Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Ethyl (Z)-3-iodoacrylate (16)

To a solution of ethylpropiolate (1.5 g, 15.3 mmol) in AcOH (15 mL), was added NaI (3.4 g, 22.9 mmol) and the reaction mixture was heated at 110° C for 3 h. The reaction mixture was cooled to 0° C then quenched with saturated aq. $NaHCO_3$ and DCM (50 mL). Aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (19:1, hexane: EtOAc) gave the ethyl (Z)-3-iodoacrylate[1] **16** (3.2 gm, 14.1 mmol, 93%) as a yellow oil.

Ethyl (Z)-5-(trimethylsilyl)pent-2-en-4-ynoate (20)

To a solution of ethyl (Z)-3-iodoacrylate**16** (1g, 4.42 mmol) and trimethylsilylacetylene (563 mg, 5.74 mmol, 0.84 mL) in dry THF (20 mL) and DIPA (8 mL) were added $[(Ph_3P)_2PdCl_2]$ (31 mg, 0.0442 mmol) and CuI (125 mg, 0.663 mmol) under nitrogen. The reaction was stirred at room temperature for 14 h. The reaction mixture was diluted with saturated aq. NH_4Cl (10 mL) and ethyl acetate (50 mL). Aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (19:1, hexane: EtOAc) gave coupled product[2] **20** (705 mg, 3.59 mmol, 81%) as a yellow oil.

(Z)-5-(Trimethylsilyl)pent-2-en-4-yn-1-ol (21)

To an ice cold solution of coupled product[2] **20** (700 mg, 3.57 mmol) in dry DCM (10 mL), was added DIBAL-H (1M in toluene) (8.56 mmol, 8.5 ml) and the reaction mixture was stirred at same temperature for 1 h. The reaction mixture was diluted with water (10 mL) and ethyl acetate (20 mL) then filtered through celite bed and collected the organic layer and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (9:1, hexane: EtOAc) gave the alcohol **21** (520 mg, 3.37 mmol, 95 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.88-5.94 (1 H, m), 5.39 (1 H, dt, *J* = 1.5 & 11.0 Hz), 4.20 (2 H, d, *J* = 6.2 Hz), 1.85 (1 H, br), -0.0002 (9 H, s) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8, 110.4, 100.9, 100.6, 61.0 and -0.06 ppm.

IR (neat): 3431, 2962, 1728, 1616, 1459, 1377, 1252, 1080, 1023, 995, 910, 848 and 483 cm^{-1}

TLC: R_f = 0.4 (9:1; hexane:EtOAc)

(Z)-Tert-butyldimethyl((5-(trimethylsilyl)pent-2-en-4-yn-1-yl)oxy)silane (22)

To an ice cold solution of alcohol **21** (500 mg, 3.24 mmol) and TBDMSCl (631 mg, 4.21 mmol) in dry DCM (10 ml) and imidazole (263 mg, 3.88 mmol) & DMAP (79 mg, 0.64 mmol) were added under nitrogen and the reaction mixture was stirred at same temperature for 2 h. The reaction mixture was diluted with water and DCM (20 mL). Aqueous layer was extracted with DCM (2 x 20 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (19:1, hexane: EtOAc) gave the protected TBS alcohol **22** (700 mg, 2.61 mmol, 80 %) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.83-5.89 (1 H, m), 5.32 (1 H, dt, *J* = 1.6 & 11.0 Hz), 4.24 (2 H, dd, *J* = 1.6 & 6.4 Hz), 0.75 (9 H, s), -0.0001(9 H, s), -0.1010 (6 H, s) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.9, 109.4, 100.9, 100.3, 61.7, 26.0, 18.5, 0.03, -4.99 ppm.

IR (neat): 2956, 2859, 1646, 1467, 1259, 1099, 909, 845, 725, 652 and 407 cm^{-1}

TLC: R_f = 0.6 (9:1; hexane:EtOAc)

(Z)-Tert-butyldimethyl(pent-2-en-4-yn-1-yloxy)silane (17)

A solution of enyne-diyne **22** (650 mg, 2.42 mmol) in MeOH (8 mL), was added K_2CO_3 (435 mg, 3.15 mmol) and the reaction mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with water and DCM (20 mL). Aqueous layer was extracted with DCM (2 x 20 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (19:1, hexane: EtOAc) gave the protected TBS alcohol (380 mg, 0.183 mmol, 76%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.98-6.04 (1 H, m), 5.35-5.44 (1 H, m), 4.35 (2 H, dt, *J* = 0.6 & 6.1 Hz), 3.05 (1 H, t, *J* = 0.8 Hz), 0.819 (9 H, s), -0.0002 (6 H, s) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 145.0, 108.0, 82.9, 79.5, 61.7, 26.0, 18.4 and -5.04 ppm.

IR (neat): 3302, 2954, 2852, 1612, 1432, 1250, 905, 842, 716 and 424 cm^{-1}

TLC: R_f = 0.5 (9:1; hexane:EtOAc)

(Z)-2-(5-((Tert-butyldimethylsilyl)oxy) pent-3-en-1-yn-1-yl)-5-methoxybenzaldehyde (23)

To a solution of 2-Iodo-5-methoxybenzaldehyde[3] **15** (500 mg, 1.90 mmol) and **(**Z)-Tert-butyldimethyl(pent-2-en-4-yn-1-yloxy)silane **17** (409 mg, 2.09 mmol) in dry THF (10 mL) and DIPA (4 mL) were added [$(Ph_3P)_2PdCl_2$] (13 mg, 0.019 mmol) and CuI (28 mg, 0.28 mmol) under nitrogen. The reaction was stirred at room temperature for 14 h. The reaction mixture was diluted with saturated aq. NH_4Cl (10 mL) and ethyl acetate (20 mL). Aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (19:1, hexane: EtOAc) gave the alcohol **23** (420 mg, 1.27 mmol, 67 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.3 (1 H, s), 7.34 (1 H, d, *J* = 8.5 Hz), 7.27-7.29 (1 H, m), 7.00 (1 H, dd, *J* = 8.6 & 2.7 Hz), 5.99-6.05 (1 H, m), 5.63-5.66 (1 H, m), 4.40 (2 H, dd, *J* = 6.2 & 1.6 Hz), 3.75 (3 H, s), 0.80 (9 H, s), -0.0002 (6 H, s) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 159.9, 143.7, 137.1, 134.5, 121.7, 119.5, 110.0, 108.7, 90.8, 90.4, 61.9, 55.7, 26.0, 18.4 and -4.99 ppm.

IR (neat): 3055, 2934, 2856, 2747, 1692, 1601, 1491, 1466, 1425, 1390, 1314, 1267, 1226, 1160, 1096, 1038, 940, 840, 737 and 595 cm^{-1}

TLC: R_f = 0.4 (8:2; hexane:EtOAc)

(Z)-1-(2-(5-((Tert-butyldimethylsilyl)oxy)pent-3-en-1-yn-1-yl)-5-methoxyphenyl)prop-2-yn-1-ol (24)

To an ice-cold solution of enyne aldehyde **23** (300 mg, 0.909 mmol) in dry THF (8 mL) was added ethynyl magnesium bromide (0.5 M solution) (374 mg, 1.8 mmol, 3.6 mL) and stirred the reaction at same temperature for 2 h, the reaction mixture was diluted with saturated aq.NH_4Cl and extracted with EtOAc (10 mL). Aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (8:2, hexane: EtOAc) gave the alkyne **24** (302 mg, 0.085 mmol, 93%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.25 (1 H, d, *J* = 8.5 Hz), 7.15 (1 H, d, *J* = 2.2 Hz), 6.70 (1 H, dd, *J* = 8.5 & 2.0 Hz), 5.92-5.98 (1 H, m), 5.69 (1 H, s), 5.63 (1 H, d, *J* = 11.0 Hz), 4.41 (2 H, dd, *J* = 1.4 & 6.1 Hz), 3.71 (3 H, s), 2.84 (1 H, br), 2.51 (1 H, d, *J* = 1.6 Hz), 0.80 (9 H, s), -0.0001(6 H, s)ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 160.1, 143.3, 142.6, 133.8, 114.4, 113.6, 112.1, 109.1, 92.1, 89.5, 82.9, 74.7, 62.8, 61.9, 55.5, 26.0, 18.4 and -4.96 ppm.

IR (neat): 3431, 3301, 3056, 2938, 1607, 1491, 1468, 1428, 1264, 1155, 1096, 1045, 889, 840, 738 and 423 cm^{-1}

HR ESI-MS: [C21H28O3NaSi]$^{+}$ = [M+Na]$^{+}$ requires 379.1706; found 379.1726

TLC: R$_f$ = 0.5 (8:2; hexane:EtOAc)

(Z)-1-(2-(5-((Tert-butyldimethylsilyl)oxy)pent-3-en-1-yn-1-yl)-5-methoxyphenyl)-5-(4-methoxyphenyl)penta-2,4-diyn-1-ol (25)

To an ice cold solution of an alkyne **24** (250 mg, 0.702 mmol), and bromo alkyne[4] **19** (157 mg, 0.84 mmol) in 1,2-DCE (8 mL) and piperidine (298 mg, 3.51 mmol, 0.36 mL freshly degassed) under nitrogen atmosphere, was added CuCl (7 mg, 0.0702 mmol), and reaction mixture was stirred at same temperature for 30 minutes, the reaction mixture was diluted with aq.NH4Cl (10 mL) then extracted with EtOAc (10 mL), Aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (10 mL) and dried over Na$_2$SO$_4$. Evaporation of the solvent and purification of the crude mixture by flash column chromatography (4:1, hexane:EtOAc) gave the corresponding diyne **25** (260 mg, 0.534 mmol, 76 %) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.28 (2 H, d, *J* = 8.8 Hz), 7.25 (1 H, d, *J* = 8.5 Hz), 7.10 (1 H, *J* = 2.6 Hz), 6.68-6.72 (3 H, m), 5.93-5.99 (1 H, m), 5.79 (1 H, s), 5.64 (1 H, dt, *J* = 2.8 & 11.0 Hz), 4.42 (2 H, dd, *J* = 1.5 & 6.1 Hz), 3.72 (3 H, s), 3.67 (3 H, s), 0.79 (9 H, s), -0.0002 (6 H, s) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 160.5, 160.2, 143.0, 142.7, 134.3, 133.9, 114.5, 114.2, 113.6, 113.4, 112.2, 109.1, 92.0, 89.7, 80.6, 79.7, 72.3, 71.4, 63.6, 61.9, 55.6, 55.4, 26.0, 18.4 and -4.95 ppm.

IR (neat): 3437, 3054, 2933, 2856, 1603, 1508, 1465, 1384, 1258, 1172, 1100, 1033, 939, 838, 777, 739 and 601 cm^{-1}

HR ESI-MS: $[C30H34O4SiNa]^+$ = $[M+Na]^+$ requires 509.2124; found 509.2136

TLC: $R_f = 0.5$ (8:2; hexane:EtOAc)

2-(((Tert-butyldimethylsilyl)oxy)methyl)-7-methoxy-1-((4-methoxyphenyl)ethynyl)-9H-fluoren-9-one (26)

A solution of enyne-diyne **25** (200 mg, 0.411 mmol) in dry EtOAc (5 mL), was added IBX (149 mg, 0.534 mmol) and the reaction mixture was heated at 80° C for 2 h. The reaction mixture was filtered through a short silica gel column (eluent: hexane/ethyl acetate 9:1) to give the cyclised product **26** (110 mg, 0.227 mmol, 55%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.47 (3 H, d, *J* = 8.8 Hz), 7.20 (2 H, t, *J* = 8.4 Hz), 7.03 (1 H, d, *J* = 2.2 Hz), 6.79 (1 H, dd, *J* = 2.3 & 8.2 Hz), 6.76 (2 H, d, *J* = 8.8 Hz), 4.80 (2 H, s), 3.69 (6 H, s), 0.82 (9 H, s), -0.002 (6 H, s) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 192.3(1C), 160.9(1C), 160.3(1C), 143.9(1C), 142.9(1C), 136.3(1C), 135.8(1C), 133.7(2C), 133.3(1C), 131.6(1C), 121.2(1C), 120.1(1C), 118.7(1C), 118.4(1C), 115.2(1C), 114.2(2C), 109.2(1C), 101.1(1C), 82.8(1C), 62.9(1C), 55.8(1C), 55.4(1C), 26.0(1C), 18.5(1C), -5.1(1C) ppm.

IR (neat): 3057, 2940, 2856, 1706, 1606, 1470, 1264, 1173, 1104, 1027, 837, 739, 538, 496 and 410 cm^{-1}

HR ESI-MS: $[C30H32O4SiNa]^+$ = $[M+Na]^+$ requires 507.1968; found 507.1951

TLC: $R_f = 0.6$ (8:2; hexane:EtOAc)

2-{[(Tert-butyldimethylsilyl)oxy]methyl}-7-methoxy-9-(4-methoxyphenyl)-1-[(4-methoxyphenyl)ethynyl]-9H-fluoren-9-ol (28)

To an ice-cold solution of cyclised product **26** (100 mg, 0.206 mmol) in THF (3 mL) was added *p*-anisyl magnesium bromide (2 mL in THF, 1.3 eq., 0.268 mmol, freshly prepared from 4-bromo anisole and Mg) at 0°C. After 2 h, the reaction mixture was quenched with saturated aq.NH_4Cl and extracted with ethyl acetate. The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by flash column chromatography gave the corresponding alcohol **28** (92 mg, 0.155 mmol, 75 %) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.45 (2 H, s), 7.40 (1 H, d, *J* = 9.0 Hz), 7.22 (2 H, d, *J* = 8.7 Hz), 7.00 (2 H, d, *J* = 8.7 Hz), 6.70 (3 H, d, *J* = 7.0 Hz), 6.67 (3 H, d, *J* = 8.7 Hz), 4.76-4.84 (2 H, m), 3.69 (3 H, s), 3.63 (3 H, s), 3.62 (3 H, s), 3.21 (1 H, br), 0.83 (9 H, s), -0.0002 (6 H, s) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 160.4(1C), 160.2(1C), 158.8(1C), 152.1(1C), 150.4(1C), 141.8(1C), 139.5(1C), 135.5(1C), 132.9(2C), 131.1(1C), 127.0(1C), 126.6(2C), 121.0(1C), 118.9(1C), 116.6(1C), 114.9(1C), 114.8(1C), 114.0(2C), 113.6(2C), 110.0(1C), 100.2(1C), 83.8(1C), 82.5(1C), 63.3(1C), 55.6(1C), 55.4(1C), 55.3(1C), 26.1(1C), 18.6(1C) and -5.07(1C) ppm..

IR (neat): 3441, 3056, 2985, 2855, 1615, 1509, 1428, 1264, 1172, 1107, 1033, 894, 835, 737 and 539 cm^{-1}

HR ESI-MS: [C37H40O5NaSi]$^+$ = [M+Na]$^+$ requires 615.2543; found 615.2510

TLC: R$_f$ = 0.5 (8:2; hexane:EtOAc)

4-(2-(Hydroxymethyl)-7-methoxy-9-(4-methoxyphenyl)-1-((4-methoxyphenyl)ethynyl)-9H-fluoren-9-yl)phenol (29)

To an ice-cold solution TBS protected *tert*-alcohol **28** (20 mg, 0.033 mmol) & phenol (6 mg, 0.067 mmol), in dry CH$_2$Cl$_2$ (2 mL) was added BF$_3$.OEt$_2$ (0.93 mg, 0.0066 mmol) to the reaction mixture and stirred reaction mixture for 30 min, at same temperature. Diluted the reaction mixture with cold water (2 mL) and CH$_2$Cl$_2$ (5 mL). The aqueous layer was extracted with 5 mL of DCM. The combined organic layer was dried over anhydrous Na$_2$SO$_4$, The crude material was purified by column chromatography (eluent: hexane/ethyl acetate 4:1) to afford phenol inserted product **29** (10 mg, 0.018 mmol, 54%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.57 (1 H, d, *J* = 8.3 Hz), 7.52 (1 H, d, *J* = 7.8 Hz), 7.23 (2 H, d, *J* = 8.9 Hz), 7.18 (2 H, d, *J* = 8.8 Hz), 7.09 (1 H, d, *J* = 8.5 Hz), 7.05 (1 H, d, *J* = 7.9 Hz), 6.93 (2 H, d, *J* = 8.8 Hz), 6.84 (1 H, dd, *J* = 2.4 & 8.4 Hz), 6.79 (2 H, t, *J* = 7.4 Hz), 6.72 (2 H, t, *J* = 8.5 Hz), 6.63 (2 H, d, *J* = 8.8 Hz), 4.85 (1 H, br), 4.12 (2 H, s), 3.79 (3 H, s), 3.73 (6 H, d, *J* = 1.4 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 160.1(1C), 159.6(1C), 158.2(1C), 155.7(1C), 154.2(1C), 153.9(1C), 152.3(1C), 142.3(1C), 138.8(1C), 135.1(1C), 135.0(1C), 132.6(1C), 132.2(2C), 130.6(2C), 130.3(2C), 128.6(1C), 120.4(1C), 119.0(1C), 115.3(2C), 114.5(2C), 114.1(2C), 113.4(1C), 113.1(1C), 111.2(1C), 100.6(1C), 86.3(1C), 65.2(1C), 55.5(1C), 55.4(1C), 55.3(1C) and 39.3(1C) ppm

^{1}H NMR (400 MHz, CD_3OD): δ = 7.60 (1 H, d, *J* = 8.4 Hz), 7.56 (1 H, d, *J* = 7.8 Hz), 7.18 (2 H, d, *J* = 8.9 Hz), 7.08 (2 H, dd, *J* = 5.3 & 8.8 Hz), 7.01 (1 H, d, *J* = 8.5 Hz), 6.89 (2 H, d, *J* = 8.9 Hz), 6.85 (1 H, dd, *J* = 1.5 & 8.4 Hz), 6.79 (2 H, d, *J* = 8.9 Hz), 6.77 (1 H, d, *J* = 2.3 Hz), 6.66 (2 H, dd, *J* = 4.7 & 8.9 Hz), 6.59 (2 H, d, *J* = 8.8 Hz), 4.58 (1 H, br), 4.04 (2 H, s), 3.75 (3 H, s), 3.68 (3 H, s), 3.66 (3 H, s) ppm.

