Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Ruthenium Catalyzed Dehydrogenative α-C–H Functionalization of β-Naphthol Using Alcohols: A Metal-Ligand Cooperative Borrowing Hydrogen Approach

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Experimental Section.

General Information. All the solvents used in the reactions were purified via distillation over sodium/benzophenone or calcium hydride, maintaining an argon atmosphere, and were stored over 4Å molecular sieves. All other reagents and chemicals were purchased from commercial sources and used without further purification. Merck60 F254 silica gel plates (0.25 mm thick) were used for analytical TLC. Merck 60 silica gel (60-120 mesh) was used for column chromatographic separation of the products. The NMR spectra were collected in a Bruker Avance Neo 400 spectrometer using tetramethylsilane as the internal standard. The HRMS experiment was performed on a Q-TOF mass spectrometer (Serial No. YEB1390).

Synthesis of Catalysts. Catalysts **1a** and **1b** were synthesized following our previous works.[1]

General Procedure for 1a-Catalyzed α-Alkylation of β-Naphthol Using Aromatic and Aliphatic Alcohols under Argon Atmosphere.

Under an argon atmosphere, catalyst **1a** (1.0 mol%, 0.005 mmol, 3.8 mg), 0.5 mmol β-naphthols, 0.6 mmol alcohols, LiO^{t}Bu (0.25 mmol, 20.0 mg), and a tiny magnetic stir bar were added to an oven-dried 35 mL of ACE high-pressure tube. 3.0 mL of dry and degassed toluene was added, and the tube was tightly capped with a PTFE screw cap. The ACE pressure tube containing the reaction mixture was then placed in an oil bath preheated at 140 ^{o}C and continued the reaction for 16 h. The reaction mixture was cooled to room temperature, and all the volatiles were removed under vacuum. The crude reaction mixture was purified by column chromatography using silica gel 60-120 mesh. Eluent: hexane/ethyl acetate.

General Procedure for 1a-Catalyzed α-Methylation/Ethylation of β-Naphthol Using Methanol/Ethanol under Argon Atmosphere.

Under an argon atmosphere, catalyst **1a** (1.0 mol%, 0.005 mmol, 3.8 mg), 0.5 mmol of β-naphthols, 1.0 mL of dry and degassed methanol/ethanol, LiO^{t}Bu (0.25 mmol, 20.0 mg), and a tiny magnetic stir bar were added to an oven-dried 35 mL of ACE high pressure sealed tube. The tube was tightly capped with a PTFE screw cap. The ACE pressure tube containing the reaction mixture was then placed in an oil bath preheated at 140 ^{o}C. The reaction was continued for 16 h. After that, the reaction mixture was cooled to room temperature. Then solvent and other volatiles were evaporated under a vacuum, and the crude reaction mixture

was purified by column chromatography using silica gel 60-120 mesh. Eluent: hexane/ethyl acetate.

General Procedure for 1a-Catalyzed α-Alkylation of β-Naphthol Using Aromatic or Hetero-Aromatic Diols under Argon Atmosphere.

Under an argon atmosphere, catalyst **1a** (1.0 mol%, 0.005 mmol, 3.8 mg), 1.0 mmol β-naphthols, 0.6 mmol aromatic diols, LiO^{t}Bu (0.5 mmol, 40.0 mg), and a tiny magnetic stir bar were added to an oven-dried 35 mL of ACE high-pressure tube. 3.0 mL of dry and degassed toluene was added, and the tube was tightly capped with a PTFE screw cap. The ACE pressure tube containing the reaction mixture was then placed in an oil bath preheated at 140 ºC and continued the reaction for 16 h. The reaction mixture was cooled to room temperature, and all the volatiles were removed under vacuum. The crude reaction mixture was purified by column chromatography using silica gel 60-120 mesh. Eluent: hexane/ethyl acetate.

General Procedure for 1a-Catalyzed Large-Scale Synthesis of α-Alkylated β-Naphthol (4a) under Argon Atmosphere.

Under an argon atmosphere, catalyst **1a** (1.0 mol%, 0.005 mmol, 3.8 mg), 1.0 gm (6.94 mmol) β-naphthol (**2a**), 8.33 mmol (0.88 mL) benzyl alcohol (**3a**), LiO^{t}Bu (3.5 mmol, 280.0 mg), and a tiny magnetic stir bar were added to an oven-dried 35 mL of ACE high-pressure tube. 8.0 mL of dry and degassed toluene was added, and the tube was tightly capped with a PTFE screw cap. The ACE pressure tube containing the reaction mixture was then placed in an oil bath preheated at 140 ºC and continued the reaction for 16 h. The reaction mixture was cooled to room temperature, and all the volatiles were removed under vacuum. The crude reaction mixture was purified by column chromatography using silica gel 60-120 mesh. Eluent: hexane/ethyl acetate (19:1). **4a** was isolated in 54% (877.0 mg) yield.

Mechanistic Investigation.

Control Experiment for Detection of N-H/N-D Stretching.[1-3] An equimolar amount of methanol (1.0 mmol), catalyst **1a** (1.0 mmol), and 0.5 equivalent of ^{t}BuOK were added in an oven-dried 35 mL of ACE high-pressure sealed tube containing a magnetic stirrer. The tube was evacuated and back-filled with argon three times. To it, 2.0 mL of dry and degassed toluene was added, and the tube was tightly capped with a PTFE screw cap. The reaction mixture was allowed to stir at room temperature for 12 h. The reaction mixture was dried under the vacuum. The IR spectrum of the resultant reaction mixture exhibited stretching frequencies at ν(N−H)= 2918 and 2958 cm^{-1}, respectively, which are the characteristic stretching frequencies of N−H bonds.

Using methanol-d[4] a similar experiment was carried out, following the above-mentioned experimental procedure. In this case, the IR spectral analysis of the resultant reaction mixture exhibits characteristic stretching due to N−D bonds: ν(N-D) 2212 and 2302 cm^{-1}.

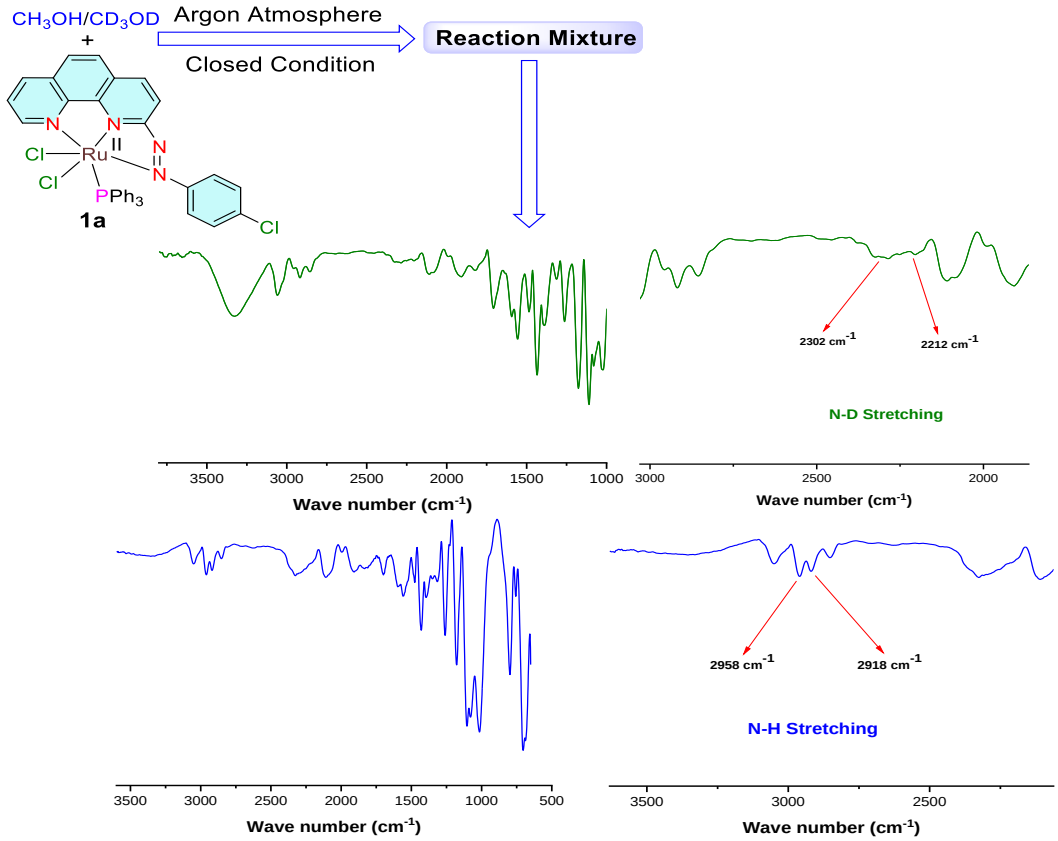


Figure S1. IR spectra of the reaction mixture showing N-H (blue) and N-D (green) stretching.

Deuterium Labeling Experiment with Methanol-d^4 in α-Methylation of β-Naphthol. Under an argon atmosphere, catalyst **1a** (1.0 mol%, 0.005 mmol, 3.8 mg), 0.5 mmol of β-naphthol (72.0 mg), 1.0 mL of dry and degassed methanol-d^4, LiO^{t}Bu (0.25 mmol, 20.0 mg), and a tiny magnetic stir bar were added to an oven-dried 35 mL of ACE high pressure sealed tube. The tube was tightly capped with a PTFE screw cap. The ACE pressure tube containing the reaction mixture was then placed in an oil bath preheated at 140 ºC. The reaction was continued for 16 h. After that, the reaction mixture was cooled to room temperature. Then solvent and other volatiles were evaporated under a vacuum, and the crude reaction mixture was purified by column chromatography using silica gel 60-120 mesh. Eluent: hexane/ethyl acetate (19:1).

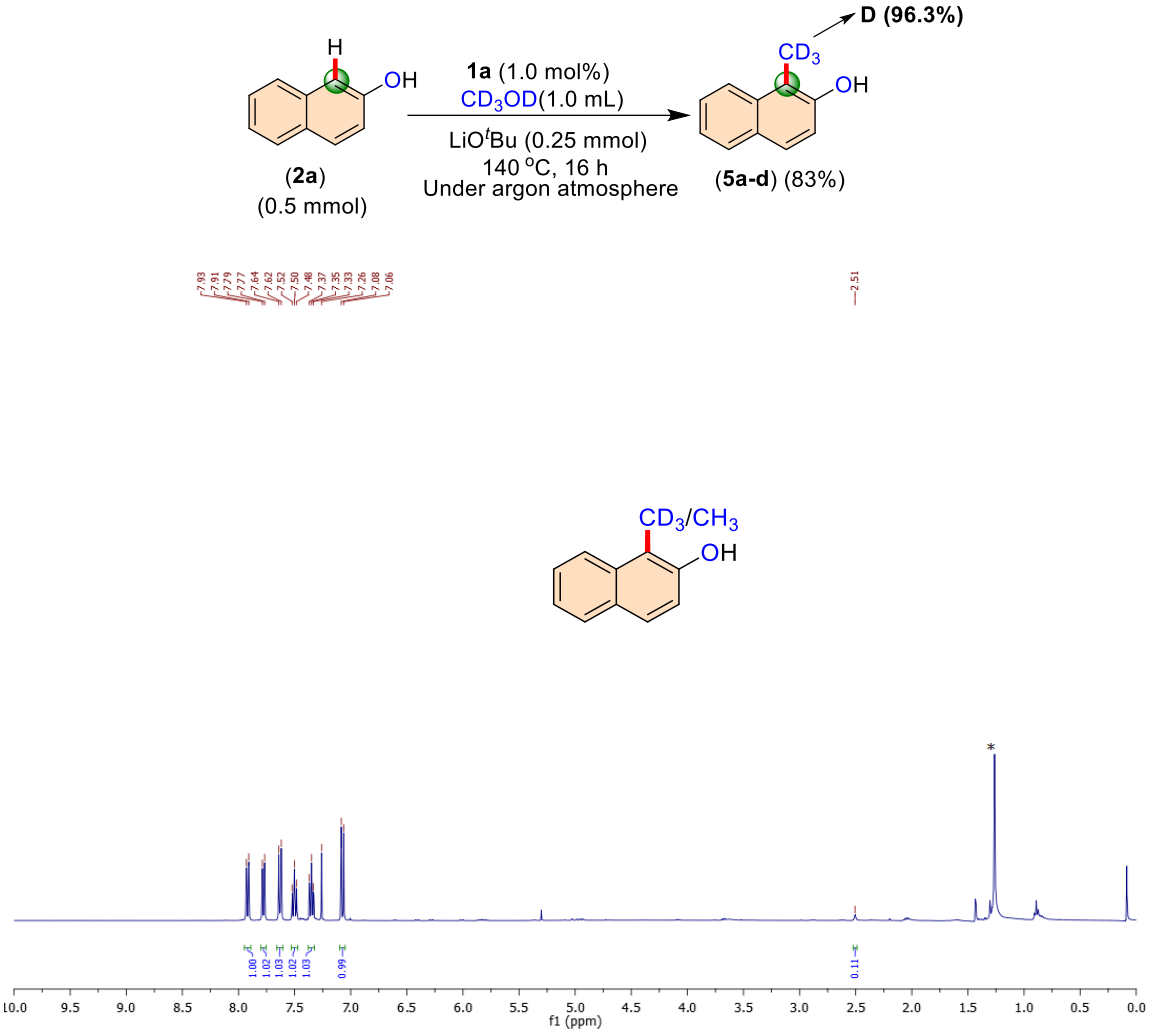


Figure S2. ^{1}H NMR spectrum of compound **5a-d** (400 MHz, $CDCl_3$) (*Hexane).

Deuterium Labeling Experiment of α-Alkylation of β-Naphthol Using Deuterated Benzyl Alcohol (3a-d).

Under an argon atmosphere, catalyst **1a** (1.0 mol%, 0.005 mmol, 3.8 mg), 0.5 mmol (72.0 mg) of β-Naphthol (**2a**), 0.6 mmol (0.06 mL) of deuterated benzyl alcohol (**3a-d**), LiO^{t}Bu (0.25 mmol, 20.0 mg), and a tiny magnetic stir bar were added to an oven-dried 35 mL of ACE high pressure sealed tube. To it, 3.0 mL of dry and degassed toluene was added, and the tube was tightly capped with a PTFE screw cap. The ACE pressure tube containing the reaction mixture was then placed in an oil bath preheated at 140 ^{o}C. The reaction was continued for 16 h. After that, the reaction mixture was cooled to room temperature. Then solvent and other volatiles were evaporated under a vacuum, and the crude reaction mixture was purified by column chromatography using silica gel 60-120 mesh. Eluent: hexane/ethyl acetate (19:1). We obtained 23% deuterium incorporated α-C–H alkylated product of β-naphthol (**4a-d**).

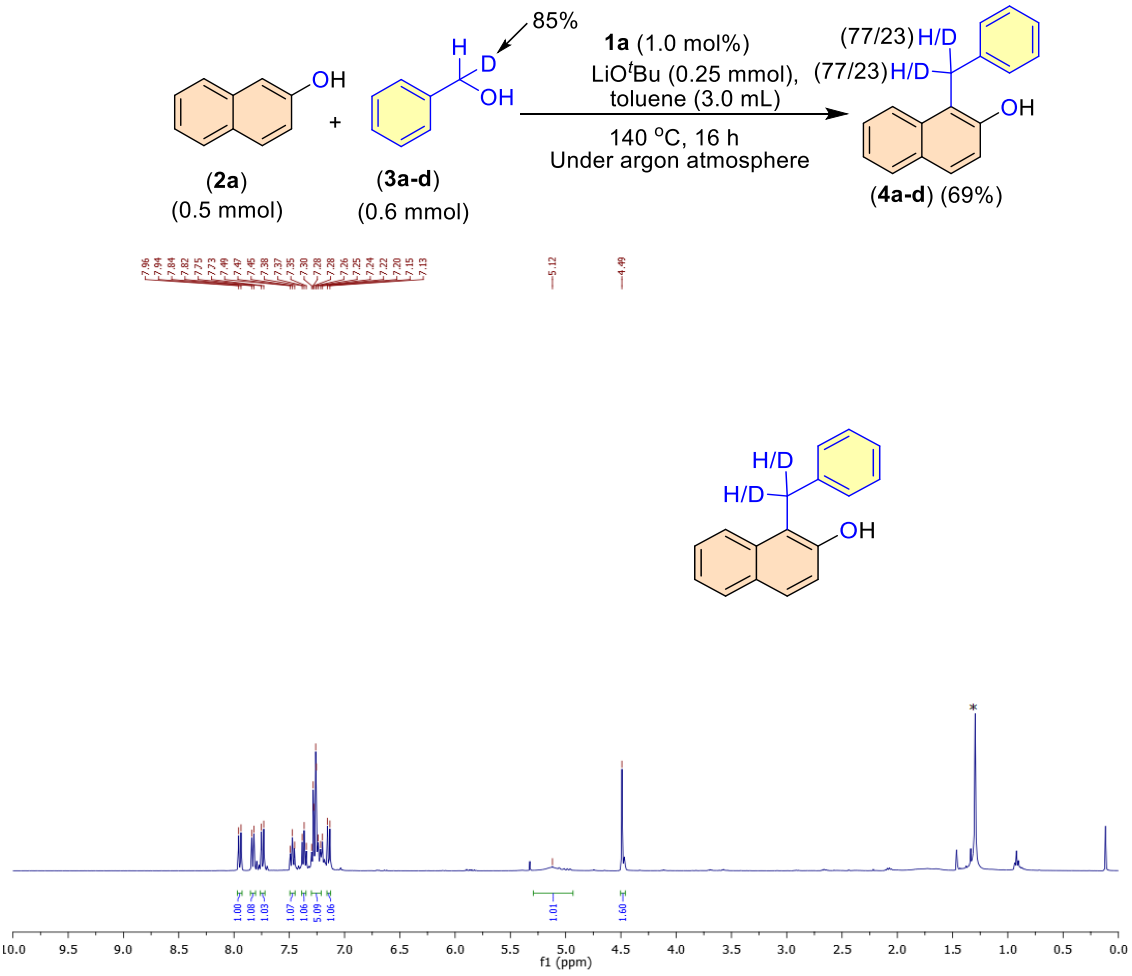
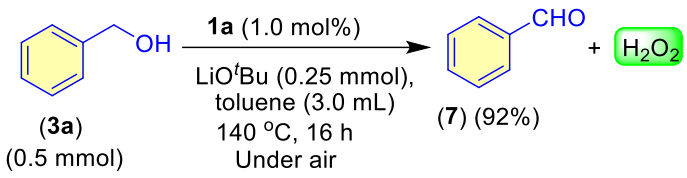


Figure S3. ^{1}H NMR spectrum of compound **4a-d** (400 MHz, $CDCl_3$) (*Hexane).

Detection of Hydrogen Peroxide During the Dehydrogenation of Benzyl Alcohol (3a) under Air.



Formation of H_2O_2 during dehydrogenation of benzyl alcohol (**3a**) was detected spectrophotometrically following the gradual development of the characteristic absorption band for I^{3-} at 354 nm. The dehydrogenation of benzyl alcohol (**3a**) was carried out under air in 35 mL oven-dried ACE pressure tube containing 0.5 mmol (0.05 mL) of **3a**, 1.0 mol% (3.8 mg) catalyst **1a**, 0.25 mmol (20.0 mg) LiO^{t}Bu in 3.0 mL of dry toluene. Then reaction mixture was stirred at 140 °C for 16 h. 10.0 mL of water was added to the reaction mixture, and the whole solution was extracted three times with dichloromethane. The separated aqueous layer was then acidified with H_2SO_4 to pH 2 to stop further oxidation. After that, 1.0 mL of a 10% solution of KI and a few drops of a 3% solution of ammonium molybdate were added. Hydrogen peroxide oxidizes I^- to I_2, which reacts with excess I^- to form I^{3-} according to the following chemical reactions:

(i) $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$; (ii) $I_2(aq) + I^- \rightarrow I_3^-$.

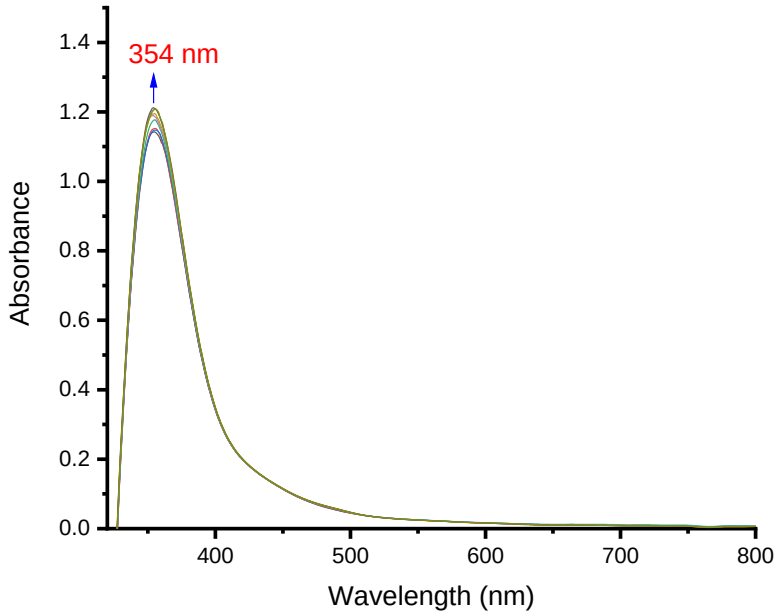
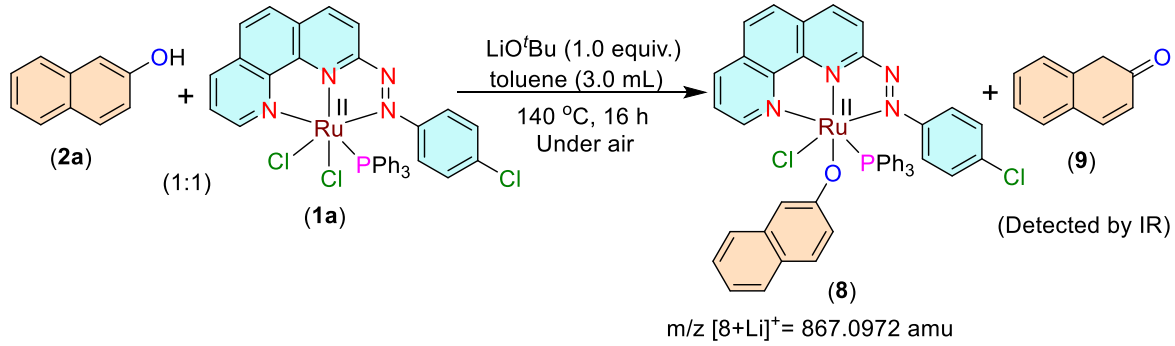


Figure S4. Detection of H_2O_2. Absorption spectral changes during the formation of I_3^- in the presence of H_2O_2.

Oxidation of β-Naphthol in Presence of Catalyst 1a and LiO^{t}Bu.

Under air, an equimolar amount of β-naphthol (**2a**) (1.0 mmol), catalyst **1a** (1.0 mmol), and 0.5 equivalent of LiO^{t}Bu (1.0 mmol) were added in an oven-dried 35 mL of ACE high-pressure sealed tube containing a magnetic stirrer. To it, 3.0 mL of dry toluene was added, and the tube was tightly capped with a PTFE screw cap. The reaction mixture was allowed to stir at 140 ^{o}C for 16 h. Then, the reaction mixture was cooled to room temperature and filtered through the Whatman 41 filter paper. The filtrate was then evaporated using a rotavator and the resulting reaction mixture was sent for HRMS and IR analysis.



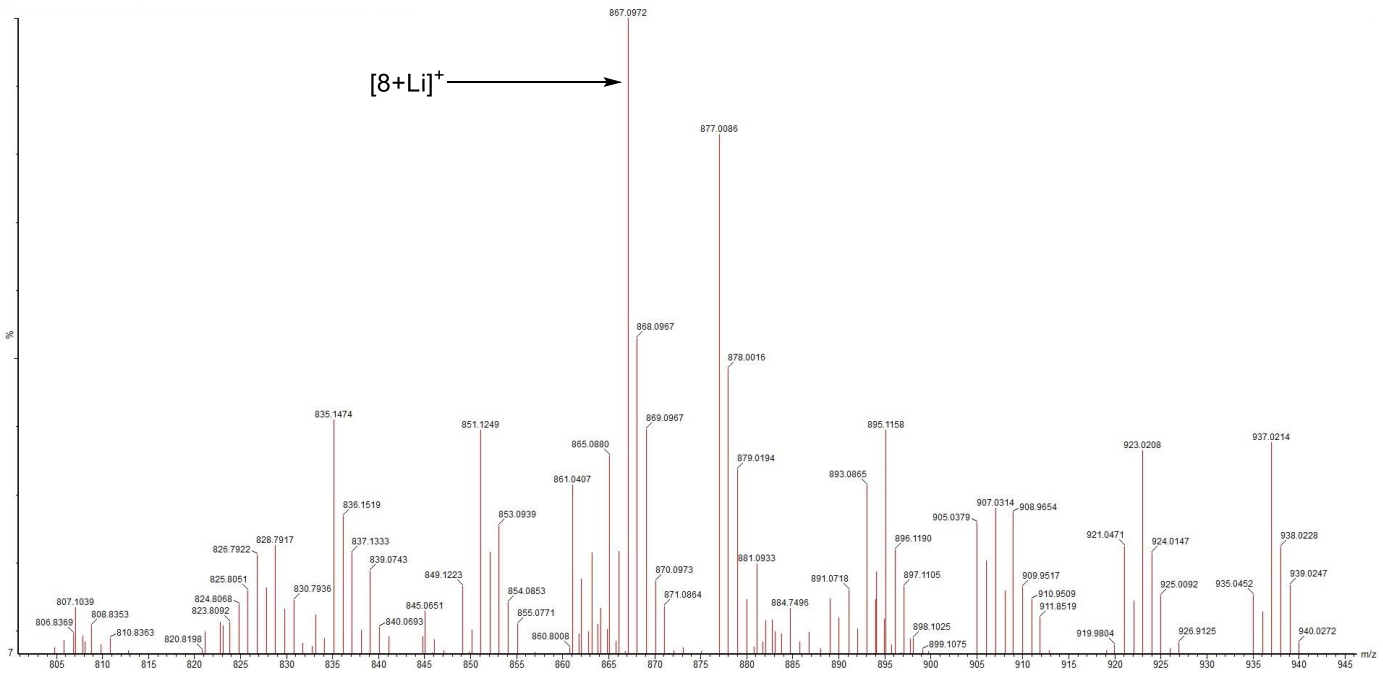


Figure S5. HRMS of **8** in reaction mixture.

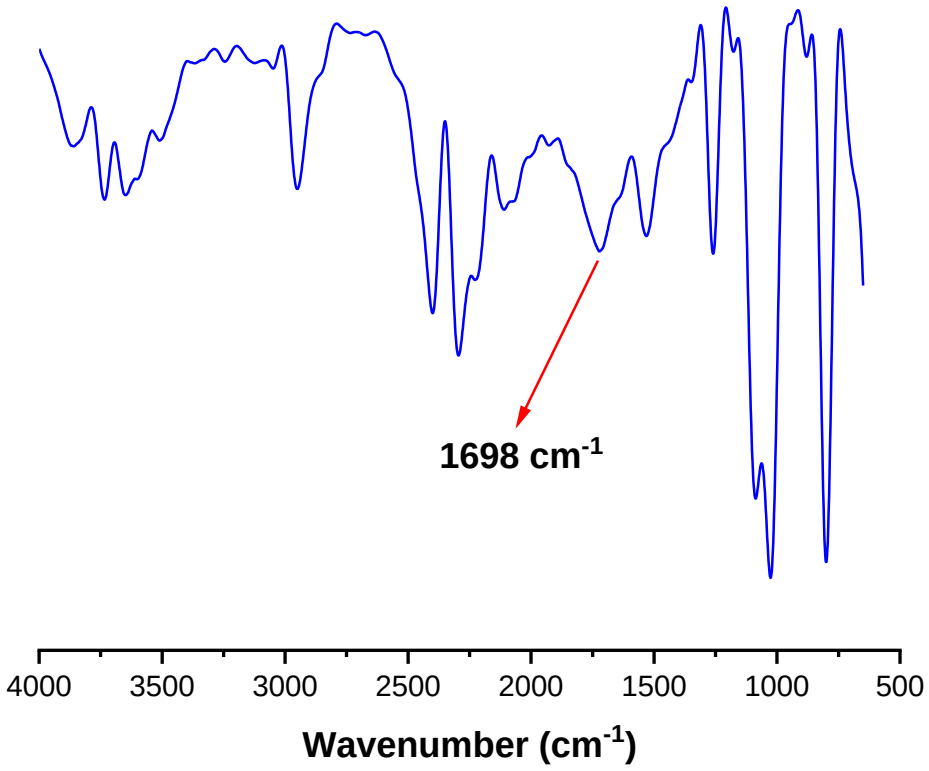
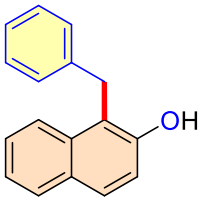
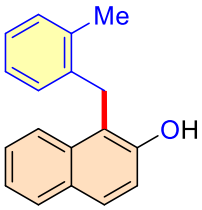


Figure S6. IR spectra of reaction mixture showing carbonyl stretching of **9**.

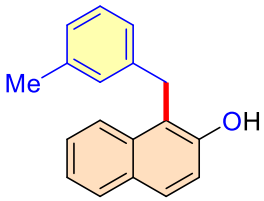
Characterization Data of the Synthesized Compounds.



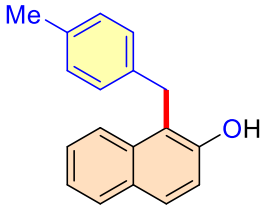
1-benzylnaphthalen-2-ol (**4a**).[4] Eluent: Hexane/ethylacetate (19:1). White solid. Yield: 89 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 775 (d, *J* = 12.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.33-7.23 (m, 5H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.20 (s br, 1H), 4.52 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.2, 140.1, 133.7, 129.5, 128.6, 128.6, 128.5, 128.3, 126.7, 126.1, 123.4, 123.3, 118.2, 117.9, 30.7.



1-(2-methylbenzyl)naphthalen-2-ol (**4b**). Eluent: Hexane/ethylacetate (19:1). Yellow oil. Yield: 81 mg, 66%. ^{1}H NMR (400 MHz, DMSO-d^{6}): δ (ppm) = 9.67 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.35–7.31 (m, 1H), 7.28–7.24 (m, 1H), 7.11–7.00 (m, 3H), 6.87 (t, *J* = 8.0 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 1H), 4.25 (s, 2H), 2.49 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^{6}): δ (ppm) = 153.5, 139.2, 136.3, 134.0, 130.0, 128.7, 128.7, 128.3, 127.1, 126.6, 126.0, 125.8, 123.5, 122.7, 118.5, 117.0, 27.7, 19.9. HRMS (ESI) m/z: [M+H]$^{+}$ calcd. for [$C_{18}H_{17}O$]$^{+}$ 249.1274; found = 249.1276.

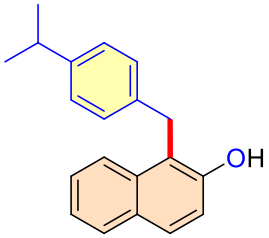


1-(3-methylbenzyl)naphthalen-2-ol (**4c**). Eluent: Hexane/ethylacetate (19:1). Yellow oil. Yield: 88 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.93 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 12.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.16-7.11 (m, 2H), 7.04-6.98 (m, 3H), 5.05 (s br, 1H), 4.42 (s, 2H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.3, 139.8, 138.2, 133.7, 129.4, 128.9, 128.5, 128.5, 127.0, 126.6, 125.2, 123.3, 123.2, 118.2, 117.9, 30.6, 21.4. HRMS (ESI) m/z: [M+H]$^{+}$ calcd. for [$C_{18}H_{17}O$]$^{+}$ 249.1274; found = 249.1278.

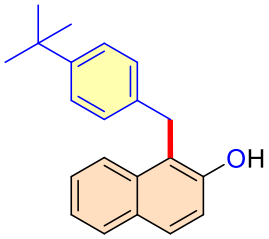


1-(4-methylbenzyl)naphthalen-2-ol (**4d**).[4] Eluent: Hexane/ethylacetate (19:1). Yellow oil. Yield: 77 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.01 (d, *J* = 12.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.21-7.12 (m, 5H), 5.21 (s br, 1H), 4.49 (s, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz,

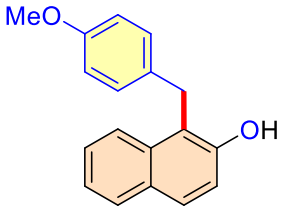
$CDCl_3$): δ (ppm) = 151.3, 137.0, 135.7, 133.8, 129.5, 129.4, 128.6, 128.5, 128.2, 126.7, 123.5, 123.3, 118.5, 118.0, 30.3, 21.1.



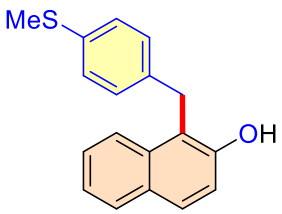
1-(4-isopropylbenzyl)naphthalen-2-ol (**4e**). Eluent: Hexane/ethylacetate (19:1). Yellow oil. Yield: 102 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.97 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.18-7.11 (m, 5H), 5.14 (s br, 1H), 4.45 (s, 2H), 2.93-2.82 (m, 1H), 1.23 (d, *J* = 4.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.2, 146.7, 137.1, 133.7, 129.5, 128.5, 128.4, 128.1, 126.7, 126.6, 123.4, 123.2, 118.4, 118.0, 33.7, 30.3, 24.0. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{20}H_{21}O]^+$ 277.1587; found = 277.1585.



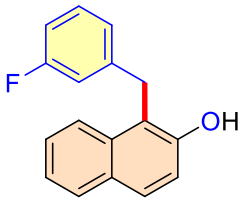
1-(4-(tert-butyl)benzyl)naphthalen-2-ol (**4f**). Eluent: Hexane/ethylacetate (19:1). Yellow oil. Yield: 110 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.97 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 5.10 (s br, 1H), 4.44 (s, 2H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.2, 149.0, 136.7, 133.7, 129.5, 128.5, 128.4, 127.8, 126.6, 125.5, 123.4, 123.2, 118.3, 118.0, 34.3, 31.3, 30.2. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{21}H_{23}O]^+$ 291.1744; found = 291.1748.



1-(4-methoxybenzyl)naphthalen-2-ol (**4g**).[4] Eluent: Hexane/ethylacetate (19:1). Yellow solid. Yield: 83 mg, 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.93 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.15-7.10 (m, 3H), 6.79 (d, *J* = 8.0 Hz, 2H), 5.28 (s br, 1H), 4.40 (s, 2H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 157.9, 151.2, 133.6, 131.9, 129.4, 129.1, 128.5, 128.4, 126.6, 123.3, 123.2, 118.5, 117.9, 114.0, 55.2, 29.8.

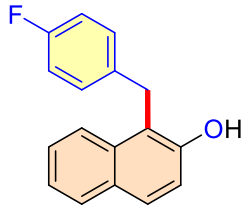


1-(4-(methylthio)benzyl)naphthalen-2-ol (**4h**).[4] Eluent: Hexane/ethylacetate (19:1). White solid. Yield: 83 mg, 60%. ^{1}H NMR (400 MHz, DMSO-d^{6}): δ (ppm) = 9.81 (s, 1H), 7.82 (d, *J* = 12.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 12.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.26–7.22 (m, 2H), 7.17–7.10 (m, 4H), 4.30 (s, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^{6}): δ (ppm) = 152.9, 138.7, 135.1, 133.6, 129.2, 128.8, 128.7, 128.3, 126.7, 126.6, 123.4, 122.7, 118.5, 118.2, 29.7, 15.5.

