Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION FOR

Nickel Catalyzed Reduction of Arenols under Mild Conditions

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1. General Information

1.1 Analytic methods

^{1}H NMR and ^{13}C NMR data were obtained on AVANCE III Bruker 400 M Hz or 500 M Hz nuclear resonance spectrometers unless otherwise noted. ^{11}B NMR data was obtained on AVANCE III Bruker 500 M Hz nuclear resonance spectrometers. $CDCl_3$ or DMSO-d_6 was used as solvent and tetramethylsilane (TMS) was used as the internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Chemical shifts were reported in units (ppm) by assigning BF_3•Et_2O (external standard) resonance in the ^{11}B NMR spectrum as 0.00 ppm. Flash chromatography was performed using 200-300 mesh silica gel with the indicated eluent according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) unless otherwise noted. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI) by the State-authorized Analytical Center in Peking University or on a GCT-MS Micromass UK spectrometer by the State-authorized Analytical Center in Institute of Chemistry Chinese Academy of Sciences.

1.2 Reagents

$Ni(cod)_2$ was purchased from Aldrich. PCy_3 was purchased from Sinocompound Catalysts Co., Ltd, and used without further purification. Anhydrous K_3PO_4 was purchased from Alfa and further heated at 450 ^{o}C for 12 h. B_2Pin_2 and other reagents were purchased from the local company and used directly without further purification otherwise noted. Toluene and tetrahydrofuran were freshly distilled over sodium under N_2 with the use of diphenyl ketone as an indicator and degassed before use. *N*, *N*-dimethylformamide (DMF) was freshly distilled over CaH_2 under reduced pressure and degassed before use. Naphthalen-2-ol (**1a**), 5-aminonaphthalen-1-ol (**12a**), naphthalen-1-ol (**21a**), naphthalene-2,6-diol (**26a**), 4-phenylphenol (**34a**), 3-phenylphenol (**35a**), 2-phenylphenol (**36a**) and 2-methylnaphthalen-1-ol (**39a**) were purchased from Alfa, *J&K*, and local company, and used as received. 6-methylnaphthalen-2-ol (**2a**), 6-isopropylnaphthalen-2-ol (**3a**), 6-hexylnaphthalen-2-ol (**4a**), 1-methylnaphthalen-2-ol (**23a**), 6-(6-((tetrahydro-2*H*-pyran-2-yl)oxy)hexyl)naphthalen-2-ol (**27a**) and 6-(3-methoxypropyl)naphthalen-2-ol (**31a**) were prepared from the corresponding Grignard reagents with 6-bromonaphthalen-2-ol or 1-bromonaphthalen-2-ol.[1] 6-phenylnaphthalen-2-ol (**5a**), 6-(4-(trifluoromethyl)phenyl)naphthalen-2-ol (**18a**), 6-(4-methoxyphenyl)naphthalen-2-ol (**19a**), 6-(4-hydroxyphenyl)naphthalen-2-ol (**20a**), 1-phenylnaphthalen-2-ol (**24a**) and 4-(4-trifluoromethylphenyl)phenol (**38a**) were prepared from the corresponding aryl boric acids and

6-bromonaphthalen-2-ol, 1-bromonaphthalen-2-ol or 4-bromophenol.[2]

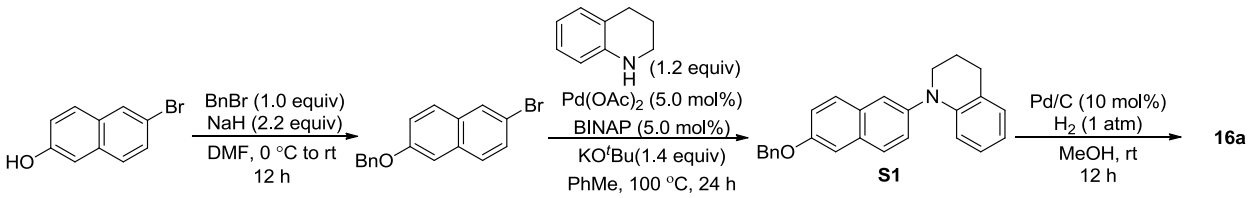
6-(trimethylsilyl)naphthalen-2-ol (**6a**) and 4-(4-trimethylsilylphenyl)phenol (**37a**) were prepared from chlorotrimethylsilane with 6-bromonaphthalen-2-ol or 4'-bromo-[1,1'-biphenyl]-4-ol.[3]

6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-ol (**7a**) was prepared from 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) with 6-bromonaphthalen-2-ol. [4]

7-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-ol (**8a**), 7-((triisopropylsilyl)oxy)naphthalen-2-ol (**9a**) and 6-((triisopropylsilyl)oxy)naphthalen-2-ol (**10a**) were prepared from the corresponding silyl chlorides with dihydroxynaphthalene. [5] 7-(dimethylamino)naphthalen-2-ol (**11a**), 7-(4-phenylpiperazin-1-yl)naphthalen-2-ol (**13a**), 7-morpholinonaphthalen-2-ol (**14a**) and 7-(4-methylpiperidin-1-yl)naphthalen-2-ol (**15a**) were prepared from the corresponding amines with dihydroxynaphthalene.[6] 9-methyl-9*H*-carbazol-2-ol (**17a**) prepared from the 9*H*-carbazol-2-ol. [7] Phenanthren-9-ol (**22a**) was prepared from 9-bromophenanthrene. [8] 1,3-diethylnaphthalen-2-ol (**25a**) was prepared from 1-bromonaphthalen-2-ol.[9] 6-(5-hydroxypentyl)naphthalen-2-ol (**32a**) was prepared from the hydrolysis of 6-(6-((tetrahydro-2*H*-pyran-2-yl)oxy)hexyl)naphthalen-2-ol (**27a**) with *p*-toluenesulfonic acid monohydrate in dichloromethane under room temperature. 5-(6-hydroxynaphthalen-2-yl)pentyl acetate (**28a**) was prepared from 6-(5-hydroxypentyl)naphthalen-2-ol (**32a**).[10] Naphthalen-2-ylmethanol (**33a**) was prepared from 2-naphthaldehyde. [11] 2-naphthol-OD **(1aa)** was prepared from 2-naphthol and DCl.[12].

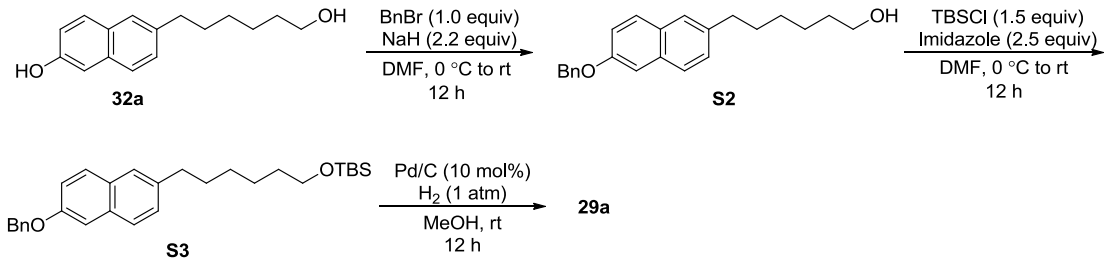
2. Synthesis of Substrates

6-(3,4-dihydroquinolin-1(2*H*)-yl)naphthalen-2-ol (**16a**)



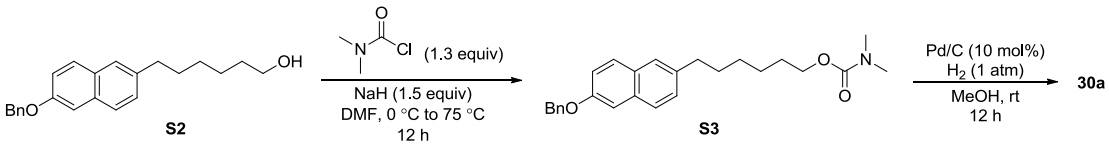
To a dispersion of NaH (0.88 g, 22.0 mmol, 60% in mineral oil) in DMF (5.0 mL) was slowly added 6-bromonaphthalen-2-ol (2.22 g, 10.0 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 30 min, and then a solution of BnBr (1.70 g, 10.0 mmol) in DMF (5.0 mL) was added dropwise. The reaction solution was stirred at room temperature for 12 h. The reaction was quenched with water (5 mL). After separation, the aqueous layer was extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with water (30 mL) and brine (30 mL), and dried over anhydrous Na_2SO_4. After filtration, the solvent was concentrated *in vacuo* to give the crude product and further purified by column chromatography on silica gel to give the product 2-(benzyloxy)-6-bromonaphthalene as a white solid (2.87g, 92%). A 25 mL tube containing 2-(benzyloxy)-6-bromonaphthalene (1.06g, 5.0 mmol), $Pd(OAc)_2$ (56 mg, 5.0 mol%, 0.25 mmol), BINAP (117 mg, 5.0 mol%, 0.25 mmol), KO^{t}Bu (0.78 g, 7.0 mmol, 1.4 equiv) was degassed for three times and then 1,2,3,4-tetrahydroquinoline (0.80 g, 6.0 mmol, 1.2 equiv) and PhMe (8.0 mL) was injected. The mixture was stirred at 100 °C for 24 h. The reaction was quenched with water (2.0 mL). After separation, the aqueous layer was extracted with dichloromethane (15 mL × 3). The combined organic layers were washed with water (15 mL) and brine (15 mL), and dried over anhydrous Na_2SO_4.

After filtration, the solvent was concentrated *in vacuo* and the crude product **S1** was mixed with Pd/C (1.05 g, 0.5 mmol, 10%) and MeOH (100 mL) carefully. Then the mixture was stirred in H_2 (1 atm) at room temperature for 12 h. After filtration, the solvent was concentrated *in vacuo* to give the crude product and further purified by column chromatography on silica gel to give the product **16a** as a white solid (0.98g, 71%)



6-(6-((*tert*-butyldimethylsilyl)oxy)hexyl)naphthalen-2-ol (29a)

To a dispersion of NaH (0.88 g, 22.0 mmol, 60% in mineral oil) in DMF (5.0 mL) was slowly added **32a** (2.44 g, 10.0 mmol) at 0 ^{o}C. The reaction mixture was stirred at the same temperature for 30 min, and then a solution of BnBr (1.70 g, 10.0 mmol) in DMF (5.0 mL) was added dropwise. The reaction solution was stirred at room temperature for 12 h. The reaction was quenched with water (5 mL). After separation, the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. After filtration, the solvent was concentrated *in vacuo* to give the crude product and further purified by column chromatography on silica gel to give the product **S2** as a white solid (2.91g, 87%). To a solution of **S2** (0.67g, 2 mmol) in DMF (2.0 mL) was added imidazole (0.34g, 5.0 mmol). TBSCl (0.45g, 3.0 mmol) was added to the mixture at 0 ^{o}C and the mixture was stirred at room temperature for 12 h. The reaction was quenched with water (2.0 mL). After separation, the aqueous layer was extracted with dichloromethane (5.0 mL × 3). The combined organic layers were washed with water (5.0 mL) and brine (5.0 mL), and dried over anhydrous Na_2SO_4. After filtration, the solvent was concentrated *in vacuo* to give the crude product **S3**. The crude product **S3** was mixed with Pd/C (0.21 g, 0.2 mmol, 10%) and MeOH (50 mL) carefully. Then the mixture was stirred in H_2 (1 atm) at room temperature for 12 h. After filtration, the solvent was concentrated *in vacuo* to give the crude product and further purified by column chromatography on silica gel to give the product **29a** as a light grey liquid (0.68g, 95%).

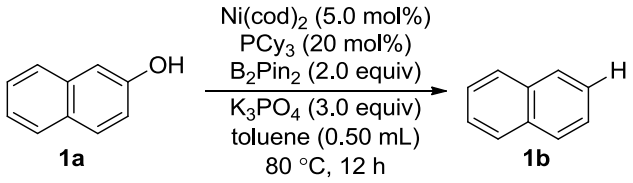


6-(6-hydroxynaphthalen-2-yl)hexyl dimethylcarbamate (30a)

To a dispersion of NaH (0.11 g, 2.6 mmol, 60% in mineral oil) in DMF (3.0 mL) was slowly added **S2** (0.68 g, 2.0 mmol) at 0 ^{o}C. The reaction mixture was stirred at the same temperature for 30 min, and then a solution of dimethylcarbamic chloride (0.27 mL, 3.0 mmol) in DMF (2.0 mL) was added dropwise. The reaction solution was warmed to 75 ^{o}C and stirred for 12 h. The reaction was quenched with water (5 mL). After separation, the aqueous layer was extracted with ethyl acetate (10 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), and dried over

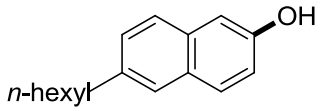
anhydrous Na_2SO_4. After filtration, the solvent was concentrated *in vacuo* to give the crude product **S3**. The crude product **S3** was mixed with Pd/C (0.21 g, 0.2 mmol, 10%) and MeOH (50 mL) carefully. Then the mixture was stirred in H_2 (1 atm) at room temperature for 12 h. After filtration, the solvent was concentrated *in vacuo* to give the crude product and further purified by column chromatography on silica gel and further recrystallized to give the product **30a** as a white solid (0.51g, 80%).

3. General procedure for the reduction of arenols



To an oven-dried schlenk tube with a stirring bar was added **1a** (28.8 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) in the air, and then K_3PO_4 (127.2 mg, 0.60 mmol, 3.0 equiv), PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of toluene (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^oC for 12 h. The mixture was then cooled to room temperature and directly purified by column chromatography with hexane as the eluant to afford compound **1b** as a white solid (20.5 mg, 80%).

4. Characterization of starting materials



6-hexylnaphthalen-2-ol (**4a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.54 (s, 1H), 7.29 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.14 –7.10 (m, 1H), 7.07 (dd, *J* = 8.8, 2.5 Hz, 1H), 4.89 (s, 1H), 2.79 – 2.69 (m, 2H), 1.74 –1.64 (m, 2H), 1.42 – 1.24 (m, 6H), 0.94 – 0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.69, 138.17, 132.90, 129.27, 129.12, 128.15, 126.20, 126.16, 117.59, 109.34, 35.90, 31.75, 31.39, 29.01, 22.60, 14.08.

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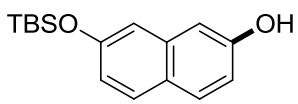
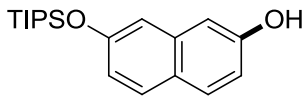


7-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-ol (**8a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (t, *J* = 9.4 Hz, 2H), 7.05 –6.98 (m, 2H), 6.93 (td, *J* = 9.1, 2.4 Hz, 2H), 4.89 (s, 1H), 1.02 (s, 9H), 0.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.12, 153.66, 135.95, 129.56, 129.19, 124.78, 119.71, 115.57, 113.71, 108.54, 25.71, 18.24, -4.35.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 275.14618, Found: 275.14605.



7-((triisopropylsilyl)oxy)naphthalen-2-ol (**9a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.62 (m, 2H), 7.08 (s, 1H), 7.04 – 6.92 (m, 3H), 5.37 (s, 1H), 1.40 – 1.28 (m, 3H), 1.22 – 1.10 (m, 18H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.58, 153.68, 136.01, 129.53, 129.11, 124.61, 119.67, 115.37, 113.24, 108.46, 17.94, 12.71.

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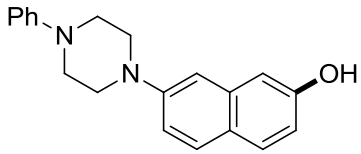
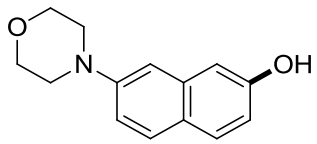


7-(4-phenylpiperazin-1-yl)naphthalen-2-ol (**13a**)

^{1}H NMR (400 MHz, Acetone) δ 8.49 (s, 1H), 7.74 –7.58 (m, 2H), 7.27 (m, 2H), 7.20 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.16 – 7.01 (m, 4H), 6.93 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.84 (t, *J* = 7.3 Hz, 1H), 3.53 –3.30 (m, 8H).

^{13}C NMR (100 MHz, Acetone) δ 156.35, 152.28, 150.42, 137.16, 129.64, 129.57, 129.03, 124.22, 120.11, 117.15, 116.73, 116.05, 109.29, 108.87, 50.02, 49.79.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 305.16484, Found: 305.16462.



7-morpholinonaphthalen-2-ol (**14a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 –7.59 (m, 2H), 7.09 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 6.91 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.20 (s, 1H), 3.92 (t, *J* = 4.8 Hz, 4H), 3.26 (t, *J* = 4.8 Hz, 4H),.

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.04, 134.48, 128.75, 128.61, 127.39, 126.71, 126.28, 123.47, 118.82, 110.01, 66.86, 49.71.

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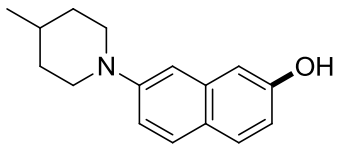

7-(4-methylpiperidin-1-yl)naphthalen-2-ol (**15a**)

^{1}H NMR (400 MHz, Acetone) δ 8.27 (s, 1H), 7.44 (dd, *J* = 8.8, 6.5 Hz, 2H), 6.96 (dd, *J* = 9.0, 2.4 Hz,

1H), 6.89 (d, *J* = 1.8 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 6.80 – 6.72 (m, 1H), 3.72 – 3.60 (m, 2H), 2.65 – 2.51 (m, 2H), 1.69 – 1.57 (m, 2H), 1.51 – 1.35 (m, 1H), 1.26 – 1.11 (m, 2H), 0.84 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, Acetone) δ156.22, 150.91, 137.26, 129.45, 128.78, 123.81, 117.58, 115.62, 109.07, 108.70, 50.39, 34.74, 31.43, 22.05.

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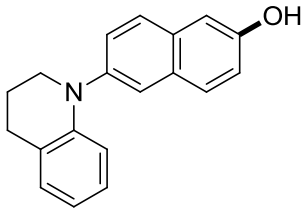
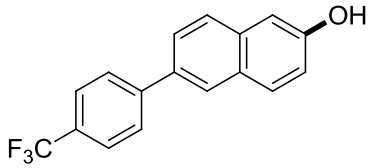


6-(3,4-dihydroquinolin-1(2*H*)-yl)naphthalen-2-ol (**16a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.08 (dd, *J* = 8.6, 2.2 Hz, 2H), 6.97 – 6.90 (m, 1H), 6.77 – 6.69 (m, 2H), 5.10 (s, 1H), 3.71 (t, *J* = 6.0 Hz, 2H), 2.89 (t, *J* = 6.4 Hz, 2H), 2.15 – 2.04 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.77, 144.65, 143.98, 131.70, 129.86, 129.32, 129.00, 127.40, 126.41, 125.79, 124.52, 121.64, 118.26, 117.96, 115.60, 109.52, 51.06, 27.75, 22.75.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 276.13829, Found: 276.13801.



6-(4-(trifluoromethyl)phenyl)naphthalen-2-ol (**18a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.86 – 7.76 (m, 4H), 7.76 – 7.65 (m, 3H), 7.22 – 7.12 (m, 2H), 5.02 (s, 1H).

^{13}C NMR (100 MHz, DMSO) δ 156.11, 144.35, 134.46, 132.67, 130.20, 127.92, 127.36, 127.05, 126.05, 125.86 (q, *J* = 3.5 Hz), 125.11, 119.39, 108.57.

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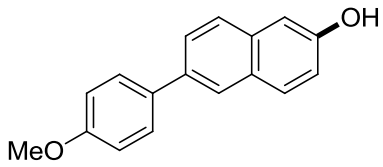

6-(4-methoxyphenyl)naphthalen-2-ol (**19a**)

^{1}H NMR (400 MHz, Acetone) δ 7.82 (s, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.61 –7.56 (s, 1H), 7.55 –7.49 (m, 3H), 7.07 (d, *J* = 2.4 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.91 – 6.85 (m, 2H), 3.69 (s, 3H).

^{13}C NMR (100 MHz, Acetone and $CDCl_3$) δ 158.10, 154.18, 134.05, 132.85, 132.38, 128.58, 127.75, 126.78, 125.62, 124.34, 123.51, 117.65, 113.18, 107.68, 53.71.

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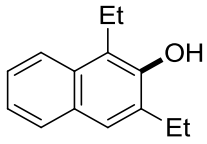
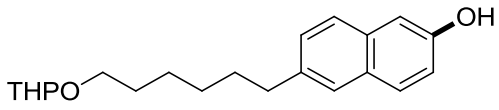


1,3-diethylnaphthalen-2-ol (**25a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.51 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 4.95 (s, 1H), 3.07 (q, *J* = 7.6 Hz, 2H), 2.82 (q, *J* = 7.5 Hz, 2H), 1.37 (t, *J* = 7.5 Hz, 3H), 1.30 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.19, 131.49, 131.41, 129.39, 128.06, 125.46, 125.43, 123.01, 122.56, 120.82, 23.72, 18.44, 14.06, 13.71.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 201.12739, Found: 201.12755.

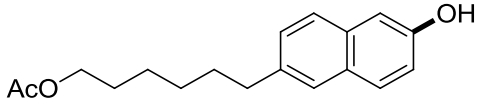


6-(6-((tetrahydro-2H-pyran-2-yl)oxy)hexyl)naphthalen-2-ol (**27a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.29 – 7.19 (m, 1H), 7.14 – 7.08 (m, 1H), 7.08 – 7.00 (m, 1H), 5.96 (s, 1H), 4.61(t, *J* = 3.2 Hz, 1H), 3.97 – 3.84 (m, 1H), 3.82 – 3.68 (m, 1H), 3.60 – 3.47 (m, 1H), 3.47 – 3.34 (m, 1H), 2.80 – 2.58 (m, 2H), 1.89 – 1.47 (m, 10H), 1.44 – 1.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.09, 137.78, 132.97, 129.15, 128.95, 127.98, 126.17, 126.13, 117.78, 109.27, 98.97, 67.77, 62.43, 35.77, 31.28, 30.74, 29.59, 29.07, 26.09, 25.43, 19.61.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 329.21112, Found: 329.21144.

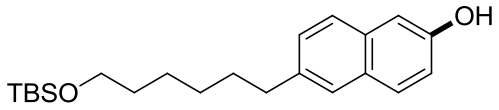


6-(6-hydroxynaphthalen-2-yl)hexyl acetate (**28a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.14 –7.10 (m, 1H), 7.08 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.95 (s, 1H), 4.06 (t, *J* = 6.7 Hz, 2H), 2.70 (t, *J* = 3.6 Hz, 2H), 2.05 (s, 3H), 1.74 – 1.56 (m, 4H), 1.44 – 1.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.79, 153.09, 137.60, 132.99, 129.13, 128.95, 127.92, 126.23, 126.15, 117.80, 109.28, 64.80, 35.72, 31.19, 28.83, 28.46, 25.77, 21.00.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 287.16417, Found: 287.16443.

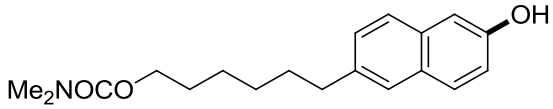


6-(6-((*tert*-butyldimethylsilyl)oxy)hexyl)naphthalen-2-ol (**29a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.16 –7.13 (m, 1H), 7.11 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.60 (s, 1H), 3.67 (t, *J* = 6.6 Hz, 2H), 2.75 (d, *J* = 8.0 Hz, 2H), 1.81 – 1.66 (m, 2H), 1.64 – 1.52 (m, 2H), 1.51 – 1.33 (m, 4H), 0.95 (s, 9H), 0.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.89, 137.91, 132.94, 129.21, 129.03, 128.04, 126.20, 126.16, 117.72, 109.33, 63.43, 35.80, 32.71, 31.36, 29.06, 25.99, 25.68, 18.40, -5.24.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 359.24008, Found: 359.24059.

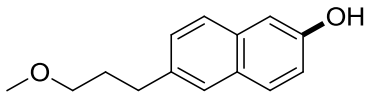


6-(6-hydroxynaphthalen-2-yl)hexyl dimethylcarbamate (**30a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 7.23 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.15 (s, 1H), 7.11 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.76 (s, 1H), 4.10 (t, *J* = 6.6 Hz, 2H), 2.91 (d, *J* = 12.0 Hz, 6H), 2.79 – 2.64 (m, 2H), 1.74 – 1.58 (m, 4H), 1.48 – 1.33 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.18, 153.53, 137.44, 133.06, 128.99, 128.81, 127.80, 126.19, 126.11, 118.00, 109.25 , 65.77, 35.73, 31.25, 28.96, 28.90, 25.81.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 316.19072, Found: 316.19140.

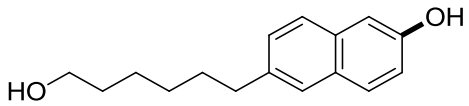


6-(3-methoxypropyl)naphthalen-2-ol (**31a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.29 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.07 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.15 (s, 1H), 3.43 (t, *J* = 6.4 Hz, 2H), 3.37 (s, 3H), 2.81 (t, *J* = 8.0 Hz, 2H), 2.03 – 1.92 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.25, 136.61, 133.07, 129.18, 128.87, 127.81, 126.35, 126.31, 117.91, 109.27, 72.08, 58.45, 32.08, 30.92.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 217.12231, Found: 217.12257.

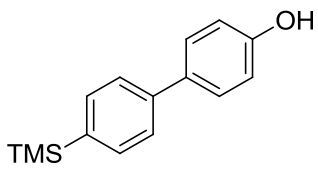


6-(6-hydroxyhexyl)naphthalen-2-ol (**32a**)

^{1}H NMR (400 MHz, Acetone) δ 8.55 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.27 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.16 (d, *J* = 2.3 Hz, 1H), 7.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.53 (t, *J* = 3.4 Hz, 2H), 2.72 (t, *J* = 8.0 Hz, 2H), 1.75 – 1.62 (m, 2H), 1.58 – 1.46 (m, 2H), 1.46 – 1.32 (m, 4H).

^{13}C NMR (100 MHz, Acetone) δ 155.33, 137.67, 134.09, 129.44, 129.27, 128.21, 126.66, 118.80, 109.33, 62.13, 36.10, 33.39, 32.01, 29.59, 26.23.

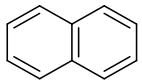
HRMS (ESI): Anal. Calcd. ($M+H^+$), 245.15361, Found: 245.15397.



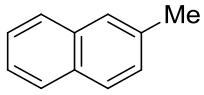
4-(4-trimethylsilylphenyl)phenol (**37a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 –7.52 (m, 4H), 7.52 – 7.46 (m, 2H), 6.93 – 6.87 (m, 2H), 4.82 (s, 1H), 0.30 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.13, 141.12, 138.53, 133.95, 133.79, 128.39, 126.05, 115.64, -1.09.
HRMS (EI): Anal. Calcd. (M^+), 242.1127, Found: 242.1125.

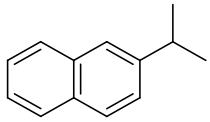
5. Characterization of products



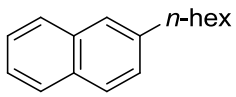
Naphthalene (**1b**) and (**21b**) (**26b**)[13]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (m, 4H), 7.61 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 133.45, 127.87, 125.80.



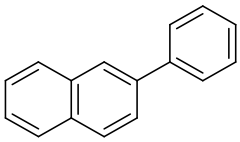
2-methylnaphthalene (**2b**) (**33b**) [14]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.76-7.70 (m, 2H), 7.60 (s, 1H), 7.47 – 7.36 (m, 2H), 7.31 (d, *J* = 8.3 Hz, 1H), 2.51 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 135.38, 133.66, 131.70, 128.08, 127.66, 127.57, 127.20, 126.81, 125.83, 124.92, 21.66.



2-isopropylnaphthalene (**3b**) [15]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 –7.75 (m, 3H), 7.66 (s, 1H), 7.50 – 7.38 (m, 3H), 3.14 – 3.03 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 146.30, 133.63, 132.07, 127.80, 127.55, 127.54, 125.78, 125.74, 125.03, 124.06, 34.22, 23.92.



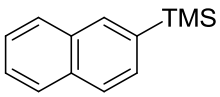
2-hexylnaphthalene (**4b**)[16]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 –7.81 (m, 3H), 7.70 (s, 1H), 7.57 – 7.46 (m, 2H), 7.42 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.86 (t, *J* = 8.0 Hz 2H), 1.88 –1.73 (m, 2H), 1.54 – 1.36 (m, 6H), 1.06 – 0.94 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.43, 133.66, 131.94, 127.70, 127.57, 127.42, 127.38, 126.26, 125.76, 124.94, 36.12, 31.77, 31.34, 29.03, 22.63, 14.10.



2-phenylnaphthalene (**5b**) [14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.95 – 7.82 (m, 3H), 7.73 (t, *J* = 8.0 Hz, 3H), 7.57 –7.43 (m, 4H), 7.37 (t, *J* = 7.4 Hz, 1H).

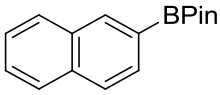
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.12, 138.55, 133.67, 132.61, 128.84, 128.39, 128.18, 127.63, 127.42, 127.33, 126.26, 125.91, 125.79, 125.58.



Trimethyl(naphthalen-2-yl)silane (**6b**) [17]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.91 – 7.80 (m, 3H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.46 (m, 2H), 0.38 (s, 9H).

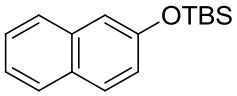
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.90, 133.74, 133.62, 132.92, 129.78, 127.99, 127.68, 126.90, 126.18, 125.85, -1.09.



4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (**7b**) [18]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.92 (m, 4H), 7.60 – 7.46 (m, 2H), 1.43 (s, 12H).

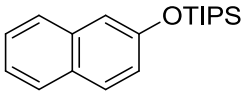
^{13}C NMR (100 MHz, $CDCl_3$) δ 136.21, 135.00, 132.79, 130.37, 128.59, 127.66, 126.93, 126.91, 125.74, 83.85, 24.87.



***Tert*-butyldimethyl(naphthalen-2-yloxy)silane** (**8b**)[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (m, 3H), 7.47 – 7.40 (m, 1H), 7.38 – 7.31 (m, 1H), 7.21 (d, *J* = 2.3 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.4 Hz, 1H), 1.04 (s, 9H), 0.27 (s, 6H).

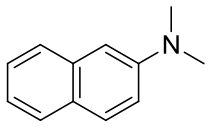
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.46, 134.64, 129.29, 129.27, 127.60, 126.66, 126.10, 123.72, 122.07, 114.90, 25.73, 18.27, -4.33.



Triisopropyl(naphthalen-2-yloxy)silane (**9b**) and (**10b**)[20]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.61 (m, 3H), 7.43 – 7.36 (m, 1H), 7.34 – 7.27 (m, 1H), 7.21 (d, *J* = 2.2 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.4 Hz, 1H), 1.36-1.27 (m, 3H), 1.11 (m, 18H).

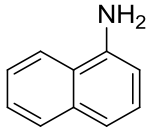
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.86, 134.68, 129.23, 129.10, 127.58, 126.61, 126.06, 123.58, 122.02, 114.45, 17.97, 12.73.



***N,N*-dimethylnaphthalen-2-amine (11b)**[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 3H), 7.38 – 7.29 (m, 1H), 7.22-7.14 (m, 1H), 7.14 –7.08 (m, 1H), 6.89 (s, 1H), 2.96 (d, *J* = 2.5 Hz, 6H).

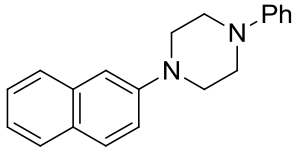
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.54, 134.92, 128.60, 127.38, 126.82, 126.12, 121.99, 116.37, 106.45, 40.76.



Naphthalen-1-amine (12b)[22]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.56 – 7.46 (m, 2H), 7.41 –7.30 (m, 2H), 6.82 (dd, *J* = 6.8, 1.6 Hz, 1H), 4.17 (s, 2H).

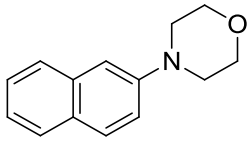
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.11, 134.38, 128.49, 126.31, 125.79, 124.78, 123.62, 120.79, 118.87, 109.62.



1-(naphthalen-2-yl)-4-phenylpiperazine (13b) [23]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (q, *J* = 8.0 Hz, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 –7.28 (m, 4H), 7.22 –7.18 (m, 1H), 7.07 – 7.00 (m, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 3.53 –3.35 (m, 8H).

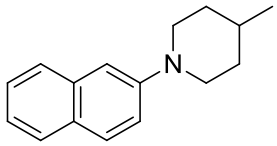
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.23, 149.05, 134.56, 129.19, 128.78, 128.68, 127.44, 126.76, 126.30, 123.51, 120.09, 119.53, 116.37, 110.55, 49.75, 49.42.



4-(Naphthalene-2-yl)morpholine (14b)[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 3H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.29 –7.23 (m, 1H), 7.13 (s, 1H), 3.92 (t, *J* = 4.4 Hz, 4H), 3.26 (t, *J* = 4.8 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.04, 134.48, 128.75, 128.61, 127.39, 126.71, 126.28, 123.47, 118.82, 110.01, 66.86, 49.71.

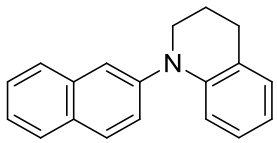


4-methyl-1-(naphthalen-2-yl)piperidine (**15b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.73 (m, 3H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.21 (d, *J* = 2.2 Hz, 1H), 3.84 (d, *J* = 12.4 Hz, 2H), 2.83 (td, *J* = 12.1, 2.2 Hz, 2H), 1.85 (d, *J* = 13.8 Hz, 2H), 1.70 – 1.57 (m, 1H), 1.55 – 1.42 (m, 2H), 1.09 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.71, 134.69, 128.42, 128.22, 127.31, 126.58, 126.01, 122.99, 120.02, 110.25, 50.22, 34.07, 30.70, 21.85.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 226.15903, Found: 226.15892.

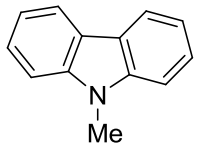


1-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinoline (**16b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 –7.80 (m, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.54 – 7.41 (m, 3H), 7.15 (d, *J* = 7.3 Hz, 1H), 7.06 – 6.97 (m, 1H), 6.95 – 6.88 (m, 1H), 6.82 (t, *J* = 7.3 Hz, 1H), 3.79 (t, *J* = 6.0 Hz, 2H), 2.93 (t, *J* = 6.5 Hz, 2H), 2.20 – 2.08 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.83, 144.11, 134.54, 130.31, 129.27, 128.75, 127.53, 127.00, 126.35, 126.14, 125.34, 124.55, 124.40, 120.12, 118.81, 116.23, 50.60, 27.66, 22.91.

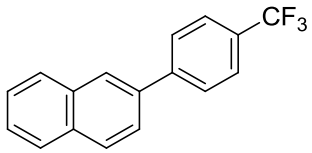
HRMS (ESI): Anal. Calcd. ($M+H^+$), 260.14338, Found: 260.14366.



9-methyl-9*H*-carbazole (**17b**)[13]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.8 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.26 (m, 2H), 3.89 (s, 3H).

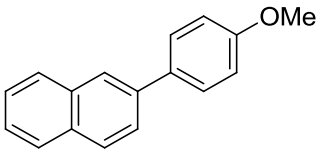
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.98, 125.64, 122.76, 120.28, 118.81, 108.39, 29.04



2-(4-(trifluoromethyl)phenyl)naphthalene (**18b**)[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.00 – 7.88 (m, 3H), 7.87-7.80 (m, 2H), 7.80 – 7.70 (m, 3H), 7.62 – 7.52 (m, 2H).

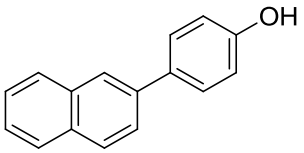
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.60, 136.98, 133.54, 132.97, 129.35 (q, *J* = 32.5 Hz), 128.74, 128.29, 127.68, 127.61, 126.57, 126.46, 126.31, 125.75 (q, *J* = 3.7 Hz), 125.14, 123.00.



2-(4-methoxyphenyl)naphthalene (19b)[25]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.91 – 7.81 (m, 3H), 7.71 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.52 –7.42 (m, 2H), 7.05 – 6.98 (m, 2H), 3.85 (s, 3H).

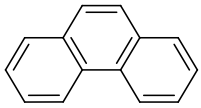
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.23, 138.12, 133.74, 133.59, 132.29, 128.39, 128.31, 128.02, 127.59, 126.19, 125.61, 125.40, 124.99, 114.30, 55.33.



4-(naphthalen-2-yl)phenol (20b)[26]

^{1}H NMR (400 MHz, DMSO) δ 9.63 (s, 1H), 8.11 (s, 1H), 8.02 – 7.83 (m, 3H), 7.79 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.57 – 7.38 (m, 2H), 6.94 (d, *J* = 8.6 Hz, 2H).

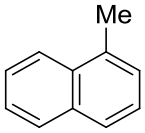
^{13}C NMR (100 MHz, DMSO) δ 157.31, 137.58, 133.47, 131.74, 130.67, 128.27, 128.06, 127.94, 127.43, 126.25, 125.57, 124.88, 123.90, 115.87.



Phenanthrene (22b)[14]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.74 (s, 2H), 7.70 – 7.55 (m, 4H).

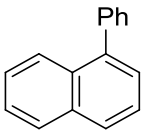
^{13}C NMR (100 MHz, $CDCl_3$) δ 132.05, 130.32, 128.56, 126.91, 126.55, 122.64.



1-methylnaphthalene (23b)[27]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 –7.92 (m, 1H), 7.86-7.78 (m, 1H), 7.72 –7.64 (s, 1H), 7.53 – 7.40 (m, 2H), 7.39 –7.26 (m, 2H), 2.67 (s, 3H).

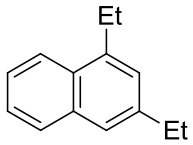
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.21, 133.58, 132.63, 128.51, 126.54, 126.36, 125.68, 125.51, 124.08, 19.32.



1-phenylnaphthalene (24b)[28]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.44 (m, 9H).

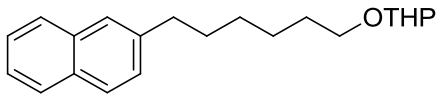
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.76, 140.26, 133.79, 131.62, 130.06, 128.24, 127.61, 127.22, 126.90, 126.02, 126.00, 125.74, 125.36.



1,3-diethylnaphthalene (**25b**)[29]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 1H), 7.81 – 7.74 (m, 1H), 7.47 (s, 1H), 7.46 – 7.37 (m, 2H), 7.19 (s, 1H), 3.07 (q, *J* = 7.5 Hz, 2H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.37 (t, *J* = 7.5 Hz, 3H), 1.31 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.42, 140.14, 134.18, 130.26, 128.25, 126.19, 125.40, 124.83, 123.95, 123.55, 29.01, 25.90, 15.42, 15.10.

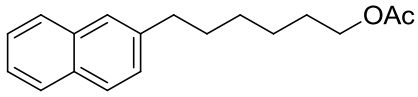


2-((6-(naphthalen-2-yl)hexyl)oxy)tetrahydro-2*H*-pyran (**27b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.74 (m, 3H), 7.63 (s, 1H), 7.50 – 7.39 (m, 2H), 7.35 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.66 – 4.55 (m, 1H), 3.95 –3.84 (m, 1H), 3.80 –3.71 (m, 1H), 3.56 –3.47 (m, 1H), 3.46-3.37 (m, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.90 – 1.39 (m, 14H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.25, 133.59, 131.89, 127.67, 127.53, 127.35, 127.33, 126.23, 125.74, 124.92, 98.79, 67.54, 62.27, 35.98, 31.22, 30.74, 29.64, 29.08, 26.11, 25.46, 19.65.

HRMS (ESI): Anal. Calcd. ($M+Na^+$), 335.19815, Found: 335.19867.

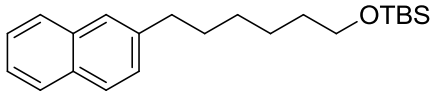


6-(naphthalen-2-yl)hexyl acetate (**28b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 3H), 7.62 (s, 1H), 7.49 – 7.40 (m, 2H), 7.34 (dd, *J* = 8.4, 1.5 Hz, 1H), 4.07 (t, *J* = 6.7 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.05 (s, 3H), 1.80 – 1.69 (m, 2H), 1.68 – 1.59 (m, 2H), 1.48 – 1.35 (m, 4H).

^{13}C NMR (100 MHz, DMSO) δ 171.17, 140.09, 133.59, 131.91, 127.74, 127.55, 127.34, 127.32, 126.26, 125.80, 125.00, 64.53, 35.95, 31.16, 28.86, 28.51, 25.80, 20.96.

HRMS (ESI): Anal. Calcd. ($M+Na^+$), 293.15120, Found: 293.15163.



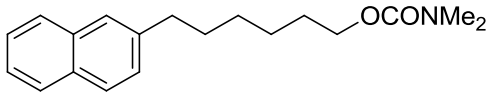
***Tert*-butyldimethyl((6-(naphthalen-2-yl)hexyl)oxy)silane** (**29b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.75 (m, 3H), 7.63 (s, 1H), 7.51 – 7.40 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.81 – 1.68 (m, 2H), 1.63 – 1.51 (m, 2H), 1.49 – 1.37 (m, 4H), 0.93 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.33, 133.64, 131.93, 127.71, 127.57, 127.41, 127.38, 126.27,

125.78, 124.96, 63.24, 36.04, 32.80, 31.33, 29.10, 25.98, 25.71, 18.36, -5.26.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 343.24517, Found: 343.24580.

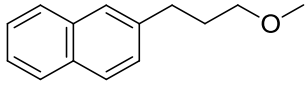


6-(naphthalen-2-yl)hexyl dimethylcarbamate (**30b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 3H), 7.62 (s, 1H), 7.50 – 7.39 (m, 2H), 7.34 (dd, *J* = 8.4, 1.5 Hz, 1H), 4.08 (t, *J* = 6.6 Hz, 2H), 2.90 (s, 6H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.83 – 1.69 (m, 2H), 1.69 – 1.57 (m, 2H), 1.52 – 1.35 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.77, 140.13, 133.57, 131.89, 127.70, 127.53, 127.32, 126.23, 125.76, 124.95, 65.35, 35.95, 31.18, 28.99, 28.90, 25.83.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 300.19581, Found: 300.19570.

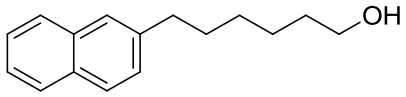


2-(3-methoxypropyl)naphthalene (**31b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 –8.76 (m, 3H), 7.65 (s, 1H), 7.52-7.41 (m, 2H), 7.36 (dd, *J* = 8.4, 1.5 Hz, 1H), 3.44 (t, *J* = 6.4 Hz, 2H), 3.38 (s, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.06 – 1.96 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.25, 136.61, 133.07, 129.18, 128.87, 127.81, 126.35, 126.31, 117.91, 109.27, 72.08, 58.45, 32.08, 30.92.

HRMS (ESI): Anal. Calcd. ($M+H^+$), 201.12739, Found: 201.12771.

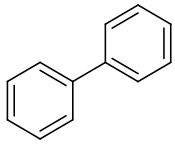


6-(naphthalen-2-yl)hexan-1-ol (**32b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 3H), 7.62 (s, 1H), 7.50 –7.39 (m, 2H), 7.34 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.81 – 1.68 (m, 2H), 1.64 – 1.52 (m, 2H), 1.50 – 1.38 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.20, 133.60, 131.91, 127.73, 127.56, 127.36, 126.26, 125.80, 124.98, 62.94, 35.98, 32.67, 31.24, 29.03, 25.60.

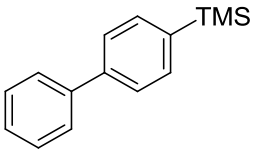
HRMS (ESI): Anal. Calcd. ($M+H^+$), 229.15869, Found: 229.15885.



1,1'-biphenyl (**34b**), (**35b**) and (**36b**)[30]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 4H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 2H).