^{13}C NMR (100 MHz, CD_3OD): δ = 162.3, 162.0, 160.5, 158.0, 157.8, 157.3, 154.8, 144.4, 140.9, 137.1, 135.8, 134.3, 132.27, 132.22, 131.8, 130.5, 122.2, 120.7, 116.9, 116.1, 115.8, 115.1, 114.7, 112.9, 102.5, 88.2, 67.2, 56.7, 56.6, 56.5 and 41.0 ppm

IR (neat): 3577, 3397, 3053, 2929, 2852, 1600, 1501, 1361, 1258, 1186, 1069, 1027, 891, 817, 740, 512 and 442 cm^{-1}

HR ESI-MS: $[C37H30O5Na]^+ = [M+Na]^+$ requires 577.1991; found 577.2000

TLC: R_f = 0.4 (8:2; hexane:EtOAc)

5-Methoxy-2-(pent-3-en-1-yn-1-yl)benzaldehyde (S0)

To a solution of 2-Iodo-5-methoxybenzaldehyde **15** (300 mg, 1.145 mmol) and pent-1-yn-3-ol[5] (105 mg, 1.25 mmol) in dry THF (5 mL) and DIPA (2 mL) were added $[(Ph_3P)_2PdCl_2]$ (8 mg, 0.01 mmol) and CuI (33 mg, 0.171 mmol) under nitrogen. The reaction was stirred at room temperature for 14 h. The reaction mixture was diluted with saturated aq. NH_4Cl (10 mL) and ethyl acetate (20 mL). Aqueous layer was extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (8:2, hexane: EtOAc) gave the alcohol **S0** (125 mg, 0.625 mmol, 54 %) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.4 (1 H, s), 7.45 (1 H, d, *J* = 8.6 Hz), 7.37 (1 H, d, *J* = 2.8 Hz), 7.09 (1 H, dd, *J* = 2.8 & 8 Hz), 4.60 (1 H, s), 3.86 (3 H, s), 2.34-2.38 (1 H, m), 1.83-1.87 (2 H, m), 1.09 (3 H, t, *J* = 7.4 Hz) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 159.9, 137.4, 134.8, 121.6, 119.0, 110.0, 95.7, 80.4, 64.3, 55.7, 31.0 and 9.66 ppm.

IR (neat): 3448, 3056, 2972, 2860, 1690, 1604, 1491, 1426, 1268, 1163, 1092, 1031, 966, 889, 833, 738, 583, 528 and 434 cm^{-1}

TLC: R_f = 0.5 (8:2; hexane:EtOAc)

2-(3-Hydroxypent-1-yn-1-yl)-5-methoxybenzaldehyde (34)

To an ice cold solution of secondary alcohol **S0** (120 mg, 0.6 mmol) in dry DCM (5 mL), was added Et_3N (1.2 mL) & Tf_2O (253 mg, 0.9 mmol, 0.15 mL) and the reaction mixture was stirred at same temperature for 1 h. The reaction mixture was diluted with water and DCM (10 mL). Aqueous layer was extracted with DCM (2 x 10 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (eluent: hexane/ethyl acetate 19:1) gave the alcohol **34** as a (1:0.3) mixture of *E:Z* geometrical isomers (60 mg, 0.176 mmol, 60%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.4 (1 H, s), 7.40 (1 H, d, *J* = 8.5 Hz), 7.32 (1 H, s), 7.03 (1 H, *J* = 7.9 Hz), 6.00-6.07 (1 H, m), 5.66 (1 H, d, *J* = 11.1 Hz), 3.79 (3 H, s), 1.90 (3 H, d, *J* = 6.6 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 191.8, 159.7, 139.7, 137.0, 134.6, 121.9, 120.2, 109.87, 109.84, 91.9, 89.4, 55.7 and 16.5 ppm.

IR (neat): 3056, 2974, 2853, 1691, 1601, 1490, 1429, 1267, 1211, 1034, 937, 896, 736, 577 and 432 cm^{-1}

HR ESI-MS: $[C13H13O2]^+ = [M+H]^+$ requires 201.0916; found = 201.0929

TLC: R_f = 0.6 (9:1; hexane:EtOAc)

1-(5-Methoxy-2-(pent-3-en-1-yn-1-yl)phenyl)prop-2-yn-1-ol (35)

To an ice-cold solution of enyne-aldehyde **34** (120 mg, 0.6 mmol) in dry THF (5 mL) was added ethynyl magnesium bromide (0.5 M solution) (1.2 mmol, 2.4 mL) and stirred the reaction at 0° C for 2 h, the reaction mixture was diluted with saturated aq.NH_4Cl and extracted with EtOAc (10 mL). Aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by column chromatography (4:1, hexane: EtOAc) gave the alkyne **35** (as a 1:0.3; mixture of *E:Z*) (100 mg, 0.442 mmol, 74%) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.38 (1 H, d, *J* = 8.5 Hz), 7.25 (1 H, d, *J* = 2.7 Hz), 6.80 (1 H, dd, *J* = 2.7 & 7.1 Hz), 6.00-6.08 (1 H, m), 5.85 (1 H, s), 5.69-5.74 (1 H, m), 3.82 (3 H, s), 2.63 (1 H, d, *J* = 2.3 Hz), 1.96 (3 H, dd, *J* = 1.7 & 6.9 Hz) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.9, 143.0, 140.0, 138.6, 133.8, 114.3, 112.0, 110.0, 90.8, 90.5, 82.9, 74.7, 62.9, 55.4 and 16.3 ppm.

IR (neat): 3465, 3300, 3054, 2983, 2846, 1604, 1492, 1428, 1266, 1158, 1110, 1032, 895, 739 and 419 cm^{-1}

HR ESI-MS: [C15H14O2Na]$^+$ = [M+H]$^+$ requires 249.0891; found = 249.0923

TLC: R_f = 0.4 (8:2; hexane:EtOAc)

1-(5-Methoxy-2-(pent-3-en-1-yn-1-yl)phenyl)-5-(4-methoxyphenyl)penta-2,4-diyn-1-ol (36)

To a solution of an alkyne **35** (80 mg, 0.353 mmol), and bromo alkyne**[4]** **19** (79 mg, 0.42 mmol) in 1,2-DCE (5 mL) and piperidine (150 mg, 1.76 mmol, 0.18 mL freshly degassed) at 0°C under nitrogen atmosphere, was added CuCl (3.5 mg, 0.035 mmol), and reaction mixture was stirred 0°C for 30 minutes , the reaction mixture was diluted with aq.NH4Cl (10 mL) then extracted with EtOAc (10 mL), Aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by flash column chromatography (8:2, hexane:EtOAc) gave the corresponding enyne-diyne (as a 1:0.28 mixture of *E:Z*) **36** (84 mg, 0.235 mmol, 67 %) as a yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.40 (3 H, t, *J* = 6.7 Hz), 7.19-7.25 (1 H, m), 6.82 (3 H, d, *J* = 8.5 Hz), 6.01-6.09 (1 H, m), 5.95 (1 H, s), 5.72 (1 H, d, *J* = 11.0 Hz), 3.83 (3 H, s), 3.79 (3 H, s), 1.99 (3 H, d, *J* = 6.8 Hz), ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 160.4, 159.9, 142.7, 138.7, 134.2, 133.9, 114.4, 114.2, 113.9, 113.3, 112.1, 110.0, 90.8, 90.7, 80.7, 79.5, 72.3, 71.3, 63.7, 55.5, 55.4 and 16.3 ppm.

IR (neat): 3440, 3054, 2983, 2844, 1603, 1501, 1428, 1264, 1171, 1104, 1030, 895, 828, 739 and 536

cm^{-1}

HR ESI-MS: [C24H20O3Na]$^+$ = [M+Na]$^+$ requires 379.1330; found = 379.1312

TLC: R_f = 0.5 (8:2; hexane:EtOAc)

7-Methoxy-1-((4-methoxyphenyl)ethynyl)-2-methyl-9H-fluoren-9-one (37)

A solution of enyne-diyne **36** (80 mg, 0.224 mmol) in dry EtOAc (5 mL), was added IBX (82 mg, 0.292 mmol) and the reaction mixture was heated at 80° C for 3 h. The reaction mixture was filtered through a short silica gel column (eluent: hexane/ethyl acetate 9:1) to give the cyclised product **37** (45 mg, 0.127

mmol, 57%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (2 H, d, *J* = 8.0 Hz), 7.31 (1 H, d, *J* = 8.0 Hz), 7.24 (1 H, d, *J* = 7.6 Hz), 7.18 (2 H, d, *J* = 8.8 Hz), 6.91 (3 H, t, *J* = 7.2 Hz), 3.83 (3 H, s), 3.82 (3 H, s), 2.46 (3 H, s) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.2(1C), 160.7(1C), 160.2(1C), 142.9(1C), 140.0(1C), 136.1(1C), 135.8(1C), 134.8(1C), 133.7(2C), 133.6 (1C), 121.3(1C), 121.0(1C), 119.9(1C), 118.4(1C), 115.5(1C), 114.1(2C), 109.1(1C), 100.4(1C), 84.3(1C), 55.7(1C), 55.4(1C) and 20.2(1C) ppm.

IR (neat): 3055, 2984, 2925, 2847, 1709, 1598, 1430, 1265, 1161, 1027, 895, 741 and 541 cm^{-1}

HR ESI-MS: $[C24H19O3]^+ = [M+H]^+$ requires 355.1334; found = 355.1333

TLC: R_f = 0.6 (8:2; hexane:EtOAc)

M.P:120-122° C

7-Methoxy-9-(4-methoxyphenyl)-1-((4-methoxyphenyl)ethynyl)-2-methyl-9H-fluoren-9-ol (S1)

To an ice-cold solution of cyclised product **40** (42 mg, 0.113 mmol) in THF (2 mL) was added *p*-anisyl magnesium bromide (2 mL in THF, 1.3 eq., 0.146 mmol, freshly prepared from 4-bromo anisole and Mg) at 0°C. After 2 h, the reaction mixture was quenched with saturated aq.NH_4Cl and extracted with ethyl acetate. The combined organic layer was washed with brine (10 mL) and dried over Na_2SO_4. Evaporation of the solvent and purification of the crude mixture by flash column chromatography gave the corresponding alcohol **S_1** (44 mg, 0.095 mmol, 84 %) as a pale yellow semi solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (1 H, d, *J* = 8.0 Hz), 7.43 (1 H, d, *J* = 7.6 Hz), 7.34 (2 H, d, *J* = 8.4 Hz), 7.23 (1 H, d, *J* = 8.0 Hz), 7.15 (2 H, d, *J* = 8.4 Hz), 6.79-6.84 (5 H, m), 6.74 (1 H, d, *J* = 4.3 Hz), 3.79 (3 H, s), 3.73 (6 H, s), 3.46 (1 H, br s), 2.46 (3 H, s) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 160.2(1C), 158.7(1C), 151.9(1C), 150.6(1C), 138.8(1C), 138.4(1C), 135.6(1C), 132.9(2C), 131.2(1C), 130.2(1C), 126.6(2C), 120.8(1C), 119.4(1C), 118.7(1C), 116.1(1C), 115.0(1C), 114.8(1C), 114.0(2C), 113.6(2C), 110.0(1C), 99.5(1C), 83.9(1C), 83.8(1C), 55.5(1C), 55.4(1C), 55.3(1C) and 20.4(1C) ppm.

IR (neat): 3433, 3055, 2930, 2846, 1604, 1509, 1458, 1260, 1172, 1111, 1032, 828, 741, 608, 530 and 483 cm^{-1}

HR ESI-MS: [C31H26O4Na]$^+$ = [M+Na]$^+$ requires 485.1729; found = 485.1710

TLC: R$_f$ = 0.4 (4:1; hexane:EtOAc)

4-(7-Methoxy-9-(4-methoxyphenyl)-1-((4-methoxyphenyl)ethynyl)-2-methyl-9H-fluoren-9-yl)phenol(33)

To an ice-cold solution *tert*-alcohol **S1** (30 mg, 0.064 mmol) & phenol (12 mg, 0.129 mmol), in dry CH$_2$Cl$_2$ (3 mL) was added Trifluoromethanesulfonic acid (0.1 M solution) (1.92 mg, 0.0128 mmol 0.1 mL) to the reaction mixture and stirred reaction mixture for 1 h, at same temperature. Diluted the reation mixture with Cold water (2 mL) and CH$_2$Cl$_2$ (5 mL). The aqueous layer was extracted with 5 mL of DCM. The combined organic layer was dried over anhydrous Na$_2$SO$_4$, The crude material was purified by column chromatography (eluent: hexane/ethyl acetate 8:2) to afford phenol inserted product **33** (25 mg, 0.046 mmol, 72%) as a pale yellow solid.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.58 (1 H, d, *J* = 8.3 Hz), 7.53 (1 H, d, *J* = 7.7 Hz), 7.16-7.24 (5 H, m), 6.97 (2 H, d, *J* = 8.8 Hz), 6.85 (1 H, dd, *J* = 2.3 & 8.3 Hz), 6.77-6.81 (3 H, m), 6.70 (2 H, d, *J* = 8.9 Hz), 6.62 (2 H, d, *J* = 8.8 Hz), 3.78 (3 H, s), 3.72 (3 H, s), 3.71 (3 H, s) ppm.

^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.9(1C), 159.5(1C), 158.2(1C), 155.5(1C), 154.2(1C), 152.1(1C), 139.0(1C), 138.3(1C), 135.1(1C), 135.0(1C), 132.6(2C), 132.4(1C), 130.5(2C), 130.3(2C), 128.8(1C), 121.0(1C), 120.3(1C), 118.8(1C), 115.9(1C), 114.5(2C), 114.0(2C), 113.3(1C), 113.0(2C), 111.2(1C), 100.5(1C), 86.3(1C), 65.0(1C), 55.5(1C), 55.4(1C), 55.3(1C) and 21.0(1C) ppm.

IR (neat): 3418, 2925, 2854, 1714, 1602, 1504, 1454, 1254, 1178, 1107, 1026, 821, 737, 524 and 444 cm^{-1}

TLC: R$_f$ = 0.5 (4:1; hexane:EtOAc)

HR ESI-MS: $[C_{37}H_{31}O_4]^+$ = $[M+H]^+$ requires 539.2222; found = 539.2272

M.P:198-200° C

References:

