Supporting Information

Alkyl Grignard cross-coupling of aryl phosphates catalyzed by new, highly active ionic iron(II) complexes containing a phosphine ligand and an imidazolium cation

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X-ray Structural Determination. Single crystals of **1**−**6** for X-ray diffraction studies were sealed in a thin-walled glass capillary. The data were collected on a Rigaku Mercury CCD area detector at 293(2) K (**1**, **3**, **4** and **5**), 273(2) K (**2**) and 173(2) K (**6**). Structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 using SHELXS-97 and SHELXL-97 programs. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

Table S1 X-ray Crystallographic Data for 1–3

	1·THF	**2**	**3**·3THF
Formula	$C_{35}H_{53}Cl_3FeN_2O_2$	$C_{45}H_{52}Cl_3FeN_2P$	$C_{57}H_{94}Cl_3FeN_2O_3P$
Formula weight	695.99	814.06	1048.51
Temperature / K	293(2)	273(2)	293(2)
Radiation used	Mo-Ka	Mo-Ka	Mo-Ka
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P21/c*	*P*na2_1	*Pnma*
Unit cell dimensions			
a / Å	12.168 (2)	17.2349(13)	17.6972(7)
b / Å	32.246(6)	14.0856(9)	16.5426(7)
c / Å	9.841(2)	17.5383(13)	22.9862(10)
β / °	96.59(3)	90	90
V / Å^3	3835.7(13)	4257.7(5)	6729.4(5)
Z	4	4	4
D_c / g cm^{-3}	1.205	1.270	1.035
μ / mm^{-1}	0.632	0.573	0.403
F(000)	1480	2398	2264
θ range / °	2.82-25.00	2.89-27.50	2.86-25.00
Reflection collected	22584	29854	32299
Independent reflections, R_{int}	6751, 0.0298	9027, 0.0319	6146, 0.0796
Goodness-of-fit on F^2	0. 989	1.163	1.198
R_1, wR_2 [$I > 2\sigma(I)$]	0.0528, 0.1213	0.0524, 0.1474	0.1008, 0.3036
R_1, wR_2 (all data)	0.0688, 0.1288	0.0542, 0.1528	0.1402, 0.3424

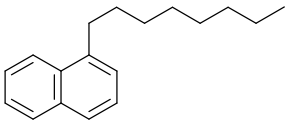
Table S2 X-ray Crystallographic Data for 4–6

	4	**5**·THF	**6**·2THF
Formula	$C_{45}H_{52}Br_3FeN_2P$	$C_{49}H_{78}Br_3FeN_2OP$	$C_{47}H_{74}Br_3FeN_2O_2P$
Formula weight	947.44	1037.65	1025.63
Temperature / K	293(2)	293(2)	173(2)
Radiation used	Mo-Ka	Mo-Ka	Mo-Ka
Crystal system	Monoclinic	Orthorhombic	triclinic
Space group	*Pna21*	$P2_12_12_1$	*P-1*
Unit cell dimensions			
a / Å	17.4631(9)	14.7396(4)	11.3255(4)
b / Å	14.2501(5)	15.5290(5)	13.2264(5)
c / Å	17.9938(10)	23.4470(5)	18.6540(9)
β / °	90	90	102.8
V / Å^3	4477.8(4)	5366.8(3)	2554.82(18)
Z	4	4	2,
D_c / g cm^{-3}	1.405	1.279	1.333
μ / mm^{-1}	3.081	2.577	2.708
F(000)	1928	2144	1064
θ range / °	2.86-25.00	2.90-25.00	2.91-25.00
Reflection collected	17111	24539	23091
Independent reflections, R_{int}	6816, 0.0491	9306, 0.0484	9001, 0.0555
Goodness-of-fit on F^2	1.013	1.026	1.068
R_1, wR_2 [$I > 2\sigma(I)$]	0.0540, 0.1179	0.0444, 0.0844	0.0782, 0.2018
R_1, wR_2 (all data)	0.0870, 0.1347	0.0789, 0.0965	0.1340, 0.2405

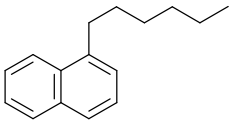
Typical procedures of attempts to synthesize the corresponding neutral iron(II) complex containing both a phosphine ligand and an NHC ligand

A Schlenk flask was charged with [HIPr][Fe(PPh_3)Br_3] (**4**) or [HIPr][Fe(PCy_3)Br_3] (**5**) (1.80 mmol), THF (40.0 mL), and a stirring bar. To this solution was added dropwise a hexane or THF solution of bases (1.80 mmol) at 0 °C. The resulting solution changed color from yellow to pale gray immediately. The reaction mixture was stirred for 0.5 h and slowly warmed to room temperature for an additional 4 h. The reaction solution was filtered, and evaporated to dryness. The residue was washed with hexane (3 × 10.0 mL), extracted with toluene (3 × 10.0 mL), and crystallized from concentrated toluene at 0 °C. The target iron(II) complex, Fe(PPh_3)(IPr)Br_2, was unsuccessfully isolated, but [HIPr][Fe(IPr)Br_3]·C_7H_8[1] was unexpectedly isolated from concentrated toluene solution.

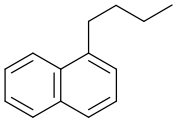
Spectral data of the cross-coupling products



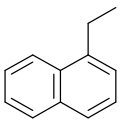
1-octylnaphthalene (**3ab**).[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 6.5 Hz, 3H), 1.25–1.46 (m, 10H), 1.70–1.78 (m, 2H), 3.05 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.43–7.50 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.7, 22.3, 28.9, 29.1, 29.4, 30.4, 31.5, 32.7, 123.5, 124.9, 125.08, 125.15, 125.4, 125.9, 128.3, 131.5, 133.4, 138.6.



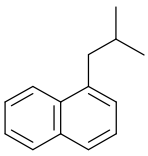
1-hexylnaphthalene (**3ac**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.25–1.45 (m, 6H), 1.68–1.76 (m, 2H), 3.02 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 6.8 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.39–7.48 (m, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.3, 22.9, 29.7, 31.0, 32.0, 33.3, 124.1, 125.5, 125.68, 125.75, 126.0, 126.5, 128.9, 132.1, 134.1, 139.2.



1-butylnaphthalene (**3aa**).[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95 (t, *J* = 7.3 Hz, 3H), 1.39–1.48 (m, 2H), 1.68–1.75 (m, 2H), 3.04 (t, *J* = 7.8 Hz,, 2H), 7.28 (d, *J* = 6.9 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.41–7.49 (m, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.6, 22.5, 32.4, 32.6, 123.5, 125.0, 125.1, 125.2, 125.5, 126.0, 128.4, 131.6, 133.5, 138.4.

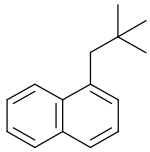


1-ethylnaphthalene (**3ad**).[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.37 (t, *J* = 7.5 Hz, 3H), 3.07–3.13 (m, 2H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.37–7.41 (m, 1H), 7.43–7.51 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.82–7.85 (m, 1H), 8.03–8.05 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.6, 25.4, 123.3, 124.4, 124.9, 125.2, 125.9, 127.4, 128.3, 131.3, 133.3, 139.8.

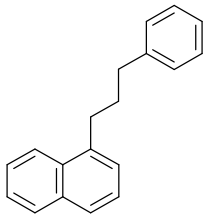


1-isobutylnaphthalene (**3af**).[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95 (d, *J* = 6.6 Hz, 6H), 2.00–2.10 (m, 1H), 2.90 (d, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.33–7.37 (m, 1H), 7.40–7.47 (m, 2H), 7.67

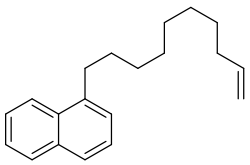
(d, J = 8.2 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 22.5, 29.2, 42.3, 123.9, 124.99, 125.01, 125.2, 126.2, 126.7, 128.4, 131.9, 133.7, 137.5.



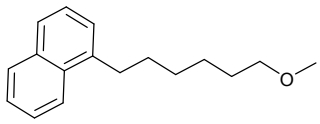
1-neopentylnaphthalene (**3ag**).[6] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.96 (s, 9H), 3.00 (s, 2H), 7.27 (d, J = 7.1 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.38–7.46 (m, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.79–7.81 (m, 1H), 8.10 (d, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 22.5, 29.2, 42.3, 123.9, 124.99, 125.01, 125.2, 126.2, 126.7, 128.4, 131.9, 133.7, 137.5.



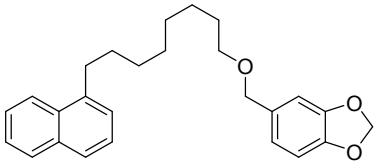
1-(3-phenylpropyl)naphthalene (**3ah**).[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.04–2.11 (m, 2H), 2.73 (t, J = 7.7 Hz, 2H), 3.08 (t, J = 7.7 Hz, 2H), 7.17–7.20 (m, 3H), 7.25–7.30 (m, 3H), 7.35–7.38 (m, 1H), 7.41– 7.48 (m, 2H), 7.68 (d, J = 8.1 Hz, 1H), 7.80–7.84 (m, 1H), 7.93–7.95 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.8, 32.1, 35.5, 123.4, 125.0, 125.1, 125.3, 125.4, 125.5, 126.1, 127.9, 128.1, 128.3, 131.5, 133.5, 138.0, 141.8.



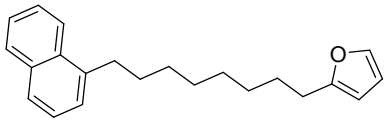
1-(dec-9-en-1-yl)naphthalene (**3ai**). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.34–1.53 (m, 8H), 1.70–1.75 (m, 2H), 1.81–1.88 (m, 2H), 2.07–2.14 (m, 2H), 3.16 (t, J = 7.6 Hz, 2H), 5.46–5.57 (m, 2H), 7.41 (d, J = 6.8 Hz, 1H), 7.47–7.50 (m, 1H), 7.54–7.61 (m, 2H), 7.79 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 7.7 Hz, 1H), 8.14 (d, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.5, 28.7, 29.0, 29.2, 29.4, 30.4, 32.2, 32.7, 123.5, 124.2, 124.9, 125.1, 125.2, 125.4, 125.9, 128.3, 131.2, 131.5, 133.5, 138.6. HRMS (CI) Calcd for $C_{20}H_{27}$ $(M+H)^+$: 267.2107, Found: 267.2115.



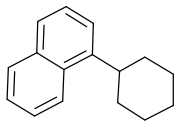
1-(6-methoxyhexyl)naphthalene (**3aj**). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.29–1.42 (m, 4H), 1.48–1.54 (m, 2H), 1.65–1.72 (m, 2H), 2.99 (t, J = 7.8 Hz, 2H), 3.25 (s, 3H), 3.29 (t, J = 6.6 Hz, 2H), 7.23 (d, J = 6.7 Hz, 1H), 7.29–7.33 (m, 1H), 7.36–7.44 (m, 2H), 7.62 (d, J = 8.1 Hz, 1H), 7.75–7.78 (m, 1H), 7.96 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.6, 29.17, 29.19, 30.3, 32.6, 58.1, 72.4, 123.4, 124.9, 125.1, 125.2, 125.4, 125.9, 128.3, 131.4, 133.4, 138.4. HRMS (CI) Calcd for $C_{17}H_{23}O$ $(M+H)^+$: 243.1743, Found: 243.1750.



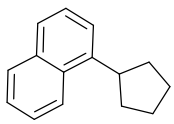
5-(((8-(naphthalen-1-yl)octyl)oxy)methyl)benzo[d][1,3]dioxole (**3ak**). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.30–1.44 (m, 8H), 1.55–1.60 (m, 2H), 1.70–1.77 (m, 2H), 3.05 (t, *J* = 7.8 Hz, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 4.38 (s, 2H), 5.91 (s, 2H), 6.74–6.78 (m, 2H), 6.84 (s, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.1 Hz, 1H), 7.44–7.51 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.75, 29.00, 29.30, 29.32, 30.38, 32.65, 69.8, 72.3, 100.5, 107.6, 107.9, 120.7, 123.4, 124.9, 125.1, 125.2, 125.4, 125.9, 128.3, 131.5, 132.2, 133.4, 138.5, 146.5, 147.3. HRMS (CI) Calcd for $C_{26}H_{31}O_3(M+H)^+$: 391.2268, Found: 391.2284.



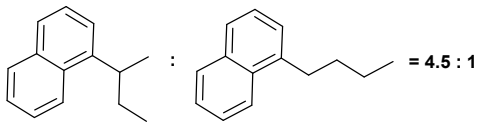
2-(6-(naphthalen-4-yl)hexyl)furan (**3al**). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.31–1.49 (m, 8H), 1.65–1.70 (m, 2H), 1.76–1.84 (m, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 3.12 (t, *J* = 7.9 Hz, 2H), 6.02–6.03 (m, 1H), 6.32–6.33 (m, 1H), 7.35–7.36 (m, 1H), 7.38 (s, 1H), 7.43 –7.47 (m, 1H), 7.50 –7.58 (m, 2H),7.76 (d, *J* = 8.2 Hz, 1H), 7.89–7.91 (m, 1H), 8.10 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 27.48, 27.54, 28.7, 28.9, 28.9, 29.3, 30.4, 32.6, 104.0, 109.5, 123.4, 124.9, 125.1, 125.1, 125.4, 125.9, 128.3, 131.4, 133.4, 138.5, 140.1, 156.1. HRMS (CI) Calcd for $C_{26}H_{31}O_3(M+H)^+$: 307.2056, Found: 307.2050.



1-cyclohexylnaphthalene (**3am**).[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.27–1.40 (m, 1H), 1.49–1.60 (m, 4H), 1.80–1.85 (m, 1H), 1.89–1.92 (m, 2H), 1.98–2.06 (m, 2H), 3.28–3.34(m, 1H), 7.36–7.38 (m, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.43–7.45 (m, 1H), 7.48–7.50 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.82–7.84 (m, 1H), 8.10 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 26.6, 27.4, 34.3, 39.3, 122.3, 123.3, 125.3, 125.6, 125.7, 126.3, 129.0, 131.4, 134.0, 143.9.

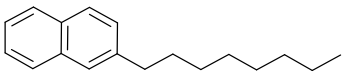


1-cyclopentylnaphthalene (**3an**).[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.75–1.85 (m, 6H), 2.17–2.18 (m, 2H), 3.72–3.80 (m, 1H), 7.37–7.41 (m, 2H), 7.41 –7.49 (m, 2H), 7.65–7.68 (m, 1H), 7.80–7.82 (m, 1H), 8.13 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.1, 33.3, 40.9, 121.7, 123.7, 124.9, 125.2, 125.3, 126.0, 128.5, 132.0, 133.6, 141.8.

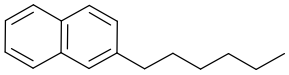


1-*sec*-butylnaphthalene (**3ao**). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.92 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 0.67H), 1.37 (t, *J* = 6.9 Hz, 3H), 1.41–1.50 (m, 0.48H), 1.65–1.77 (m, 1.5H), 1.80–1.91 (m,

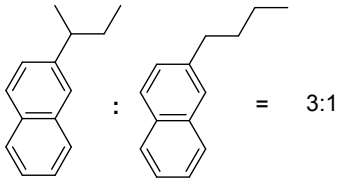
1H), 3.06 (t, *J* = 7.8 Hz, 0.45H), 3.06 (t, *J* = 7.8 Hz, 0.45H), 3.47–3.55 (m, 1H), 7.31 (d, *J* = 7.8 Hz, 0.24H), 7.36–7.40 (m, 1H), 7.42–7.52 (m, 3.45H), 7.69 (d, *J* = 8.1 Hz, 3.45H), 7.84–7.86 (m, 1H), 8.04 (d, *J* = 8.2 Hz, 0.22H), 8.12 (d, *J* = 8.3 Hz, 1H).



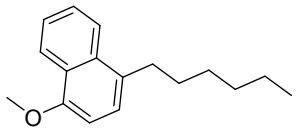
2-octylnaphthalene (**3bb**).[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.87 (t, *J* = 7.0 Hz, 3H), 1.10–1.46 (m, 10H), 1.63–1.68 (m, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.34–7.41 (m, 2H), 7.56 (s, 1H), 7.70–7.76 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8, 22.4, 29.0, 29.1, 29.2, 31.1, 31.6, 35.8, 124.6, 125.4, 125.9, 127.06, 127.09, 127.3, 127.4, 131.6, 133.3, 140.1.



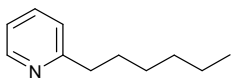
2-hexylnaphthalene (**3bc**).[9] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.25–1.38 (m, 6H), 1.65–1.72 (m, 2H), 2.75 (t, *J* = 7.8 Hz, 2H), 7.30–7.33 (m, 1H), 7.37–7.44 (m, 2H), 7.59 (s, 1H), 7.73–7.79 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.2, 22.7, 29.1, 31.4, 31.8, 36.2, 125.0, 125.8, 126.3, 127.4, 127.5, 127.8, 132.0, 133.7, 140.5.



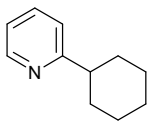
2-*sec*-butylnaphthalene (**3bo**). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.85 (t, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.34–1.44 (m, 0.76H), 1.61–1.76 (m, 2.75H), 2.72–2.81 (m, 1.71H), 7.32–7.36 (m, 1.31H), 7.38–7.46 (m, 2.67H), 7.60 (s, 1H), 7.74–7.80 (m, 4H).



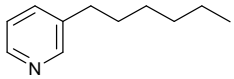
1-hexyl-4-methoxynaphthalene (**3cc**). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95 (t, *J* = 7.1 Hz, 3H), 1.37–1.40 (m, 4H), 1.44–1.50 (m, 2H), 1.63 (s, 3H), 1.72–1.80 (m, 2H), 3.03 (t, *J* = 7.8 Hz, 2H), 4.04 (s, 3H), 6.79 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.50–7.59 (m, 2H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.34–8.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.7, 22.2, 29.0, 30.4, 31.3, 32.2, 55.0, 102.9, 122.0, 123.3, 124.2, 124.9, 125.4, 125.6, 130.4, 132.2, 153.5. HRMS (CI) Calcd for $C_{17}H_{23}O$ $(M+H)^+$: 243.1743, Found: 243.1750.



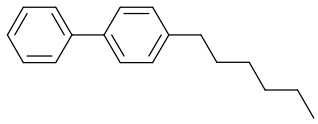
2-hexylpyridine (**3dc**).[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.78 (t, *J* = 7.0 Hz, 3H), 1.19–1.28 (m, 6H), 1.59–1.67 (m, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 6.95–6.98 (m, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 7.43–7.47 (m, 1H), 8.41–8.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.5, 22.0, 28.5, 29.3, 31.2, 37.9, 120.2, 122.1, 135.6, 148.6, 161.9.



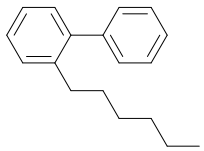
2-cyclohexylpyridine (**3dm**).[10] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23–1.34 (m, 1H), 1.36–1.47 (m, 2H), 1.48–1.58 (m, 2H), 1.72–1.79 (m, 1H), 1.84–1.89 (m, 2H), 1.94–1.97 (m, 2H), 2.66–2.74 (m, 1H), 7.07–7.10 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.57–7.62 (m, 1H), 8.52–8.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 25.6, 26.1, 32.4, 46.1, 120.5, 135.9, 148.5, 166.0.



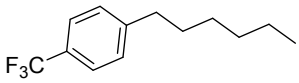
3-hexylpyridine (**3ec**).[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 6.9 Hz, 3H), 1.25–1.36 (m, 6H), 1.57–1.64 (m, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 7.17–7.20 (m, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 8.41–8.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.5, 22.0, 28.3, 30.6, 31.1, 32.5, 122.7, 135.4, 137.5, 146.5, 149.3.



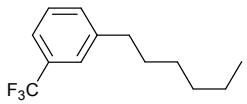
4-hexyl-1,1'-Biphenyl (**3fc**).[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.89 (t, *J* = 6.9 Hz, 3H), 1.29–1.38 (m, 6H), 1.60–1.68 (m, 2H), 2.63 (t, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.28–7.32 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.49–7.51 (m, 2H), 7.56–7.59 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.7, 22.2, 28.6, 31.1, 31.3, 35.2, 126.51, 126.55, 128.3, 128.4, 138.1, 140.8, 141.7.



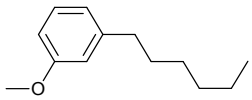
2-hexyl-1,1'-biphenyl (**3gc**).[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.84 (t, *J* = 6.9 Hz, 3H), 1.16–1.28 (m, 6H), 1.44–1.51 (m, 2H), 2.58 (t, *J* = 7.9 Hz, 2H), 7.21–7.26 (m, 2H), 7.27–7.30 (m, 1H), 7.30–7.32 (m, 2H), 7.33–7.35 (m, 1H), 7.35–7.38 (m, 1H), 7.41–7.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.5, 22.0, 26.1, 30.6, 32.2, 44.7, 115.3, 120.4, 127.4, 127.6, 128.6, 128.7, 128.8, 129.8, 136.6, 151.9.



1-hexyl-4-(trifluoromethyl)benzene (**3hc**).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.94 (t, *J* = 6.9 Hz, 3H), 1.32–1.43 (m, 6H), 1.64–1.71 (m, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.58, 13.64, 22.1, 22.22, 28.4, 28.9, 29.19, 29.23, 30.7, 31.2, 31.5, 35.3, 124.6, 124.6, 124.67, 124.71, 128.2.

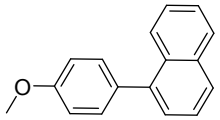


1-hexyl-3-(trifluoromethyl)benzene (**3ic**). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.26–1.35 (m, 6H), 1.58–1.66 (m, 2H), 2.65 (t, *J* = 7.9 Hz, 2H), 7.33–7.39 (m, 2H), 7.42–7.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.6, 22.1, 28.4, 30.8, 31.2, 35.3, 121.97, 122.01, 124.55, 124.59, 128.1, 131.30, 131.31, 143.3. HRMS (CI) Calcd for $C_{13}H_{18}F_3(M+H)^+$: 231.1355, Found: 231.1355.



1-hexyl-3-methoxybenzene (**3jc**).[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, *J* = 6.6 Hz, 3H), 1.30–

1.36 (m, 6H), 1.56–1.64 (m, 2H), 2.57 (t, *J* = 7.9 Hz, 2H), 3.77 (s, 3H), 6.70–6.72 (m, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 7.15–7.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.7, 22.2, 28.6, 30.9, 31.3, 35.6, 54.6, 110.3, 113.7, 120.4, 128.7, 144.2, 159.1.



1-(4-methoxyphenyl)naphthalene (**3aq**).[13] ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.96 (s, 3H), 7.10–7.12 (m, 2H), 7.47–7.52 (m, 4H), 7.54–7.60 (m, 2H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.96–8.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 54.9, 113.3, 124.9, 125.2, 125.5, 125.6, 126.5, 126.9, 127.8, 130.7, 131.37, 132.7, 133.4, 139.5.

