Electronic Supplementary Information

Multi-component synthesis of 3-substituted indoles and their cyclisation to α-carbolines *via* I_2-promoted intramolecular C2 oxidative amination/aromatisation at room temperature

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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 Bruker Avance DPX-300 and -500 NMR spectrometer with tetramethylsilane (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 iodine vapour. Column chromatography was performed on silica gel (100-200 mesh, Merck) using ethyl acetate/hexane as eluent.

Preparation of 3:[1]

A solution of 3-aminocrotonitrile (1.7 g, 10 mmol in 15 mL of 1N HC1) and phenylhydrazine (1 mL, 10 mmol) was refluxed for 16 h. The resulting reddish liquid was dissolved in EtOAc and washed with H_2O (2 x 50 mL). Separated the organic layer and dried with anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator which gave the product as light brown solid; yield 1.6 g (95%).

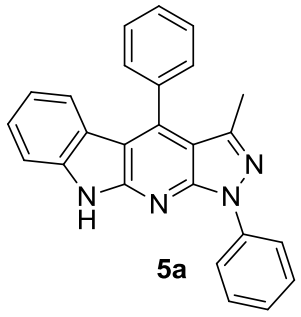
Preparation of 1, 3-diphenyl-1H-pyrazol-5-amine:[2]

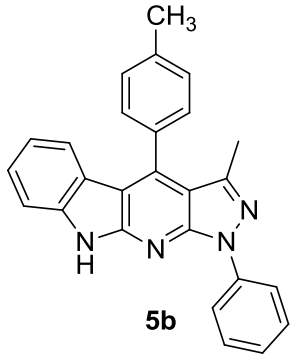
First we prepared 1-amino-1-phenylacrylonitrile (**A**). Benzonitrile (2 g, 20 mmol) was dissolved in benzene (50 mL). To this, acetonitrile (1.6 g, 40 mmol) was added, followed by portions of potassium *tert*-butoxide (9 g, 80 mmol). The mixture was stirred for 24 h at 20°C. Diethyl ether (40 mL) was added, followed by 2% $NaHCO_3$ (20 mL). Separated the organic layer and washed with 5 N NaCl (20 mL). The organic layer was dried with anhyd. Na_2SO_4. Evaporated the solvent and recrystallized from *i*-Pr_2O (20 mL) which gave 2 g of **A** (70%). Then (1.4 g, 10 mmol) of **A** was suspended in 2.5 N HCl (10 mL, 25 mmol) and heated to 50 °C. Phenylhydrazine (1.2 g, 11 mmol) was then added, followed by 12 N HCl (5 mL, 60 mmol) and the mixture was heated to 110 °C for 20 mins. After cooling by adding pieces of ice, 14 N NH_4OH was added drop wise until the solution became basic (7 mL, 100 mmol). Extracted the product with EtOAc and washed with H_2O (2 x 100 mL). The organic fraction

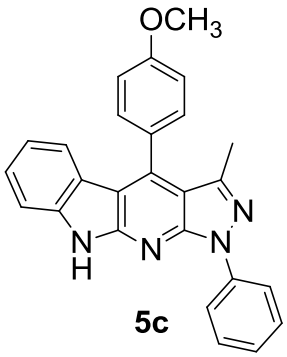
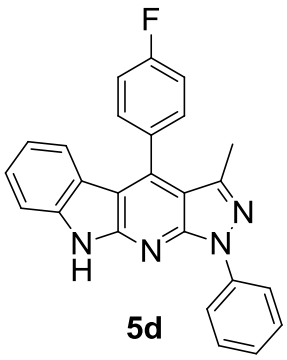
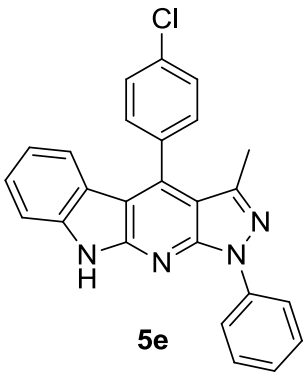
was then dried with anhyd. Na_2SO_4 and evaporation of the solvent gave us the crude product. Recrystallization from *i*-Pr_2O (10 mL) gave 0.91 g (39 %) of product as brown solid.

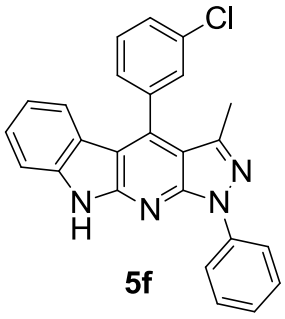
General Procedure for the Synthesis of 5:

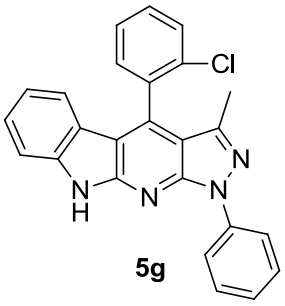
Compound **1** (1.0 mmol), **2** (1.0 mmol), and **3** (1.0 mmol) were stirred in presence of CAN (10 mol %) at room temperature for mentioned hours. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was dissolved in EtOAc and washed with H_2O (2 x 25 mL). Separated the organic layer and dried with anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator which gave **4** as crude product. The crude **4** was then dissolved in DCE and I_2 (1 eq.) was added to this. The reaction mixture was stirred at room temperature for the appropriate time. Removed the solvent using a rotary evaporator and the crude product was purified by column chromatography (silica gel, 100-200 mesh; ethyl acetate/hexane).

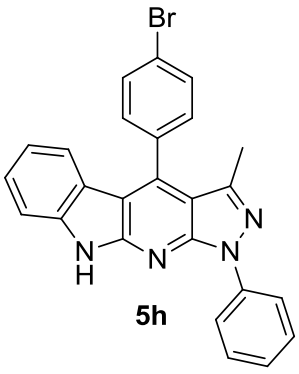
 **5a**	**3-methyl-1,4-diphenyl-1,9-dihydropyrazolo[4',3':5,6]pyrido [2,3-b]indole (5a):** Brown solid, (284 mg, yield- 76%); M.P.: 146-148 ^oC ; R_f = 0.8 (hexane/EtOAc, 5:1); IR (KBr): 3350, 3060, 2922, 1597, 1511, 1462, 1364, 1335, 1248, 1139, 1077, 1016, 885, 765, 730, 692, 611, 520 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.36 (bs, 1H), 8.41 (d, *J* = 7.9 Hz, 2H), 7.64-7.48 (m, 7H), 7.27-7.15 (m, 2H), 7.02-6.90 (m, 2H), 6.76 (d, *J* = 7.9 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.2, 149.3, 144.1, 140.5, 139.6, 139.3, 135.8, 129.2, 128.8, 128.7, 128.5, 126.1, 125.7, 121.5, 121.3, 121.2, 119.9, 112.2, 111.7, 110.6, 14.5; HRMS (ESI) exact mass calculated for $C_{25}H_{19}N_4$ $[M+H]^+$: 375.1604; Found: 375.1609.

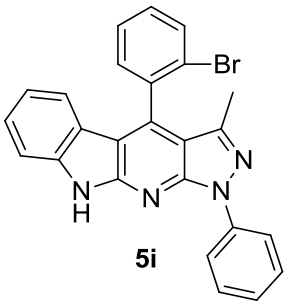
 **5b**	**3-methyl-1-phenyl-4-(p-tolyl)-1,9-dihydropyrazolo[4',3':5,6] pyrido[2,3-b]indole (5b):** White solid, (279 mg, yield- 72%); M.P.: 191-193 ^oC; R_f = 0.8 (hexane/EtOAc, 5:1); IR (KBr): 3344, 3066, 2918, 2652, 1596, 1511, 1463, 1367, 1338, 1245, 1181, 1142, 1021, 888, 807, 748, 693, 657, 506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 10.15 (bs, 1H), 8.38 (d, *J* = 7.8 Hz, 2H), 7.49-7.40 (m, 6H), 7.21-7.14 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.92-6.89 (m, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 2.54 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 149.3, 144.2, 140.8, 140.7, 139.3, 138.6, 132.8, 129.3, 129.2, 128.4, 126.0, 125.6, 121.6, 121.4, 121.2, 119.9, 112.3, 111.9, 110.5, 21.5, 14.9; HRMS (ESI) exact mass calculated for $C_{26}H_{21}N_4$ $[M+H]^+$: 389.1761; Found: 389.1766.

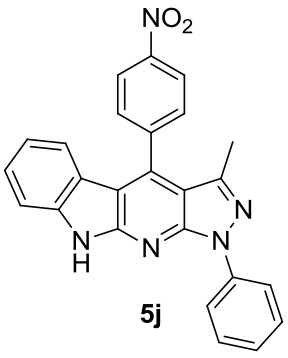
 **5c**	**4-(4-methoxyphenyl)-3-methyl-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5c):** Brown solid, (262 mg, yield-65%); M.P.: 184-186 ^{o}C; R_f = 0.7 (hexane/EtOAc, 4:1); IR (KBr): 3406, 2924, 2853, 1596, 1512, 1460, 1334, 1291, 1248, 1175, 1030, 852, 814, 738, 689, 627, 582, 519, cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.99 (bs, 1H), 8.36 (d, J = 7.6 Hz, 2H), 7.49-7.43 (m, 4H), 7.22-7.16 (m, 2H), 7.13-7.12 (m, 2H), 7.10-7.09 (m, 1H), 6.94-6.91 (m, 1H), 6.83-6.79 (m, 1H), 3.96 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 153.2, 149.4, 144.1, 140.6, 139.7, 139.3, 134.3, 134.3, 129.9, 129.1, 127.9, 126.0, 125.6, 121.6, 121.2, 119.9, 114.2, 114.1, 112.1, 110.6, 55.4, 15.0; HRMS (ESI) exact mass calculated for $C_{26}H_{21}N_4O$ $[M+H]^+$: 405.1710; Found: 405.1718.
 **5d**	**4-(4-fluorophenyl)-3-methyl-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5d):** Orange solid, (333 mg, yield-85%); M.P.: 160-162 ^{o}C; R_f = 0.8 (hexane/EtOAc, 4:1); IR (KBr): 3357, 2922, 2852, 1595, 1508, 1460, 1384, 1334, 1244, 1155, 1136, 1014, 904, 852, 812, 736, 694, 655, 572, 522, 511cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.17 (bs, 1H), 8.24 (d, J = 8.6 Hz, 2H), 7.50-7.41 (m, 4H), 7.29-7.24 (m, 2H), 7.23-7.21 (m, 1H), 7.19-7.18 (m, 1H), 7.09 (d, J = 7.9 Hz, 1H), 6.96-6.95 (m, 1H), 6.92-6.91 (m, 1H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.1 (d, $J_{C\text{-}F}$ = 248.0 Hz), 152.9, 149.4, 143.7, 139.6, 139.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 131.8, 130.4 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.1, 126.4, 125.6, 124.5, 121.6, 121.3, 121.2, 120.2, 115.9(d, $J_{C\text{-}F}$ = 21.8 Hz), 112.2, 111.8. 110.7, 14.9; HRMS (ESI) exact mass calculated for $C_{25}H_{18}FN_4$ $[M+H]^+$: 393.1510; Found: 393.1518.
 **5e**	**4-(4-chlorophenyl)-3-methyl-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5e):** Brown solid, (327 mg, yield-80%); M.P.: 167-169 ^{o}C; R_f = 0.7 (hexane/EtOAc, 5:1); IR (KBr): 3353, 3050, 2928, 2853, 1595, 1506, 1461, 1385, 1334, 1245, 1146, 1087, 1017, 766, 722, 691 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.22 (bs, 1H), 8.36-8.34 (m, 2H), 7.66-7.64 (m, 2H), 7.56-7.53 (m, 4H), 7.35-7.32 (m, 1H), 7.31-7.29 (m, 1H), 7.19 (d, J = 7.9 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.04-7.00 (m, 1H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 149.5, 143.6, 139.6, 139.2, 138.8, 135.0, 134.4, 130.1, 129.1(2C), 126.5, 125.6, 121.7, 121.3, 121.2, 120.3, 112.0, 111.6, 110.7, 15.0; HRMS (ESI) exact mass calculated for $C_{25}H_{18}ClN_4$ $[M+H]^+$: 409.1215; Found: 409.1219.

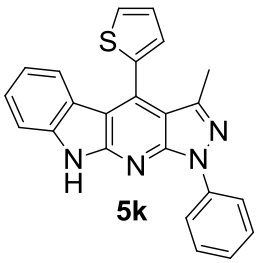
 **5f**	**4-(3-chlorophenyl)-3-methyl-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5f):** Yellow solid, (318 mg, yield-78%); M.P.: 140-142 ^{o}C; R_f = 0.8 (hexane/EtOAc, 4:1); IR (KBr): 3317, 3063, 2923, 2853, 1598, 1509, 1462, 1377, 1335, 1244, 1136, 1042, 1015, 885, 834, 741, 690, 525 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.25 (bs, 1H), 8.37 (d, *J* = 7.5 Hz, 2H), 7.61-7.53 (m, 3H), 7.48-7.44 (m, 3H), 7.20- 7.15 (m, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.95- 6.92 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1, 149.2, 143.6, 139.6, 139.4, 138.4, 137.7, 134.7, 130.1, 129.2, 128.8, 127.9, 126.4, 125.7, 121.4, 121.3, 120.9, 120.1, 112.0, 111.4, 110.7, 14.9; HRMS (ESI) exact mass calculated for $C_{25}H_{18}ClN_4$ $[M+H]^+$: 409.1215; Found: 409.1216.

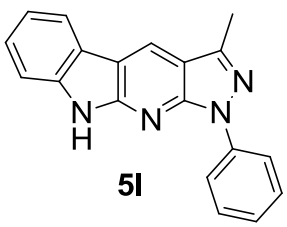
 **5g**	**4-(2-chlorophenyl)-3-methyl-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5g):** White solid, (327 mg, yield-80%); M.P.: 155-157 ^{o}C; R_f = 0.7 (hexane/EtOAc, 5:1); IR (KBr): 3314, 2923, 2853, 1598, 1508, 1462, 1374, 1335, 1244, 1136, 1042, 1015, 885, 834, 741, 690, 525 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.58 (bs, 1H), 8.30 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.48-7.34 (m, 5H), 7.10-6.96 (m, 2H), 6.81-6.73 (m, 2H), 6.49 (d, *J* = 8.1 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.4, 149.2, 143.9, 139.6, 139.5, 136.7, 134.7, 133.0, 130.5, 130.3, 129.9, 129.2, 127.2, 126.3, 125.8, 121.3, 121.1, 120.8, 112.3, 111.3, 110.7, 13.9; HRMS (ESI) exact mass calculated for $C_{25}H_{18}ClN_4$ $[M+H]^+$: 409.1215; Found: 409.1221.

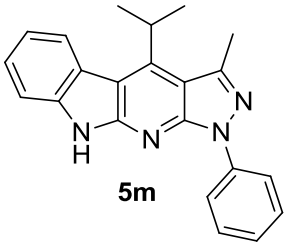
 **5h**	**4-(4-bromophenyl)-3-methyl-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5h):** Yellow solid, (371 mg, yield-82%); M.P.: 179-181 ^{o}C; R_f = 0.8 (hexane/EtOAc, 5:1); IR (KBr): 3343, 2929, 2854, 1596, 1508, 1463, 1388, 1336, 1248, 1146, 1076, 1012, 1146, 1076, 1012, 807, 739, 694, 655, cm^{-1}; ^{1}H NMR (500 MHz, DMSO): δ 12.14 (bs, 1H), 8.36-8.34 (m, 2H), 7.89-7.87 (m, 2H), 7.62-7.55 (m, 4H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.39-7.36 (m, 1H), 7.32-7.29 9 (m, 1H), 7.01-6.98 (m, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, DMSO): δ 152.9, 149.3, 143.0, 140.1, 139.6, 138.3, 134.6, 131.8, 130.9, 129.1, 126.5, 125.0, 122.5, 121.0, 120.5, 120.1, 119.7, 111.3, 111.2, 110.5, 14.7; HRMS (ESI) exact mass calculated for $C_{25}H_{18}BrN_4$ $[M+H]^+$: 453.0709; Found: 453.0711.

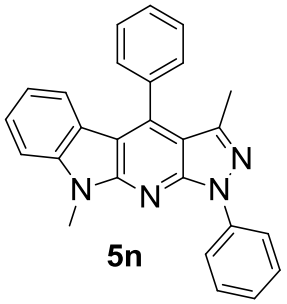
 **5i**	**4-(2-bromophenyl)-3-methyl-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5i):** White solid, (362 mg, yield-80%); M.P.: 118-120 ^{o}C; R_f = 0.6 (hexane/EtOAc, 5:1); IR (KBr): 3415, 3061, 2924, 2854, 1598, 1509, 1462, 1376, 1245, 886, 835, 740, 692 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (bs, 1H), 8.34 (d, *J* = 7.6 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.60-7.48 (m, 5H), 7.36-7.23 (m, 3H), 7.03- 6.98 (m, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.0, 149.6, 143.7, 139.7, 139.2, 138.1, 136.9, 133.1, 130.5, 130.3, 129.1, 127.8, 126.5, 125.5, 122.7, 121.5, 121.3, 121.1, 120.4, 113.4, 111.8, 110.7, 14.1; HRMS (ESI) exact mass calculated for $C_{25}H_{18}BrN_4$ $[M+H]^+$: 453.0709; Found: 453.0717.

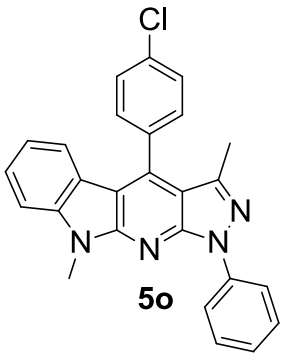
 **5j**	**3-methyl-4-(4-nitrophenyl)-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5j):** Brown solid, (364 mg, yield-87%); M.P.: 150-156 ^{o}C; R_f = 0.7 (hexane/EtOAc, 5:1); IR (KBr): 3437, 3017, 2892, 2840, 1594, 1508, 1440, 1373, 1313, 1231, 1133, 1008, 852, 736, 694, 656, 581, 501cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.36 (bs, 1H), 8.53 (d, *J* = 8.6 Hz, 2H), 8.32 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.54-7.51 (m, 2H), 7.34-7.28 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.00-6.97 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 149.3, 148.3, 143.0, 142.9, 139.5, 139.4, 137.1, 130.0, 129.1, 126.8, 125.8, 124.0, 121.3 (2C), 120.8, 120.4, 111.5, 111.0, 110.9, 15.0; HRMS (ESI) exact mass calculated for $C_{25}H_{18}N_5O_2$ $[M+H]^+$: 420.1455; Found: 420.1459.

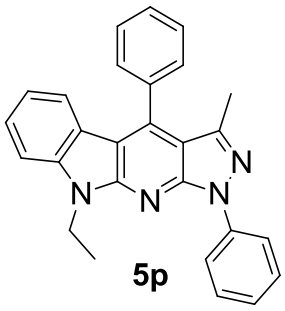
 **5k**	**3-methyl-1-phenyl-4-(thiophen-2-yl)-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5k):** Brown solid, (235 mg, yield-62%); M.P.: 122-128 ^{o}C; R_f = 0.8 (hexane/EtOAc, 4:1); IR (KBr): 3434, 2921, 2852, 1595, 1506, 1461, 1377, 1339, 1246, 1133, 1105, 1016, 883, 850, 793, 748, 691, 632, 571, 523 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75 (bs, 1H), 8.34 (d, *J* = 8.1 Hz, 2H), 7.65-7.64 (m, 1H), 7.51-7.48 (m, 2H), 7.33-7.31 (m, 1H), 7.29-7.28 (m, 1H), 7.25-7.21 (m, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.01-6.98 (m, 1H), 6.93- 6.91 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 149.2, 143.9, 139.6, 139.4, 135.3, 132.7, 129.2, 127.8, 127.6, 127.1, 126.5, 125.7, 121.9, 121.3, 121.1, 120.3, 114.0, 112.8, 110.6, 14.3; HRMS (ESI) exact mass calculated for $C_{23}H_{17}N_4S$ $[M+H]^+$: 381.1168; Found: 381.1175.

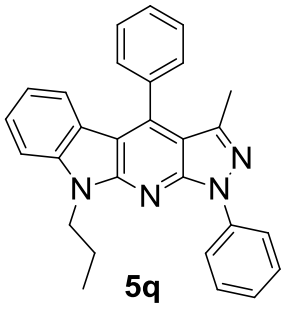
 **5l**	**3-methyl-1-phenyl-1,9-dihydropyrazolo[4',3':5,6]pyrido[2,3-b]indole (5l):** Brown solid, (149 mg, yield- 50%); M.P.: 195-197 ^{o}C; R_f = 0.6 (hexane/EtOAc, 4:1); IR (KBr): 3408, 2925, 2854, 1595, 1511, 1461, 1398, 1330, 1258, 1189, 1121, 1074, 1012, 969, 911, 751, 690, 649, 605, 518 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.89 (bs, 1H), 8.58 (s, 1H), 8.33-8.32 (m, 2H), 8.07-8.06 (m,1H), 7.54-7.50 (m, 2H), 7.43-7.40 (m, 1H), 7.30-7.25 (m, 3H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 149.6, 143.6, 139.8, 139.3, 139.1, 129.1, 126.6, 125.3, 121.6, 121.3, 120.9, 120.5, 120.2, 114.1, 113.7, 112.9, 110.8, 14.1; HRMS (ESI) exact mass calculated for $C_{19}H_{15}N_4$ $[M+H]^+$: 299.1291.; Found: 299.1295.

