A domino transformation of D-glucal to α-substituted α-hydroxymethyl furfuryl derivatives

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Supporting Information

Section A: General Information S2

Section B: Experimental procedures and spectral analysis S2-S13

Section C: 1H NMR and 13C NMR Spectra S14-S32

Section A: General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 200 and 500 MHz spectrometers with TMS as the internal standard. Chemical shifts were expressed in parts per million (δ ppm). MS were recorded on JEOL MSD-300 and Bruker Esquire 3000 LCMass spectrometer. Silica gel coated aluminium plates were used for TLC. Elemental analyses were performed on Elementar Vario EL-III. Optical rotations were measured on Perkin-Elmer 241 polarimeter at 25 oC using sodium D light. Reagents and solvents used were mostly of LR grade.

Section B: Experimental procedure

(1) General procedure for $In(OTf)_3$ catalysed synthesis of α-substituted α-hydroxy methyl furfuryl derivatives

The nucleophile (1.5 equiv.) and $In(OTf)_3$ (1 mol %) were successively added to a solution of glucal (1eqv.) in acetonitrile (3 mL/mmol substrate) and stirred for the specified time (Table 1). The reaction mixture was concentrated, diluted with ethyl acetate and washed with saturated sodium bicarbonate solution (10 mL). The organic layer was separated, evaporated and the crude mixture was subjected to flash chromatography over silica gel (100-200 mesh) to afford corresponding pure product. The following nucleophiles were used for the transformations.

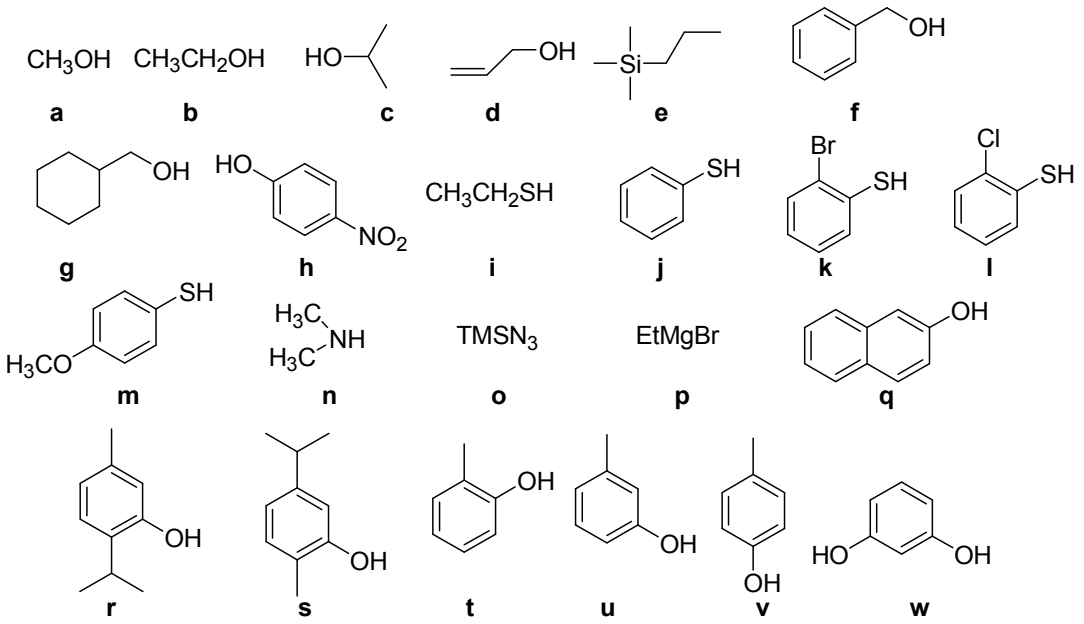


Figure 1. Nucleophiles **a-w** employed in the reaction with glucal

On a larger scale (~20 mol of the substrate), the reaction proceeded in a similar manner even with a lower catalyst loading (0.5 mol %) thus making this process amenable for easy scale up.

(2) Optimization of the protocol

(a) Comparison of catalytic efficacy of different Lewis acids

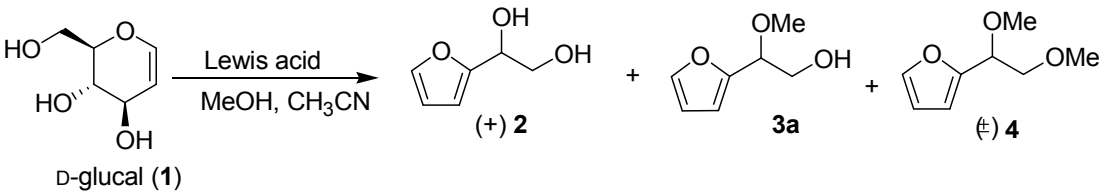


Table 1: Reaction of D-glucal (1 eqv.) with MeOH (1.5 eqv.) in the presence of different Lewis acids:

Entry	Acid catalyst[a]	Time (h)	Yield[b](**2c**:**3**:**4**)%
1	$InCl_3$	1.2	40 (3:6:1)
2	$InBr_3$	.5	65 (2:7:1)
3	$Sc(OTf)_3$	.5	60 (1:5.5:2)
4	$In(OTf)_3$	.2	76 (1.1:9:1)
5	$HClO_4$.silica	1.5	35 (2:1.5:1)
6	InCl3.H2O	1.2)	30 (4:3:1)
7	$HgSO_4$	1.8	20 (3:1.5:1)

a. Catalyst loading 1 mol %
b. Isolated yield of compound **3a** after column chromatography.
c. Rotation value of compound **2** is +34 (c 1.3, $CHCl_3$)

(b) Solvent effect on domino reaction

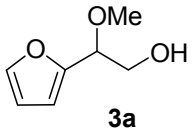
Table 2: Solvent effect on reaction of D-glucal (1eqv.) with MeOH (1.5eqv.) in presence of 1mol% $In(OTf)_3$

Entry	Solvent[a]	Time (h)	Yield[b]%
1	DMF	1.2	52
2	THF	1.8	45
3	Acetone	2.3	60
4	Acetonitrile	0.2	76
5	Ionic liquid	1	55

a. In every case 3 ml/mmol of solvent was used .
b. Isolated yield after column chromatography.

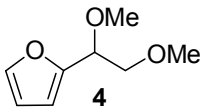
(3) Experimental procedure for the reaction of D-glucal with $TMSN_3$ using water as a solvent: $TMSN_3$ (1.5eqv.), $In(OTf)_3$ (1mol %) were successively added to a solution of glucal (1eqv.) in water (3 mL/mmol) and stirred for 2 h. The reaction mixture was extracted with ethyl acetate, washed with saturated sodium bicarbonate solution (10 mL). The organic layer was separated, evaporated and the crude mixture was subjected to flash chromatography over silica gel (60-120 mesh) to afford the pure product. (Caution: Care should be taken while using $TMSN_3$ in water due to the formation of hydrazoic acid.)

(4) Spectral analysis:



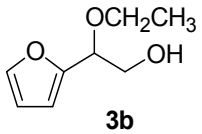
3a

2-(Furan-2-yl)-2-methoxy-ethanol (3a).[3f] Prepared by the general procedure **1** and purified on silica gel (EtOAc/PE: 8/92) to obtain the product (76%) as oily liquid; ^1H NMR (200 MHz, $CDCl_3$): δ 7.34 (bs, 1H), 6.29 (bs, 2H), 4.27 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.83 (dd, *J* = 11.6, 8.1 Hz, 1H), 3.67 (dd, *J* = 11.6, 3.9 Hz, 1H), 3.26 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.0, 141.0, 109.0, 107.0, 77.0, 63.0, 55.0; ESI-MS (M^++Na) =165; Anal. Calc for $C_7H_{10}O_3$:C, 59.14; H, 7.09; Found; C, 59.10; H, 7.19.



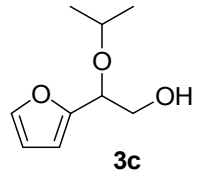
4

2-(1, 2-Dimethoxy-ethyl)-furan (4). Prepared by the general procedure **1** and purified on silica gel (EtOAc/PE: 3/97) to obtain (7%) as oily liquid; ^1H NMR (200 MHz, $CDCl_3$): δ 7.41-7.43 (m, 1H), 6.38 (d, *J* = 1.6 Hz, 1H), 6.35 (d, *J* = 1.6 Hz, 1H), 4.43 (dd, *J* = 7.8, 4.4 Hz, 1H), 3.76 (dd, *J* = 10.2, 7.6 Hz, 1H), 3.60 (dd, 10.2, 4.3Hz, 1H), 3.40 (s, 3H), 3.20 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 150.9, 141.6, 109.1, 107.6, 74.7, 73.0, 58.3, 55.8; ESI-MS (M^++Na) =179; Anal. Calc for $C_8H_{12}O_3$: C, 61.52; H, 7.74; Found; C, 61.58.10; H, 7.79.



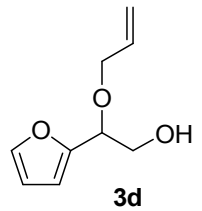
3b

2-Ethoxy-2-(furan-2-yl)-ethanol (3b).[3f] Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 5/95) to obtain the product (79%) as oily liquid; ^{1}H NMR (200 MHz, CDCl3): δ 7.4 (s,1H), 6.31-6.36 (m, 2H), 4.41-4.47 (m, 1H), 3.71-3.88 (m, 2H), 3.42-3.55 (m, 2H), 2.1 (bs, 1H), 1.20 (t, *J* =7.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 152.6, 142.9, 110.5, 108.7, 75.9, 70.2, 68.2, 15.5; ESI-MS (M^++Na) =179; Anal. Calc for $C_8H_{12}O_3$; C, 61.52; H, 7.74; Found; C, 61.47; H, 7.79.



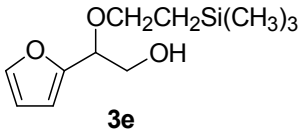
3c

2-Furan-2-yl-2-isopropoxy-ethanol (3c). Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 4/96) to obtain the product (78%) as oily liquid;. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.39-7.40 (m, 1H), 6.30-6.36 (m, 2H), 4.36 (dd, *J* = 7.96, 4.46 Hz, 1H), 3.65- 3.88 (m, 3H), 1.23 (d, *J* = 9.50 Hz, 3H), 1.10 (d, 1H, *J* = 6.19 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 153.0, 142.5, 110.2, 108.0, 73.3, 70.2, 64.6, 23.0, 22.0; ESI-MS (M^++Na) 193; Anal. Calc for $C_9H_{14}O_3$; C, 63.51; H, 8.29; Found; 63.48; H, 8.32.



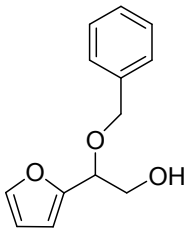
3d

2-Allyloxy-2-furan-2-yl-ethanol (3d).[3f] Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 4/96) to obtain the product (80%) as oily liquid;. ^{1}H NMR (200 MHz, CDCl3): δ 7.39-7.40 (m, 1H), 6.34-6.35 (m, 2H), 5.79-5.95 (m, 1H), 5.15-5.30 (m, 2H), 4.51 (dd, *J* = 7.9, 4.2 Hz, 1H), 3.71- 4.07 (m, 4H), 2.72 (bs, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.9, 142.7, 134.4, 117.3, 110.2, 107.6, 75.0, 69.9, 64.2; ESI-MS (M^++Na) =191; Anal. Calc for $C_9H_{12}O_3$; C, 64.27; H, 7.19; Found; C, 64.21; H, 7.24



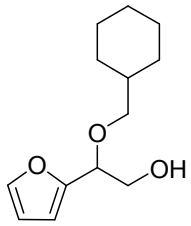
3e

2-Furan-2-yl-2-(2-trimethylsilanyl-ethoxy)-ethanol (3e). Prepared by the general procedure **1** and purified on silica gel (EtOAc/PE: 3/97) to obtain the product (75%) as oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 1.0 Hz, 1H), 6.41 – 6.31 (m, 2H), 4.51 – 4.43 (m, 1H), 3.89 (dd, *J* = 11.4, 8.3 Hz, 1H), 3.81 – 3.70 (m, 1H), 3.65 – 3.55 (m, 1H), 3.57 – 3.44 (m, 1H), 1.06 – 0.88 (m, 2H), 0.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4, 143.9, 111.5, 109.7, 76.7, 67.9, 65.7, 19.6, 0.01; ESI-MS (M^++Na) =251; Anal. Calc for $C_{11}H_{20}O_3Si$; C, 57.85; H, 8.83; Found; C, 57.80; H, 8.88.



3f

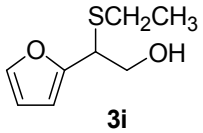
2-benzyloxy-2-furan-2-yl-ethanol (3f). Prepared by the general procedure **1** and purified on silica gel (EtOAc/PE: 3/96) to obtain the product (78%) as oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.40 – 7.27 (m, 5H), 6.40 – 6.35 (m, 2H), 4.63 – 4.53 (m, 2H), 4.41 (d, *J* = 11.6 Hz, 1H), 4.00 – 3.90 (m, 1H), 3.76 (dd, *J* = 9.9, 4.9 Hz, 1H), 2.25 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 142.8, 137.7, 128.7, 128.6, 128.2, 128.1, 127.9, 110.4, 109.1, 74.9, 70.9, 64.2. ESI-MS (M^++Na) =241; Anal.Calc for $C_{13}H_{14}O_3$; C, 71.54; H, 6.47; Found; C, 71.49; H, 6.52.



3g

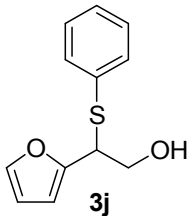
2-(Cyclohexylmethoxy)-2-(furan-2-yl) ethanol (3g). Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 2/96) to obtain the product (76%) as oily liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 4.9 Hz, 1H), 6.33 (m, 2H), 4.40 (dd, *J* = 8.3, 4.0 Hz, 1H), 3.93 – 3.85 (m, 1H), 3.46 (dd, *J* = 15.4, 4.5 Hz, 1H), 3.28 (dd, *J* = 8.9, 6.8 Hz, 1H), 3.20

(dd, *J* = 9.0, 6.6 Hz, 1H), 2.27 (s, 1H), 1.69 (m, 6H), 1.31 – 1.11 (m, 3H), 0.96 – 0.86 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.2, 142.5, 110.1, 108.3, 75.8, 75.1, 64.4, 38.0, 30.0, 29.9, 26.5, 25.8, 25.7. ESI-MS (M^++Na) =247; Anal. Calc for $C_{13}H_{20}O_3$; C, 69.60; H, 8.99; Found; C, 69.54; H, 9.05.



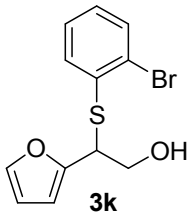
3i

2-Ethylsulfanyl-2-furan-2-yl-ethanol (3i). Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 6/94) to obtain the product (79%) as oily liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.39 (t, *J* = 0.8 Hz, 1H), 6.36 (t, *J* = 3.0 Hz, 1H), 6.26 (d, *J* = 3.0 Hz, 1H), 3.81-4.11 (m, 3H), 2.47-2.59 (m, 2H), 2.25 (bs, 1H), 1.26 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 152.5, 142.2, 110.4, 107.4, 63.0, 45.6, 24.7, 14.8; ESI-MS (M^++Na) =195; Anal.Calc $C_8H_{12}O_2S$; C, 55.78; H, 7.02; S, 18.40; Found; C, 55.72; H, 7.07; S, 18.40.