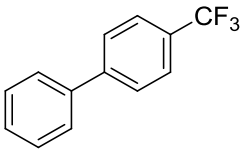
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.18, 128.71, 127.20, 127.11.



[1,1'-biphenyl]-4-yltrimethylsilane (**37b**)[31]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 6H), 7.72 – 7.64 (m, 2H), 7.59 – 7.52 (m, 1H), 0.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.60, 141.16, 139.17, 133.81, 128.75, 127.31, 127.15, 126.50, -1.07.



4-(trifluoromethyl)-1,1'-biphenyl (**38b**)[32]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 4H), 7.72 –7.64 (m, 2H), 7.59 – 7.53 (m, 2H), 7.53-7.46 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.69, 139.70, 129.31 (q, *J* = 32.3 Hz), 128.97, 128.18, 127.37, 127.23, 125.68 (q, *J* = 3.7 Hz), 123.03

6. Experimental details for Scheme 2

Experimental details for equation 1 in Scheme 2: To an oven-dried schlenk tube with a stirring bar was added 2-naphthol-OD **(1aa)** (29.0 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) in the air, and then K_3PO_4 (127.2 mg, 0.60 mmol, 3.0 equiv), PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of toluene (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^{o}C for 12 h. The mixture was then cooled to room temperature and directly purified by column chromatography on silica gel with hexane/ ethyl acetate (1:0 to 20:1) as the eluant to afford naphthalene as a white solid (19.3 mg, 75%) and no deuterium incorporation was occurred in the product from the ^{11}H NMR analyses.

Experimental details for equation 2 in Scheme 2: To an oven-dried schlenk tube with a stirring bar was added phenanthren-9-ol (**22a**) (38.8 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) in the air, and then K_3PO_4 (127.2 mg, 0.60 mmol, 3.0 equiv), PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of benzene-*d6* (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^{o}C for 12 h. After the mixture was cooled to room temperature, dodecane (34.0 mg, 0.2 mmol) was added and then the mixture was diluted with ethyl acetate (5.0 mL), followed by stirring for 15 min. After centrifugation and sedimentation of the mixture, the clear organic layer was subjected to GC analyses. GC analysis of the reaction mixture showed the formation of phenanthrene (70%). Then the solvent was concentrated *in vacuo* and the residues was directly purified by column chromatography on silica gel with hexane/ ethyl acetate (1:0 to 20:1) as the eluant and 52% deuterium incorporation was occurred in the product from the ^{11}H NMR analyses.

Experimental details for equation 3 in Scheme 2: To an oven-dried schlenk tube with a stirring bar was added phenanthren-9-ol (**22a**) (38.8 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) in the

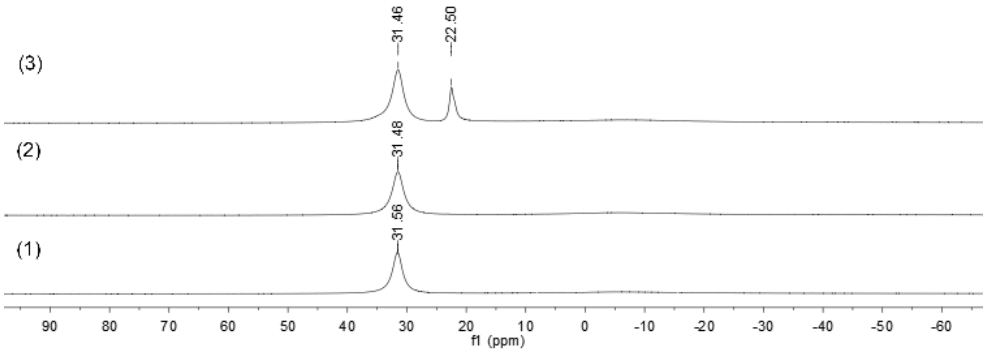
air, and then K_3PO_4 (127.2 mg, 0.60 mmol, 3.0 equiv), PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of toluene (0.50 mL) and D_2O (4.0 mg, 0.2 mmol, 1.0 equiv) in glove box. The tube was sealed up and the mixture was stirred at 80 ^oC for 12 h. After the mixture was cooled to room temperature, dodecane (34.0 mg, 0.2 mmol) was added and then the mixture was diluted with ethyl acetate (5.0 mL), followed by stirring for 15 min. After centrifugation and sedimentation of the mixture, the clear organic layer was subjected to GC analyses. GC analysis of the reaction mixture showed the formation of phenanthrene (35%). Then the solvent was concentrated *in vacuo* and the residues was directly purified by column chromatography on silica gel with hexane/ ethyl acetate (1:0 to 20:1) as the eluant and 68% deuterium incorporation was occurred in the product from the ^{11}H NMR analyses.

Experimental details for equation 4 in Scheme 2: To an oven-dried schlenk tube with a stirring bar was added 2-methylnaphthalen-1-ol (**39a**) (31.6 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) in the air, and then K_3PO_4 (127.2 mg, 0.60 mmol, 3.0 equiv), PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of benzene-*d6* (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^oC for 12 h. After the mixture was cooled to room temperature, dodecane (34.0 mg, 0.2 mmol) was added and then the mixture was diluted with ethyl acetate (5.0 mL), followed by stirring for 15 min. After centrifugation and sedimentation of the mixture, the clear organic layer was subjected to GC analyses. GC analysis of the reaction mixture showed the formation of 2-methylnaphthalene (30%). Then the solvent was concentrated *in vacuo* and the residues was directly purified by column chromatography on silica gel with hexane/ ethyl acetate (1:0 to 20:1) as the eluant and 77%, 17%, 17%, 11% deuterium incorporations were occurred in the product from the ^{11}H NMR analyses.

Experimental details for equation 5 in Scheme 2: To an oven-dried schlenk tube with a stirring bar was added 4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (**7b**) (50.8 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) in the air, and then K_3PO_4 (127.2 mg, 0.60 mmol, 3.0 equiv), PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of toluene (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^oC for 12 h. Then the mixture was cooled to room temperature and diluted with ethyl acetate (5.0 mL), followed by stirring for 15 min. After centrifugation and sedimentation of the mixture, the clear organic layer was subjected to GC-MS analyses. GC-MS analysis of the reaction mixture showed the formation of naphthalene.

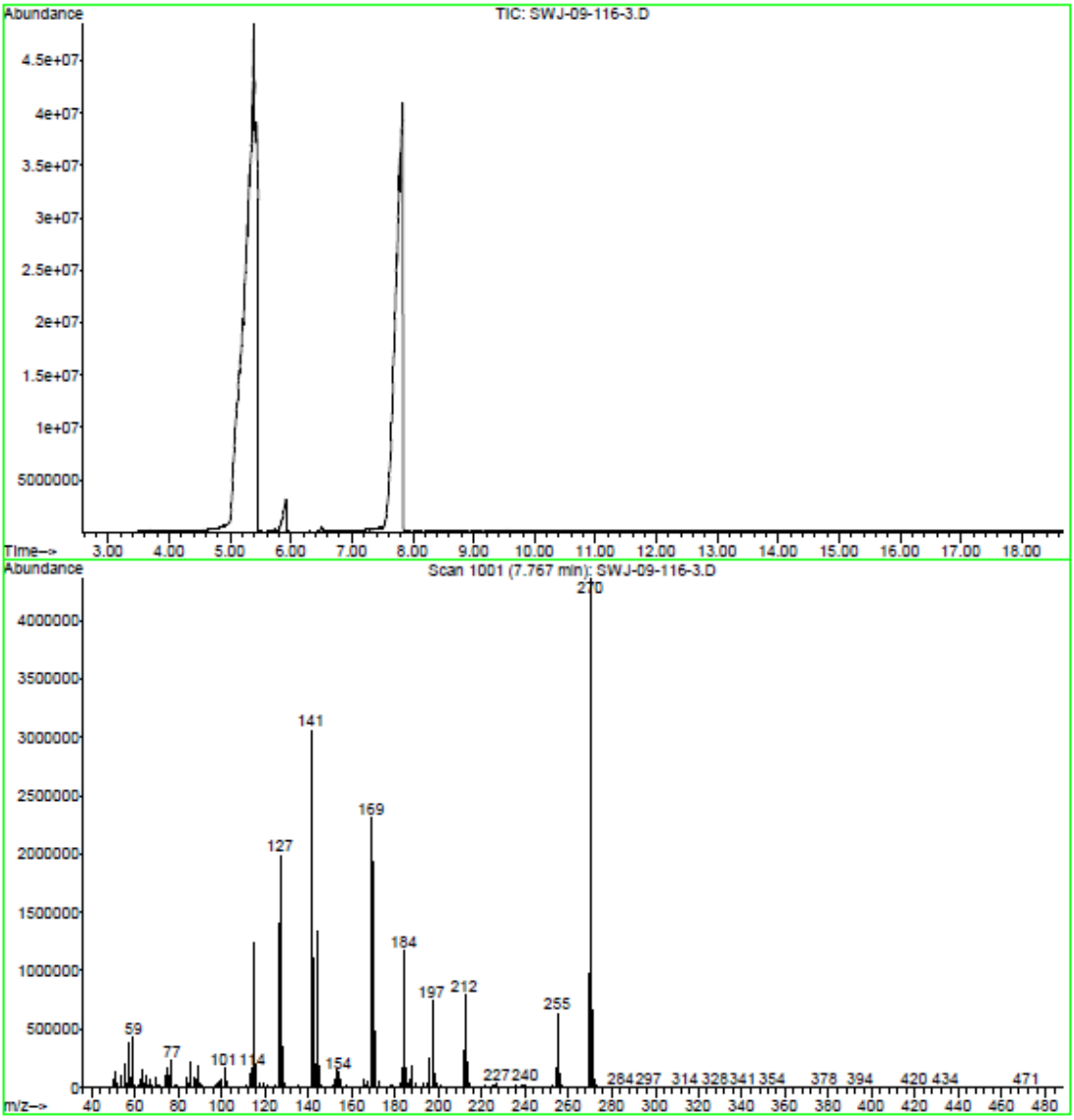
Experimental details for equation 6 in Scheme 2: To an oven-dried schlenk tube with a stirring bar was added 2-naphthol **(1a)** (28.8 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) and 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) (6.1 mg, 0.04 mmol, 20 mol%) in the air, and then K_3PO_4 (127.2 mg, 0.60 mmol, 3.0 equiv), PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of toluene (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^oC for 12 h. After the mixture was cooled to room temperature, dodecane (34.0 mg, 0.2 mmol) was added and then the mixture was diluted with ethyl acetate (5.0 mL), followed by stirring for 15 min. After centrifugation and sedimentation of the mixture, the clear organic layer was subjected to GC analyses. GC analysis of the reaction mixture showed the formation of naphthalene (80%).

7. Scheme S1-S3 and experimental details



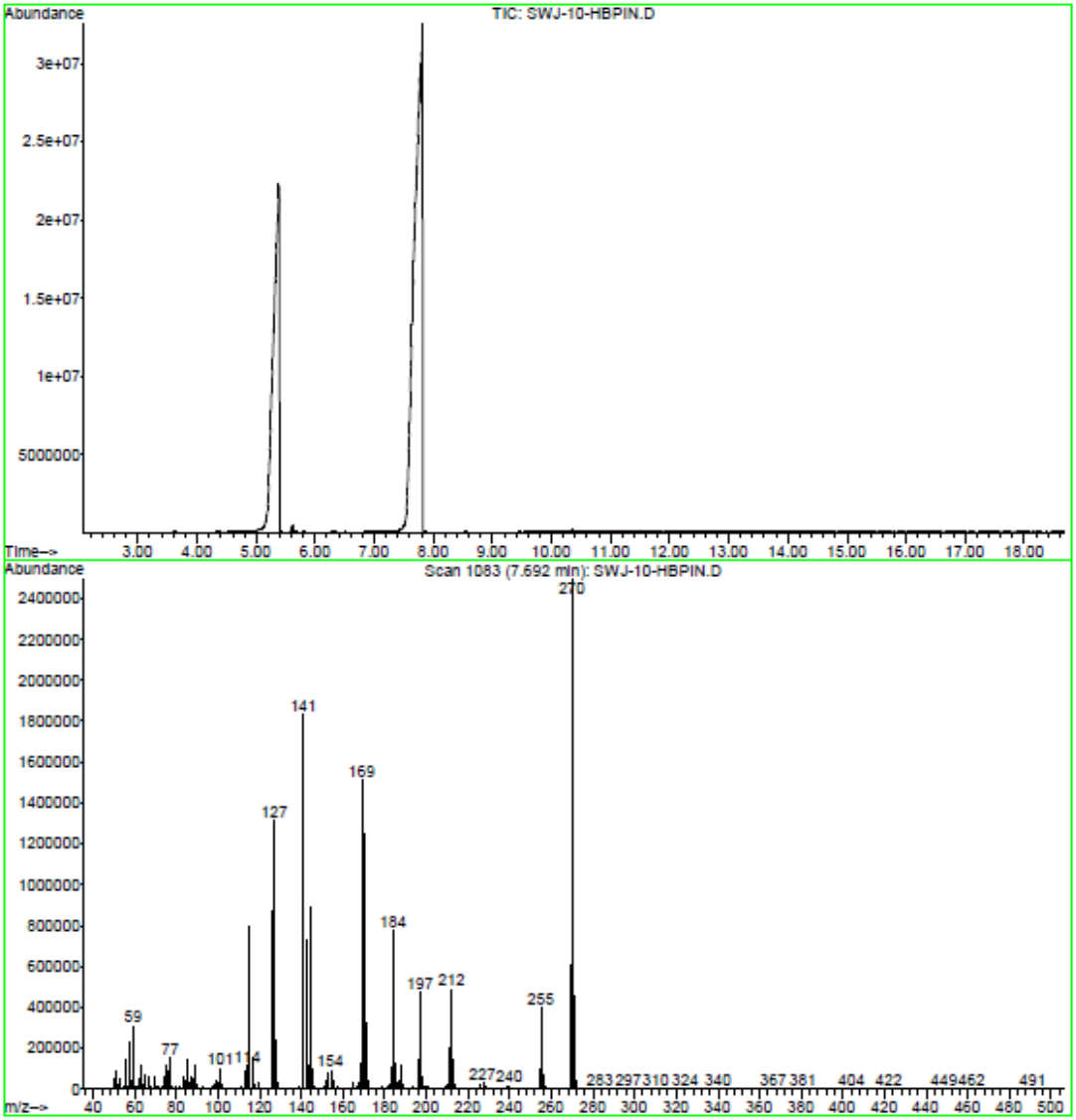
Scheme S1. ^{11}B NMR spectra: (1) B_2Pin_2, δ = 31.56 ppm; (2) NapOH + B_2Pin_2 (2 equiv), δ = 31.48 ppm; (3) NapOH + B_2Pin_2 (2 equiv) + $Ni(cod)_2$ (5 mol%) + PCy_3 (20 mol%) at 80 °C for 30 min, δ = 31.46 and 22.50 ppm. Nap = naphthyl.

Experimental details for equation 3 in Scheme S1: To an oven-dried schlenk tube with a stirring bar was added 2-naphthol **(1a)** (28.8 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) in the air, and then PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of toluene (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^{o}C for 30 min. After the mixture was cooled to room temperature, the tube was removed into the glove box and the clear mixture was added to a nuclear magnetic tube in the glove box and subjected to ^{11}B NMR analyses.



Scheme S2. Detection of Nap-OBpin on GC-MS with B_2pin_2 as the reductant.

Experimental details for Scheme S2: To an oven-dried schlenk tube with a stirring bar was added 2-naphthol **(1a)** (28.8 mg, 0.20 mmol), B_2Pin_2 (101.6 mg, 0.40 mmol, 2.0 equiv) in the air, and then PCy_3 (11.2 mg, 0.04 mmol, 20 mol%) and $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) were added, followed by the injection of toluene (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^oC for 30 min. After the mixture was cooled to room temperature, the clear mixture was directly subjected to GC-MS analyses.



Scheme S3. Detection of naphthalene and Nap-OBpin with HBpin as the reductant.

Experimental details for e Scheme S3: To an oven-dried schlenk tube with a stirring bar was added 2-naphthol **(1a)** (28.8 mg, 0.20 mmol) in the air, and then PCy_3 (11.2 mg, 0.04 mmol, 20 mol%), $Ni(cod)_2$ (2.8 mg, 0.01 mmol, 5.0 mol%) and HBpin (102.4 mg, 0.8 mmol, 4 equiv) were added, followed by the injection of toluene (0.50 mL) in glove box. The tube was sealed up and the mixture was stirred at 80 ^{o}C for 30 min. The mixture was cooled to room temperature, diluted with ethyl acetate (5.0 mL), followed by stirring for 15 min. After centrifugation and sedimentation of the mixture, the clear organic layer was subjected to GC-MS analyses.

8. References

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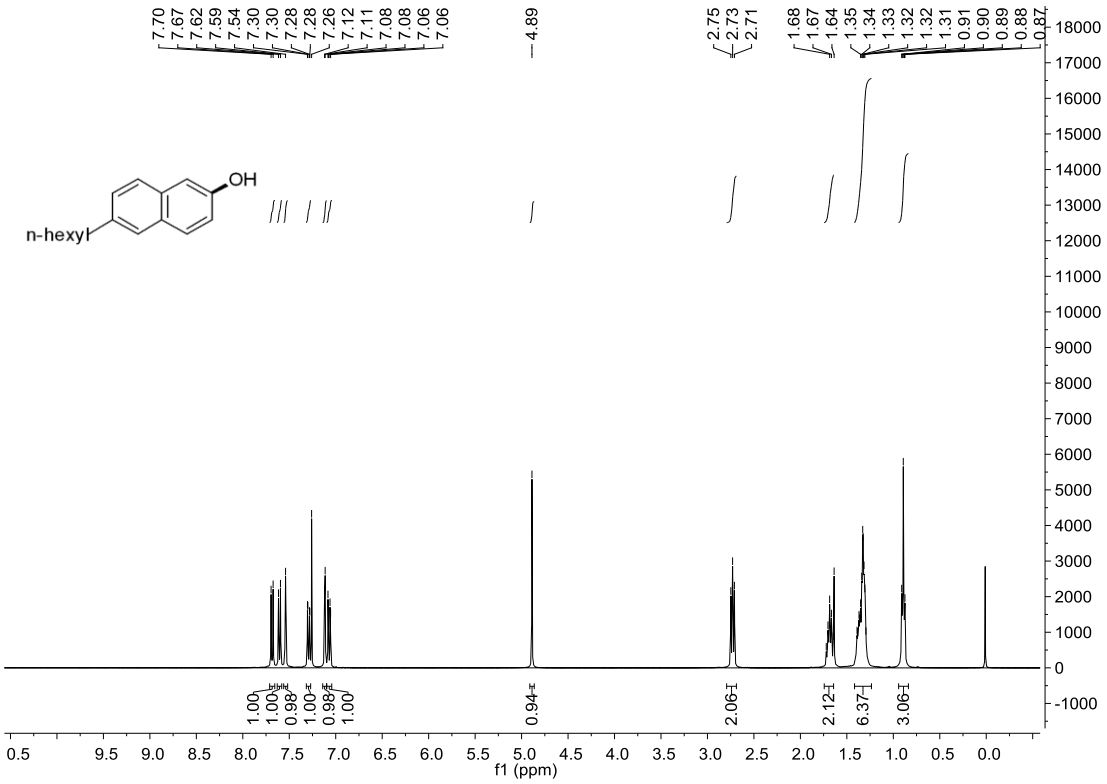
9. NMR Spectra



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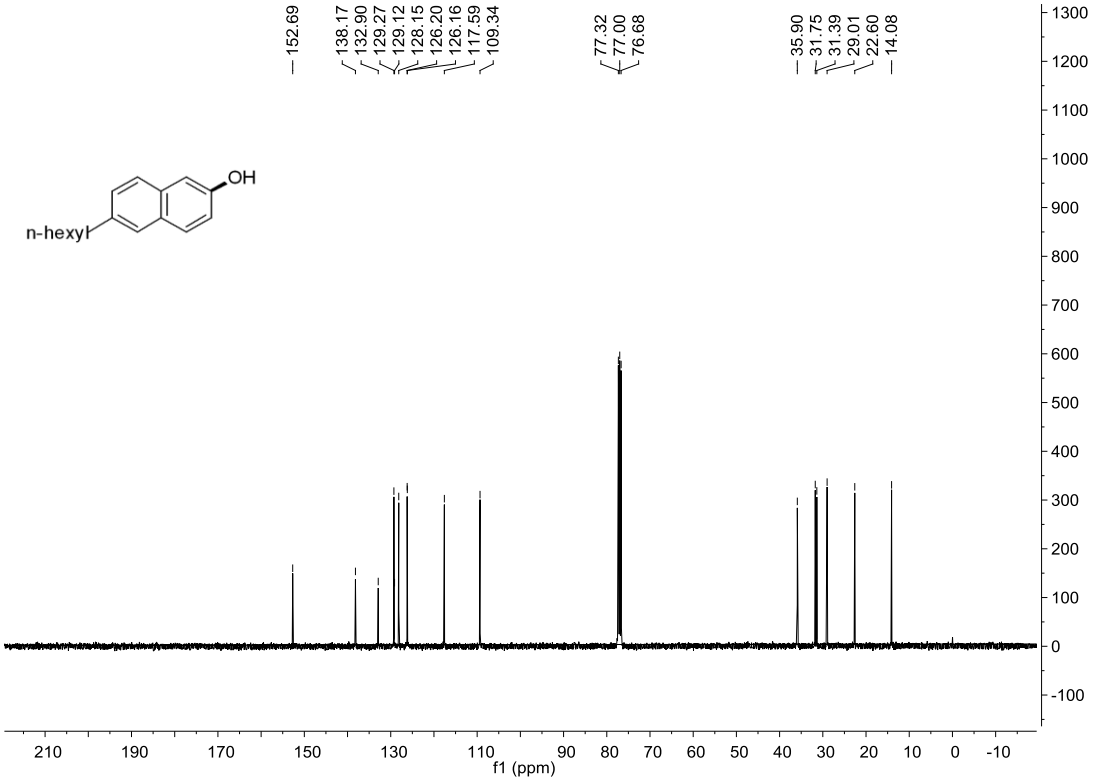

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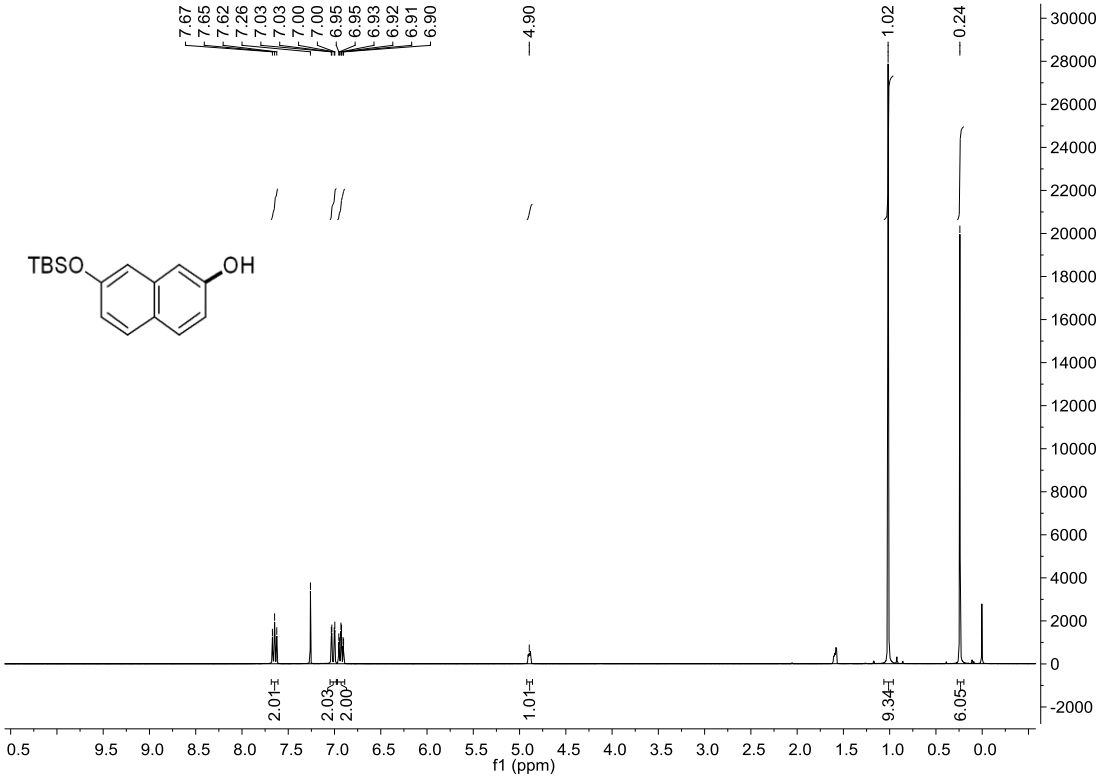

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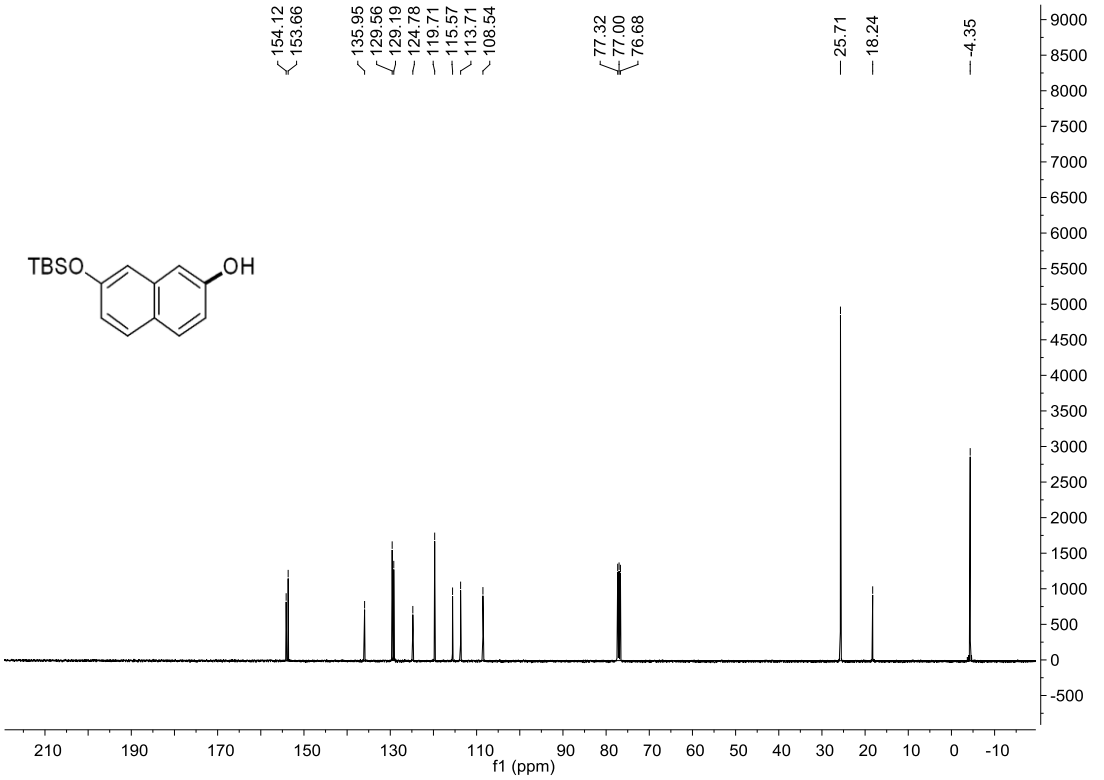

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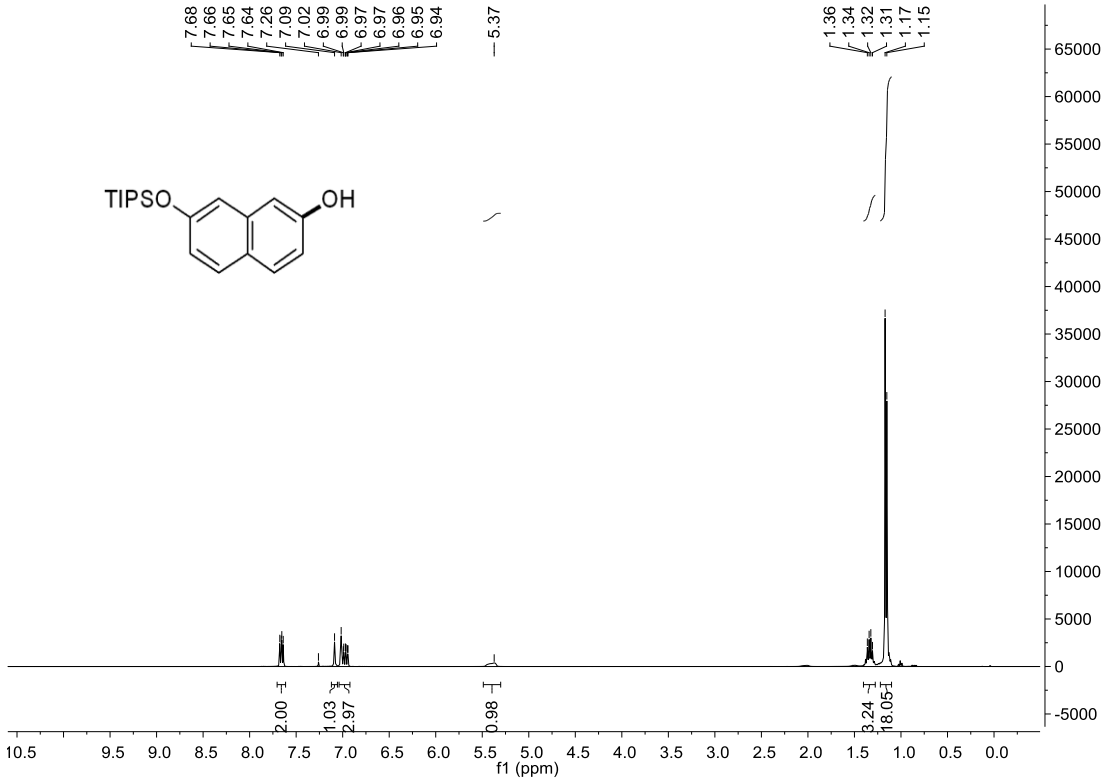

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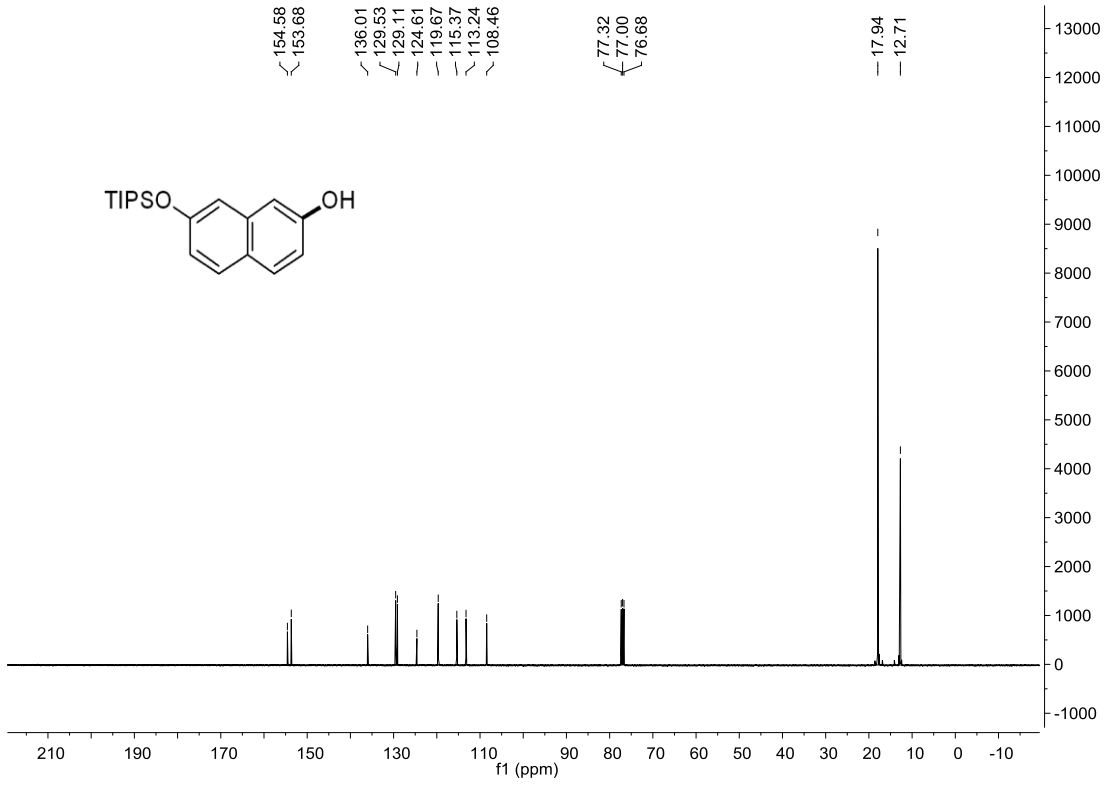

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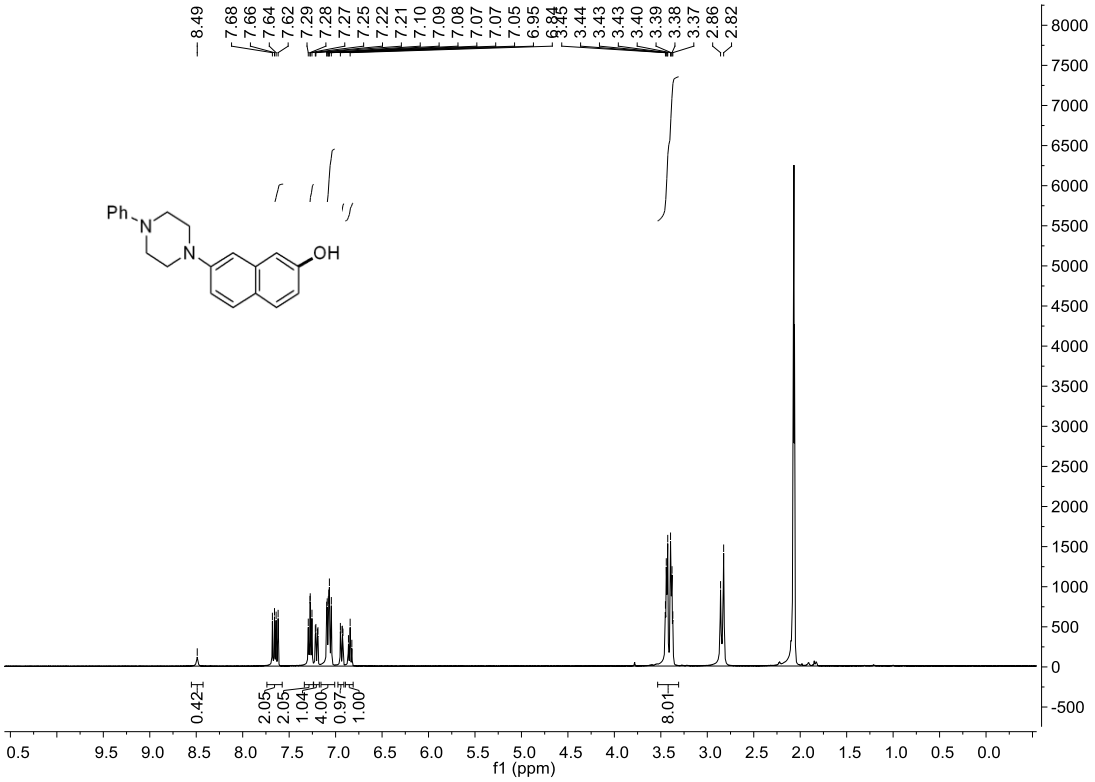

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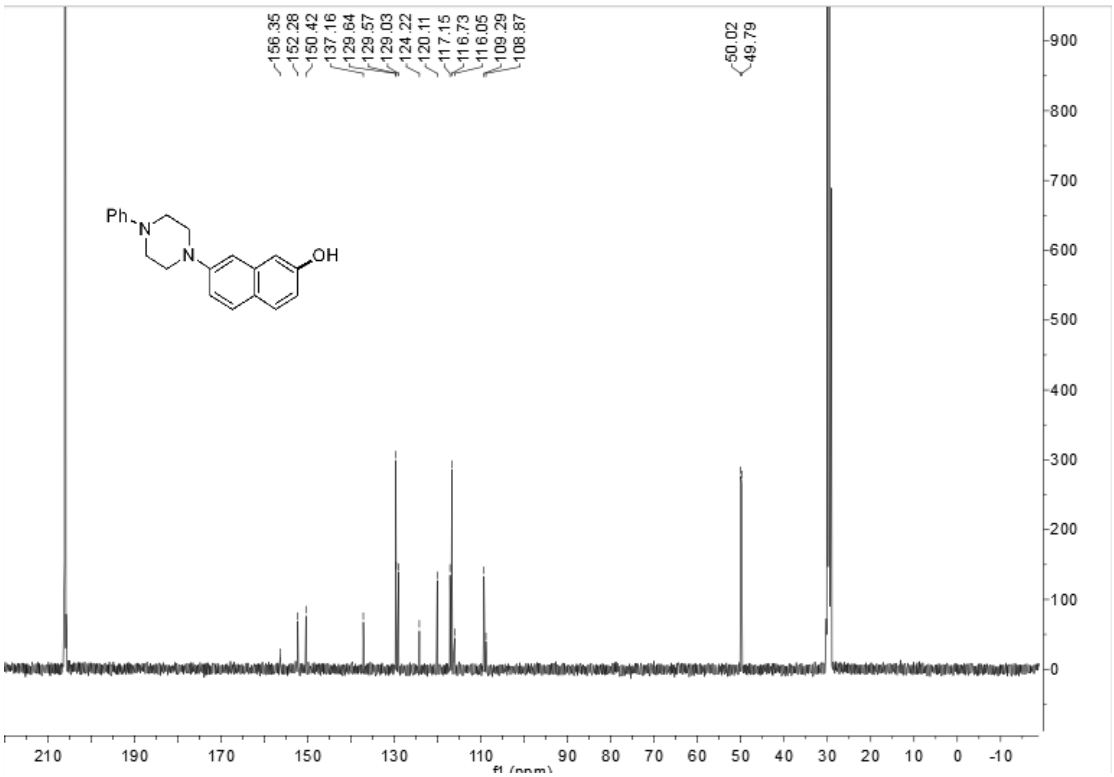

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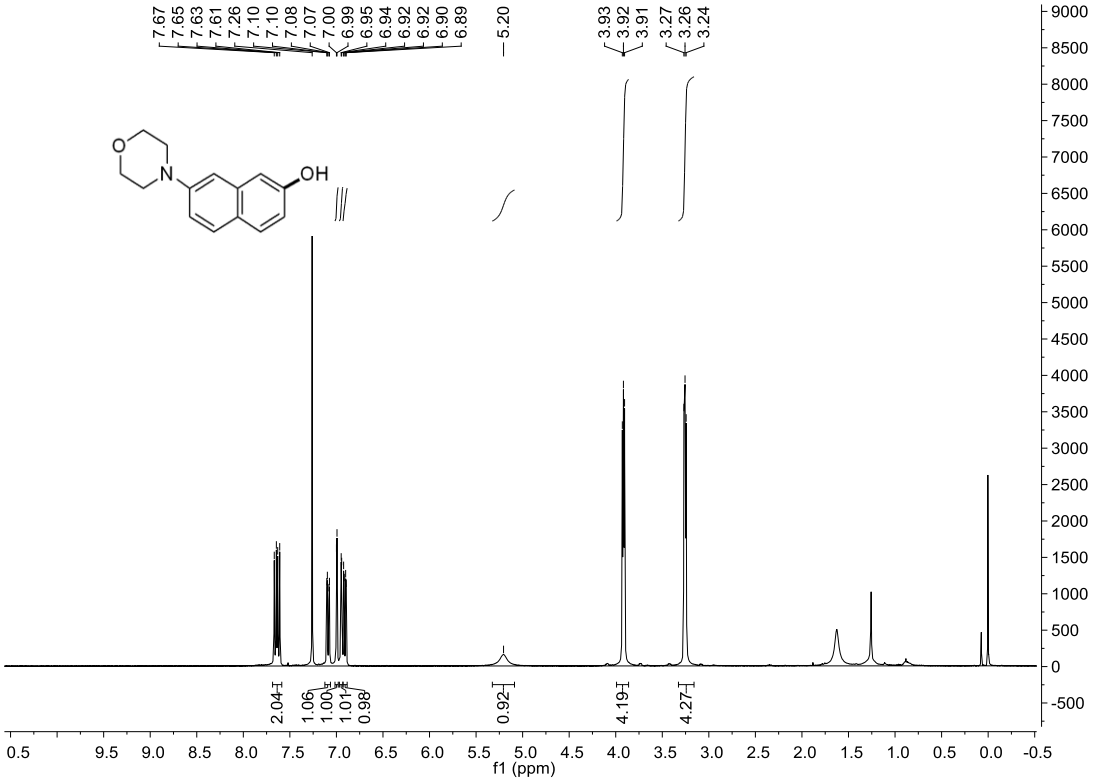

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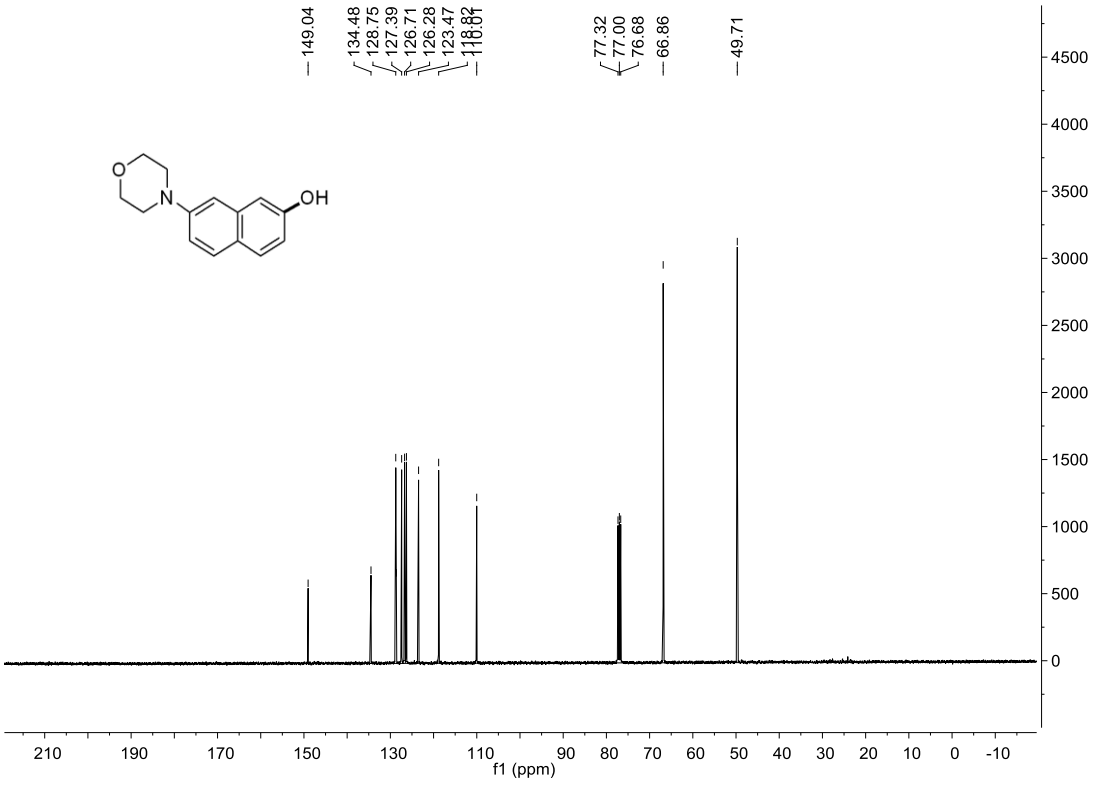