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Copies of NMR Spectra for All Compounds

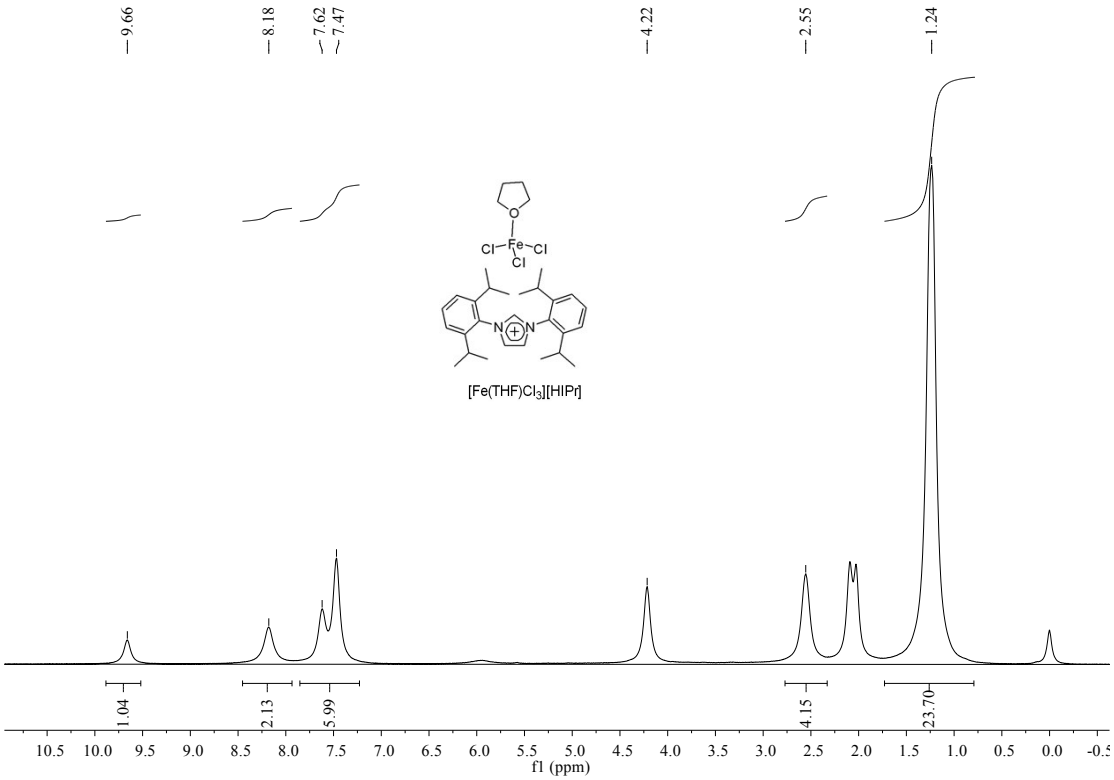

Figure S1. ^{1}H NMR spectrum of **[HIPr][Fe(C_4H_8O)Cl_3]** (**1**) in $(CD_3)_2CO$.

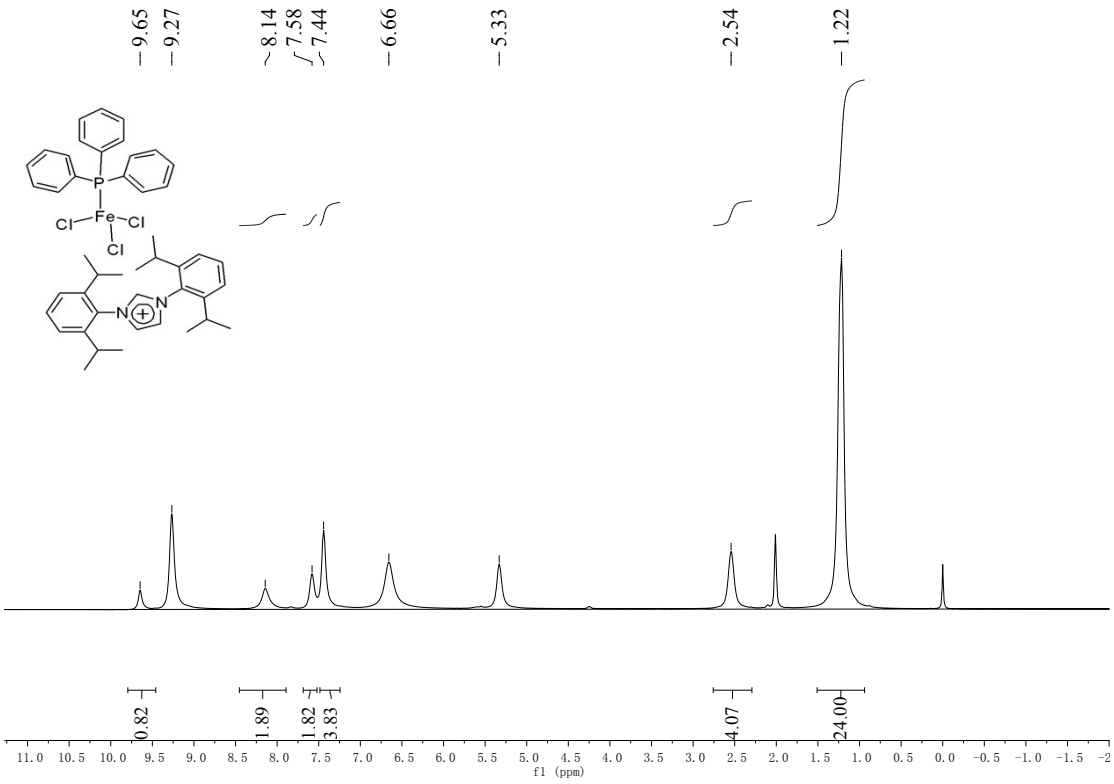

Figure S2. ^{1}H NMR spectrum of **[HIPr][Fe(PPh$_3$)Cl$_3$]** (**2**) in $(CD_3)_2CO$.

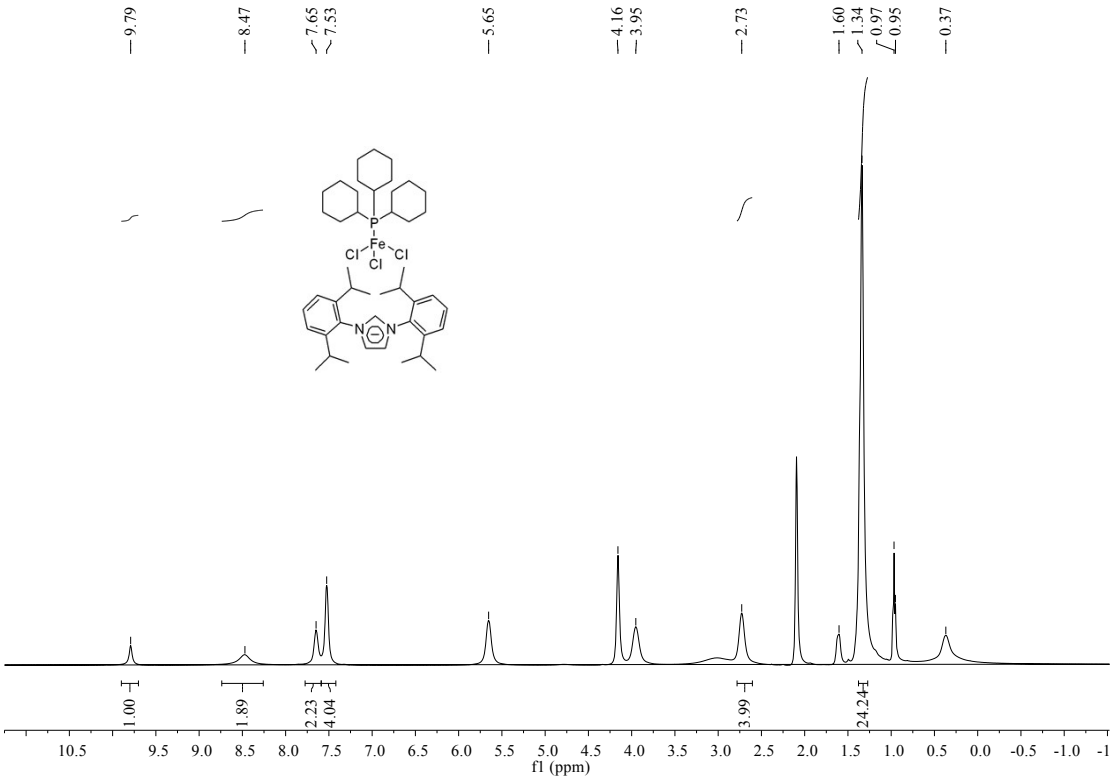

Figure S3. ^{1}H NMR spectrum of **[HIPr][Fe(PCy$_3$)Cl$_3$]** (**3**) in $(CD_3)_2CO$.

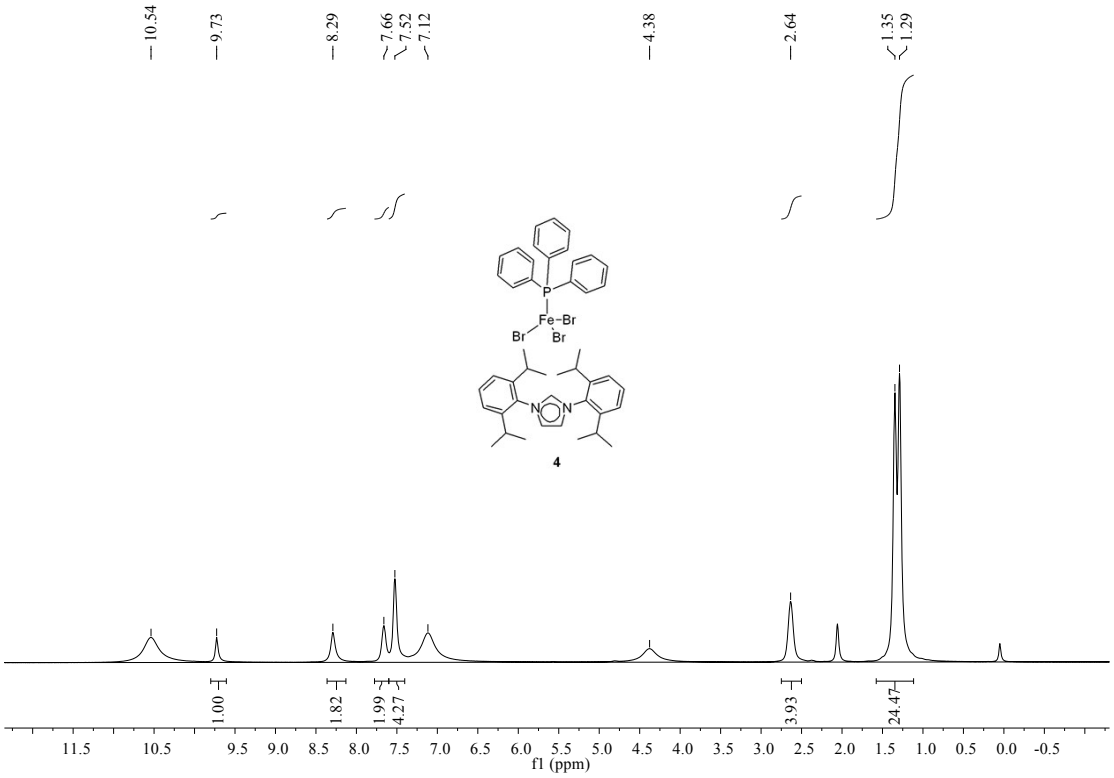

Figure S4. ^{1}H NMR spectrum of **[HIPr][Fe(PPh$_3$)Br$_3$]** (**4**) in $(CD_3)_2CO$.

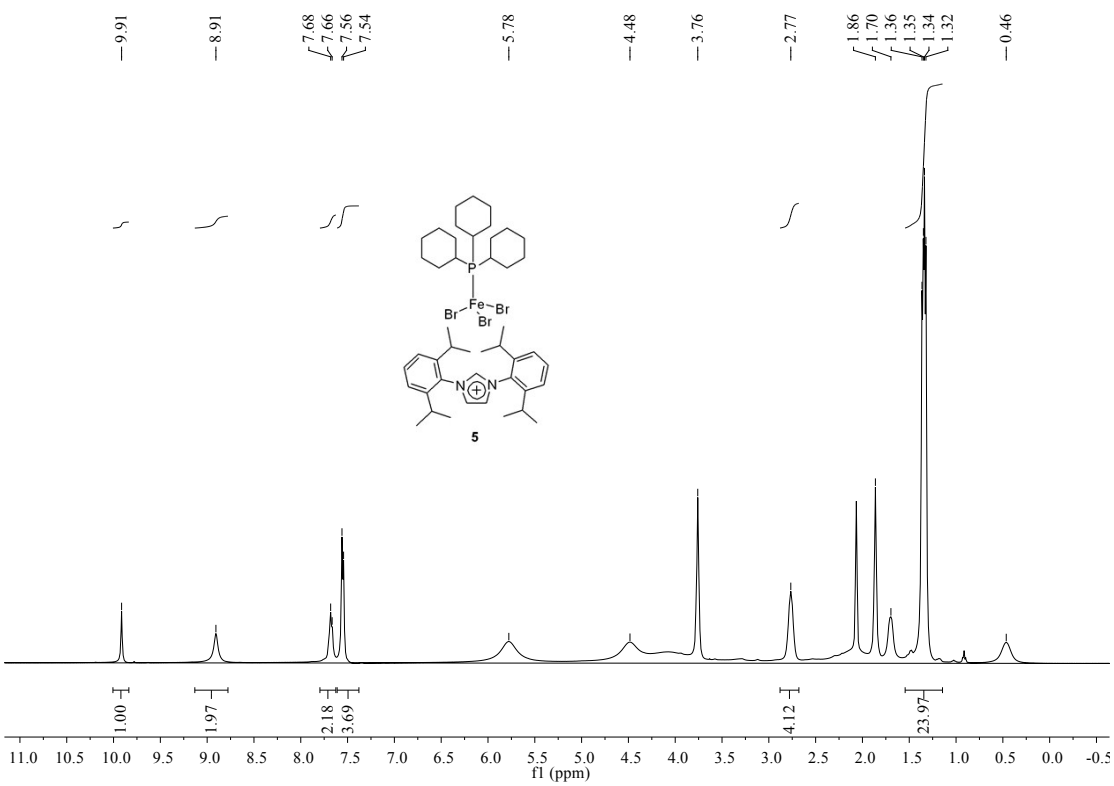

Figure S5. ^{1}H NMR spectrum of **[HIPr][Fe(PCy$_3$)Br$_3$]** (**5**) in $(CD_3)_2CO$.

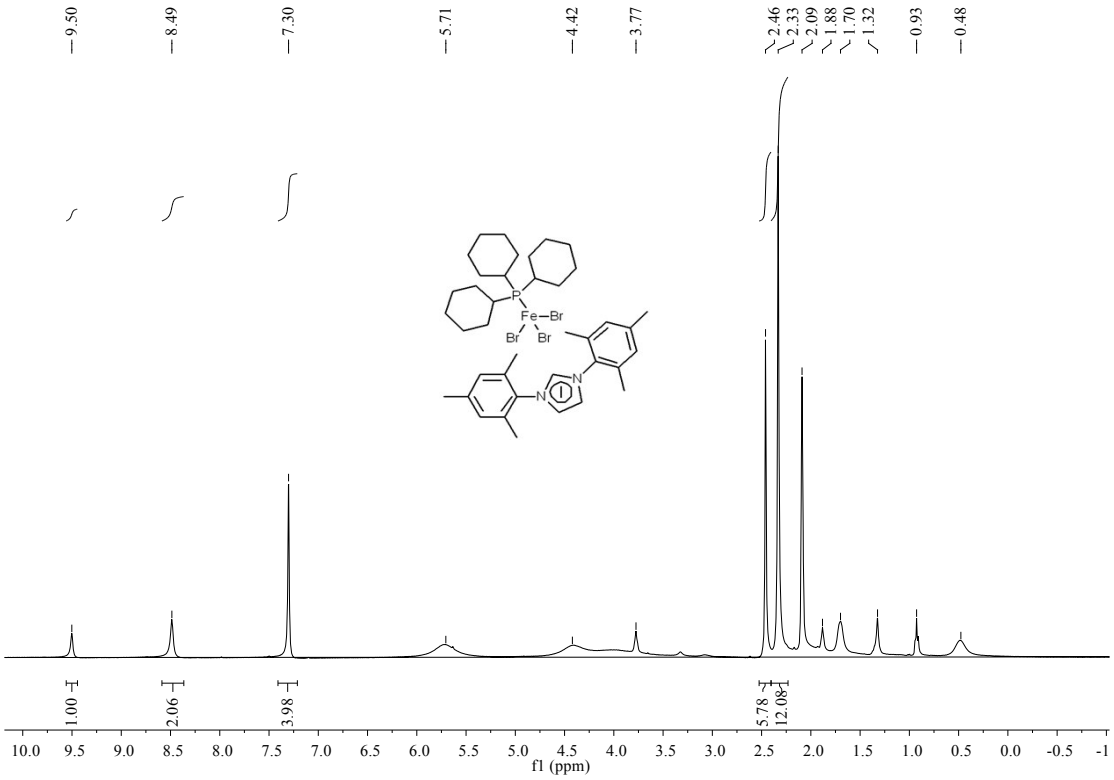

Figure S6. ^{1}H NMR spectrum of **[HIMes][Fe(PCy$_3$)Br$_3$]** (**6**) in $(CD_3)_2CO$.

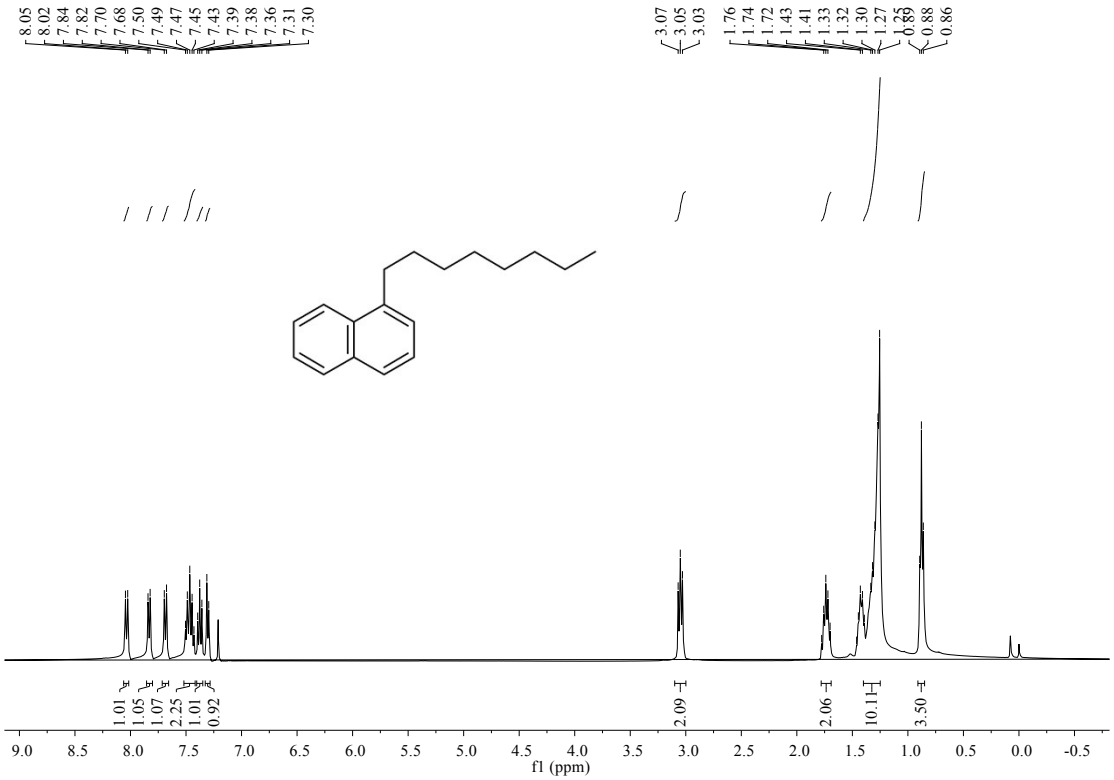

Figure S7. ^{1}H NMR spectrum of **1-octylnaphthalene** (**3ab**) in $CDCl_3$.

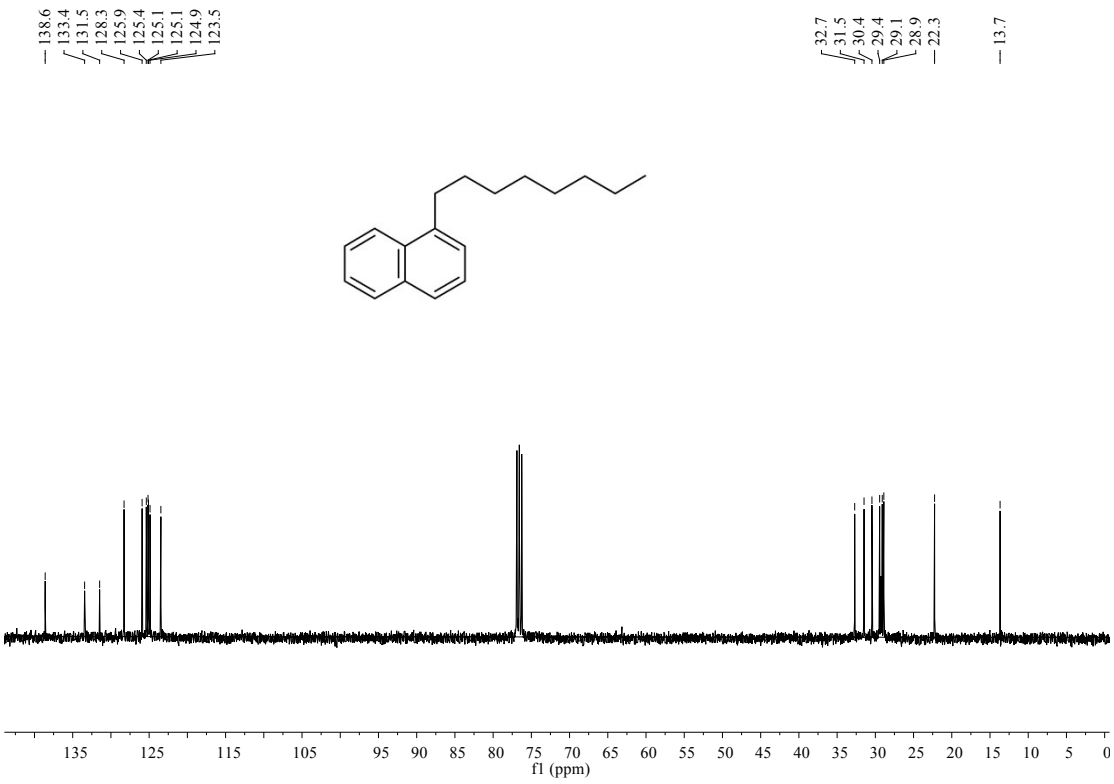

Figure S8. ^{13}C NMR spectrum of **1-octylnaphthalene** (**3ab**) in $CDCl_3$.

