Ultrasound-mediated One-pot Synthesis of The Fully Funtionalized *N*,*N′*-(1,3-Propane)-Bispyrrole

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General Information

Melting points were recorded on a Yanaco hot-stage melting point apparatus and uncorrected. Purification of reaction products was carried out by flash chromatography using EM Reagent silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz using a JEOL ECA 400 or ECX 400 spectrometer. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration). Elemental analyses were performed with a Yanaco MT-5 CHN-Corder. All high resolution mass spectra were obtained on a micro TOF-QII 10203 spectrometer. Ultrasonication was done in a KQ5200DE and a frequency of 40 kHz ultrasound clear with an out power 200W. All of the organic solvents used in this study were dried over appropriate drying agents. Bisimines were prepared using literature procedures.[2]

A two–neck round bottom flask equipped with a magnetic bar was charged the bisimine (0.1 mmol, 1 equiv.), aroyl chloride (0.22 mmol, 2.2 equiv.) and acetonitrile (2 mL), and stirring; After 0.5 h, at room temperature, *tert*-butyl isocyanide (0.22 mmol, 2.2 equiv.) was injected by syringe. After 0.5 h, at room temperature, diisopropylethylamine (0.22 mmol, 2.2 equiv.) was injected. After 0.5 h, at room temperature, DMAD (0.22 mmol, 2.2 equiv.) was injected and the reaction was carried out under ultrasonic irradiation for 2 or 3 h. The solution was concentrated in vacuo, the crude products were purified by silica gel chromatography using dichloromethane/ethyl acetate (*V*:*V* = 4:1) as eluent.

Tetramethyl 1,1′-(propane-1,3-diyl) bis(2,5-diphenyl-1*H*-pyrrole-3,4-dicarboxylate) [3a]

Colorless solid, yield: 72.5%. mp 119–121 °C. R_f = 0.75. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.06–1.12 (m, 2H, CH_2), 3.16–3.20 (t, *J* = 7.6 Hz, 4H, CH_2), 3.61 (s, 12H, CH_3), 7.02–7.09 (d, *J* = 8.4 Hz, 8H, ArH), 7.33–7.42 (m, 12H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.5, 41.6,51.6, 114.7, 128.5, 128.9, 130.2, 130.3,136.0, 166.1. HRMS (ESI^+) calcd for $C_{43}H_{38}N_2O_8$ (MH^+) 711.7768, found 711.7766. Anal. Calcd for. $C_{43}H_{38}N_2O_8$: C, 72.66; H, 5.39; N, 3.94%. Found: C, 72.43; H, 5.43; N, 3.81.

Tetramethyl 1,1′-(propane-1,3-diyl) bis[2-phenyl-5-(4-methoxyphenyl)-1*H*-pyrrole-3,4-dicarboxylate] [3b]

Colorless solid, yield: 74.6%. mp 82–85 °C. R_f = 0.67. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.07–1.15 (m, 2H, CH_2), 3.16–3.20 (t, *J* = 8.0 Hz, 4H, CH_2), 3.60 (s, 6H, CH_3), 3.62 (s, 6H, CH_3), 3.87 (s, 6H, CH_3), 6.87–6.89 (d, *J* = 8.8 Hz, 4H, ArH), 7.00–7.02 (d, *J* = 8.8 Hz, 4H, ArH), 7.06–7.08 (d, *J* = 6.8 Hz, 4H, ArH), 7.30–7.42 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.6, 41.6, 51.6, 55.3, 113.9, 114.5, 114.6, 122.3, 128.5, 128.8, 130.2, 130.4, 131.5, 135.7, 135.9, 159.9, 165.2, 165.3. HRMS (ESI^+) calcd for $C_{45}H_{42}N_2O_{10}$ (MH^+) 771.8286, found 771.8285. Anal. Calcd for. $C_{45}H_{42}N_2O_{10}$: C, 70.12; H, 5.49; N, 3.63%. Found: C, 69.75; H, 5.57; N, 3.87.