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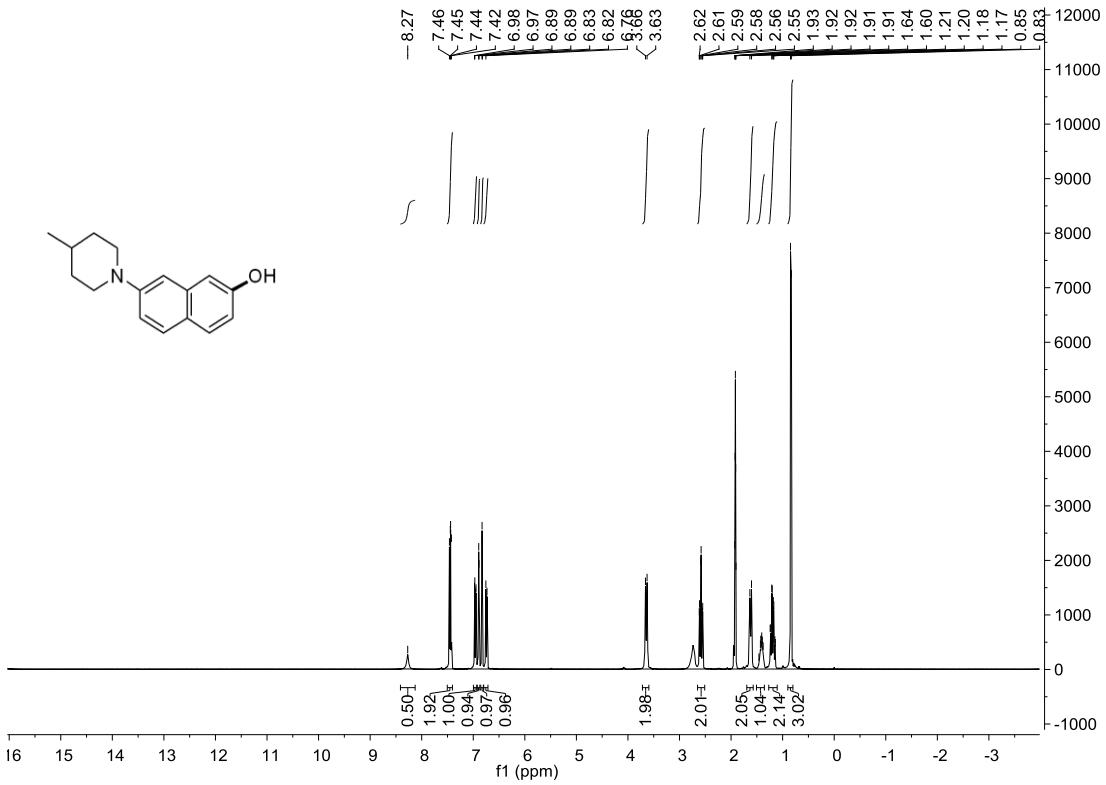

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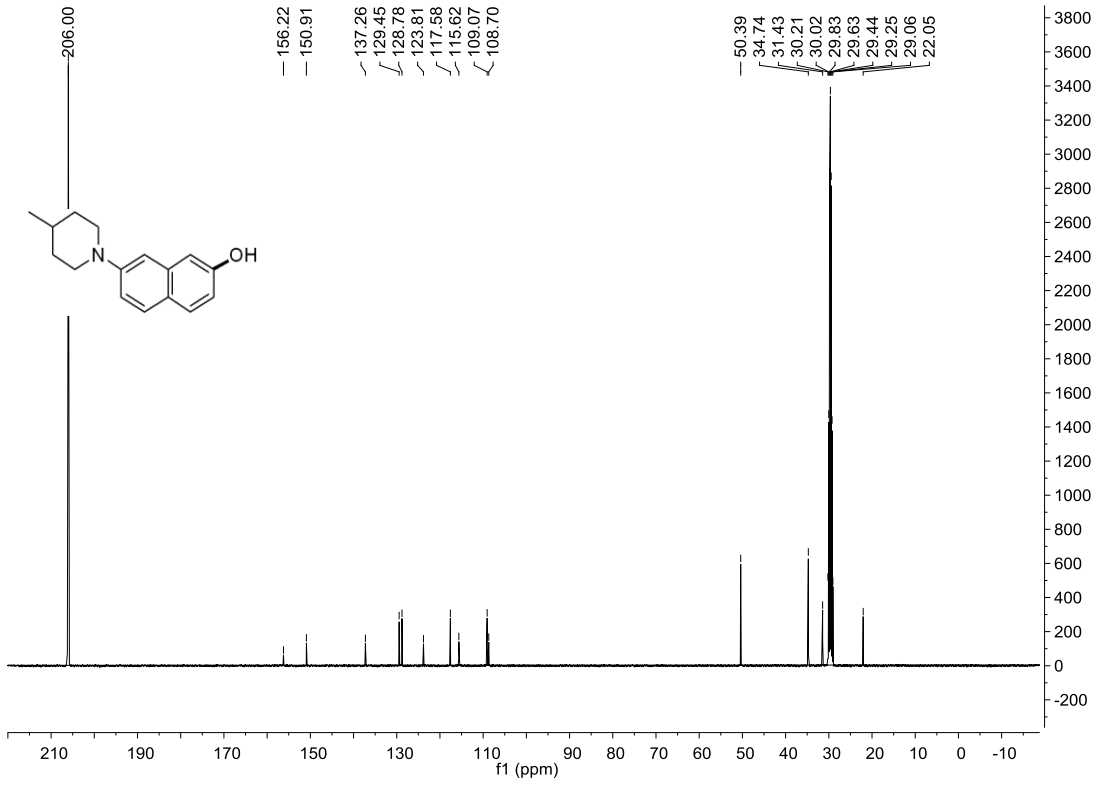

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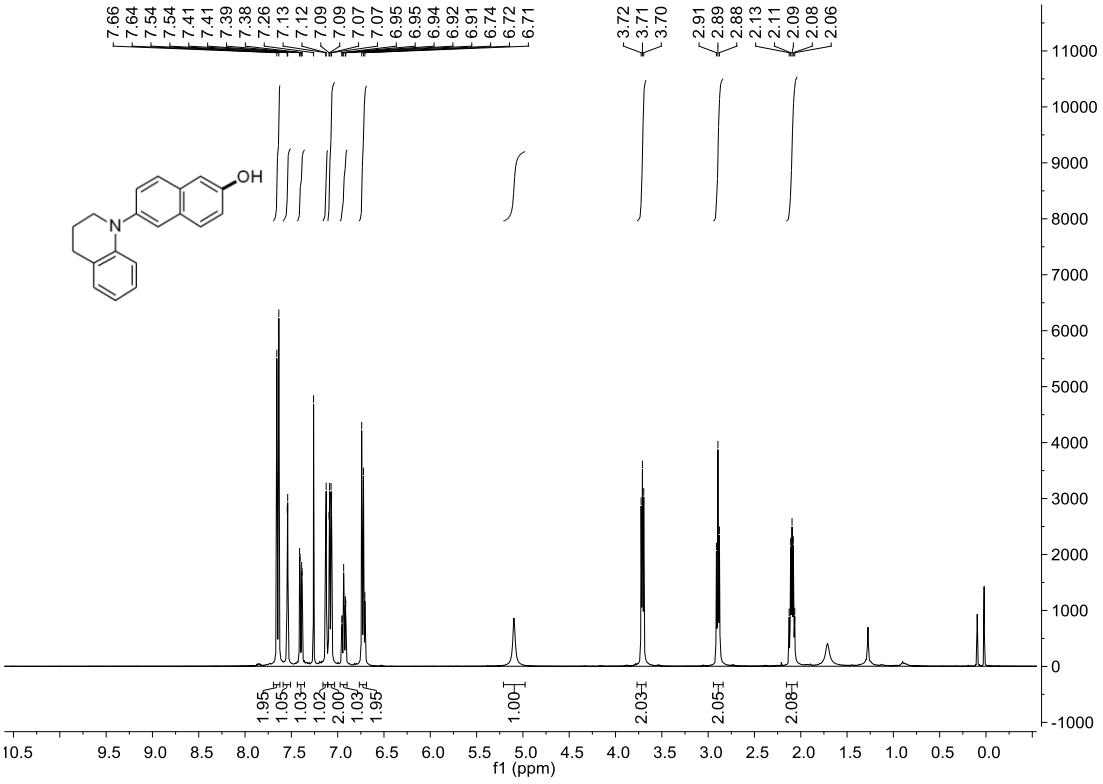

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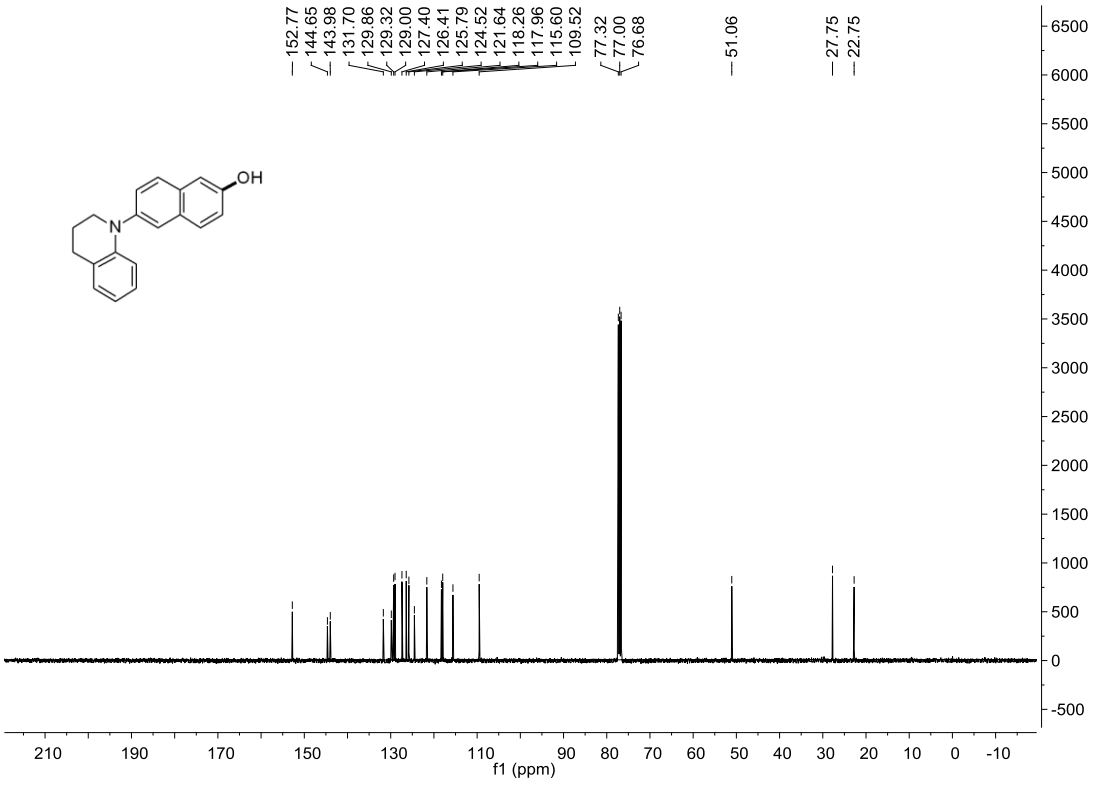

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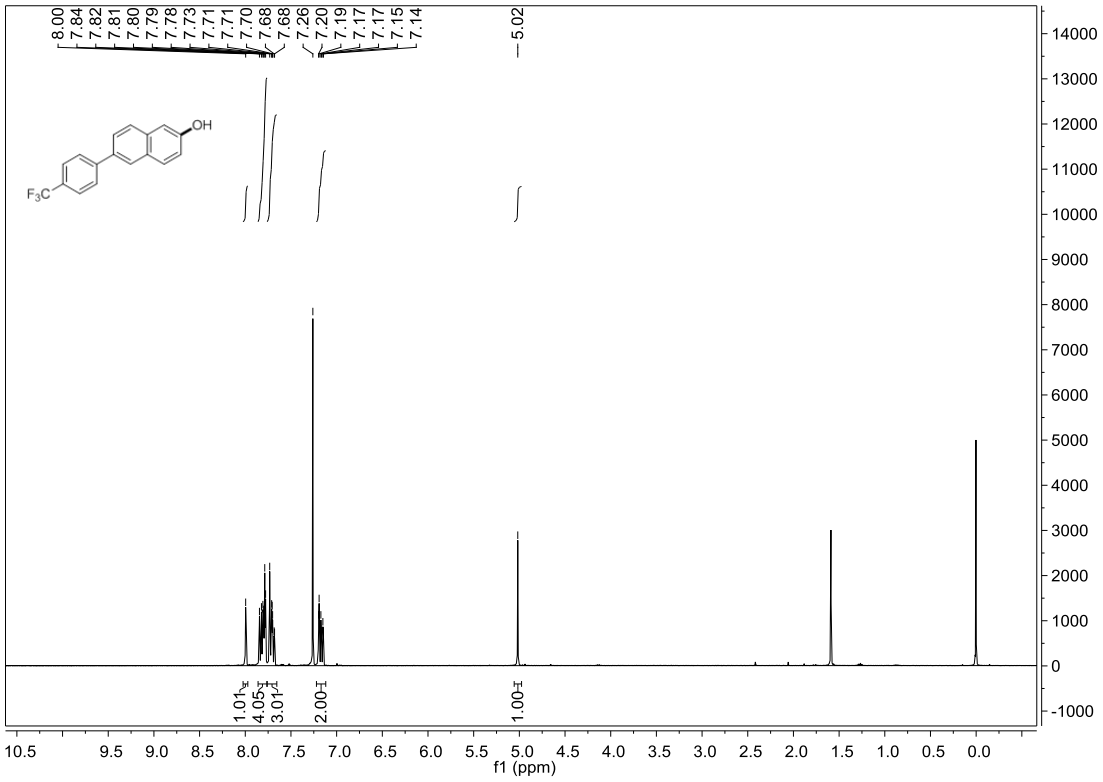

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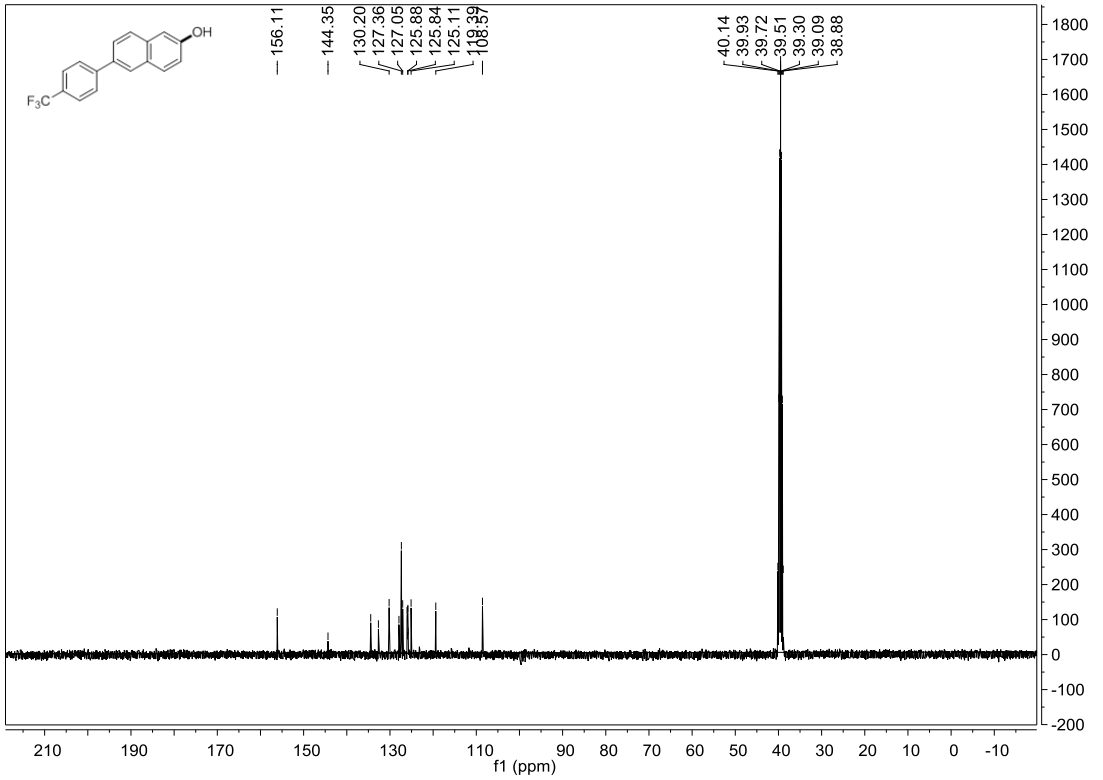

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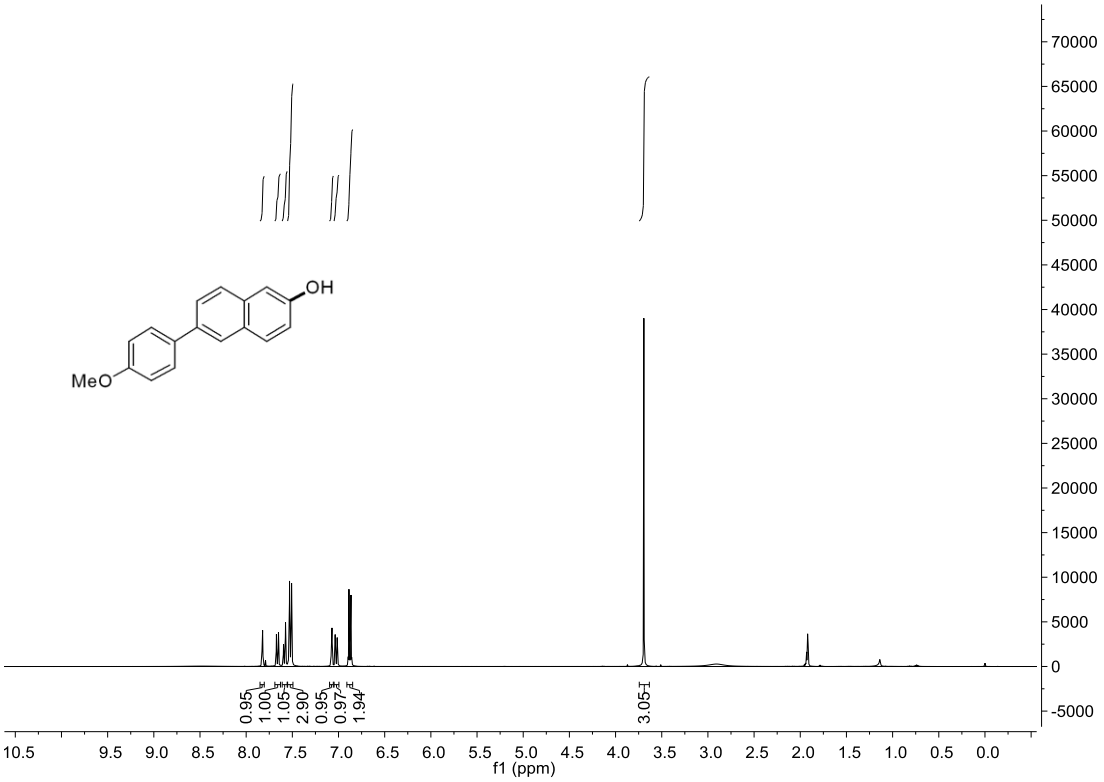

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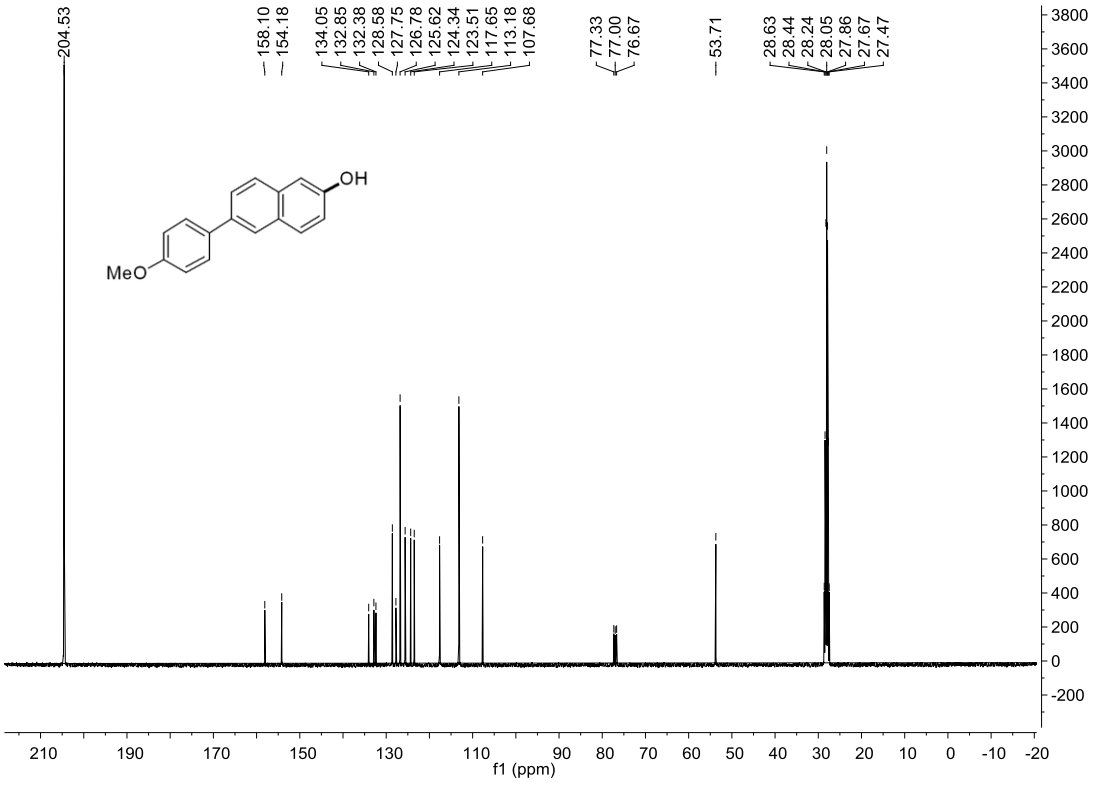

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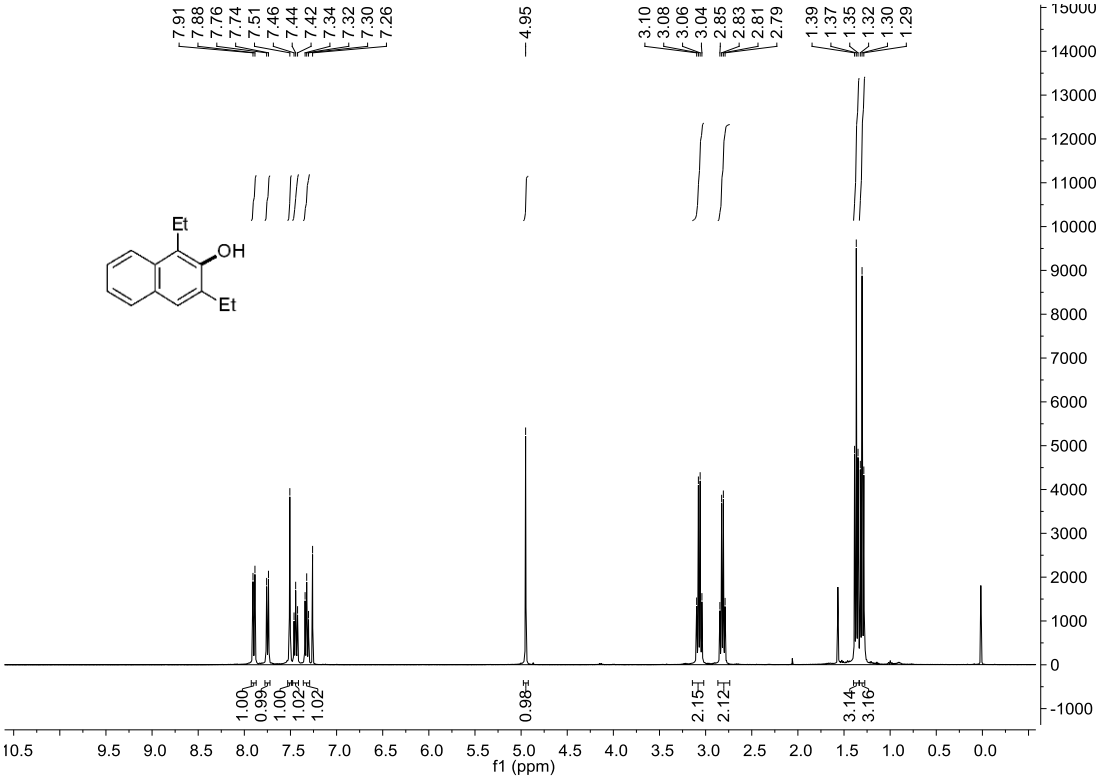

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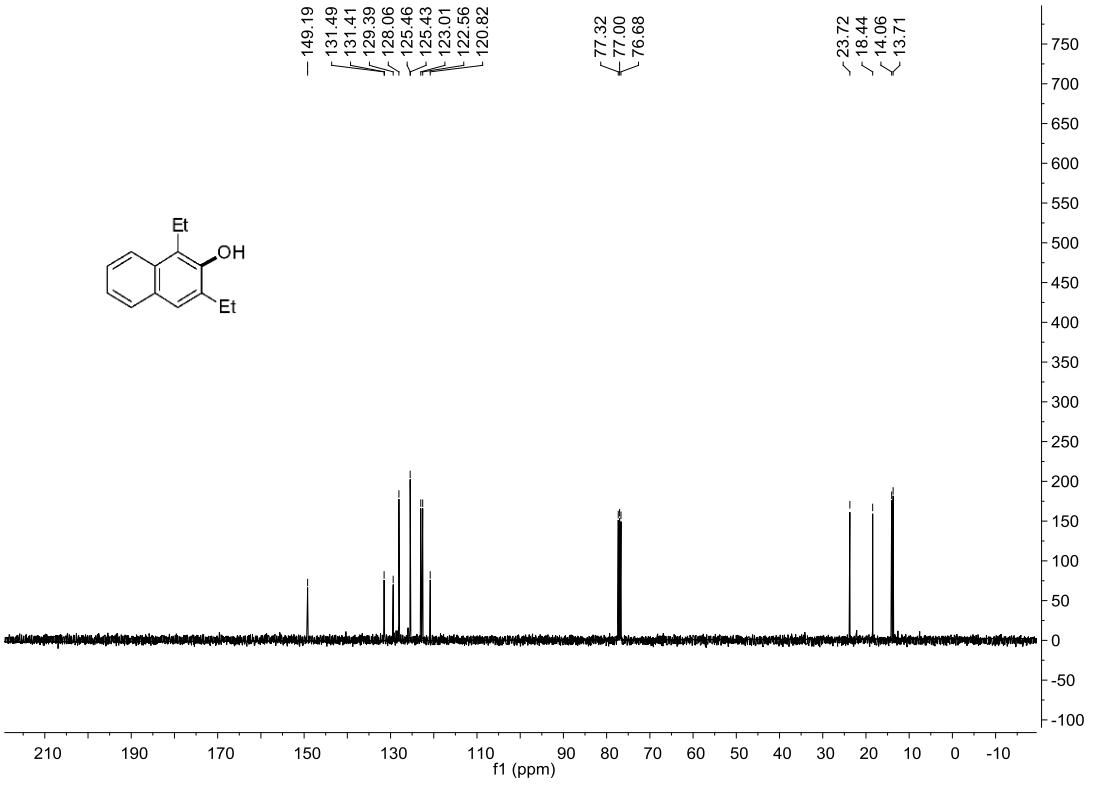

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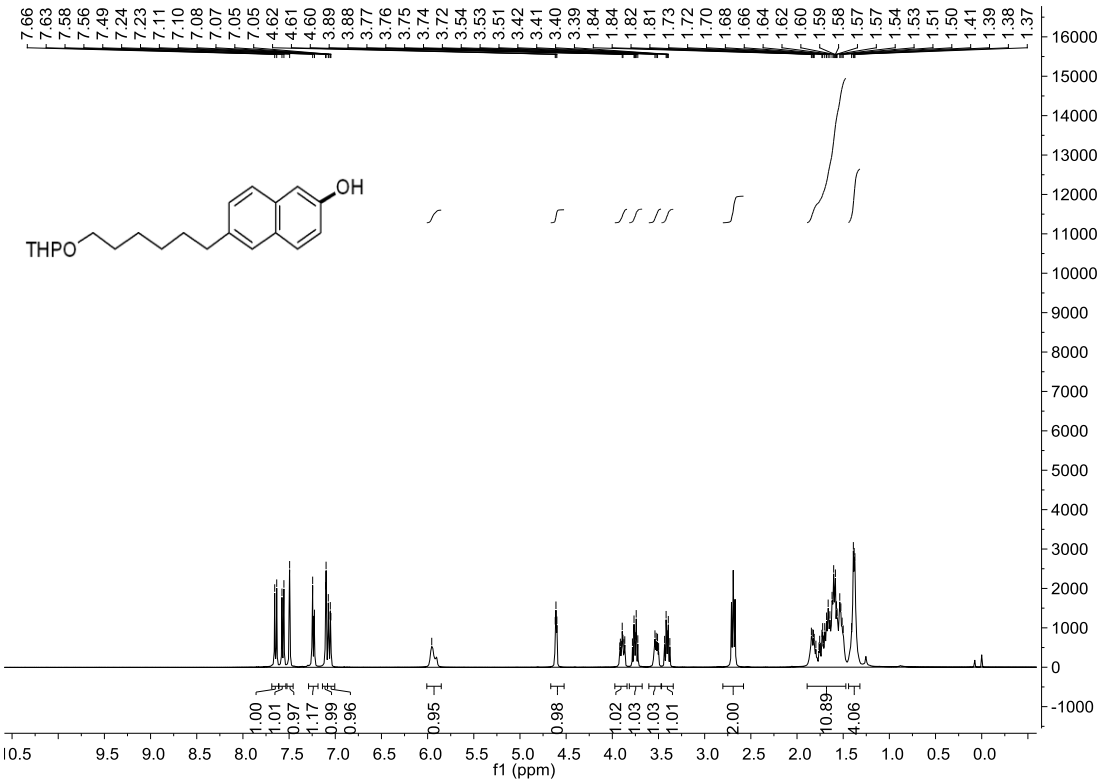

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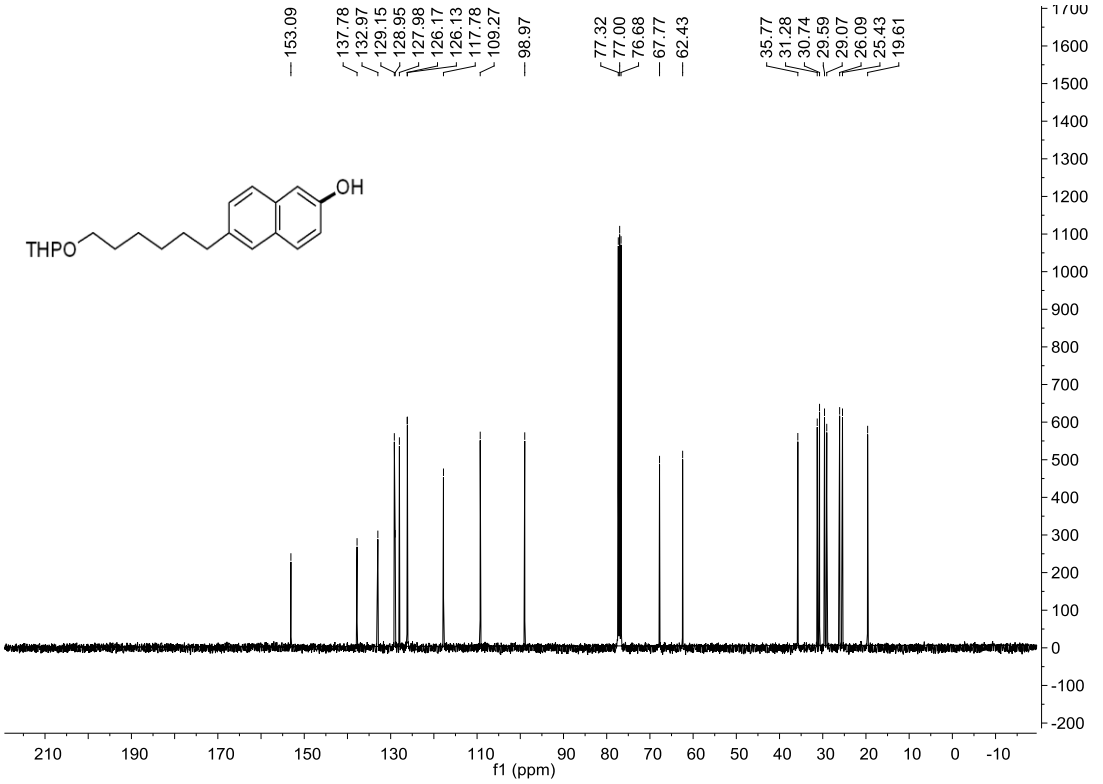

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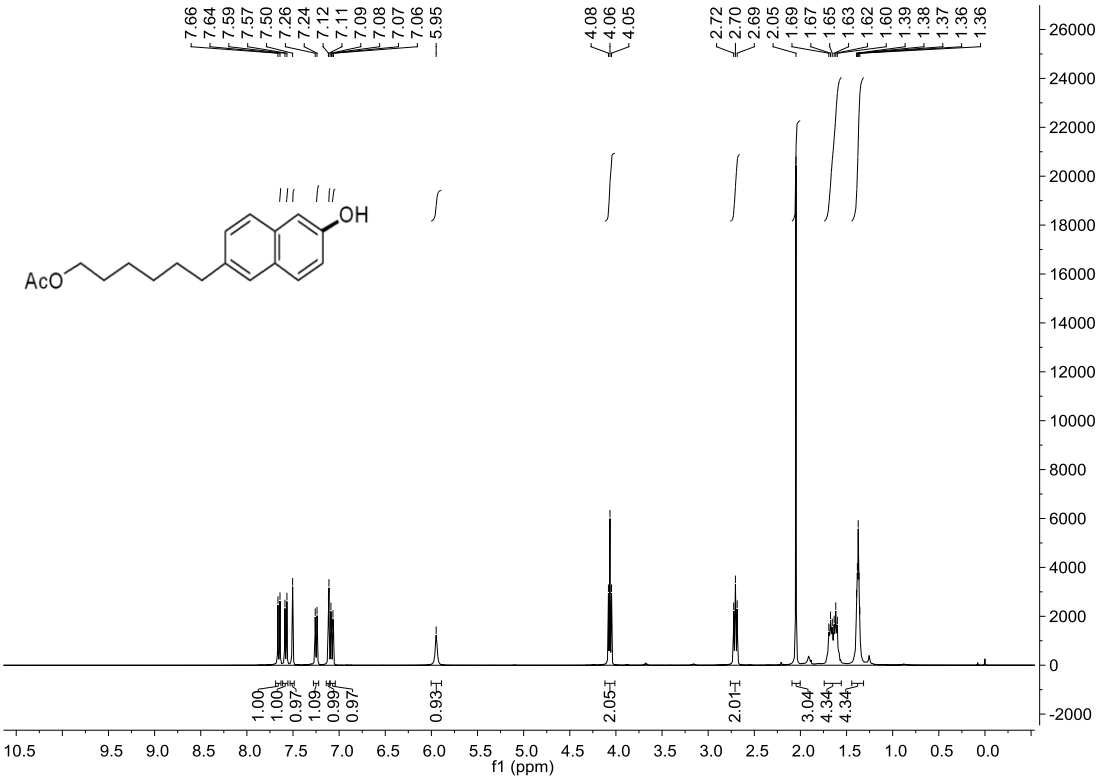

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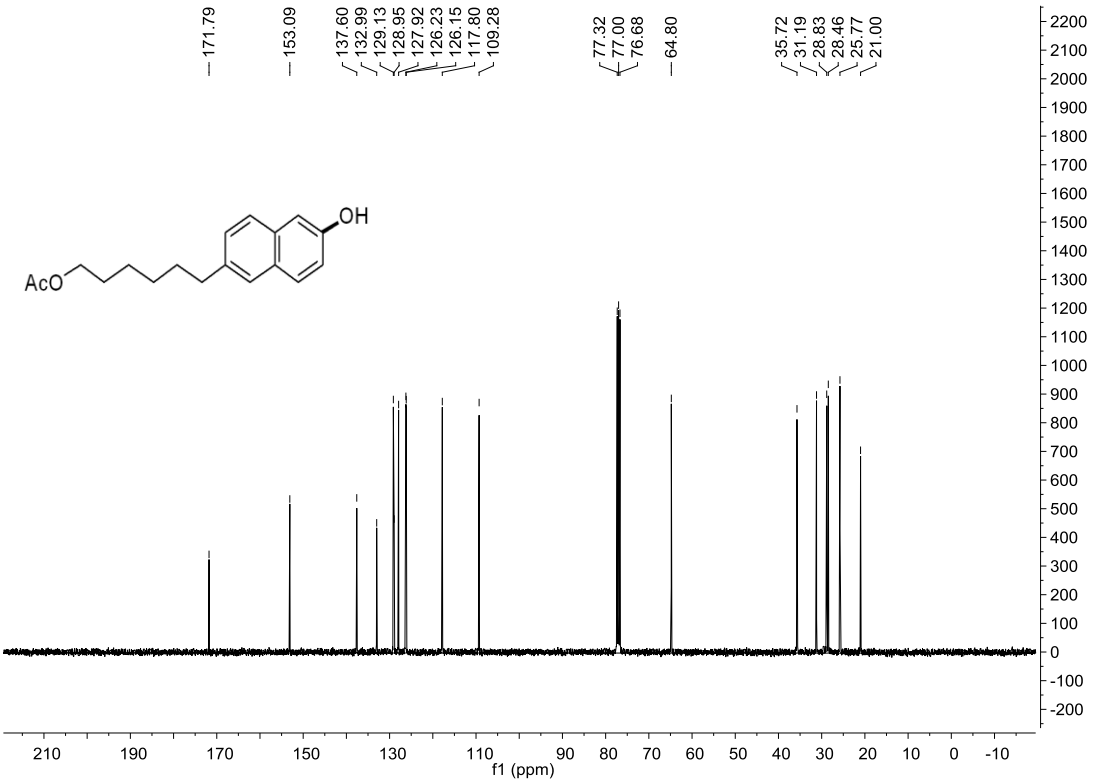

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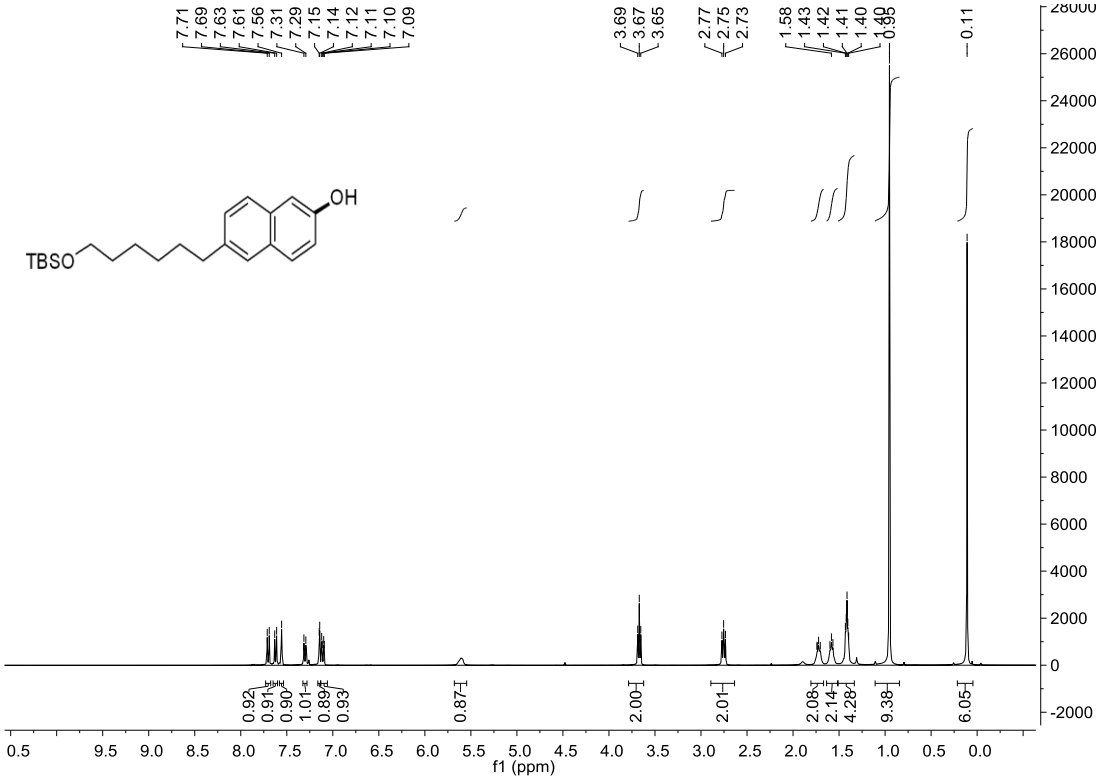

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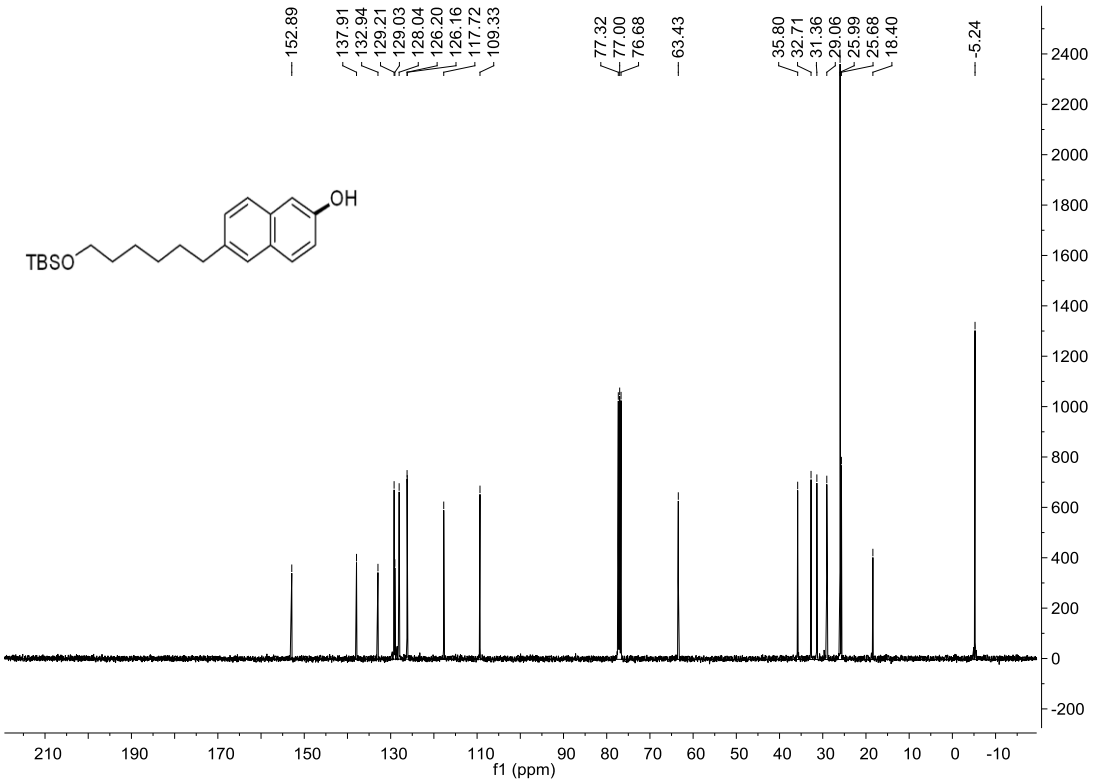