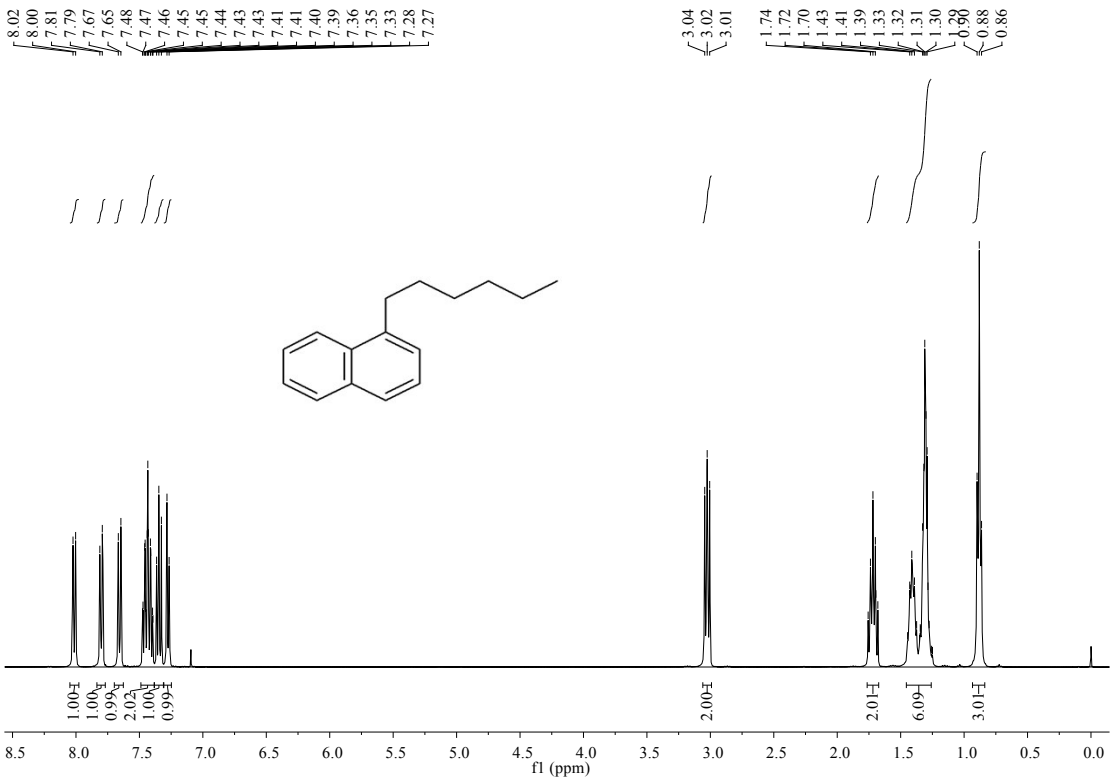

Figure S9. ^{1}H NMR spectrum of **1-hexylnaphthalene** (**3ac**) in $CDCl_3$.

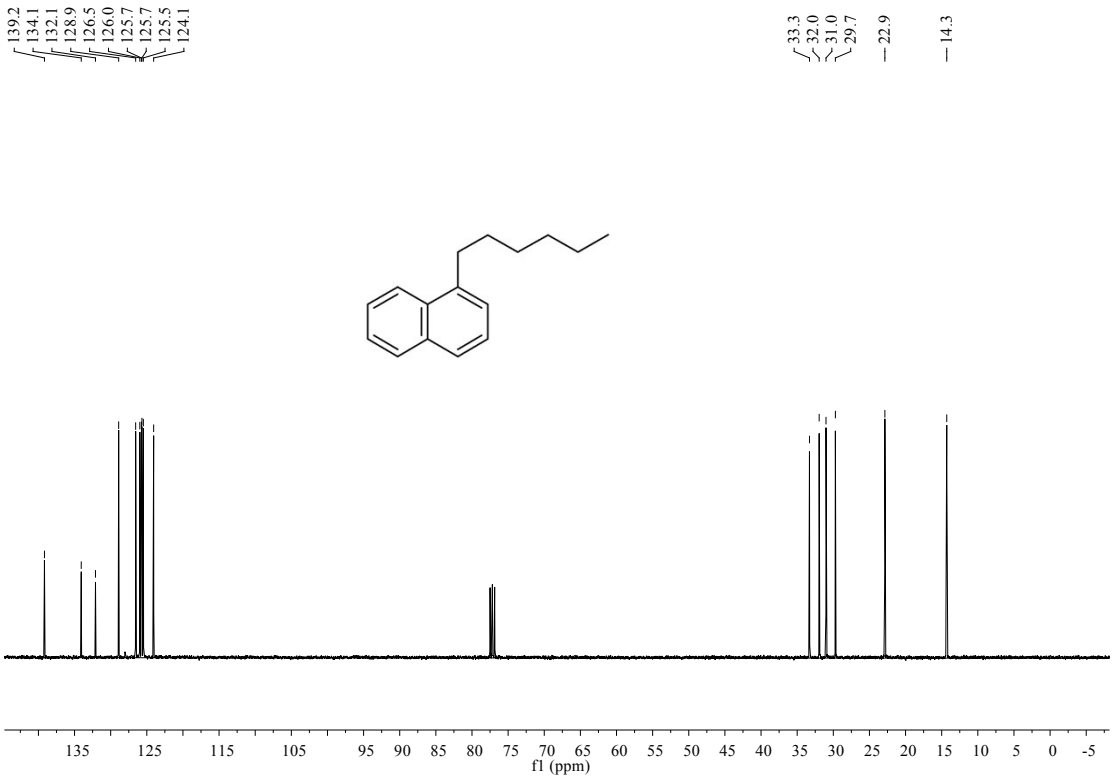

Figure S10. ^{13}C NMR spectrum of **1-hexylnaphthalene** (**3ac**) in $CDCl_3$.

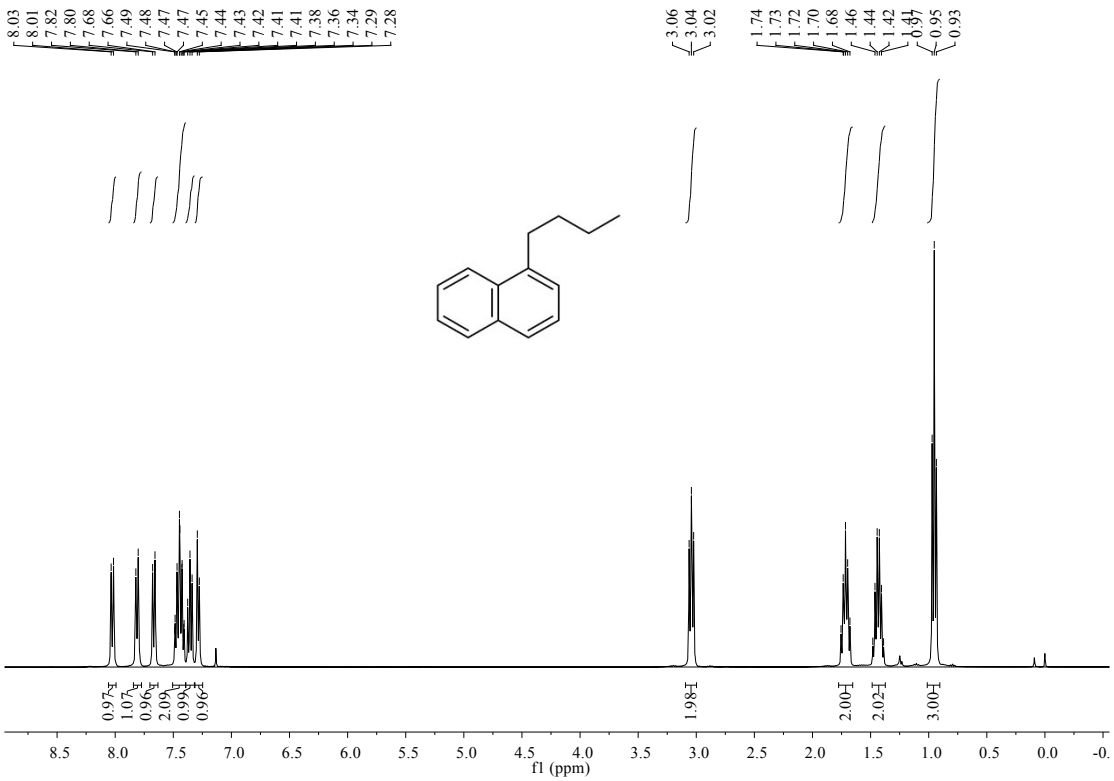

Figure S11. ^{1}H NMR spectrum of **1-butylnaphthalene** (**3aa**) in $CDCl_3$.

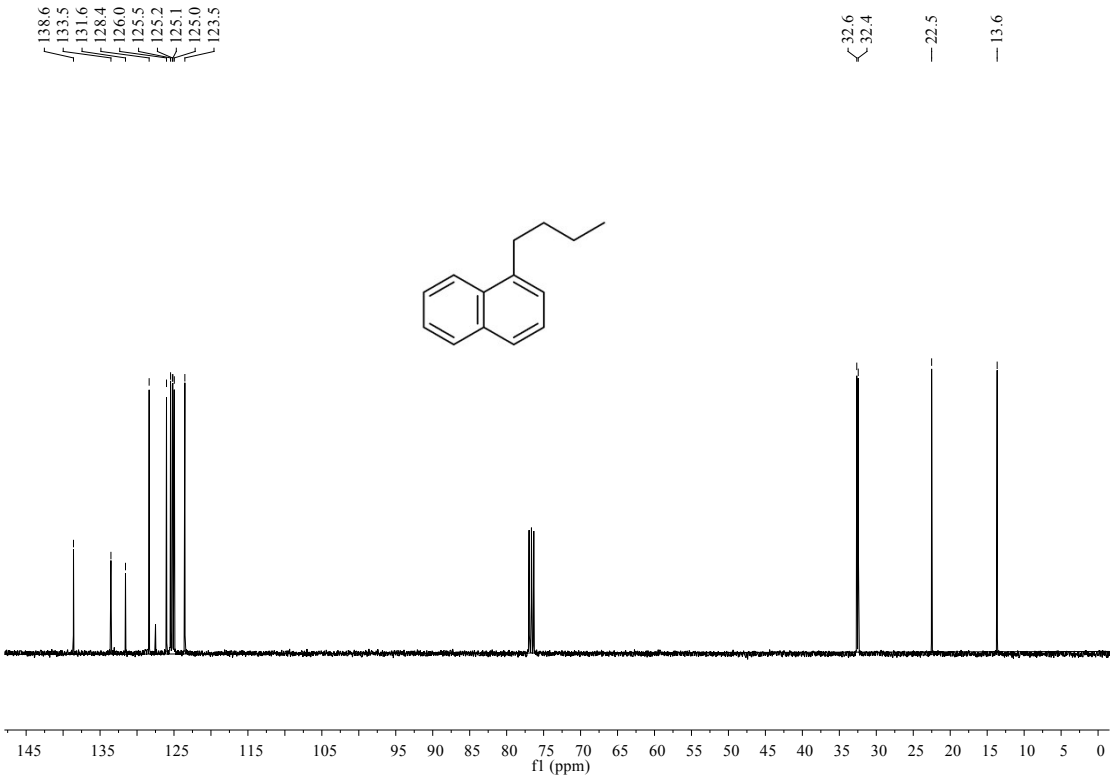

Figure S12. ^{13}C NMR spectrum of **1-butylnaphthalene** (**3aa**) in $CDCl_3$.

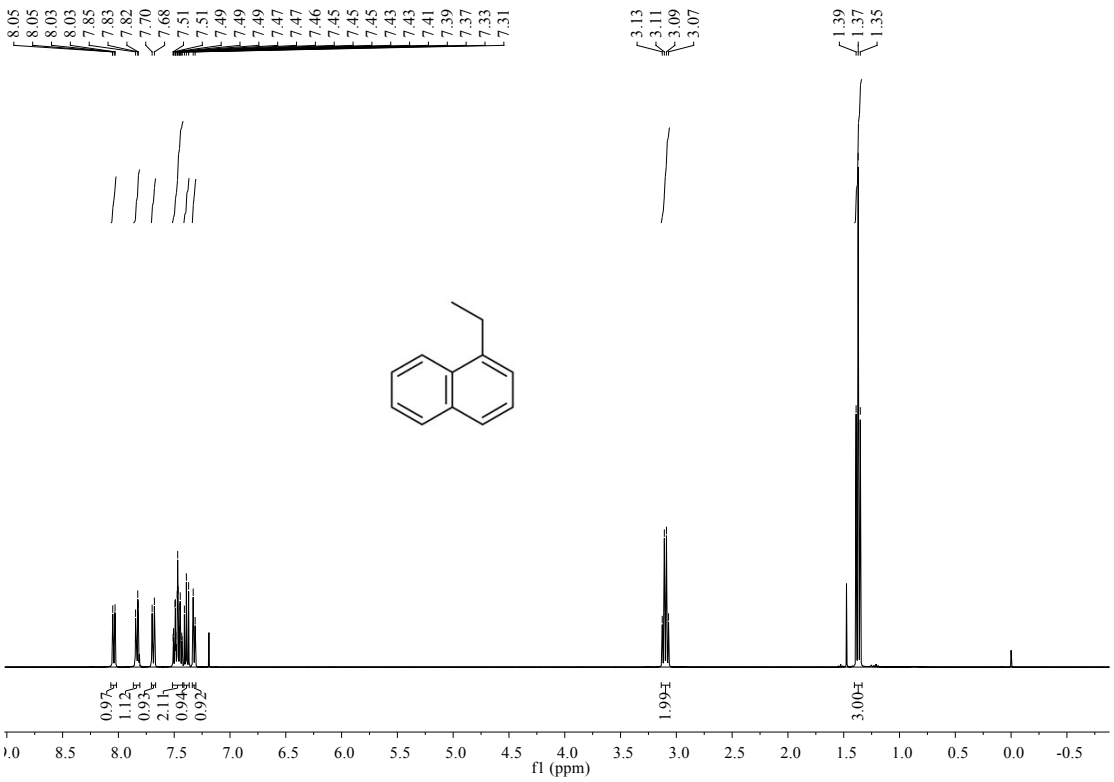

Figure S13. ^{1}H NMR spectrum of **1-ethylnaphthalene** (**3ad**) in $CDCl_3$.

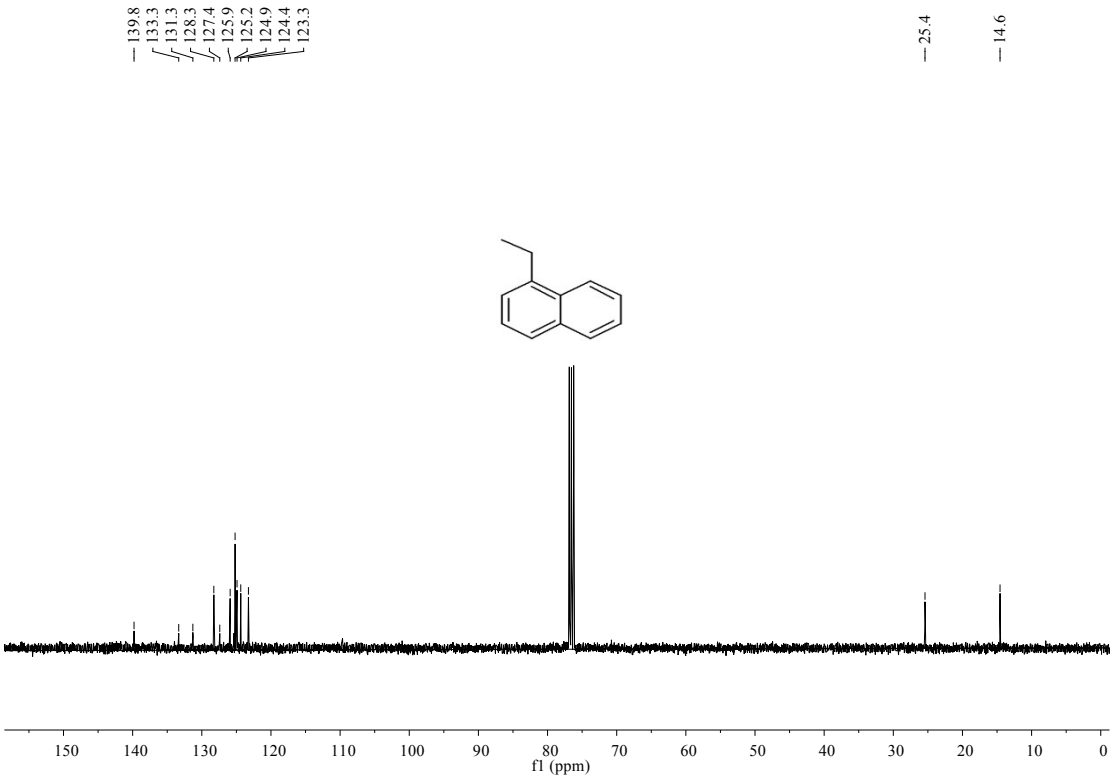

Figure S14. ^{13}C NMR spectrum of **1-ethylnaphthalene** (**3ad**) in $CDCl_3$.

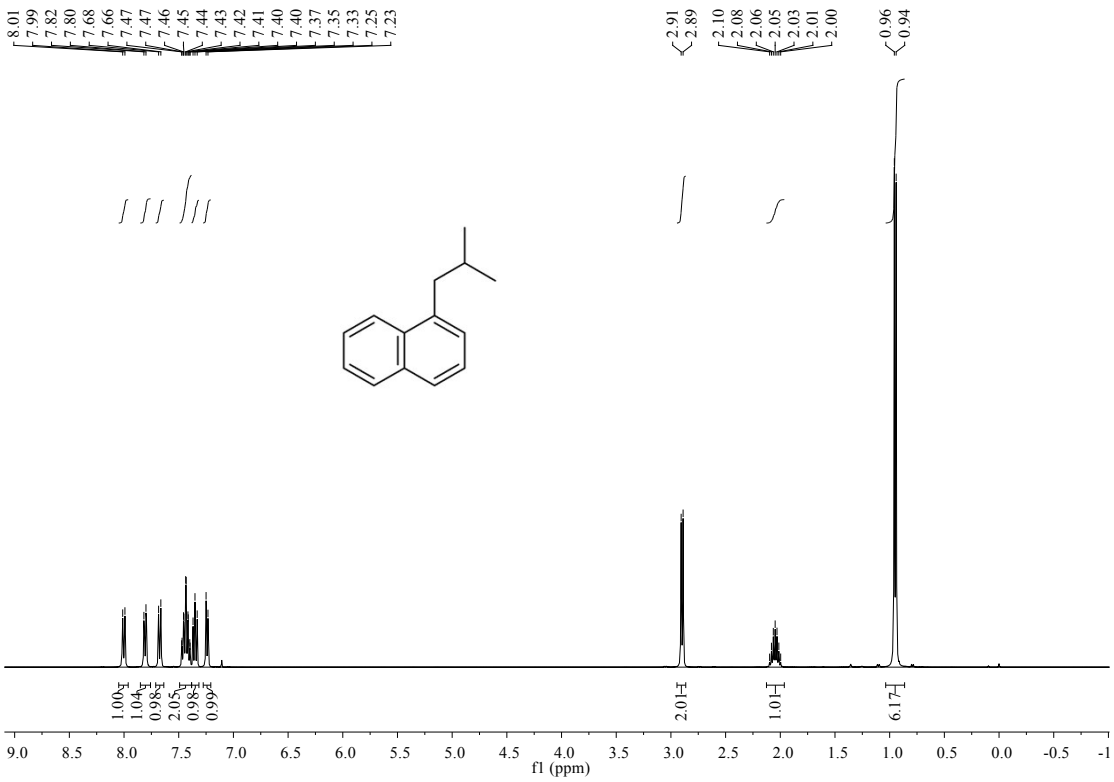

Figure S15. ^{1}H NMR spectrum of **1-isobutylnaphthalene** (**3af**) in $CDCl_3$.

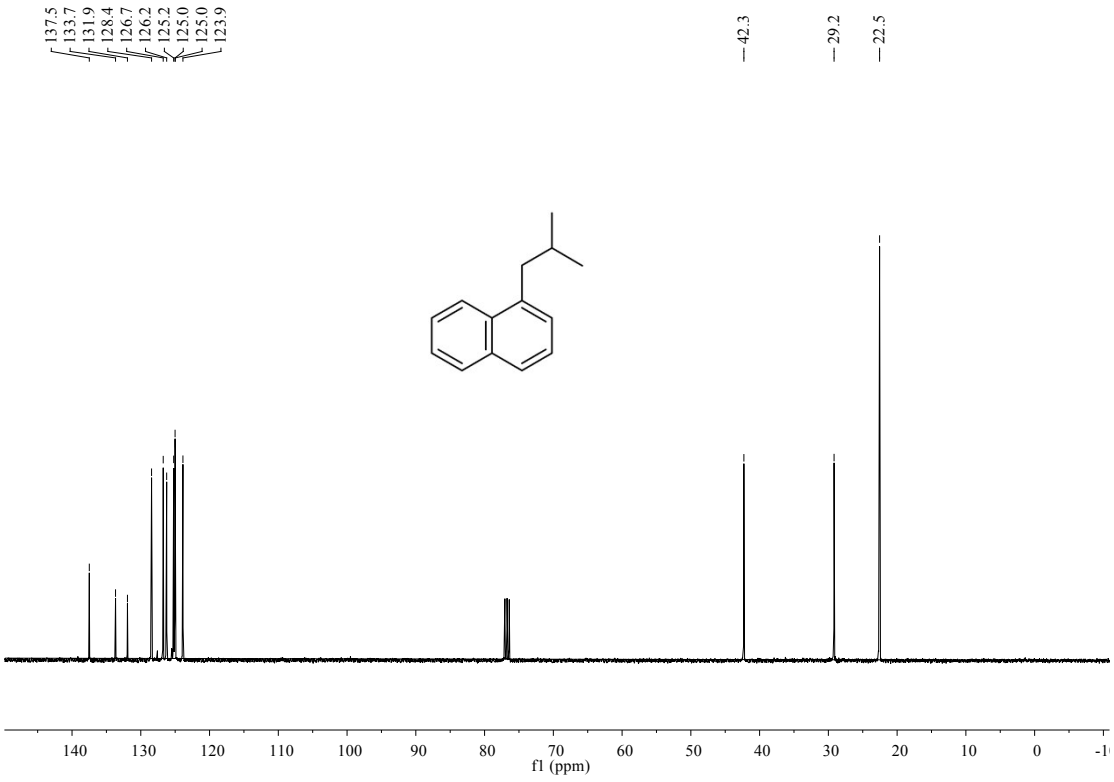

Figure S16. ^{13}C NMR spectrum of **1-isobutylnaphthalene** (**3af**) in $CDCl_3$.

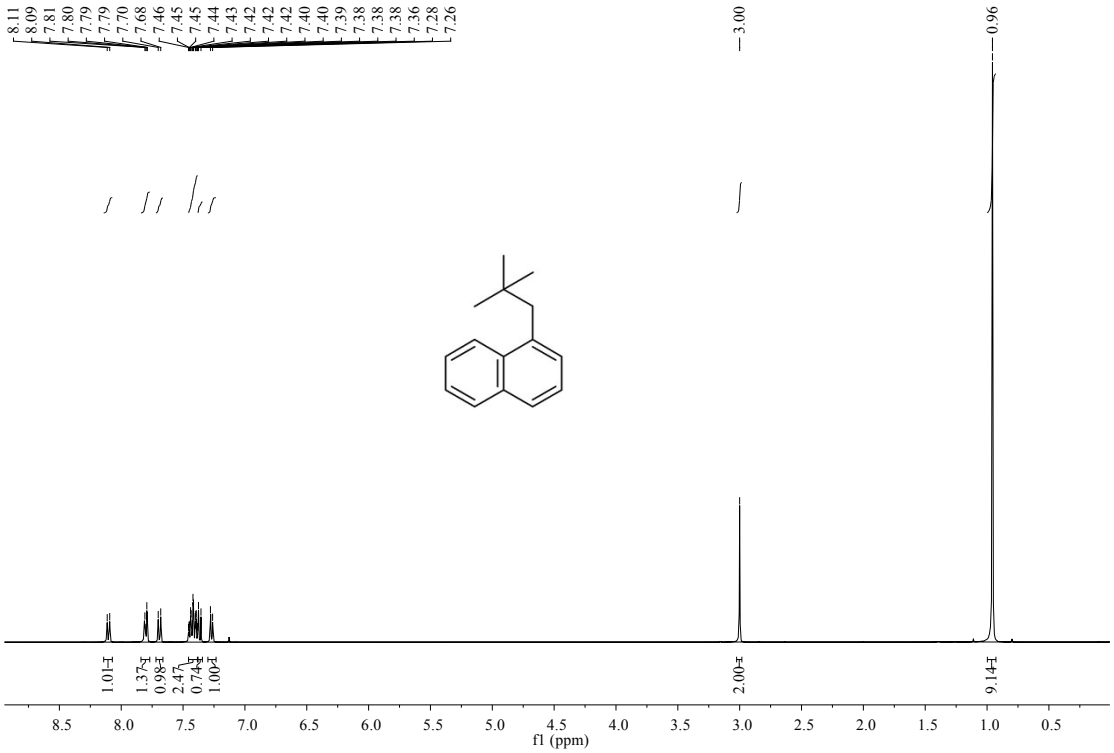

Figure S17. ^{1}H NMR spectrum of **1-neopentylnaphthalene** (**3ag**) in $CDCl_3$.