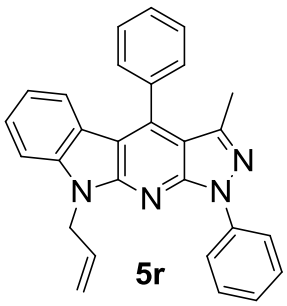
 **5m**	**4-isopropyl-3-methyl-1-phenyl-1,9-dihydropyrazolo[4',3':5,6] pyrido[2,3-b]indole (5m):** Yellow solid, (197 mg, yield- 58%); M.P.: 149-151 ^{o}C; R_f = 0.8 (hexane/EtOAc, 4:1); IR (KBr): 3407, 3051, 2960, 2924, 2853, 1593, 1505, 1464, 1383, 1338, 1249, 1157, 1123, 1072, 1013, 895, 815, 752, 666, 629, 542 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.91 (bs, 1H), 8.32 (d, J = 8.3 Hz, 2H), 8.22 (d, J = 7.2 Hz, 1H), 7.50-7.44 (m, 2H), 7.29-7.18 (m, 3H), 6.94-9.92 (m, 1H), 4.37 (s, 1H), 2.91 (s, 3H), 1.77 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.9, 149.8, 143.3, 143.2, 139.6, 139.2, 129.1, 125.6, 125.5, 121.2, 120.7, 119.7, 111.6, 111.1, 110.6, 29.5, 22.7, 14.1; ; HRMS (ESI) exact mass calculated for $C_{22}H_{21}N_4$ $[M+H]^+$: 341.1761; Found: 341.1765.

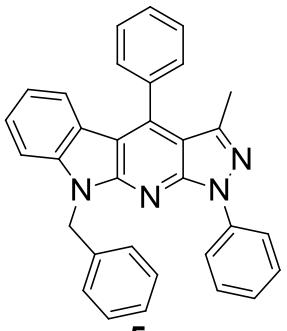
 **5n**	**3,9-dimethyl-1,4-diphenyl-1,9-dihydropyrazolo[4',3':5,6]pyrido [2,3-b]indole (5n):** Brown solid, (330 mg, yield- 85%); M.P.: 184-186 ^{o}C; R_f = 0.8 (hexane/EtOAc, 5:1); IR (KBr): 3029, 2928, 2854, 1586, 1498, 1431, 1382, 1290, 1250, 1208, 1150, 1029, 1017, 919, 859, 797, 746, 715, 667, 610, 558, 504 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (d, J = 8.2 Hz, 2H), 7.60- 7.59 (m, 3H), 7.56-7.53 (m, 4H), 7.42-7.39 (m, 1H), 7.35-7.34 (m, 1H), 7.28-7.25 (m, 1H), 7.05 (d, J = 7.8 Hz, 1H), 7.00-6.97 (m, 1H), 3.95 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 149.7, 143.8, 141.4, 140.1, 139.9, 136.0, 128.9, 128.7, 128.6, 126.1, 124.8, 121.7, 121.0, 120.4, 119.8, 111.5, 111.3, 108.6, 27.8, 14.8; HRMS (ESI) exact mass calculated for $C_{26}H_{21}N_4$ $[M+H]^+$: 389.1761; Found: 389.1765.

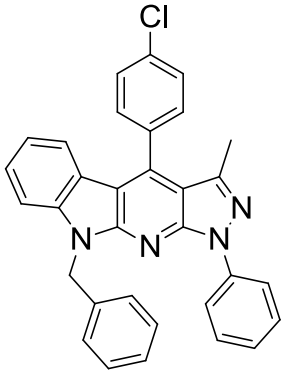
 **5o**	**4-(4-chlorophenyl)-3,9-dimethyl-1-phenyl-1,9-dihydropyrazolo [4',3':5,6]pyrido[2,3-b]indole (5o)**: White solid, (359 mg, yield- 85%); M.P.: 210-212 ^{o}C; R_f = 0.7 (hexane/EtOAc, 5:1); IR (KBr): 3047, 2927, 2793, 2658, 1590, 1506, 1431, 1382, 1294, 1255, 1205, 1150, 1088, 1015, 905, 836, 827, 751, 739, 693, 614, 562, 498 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46-8.44 (m, 2H), 7.56-7.52 (m, 2H), 7.47-7.45 (m, 2H), 7.44-7.41 (m, 1H), 7.36-7.34 (m, 1H). 7.29-7.26 (m, 1H), 7.08-7.06 (m, 1H), 7.04-7.01 (m, 1H), 3.92 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 149.6, 143.5, 141.4, 140.0, 138.3, 134.8, 134.4, 130.2, 129.0, 128.9, 126.3, 124.9, 121.6, 120.7, 120.4, 119.9, 111.4, 111.1, 108.7, 27.8, 15.0; HRMS (ESI) exact mass calculated for $C_{26}H_{20}ClN_4$ $[M+H]^+$: 423.1371; Found: 423.1376.

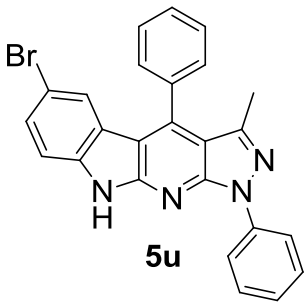
 **5p**	**9-ethyl-3-methyl-1,4-diphenyl-1,9-dihydropyrazolo[4',3':5,6] pyrido[2,3-b]indole (5p):** White solid, (309 mg, yield- 77%); M.P.: 147-149 ^{o}C; R_f = 0.8 (hexane/EtOAc, 5:1); IR (KBr): 3046, 2972, 2929, 2854, 2316, 2246, 1569, 1510, 1449, 1385, 1354, 1239, 1149, 1126, 1058, 1016, 926, 858, 750, 721, 665, 611, 556, 498 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50-8.48 (m, 2H), 7.60-7.58 (m, 3H), 7.56-7.52 (m, 4H), 7.39-7.38 (m, 2H), 7.28-7.25 (m, 1H), 7.06-7.04 (m, 1H), 6.98-6.95 (m, 1H), 4.57-4.53 (q, J =7.2 Hz, J = 7.3 Hz, 2H), 2.13 (s, 3H), 1.51 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.2, 149.7, 143.8, 140.3, 140.2, 139.8, 136.1, 128.8, 128.6(2C), 126.0, 124.7, 121.9, 121.2, 120.3, 119.6, 111.5, 111.3, 108.7, 36.4, 14.8, 13.6; HRMS (ESI) exact mass calculated for $C_{27}H_{23}N_4$ $[M+H]^+$: 403.1917; Found: 403.1920.

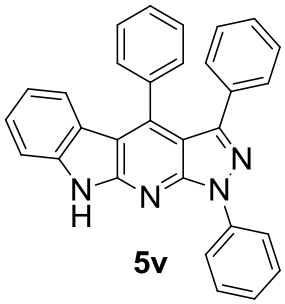
 **5q**	**3-methyl-1,4-diphenyl-9-propyl-1,9-dihydropyrazolo[4',3':5,6] pyrido[2,3-b]indole (5q):** White solid, (304 mg, yield- 73%); M.P.: 157-159 ^{o}C; R_f = 0.9 (hexane/EtOAc, 5:1); IR (KBr): 3058, 2930, 2873, 1570, 1510, 1446, 1397, 1296, 1237, 1150, 1061, 1016, 903, 856, 750, 718, 657, 610, 557, 499 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, J = 7.8 Hz, 2H), 7.60-7.58 (m, 3H), 7.55-7.52 (m, 4H), 7.38-7.37 (m, 2H), 7.55-7.52 (m, 4H), 7.38-7.37 (m, 2H), 7.28-7.25 (m, 1H), 7.06-7.05 (m, 1H), 6.98-6.95 (m, 1H), 4.47 (t, J = 7.0 Hz, 2H), 2.13 (s, 3H), 2.05-1.98 (m,2H), 1.03 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7, 149.6, 143.8, 140.8, 140.2, 139.8, 136.1, 128.8, 128.7, 128.6(2C), 126.0, 124.6, 121.8, 121.1, 120.2, 119.6, 111.4(2C), 108.9, 43.3, 21.9, 14.8, 11.9; HRMS (ESI) exact mass calculated for $C_{28}H_{25}N_4$ $[M+H]^+$: 417.2074; Found: 417.2082.

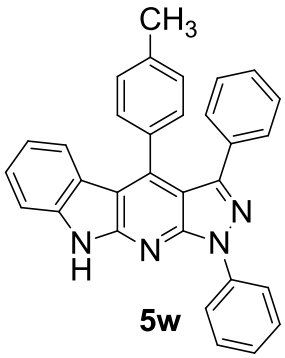
 **5r**	**9-allyl-3-methyl-1,4-diphenyl-1,9-dihydropyrazolo[4',3':5,6] pyrido[2,3-b]indole (5r):** Brown solid, (339 mg, yield- 82%); M.P.: 120-122 ^{o}C; R_f = 0.8 (hexane/EtOAc, 5:1); IR (KBr): 3058, 2924, 2851, 1571, 1509, 1383, 1295, 1224, 1148, 1057, 1017, 903, 856, 799, 750, 692, 610, 541, 498 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47-8.46 (m, 2H), 7.61-7.60 (m, 3H), 7.55-7.52 (m, 4H), 7.37-7.35 (m, 2H), 7.28-7.25 (m, 1H), 7.06-7.05 (m,1H), 6.99-6.96 (m, 1H), 6.12-6.04 (m, 1H), 5.27-5.22 (m, 2H), 5.14 (d, J = 5.3 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 149.6, 143.8, 140.6, 140.1, 140.0, 136.0, 132.5, 128.9, 128.7(2C), 128.6, 126.0, 124.8, 121.8, 121.2, 120.3, 119.9, 117.3, 111.6, 111.5, 109.3, 44.1, 14.8; HRMS (ESI) exact mass calculated for $C_{28}H_{23}N_4$ $[M+H]^+$: 415.1917; Found: 415.1920.

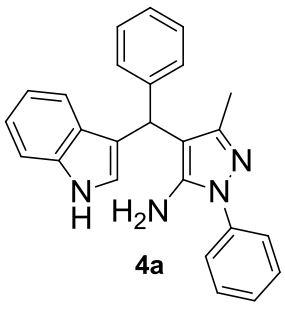
 **5s**	**9-benzyl-3-methyl-1,4-diphenyl-1,9-dihydropyrazolo[4',3':5,6] pyrido[2,3-b]indole (5s):** Yellow solid, (301 mg, yield- 65%); M.P.: 145-147 ^{o}C; R_f = 0.8 (hexane/EtOAc, 5:1); IR (KBr): 3052, 2926, 2853, 1716, 1593, 1498, 1439, 1380, 1326, 1115, 756, 693, 505 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (d, J = 8.6 Hz, 2H), 7.57-7.53 (m, 3H), 7.49-7.48 (m, 2H), 7.45-7.42 (m, 2H), 7.33-7.32 (m, 2H), 7.25-7.21 (m, 4H), 7.19-7.16 (m, 2H), 6.98 (d, J = 7.8 Hz, 1H), 6.92-6.87 (m, 1H), 5.63 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7, 149.6, 143.9, 140.7, 140.1, 137.3, 136.0, 128.9 (2C), 128.8, 128.7 128.6, 127.5 (2C), 126.1, 124.8, 123.6, 121.8, 121.3, 120.4, 120.0, 111.7, 111.5, 109.4, 45.4, 14.8; HRMS (ESI) exact mass calculated for $C_{32}H_{25}N_4$ $[M+H]^+$: 465.2074; Found: 465.2075.

 **5t**	**9-benzyl-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,9-dihydro pyrazolo [4',3':5,6]pyrido[2,3-b]indole (5t):** Brown solid, (364 mg, yield- 73%); M.P.: 180-182 ^{o}C; R_f = 0.8 (hexane/EtOAc, 5:1); IR (KBr): 3059, 3027, 2924, 2854, 1570, 1506, 1443, 1381, 1336, 1294, 1145, 1088, 1017, 902, 834, 748, 697, 621, 574, 504 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (d, J = 7.6 Hz, 2H), 7.62-7.60 (m, 2H), 7.53-7.49 (m, 4H), 7.40- 7.37 (m, 2H), 7.35- 7.33 (m, 2H), 7.32-7.24 (m, 4H), 7.09 42 (d, J = 7.9 Hz, 1H), 7.02-6.99 (m, 1H), 5.69 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.6, 149.5, 143.5, 140.7, 140.0, 138.5, 137.2, 134.9, 134.5, 130.2, 129.0, 128.9, 128.7, 127.6, 127.5, 126.4, 124.9, 121.7, 121.0, 120.4, 120.2, 111.5(2C), 109.5, 45.4, 15.0; HRMS (ESI) exact mass calculated for $C_{32}H_{24}ClN_4$ $[M+H]^+$: 499.1684; Found: 499.1691.

 **5u**	**6-bromo-3-methyl-1,4-diphenyl-1,9-dihydropyrazolo[4',3':5,6] pyrido[2,3-b]indole (5u):** Black solid, (271 mg, yield- 60%); M.P.: 177-179 ^{o}C; R_f = 0.8 (hexane/EtOAc, 4:1); IR (KBr): 3338, 2924, 2853, 1596, 1508, 1463, 1388, 1336, 1248, 1146, 1076, 1012, 887, 807, 739, 694, 655 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.01 (bs, 1H), 8.34-8.32 (m, 2H), 7.67-7.65 (m, 3H), 7.57-7.54 (m, 2H), 7.52-7.48 (m, 2H), 7.30-7.28 (m, 1H), 7.27-7.23 (m, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 6.72 (d, *J* = 8.7 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.1, 149.5, 144.2, 141.2, 139.5, 137.9, 135.2, 129.2, 128.9, 128.8, 128.4, 125.9, 124.3, 123.2, 121.4, 112.8, 112.0 (2C), 111.2, 14.8; HRMS (ESI) exact mass calculated for $C_{25}H_{18}BrN_4$ $[M+H]^+$: 453.0709; Found: 453.0717.

 **5v**	**1,3,4-triphenyl-1,9-dihydropyrazolo[4',3':5,6]pyrido[2,3-b] indole (5v):**[3] Brown solid, (340 mg, yield- 78%); M.P.: 240-244 ^{o}C; R_f = 0.7 (hexane/EtOAc, 4:1); IR (KBr):, 3447, 2913, 2365, 1596, 1481, 1352, 1240, 1129, 975, 880, 775, 720, 697, 508 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.86 (bs, 1H), 8.44-8.42 (m, 2H), 7.58-7.55 (m, 2H), 7.38-7.32 (m, 6H), 7.30-7.29 (m, 2H), 7.24-7.22 (m, 1H), 7.19-7.15 (m, 3H), 7.08-7.05 (m, 2H), 7.00-6.96 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 149.7, 147.2, 140.6, 139.7, 139.4, 135.4, 133.1, 129.2, 129.1, 129.0, 128.5, 128.3, 127.4, 126.5, 125.8, 122.3, 121.7(2C), 120.2, 112.3, 112.0, 110.6; HRMS (ESI) exact mass calculated for $C_{30}H_{21}N_4$ $[M+H]^+$: 437.1761; Found: 437.1763.

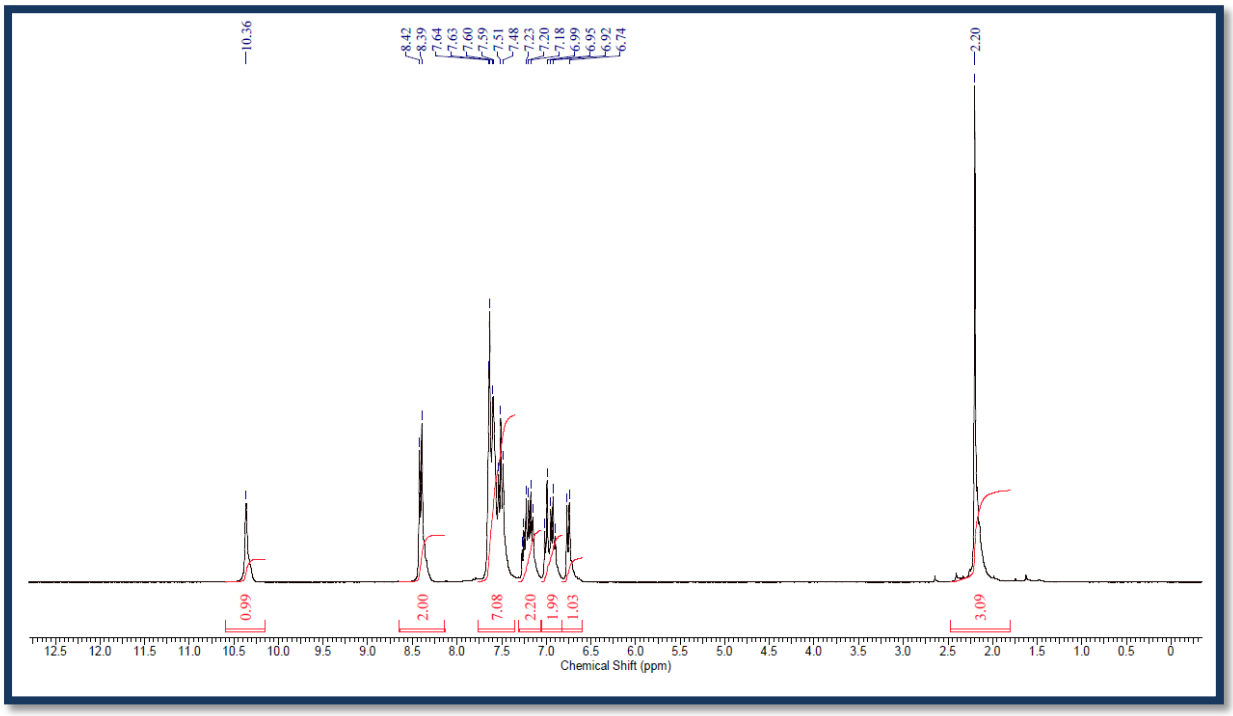
 **5w**	**1,3-diphenyl-4-(p-tolyl)-1,9-dihydropyrazolo[4',3':5,6]pyrido [2,3-b]indole (5w):**[3] Green solid, (337 mg, yield- 75%); M.P.: 255-257 ^{o}C; R_f = 0.7 (hexane/EtOAc, 4:1); IR (KBr): 3363, 2918, 2360, 1593, 1490, 1382, 1247, 1143, 989, 885, 796, 736, 692, 511 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.51 (bs, 1H), 8.38-8.36 (m, 2H), 7.47-7.43 (m, 2H), 7.23-7.22 (m, 1H), 7.21-7.16 (m, 2H), 7.13-7.08 (m, 5H), 7.00-6.95 (m, 5H), 6.89-6.86 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 149.6, 147.4, 141.1, 139.7, 139.5, 138.3, 133.2, 132.6, 129.3, 129.1, 129.0, 128.8, 127.3, 127.2, 126.3, 125.9, 122.2, 121.8, 121.6, 120.0, 112.4, 111.0, 110.6, 21.3; HRMS (ESI) exact mass calculated for $C_{31}H_{23}N_4$ $[M+H]^+$: 451.1917; Found: 451.1927.

 **4a**	**4-((1H-indol-3-yl)(phenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-amine (4a):**[4] White solid, (340 mg, yield- 90%); M.P.: 210-212 ^{o}C; R_f = 0.4 (hexane/EtOAc, 4:1); IR (KBr): 3409, 3345, 2931, 1621, 1458, 1315, 740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (bs, 1H), 7.52-7.49 (m, 2H), 7.42-7.32 (m, 8H), 7.29-7.17 (m, 3H), 7.06-7.01 (m, 1H), 6.66 (s, 1H), 5.53 (s, 1H), 3.26 (bs, 2H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.2, 142.9, 142.6, 138.4, 136.7, 129.3, 128.5, 128.4, 126.8, 126.6, 126.4, 123.8, 123.7, 122.2, 119.6, 119.4, 117.5, 111.2, 102.9, 38.1, 12.4; HRMS (ESI) exact mass calculated for $C_{25}H_{23}N_4$ $[M+H]^+$: 379.1917; Found: 379.1921.

Reference

1. N. Griebenow, L. Bärfacker, H. Meier, D. Schneider , N. Teusch , K. Lustig, R. Kast and P. Kolkhof, *Bioorg. Med. Chem. Lett.* 2010, **20**, 5891.
2. T. D. Paulis, K. Hemstapat, Y. Chen, Y. Zhang, S. Saleh, D. Alagille, R. M. Baldwin, G. D. Tamagnan and P. J. Conn, *J. Med. Chem.* 2006**, 49***,* 3332.
3. R. Ghahremanzadeh, S. Ahadi and A. Bazgir, *Tetrahedron Lett.,* 2009**, 50***,* 7379.
4. M. L. Deb, C. Das, B. Deka, P. J. Saikia and P. K. Baruah, *Synlett,* 2016**, 27**, 2788.

