Electronic Supplementary Information

Palladium-Catalyzed Aerobic Synthesis of *ortho*-Substituted Phenols from Cyclohexanones and Primary Alcohols

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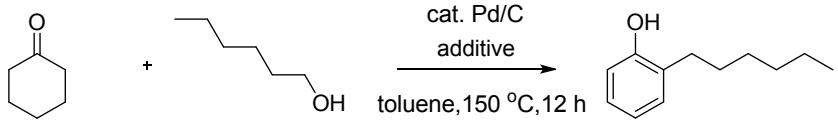
I. General information

All reagents were purchased from commercial sources and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out in air atmosphere unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents (unless otherwise stated). ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz and 600 MHz NMR spectrometers in $CDCl_3$ (unless otherwise stated) at room temperature. The chemical shifts are referenced to internal TMS. HRMS analyses were made by Lanzhou University by means of ESI. Melting points were measured on micro melting point apparatus and uncorrected. All solvents were purified and dried by standard techniques.

II. Optimization of the reaction conditions

1) Screening acid and base

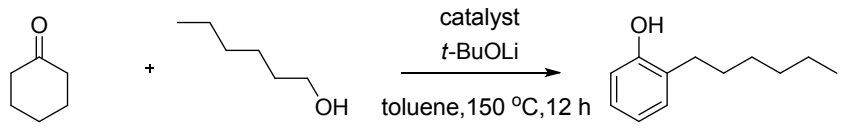


1a **2a** **3a**

Entry	Acids and bases	Yield[a]%
1	-	N.P.
2	NaOH	35
3	NaH	40
4	*t*-BuOK	45
5	*t*-BuOLi	68
6	LiOH	57
7	DBU	N.P.
8	TFA	N.P.
9	$PhCO_2H$	N.P.

General conditions: Cyclohexanone (0.3 mmol), 1-hexanol (0.2 mmol), Pd/C (10 mol%), additive (12.5 mol%), and toluene (1.0 mL) at 150 °C for 12 h under an air atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

2) Screening catalysts

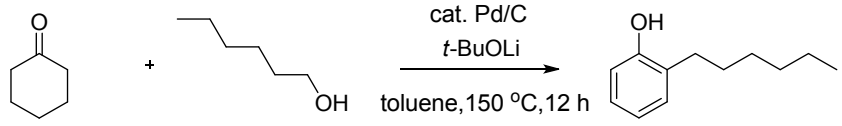


1a 2a 3a

Entry	Catalyst	Yield[a]%
1	-	N.P.
2	Pd/C	68
3	Pd/Al_2O_3	26
4	$Pd(OH)_2/C$	52
5	$Pd(OAc)_2$	N.P.
6	$PdCl_2$	N.P.

General conditions: Cyclohexanone (0.3 mmol), 1-hexanol (0.2 mmol), catalyst (10 mol%), *t*-BuOLi (12.5 mol%), and toluene (1.0 mL) at 150 °C for 12 h under an air atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

3) Screening the amount of *t*-BuOLi

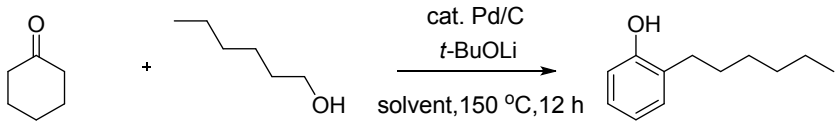


1a 2a 3a

Entry	*t*-BuOLi	Yield[a]%
1	6.25 mol%	25
2	12.5 mol%	68
3	25 mol%	60
4	50 mol%	52
5	1.0 equiv	48

General conditions: Cyclohexanone (0.3 mmol), 1-hexanol (0.2 mmol), Pd/C (10 mol%), *t*-BuOLi, and toluene (1.0 mL) at 150 °C for 12 h under an air atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

4) Screening solvents



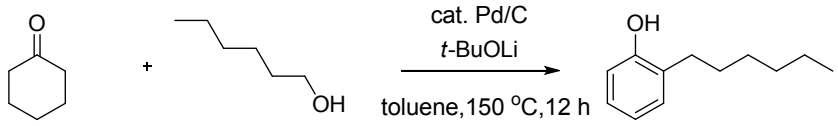
1a 2a 3a

Entry	Solvents	Yield[a]%
1	toluene	68
2	*o*-xylene	N.P.
3	*m*-xylene	N.P.
4	*p*-xylene	N.P.
5	heptane	61

6	cyclohexane	43
7	DMA	N.P.
8	DMSO	N.P.
9	H_2O	N.P.

General conditions: Cyclohexanone (0.3 mmol), 1-hexanol (0.2 mmol), Pd/C (10 mol%), *t*-BuOLi (12.5 mol%), and solvent (1.0 mL) at 150 °C for 12 h under an air atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

5) Screening the amount of O_2

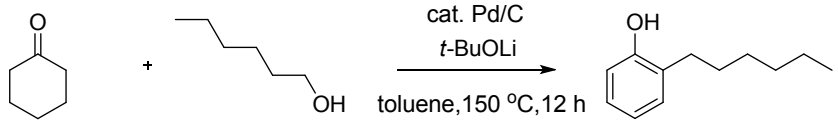


1a **2a** **3a**

Entry	O_2	Yield[a]%
1	Ar	42
2	0.5 mL	55
3	1.0 mL	64
4	2.0 mL	65
5	4.0 mL	55
6	O_2	50
7	air	68

General conditions: Cyclohexanone (0.3 mmol), 1-hexanol (0.2 mmol), Pd/C (10 mol%), *t*-BuOLi (12.5 mol%), and toluene (1.0 mL) at 150 °C for 12 h. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

6) Screening the amount of cyclohexanone

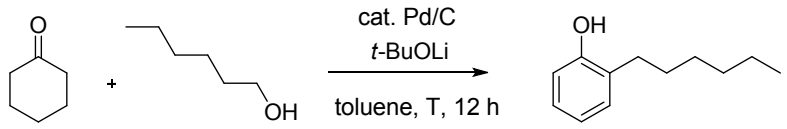


1a **2a** **3a**

Entry	Cyclohexanone	Yield[a]%
1	0.2 mmol	65
2	0.3 mmol	68
3	0.4 mmol	65
4	0.6 mmol	56

General conditions: Cyclohexanone, 1-hexanol (0.2 mmol), Pd/C (10 mol%), *t*-BuOLi (12.5 mol%), and toluene (1.0 mL) at 150 °C for 12 h under an air atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

7) Screening reaction temperature

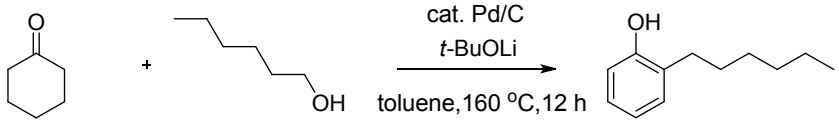


1a 2a 3a

Entry	Temperature/ °C	Yield[a]%
1	140	55
2	150	68
3	160	75
4	170	77

General conditions: Cyclohexanone (0.3 mmol), 1-hexanol (0.2 mmol), Pd/C (10 mol%), *t*-BuOLi (12.5 mol%), and toluene (1.0 mL) for 12 h under an air atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

8) Screening the amount of catalyst

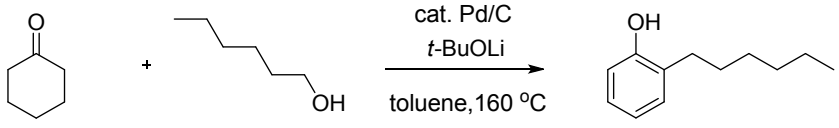


1a 2a 3a

Entry	Pd/C	Yield[a]%
1	5 mol%	71
2	7 mol%	75
3	10 mol%	75
4	15 mol%	27

General conditions: Cyclohexanone (0.3 mmol), 1-hexanol (0.2 mmol), Pd/C, *t*-BuOLi (12.5 mol%), and toluene (1.0 mL) at 160 °C for 12 h under an air atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

9) Screening reaction time

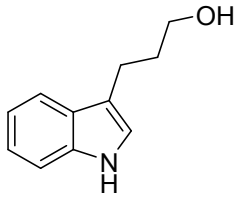


1a 2a 3a

Entry	Time	Yield[a]%
1	5 h	60
2	12 h	75
3	24 h	75

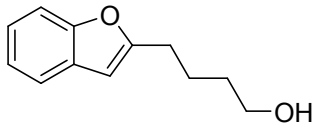
General conditions: Cyclohexanone (0.3 mmol), 1-hexanol (0.2 mmol), Pd/C (7 mol%), *t*-BuOLi (12.5 mol%), and toluene (1.0 mL) at 160 °C under an air atmosphere. [a]Yields were determined by ^{1}H NMR with nitromethane as internal standard.

III. Preparation and characterization of the starting materials



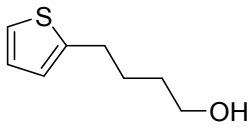
3-(1H-indol-3-yl)propan-1-ol (2k)

The alcohol was synthesized according to the literature procedures for $LiAlH_4$ reduction of carboxylic acid compounds.[1] ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.11 (t, *J* = 6.8 Hz, 1H), 6.96 (s, 1H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.03–1.92 (m, 2H), 1.58 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 127.6, 122.1, 121.4, 119.3, 119.0, 116.1, 111.2, 62.8, 33.1, 21.5.



4-(benzofuran-2-yl)butan-1-ol (2l)

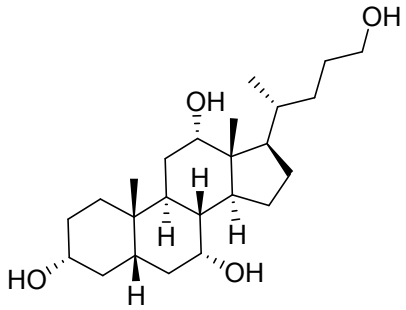
The alcohol was synthesized according to the literature procedures.[2] ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.44 (m, 1H), 7.43–7.37 (m, 1H), 7.23–7.12 (m, 2H), 6.38 (s, 1H), 3.67 (t, *J* = 6.5 Hz, 2H), 2.80 (t, *J* = 7.4 Hz, 2H), 1.90–1.77 (m, 2H), 1.73–1.61 (m, 2H), 1.59 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 154.8, 129.1, 123.3, 122.5, 120.3, 110.8, 102.2, 62.7, 32.3, 28.3, 24.1.



4-(thiophen-2-yl)butan-1-ol (2m)

The alcohol was synthesized according to the literature procedures.[2] ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.80–6.76 (m, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 1.81 (s, 1H), 1.80–

1.70 (m, 2H), 1.67–1.57 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 126.8, 124.2, 123.0, 62.7, 32.2, 29.7, 28.0.

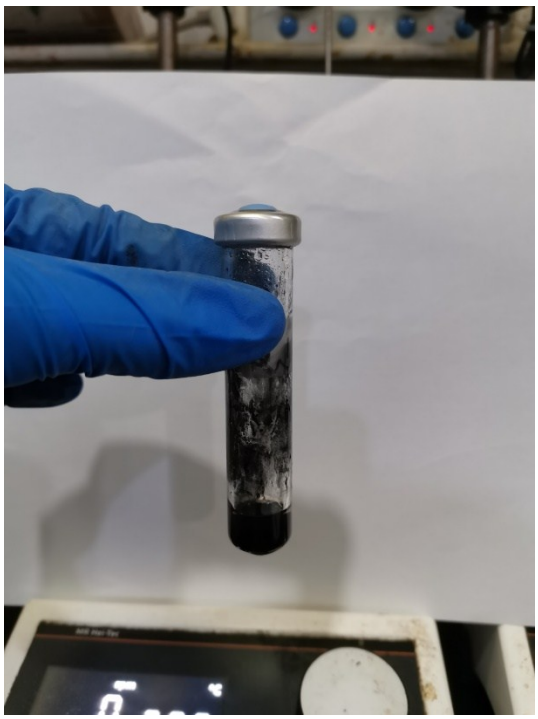
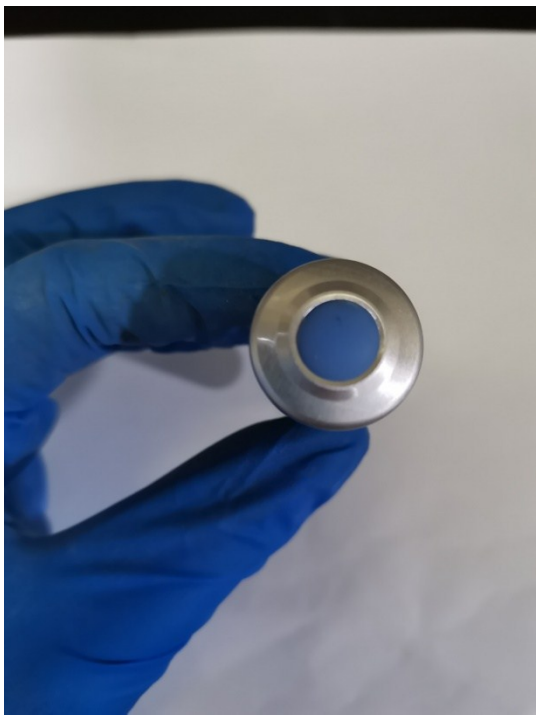


Cholic alcohol (2p)

The alcohol was synthesized according to the literature procedures.[1] ^{1}H NMR (600 MHz, CD_3OD) δ 3.96 (m, 1H), 3.79 (m, 1H), 3.57–3.46 (m, 2H), 3.40–3.30 (m, 1H), 2.32–2.21 (m, 2H), 2.00–1.35 (m, 19H), 1.32–1.25 (m, 1H), 1.16–1.06 (m, 2H), 1.02 (d, J = 6.6 Hz, 3H), 0.91 (s, 3H), 0.71 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 74.1, 72.9, 69.1, 63.6, 48.3, 47.5, 43.2, 43.0, 41.1, 40.5, 37.1, 36.5, 35.9, 35.8, 33.2, 31.2, 30.4, 29.6, 28.8, 27.9, 24.2, 23.2, 18.1, 13.0.

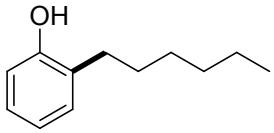
IV. General procedure for the cross-coupling of cyclohexanones with primary alcohols

An oven-dried microwave reacting tube (10 mL) was charged with a magnetic stir-bar, Pd/C (10 wt%, 15 mg, 7 mol% based on Pd contents, vacuum drying under reduced pressure for six hours) and lithium *tert*-butoxide (2.0 mg, 0.025 mmol). Under an air atmosphere, toluene (1.0 mL), cyclohexanone (0.3 mmol) and alcohol (0.2 mmol) was added. Then the tube was sealed with an aluminum cover with a teflon pad and placed in a preheated oil bath at 160 °C and the mixture was stirred vigorously for 24 h. The reaction mixture was cooled to room temperature and filtered through the pad of silica gel. The filtrate was concentrated and the resulting residue was purified via the column chromatography.

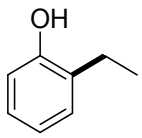
The photo of the reaction device

V. Characterization data of products



2-hexylphenol (3a)

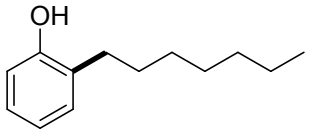
Yellow oil; IR (film): 3423, 2957, 2929, 2858, 1591, 1504, 1455, 1233, 1172, 1120, 844, 751cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.01 (m, 2H), 6.86 (t, J = 7.4 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 4.88 (s, 1H), 2.59 (t, J = 8.0 Hz, 2H), 1.65–1.54 (m, 2H), 1.42–1.22 (m, 6H), 0.88 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 130.3, 128.8, 127.1, 120.9, 115.3, 31.9, 30.1, 29.9, 29.4, 22.8, 14.3. HRMS (ESI) calcd. for $C_{12}H_{19}O$ ($[M+H]^+$): 179.1430, found: 179.1435.



2-ethylphenol (3b) [3]

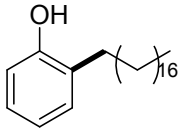
Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, J = 7.5 Hz, 1H), 7.09 (t, J = 7.7

Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.9 Hz, 1H), 4.72 (s, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.4, 130.0, 129.4, 127.1, 121.0, 115.2, 23.1, 14.1.



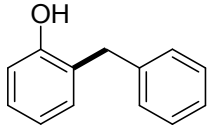
2-heptylphenol (3c)

Yellow oil; IR (film): 3444, 2957, 2927, 2857, 1591, 1504, 1455, 1233, 1172, 1120, 751cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.04 (m, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 4.72 (s, 1H), 2.59 (t, *J* = 8.0 Hz, 2H), 1.66–1.54 (m, 2H), 1.41–1.21 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 130.3, 128.7, 127.1, 120.9, 115.3, 32.0, 30.1, 29.9, 29.7, 29.4, 22.8, 14.3. HRMS (ESI) calcd. for $C_{13}H_{21}O$ ($[M+H]^+$): 193.1587, found: 193.1591.



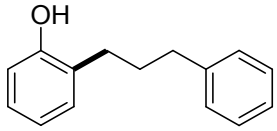
2-octadecylphenol (3d)

White solid; M.p. 62–63 ^{o}C; IR (film): 3341, 2920, 2849, 1466, 1384, 1235, 1215, 1121, 747cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.03 (m, 2H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 4.72 (s, 1H), 2.59 (t, *J* = 8.0 Hz, 2H), 1.66–1.54 (m, 2H), 1.43–1.17 (m, 30H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 130.3, 128.7, 127.1, 120.9, 115.3, 32.1, 30.1, 29.9, 29.9(9C), 29.8, 29.7, 29.7, 29.5, 22.9, 14.3. HRMS (ESI) calcd. for $C_{24}H_{43}O$ ($[M+H]^+$): 347.3308, found: 347.3313.



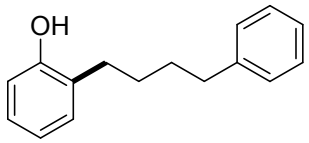
2-benzylphenol (3e) [4]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.26 (m, 2H), 7.25–7.18 (m, 3H), 7.16–7.08 (m, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.72 (s, 1H), 3.99 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 139.9, 131.1, 128.8, 128.8, 128.0, 127.1, 126.5, 121.1, 115.8, 36.5.



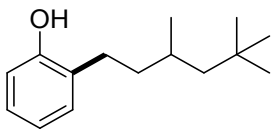
2-(3-phenylpropyl)phenol (3f)[5]

Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 7.23–7.15 (m, 3H), 7.14–7.03 (m, 2H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 4.72 (s, 1H), 2.71–2.59 (m, 4H), 2.01–1.89 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 142.4, 130.3, 128.6, 128.4, 128.2, 127.3, 125.9, 120.9, 115.3, 35.7, 31.3, 29.6.



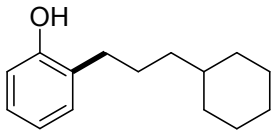
2-(4-phenylbutyl)phenol (3g)

Colorless solid; M.p. 77–79 ^{o}C; IR (film): 3511, 3065, 3028, 2935, 2857, 1593, 1496, 1455, 1330, 1233, 1172, 1099, 846, 751, 700cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.23 (m, 2H), 7.20–7.15 (m, 3H), 7.12–7.04 (m, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 4.69 (s, 1H), 2.69–2.58 (m, 4H), 1.75–1.60 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 142.7, 130.4, 128.6, 128.4, 128.4, 127.2, 125.8, 120.9, 115.3, 35.9, 31.4, 29.9, 29.5. HRMS (ESI) calcd. for $C_{16}H_{19}O$ ($[M+H]^+$): 227.1430, found: 227.1434.



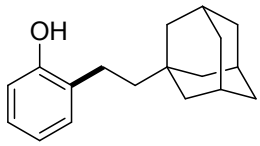
2-(3,5,5-trimethylhexyl)phenol (3h)

Colorless oil; IR (film): 3470, 2955, 2912, 2868, 1591, 1455, 1366, 1235, 1172, 1105, 751cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.1 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 4.66 (s, 1H), 2.65–2.52 (m, 2H), 1.63–1.52 (m, 2H), 1.49–1.39 (m, 1H), 1.30 (dd, *J* = 13.9, 3.5 Hz, 1H), 1.09 (dd, *J* = 13.9, 6.0 Hz, 1H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.89 (s, 9H). ^{13}C NMR (151 MHz, CDCl3) δ 153.5, 130.1, 129.0, 127.1, 121.0, 115.3, 51.3, 39.6, 31.3, 30.2, 29.6, 27.8, 22.7. HRMS (ESI) calcd. for $C_{15}H_{25}O$ ([M+H]$^+$): 221.1900, found: 221.1902.



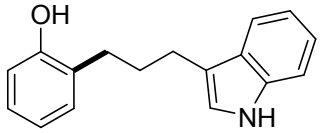
2-(3-cyclohexylpropyl)phenol (3i)

Colorless solid; M.p. 33–34 ^{o}C; IR (film): 3431, 2924, 2853, 1591, 1455, 1235, 751cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.04 (m, 2H), 6.87 (t, *J* = 7.6 HZ, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.72 (s, 1H), 2.57 (t, *J* = 8.0 HZ, 2H), 1.75–1.56(m, 7H), 1.30–1.06 (m, 6H), 0.93–0.80 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 130.2, 128.7, 127.1, 120.9, 115.3, 37.7, 37.5, 33.5, 30.3, 27.2, 26.9, 26.6. HRMS (ESI) calcd. for $C_{15}H_{23}O$ ([M+H]$^+$): 219.1743, found: 219.1744.



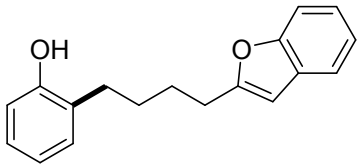
2-(2-(adamantan-1-yl)ethyl)phenol (3j)

White solid; M.p. 120–121 ^{o}C; IR (film): 3285, 2901, 2845, 1591, 1455, 1230, 913, 749 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.70 (s, 1H), 2.61–2.50 (m, 2H), 1.98 (s, 3H), 1.72 (d, *J* = 12.1 Hz, 3H), 1.65 (d, *J* = 12.0 Hz, 3H), 1.57 (s, 6H), 1.39–1.32 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.4, 130.0, 129.4, 127.0, 121.0, 115.3, 44.8, 42.4, 37.4, 32.6, 28.9, 23.1. HRMS (ESI) calcd. for $C_{18}H_{25}O$ ([M+H]$^+$): 257.1900, found: 257.1904.