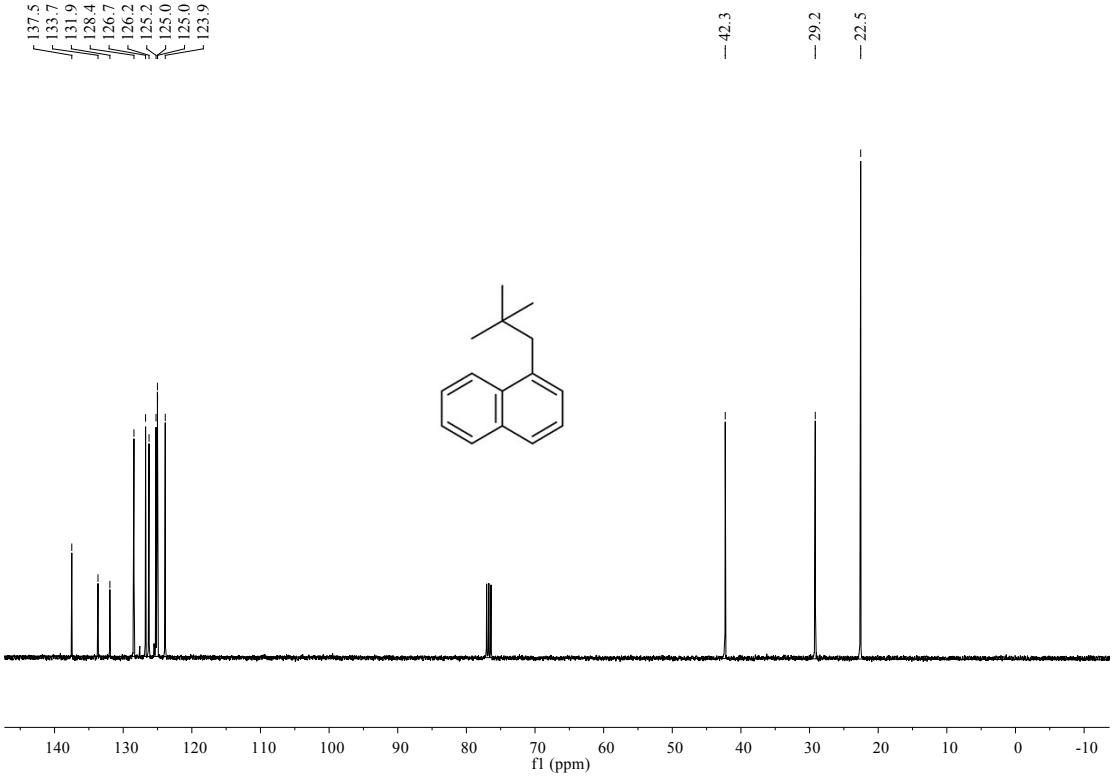

Figure S18. ^{13}C NMR spectrum of **1-neopentylnaphthalene** (**3ag**) in $CDCl_3$.

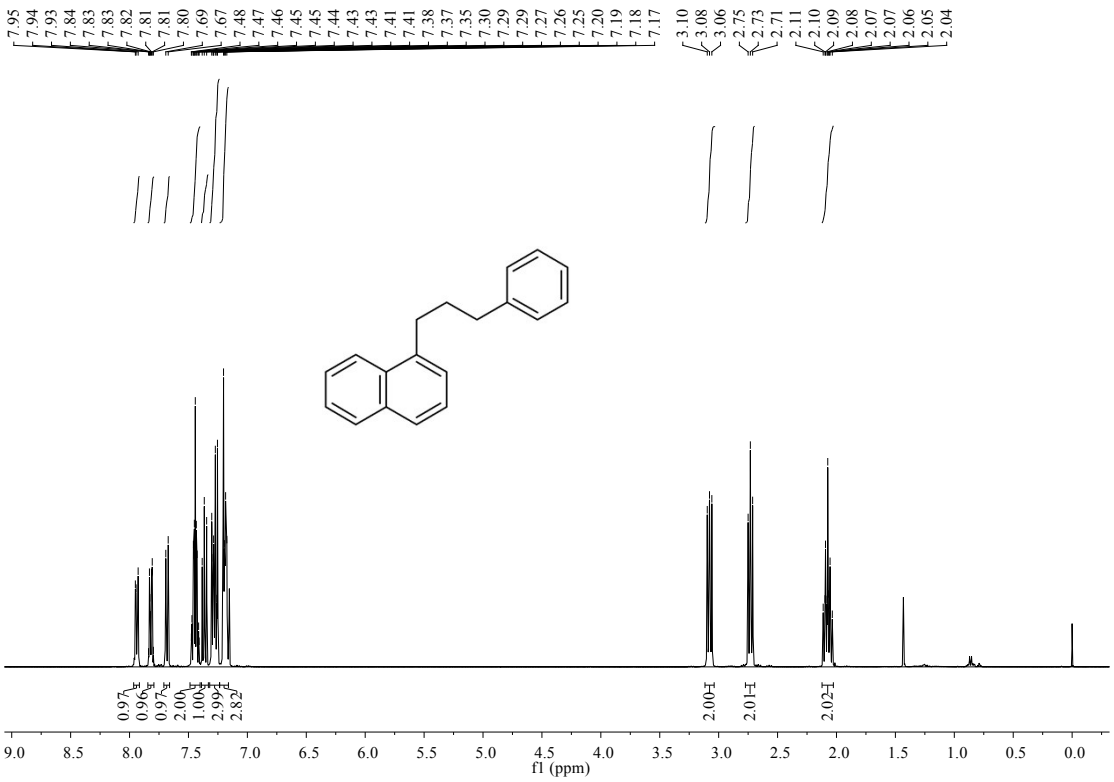

Figure S19. ^{1}H NMR spectrum of **1-neopentylnaphthalene** (**3ah**) in $CDCl_3$.

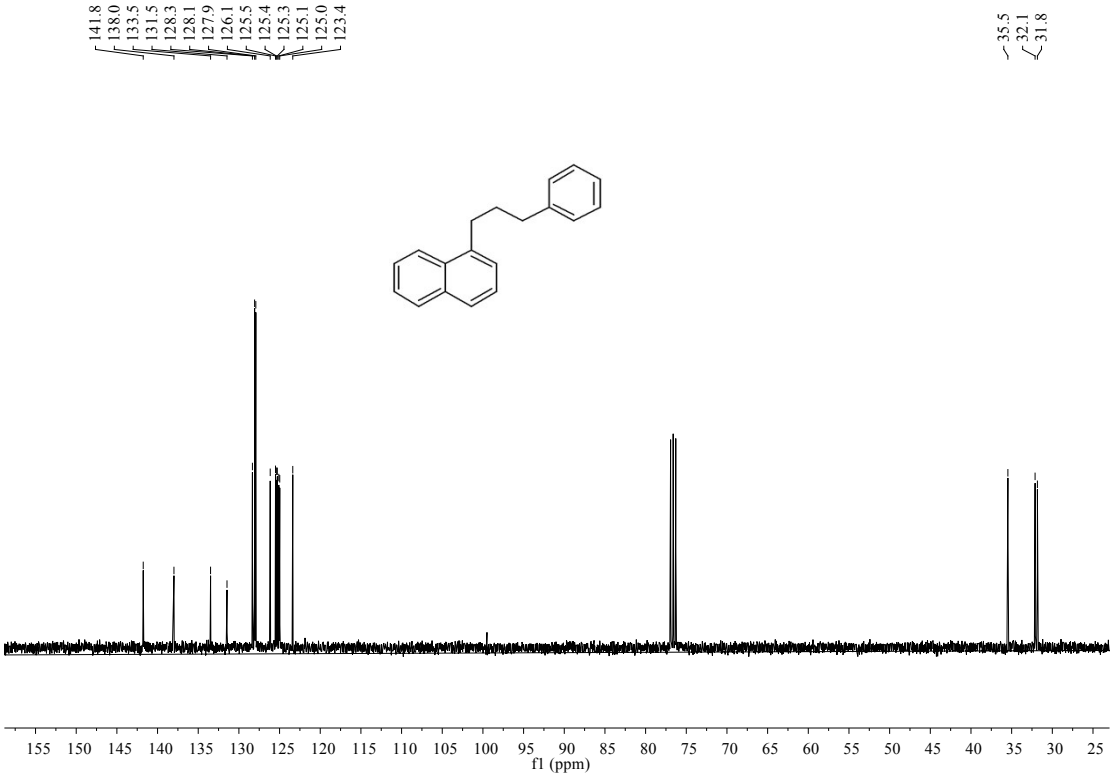

Figure S20. ^{13}C NMR spectrum of **1-neopentylnaphthalene** (**3ah**) in $CDCl_3$.

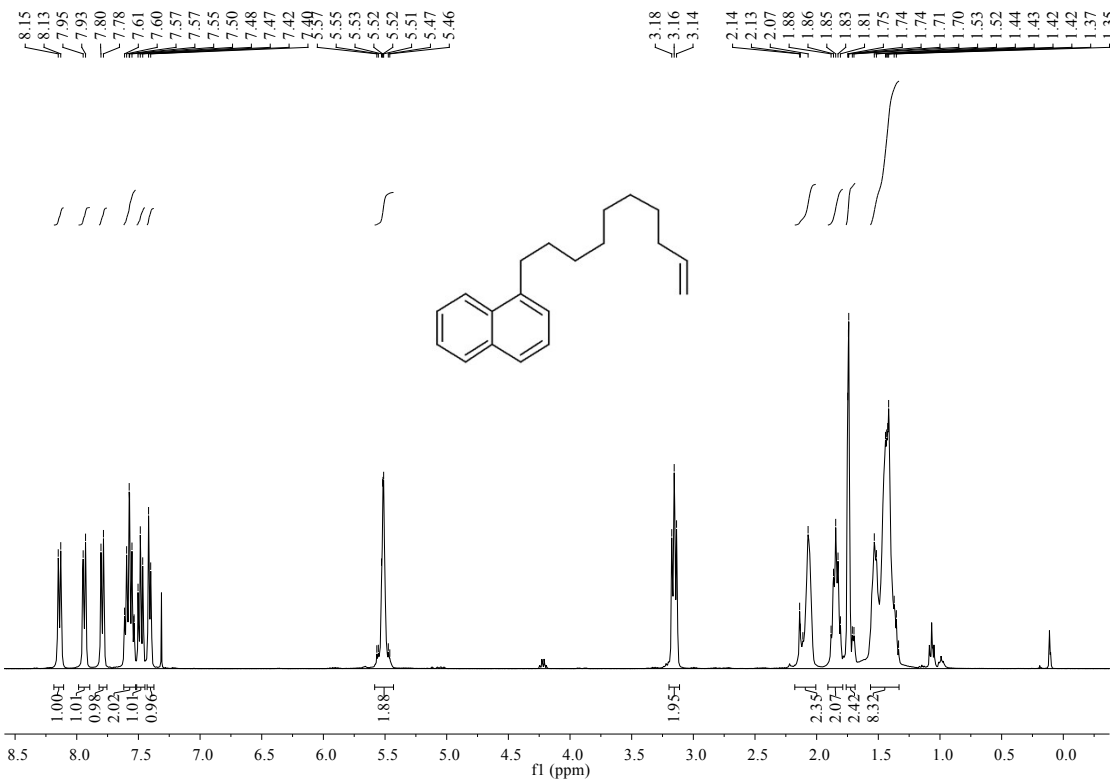

Figure S21. ^{1}H NMR spectrum of **1-(dec-9-en-1-yl)naphthalene** (**3ai**) in $CDCl_3$.

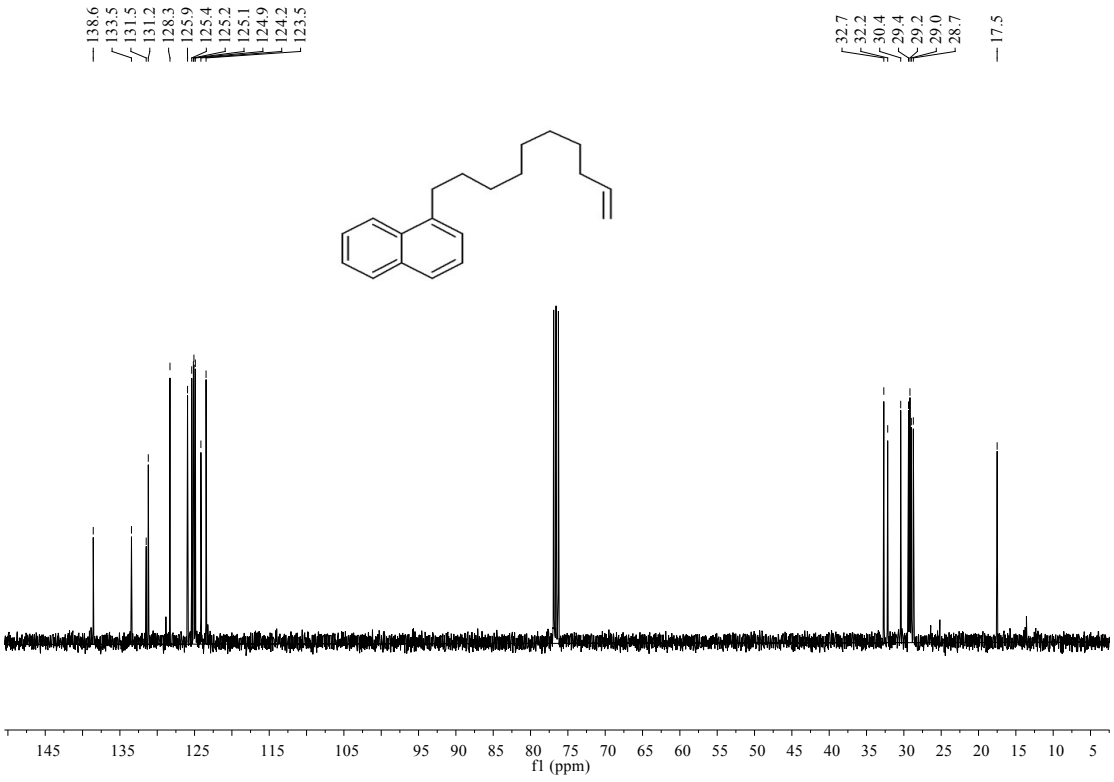

Figure S22. ^{13}C NMR spectrum of **1-(dec-9-en-1-yl)naphthalene** (**3ai**) in $CDCl_3$.

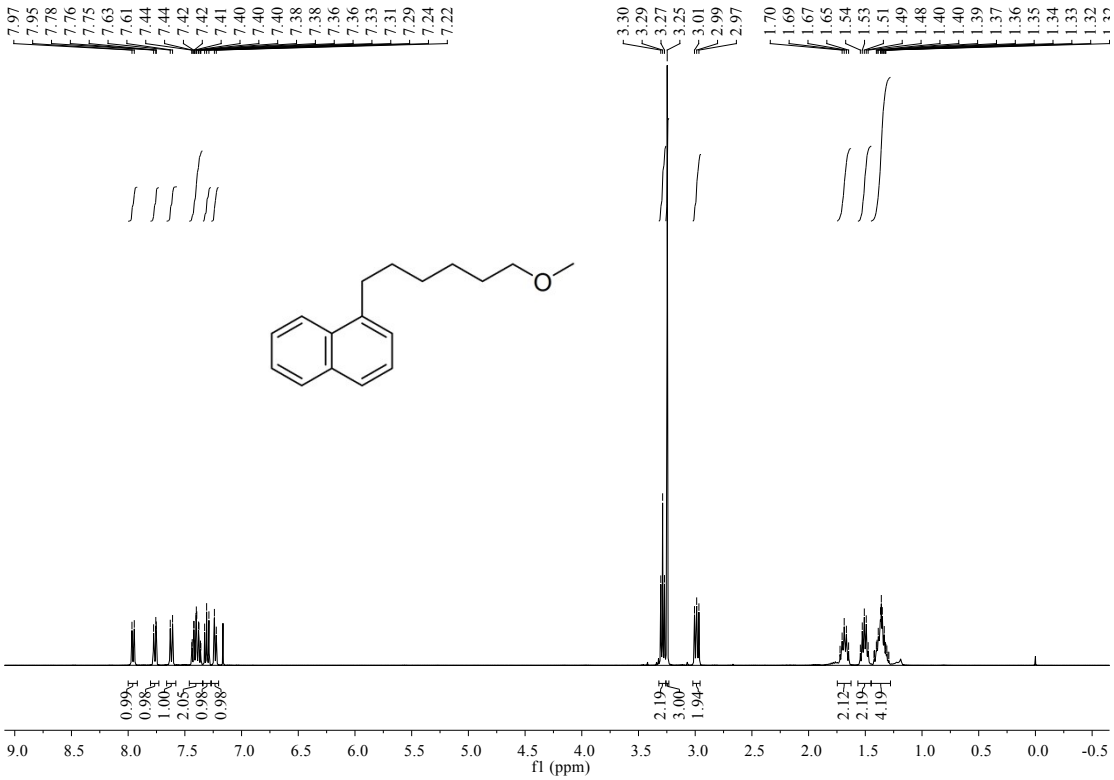

Figure S23. ^{1}H NMR spectrum of **1-(6-methoxyhexyl)naphthalene** (**3aj**) in $CDCl_3$.

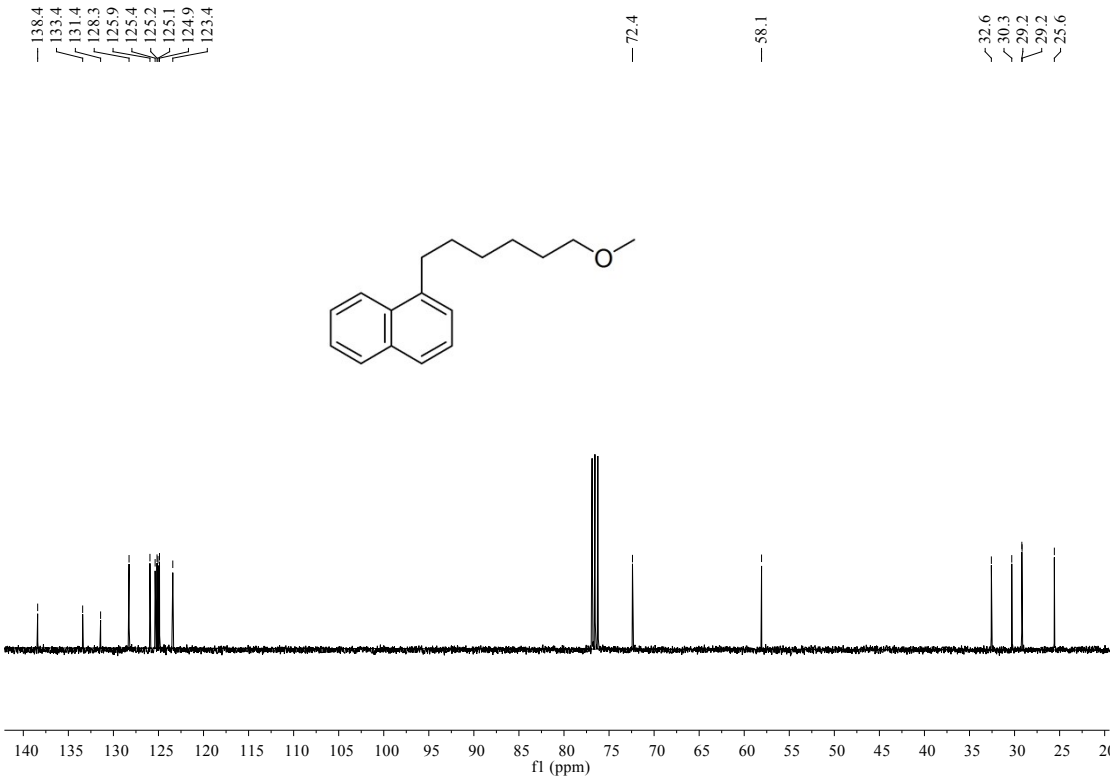

Figure S24. ^{13}C NMR spectrum of **1-(6-methoxyhexyl)naphthalene** (**3aj**) in $CDCl_3$.

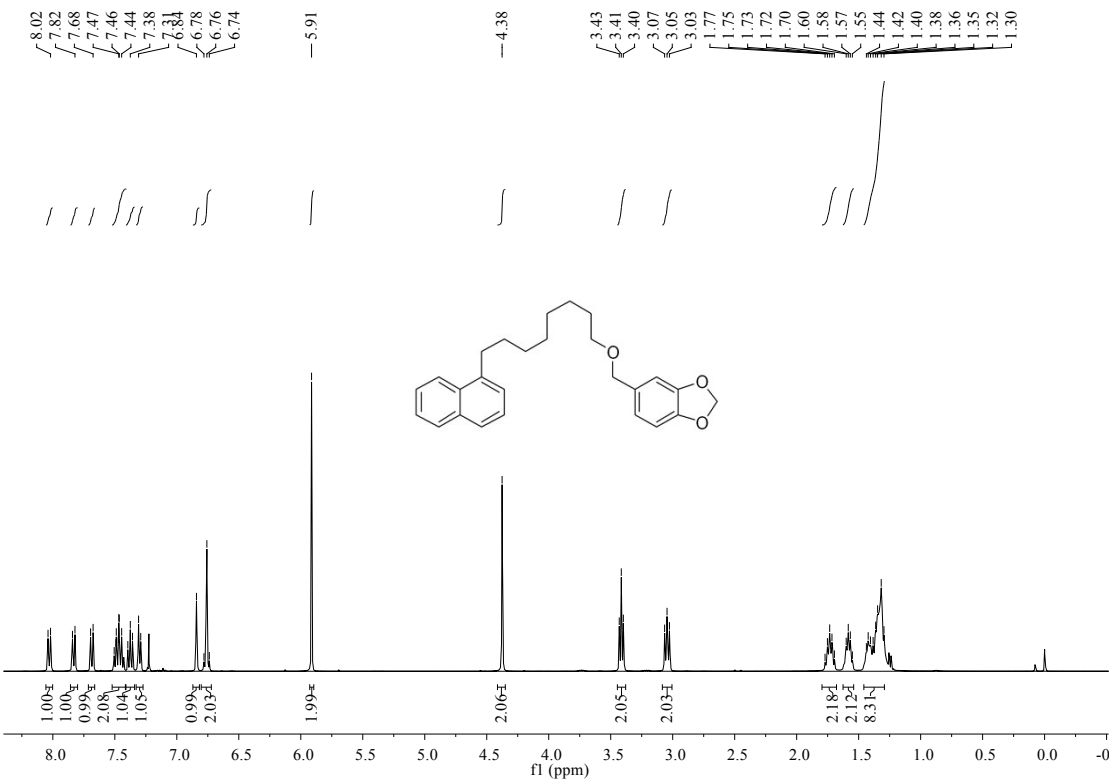

Figure S25. ^{1}H NMR spectrum of **5-(((8-(naphthalen-1-yl)octyl)oxy)methyl)benzo[d][1,3]dioxole** (**3ak**) in $CDCl_3$.