^{1}H-NMR of 5a



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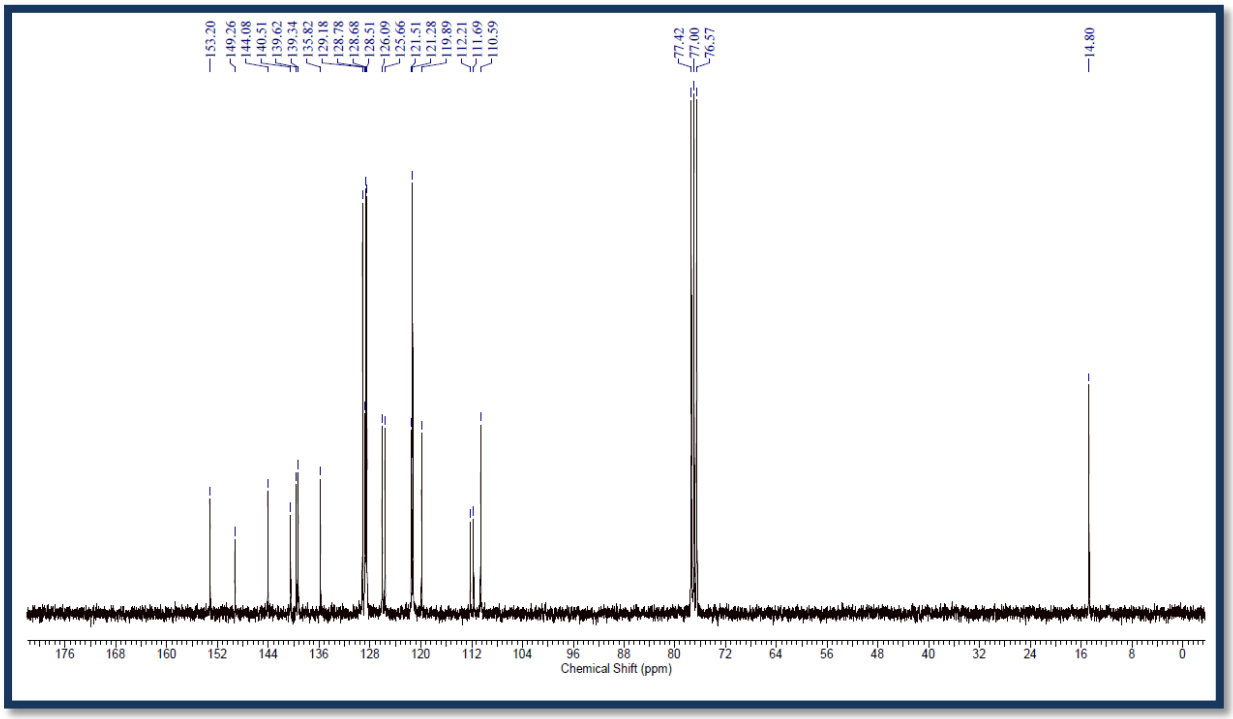
^{13}C-NMR of 5a



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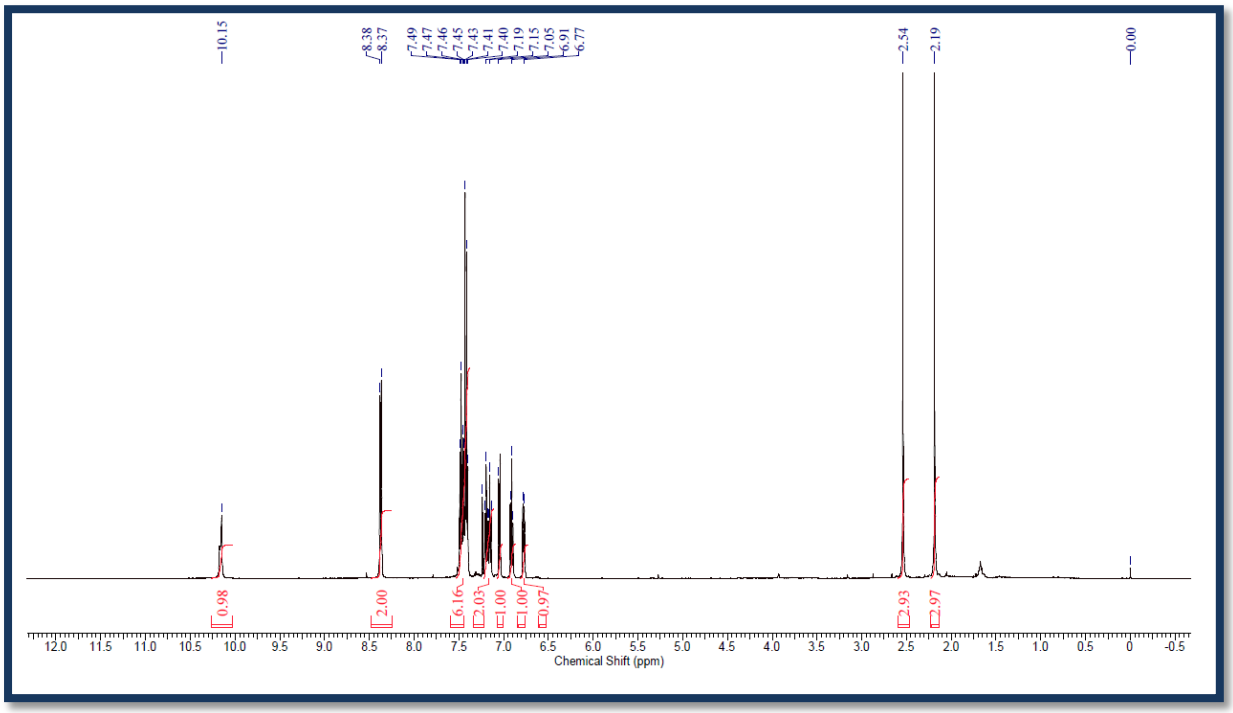

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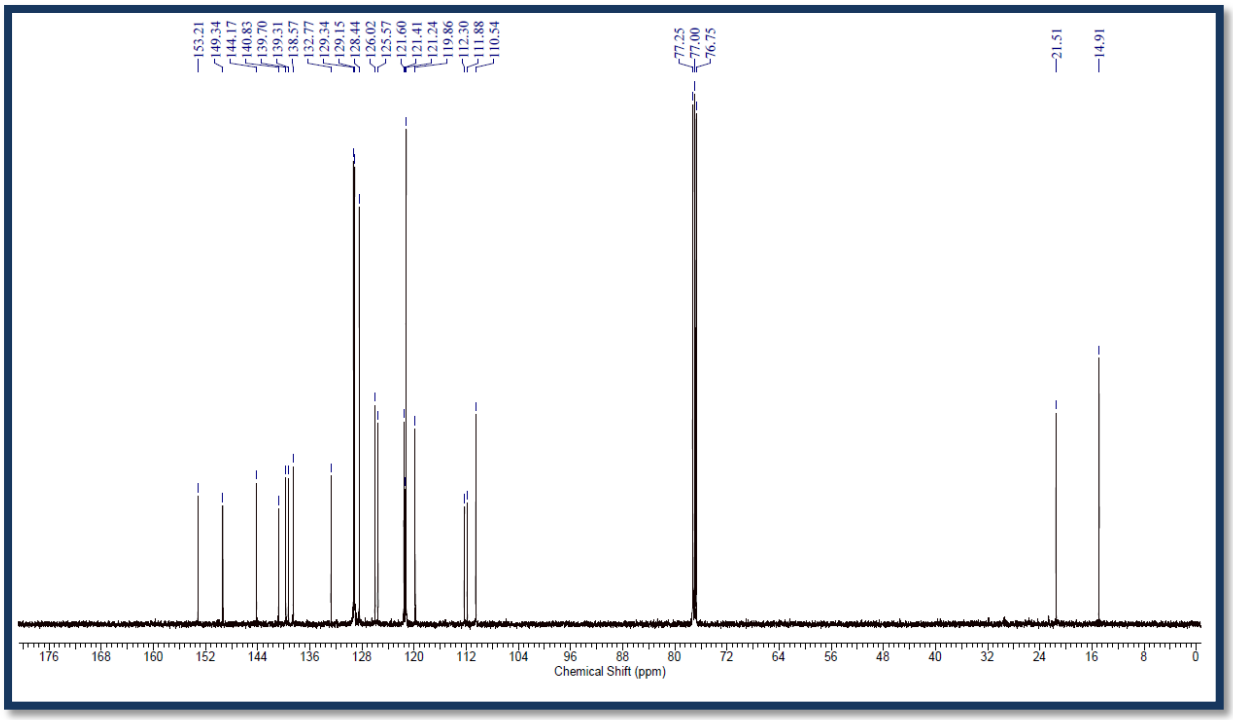

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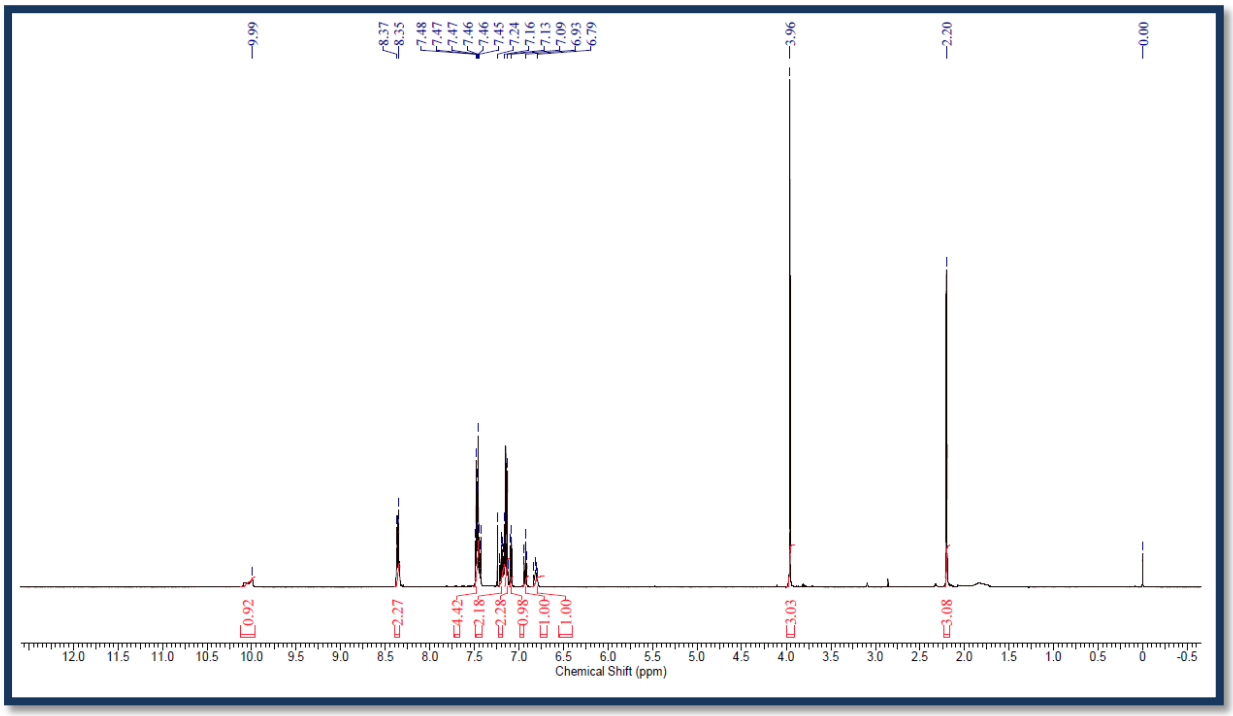

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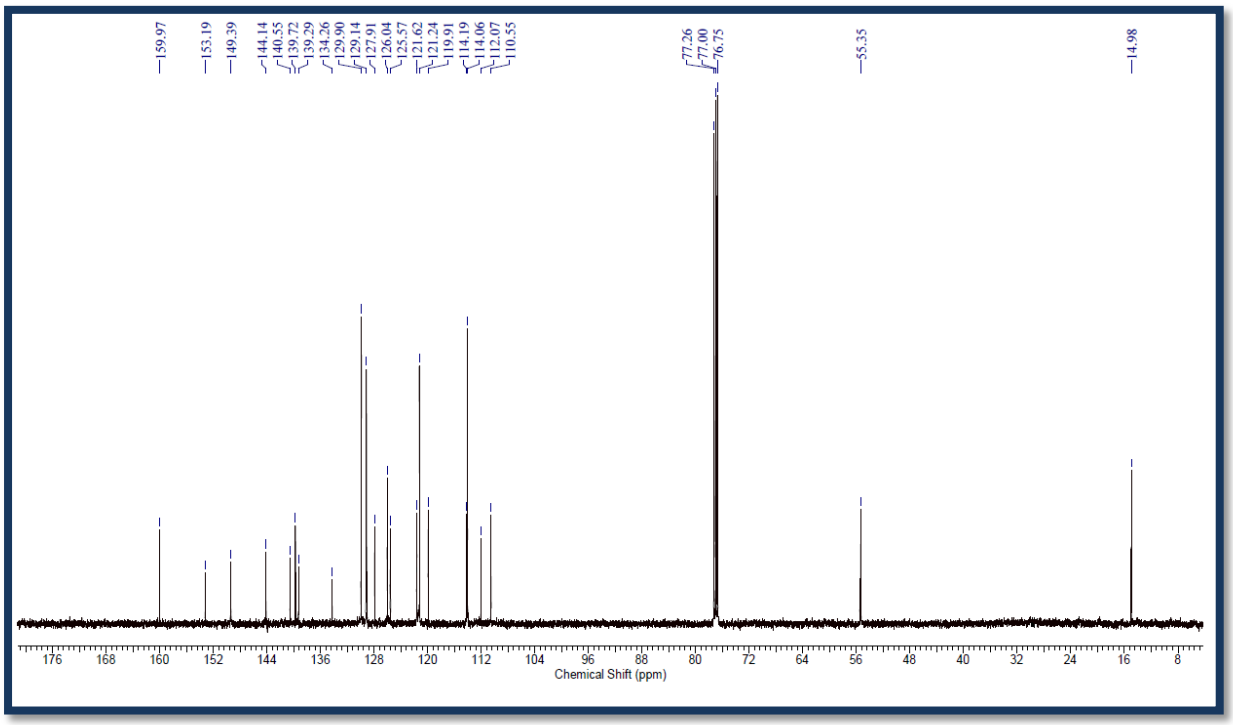

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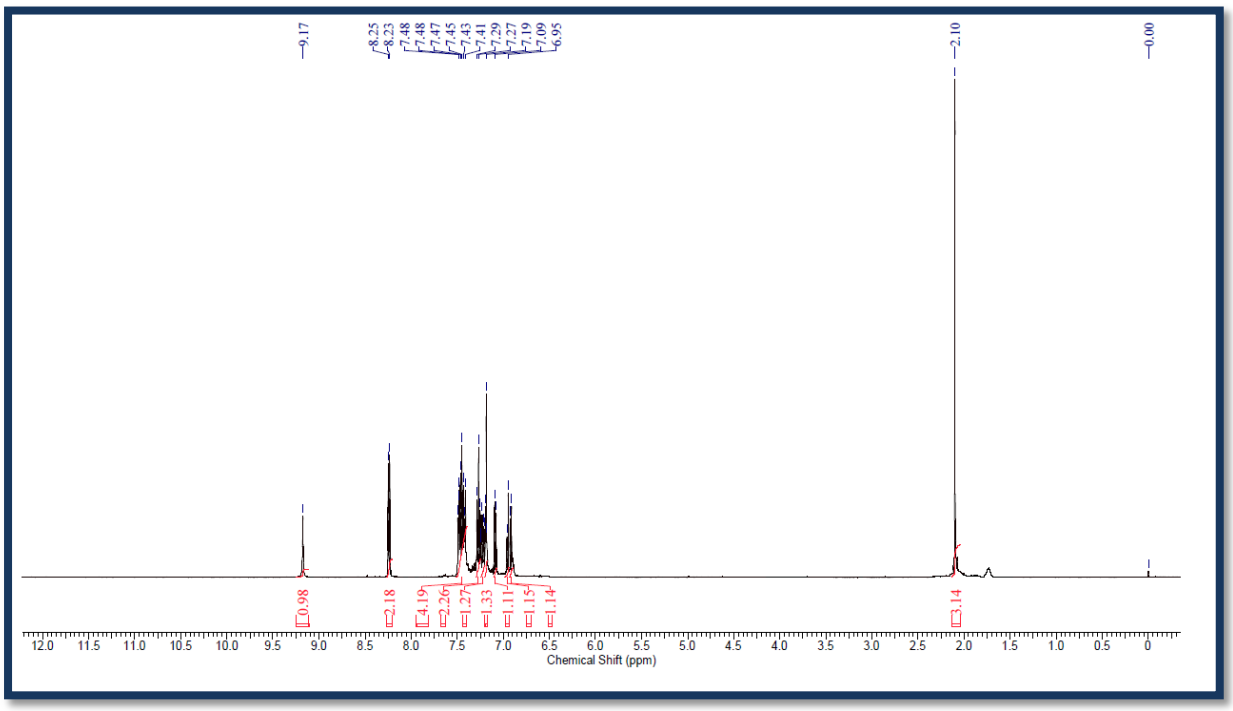

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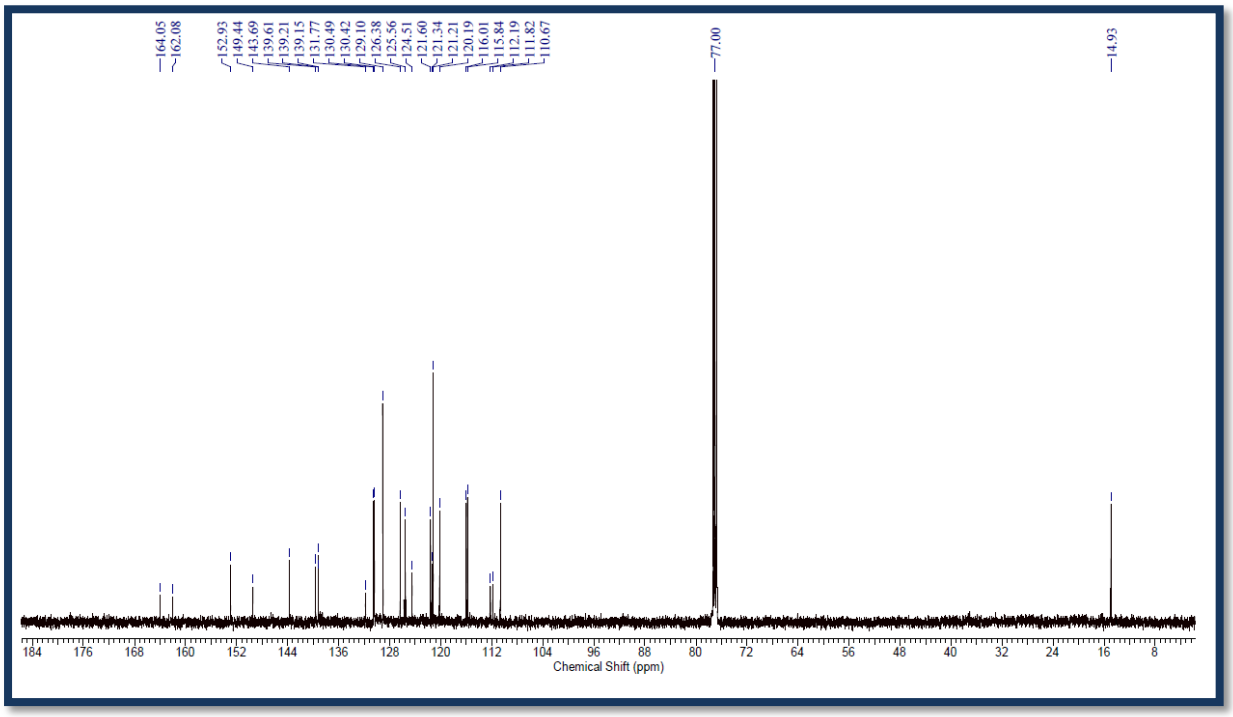

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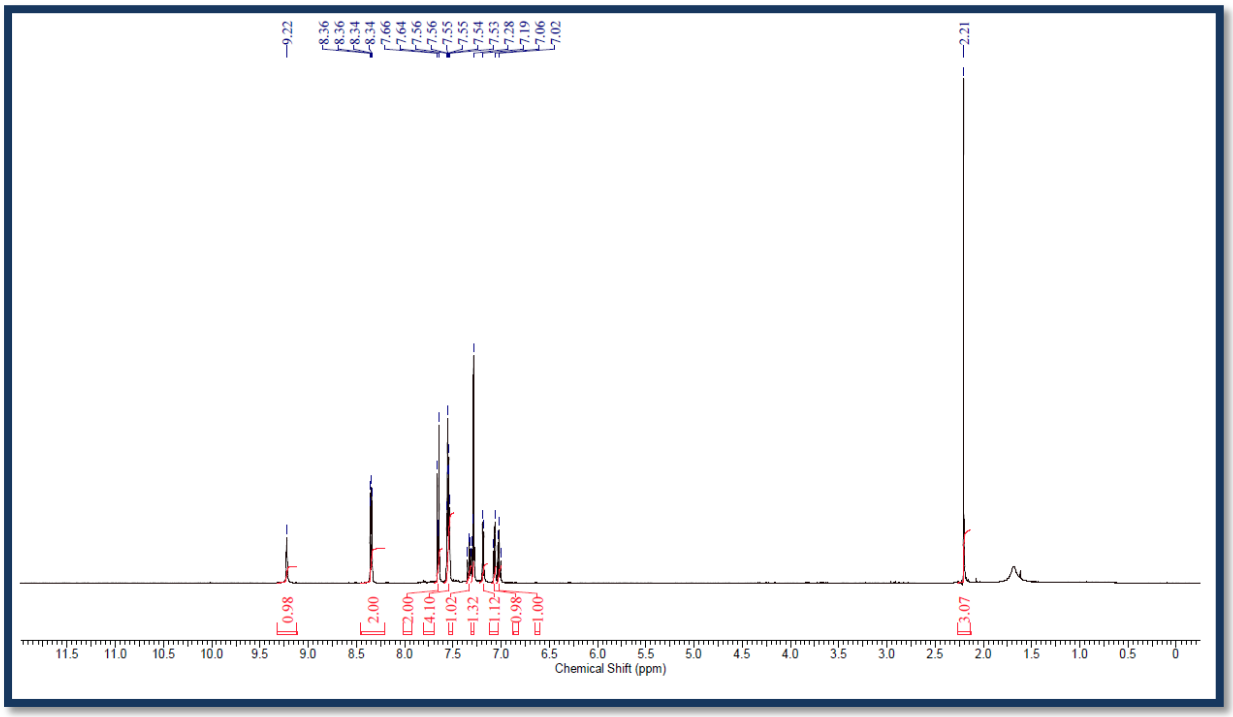