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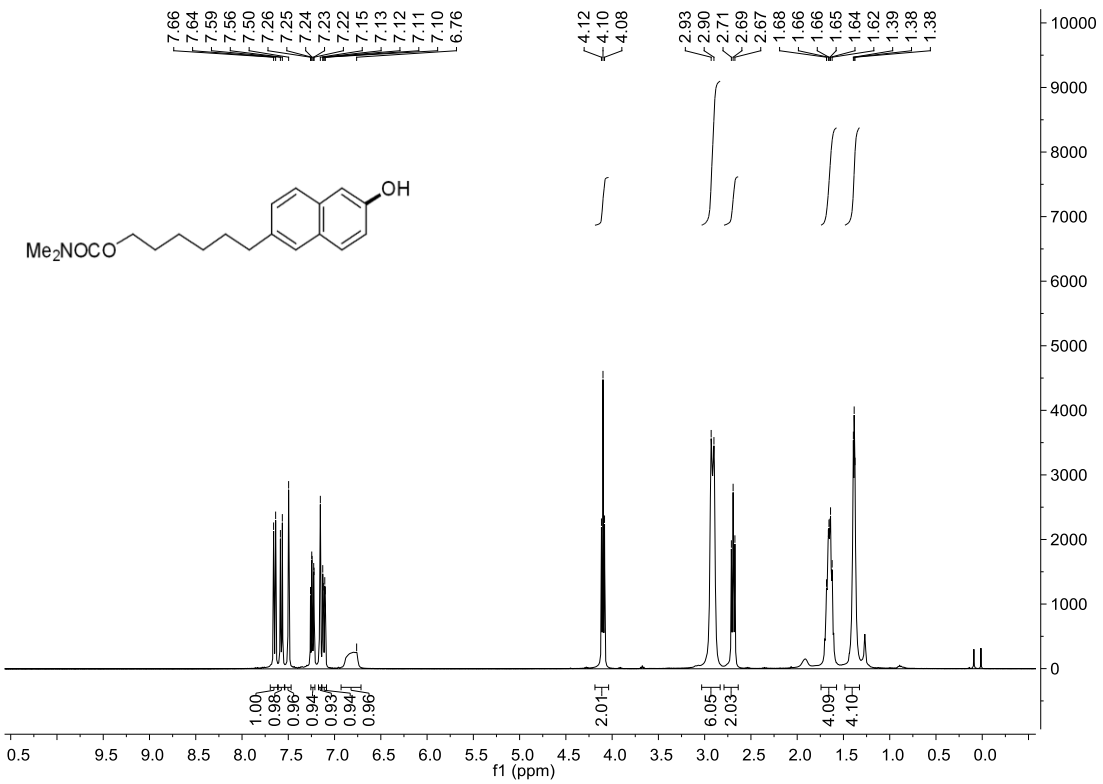

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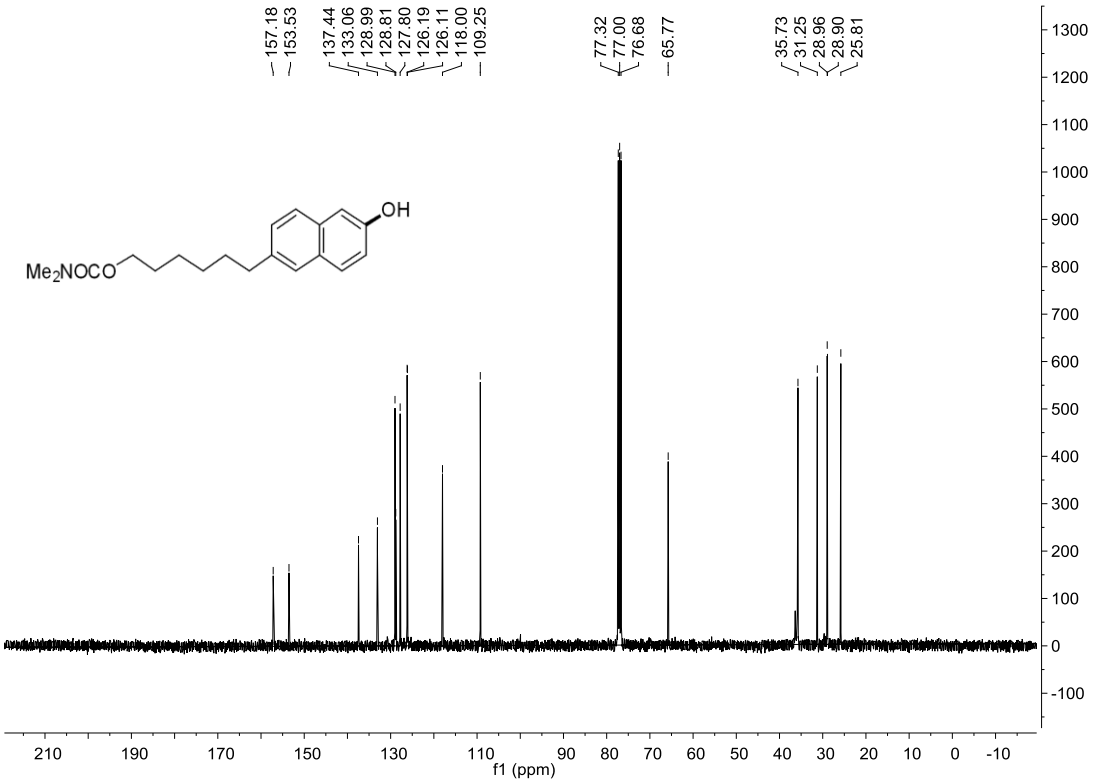

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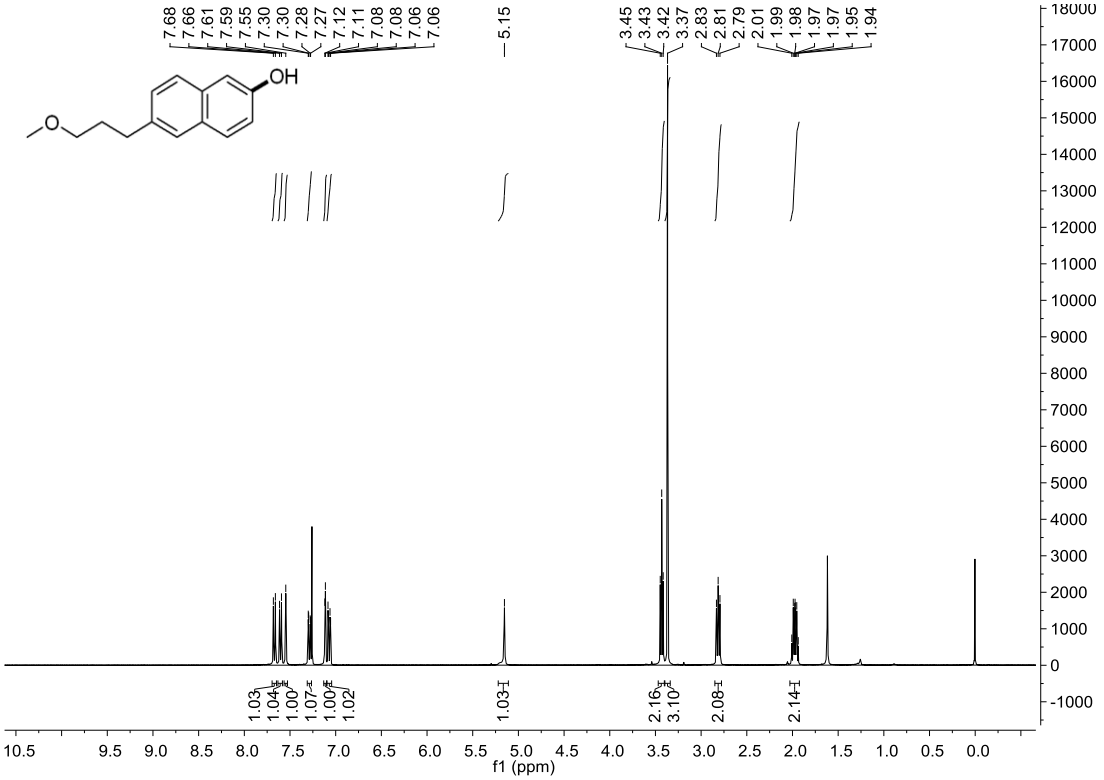

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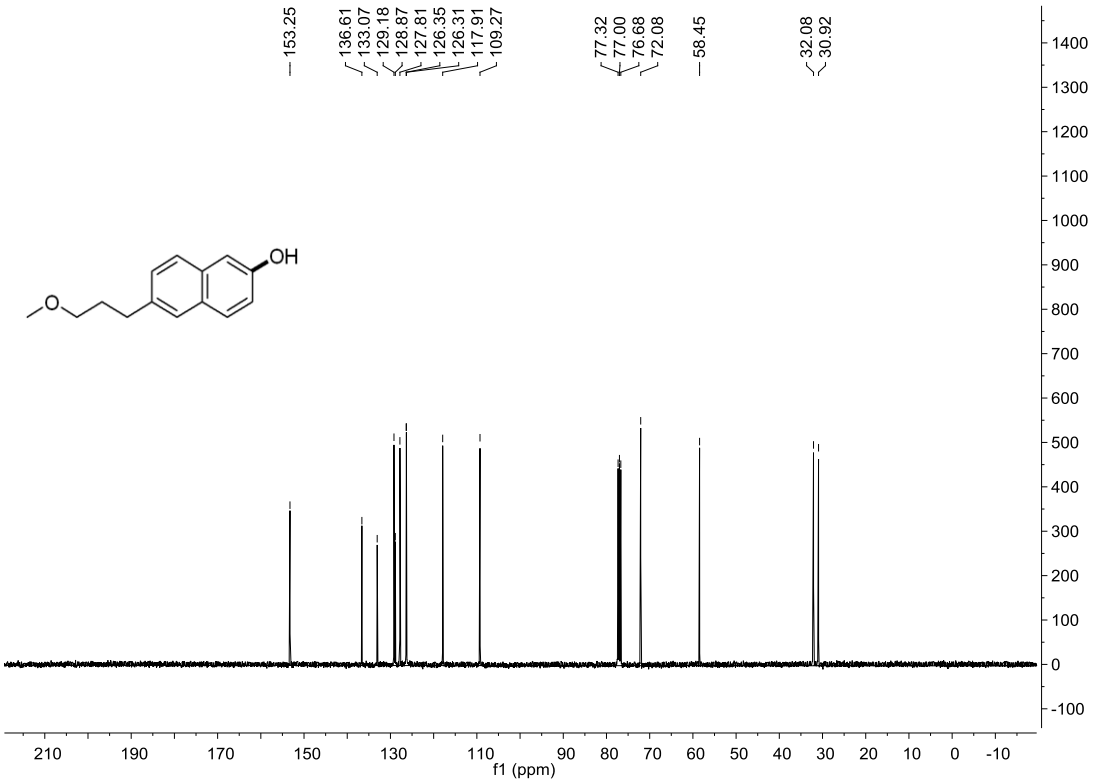

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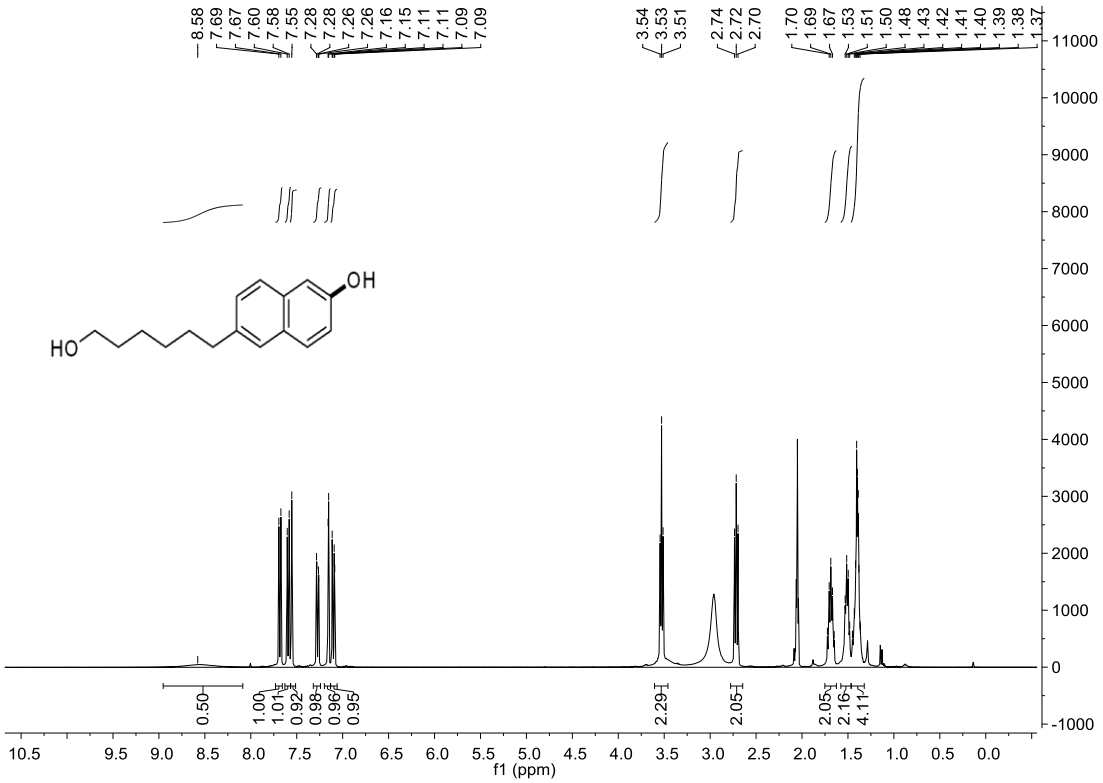

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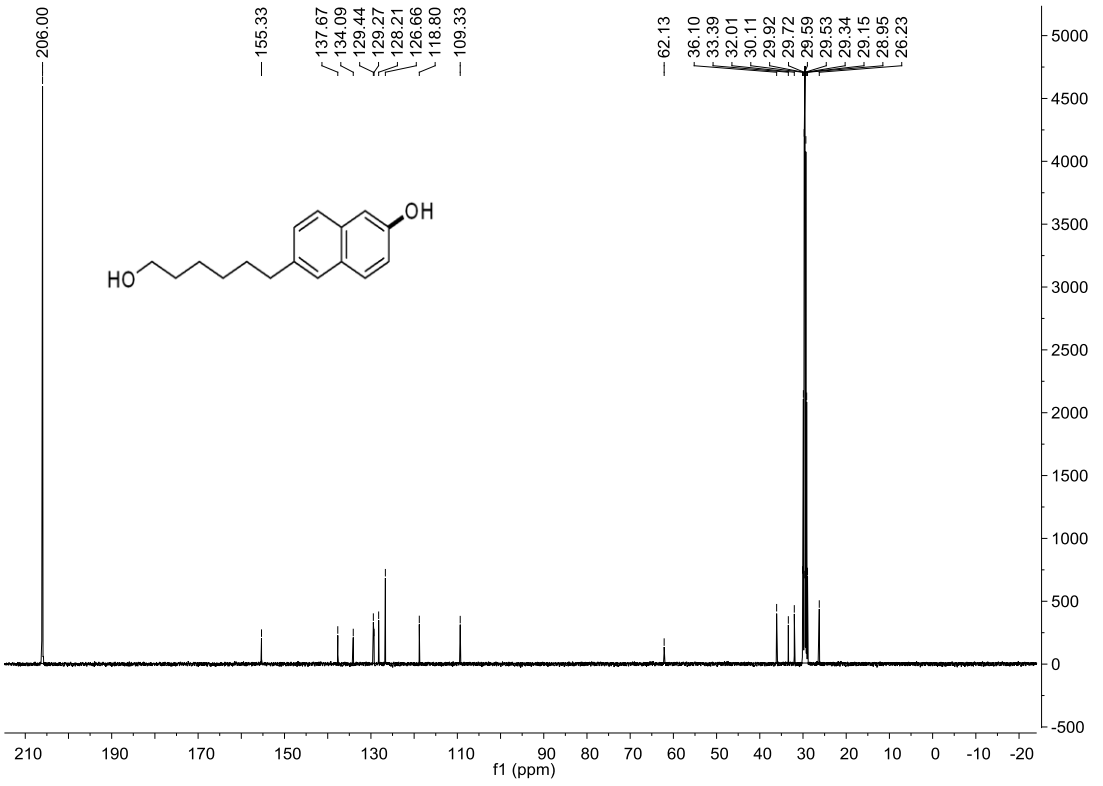

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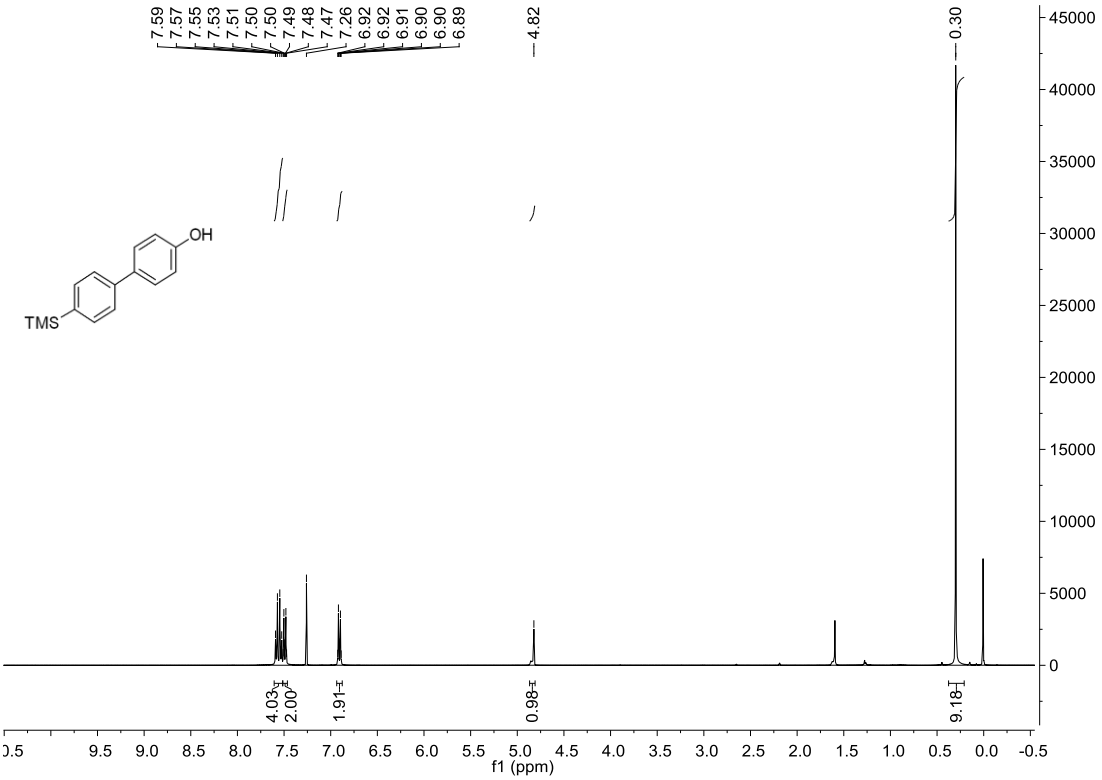

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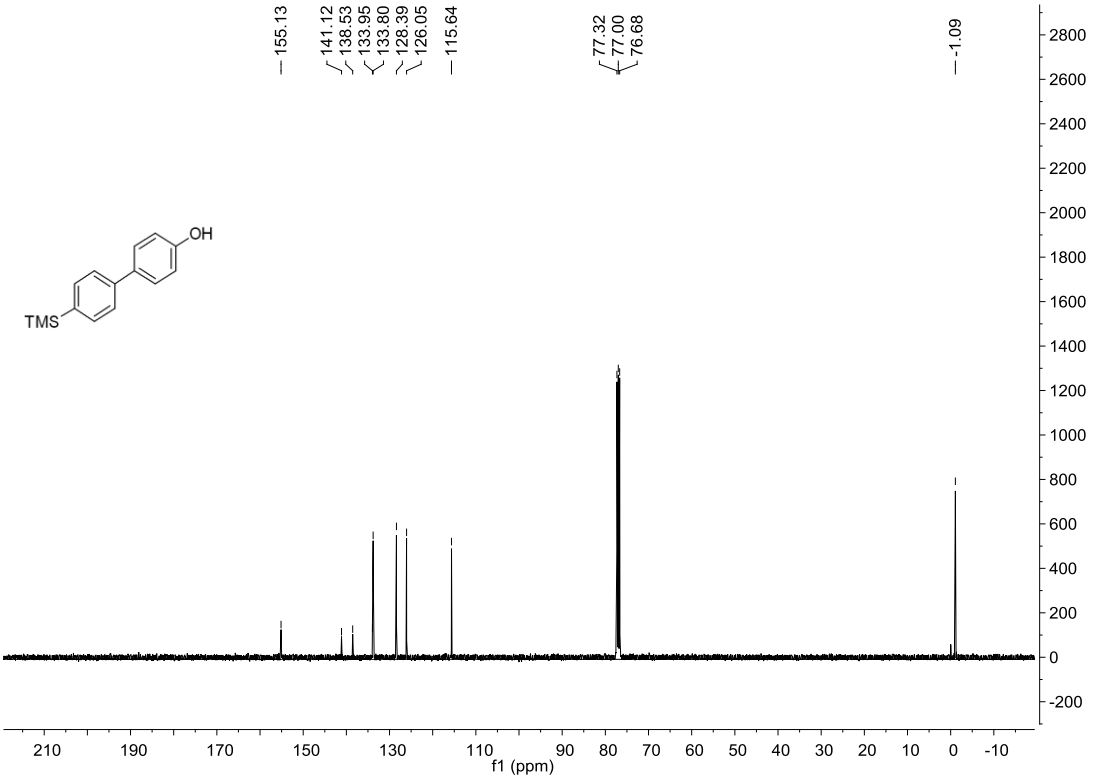

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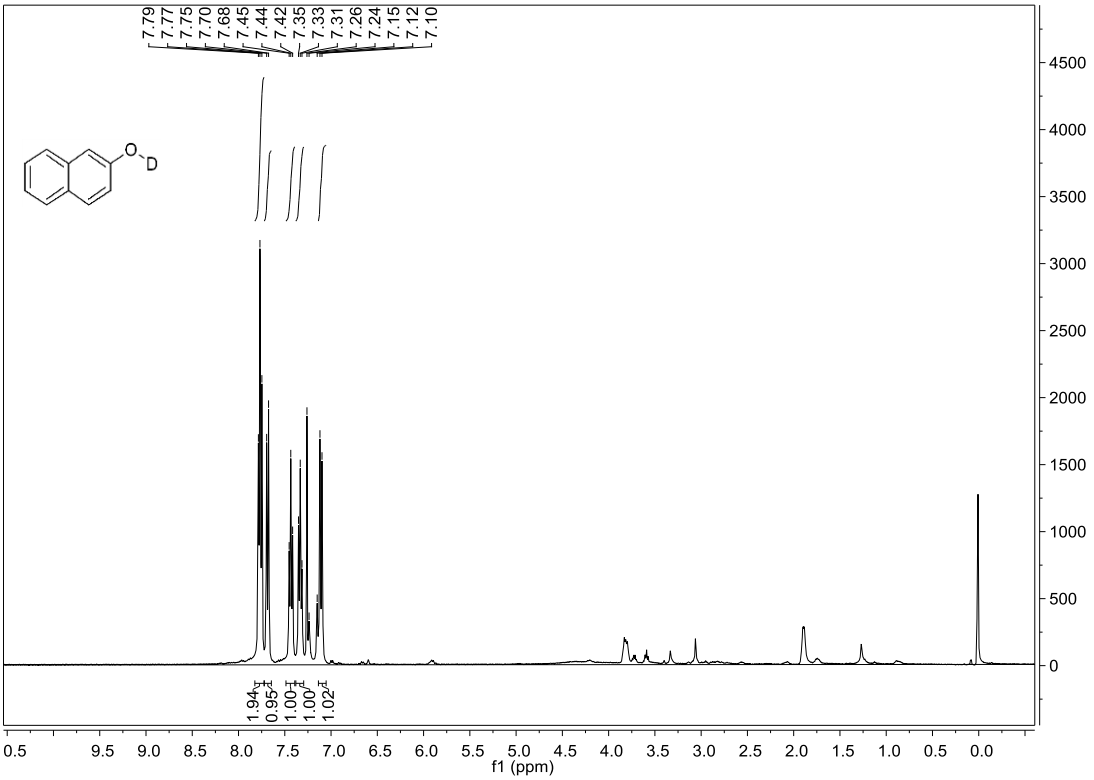
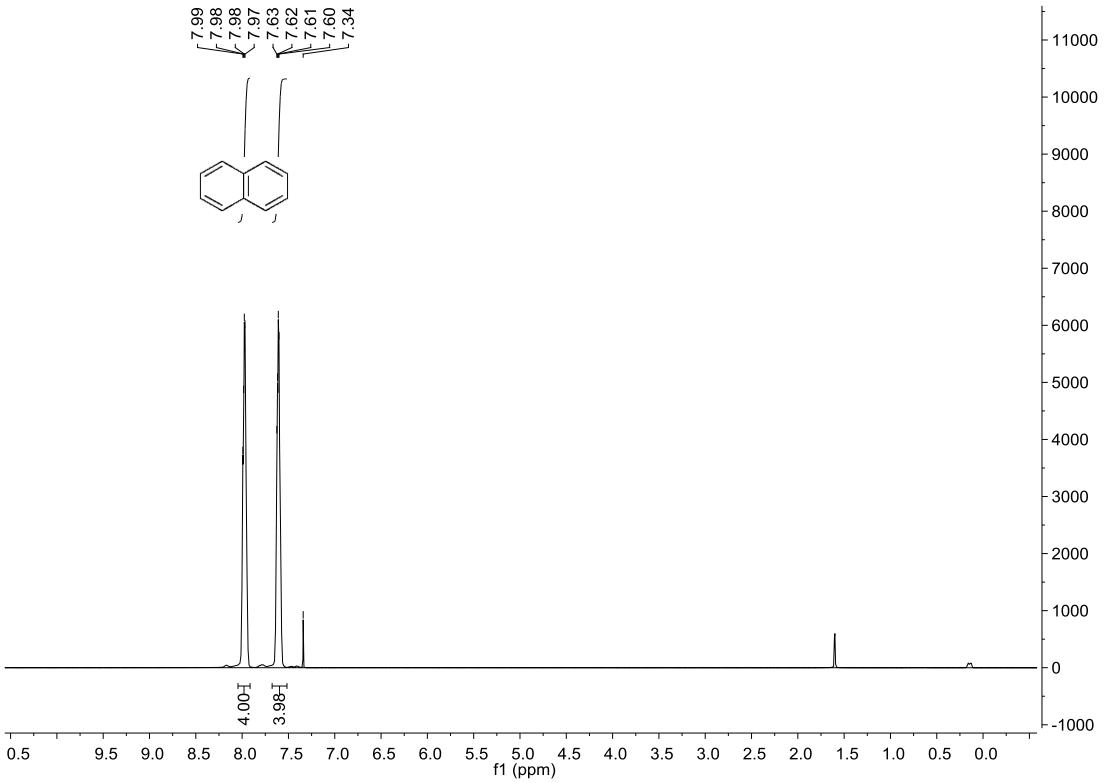
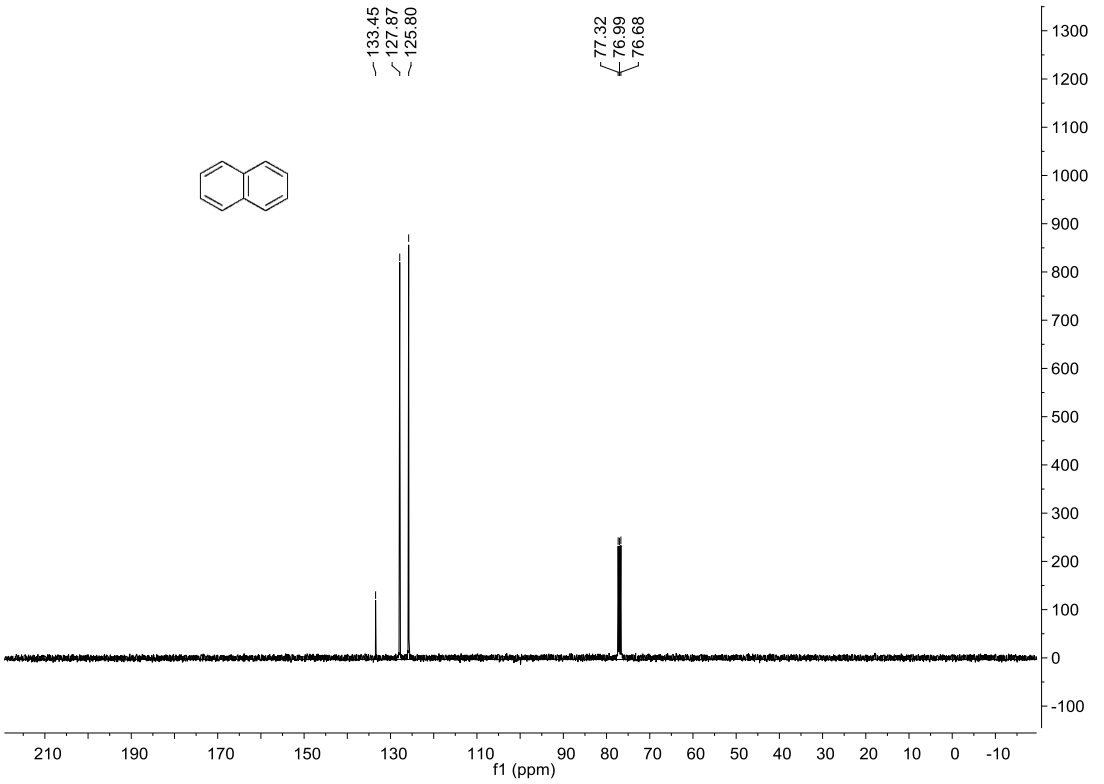


