

Supporting Information

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Supporting Information

Pd/RHA and Pd/BPA as eco-friendly heterogeneous catalysts: Microwave-assisted C–S cross-coupling reaction in DMF

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Supporting Information

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General Information:

All the chemicals were purchased from Sigma Aldrich with purity not less than 99.9%. Analytical Thin Layer Chromatography (TLC) was carried out by using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp of I₂ stain. All the products were characterized by their NMR and Mass spectra. ¹H NMR and ¹³C NMR were recorded on 400 in DMSO and CDCl₃, and the chemical shifts were reported in parts per million (ppm, δ) downfield from the tetramethylsilane. All reactions were carried out in sealed glass tubes with a volume of 10 mL in a commercially available monomode microwave reactor (CEM, Matthews, NC, USA) equipped with infrared monitoring and a non-invasive pressure transducer.

General procedure for the synthesis of 5-phenylthio-2,1,3-benzothiadiazoles:¹

Benzene thiols (0.45 mmol), 5-bromo-2,1,3-benzothiadiazole (0.3 mmol), a catalytic amount of Pd/RHA or Pd/BPA (0.025 mol%), K₂CO₃ (0.6 mmol) and DMF (2 mL) were added to a microwave reaction vessel armed with a magnetic stirrer bar. The reaction mixture was subjected to microwave irradiation (a CEM Discover MW reactor) (200W, 75 °C) for 15-25 min. The progress of the reaction was observed by TLC (eluent: EtOAc/hexane, 10:90). The reaction mixture was cooled to room temperature and the crude residue was extracted with ethyl acetate (3 x 10 mL) and water. Then, combined all the organic layers and dried over anhydrous Na₂SO₄. The remaining solvent was evaporated under reduced pressure. Further, the crude product was purified by column chromatography over silica gel to afford the corresponding product, and yields were obtained in 51-92% as shown in **Scheme 2**.

General procedure for the synthesis of of bis-arylsulfenyl- and bis-arylselenanyl-benzo-2,1,3-thiadiazoles:

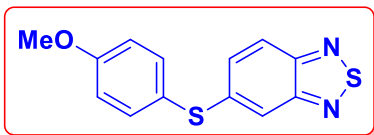
Benzene thiols (0.6 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (0.3 mmol), a catalytic amount of Pd/RHA (0.025 mol%), K₂CO₃ (0.9 mmol) and DMF (2 mL) were added to a microwave reaction vessel armed with a magnetic stirrer bar. The reaction mixture was subjected to microwave irradiation (a CEM Discover MW reactor) (200W, 75 °C) for 20 min. The progress of the reaction was observed by TLC (eluent: EtOAc/hexane, 10:90). The reaction mixture was cooled to room temperature and the crude residue was extracted with ethyl acetate (3 x 10 mL) and water. Then, combined all the organic layers and dried over anhydrous Na₂SO₄. The remaining solvent was evaporated under reduced pressure. Further, the crude product was purified by column chromatography over silica gel to

afford the corresponding product, and yields were obtained in 83-94% as shown in **Scheme 3**.

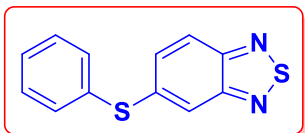
Reference:

1. Santos, B. F., Pereira, C. F., Pinz, M. P., Oliveira, A. R., Brand, G., Katla, R., Domingues, N. L. C. *Appl Organometal Chem.* **2020**, e5650.

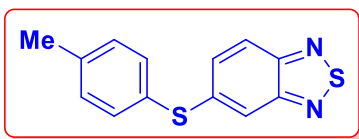
SPECTRAL DATA OF COMPOUNDS:



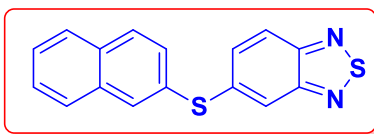
5-((4-methoxyphenyl)thio)benzo[c][1,2,5]thiadiazole (3a)¹: Yield: 74.25 mg (92%); light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 1.5 Hz, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.66 (dd, *J*₁ = 9.3 Hz, *J*₂ = 1.8 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.88, 155.25, 153.32, 133.18, 132.61, 128.41, 123.80, 122.15, 114.58, 55.33. MS (ESI): *m/z* = 275 [M + H]⁺.



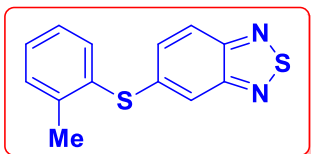
5-(phenylthio)benzo[c][1,2,5]thiadiazole (3b)¹: Yield: 67.62 mg (92%); yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 1.6 Hz, 1H), 7.86 (dd, *J*₁ = 8.9 Hz, *J*₂ = 5.0 Hz, 1H), 7.66 (dd, *J*₁ = 9.3 Hz, *J*₂ = 1.8 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.30 (dd, *J*₁ = 10.2 Hz, *J*₂ = 4.8 Hz, 2H), 7.22 (q, *J* = 7.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 155.25, 153.31, 137.00, 133.17, 129.02, 127.48, 127.11, 124.49, 123.80, 122.14. MS (ESI): *m/z* = 245 [M + H]⁺.



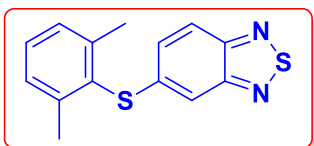
5-(p-tolylthio)benzo[c][1,2,5]thiadiazole (3c)¹: Yield: 46.62 mg (60%); yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 9.2 Hz, 1H), 7.41 – 7.30 (m, 1H), 7.24 (t, *J* = 4.9 Hz, 1H), 7.13 – 7.06 (m, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.37, 153.16, 143.91, 143.37, 141.76, 134.70, 130.16, 129.18, 128.86, 128.00, 121.12, 114.18, 21.40. MS (ESI): *m/z* = 259 [M + H]⁺.



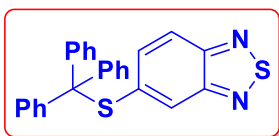
5-(naphthalen-2-ylthio)benzo[c][1,2,5]thiadiazole (3d): Yield: 75.22 mg (85%); yellow solid; mp 118–120 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 40.3 Hz, 1H), 7.91 – 7.40 (m, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 155.15, 153.54, 141.26, 133.42, 130.63, 130.24, 129.62, 128.94, 127.78, 127.44, 127.01, 126.63, 126.21, 125.65, 121.35, 118.67. MS (ESI): *m/z* = 295 [M + H]⁺. Anal. Calcd for: (C₁₆H₁₀N₂S₂) C: 65.28, H: 3.42, N: 9.52, S: 21.78; found C: 65.24, H: 3.35, N: 9.48, S: 21.73.



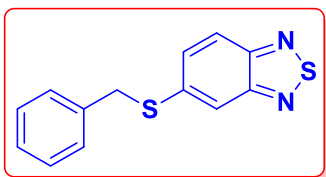
5-(o-tolylthio)benzo[c][1,2,5]thiadiazole (3e)¹: Yield: 61.38 mg (79%); yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 9.2 Hz, 1H), 7.51 – 7.40 (m, 4H), 7.27 – 7.24 (m, 2H), 2.41 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.21, 153.40, 142.53, 139.66, 134.53, 130.70, 130.13, 127.68, 121.14, 117.31, 21.28. MS (ESI): *m/z* = 259 [M + H]⁺.



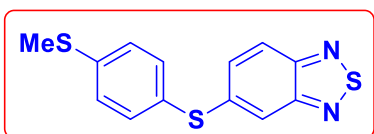
5-((2,6-dimethylphenyl)thio)benzo[c][1,2,5]thiadiazole (3f): Yield: 71.25 mg (87%); yellow solid; mp 82-84 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 9.2 Hz, 1H), 7.39 (dd, *J*₁ = 9.2 Hz, *J*₂ = 1.8 Hz, 1H), 7.31 – 7.29 (m, 1H), 7.25 (s, 1H), 7.10 (d, *J* = 1.2 Hz, 1H), 7.01 (s, 1H), 2.44 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 155.38, 153.17, 143.93, 141.77, 130.17, 129.23, 128.86, 128.00, 121.12, 114.16, 21.56. MS (ESI): *m/z* = 273 [M + H]⁺. Anal. Calcd for: (C₁₄H₁₂N₂S₂) C: 61.73, H: 4.44, N: 10.28, S: 23.54; found C: 61.70, H: 4.41, N: 10.31, S: 23.49.



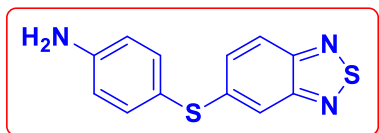
5-(tritylthio)benzo[c][1,2,5]thiadiazole (3g): Yield: 108.5 mg (88%); yellow solid; mp 90-92 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.34 (dd, *J*₁ = 12.6 Hz, *J*₂ = 6.5 Hz, 9H), 7.28 – 7.24 (m, 3H), 7.17 (d, *J* = 7.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 146.90, 143.94, 129.49, 128.34, 127.97, 127.30, 126.33, 56.88. MS (ESI): *m/z* = 411 [M + H]⁺. Anal. Calcd for: (C₂₅H₁₈N₂S₂) C: 73.14, H: 4.42, N: 6.82, S: 15.62; found C: 73.09, H: 4.35, N: 6.77, S: 15.57.



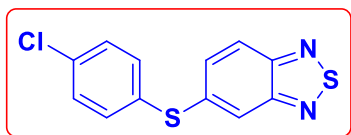
5-(benzylthio)benzo[c][1,2,5]thiadiazole (3h)¹: Yield: 71.48 mg (92%); yellow semi solid. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 1.6 Hz, 1H), 7.86 (dd, *J*₁ = 14.0 Hz, *J*₂ = 9.2 Hz, 2H), 7.74 (d, *J* = 1.5 Hz, 1H), 7.67 (dd, *J*₁ = 9.3 Hz, *J*₂ = 1.8 Hz, 1H), 7.46 – 7.39 (m, 3H), 4.28 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.22, 153.30, 140.82, 137.34, 133.20, 130.58, 129.39, 128.45, 127.65, 127.40, 123.81, 122.16, 121.00, 116.65, 43.26. MS (ESI): *m/z* = 259 [M + H]⁺.



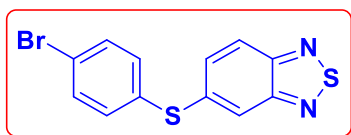
5-((4-(methylthio)phenyl)thio)benzo[c][1,2,5]thiadiazole (3i): Yield: 54.12 mg (62%); yellow semi solid. ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 8.4$ Hz, 1H), 7.40 (dd, $J_1 = 11.5$ Hz, $J_2 = 5.0$ Hz, 3H), 7.29 (d, $J = 8.4$ Hz, 1H), 7.16 (d, $J = 8.4$ Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.56, 139.67, 137.44, 134.54, 133.90, 133.23, 130.72, 130.15, 129.78, 128.55, 124.54, 123.86, 122.20, 121.17, 117.34, 21.04. MS (ESI): $m/z = 291$ $[\text{M} + \text{H}]^+$. Anal. Calcd for: ($\text{C}_{13}\text{H}_{10}\text{N}_2\text{S}_3$) C: 53.77, H: 3.47, N: 9.65, S: 33.12; found C: 53.72, H: 3.41, N: 9.59, S: 33.08.



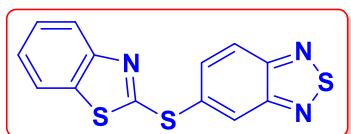
4-(benzo[c][1,2,5]thiadiazol-5-ylthio)aniline (3j)¹: Yield: 64.74 mg (83%); yellow semi solid. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 1.3$ Hz, 1H), 7.87 (t, $J = 9.4$ Hz, 2H), 7.67 (dd, $J_1 = 9.3$ Hz, $J_2 = 1.7$ Hz, 1H), 7.42 – 7.38 (m, 2H), 6.84 (s, 1H), 4.33 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.46, 148.74, 136.94, 133.34, 131.71, 123.95, 122.30, 118.35, 115.34. MS (ESI): $m/z = 260$ $[\text{M} + \text{H}]^+$.



5-((4-chlorophenyl)thio)benzo[c][1,2,5]thiadiazole (3k)¹: Yield: 46 mg (55%); light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 9.2$ Hz, 1H), 7.63 (d, $J = 1.3$ Hz, 1H), 7.47 – 7.39 (m, 4H), 7.27 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.05, 153.54, 140.53, 134.88, 130.53, 130.03, 129.29, 121.55, 118.97. MS (ESI): $m/z = 279$ $[\text{M} + \text{H}]^+$.

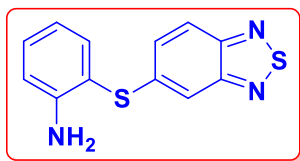


5-((4-bromophenyl)thio)benzo[c][1,2,5]thiadiazole (3l): Yield: 62.2 mg (64%); yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.89 (dd, $J_1 = 9.2$ Hz, $J_2 = 0.4$ Hz, 1H), 7.66 (d, $J = 1.2$ Hz, 1H), 7.56 – 7.53 (m, 2H), 7.44 – 7.38 (m, 2H), 7.35 – 7.32 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.98, 132.98, 132.20, 130.64, 129.38, 121.59, 119.20. MS (ESI): $m/z = 324$ $[\text{M} + \text{H}]^+$. Anal. Calcd for: ($\text{C}_{12}\text{H}_7\text{BrN}_2\text{S}_2$) C: 44.59, H: 2.18, N: 8.67, S: 19.84; found C: 44.52, H: 2.12, N: 8.71, S: 19.80.