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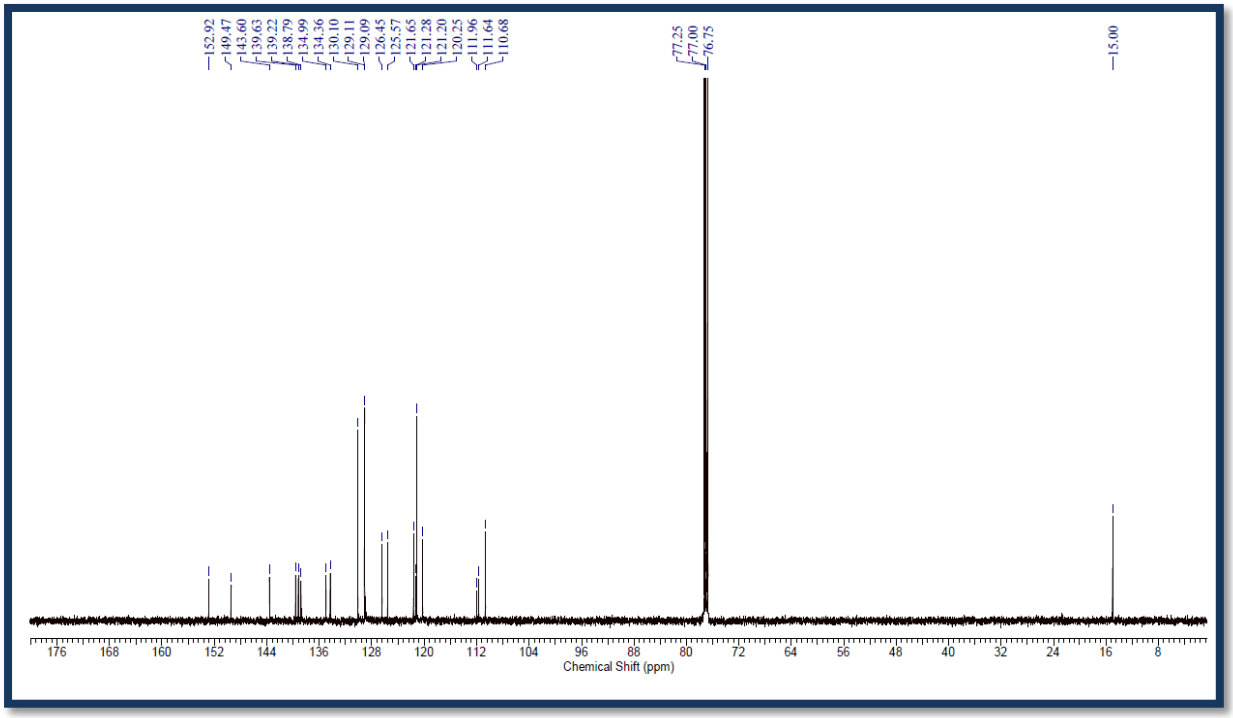

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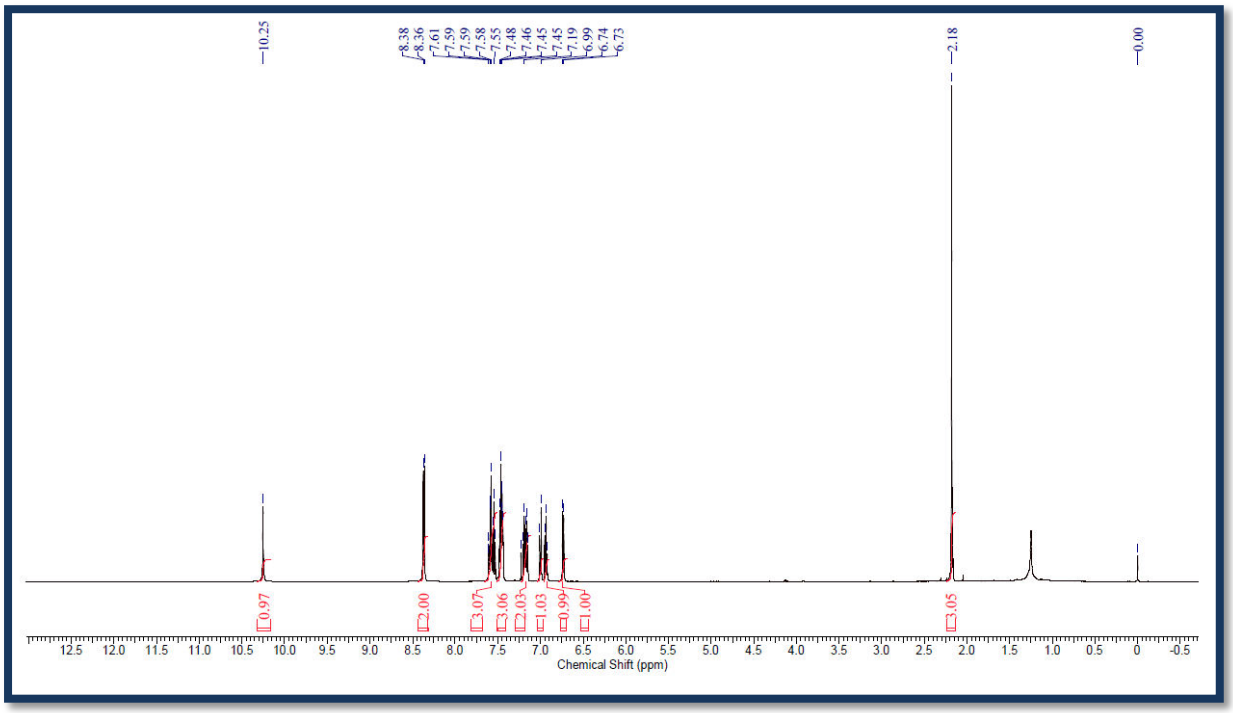

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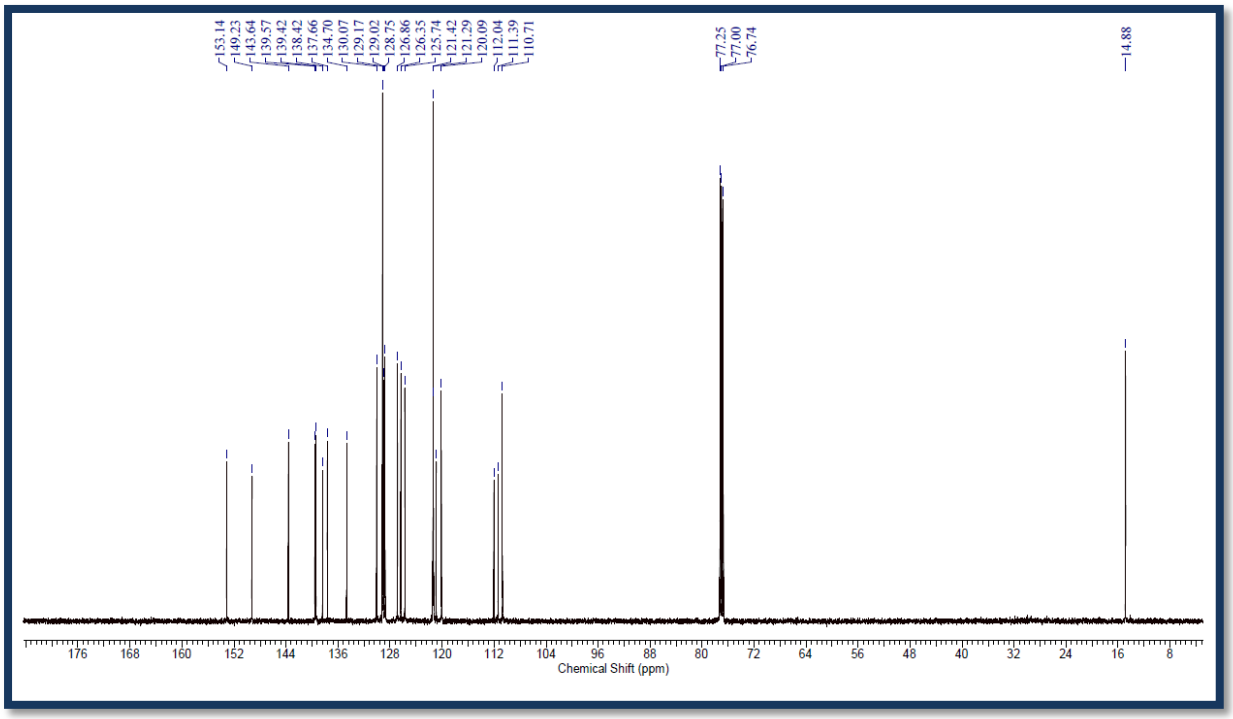

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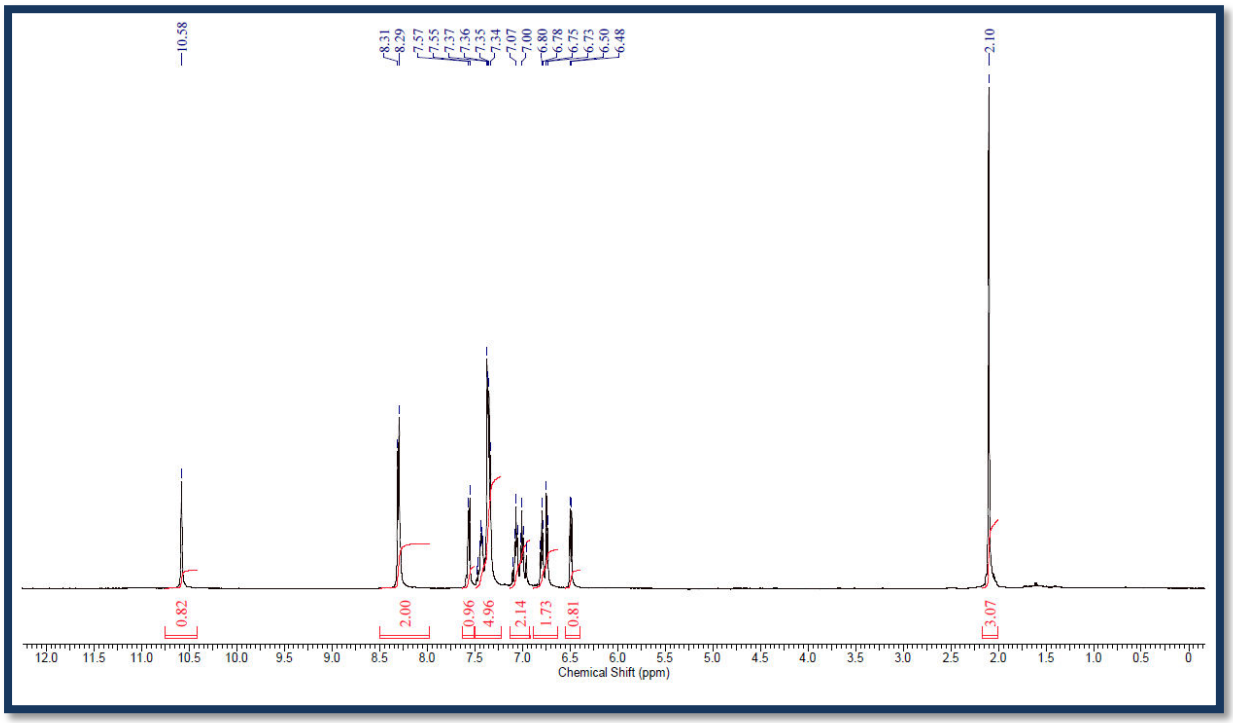

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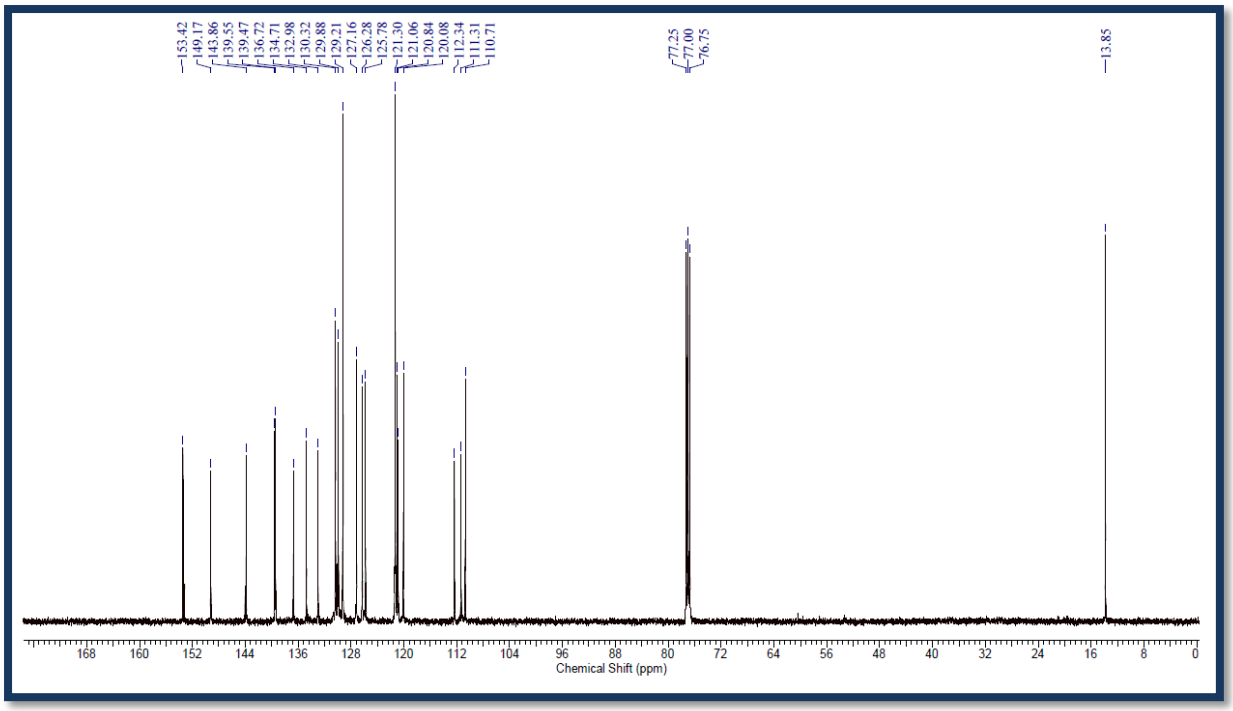

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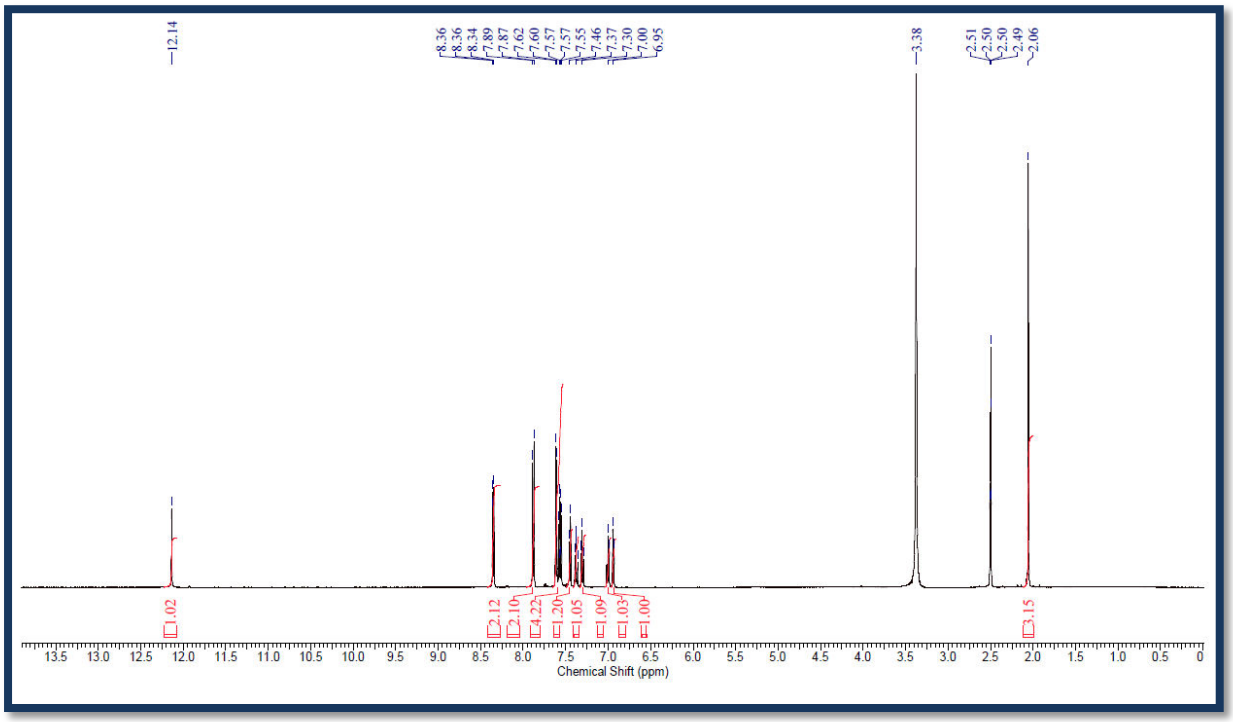

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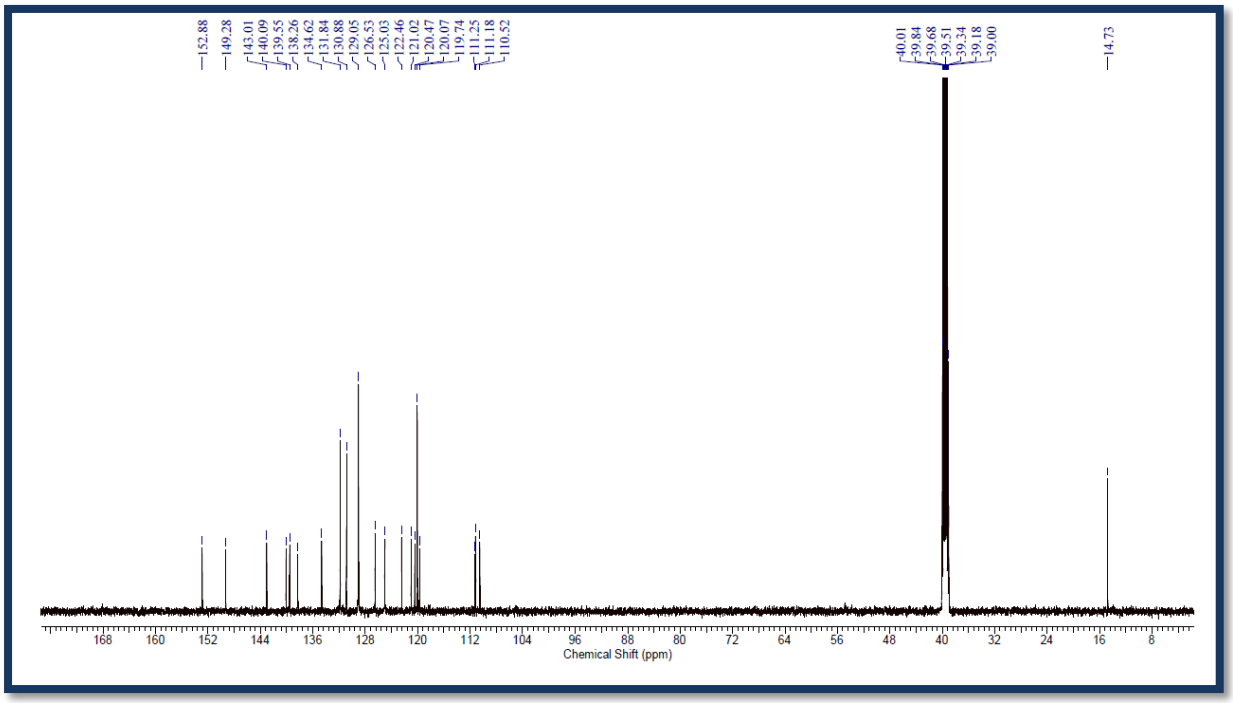

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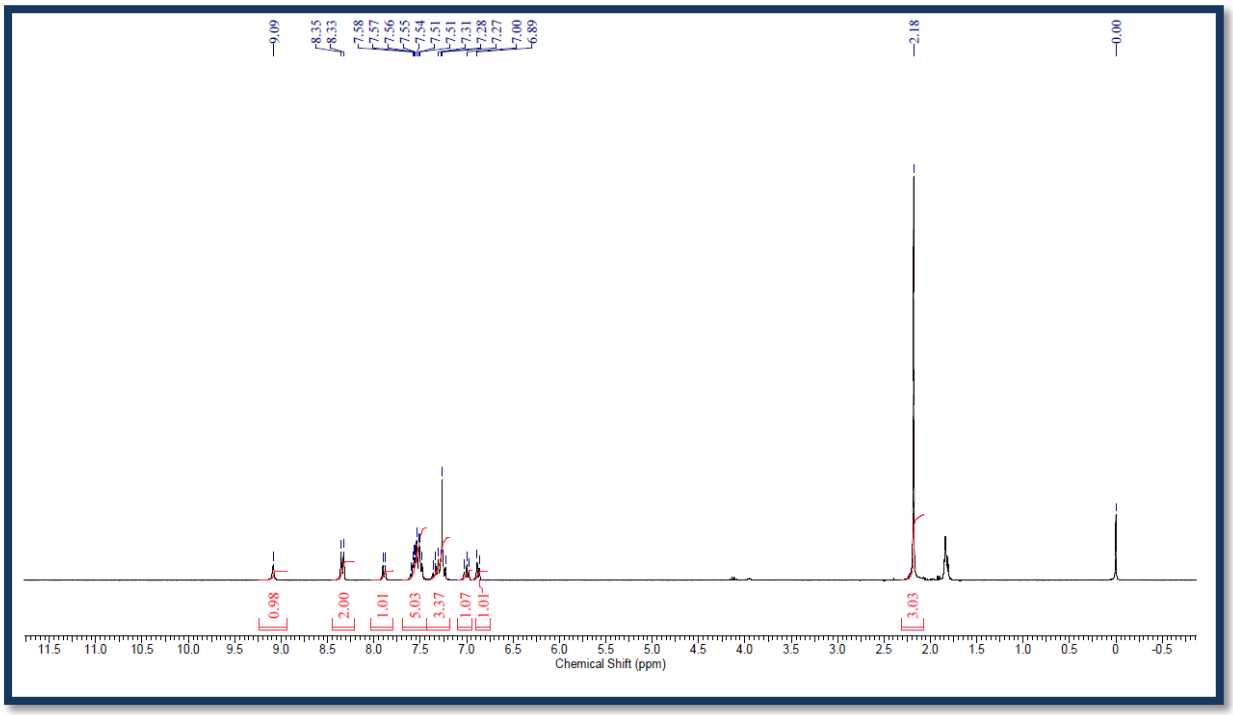