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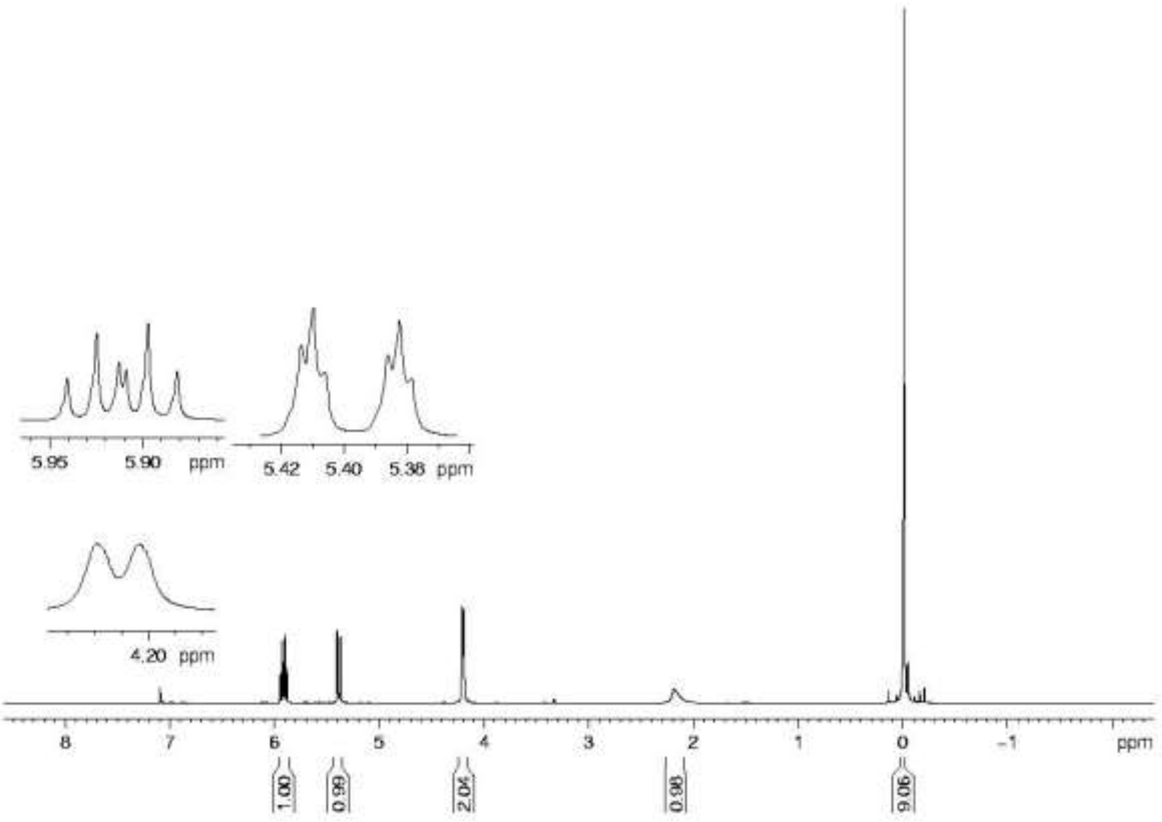
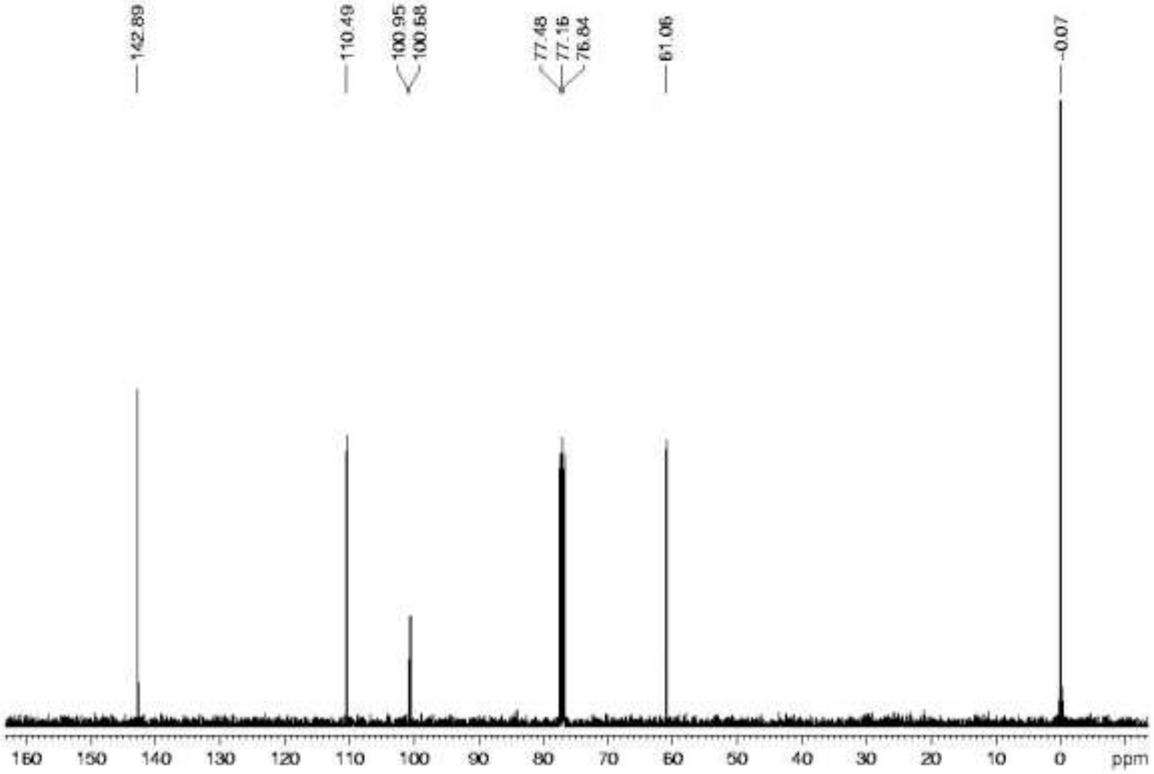
2) S. Arai, Y. Koike, H. Hada and Atsushi Nishida, *J. Am. Chem. Soc*., **2010**, *132*, 4522–4523.
3) B. S. Chinta and B. Baire, *Org. Biomol. Chem*., **2017**, 15, 5908–5911
4) Z. Chen , H. Jiang, Y. Li and C. Qi, Chem. Commun., **2010**, ***46***, 8049-8051.
5) Z. Lu, and S. Ma, *J. Org. Chem*., **2006**, *71*, 2655–2660