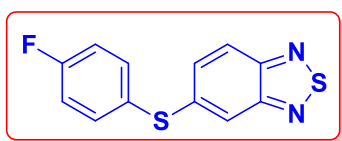


5-(benzo[d]thiazol-2-ylthio)benzo[c][1,2,5]thiadiazole (3m): Yield: 50.7 mg (56%); yellow semi solid. ^1H NMR (400 MHz, DMSO) δ 8.33 (d, $J = 1.8$ Hz, 1H), 8.15 (s, 1H), 8.01 (d, $J = 9.2$ Hz, 2H), 7.77 (dd, $J_1 = 9.2$ Hz, $J_2 = 1.6$ Hz, 2H), 7.38 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ 164.31, 151.95, 135.63, 132.97, 130.50, 130.43, 127.14, 124.77, 123.79, 121.26, 120.25, 117.21, 115.63. MS (ESI): $m/z = 302$ $[\text{M} + \text{H}]^+$. Anal. Calcd for:

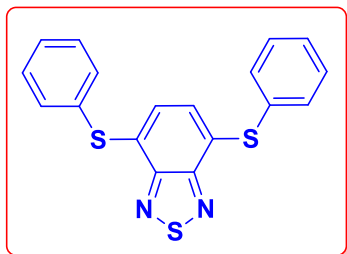
(C₁₃H₇N₃S₃) C: 51.81, H: 2.34, N: 13.94, S: 31.91; found C: 51.74, H: 2.27, N: 13.87, S: 31.83.



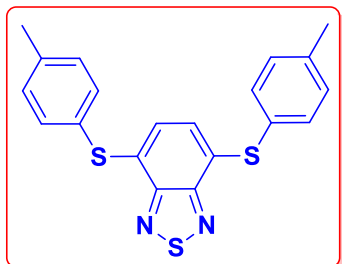
2-(benzo[c][1,2,5]thiadiazol-5-ylthio)aniline (3n)¹: Yield: 63.18 mg (81%); yellow semi solid. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 1.4 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.69 (dd, *J*₁ = 9.2 Hz, *J*₂ = 1.8 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 2H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.60 (t, *J* = 7.5 Hz, 1H), 4.36 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 155.30, 153.37, 148.65, 136.84, 133.24, 131.62, 123.85, 122.20, 118.25, 115.25. MS (ESI): *m/z* = 260 [M + H]⁺.



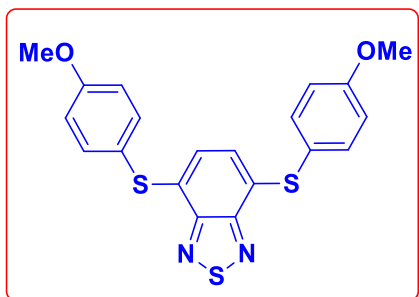
5-((4-fluorophenyl)thio)benzo[c][1,2,5]thiadiazole (3o)¹: Yield: 55.23 mg (70%); yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 9.2 Hz, 1H), 7.56 (ddd, *J*₁ = 15.4 Hz, *J*₂ = 9.4 Hz, *J*₃ = 1.5 Hz, 3H), 7.17 (t, *J* = 8.6 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 164.69, 162.20, 155.13, 153.45, 141.78, 136.63, 131.33, 130.02, 121.41, 117.71, 117.29, 116.40. MS (ESI): *m/z* = 263 [M + H]⁺.



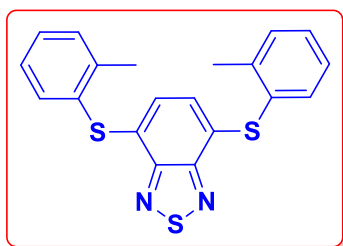
4,7-bis(phenylthio)benzo[c][1,2,5]thiadiazole (4a): Yield: 77.6 mg (88%); yellow solid; mp 125-127 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.35 (m, 8H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 6.94 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 152.97, 136.98, 134.40, 133.52, 132.23, 131.50, 129.62, 129.00, 128.66, 127.72, 127.48, 127.10. MS (ESI): *m/z* = 353 [M + H]⁺. MS (ESI): *m/z* = 295 [M + H]⁺.



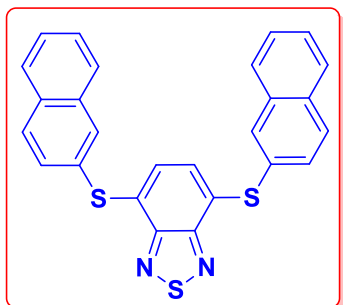
4,7-bis(p-tolylthio)benzo[c][1,2,5]thiadiazole (4b): Yield: 102.6 mg (90%); Orange oil. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (s, 1H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.50 (s, 1H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.28 (s, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.82 (s, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.92, 152.07, 139.12, 134.93, 134.13, 132.24, 130.73, 130.44, 129.35, 127.49, 126.84, 125.37, 113.88, 110.14, 21.20. MS (ESI): $m/z = 381$ $[\text{M} + \text{H}]^+$.



4,7-bis((4-methoxyphenyl)thio)benzo[c][1,2,5]thiadiazole (4c): Yield: 116 mg (94%); orange oil. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.8$ Hz, 4H), 6.93 (d, $J = 8.8$ Hz, 4H), 6.71 (s, 2H), 3.83 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.58, 152.51, 137.45, 136.59, 129.92, 127.62, 125.83, 121.03, 115.78, 115.34, 114.61, 55.39. MS (ESI): $m/z = 413$ $[\text{M} + \text{H}]^+$.

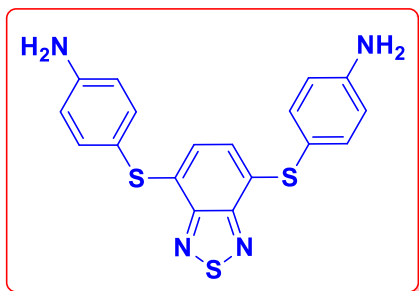


4,7-bis(o-tolylthio)benzo[c][1,2,5]thiadiazole (4d): Yield: 94.6 mg (83%); yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (s, 1H), 7.58 (s, 1H), 7.46 (d, $J = 7.6$ Hz, 1H), 7.40 (d, $J = 3.1$ Hz, 1H), 7.33 – 7.29 (m, 3H), 7.20 (dd, $J_1 = 5.1$ Hz, $J_2 = 2.9$ Hz, 1H), 6.61 (s, 1H), 6.55 (d, $J = 7.7$ Hz, 1H), 2.42 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 152.78, 141.92, 136.31, 135.38, 132.21, 130.98, 129.47, 127.11, 125.88, 124.44, 113.86, 109.92, 20.53. MS (ESI): $m/z = 381$ $[\text{M} + \text{H}]^+$. Anal. Calcd for: ($\text{C}_{20}\text{H}_{16}\text{N}_2\text{S}_3$) C: 63.13, H: 4.24, N: 7.36, S: 25.27; found C: 63.09, H: 4.17, N: 7.28, S: 25.18.



4,7-bis(naphthalen-2-ylthio)benzo[c][1,2,5]thiadiazole (4e): Yield: 116.6 mg (86%); yellow solid; mp 105-107 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.04 (s, 2H), 7.85 – 7.76 (m, 6H), 7.54 – 7.48 (m, 6H), 6.96 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 153.10, 133.86, 133.01, 130.07, 129.38, 129.05, 128.76, 127.98, 127.68, 126.95, 126.78. MS (ESI): m/z

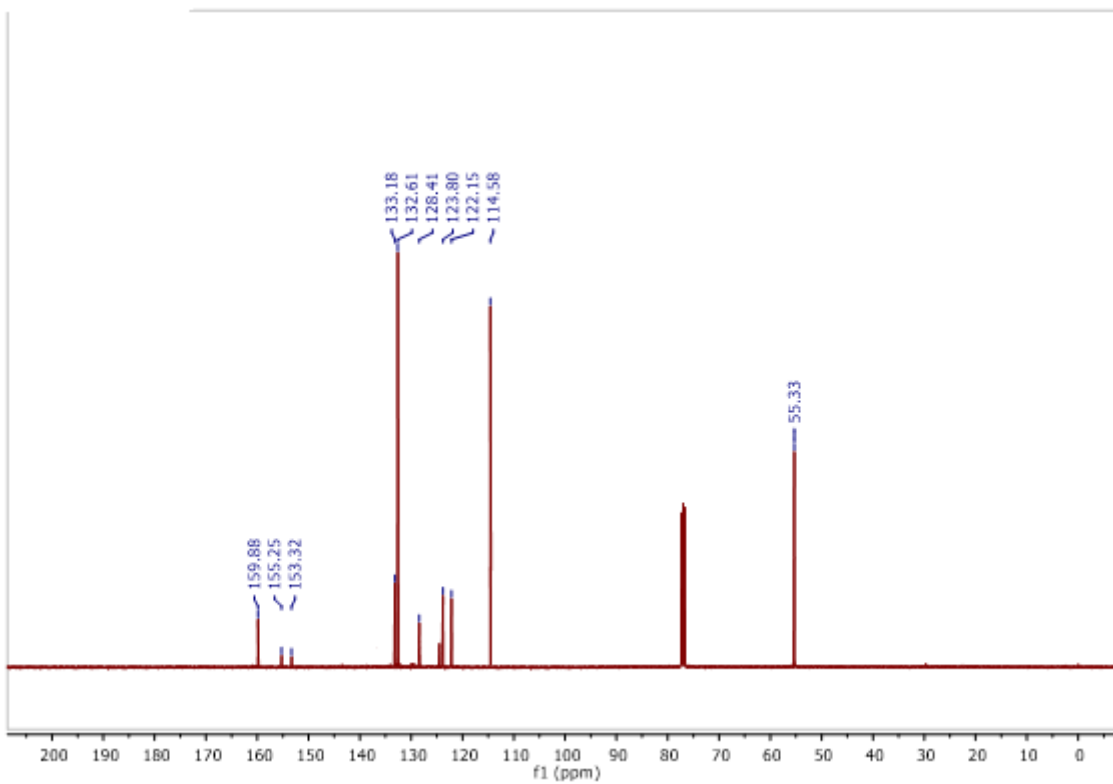
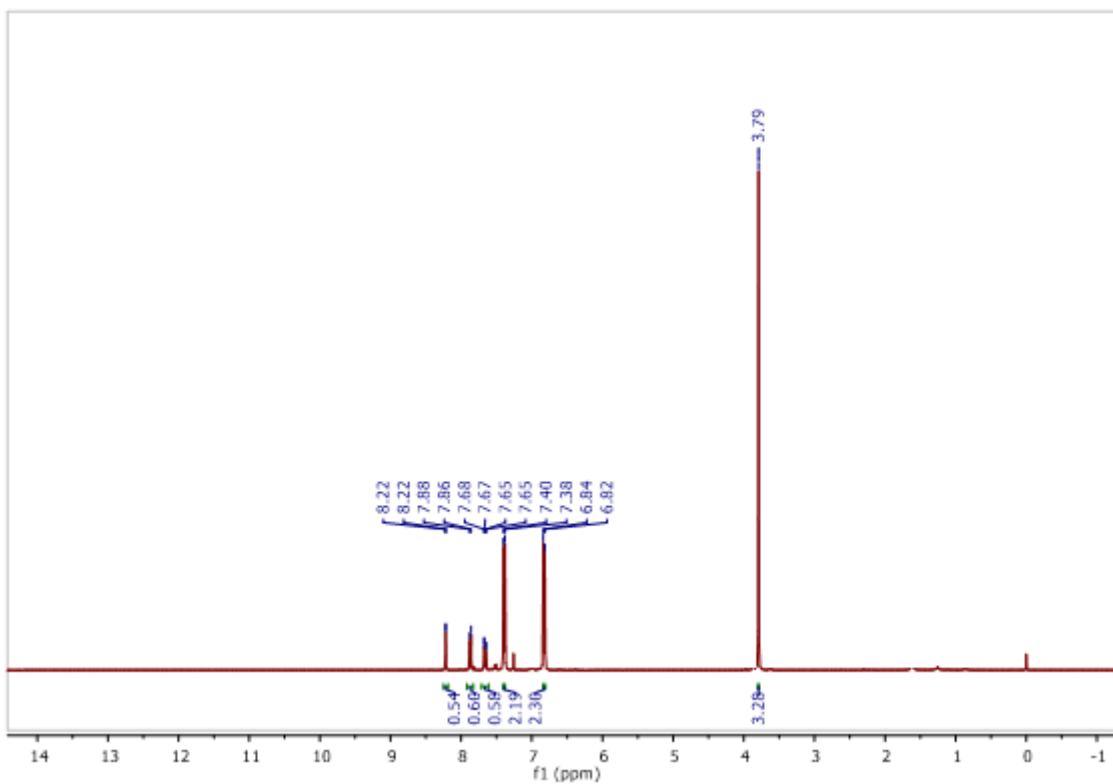
= 453 [M + H]⁺. Anal. Calcd for: (C₂₆H₁₆N₂S₃) C: 69.00, H: 3.56, N: 6.19, S: 21.25; found C: 68.92, H: 3.46, N: 6.12, S: 21.14.