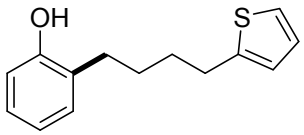
2-(3-(1H-indol-3-yl)propyl)phenol (3k)

Brown solid; M.p. 100–102 ^{o}C; IR (film): 3418, 3056, 2931, 2857, 1591, 1504, 1489, 1455, 1340, 1241, 1097, 745cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.22–7.04 (m, 4H), 6.99 (s, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 4.69 (s, 1H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.11–2.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 136.5, 130.4, 128.4, 127.7, 127.2, 122.1, 121.4, 120.9, 119.3, 119.1, 116.6, 115.4, 111.2, 30.0, 29.8, 25.0. HRMS (ESI) calcd. for $C_{17}H_{18}NO$ ([M+H]$^{+}$): 252.1383, found: 252.1379.



2-(4-(benzofuran-2-yl)butyl)phenol (3l)

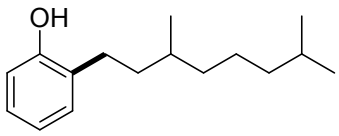
Yellow oil; IR (film): 3529, 3065, 3035, 2937, 2860, 1589, 1504, 1455, 1328, 1254, 1174, 1099, 944, 799, 751cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.44 (m, 1H), 7.43–7.37 (m, 1H), 7.22–7.13 (m, 2H), 7.13–7.02 (m, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.35 (s, 1H), 4.76 (s, 1H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.88–1.67 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 154.8, 153.6, 130.4, 129.1, 128.3, 127.3, 123.2, 122.5, 121.0, 120.3, 115.4, 110.9, 102.1, 29.7, 29.4, 28.4, 27.6. HRMS (ESI) calcd. for $C_{18}H_{19}O_2$ ([M+H]$^{+}$): 267.1380, found: 267.1385.



2-(4-(thiophen-2-yl)butyl)phenol (3m)

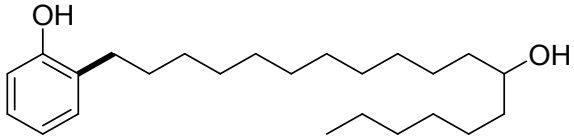
Yellow oil; IR (film): 3526, 3104, 3069, 3037, 2931, 2858, 1591, 1504, 1455, 1328,

1235, 1172, 1097, 849, 754, 695cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.03 (m, 3H), 6.93–6.82 (m, 2H), 6.79–6.70 (m, 2H), 4.68 (s, 1H), 2.86 (t, *J* = 7.0 Hz, 2H), 2.63(t, *J* = 7.6 Hz, 2H), 1.80–1.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 145.6, 130.4, 128.4, 127.2, 126.8, 124.2, 123.0, 121.0, 115.4, 31.7, 29.9, 29.8, 29.3. HRMS (ESI) calcd. for $C_{14}H_{17}OS$ ($[M+H]^+$): 233.0995, found: 233.0999.



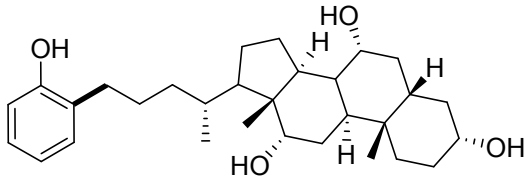
2-(3,7-dimethyloctyl)phenol (3n)

Yellow oil; IR (film): 3419, 2955, 2927, 2870, 1591, 1504, 1455, 1379, 1235, 1172, 1121, 844, 751cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.03 (m, 2H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 4.72 (s, 1H), 2.69–2.50 (m, 2H), 1.76–1.07 (m, 10H), 0.94 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 130.2, 129.0, 127.1, 121.0, 115.3, 39.5, 37.3, 37.2, 32.9, 28.1, 27.6, 24.8, 22.9, 22.8, 19.8. HRMS (ESI) calcd. for $C_{16}H_{27}O$ ($[M+H]^+$): 235.2056, found: 235.2054.



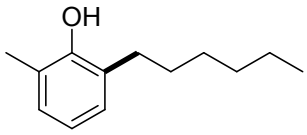
2-(12-hydroxyoctadecyl)phenol (3o)

White solid; M.p. 67–68 ^{o}C; IR (film): 3523, 3341, 2918, 2849, 1591, 1453, 1333, 1257, 1117, 1078, 844, 757, 726 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (d, *J* = 6.9 Hz, 1H), 7.05 (t, *J* = 7.0 Hz, 1H), 6.84 (t, *J* = 7.0 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.56 (s, 1H), 3.61 (s, 1H), 2.59 (t, *J* = 7.3 Hz, 2H), 1.70–1.13 (m, 31H), 0.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.9, 130.2, 129.0, 127.0, 120.6, 115.3, 72.4, 37.6, 37.6, 32.0, 30.1, 29.9, 29.8, 29.7(4C), 29.6(3C), 29.5, 25.8, 22.8, 14.2. HRMS (ESI) calcd. for $C_{24}H_{43}O_2$ ($[M+H]^+$): 363.3258, found: 363.3260.



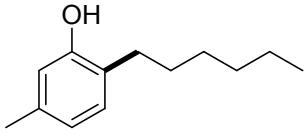
(3R,5S,7R,9S,10S,12S,13R,14S)-17-((R)-5-(2-hydroxyphenyl)pentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triol (3p)

White solid; M.p. 148–150 °C; IR (film): 3386, 2937, 2868, 1662, 1593, 1455, 1377, 1239, 1077, 1041, 751, 736cm^{-1}. ^{1}H NMR (400 MHz, MeOD) δ 7.04–6.92 (m, 2H), 6.75–6.67 (m, 2H), 3.98–3.91 (m, 1H), 3.82–3.75 (m, 1H), 3.41–3.32 (m, 1H), 2.64–2.44 (m, 2H), 2.34–2.18 (m, 2H), 2.01–1.04 (m, 22H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.90 (s, 3H), 0.70 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 154.8, 129.6, 129.0, 126.2, 119.0, 114.4, 72.7, 71.5, 67.7, 47.0, 46.0, 41.8, 41.6, 39.6, 39.1, 35.7, 35.6, 35.1, 34.5, 34.4, 30.2, 29.8, 28.2, 27.4, 26.5, 26.3, 22.9, 21.8, 16.7, 11.7. HRMS (ESI) calcd. for $C_{30}H_{46}O_4Na$ ([M+Na]$^+$): 493.3288, found: 493.3277.



2-hexyl-6-methylphenol (3q)

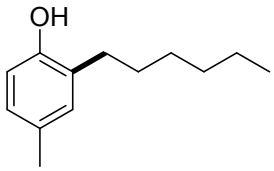
Yellow oil; IR (film): 3470, 2955, 2929, 2858, 1468, 1261, 1192, 773, 743cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 7.5 Hz, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 4.62 (s, 1H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.25 (s, 3H), 1.65–1.55 (m, 2H), 1.43–1.24 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 128.6, 128.0, 127.9, 123.1, 120.3, 31.9, 30.3, 29.9, 29.4, 22.8, 16.1, 14.3. HRMS (ESI) calcd. for $C_{13}H_{21}O$ ([M+H]$^+$): 193.1587, found: 193.1591.



2-hexyl-5-methylphenol (3r)

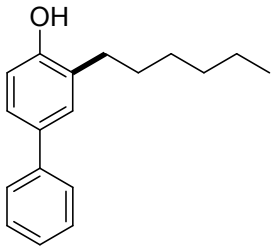
Yellow oil; IR (film): 3404, 2955, 2927, 2858, 1625, 1587, 1520, 1457, 1420, 1272,

1231, 1121, 944, 810cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.59 (s, 1H), 4.57 (s, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.27 (s, 3H), 1.64–1.53 (m, 2H), 1.41–1.25 (m, 6H), 0.88 (t, *J* = 7.2Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 137.1, 130.1, 125.5, 121.6, 116.1, 31.9, 30.1, 29.7, 29.4, 22.8, 21.1, 14.3. HRMS (ESI) calcd. for $C_{13}H_{21}O$ ([M+H]$^+$): 193.1587, found: 193.1590.



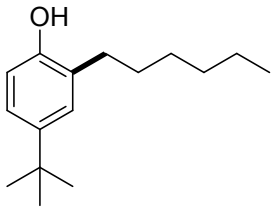
2-hexyl-4-methylphenol (3s)

Yellow oil; IR (film): 3403, 3015, 2957, 2933, 2860, 1613, 1509, 1463, 1258, 1203, 1123, 810cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 4.66 (s, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.25 (s, 3H), 1.64–1.53 (m, 2H), 1.41–1.24 (m, 6H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 130.9, 130.0, 128.5, 127.4, 115.1, 31.9, 30.1, 30.1, 29.4, 22.8, 20.7, 14.3. HRMS (ESI) calcd. for $C_{13}H_{21}O$ ([M+H]$^+$): 193.1587, found: 193.1591.



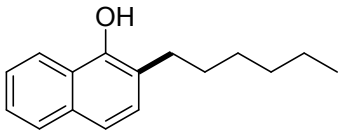
3-hexyl-[1,1'-biphenyl]-4-ol (3t)

Yellow solid; M.p. 59–60 ^{o}C; IR (film): 3427, 3065, 3034, 2957, 2929, 2858, 1608, 1487, 1455, 1414, 1261,1231, 1192, 1123, 820, 762, 698cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.51 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.38–7.26 (m, 3H), 6.83 (d, *J* = 8.2 Hz, 1H), 4.83 (s, 1H), 2.65 (t, *J* = 8.0 Hz, 2H), 1.70–1.59 (m, 2H), 1.45–1.22 (m, 6H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 141.2, 134.0, 129.1, 129.0, 128.8, 126.9, 126.7, 125.8, 115.6, 31.9, 30.3, 30.0, 29.4, 22.8, 14.3. HRMS (ESI) calcd. for $C_{18}H_{23}O$ ([M+H]$^+$): 255.1743, found: 255.1742.



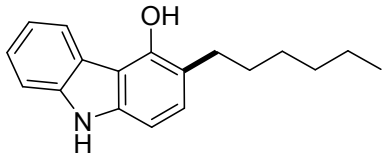
4-(tert-butyl)-2-hexylphenol (3u)

Colorless oil; IR (film): 3401, 2957, 2931, 2860, 1612, 1507, 1466, 1364, 1271, 1131, 820cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.05 (m, 2H), 6.69 (d, *J* = 8.3 Hz, 1H), 4.70 (s, 1H), 2.59 (t, *J* = 7.6 Hz,2H), 1.66–1.55 (m, 2H), 1.43–1.23 (m, 15H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 143.5, 128.0, 127.3, 123.8, 114.8, 34.2, 31.9, 31.7, 30.6, 30.1, 29.5, 22.8, 14.3. HRMS (ESI) calcd. for $C_{16}H_{27}O$ ([M+H]$^+$): 235.2056, found: 235.2061.



2-hexylnaphthalen-1-ol (3v) [4]

Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.80–7.75 (m, 1H), 7.49–7.37 (m, 3H), 7.27–7.22 (m, 1H), 5.13 (s, 1H), 2.74 (t, *J* = 7.6 Hz, 2H), 1.74–1.63 (m, 2H), 1.46–1.27 (m, 7H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 133.4, 128.3, 127.8, 125.6, 125.4, 124.5, 121.5, 121.1, 120.4, 31.9, 30.2, 30.2, 29.4, 22.8, 14.2.



3-hexyl-9H-carbazol-4-ol (3w)

Red solid; M.p. 95–97 ^{o}C; IR (film): 3544, 3431, 2955, 2926, 2858, 1638, 1587, 1498, 1451, 1336, 1202, 1034, 1008, 799, 747, 734cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.8 Hz, 1H), 7.87 (s, 1H), 7.40–7.31 (m, 2H), 7.26–7.20 (m, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 5.28 (s, 1H), 2.70 (t, *J* = 6.9 Hz, 2H), 1.71–1.61

(m, 2H), 1.45–1.23 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 139.9, 139.2, 128.0, 125.1, 122.6, 122.5, 119.6, 117.4, 112.0, 110.2, 103.0, 31.9, 30.8, 29.4, 29.4, 22.8, 14.3. HRMS (ESI) calcd. for $C_{18}H_{22}NO$ ($[M+H]^+$): 268.1696, found: 268.1696.

VI. References

[1] Dai, X.-J.; Li, C.-J. *J. Am. Chem. Soc.* **2016**, *138*, 5433−5440.

[2] Tofi, M.; Montagnon, T.; Georgiou, T.; Vassilikogiannakis, G. *Org. Biomol. Chem*. **2007**, *5*, 772–777.

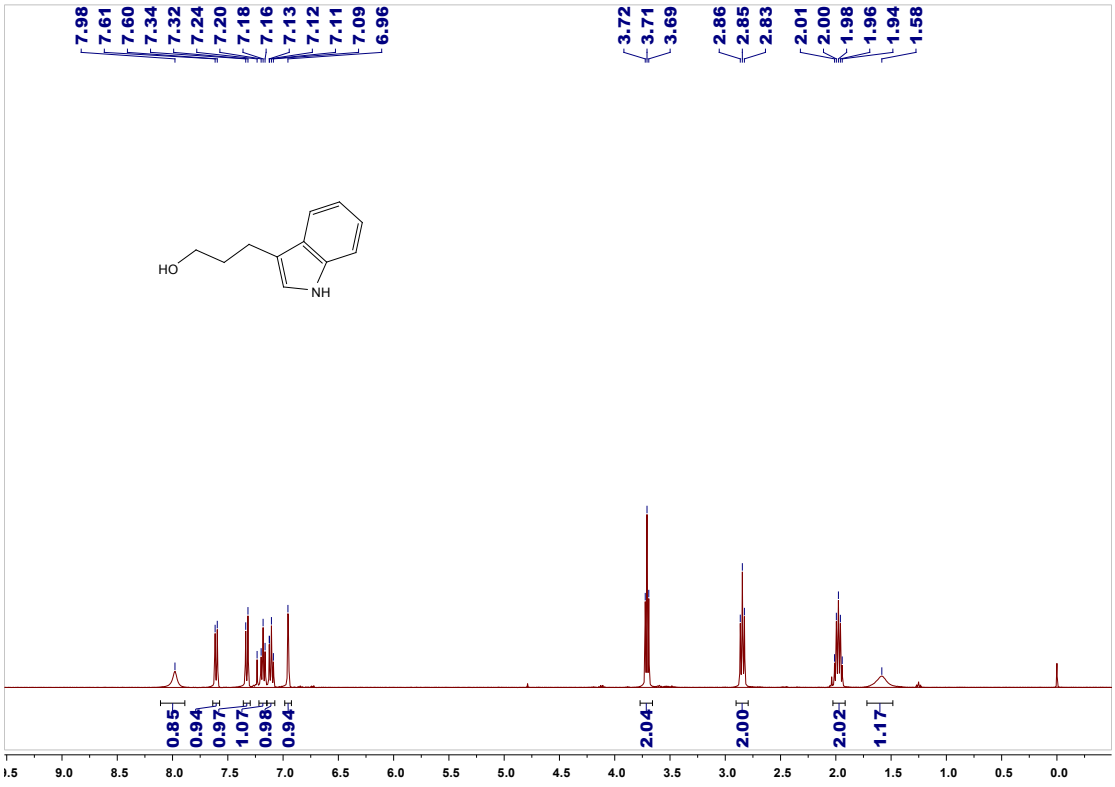
[3] Costanzo, M. J.; Patel, M. N.; Petersen, K. A.; Vogt, P. F. *Tetrahedron Lett.* **2009**, *50*, 5463–5466.

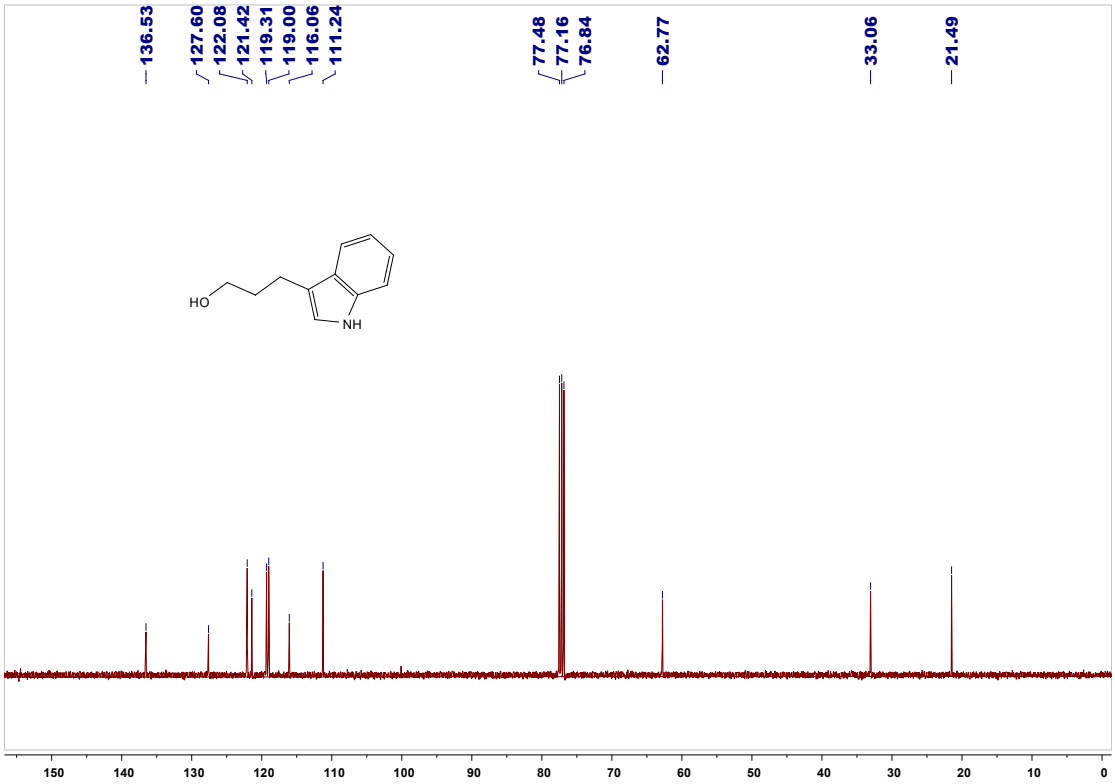
[4] Lee, D.-H.; Kwon, K.-H.; Yi, C. S. *J. Am. Chem. Soc.* **2012**, *134*, 7325–7328.

[5] Kalutharage, N.; Yi, C. S. *J. Am. Chem. Soc.* **2015**, *137*, 11105–11114.

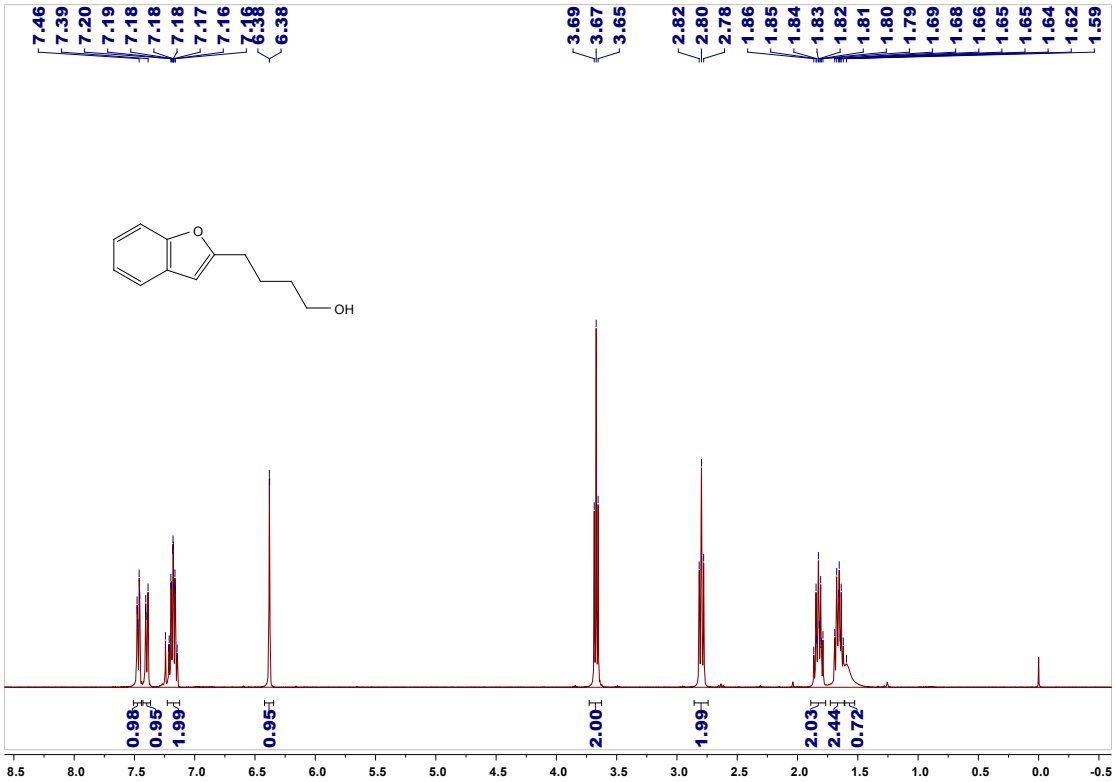
VII. Copies of NMR spectra

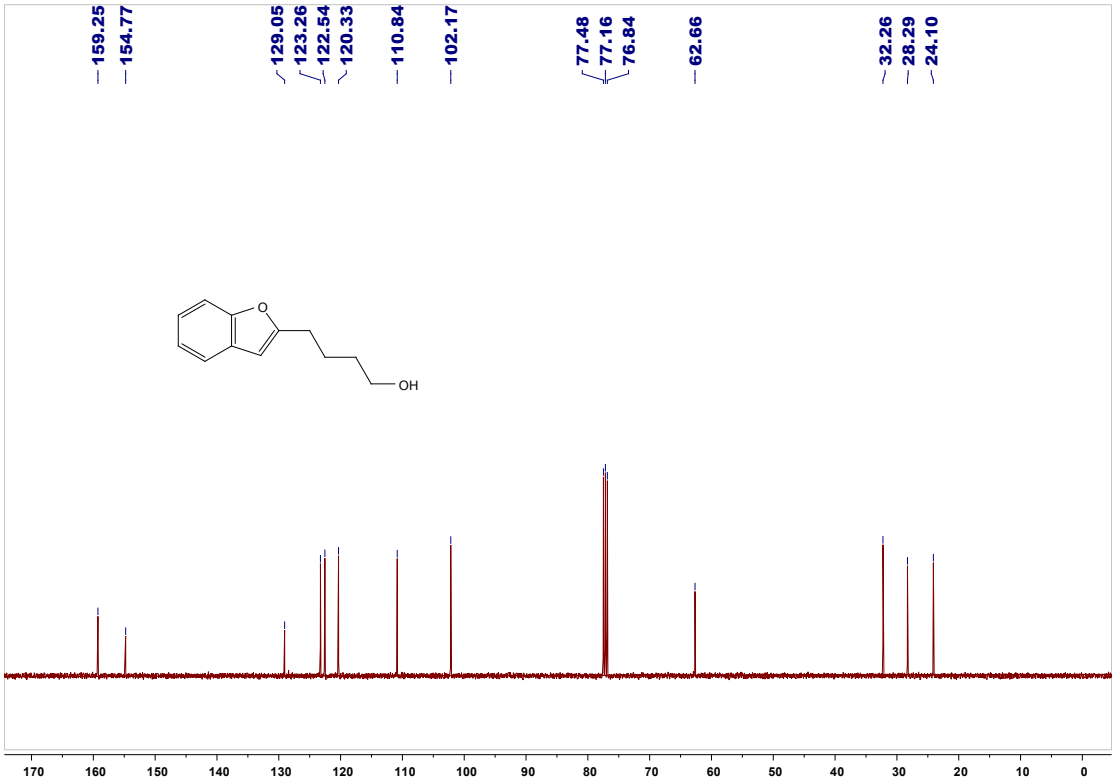
^{1}H and ^{13}C NMR spectra of compound **2k**



