A Mild and Practical Method for Deprotection of Aryl Methyl/Benzyl/Allyl Ethers with $HPPh_2$ and ^tBuOK

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Supporting Information

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I. General Information

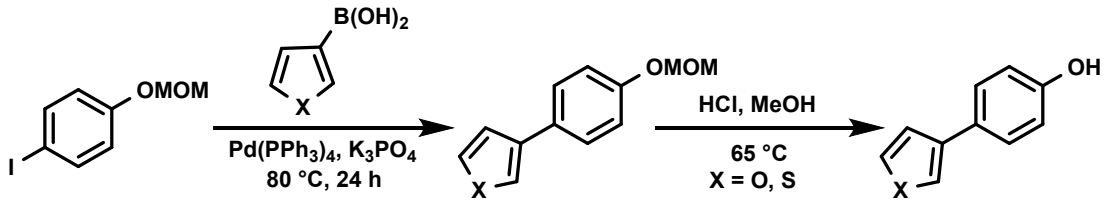
All air or moisture-sensitive manipulations were performed under nitrogen atmosphere, using an oven-dried vial with a magnetic stirrer. $HPPh_2$, anhydrous DMF, anhydrous THF, anhydrous toluene, anhydrous ^{t}BuOK, $Pd(PPh_3)_4$ were purchased from Energy Chemicals Inc and used as received. Analytical thin layer chromatography (TLC) was performed using silica gel plates. Visualisation was performed by ultraviolet fluorescence, and/or phosphomolybdic acid, and/or $KMnO_4$.

^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR) and ^{13}C-Nuclear Magnetic Resonance (^{13}C-NMR) spectra were recorded on Bruker 400 MHz at 20 °C with $CDCl_3$, DMSO-d_6 or $(CD_3)_2CO$ as solvent. The chemical shifts of ^{1}H NMR spectra were referenced to TMS or internal solvent resonances and the chemical shifts of ^{13}C NMR spectra were referenced to internal solvent resonances: ^{1}H NMR reference for $CDCl_3$ was 7.26 ppm, DMSO-d_6 was 2.50 ppm and $(CD_3)_2CO$ was 2.05 ppm; ^{13}C NMR reference for $CDCl_3$ was 77.16 ppm, DMSO-d_6 was 39.52 ppm and $(CD_3)_2CO$ was 29.84 ppm. The data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant J (Hz), and integration. High resolution mass spectra were recorded on a Bruker Maxis System. IR spectra were collected on a Spectrum BX FTIR from Perkin-Elmer and reported in unit of cm^{-1}.

II. Synthesis and Characterization of Substrates

Aryl methyl ether **1a-aa**[1], **1ac-ad**[1], Aryl benzyl ethers **2a-c**[2], **2g-k**[2], **2n**[2], **2q-r**[2], **2v-w**[2], Aryl allyl ether **3a-c**[3], **3e**[3], **3g**[3], **3n-r**[3], **3v-w**[3] and **3ab**[4] were prepared following the reported procedure.

General procedure A for the synthesis of 4-heteroarylphenols

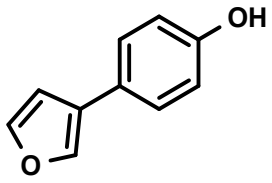


1-Iodo-4-(methoxymethoxy)benzene was synthesized according to the method reported in the literature.[5]

In the glove box, $Pd(PPh_3)_4$ (0.45 mmol, 0.05 equiv), anhydrous K_3PO_4 (27 mmol, 3 equiv) and DMF (15 mL) were added to a 35 mL pressure bottle pre-filled with 1-iodo-4-(methoxymethoxy)benzene (9 mmol, 1 equiv) and heteroarylboronic acid (10.8 mmol, 1.2 equiv). The mixture was stirred at 80 °C for 24 h, and then the resulting solution was quenched with water (100 mL). The aqueous solution was extracted with ethyl acetate (3 × 50 mL), and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The desired product 1-heteroaryl-4-(methoxymethoxy)benzene was obtained by silica gel column chromatography (eluent: petroleum ether/EtOAc = 60:1).

To a solution of 1-heteroaryl-4-(methoxymethoxy)benzene (6.5 mmol) in methanol (82 mL) was added concentrated HCl (1.3 mL), and the reaction solution was stirred at 65 °C for 2 h. The reaction was quenched with water (100 mL), and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic phases were dried over $MgSO_4$, and the solvent were removed under reduced pressure. The residue were separated by column chromatography (eluent: petroleum ether/EtOAc).

4-(Furan-3-yl)phenol



4-(furan-3-yl)phenol was prepared as a white solid in 82% yield (0.85 g, eluent: petroleum ether/EtOAc = 10:1) following the general procedure A.

m.p. 146-147 °C

R_f = 0.45 (petroleum ether/EtOAc = 5:1)

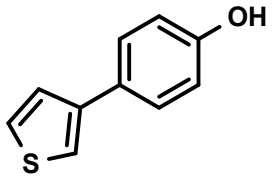
^{1}H NMR (400 MHz, DMSO) δ 9.47 (s, 1H), 7.98 (s, 1H), 7.66 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 6.90–6.75 (m, 3H).

^{13}C NMR (101 MHz, DMSO) δ 156.55, 143.91, 137.75, 126.83, 125.92, 122.86, 115.67, 108.71.

HRMS (ESI$^+$): calcd for $C_{10}H_8O_2$ [M-H]$^+$: 159.0446, found: 159.0450.

IR (neat, cm^{-1}): 3414, 3152, 3134, 2925, 1611, 1522, 1450, 1260, 1161, 1053, 875, 834, 781, 594, 521.

4-(Thiophen-3-yl)phenol



4-(thiophen-3-yl)phenol was prepared as a white solid in 90% yield (1.03 g, eluent: petroleum ether/EtOAc = 10:1) following the general procedure A.

m.p. 185-186 °C

R_f = 0.41 (petroleum ether/EtOAc = 5:1)

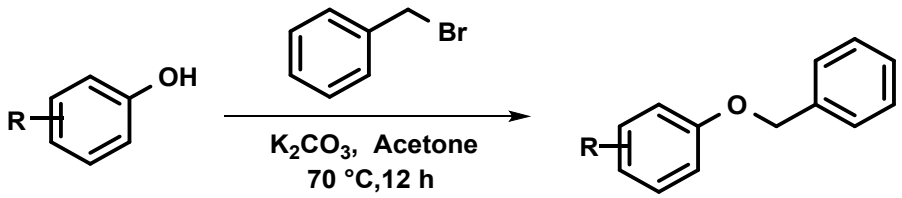
^{1}H NMR (400 MHz, DMSO) δ 9.50 (s, 1H), 7.61 (s, 1H), 7.57–7.48 (m, 3H), 7.44 (d, *J* = 4.8 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 156.70, 141.61, 127.28, 126.63, 126.42, 125.96, 118.50, 115.61.

HRMS (ESI$^+$): calcd for $C_{10}H_8OS$ [M-H]$^+$: 175.0218, found: 175.0221.

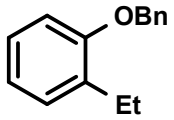
IR (neat, cm^{-1}): 3413, 3100, 3033, 2925, 1608, 1536, 1504, 1449, 1380, 1259, 1200, 834, 776, 714, 518.

General procedure B for the synthesis of aryl benzyl ethers



Anhydrous K_2CO_3 (10 mmol, 2 equiv), aryl phenol (7.5 mmol, 1.5 equiv) and benzylbromide (5 mmol, 1 equiv) were sequentially added to a 35 mL sealed tube equipped with a stir bar. Acetone (10 mL) was then added, and the mixture was stirred at 70 °C for 12 h. The resulting solution was then filtered, washed with ethyl acetate, and concentrated under reduced pressure. The desired product was obtained by silica gel column chromatography (eluent: petroleum ether/ethyl acetate).

1-Benzyloxy-2-ethylbenzene



2d was prepared as a colorless oil in 90% yield (0.95 g, eluent: petroleum ether) following the general procedure B.

$\mathbf{R}_f$ = 0.80 (petroleum ether)

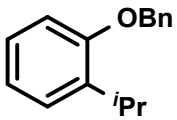
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 1H), 7.18 (dd, *J* = 16.7, 7.7 Hz, 2H), 6.93 (t, *J* = 8.7 Hz, 2H), 5.11 (s, 2H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.73, 137.83, 133.28, 129.31, 128.74, 127.93, 127.30, 126.99, 121.01, 111.80, 70.05, 23.64, 14.46.

HRMS (ESI^+): calcd for $C_{15}H_{16}O$ $[M+Na]^+$: 235.1093, found: 235.1092.

IR (neat, cm^{-1}): 3033, 2966, 2931, 2872, 1493, 1451, 1236, 1124, 1043, 1020, 741, 695.

1-Benzyloxy-2-isopropylbenzene



2e was prepared as a colorless oil in 95% yield (1.08 g, eluent: petroleum ether)

following the general procedure B.

$\mathbf{R}_f$ = 0.75 (petroleum ether)

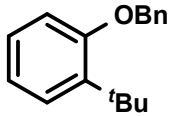
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.98–6.87 (m, 2H), 5.08 (s, 2H), 3.42 (heptet, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.04, 137.73, 137.52, 128.65, 127.84, 127.23, 126.67, 126.29, 121.05, 111.87, 70.12, 27.00, 22.86.

HRMS (ESI^+): calcd for $C_{16}H_{18}O$ $[M+Na]^+$: 249.1250, found: 249.1248.

IR (neat, cm^{-1}): 3033, 2961, 2869, 1598, 1491, 1450, 1382, 1289, 1234, 1088, 1022, 746, 696.

1-Benzyloxy-2-*tert*-butylbenzene



2f was prepared as a colorless oil in 93% yield (1.12 g, eluent: petroleum ether) following the general procedure B.

$\mathbf{R}_f$ = 0.83 (petroleum ether)

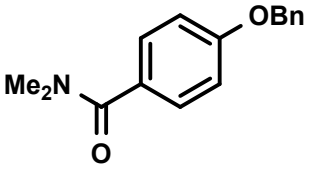
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.38–7.31 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.97–6.92 (m, 2H), 5.14 (s, 2H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 138.48, 137.59, 128.67, 127.83, 127.45, 127.15, 126.86, 120.68, 112.58, 70.21, 35.02, 29.98.

HRMS (ESI^+): calcd for $C_{17}H_{20}O$ $[M+Na]^+$: 263.1406, found: 263.1405.

IR (neat, cm^{-1}): 3033, 2956, 2912, 2869, 1489, 1443, 1225, 1094, 1021, 746, 697.

4-(Benzyloxy)-*N*,*N*-dimethylbenzamide



2l was prepared as a white solid in 90% yield (1.15 g, eluent: petroleum ether/EtOAc = 1:1) following the general procedure B.

m.p. 84-85 °C

R_f = 0.40 (EtOAc)

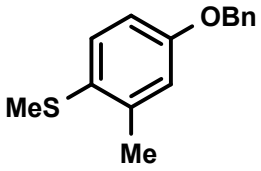
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.29 (m, 7H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 2H), 3.04 (d, *J* = 13.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.46, 159.75, 136.55, 129.18, 128.67, 128.13, 127.50, 114.46, 70.00, 39.83, 35.57.

HRMS (ESI^+): calcd for $C_{15}H_{16}O$ $[M+H]^+$: 256.1332, found: 256.1331.

IR (neat, cm^{-1}): 3034, 2927, 1625, 1605, 1386, 1240, 1171, 1079, 838, 696.

4-Benzyloxy-2-methyl-1-methylsulfanylbenzene



2m was prepared as a white solid in 84% yield (1.03 g, eluent: petroleum ether) following the general procedure B.

m.p. 46-47 °C

R_f = 0.45 (petroleum ether)

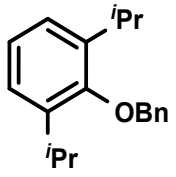
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.27 (m, 5H), 7.25–7.13 (m, 1H), 6.90–6.70 (m, 2H), 5.02 (d, *J* = 6.4 Hz, 2H), 2.37 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.35, 139.14, 137.16, 129.36, 128.67, 128.60, 128.04, 127.54, 117.13, 112.95, 70.18, 20.58, 17.22.

HRMS (ESI^+): calcd for $C_{15}H_{16}OS$ $[M+Na]^+$: 267.0814, found: 267.0813.

IR (neat, cm^{-1}): 3032, 2979, 2917, 2865, 1595, 1477, 1294, 1232, 1170, 1027, 801, 733, 697.

2-Benzyloxy-1,3-diisopropylbenzene



2o was prepared as a white solid in 86% yield (1.15 g, eluent: petroleum ether) following the general procedure B.

m.p. 36-37 °C

R_f = 0.66 (petroleum ether)

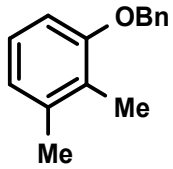
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.16 (s, 3H), 4.84 (s, 2H), 3.43 (heptet, *J* = 6.9 Hz, 2H), 1.27 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.28, 142.08, 137.91, 128.70, 128.05, 127.52, 124.87, 124.21, 76.53, 26.73, 24.26.

HRMS (ESI^+): calcd for $C_{19}H_{24}O$ $[M+Na]^+$: 291.1719, found: 291.1717.

IR (neat, cm^{-1}): 3031, 2962, 2929, 2868, 1447, 1324, 1253, 1181, 1048, 1016, 760, 733, 697.

1-Benzyloxy-2,3-dimethylbenzene



2p was prepared as a colorless oil in 90% yield (0.96 g, eluent: petroleum ether) following the general procedure B.

R_f = 0.83 (petroleum ether)

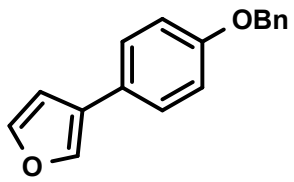
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.81 (t, *J* = 8.6 Hz, 2H), 5.09 (s, 2H), 2.32 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.86, 138.14, 137.83, 128.62, 127.81, 127.27, 125.91, 125.68, 122.67, 109.59, 70.32, 20.24, 11.95.

HRMS (ESI^+): calcd for $C_{15}H_{16}O$ $[M+Na]^+$: 235.1093, found: 235.1092.

IR (neat, cm^{-1}): 3032, 2921, 2864, 1583, 1457, 1381, 1307, 1257, 1102, 1014, 766, 735, 696.

3-(4-Benzyloxyphenyl)furan



2s was prepared as a white solid in 80% yield (1.00 g, eluent: petroleum ether/EtOAc = 60:1) following the general procedure B.

m.p. 117-118 °C

$\mathbf{R}_f$ = 0.52 (petroleum ether/EtOAc = 30:1)

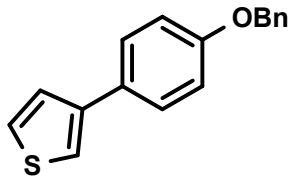
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.41 (m, 8H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.67 (s, 1H), 5.10 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.09, 143.64, 137.84, 137.12, 128.73, 128.11, 127.60, 127.17, 126.20, 125.48, 115.37, 109.00, 70.22.

HRMS (ESI$^+$): calcd for $C_{17}H_{14}O_2$ $[M+H]^+$: 251.1067, found: 251.1065.

IR (neat, cm^{-1}): 3040, 2912, 2861, 1587, 1516, 1291, 1248, 1159, 1016, 874, 828, 781, 741, 695, 594.

3-(4-Benzyloxyphenyl)thiophene



2t was prepared as a white solid in 81% yield (1.09 g, eluent: petroleum ether/EtOAc = 60:1) following the general procedure B.

m.p. 146-147 °C

$\mathbf{R}_f$ = 0.52 (petroleum ether/EtOAc = 30:1)

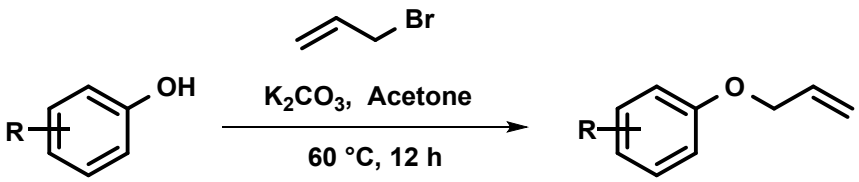
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.50–7.28 (m, 8H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.11 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.22, 142.11, 137.11, 129.14, 128.74, 128.13, 127.70, 127.61, 126.37, 126.20, 119.13, 115.30, 70.24.

HRMS (ESI$^+$): calcd for $C_{17}H_{14}OS$ $[M+H]^+$: 267.0838, found: 267.0838.

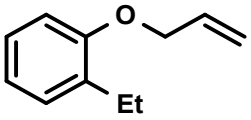
IR (neat, cm^{-1}): 3100, 3040, 2918, 2861, 1608, 1535, 1501, 1381, 1290, 1247, 1182, 1014, 838, 776, 740, 692.

General procedure C for the synthesis of aryl allyl ethers



Anhydrous potassium carbonate (10 mmol, 2 equiv), phenol (5 mmol, 1 equiv), allylbromide (7.5 mmol, 1.5 equiv) and acetone (10 mL) were sequentially added to a 35 mL sealed tube, and the mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the resulting solution was filtered, extracted with ethyl acetate, and concentrated under reduced pressure. The desired product was obtained by silica gel column chromatography (eluent: petroleum ether/ethyl acetate).

1-Allyloxy-2-ethylbenzene



3d was prepared as a colorless oil in 80% yield (0.65 g, eluent: petroleum ether) following the general procedure C.

R_f = 0.77 (petroleum ether)

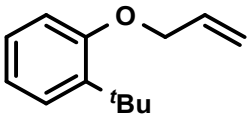
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 8.9 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.09 (m, 1H), 5.45 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.56 (d, *J* = 4.4 Hz, 2H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.50, 133.83, 133.11, 129.17, 126.81, 120.78, 116.87, 111.64, 68.78, 23.50, 14.32.

HRMS (EI^+): calcd for $C_{11}H_{14}O$ [M]: 162.1045, found: 162.1049.

IR (neat, cm^{-1}): 2962, 2926, 2857, 1492, 1455, 1240, 1127, 1023, 999, 924, 749.

1-Allyloxy-2-*tert*-butylbenzene



3f was prepared as a colorless oil in 82% yield (0.78 g, eluent: petroleum ether) following the general procedure C.

R_f = 0.87 (petroleum ether)

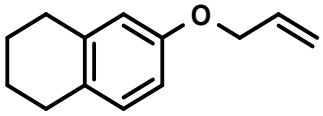
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 6.90 (dd, *J* = 17.5, 8.0 Hz, 2H), 6.13 (m, 1H), 5.47 (d, *J* = 17.3 Hz, 1H), 5.30 (d, *J* = 10.6 Hz, 1H), 4.59 (d, *J* = 4.1 Hz, 2H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.58, 138.50, 133.81, 127.07, 126.79, 120.60, 117.06, 112.67, 68.96, 35.01, 29.93.

HRMS (ESI^+): calcd for $C_{13}H_{18}O$ $[M+Na]^+$: 213.1250, found: 213.1249.

IR (neat, cm^{-1}): 2957, 2915, 2869, 1489, 1443, 1229, 1093, 1023, 996, 926, 748.

6-Allyloxy-1,2,3,4-tetrahydronaphthalene



3h was prepared as a colorless oil in 88% yield (0.83 g, eluent: petroleum ether) following the general procedure C.

R_f = 0.66 (petroleum ether)

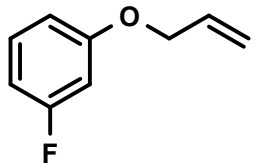
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.67 (s, 1H), 6.09 (m, 1H), 5.44 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.5 Hz, 1H), 4.54 (d, *J* = 4.6 Hz, 2H), 2.76 (d, *J* = 15.6 Hz, 4H), 1.82 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.51, 138.23, 133.78, 129.99, 129.55, 117.44, 114.81, 112.63, 68.94, 29.82, 28.69, 23.56, 23.29.

HRMS (ESI^+): calcd for $C_{13}H_{16}O$ $[M+Na]^+$: 211.1093, found: 211.1092.

IR (neat, cm^{-1}): 3016, 2925, 2857, 1611, 1500, 1424, 1248, 1230, 1158, 1029, 923, 825, 799.

1-Allyloxy-3-fluorobenzene



3j was prepared as a light yellow oil in 89% yield (0.68 g, eluent: petroleum ether) following the general procedure C.

R_f = 0.70 (petroleum ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.16 (m, 1H), 6.74–6.58 (m, 3H), 6.04 (m, 1H), 5.41 (d, *J* = 17.3 Hz, 1H), 5.30 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 5.3 Hz, 2H).

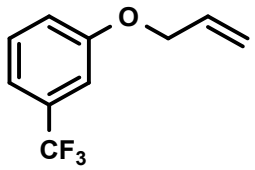
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.71 (d, *J* = 246.4 Hz), 160.04 (d, *J* = 11.1 Hz), 132.89, 130.29 (d, *J* = 10.1 Hz), 118.11, 110.64, 107.74 (d, *J* = 21.2 Hz), 102.54 (d, *J* = 24.2 Hz), 69.12.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.72.

HRMS (ESI$^+$): calcd for $C_9H_{10}OF$ $[M+H]^+$: 153.0710, found: 153.0719.

IR (neat, cm^{-1}): 2925, 2855, 1610, 1593, 1489, 1282, 1264, 1169, 1134, 1028.

1-Allyloxy-3-trifluoromethylbenzene



3k was prepared as a light yellow oil in 91% yield (0.92 g, eluent: petroleum ether) following the general procedure C.

R_f = 0.73 (petroleum ether)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.15 (s, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 6.06 (m, 1H), 5.44 (d, *J* = 17.3 Hz, 1H), 5.33 (d, *J* = 10.5 Hz, 1H), 4.58 (d, *J* = 5.2 Hz, 2H).

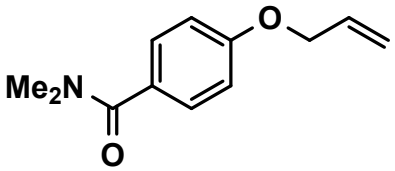
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.79, 132.70, 131.93 (q, *J* = 32.3 Hz), 130.08, 124.10 (q, *J* = 273.4 Hz), 118.36, 118.27, 117.64 (q, *J* = 4.0 Hz), 111.63 (q, *J* = 4.0 Hz), 69.12.

^{19}F NMR (376 MHz, CDCl3) δ -62.72.

HRMS (ESI$^+$): calcd for $C_{10}H_9F_3O$ $[M+H]^+$: 203.0678, found: 203.0680.

IR (neat, cm^{-1}): 2927, 2855, 1450, 1328, 1168, 1128, 1067, 1028, 697.

4-Allyloxy-*N*,*N*-dimethylbenzamide



3l was prepared as a light yellow oil in 88% yield (0.90 g, eluent: petroleum ether/EtOAc = 1:1) following the general procedure C.

R_f = 0.45 (EtOAc)

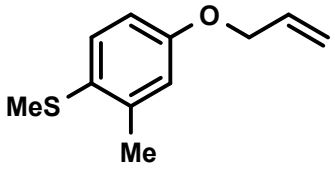
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.01 (m, 1H), 5.37 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 4.52 (d, *J* = 5.1 Hz, 2H), 3.01 (d, *J* = 12.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.25, 159.59, 132.86, 129.13, 128.55, 117.96, 114.32, 68.80, 39.82, 35.57.

HRMS (ESI^+): calcd for $C_{12}H_{15}O_2N$ $[M+H]^+$: 206.1176, found: 206.1177.

IR (neat, cm^{-1}): 2928, 1625, 1605, 1387, 1242, 1221, 1173, 1080, 840, 763.

4-Allyloxy-2-methyl-1-methylsulfanylbenzene



3m was prepared as a colorless oil in 85% yield (0.83 g, eluent: petroleum ether) following the general procedure C.

R_f = 0.57 (petroleum ether)

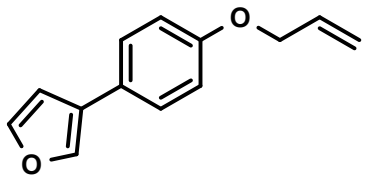
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 1H), 6.85–6.69 (m, 2H), 6.05 (m, 1H), 5.41 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.51 (d, *J* = 4.4 Hz, 2H), 2.39 (d, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.18, 139.16, 133.45, 129.42, 128.45, 117.69, 117.01, 112.90, 69.02, 20.59, 17.28.

HRMS (ESI^+): calcd for $C_{11}H_{14}OS$ $[M+Na]^+$: 217.0658, found: 217.0657.

IR (neat, cm^{-1}): 2980, 2919, 2856, 1595, 1478, 1429, 1294, 1233, 1171, 1027, 992, 925, 801.

3-(4-Allyloxyphenyl)furan



3s was prepared as a light yellow solid in 81% yield (0.82 g, eluent: petroleum ether) following the general procedure C.

m.p. 74-75 °C

R_f = 0.34 (petroleum ether)

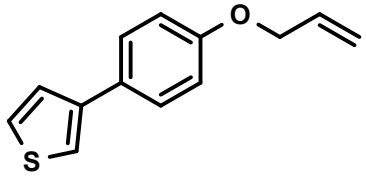
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.46 (s, 1H), 7.41 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.66 (s, 1H), 6.08 (m, 1H), 5.43 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.5 Hz, 1H), 4.56 (d, *J* = 5.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.90, 143.64, 137.83, 133.40, 127.14, 126.22, 125.38, 117.84, 115.25, 109.00, 69.03.

HRMS (ESI^+): calcd for $C_{13}H_{12}O_2$ $[M+Na]^+$: 223.0730, found: 223.0728.

IR (neat, cm^{-1}): 3128, 2921, 2865, 1737, 1590, 1518, 1244, 1158, 1015, 835, 786.

3-(4-Allyloxyphenyl)thiophene



3t was prepared as a white solid in 80% yield (0.87 g, eluent: petroleum ether) following the general procedure C.

m.p. 102-103 °C

R_f = 0.34 (petroleum ether)

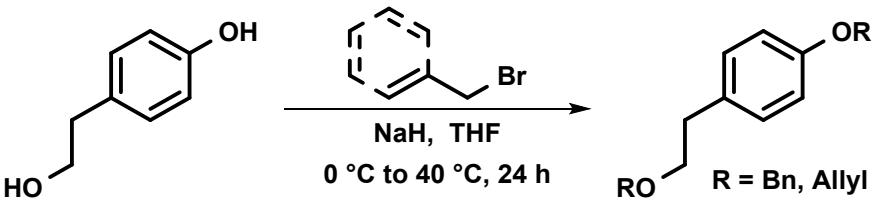
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.35 (s, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.09 (m, 1H), 5.45 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.5 Hz, 1H), 4.58 (d, *J* = 4.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.02, 142.11, 133.39, 129.03, 127.65, 126.36, 126.18, 119.09, 117.85, 115.16, 69.02.

HRMS (ESI^+): calcd for $C_{13}H_{12}OS$ $[M+Na]^+$: 239.0501, found: 239.0500.

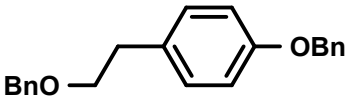
IR (neat, cm^{-1}): 3053, 2926, 2858, 1609, 1538, 1502, 1263, 1017, 997, 836, 779, 735.

General procedure D for the synthesis of aryl dialkyl ethers



NaH (25 mmol, 5 equiv) was dissolved in 10 ml of dry THF under N_2 and placed in an ice bath, a phenol (5 mmol, 1 equiv, dissolved in 10 ml dry THF) solution was added dropwised, and the reaction mixture was stirred for 30 min. Allylbromide (50 mmol, 10 equiv) or benzylbromide (50 mmol, 10 equiv) was added to the above solution, and the mixture was further stirred at 40 °C for 24 h. Upon completion, the solution was cooled to room temperature, and carefully added ice-water. After the effervescence ceased, the mixture was extracted with ethyl acetate, and the organic layer was separated and concentrated under reduced pressure. The desired product was obtained by silica gel column chromatography (eluent: petroleum ether/ethyl acetate).

1-benzyloxy-4-(2-benzyloxyethyl)benzene



2ab was prepared as a white solid in 90% yield (1.43 g, eluent: petroleum ether/EtOAc = 60:1) following the general procedure D.

m.p. 87-88 °C

R$_f$ = 0.43 (petroleum ether/EtOAc = 20:1)

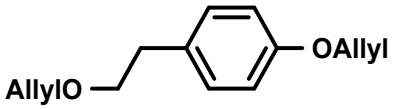
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.25 (m, 10H), 7.19 – 7.13 (m, 2H), 6.96 – 6.89 (m, 2H), 5.06 (s, 2H), 4.54 (s, 2H), 3.67 (t, *J* = 7.2 Hz, 2H), 2.89 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 157.44, 138.57, 137.32, 131.46, 130.02, 128.70, 128.49, 128.03, 127.75, 127.66, 127.59, 114.89, 73.08, 71.60, 70.17, 35.62.

HRMS (ESI$^+$): calcd for $C_{22}H_{22}O_2Na$ $[M+Na]^+$: 341.1517, found: 341.1520.

IR (neat, cm^{-1}): 2919.42, 2852.69, 1611.47, 1510.81, 1453.61, 1238.97, 1098.81, 1026.6, 733.58, 695.54.

1-allyloxy-4-(2-allyloxyethyl)benzene



3ac was prepared as a light yellow oil in 85% yield (0.93 g, eluent: petroleum ether) following the general procedure D.

R$_f$ = 0.52 (petroleum ether/EtOAc = 20:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18–7.12 (m, 2H), 6.90–6.82 (m, 2H), 6.07 (ddd, *J* = 12.0, 10.5, 5.2 Hz, 1H), 5.90 (d, *J* = 10.4 Hz, 1H), 5.42 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.33 – 5.23 (m, 2H), 5.18 (dq, *J* = 10.4, 1.5 Hz, 1H), 4.52 (dt, *J* = 5.2, 1.6 Hz, 2H), 4.00 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.86 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 157.20, 134.98, 133.57, 131.29, 129.90, 117.60, 116.89, 114.74, 71.95, 71.56, 68.92, 35.56.

HRMS (ESI$^+$): calcd for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1385, found: 219.1389.

IR (neat, cm^{-1}): 2921.01, 2856.22, 1612.29, 1511.55, 1241.16, 1177.76, 1099.09, 1024.62, 997.64, 923.89, 827.18

III. References

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2. L. Bering, K. Jeyakumar and A. P. Antonchick, *Org. Lett.*, 2018, **20**, 3911.

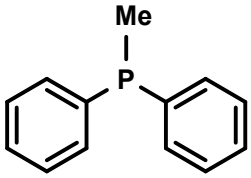
3. M. Chouhan, K. Kumar, R. Sharma, V. Grover and V. A. Nair, *Tetrahedron Lett.*, **2013**, *54*, 4540.

4. T.-Z. Li, C.-A. Geng and J.-J. Chen, *Tetrahedron Lett*., 2019, **60**, 151059.

5. K. Gebauer and A. Furstner, *Angew. Chem. Int. Ed.*, 2014, **53**, 6393.

IV. Copies of NMR Spectra of Ph_2PMe

methyldiphenylphosphane

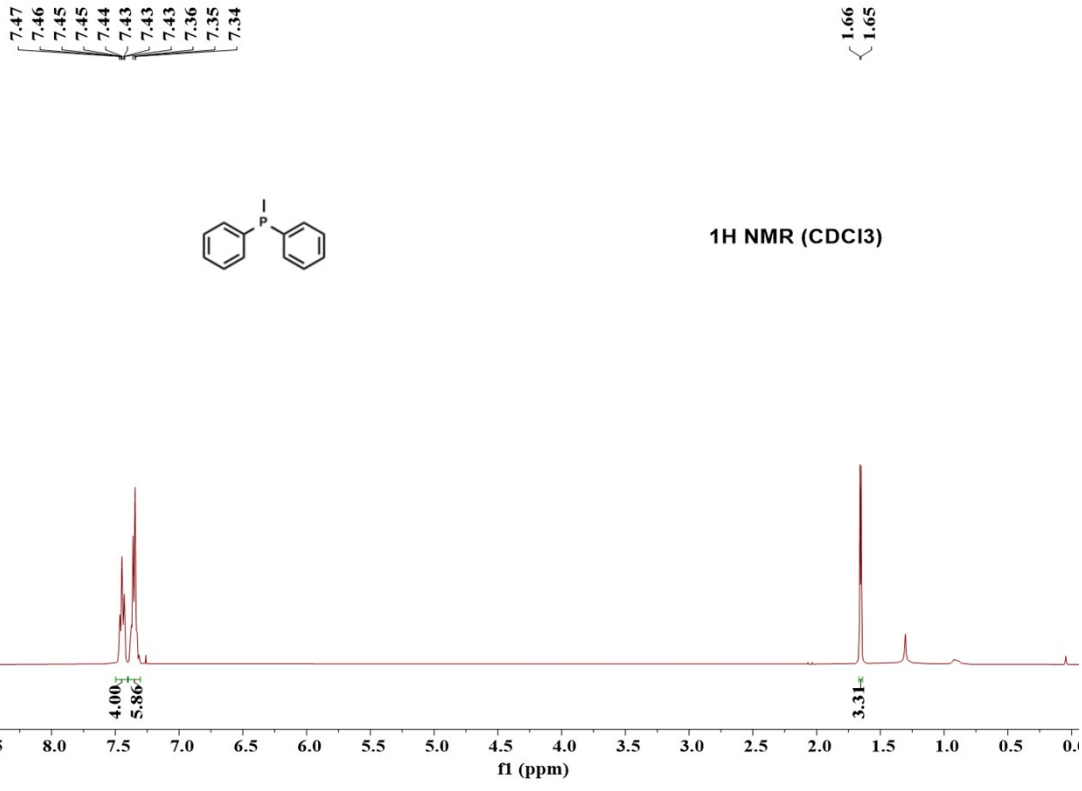


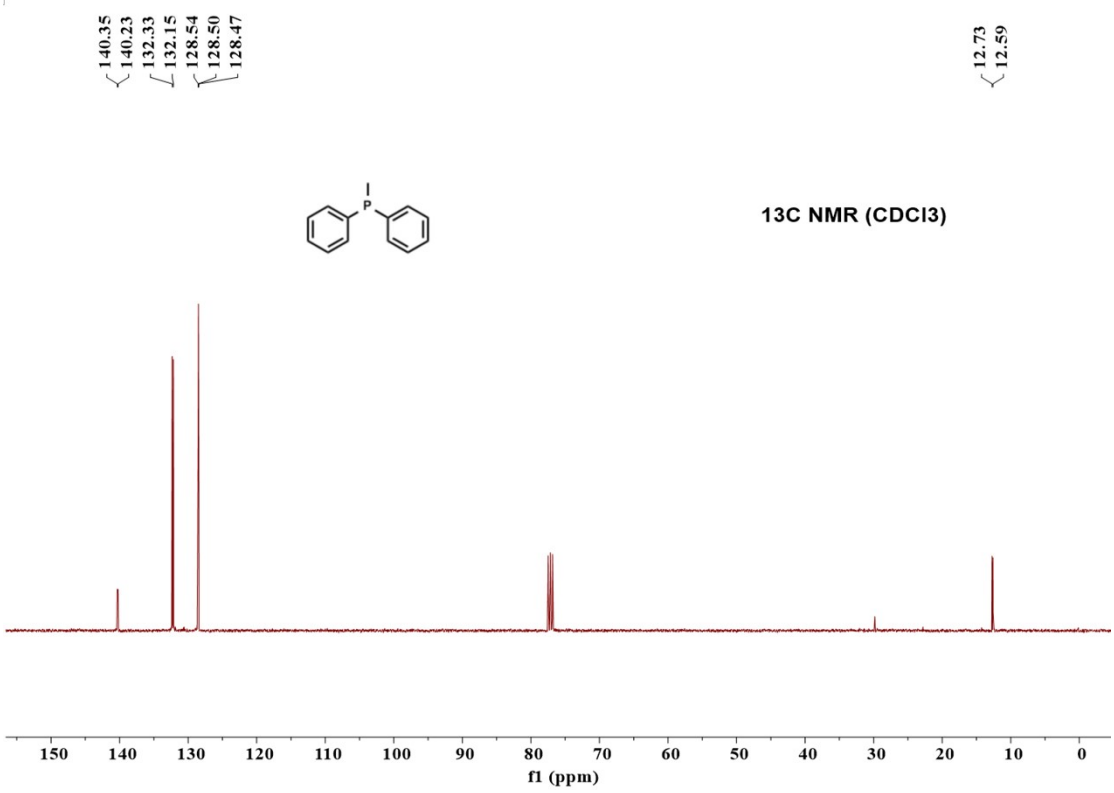
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.40 (m, 4H), 7.35 (d, J = 6.4 Hz, 6H), 1.66 (d, $J_{P,H}$ = 3.5 Hz, 3H).

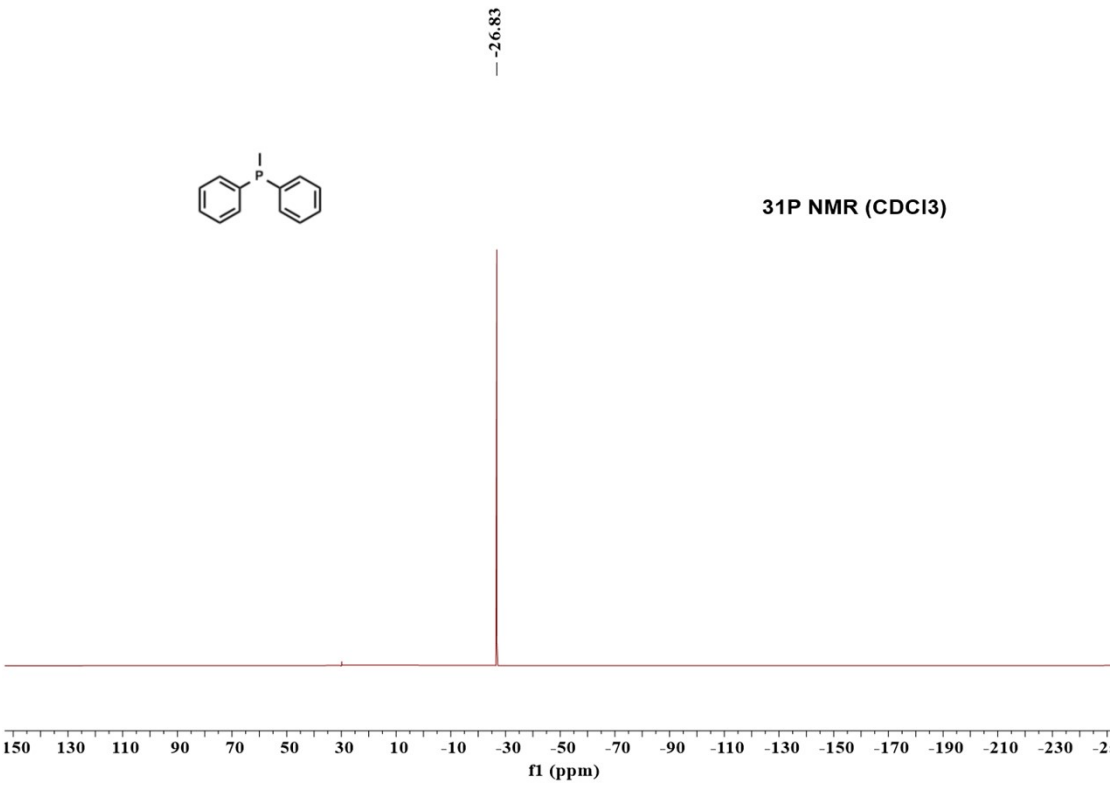
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.29 (d, $J_{P,C}$ = 12.1 Hz), 132.24 (d, $J_{P,C}$ = 18.2 Hz), 128.51 (d, $J_{P,C}$ = 7.1 Hz), 128.50, 12.66 (d, $J_{P,C}$ = 14.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ -26.83.

GCMS : calcd for $C_{13}H_{13}P$ $[M+H]^+$: 200.07, found: 200.1.