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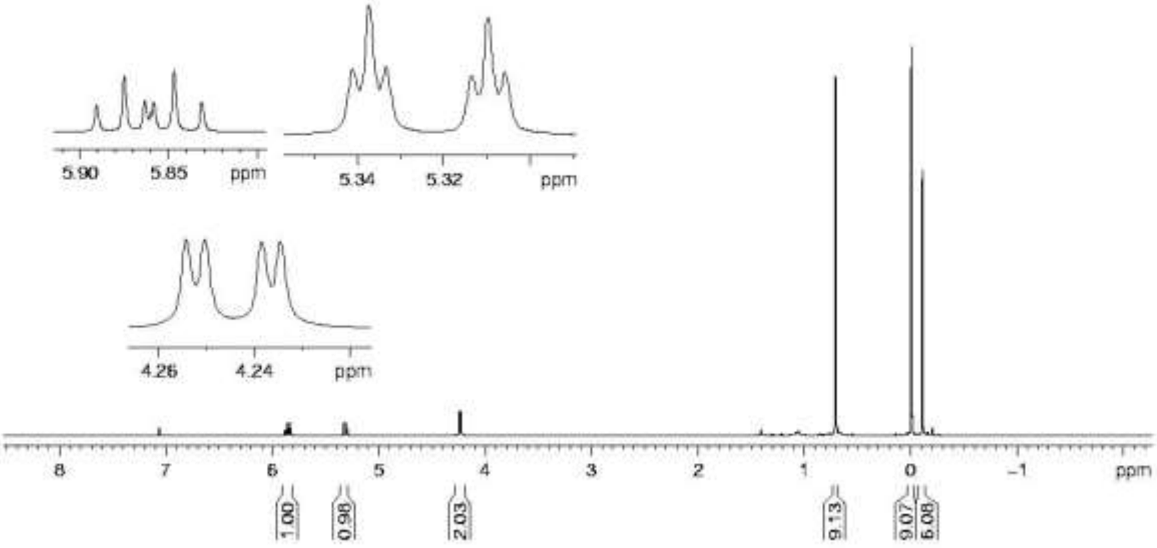
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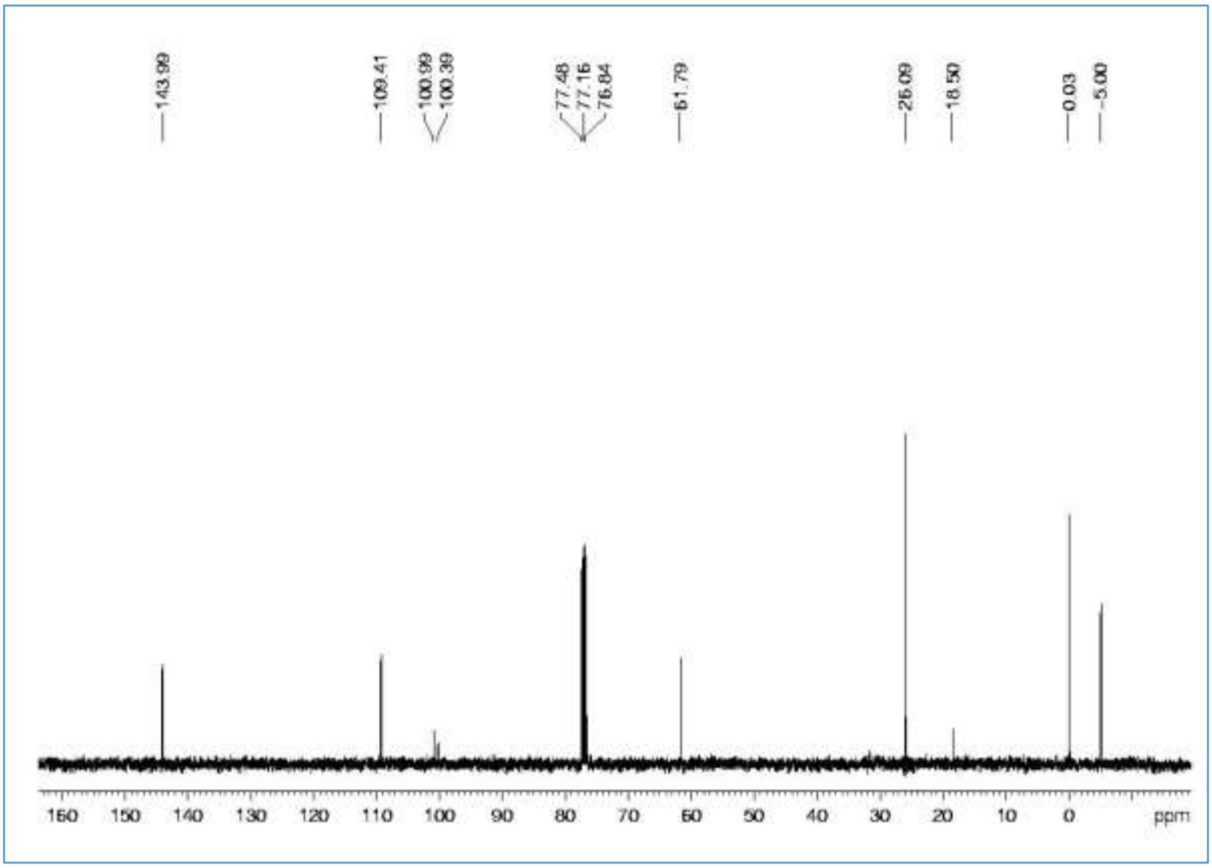
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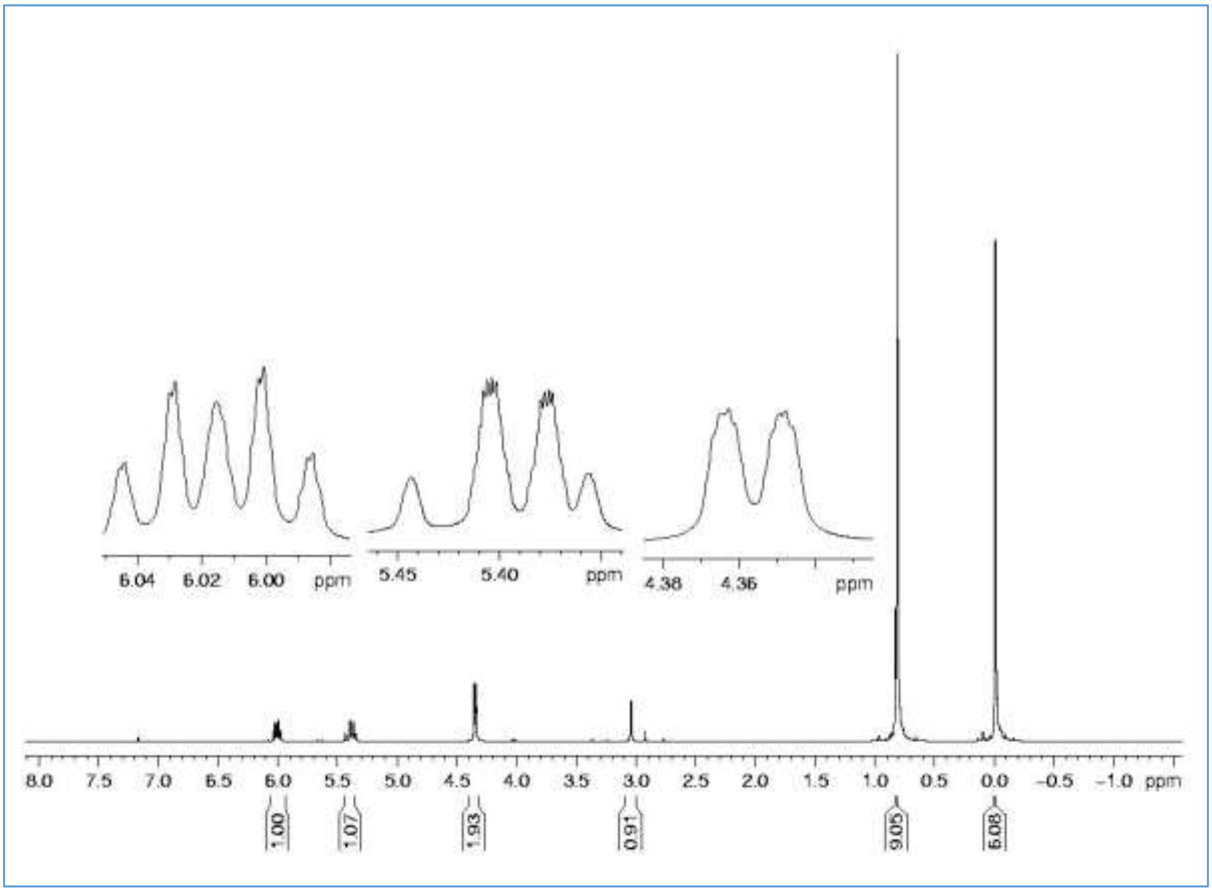
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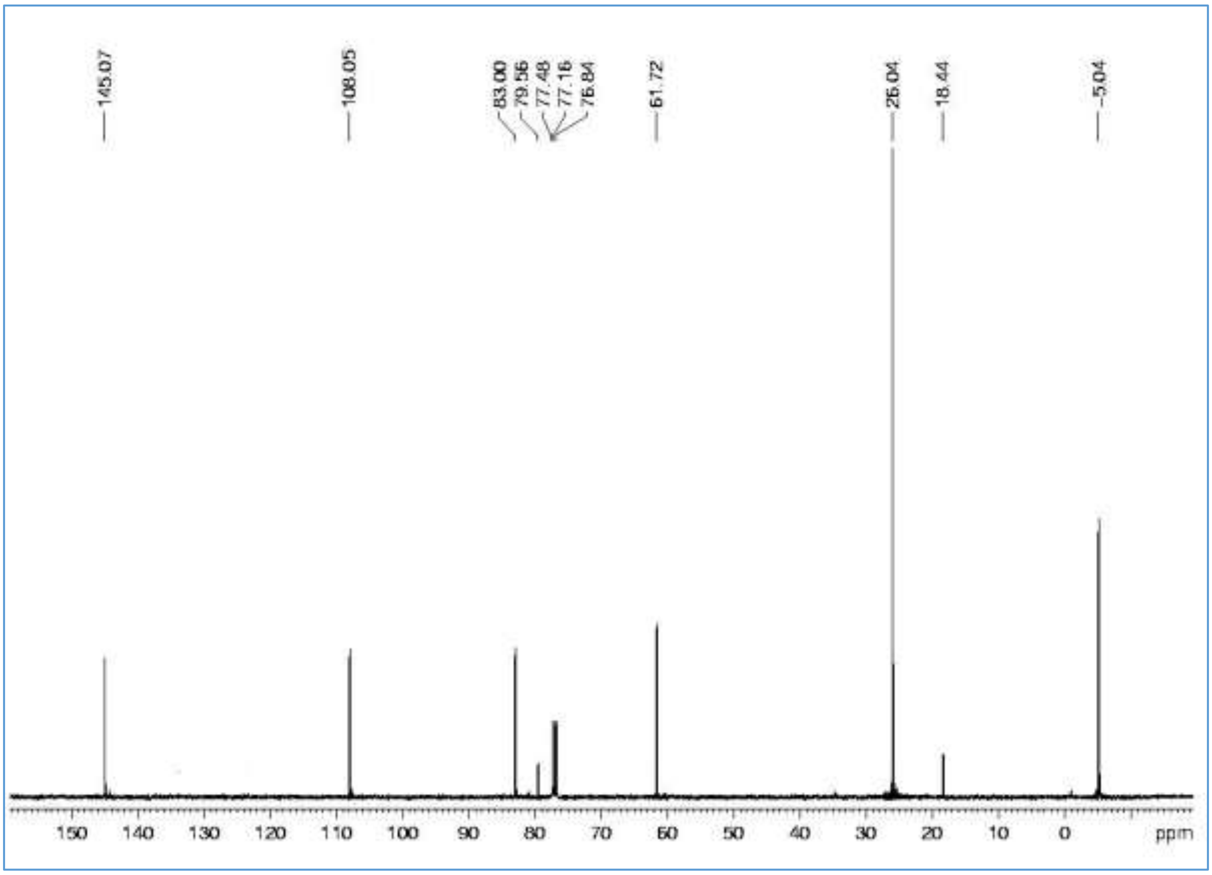
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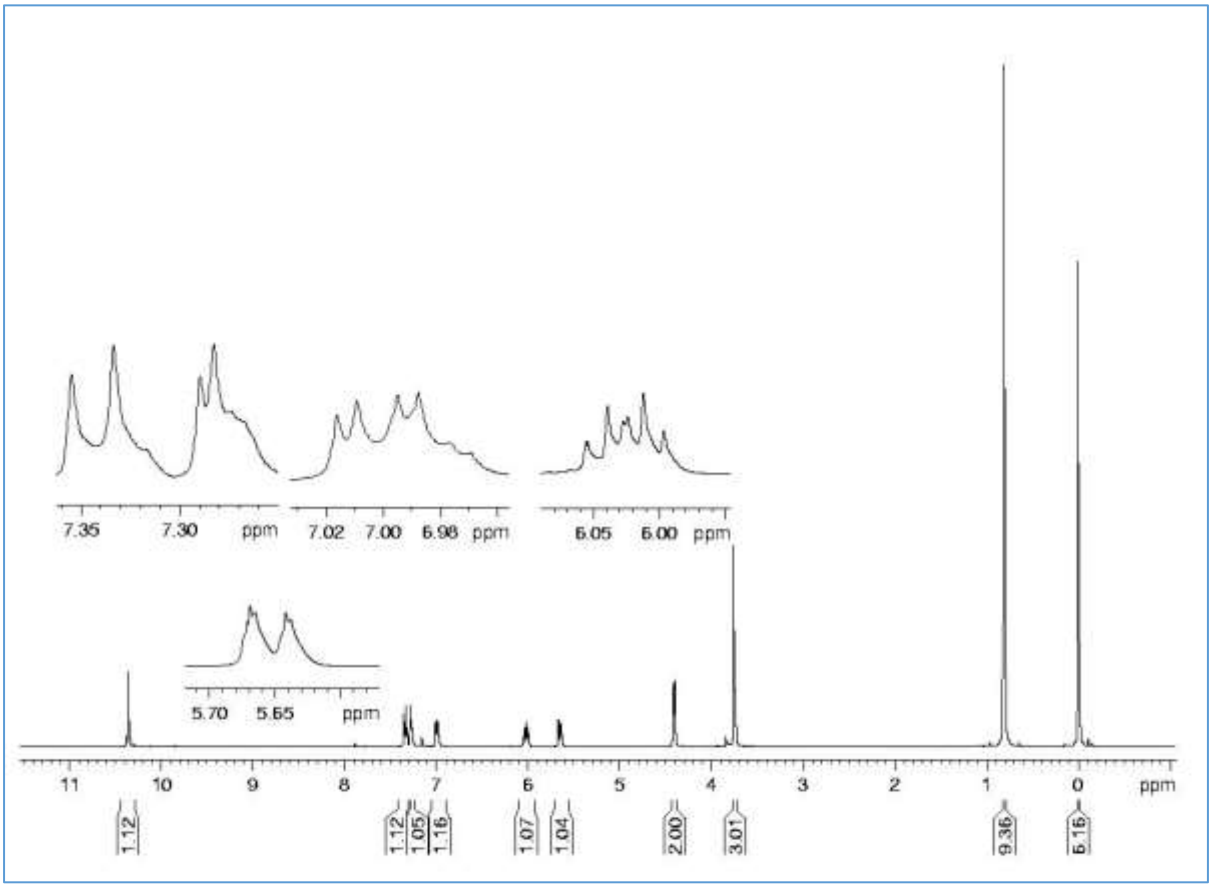
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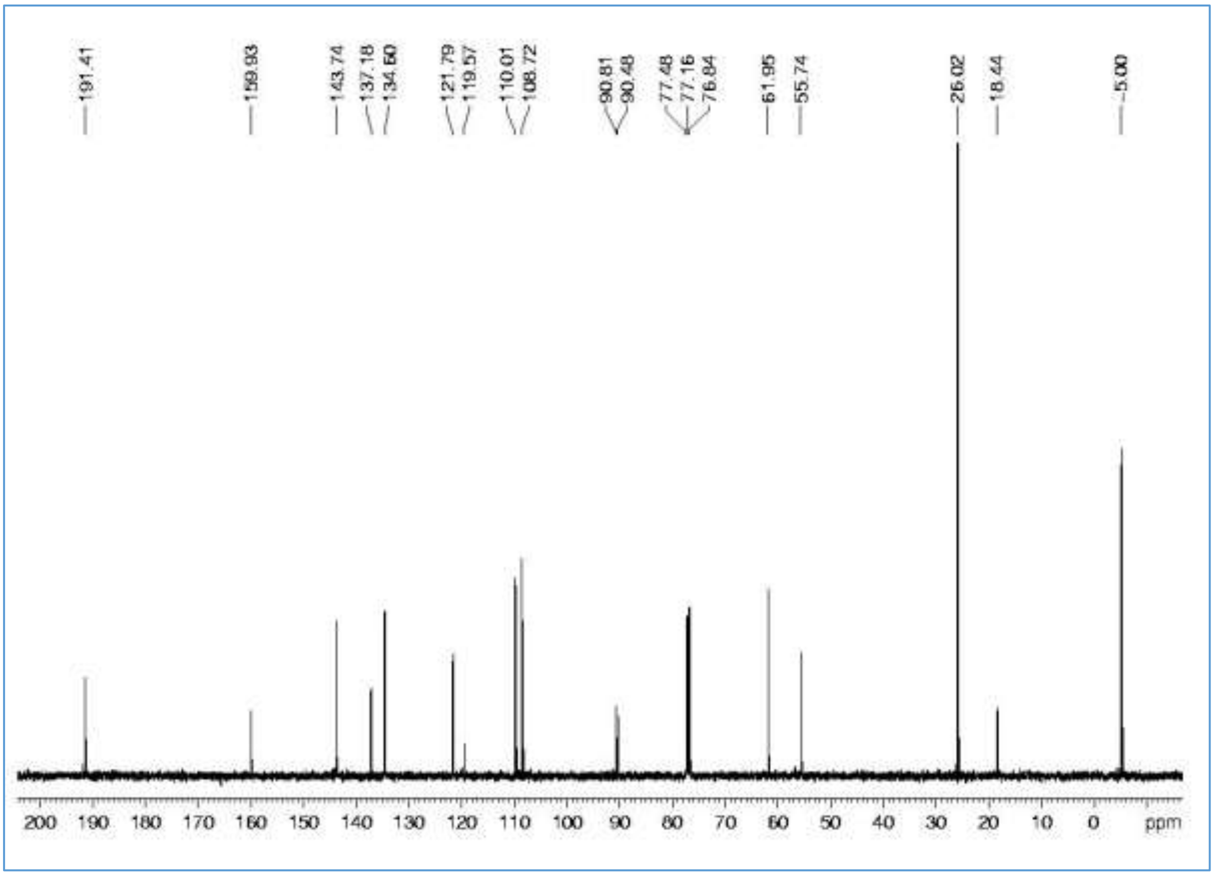
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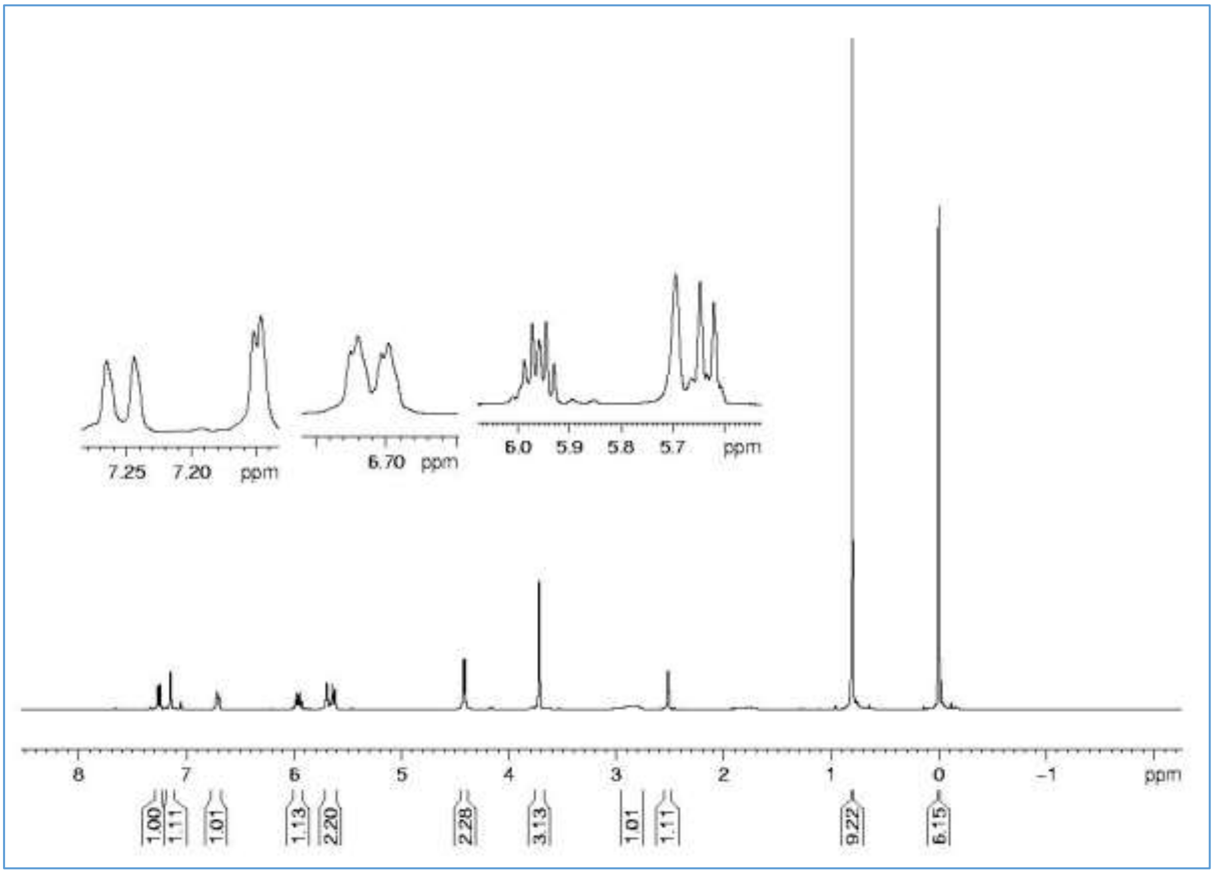
