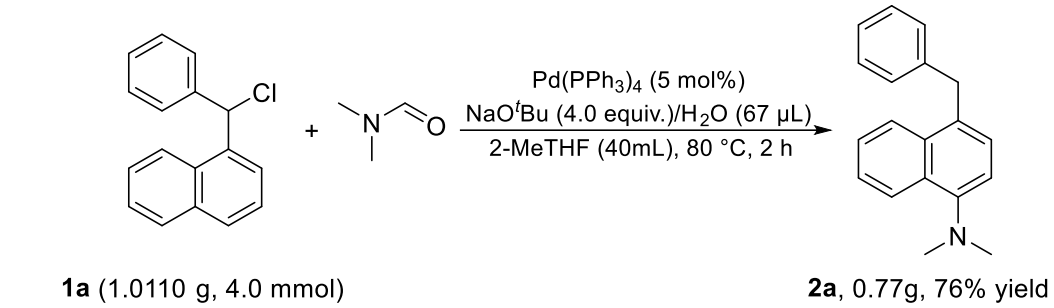
Method B:

Representative Procedure for Obtaining Products 2i-2m:

An oven-dried 25-mL Schlenk tube was charged with a mixture of 1-(1-chloroethyl) naphthalene (**1i**, 0.3 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (0.0173 g, 5 mol%), NaO^{t}Bu (0.1152 g, 1.2 mmol, 4.0 equiv.), H_2O (5.0 μL) and dry DMF (3.0 mL). The reaction mixture was stirred for 1 h under a N_2 atmosphere. After cooled to room temperature, the reaction mixture was quenched by H_2O (10 mL). Then the reaction mixture was extracted with ethyl acetate (10 mL × 3). And the combined organic layers were washed with brine (10 mL × 3), dried over anhydrous Na_2SO_4 and

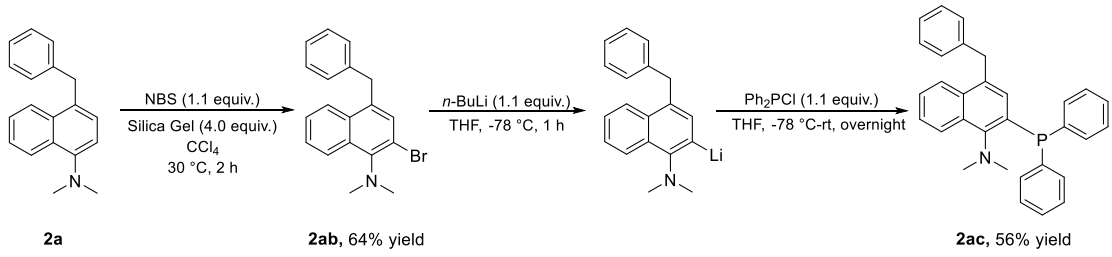
filtered. The solvent was removed under reduced pressure and the residue obtained was purified via silica gel chromatography (eluent: hexane/ethyl acetate = 100:1) to afford 4-ethyl-*N*,*N*-dimethylnaphthalen-1-amine (**2i**) in 44% yield (26.3 mg) as a brown oil.

6. Gram-scale reaction and derivatization



Scheme S1. Gram-scale reaction.

An oven-dried 100-mL Schlenk tube was charged with a mixture of 1-(chloro-(phenyl)methyl)naphthalene (**1a**, 1.011 g, 4.0 mmol,), DMF (0.9232 mL, 1.2 mmol, 3.0 equiv.), $Pd(PPh_3)_4$ (0.2267 g, 5 mol%), NaO^tBu (1.536 g, 16 mmol, 4.0 equiv.), H_2O (66.67 μL) and dry 2-MeTHF (40.0 mL). The reaction mixture was stirred for 2 h under a N_2 atmosphere. After cooled to room temperature, the reaction mixture was concentrated in a vacuum. And then the residue was extracted with H_2O (10 mL × 3). The combined aqueous layers ware washed by ethyl acetate (30 mL × 3). And the combined organic layers were washed with brine (30 mL × 3), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the residue obtained was purified via silica gel chromatography (eluent: hexane/ethyl acetate = 100:1) to afford 4-benzyl-*N*,*N*-dimethylnaphthalen-1-amine (**2a**) in 76% yield (0.768 g) as a yellowish solid.

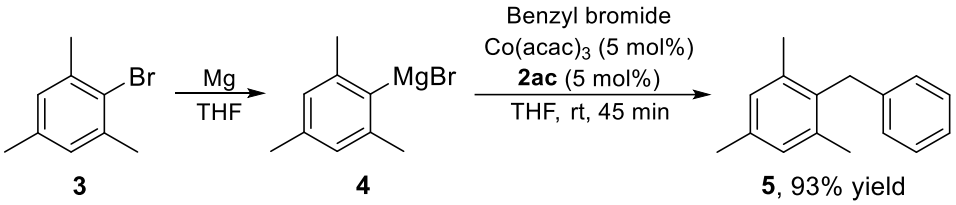


Scheme S2. Derivatization.

The amination product **2a** was obtained by means of **Method A**. To a solution of **2a** in CCl_4 (3.0 mL), NBS (58.8 mg, 0.33 mmol, 1.1 equiv.) and Silica Gel (72.0 mg, 1.2 mmol, 4.0 equiv.) were added. After the mixture was stirred at 30 ℃ for 2 h, the insoluble material was removed by filtration, washed with aqueous sodium thiosulfate, and dried over anhydrous Na_2SO_4. Filtration, removal of the solvent, and the residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 50:1) to afford the corresponding brominated product **2ab** (65.1 mg, 64% yield).

n-BuLi (0.25 mL, 0.55 mmol, 2.5 M in *n*-hexane) was added dropwise at −78 °C to a solution of 4-benzyl-2-bromo-*N*,*N*-dimethylnaphthalen-1-amine (0.5 mmol) in anhydrous THF (10.0 mL).

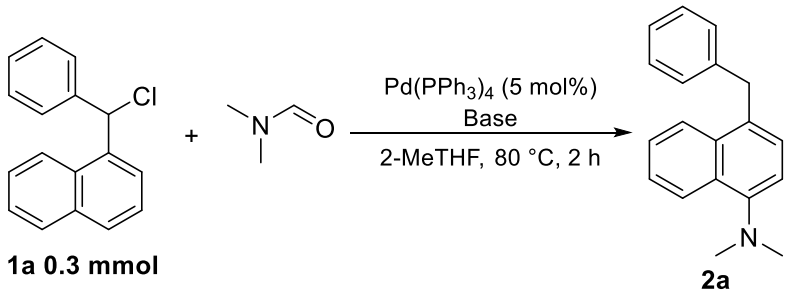
After this solution was stirred for 1 h at −78 °C, Chlorodiphenyl phosphine (97.0 mL, 5.5 mmol, 1.1 equiv.) was added to this solution at −78 °C. Then the reaction mixture was stirred overnight at room temperature. The solvent was evaporated at reduced pressure, and the residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 50:1) to afford the phosphine compound **2ac** (123.6 mg, 56% yield).



Scheme S3. The application of **2ac**.

In a round bottom flask (10 mL) magnesium ribbon (0.0960 g, 2.0 equiv) was added in 2 mL of THF. A solution of 2-bromomesitylene (0.3981 g, 2 mmol) in 2 mL of THF was added dropwise to the flask under strong stirring. Keep the mixture slightly boiling. After two hours of reaction, the crude product of MesMgBr was obtained. Benzyl bromide (1 mmol), cobalt tris-(acetylacetonate) (0.018 g, 0.05 mmol), and **2ac** (0.015 g, 0.05 mmol) were weighed neat into a vial (20 mL). THF was added (5 mL), and the reaction was stirred until homogeneous. The solution of MesMgBr was then added, and the reaction mixture was stirred for 45 min. Following this, the reaction mixture was concentrated to dryness. The resulting residue was extracted with hexanes (2 mL × 3) and concentrated. The crude product was then purified by silica gel chromatography and eluted from pure hexanes to afford the 2-benzyl-1,3,5-trimethylbenzene (**5**, 195.6 mg, 93% yield).

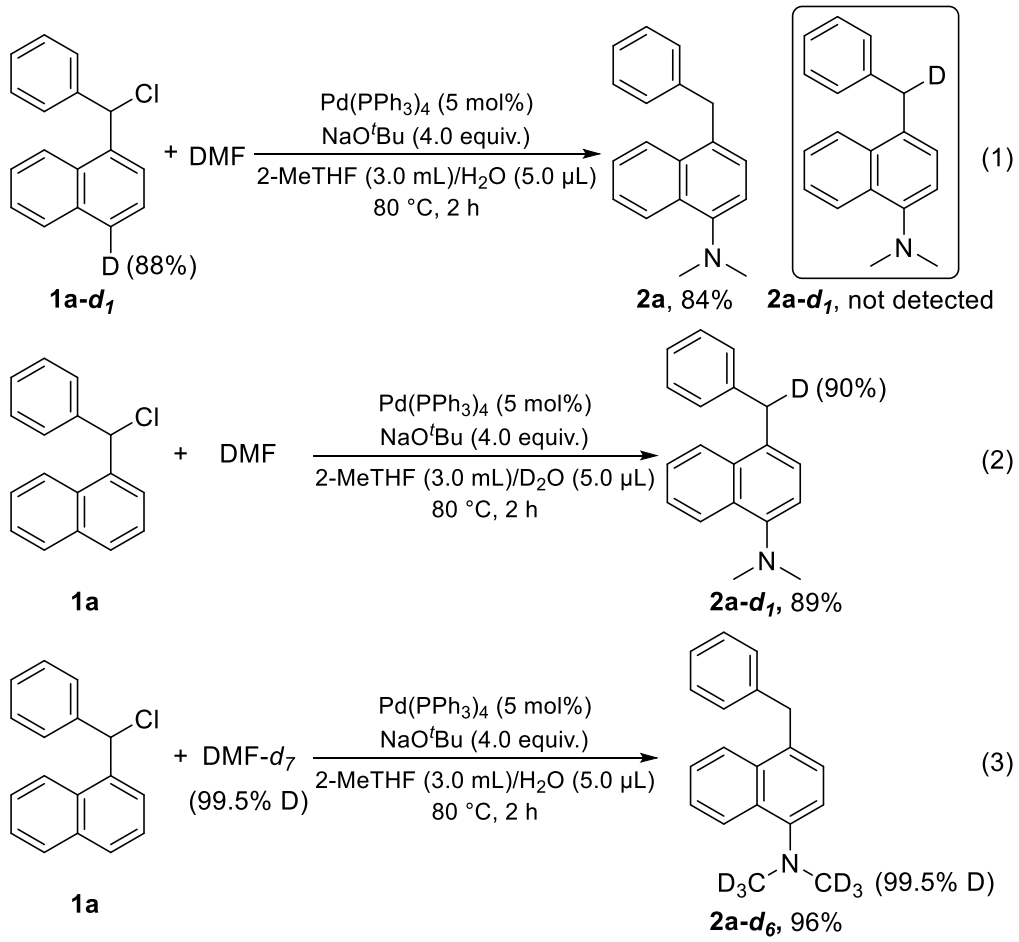
7. Control experiments



Bases	yield
1) 1.2 mmol NaO^{t}Bu, 5μL H_2O	97%
2) 0.9222 mmol NaO^{t}Bu, 0.2778 mmol NaOH, 0.2778 mmol ^{t}BuOH	97%
3) 0.9222 mmol NaO^{t}Bu, 0.2778 mmol NaOH	98%
4) 0.9222 mmol NaO^{t}Bu, 0.2778 mmol ^{t}BuOH	77%
5) 1.2 mmol NaOH	87%

Scheme S4. The role of the base and H_2O.

An oven-dried 25-mL Schlenk tube was charged with a mixture of 1-(chloro(phenyl)methyl)naphthalene (**1a**, 0.3 mmol, 1.0 equiv.), DMF (69.24 μL, 0.9 mmol, 3.0 equiv.), $Pd(PPh_3)_4$ (0.0173 g, 5 mol%), NaO^tBu (0.9222 - 1.2 mmol), NaOH (0 - 1.2 mmol), ^tBuOH (0 - 0.2778 mmol), H_2O (0 - 5.0 μL) and dry 2-MeTHF (3.0 mL). The reaction mixture was stirred for 2 h under a N_2 atmosphere. After cooled to room temperature, the reaction mixture was filtered through celite and the conversion of amide was determined by ^1H NMR using CH_2Br_2 as an internal standard.



Scheme S5. Deuterium experiment

An oven-dried 25-mL Schlenk tube was charged with a mixture of **1a** or **1a**-d_1 (0.3 mmol, 1.0 equiv.), DMF or DMF-d_7 (69.24 μL, 0.9 mmol, 3.0 equiv.), $Pd(PPh_3)_4$ (0.0173 g, 5 mol%), NaO^tBu (0.1152 g, 1.2 mmol, 4.0 equiv.), H_2O or D_2O (5.0 μL) and dry 2-MeTHF (3.0 mL). The reaction mixture was stirred for a certain period under a N_2 atmosphere. After cooled to room temperature, the solvent was removed in *vacuo*. The residue obtained was purified via silica gel chromatography (eluent: hexane/ethyl acetate = 100:1) to afford the corresponding product.

8. Plausible mechanism about DMF and Base.

An oven-dried 25-mL Schlenk tube was charged with a mixture of 1-(chloro(phenyl) methyl)naphthalene (**1a**, 0.3 mmol, 1.0 equiv.), DMF (69.24 μL, 0.9 mmol, 3.0 equiv.), $Pd(PPh_3)_4$ (0.0173 g, 5 mol%), NaO^tBu (0.1152 g, 1.2 mmol, 4.0 equiv.), H_2O (5.0 μL) and dry 2-MeTHF (3.0 mL). The reaction mixture was stirred for 2 h at 80 ℃ under a N_2 atmosphere. After cooled

to room temperature, the solvent was filtered through filter paper and the insoluble solid was determined by ^{1}H NMR and ^{13}C NMR using D_2O as the deuterated solvent.

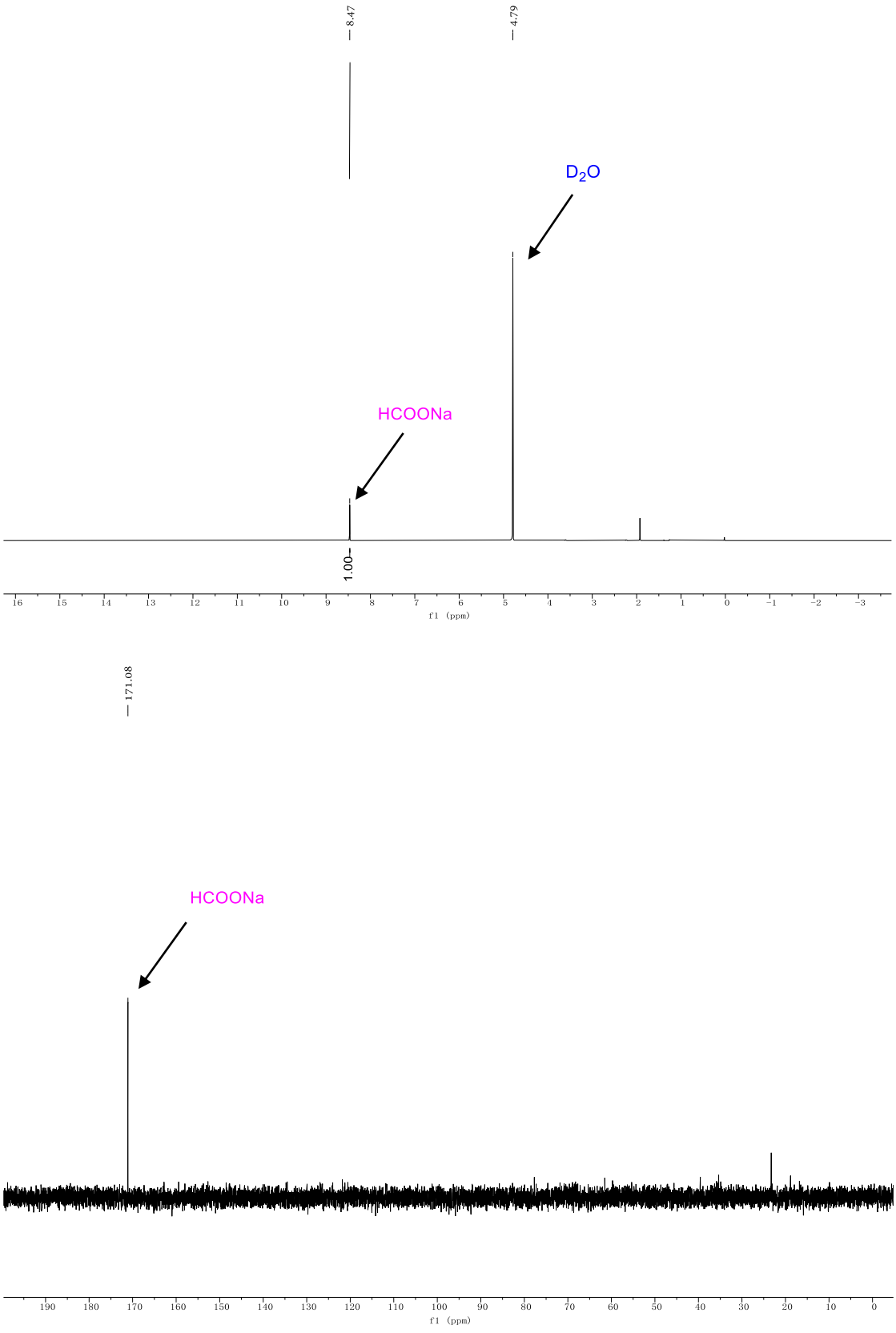
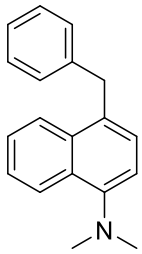


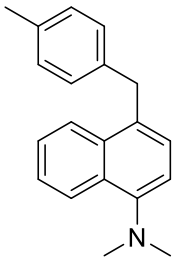
Figure 1. ^{1}H and ^{13}C NMR spectra of the solid.

9. Characterization Data for All Compounds



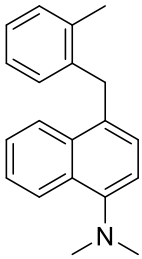
4-benzyl-*N*,*N*-dimethylnaphthalen-1-amine (2a)

Yellowish solid (74.5 mg, 95% yield) mp 80-82 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, J = 8.3, 1.6 Hz, 1H), 7.92 (dd, J = 8.2, 1.5 Hz, 1H), 7.46–7.37 (m, 2H), 7.25–7.09 (m, 6H), 6.97 (d, J = 7.6 Hz, 1H), 4.33 (s, 2H), 2.83 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 141.1, 133.3, 131.3, 129.3, 128.8, 128.6, 128.5, 127.3, 126.1, 125.9, 125.0, 124.9, 124.8, 113.8, 77.5, 77.2, 76.8, 45.5, 38.9; IR (KBr) 3060, 3026, 2925, 2854, 1584, 1493, 1453, 1391, 1304, 1265, 1188, 1043, 907, 845, 766, 717 cm^{-1}; HRMS (ESI) calcd for C19H20N: 262.1596 [M+H]+; found: 262.1585.



***N*,*N*-dimethyl-4-(4-methylbenzyl)naphthalen-1-amine (2b)**

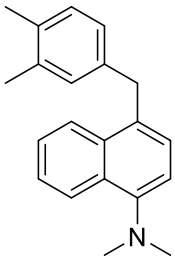
Brown solid (77.5 mg, 94% yield) mp 78-80 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, J = 7.9, 1.7 Hz, 1H), 7.99–7.87 (m, 1H), 7.52–7.40 (m, 2H), 7.28–7.15 (m, 1H), 7.12–7.03 (m, 4H), 7.01 (d, J = 7.6 Hz, 1H), 4.33 (s, 2H), 2.87 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 135.4, 133.2, 131.5, 129.3, 129.1, 128.6, 127.1, 125.8, 124.9, 124.8, 124.7, 113.7, 77.4, 77.1, 76.7, 45.4, 38.4, 21.0. IR (KBr) 3045, 2933, 2861, 2827, 2782, 1654, 1582, 1512, 1454, 1390, 1306, 1187, 1143, 1043, 1015, 910, 823, 767, 737 cm^{-1}; HRMS (ESI) calcd for C20H22N: 276.1752. [M+H]+; found: 276.1743.



***N*,*N*-dimethyl-4-(2-methylbenzyl)naphthalen-1-amine (2c)**

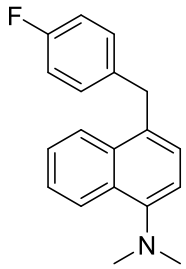
Brown oil (71.8 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, J = 7.9, 1.8 Hz, 1H), 7.97–7.90 (m, 1H), 7.54–7.41 (m, 2H), 7.22 (d, J = 7.7 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.99–6.87 (m, 3H), 4.32 (s, 2H), 2.87 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 138.8, 136.7, 133.4, 130.7, 130.1, 129.7, 129.1, 126.4, 126.3, 126.1, 125.9, 125.0, 124.8, 124.4, 113.9, 77.4, 77.1, 76.8, 45.5, 36.0, 19.7. IR (neat) 3066, 2934, 2860, 2827, 1584, 1511, 1455, 1390, 1304, 1187, 1144, 1097, 1045, 1012, 910, 826, 770, 737 cm^{-1}; HRMS (ESI) calcd for C20H22N: 276.1752. [M+H]+; found: 276.1741.



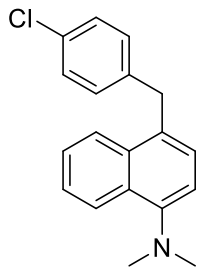
4-(3,4-dimethylbenzyl)-*N*,*N*-dimethylnaphthalen-1-amine (2d)

Brown oil (75.5 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31–8.25 (m, 1H), 7.97 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.49–7.36 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.04–6.97 (m, 1H), 6.99 (s, 2H), 6.91 (dd, *J* = 7.7, 1.9 Hz, 1H), 4.30 (s, 2H), 2.86 (s, 6H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 138.4, 136.5, 134.1, 133.3, 131.7, 130.1, 129.7, 129.3, 127.1, 126.2, 125.9, 124.9, 124.8, 124.7, 113.8, 77.4, 77.1, 76.8, 45.5, 38.5, 19.9, 19.4. IR (neat) 3068, 2935, 2859, 2827, 2783, 1581, 1504, 1453, 1390, 1301, 1265, 1188, 1143, 1043, 907, 822, 768, 739 cm^{-1}; HRMS (ESI) calcd for C21H24N: 290.1909. [M+H]+; found: 290.1908.



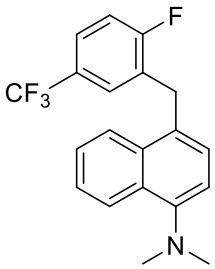
4-(4-fluorobenzyl)-*N*,*N*-dimethylnaphthalen-1-amine (2e)

Brown oil (74.5 mg, 89 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.47–7.35 (m, 2H), 7.18–7.07 (m, 3H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.97–6.87 (m, 2H), 4.31 (s, 2H), 2.86 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 239.5 Hz), 160.2, 150.2, 136.7 (d, *J* = 3.3 Hz), 133.2, 131.0, 130.1 (d, *J* = 7.8 Hz), 129.4, 127.2, 125.9, 125.0, 124.9, 124.8, 115.2 (d, *J* = 21.3 Hz), 113.7, 77.4, 77.1, 76.8, 45.4, 38.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.54. IR (neat) 3069, 2981, 2938, 2829, 1582, 1508, 1454, 1391, 1305, 1221, 1156, 1093, 1044, 1014, 907, 824, 769 cm^{-1}; HRMS (ESI) calcd for C19H19FN: 280.1502. [M+H]+; found: 280.1489.



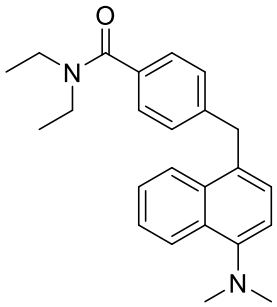
4-(4-chlorobenzyl)-*N*,*N*-dimethylnaphthalen-1-amine (2f)

Brown oil (51.4 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32–8.25 (m, 1H), 7.90–7.83 (m, 1H), 7.49–7.34 (m, 2H), 7.21–7.03 (m, 6H), 7.00 (d, J = 7.6 Hz, 1H), 4.31 (s, 2H), 2.87 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 139.6, 133.1, 131.7, 130.6, 130.1, 129.4, 128.5, 127.3, 125.9, 125.0, 124.9, 124.6, 113.7, 77.3, 77.1, 76.9, 45.4, 38.3. IR (neat) 3068, 2925, 2853, 2783, 1666, 1582, 1509, 1490, 1390, 1304, 1264, 1187, 1043, 1014, 907, 821, 766, 740 cm^{-1}; HRMS (ESI) calcd for C19H19ClN: 296.1206. [M+H]+; found: 296.1197.



4-(2-fluoro-5-(trifluoromethyl)benzyl)-*N*,*N*-dimethylnaphthalen-1-amine (2g)

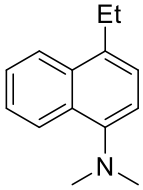
Yellow oil (65.6 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26–8.22 (m, 1H), 7.86–7.79 (m, 1H), 7.46–7.35 (m, 3H), 7.25–7.19 (m, 1H), 7.12–7.06 (m, 1H), 6.94 (d, J = 7.6 Hz, 1H), 4.32 (s, 2H), 2.81 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, J_{CF} = 7.6 Hz, 1H), 150.6, 133.0, 129.4, 129.1, 128.9, 128.4 (qd, J_{CF} = 4.1 Hz, 9.1Hz), 127.1, 126.2, 125.4 (dq, J_{CF} = 3.9 Hz, 9.3Hz), 125.1, 125.0, 124.0, 123.9 (q, J_{CF} = 273.0 Hz, CF_3), 115.8 (d, J_{CF} = 24.6 Hz), 113.7, 77.3, 77.0, 76.7, 45.3, 31.2 (d, J_{CF} = 3.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.89, -112.06. IR (neat) 3064, 2927, 2855, 1622, 1603, 1502, 1430, 1330, 1267, 1165, 1128, 1072, 1017, 910, 831, 779, 739 cm^{-1}; HRMS (ESI) calcd for C20H18F4N: 348.1375. [M+H]+; found: 348.1367.



4-((4-(dimethylamino)naphthalen-1-yl)methyl)-*N*,*N*-diethylbenzamide (2h)

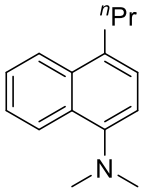
Yellowish oil (31.0 mg, 29% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.3 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.40–7.30 (m, 2H), 7.22–7.16 (m, 2H), 7.15–7.07 (m, 3H), 6.94 (d, J = 7.6 Hz, 1H), 4.30 (s, 2H), 3.30 (br, s, 4H), 2.80 (s, 6H), 1.07 (br, s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

171.4, 150.2, 142.2, 134.9, 133.2, 130.6, 129.3, 128.7, 128.6, 127.4, 126.6, 125.9, 124.9, 124.8, 124.7, 113.7, 77.3, 77.1, 76.9, 45.4, 43.3, 39.3, 38.7, 14.3, 12.9. IR (neat) 3064, 2973, 1915, 1632, 1510, 1424, 1390, 1287, 1188, 1095, 1043, 909, 827, 769, 735 cm^{-1}; HRMS (ESI) calcd for C24H29N2O: 361.2280 [M+H]+; found: 361.2274.



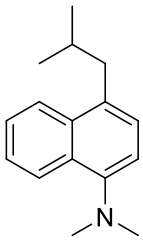
4-ethyl-*N*,*N*-dimethylnaphthalen-1-amine (2i)

Brown oil (26.3 mg, 44% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.32–8.25 (m, 1H), 8.04–7.99 (m, 1H), 7.53–7.42 (m, 2H), 7.24 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 3.10–2.98 (m, 2H), 2.86 (s, 6H), 1.35 (t, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 134.9, 132.9, 129.2, 125.6, 124.8, 124.7, 124.2, 113.9, 77.4, 77.1, 76.8, 45.4, 25.7, 15.1. IR (neat) 3064, 2958, 2867, 2828, 2781, 1732, 1659, 1583, 1495, 1454, 1390, 1265, 1187, 1154, 1043, 965, 900, 832, 766, 738 cm^{-1}; HRMS (ESI) calcd for C14H18N: 200.1439. [M+H]+; found: 200.1439.



***N*,*N*-dimethyl-4-propylnaphthalen-1-amine (2j)**

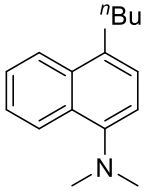
Brown oil (41.6 mg, 65% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.31–8.27 (m, 1H), 8.07–7.95 (m, 1H), 7.52–7.45 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 2.98 (dd, J = 8.7, 6.8 Hz, 2H), 2.86 (s, 6H), 1.81–1.71 (m, 2H), 1.02 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0, 129.1, 125.7, 125.6, 124.8, 124.7, 124.4, 113.9, 77.4, 77.1, 76.7, 45.5, 35.0, 24.0, 14.3. IR (neat) 3068, 2956, 2868, 2828, 2782, 1663, 1583, 1511, 1458, 1391, 1303, 1188, 1045, 993, 911, 828, 765 cm^{-1}; HRMS (ESI) calcd for C15H20N: 214.1596. [M+H]+; found: 214.1585.



4-isobutyl-*N*,*N*-dimethylnaphthalen-1-amine (2k)

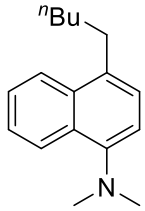
Brown oil (60.0 mg, 88% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, J = 6.5, 3.5 Hz, 1H), 7.90 (dd, J = 6.5, 3.4 Hz, 1H), 7.38 (dd, J = 6.7, 3.4 Hz, 2H), 7.09 (d, J = 7.5 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 2.77 (s, 7H), 2.75 (s, 1H), 2.00–1.88 (m, 1H), 0.88 (dd, J = 6.6, 1.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 133.3, 132.5, 129.3, 126.9, 125.4, 124.7, 124.6, 113.6, 77.4, 77.1, 76.7, 45.4, 42.5, 29.4, 29.2, 22.9. IR (neat) 3069, 2952, 2865, 2827, 2782, 1659, 1583, 1511, 1461, 1303, 1254, 1188, 1144, 1046, 1008, 909, 840, 812, 765 cm^{-1}; HRMS (ESI) calcd for

C16H22N: 228.1752. [M+H]+; found: 228.1742.



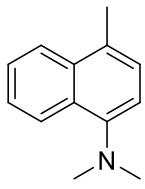
4-butyl-*N*,*N*-dimethylnaphthalen-1-amine (2l)

Brown oil (44.3 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33–8.24 (m, 1H), 8.06–7.96 (m, 1H), 7.52–7.42 (m, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 3.06–2.94 (m, 2H), 2.85 (s, 6H), 1.75–1.67 (m, 2H), 1.49–1.40 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 133.7, 133.0, 129.3, 125.7, 125.5, 124.8, 124.4, 113.8, 77.4, 77.1, 76.8, 45.4, 33.1, 32.7, 23.0, 14.1. IR (neat) 3068, 2954, 2931, 2861, 2827, 2782, 1663, 1583, 1458, 1391, 1296, 1185, 1044, 1002, 904, 830, 765 cm^{-1}; HRMS (ESI) calcd for C16H22N: 228.1752. [M+H]+; found: 228.1742.



