Electronic supplementary information

A simple copper-catalysed tandem cyclisation of ynamides leading to triazolo-1,2,4-benzothiadiazine-1,1-dioxides in PEG-400 medium

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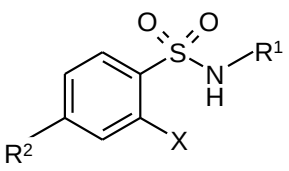
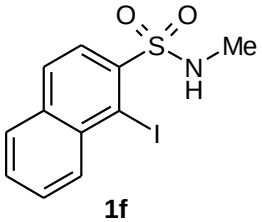
General: Chemicals were purified when required according to standard procedures.[1] All reactions, unless stated otherwise, were performed in a dry nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded using a 400 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$). Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Microanalyses were performed using a CHNS analyzer. For TLC, glass microslides were coated with silica-gel-GF_{254} (mesh size 75μ) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of 100-200 mesh size was used. LC-MS or GC-MS equipment were used to record mass spectra for isolated compounds where appropriate. LC-MS data were obtained using electrospray ionization on a C-18 column at a flow rate 0.2 mL/ min using MeOH/water (90:10) as eluent. GC-MS data were obtained on EI mode using ZB-1 column. DMF was distilled on CaH_2 and stored on molecular sieves.

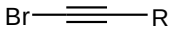
The substituted 2-halo-benzenesulfonamides **1a-h**,[2] 2-bromo-*N*,4-dimethylbenzenesulfonamide **1i**[3] and substituted (bromoethynyl)benzene precursors **2a-g**[4] were prepared following literature reports.



1a-i



1f



2a-g

For X = -I

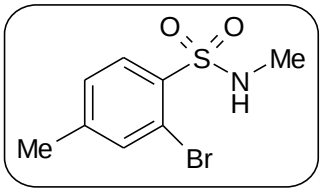
R^1 = -Me, R^2 = -Me	**1a**
R^1 = -Me, R^2 = -*t*-Bu	**1b**
R^1 = -Me, R^2 = -OMe	**1c**
R^1 = -Me, R^2 = -Ph	**1d**
R^1 = -*i*-Pr, R^2 = -Me	**1e**

For X = -Br

R^1 = -Me, R^2 = -H	**1g**
R^1 = -*n*-Butyl, R^2 = -H	**1h**
R^1 = -Me, R^2 = -Me	**1i**

R = -Ph	**2a**
R = -*p*-Tolyl	**2b**
R = -*n*-Hexyl	**2c**
R = $-CH_2OBn$	**2d**
R = $-3\text{-}F\text{-}C_6H_4$	**2e**
R = -tips	**2f**
R = -biphenyl	**2g**

2-bromo-N,4-dimethylbenzenesulfonamide (1i)

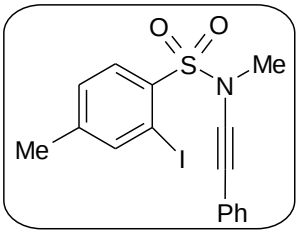


White solid; Yield 0.73 g (72%); Mp 74 ^{o}C; IR υ_{max} (KBr): 3320, 3090, 2926, 1594, 1408, 1331, 1172, 1112, 1024, 827, 651 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, Ar-CH_3), 2.60 (d, *J* = 5.2 Hz, 3H, NCH_3), 5.02-5.03 (m, 1H, SO_2N*H)*, 7.27-7.28 (m, 1H, Ar-*H*), 7.57 (s, 1H, Ar-*H*), 8.01 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (ArCH_3), 29.3 (NCH_3), 119.4, 128.5, 131.9, 134.4, 135.5,145.2; LC/MS: *m/z* 264 and 266 $[M]^+$. Anal.Calcd. for $C_8H_{10}BrNO_2S$: C, 36.28; H, 3.82; N, 5.30. Found: C, 36.29; H, 3.86; N, 5.25.

Experimental procedures and characterisation data for compounds 3a-p and acetamides 5 (and A-D)

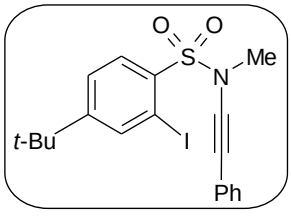
Synthesis of ynamides 3a-p: Representative procedure for 2-iodo-N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide (3a)

These compounds were prepared following a known procedure.[5] Compound **3a** was synthesised by using 2-iodo-*N*,4-dimethylbenzenesulfonamide **1a** (1.00 g, 3.21 mmol), $CuSO_4 \cdot 5H_2O$ (0.08 g, 0.32 mmol), 1,10-phenanthroline monohydrate (0.127 g, 0.64 mmol) and K_2CO_3 (1.11 g, 8.03 mmol).. Later, dry toluene (5 mL) and (bromoethynyl)benzene **2a** (0.46 mL, 3.85 mmol) were added. The vessel was stoppered under nitrogen atmosphere and heated on an oil-bath maintained at 80 ^oC overnight. The mixture was passed through celite and concentrated in vaccum. The crude residue was then purified by using silica gel column chromatography to obtain the pure ynamide **3a** by using hexane-ethyl acetate (9:1) as the eluent.



White solid; Yield 1.13 g (86%); Mp 96 ^oC; IR υ_{max} (KBr): 2241, 1584, 1441, 1353, 1260, 1167, 1096, 1019, 964, 756, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H, Ar-CH_3), 3.41 (s, 3H, NCH_3), 7.26-7.27 (m, 5H, Ar-*H)*, 7.33 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.99 (s, 1H, Ar-*H*), 8.10 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9 (Ar*C*H_3), 39.7 (N*C*H_3), 70.2, 83.3, 92.2 (*C*I), 122.7, 127.8, 128.3, 129.0, 131.2, 132.6, 136.9, 143.8, 145.7; HRMS (ESI): Calcd. for $C_{16}H_{15}INO_2S$ [M^++H]: *m/z* 411.9868. Found: 411.9866.

4-(tert-butyl)-2-iodo-N-methyl-N-(phenylethynyl)benzenesulfonamide (3b)

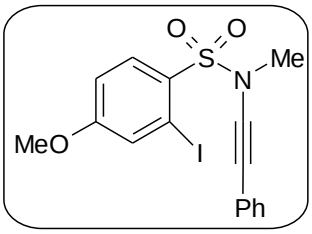


Here, 4-*tert*-butyl-2-iodo-*N*-methylbenzenesulfonamide **1b** (1.00 g, 2.82 mmol) and (bromoethynyl)benzene **2a** (0.40 mL, 3.39 mmol) were used.

White solid; Yield 1.12 g (88%); Mp 68 ^oC; IR υ_{max} (KBr): 2225, 1584, 1540, 1458, 1337, 1178,

959, 751, 663 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 0.99 (s, 9H, C(CH_3)$_3$), 3.15 (s, 3H, NCH_3), 7.04-7.09 (m, 4H, Ar-H), 7.33-7.34 (m, 2H, Ar-*H*), 8.08 (s, 1H, Ar-*H*), 8.22 (d, *J* = 8.4 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 30.3 (C(CH_3)$_3$), 34.4 (C(CH_3)$_3$), 39.2 (NCH_3), 70.5, 84.3, 92.8 (*C*I), 123.2, 125.5, 127.7, 128.3, 131.4, 132.7, 137.8, 140.4, 158.1; HRMS (ESI): Calcd. for $C_{19}H_{21}INO_2S$ [M^++H]: *m/z* 454.0337. Found: 454.0342.

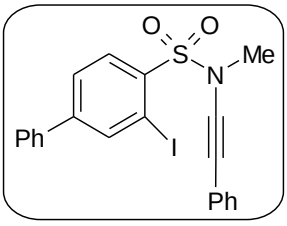
2-iodo-4-methoxy-N-methyl-N-(phenylethynyl)benzenesulfonamide (3c)



Here, 2-iodo-4-methoxy-*N*-methylbenzenesulfonamide **1c** (1.00 g, 3.05 mmol) and (bromoethynyl)benzene **2a** (0.43 mL, 3.66 mmol) were used.

Gummy liquid; Yield 1.20 g (92%); IR υ_{max}(neat): 2236, 1584, 1474, 1364, 1162, 1014, 959, 762 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 2.92 (s, 3H, NCH_3), 3.16 (s, 3H, Ar-OCH_3), 6.35 (dd, *J* = 8.8 and 2.4 Hz, 1H, Ar-*H*), 7.02 (d, *J* = 6.8 Hz, 3H, Ar-*H*), 7.38-7.42 (m, 3H, Ar-*H*), 8.21 (d, 1H, *J* = 8.8 Hz, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 39.2 (NCH_3), 55.1 (Ar-OCH_3), 70.4, 84.4, 93.6 (*C*I), 113.1, 123.2, 127.7, 128.4, 128.5, 131.4, 131.9, 134.3, 162.7; LC/MS: *m/z* 428 $[M+1]^+$. Anal.Calcd. for $C_{16}H_{14}INO_3S$: C, 44.98; H, 3.30; N, 3.28. Found: C, 44.85; H, 3.36; N, 3.23.

3-iodo-N-methyl-N-(phenylethynyl)-[1,1'-biphenyl]-4-sulfonamide (3d)

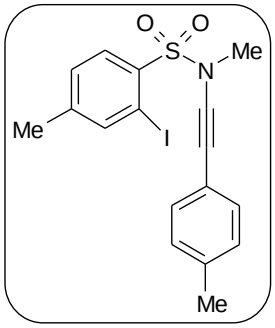


Here, 3-iodo-*N*-methylbiphenyl-4-sulfonamide **1d** (0.50 g, 1.33 mmol) and (bromoethynyl)benzene **2a** (0.19 mL, 1.60 mmol) were used.

Gummy liquid; Yield 0.59 g (94%); IR υ_{max}(neat): 2236, 1584, 1540, 1458, 1364, 1167, 964, 805, 756 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 3.17 (s, 3H, NCH_3), 7.02-7.04 (m, 3H, Ar-*H*), 7.11-

7.19 (m, 6H, Ar-*H*), 7.40 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 8.13 (s, 1H, Ar-*H*), 8.29 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 39.3 (N*C*H$_3$), 70.6, 84.1, 93.0 (*C*I), 123.1, 126.5, 127.3, 128.4, 128.6, 128.8, 129.0, 131.5, 133.0, 137.4, 138.9, 141.5, 146.8; HRMS (ESI): Calcd. for $C_{21}H_{17}INO_2S$ [M^++H]: *m/z* 474.0024. Found: 474.0020.

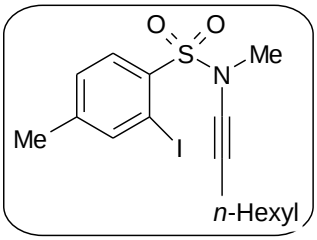
2-iodo-N,4-dimethyl-N-(p-tolylethynyl)benzenesulfonamide (3e)



Here, 2-iodo-*N*,4-dimethylbenzenesulfonamide **1a** (0.50 g, 1.60 mmol) and 1-(bromoethynyl)-4-methylbenzene **2b** (0.26 mL, 1.92 mmol) were used.

White solid; Yield 0.56 g (82%); Mp: 102 ^{o}C; IR υ_{max} (KBr): 2230, 1584, 1452, 1353, 1162, 1030, 953, 816, 729, 658 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ 1.60 (s, 3H, Ar-C*H*$_3$), 1.99 (s, 3H, Ar-C*H*$_3$), 3.13 (s, 3H, NC*H*$_3$), 6.53 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.82 (d, *J* = 7.6 Hz, 2H, Ar-*H)*, 7.33 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.53 (s, 1H, Ar-*H*), 8.15 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 20.0 (Ar-*C*H$_3$), 21.0 (Ar*C*H$_3$), 39.3 (N*C*H$_3$), 70.3, 83.5, 92.5 (*C*I), 120.1, 128.7, 129.1, 131.7, 132.5, 137.7, 137.8, 143.6, 145.0; HRMS (ESI): Calcd. for $C_{17}H_{17}INO_2S$ [M^++H]: *m/z* 426.0024. Found: 426.0022.

2-iodo-N,4-dimethyl-N-(oct-1-yn-1-yl)benzenesulfonamide (3f)

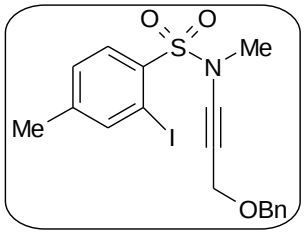


Here, 2-iodo-*N*,4-dimethylbenzenesulfonamide **1a** (0.50 g, 1.60 mmol) and 1-bromooct-1-yne **2c** (0.20 mL, 1.92 mmol) were used.

Gummy liquid; Yield 0.57 g (84%); IR υ_{max}(neat): 2251, 1588, 1459, 1356, 1283, 1169, 1024,

828, 672 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 0.93 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.15-1.35 (m, 8H, 4 C*H*$_2$), 1.71 (s, 3H, Ar-C*H*$_3$), 2.09 (t, *J* = 6.8 Hz, 2H, C*H*$_2$), 3.17 (s, 3H, NC*H*$_3$), 6.68 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.60 (s, 1H, Ar-*H*), 8.20 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 14.1, 18.5, 20.1, 22.7 (Ar-*C*H$_3$), 28.4, 28.9, 31.4, 39.3 (N*C*H$_3$), 69.5, 74.9, 92.5 (*C*I), 128.5, 132.4, 138.0, 143.4, 144.7; HRMS (ESI): Calcd. for $C_{16}H_{23}INO_2S$ [M^++H]: *m/z* 420.0494. Found: 420.0496.

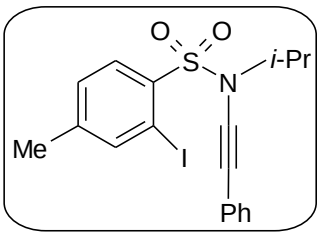
N-(3-(benzyloxy)prop-1-yn-1-yl)-2-iodo-N,4-dimethylbenzenesulfonamide (3g)



Here, 2-iodo-*N*,4-dimethylbenzenesulfonamide **1a** (0.50 g, 1.60 mmol) and ((3-bromoprop-2-ynyloxy)methyl)benzene **2d** (0.30 mL, 1.92 mmol) were used.

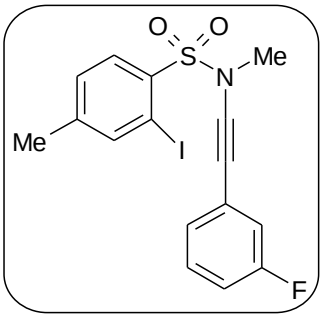
Gummy liquid; Yield 0.654 g (89%); IR υ_{max}(neat): 2241, 1589, 1452, 1348, 1167, 1063, 1019, 701 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 1.64 (s, 3H, Ar-C*H*$_3$), 3.07 (s, 3H, NC*H*$_3$), 4.11 (s, 2H, OC*H*$_2$), 4.42 (s, 2H, OC*H*$_2$), 6.60 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.17-7.23 (m, 3H, Ar-*H)*, 7.33 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.55 (s, 1H, Ar-*H*), 8.14 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 20.2 (Ar-*C*H$_3$), 39.2 (N*C*H$_3$), 57.3 (O*C*H$_2$), 67.3, 70.7 (O*C*H$_2$), 81.2, 92.4 (*C*I), 127.6, 128.0, 128.3, 128.9, 132.4, 137.3, 138.1, 143.6, 145.5; HRMS (ESI): Calcd. for $C_{18}H_{19}INO_3S$ [M^++H]: *m/z* 456.0130. Found: 456.0129.

2-iodo-N-isopropyl-4-methyl-N-(phenylethynyl)benzenesulfonamide (3h)



Here, 2-iodo-4-methyl-*N*-(*i*-propyl)benzenesulfonamide **1e** (0.50 g, 1.47 mmol), $CuSO_4 \cdot 5H_2O$ (0.072 g, 0.29 mmol), 1,10-phenanthroline monohydrate (0.114 g, 0.58 mmol), K_2CO_3 (0.507 g, 3.67 mmol), dry toluene (3 mL) and (bromoethynyl)benzene **2a** (0.21 mL, 1.76 mmol) were used. White solid; Yield 0.23 g (36%); Mp 80 ^oC; IR υ_{max} (KBr): 2230, 1584, 1353, 1178, 1025, 970, 756, 674 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 1.35 (d, *J* = 6.4 Hz, 6H, $CH(CH_3)_2$), 1.64 (s, 3H, Ar-CH_3), 4.55-4.58 (m, 1H, NC*H*), 6.59 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.00-7.05 (m, 3H, Ar-*H*), 7.40 (dd, *J* = 8.0 and 1.6 Hz, 2H, Ar-*H*), 7.57 (s, 1H, Ar-*H*), 8.25 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 20.0 ($CH(CH_3)_2$), 20.9 (Ar-CH_3), 52.6 (NCH), 74.0, 80.0, 92.6 (CI), 123.6, 128.3, 128.6, 131.4, 132.6, 138.3, 143.5, 144.9; HRMS (ESI): Calcd. for $C_{18}H_{18}INO_2S$ $[M^+ + H]$: *m/z* 440.0181. Found: 440.0181.

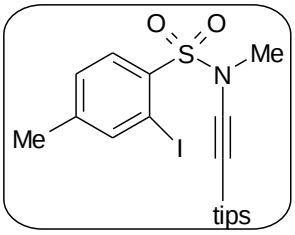
N-((3-fluorophenyl)ethynyl)-2-iodo-N,4-dimethylbenzenesulfonamide (3i)



Here, 2-iodo-*N*,4-dimethylbenzenesulfonamide **1a** (0.50 g, 1.60 mmol) and 1-(bromoethynyl)-3-fluorobenzene **2e** (0.23 mL, 1.92 mmol) were used.

Gummy liquid; Yield 0.664 g (96%); IR υ_{max}(neat): 2236, 1578, 1436, 1353, 1260, 1173, 1025, 888, 734, 679 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 1.65 (s, 3H, Ar-CH_3), 3.09 (s, 3H, NCH_3), 6.58 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.65-6.69 (m, 1H, Ar-*H*), 6.73-6.79 (m, 1H, Ar-*H*), 7.03 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.55 (s, 1H, Ar-*H*), 8.13 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 20.2 (Ar-CH_3), 39.1 (NCH_3), 69.5, 85.2, 92.4 (CI), 114.8 (d, $J_{C\text{-}F}$ = 20 Hz), 117.7 (d, $J_{C\text{-}F}$ = 20 Hz), 125.1 (d, $J_{C\text{-}F}$ = 10 Hz), 126.9, 128.8, 130.0 (d, $J_{C\text{-}F}$ = 10 Hz), 132.4, 137.2, 143.7, 145.6, 163.5 (d, $J_{C\text{-}F}$ = 240 Hz); HRMS (ESI): Calcd. for $C_{16}H_{15}INO_2S$ $[M^+ + H]$: *m/z* 429.9774. Found: 429.9773.

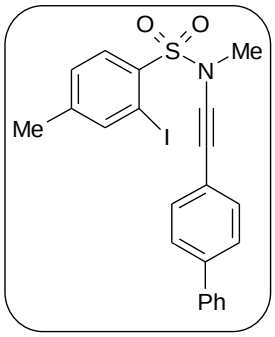
2-iodo-N,4-dimethyl-N-((triisopropylsilyl)ethynyl)benzenesulfonamide (3j)



Here, 2-iodo-*N*,4-dimethylbenzenesulfonamide **1a** (0.50 g, 1.60 mmol) and (bromoethynyl)triisopropylsilane **2f** (0.46 mL, 1.92 mmol) were used.

White solid; Yield 0.746 g (95%); Mp: 52 ^{o}C; IR υ_{max} (KBr): 2164, 1584, 1463, 1337, 1167, 1030, 981, 888, 729, 674 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ 1.13-1.14 (m, 21H, Si(C*H*(CH_3)$_2$)$_3$), 1.71 (s, 3H, Ar-CH_3), 3.13 (s, 3H, NCH_3), 6.67 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 7.57 (s, 1H, Ar-*H*), 8.20 (d, *J* = 8.4 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 11.4 (*C*H), 18.6 (*C*H_3), 20.0 (Ar-*C*H_3), 39.0 (N*C*H_3), 68.3, 92.5, 98.0 (*C*I), 128.6, 132.9, 137.4, 143.3, 145.0; LC/MS: *m/z* 490 [M-1]$^{+}$. Anal.Calcd. for $C_{19}H_{30}ISNO_2Si$: C, 46.43; H, 6.15; N, 2.85. Found: C, 46.52; H, 6.20; N, 2.81.

N-([1,1'-biphenyl]-4-ylethynyl)-2-iodo-N,4-dimethylbenzenesulfonamide (3k)

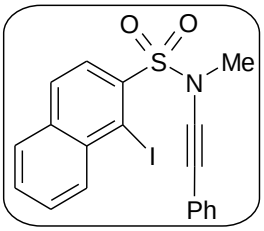


Here, 2-iodo-*N*,4-dimethylbenzenesulfonamide **1a** (0.5 g, 1.60 mmol) and 1-(bromoethynyl)biphenyl **2g** (0.495 g, 1.92 mmol) were used.

Gummy liquid; Yield 0.704 g (90%); IR υ_{max}(neat): 2235, 1588, 1490, 1358, 1161, 1019, 964, 838, 723 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ 1.66 (s, 3H, Ar-CH_3), 3.18 (s, 3H, NCH_3), 6.61 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.20 (d, *J* = 7.2 Hz, 1H, Ar-*H)*, 7.21-7.26 (m, 2H, Ar-*H*), 7.34 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.41 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.46 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.59 (s, 1H, Ar-*H*), 8.21 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 20.1 (Ar-*C*H_3), 39.3 (N*C*H_3), 70.4, 84.8, 92.5 (*C*I), 122.0, 127.0, 127.1, 127.3, 128.8, 128.9, 131.9, 132.5, 137.6, 140.4, 140.6,

143.6, 145.3; HRMS (ESI): Calcd. for $C_{22}H_{18}INO_2S$ [M^++Na]: *m/z* 510.0001. Found: 510.0001.

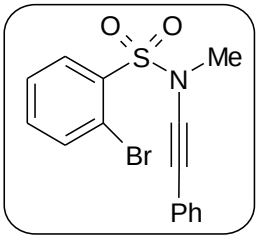
1-iodo-N-methyl-N-(phenylethynyl)naphthalene-2-sulfonamide (3l)



Here, 1-iodo-*N*-methylnaphthalene-2-sulfonamide **1f** (0.50 g, 1.44 mmol) and (bromoethynyl)benzene **2a** (0.20 mL, 1.92 mmol) were used. Two isomers in the ratio 3:1 were present; the mixture was used as such.

Gummy liquid; Yield 0.40 g (62%); IR υ_{max}(neat): 2236, 1540, 1441, 1364, 1173, 970, 762, 674 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6, major isomer): δ 3.15 (s, 3H, NC*H*$_3$), 6.98-6.99 (m, 3H, Ar-*H*), 7.15-7.22 (m, 3H, Ar-*H*), 7.32-7.34 (m, 3H, Ar-*H*), 8.36 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 8.41 (d, *J* = 8.4 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6, major isomer): δ 39.3 (N*C*H$_3$), 70.7, 84.1, 123.0, 127.7, 128.3, 128.9, 129.1, 131.4, 134.8, 135.8, 140.2; LC/MS: *m/z* 448 $[M+1]^+$. Anal.Calcd. for $C_{19}H_{14}INO_2S$: C, 51.02; H, 3.15; N, 3.13. Found: C, 51.16; H, 3.21; N, 3.18.

2-bromo-N-methyl-N-(phenylethynyl)benzenesulfonamide (3m)

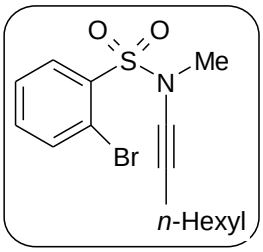


Here, 2-bromo-*N*-methylbenzenesulfonamide **1g** (0.50 g, 1.99 mmol) and (bromoethynyl)benzene **2a** (0.28 mL, 1.92 mmol) were used.

Gummy liquid; Yield 0.645 g (92%); IR υ_{max}(neat): 2230, 1567, 1447, 1375, 1260, 1156, 1030, 970, 762 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ 3.06 (s, 3H, NC*H*$_3$), 6.55 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 6.68 (t, *J* = 7.8 Hz, 1H, Ar-*H*), 7.00-7.01 (m, 3H, Ar-*H*), 7.22 (s, 1H, Ar-*H*), 7.34-7.36 (m, 2H, Ar-*H*), 8.19 (dd, *J* = 7.8 and 1.4 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 39.0 (N*C*H$_3$), 70.3, 83.7, 120.4, 122.9, 127.4, 128.4, 128.6, 131.4, 133.0, 135.7, 134.3, 137.1; LC/MS: *m/z* 350

and 352 $[M]^+$. Anal.Calcd. for $C_{15}H_{12}BrNO_2S$: C, 51.44; H, 3.45; N, 4.00. Found: C, 51.36; H, 3.49; N, 4.07.

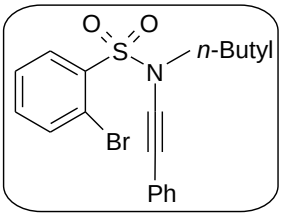
2-bromo-N-methyl-N-(oct-1-yn-1-yl)benzenesulfonamide (3n)



Here, 2-bromo-*N*-methylbenzenesulfonamide **1g** (0.36 g, 1.43 mmol) and 1-bromooct-1-yne **2c** (0.27 mL, 1.72 mmol) were used.

Gummy liquid; Yield 0.42 g (82%); IR υ_{max}(neat): 2258, 1573, 1447, 1364, 1173, 1036, 767, 652 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 0.93 (t, *J* = 7.2 Hz, 3H, C*H*$_3$), 1.14-1.33 (m, 8H, 4C*H*$_2$), 2.06 (t, *J* = 6.8 Hz, 2H), 3.09 (s, 3H, NC*H*$_3$), 6.61 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 6.78 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.28 (s, 1H, Ar-*H*), 8.24 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 14.0, 18.3, 22.7, 28.3, 28.9, 31.3, 39.1 (N*C*H$_3$), 69.5, 74.4, 120.5, 127.1, 133.0, 133.8, 135.5, 137.7; LC/MS: *m/z* 358 and 360 $[M]^+$. Anal.Calcd. for $C_{15}H_{20}BrNO_2S$: C, 50.28; H, 5.63; N, 3.91. Found: C, 50.14; H, 5.68; N, 3.85.

2-bromo-N-butyl-N-(phenylethynyl)benzenesulfonamide (3o)

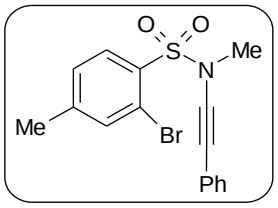


Here, 2-bromo-*N*-butylbenzenesulfonamide **1h** (0.58 g, 1.60 mmol) and (bromoethynyl)benzene **2a** (0.28 mL, 2.38 mmol) were used.

Gummy liquid; Yield 0.63 g (82%); IR υ_{max}(neat): 2230, 1573, 1452, 1364, 1184, 1030, 932, 756 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 0.85 (t, *J* = 7.2 Hz, 3H, C*H*$_3$), 1.33-1.39 (m, 2H, C*H*$_2$), 1.72-1.79 (m, 2H, C*H*$_2$), 3.69 (t, *J* = 7.2 Hz, 2H, C*H*$_2$), 6.59 (dt, *J* = 7.6 1.2 Hz, 1H, Ar-*H*), 6.73 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 7.01-7.00 (m, 3H, Ar-*H*), 7.28 (s, 1H, Ar-*H*), 7.34-7.35 (m, 2H, Ar-*H*),

8.26 (dd, 1H, *J* = 8.0 and 1.6 Hz , Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 13.4, 19.5, 30.7, 52.0, 71.8, 82.4, 120.5, 123.2, 127.1, 127.7, 128.3, 131.4, 133.1, 133.8, 135.5, 137.8; LC/MS: *m/z* 392 and 394 $[M]^+$. Anal.Calcd. for $C_{18}H_{18}BrNO_2S$: C, 55.11; H, 4.62; N, 3.57. Found: C, 55.21; H, 4.58; N, 3.62.

2-bromo-N,4-dimethyl-N-(phenylethynyl)benzenesulfonamide (3p)



Here, 2-bromo-*N*,4-dimethylbenzenesulfonamide **1i** (0.50 g, 1.90 mmol) and (bromoethynyl)benzene **2a** (0.28 mL, 2.28 mmol) were used.

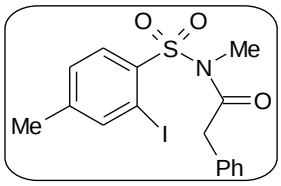
White solid; Yield 0.59 g (86%); Mp: 68 ^{o}C; IR υ_{max} (KBr): 2230, 1584, 1447, 1353, 1260, 1167, 1036, 948, 762 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ 1.68 (s, 3H, Ar-C*H*$_3$), 3.12 (s, 3H, NC*H*$_3$) , 6.54 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.02-7.00 (m, 3H, Ar-*H*), 7.12 (s, 1H, Ar-*H*), 7.39 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 8.15 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, C_6D_6): δ 20.4 (Ar-*C*H$_3$), 39.0 (N*C*H$_3$), 70.2, 83.9, 123.1, 120.3, 127.7, 128.3, 131.4, 132.9, 134.4, 136.2, 145.7; LC/MS: *m/z* 364 and 366 $[M]^+$. Anal.Calcd. for $C_{16}H_{14}BrNO_2S$: C, 52.76; H, 3.87; N, 3.85. Found: C, 52.65; H, 3.92; N, 3.81.

General procedure for the synthesis of acetamides 5 and A-D

Compound **5** was initially obtained in 36% yield along with **4** when water was used as the medium (cf. Scheme 1 and procedure given above for **4**). A general procedure is given below.

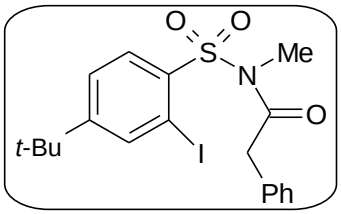
The ynamide **3a** (0.24 mmol) was dissolved in chloroform (2 mL) and stirred in open air at room temperature overnight. After completion of the reaction the solvent was removed under reduced pressure. The obtained crude reaction mixture was purified by using silica gel column chromatography using hexane-ethyl acetate (9:1) as the eluent. Similarly, compounds **A**-**D** could be obtained using **3b-d** or **3h**, respectively.