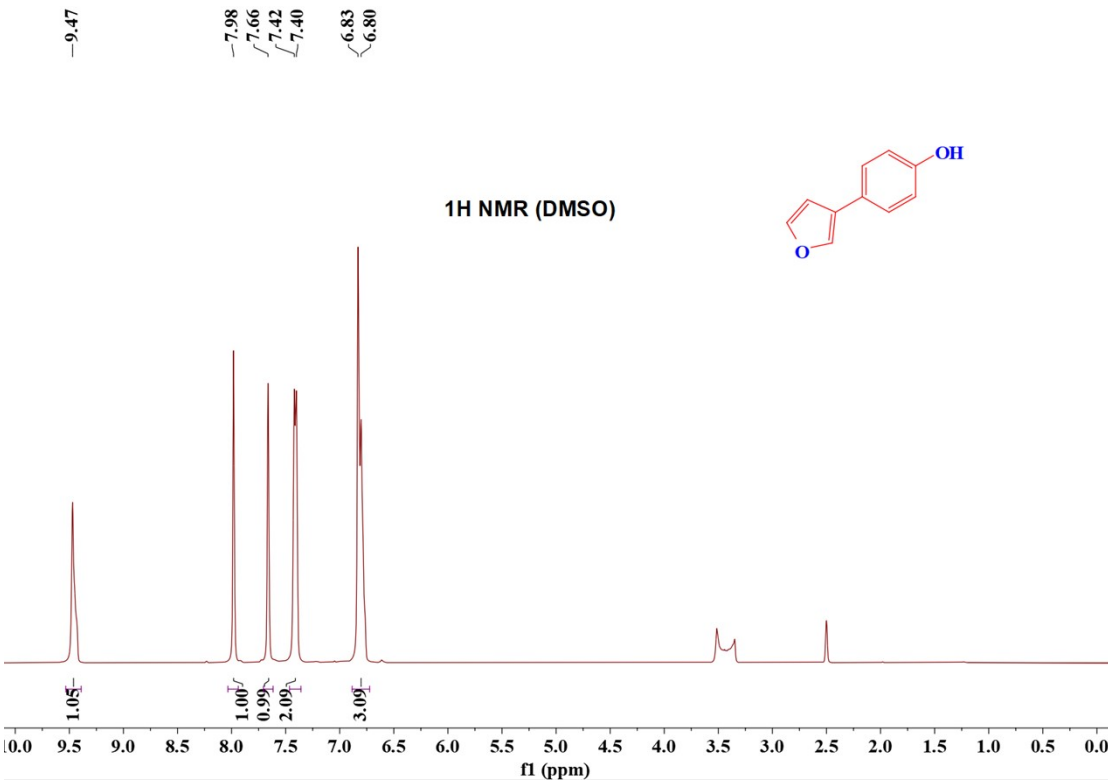


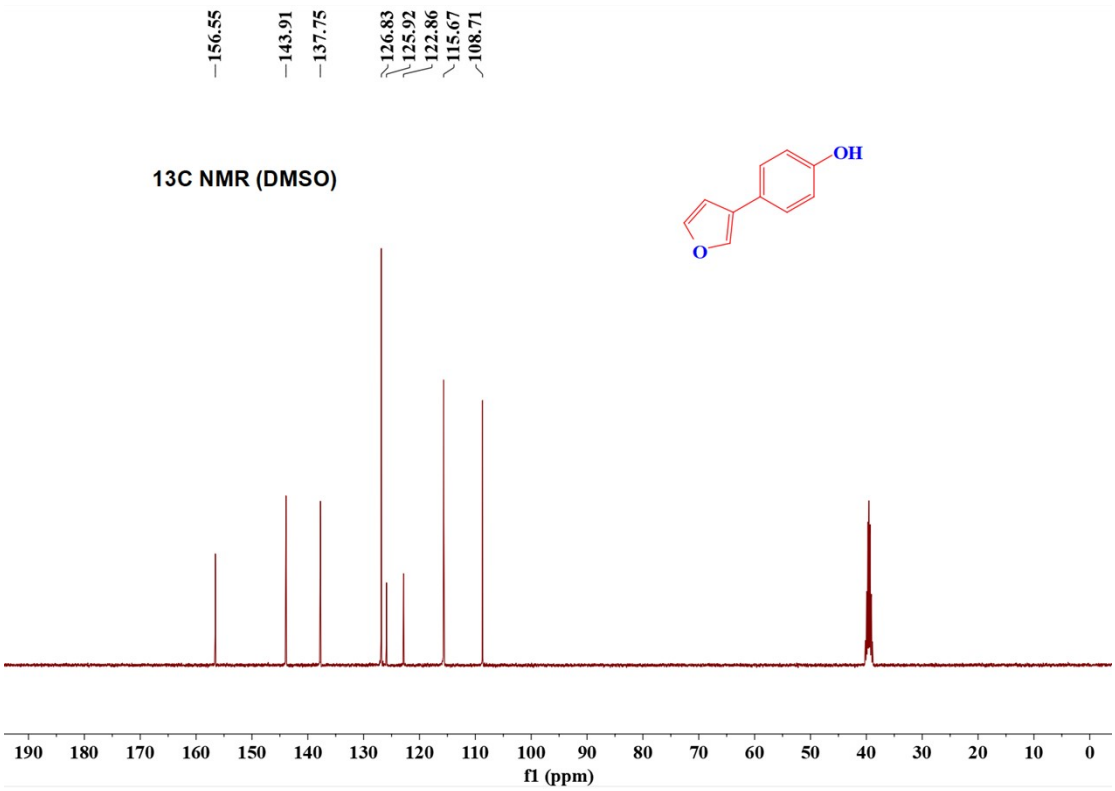

140.35
140.23
132.33
132.15
128.54
128.50
128.47
12.73
12.59
13C NMR (CDCl3)
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-26.83
31P NMR (CDCl3)
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

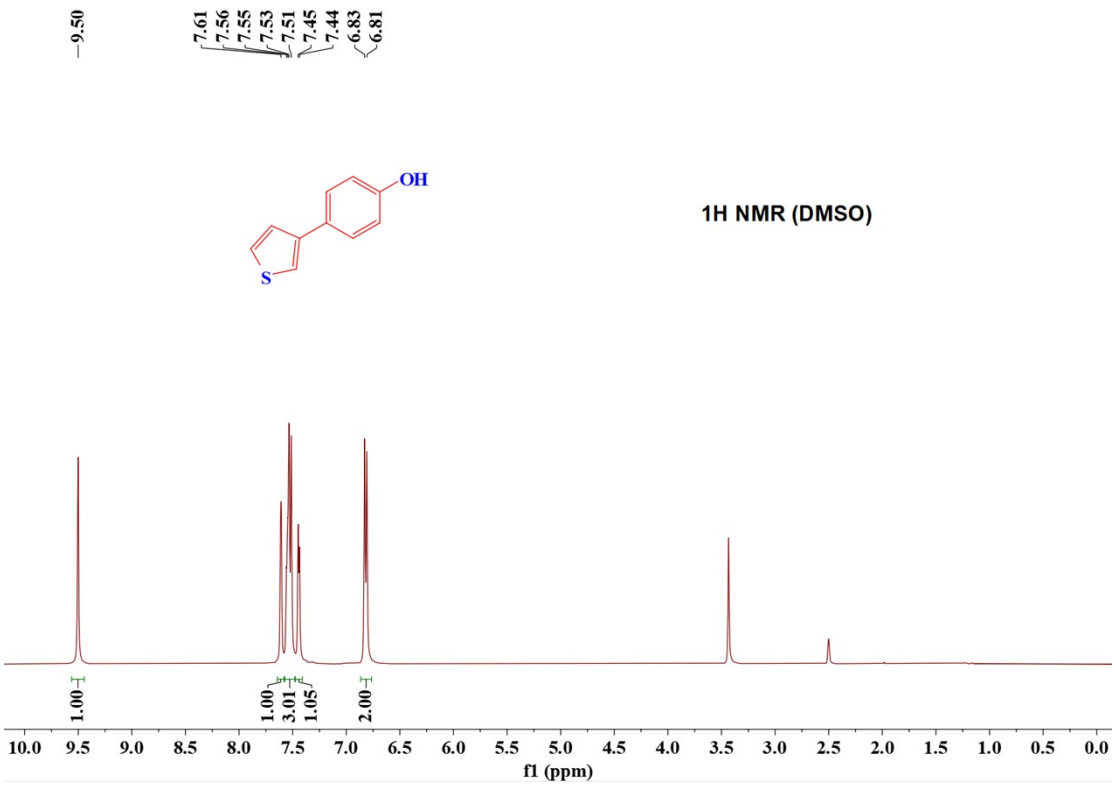
V. Copies of NMR Spectra of Unknown Aryl Benzyl/Allyl Ether

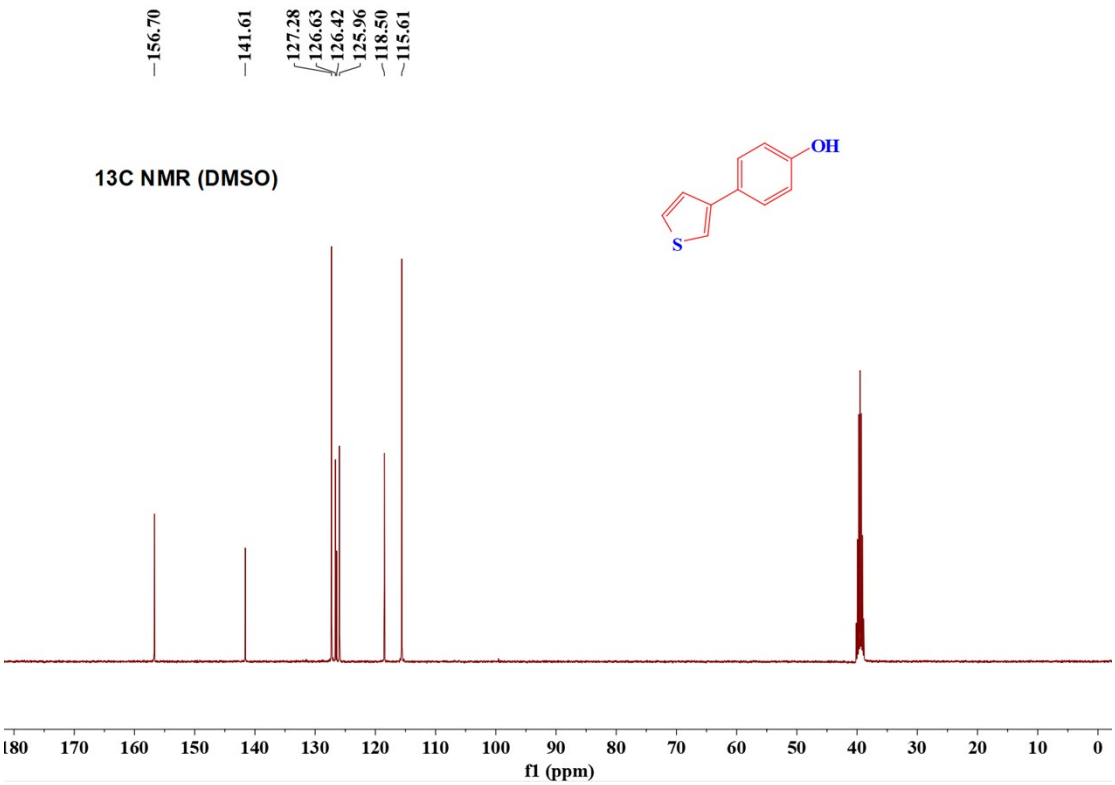
1. 4-(furan-3-yl)phenol



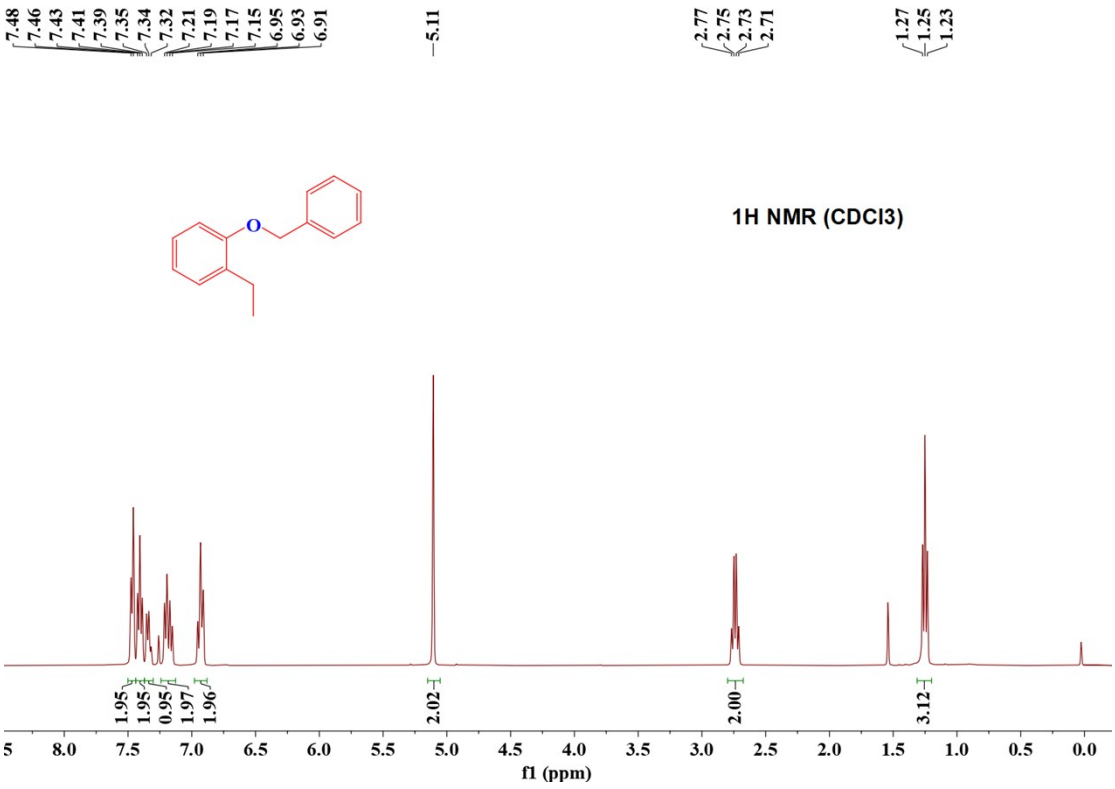


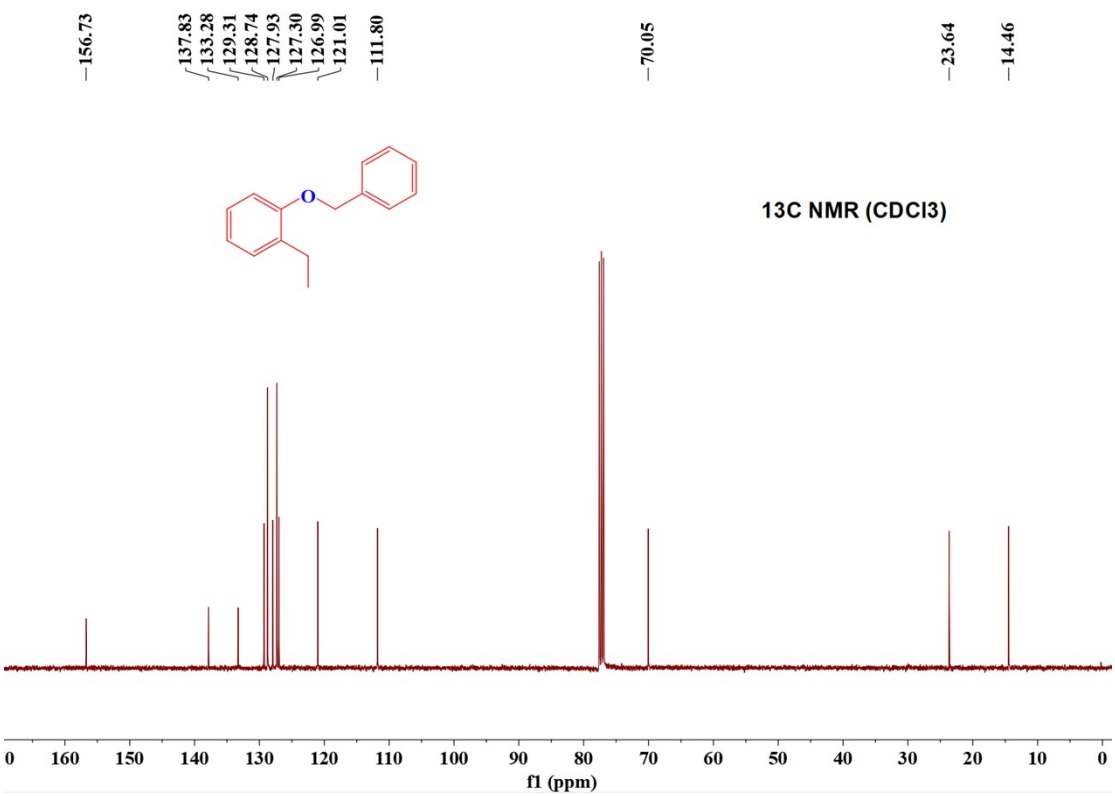
2. 4-(thiophen-3-yl)phenol



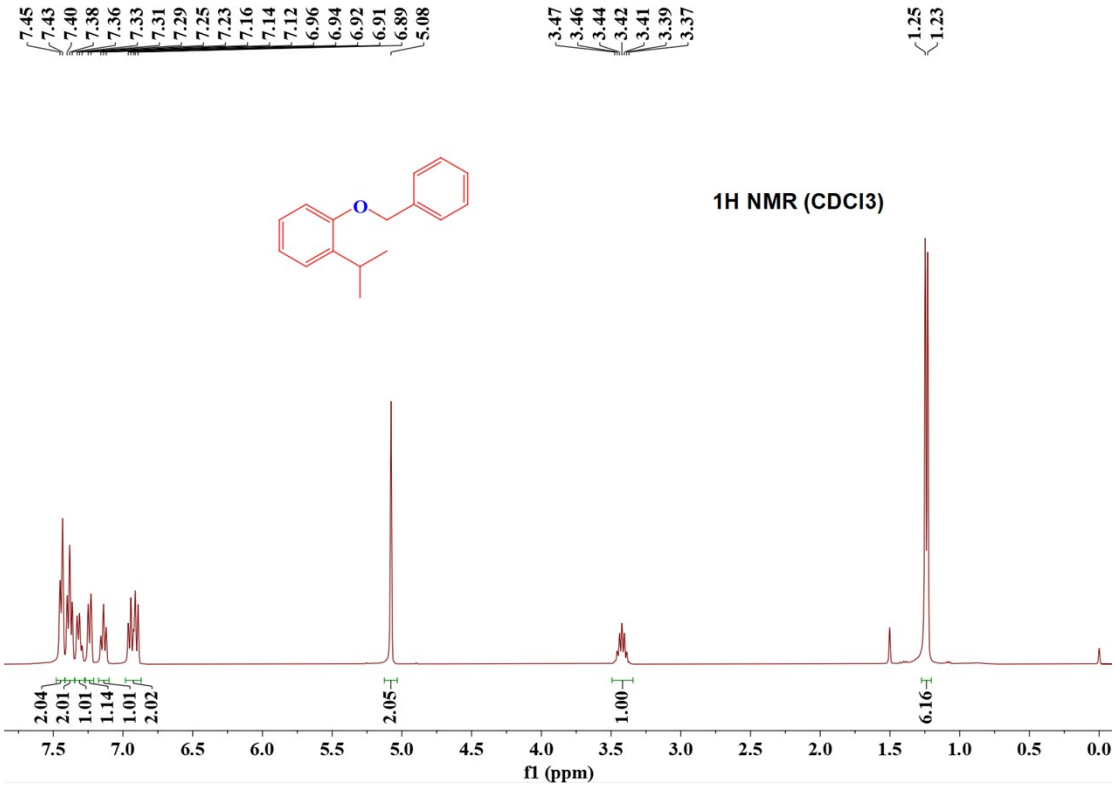


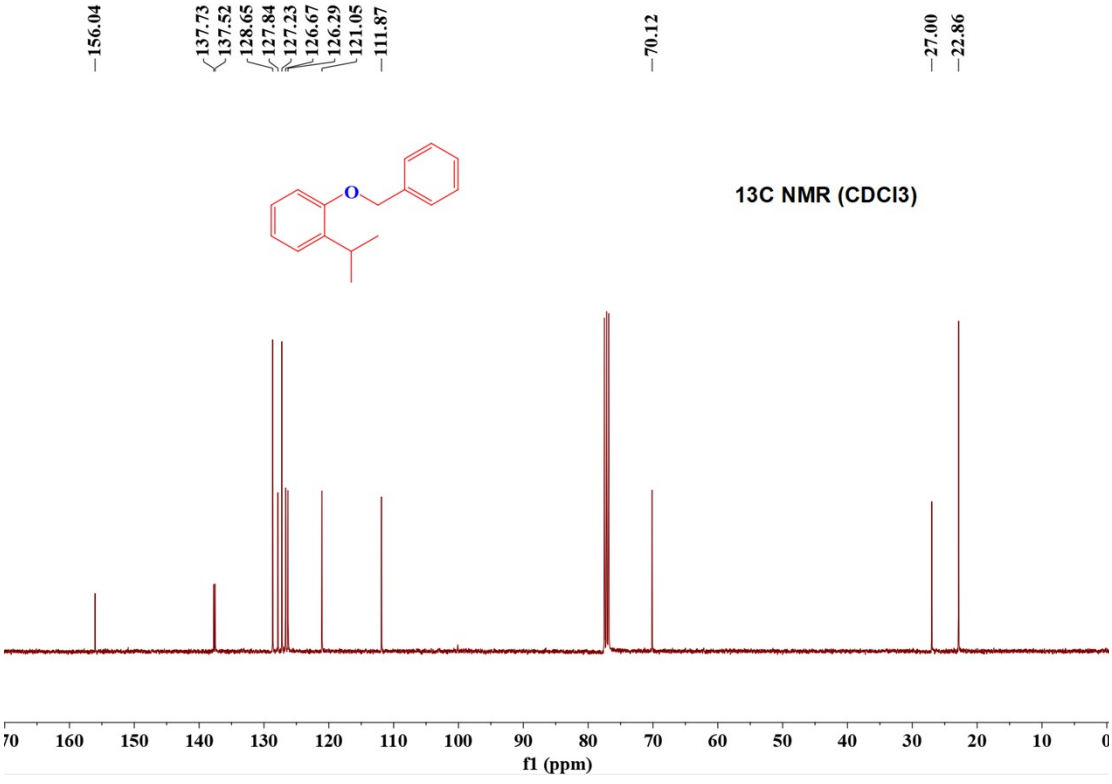
3. 1-benzyloxy-2-ethylbenzene (**2d**)



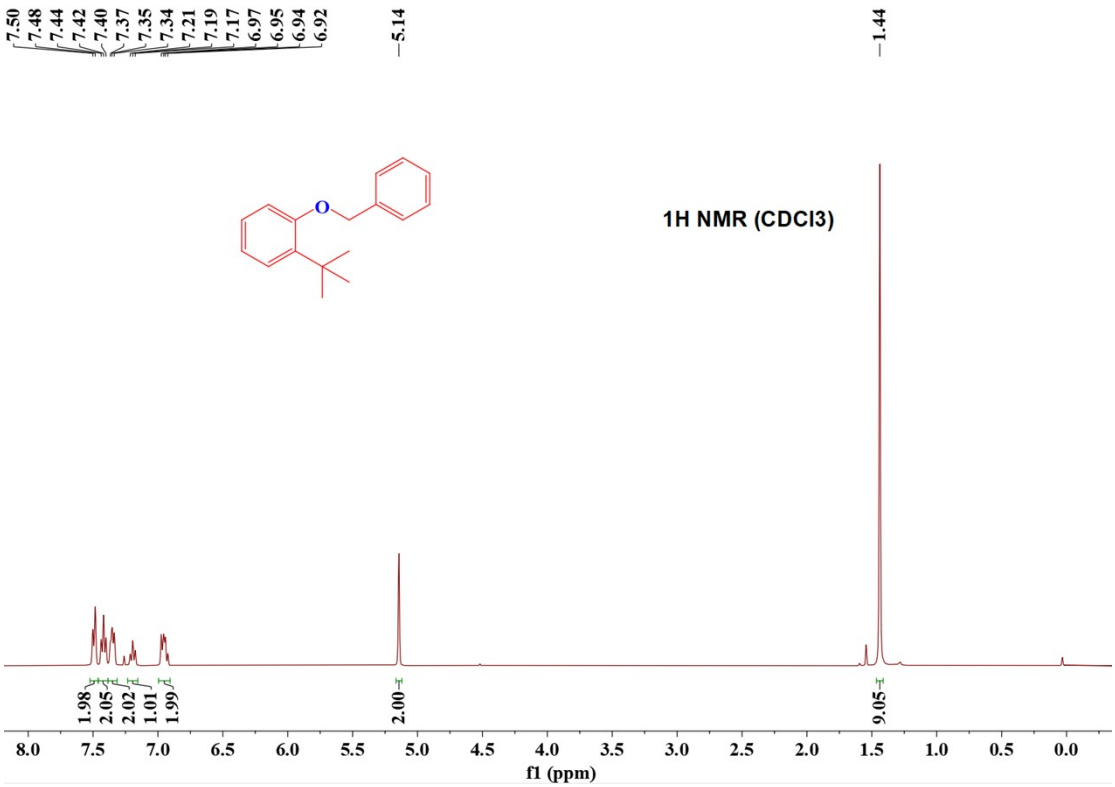


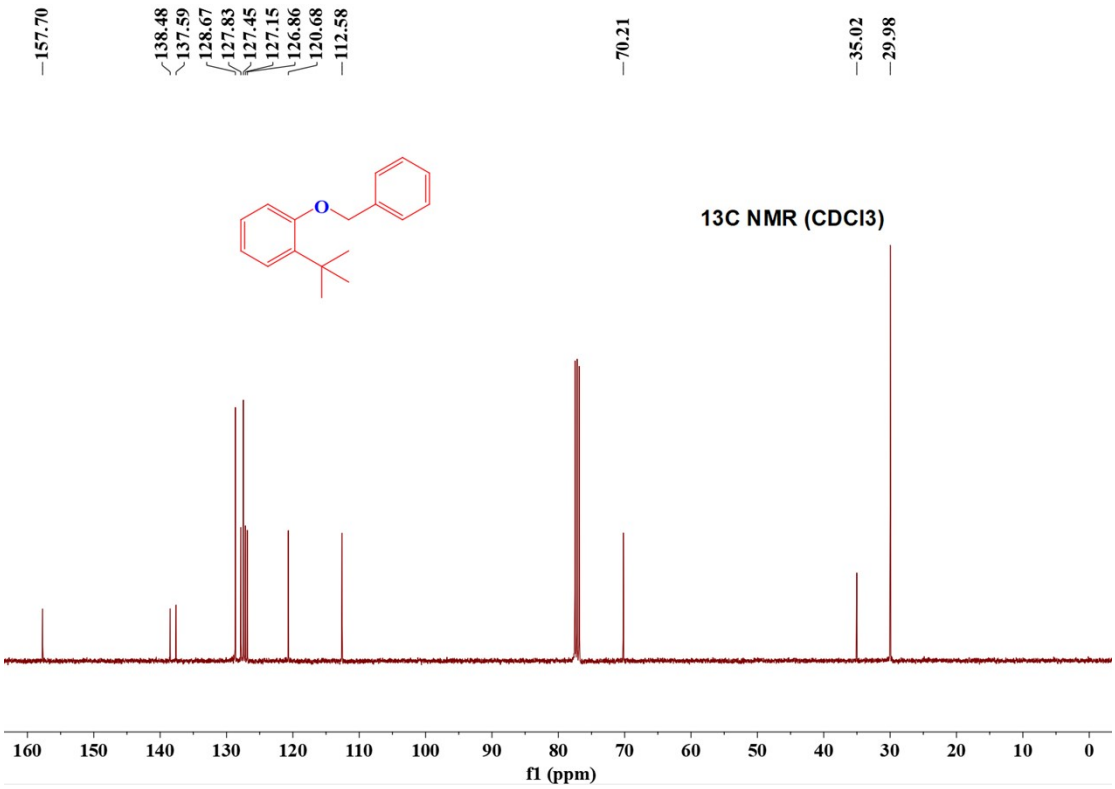
4. 1-benzyloxy-2-isopropylbenzene (**2e**)



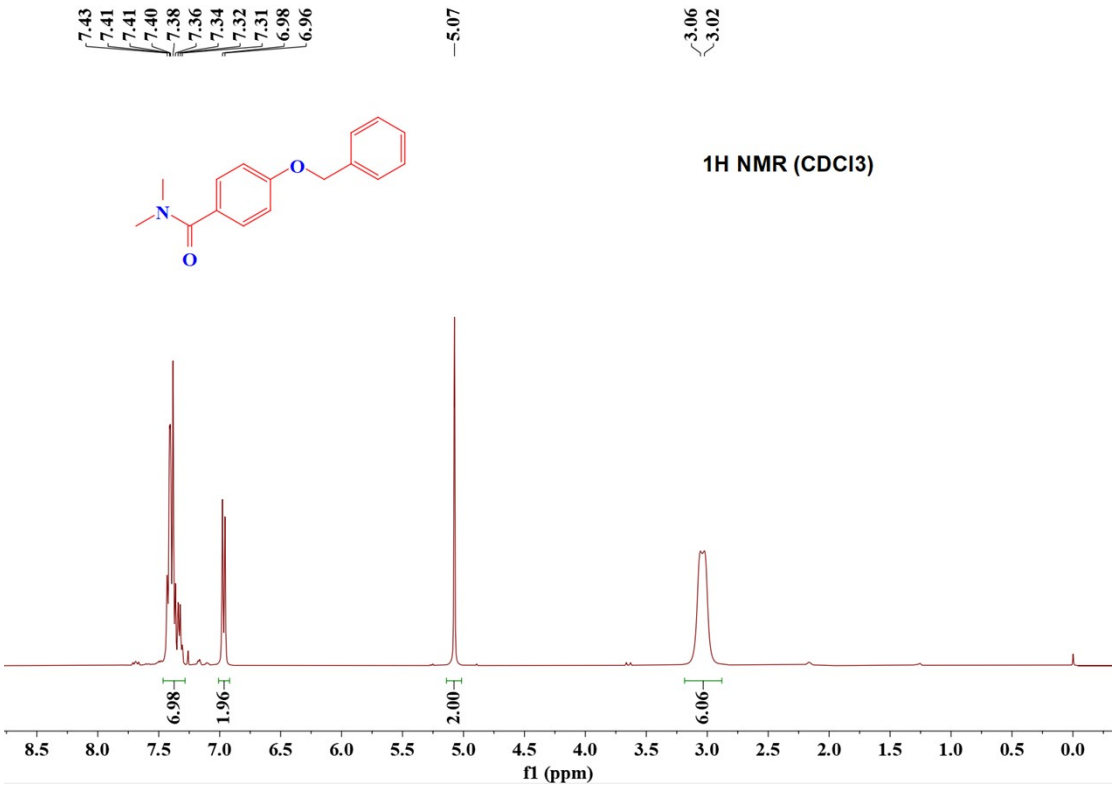


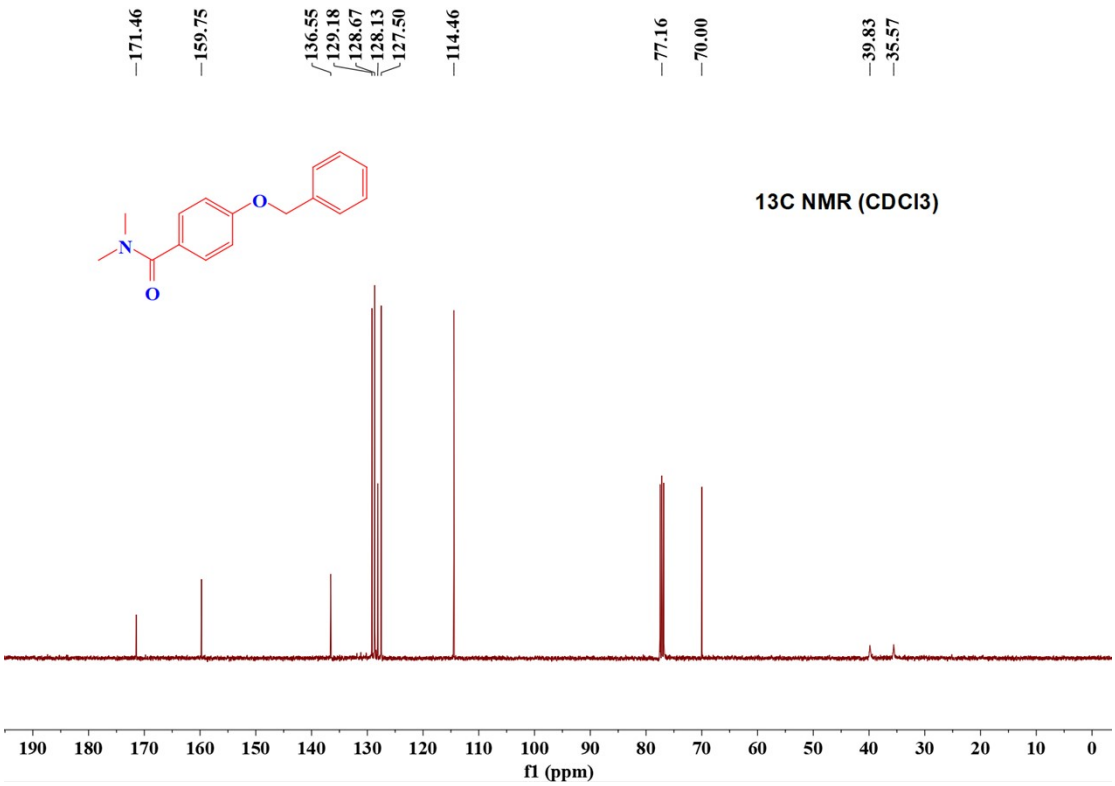
5. 1-benzyloxy-2-*tert*-butylbenzene (**2f**)



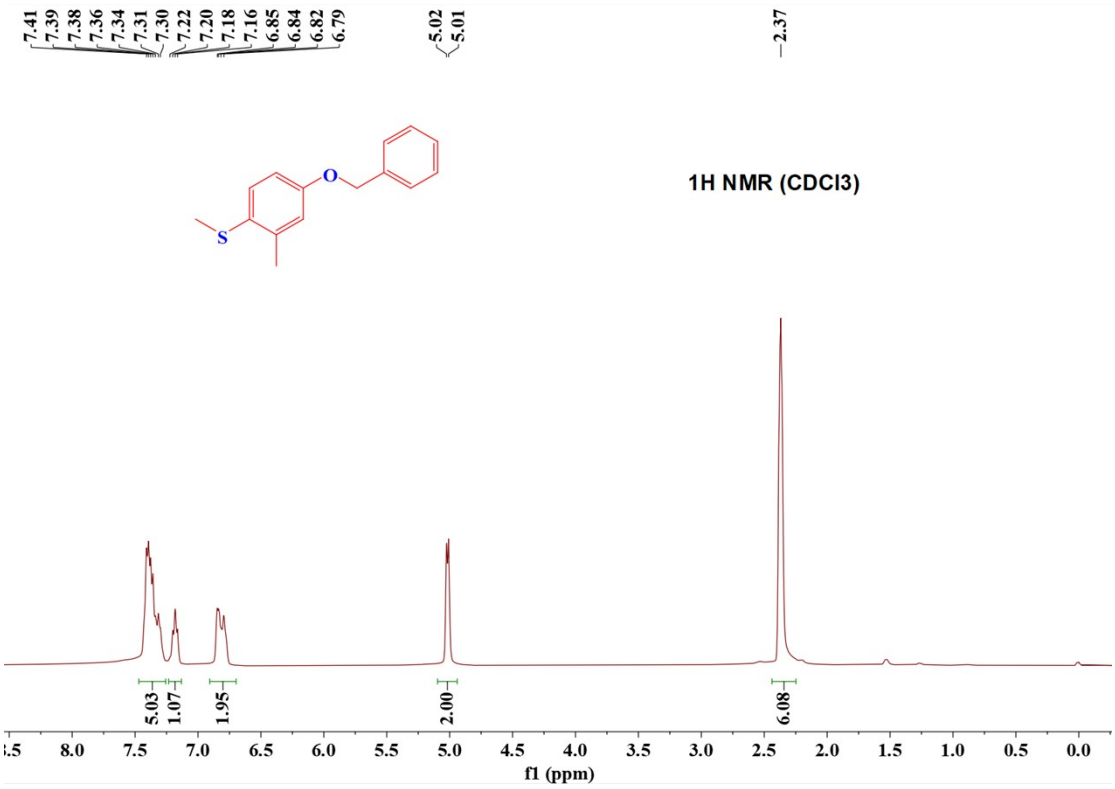


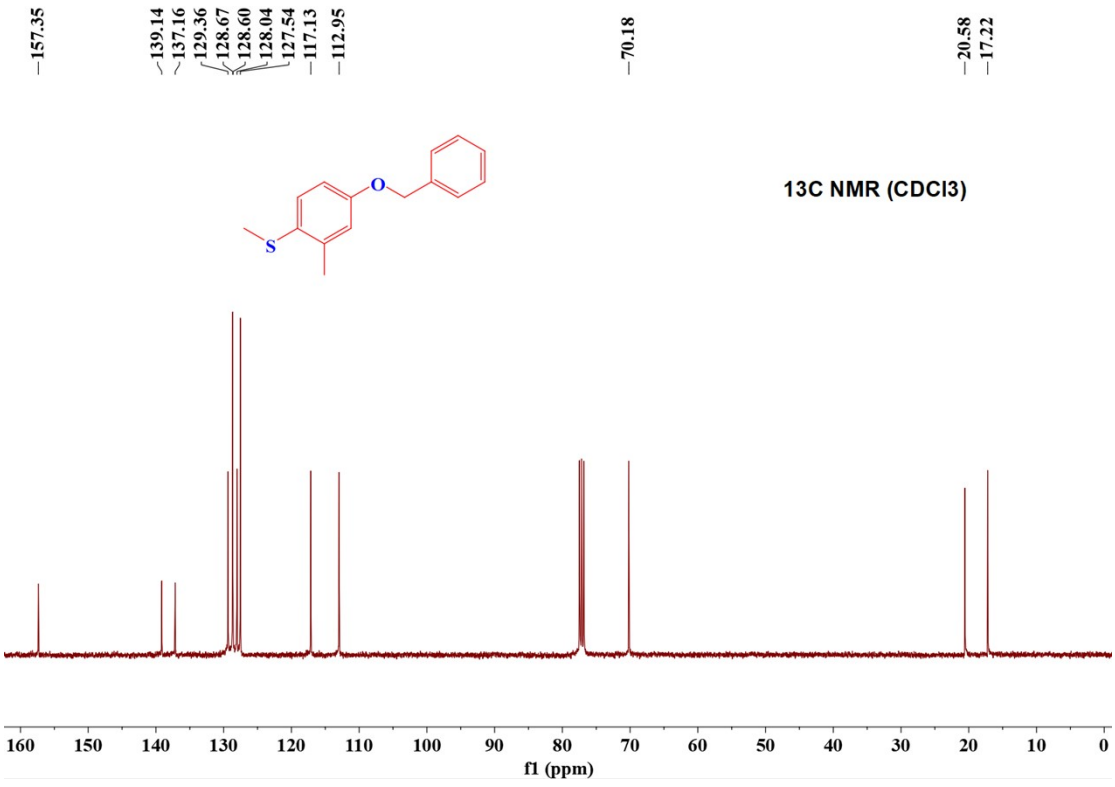
6. 4-benzyloxy-*N*,*N*-dimethylbenzamide (**2l**)



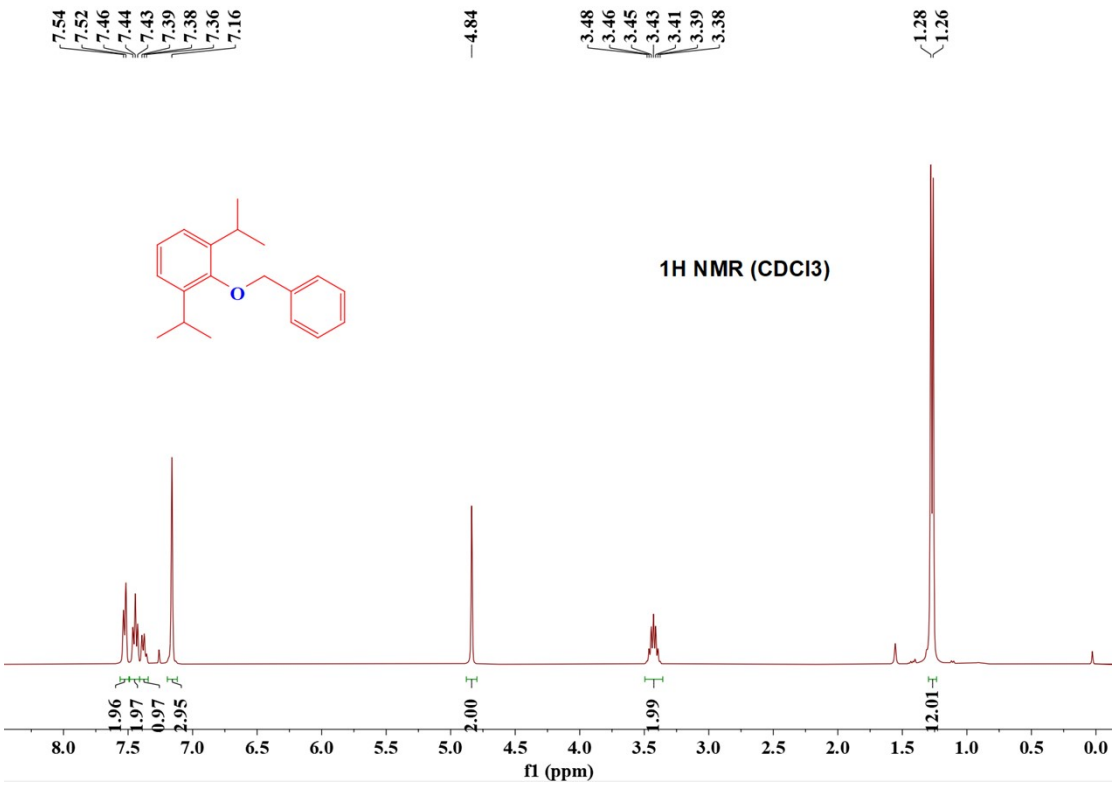


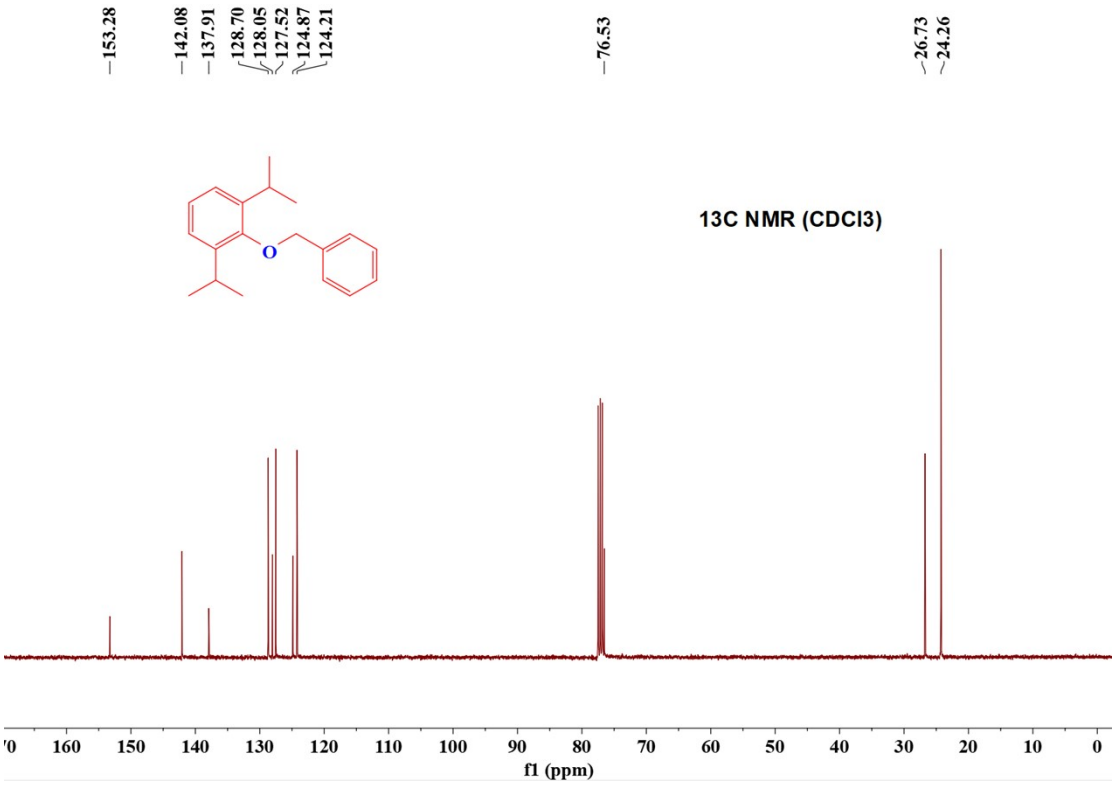
7. 4-benzyloxy-2-methyl-1-methylsulfanylbenzene (**2m**)



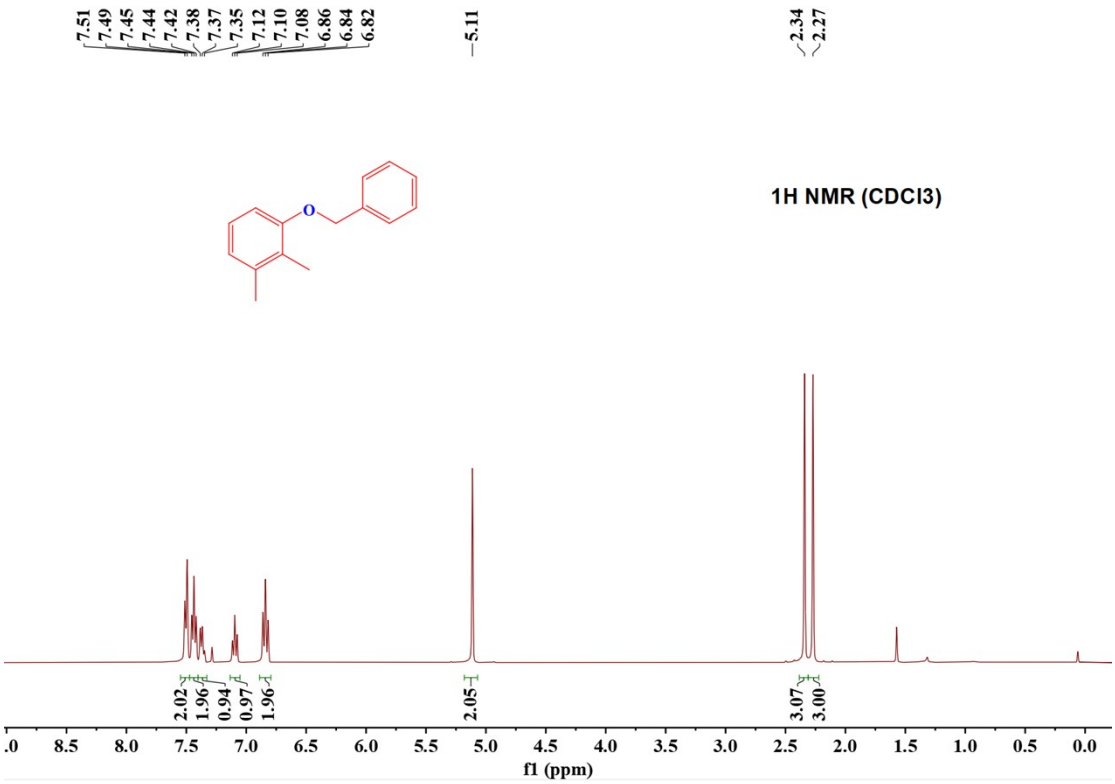


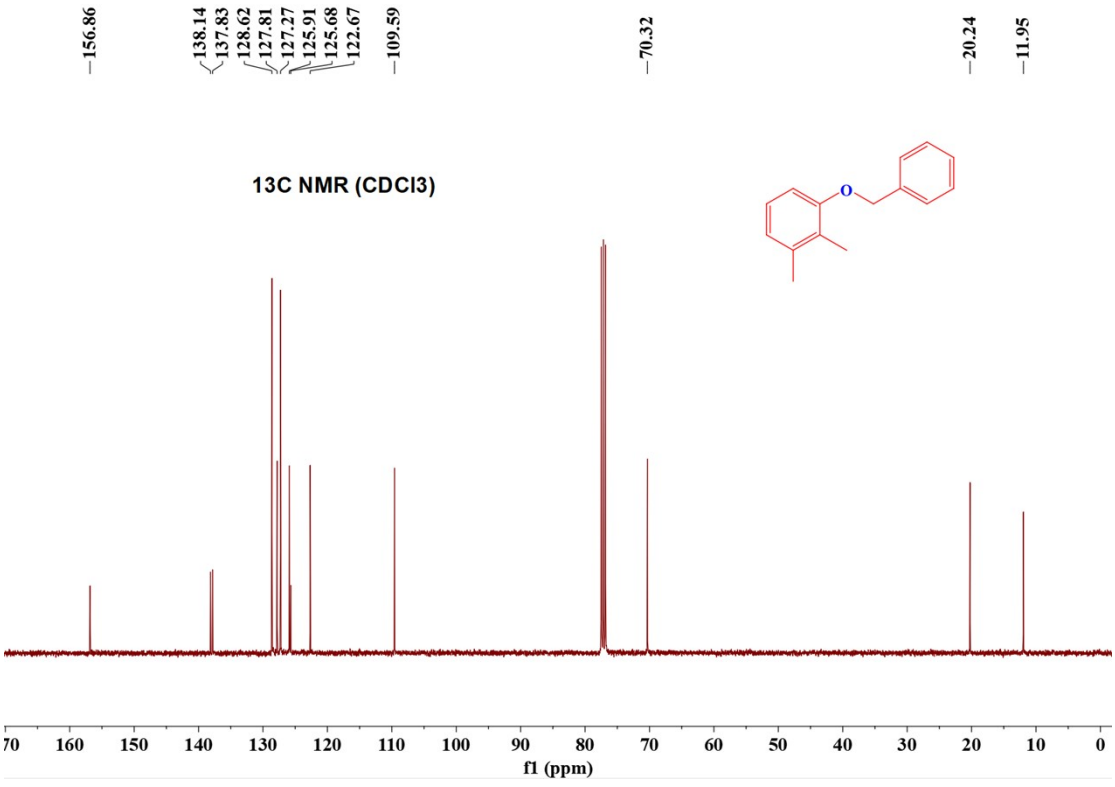
8. 2-benzyloxy-1,3-diisopropylbenzene (**2o**)