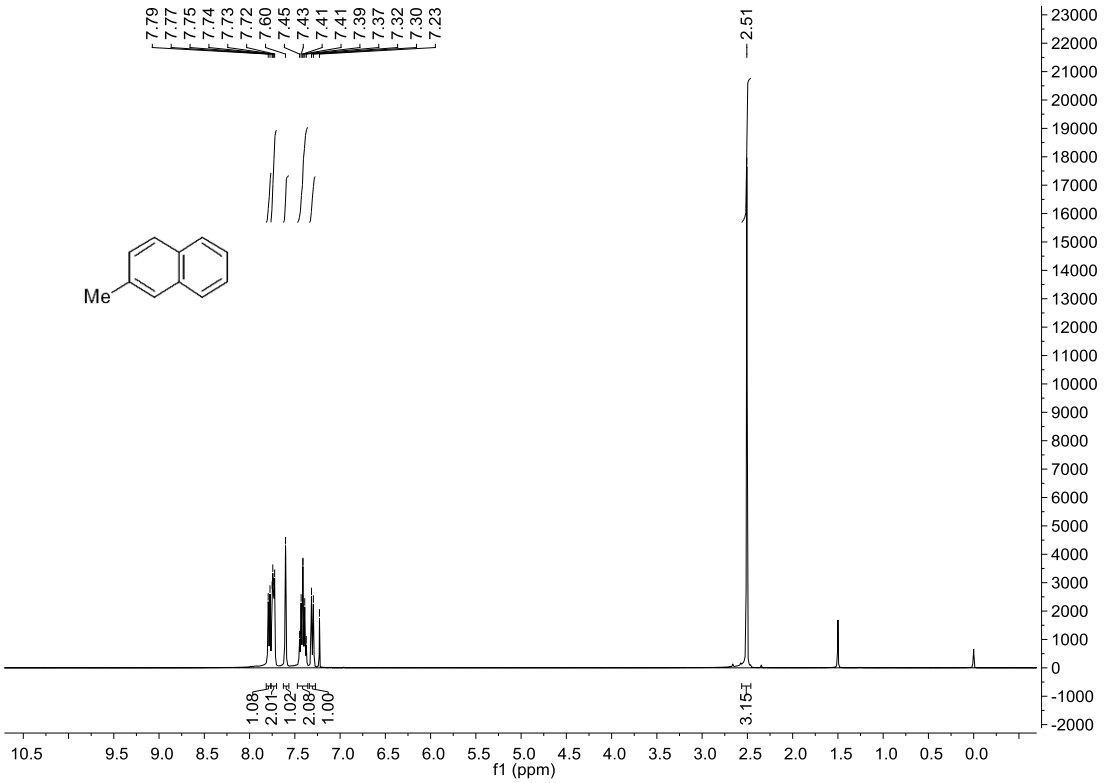
^{1}H NMR of compound 1aa



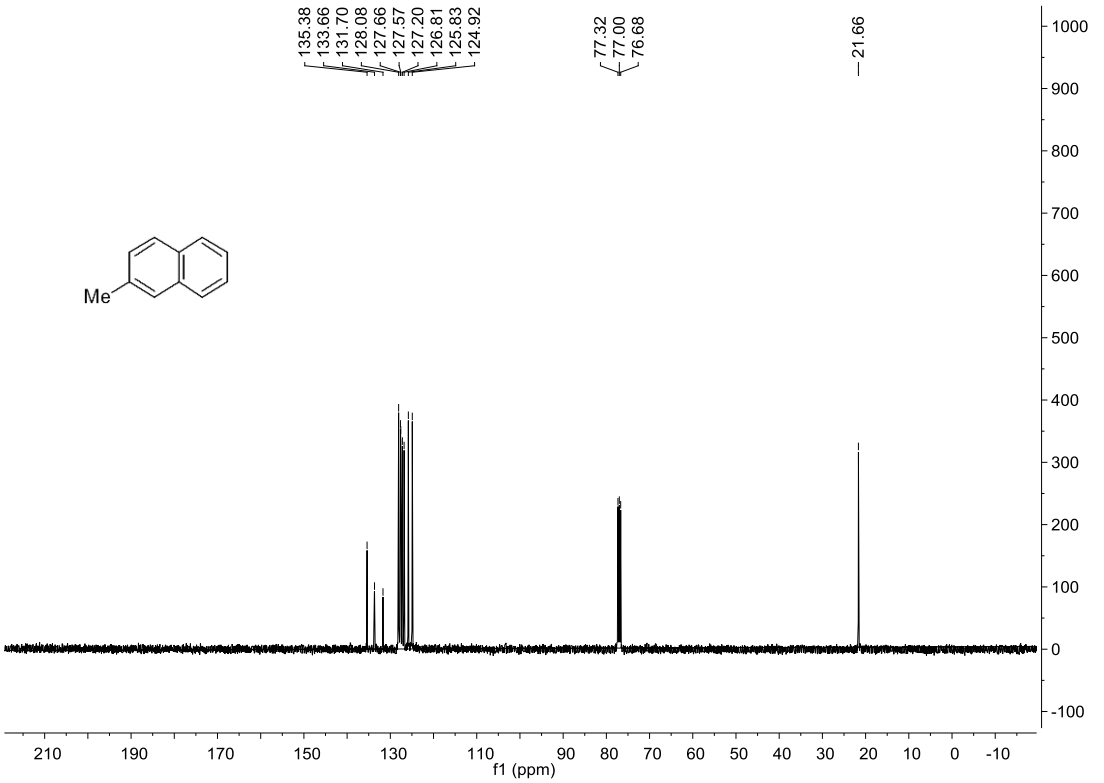
^{1}H NMR of compound 1b, 21b and 26b



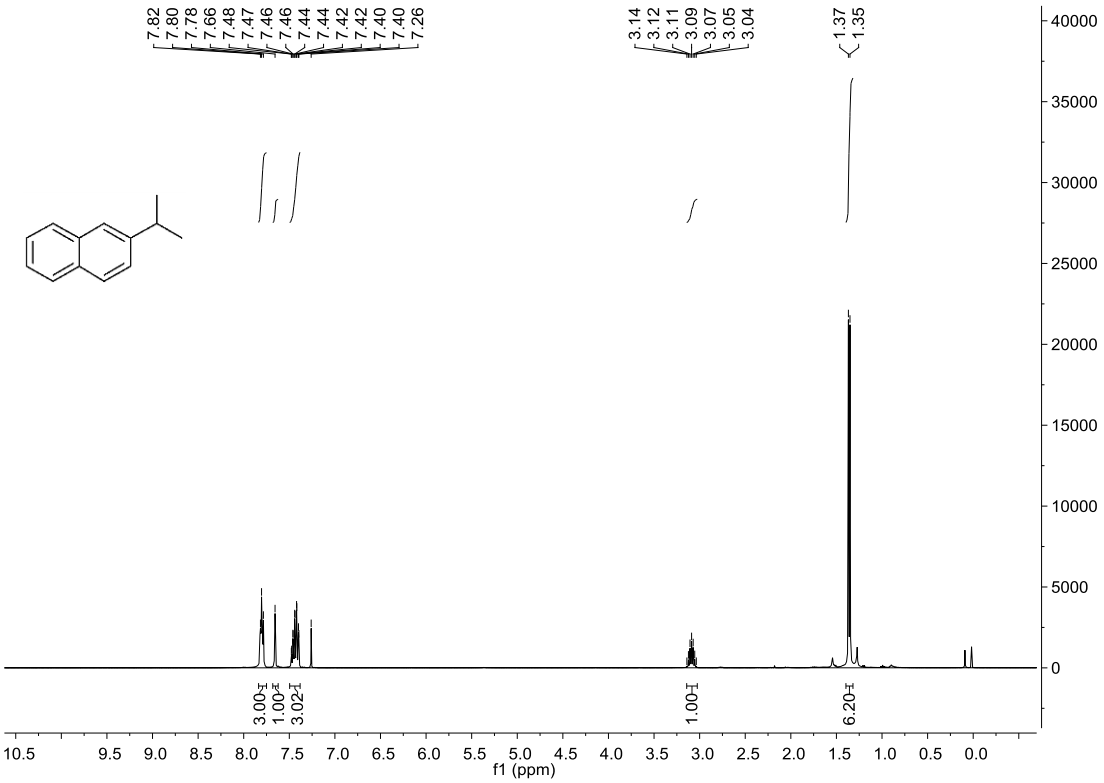
^{13}C NMR of compound 1b, 21b and 26b



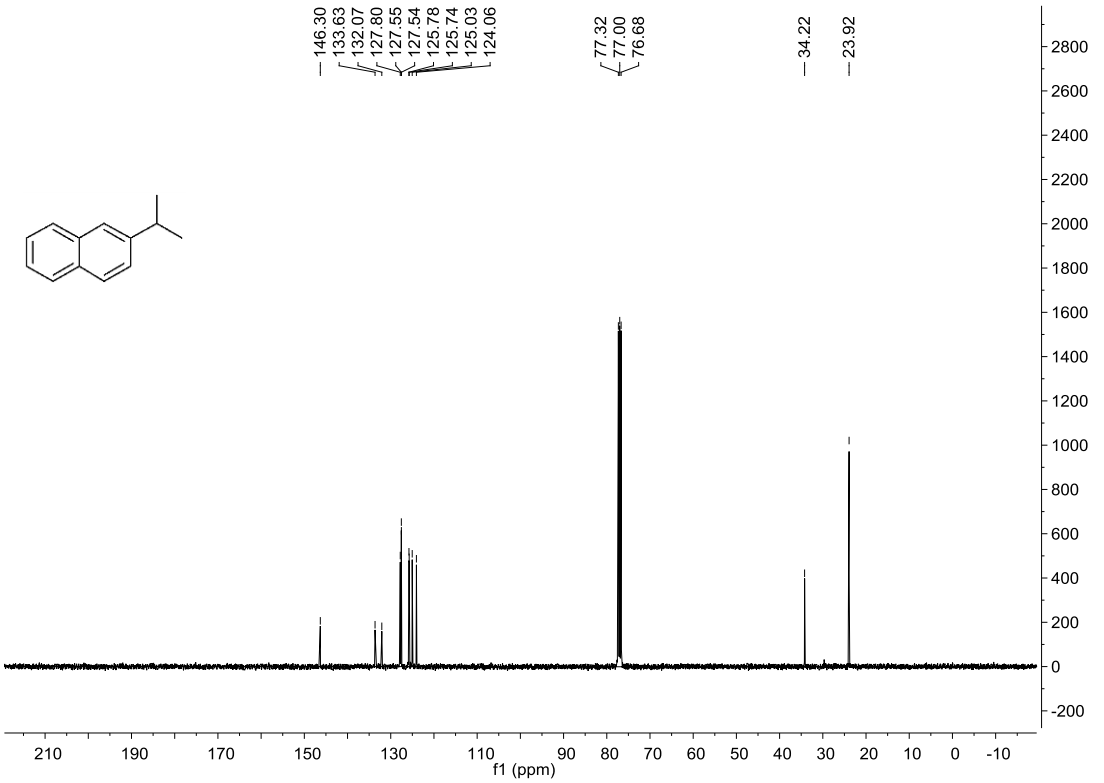
^{1}H NMR of compound 2b and 33b



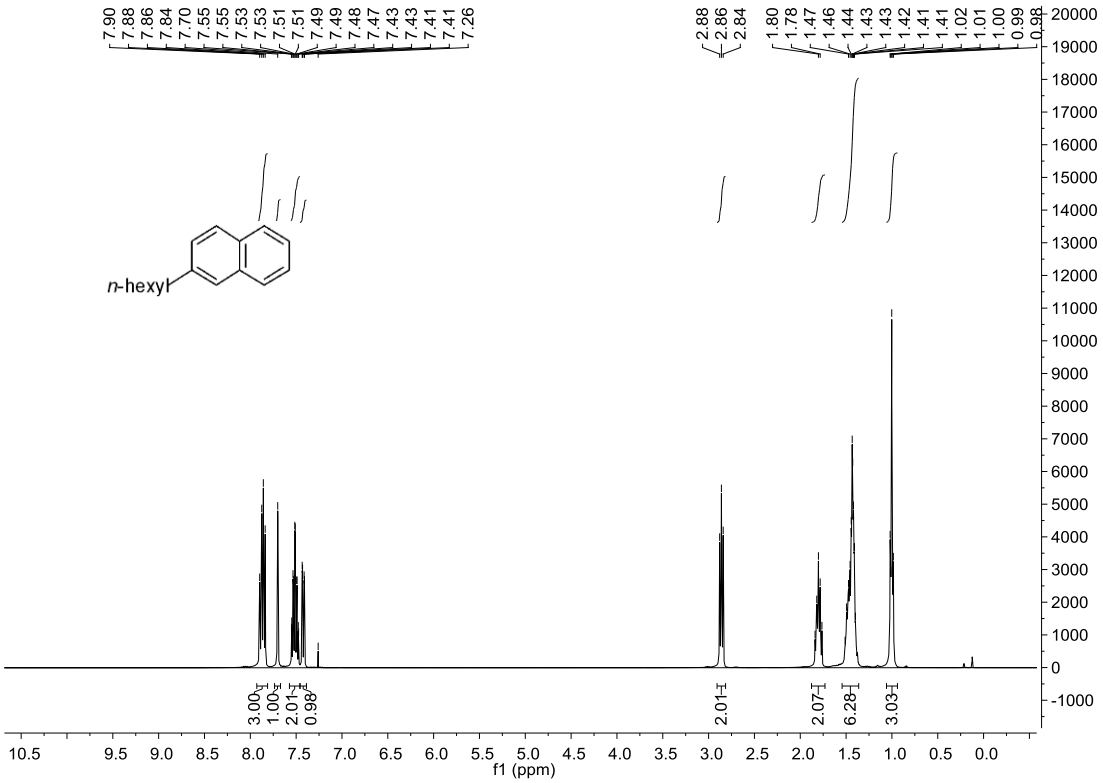
^{13}C NMR of compound 2b and 33b



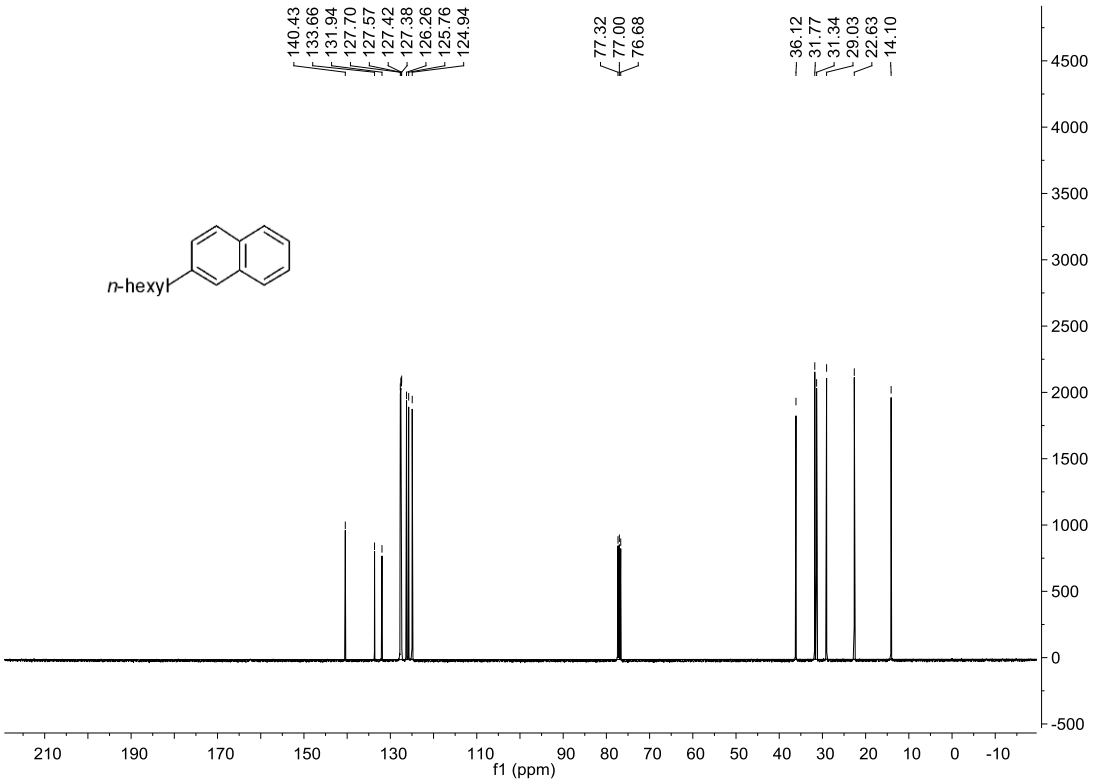
^{1}H NMR of compound 3b



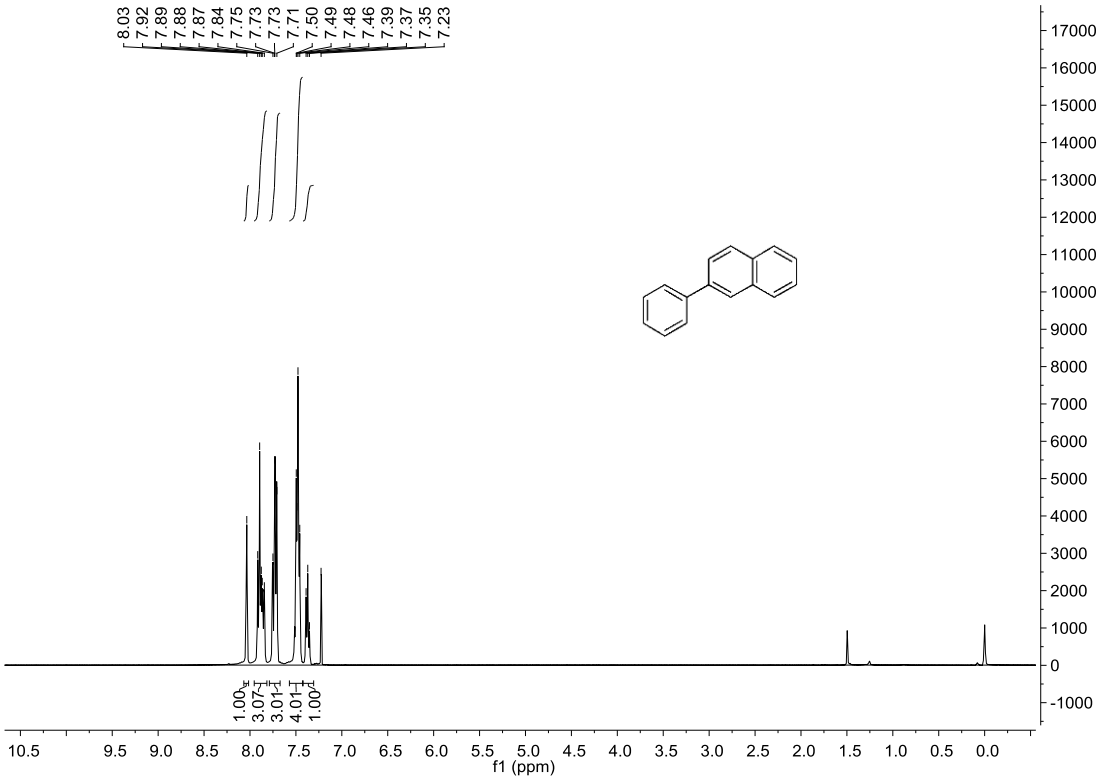
^{13}C NMR of compound 3b



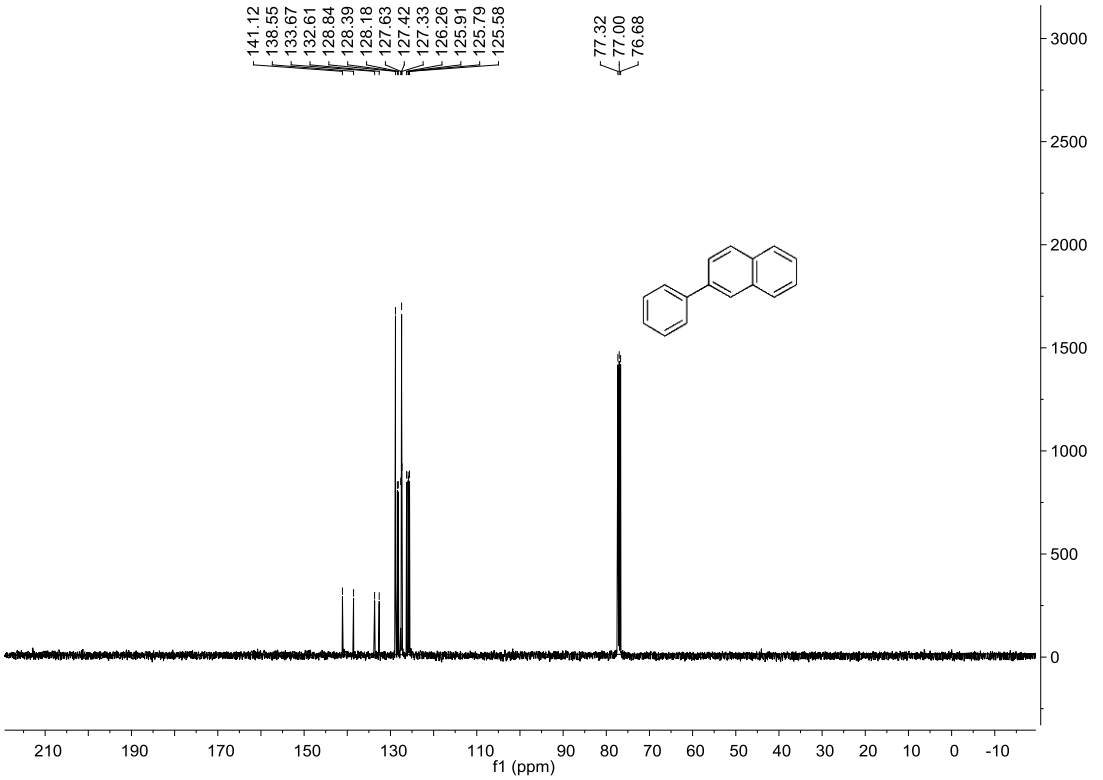
^{1}H NMR of compound 4b



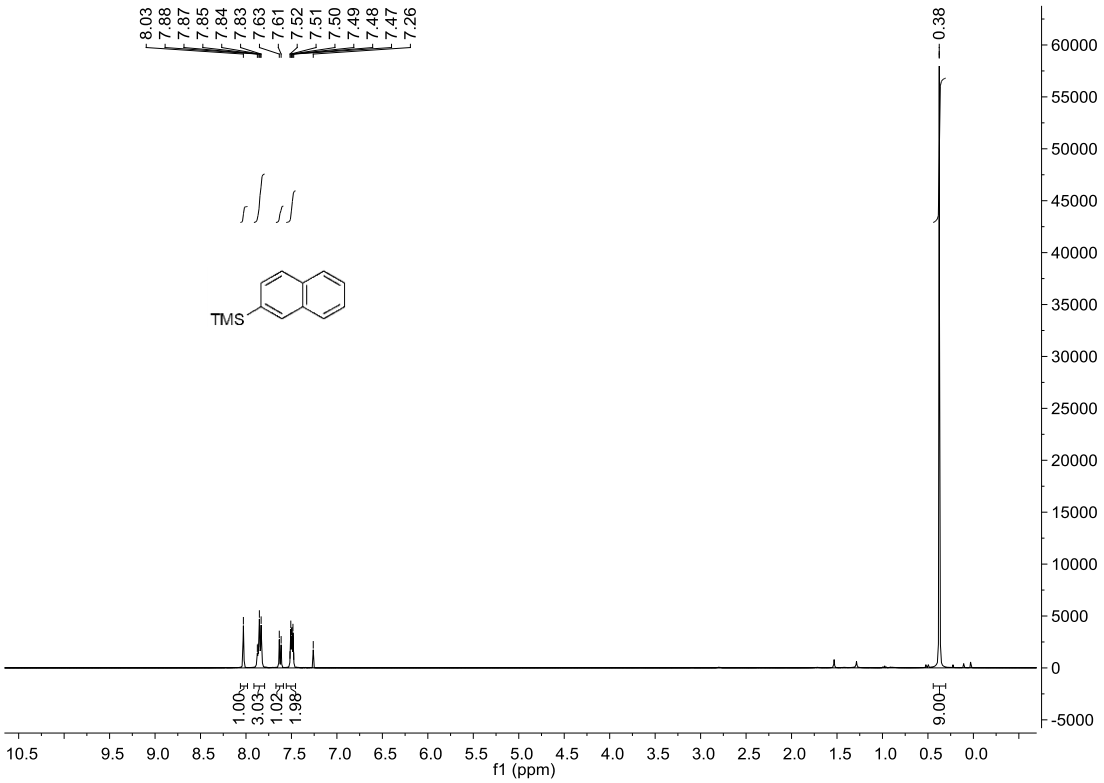
^{13}C NMR of compound 4b



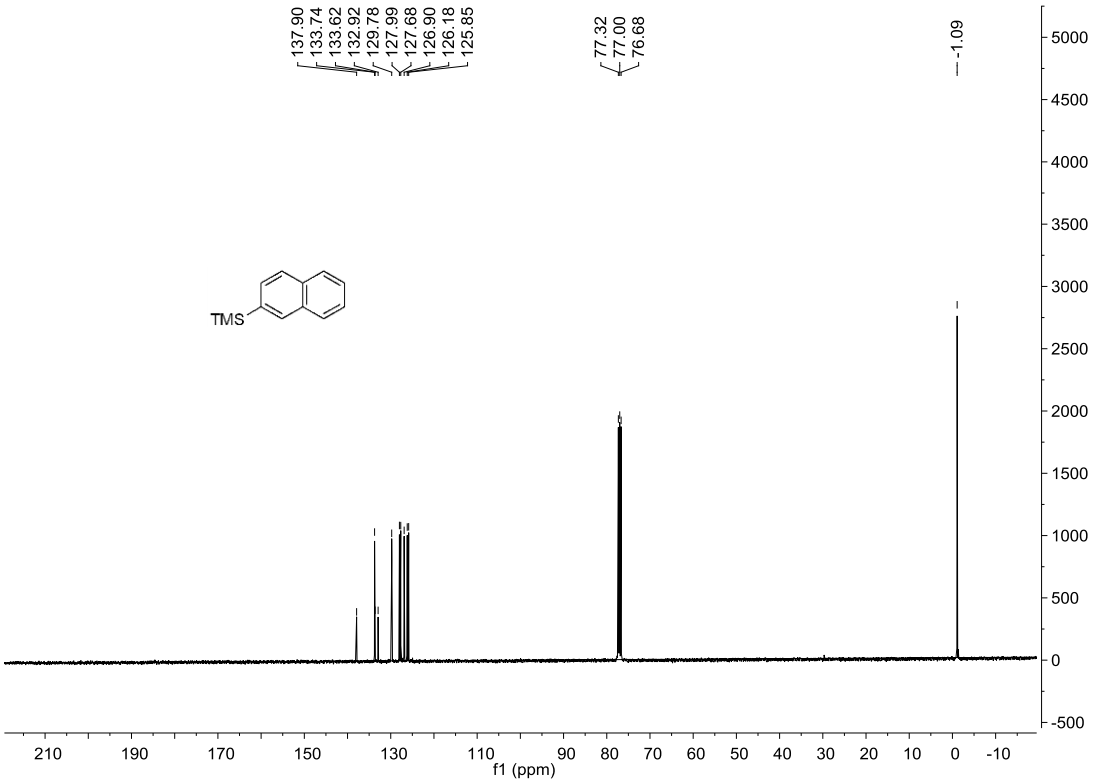
^{1}H NMR of compound 5b



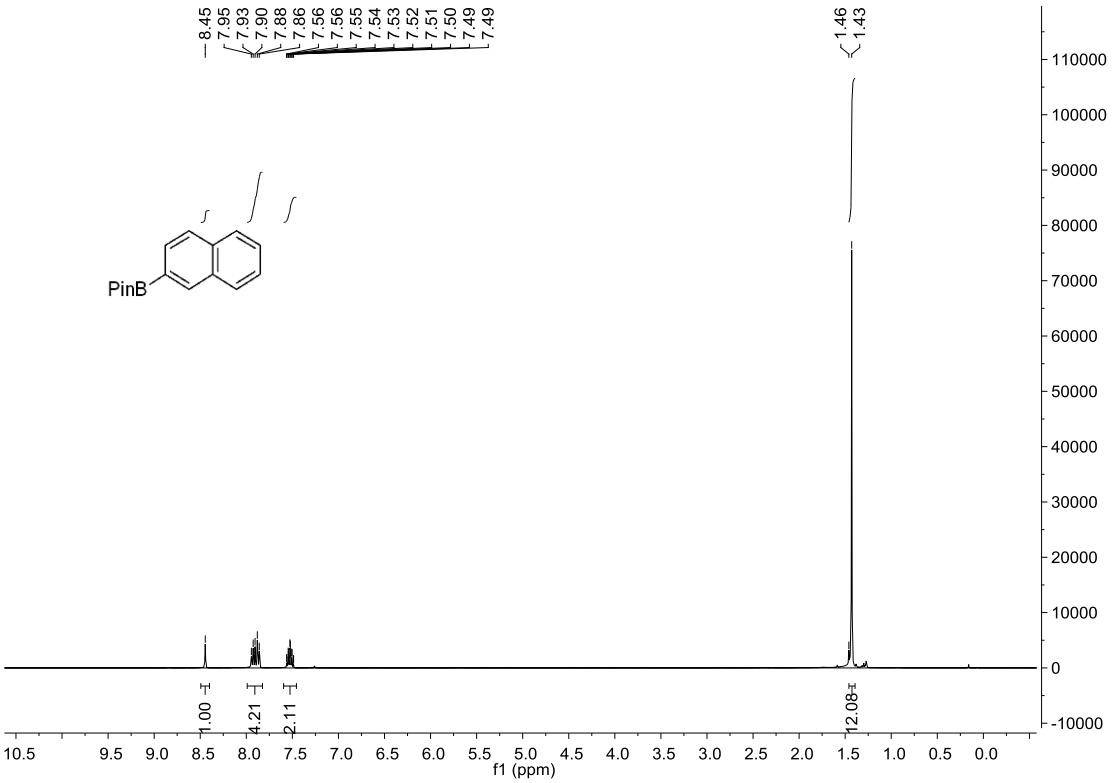
^{13}C NMR of compound 5b



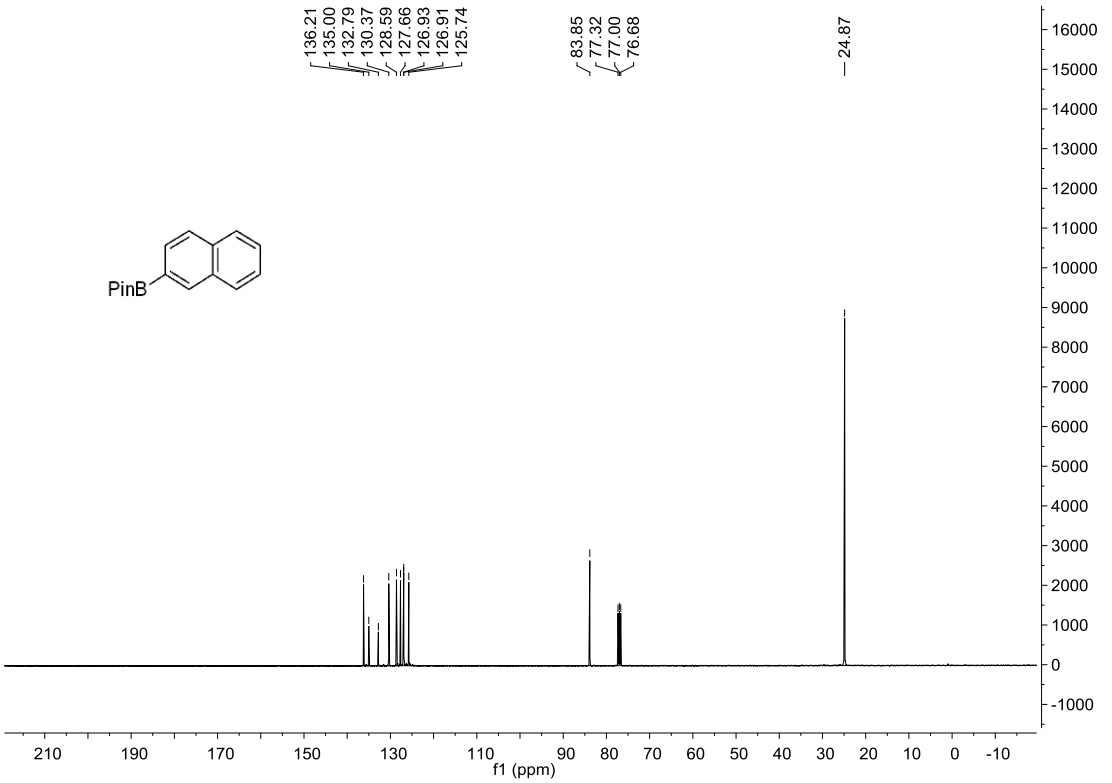
^{1}H NMR of compound 6b



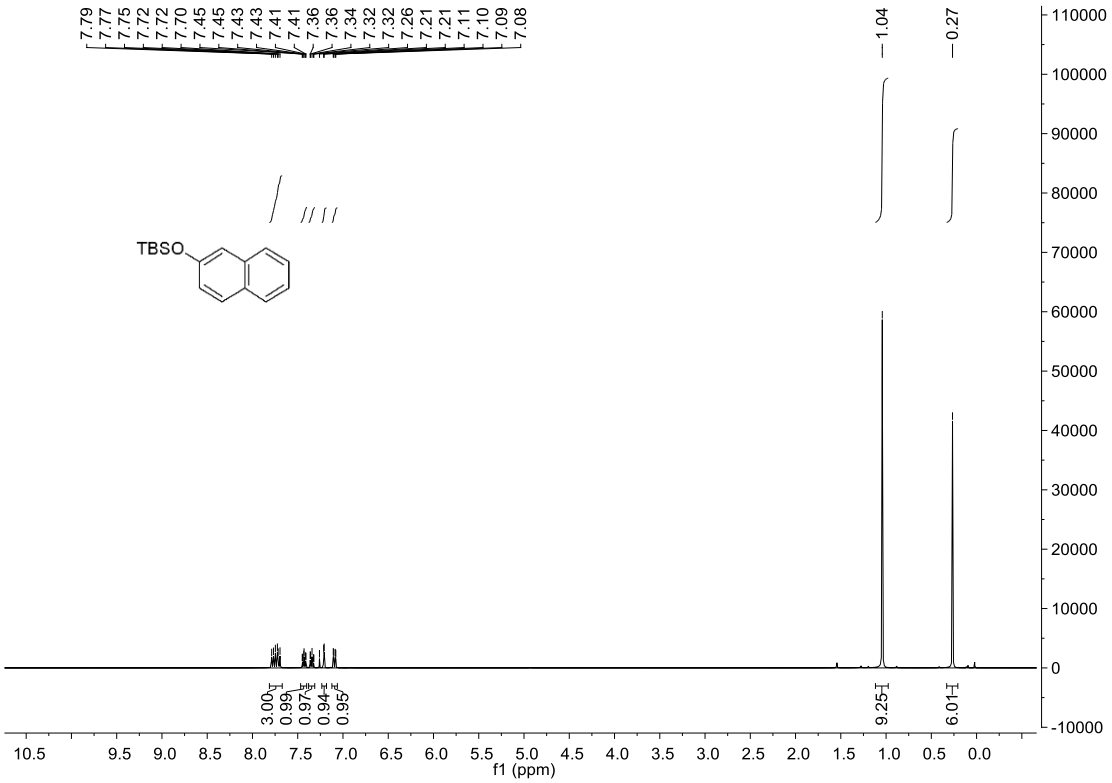
^{13}C NMR of compound 6b



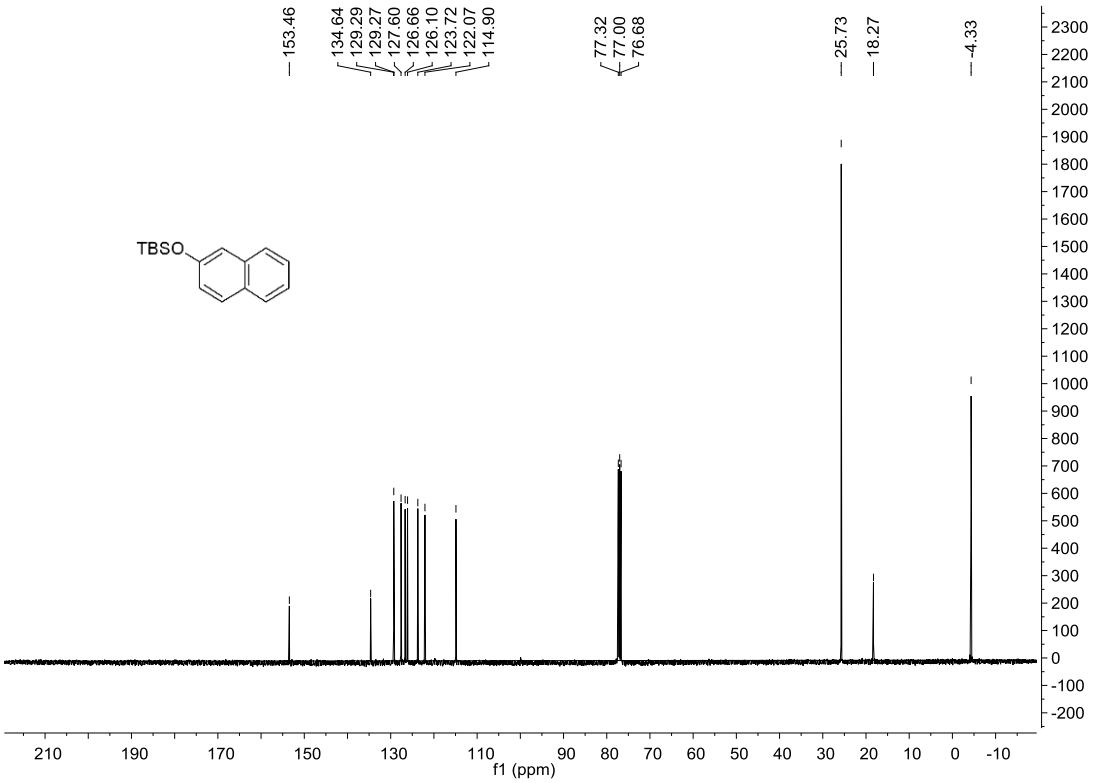
^{1}H NMR of compound 7b



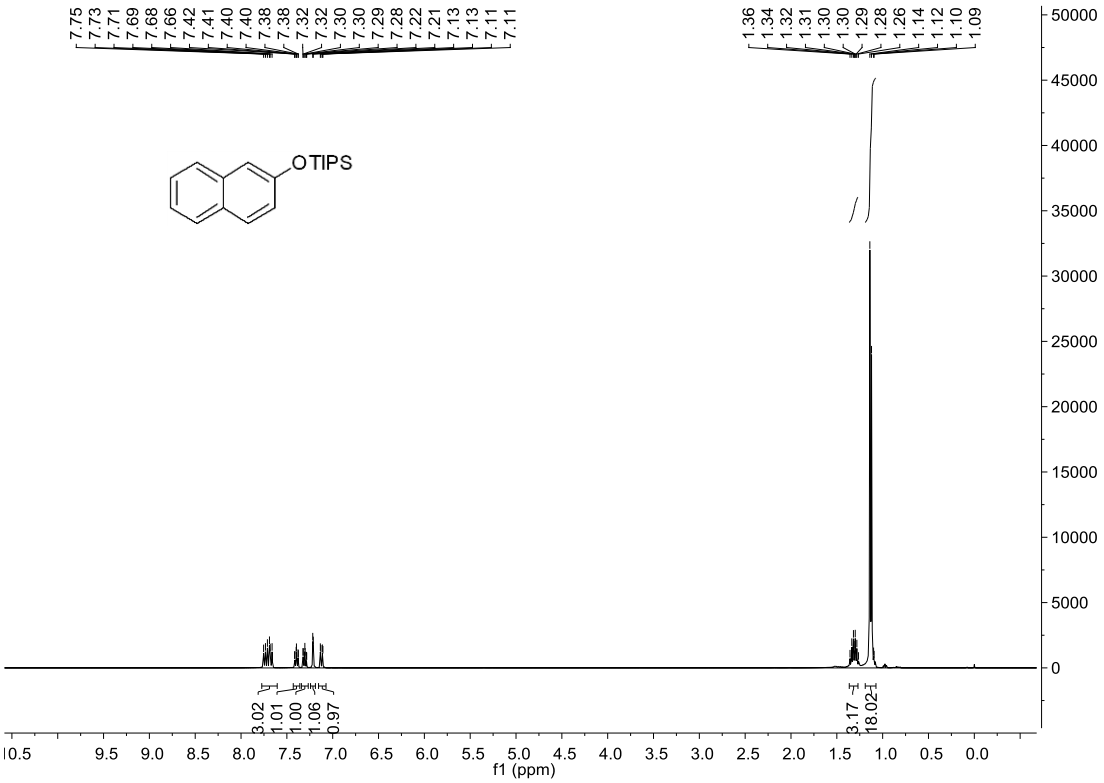
^{13}C NMR of compound 7b



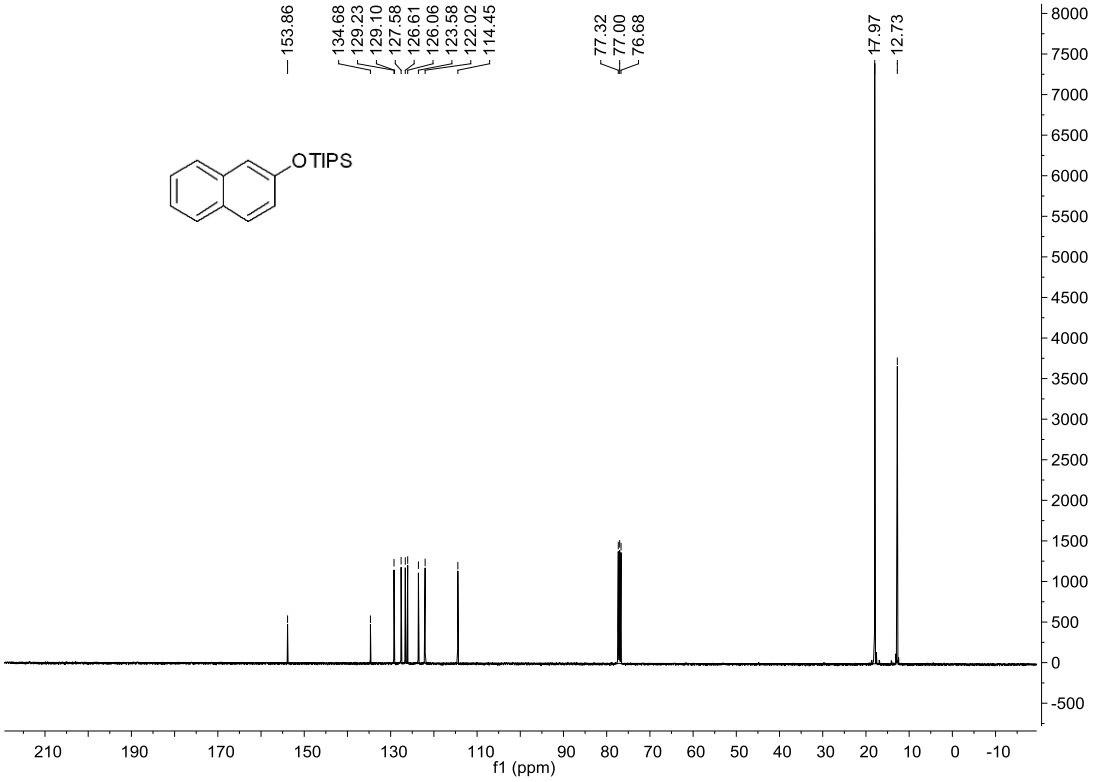
^{1}H NMR of compound 8b



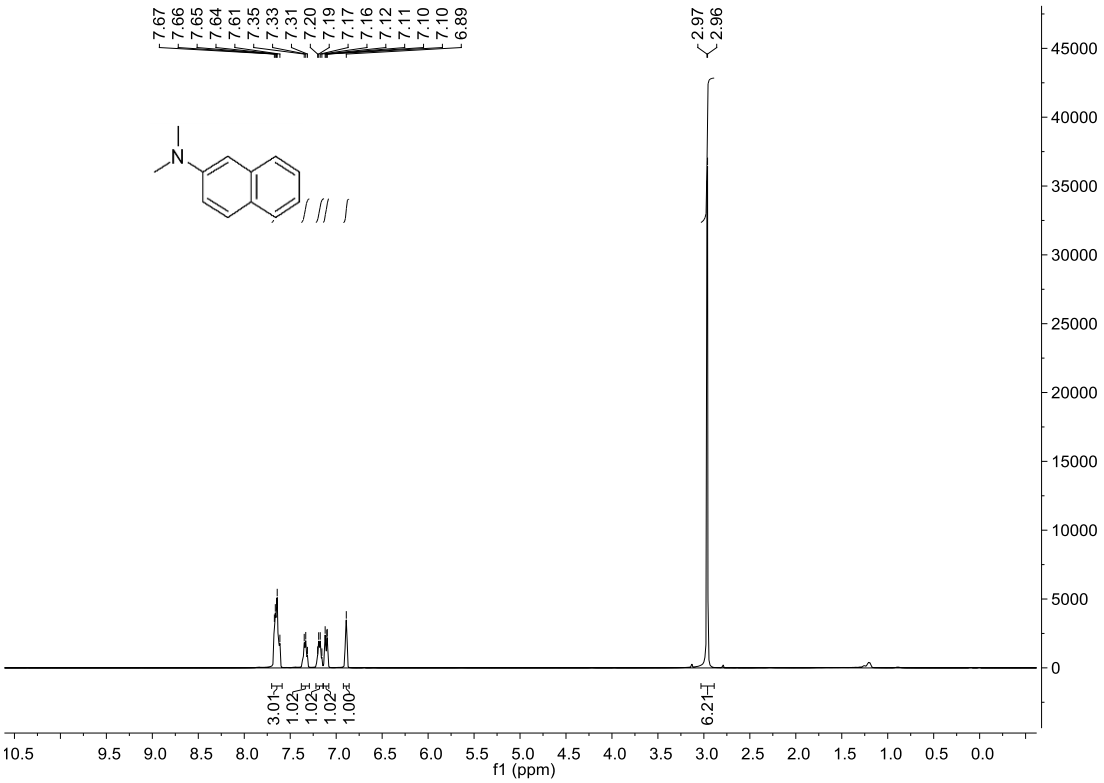
^{13}C NMR of compound 8b



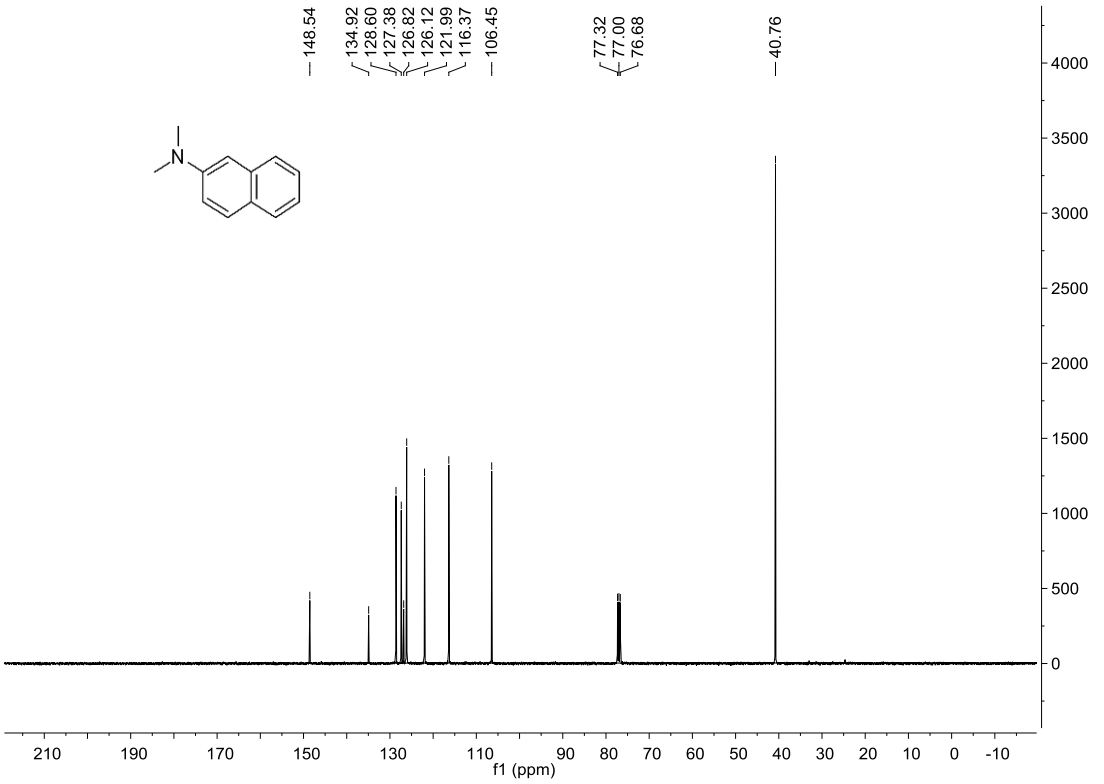
^{1}H NMR of compound 9b and 10b



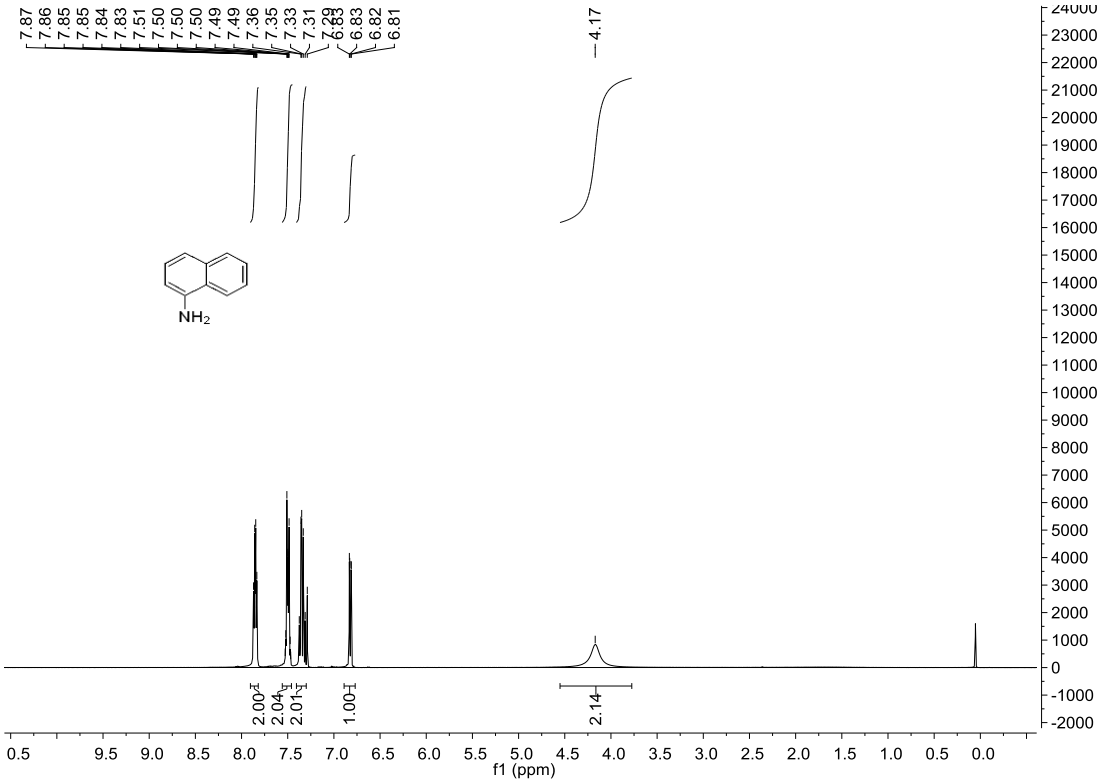
^{13}C NMR of compound 9b and 10b



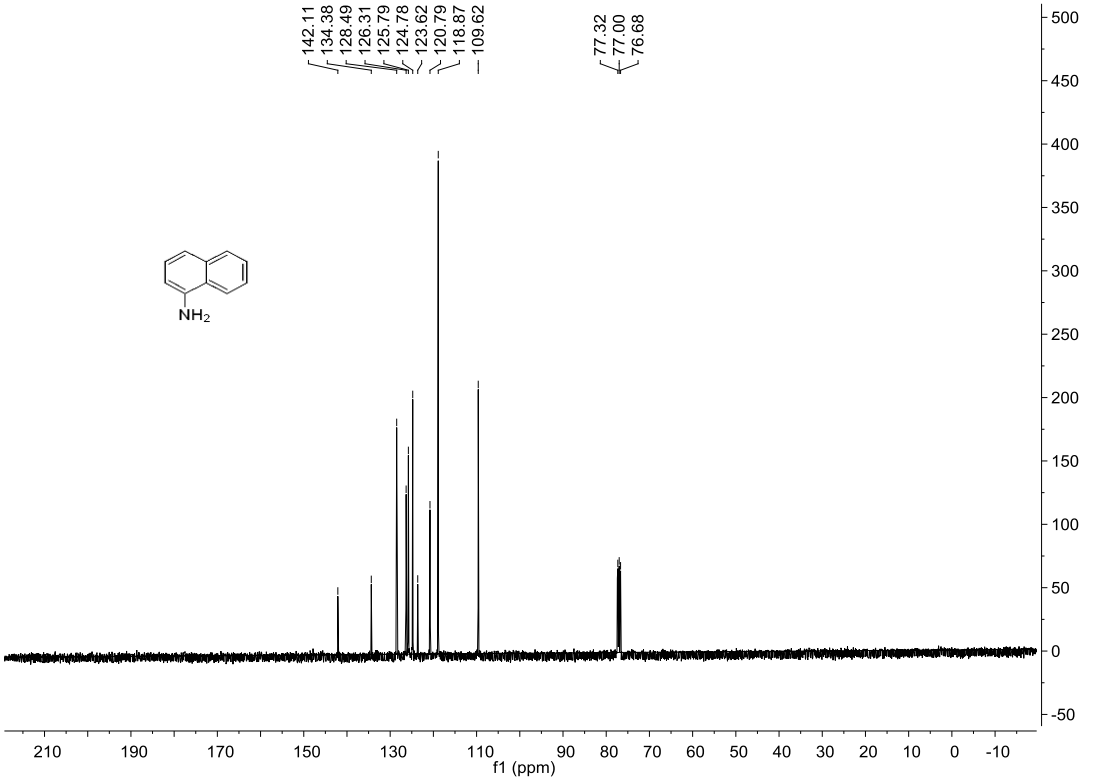