N-((2-iodo-4-methylphenyl)sulfonyl)-N-methyl-2-phenylacetamide (5)



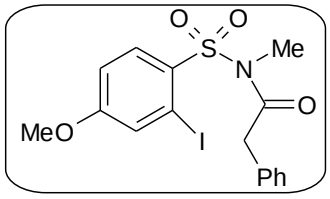
White solid; Yield 0.091 g (90%); Mp 106 ^{o}C; IR υ_{max} (KBr): 2942, 2909, 1704, 1578, 1457, 1336, 1161, 1073, 865, 766, 673 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H, Ar-C*H*$_3$), 3.39 (s, 3H, NC*H*$_3$), 3.96 (s, 2H, C*H*$_2$), 7.16 (d, *J* = 7.2 Hz, 1H, Ar-*H*), 7.27-7.34 (m, 4H, Ar-*H)*, 7.88 (s, 1H, Ar-*H*), 8.17 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9 (Ar-*C*H$_3$), 34.0 (N*C*H$_3$), 43.3 (*C*H$_2$), 127.3, 91.4 (*C*I), 129.3, 128.7, 132.8, 129.4, 143.1, 138.6, 145.7, 171.3; HRMS (ESI): Calcd. for $C_{16}H_{17}INO_3S$ [M^{+}+H]: *m/z* 429.9974. Found: 429.9969.

N-((4-(tert-butyl)-2-iodophenyl)sulfonyl)-N-methyl-2-phenylacetamide (A)



White solid; Yield 0.100 g (90%); Mp 98 ^{o}C; IR υ_{max} (KBr): 2959, 1709, 1572, 1451, 1336, 1177, 1073, 860, 777, 662 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H, C(C*H*$_3$)$_3$), 3.39 (s, 3H, NC*H*$_3$), 3.99 (s, 2H, C*H*$_2$), 7.15-7.16 (m, 2H, Ar-*H*), 7.27-7.32 (m, 3H, Ar-*H*), 7.53 (dd, *J* = 8.4 and 2.0 Hz, 1H, Ar-*H*), 8.02 (d, *J* = 1.6 Hz, 1H, Ar-*H*), 8.19 (d, *J* = 8.4 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.9 (C(*C*H$_3$)$_3$), 34.0 (N*C*H$_3$), 35.1 (*C*(CH$_3$)$_3$), 43.4 (N*C*H$_2$), 91.6 (*C*I), 125.8, 127.3, 128.7, 129.4, 132.7, 132.8, 138.5, 140.0, 158.6, 171.3; LC/MS: *m/z* 470 [M-1]$^{+}$. Anal.Calcd. for $C_{19}H_{22}INO_3S$: C, 48.42; H, 4.70; N, 2.97. Found: C, 48.56; H, 4.79; N, 2.85.

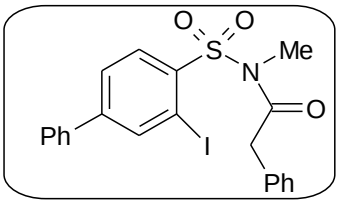
N-((2-iodo-4-methoxyphenyl)sulfonyl)-N-methyl-2-phenylacetamide (B)



White solid; Yield 0.102 g (94%); Mp 116 ^{o}C; IR υ_{max} (KBr): 2953, 1698, 1583, 1468, 1353,

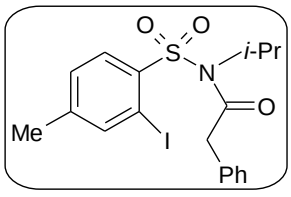
1172, 1073, 860, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.39 (s, 3H, Ar-CH_3), 3.86 (s, 3H, NCH_3), 3.96 (s, 2H, CH_2), 7.00 (dd, *J* = 8.8 and 2.4 Hz, 1H, Ar-*H*), 7.16 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 7.27-7.32 (m, 3H, Ar-*H)*, 7.54 (d, *J* = 2.4 Hz, 1H, Ar-*H*), 8.22 (d, *J* = 8.8 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.0 (N*C*H_3), 43.4 (*C*H_2), 56.0 (O*C*H_3), 92.5 (*C*I), 113.4, 127.3, 128.2, 128.7, 129.4, 132.9, 133.0, 134.7, 162.9, 171.3; LC/MS: *m/z* 446 $[M+1]^+$. Anal.Calcd. for $C_{16}H_{16}INO_4S$: C, 43.16; H, 3.62; N, 3.15. Found: C, 43.28; H, 3.56; N, 3.23.

N-((3-iodo-[1,1'-biphenyl]-4-yl)sulfonyl)-N-methyl-2-phenylacetamide (C)



White solid; Yield 0.100 g (84%); Mp: 96 ^oC; IR υ_{max} (KBr): 3079, 3030, 1704, 1583, 1451, 1336, 1166, 1073, 871, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.46 (s, 3H, NCH_3), 3.99 (s, 2H, CH_2), 7.18 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 7.27-7.33 (m, 3H, Ar-*H*), 7.45-7.52 (m, 3H, Ar-*H*), 7.59 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.73 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 8.25 (s, 1H, Ar-*H*), 8.34 (d, *J* = 8.4 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.1 (N*C*H_3), 43.3 (*C*H_2), 91.9 (*C*I), 127.1, 127.4, 128.8, 129.2, 129.4, 132.7, 133.3, 137.5, 140.0, 141.0, 147.3, 171.3; LC/MS: *m/z* 490 $[M-1]^+$. Anal.Calcd. for $C_{21}H_{18}INO_3S$: C, 51.33; H, 3.69; N, 2.85. Found: C, 51.45; H, 3.62; N, 2.79.

N-((2-iodo-4-methylphenyl)sulfonyl)-N-isopropyl-2-phenylacetamide (D)



White solid; Yield 0.094 g (86%); Mp: 96 ^oC; IR υ_{max} (KBr): 3030, 1709, 1578, 1462, 1347, 1183, 1090, 986, 728, 662 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 2.41 (s, 3H, Ar-CH_3), 3.91-3.98 (m, 1H, NC*H*), 4.32 (s, 2H, CH_2), 7.24-7.35 (m, 6H, Ar-*H*), 7.97 (s, 1H, Ar-*H*), 8.10 (d, *J* = 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7

(CH(CH$_3$)$_2$), 20.9 (Ar-CH$_3$), 46.2 (CH$_2$), 53.9 (NCH), 93.1 (CI), 127.0, 128.4, 129.3, 129.9, 132.0, 134.2, 137.9, 143.6, 145.8, 172.6; LC/MS: *m/z* 458 $[M+1]^+$. Anal.Calcd. for $C_{18}H_{20}INO_3S$: C, 47.27; H, 4.41; N, 3.06. Found: C, 47.36; H, 4.35; N, 3.12.

References:

1. D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*; Pergamon: Oxford, UK, 1986.
2. (a) J. S. Reddy, E. V. Bharathi, D. Dastagiri, A. Kamal, *Tetrahedron Lett.* 2008, **49**, 2320-2323. (b) B. Deepak Kumar, Y. C. Tu, V. Kavala, C. W. Kuo, C. F. Yao, *Adv. Synth. Catal*. 2011, **353**, 41-48.
3. S. L. Macneil, O. B. Familoni, V. Snieckus, *J. Org. Chem.* 2001, **66**, 3662-3670.
4. X. Nie, G. Wang, *J. Org. Chem.* 2006, **71**, 4734-4741.
5. (a) Y. Zhang, R. P. Hsung, M. R. Tracey, K. C. M. Kurtz, E. L. Vera, *Org. Lett*. 2004, **6**, 1151-1154. (b) R. B. Dateer, B. S. Shaibu, R. S. Liu, *Angew. Chem. Int. Ed*. 2012, **51**, 113 –117.