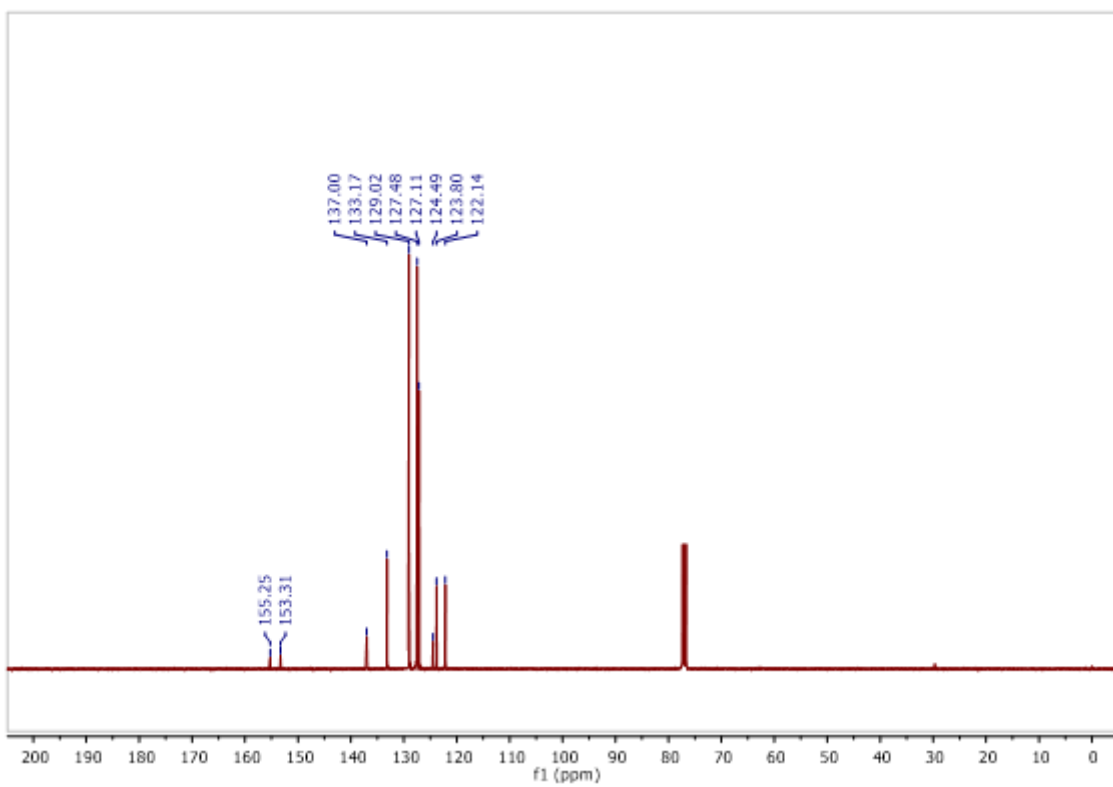
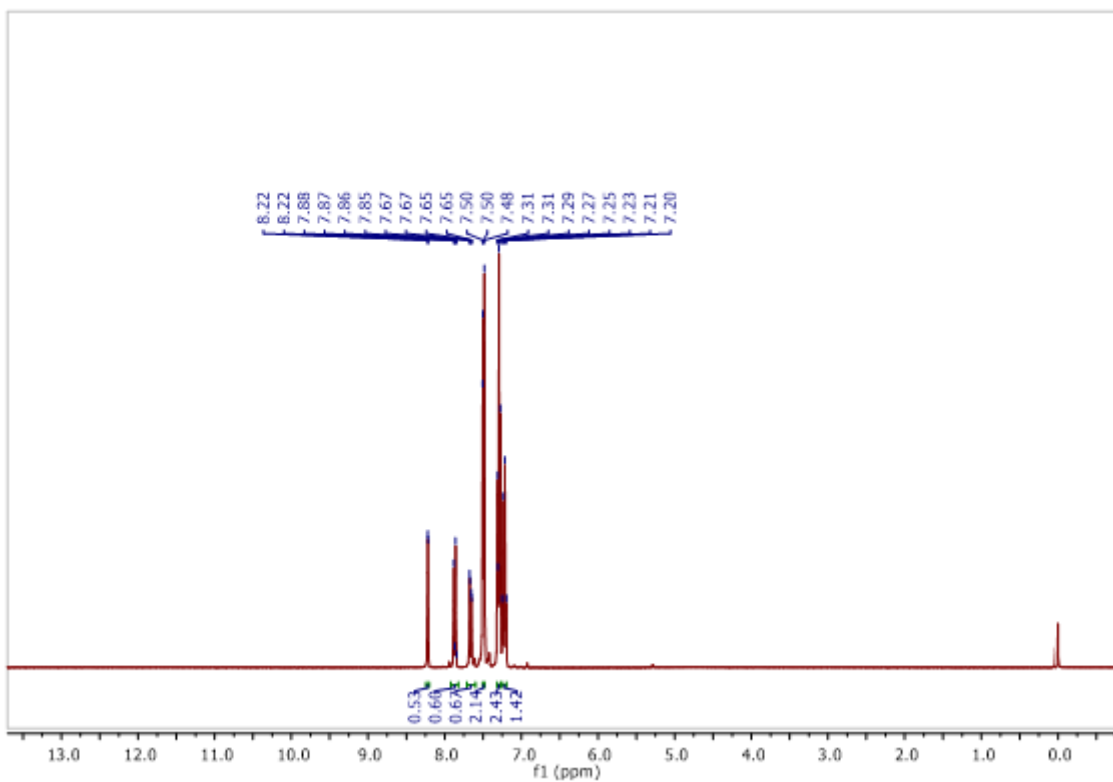
4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diylbis(sulfaneyl))dianiline (4f): Yield: 100.8 mg (88%); yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, *J*₁ = 7.7 Hz, *J*₂ = 1.5 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.14 (ddd, *J*₁ = 7.2 Hz, *J*₂ = 3.9 Hz, *J*₃ = 1.5 Hz, 3H), 6.71 (ddd, *J*₁ = 9.6 Hz, *J*₂ = 8.5 Hz, *J*₃ = 4.4 Hz, 3H), 6.60 – 6.54 (m, 2H), 4.34 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 162.47, 152.60, 149.09, 148.56, 136.71, 131.50, 126.71, 124.65, 118.12, 115.15, 111.52. MS (ESI): *m/z* = 383 [M + H]⁺. Anal. Calcd for: (C₁₈H₁₄N₄S₃) C: 56.52, H: 3.69, N: 14.65, S: 25.14; found C: 56.46, H: 3.62, N: 14.60, S: 25.08.

¹H AND ¹³C SPECTRAS OF THE COMPOUNDS:

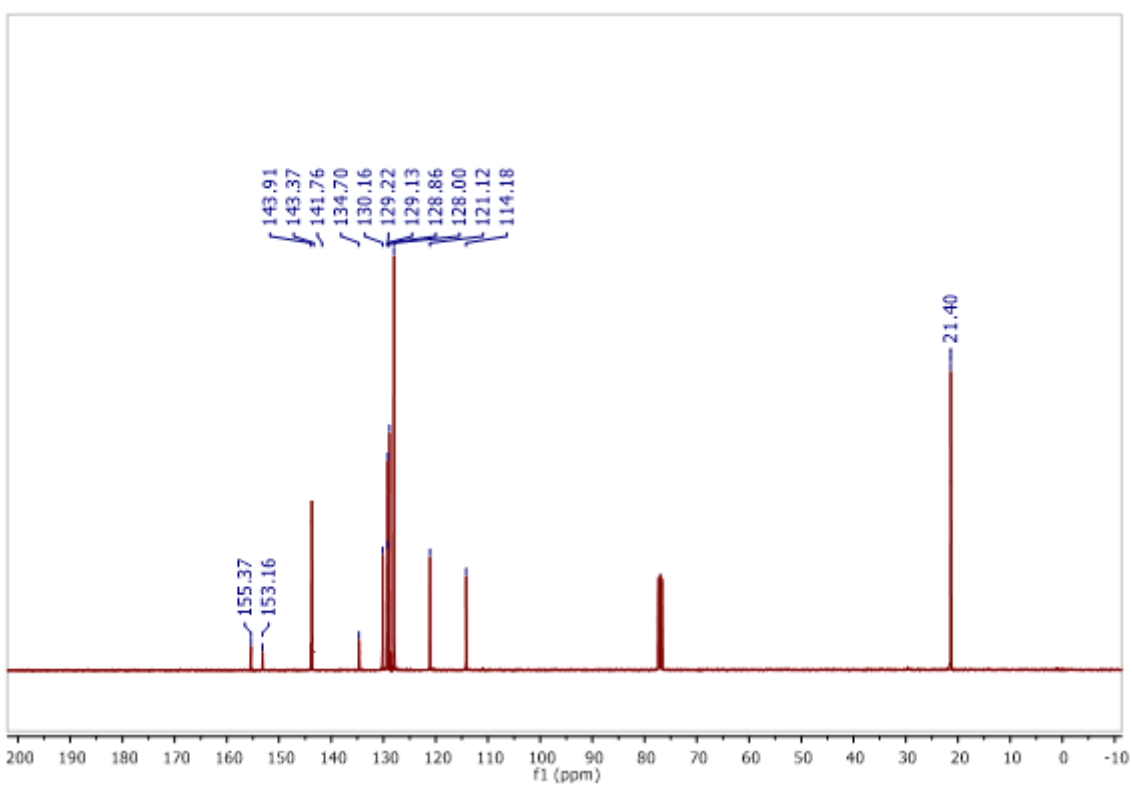
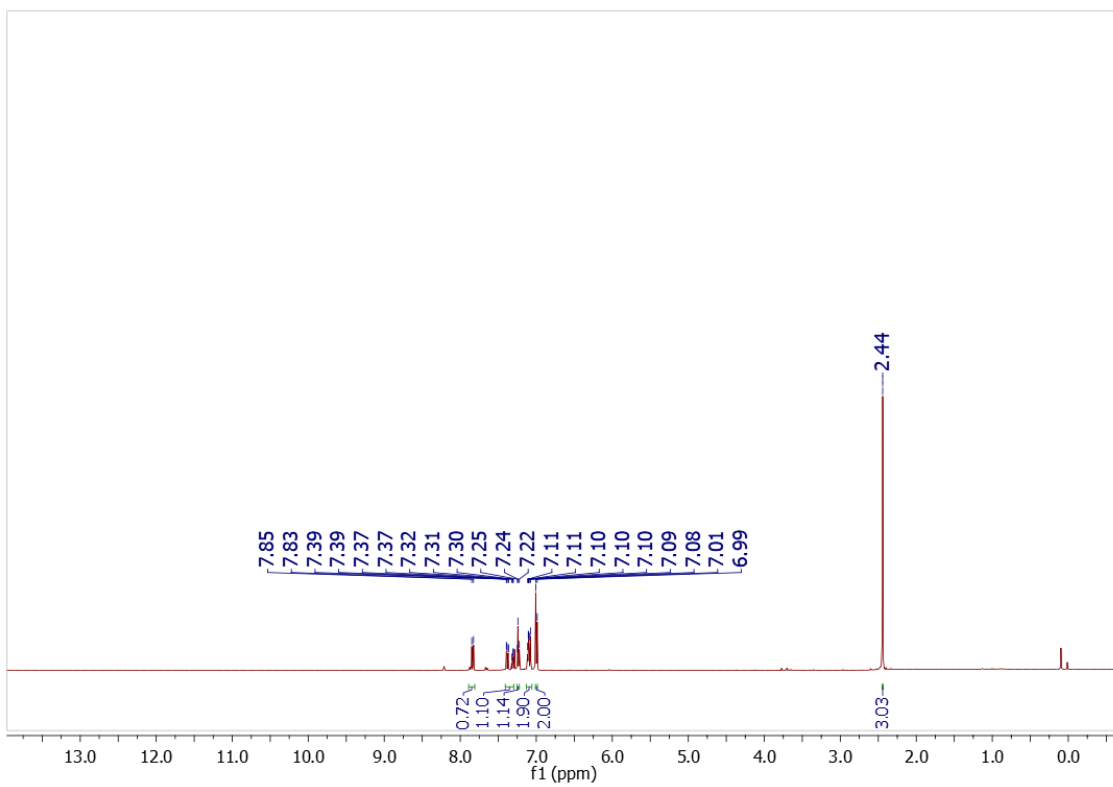
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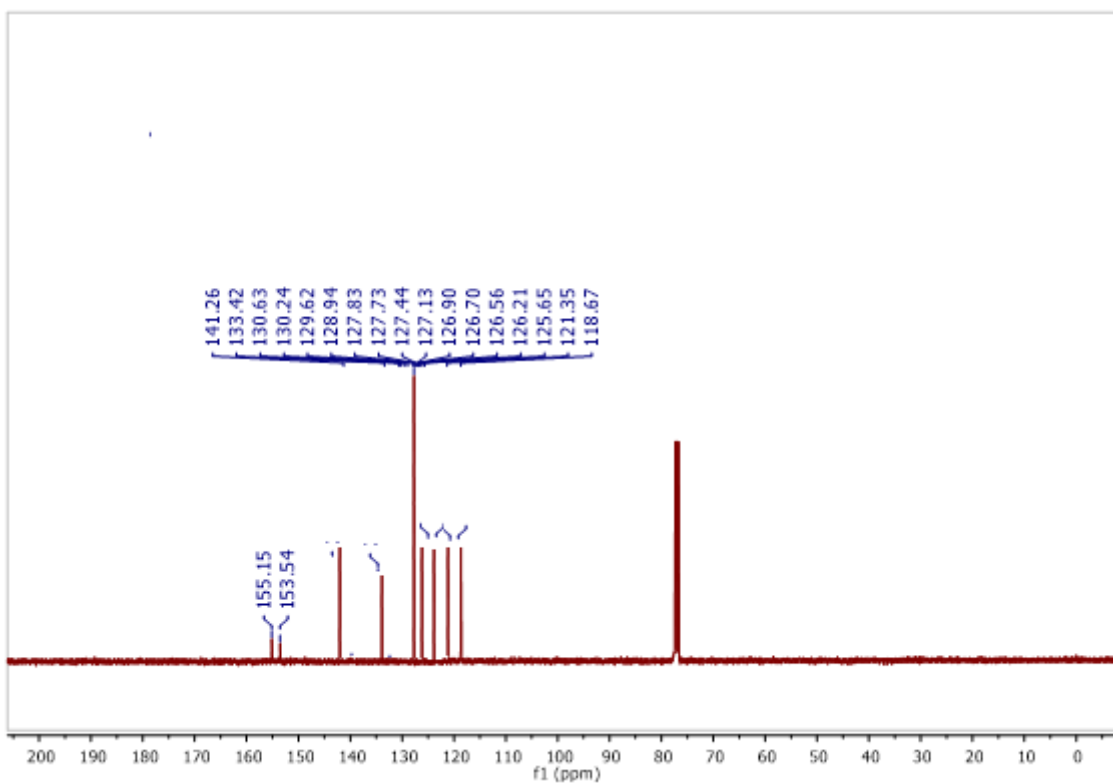
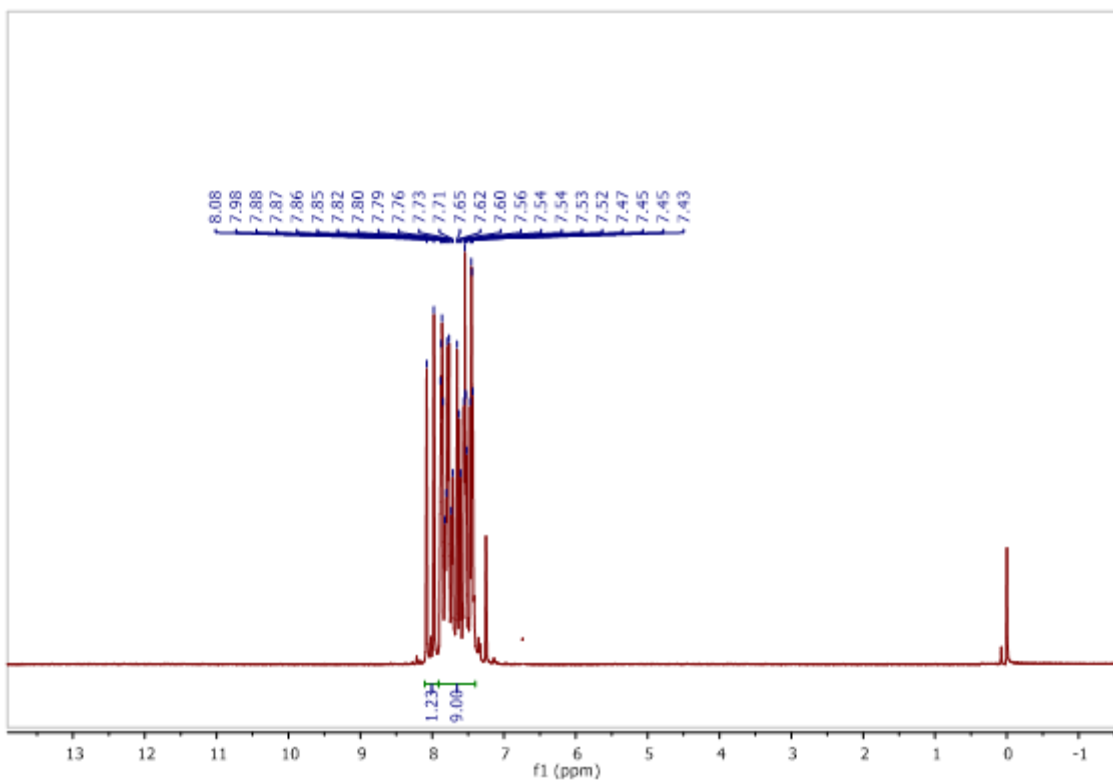
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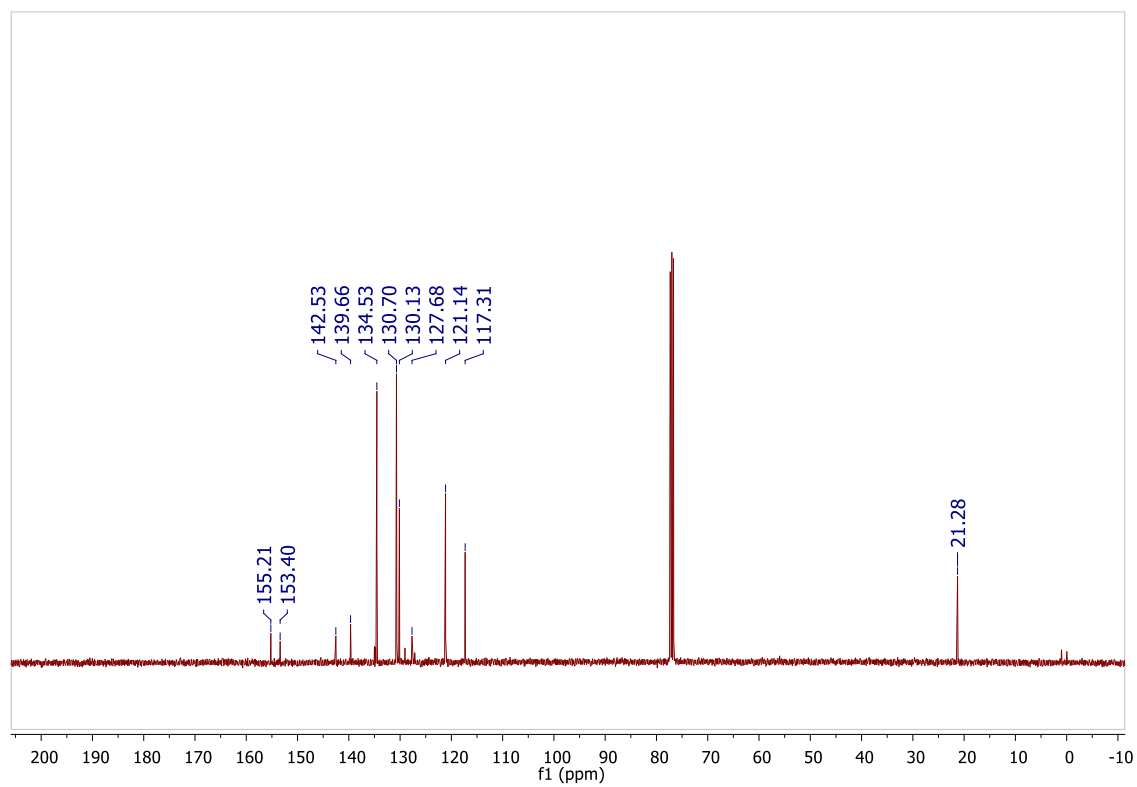
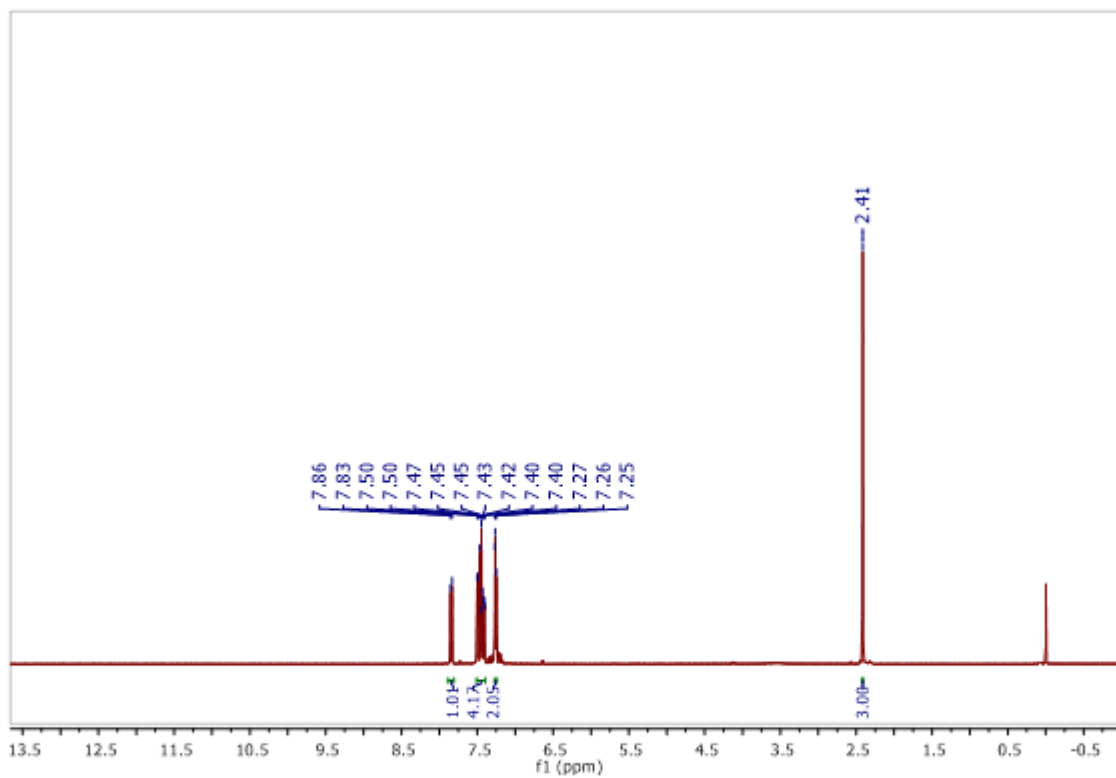