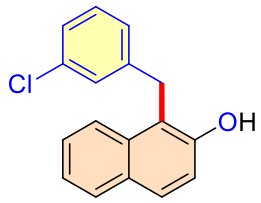


1-(3-fluorobenzyl)naphthalen-2-ol (**4i**). Eluent: Hexane/ethylacetate (19:1). Colourless oil. Yield: 109 mg, 87%. ^{1}H NMR (400 MHz, DMSO-d^{6}): δ (ppm) = 9.84 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.28–7.24 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.01–6.92 (m, 2H), 4.37 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^{6}): δ (ppm) = 162.6 (d, $^{1}J_{C\text{-}F}$ = 241.0 Hz), 153.1, 144.9 (d, $^{3}J_{C\text{-}F}$ = 7.0 Hz), 133.6, 130.4 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 128.8, 128.7, 128.5, 126.8, 124.7 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz),

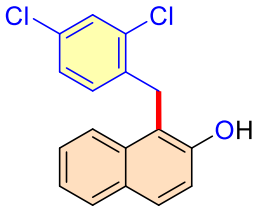
123.3, 122.8, 118.5, 117.7, 115.1 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 112.7 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 30.0. $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d^{6}): δ (ppm) = -113.9. HRMS (ESI) m/z: $[M+H]^{+}$ calcd. for $[C_{17}H_{14}FO]^{+}$ 253.1024; found = 253.1025.



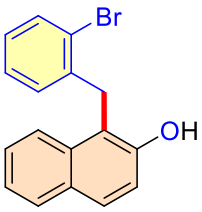
1-(4-fluorobenzyl)naphthalen-2-ol (**4j**).[4] Eluent: Hexane/ethylacetate (19:1). White solid. Yield: 114 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.20-7.16 (m, 2H), 7.12-7.09 (m, 1H), 6.96-6.91 (m, 2H), 5.18 (s br, 1H), 4.43 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 161.3 (d, $^{1}J_{C\text{-}F}$ = 242.0 Hz), 151.0, 135.8 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 133.5, 129.6 (d, $^{3}J_{C\text{-}F}$ = 7.0 Hz), 129.5, 128.6, 126.8, 123.3, 123.2, 118.2, 117.8, 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 29.8. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ (ppm) = -117.3.



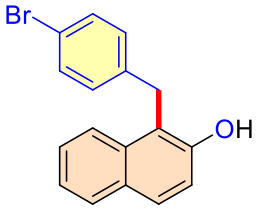
1-(3-chlorobenzyl)naphthalen-2-ol (**4k**).[4] Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 96 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.85 (d, *J* = 12.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.21 (s, 1H), 7.16-7.09 (m, 4H), 5.19 (s br, 1H), 4.43 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.1, 142.5, 134.3, 133.5, 129.7, 129.4, 128.7, 128.6, 128.3, 126.8, 126.4, 126.2, 123.3, 123.1, 117.7, 117.5, 30.3.



1-(2,4-dichlorobenzyl)naphthalen-2-ol (**4l**). Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 106 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.82 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.46-7.41 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.62-6.59 (m, 1H), 5.24 (s br, 1H), 4.46 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.4, 136.2 134.6, 133.6, 132.2, 130.0, 129.4, 129.0, 128.9, 128.6, 127.1, 127.0, 123.5, 123.1, 117.7, 116.2, 27.7. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{17}H_{13}Cl_2O]^+$ 303.0338; found = 303.0340.

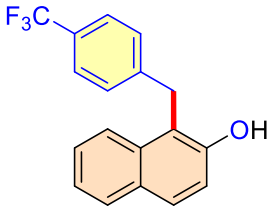


1-(2-bromobenzyl)naphthalen-2-ol (**4m**).[4] Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 96 mg, 62%. ^{1}H NMR (400 MHz, DMSO-d^6): δ (ppm) = 9.85 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.69–7.66 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.30–7.24 (m, 1H), 7.21–7.20 (m, 1H), 7.11–7.09 (m, 2H), 6.53–6.51 (m, 1H), 4.35 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^6): δ (ppm) = 153.6, 139.9, 133.7, 132.7, 129.4, 128.9, 128.9, 128.7, 128.6, 128.3, 128.1, 127.0, 124.6, 122.9, 118.5, 116.1, 30.9.

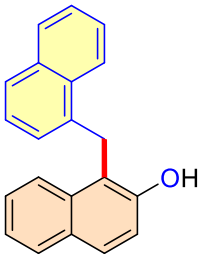


1-(4-bromobenzyl)naphthalen-2-ol (**4n**). Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 98 mg, 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 12.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.35-7.31 (m, 3H), 7.09 (t, *J* = 8.0 Hz, 3H), 5.10 (s br, 1H), 4.40 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm)

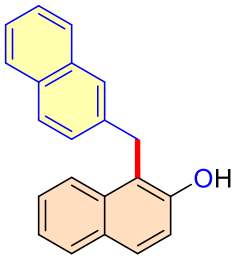
= 151.0, 139.3, 133.5, 131.5, 130.0, 129.4, 128.7, 128.6, 126.8, 123.3, 123.1, 119.7, 117.7, 30.1. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{17}H_{14}BrO]^+$ 313.0223; found = 313.0221.



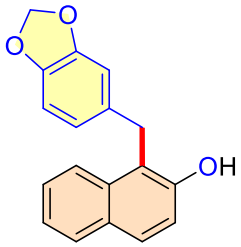
1-(4-(trifluoromethyl)benzyl)naphthalen-2-ol (**4o**).[4] Eluent: Hexane/ethylacetate (19:1). Reddish solid. Yield: 123 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.91-7.86 (m, 2H), 7.75 (d, *J* = 12.0 Hz, 1H), 7.54-7.49 (m, 3H), 7.43-7.35 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 5.42 (s br, 1H), 4.55 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.1, 144.7, 133.6, 129.5, 128.9, 128.8, 128.6, 128.1, 127.8, 127.0, 125.4 (q, $^3J_{C-F}$ = 4.0 Hz), 124.4 (q, $^1J_{C-F}$ = 270.0 Hz), 123.5, 123.2, 123.1, 117.7, 117.6, 30.5. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ (ppm) = -62.0.



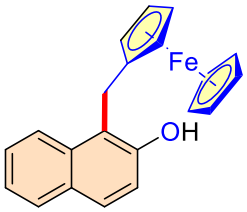
1-(naphthalen-1-ylmethyl)naphthalen-2-ol (**4p**). Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 109 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.36 (d, *J* = 12.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.86-7.84 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.75-7.71 (m, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.39-7.33 (m, 2H), 7.23-7.17 (m, 2H), 6.79 (d. *J* = 8.0 Hz, 1H), 5.20 (s br, 1H), 4.87 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.7, 134.8, 133.9, 133.8, 132.1, 129.5, 128.9, 128.7, 128.5, 126.9, 126.7, 126.2, 125.7, 125.7, 124.6, 123.4, 123.3, 123.3, 118.0, 116.8, 27.6. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{21}H_{17}O]^+$ 285.1274; found = 285.1271.



1-(naphthalen-2-ylmethyl)naphthalen-2-ol (**4q**).[4] Eluent: Hexane/ethylacetate (19:1). White solid. Yield: 108 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, *J* = 8.0 Hz, 1H), 7.85-7.74 (m, 4H), 7.70-7.68 (m, 1H), 7.59 (s, 1H), 7.47-7.41 (m, 4H), 7.38-7.35 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 5.20 (s br, 1H), 4.63 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.3, 137.6, 133.7, 133.6, 132.1, 129.5, 128.7 128.6, 128.2, 127.6, 127.1, 126.8, 126.2, 126.0, 125.3, 123.4, 123.3, 118.0, 118.0, 30.9.

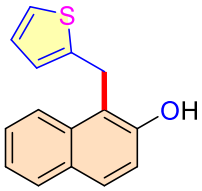


1-(benzo[d][1,3]dioxol-5-ylmethyl)naphthalen-2-ol (**4r**).[4] Eluent: Hexane/ethylacetate (19:1). White solid. Yield: 80 mg, 58%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 3H), 5.87 (s, 2H), 4.60 (s, 1H), 4.37 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.2, 147.8, 145.8, 134.0, 133.6, 129.4, 128.6, 128.5, 126.7, 123.2, 123.2, 121.0, 118.3, 117.9, 108.8, 108.2, 100.8, 30.3.

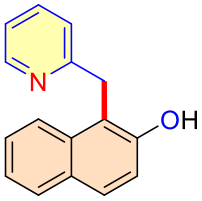


1-(Ferrocene-2-ylmethyl)naphthalen-2-ol (**4s**).[4] Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 107 mg, 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.02-7.01 (m, 6H), 5.35 (s br, 1H), 4.81-4.14 (m, 11H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.6, 133.0,

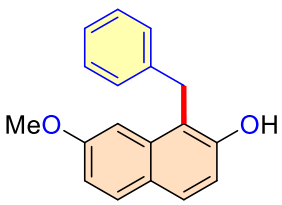
129.2, 128.5, 128.1, 126.3, 123.2, 123.0, 119.3, 117.7, 73.3, 71.5, 70.4, 69.7, 69.7, 69.1, 69.1, 68.5, 24.6.



1-(thiophen-2-ylmethyl)naphthalen-2-ol (**4t**).[4] Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 74 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.07 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.16-7.12 (m, 2H), 6.94-6.92 (m, 1H), 6.87 (s, 1H), 5.95 (s br, 1H), 4.69 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.1, 143.7, 133.3, 129.5, 128.8, 128.7, 126.8, 124.8, 123.6, 123.4, 123.2, 118.4, 118.1, 25.5.

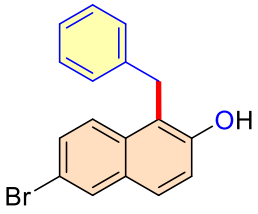


1-(pyridin-2-ylmethyl)naphthalen-2-ol (**4u**). Eluent: Hexane/ethylacetate (4:1). White solid. Yield: 95 mg, 81%. ^{1}H NMR (400 MHz, DMSO-d^{6}): δ (ppm) = 10.09 (s br, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 2H), 7.16-7.13 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.49 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^{6}): δ (ppm) = 161.4, 153.1, 149.0, 137.2, 133.8, 128.7, 128.7, 128.5, 126.7, 123.5, 122.8, 122.7, 121.7, 118.7, 117.2, 33.6. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{16}H_{14}NO]^+$ 236.1070; found = 236.1074.

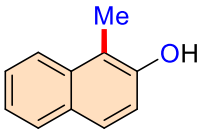


1-benzyl-7-methoxynaphthalen-2-ol (**4v**).[4] Eluent: Hexane/ethylacetate (19:1). White solid. Yield: 103 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.72 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.30-7.29 (m, 4H), 7.24-7.20 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J*

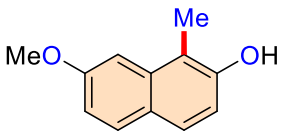
= 8.0 Hz, 1H), 5.20 (s br, 1H), 4.46 (s, 2H), 3.86 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.4, 151.8, 140.2, 135.0, 130.1, 128.6, 128.2, 128.2, 126.1, 124.9, 117.5, 115.4, 115.3, 102.7, 55.2, 31.0.



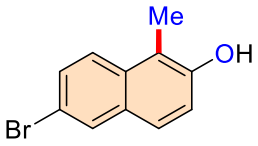
1-benzyl-6-bromonaphthalen-2-ol (**4w**).[4] Eluent: Hexane/ethylacetate (19:1). White solid. Yield: 84 mg, 54%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.93 (s, 1H), 7.78-7.75 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.24-7.23 (m, 2H), 7.18-7.12 (m, 4H), 5.29 (s, br, 1H), 4.42 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 151.5, 139.6, 132.2, 130.6, 130.4, 129.8, 128.6, 128.2, 128.1, 127.6, 126.2, 125.2, 119.0, 118.5, 117.0, 30.6.



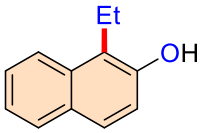
1-methylnaphthalen-2-ol (**5a**).[5] Eluent: Hexane/ethylacetate (19:1). Light yellow solid. Yield: 66 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 5.34 (s, br, 1H), 2.59 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.5, 133.9, 129.2, 128.5, 127.4, 126.4, 123.2, 123.2, 117.7, 115.5, 10.6.



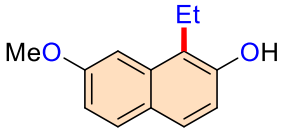
7-methoxy-1-methylnaphthalen-2-ol (**5b**). Eluent: Hexane/ethylacetate (19:1). Brown solid. Yield: 67 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.67 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 7.05-7.02 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.33 (s, br, 1H), 3.96 (s, 3H), 2.50 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) = 158.1, 151.1, 135.1, 130.0, 127.0, 124.5, 115.3, 115.1, 114.4, 102.2, 55.3, 10.7. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{12}H_{13}O_2]^+$ 189.0911; found = 189.0914.



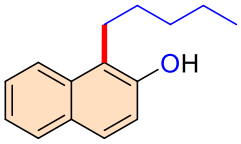
6-bromo-1-methylnaphthalen-2-ol (**5c**). Eluent: Hexane/ethylacetate (19:1). White solid. Yield: 64 mg, 54%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.96-7.93 (m, 1H), 7.82-7.78 (m, 1H), 7.66-7.51 (m, 2H), 7.11-7.08 (m, 1H), 5.38 (s br, 1H), 2.53 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.8, 130.3, 129.4, 128.5, 127.3, 126.4, 125.1, 123.1, 118.6, 117.6, 10.5. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{11}H_{10}BrO]^+$ 236.9910; found = 236.9908.



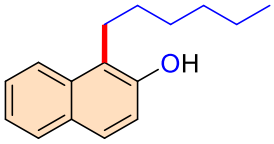
1-ethylnaphthalen-2-ol (**5d**). Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 58 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.95 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 12.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 5.59 (s br, 1H), 3.11-3.05 (m, 2H), 1.29 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.0, 132.9, 129.3, 128.5, 127.4, 126.2, 122.9, 122.8, 121.8, 117.7, 18.1, 14.1. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{12}H_{13}O]^+$ 173.0961; found = 173.0964.



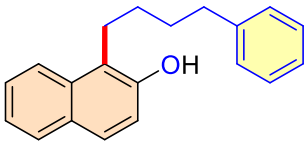
1-ethyl-7-methoxynaphthalen-2-ol (**5e**). Eluent: Hexane/ethylacetate (19:1). Brown oil. Yield: 50 mg, 50%. ^{1}H NMR (400 MHz, DMSO-d^6): δ (ppm) = 9.45 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 4.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.93-6.90 (m, 1H), 3.87 (s, 3H), 2.98-2.92 (m, 2H), 1.15 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^6): δ (ppm) = 158.0, 152.7, 134.4, 130.3, 127.0, 123.9, 120.5, 115.8, 114.5, 101.8, 55.3, 18.0, 14.2. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $[C_{13}H_{15}O_2]^+$ 203.1067; found = 203.1071.



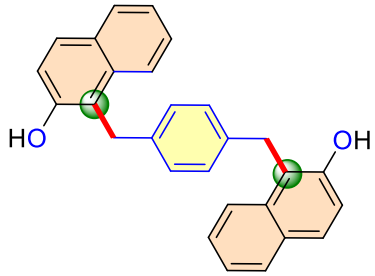
1-pentylnaphthalen-2-ol (**5f**).[4] Eluent: Hexane/ethylacetate (49:1). Colourless oil. Yield: 53 mg, 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.96 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 5.28 (s br, 1H), 3.05 (t, *J* = 8.0 Hz, 2H), 1.74-1.66 (m, 2H), 1.53-1.38 (m, 4H), 0.94 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.3, 133.2, 129.4, 128.6, 127.5, 126.2, 123.0, 122.9, 120.3, 117.6, 32.1, 29.5, 25.1, 22.7, 14.1.



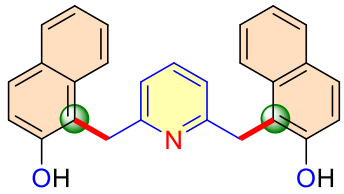
1-hexylnaphthalen-2-ol (**5g**).[4] Eluent: Hexane/ethylacetate (49:1). Colourless oil. Yield: 47 mg, 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.94 (d, *J* = 12.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 5.10 (s br, 1H), 3.04 (t, *J* = 8.0 Hz, 2H), 1.72-1.64 (m, 2H), 1.53-1.45 (m, 2H), 1.40-1.32 (m, 4H), 0.92 (t, *J* = 8.0 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.3, 133.2, 129.4, 128.6, 127.5, 126.3, 123.0, 123.0, 120.4, 117.6, 31.8, 29.8, 29.7, 25.1, 22.7, 14.1.



1-(4-phenylbutyl)naphthalen-2-ol (**5h**).[4] Eluent: Hexane/ethylacetate (49:1). Colourless oil. Yield: 84 mg, 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.63 (d *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.37-7.28 (m, 3H), 7.22-7.19 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 1H), 4.91 (s br, 1H), 3.08 (t, *J* = 8.0 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 1.87-1.71 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) = 150.4, 142.6, 133.2, 129.4, 128.6, 128.4, 128.3, 127.6, 126.3, 125.7, 123.0, 120.2, 117.6, 35.8, 31.6, 29.4, 24.9.



1,1'-(1,4-phenylenebis(methylene)bis(naphthalen-2-ol)) (**6a**). Eluent: Hexane/ethylacetate (4:1). Brown oil. Yield: 145 mg, 62%. ^{1}H NMR (400 MHz, DMSO-d^{6}): δ (ppm) = 9.72 (s, 2H), 7.80-7.73 (m, 4H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.24-7.19 (m, 4H), 7.04 (s, 4H), 4.25 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^{6}): δ (ppm) = 160.3, 153.2, 138.2, 133.8, 128.7, 128.6, 126.7, 123.6, 122.8, 120.2, 118.8, 117.2, 33.6. HRMS (ESI) m/z: $[M+H]^{+}$ calcd. for $[C_{28}H_{23}O_2]^{+}$ 391.1693; found = 391.1692.



1,1'-(pyridine-2,6-diylbis(methylene))bis(naphthalen-2-ol) (**6b**). Eluent: Hexane/ethylacetate (1:1). Brown oil. Yield: 159 mg, 68%. ^{1}H NMR (400 MHz, DMSO-d^{6}): δ (ppm) = 10.22 (s br, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.79-7.71 (m, 4H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.36-7.24 (m, 6H), 6.89 (d, *J* = 4.0 Hz, 2H), 4.53 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d^{6}): δ (ppm) = 160.3, 153.2, 138.2, 133.8, 128.7, 128.6, 126.7, 123.6, 122.8, 120.2, 118.8, 117.2, 33.6. HRMS (ESI) m/z: $[M+H]^{+}$ calcd. for $[C_{27}H_{22}NO_2]^{+}$ 392.1646; found = 392.1649.

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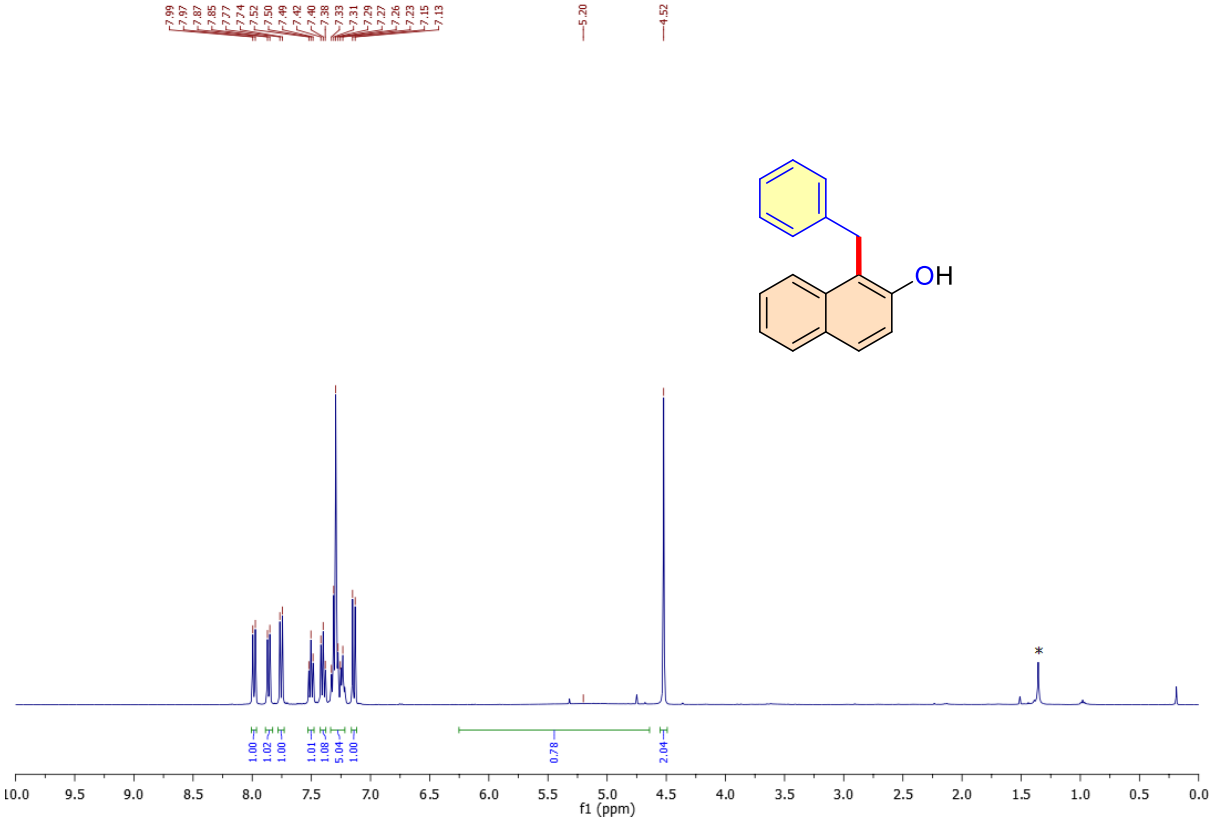

Figure S7. ^{1}H NMR spectrum of compound **4a** (400 MHz, $CDCl_3$) (*Hexane).

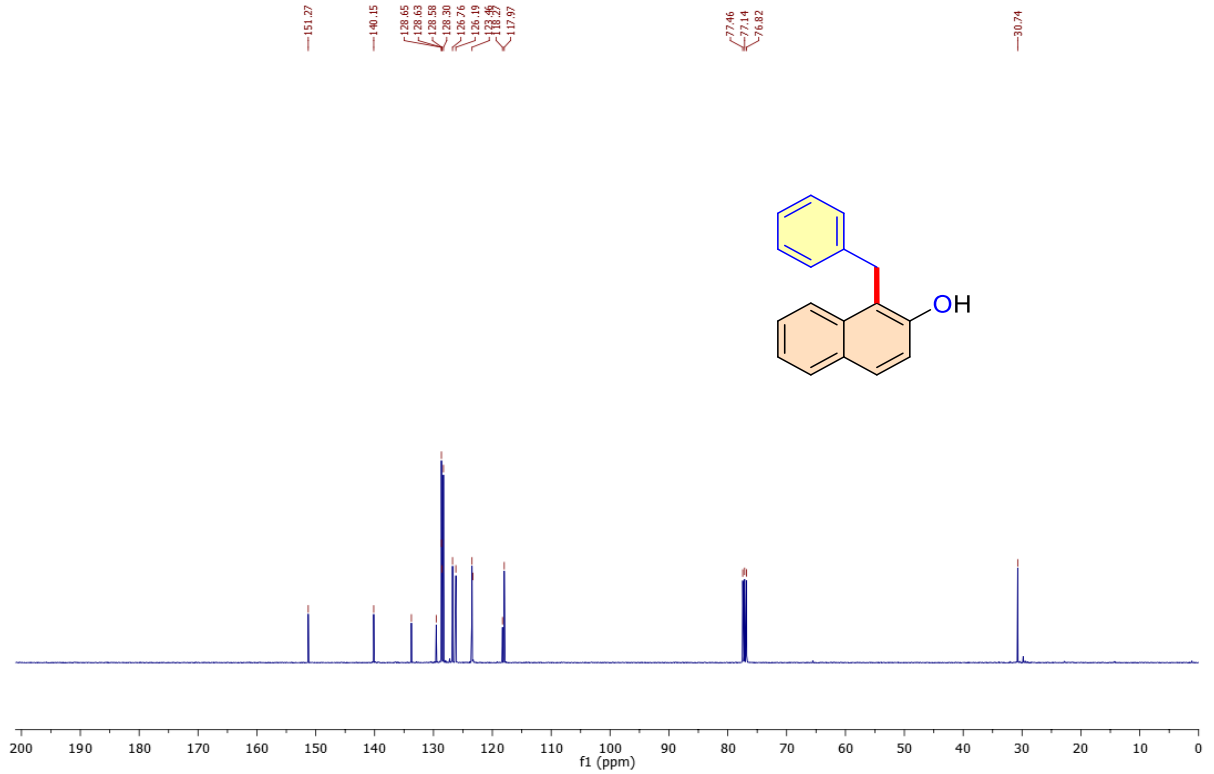

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4a** (100 MHz, $CDCl_3$).

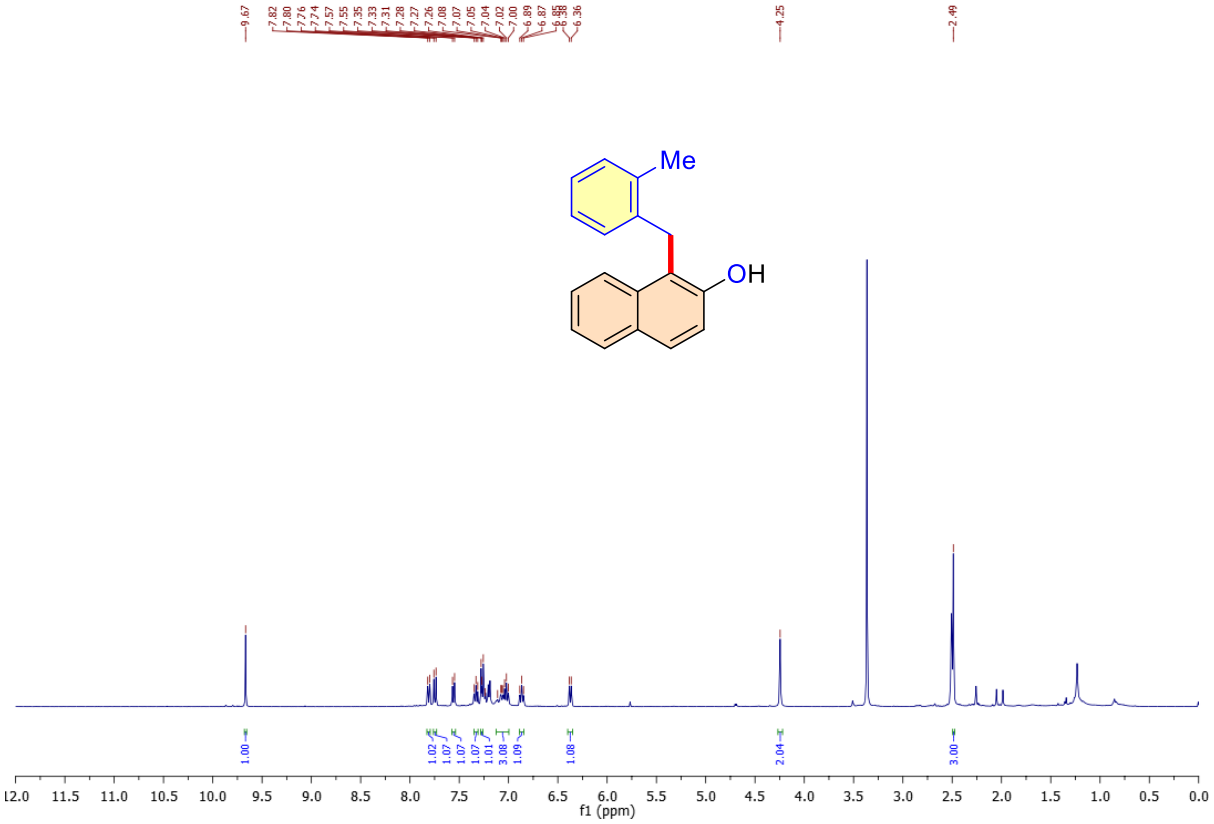

Figure S9. ^{1}H NMR spectrum of compound **4b** (400 MHz, DMSO-d^{6}).

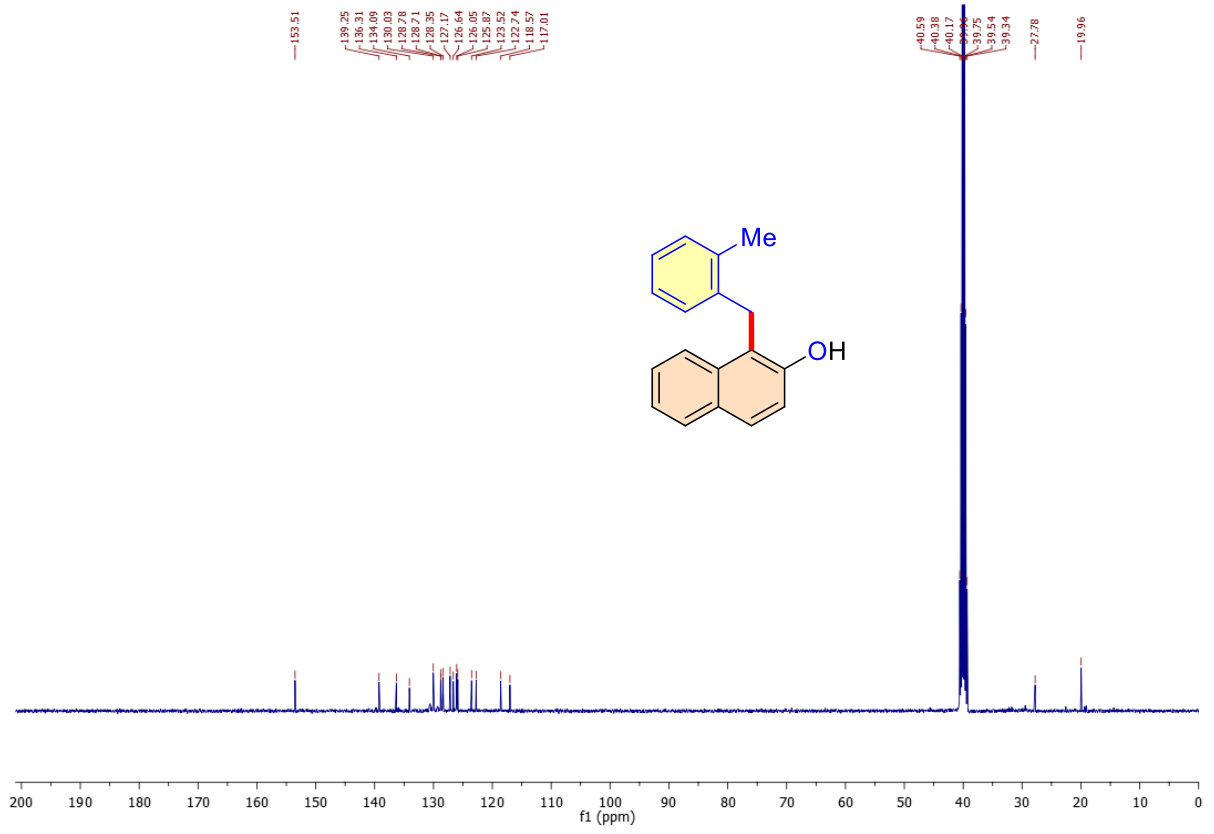

Figure S10. ^{13}C{^{1}H} NMR spectrum of compound **4b** (100 MHz, DMSO-d^{6}).

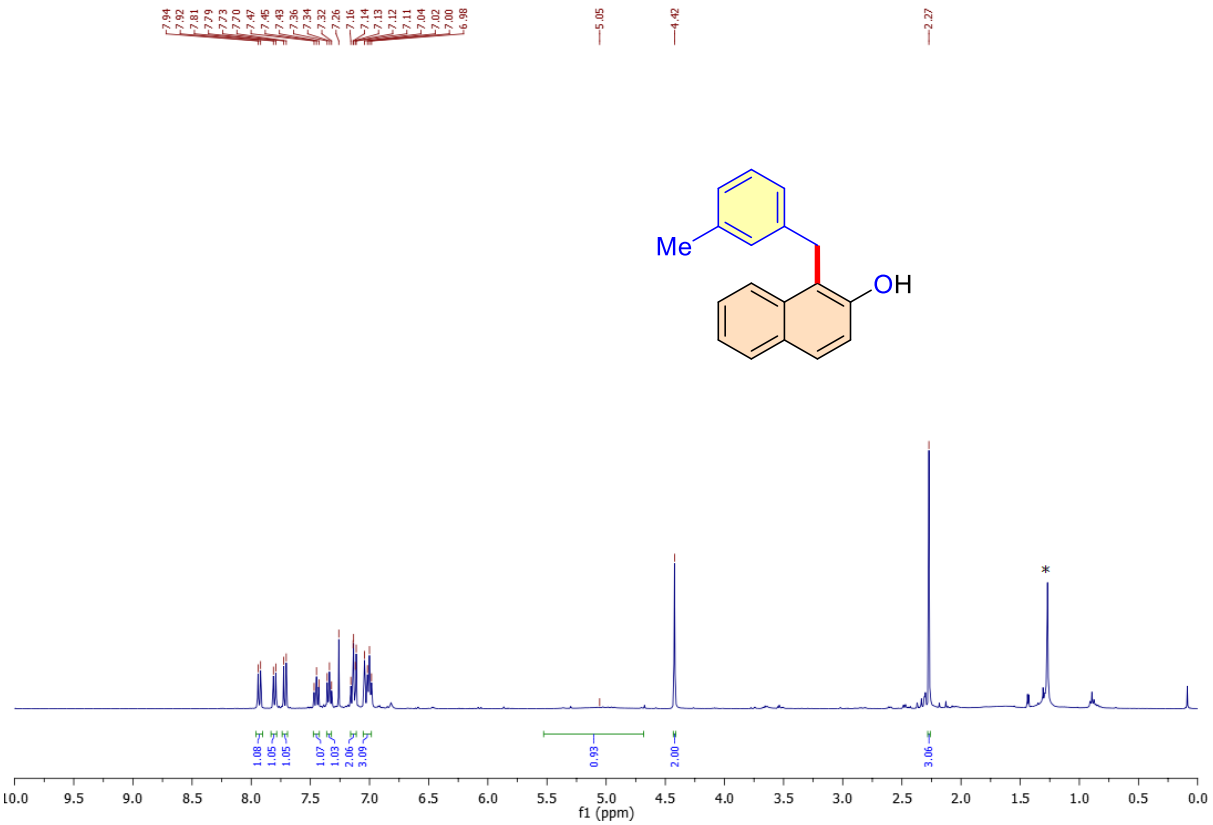

Figure S11. ^{1}H NMR spectrum of compound **4c** (400 MHz, $CDCl_3$) (*Hexane).