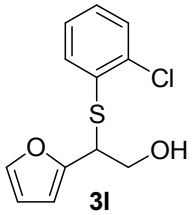
3j

2-Furan-2-yl-2-phenylsulfanyl-ethanol (3j). Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 4/96) to obtain the product (80%) as oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 3H), 7.32 – 7.25 (m, 3H), 6.30 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.12 (d, *J* = 3.2 Hz, 1H), 4.37 (t, *J* = 6.7 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.86 (d, *J* = 6.9 Hz, 1H), 2.24 (s, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 142.3, 133.6, 133.4, 132.6, 128.8, 128.6, 128.1, 110.5, 108.1, 62.9, 49.5; ESI-MS (M^++Na) =243; Anal. Calc for $C_{12}H_{12}O_2S$. C, 63.74; H, 5.35; S, 14.56; Found; C, 63.70; H, 5.31; S, 14.62.



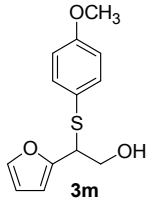
3k

2-(2-Bromo-phenylsulphanyl)-2-furan-2-yl-ethanol (3k). Prepared by the general procedure and purified on silica gel (EtOAc/PE: 4/96) to obtain the product (81%) as oily liquid;. ^{1}H NMR (200 MHz, CDCl3): δ 7.60 (dd, *J* = 7.74, 1.55 Hz, 1H), 7.4 (dd, *J* = 3.3, 1.7 Hz, 1H), 7.13-7.35 (m, 3H), 6.33 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.23 (d, *J* = 3.2 Hz, 1H), 4.54 (t, *J* = 6.4 Hz, 1H), 3.89-4.06 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.2, 142.5, 134.4, 134.1, 133.3, 129.1, 127.9, 127.9, 110.6, 108.5, 63.1, 48.9; ESI-MS (M^++Na) = 323: 321(1:1); Anal.Calc for $C_{12}H_{11}BrO_2S$.; C, 48.17; H, 3.71; S, 10.72; Found; C, 48.12; H, 3.77; S, 10.80



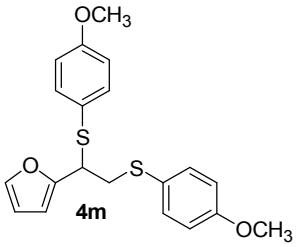
3l

2-(2-Chloro-phenylsulphanyl)-2-furan-2-yl-ethanol (3l). Prepared by the general procedure and purified on silica gel (EtOAc /PE: 4/96) to get the product (80%) as oily liquid;. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.15 -7.33 (m, 5H), 6.21-6.24 (m, 1H), 6.01 (d, *J* = 3.2 Hz, 1H), 4.25 (t, *J* = 6.2 Hz, 1H), 3.81-3.87 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 151.7, 141.3, 133.9, 133.4, 128.3, 130.1,128.0, 109.5, 107.2, 61.8, 48.4; ESI-MS (M^++Na) = 277; Anal. Calc for $C_{12}H_{11}ClO_2S$.; C, 56.58; H, 4.35; S, 12.59 Found; C, 56.50; H, 4.31; S, 12.50.



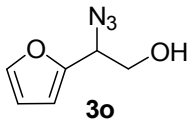
3m

2-Furan-2-yl-2-(4-methoxy-phenylsulfanyl)-ethanol. (3m). Prepared by the general procedure **1** and purified on silica gel (EtOAc/PE: 4/96) to get the product (85%) as oily liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.48-7.25 (m, 3H), 6.83 (m, 2H), 6.29 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.05 (d, *J* = 3.2, 1H), 4.19 (m, 1H), 3.86 -3.78 (m, 5H), 2.65 (s. 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 160.2, 151.7, 142.2, 136.8, 136.2, 122.1, 114.7, 114.5, 110.4, 107.9, 62.6, 55.4, 50.2; ESI-MS (M^++Na) = 273; Anal.Calc $C_{13}H_{14}O_3S$.; C, 62.38; H, 5.64; S, 12.81; Found; C, 62.30; H, 5.56; S, 12.89.



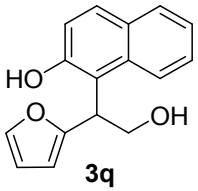
4m

2-(1,2-Bis(4-methoxyphenylthio)ethyl)furan: Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 2/98) to get the product (85%) as oily liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.3 (s, 1H), 7.1- 7.2 (m, 4H), 6.7-6.8 (m, 4H), 6.2-6.3 (m,1H), 5.9 (d, *J* = 3.16 Hz, 1H), 4.13 (t, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.27 (d, *J* =7.4 Hz, 2H). ESI-MS (M^++Na) = 372; Anal.Calc $C_{20}H_{20}O_3S_2$.; C, 64.49; H, 5.41; S, 17.22; Found; C, 64.41; H, 5.49; S, 17.30.



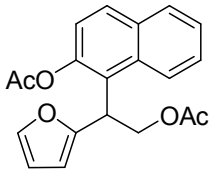
3o

2-Hydroxy-1-(2-furyl) ethyl azide (3o).[2a] Prepared by the general procedure 1 and purified on silica gel (EtOAc /PE: 8/92) to obtain the product (80%) as oily liquid; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.38-7.43 (m, 1H), 6.39 (s, 2H), 4.63 (t, *J* = 6.20 Hz, 1H), 3.89 (m, 2H), 2.47 (bs, -OH); ^{13}C NMR (50 MHz, $CDCl_3$): δ 149.8, 143.0, 110.4, 108.6, 63.1, 60.6; ESI-MS (M^++Na) =176; Anal. Calc for $C_6H_7N_3O_2$; C, 47.06; H, 4.61; N, 27.44; Found; C, 47.0; H, 4.67; N, 27.47.

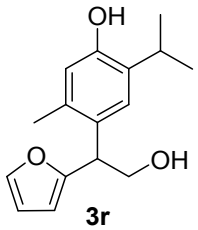


3q

2-Furan-2-yl-2-(2-hydroxynaphthyl)-ethanol (3q). Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 10/90) to obtain the product (80%) as oily liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.14 Hz, 1H), 7.69 (d, J = 8.79, 1H), 7.51 (d, *J* = 8.38, 1H), 7.23-7.33 (m, 2H), 7.11-7.17 (m, 2H), 6.21 (dd, *J* = 1.7, 3.1, 1H), 5.94 (d, *J* = 3.1 Hz, 1H), 4.99-5.01 (m, 1H), 4.82-4.86 (m, 1H), 4.69-4.72 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 158.2, 155.3, 142.1, 130.9, 130.5, 129.4,129.2, 129.0, 128.4, 127.1, 123.1, 122.7, 118.6, 112.5, 110.6, 106.6, 77.0, 41.5, ESI-MS (M^++Na) = 277; Anal. Calc for $C_{16}H_{14}O_3$.;C, 75.57; H, 5.55;Found; C, 75.51; H, 5.59.

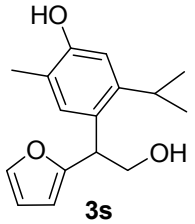


Diacetylated derivative of (3q). Obtained after acetylation of **3q** with acetic anhydride and pyridine in quantitative yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 –7.87 (m,1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.46-7.48 (m, 2H), 7.26-7.31 (m, 2H), 7.22 (d, *J* = 8.9 Hz, 1H), 6.33-6.35 (m,1H), 6.18(d, *J* = 3.3 Hz, 1H), 5.34 (t, *J* = 7.3, 1H), 5.04 (dd, *J* = 10.9, 7.5 Hz, 1H), 4.68 (dd, *J* = 10.9, 3.8 Hz, 1H), 2.23 (s, 3H), 1.97 (s, 3H); ESI-MS (M^++Na) = 361; ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.5, 169.7, 154.1, 147.8, 141.9, 133.0, 132.7, 129.8, 129.4, 126.8, 125.8, 124.8, 124.2, 122.6, 110.7, 106.3, 64.9, 37.1, 21.4, 21.3. Anal. Calc for $C_{20}H_{18}O_5$.; C, 70.99; H, 5.36; Found; C, 70.91; H, 5.28.



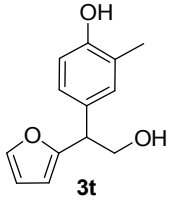
3r

4-(1-Furan-2-yl-2-hydroxy-ethyl)-2-isopropyl-5-methyl-phenol (3r). Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 8/92) to obtain the product (83%) as oily liquid;^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (m, 1H), 7.01 (s, 1H), 6.57 (s, 1H), 6.32 (dd, *J* = 3.1,1.9 Hz, 1H), 6.07 (d, *J*= 1 HZ, 1H), 5.58 (bs, 1H), 4.42 (t, *J* = 7.1 Hz, 1H), 4.16 (dd, *J* = 10.9, 7.6 Hz, 1H), 3.99 (dd, *J* = 10.9, 6.7Hz, 1H), 3.13-3.18 (m, 1H), 2.27 (d, *J* = 6.90 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.6, 151.9, 141.7, 135.0, 132.4, 128.8, 125.4, 117.5, 110.2, 106.6, 65.1, 43.3, 27.0, 22.7, 22.6; ESI-MS (M^++Na) = 283; Anal. Calc for $C_{16}H_{20}O_3$.; C, 73.82; H, 7.74; Found; C, 73.76; H, 7.79.



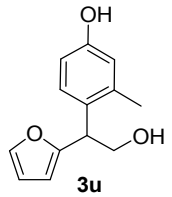
3s

4-(1-Furan-2-yl-2-hydroxy-ethyl)-5-isopropyl-2-methyl-phenol (3s). Prepared by the general procedure and purified on silica gel (EtOAc /PE: 8/92) to obtain the product (76%) as oily liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (m, 1H), 6.93 (s, 1H), 6.73 (s, 1H), 6.31 (dd, *J* = 3.1, 1.9Hz, 1H), 6.09 (m, 1H), 4.52 (t, *J* = 7.14, 1H), 4.10-4.19 (m, 1H), 3.92-3.97 (m, 1H), 3.21-3.26 (m, 1H), 2.17 (s, 3H, with traces of acetone), 1.24 (d, *J* = 6.8, 3H), 1.19 (d, *J* = 6.8, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.9, 153.1, 146.5, 141.7, 130.1, 127.7, 121.3, 112.2, 110.2, 106.4, 65.6, 42.1, 28.4, 24.3, 15.5; ESI-MS (M^++Na) =283; Anal. Calc for $C_{16}H_{20}O_3$.; C, 73.82; H, 7.74; Found; C, 73.76; H, 7.78.



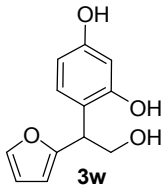
3t

4-(1-Furan-2-yl-2-hydroxy-ethyl)-2-methyl-phenol (3t). Prepared by the general procedure and purified on silica gel (EtOAc/PE: 10/90) to obtain the product (79%) as oily liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (m, 1H), 7.0 (s, 1H), 6.95 (dd, *J* = 1.8, 8.1 Hz,1H), 6.69 (d, *J* = 8.1 Hz ,1H), 6.32 (m, 1H), 6.11 (dd, *J* = 2.1, 2.6 Hz, 1H), 4.09-4.13 (m, 2H), 3.94-3.98 (m, 1H), 2.20 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.3, 153.3, 141.8, 130.9, 130.9, 126.8, 124.4, 115.2, 110.3, 106.5, 65.6, 47.4, 15.9; ESI-MS (M^++Na) = 241; Anal. Calc for $C_{13}H_{14}O_3$.; C, 71.54; H, 6.47; Found; C, 71.47; H, 6.54.



3u

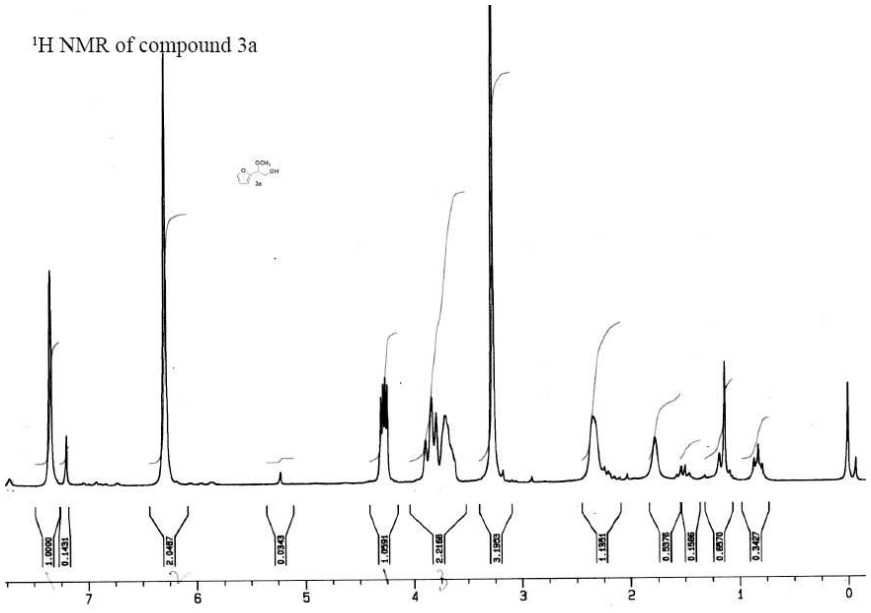
4-(1-Furan-2-yl-2-hydroxy-ethyl)-3-methyl-phenol (3u). Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 10/90) to obtain the product (73%) as oily liquid;^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (s, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.63-6.69 (m, 2H), 6.30 (t, *J* = 1.5 Hz, 1H), 6.06 (d, *J* = 2.4 Hz, 1H), 4.46-4.53 (m, 1H), 4.17-4.21(m, 1H), 4.06-4.09 (m, 1H), 2.20 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.4, 154.5, 141.8, 137.0, 129.4, 128.6, 117.6, 113.2, 110.3, 106.6, 65.0, 43.1, 14.2; ESI-MS (M^++Na) =241; Anal. Calc for $C_{13}H_{14}O_3$.; C, 71.54; H, 6.47; Found; C, 71.46; H, 6.53.