NMR spectra for the all new compounds

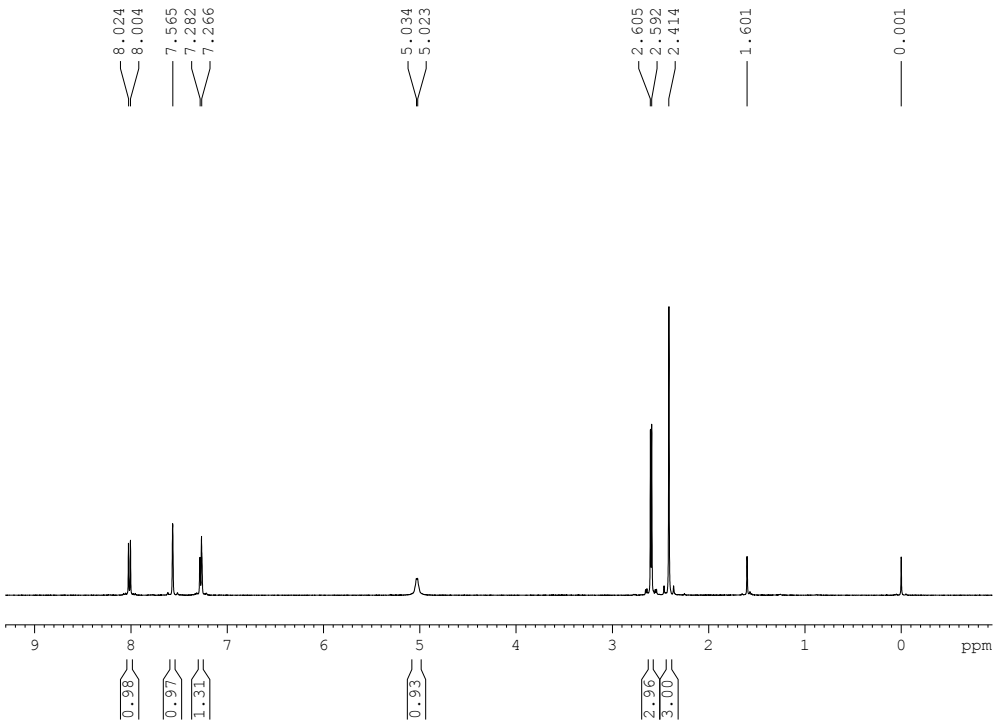


Figure S1. ^{1}H NMR spectrum of compound **1i**

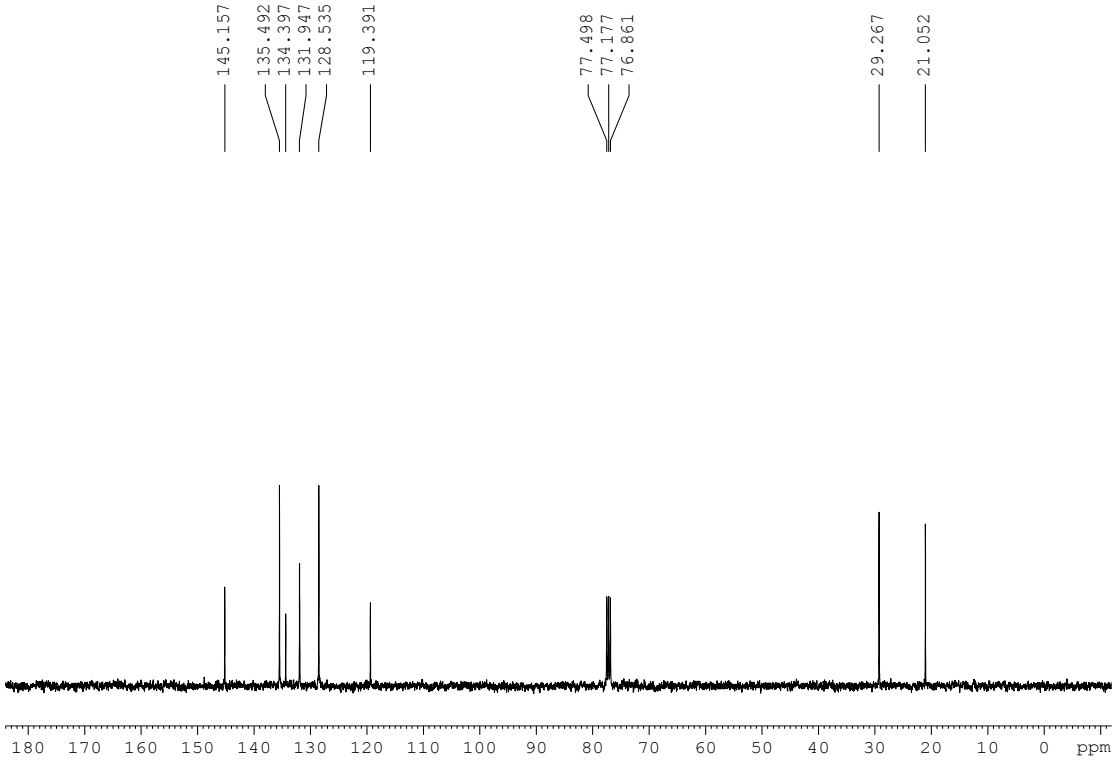


Figure S2. ^{13}C NMR spectrum of compound **1i**

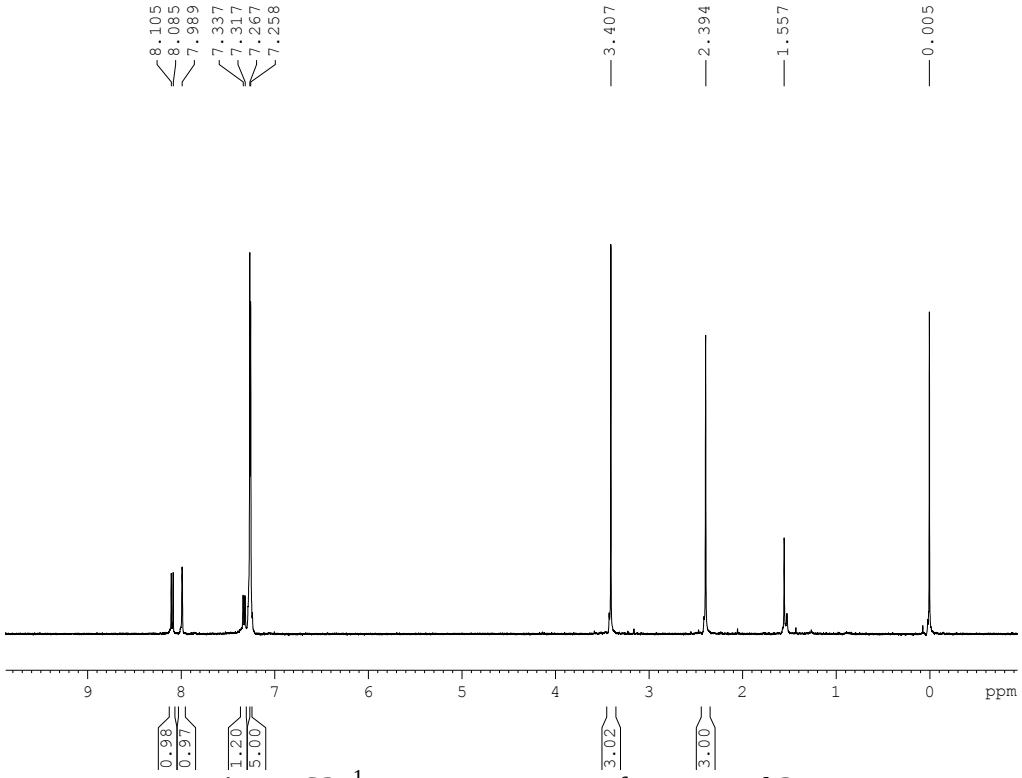


Figure S3. ^{1}H NMR spectrum of compound **3a**

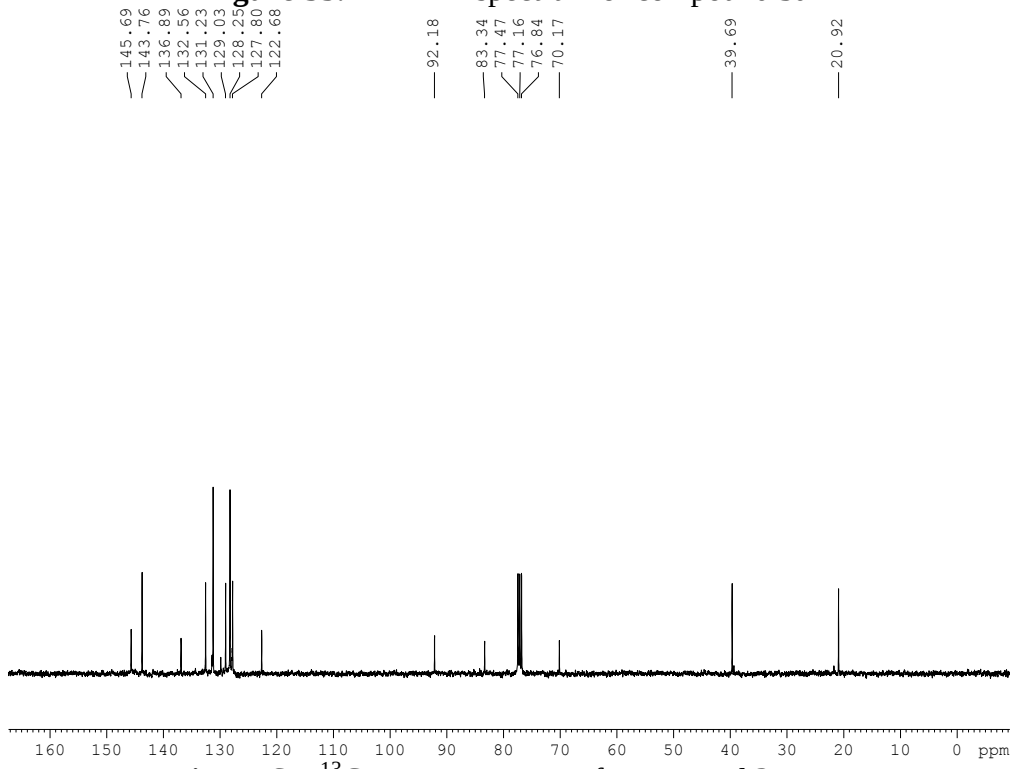


Figure S4. ^{13}C NMR spectrum of compound **3a**

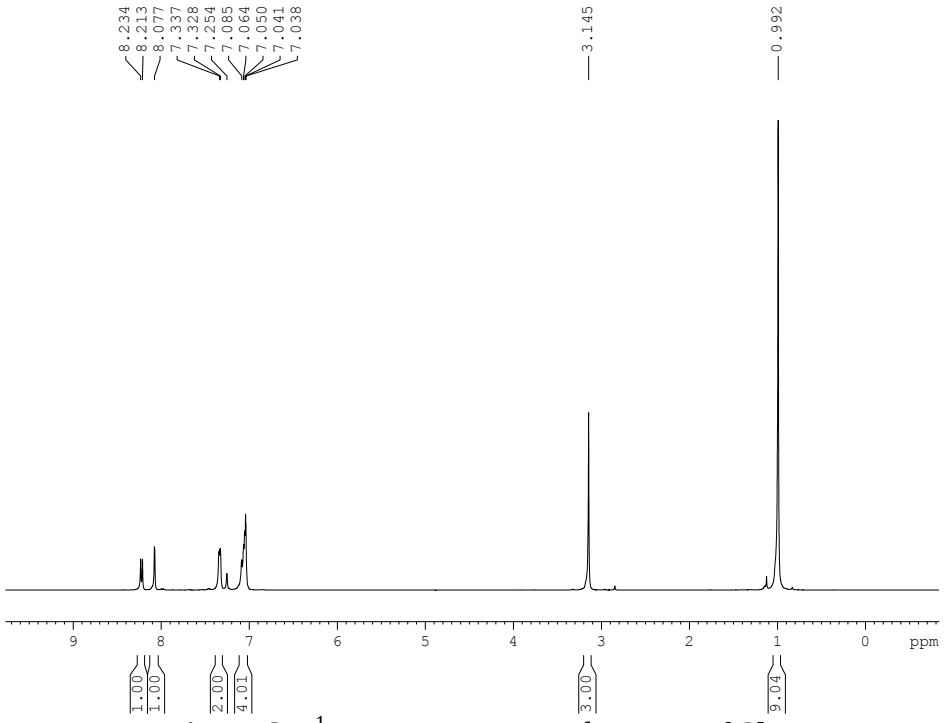


Figure S5. ^{1}H NMR spectrum of compound **3b**

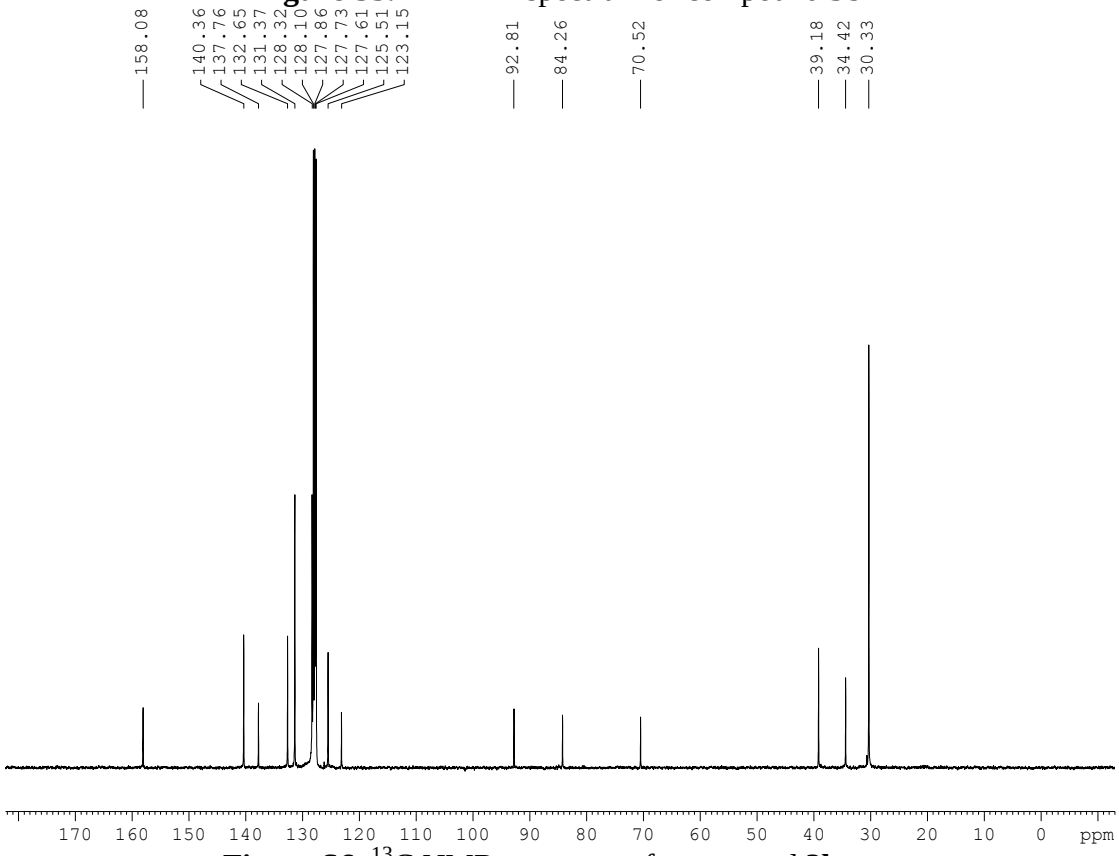


Figure S6. ^{13}C NMR spectrum of compound **3b**

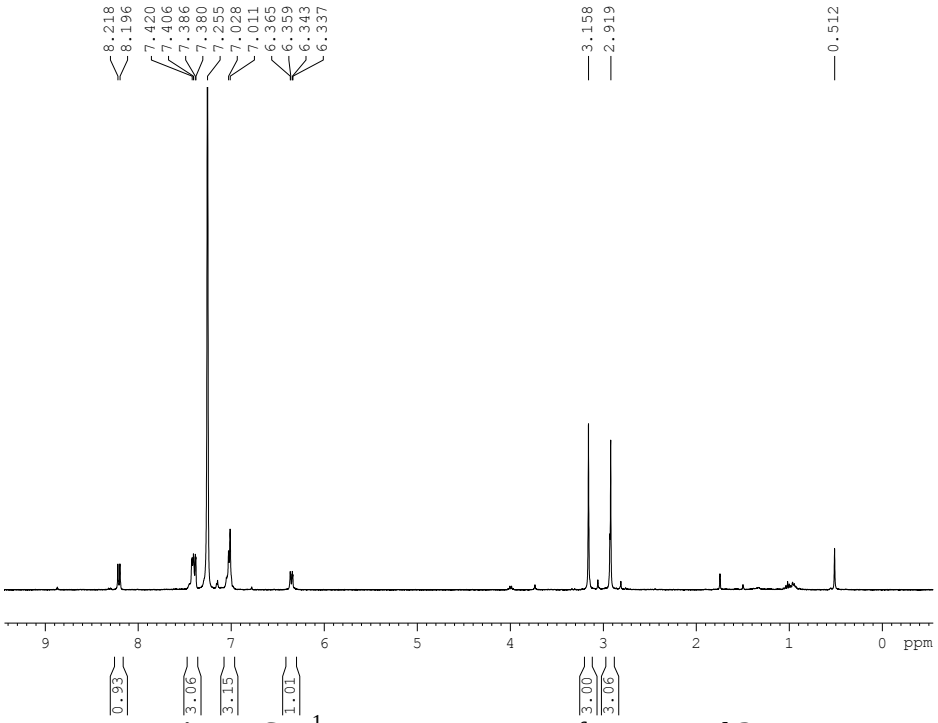


Figure S7. ^{1}H NMR spectrum of compound **3c**

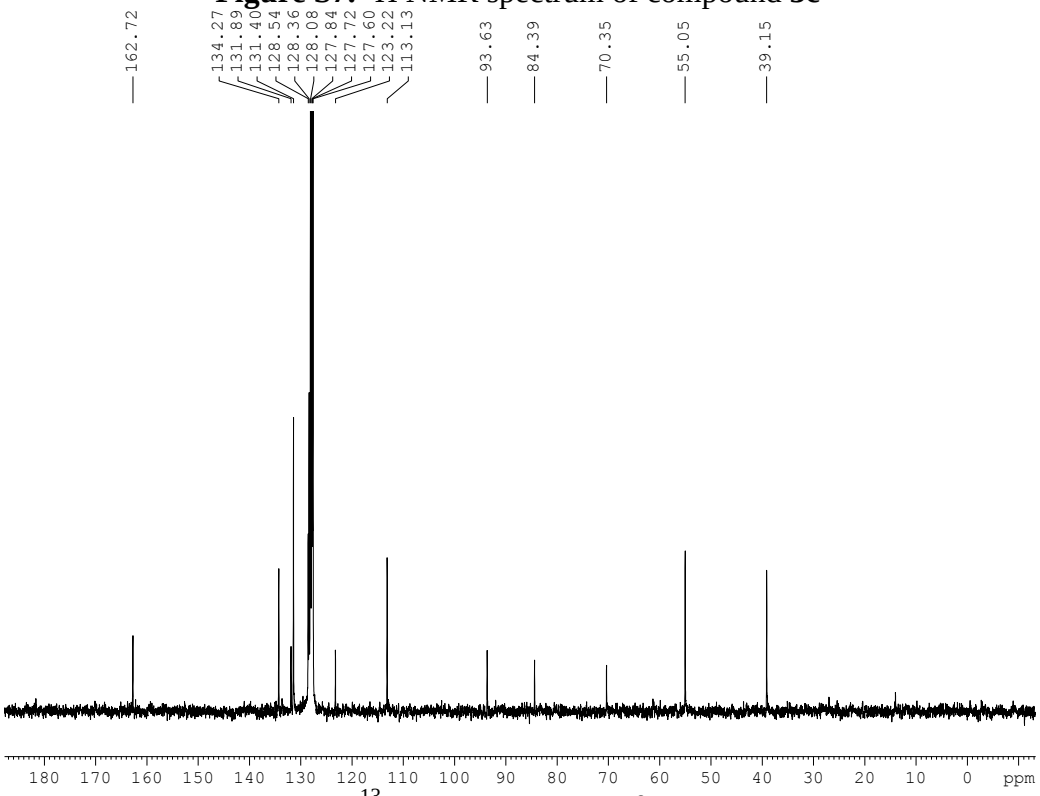


Figure S8. ^{13}C NMR spectrum of compound **3c**

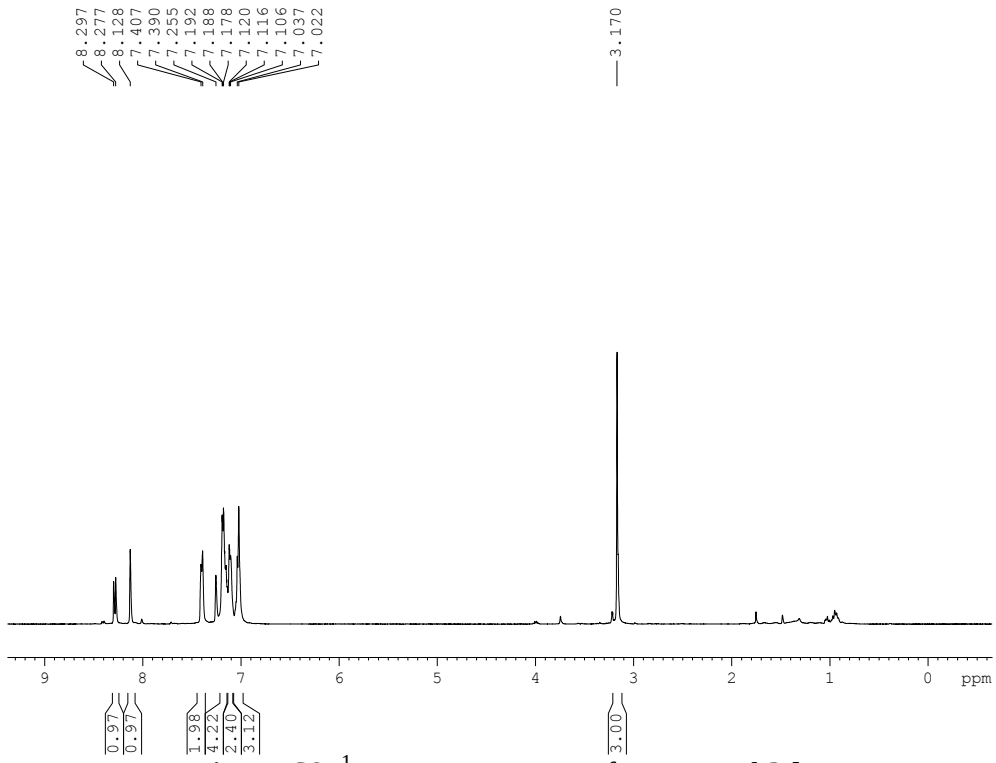


Figure S9. ^{1}H NMR spectrum of compound **3d**

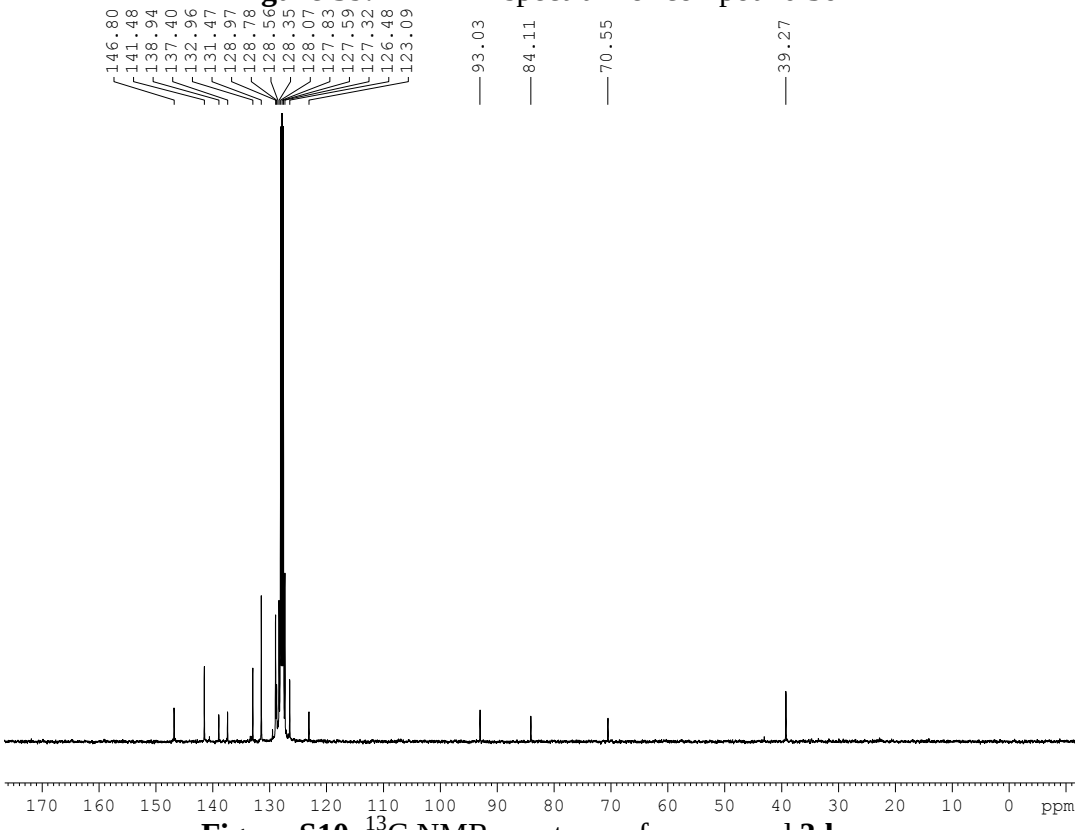


Figure S10. ^{13}C NMR spectrum of compound **3d**

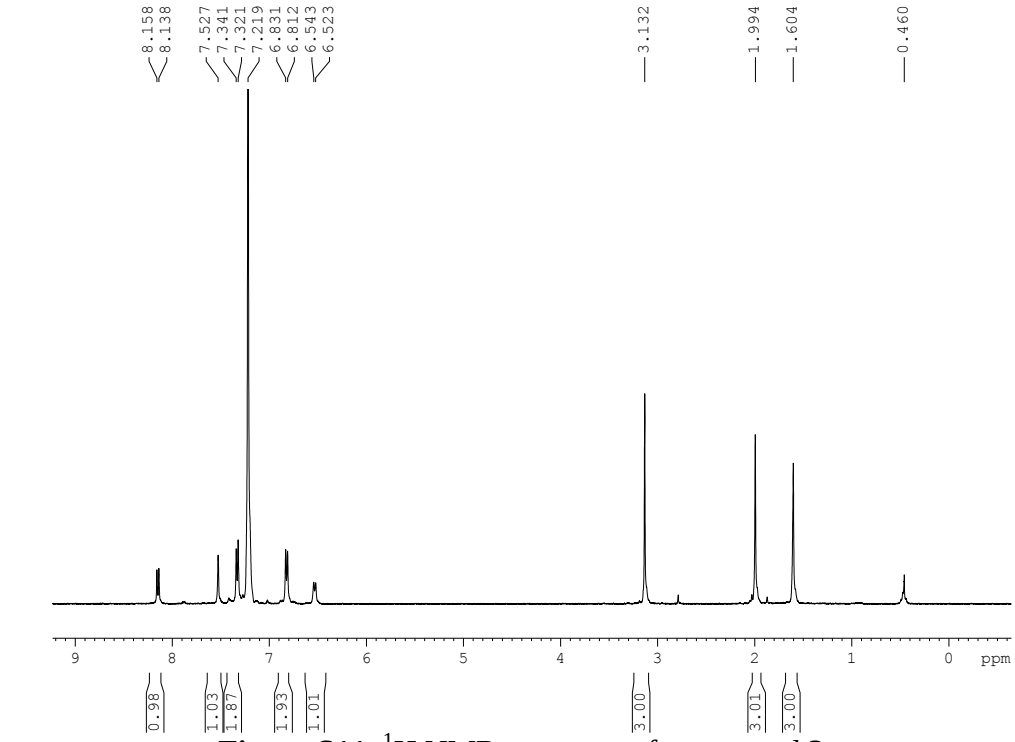


Figure S11. ^{1}H NMR spectrum of compound **3e**

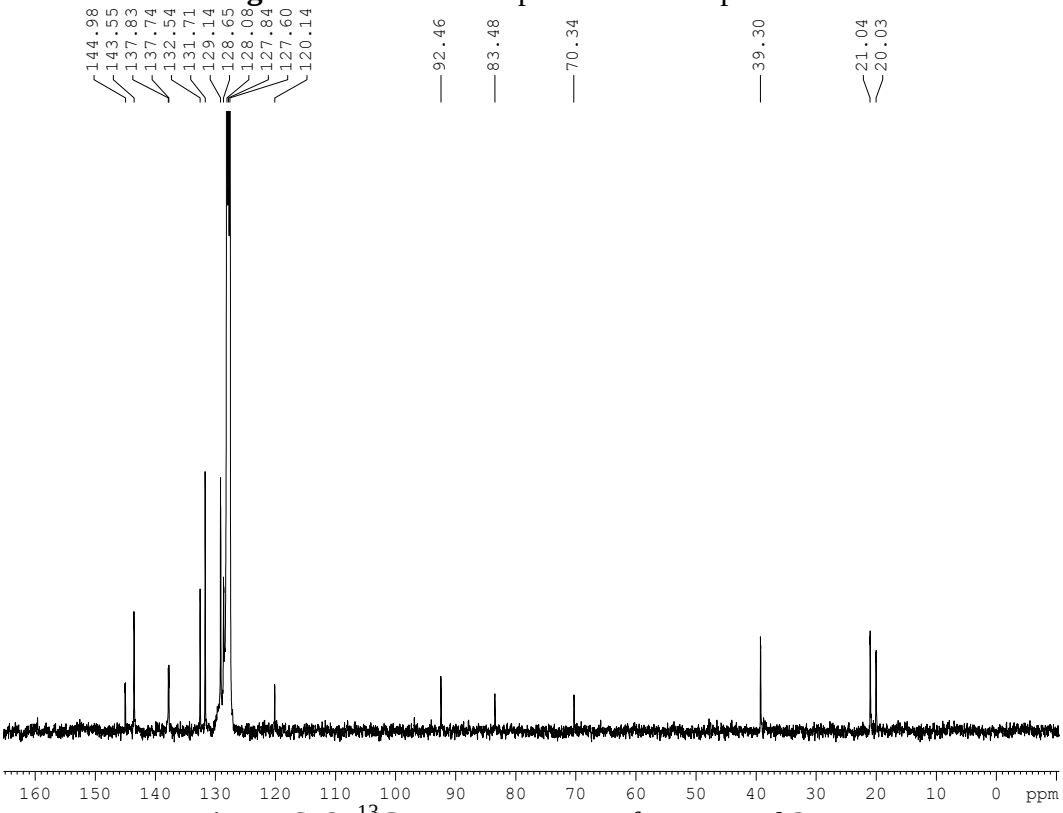


Figure S12. ^{13}C NMR spectrum of compound **3e**

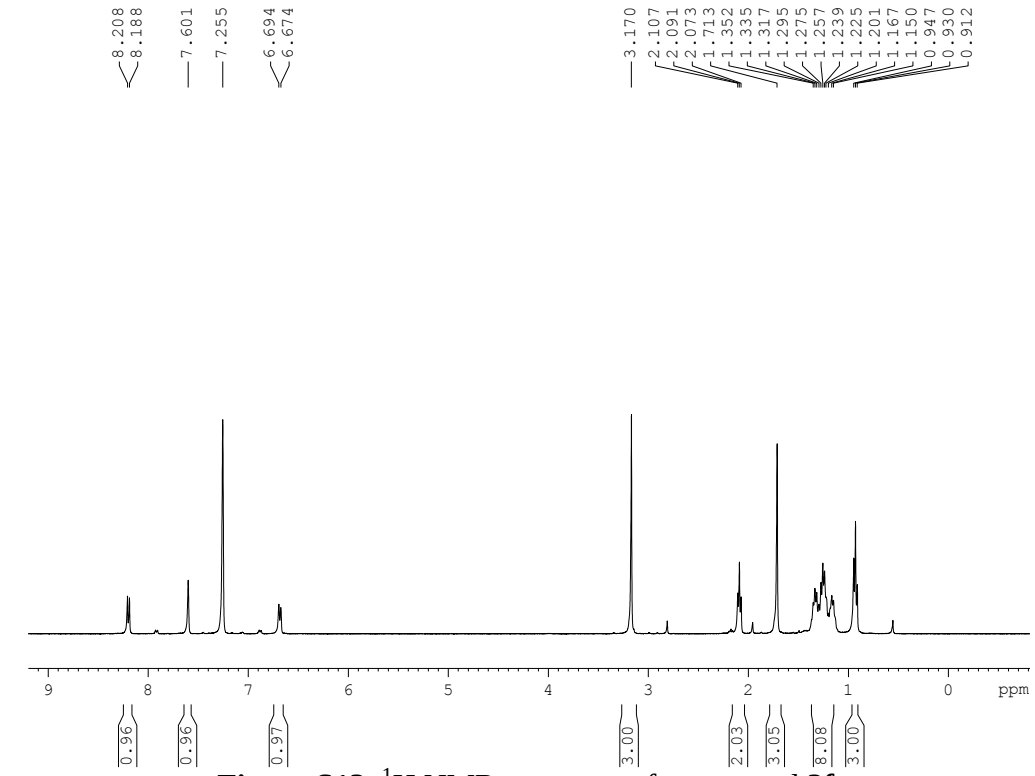


Figure S13. ^{1}H NMR spectrum of compound **3f**