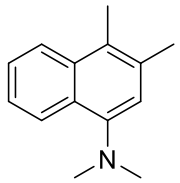
***N*,*N*-dimethyl-4-pentylnaphthalen-1-amine (2m)**

Brown oil (47.1 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–8.27 (m, 1H), 8.06–7.96 (m, 1H), 7.52–7.41 (m, 2H), 7.21 (s, 1H), 7.00 (dd, J = 7.6, 2.0 Hz, 1H), 2.98 (t, J = 7.9 Hz, 2H), 2.85 (d, J = 2.1 Hz, 6H), 1.73 (t, J = 7.7 Hz, 2H), 1.49–1.30 (m, 4H), 0.93–0.89 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 133.7, 133.0, 129.3, 125.6, 125.5, 124.8, 124.7, 124.4, 113.8, 77.4, 77.1, 76.7, 45.4, 32.9, 32.1, 30.7, 22.7, 14.2. IR (neat) 3068, 2954, 2859, 2782, 1667, 1583, 1503, 1459, 1390, 1303, 1188, 1120, 1095, 1046, 910, 828, 765, 719 cm^{-1}; HRMS (ESI) calcd for C17H24N: 242.1909. [M+H]+; found: 242.1898.



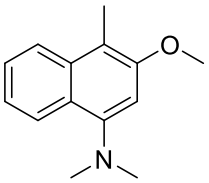
***N*,*N*-4-trimethylnaphthalen-1-amine (2n)[5]**

Brown oil (46.7 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28–8.15 (m, 1H), 7.93–7.84 (m, 1H), 7.45–7.40 (m, 2H), 7.20–7.10 (m, 1H), 6.92 (dd, J = 7.5, 1.7 Hz, 1H), 2.80 (d, J = 1.8 Hz, 6H), 2.56 (d, J = 1.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.7, 128.9, 126.3, 125.6, 125.0, 124.6, 124.5, 113.8, 77.4, 77.0, 76.7, 45.5, 19.2.



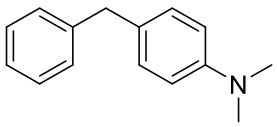
***N*,*N*,3,4-tetramethylnaphthalen-1-amine (2o)**

Brown oil (16.2 mg, 27% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–8.21 (m, 1H), 8.03–7.96 (m, 1H), 7.50–7.37 (m, 2H), 6.91 (s, 1H), 2.86 (s, 6H), 2.53 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 134.0, 132.8, 127.6, 125.9, 125.7, 124.4, 124.1, 123.9, 117.5, 77.4, 77.1, 76.7, 45.4, 21.1, 14.3. IR (neat) 3069, 2935, 2864, 2826, 2781, 1732, 1594, 1516, 1454, 1411, 1387, 1285, 1265, 1189, 1145, 1097, 1042, 907, 859, 760, 739 cm^{-1}; HRMS (ESI) calcd for C14H18N: 200.1439. [M+H]+; found: 200.1431.



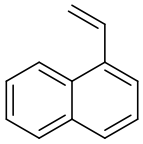
3-methoxy-*N*,*N*,4-trimethylnaphthalen-1-amine (2p)

Brown solid (55.5 mg, 86% yield) mp 55-57 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.48–7.44 (m, 1H), 7.36 (t, J = 7.6 Hz, 1H), 6.91 (s, 1H), 3.94 (s, 3H), 2.90 (s, 6H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 150.5, 134.6, 126.2, 124.7, 124.4, 123.9, 122.7, 114.3, 103.6, 77.3, 77.0, 76.7, 68.0, 57.1, 45.4, 10.3. IR (KBr) 3070, 2987, 2936, 2828, 2782, 1616, 1585, 1455, 1385, 1294, 1239, 1110, 1028, 906, 840, 756, 709 cm^{-1}; HRMS (ESI) calcd for C14H18NO: 216.1388. [M+H]+; found: 216.1379.



4-benzyl-*N*,*N*-dimethylaniline (2q)[6]

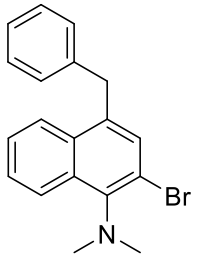
Yellow oil (11.4 mg, 21% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 2H), 7.10 (d, J = 7.2 Hz, 3H), 6.98 (d, J = 8.5 Hz, 2H), 6.61 (d, J = 8.5 Hz, 2H), 3.81 (s, 2H), 2.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 142.1, 129.6, 129.5, 128.8, 128.4, 125.8, 113.0, 77.4, 77.1, 76.7, 41.0, 40.9.



1-vinylnaphthalene (2ib)[7]

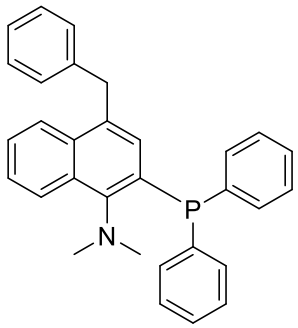
Colorless oil (8.4 mg, 18% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.06 (m, 1H), 7.87–7.79 (m, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.66–7.58 (m, 1H), 7.57–7.38 (m, 4H), 5.78 (dd, J = 17.3, 1.6

Hz, 1H), 5.46 (dd, J = 10.9, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 134.4, 133.6, 131.2, 128.6, 128.2, 126.1, 125.8, 125.7, 123.8, 123.7, 117.2, 77.4, 77.1, 76.8.



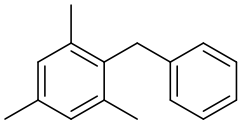
4-benzyl-2-bromo-*N*,*N*-dimethylnaphthalen-1-amine (2ab)

Colorless solid (65.1 mg, 64% yield) mp 56-58 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36–8.30 (m, 1H), 7.90–7.87 (m, 1H), 7.47–7.37 (m, 2H), 7.35 (d, J = 0.9 Hz, 1H), 7.27–7.19 (m, 2H), 7.17–7.12 (m, 3H), 4.29 (s, 2H), 2.99 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 140.1, 135.9, 134.9, 132.5, 132.4, 128.8, 128.7, 126.4, 126.3, 126.2, 125.4, 124.8, 119.9, 77.5, 77.2, 76.9, 42.8, 38.6. IR (KBr) 3063, 2924, 2855, 2787, 1732, 1651, 1494, 1453, 1386, 1265, 1048, 960, 830, 757, 737, 699 cm^{-1}; HRMS (ESI) calcd for C19H19BrN: 340.0701. [M+H]+; found: 340.0694.



4-benzyl-2-(diphenylphosphaneyl)-*N*,*N*-dimethylnaphthalen-1-amine (2ac)

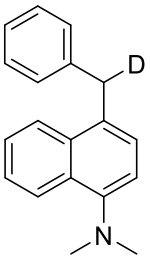
Yellowish oil (123.6 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 19.4, 8.1 Hz, 2H), 7.44–7.36 (m, 2H), 7.31–7.25 (m, 10H), 7.12 (dd, J = 19.4, 7.1 Hz, 3H), 7.02 (d, J = 7.4 Hz, 2H), 6.78 (d, J = 3.1 Hz, 1H), 4.21 (s, 2H), 2.84 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 152.0, 140.5, 138.9, 138.8, 135.9, 134.8, 134.2, 134.1, 133.9, 132.7, 131.4, 128.7, 128.6, 128.5, 128.4, 126.3, 126.1, 125.6, 125.5, 125.1, 125.0, 77.6, 77.2, 76.9, 44.3, 44.2, 39.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ -14.12. IR (neat) 3064, 2926, 2855, 2784, 1735, 1643, 1492, 1454, 1380, 1282, 1177, 1049, 961, 744, 699 cm^{-1}; HRMS (ESI) calcd for C31H29NP: 446.2038. [M+H]+; found: 446.2032.



2-benzyl-1,3,5-trimethylbenzene (5)[8]

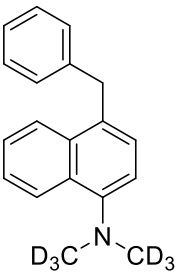
Colourless oil (195.6 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 7.7 Hz, 2H), 7.17–7.07 (m, 1H), 7.07–6.95 (m, 2H), 6.88 (s, 2H), 4.00 (s, 2H), 2.28 (s, 3H), 2.19 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 137.2, 135.8, 133.9, 129.0, 128.5, 128.0, 125.8, 77.5, 77.2, 76.9,

34.8, 21.1, 20.3.



***N*,*N*-dimethyl-4-(phenylmethyl-*d*)naphthalen-1-amine (2a-d_1)**

Yellowish oil (70.1 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–8.25 (m, 1H), 7.92 (dd, J = 8.2, 1.4 Hz, 1H), 7.47–7.34 (m, 2H), 7.25–7.10 (m, 6H), 6.97 (d, J = 7.6 Hz, 1H), 4.34 (s, 1H), 2.83 (s, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 141.1, 133.3, 131.3, 129.3, 128.8, 128.5, 128.4, 127.3, 126.0, 125.9, 124.9, 124.8, 124.7, 113.7, 77.4, 77.1, 76.8, 45.4, 38.9. IR (neat) 3062, 2979, 2862, 2827, 2783, 1731, 1581, 1512, 1494, 1453, 1391, 1306, 1188, 1144, 1013, 910, 826, 767, 713 cm^{-1}; HRMS (ESI) calcd for C19H19DN: 263.1659. [M+H]+; found: 263.1650.



4-benzyl-*N*,*N*-bis(methyl-d_3)naphthalen-1-amine (2a-d_6)

Yellowish oil (77.0 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.43–7.26 (m, 2H), 7.17–7.13 (m, 2H), 7.12–7.02 (m, 4H), 6.89 (d, J = 7.6 Hz, 1H), 4.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 141.1, 133.3, 131.3, 129.3, 128.8, 128.6, 128.5, 127.3, 126.0, 125.9, 125.0, 124.9, 124.8, 113.7, 77.4, 77.1, 76.8, 38.9. IR (neat) 3062, 3026, 2183, 2045, 1582, 1494, 1435, 1393, 1297, 1168, 1124, 1054, 965, 834, 766, 715 cm^{-1}; HRMS (ESI) calcd for C19H14D6N: 268.1972 [M+H]+; found: 268.1967.

10. References.

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[7] Gao Y., Ou Y., and Goo ßen L. J. *Chem. Eur. J.* **2019**, 25(37), 8709–8712.

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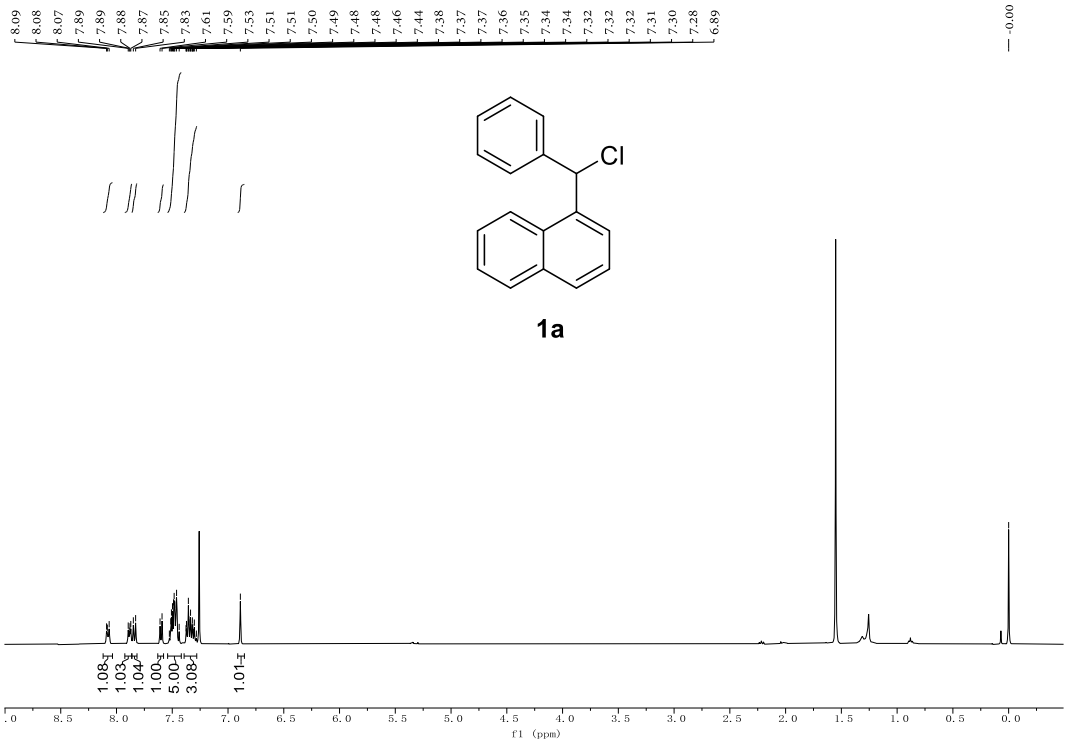
11. Copies of ^{1}H, ^{13}C, ^{19}F , ^{31}P NMR and HMBC Spectra

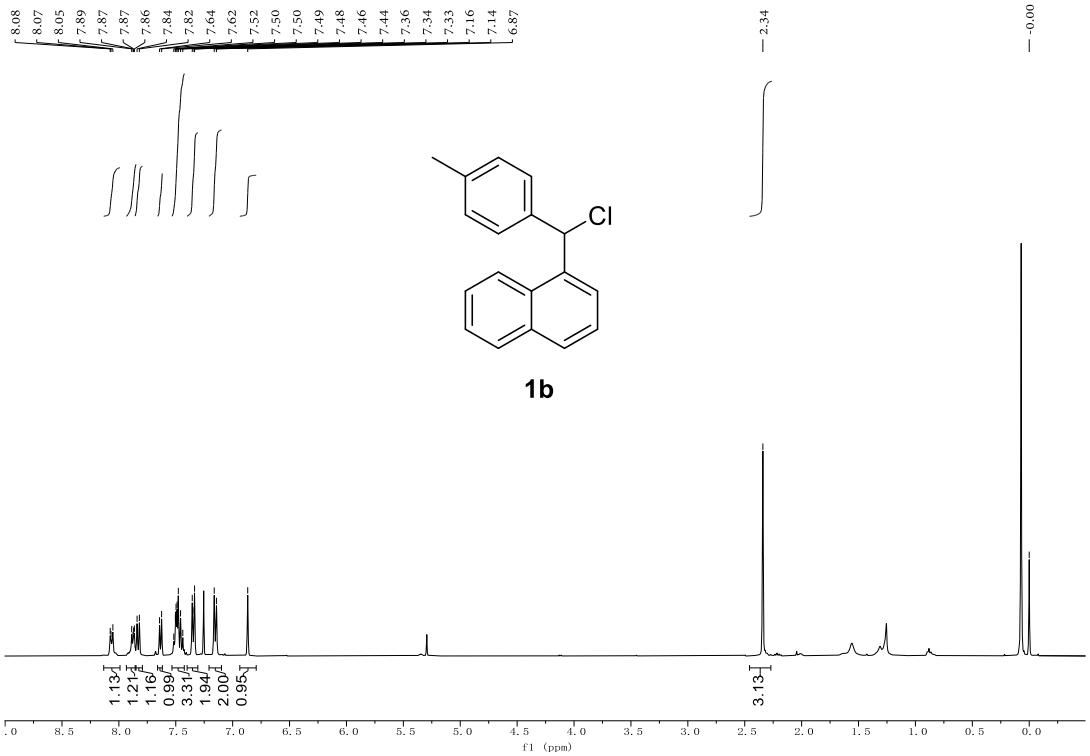
1-(chloro(phenyl)methyl) naphthalene (**1a**)

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



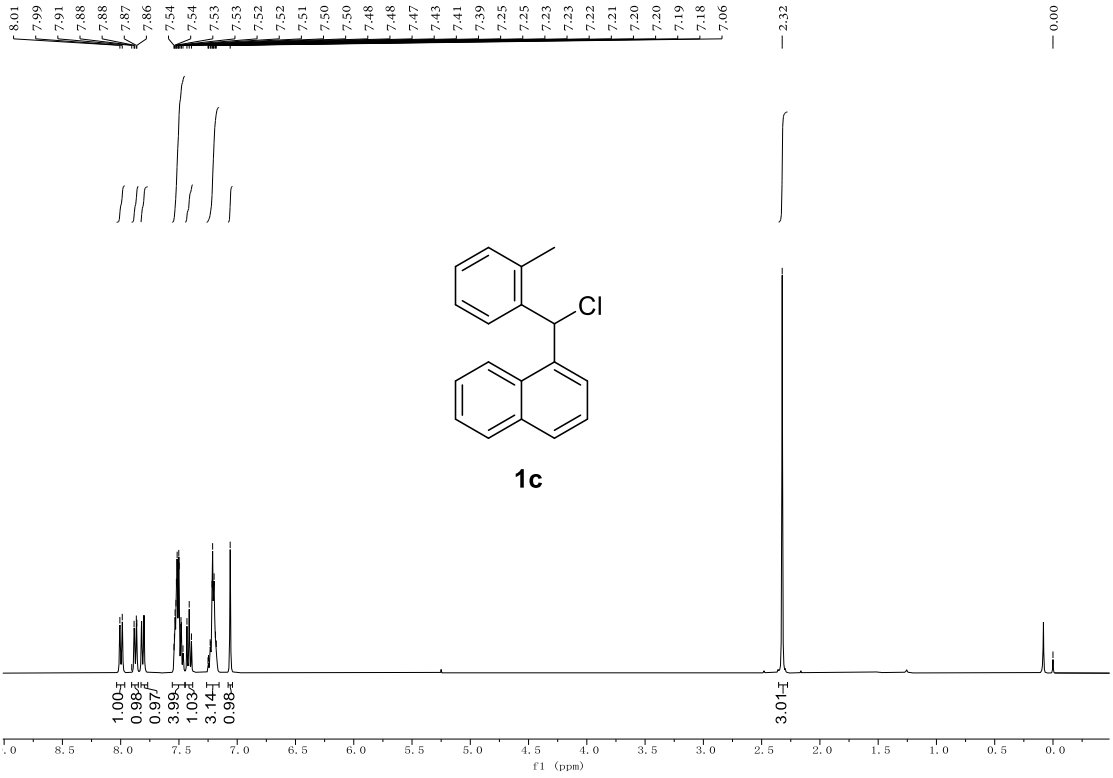
1-(chloro(*p*-tolyl)methyl)naphthalene (**1b**)

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

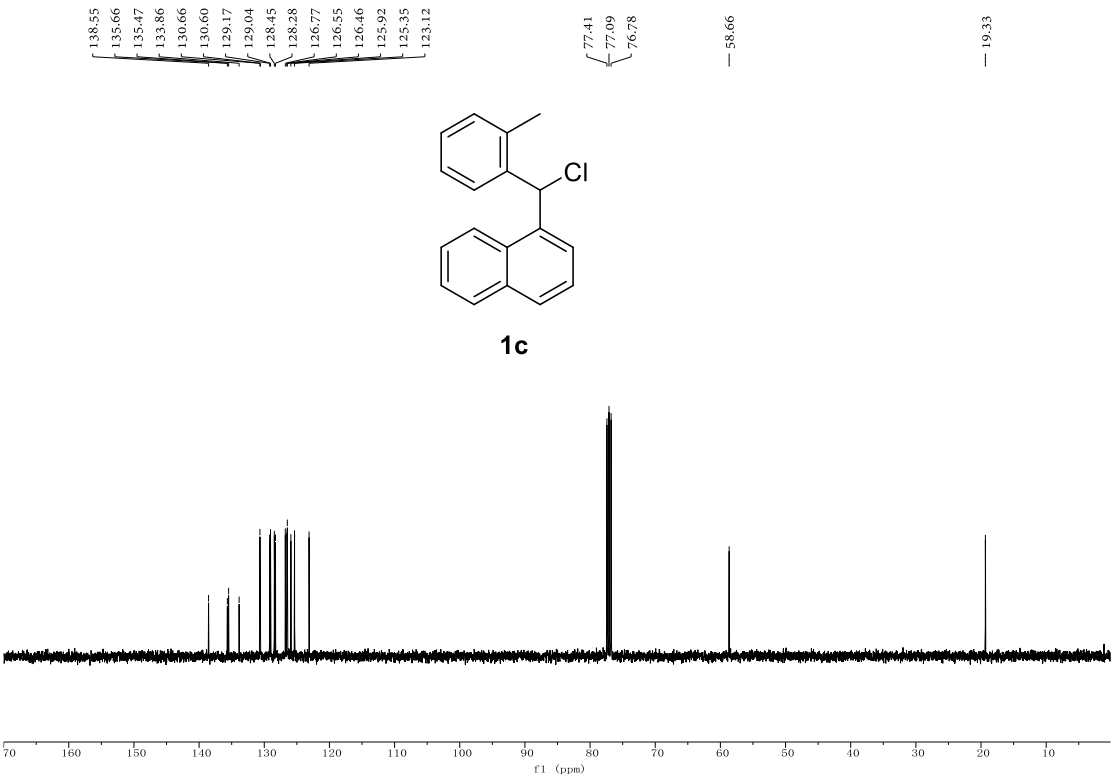


1-(chloro(*o*-tolyl)methyl)naphthalene (**1c**)

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

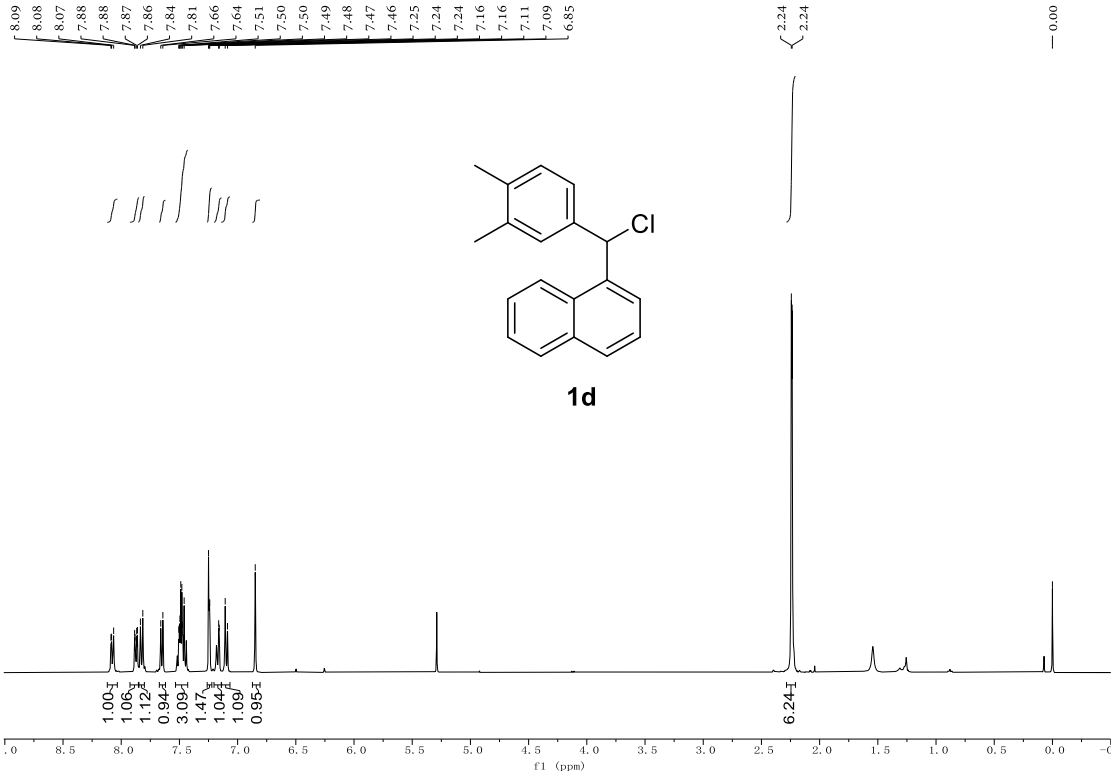


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

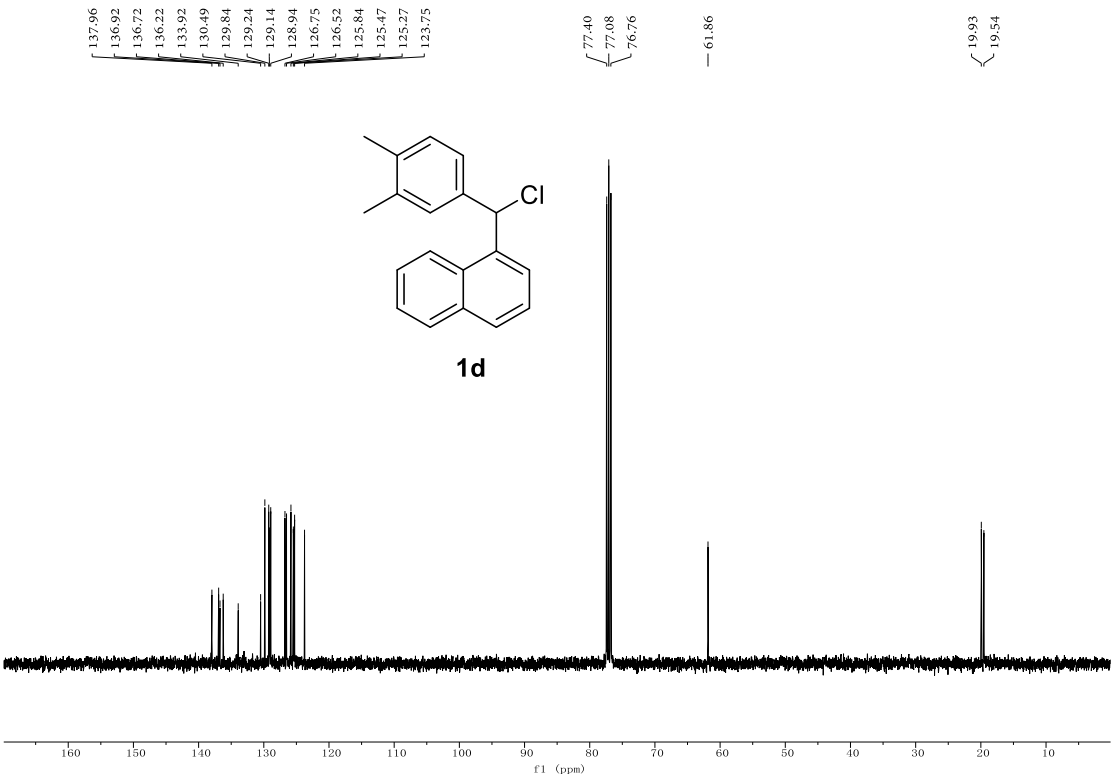


1-(chloro(3,4-dimethylphenyl)methyl)naphthalene (**1d**)

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

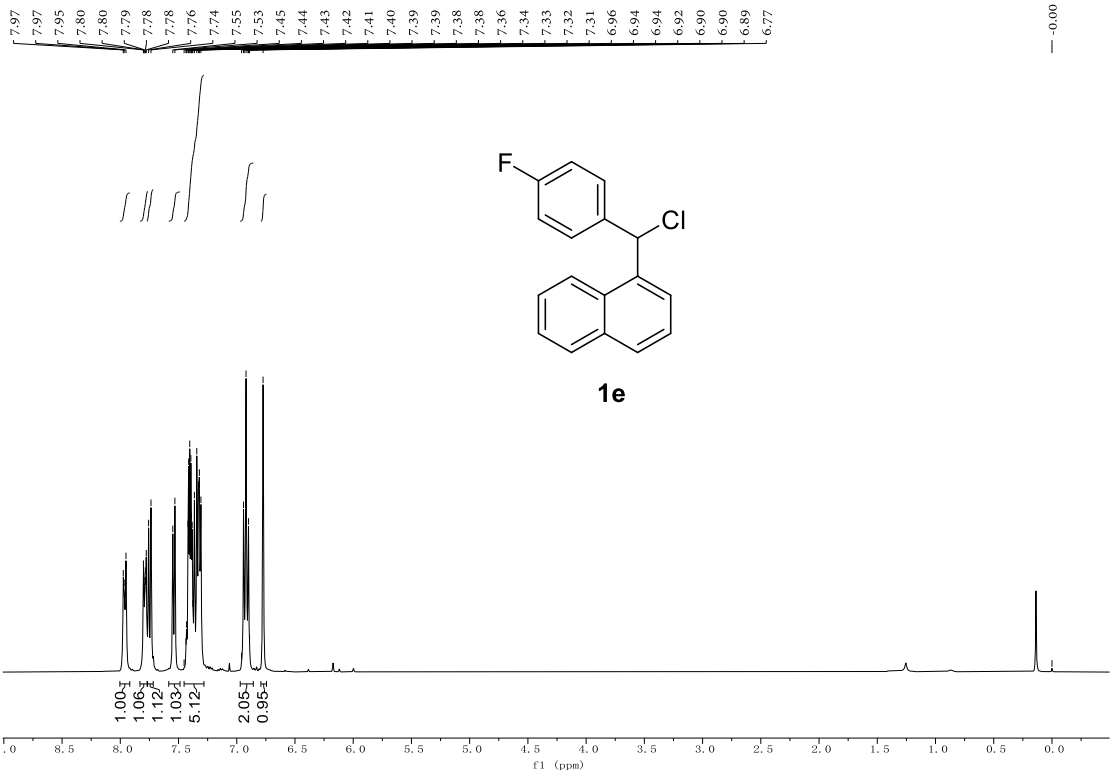


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

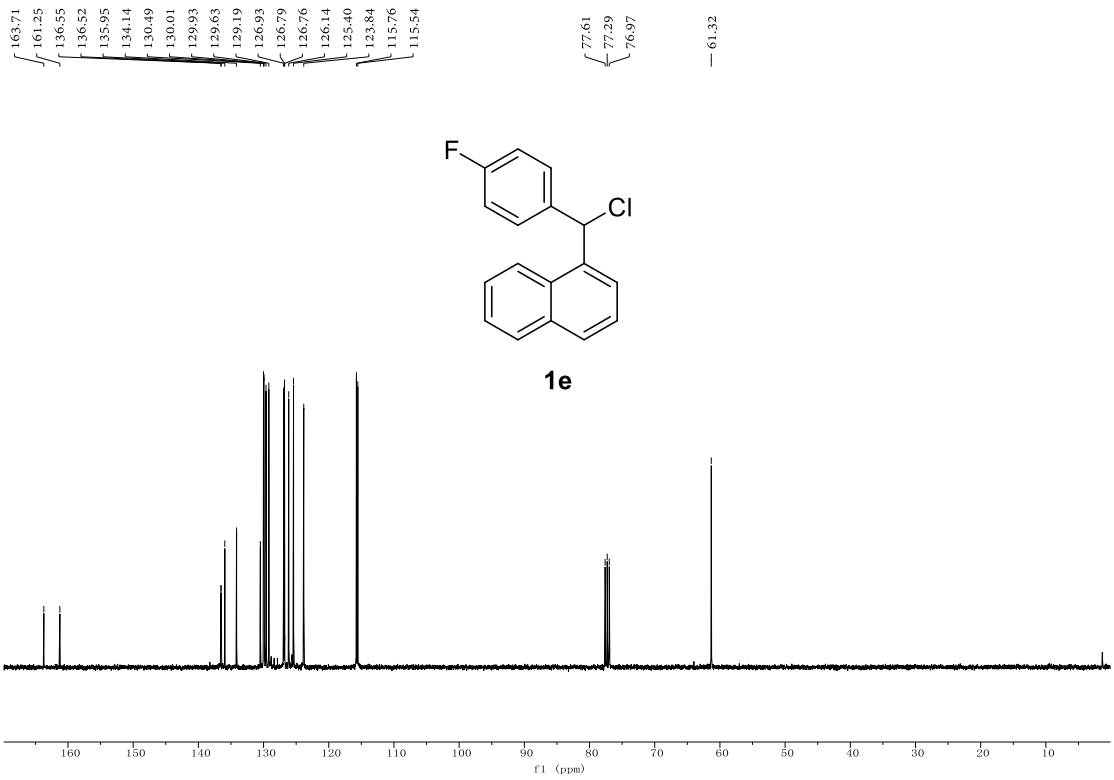


1-(chloro(4-fluorophenyl)methyl)naphthalene (**1e**)