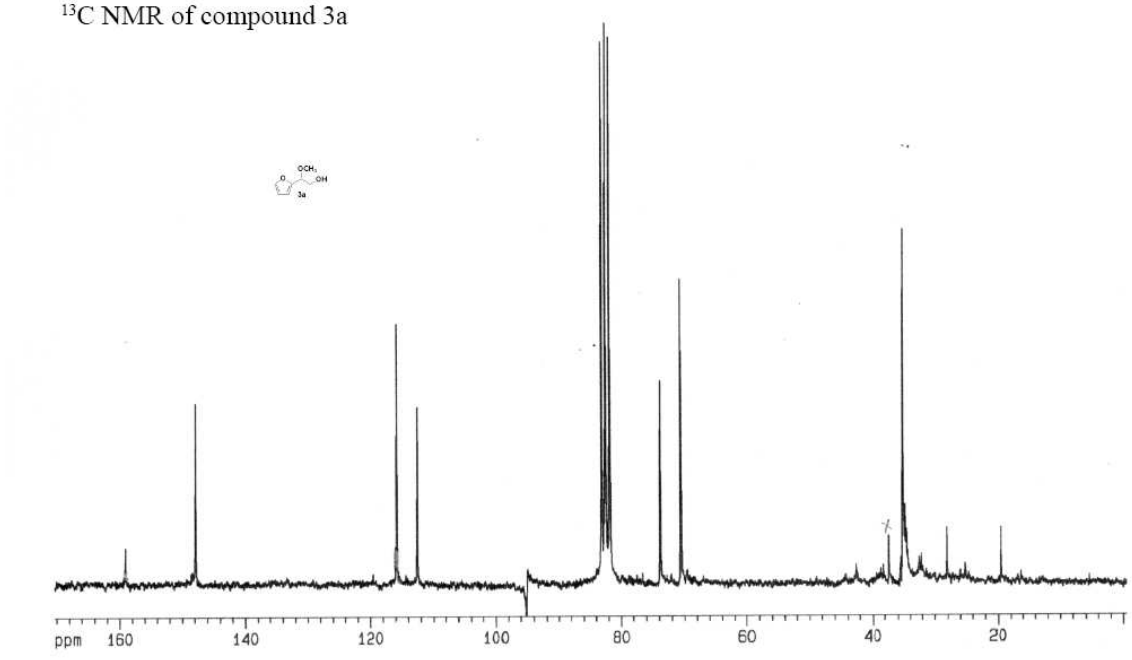
3w

4-(1-Furan-2-yl-2-hydroxy-ethyl)-benzene-1,3-diol (3w). Prepared by the general procedure **1** and purified on silica gel (EtOAc /PE: 16/84) to obtain the product (81%) as oily liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, MeOD) δ 7.27 (d, *J* = 8.8 Hz, 1H), 6.65 (t, *J* = 9.1 Hz, 1H), 6.24 – 6.21 (m, 1H), 6.19 (d, *J* = 2.2 Hz, 1H), 6.10 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.05 (d, *J* = 3.0 Hz, 1H), 4.41 (t, *J* = 6.9 Hz, 1H), 3.88 – 3.77 (m, 2H). ^{13}C NMR (125 MHz, MeOD): δ 160.6, 159.6, 159.3, 145.7, 134.3, 122.2, 114.5, 111.6, 110.9, 107.6, 68.9, 45.7; ESI-MS (M^{+}+Na) = 243; Anal. Calc for $C_{12}H_{12}O_4$.; C, 65.45; H, 5.49; Found; C, 65.51; H, 5.53.

