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Electronic Supplementary Information

Catalyst-free multi-component cascade C-H-functionalization in water using molecular oxygen: An approach to 1,3-oxazines

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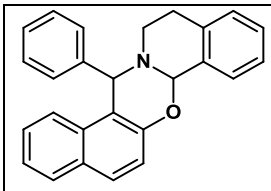
General information

All the commercially available reagents were used as received. Melting points were determined in open capillary tubes with a Buchi-540 micro melting point apparatus and were uncorrected. I.R. spectra were recorded on a Perkin-Elmer system 2000 FT-IR spectrometer. Mass spectra (ESI-HRMS) were recorded on Agilent Accurate-Mass Q-TOF LC/MS 6520. NMR spectra were recorded on a Bruker Avance DPX-300 and -500 NMR spectrometer with TMS as the internal standard at room temperature. Chemical shifts (δ) are quoted in ppm and coupling constants (*J*) are measured in Hertz (Hz). All the experiments were monitored by thin layer chromatography (TLC) on pre-coated silica gel plates (Merck) and visualized under UV lamp at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ warming in a hot air oven or by iodine vapor. Column chromatography was performed on silica gel (100-200 mesh, Merck) using ethyl acetate/hexane as eluent.

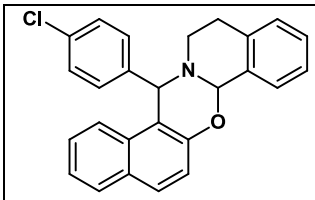
The representative procedure for the synthesis of 4a is as follows:

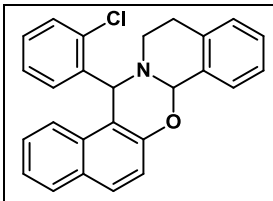
2-naphthol (**1a**, 144 mg, 1 mmol), benzaldehyde (**2a**, 106 mg, 1 mmol), tetrahydroisoquinoline (**3**, 133 mg, 1 mmol) and water (1.5 mL) were added in a round-bottom flask equipped with a magnetic stirring bar and a reflux condenser. The whole apparatus was efficiently flushed with oxygen gas and then connected to a balloon filled with oxygen. After vigorous stirring at 100 ^oC for 12 h, water was removed under vacuum and purified the reaction mixture by column chromatography (100-200 mesh silica gel, hexane-ethyl acetate) to obtain the product **4a** as white solid. The other 1,3-oxazines were synthesized and purified by following the procedure described above.

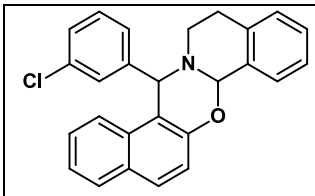


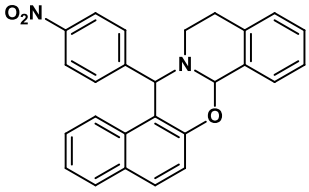
4a

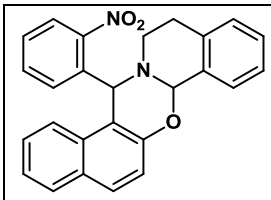
15-phenyl-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3]oxazino[2,3-a]isoquinoline (4a):[1] White solid; Yield 61 %, 221 mg; ^1H NMR (500 MHz, $CDCl_3$): δ 7.79-7.77 (m, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.43-7.41 (m, 1H), 7.33-7.28 (m, 8H), 7.24-7.19 (m, 3H), 7.11 (d, *J* = 8.9 Hz, 1H), 5.65 (s, 1H), 5.44 (s, 1H), 3.40-3.26 (m, 2H), 3.12-3.09 (m, 1H), 2.90-2.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 142.3, 135.0, 133.0, 132.4, 129.3, 129.1, 128.9, 128.8 (2C), 128.7, 128.6, 128.2, 127.4, 126.5, 126.2, 123.1, 122.7, 118.9, 110.9, 82.2, 62.6, 45.4, 29.4; HRMS (ESI) exact mass calculated for $C_{26}H_{21}NO$ $[M+H]^+$: 364.1701; found: 364.1705.

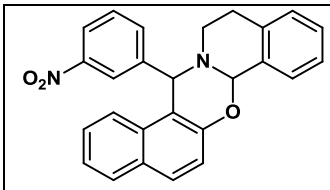
 **4b**	**15-(4-chlorophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4b):**[1b] Off white solid; Yield 64 %, 254 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80-7.78 (m, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.36-7.29 (m, 5H), 7.25-7.19 (m, 6H), 7.11 (d, *J* = 9.0 Hz, 1H), 5.58 (s, 1H), 5.38 (s, 1H), 3.39-3.25 (m, 2H), 3.10-3.07 (m, 1H), 2.89-2.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 140.9, 134.9, 133.2, 132.8, 132.2, 130.7, 129.4, 128.9 (2C), 128.8, 128.7 (2C), 128.4, 126.7, 126.2, 123.3, 122.4, 119.0, 110.4, 82.2, 61.9, 45.3, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}ClNO$ $[M+H]^+$: 398.1312; found: 398.1318.

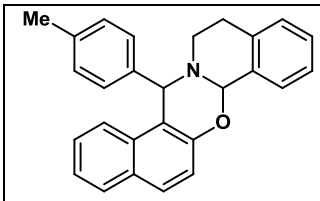
 **4c**	**15-(2-chlorophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4c):** Off white solid; Yield 59 %, 234 mg; Mp = 155-156 ºC; IR (KBr): 3060, 2926, 2855, 1624, 1467, 1405, 1237, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.73 (m, 2H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.36-7.13 (m, 9H), 7.04-6.93 (m, 2H), 5.71 (s, 2H), 3.41-3.22 (m, 3H), 2.85-2.82 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.5, 139.8, 135.3, 134.8, 132.7, 131.8, 130.2, 129.4, 129.0, 128.9, 128.8 (2C), 128.7, 128.6, 126.7, 126.2, 126.1, 123.3, 122.6, 118.9, 110.1, 82.0, 59.9, 45.2, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}ClNO$ $[M+H]^+$: 398.1312; found: 398.1308.

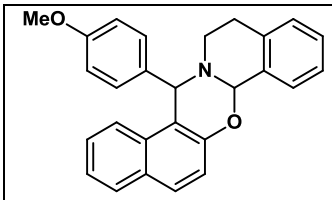
 **4d**	**15-(3-chlorophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4d):**[1b] Off white solid; Yield 60 %, 238 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81-7.79 (m, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.38-7.30 (m, 6H), 7.25-7.17 (m, 5H), 7.11 (d, *J* = 9.0 Hz, 1H), 5.60 (s, 1H), 5.39 (s, 1H), 3.39-3.26 (m, 2H), 3.11-3.07 (m, 1H), 2.90-2.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 144.5, 134.9, 134.2, 132.8, 132.2, 129.5, 129.4 (2C), 129.0, 128.9, 128.8, 128.7 (2C), 127.7, 127.6, 126.8, 126.2, 123.3, 122.4, 118.9, 110.1, 82.1, 62.1, 45.4, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}ClNO$ $[M+H]^+$: 398.1312; found: 398.1316.

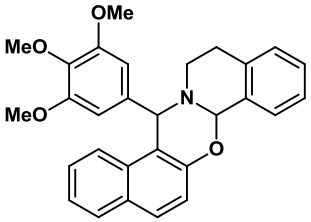
 **4e**	**15-(4-nitrophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4e):** Brown solid; Yield 66 %, 269 mg; Mp = 146-148 ºC; IR (KBr): 3065, 2922, 2863, 1623, 1531, 1460, 1364, 1233, 745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14-8.12 (m, 2H), 7.83-7.81 (m, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.51-7.49 (m, 2H), 7.38-7.33 (m, 2H), 7.32-7.29 (m, 3H), 7.25-7.21 (m, 2H), 7.13 (d, *J* = 8.9 Hz, 1H), 5.50 (s, 1H), 5.47 (s, 1H), 3.44-3.39 (m, 1H), 3.35-3.28 (m, 1H), 3.16-3.12 (m, 1H), 2.92-2.89 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0, 149.4, 147.3, 134.7, 132.5, 132.1, 130.2, 129.8, 129.1, 129.0, 128.9, 128.8, 128.7, 127.0, 126.3, 123.5, 122.1, 119.0, 109.5, 82.3, 61.9, 45.5, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}N_2O_3$ $[M+H]^+$: 409.1552; found: 409.1559.

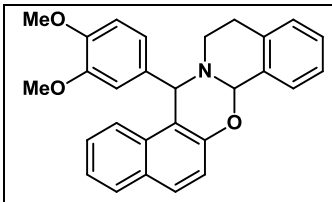
 **4f**	**15-(2-nitrophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4f):** Brown solid; Yield 60 %, 245 mg; Mp = 130-133 ºC; IR (KBr): 3063, 2928, 2852, 1625, 1530, 1467, 1235, 986, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.82-7.77 (m, 3H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.41-7.24 (m, 6H), 7.21-7.11 (m, 3H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.30 (s, 1H), 5.41 (s, 1H), 3.30-3.12 (m, 2H), 3.07-3.04 (m, 1H), 2.76-2.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 149.7, 136.3, 135.2, 132.3, 132.2, 131.7, 131.5, 129.8, 128.9, 128.8, 128.7, 128.5, 128.4, 127.0, 126.0, 125.0, 123.5, 122.5, 119.1, 109.0, 82.2, 57.5, 45.4, 28.9; HRMS (ESI) exact mass calculated for $C_{26}H_{20}N_2O_3$ $[M+H]^+$: 409.1552; found: 409.1557.

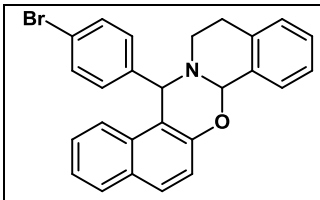
 **4g**	**15-(3-nitrophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4g):[1b]** Light yellow solid; Yield 63 %, 257 mg; ^1H NMR (500 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.12-8.10 (m, 1H), 7.86-7.81 (m, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.59-7.51 (m, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.38-7.30 (m, 5H), 7.25-7.21 (m, 2H), 7.13 (d, *J* = 8.9 Hz, 1H), 5.52 (s, 1H), 5.48 (s, 1H), 3.45-3.39 (m, 1H), 3.36-3.30 (m, 1H), 3.17-3.14 (m, 1H), 2.92-2.89 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 148.5, 144.6, 135.4, 134.8, 132.5, 132.0, 129.9, 129.1 (2C), 129.0, 128.9, 128.8, 128.7, 127.0, 126.3, 124.4, 123.5, 122.6, 122.0, 119.0, 109.3, 82.1, 61.9, 45.5, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}N_2O_3$ $[M+H]^+$: 409.1552; found: 409.1547.

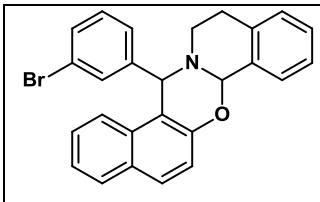
 **4h**	**15-(p-tolyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3]oxazino [2,3-a]isoquinoline (4h):[1b]** Off white solid; Yield 60 %, 226 mg; ^1H NMR (500 MHz, $CDCl_3$): δ 7.78-7.77 (m, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.34-7.27 (m, 3H), 7.24-7.18 (m, 4H), 7.11-7.06 (m, 4H), 5.66 (s, 1H), 5.40 (s, 1H), 3.38-3.24 (m, 2H), 3.10-3.07 (m, 1H), 2.88-2.85 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 139.5, 137.0, 135.0, 133.1, 132.4, 129.2, 129.0, 128.8 (2C), 128.7 (2C), 128.5, 128.4, 126.5, 126.1, 123.1, 122.7, 118.9, 111.1, 82.2, 62.4, 45.3, 29.3, 21.1; HRMS (ESI) exact mass calculated for $C_{27}H_{23}NO$ $[M+H]^+$: 378.1858; found: 378.1852.

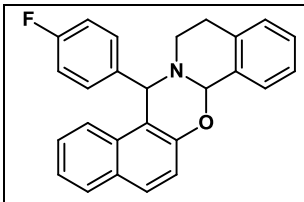
 **4i**	**15-(4-methoxyphenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6] [1,3]oxazino[2,3-a]isoquinoline (4i):**[1b] White solid; Yield 59 %, 232 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78-7.77 (m, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.35-7.27 (m, 5H), 7.25-7.18 (m, 3H), 7.10 (d, *J* = 8.9 Hz, 1H), 6.80-6.78 (m, 2H), 5.66 (s, 1H), 5.39 (s, 1H), 3.75 (s, 3H), 3.38-3.24 (m, 2H), 3.09-3.06 (m, 1H), 2.88-2.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 151.8, 135.0, 134.6, 133.0, 132.3, 130.4, 129.0, 128.8 (3C), 128.7, 128.5, 126.5, 126.1, 123.1, 122.7, 118.9, 113.5, 111.2, 82.1, 62.0, 55.2, 45.2, 29.3; HRMS (ESI) exact mass calculated for $C_{27}H_{23}NO_2$ $[M+H]^+$: 394.1807; found: 394.1809.

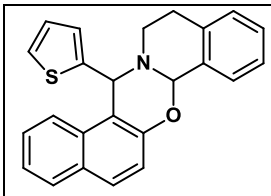
 **4j**	**15-(3,4,5-trimethoxyphenyl)-7a,12,13,15-tetrahydronaphtho [1',2': 5,6][1,3]oxazino[2,3-a]isoquinoline (4j):**[1b] White solid; Yield 56 %, 254 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78-7.76 (m, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.38-7.34 (m, 2H), 7.32-7.29 (m, 2H), 7.27-7.24 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 6.54 (bs, 2H), 5.73 (s, 1H), 5.36 (s, 1H), 3.81 (s, 3H), 3.67 (s, 6H), 3.36-3.26 (m, 2H), 3.10-3.06 (m, 1H), 2.91-2.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 151.7, 138.0, 137.1, 134.9, 133.0, 132.4, 129.2, 128.9, 128.8, 128.7, 128.5, 126.5, 126.2, 123.1, 122.7, 118.8, 110.7, 106.5, 82.3, 62.8, 60.8, 56.0, 45.2, 29.3; HRMS (ESI) exact mass calculated for $C_{29}H_{27}NO_4$ $[M+H]^+$: 454.2018; found: 454.2013.

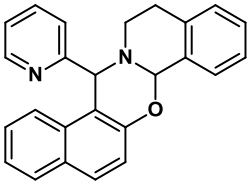
 **4k**	**15-(3,4-dimethoxyphenyl)-7a,12,13,15-tetrahydronaphtho [1',2':5, 6][1,3]oxazino[2,3-a]isoquinoline (4k):** White solid; Yield 58 %, 245 mg; Mp = 171-173 ºC; IR (KBr): 3062, 2926, 2864, 1620, 1511, 1465, 1251, 1033, 813, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.36-7.29 (m, 4H), 7.20 (d, *J* = 7.5 Hz,, 1H), 7.11-7.03 (m, 1H), 7.03 (bs, 1H), 6.69-6.65 (m, 2H), 5.70 (s, 1H), 5.38 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.40-3.26 (m, 2H), 3.09-3.07 (m, 1H), 2.89-2.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 151.8, 135.0, 134.6, 133.0, 132.4, 129.7, 129.1, 128.8, 128.5, 127.7, 126.4, 126.3, 126.2, 123.5, 122.7, 121.8, 118.8, 117.8, 112.3, 110.3, 109.4, 82.2, 62.4, 55.8 (2C), 45.2, 29.3; HRMS (ESI) exact mass calculated for $C_{28}H_{25}NO_3$ $[M+H]^+$: 424.1913; found: 424.1909.

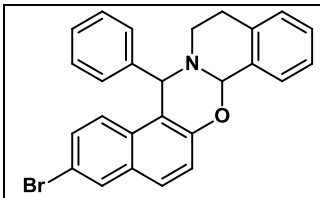
 **4l**	**15-(4-bromophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4l):**[1b] White solid; Yield 62 %, 273 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80-7.78 (m, 1H), 7.76-7.73 (m, 1H), 7.40-7.34 (m, 4H), 7.33-7.29 (m, 4H), 7.25-7.19 (m, 3H), 7.11 (d, *J* = 9.0 Hz, 1H), 5.58 (s, 1H), 5.36 (s, 1H), 3.39-3.34 (m, 2H), 3.10-3.07 (m, 1H), 2.89-2.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 141.4, 134.8, 132.8, 132.4, 132.2, 131.3, 131.1, 129.4, 128.9 (2C), 128.8, 128.7 (2C), 126.7, 126.2, 123.3, 122.4, 121.5, 118.9, 110.3, 82.1, 62.0, 45.3, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}BrNO$ $[M+H]^+$: 442.0807; found: 442.0813.

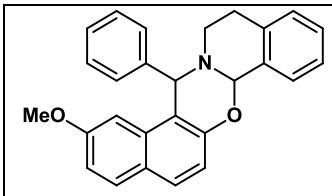
 **4m**	**15-(3-bromophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4m):** White solid; Yield 59 %, 261 mg; Mp = 139-141 ºC; IR (KBr): 3061, 2927, 2851, 1622, 1477, 1402, 1230, 1016, 745 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.3 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.62-7.52 (m, 2H), 7.38-7.35 (m, 3H), 7.33-7.29 (m, 4H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 2H), 5.60 (s, 1H), 5.38 (s, 1H), 3.38-3.28 (m, 2H), 3.09-3.06 (m, 1H), 2.89-2.85 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0, 144.7, 134.9, 132.8, 132.3, 130.6, 129.7, 129.5, 128.9 (2C), 128.8, 128.7 (2C), 128.0, 126.8, 126.4, 126.2, 123.3, 122.6, 122.4, 118.9, 110.0, 82.1, 62.1, 45.4, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}BrNO$ $[M+H]^+$: 442.0807; found: 442.0810.

 **4n**	**15-(4-fluorophenyl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4n):** White solid; Yield 66 %, 251 mg; Mp = 110-112 ºC; IR (KBr): 3066, 2919, 2864, 1605, 1505, 1233, 813, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.78 (m, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.39-7.19 (m, 9H), 7.11 (d, *J* = 9.0 Hz, 1H), 6.94 (t, *J* = 8.7 Hz, 2H), 5.60 (s, 1H), 5.39 (s, 1H), 3.38-3.24 (m, 2H), 3.09-3.06 (m, 1H), 2.89-2.84 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0 (d, $J_{C\text{-}F}$ = 246.1 Hz), 151.9, 138.1 (d, $J_{C\text{-}F}$ = 2.7 Hz), 134.9, 132.9, 132.2, 130.9 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.3, 128.9 (2C), 128.8, 128.7, 128.6, 126.6, 126.2, 123.2, 122.5, 118.9, 115.1 (d, $J_{C\text{-}F}$ = 20.9 Hz), 110.7, 82.1, 61.9, 45.2, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}FNO$ $[M+H]^+$: 382.1607; found: 382.1599.

 **4o**	**15-(thiophen-2-yl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4o):**[1b] Off white solid; Yield 60 %, 221 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.42-7.39 (m, 1H), 7.37-7.30 (m, 3H), 7.27-7.24 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 9.0 Hz, 1H), 6.83-6.81 (m, 1H), 6.63-6.62 (m, 1H), 5.87 (s, 1H), 5.60 (s, 1H), 3.33-3.26 (m, 2H), 3.10-3.03 (m, 1H), 2.90-2.83 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.3, 147.2, 135.0, 132.8, 132.1, 129.4, 128.9 (2C), 128.8 (2C), 128.5, 127.7, 126.6, 126.4, 126.2, 125.7, 123.2, 122.5, 118.9, 111.5, 82.2, 58.6, 44.6, 29.3; HRMS (ESI) exact mass calculated for $C_{24}H_{19}NOS$ $[M+H]^+$: 370.1266; found: 370.1261.

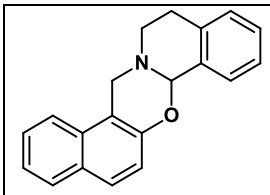
 **4p**	**15-(pyridin-2-yl)-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4p):** Brown solid; Yield 61 %, 222 mg; Mp = 165-167 ºC; IR (KBr): 3051, 2924, 1622, 1581, 1469, 1238, 816, 747 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.71 (dd, *J* = 4.7, 0.8 Hz, 1H), 7.78-7.73 (m, 2H), 7.58-7.54 (m, 1H), 7.36-7.33 (m, 2H), 7.32-7.27 (m, 3H), 7.25-7.21 (m, 1H), 7.18-7.16 (m, 2H), 7.15-7.13 (m, 2H), 5.81 (s, 1H), 5.56 (s, 1H), 3.47-3.42 (m, 1H), 3.36-3.29 (m, 1H), 3.22-3.18 (m, 1H), 2.87 (dd, *J* = 16.3, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.2, 152.0, 150.1, 136.6, 135.0, 132.7, 132.0, 129.4, 129.1, 128.9, 128.8, 128.7, 128.6, 126.6, 126.1, 123.7, 123.2, 122.5 (2C), 118.9, 110.3, 82.2, 65.1, 45.7, 29.2; HRMS (ESI) exact mass calculated for $C_{25}H_{20}N_2O$ $[M+H]^+$: 365.1654; found: 365.1652.

 **4q**	**3-bromo-15-phenyl-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3] oxazino[2,3-a]isoquinoline (4q):** White solid; Yield 63 %, 288 mg; Mp = 172-174 ºC; IR (KBr): 3066, 2924, 2853, 1623, 1486, 1230, 1011, 814, 748 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.39-7.37 (m, 2H), 7.31-7.27 (m, 6H), 7.25-7.19 (m, 3H), 7.13 (d, *J* = 9.0 Hz, 1H), 5.64 (s, 1H), 5.39 (s, 1H), 3.38-3.26 (m, 2H), 3.13-3.09 (m, 1H), 2.91-2.87 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.2, 142.0, 134.9, 132.7, 130.9, 130.5, 130.1, 129.7, 129.3, 129.2, 128.9, 128.8, 128.7, 128.3, 128.2, 127.6, 126.2, 124.4, 120.1, 116.7, 111.2, 82.4, 62.5, 45.4, 29.3; HRMS (ESI) exact mass calculated for $C_{26}H_{20}BrNO$ $[M+H]^+$: 442.0807; found: 442.0802.



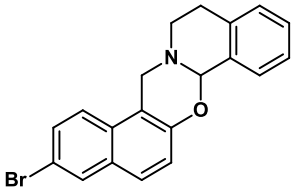
4r

2-methoxy-15-phenyl-7a,12,13,15-tetrahydronaphtho[1',2':5,6] [1,3]oxazino[2,3-a]isoquinoline (4r): White solid; Yield 57 %, 224 mg; Mp = 148-150 ºC; IR (KBr): 3065, 2925, 2859, 1609, 1510, 1465, 1248, 1031, 815, 748 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.32-7.18 (m, 9H), 6.98-6.95 (m, 2H), 6.67 (m, 1H), 5.66 (s, 1H), 5.33 (s, 1H), 3.64 (s, 3H), 3.42-3.36 (m, 1H), 3.32-3.25 (m, 1H), 3.12-3.09 (m, 1H), 2.90-2.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 152.5, 142.0, 135.0, 133.6, 133.0, 130.1, 129.2, 128.8 (3C), 128.7, 128.3, 127.4, 126.1, 124.1, 116.3, 114.7, 110.2, 102.4, 82.1, 62.9, 55.1, 45.4, 29.3; HRMS (ESI) exact mass calculated for $C_{27}H_{23}NO_2$ $[M+H]^+$: 394.1807; found: 394.1811.