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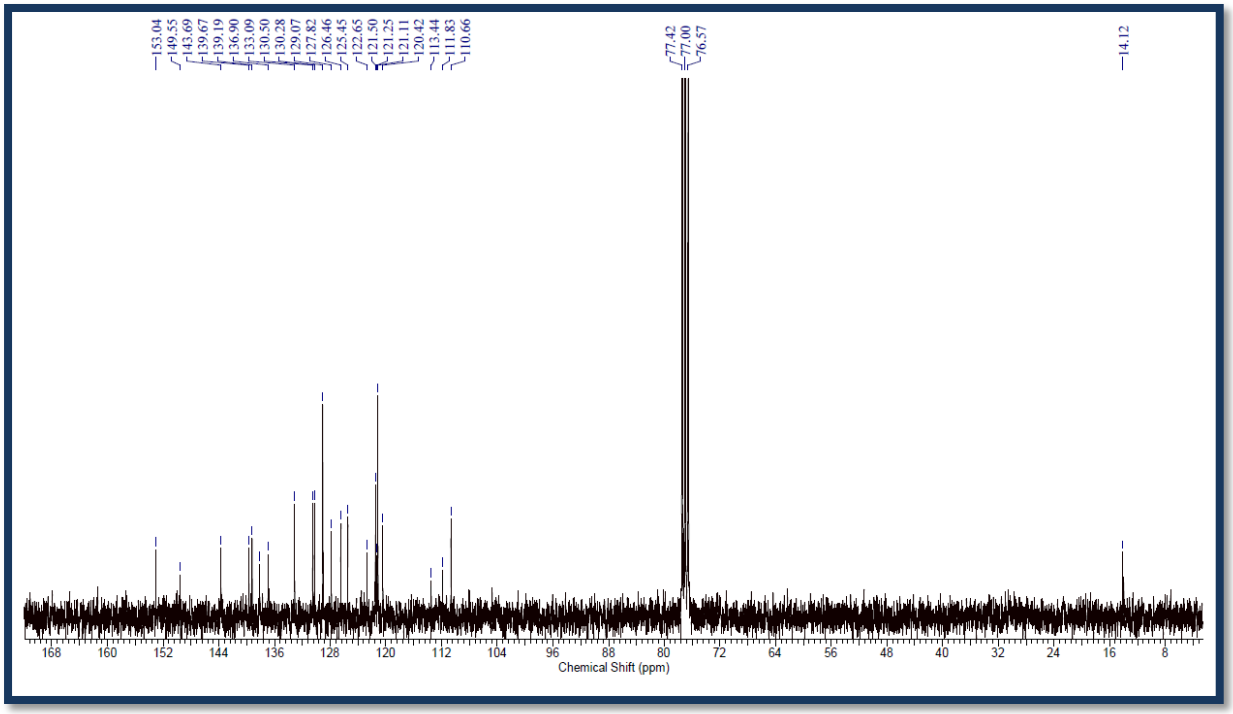

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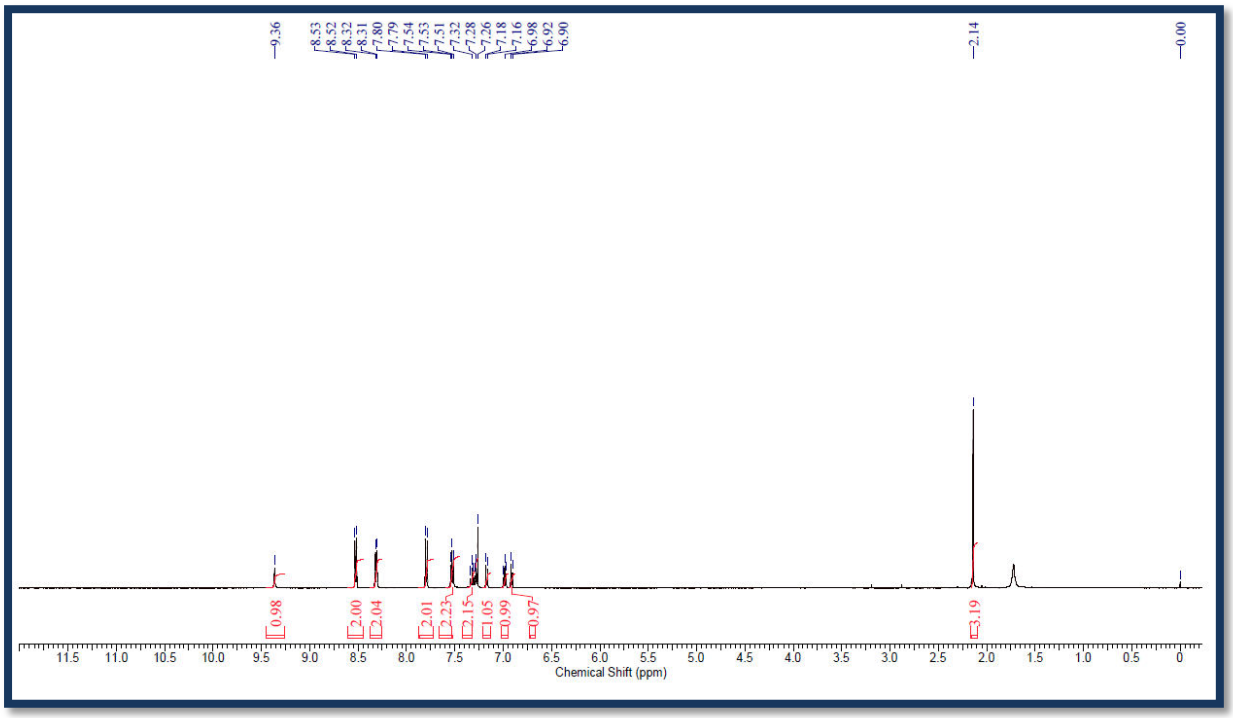

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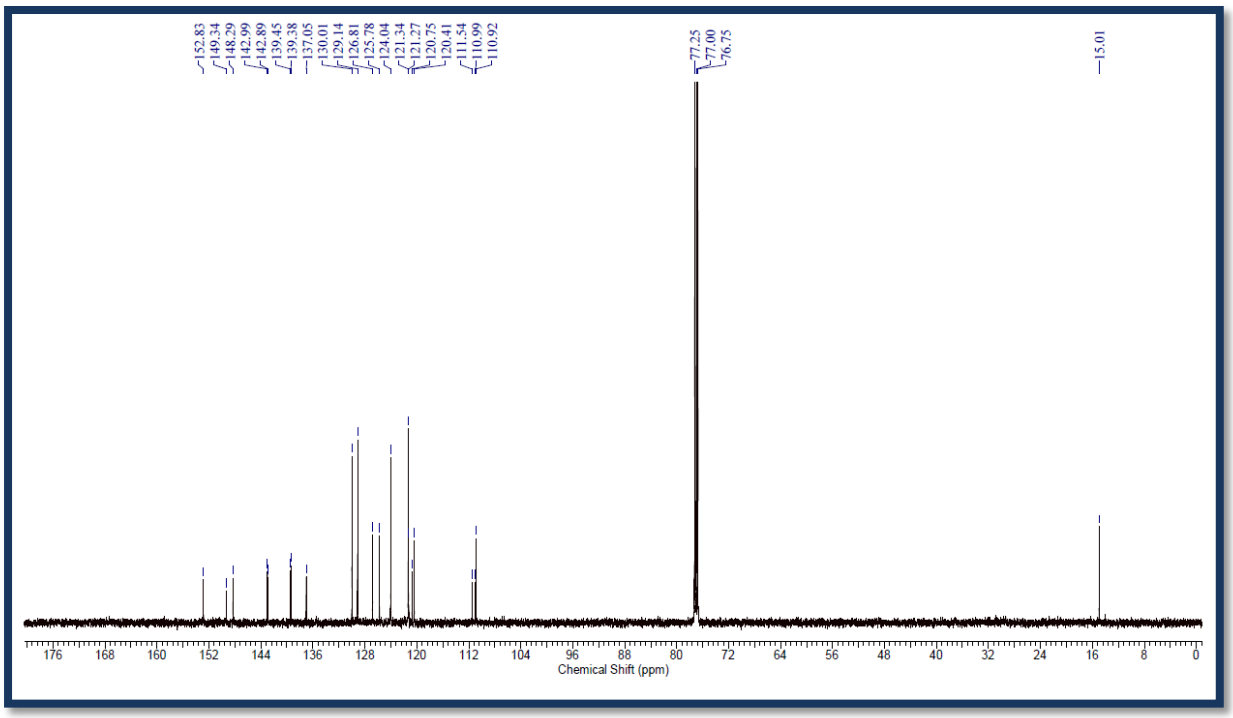

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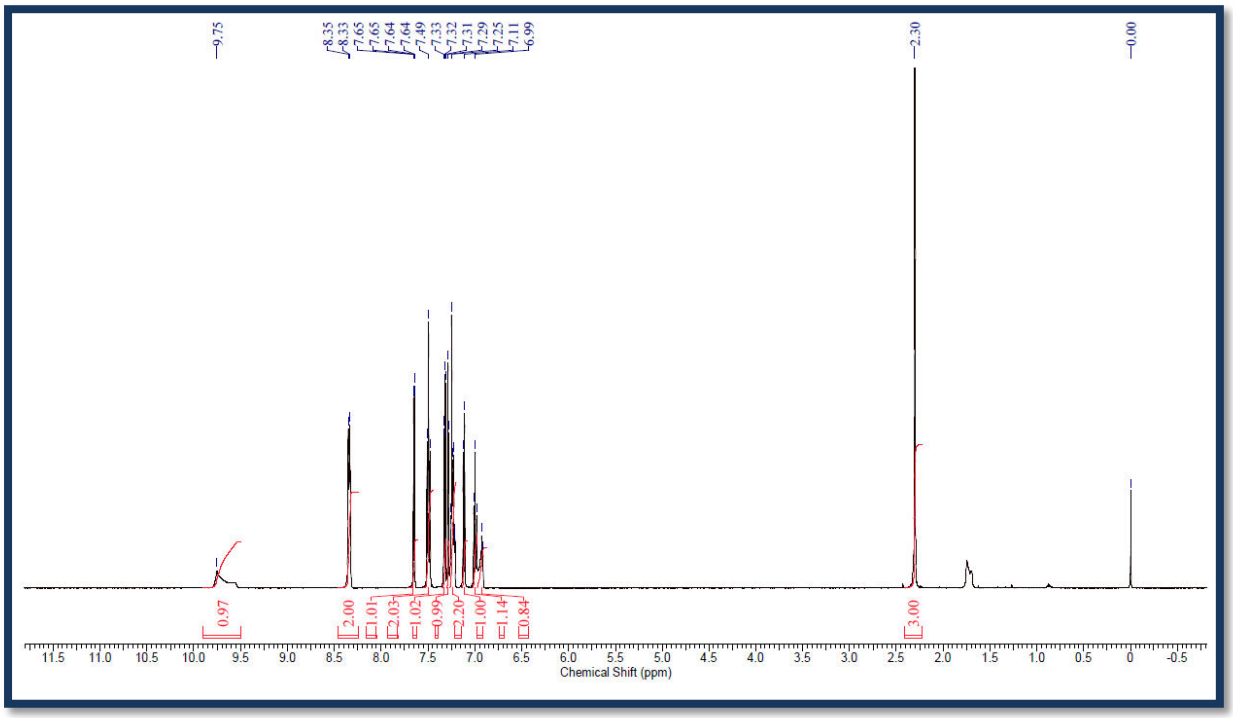

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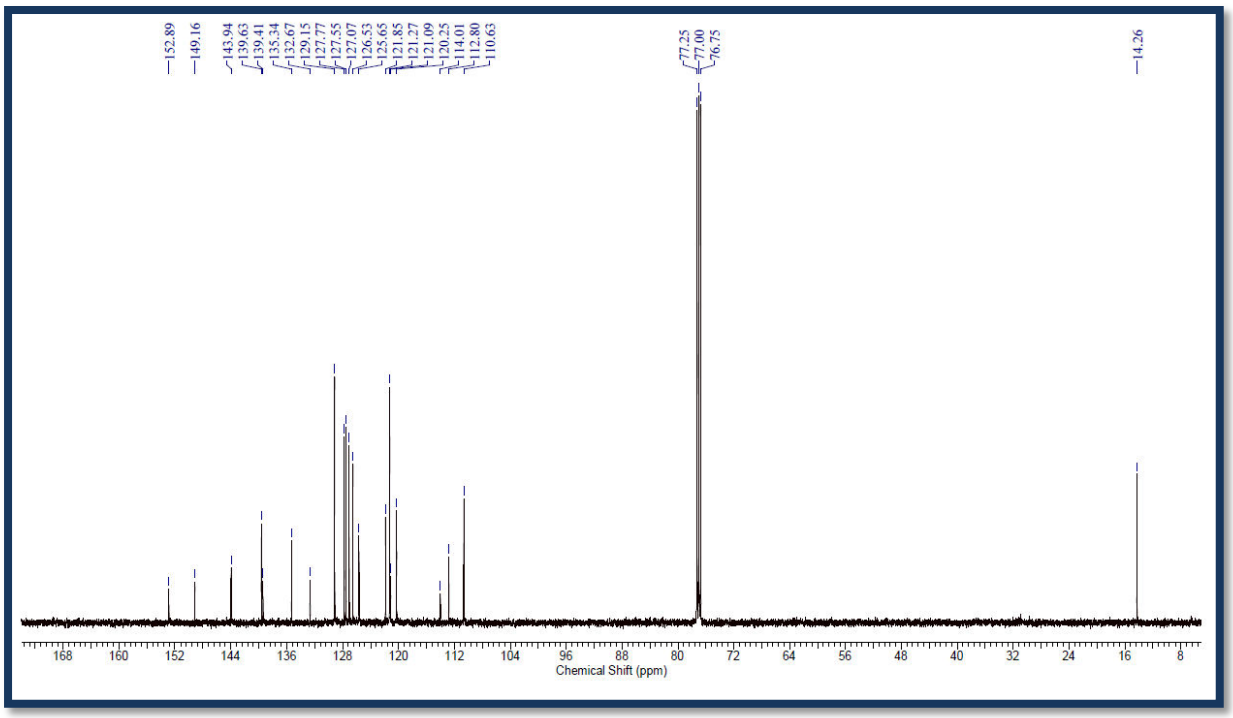

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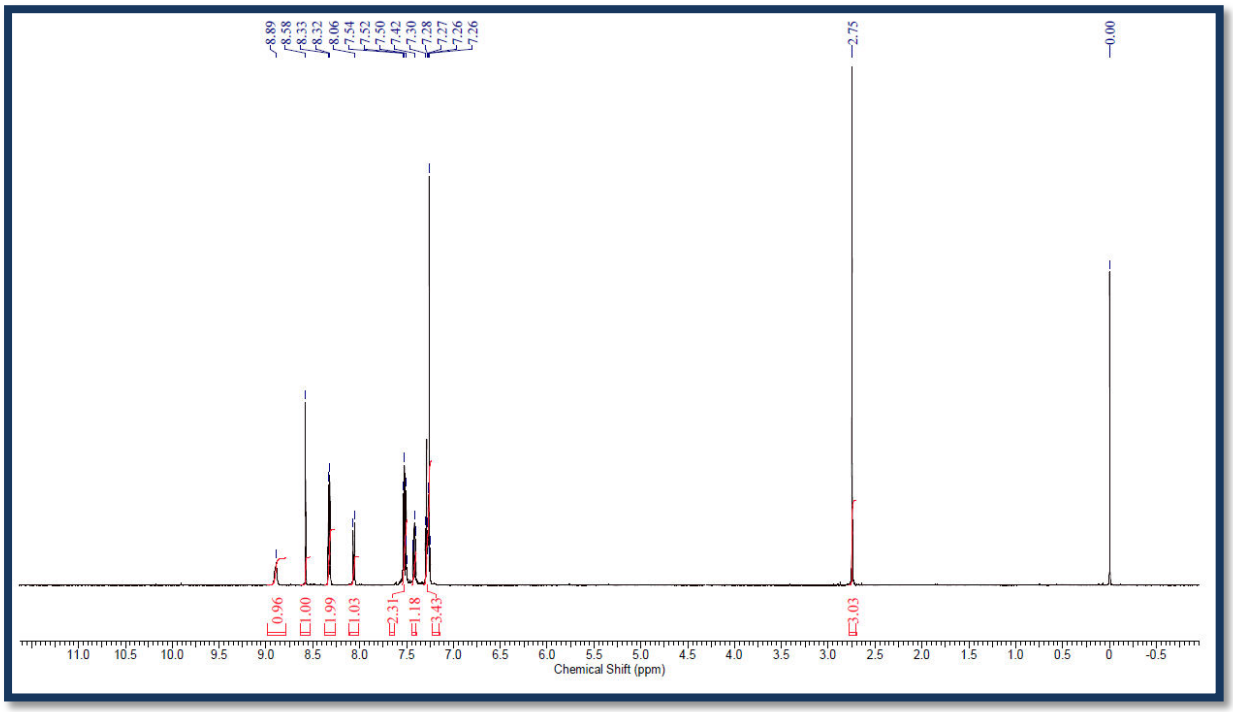

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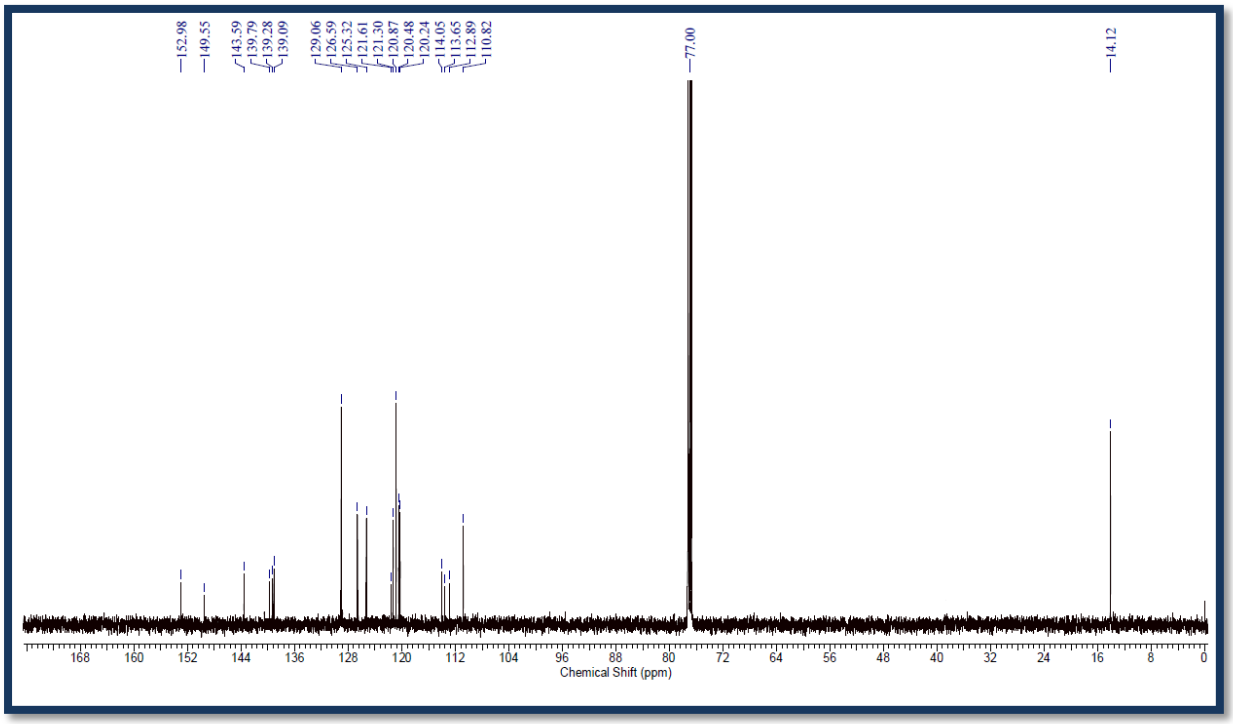