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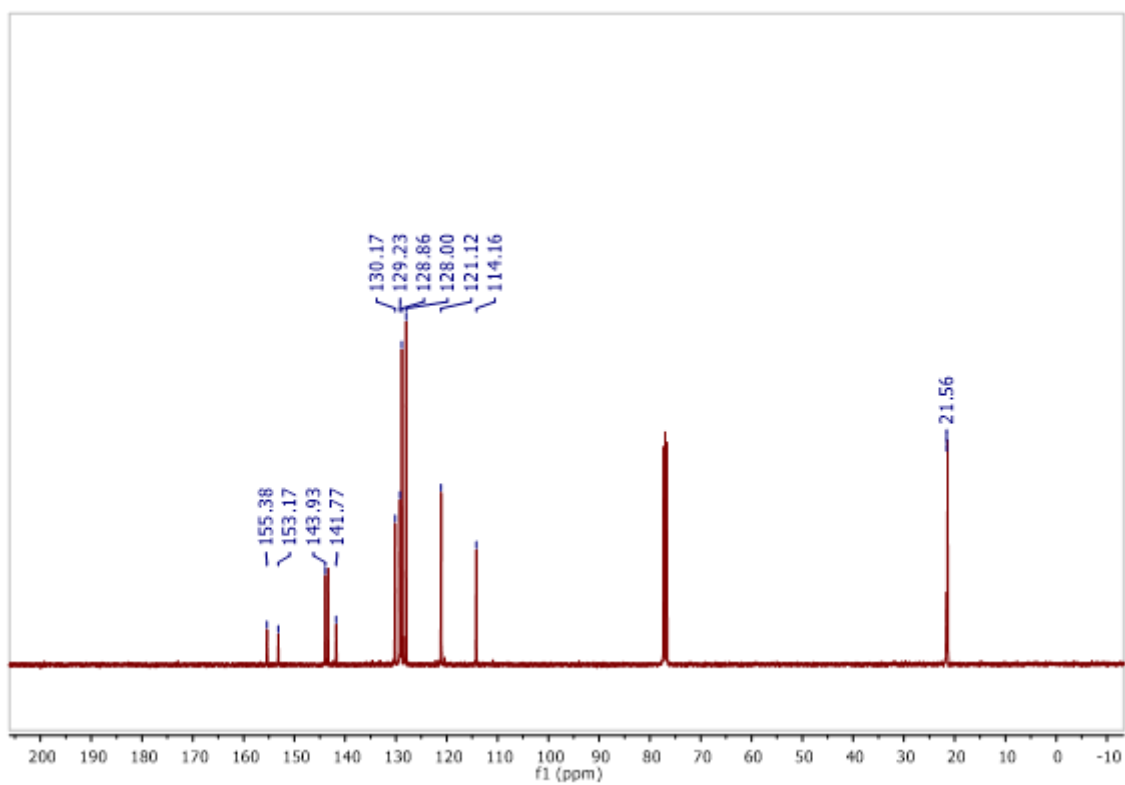
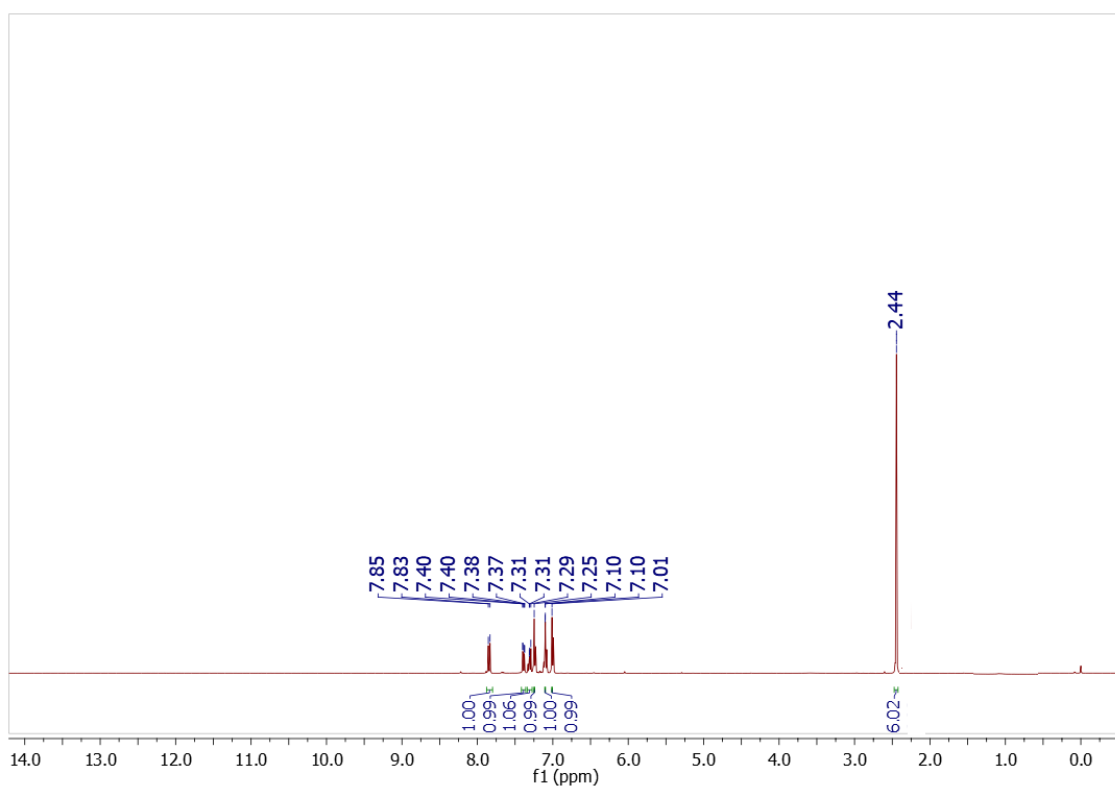
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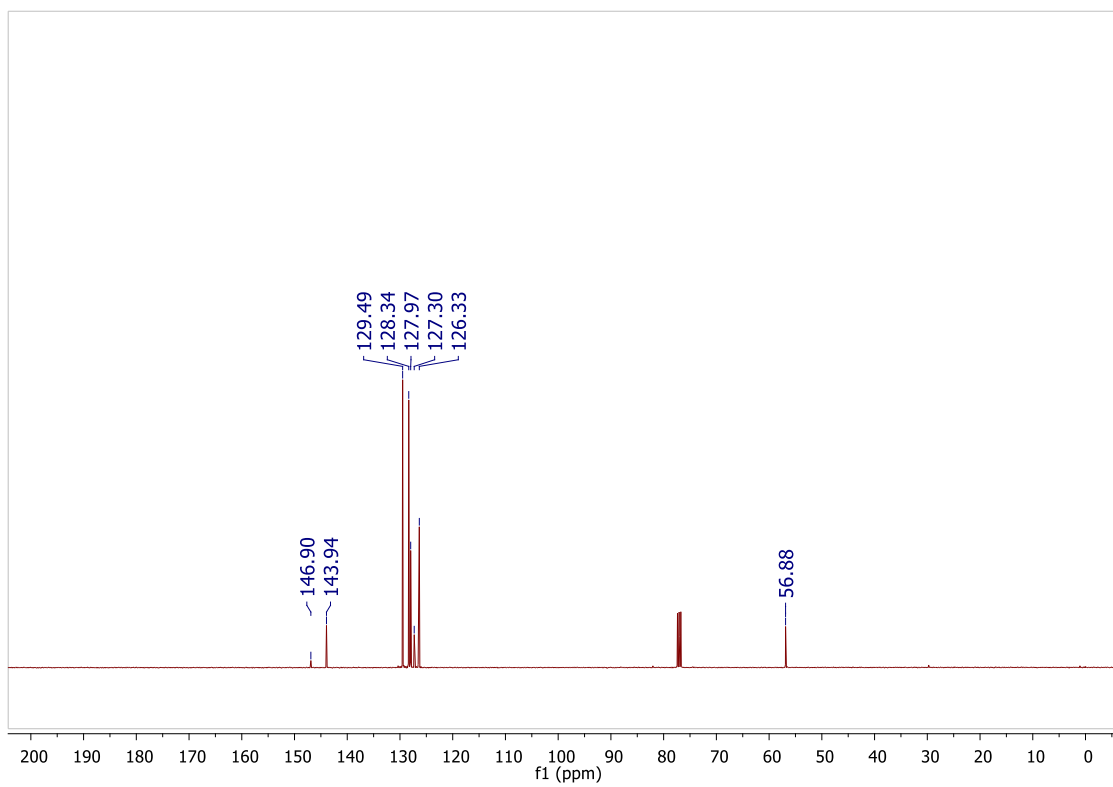
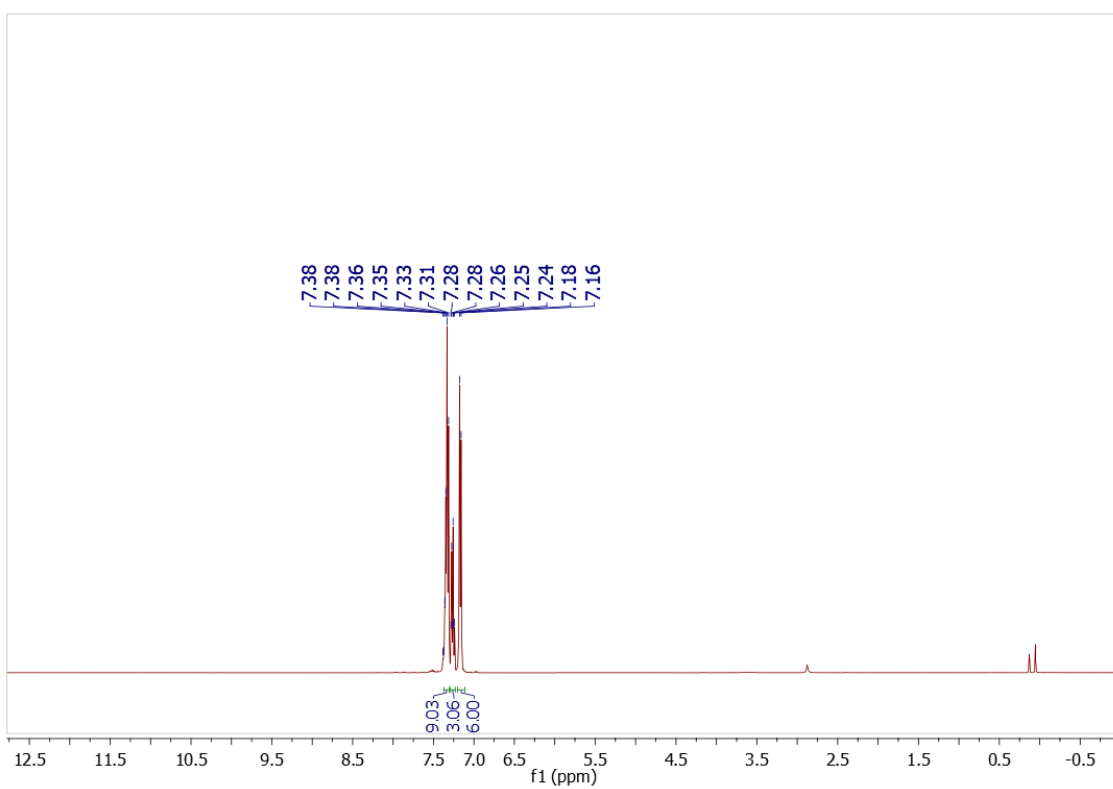
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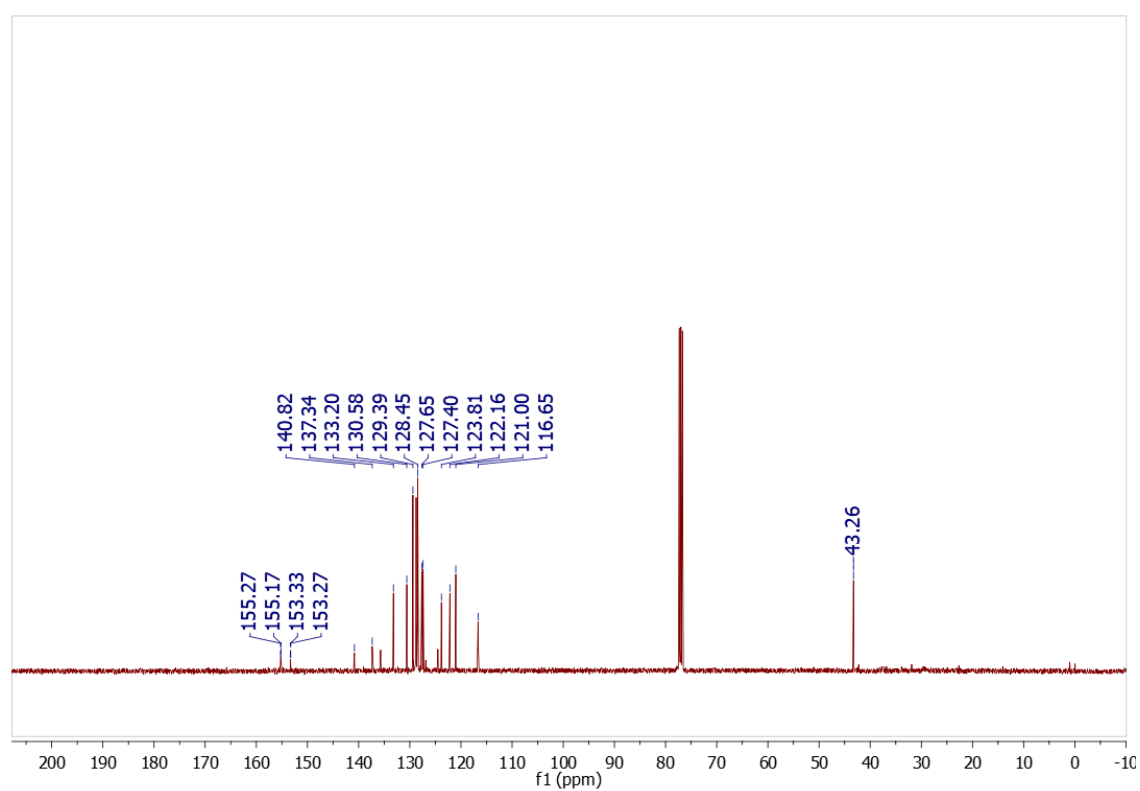
