Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Indium(III) catalysed regio- and stereoselective hydrothiolation of bromoalkynes

Nimmakuri Rajesh and Dipak Prajapati*

Medicinal Chemistry Division, CSIR-North-East Institute of Science & Technology, Jorhat, Assam 785006, India

E-mail: dr_dprajapati2003@yahoo.co.uk

Table of Contents

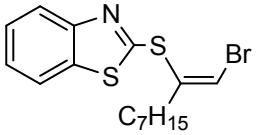
General information

All the commercially available reagents were used as received. IR Spectra were recorded on a SHIMADZU FTIR-8400 instrument. NMR spectra were recorded on Advance DPX 300 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded on ESQUIRE 3000 Mass spectrometer. All the experiments were monitored by thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Merck). After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ warming in a hot air oven. Column chromatography was performed on silica gel (100-200 mesh, Merck) using ethyl acetate: hexane as eluent.

Experimental data

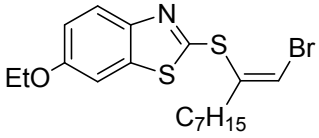
General procedure for hydrothiolation of bromoalkyne: Thiol (1 mmol), bromoalkyne (1 mmol) and 5 mol% $In(OTf)_3$ were taken in a round bottomed flask containing 5 ml of toluene. Allow the reaction mixture to reflux in toluene for appropriate time. After completion of reaction as indicated by TLC, the solvent was distilled off under reduced pressure and the crude product was separated through coloum chromatography by using hexane:ethylacetate as elutent to obtain desired product **3** or **5.**

Characterization data of the Products



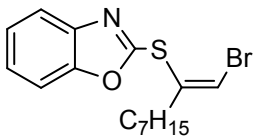
(*Z*)-2-((1-bromonon-1-en-2-yl)thio)benzo[*d*]thiazole (3a)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 1H), 7.71(d, J = 7.95 Hz, 1H), 7.39 (t, 1H), 7.34 (t, 1H), 6.65 (s, IH), 2.47 (t, 2H), 1.49 (m, 2H), 1.35 (m, 8H), 0.78 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163, 153.6, 139.2, 136.1, 126.3, 124.9, 122.4, 121, 112.9, 37.7, 31.6, 28.8, 28.6, 28.2, 22.5, 14; MS (LCMS, m/z) 369 [M]+; Anal. Calcd. for $C_{16}H_{20}BrNS_2$: C, 51.89; H, 5.44; Br, 21.57; N, 3.78; S, 17.32. Found: C, 51.87; H, 5.41; Br, 21.58; N, 3.72; S, 17.33.



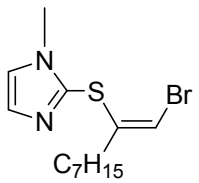
(*Z*)-2-((1-bromonon-1-en-2-yl)thio)-6-ethoxybenzo[*d*]thiazole (3b)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 8.9 Hz, 1H), 7.23 (s, 1H), 7.06 (d, J = 8.9 Hz, 1H), 6.62 (s, 1H), 4.1 (q, 2H), 2.48 (t, 2H), 1.55 (m, 2H), 1.47 (t, 3H), 1.20 (m, 8H), 0.85 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 157, 148, 139.7, 137.9, 123.1, 115.9, 110.6, 104.4, 64.1, 37.4, 31.6, 28.8, 28.6, 28.1, 22.5, 14.8, 14; MS (LCMS, m/z) 414 [M]+; Anal. Calcd. for $C_{18}H_{24}BrNOS_2$: C, 52.17; H, 5.84; Br, 19.28; N, 3.38; O, 3.86; S, 15.47. Found: C, 52.14; H, 5.84; Br, 19.27; N, 3.39; O, 3.88; S, 15.48.



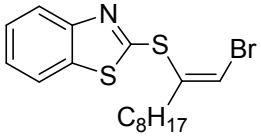
(*Z*)-2-((1-bromonon-1-en-2-yl)thio)benzo[*d*]oxazole (3c)

Light reddish oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.49 (m, 1H), 7.31 (t, 2H), 6.71 (s, 1H), 2.59 (t, 2H), 1.56 (m, 2H), 1.21 (m, 8H), 0.86 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 151.8, $_{141}$.8, 136.8, 124.7, 124.5, 119.2, 112.2, 110.1, 37.6, 31.6, 28.9, 28.8, 28, 22.5, 14; MS (LCMS, m/z) 354 [M]+; Anal. Calcd. for $C_{16}H_{20}BrNOS$: C, 54.24; H, 5.69; Br, 22.55; N, 3.95; O, 4.52; S, 9.05. Found: C, 54.26; H, 5.70; Br, 22.54; N, 3.95; O, 4.51; S, 9.04.



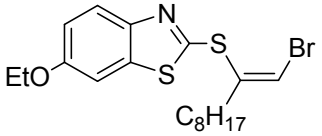
(*Z*)-2-((1-bromonon-1-en-2-yl)thio)-1-methyl-1H-imidazole (3d)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.08 (s, 1H), 6.25 (s, 1H), 3.7 (s, 3H), 2.01 (t, 2H), 1.37 (m, 2H), 1.25 (m, 8H), 0.87 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 136.4, 129.5, 123.8, 103.1, 36.2, 34, 31.6, 28.8, 28.6, 27.7, 22.5, 14; MS (LCMS, m/z) 317 [M]+; Anal. Calcd. for $C_{13}H_{21}BrN_2S$: C, 49.21; H, 6.67; Br, 25.18; N, 8.83; S, 10.11. Found: C, 49.24; H, 6.65; Br, 25.17; N, 8.81; S, 10.13.



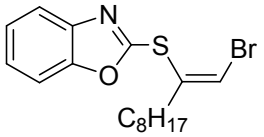
(*Z*)-2-((1-bromodec-1-en-2-yl)thio)benzo[*d*]thiazole (3e)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 7.95 Hz, 1H), 7.44 (t, 1H), 7.34 (t, 1H), 6.71 (s, IH), 2.47 (t, 2H), 1.49 (m, 2H), 1.29 (m, 10H), 0.85 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163, 153.6, 139.2, 136.1, 126.3, 124.9, 122.4, 121, 112.9, 37.7, 31.7, 29.1, 29, 28.6, 28.2, 22.5, 14.1; MS (LCMS, m/z) 384 [M]+; Anal. Calcd. for $C_{17}H_{22}BrNS_2$: C, 53.12; H, 5.77; Br, 20.79; N, 3.64; S, 16.68. Found: C, 53.10; H, 5.79; Br, 20.77; N, 3.62; S, 16.72.



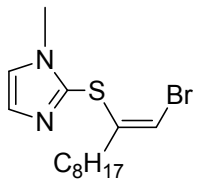
(*Z*)-2-((1-bromodec-1-en-2-yl)thio)-6-ethoxybenzo[*d*]thiazole (3f)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.9 Hz, 1H), 7.18 (s, 1H), 6.98 (d, J = 8.9 Hz, 1H), 6.54 (s, 1H), 4.02 (q, 2H), 2.4 (t, 2H), 1.47 (m, 2H), 1.38 (t, 3H), 1.11 (m, 10H), 0.79 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 157, 147.9, 139.7, 137.8, 123.1, 115.9, 110.8, 104.4, 64.1, 37.4, 31.7, 29.1, 28.7, 28.1, 22.6, 14.8, 14.1; MS (LCMS, m/z) 428 [M]+; Anal. Calcd. for $C_{19}H_{26}BrNOS_2$: C, 53.26; H, 6.12; Br, 18.65; N, 3.27; O, 3.73; S, 14.97. Found: C, 53.29; H, 6.13; Br, 18.66; N, 3.25; O, 3.73; S, 14.94.



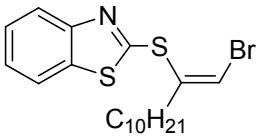
(*Z*)-2-((1-bromodec-1-en-2-yl)thio)benzo[*d*]oxazole (3g)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.49 (m, 1H), 7.31 (t, 2H), 6.71 (s, 1H), 2.59 (t, 2H), 1.56 (m, 2H), 1.21 (m, 10H), 0.87 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 151.8, 140.9, 136.8, 124.7, 124.5, 119.2, 112.2, 110.1, 37.6, 31.7, 29.1, 28.8, 28.6, 28, 22.6, 14; MS (LCMS, m/z) 367 [M]+; Anal. Calcd. for $C_{17}H_{22}BrNOS$: C, 55.43; H, 6.02; Br, 21.69; N, 3.8; O, 4.34; S, 8.71. Found: C, C, 55.45; H, 6.01; Br, 21.71; N, 3.5; O, 4.32; S, 8.75.



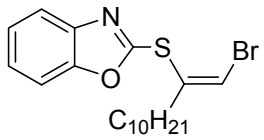
(*Z*)-2-((1-bromodec-1-en-2-yl)thio)-1-methyl-1H-imidazole (3h)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (s, 1H), 7.06 (s, 1H), 6.25 (s, 1H), 3.7 (s, 3H), 2.01 (t, 2H), 1.36 (m, 2H), 1.26 (m, 10H), 0.87 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 136.4, 129.4, 123.7, 103.3, 36.3, 34.1, 31.7, 29.1, 28.7, 28.6, 27.7, 22.6, 14.1; MS (LCMS, m/z) 330 [M]+; Anal. Calcd. for $C_{14}H_{23}BrN_2S$: C, 50.75; H, 7.00; Br, 24.12; N, 8.46; S, 9.86. Found: C, 50.71; H, 7.00; Br, 24.11; N, 8.42; S, 9.82.



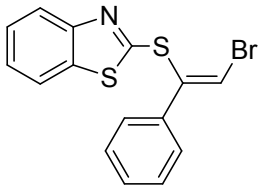
(*Z*)-2-((1-bromododec-1-en-2-yl)thio)benzo[*d*]thiazole (3i)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, J = 8.1 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.47 (t, 1H), 7.37 (t, 1H), 6.73 (s, IH), 2.55 (t, 2H), 1.57 (m, 2H), 1.21 (m, 12H), 0.88 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 153.6, 139.2, 136.1, 126.2, 124.9, 122.4, 121, 112.8, 37.7, 31.9, 29.5, 29.4, 29.29, 29.24, 28.7, 28.2, 25.6, 22.6, 14.1; MS (LCMS, m/z) 412 [M]+; Anal. Calcd. for $C_{19}H_{26}BrNS_2$: C, 55.33; H, 6.35; Br, 19.37; N, 3.40; S, 15.55. Found: C, 55.31; H, 6.34; Br, 19.38; N, 3.41; S, 15.56.



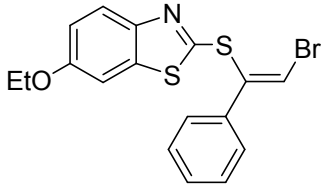
(*Z*)-2-((1-bromododec-1-en-2-yl)thio)benzo[*d*]oxazole (3j)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.31 (m, 1H), 7.31 (t, 2H), 6.71 (s, 1H), 2.59 (t, 2H), 1.56 (m, 2H), 1.21 (m, 12H), 0.88 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 151.8, 141.8, 136.8, 124.7, 124.5, 119.2, 112.2, 110.1, 37.6, 31.8, 29.7, 29.5, 29.4, 29.2, 28.6, 28, 22.6, 14.1; MS (LCMS, m/z) 396 [M]+; Anal. Calcd. for $C_{19}H_{26}BrNOS$: C, 57.57; H, 6.61; Br, 20.16; N, 3.53; O, 4.04; S, 8.09. Found: C, 57.59; H, 6.58; Br, 20.17; N, 3.56; O, 4.03; S, 8.07.



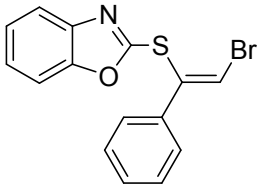
(*Z*)-2-((2-bromo-1-phenyvinyl)thio)benzo[*d*]thiazole (5a)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 8Hz, 1H), 7.63 (m, 3H), 7.38 (m, 5H), 7.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 153.1, 138.6, 137.5, 136, 129.8, 128.8, 127.9, 126.2, 124.7, 122.2, 120.9, 116.1; MS (LCMS, m/z) 346 [M]+; Anal. Calcd. for $C_{15}H_{10}BrNS_2$: C, 51.73; H, 2.89; Br, 22.94; N, 4.02; S, 18.41. Found: C, 51.75; H, 2.92; Br, 22.93; N, 4.01; S, 18.39.



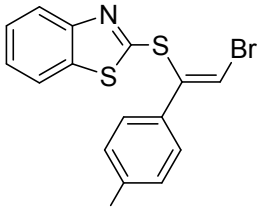
(*Z*)-2-((2-bromo-1-phenyvinyl)thio)-6-ethoxybenzo[*d*]thiazole (5b)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 9Hz, 1H), 7.5 (m, 2H), 7.23 (m, 4H), 7.0 (m, 1H), 6.98 (s, 1H), 6.9 (d, J = 8.8 Hz, 1H), 4.0 (q, 2H), 1.34 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 156.7, 147.4, 139.1, 137.6, 137.5, 129.1, 128.7, 127.9, 122.8, 115.7, 114.5, 104, 64, 29.7, 14.7; MS (LCMS, m/z) 392 [M]+; Anal. Calcd. for $C_{17}H_{14}BrNOS_2$: C, 52.04; H, 3.60; Br, 20.37; N, 3.57; O, 4.08; S, 16.35. Found: 52.03; H, 3.63; Br, 20.39; N, 3.52; O, 4.07; S, 16.36.



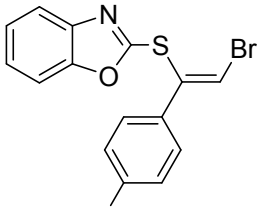
(*Z*)-2-((2-bromo-1-phenyvinyl)thio)benzo[*d*]oxazole (5c)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (m, 3H), 7.32-7.18 (m, 6H), 7.06 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 151.9, 141.7, 137.9, 136.8, 129.1, 128.6, 127.5, 124.6, 124.4, 119.2, 114.6, 110; MS (LCMS, m/z) 332 [M]+; Anal. Calcd. for $C_{15}H_{10}BrNOS$: C, 54.23; H, 3.03; Br, 24.05; N, 4.22; O, 4.82; S, 9.65. Found: C, 54.24; H, 3.01; Br, 24.07; N, 4.21; O, 4.82; S, 9.65.



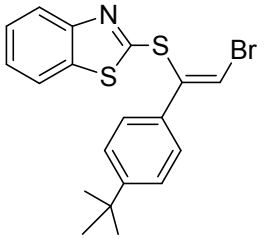
(*Z*)-2-((2-bromo-1-(*p*-tolyl)vinyl)phenyl)thio)benzo[*d*]thiazole (5d)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.3 Hz, 1H), 7.5 (d, J = 8.1 Hz, 2H), 7.4 (t, 1H), 7.28 (t, 1H), 7.14 (m, 3H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 153.2, 139.5, 138.5, 136.1, 134.6, 129.5, 127.7, 126.1, 124.5, 122.2, 122, 115.2, 21.2; MS (LCMS, m/z) 362 [M]+; Anal. Calcd. for $C_{16}H_{12}BrNS_2$: C, 53.04; H, 3.34; Br, 22.05; N, 3.87; S, 17.70. Found: C, 53.01; H, 3.31; Br, 22.07; N, 3.89; S, 17.72.