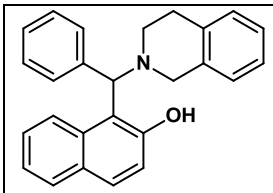
4s

7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3]oxazino[2,3-a] isoquinoline (4s):[1a] White solid; Yield 52 %, 149 mg; ^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.70-7.65 (m, 2H), 7.55-7.47 (m, 2H), 7.41-7.31 (m, 3H), 7.27-7.22 (m, 1H), 7.08 (d, *J* = 8.7 Hz, 1H), 5.81 (s, 1H), 4.82 (d, *J* = 16.2 Hz, 1H), 4.31 (d, *J* = 16.6 Hz, 1H), 3.50-3.42 (m, 1H), 3.18-3.13 (m, 1H), 2.99-2.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 134.9, 133.0, 131.5, 129.0, 128.8 (2C), 128.5, 128.2, 126.5, 126.3, 123.5, 121.2, 118.8, 111.1, 86.9, 51.3, 45.2, 29.2; HRMS (ESI) exact mass calculated for $C_{20}H_{17}NO$ $[M+H]^+$: 288.1388; found: 288.1381.



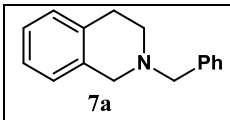
4t

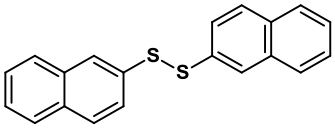
3-bromo-7a,12,13,15-tetrahydronaphtho[1',2':5,6][1,3]oxazino[2,3-a]isoquinoline (4t):[2] White solid; Yield 54 %, 198 mg; ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 2.0 Hz, 1H), 7.58-7.53 (m, 3H), 7.47-7.46 (m, 1H), 7.37-7.30 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 5.80 (s, 1H), 4.78 (d, *J* = 16.6 Hz, 1H), 4.25 (d, *J* = 16.6 Hz, 1H), 3.44-3.39 (m, 1H), 3.21-3.14 (m, 1H), 2.97-2.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.9, 134.8, 132.7, 130.6, 130.1, 129.9, 129.7, 129.0, 128.8, 128.4, 127.2, 126.3, 122.9, 119.9, 117.1, 111.3, 86.9, 51.1, 45.1, 29.0; HRMS (ESI) exact mass calculated for $C_{20}H_{16}BrNO$ $[M+H]^+$: 366.0494; found: 366.0501.

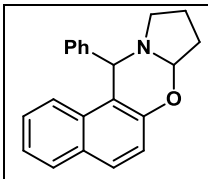


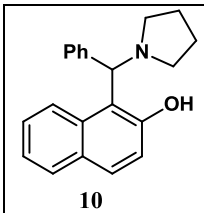
5a

1-((3,4-dihydroisoquinolin-2(1H)-yl)(phenyl)methyl)naphthalen-2-ol (5a):[1a] The intermediate was purified by column chromatography using 100-200 mesh silica gel and hexane-ethyl acetate as eluent. White solid; ^1H NMR (300 MHz, $CDCl_3$): δ 13.37 (s, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.78-7.64 (m, 4H), 7.43-7.23 (m, 5H), 7.18-7.09 (m, 4H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.30 (s, 1H), 3.67-3.62 (m, 1H), 3.40-2.57 (m, 5H); HRMS (ESI) exact mass calculated for $C_{26}H_{23}NO$ $[M+H]^+$: 366.1858; found: 366.1851. Minor peaks seen in the ^1H-NMR spectra are for the **6a**, which could not be separated.

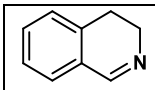
 7a	**2-benzyl-1,2,3,4-tetrahydroisoquinoline (7a):**[3] The by-product was purified by column chromatography using 100-200 mesh silica gel and hexane-ethyl acetate as eluent. Colorless viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.36-7.33 (m, 2H), 7.30-7.27 (m, 1H), 7.13-7.10 (m, 3H), 6.99 (d, *J* = 8.2 Hz, 1H), 3.71 (s, 2H), 3.66 (s, 2H), 2.92 (t, *J* = 5.8 Hz, 2H), 2.78 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 134.5, 134.2, 129.2, 128.7, 128.3, 127.2, 126.6, 126.2, 125.6, 62.6, 55.9, 50.5, 28.9; HRMS (ESI) exact mass calculated for $C_{16}H_{17}N$ $[M+H]^+$: 224.1439; found: 224.1445.

 8	**1,2-di(naphthalen-2-yl)disulfane (8):**[4] The reaction was performed at 1.0 mmol scale using 2-thionaphthol (160 mg), benzaldehyde (106 mg), tetrahydroisoquinoline (133 mg) and water (1.5 mL) by following the same procedure as **4**. The compound was purified by column chromatography using 60-120 mesh silica gel and hexane-ethyl acetate as eluent. White solid; Yield 42 %, 134 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 2H), 7.78-7.71 (m, 6H), 7.62-7.60 (m, 2H), 7.44 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.2, 133.4, 132.4, 129.0, 127.7, 127.4, 126.7, 126.5, 126.2, 125.6; HRMS (ESI) exact mass calculated for $C_{20}H_{14}S_2$ $[M+H]^+$: 319.0615; found: 319.0612.

 9	**12-phenyl-8,9,10,12-tetrahydro-7aH-naphtho[1,2-e]pyrrolo[2,1-b] [1,3]oxazine (9):**[1a] The reaction was performed at 1.0 mmol scale by taking 2-naphthol (144 mg), benzaldehyde (106 mg), pyrrolidine (71 mg) and water (1.5 mL) following the same procedure as **4**. The compound was purified by column chromatography using 100-200 mesh silica gel and hexane-ethyl acetate as eluent. White solid; Yield - trace; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.71 (m, 2H), 7.39-7.37 (m, 1H), 7.29-7.21 (m, 7H), 7.07 (d, *J* = 8.9 Hz, 1H), 5.45 (s, 1H), 5.09 (d, *J* = 3.7 Hz, 1H) 3.35-3.31 (m, 1H), 2.94-2.89 (m, 1H), 2.12-1.96 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.7, 143.3, 132.4, 128.9, 128.8, 128.7, 128.5, 128.4, 127.2, 126.4, 122.9, 122.6, 118.8, 110.2, 86.3, 56.3, 50.4, 32.0, 20.9; HRMS (ESI) exact mass calculated for $C_{21}H_{19}NO$ $[M+H]^+$: 302.1545; found: 302.1552.

 10	**1-(phenyl(pyrrolidin-1-yl)methyl)naphthalen-2-ol (10):**[1a] The reaction was performed at 1.0 mmol scale using **5a** (365 mg), pyrrolidine (71 mg) and water (2.0 mL) by following the same procedure as **4**. The compound was purified by column chromatography using 100-200 mesh silica gel and hexane-ethyl acetate as eluent. White solid; Yield 66 %, 200 mg; ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.90 (bs, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.72-7.61 (m, 4H), 7.41-7.36 (m, 1H), 7.28-7.15 (m, 5H), 5.14 (s, 1H), 3.44-3.15 (m, 1H), 2.89-2.10 (m, 3H), 1.87 (bs, 4H); ^{13}C NMR (75 MHz,

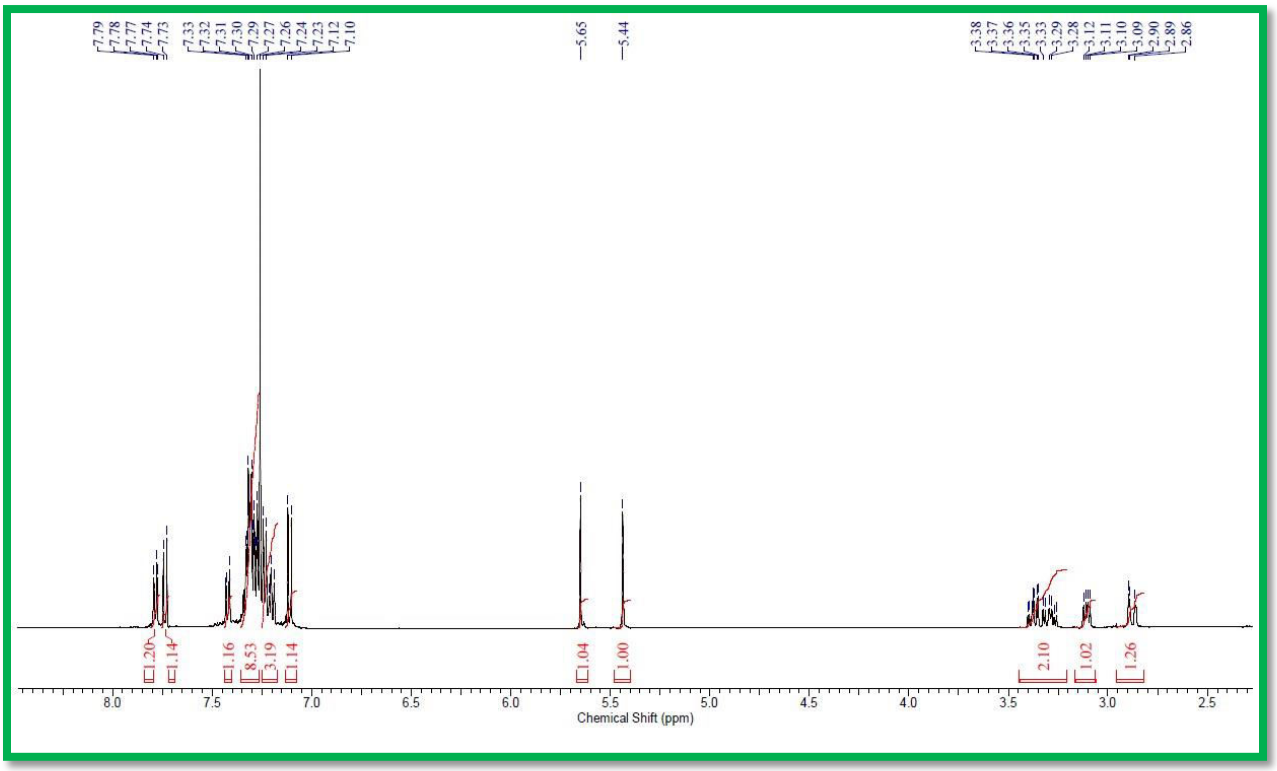
	$CDCl_3$): δ 155.6, 141.4, 131.8, 129.6, 128.8 (2C), 128.6, 128.5, 127.8, 126.3, 122.4, 121.2, 119.9, 116.5, 70.9, 23.5; HRMS (ESI) exact mass calculated for $C_{21}H_{21}NO$ $[M+H]^+$: 304.1701; found: 304.1692.

 **11**	**3,4-dihydroisoquinoline (11):**[5] The compound was purified by column chromatography using 100-200 mesh silica gel and hexane-ethyl acetate as eluent. Light yellow solid; Yield 38 %, 50 mg; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (bs, 1H), 7.36-7.26 (m, 3H), 7.18-7.15 (m, 1H), 3.78 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H).

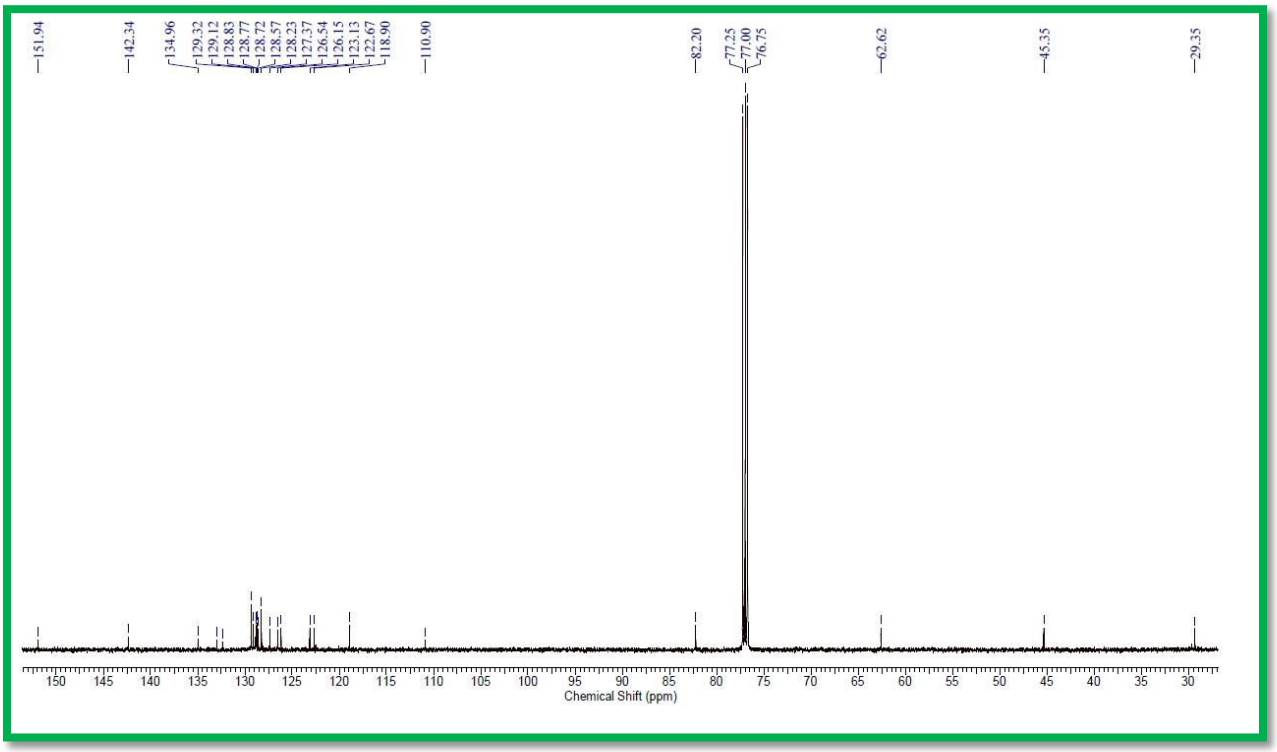
References:

1. (a) M. L. Deb, S. S. Dey, I. Bento, M. T. Barros, C. D. Maycock, *Angew. Chem. Int. Ed.,* 2013, **52**, 9791; (b) K. S. V. Gupta, D. V. Ramana, B. Vinayak, B. Sridhar, M. Chandrasekharam, *New J. Chem.,* 2016, **40**, 6389.
2. M. L. Deb, P. J. Borpatra, P. J. Saikia, P. K. Baruah, *Synlett*, 2017, **28**, 461.
3. Q. Zou, C. Wang, J. Smith, D. Xue, J. Xiao, *Chem. - A Eur. J.* 2015, **21**, 9656.
4. Y. Dou, X. Huang, H. Wang, L. Yang, H. Li, B. Yuan and G. Yang, Green Chem., 2017, DOI: 10.1039/C7GC00401J.
5. G. Lahm, J.-G. Deichmann, A. L. Rauen, T. Opatz, *J. Org. Chem.*, 2015, **80**, 2010.

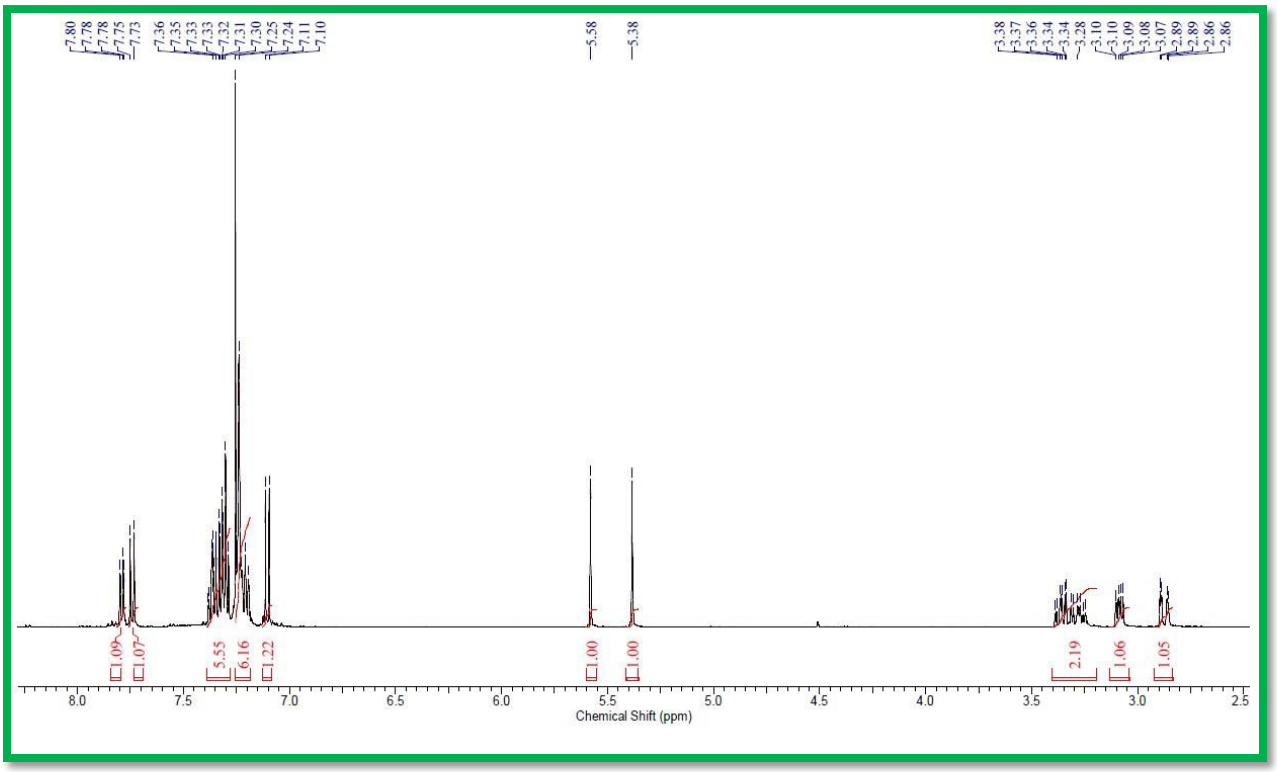
^{1}H-NMR of 4a (500 MHz)



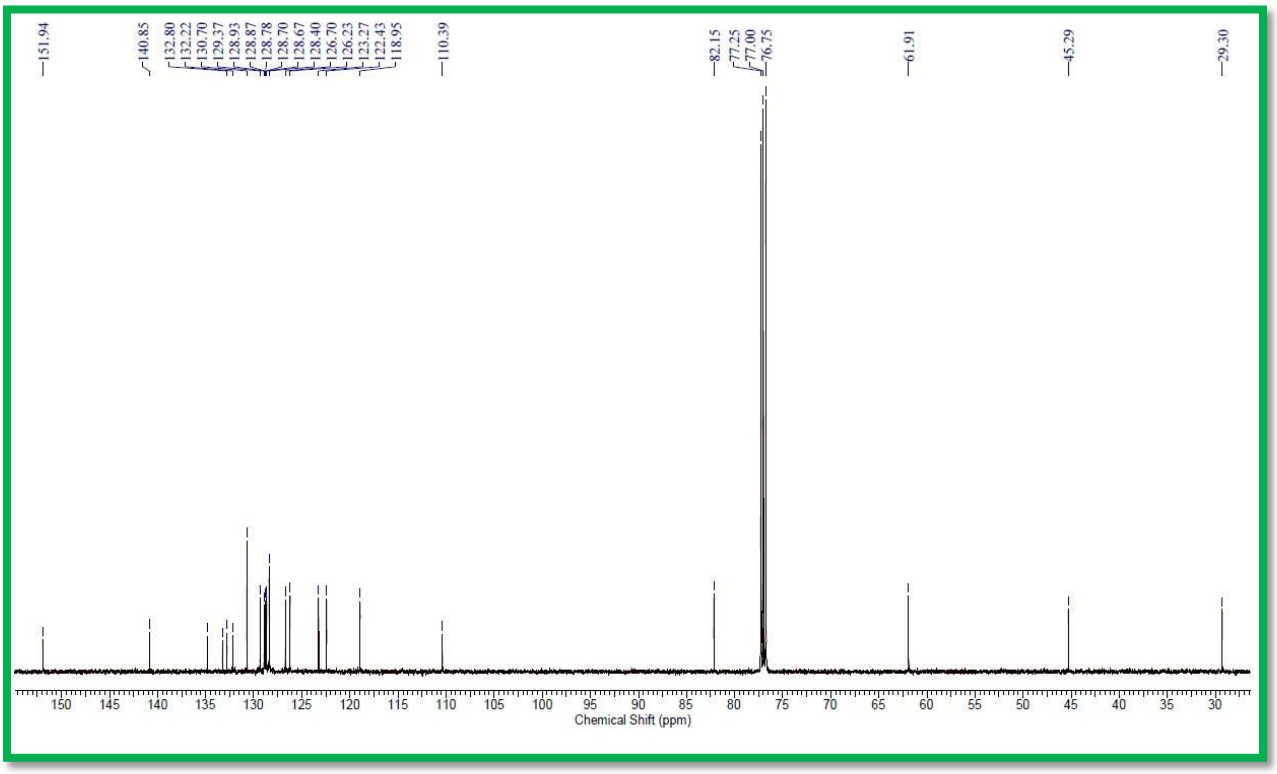
^{13}C-NMR of 4a (125 MHz)



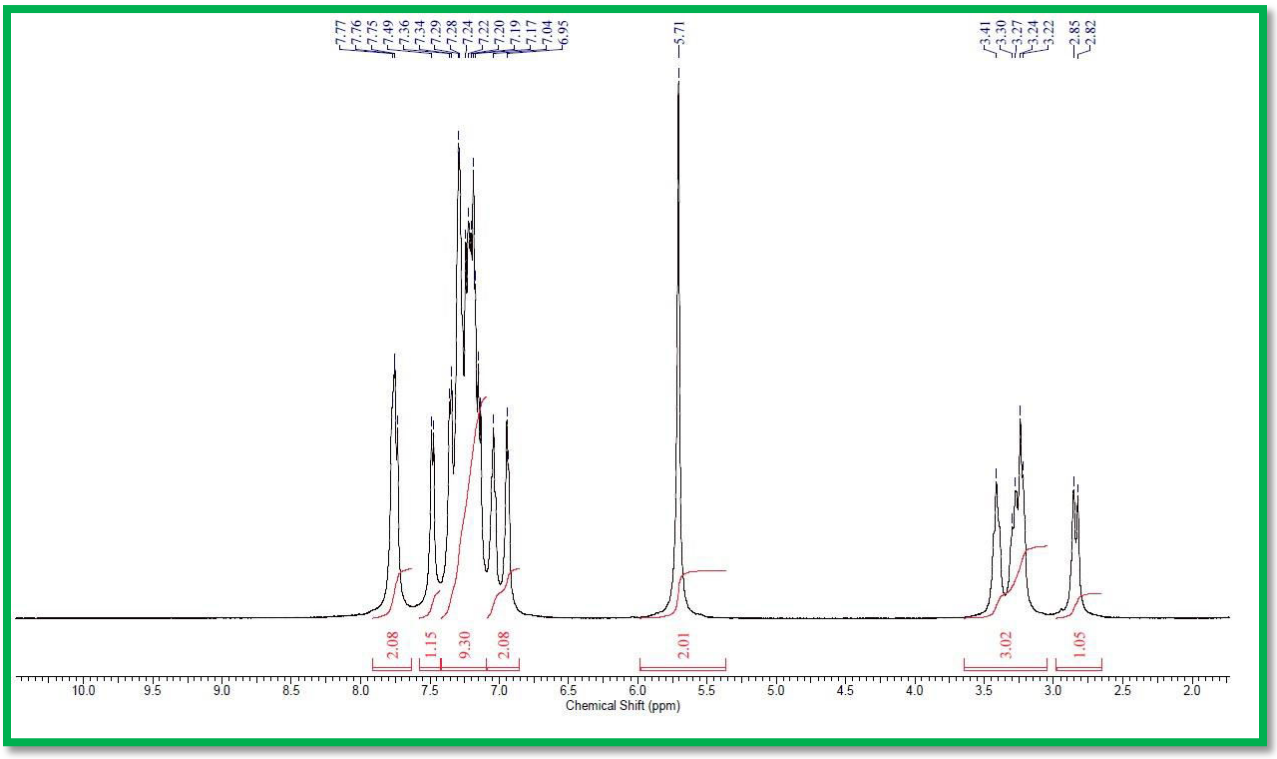
^{1}H-NMR of 4b (500 MHz)