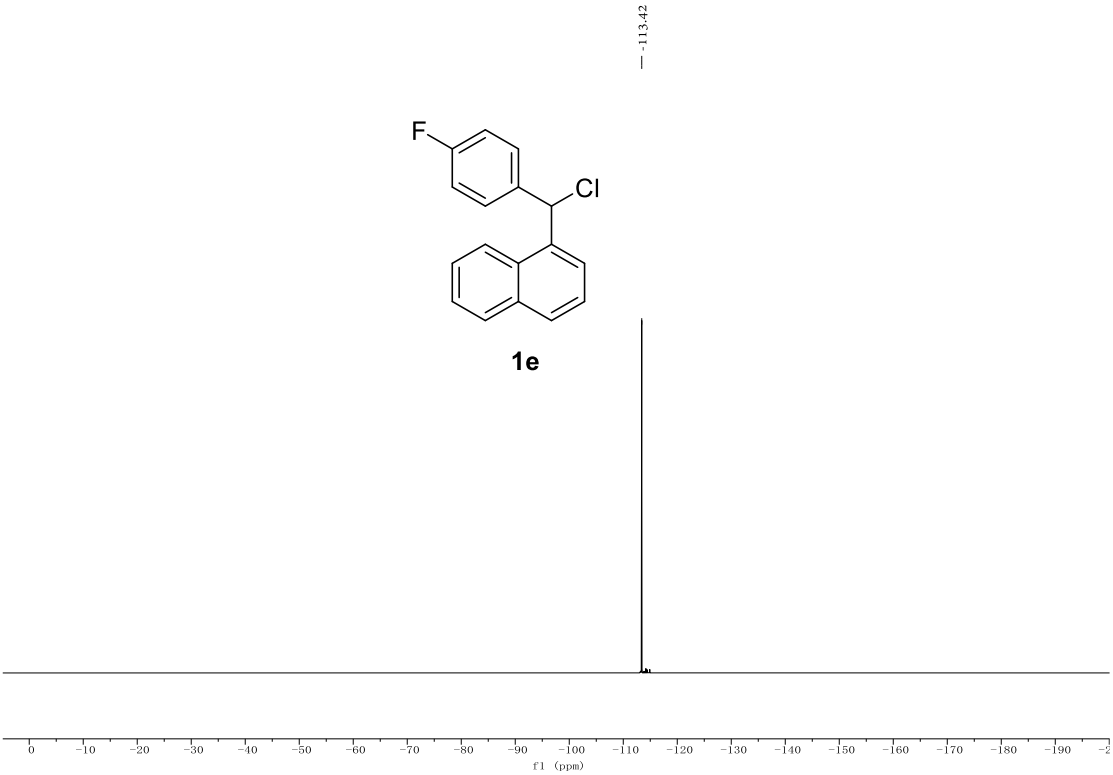
^{1}H NMR, 400 MHz, $CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

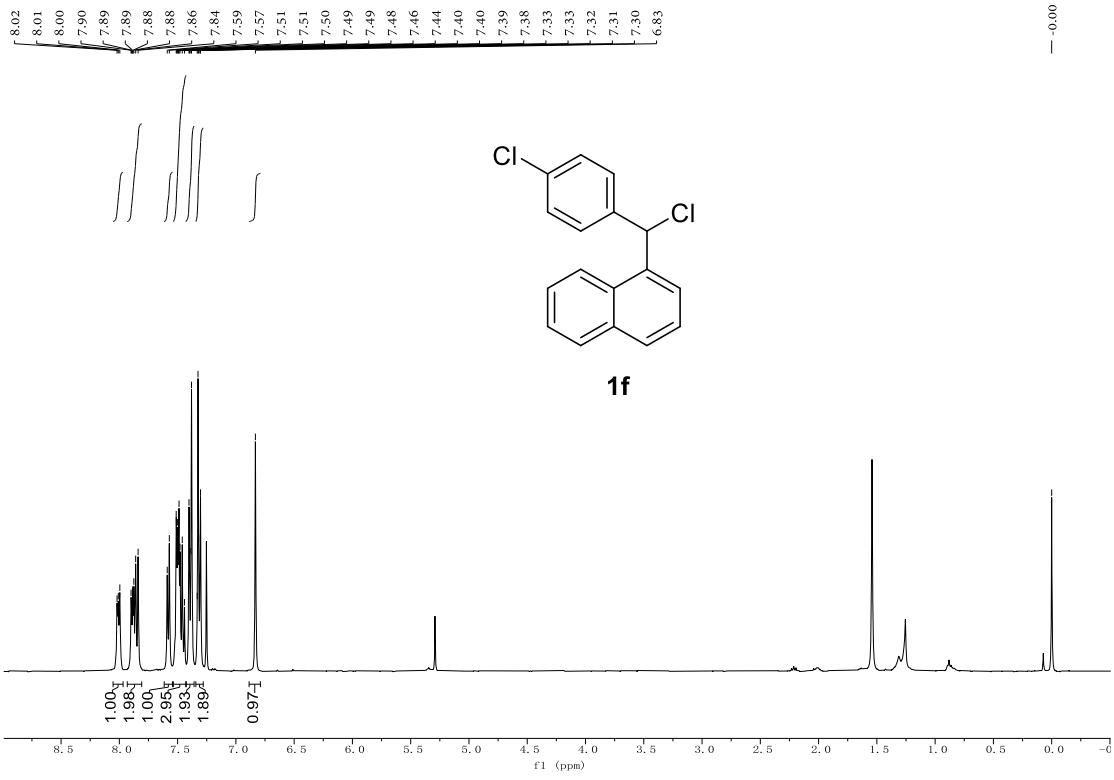


^{19}F NMR, 376 MHz, $CDCl_3$

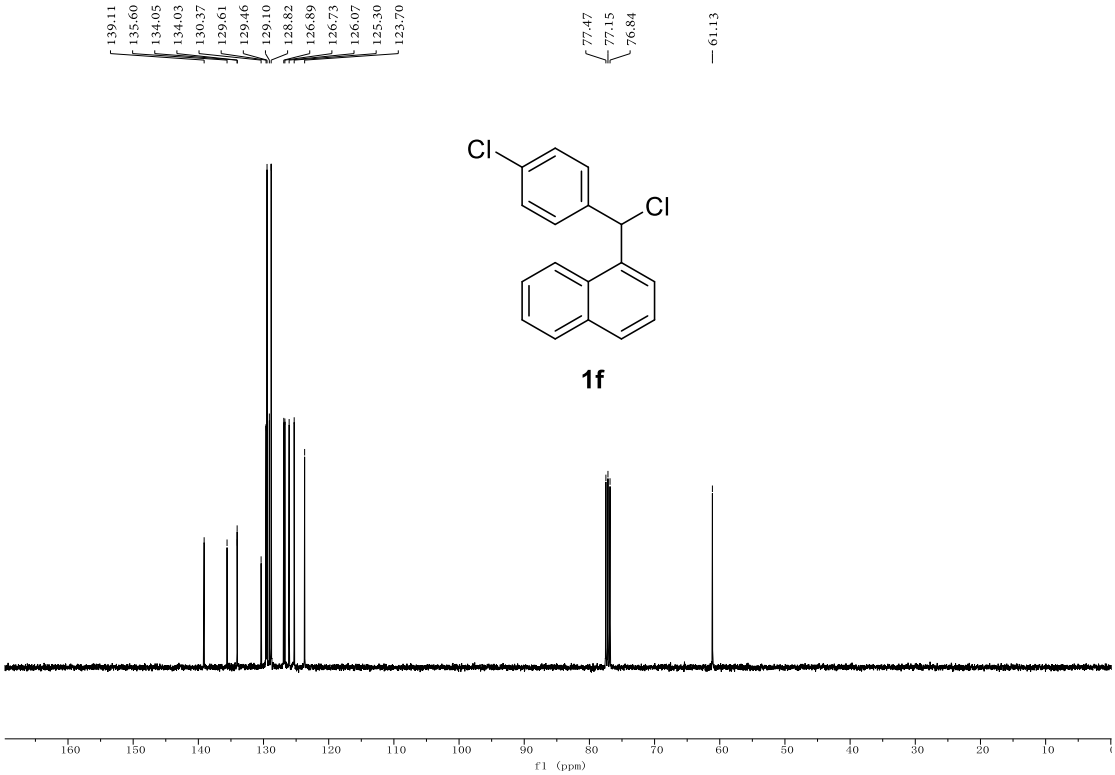


1-(chloro(4-chlorophenyl)methyl)naphthalene (**1f**)

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

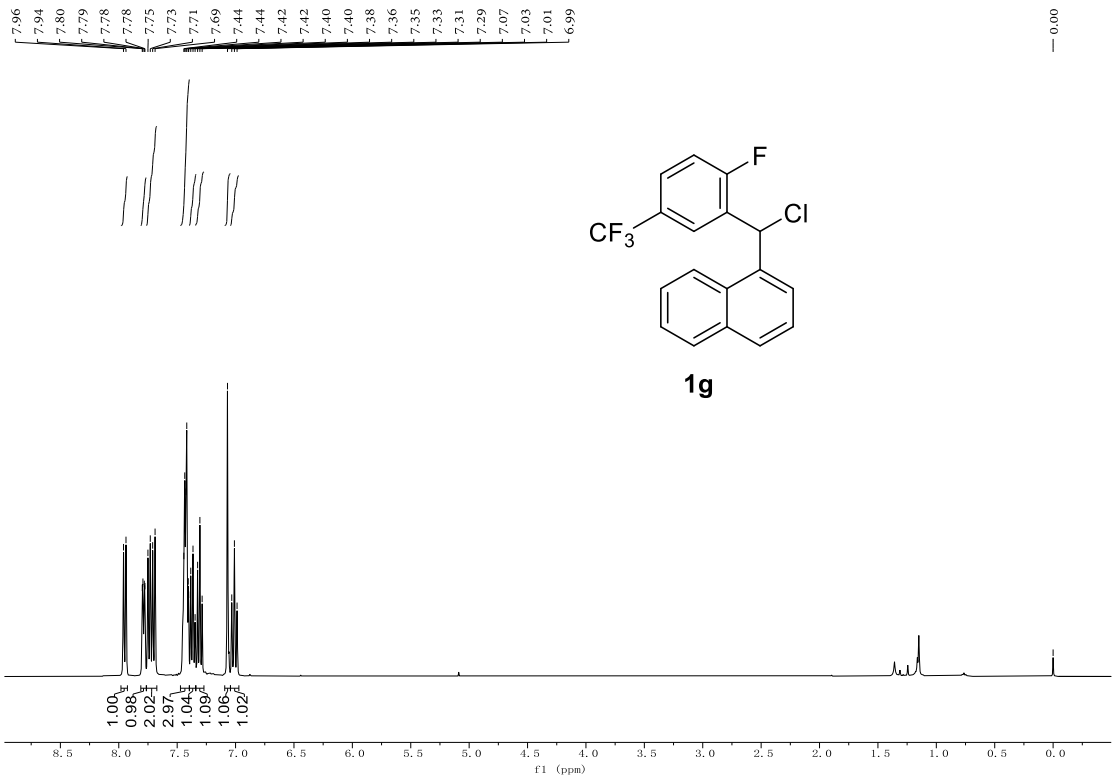


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

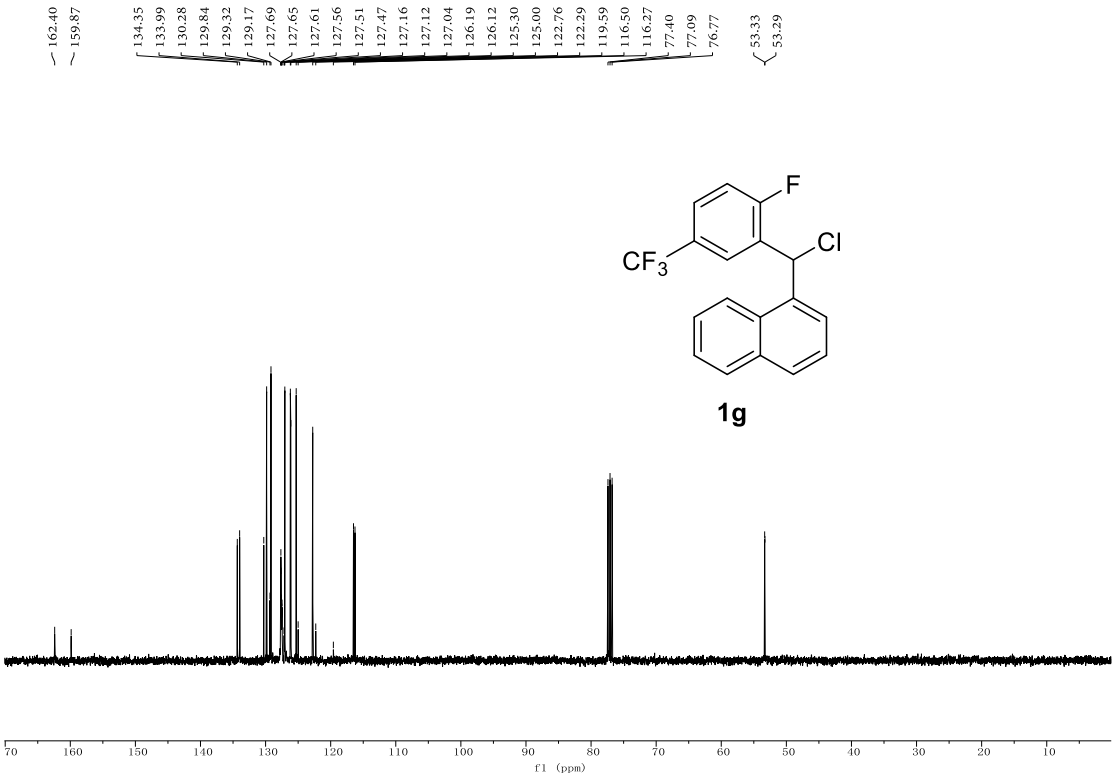


1-(chloro(2-fluoro-5-(trifluoromethyl)phenyl)methyl)naphthalene (**1g**)

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



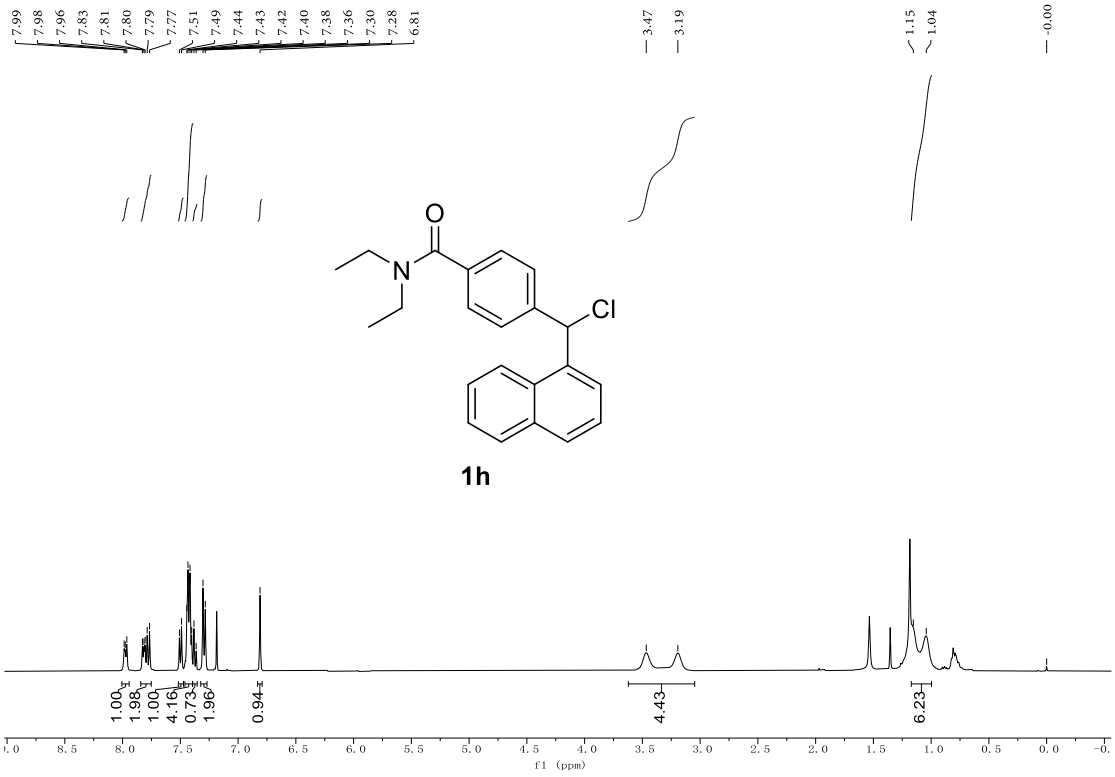
$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



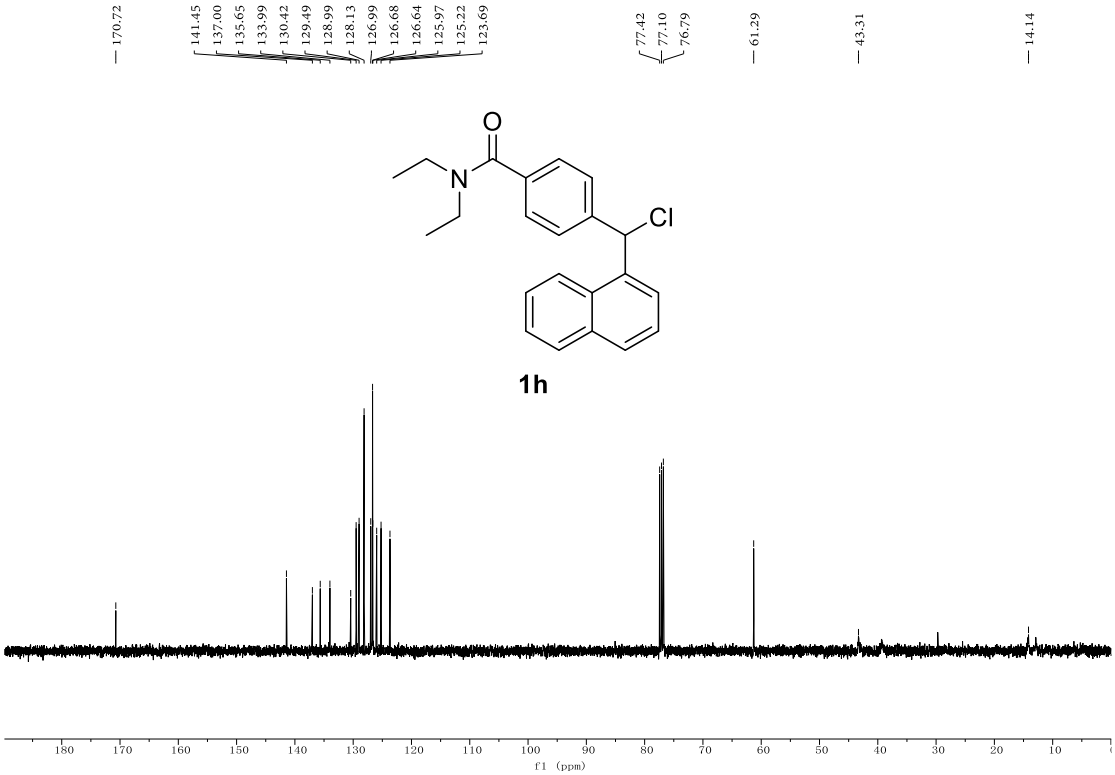
^{19}F NMR, 376 MHz, $CDCl_3$

4-(chloro(naphthalen-1-yl)methyl)-*N*,*N*-diethylbenzamide (**1h**)

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

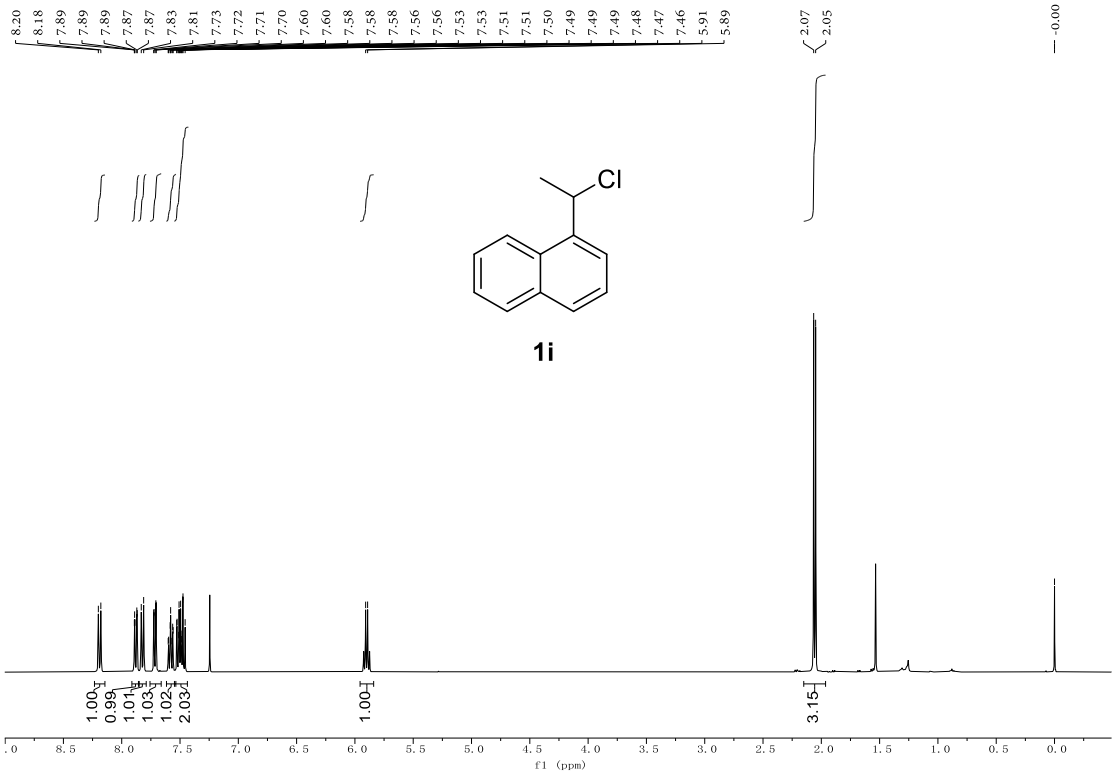


^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$



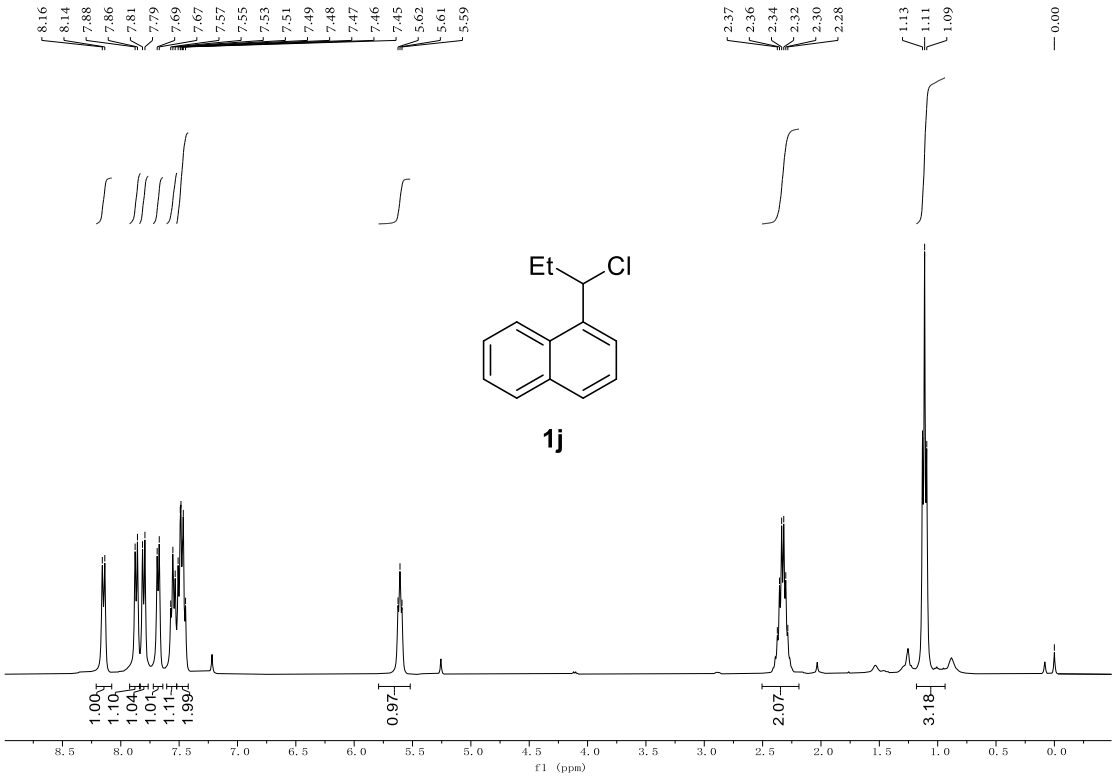
1-(1-chloroethyl)naphthalene (**1i**)

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



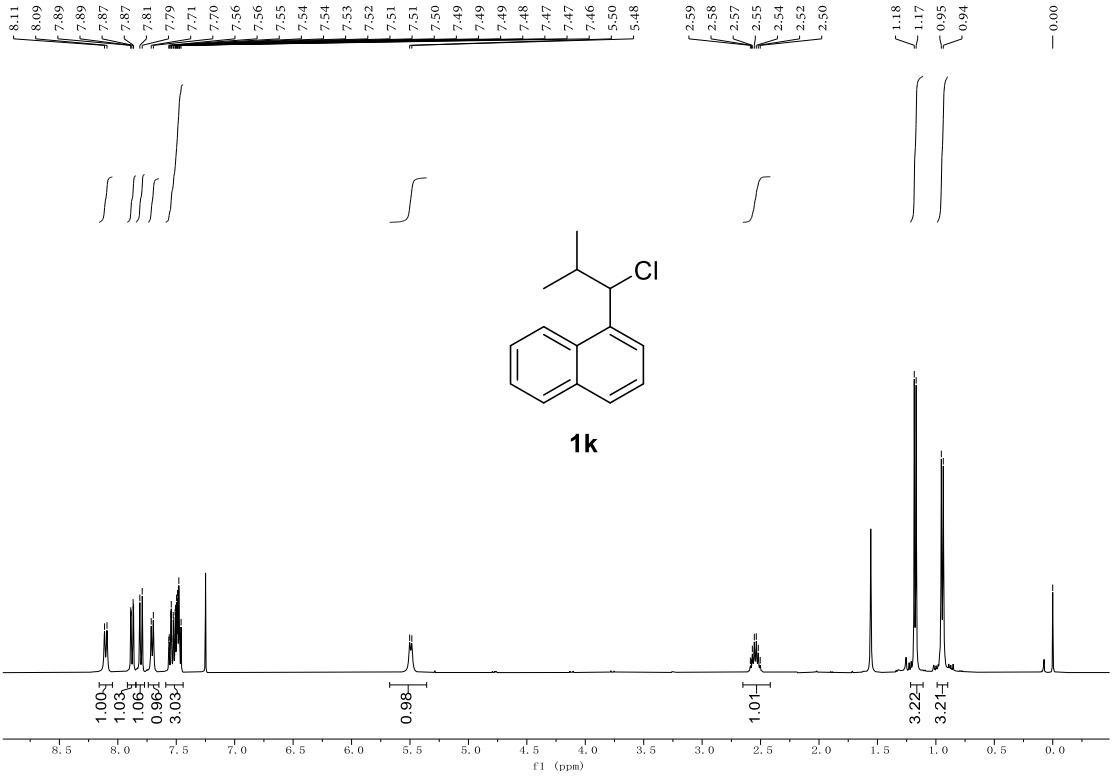
1-(1-chloropropyl)naphthalene (**1j**)

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



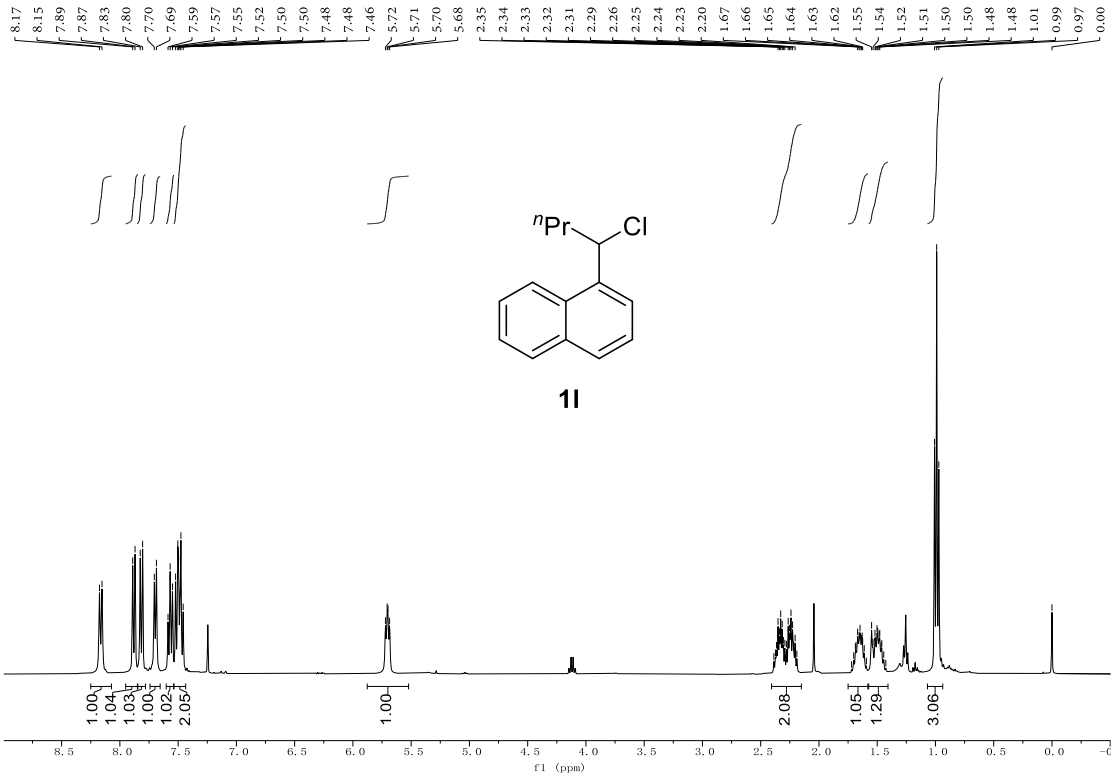
1-(1-chloro-2-methylpropyl)naphthalene (**1k**)