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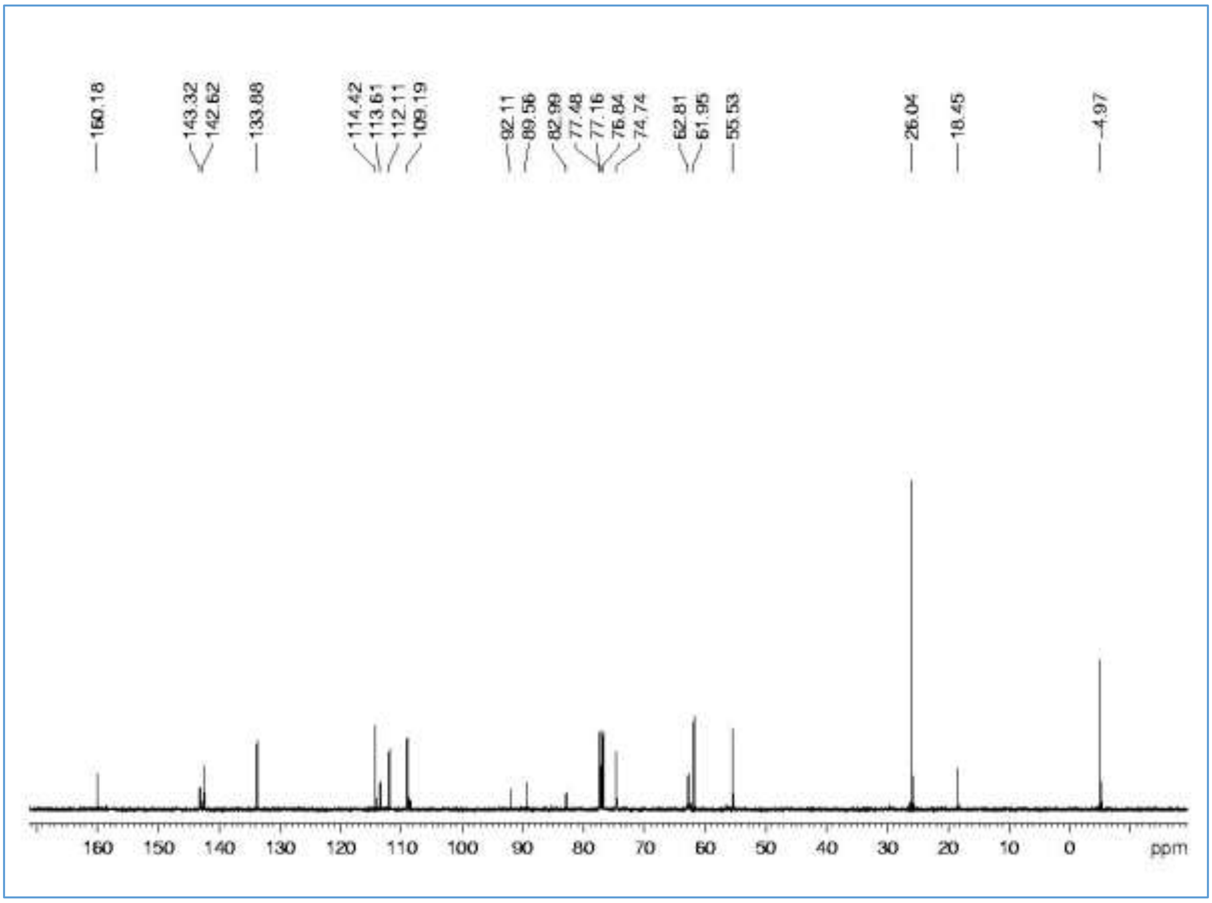
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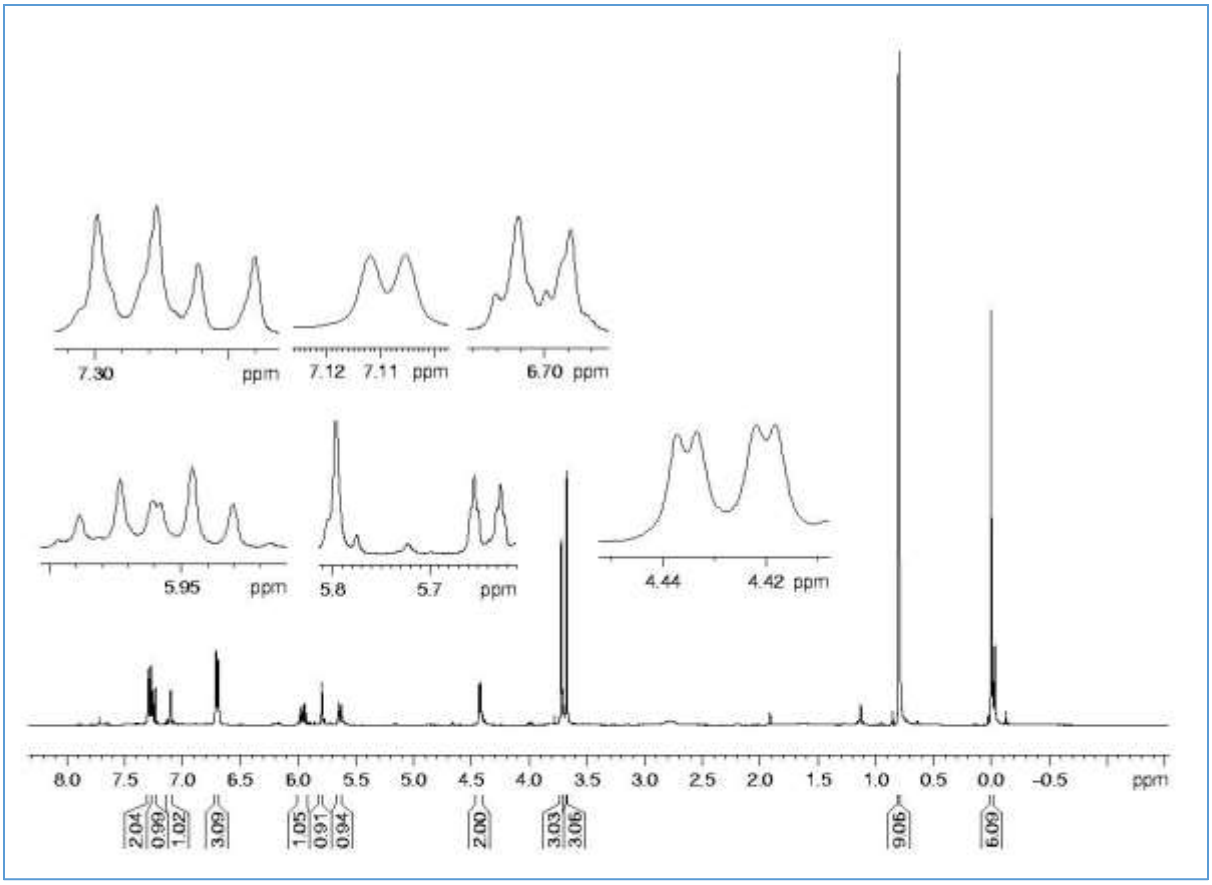
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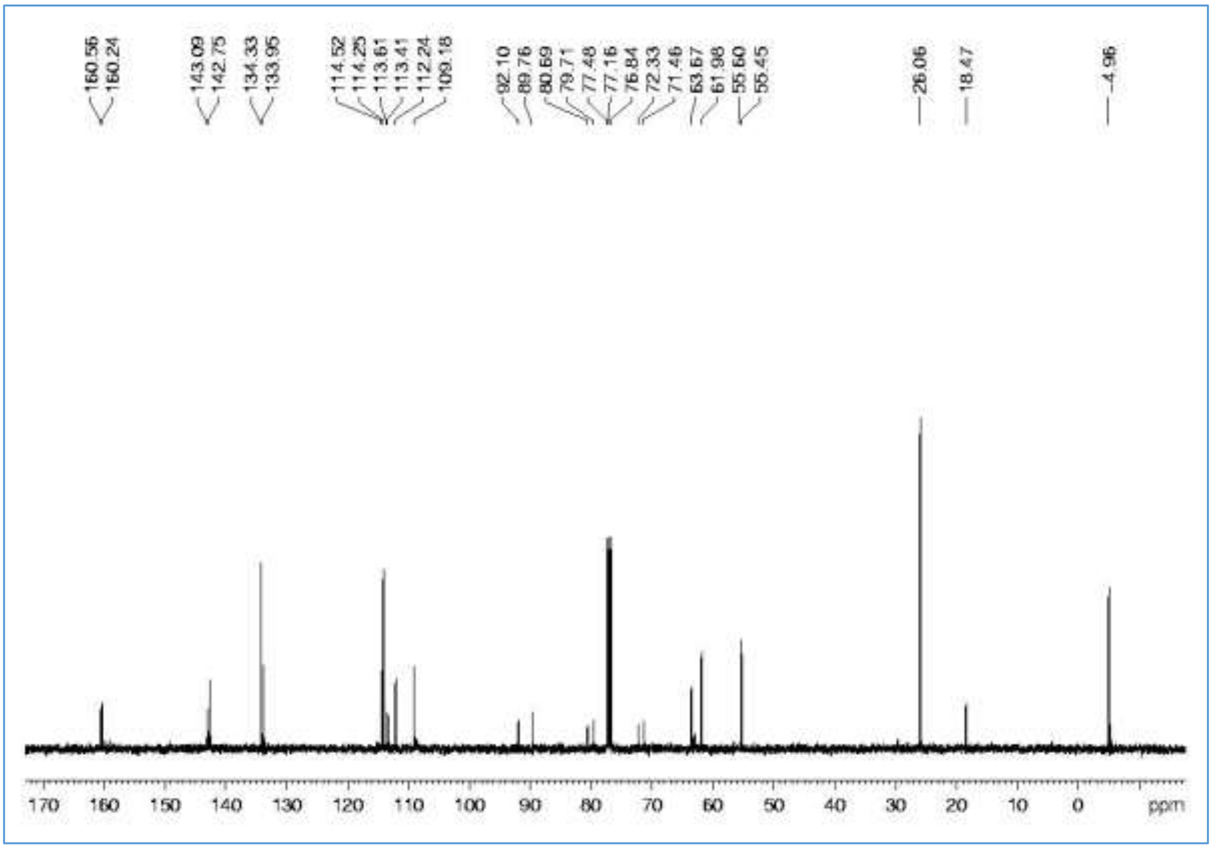
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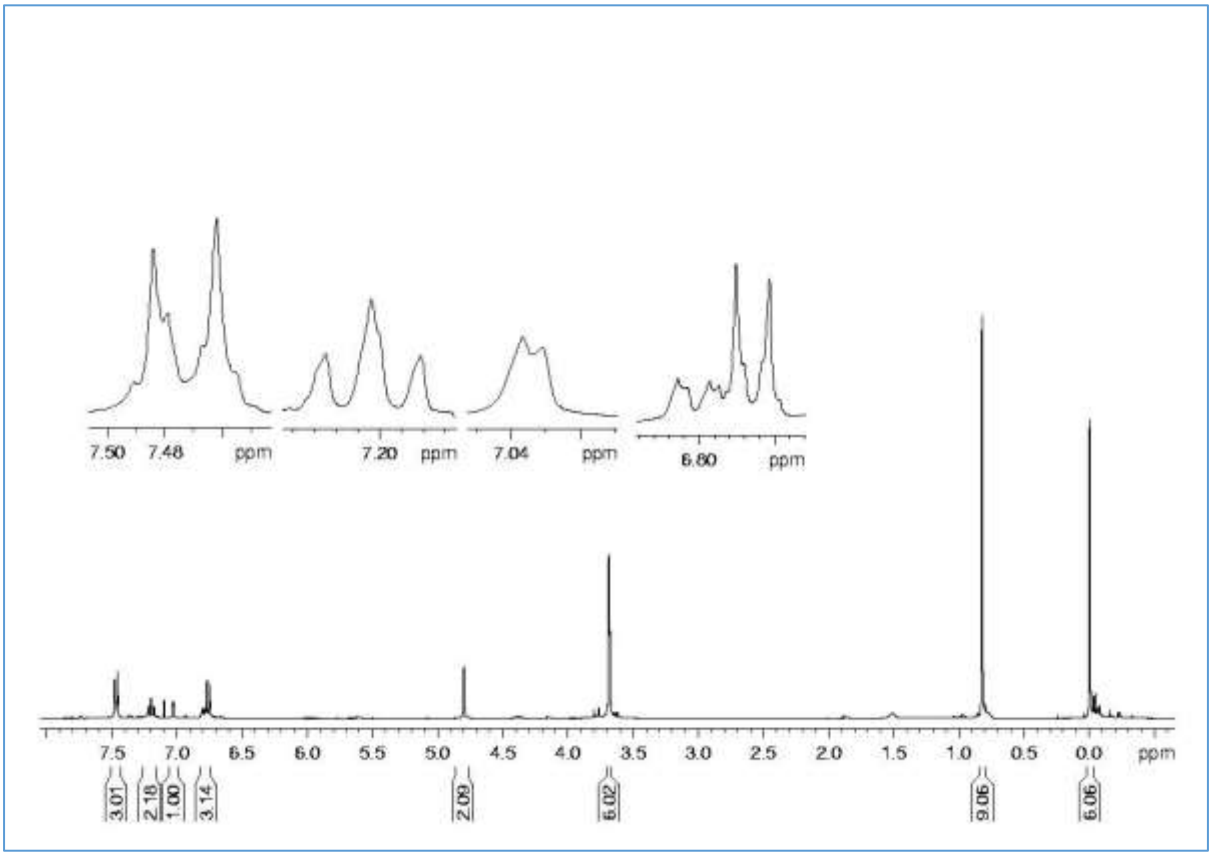
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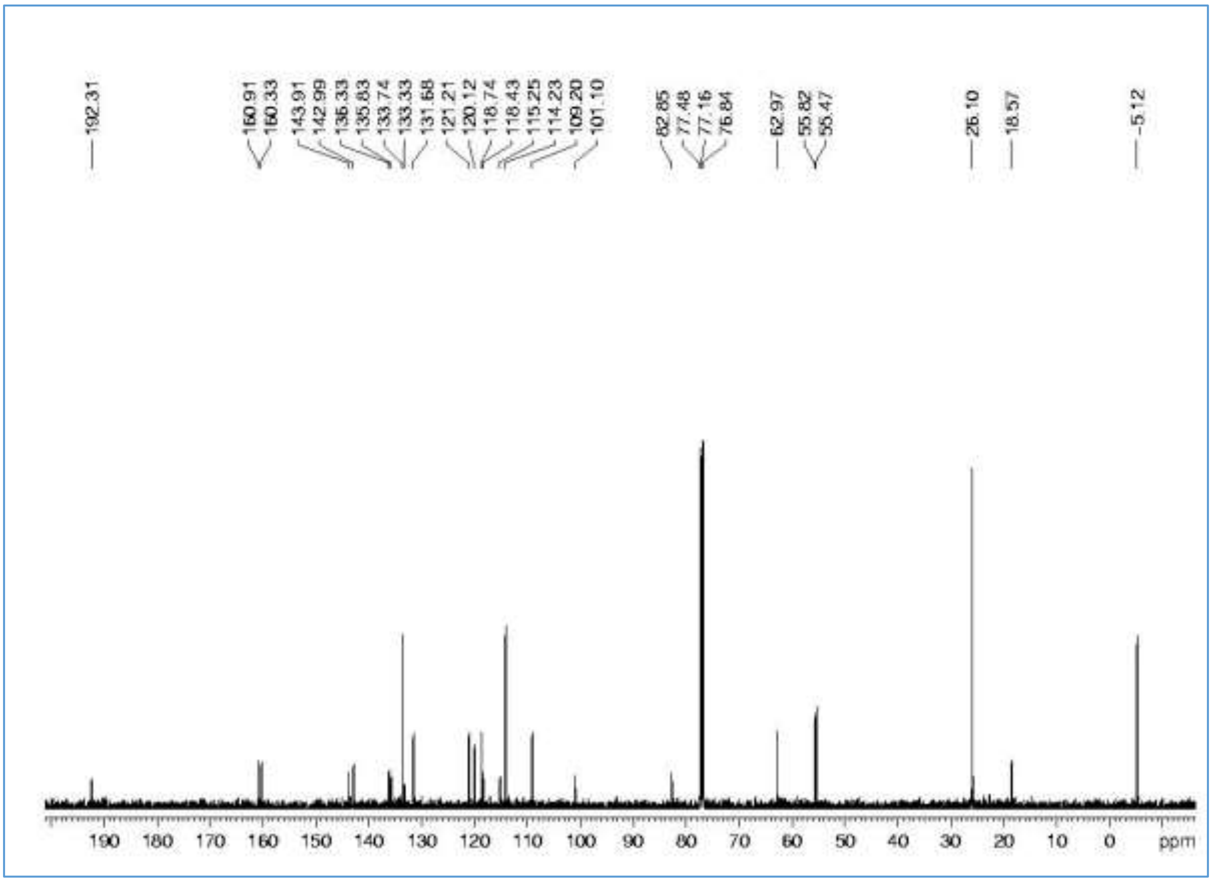
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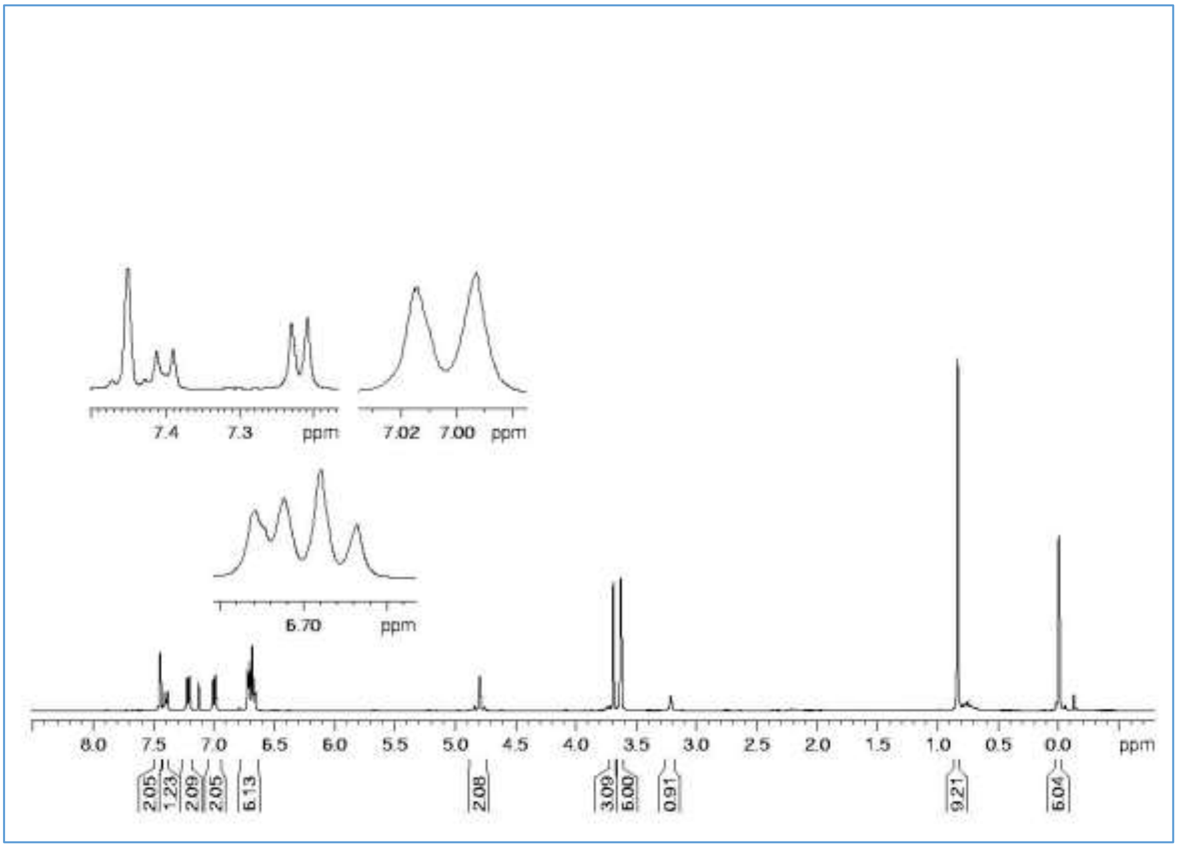
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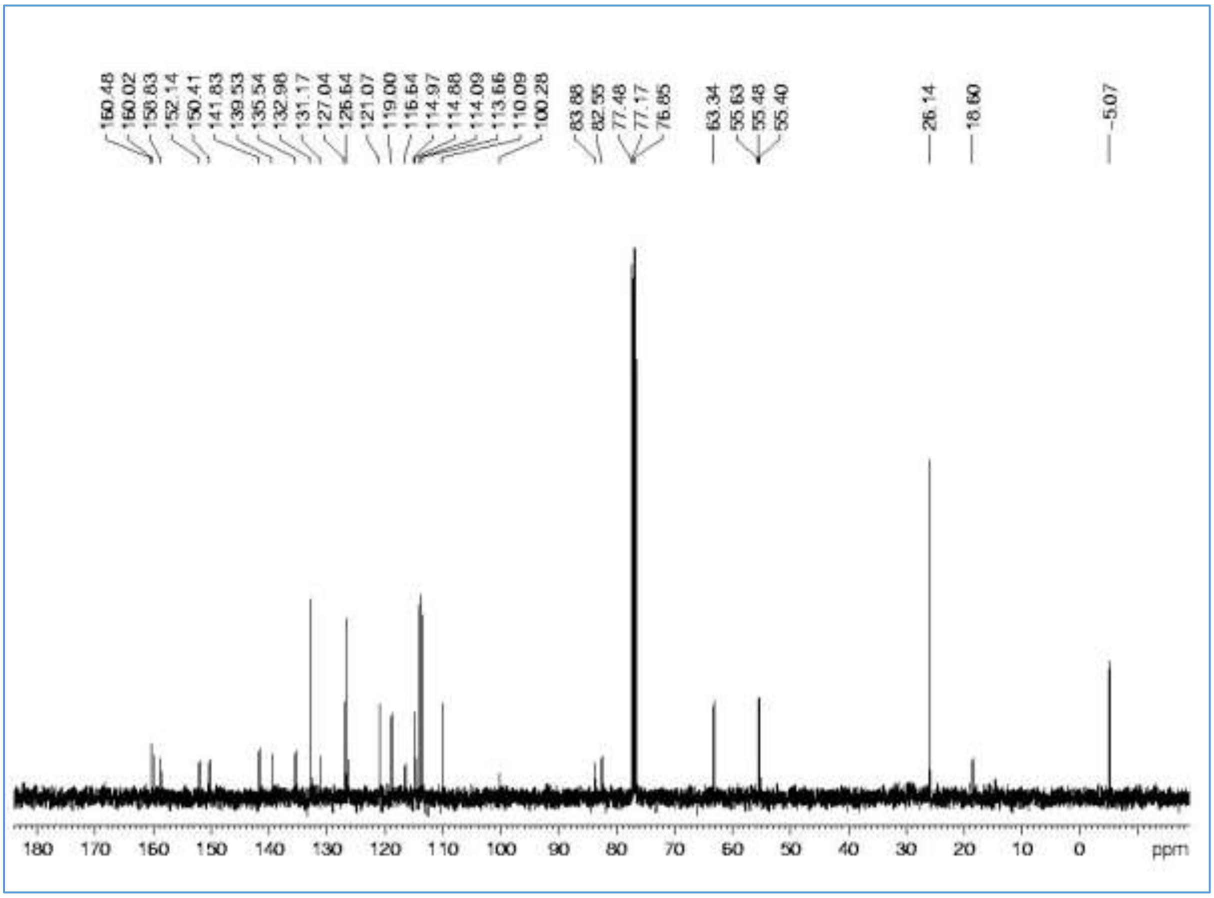
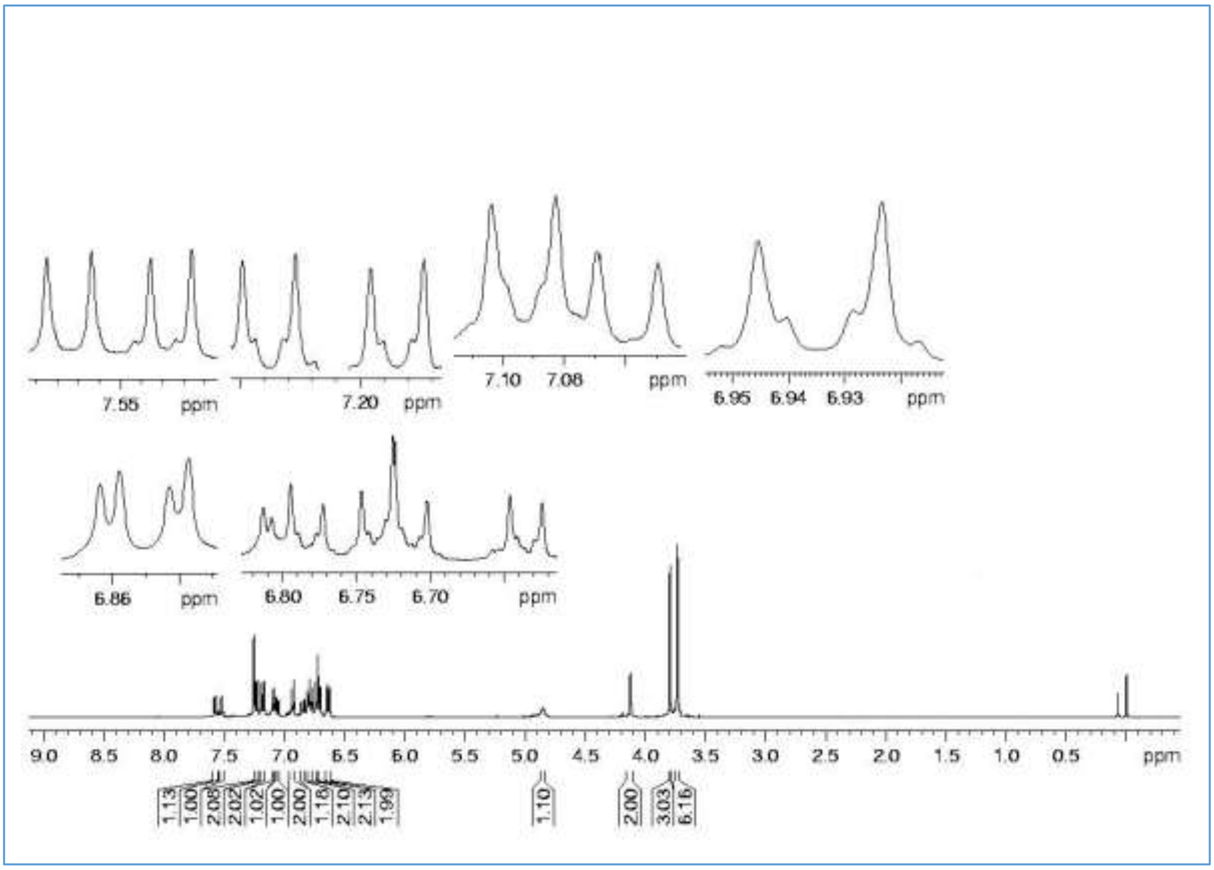