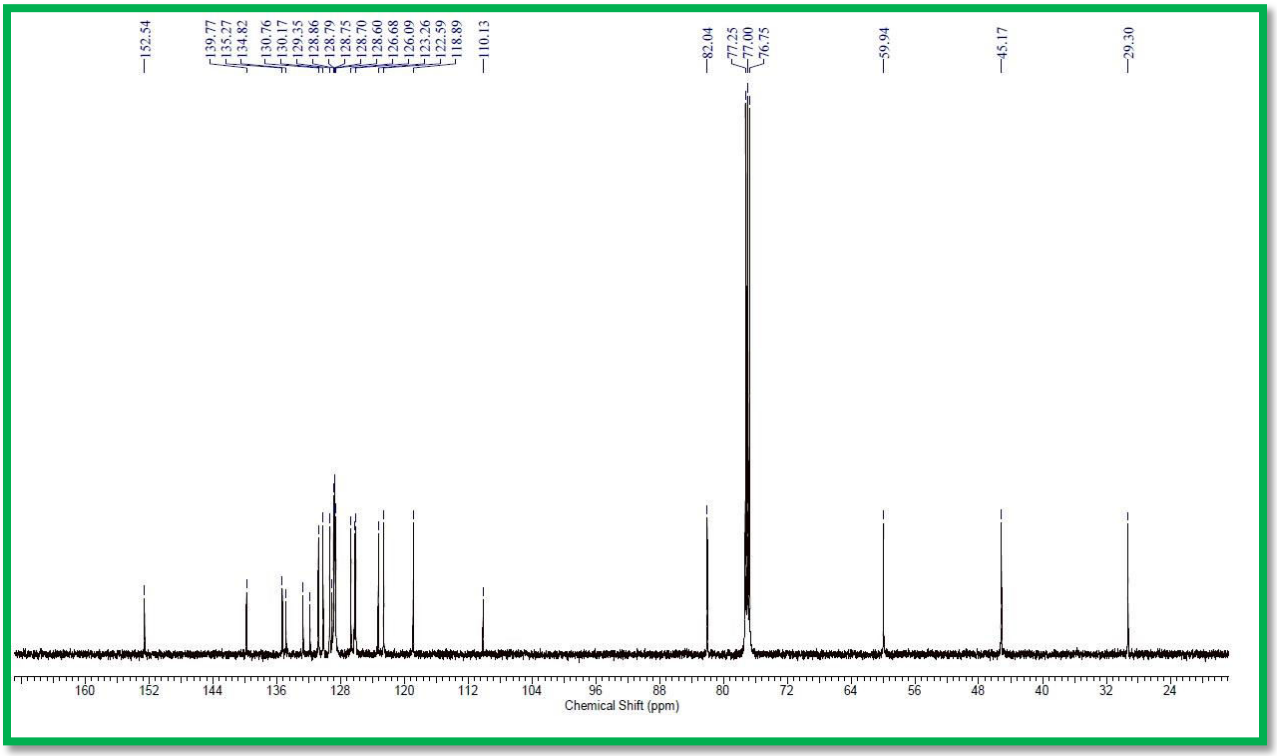
^{13}C-NMR of 4b (125 MHz)



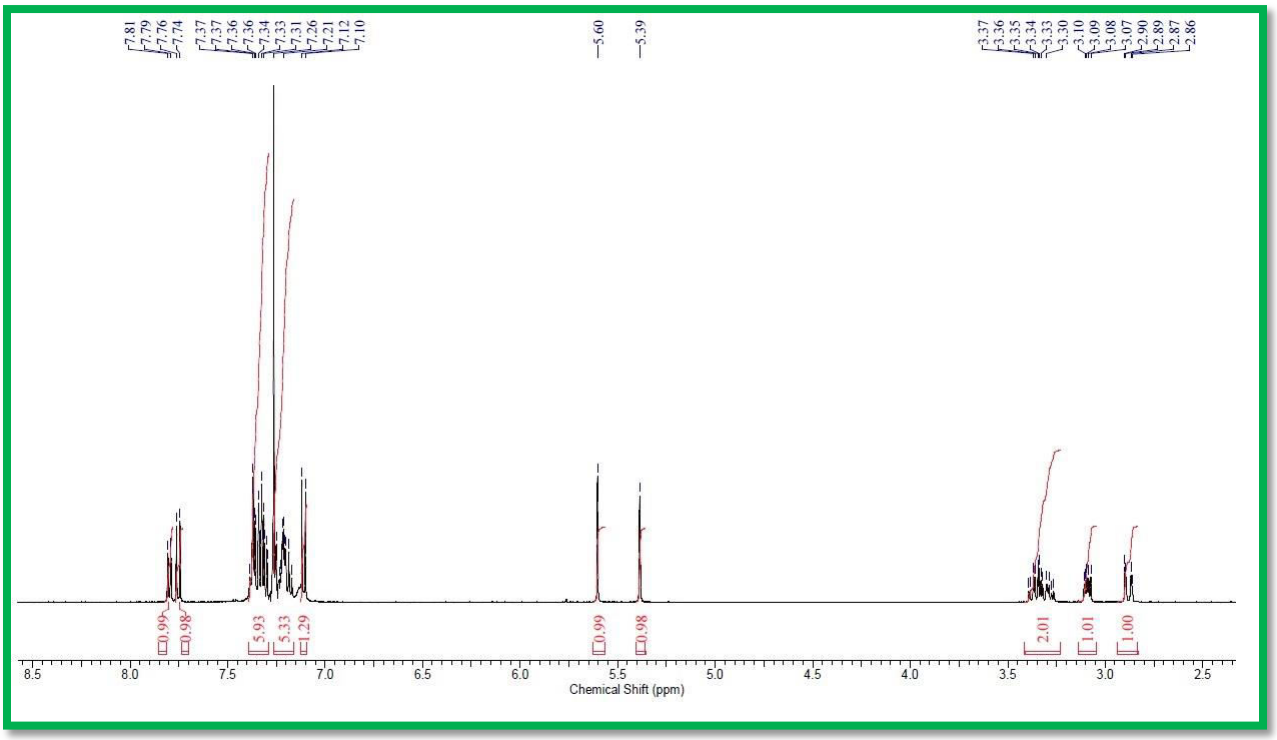
^{1}H-NMR of 4c (500 MHz)



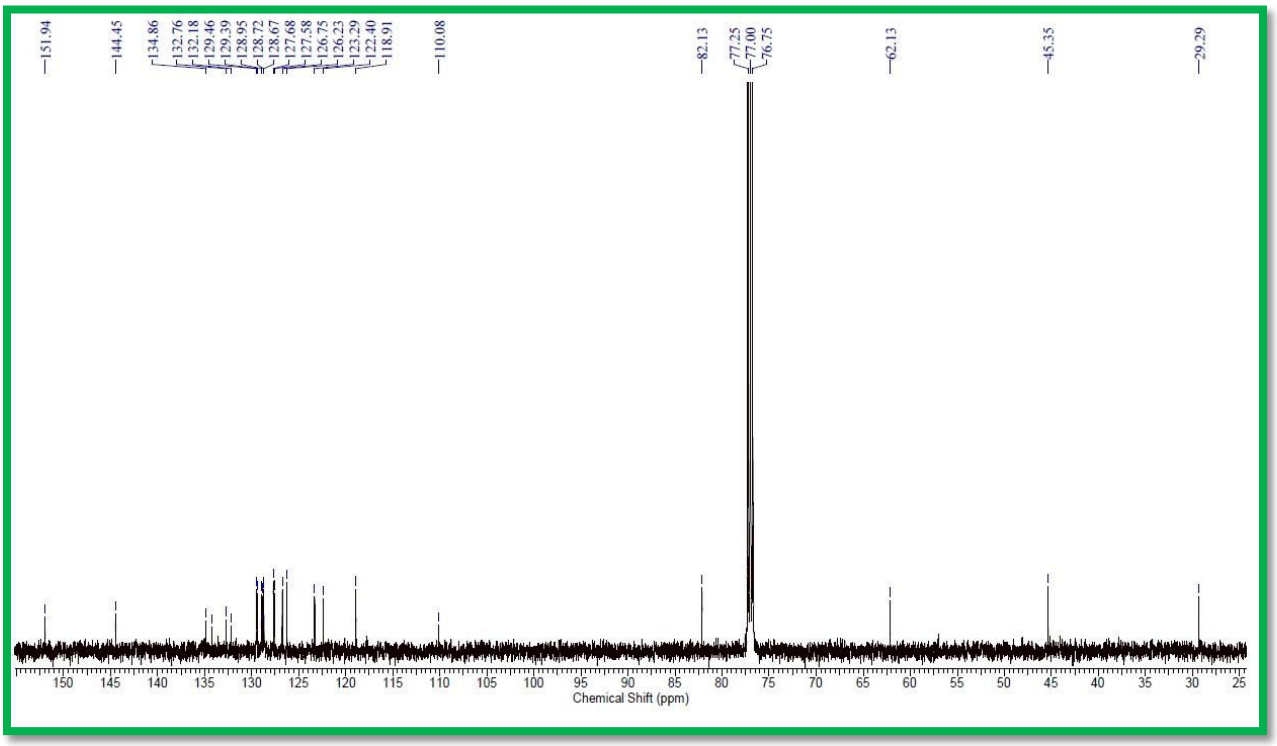
^{13}C-NMR of 4c (500 MHz)



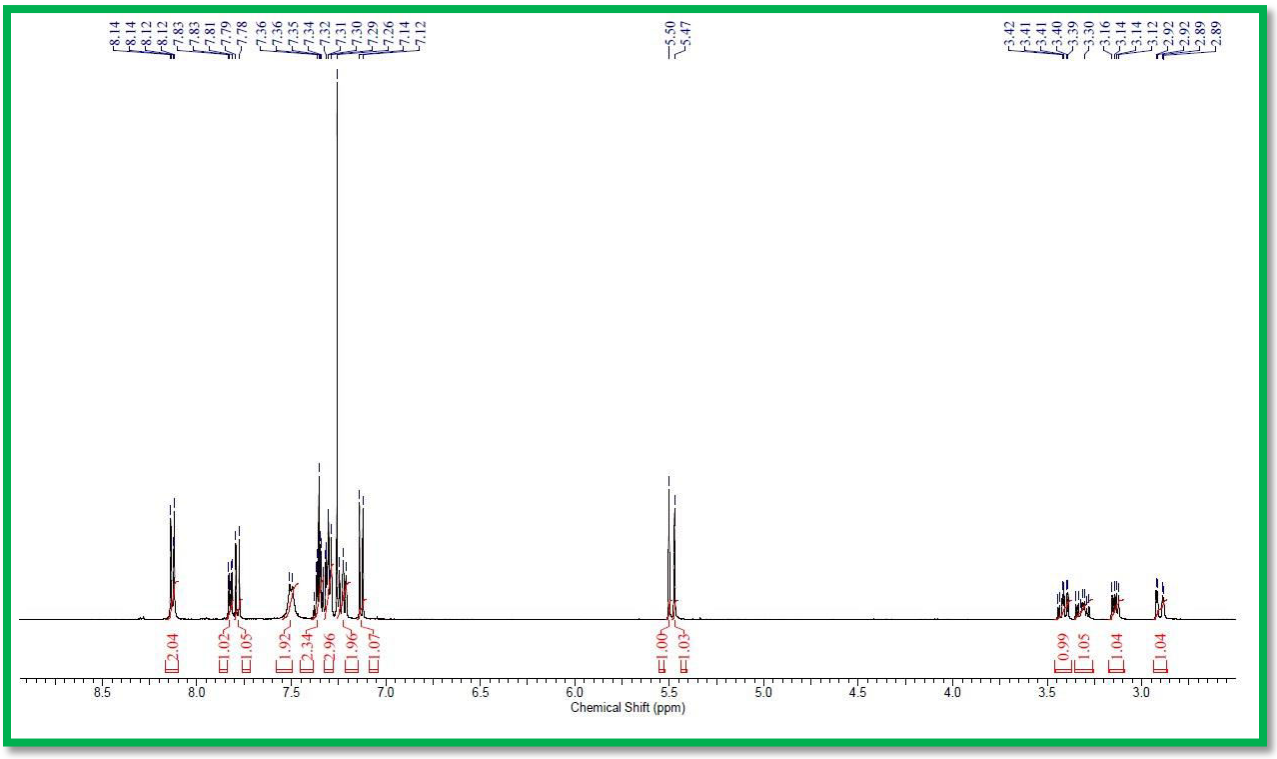
^{1}H-NMR of 4d (500 MHz)



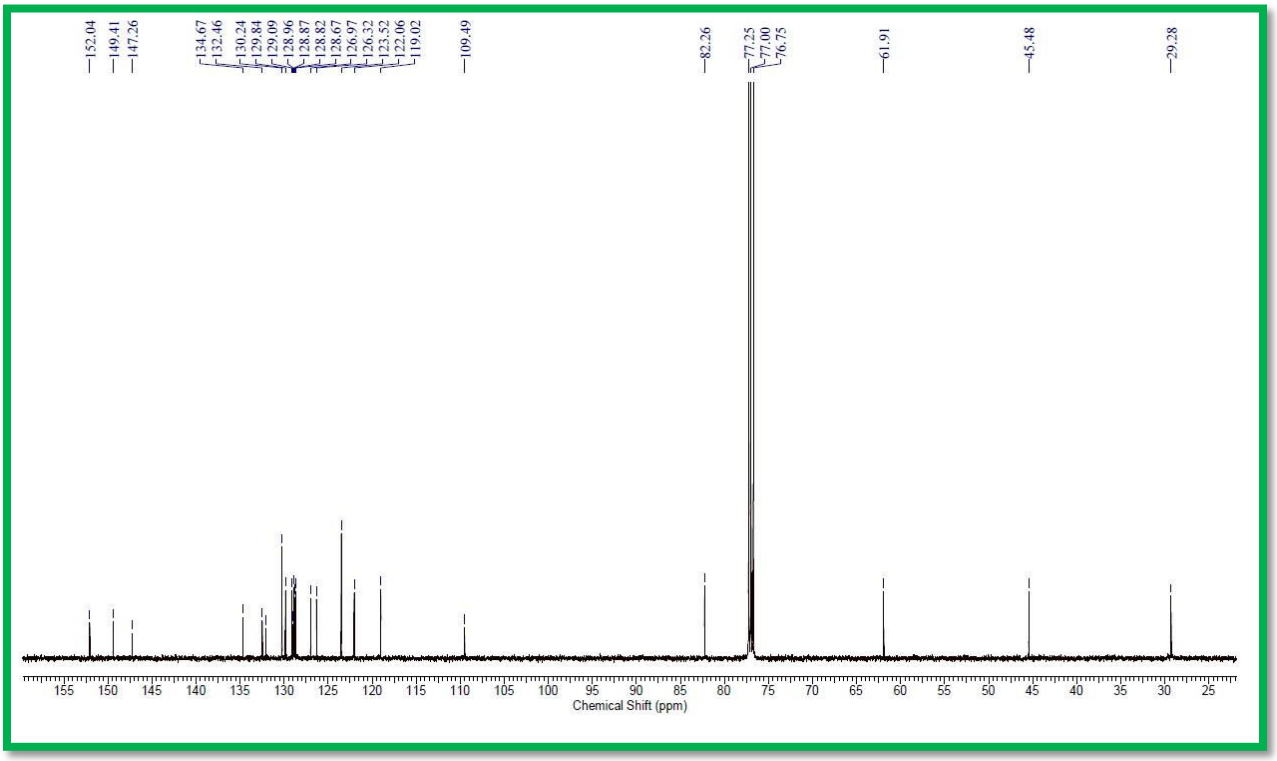
^{13}C-NMR of 4d (125 MHz)



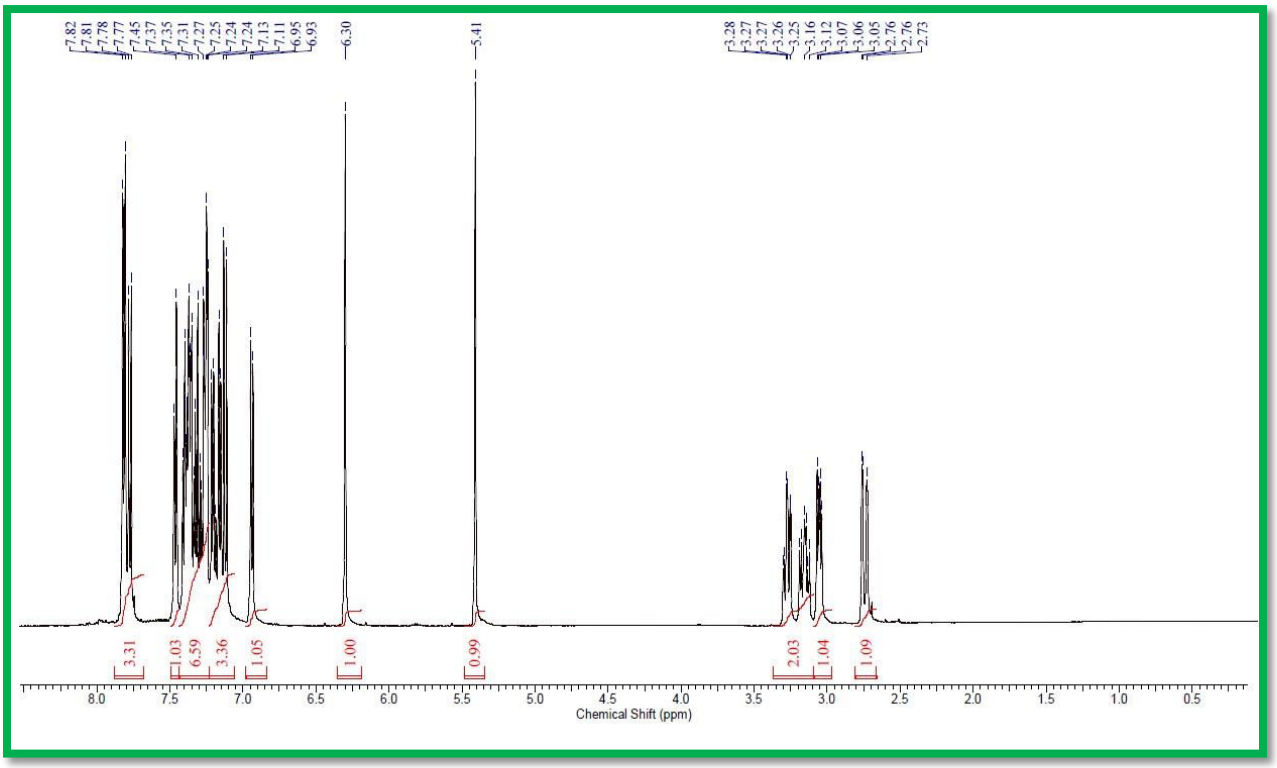
^{1}H-NMR of 4e (500 MHz)



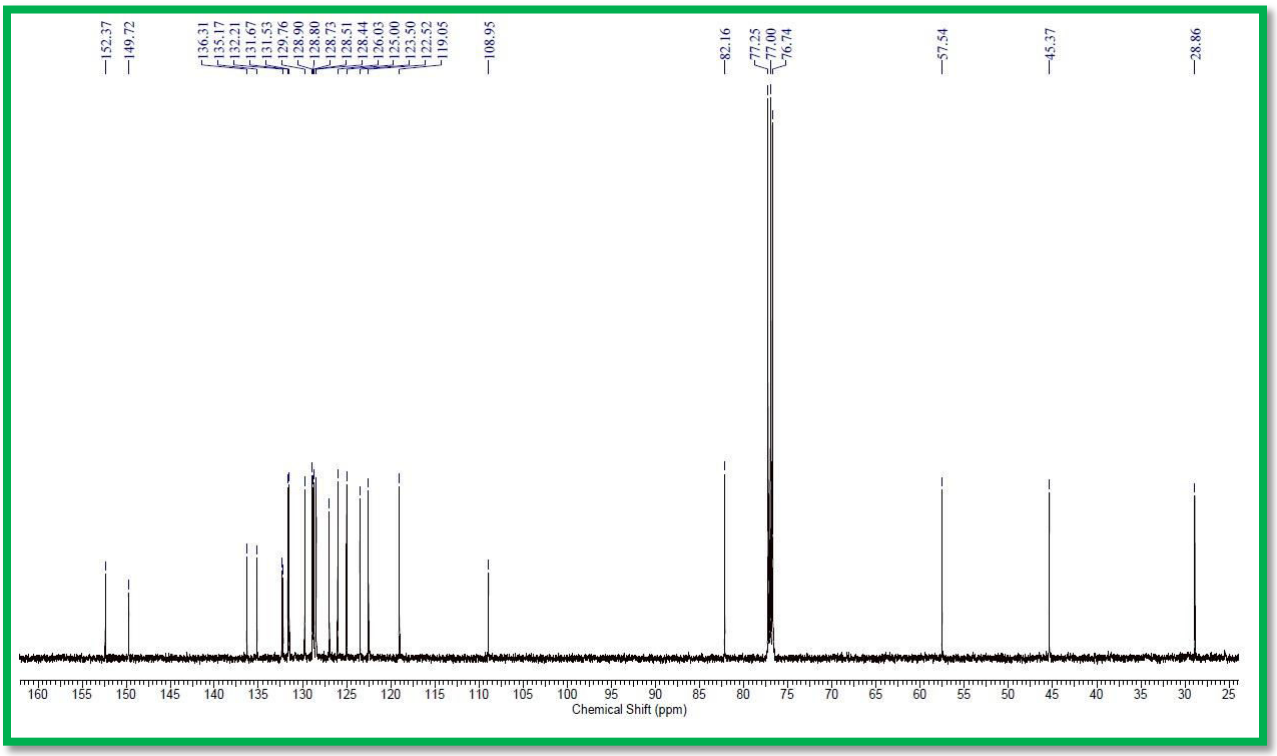
^{13}C-NMR of 4e (125 MHz)