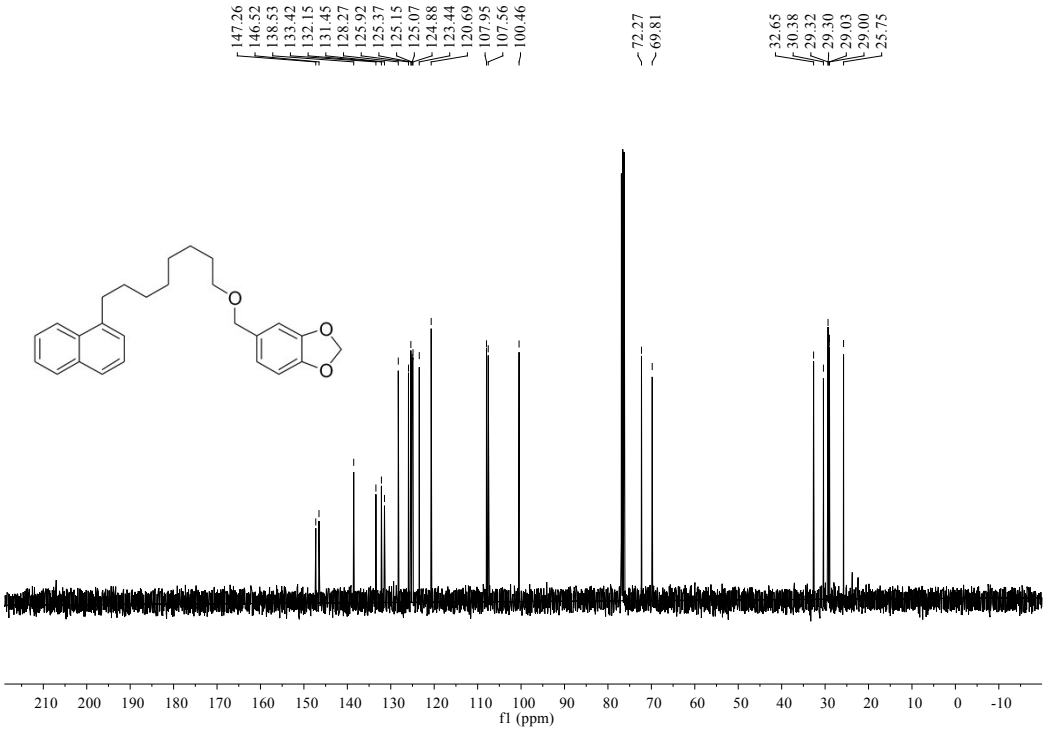

Figure S26. ^{13}C NMR spectrum of **5-(((8-(naphthalen-1-yl)octyl)oxy)methyl)benzo[d][1,3]dioxole** (**3ak**) in $CDCl_3$.

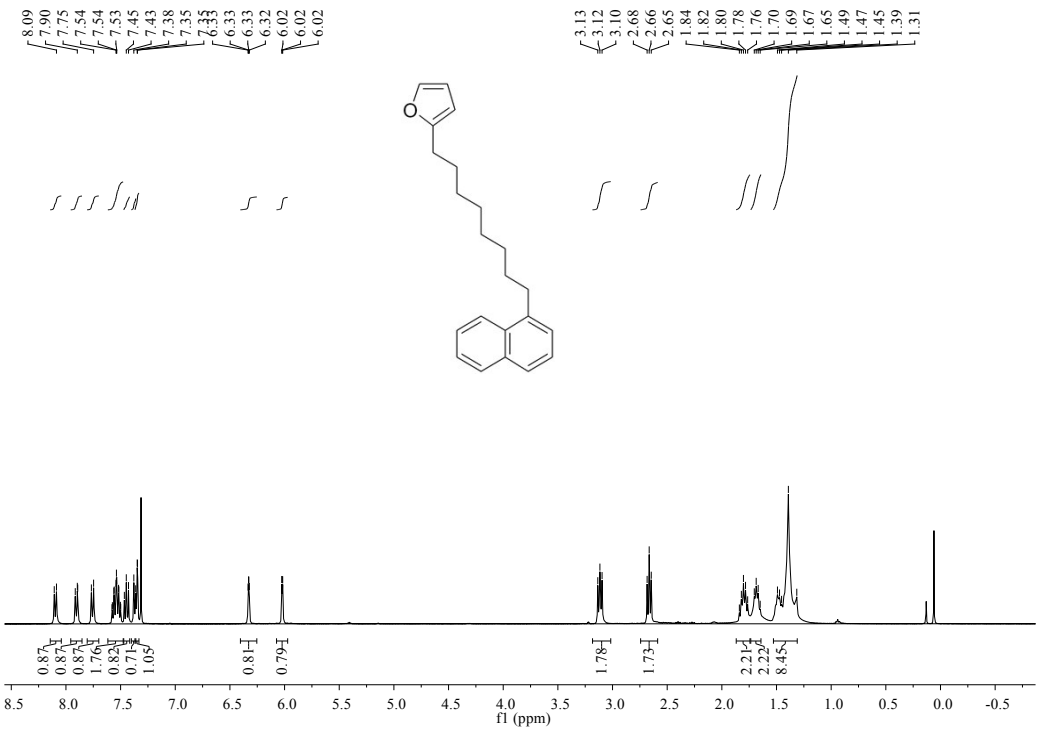

Figure S27. ^{1}H NMR spectrum of **2-(8-(naphthalen-1-yl)octyl)furan** (**3al**) in $CDCl_3$.

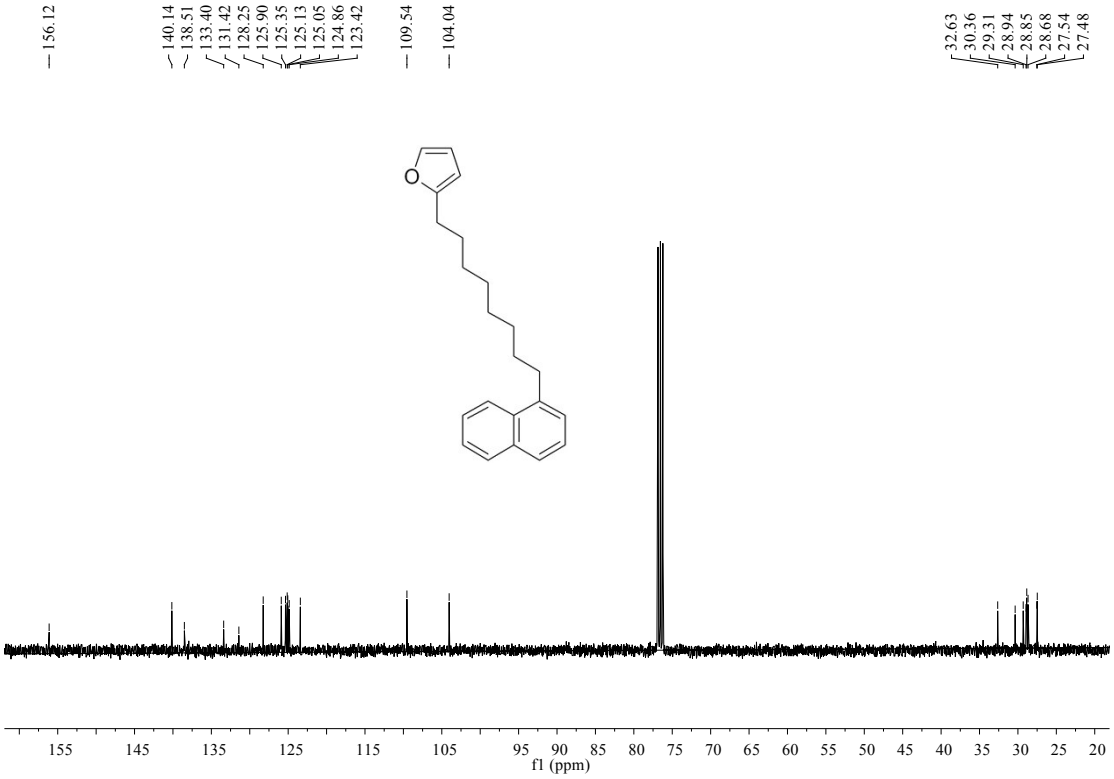

Figure S28. ^{13}C NMR spectrum of **2-(8-(naphthalen-1-yl)octyl)furan** (**3al**) in $CDCl_3$.

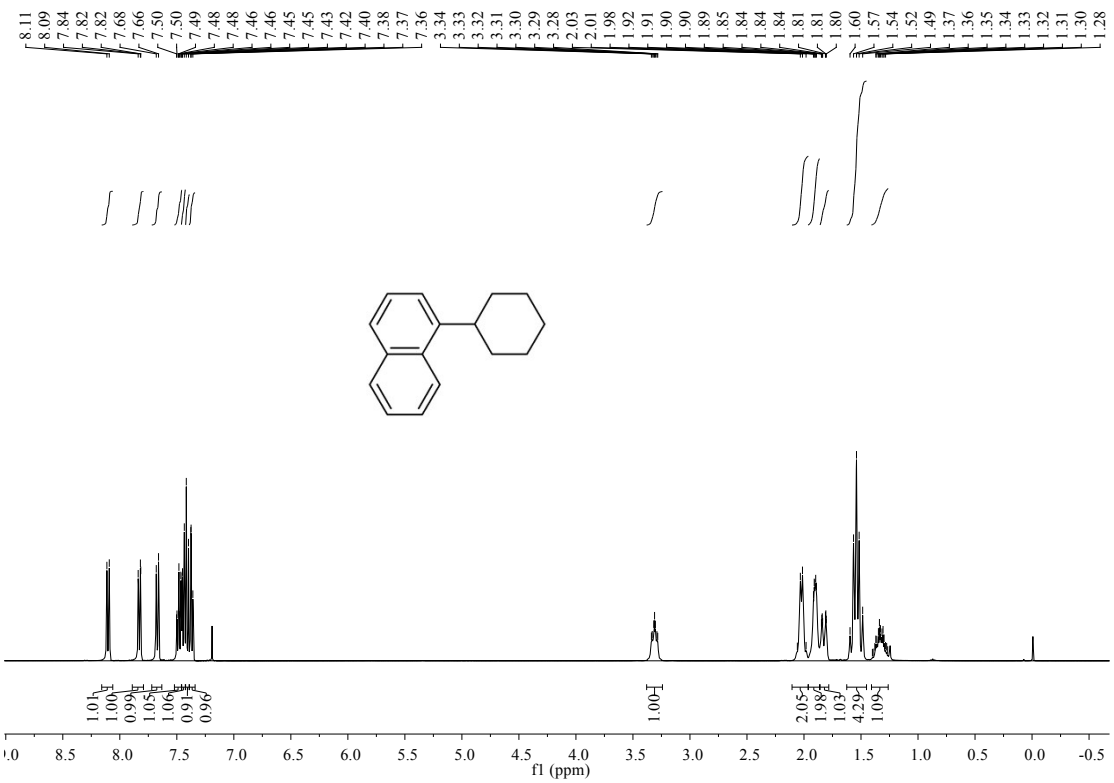

Figure S29. ^{1}H NMR spectrum of **1-cyclohexylnaphthalene** (**3am**) in $CDCl_3$.

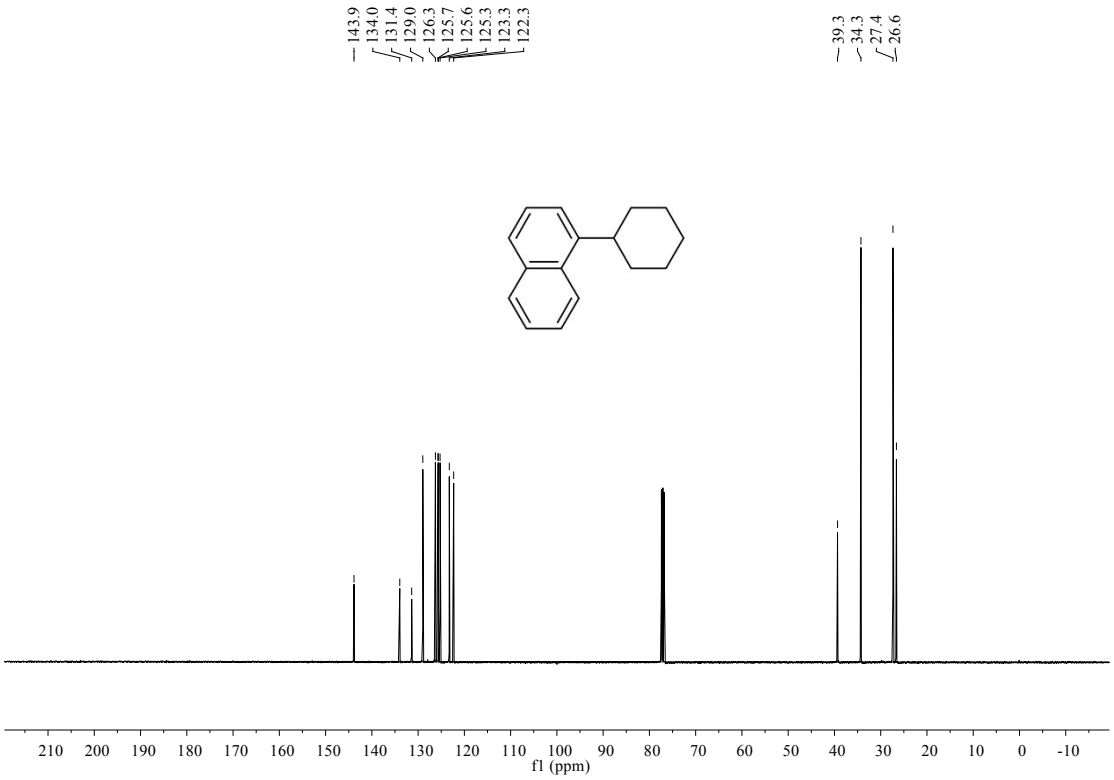

Figure S30. ^{13}C NMR spectrum of **1-cyclohexylnaphthalene** (**3am**) in $CDCl_3$.

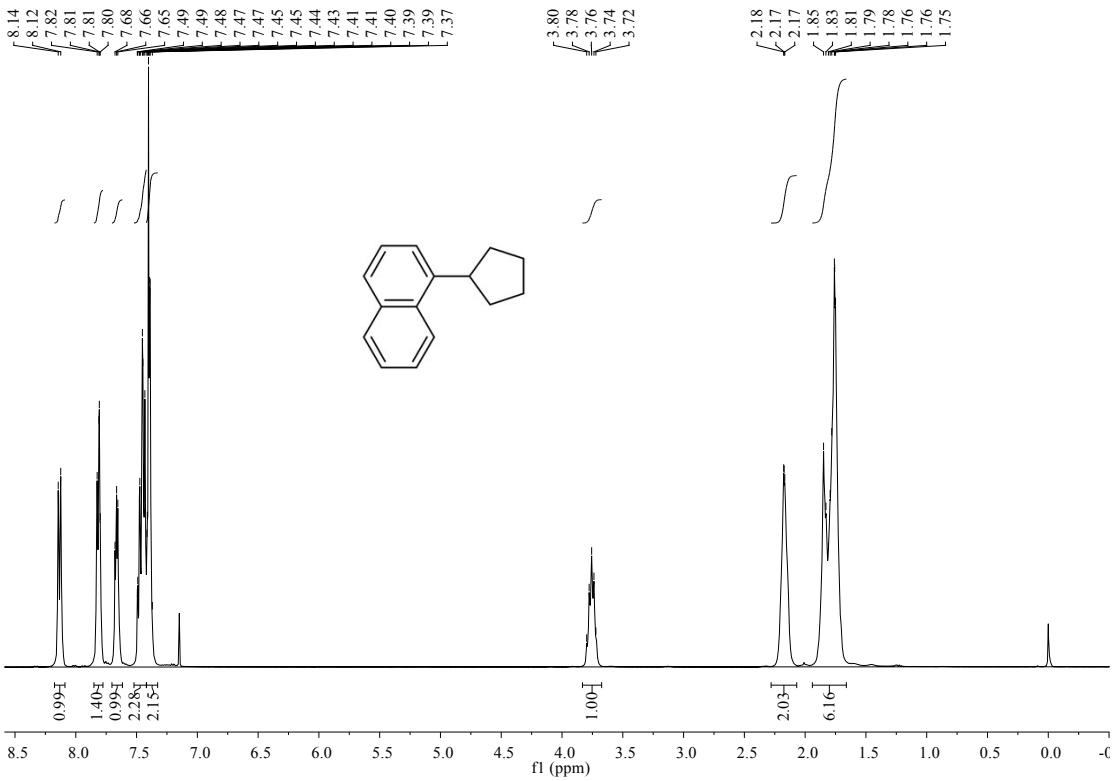

Figure S31. ^{1}H NMR spectrum of **1-cyclopentylnaphthalene** (**3an**) in $CDCl_3$.

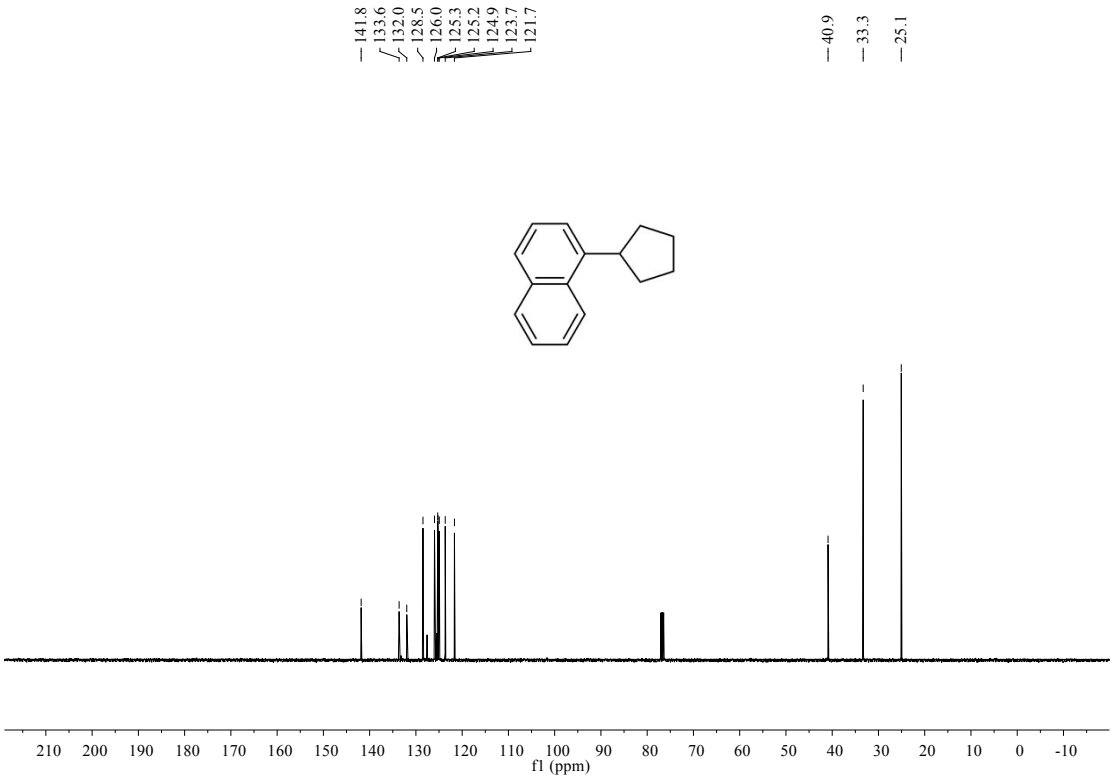

Figure S32. ^{13}C NMR spectrum of **1-cyclopentylnaphthalene** (**3an**) in $CDCl_3$.

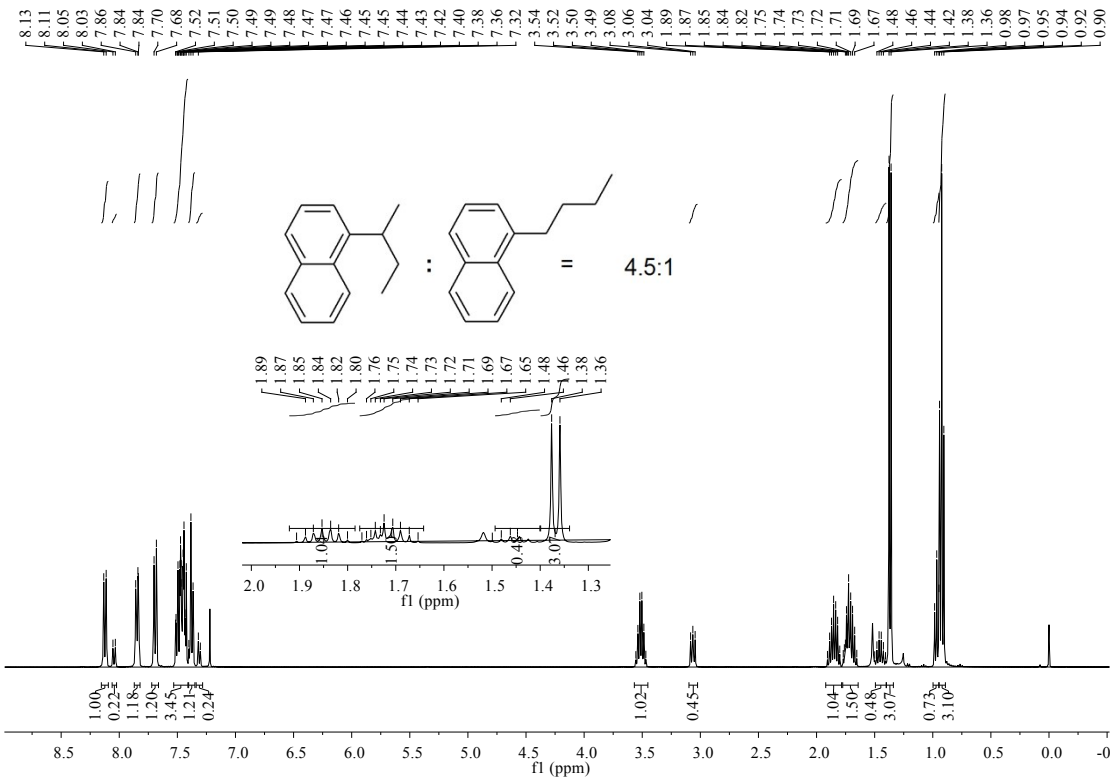

Figure S33. ^{1}H NMR spectrum of **1-*sec*-butylnaphthalene** (**3ao**) in $CDCl_3$.

