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Electronic Supplementary Information

Microwave-promoted regio- and stereoselective vinylation of heterocyclic thiols

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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. The microwave reactor used is Anton Paar Synthos 3000 microwave reactor.

Microwave Instrumentation

All microwave reactions were carried out in a Synthos 3000 (Anton Paar) microwave reactor. The multitude microwave has a twin magnetron (2.45 GHz) with maximum output power of 1400 W. The output power can be controlled in unpulsed control mode over whole power which is adjustable in 1 W increment. A 68xxx series microprocessor system control is used to measure power, pressure, time and temperature during the reaction. The temperature and pressure were monitored throughout the reaction by an infrared detector. The temperature can be measured from 0 to 280 ^{o}C with uncertainty ±1%. The pressure can be measured from 0 to 86 bar with uncertainty ±0.2 bar. The MW power is initially set at 700 W and the reaction is run. However, during the course of the reaction, once the set temperature and pressure limit is reached, the reactor automatically adjusts the power by lowering it.

Experimental data

General procedure for the vinylation of heterocyclic thiols

Heterocyclic thiol (1 mmol) and activated terminal alkyne (1.3 mmol) were irradiated in a closed vessel by employing methanol (4ml) as solvent inside a microwave reactor at 500 Watt, 100 ^{0}C and 12 bar for specified time. After completion of reaction, solvent was distilled off and crude mixture is purified by coloum chromatography using ethylacetate: hexane as the eluent to give the desired products **(3aa-3hb).**

General procedure for the vinylation of aromatic thiols

Aromatic thiol (1 mmol) and activated terminal alkyne (1.1 mmol) were irradiated in a closed vessel by employing methanol (4ml) as solvent inside a microwave reactor at 500 Watt, 100 ^{0}C and 12 bar for specified time. After completion of reaction, solvent was distilled off and crude mixture is purified by coloum chromatography using ethylacetate: hexane as the eluent to give the desired products **(5a-f).**

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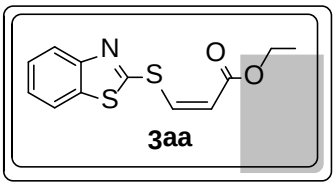
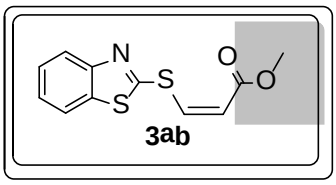
Characterization data of the Products



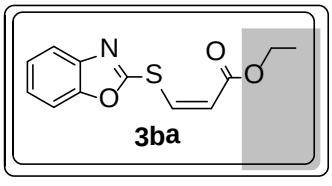
(*Z*)-Ethyl-3-(benzo[*d*]thiazol-2-ylthio)acrylate (3aa)

White solid; m.p. 80.5-82 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, J = 9.9 Hz, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.51 (t, 1H), 7.38 (t, 1H), 6.19 (d, J = 9.9 Hz, 1H), 4.31 (q, 2H), 1.36 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 164.3, 152.6, 140.6, 135.4, 126.4, 125, 122.1, 121.3, 115.7, 60.9, 14.3; MS (GCMS, m/z) 265 [M]+ ; Anal. Calcd. for $C_{12}H_{11}NO_2S_2$: C, 54.32; H, 4.18; N, 5.28; O, 12.06; S, 24.17. Found C, 54.22; H, 4.12; N, 5.20; O, 12.13; S, 24.33.



(*Z*)-Methyl-3-(benzo[*d*]thiazol-2-ylthio)acrylate (3ab)

White solid; m.p. 96-97.5 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.4 (d, J = 10 Hz, 1H), 7.96 (d, J = 8 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.5 (t, 1H), 7.39 (t, 1H), 6.2 (d, J = 9.9 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 164.1, 152.6, 141, 135.4, 126.4, 125, 122.1, 121.3, 115.2, 51.9; MS (GCMS, m/z) 251 [M]+ ; Anal. Calcd. for $C_{11}H_9NO_2S_2$: C, 52.57; H, 3.61; N, 5.57; O, 12.73; S, 25.52. Found C, 52.59; H, 3.6; N, 5.62; O, 12.68; S, 25.51.



(*Z*)-Ethyl-3-(benzo[*d*]oxazol-2-ylthio)acrylate (3ba)

White solid; m.p. 111-112.2 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 9.8 Hz, 1H), 7.6 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 8.9 Hz, 1H), 7.34 (t, 2H), 6.26 (d, J = 9.9 Hz, 1H), 4.32 (q, 2H), 1.37 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 162.8, 152, 141.2, 139.3, 124.7, 124.6, 118.9, 117, 110.3, 61, 14.2; MS (GCMS, m/z) 249 [M]+ ; Anal. Calcd. for $C_{12}H_{11}NO_3S$: C, 57.82; H, 4.45; N, 5.62; O, 19.25; S, 12.86. Found C, 57.77; H, 4.52; N, 5.53; O, 19.26; S, 12.92.

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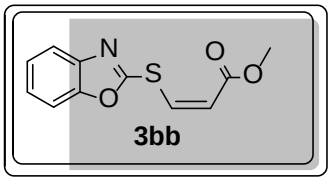
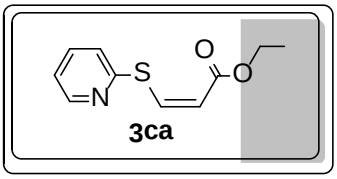


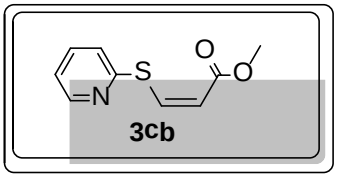
(*Z*)-Methyl-3-(benzo[*d*]oxazol-2-ylthio)acrylate (3bb)

White solid; m.p. 92-93.5 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 9.8 Hz, 1H), 7.6 (d, J = 9 Hz, 1H), 7.52 (d, J = 9.1 Hz, 1H), 7.34 (t, 2H), 6.27 (d, J = 9.9 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 162.7, 152, 141.2, 139.7, 124.7, 124.6, 118.9, 116.5, 110.3, 52, 30.9; MS (GCMS, m/z) 235 [M]+ ; Anal. Calcd. for $C_{11}H_9NO_3S$: C, 56.16; H, 3.86; N, 5.95; O, 20.40; S, 13.63. Found C, 56.11; H, 3.91; N, 5.89; O, 20.42; S, 13.67.



(*Z*)-Ethyl-3-(pyridin-2-ylthio)acrylate (3ca)

White solid; m.p. 96-97.5 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, J = 10.1 Hz, 2H), 7.62 (t, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.15 (t, 1H), 6.11 (d, J = 10.2 Hz, 1H), 4.29 (q, 2H), 1.35 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 155.3, 149.6, 141.8, 136.8, 123.2, 121.2, 113.9, 60.4, 14.3; MS (GCMS, m/z) 209 [M]+ ; Anal. Calcd. for $C_{10}H_{11}NO_2S$: C, 57.39; H, 5.30; N, 6.69; O, 15.29; S, 15.32. Found C, 57.41; H, 5.23; N, 6.75; O, 15.27; S, 15.34.



(*Z*)-Methyl-3-(pyridin-2-ylthio)acrylate (3cb)

White solid; m.p. 72-72.5 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, J = 10.2 Hz, 2H), 7.62 (t, 1H), 7.33 (d, J = 7.9 Hz, 1H), 7.15 (t, 1H), 6.12 (d, J = 10.2 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 155, 149.6, 142.3, 136.8, 123.3, 121.3, 113.4, 51.5; MS (GCMS, m/z) 195 [M]+ ; Anal. Calcd. for $C_9H_9NO_2S$: C, 55.37; H, 4.65; N, 7.17; O, 16.39; S, 16.42. Found C, 55.41; H, 4.62; N, 7.18; O, 16.28; S, 16.51.

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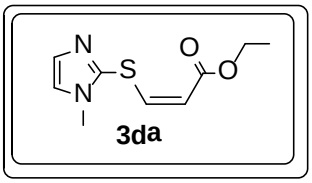
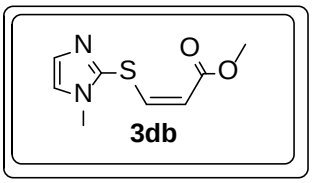


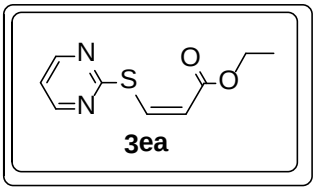
(Z)-Ethyl-3-(1-methyl-1H-imadazol-2-ylthio)acrylate (3da)

Colourless liquid ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 9.8 Hz, 1H), 7.08 (d, J = 0.75 Hz, 1H), 6.98 (d, J = 0.87 Hz, 1H), 6.07 (d, J = 9.9 Hz, 1H), 4.2 (q, 2H), 3.6 (s, 3H), 1.35 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 144.5, 140.4, 129.1, 123, 114.6, 60.4, 33.2, 14.1; MS (GCMS, m/z) 212 [M]+ ; Anal. Calcd. for $C_9H_{12}N_2O_2S$: C, 50.92; H, 5.70; N, 13.20; O, 15.07; S, 15.17. Found C, 50.96; H, 5.62; N, 13.25; O, 15.05; S, 15.12.



(*Z*)-Methyl-3-(1-methyl-1H-imadazol-2-ylthio)acrylate (3db)

White solid; m.p. 52-52.9 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 9.8 Hz, 1H), 7.10 (d, J = 1.05 Hz, 1H), 6.98 (d, J = 1.05 Hz, 1H), 6.09 (d, J = 9.9 Hz, 1H), 3.8 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167, 145, 140.6, 129.5, 123, 114.2, 51.6, 33.2; MS (GCMS, m/z) 198 [M]+ ; Anal. Calcd. for $C_8H_{10}N_2O_2S$: C, 48.47; H, 5.08; N, 14.13; O, 16.14; S, 16.17. Found C, 48.53; H, 4.99; N, 14.1; O, 16.16; S, 16.22.



(*Z*)-Ethyl-3-(pyrimidin-2-ylthio)acrylate (3ea)

White solid; m.p. 80-81 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, J = 4.8 Hz, 2H), 8.54 (d, J = 10.4 Hz, 1H), 7.13 (t, 1H), 6.13 (d, J = 10.4 Hz, 1H), 4.3, (q, 2H), 1.36 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 166.6, 157.8, 157.6, 141.6, 118.1, 114.5, 60.6, 14.2; MS (GCMS, m/z) 210 [M]+ ; Anal. Calcd. for $C_9H_{10}N_2O_2S$: C, 51.41; H, 4.79; N, 13.32; O, 15.22; S, 15.25. Found C, 51.34; H, 4.8; N, 13.34; O, 15.36; S, 15.16.

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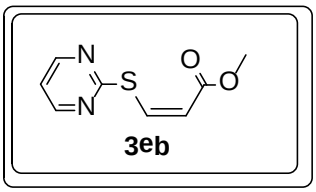
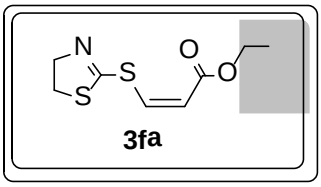


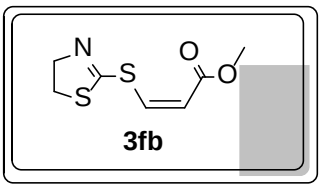
(*Z*)-Methyl-3-(pyrimidin-2-ylthio)acrylate (3eb)

White solid; m.p. 115-116.2 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, J = 4.8 Hz, 2H), 8.56 (d, J = 10.4 Hz, 1H), 7.13 (t, 1H), 6.14 (d, J = 10.3 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.9, 157.8, 157.6, 141.9, 118.1, 114.4, 51.6; MS (GCMS, m/z) 196 [M]+ ; Anal. Calcd. for $C_8H_8N_2O_2S$: C, 48.97; H, 4.11; N, 14.28; O, 16.31; S, 16.34. Found C, 49.07; H, 4.19; N, 14.34; O, 16.19; S, 16.21.



(*Z*)-Ethyl-3-((4,5-dihydrothiazol-2-yl)thio)acrylate (3fa)

Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J = 10 Hz, 1H), 6.04 (d, J = 10 Hz, 1H), 3.49 (q, 2H), 1.33 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 164.2, 140.5, 115.3, 63.9, 60.7, 35.5, 14.2; MS (GCMS, m/z) 217 [M]+ ; Anal. Calcd. for $C_8H_{11}NO_2S_2$: C, 44.22; H, 5.10; N, 6.45; O, 14.73; S, 29.51. Found C, 44.19; H, 5.06; N, 6.45; O, 14.77; S, 29.53.



(*Z*)-Methyl-3-((4,5-dihydrothiazol-2-yl)thio)acrylate (3fb)

Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, J = 10 Hz, 1H), 6.06 (d, J = 10 Hz, 1H), 4.3 (t, 2H), 3.77 (s, 3H), 3.49 (t, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 164, 140.8, 114.8, 63.9, 51.7, 35.5; MS (GCMS, m/z) 203 [M]+ ; Anal. Calcd. for $C_7H_9NO_2S_2$: C, 41.36; H, 4.46; N, 6.89; O, 15.74; S, 31.55. Found C, 41.39; H, 4.46; N, 6.78; O, 15.66; S, 31.71.

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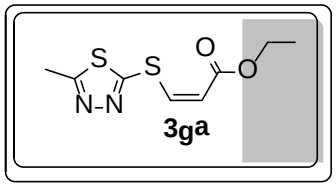
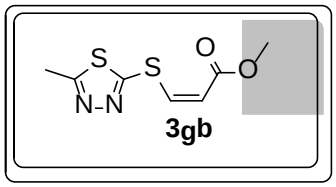


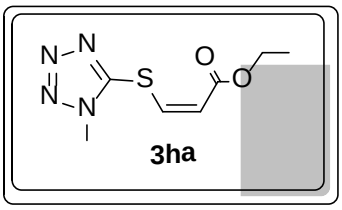
(*Z*)-Ethyl-3-((5-methyl-1,3,4-thiadiazol-2-yl)thio)acrylate (3ga)

White solid; m.p. 69.2-71 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, J = 9.8 Hz, 1H), 6.16 (d, J = 9.8 Hz, 1H), 4.3 (q, 2H), 2.78 (s, 3H), 1.35 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 166.3, 163.6, 140.5, 116, 60.9, 15.7, 14.2; MS (GCMS, m/z) 230 [M]+ ; Anal. Calcd. for $C_8H_{10}N_2O_2S_2$: C, 41.72; H, 4.38; N, 12.16; O, 13.89; S, 27.85. Found C, 41.56; H, 4.52; N, 12.15; O, 13.86; S, 27.91.



(*Z*)-Methyl-3-((5-methyl-1,3,4-thiadiazol-2-yl)thio)acrylate (3gb)

White solid; m.p. 115-116.2 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 9.8 Hz, 1H), 6.17 (d, J = 9.8 Hz, 1H), 3.81 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 166.3, 163.5, 140.9, 115.5, 51.9, 15.7; MS (GCMS, m/z) 216 [M]+ ; Anal. Calcd. for $C_7H_8N_2O_2S_2$: C, 38.87; H, 3.73; N, 12.95; O, 14.80; S, 29.65. Found C, 38.96; H, 3.71; N, 12.95; O, 14.86; S, 29.52.



(*Z*)-Ethyl-3-((1-methyl-1H-tetrazol-5-yl)thio)acrylate (3ha)

White solid; m.p. 107-107.5 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 9.6 Hz, 1H), 6.29 (d, J = 9.6 Hz, 1H), 4.32 (q, 2H), 4.02 (s, 3H), 1.37 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 153.1, 138.7, 117.5, 61.2, 33.6, 14.2; MS (GCMS, m/z) 214 [M]+ ; Anal. Calcd. for $C_7H_{10}N_4O_2S$: C, 39.24; H, 4.70; N, 26.15; O, 14.94; S, 14.97. Found C, 39.21; H, 4.66; N, 26.21; O, 15.02; S, 14.9.

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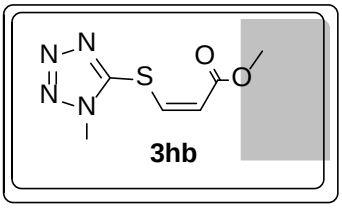
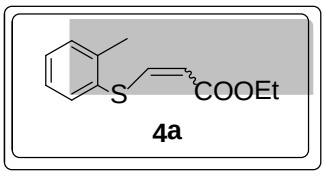


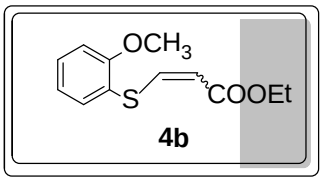
(*Z*)-Methyl-3-((1-methyl-1H-tetrazol-5-yl)thio)acrylate (3hb)

White solid; m.p. 111.9-113 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 9.6 Hz, 1H), 6.3 (d, J = 9.6 Hz, 1H), 4.02 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167, 153, 139.1, 117.1, 52.1, 33.6; MS (GCMS, m/z) 200 [M]+ ; Anal. Calcd. for $C_6H_8N_4O_2S$: C, 35.99; H, 4.03; N, 27.98; O, 15.98; S, 16.02. Found C, 36.09; H, 3.94; N, 27.88; O, 15.92; S, 16.17.