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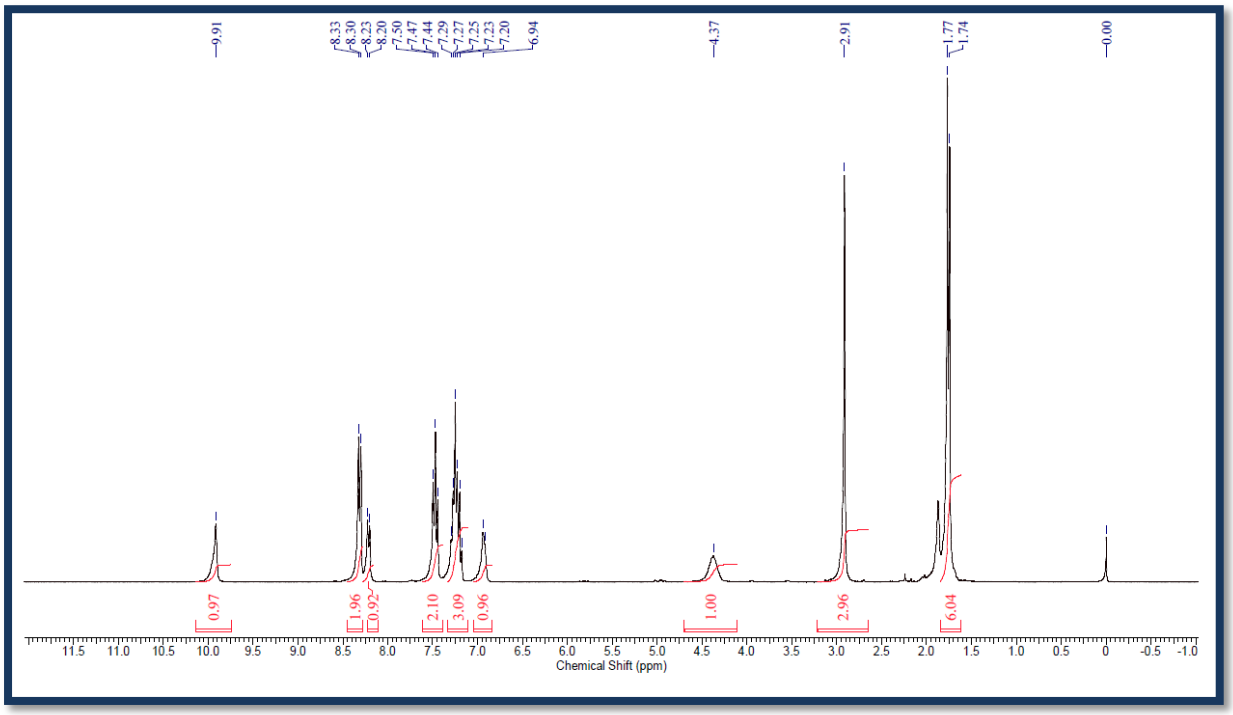

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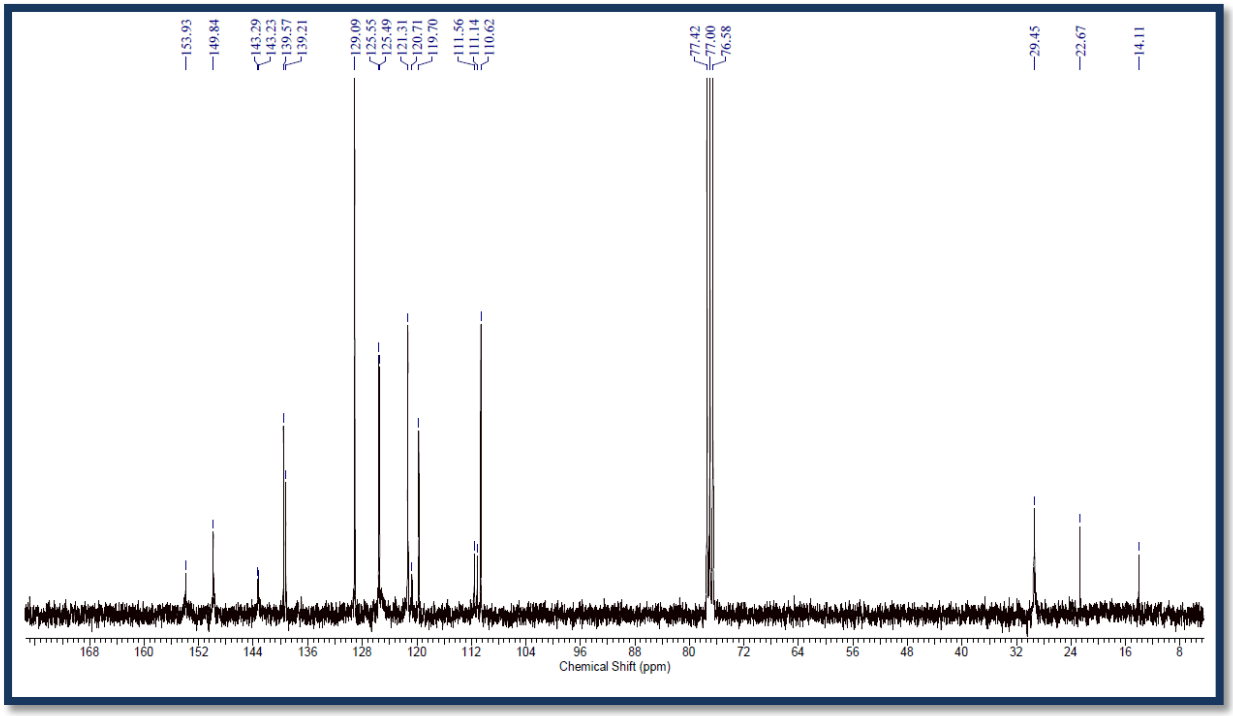

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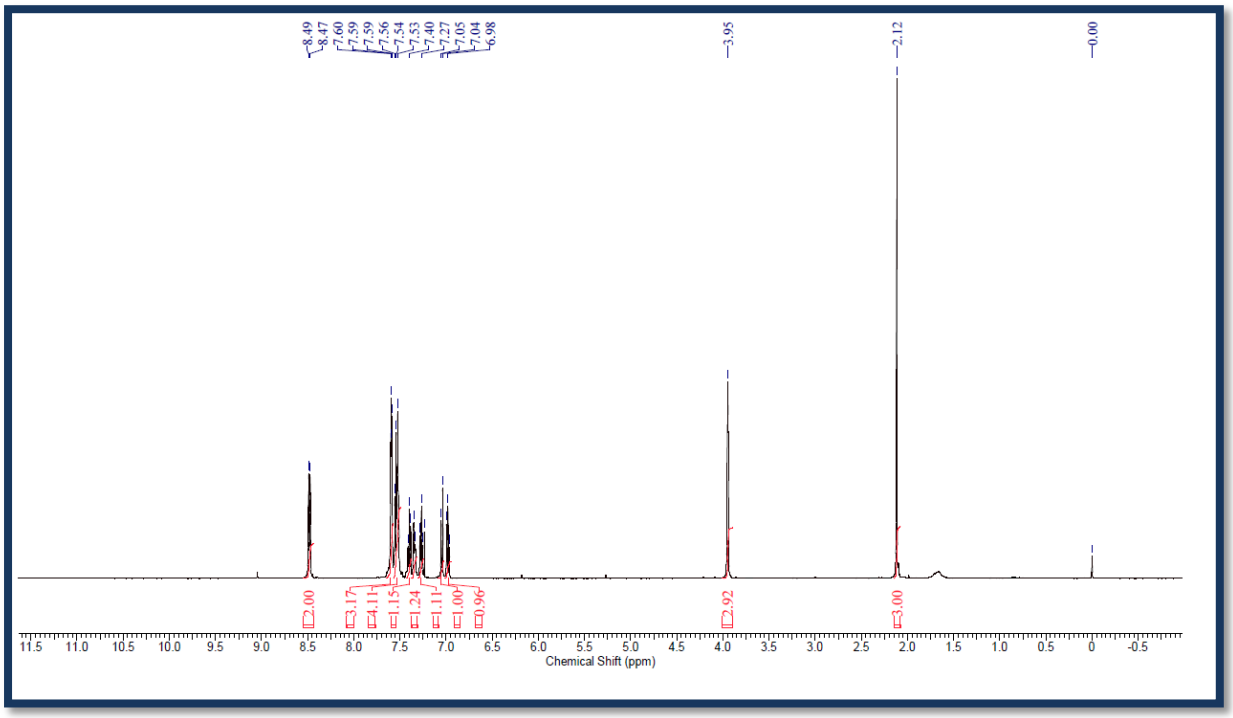

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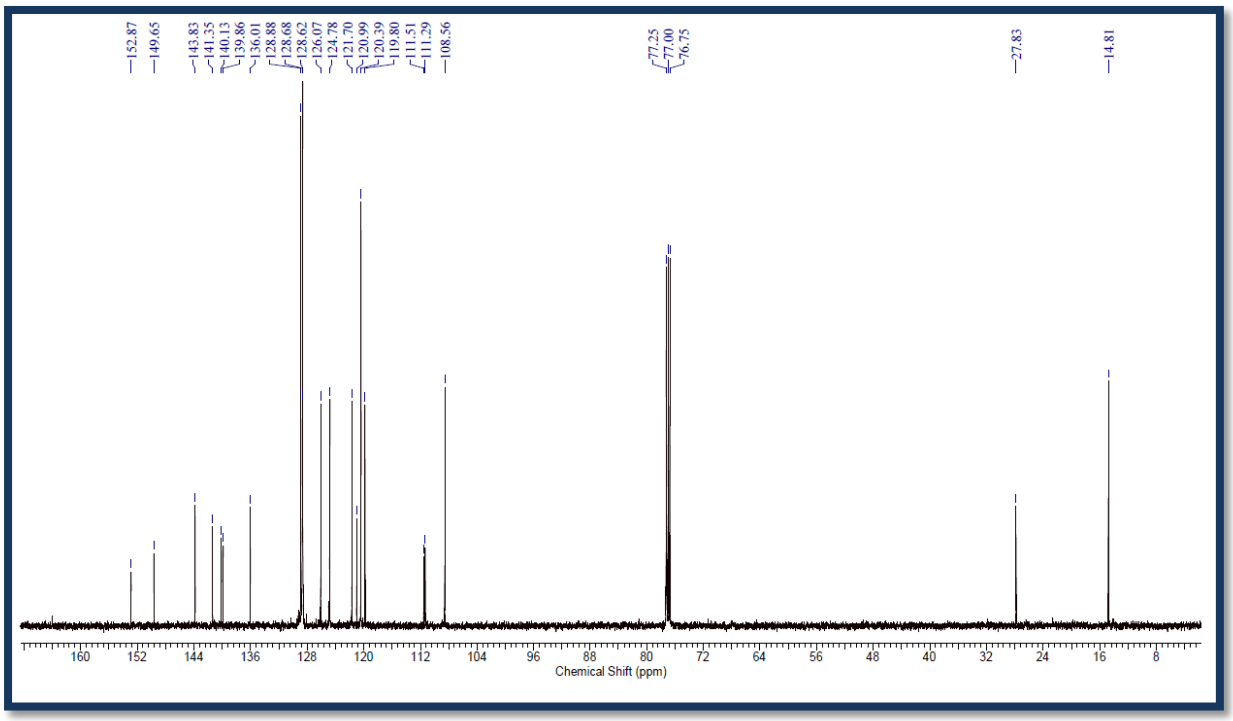

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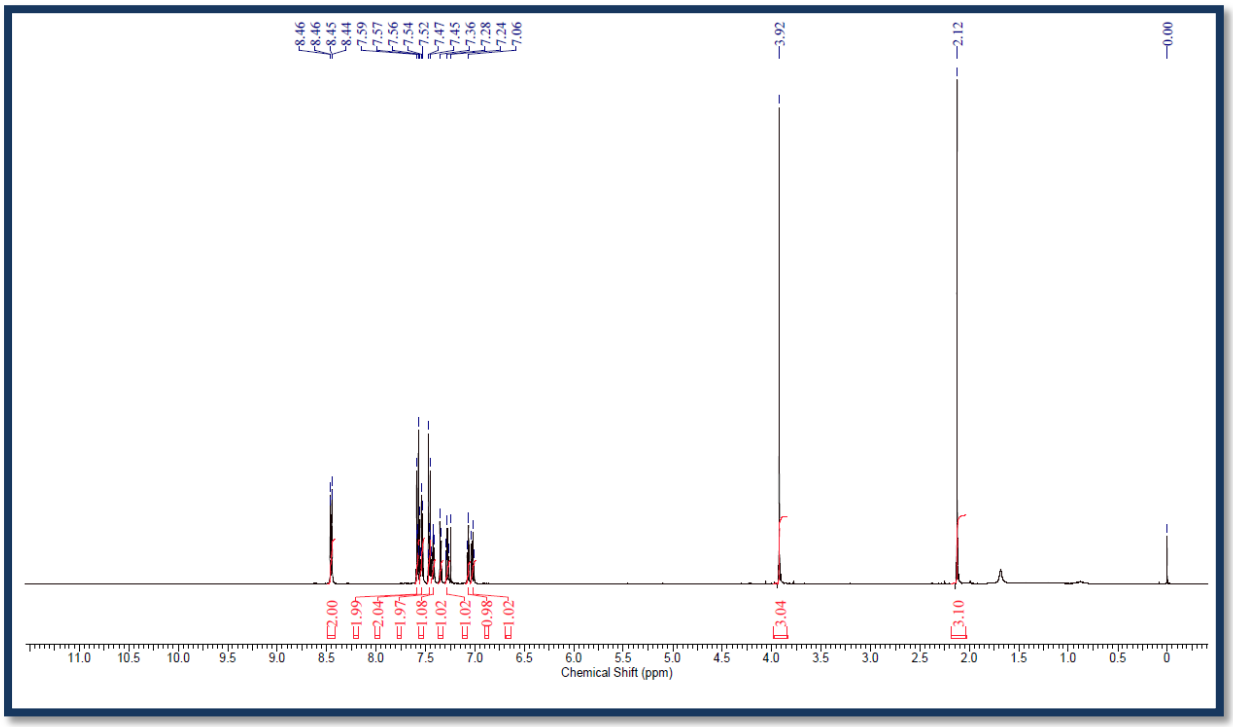

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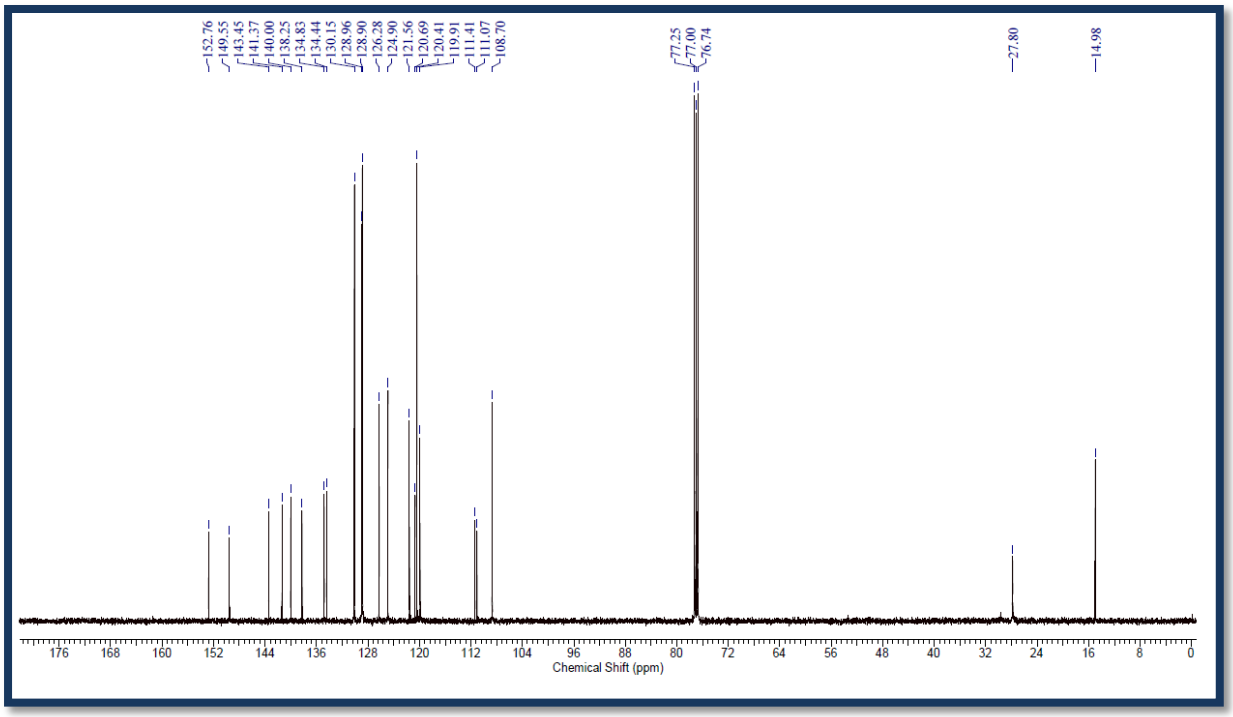

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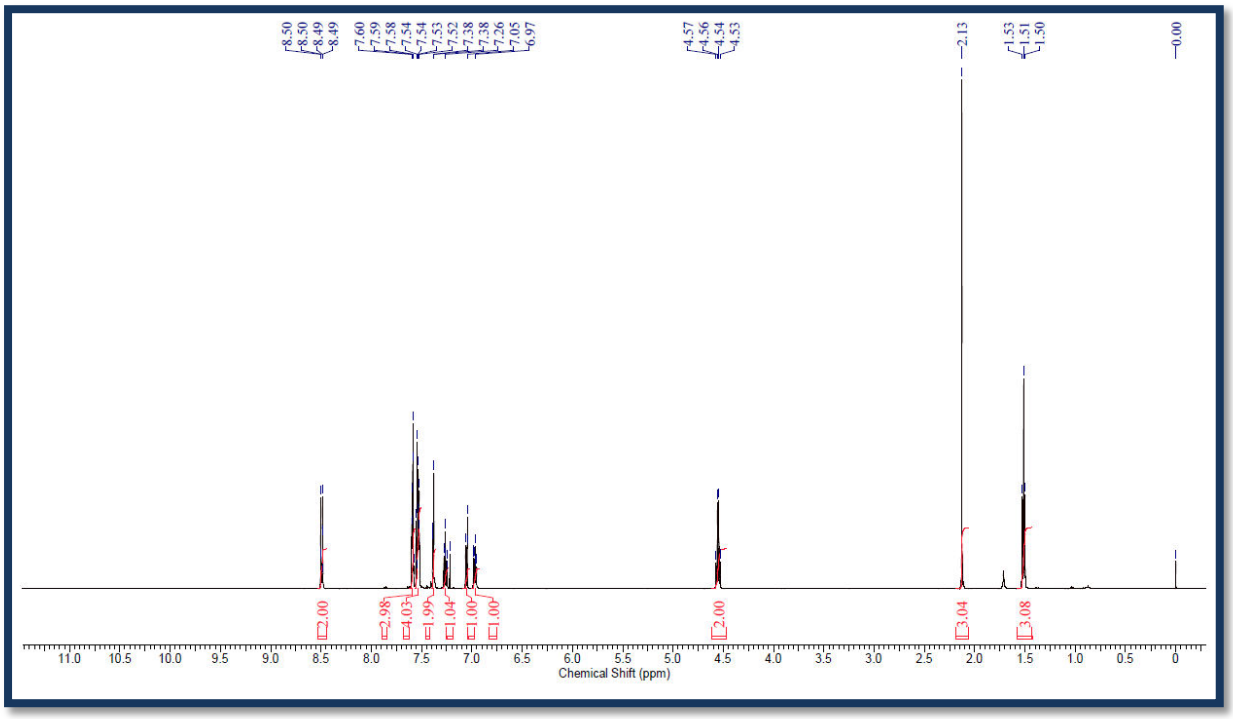

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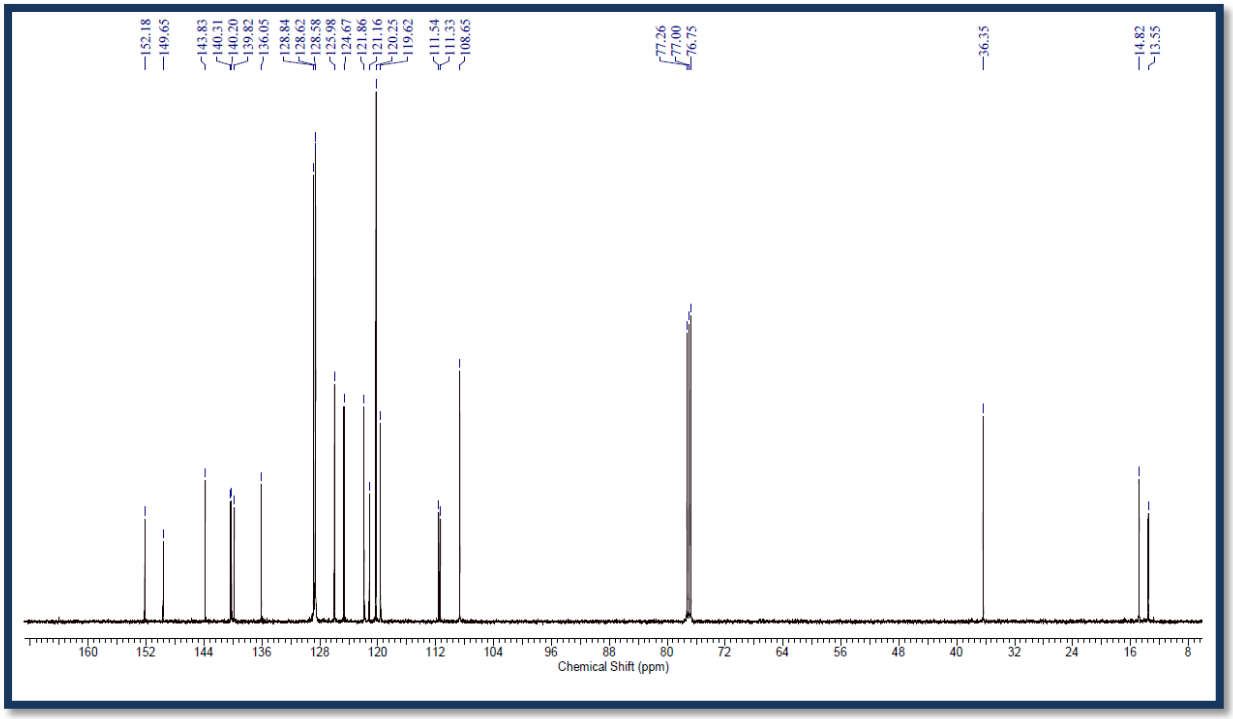