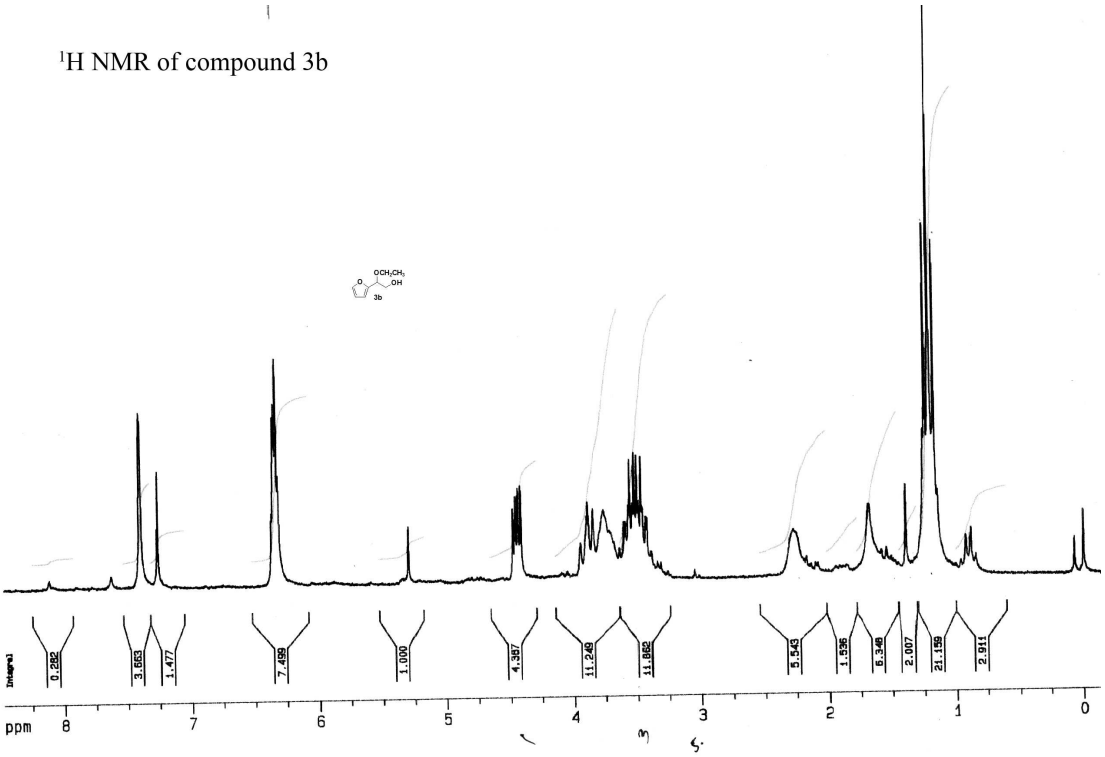
^{1}H NMR of compound 3a



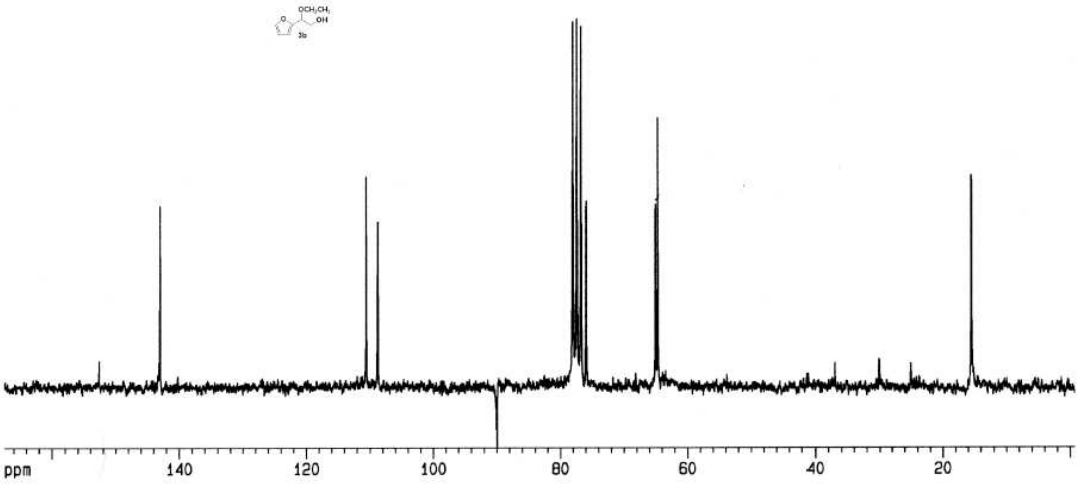
^{13}C NMR of compound 3a



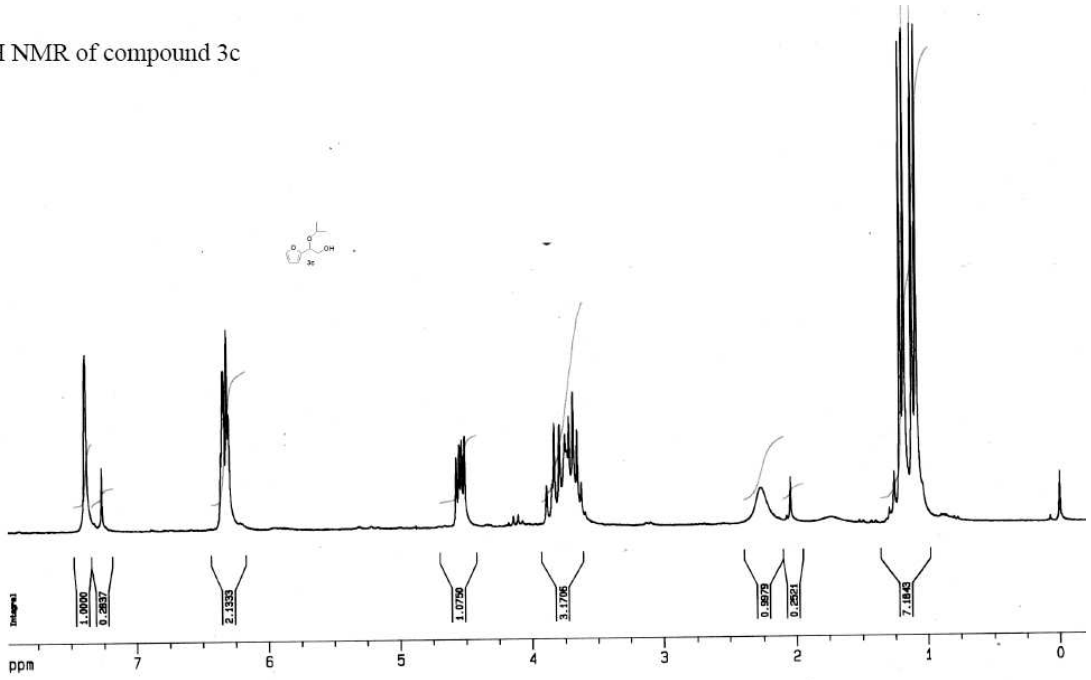
^{1}H NMR of compound 3b



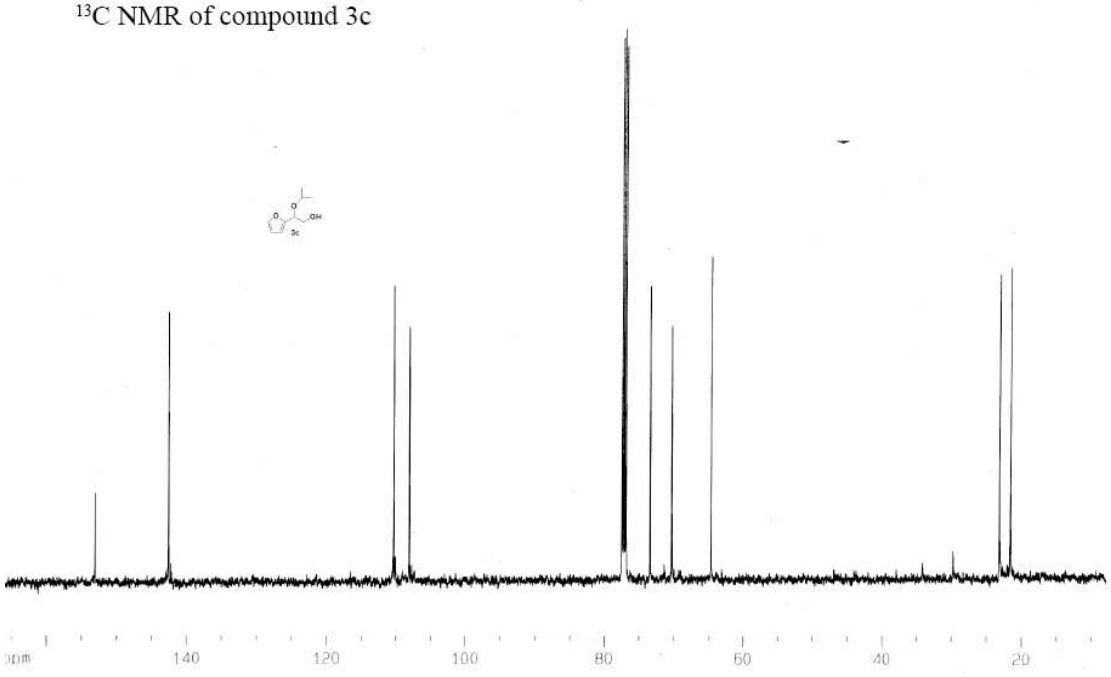
^{13}C NMR of compound 3b



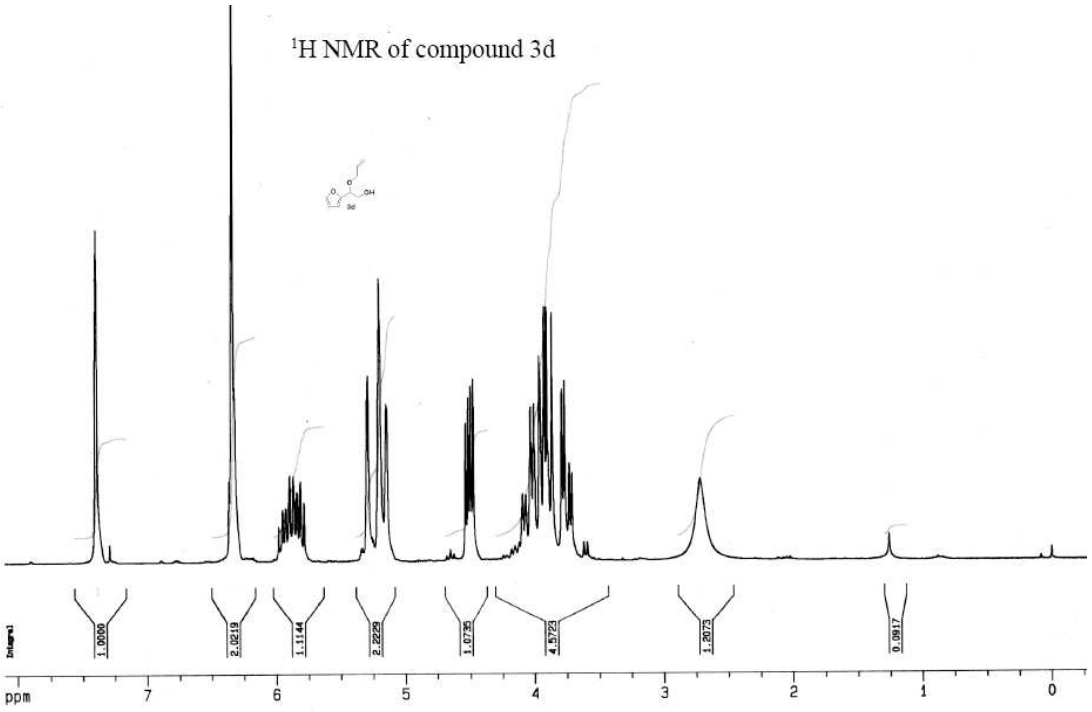
^{1}H NMR of compound 3c



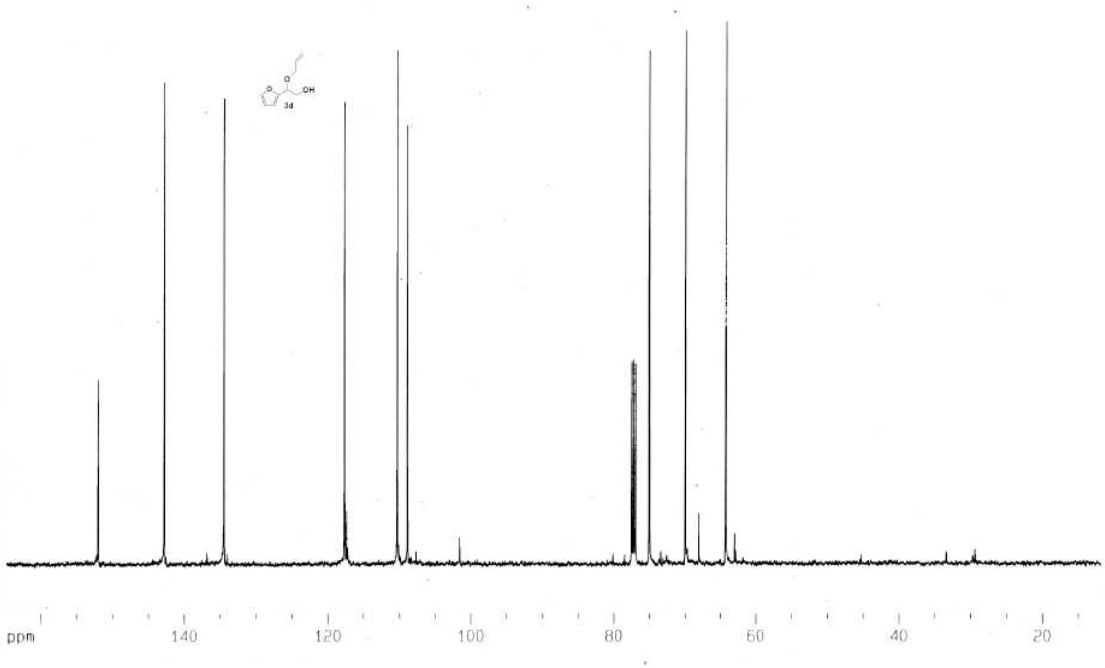
^{13}C NMR of compound 3c

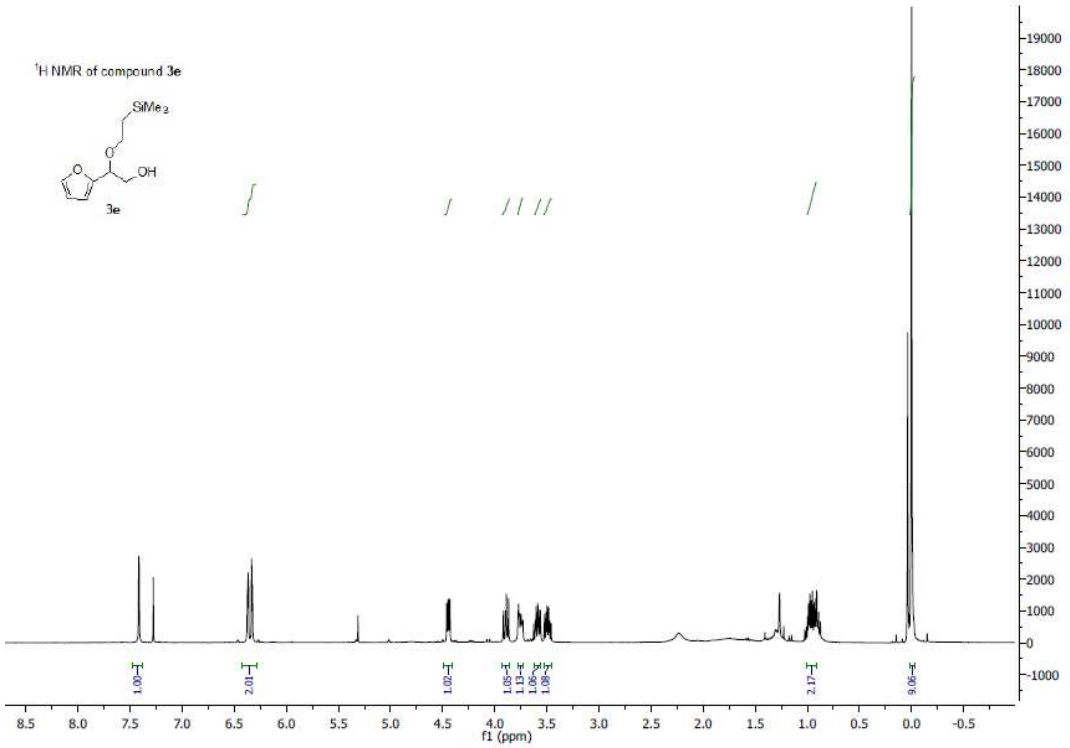


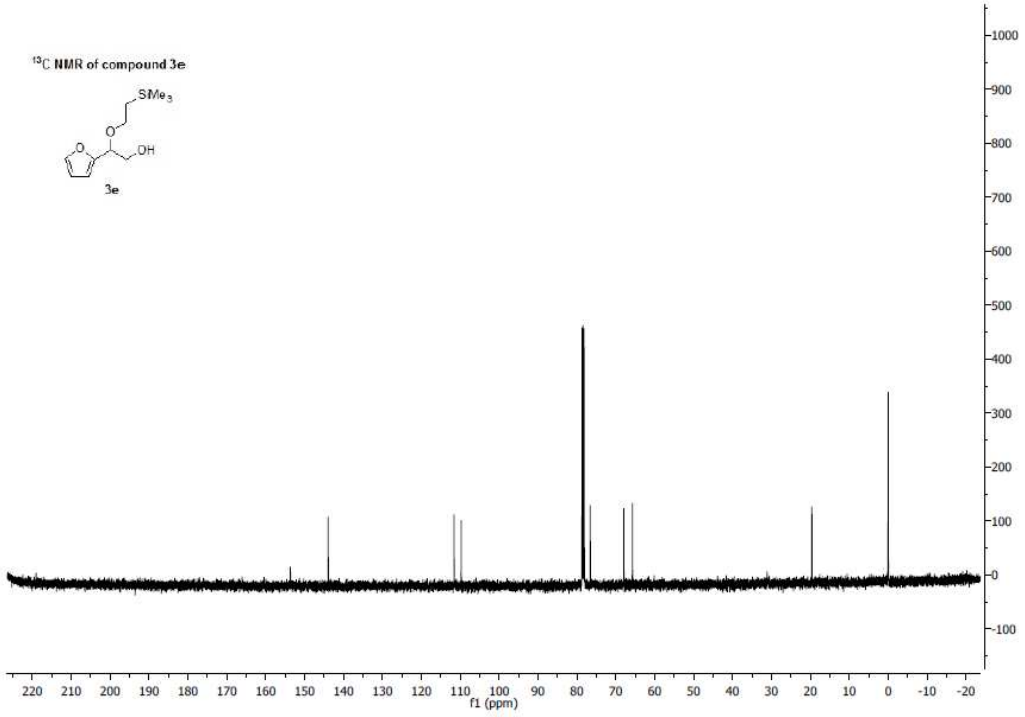
^{1}H NMR of compound 3d

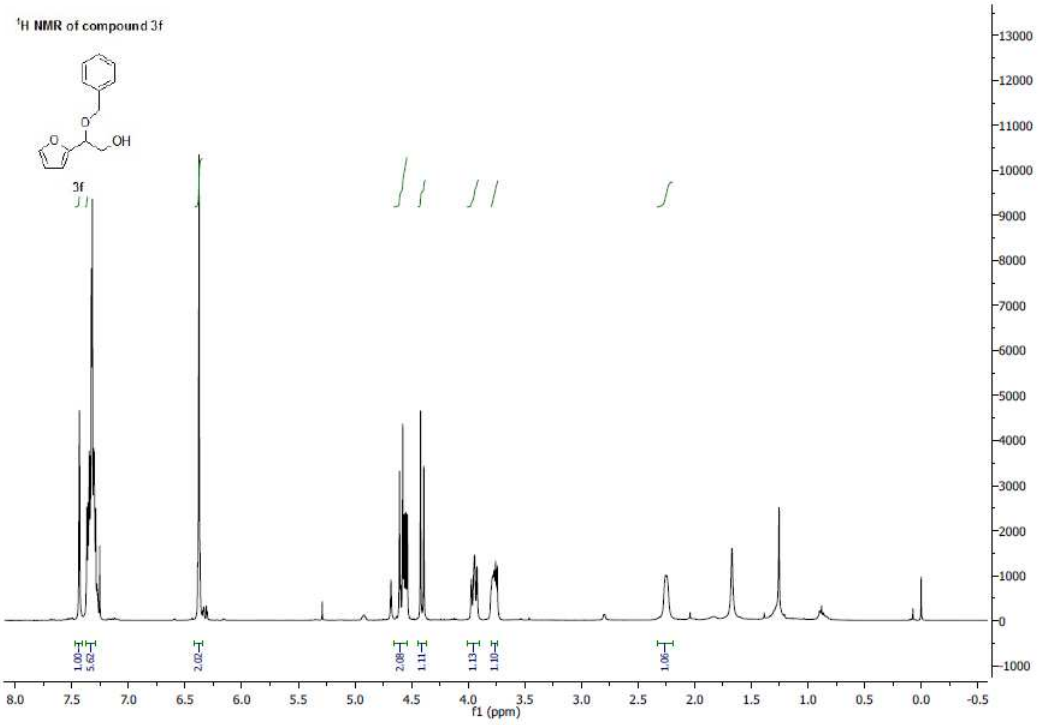


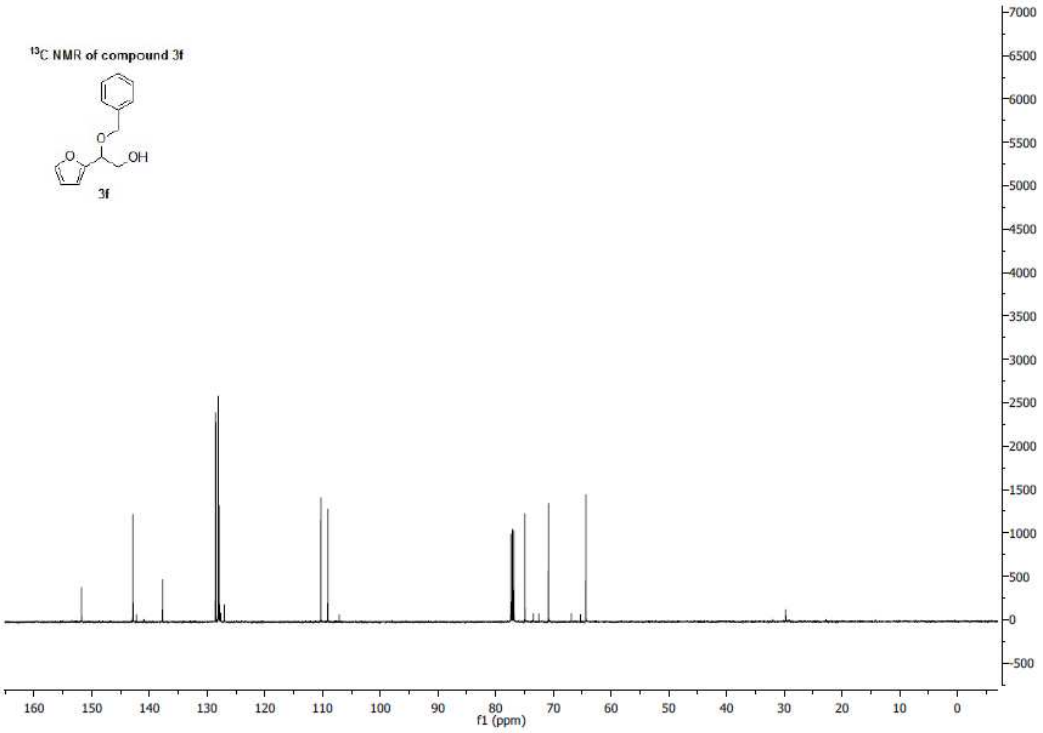
^{13}C NMR of compound 3d

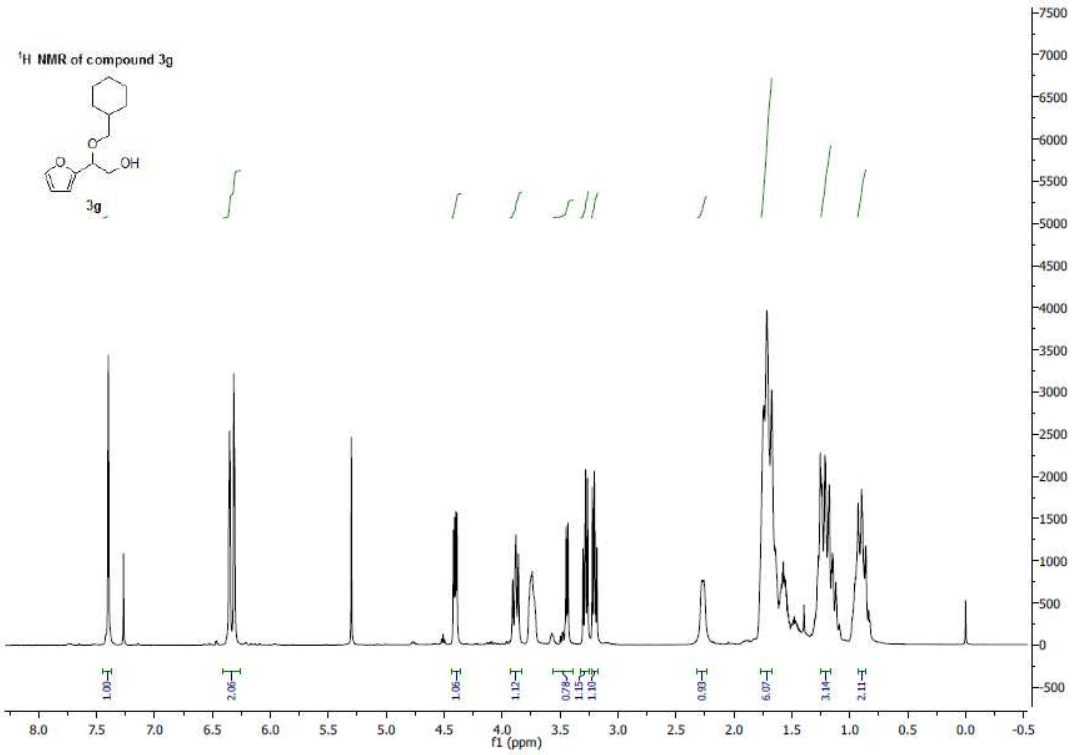


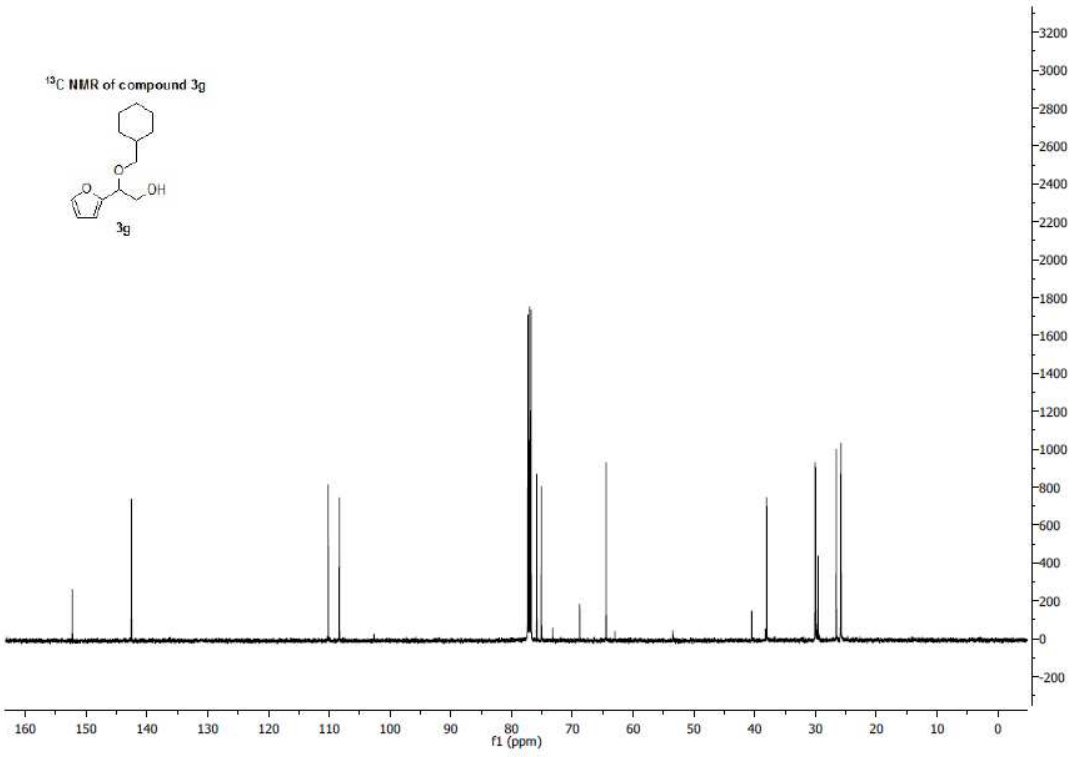

^{1}H NMR of compound 3e
SiMe$_3$
O
OH
3e
1.00
2.01
1.02
1.05
1.13
1.05
1.08
2.17
9.06
f1 (ppm)