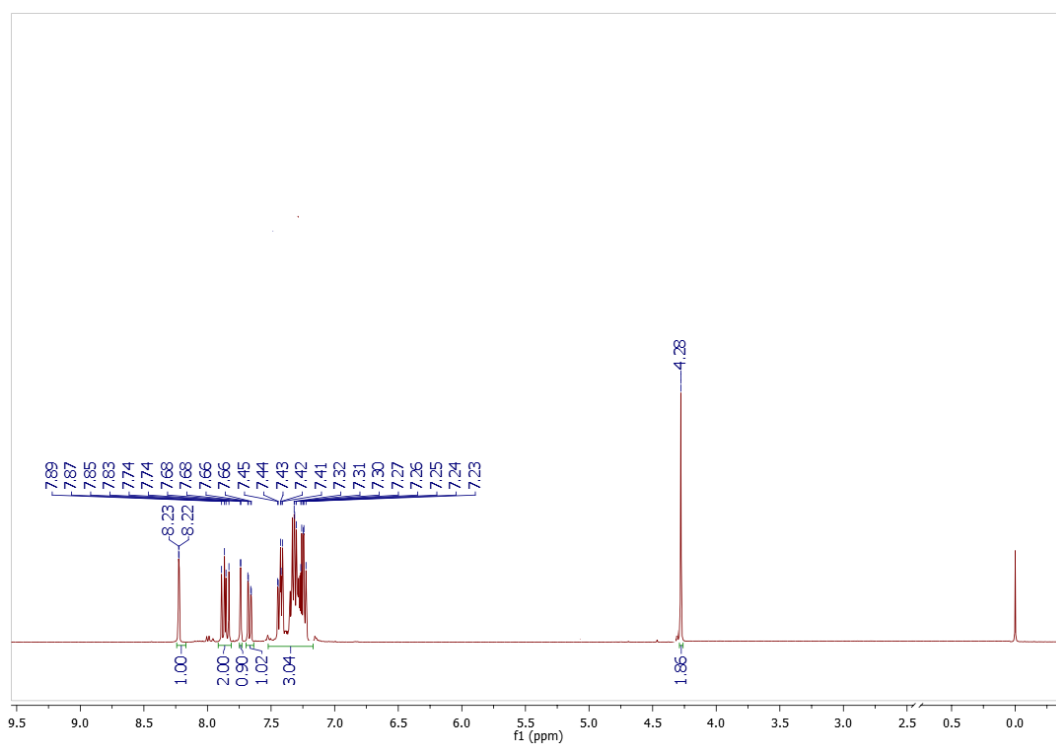
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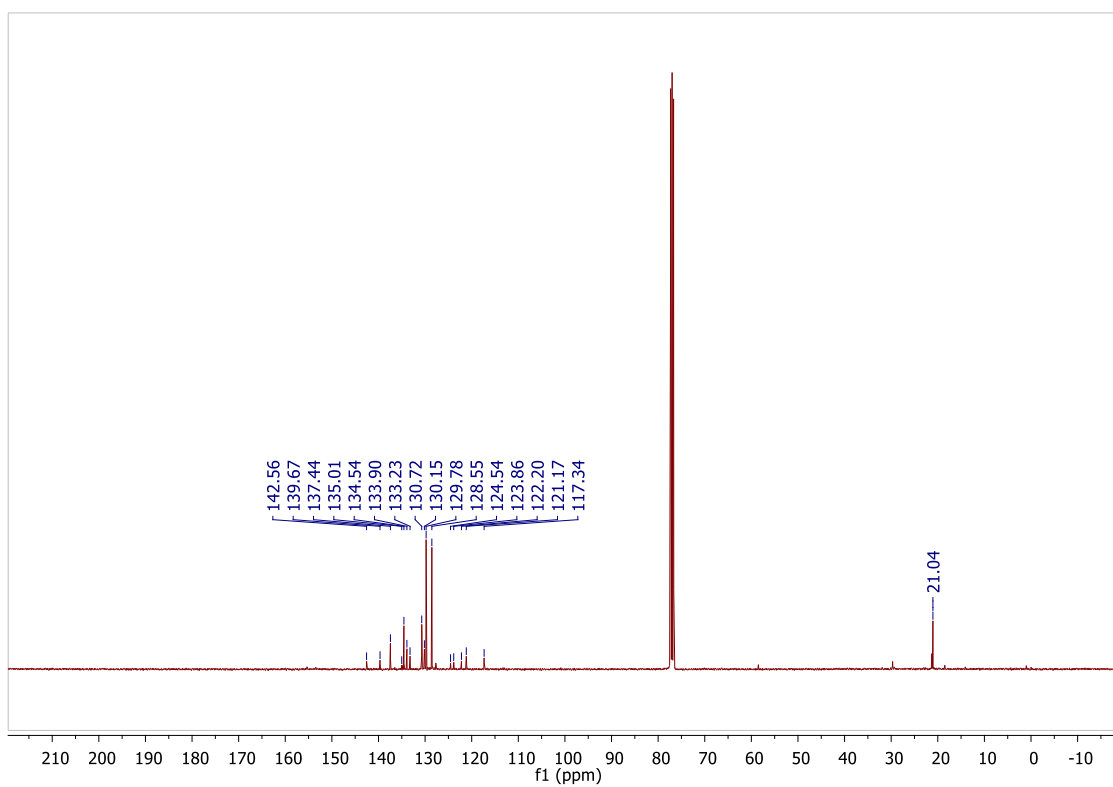
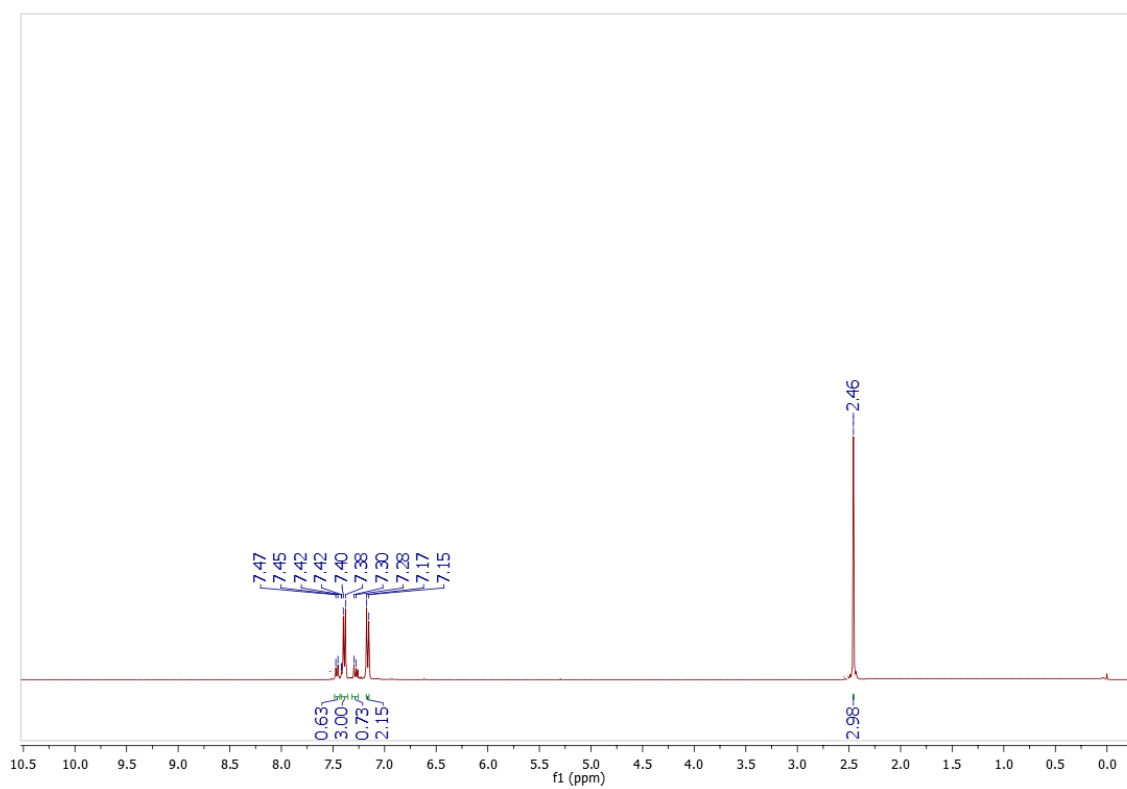
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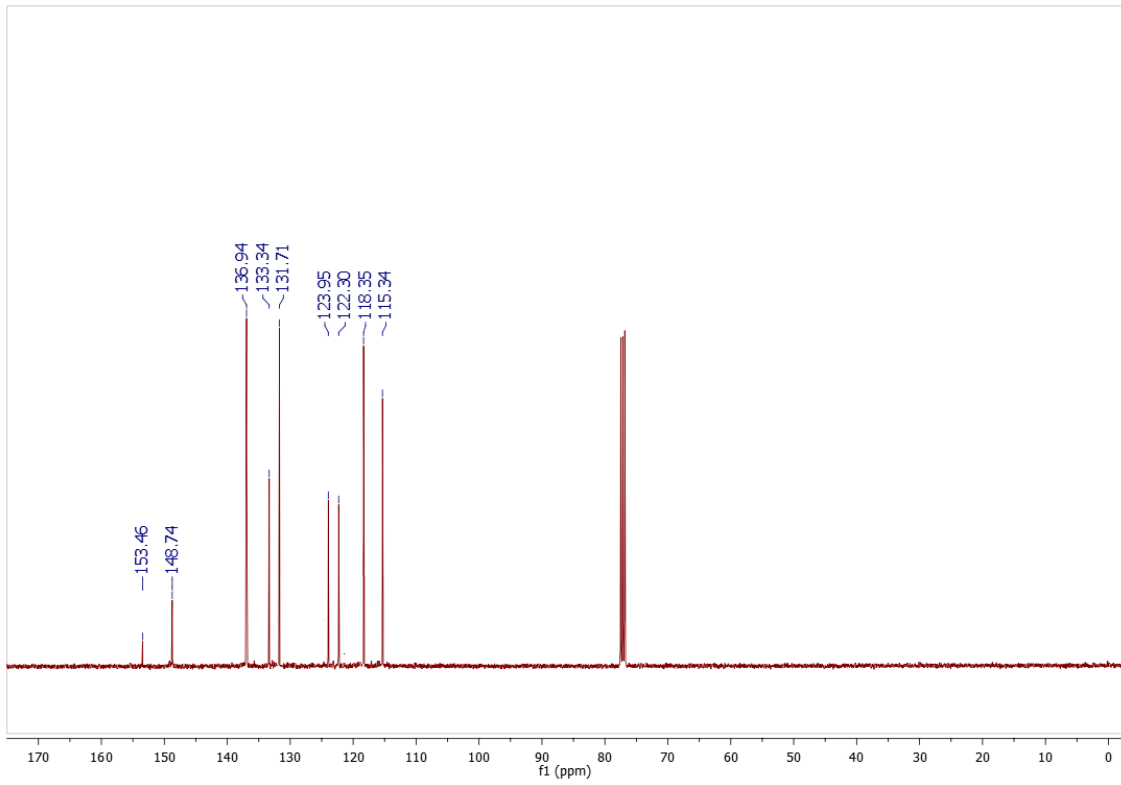
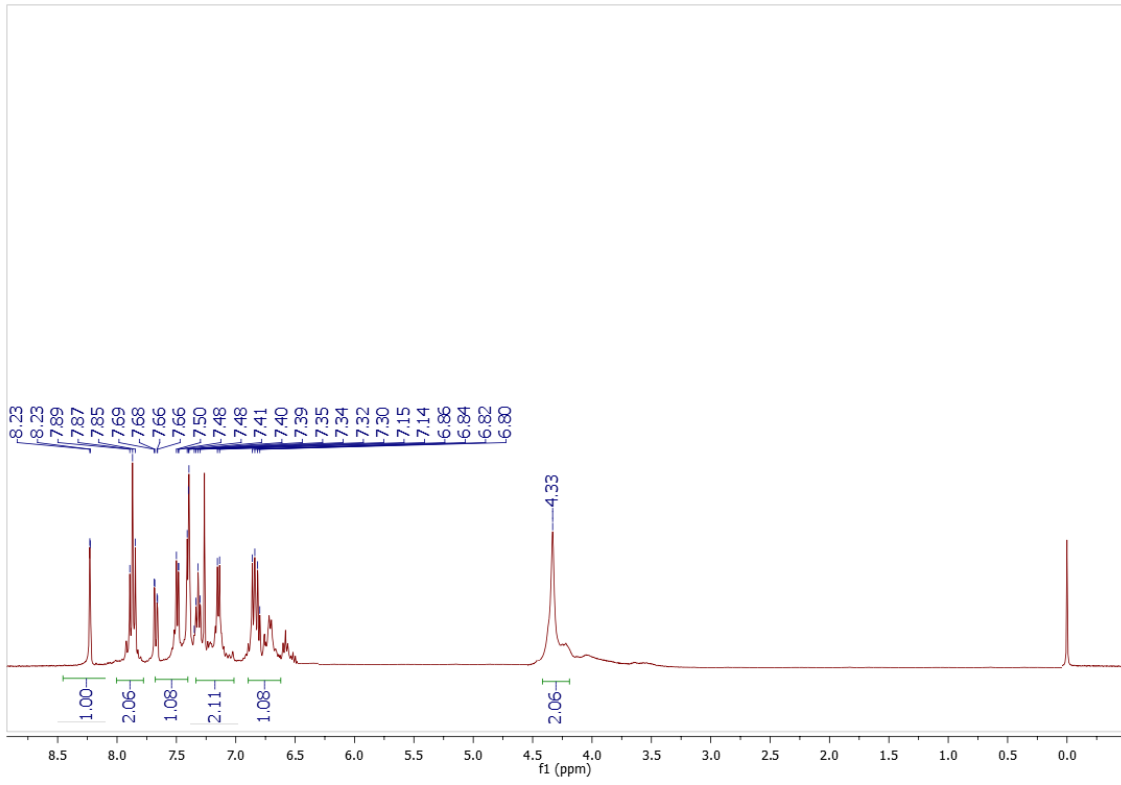
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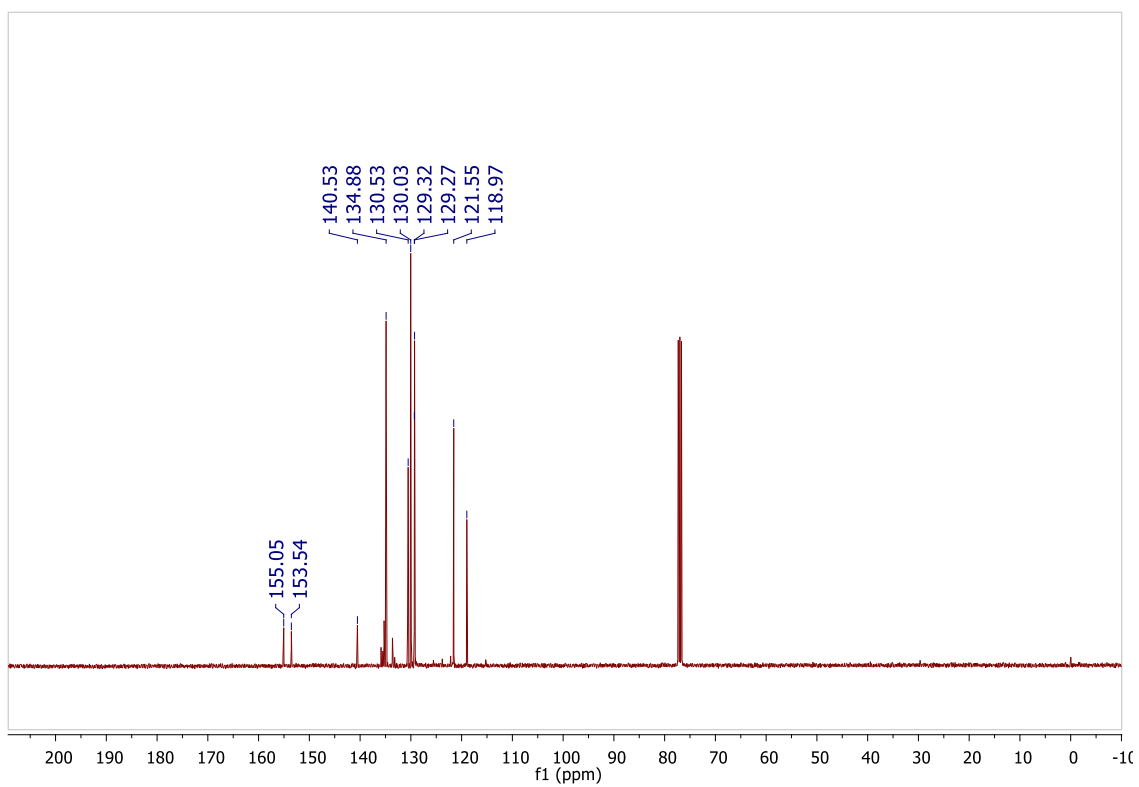