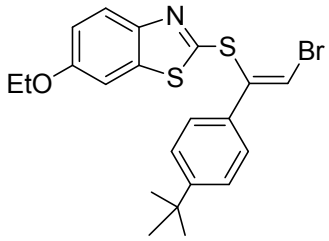
(*Z*)-2-((2-bromo-1-(*p*-tolyl)vinyl)phenyl)thio)benzo[*d*]oxazole (5e)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 6.9 Hz, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 6.9 Hz, 1H), 7.24 (m, 2H), 7.09 (d, J = 8 Hz, 2H), 7.04 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1, 151.9, 141.8, 139.2, 136.7, 135, 129.3, 127.3, 124.5, 124.4, 119.2, 113.9, 110, 21.2; MS (LCMS, m/z) 346 [M]+; Anal. Calcd. for $C_{16}H_{12}BrNOS$: C, 55.50; H, 3.49; Br, 23.08; N, 4.05; O, 4.62; S, 9.26. Found: C, 55.51; H, 3.45; Br, 23.09; N, 4.03; O, 4.61; S, 9.31.



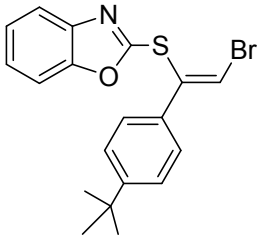
(*Z*)-2-((2-bromo-1-(4-(*tert*-butyl)vinyl)phenyl)thio)benzo[*d*]thiazole (5f)

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.8 (d, J = 3 Hz, 1H), 7.59 (d, J = 6.5 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.32 (t, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.21 (t, 1H), 7.13 (s, 1H), 1.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 153.1, 152.5, 138.1, 135.8, 134.5, 127.4, 126.1, 126, 124.5, 122, 120.8, 116.1, 34.6, 31; MS (LCMS, m/z) 405 [M]+; Anal. Calcd. for $C_{19}H_{18}BrNS_2$: C, 56.43; H, 4.49; Br, 19.76; N, 3.46; S, 15.86. Found: C, 56.46; H, 4.47; Br, 19.79; N, 3.45; S, 15.83.



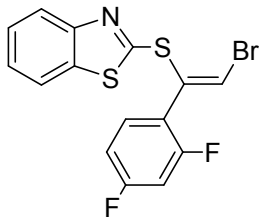
(*Z*)-2-((2-bromo-1-(4-(*tert*-butyl)vinyl)phenyl)thio)-6-ethoxy-benzo[*d*]thiazole (5g)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.9 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.11 (m, 2H), 7.0 (m, 1H), 4.07 (q, 2H), 1.44 (t, 3H), 1.26 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 156.6, 152.5, 147.5, 138.7, 137.5, 134.6, 127.5, 125.7, 122.8, 115.6, 104.4, 64, 34.7, 31.1, 14.8; MS (LCMS, m/z) 449 [M]+; Anal. Calcd. for $C_{21}H_{22}BrNOS_2$: C, 56.24; H, 4.94; Br, 17.82; N, 3.12; O, 3.57; S, 14.30. Found: C, 56.24; H, 4.92; Br, 17.80; N, 3.10; O, 3.59; S, 14.35.



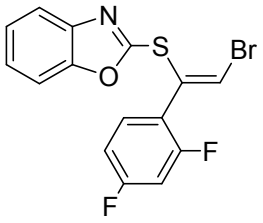
(*Z*)-2-((2-bromo-1-(4-(*tert*-butyl)vinyl)phenyl)thio)benzo[*d*]oxazole (5h)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 2 Hz, 1H), 7.52 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 6.5 Hz, 1H), 7.3 (d, J = 7.4 Hz, 2H), 7.25 (t, 1H), 7.09 (s, 1H), 1.24 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 153.5, 143.8, 131.6, 129.5, 127.3, 126.1, 125.3, 124, 122.5, 116.6, 111.3, 109.9, 34.8, 31.2; MS (LCMS, m/z) 389 [M]+; Anal. Calcd. for $C_{19}H_{18}BrNOS$: C, 58.77; H, 4.67; Br, 20.58; N, 3.61; O, 4.13; S, 8.26. Found: C, 58.79; H, 4.65; Br, 20.62; N, 3.61; O, 4.10; S, 8.23.



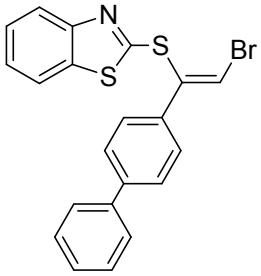
***Z*)-2-((2-bromo-1-(2,4-difluorophenyl)vinyl)thio)benzo[*d*]thiazole (5i)**

Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.5 Hz, 1H), 7.75 (d, J = 8 Hz, 1H), 7.58 (m, 1H), 7.45 (t, 1H), 7.34 (t, 1H), 7.19 (s, 1H), 6.86 (q, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 153, 135.9, 131.9, 126.2, 124.8, 122.2, 121.3, 118.5, 111.6, 104.4; MS (LCMS, m/z) 384 [M]+; Anal. Calcd. for $C_{15}H_8BrF_2NS_2$: C, 46.88; H, 2.10; Br, 20.79; F, 9.89; N, 3.65; S, 16.69. Found: C, 46.85; H, 2.12; Br, 20.78; F, 9.85; N, 3.67; S, 16.73.



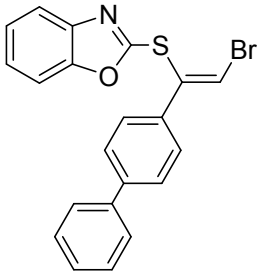
(*Z*)-2-((2-bromo-1-(2,4-difluorophenyl)vinyl)thio)benzo[*d*]oxazole (5j)

Light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6 (m, 2H), 7.4 (d, J = 8.5 Hz, 1H), 7.28 (m, 2H), 7.12 (s, 1H), 6.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 151.6, 140.2, 131.9, 125.2, 125, 122.5, 124, 118.9, 110.2, 104.5; MS (LCMS, m/z) 366 [M]+; Anal. Calcd. for $C_{15}H_8BrF_2NOS$: C, 48.93; H, 2.19; Br, 21.70; F, 10.32; N, 3.80; O, 4.35; S, 8.67. Found: C, C, 48.96; H, 2.17; Br, 21.73; F, 10.31; N, 3.82; O, 4.33; S, 8.68.



(*Z*)-2-((1-([1,1[1]-biphenyl]-4-yl-)-2-bromovinyl)thio)benzo[*d*]thiazole (5k)

Yellow oil; [1]H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 1H), 7.68 (t, 3H), 7.54 (m, 4H), 7.4 (m, 3H), 7.27 (m, 1H), 7.21(s, 1H); [13]C NMR (75 MHz, $CDCl_3$) δ 163.9, 153.2, 142, 139.9, 138.2, 136.4, 136, 128.2, 127.8, 127, 126.2, 124.7, 120.9, 116.3; MS (LCMS, m/z) 424 [M]+; Anal. Calcd. for $C_{21}H_{14}BrNS_2$: C, 59.43; H, 3.33; Br, 18.83; N, 3.30; S, 15.11. Found: C, 59.44; H, 3.30; Br, 18.85; N, 3.34; S, 15.07.



(*Z*)-2-((1-([1,1[1]-biphenyl]-4-yl-)-2-bromovinyl)thio)benzo[*d*]oxazole (5l)

Yellow oil; [1]H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J = 8Hz, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.55 (m, 5H), 7.39 (m, 3H), 7.22 (m, 2H), 7.14 (s, 1H); [13]C NMR (75 MHz, $CDCl_3$) δ 160, 151.9, 141.8, 139.9, 136.4, 128.8, 127.9, 127.7, 127, 126.9, 124.6, 124.4, 119.2, 114.9, 110; MS (LCMS, m/z) 409 [M]+; Anal. Calcd. for $C_{21}H_{14}BrNOS$: C, 61.77; H, 3.46; Br, 19.57; N, 3.43; O, 3.92; S, 7.85. Found: C, 61.77; H, 3.45; Br, 19.58; N, 3.41; O, 3.94; S, 7.85.

NMR Spectra of the Products:

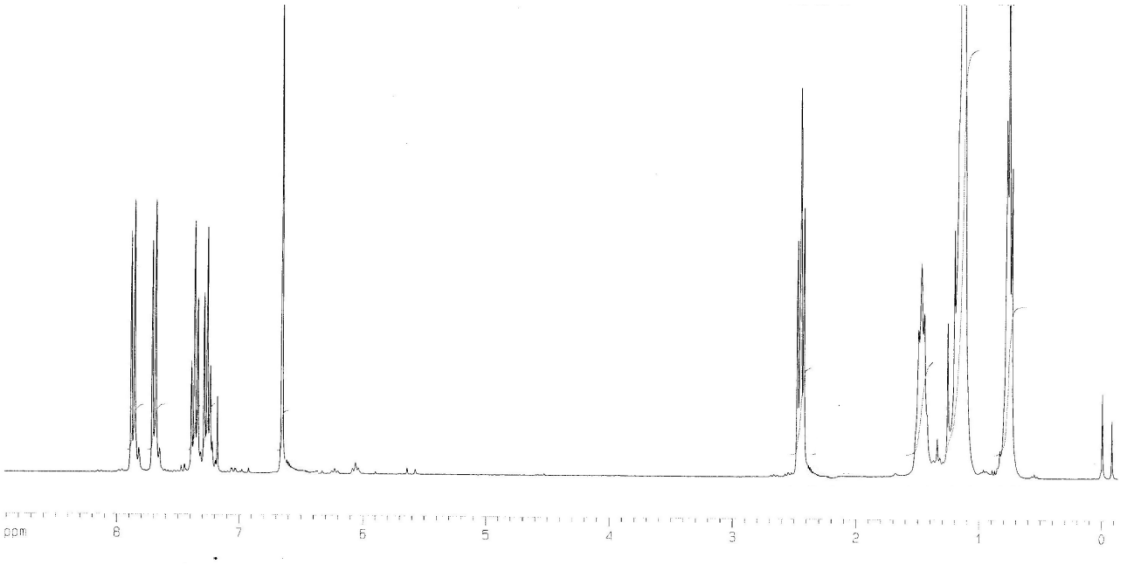


Fig S-1: ^{1}H NMR Spectrum of Product **3a**

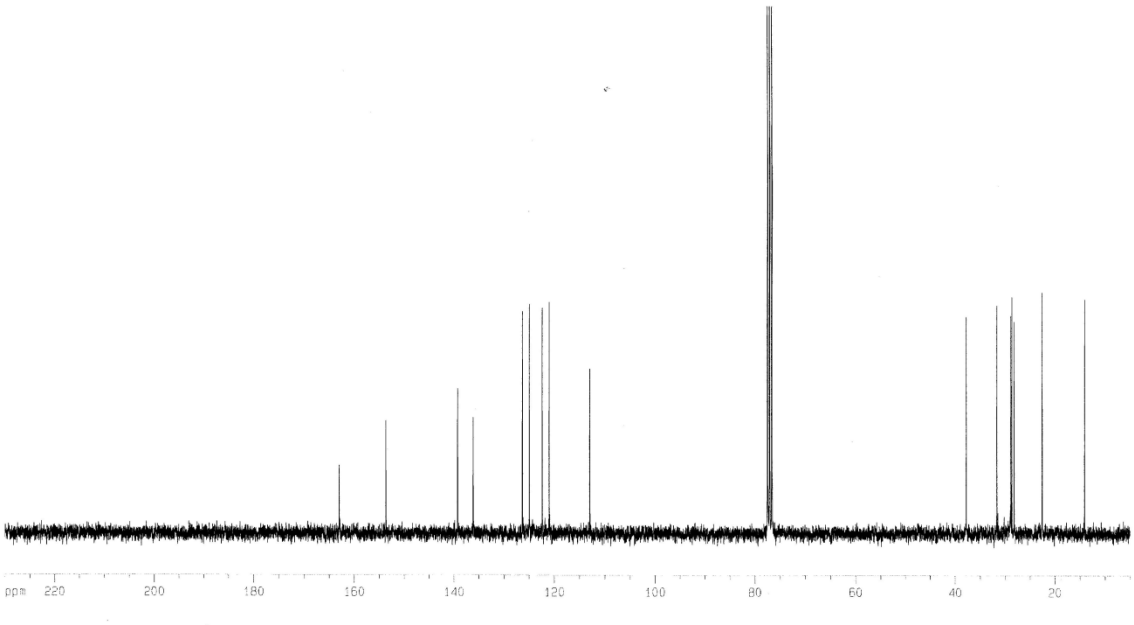


Fig S-2: ^{13}C NMR Spectrum of Product **3a**

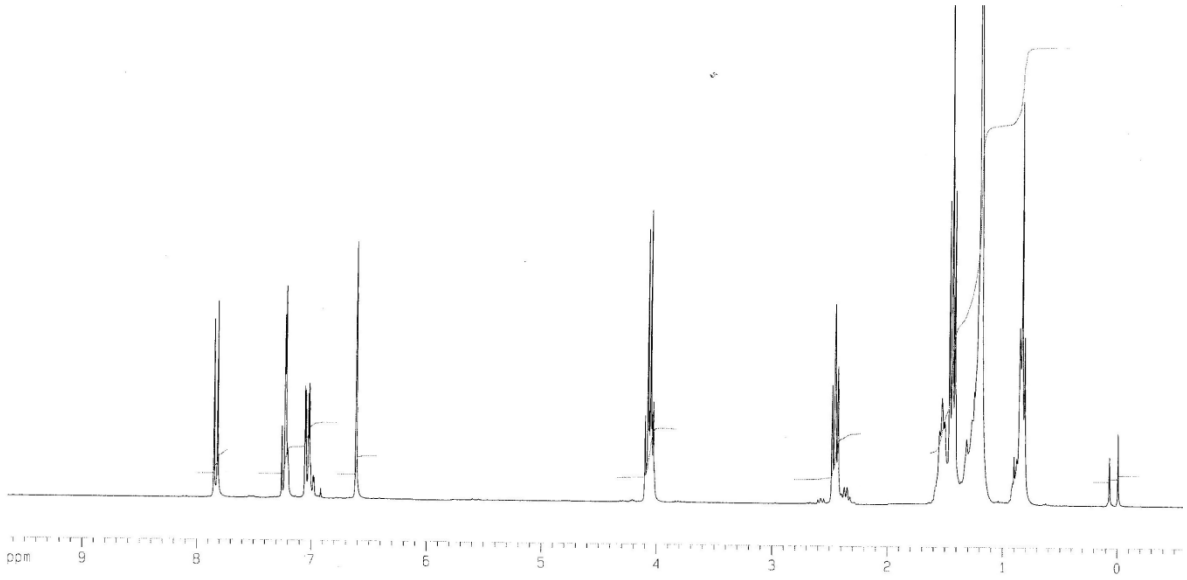


Fig S-3: ^{1}H NMR Spectrum of Product **3b**

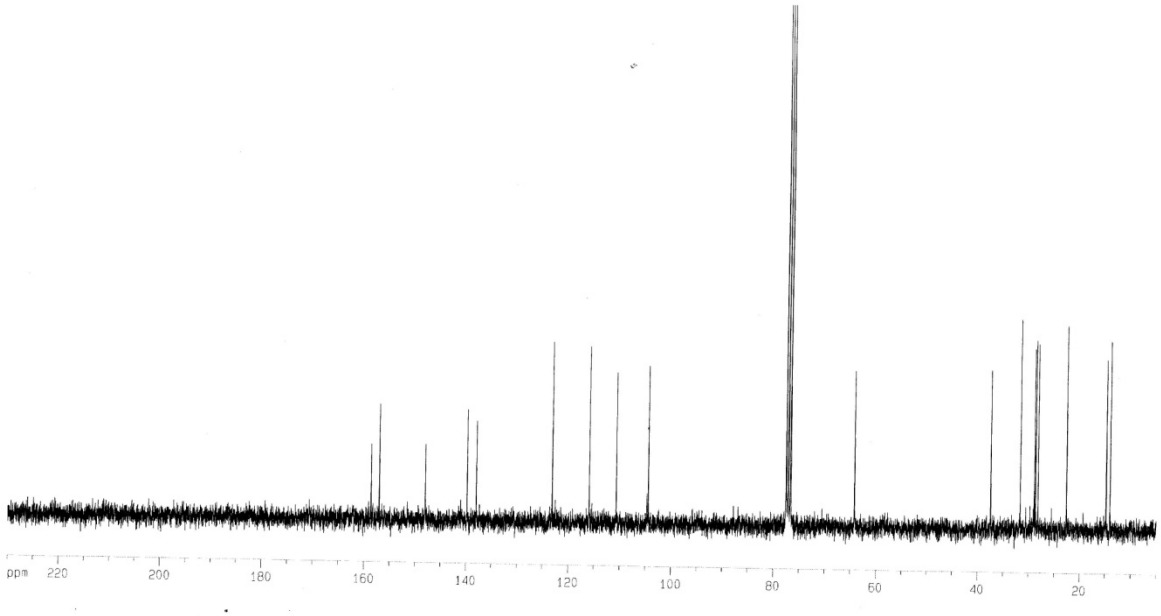


Fig S-4: ^{13}C NMR Spectrum of Product **3b**

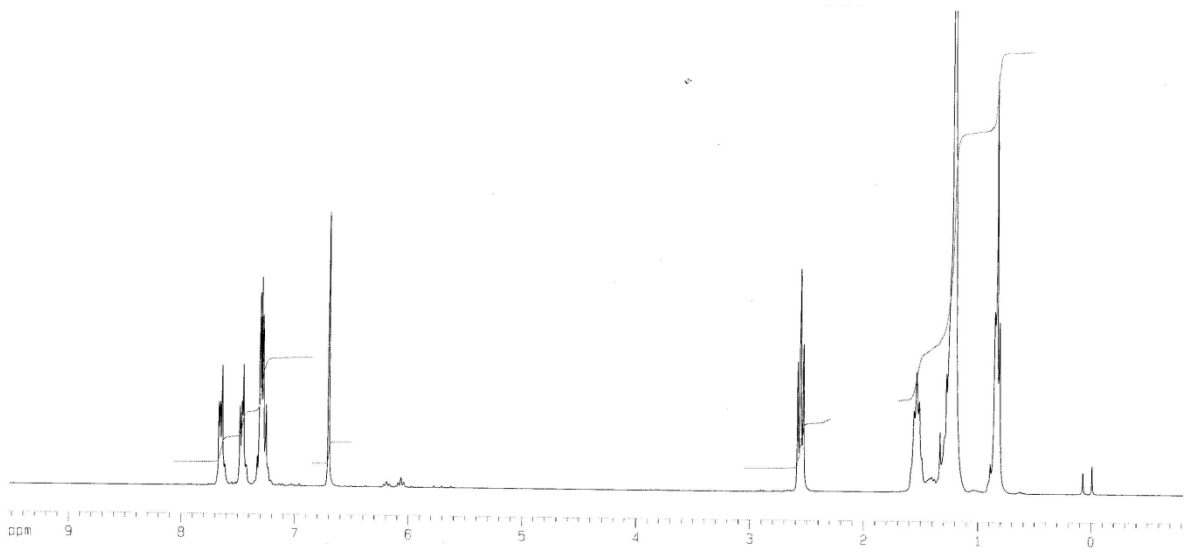


Fig S-5: ^{1}H NMR Spectrum of Product **3c**

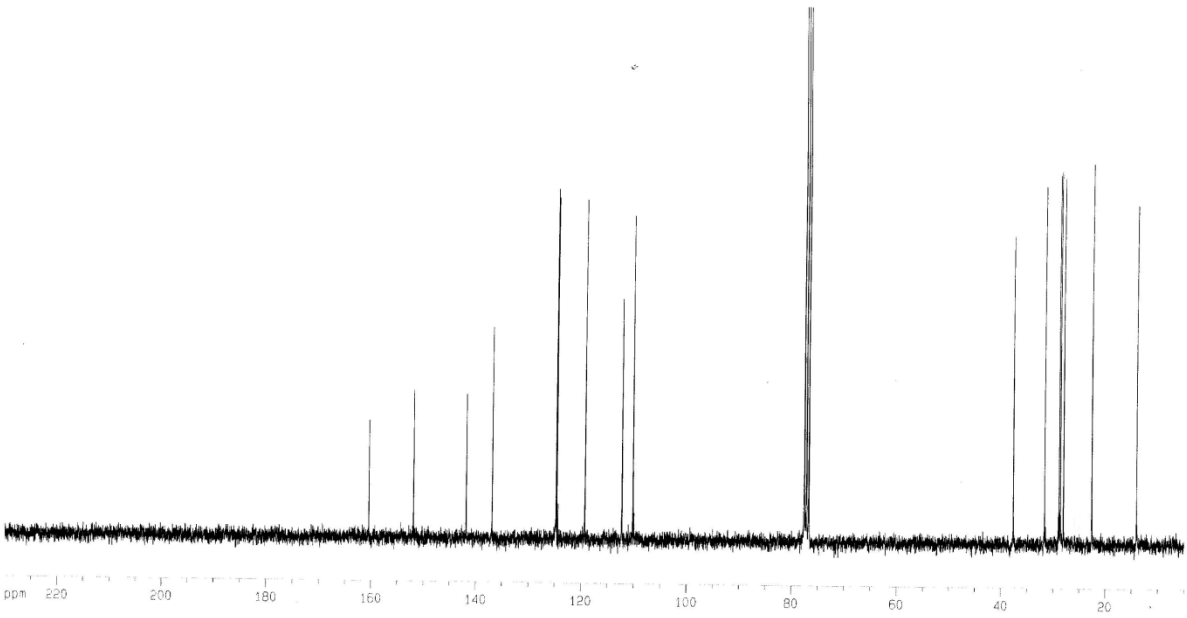


Fig S-6: ^{13}C NMR Spectrum of Product **3c**

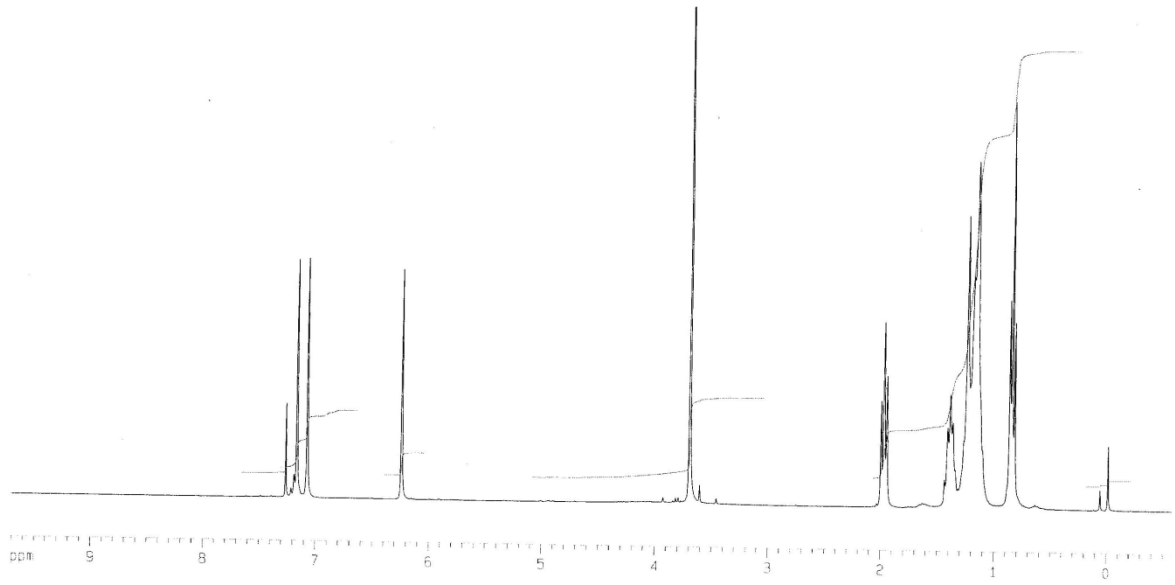


Fig S-7: ^{1}H NMR Spectrum of Product **3d**