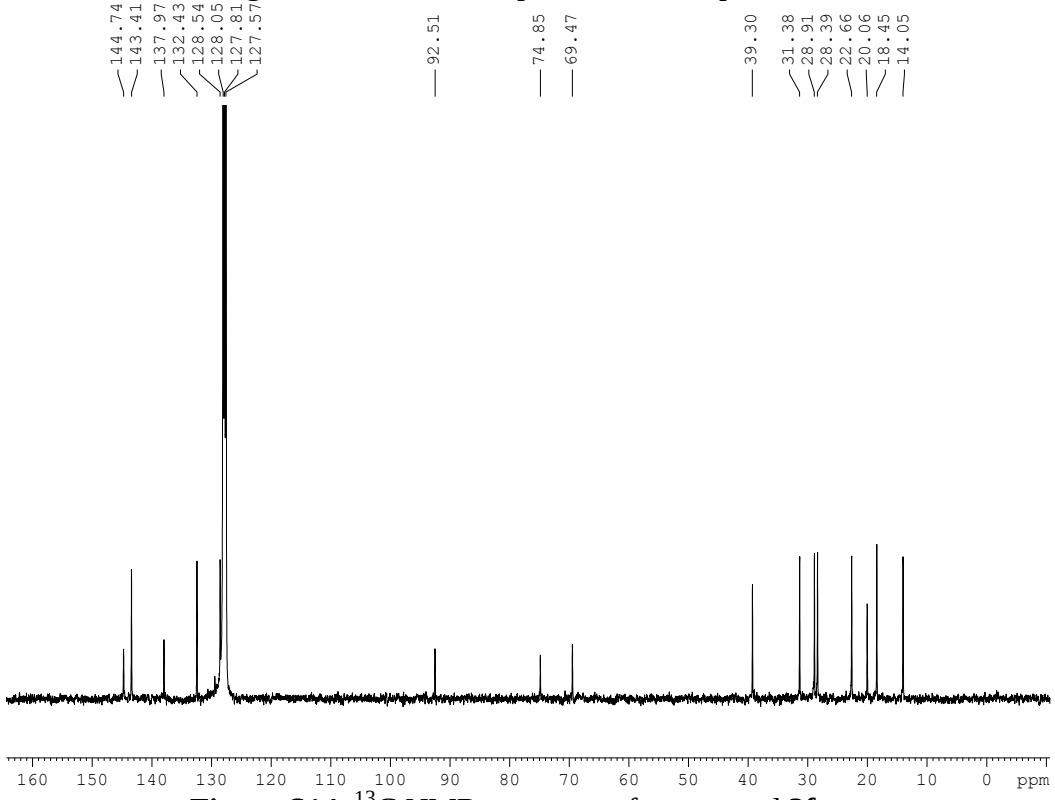


Figure S14. ^{13}C NMR spectrum of compound **3f**

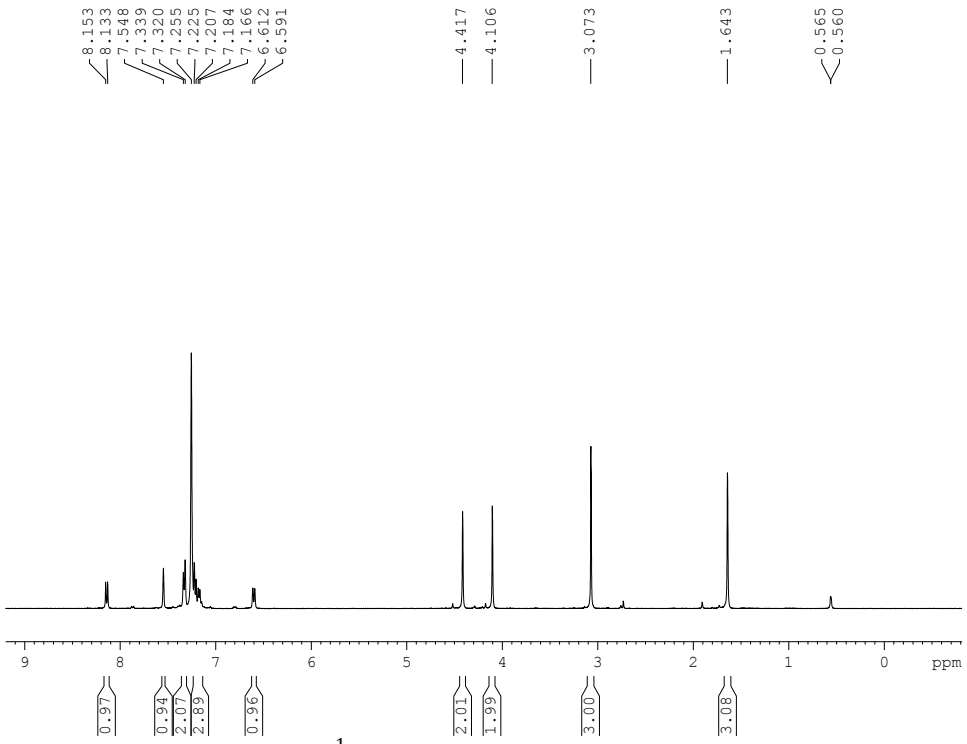


Figure S15. ^{1}H NMR spectrum of compound **3g**

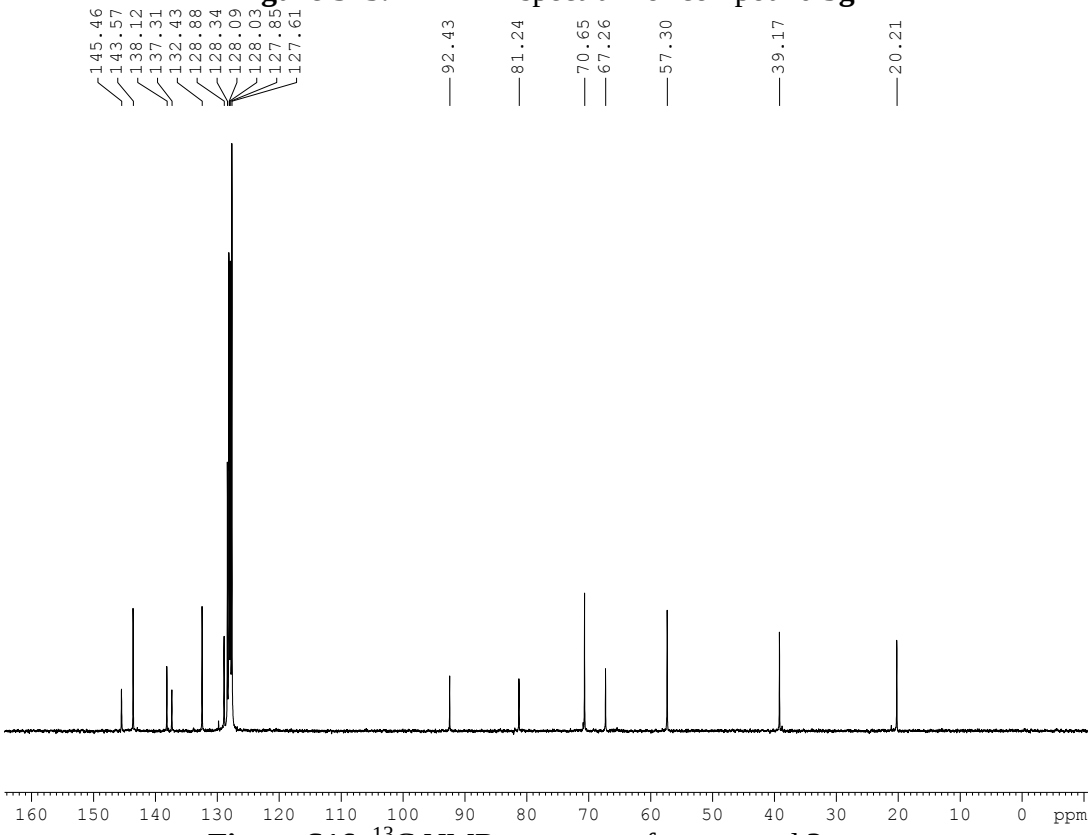


Figure S16. ^{13}C NMR spectrum of compound **3g**

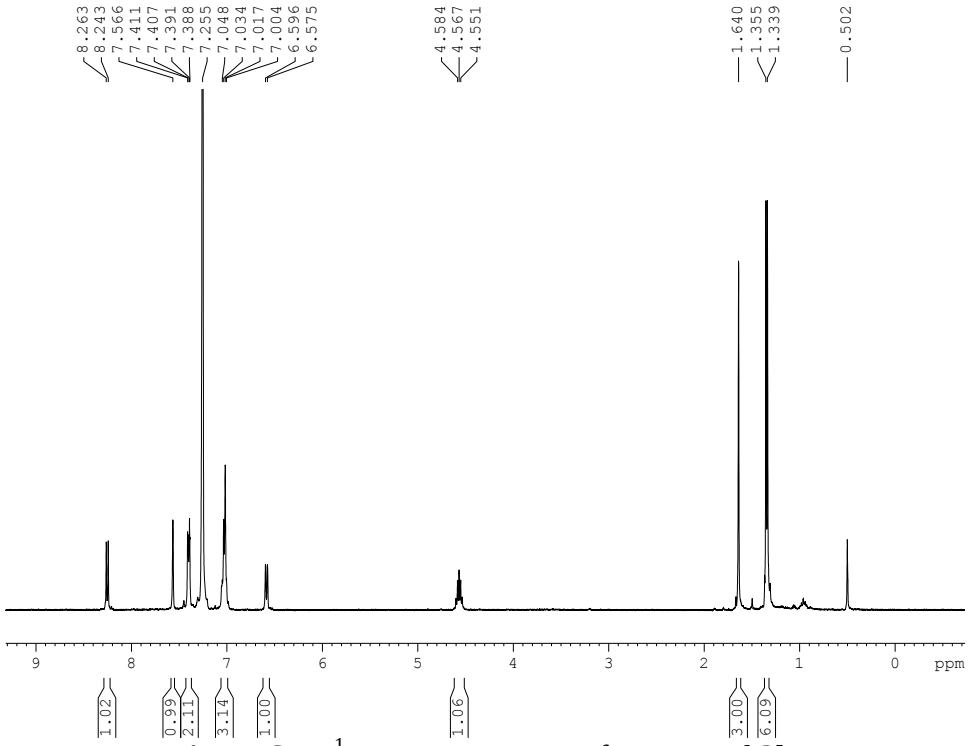


Figure S17. ^{1}H NMR spectrum of compound **3h**

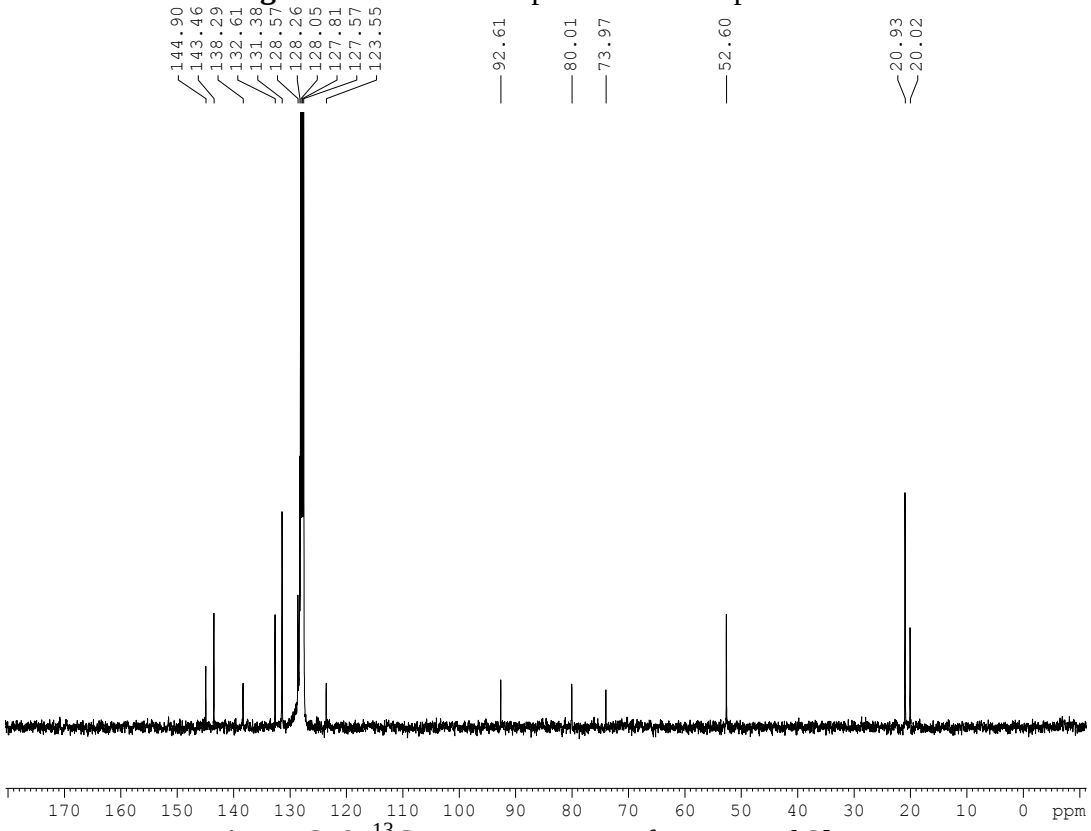


Figure S18. ^{13}C NMR spectrum of compound **3h**

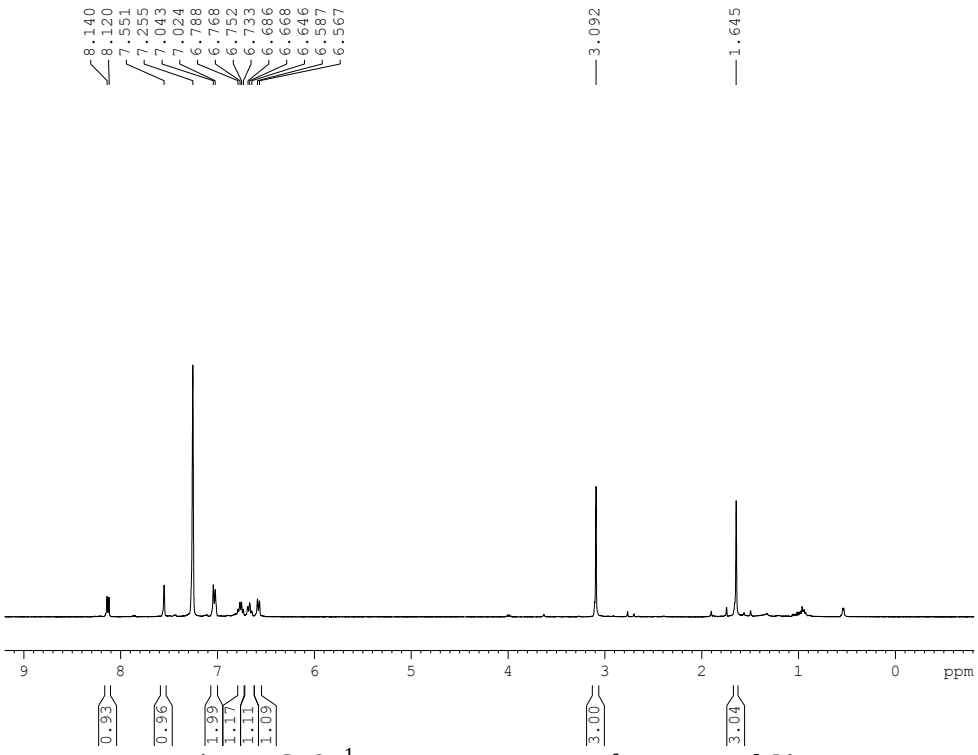


Figure S19. ^{1}H NMR spectrum of compound **3i**

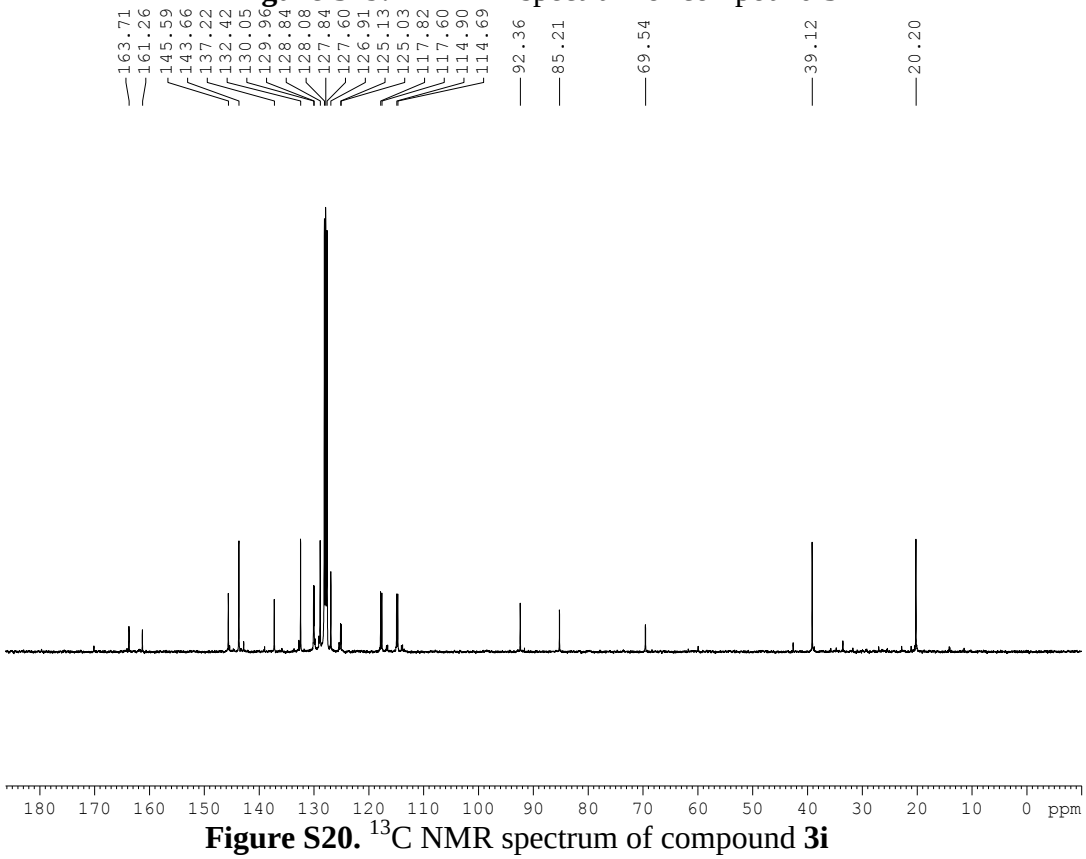


Figure S20. ^{13}C NMR spectrum of compound **3i**

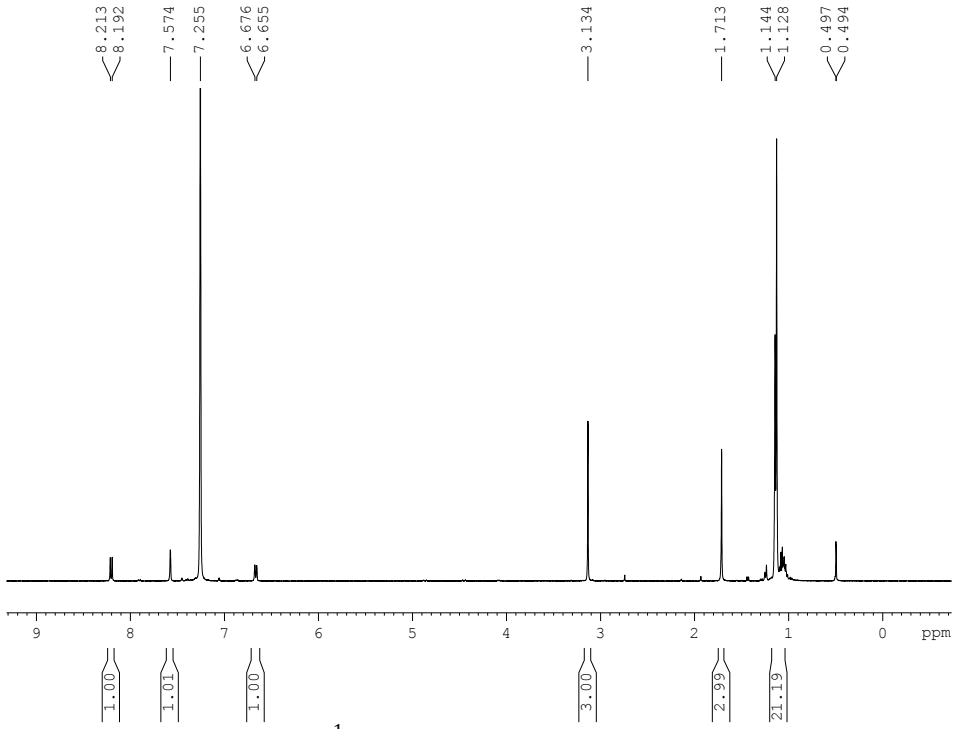


Figure S21. ^{1}H NMR spectrum of compound **3j**

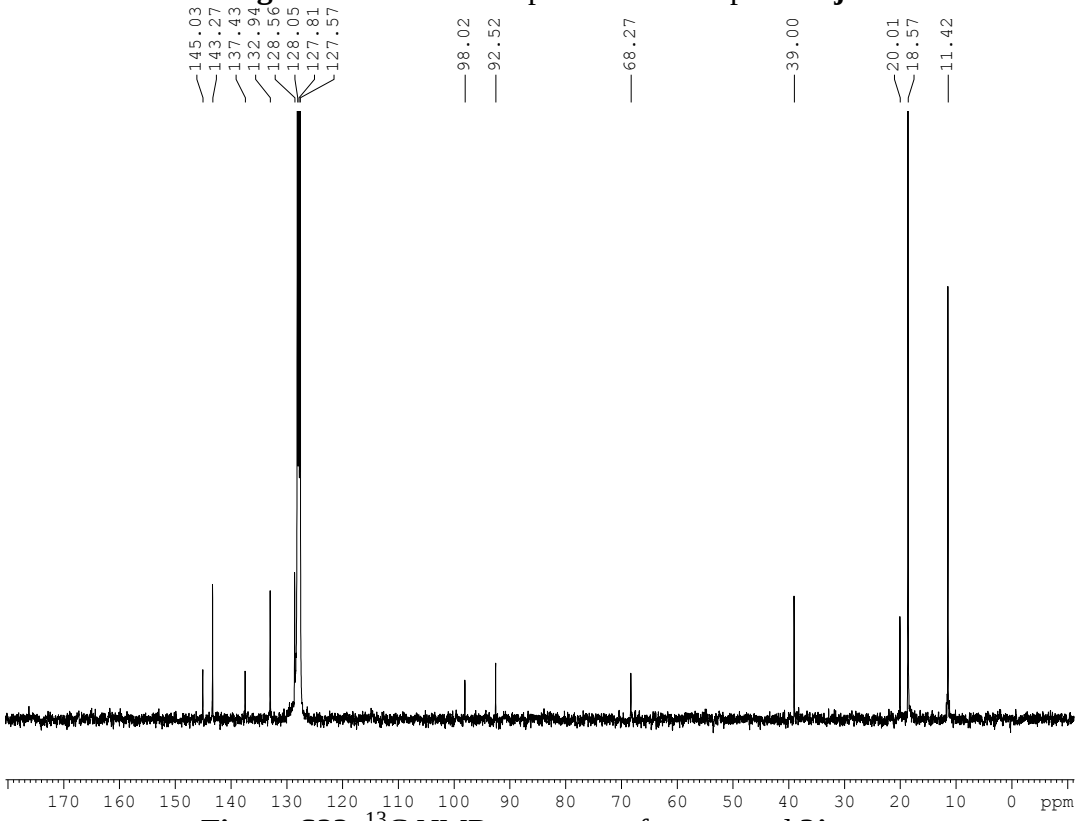


Figure S22. ^{13}C NMR spectrum of compound **3j**

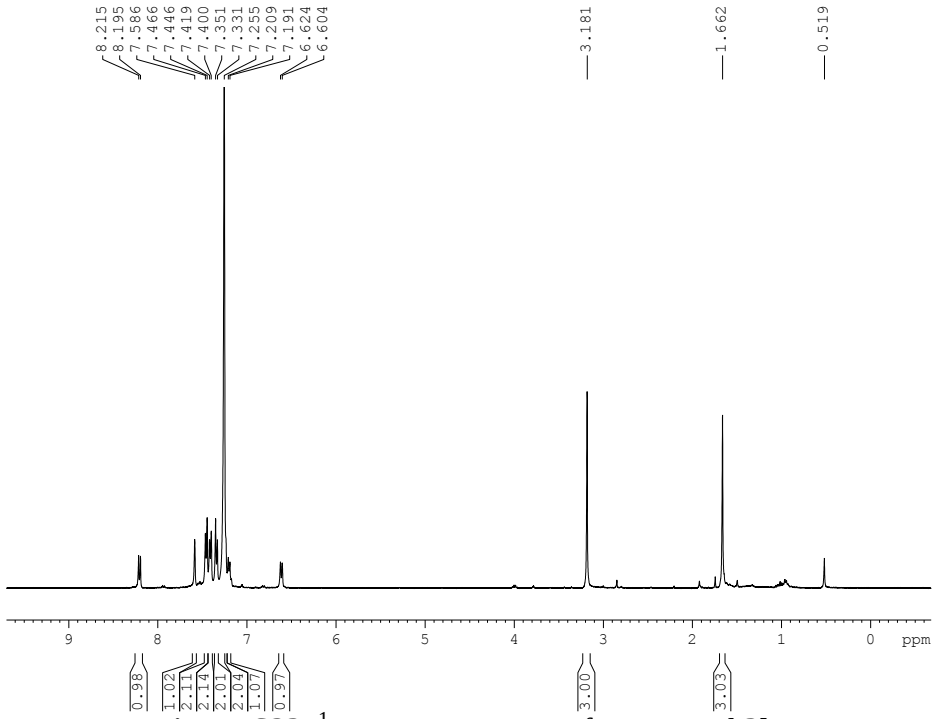


Figure S23. ^{1}H NMR spectrum of compound **3k**

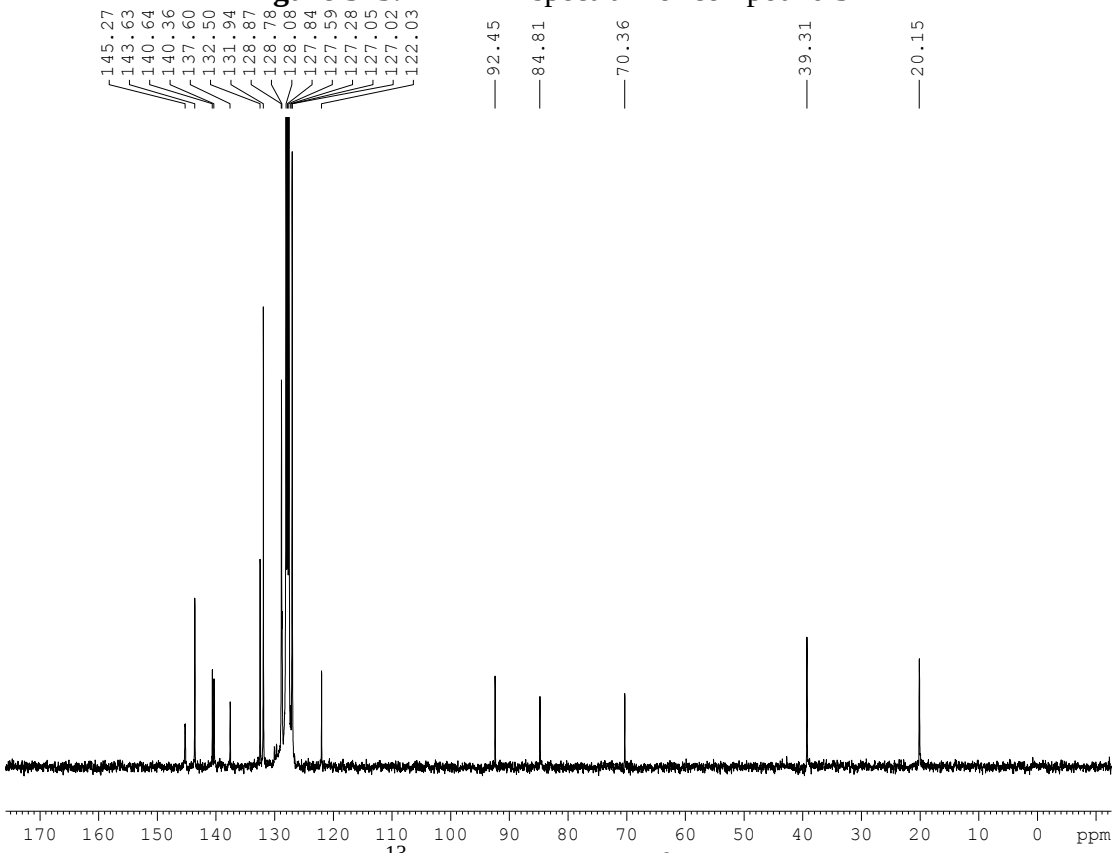


Figure S24. ^{13}C NMR spectrum of compound **3k**

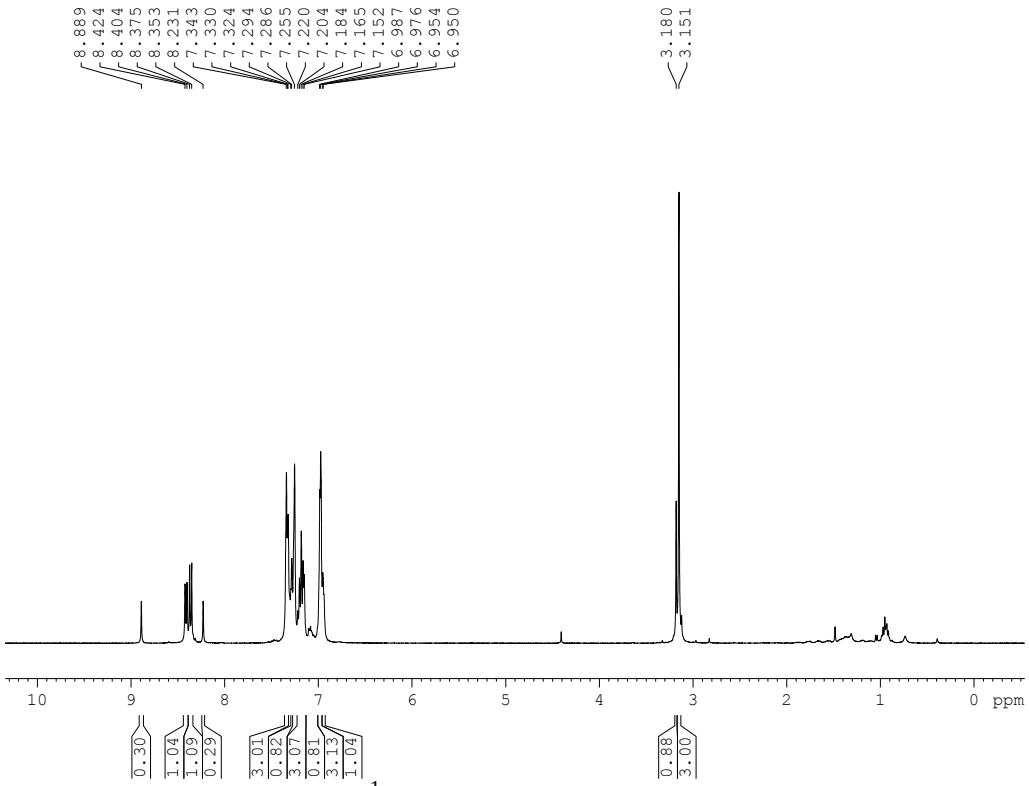


Figure S25. ^{1}H NMR spectrum of compound **3l**

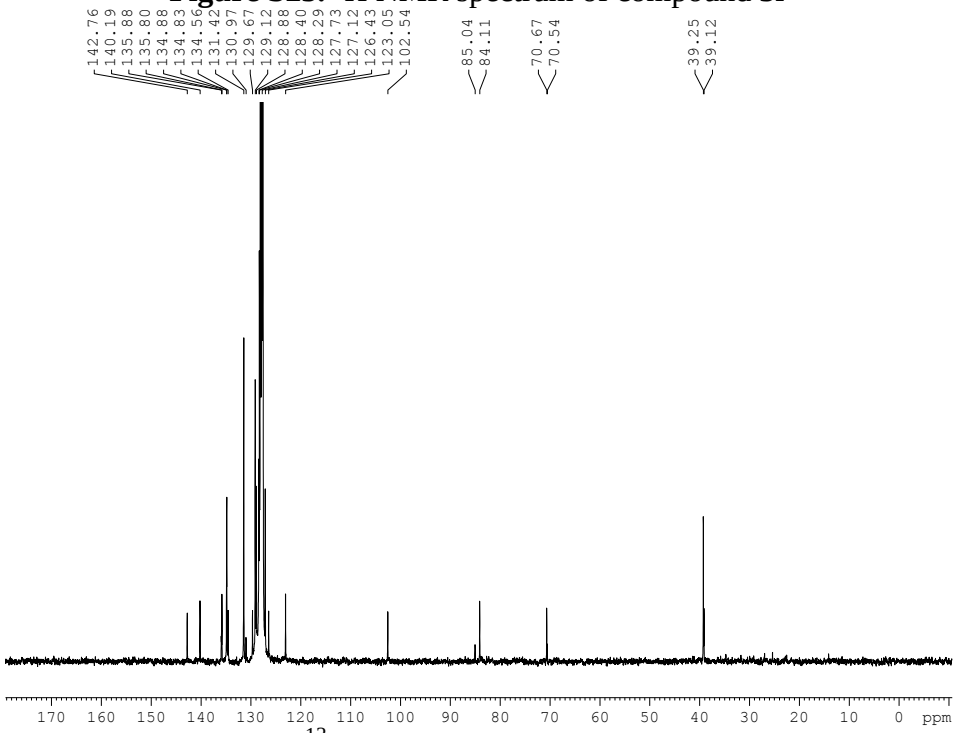


Figure S26. ^{13}C NMR spectrum of compound **3l**

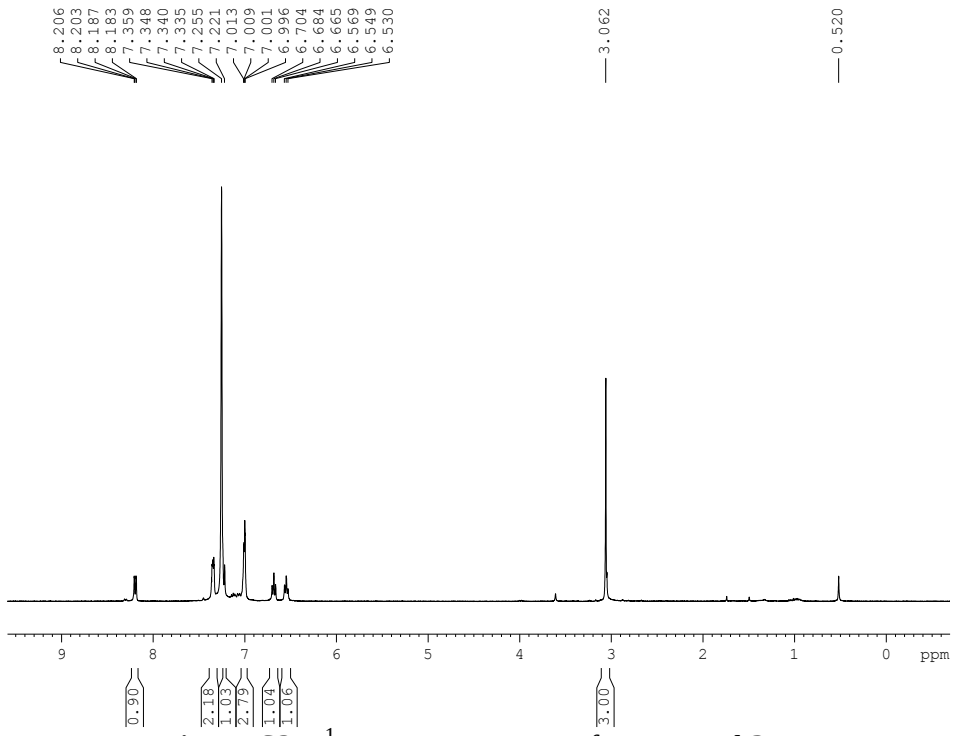