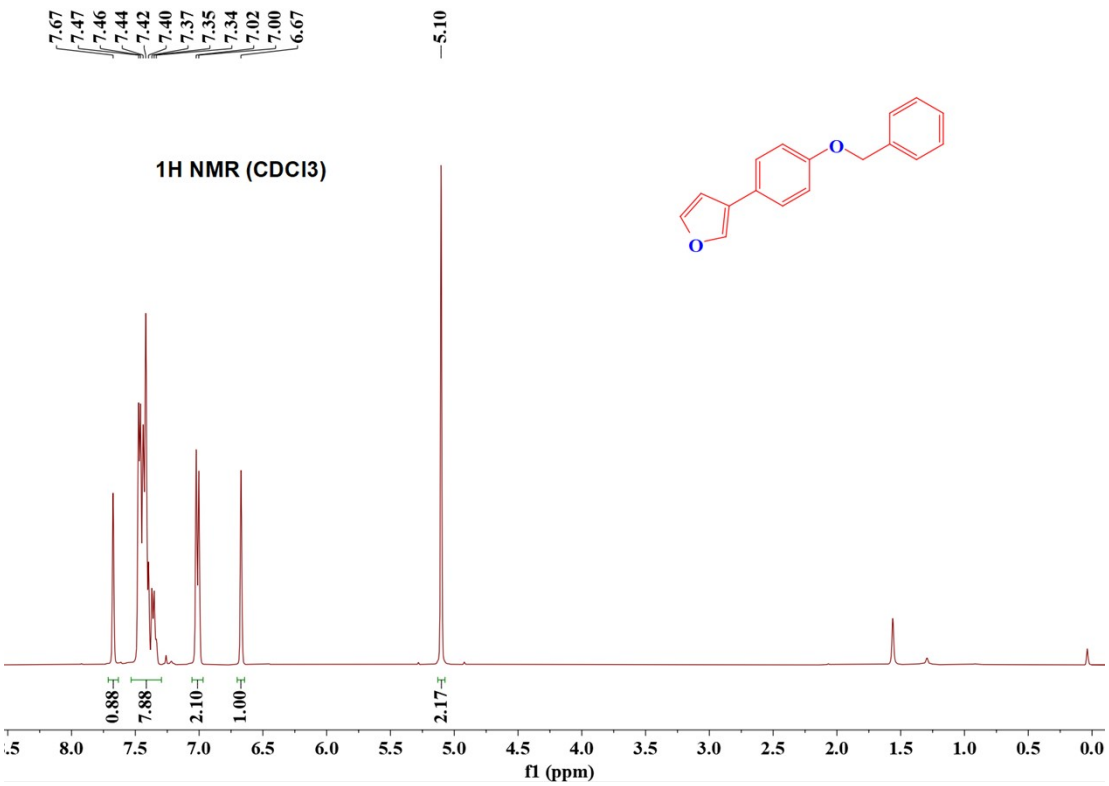


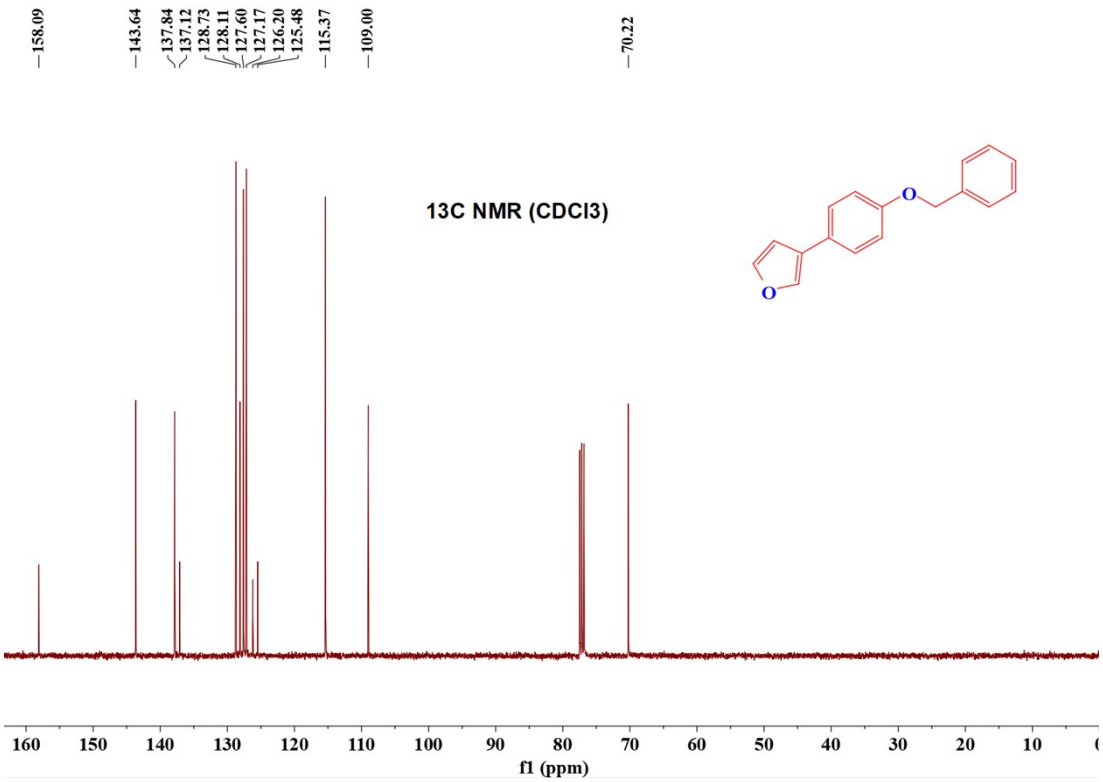
9. 1-benzyloxy-2,3-dimethylbenzene (**2p**)



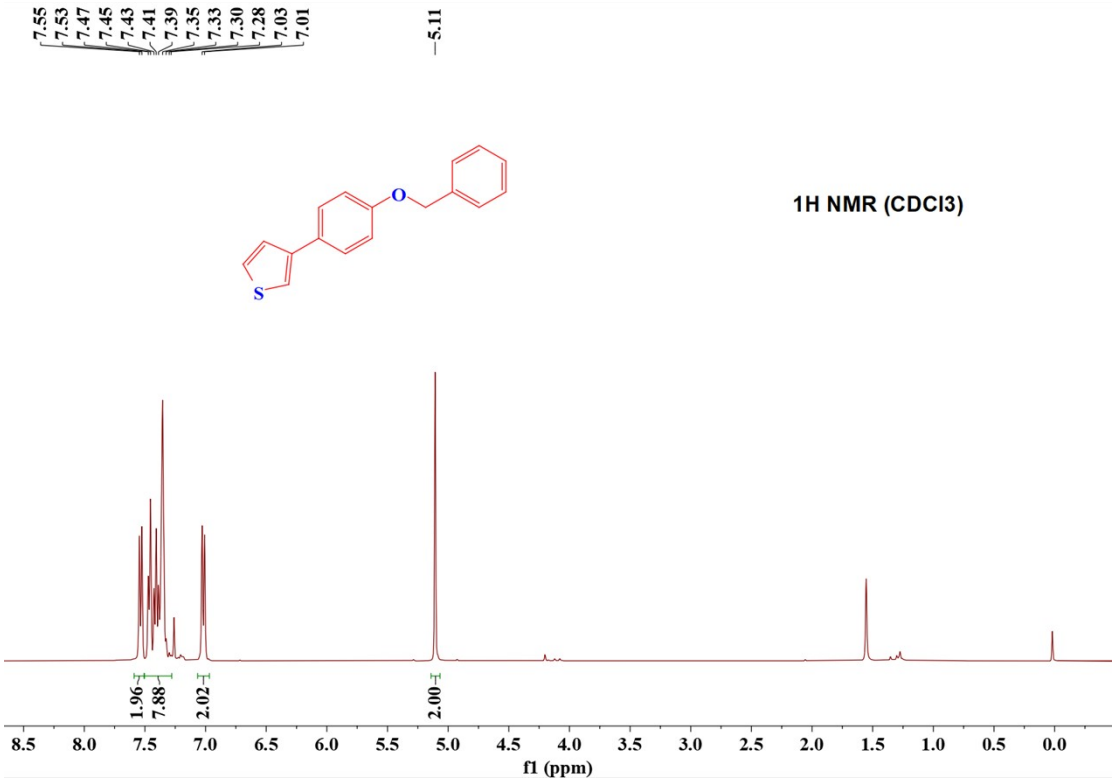


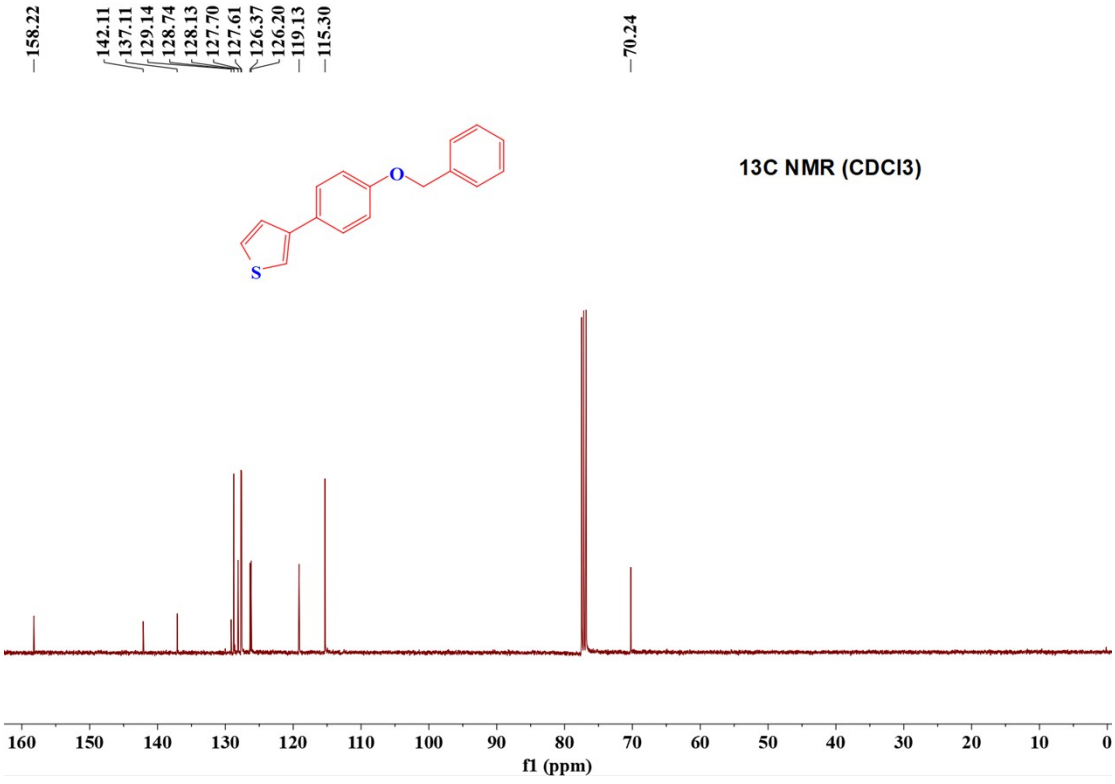
10. 3-(4-benzyloxyphenyl)furan (**2s**)



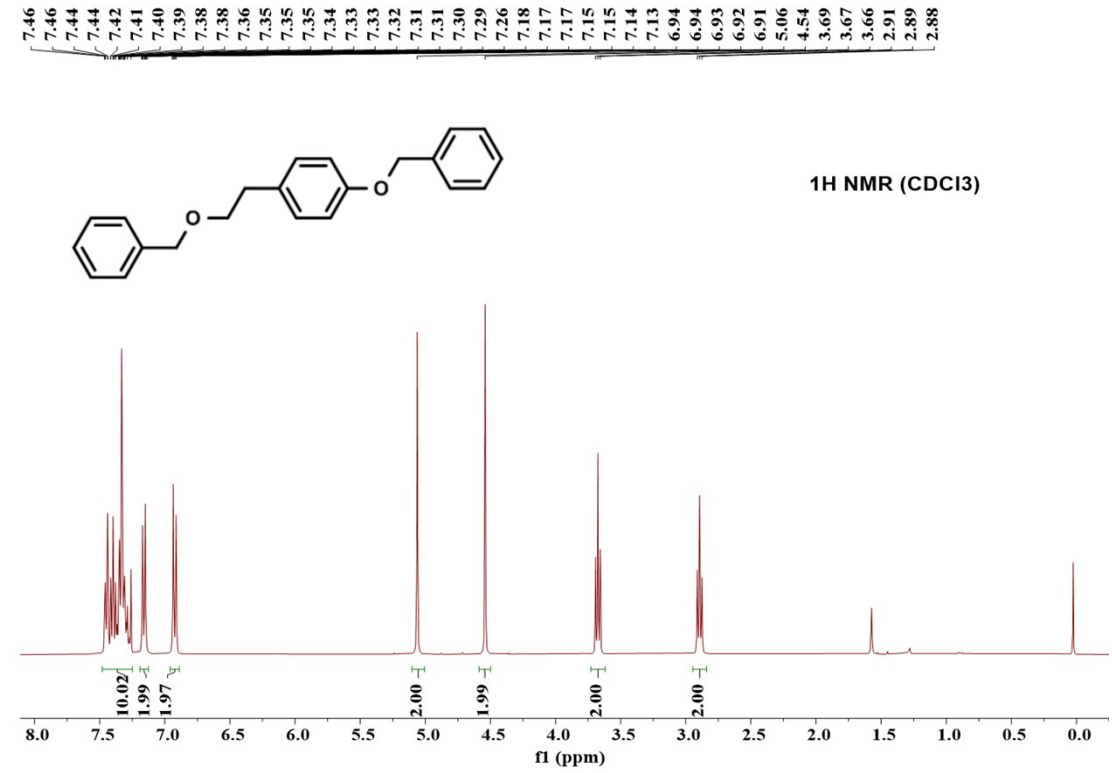


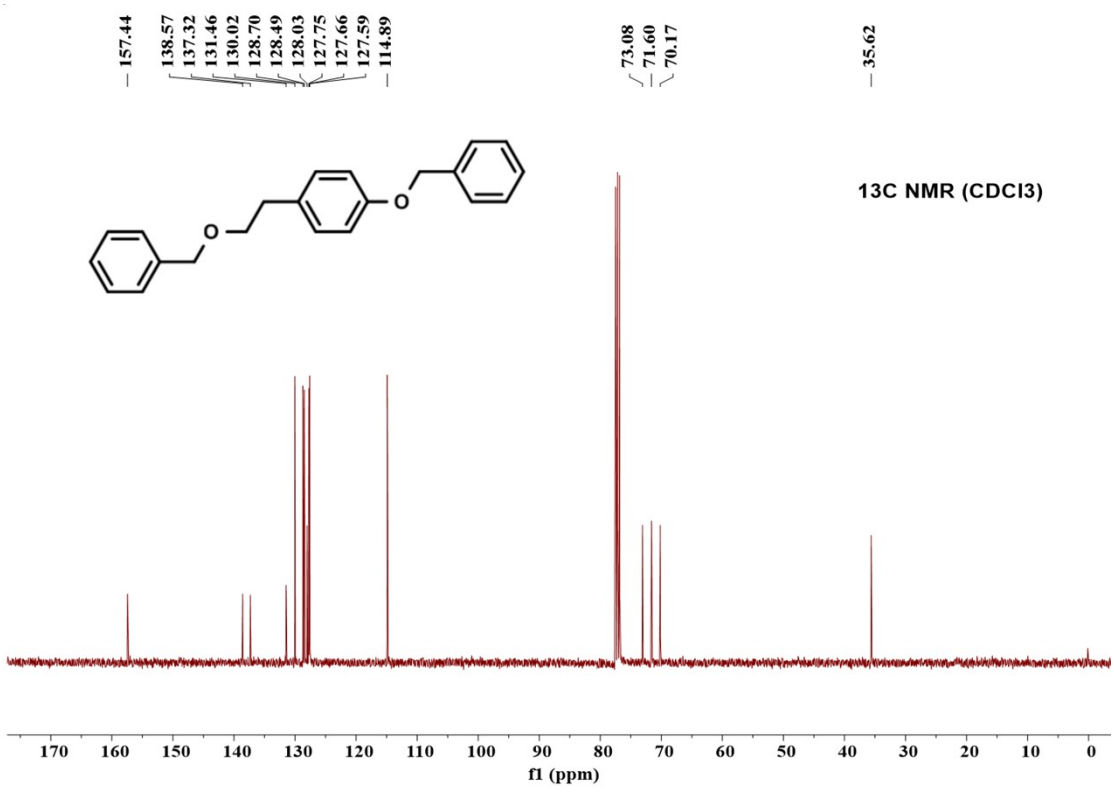
11. 3-(4-benzyloxyphenyl)thiophene (**2t**)



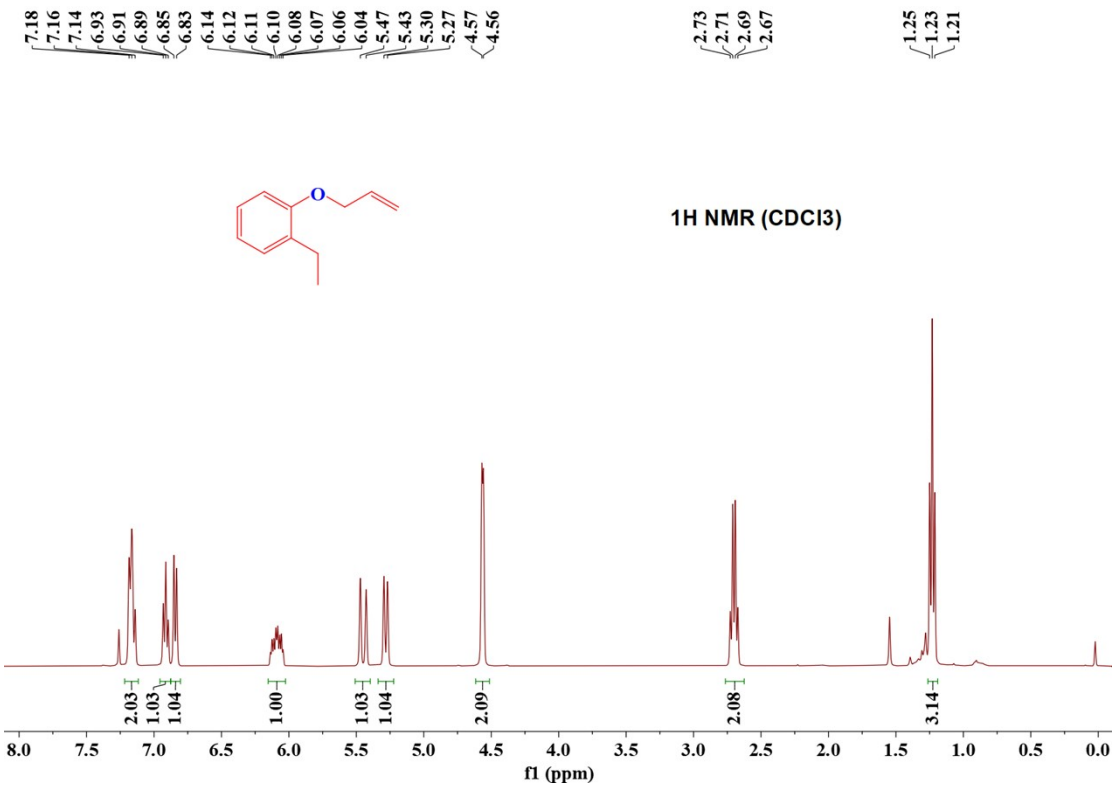


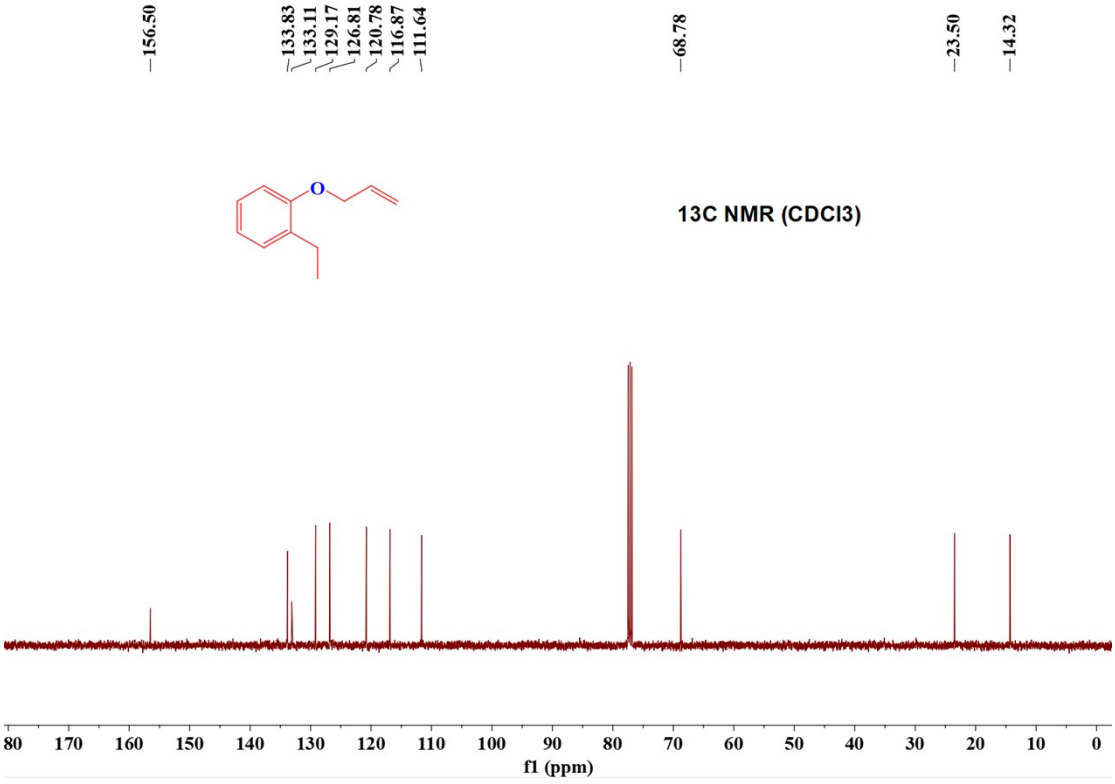
12. 1-benzyloxy-4-(2-benzyloxyethyl)benzene (**2ab**)



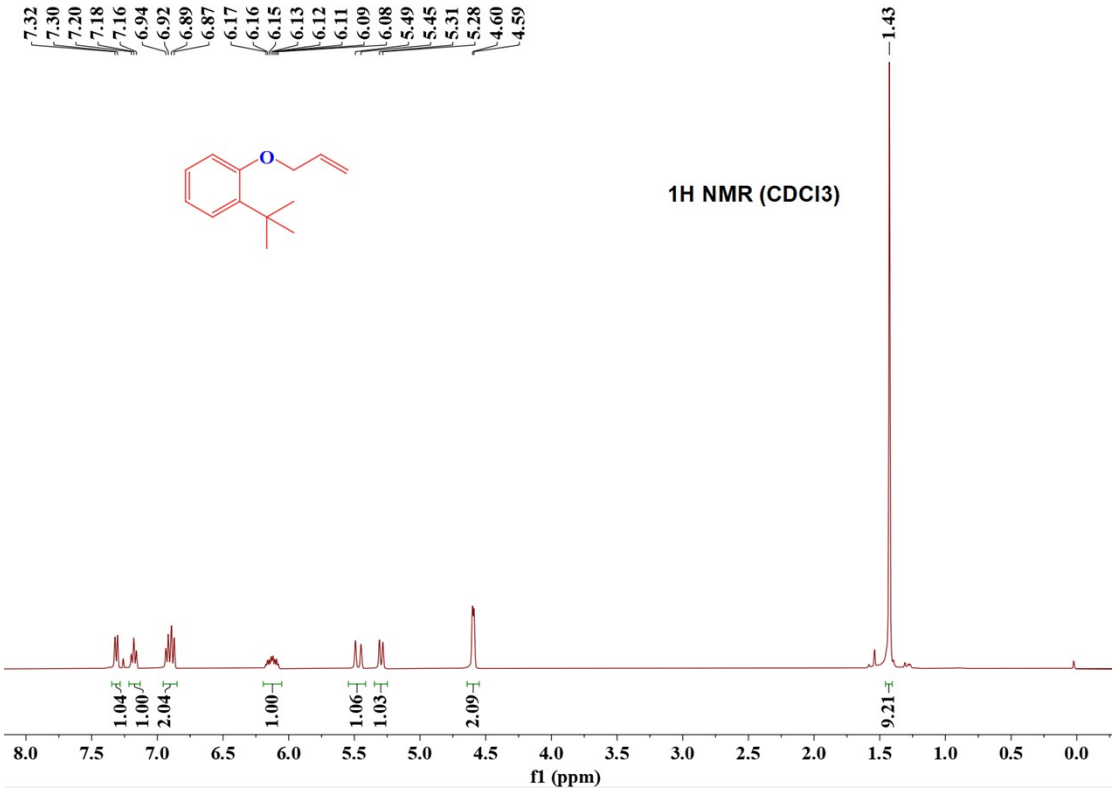


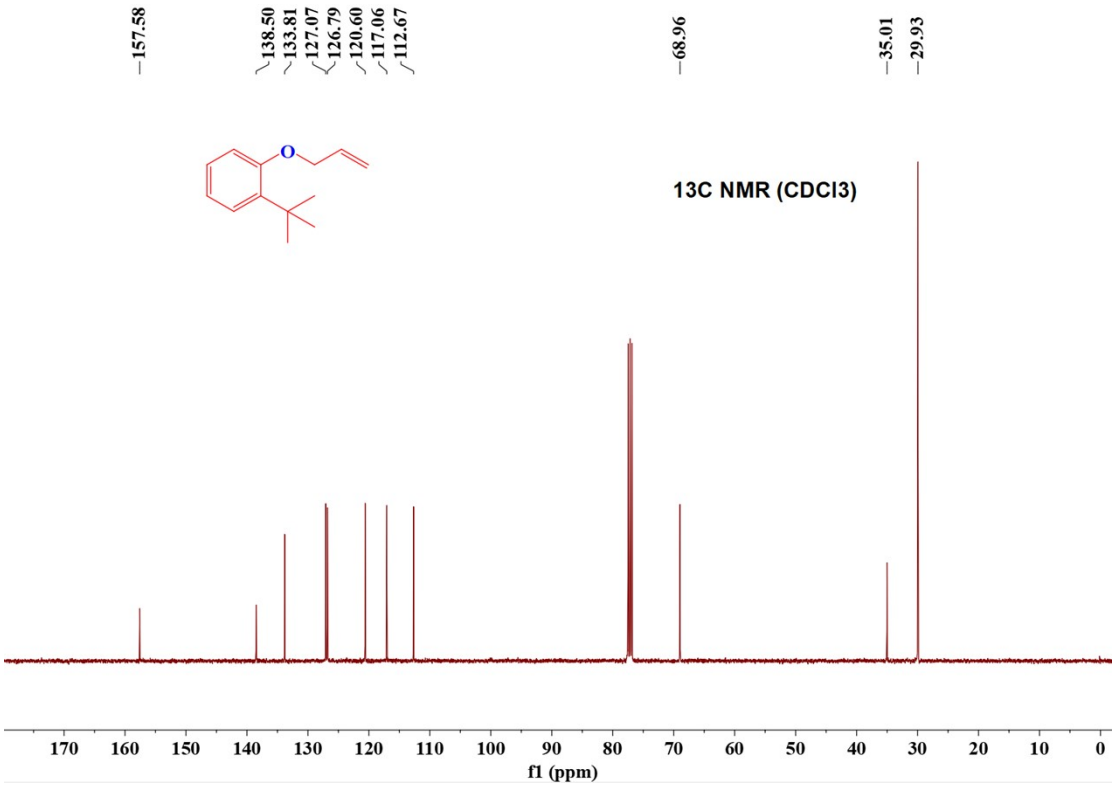
13. 1-allyloxy-2-ethylbenzene (**3d**)



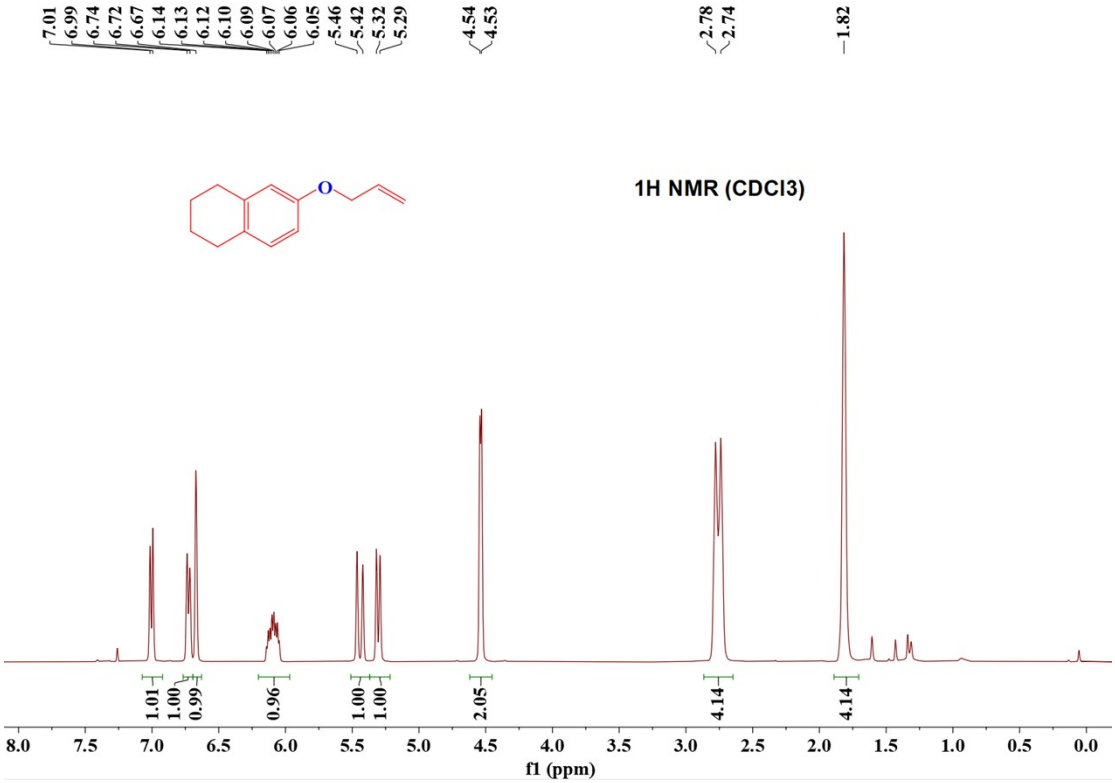


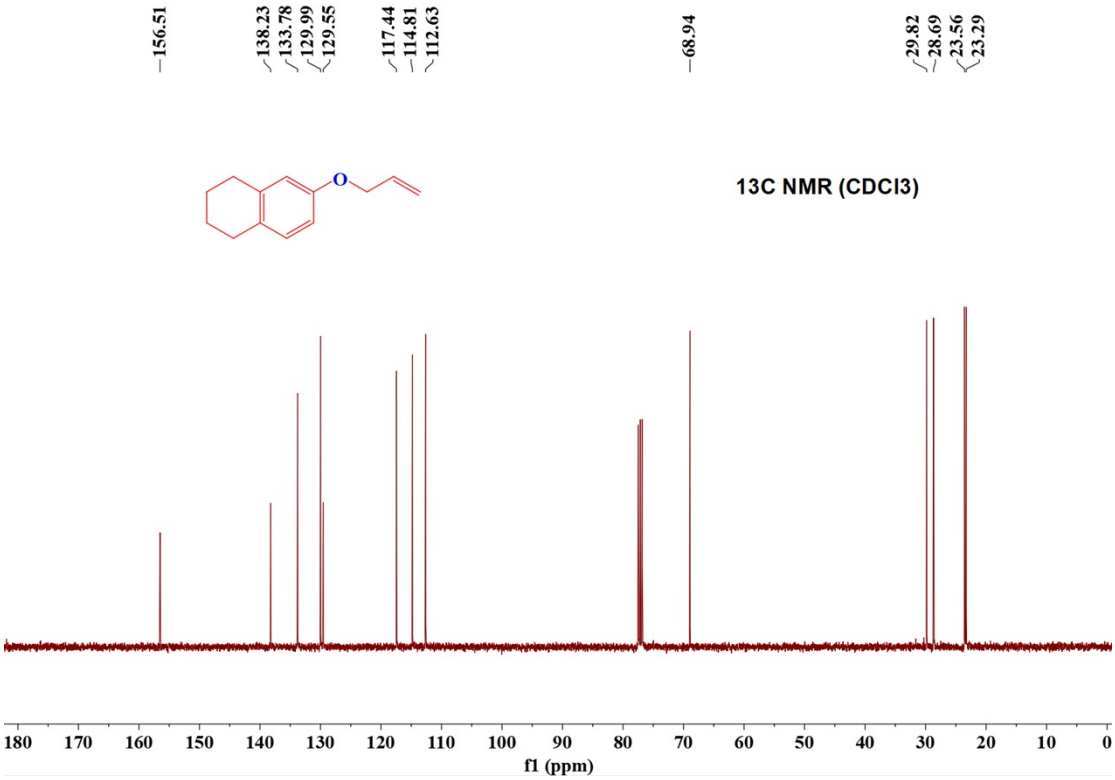
14. 1-allyloxy-2-*tert*-butylbenzene (**3f**)



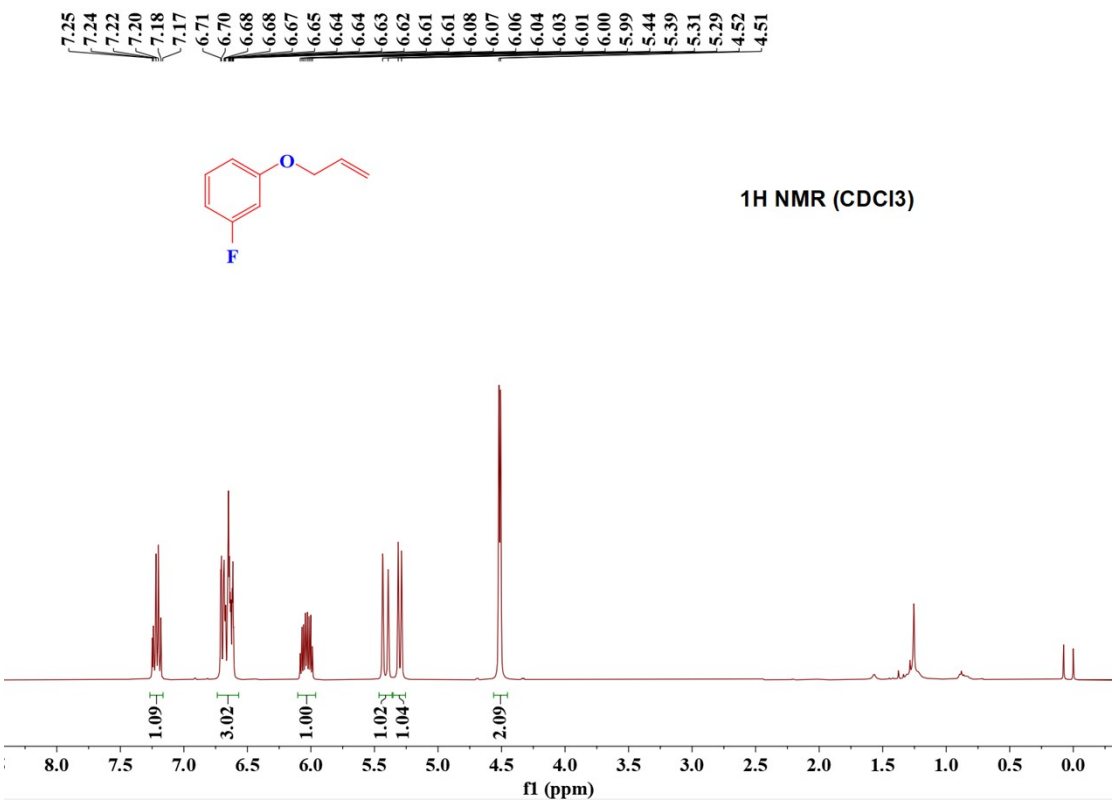


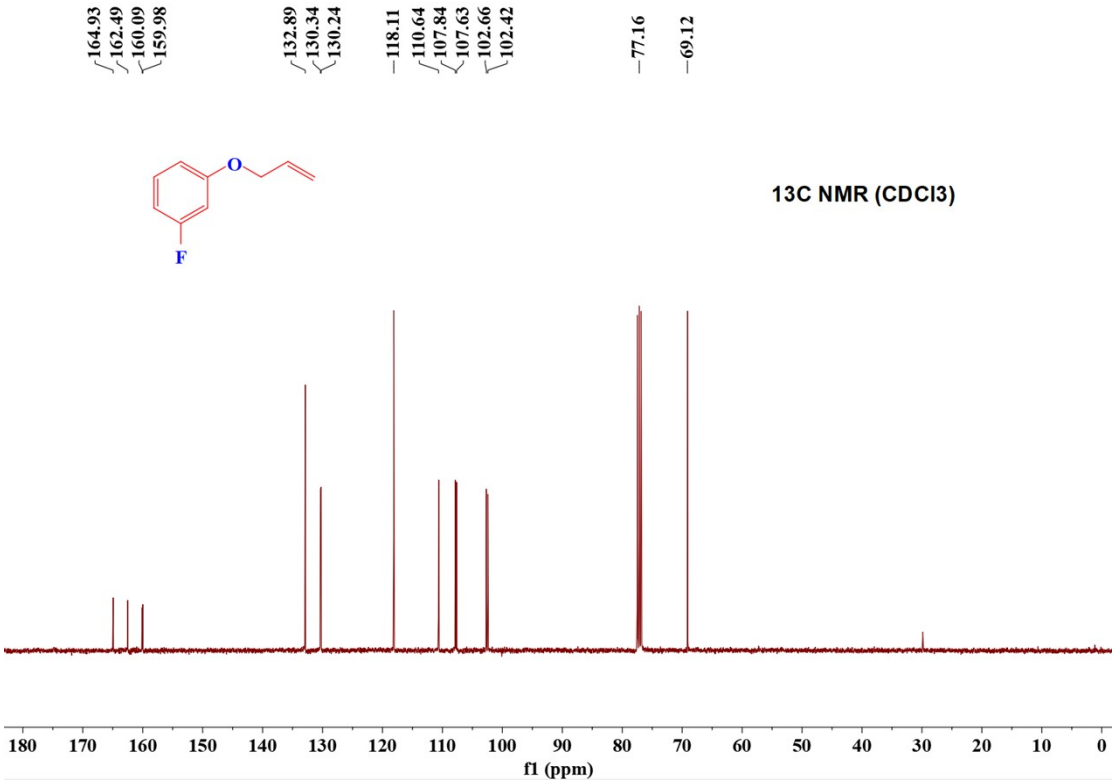
15. 6-allyloxy-1,2,3,4-tetrahydronaphthalene (**3h**)

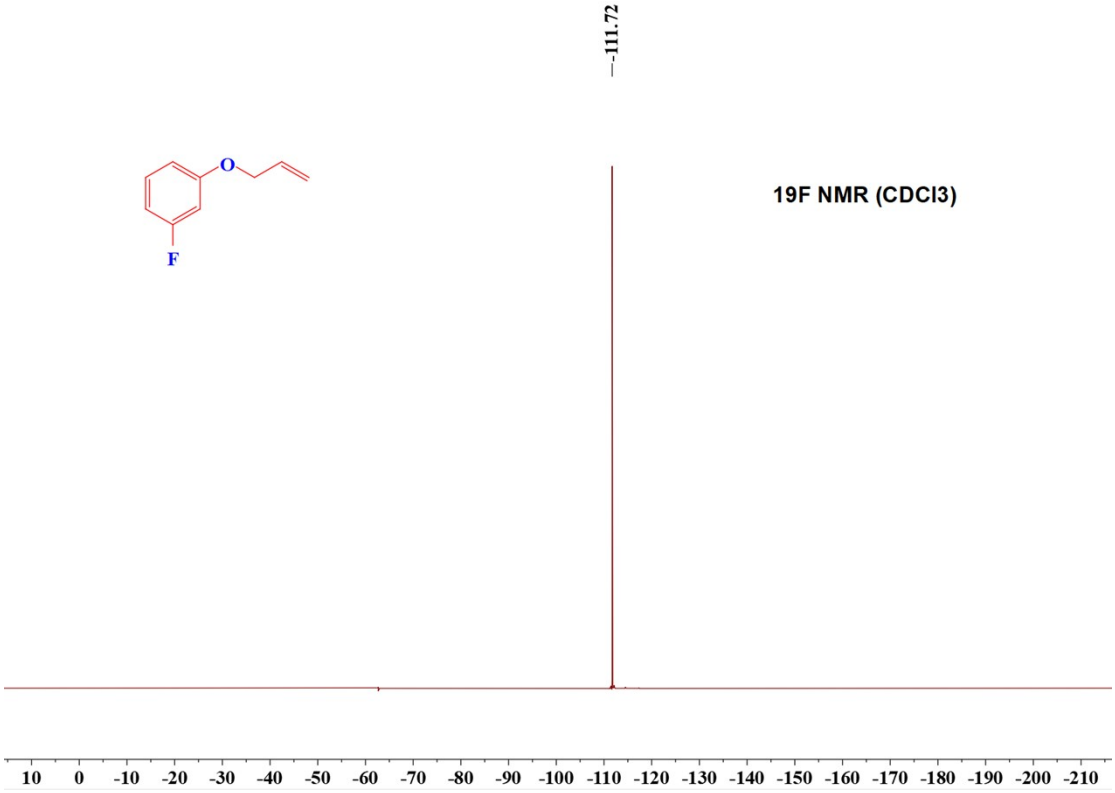




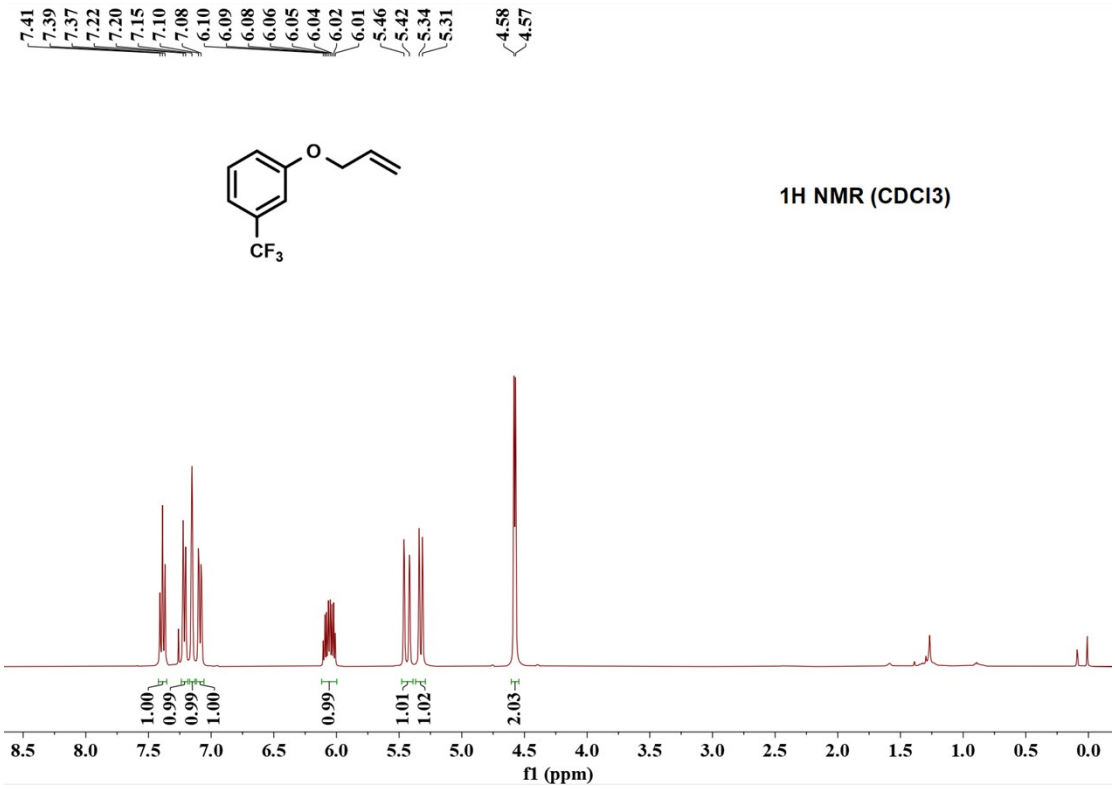
16. 1-allyloxy-3-fluorobenzene (**3j**)