Ethyl-3-(*o*-tolylthio) acrylate (5a)

Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 7.05 Hz, 1H), 7.31 (m, 3H), 7.13 (d, J = 10 Hz, 1H), 5.93 (d, J = 10 Hz, 1H), 4.29 (q, 2H), 2.45 (s, 3H), 1.35 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 150.2, 139.8, 135.2, 132.7, 130.6, 128.7, 126.9, 113.3, 60.3, 20.9, 14.3; MS (GCMS, m/z) 222 [M]+ ; Anal. Calcd. for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; O, 14.39; S, 14.42. Found C, 64.92; H, 6.24; O, 14.28; S, 14.56.



Ethyl-3-((2-methoxyphenyl)thio)acrylate (5b)

Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.21 (d, J = 10.1 Hz, 1H), 6.95 (m, 2H), 5.9 (d, J = 10.1 Hz, 1H), 4.28 (q, 2H), 3.87 (s, 3H), 1.34 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 158.2, 150.3, 133.4, 130.2, 123.4, 121.1, 112.9, 111.4, 60.2, 55.8, 14.3; MS (GCMS, m/z) 238 [M]+ ; Anal. Calcd. for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92; O, 20.14; S, 13.46. Found C, 60.49; H, 5.96; O, 20.12; S, 13.43.

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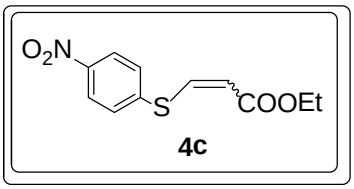
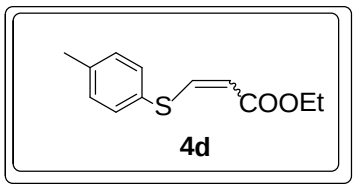


4c

Ethyl-3-((4-nitrophenyl)thio)acrylate (5c)

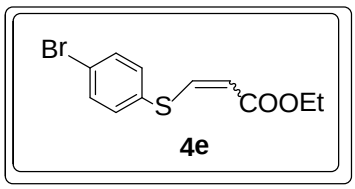
Yellow solid; m.p. 109-111.2 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 10 Hz, 1H), 6.1 (d, J = 9.9 Hz, 1H), 4.3 (q, 2H), 1.34 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 147, 144.9, 144.7, 129.9, 124.3, 115.9, 66.7, 14.3; MS (GCMS, m/z) 253 [M]+ ; Anal. Calcd. for $C_{11}H_{11}NO_4S$: C, 52.16; H, 4.38; N, 5.53; O, 25.27; S, 12.66. Found C, 52.12; H, 4.42; N, 5.5; O, 25.24; S, 12.72.



4d

Ethyl-3-(p-tolyithio)acrylate (5d)[1]

Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.2 (d, J = 9.9 Hz, 1H), 5.95 (d, J = 10 Hz, 1H), 4.28 (q, 2H), 1.34 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 150.5, 147.4, 138.4, 133.3, 131.3, 130.4, 130, 113, 60.2, 21.2, 14.3; MS (GCMS, m/z) 222 [M]+ ; Anal. Calcd. for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; O, 14.39; S, 14.42. Found C, 64.81; H, 6.32; O, 14.43; S, 14.44.



4e

Ethyl-3-((4-bromophenyl)thio)acrylate (5e) [2]

Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.2 (d, J = 10 Hz, 1H), 5.95 (d, J = 9.9 Hz, 1H), 4.28 (q, 2H), 1.34 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 148.5, 145.7, 135.3, 134.3, 132.8, 132.5, 116.2, 114, 60.4, 14.3; MS (GCMS, m/z) 287.9 [M]+ ; Anal. Calcd. for $C_{11}H_{11}BrO_2S$: C, 46.01; H, 3.86; Br, 27.82; O, 11.14; S, 11.17. Found C, 45.91; H, 4.12; Br, 27.71; O, 11.11; S, 11.15.

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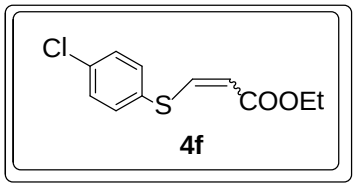

4f

Ethyl-3-((4-chlorophenyl)thio)acrylate (5f) [2]

Colourless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 7.2 (d, J = 10 Hz, 1H), 5.95 (d, J = 10 Hz, 1H), 4.28 (q, 2H), 1.35 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 148.8, 134.7, 132.4, 129.5, 113.9, 60.4, 14.3; MS (GCMS, m/z) 242 [M]+ ; Anal. Calcd. for $C_{11}H_{11}ClO_2S$: C, 54.43; H, 4.57; Cl, 14.61; O, 13.18; S, 13.21. Found C, 54.40; H, 4.52; Cl, 14.71; O, 13.19; S, 13.18.

NMR Spectra of the Products

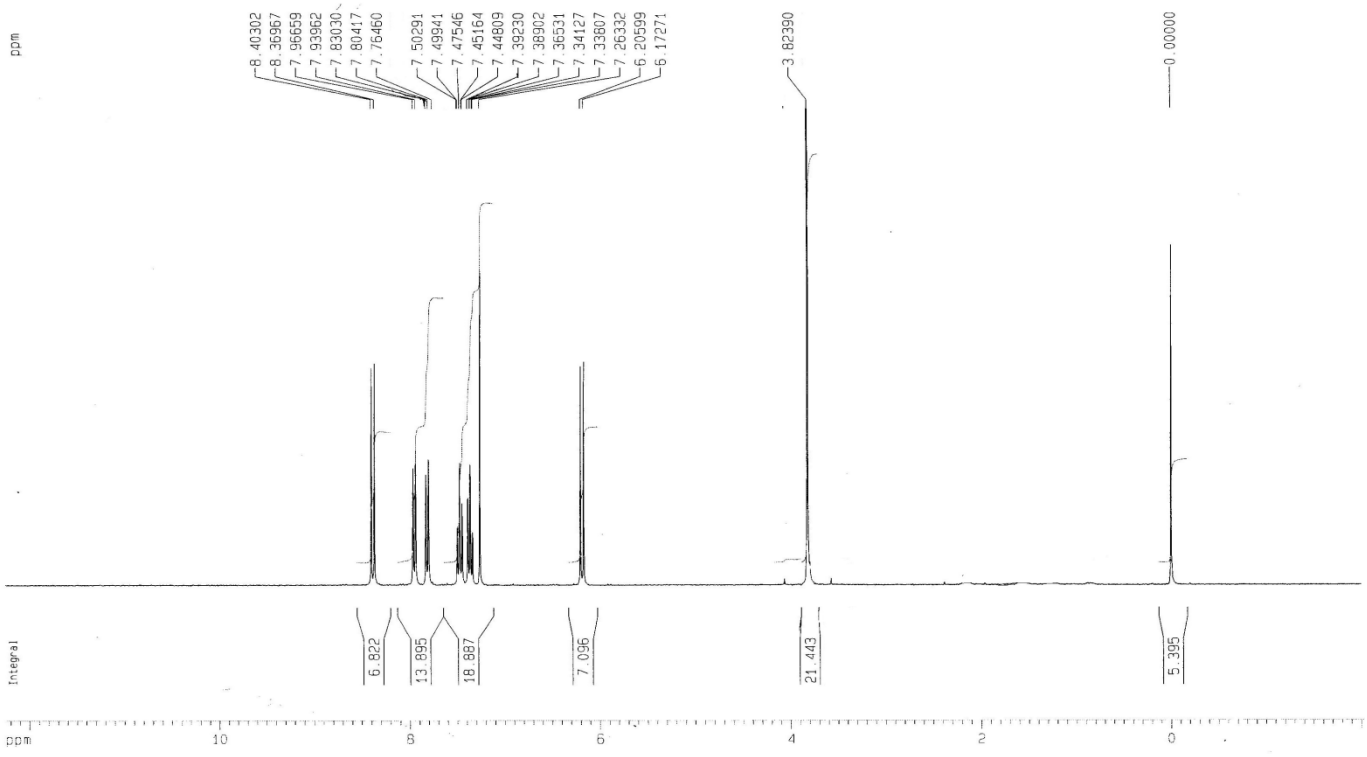

Fig S-1: ^{1}H NMR Spectrum of Product **3ab**

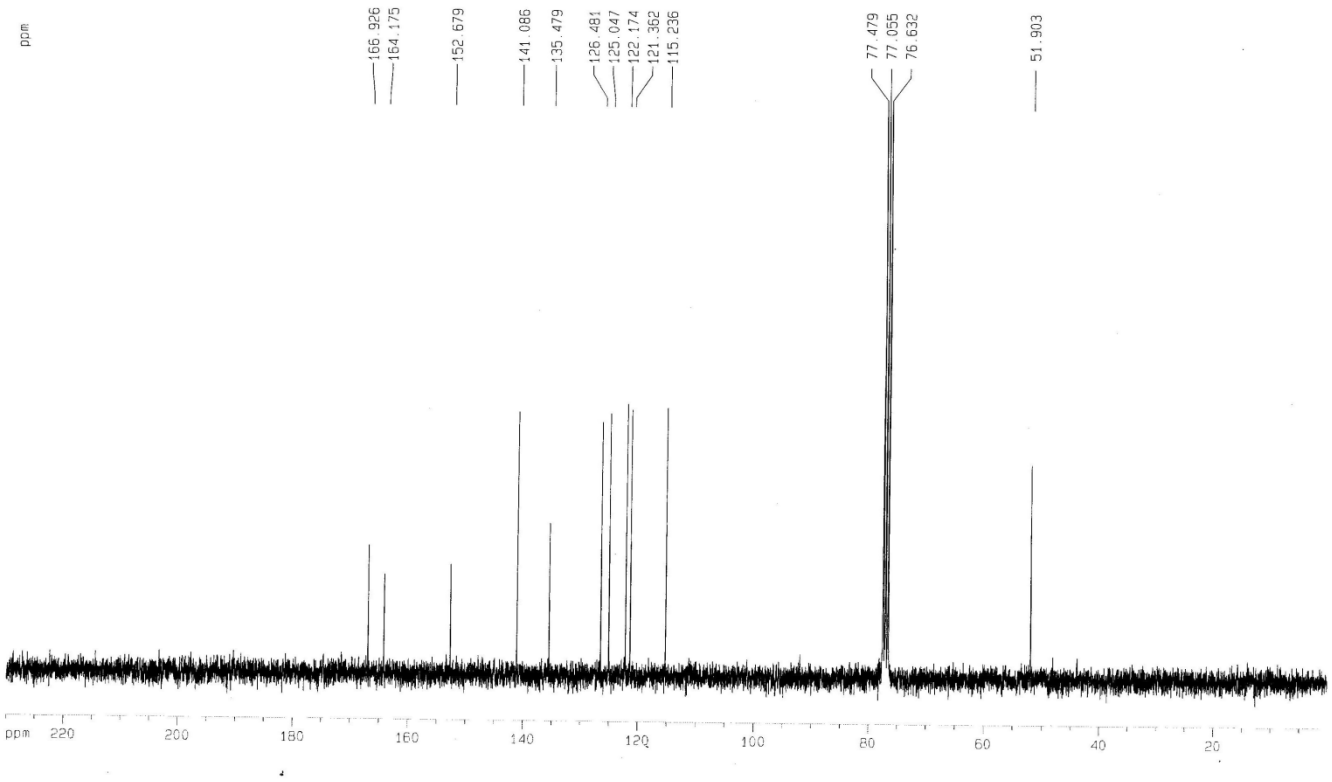

Fig S-2: ^{13}C NMR Spectrum of Product **3ab**

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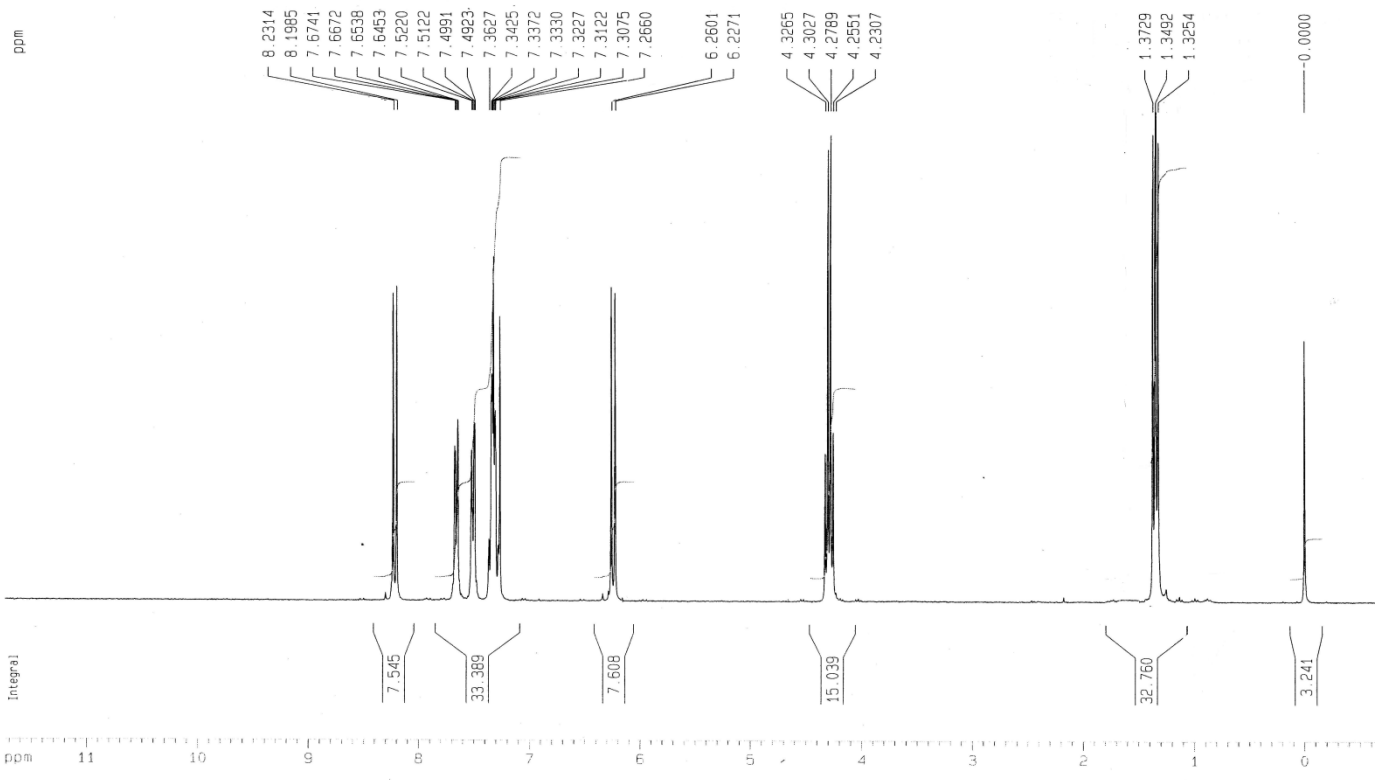