Yin et.al reported selaginpulvilin-A ^{1}H & ^{13}C NMR spectral data (CD3OD)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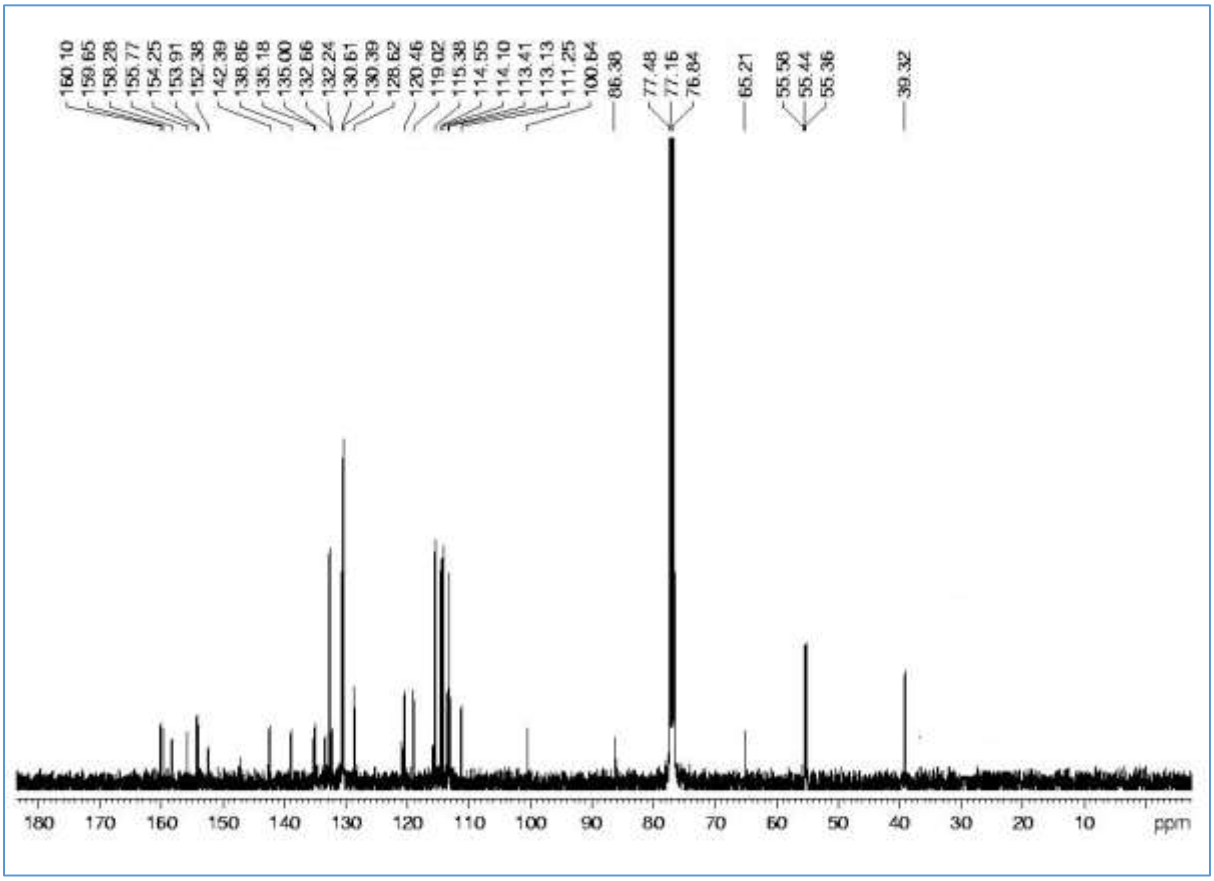
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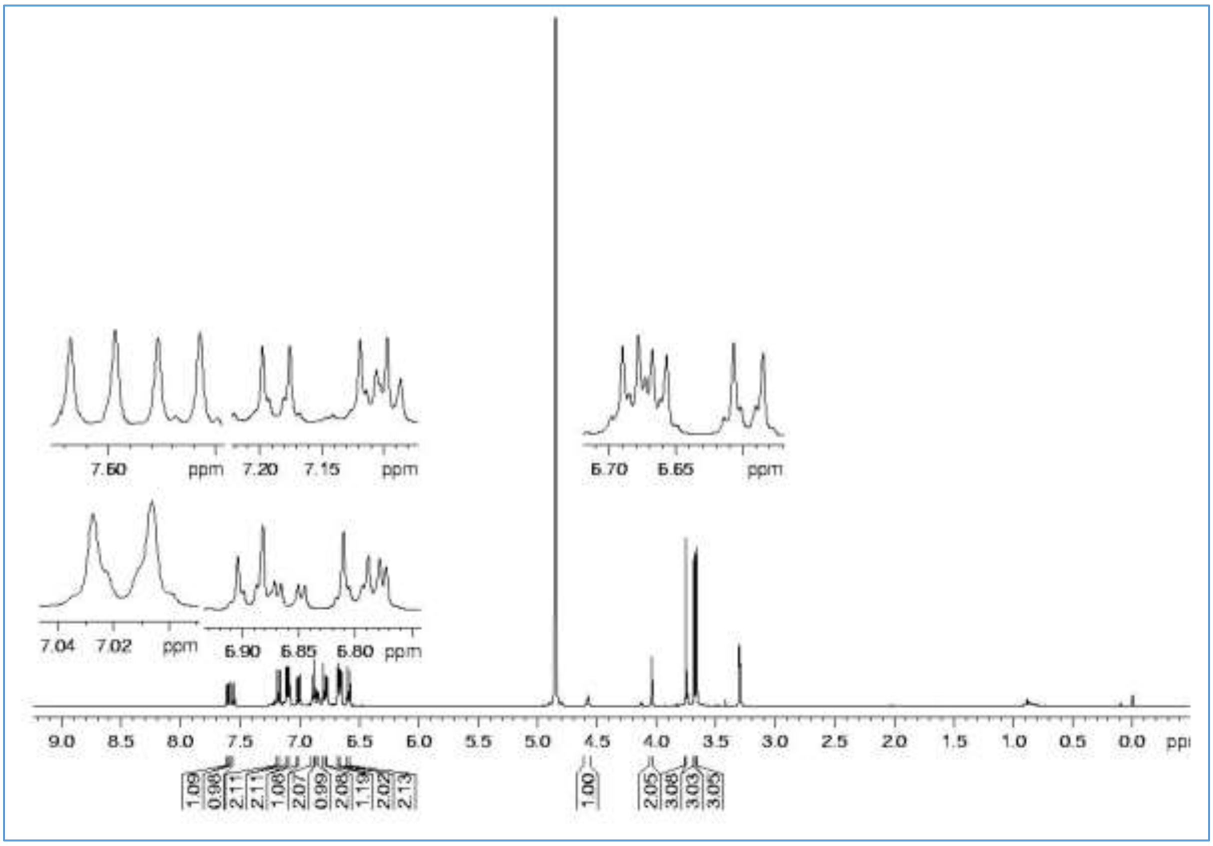
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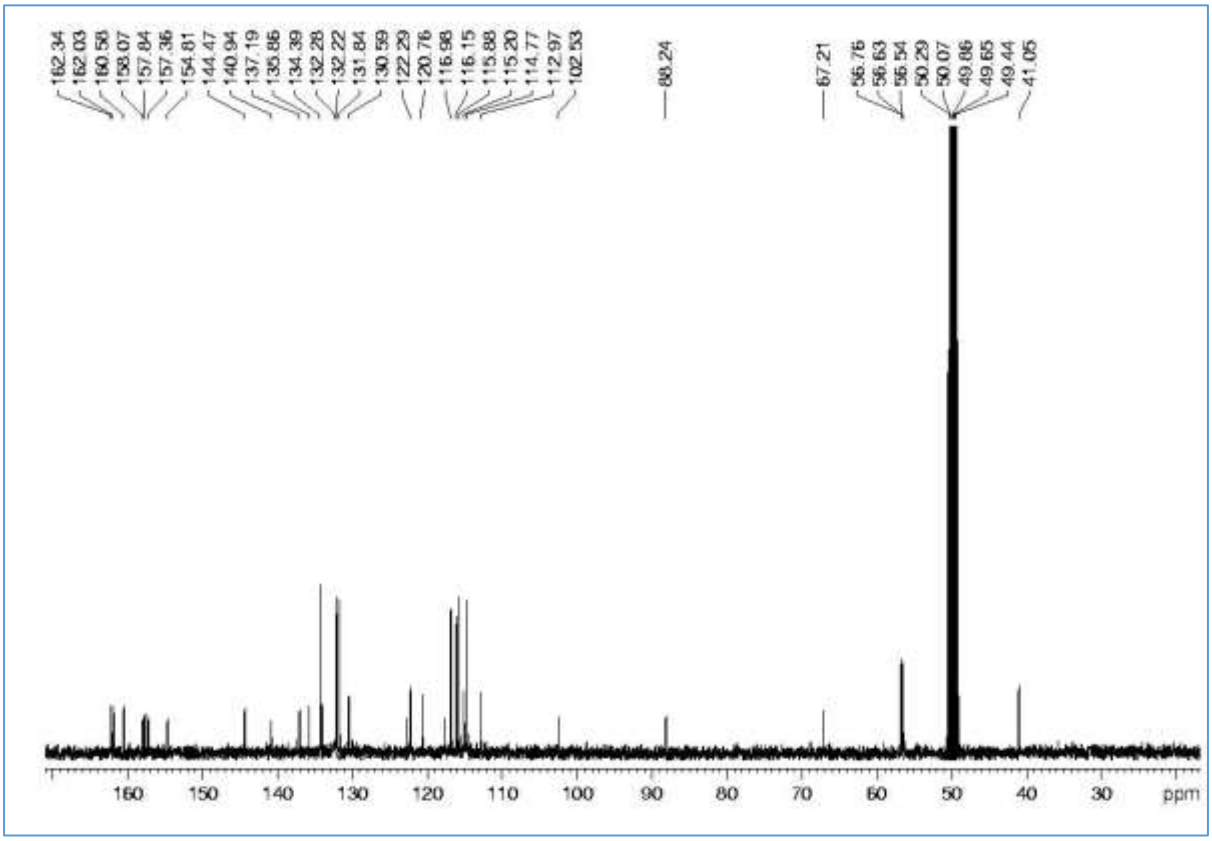
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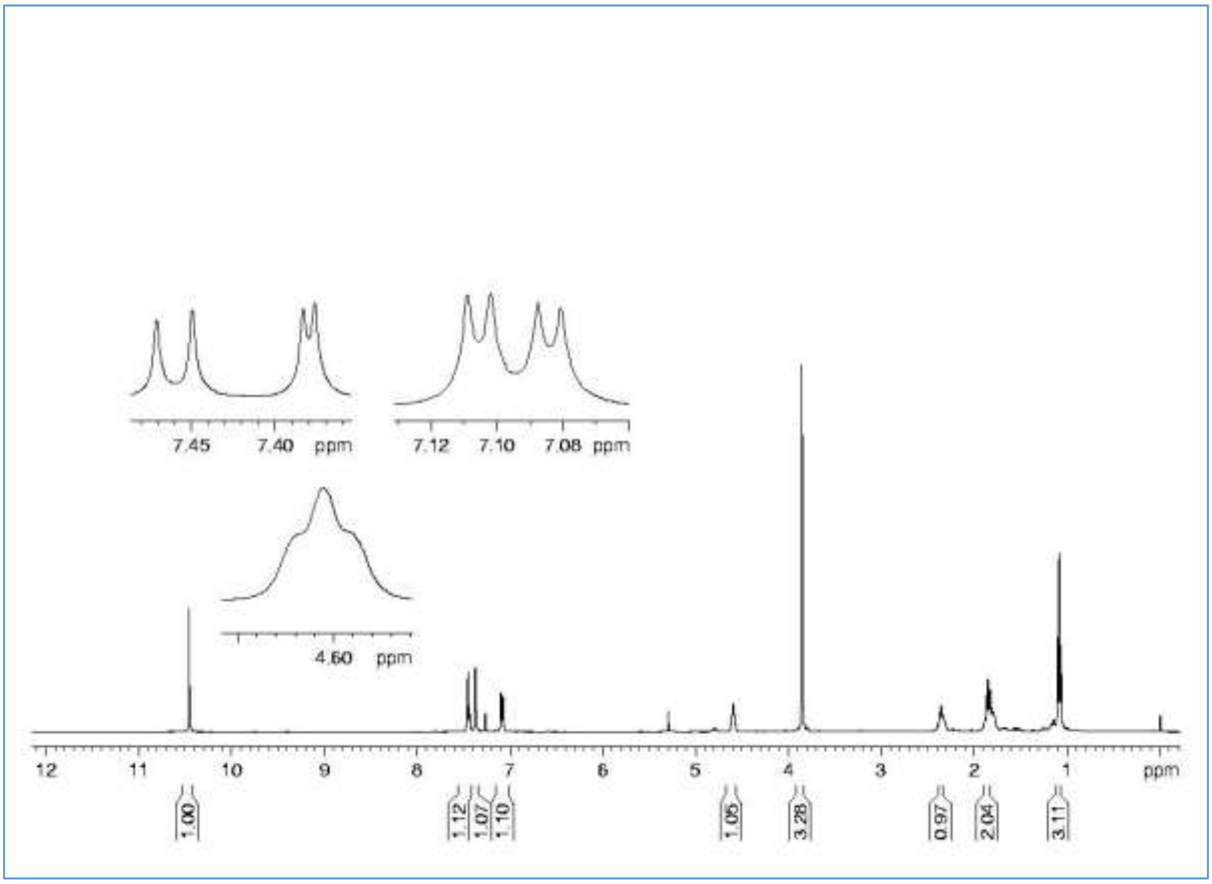
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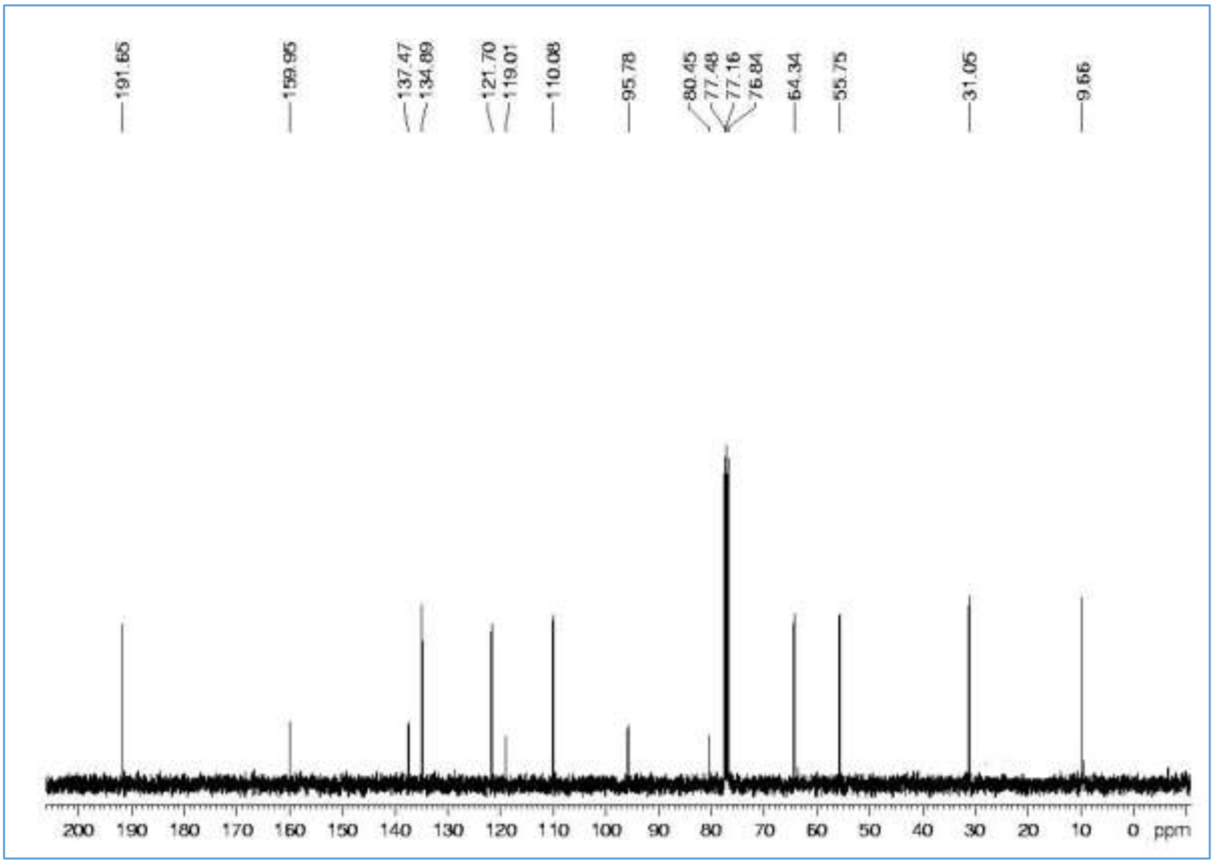
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77.16
76.84
64.34
55.75
31.05
9.66
200
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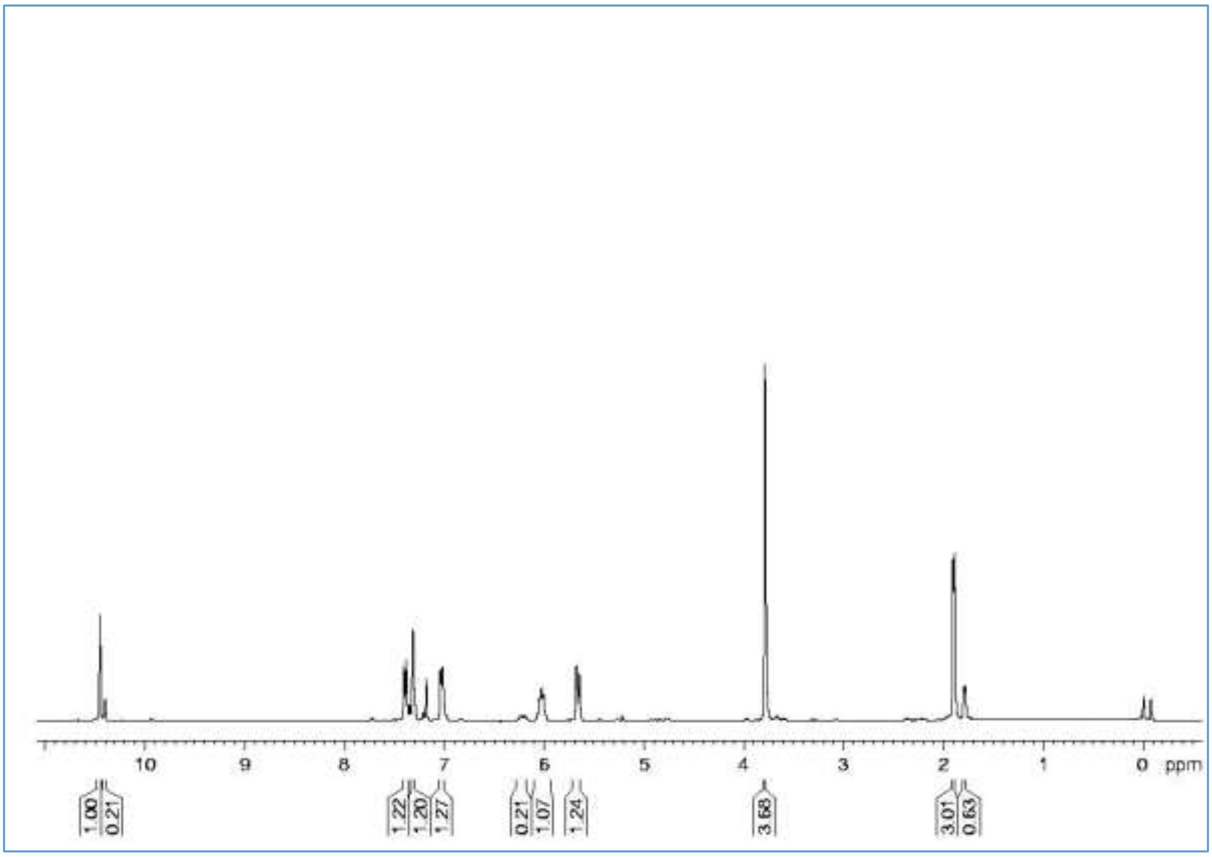
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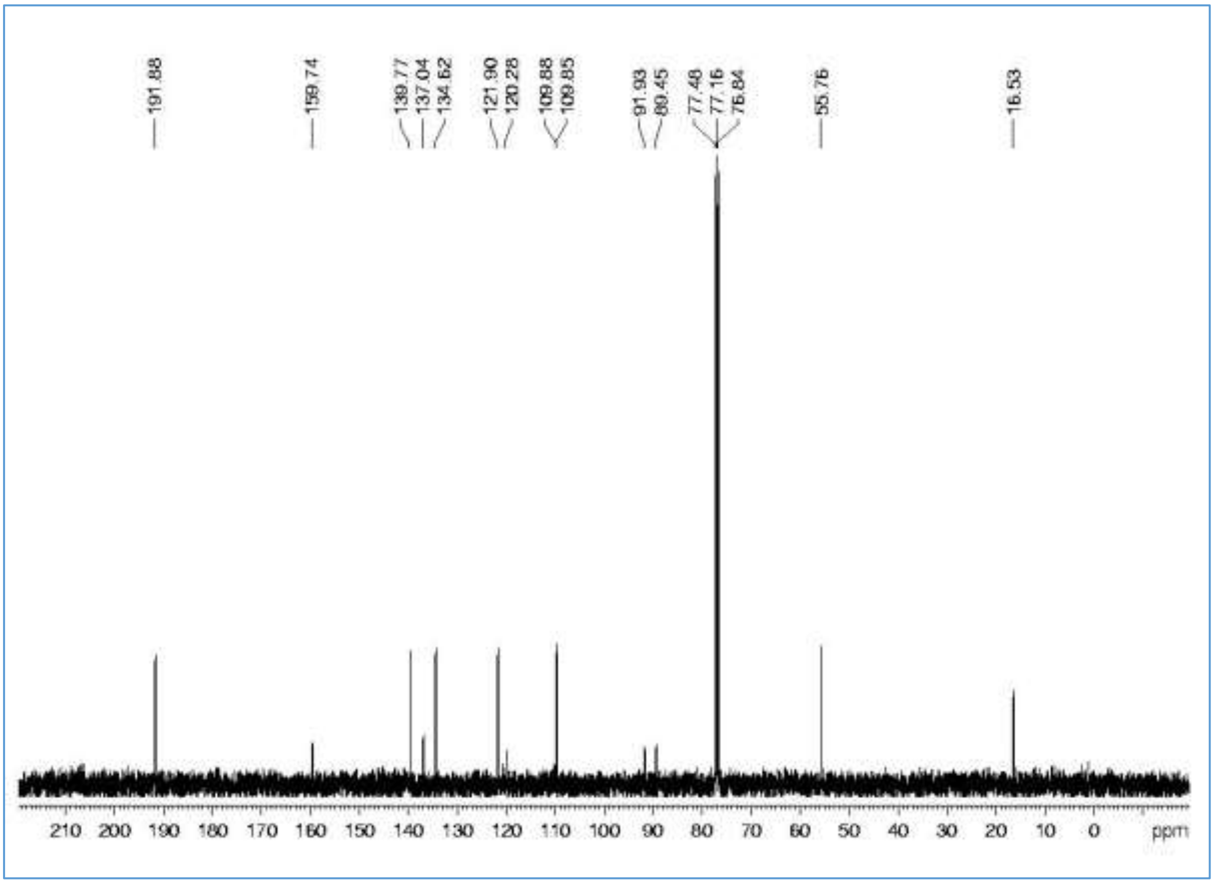
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76.84
55.76
16.53
210
200
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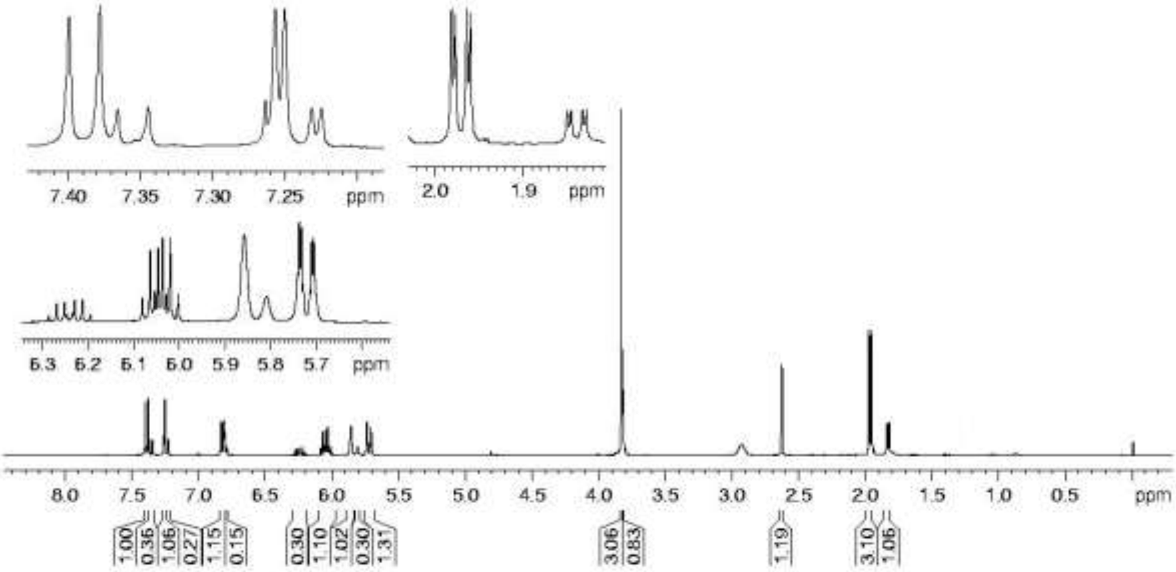
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5.8
5.7
ppm
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.10
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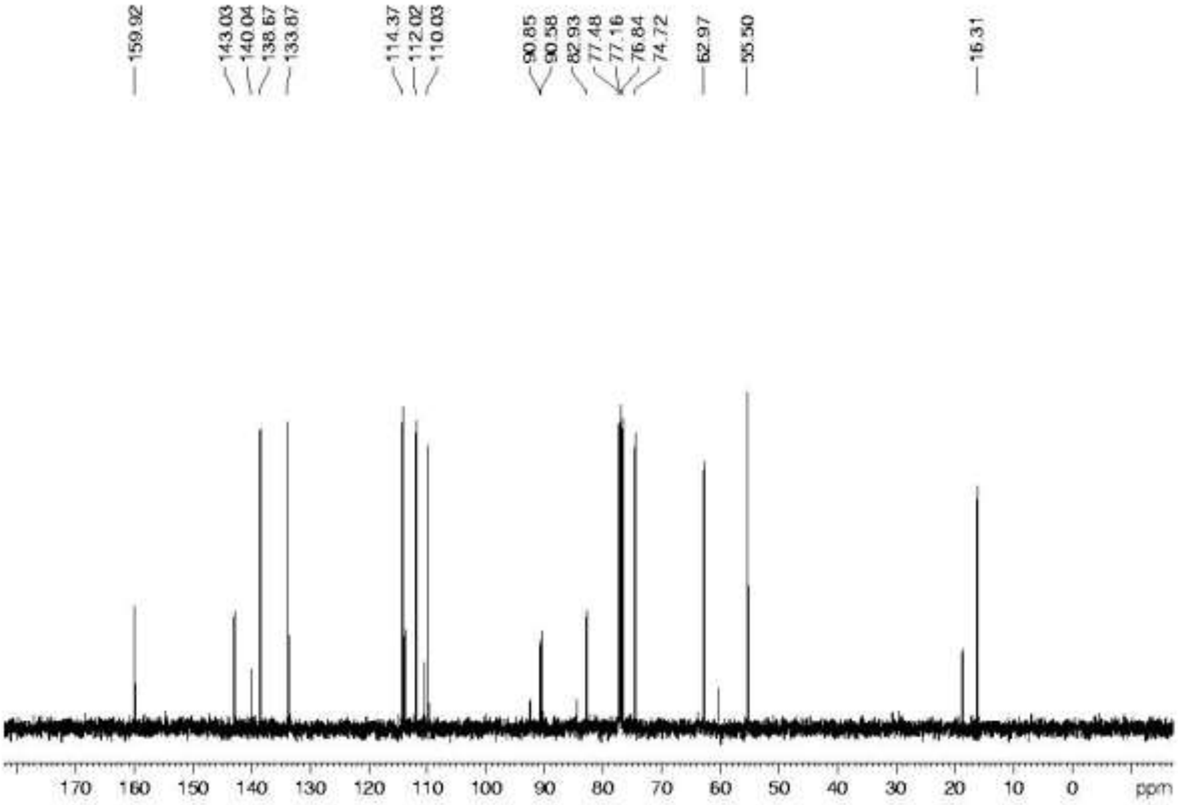
1.06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76.84
74.72
62.97
55.50