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



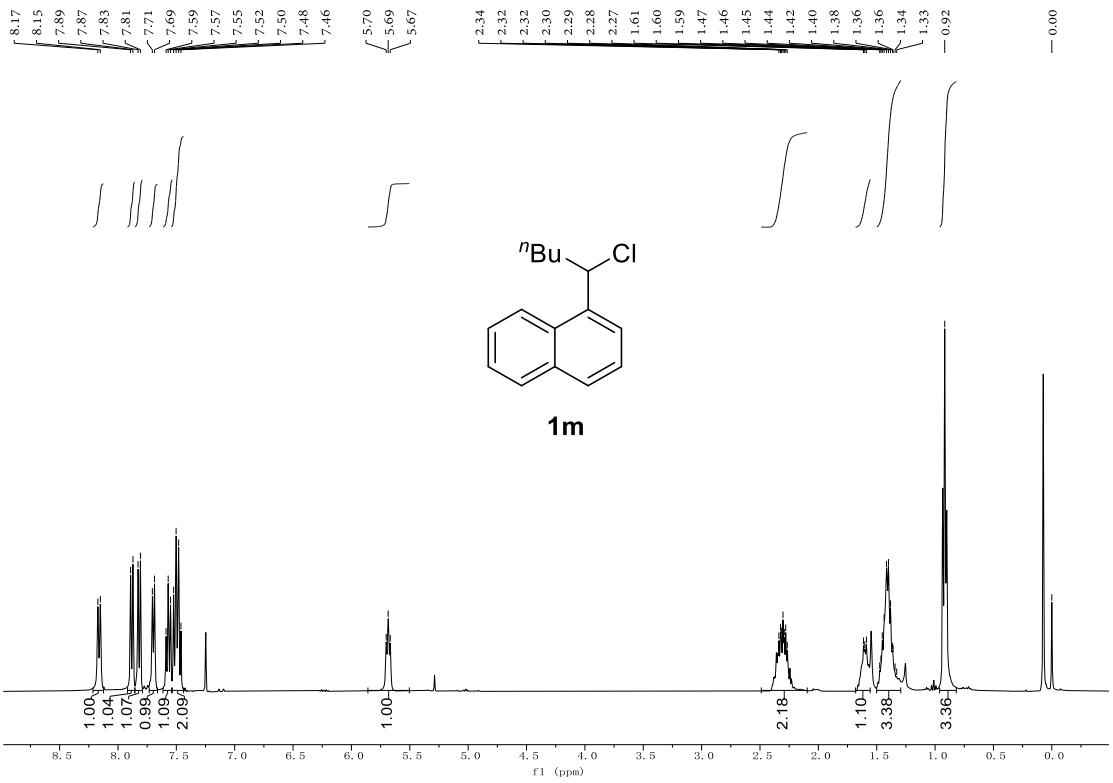
1-(1-chlorobutyl)naphthalene (**1l**)

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



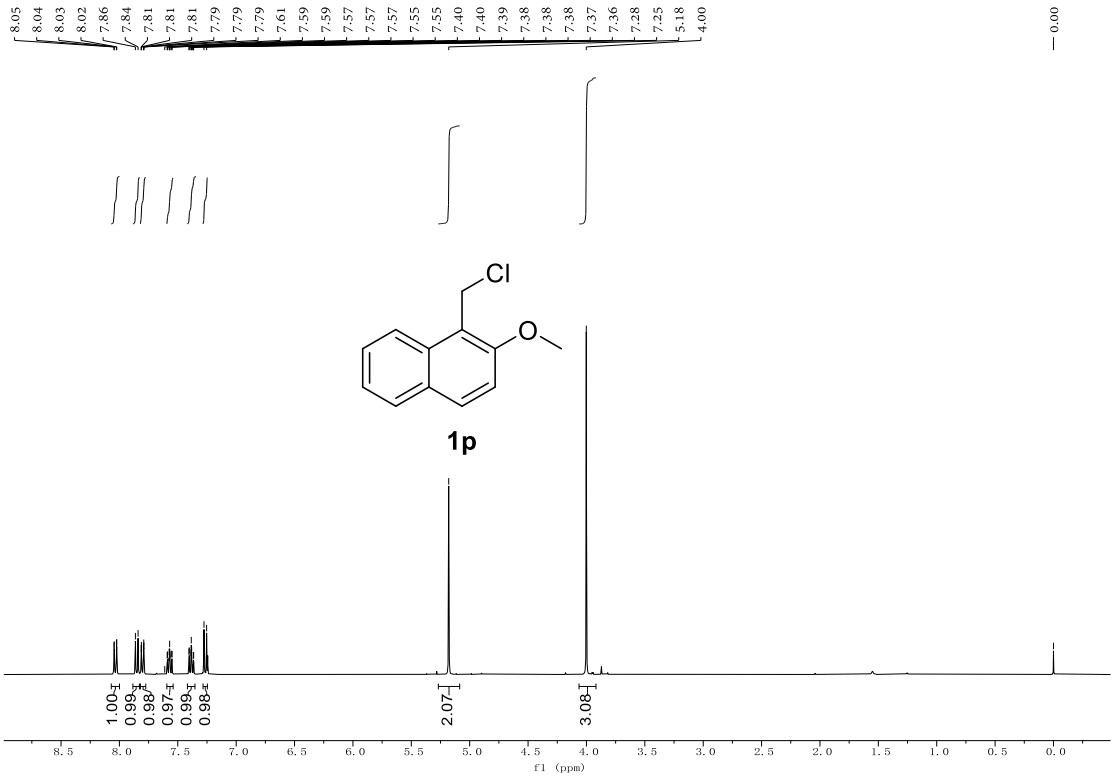
1-(1-chloropentyl)naphthalene (**1m**)

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

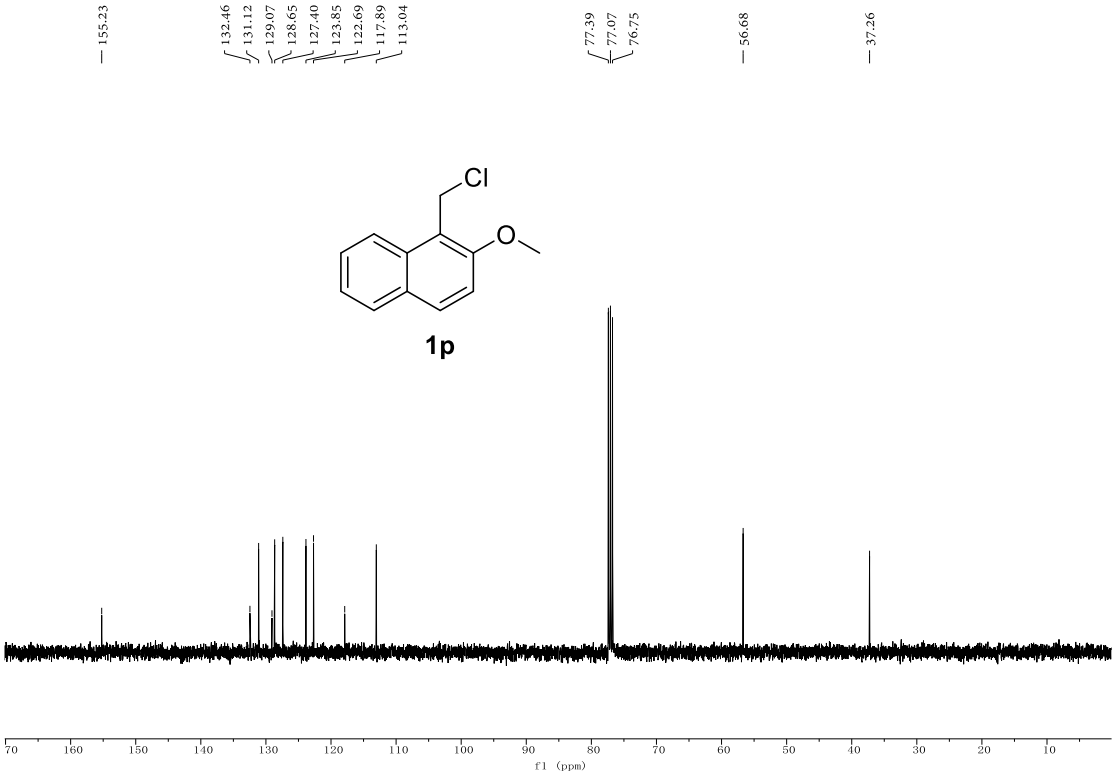


1-(chloromethyl)-2-methoxynaphthalene (**1p**)

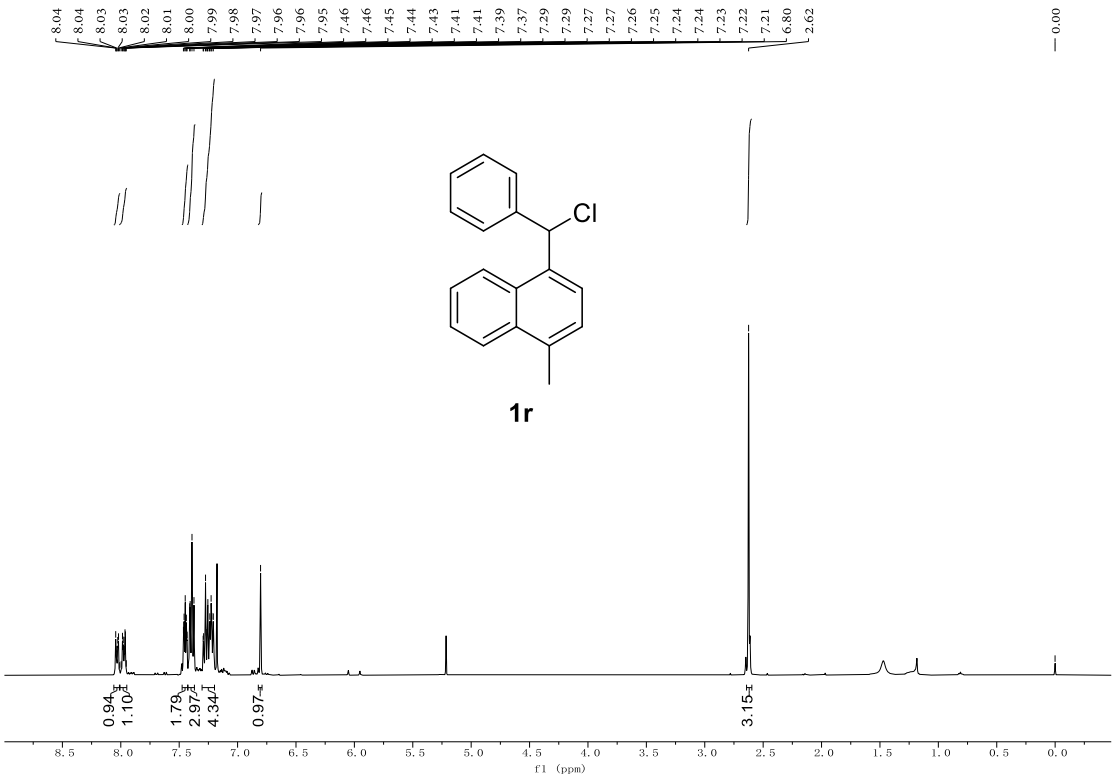
^{1}H NMR, 400 MHz, $CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

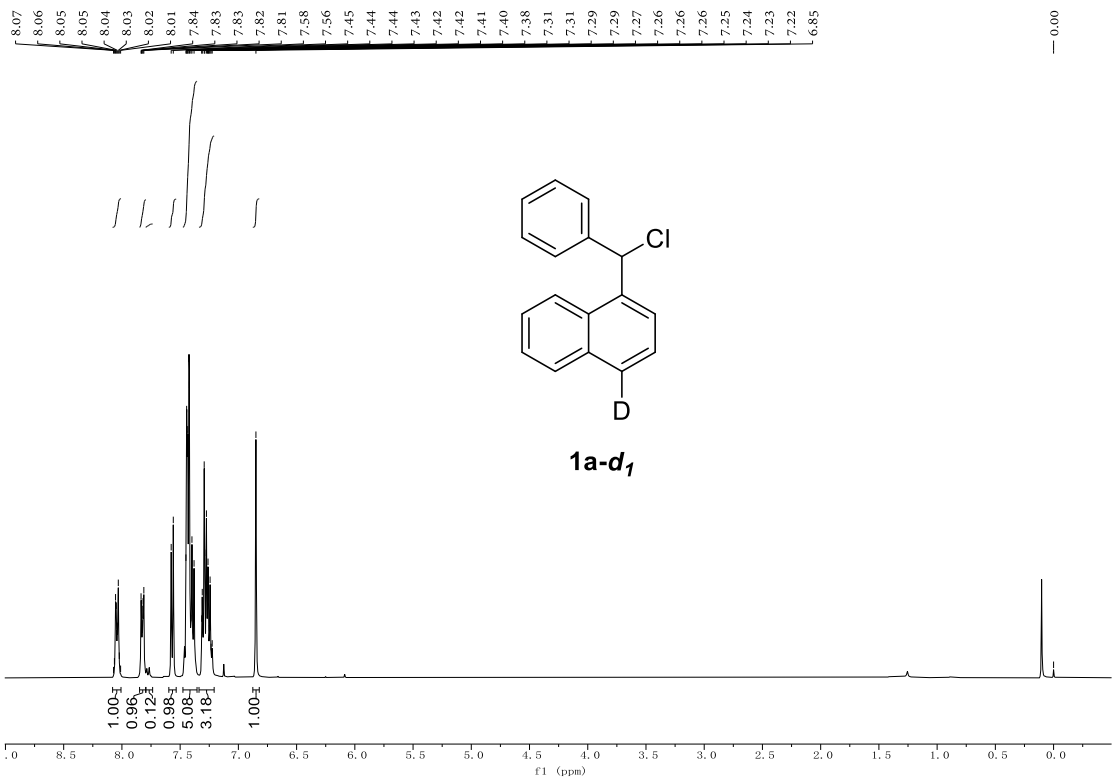


1-(chloro(phenyl)methyl)-4-methylnaphthalene(**1r**)

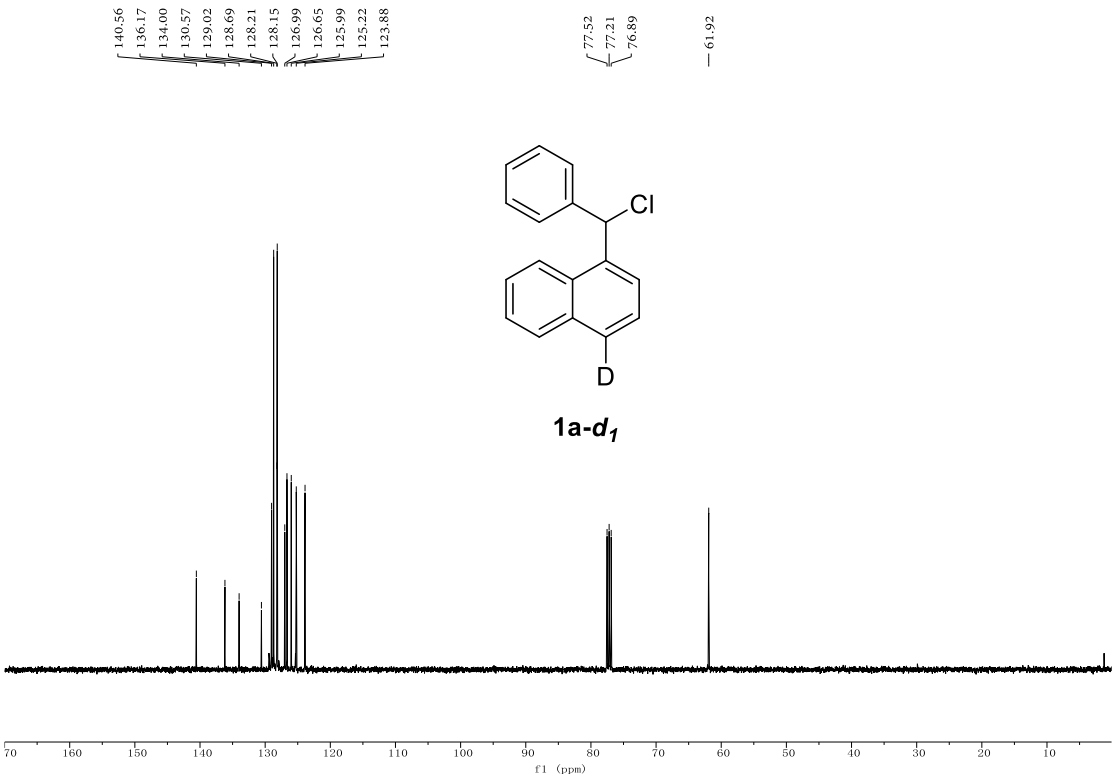


1-(chloro(phenyl)methyl)naphthalene-4-*d* (**1a**-d_1)

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

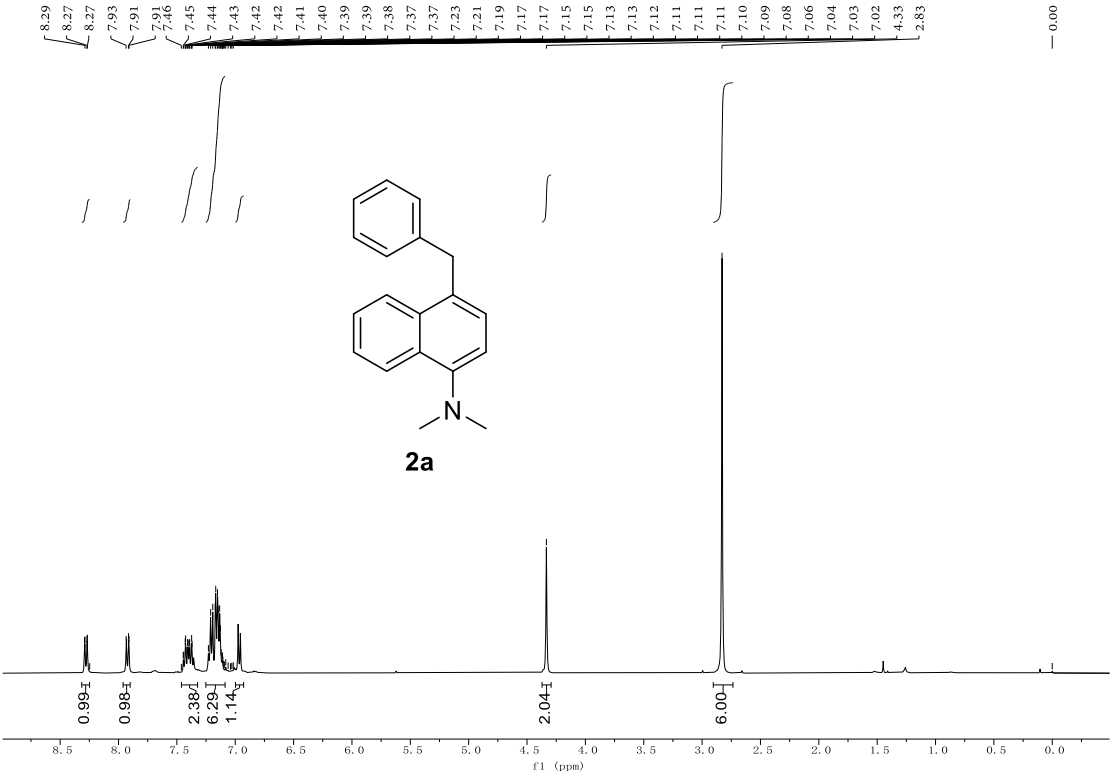


^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$

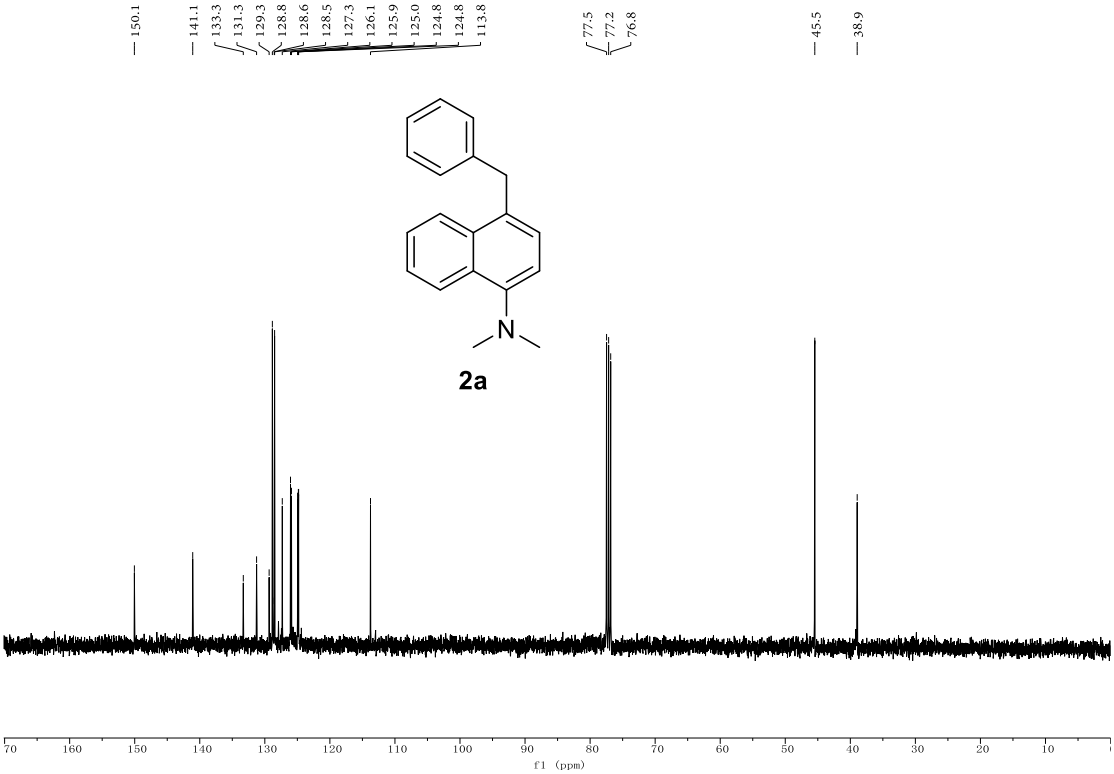


4-benzyl-*N*,*N*-dimethylnaphthalen-1-amine (**2a**)

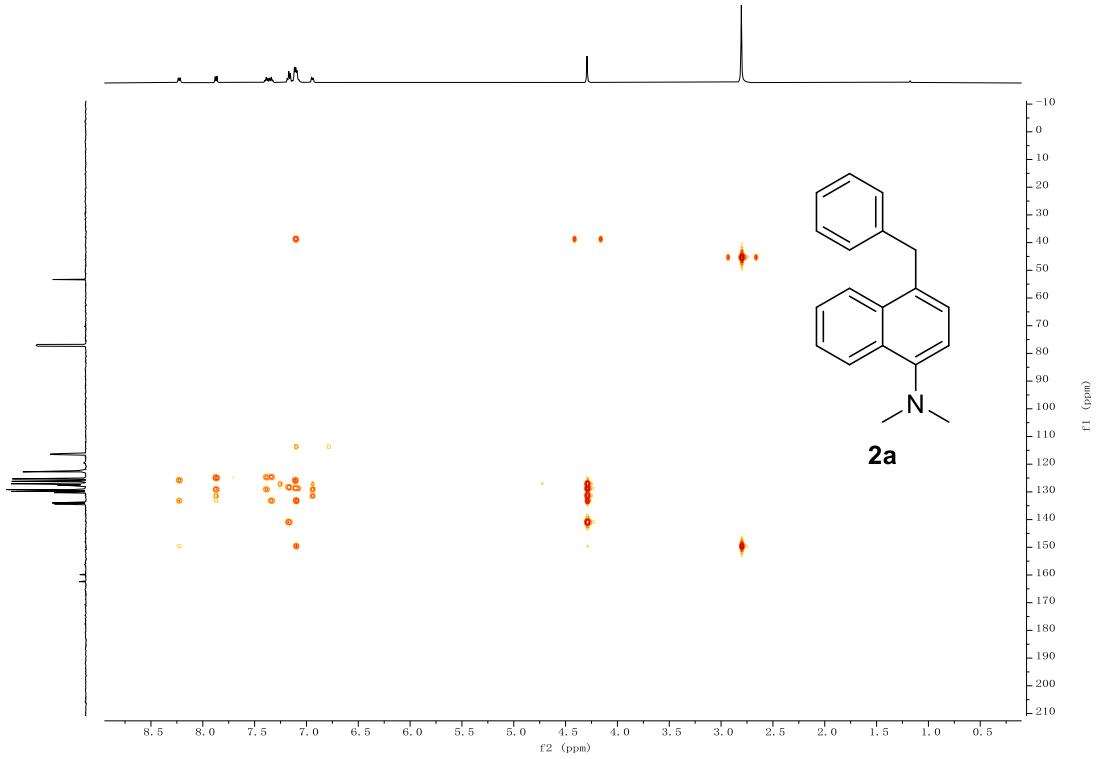
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$

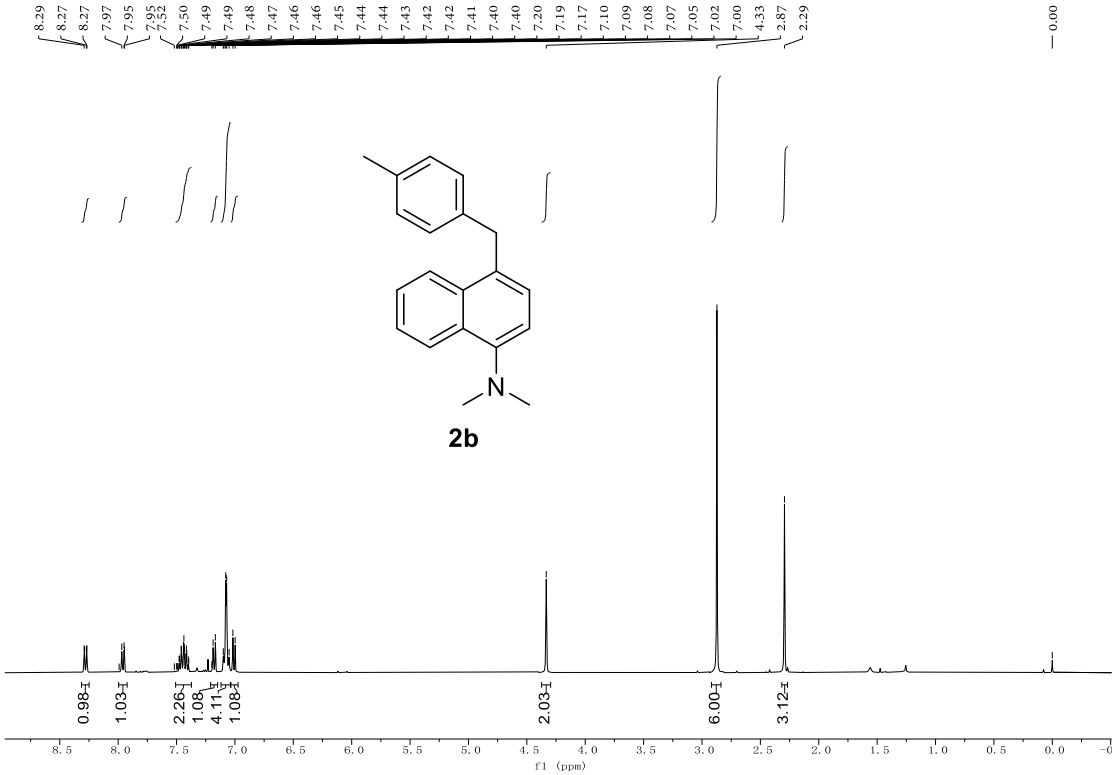


HMBC spectrum

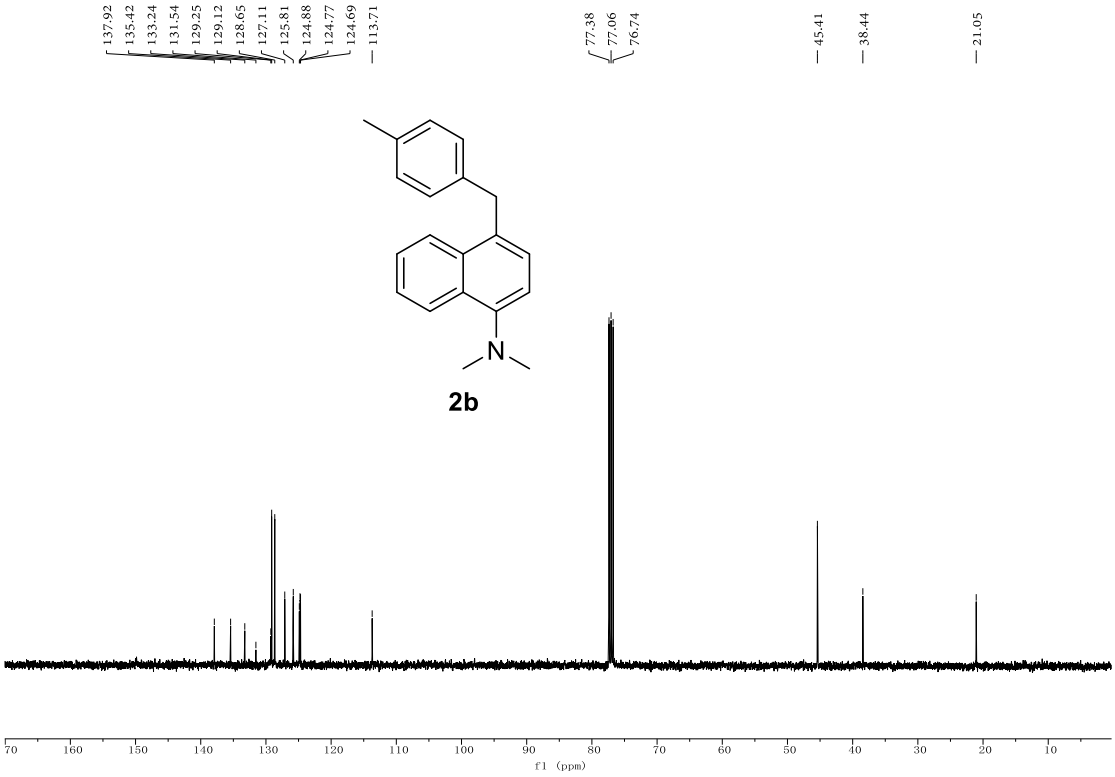


N,*N*-dimethyl-4-(4-methylbenzyl)naphthalen-1-amine (**2b**)