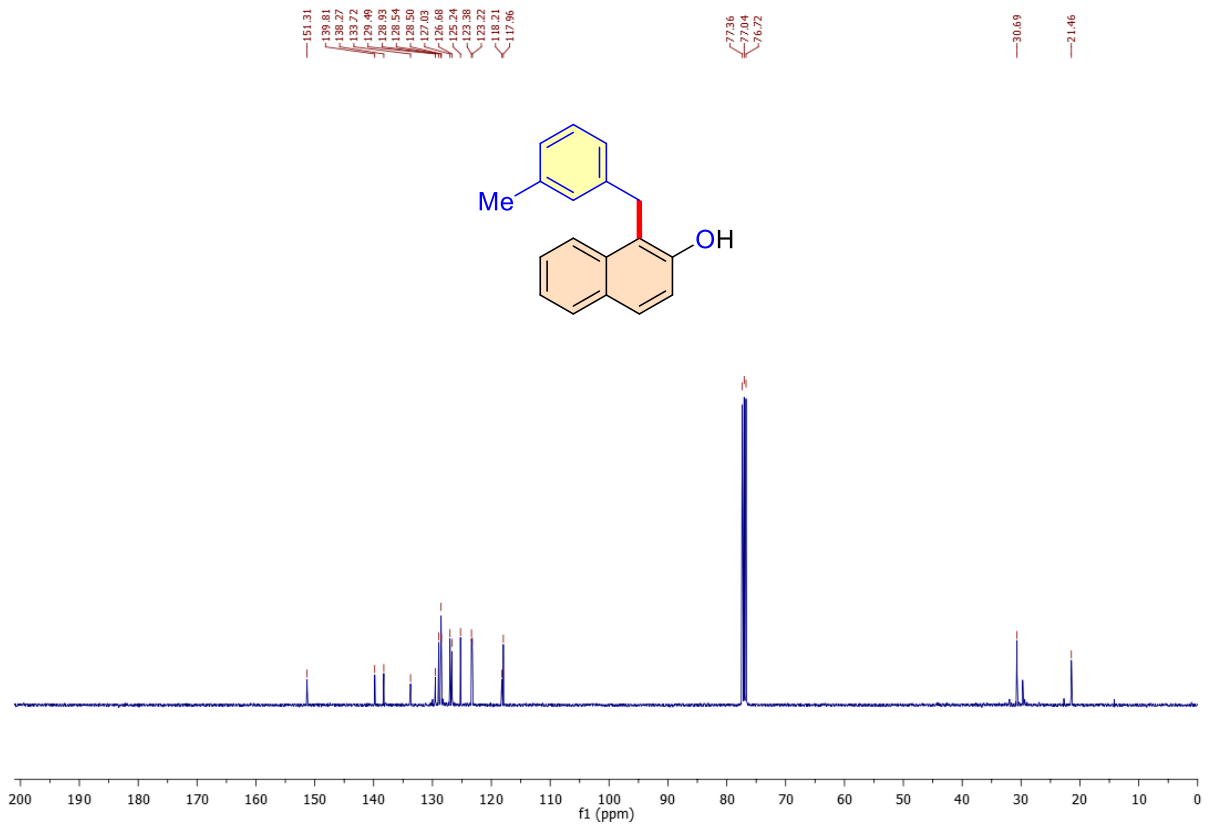

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4c** (100 MHz, $CDCl_3$).

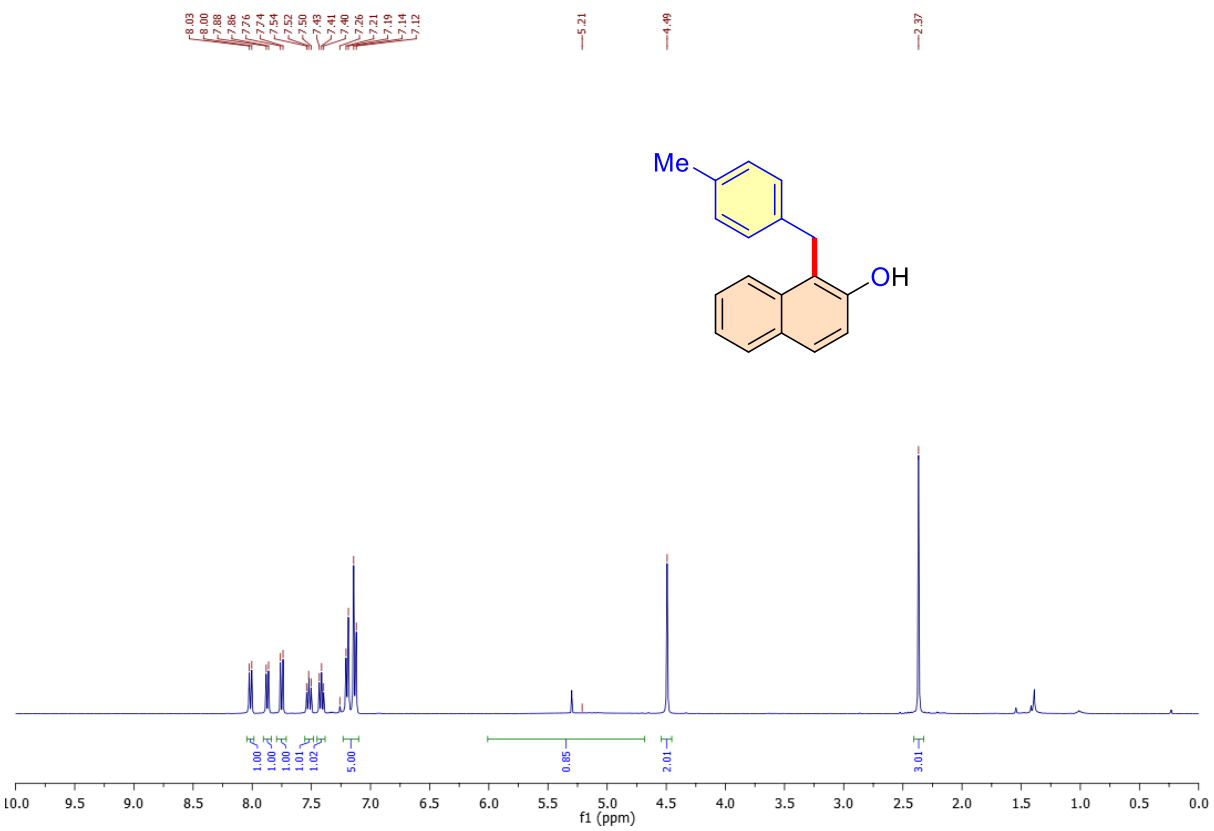

Figure S13. ^{1}H NMR spectrum of compound **4d** (400 MHz, $CDCl_3$).

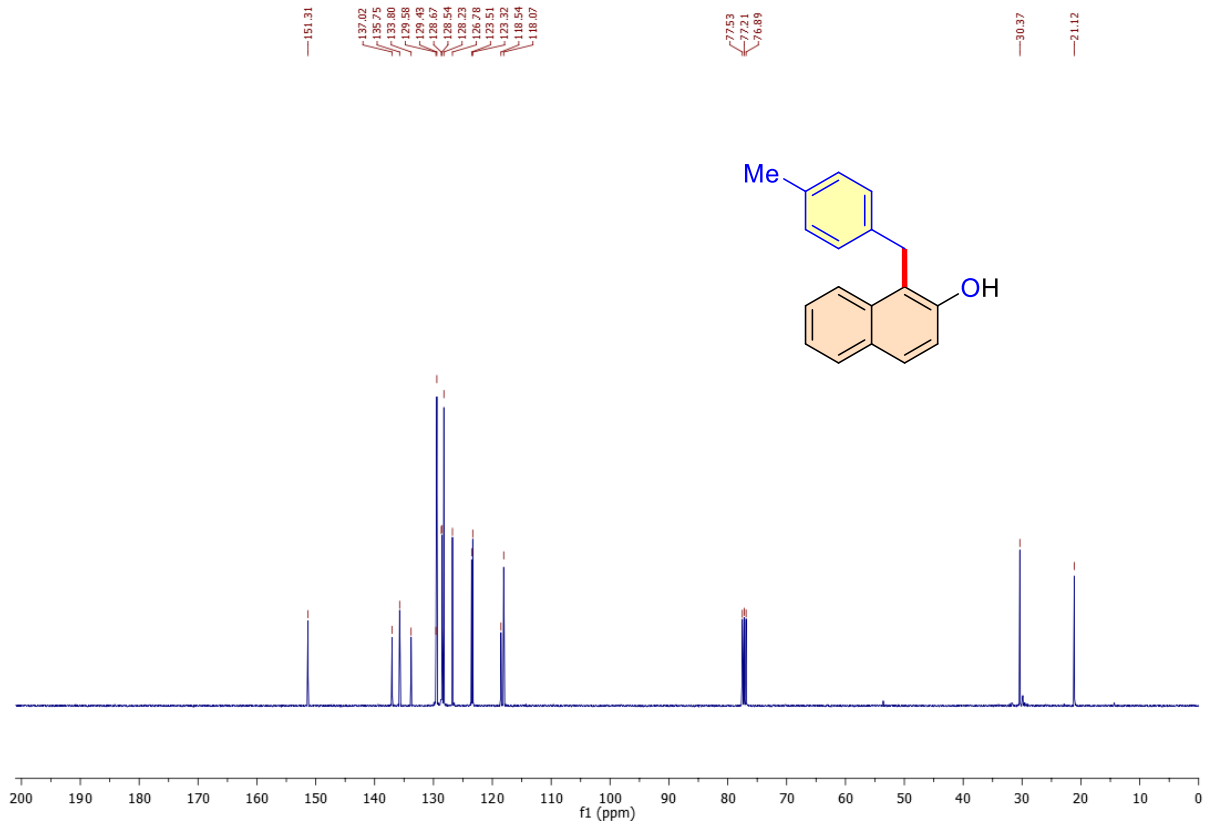

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4d** (100 MHz, $CDCl_3$).

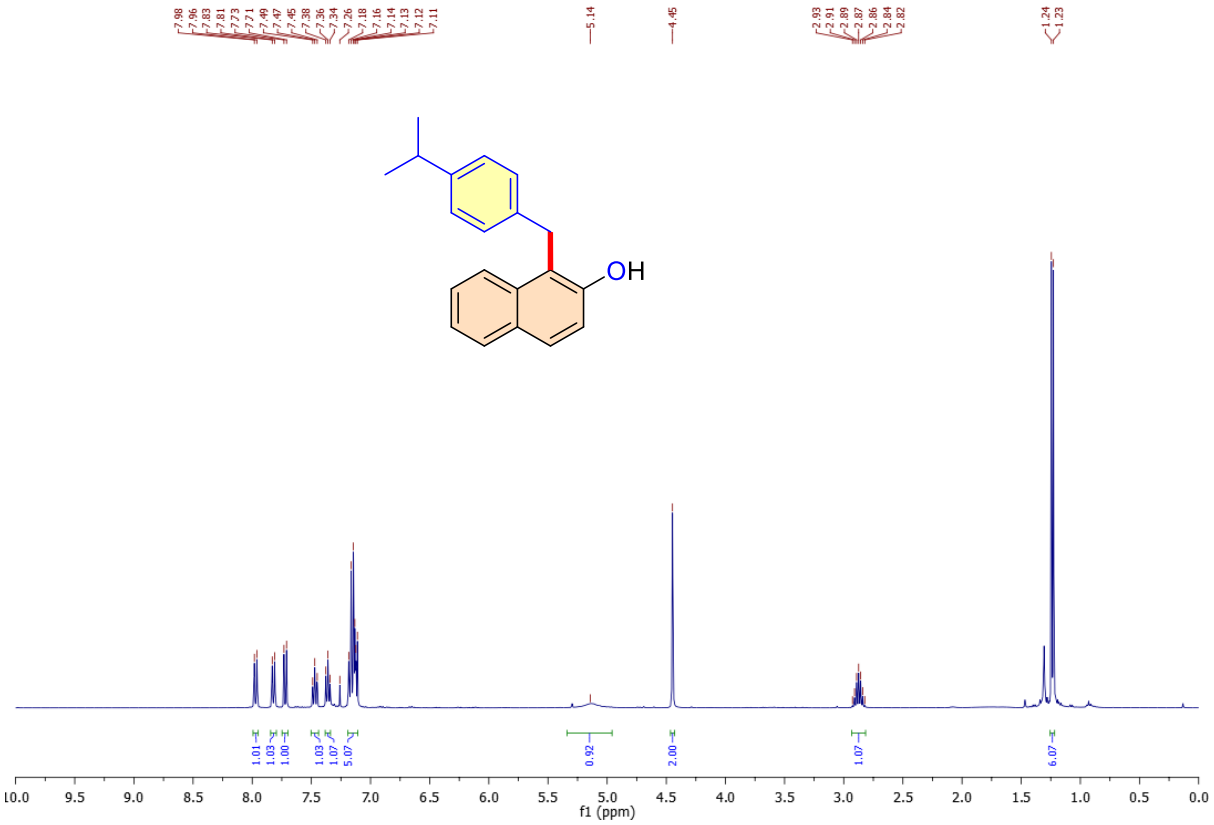

Figure S15. ^{1}H NMR spectrum of compound **4e** (400 MHz, $CDCl_3$).

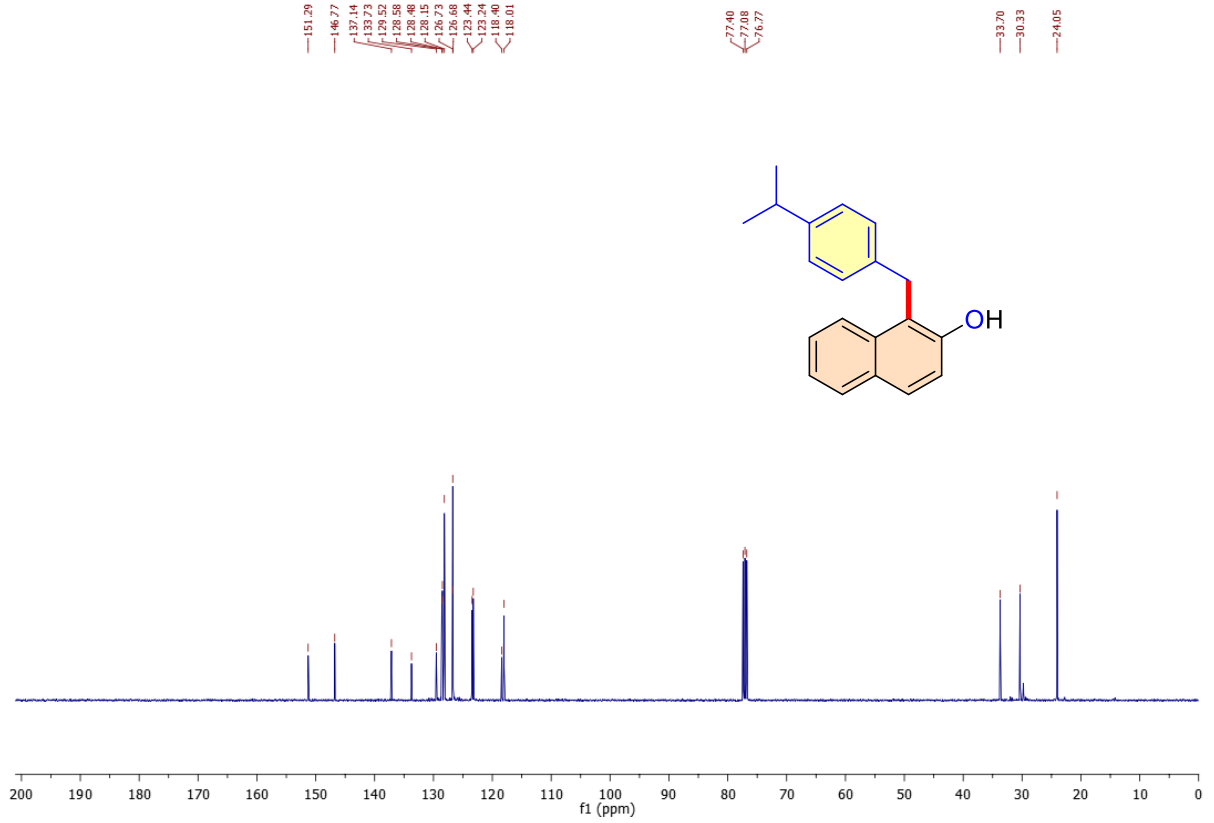

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4e** (100 MHz, $CDCl_3$).

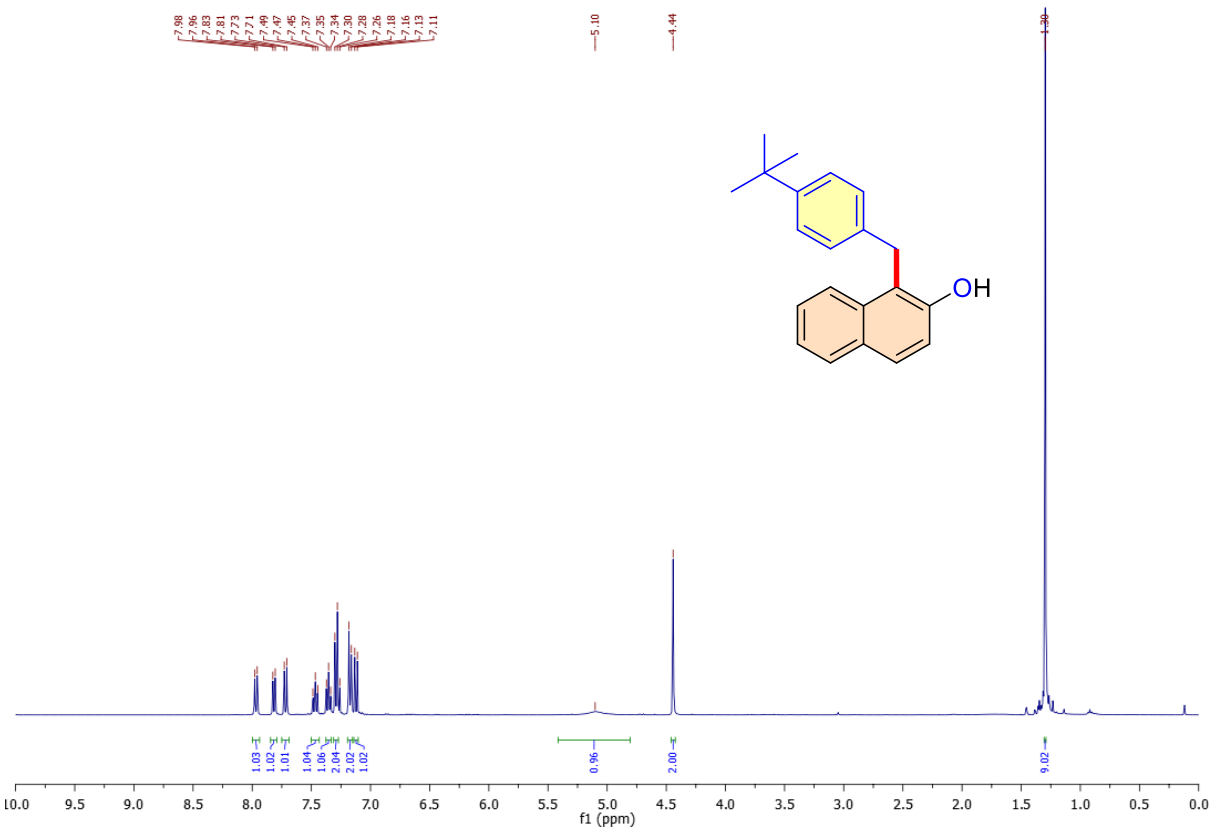

Figure S17. ^{1}H NMR spectrum of compound **4f** (400 MHz, $CDCl_3$).

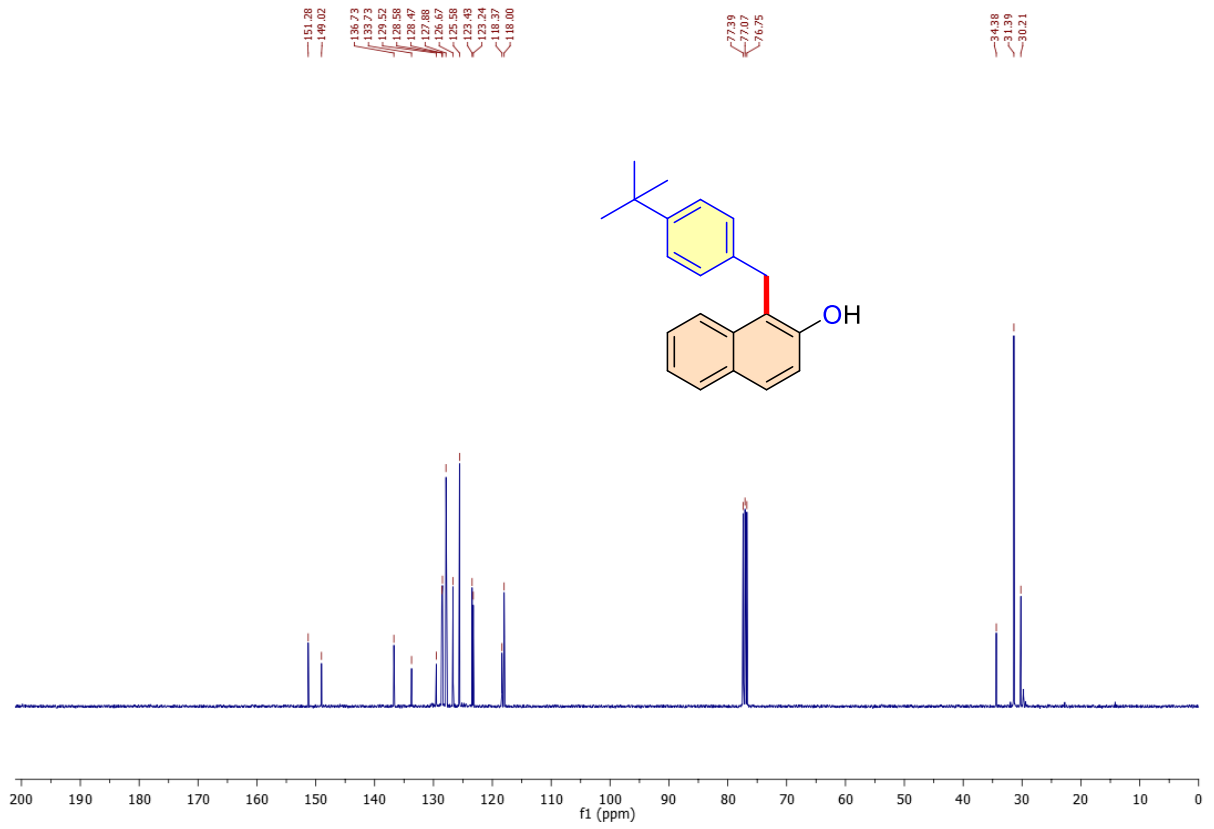

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4f** (100 MHz, $CDCl_3$).

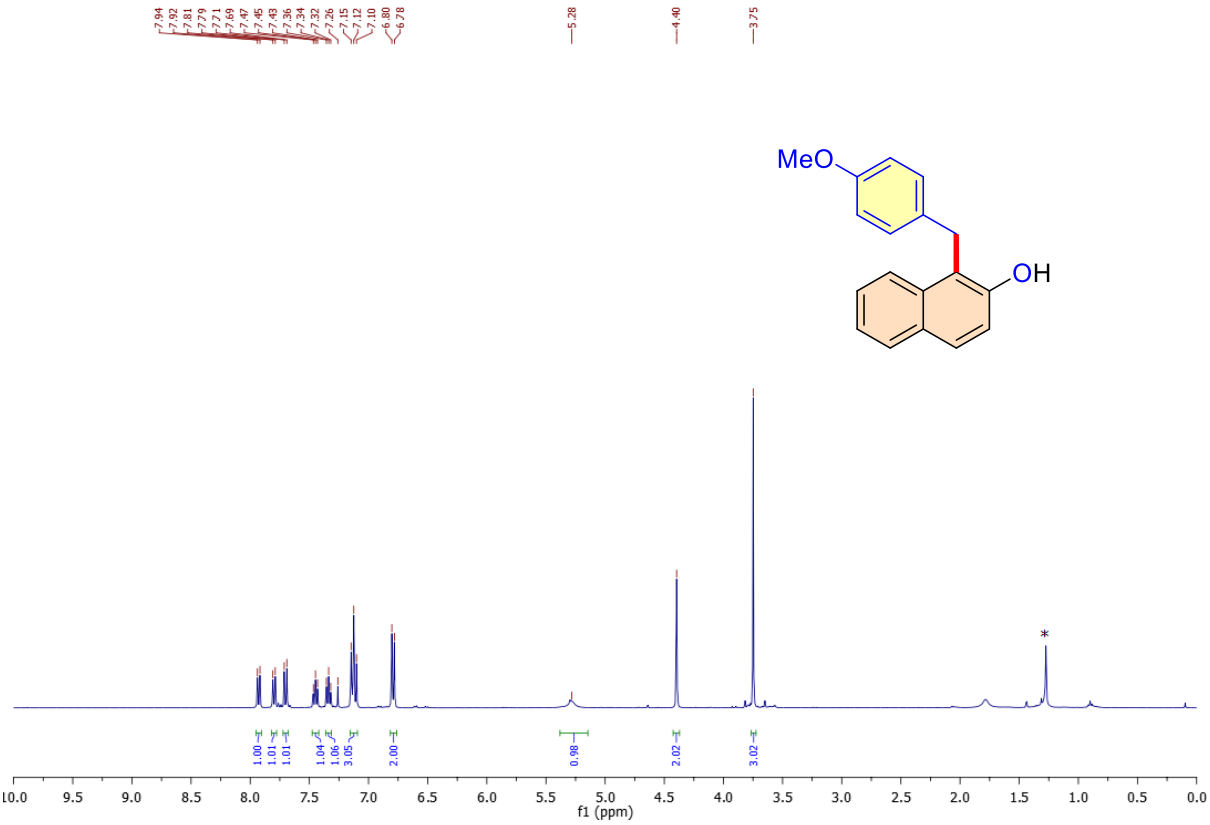

Figure S19. ^{1}H NMR spectrum of compound **4g** (400 MHz, $CDCl_3$) (*Hexane).

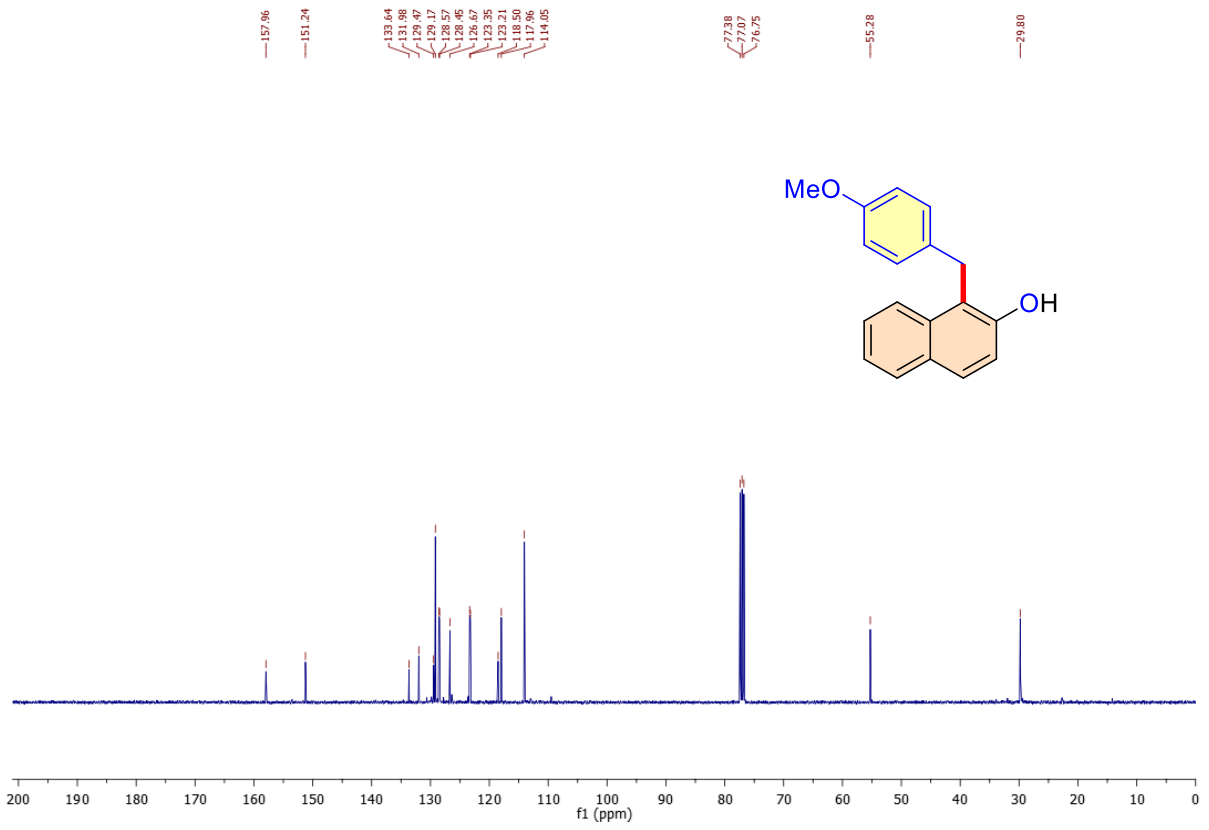

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4g** (100 MHz, $CDCl_3$).

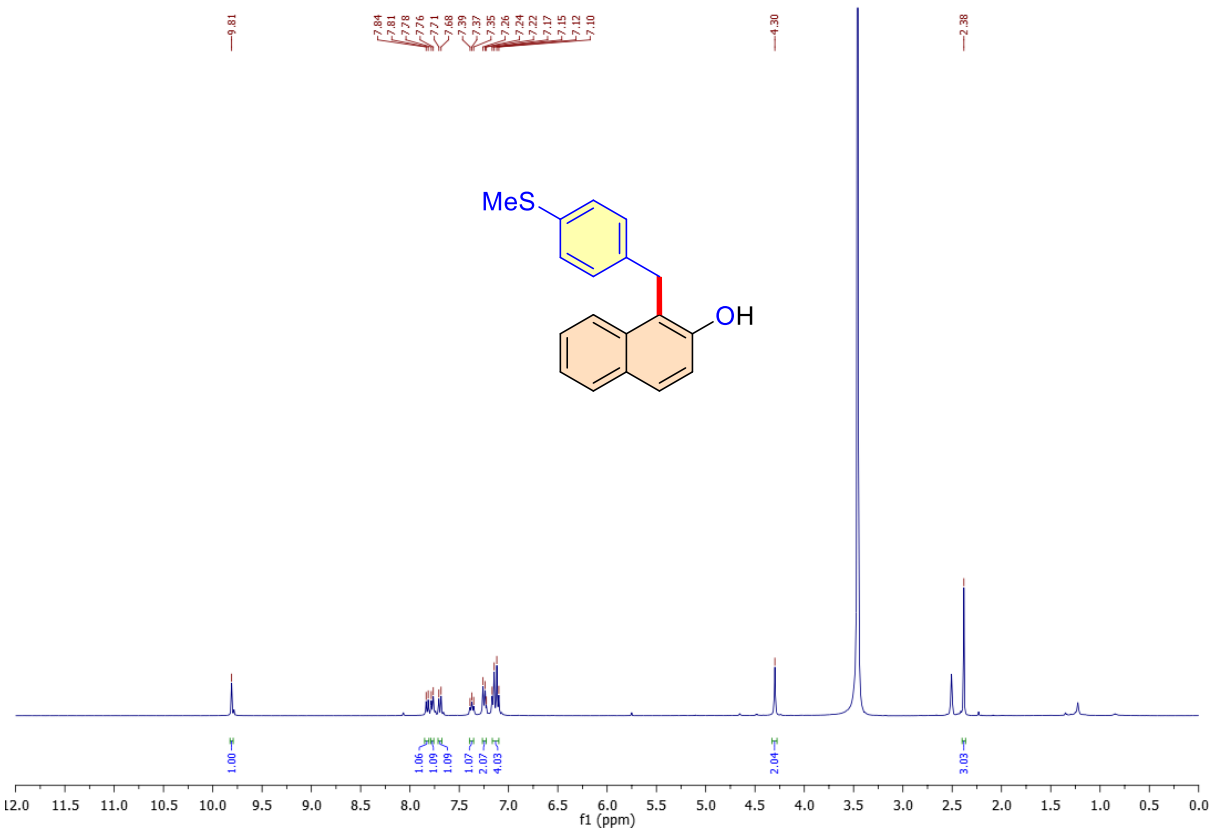

Figure S21. ^{1}H NMR spectrum of compound **4h** (400 MHz, DMSO-d^{6}).

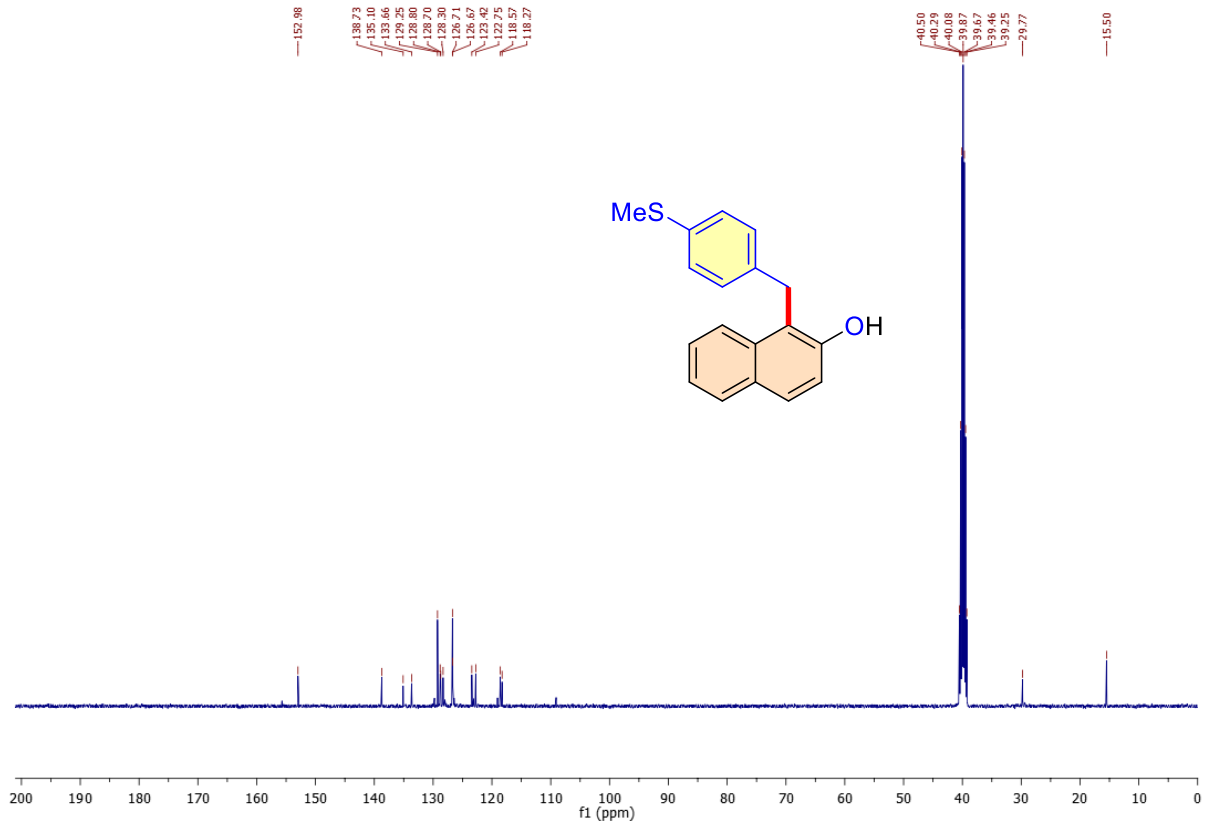

Figure S22. ^{13}C{^{1}H} NMR spectrum of compound **4h** (100 MHz, DMSO-d^{6}).