^{13}C NMR of compound 3e
SiMe$_3$
O
OH
3e
f1 (ppm)

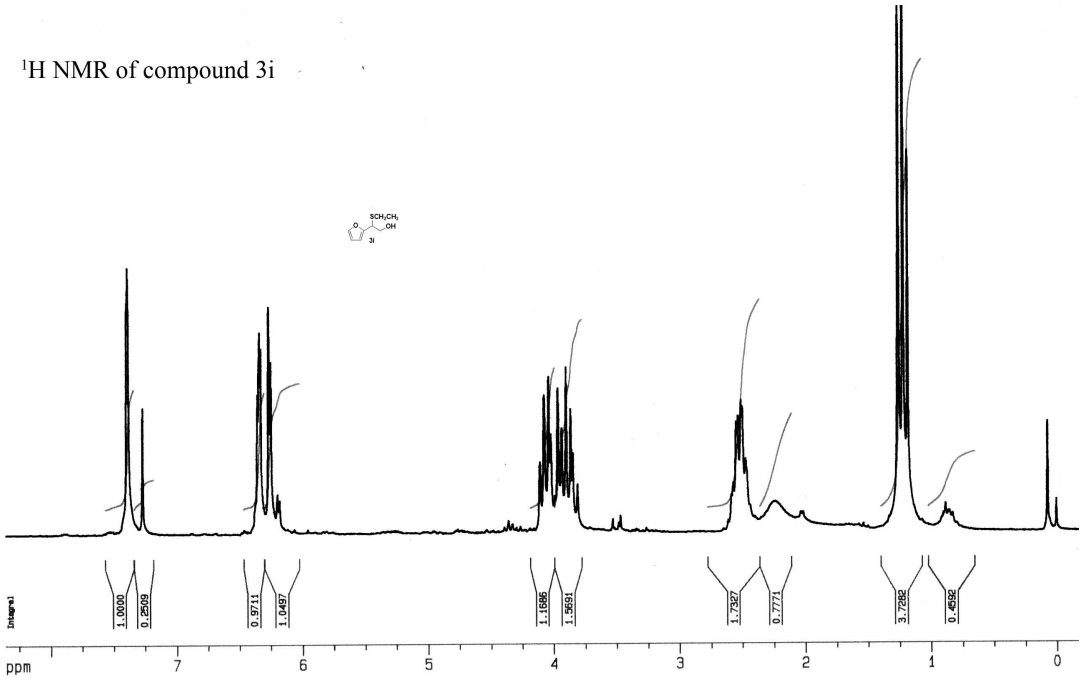

^{1}H NMR of compound 3f
OH
3f
1.00
5.62
2.02
2.08
1.11
1.13
1.10
1.06
f1 (ppm)


^{13}C NMR of compound 3f
OH
3f
f1 (ppm)

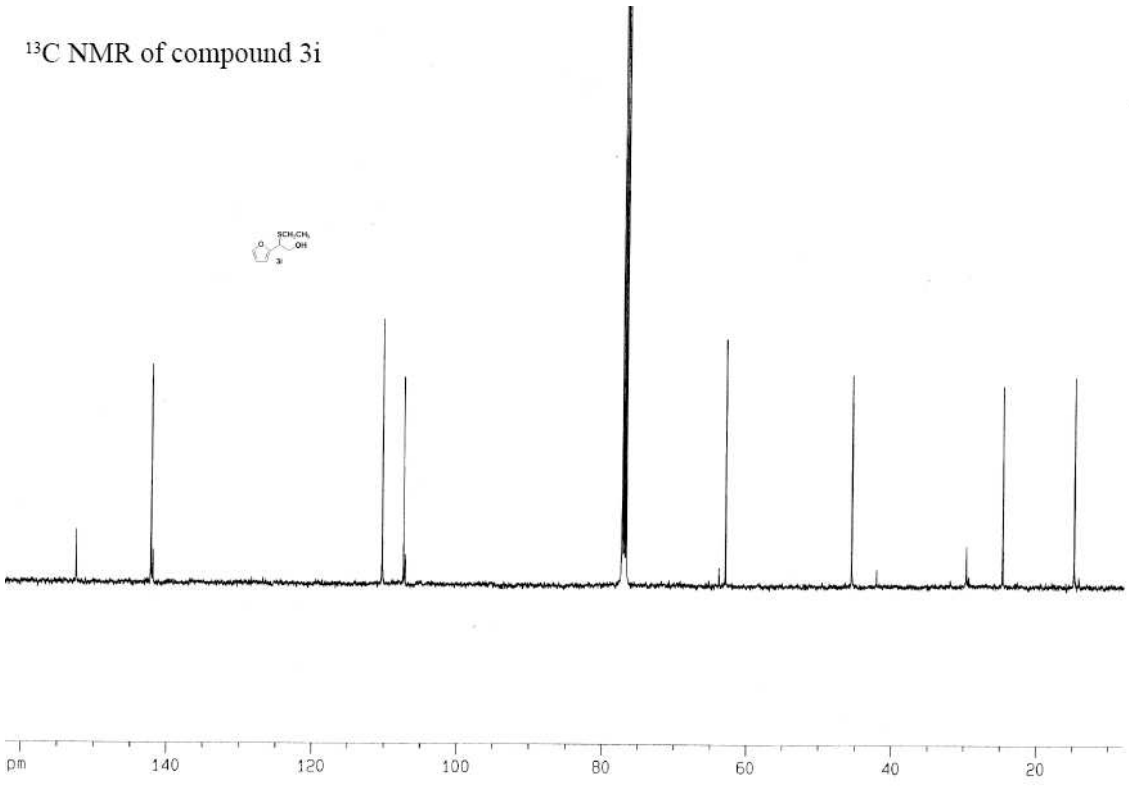

^{1}H NMR of compound 3g
OH
3g
1.00
2.06
1.06
1.12
0.78
1.15
1.10
0.93
6.07
3.14
2.11
f1 (ppm)

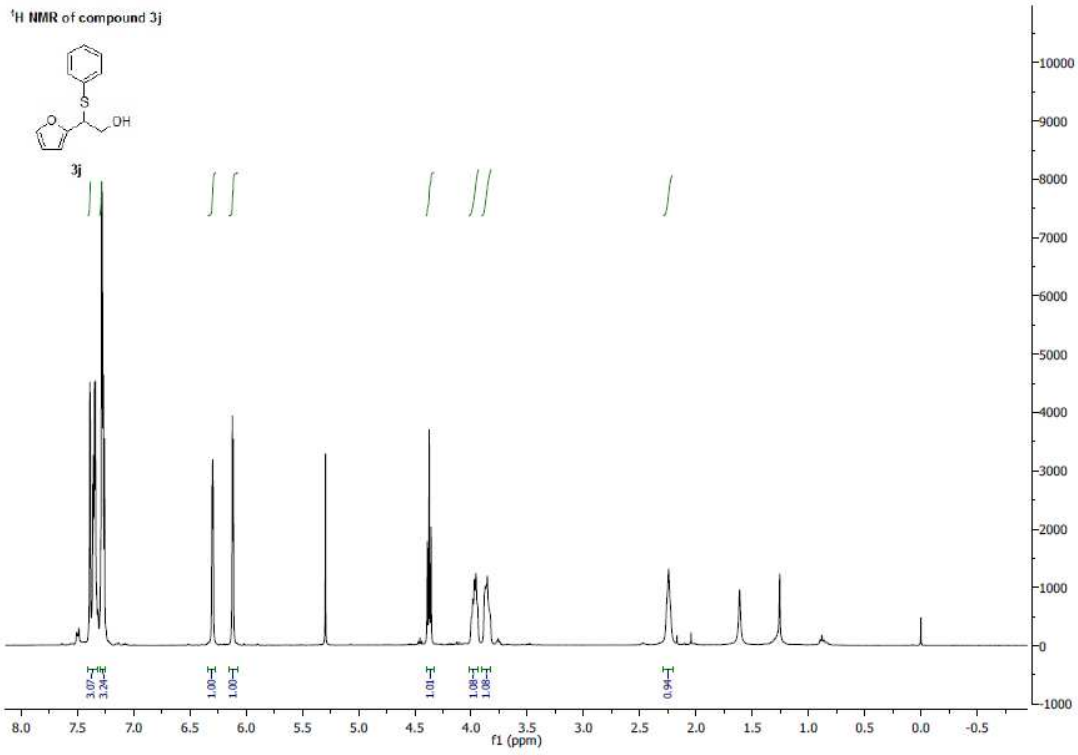

^{13}C NMR of compound 3g
OH
3g
f1 (ppm)