Fig S-3: ^{1}H NMR Spectrum of Product **3ba**

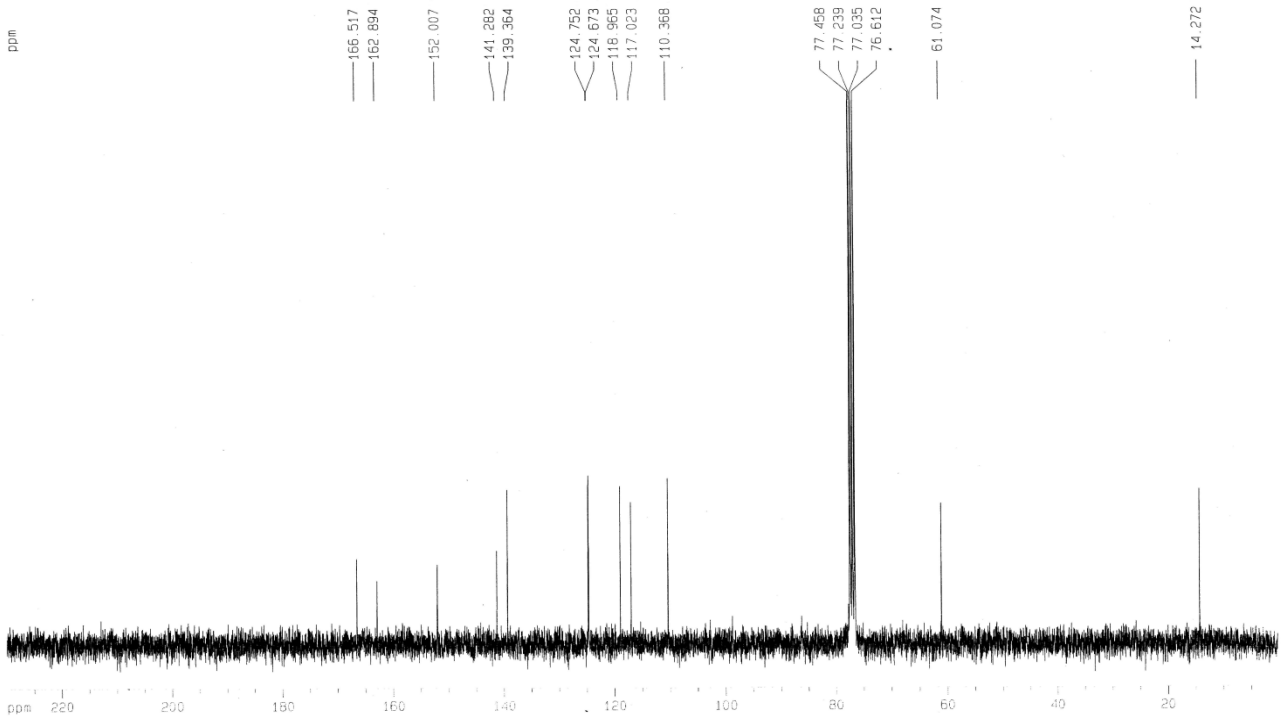

Fig S-4: ^{13}C NMR Spectrum of Product **3ba**

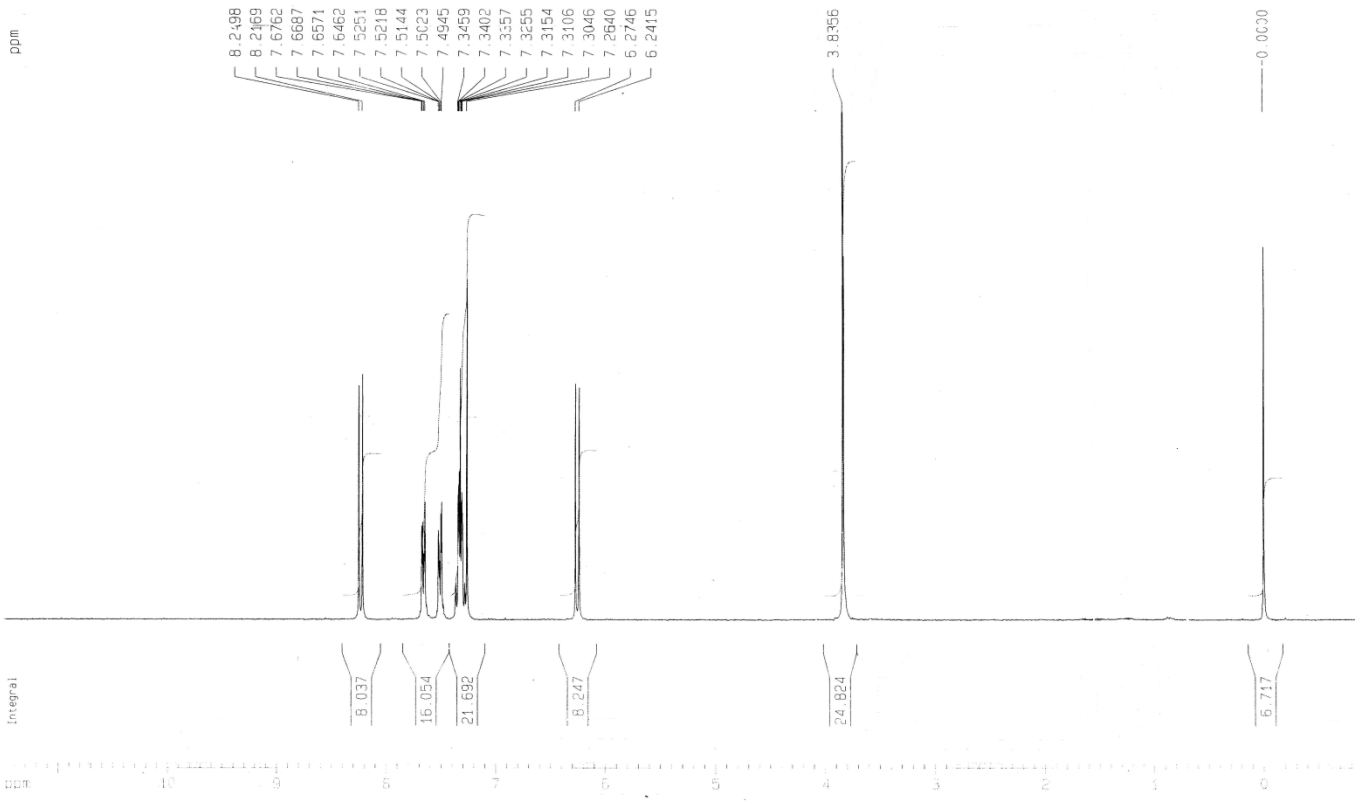

Fig S-5: ^{1}H NMR Spectrum of Product **3bb**

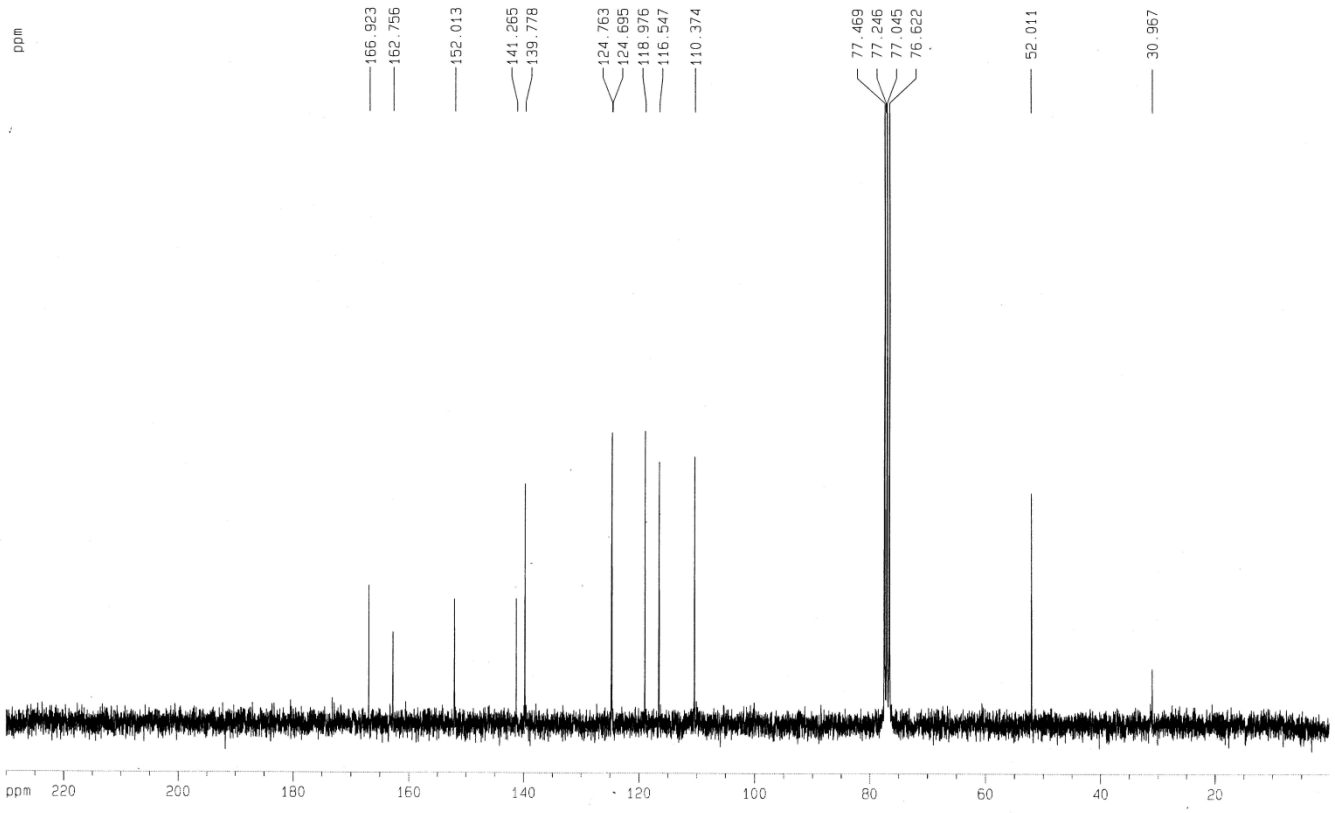

Fig S-6: ^{13}C NMR Spectrum of Product **3bb**

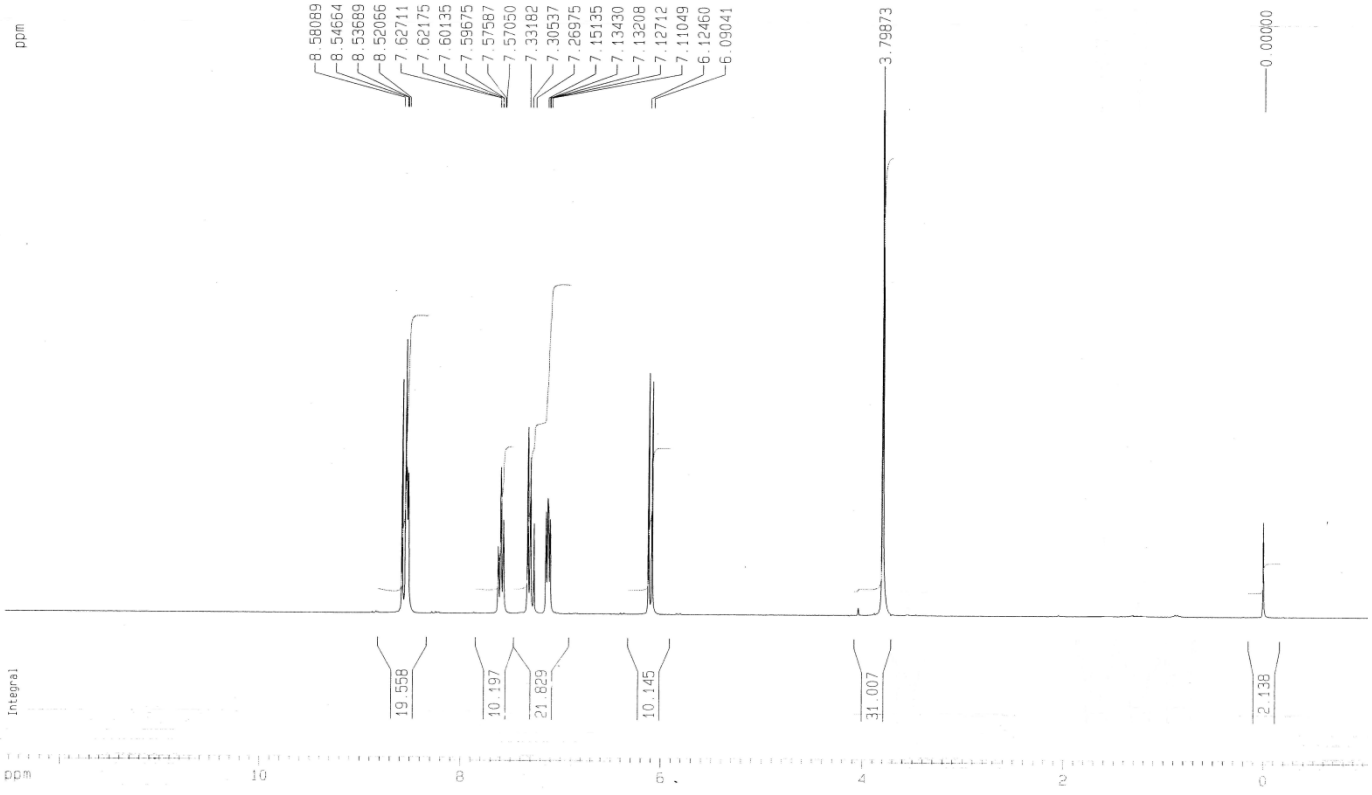

Fig S-7: ^{1}H NMR Spectrum of Product **3cb**

