Electronic Supplementary Information for

Efficient construction of a β-naphthol library under continuous flow conditions

Chao Shan,* Ranran Li and Xinchao Wang*

Heze University, Heze, Shandong Province, 274015, China

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1. General information

All common reagents and solvents were commercially available and used without further purification. CH_2Cl_2 was dried over 3 Å molecular sieve before being used. Commercially available 3 Å molecular sieves were predried at 300 °C for 24 h immediately before use. All reactions were carried out under a nitrogen atmosphere, and all reaction vessels were predried. ^1H, ^{13}C NMR spectral data were recorded using a Bruker AVANCE III 400 or Bruker Ascend 600 spectrometer. Chemical shifts for protons were reported in parts per million downfield from tetramethylsilane or referenced to residual solvent. Chemical shifts for carbons were reported in parts per million downfield from tetramethylsilane or referenced to residual solvent. NMR data were reported as follows: chemical shift, integration, multiplicity (s: singlet, d: doublet, t: triplet, q: quadruplet, br: broad, m: multiplet), coupling constants (J in Hz). High resolution mass spectrometry (ESI) was carried out using a Waters Quatro Macro triple quadrupole mass spectrometer. The HPLC pumps with flow rate 0.01 ~ 20 mL/min were purchased from Bejing Xingda Science & Technology Development Co. Ltd. The T-mixer (Peek, 1/16" I.D.) was used to mix two separate feed streams, and the mixture was channeled into the coil reactor (PFA, 1/16" O.D.).

2. General procedures

General procedure 1: Synthesis of aryl acetyl chloride.

Apart from phenylacetyl chloride, the arylacetyl chlorides used in this work were synthesized by general procedure.

The preparation of 4-methylphenylacetyl chloride was taken as an example. A three-neck flask fitted with a reflux condenser tube was charged with 4-methylphenylacetic acid (1.50 g, 10 mmol, 1.0 equiv.) and thionyl chloride (14.5 mL, 200 mmol, 20.0 equiv.) under nitrogen atmosphere. The reaction was carried out at reflux temperature for 3 h. After cooling to ambient temperature, the excess thionyl chloride was removed by a rotary evaporator equipped with an acid gas absorption device. The residue was 4-methylphenyl acetyl chloride, which could be used directly without further purification.

General procedure 2: Synthesis of β-naphthol under continuous flow conditions.

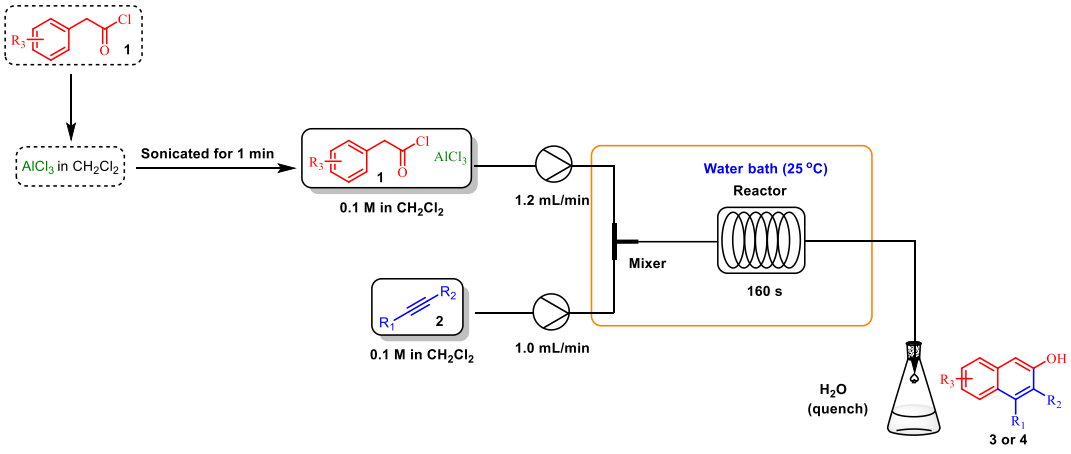


Fig. S1 The flow system for the synthesis of β-naphthols.

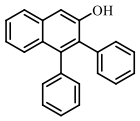
As shown in Fig. S1, the continuous flow system consisted of two HPLC pumps, a T-shaped mixer (**Mixer**, PEEK, 1/16" I.D.), and a coil reactor (**Reactor**, PFA, 1/16" O.D., 5.9 mL internal volume). The coil reactor was dipped in a water bath (25 °C). A flask containing a stirred H_2O was placed at the end of the flow system. The reaction solution was quenched as it dropped into this flask.

Prior to the start of the reaction, the continuous flow system was flushed with anhydrous CH_2Cl_2 and purged with N_2, arylacetyl chloride **1** and $AlCl_3$ (1.3 equiv. relative to **1**) were mixed in CH_2Cl_2 and sonicated for 1 min to provide clear complex solution. **1**-$AlCl_3$ solution (0.1 M in CH_2Cl_2) was driven by a HPLC pump at a flow rate of 1.2 mL/min into **Mixer**, where it was mixed with **2** solution (0.1 M in CH_2Cl_2) delivered by the other HPLC pump at a flow rate of 1.0 mL/min. The combined stream was passed through **Reactor** with a residence time of 160 s and subsequently quenched by H_2O. After a steady state was reached, the product solution was collected for 5 min (0.5 mmol). At the end of the reaction, the reaction stream was replaced with anhydrous CH_2Cl_2 to avoid substance deposition. The organic phase of the collected liquid mixture was separated, and the aqueous phase was extracted with CH_2Cl_2, the combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The target product β-naphthol **3** or **4** was isolated by column chromatography (hexane/ethyl acetate = 15: 1 ~ 5: 1).

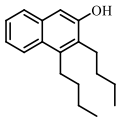
3. Scale-up preparation of 3g under continuous flow conditions

A solution of **1a**-$AlCl_3$ (0.2 M in CH_2Cl_2, 1.3 equiv. $AlCl_3$ relative to **1**, 2.4 mL/min) and a solution of **2g** (0.2 M in CH_2Cl_2, 2.0 mL/min) were introduced into a coil reactor with an internal volume of 11.8 mL by two HPLC pumps at 25 ℃. After a steady state was reached, the continuous flow system was running for 1.5 h, and 7.05 g of 4-octylnaphthalen-2-ol (**3g**) was straightforwardly produced with 76% yield (4.70 $g \cdot h^{-1}$ throughput).

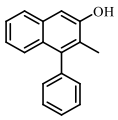
4. Synthesis of compounds



3,4-Diphenylnaphthalen-2-ol (3a): Following general procedure 2, using phenylacetyl chloride and diphenylacetylene, the product **3a** was isolated as a yellow solid. 83% yield. Mp: 142-145 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.45–7.39(m, 2H), 7.30–7.18 (m, 7H), 7.17–7.09 (m, 4H), 5.04 (br, s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.81, 140.20, 138.67, 135.11, 134.54, 131.04, 131.00, 129.72, 128.87, 128.21, 127.91, 127.74, 127.07, 126.85, 126.71, 126.53, 123.83, 109.51. HRMS (ESI) m/z calcd for $C_{22}H_{16}O$ $[M+H]^+$: 296.1201, found: 296.1204.

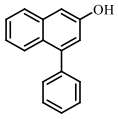


3, 4-Dibutylnaphthalen-2-ol (3b): Following general procedure 2, using phenylacetyl chloride and 5-decyne, the product **3b** was isolated as a yellow solid. 70% yield. Mp: 105-107 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.42–7.33 (m, 2H), 6.97 (s, 1H), 5.12 (br, s, 1H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 1.73–1.47 (m, 8H), 1.09–0.99 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.41, 138.29, 133.53, 129.16, 128.03, 126.84, 125.30, 124.26, 123.45, 107.91, 33.41, 32.58, 28.54, 26.85, 23.52, 23.36, 14.18, 14.15. HRMS (ESI) m/z calcd for $C_{18}H_{24}O$ $[M+H]^+$: 256.1827, found: 256.1832.

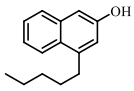


3-Methyl-4-phenylnaphthalen-2-ol (3c): Following general procedure 2, using phenylacetyl chloride and 1-phenyl-1-propyne, the product **3c** was isolated as a yellow solid. 81% yield. Mp:

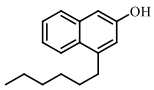
129-130 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.30–7.22 (m, 3H), 7.19–7.11 (m, 2H), 5.43 (br, s, 1H), 2.13 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 152.56, 140.55, 139.65, 133.09, 130.24, 128.78, 128.47, 127.25, 126.58, 126.12, 125.56, 124.69, 123.47, 108.68, 14.10. HRMS (ESI) m/z calcd for $C_{17}H_{14}O$ $[M+H]^+$: 234.1045, found: 234.1043.



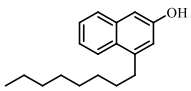
4-Phenylnaphthalen-2-ol (3d): Following general procedure 2, using phenylacetyl chloride and phenylacetylene, the product **3d** was isolated as a yellow solid. 74% yield. Mp: 125-127 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.54–7.43 (m, 6H), 7.34–7.29 (m, 1H), 7.21 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 5.98 (br, s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.69, 142.53, 140.15, 135.29, 129.98, 128.36, 127.54, 127.38, 126.96, 126.57, 126.16, 123.86, 118.86, 109.43. HRMS (ESI) m/z calcd for $C_{16}H_{12}O$ $[M+H]^+$: 220.0888, found: 220.0883.



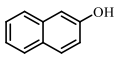
4-Pentylnaphthalen-2-ol (3e): Following general procedure 2, using phenylacetyl chloride and 1-heptyne, the product **3e** was isolated as a yellow oil. 77% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.47–7.41 (m, 1H), 7.41–7.35 (m, 1H), 7.02 (dd, *J* = 12.0, 2.4 Hz, 2H), 5.79 (br, s, 1H), 3.03 (t, *J* = 7.6 Hz, 2H), 1.76 (p, *J* = 7.6 Hz, 2H), 1.49–1.36 (m, 4H), 0.94 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.97, 141.74, 135.36, 127.62, 127.36, 126.21, 123.99, 123.45, 117.79, 107.98, 33.01, 32.06, 30.41, 22.68, 14.17. HRMS (ESI) m/z calcd for $C_{15}H_{18}O$ $[M+H]^+$: 214.1358, found: 214.1355.



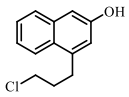
4-Hexylnaphthalen-2-ol (3f): Following general procedure 2, using phenylacetyl chloride and 1-octyne, the product **3f** was isolated as a yellow oil. 75% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.47–7.41 (m, 1H), 7.40–7.34 (m, 1H), 7.01 (dd, *J* = 13.6, 2.4 Hz, 2H), 5.55 (br, s, 1H), 3.03 (t, *J* = 7.6 Hz, 2H), 1.75 (p, *J* = 7.6 Hz, 2H), 1.50–1.28 (m, 6H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.94, 141.78, 135.35, 127.64, 127.36, 126.24, 124.01, 123.47, 117.75, 107.96, 33.07, 31.86, 30.71, 29.60, 22.78, 14.24. HRMS (ESI) m/z calcd for $C_{16}H_{20}O$ $[M+H]^+$: 228.1514, found: 228.1516.