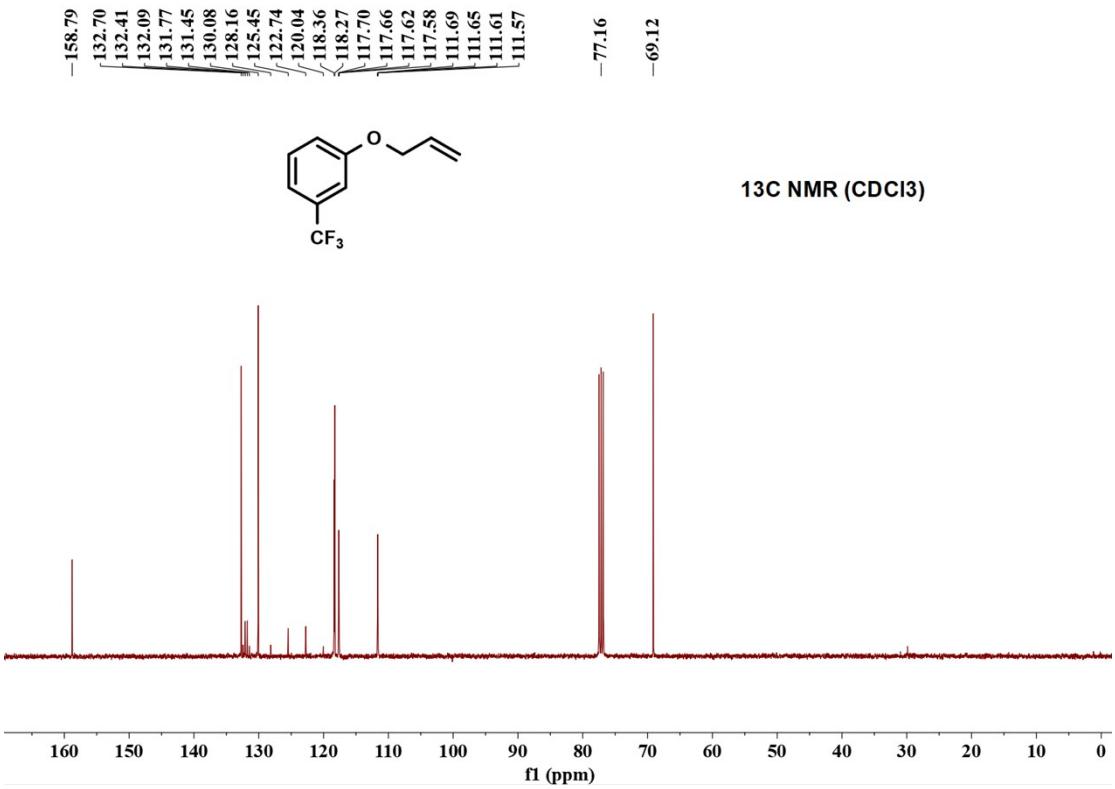


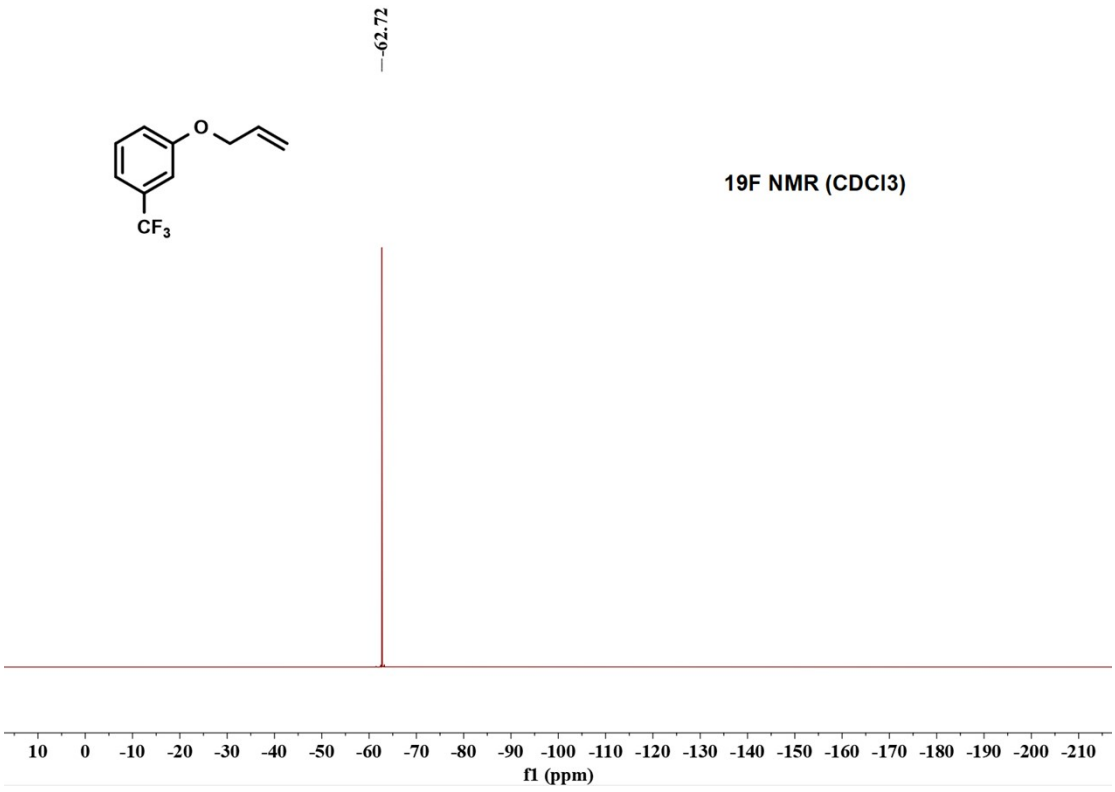




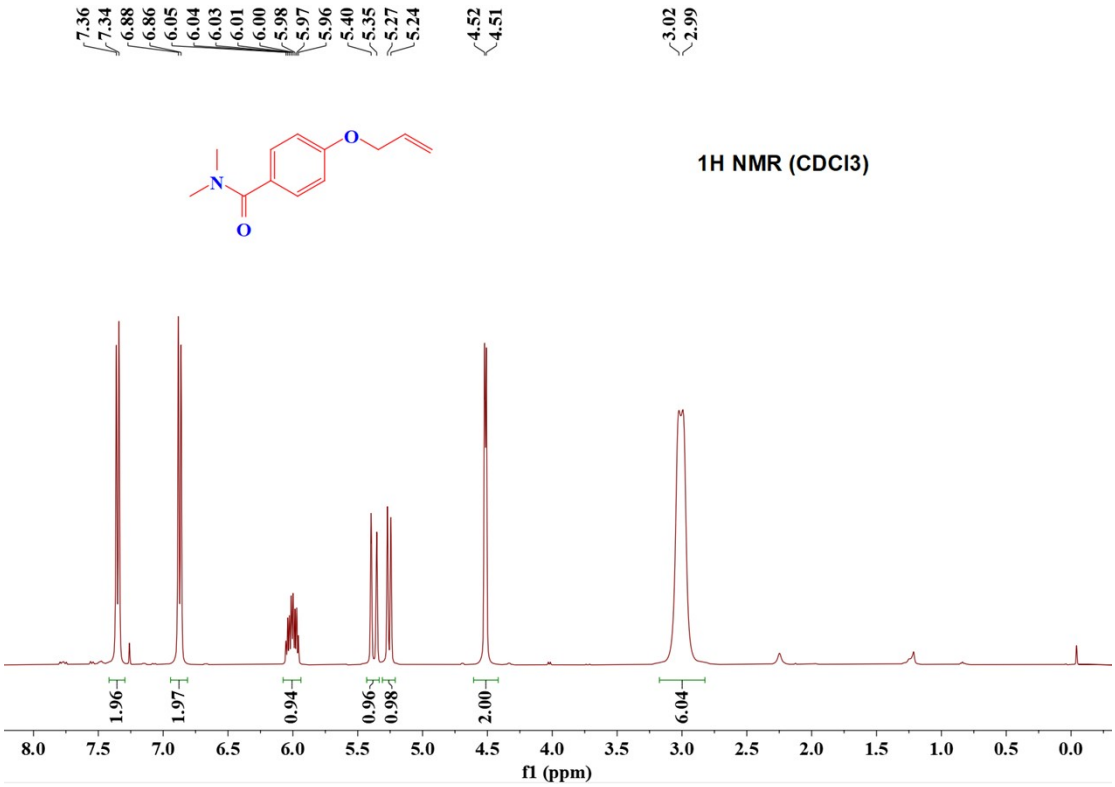
17. 1-allyloxy-3-trifluoromethylbenzene (**3k**)

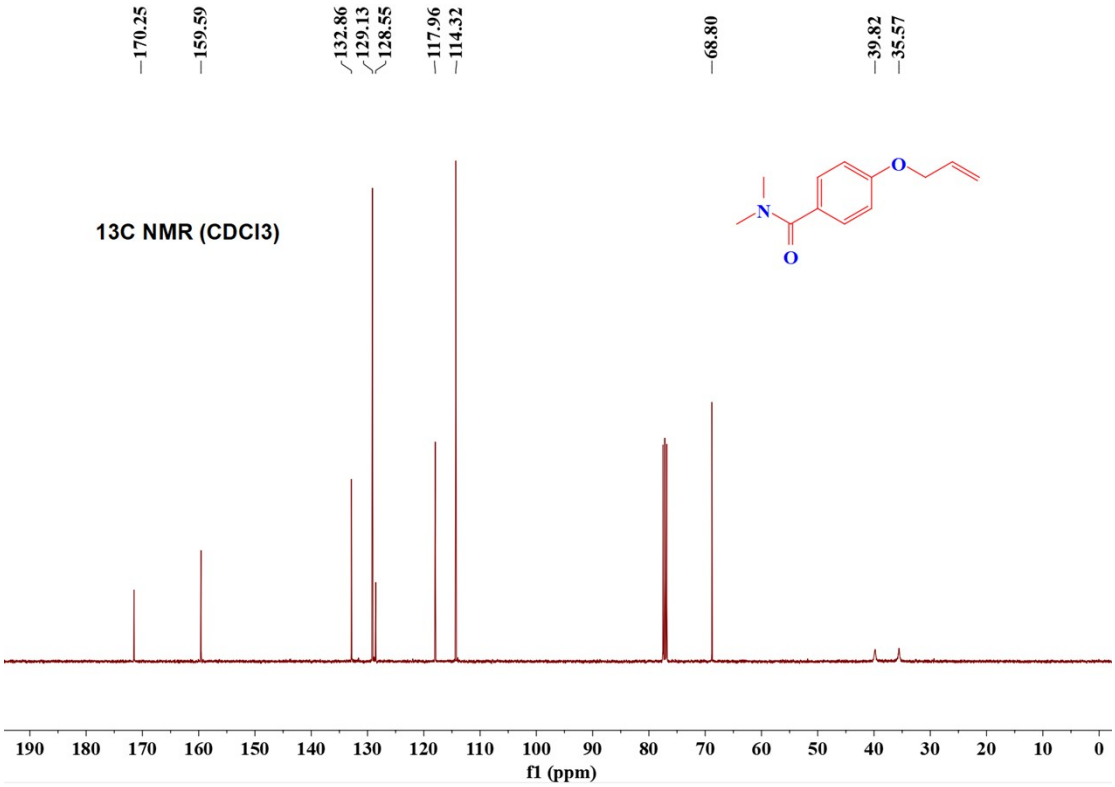



158.79
132.70
132.41
132.09
131.77
131.45
130.08
128.16
125.45
122.74
120.04
118.36
118.27
117.70
117.66
117.62
117.58
111.69
111.65
111.61
111.57
77.16
69.12
O
CF3
13C NMR (CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

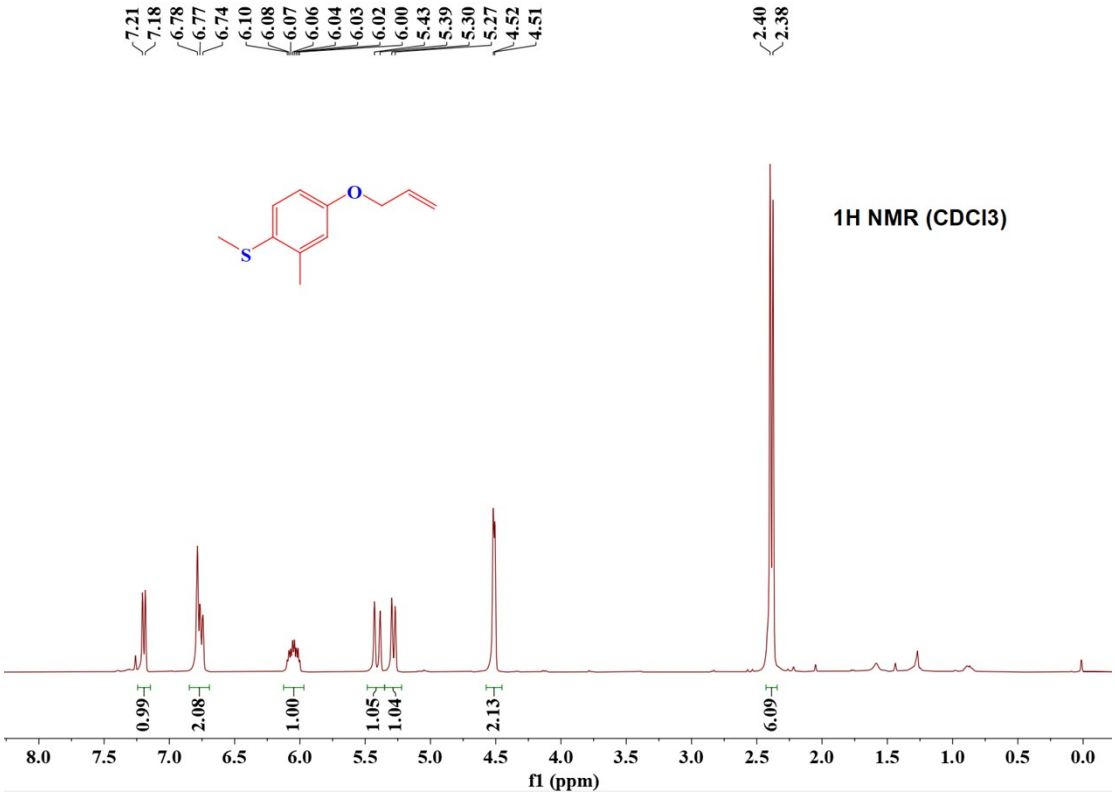

62.72
O
CF3
19F NMR (CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

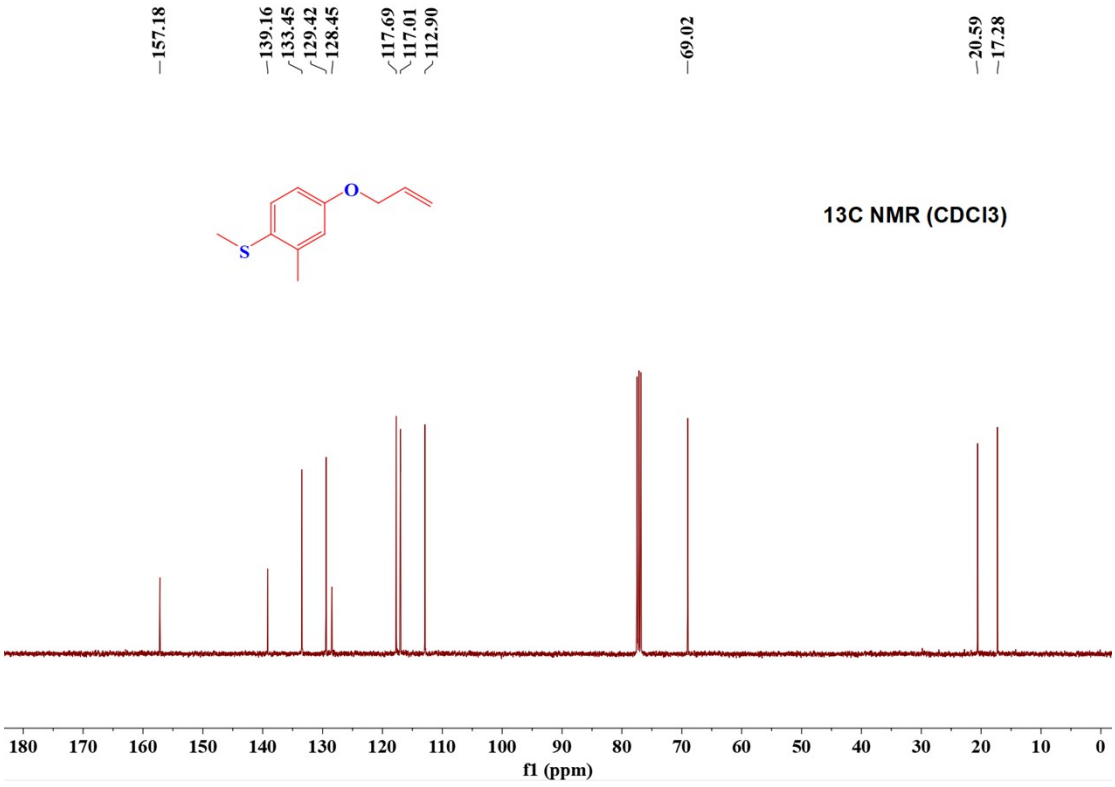
18. 4-allyloxy-*N*,*N*-dimethylbenzamide (**3l**)



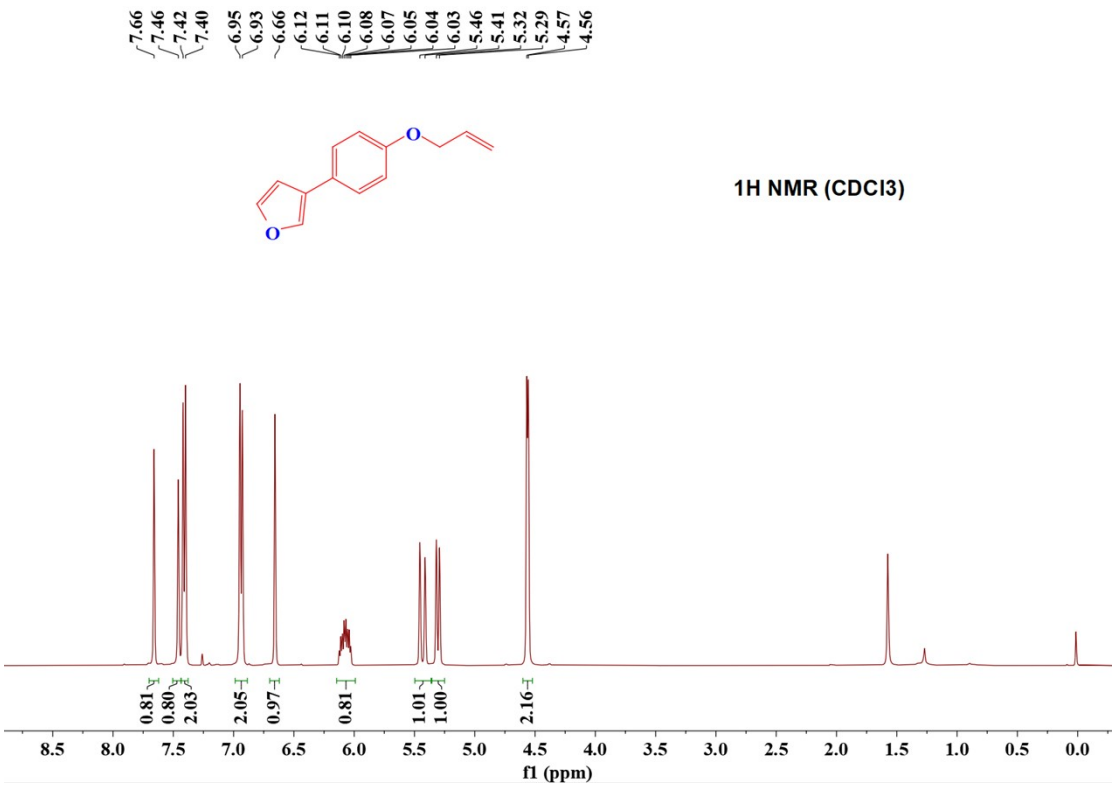


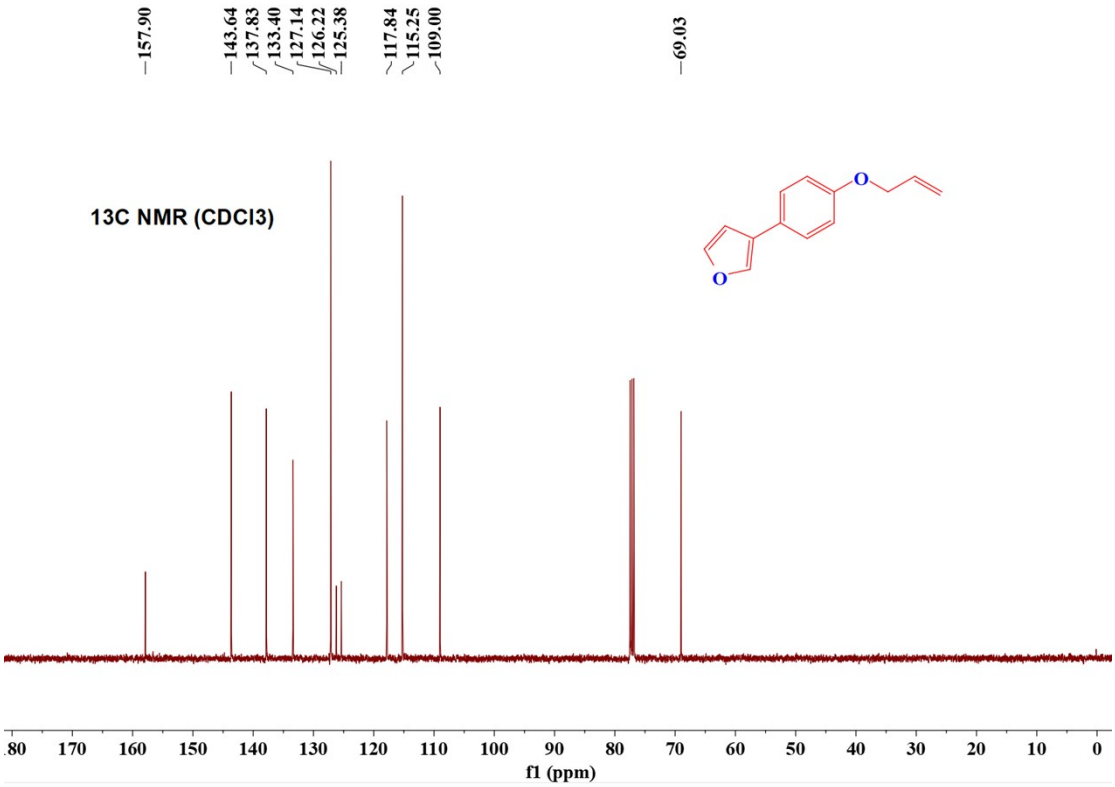
19. 4-allyloxy-2-methyl-1-methylsulfanylbenzene (**3m**)



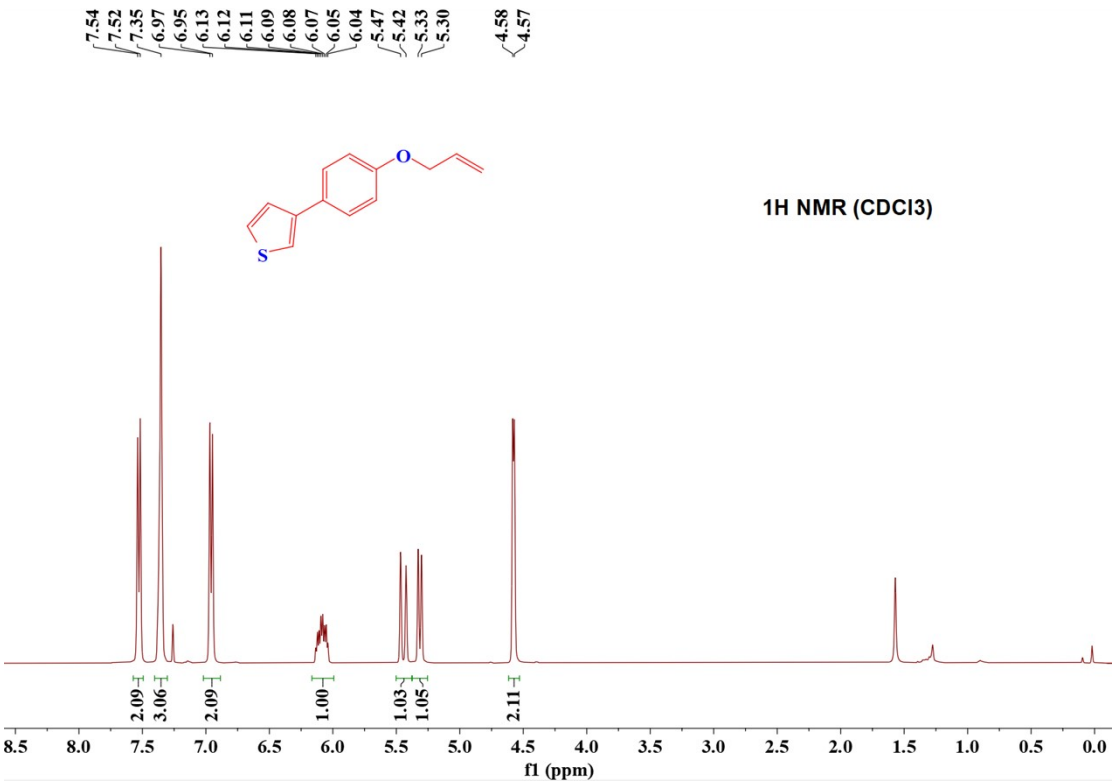


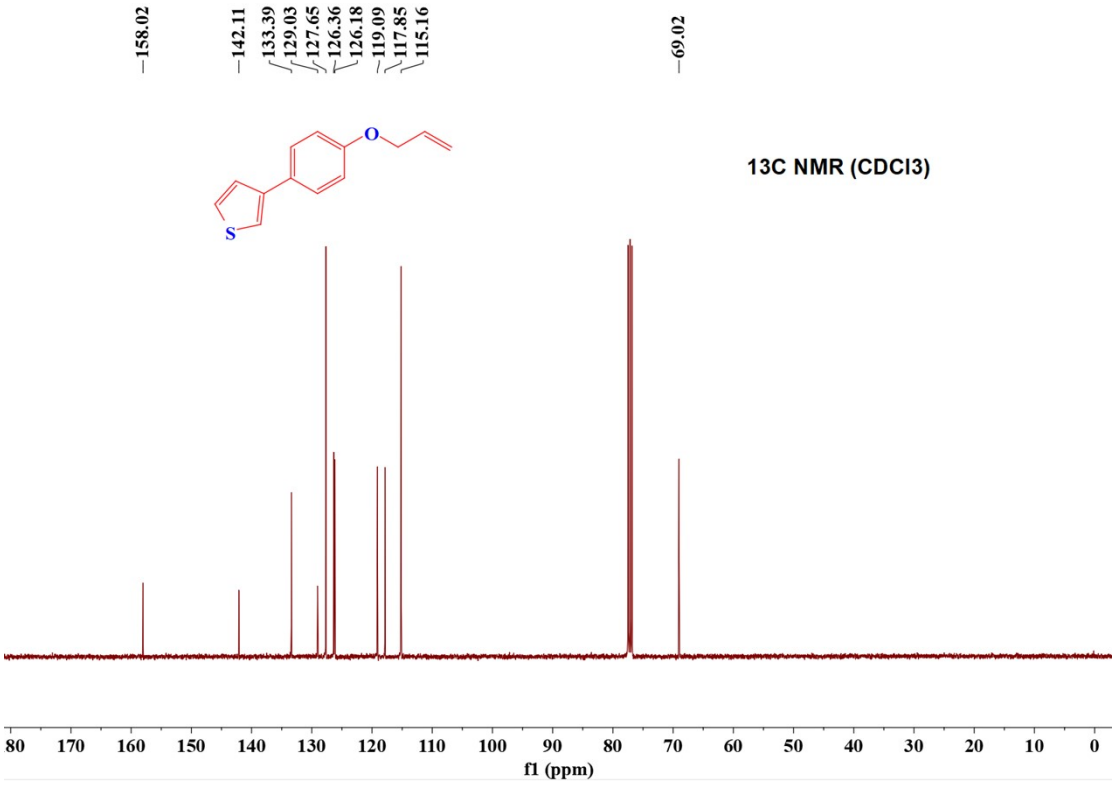
20. 3-(4-allyloxyphenyl)furan (**3s**)



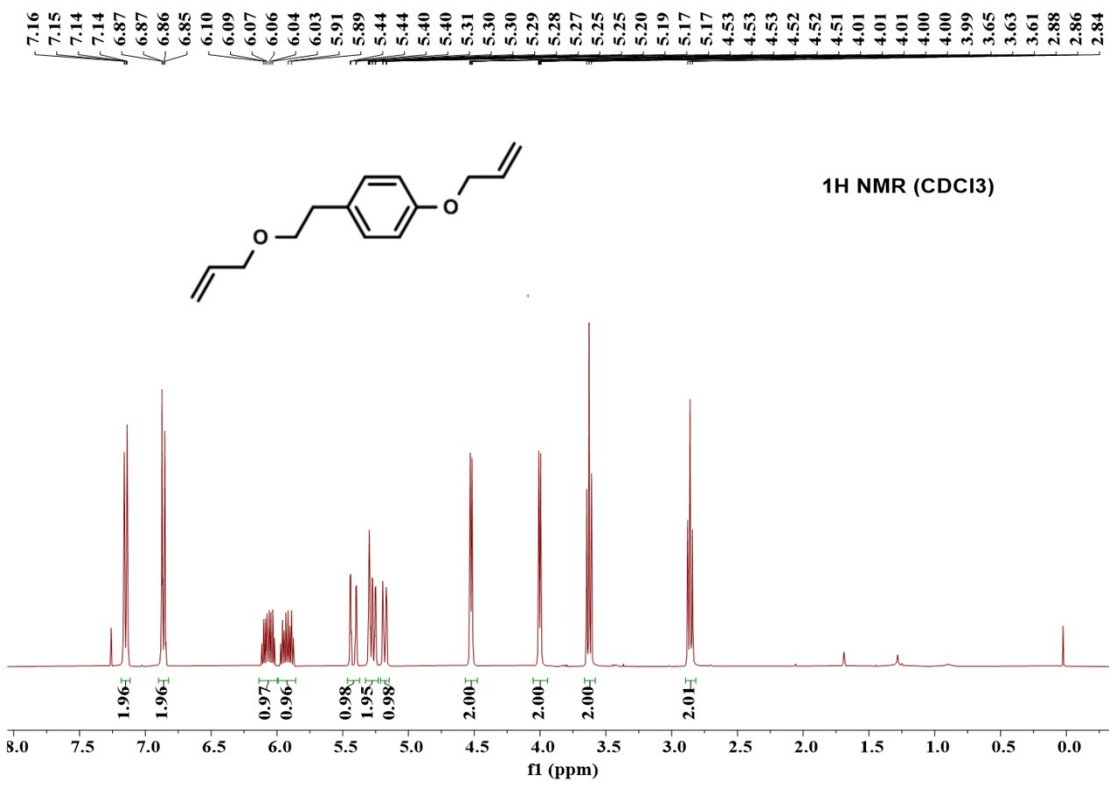


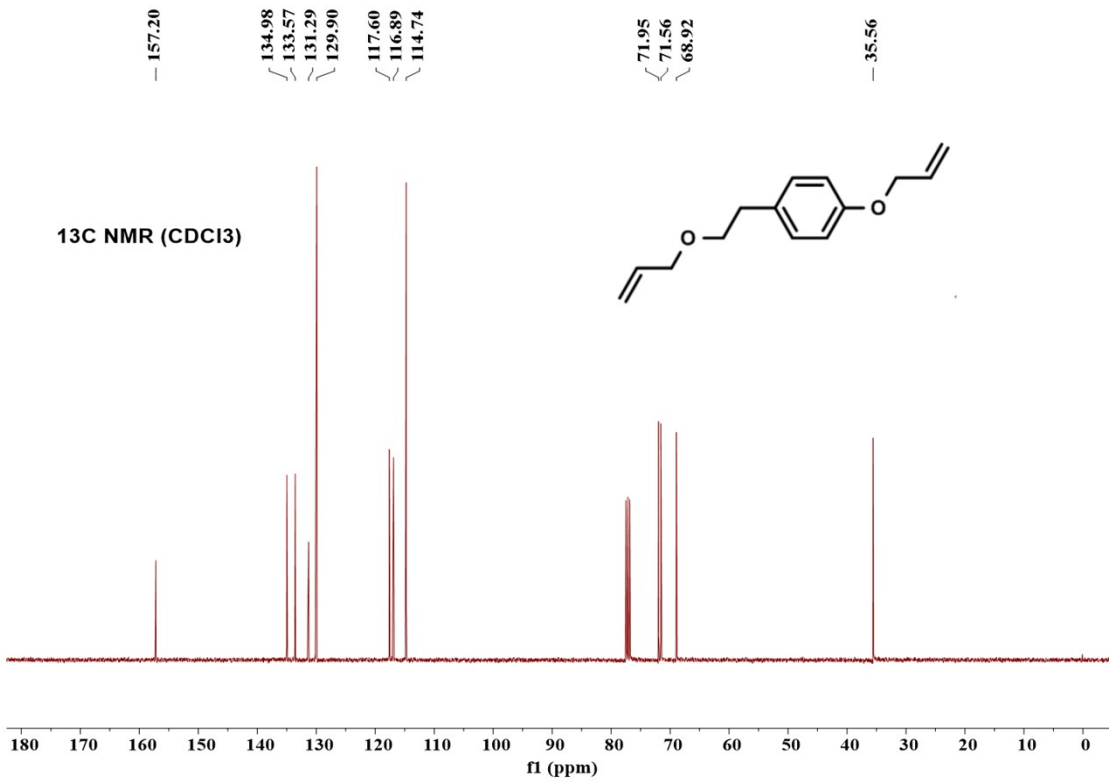
21. 3-(4-allyloxyphenyl)thiophene (**3t**)





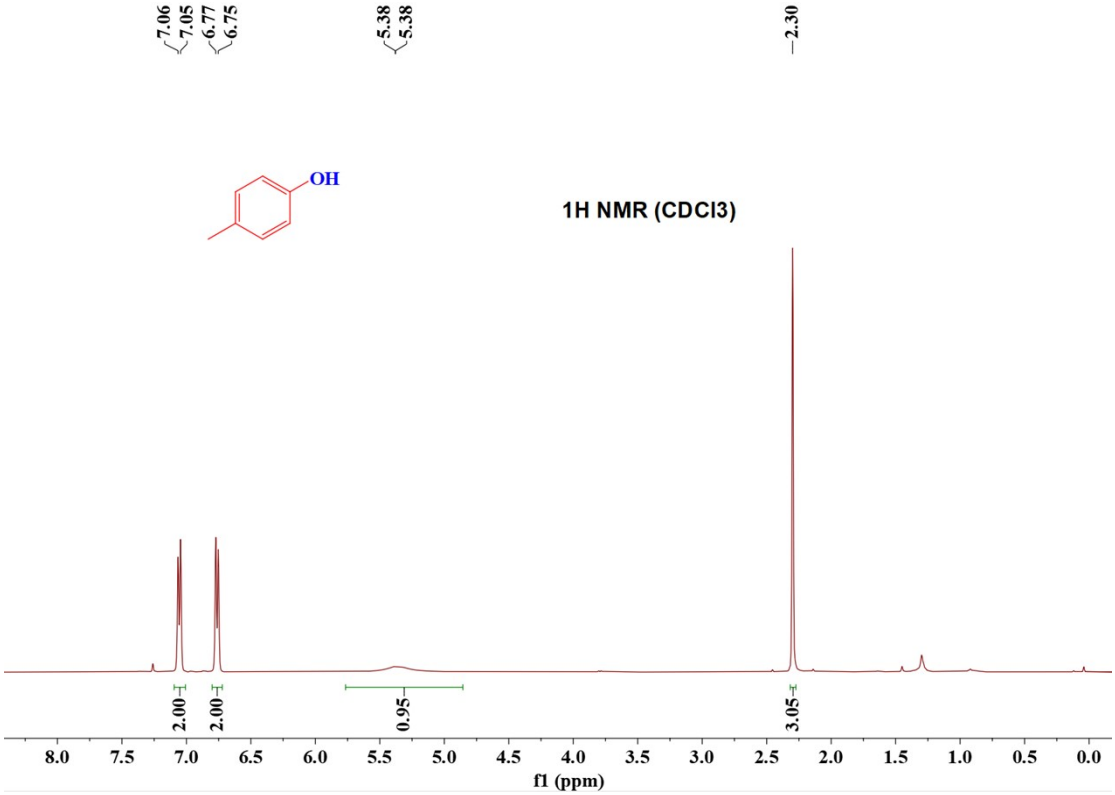
22. 1-allyloxy-4-(2-allyloxyethyl)benzene (**3ac**)

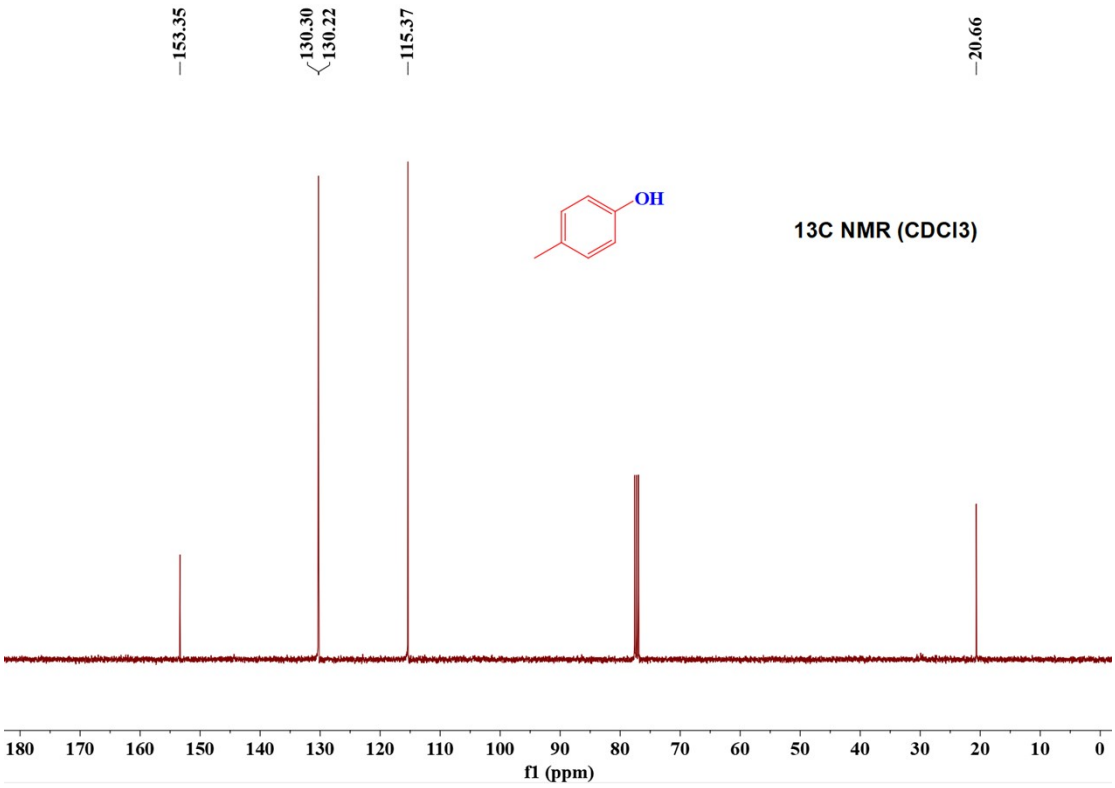




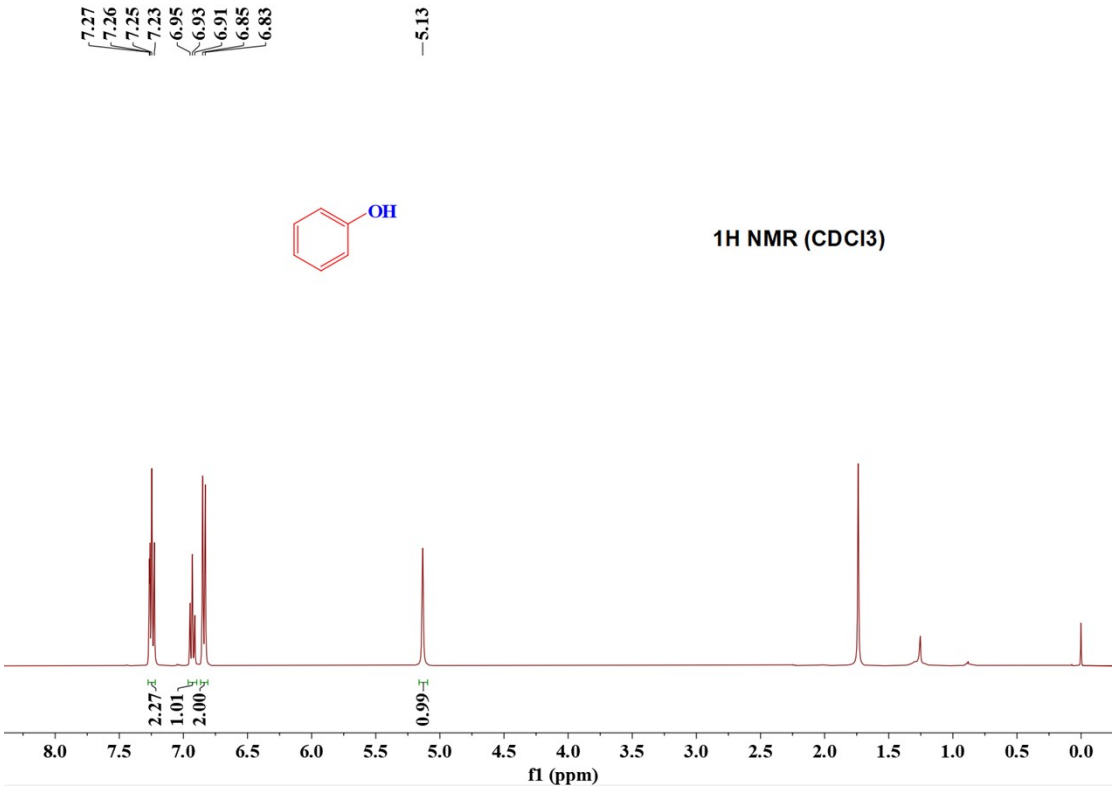
VI. Copies of NMR Spectra of Deprotection Products Aryl Phenols