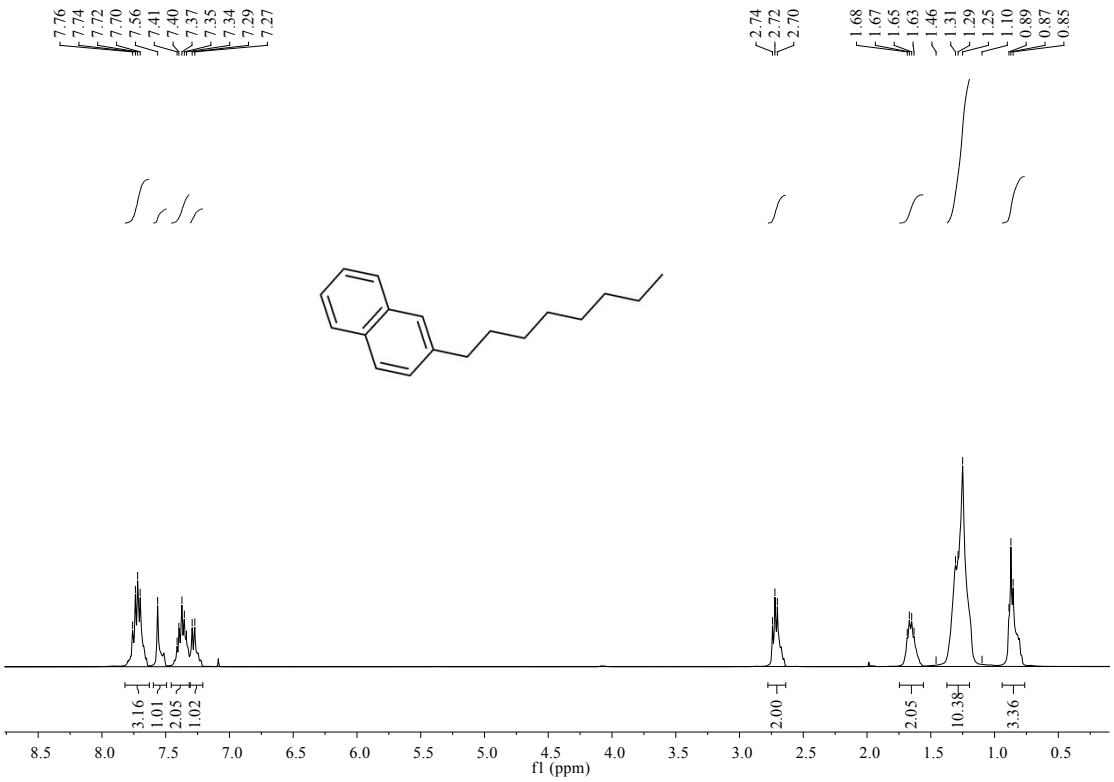

Figure S34. ^{1}H NMR spectrum of **2-octylnaphthalene** (**3bb**) in $CDCl_3$.

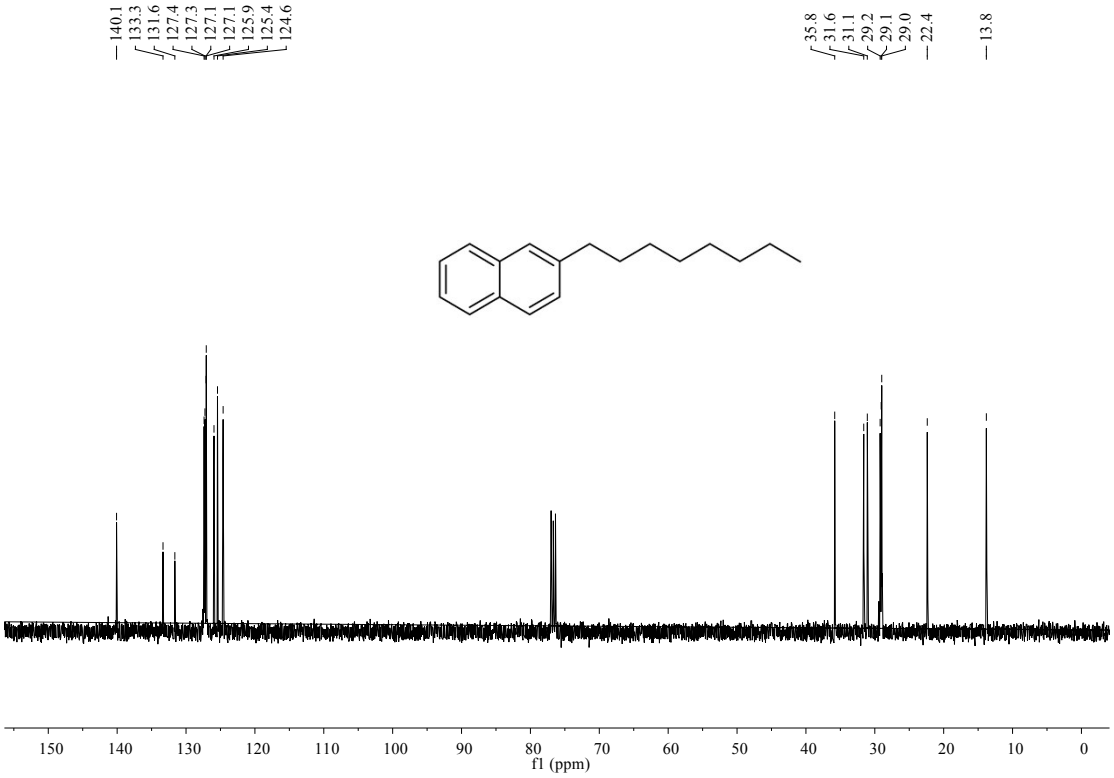

Figure S35. ^{13}C NMR spectrum of **2-octylnaphthalene** (**3bb**) in $CDCl_3$.

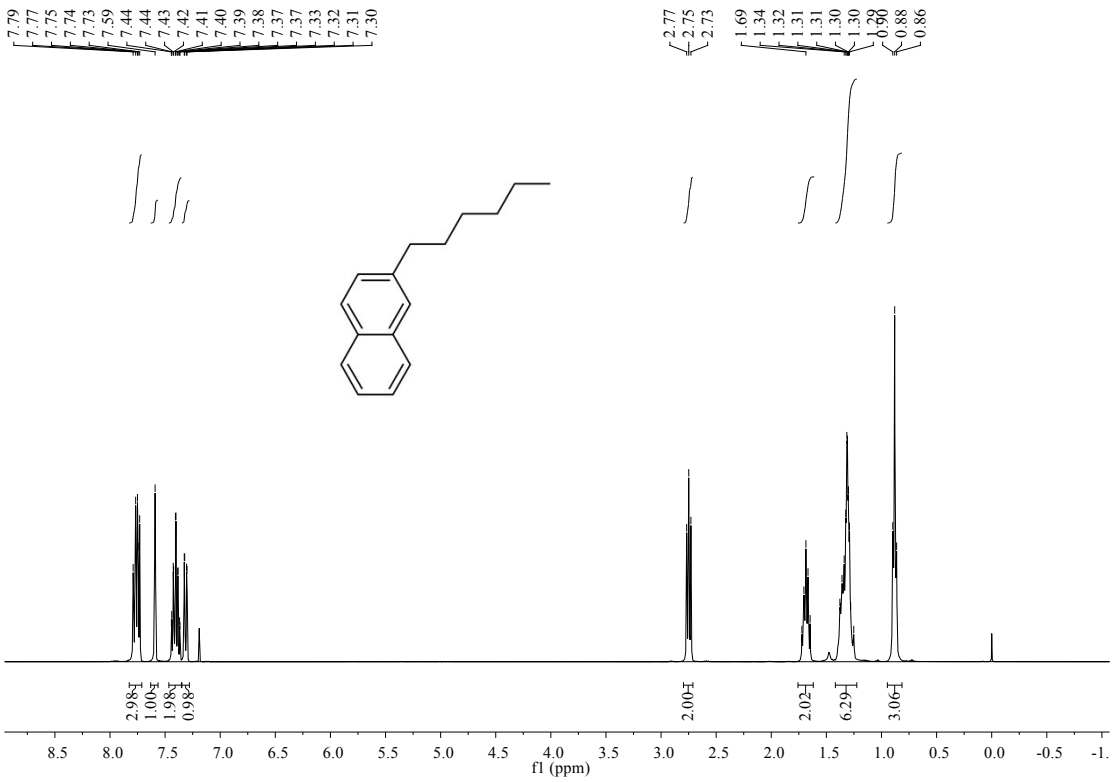

Figure S36. ^{1}H NMR spectrum of **2-hexylnaphthalene** (**3bc**) in $CDCl_3$.

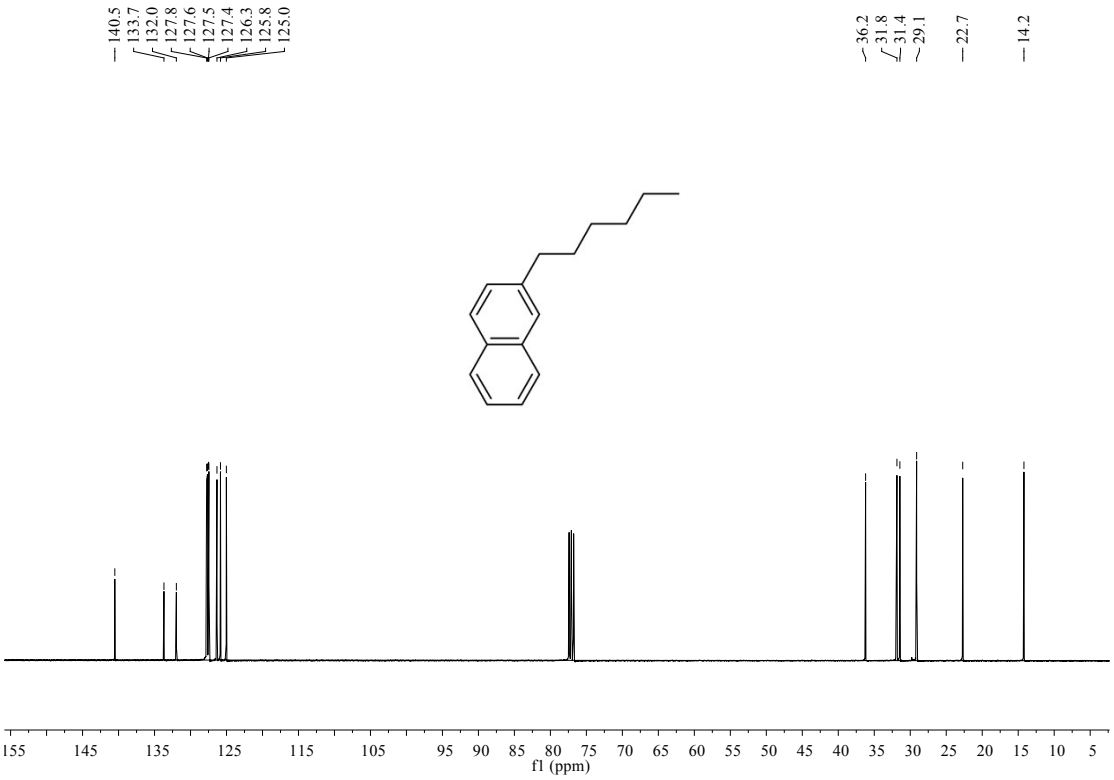

Figure S37. ^{13}C NMR spectrum of **2-hexylnaphthalene** (**3bc**) in $CDCl_3$.

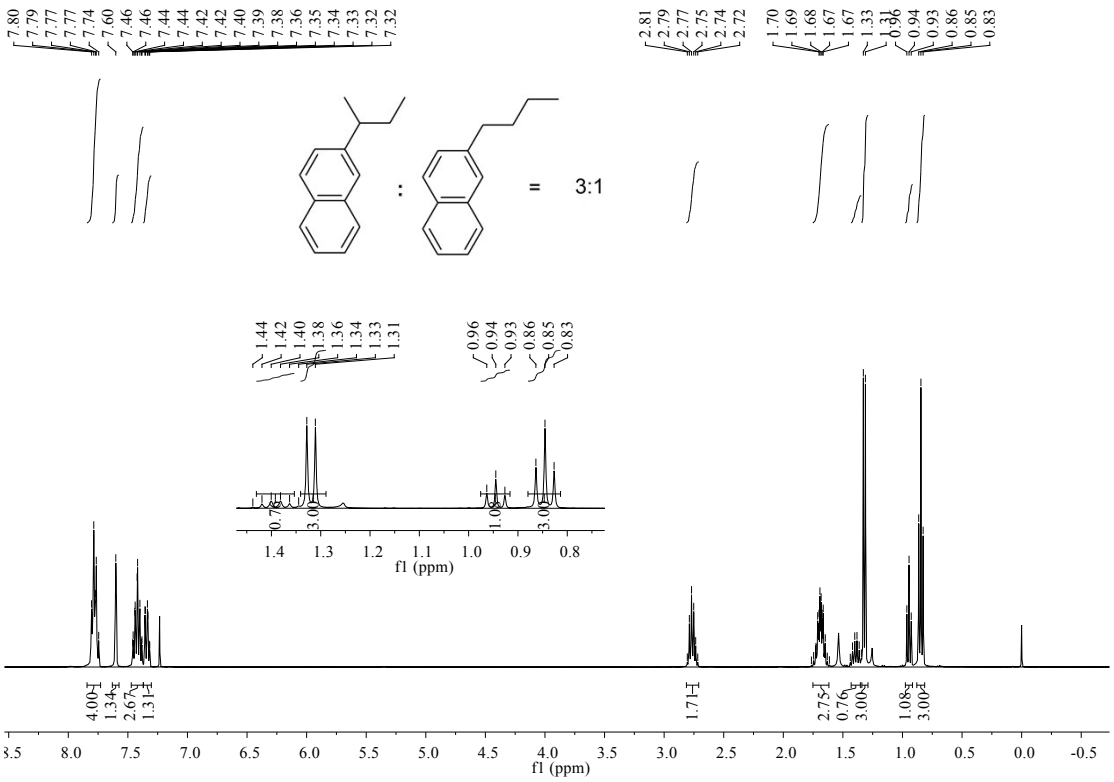

Figure S38. ^{1}H NMR spectrum of **2-*sec*-butylnaphthalene** (**3bo**) in $CDCl_3$.

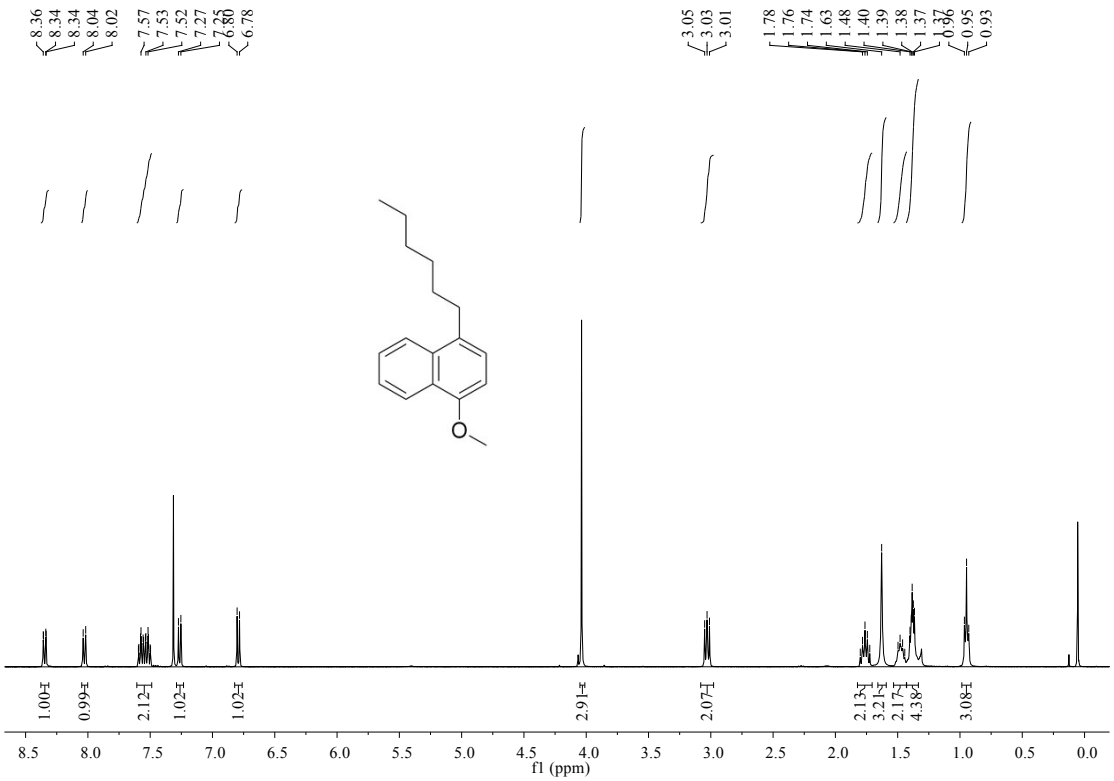

Figure S39. ^{1}H NMR spectrum of **1-hexyl-4-methoxynaphthalene** (**3cc**) in $CDCl_3$.

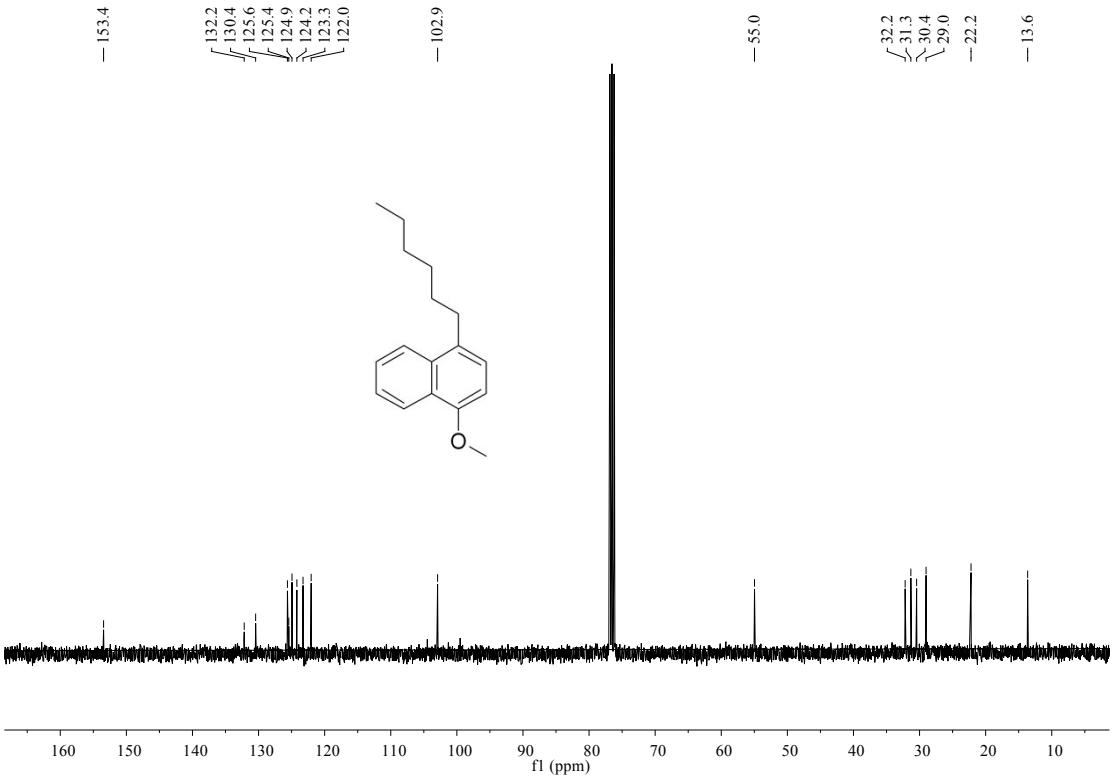

Figure S40. ^{13}C NMR spectrum of **1-hexyl-4-methoxynaphthalene** (**3cc**) in $CDCl_3$.

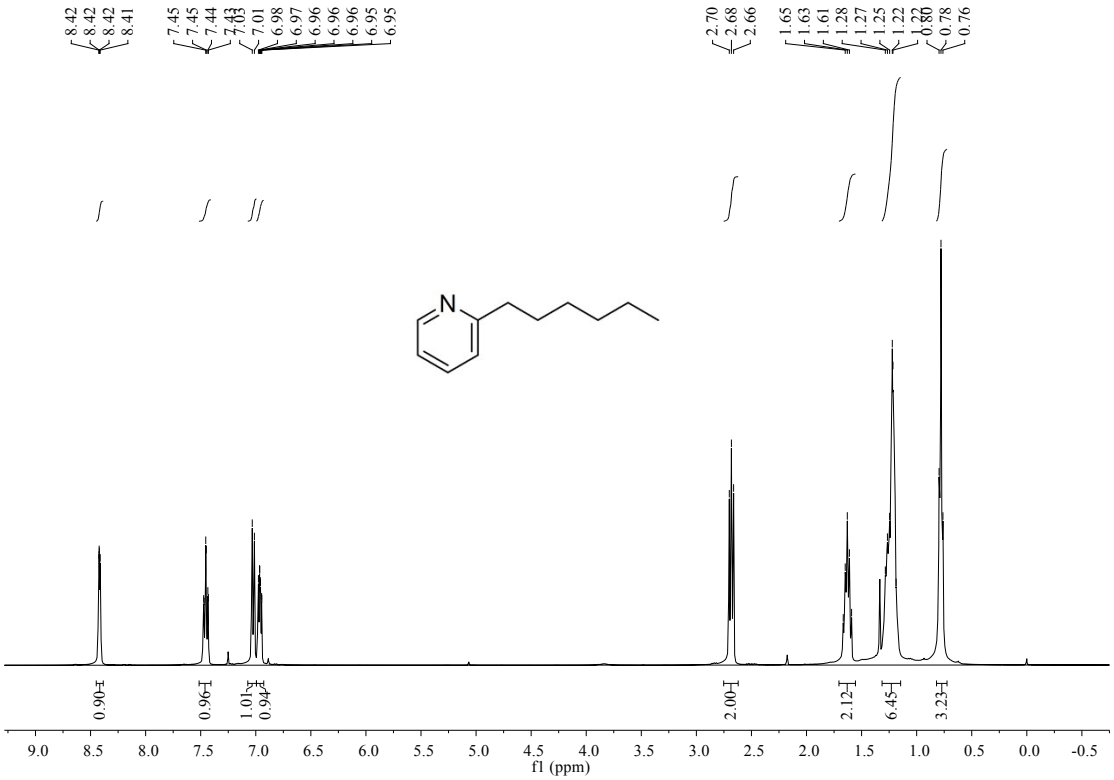

Figure S41. ^{1}H NMR spectrum of **2-hexylpyridine** (**3dc**) in $CDCl_3$.