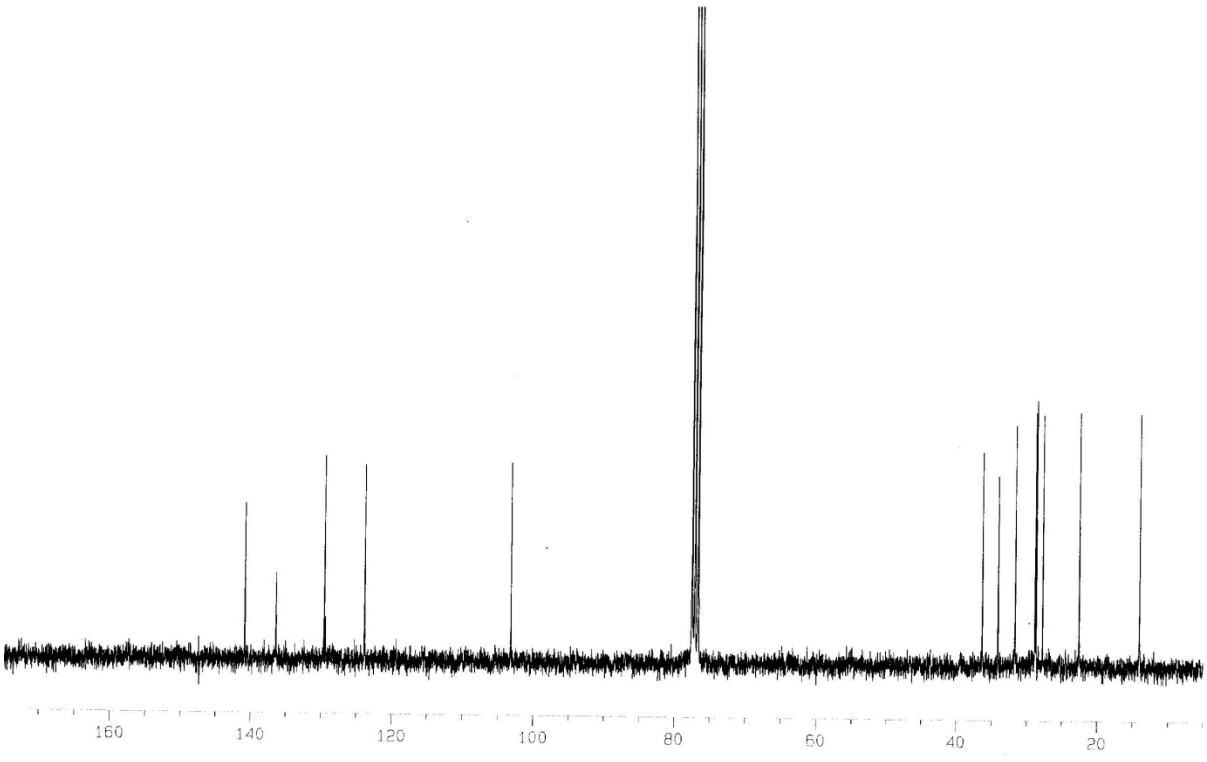


Fig S-8: ^{13}C NMR Spectrum of Product **3d**

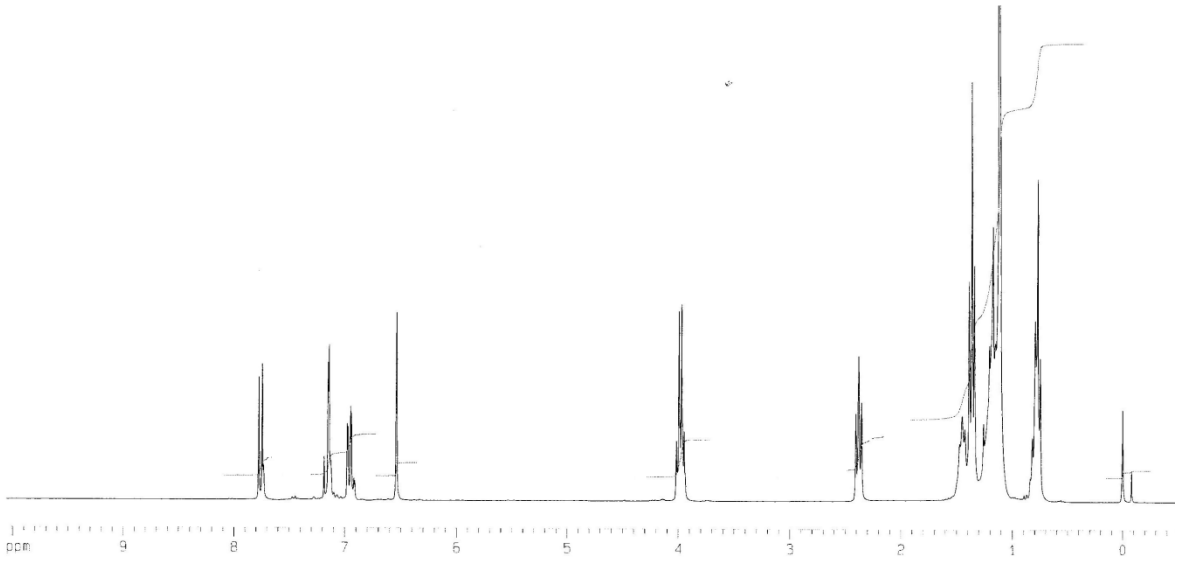


Fig S-9: ^{1}H NMR Spectrum of Product **3f**

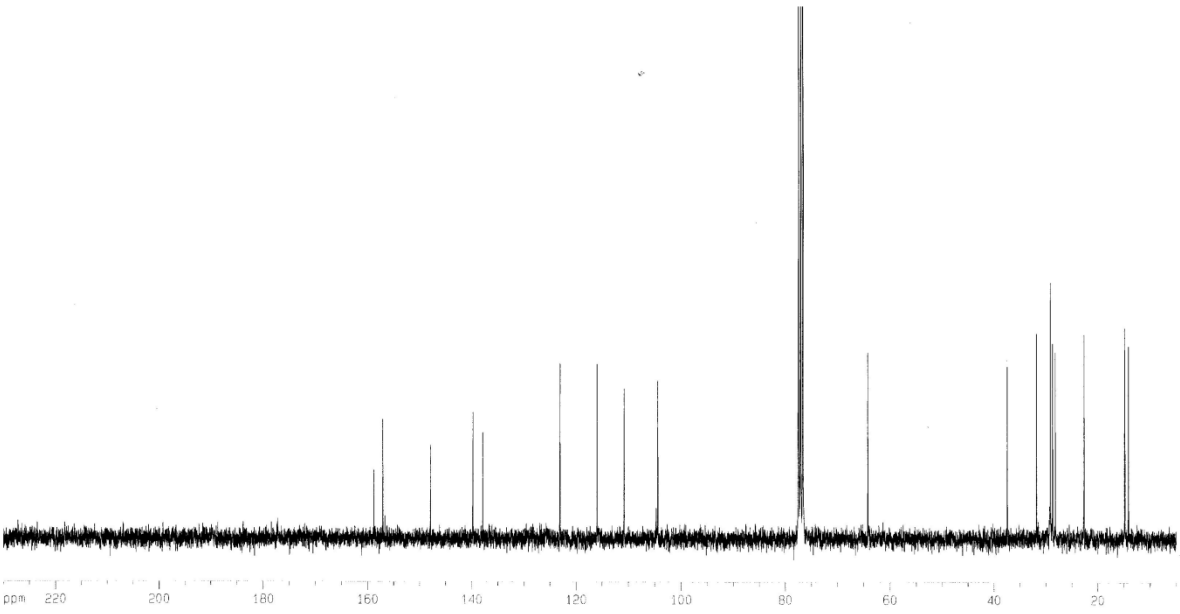


Fig S-10: ^{13}C NMR Spectrum of Product **3f**

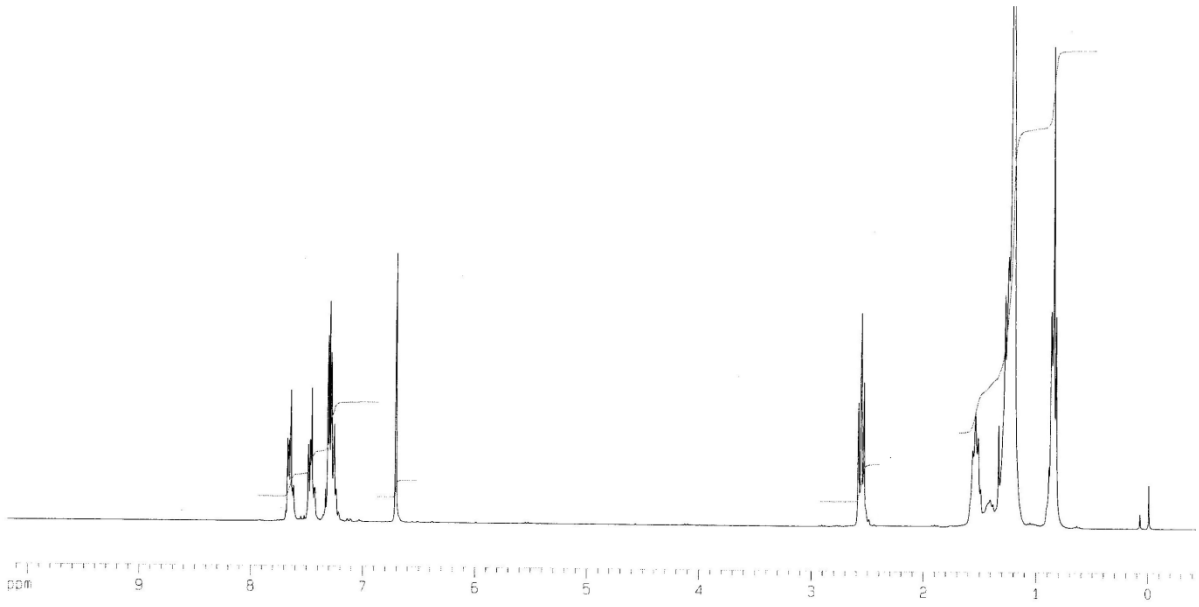


Fig S-11: ^{1}H NMR Spectrum of Product **3g**

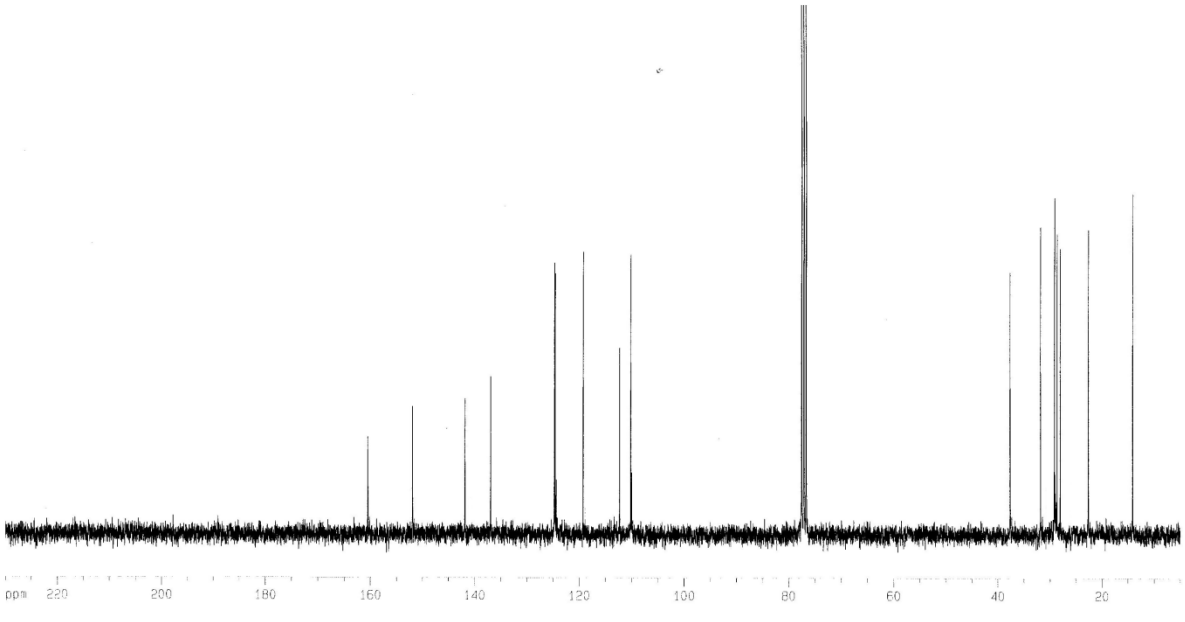


Fig S-12: ^{13}C NMR Spectrum of Product **3g**

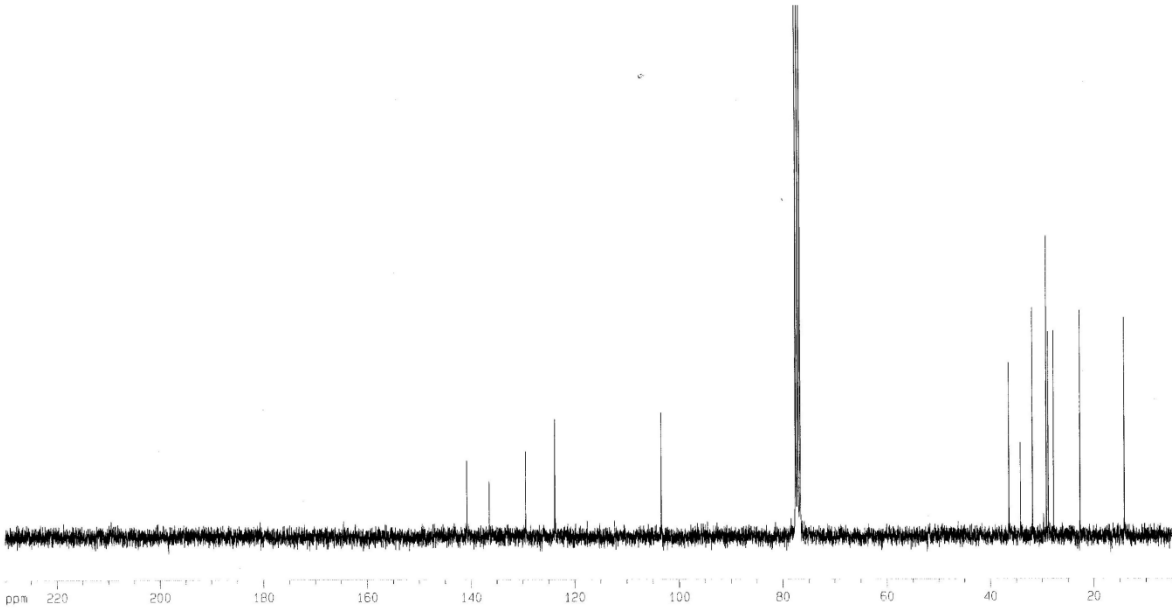


Fig S-13: ^{13}C NMR Spectrum of Product **3h**

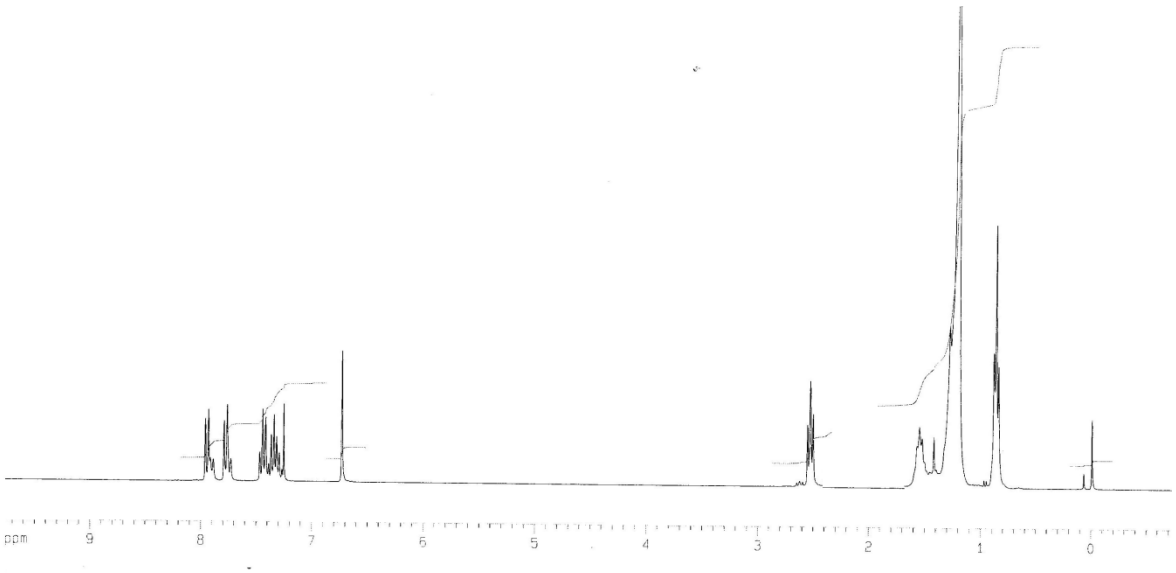