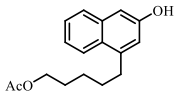
4-Octylnaphthalen-2-ol (3g): Following general procedure 2, using phenylacetyl chloride and 1-decyne, the product **3g** was isolated as a yellow oil. 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.01 (dd, *J* = 12.4, 2.0 Hz, 2H), 3.03 (t, *J* = 8.0 Hz, 2H), 1.75 (p, *J* = 7.6 Hz, 2H), 1.50–1.25 (m, 10H), 0.93 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.94, 141.77, 135.35, 127.63, 127.36, 126.22, 124.00, 123.46, 117.76, 107.97, 33.06, 32.02, 30.74, 29.93, 29.61, 29.42, 22.80, 14.24. HRMS (ESI) m/z calcd for $C_{18}H_{24}O$ $[M+H]^+$: 256.1827, found: 256.1831.



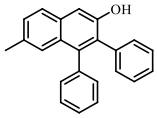
Naphthalen-2-ol (3h): Following general procedure 2, using phenylacetyl chloride and trimethylsilylacetylene, the product **3h** was isolated as a white solid. 82% yield. Mp: 121-123 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (t, *J* = 9.2 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.49–7.42 (m, 1H), 7.40–7.32 (m, 1H), 7.18–7.10 (m, 2H), 5.43 (br, s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.41, 134.70, 129.98, 129.05, 127.88, 126.65, 126.50, 123.75, 117.88, 109.67. HRMS (ESI) m/z calcd for $C_{10}H_8O$ [M+H]$^+$: 144.0575, found: 144.0580.



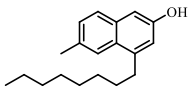
4-(3-Chloropropyl)naphthalen-2-ol (3i): Following general procedure 2, using phenylacetyl chloride and 5-chloro-1-pentyne, the product **3i** was isolated as a yellow oil. 53% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.48–7.42 (m, 1H), 7.42–7.36 (m, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 5.84 (br, s, 1H), 3.58 (t, *J* = 6.4 Hz, 2H), 3.19 (t, *J* = 7.6 Hz, 2H), 2.23–2.14 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.79, 139.42, 135.37, 127.44, 127.37, 126.41, 123.78, 123.69, 118.26, 108.60, 44.69, 33.05, 29.79. HRMS (ESI) m/z calcd for $C_{13}H_{13}ClO$ [M+H]$^+$: 220.0655, found: 220.0660.



5-(3-Hydroxynaphthalen-1-yl)pentyl acetate (3j): Following general procedure 2, using phenylacetyl chloride and hept-6-yn-1-yl acetate, the product **3j** was isolated as a yellow oil. 39% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.45–7.38 (m, 1H), 7.37–7.31 (m, 1H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 1H), 5.65 (br, s, 1H), 4.09 (t, *J* = 6.6 Hz, 2H), 3.03 (t, *J* = 7.8 Hz, 2H), 2.06 (s, 3H), 1.78 (p, *J* = 7.8 Hz, 2H), 1.69 (p, *J* = 7.2 Hz, 2H), 1.52–1.45 (m, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.78, 153.22, 140.99, 135.43, 127.47, 127.38, 126.25, 123.88, 123.46, 117.96, 108.04, 64.75, 32.81, 30.18, 28.59, 26.05, 21.18. HRMS (ESI) m/z calcd for $C_{17}H_{20}O_3$ [M+H]$^+$: 272.1412, found: 272.1416.

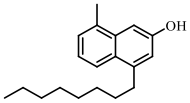


6-Methyl-3,4-diphenylnaphthalen-2-ol (4a): Following general procedure 2, using 4-methylphenylacetyl chloride and diphenylacetylene, the product **4a** was isolated as a yellow solid. 73% yield. Mp: 147-149 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 1H), 7.19–7.07 (m, 9H), 7.05–6.98 (m, 4H), 4.94 (br, s, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.17, 139.45, 138.83, 135.39, 133.23, 132.67, 131.02, 129.74, 128.76, 128.69, 128.27, 127.69, 127.67, 126.71, 126.59, 125.84, 109.40, 21.86. HRMS (ESI) m/z calcd for $C_{23}H_{18}O$ [M+H]$^+$: 310.1358, found: 310.1356.

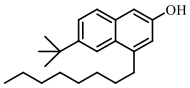


6-Methyl-4-octylnaphthalen-2-ol (4b): Following general procedure 2, using 4-methylphenylacetyl chloride and 1-decyne, the product **4b** was isolated as a yellow oil. 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.28 (dd, *J* = 8.4, 1.6 Hz,

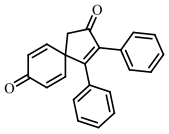
1H), 6.97 (dd, *J* = 10.8, 2.4 Hz, 2H), 5.47 (br, s, 1H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.54 (s, 3H), 1.75 (p, *J* = 7.6 Hz, 2H), 1.50–1.25 (m, 10H), 0.93 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.35, 140.91, 133.41, 132.78, 128.40, 127.75, 127.22, 123.09, 117.75, 107.80, 32.99, 32.05, 30.62, 29.92, 29.63, 29.43, 22.82, 22.00, 14.25. HRMS (ESI) m/z calcd for $C_{19}H_{26}O$ $[M+H]^+$: 270.1984, found: 270.1987.



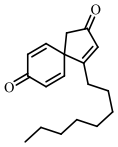
8-Methyl-4-octylnaphthalen-2-ol (4c): Following general procedure 2, using 2-methylphenylacetyl chloride and 1-decyne, the product **4c** was isolated as a pale yellow oil. 74% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94–7.86 (m, 1H), 7.36–7.28 (m, 2H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 5.84 (br, s, 1H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.60 (s, 3H), 1.76 (p, *J* = 7.6 Hz, 2H), 1.51–1.28 (m, 10H), 0.96 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.75, 142.33, 134.53, 133.41, 127.56, 127.00, 123.07, 122.29, 117.33, 104.80, 33.49, 32.03, 30.92, 29.96, 29.62, 29.43, 22.81, 20.01, 14.25. HRMS (ESI) m/z calcd for $C_{19}H_{26}O$ $[M+H]^+$: 270.1984, found: 270.1988.



6-(*tert*-Butyl)-4-octylnaphthalen-2-ol (4d): Following general procedure 2, using 4-*tert*-butyl phenylacetyl chloride and 1-decyne, the product **4d** was isolated as a yellow oil. 78% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 1.6 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.54 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.98 (dd, *J* = 9.6, 2.4 Hz, 2H), 5.43 (br, s, 1H), 3.04 (t, *J* = 7.6 Hz, 2H), 1.77 (p, *J* = 7.6 Hz, 2H), 1.51–1.25 (m, 19H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.60, 145.91, 141.52, 133.38, 127.33, 127.06, 125.04, 118.99, 117.73, 107.58, 34.96, 33.11, 32.03, 31.50, 30.63, 29.91, 29.62, 29.41, 22.82, 14.25. HRMS (ESI) m/z calcd for $C_{22}H_{32}O$ $[M+H]^+$: 312.2453, found: 312.2450.

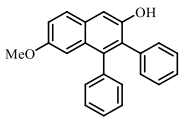


3,4-Diphenylspiro[4.5]deca-3,6,9-triene-2,8-dione (4e): Following general procedure 2, using 4-hydroxyphenylacetyl chloride or 4-methoxyphenylacetyl chloride and diphenylacetylene, the product **4e** was isolated as a gray solid. 65% or 63% yield. Mp: 144-146 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27–7.23 (m, 4H), 7.22–7.16 (m, 4H), 7.11–7.06 (m, 2H), 6.94–6.88 (m, 2H), 6.43–6.33 (m, 2H), 2.91 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.89, 184.80, 169.09, 150.77, 141.23, 133.85, 130.38, 130.33, 129.63, 128.53, 128.40, 128.27, 127.73, 50.95, 45.93. HRMS (ESI) m/z calcd for $C_{22}H_{16}O_2$ $[M+H]^+$: 312.1150, found: 312.1152.

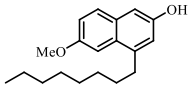


4-Octylspiro[4.5]deca-3,6,9-triene-2,8-dione (4f): Following general procedure 2, using 4-hydroxyphenylacetyl chloride or 4-methoxyphenylacetyl chloride and 1-decyne, the product **4f** was isolated as a yellow oil. 55% or 75% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.68–6.61 (m, 2H), 6.46–6.38 (m, 2H), 6.19 (t, *J* = 1.6 Hz, 1H), 2.62 (s, 2H), 2.11–2.03 (m, 2H), 1.56–1.45 (m, 2H), 1.34–

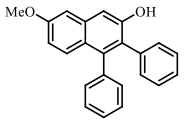
1.14 (m, 10H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.67, 184.96, 181.76, 150.06, 130.73, 130.70, 52.74, 45.19, 31.84, 29.31, 29.24, 29.18, 27.62, 22.70, 14.17. HRMS (ESI) m/z calcd for $C_{18}H_{24}O_2$ $[M+H]^+$: 272.1776, found: 272.1771.



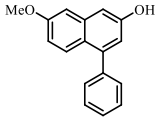
6-Methoxy-3,4-diphenylnaphthalen-2-ol (4g): Following general procedure 2, using 4-methoxyphenylacetyl chloride and diphenylacetylene, the product **4g** was isolated as a yellow solid. 21% yield. Mp: 150-153 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.8 Hz, 1H), 7.20–7.07 (m, 7H), 7.06–6.98 (m, 5H), 6.70 (d, *J* = 2.4 Hz, 1H), 4.85 (br, s, 1H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.18, 149.27, 138.89, 138.87, 135.40, 130.99, 130.93, 130.05, 129.89, 128.95, 128.79, 128.18, 127.83, 127.79, 126.82, 118.98, 109.62, 105.87, 55.23. HRMS (ESI) m/z calcd for $C_{23}H_{18}O_2$ $[M+H]^+$: 326.1307, found: 326.1303.



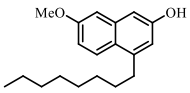
6-Methoxy-4-octylnaphthalen-2-ol (4h): Following general procedure 2, using 4-methoxyphenylacetyl chloride and 1-decyne, the product **4h** was isolated as a yellow oil. 12% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 9.0 Hz, 1H), 7.24 (d, *J* = 1.8 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.95 (dd, *J* = 7.8, 2.4 Hz, 2H), 5.39 (br, s, 1H), 3.91 (s, 3H), 2.94 (t, *J* = 7.8 Hz, 2H), 1.72 (p, *J* = 7.8 Hz, 2H), 1.43 (p, *J* = 7.2 Hz, 2H), 1.36–1.21 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.97, 151.49, 140.12, 130.52, 128.76, 128.32, 118.33, 118.12, 108.02, 103.36, 55.47, 33.15, 32.03, 30.19, 29.91, 29.63, 29.42, 22.81, 14.24. HRMS (ESI) m/z calcd for $C_{19}H_{26}O_2$ $[M+H]^+$: 286.1933, found: 286.1936.