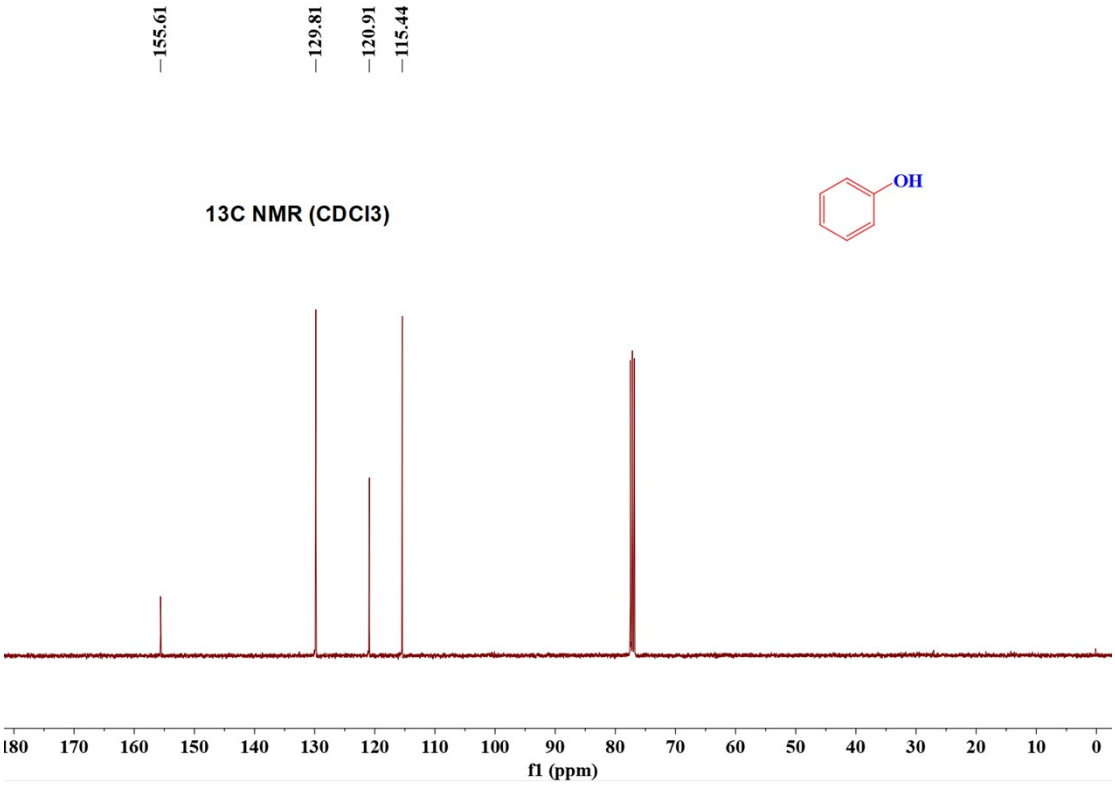
1. *p*-cresol (**4a**)



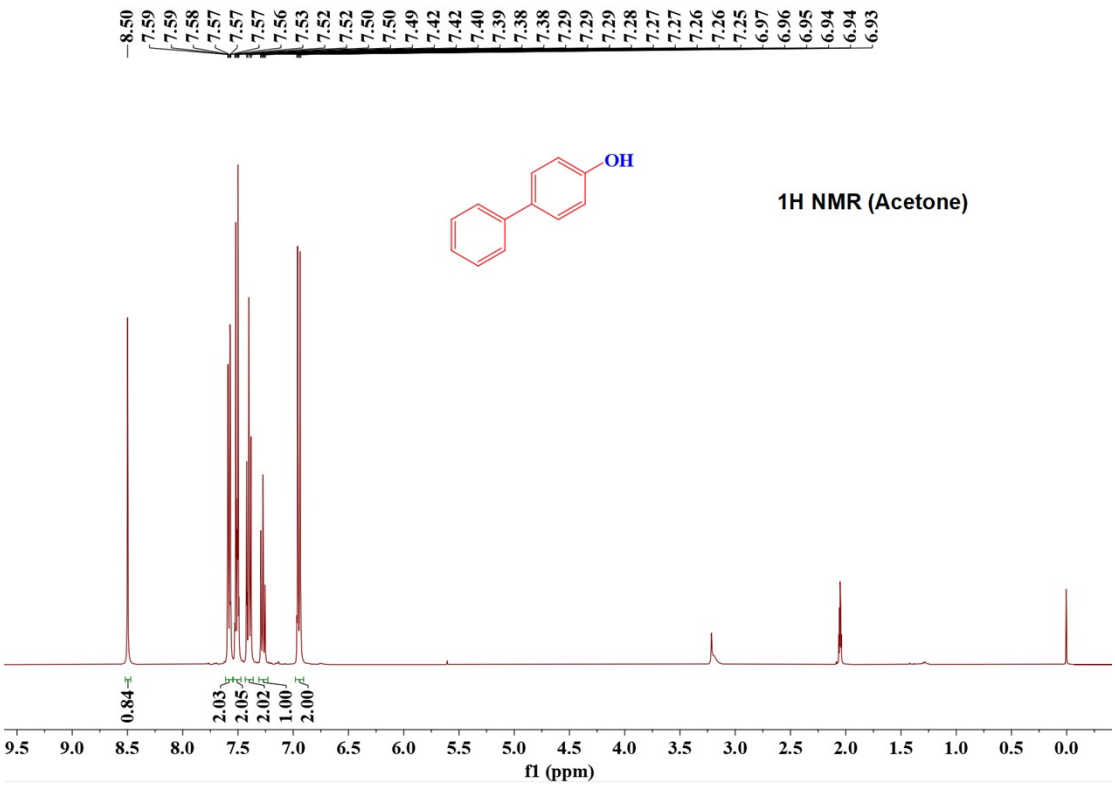


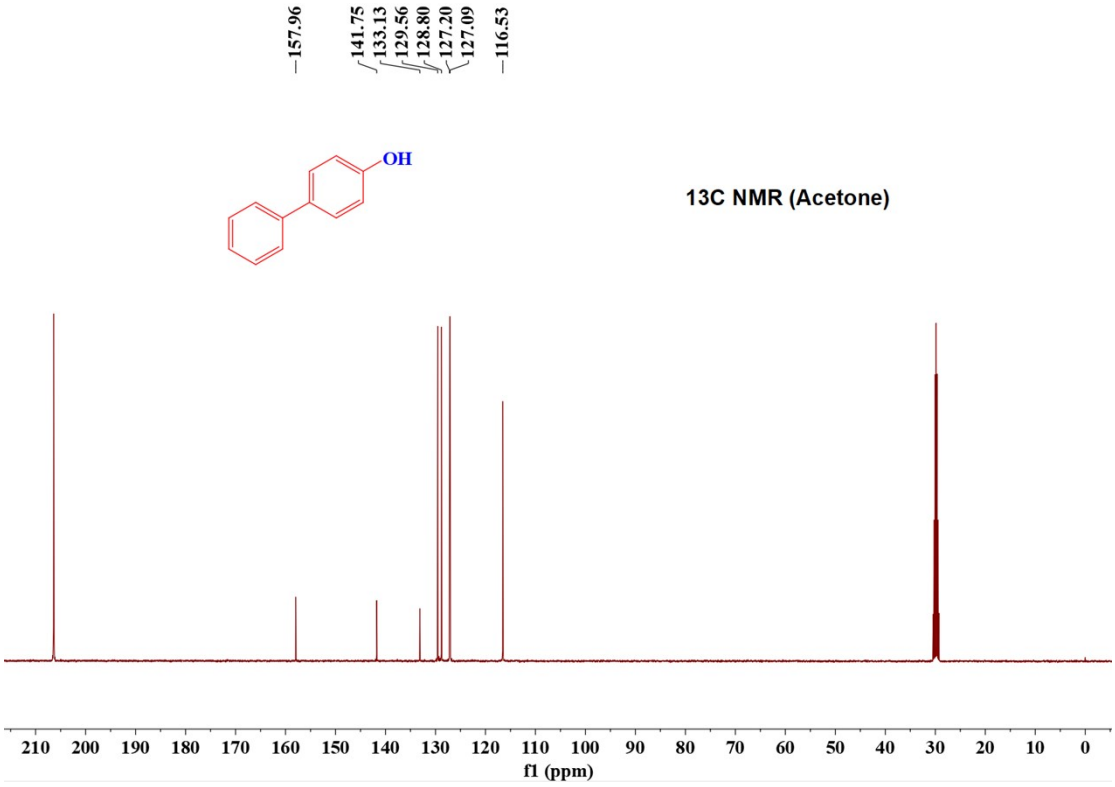
2. phenol (**4b**)


7.27
7.26
7.25
7.23
6.95
6.93
6.91
6.85
6.83
5.13
OH
1H NMR (CDCl3)
2.27
1.01
2.00
0.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

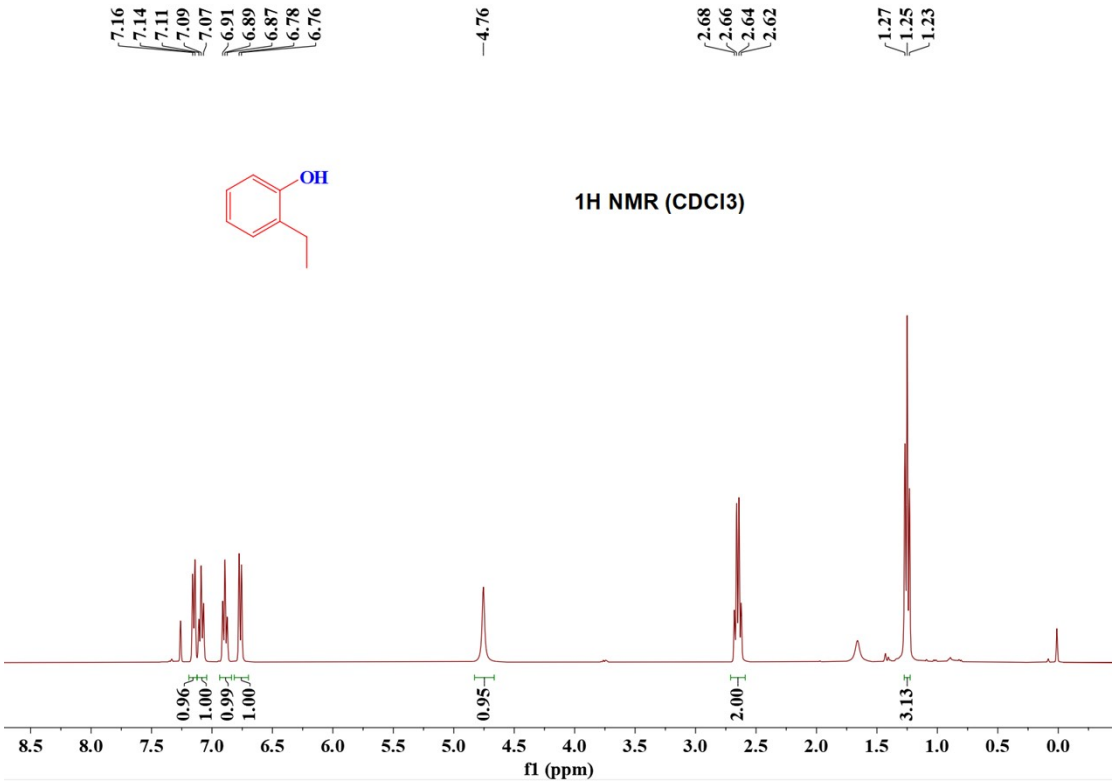

155.61
129.81
120.91
115.44
13C NMR (CDCl3)
OH
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

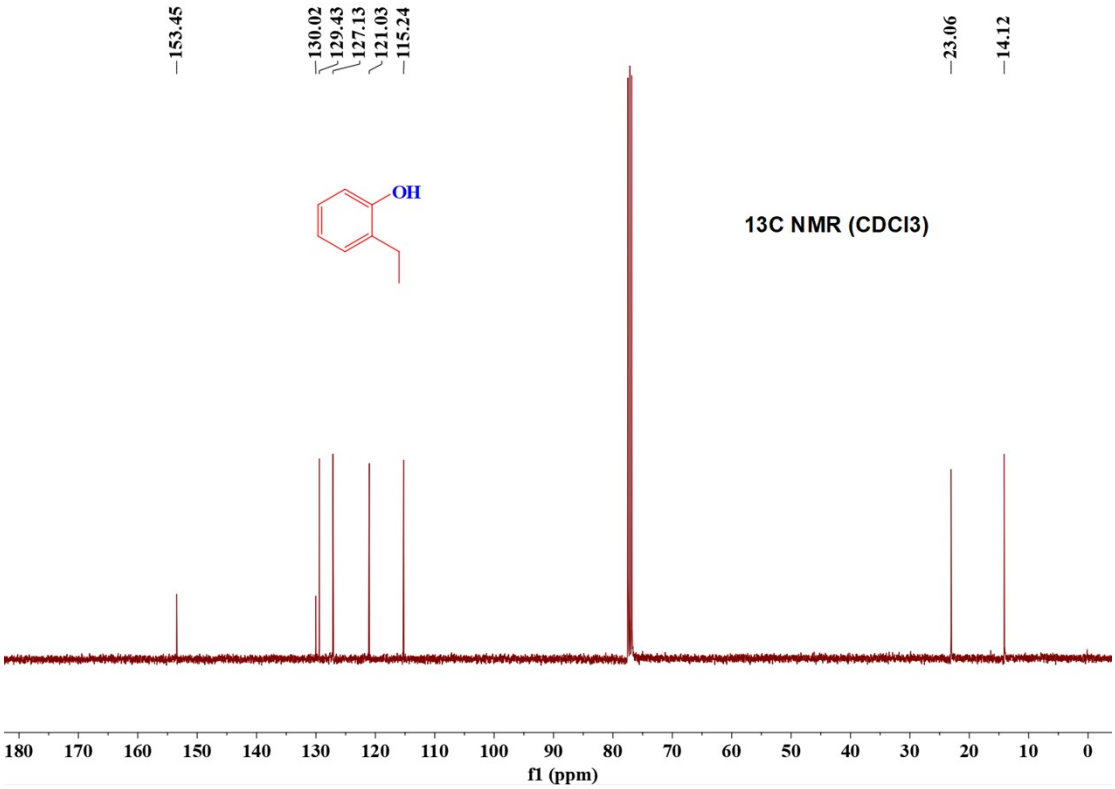
3. [1,1'-biphenyl]-4-ol (**4c**)



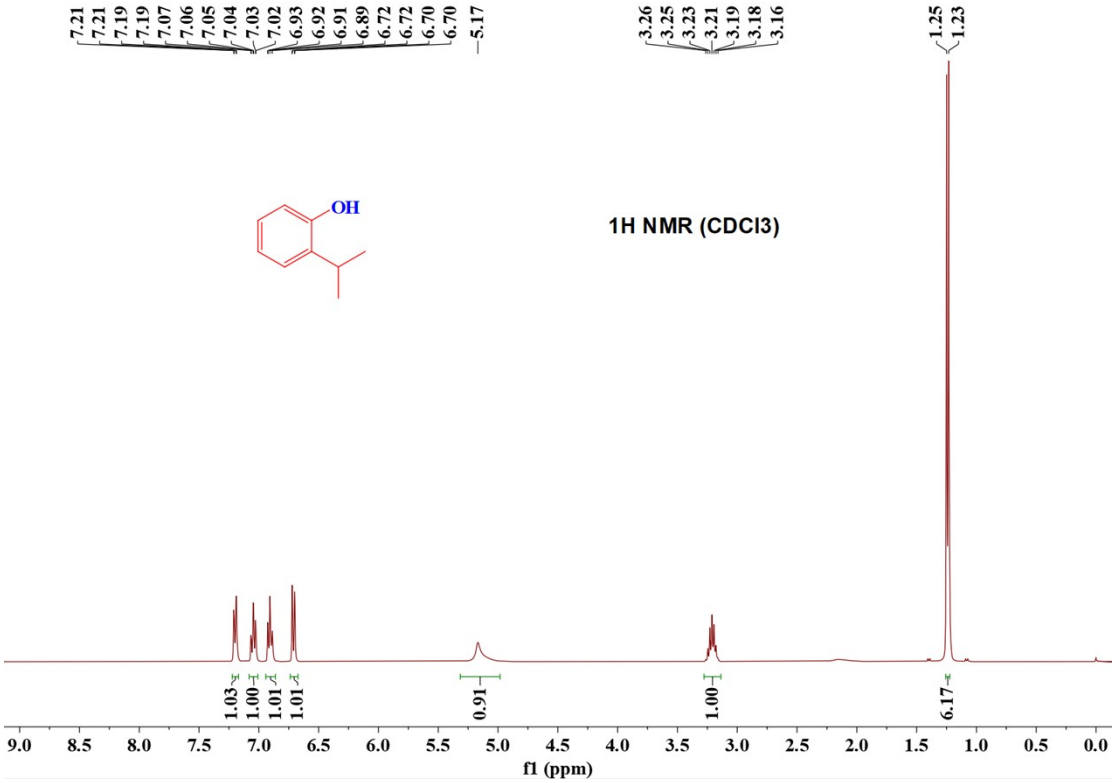


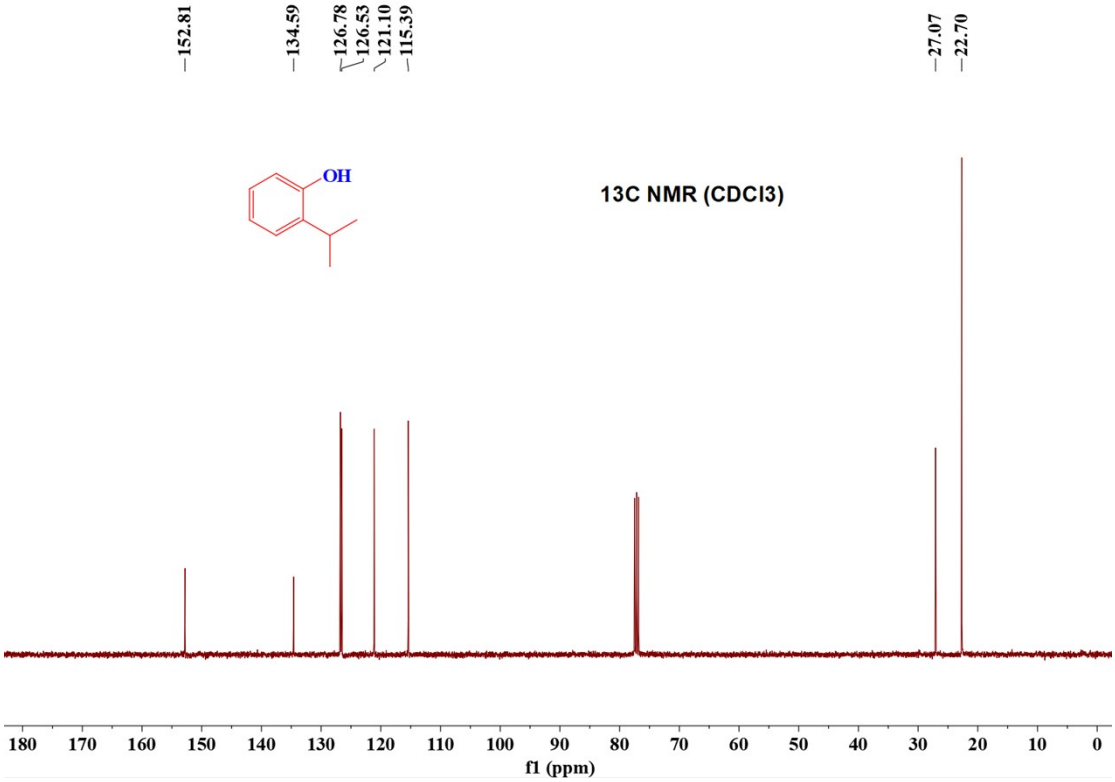
4. 2-ethylphenol (**4d**)



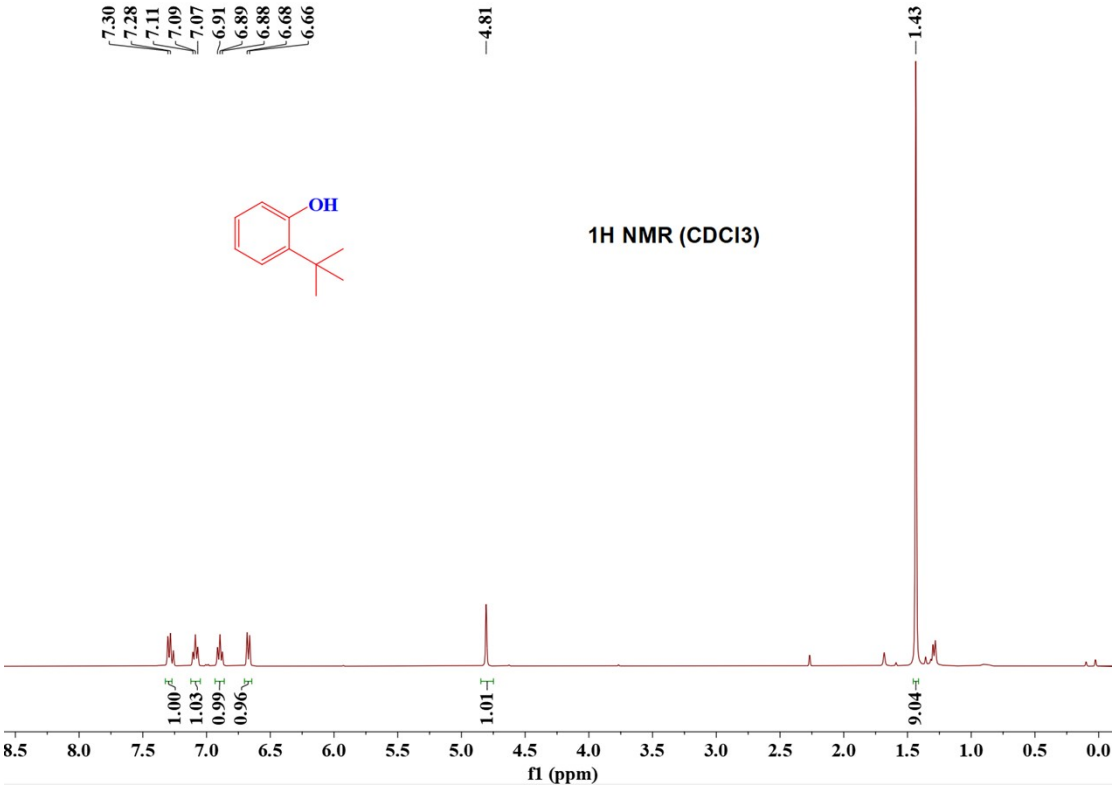


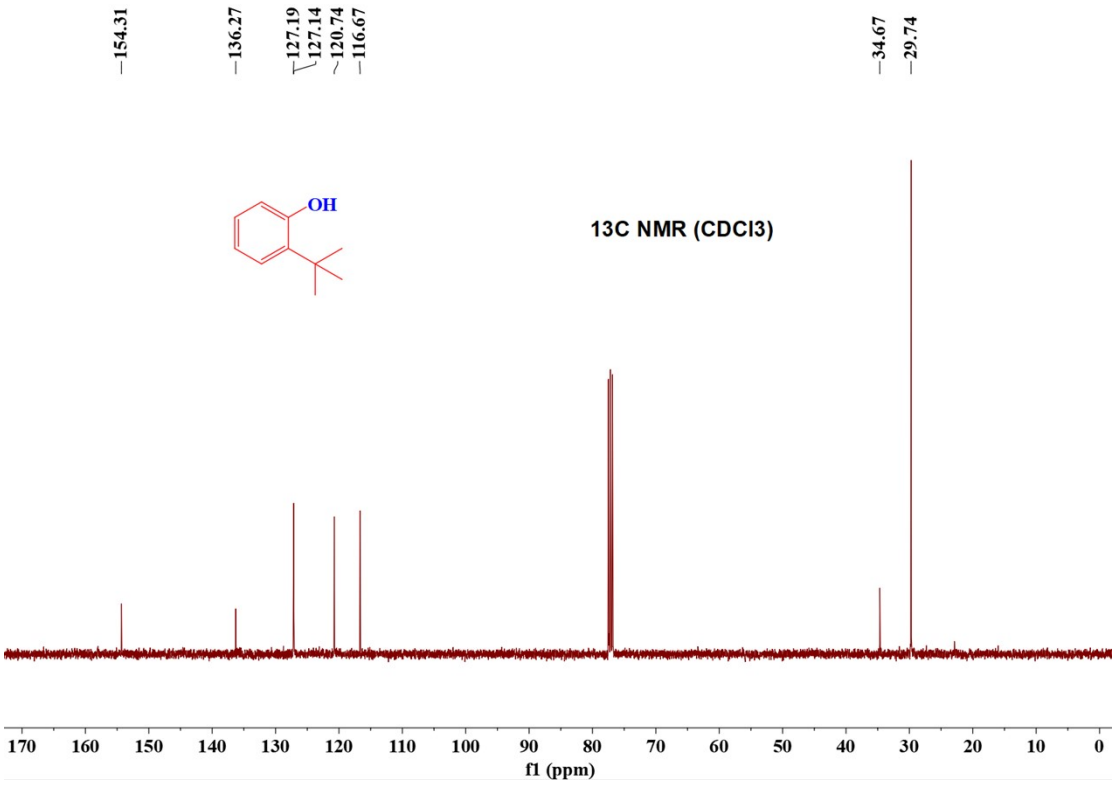
5. 2-isopropylphenol (**4e**)



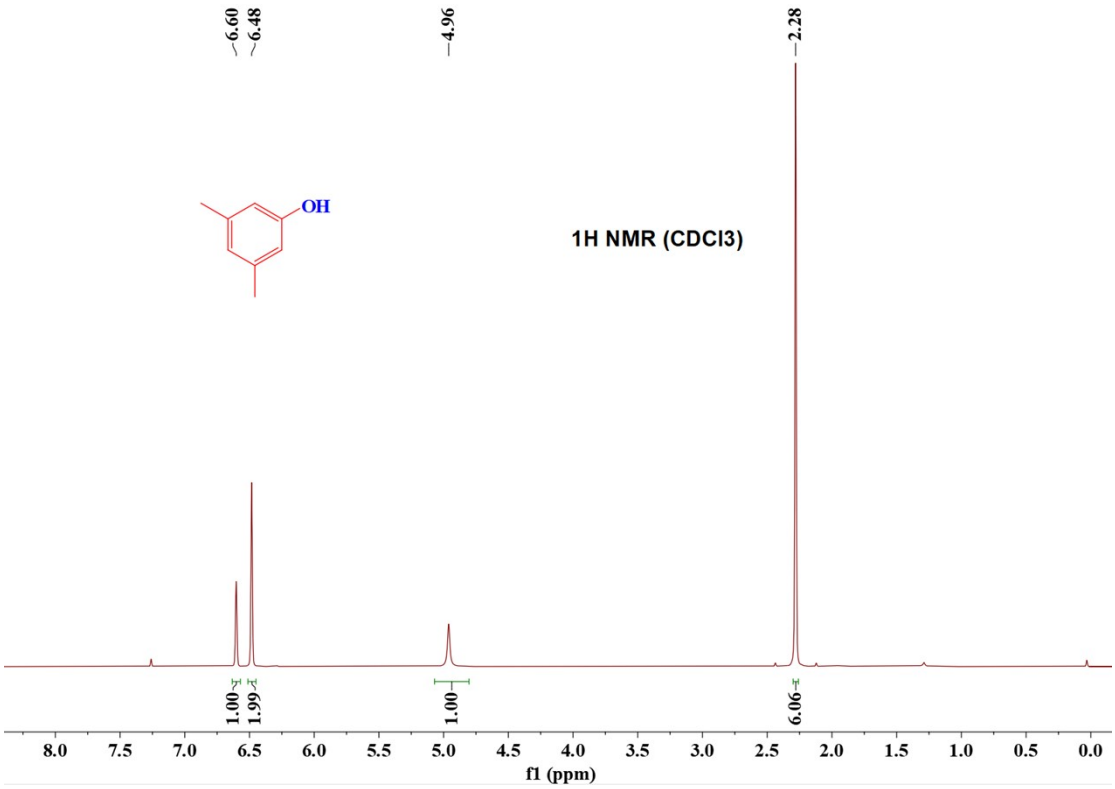


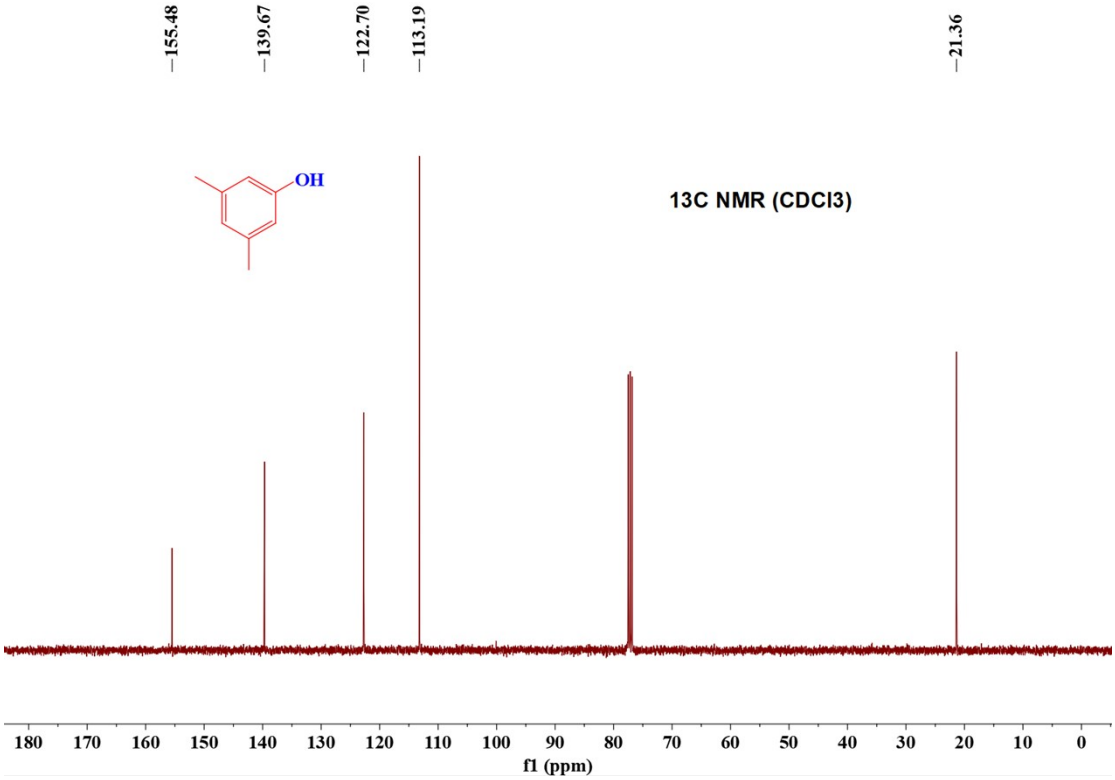
6. 2-*tert*-butylphenol (**4f**)



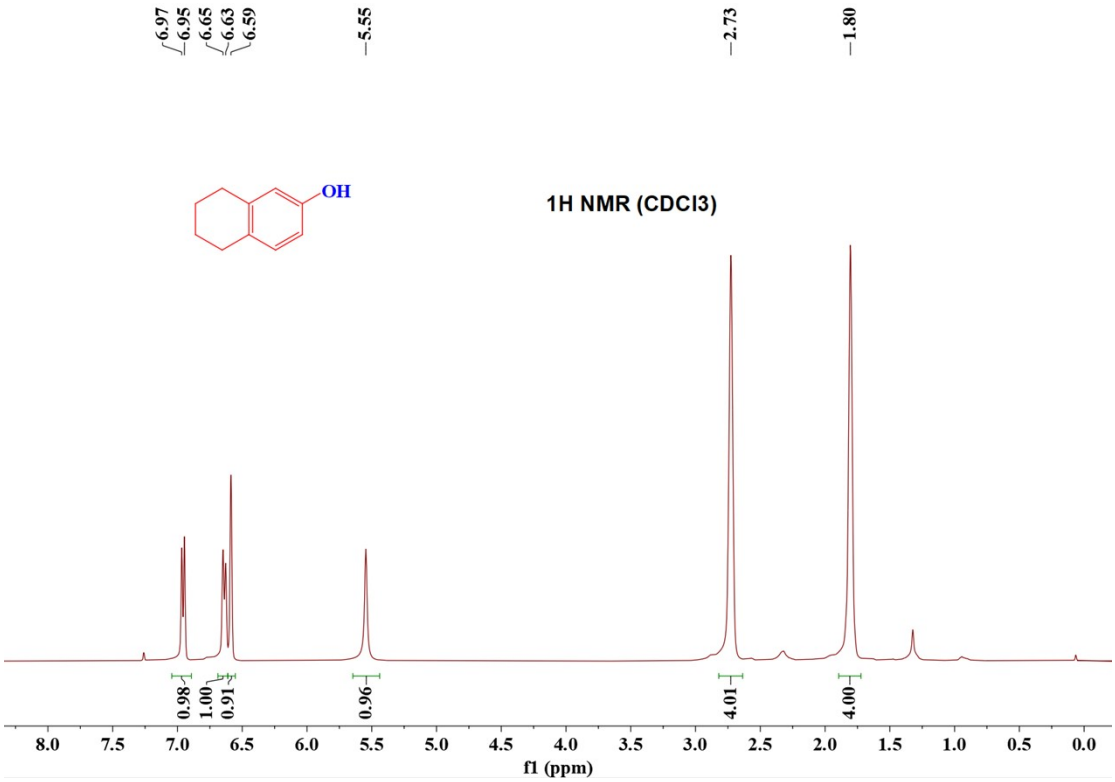


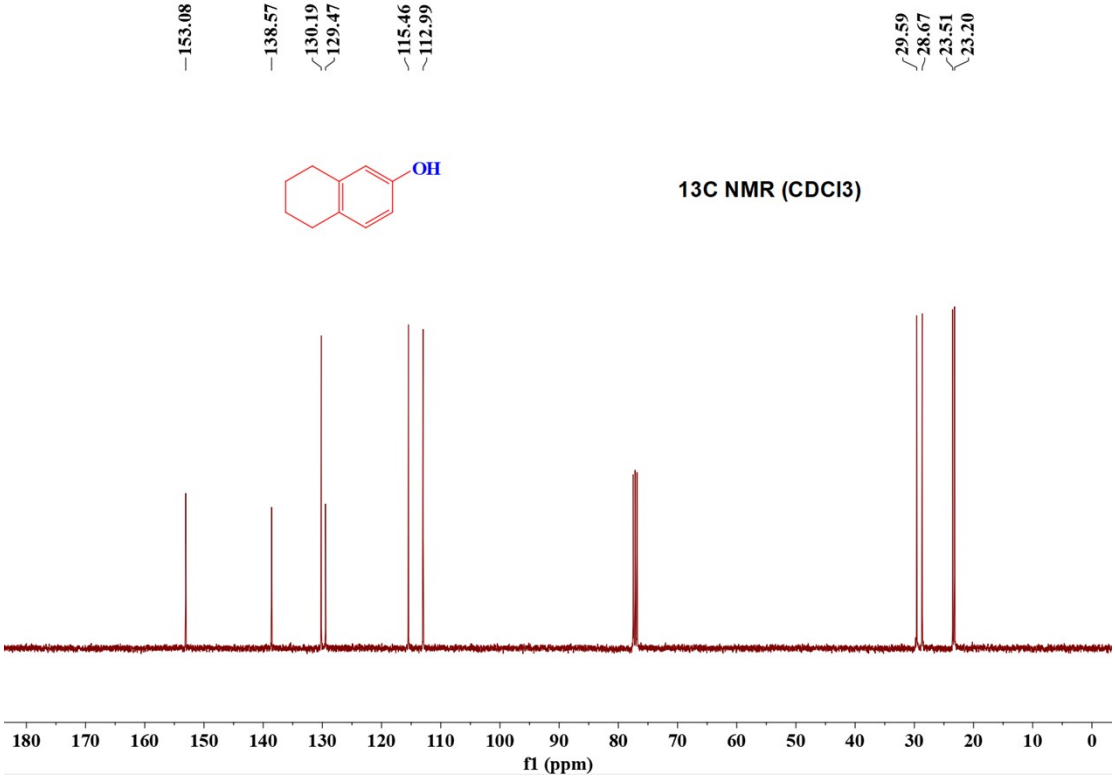
7. 3,5-dimethylphenol (**4g**)



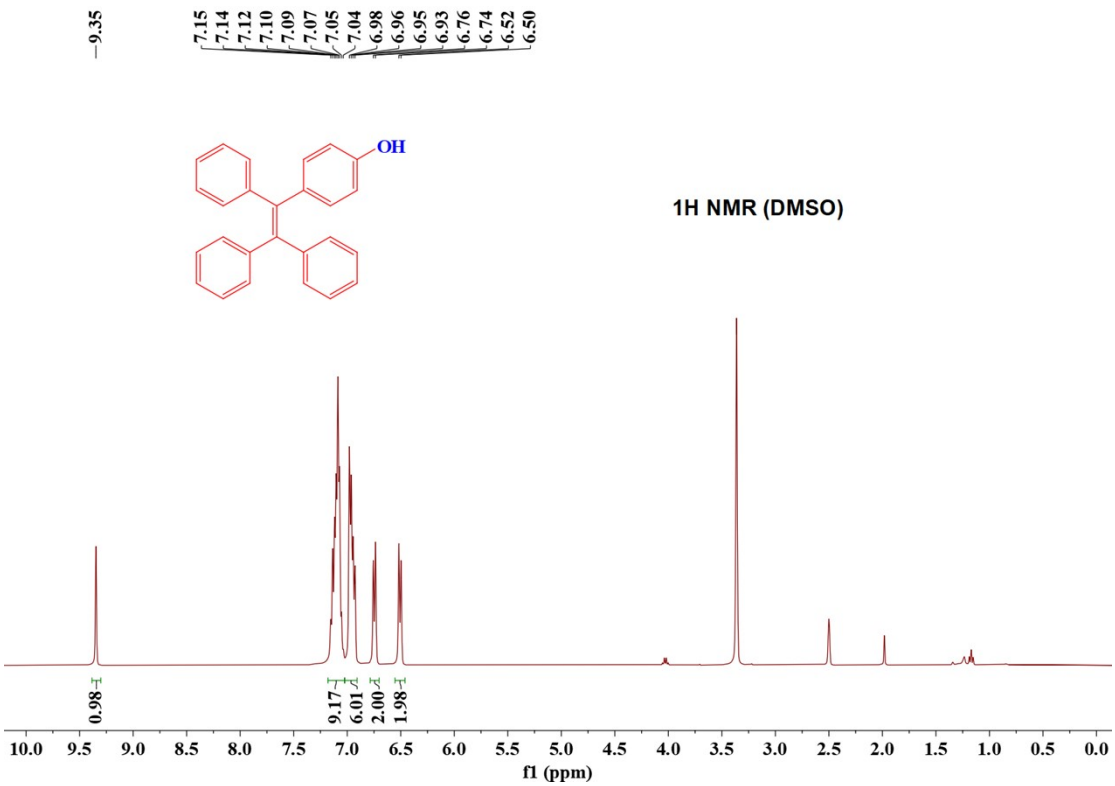


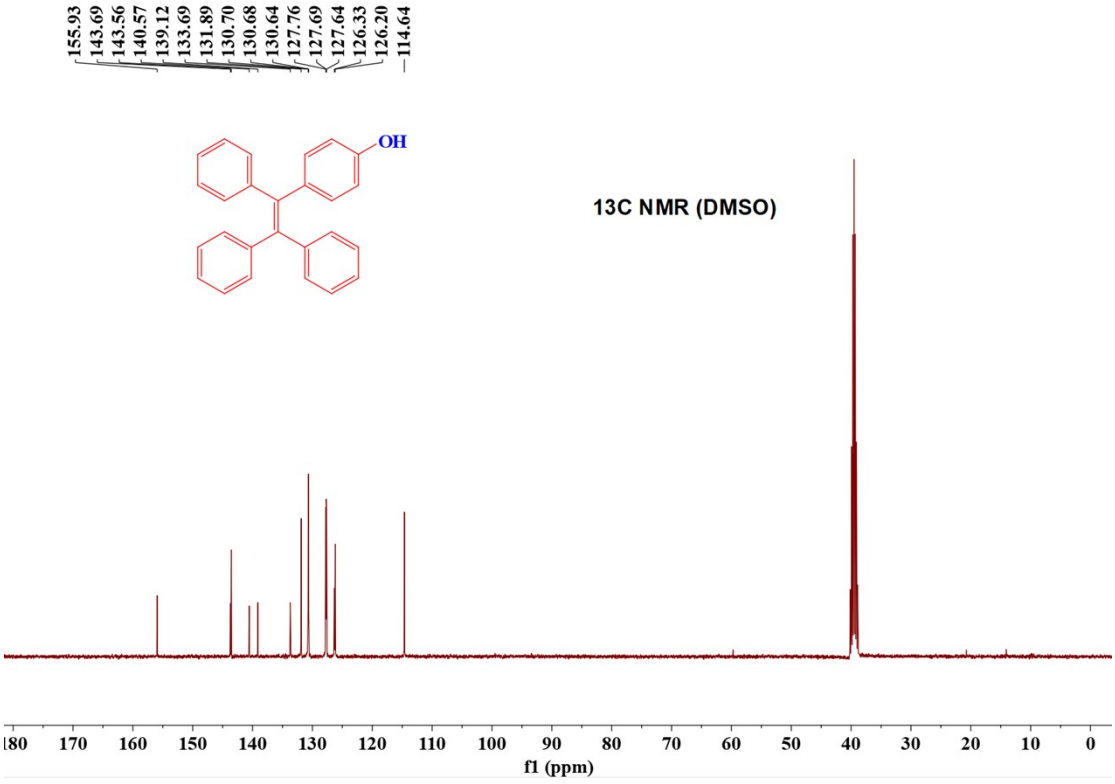
8. 5,6,7,8-tetrahydro-2-naphthol (**4h**)