Fig S-14: ^{1}H NMR Spectrum of Product **3i**

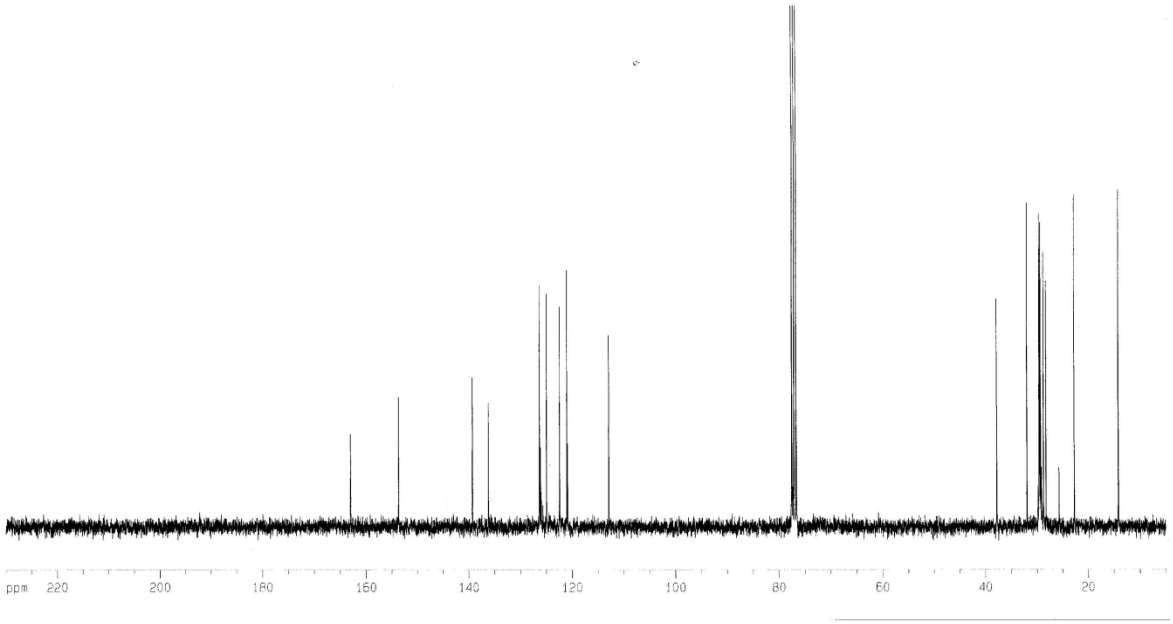


Fig S-15: ^{13}C NMR Spectrum of Product **3i**

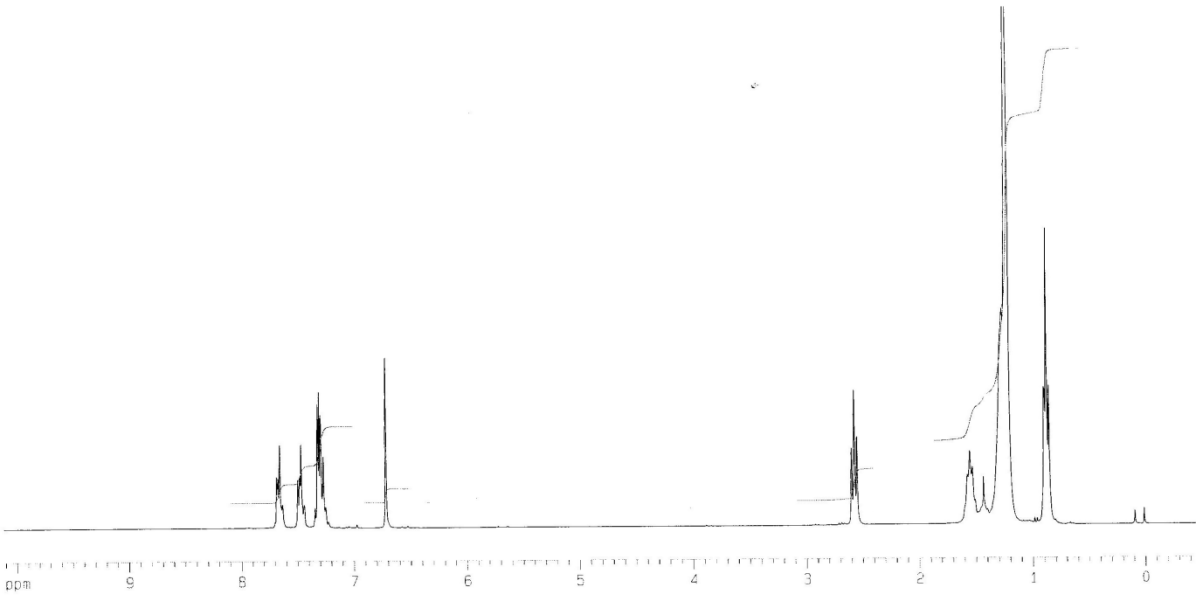


Fig S-16: ^{1}H NMR Spectrum of Product **3j**

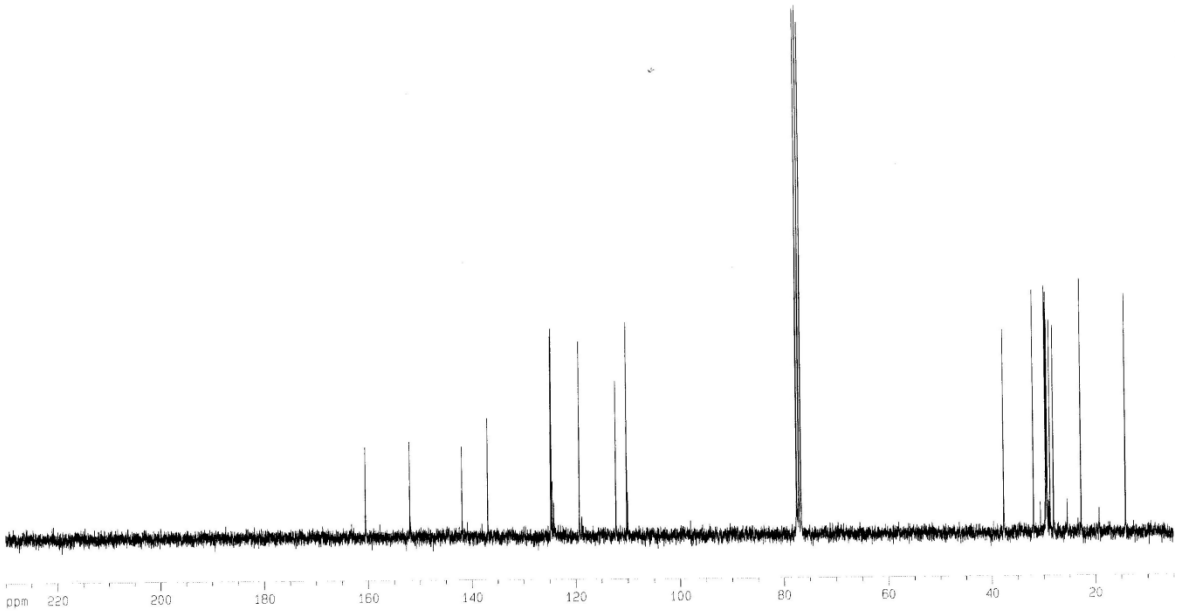


Fig S-17: ^{13}C NMR Spectrum of Product **3j**

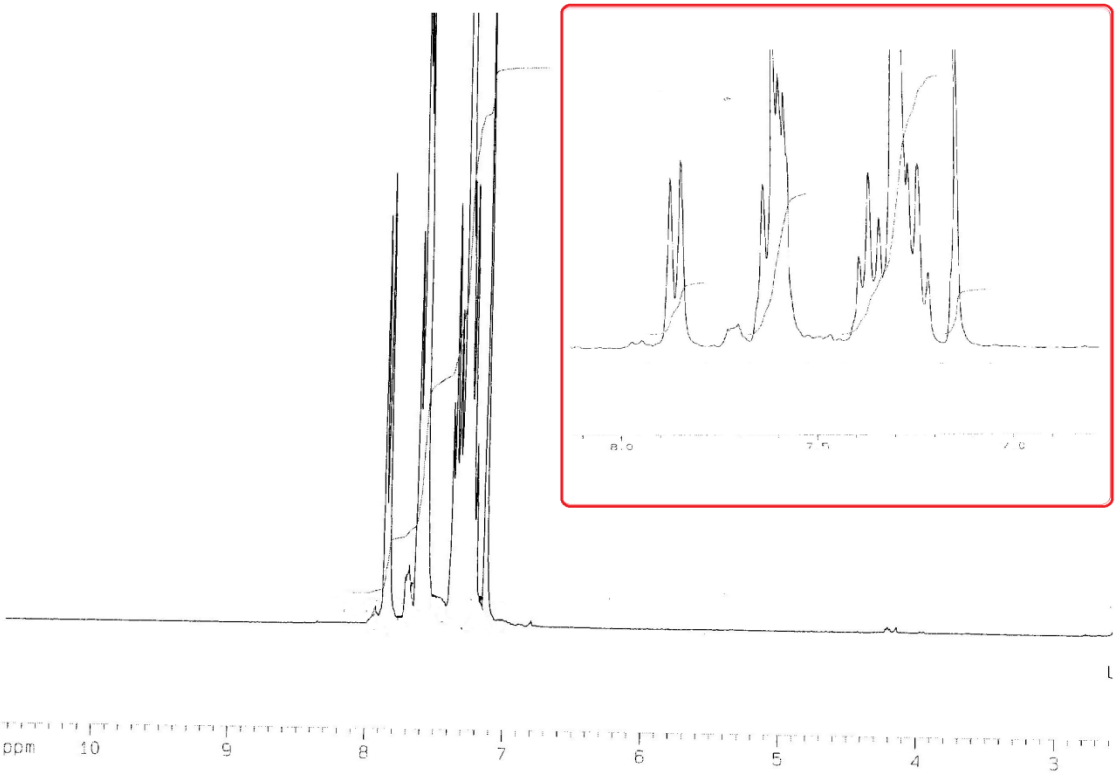


Fig S-18: ^{1}H NMR Spectrum of Product **5a**

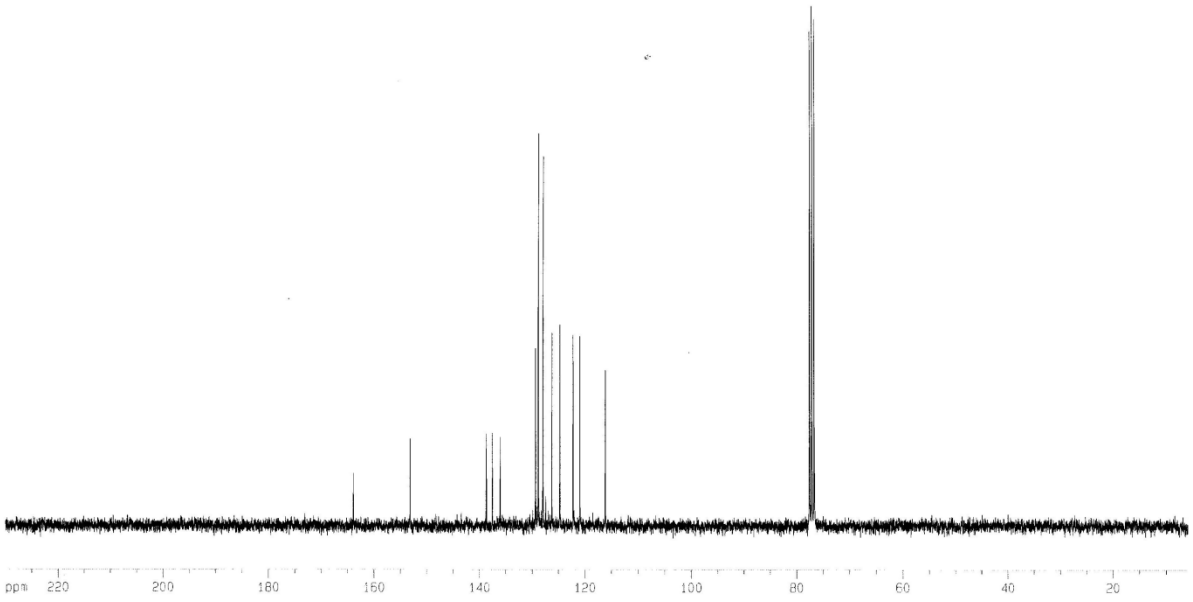


Fig S-19: ^{13}C NMR Spectrum of Product **5a**

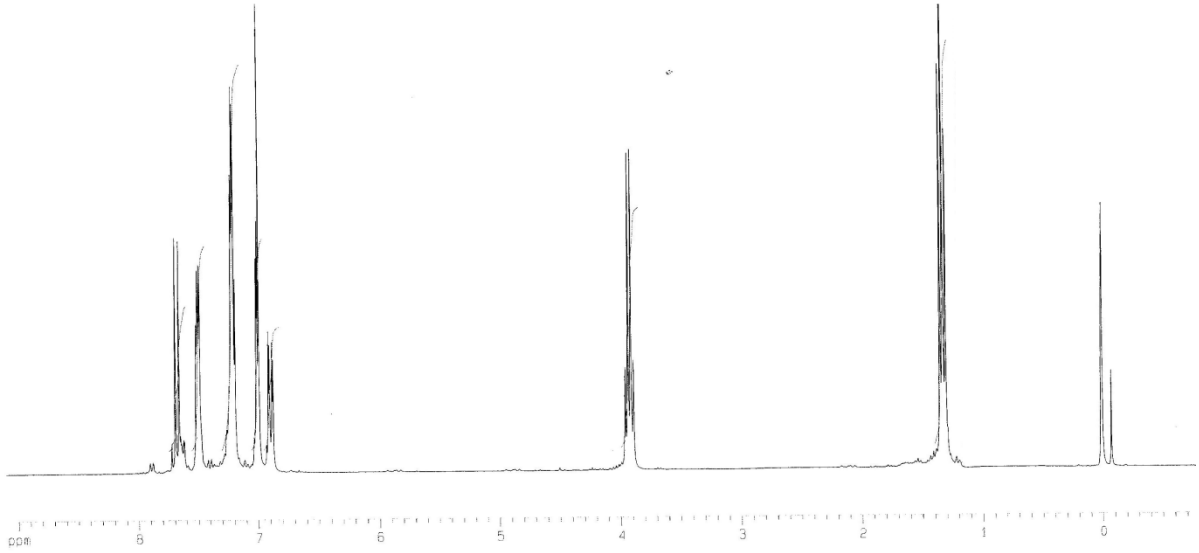


Fig S-20: ^{1}H NMR Spectrum of Product **5b**

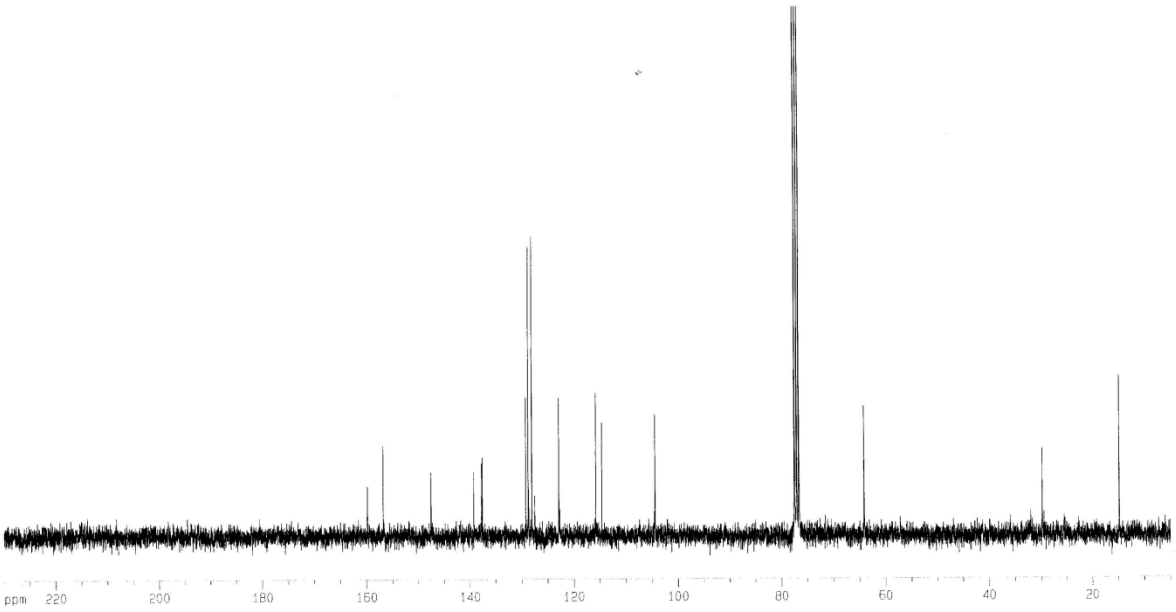