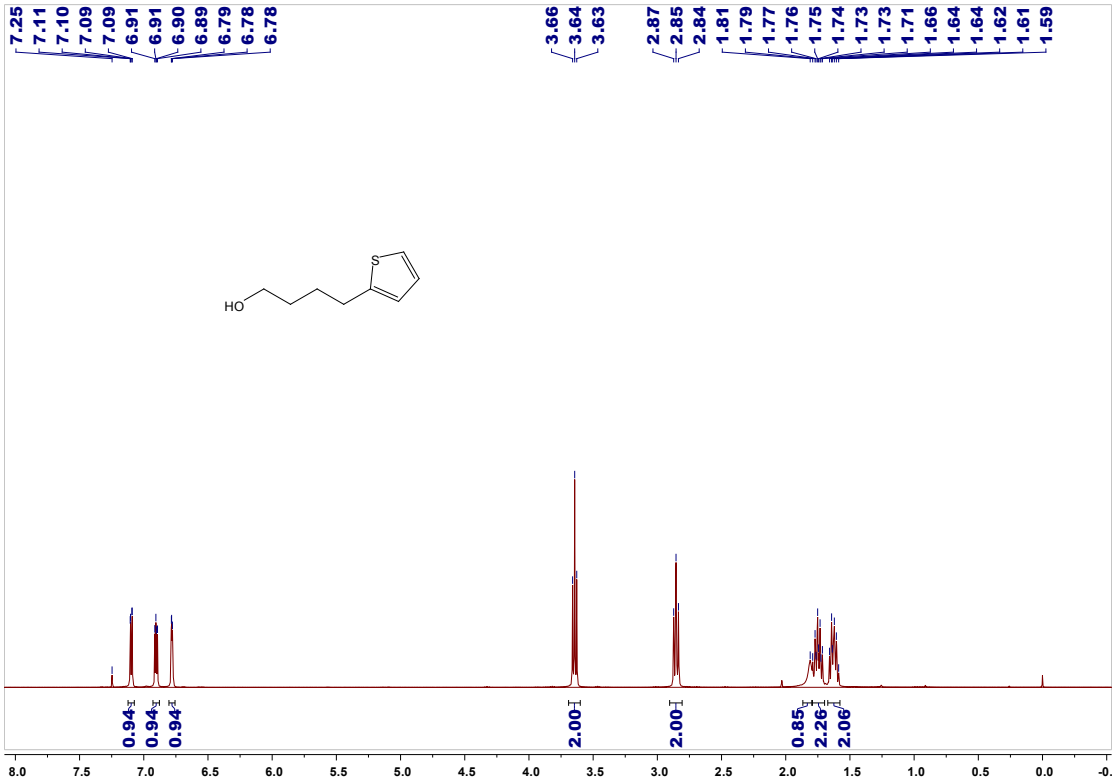


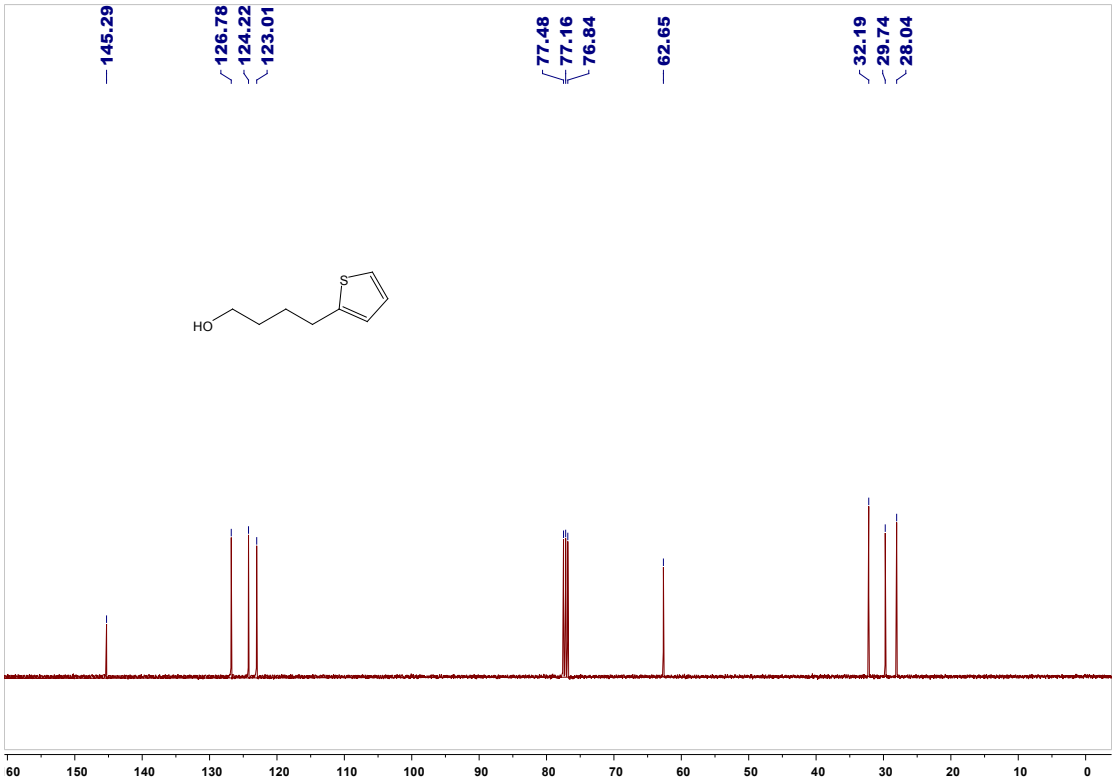
^{1}H and ^{13}C NMR spectra of compound **2l**



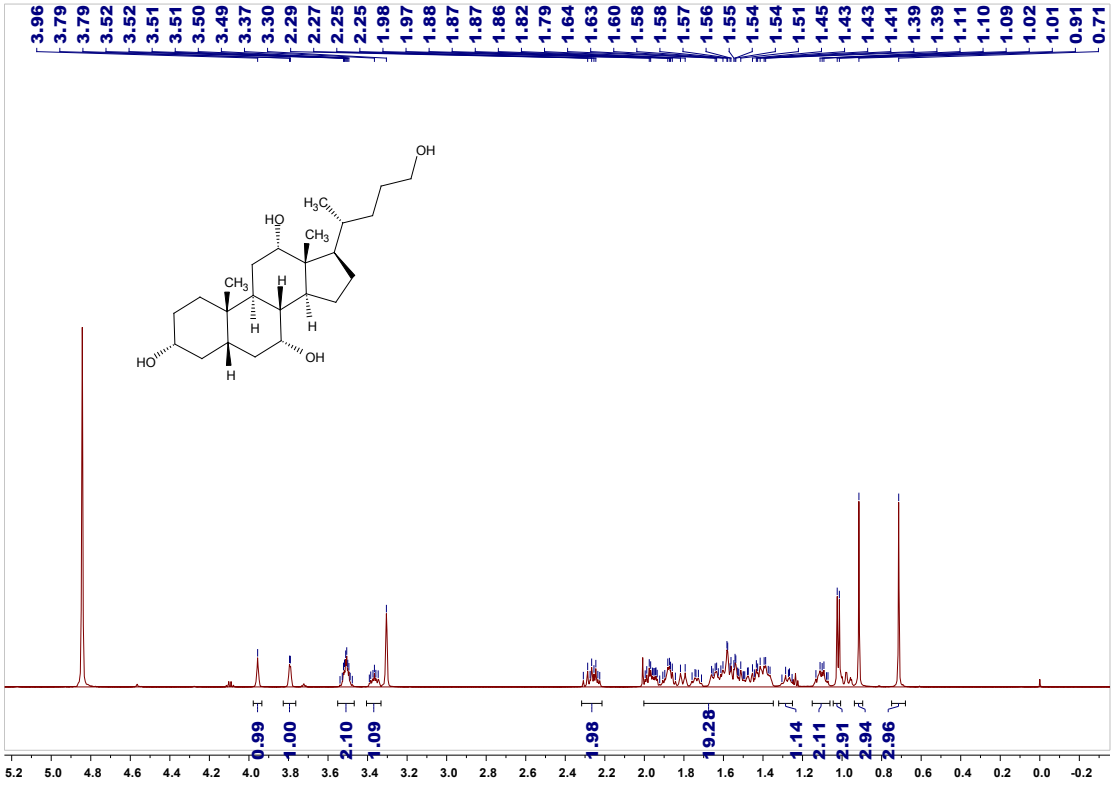


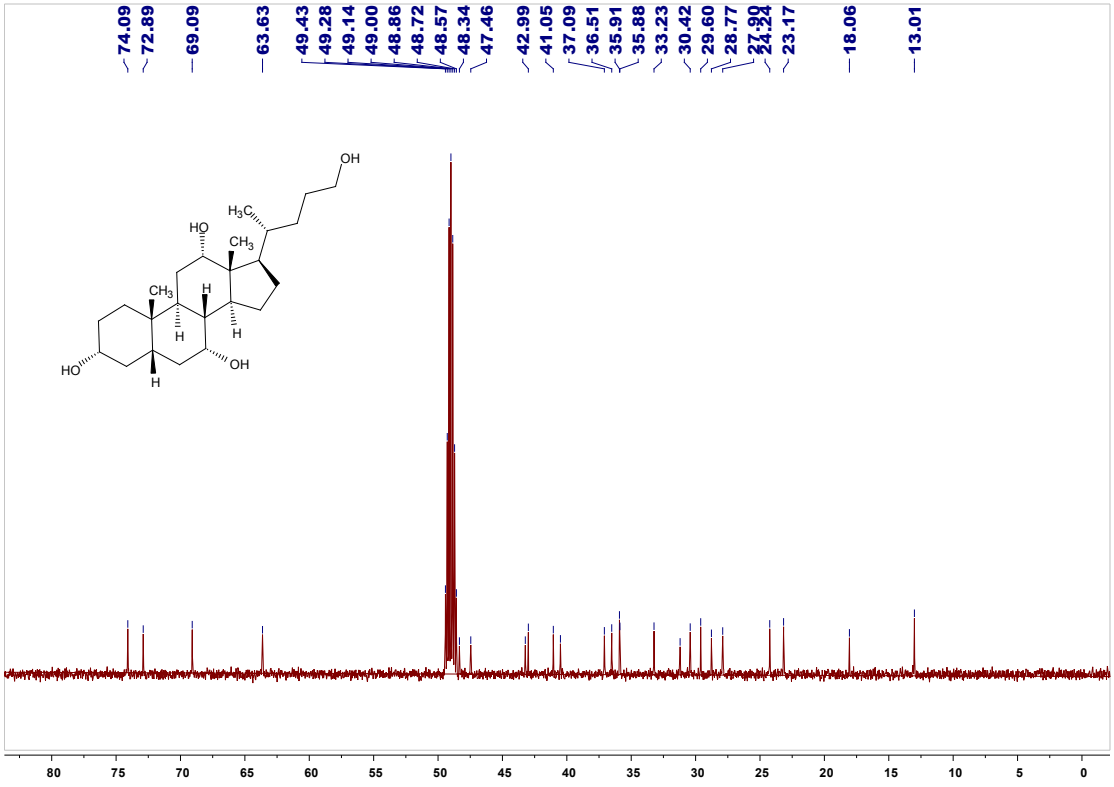
^{1}H and ^{13}C NMR spectra of compound **2m**



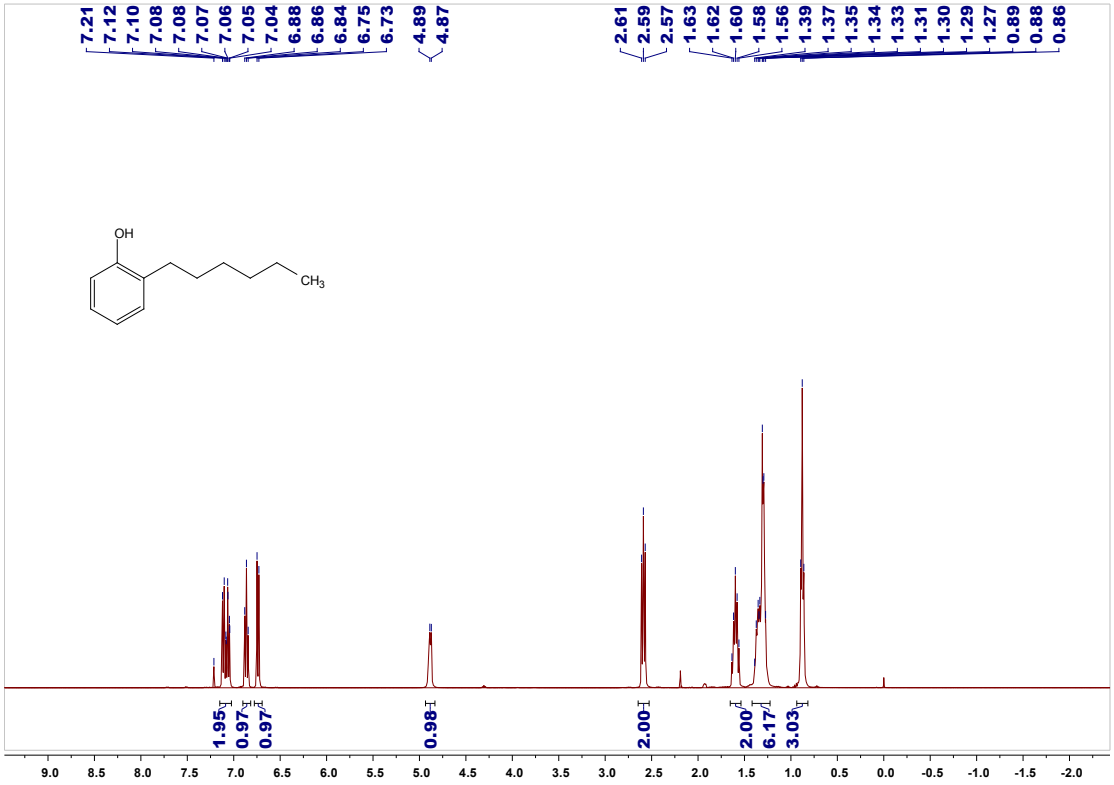


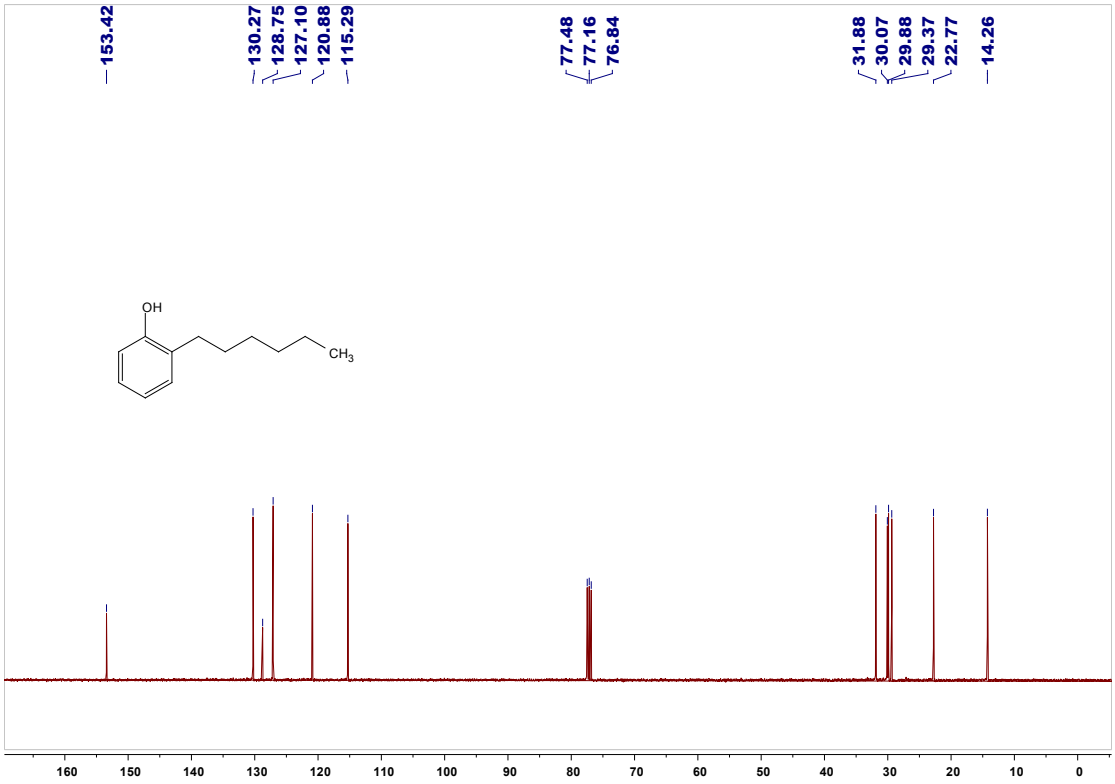
^{1}H and ^{13}C NMR spectra of compound **2p**



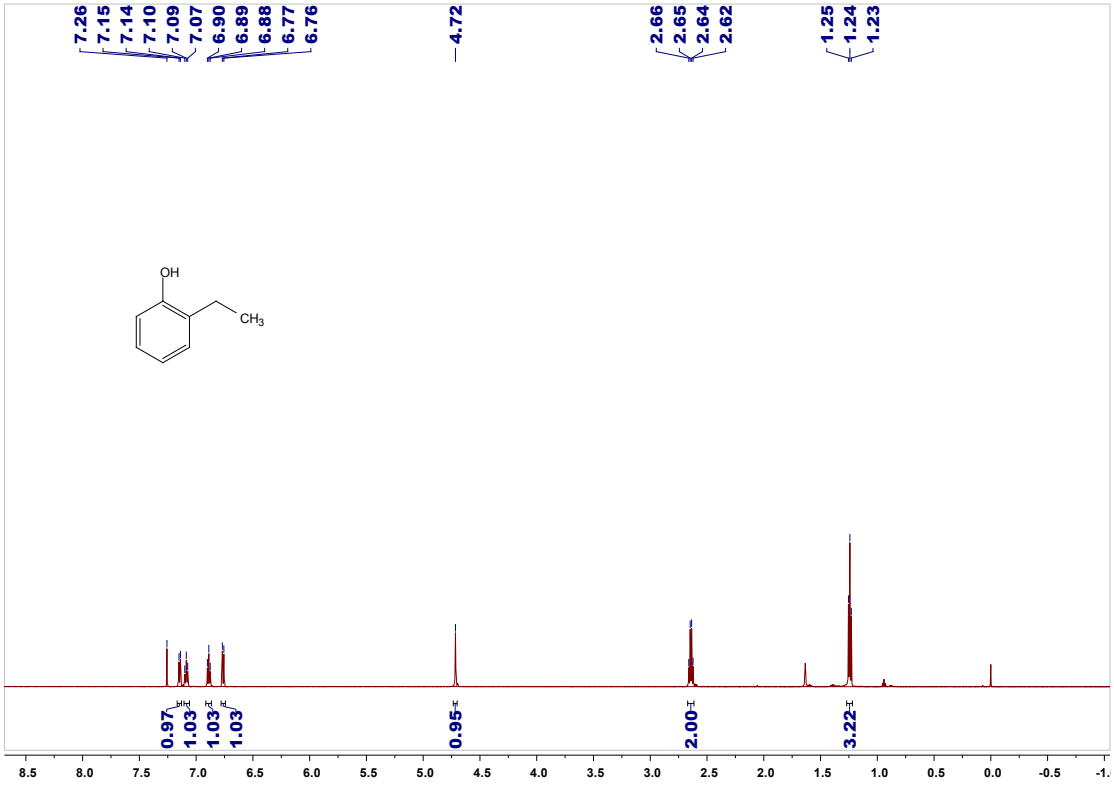


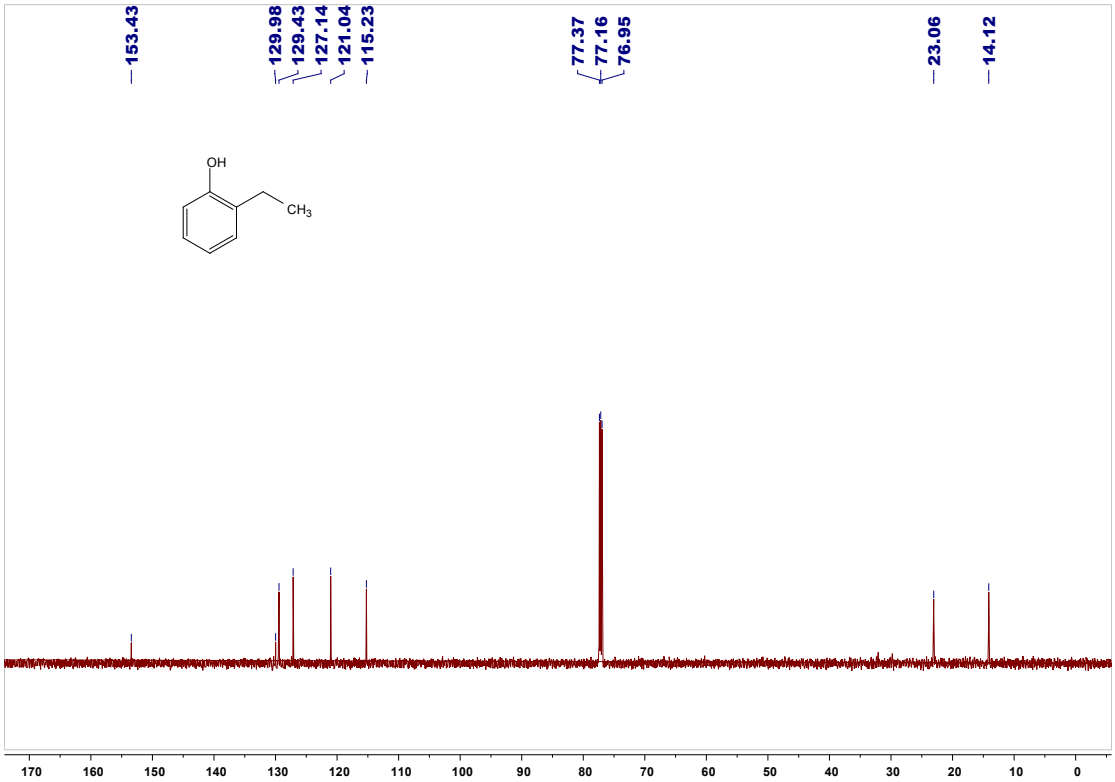
^{1}H and ^{13}C NMR spectra of compound **3a**