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

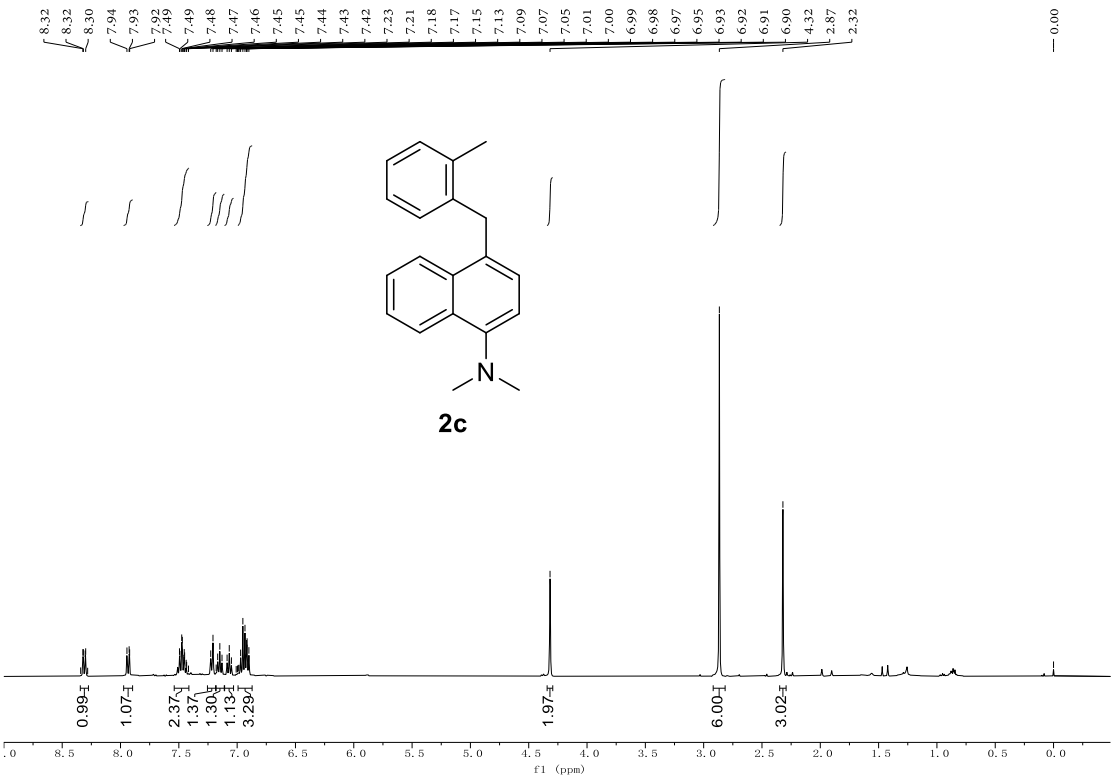


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

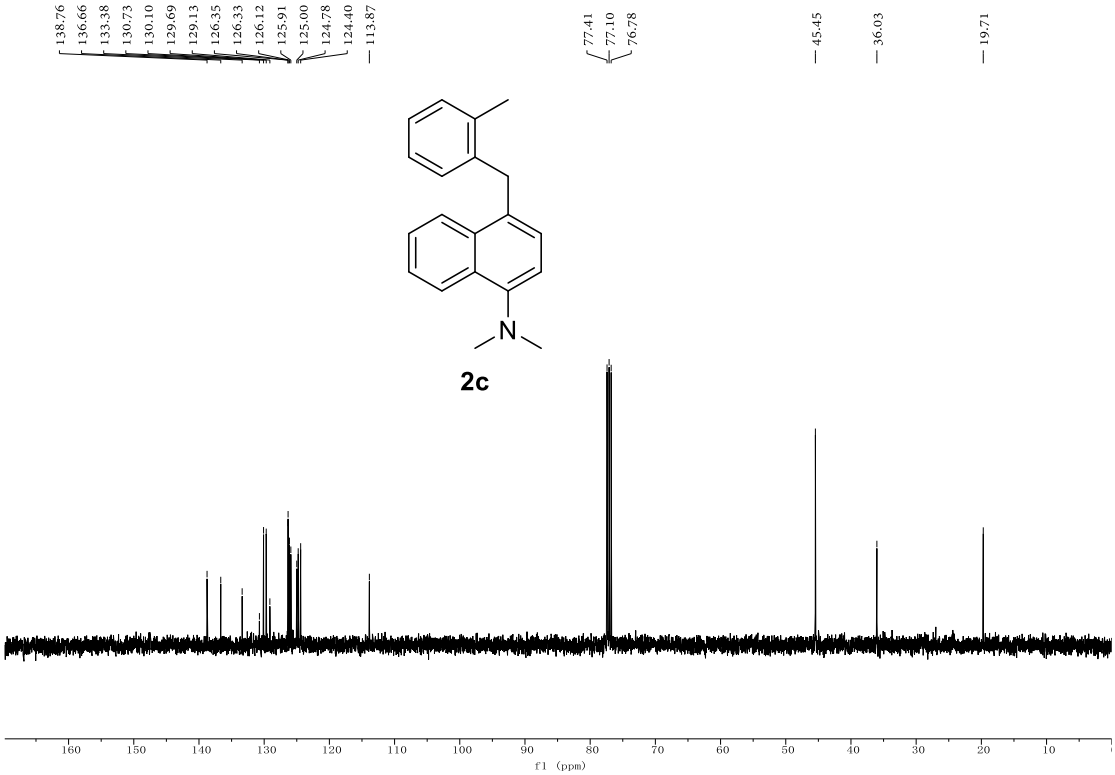


N,*N*-dimethyl-4-(2-methylbenzyl)naphthalen-1-amine (**2c**)

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

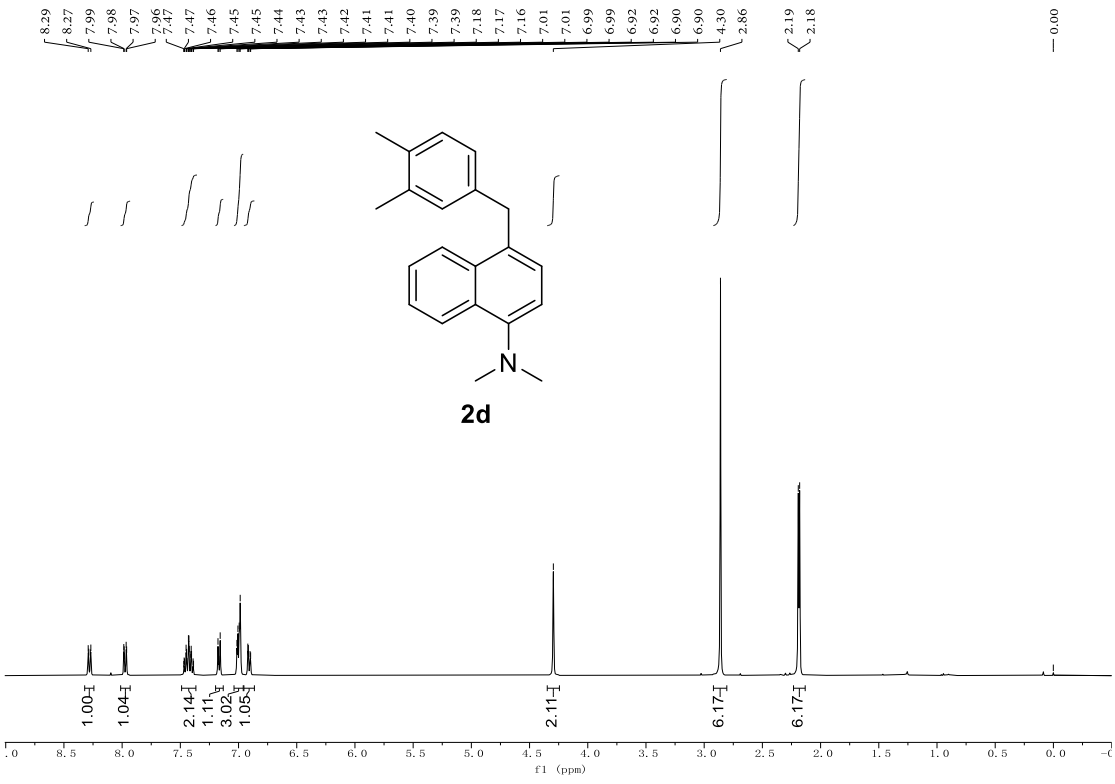


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

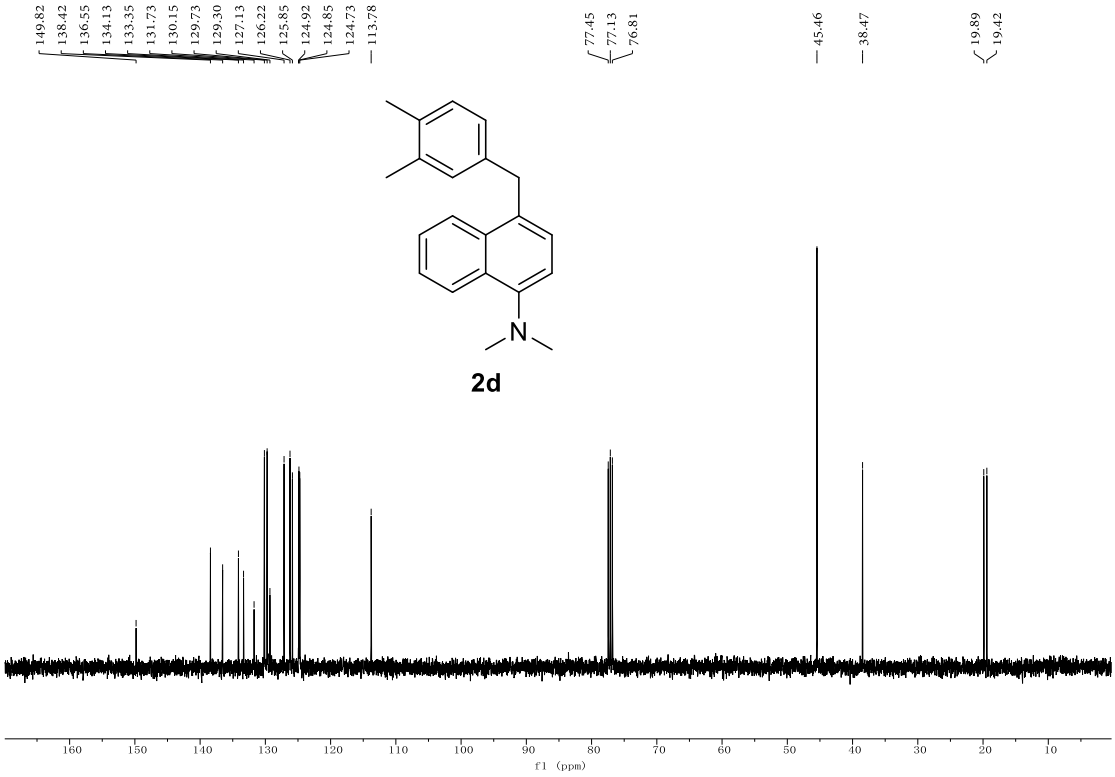


4-(3,4-dimethylbenzyl)-*N*,*N*-dimethylnaphthalen-1-amine (**2d**)

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

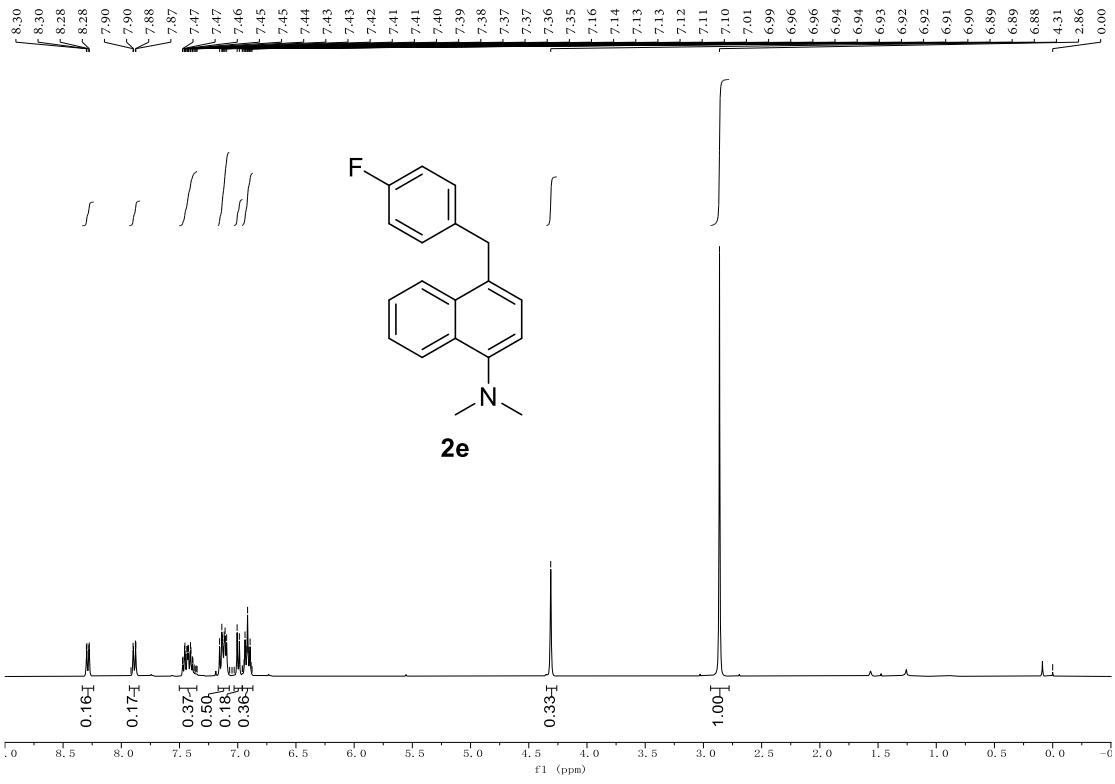


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

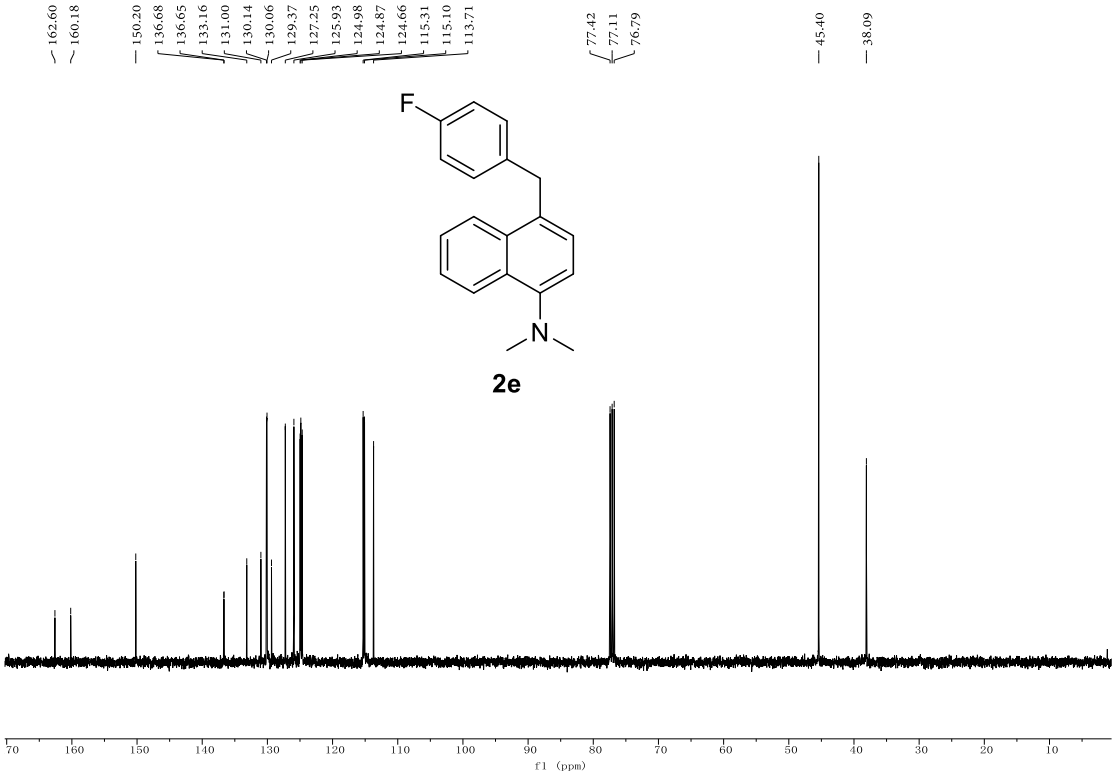


4-(4-fluorobenzyl)-*N*,*N*-dimethylnaphthalen-1-amine (**2e**)

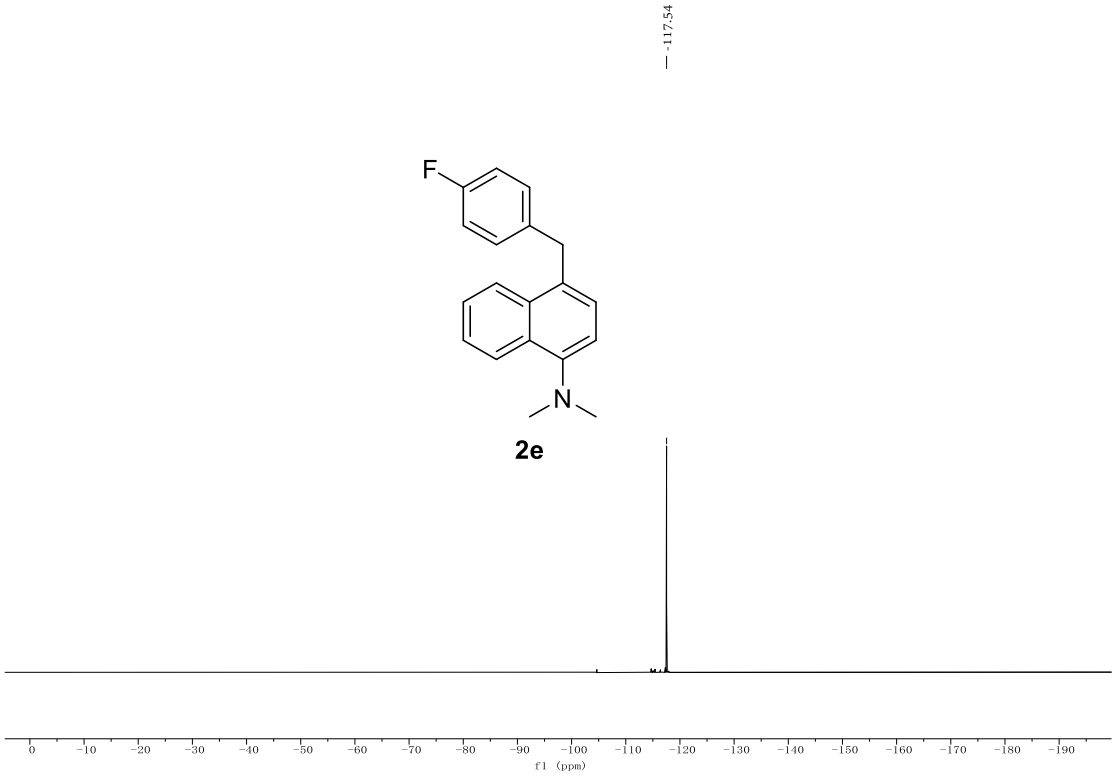
^{1}H NMR, 400 MHz, $CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

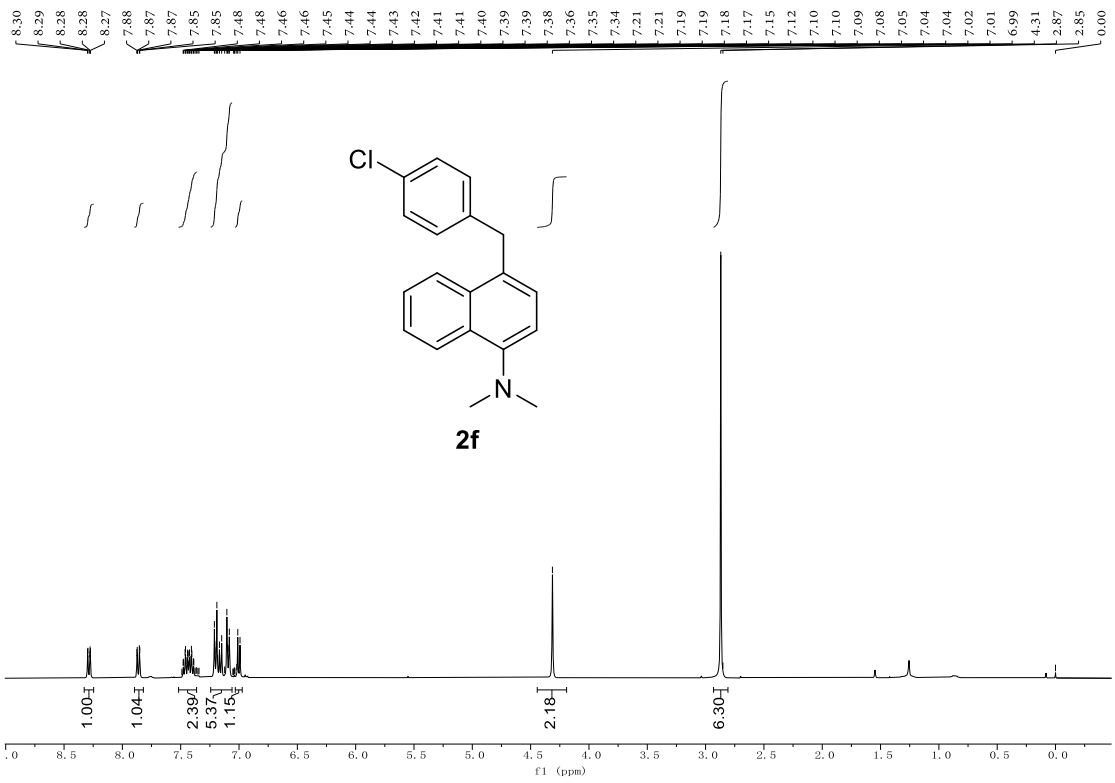


^{19}F NMR, 376 MHz, $CDCl_3$

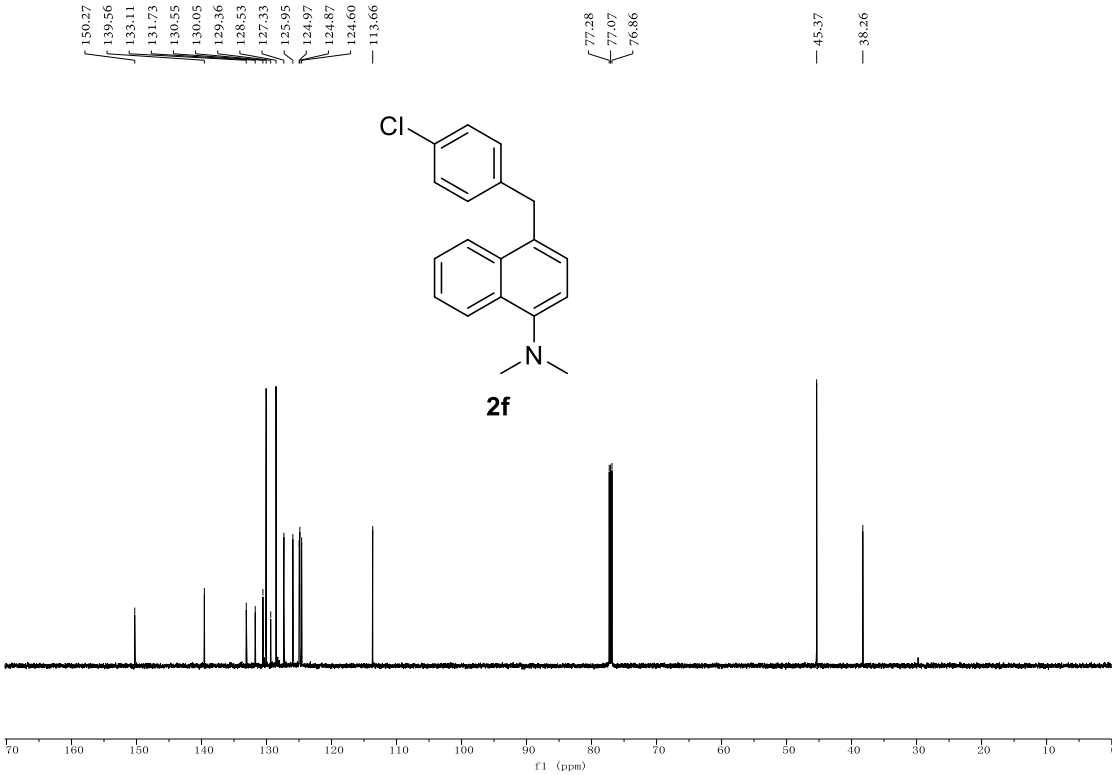


4-(4-chlorobenzyl)-*N*,*N*-dimethylnaphthalen-1-amine (**2f**)

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

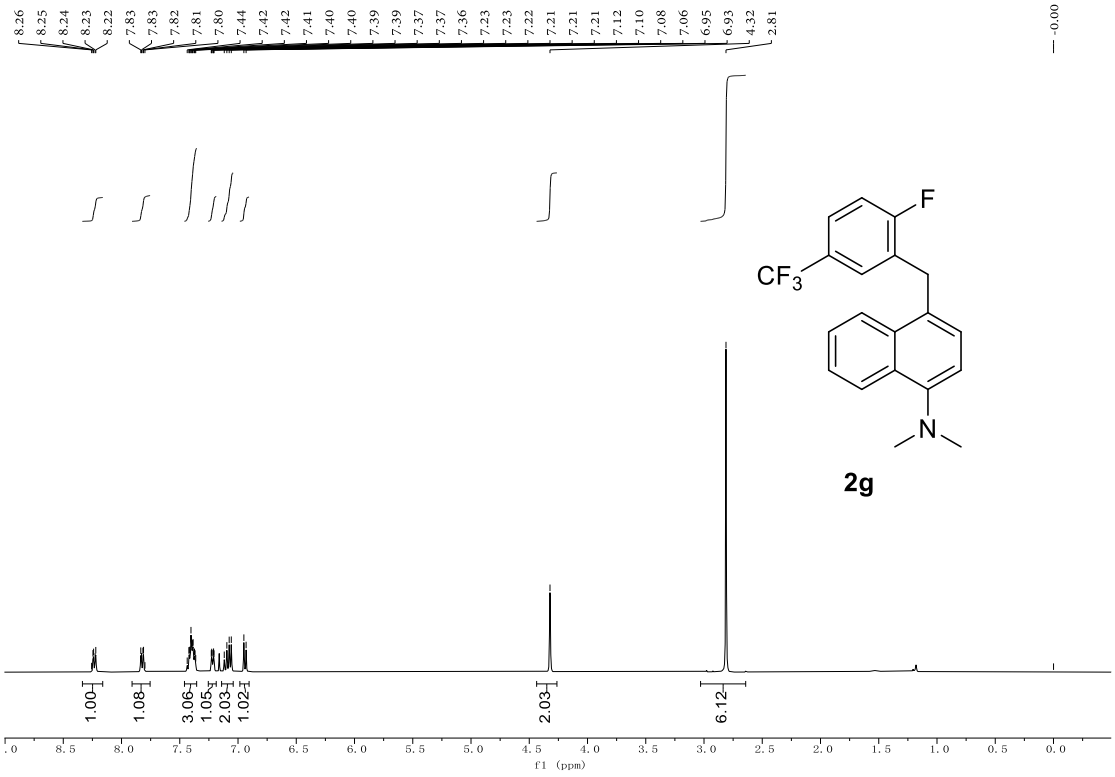


^{13}C{^{1}H} NMR, 151 MHz, $CDCl_3$

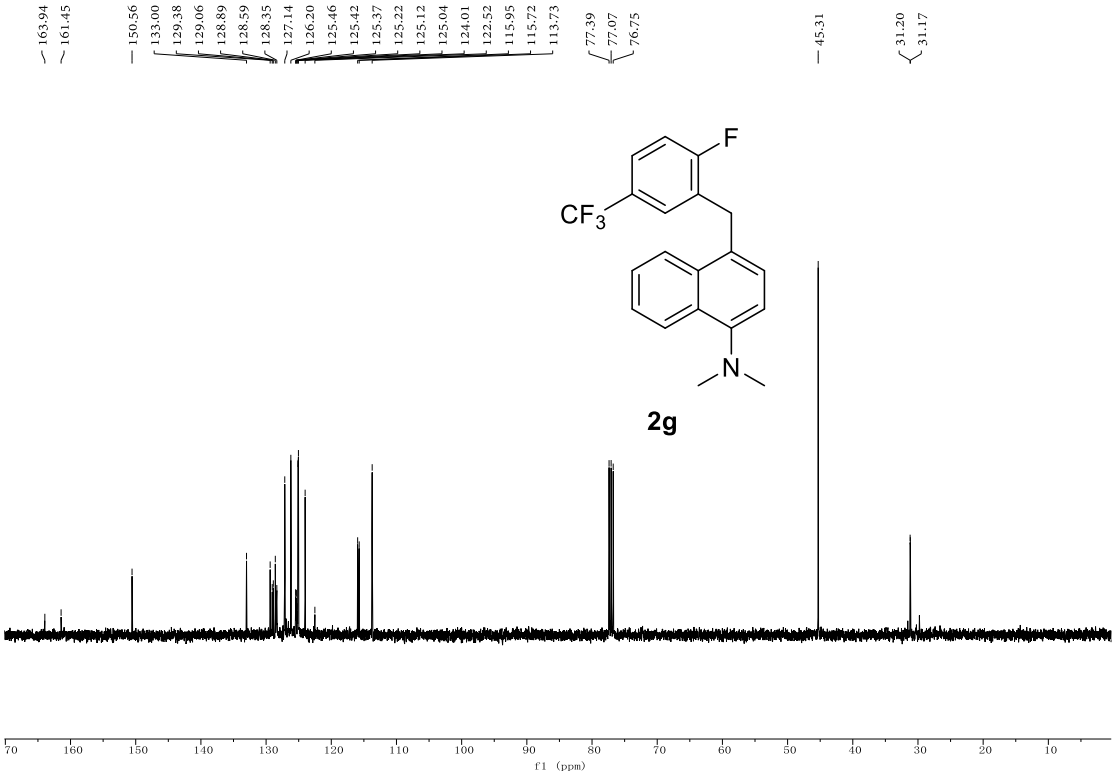


4-(2-fluoro-5-(trifluoromethyl)benzyl)-*N*,*N*-dimethylnaphthalen-1-amine (**2g**)