Figure S27. ^{1}H NMR spectrum of compound **3m**

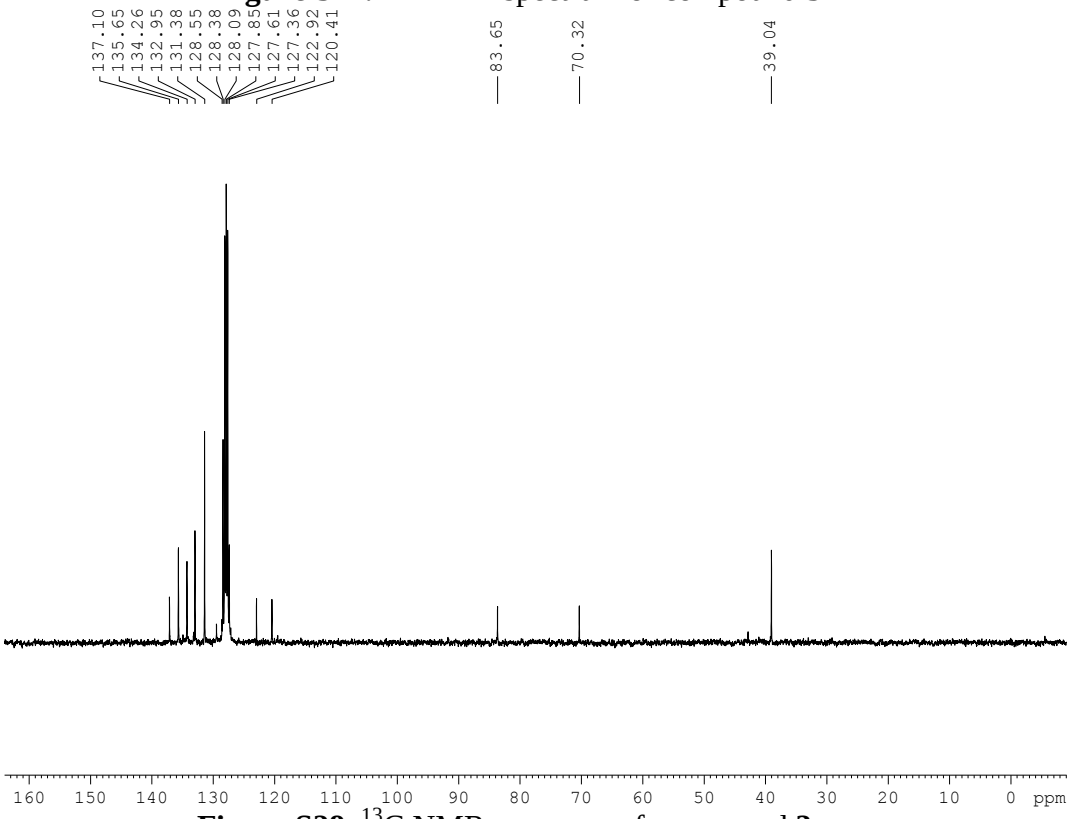


Figure S28. ^{13}C NMR spectrum of compound **3m**

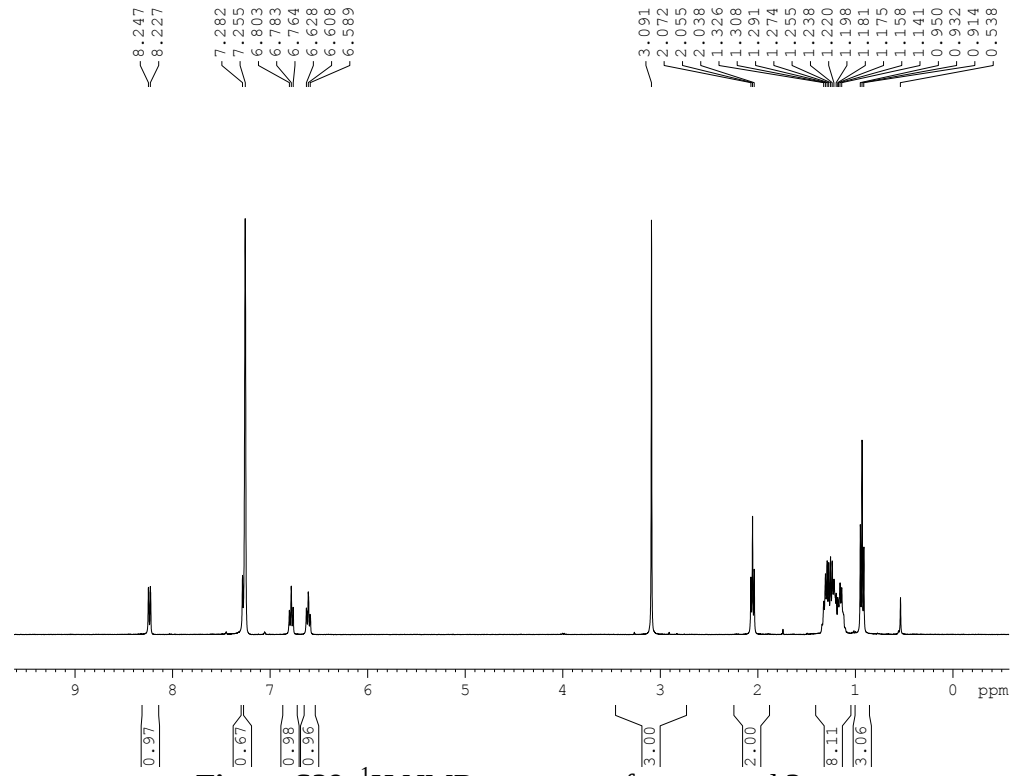


Figure S29. ^{1}H NMR spectrum of compound **3n**

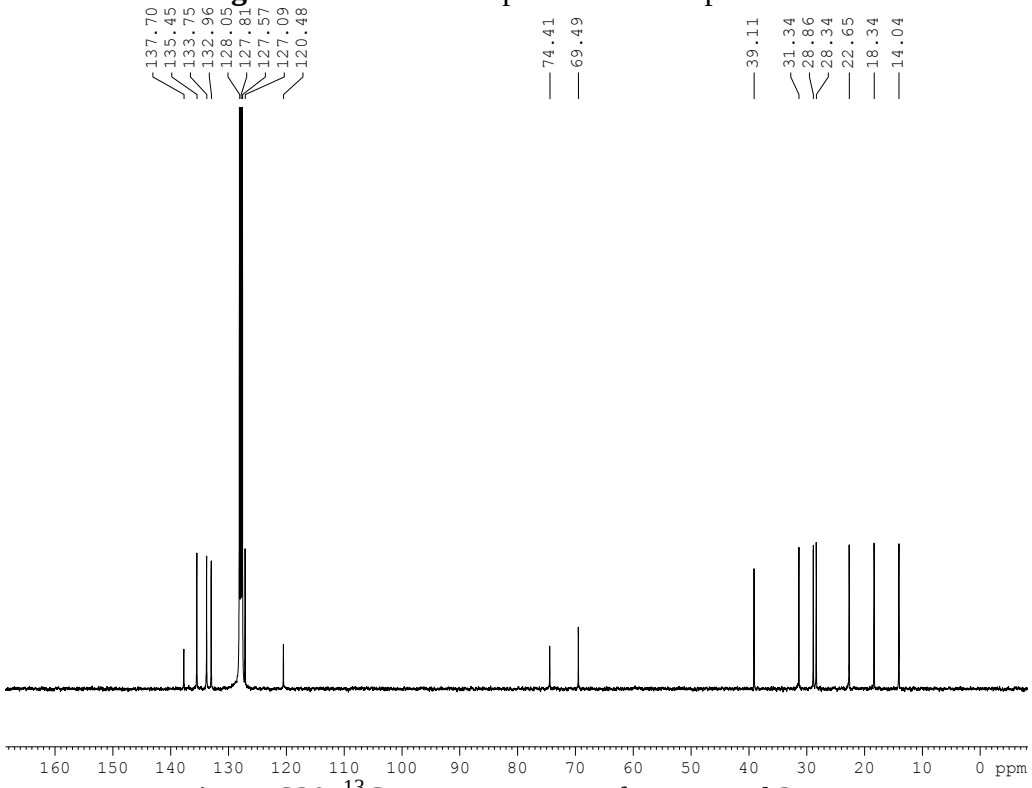


Figure S30. ^{13}C NMR spectrum of compound **3n**

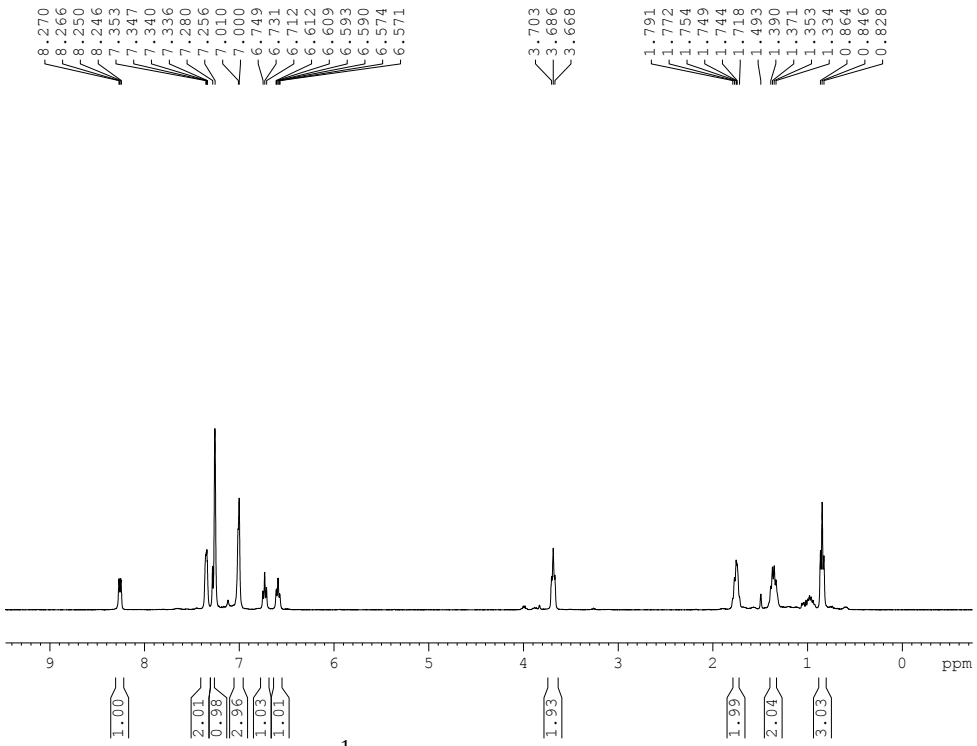


Figure S31. ^{1}H NMR spectrum of compound **3o**

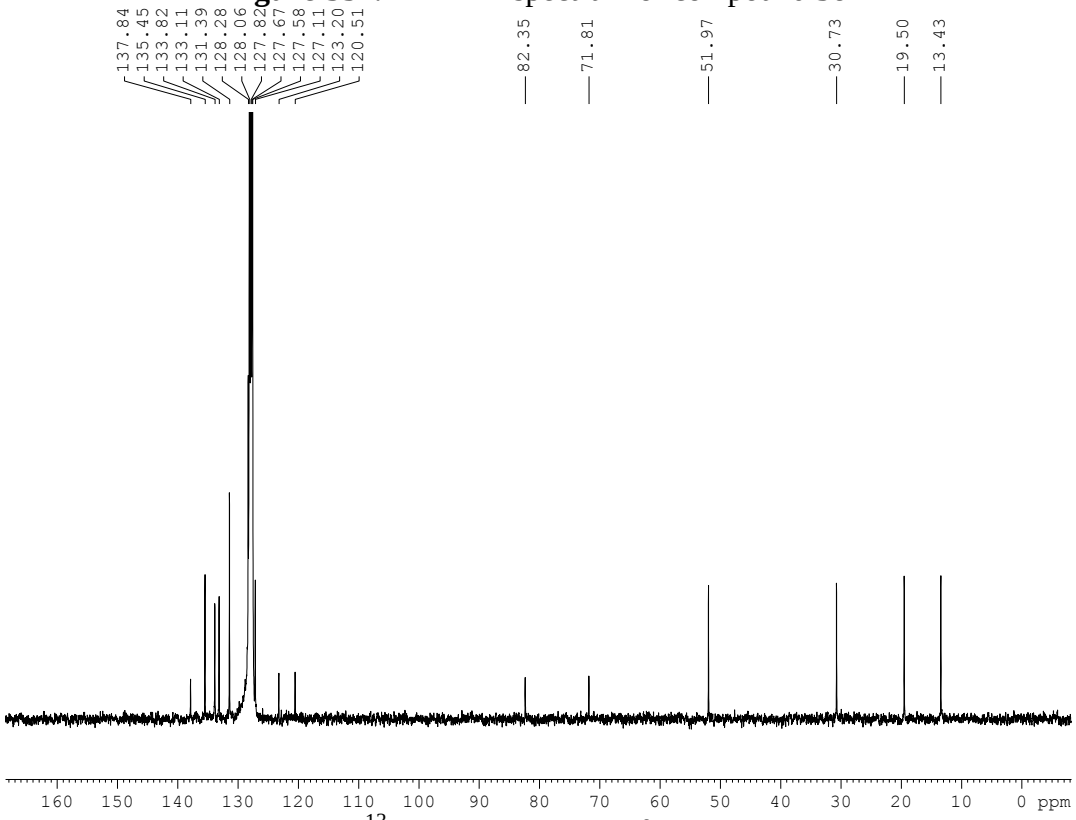


Figure S32. ^{13}C NMR spectrum of compound **3o**

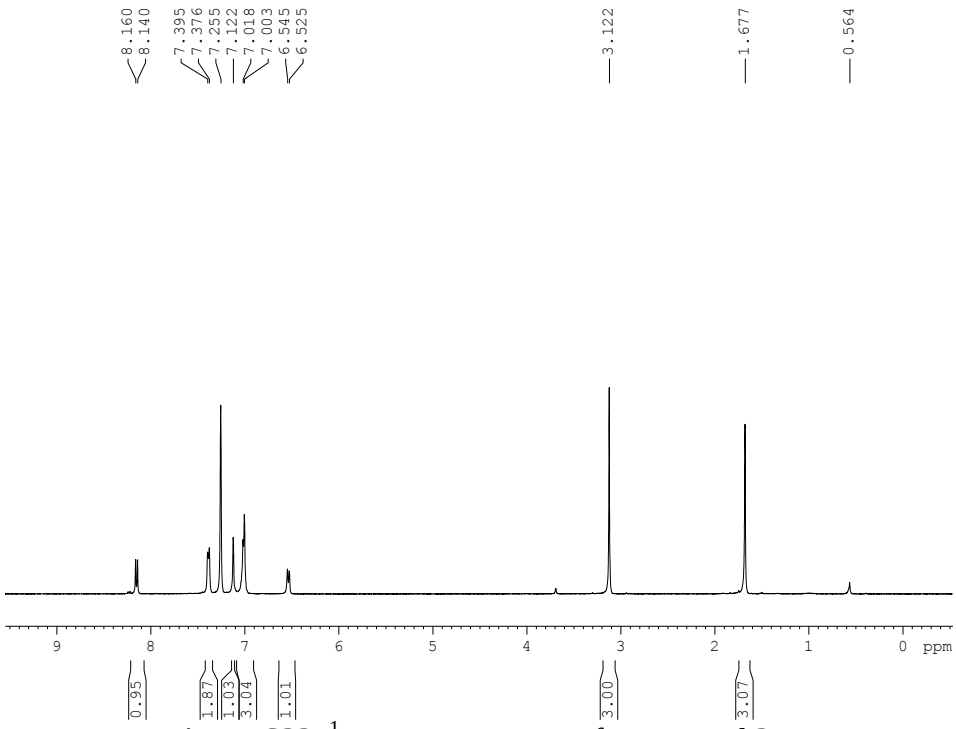


Figure S33. ^{1}H NMR spectrum of compound **3p**

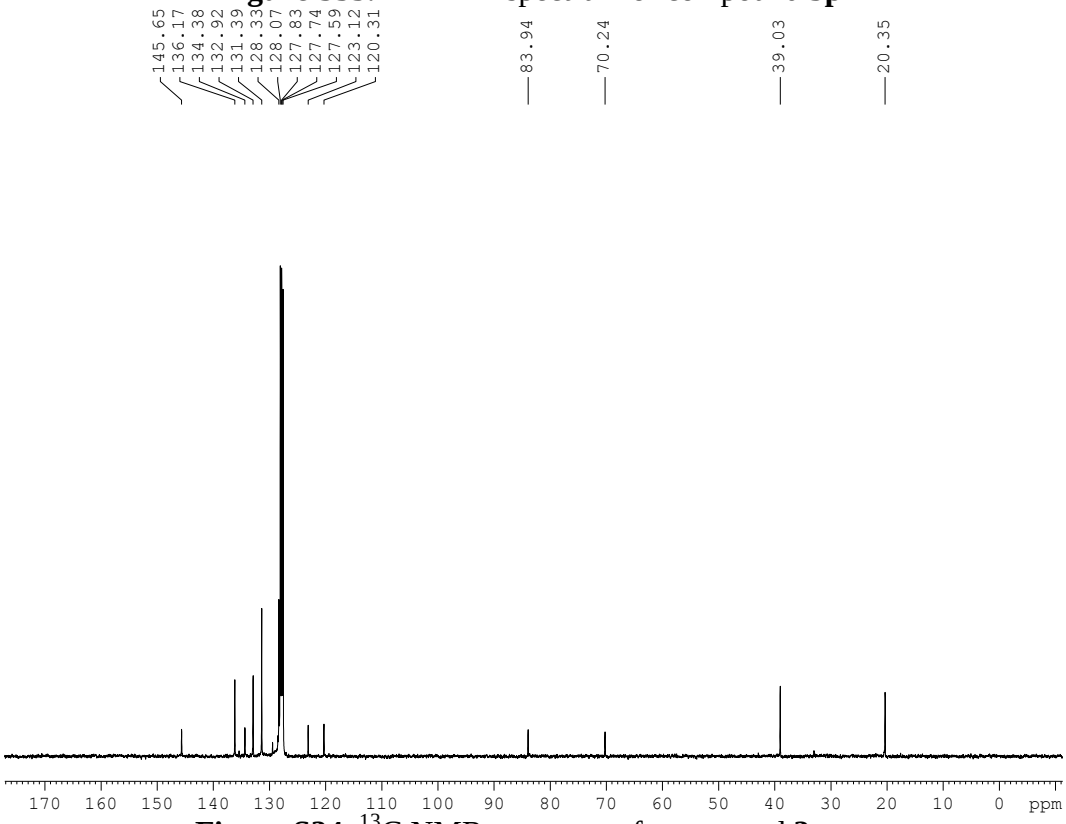


Figure S34. ^{13}C NMR spectrum of compound **3p**

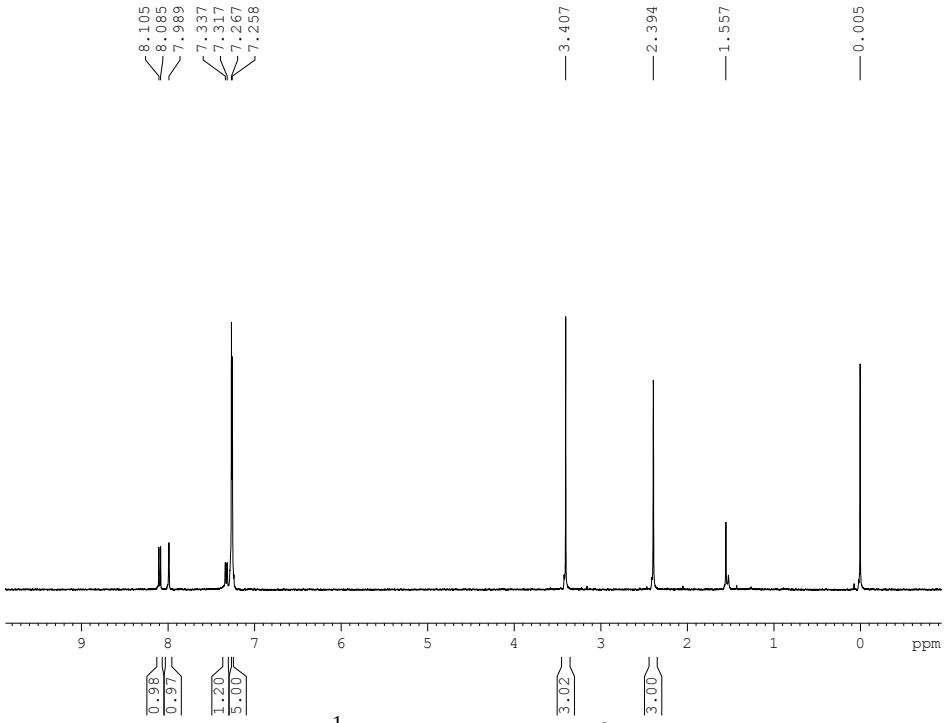


Figure S35. ^{1}H NMR spectrum of compound **4**

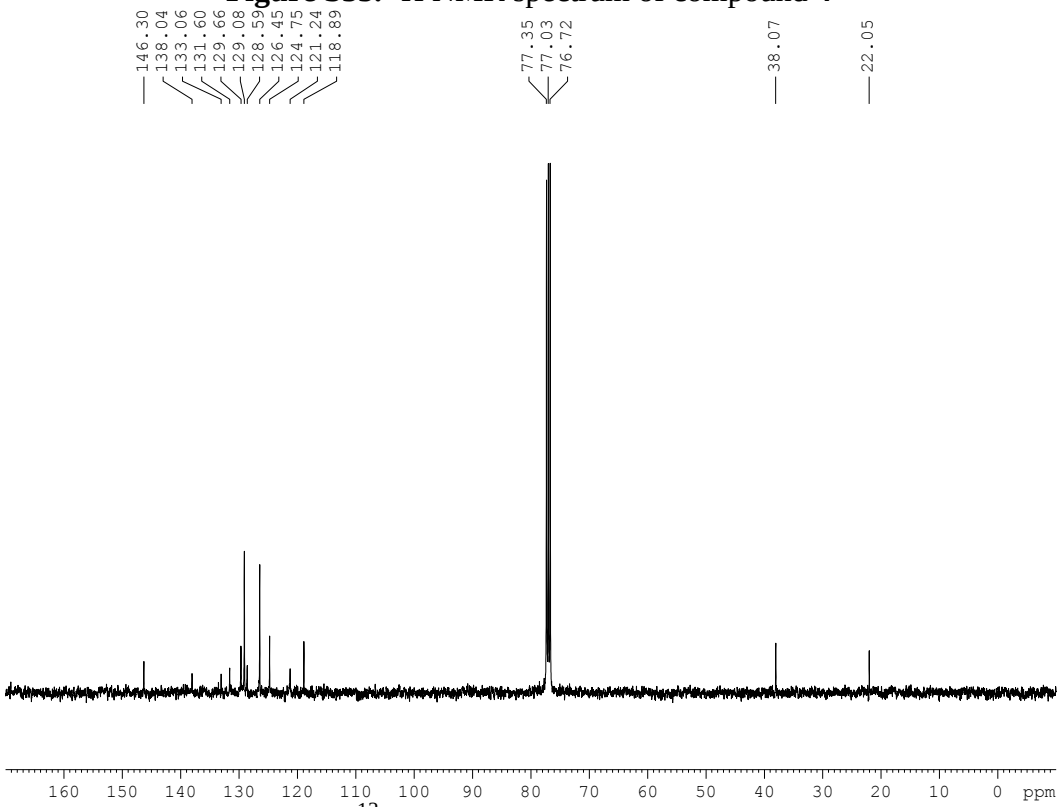


Figure S36. ^{13}C NMR spectrum of compound **4**

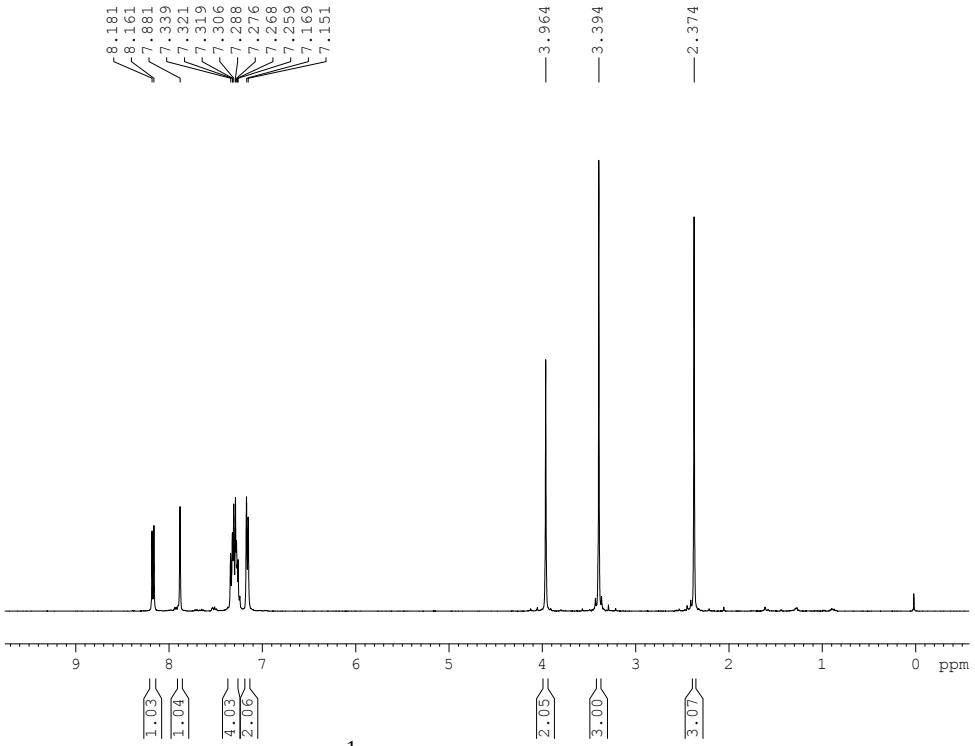


Figure S37. ^{1}H NMR spectrum of compound **5**

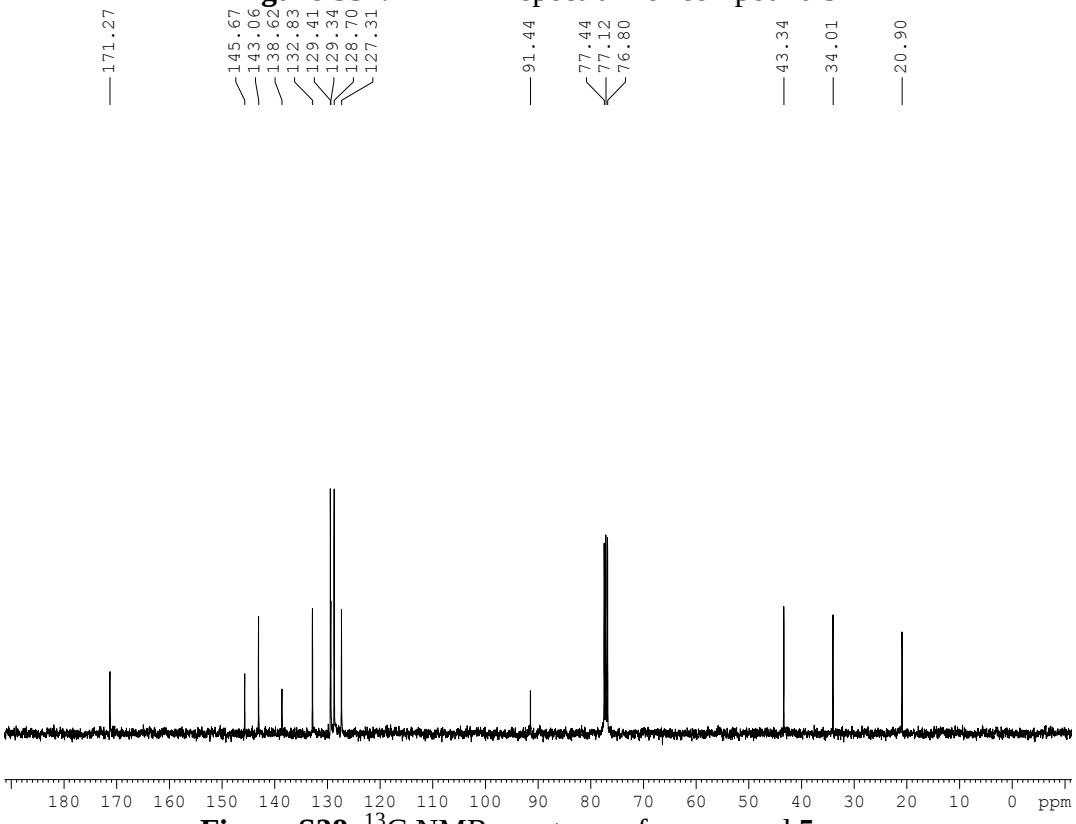


Figure S38. ^{13}C NMR spectrum of compound **5**

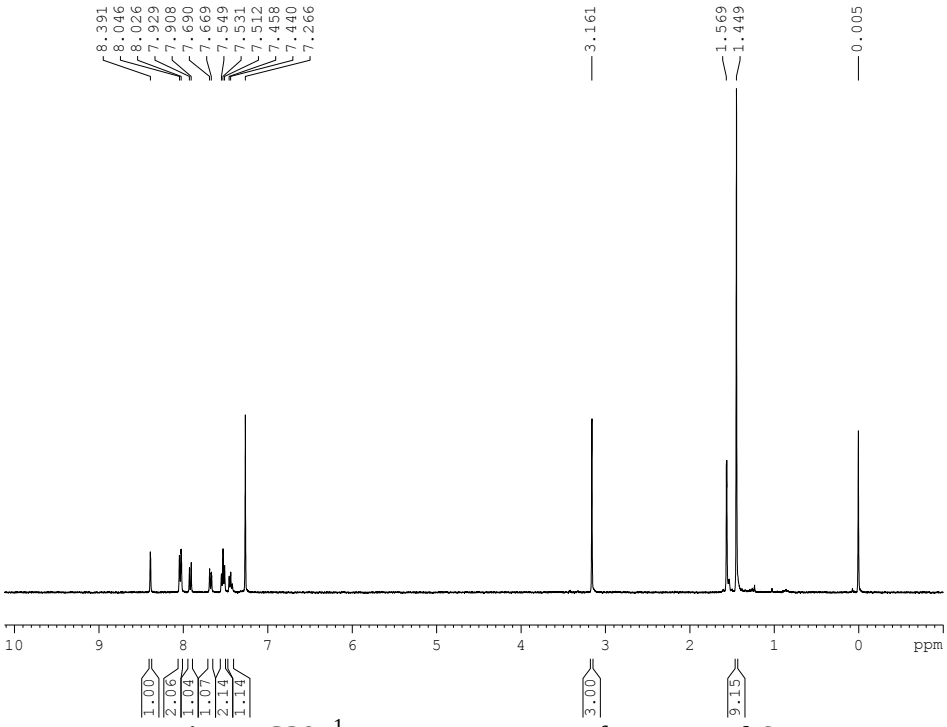


Figure S39. ^{1}H NMR spectrum of compound **6**

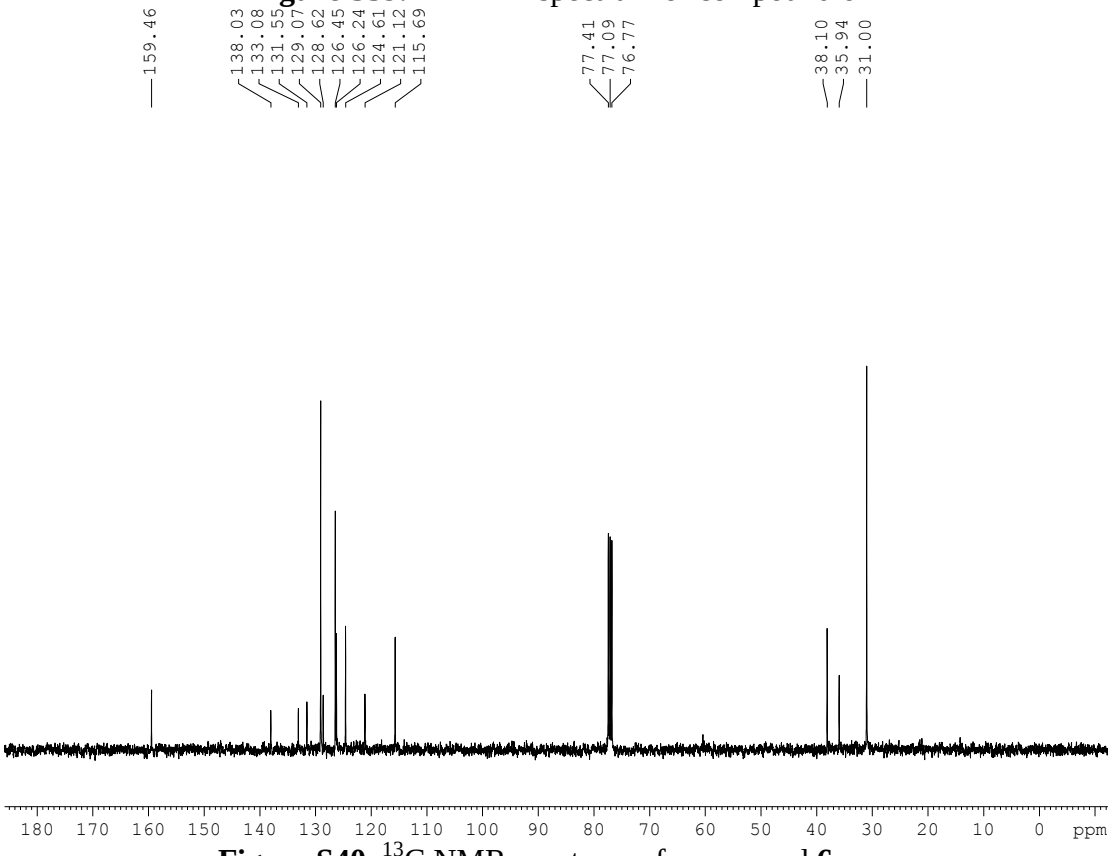


Figure S40. ^{13}C NMR spectrum of compound **6**