Fig S-21: ^{13}C NMR Spectrum of Product **5b**

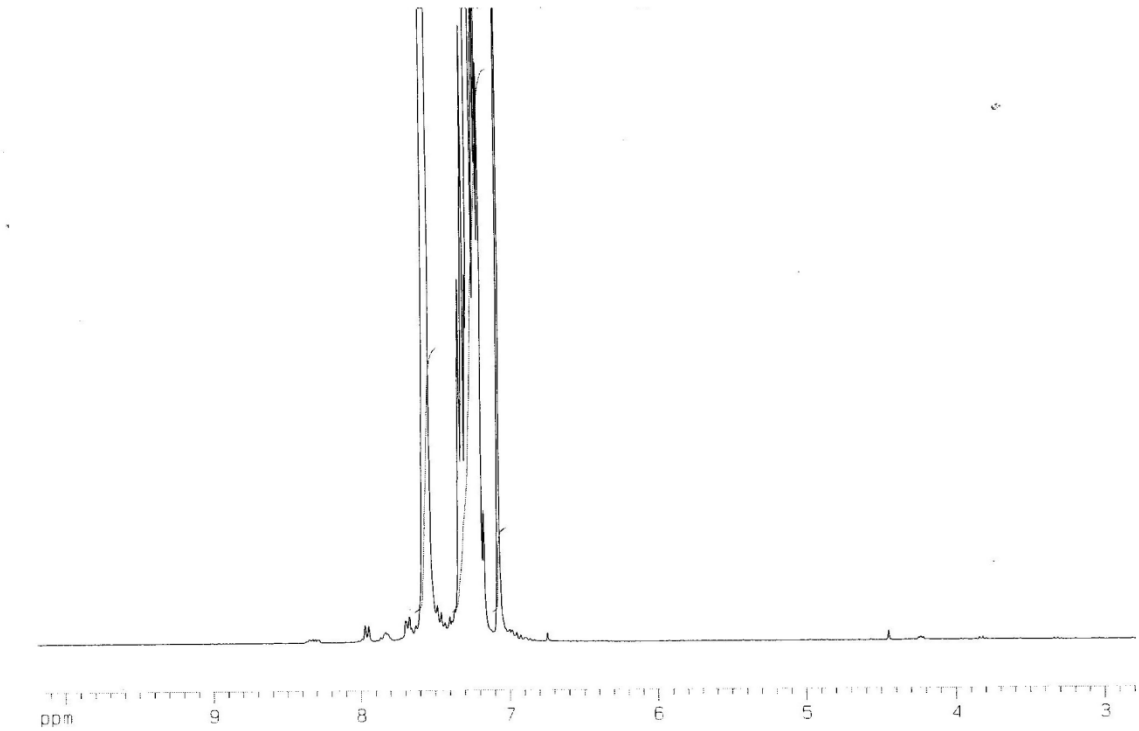


Fig S-22: ^{1}H NMR Spectrum of Product **5c**

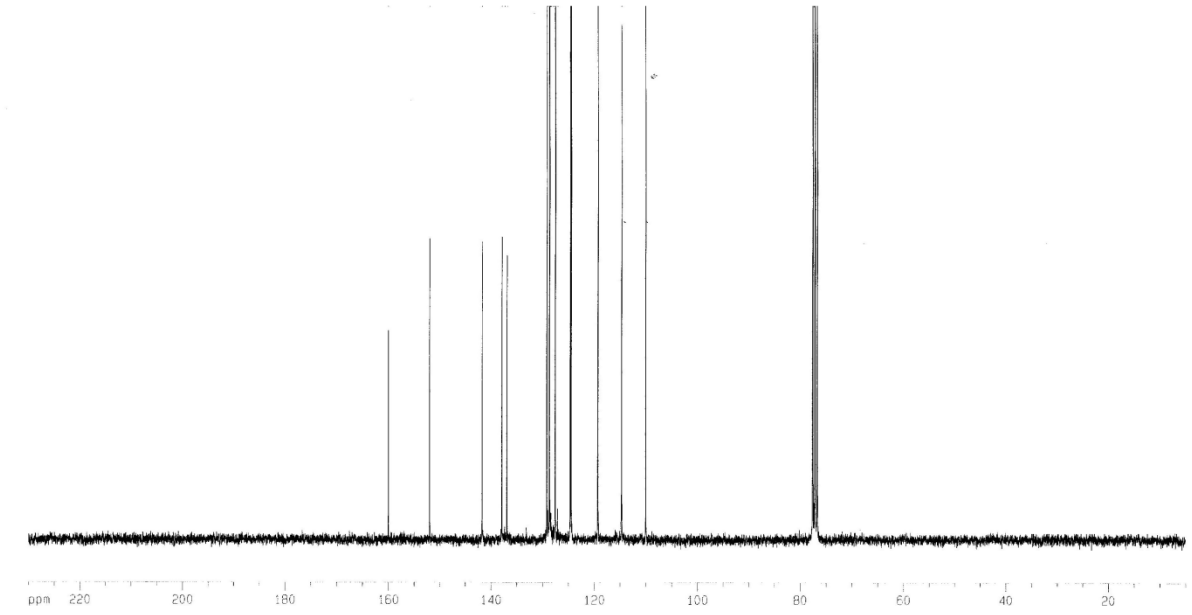


Fig S-23: ^{13}C NMR Spectrum of Product **5c**

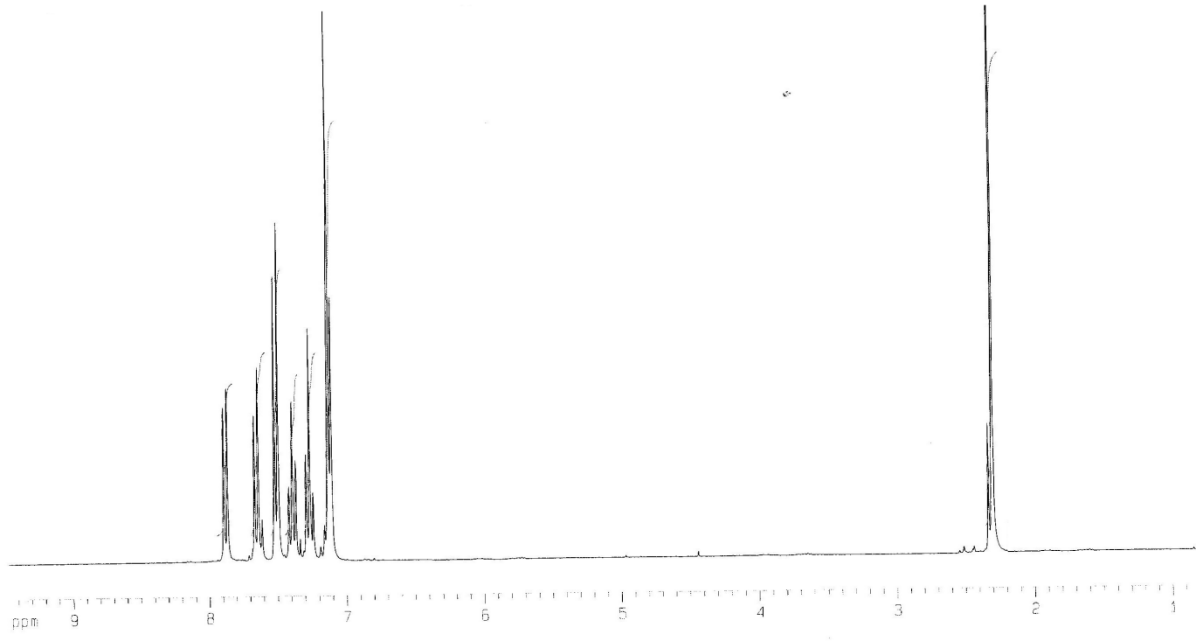


Fig S-24: ^{1}H NMR Spectrum of Product **5d**

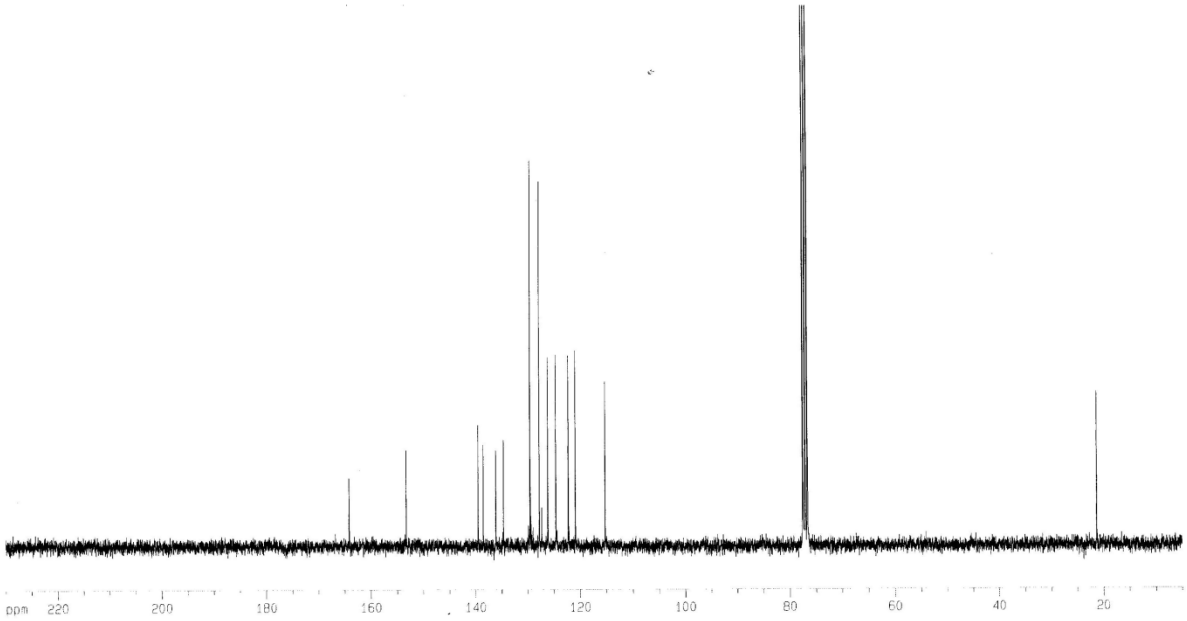


Fig S-25: ^{13}C NMR Spectrum of Product **5d**

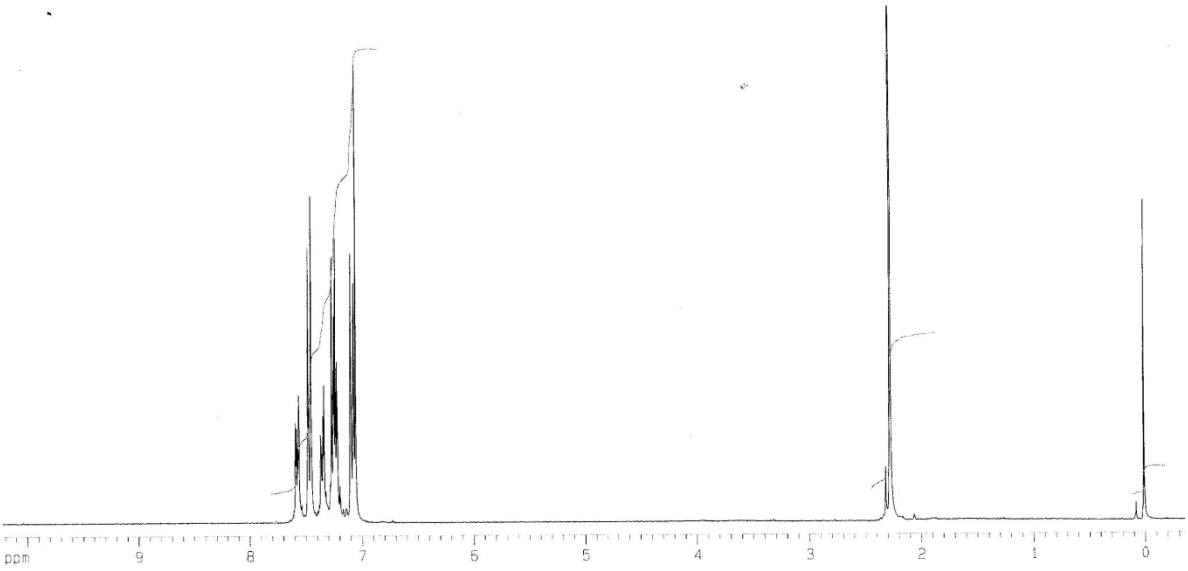


Fig S-26: ^{1}H NMR Spectrum of Product **5e**

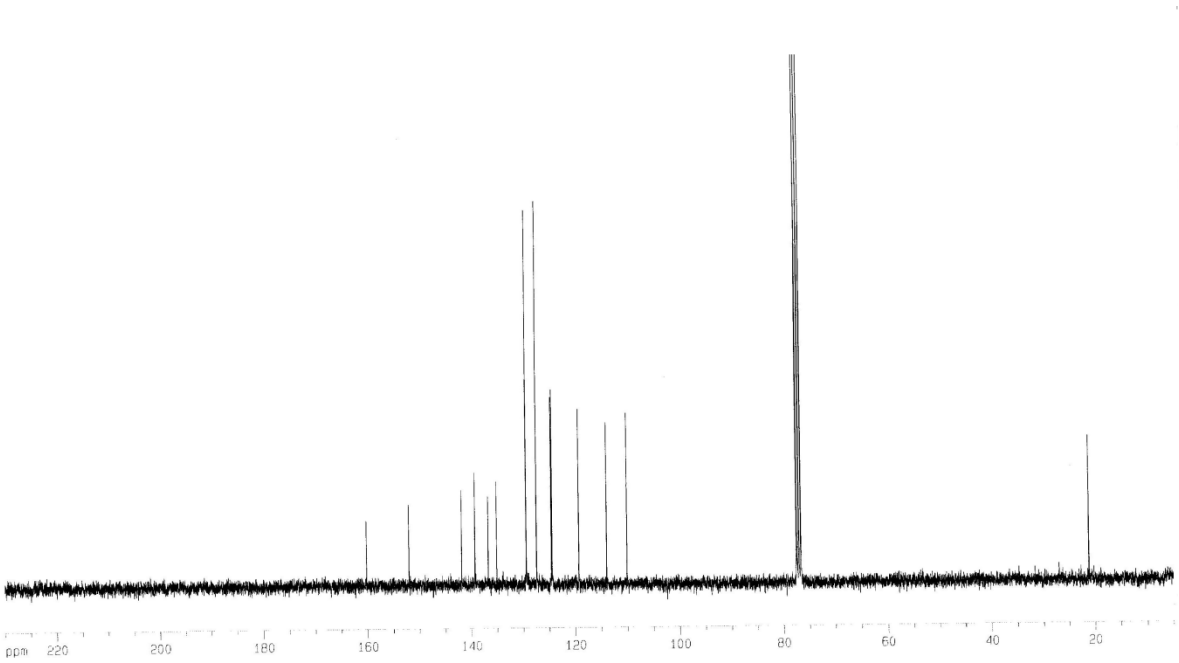


Fig S-27: ^{13}C NMR Spectrum of Product **5e**

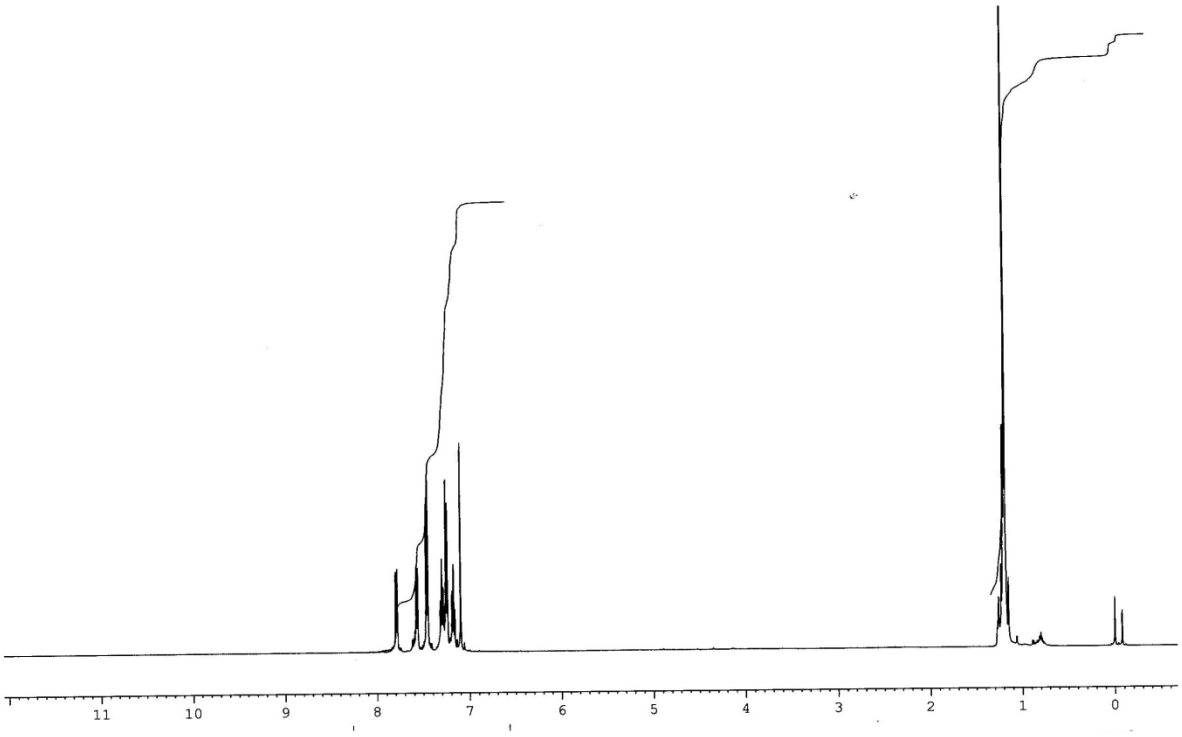