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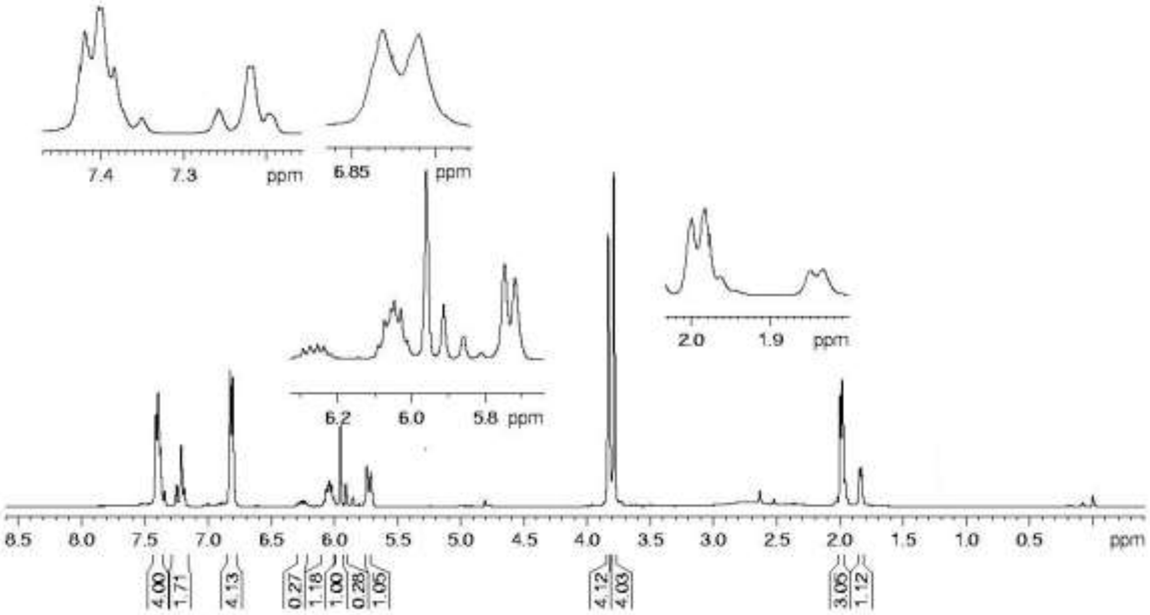
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ppm
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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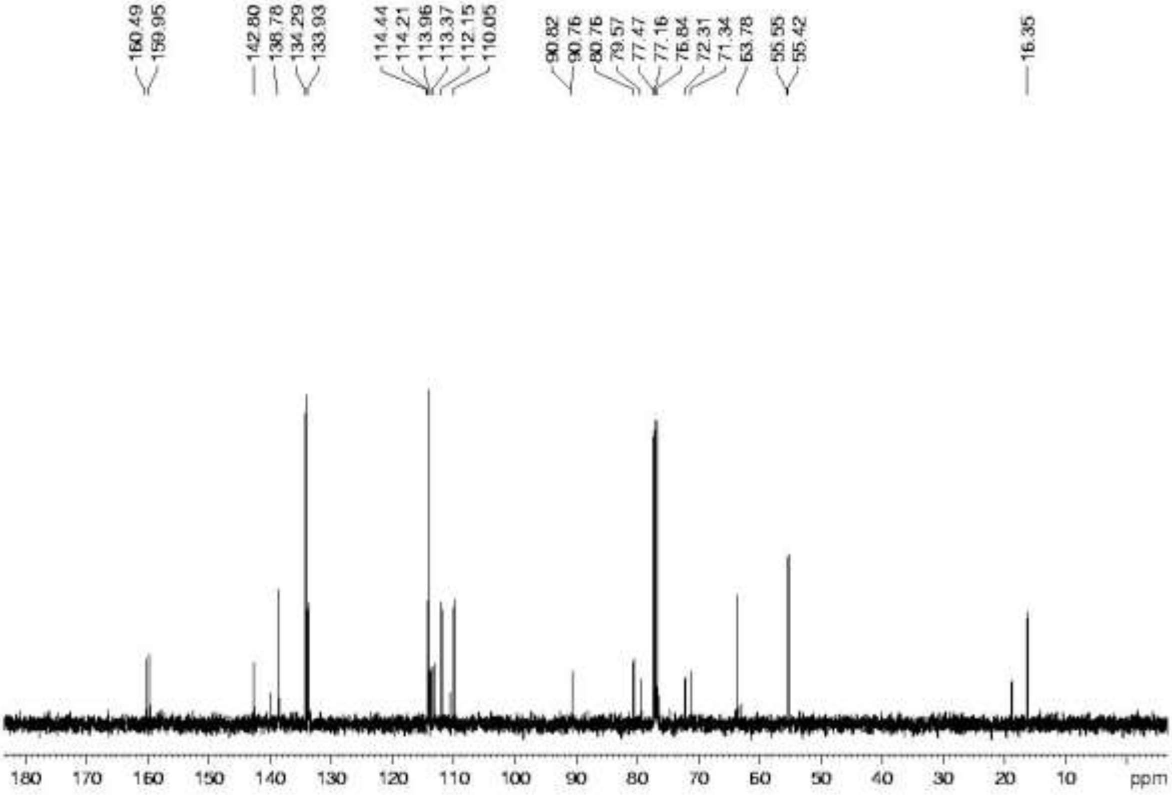
1.12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90.76
80.76
79.57
77.47
77.16
76.84
72.31
71.34
63.78
55.55
55.42
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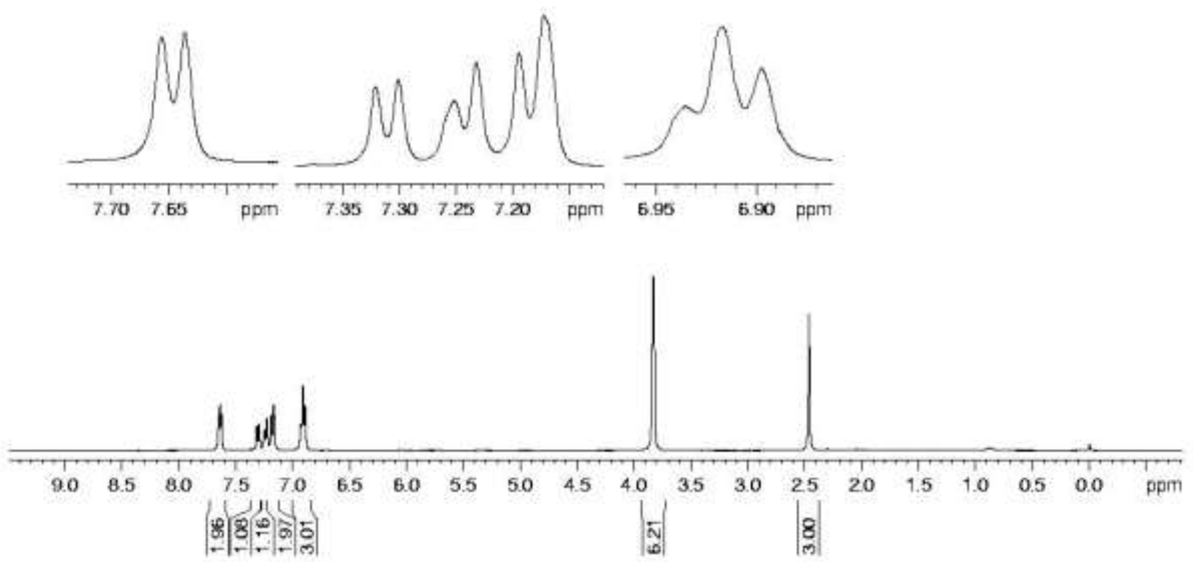
ppm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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
0.0
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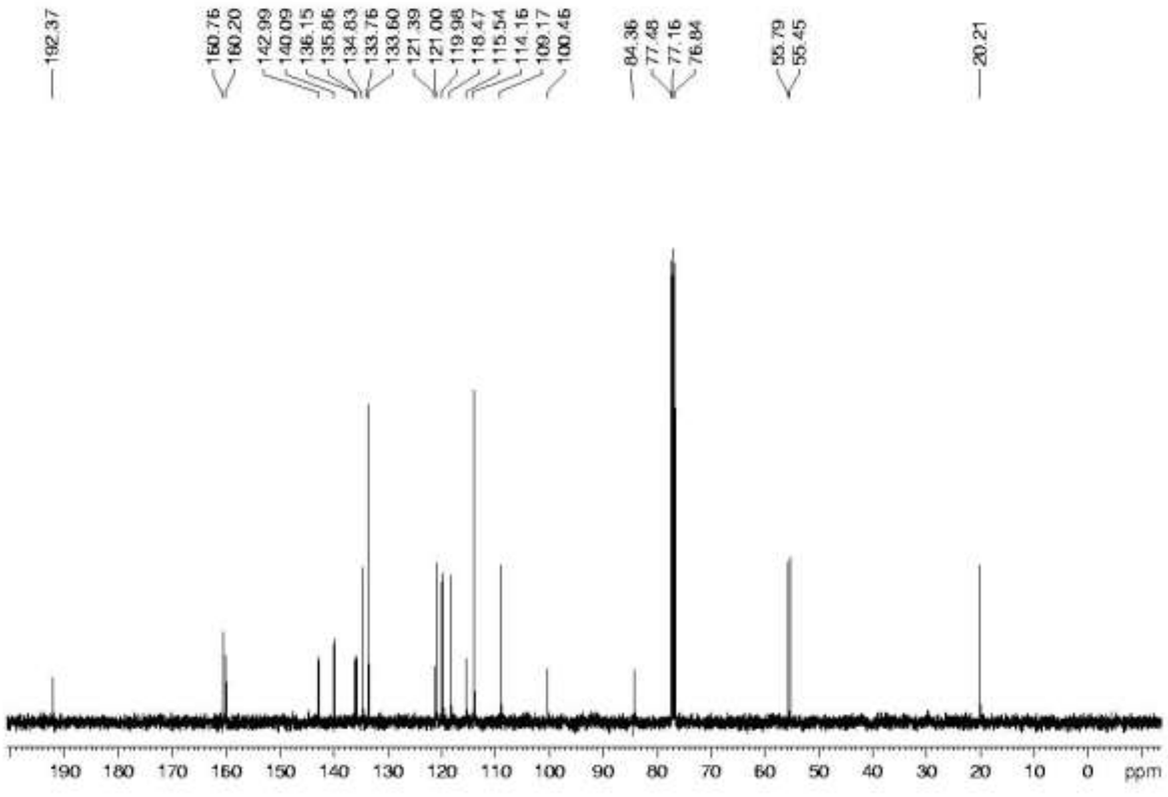
1.16
1.97
3.01
6.21
3.00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115.54
114.16
109.17
100.46
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77.48
77.16
76.84
55.79
55.45
20.21
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140
130
120
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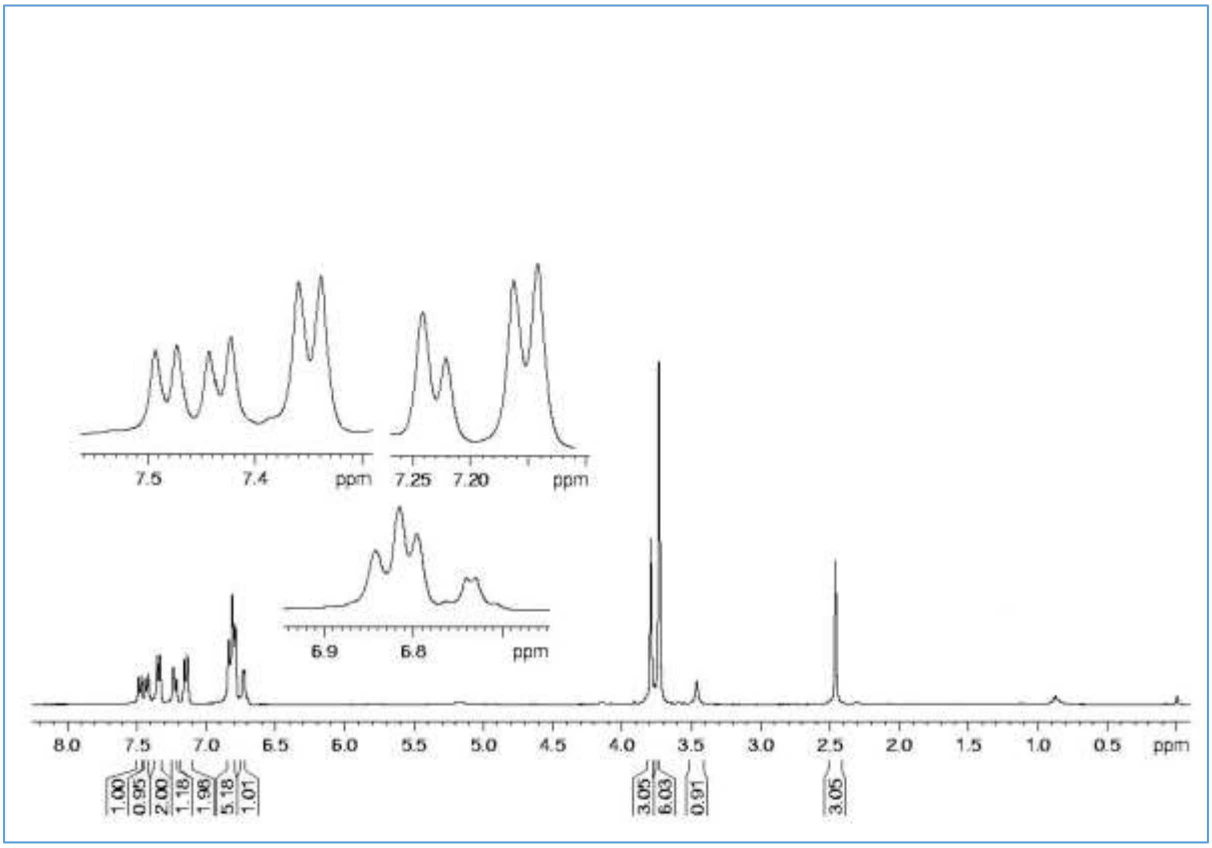
ppm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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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ppm
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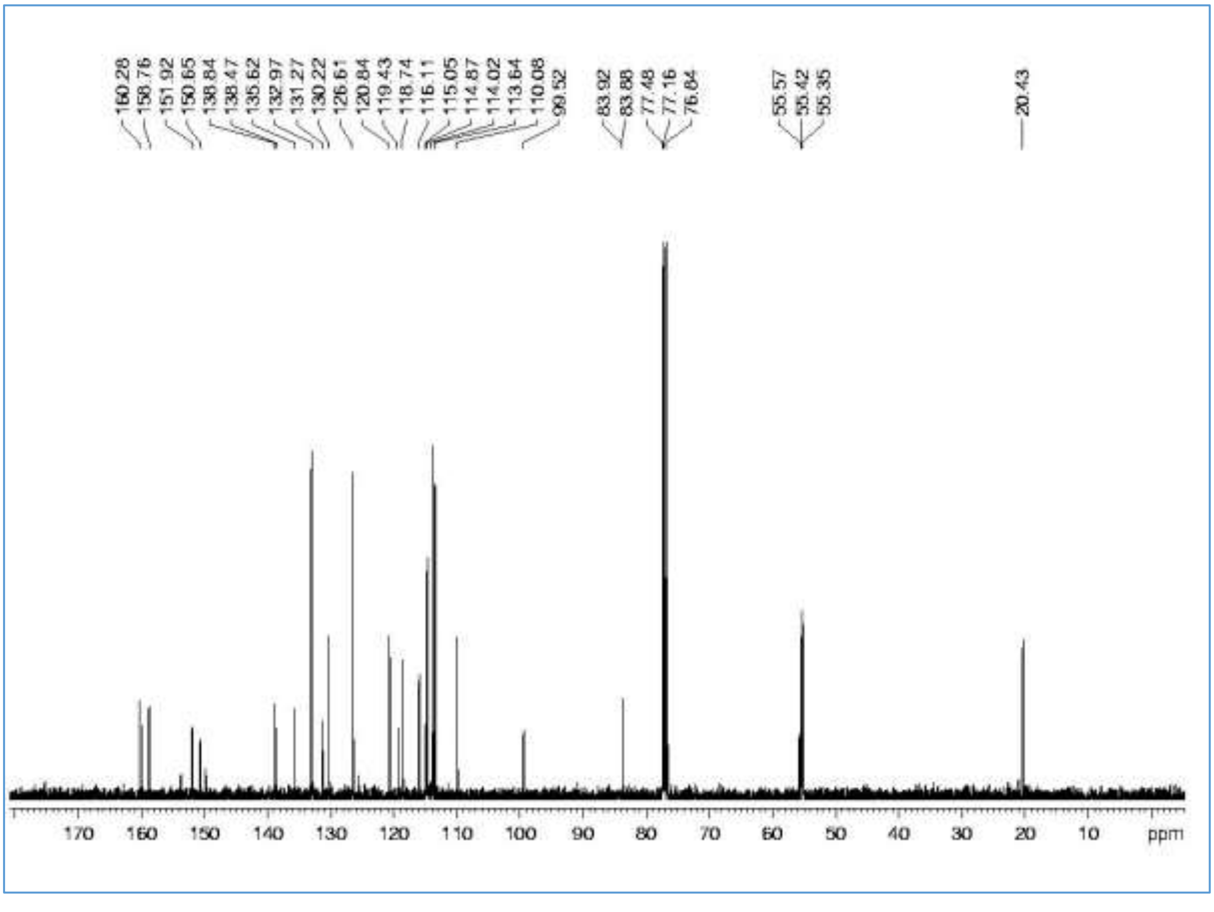
2.00
1.18
1.98
5.18
1.01
3.05
6.03
0.91