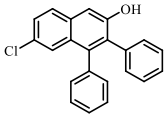
7-Methoxy-3,4-diphenylnaphthalen-2-ol (4i): Following general procedure 2, using 3-methoxyphenylacetyl chloride and diphenylacetylene, the product **4i** was isolated as a yellow solid. 72% yield. Mp: 152-154 ℃**.** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 9.2 Hz, 1H), 7.24–7.00 (m, 12H), 6.84 (dd, *J* = 9.2, 2.8 Hz, 1H), 5.06 (br, s, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.20, 151.42, 140.10, 138.80, 135.88, 135.27, 131.17, 130.92, 128.73, 128.67, 127.67, 127.33, 126.77, 123.55, 116.39, 108.71, 104.76, 55.39. HRMS (ESI) m/z calcd for $C_{23}H_{18}O_2$ $[M+H]^+$: 326.1307, found: 326.1303.



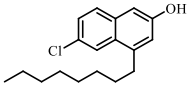
7-Methoxy-4-phenylnaphthalen-2-ol (4j): Following general procedure 2, using 3-methoxyphenylacetyl chloride and phenylacetylene, the product **4j** was isolated as a yellow solid. 64% yield. Mp: 132-133 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 9.2 Hz, 1H), 7.51– 7.40 (m, 5H), 7.09 (d, *J* = 2.4 Hz, 1H), 7.03 (d, *J* = 2.8 Hz, 1H), 6.99–6.91 (m, 2H), 5.91 (br, s, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.09, 153.56, 142.42, 140.34, 136.80, 129.90, 128.33, 127.78, 127.49, 122.72, 116.51, 116.21, 108.68, 105.26, 55.37. HRMS (ESI) m/z calcd for $C_{17}H_{14}O_2$ $[M+H]^+$: 250.0994, found: 250.0995.



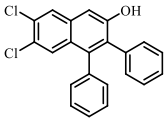
7-Methoxy-4-octylnaphthalen-2-ol (4k): Following general procedure 2, using 3-methoxyphenylacetyl chloride and 1-decyne, the product **4k** was isolated as a yellow oil. 69% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 9.2 Hz, 1H), 7.04 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.98 (d, *J* = 2.8 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 5.76 (br, s, 1H), 3.89 (s, 3H), 2.96 (t, *J* = 8.0 Hz, 2H), 1.71 (p, *J* = 7.6 Hz, 2H), 1.47–1.23 (m, 10H), 0.97–0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.86, 153.74, 141.74, 136.81, 125.62, 122.97, 115.76, 115.48, 107.33, 105.73, 55.34, 33.15, 32.01, 30.85, 29.91, 29.61, 29.41, 22.79, 14.23. HRMS (ESI) m/z calcd for $C_{19}H_{26}O_2$ $[M+H]^+$: 286.1933, found: 286.1937.



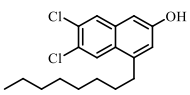
6-Chloro-3,4-diphenylnaphthalen-2-ol (4l): Following general procedure 2, using 4-chlorophenylacetyl chloride and diphenylacetylene, the product **4l** was isolated as a yellow solid. 58% yield. Mp: 148-150 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 1.6 Hz, 1H), 7.40–7.35 (m, 2H), 7.31–7.20 (m, 6H), 7.16–7.12 (m, 2H), 7.11–7.06 (m, 2H), 5.08 (br, s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.10, 139.59, 137.95, 134.70, 132.81, 130.90, 130.72, 129.56, 128.99, 128.90, 128.29, 128.14, 127.97, 127.42, 127.19, 125.84, 109.53. HRMS (ESI) m/z calcd for $C_{22}H_{15}ClO$ $[M+H]^+$: 330.0811, found: 330.0816.



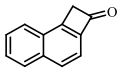
6-Chloro-4-octylnaphthalen-2-ol (4m): Following general procedure 2, using 4-chlorophenylacetyl chloride and 1-decyne, the product **4m** was isolated as a yellow oil. 51% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.59 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.34 (td, *J* = 8.8, 1.6 Hz, 1H), 6.98 (s, 2H), 2.95 (t, *J* = 8.0 Hz, 2H), 1.71 (p, *J* = 7.6 Hz, 2H), 1.47–1.21 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 153.45, 140.98, 133.63, 129.12, 128.80, 128.27, 126.97, 123.12, 118.78, 107.85, 32.91, 32.03, 30.58, 29.85, 29.60, 29.41, 22.82, 14.26. HRMS (ESI) m/z calcd for $C_{18}H_{23}ClO$ $[M+H]^+$: 290.1437, found: 290.1435.



6,7-Dichloro-3,4-diphenylnaphthalen-2-ol (4n): Following general procedure 2, using 3,4-dichlorophenylacetyl chloride and diphenylacetylene, the product **4n** was isolated as a yellow solid. 44% yield. Mp: 155-156 ℃. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.55 (s, 1H), 7.31–7.27 (m, 3H), 7.26–7.22 (m, 4H), 7.15–7.10 (m, 2H), 7.09–7.04 (m, 2H), 5.16 (br, s, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 151.92, 139.64, 137.59, 134.37, 133.60, 130.97, 130.91, 130.83, 130.79, 129.06, 128.29, 128.18, 128.07, 127.87, 127.43, 127.39, 108.55. HRMS (ESI) m/z calcd for $C_{22}H_{14}Cl_2O$ $[M+H]^+$: 364.0422, found: 364.0418.



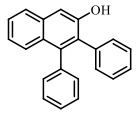
6,7-Dichloro-4-octylnaphthalen-2-ol (4o): Following general procedure 2, using 3,4-dichlorophenylacetyl chloride and 1-decyne, the product **4o** was isolated as a yellow oil. 37% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.76 (s, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 5.29 (br, s, 1H), 2.94 (t, *J* = 7.8 Hz, 2H), 1.70 (p, *J* = 7.8 Hz, 2H), 1.45–1.22 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 154.15, 141.20, 134.54, 130.55, 127.96, 127.48, 126.81, 125.42, 118.91, 106.87, 32.90, 32.02, 30.54, 29.78, 29.58, 29.39, 22.82, 14.25. HRMS (ESI) m/z calcd for $C_{18}H_{22}Cl_2O$ $[M+H]^+$: 324.1048, found: 324.1046.



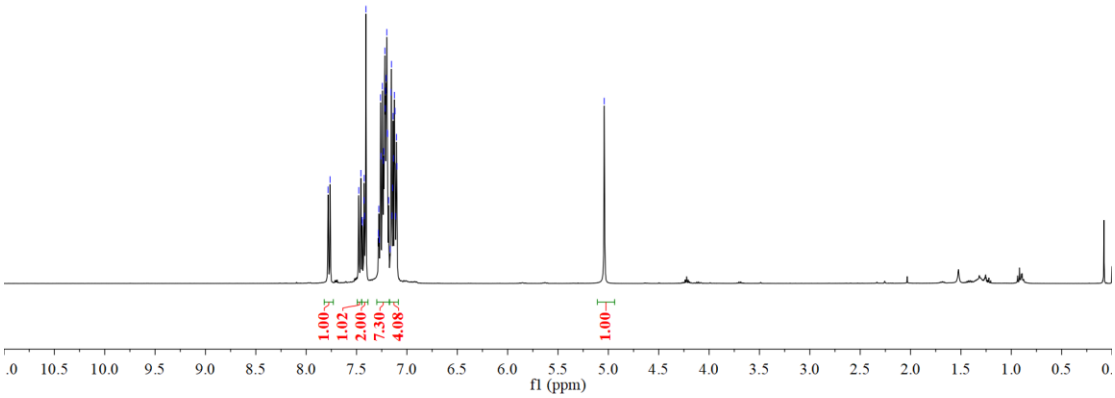
Cyclobuta[a]naphthalen-2(1H)-one (4p): Following general procedure 2, using 1-naphthalacetyl chloride and 1-decyne, the product **4p** was isolated as a white solid. 91% yield. Mp: 75-77 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.38 (d, *J* = 6.8 Hz, 1H), 3.72 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.77, 142.71, 134.86, 134.49, 131.33, 130.77, 128.27, 127.85, 123.83, 121.24, 120.89, 41.85. HRMS (ESI) m/z calcd for $C_{12}H_8O$ $[M+H]^+$: 168.0575, found: 168.0577.

5. ^{1}H-NMR, ^{13}C-NMR spectra of compounds

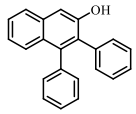
^{1}H NMR (400 MHz, $CDCl_3$)



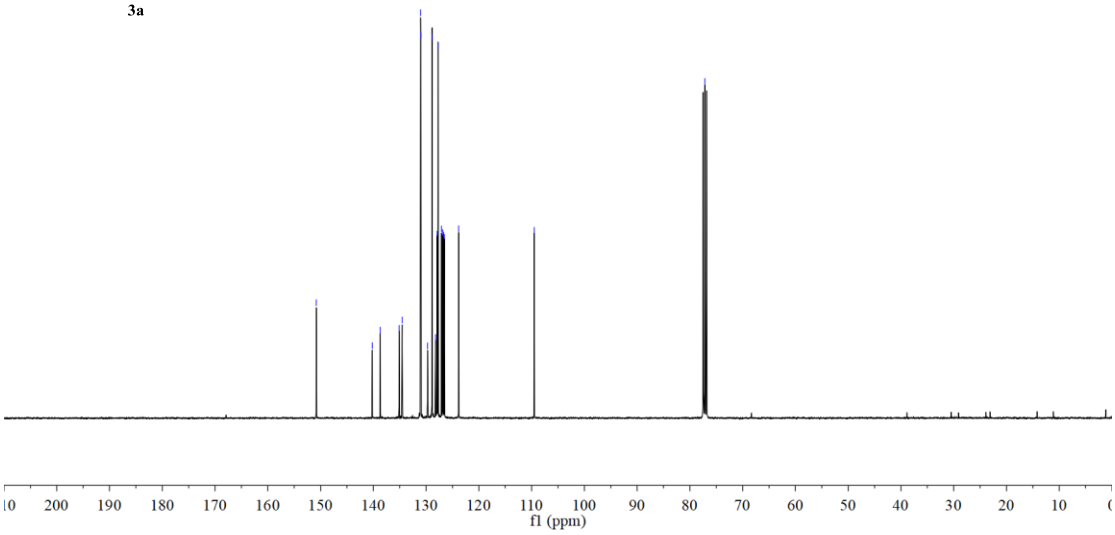
3a



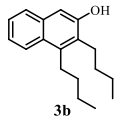
^{13}C NMR (100 MHz, $CDCl_3$)