Tetramethyl 1,1′-(propane-1,3-diyl) bis[2-phenyl-5-(4-nitrophenyl)-1*H*-pyrrole-3,4-dicarboxylate] [3c]

Yellow solid, yield: 69%. mp 199–201 °C. R_f = 0.70. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.96–1.04 (m, 2H, CH_2), 3.23–3.27 (t, *J* = 7.6 Hz, 4H, CH_2), 3.62 (s, 6H, CH_3), 3.63 (s, 6H, CH_3), 7.12–7.14 (t, *J* = 7.6 Hz, 4H, ArH), 7.24–7.26 (d, *J* = 8.8 Hz, 4H, ArH), 7.37–7.47(m, 6H, ArH), 8.19–8.21 (d, *J* = 8.8 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 29.7, 41.8, 51.9, 53.5, 115.7, 116.0, 123.7, 128.7, 129.4, 129.6, 130.1, 131.2, 133.4, 136.7, 136.8, 147.8, 164.3, 164.8. HRMS (ESI^+) calcd for $C_{43}H_{36}N_4O_{12}$ (MH^+) 801.7720, found 801.7716. Anal. Calcd for. $C_{43}H_{36}N_4O_{12}$: C, 64.50; H, 4.53; N, 7.00%. Found: C, 65.09; H, 5.17; N, 6.50.

Tetramethyl 1,1′-(propane-1,3-diyl) bis[2,5-di(4-methoxyphenyl)-1*H*-pyrrole-3,4-dicarboxylate] [3d]

Colorless solid, yield: 77.7%. mp 261–262 °C. R_f = 0.70. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.11–1.19 (m, 2H, CH_2), 3.16–3.20 (t, *J* = 7.6 Hz, 4H, CH_2), 3.62 (s, 12H, CH_3), 3.87 (s, 12H, CH_3), 6.87–6.89 (d, *J* = 8.8 Hz, 8H, ArH),

7.00–7.02 (d, J = 8.4 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.7, 41.5, 51.6, 55.3, 113.9, 114.4, 122.4, 131.5, 135.7, 159.9, 165.4. HRMS (ESI^+) calcd for $C_{47}H_{46}N_2O_{12}$ (MH^+) 831.8804, found 831.8800. Anal. Calcd for. $C_{47}H_{46}N_2O_{12}$: C, 67.94; H, 5.58; N, 3.37%. Found: C, 67.94; H, 5.77; N, 3.37.

Tetramethyl 1,1′-(propane-1,3-diyl) bis[2-(4-methoxyphenyl)-5-(4-nitrophenyl)-1*H*-pyrrole-3,4-dicarboxylate] [3e]

Yellow solid, yield: 62.5%. mp 98–101 °C. R_f = 0.55. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.01–1.09 (m, 2H, CH_2), 3.22–3.26 (t, J = 7.6 Hz, 4H, CH_2), 3.62 (s, 6H, CH_3), 3.64 (s, 6H, CH_3), 3.89 (s, 6H, CH_3), 6.92–6.94 (d, J = 8.8 Hz, 4H, ArH), 7.07–7.09 (d, J = 8.8 Hz, 4H, ArH), 7.23–7.25 (d, J = 7.6 Hz, 4H, ArH), 8.19–8.21 (d, J = 8.0 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.5, 41.8, 51.9, 55.4, 113.9, 114.1, 115.6, 115.7, 121.5, 123.6, 131.2, 131.5, 133.1, 136.7, 136.9, 147.9, 160.3, 164.5, 164.9. HRMS (ESI^+) calcd for $C_{45}H_{40}N_4O_{14}$ (MH^+) 862.8317, found 862.8317. Anal. Calcd for. $C_{45}H_{40}N_4O_{14}$: C, 62.79; H, 4.68; N, 6.51%. Found: C, 62.55; H, 5.06; N, 6.15.