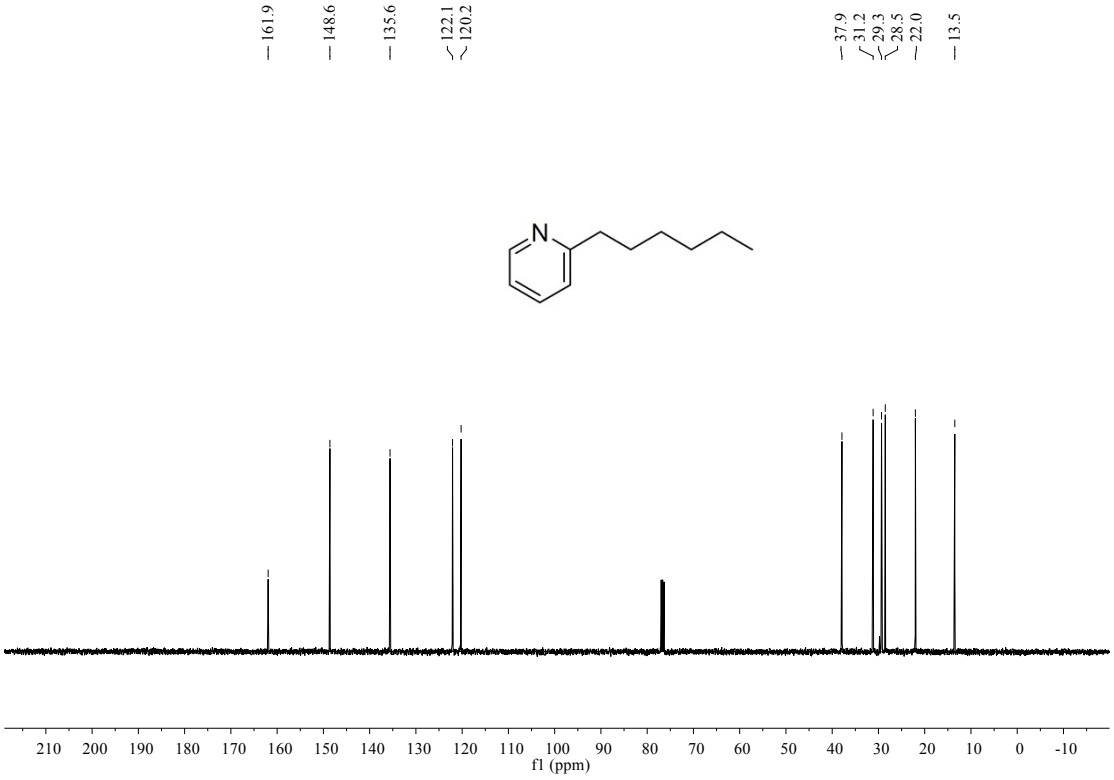

Figure S42. ^{13}C NMR spectrum of **2-hexylpyridine** (**3dc**) in $CDCl_3$.

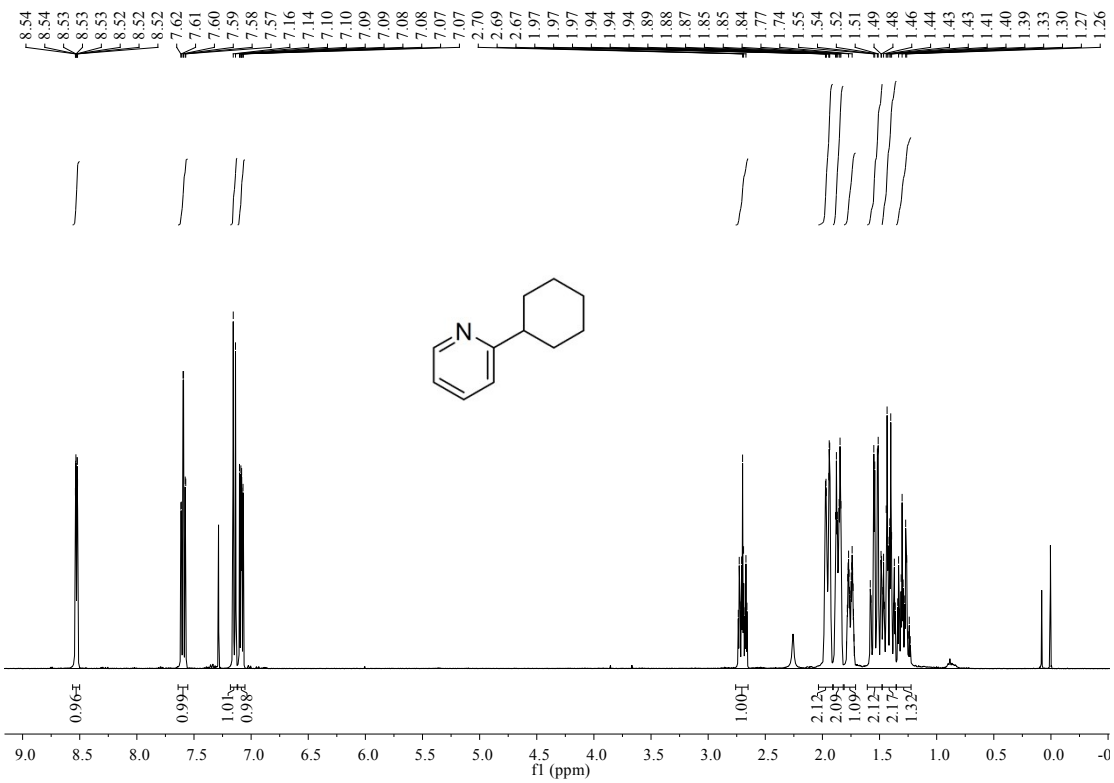

Figure S43. ^{1}H NMR spectrum of **2-cyclohexylpyridine** (**3dm**) in $CDCl_3$.

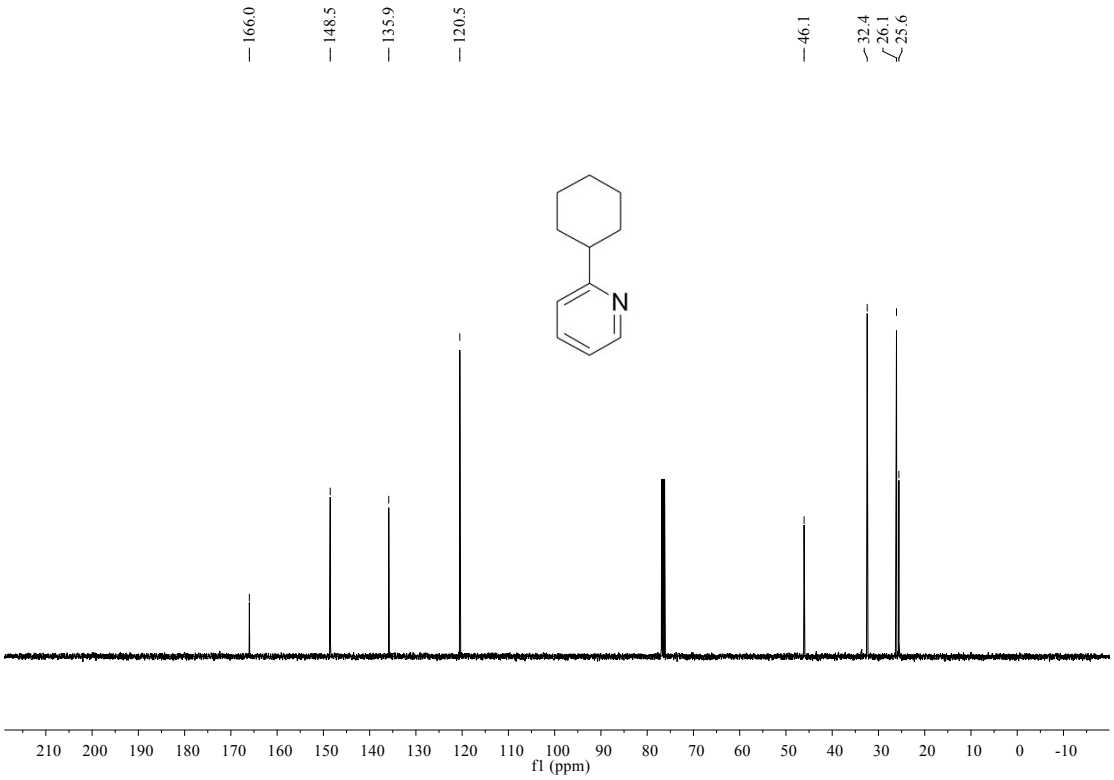

Figure S44. ^{13}C NMR spectrum of **2-cyclohexylpyridine** (**3dm**) in $CDCl_3$.

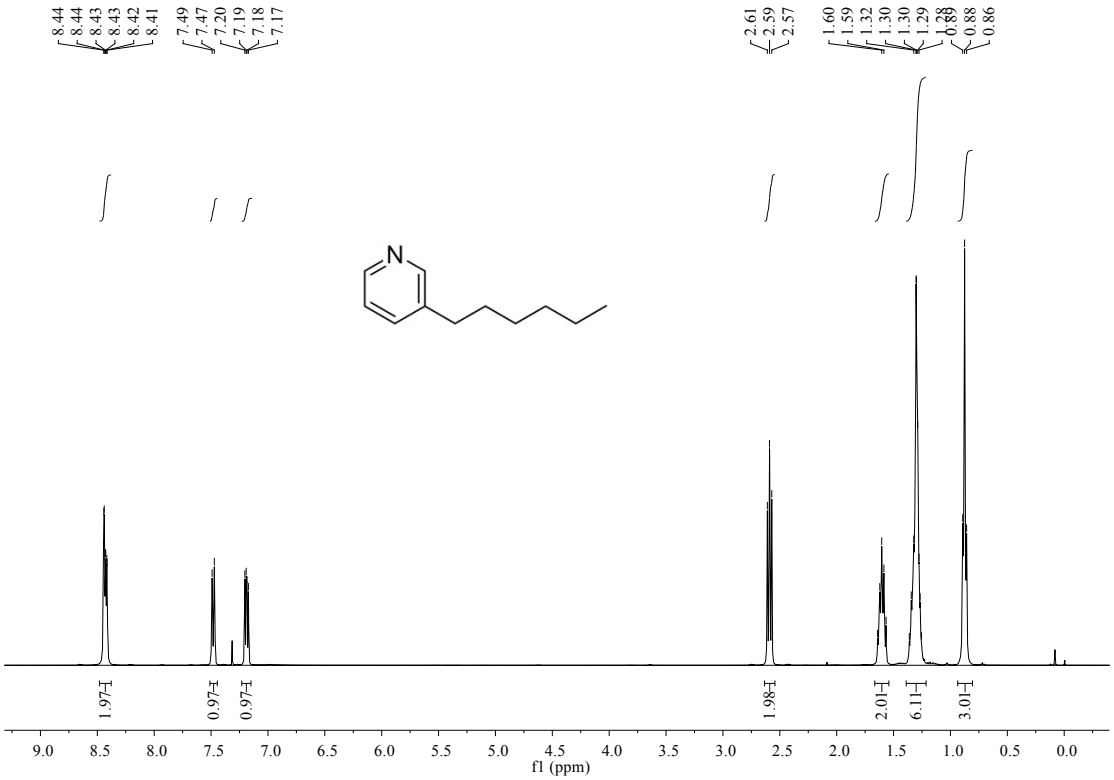

Figure S45. ^{1}H NMR spectrum of **3-hexylpyridine** (**3ec**) in $CDCl_3$.

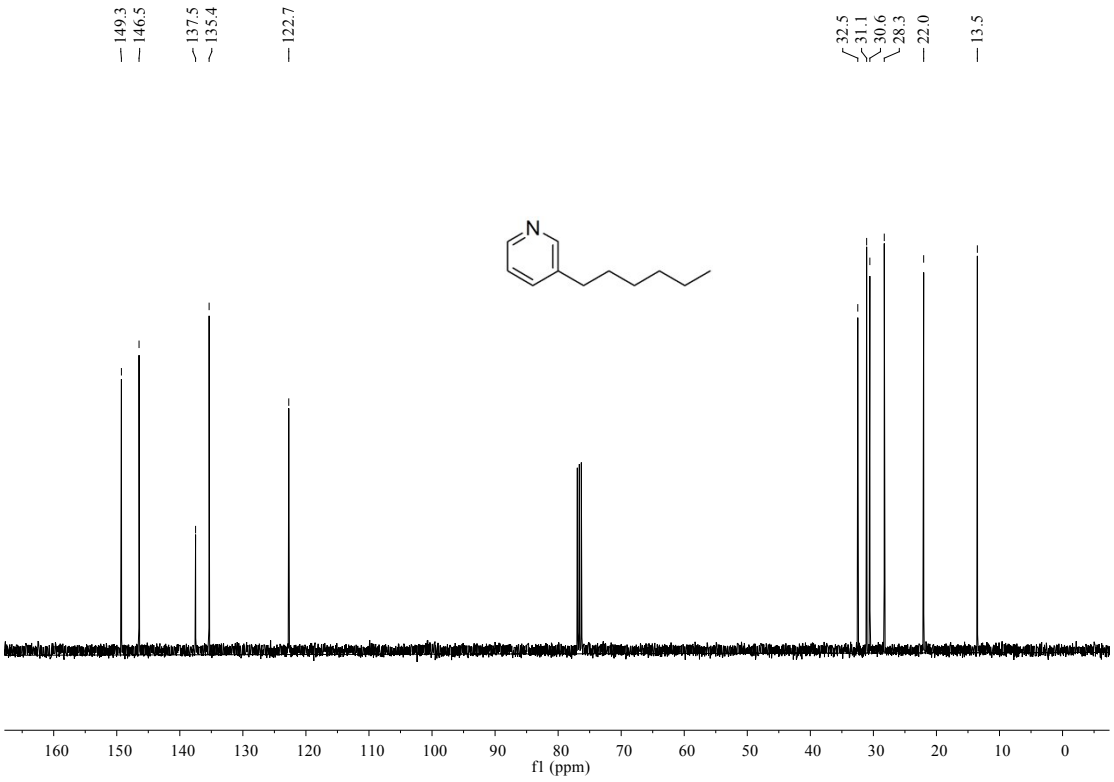

Figure S46. ^{13}C NMR spectrum of **3-hexylpyridine** (**3ec**) in $CDCl_3$.

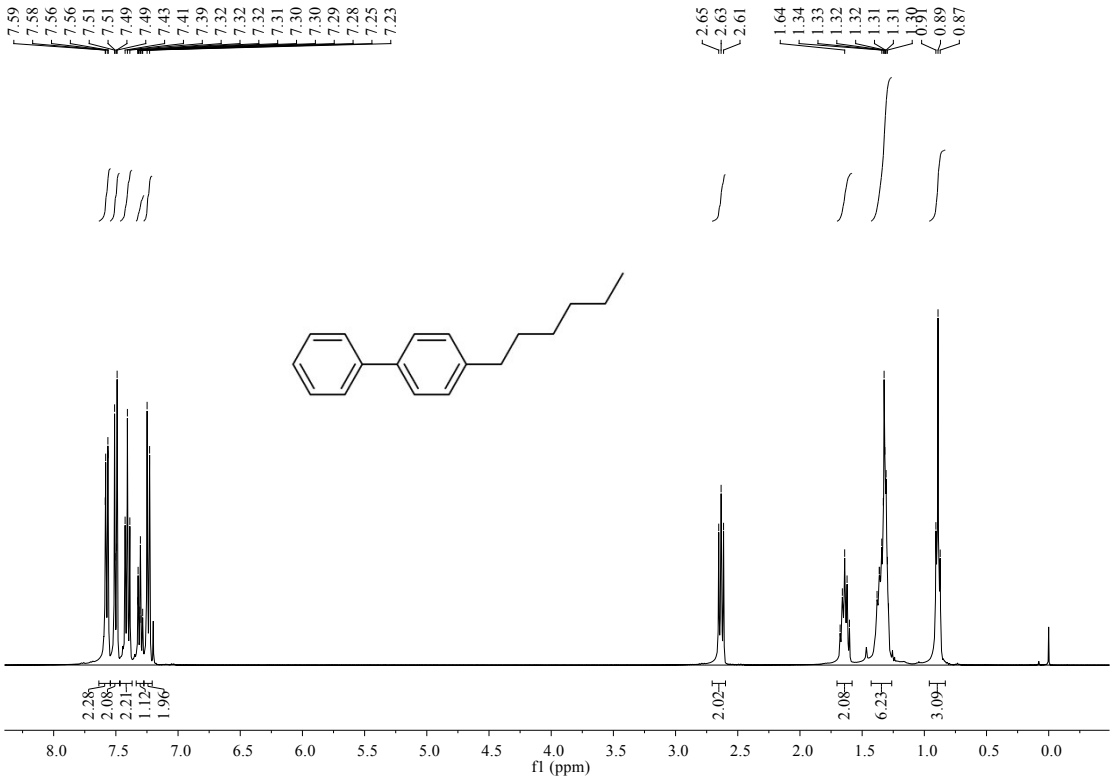

Figure S47. ^{1}H NMR spectrum of **4-hexyl-1,1'-Biphenyl** (**3fc**) in $CDCl_3$.

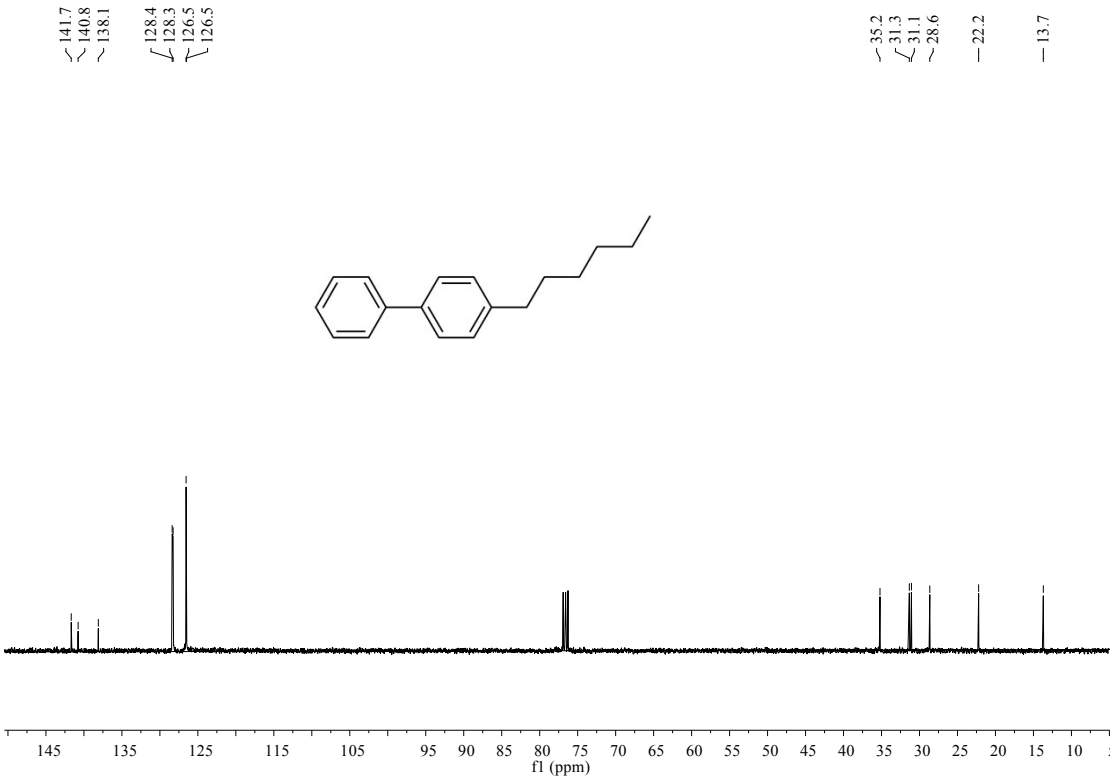

Figure S48. ^{13}C NMR spectrum of **4-hexyl-1,1'-Biphenyl** (**3fc**) in $CDCl_3$.

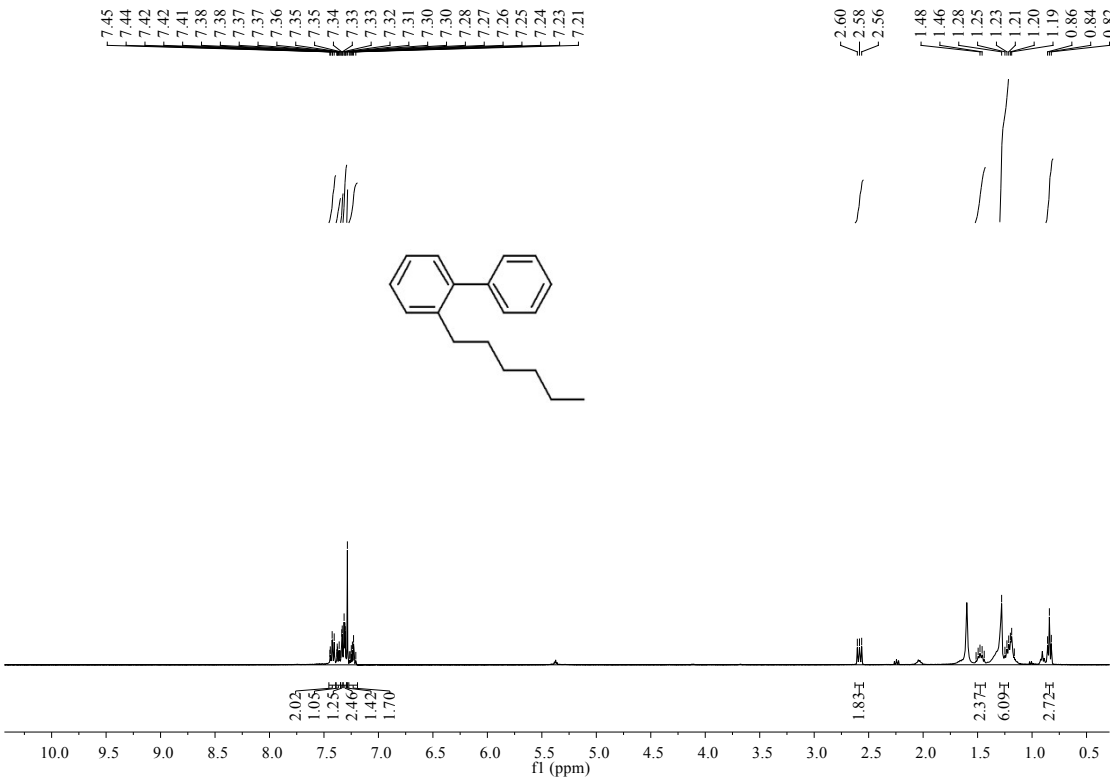

Figure S49. ^{1}H NMR spectrum of **2-hexyl-1,1'-Biphenyl** (**3gc**) in $CDCl_3$.

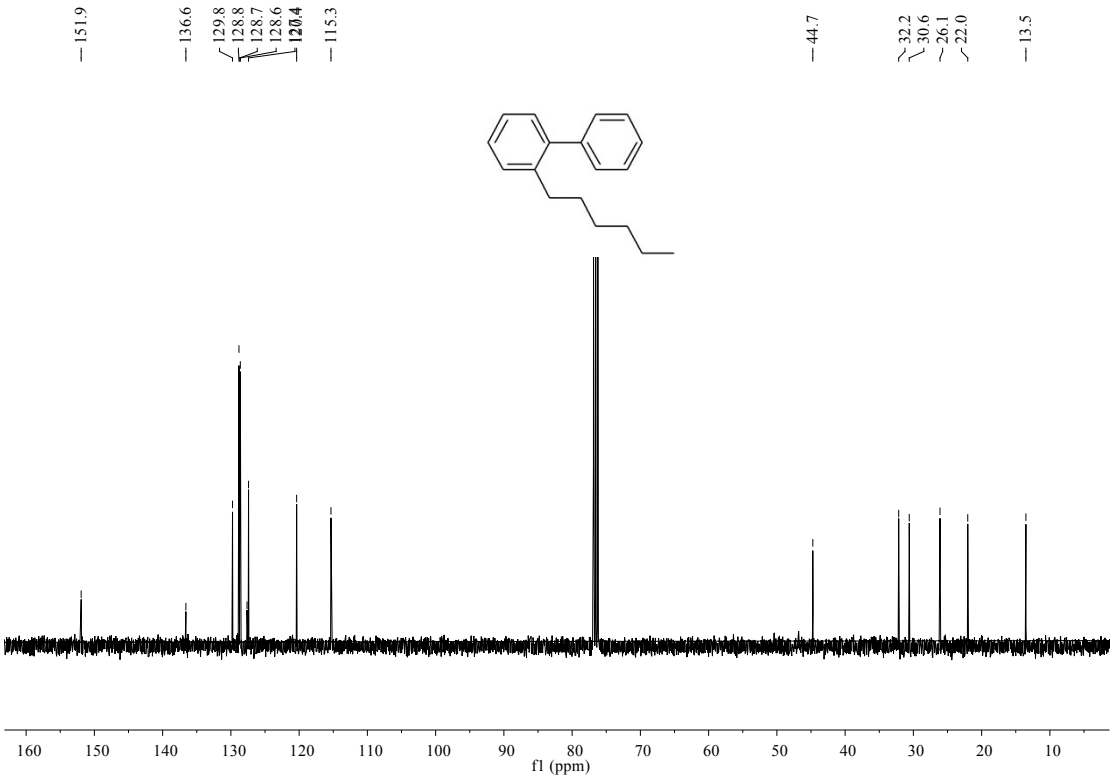

Figure S50. ^{13}C NMR spectrum of **2-hexyl-1,1'-Biphenyl** (**3gc**) in $CDCl_3$.