^{1}H NMR of compound 11b



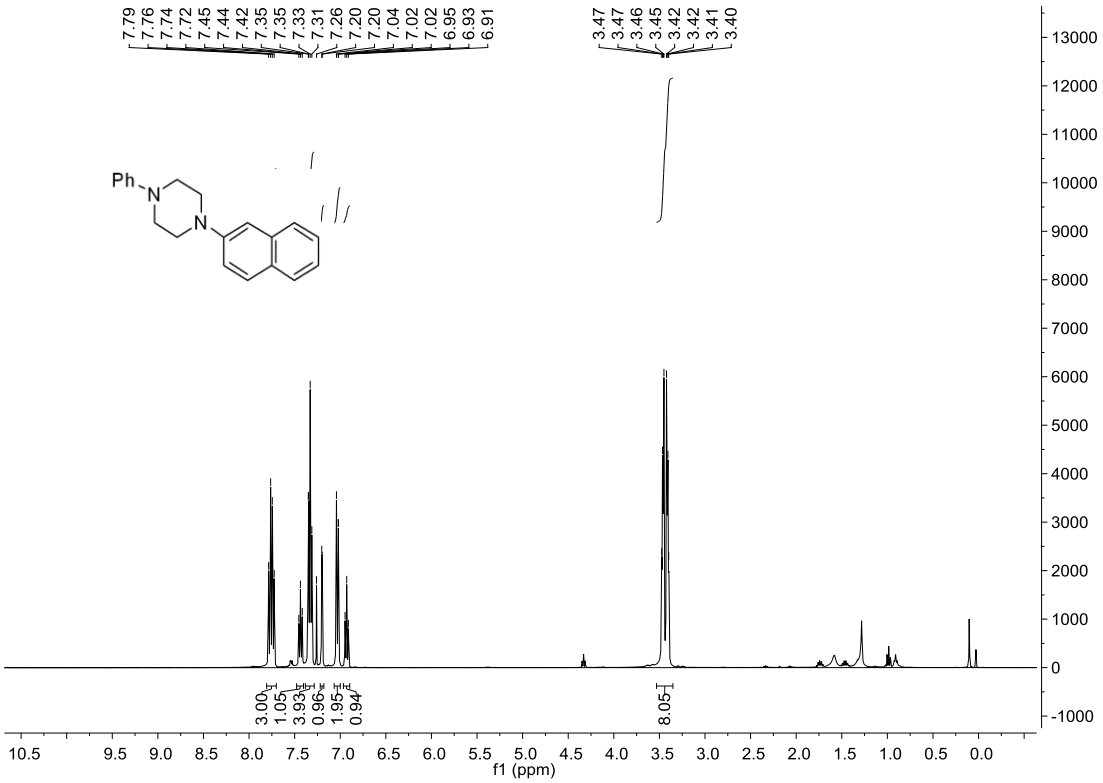
^{13}C NMR of compound 11b



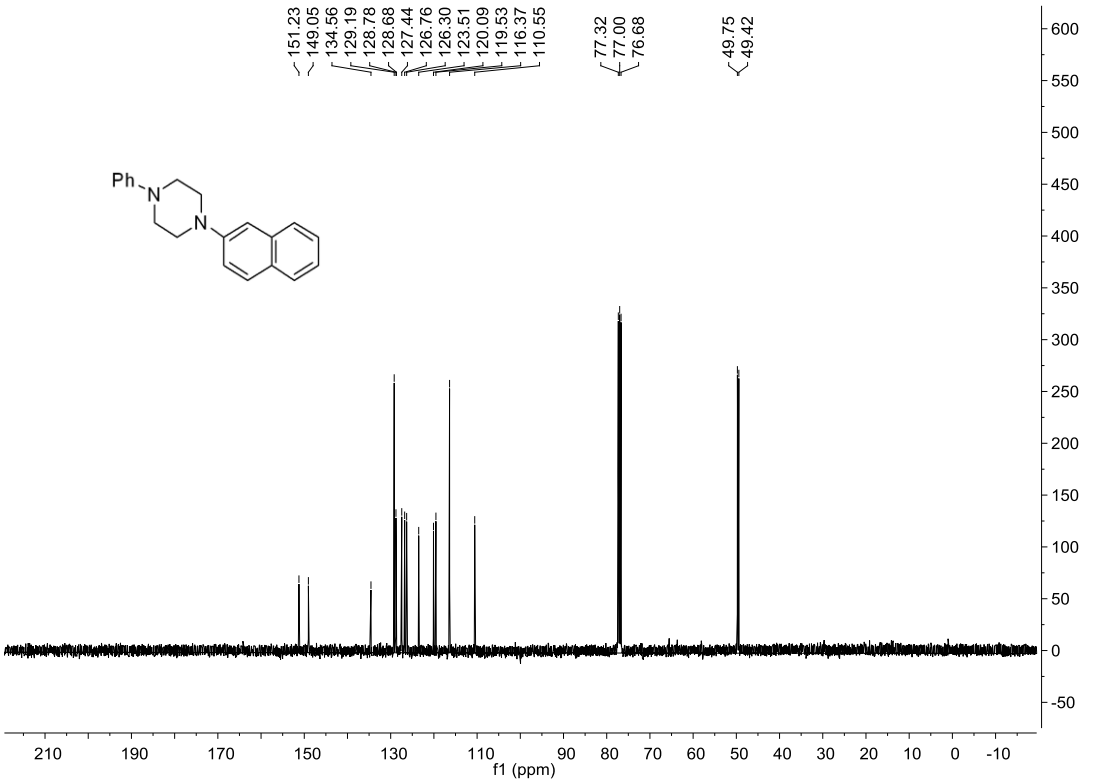
.^{1}H NMR of compound 12b



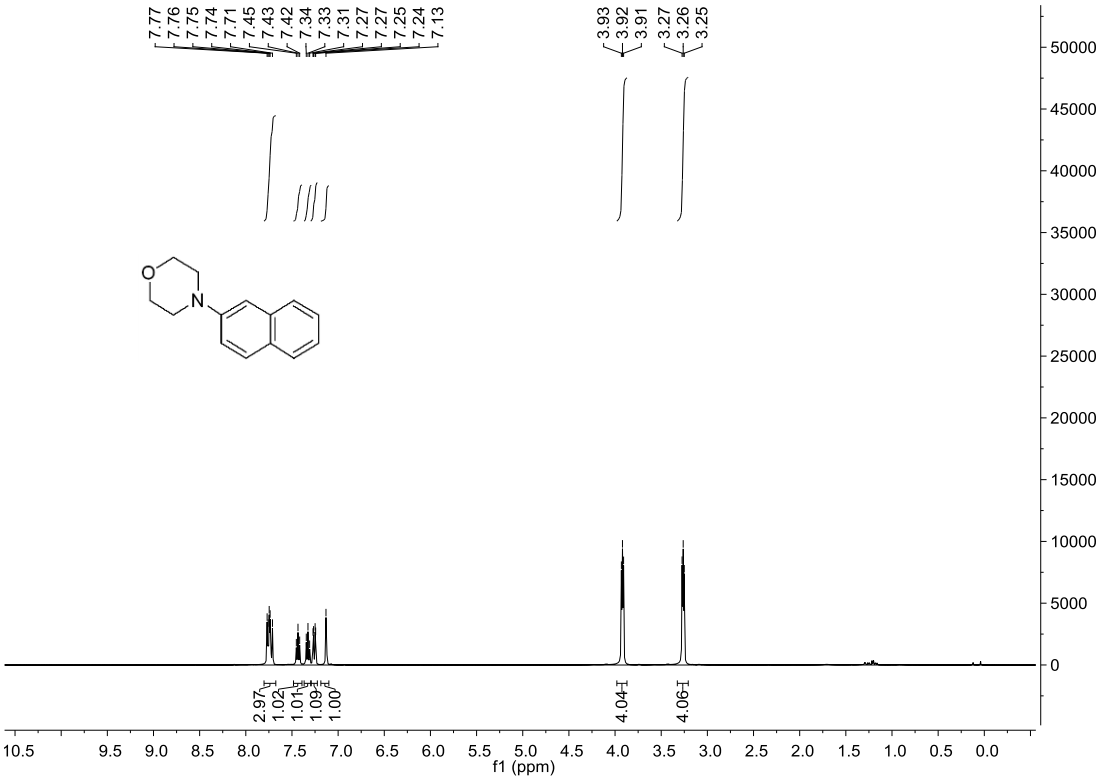
^{13}C NMR of compound 12b



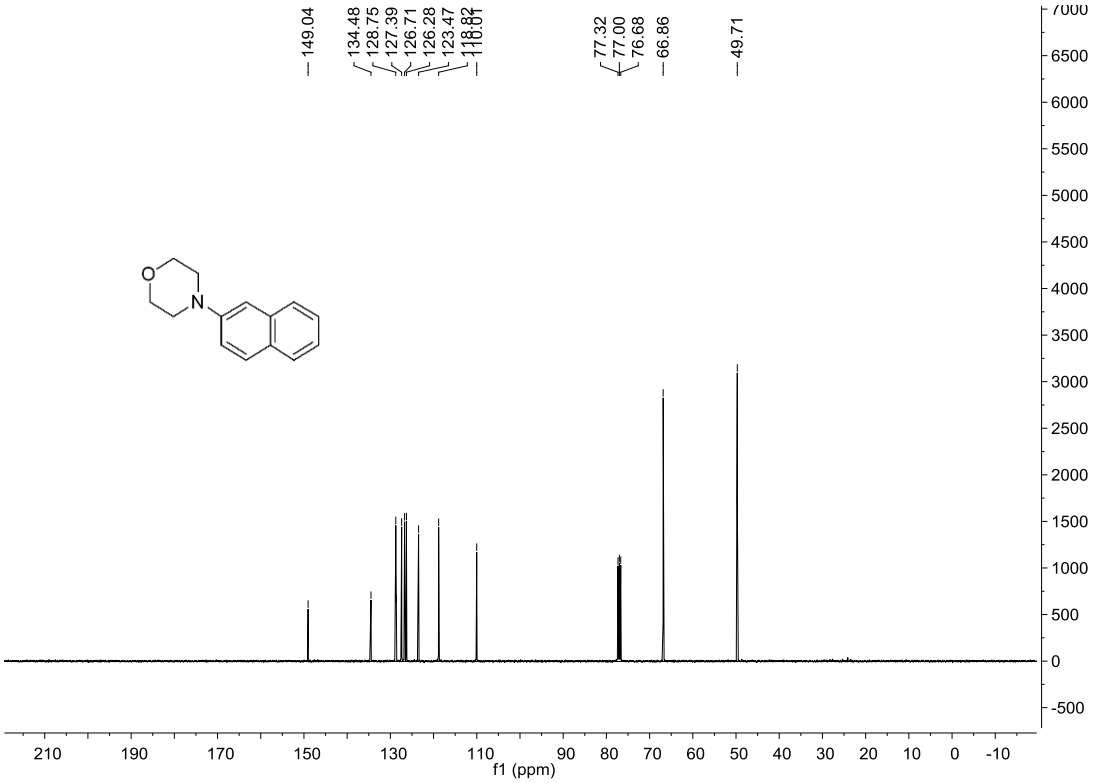
^{1}H NMR of compound 13b



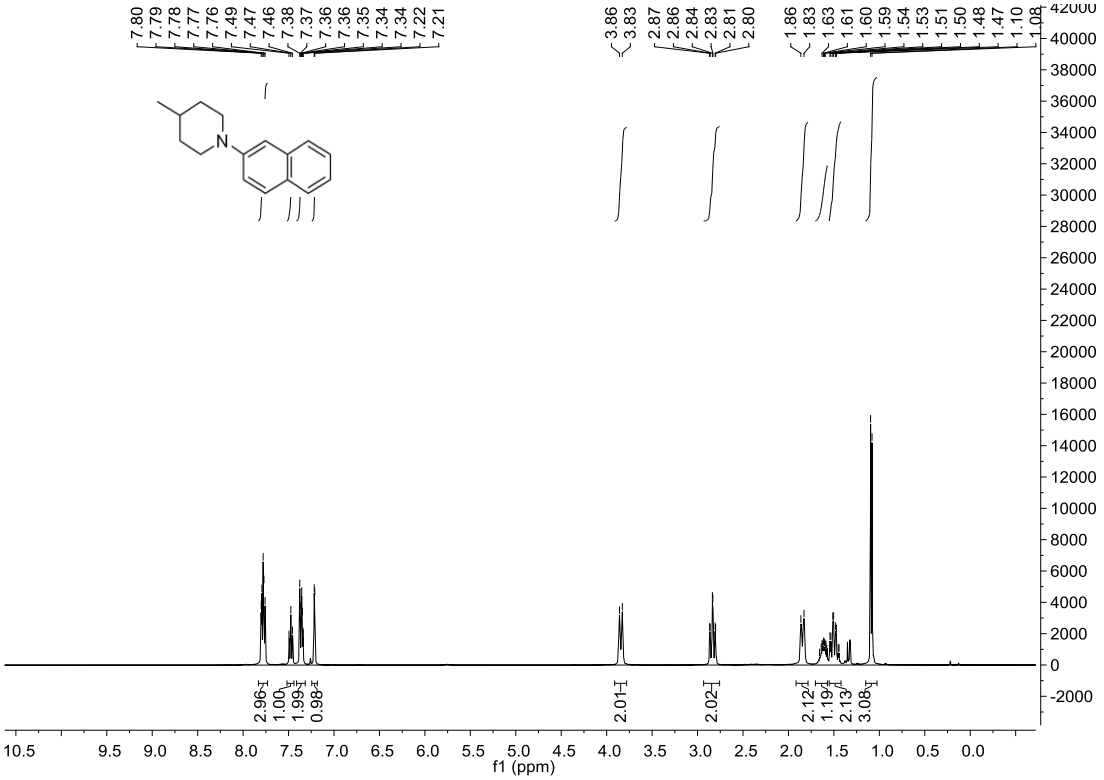
^{13}C NMR of compound 13b



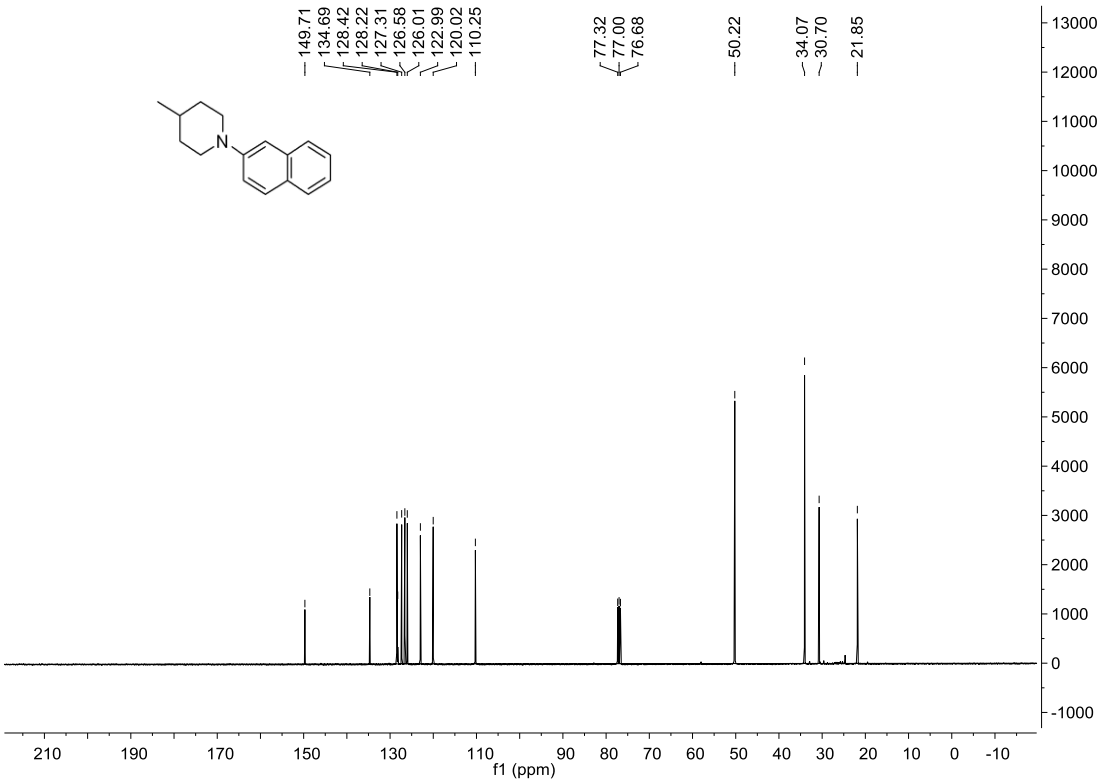
^{1}H NMR of compound 14b



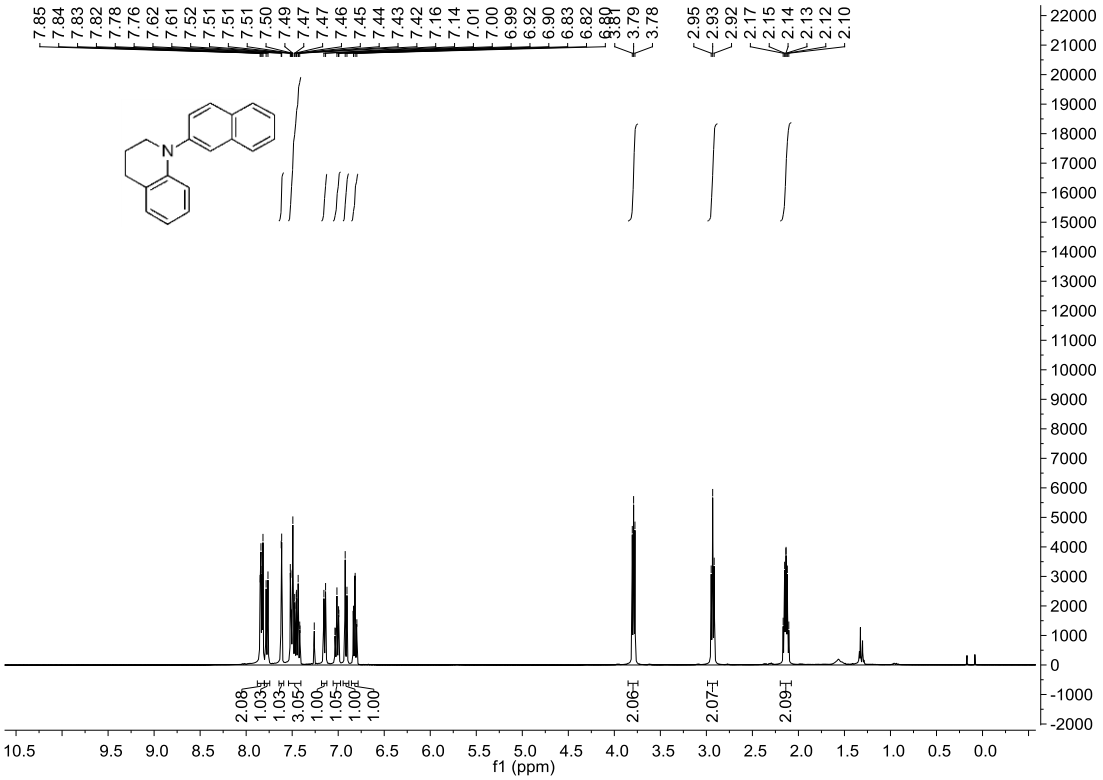
^{13}C NMR of compound 14b



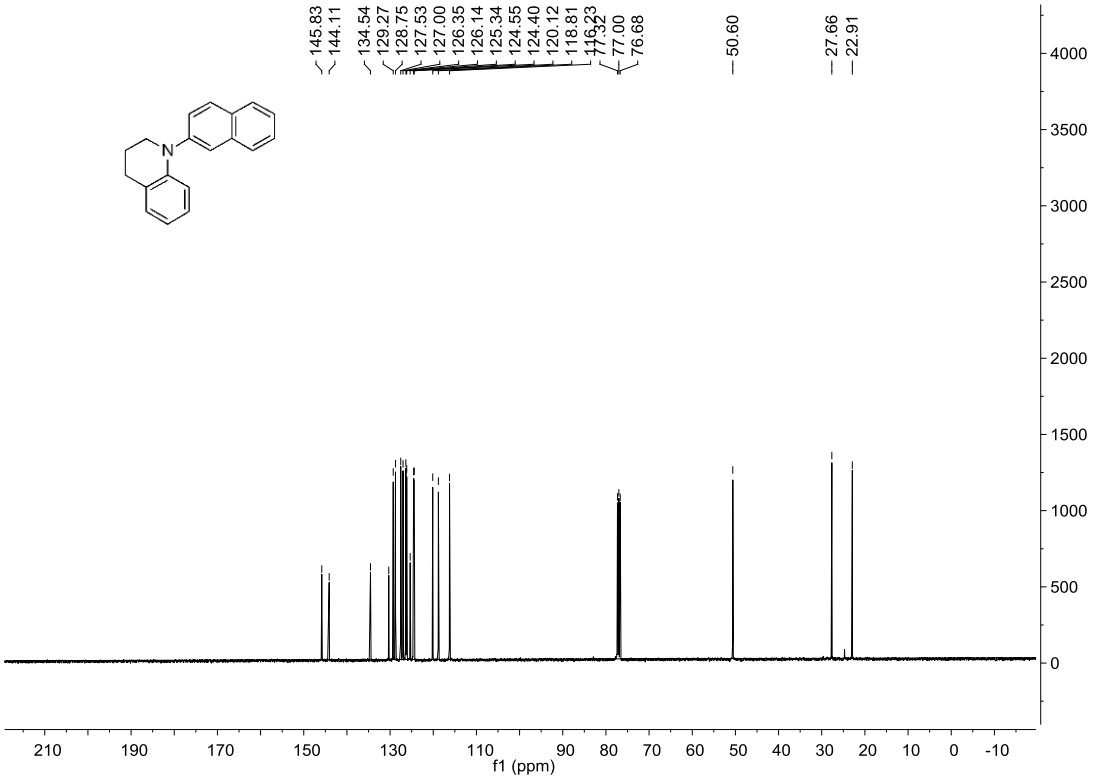
^{1}H NMR of compound 15b



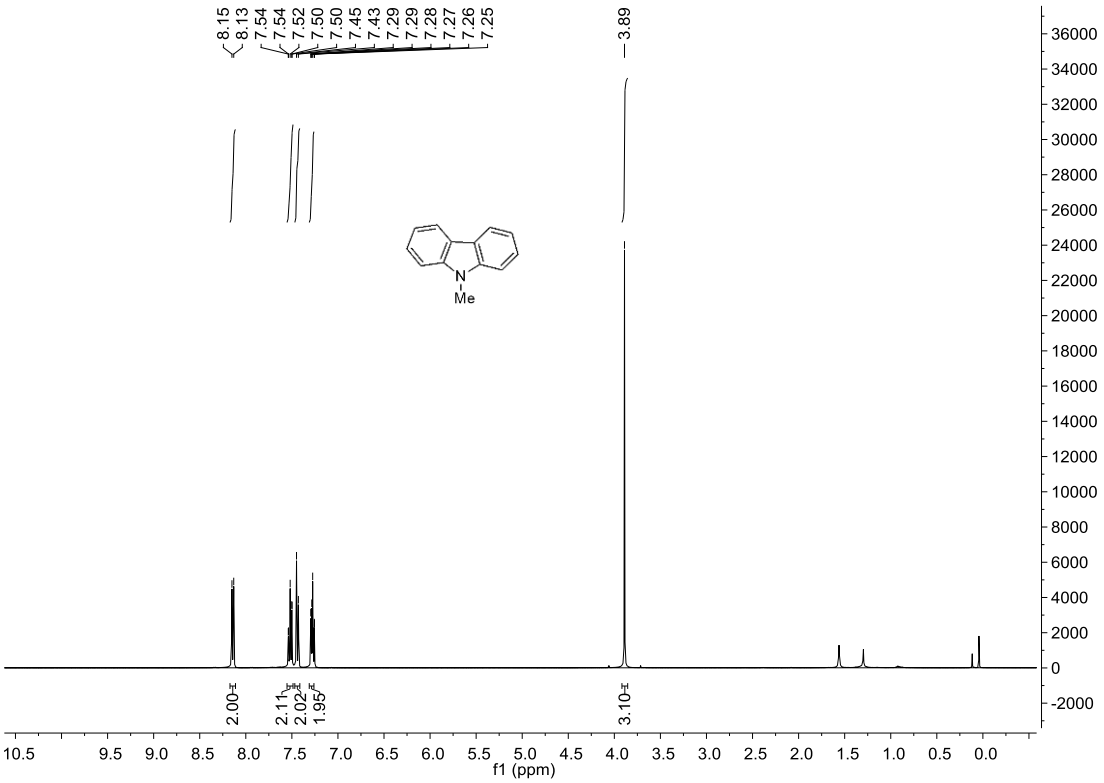
^{13}C NMR of compound 15b



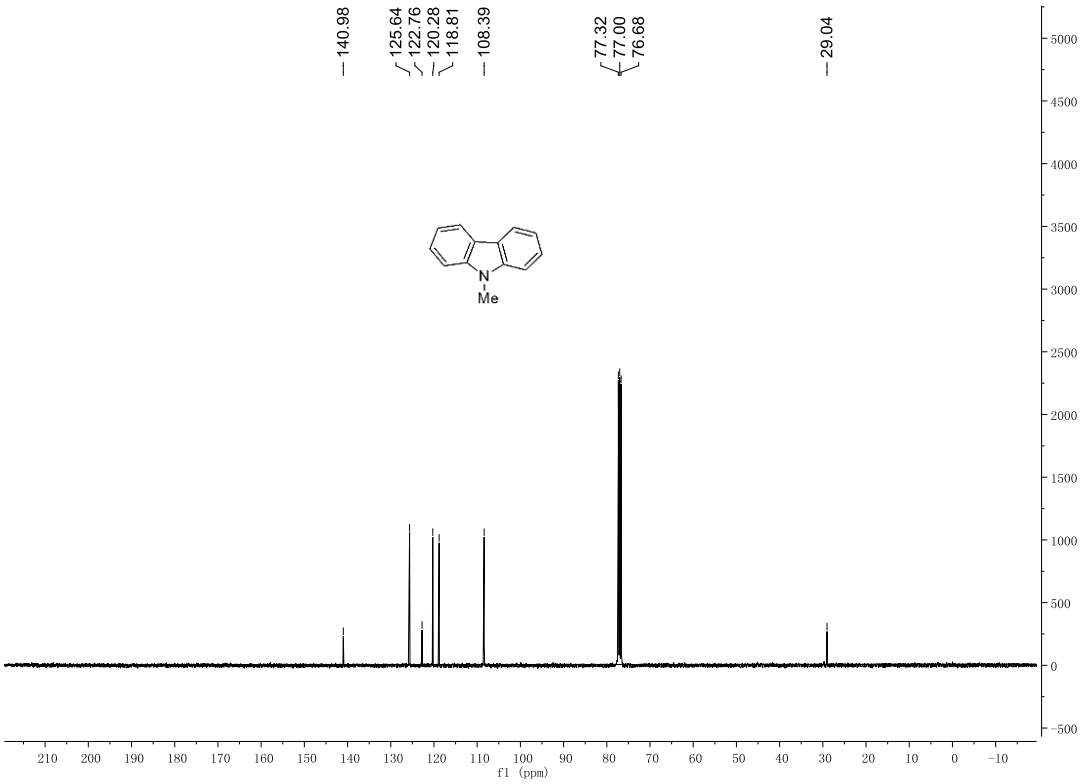
^{1}H NMR of compound 16b



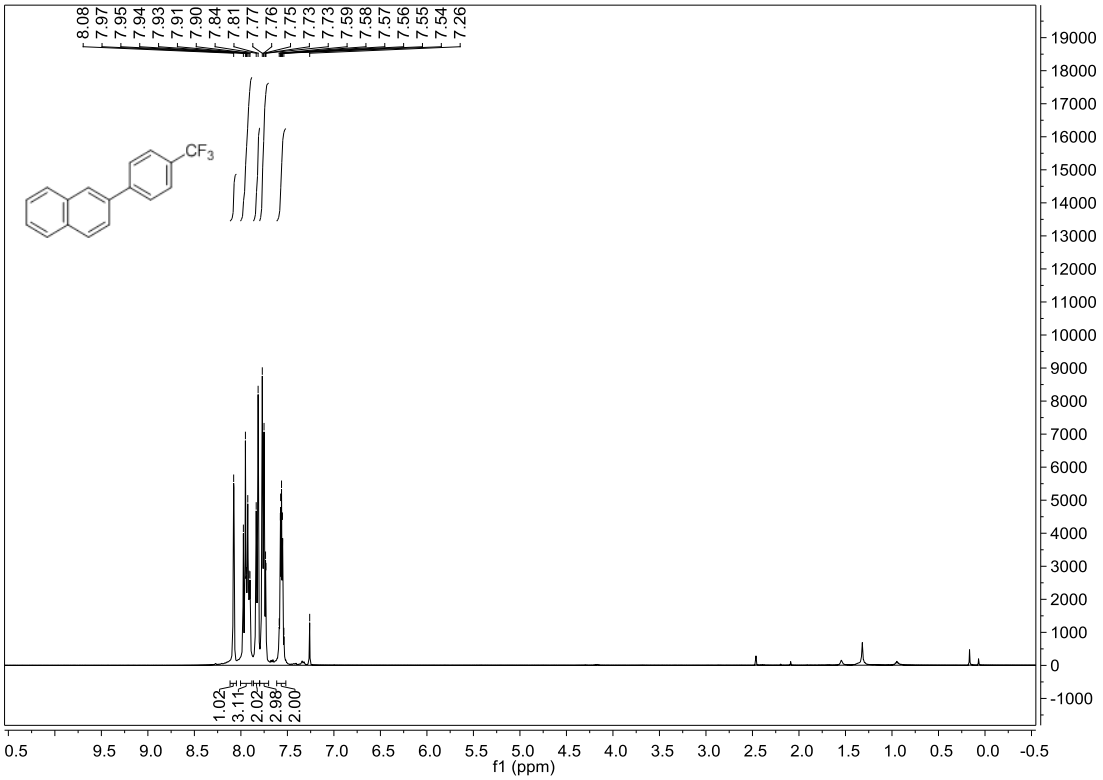
^{13}C NMR of compound 16b



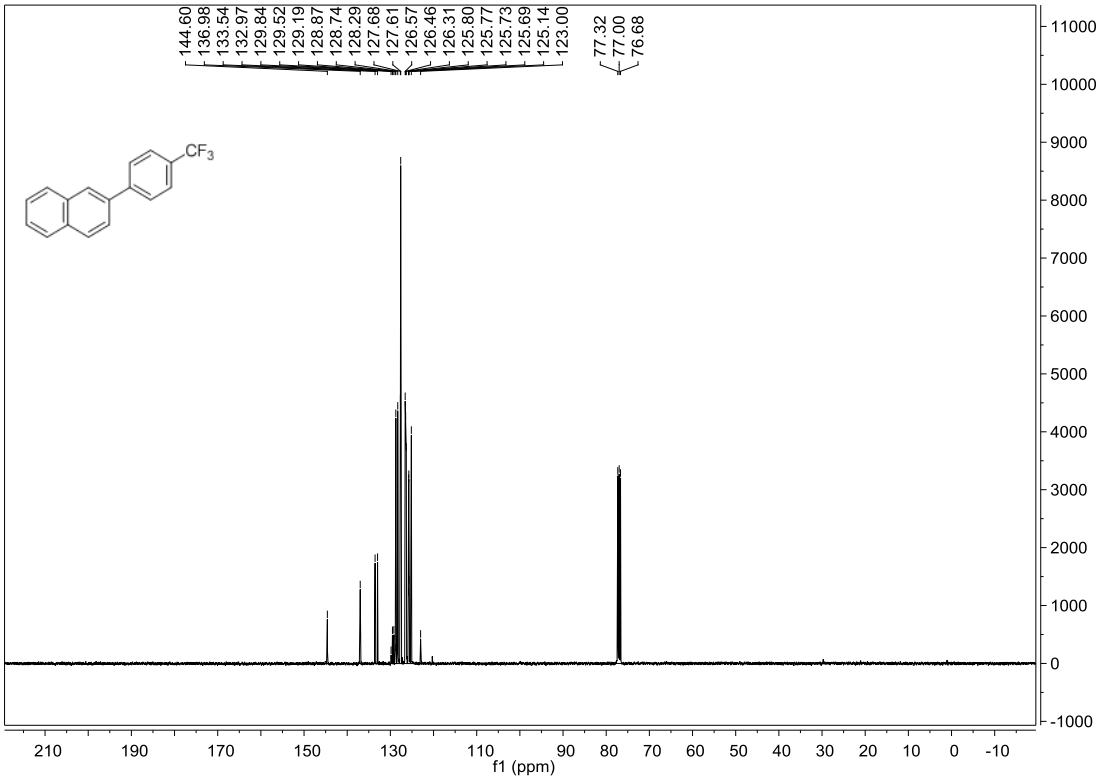
^{1}H NMR of compound 17b



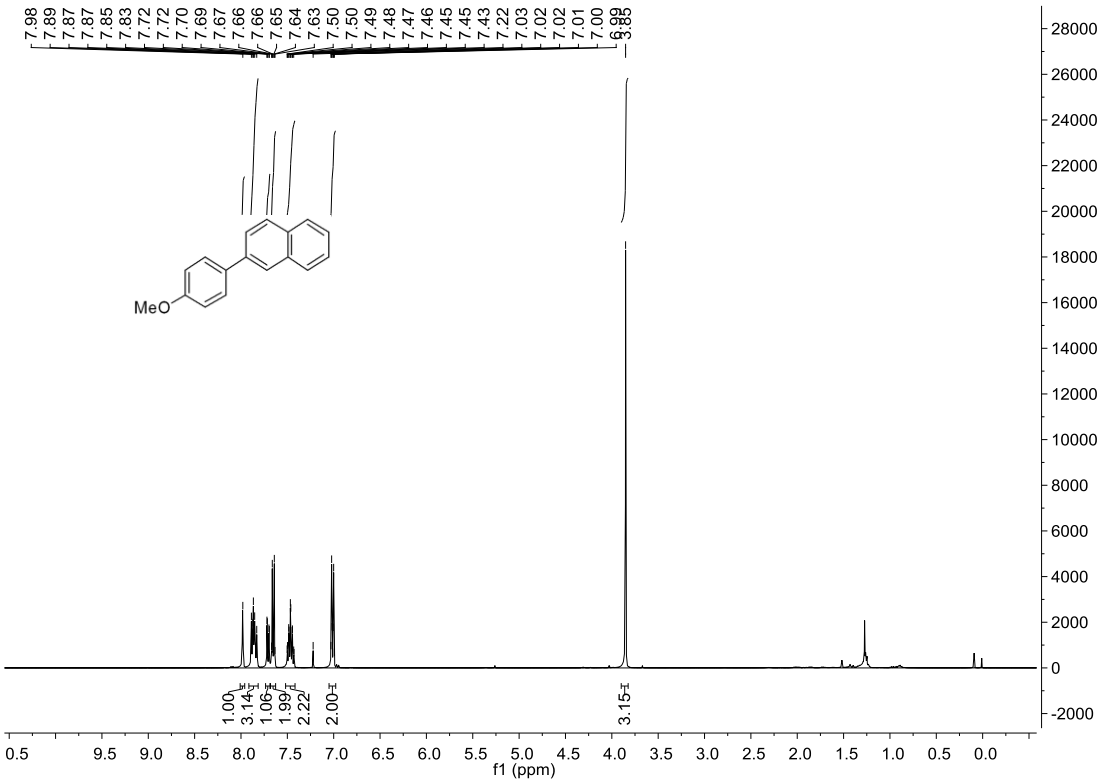
^{13}C NMR of compound 17b



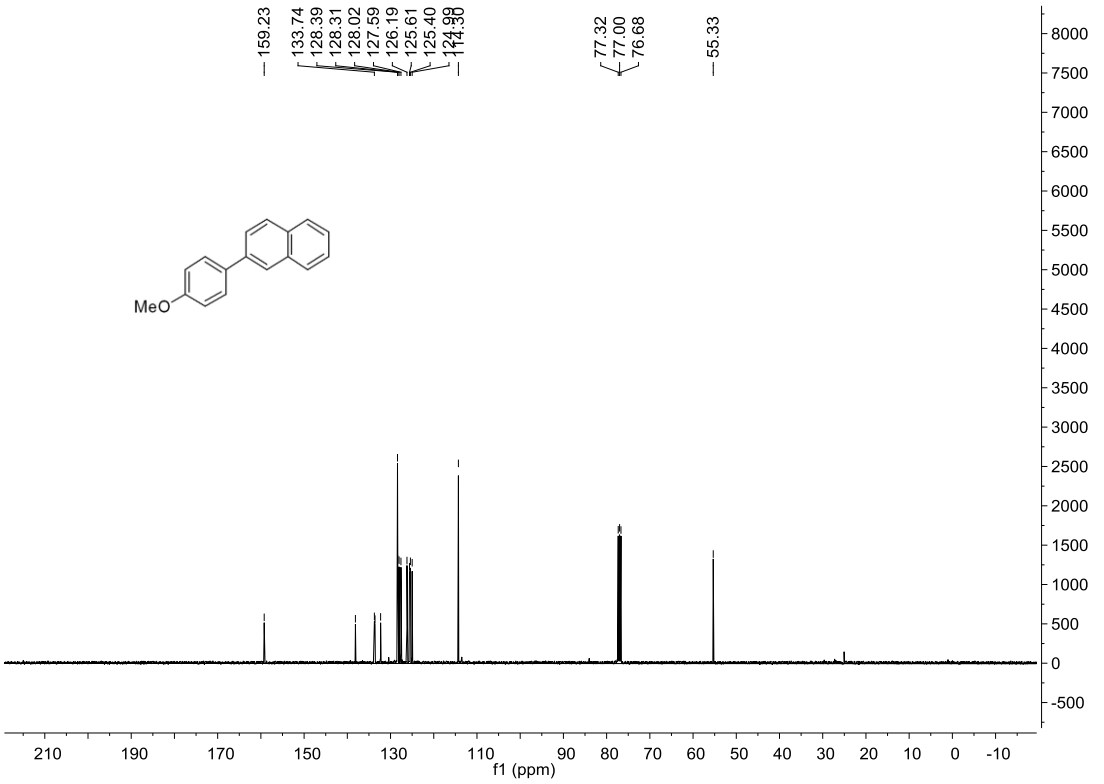
^{1}H NMR of compound 18b



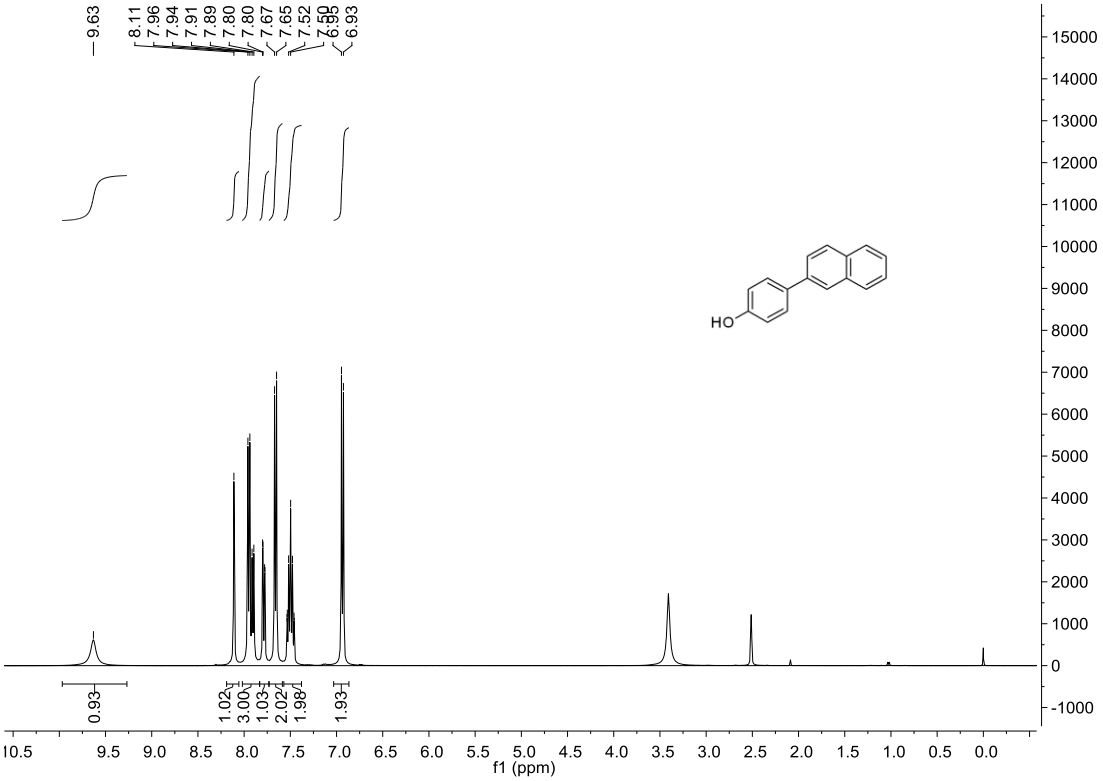
^{13}C NMR of compound 18b



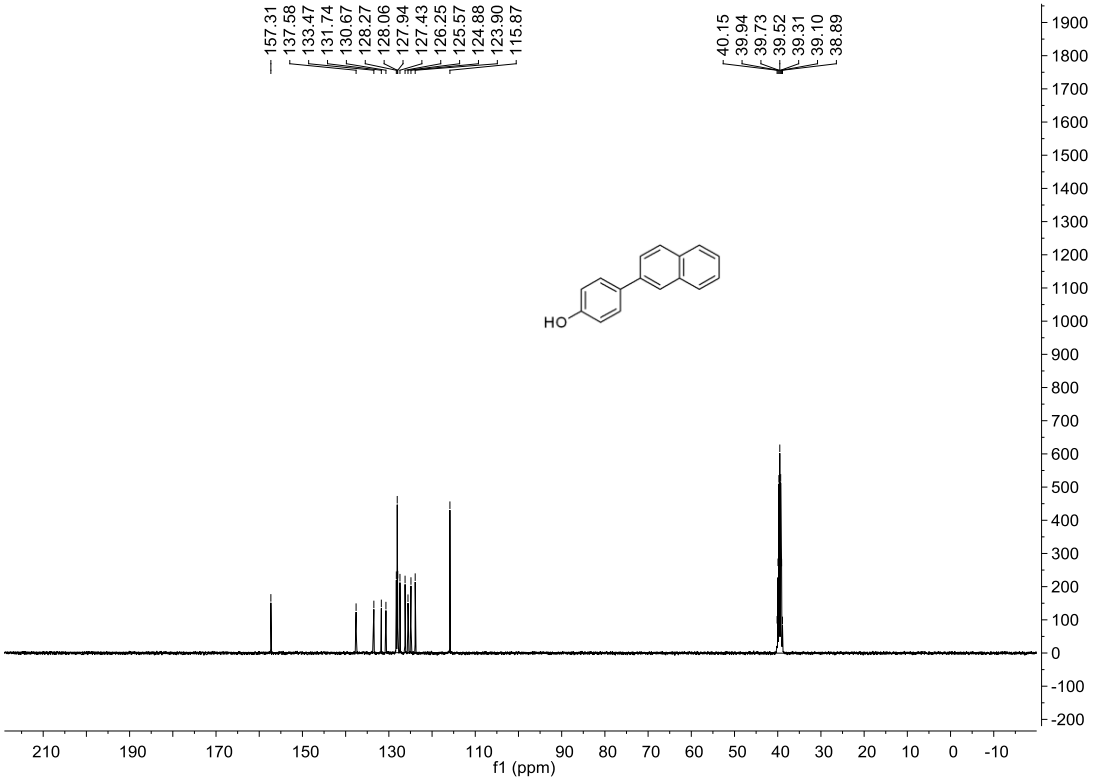
^{1}H NMR of compound 19b



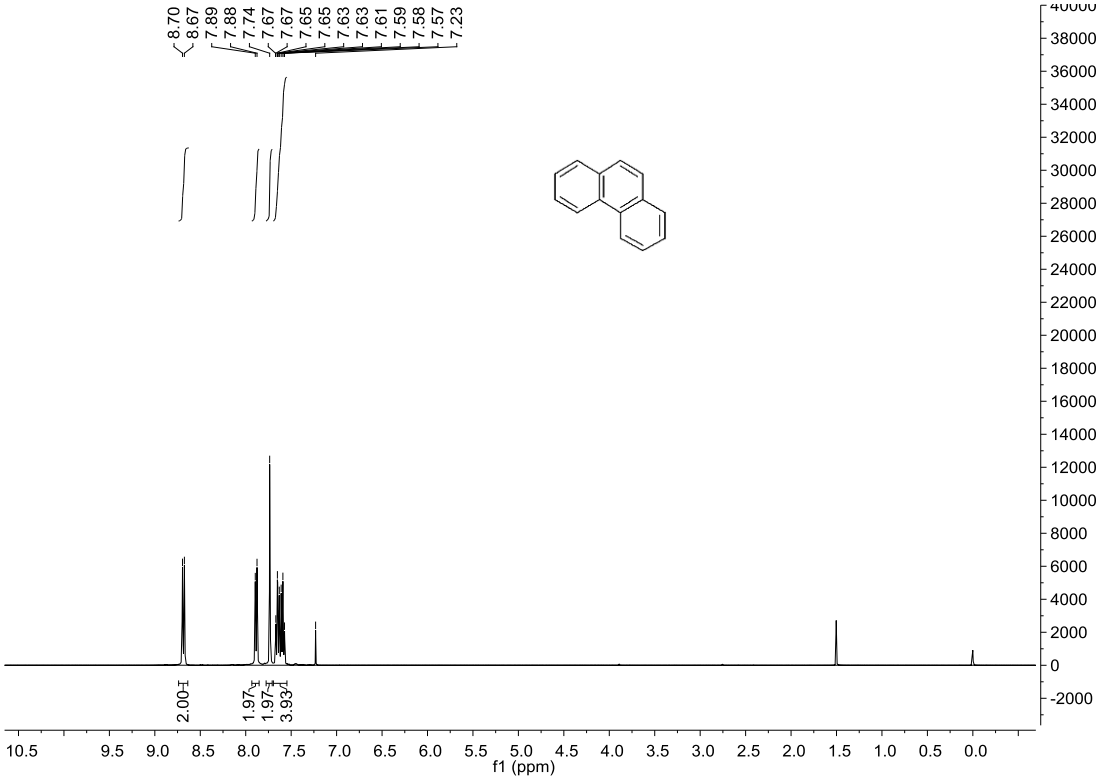
^{13}C NMR of compound 19b



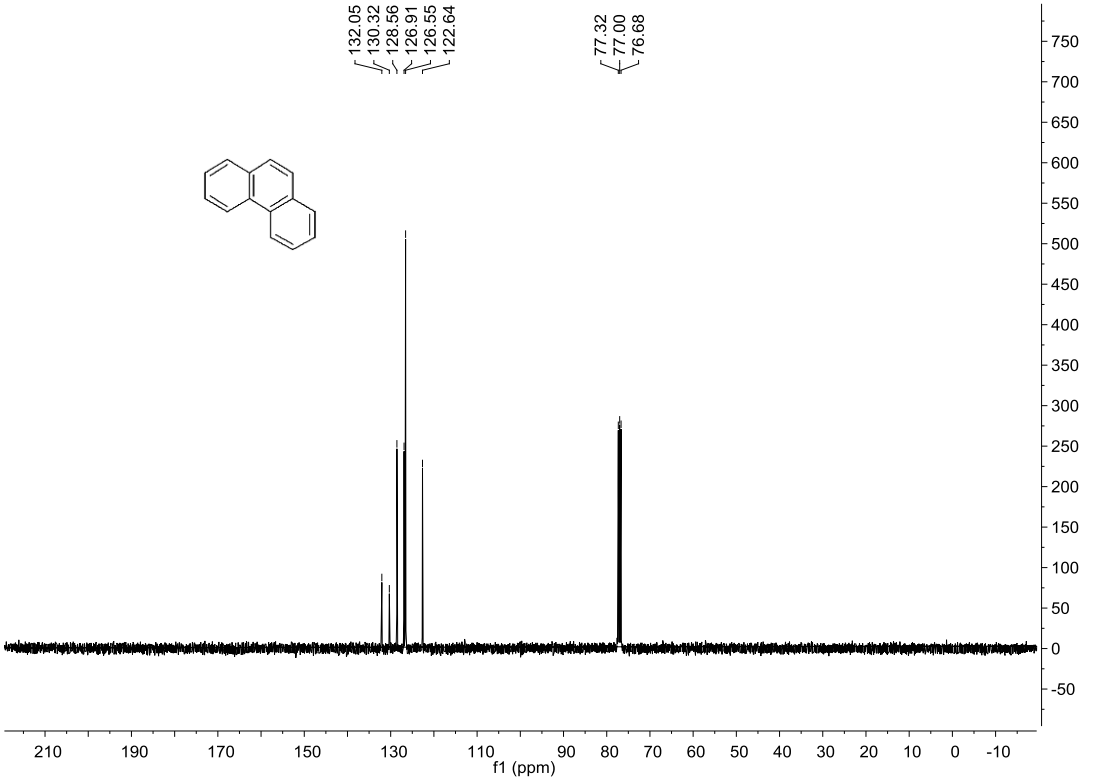
^{1}H NMR of compound 20b



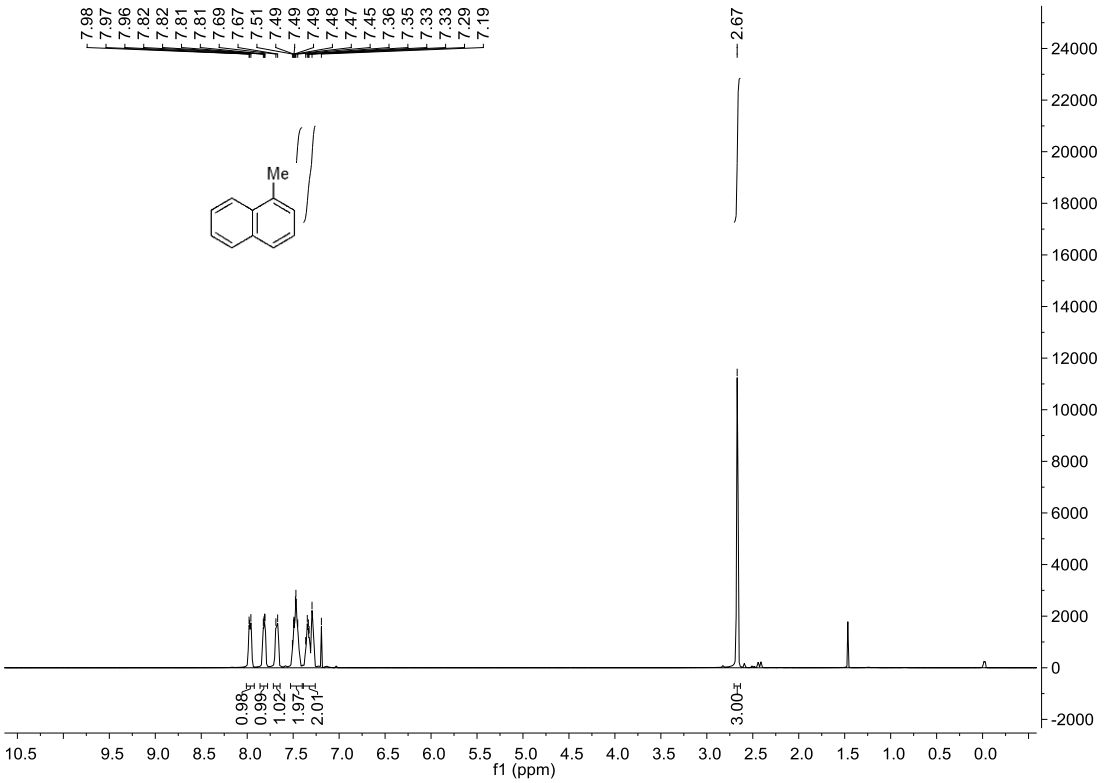
^{13}C NMR of compound 20b



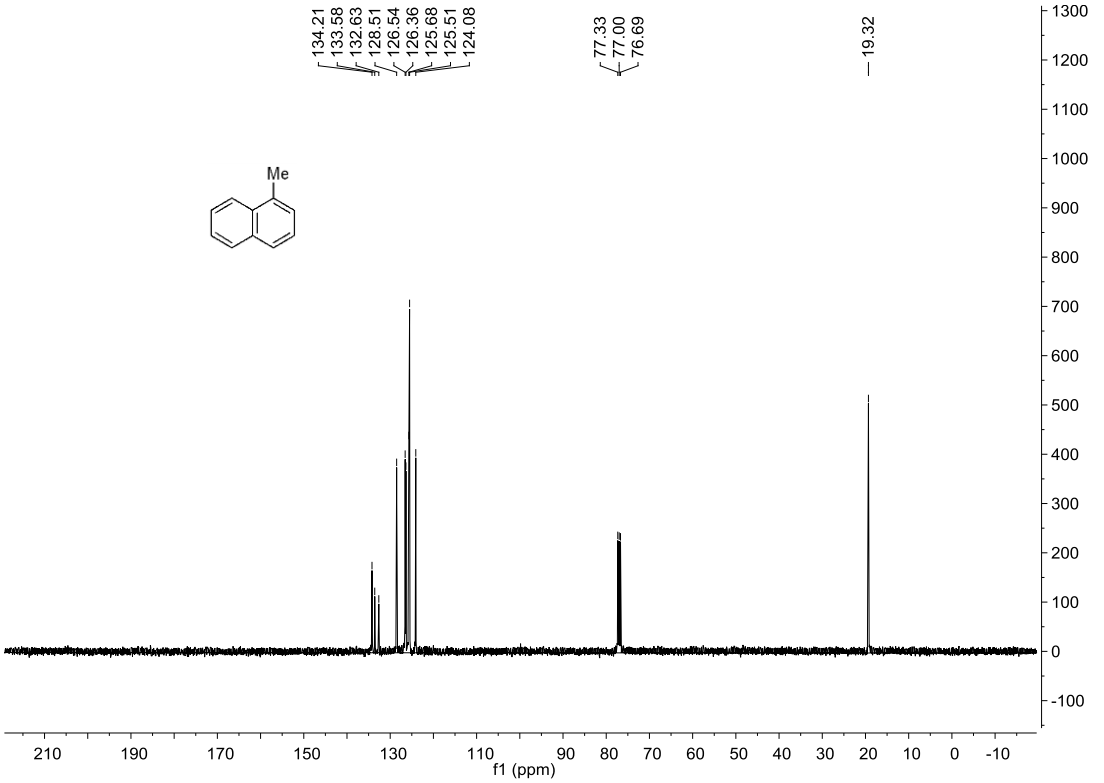
^{1}H NMR of compound 22b