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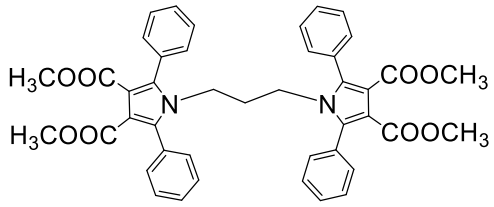
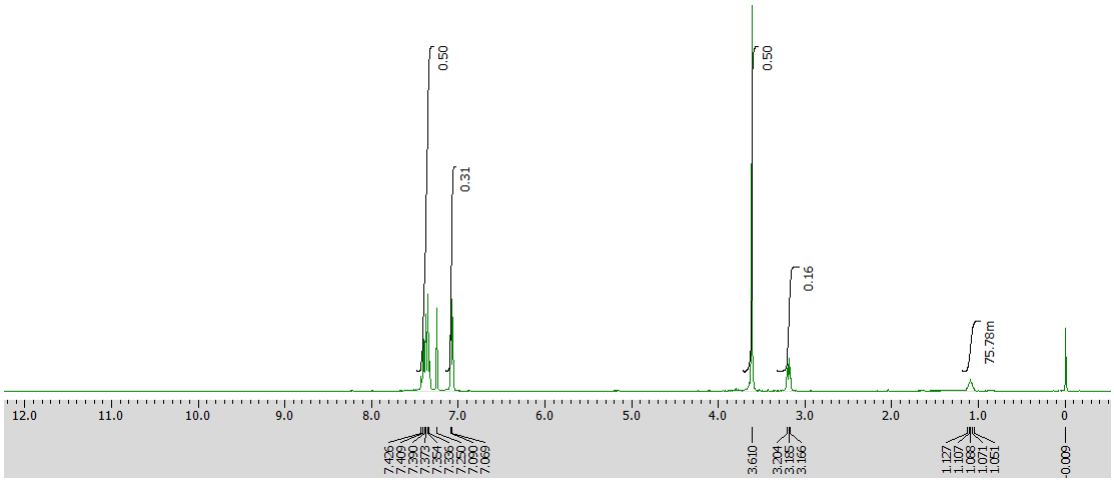
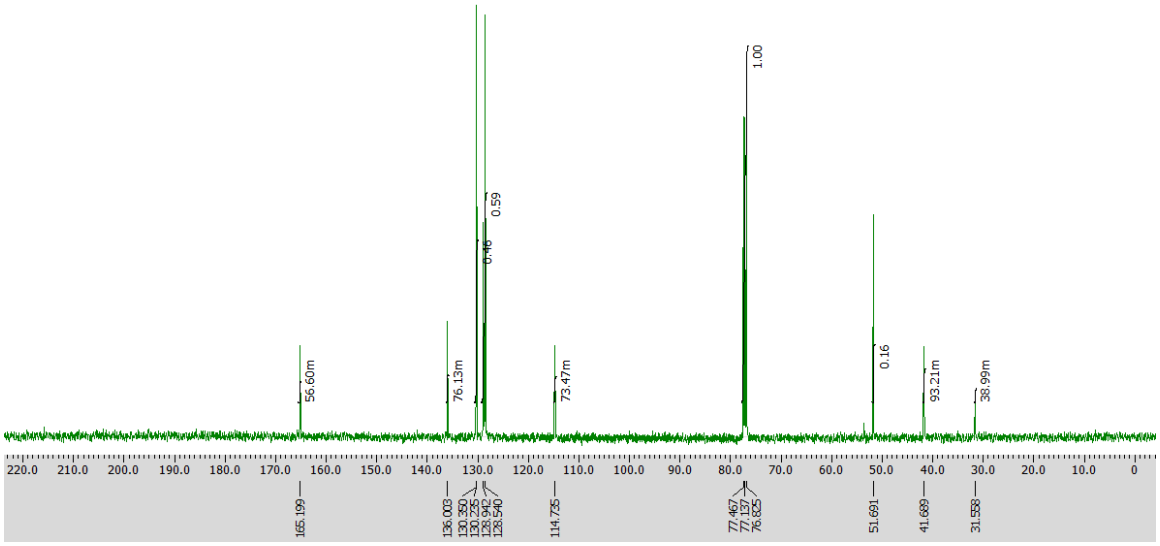
[1]. R. W. Layer, *Chem. Ber.*, 1963, **63**, 489.