3.05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126.61
120.84
119.43
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116.11
115.05
114.87
114.02
113.64
110.08
99.52
83.92
83.88
77.48
77.16
76.84
55.57
55.42
55.35
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150
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30
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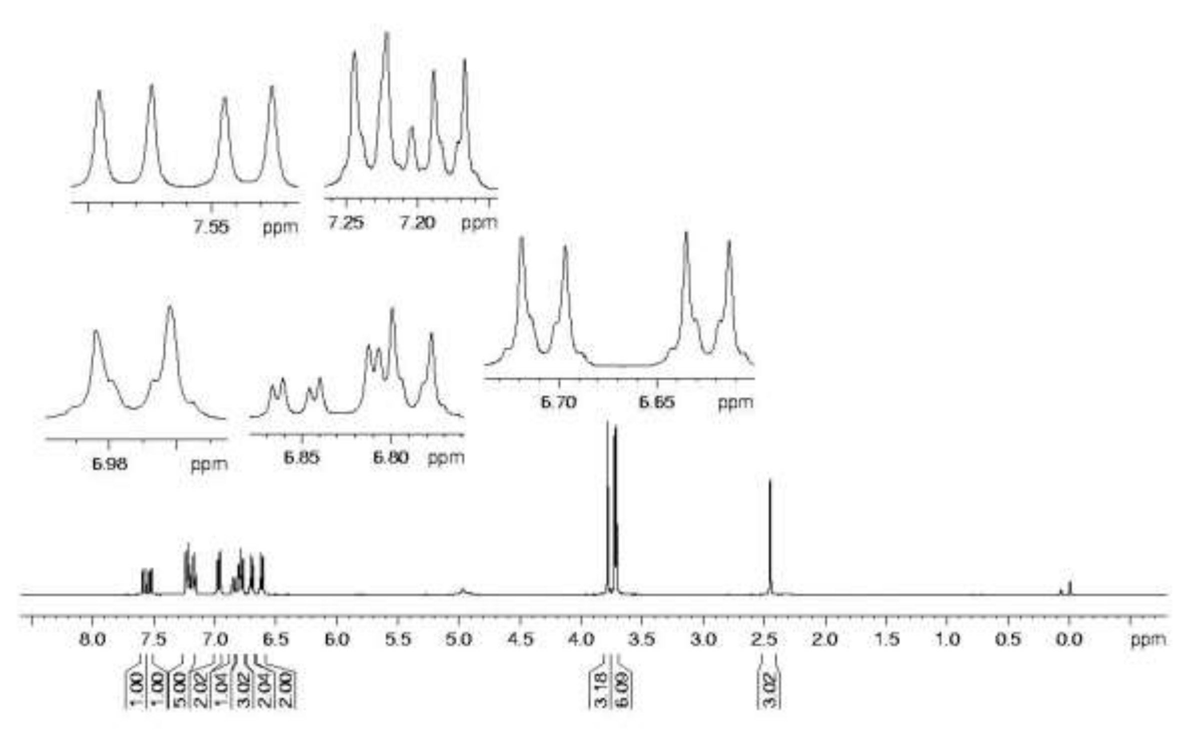
10
ppm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ppm
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ppm
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6.80
ppm
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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5.00
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2.04
2.00
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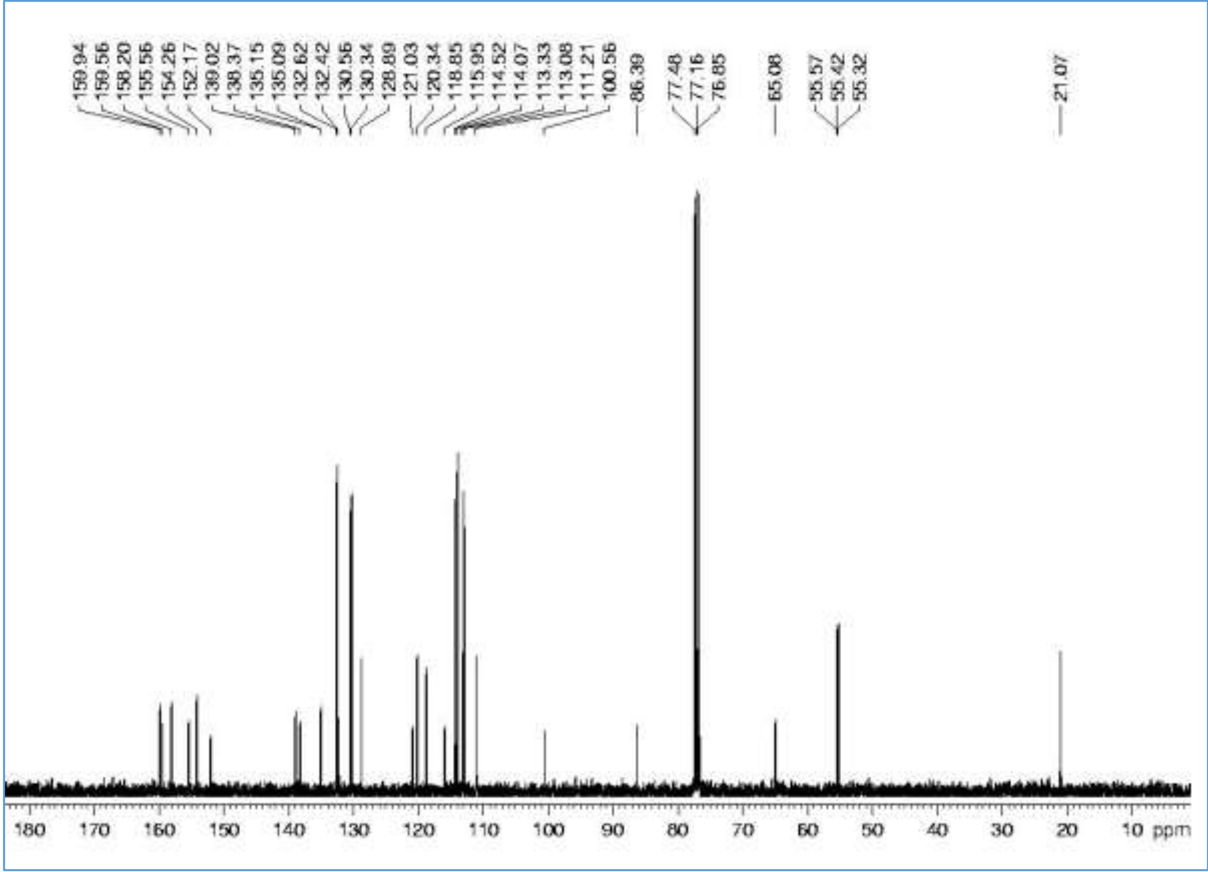
6.09
3.02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120.34
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115.95
114.52
114.07
113.33
113.08
111.21
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86.39
77.48
77.16
76.85
65.08
55.57
55.42
55.32
21.07
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170
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100
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40
30
20
10
ppm