3a

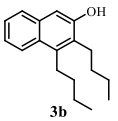


^{1}H NMR (400 MHz, $CDCl_3$)



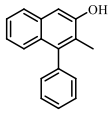
3b

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



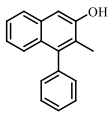
3b

^{1}H NMR (600 MHz, $CDCl_3$)

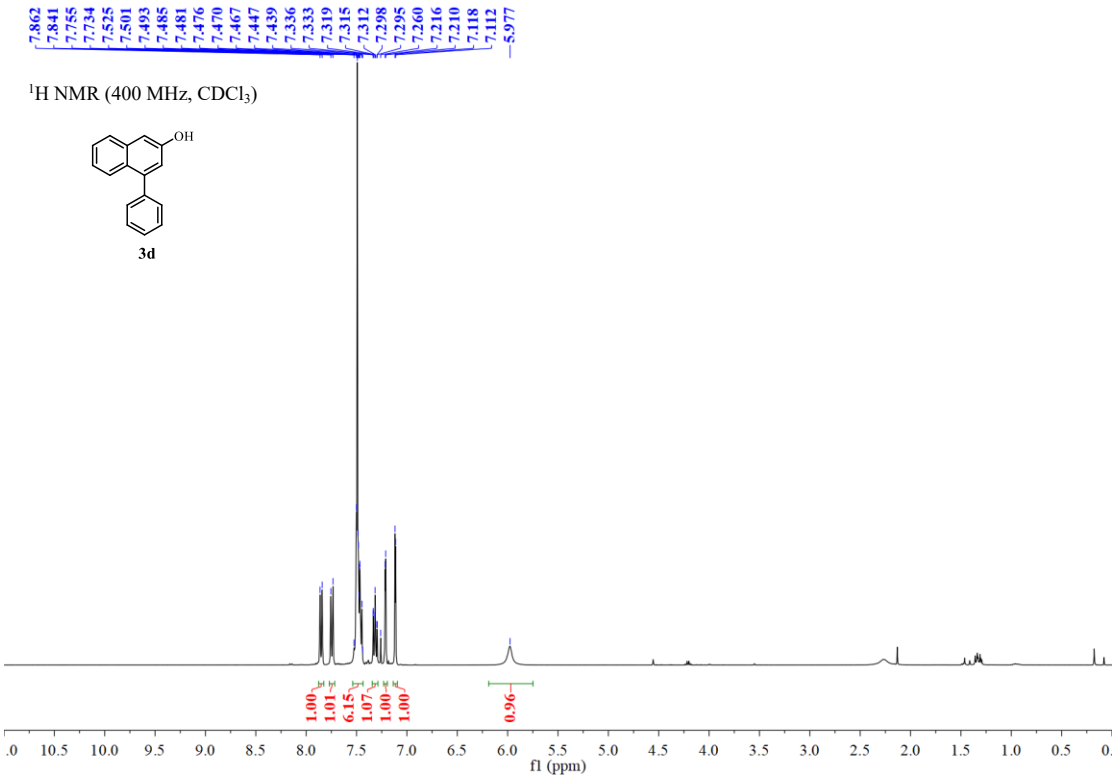


3e

^{13}C NMR (150 MHz, $CDCl_3$)

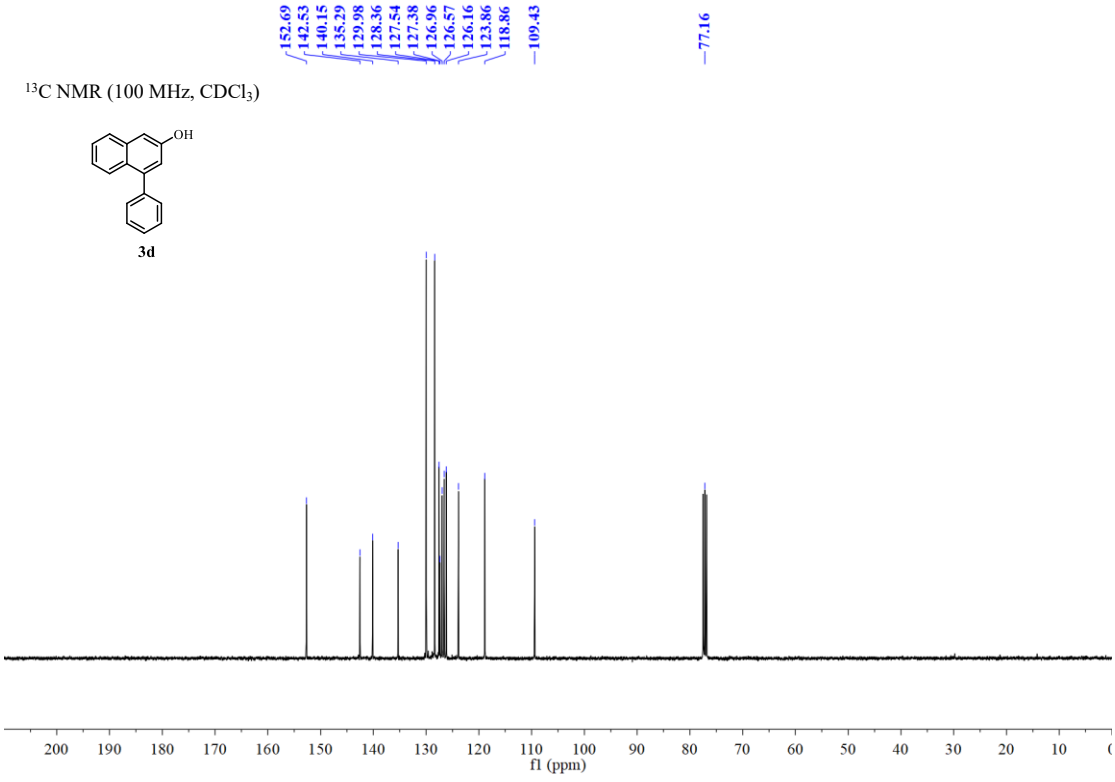


3e



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

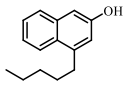
3d



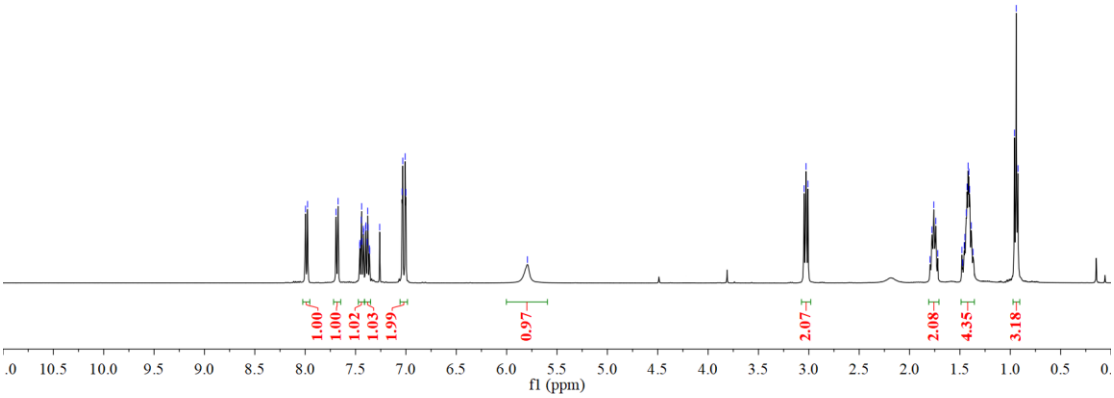
^{13}C NMR (100 MHz, $CDCl_3$)

3d

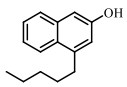
^{1}H NMR (400 MHz, $CDCl_3$)



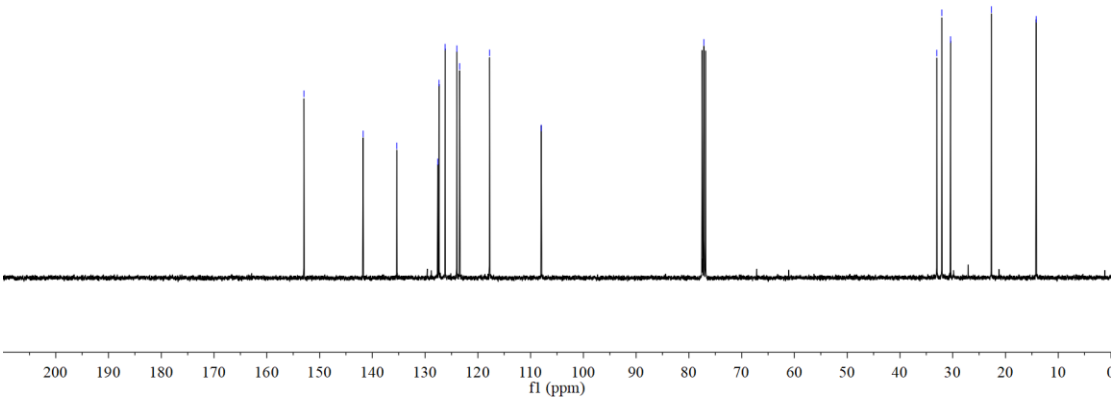
3e



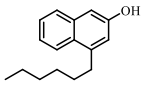
^{13}C NMR (100 MHz, $CDCl_3$)



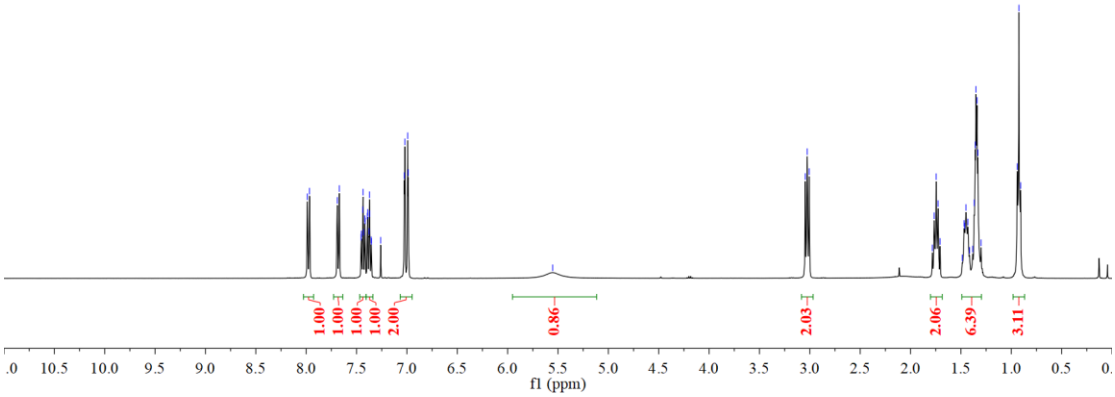
3e



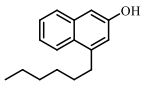
^{1}H NMR (400 MHz, $CDCl_3$)



3f



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



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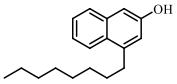
^{1}H NMR (400 MHz, $CDCl_3$)