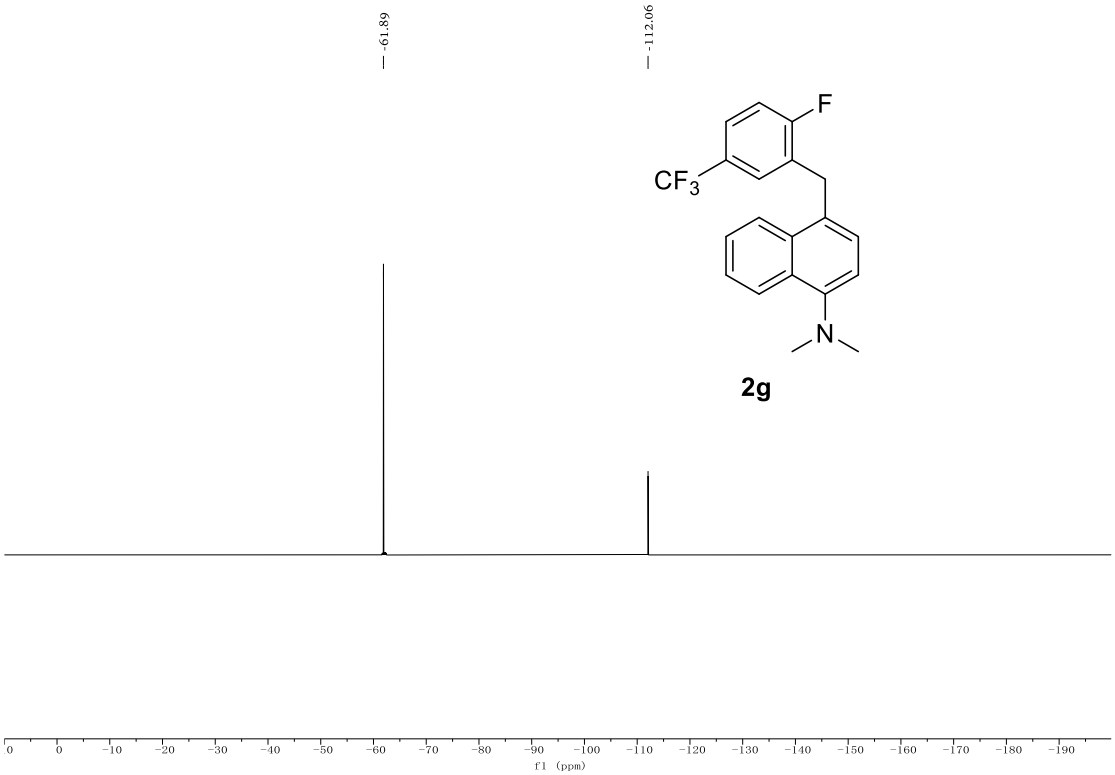
^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$

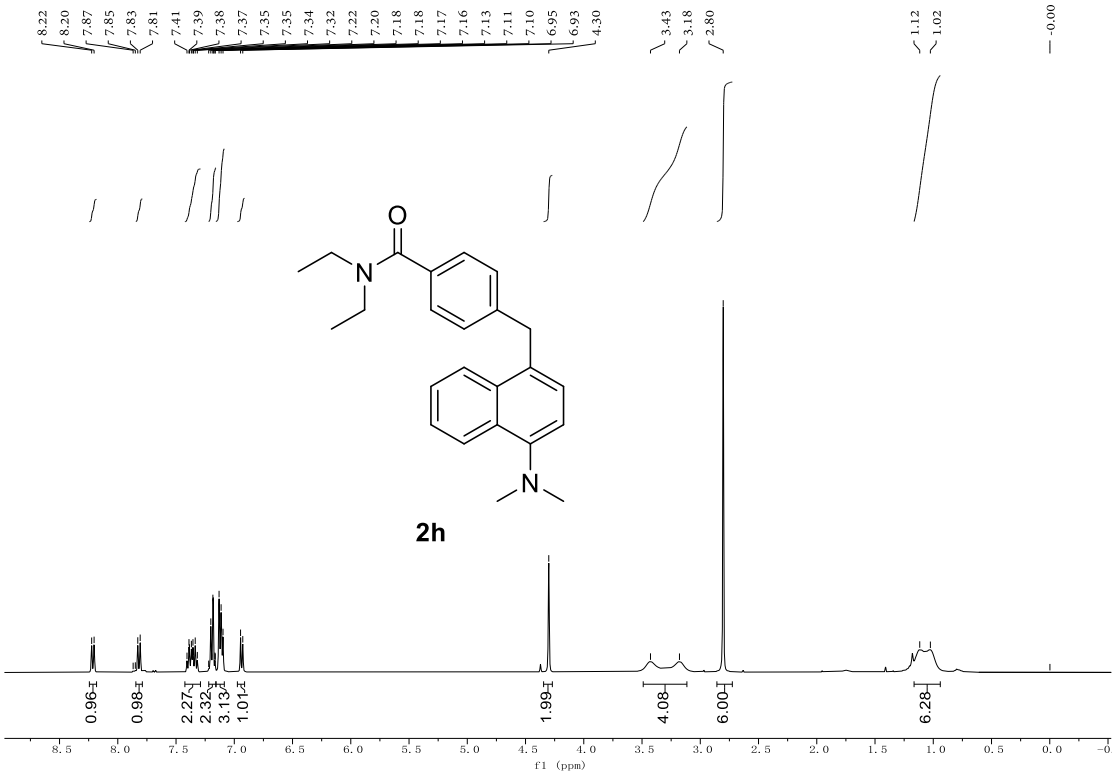


^{19}F NMR, 376 MHz, $CDCl_3$

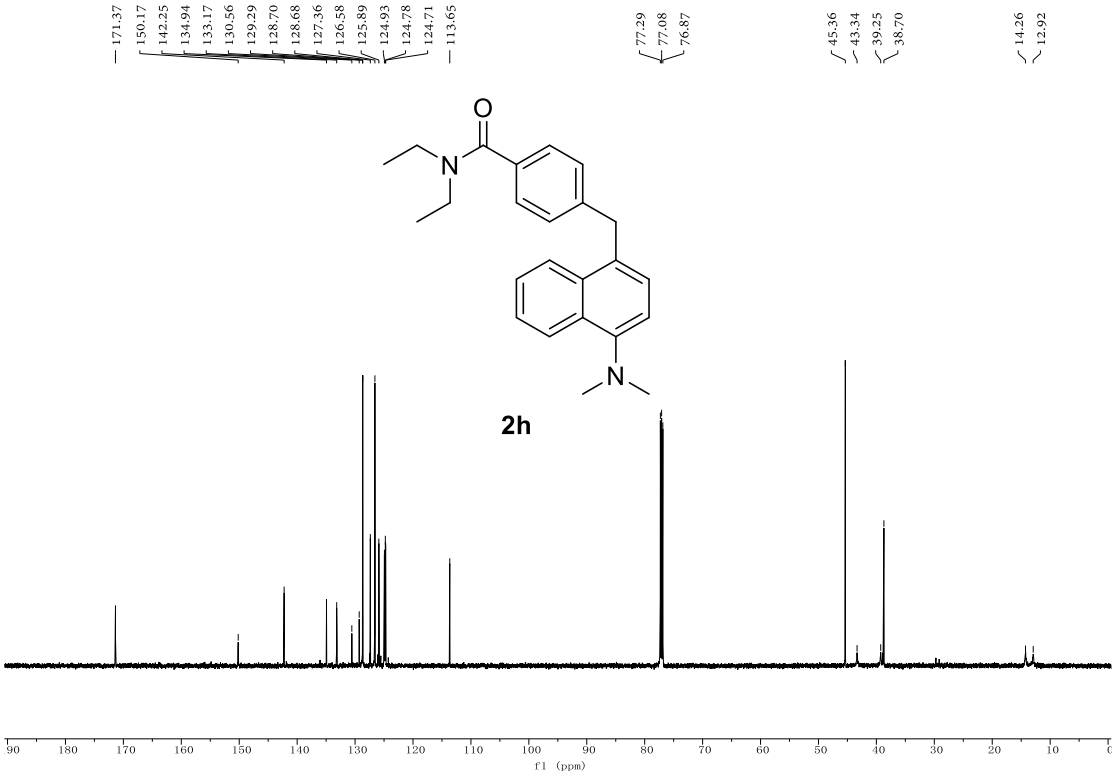


4-((4-(dimethylamino)naphthalen-1-yl)methyl)-*N*,*N*-diethylbenzamide (**2h**)

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

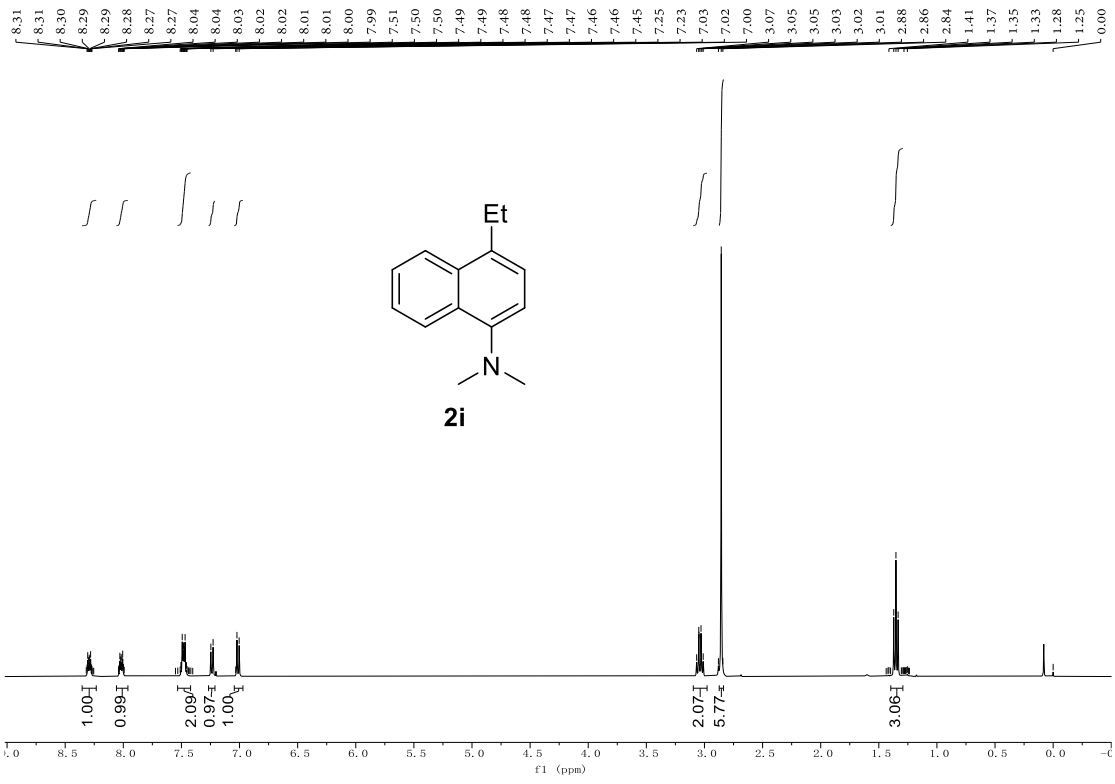


$^{13}C\{^{1}H\}$ NMR, 151 MHz, $CDCl_3$

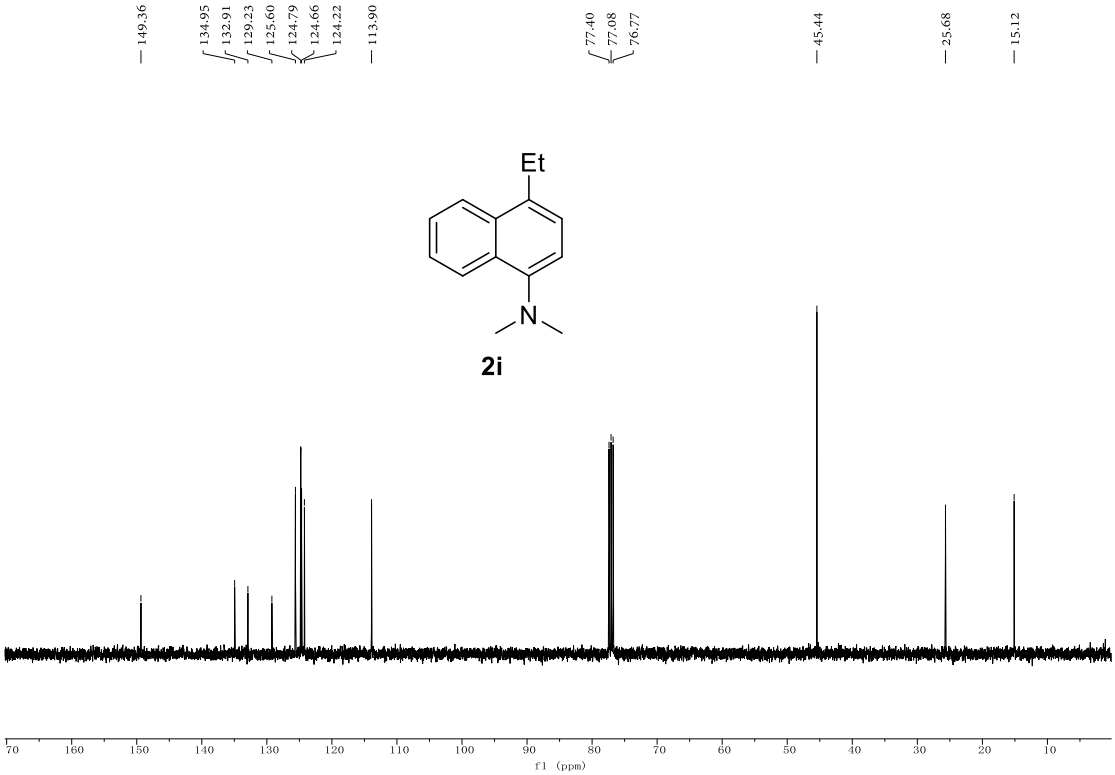


4-ethyl-*N*,*N*-dimethylnaphthalen-1-amine (**2i**)

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

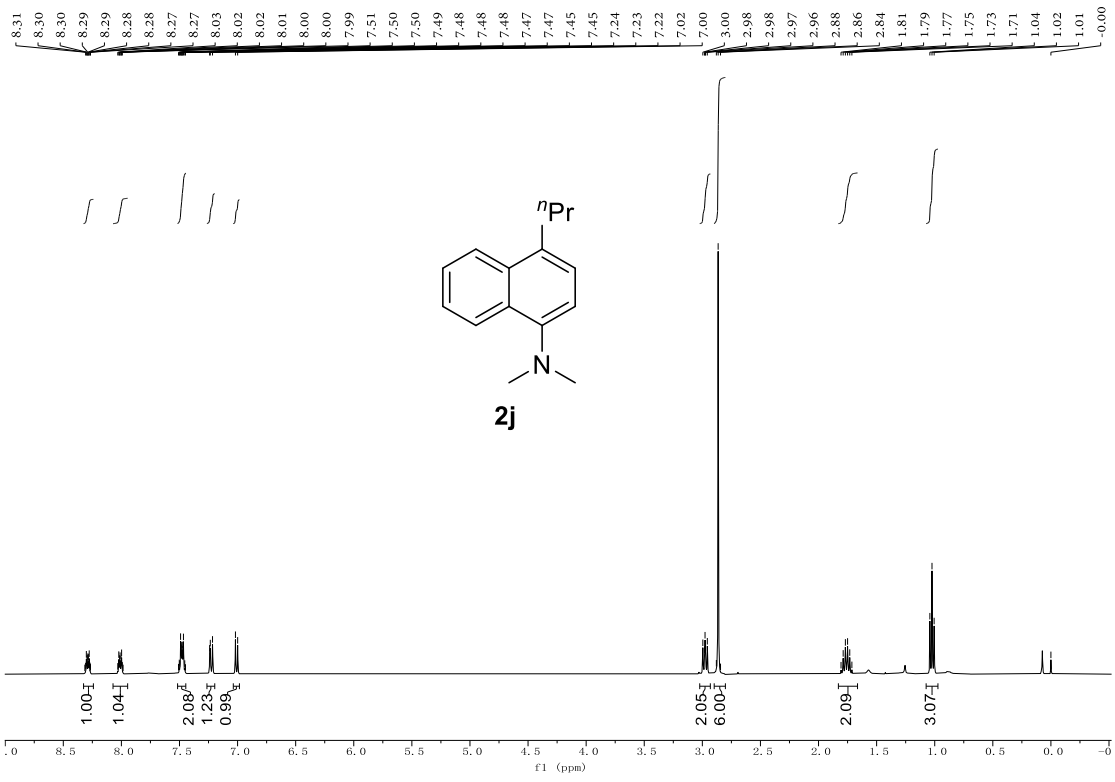


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

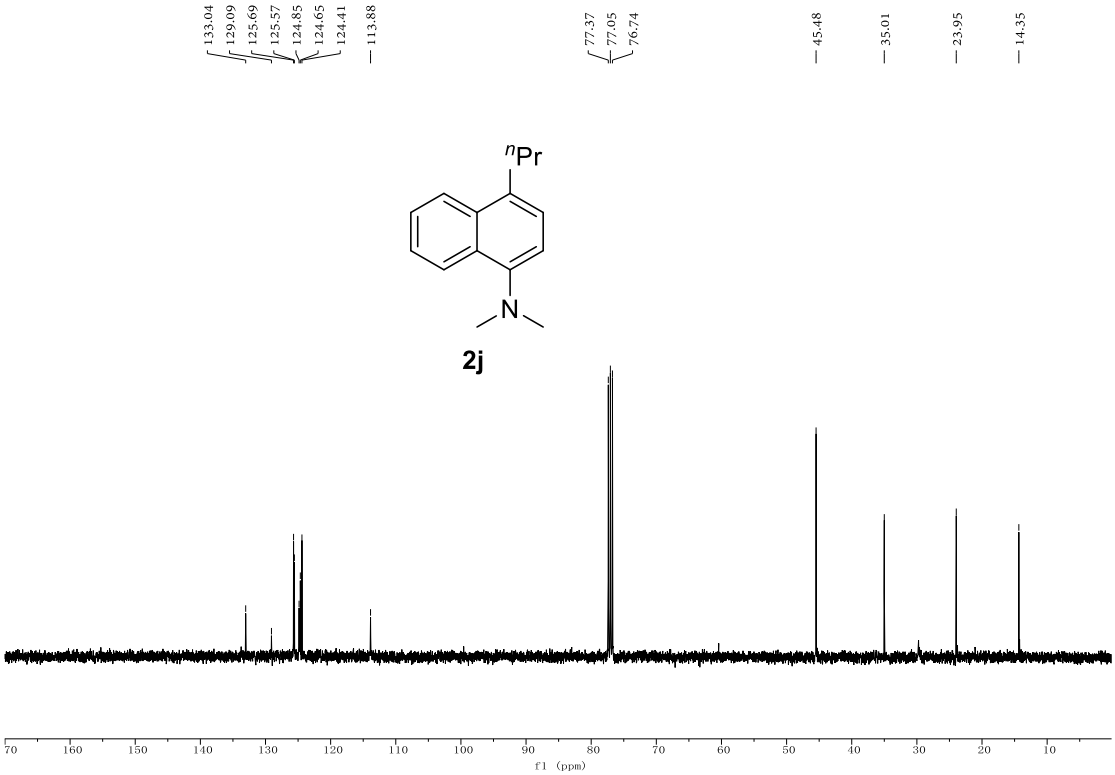


N,*N*-dimethyl-4-propylnaphthalen-1-amine (**2j**)

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

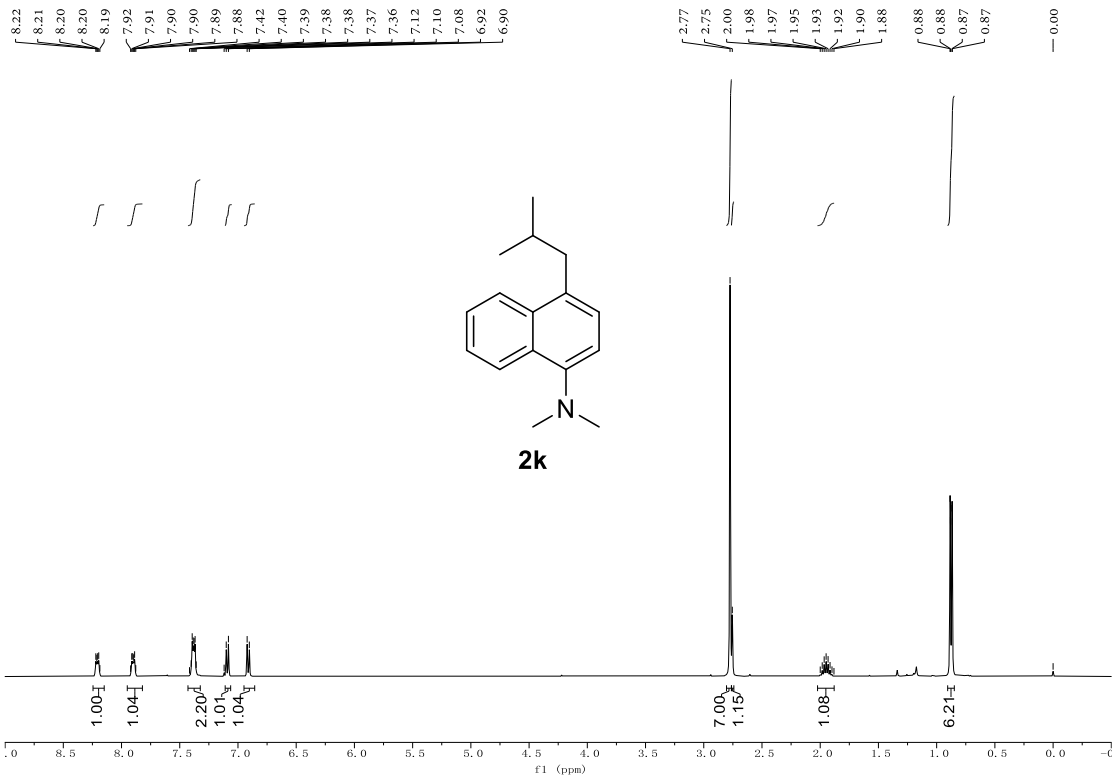


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

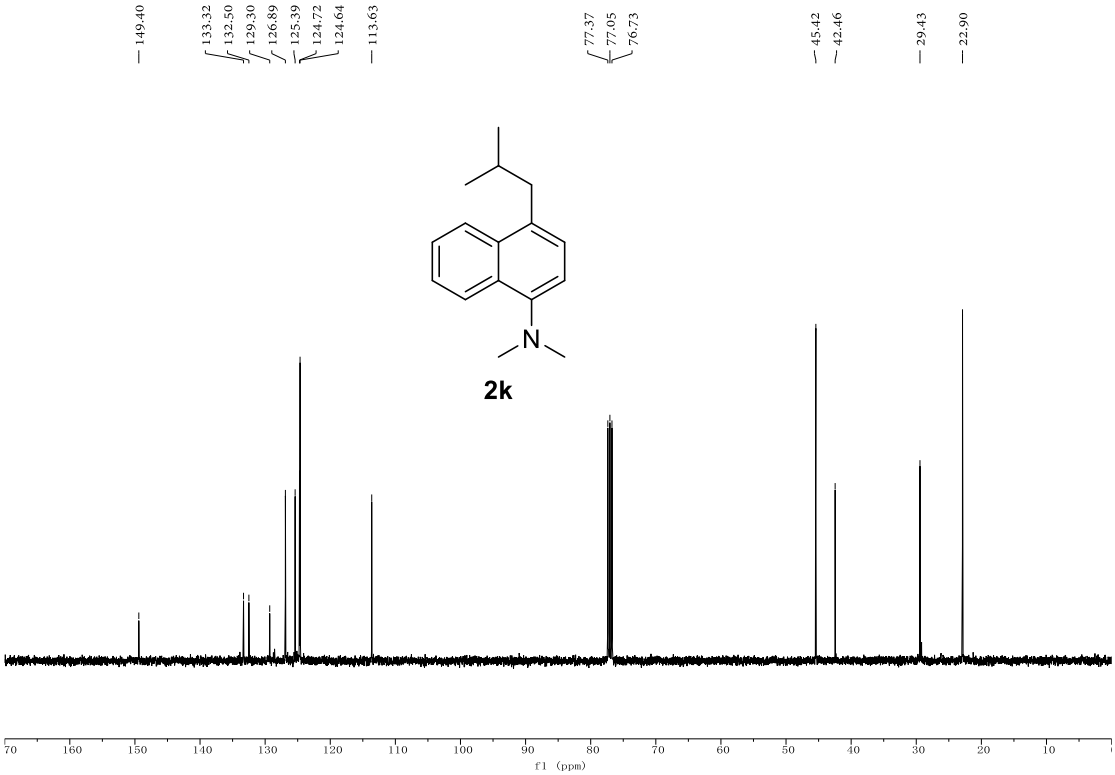


4-isobutyl-*N*,*N*-dimethylnaphthalen-1-amine (**2k**)

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

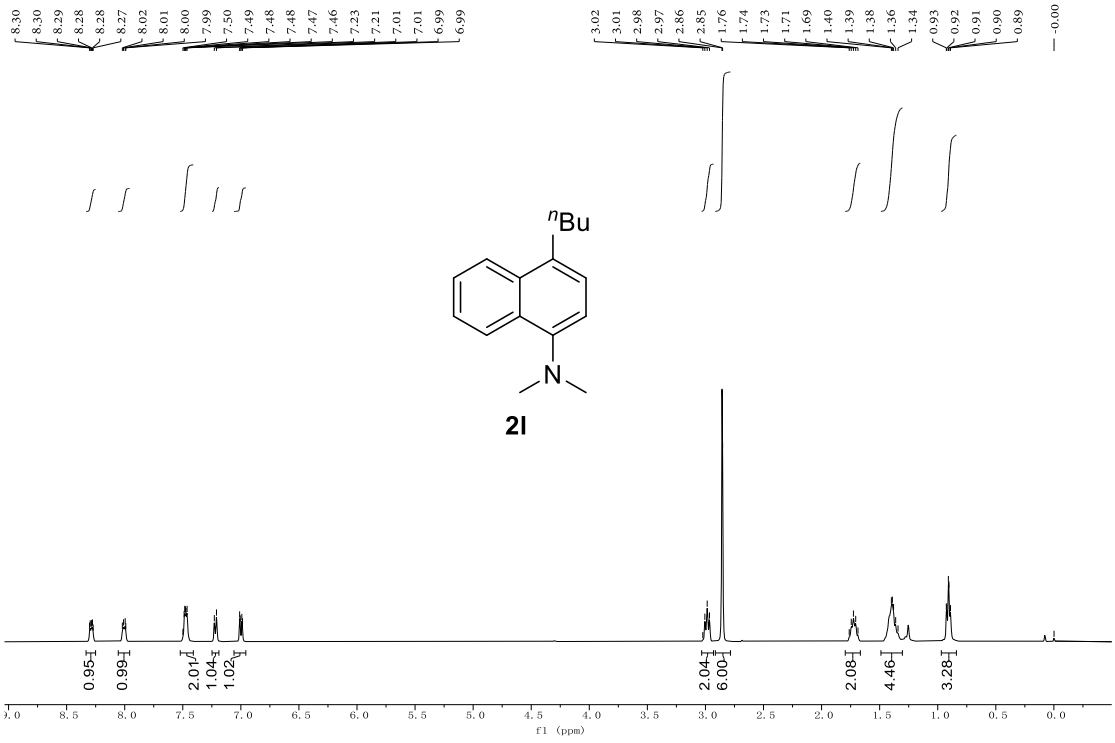


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

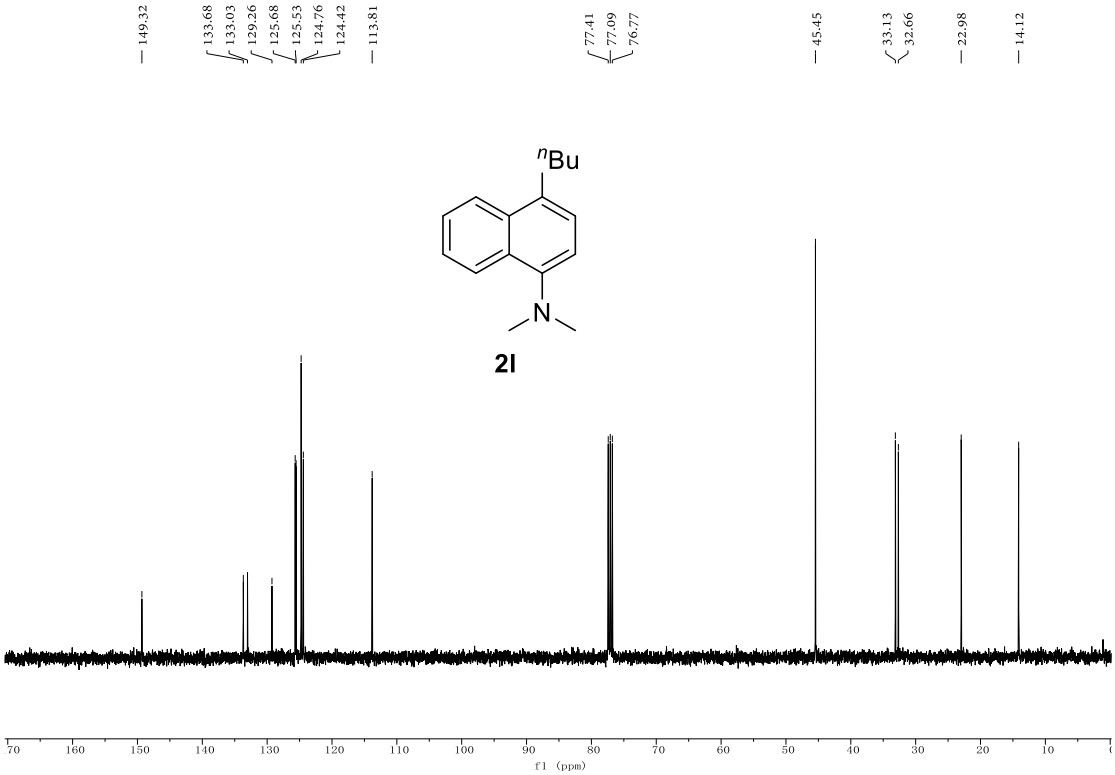


4-butyl-*N*,*N*-dimethylnaphthalen-1-amine (**2l**)