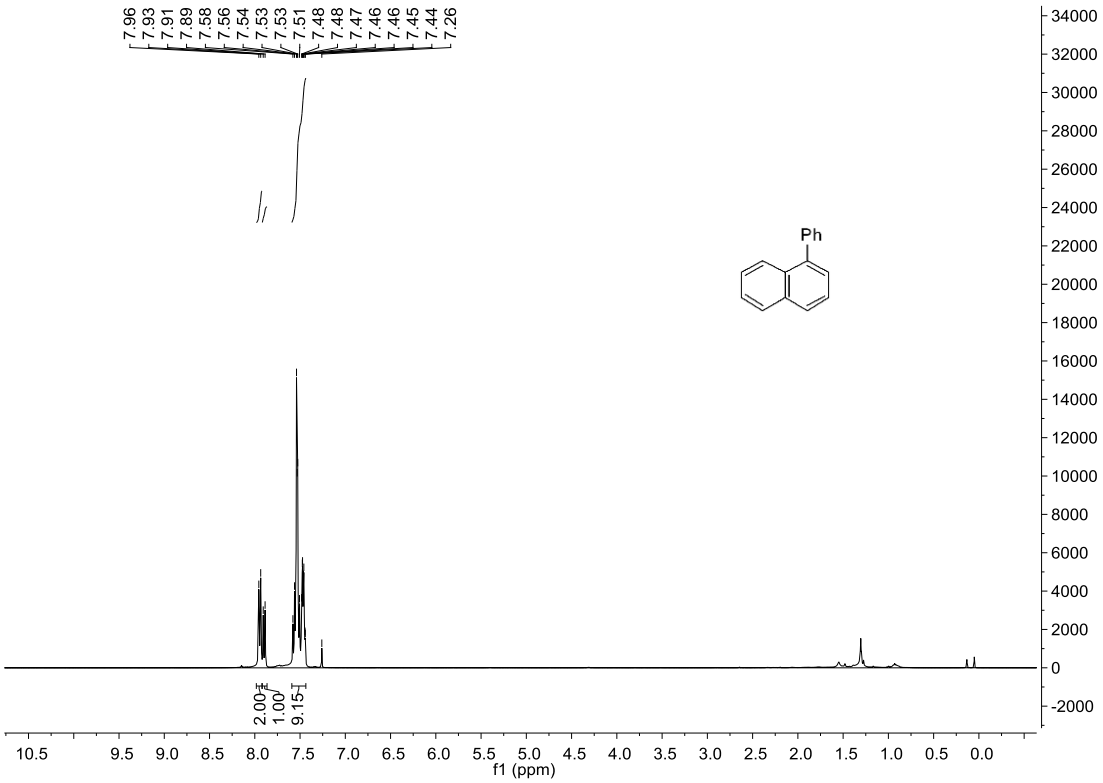
^{13}C NMR of compound 22b



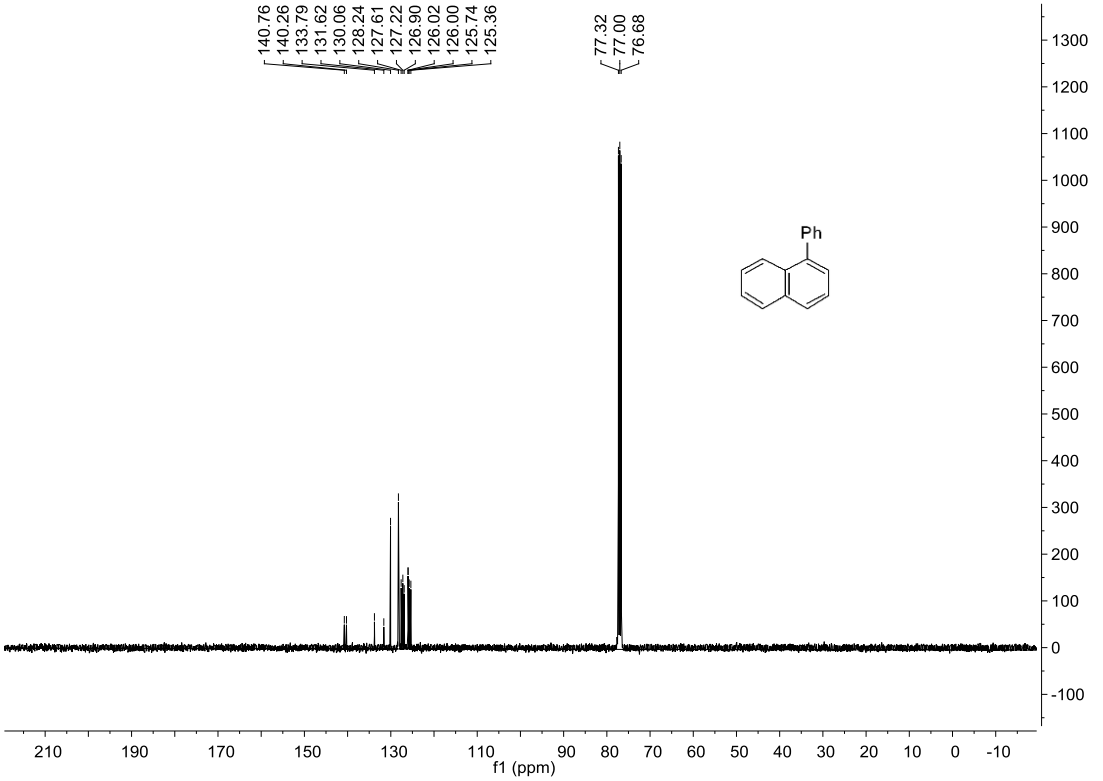
^{1}H NMR of compound 23b



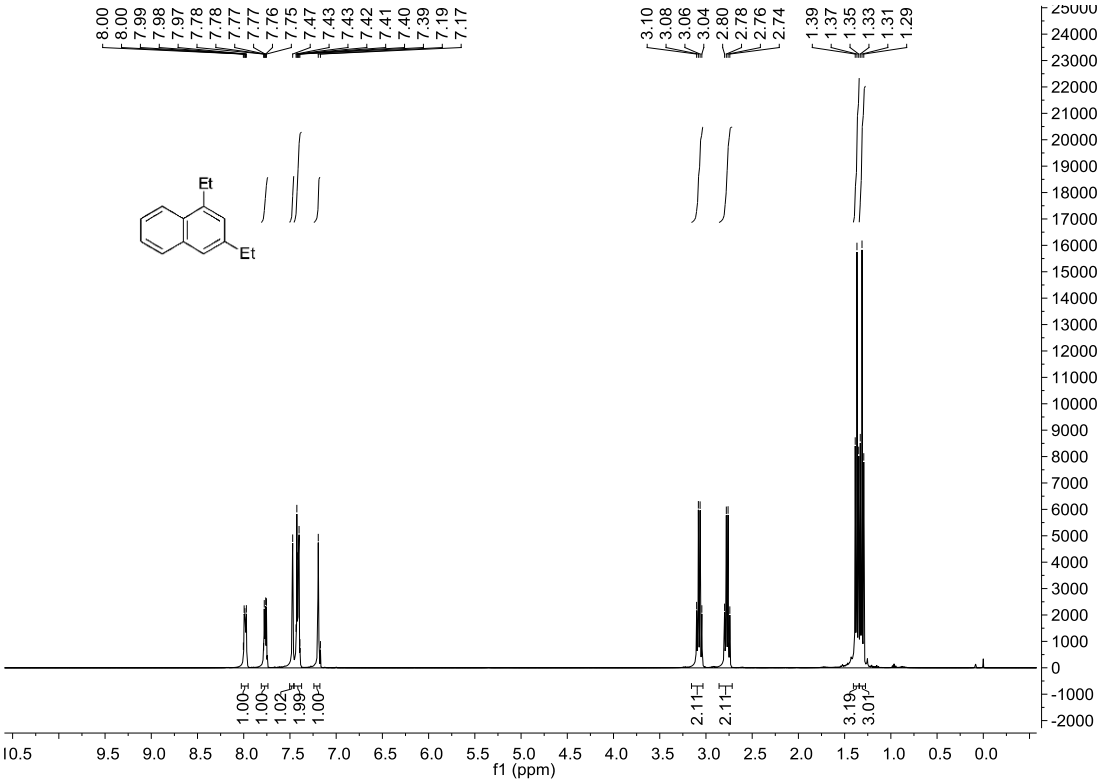
^{13}C NMR of compound 23b



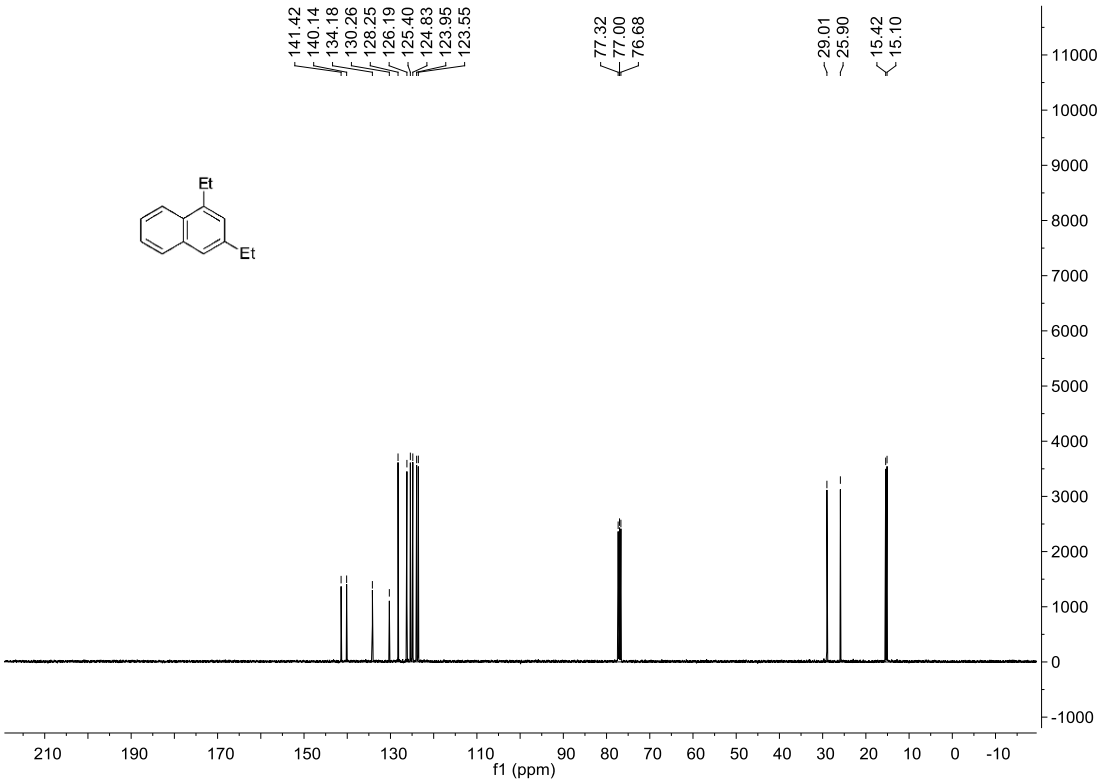
^{1}H NMR of compound 24b



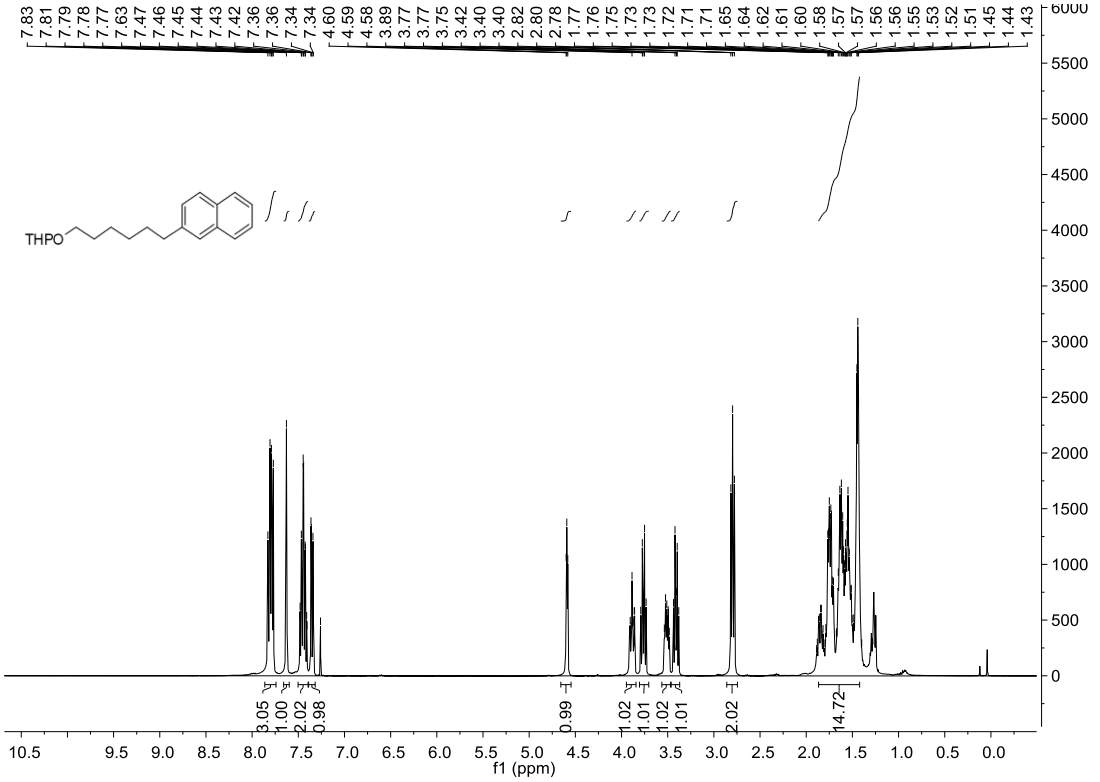
^{13}C NMR of compound 24b



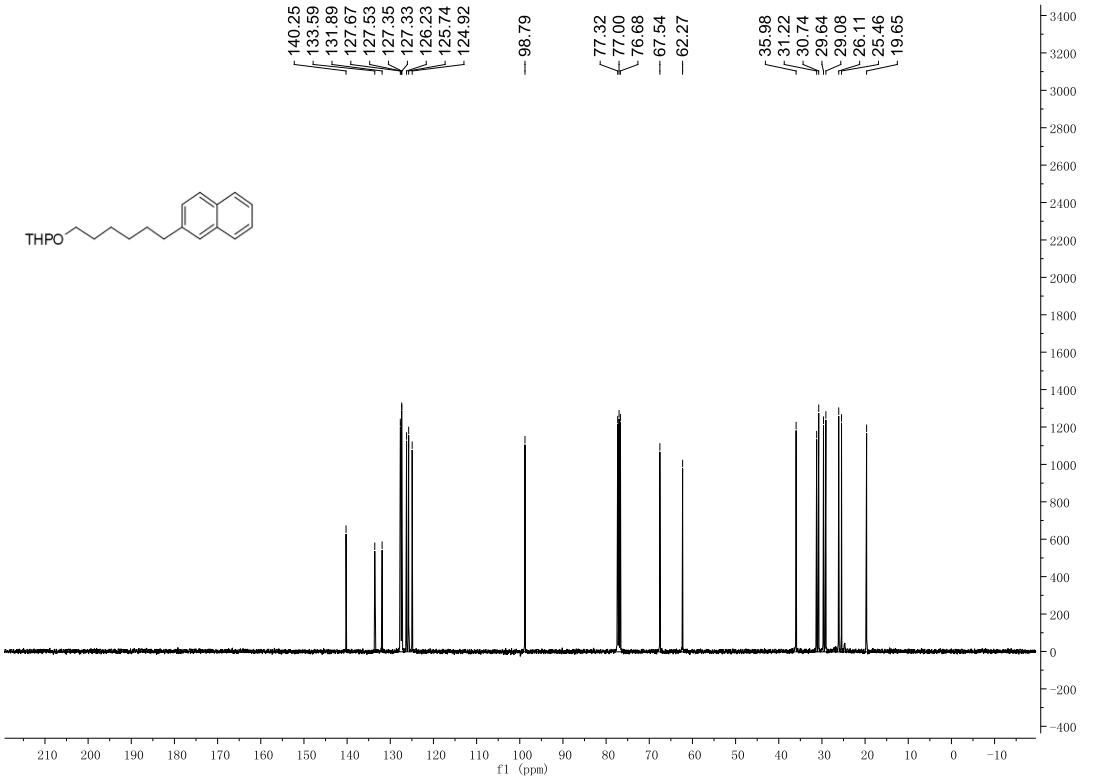
^{1}H NMR of compound 25b



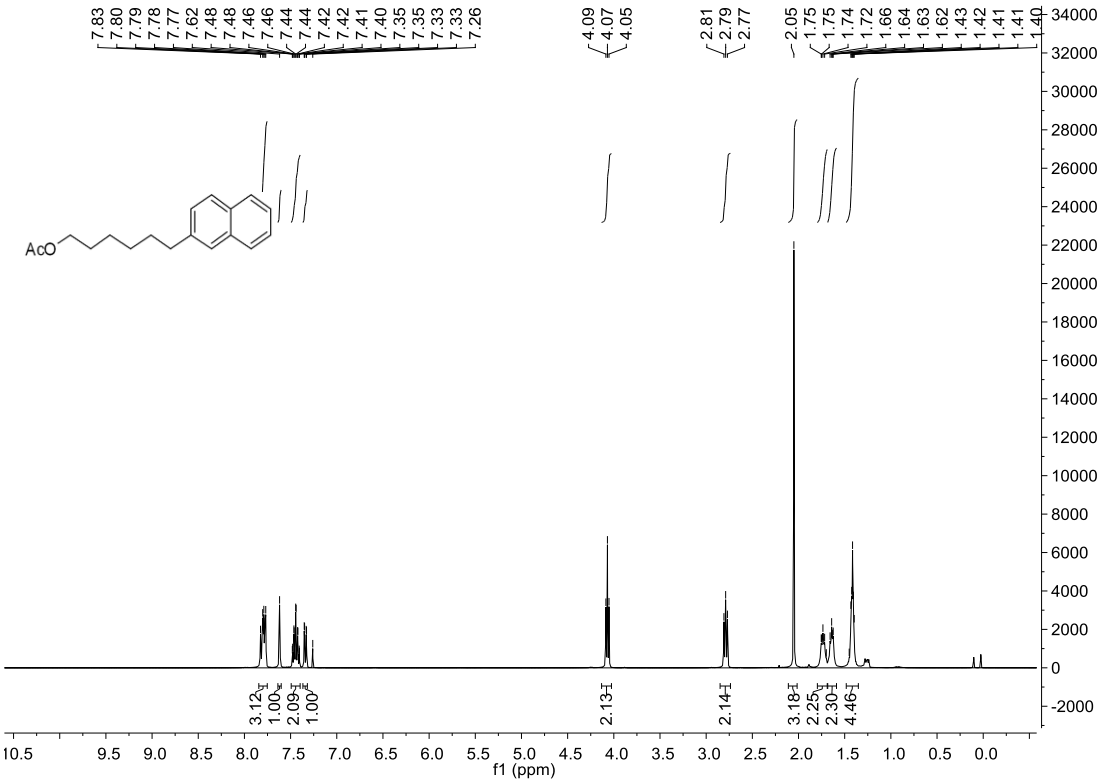
^{13}C NMR of compound 25b



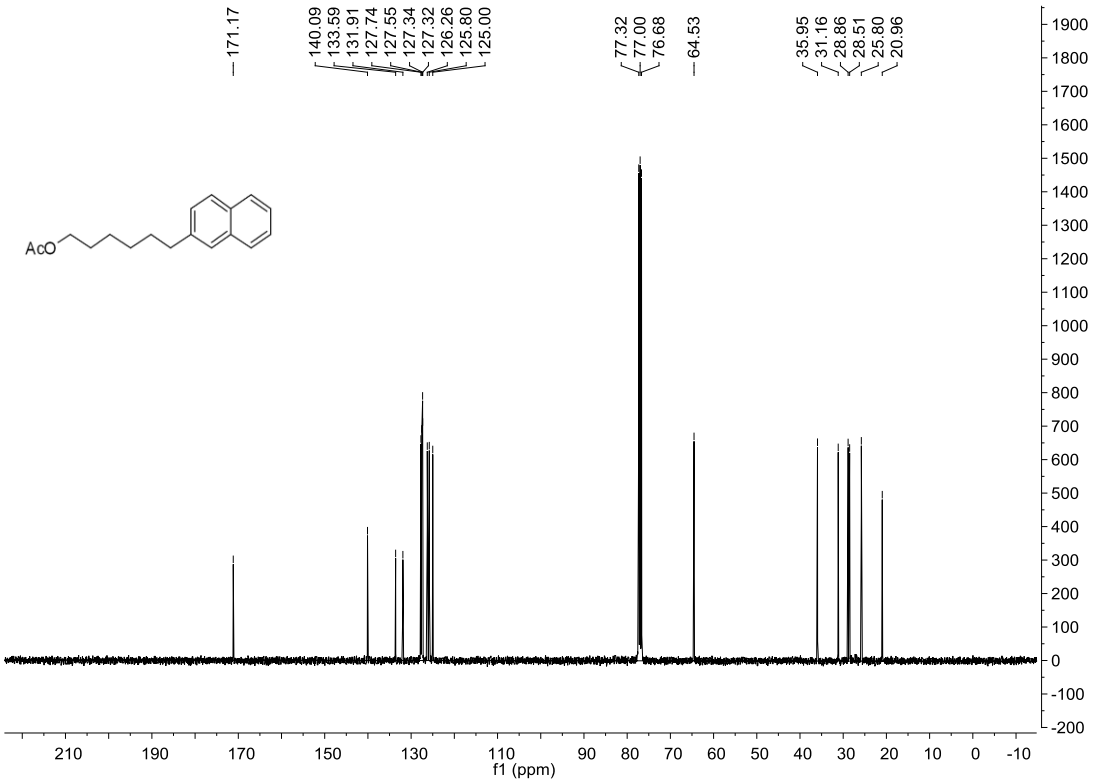
^{1}H NMR of compound 27b



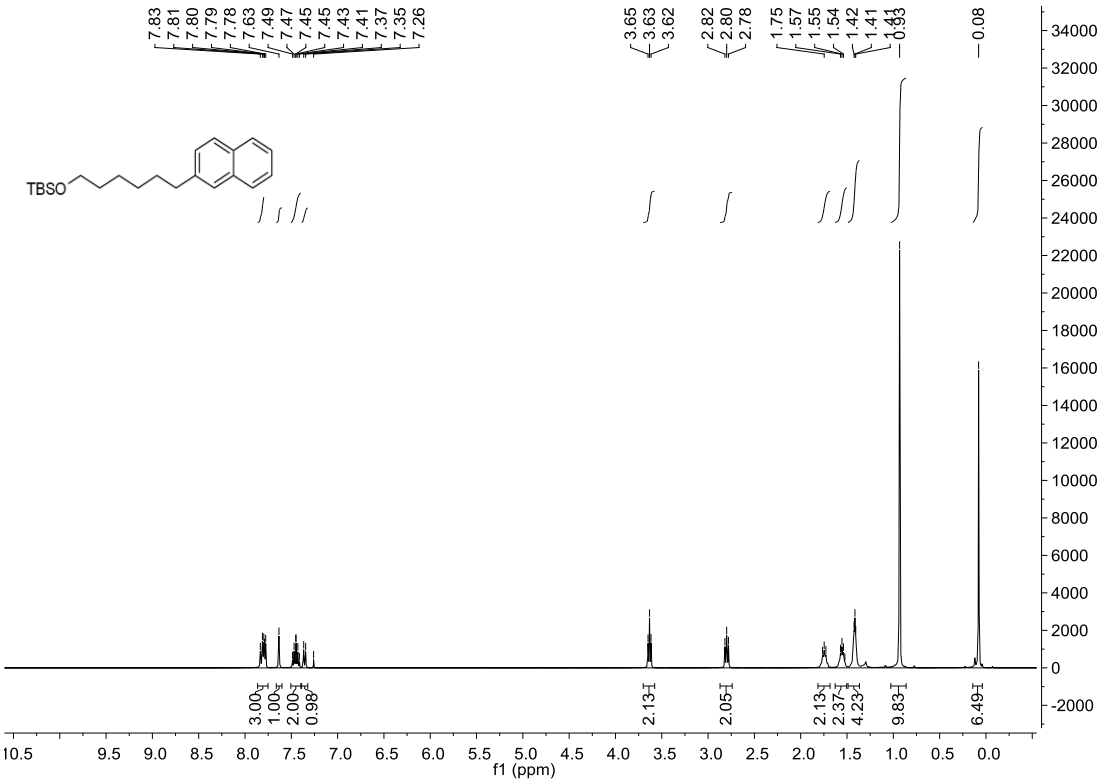
^{13}C NMR of compound 27b



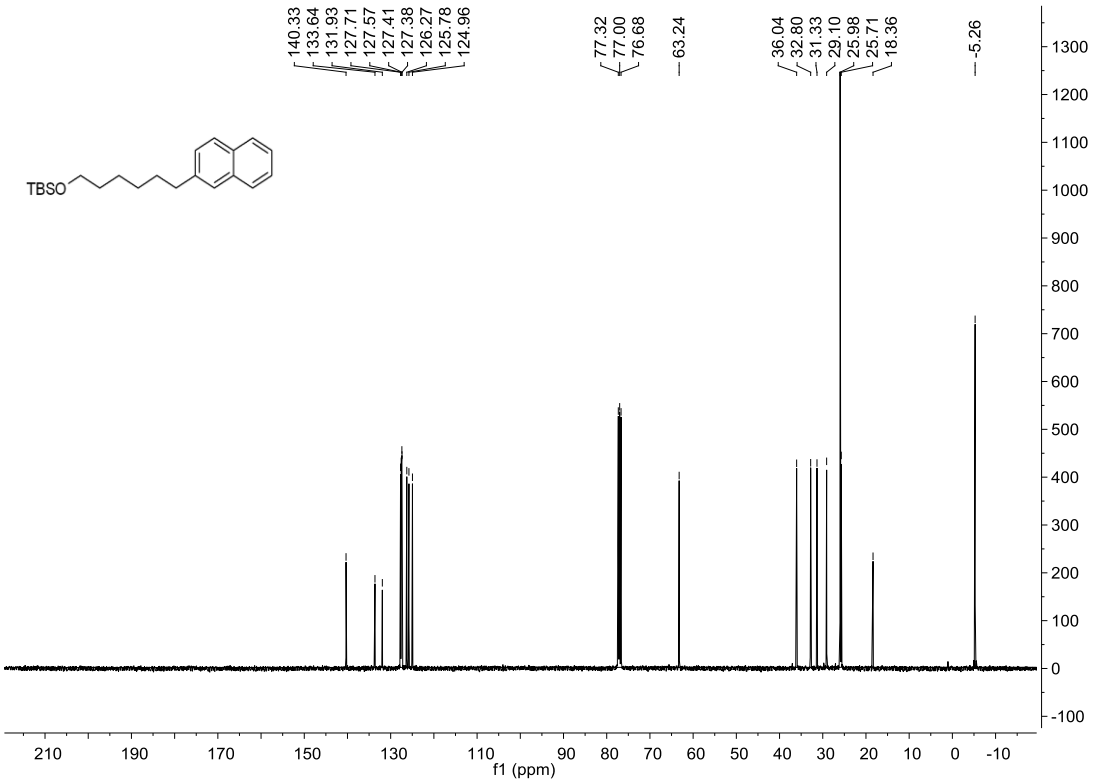
^{1}H NMR of compound 28b



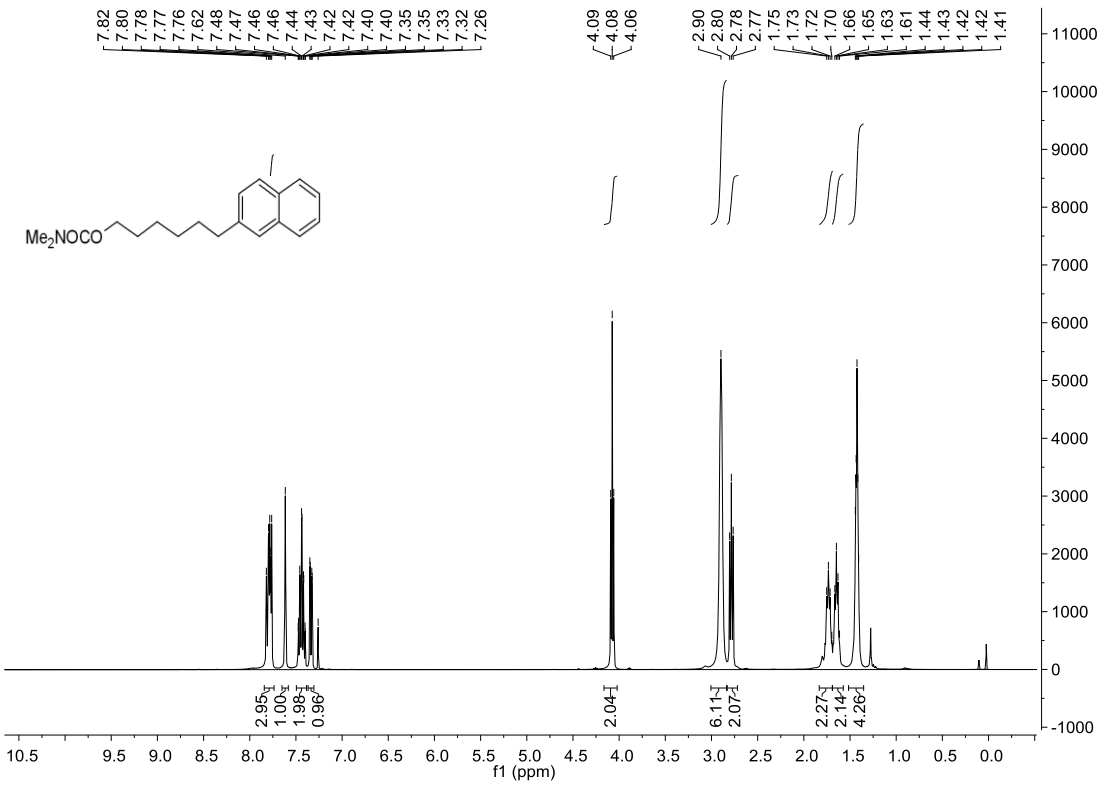
^{13}C NMR of compound 28b



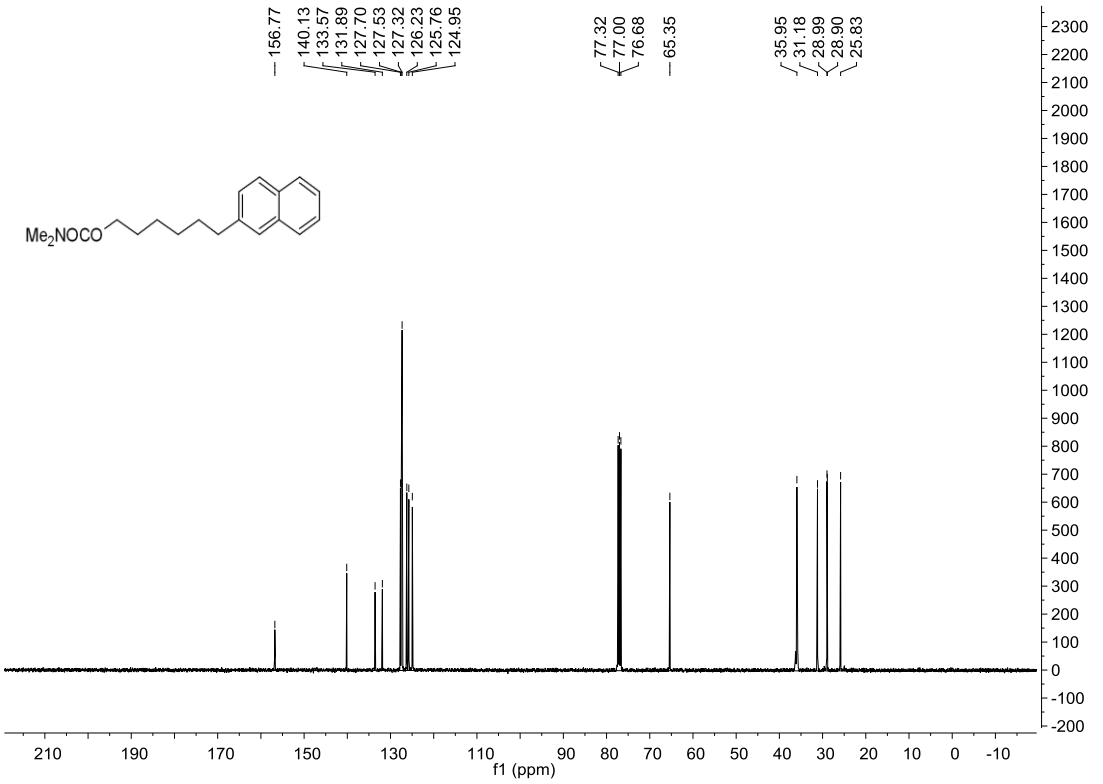
^{1}H NMR of compound 29b



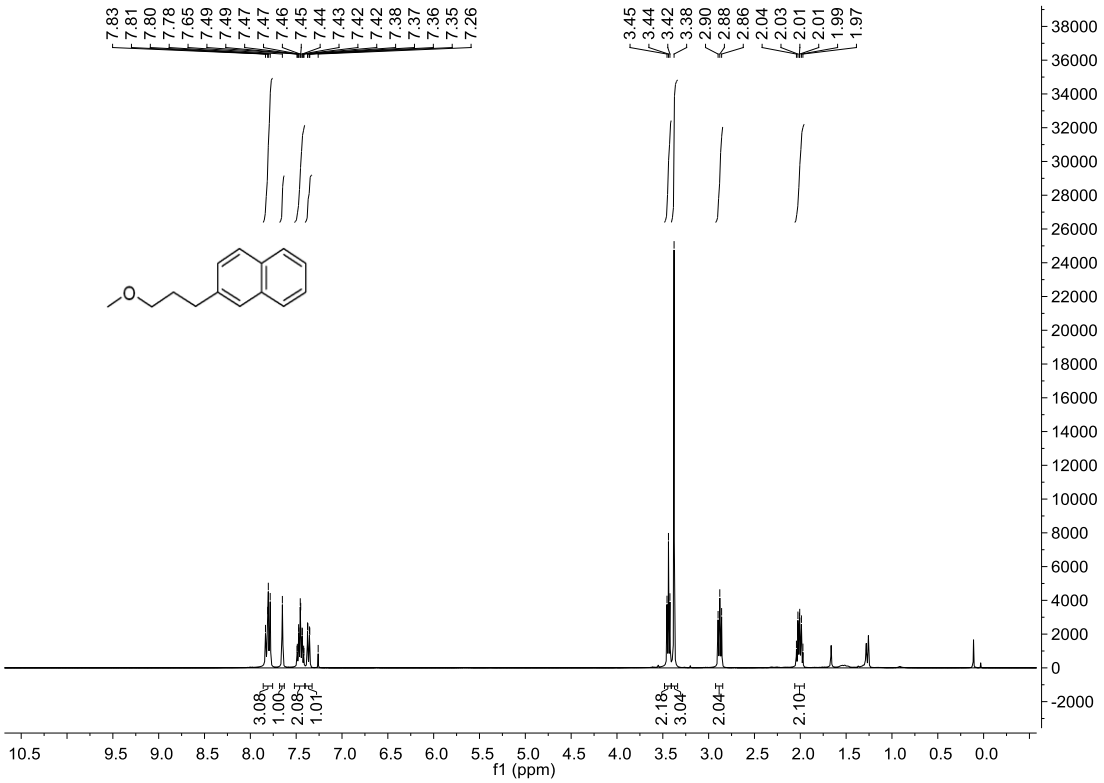
^{13}C NMR of compound 29b



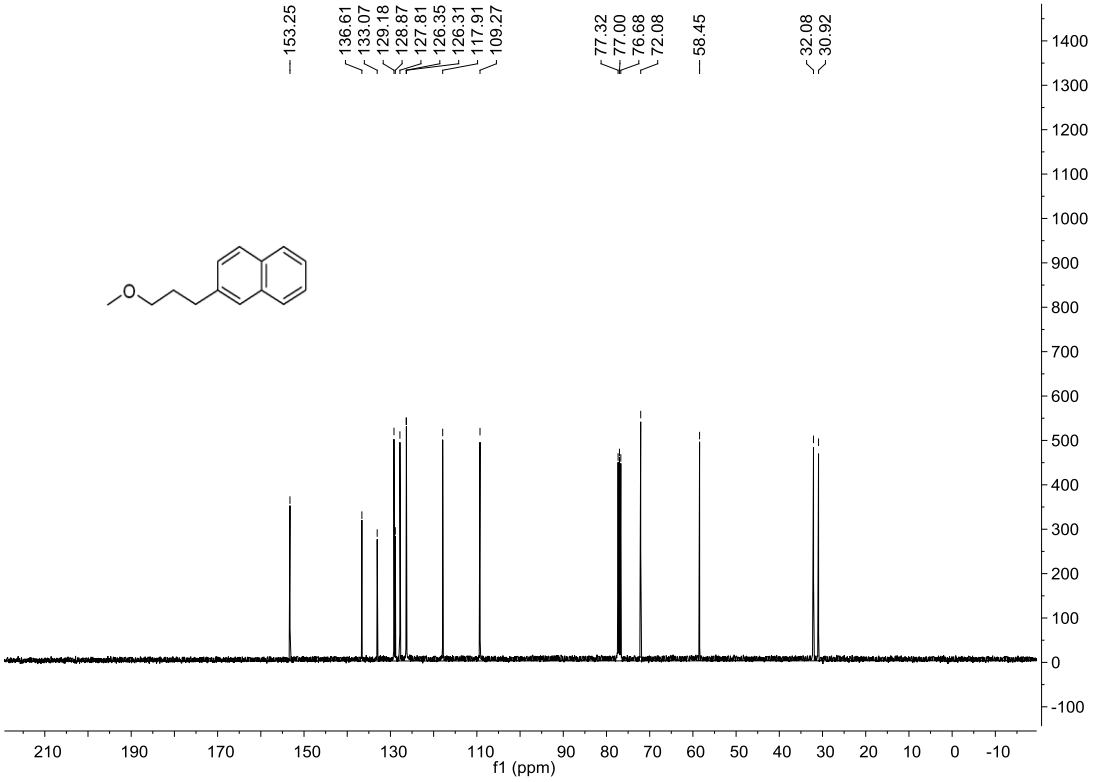
^{1}H NMR of compound 30b



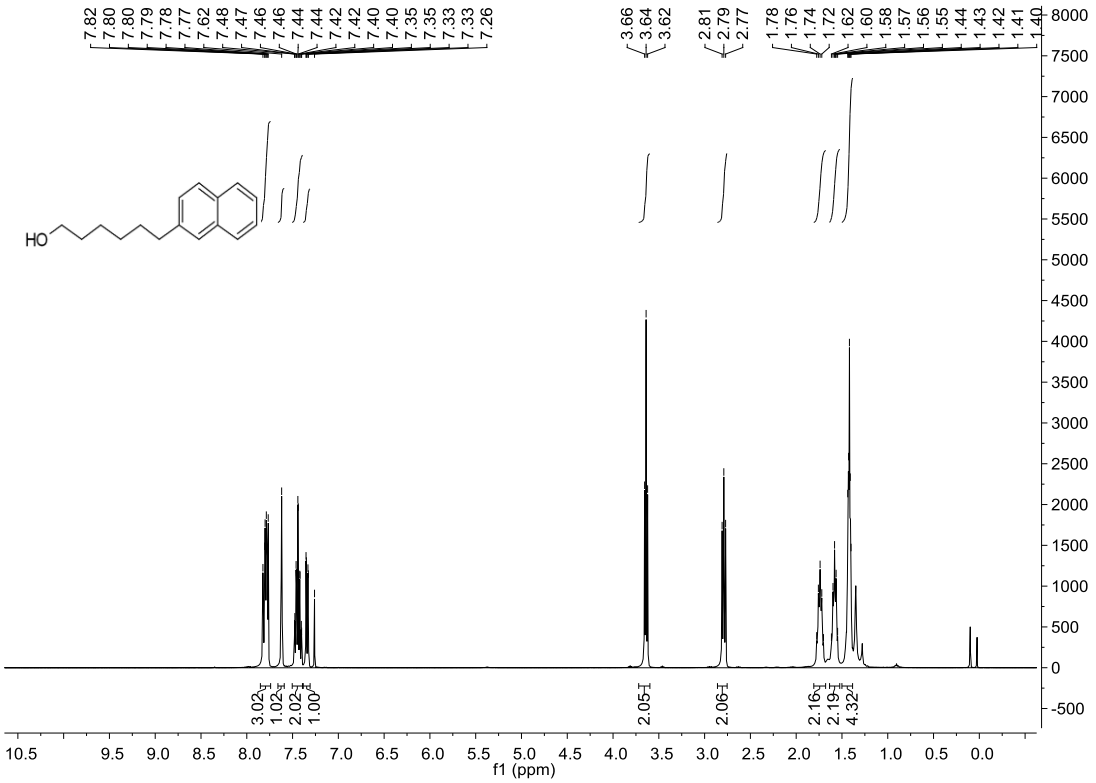
^{13}C NMR of compound 30b



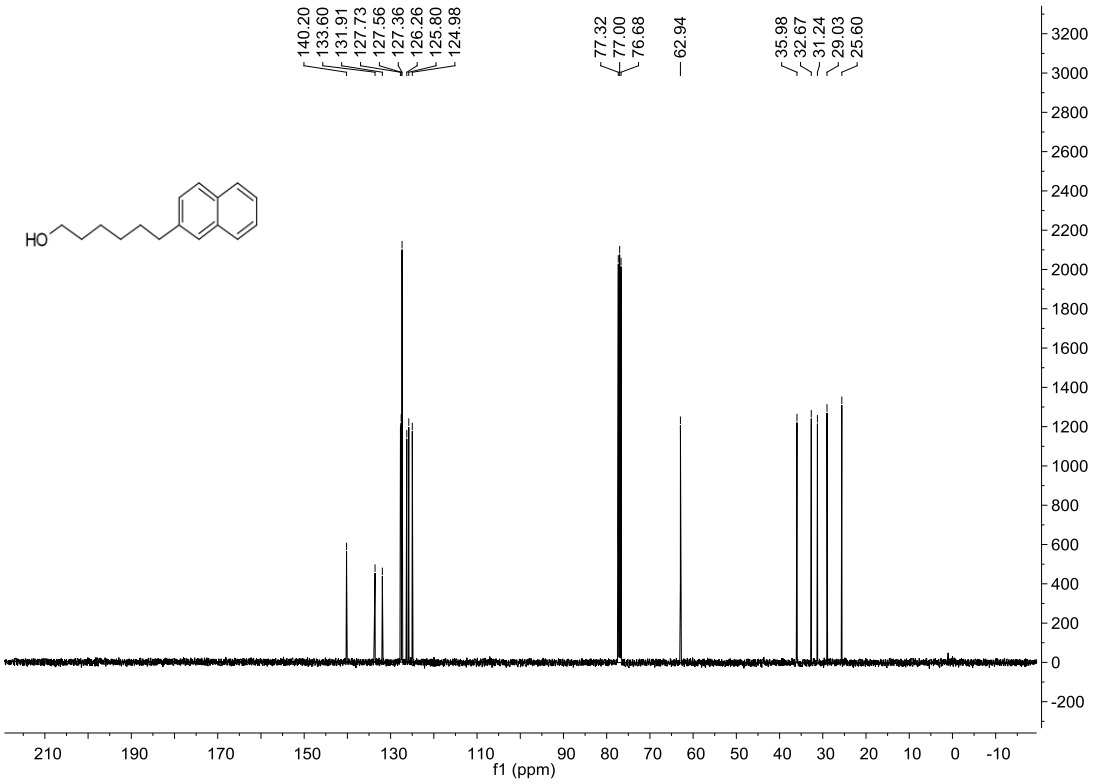
^{1}H NMR of compound 31b



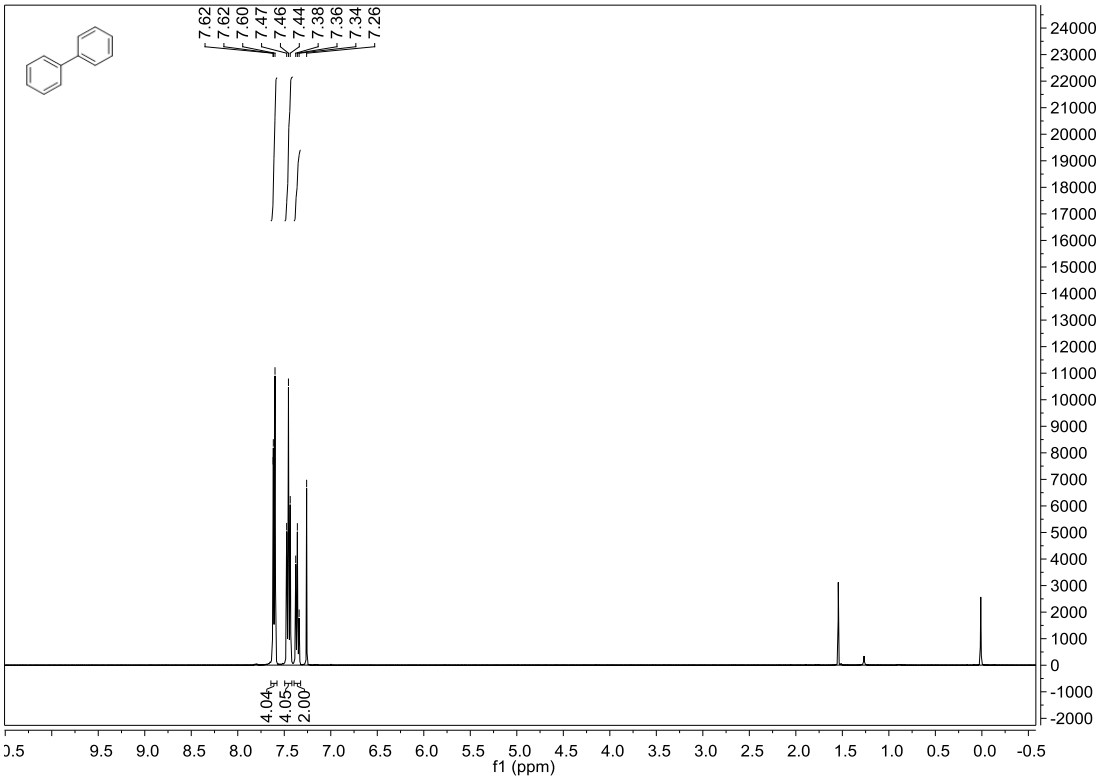
^{13}C NMR of compound 31b



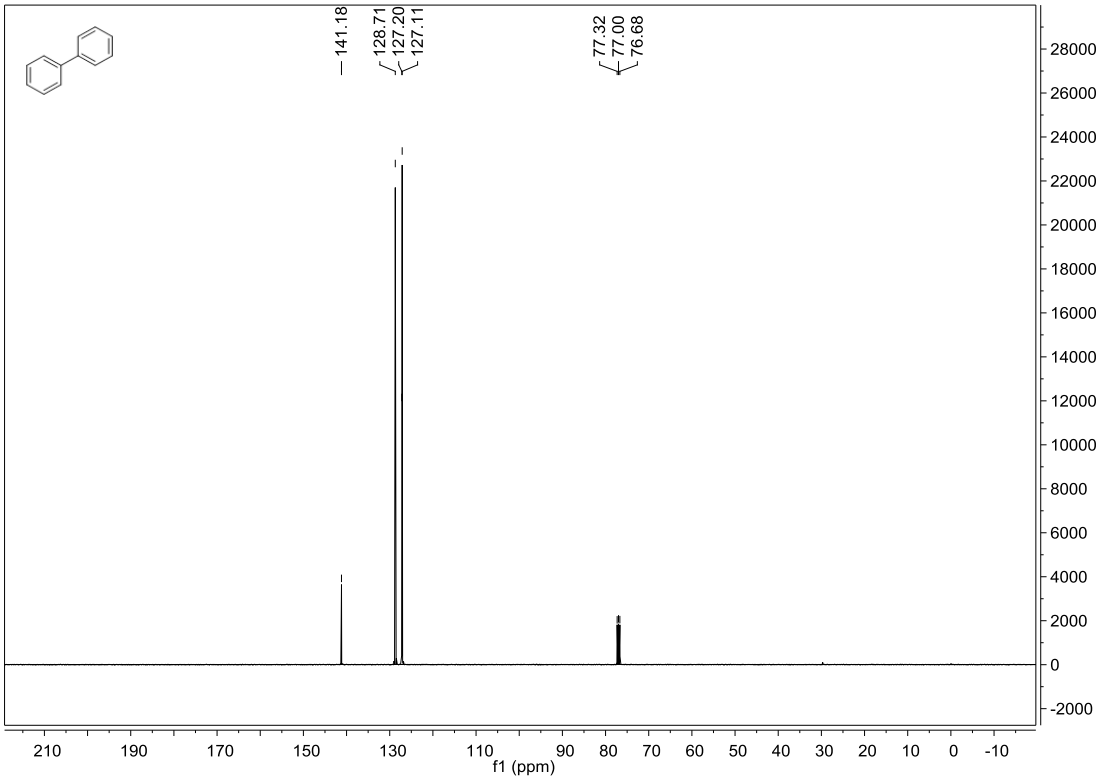
^{1}H NMR of compound 32b



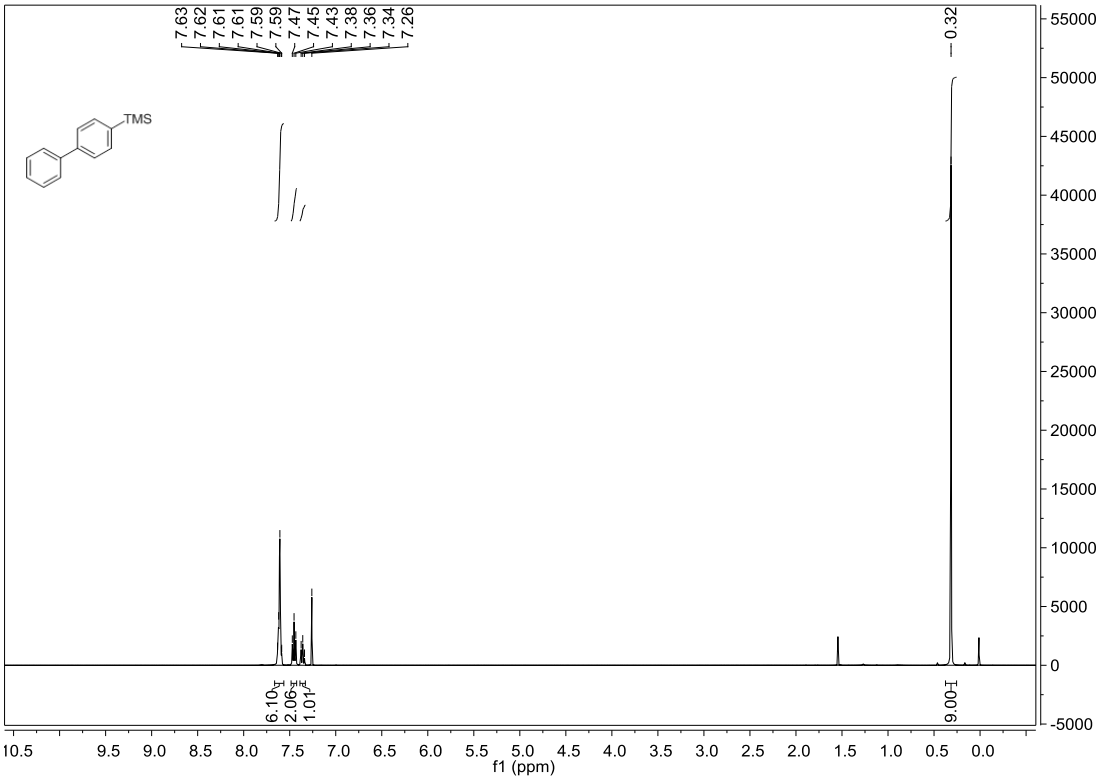
^{13}C NMR of compound 32b



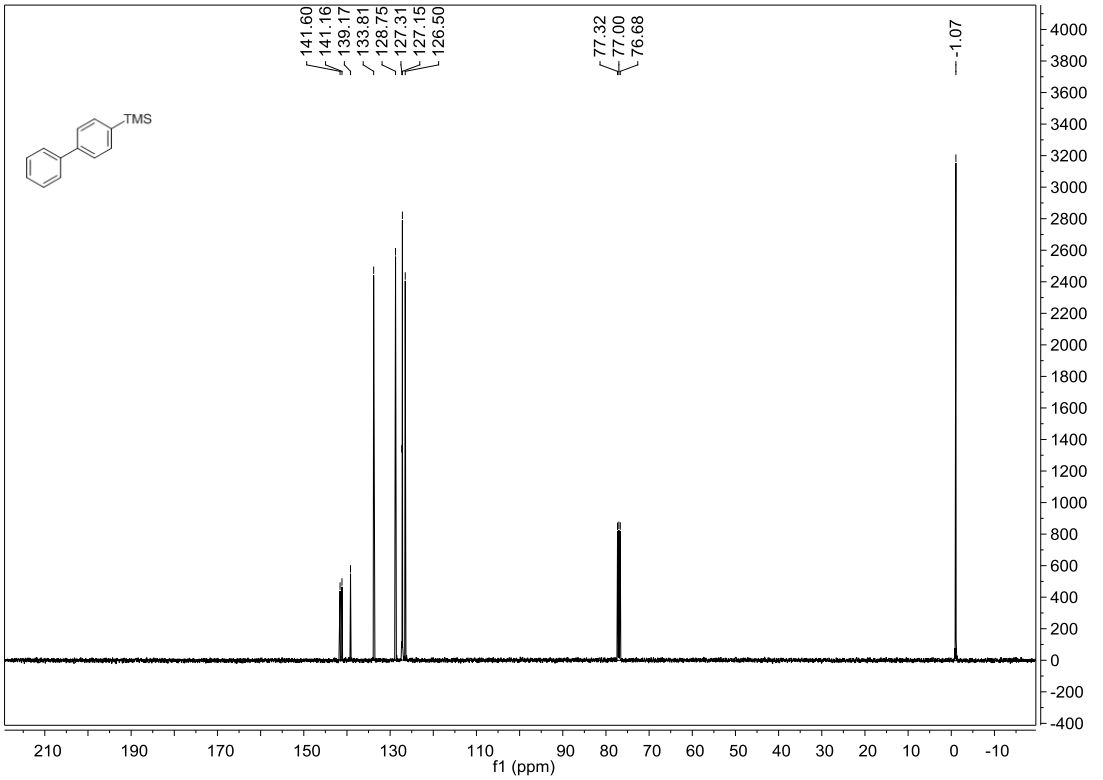
^{1}H NMR of compound 34b, 35b and 36b