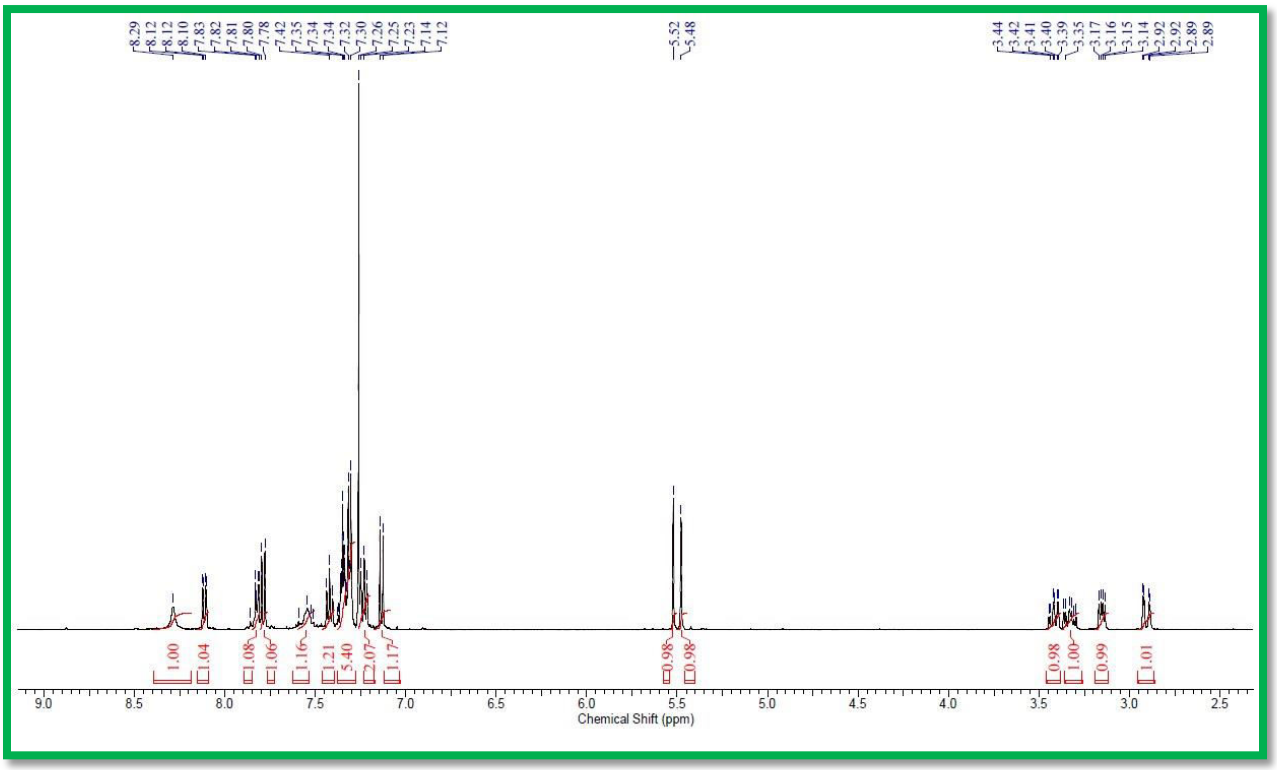
^{1}H-NMR of 4f (500 MHz)



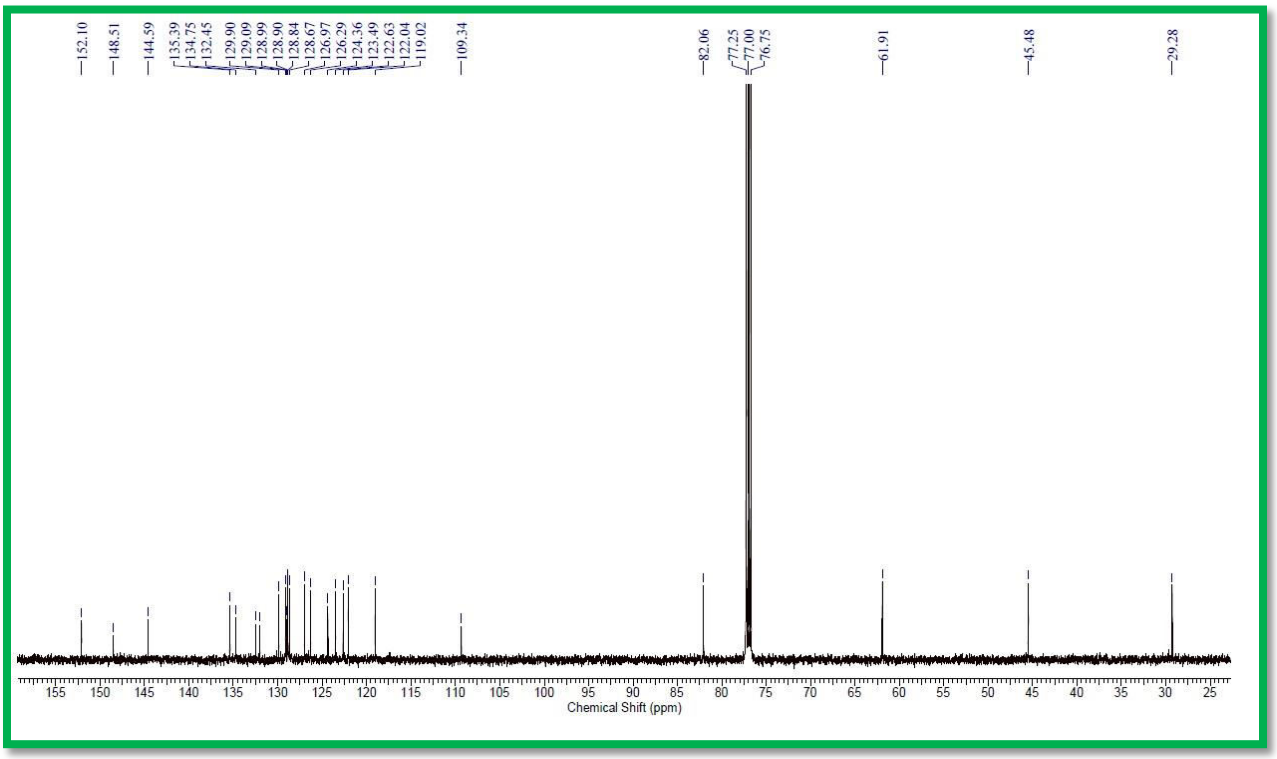
^{13}C-NMR of 4f (125 MHz)



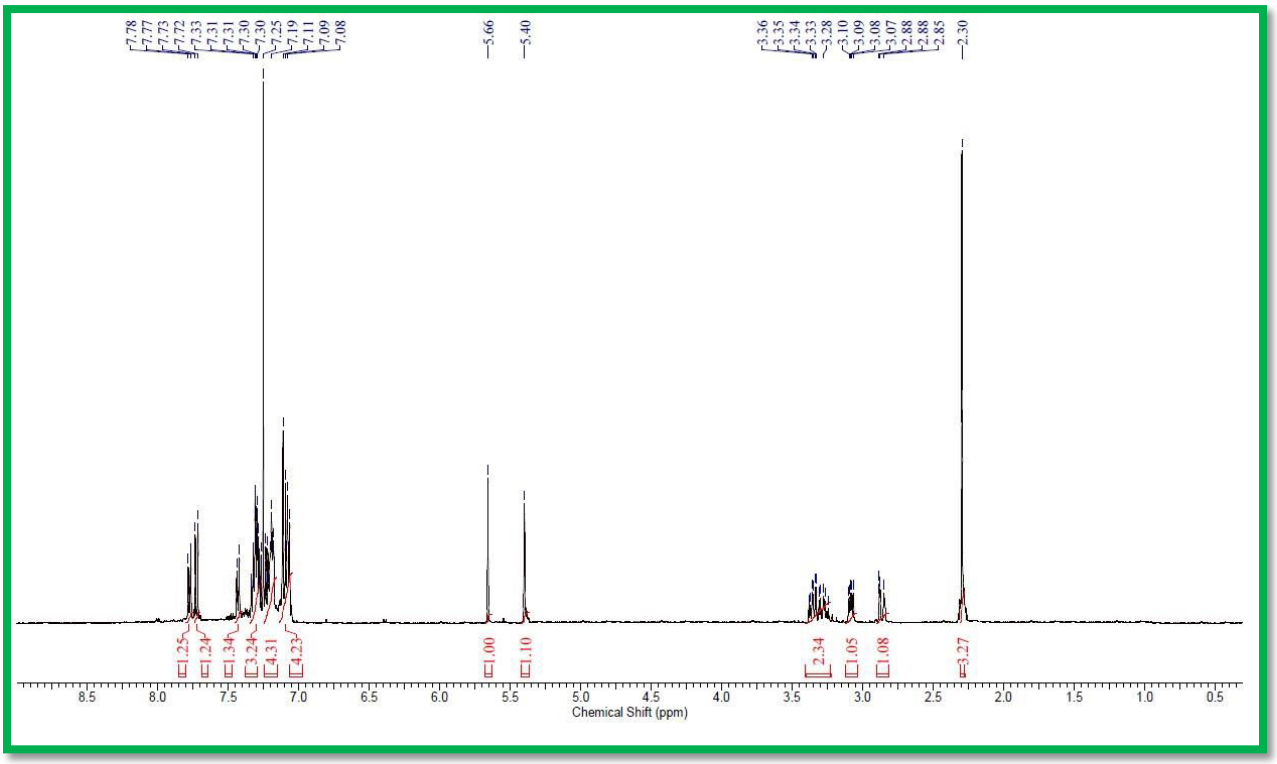
^{1}H-NMR of 4g (500 MHz)



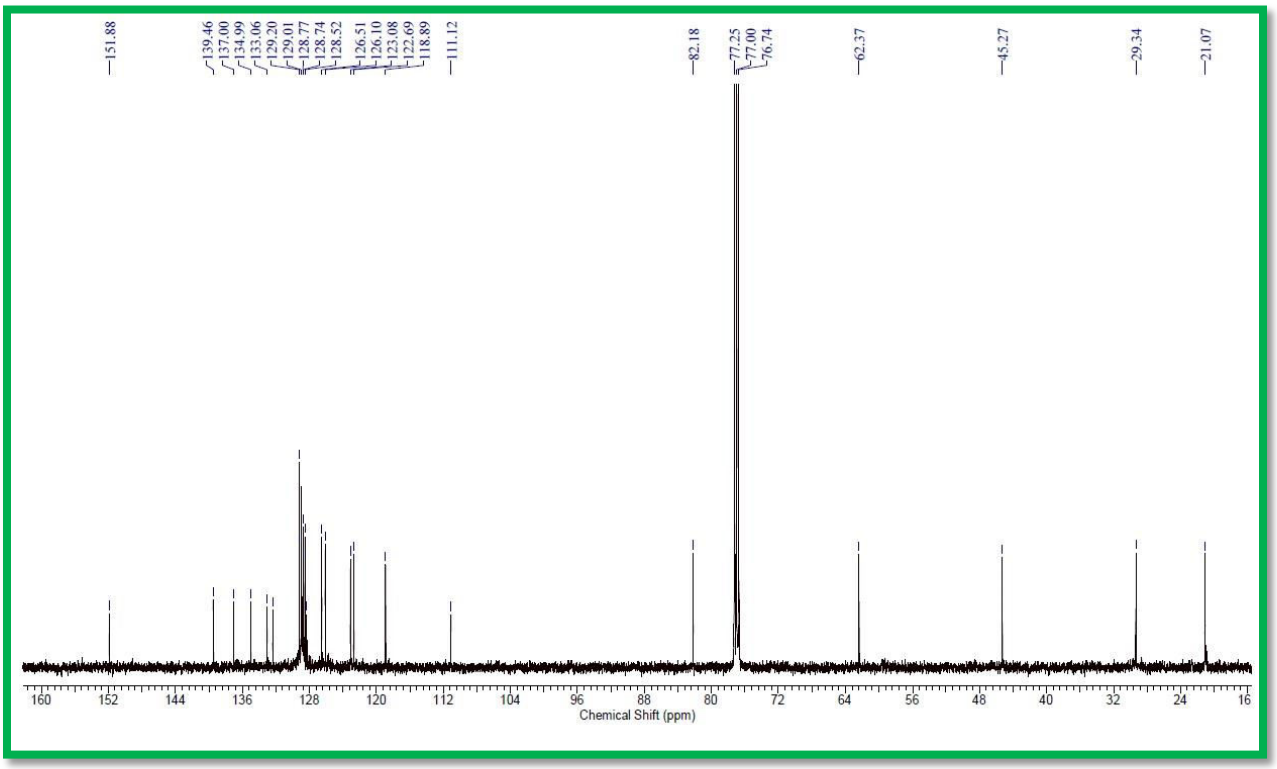
^{13}C-NMR of 4g (125 MHz)



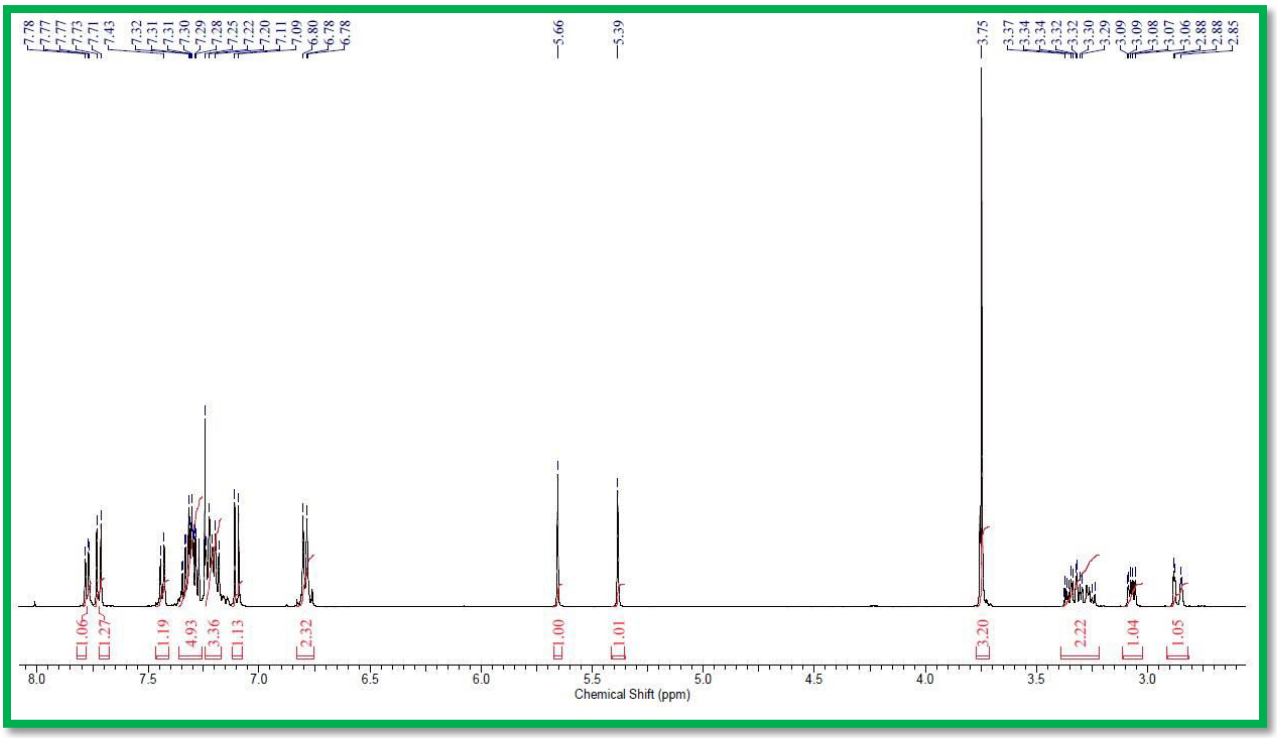
^{1}H-NMR of 4h (500 MHz)



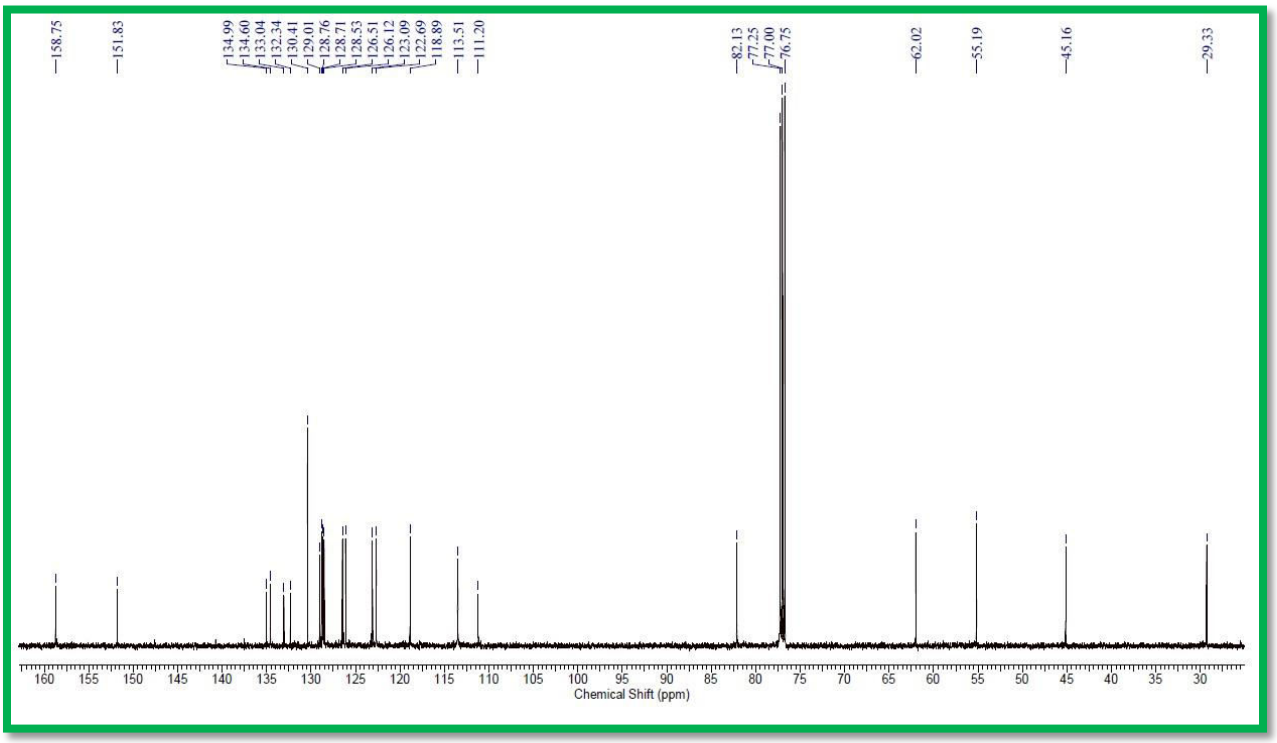
^{13}C-NMR of 4h (125 MHz)



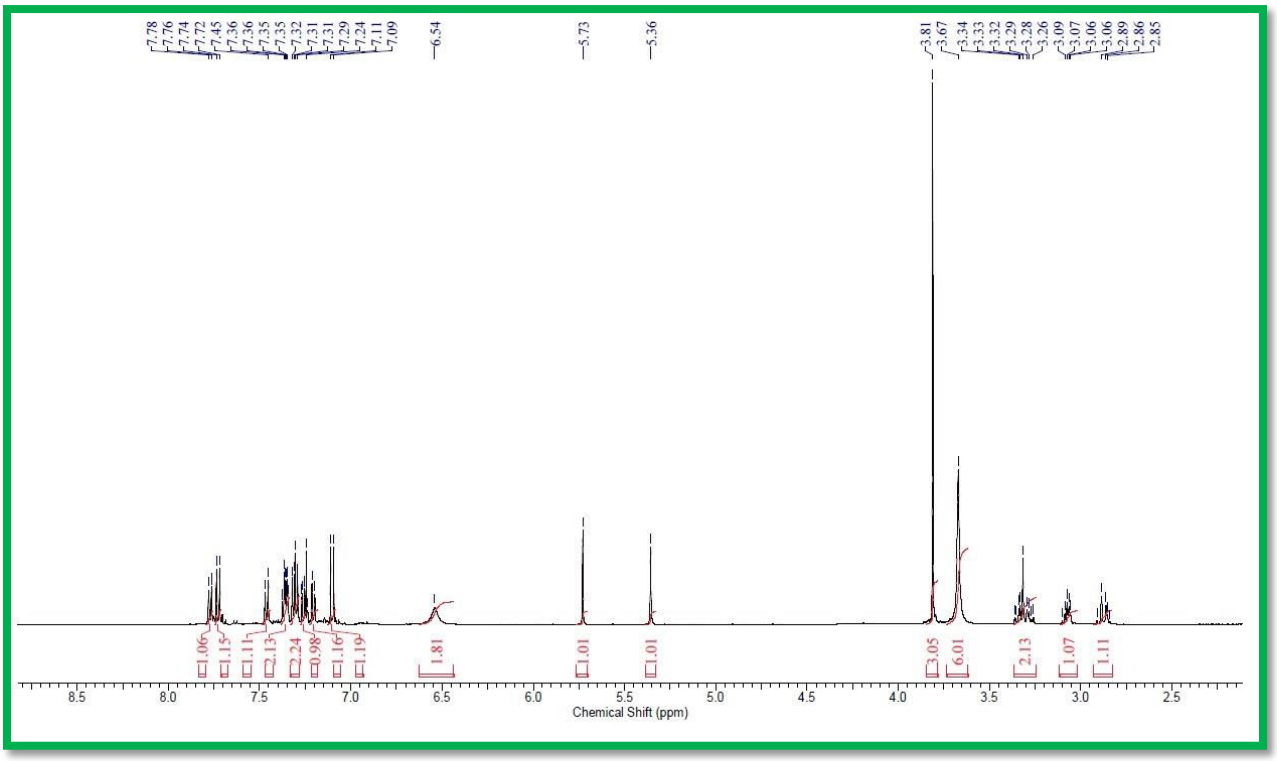
^{1}H-NMR of 4i (500 MHz)