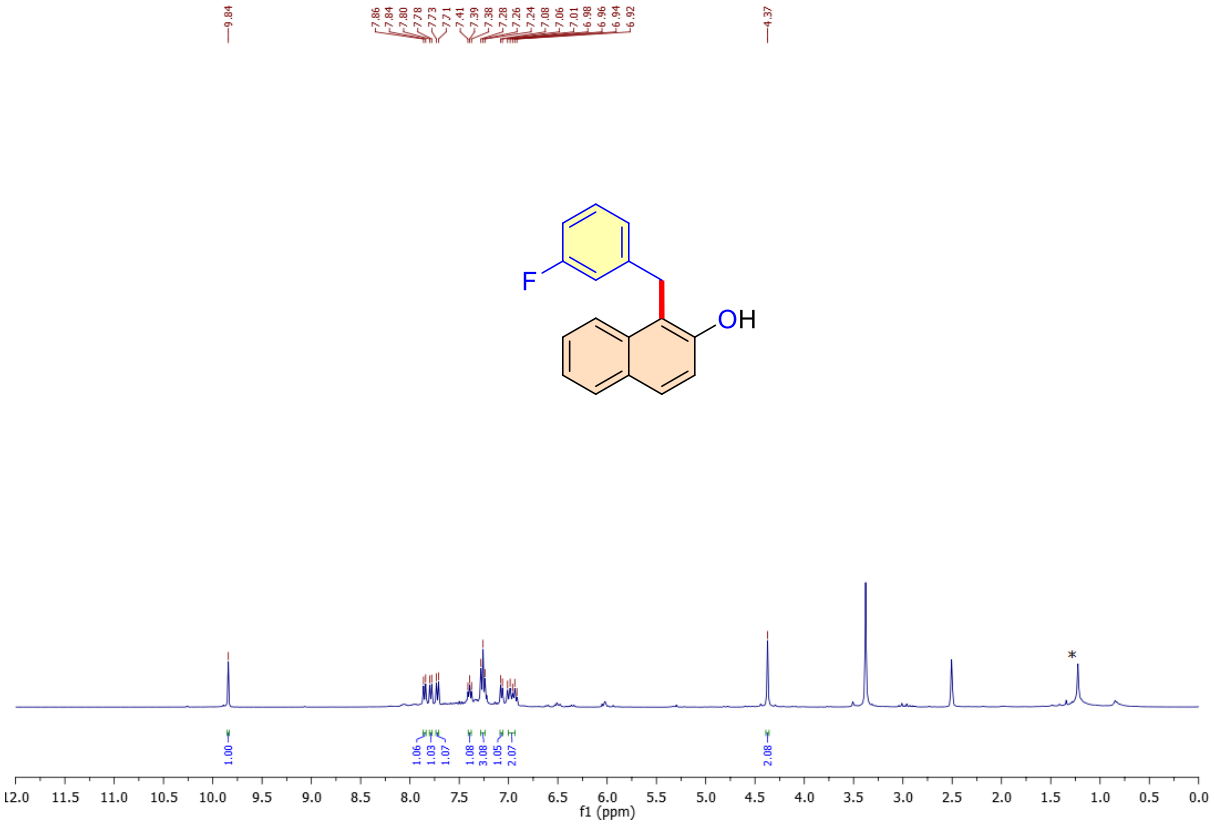

Figure S23. ^{1}H NMR spectrum of compound **4i** (400 MHz, DMSO-d^{6}) (*Hexane).

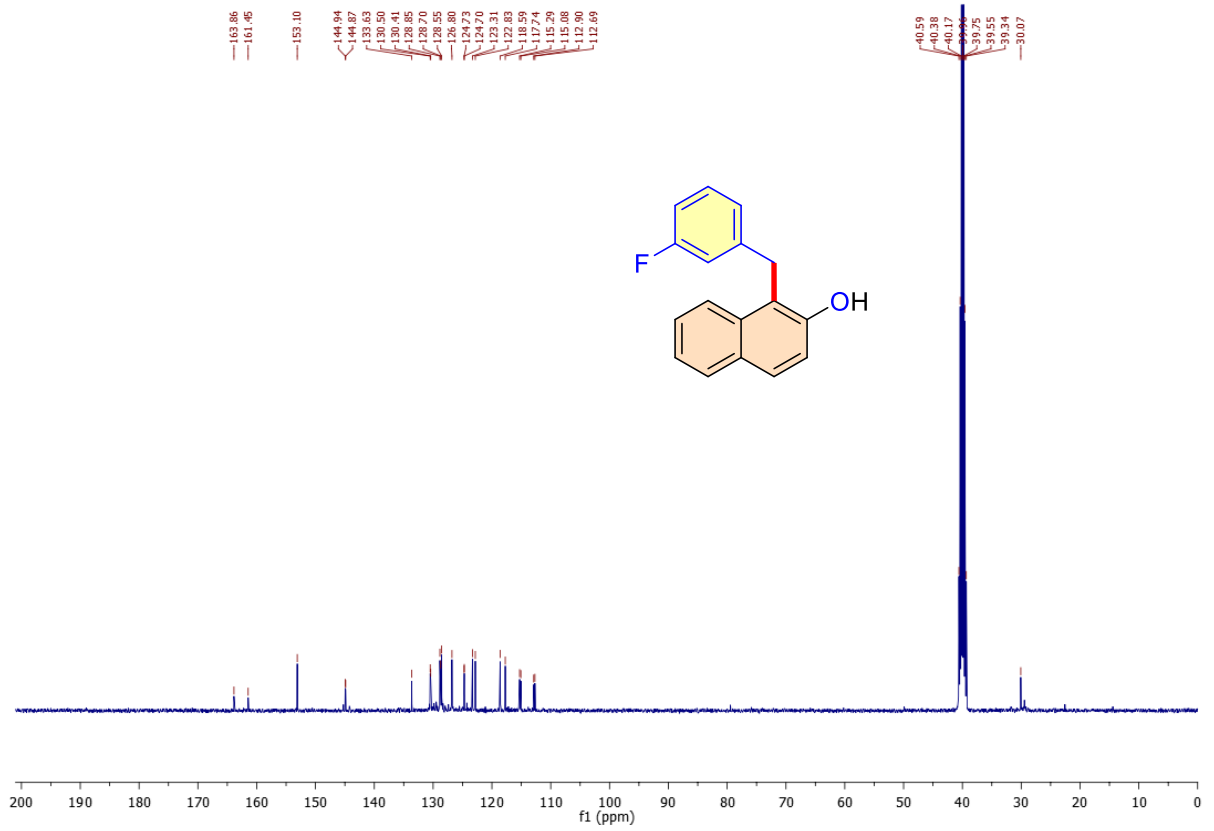

Figure S24. ^{13}C{^{1}H} NMR spectrum of compound **4i** (100 MHz, DMSO-d^{6}).

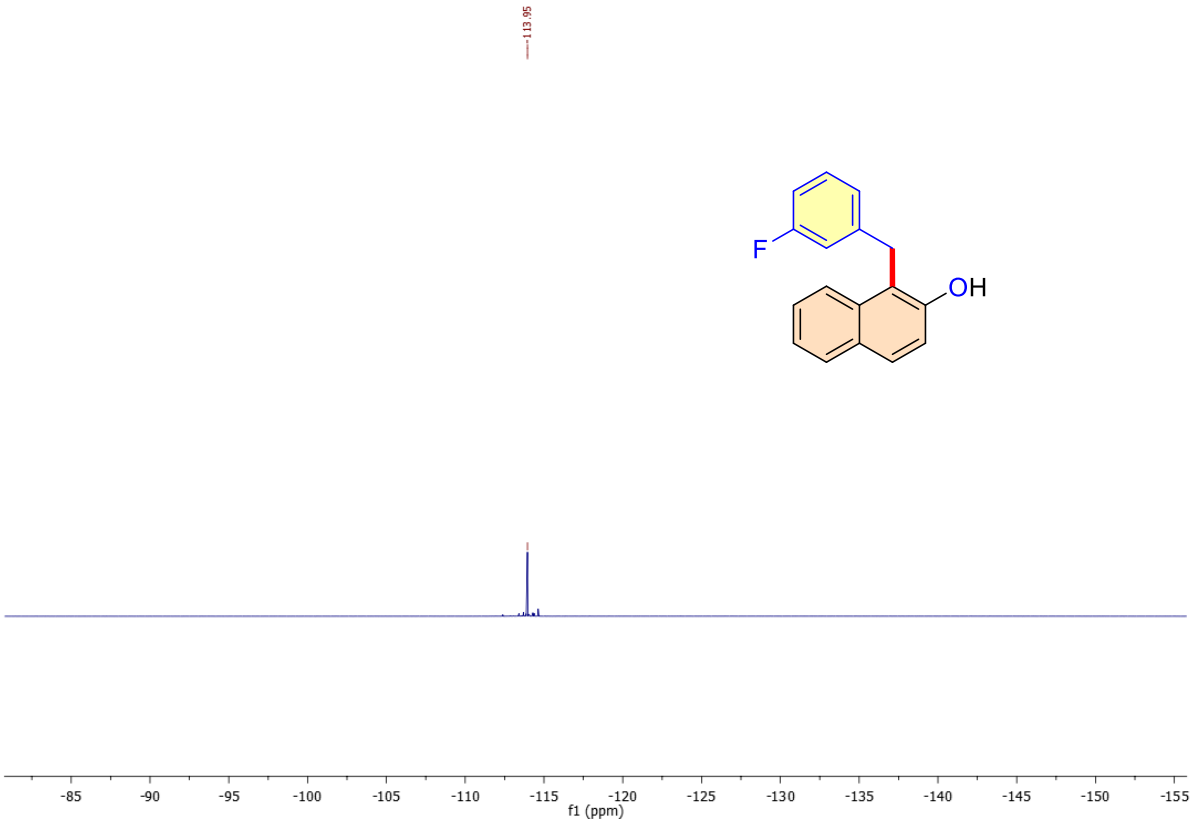

Figure S25. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4i** (376 MHz, DMSO-d^6).

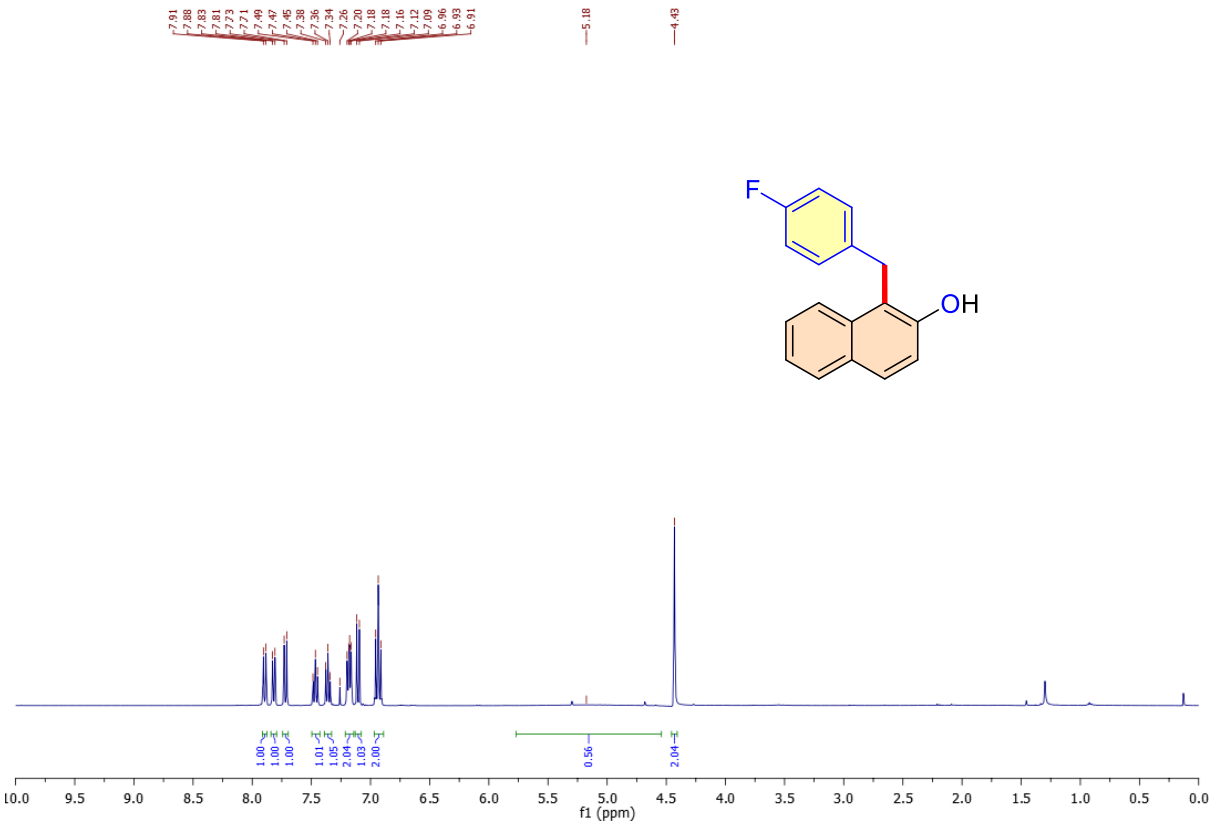

Figure S26. ^{1}H NMR spectrum of compound **4j** (400 MHz, $CDCl_3$).

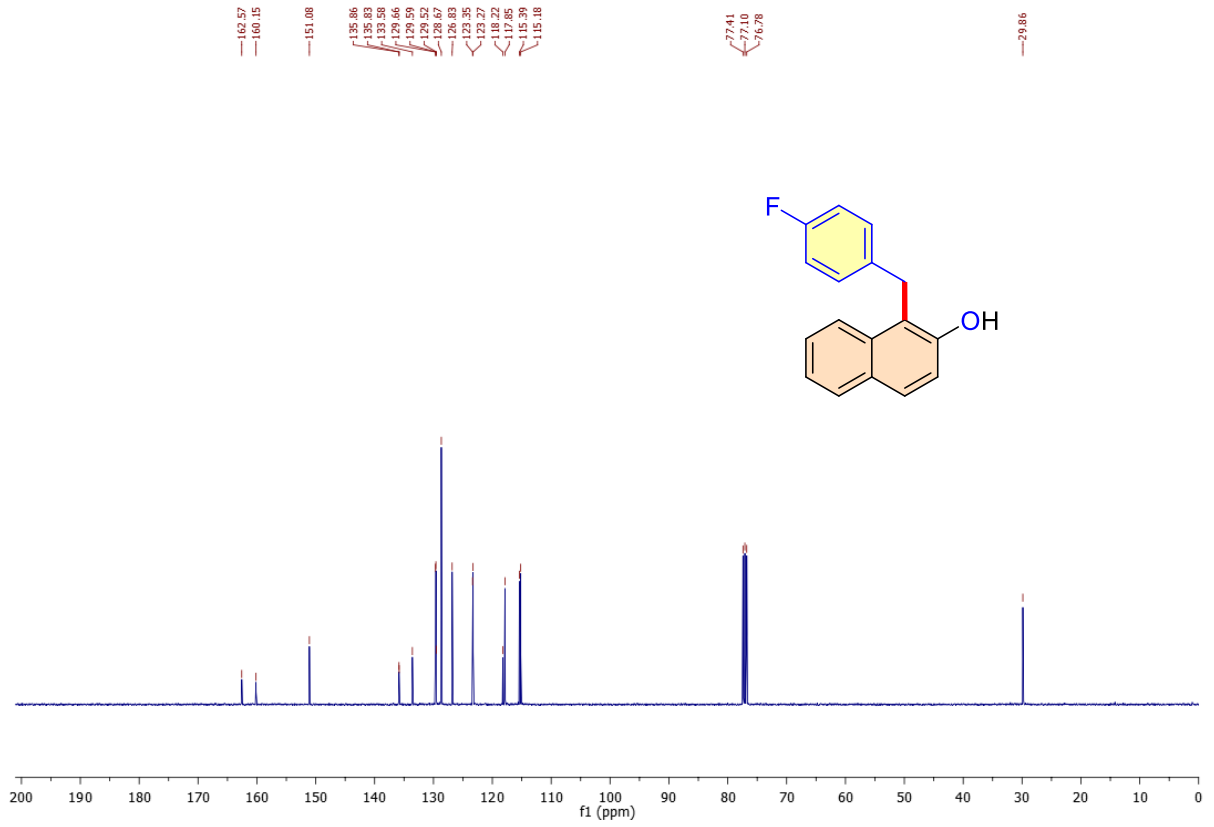

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4j** (100 MHz, $CDCl_3$).

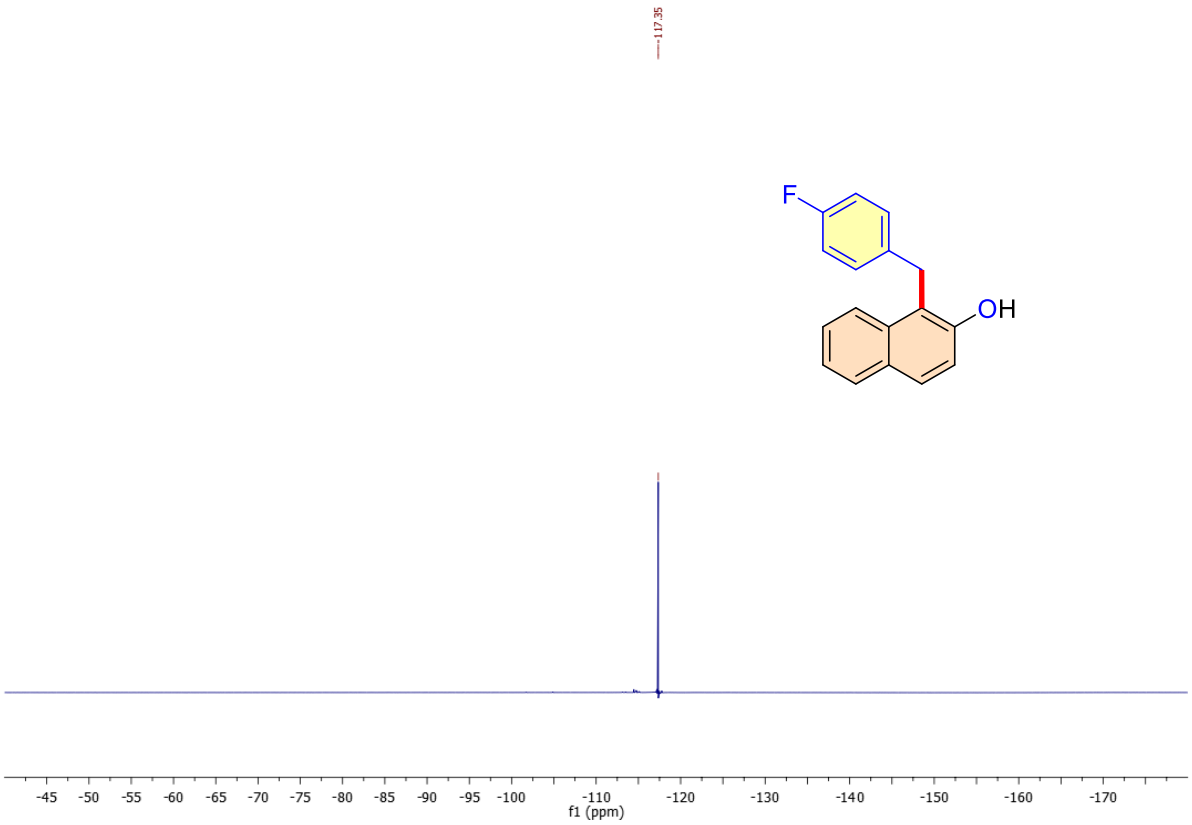

Figure S28. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4j** (376 MHz, $CDCl_3$).

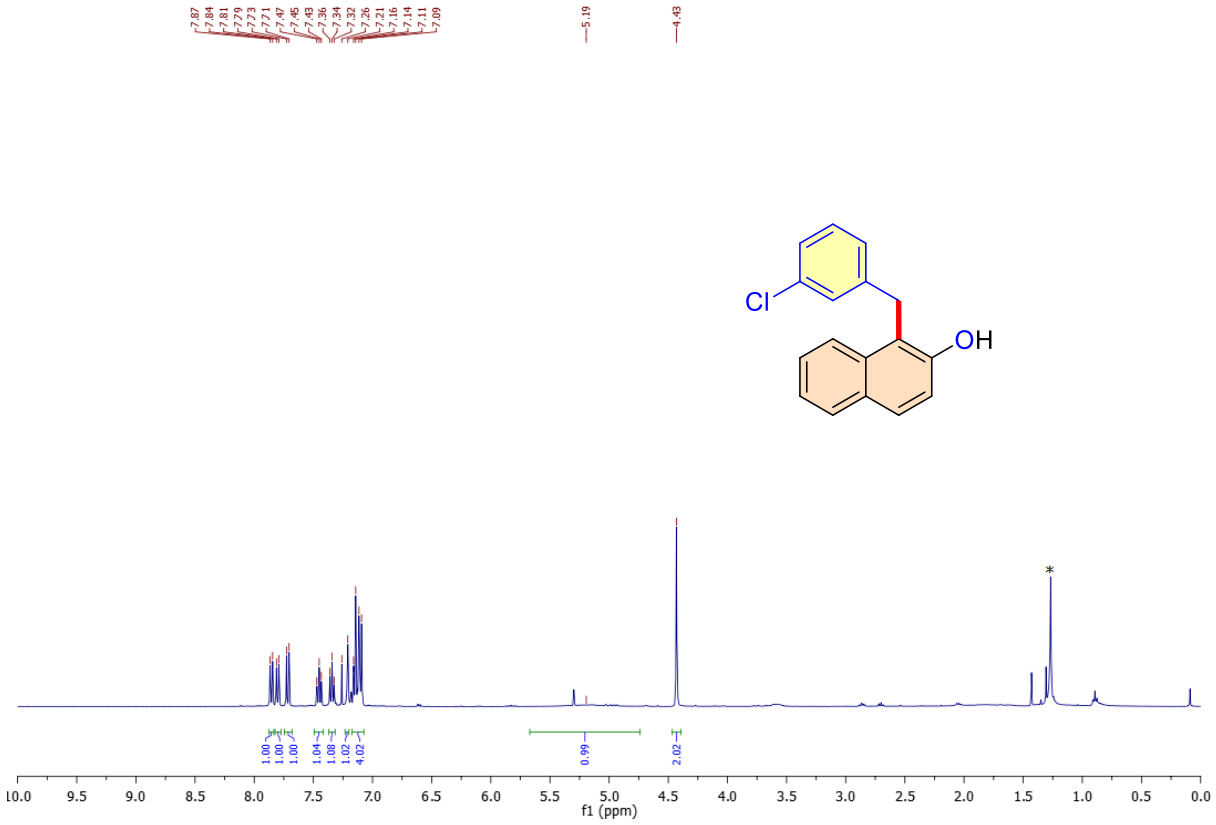

Figure S29. ^{1}H NMR spectrum of compound **4k** (400 MHz, $CDCl_3$) (*Hexane).

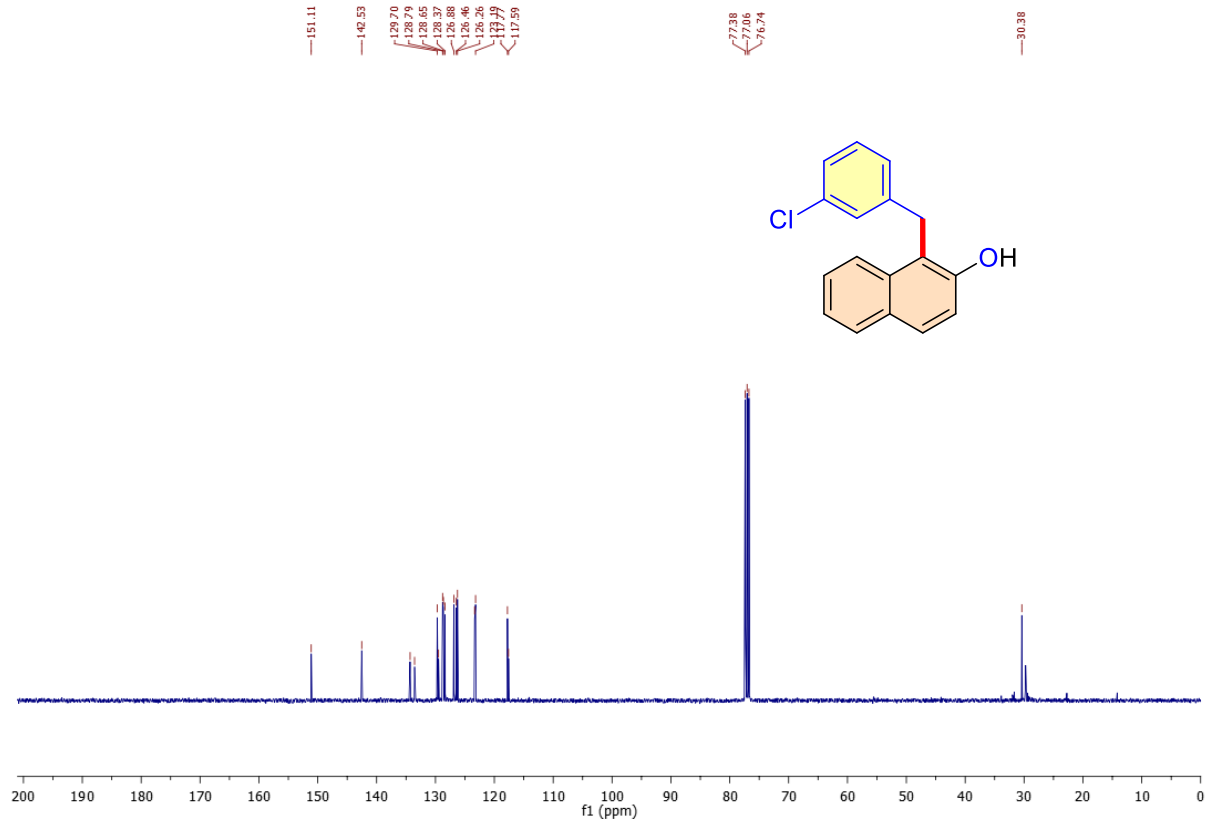

Figure S30. ^{13}C{^{1}H} NMR spectrum of compound **4k** (100 MHz, $CDCl_3$).

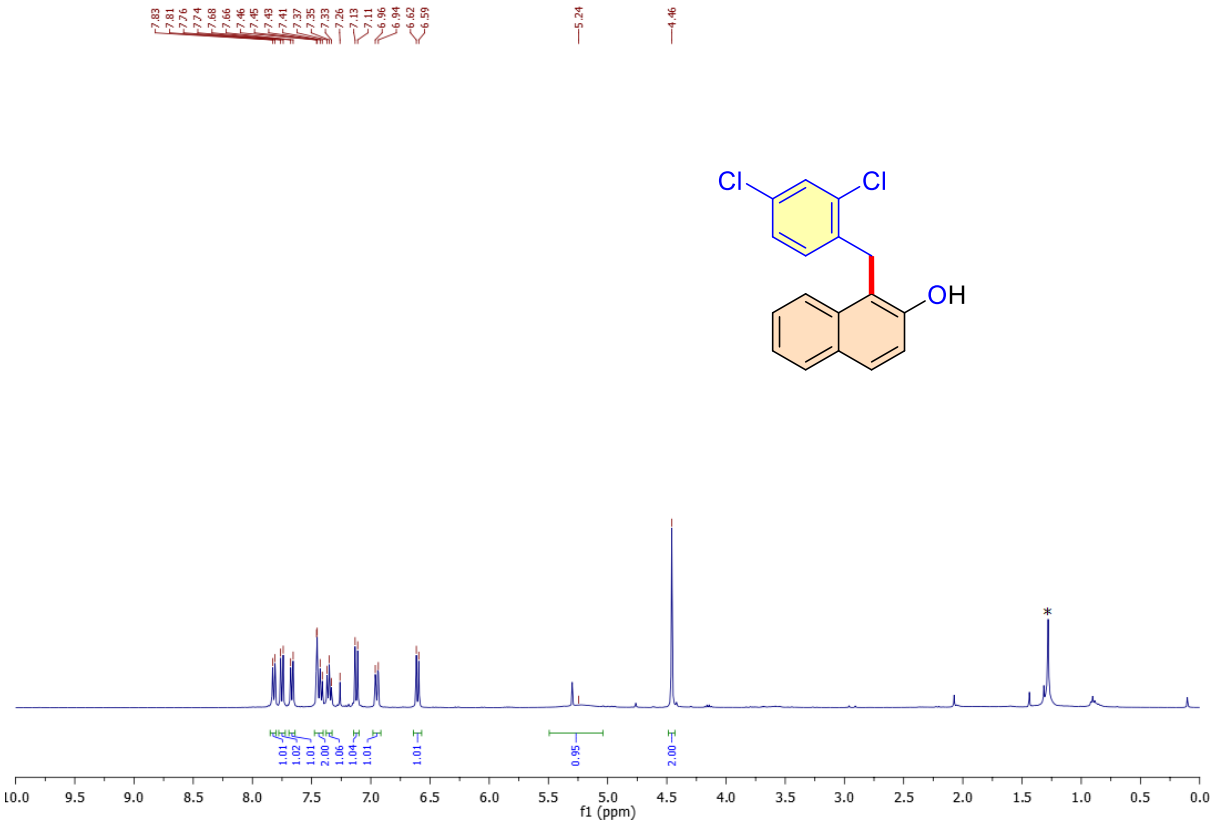

Figure S31. ^{1}H NMR spectrum of compound **4l** (400 MHz, $CDCl_3$) (*Hexane).

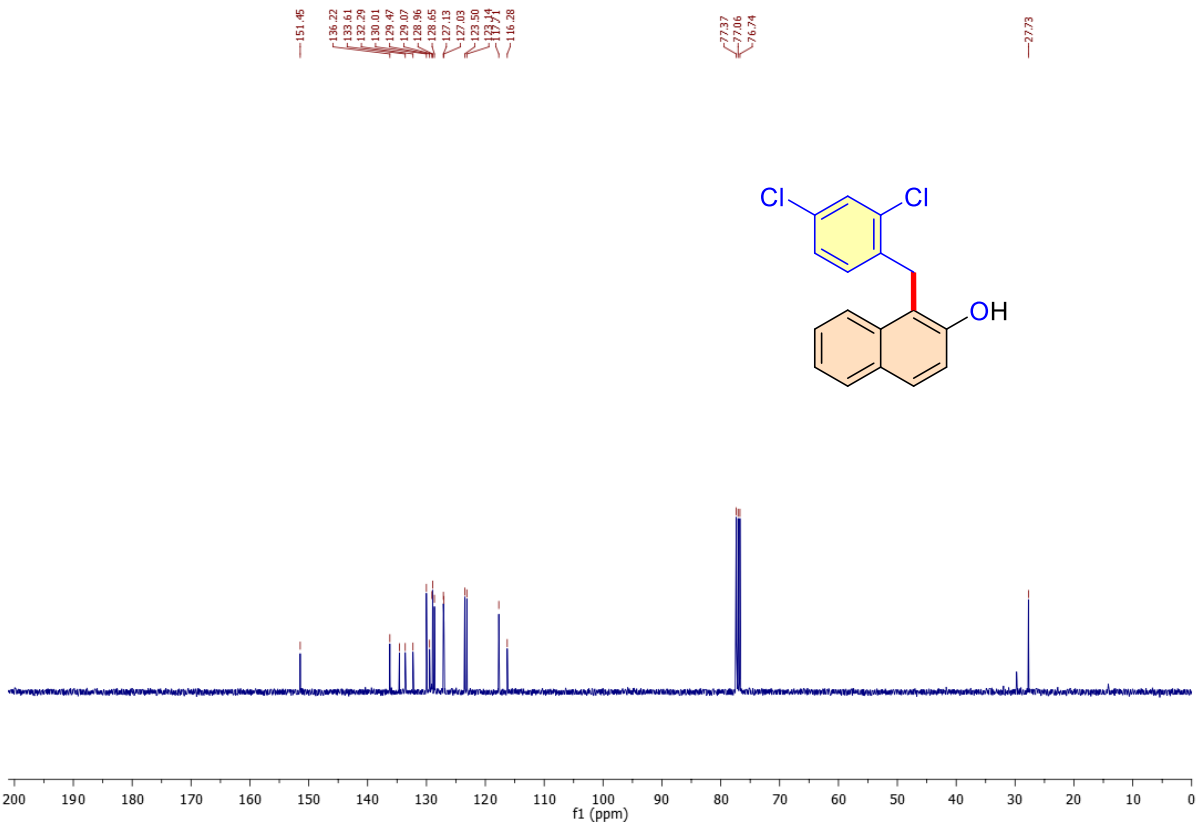

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4l** (100 MHz, $CDCl_3$).

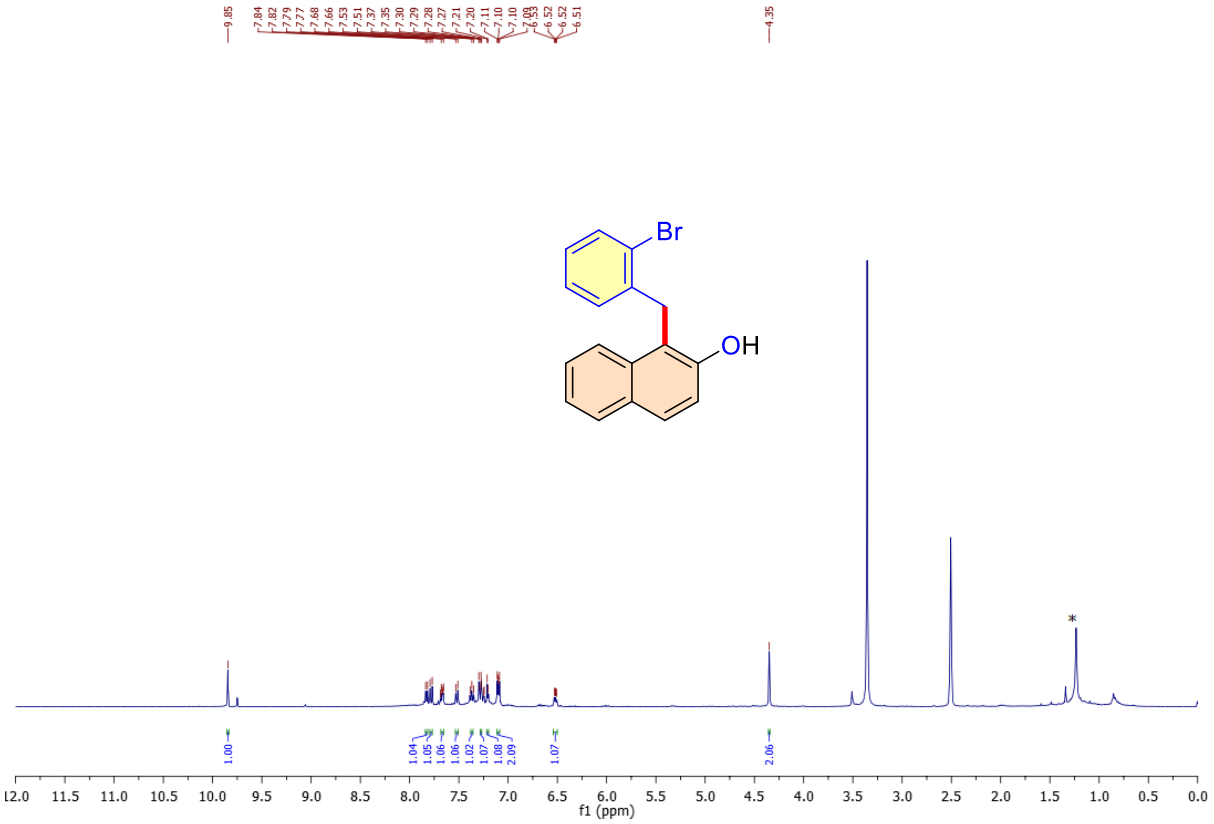

Figure S33. ^{1}H NMR spectrum of compound **4m** (400 MHz, DMSO-d^{6}) (*Hexane).