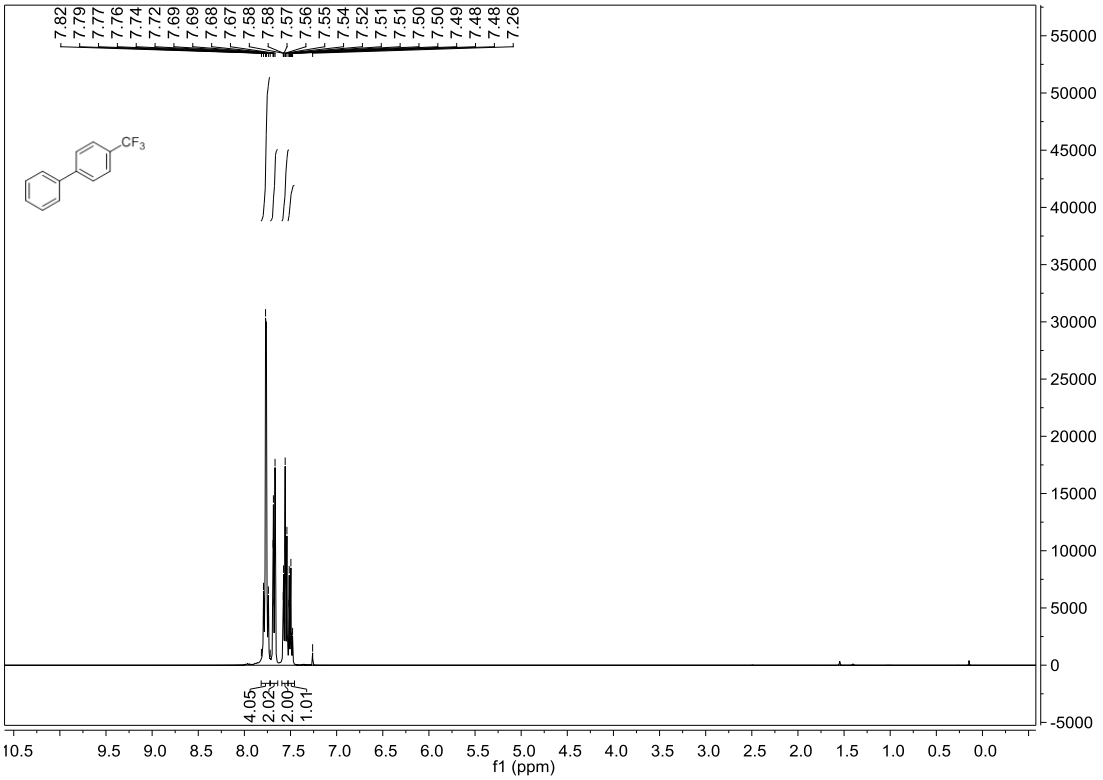
^{13}C NMR of compound 34b, 35b and 36b



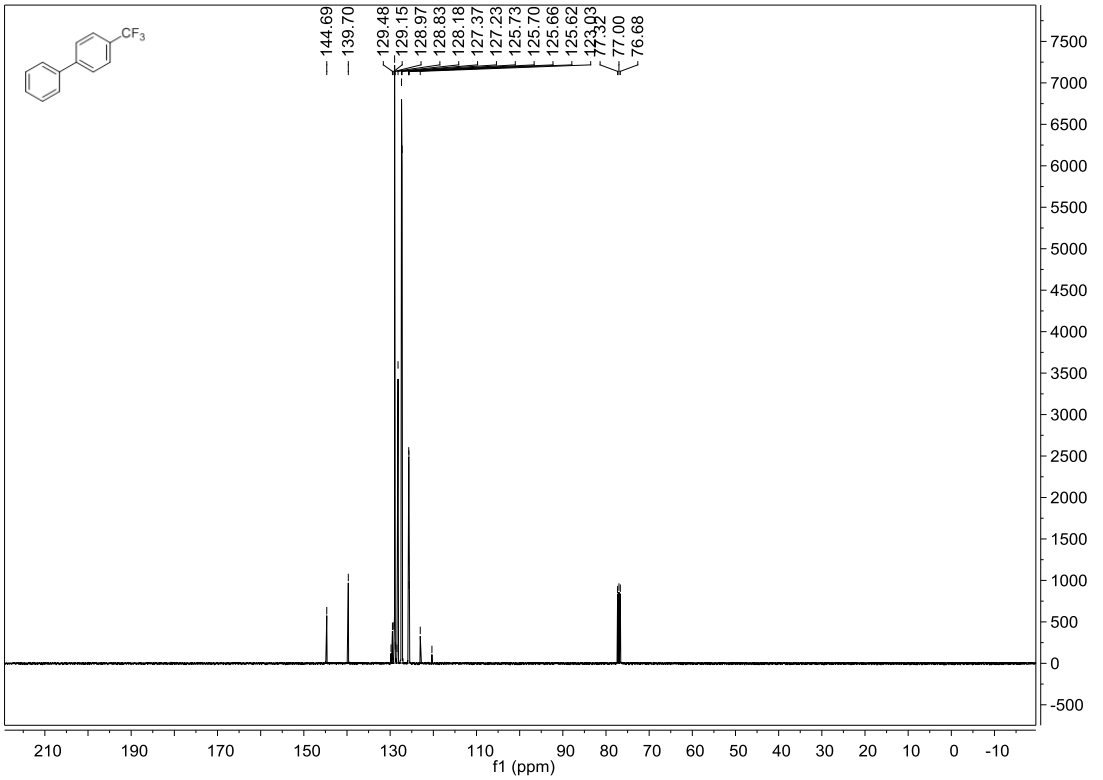
^{1}H NMR of compound 37b



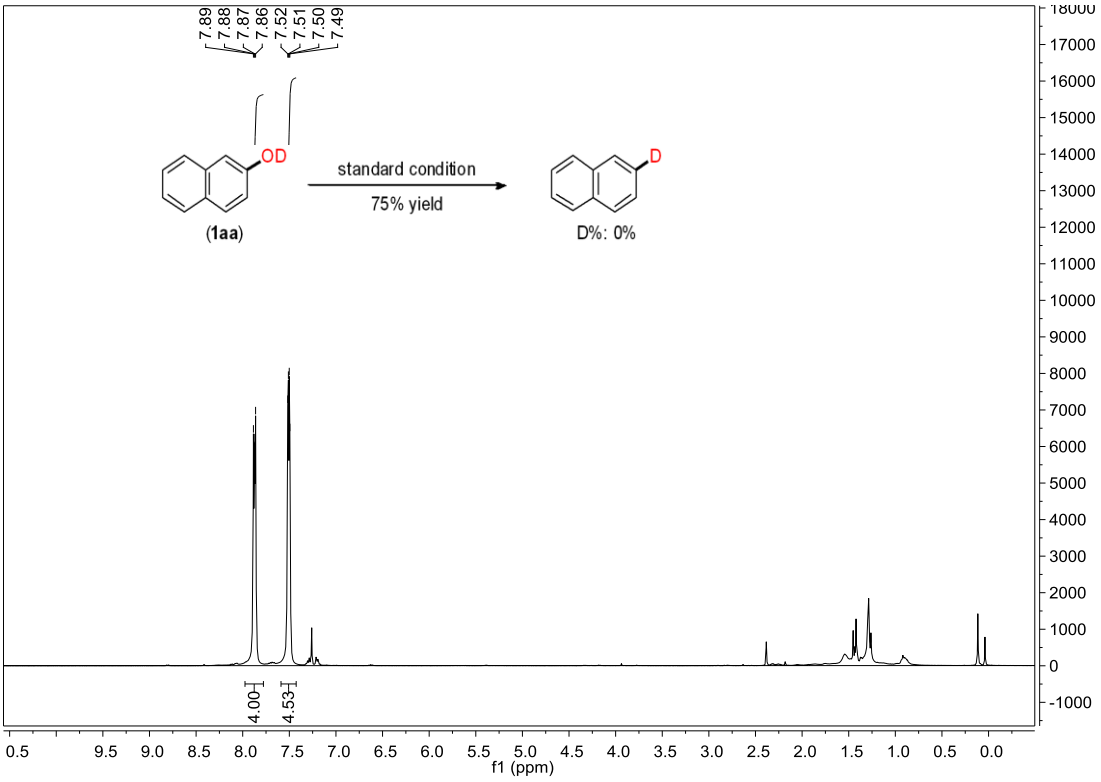
^{13}C NMR of compound 37b

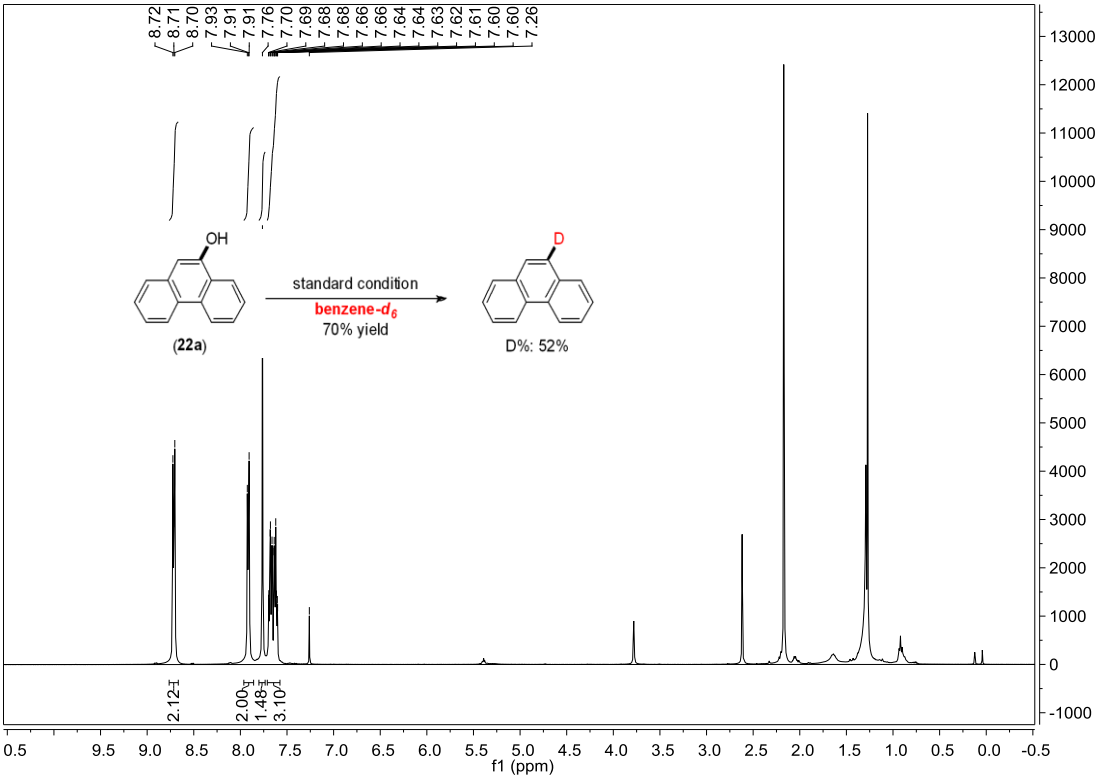


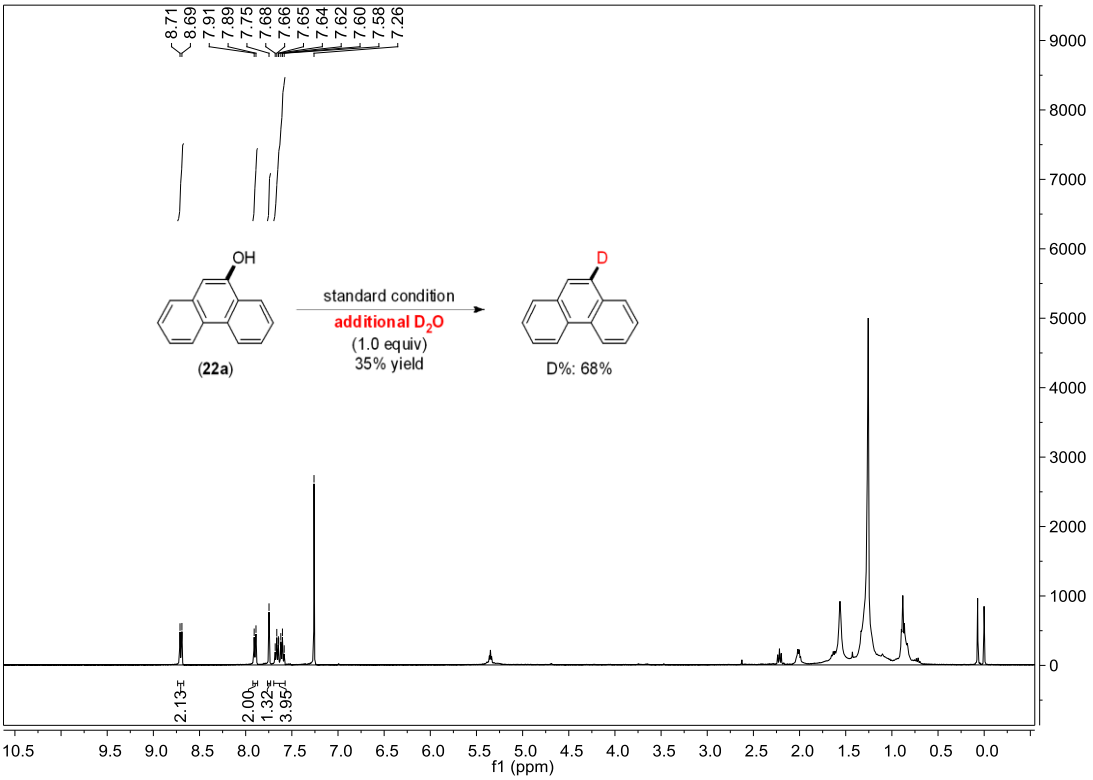
^{1}H NMR of compound 38b

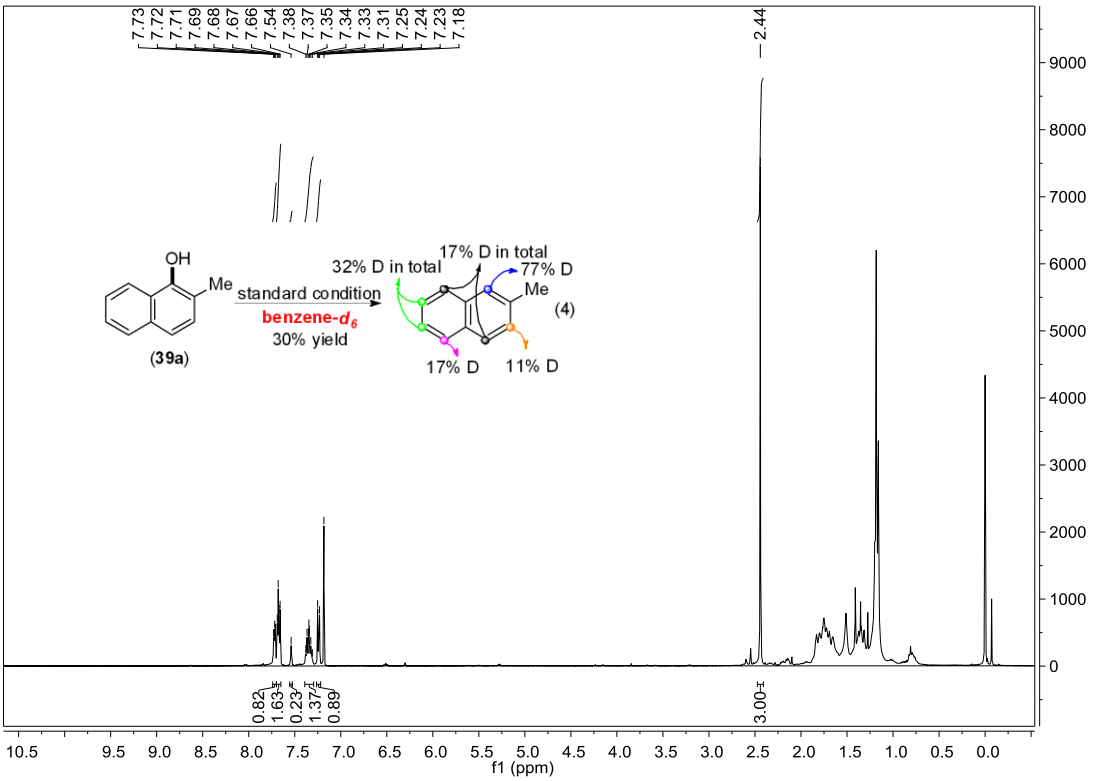


^{13}C NMR of compound 38b

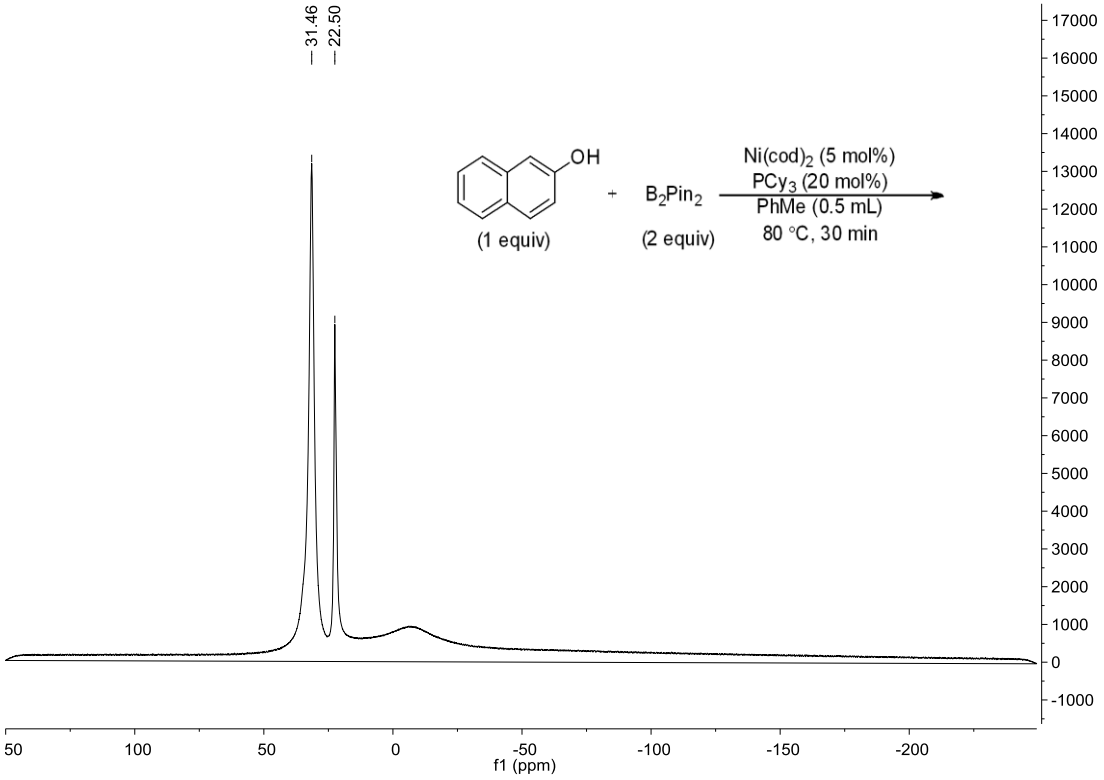

7.89
7.88
7.87
7.86
7.52
7.51
7.50
7.49
OD
standard condition
75% yield
(1aa)
D
D%: 0%
4.00
4.53
f1 (ppm)

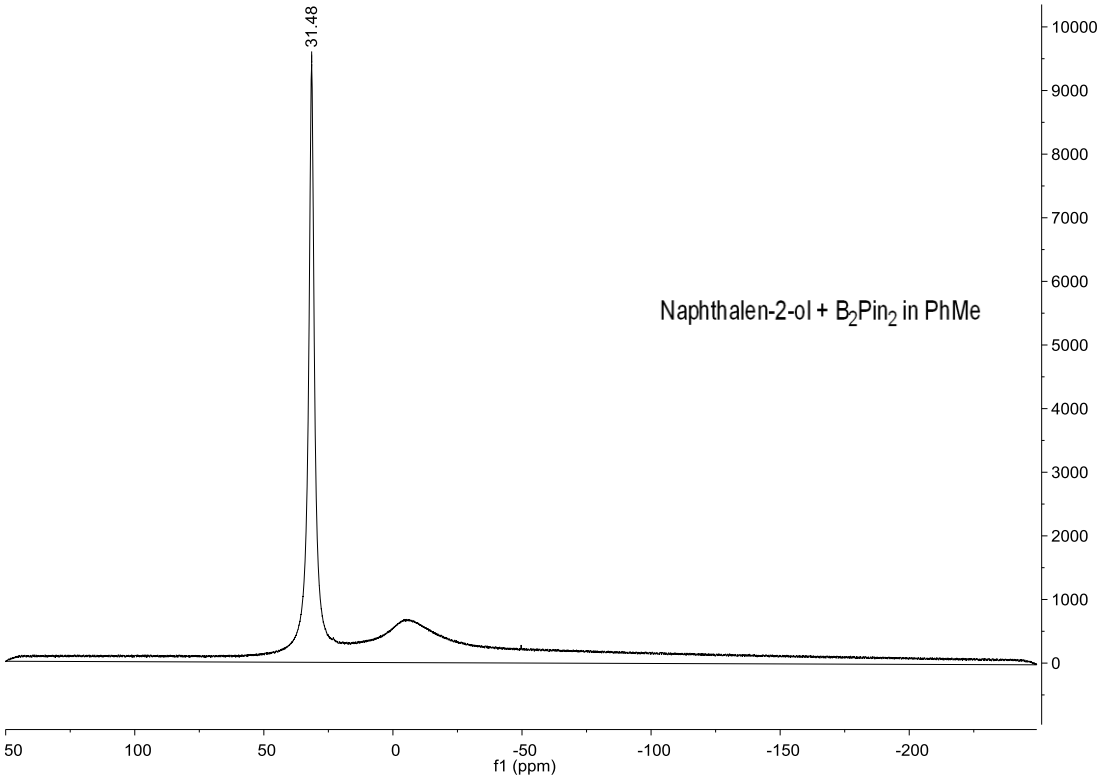

8.72
8.71
8.70
7.93
7.91
7.76
7.70
7.69
7.68
7.68
7.66
7.66
7.64
7.64
7.63
7.62
7.61
7.60
7.60
7.26
OH
standard condition
benzene-d6
70% yield
(22a)
D
D%: 52%
2.12
2.00
1.48
3.10
f1 (ppm)

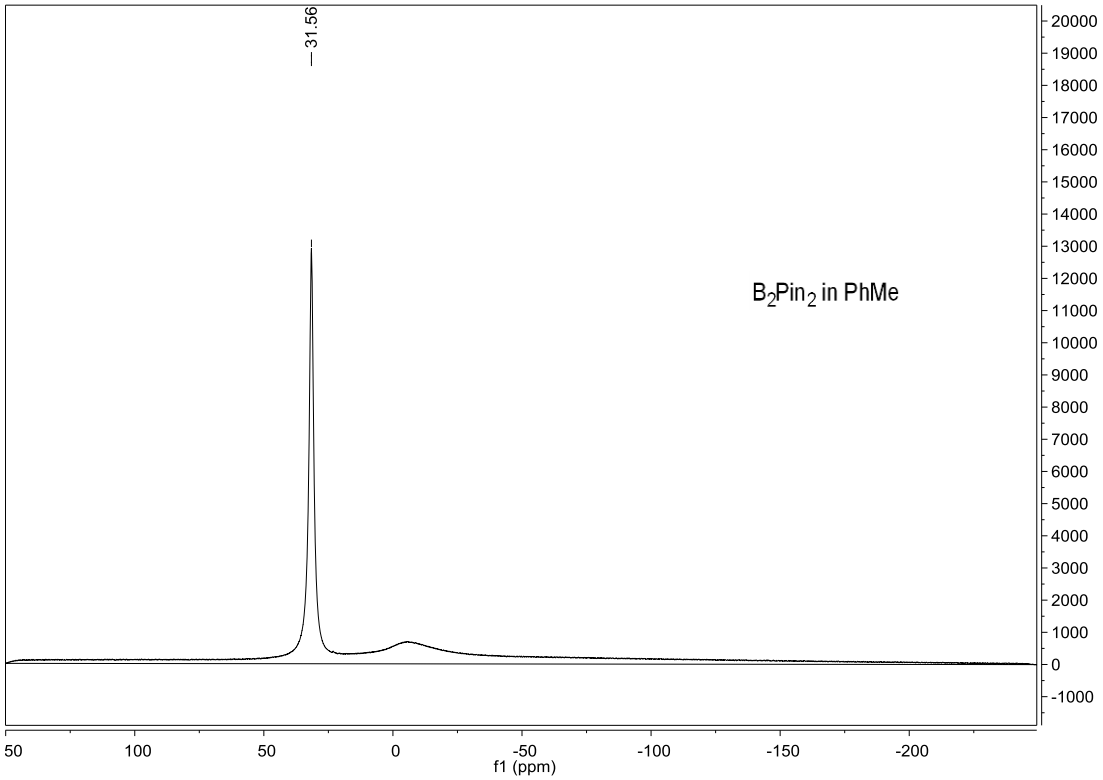

8.71
8.69
7.91
7.89
7.75
7.68
7.66
7.65
7.64
7.62
7.60
7.58
7.26
OH
(22a)
standard condition
additional D2O
(1.0 equiv)
35% yield
D
D%: 68%
2.13
2.00
1.32
3.95
f1 (ppm)


7.73
7.72
7.71
7.69
7.68
7.67
7.66
7.54
7.38
7.37
7.35
7.34
7.33
7.31
7.25
7.24
7.23
7.18
2.44
OH
Me
(39a)
standard condition
benzene-d6
30% yield
32% D in total
17% D in total
77% D
Me
(4)
17% D
11% D
0.82
1.63
0.23
1.37
0.89
3.00
f1 (ppm)

^{11}B NMR (with BF_3•Et_2O as external standard, 0.00 ppm) in Scheme S1






31.56
B2Pin2 in PhMe
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
50
100
50
0
-50
-100
-150
-200
f1 (ppm)