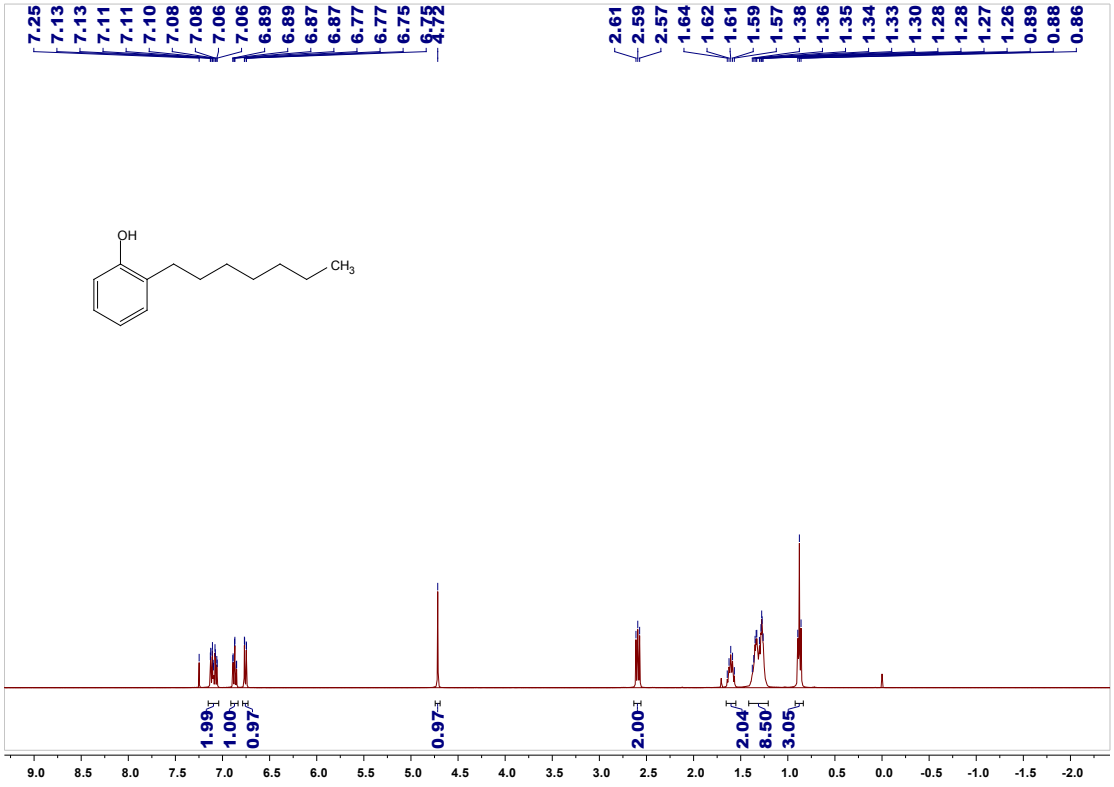


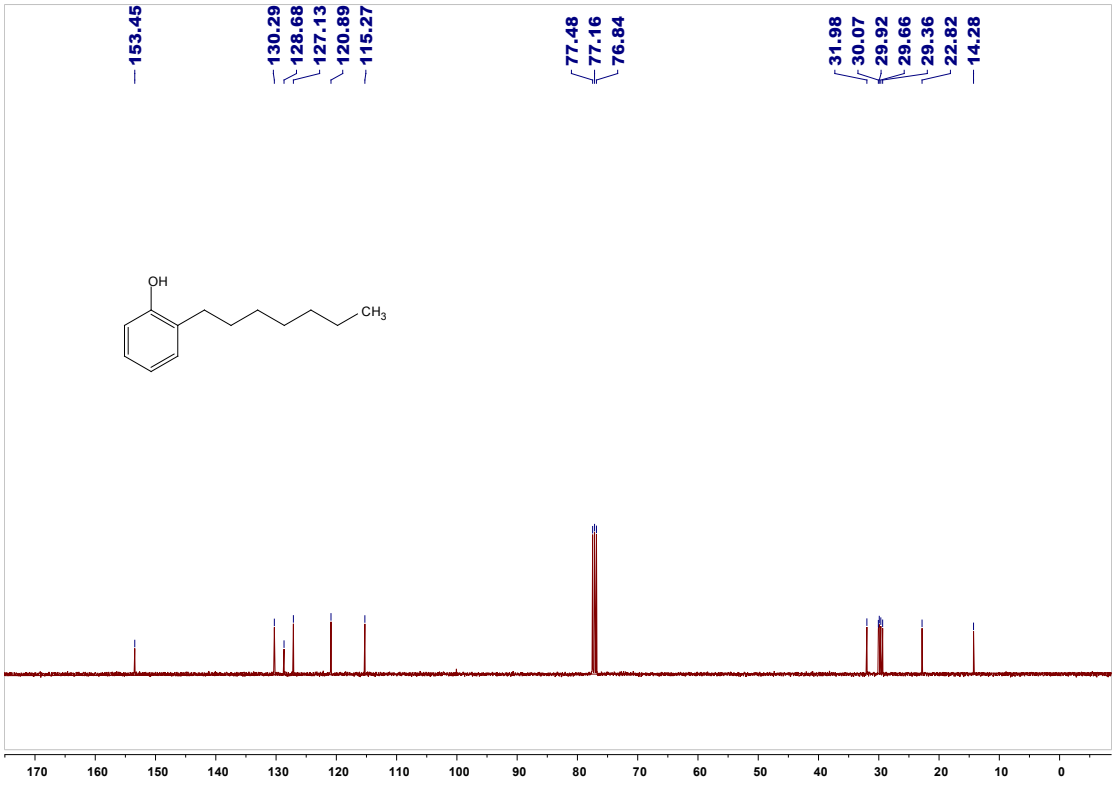
^{1}H and ^{13}C NMR spectra of compound **3b**



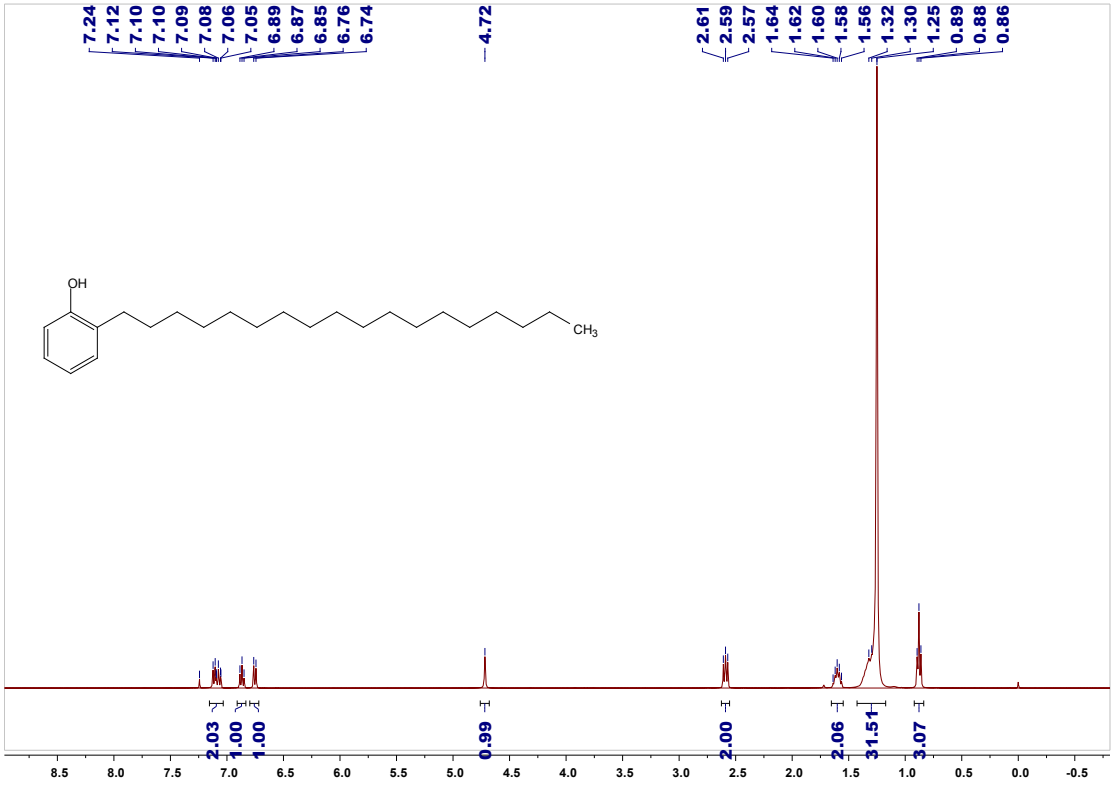


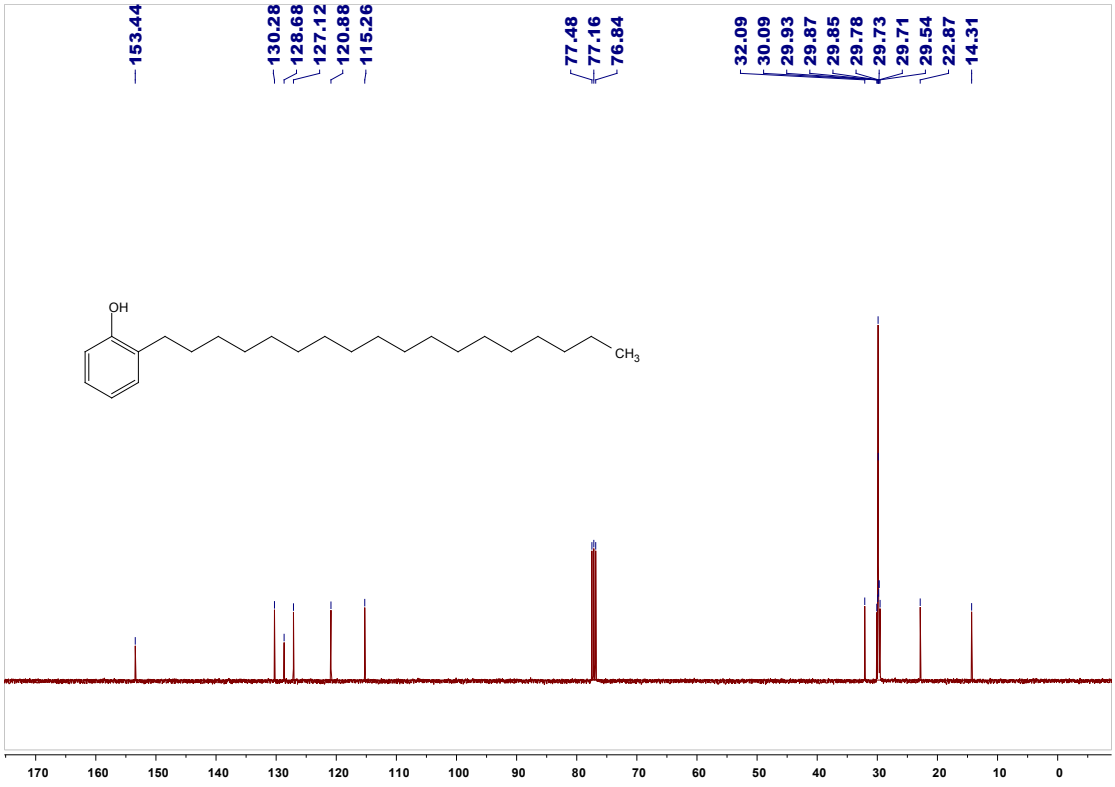
^{1}H and ^{13}C NMR spectra of compound **3c**



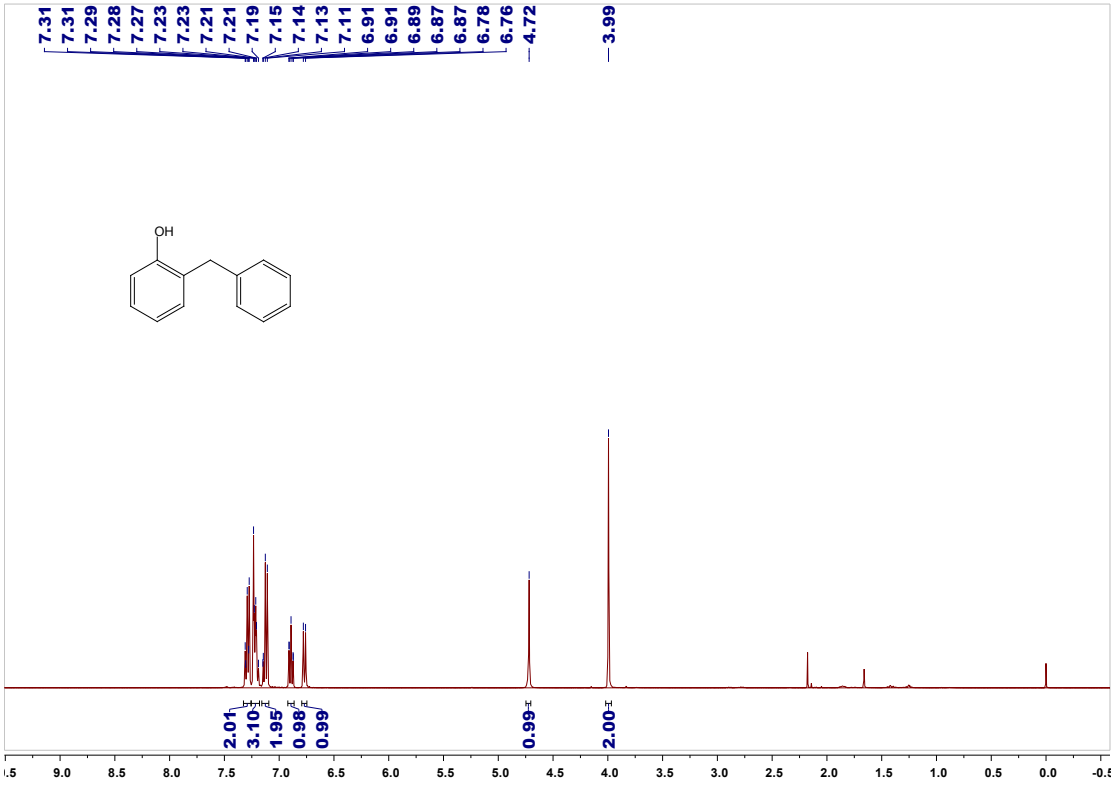


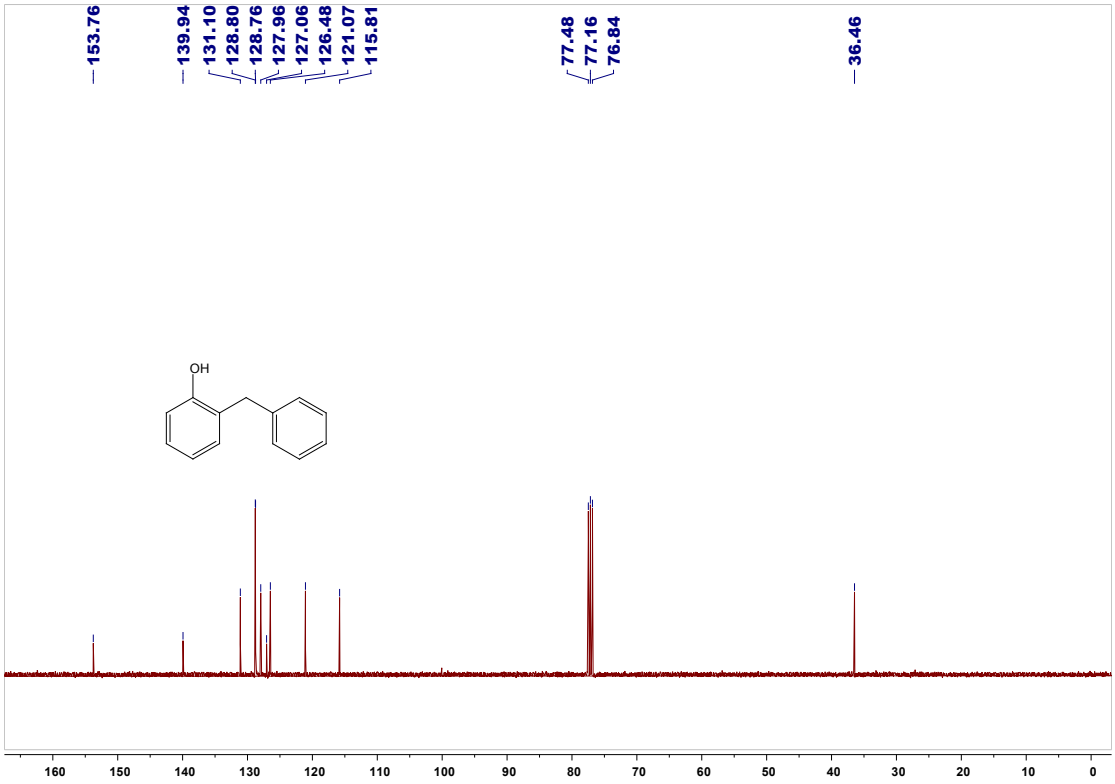
^{1}H and ^{13}C NMR spectra of compound **3d**



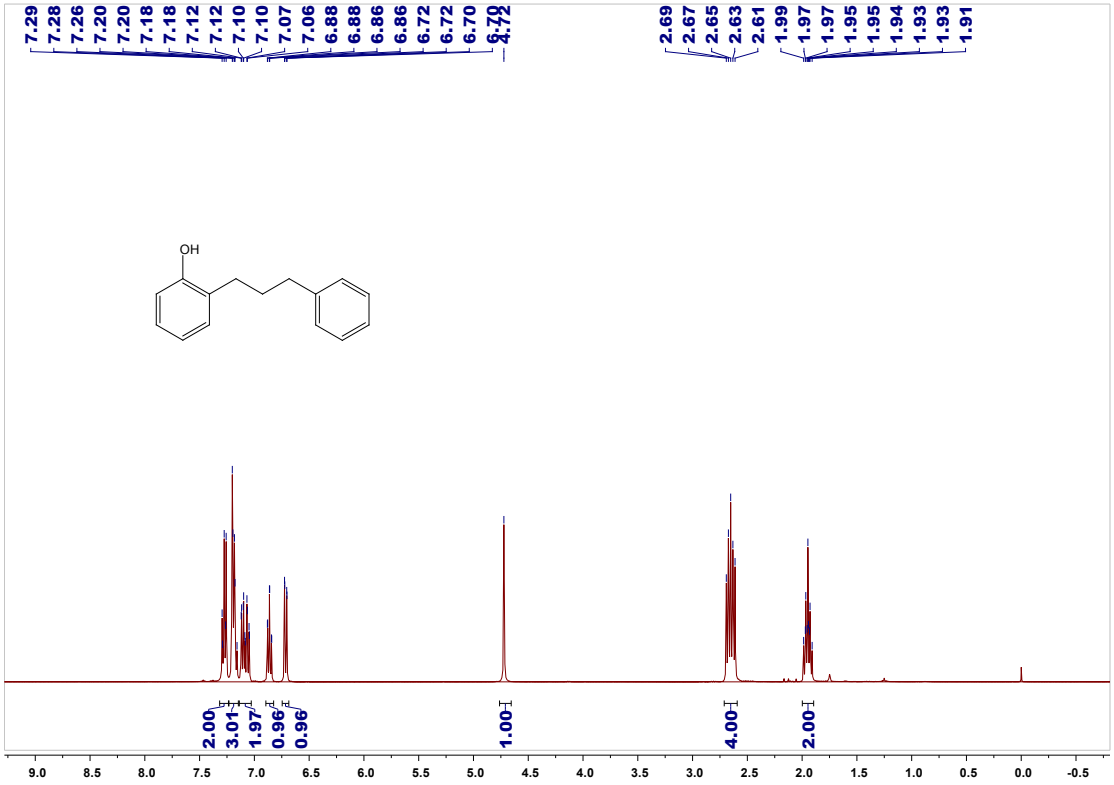


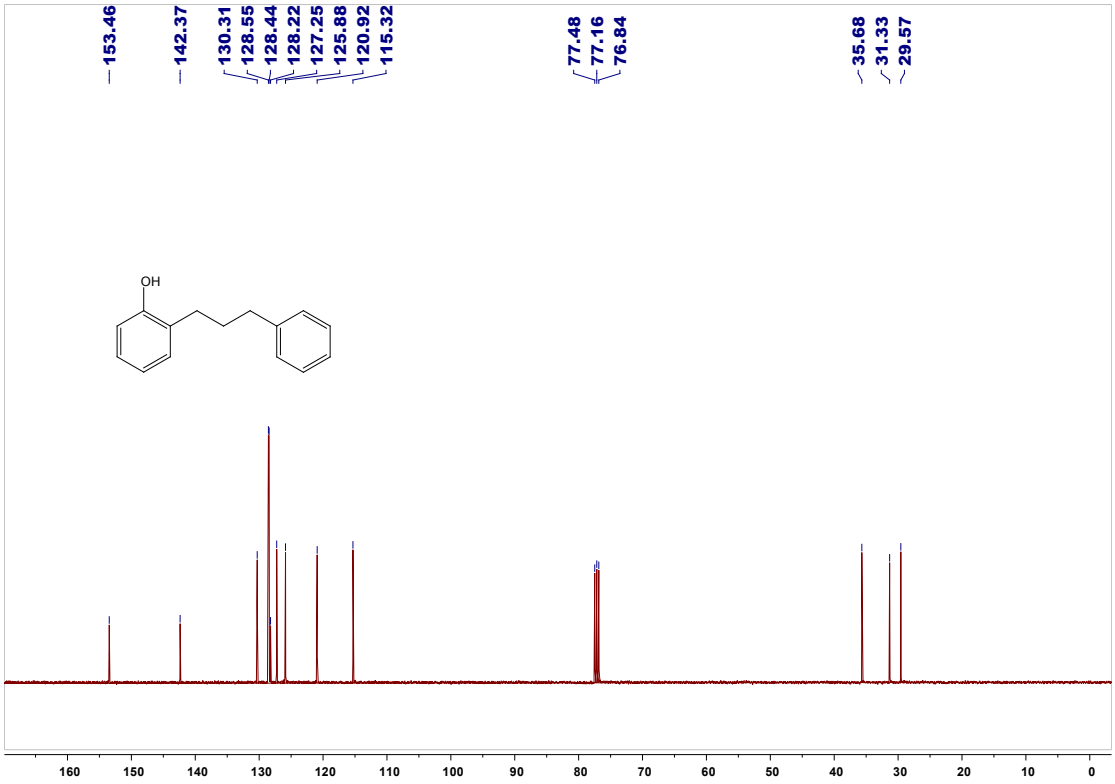
^{1}H and ^{13}C NMR spectra of compound **3e**