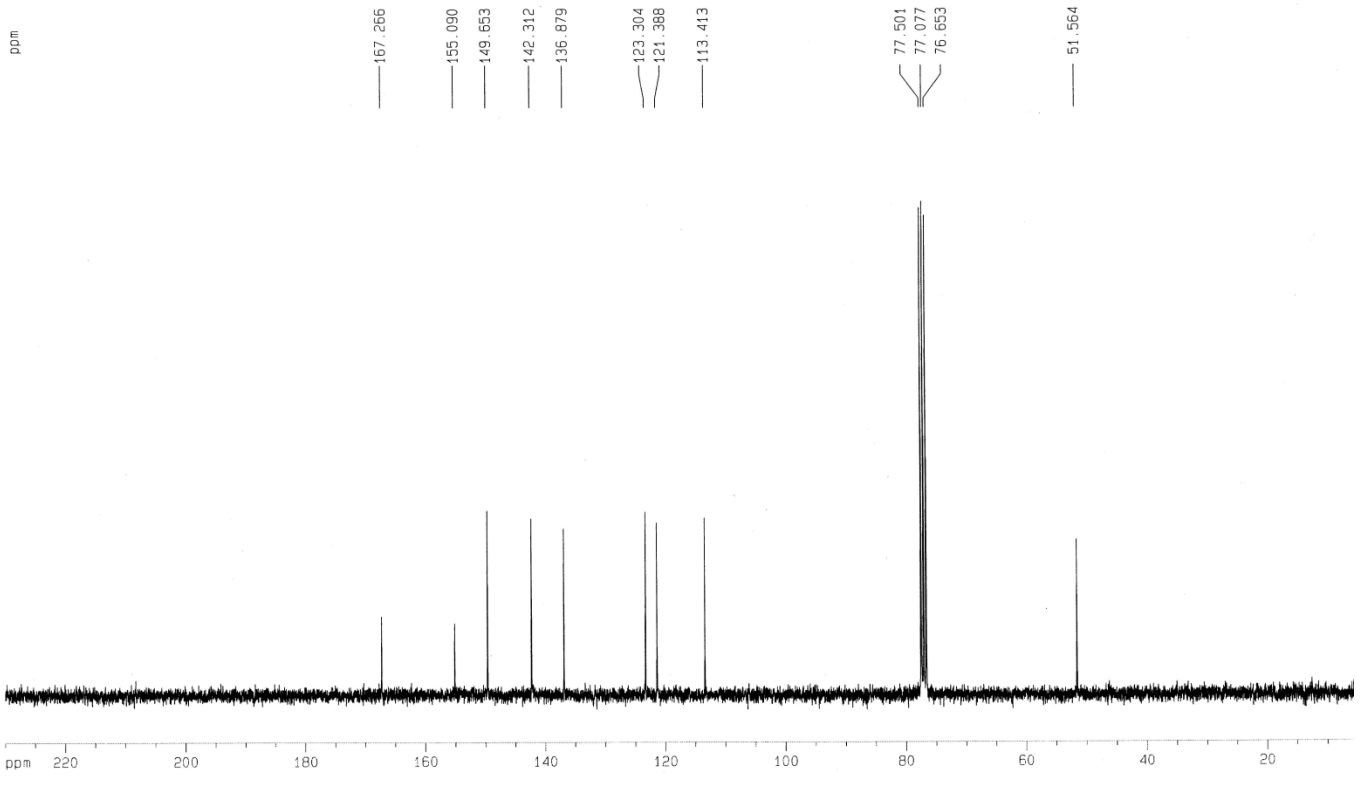

Fig S-8: ^{13}C NMR Spectrum of Product **3cb**

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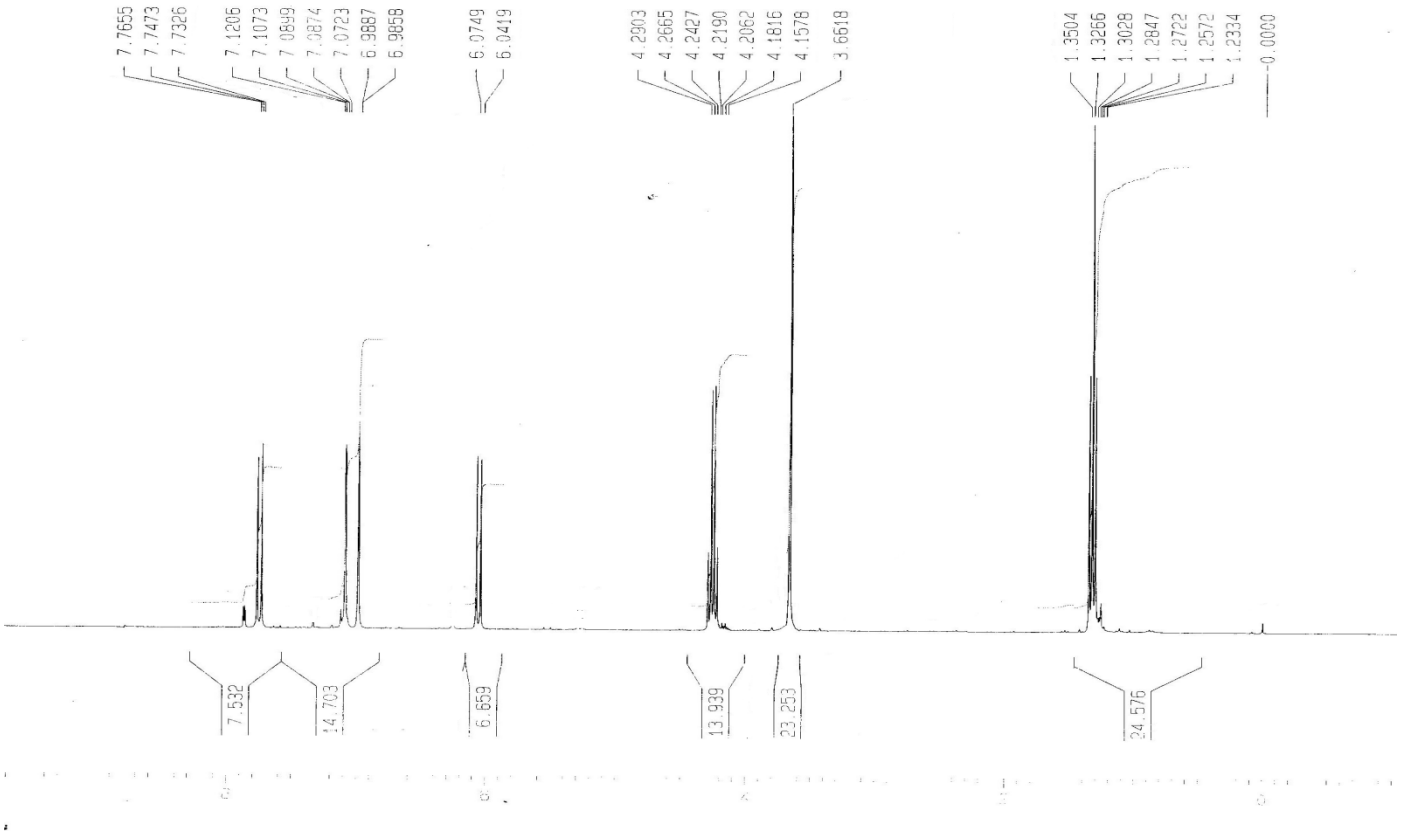

Fig S-9: ^{1}H NMR Spectrum of Product 3da

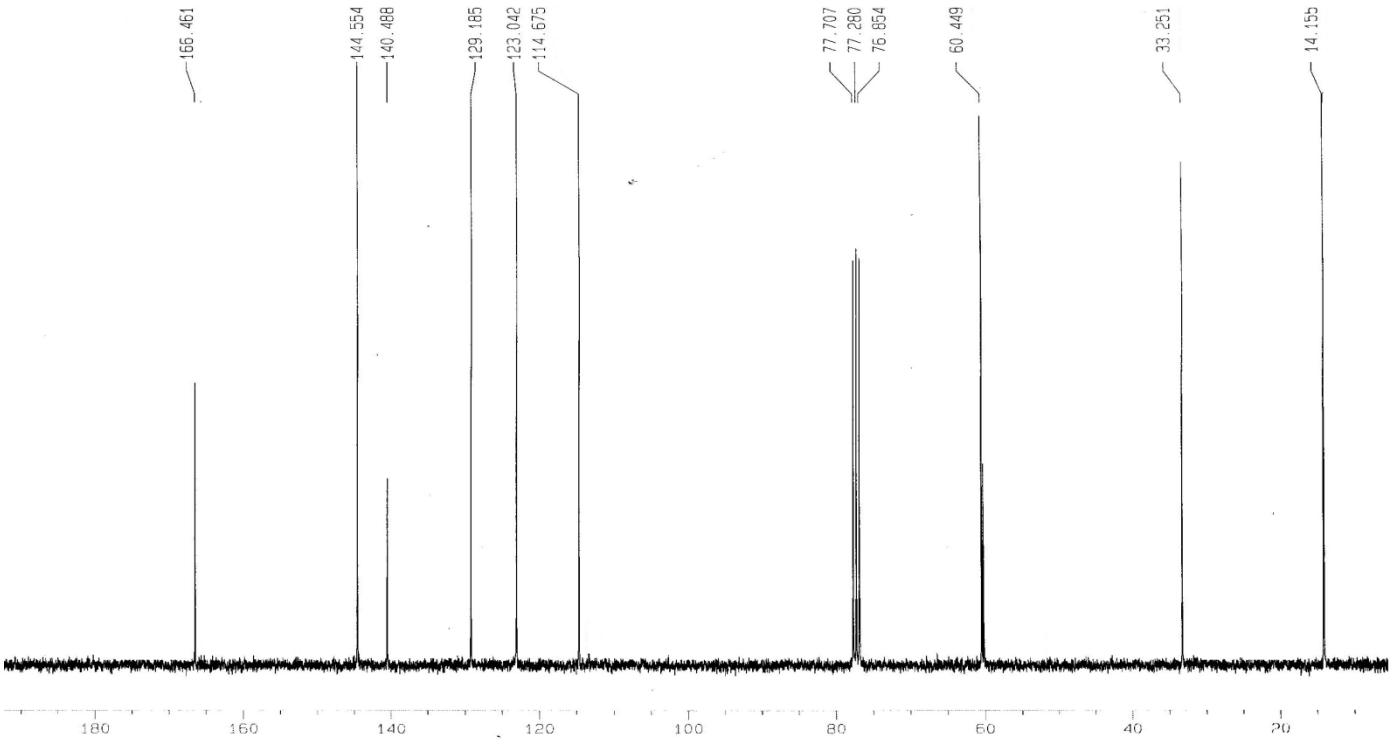

Fig S-10: ^{13}C NMR Spectrum of Product 3da

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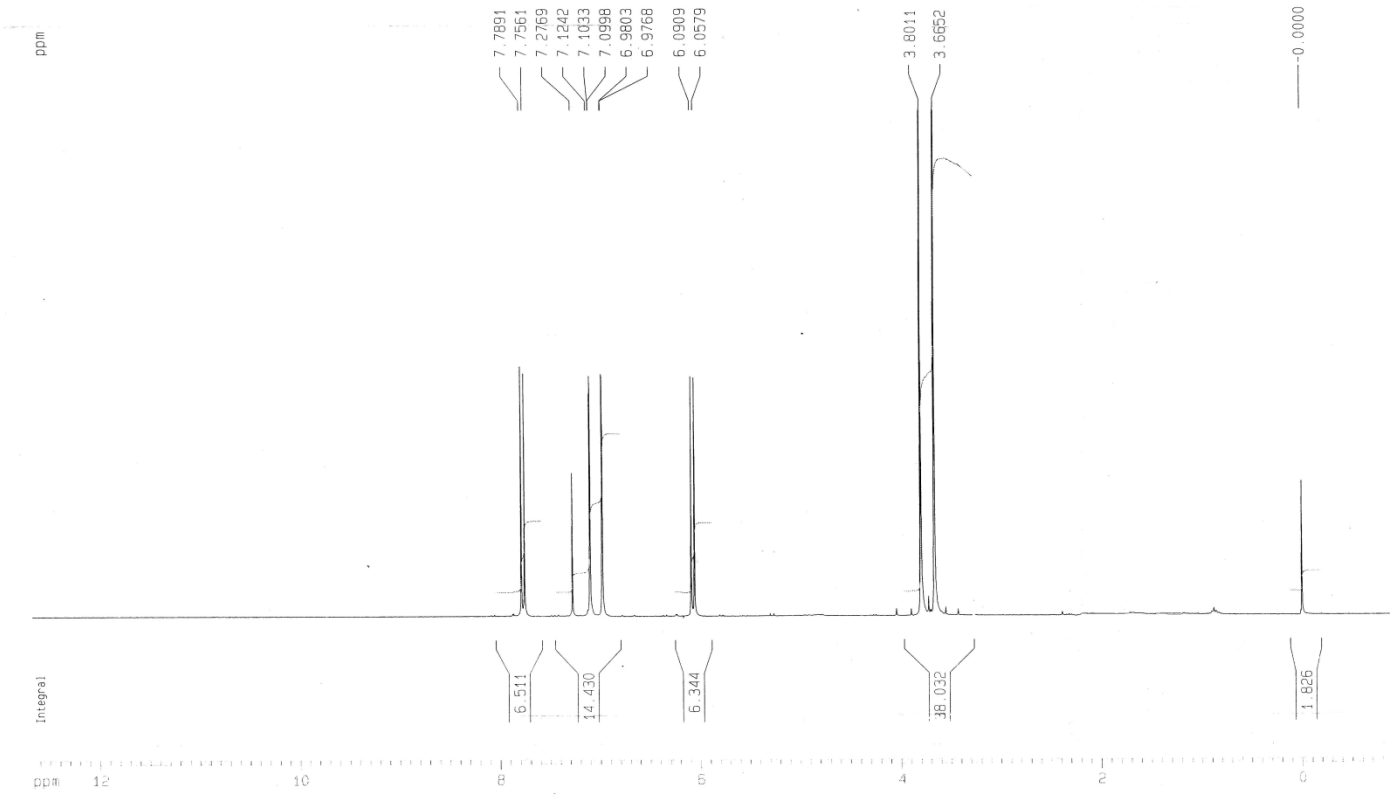