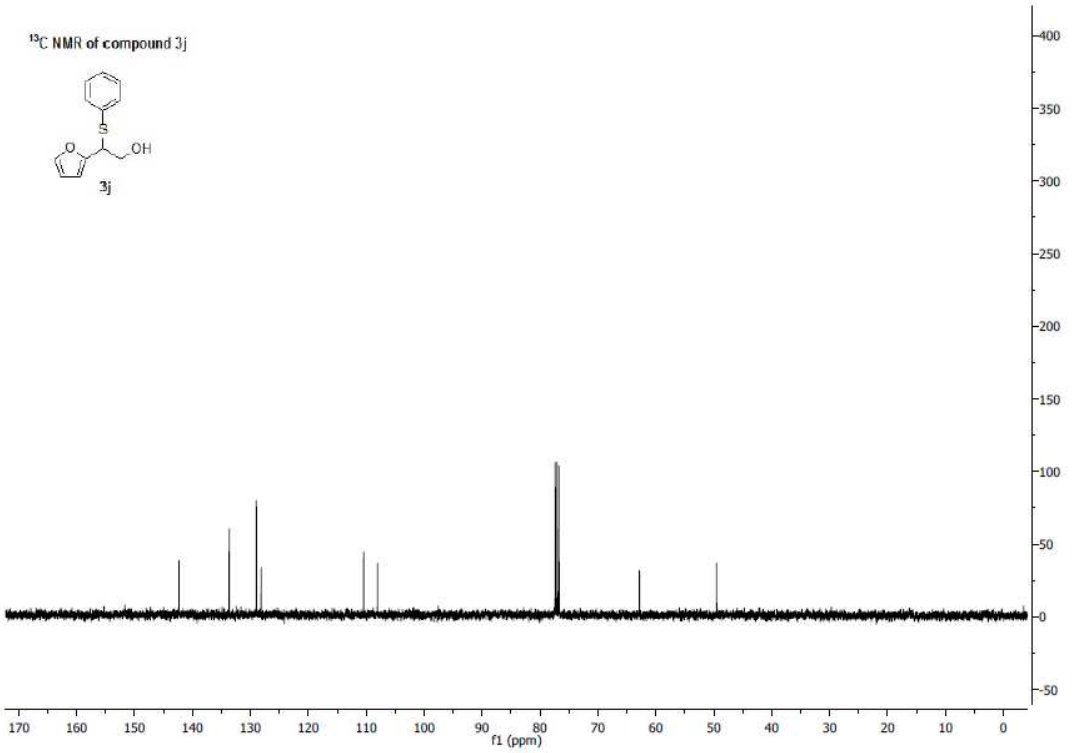
^{1}H NMR of compound 3i



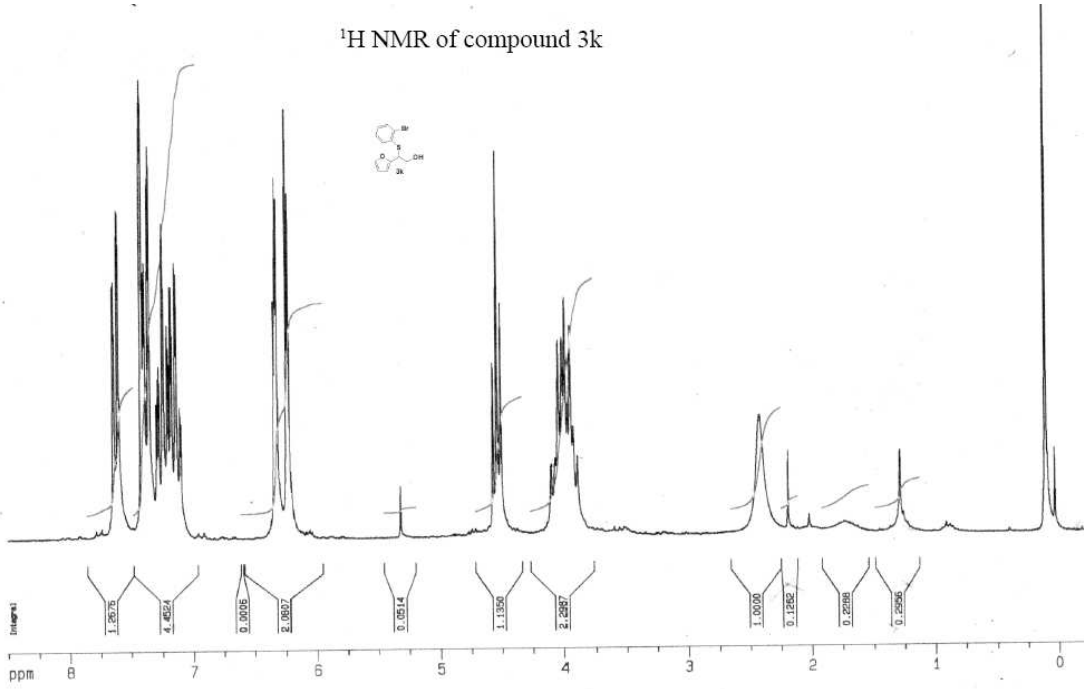
^{13}C NMR of compound 3i



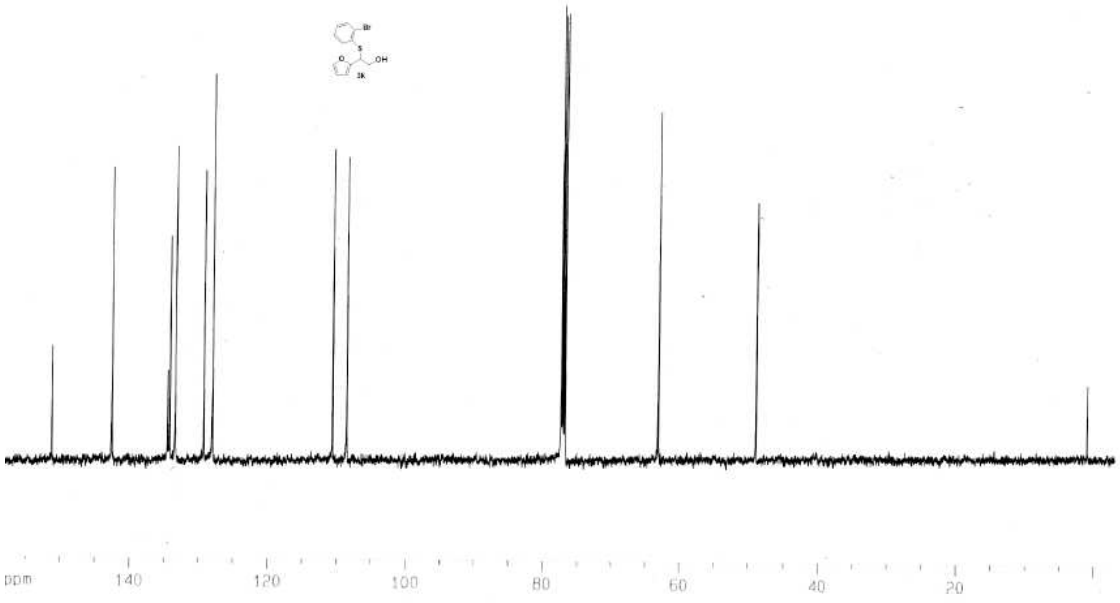

¹H NMR of compound 3j
3j
3.07
3.24
1.00
1.00
1.01
1.08
1.08
0.94
f1 (ppm)


¹³C NMR of compound 3j
3j
f1 (ppm)