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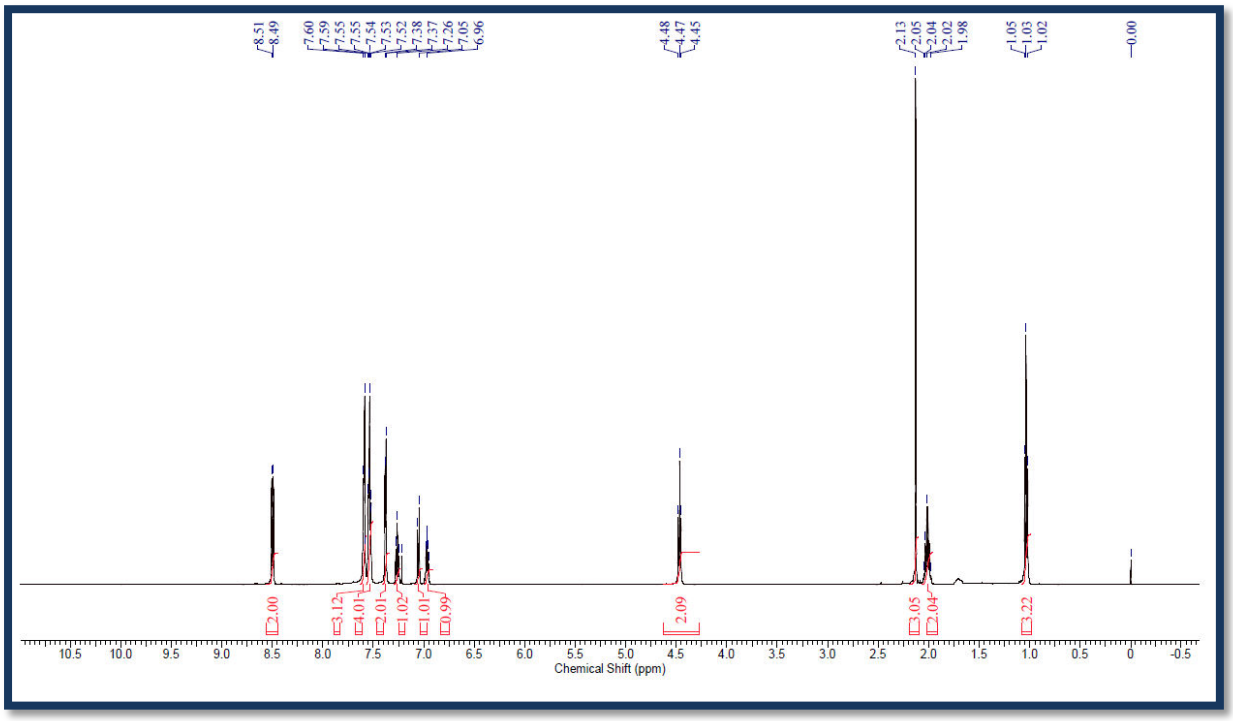

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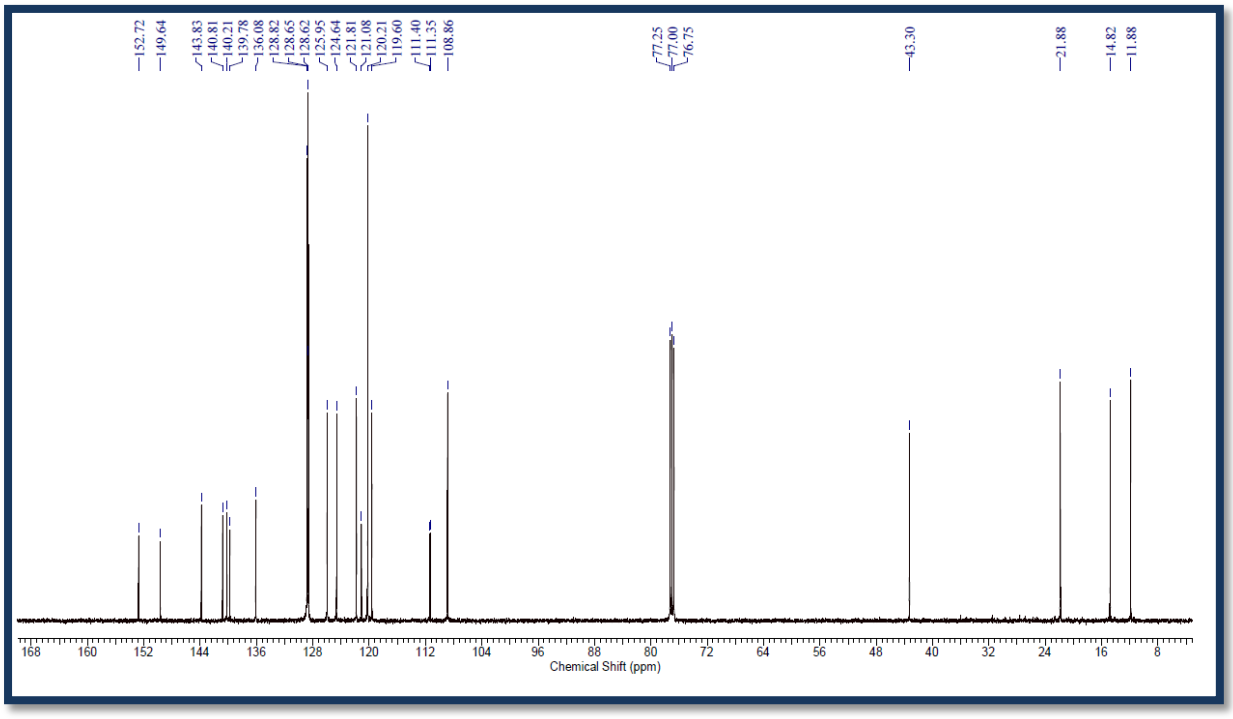

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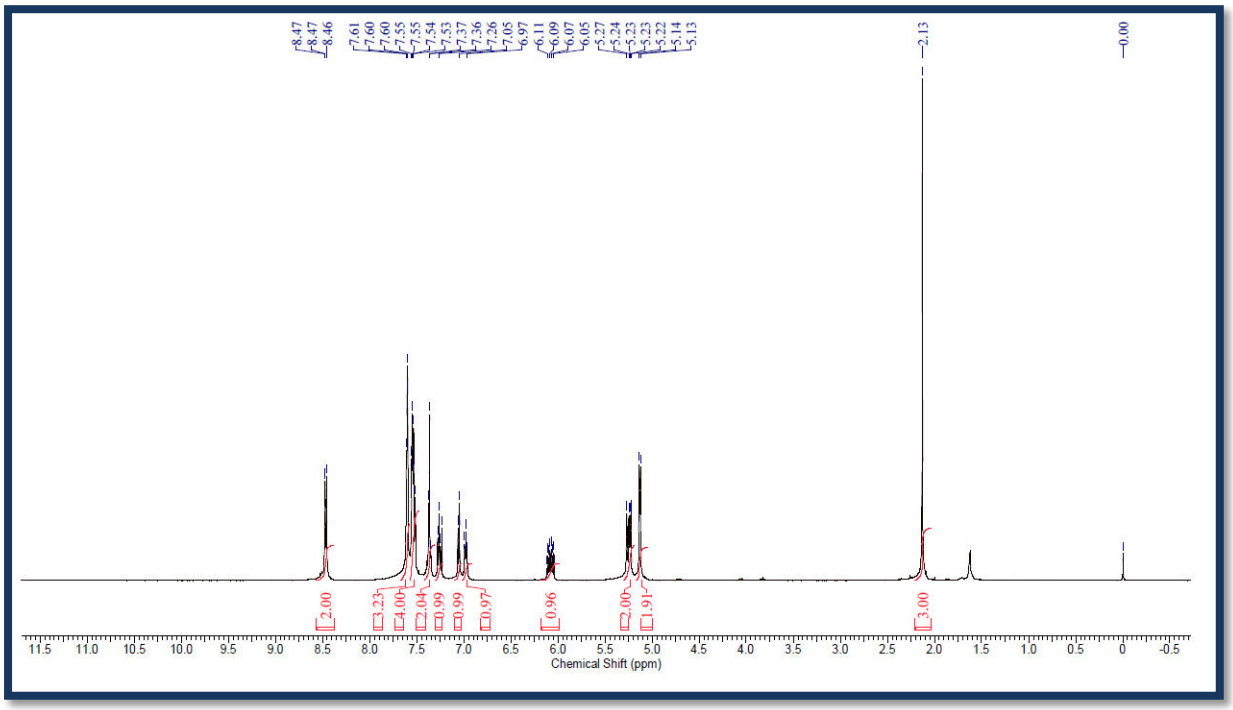

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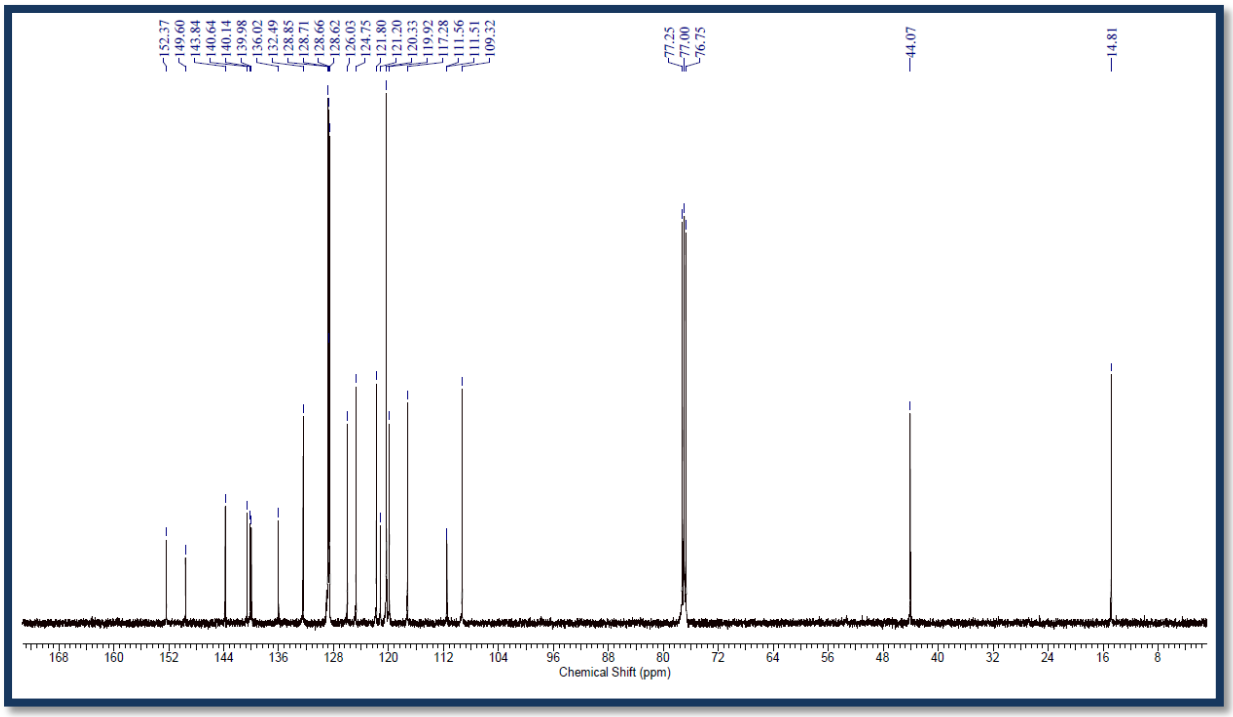

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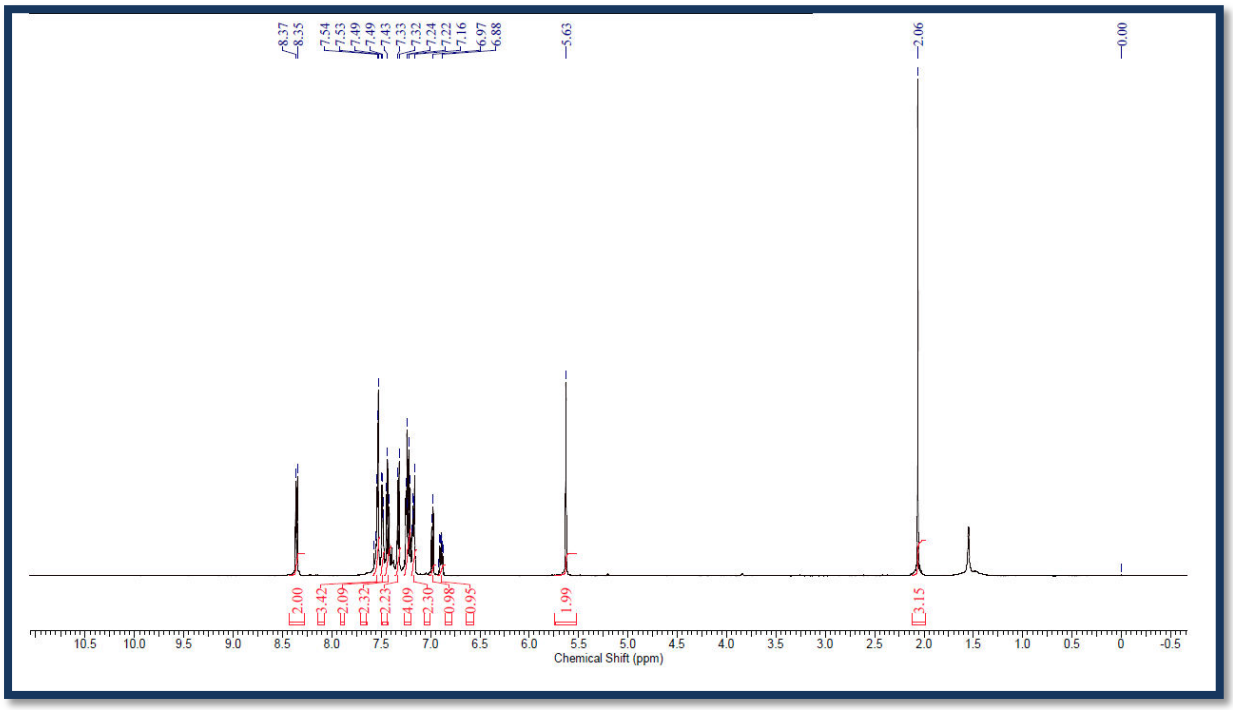

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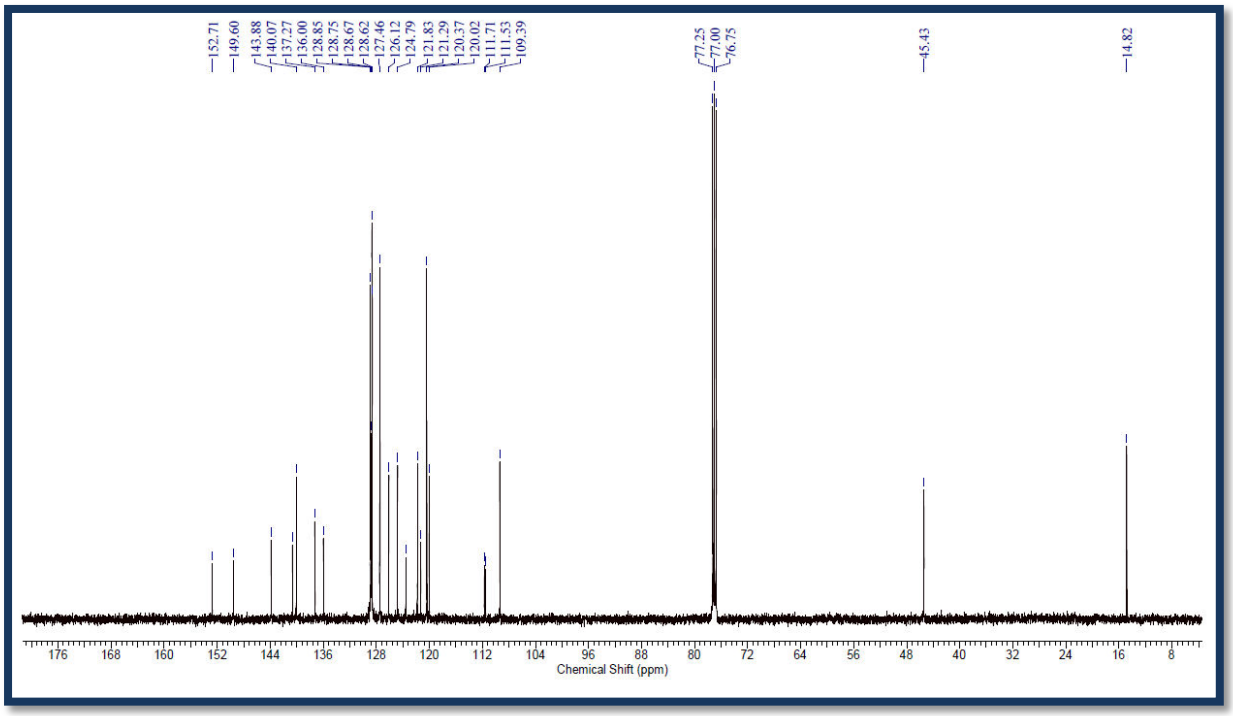

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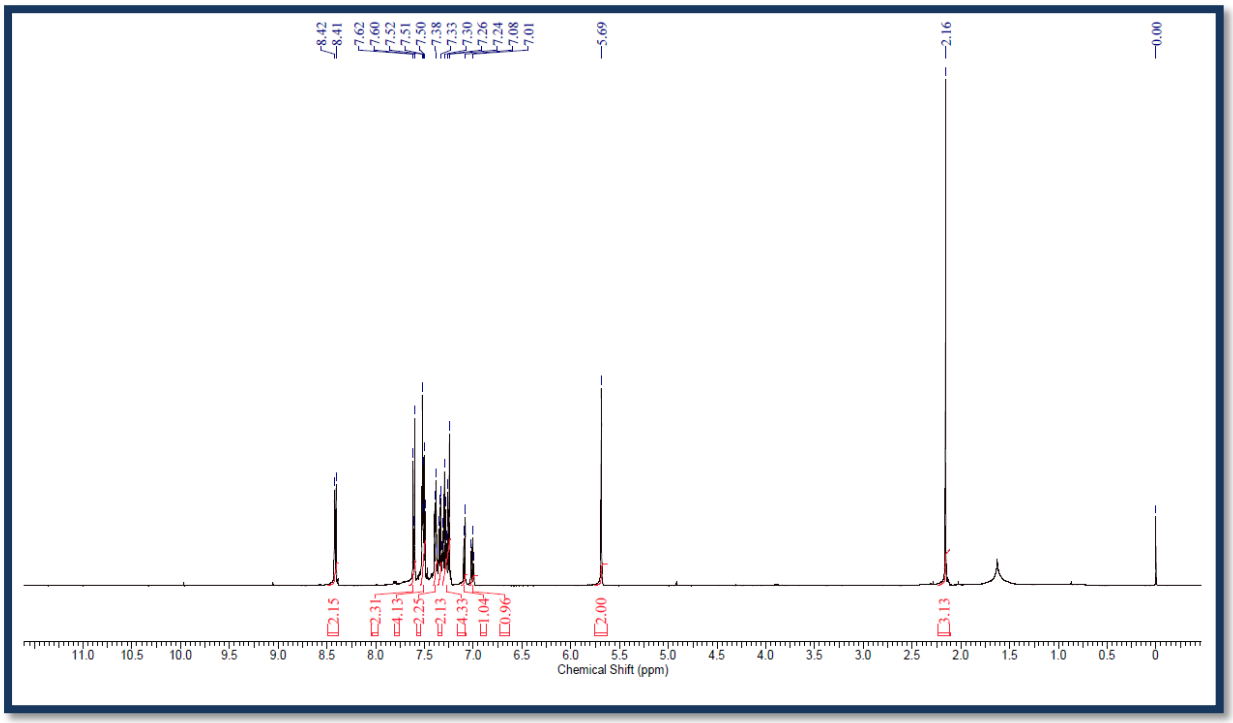