Fig S-11: ^{1}H NMR Spectrum of Product **3db**

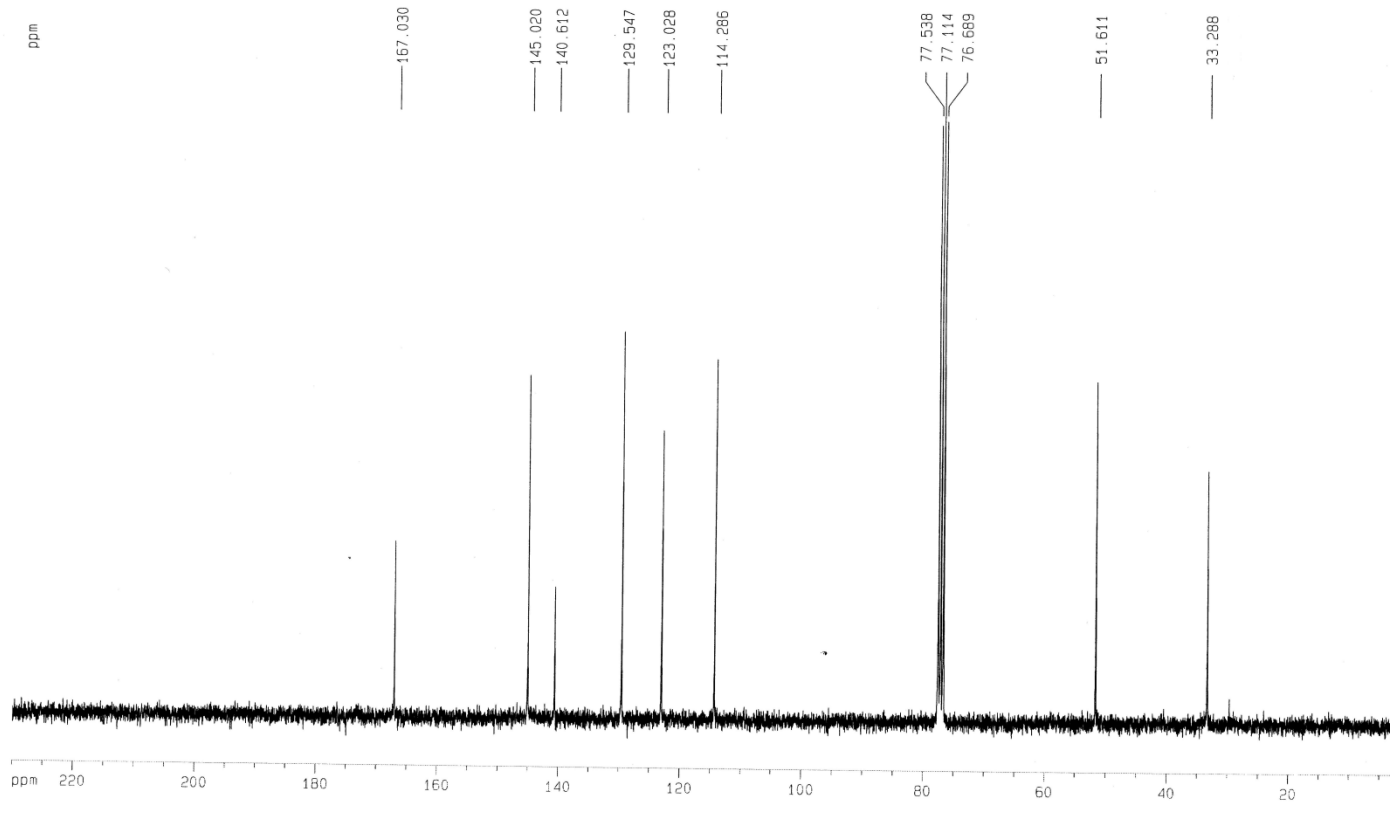

Fig S-12: ^{13}C NMR Spectrum of Product **3db**

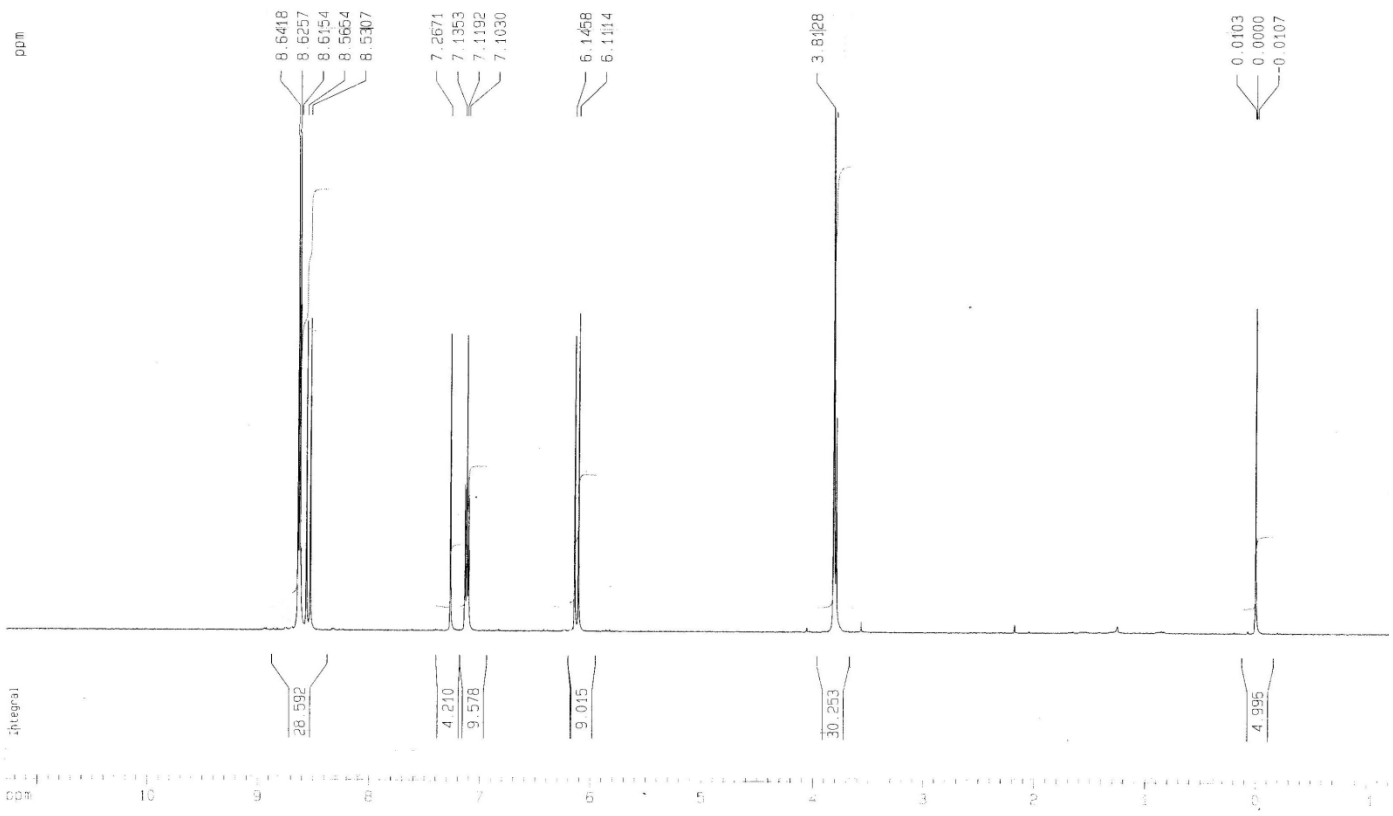

Fig S-13: ^{1}H NMR Spectrum of Product **3eb**

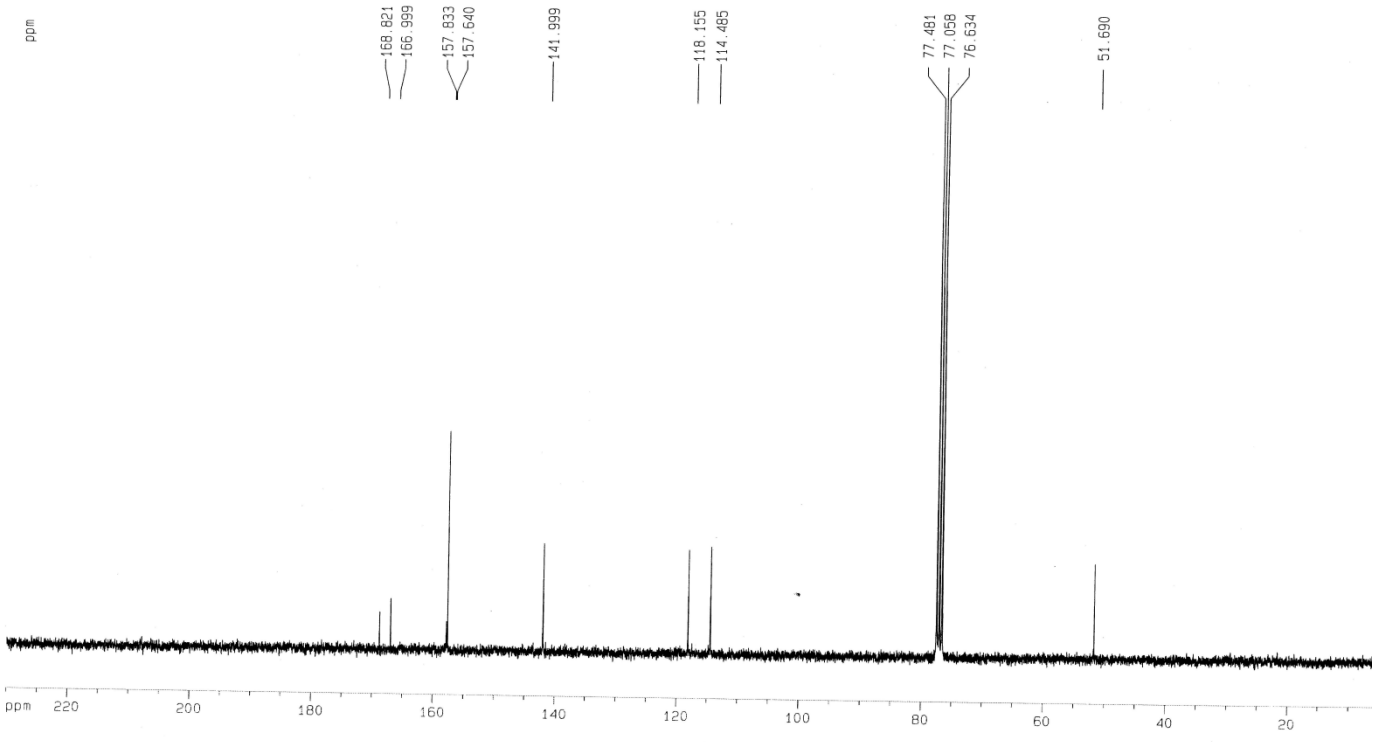

Fig S-14: ^{13}C NMR Spectrum of Product **3eb**

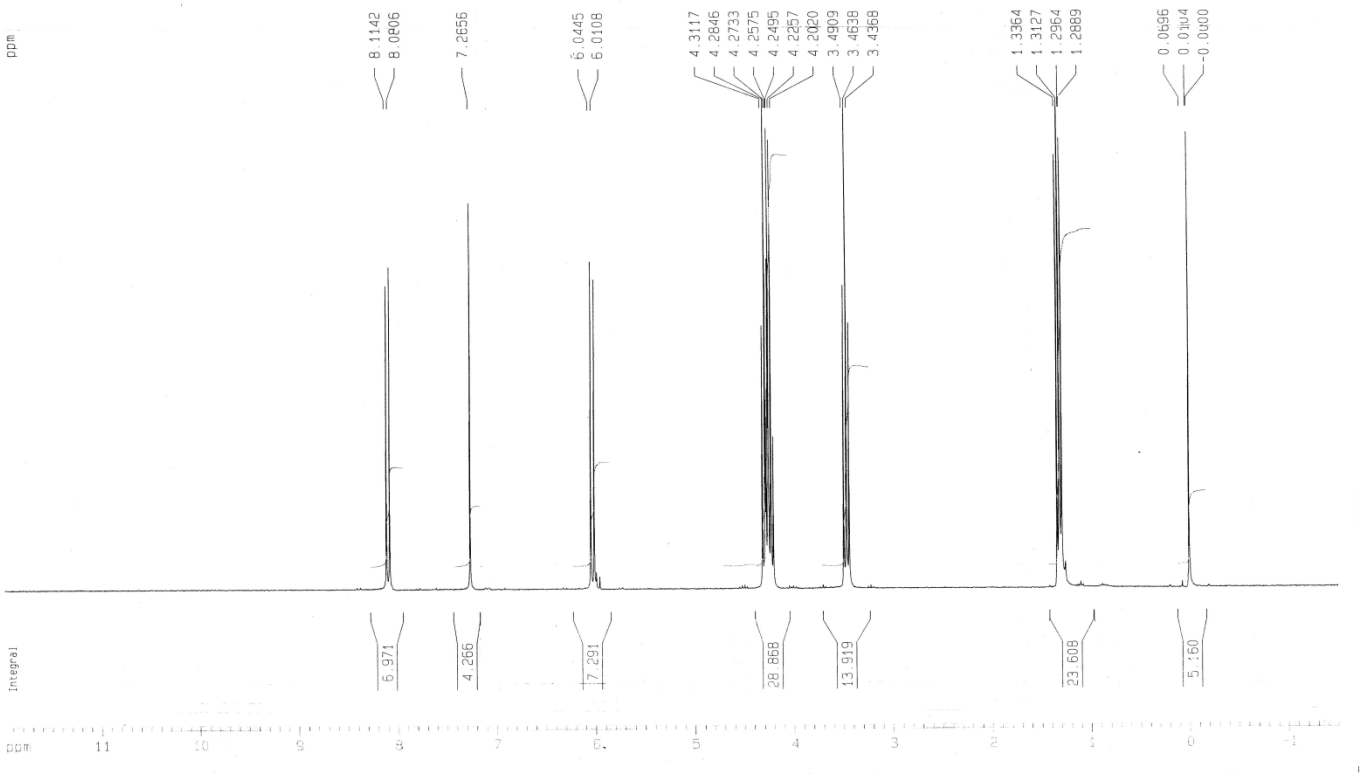

Fig S-15: ^{1}H NMR Spectrum of Product **3fa**