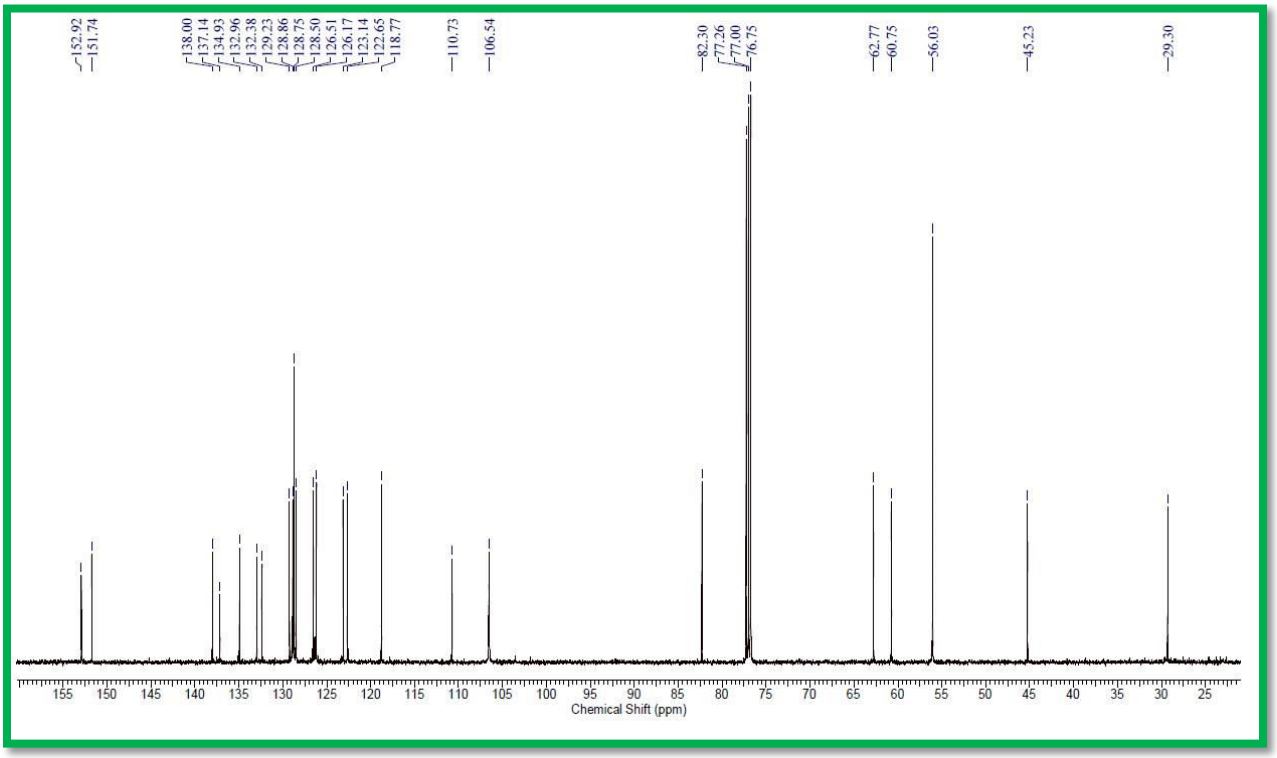
^{13}C-NMR of 4i (125 MHz)



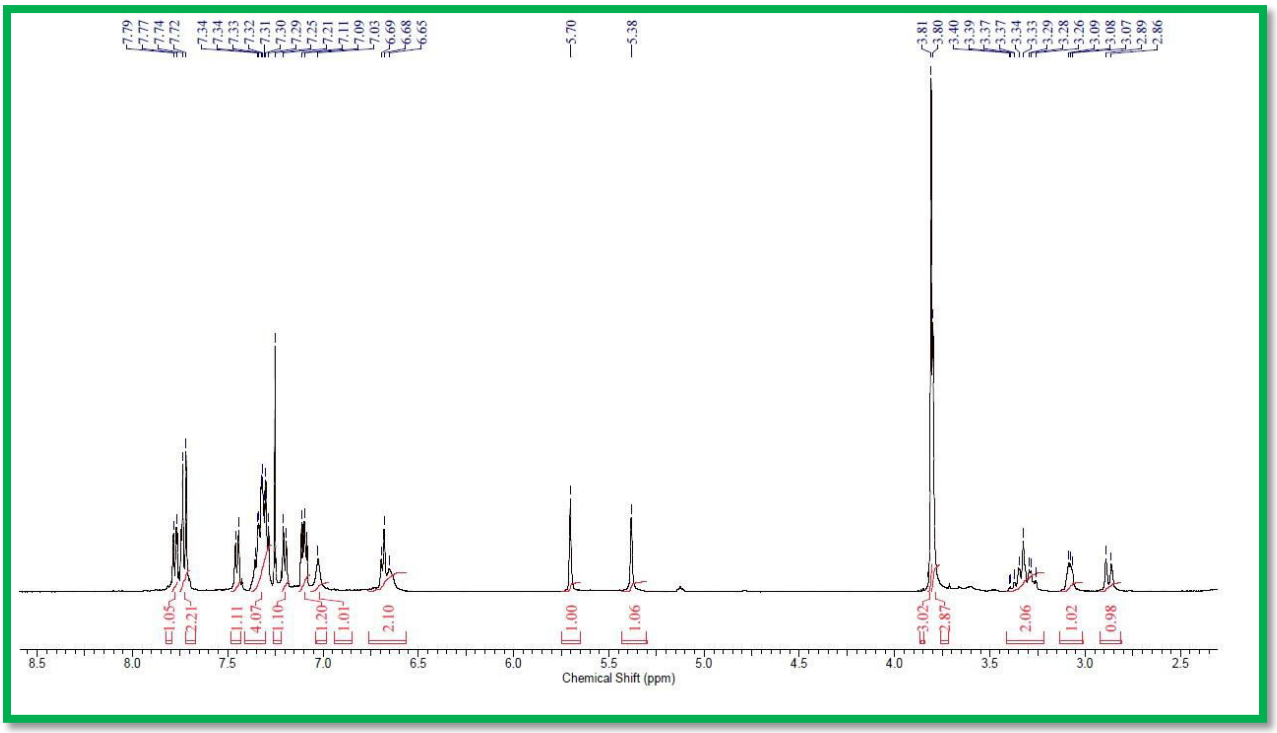
^{1}H-NMR of 4j (500 MHz)



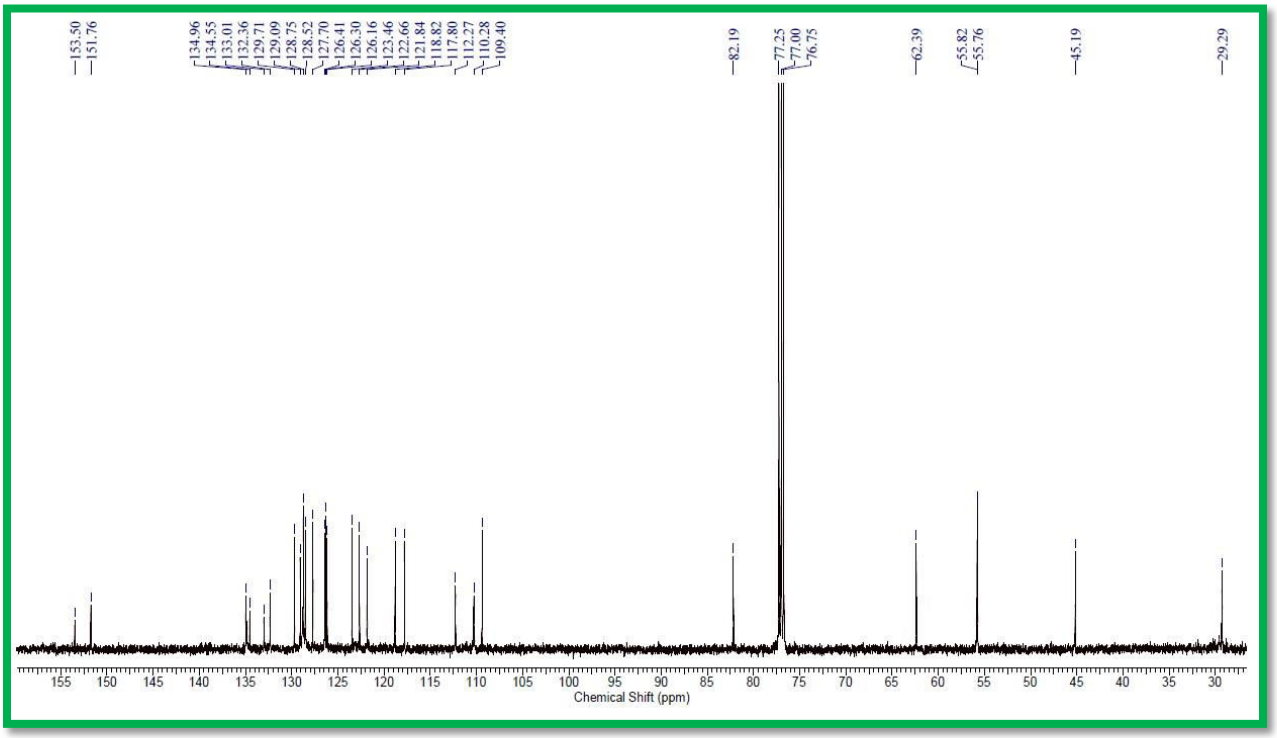
^{13}C-NMR of 4j (125 MHz)



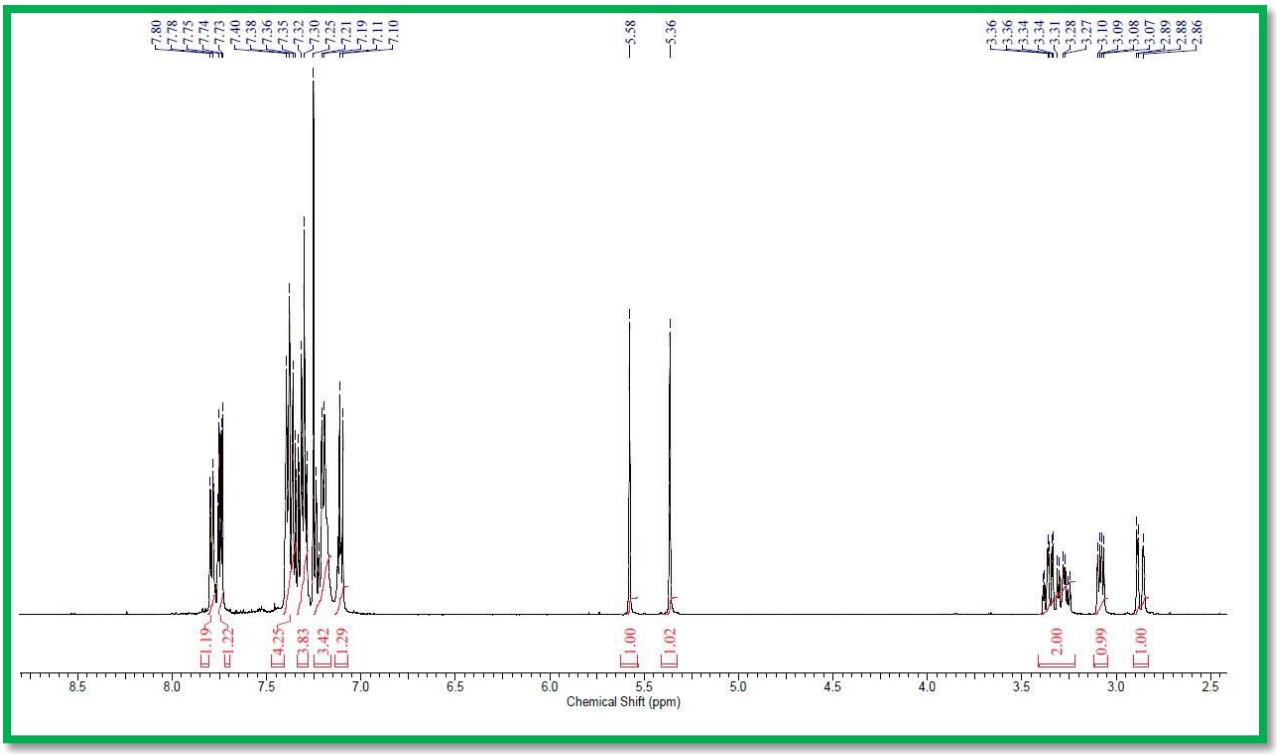
^{1}H-NMR of 4k (500 MHz)



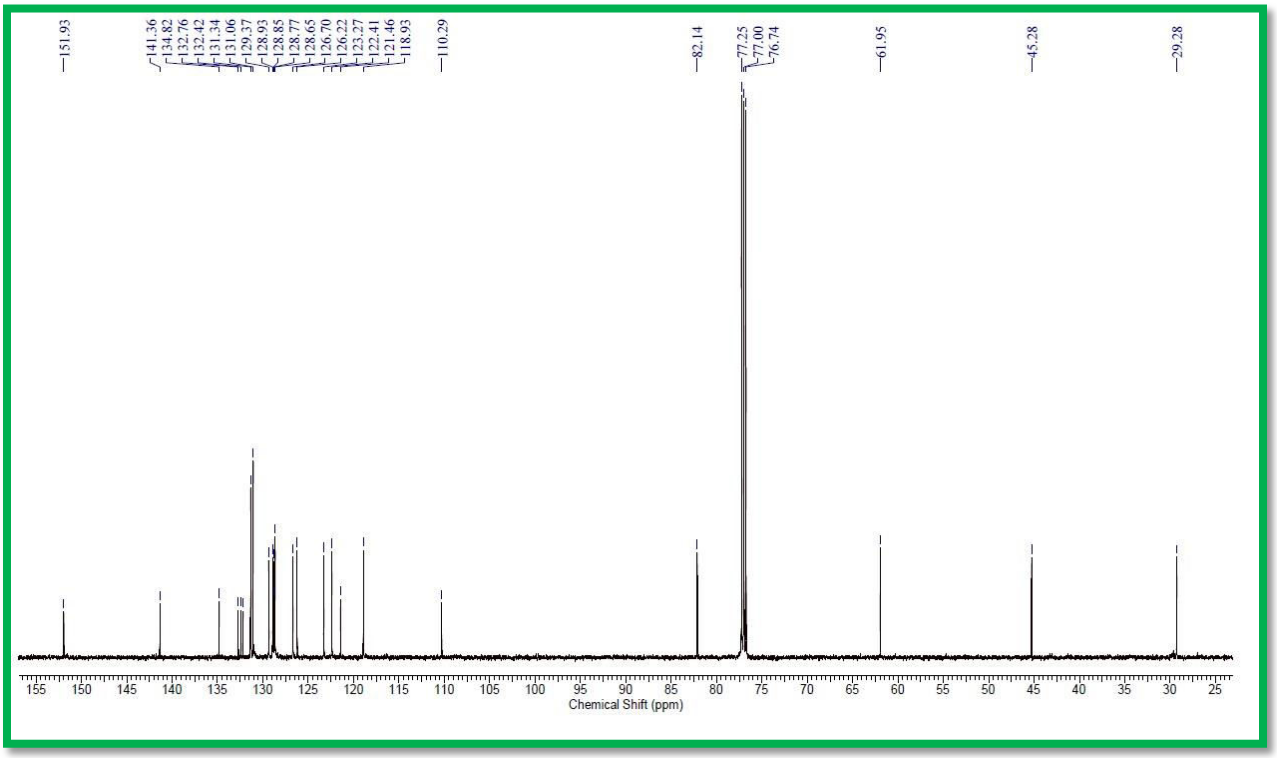
^{13}C-NMR of 4k (125 MHz)



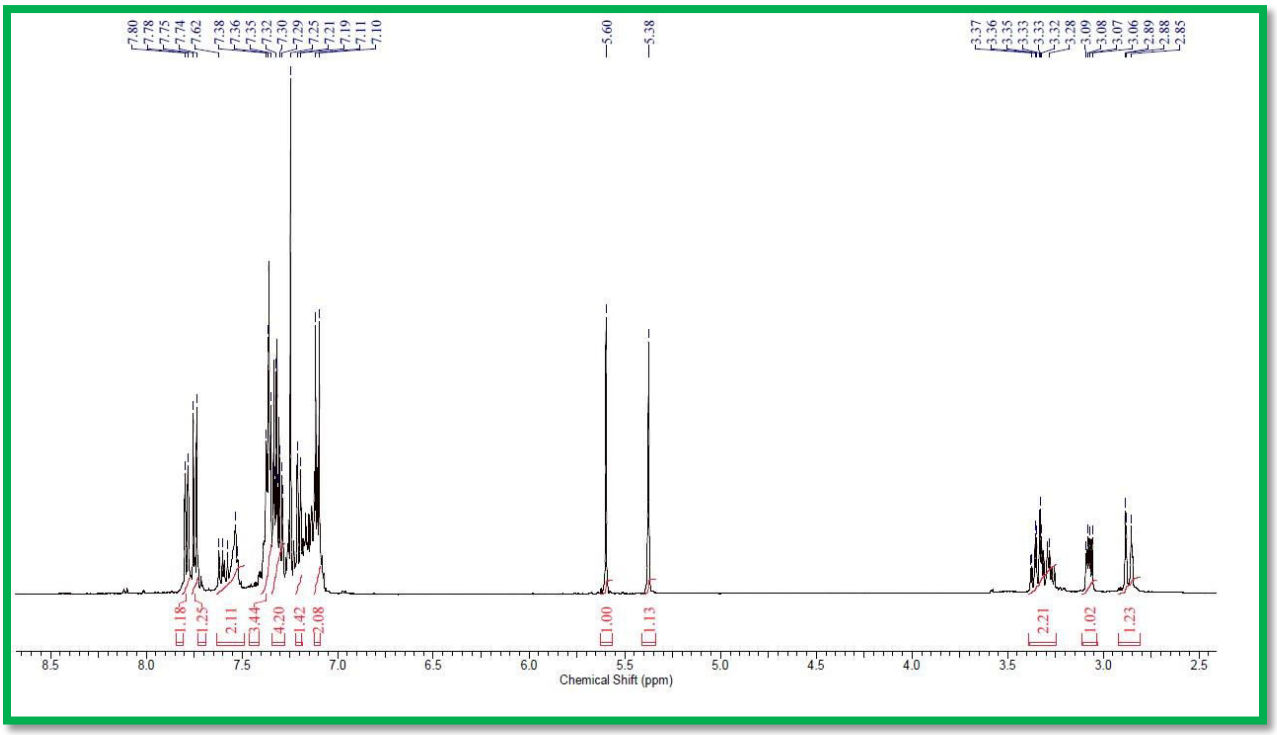
^{1}H-NMR of 4l (500 MHz)



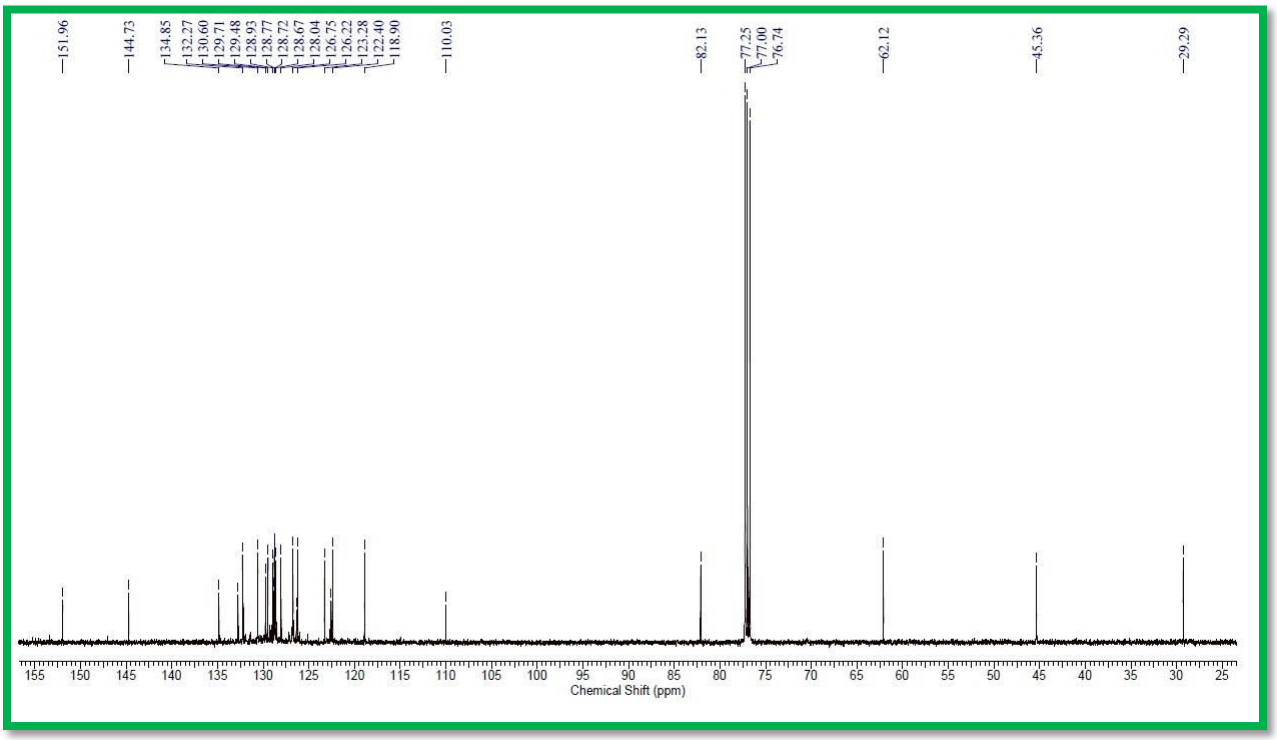
^{13}C-NMR of 4l (125 MHz)



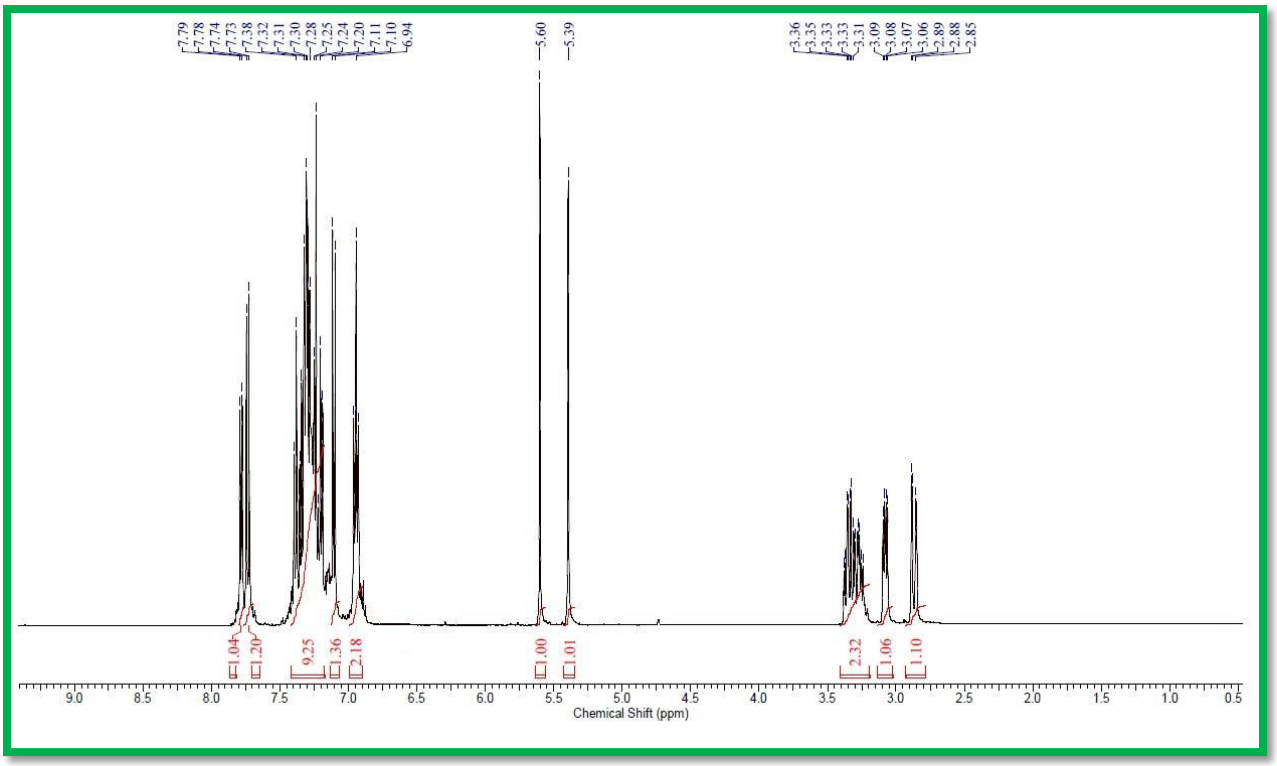
^{1}H-NMR of 4m (500 MHz)