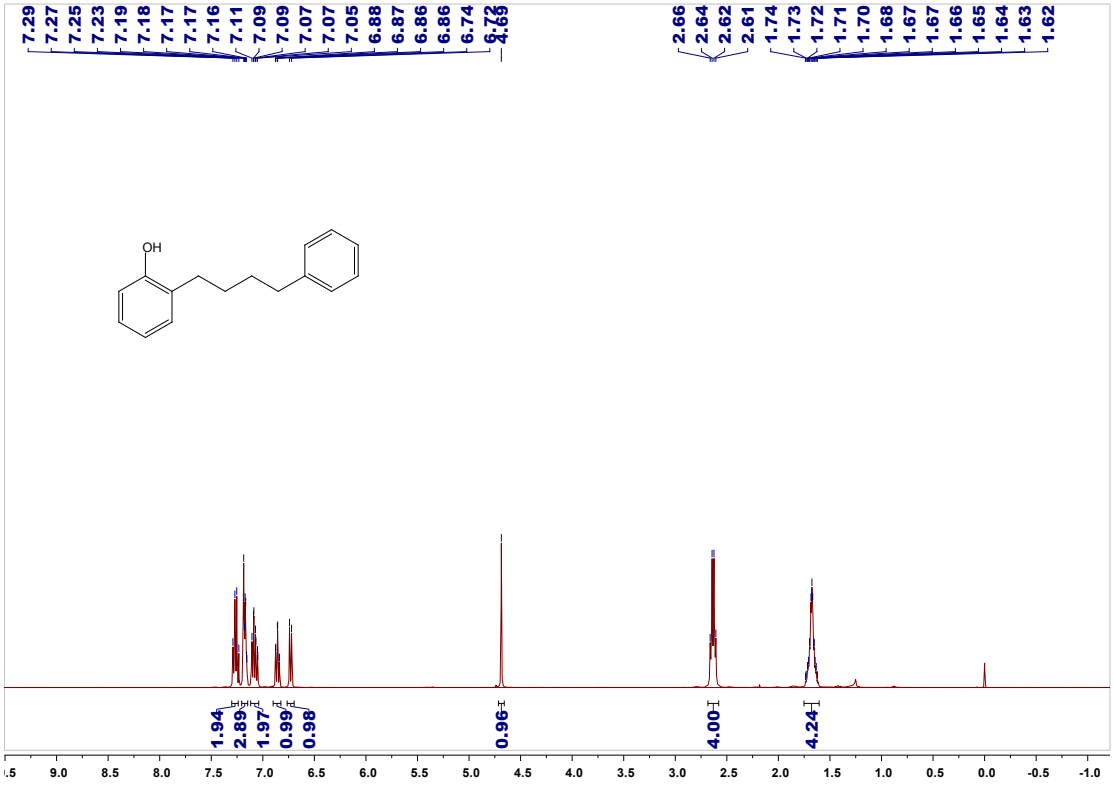


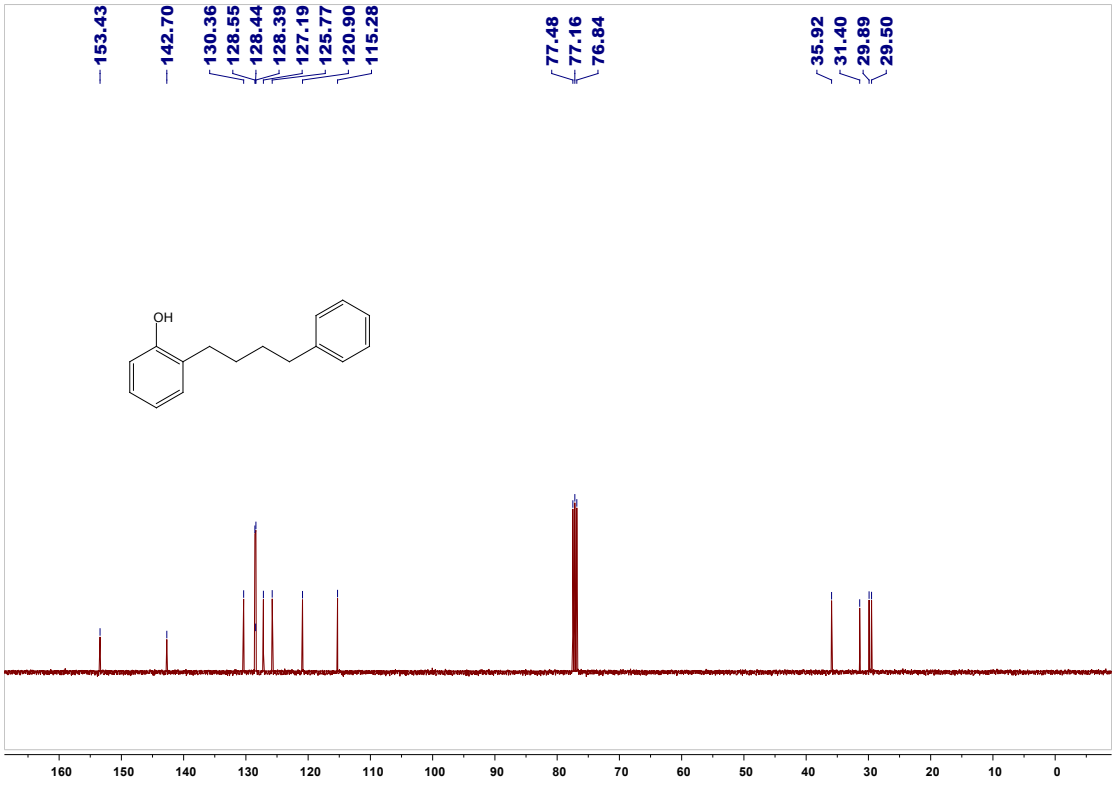
^{1}H and ^{13}C NMR spectra of compound **3f**



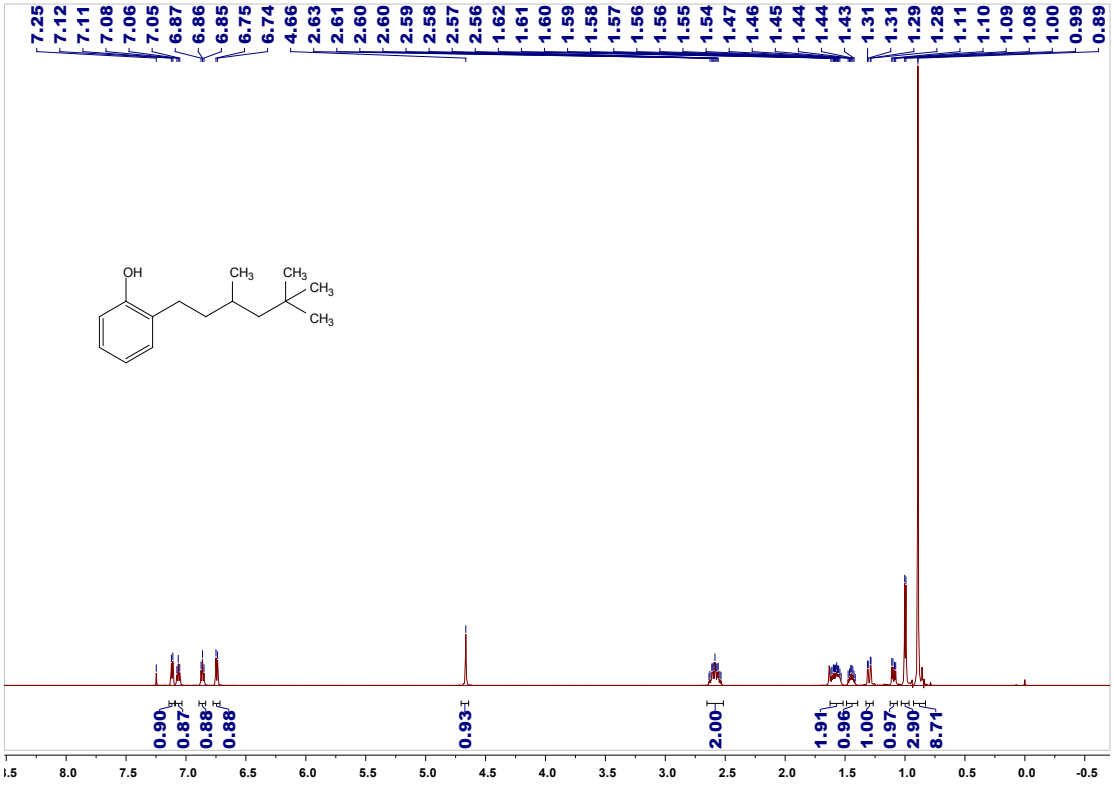


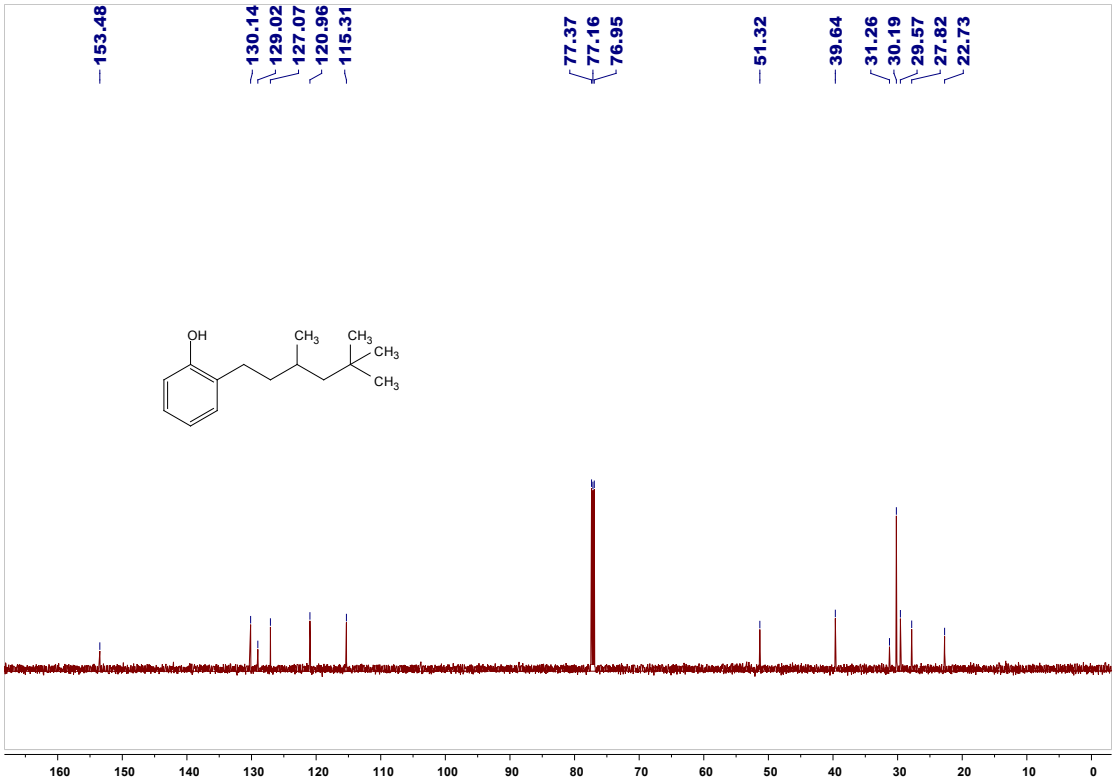
^{1}H and ^{13}C NMR spectra of compound **3g**



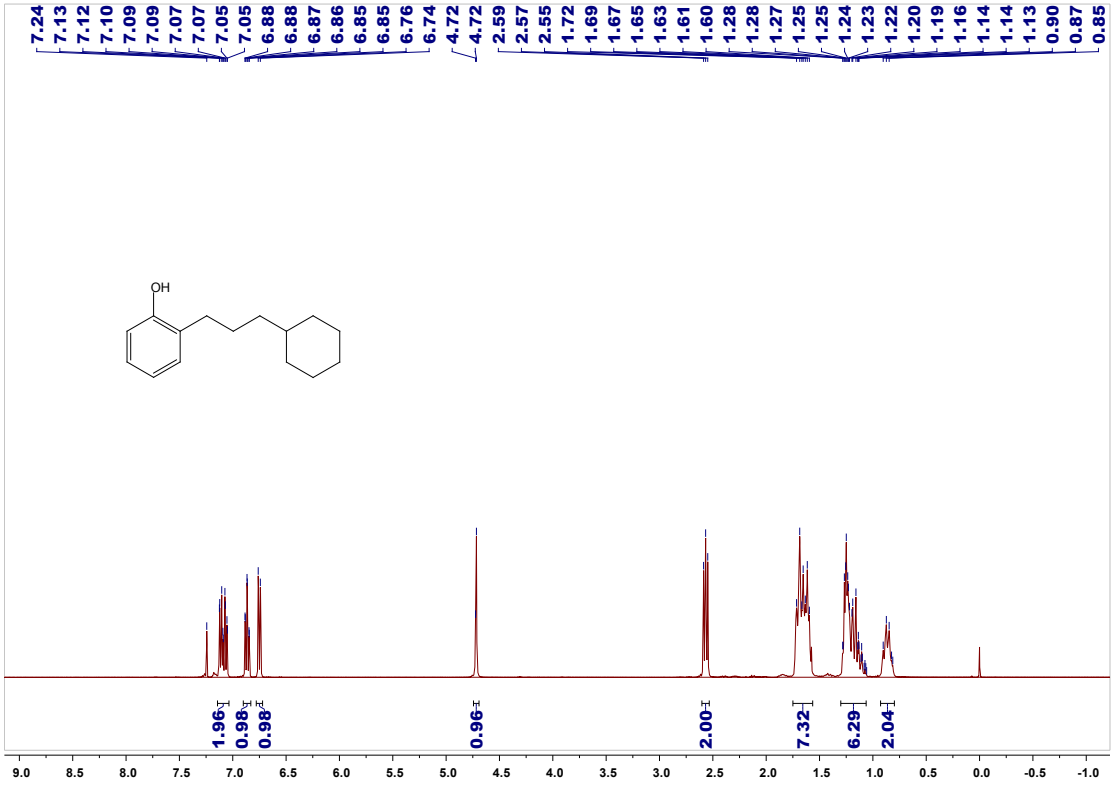


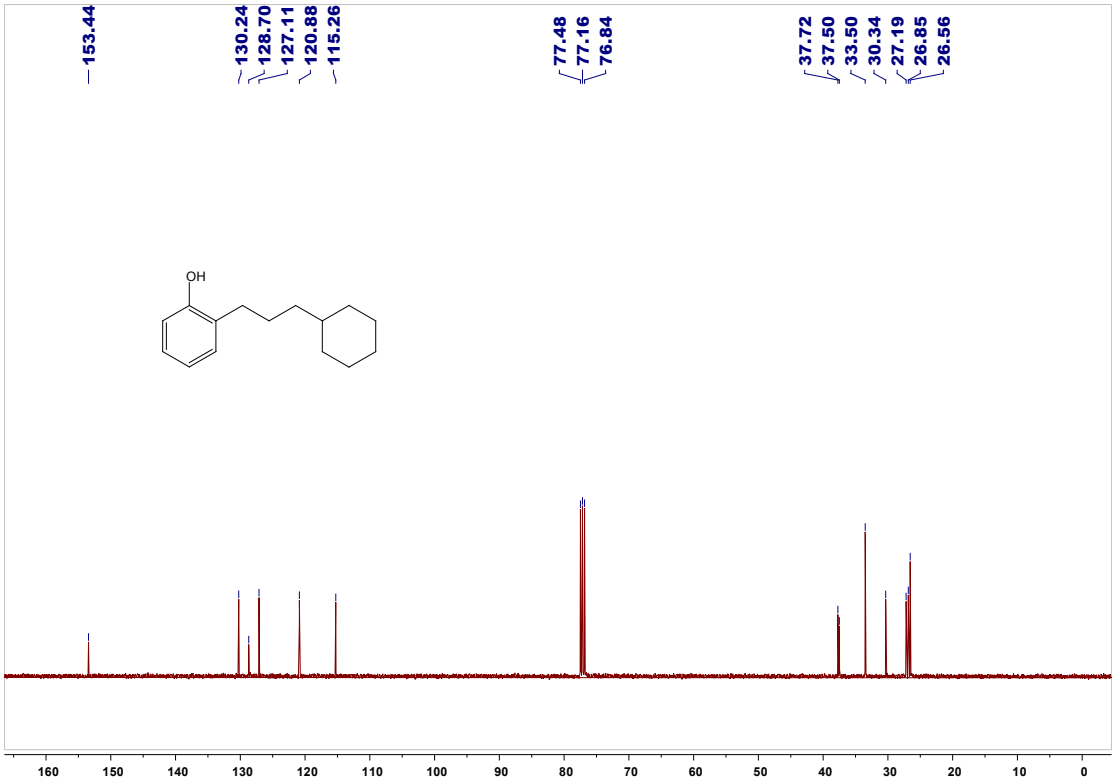
^{1}H and ^{13}C NMR spectra of compound **3h**



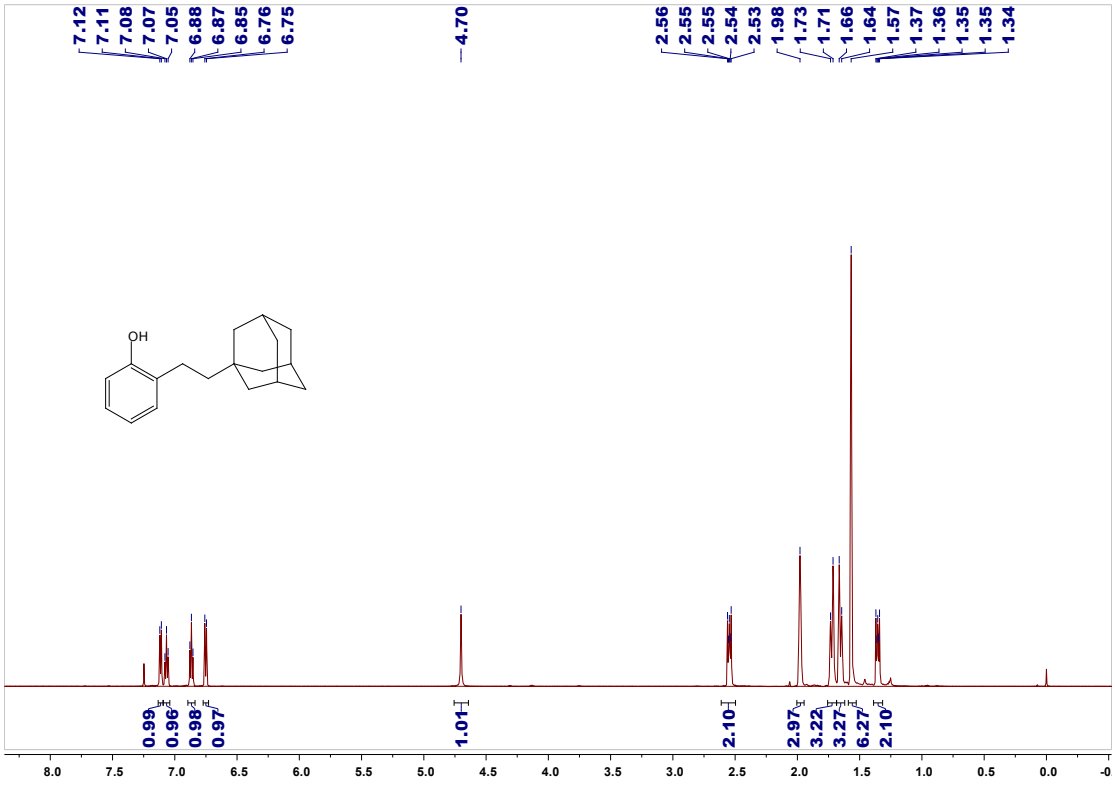


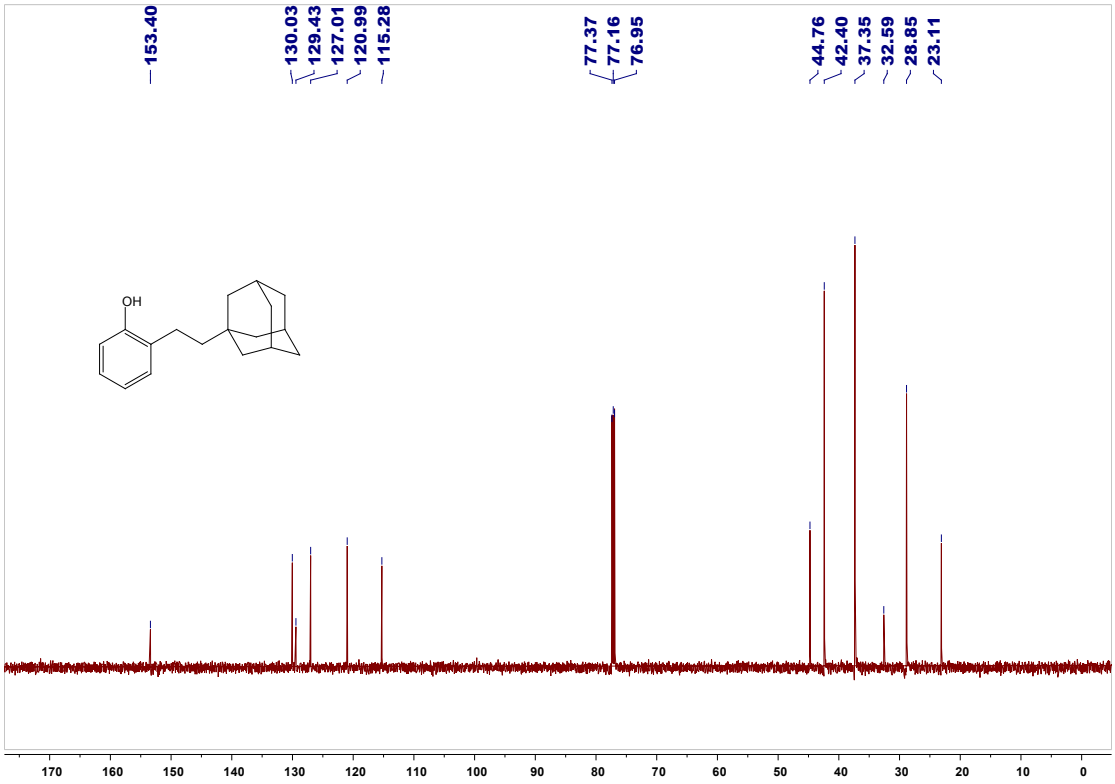
^{1}H and ^{13}C NMR spectra of compound **3i**