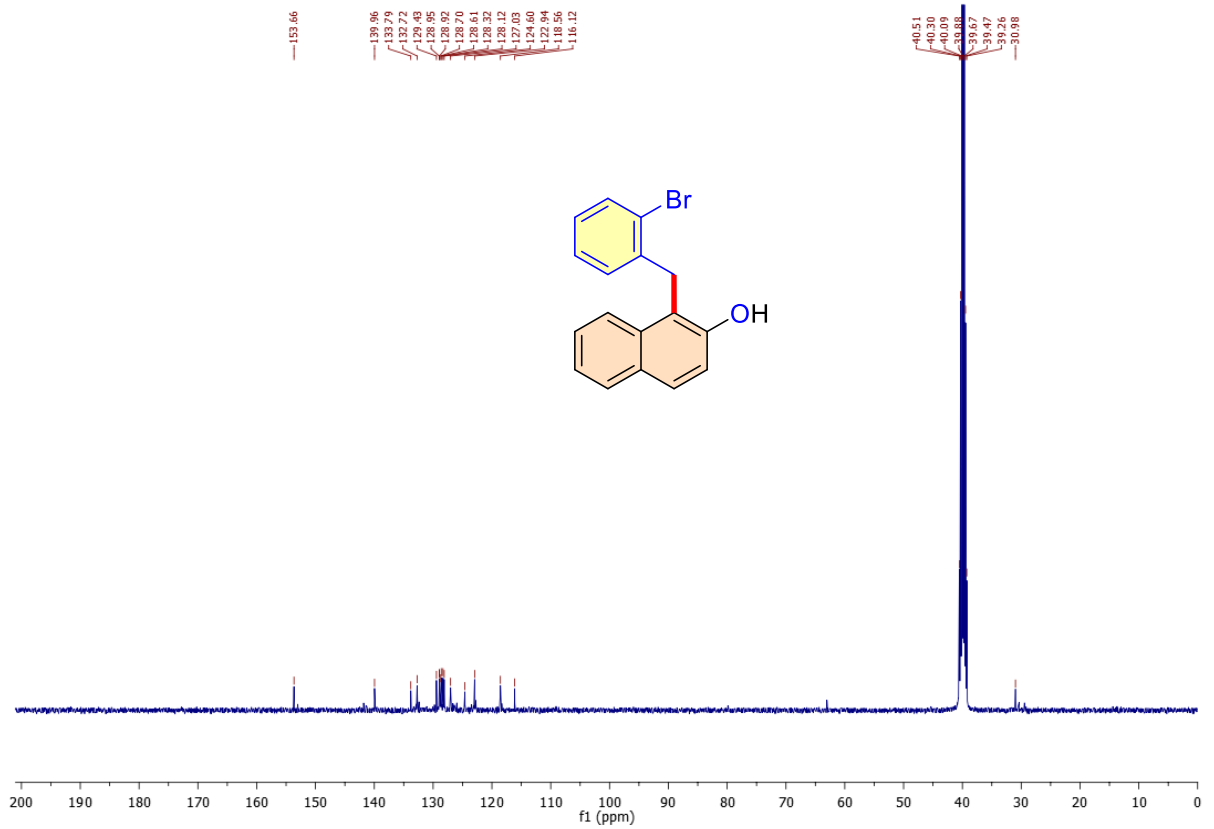

Figure S34. ^{13}C{^{1}H} NMR spectrum of compound **4m** (100 MHz, DMSO-d^{6}).

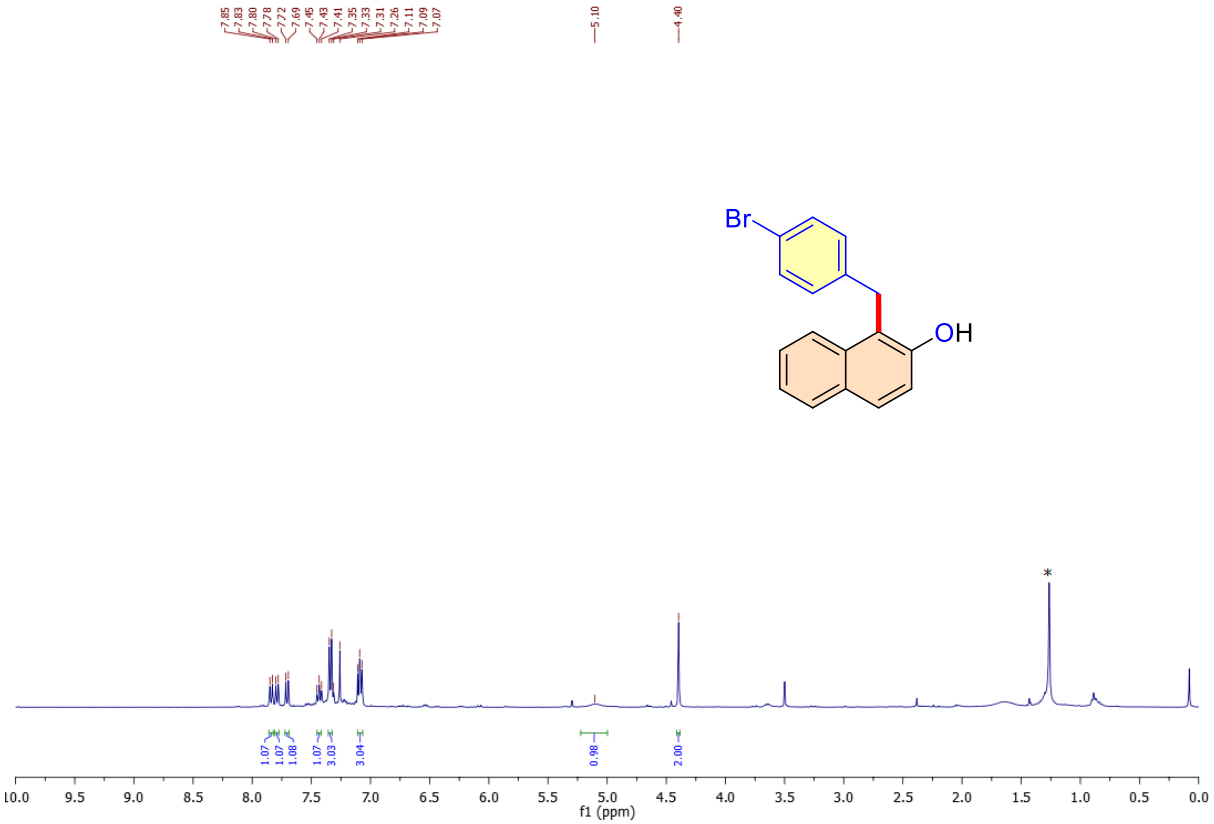

Figure S35. ^{1}H NMR spectrum of compound **4n** (400 MHz, $CDCl_3$) (*Hexane).

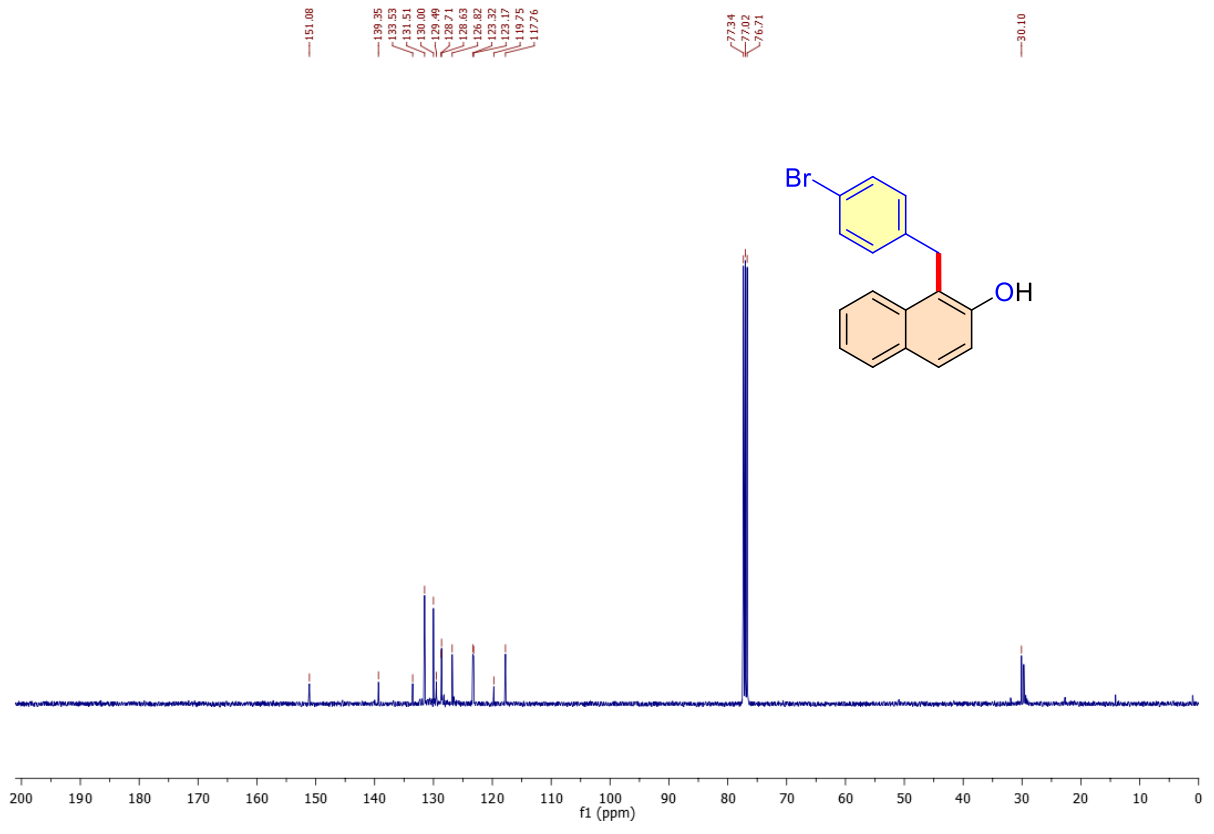

Figure S36. ^{13}C{^{1}H} NMR spectrum of compound **4n** (100 MHz, $CDCl_3$).

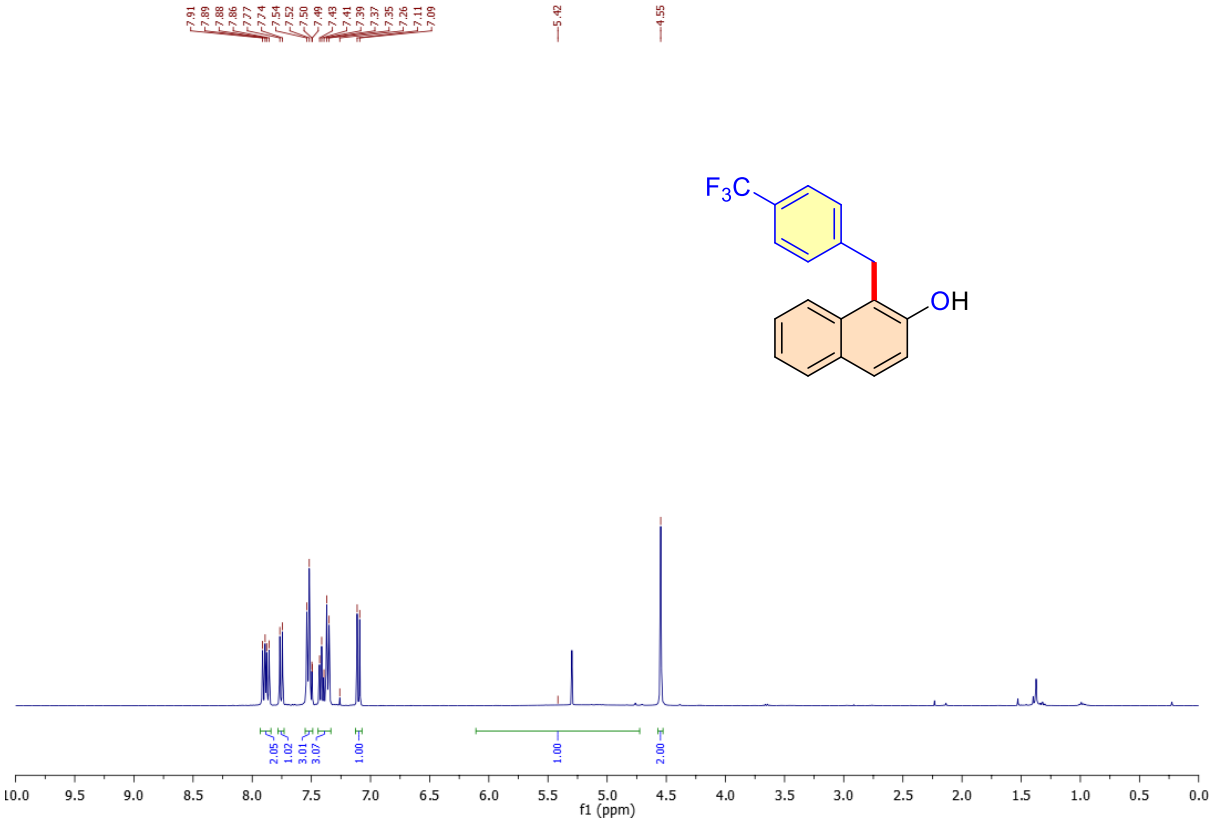

Figure S37. ^{1}H NMR spectrum of compound **4o** (400 MHz, $CDCl_3$).

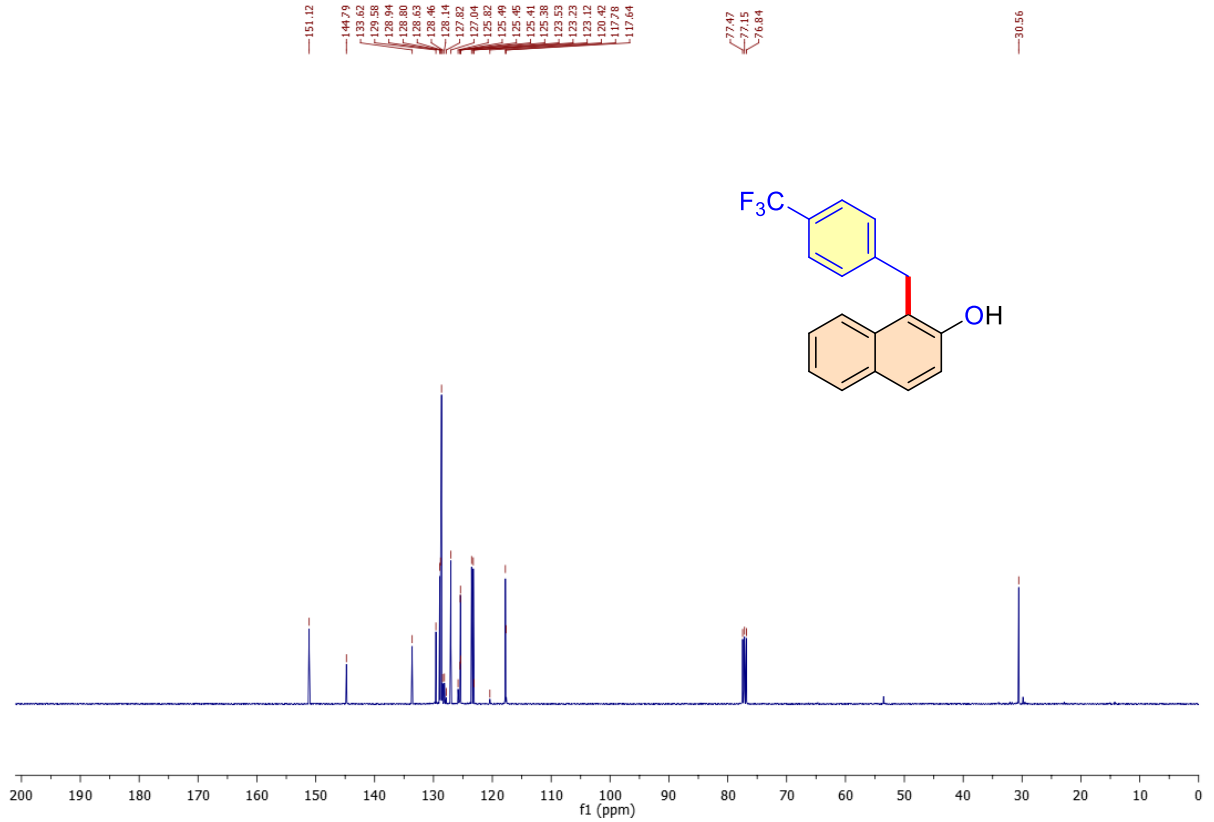

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4o** (100 MHz, $CDCl_3$).

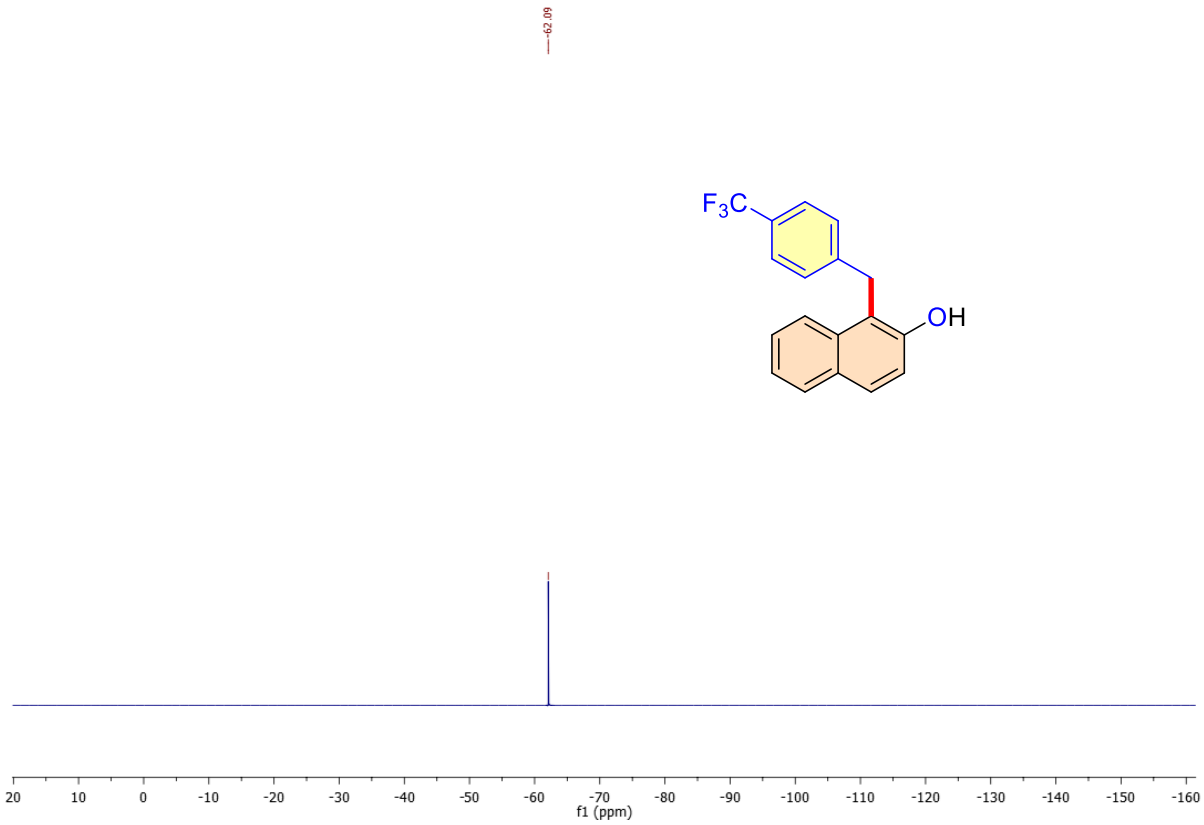

Figure S39. $^{19}F\{^{1}H\}$ NMR spectrum of compound **4o** (376 MHz, $CDCl_3$).

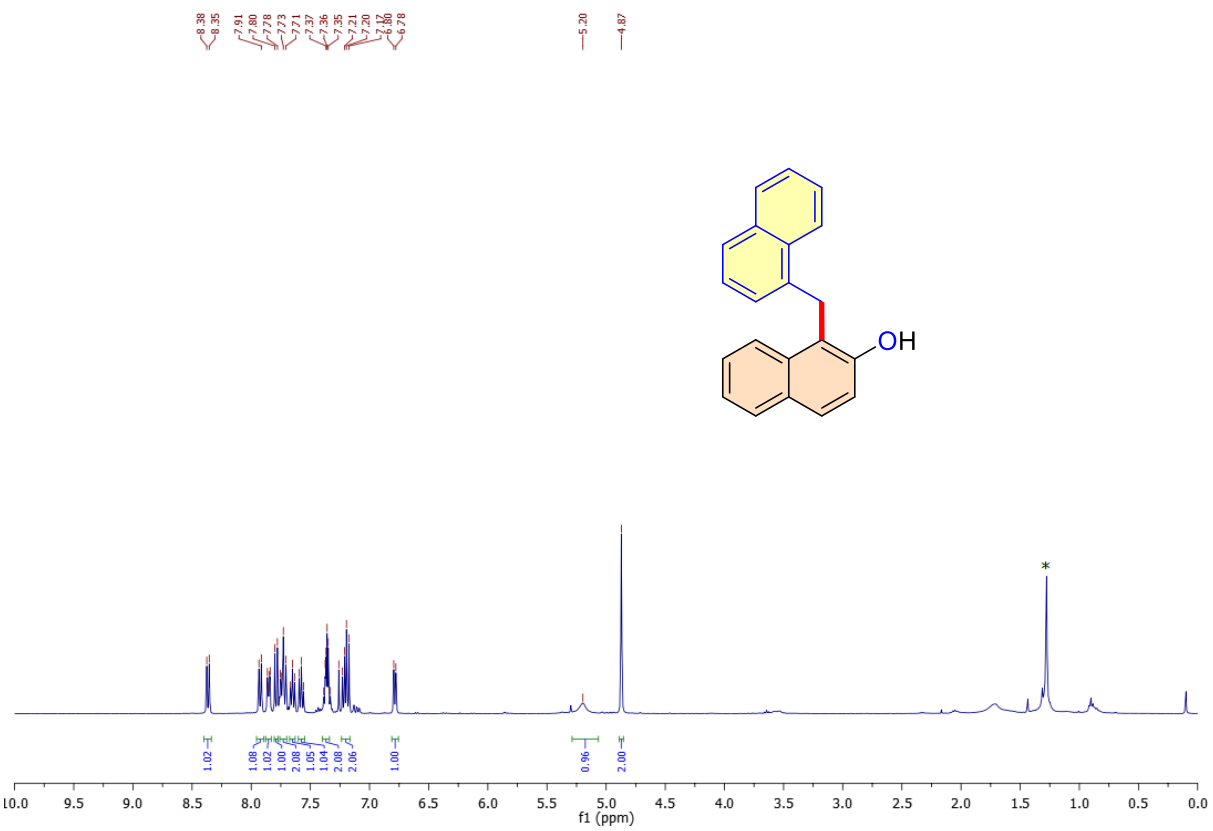

Figure S40. ^{1}H NMR spectrum of compound **4p** (400 MHz, $CDCl_3$) (*Hexane).

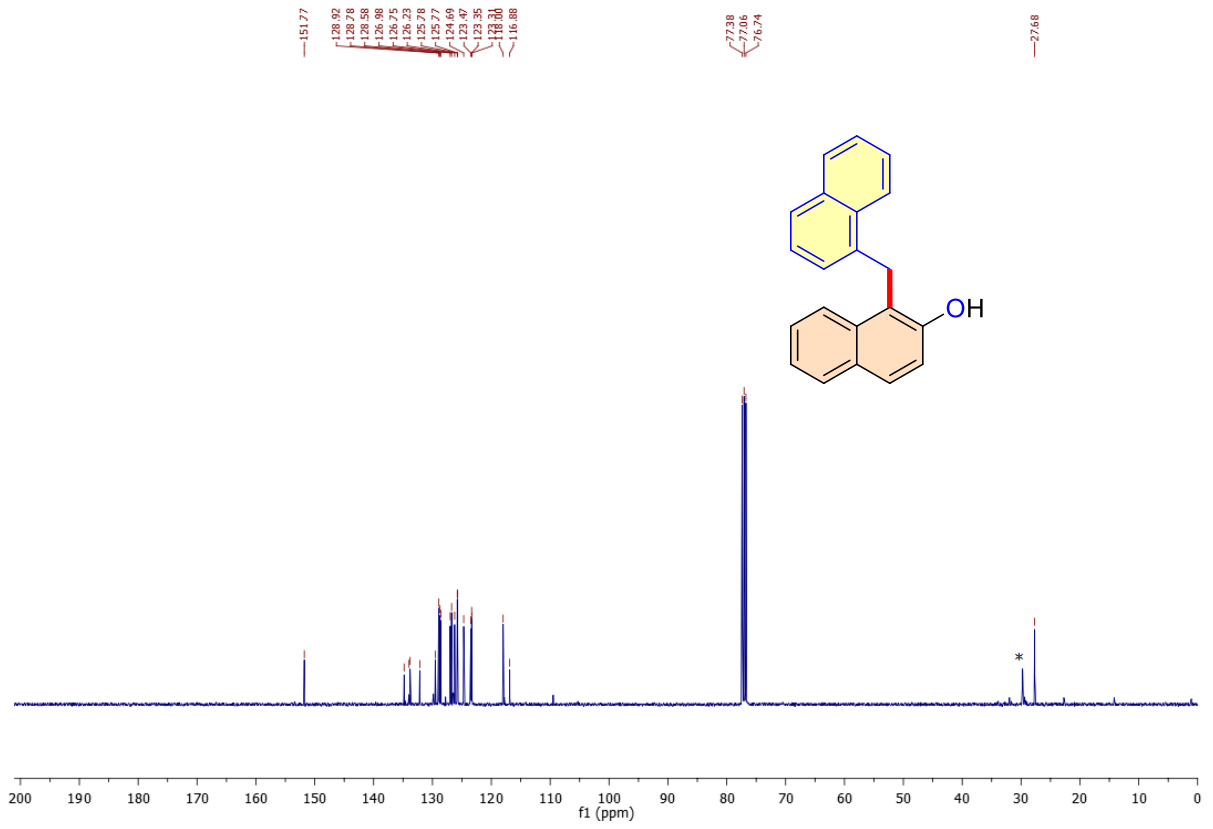

Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4p** (100 MHz, $CDCl_3$) (*Hexane).

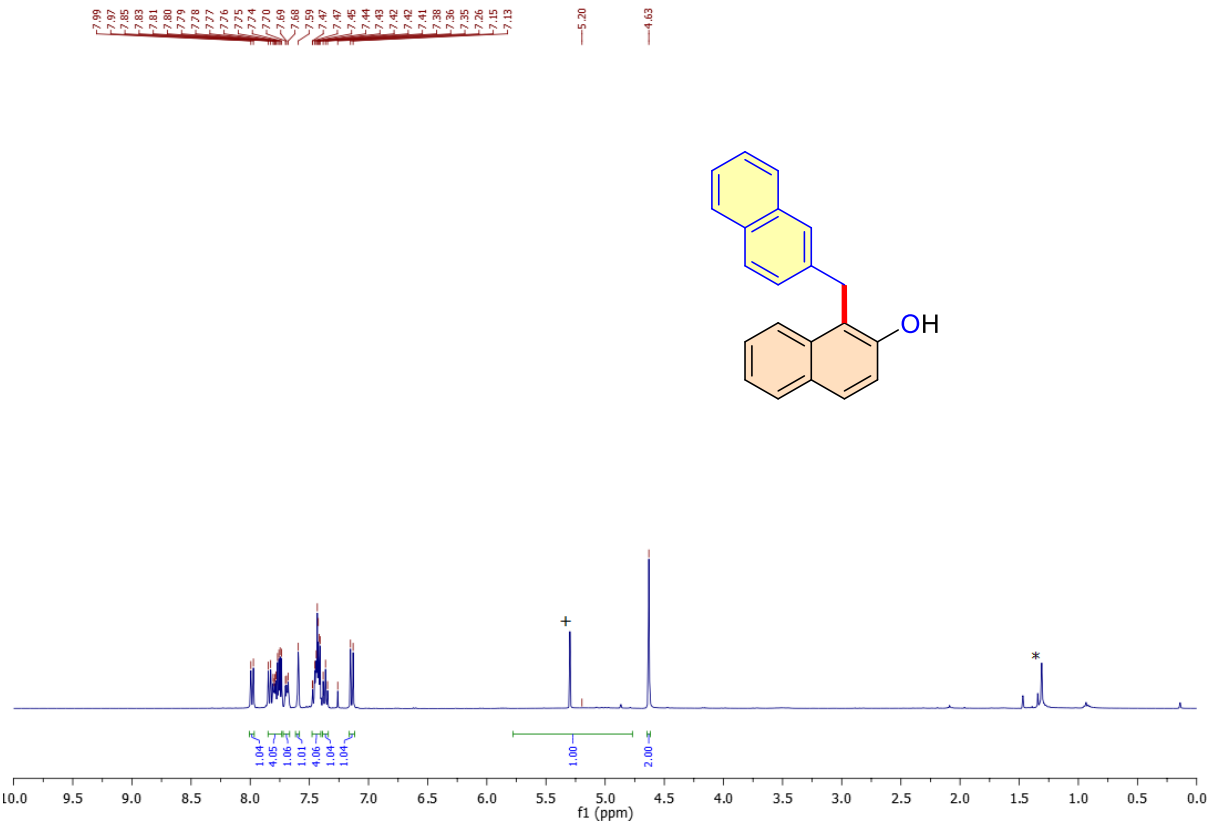

Figure S42. ^{1}H NMR spectrum of compound **4q** (400 MHz, $CDCl_3$) (*Hexane, $^{+}$Dichloromethane).

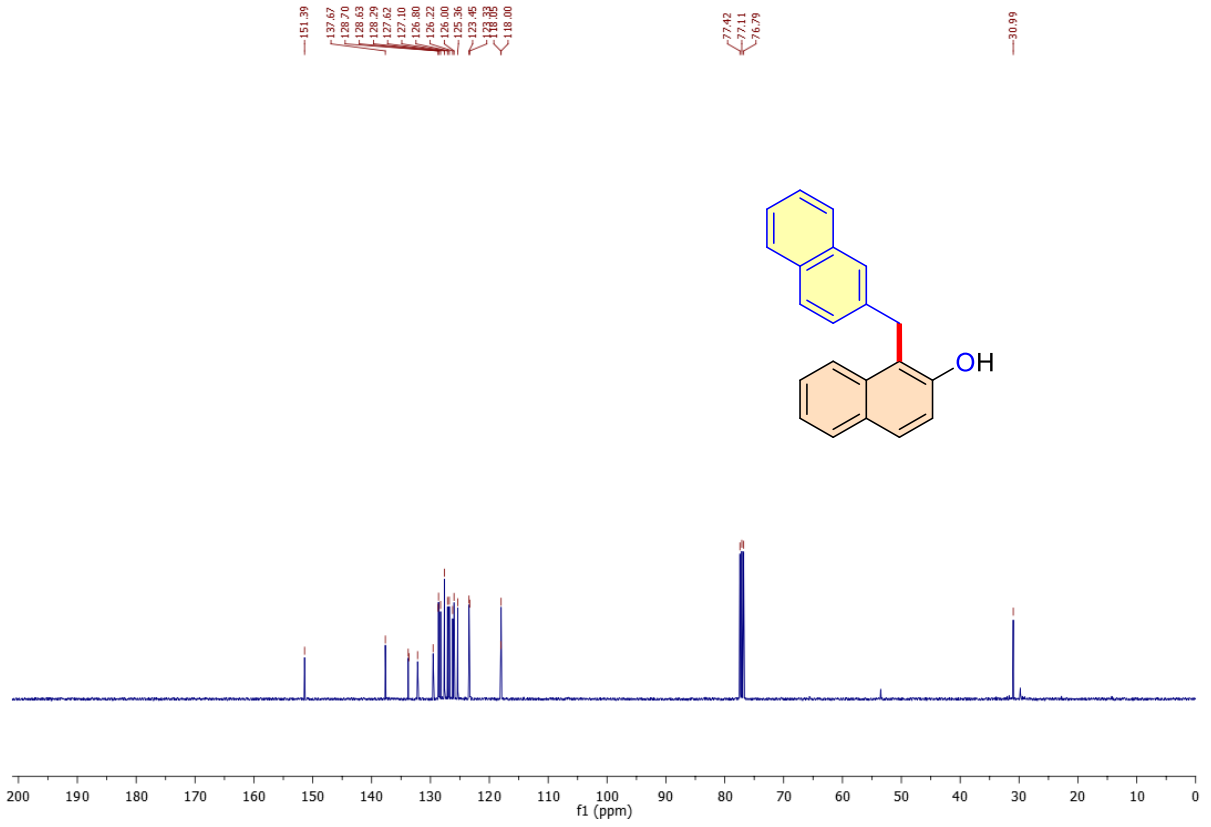

Figure S43. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4q** (100 MHz, $CDCl_3$).

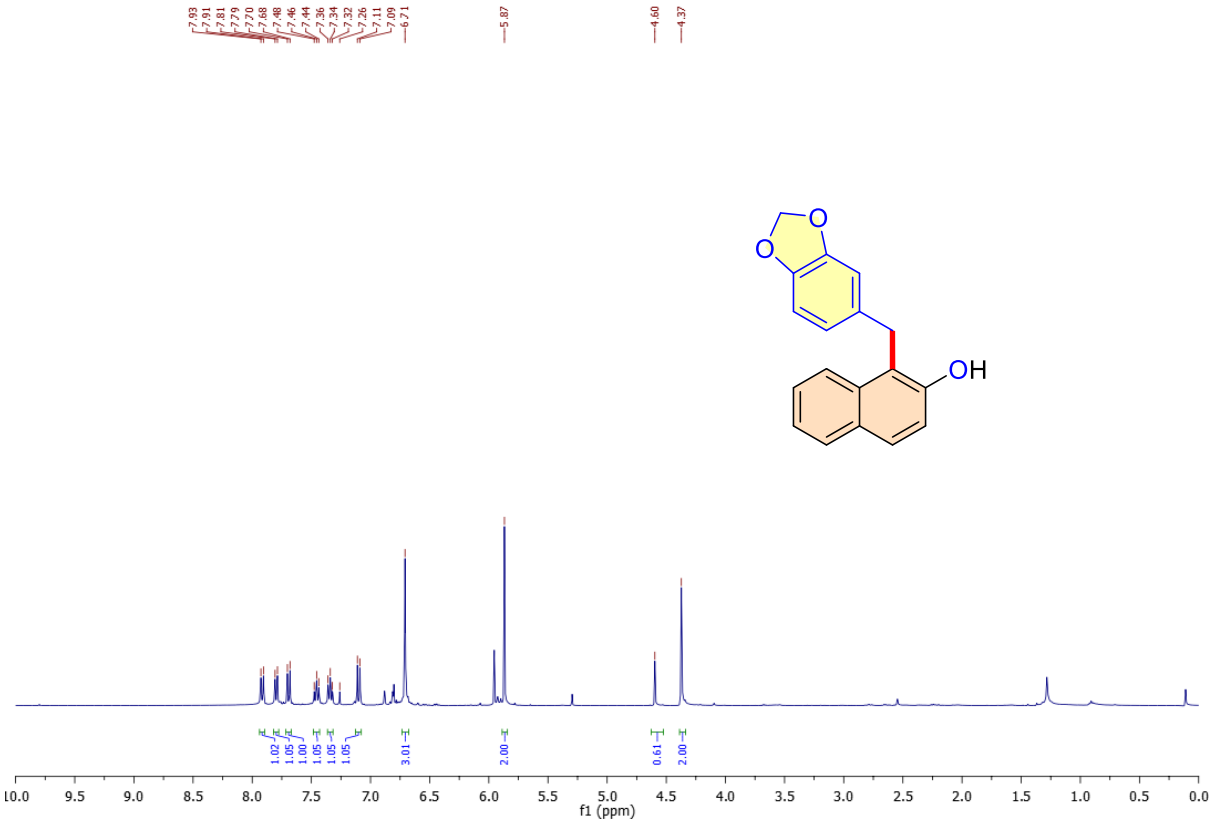

Figure S44. ^{1}H NMR spectrum of compound **4r** (400 MHz, $CDCl_3$).