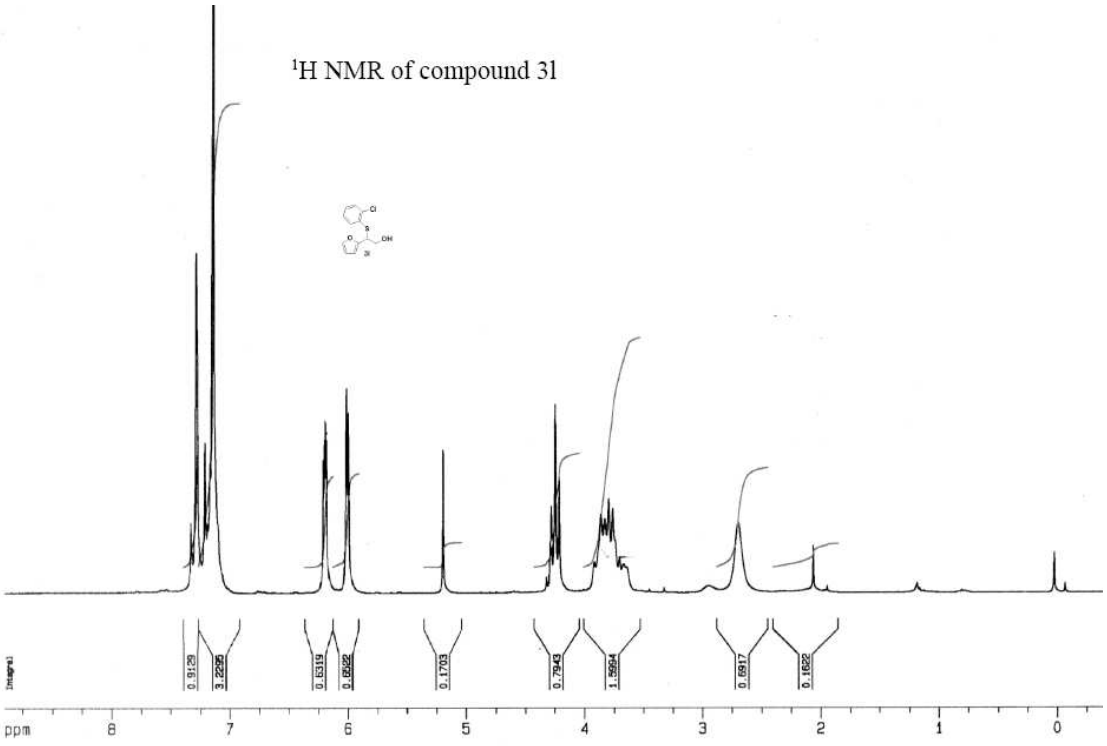
^{1}H NMR of compound 3k



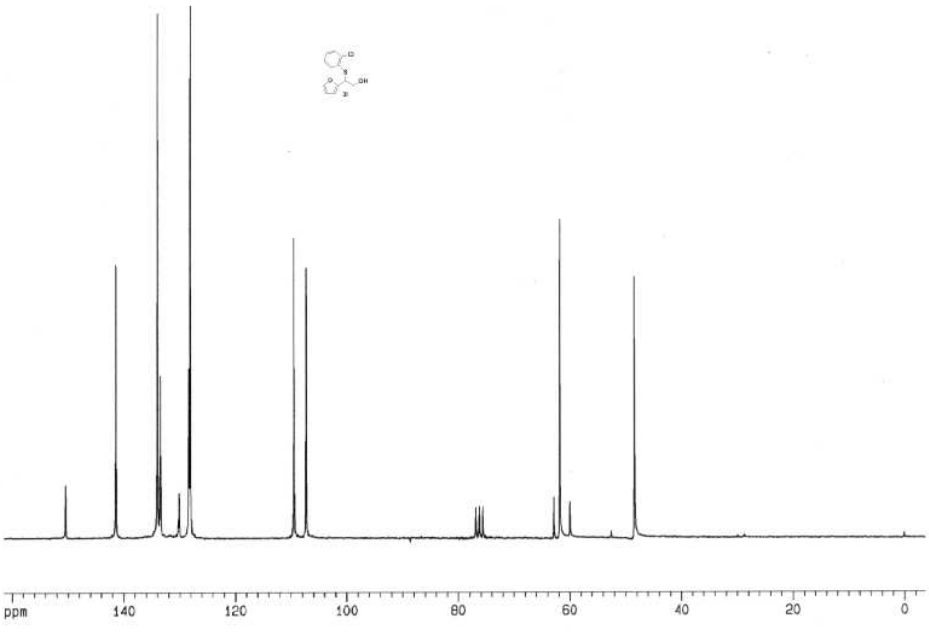
^{13}C NMR of copound 3k



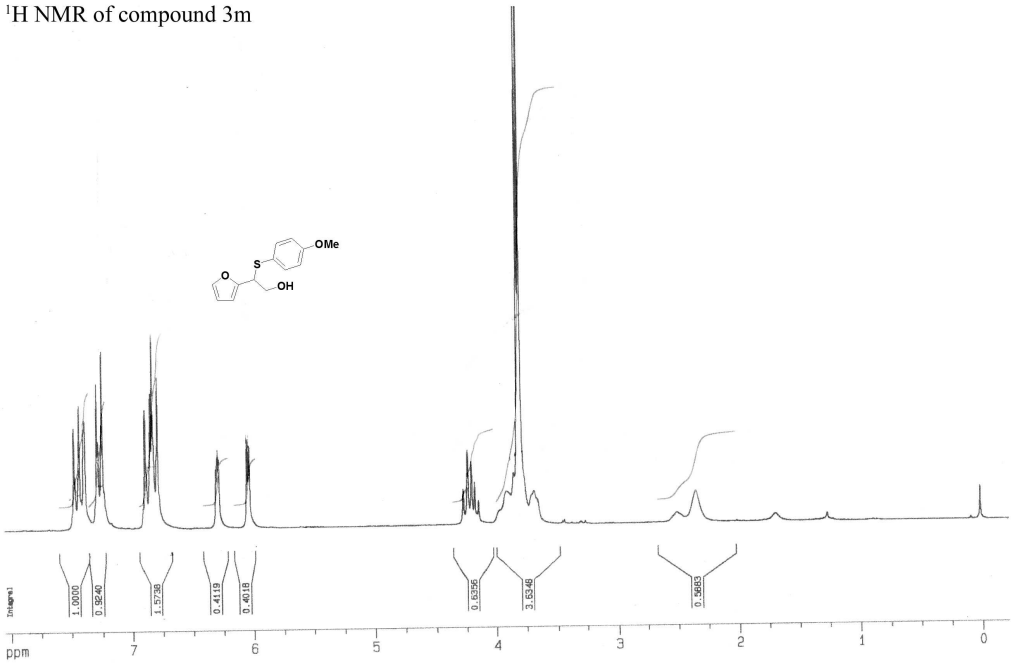
^{1}H NMR of compound 31



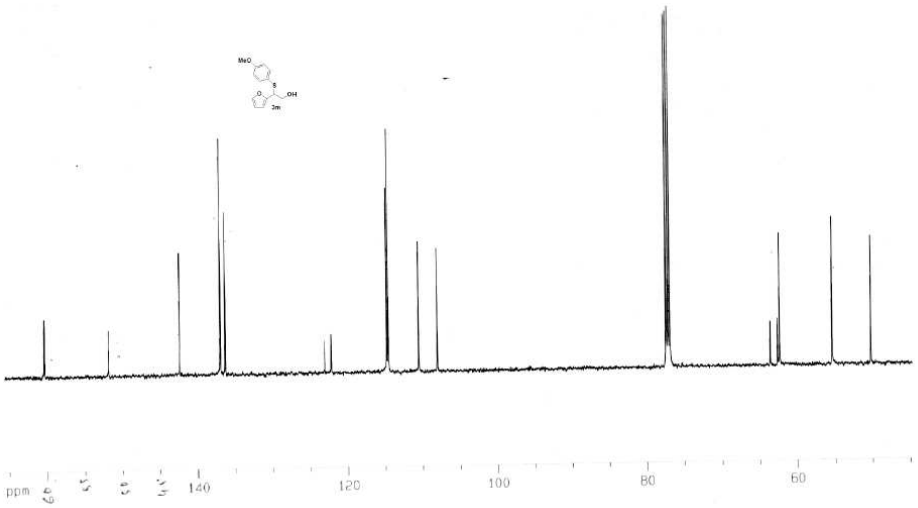
^{13}C NMR of compound 31



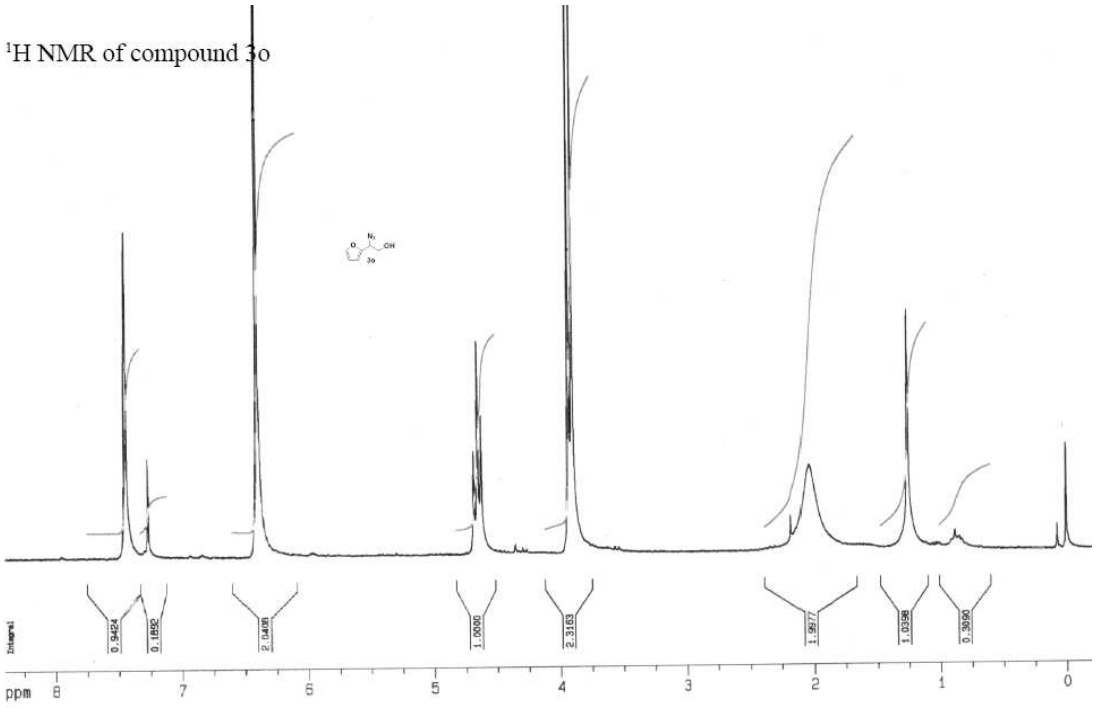
^{1}H NMR of compound 3m



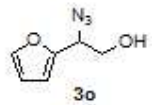
^{13}C NMR of compound 3m



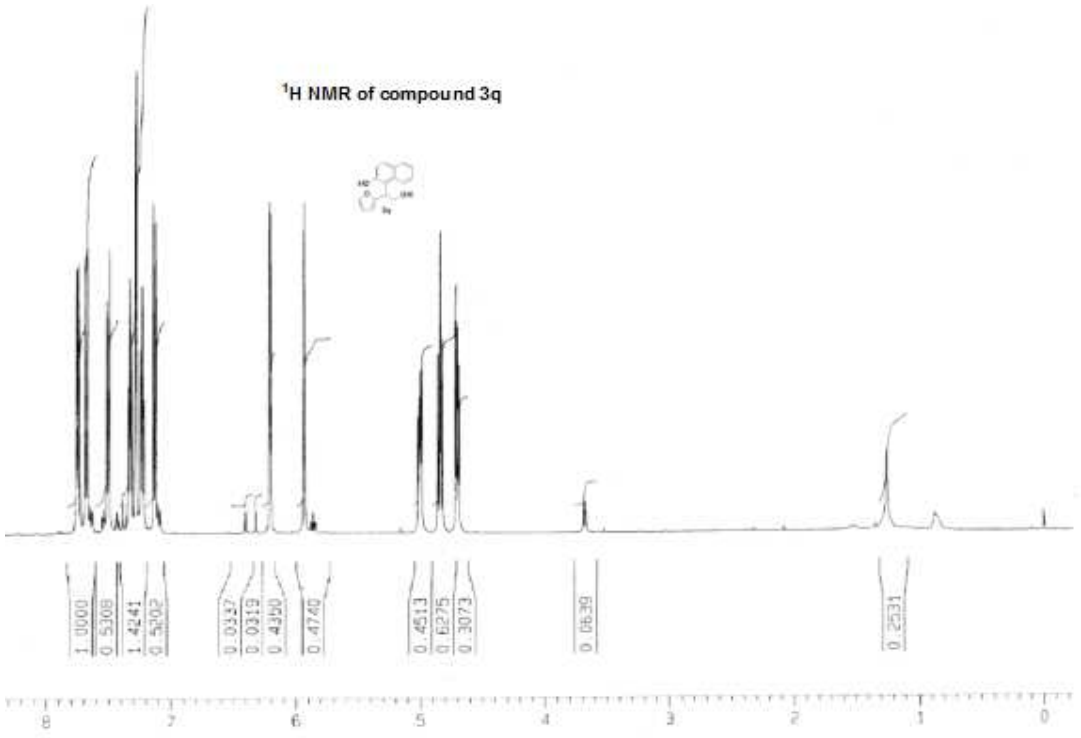
^{1}H NMR of compound 3o



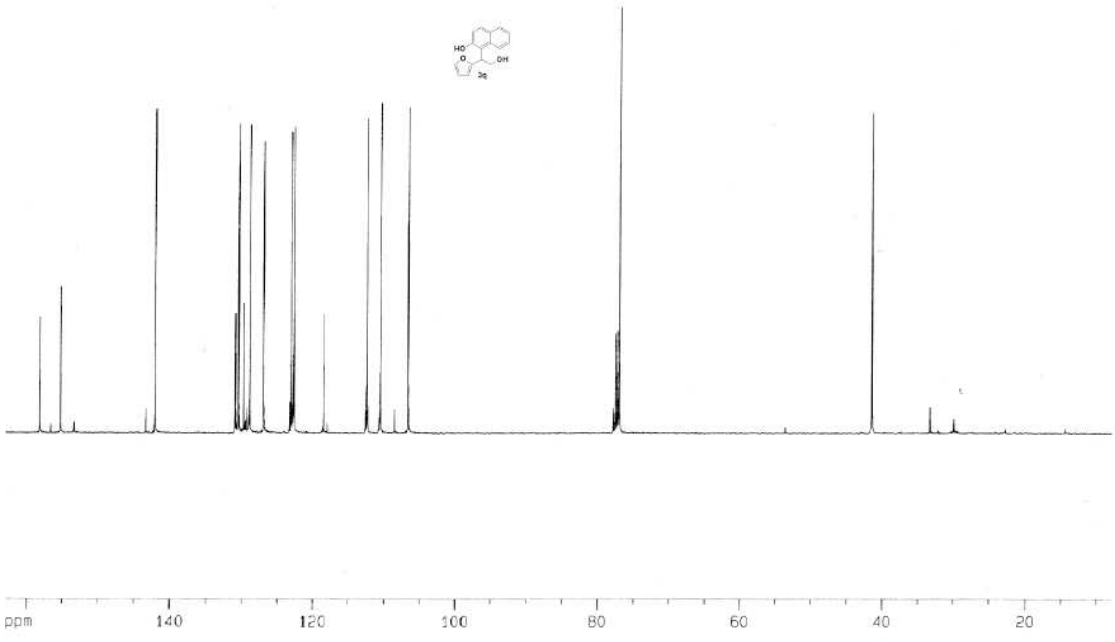
^{13}C NMR of compound 3o



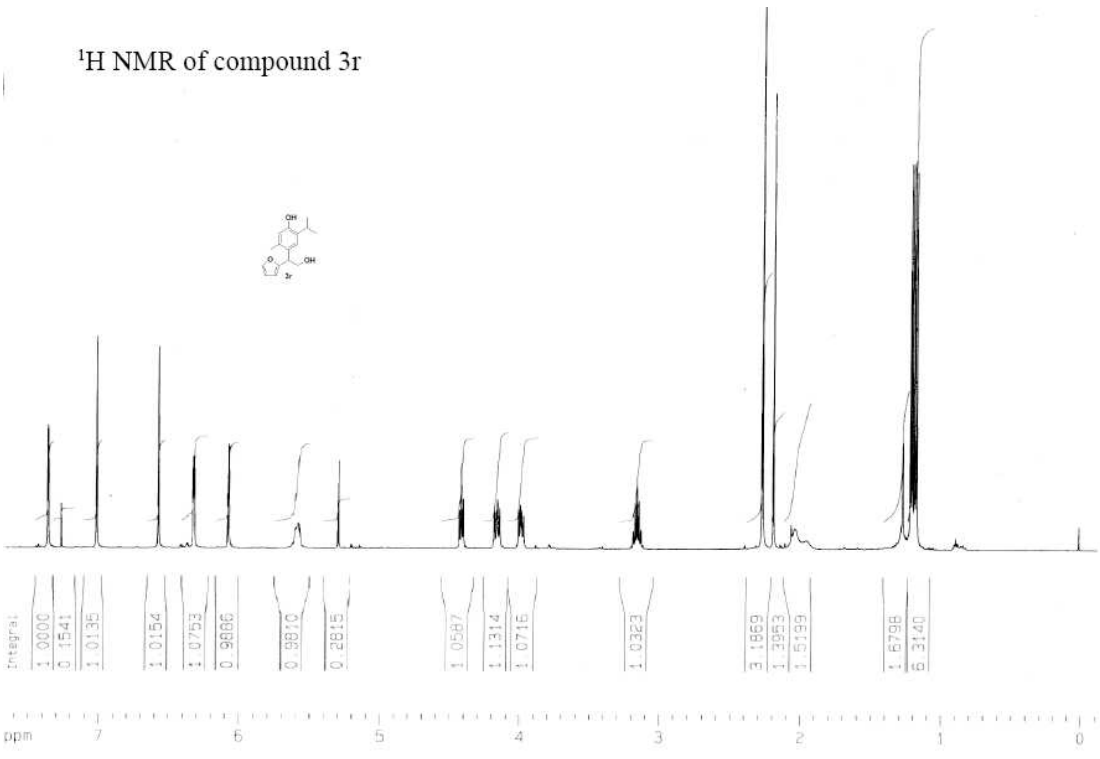
3o



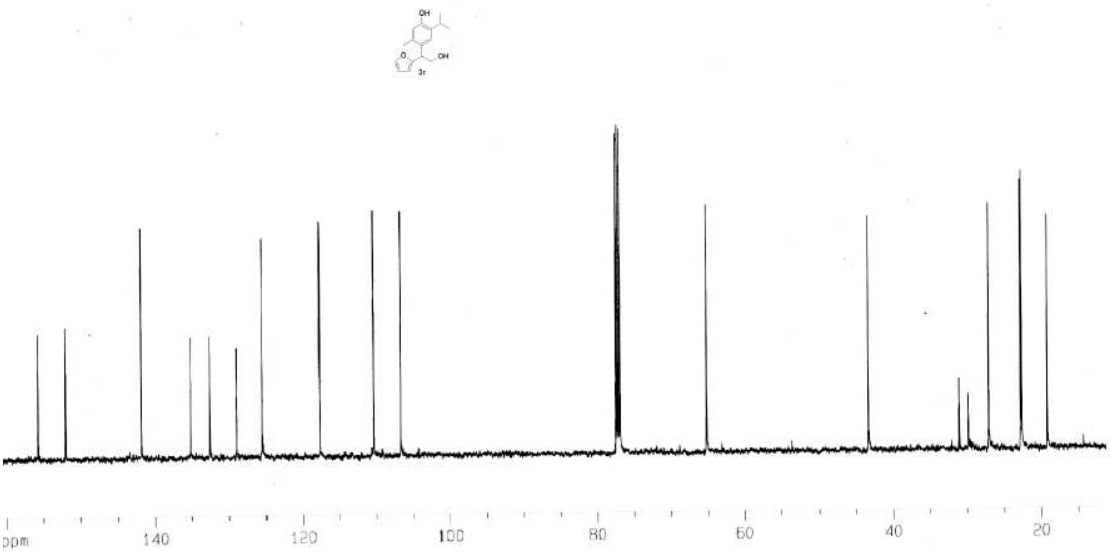
^{13}C NMR of compound 3q