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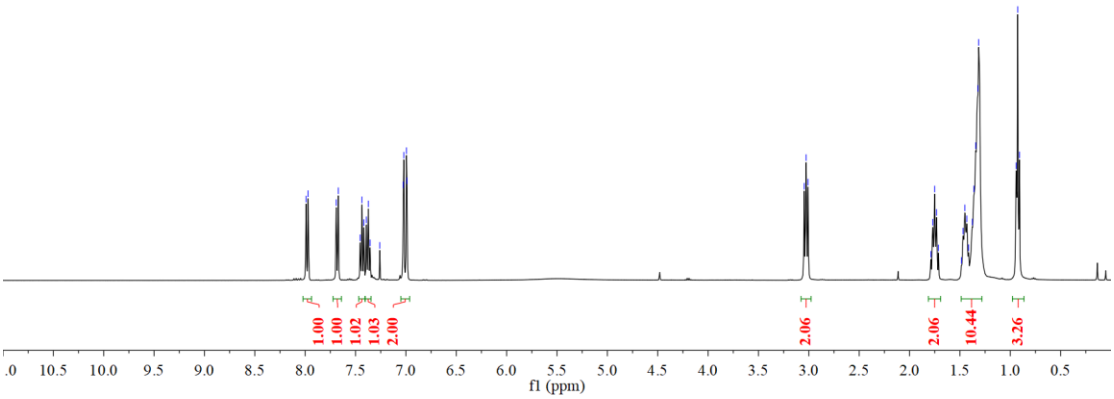
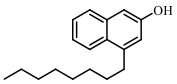


^{13}C NMR (100 MHz, $CDCl_3$)



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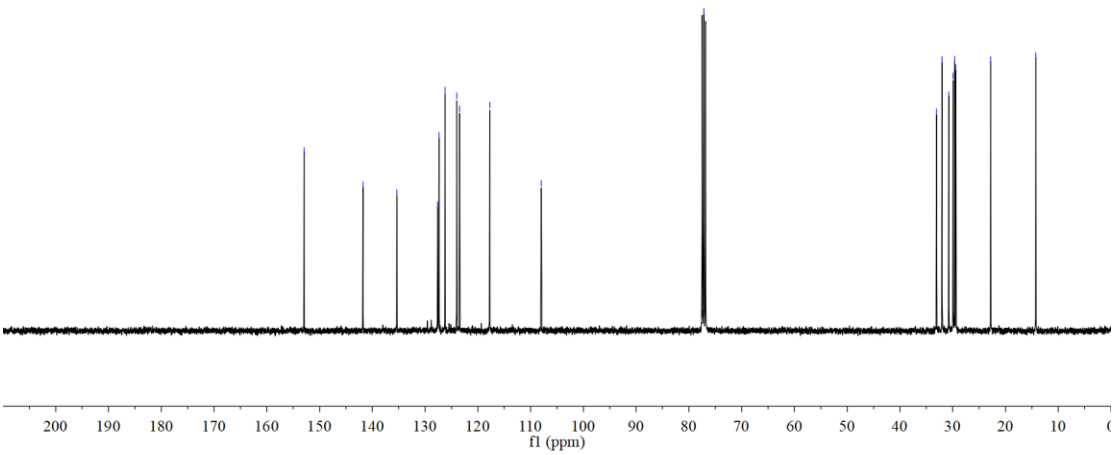
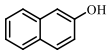


^{1}H NMR (400 MHz, $CDCl_3$)



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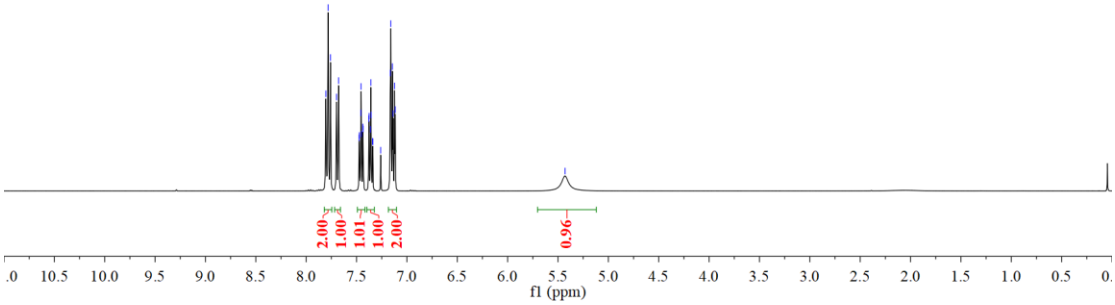
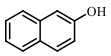
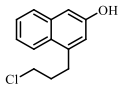


^{13}C NMR (100 MHz, $CDCl_3$)



3h

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



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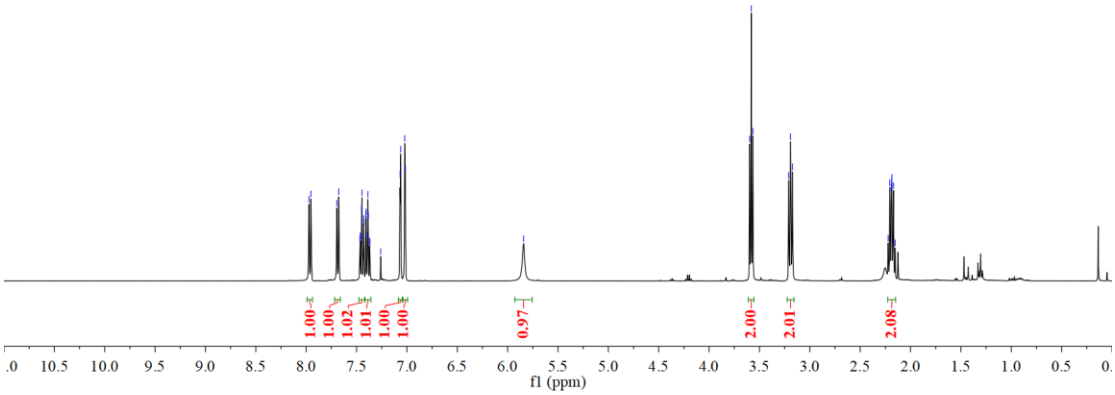
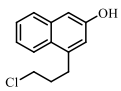


^{13}C NMR (100 MHz, $CDCl_3$)



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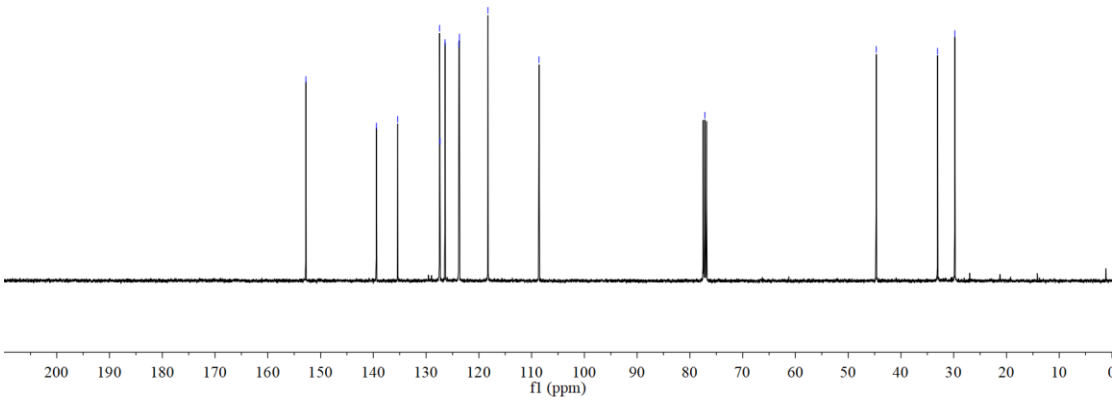
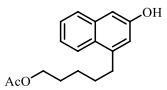
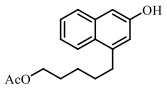


^{1}H NMR (600 MHz, $CDCl_3$)



3j

^{13}C NMR (150 MHz, $CDCl_3$)



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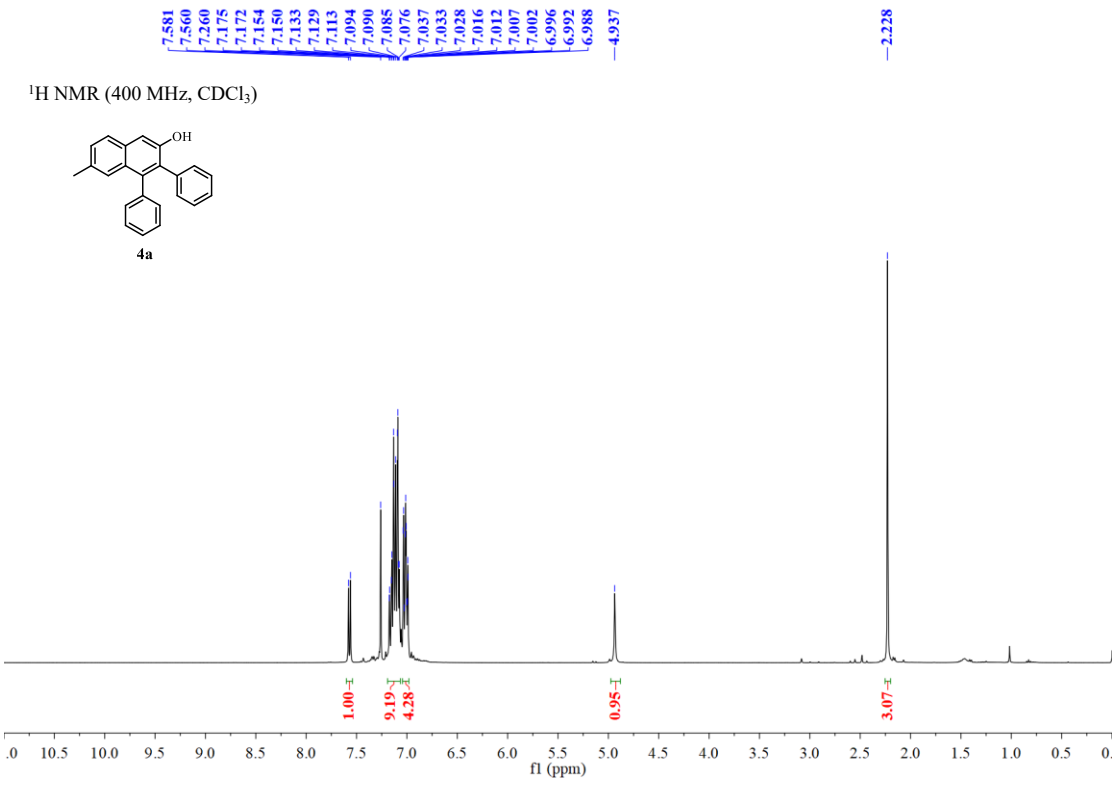
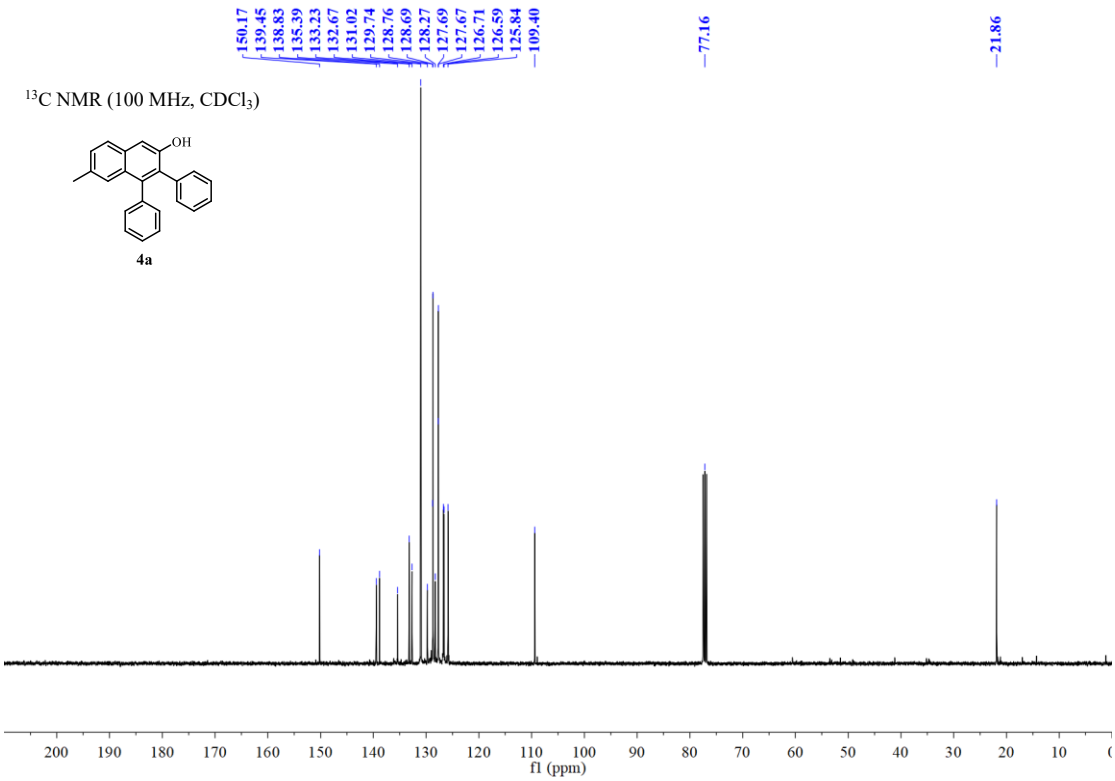