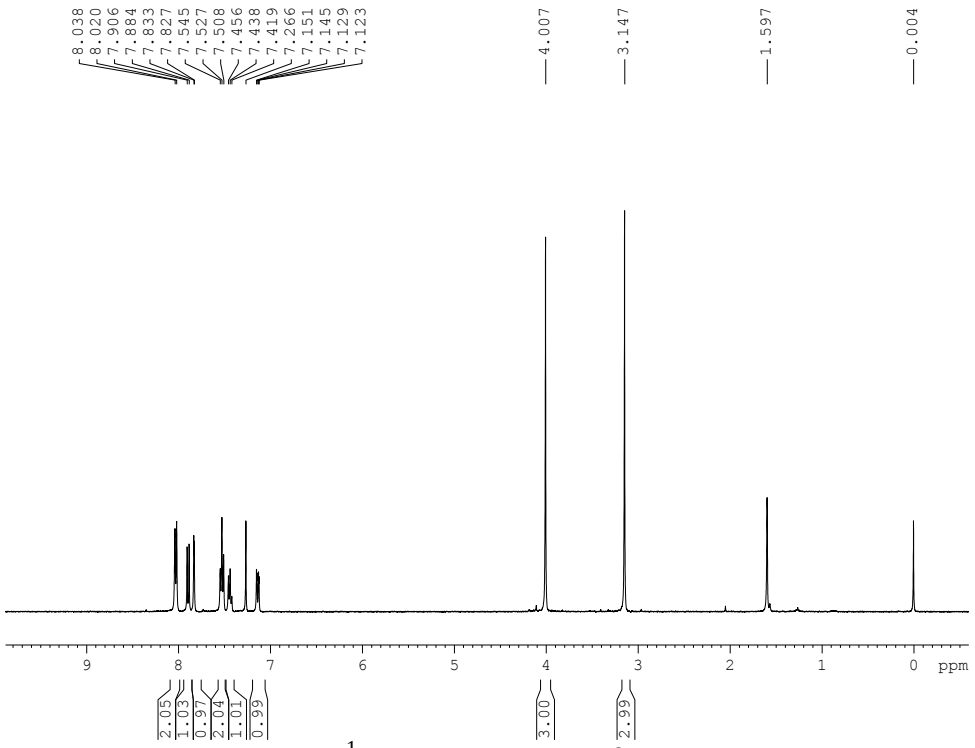


Figure S41. ^{1}H NMR spectrum of compound **7**

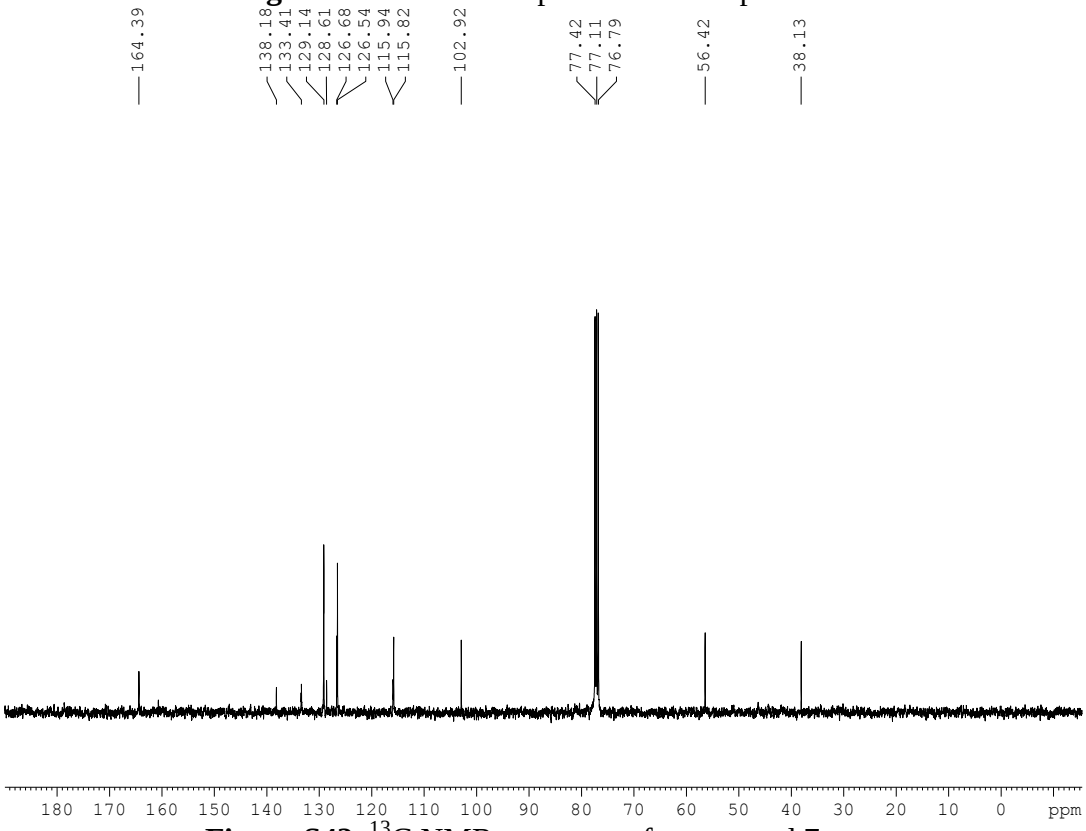


Figure S42. ^{13}C NMR spectrum of compound **7**

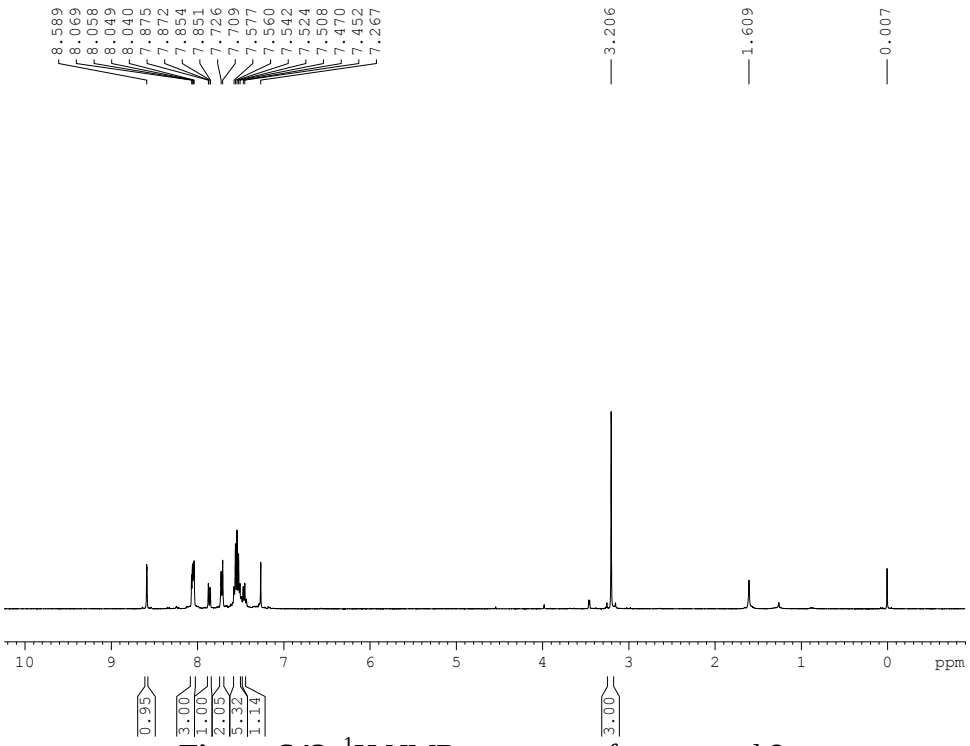


Figure S43. ^{1}H NMR spectrum of compound **8**

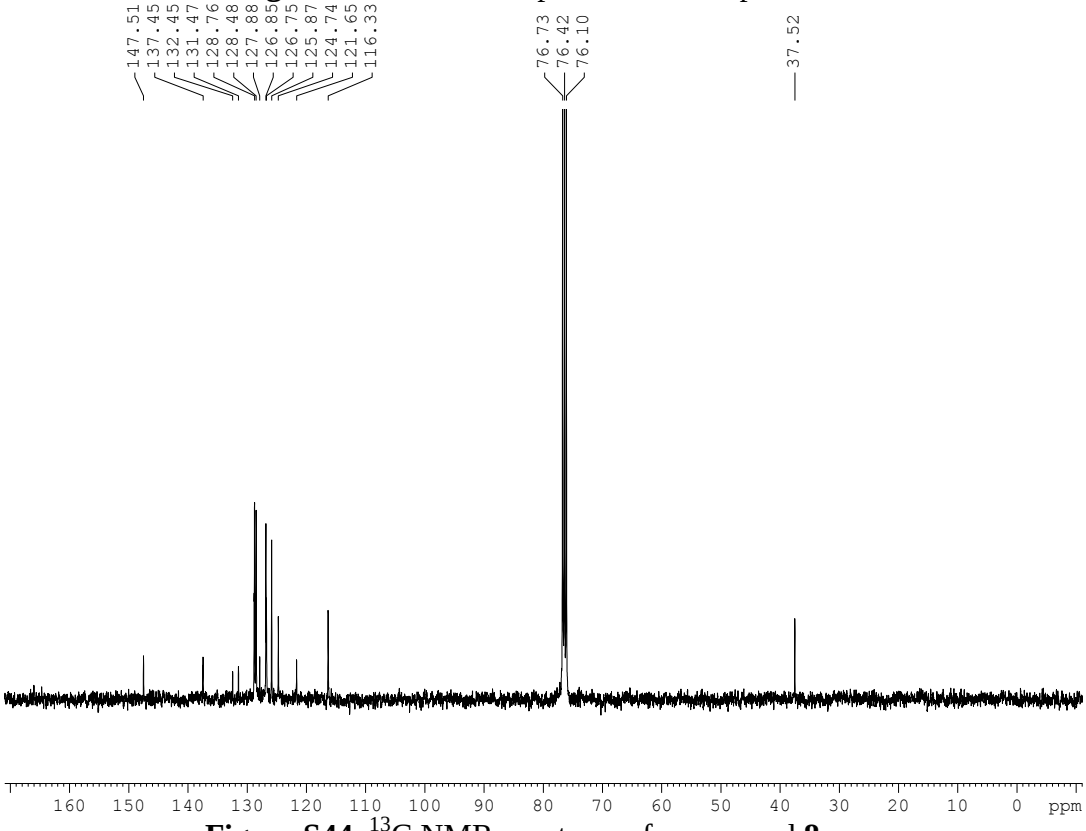


Figure S44. ^{13}C NMR spectrum of compound **8**

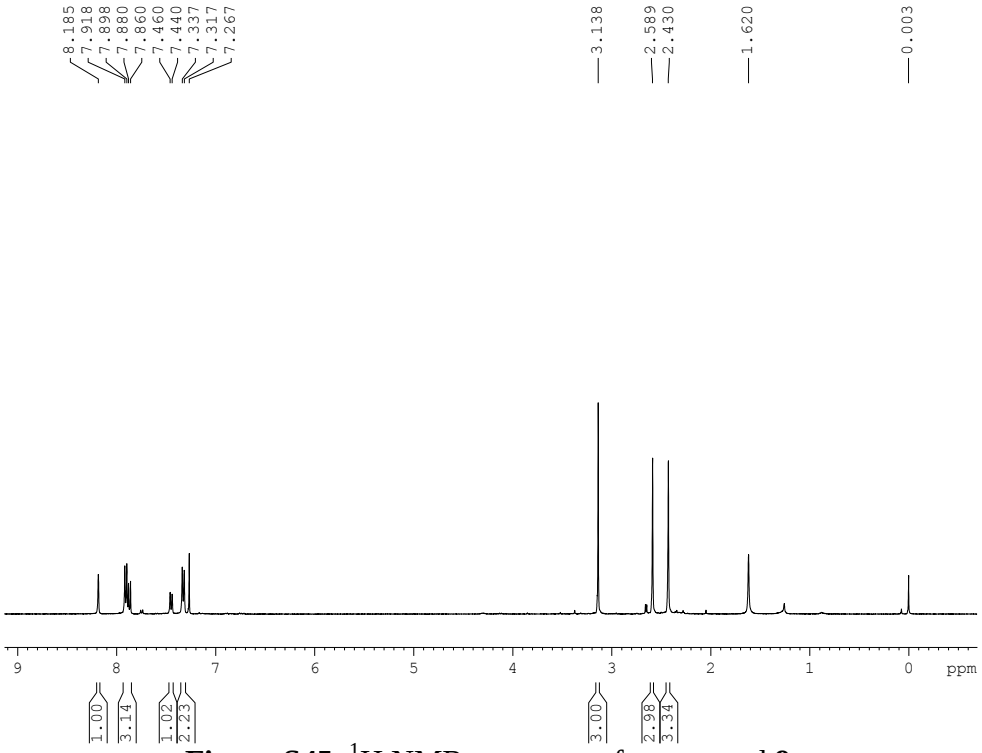


Figure S45. ^{1}H NMR spectrum of compound **9**

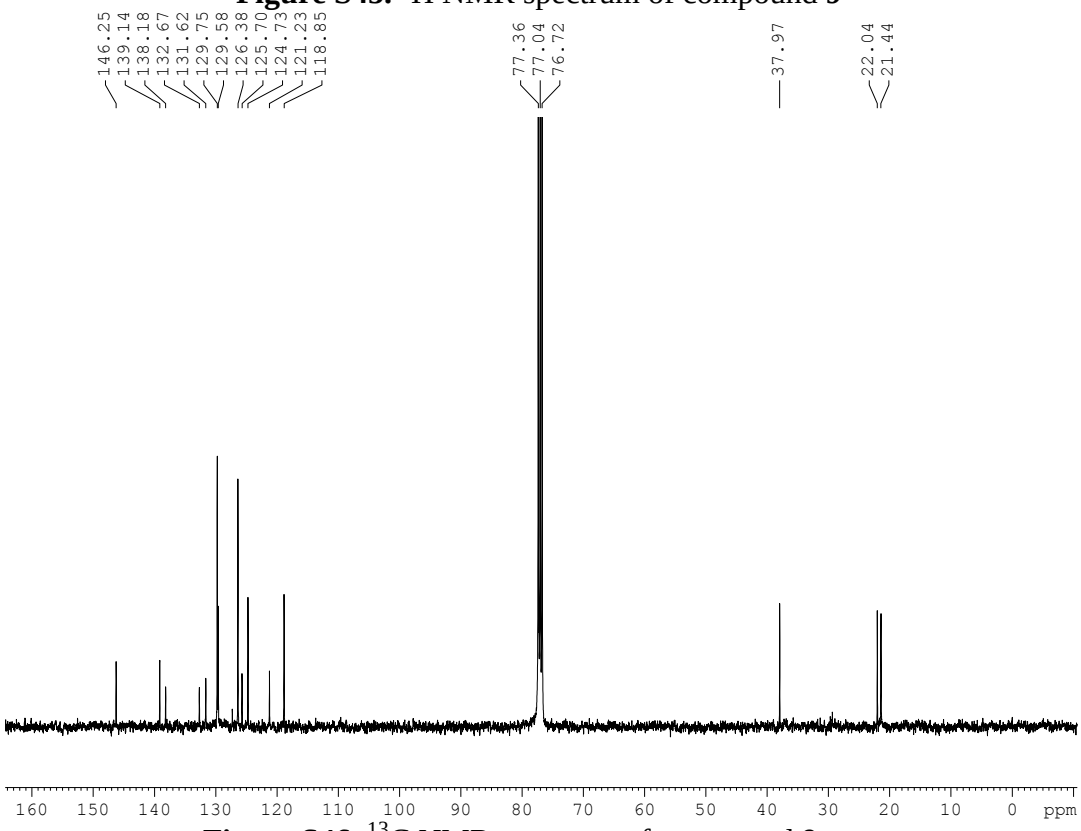


Figure S46. ^{13}C NMR spectrum of compound **9**

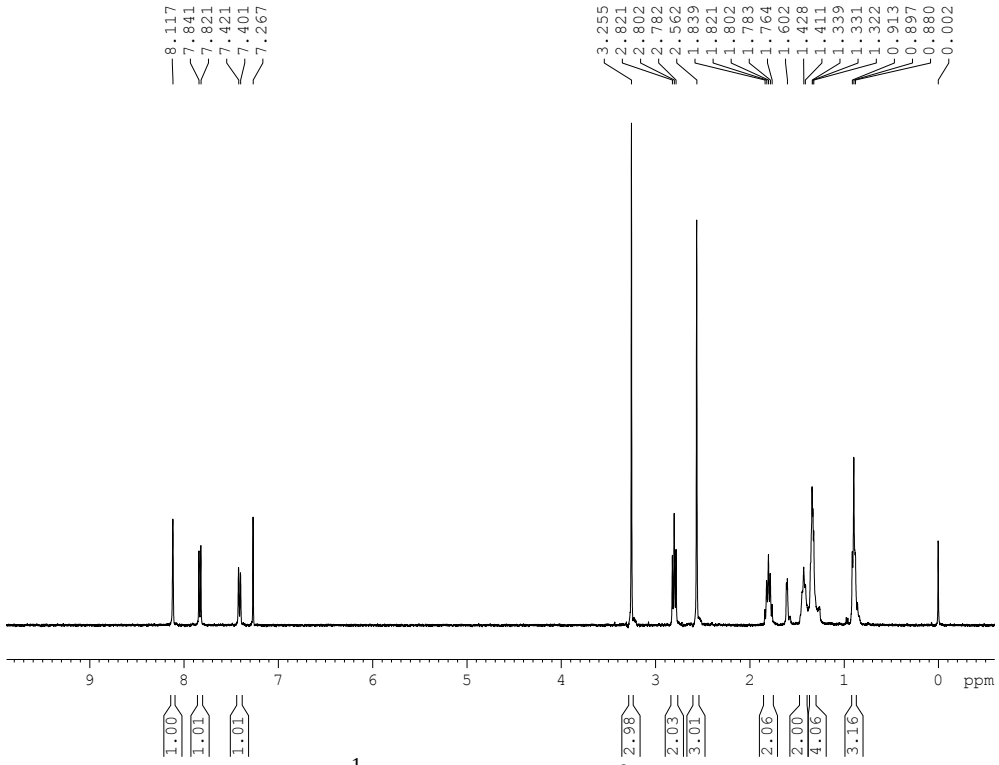


Figure S47. ^{1}H NMR spectrum of compound **10**

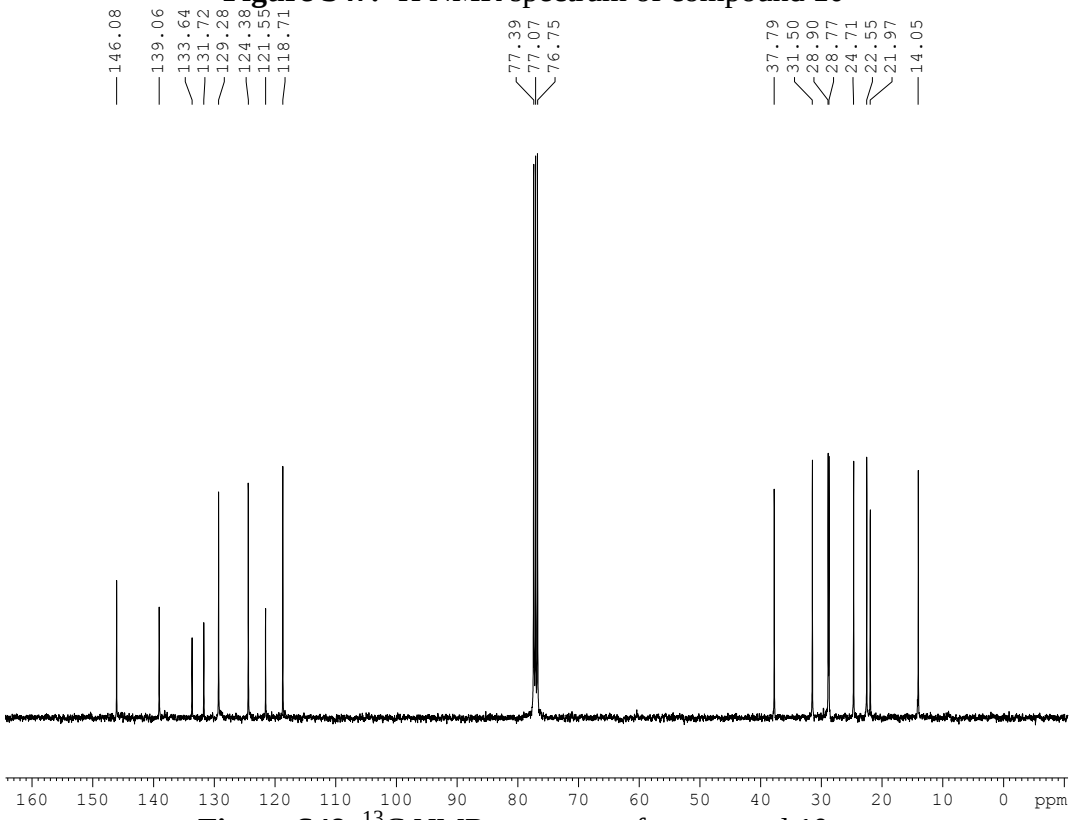


Figure S48. ^{13}C NMR spectrum of compound **10**

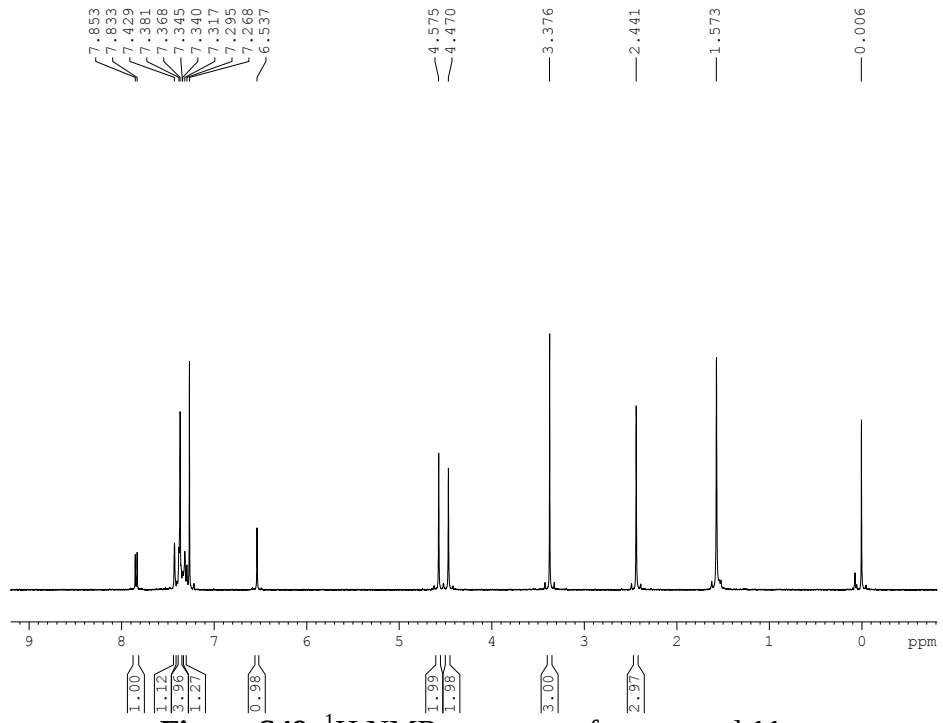


Figure S49. ^{1}H NMR spectrum of compound **11**

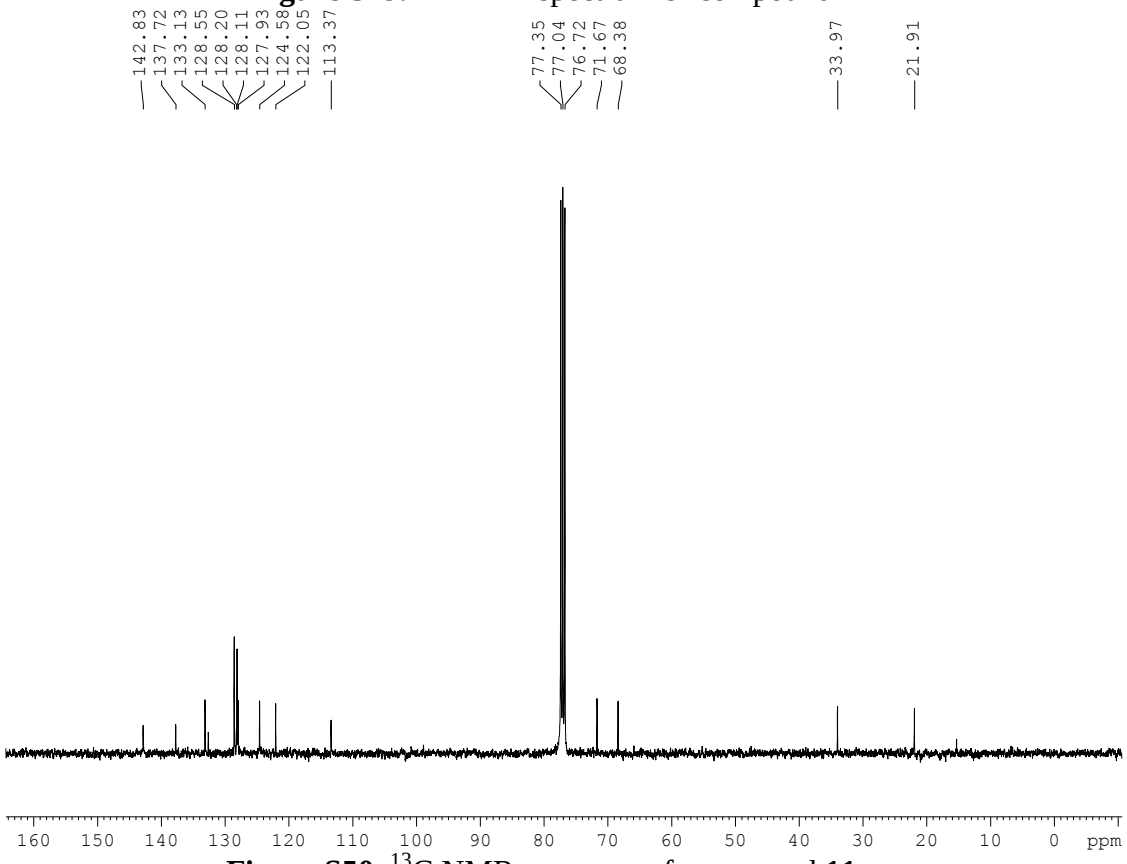


Figure S50. ^{13}C NMR spectrum of compound **11**

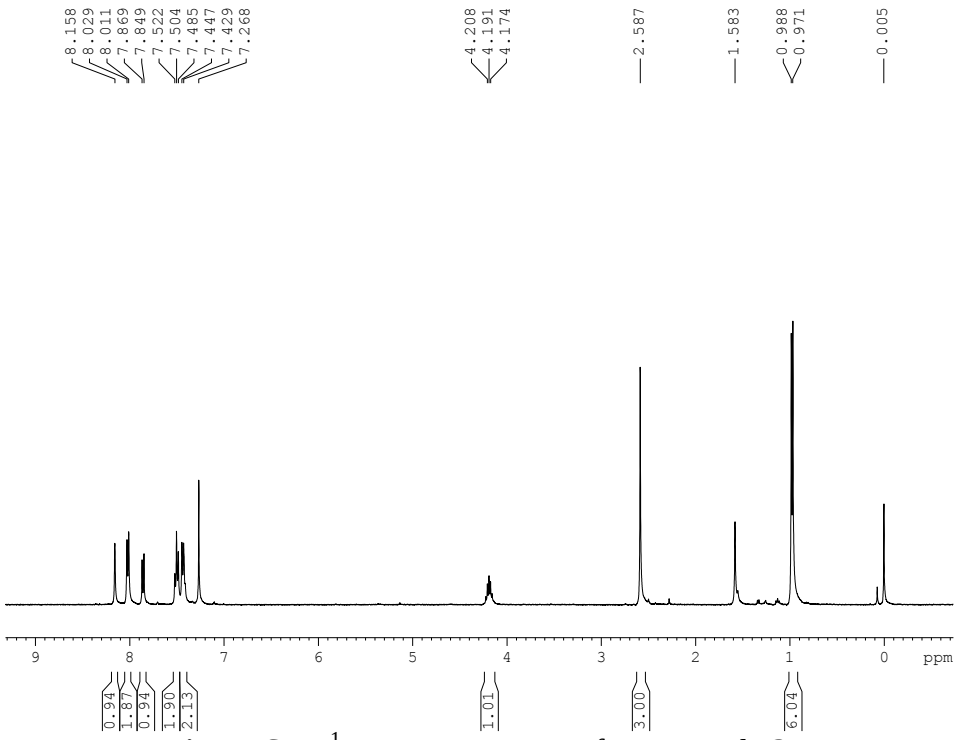


Figure S51. ^{1}H NMR spectrum of compound **12**

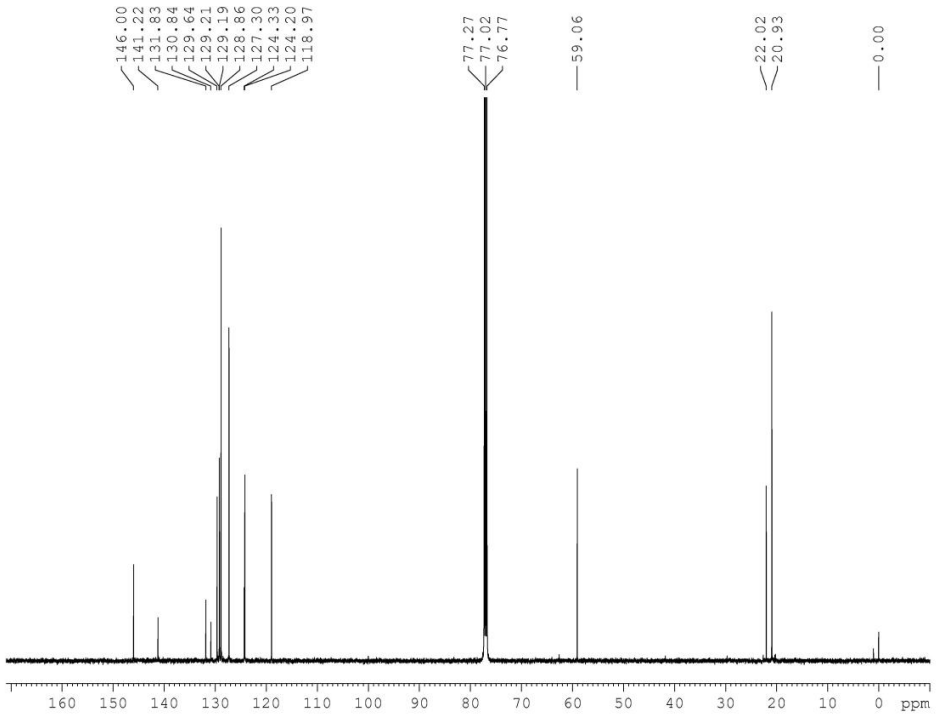


Figure S52. ^{13}C NMR spectrum of compound **12**

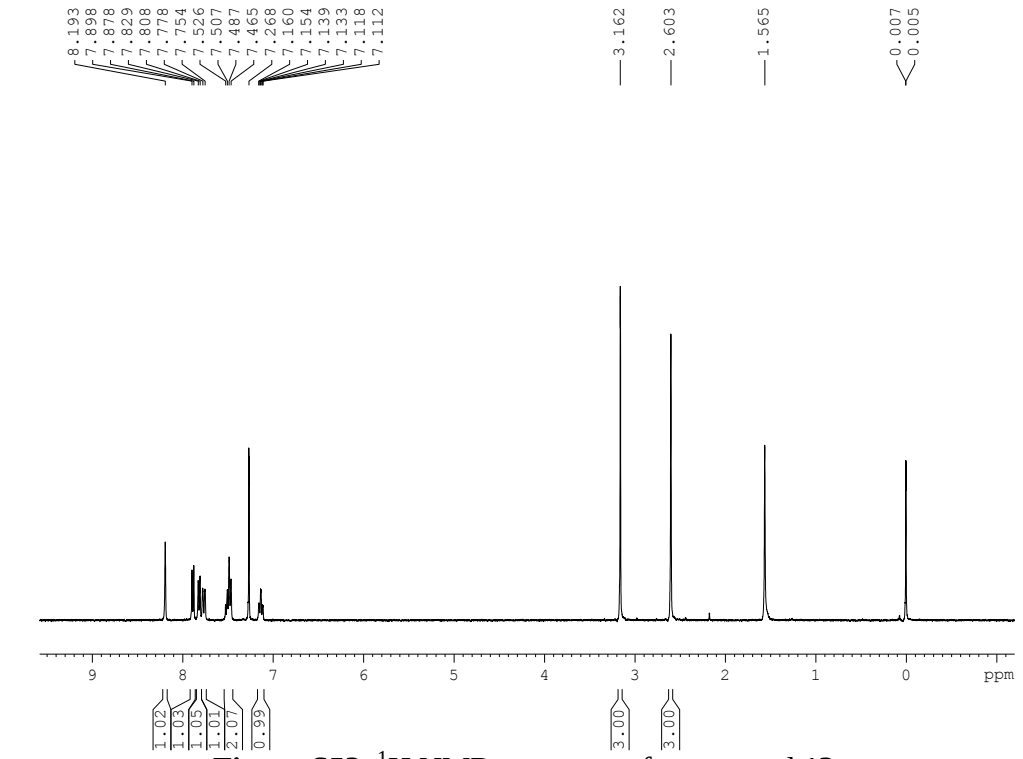


Figure S53. ^{1}H NMR spectrum of compound **13**