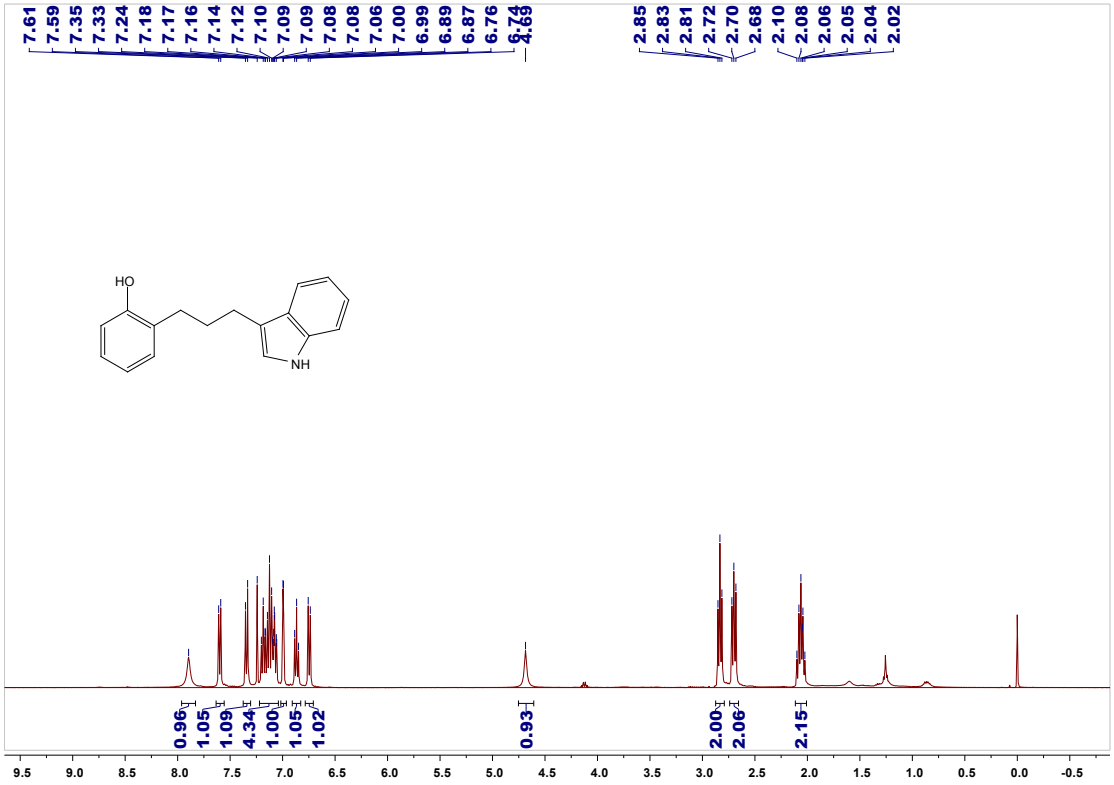


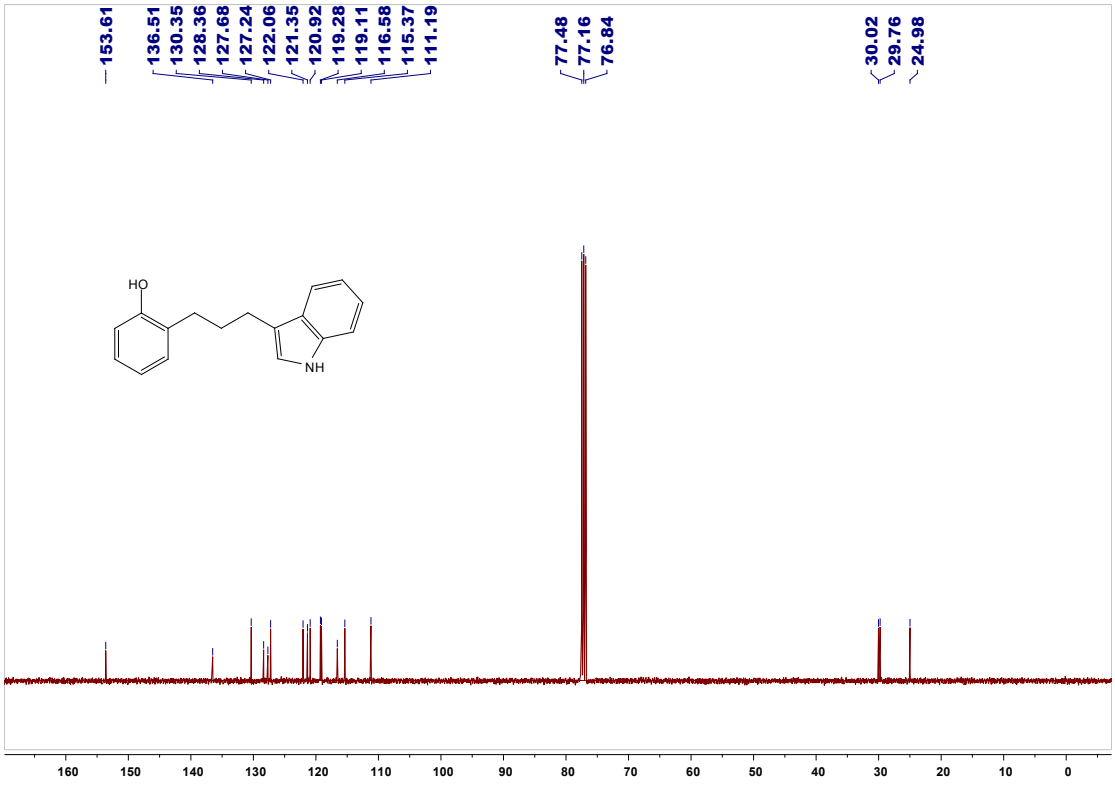
^{1}H and ^{13}C NMR spectra of compound **3j**



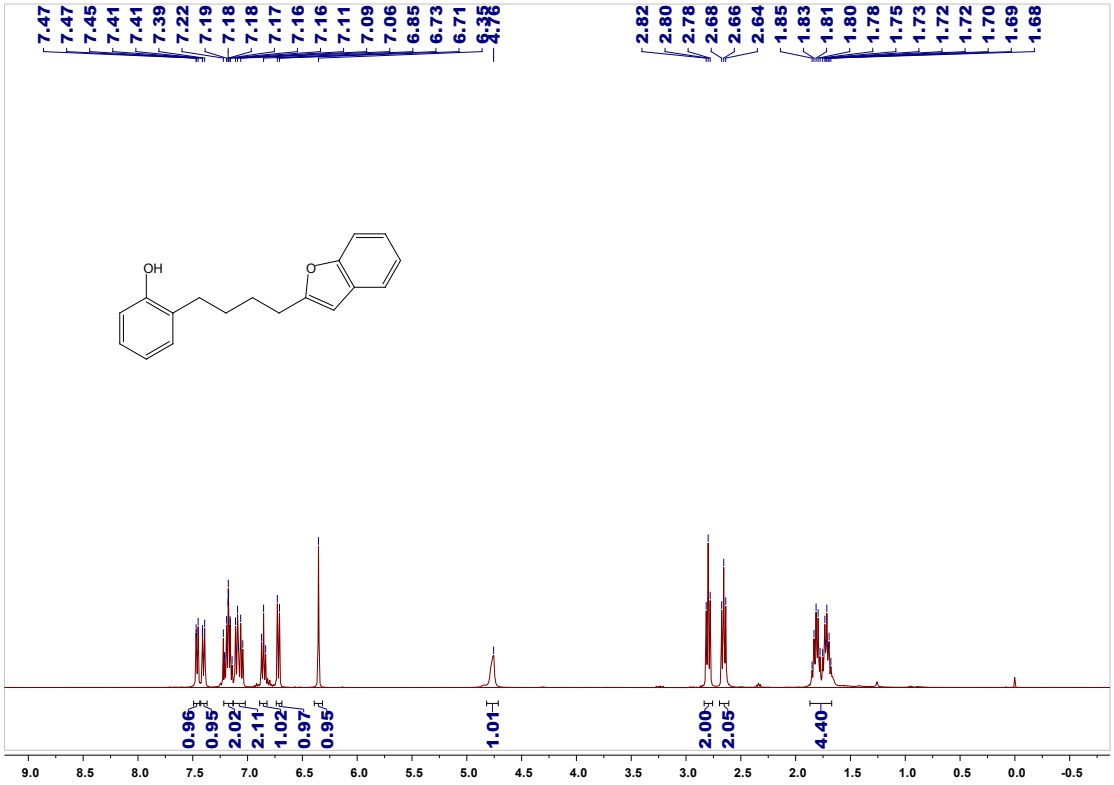


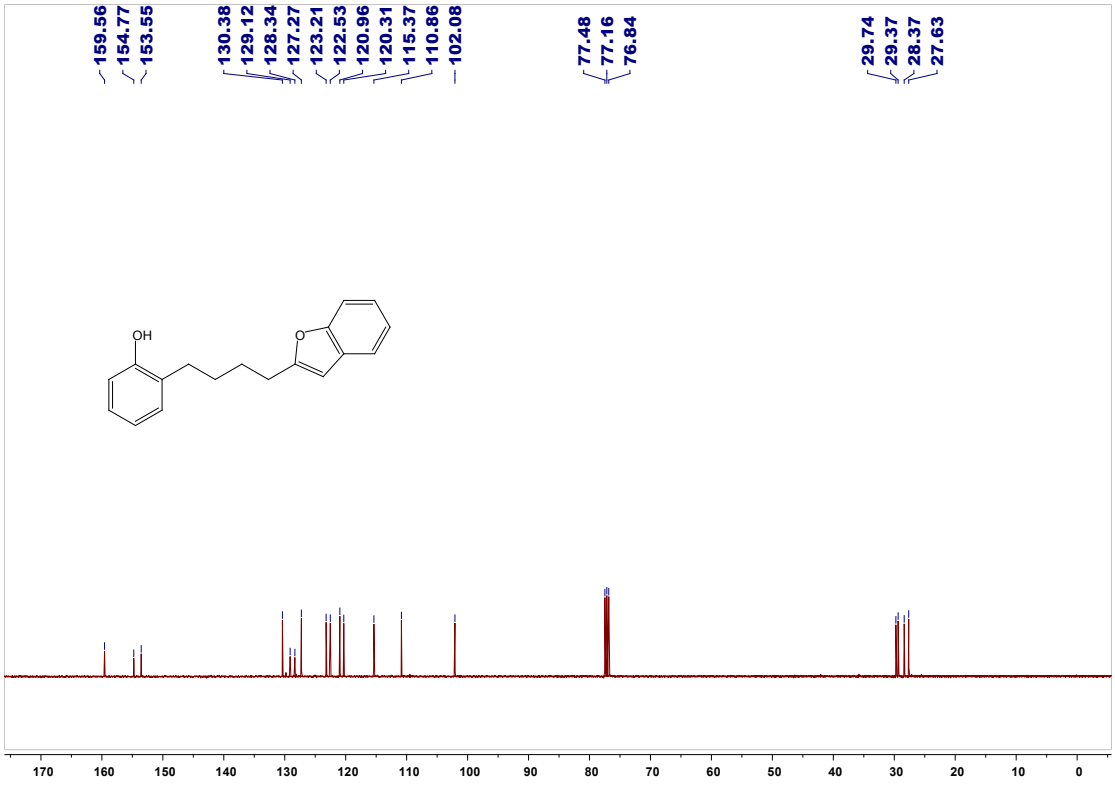
^{1}H and ^{13}C NMR spectra of compound **3k**



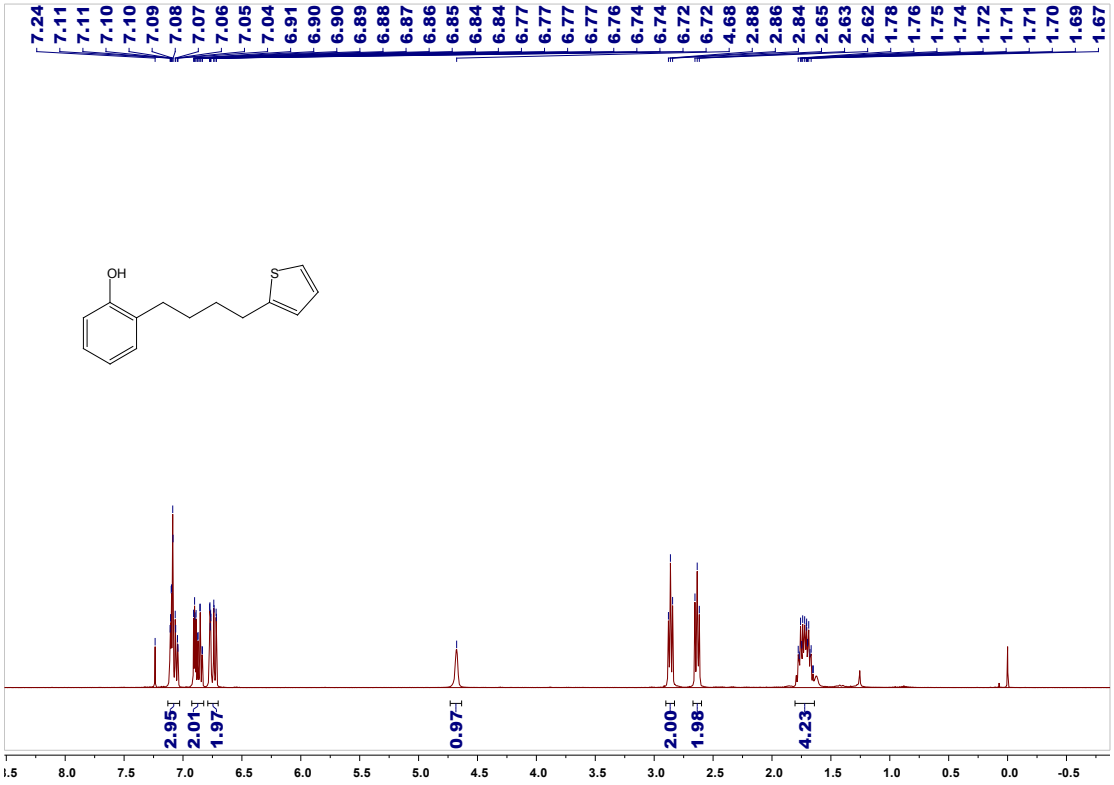


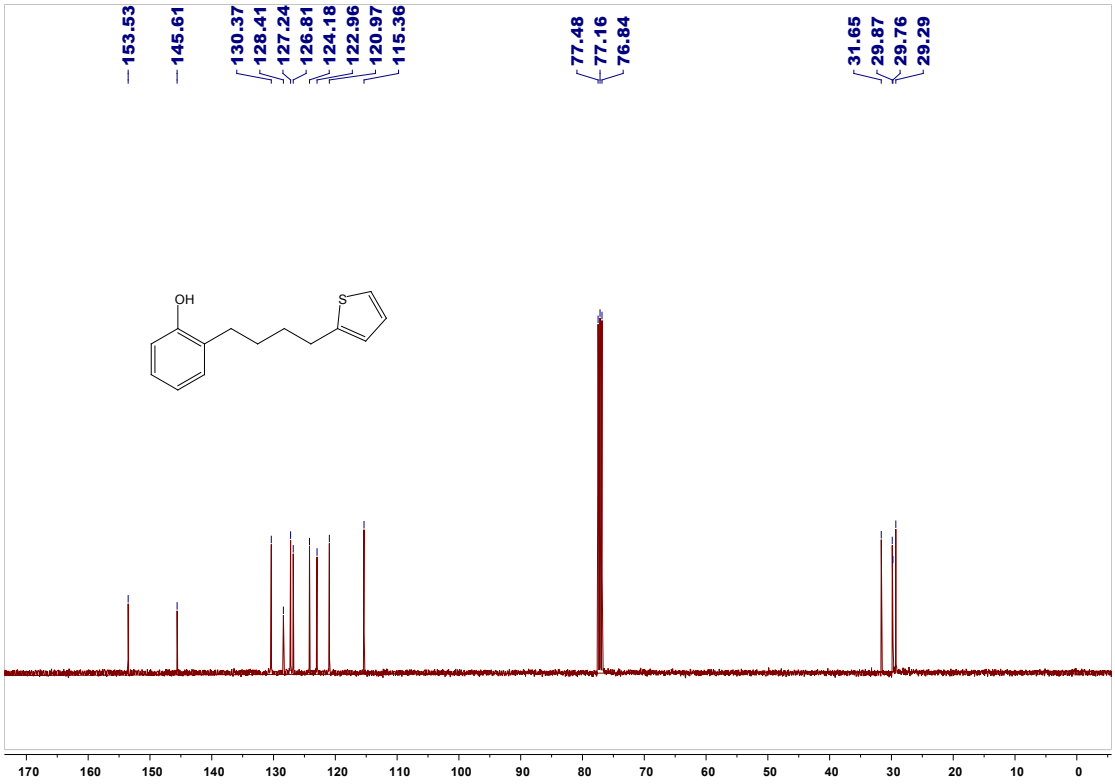
^{1}H and ^{13}C NMR spectra of compound **3l**



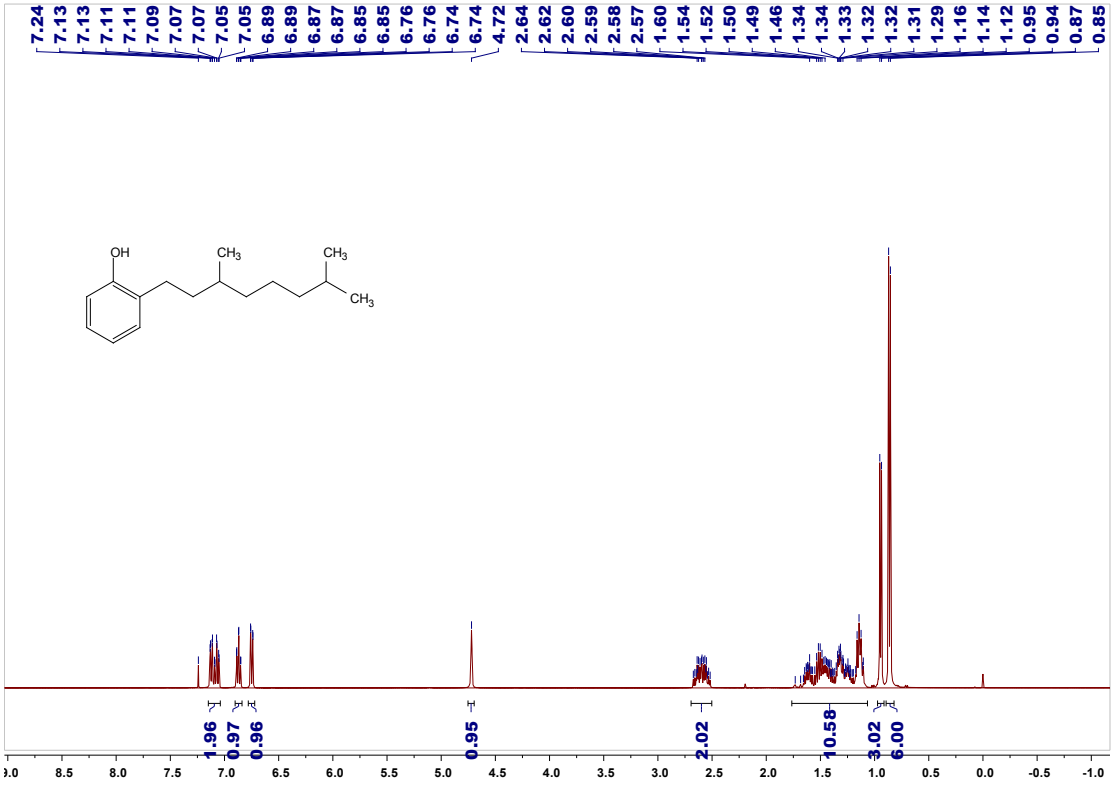


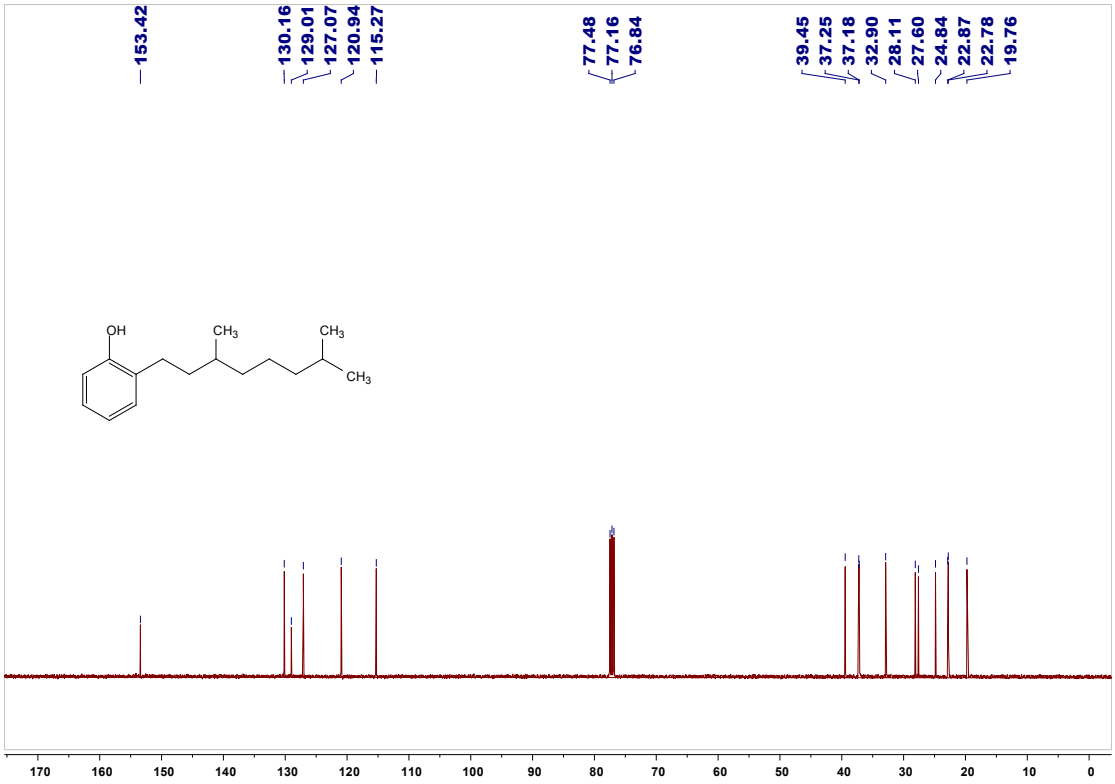
^{1}H and ^{13}C NMR spectra of compound **3m**