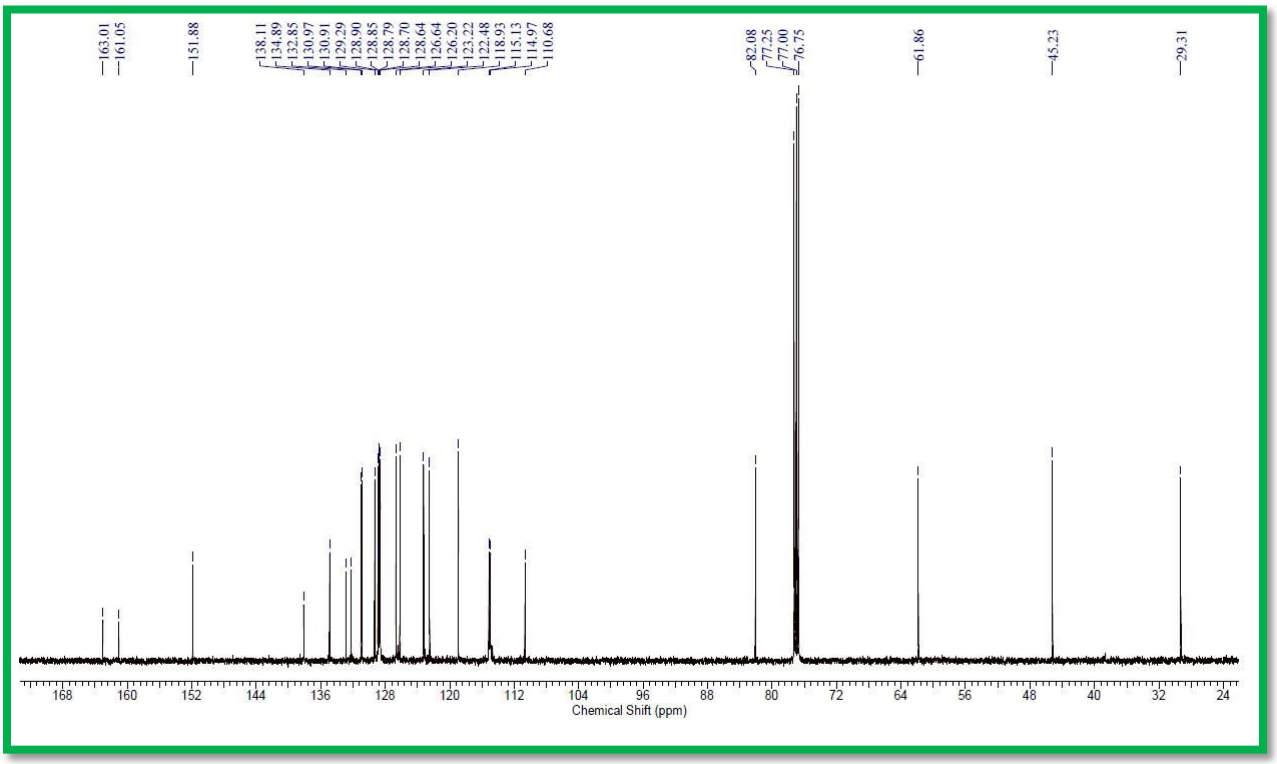
^{13}C-NMR of 4m (125 MHz)



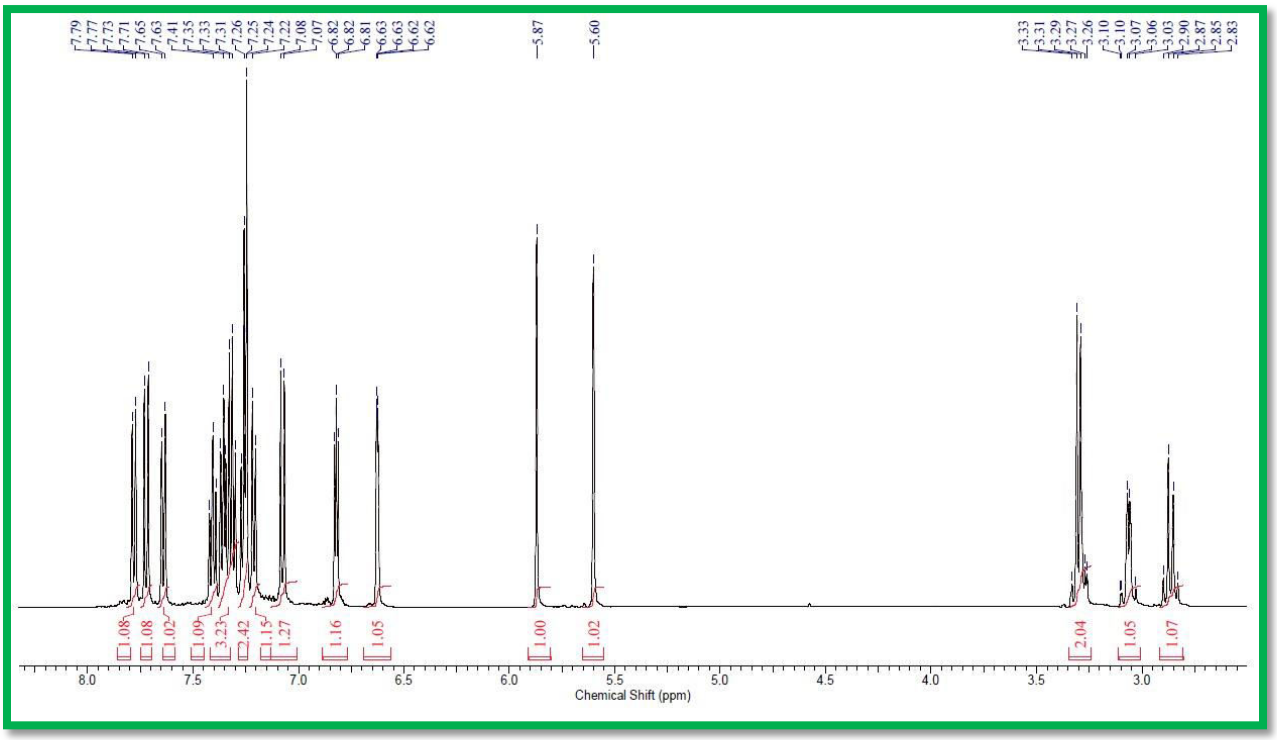
^{1}H-NMR of 4n (500 MHz)



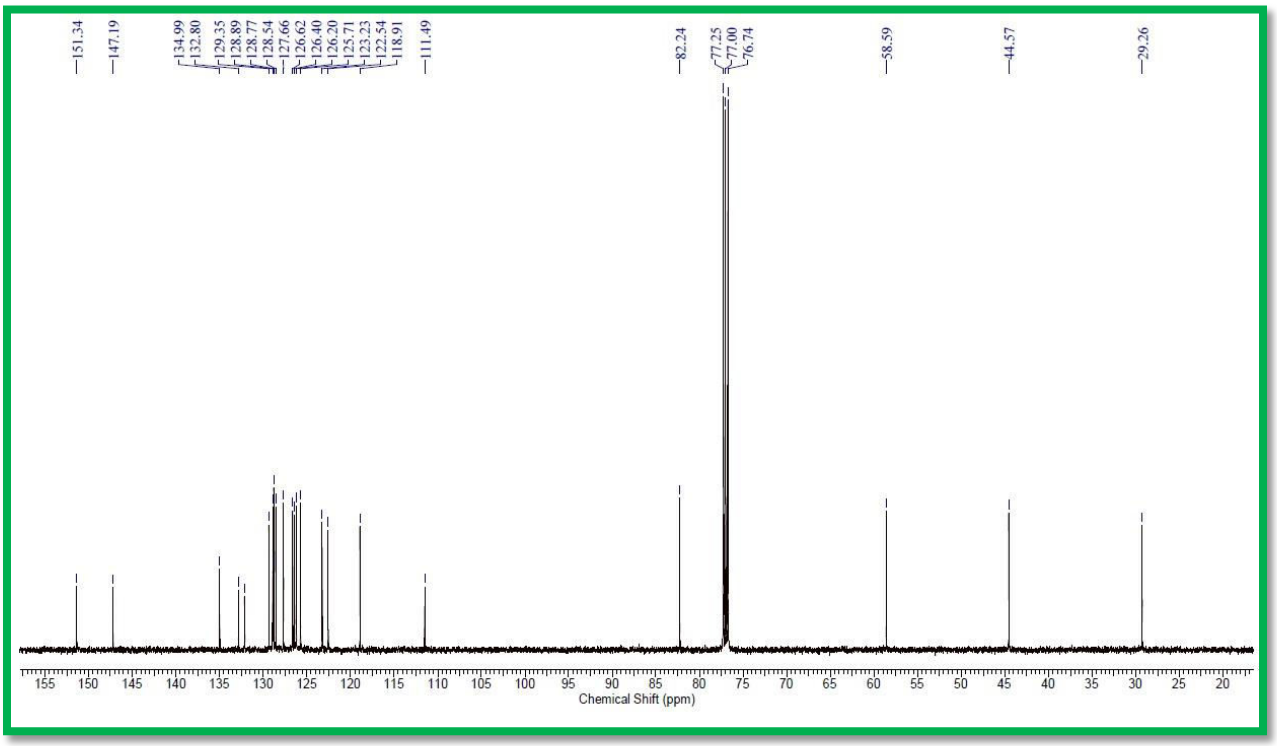
^{13}C-NMR of 4n (125 MHz)



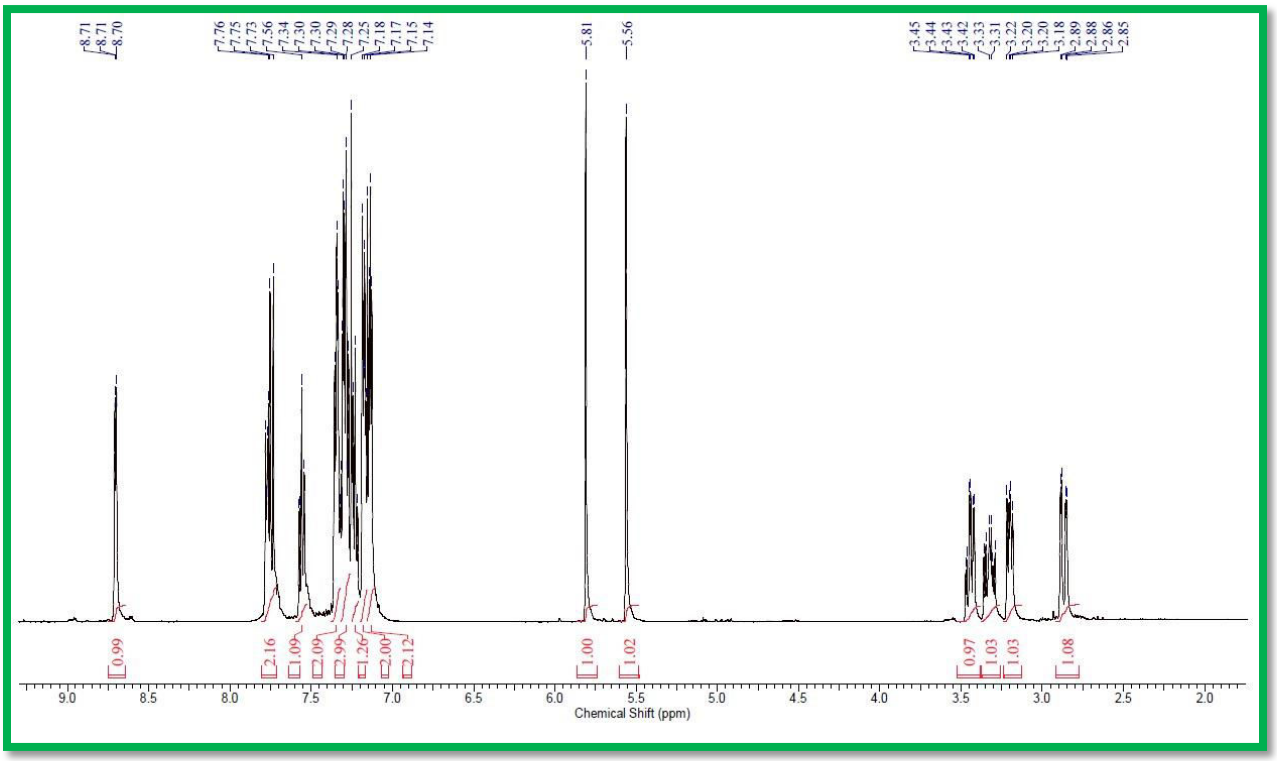
^{1}H-NMR of 4o (500 MHz)



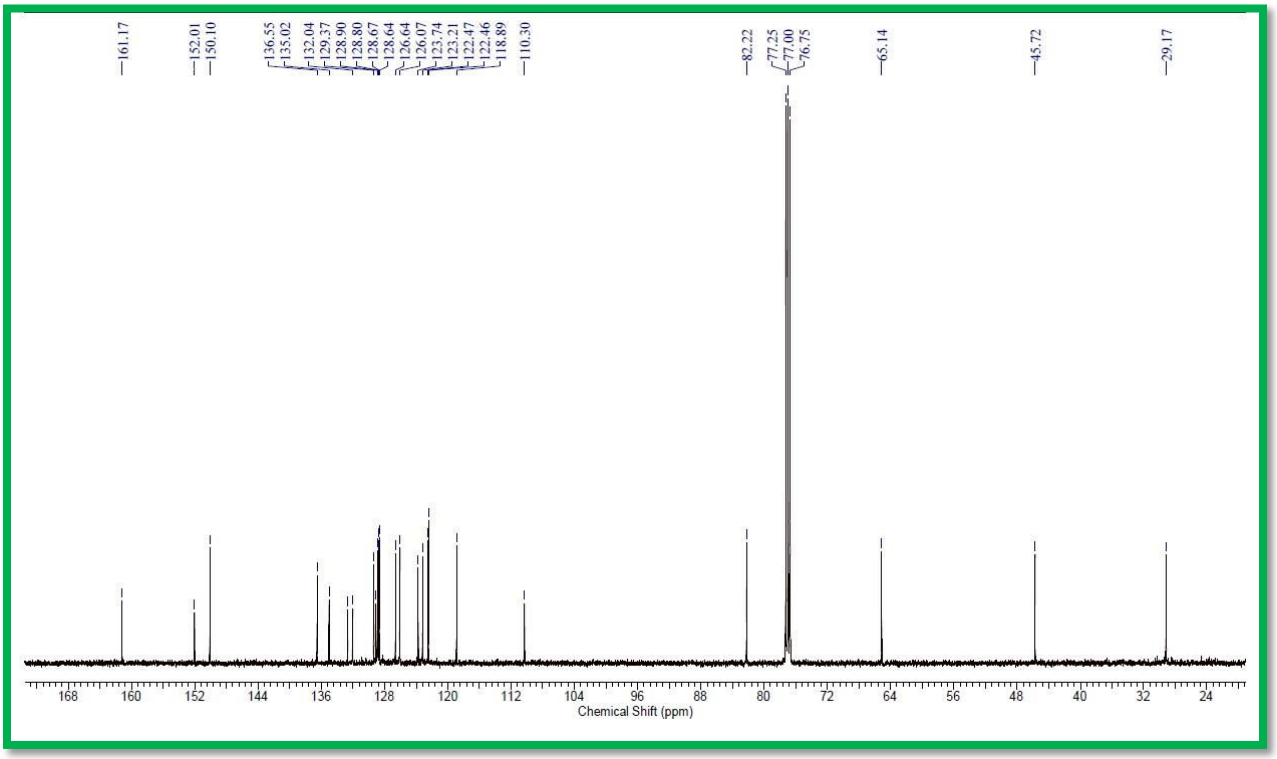
^{13}C-NMR of 4o (125 MHz)



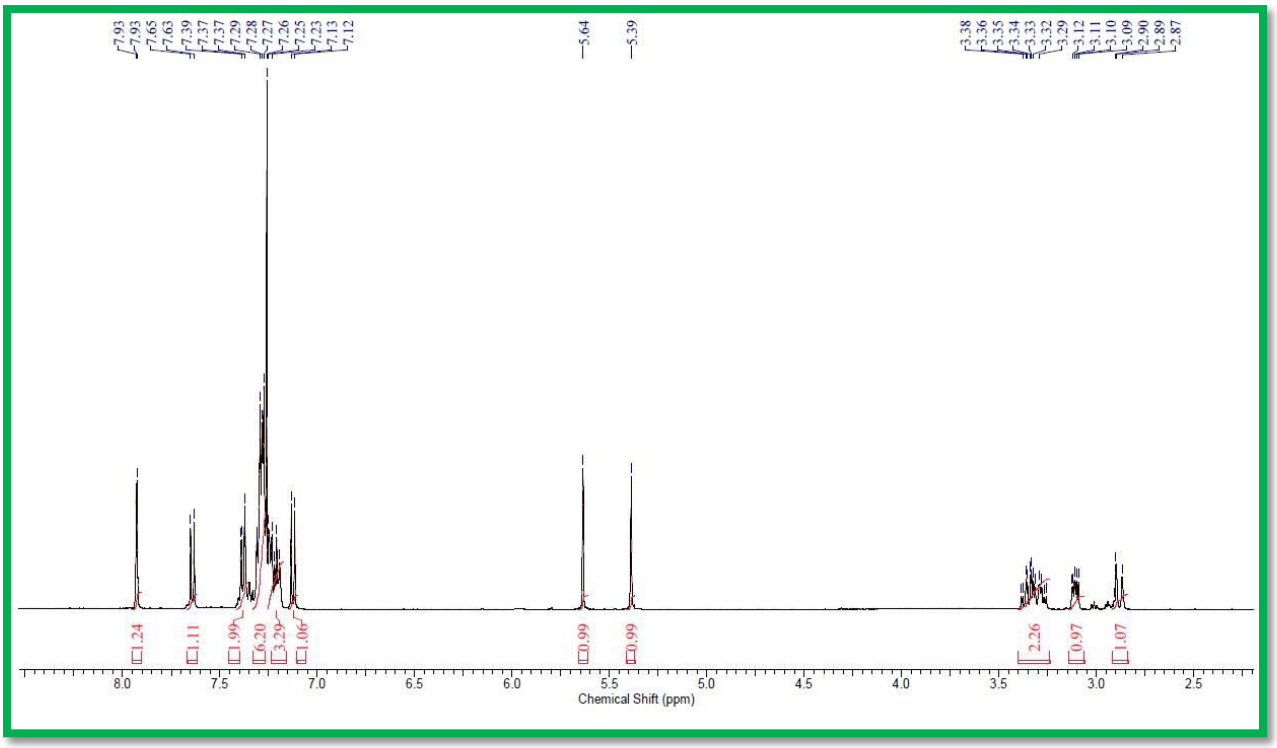
^{1}H-NMR of 4p (500 MHz)



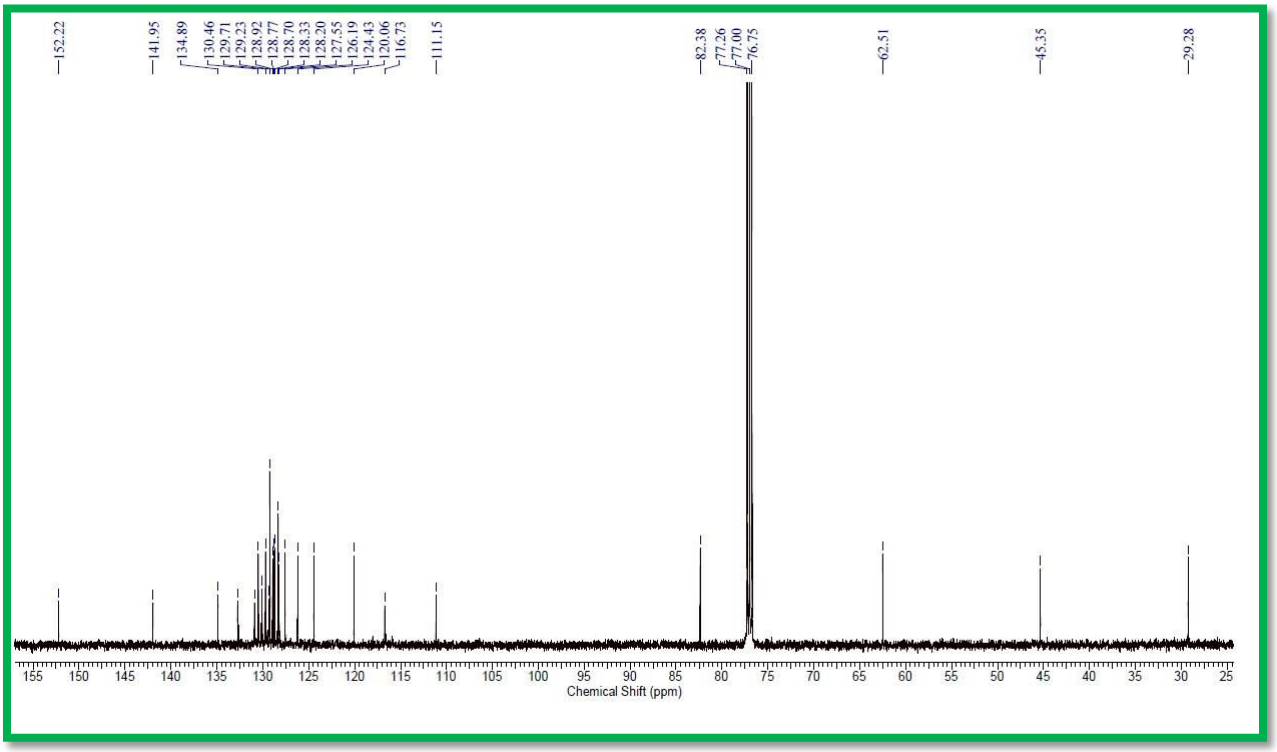
^{13}C-NMR of 4p (125 MHz)