^{1}H NMR (400 MHz, $CDCl_3$)

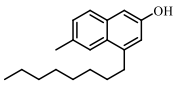
4a



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

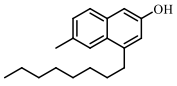
4a

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



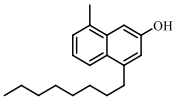
4b

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



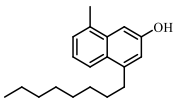
4b

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



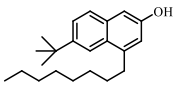
4c

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



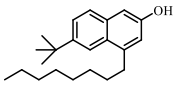
4c

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



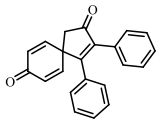
4d

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

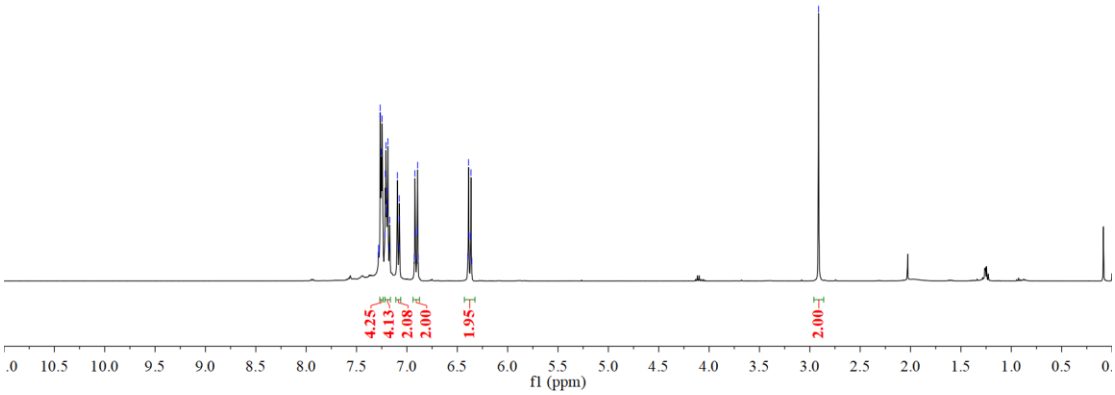


4d

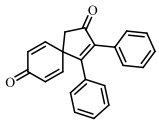
^{1}H NMR (400 MHz, $CDCl_3$)



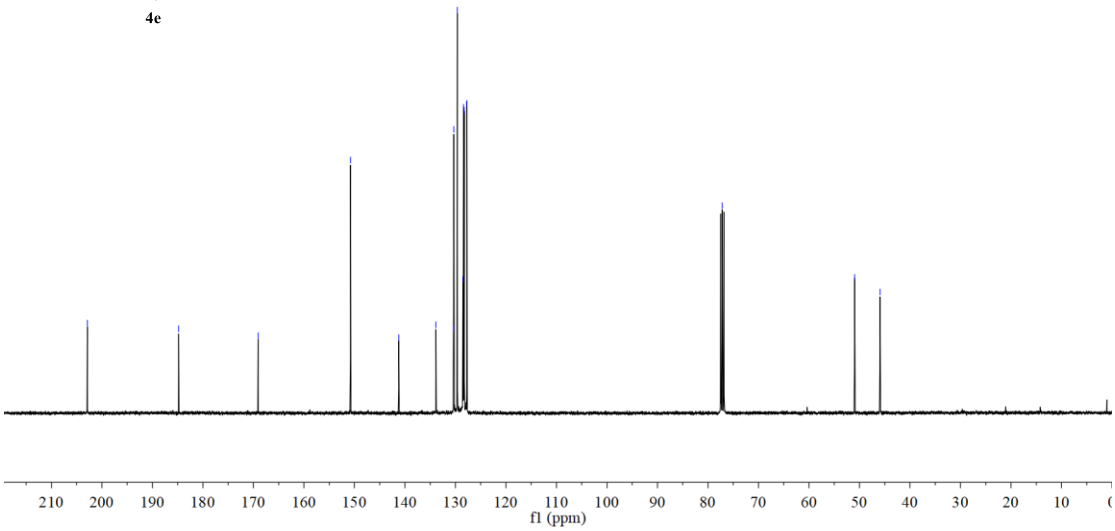
4e



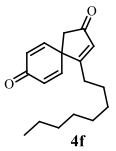
^{13}C NMR (100 MHz, $CDCl_3$)



4e

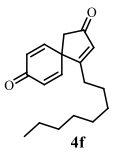


^{1}H NMR (400 MHz, $CDCl_3$)