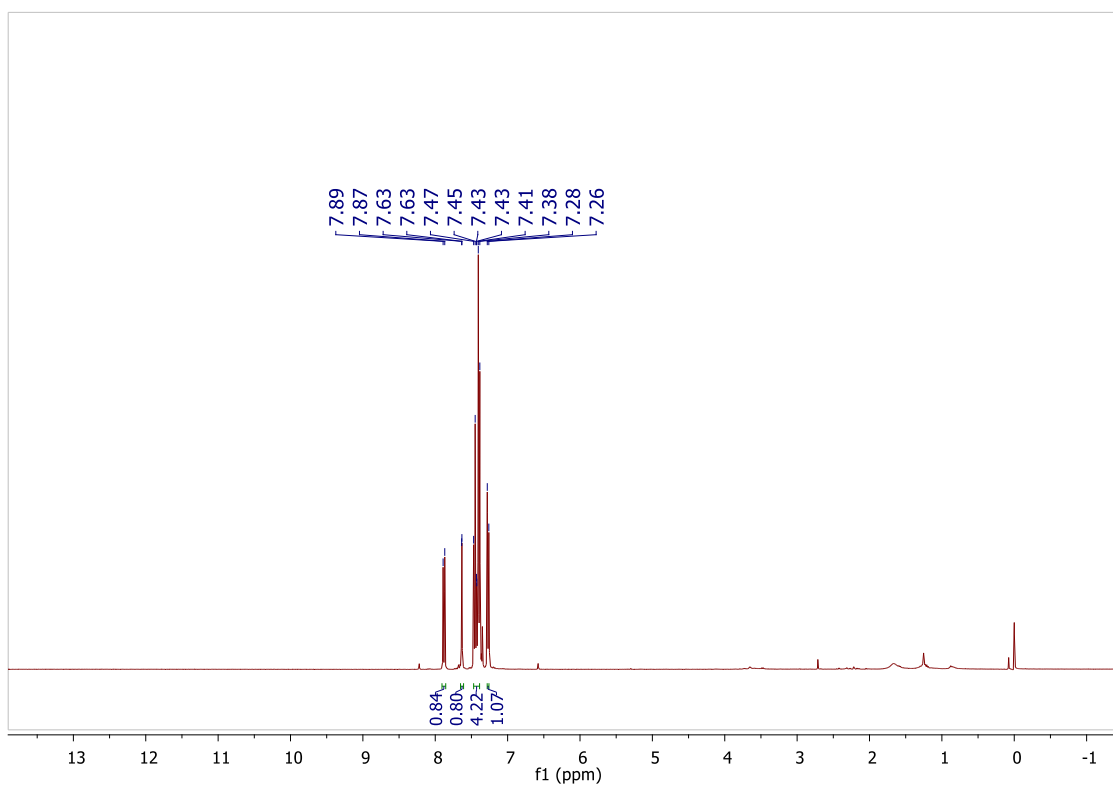
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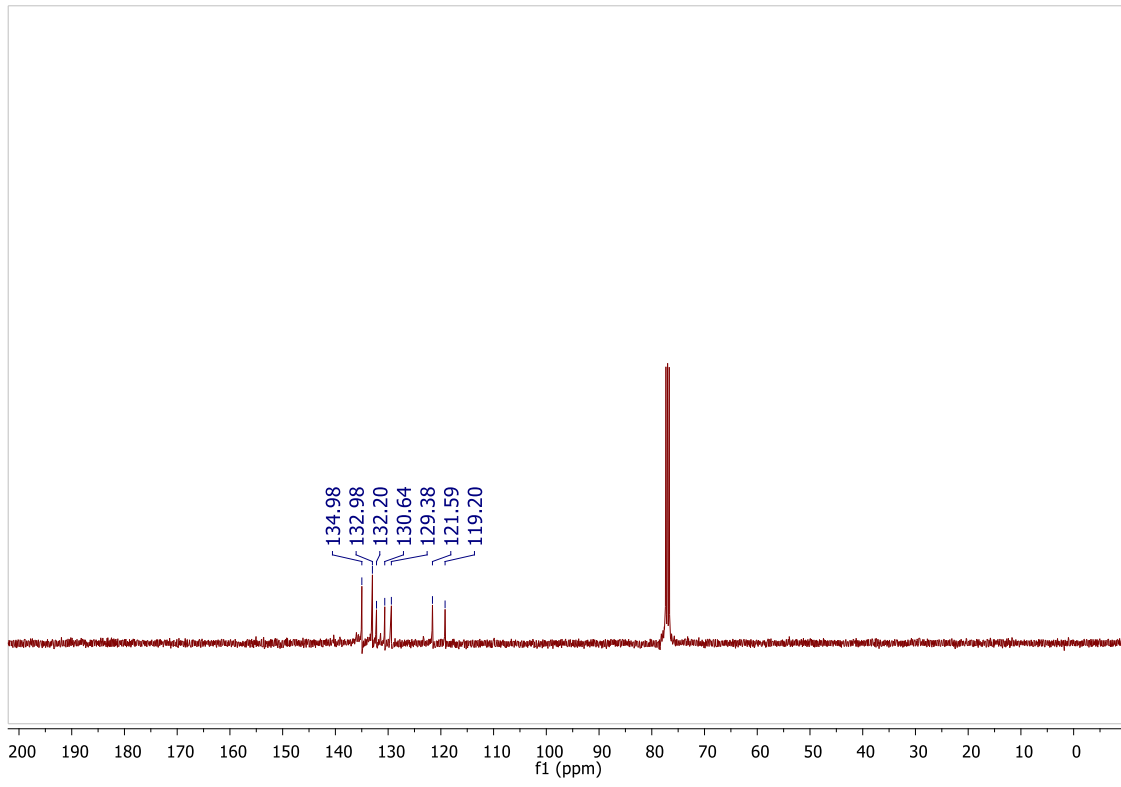
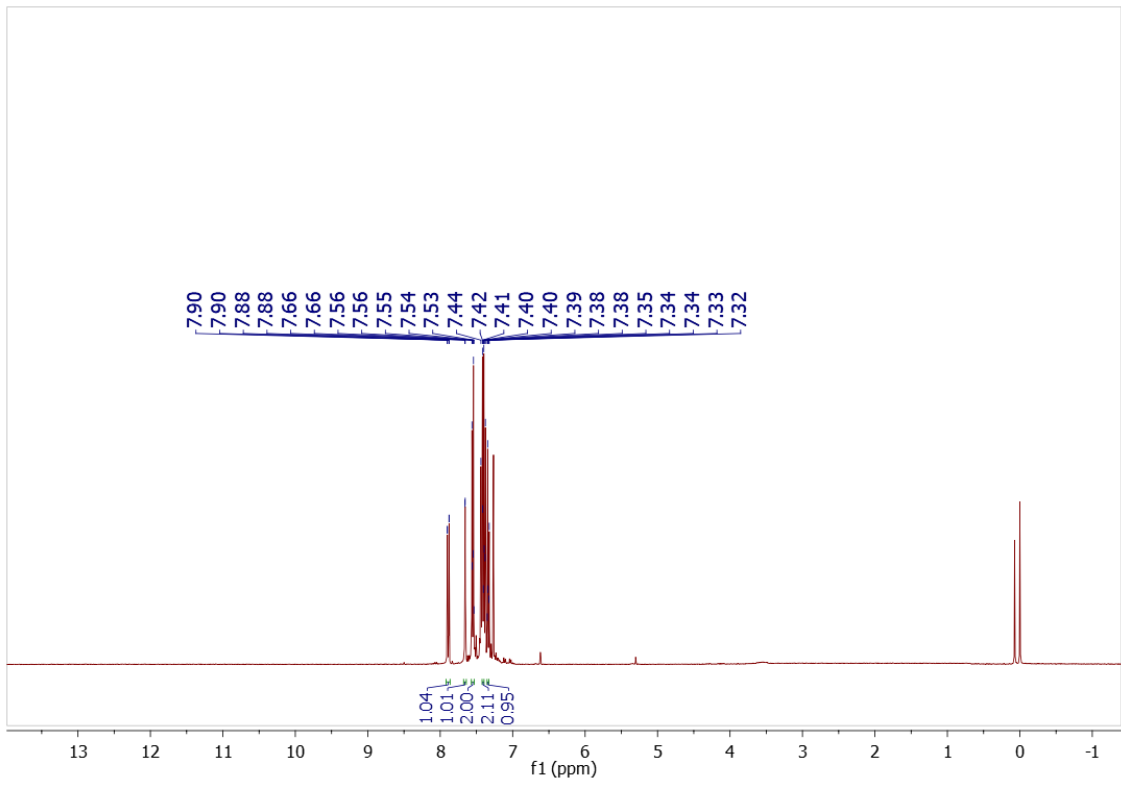
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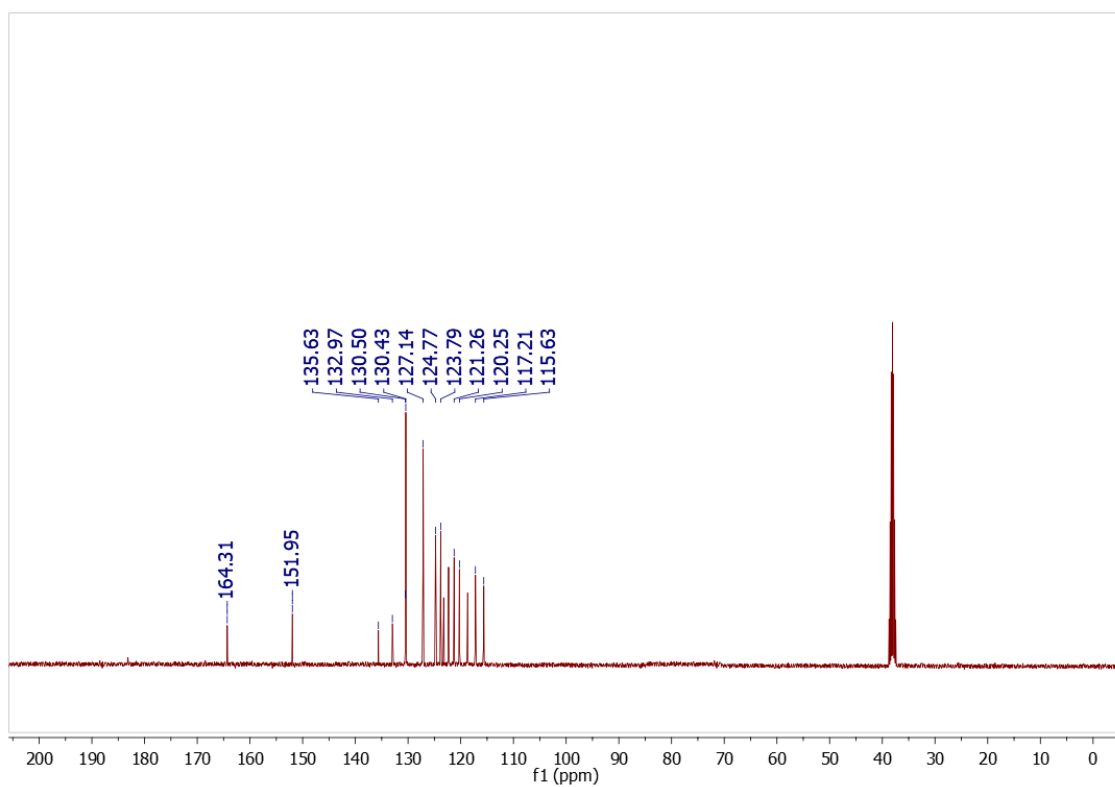
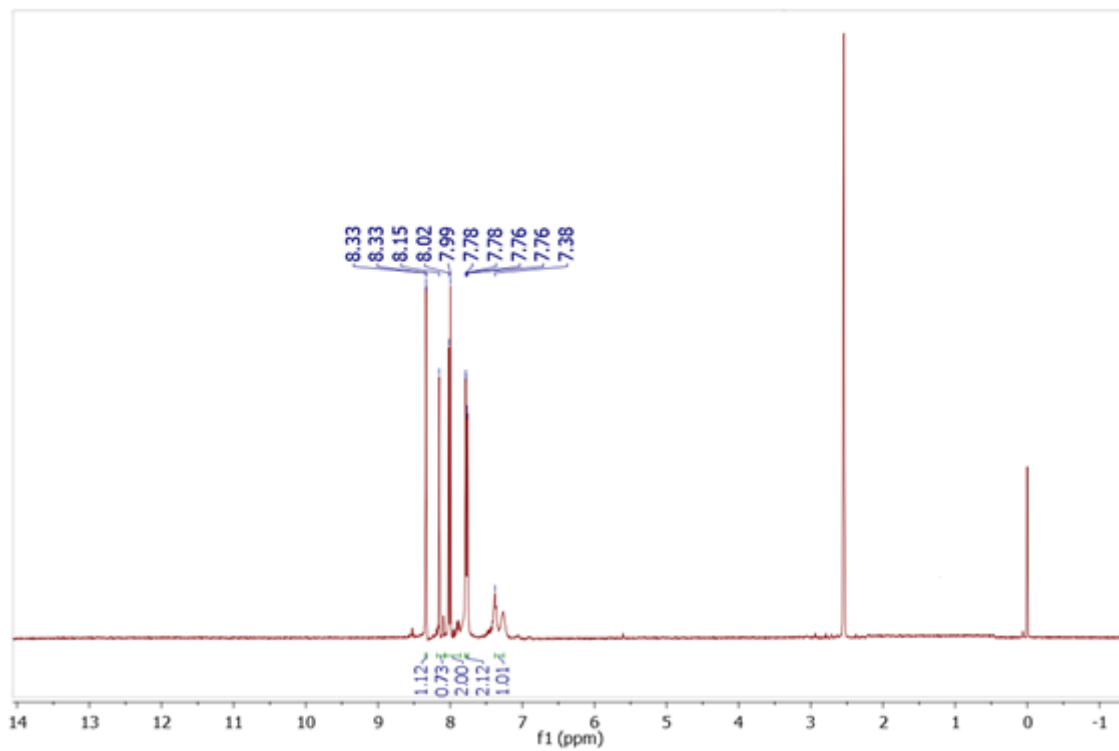