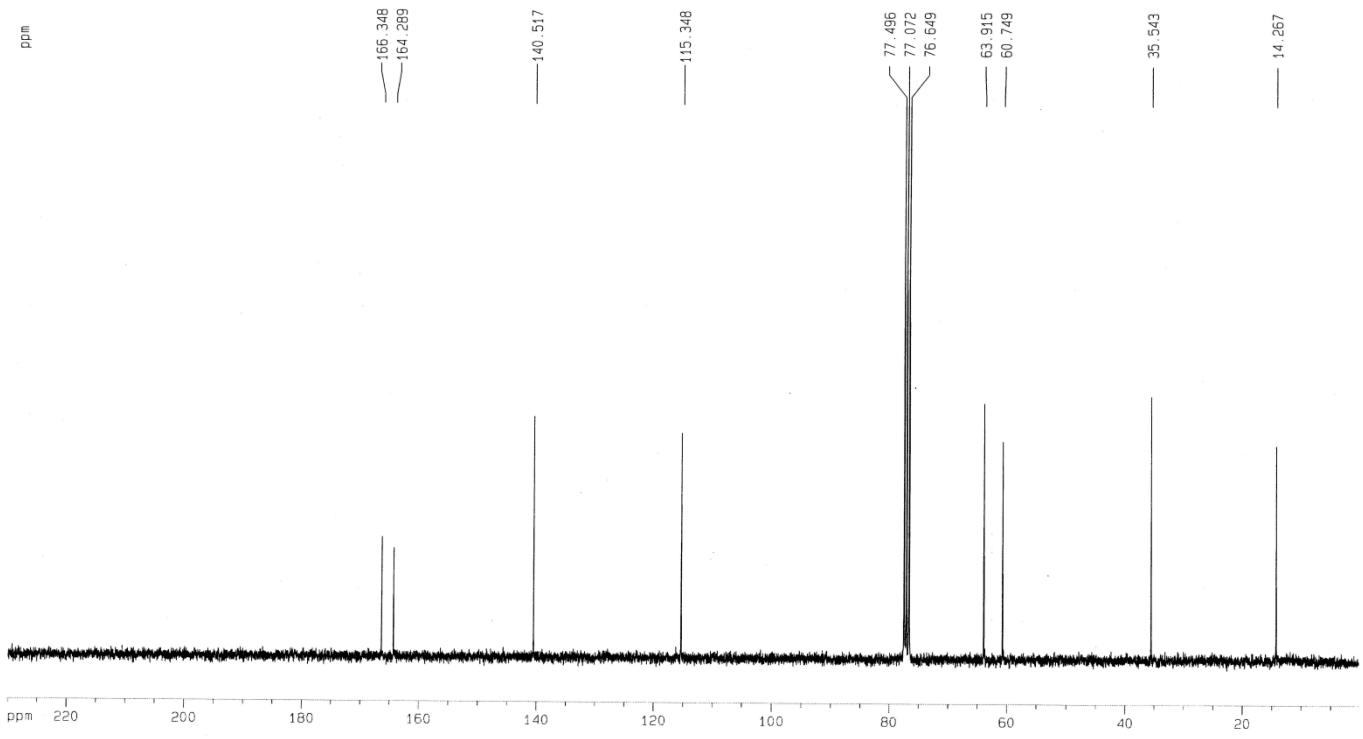

Fig S-16: ^{13}C NMR Spectrum of Product **3fa**

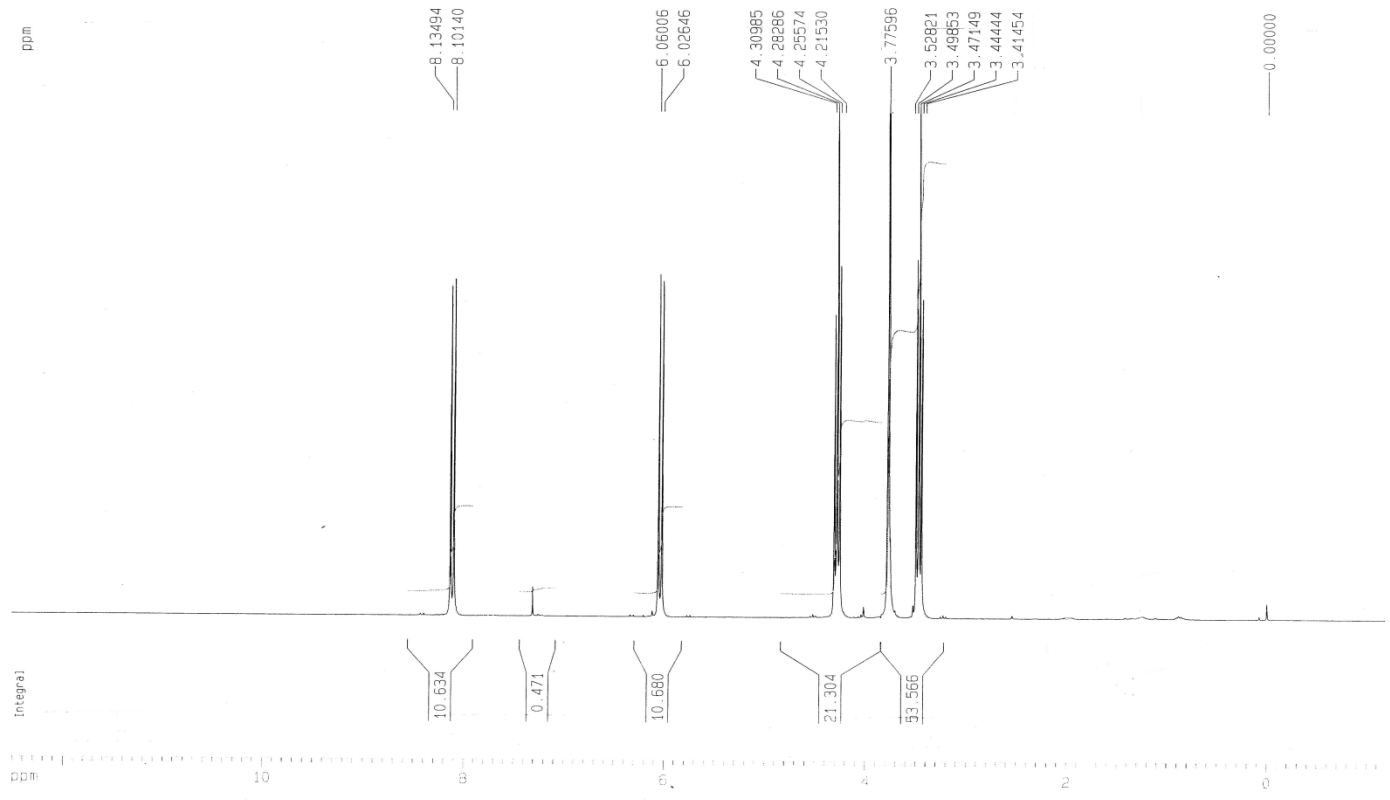

Fig S-17: ^{1}H NMR Spectrum of Product **3fb**

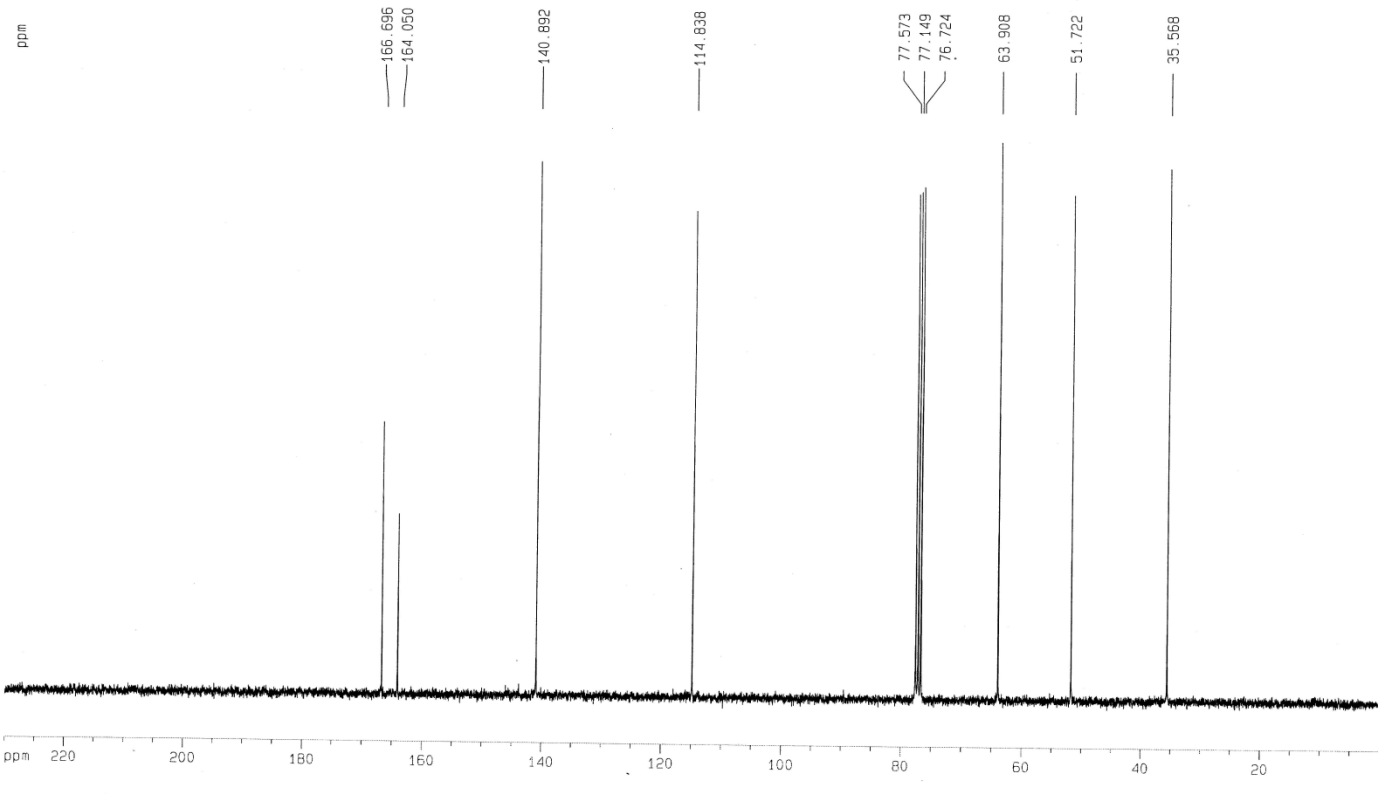

Fig S-18: ^{13}C NMR Spectrum of Product **3fb**

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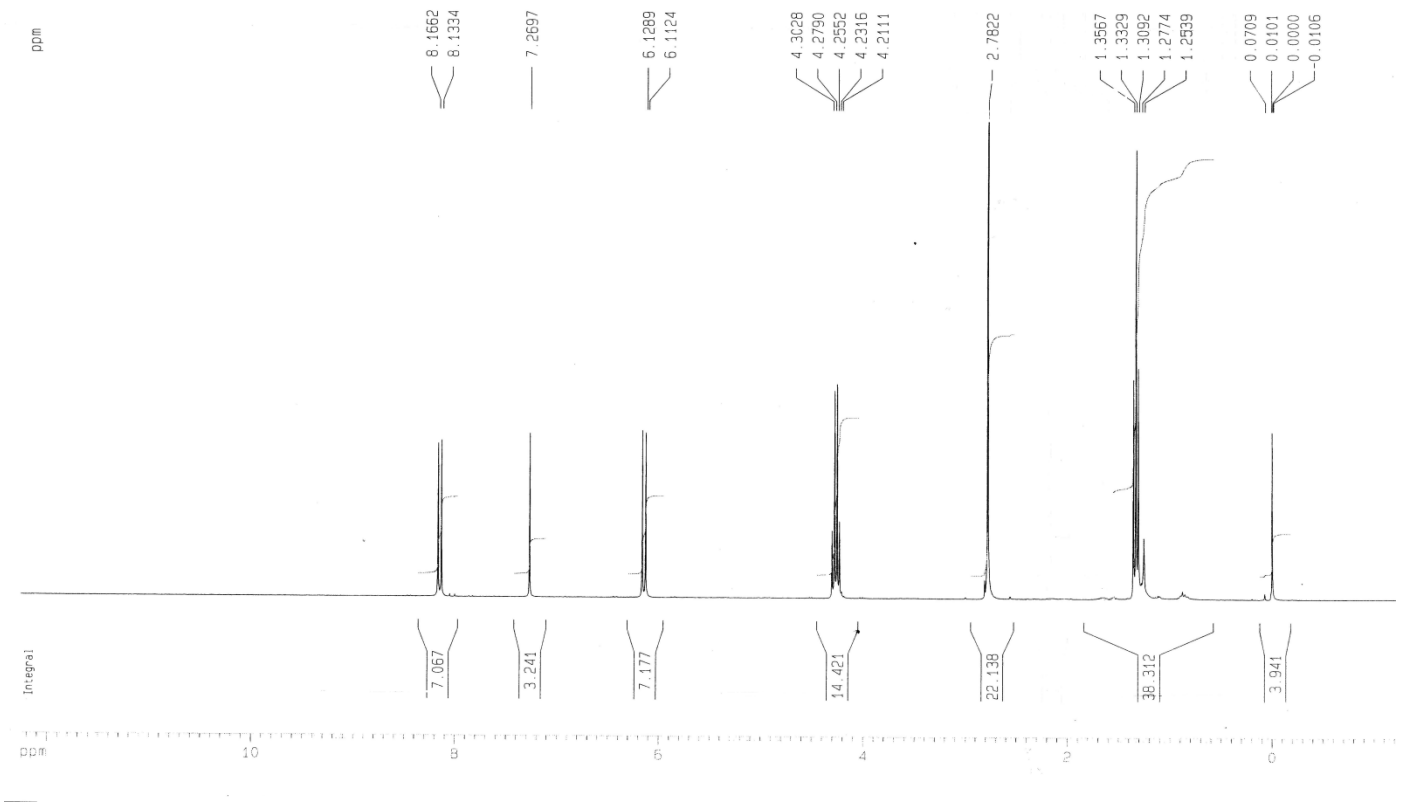