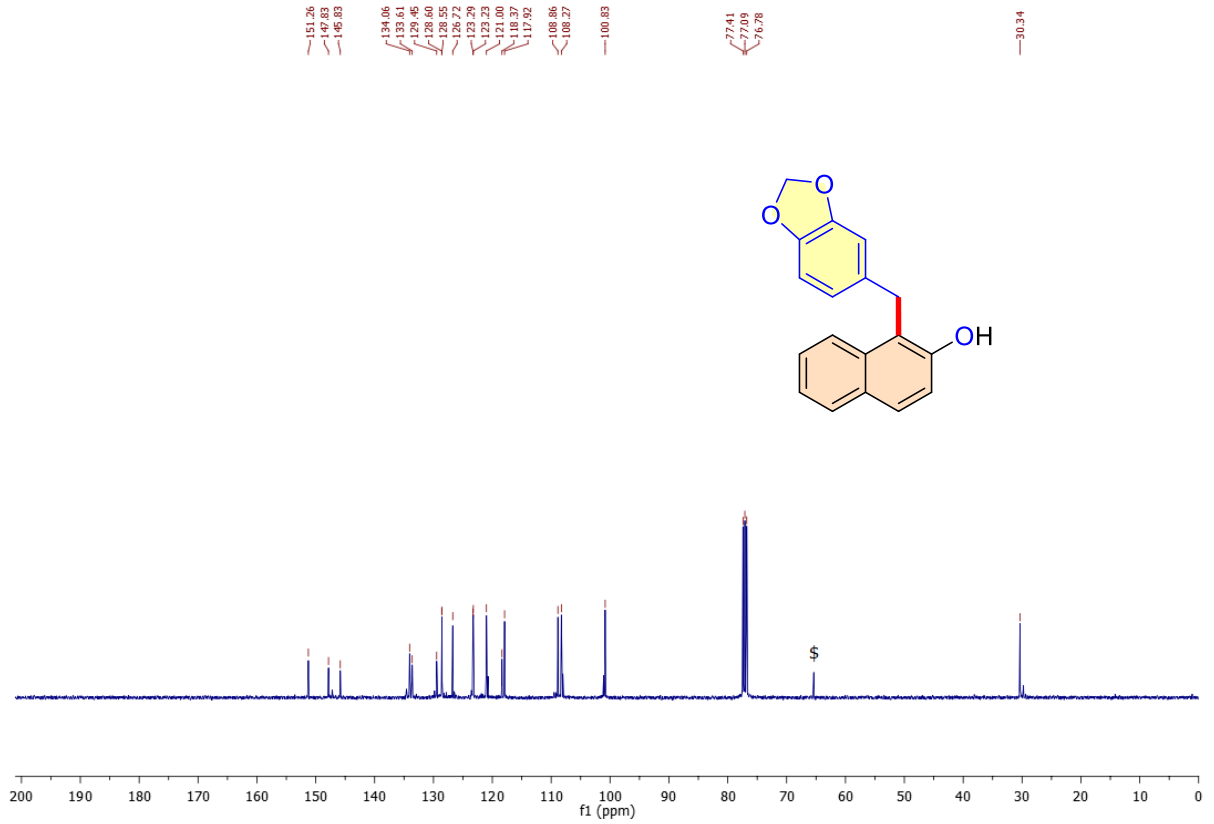

Figure S45. ^{13}C{^{1}H} NMR spectrum of compound **4r** (100 MHz, $CDCl_3$) ($^{\$}$Diethylether).

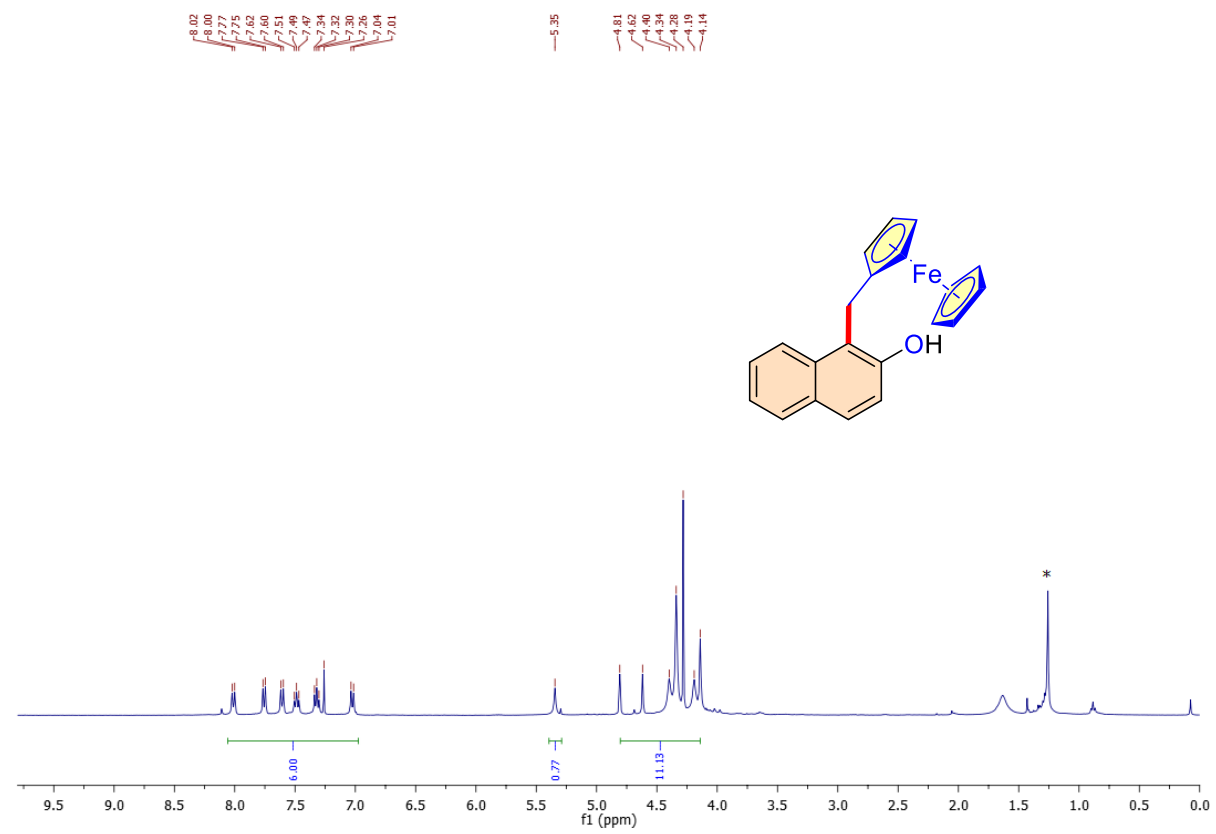

Figure S46. ^{1}H NMR spectrum of compound **4s** (400 MHz, $CDCl_3$) (*Hexane).

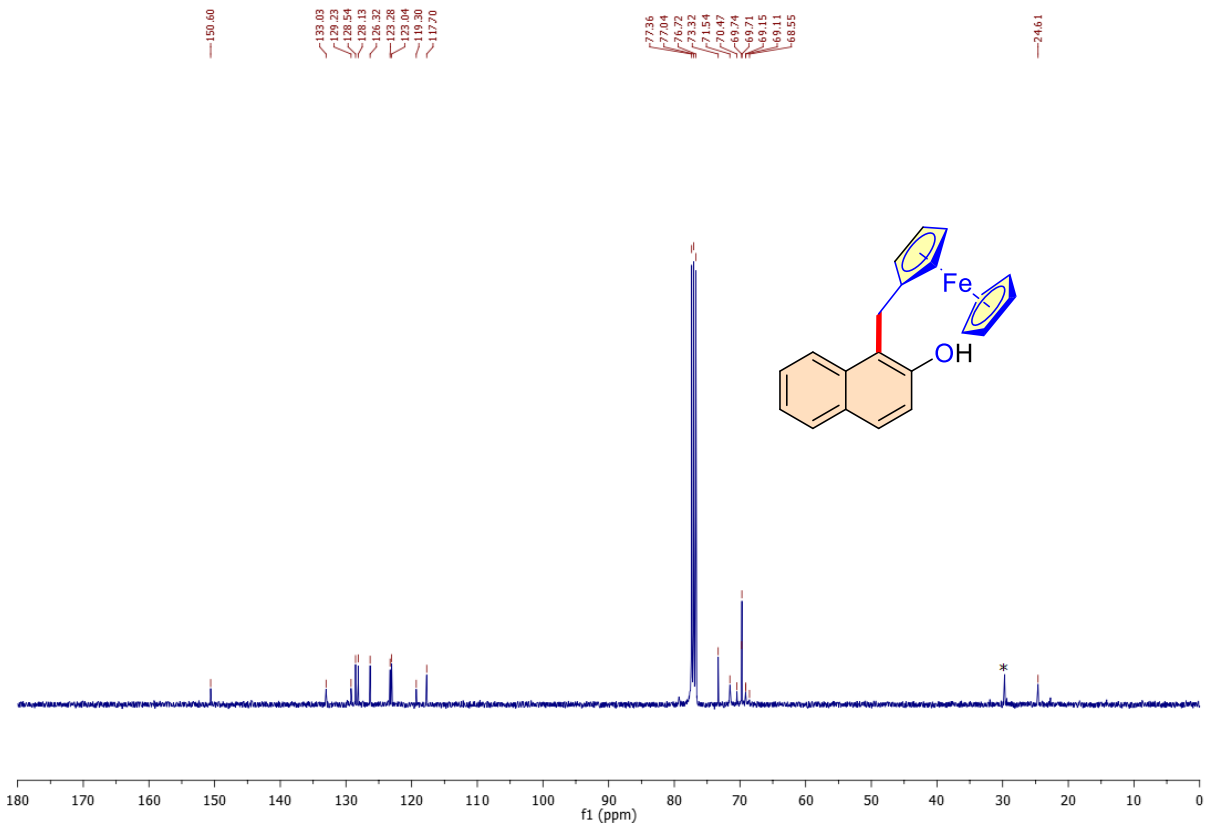

Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4s** (100 MHz, $CDCl_3$) (*Hexane).

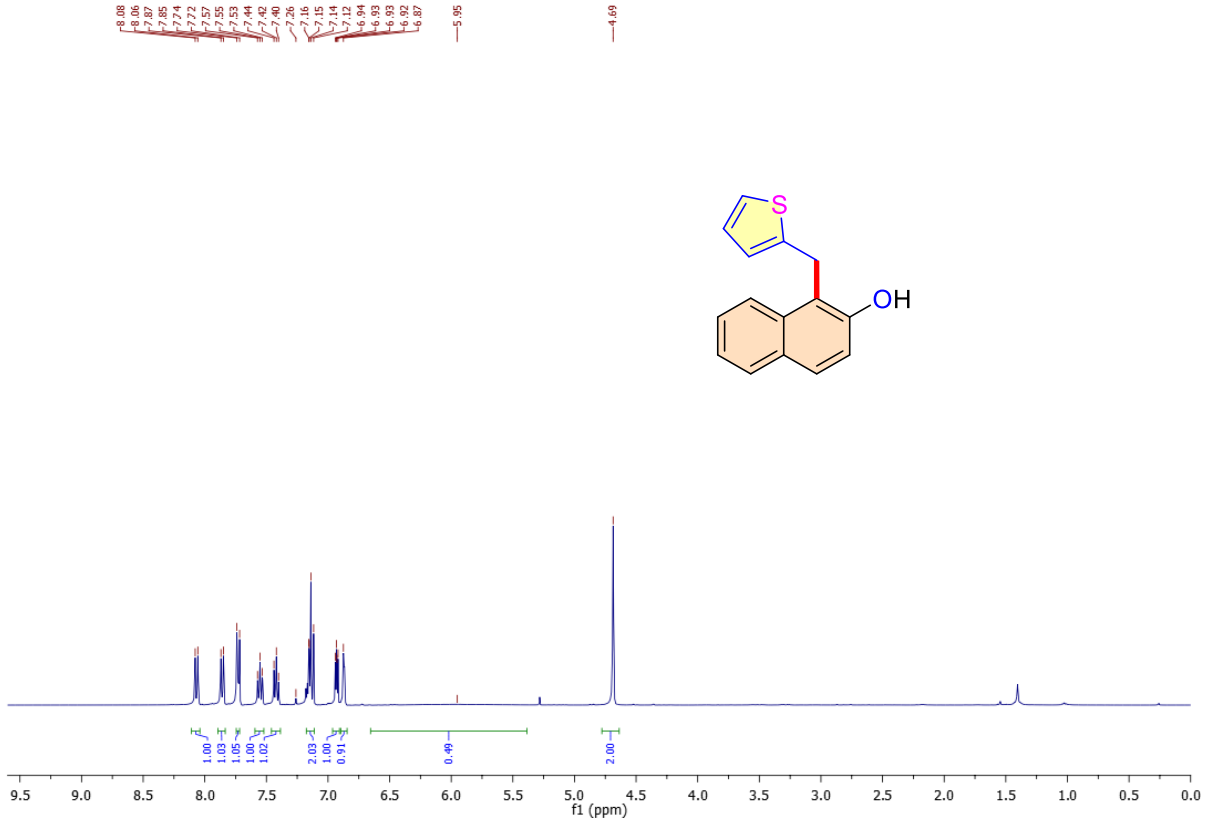

Figure S48. ^{1}H NMR spectrum of compound **4t** (400 MHz, $CDCl_3$).

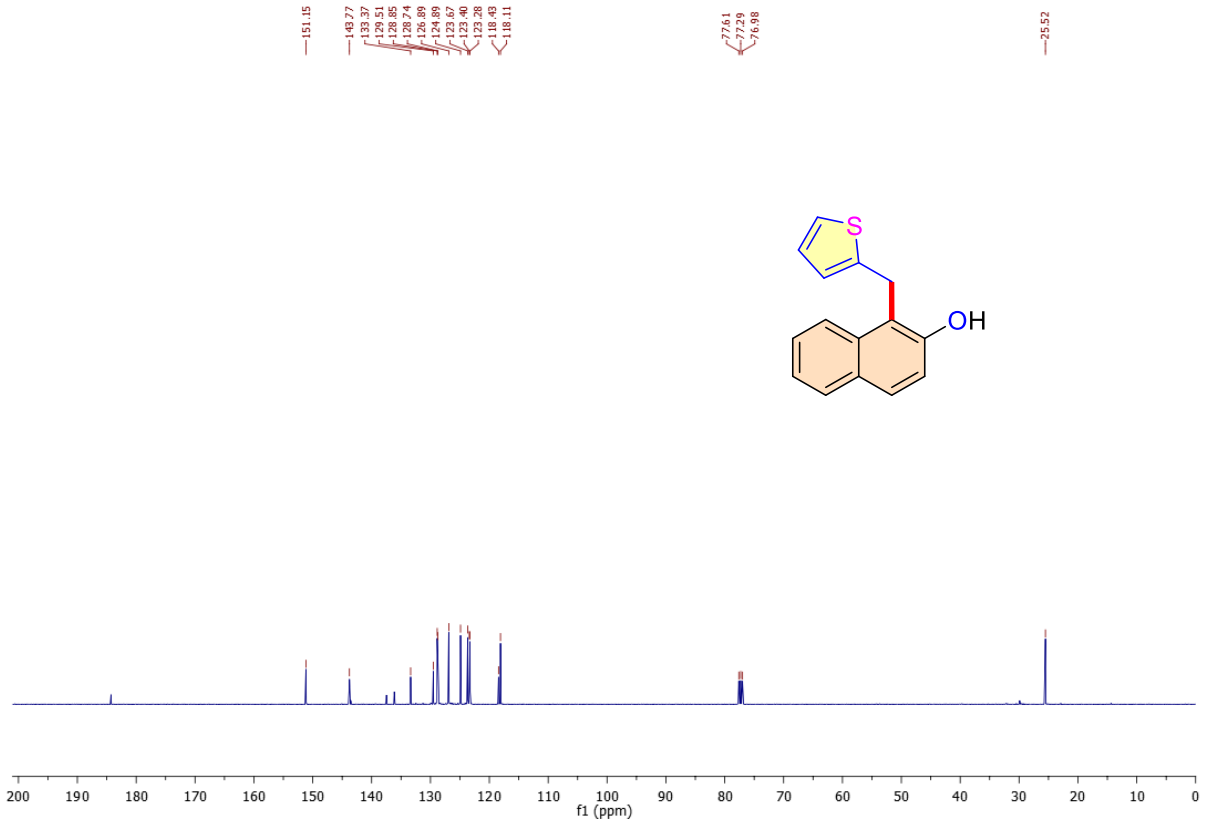

Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4t** (100 MHz, $CDCl_3$).

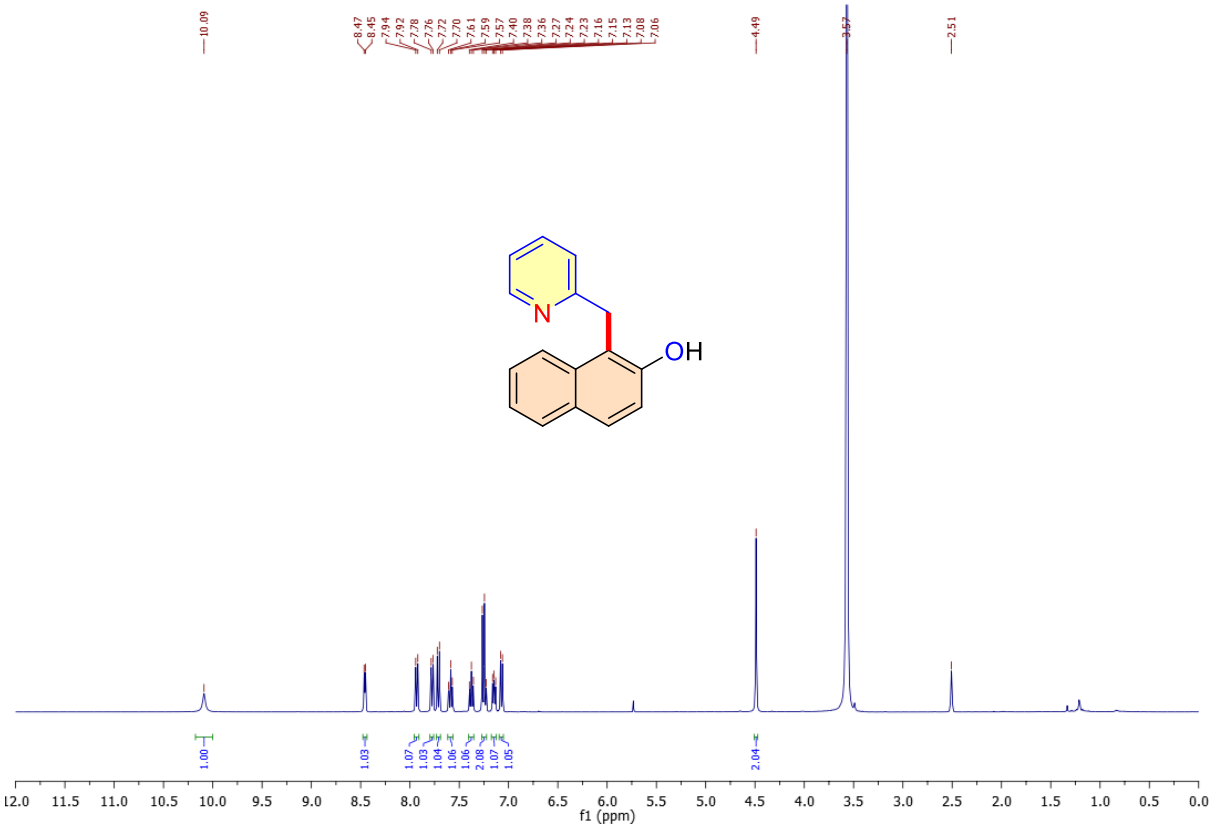

Figure S50. ^{1}H NMR spectrum of compound **4u** (400 MHz, DMSO-d^{6}).

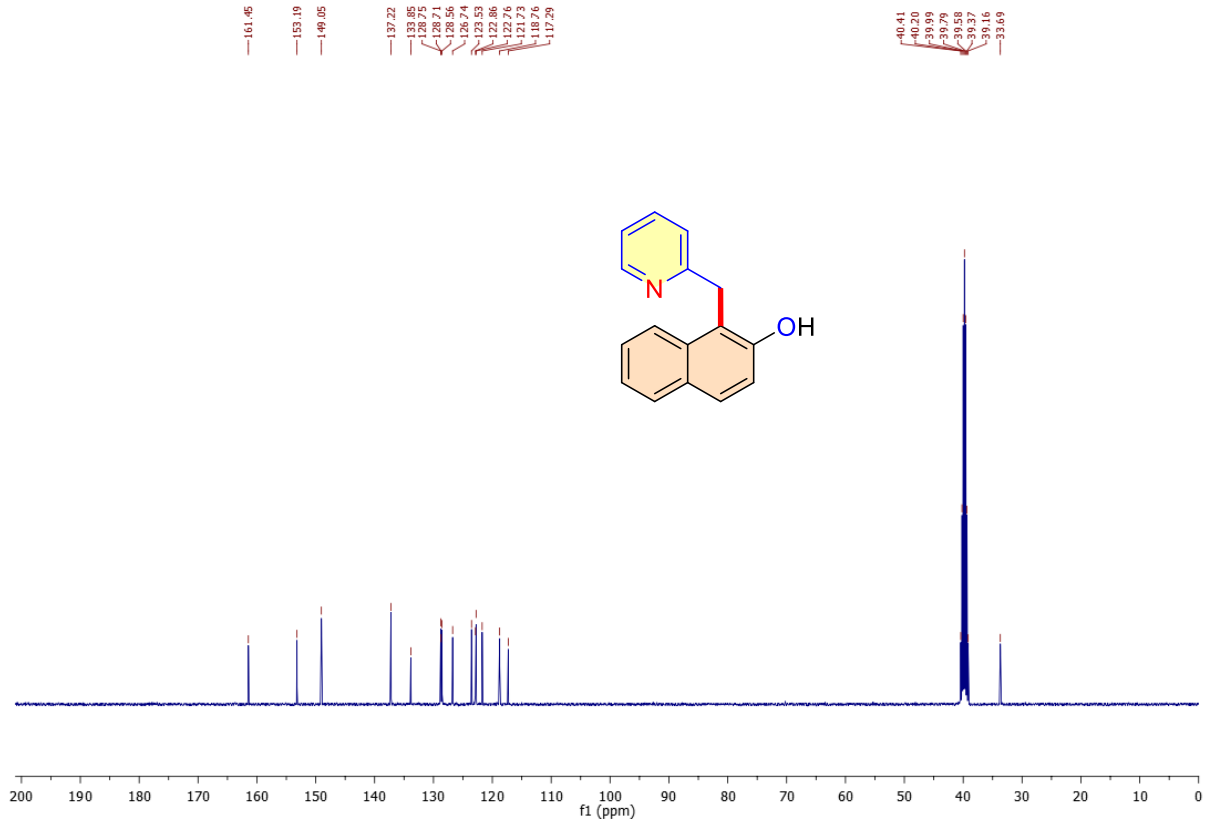

Figure S51. ^{13}C{^{1}H} NMR spectrum of compound **4u** (100 MHz, DMSO-d^{6}).

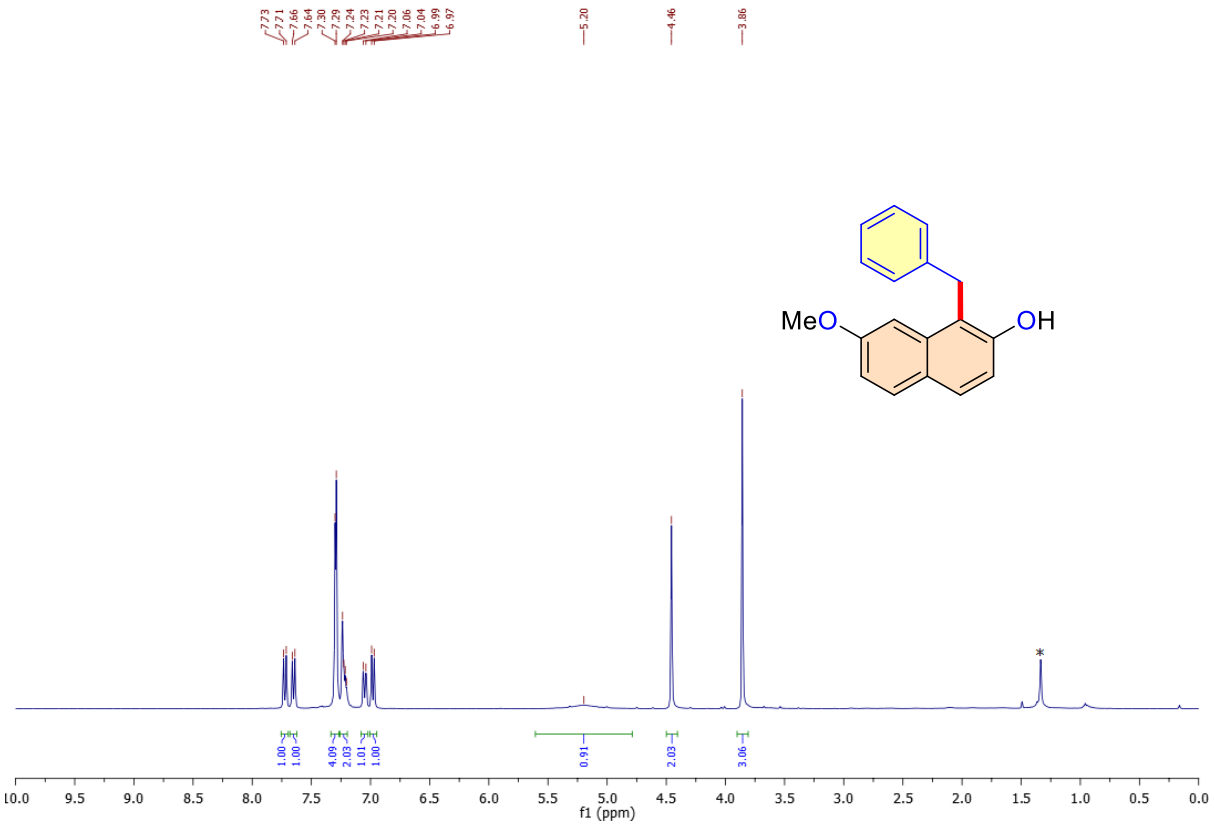

Figure S52. ^{1}H NMR spectrum of compound **4v** (400 MHz, $CDCl_3$) (*Hexane).

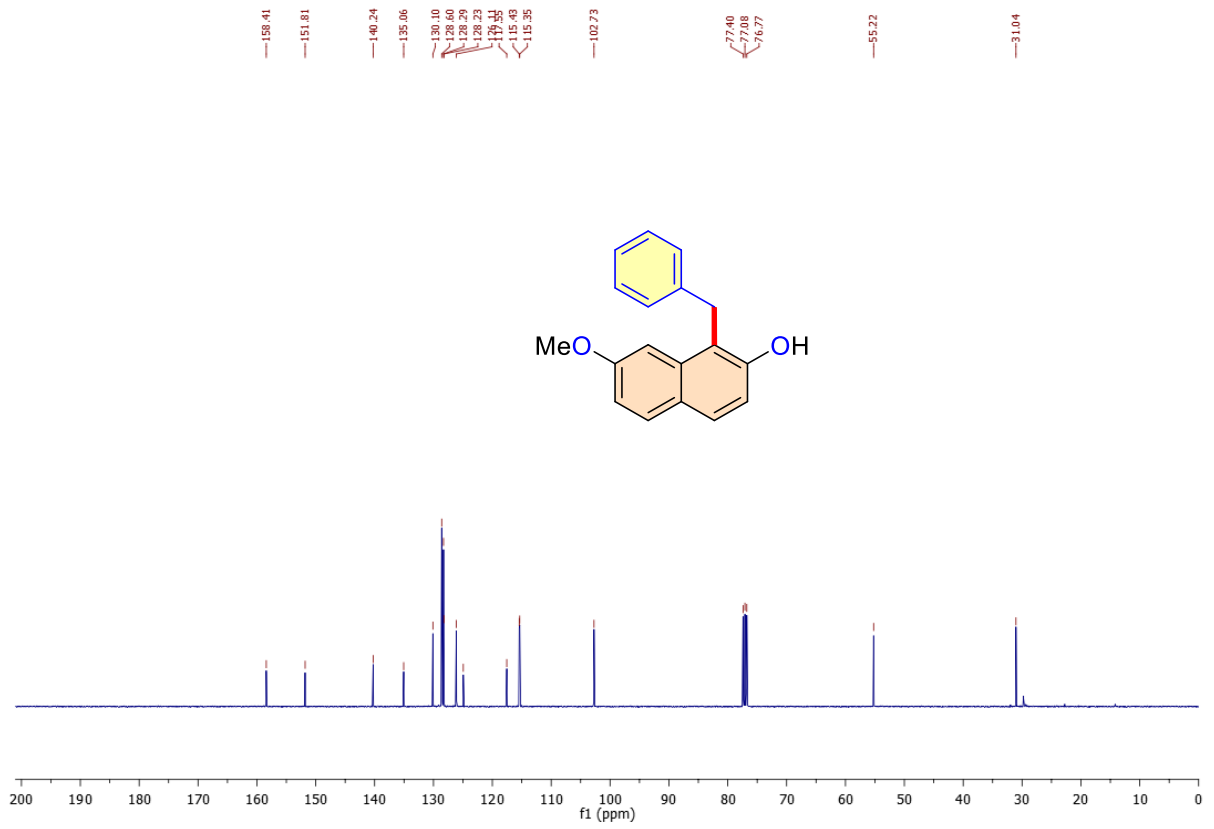

Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4v** (100 MHz, $CDCl_3$).

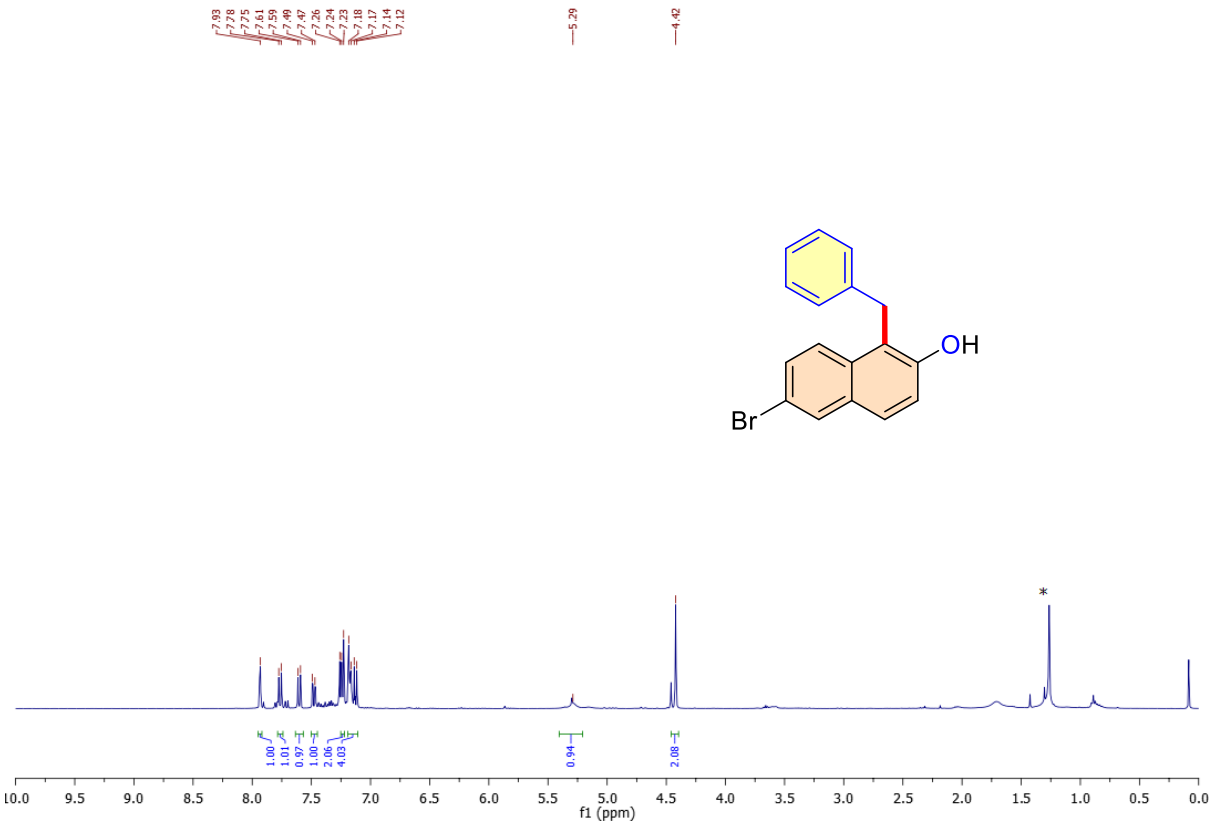

Figure S54. ^{1}H NMR spectrum of compound **4w** (400 MHz, $CDCl_3$) (*Hexane).

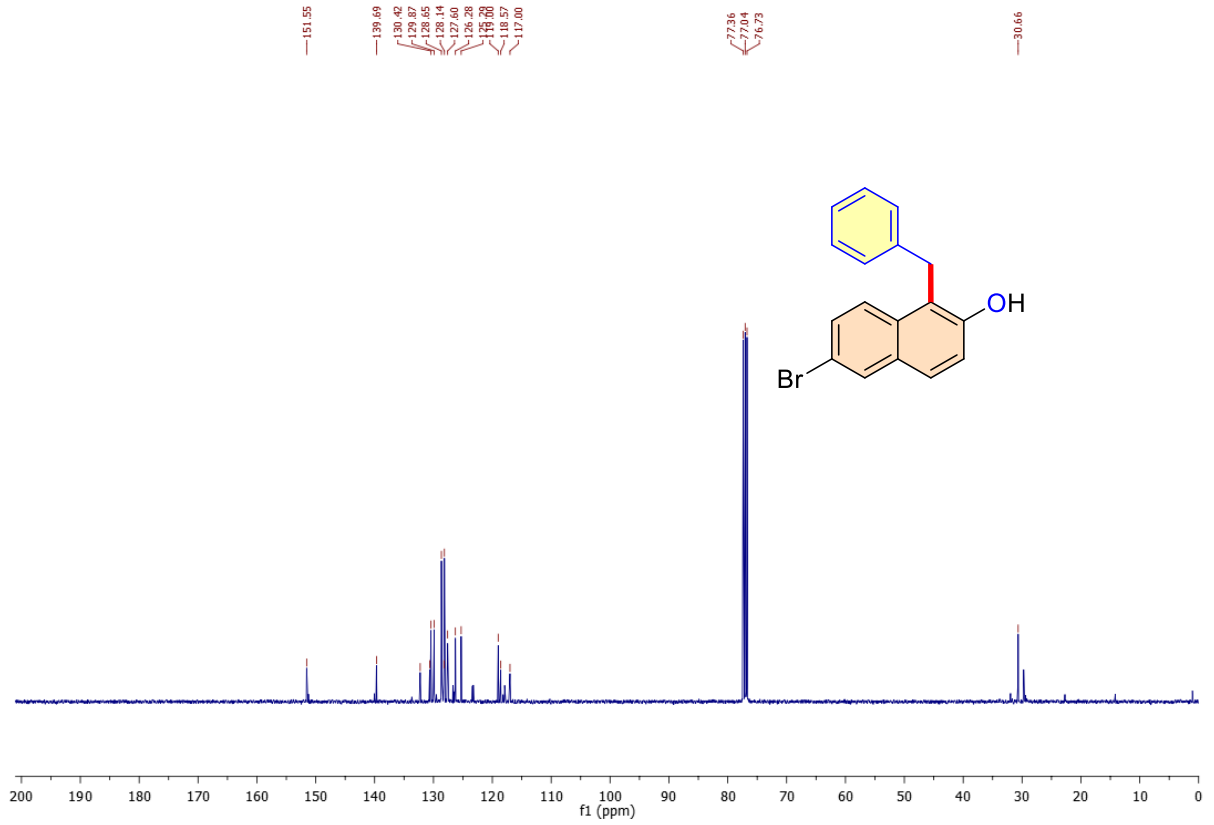

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4w** (100 MHz, $CDCl_3$).