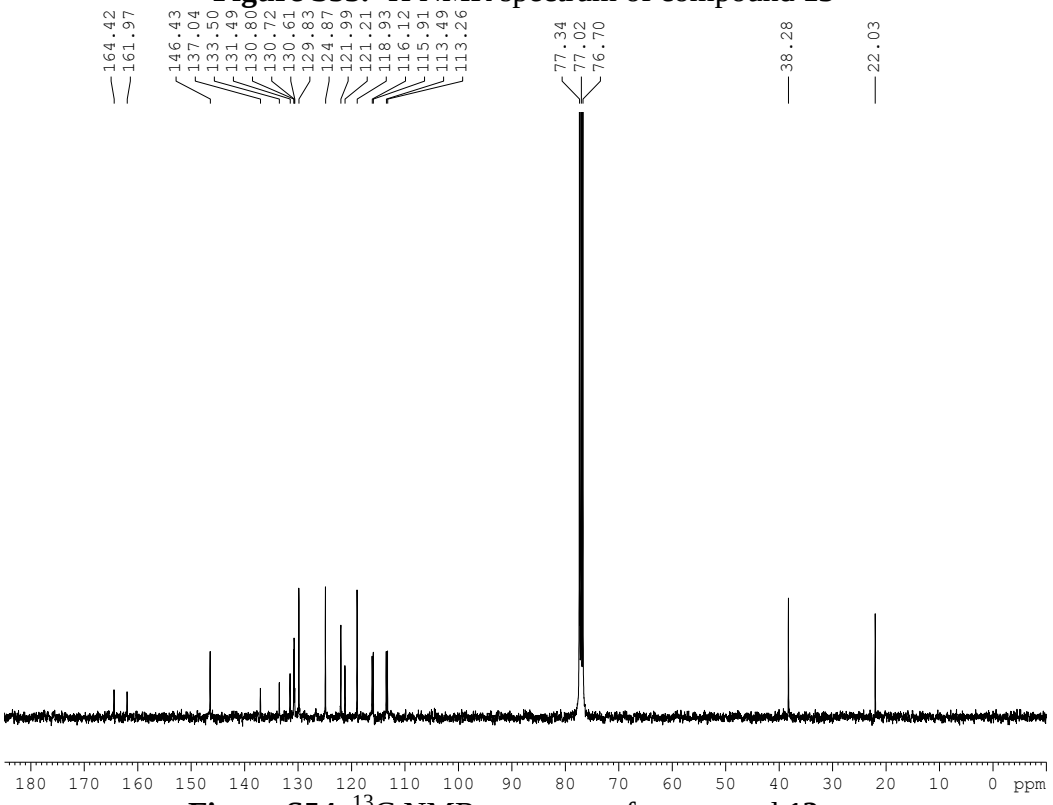


Figure S54. ^{13}C NMR spectrum of compound **13**

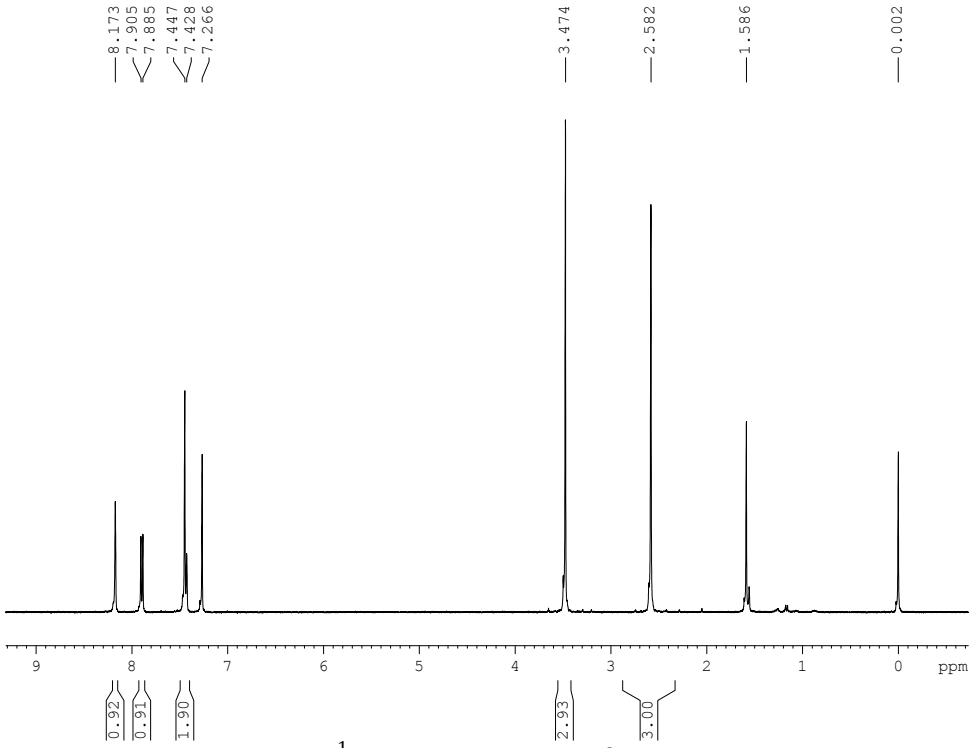


Figure S55. ^{1}H NMR spectrum of compound **14**

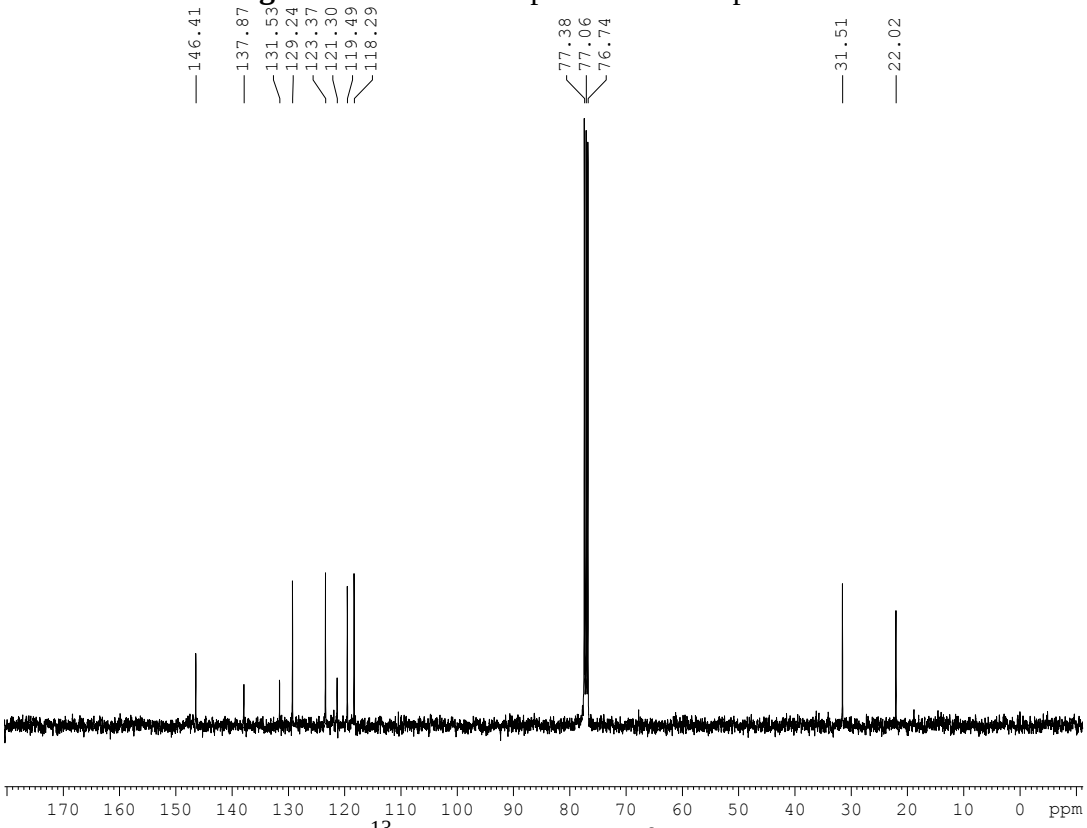


Figure S56. ^{13}C NMR spectrum of compound **14**

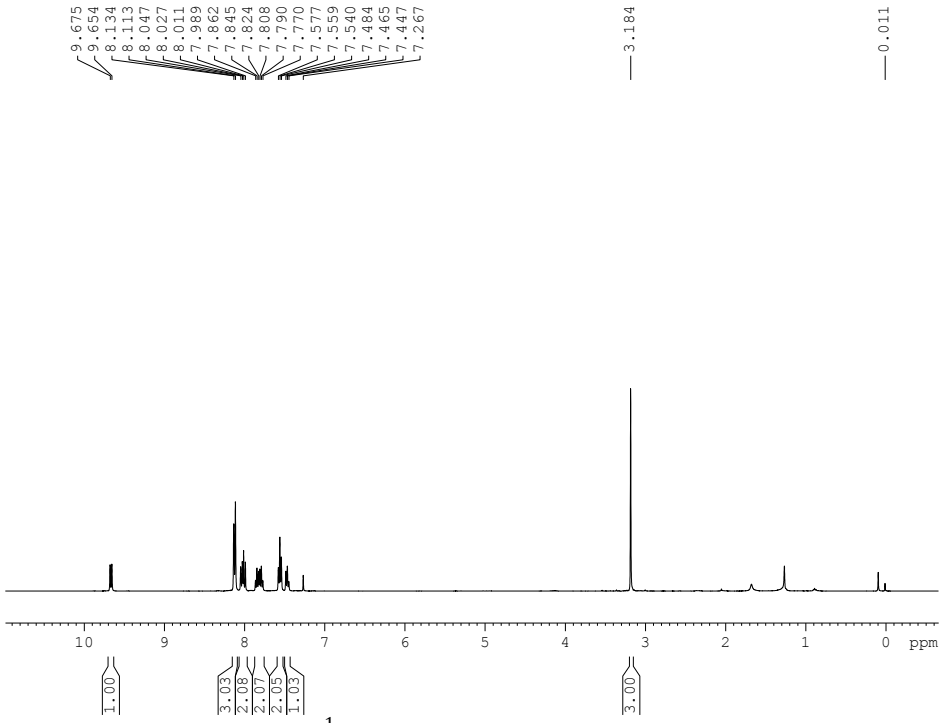


Figure S57. ^{1}H NMR spectrum of compound **15**

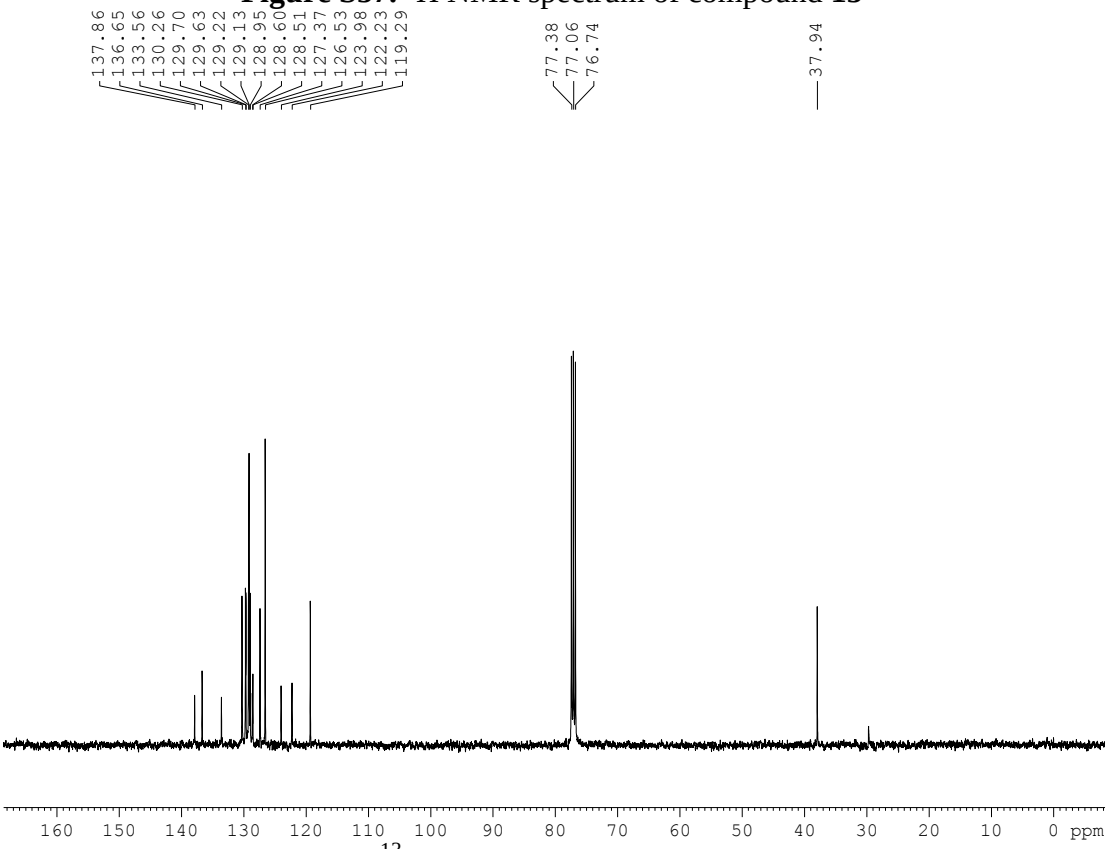


Figure S58. ^{13}C NMR spectrum of compound **15**

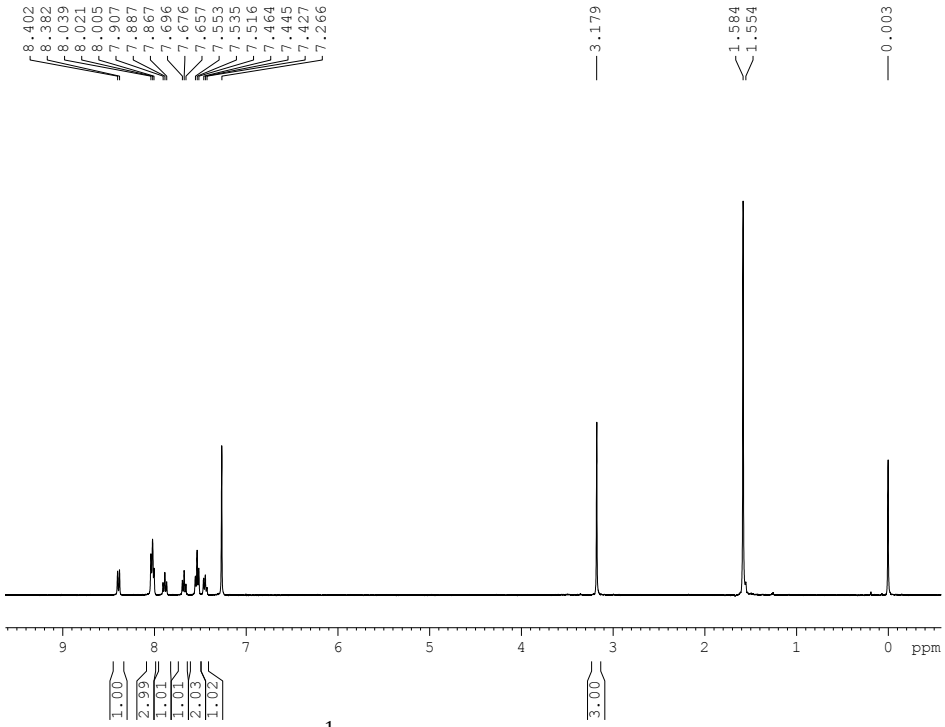


Figure S59. ^{1}H NMR spectrum of compound **16**

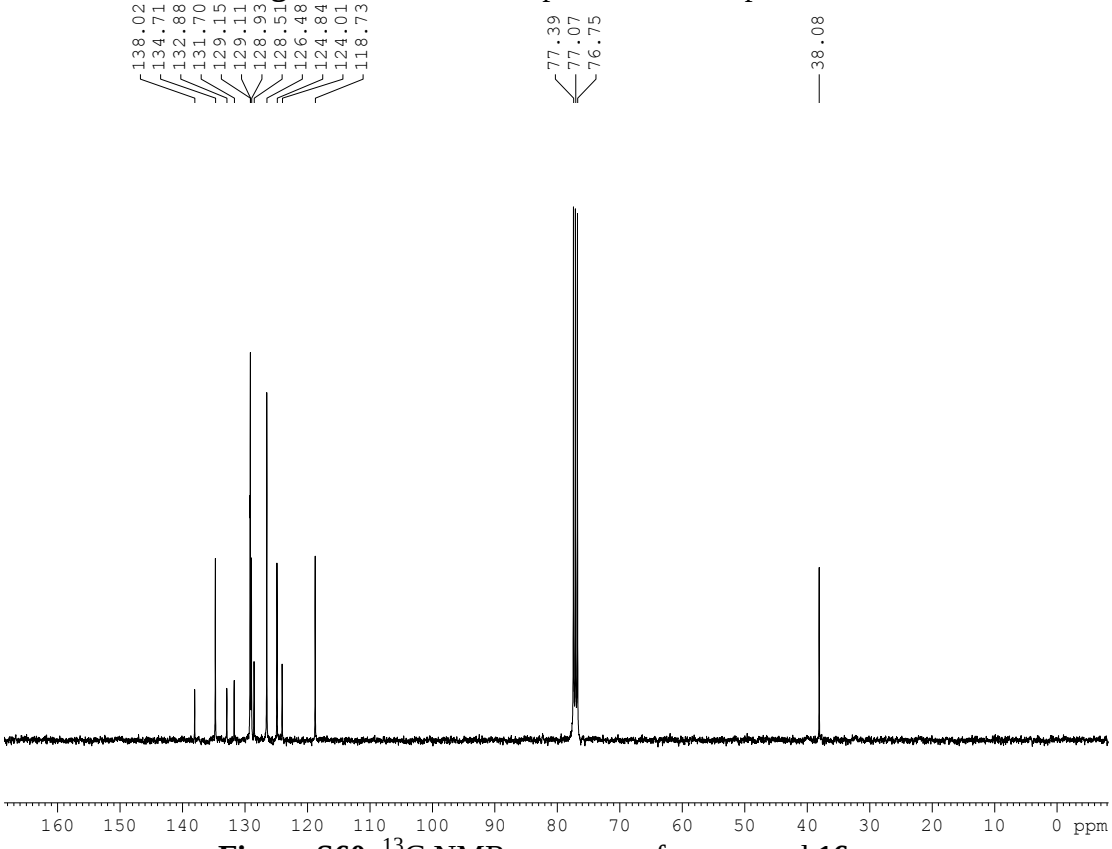


Figure S60. ^{13}C NMR spectrum of compound **16**

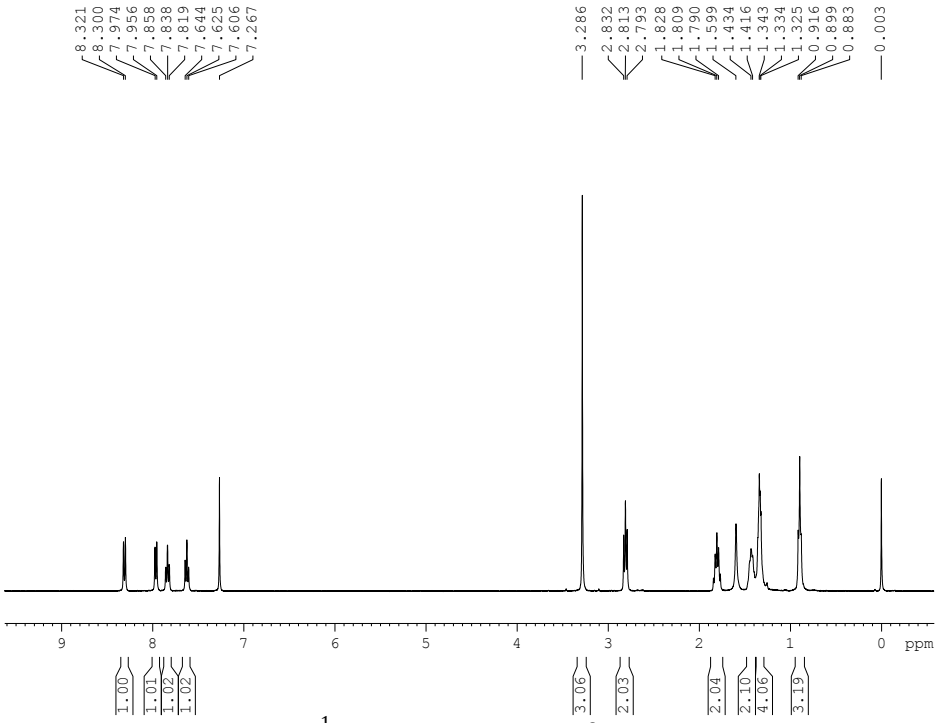


Figure S61. ^{1}H NMR spectrum of compound **17**

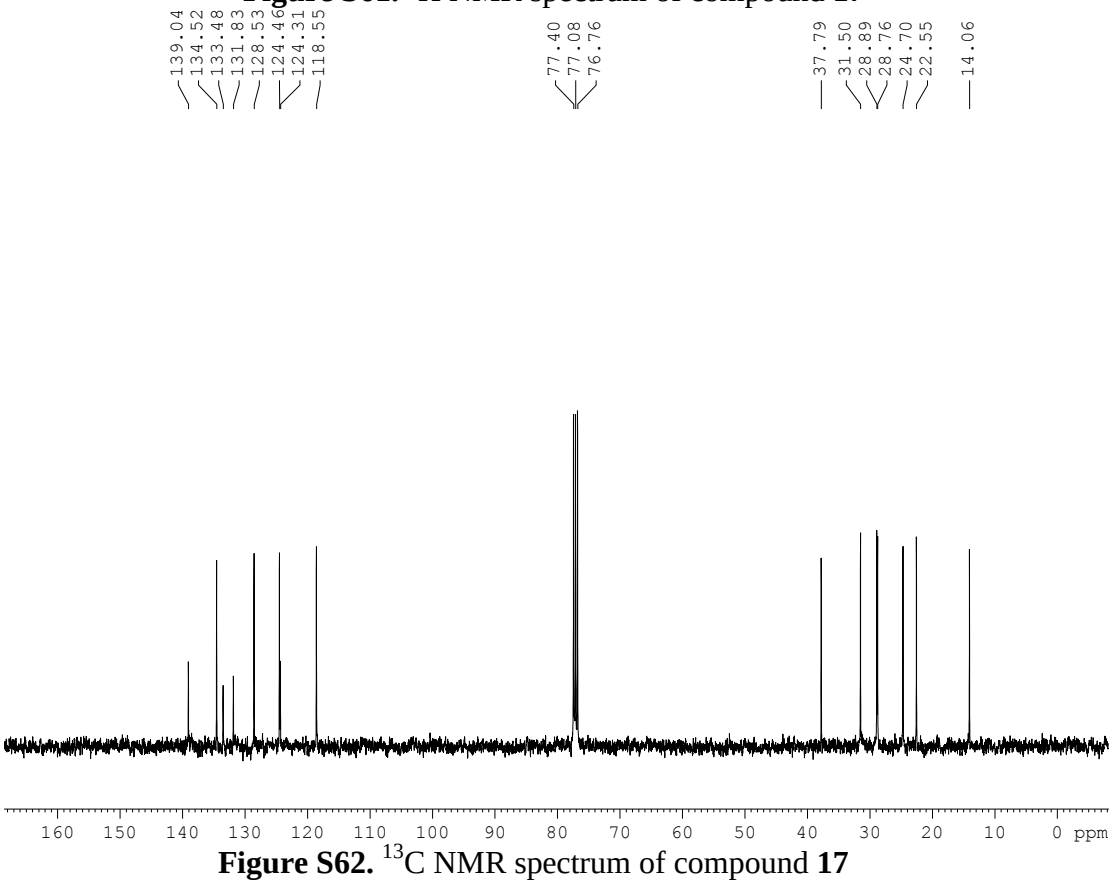


Figure S62. ^{13}C NMR spectrum of compound **17**

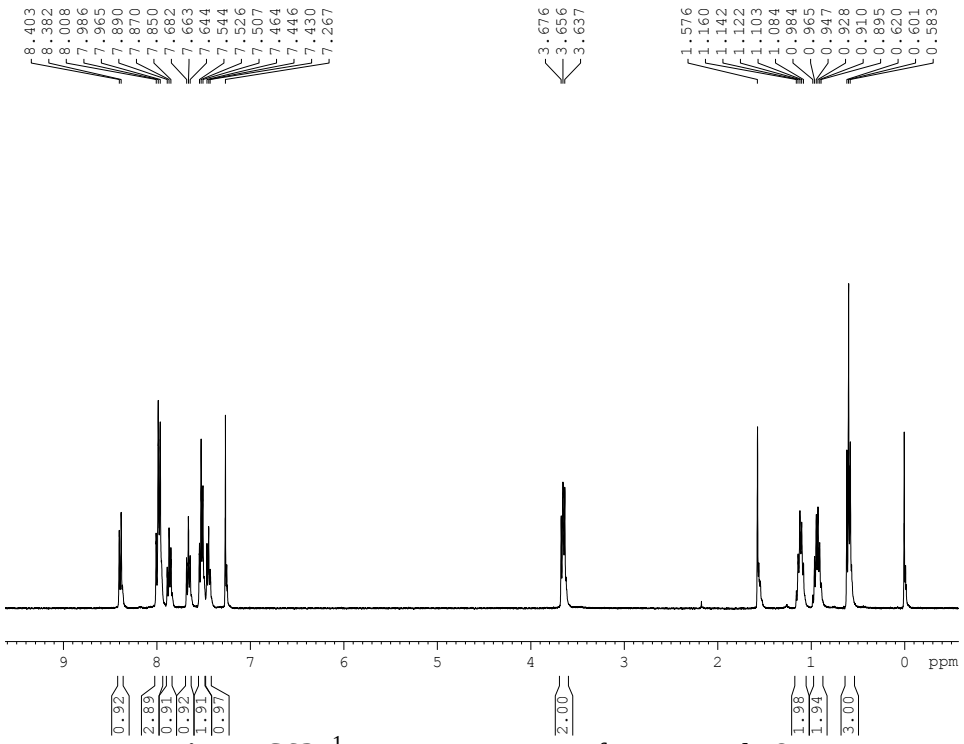


Figure S63. ^{1}H NMR spectrum of compound **18**

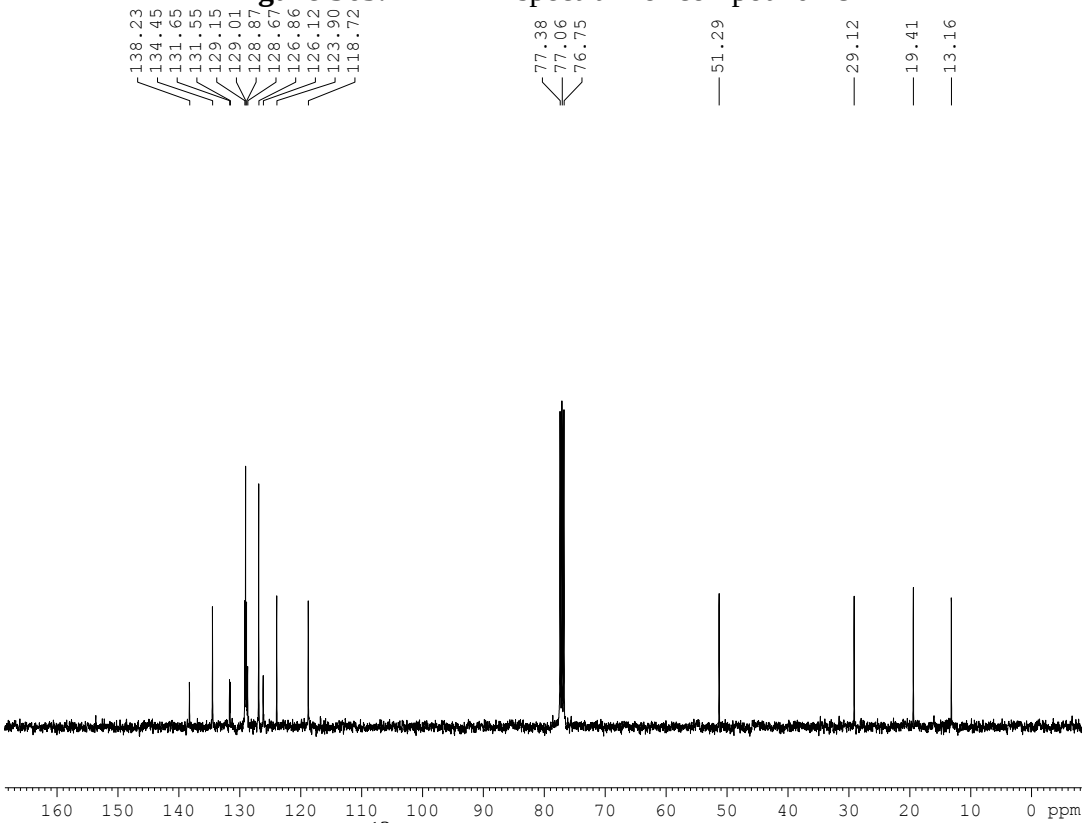


Figure S64. ^{13}C NMR spectrum of compound **18**

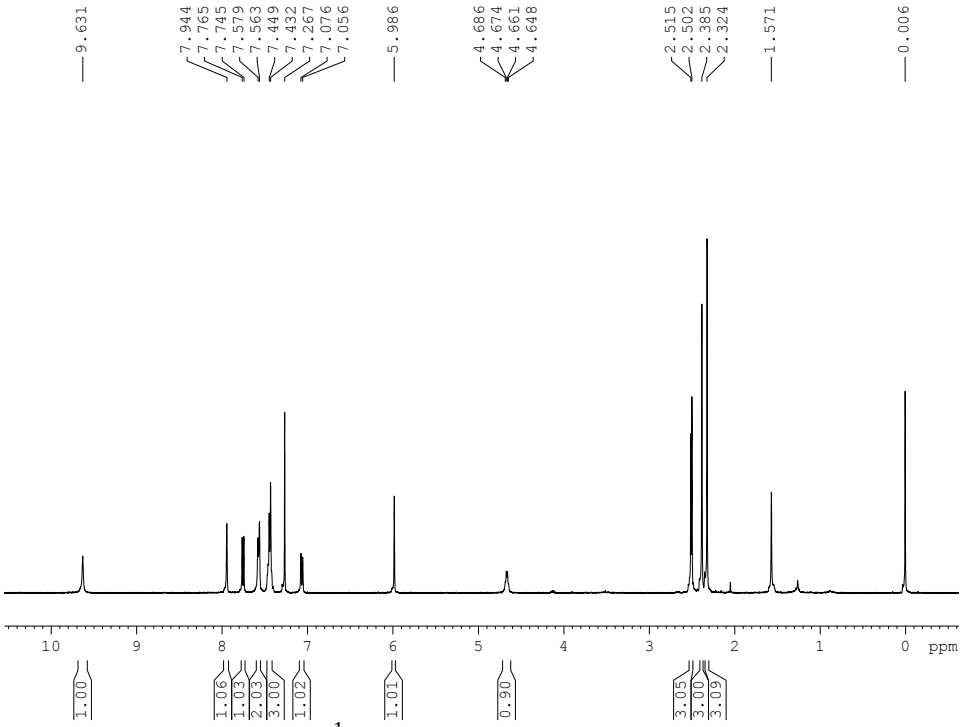


Figure S65. ^{1}H NMR spectrum of compound **21**

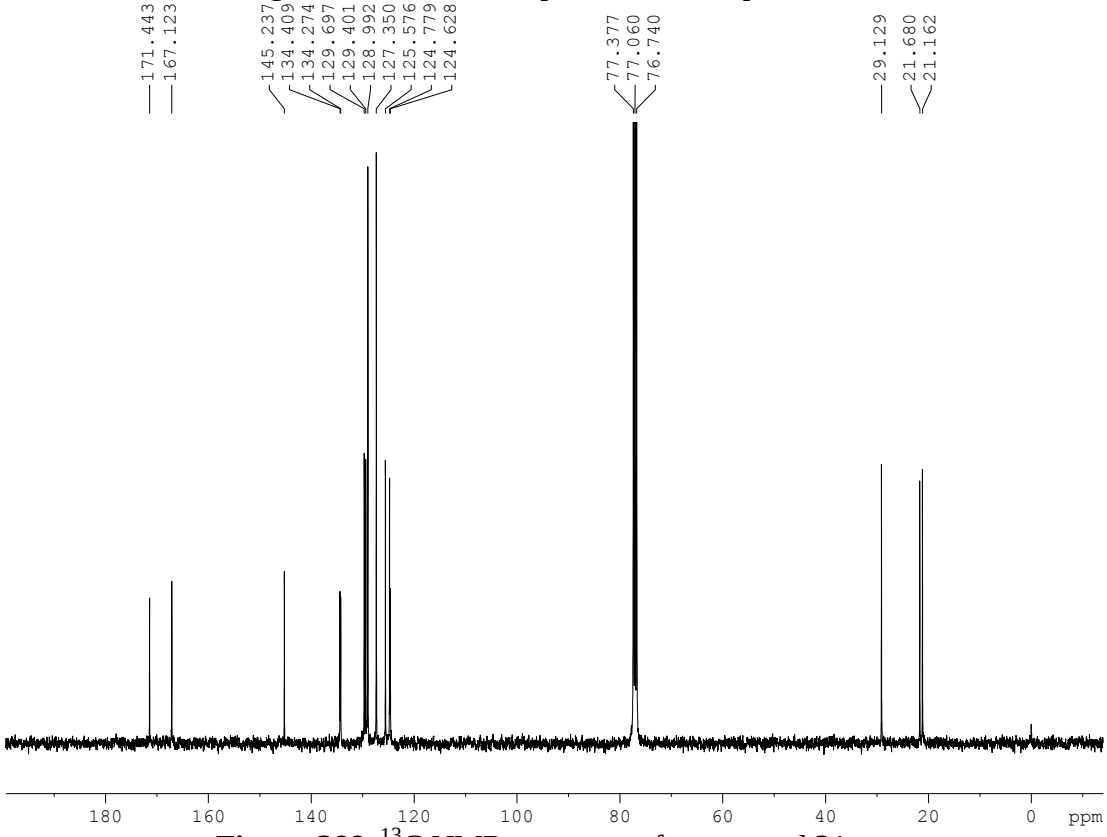


Figure S66. ^{13}C NMR spectrum of compound **21**

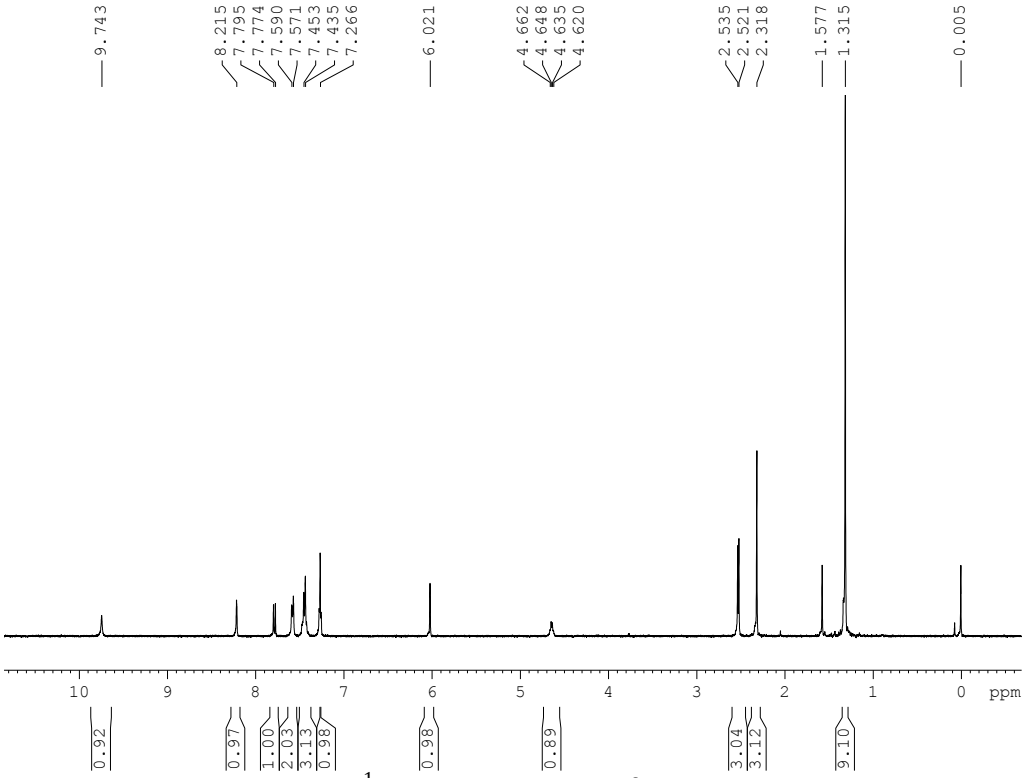