^{1}H and ^{13}C NMR Spectra

3a







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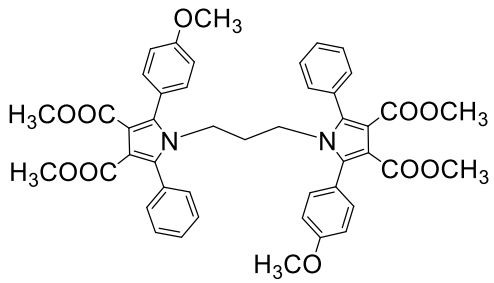
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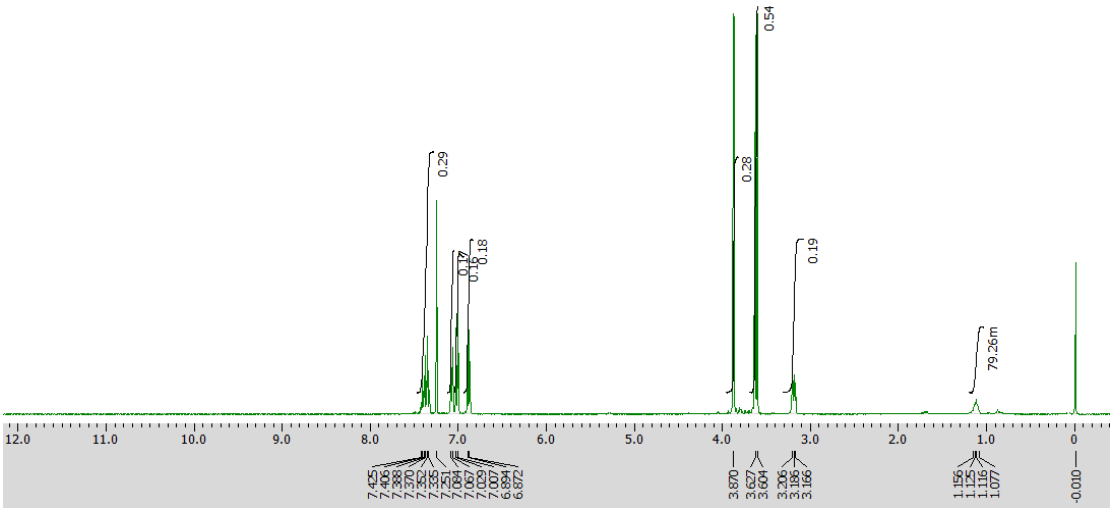
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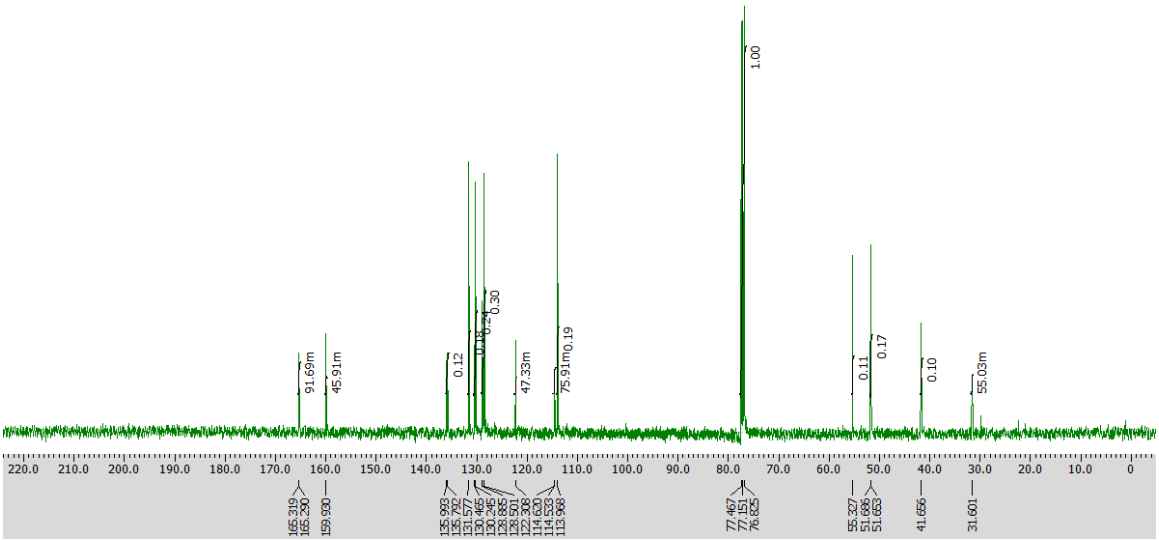
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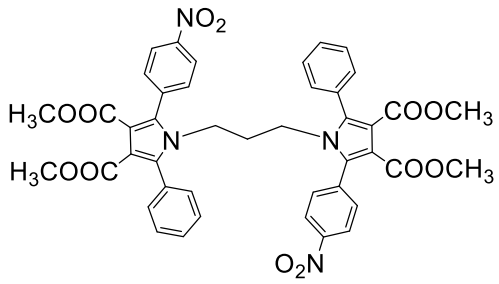