Fig S-19: ^{1}H NMR Spectrum of Product **3ga**

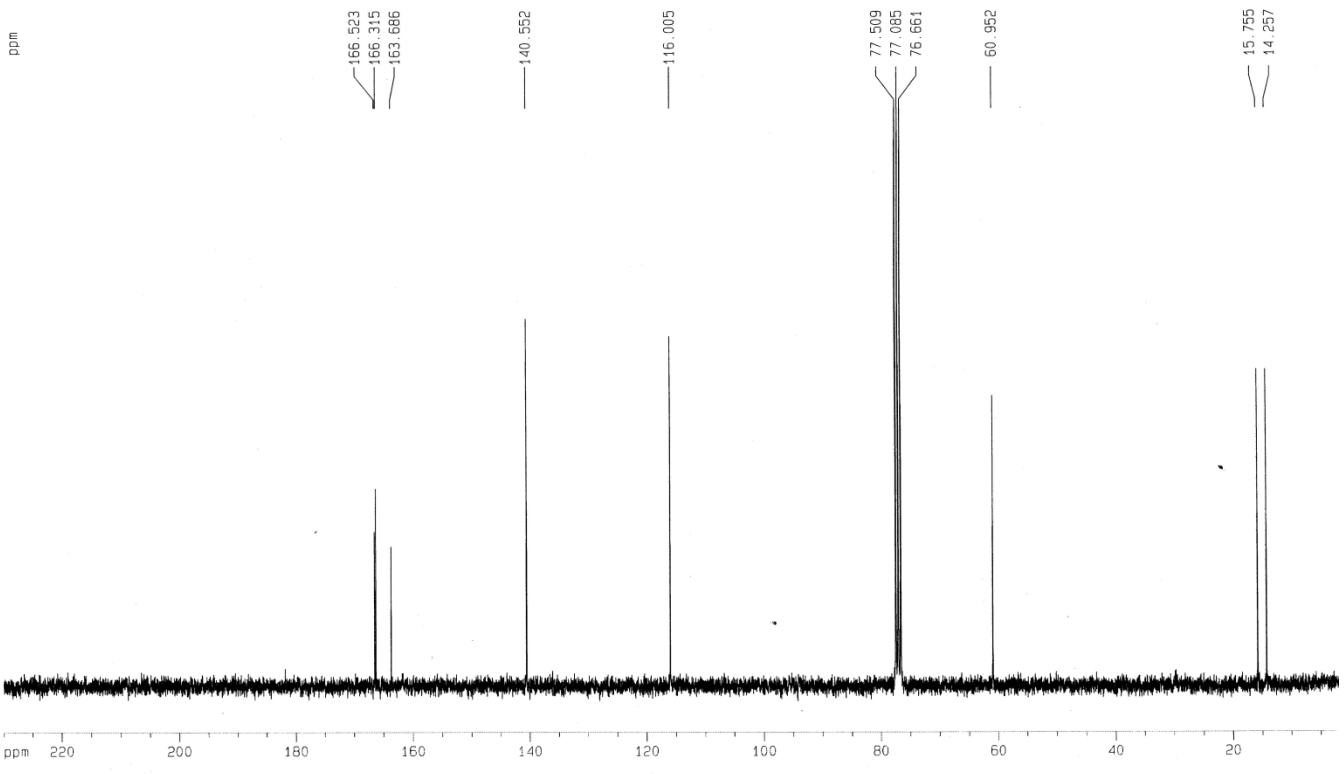

Fig S-20: ^{13}C NMR Spectrum of Product **3ga**

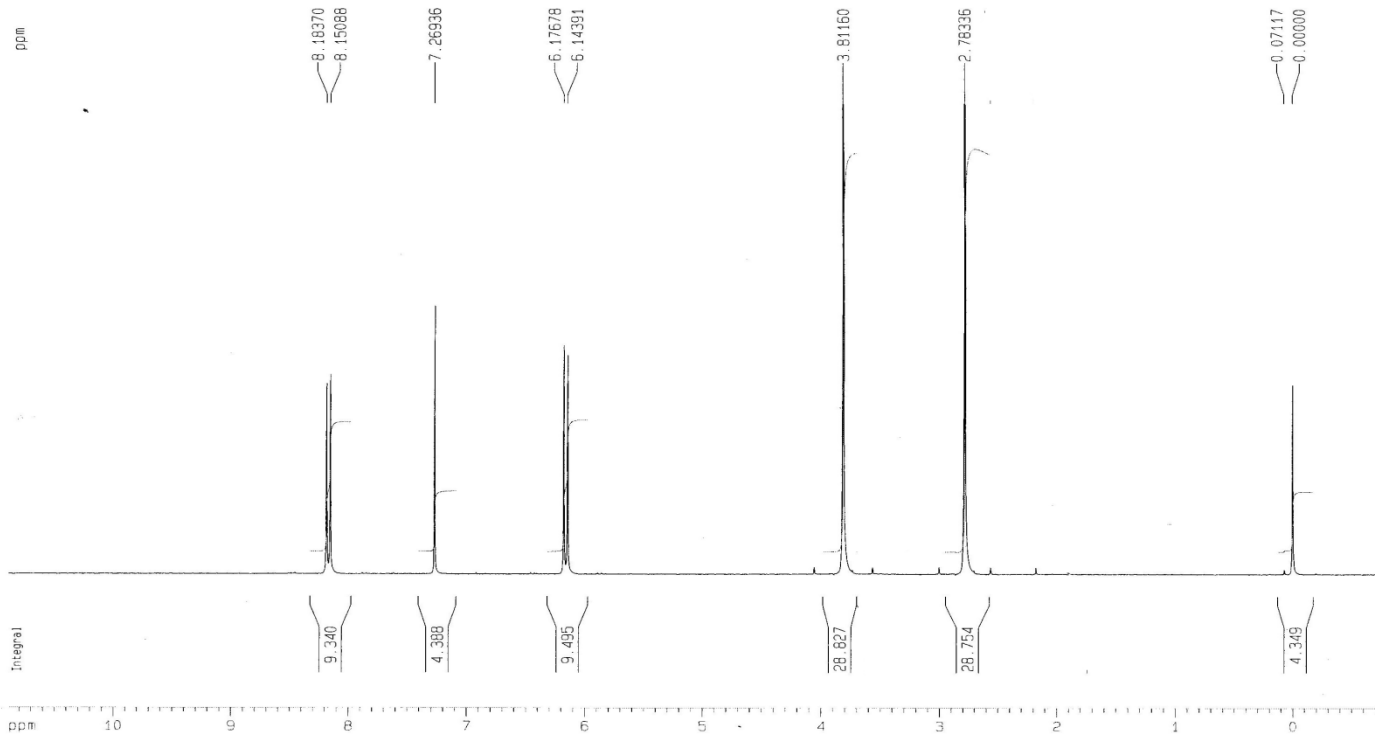

Fig S-21: ^{1}H NMR Spectrum of Product **3gb**

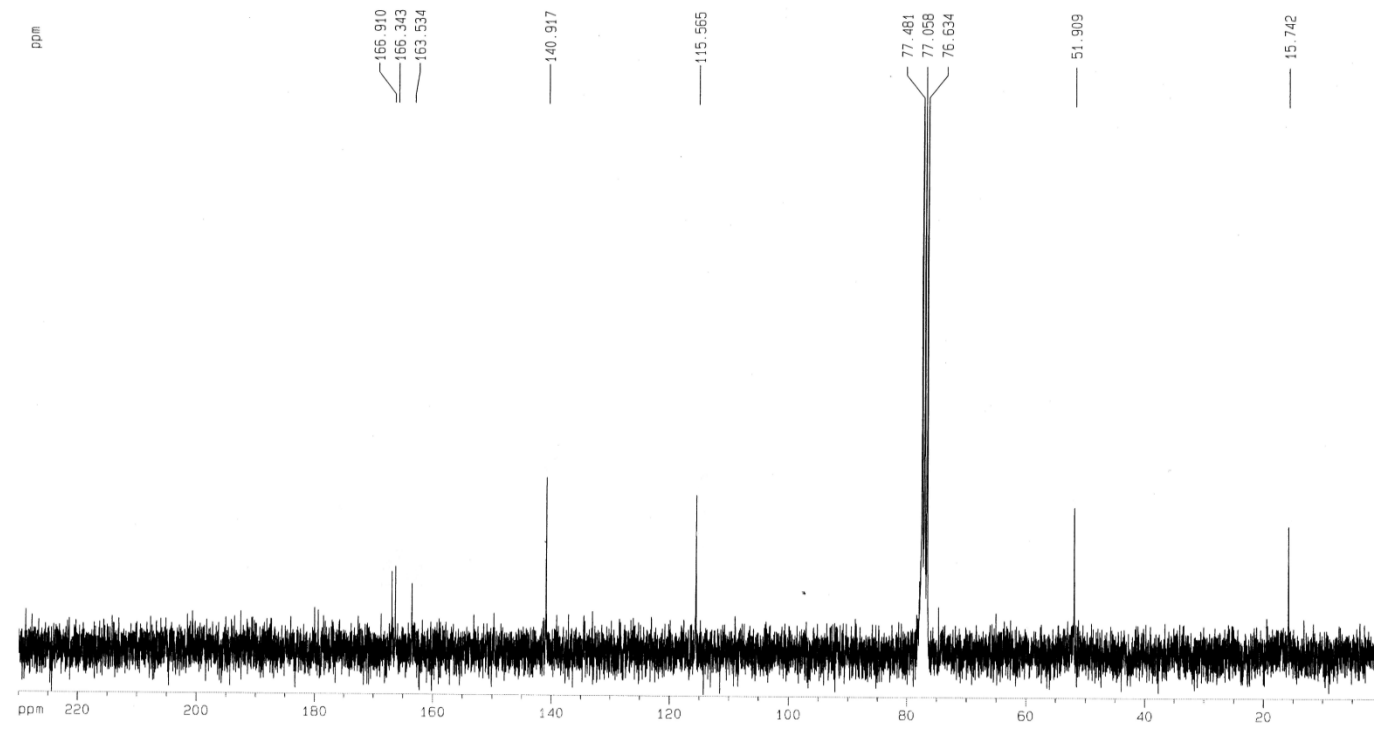

Fig S-22: ^{13}C NMR Spectrum of Product **3gb**

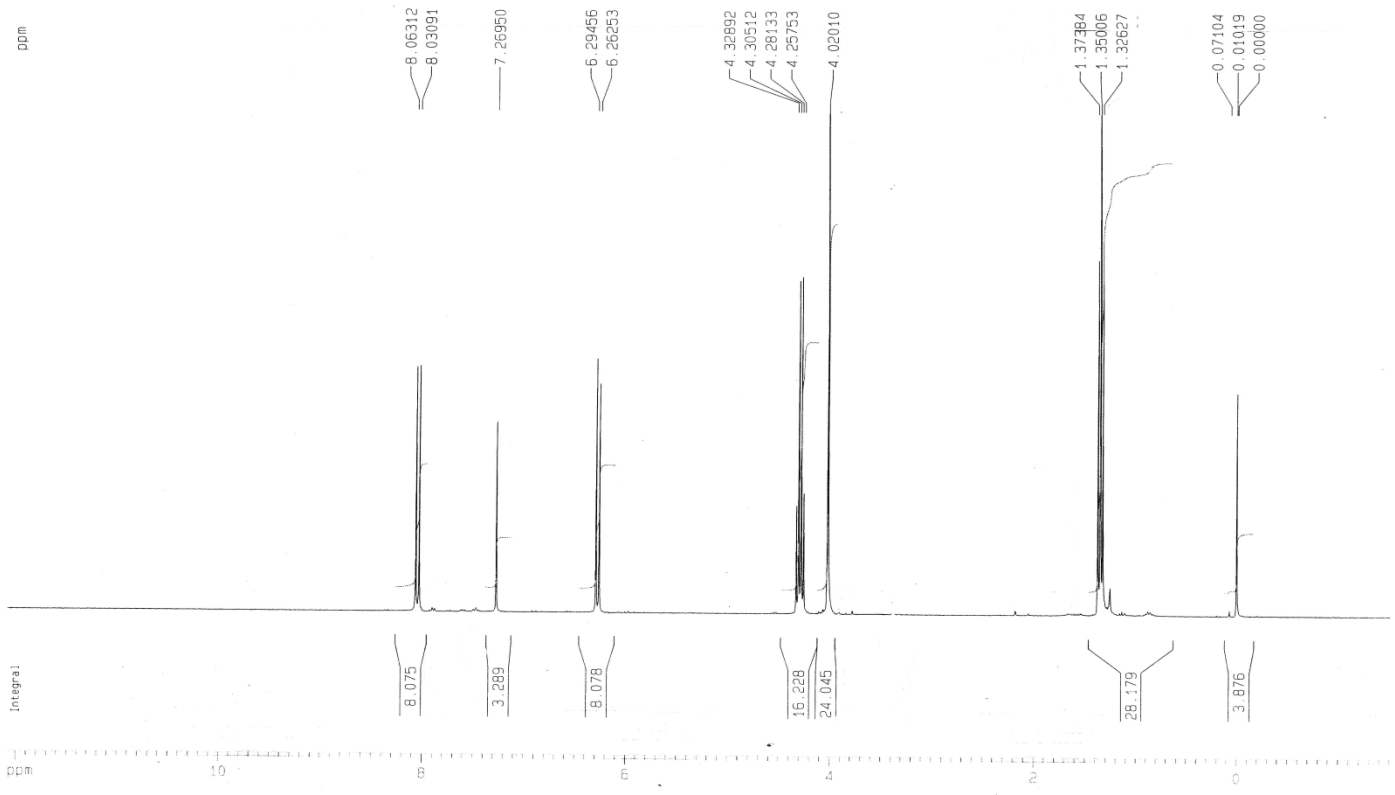

Fig S-23: ^{1}H NMR Spectrum of Product **3ha**

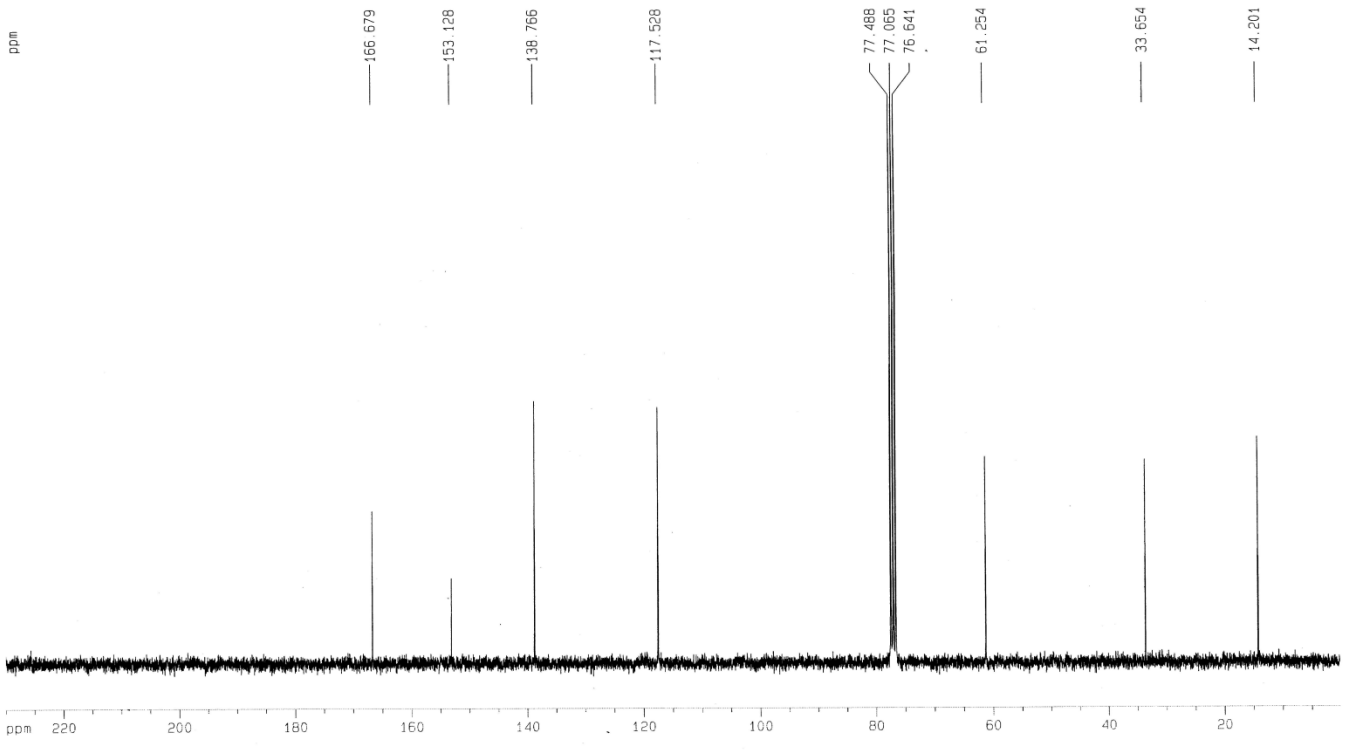

Fig S-24: ^{13}C NMR Spectrum of Product **3ha**

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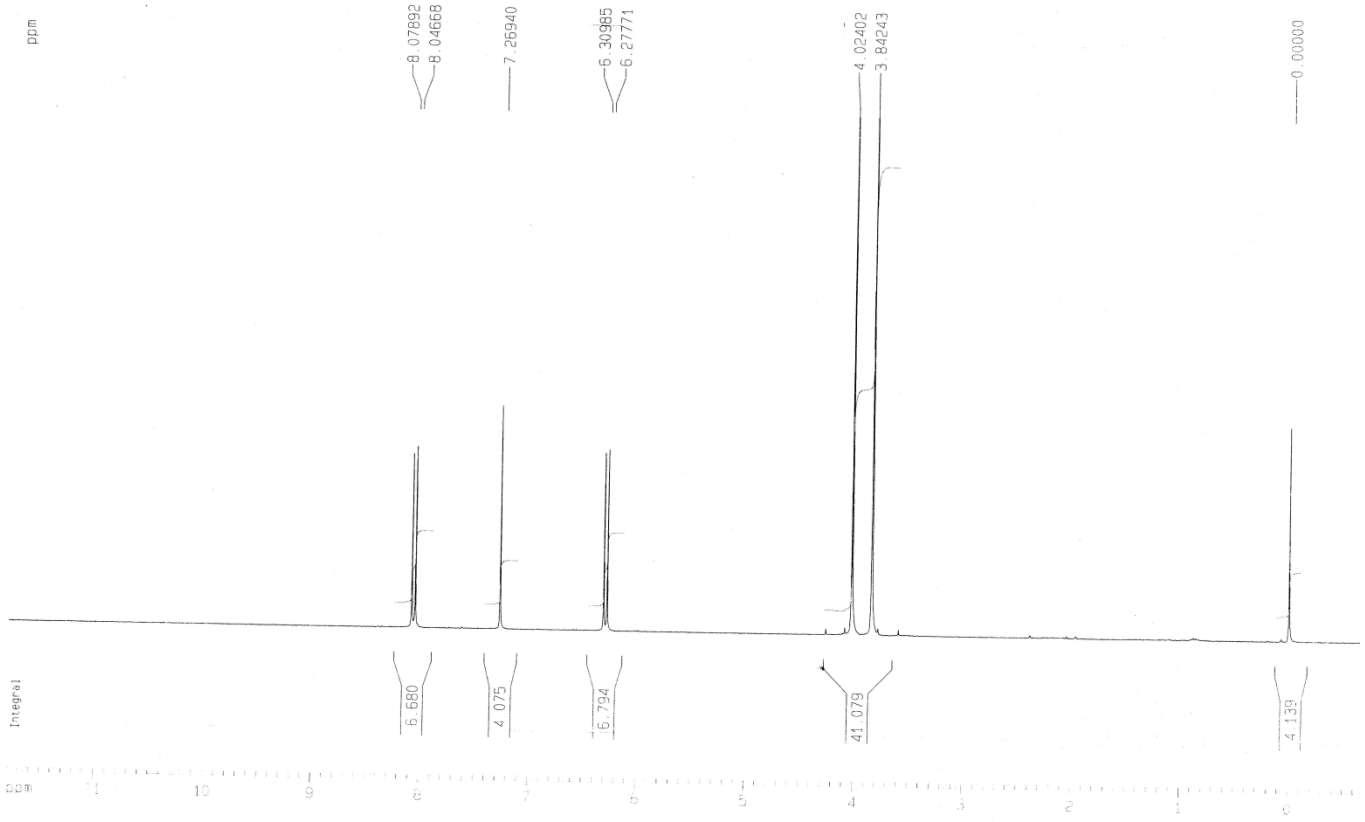