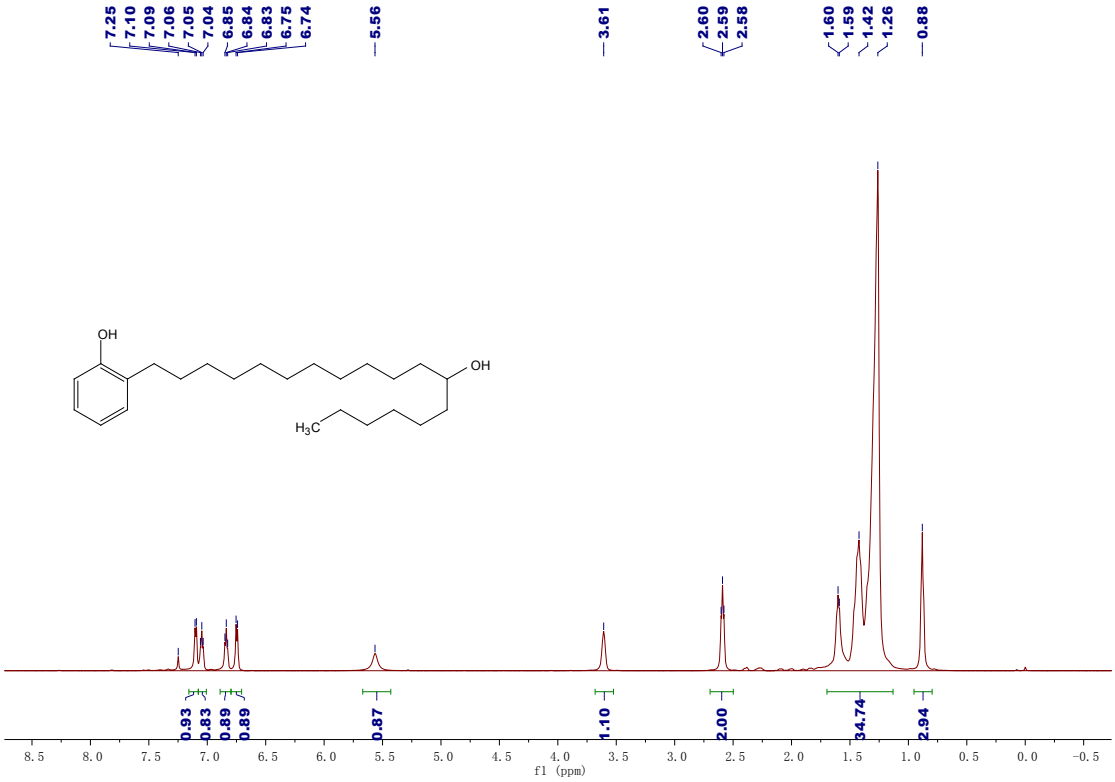


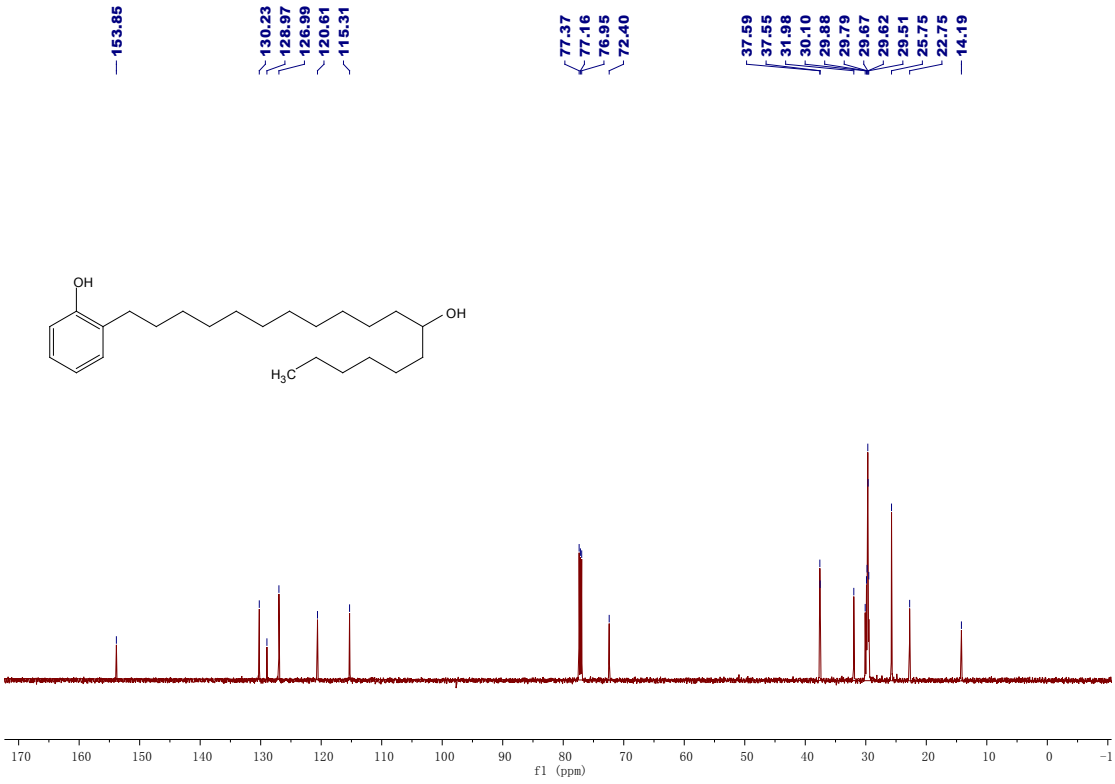
^{1}H and ^{13}C NMR spectra of compound **3n**



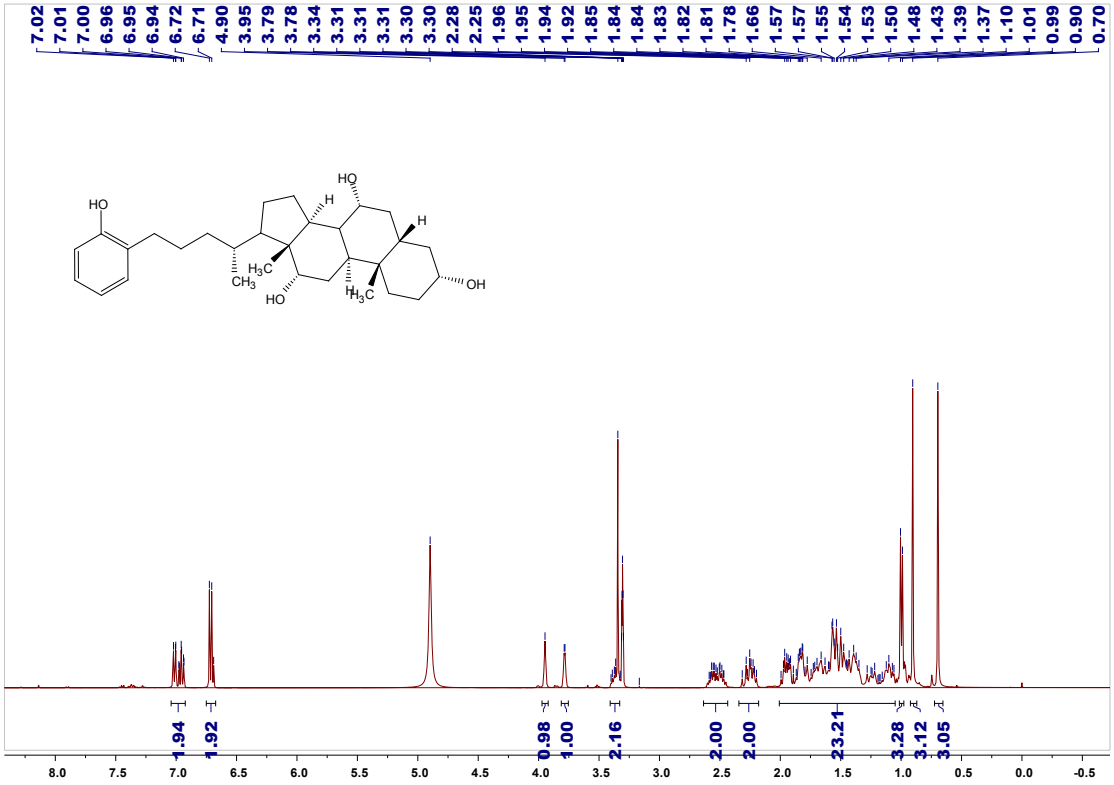


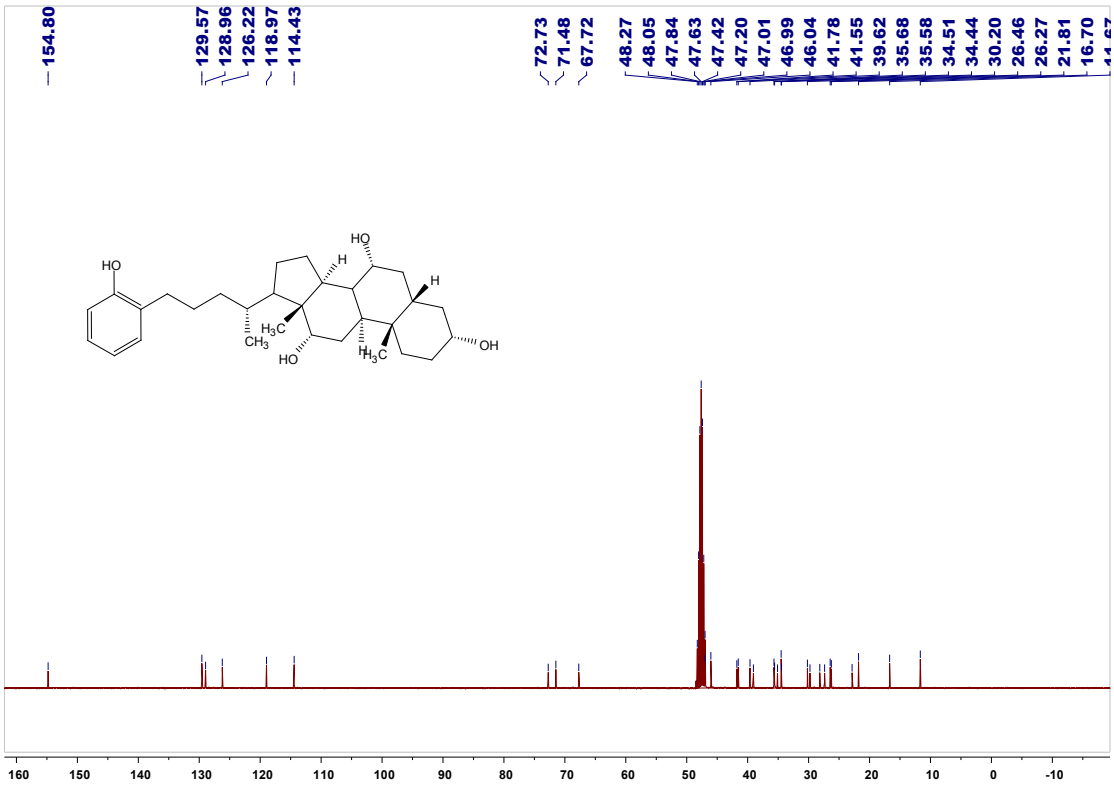
^{1}H and ^{13}C NMR spectra of compound **3o**



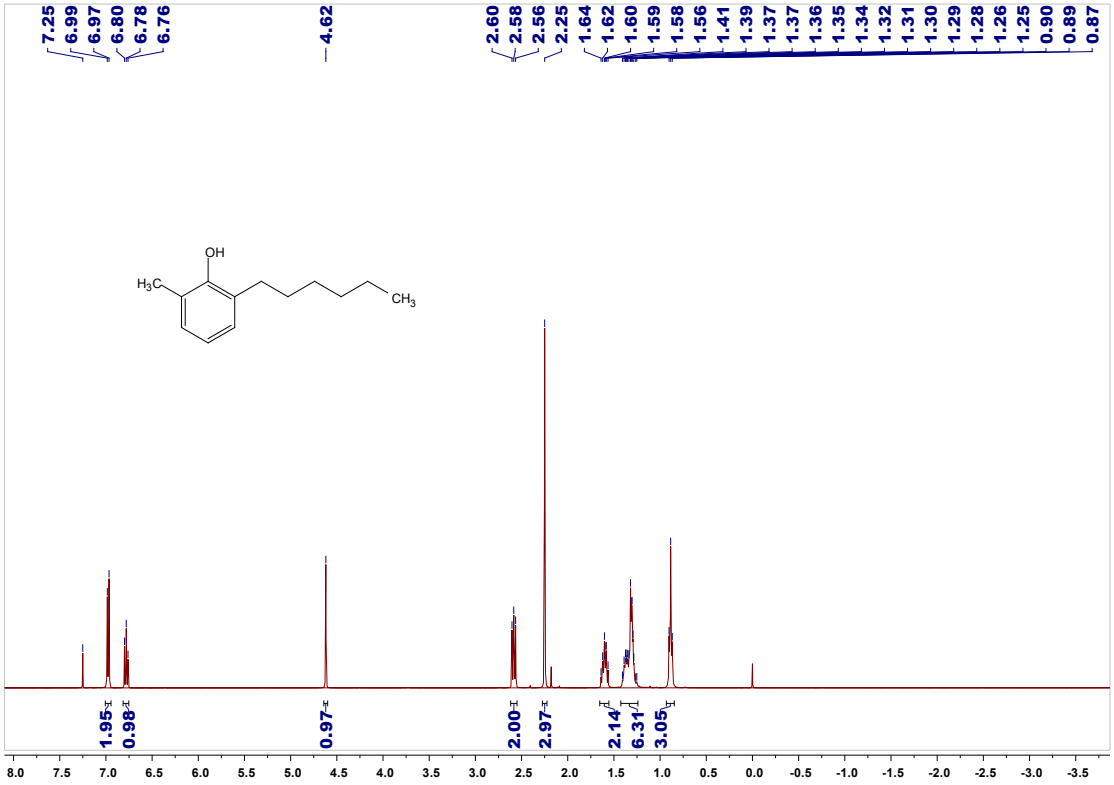


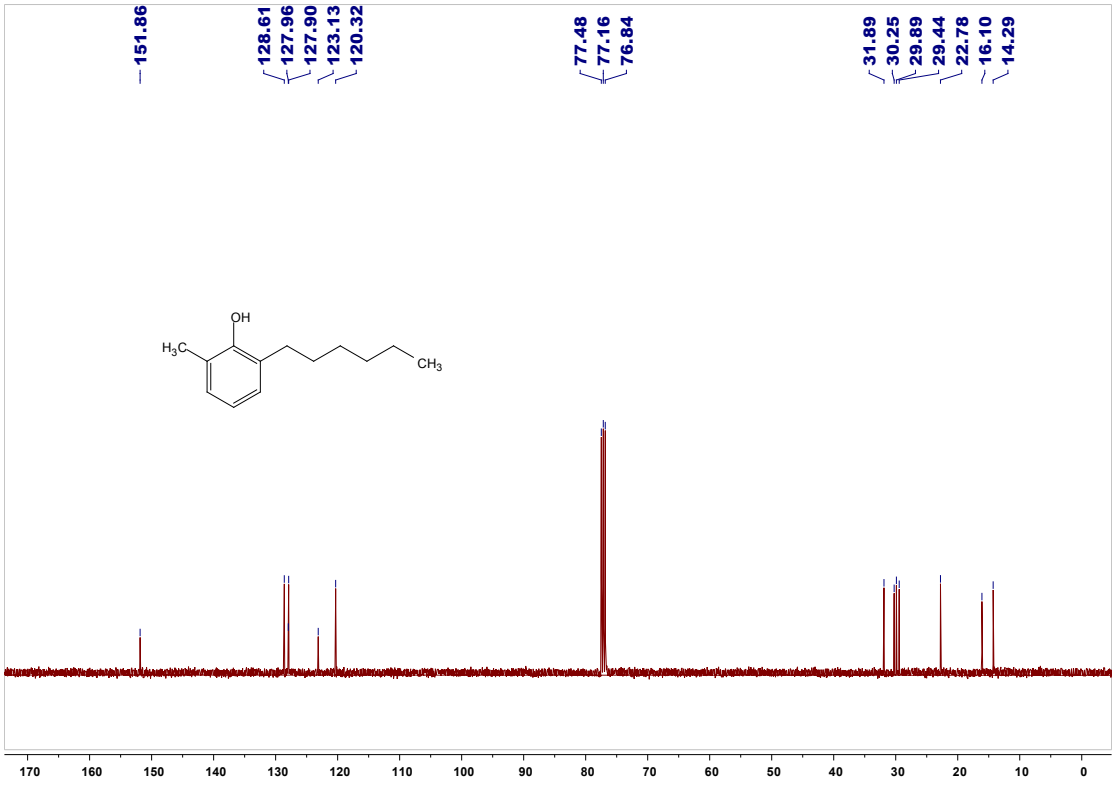
^{1}H and ^{13}C NMR spectra of compound **3p**



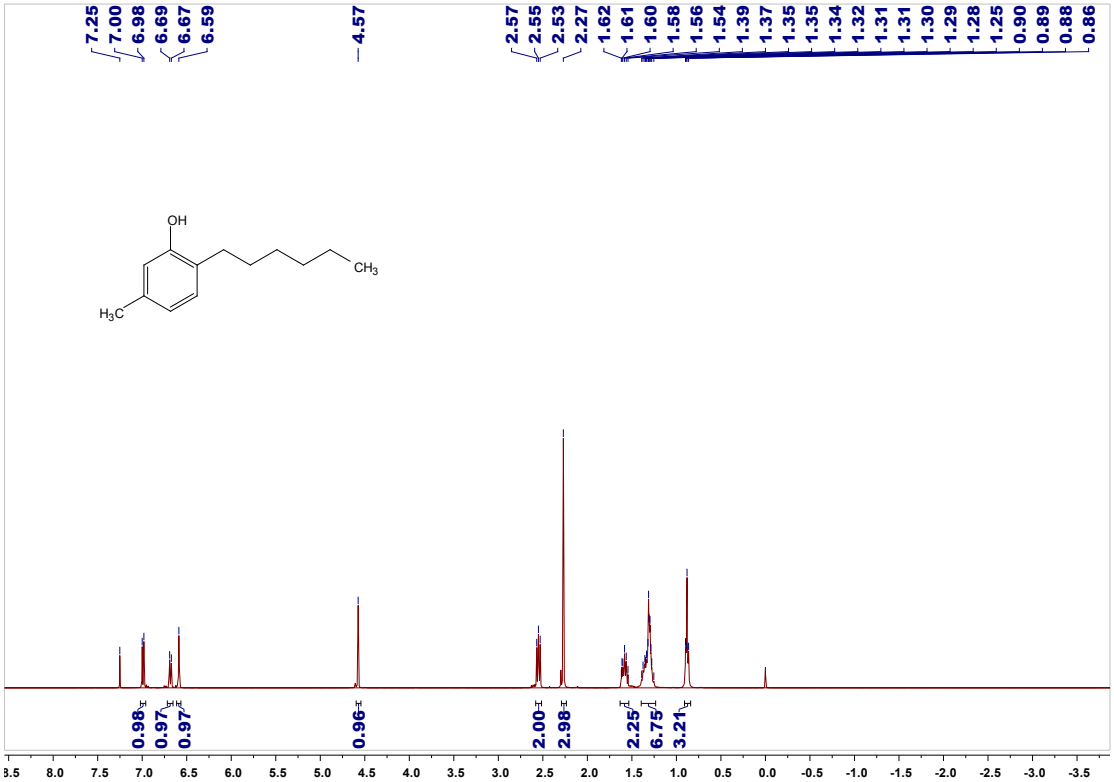


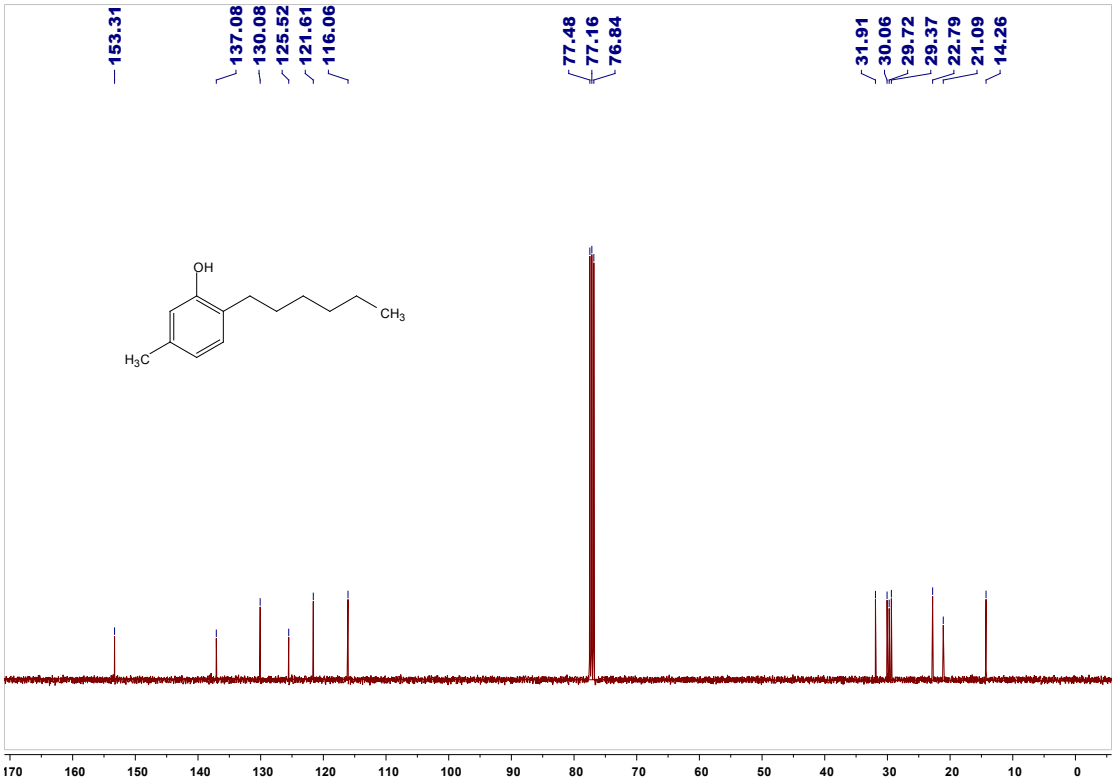
^{1}H and ^{13}C NMR spectra of compound **3q**