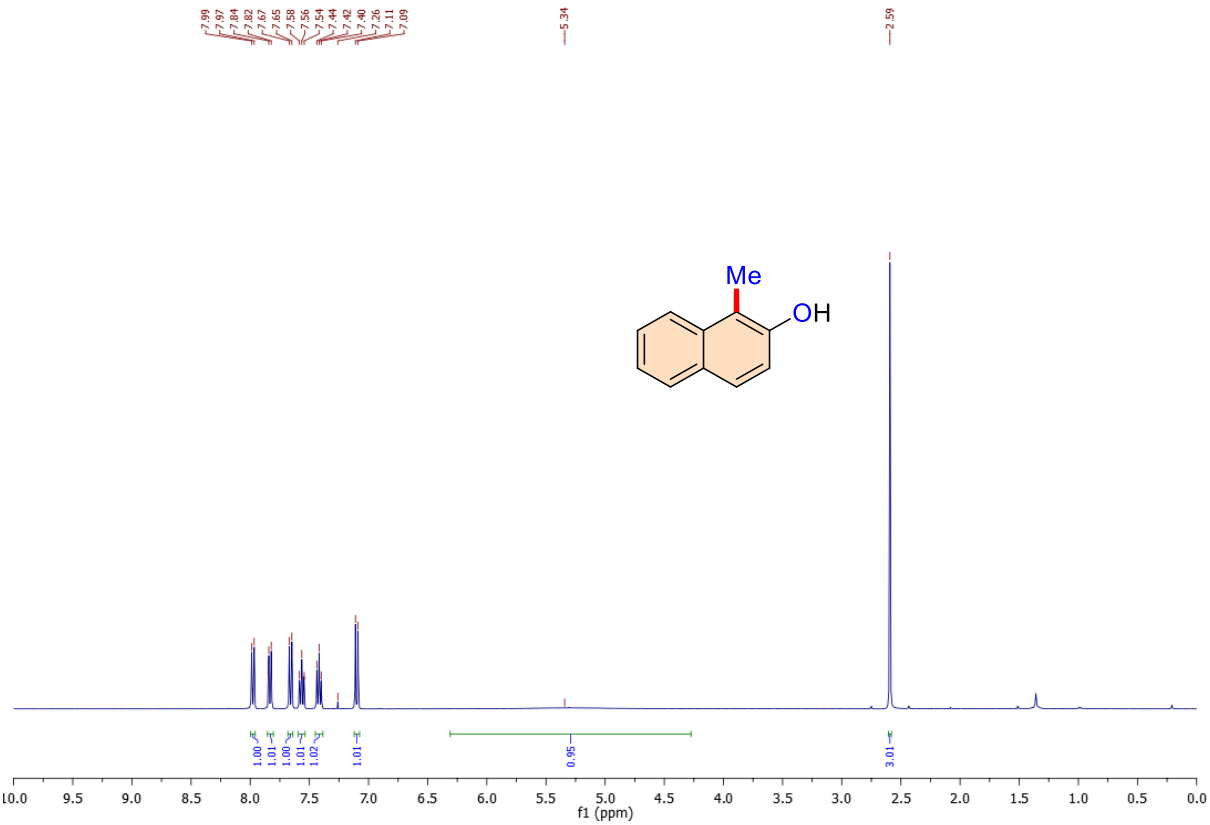

Figure S56. ^{1}H NMR spectrum of compound **5a** (400 MHz, $CDCl_3$).

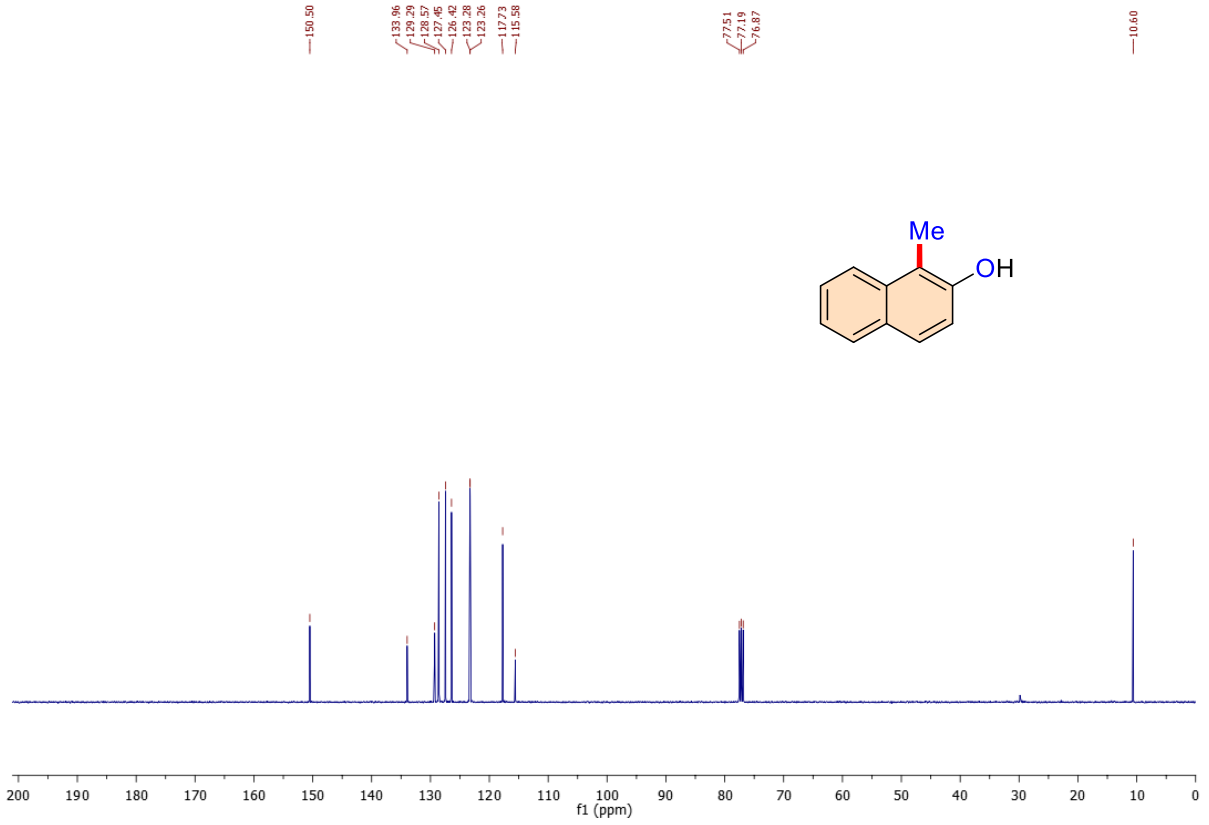

Figure S57. ^{13}C{^{1}H} NMR spectrum of compound **5a** (100 MHz, $CDCl_3$).

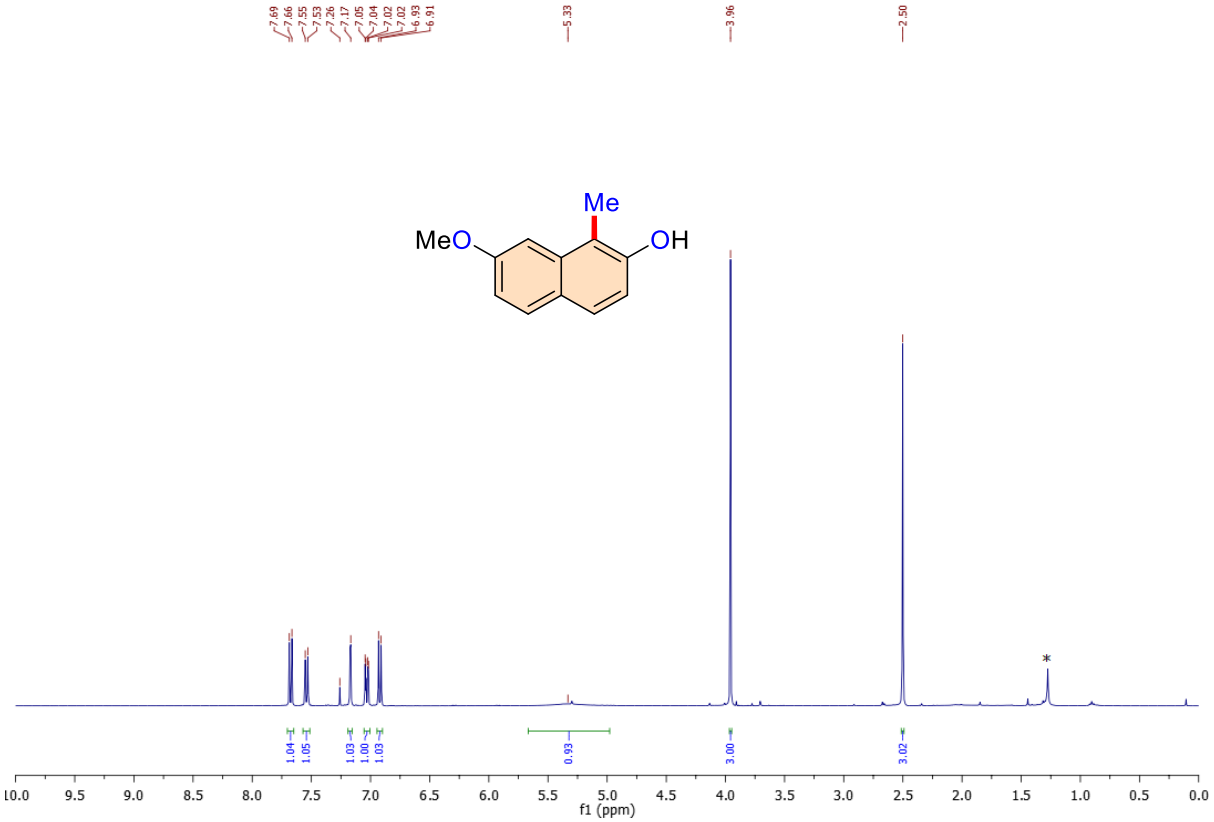

Figure S58. ^{1}H NMR spectrum of compound **5b** (400 MHz, $CDCl_3$) (*Hexane).

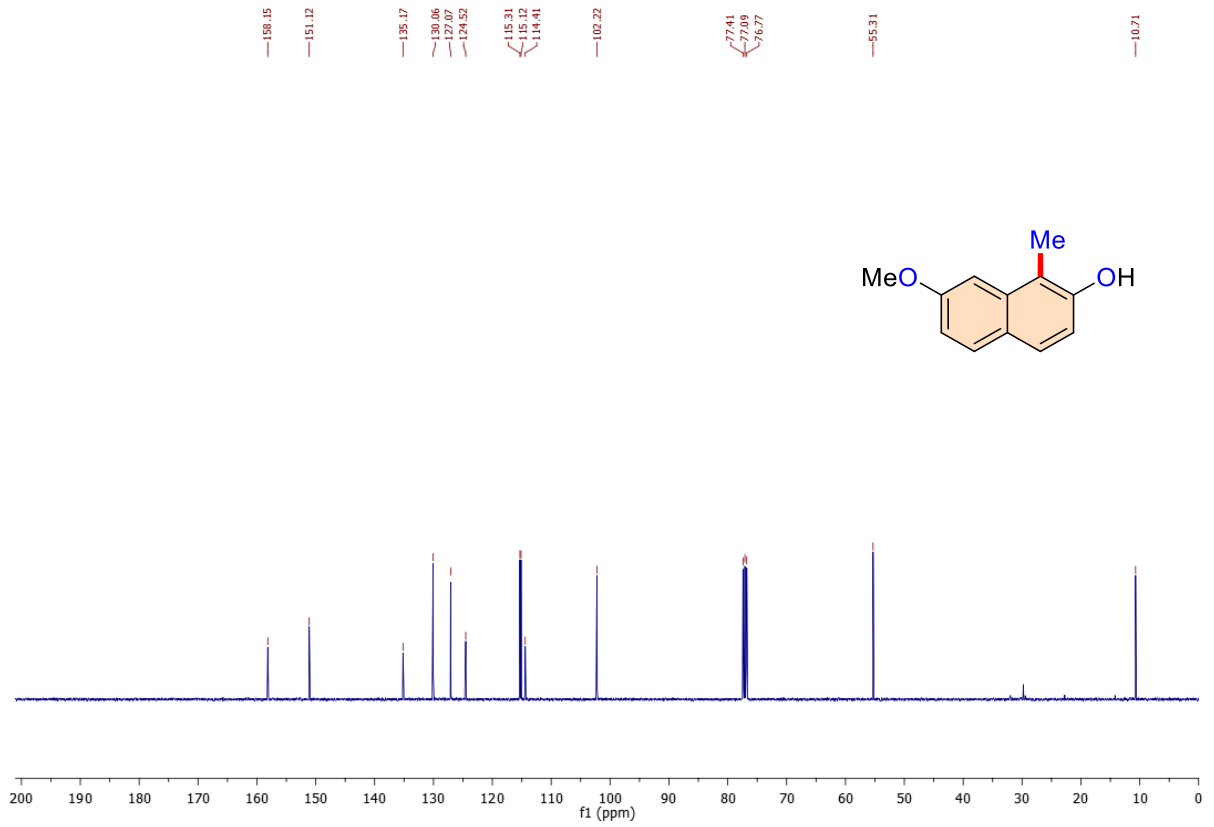

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5b** (100 MHz, $CDCl_3$).

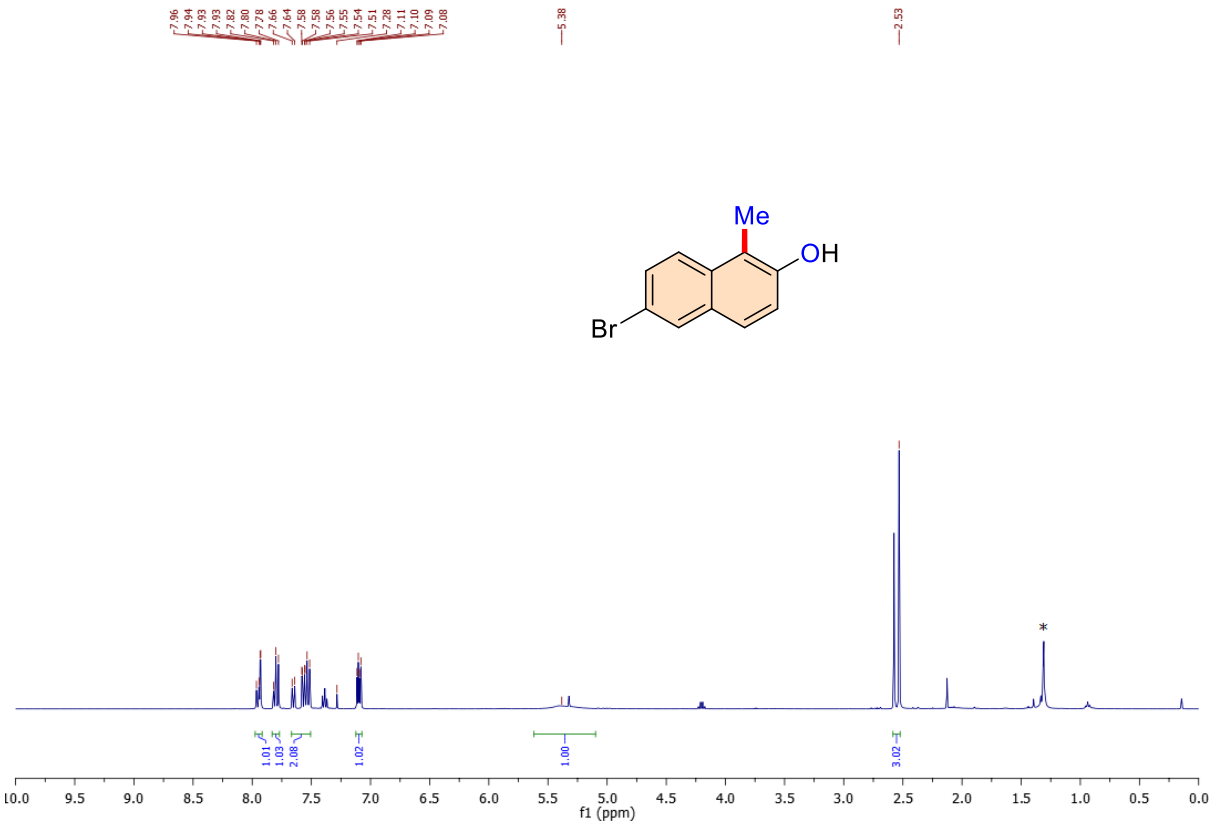

Figure S60. ^{1}H NMR spectrum of compound **5c** (400 MHz, $CDCl_3$) (*Hexane).

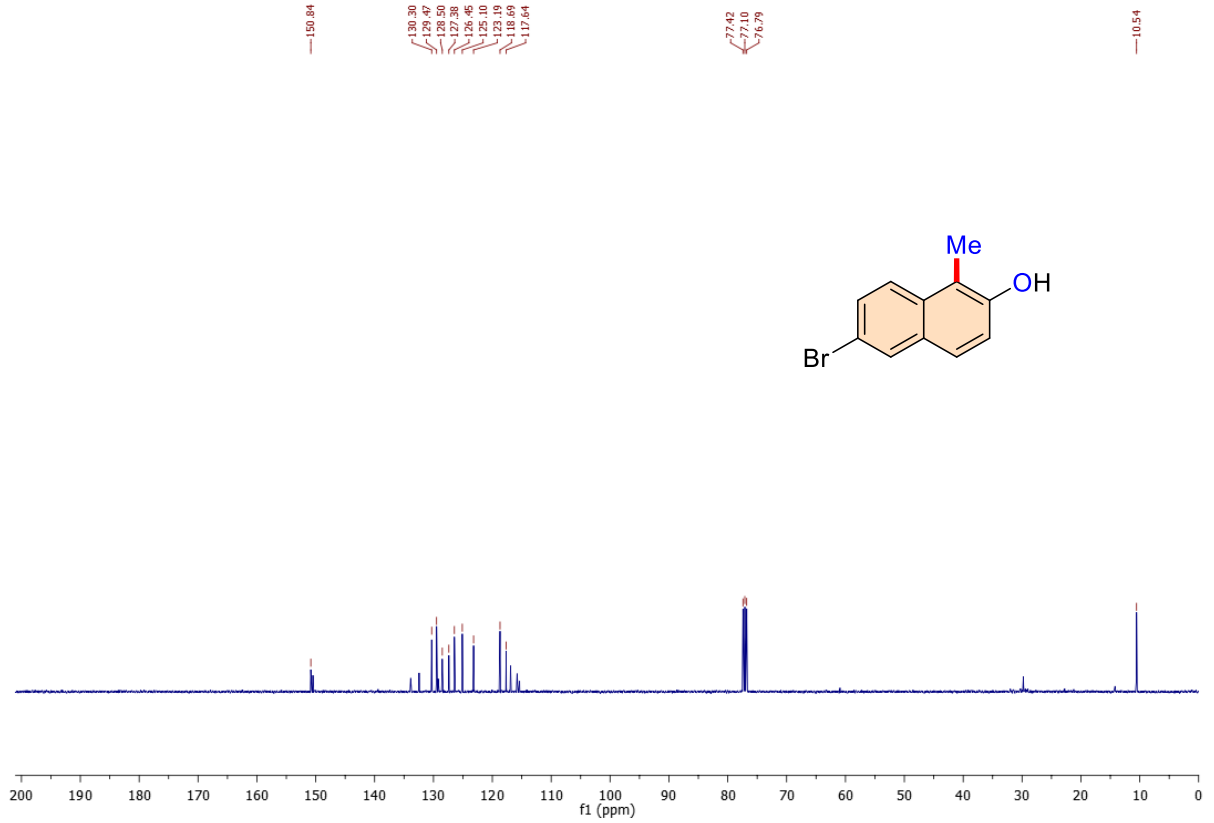

Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5c** (100 MHz, $CDCl_3$).

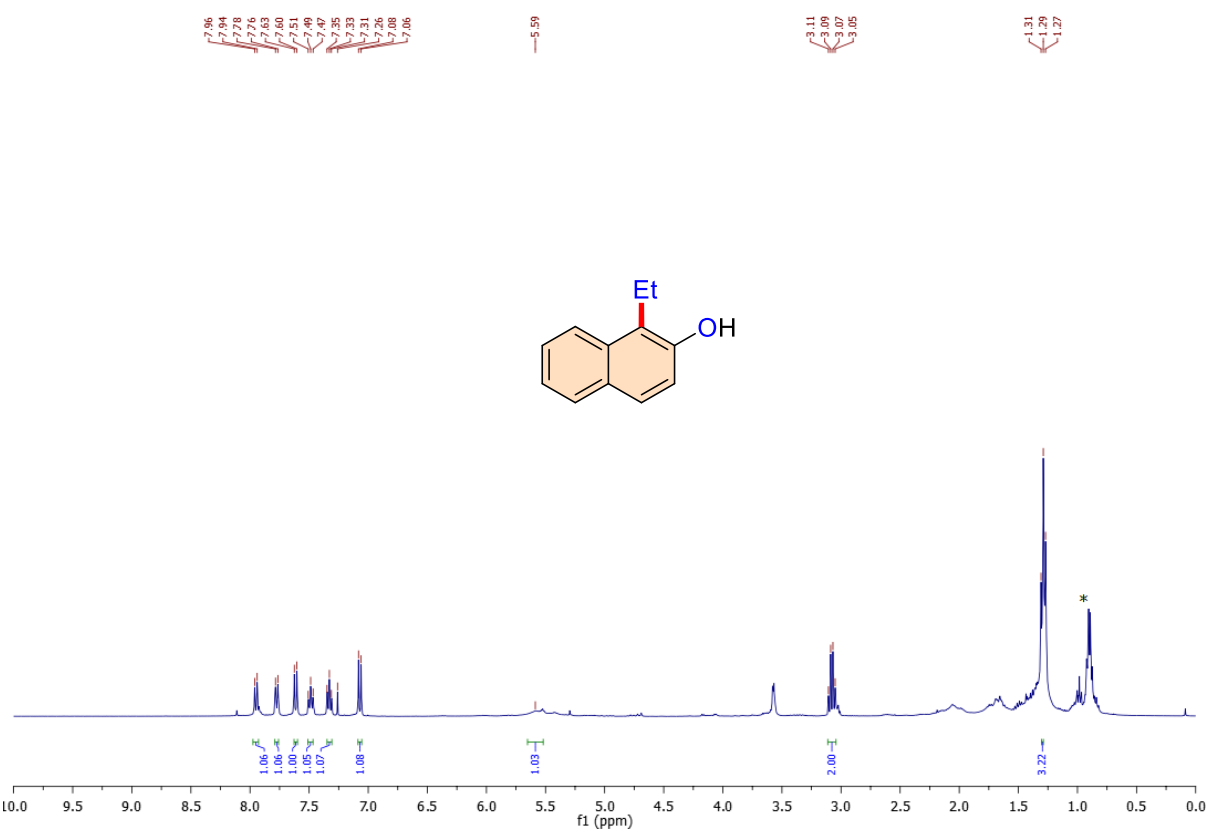

Figure S62. ^{1}H NMR spectrum of compound **5d** (400 MHz, $CDCl_3$) (*Hexane).

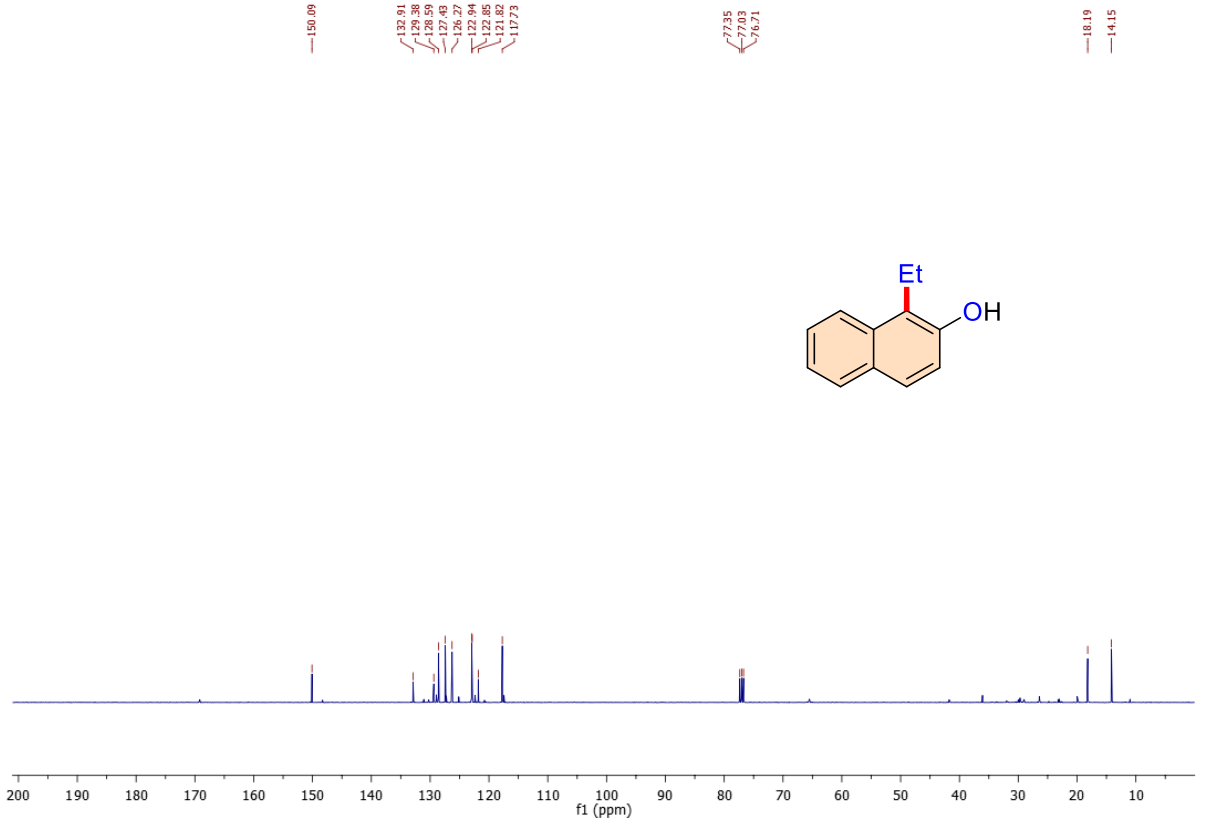

Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5d** (100 MHz, $CDCl_3$).

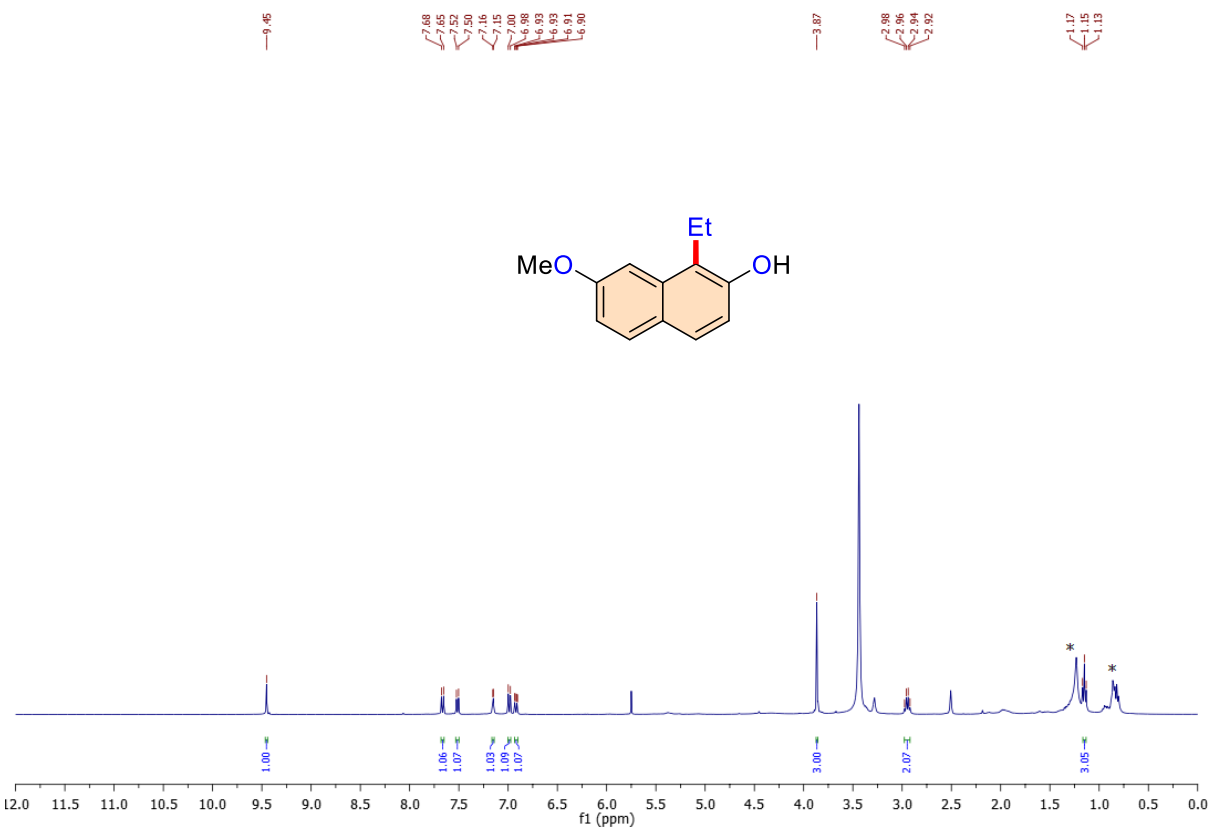

Figure S64. ^{1}H NMR spectrum of compound **5e** (400 MHz, DMSO-d^{6}) (*Hexane).

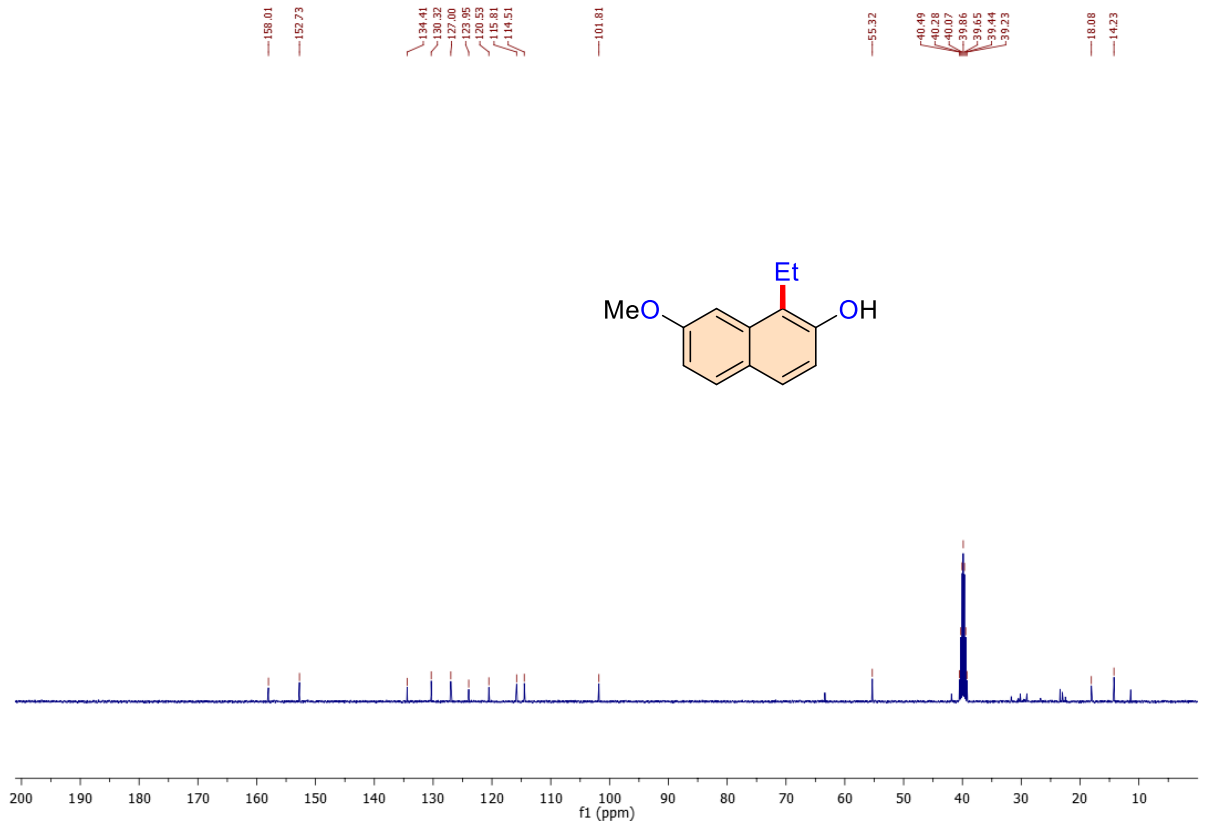

Figure S65. ^{13}C{^{1}H} NMR spectrum of compound **5e** (100 MHz, DMSO-d^{6}).

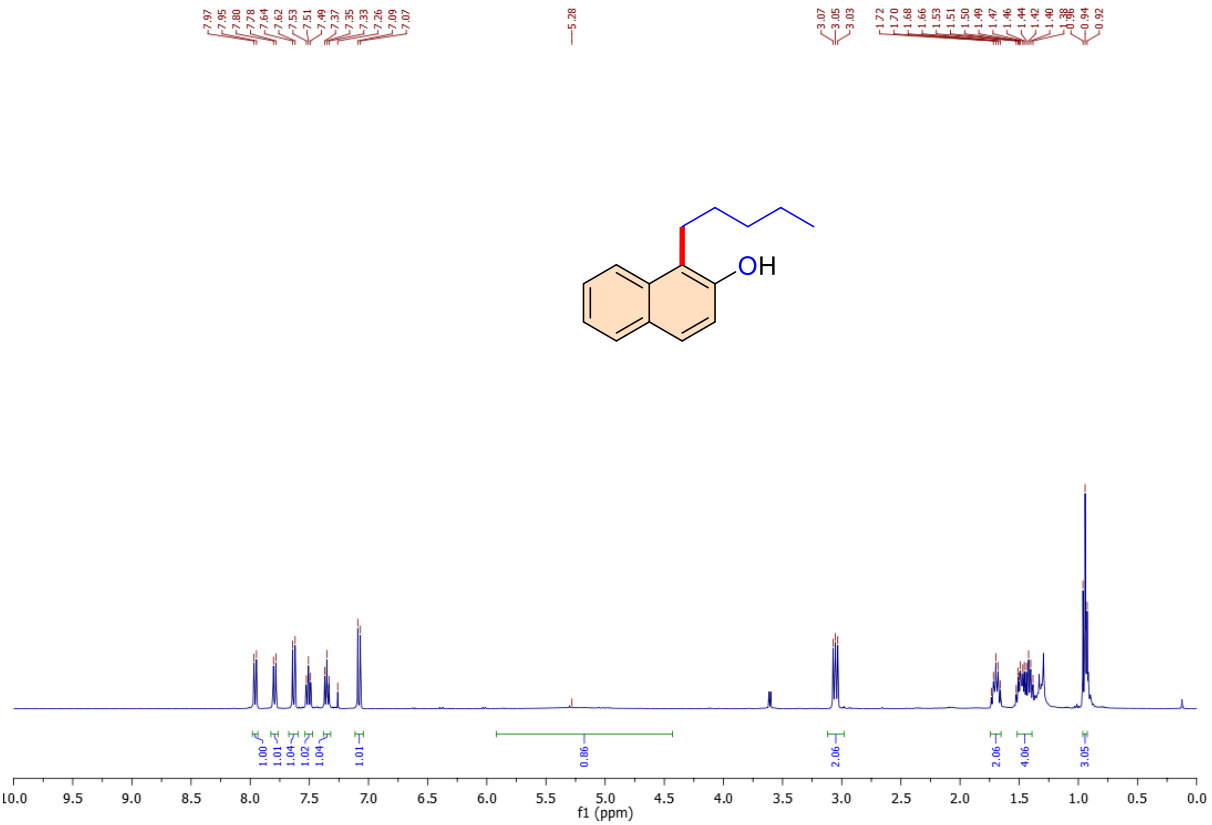

Figure S66. ^{1}H NMR spectrum of compound **5f** (400 MHz, $CDCl_3$).