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

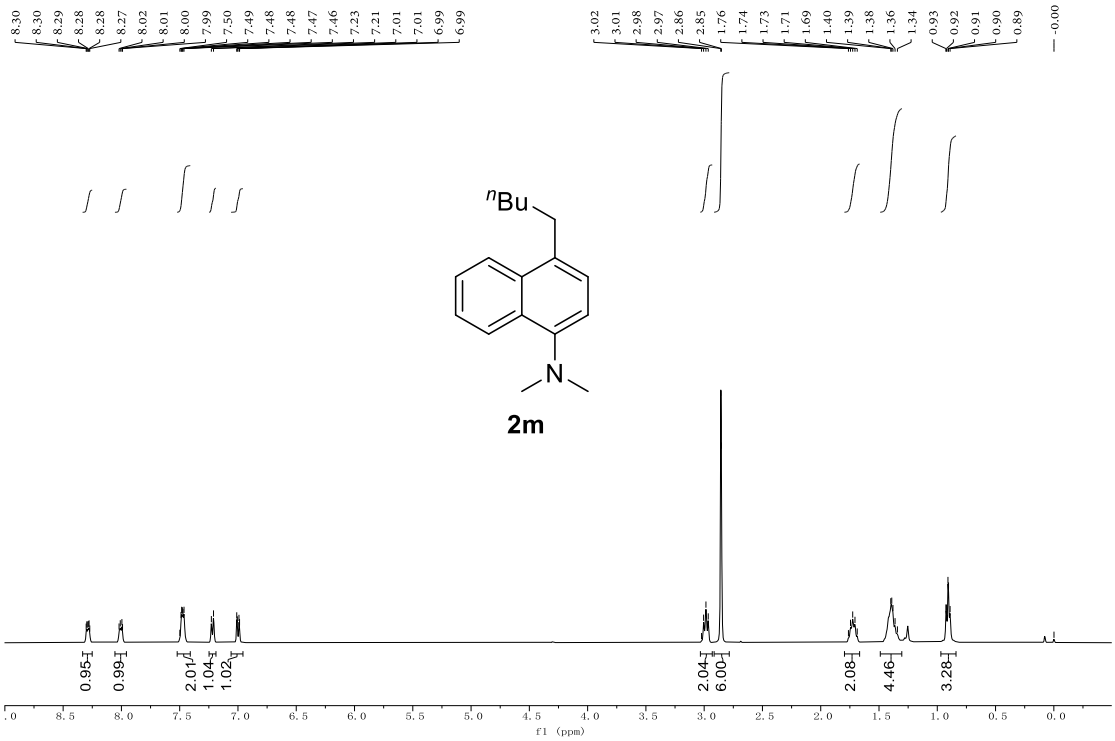


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

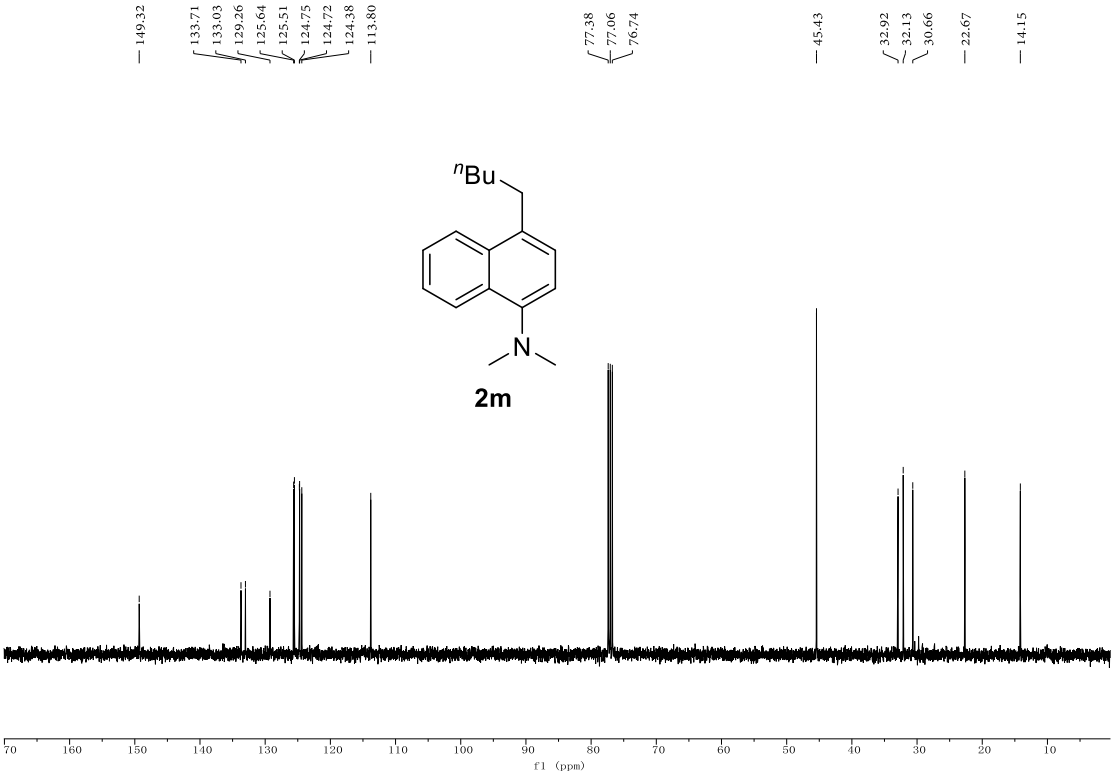


N,*N*-dimethyl-4-pentylnaphthalen-1-amine (**2m**)

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

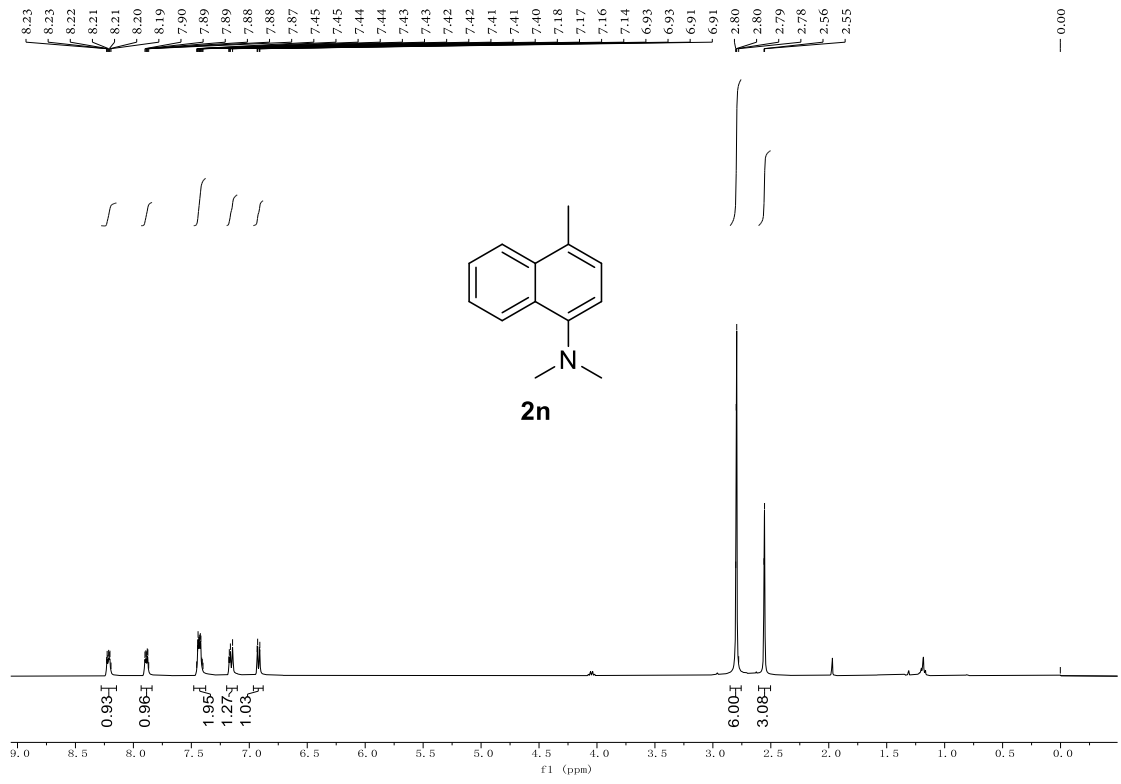


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

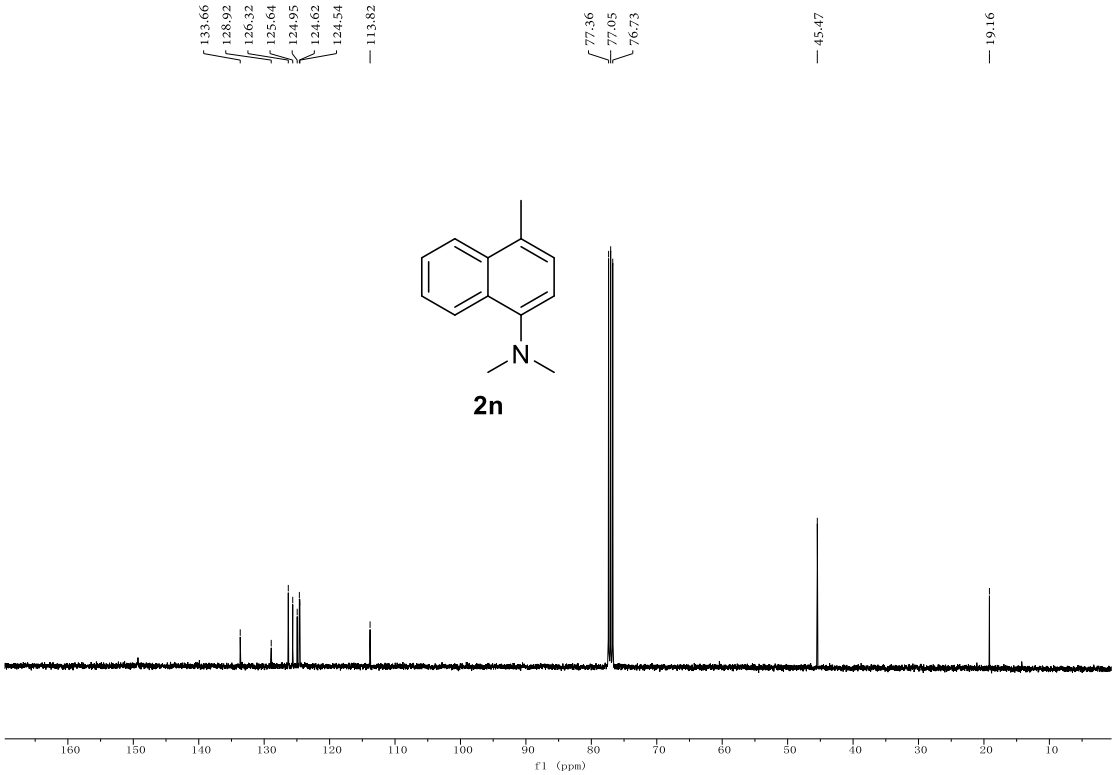


N,*N*,4-trimethylnaphthalen-1-amine (**2n**)

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

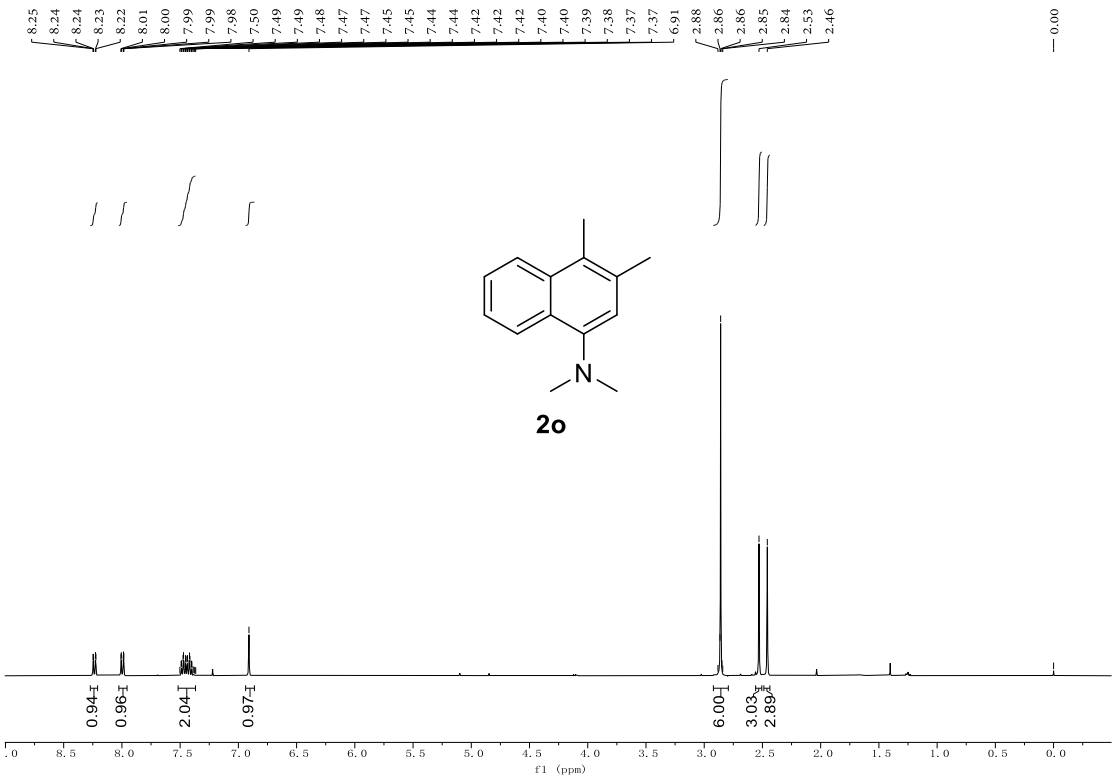


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

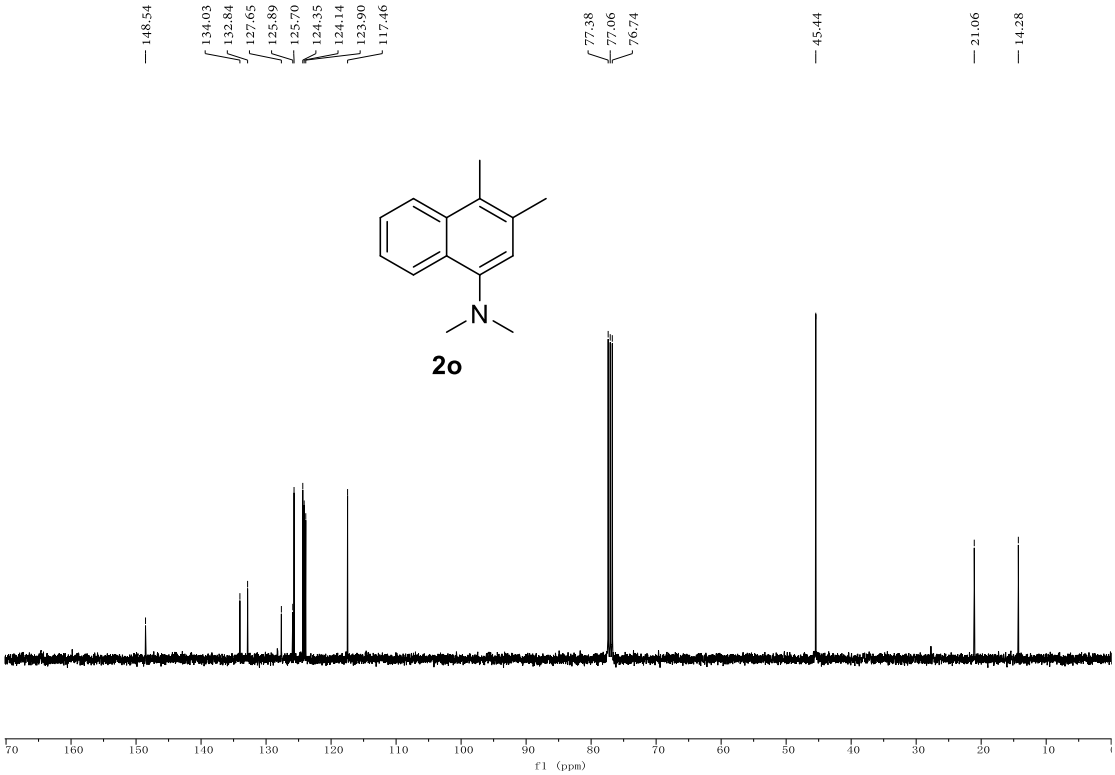


N,*N*,3,4-tetramethylnaphthalen-1-amine (**2o**)

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

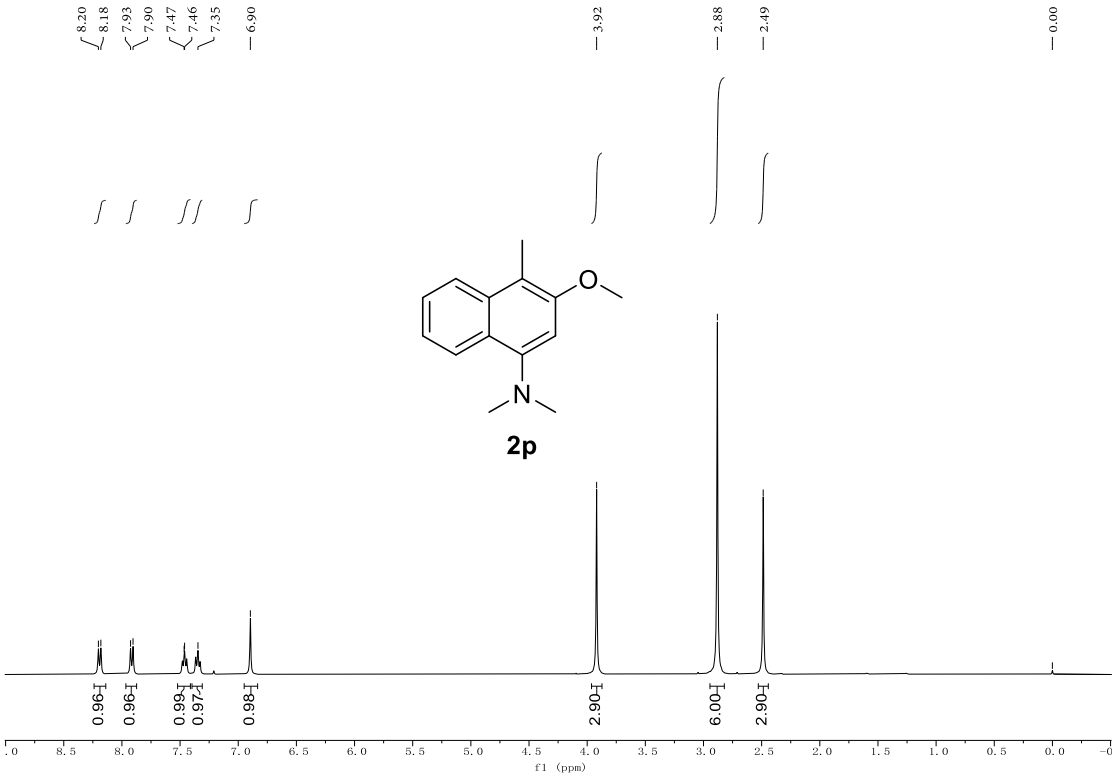


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

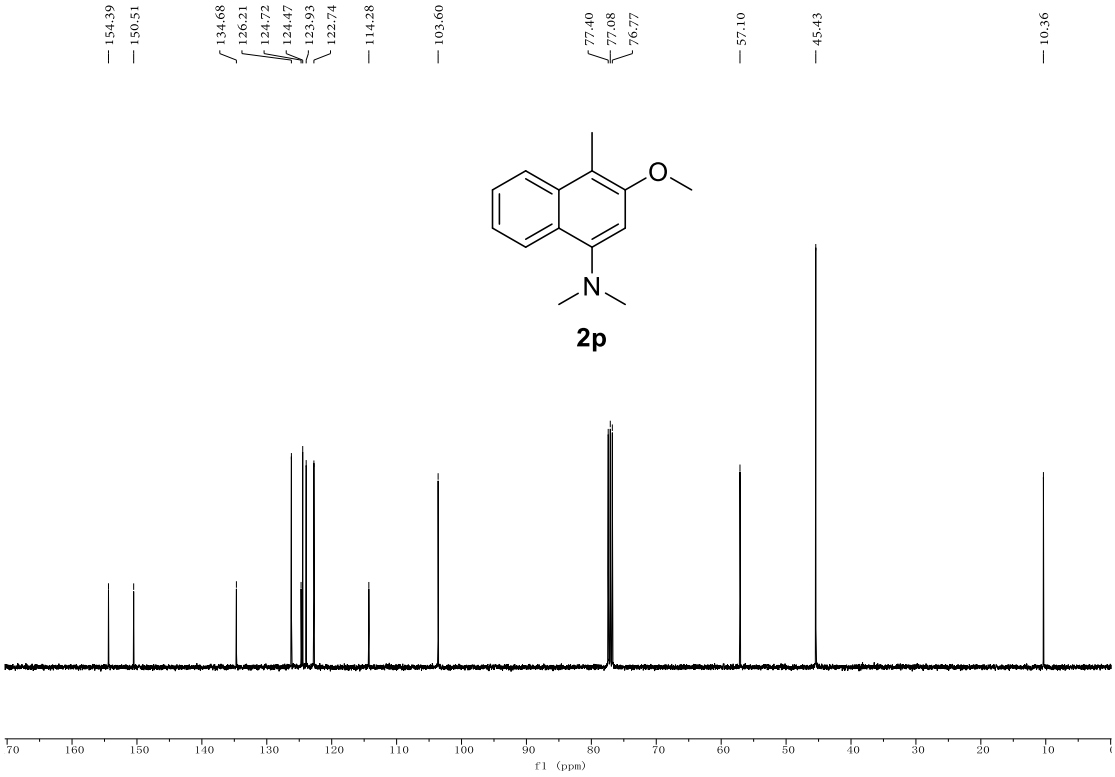


3-methoxy-*N*,*N*,4-trimethylnaphthalen-1-amine (**2p**)