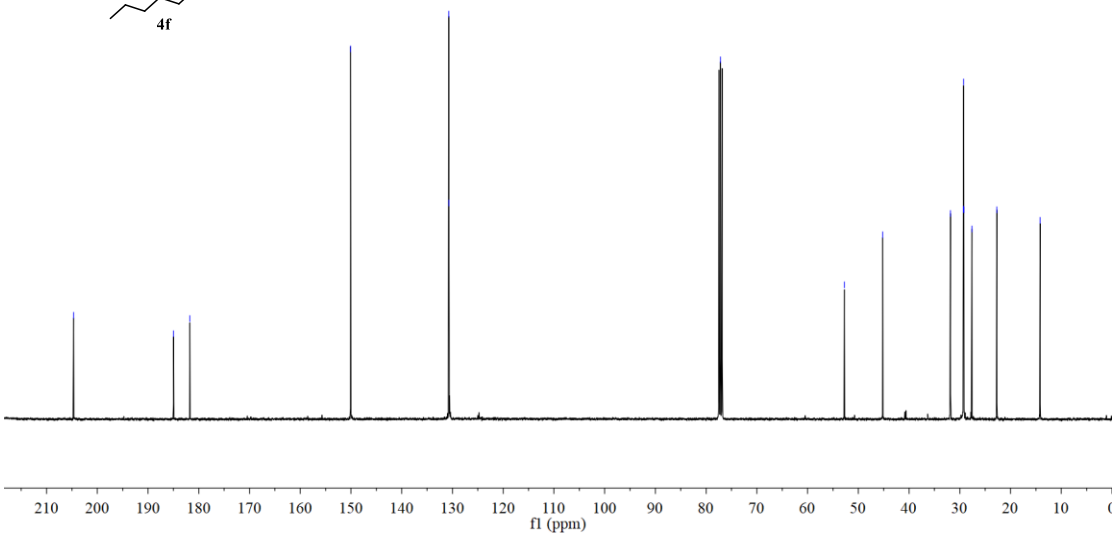


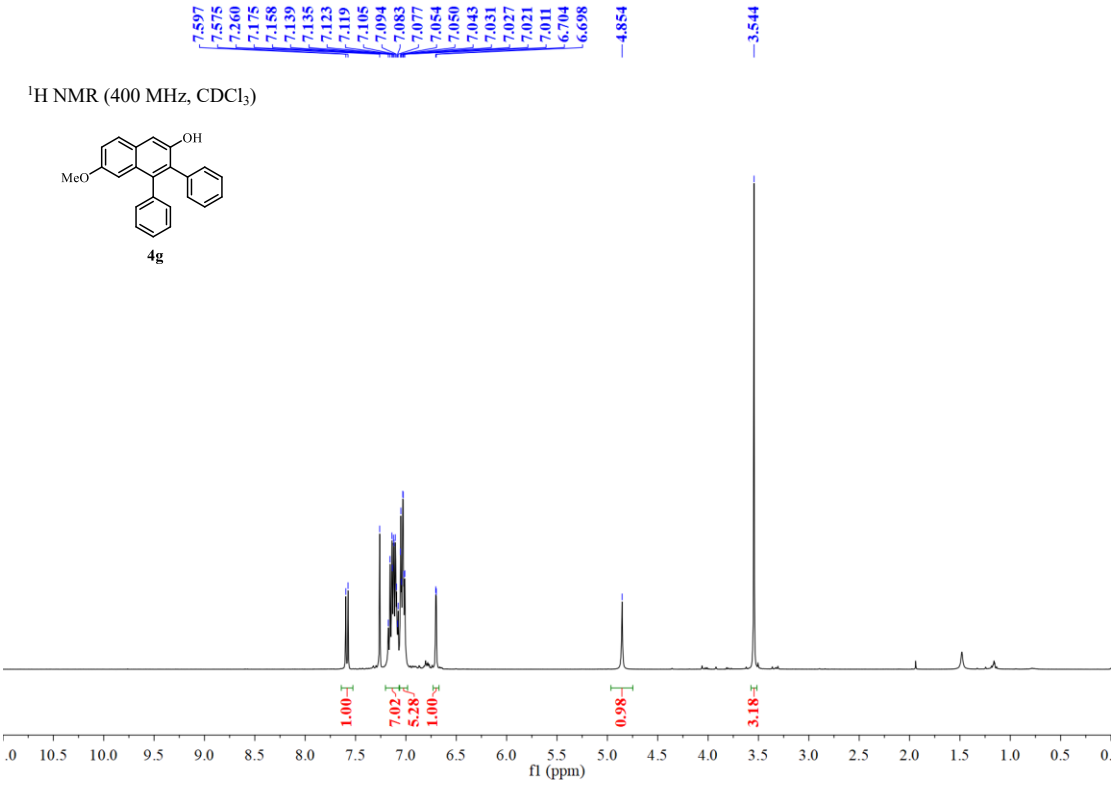
4f

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



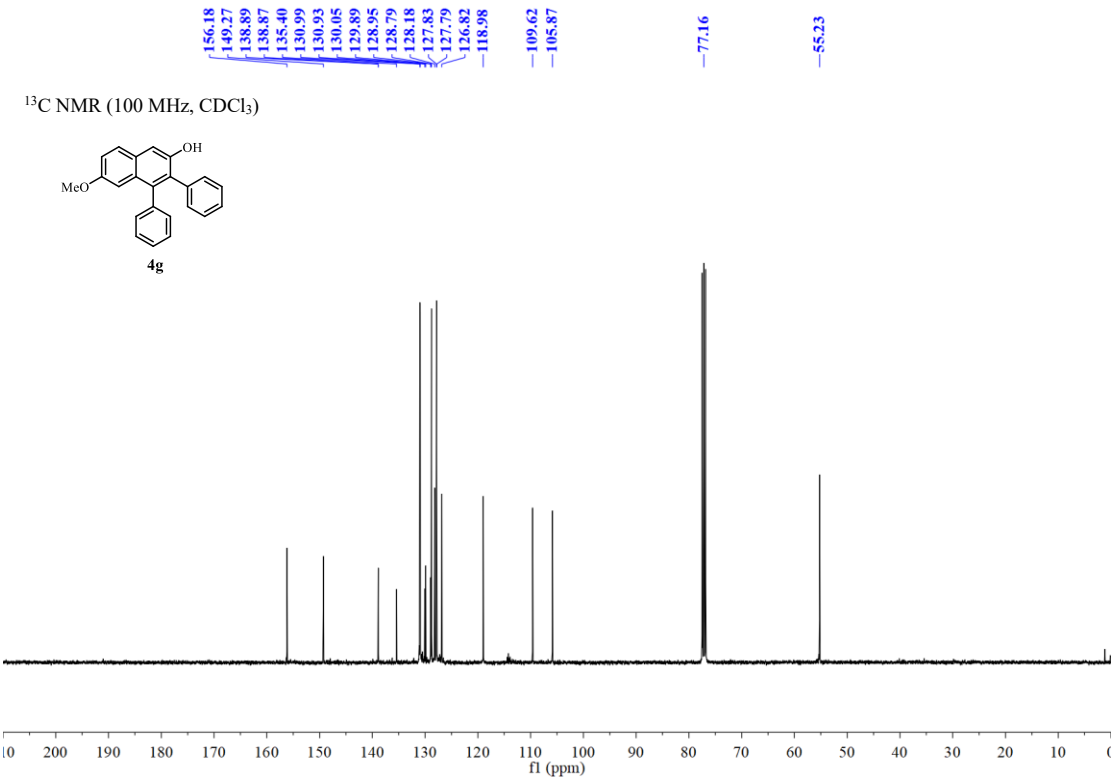
4f





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

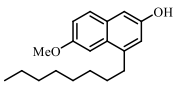
4g



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

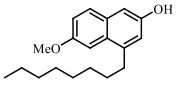
4g

^{1}H NMR (600 MHz, $CDCl_3$)



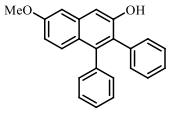
4h

^{13}C NMR (150 MHz, $CDCl_3$)