Fig S-28: ^{1}H NMR Spectrum of Product **5f**

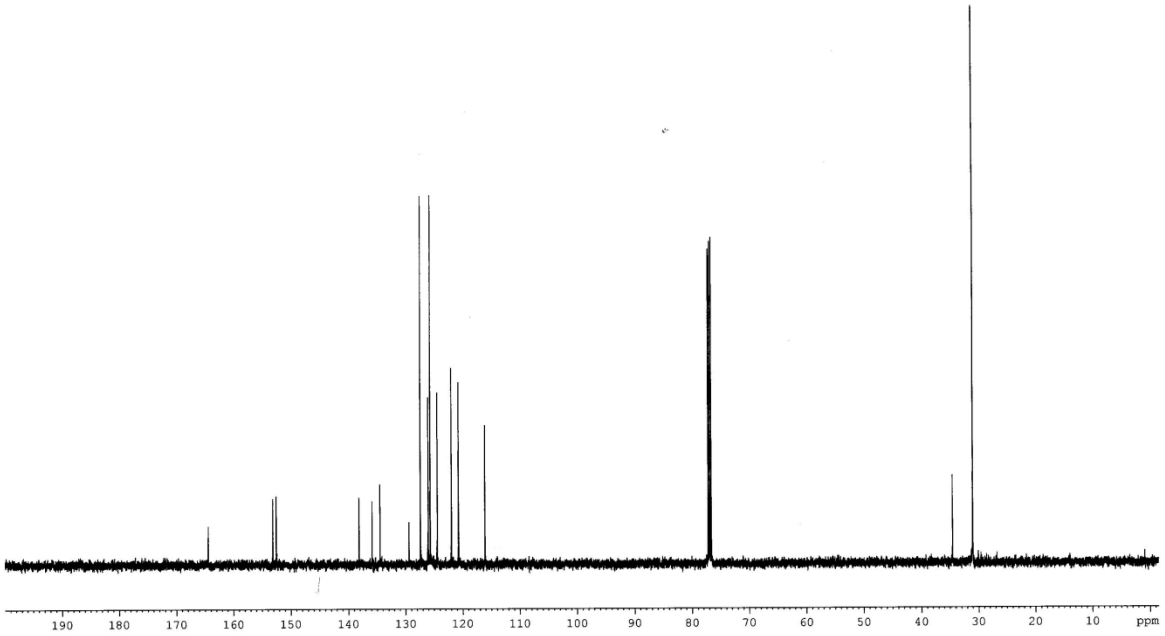


Fig S-29: ^{13}C NMR Spectrum of Product **5f**

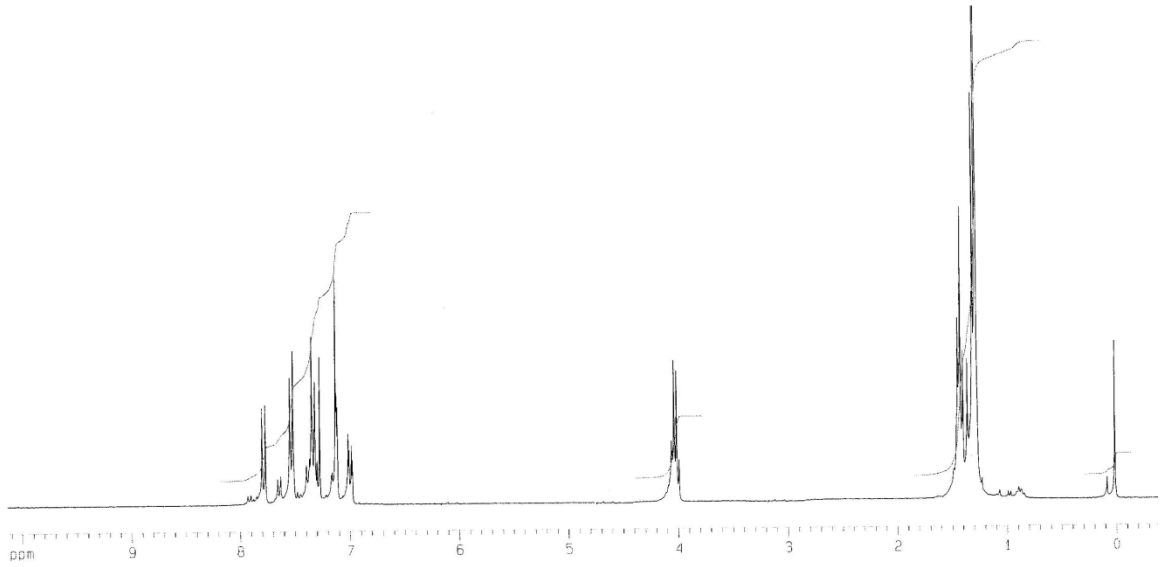


Fig S-30: ^{1}H NMR Spectrum of Product **5g**

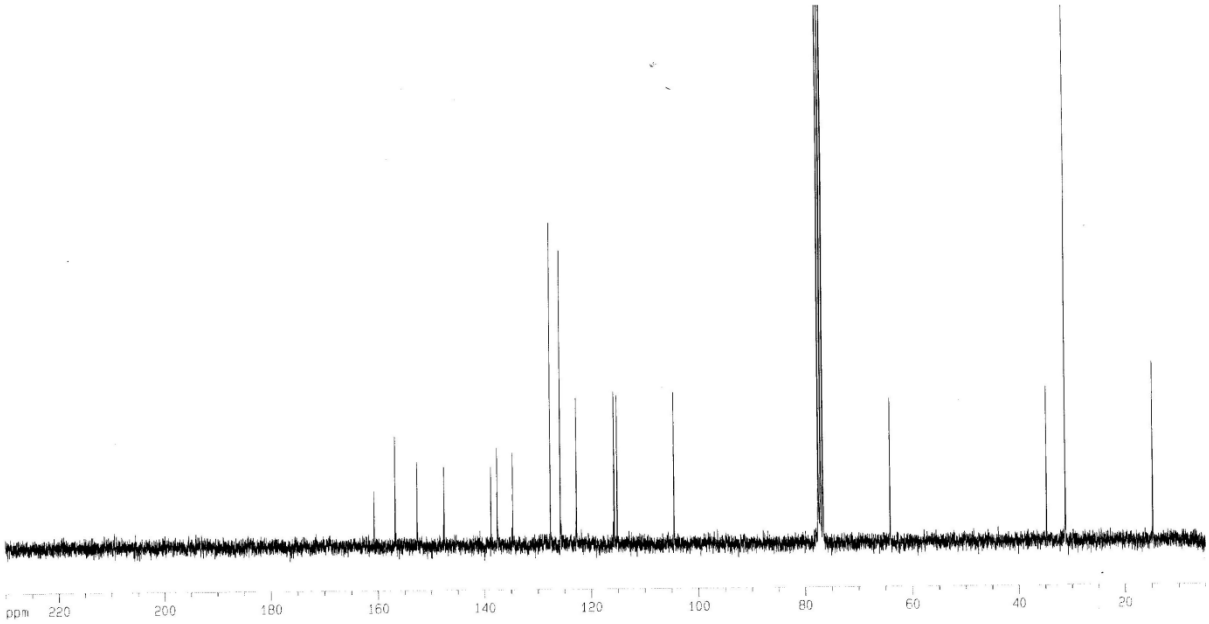


Fig S-31: ^{13}C NMR Spectrum of Product **5g**

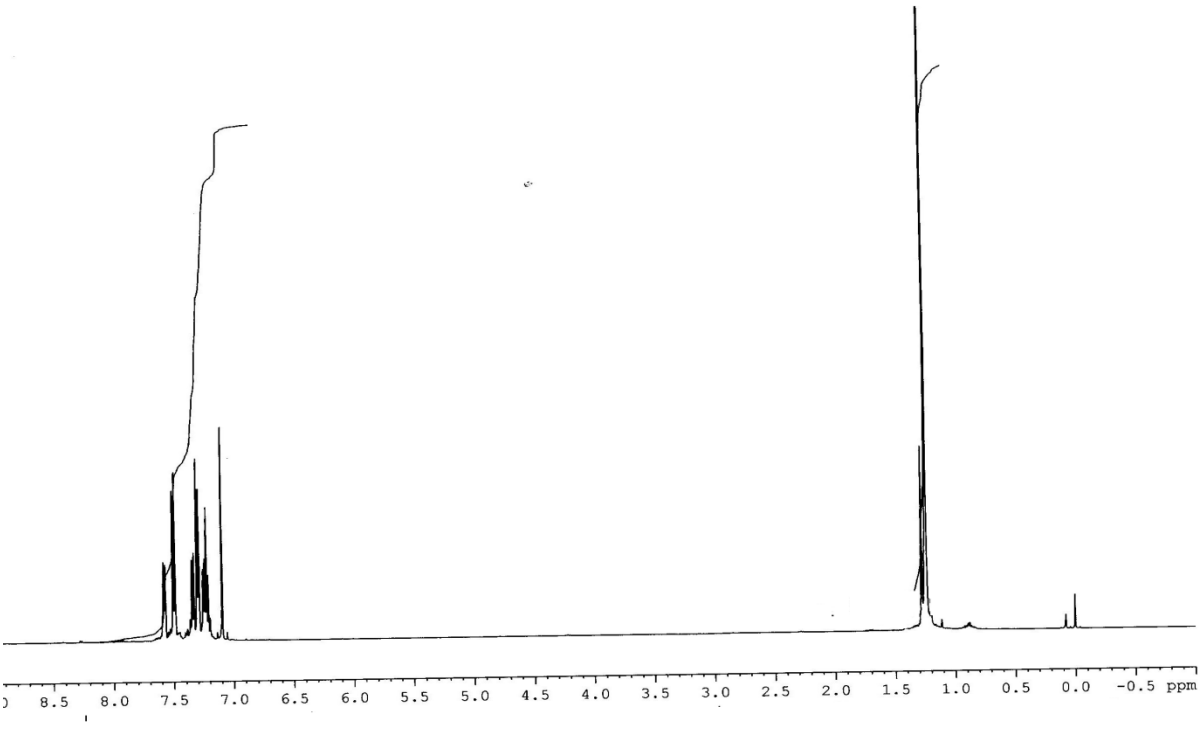


Fig S-32: ^{1}H NMR Spectrum of Product **5h**

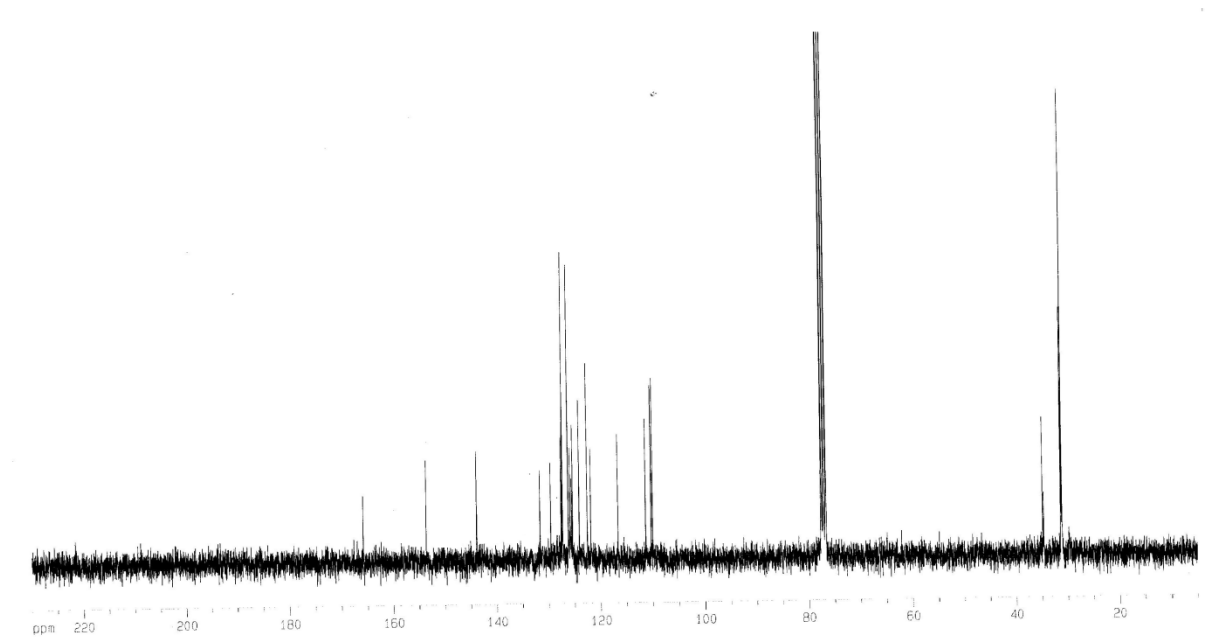


Fig S-33: ^{13}C NMR Spectrum of Product **5h**

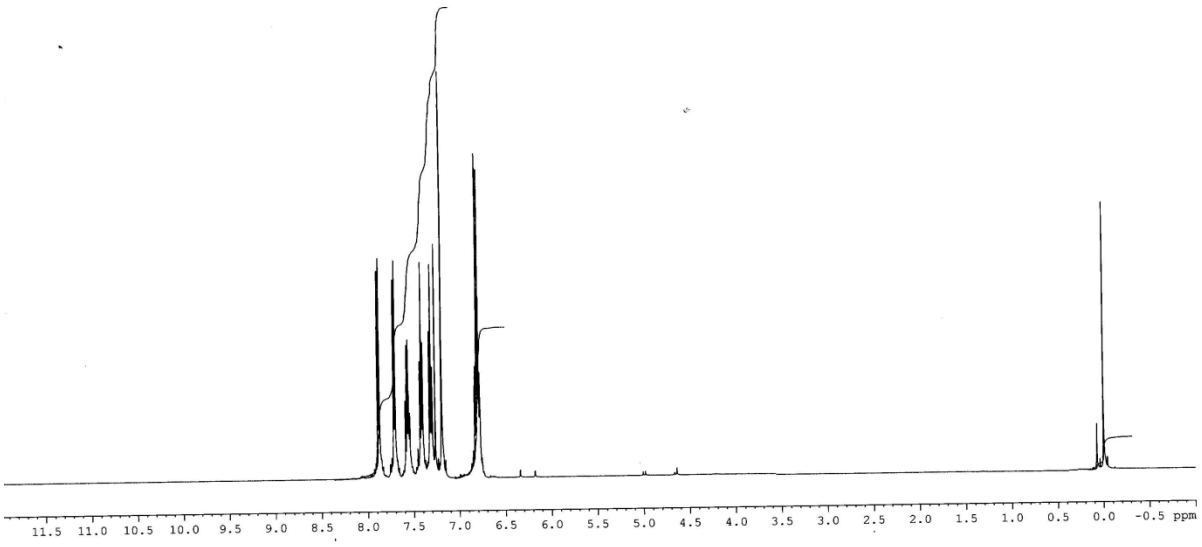


Fig S-34: ^{1}H NMR Spectrum of Product **5i**