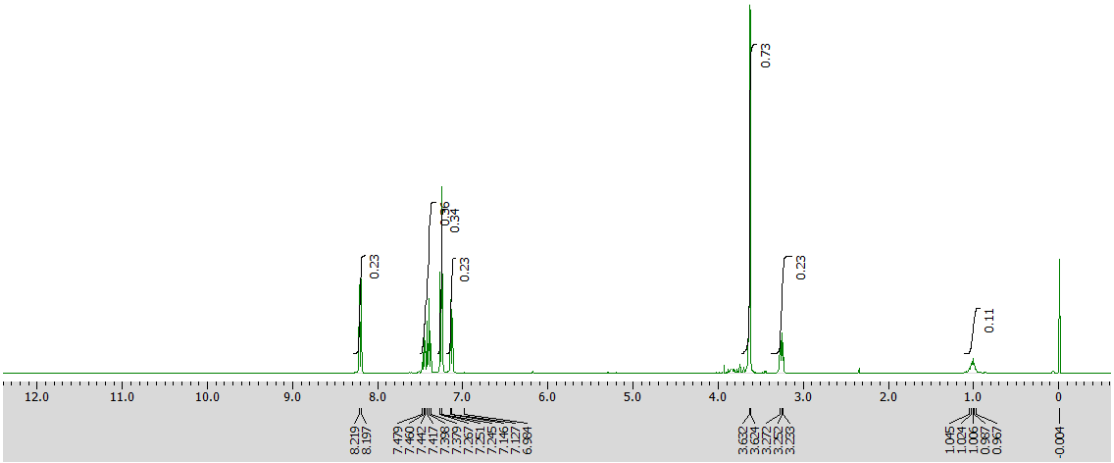

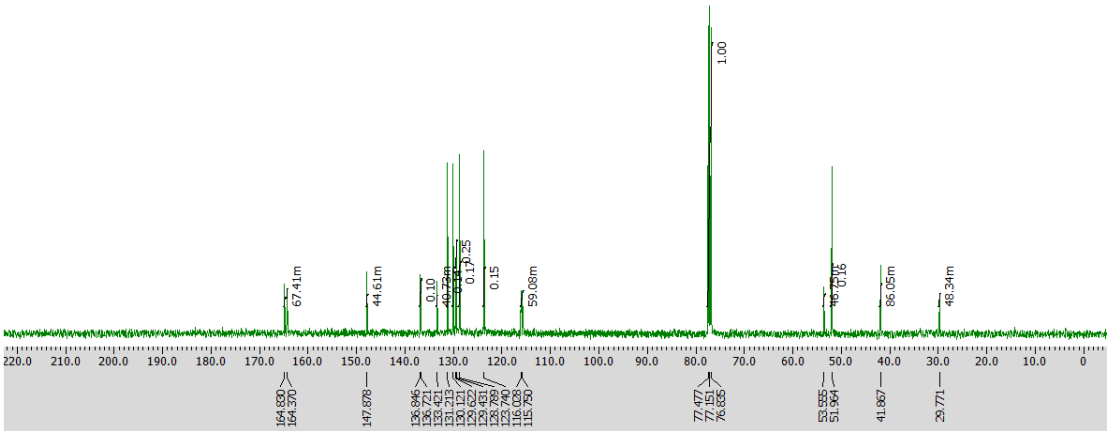

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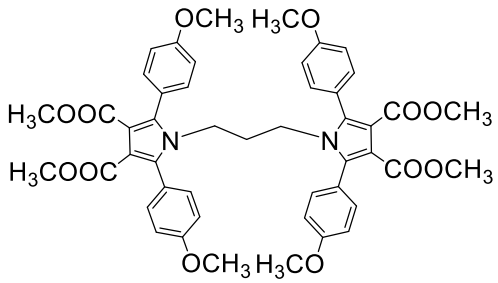
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