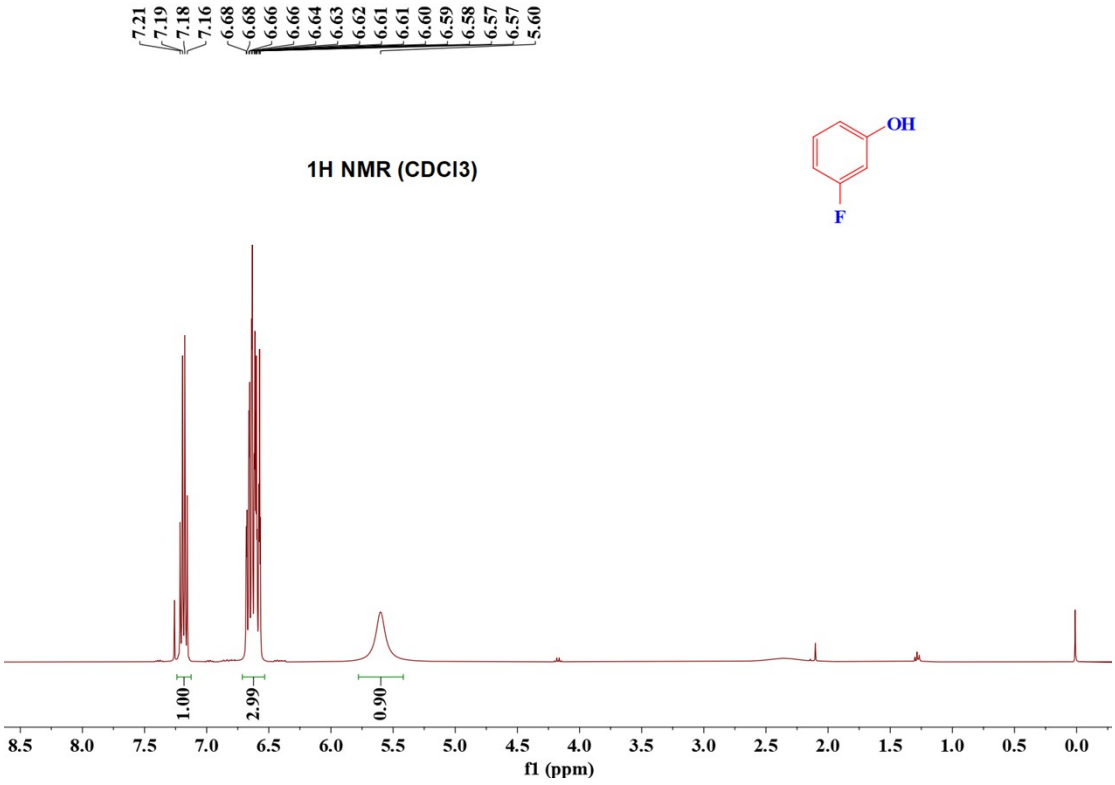


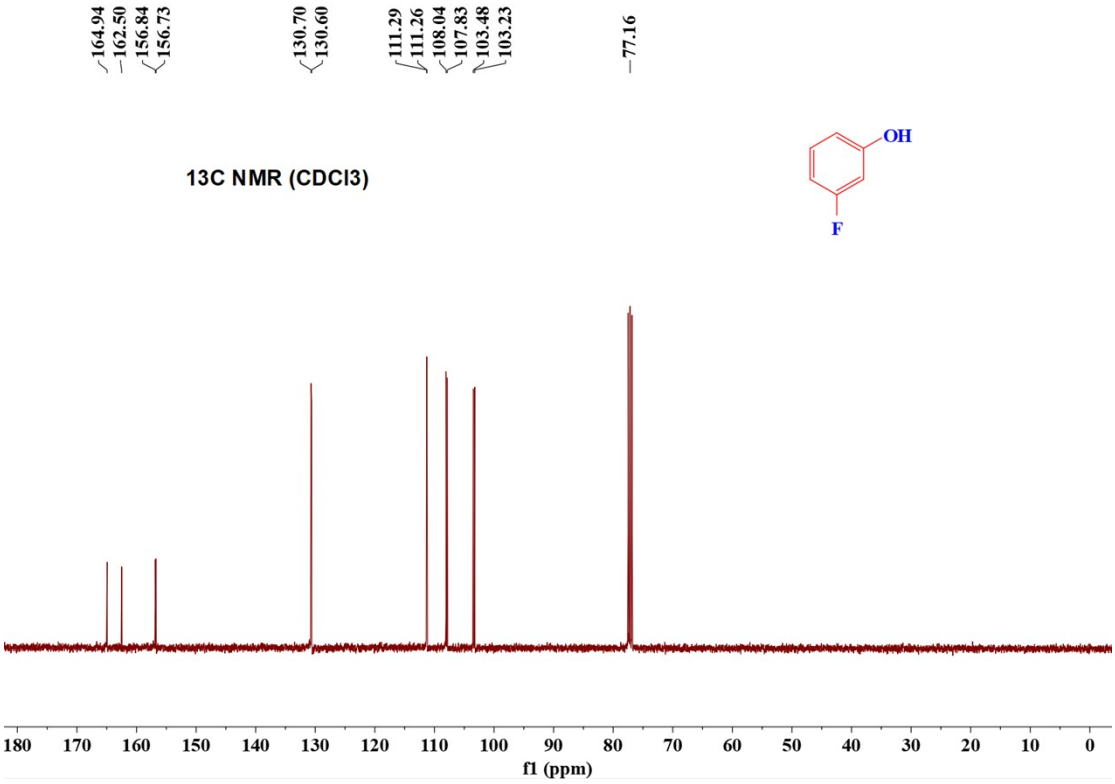
9. 4-(1,2,2-triphenylvinyl)phenol (**4i**)

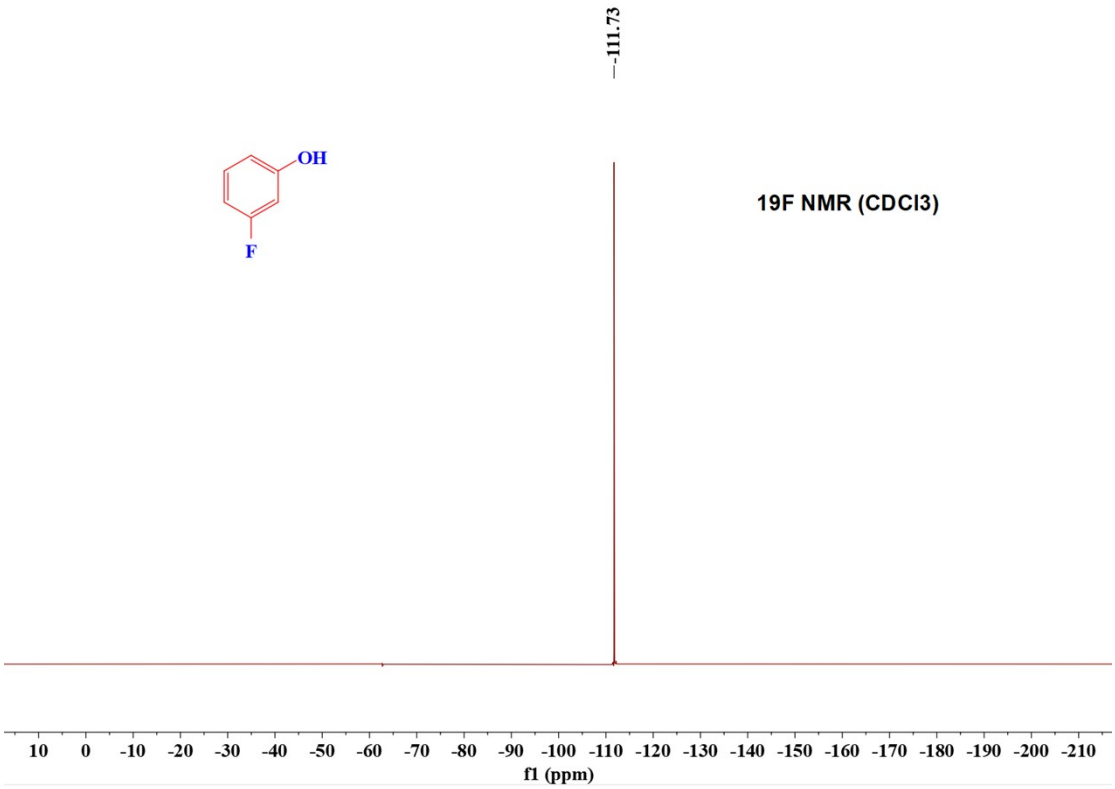




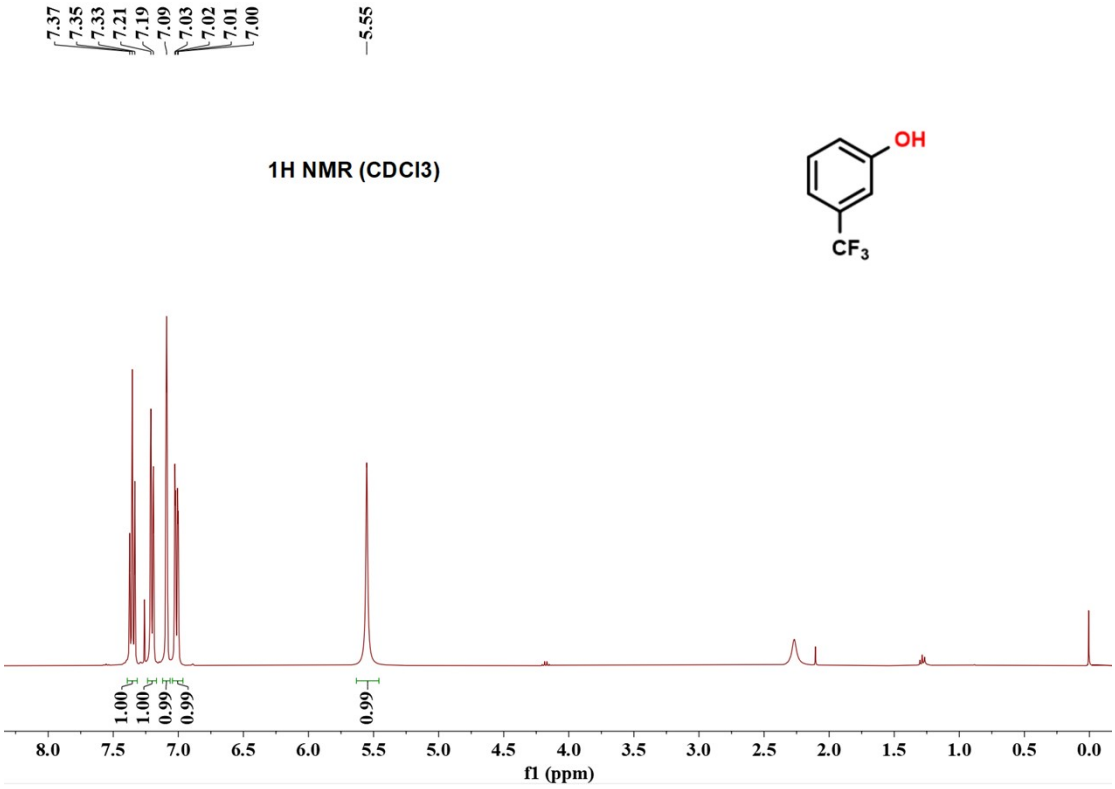
10. 3-fluorophenol (**4j**)

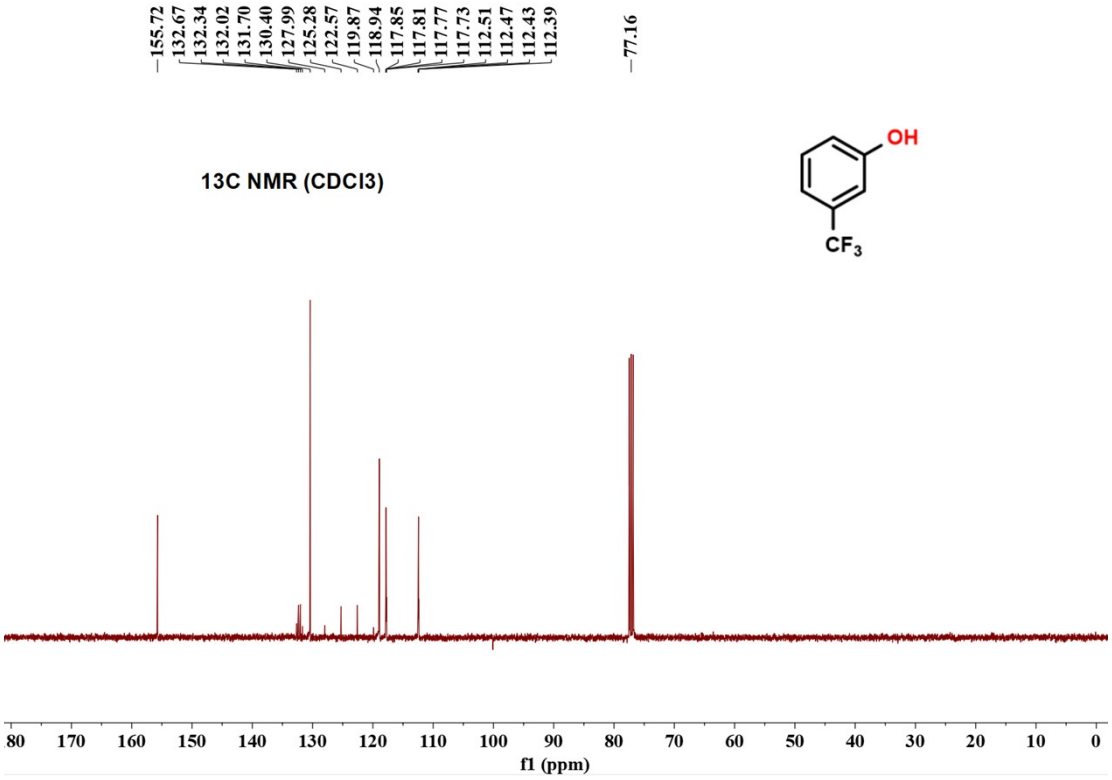


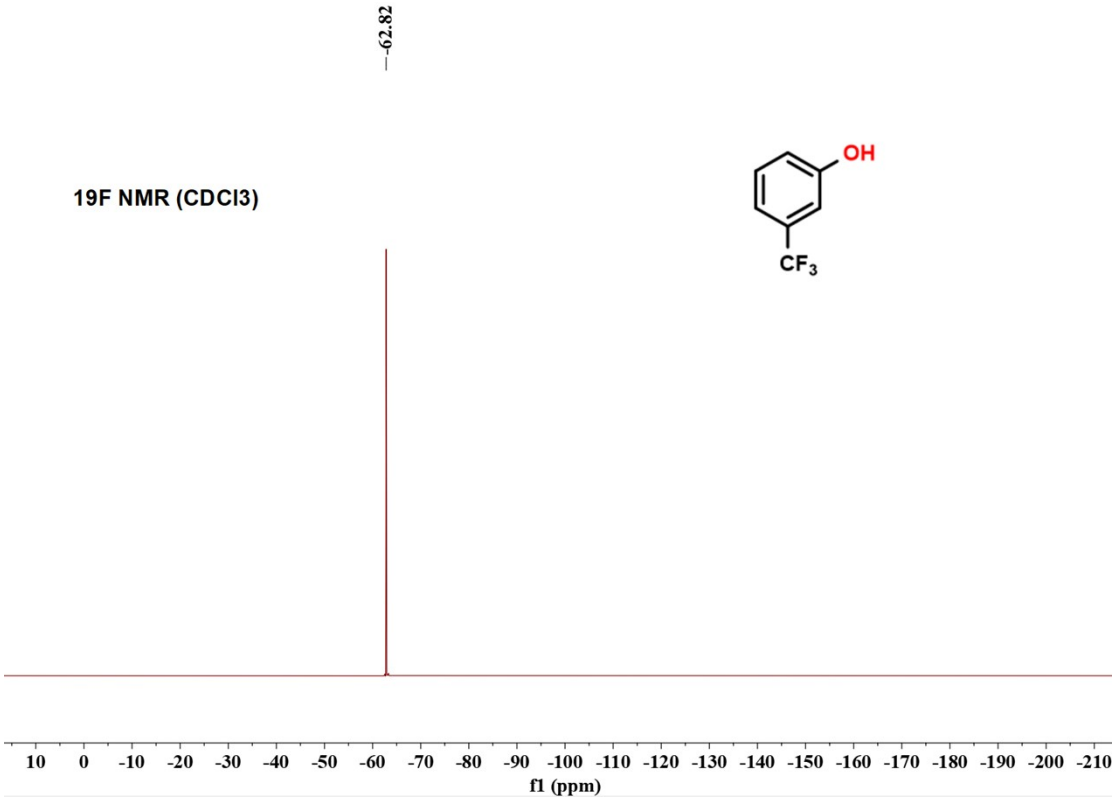




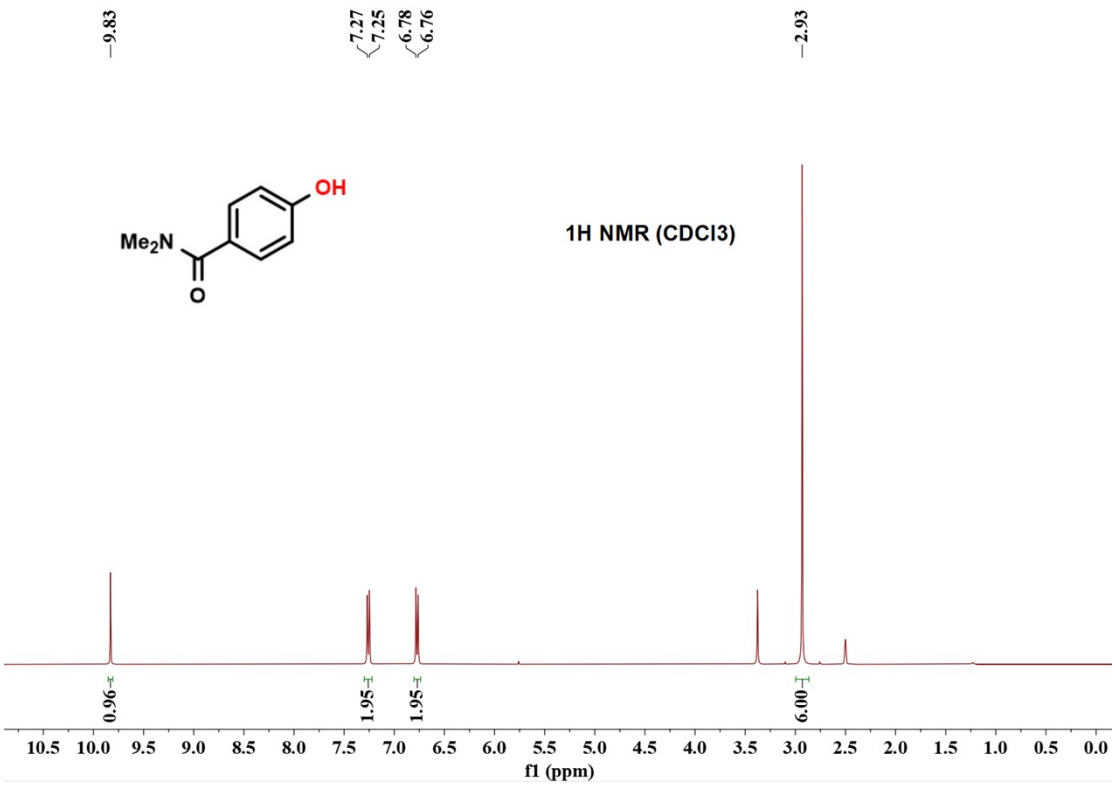
11. 3-trifluoromethylphenol (**4k**)

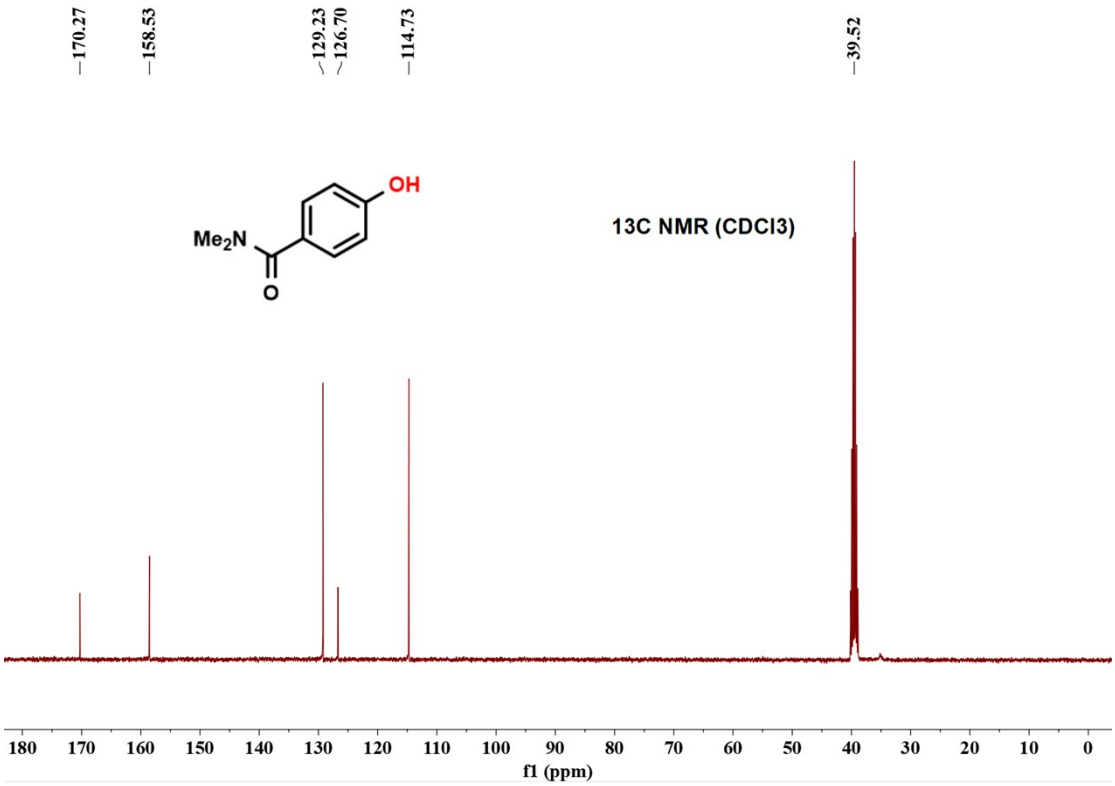



155.72
132.67
132.34
132.02
131.70
130.40
127.99
125.28
122.57
119.87
118.94
117.85
117.81
117.77
117.73
112.51
112.47
112.43
112.39
77.16
13C NMR (CDCl3)
OH
CF3
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

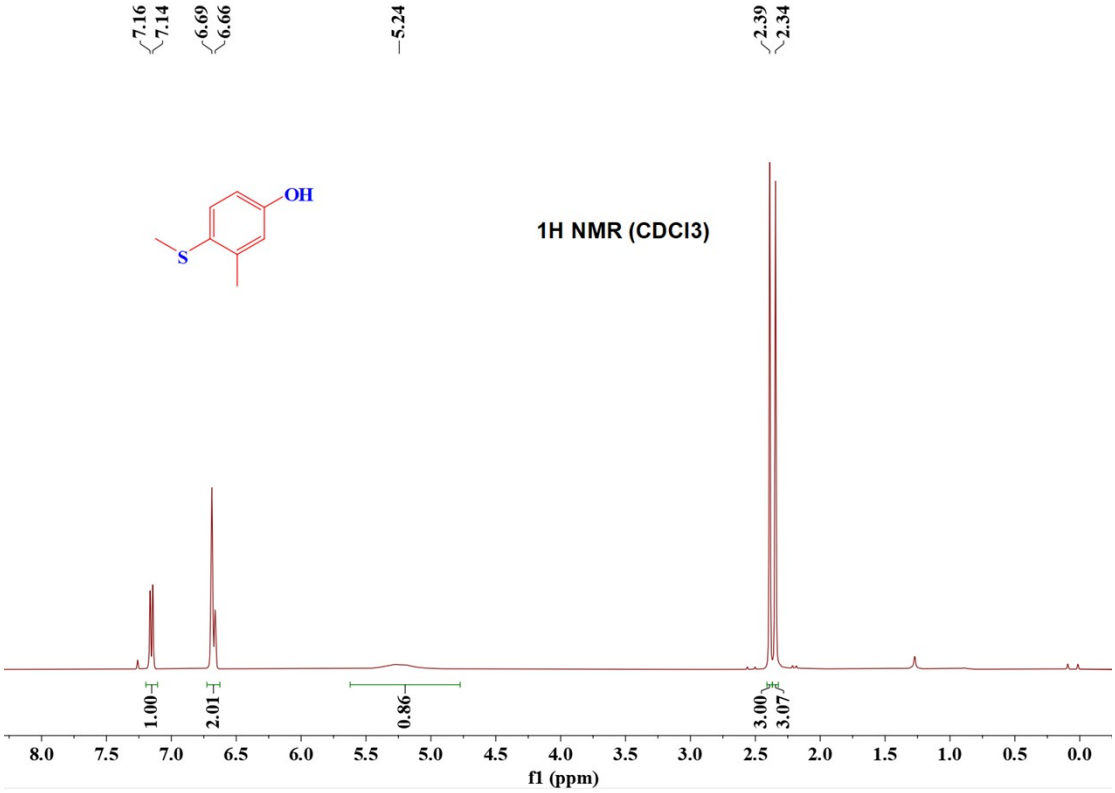

-62.82
19F NMR (CDCl3)
OH
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

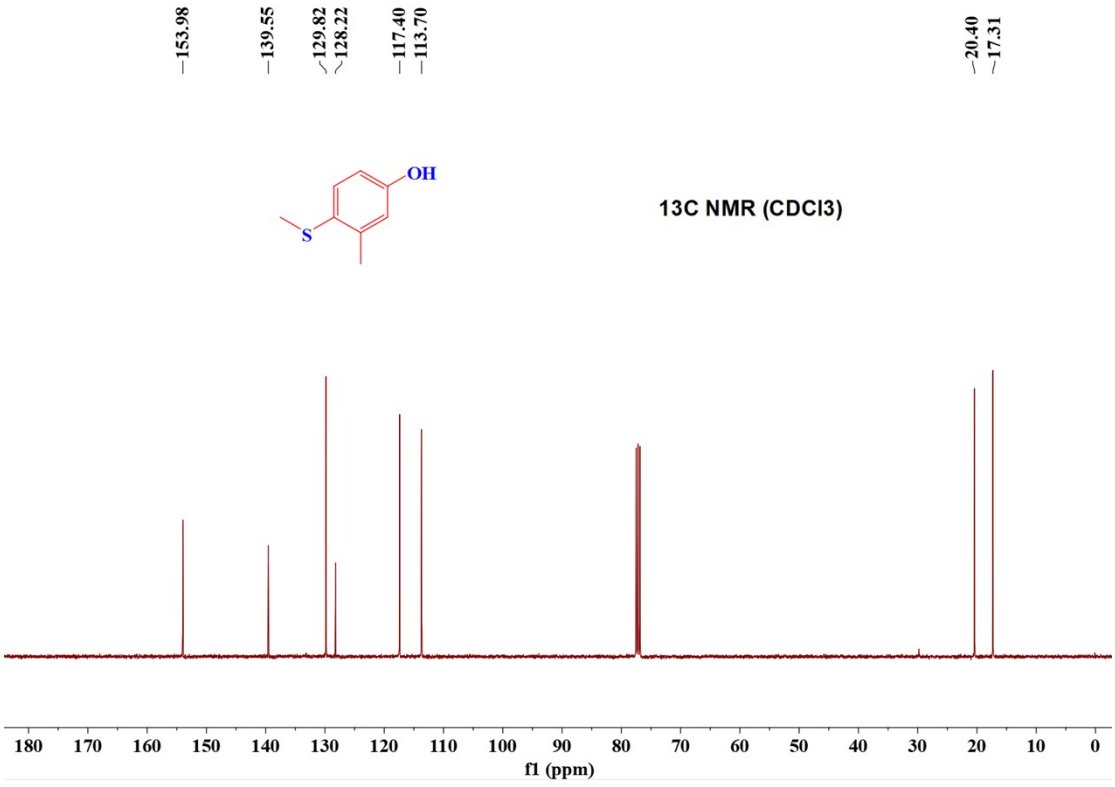
12. 4-hydroxy-*N*,*N*-dimethylbenzamide (**4l**)



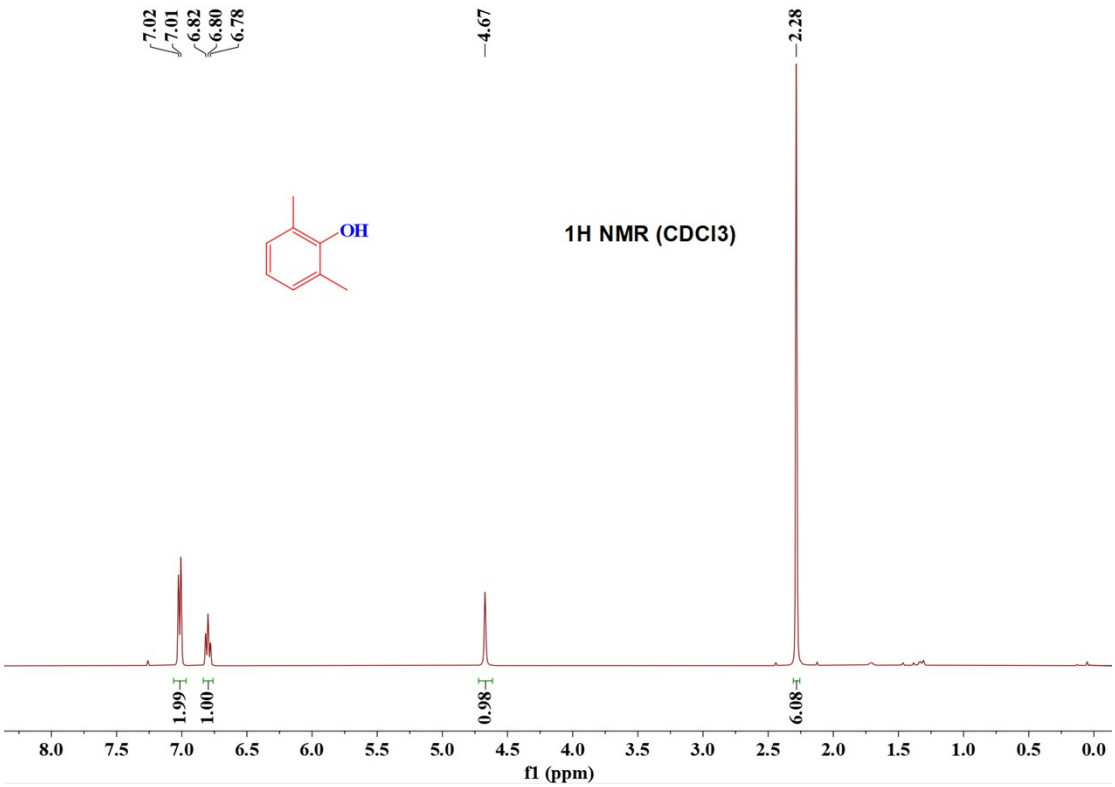


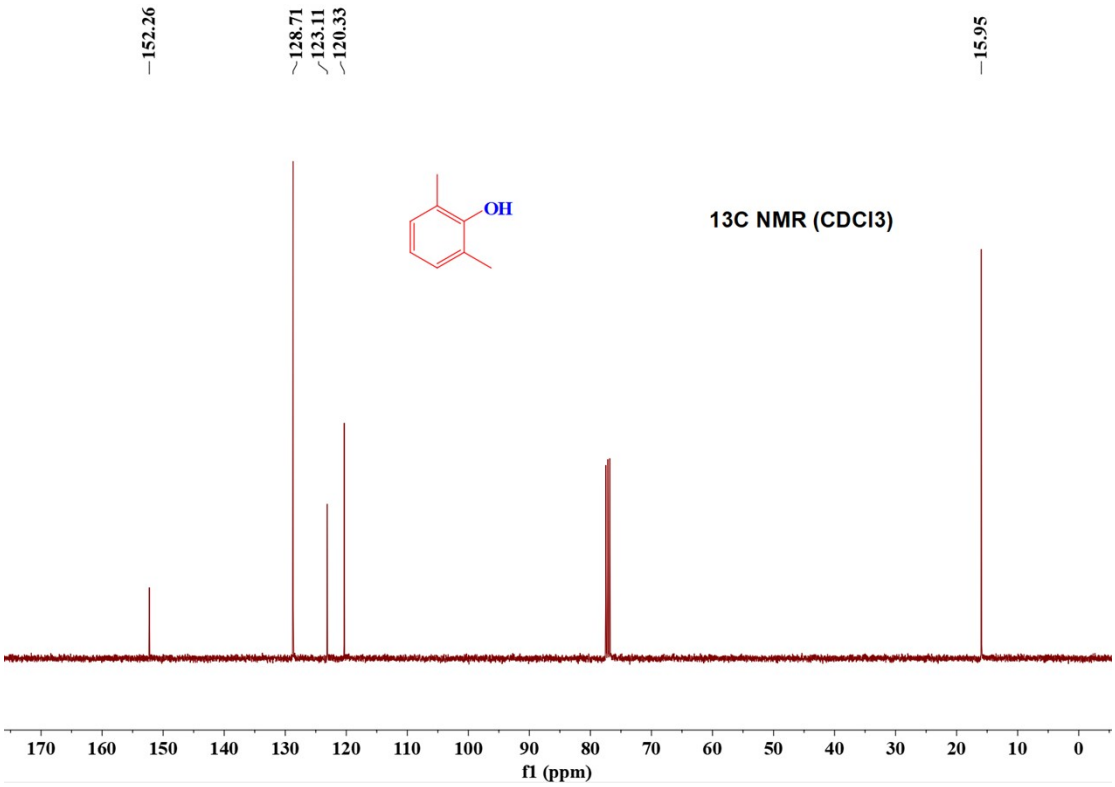
13. 3-methyl-4-methylthiophenol (**4m**)



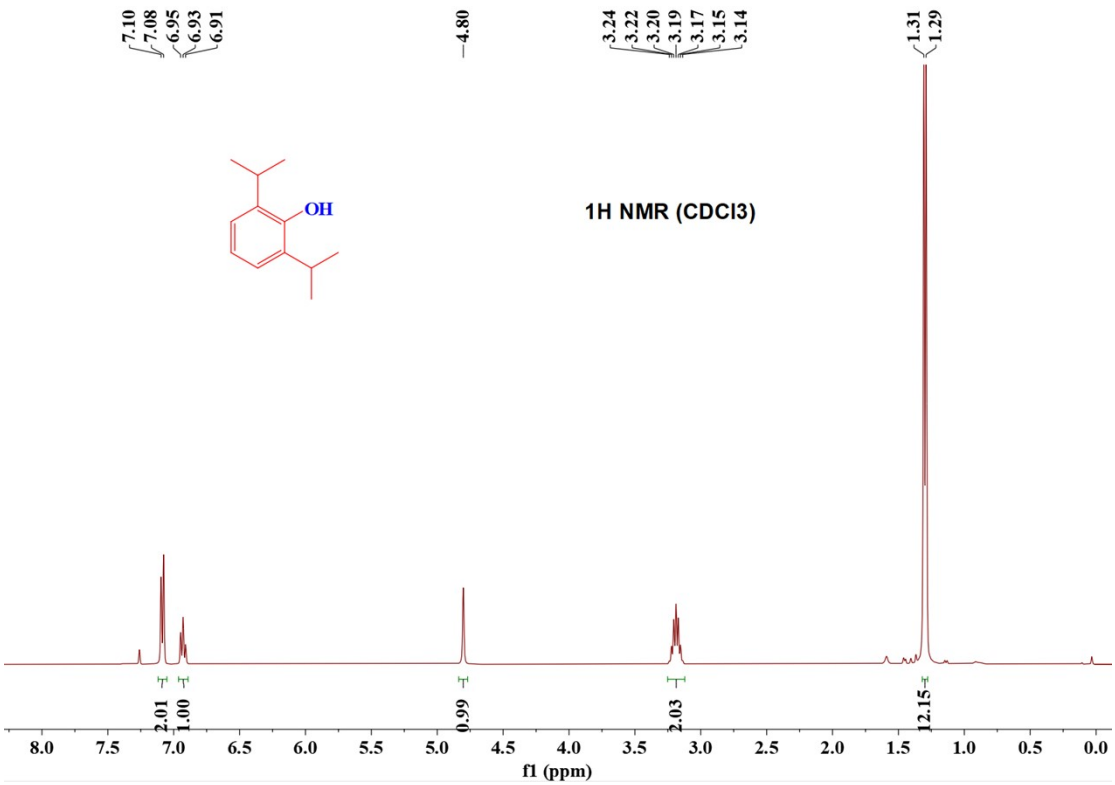


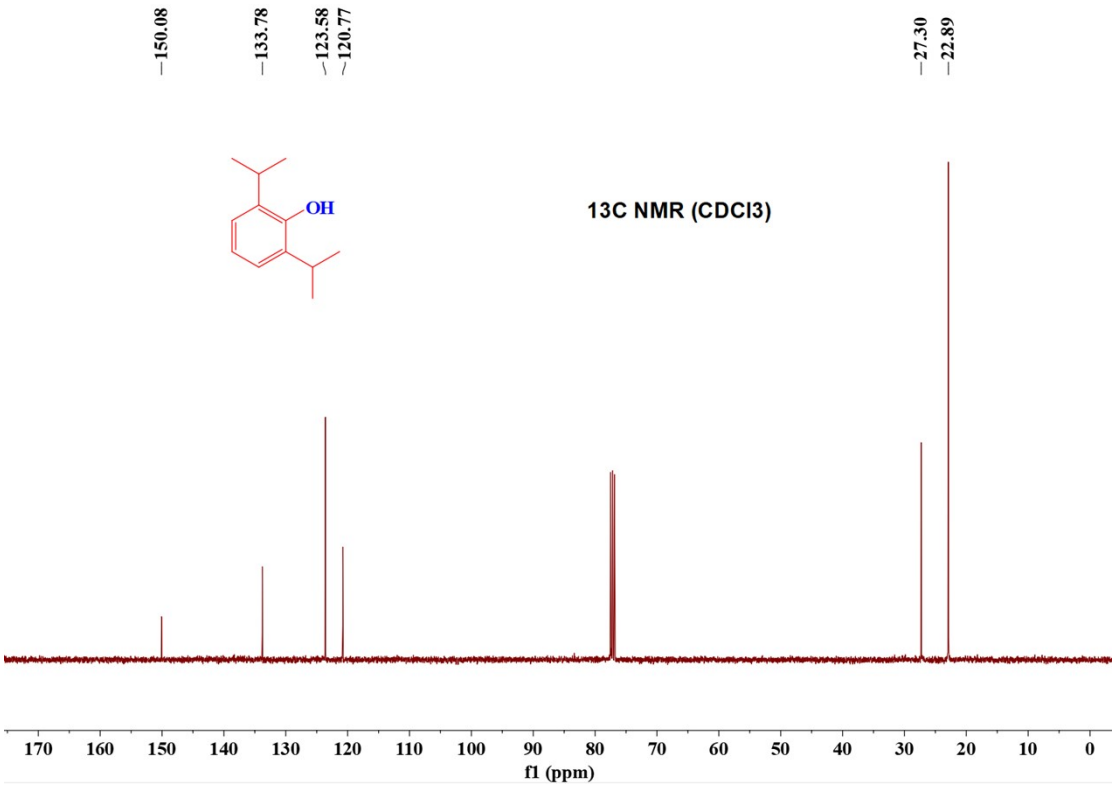
14. 2,6-dimethylphenol (**4n**)



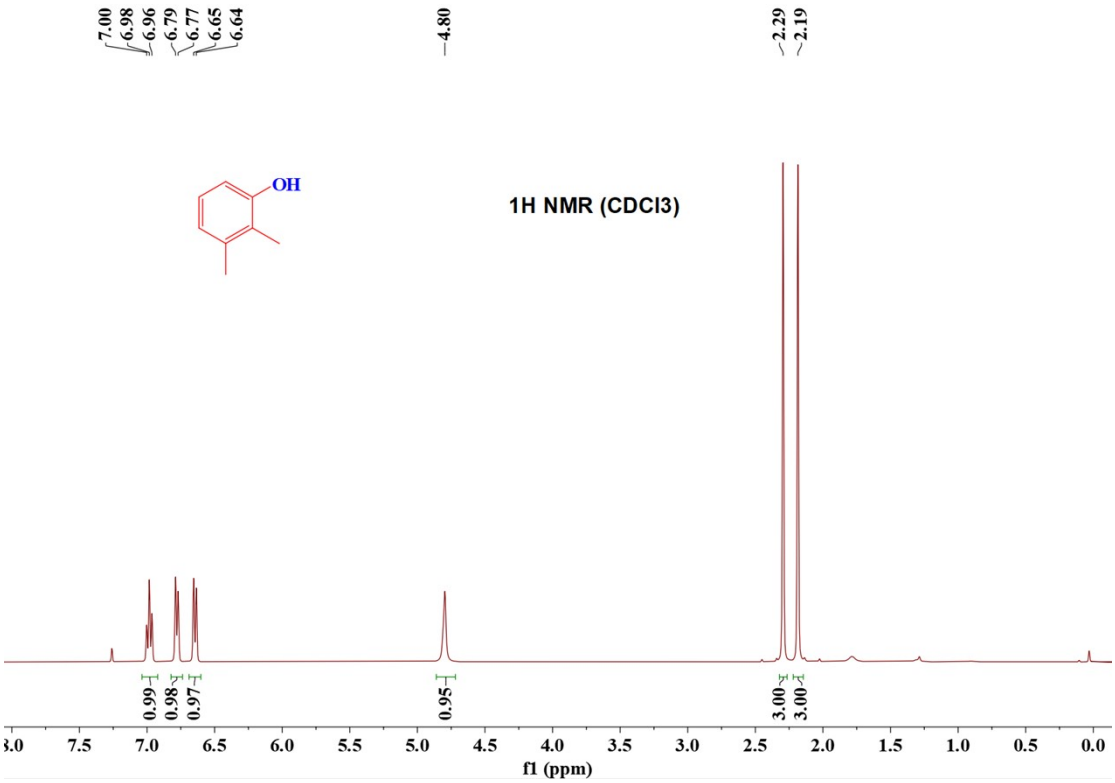


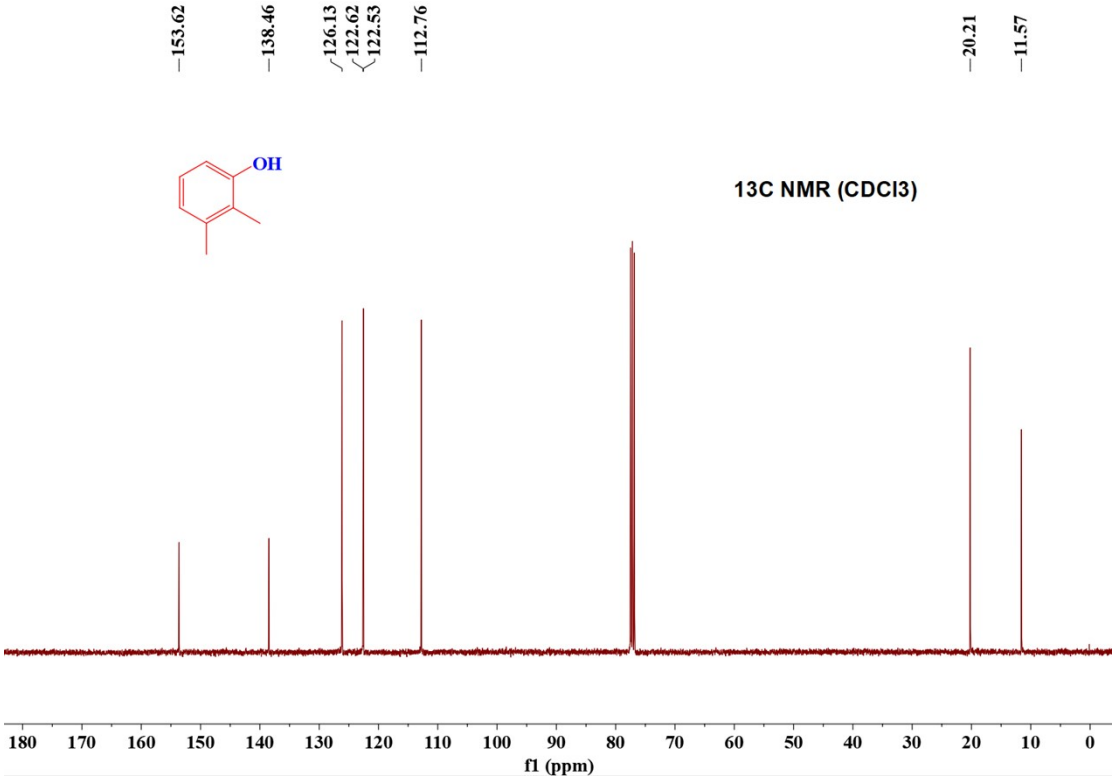
15. 2,6-diisopropylphenol (**4o**)