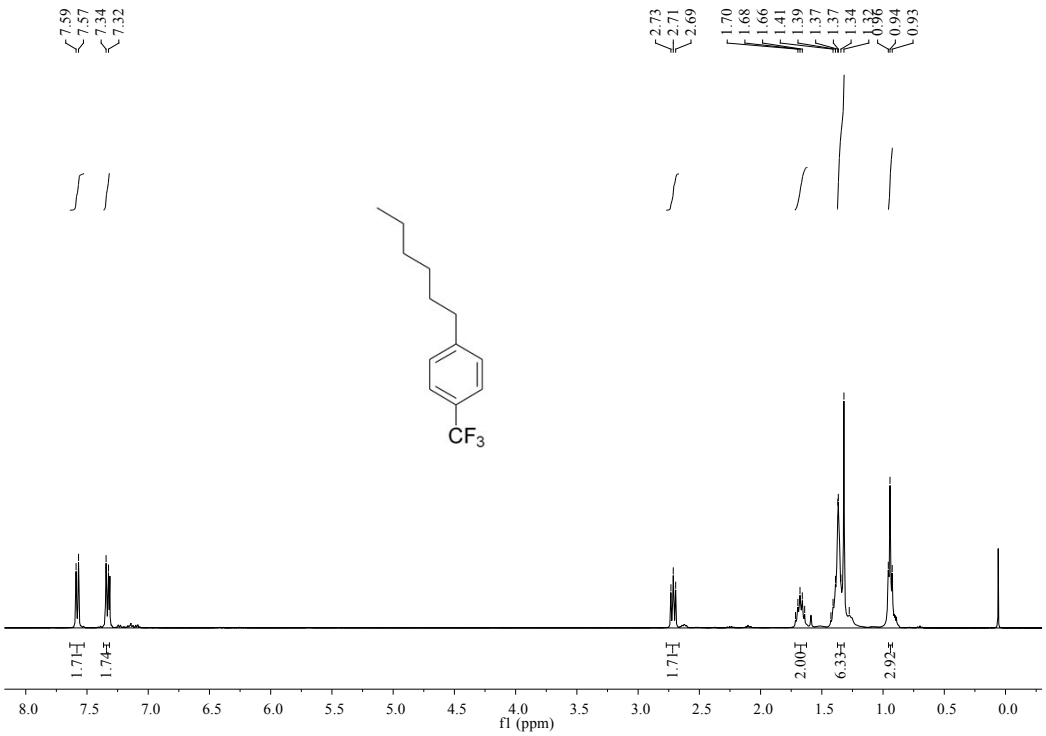

Figure S51. ^{1}H NMR spectrum of **1-hexyl-4-(trifluoromethyl)benzene** (**3hc**) in $CDCl_3$.

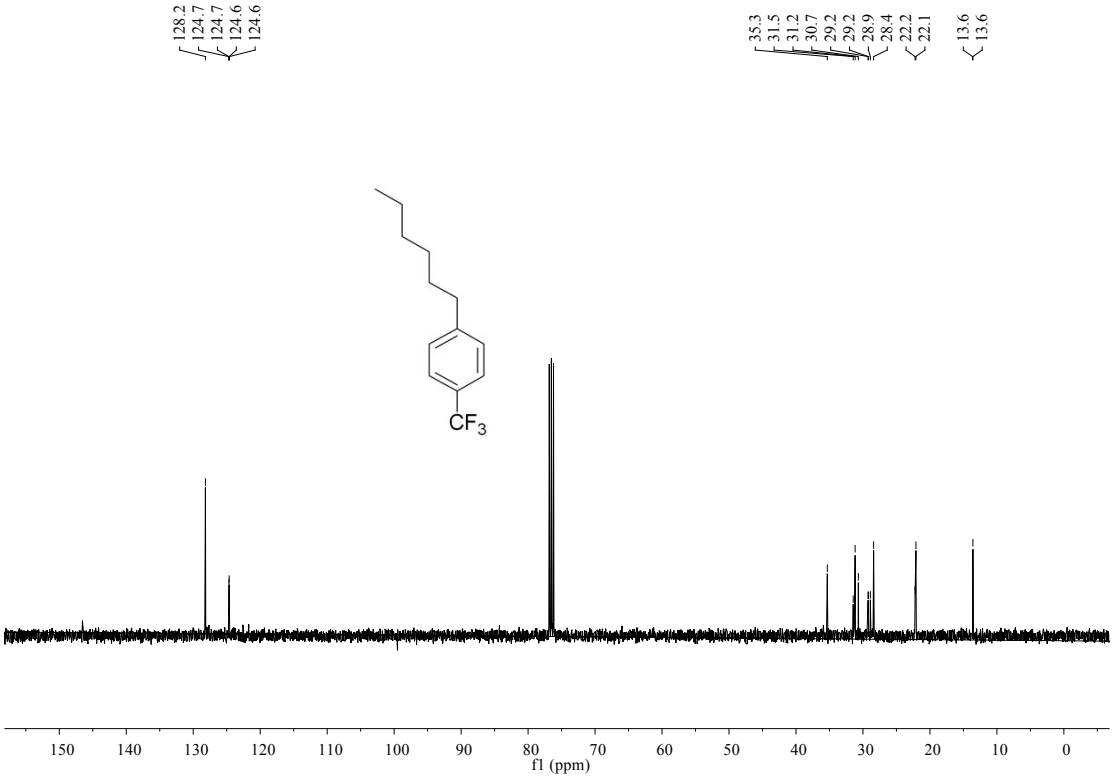

Figure S52. ^{13}C NMR spectrum of **1-hexyl-4-(trifluoromethyl)benzene** (**3hc**) in $CDCl_3$.

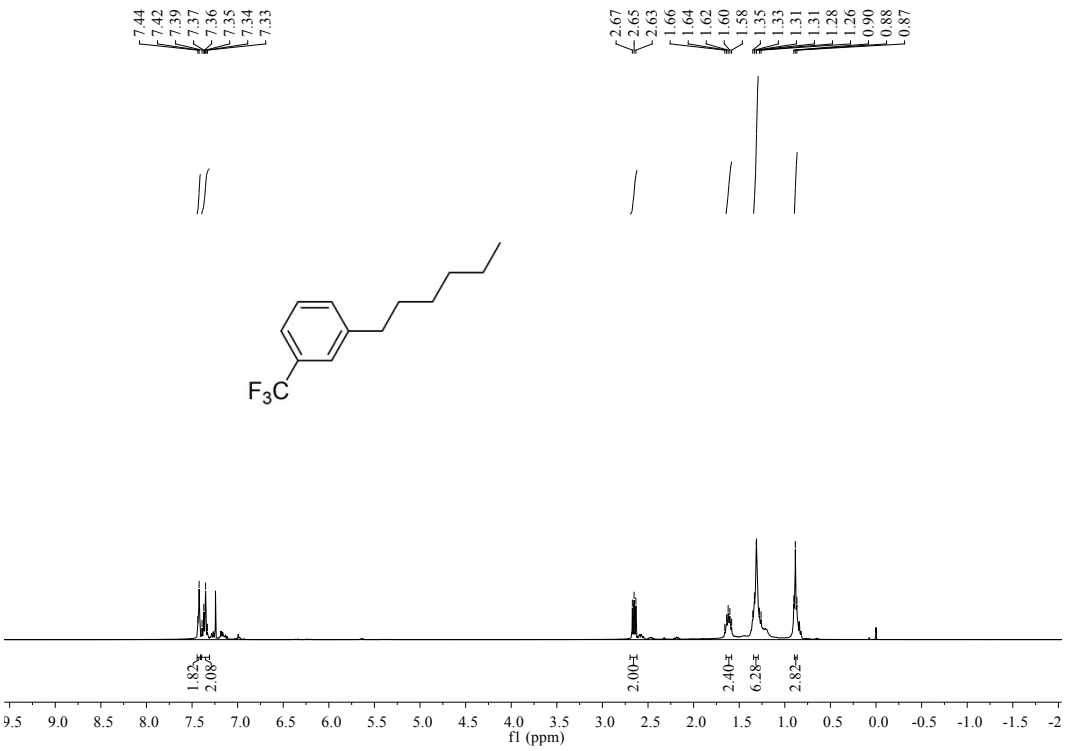

Figure S53. ^{1}H NMR spectrum of **1-(trifluoromethyl)-3-hexylbenzene** (**3ic**) in $CDCl_3$.

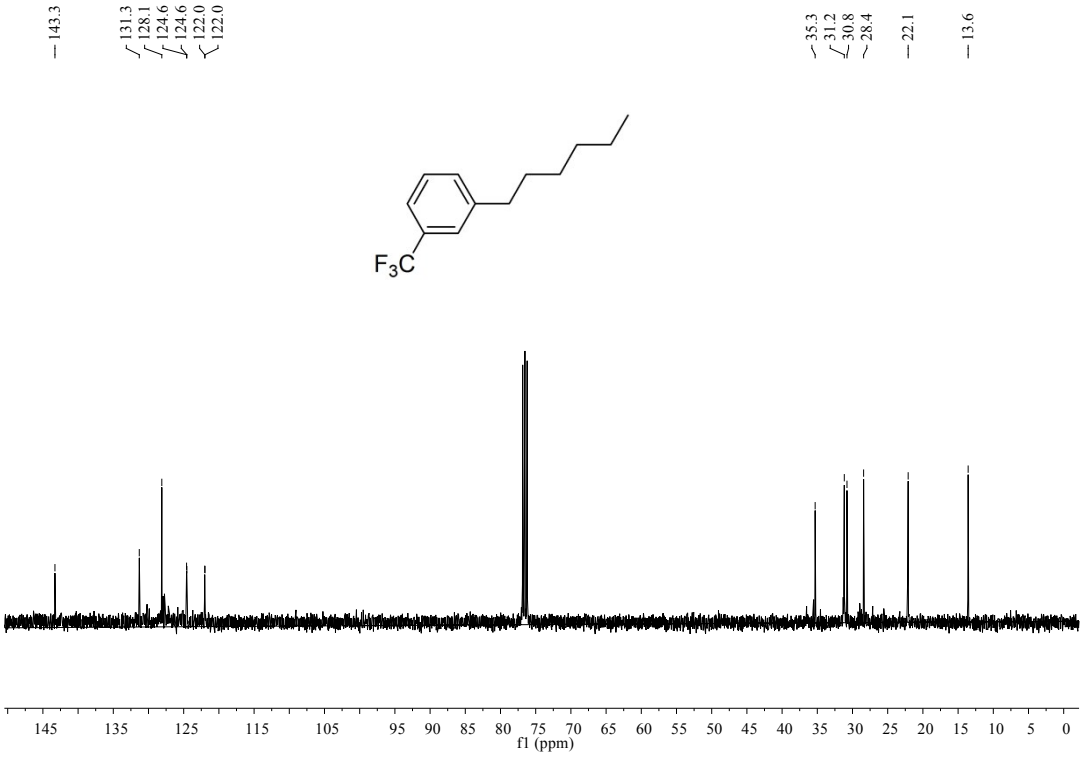

Figure S54. ^{13}C NMR spectrum of **1-(trifluoromethyl)-3-hexylbenzene** (**3ic**) in $CDCl_3$.

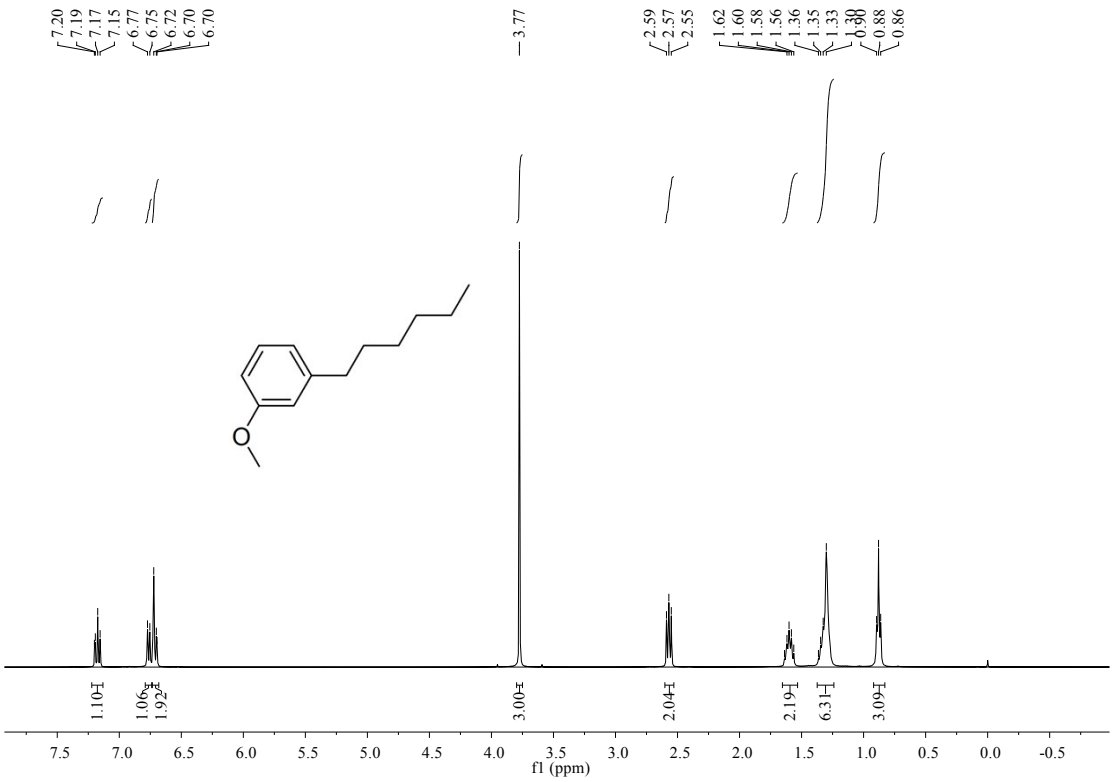

Figure S55. ^{1}H NMR spectrum of **1-hexyl-3-methoxybenzene** (**3jc**) in $CDCl_3$.

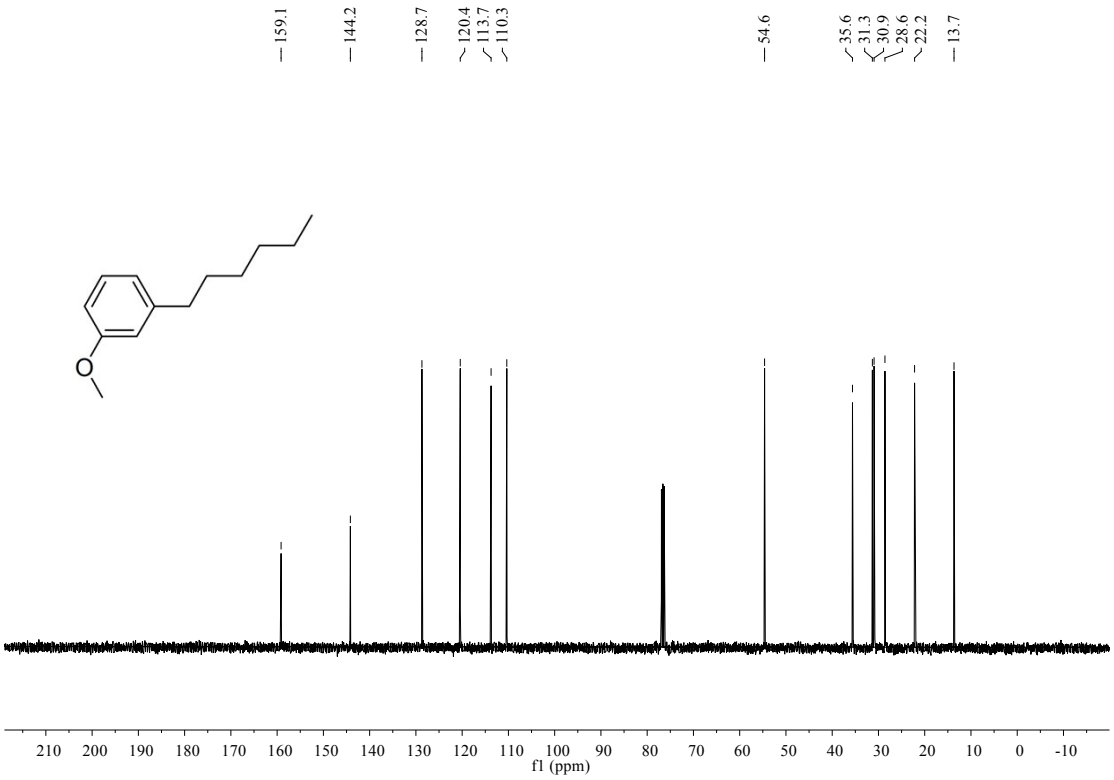

Figure S56. ^{13}C NMR spectrum of **1-hexyl-3-methoxybenzene** (**3jc**) in $CDCl_3$.

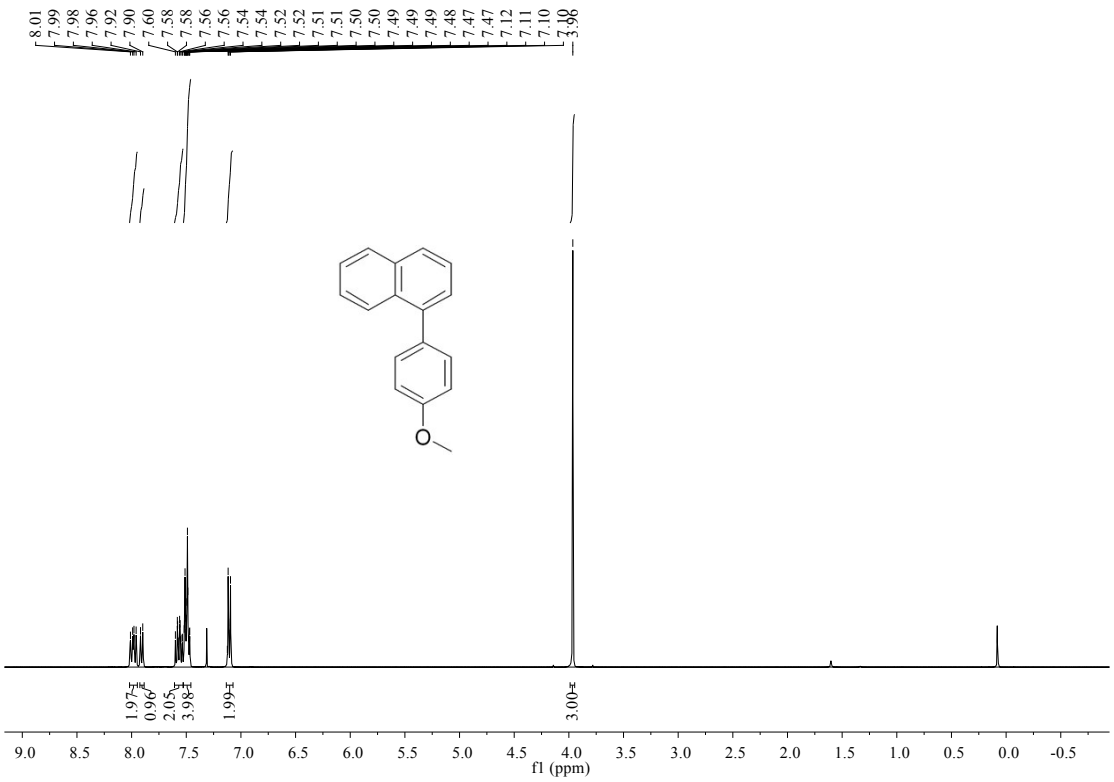

Figure S57. ^{1}H NMR spectrum of **1-(4-methoxyphenyl)naphthalene** (**3aq**) in $CDCl_3$.

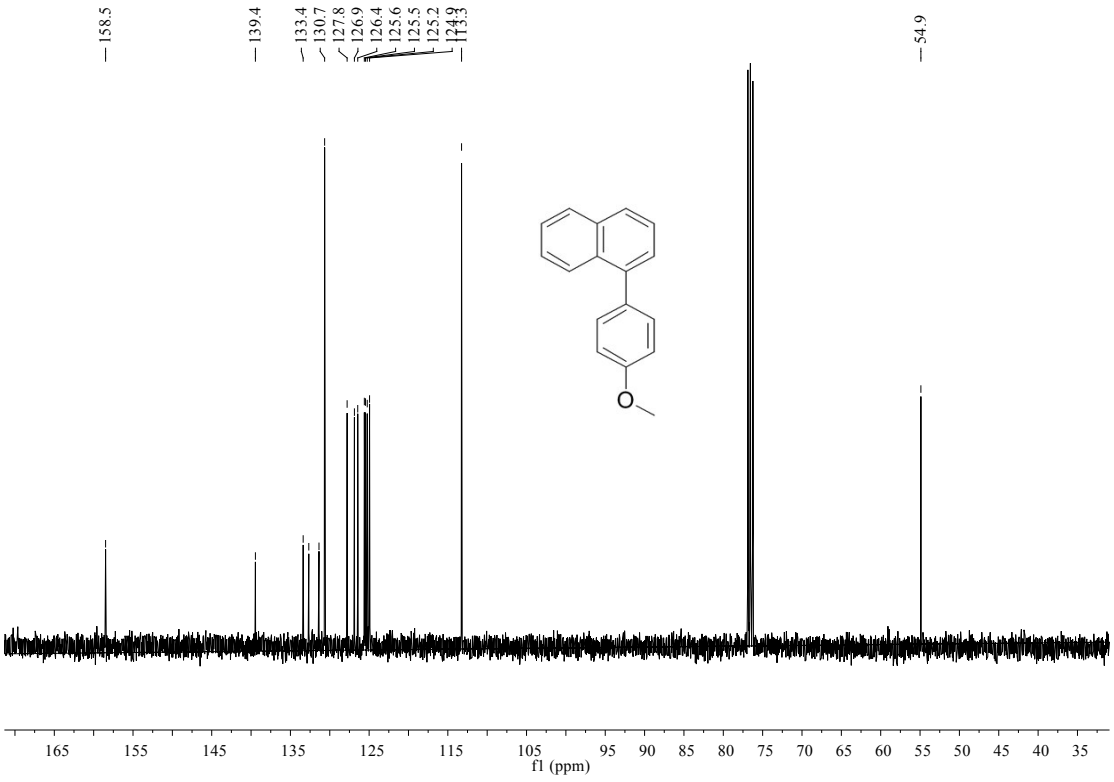

Figure S58. ^{1}C NMR spectrum of **1-(4-methoxyphenyl)naphthalene** (**3aq**) in $CDCl_3$.

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