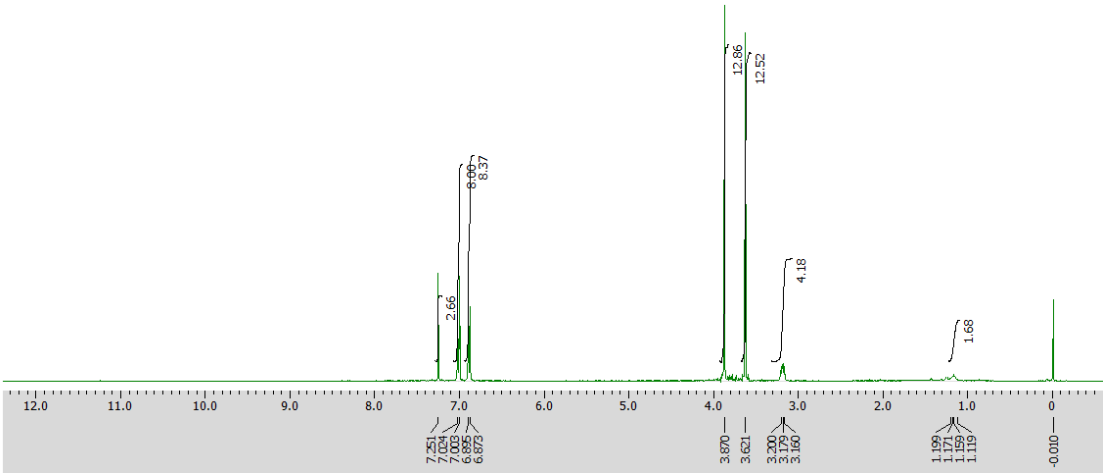
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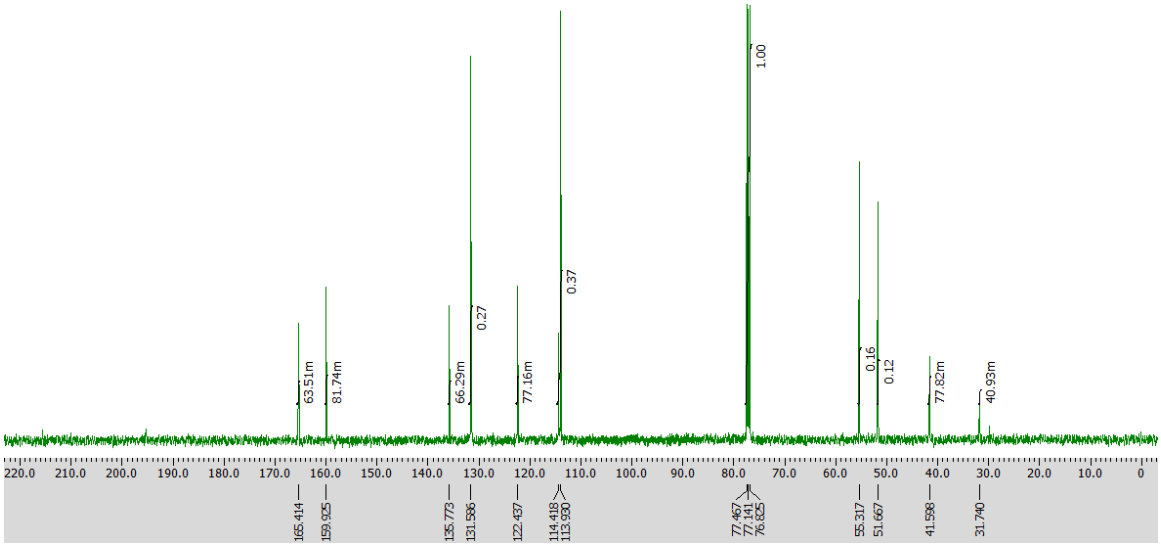
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3e