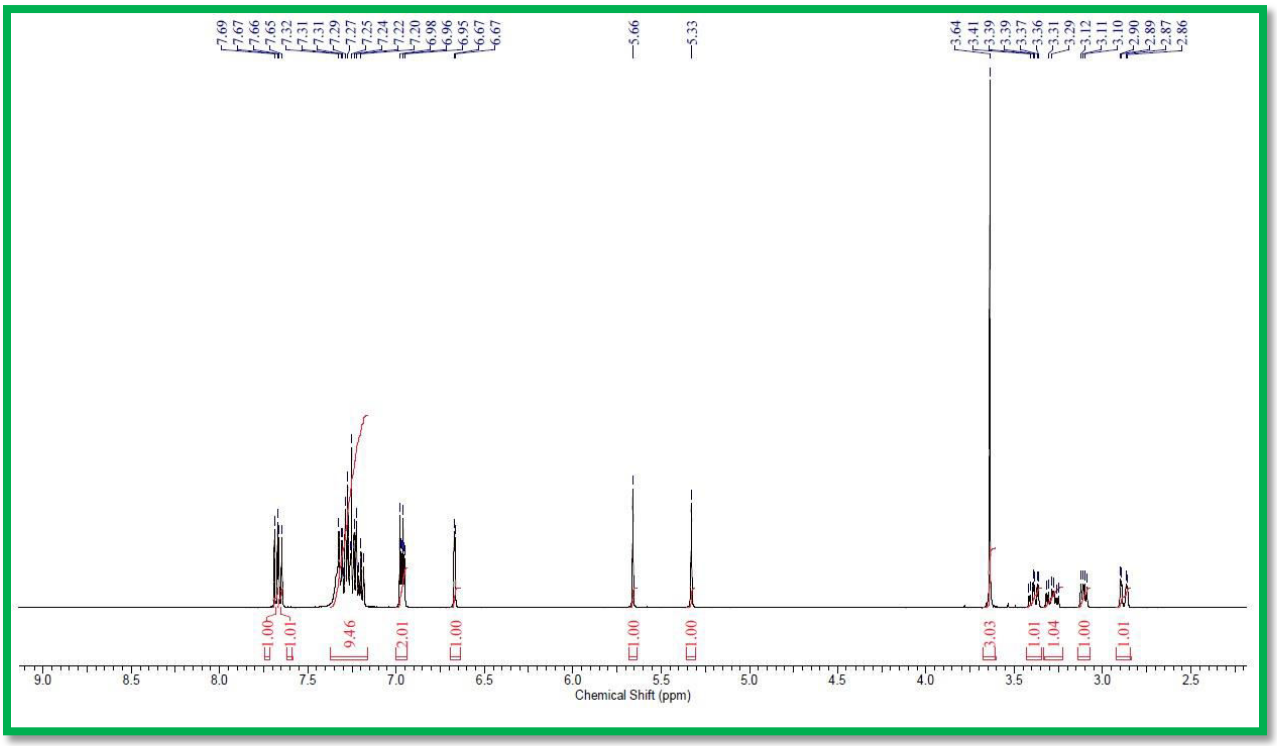
^{1}H-NMR of 4q (500 MHz)



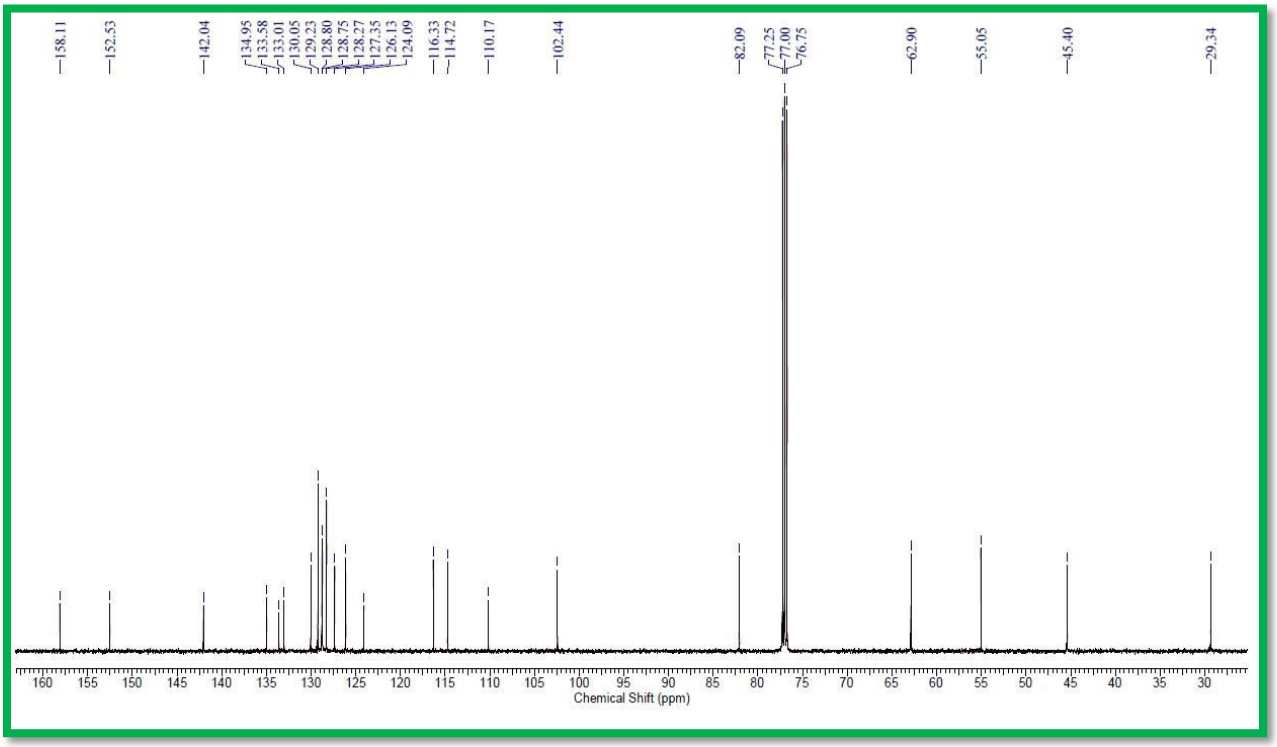
^{13}C-NMR of 4q (125 MHz)



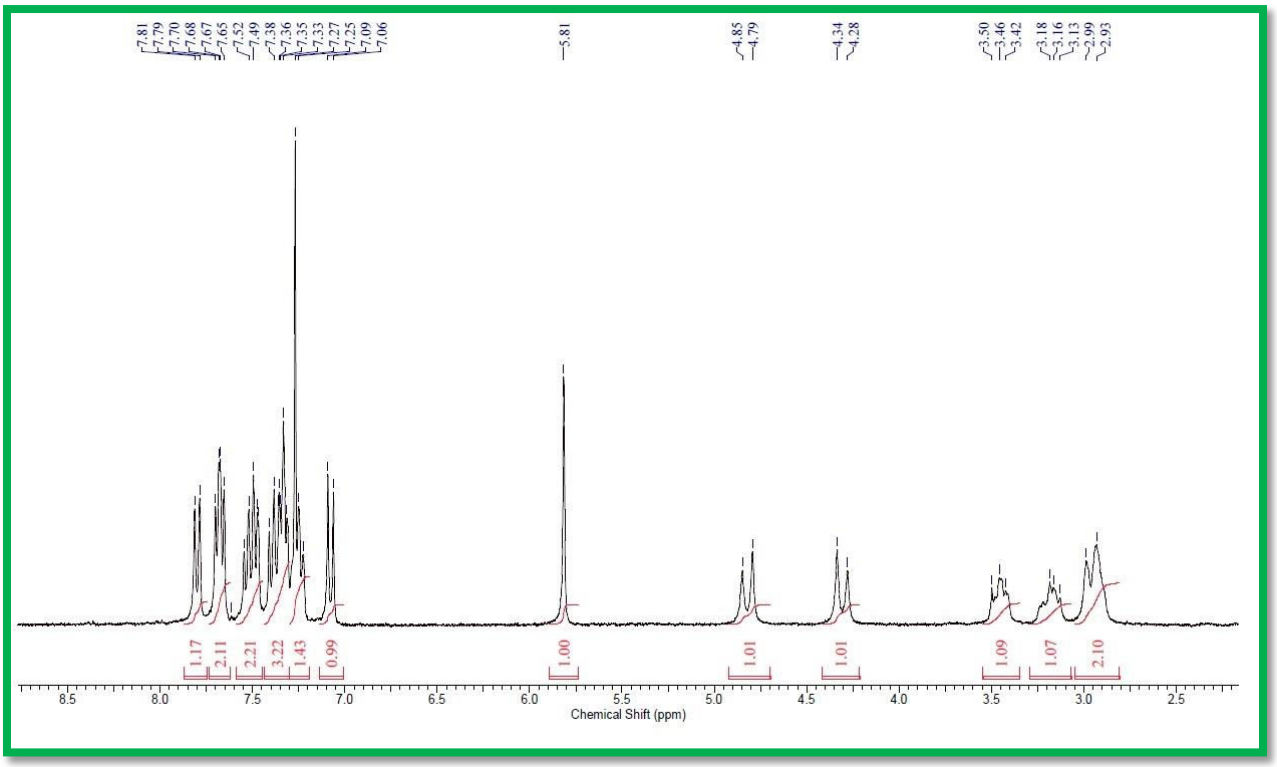
^{1}H-NMR of 4r (500 MHz)



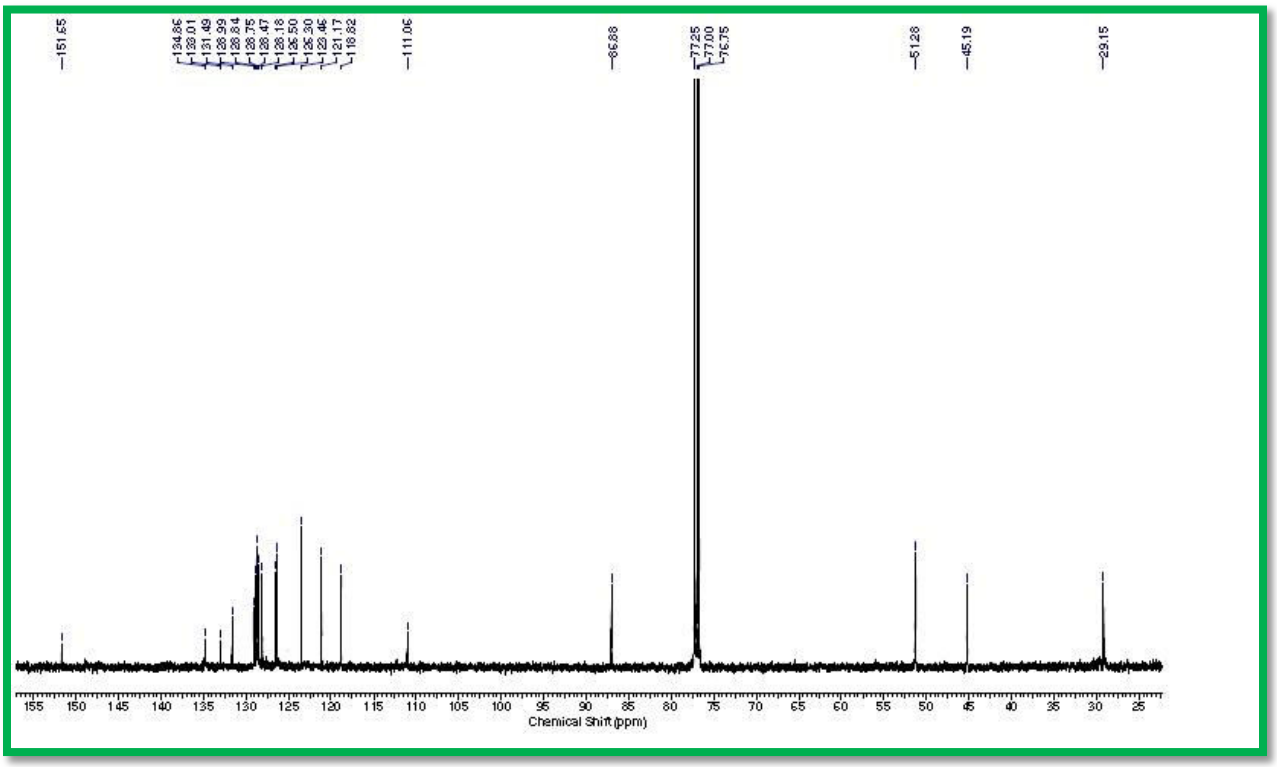
^{13}C-NMR of 4r (125 MHz)



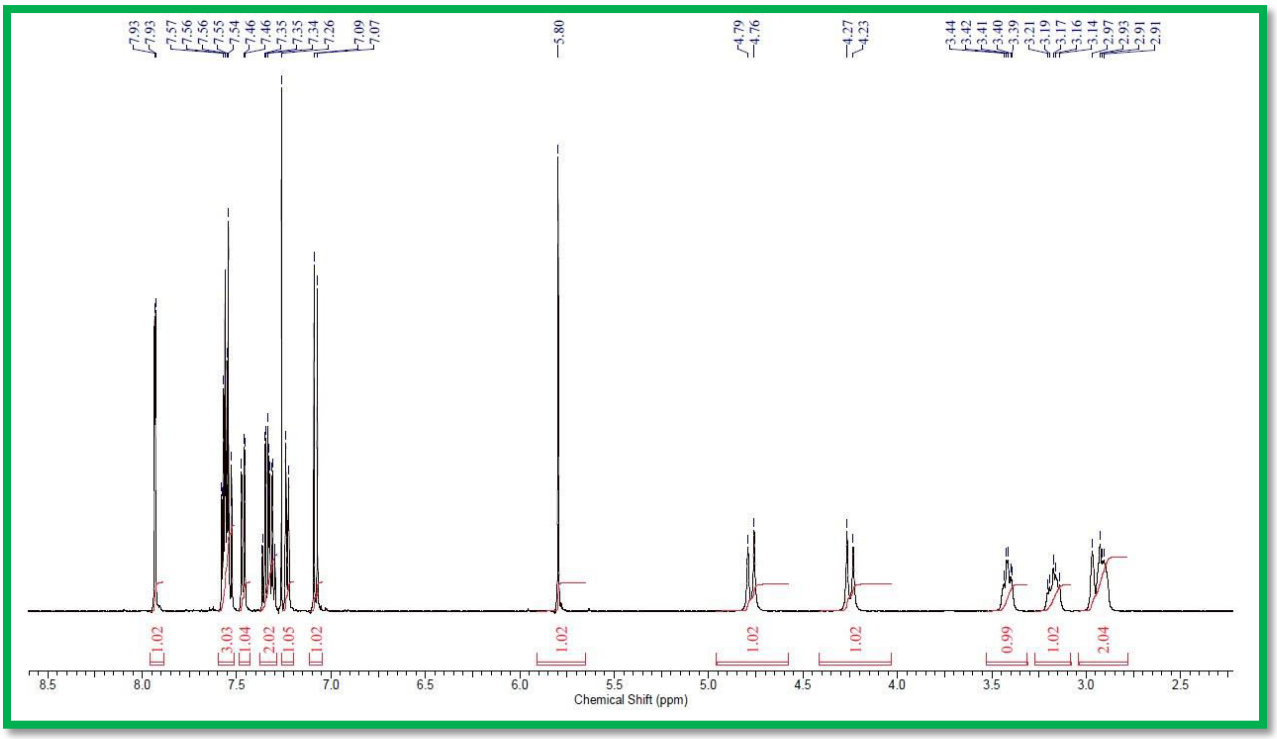
^{1}H-NMR of 4s (300 MHz)



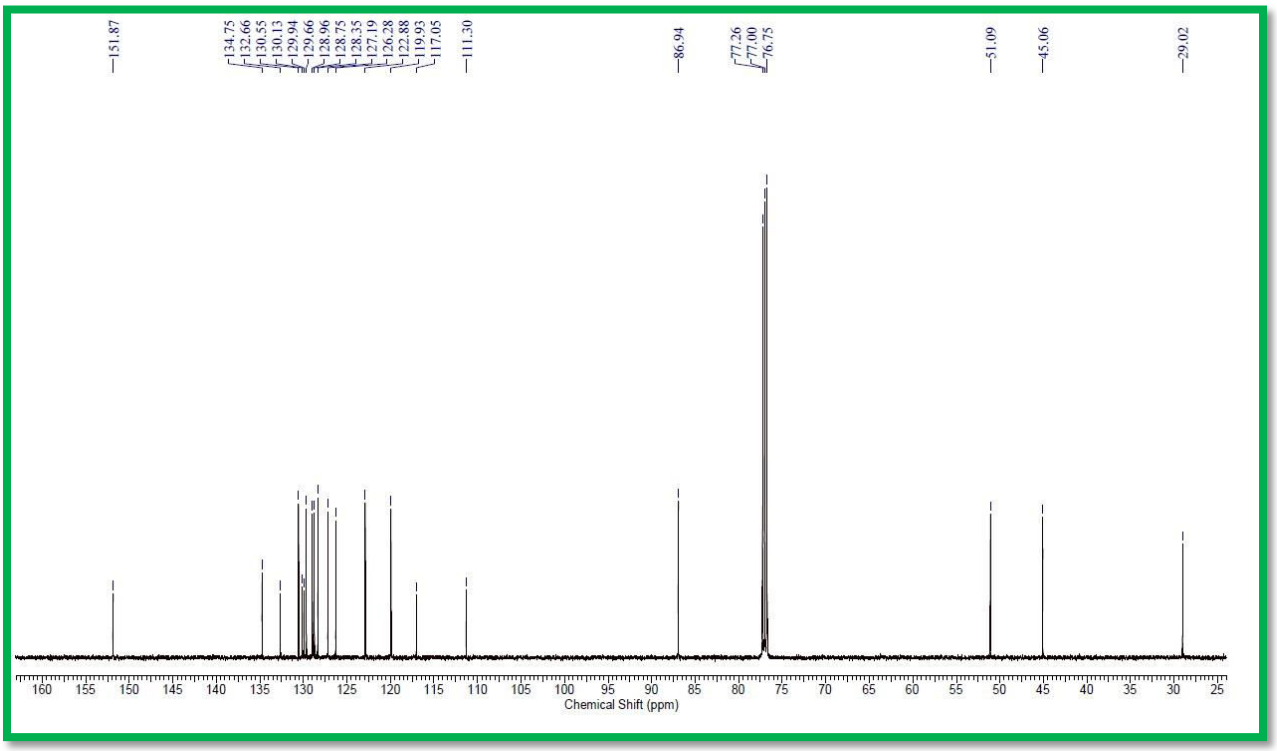
^{13}C-NMR of 4s (125 MHz)



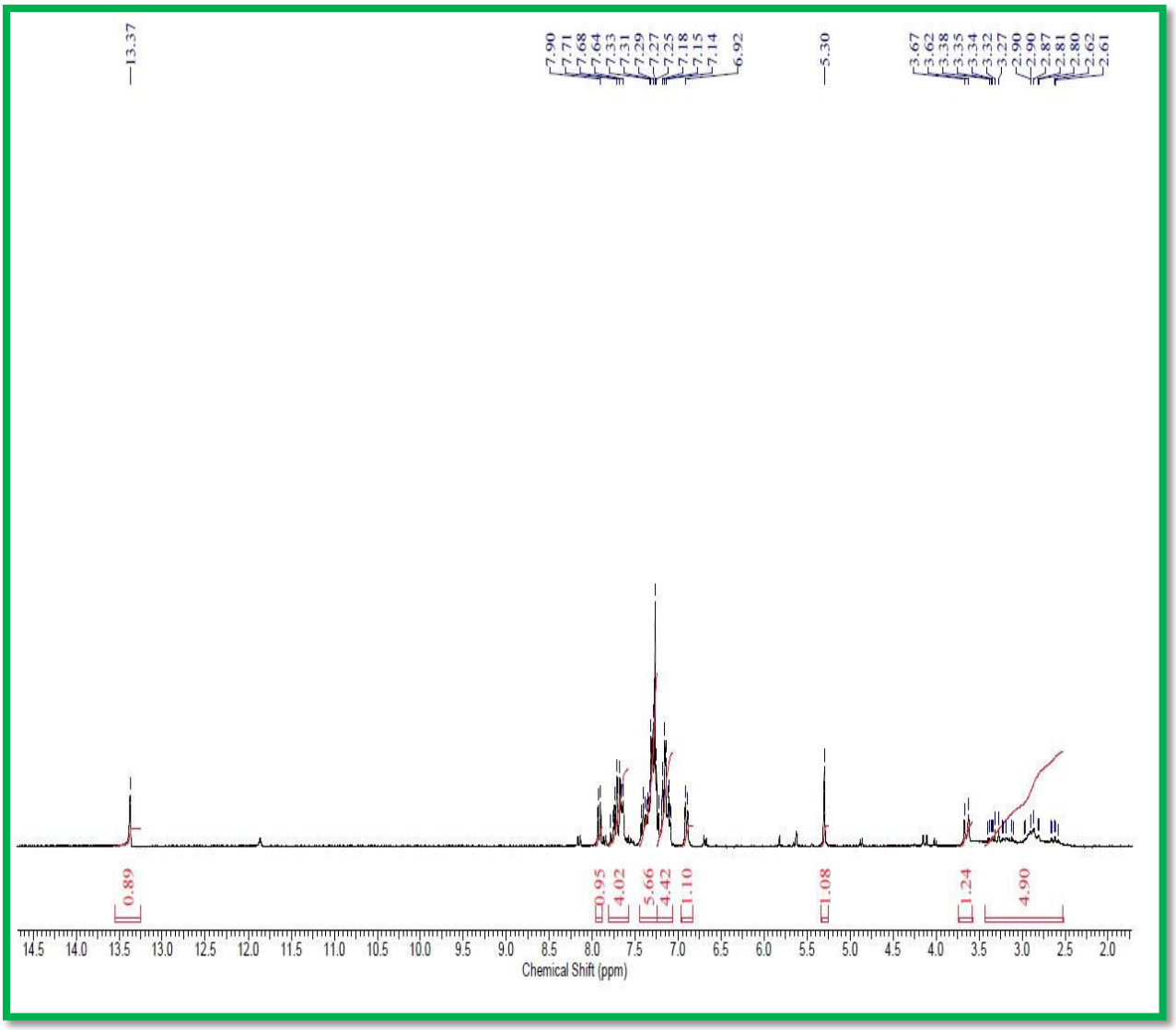
^{1}H-NMR of 4t (500 MHz)



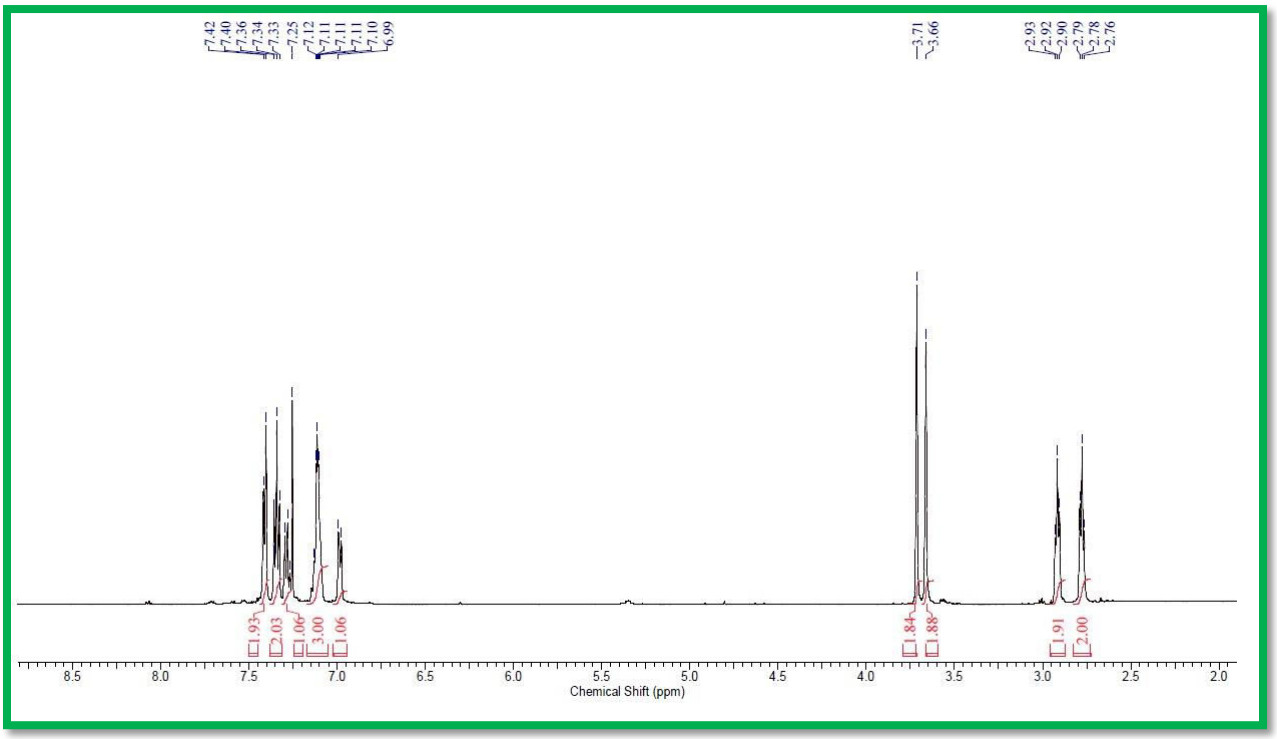
^{13}C-NMR of 4t (125 MHz)