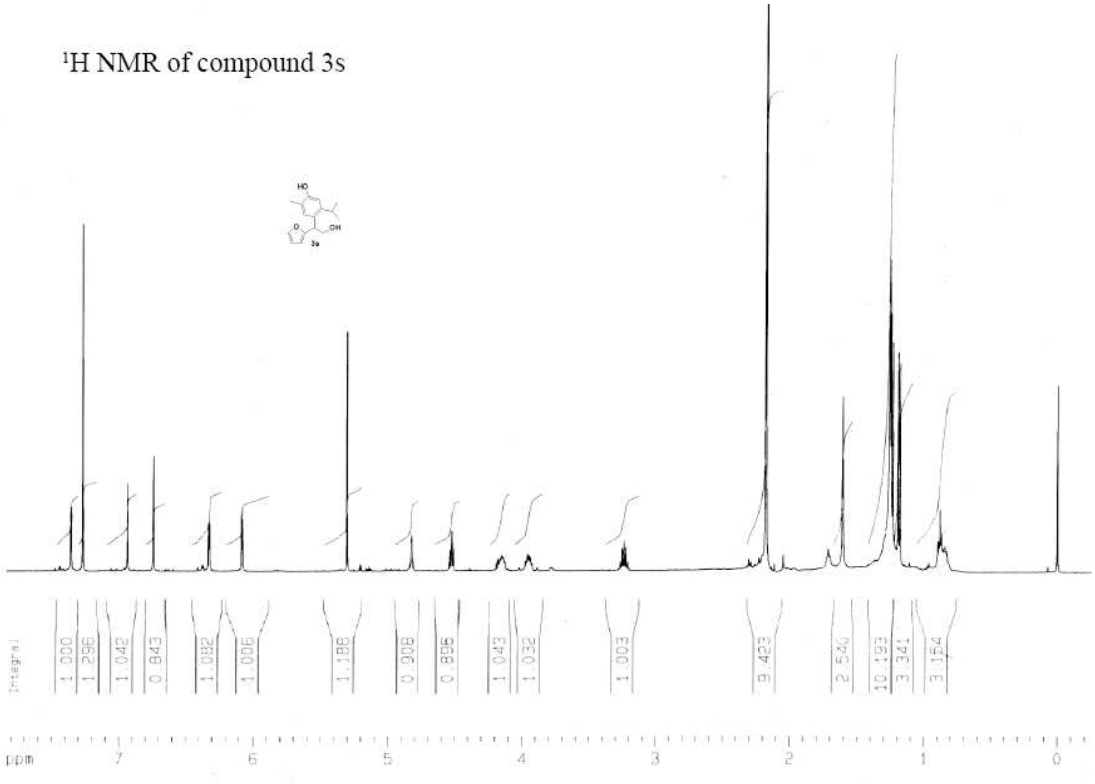
^{1}H NMR of compound 3r



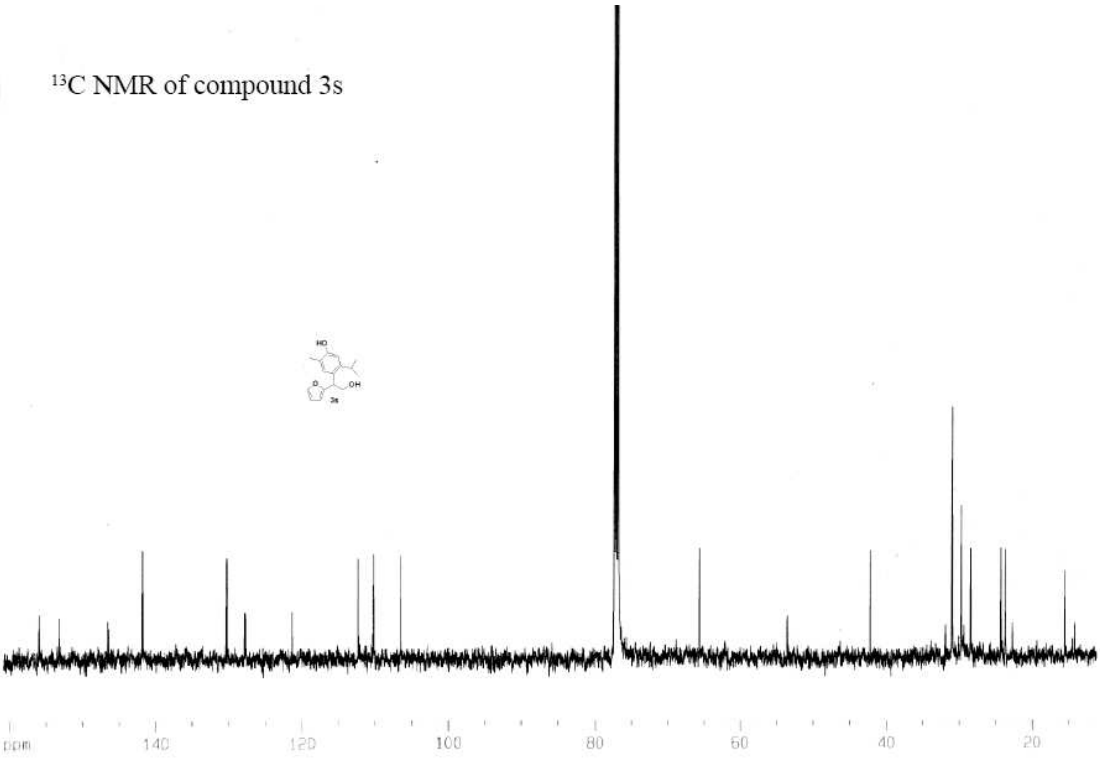
^{13}C NMR of compound 3r



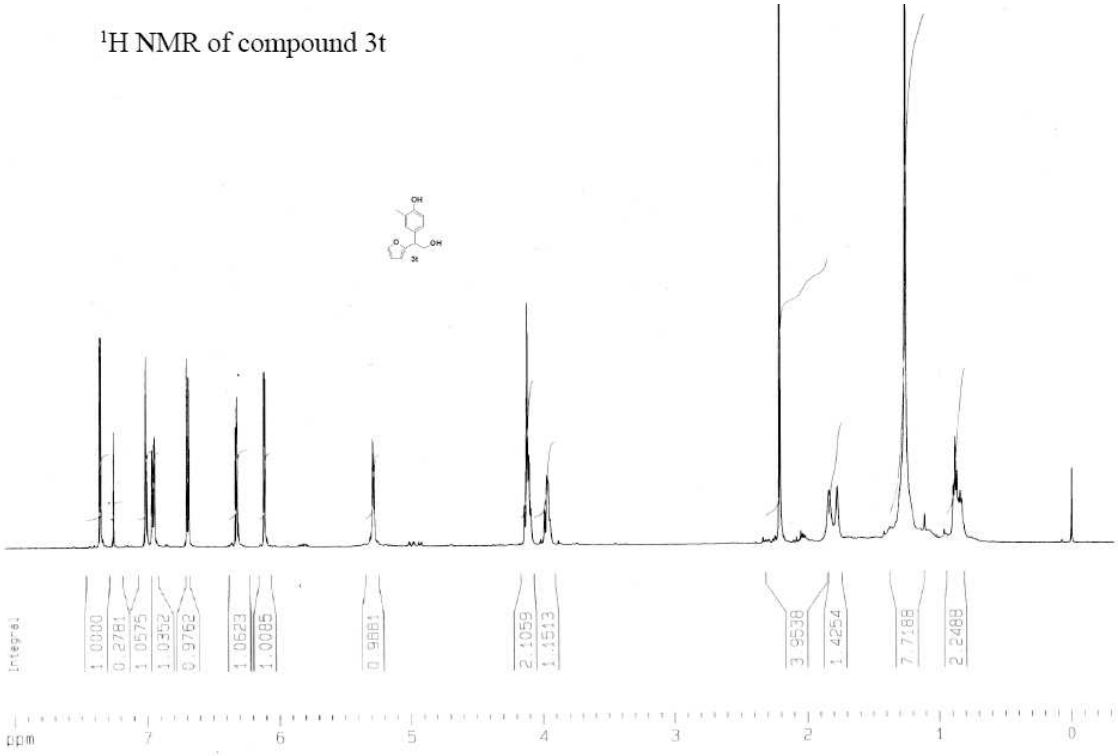
^{1}H NMR of compound 3s



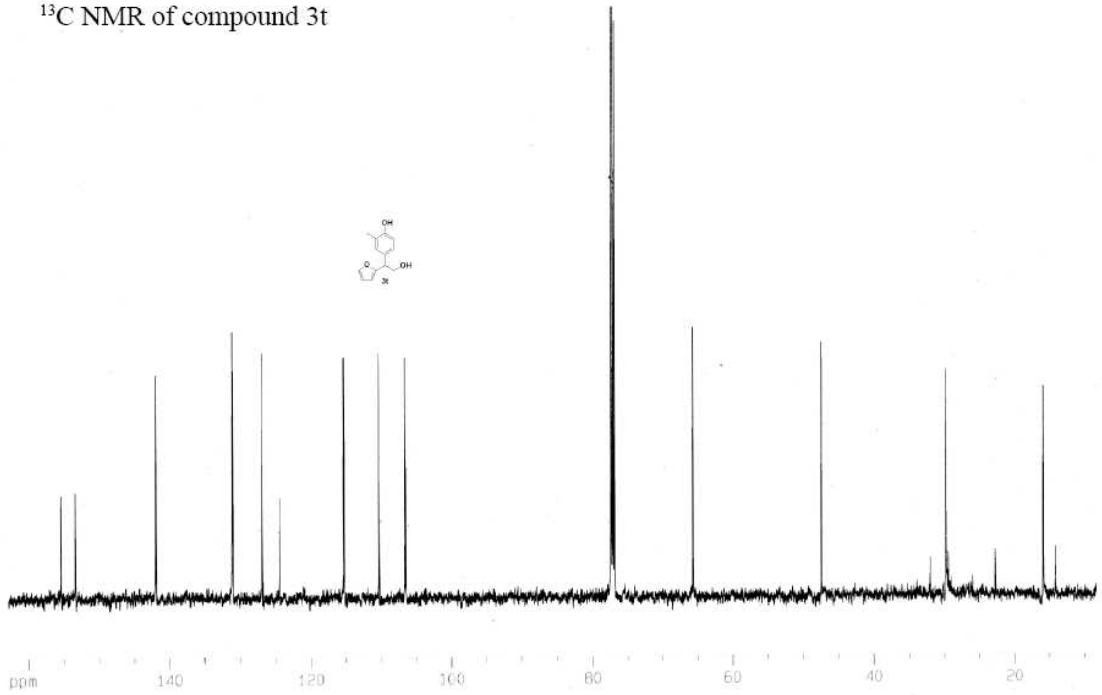
^{13}C NMR of compound 3s



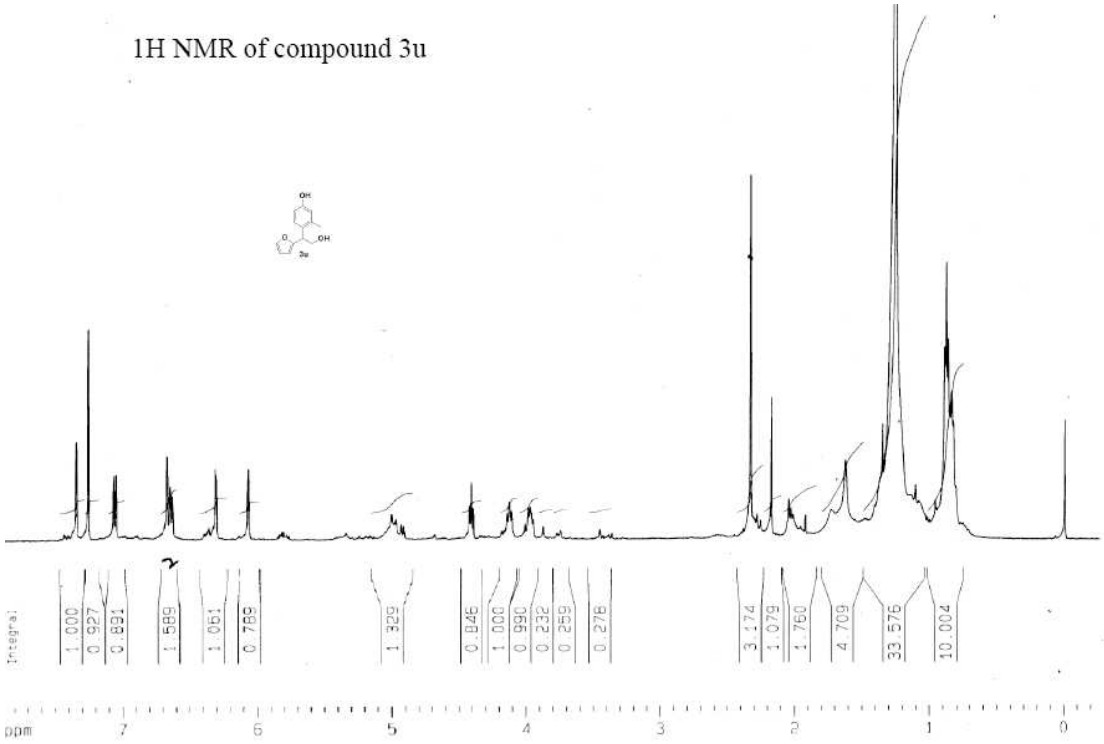
^{1}H NMR of compound 3t



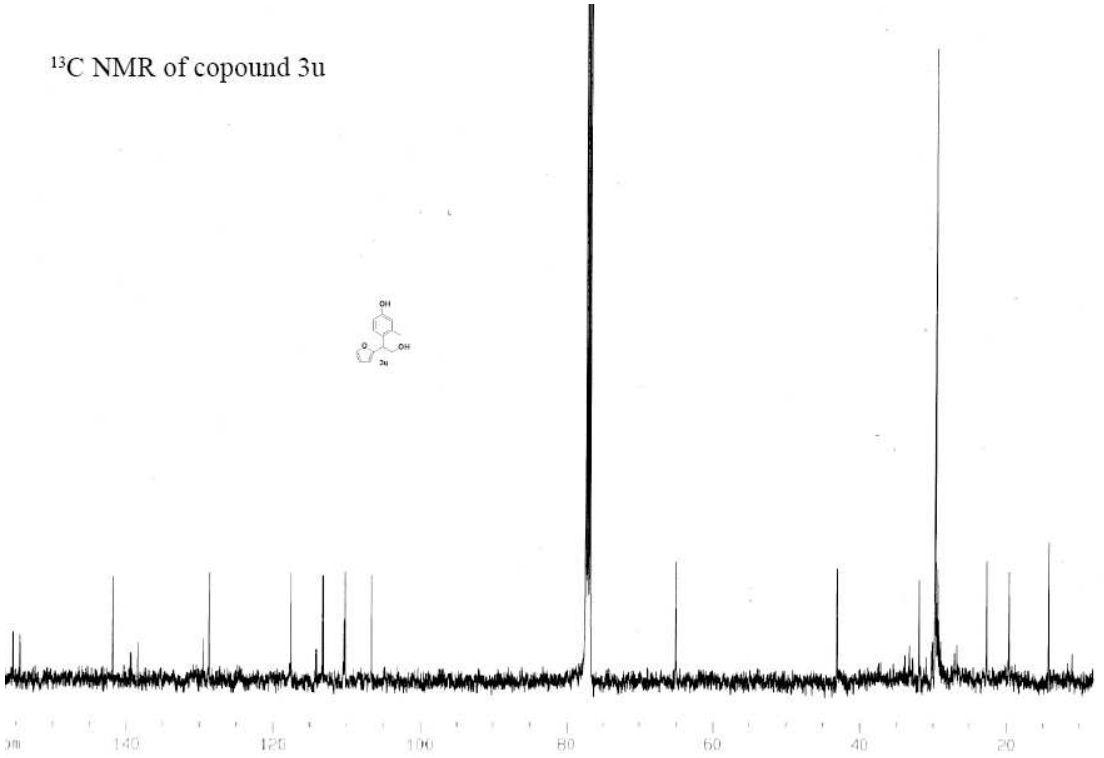
^{13}C NMR of compound 3t

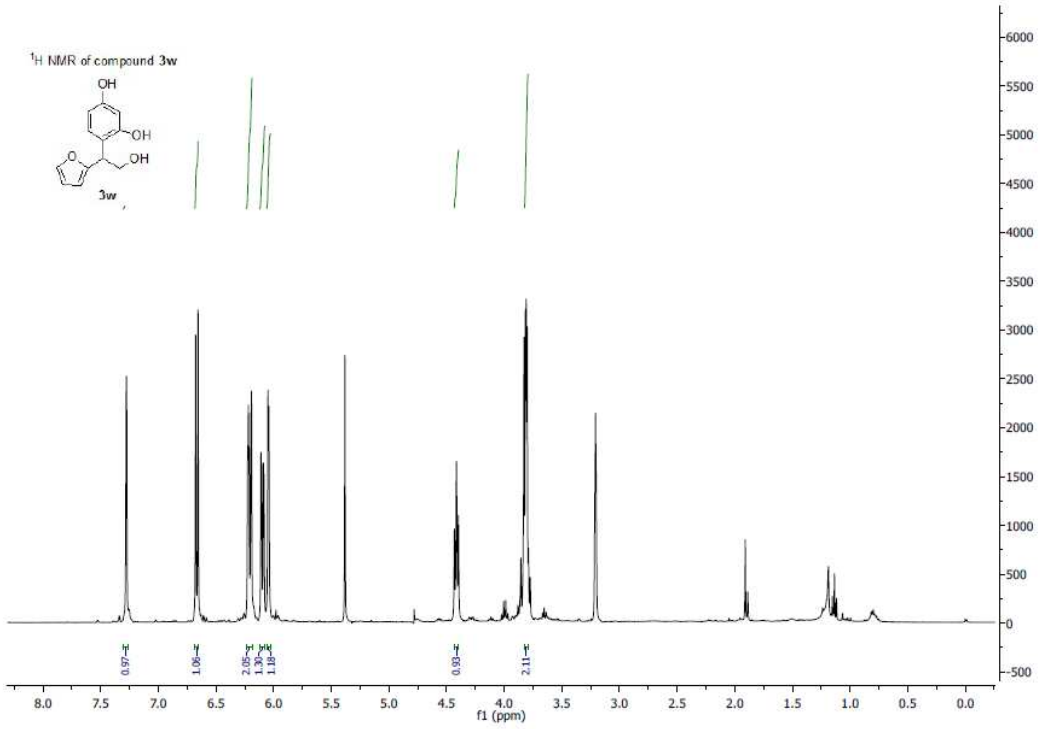


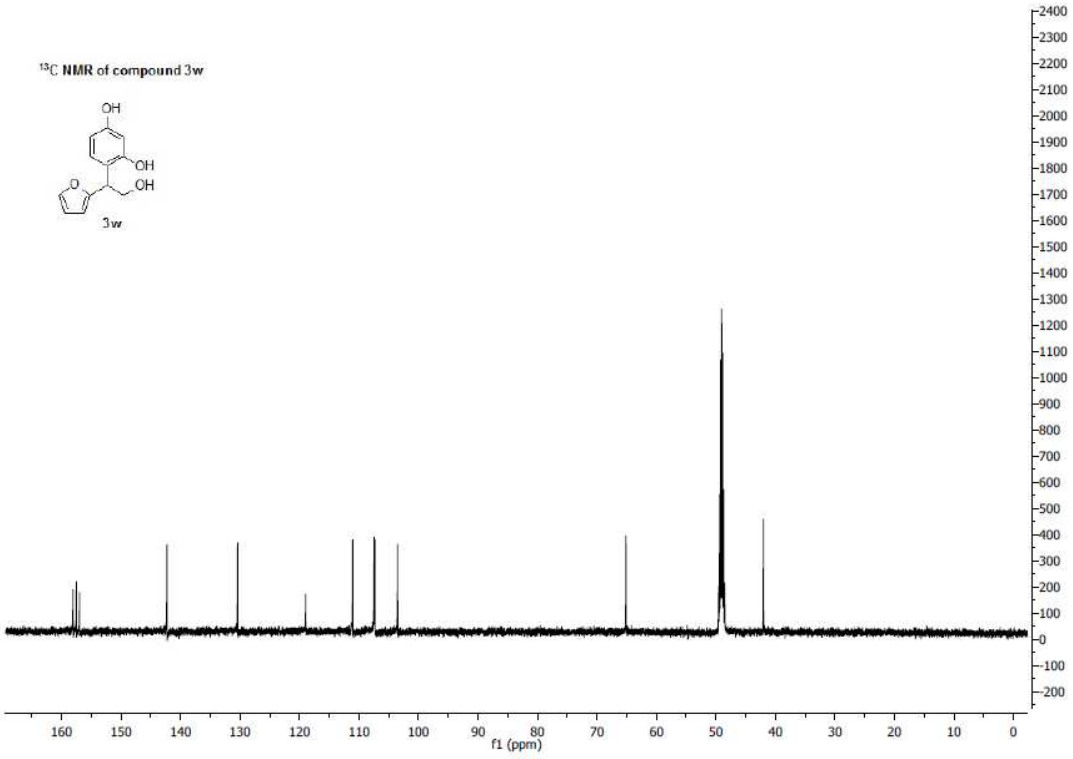
1H NMR of compound 3u



^{13}C NMR of copound 3u




1H NMR of compound 3w
OH
OH
OH
O
3w
0.97
1.06
2.05
1.30
1.18
0.93
2.11
f1 (ppm)


13C NMR of compound 3w
OH
OH
OH
O
3w
f1 (ppm)