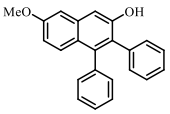
4h

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

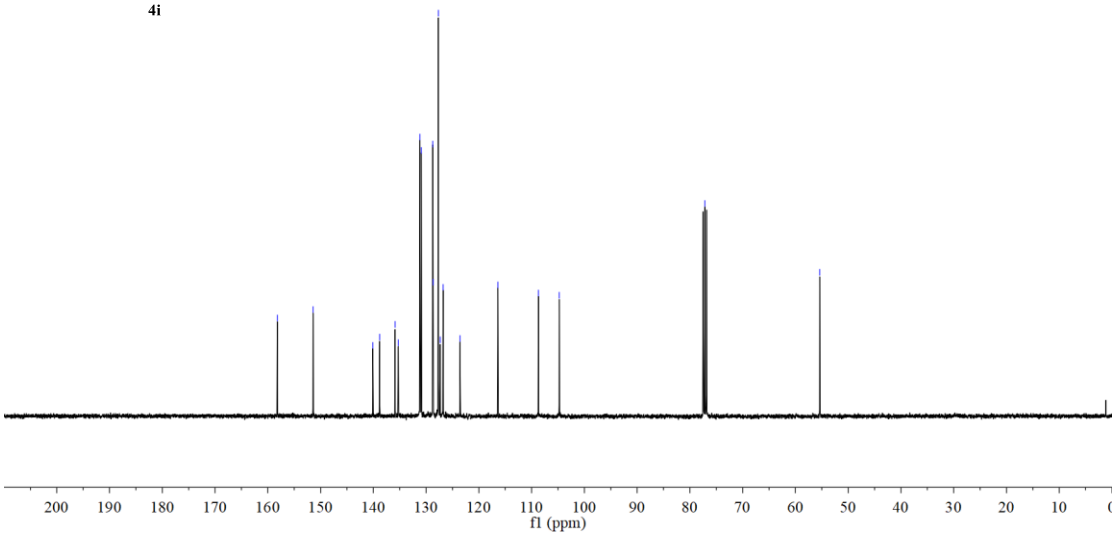


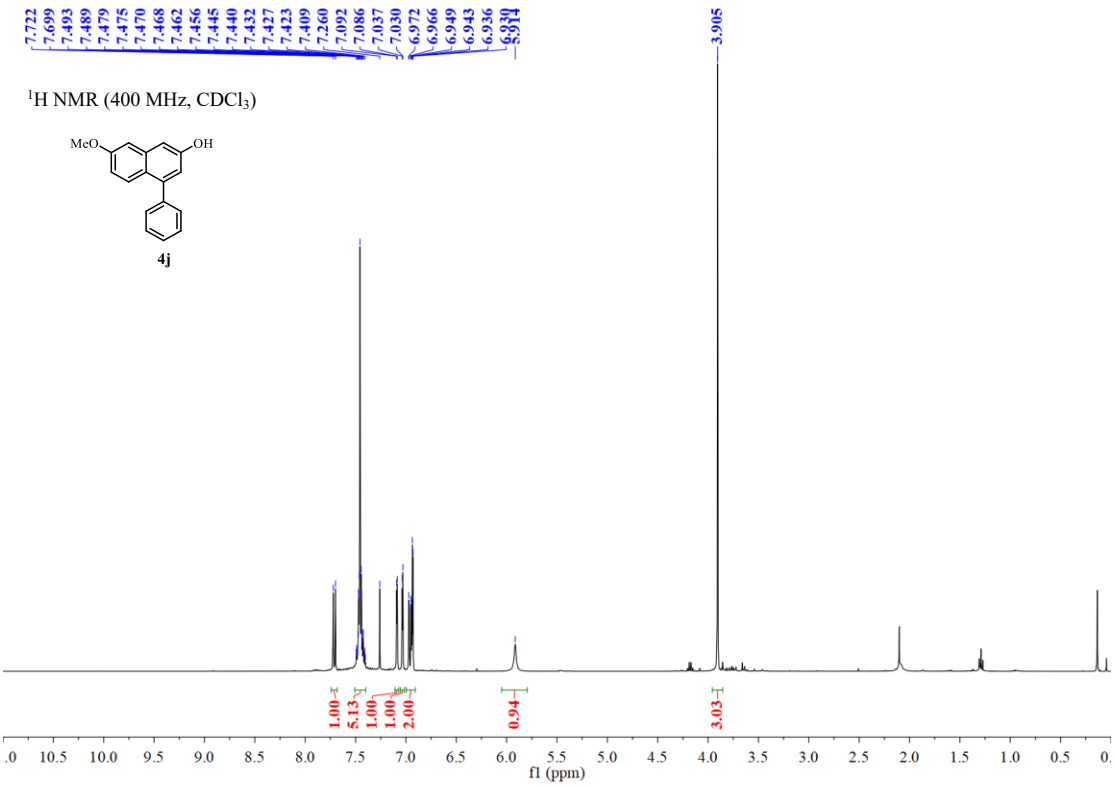
4i

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



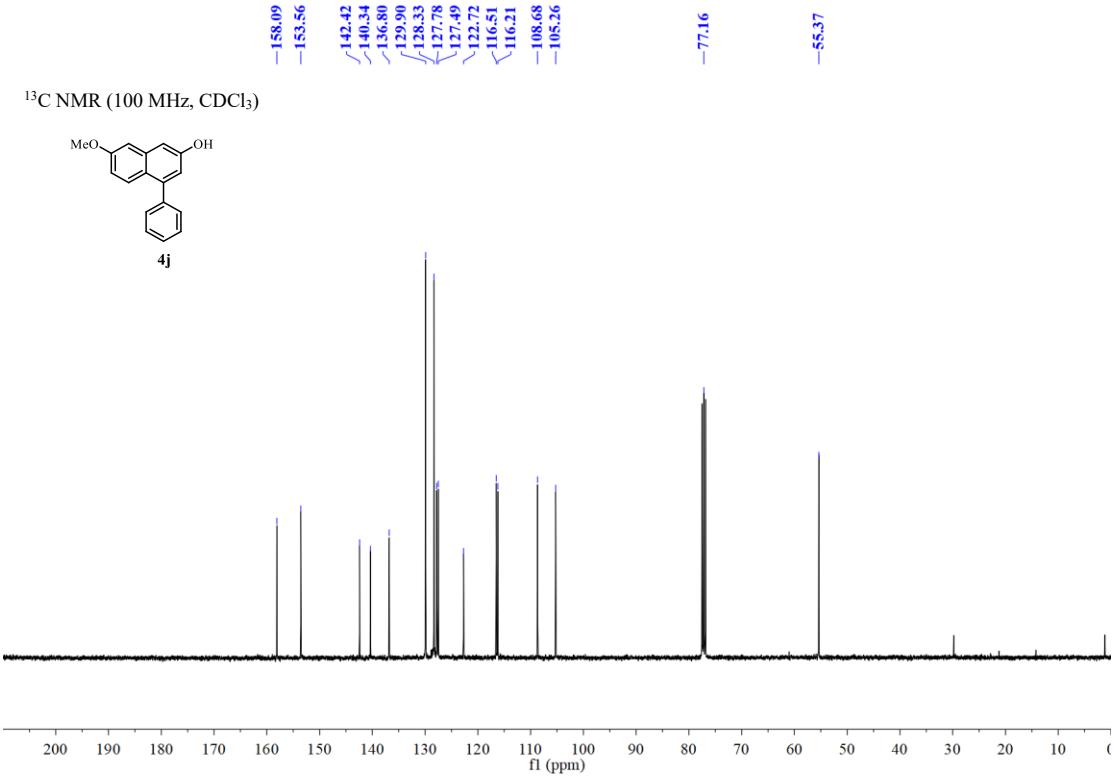
4i





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

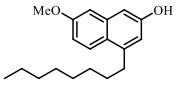
4j



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

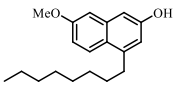
4j

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



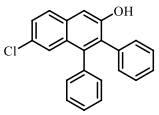
4k

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

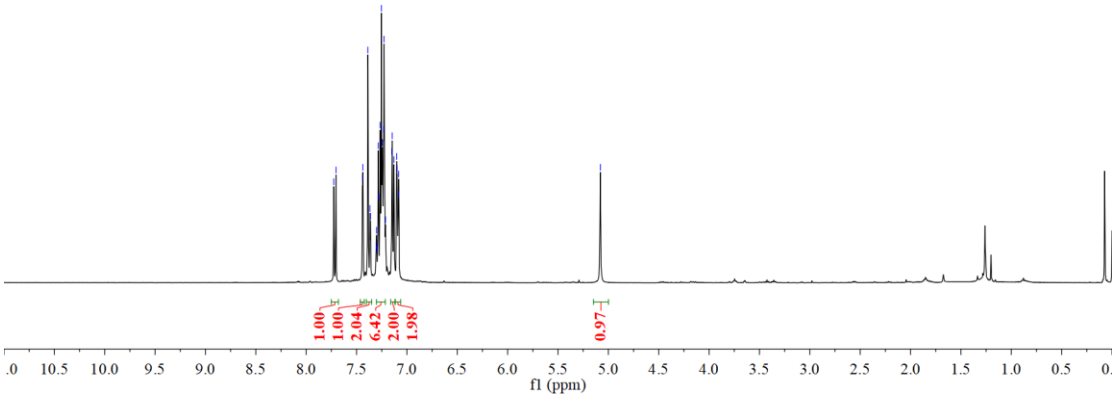


4k

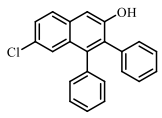
^{1}H NMR (400 MHz, $CDCl_3$)



4l

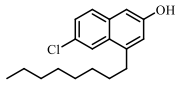


^{13}C NMR (100 MHz, $CDCl_3$)



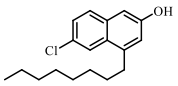
4l

^{1}H NMR (600 MHz, $CDCl_3$)



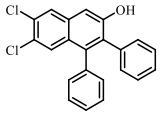
4m

^{13}C NMR (150 MHz, $CDCl_3$)

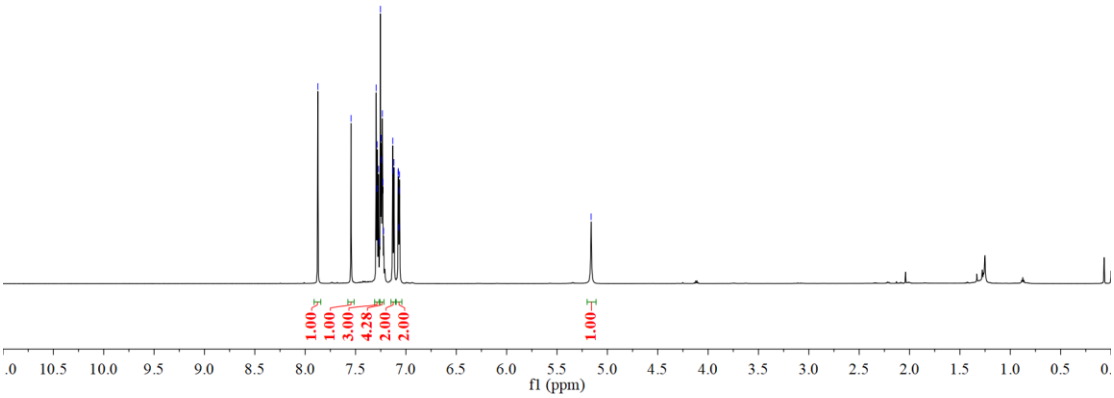


4m

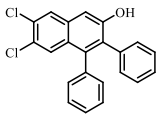
^{1}H NMR (600 MHz, $CDCl_3$)



4n

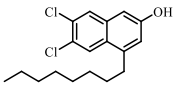


^{13}C NMR (150 MHz, $CDCl_3$)



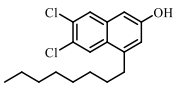
4n

^{1}H NMR (600 MHz, $CDCl_3$)

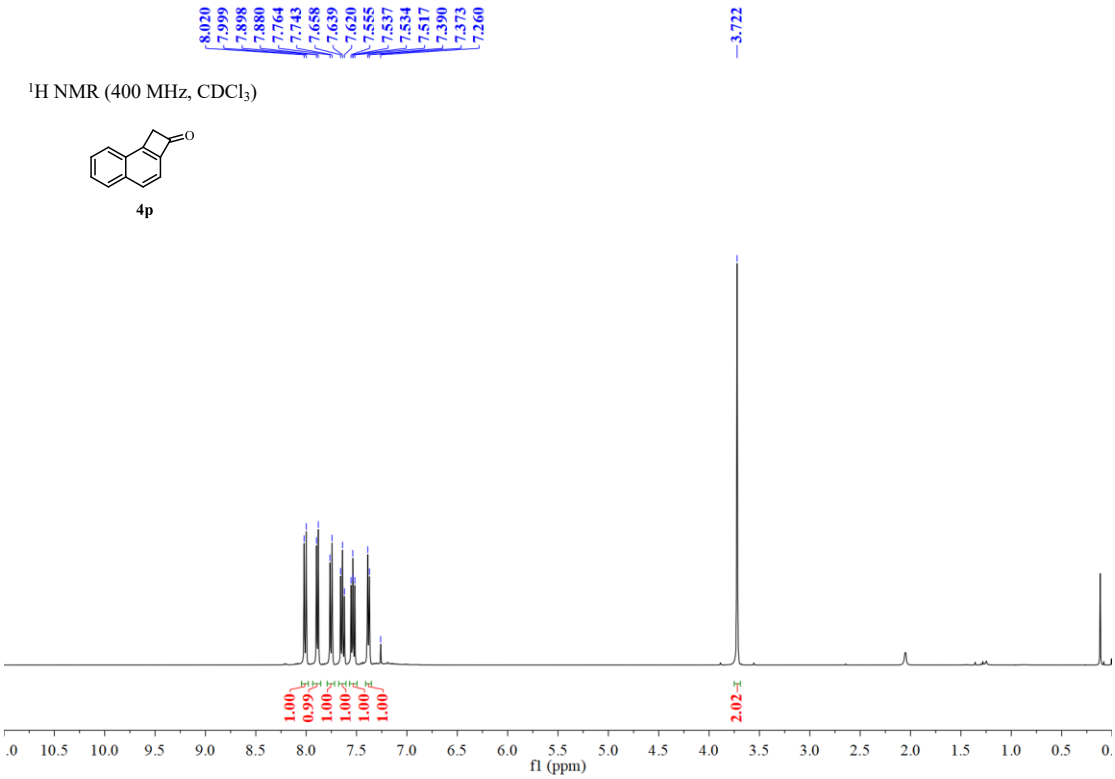


4o

^{13}C NMR (150 MHz, $CDCl_3$)

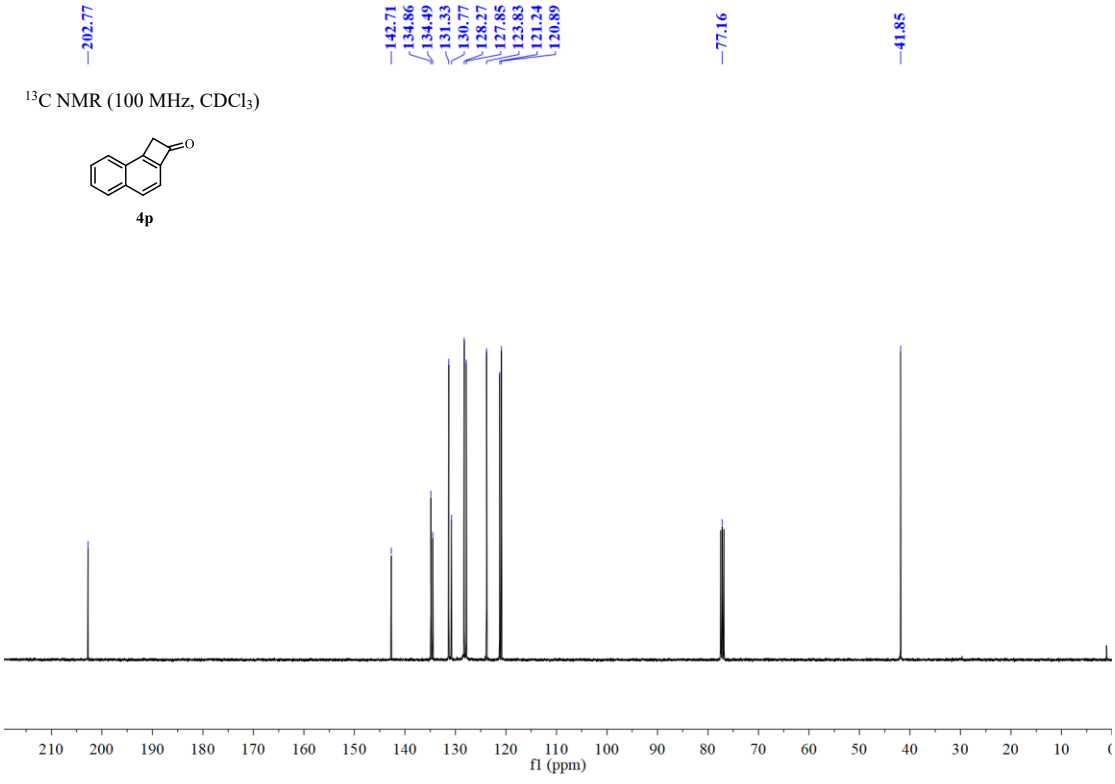


4o



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

4p



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

4p