Figure S67. ^{1}H NMR spectrum of compound **22**

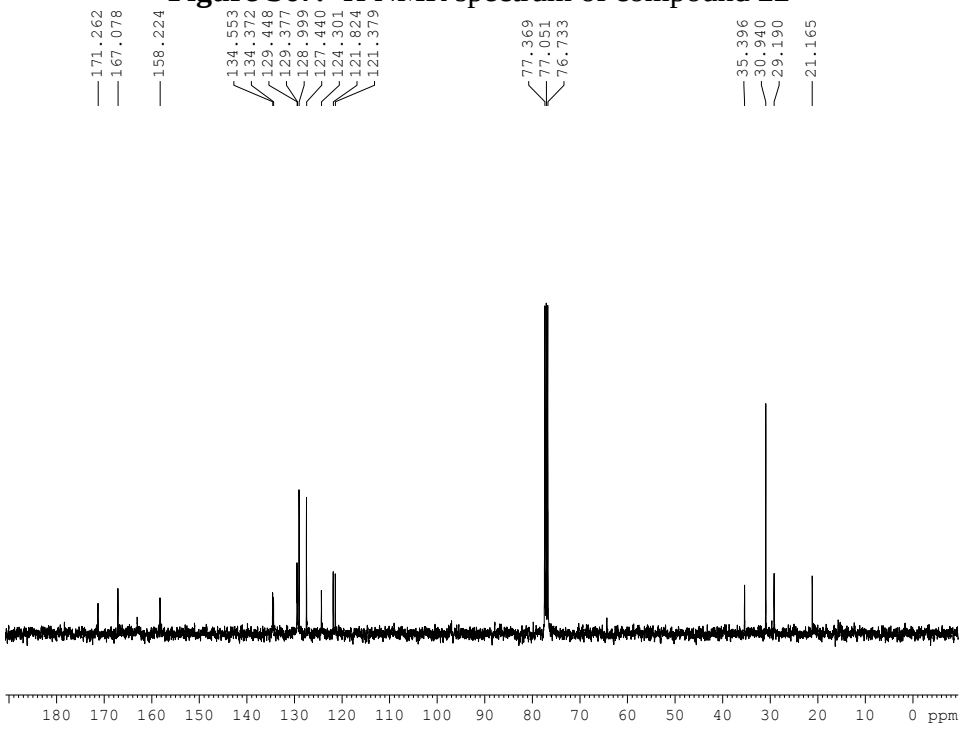


Figure S68. ^{13}C NMR spectrum of compound **22**

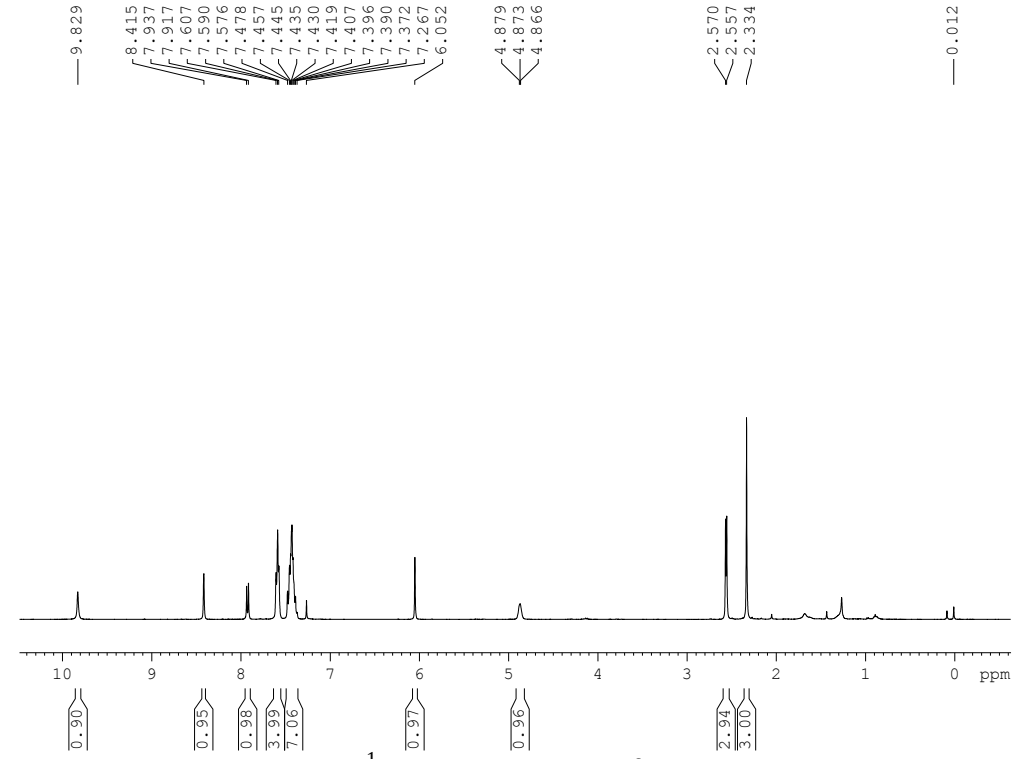


Figure S69. ^{1}H NMR spectrum of compound **23**

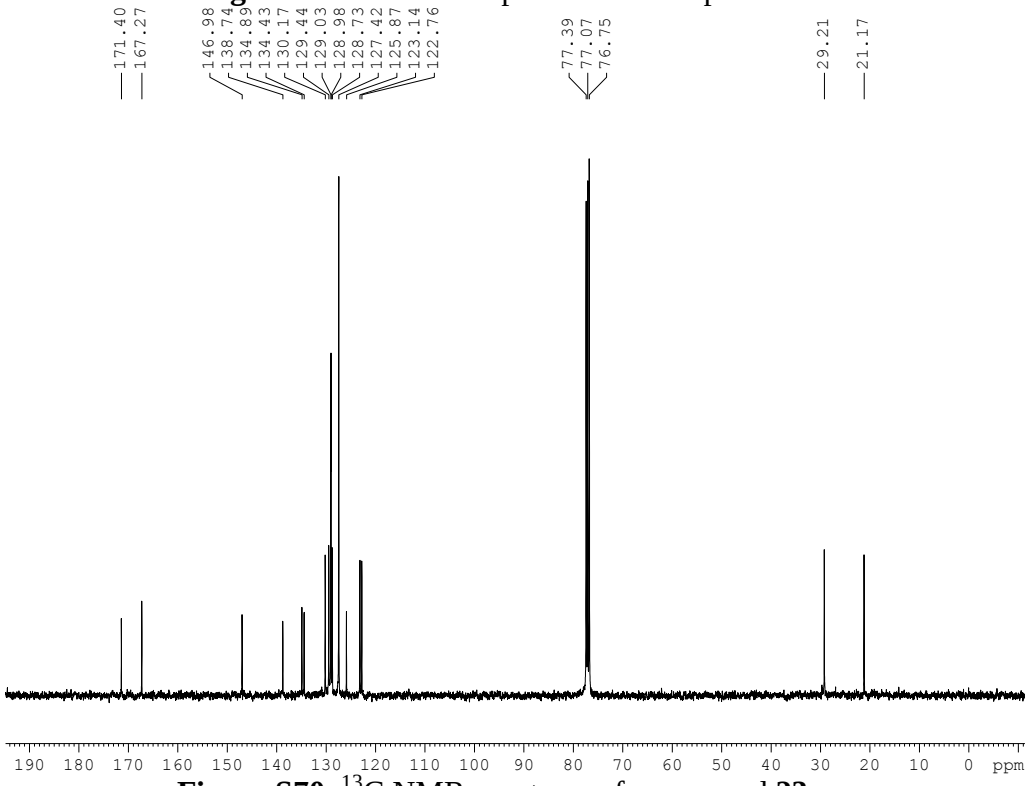


Figure S70. ^{13}C NMR spectrum of compound **23**

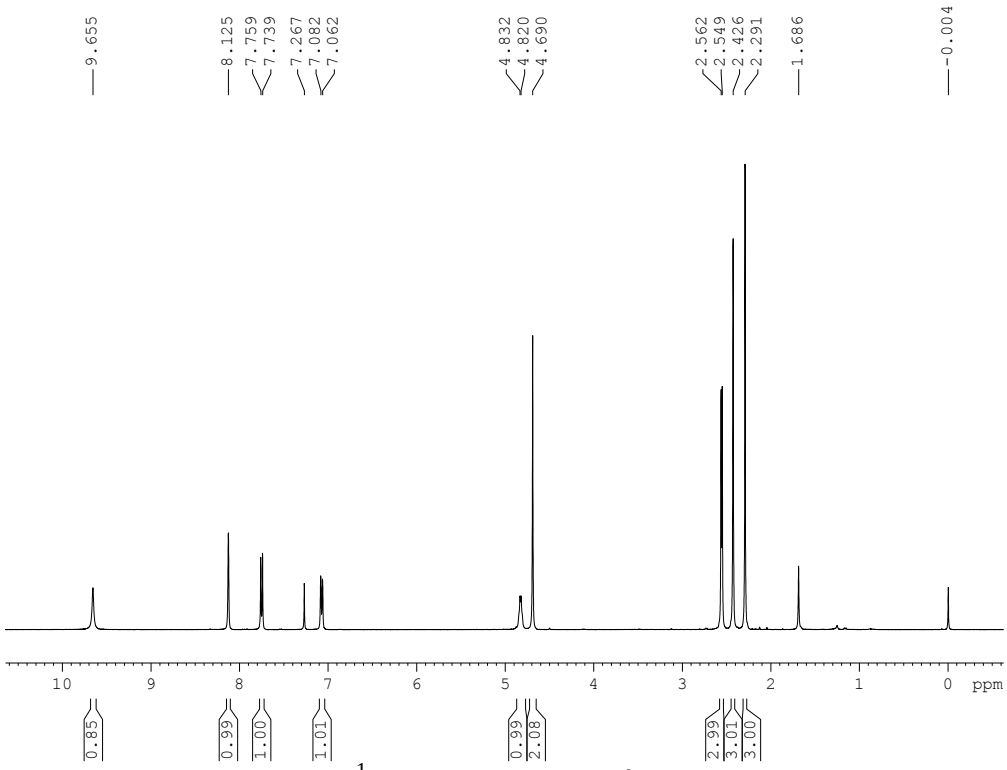


Figure S71. ^{1}H NMR spectrum of compound **24**

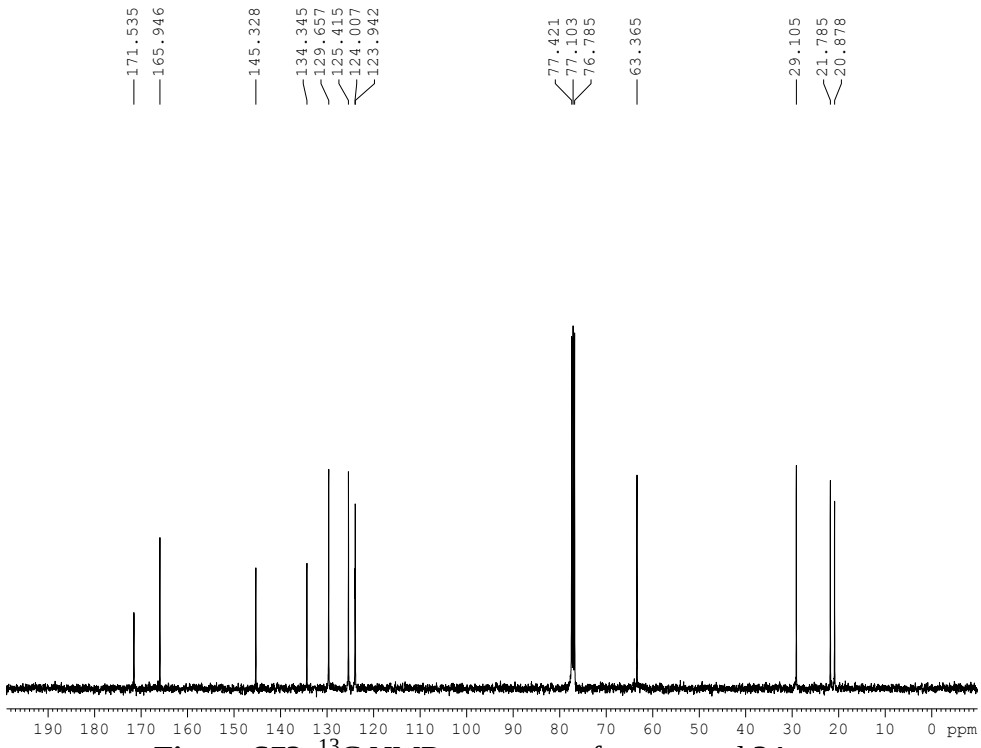


Figure S72. ^{13}C NMR spectrum of compound **24**

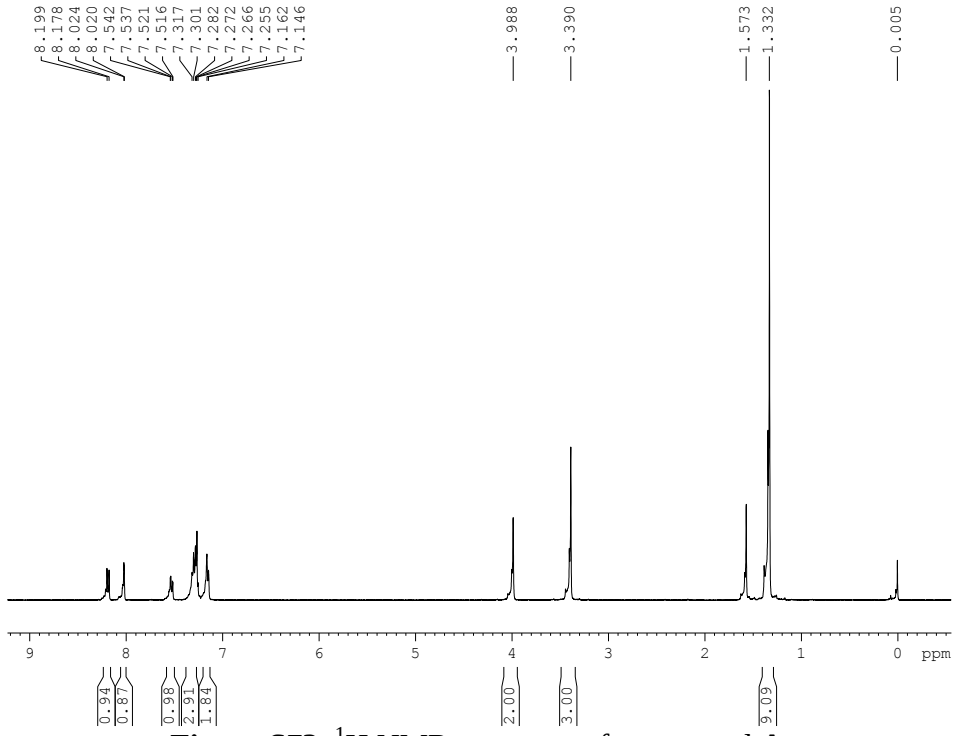


Figure S73. ^{1}H NMR spectrum of compound **A**

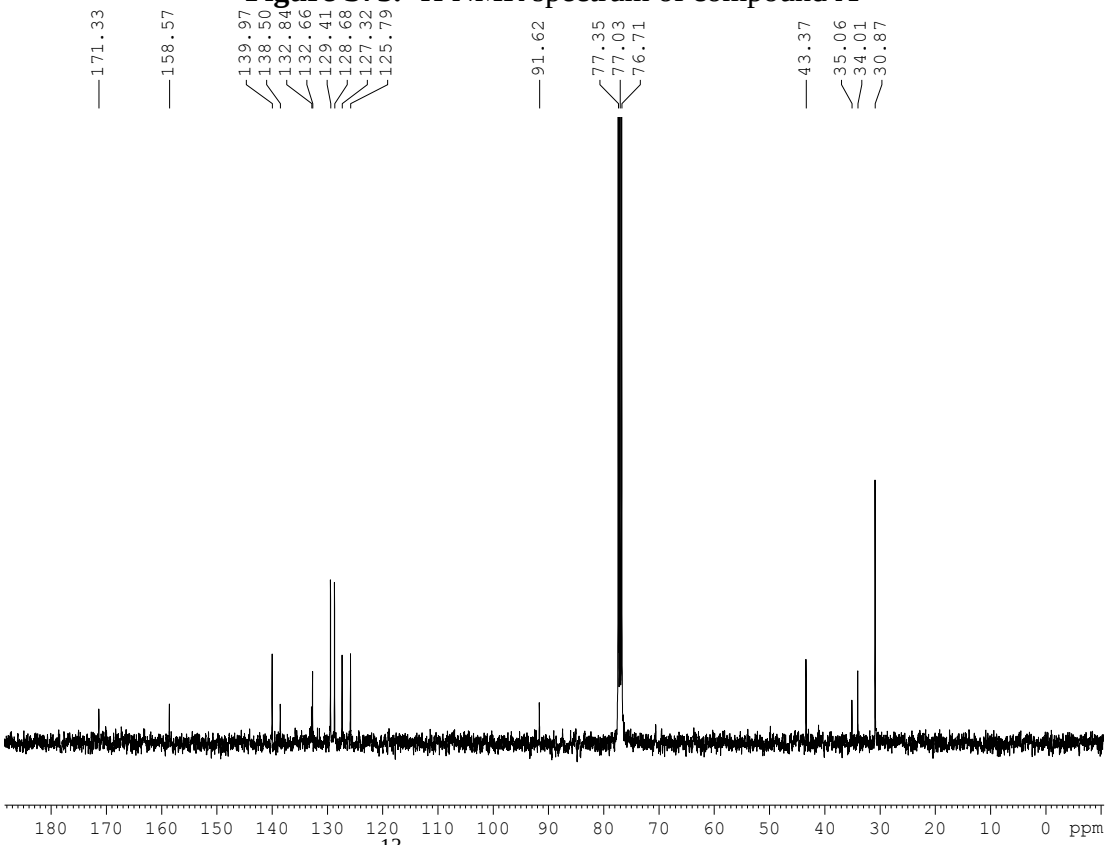


Figure S74. ^{13}C NMR spectrum of compound **A**

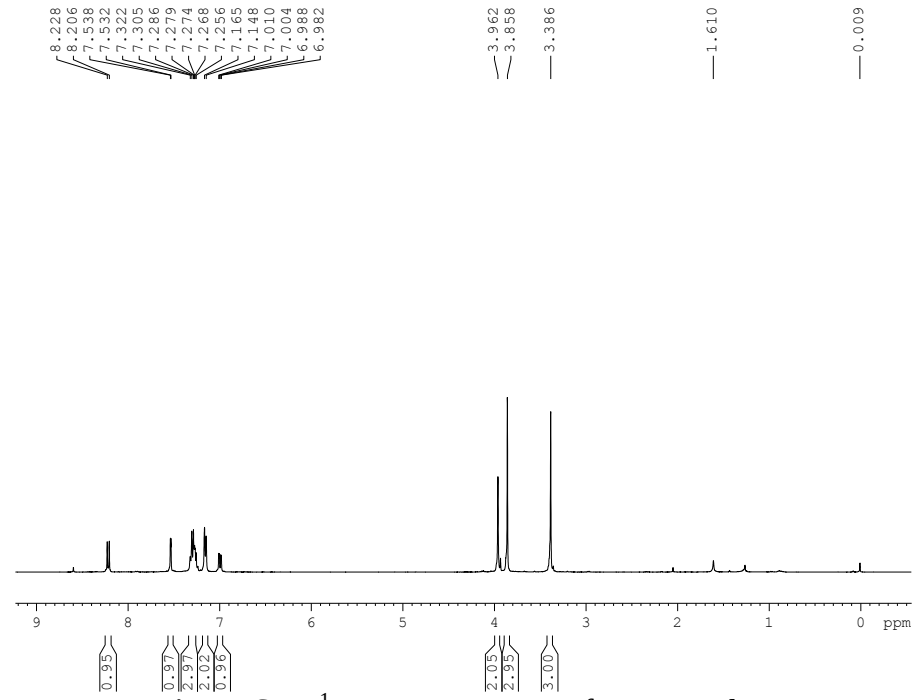


Figure S75. ^{1}H NMR spectrum of compound **B**

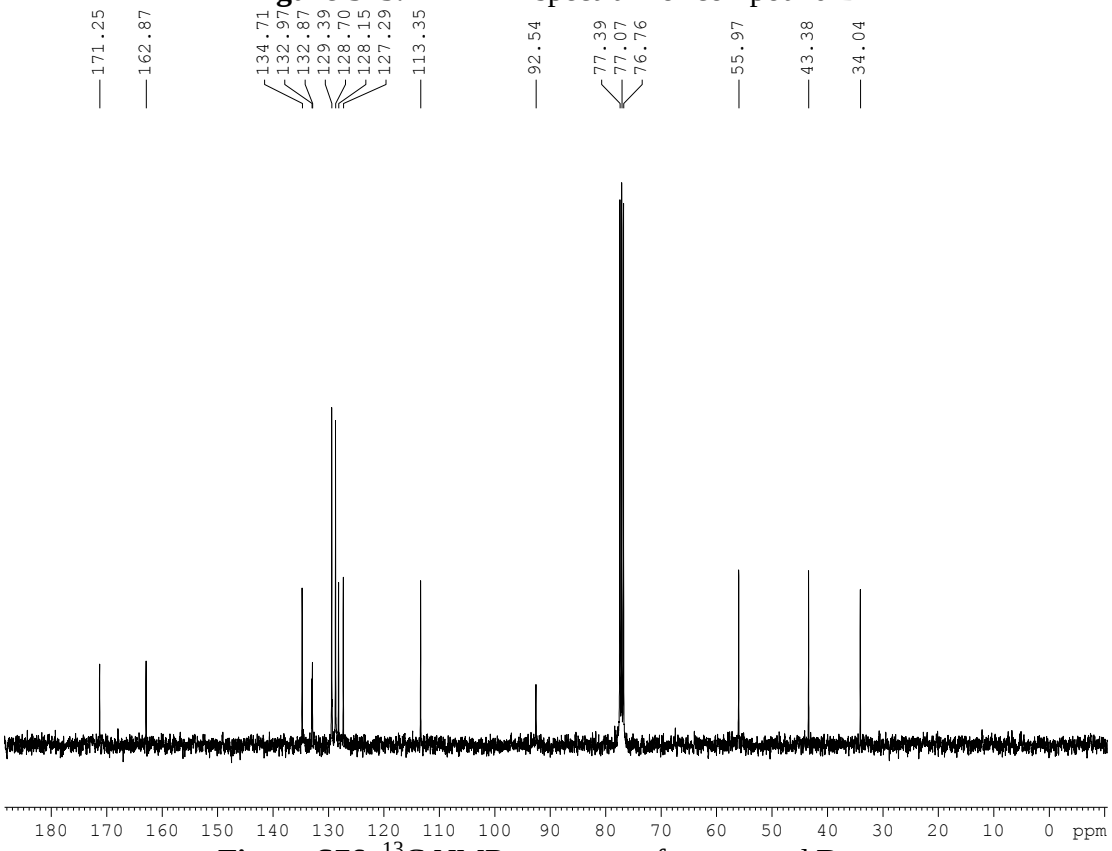


Figure S76. ^{13}C NMR spectrum of compound **B**

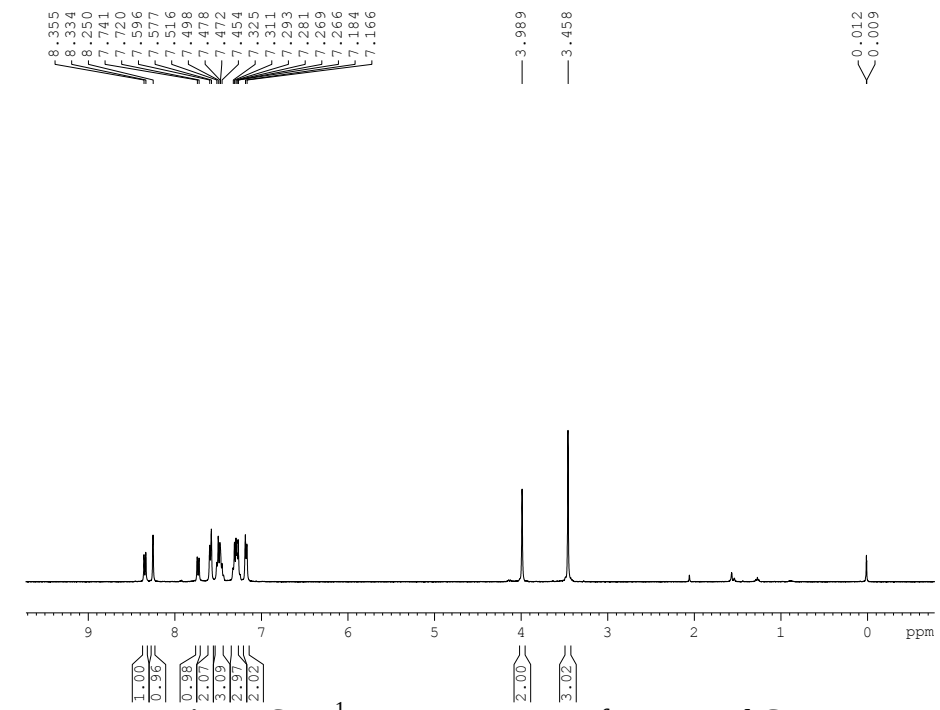


Figure S77. ^{1}H NMR spectrum of compound **C**

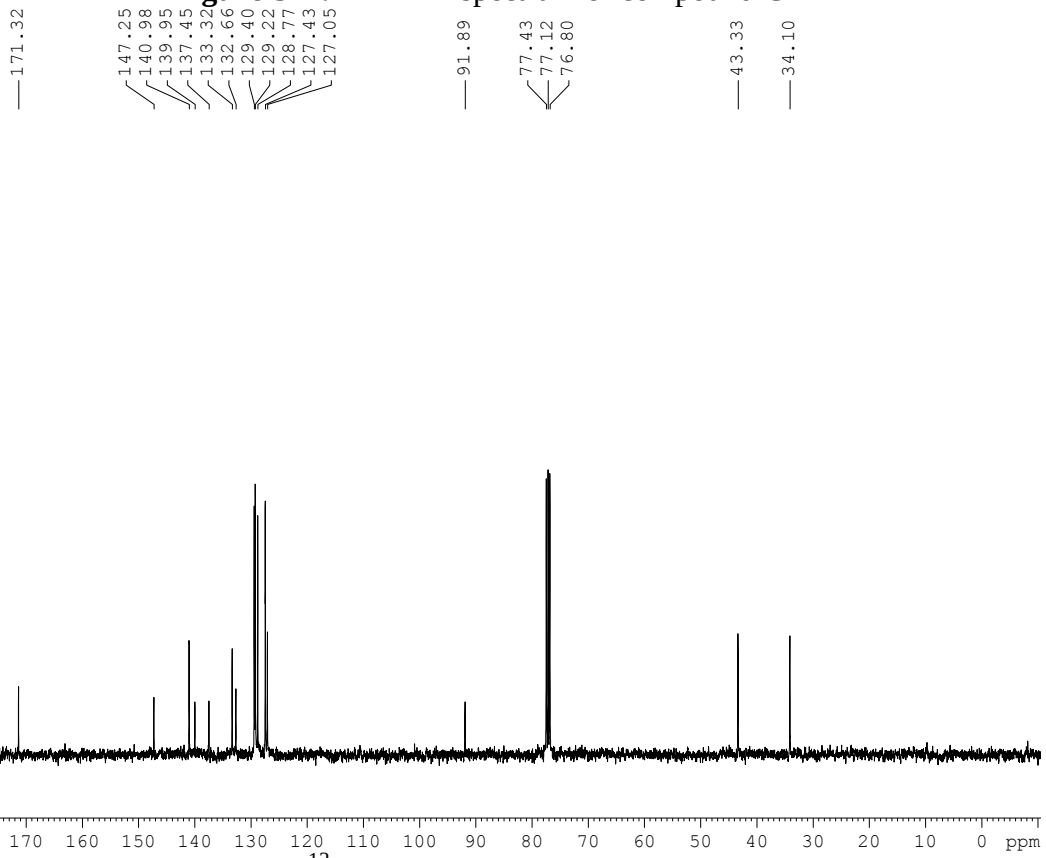


Figure S78. ^{13}C NMR spectrum of compound **C**

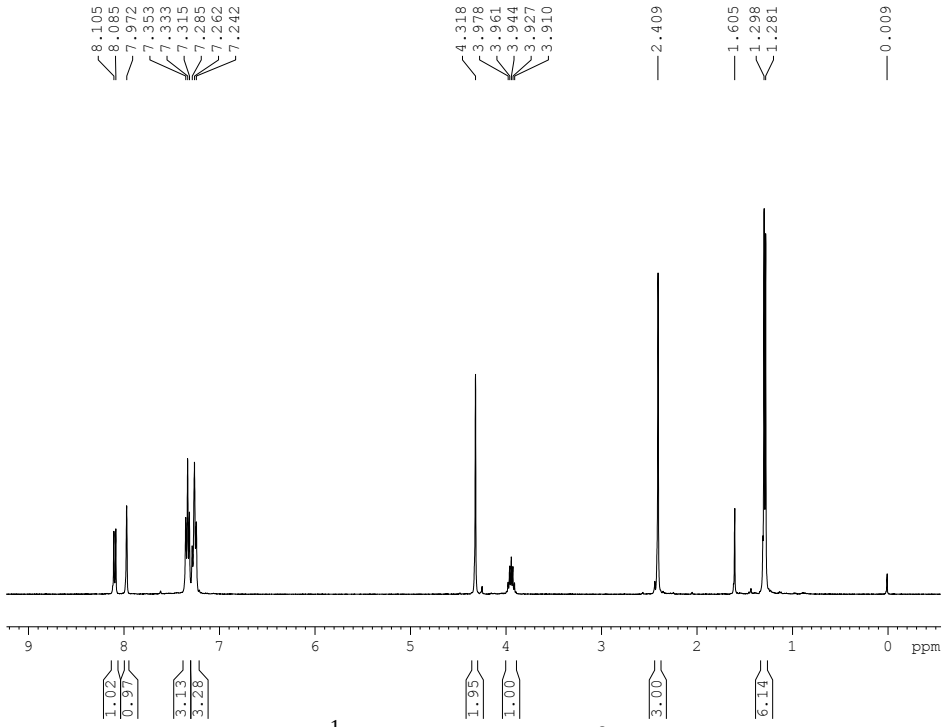


Figure S79. ^{1}H NMR spectrum of compound **D**

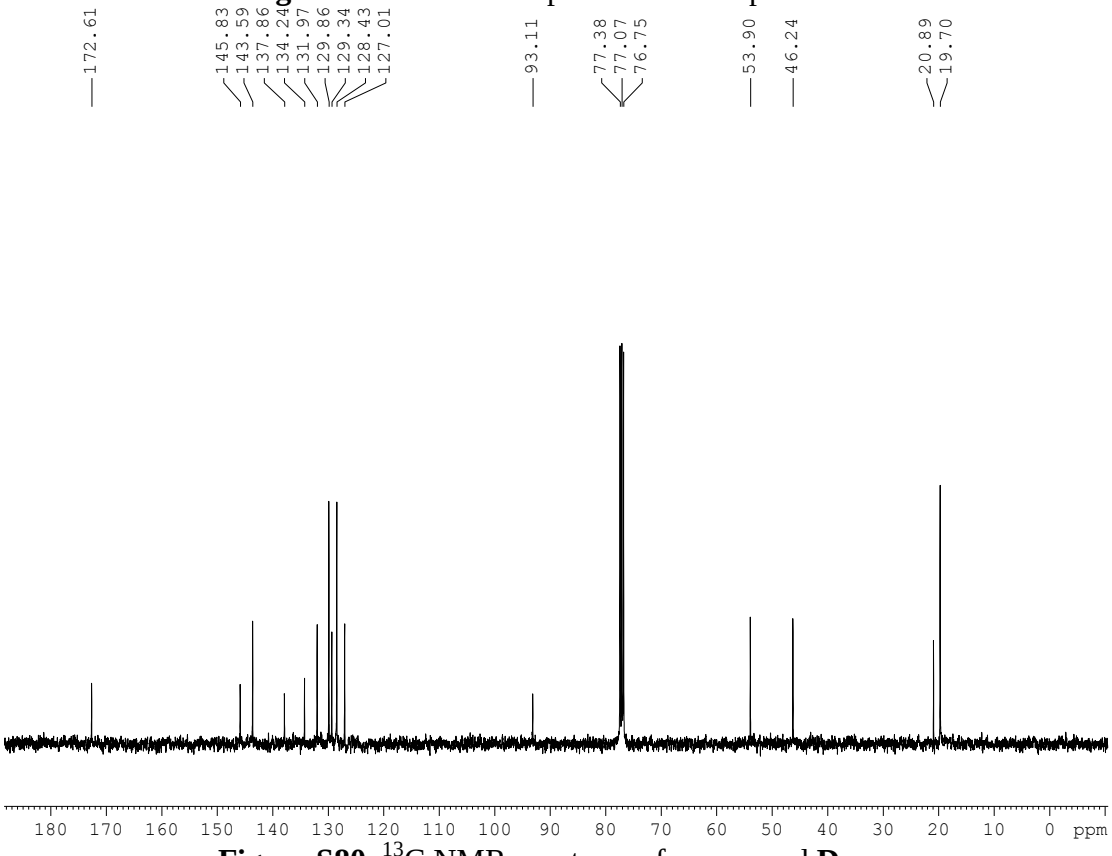


Figure S80. ^{13}C NMR spectrum of compound **D**