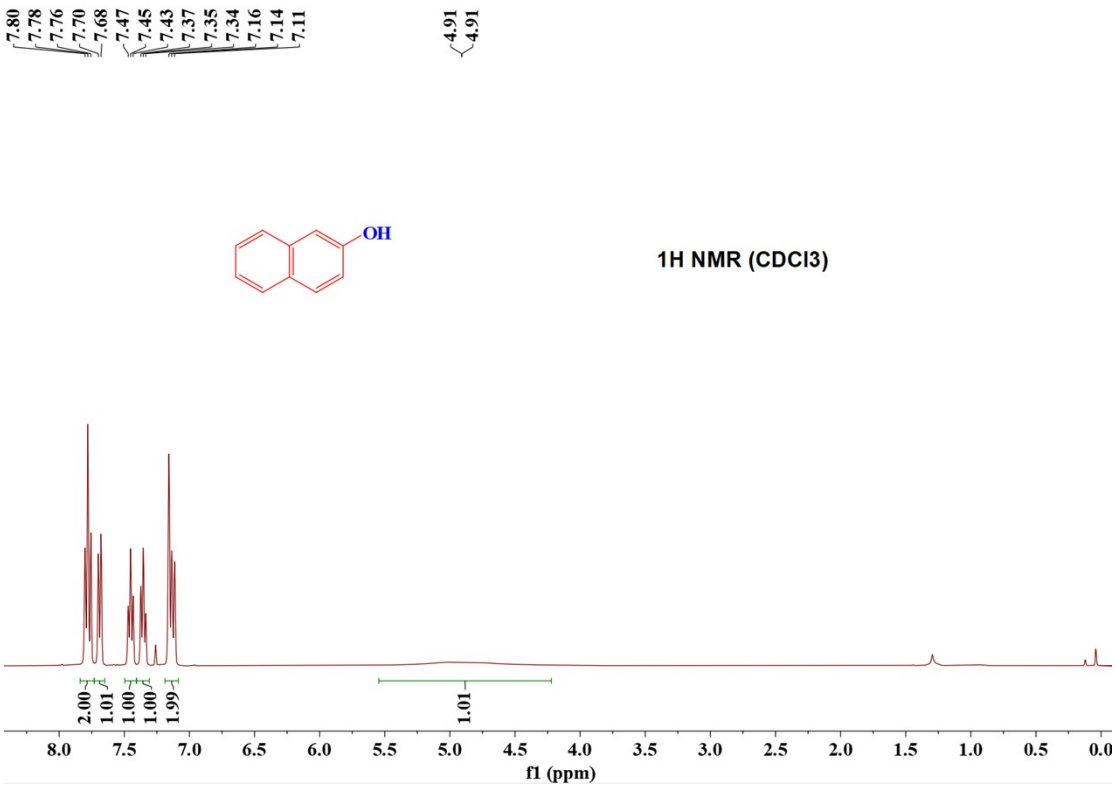


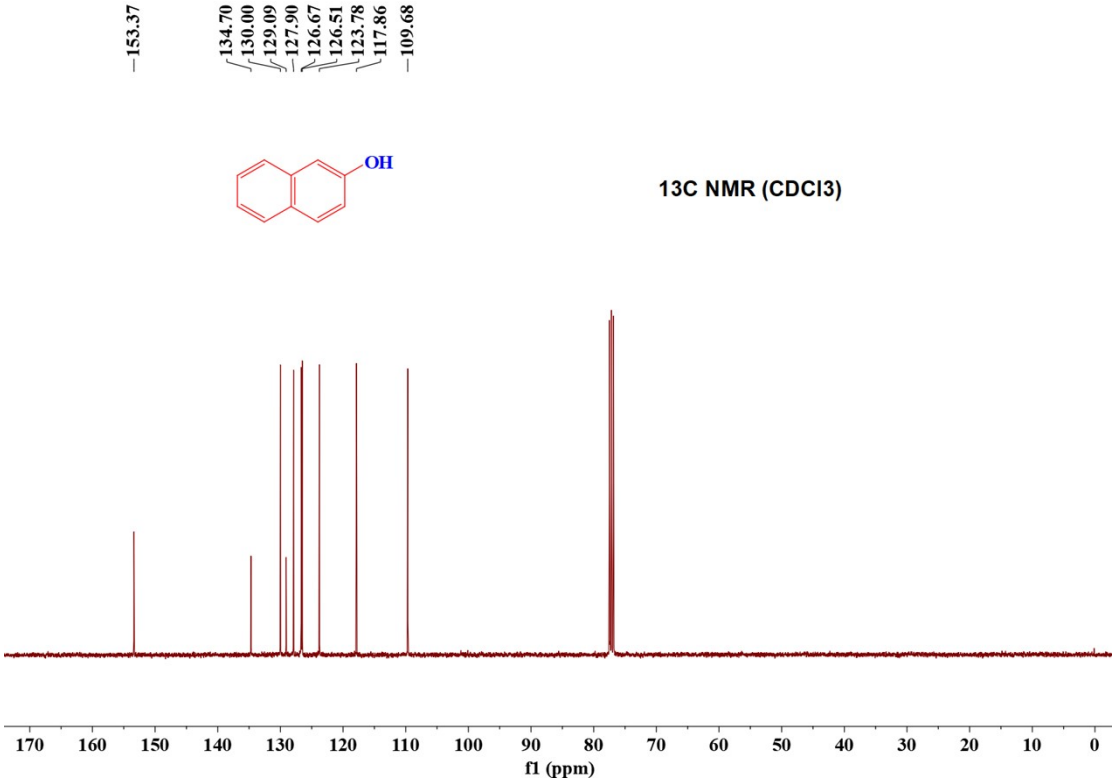
16. 2,3-dimethylphenol (**4p**)



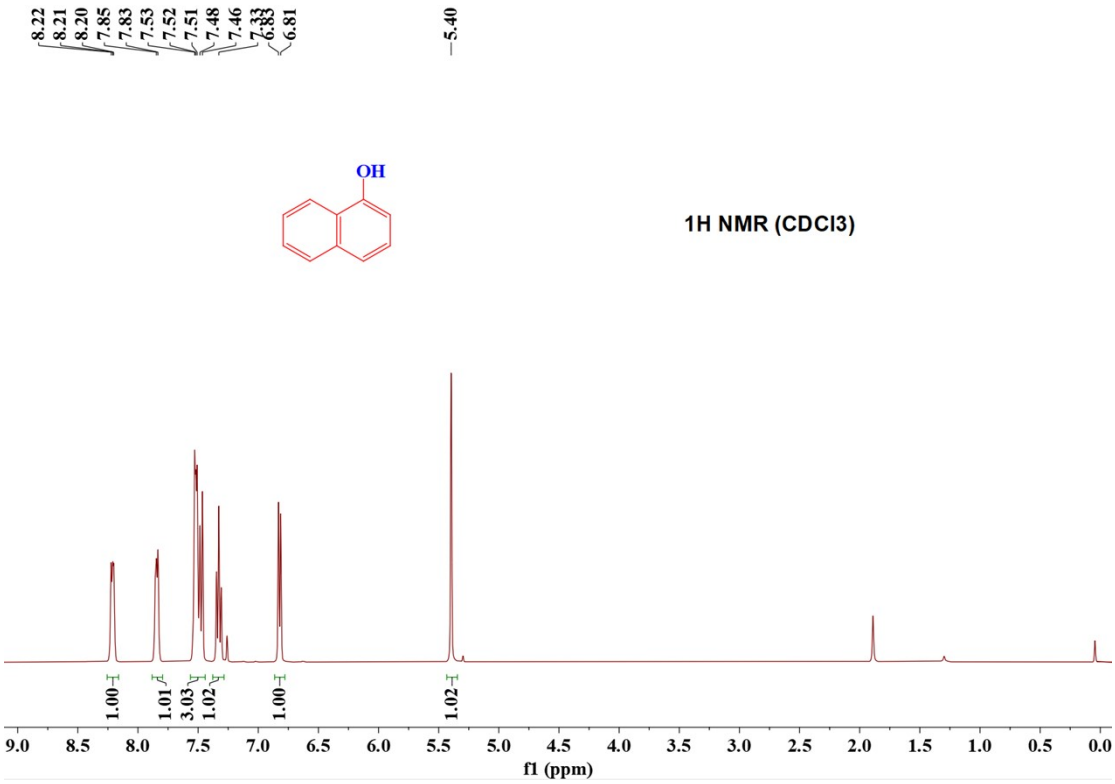


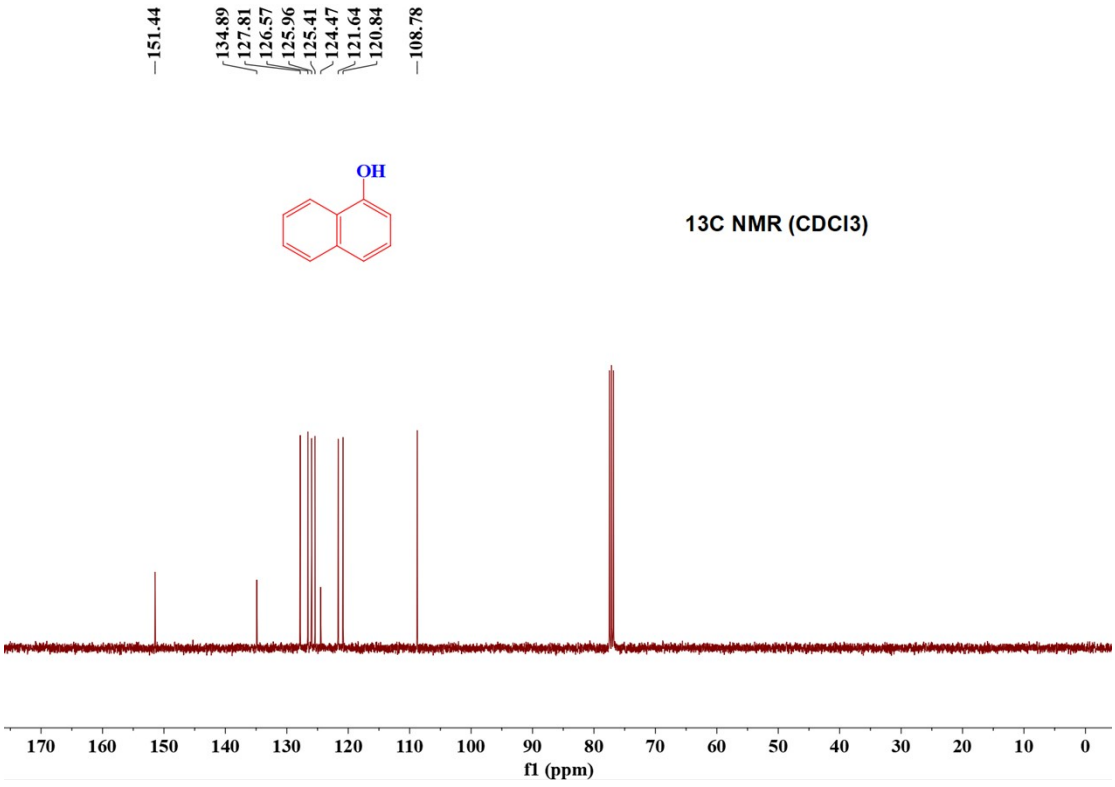
17. 2-naphthalenol (**4q**)



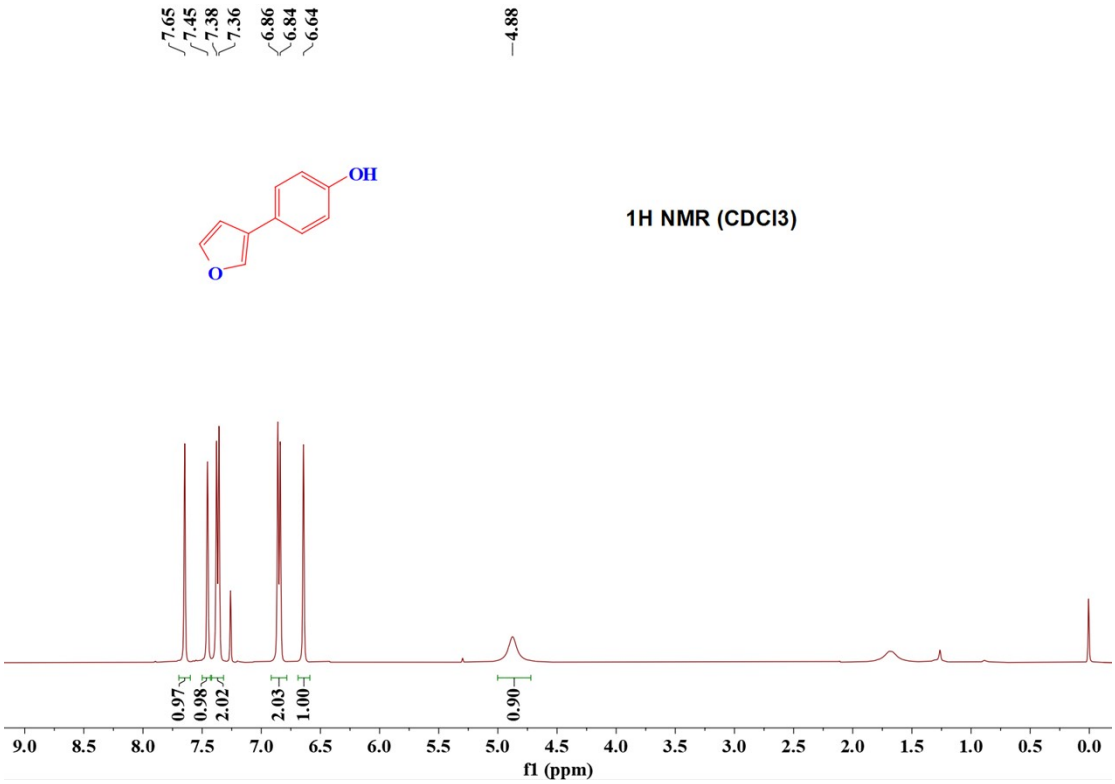


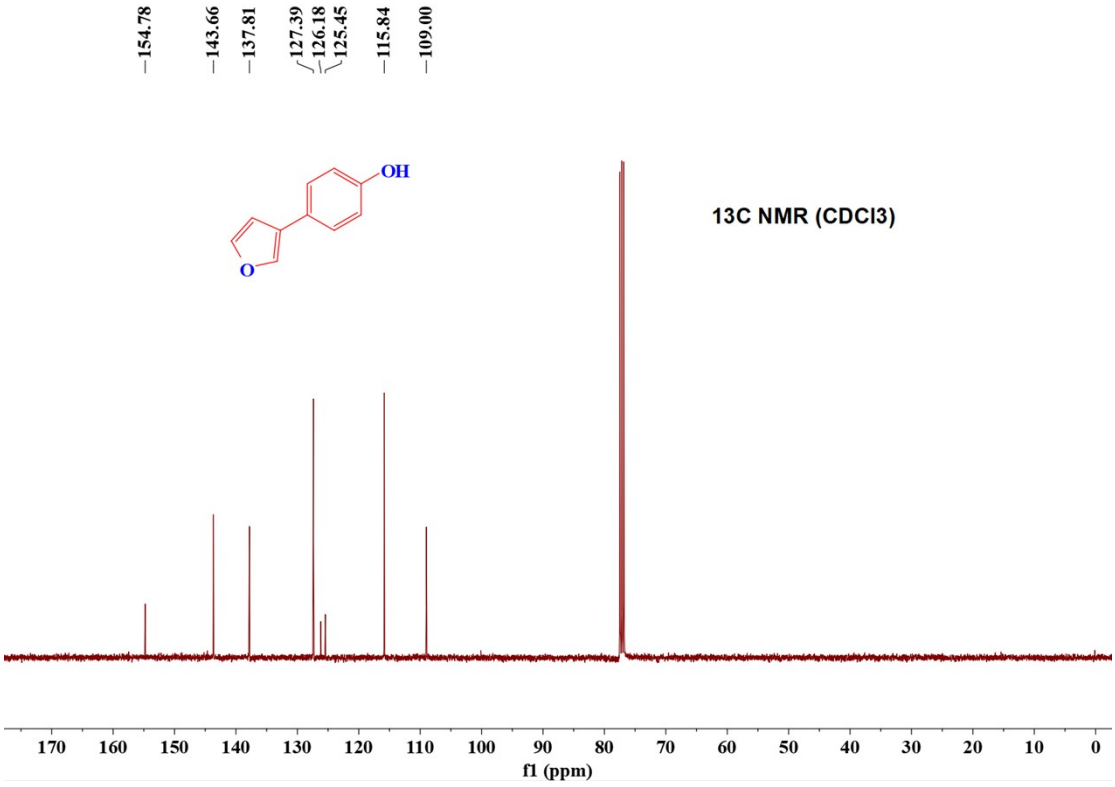
18. 1-naphthalenol (**4r**)



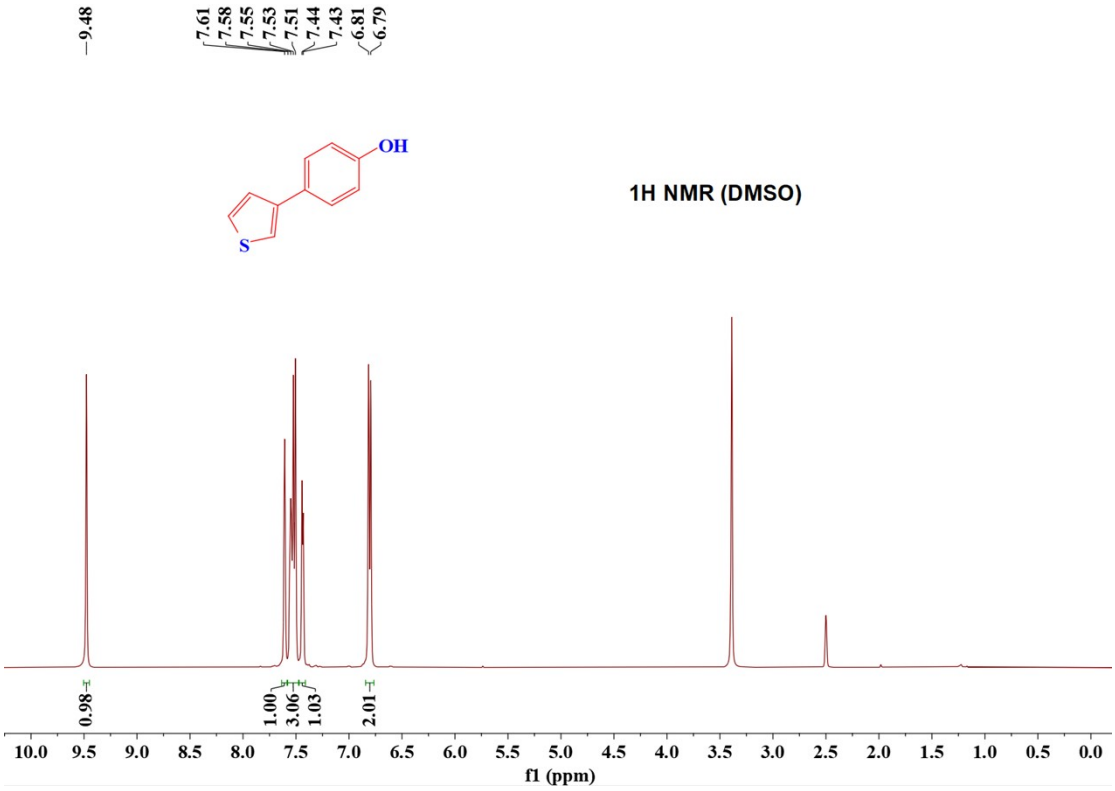


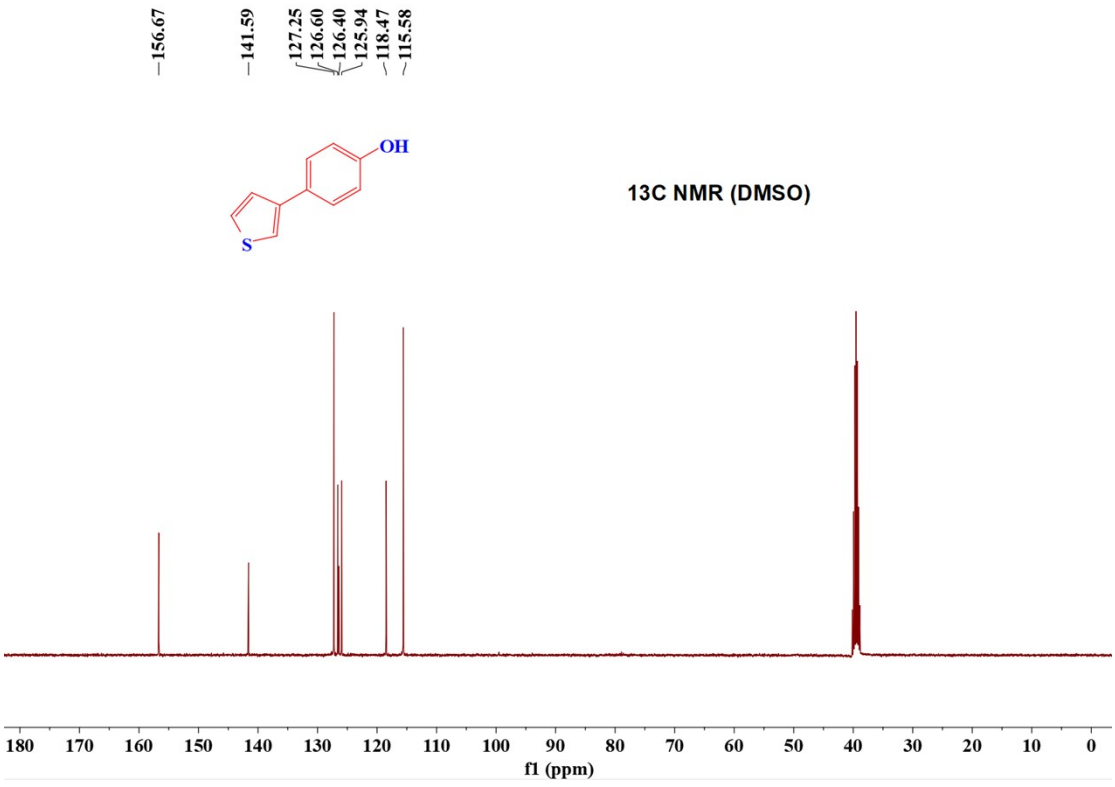
19. 4-(furan-3-yl)phenol (**4s**)



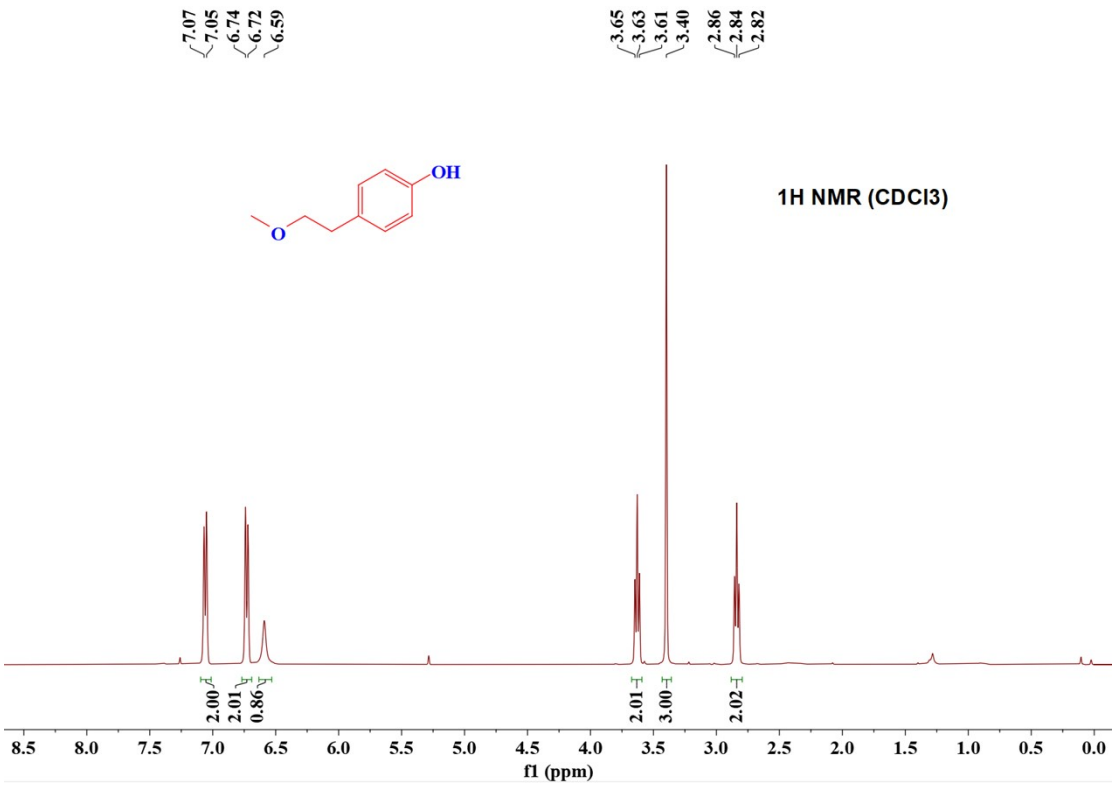


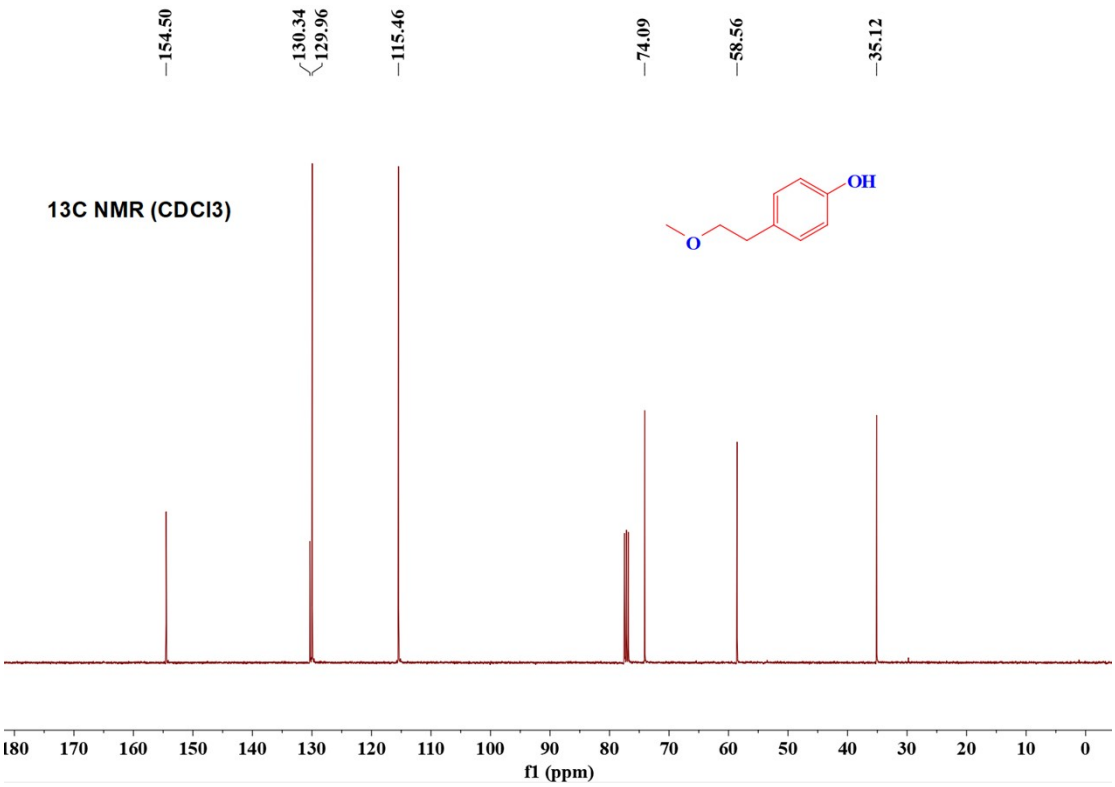
20. 4-(thiophen-3-yl)phenol (**4t**)



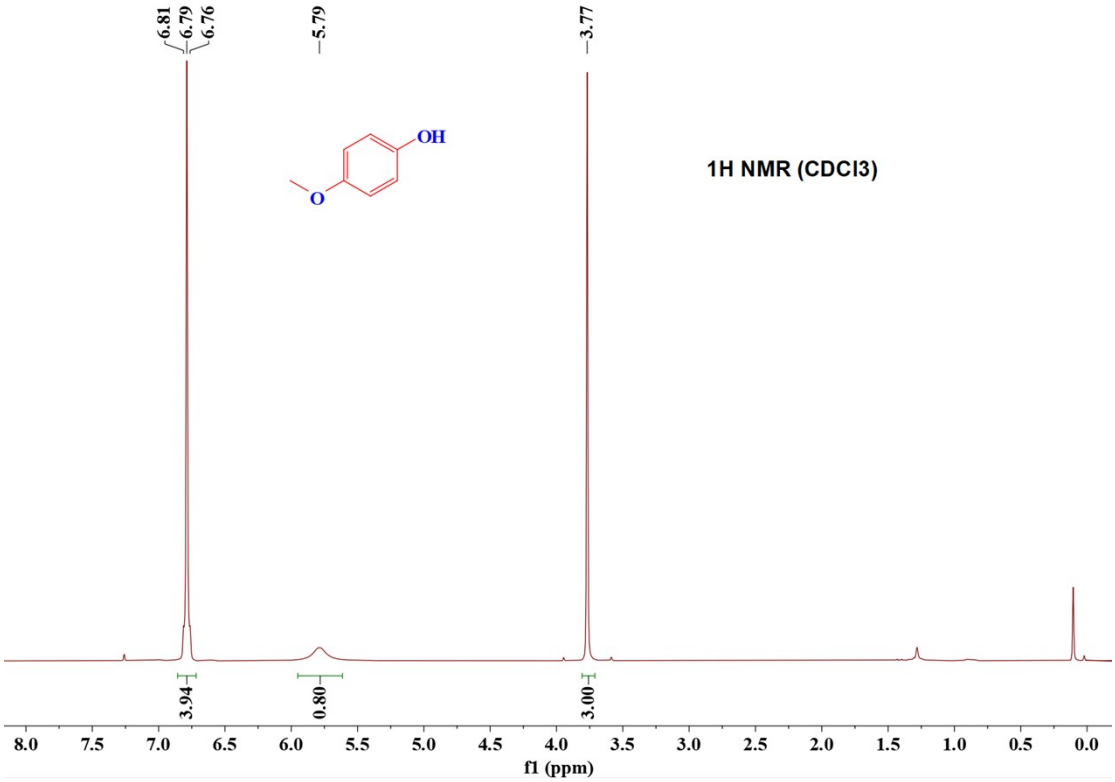


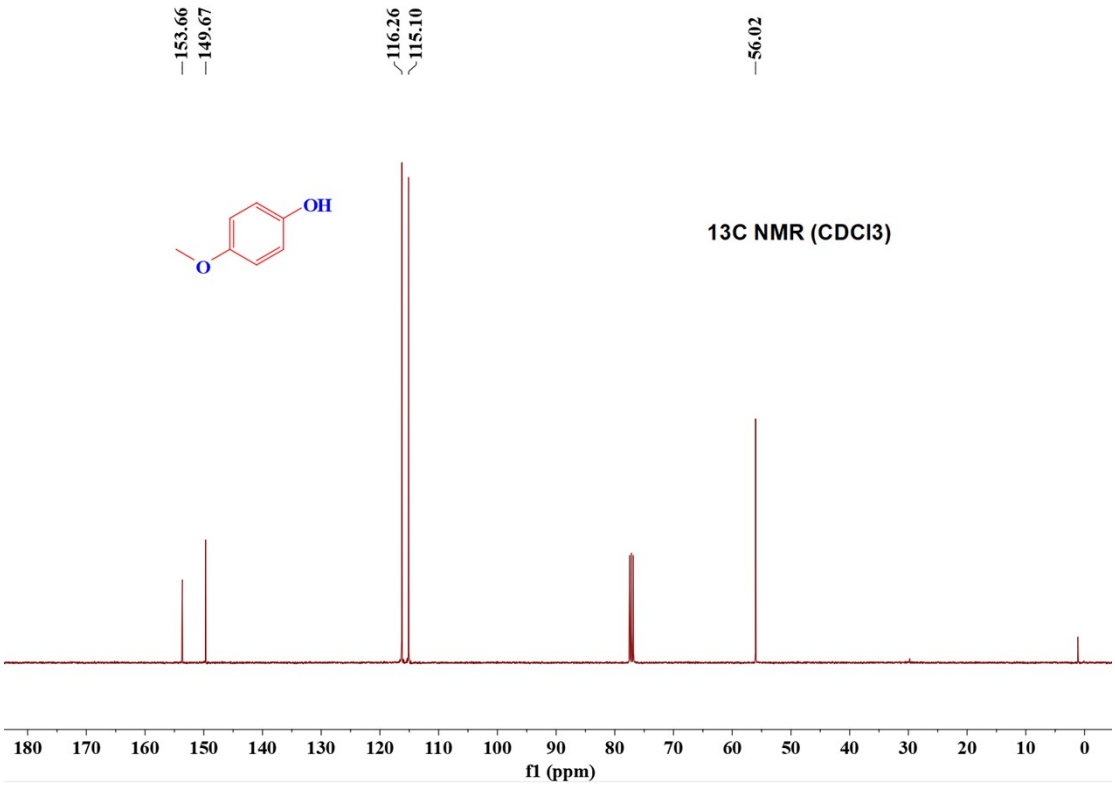
21. 4-(2-methoxyethyl)phenol (**4u**)



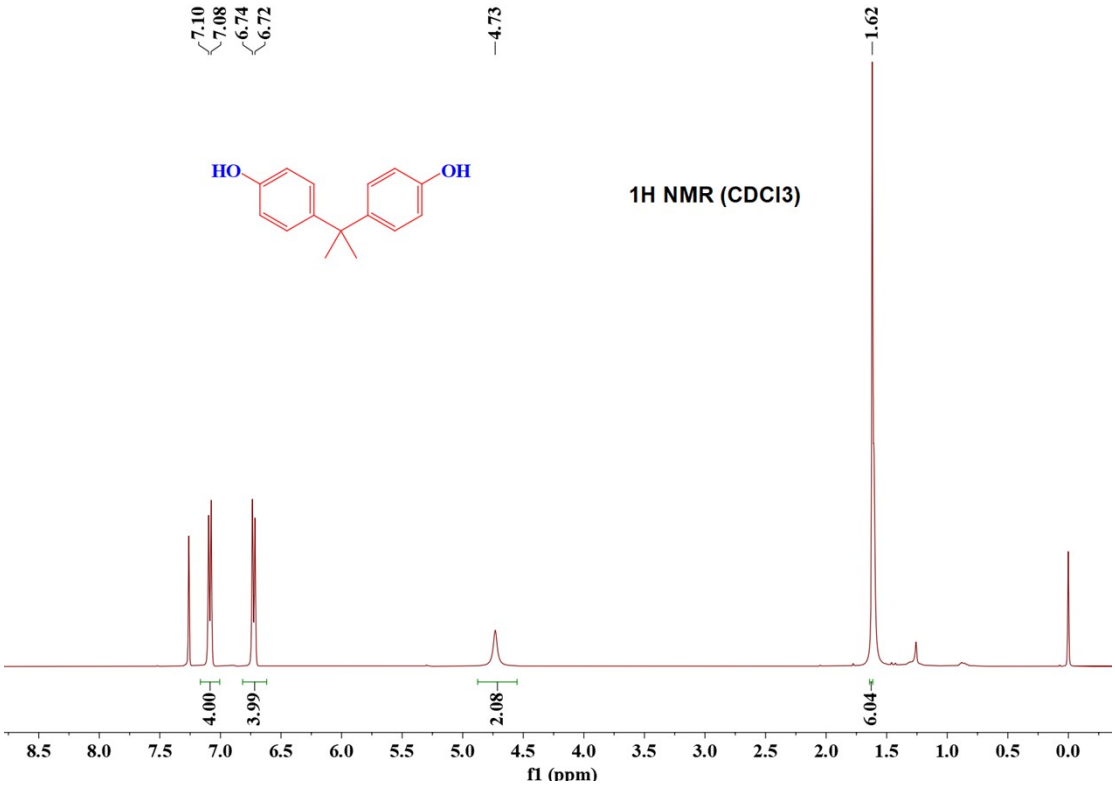


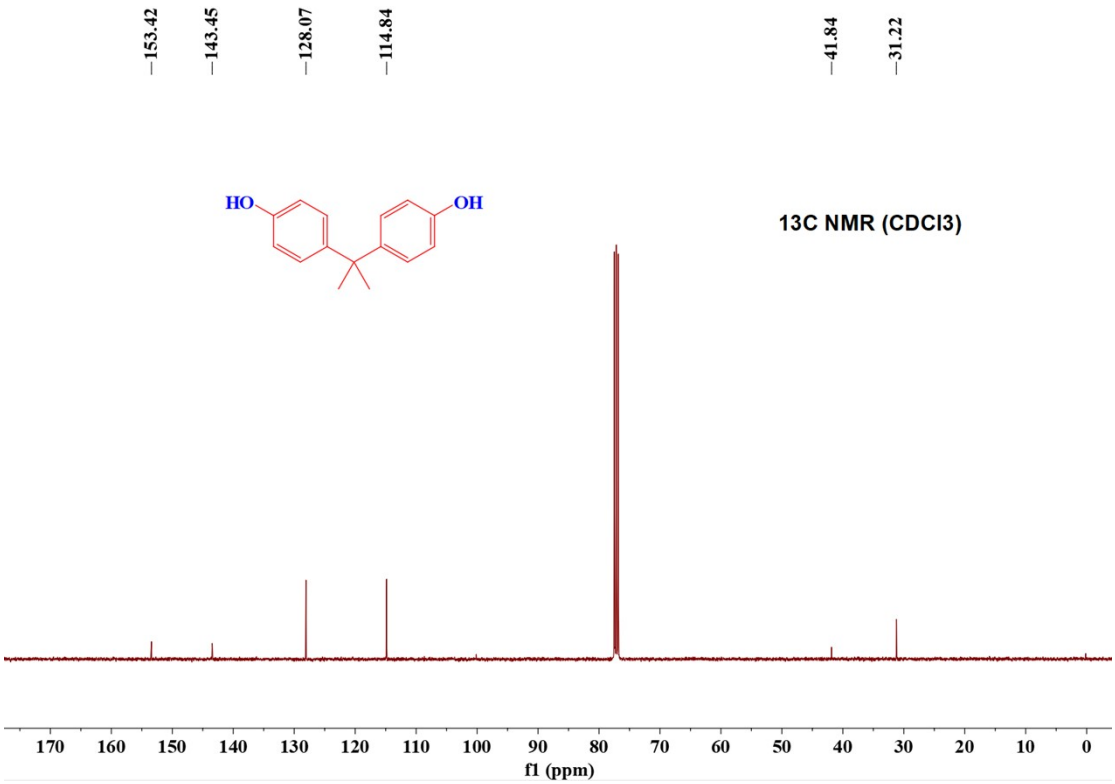
22. 4-methoxyphenol (**4v**)



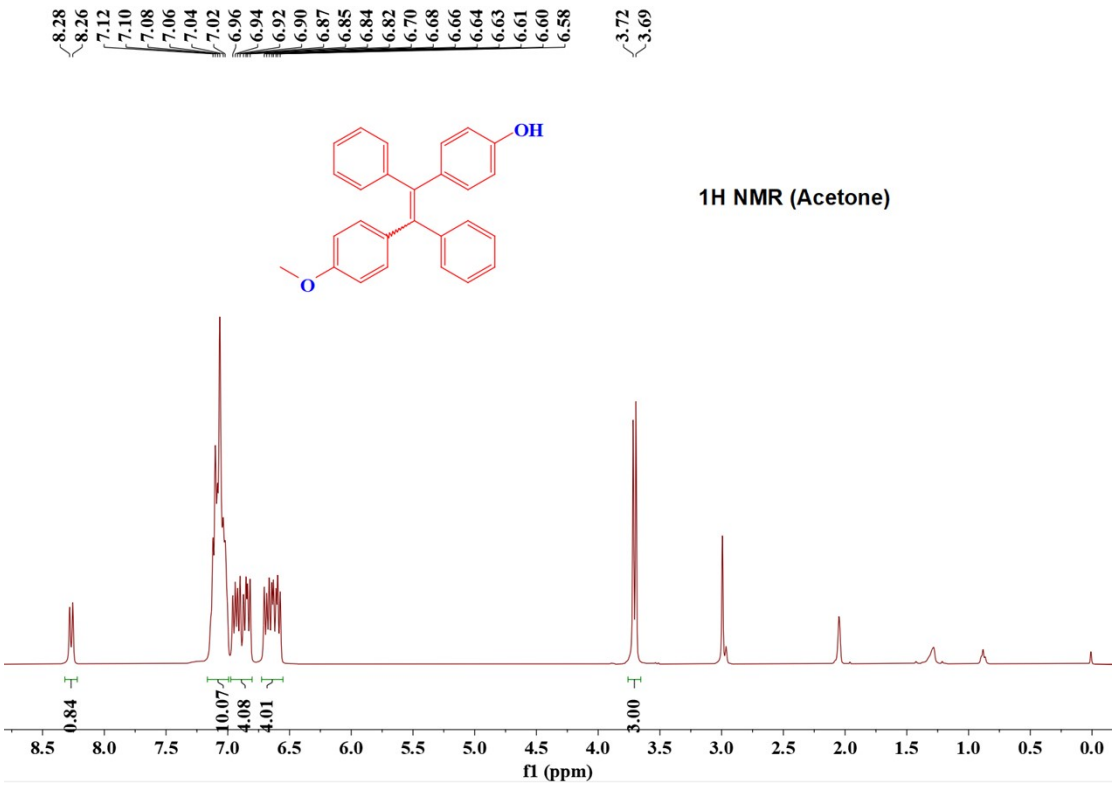


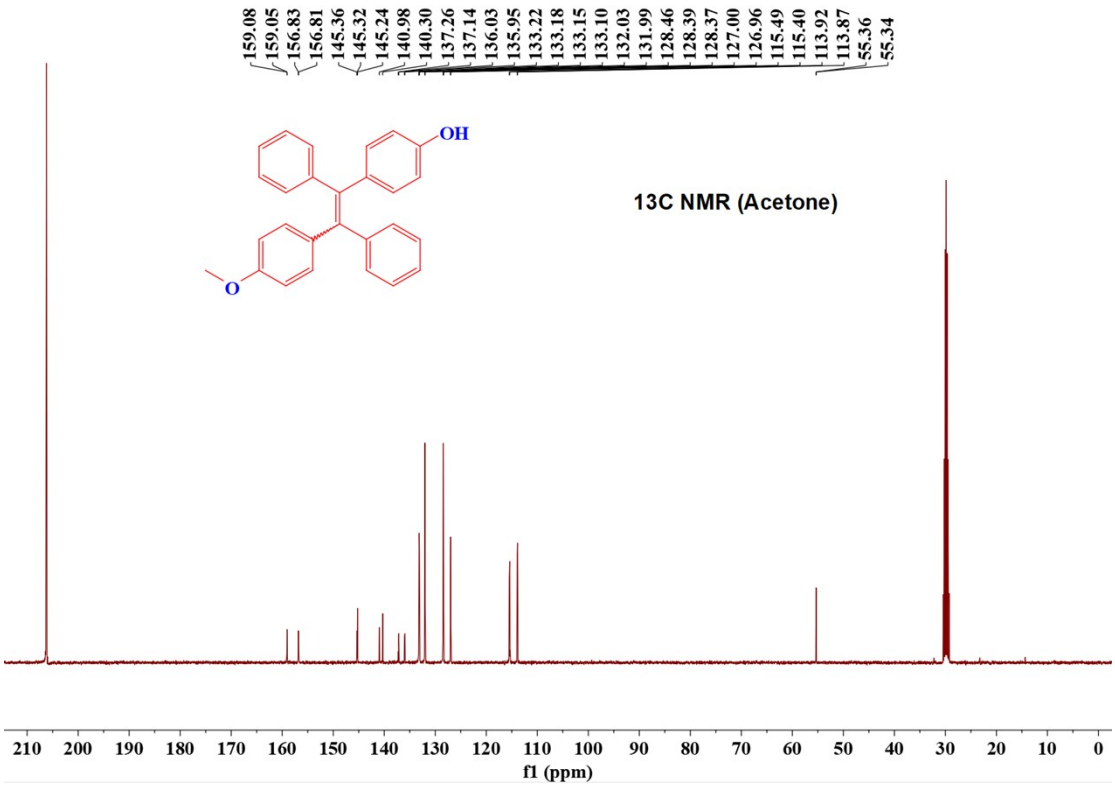
23. 4,4'-(1-methylethylidene)diphenol (**4w**)