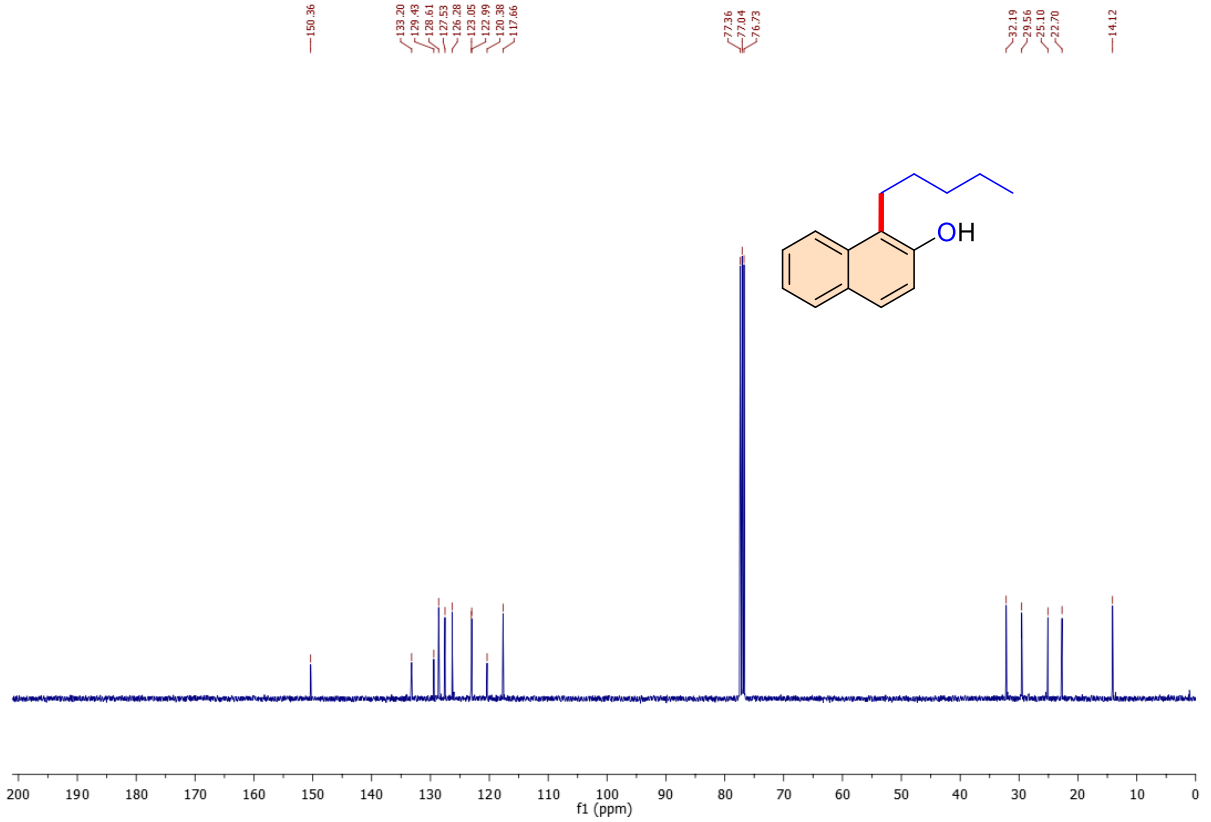

Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5f** (100 MHz, $CDCl_3$).

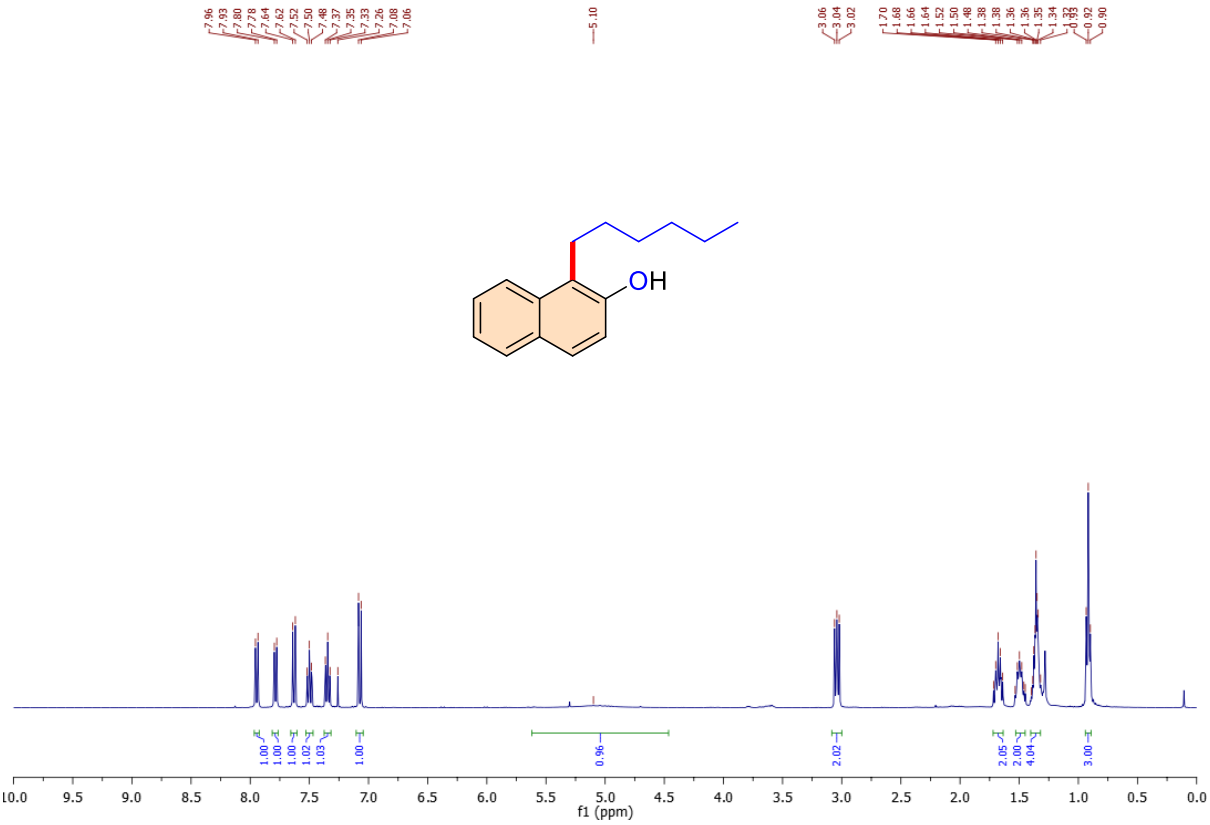

Figure S68. ^{1}H NMR spectrum of compound **5g** (400 MHz, $CDCl_3$).

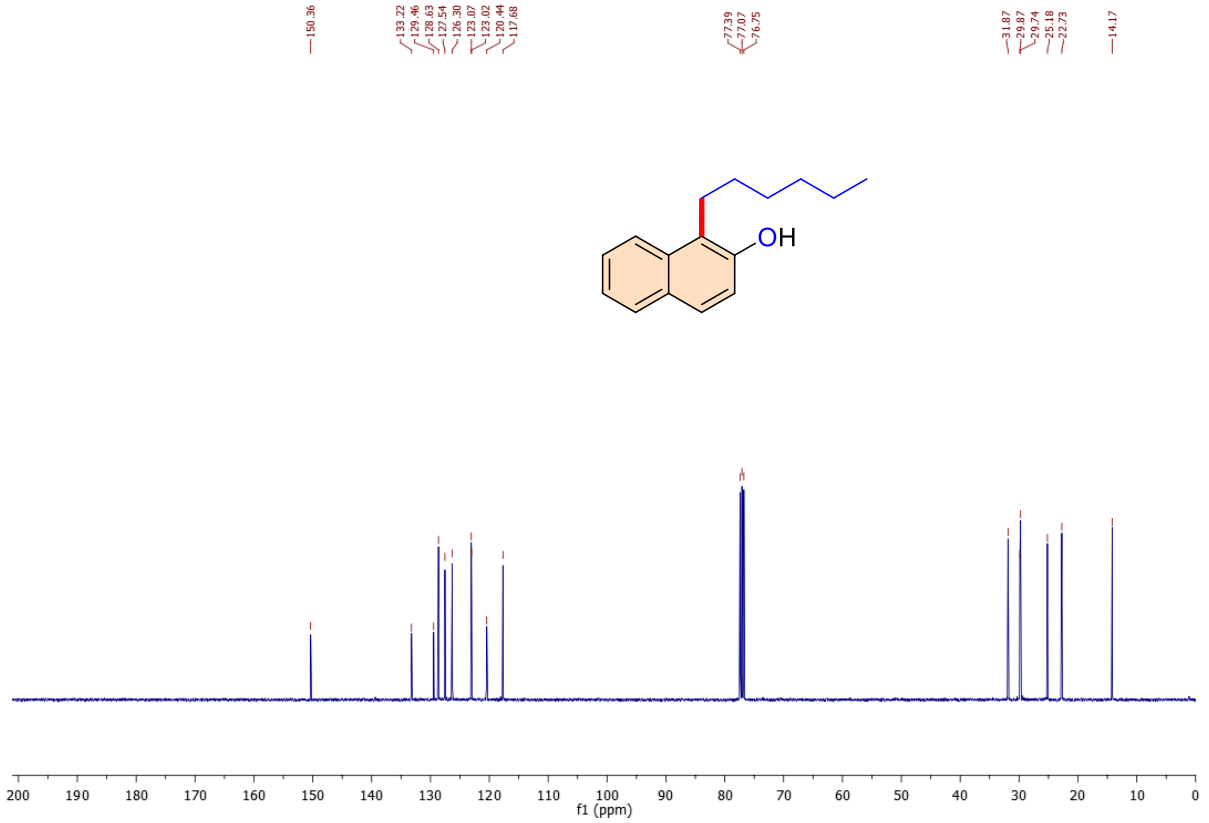

Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5g** (100 MHz, $CDCl_3$).

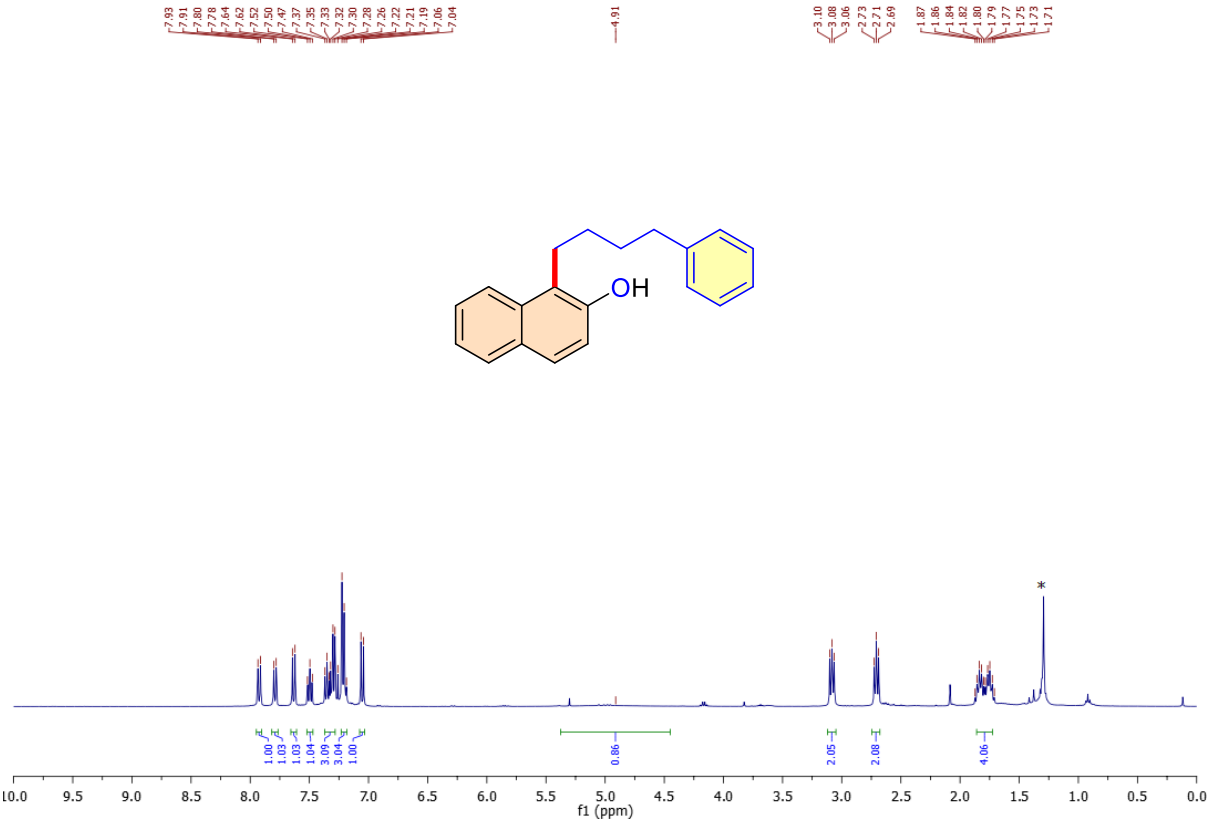

Figure S70. ^{1}H NMR spectrum of compound **5h** (400 MHz, $CDCl_3$) (*Hexane).

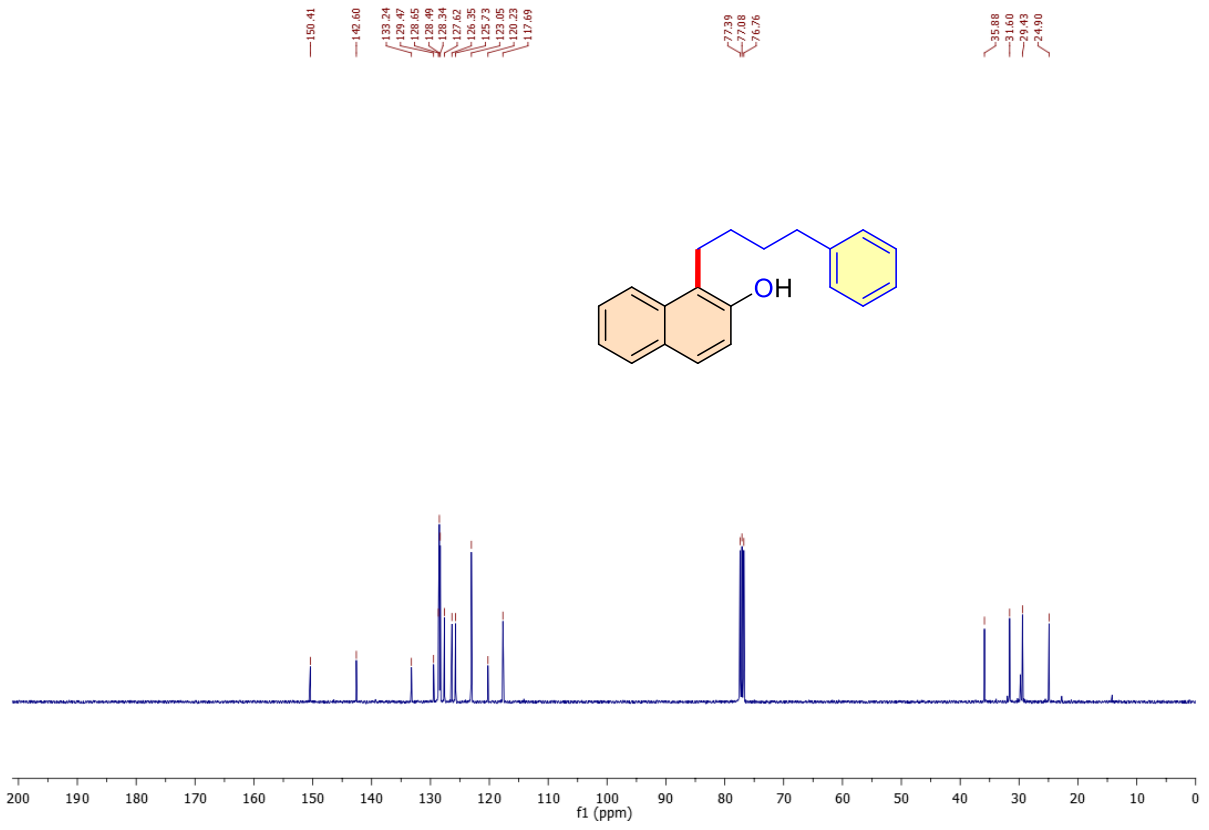

Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5h** (100 MHz, $CDCl_3$).

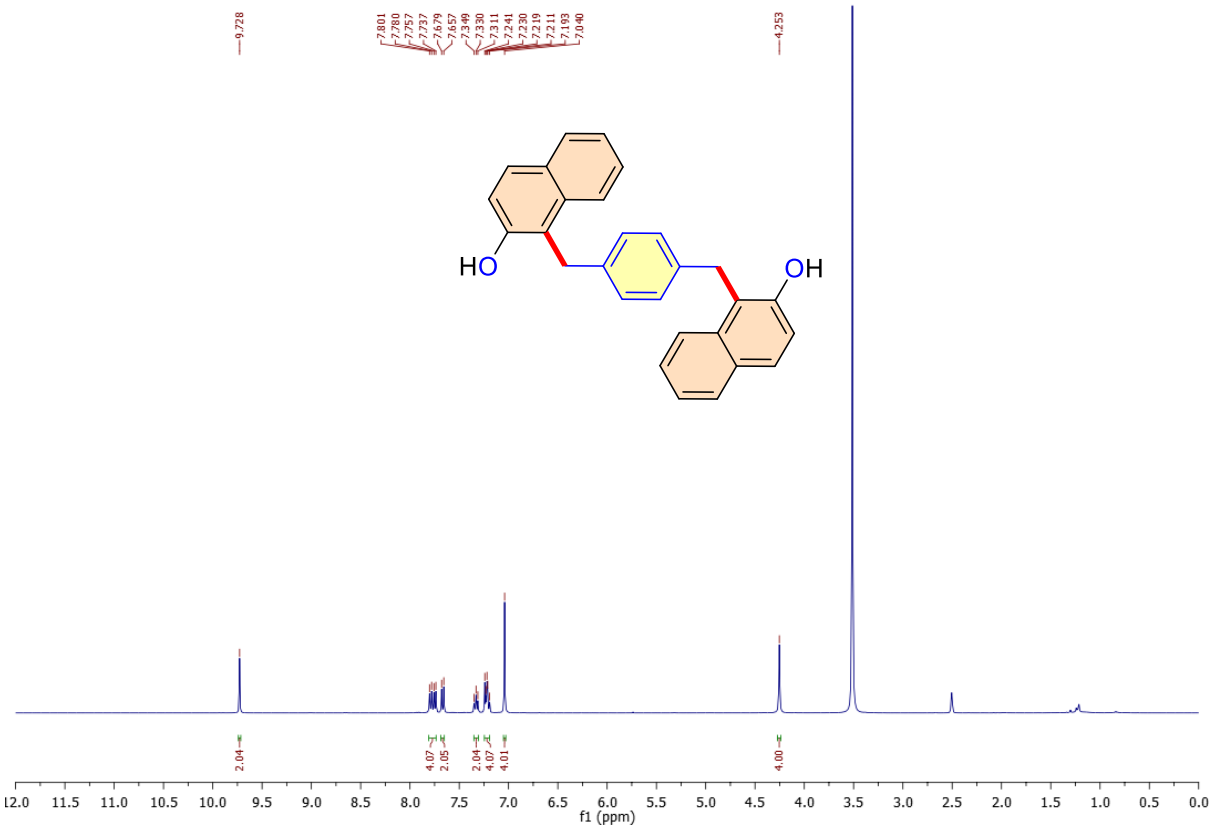

Figure S72. ^{1}H NMR spectrum of compound **6a** (400 MHz, DMSO-d^{6}).

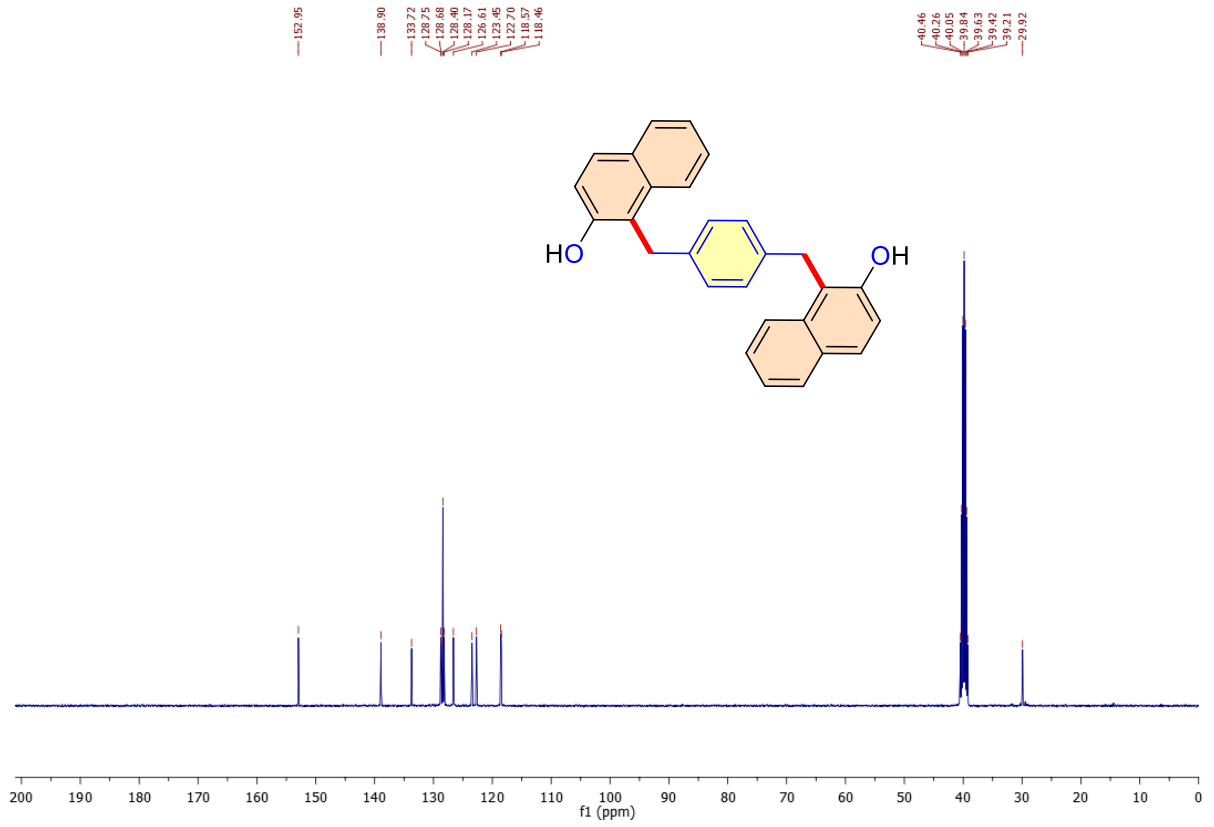

Figure S73. ^{13}C{^{1}H} NMR spectrum of compound **6a** (100 MHz, DMSO-d^{6}).

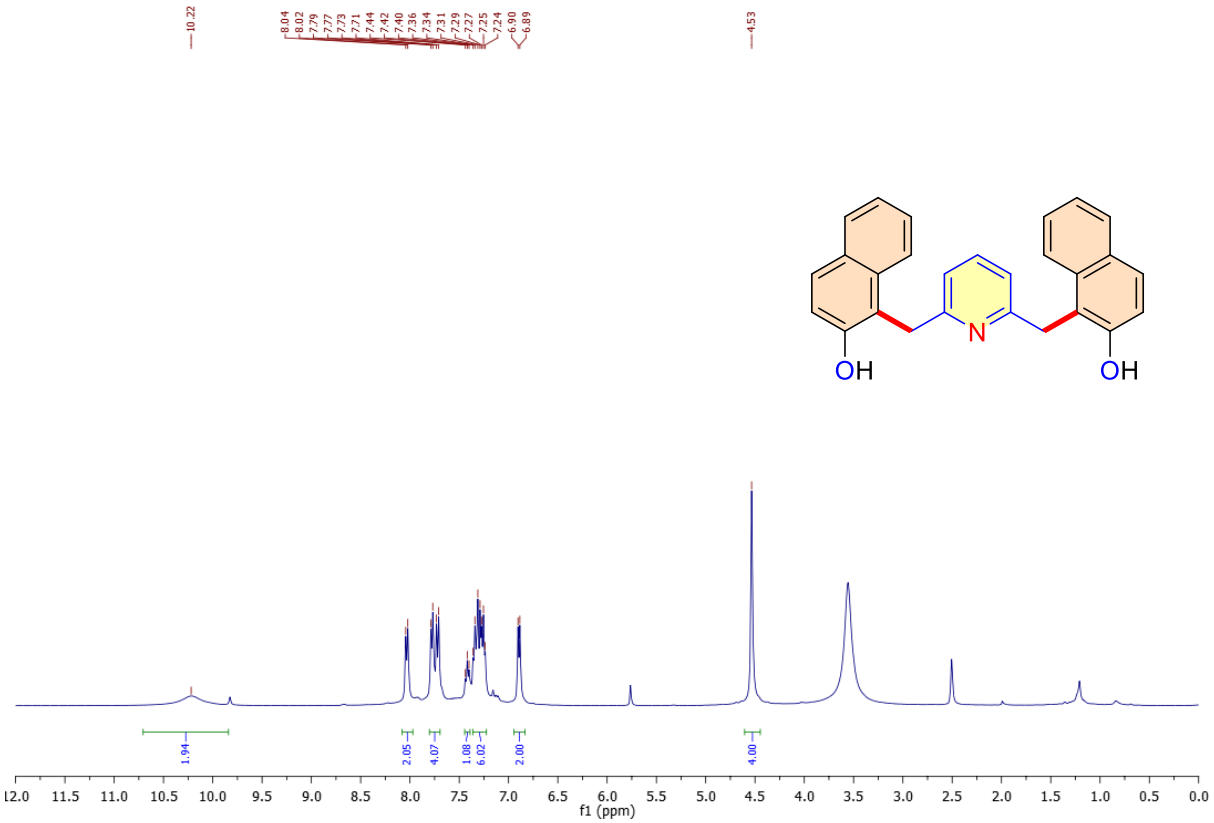

Figure S74. ^{1}H NMR spectrum of compound **6b** (400 MHz, DMSO-d^{6}).

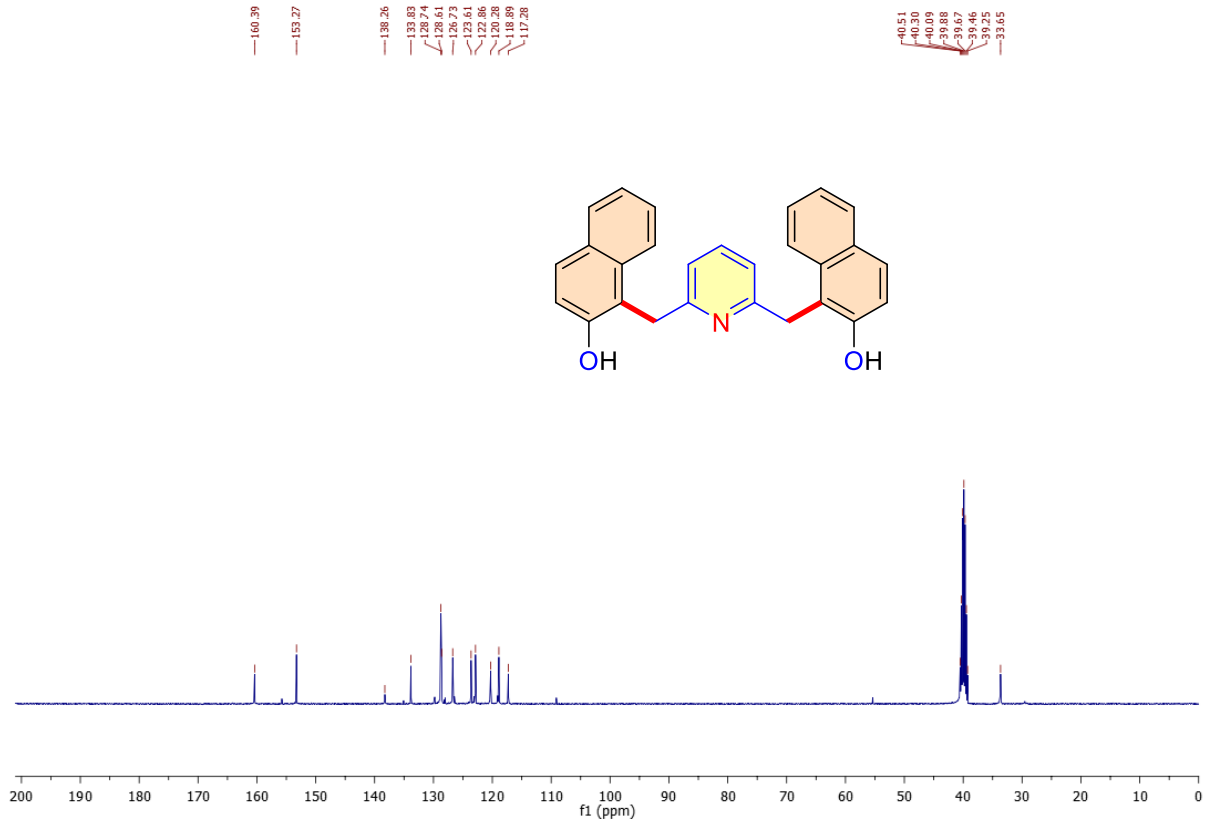

Figure S75. ^{13}C{^{1}H} NMR spectrum of compound **6b** (100 MHz, DMSO-d^{6}).

Dehydrogenation of Radical Clock Substrate Cyclobutanol.[1-3]

A mixture of catalyst **1a** (1.0 mol%, 0.0025 mmol, 1.9 mg), LiO^tBu (0.125 mmol, 10 mg), cyclobutanol (0.25 mmol, 0.025 mL) were added to a 50 mL round-bottom flask. To it, 3.0 mL of toluene was added, after that the round-bottom flask containing the reaction mixture was fitted with a water condenser and placed in an oil bath preheated at 60 ^oC for 16 h. Once the reaction was complete, the resulting mixture was cooled to room temperature, and the resulting mixture was passed through celite. Next, solvent and other volatiles were removed under a vacuum using a rotary evaporator. Then the reaction mixture was diluted by adding chloroform-D ($CDCl_3$), and the resulting solution was taken in an NMR tube. 1.0 mmol (0.1 mL) 1,1,2,2-tetrachloroethane (reference standard) was added to the NMR tube containing the reaction mixture and the sample was sent for NMR analysis.

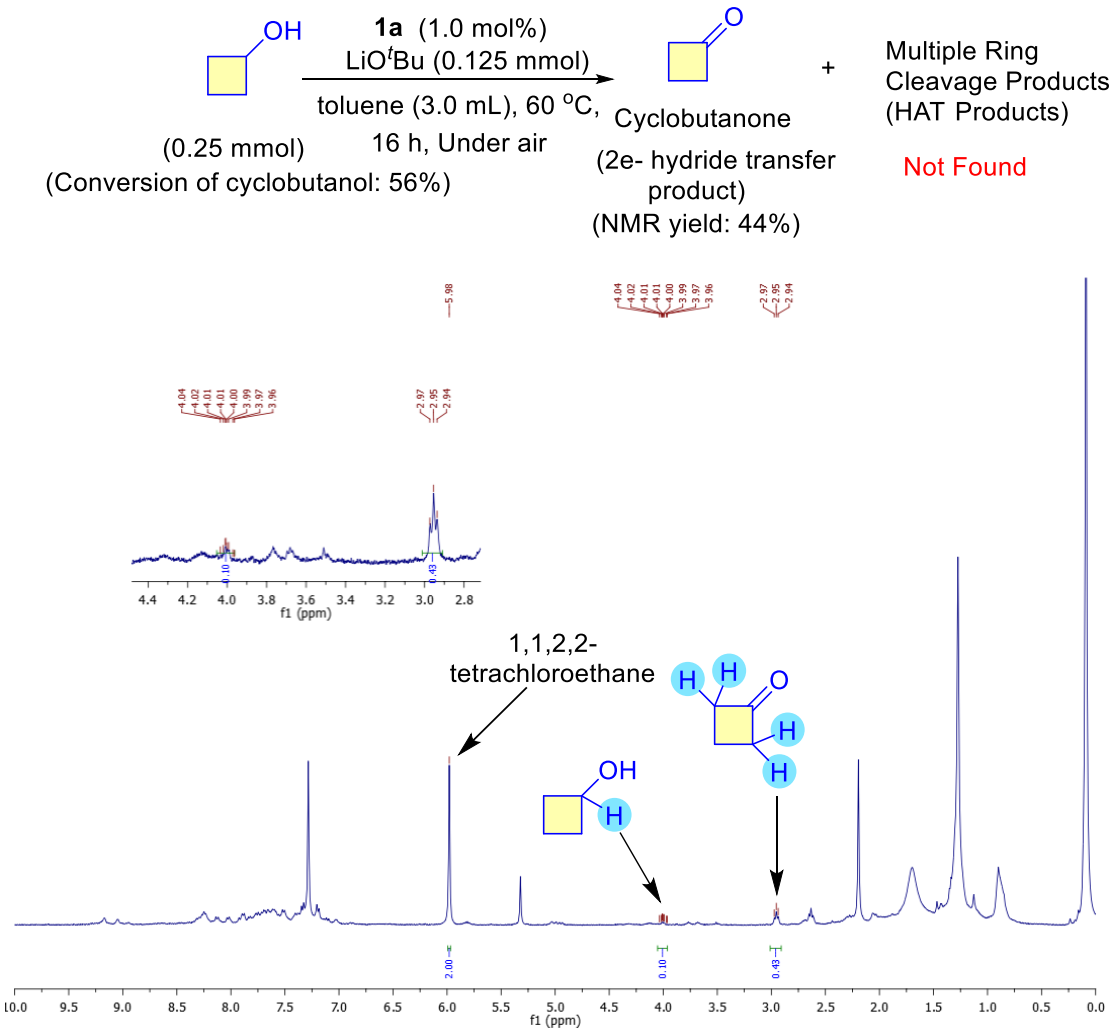

Figure S76. ^1H NMR spectrum of the reaction mixture of dehydrogenation of cyclobutanol (400 MHz, $CDCl_3$).

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1 A. K. Guin, R. Mondal, G. Chakraborty, S. Pal and N. D. Paul, *J. Org. Chem.*, 2022, **87**, 7106–7123.

2 A. K. Guin, S. Pal, S. Chakraborty, S. Chakraborty and N. D. Paul, *J. Org. Chem.*, 2023, **88**, 5944–5961.

3 A. K. Guin, S. Pal, S. Chakraborty, S. Chakraborty and N. D. Paul, *J. Org. Chem.*, 2023, **88**, 16755–16772.

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5 S. Kim and S. H. Hong, *Adv. Synth. Catal.*, 2017, **359**, 798–810.