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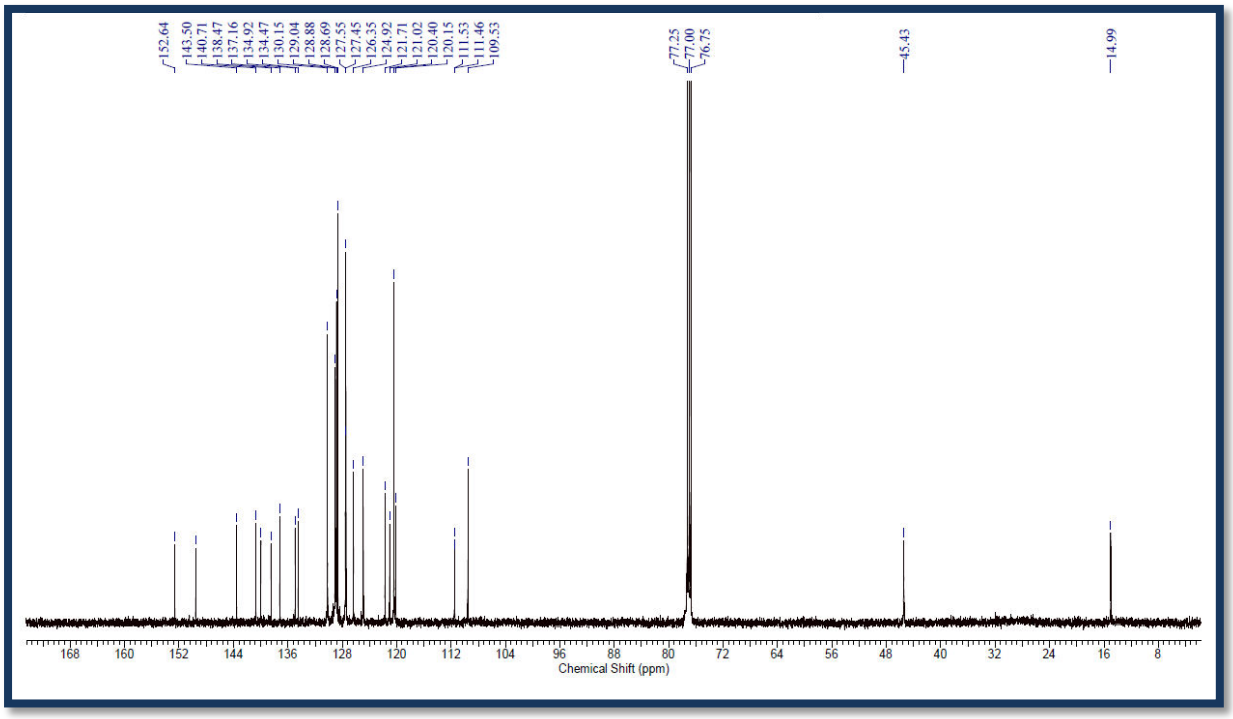

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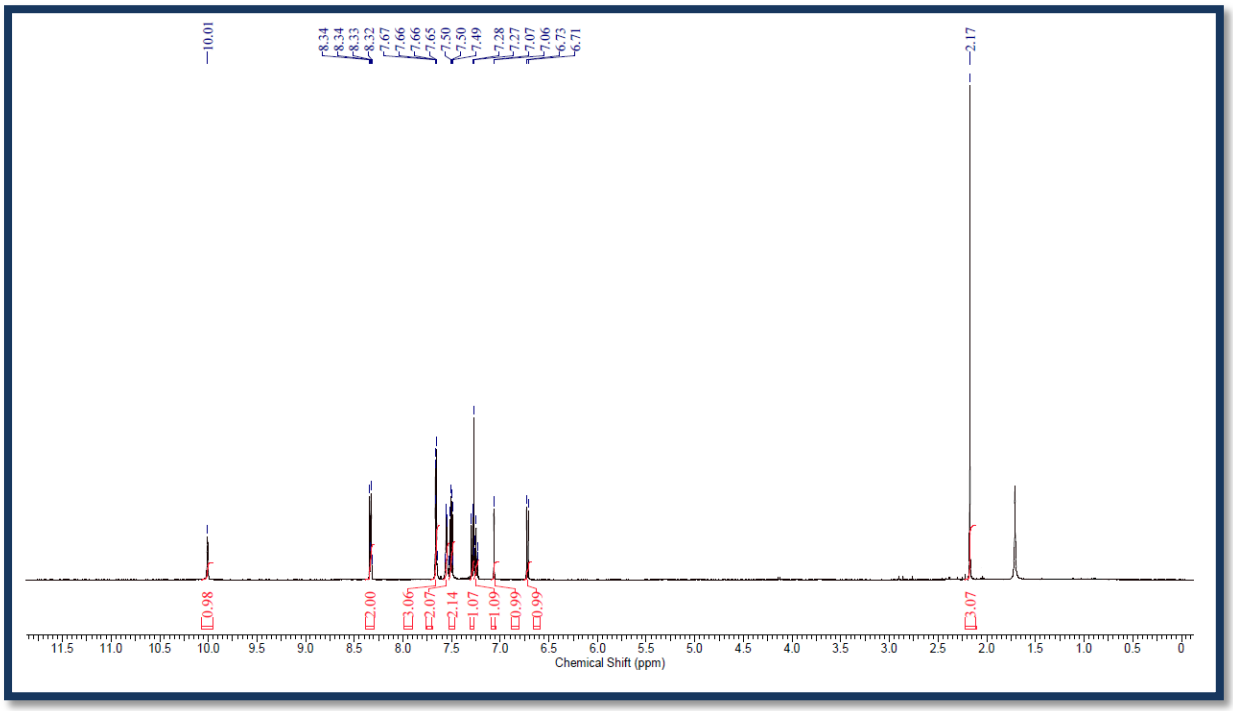

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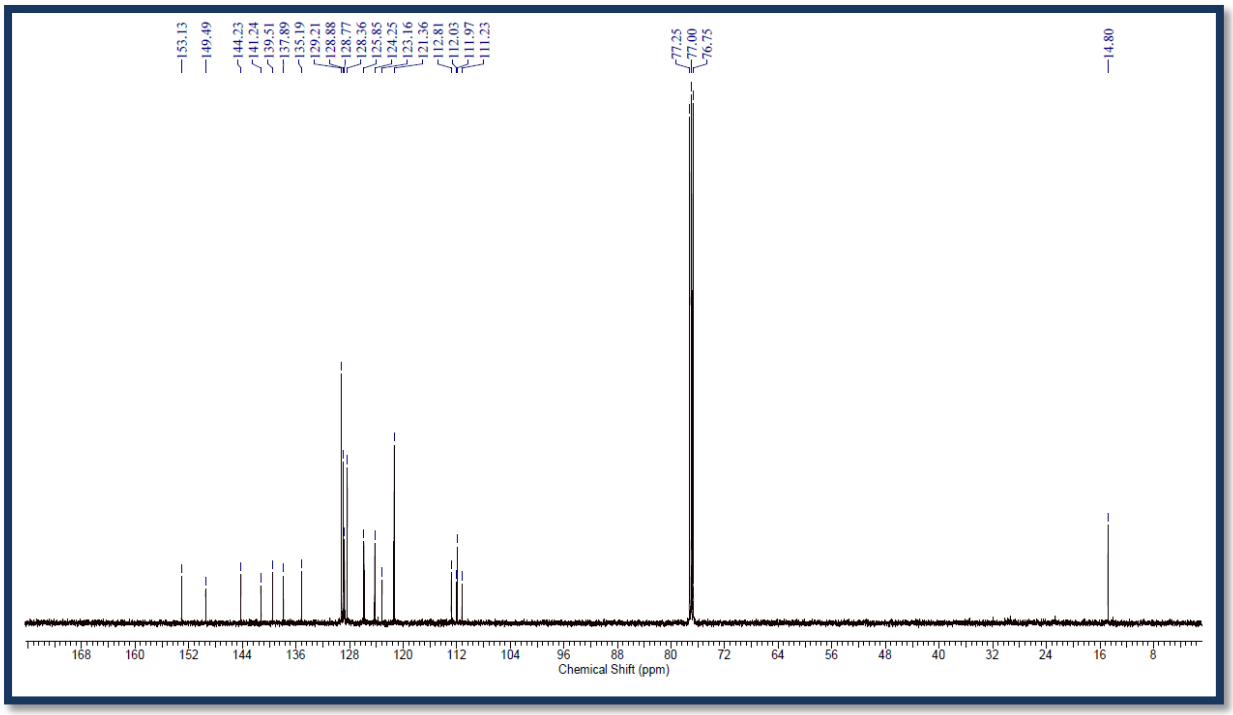

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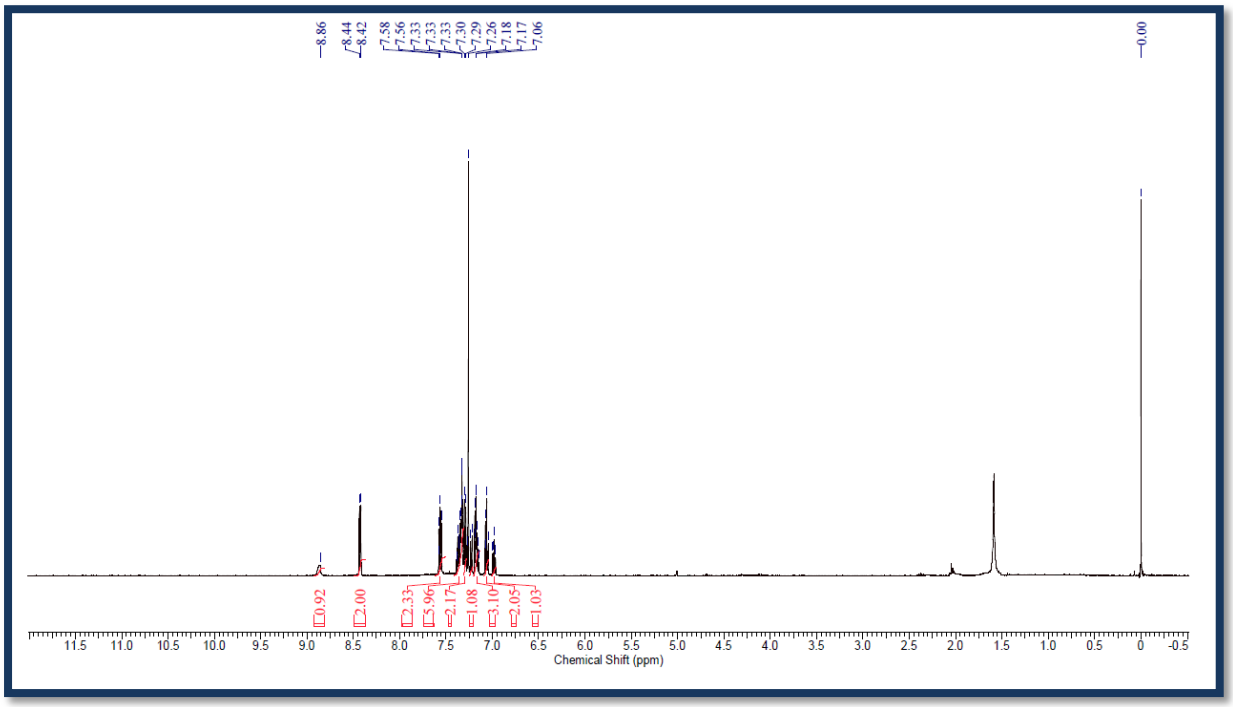

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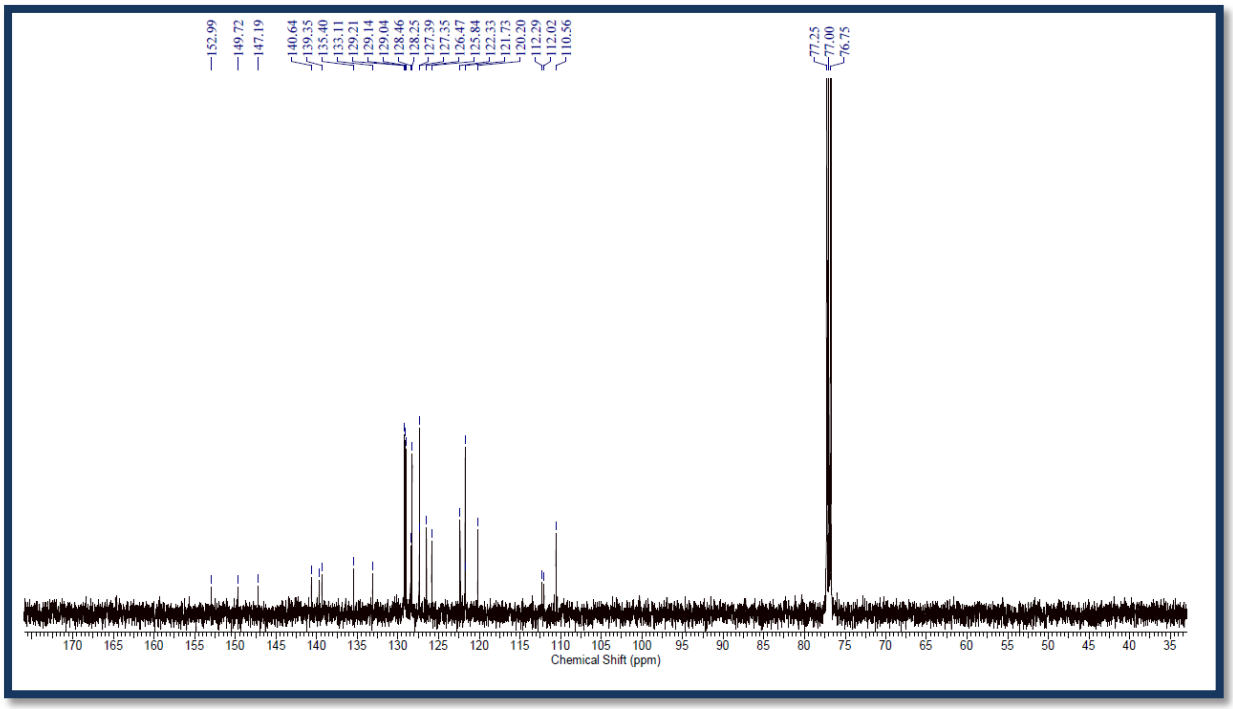

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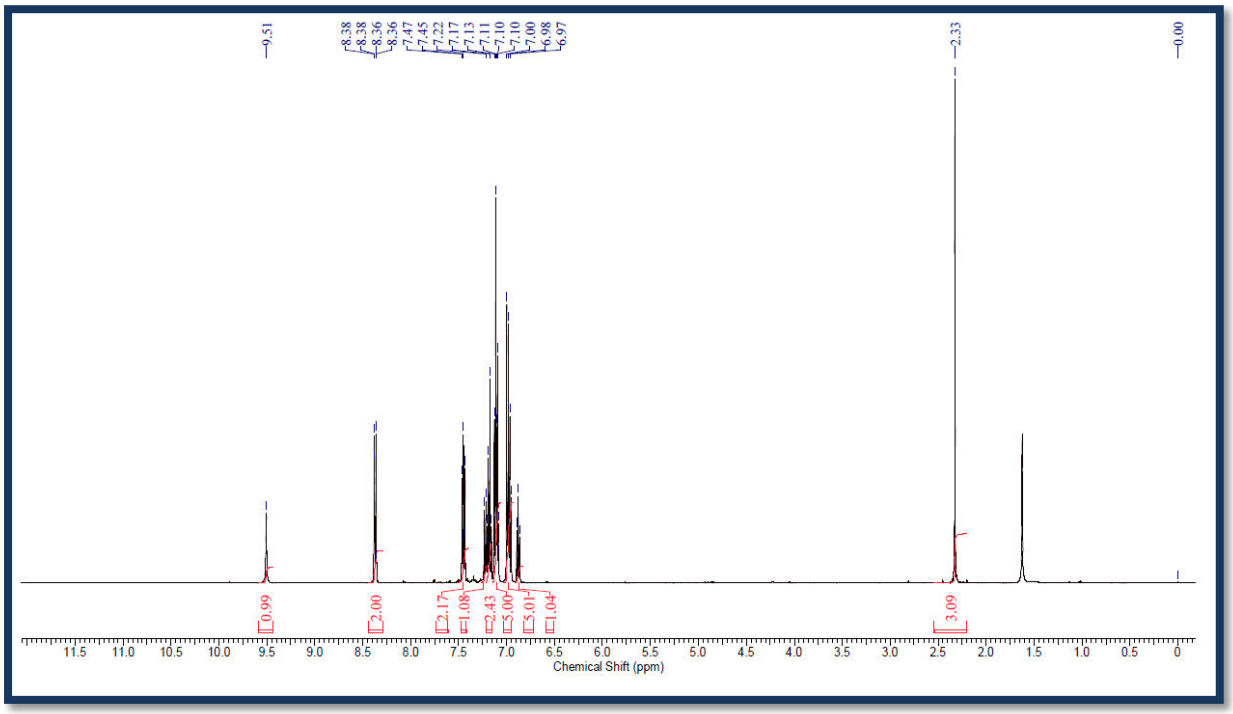

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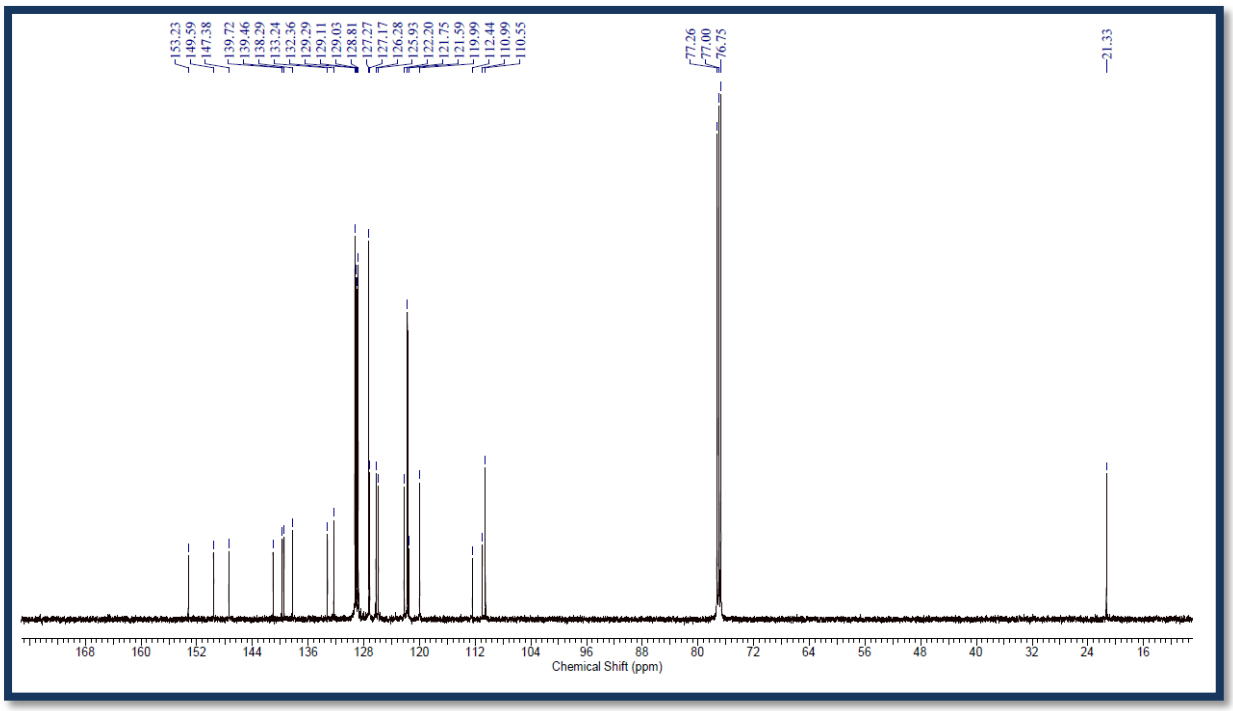

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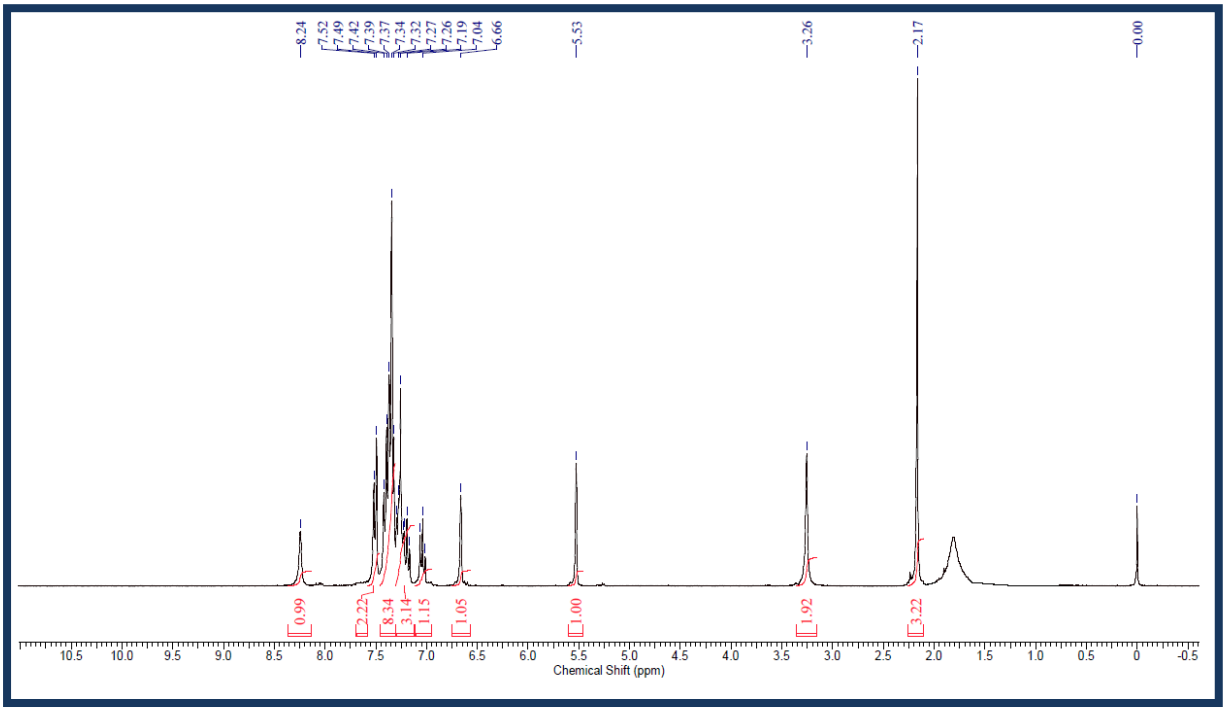

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