Fig S-25: ^{1}H NMR Spectrum of Product **3hb**

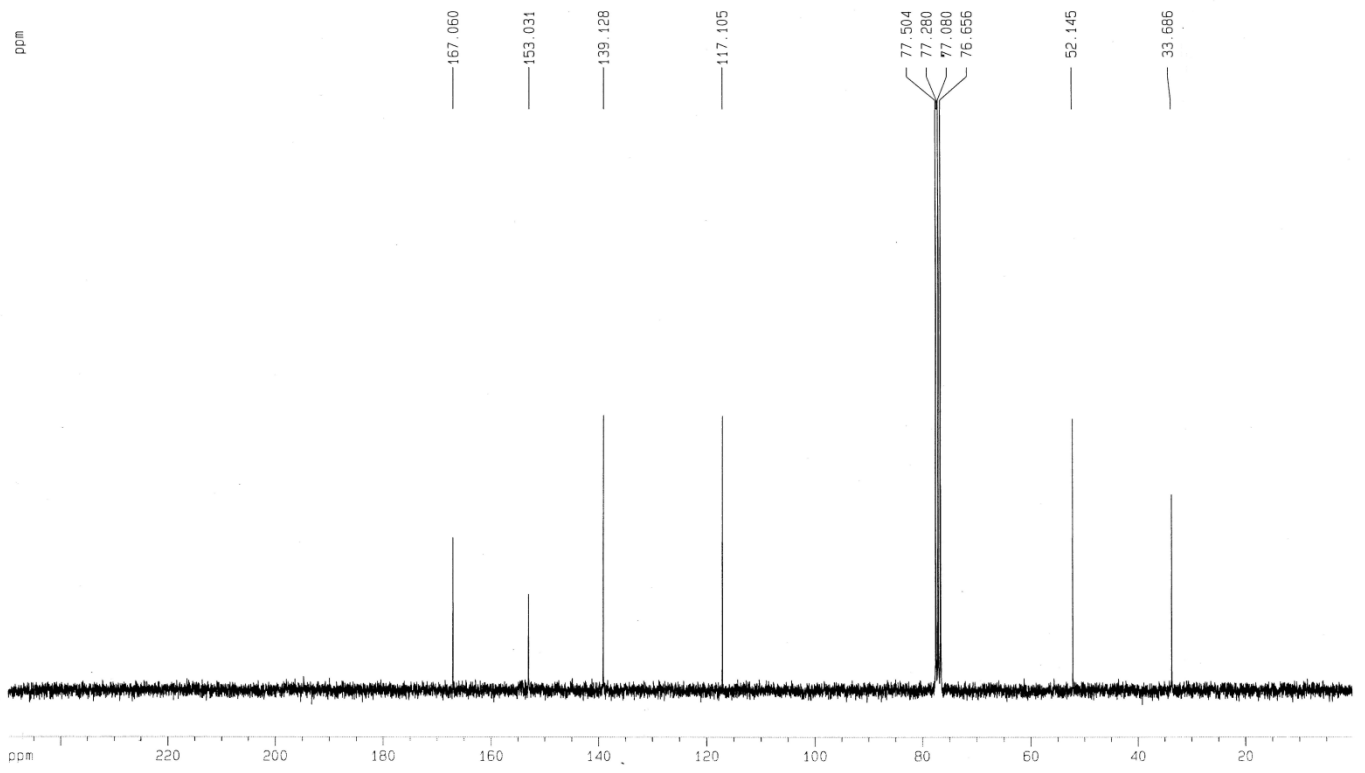

Fig S-26: ^{13}C NMR Spectrum of Product **3hb**

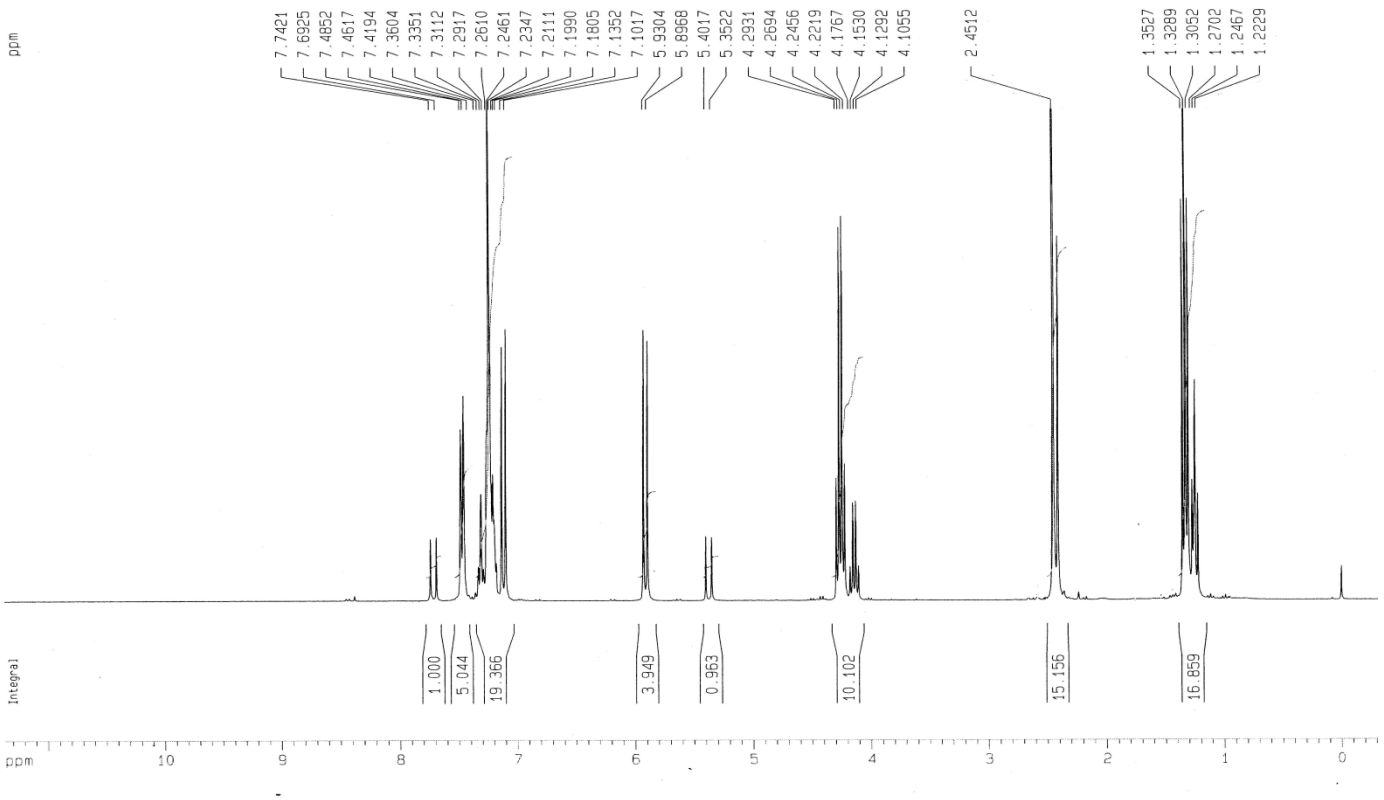

Fig S-27: ^{1}H NMR Spectrum of Product **5a**

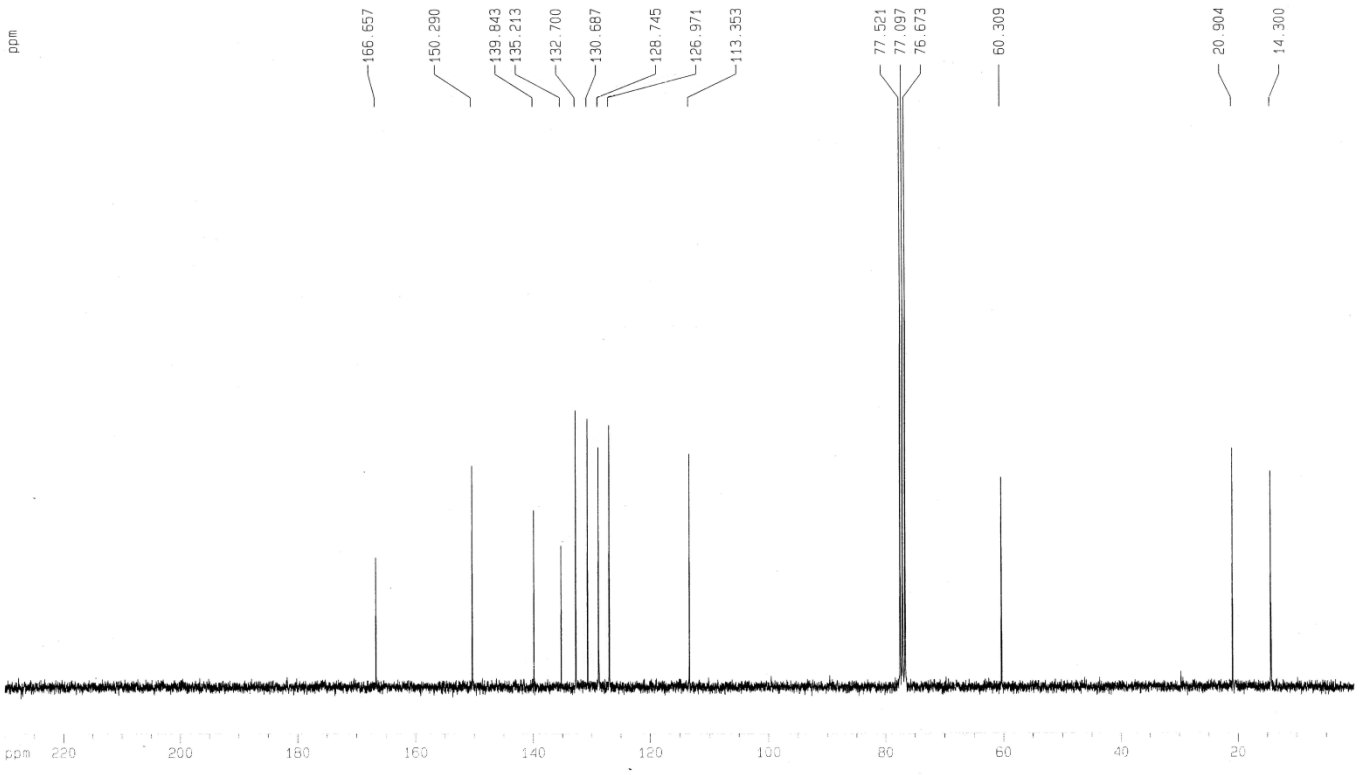

Fig S-28: ^{13}C NMR Spectrum of Product **5a**

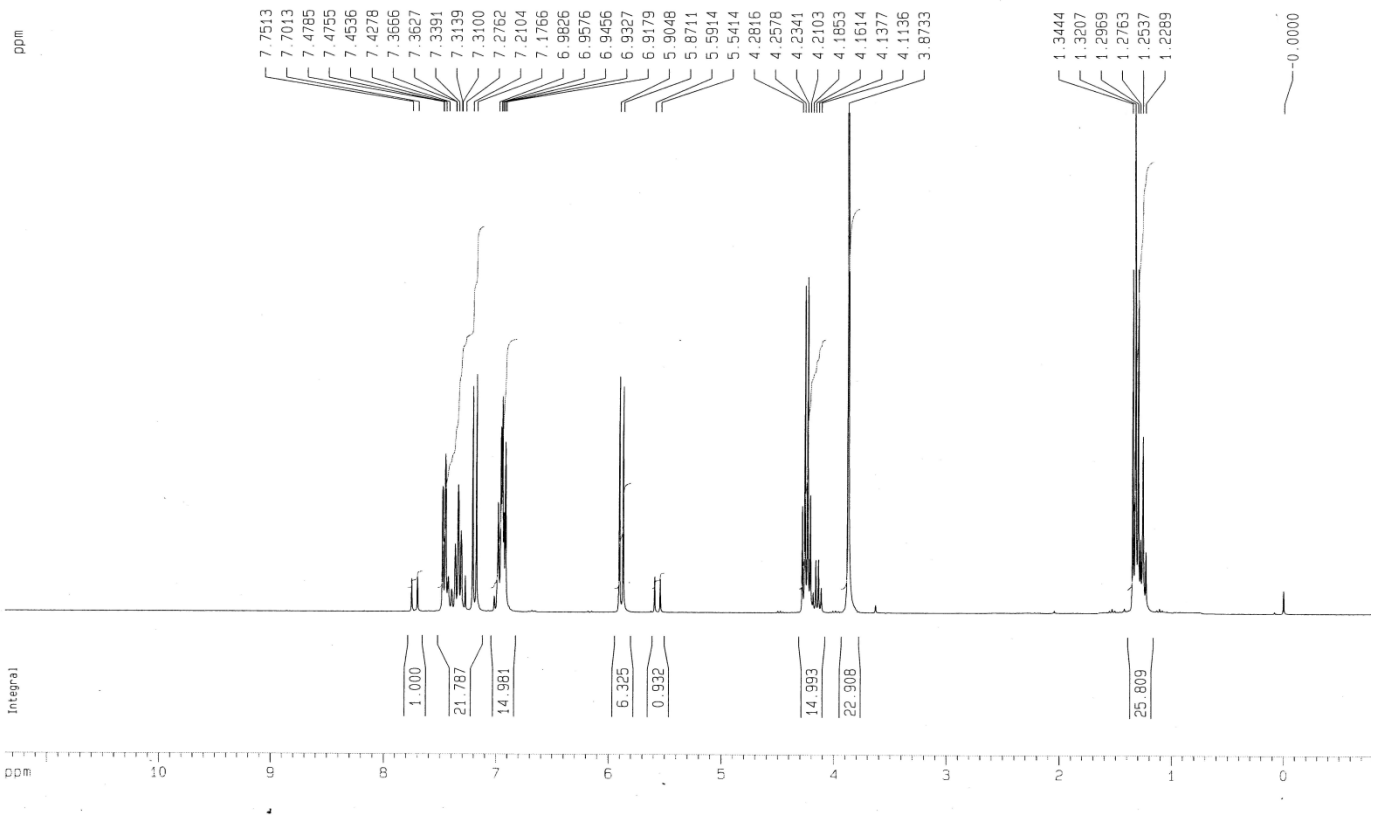

Fig S-29: ^{1}H NMR Spectrum of Product **5b**

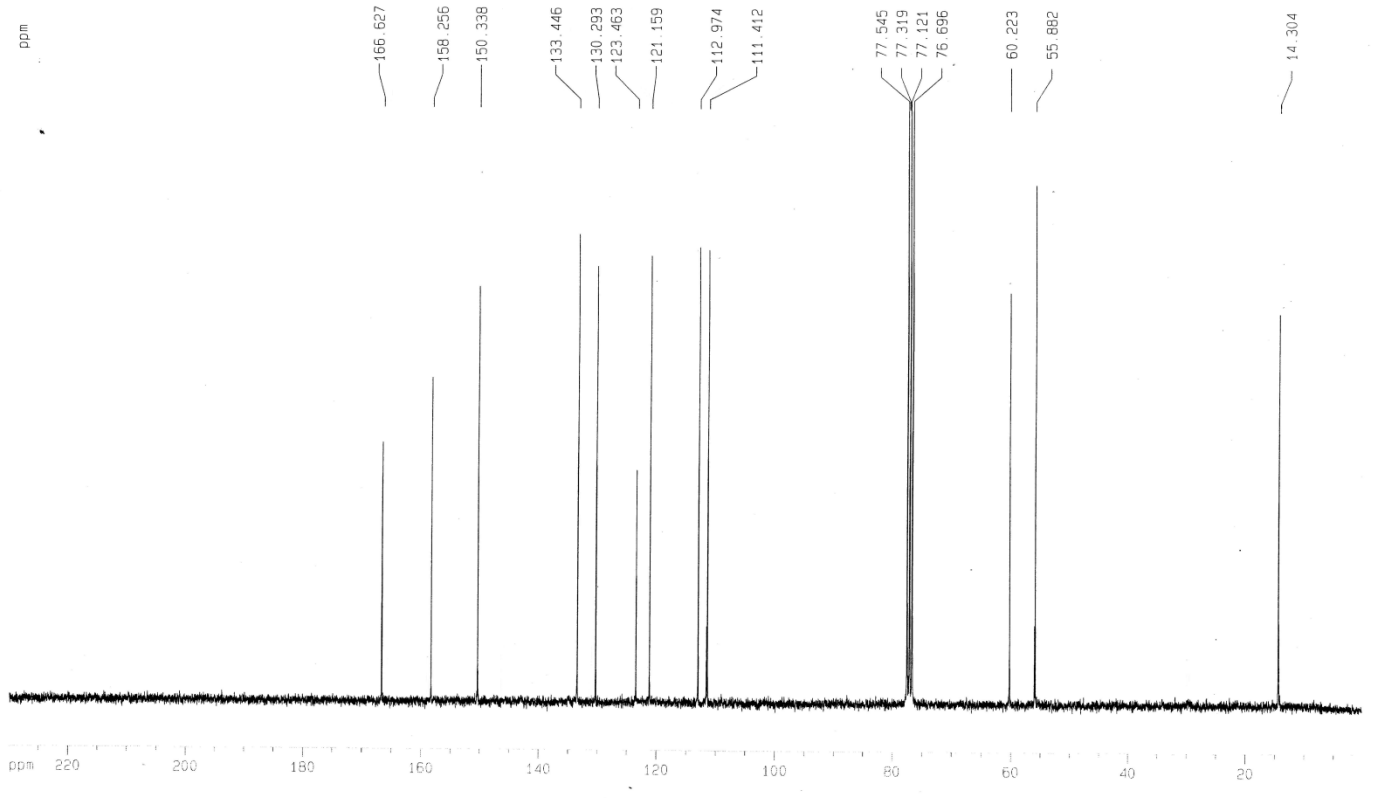

Fig S-30: ^{13}C NMR Spectrum of Product **5b**

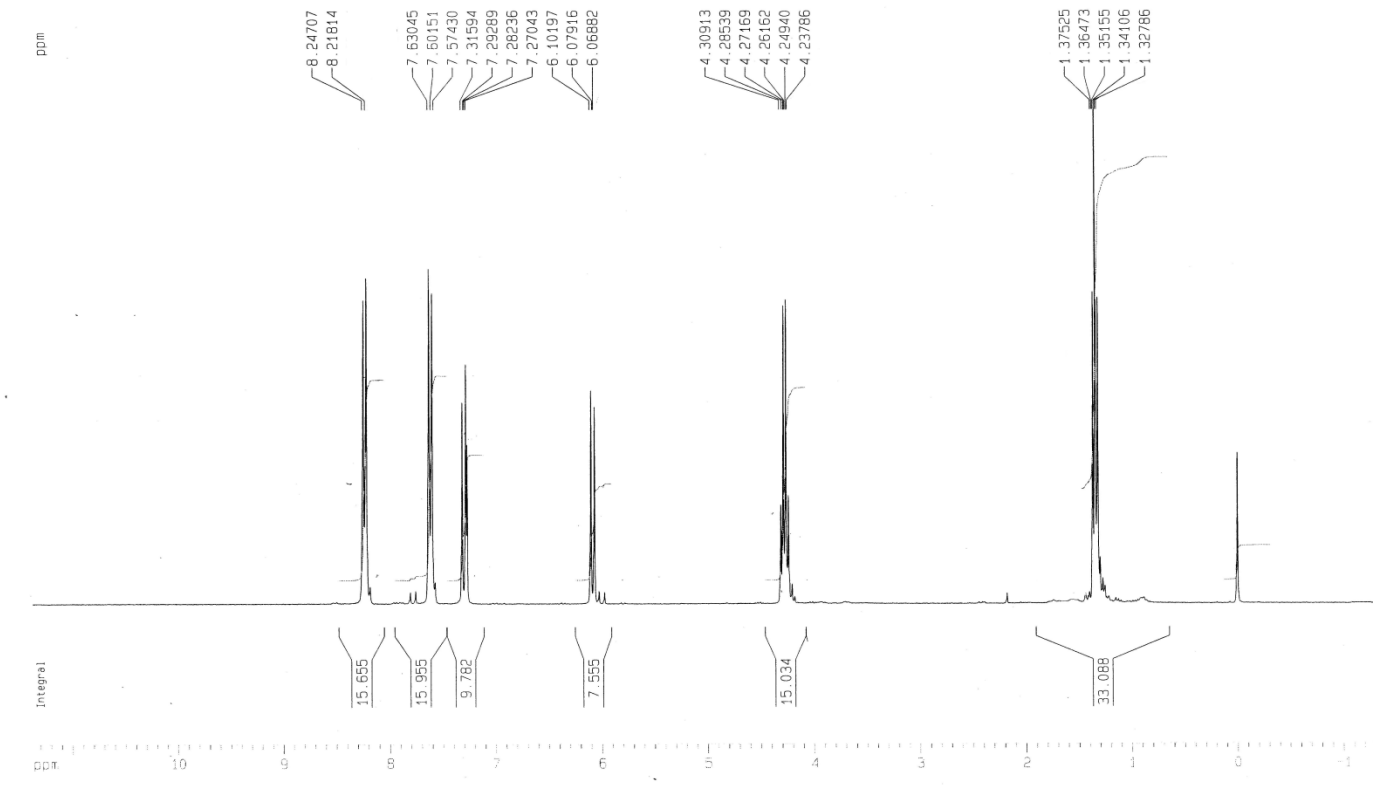

Fig S-31: ^{1}H NMR Spectrum of Product **5c**

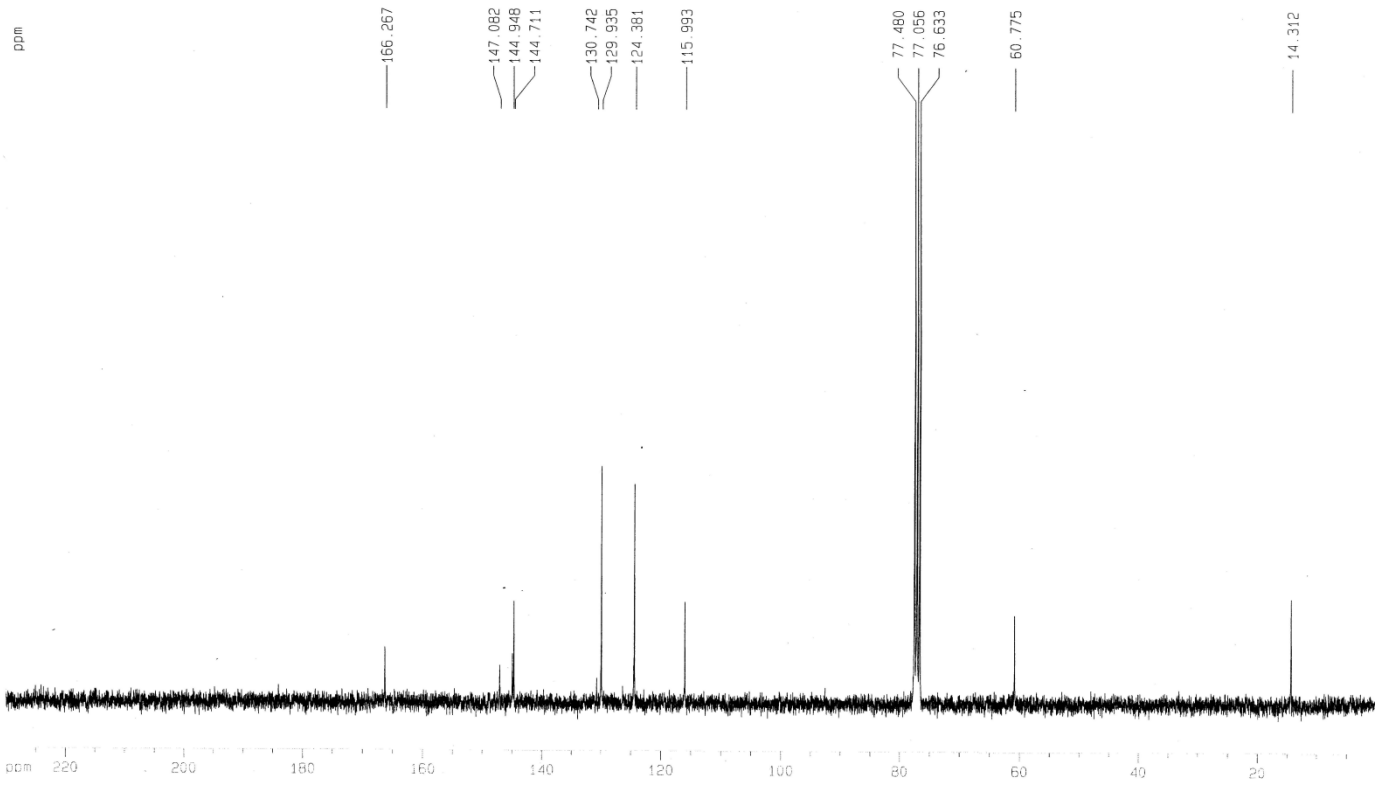

Fig S-32: ^{13}C NMR Spectrum of Product **5c**

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1. C. W. Downey, S. Craciun, A. M. Neferu, C. A. Vivelo, C. J. Mueller, B. C. Southall, S. Corsi, Eric W. Etchill, R. J. Sault, *Tetrahedron. Lett.,* **2012,** *53*, 5763–5765.
2. N. A. Randive, V. Kumar, V. A. Nair, *Monatsh Chem.*, **2010**, *141*, 1329–1332.