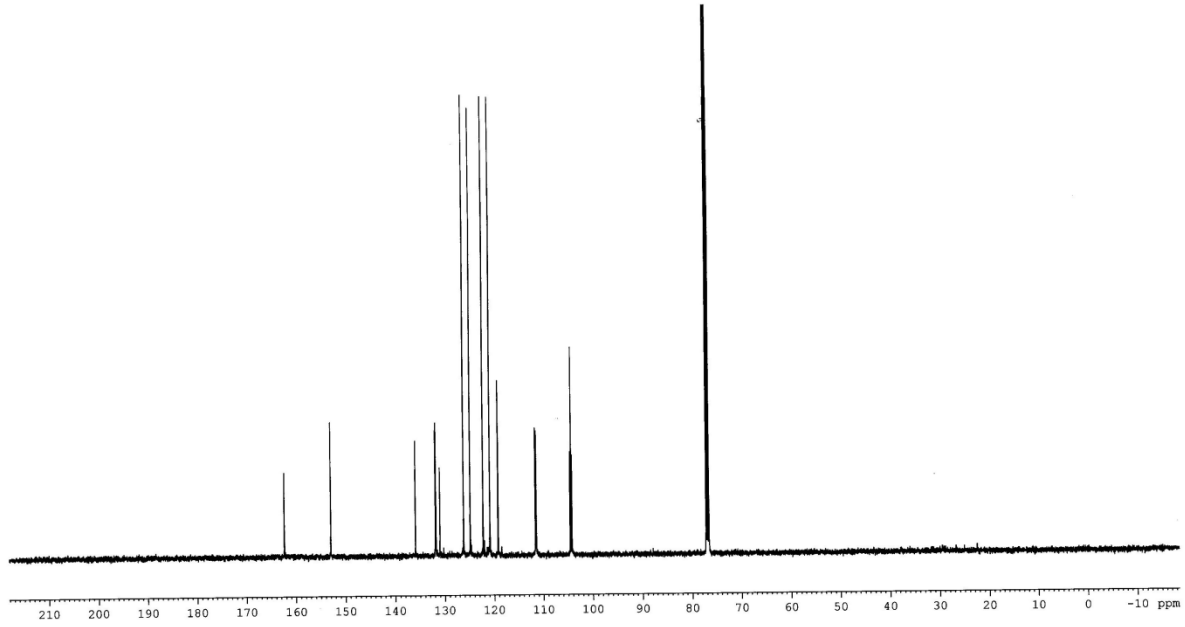


Fig S-35: ^{13}C NMR Spectrum of Product **5i**

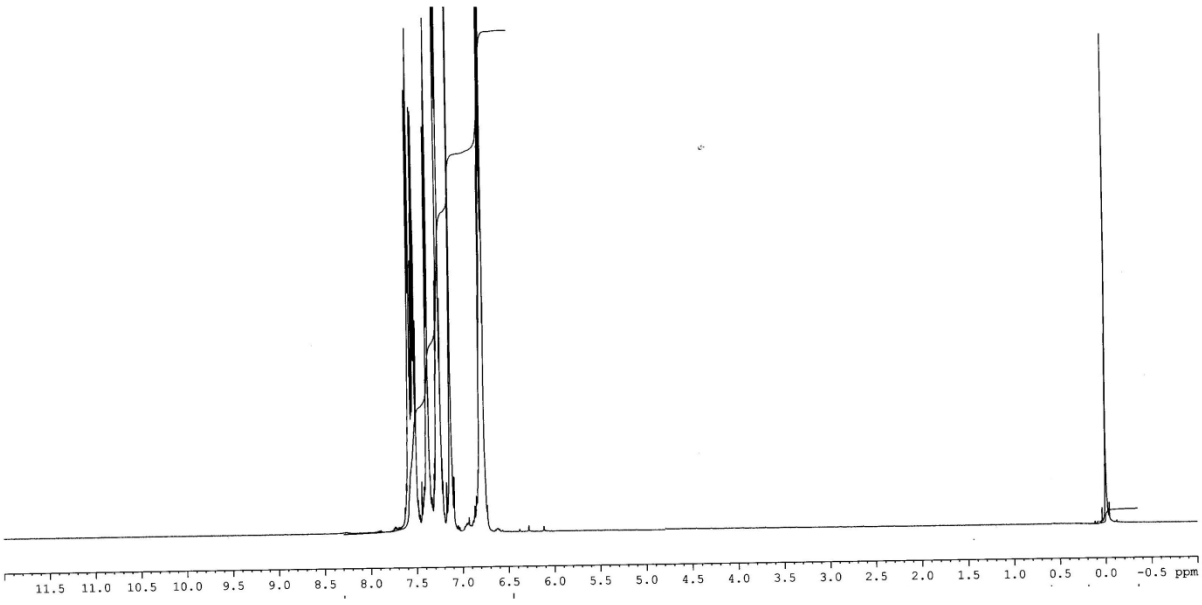


Fig S-36: ^{1}H NMR Spectrum of Product **5j**

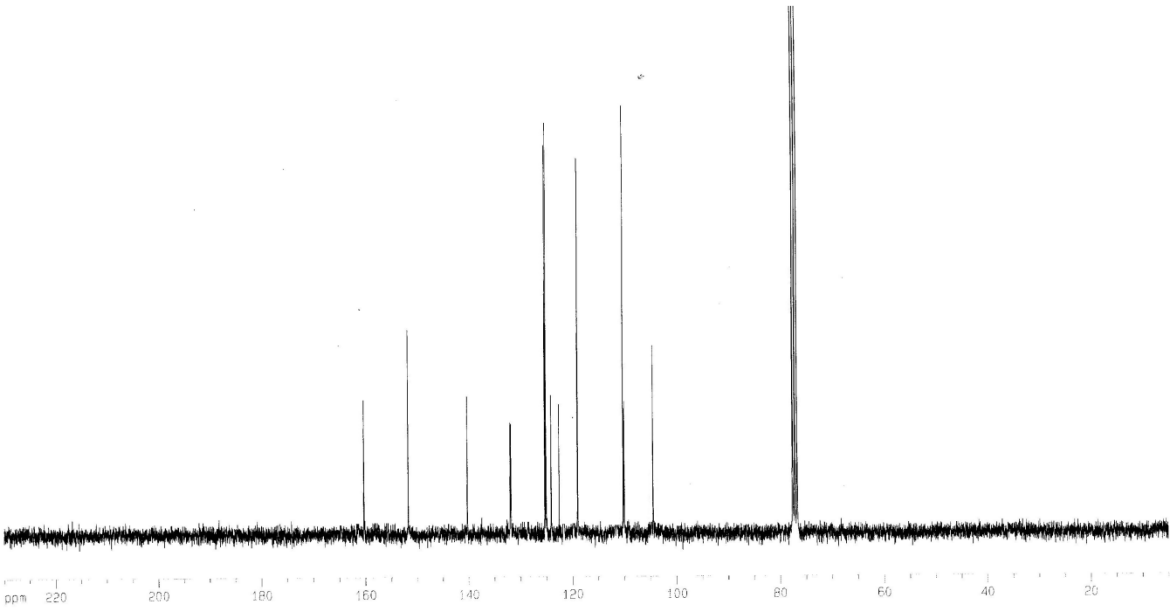


Fig S-37: ^{13}C NMR Spectrum of Product **5j**

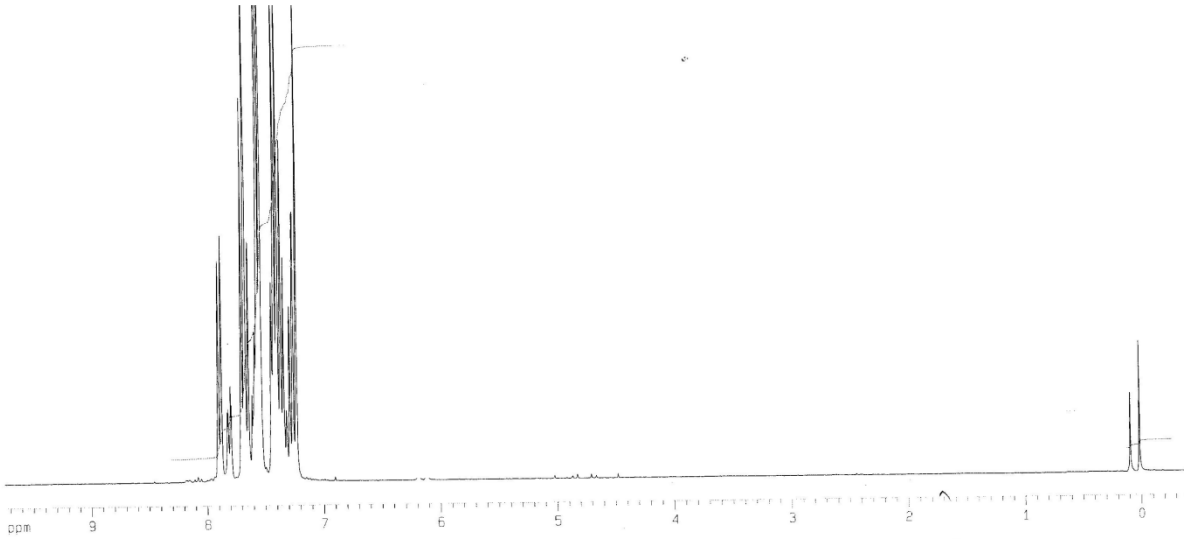


Fig S-38: ^{1}H NMR Spectrum of Product **5k**

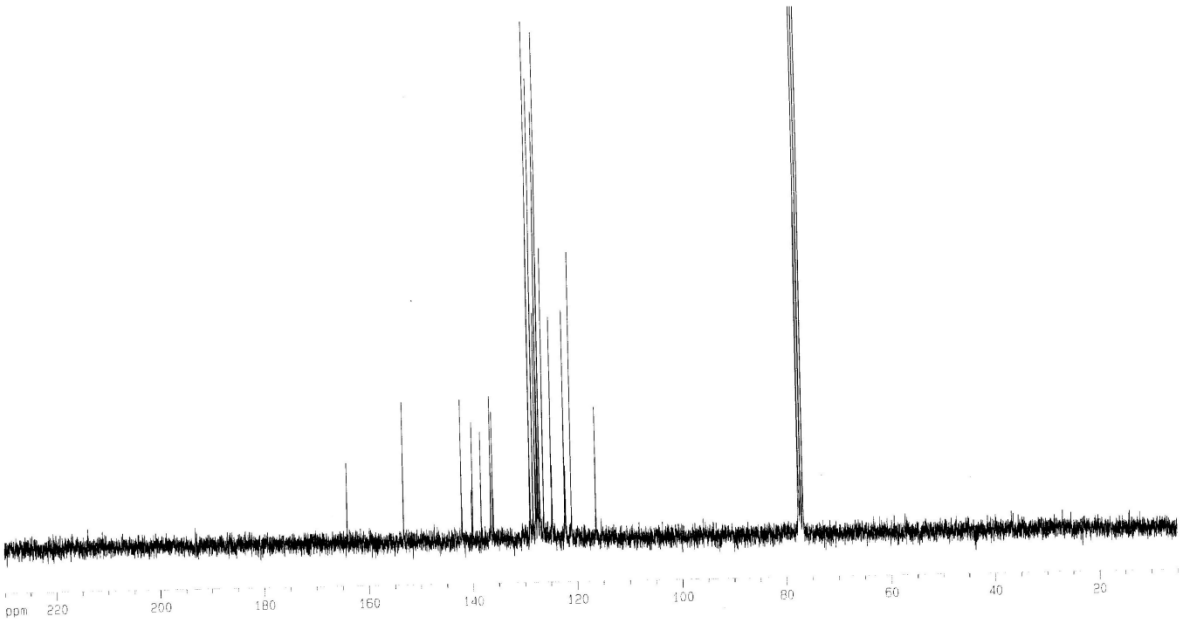


Fig S-39: ^{13}C NMR Spectrum of Product **5k**

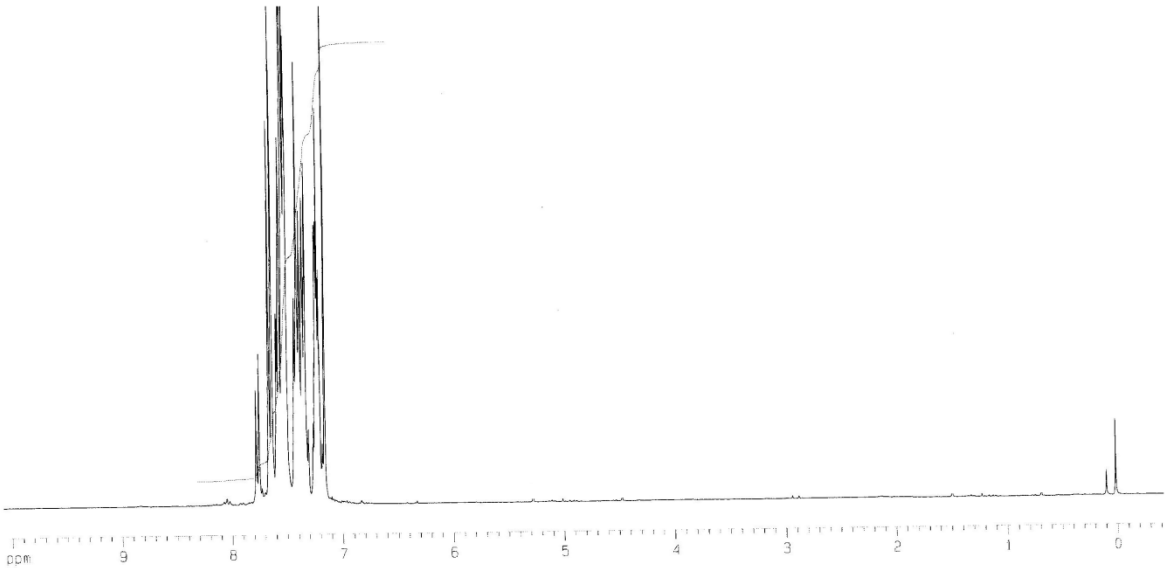


Fig S-40: ^{1}H NMR Spectrum of Product **5l**

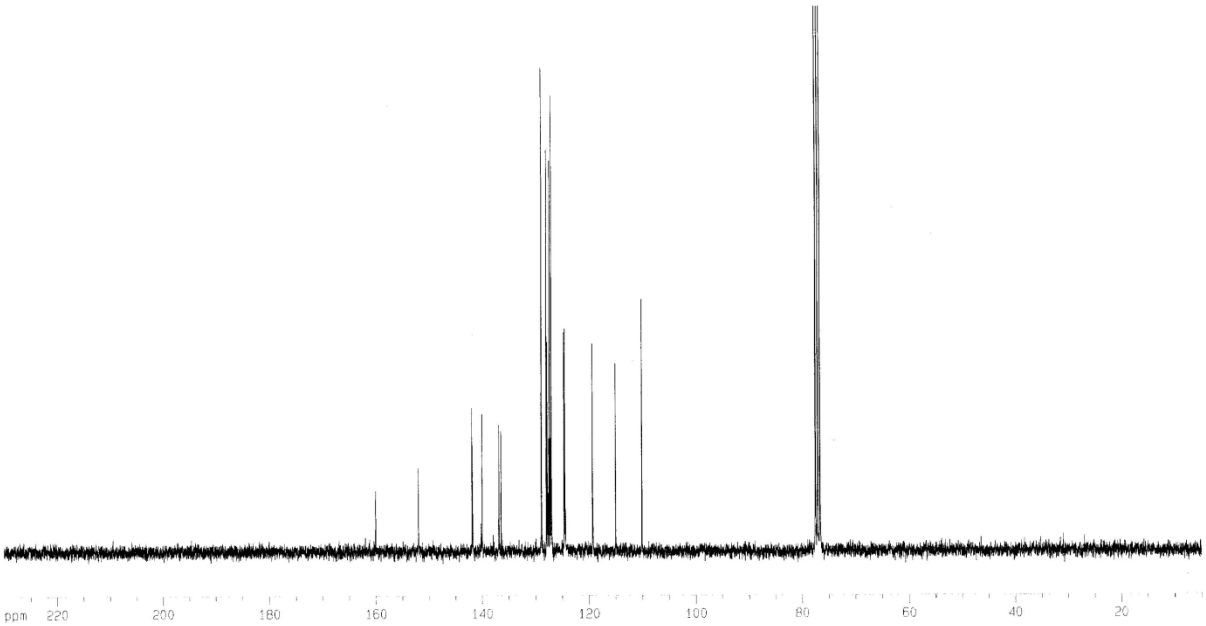


Fig S-41: ^{13}C NMR Spectrum of Product **5l**