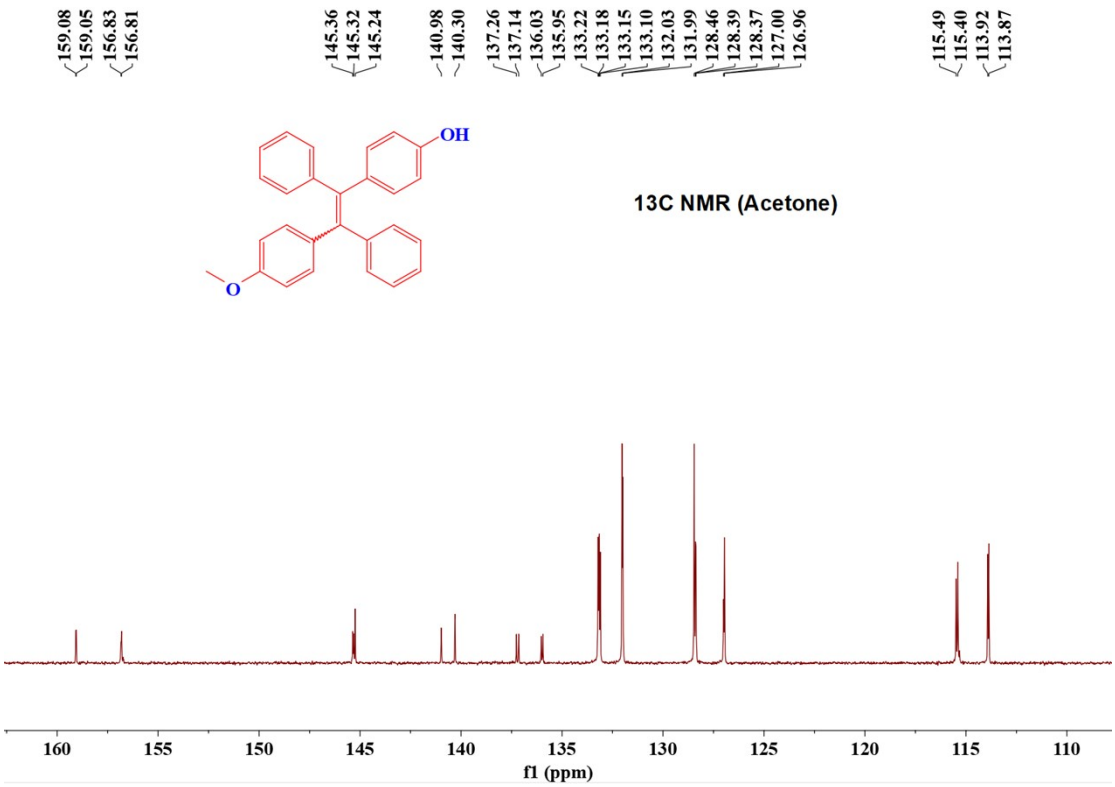




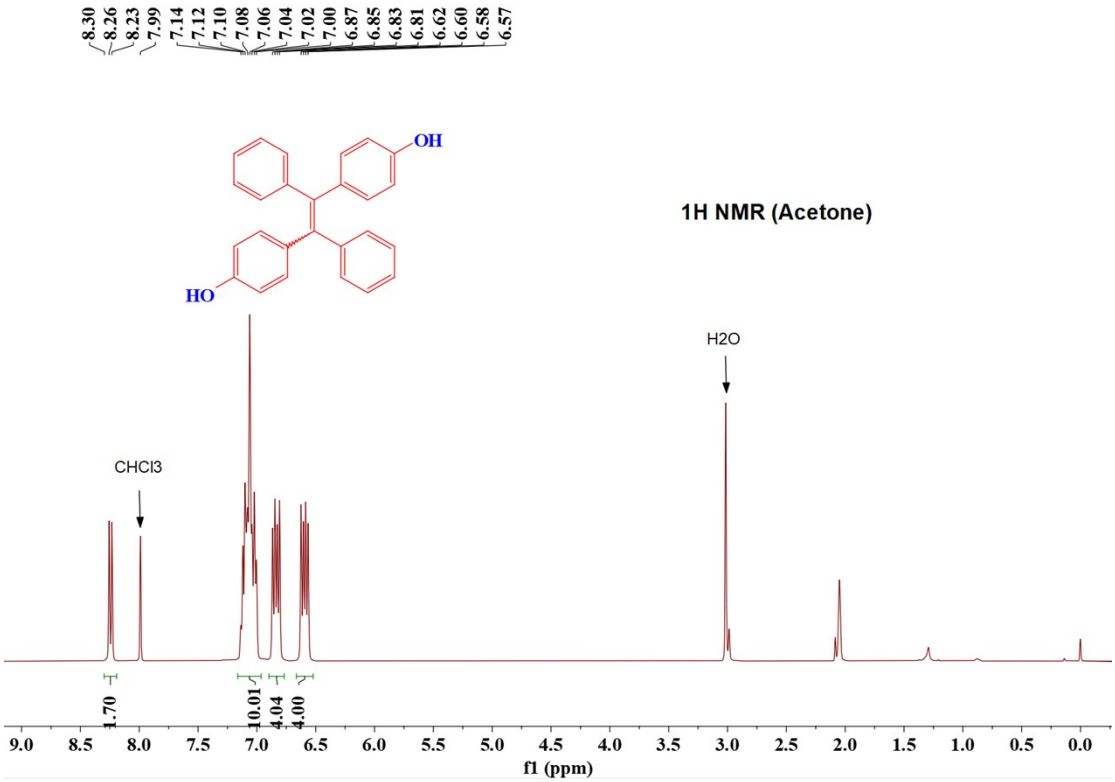
24. 4-(2-(4-methoxyphenyl)-1,2-diphenylvinyl)phenol (**4x**)

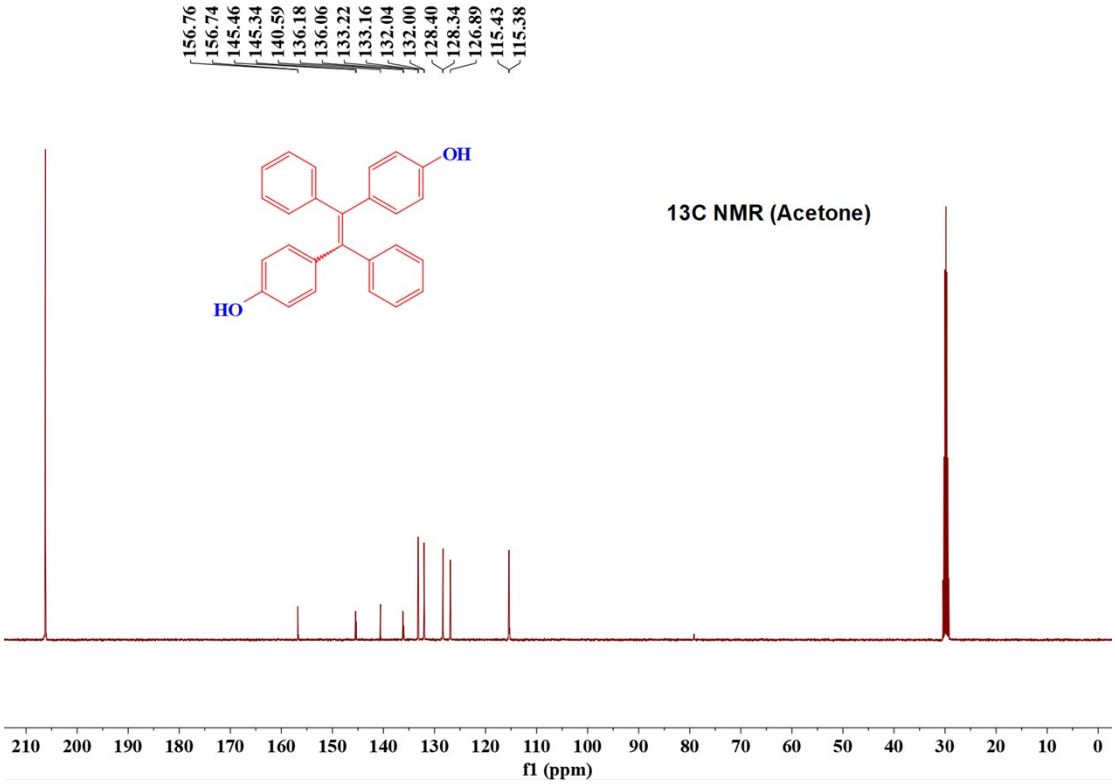


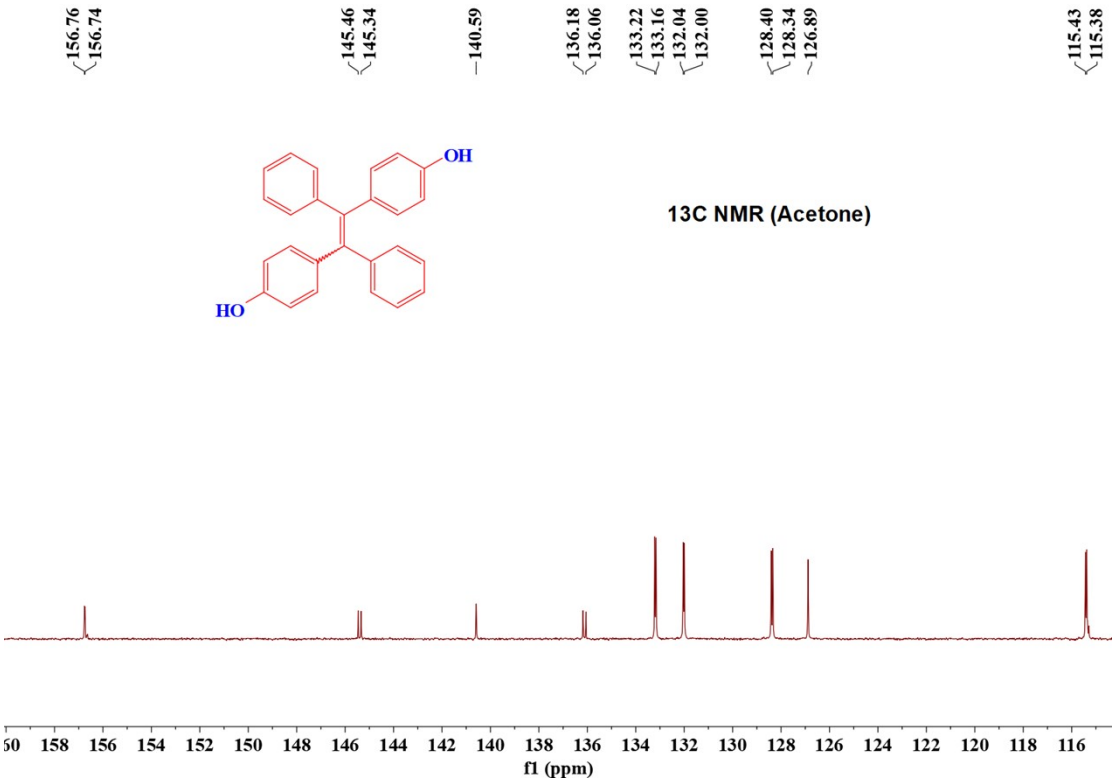




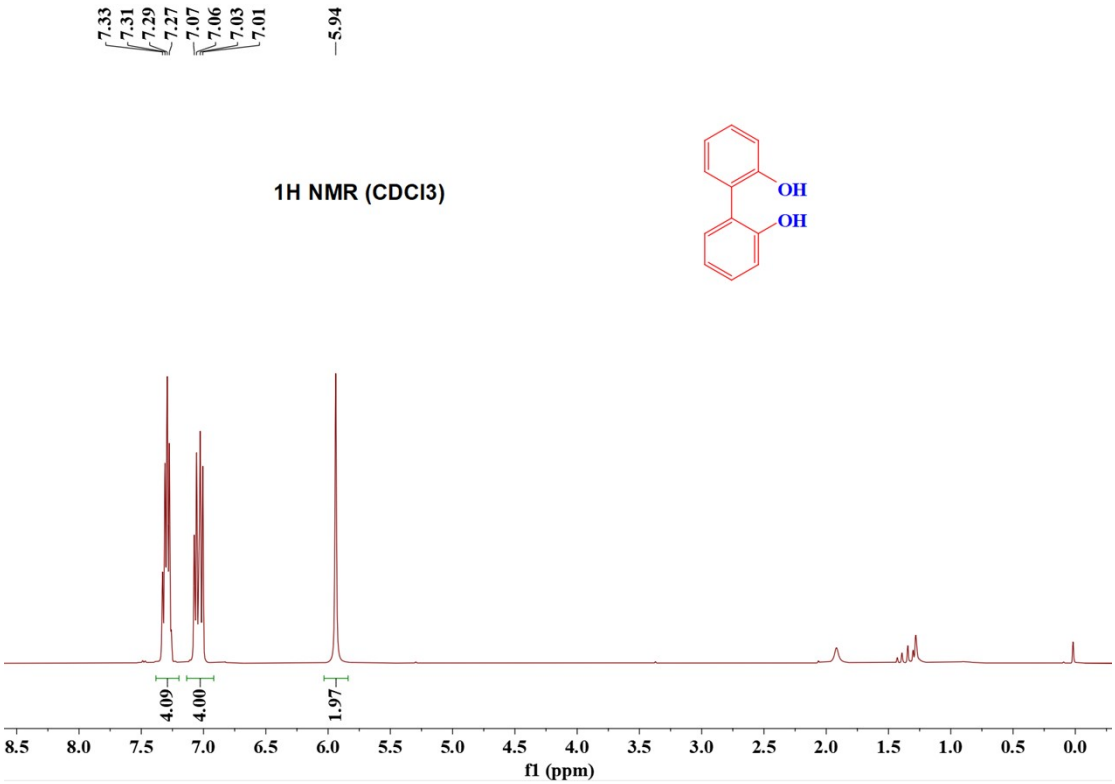
25. 4,4'-(1,2-diphenylethene-1,2-diyl)diphenol (**4y**)

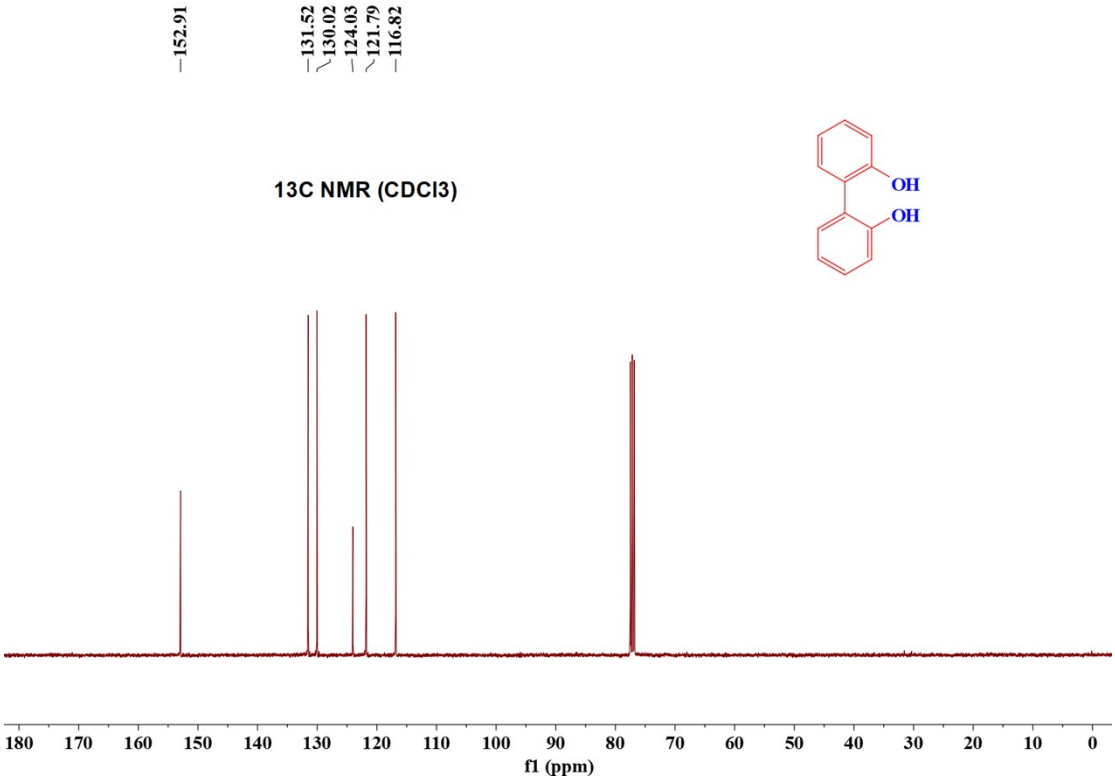



156.76
156.74
145.46
145.34
140.59
136.18
136.06
133.22
133.16
132.04
132.00
128.40
128.34
126.89
115.43
115.38
OH
HO
13C NMR (Acetone)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

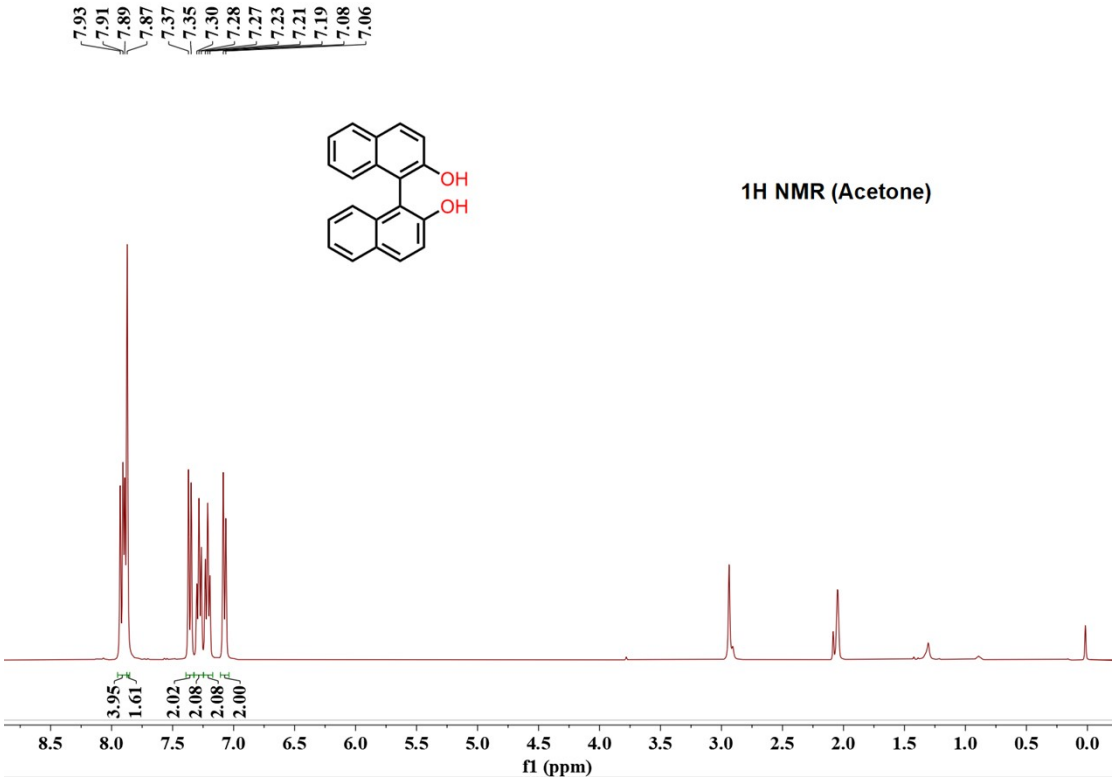

156.76
156.74
145.46
145.34
140.59
136.18
136.06
133.22
133.16
132.04
132.00
128.40
128.34
126.89
115.43
115.38
OH
HO
13C NMR (Acetone)
50 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)

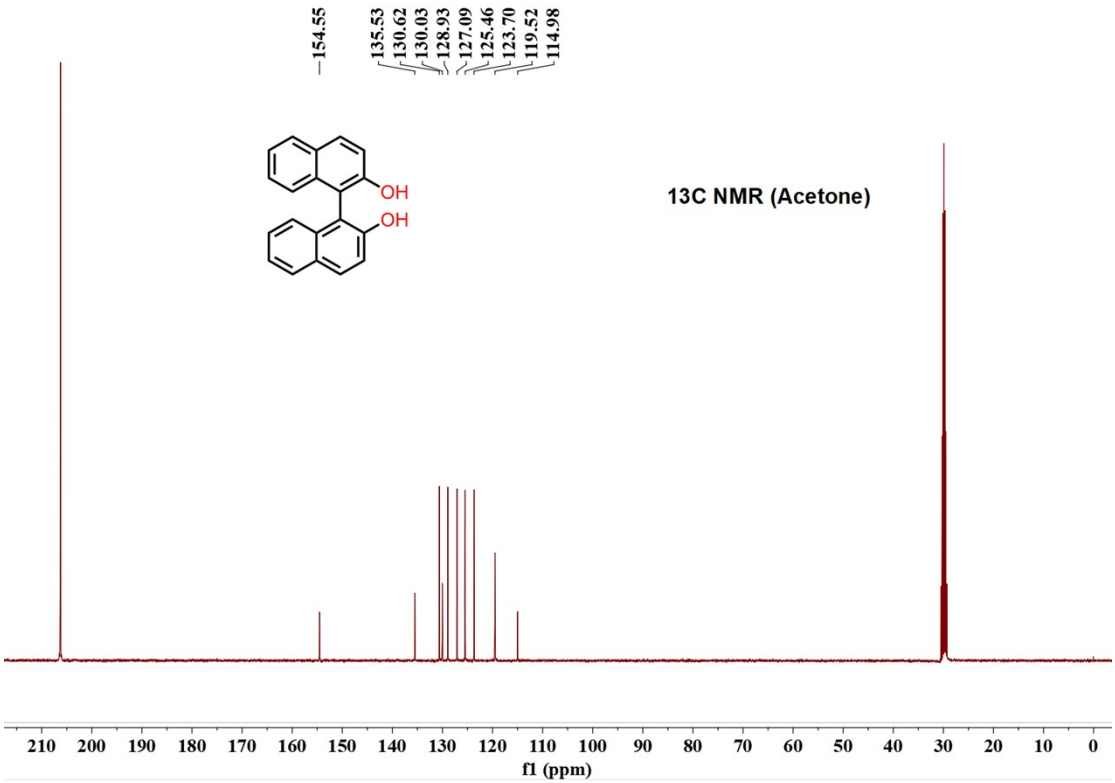
26. [1,1'-biphenyl]-2,2'-diol (**4z**)



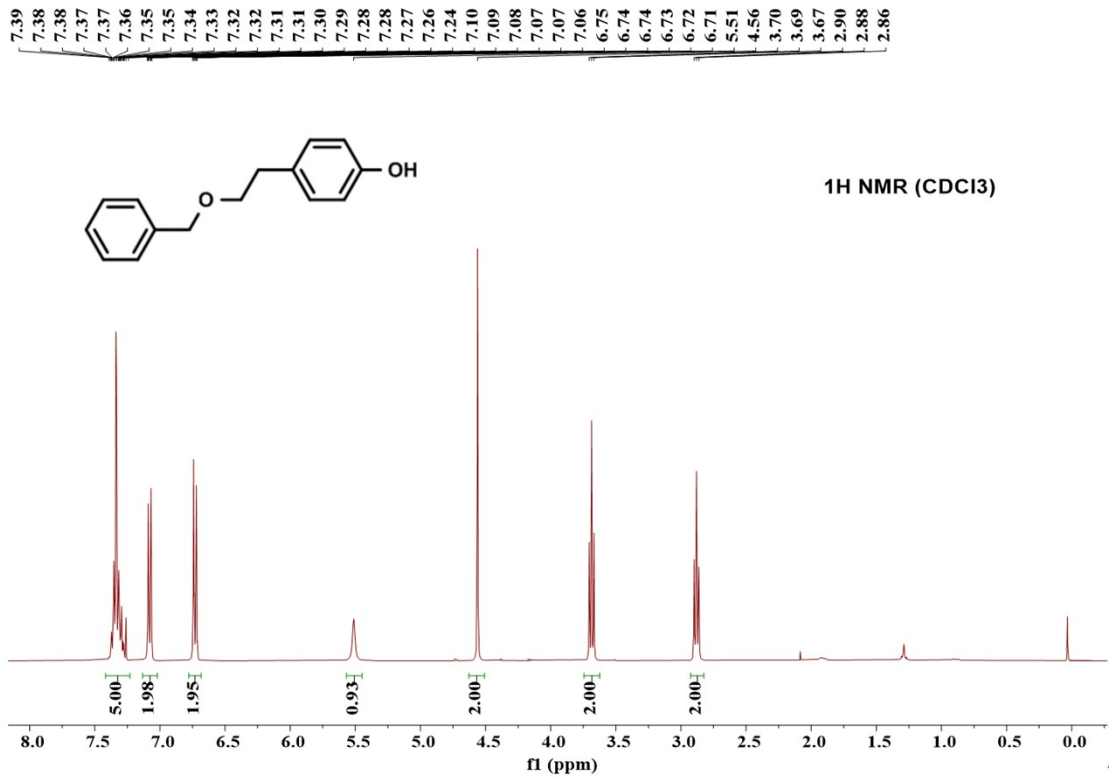


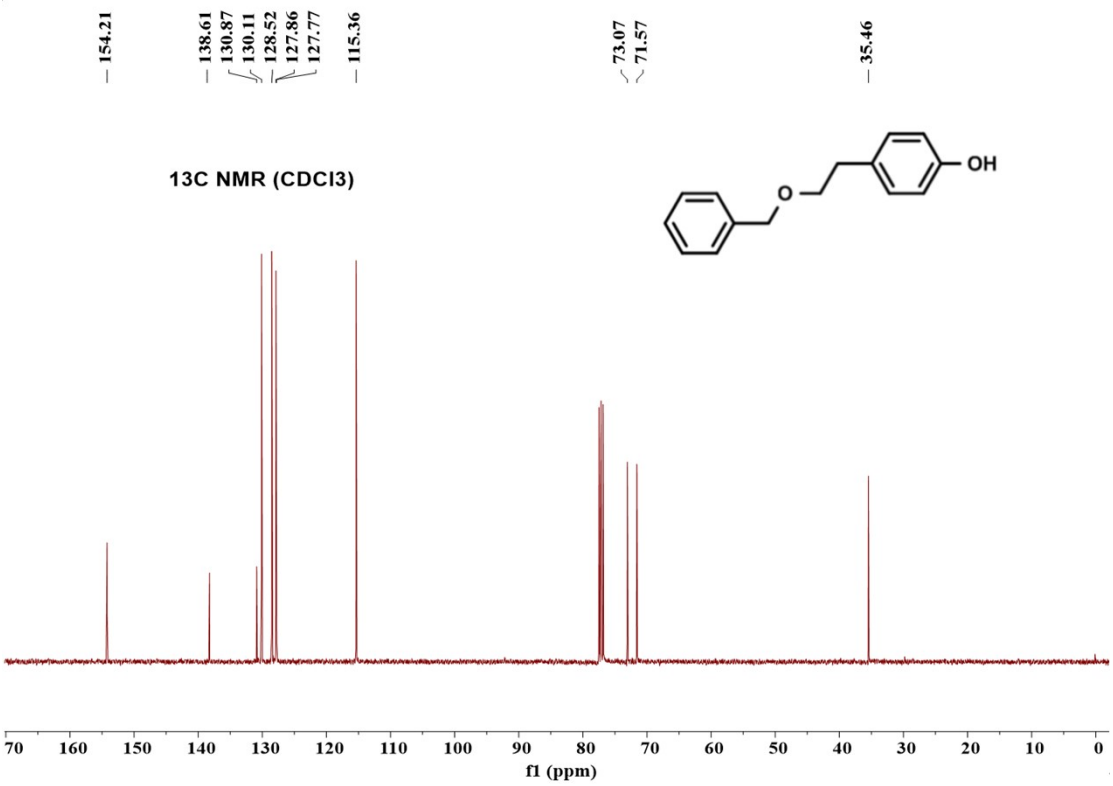
27. 1-(2-hydroxynaphthalen-1-yl)naphthalen-2-ol (**4aa**)



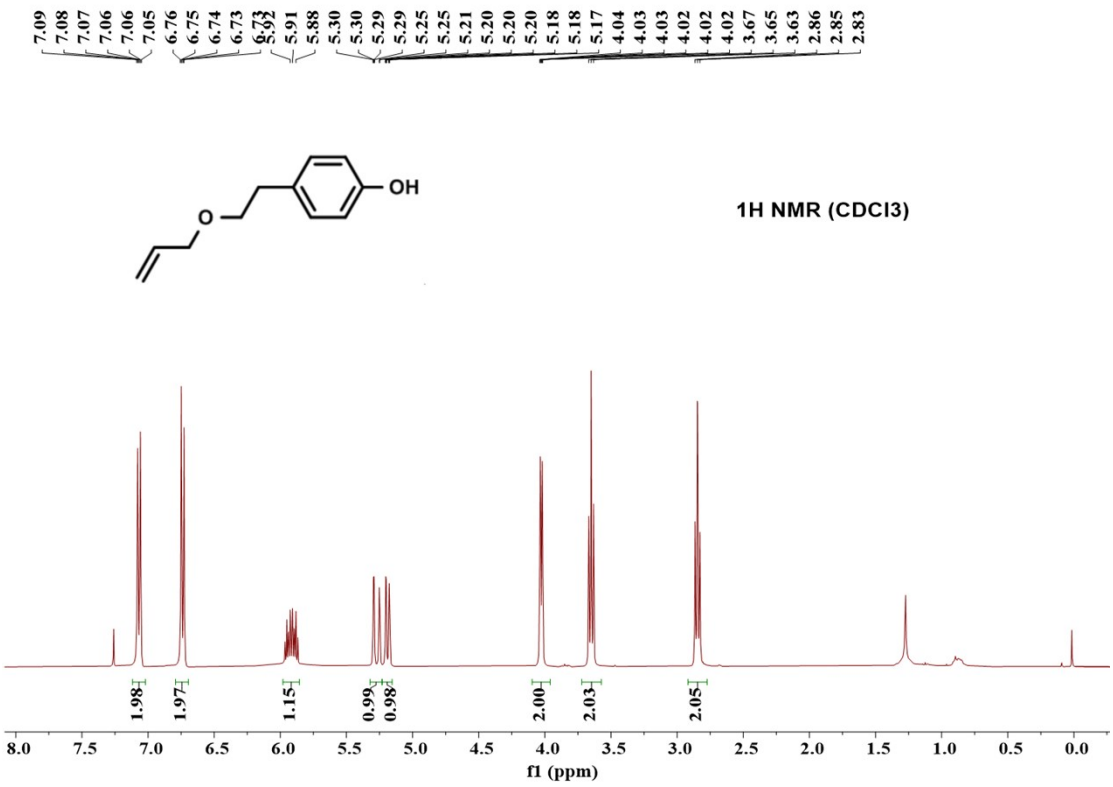


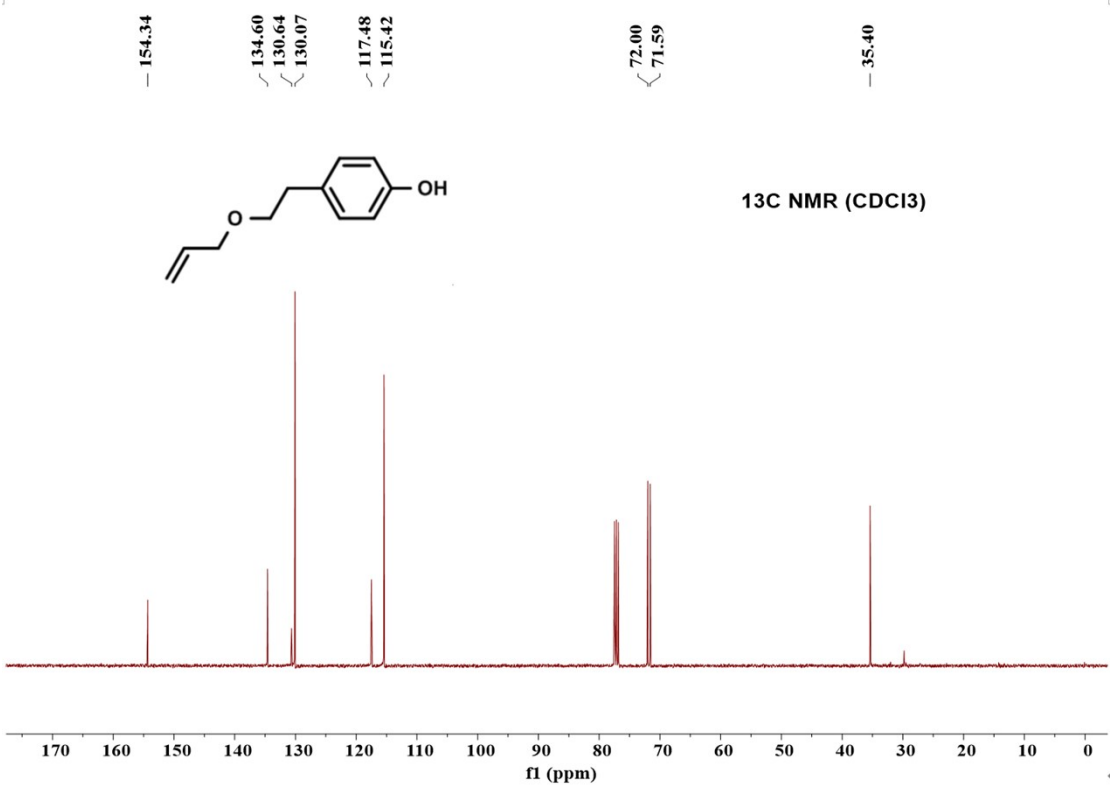
28. 4-(2-benzyloxyethyl)phenol (**4ab**)



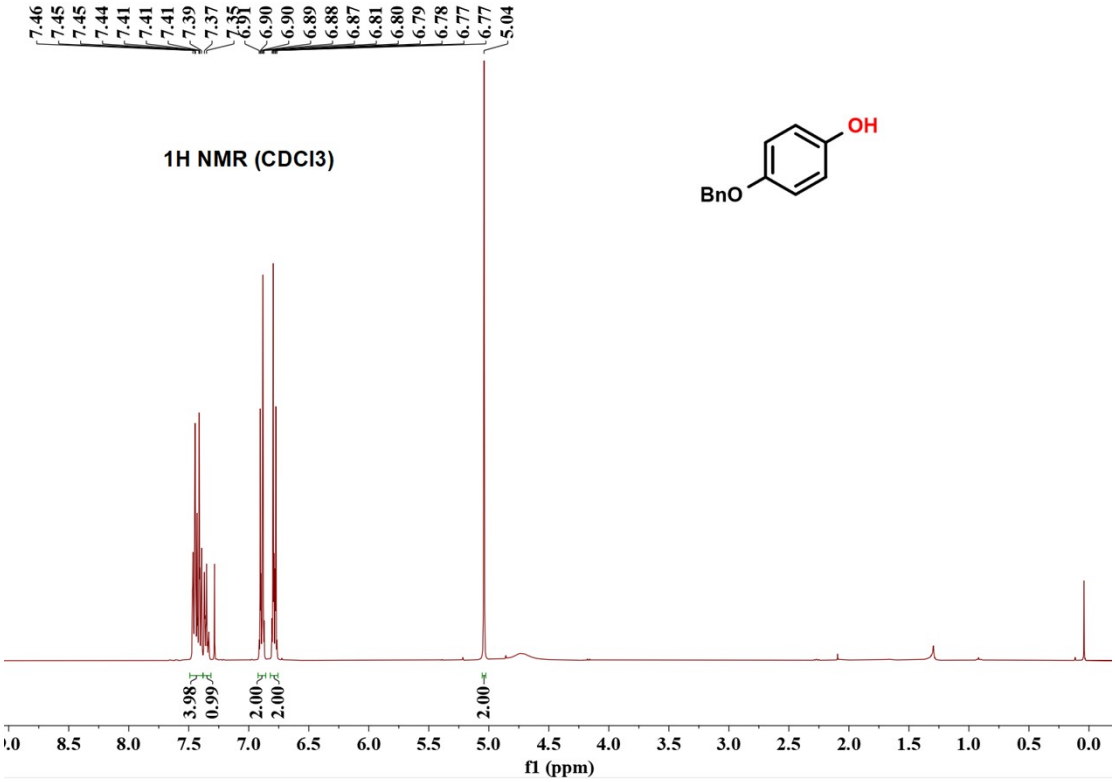


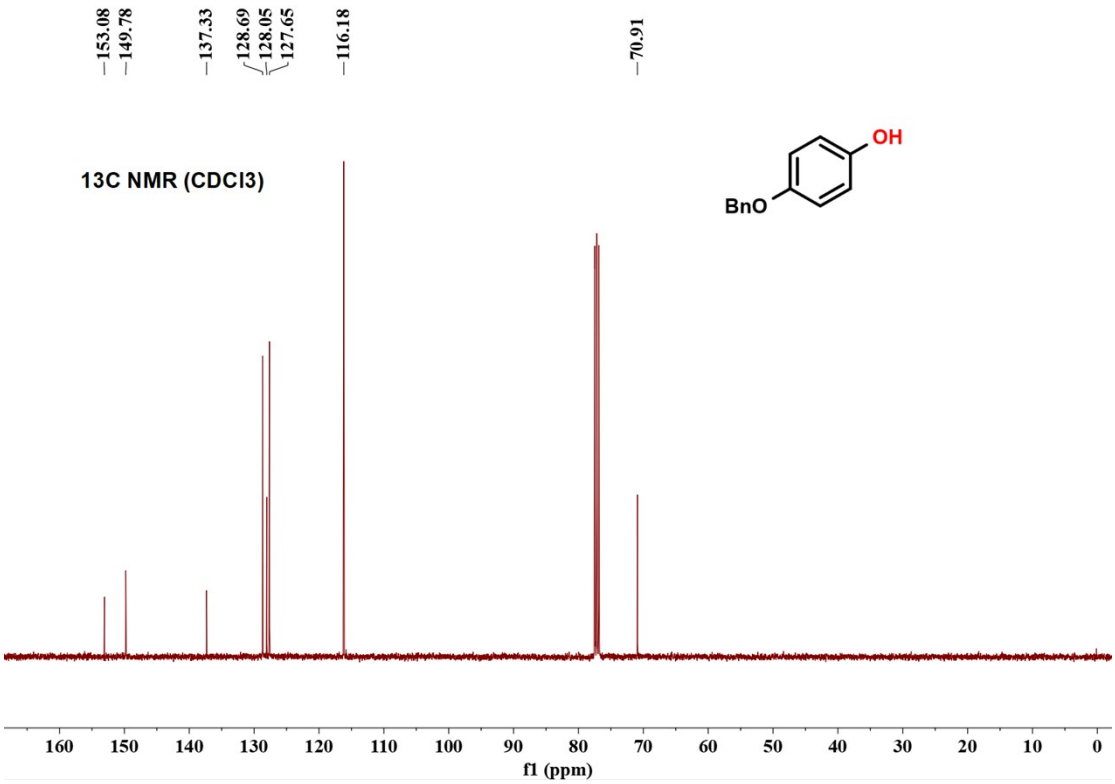
29. 4-(2-allyloxyethyl)phenol (**4ac**)



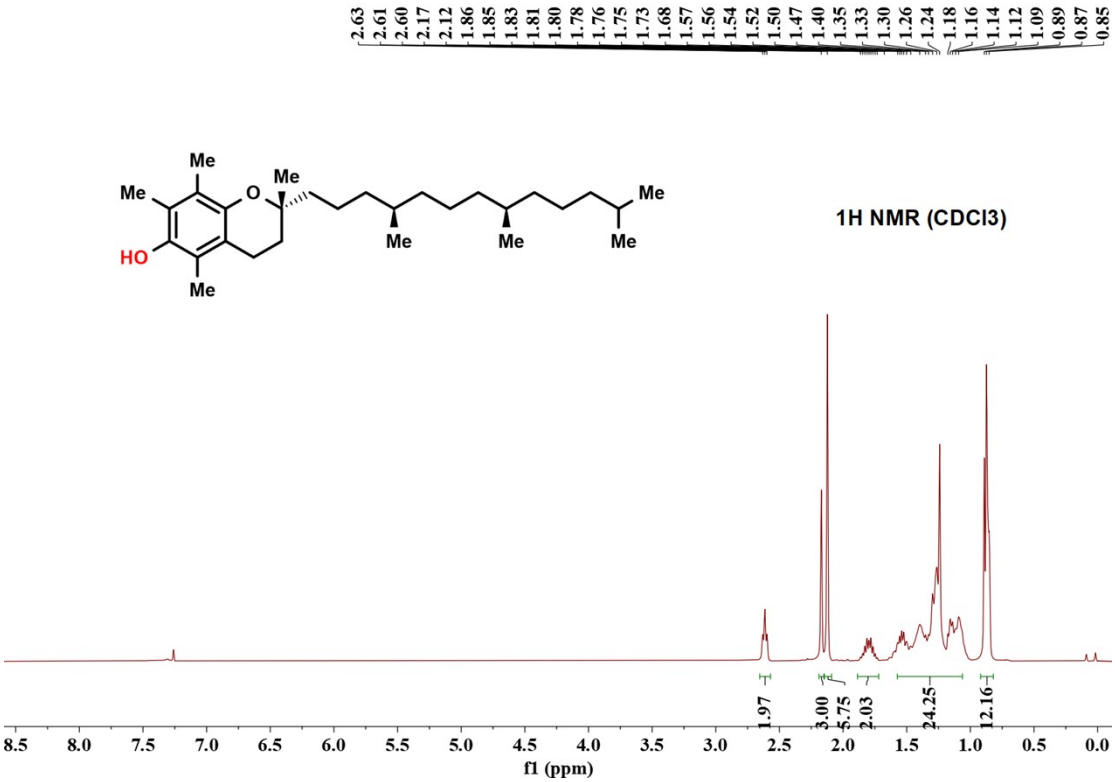


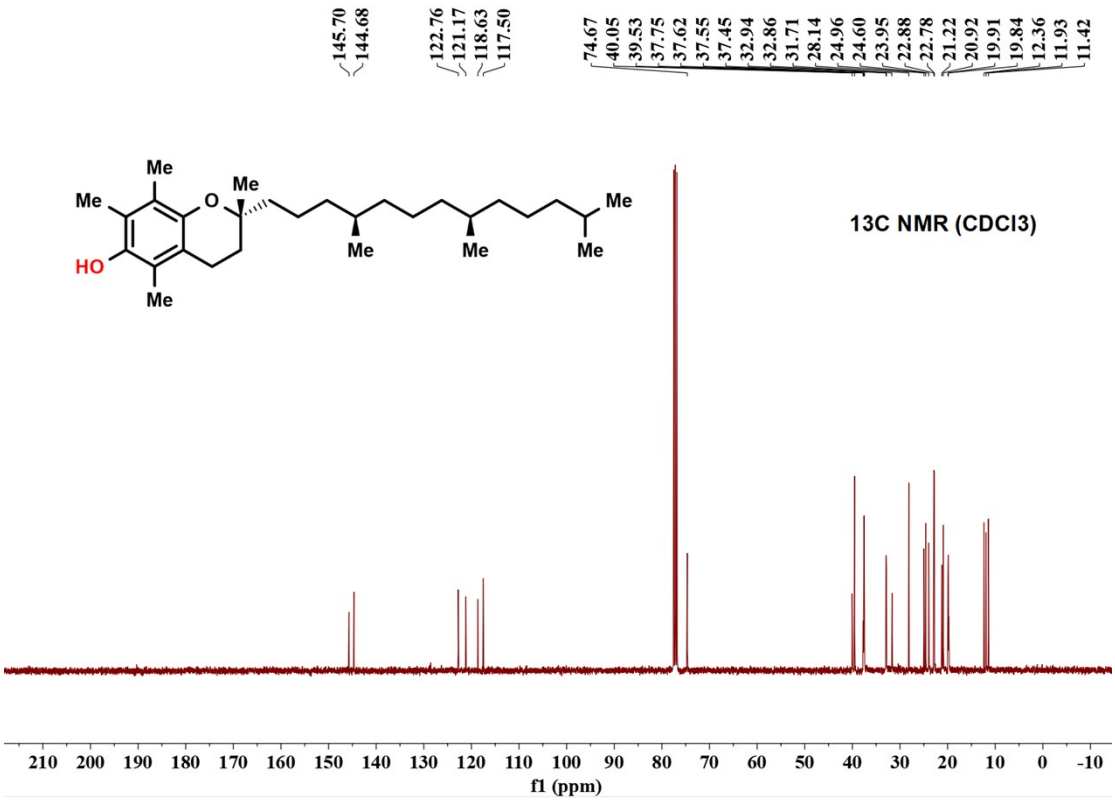
30. 4-Benzyloxyphenol (**4ad**)





31. D-α-tocopherol (**4ae**)





32. 17-methoxy-1,3,5(10)-estratrien-3-ol (**4af**)