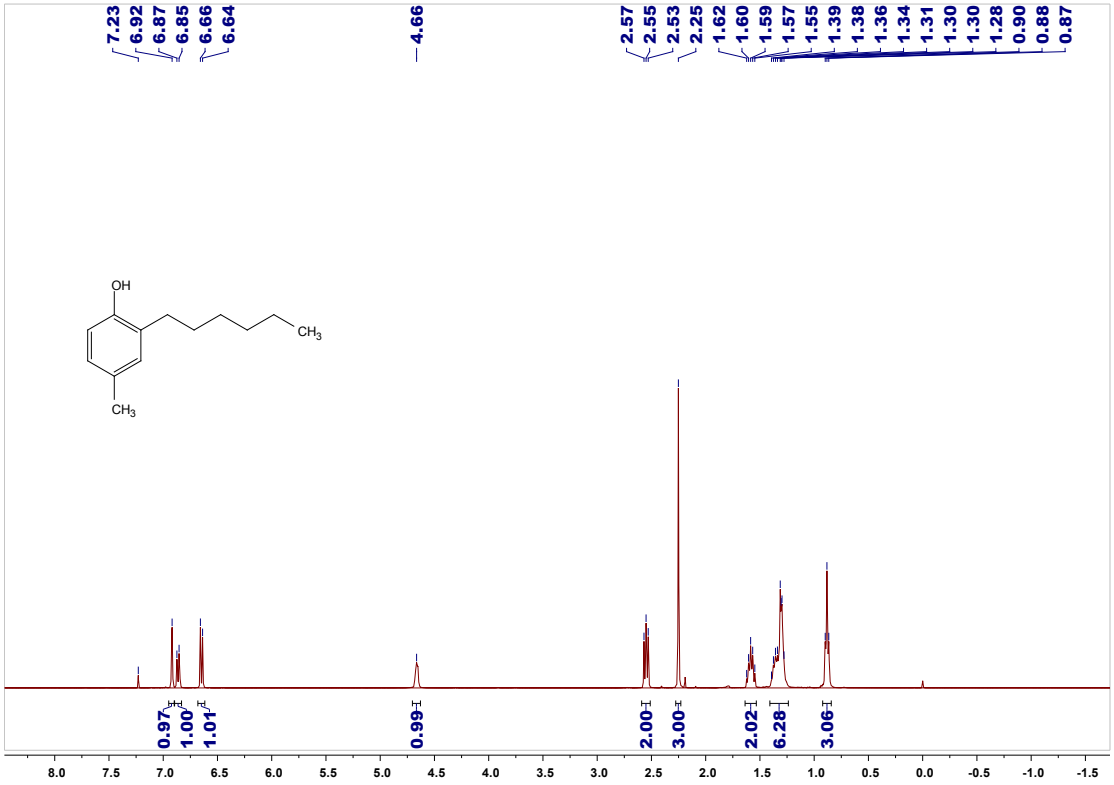


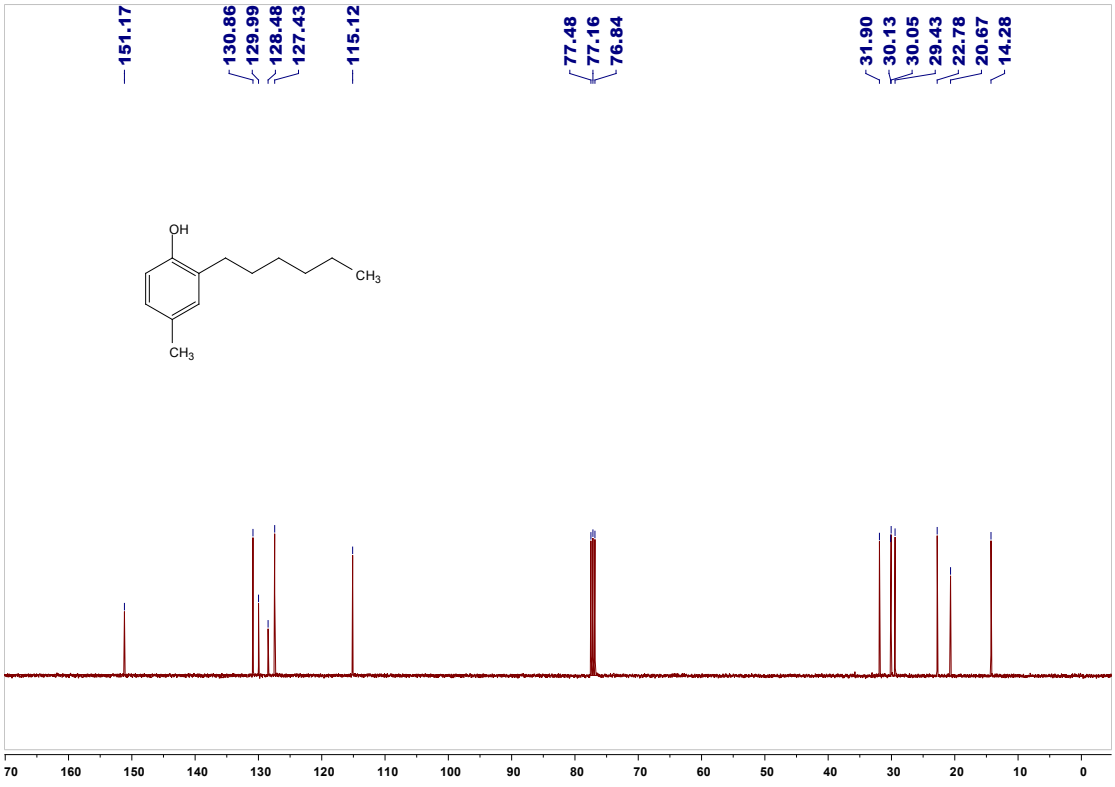
^{1}H and ^{13}C NMR spectra of compound **3r**



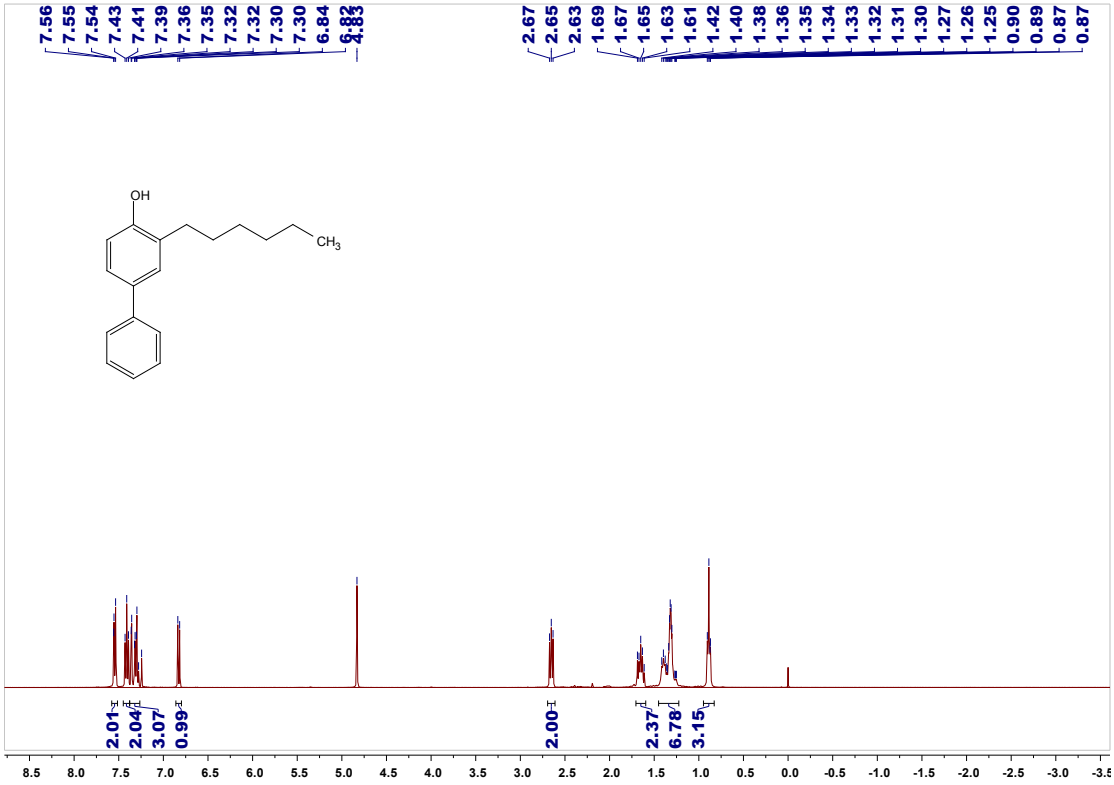


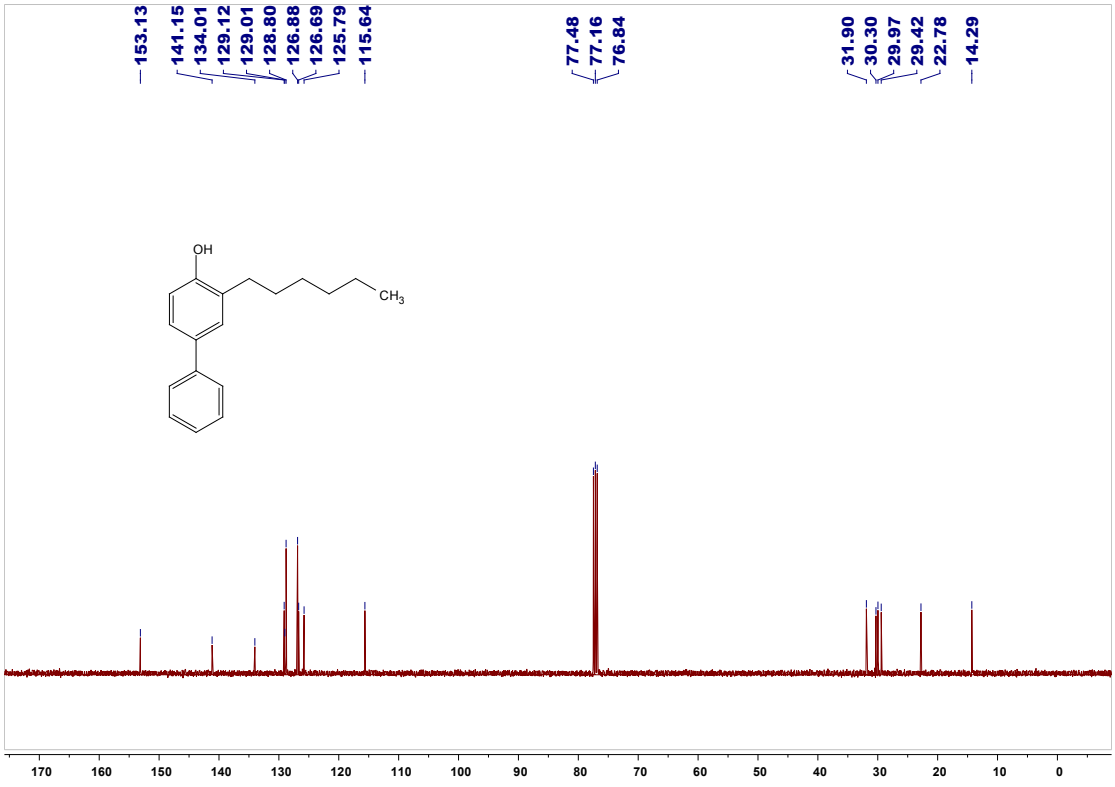
^{1}H and ^{13}C NMR spectra of compound **3s**



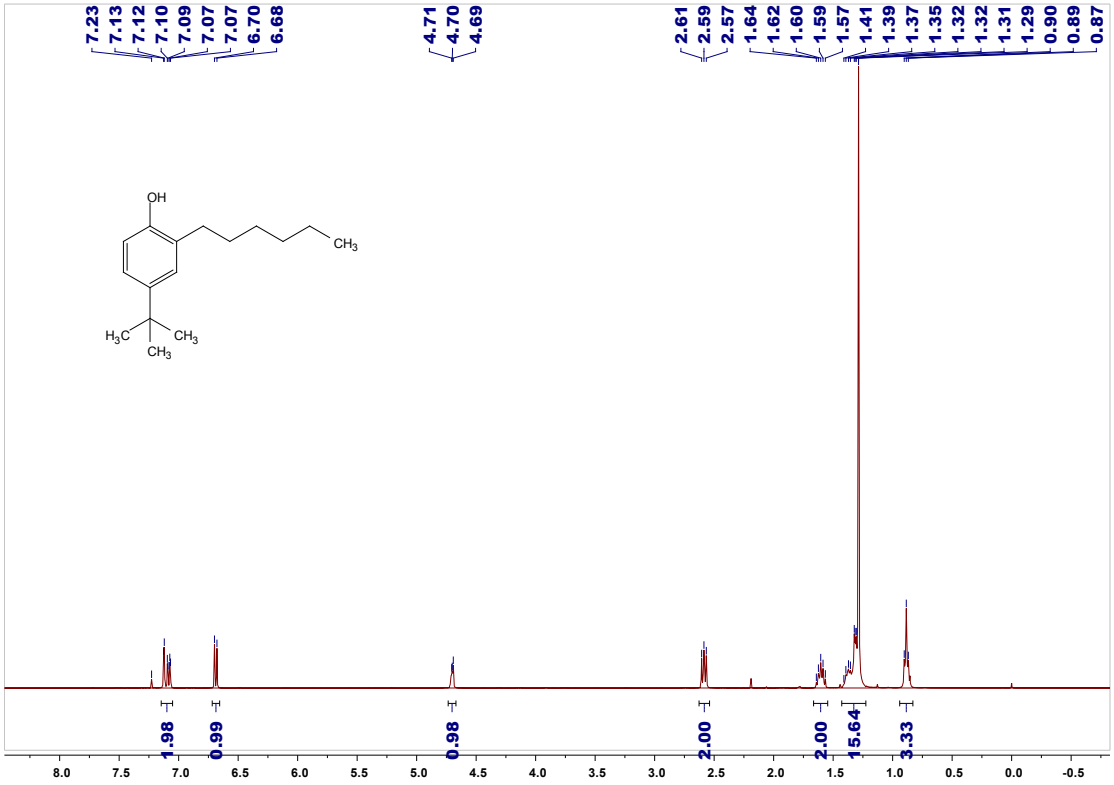


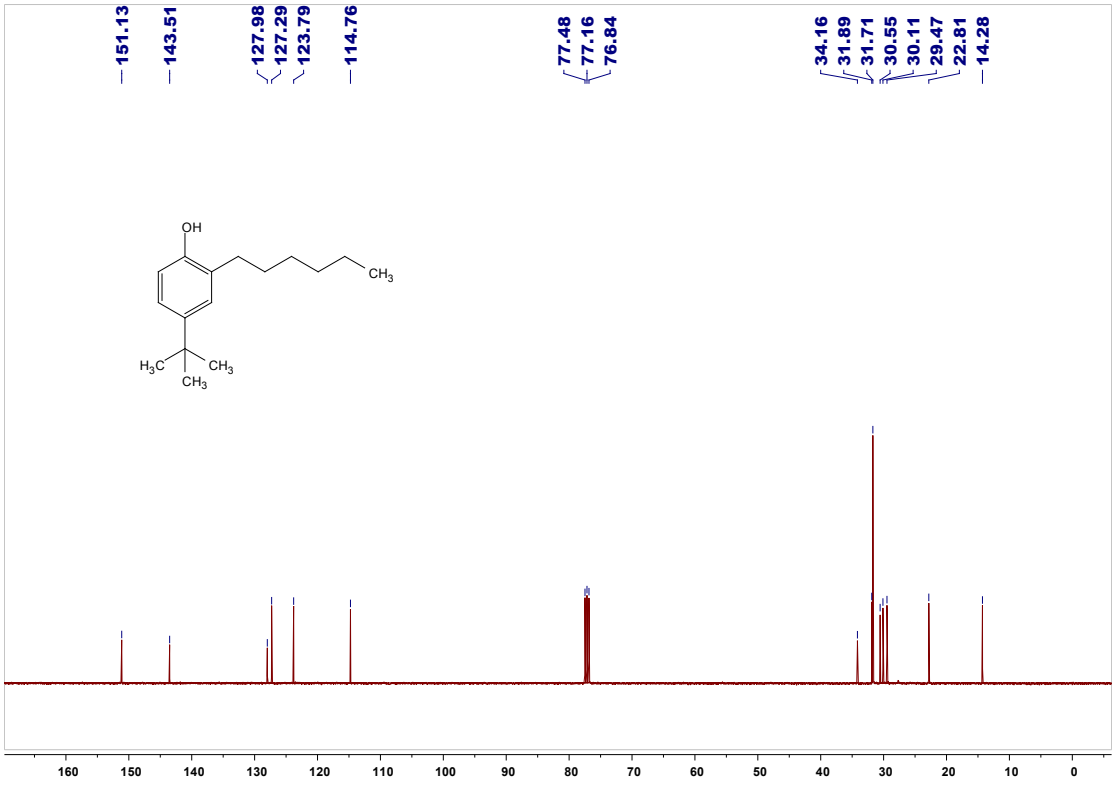
^{1}H and ^{13}C NMR spectra of compound **3t**



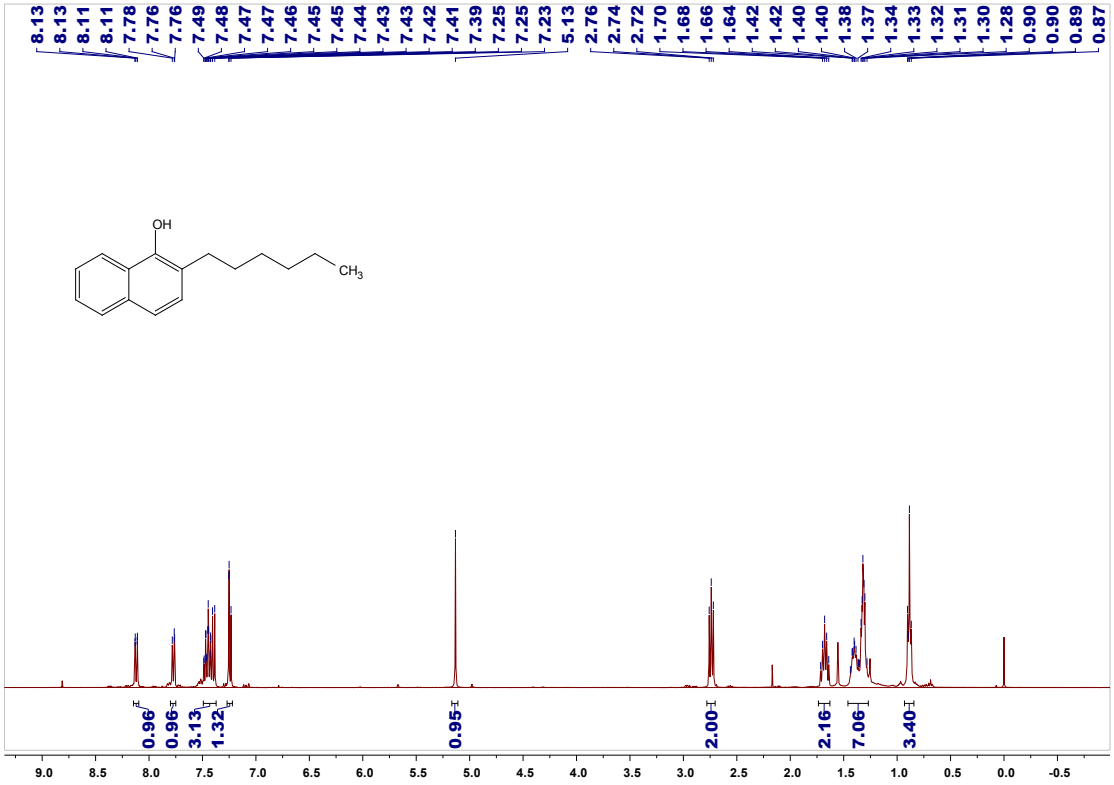


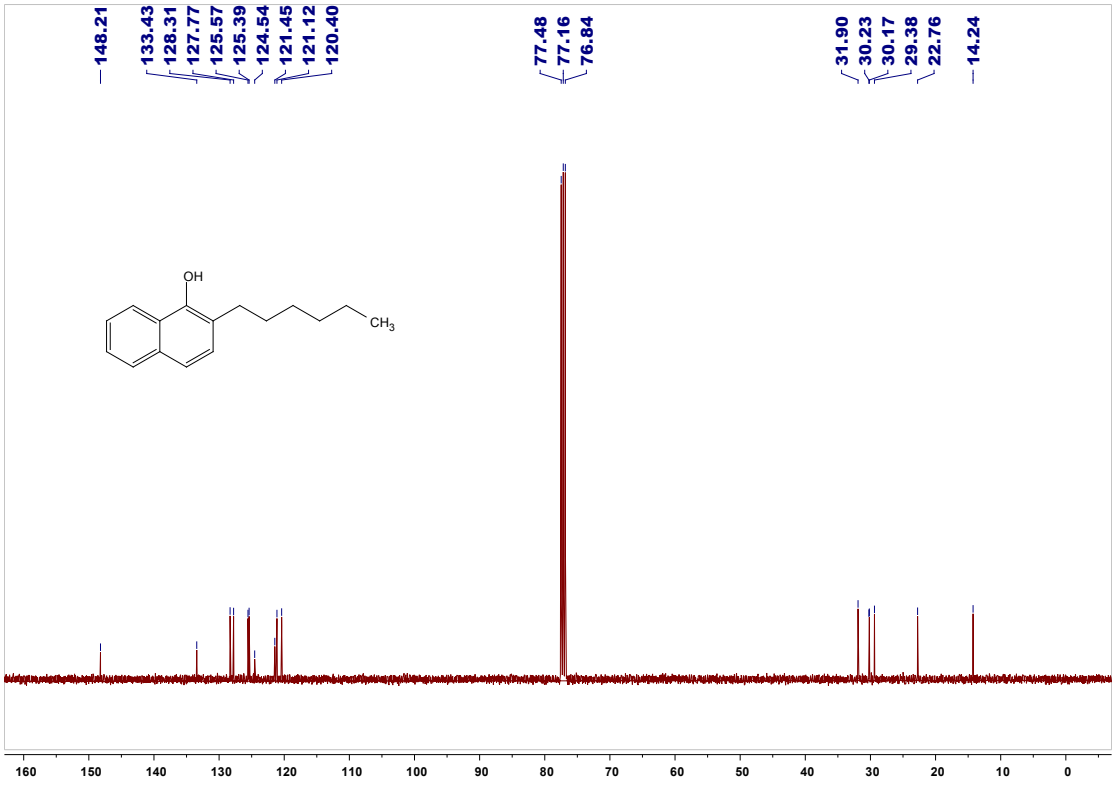
^{1}H and ^{13}C NMR spectra of compound **3u**





^{1}H and ^{13}C NMR spectra of compound **3v**





^{1}H and ^{13}C NMR spectra of compound **3w**