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

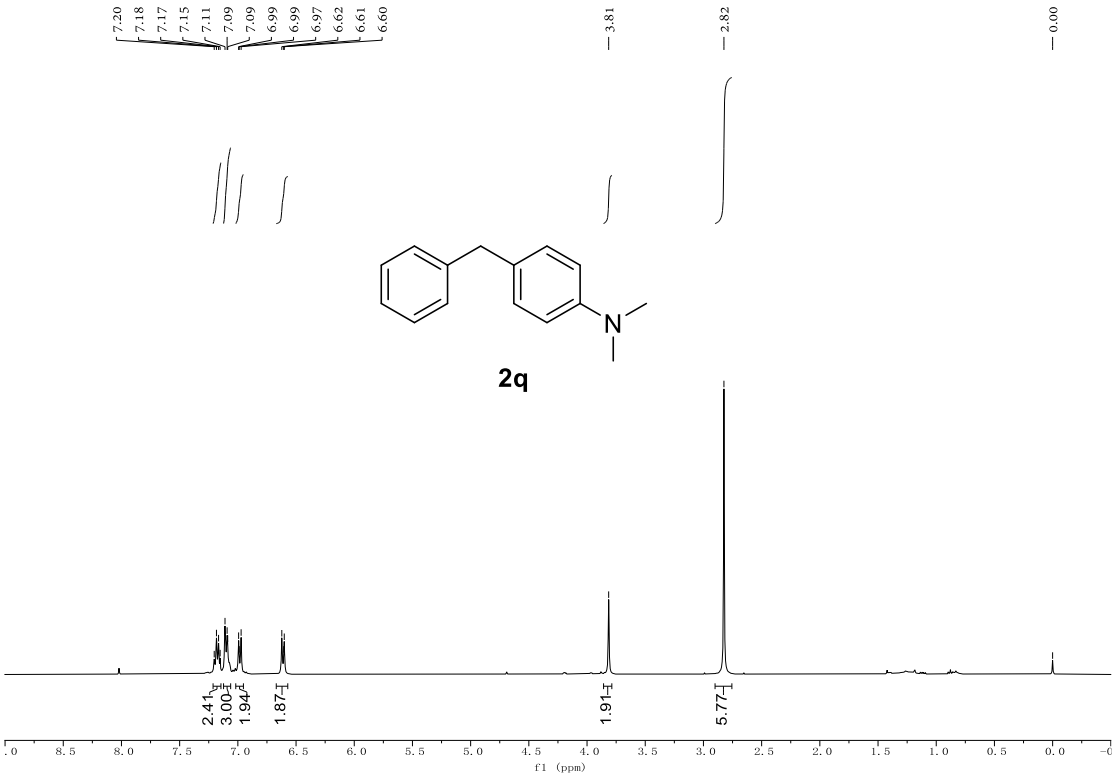


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

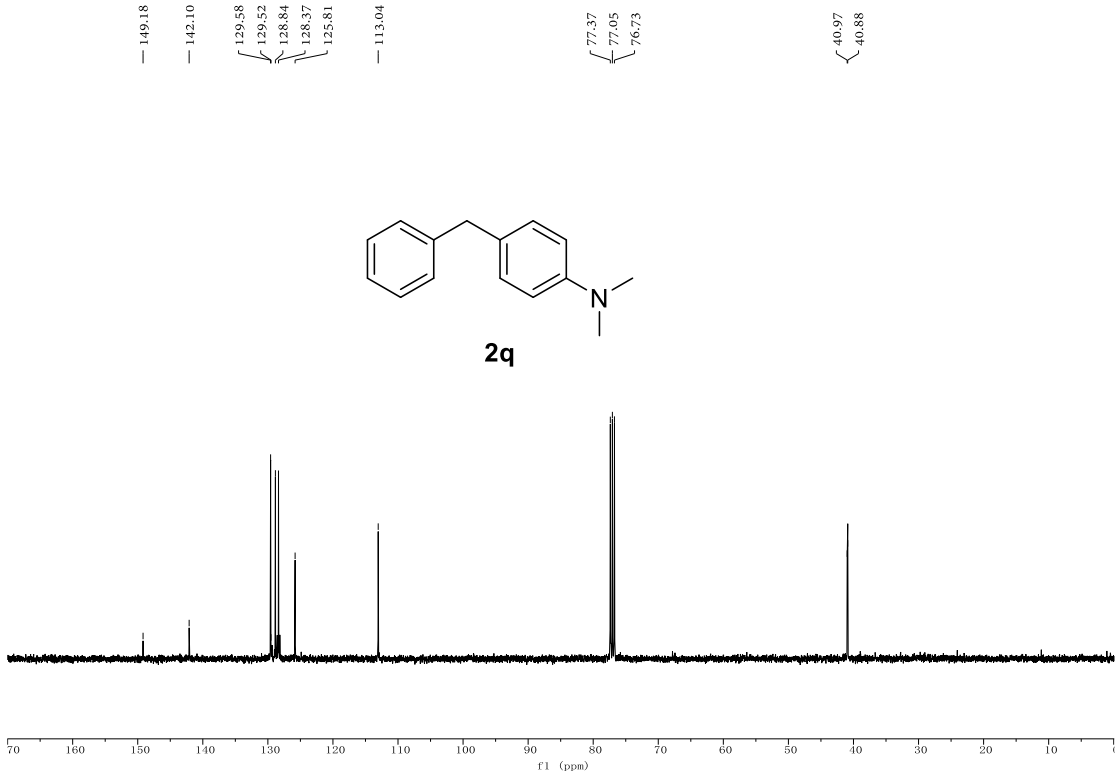


4-benzyl-*N*,*N*-dimethylaniline **(2q)**

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

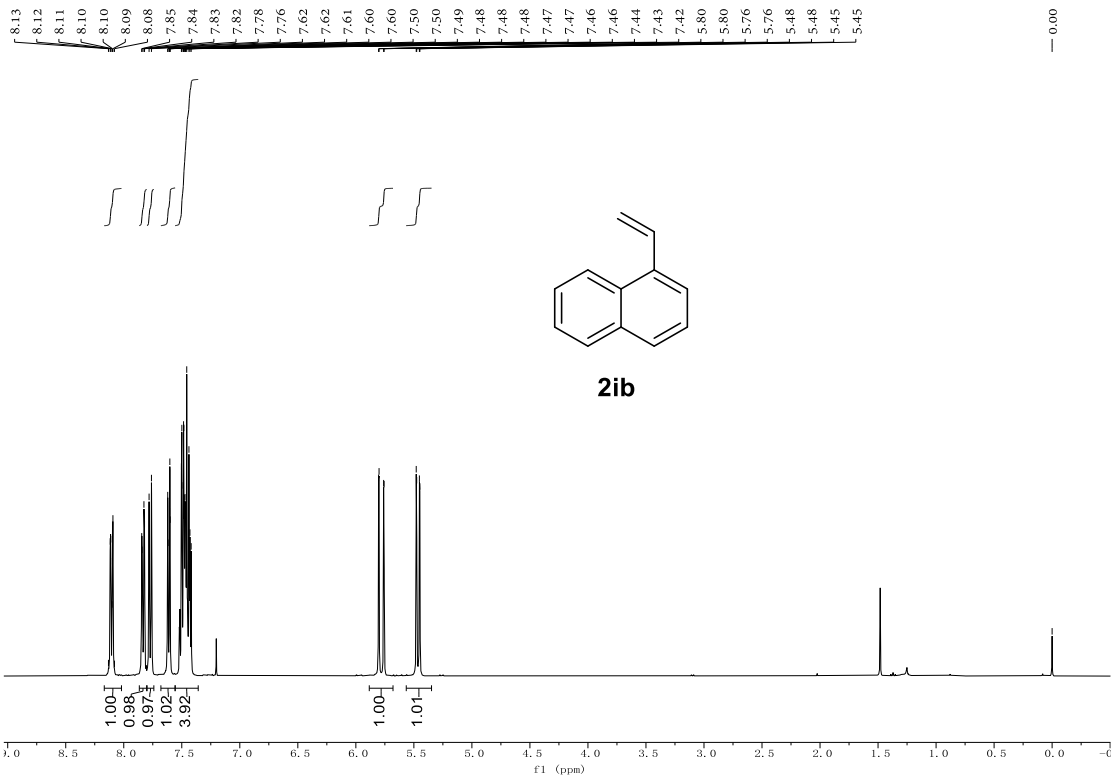


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

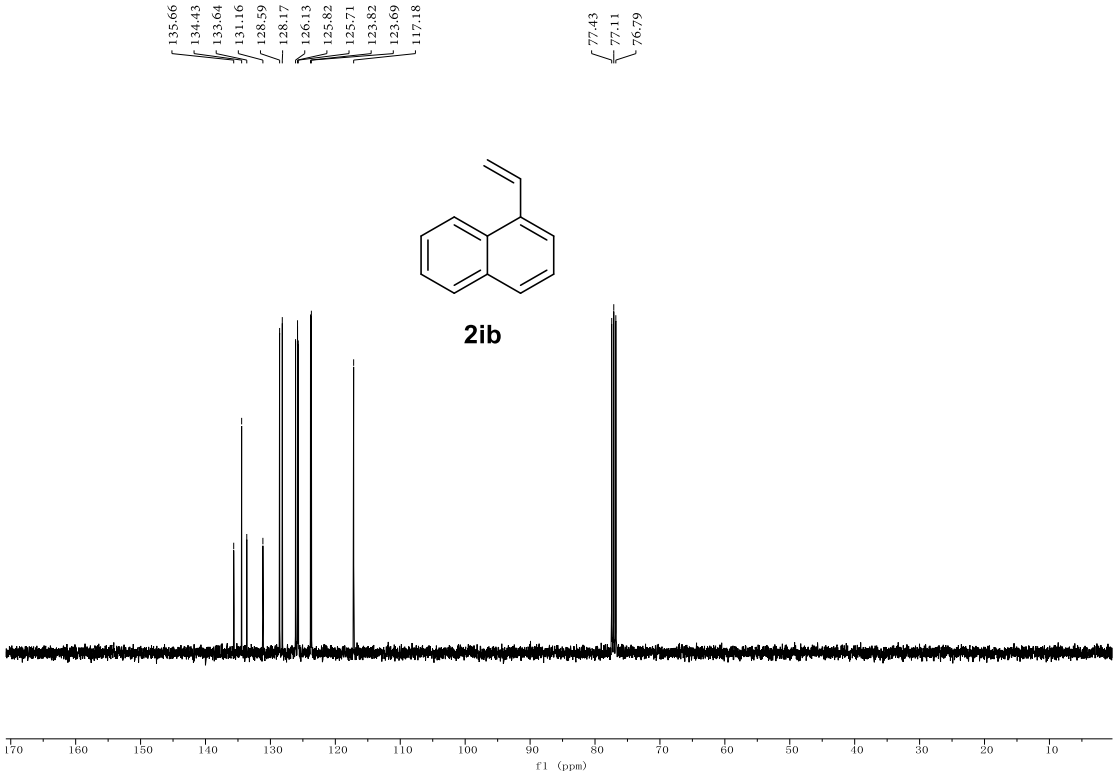


1-vinylnaphthalene **(2ib)**

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

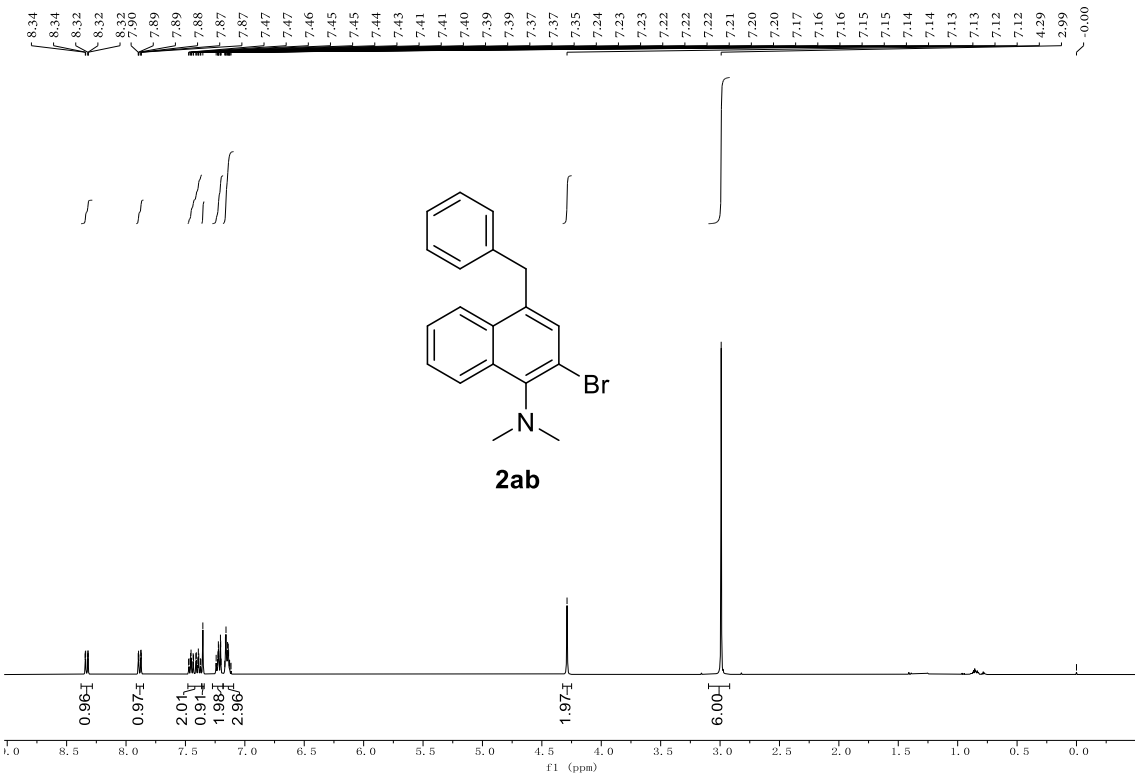


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

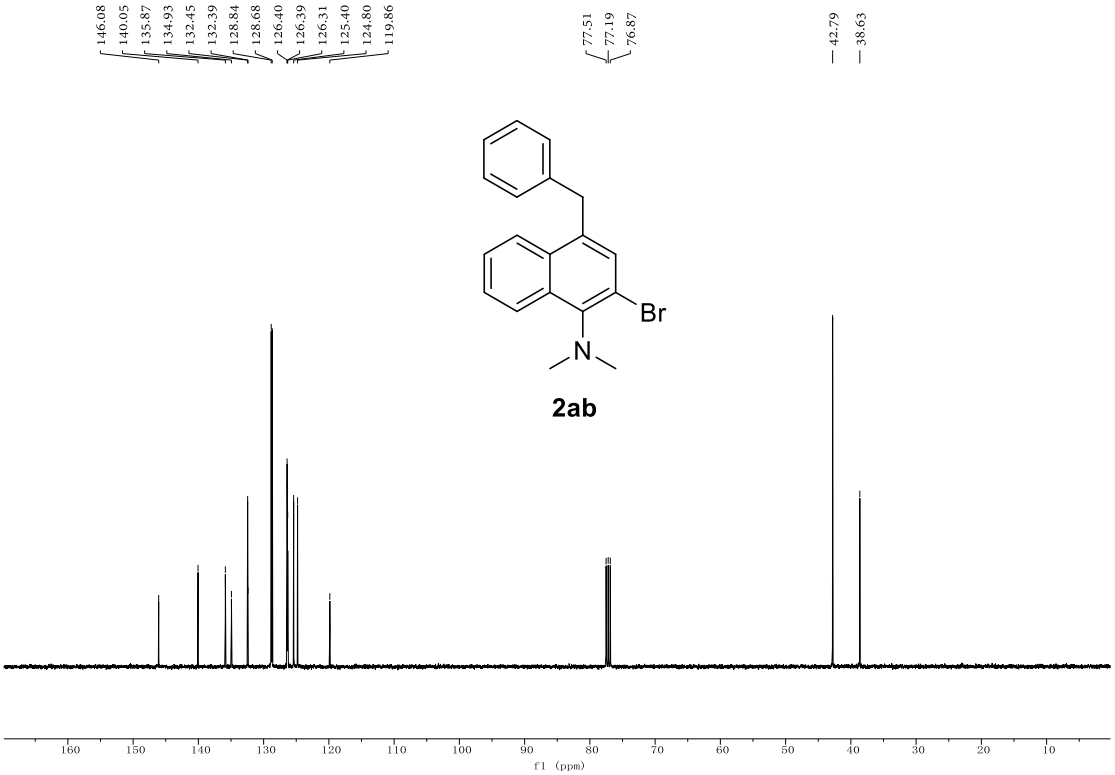


4-benzyl-2-bromo-*N*,*N*-dimethylnaphthalen-1-amine (**2ab**)

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

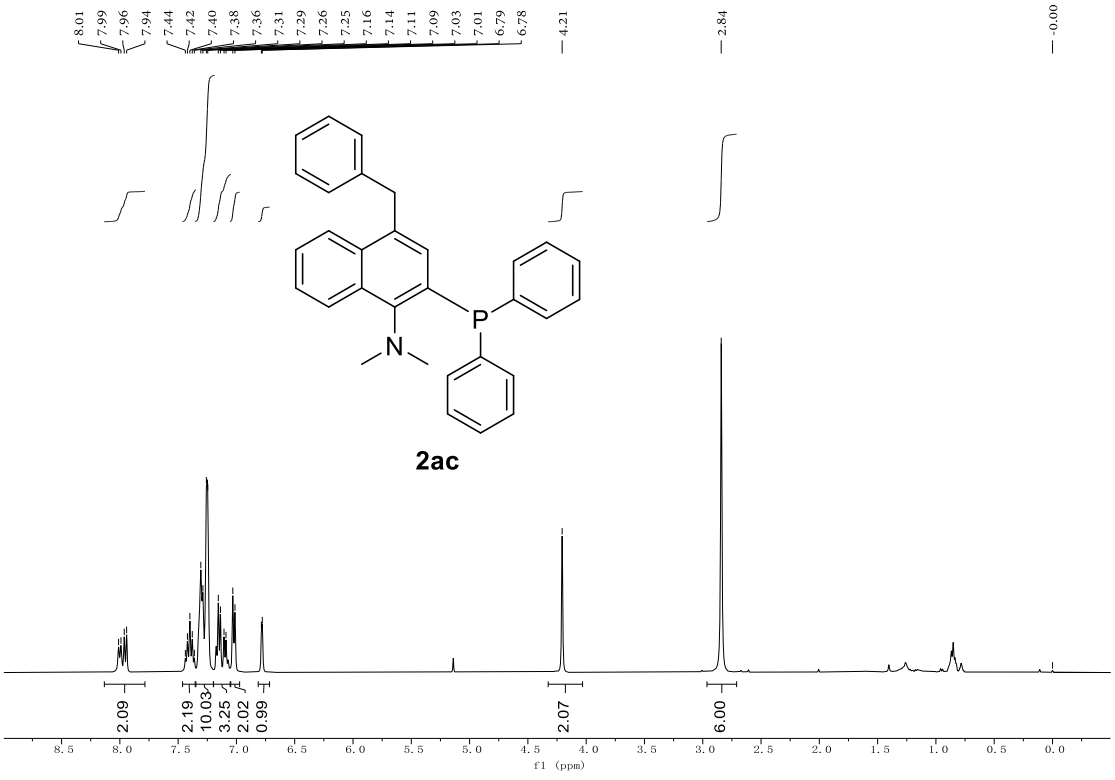


$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

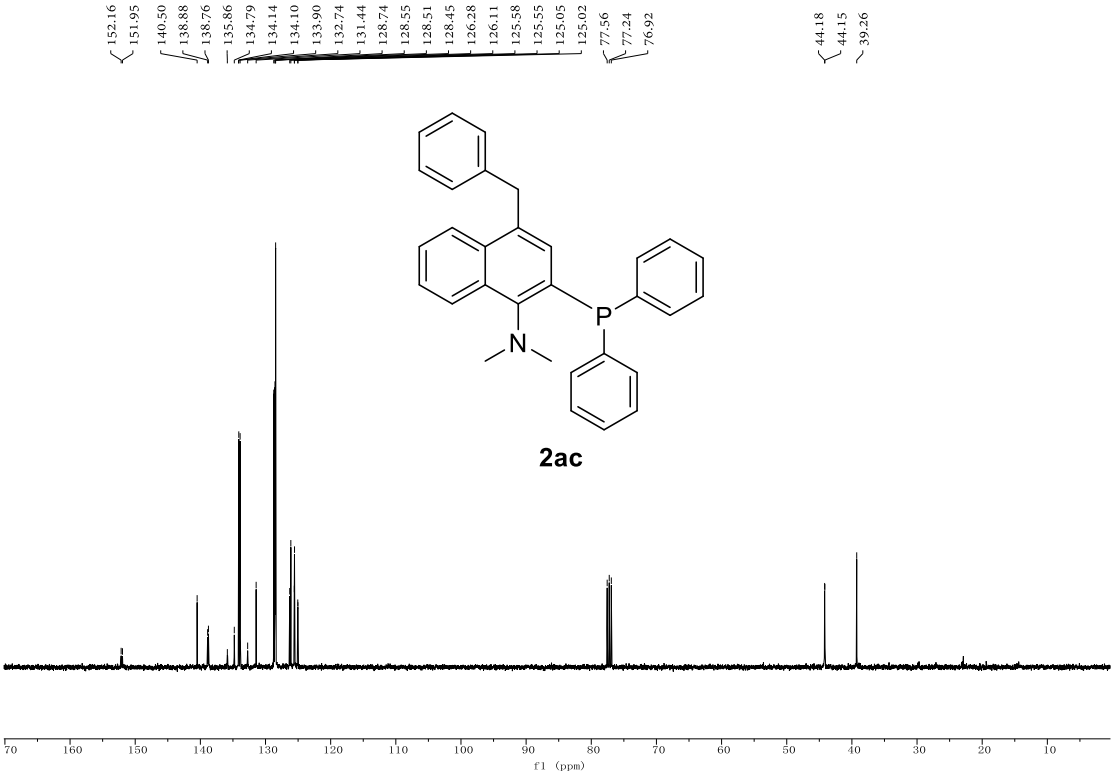


4-benzyl-2-(diphenylphosphaneyl)-*N*,*N*-dimethylnaphthalen-1-amine **(2ac)**

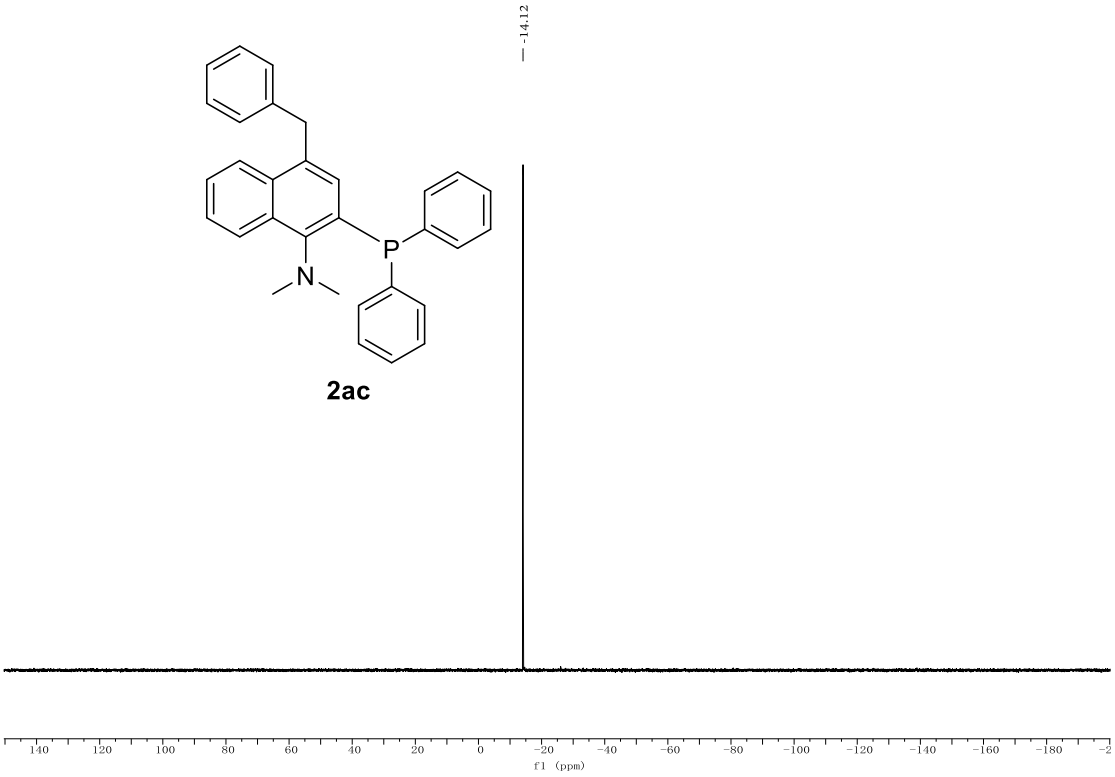
^{1}H NMR, 400 MHz, $CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

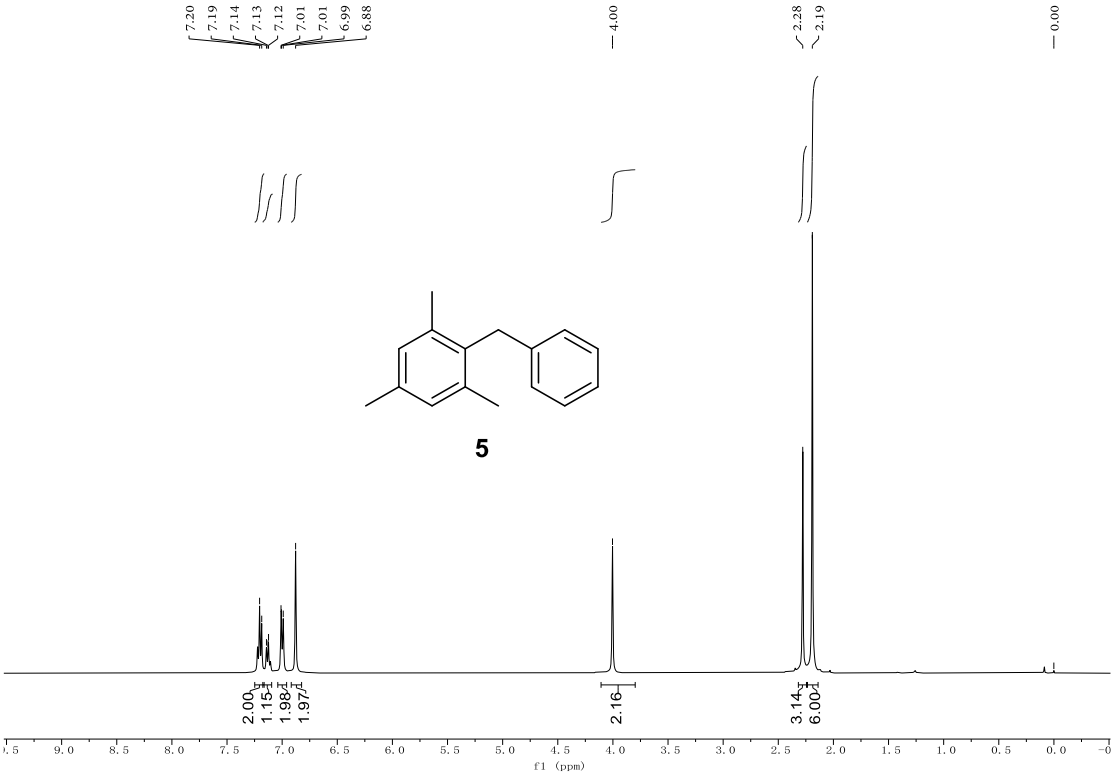


^{31}P NMR, 162 MHz, $CDCl_3$

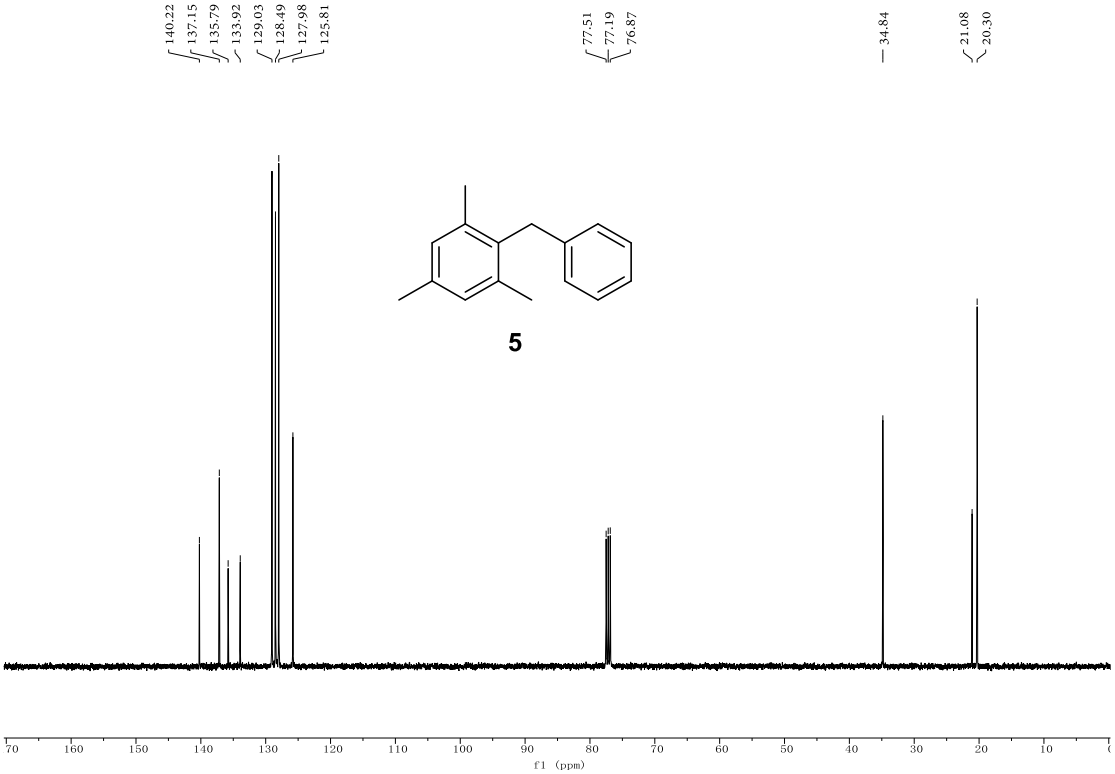


2-benzyl-1,3,5-trimethylbenzene **(5)**

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

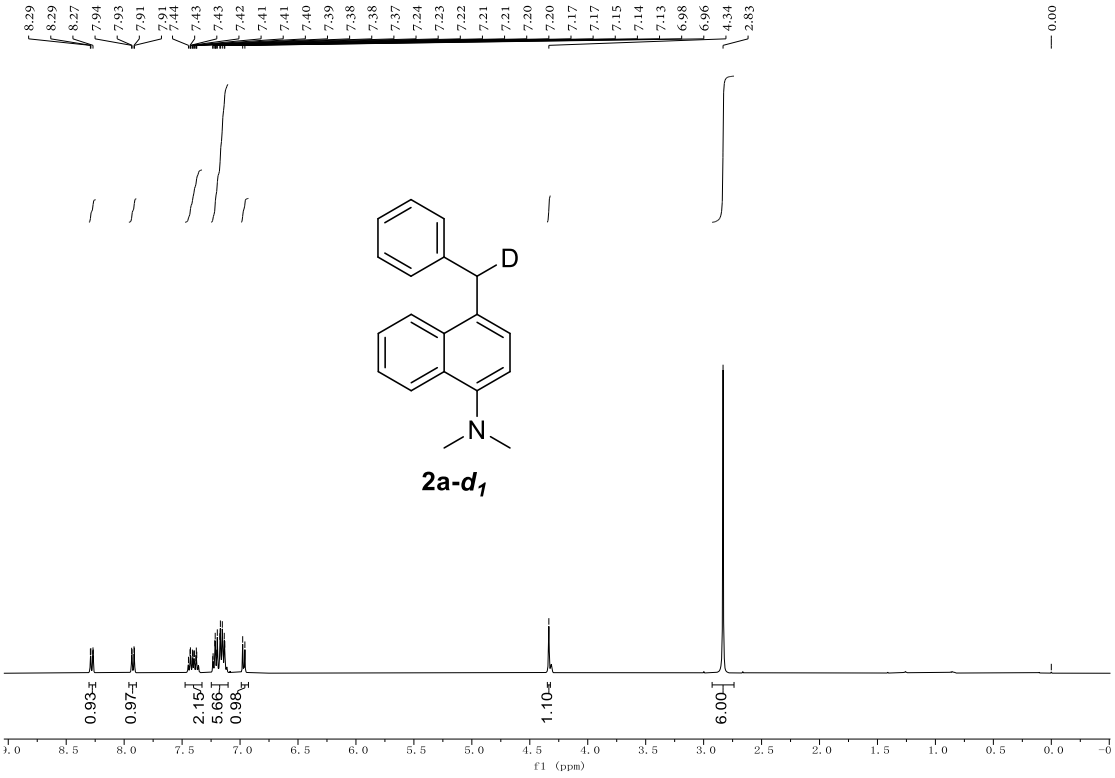


^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$

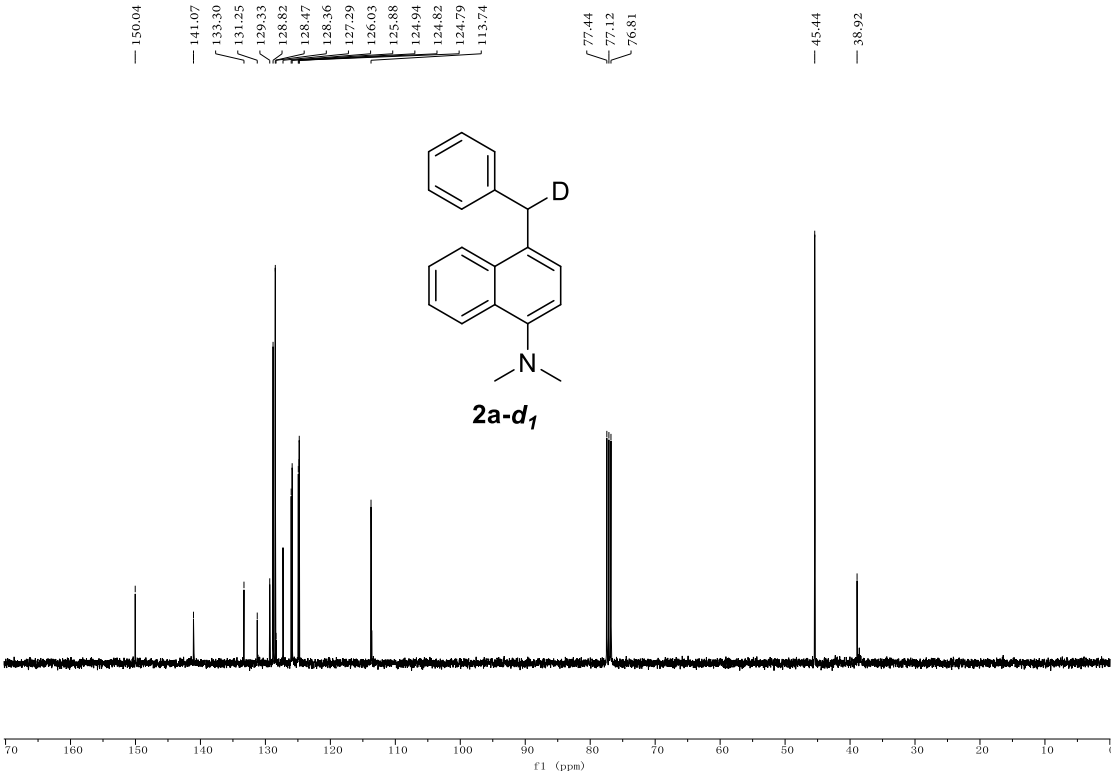


N,*N*-dimethyl-4-(phenylmethyl-*d*)naphthalen-1-amine **(2a-*d*$_1$)**

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

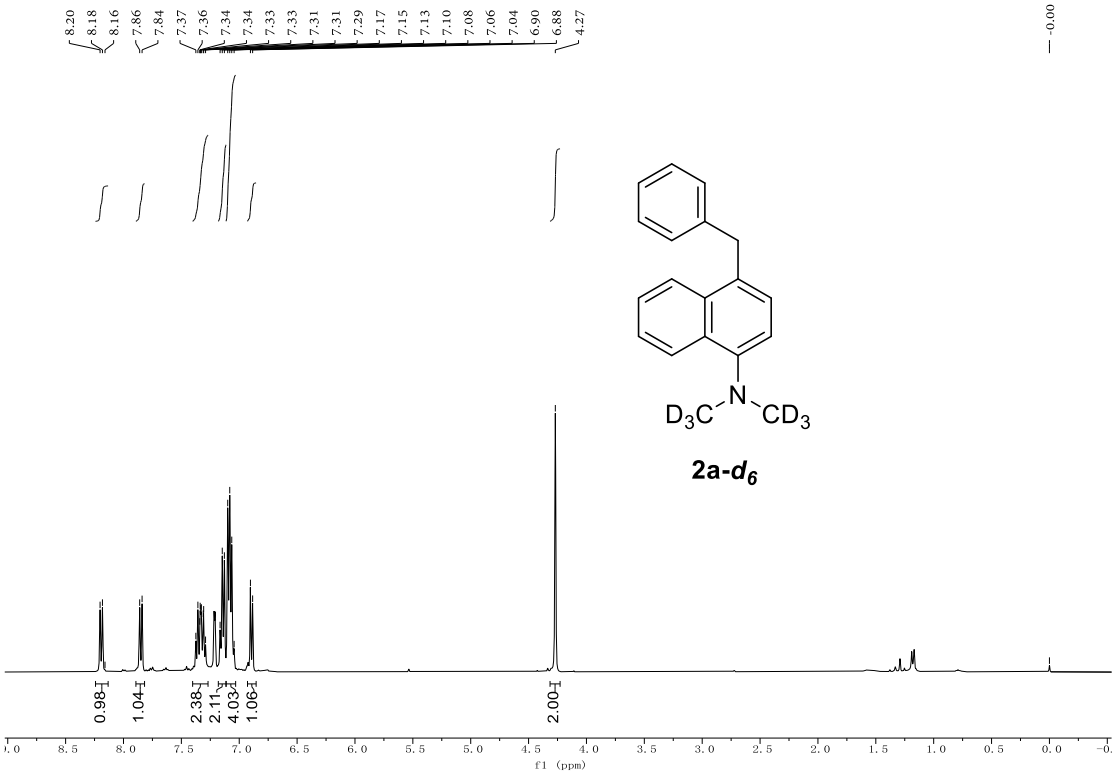


^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$



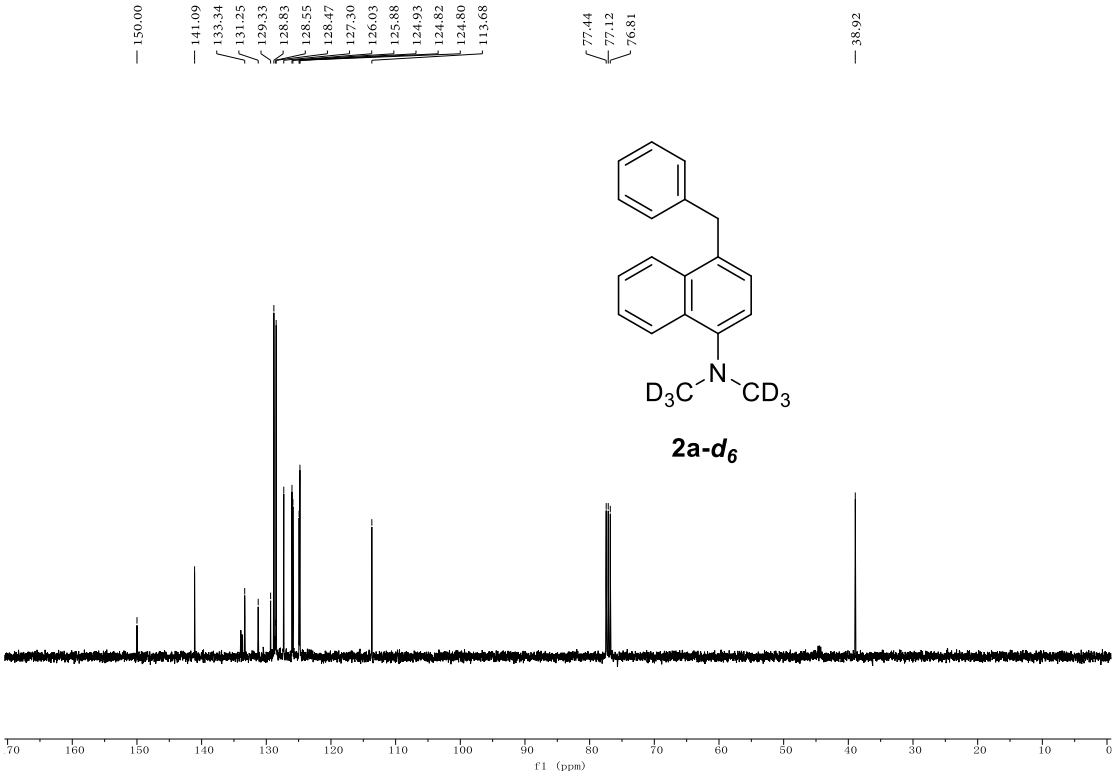
4-benzyl-*N*,*N*-bis(methyl-d_3)naphthalen-1-amine (**2a-*d*$_6$**)

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



2a-*d*$_6$

^{13}C{^{1}H} NMR, 101 MHz, $CDCl_3$



2a-*d*$_6$