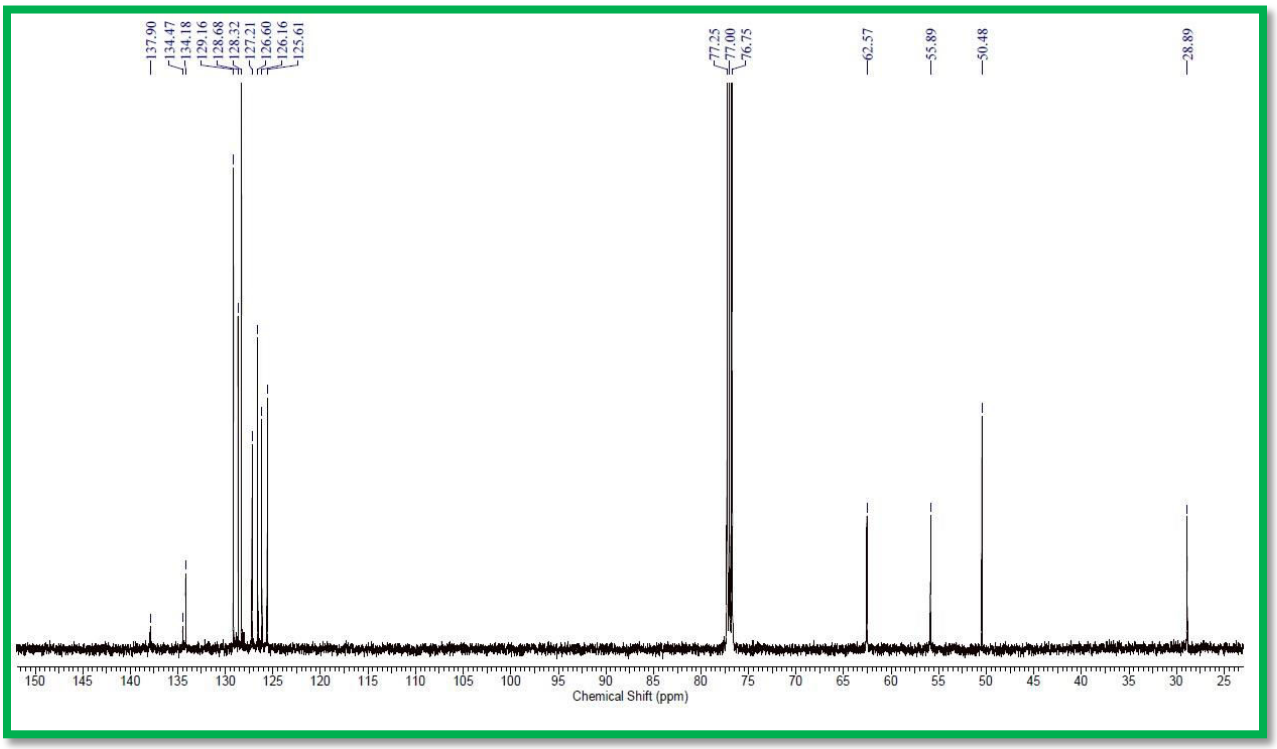
^{1}H-NMR of 5a (300 MHz)



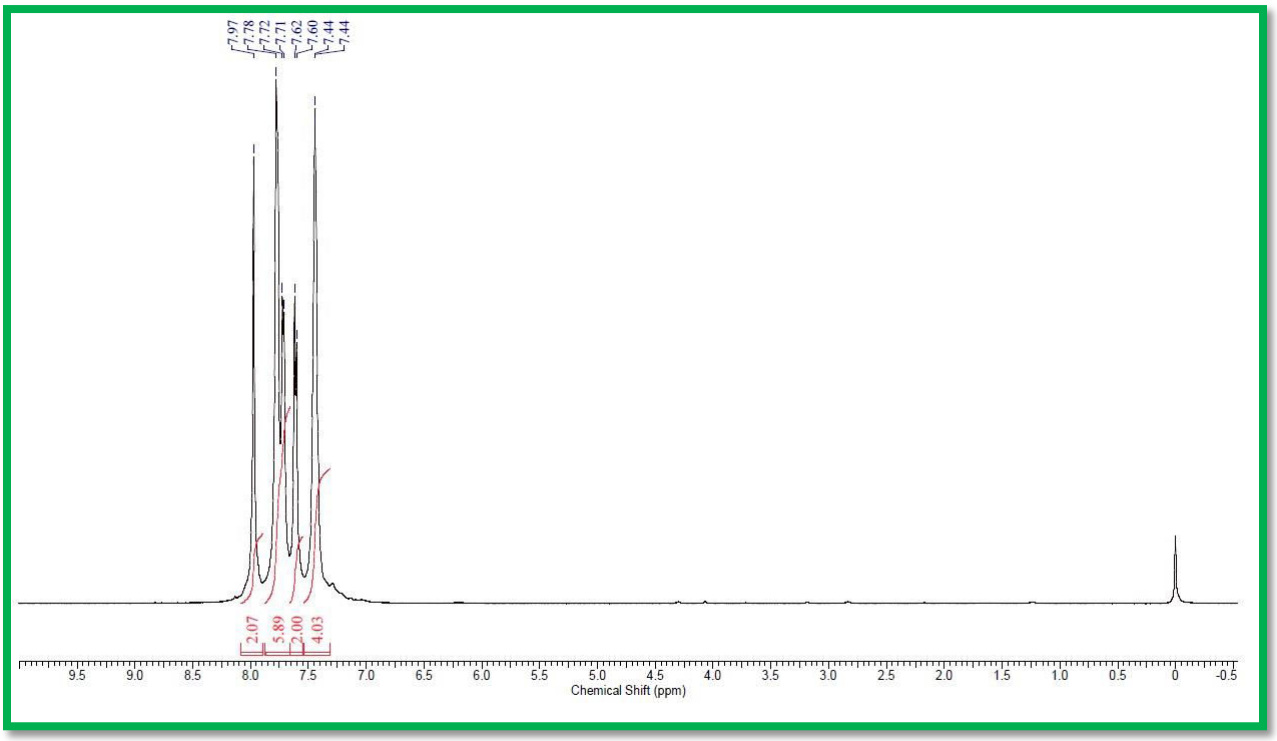
^{1}H-NMR of 7a (500 MHz)



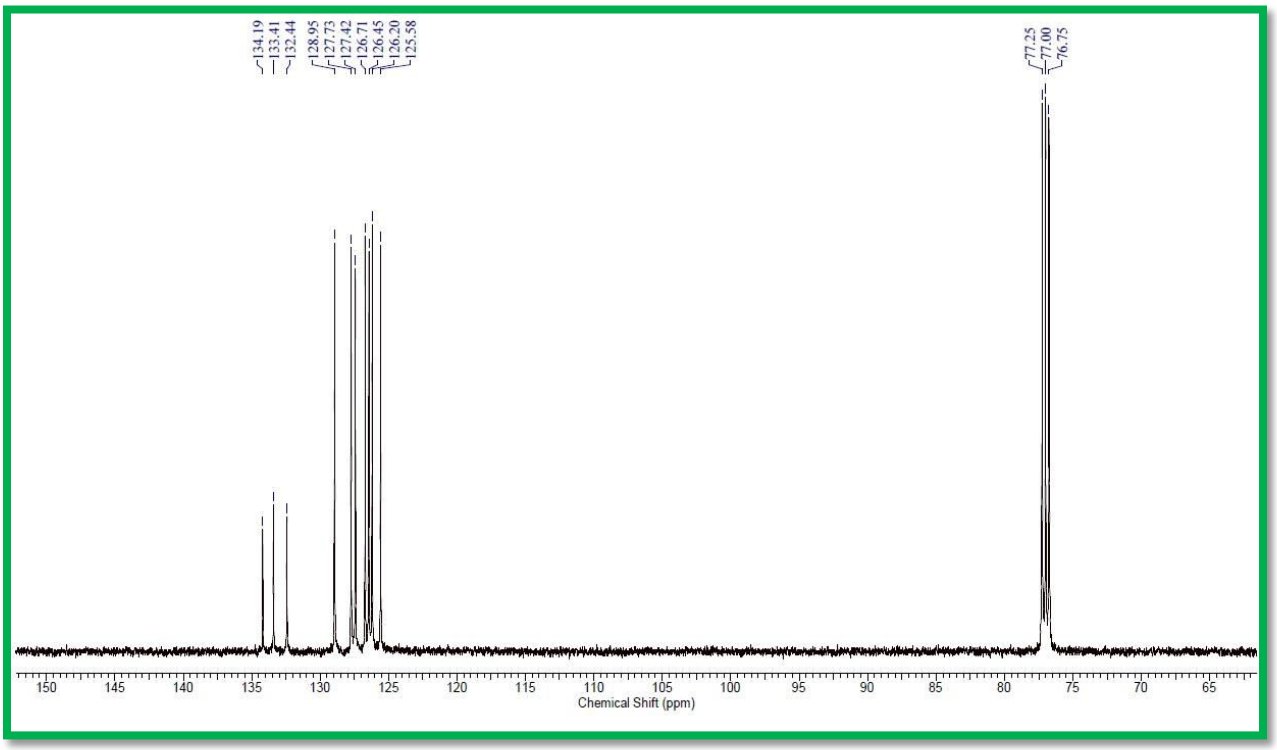
^{13}C-NMR of 7a (125 MHz)



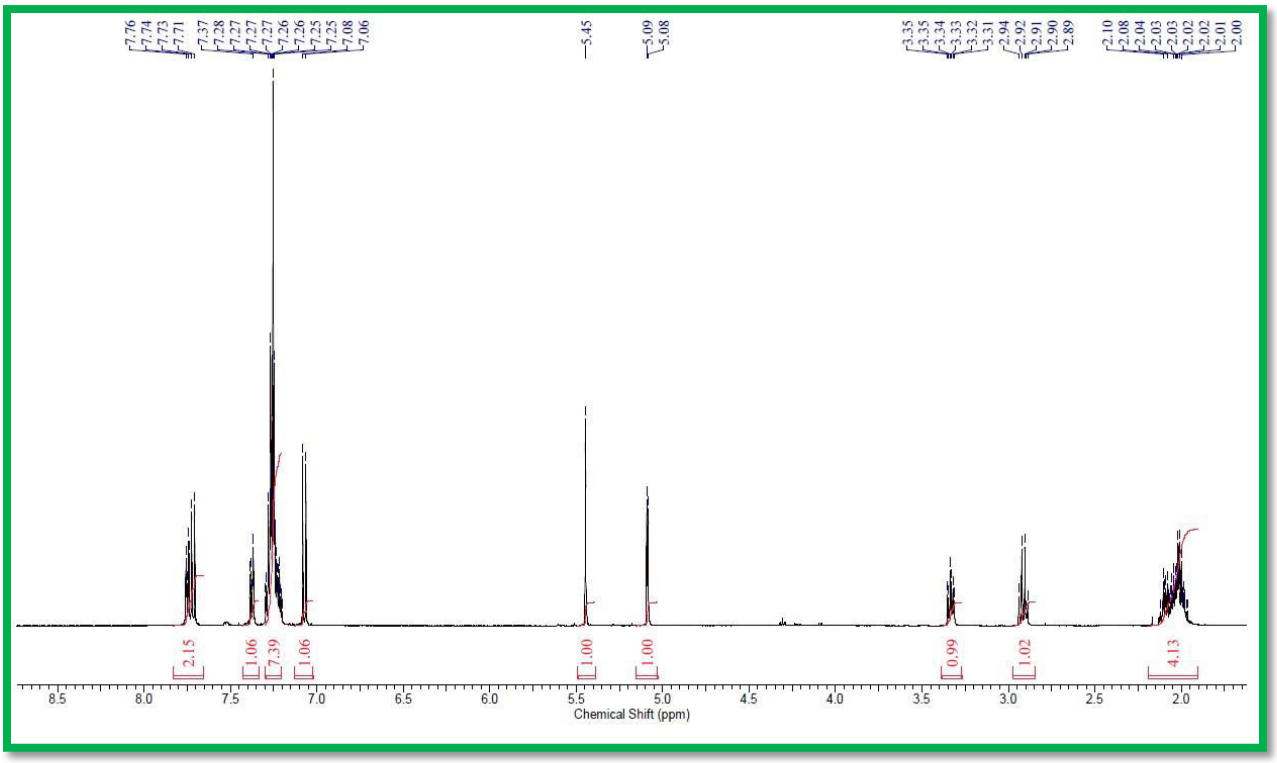
^{1}H-NMR of 8 (500 MHz)



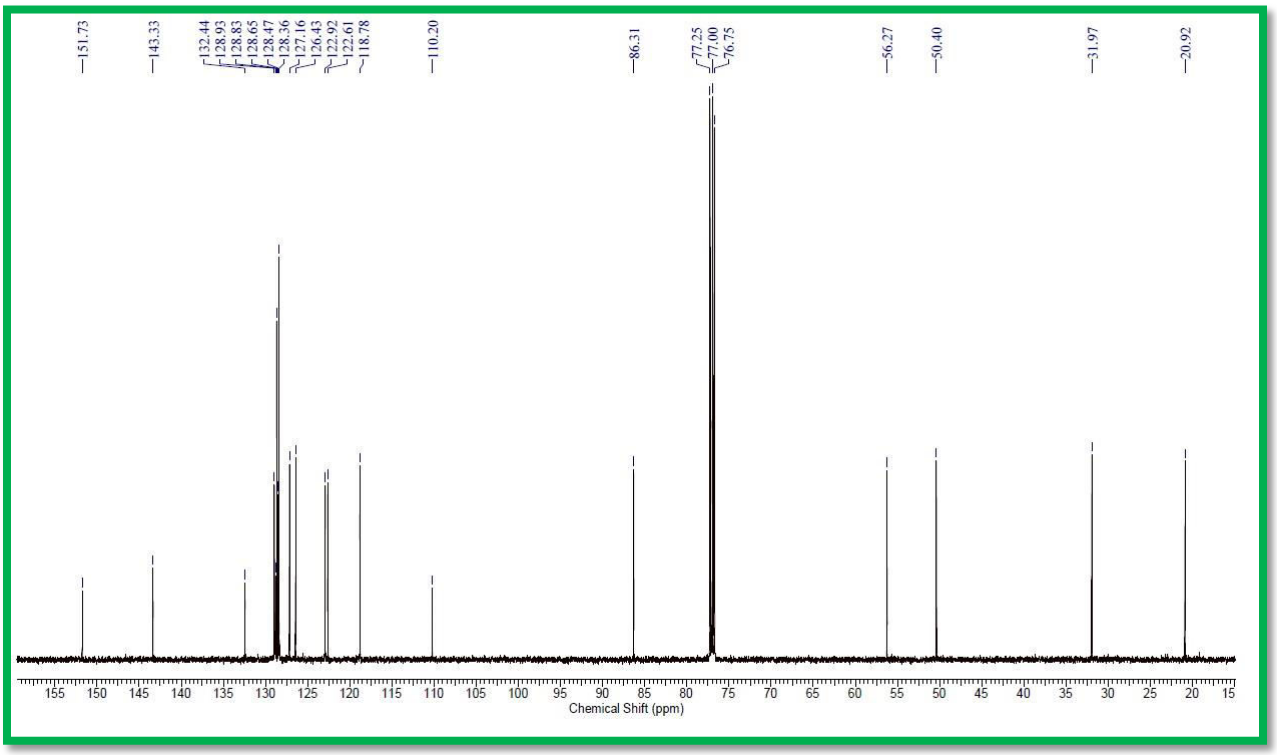
^{13}C-NMR of 8 (125 MHz)



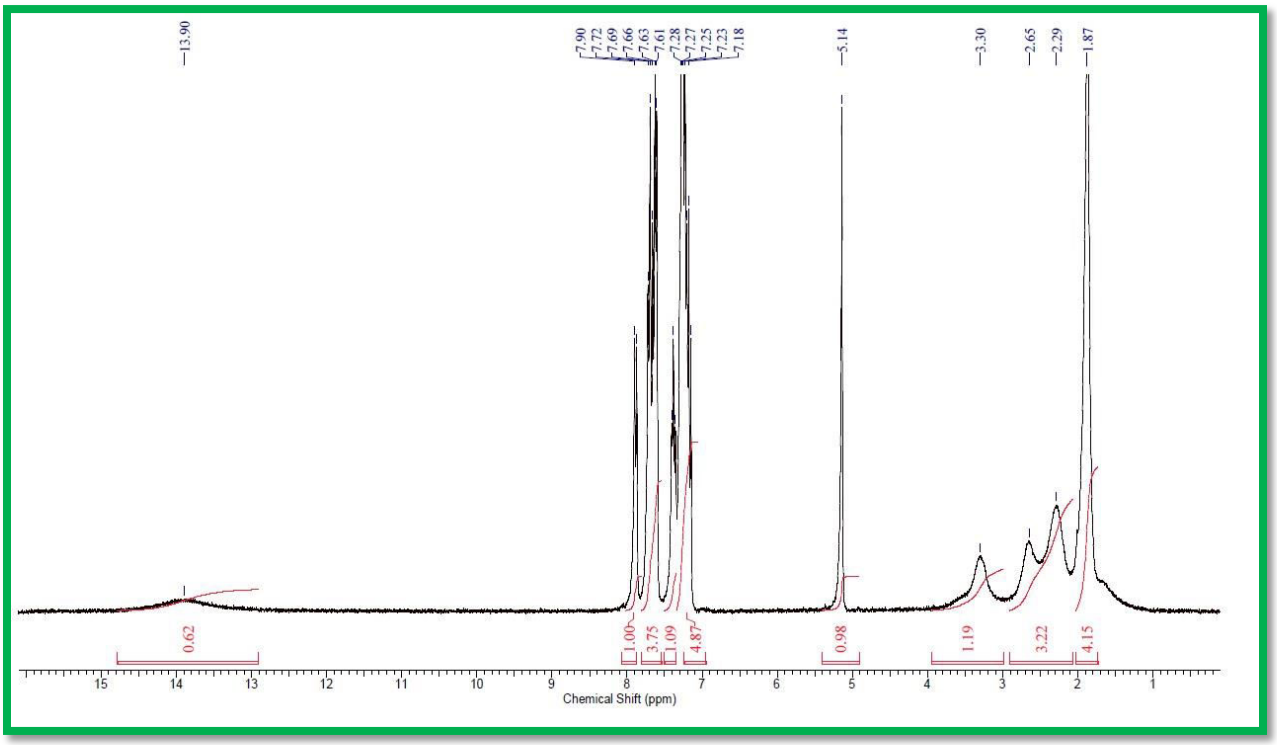
^{1}H-NMR of 9 (500 MHz)



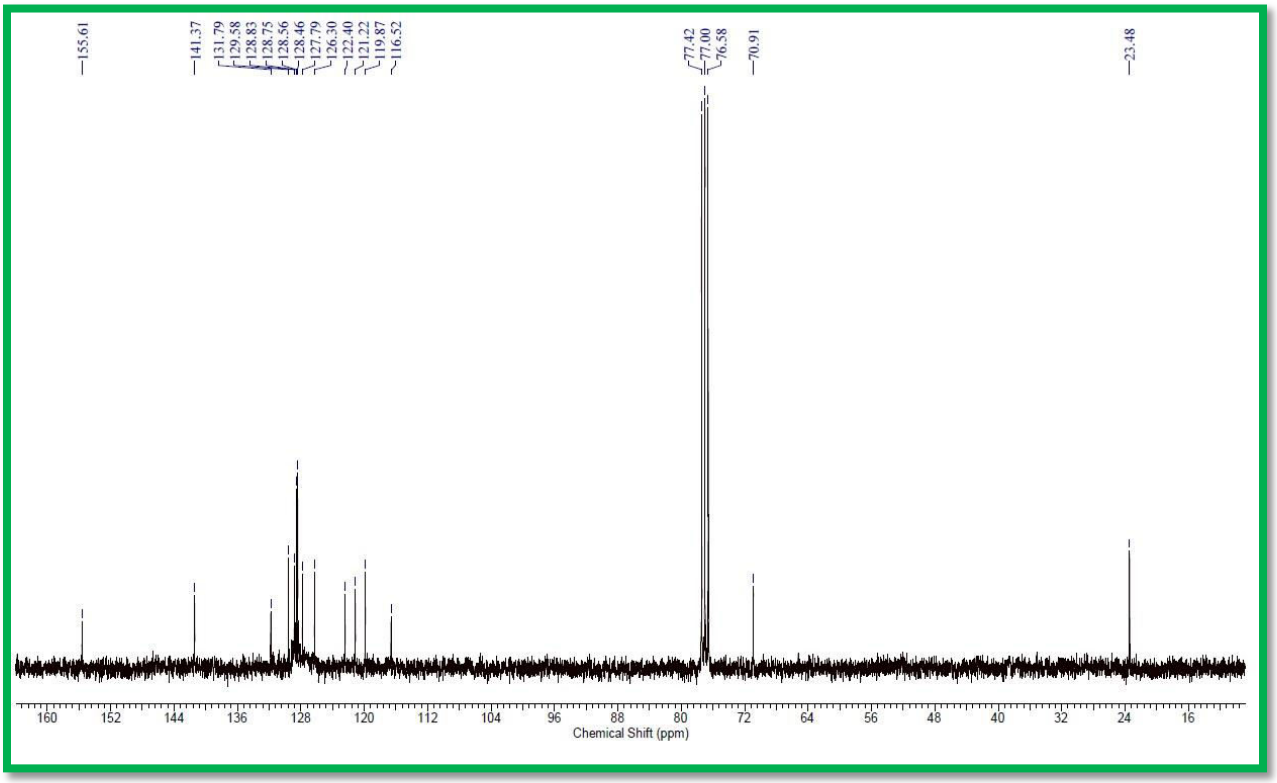
^{13}C-NMR of 9 (125 MHz)



^{1}H-NMR of 10 (300 MHz)



^{13}C-NMR of 10 (75 MHz)



^{1}H-NMR of 11 (300 MHz)