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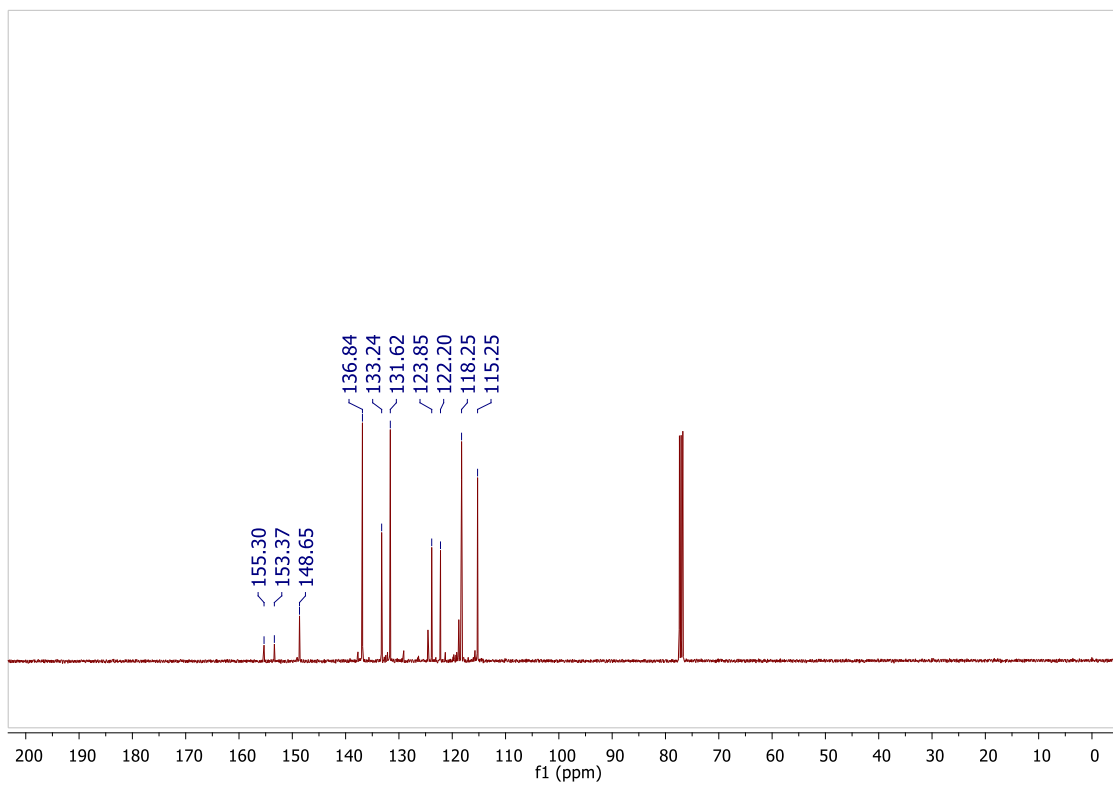
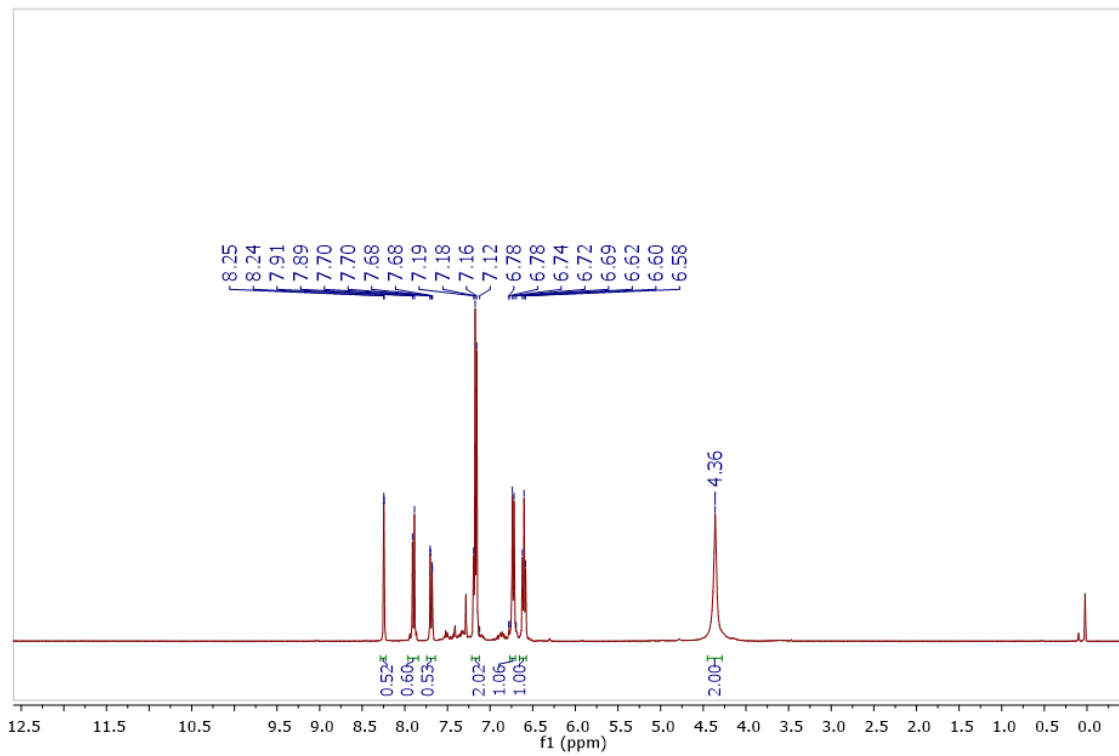
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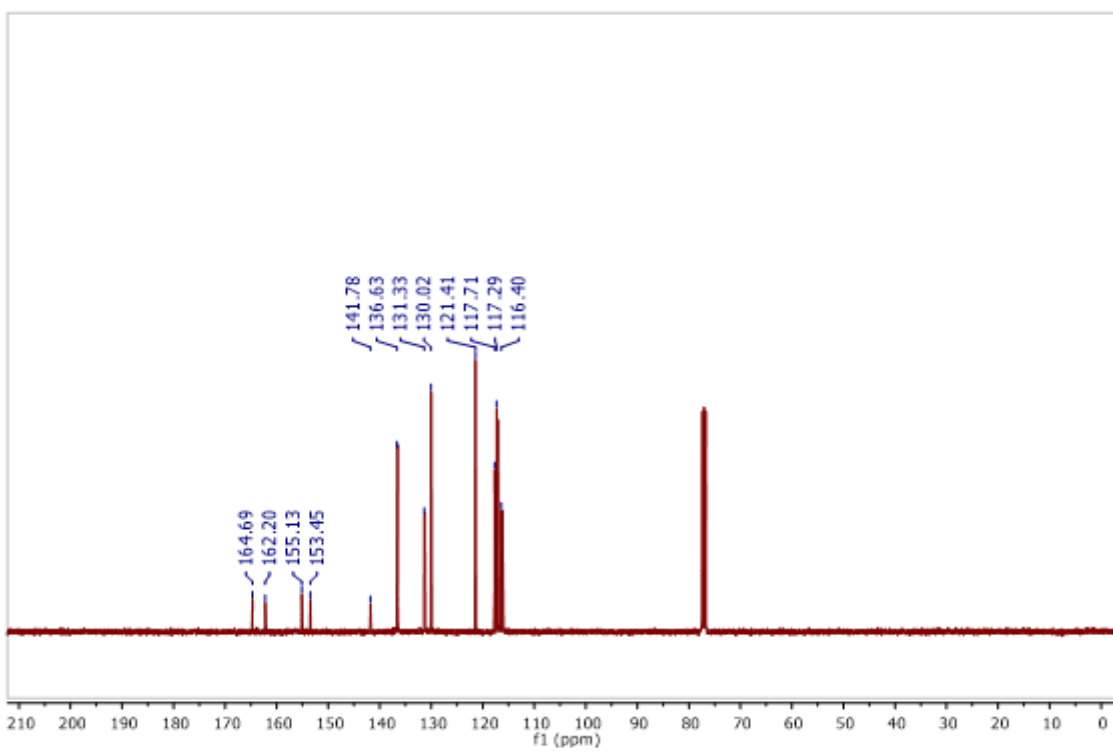
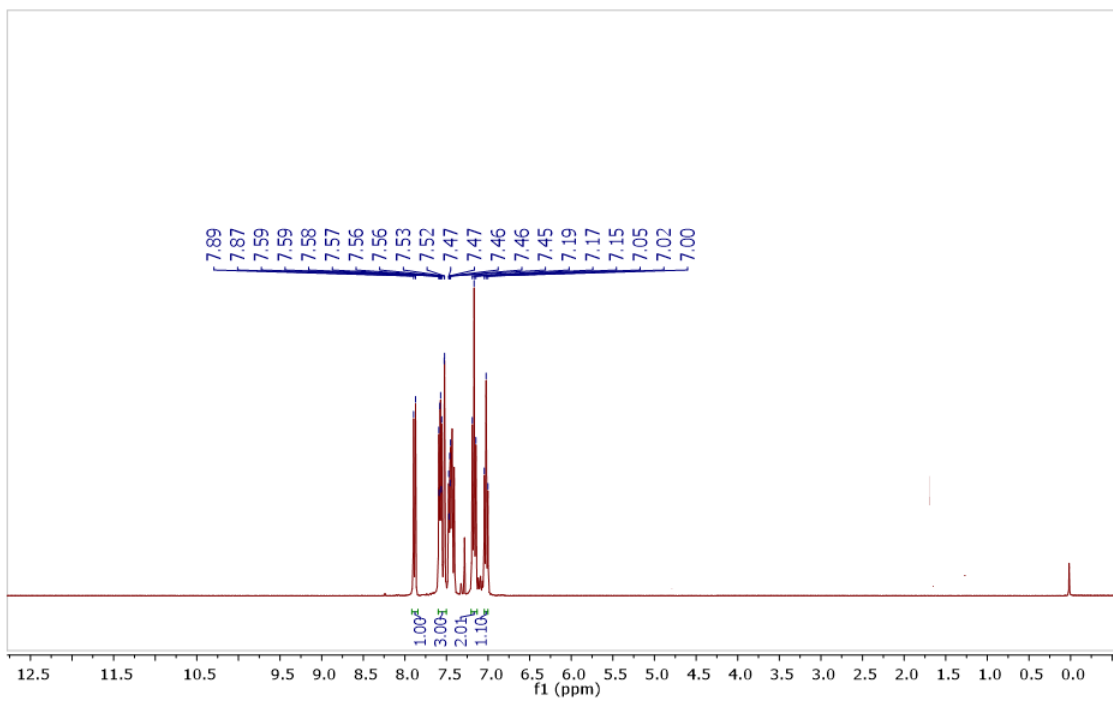
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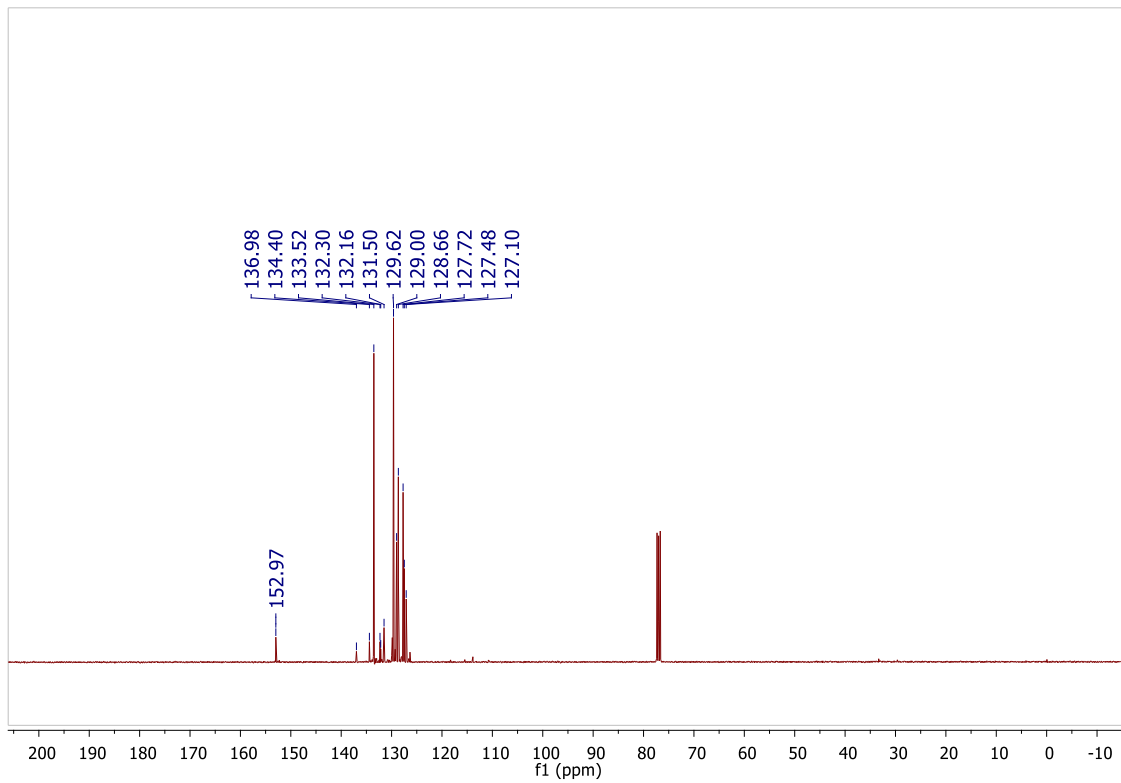
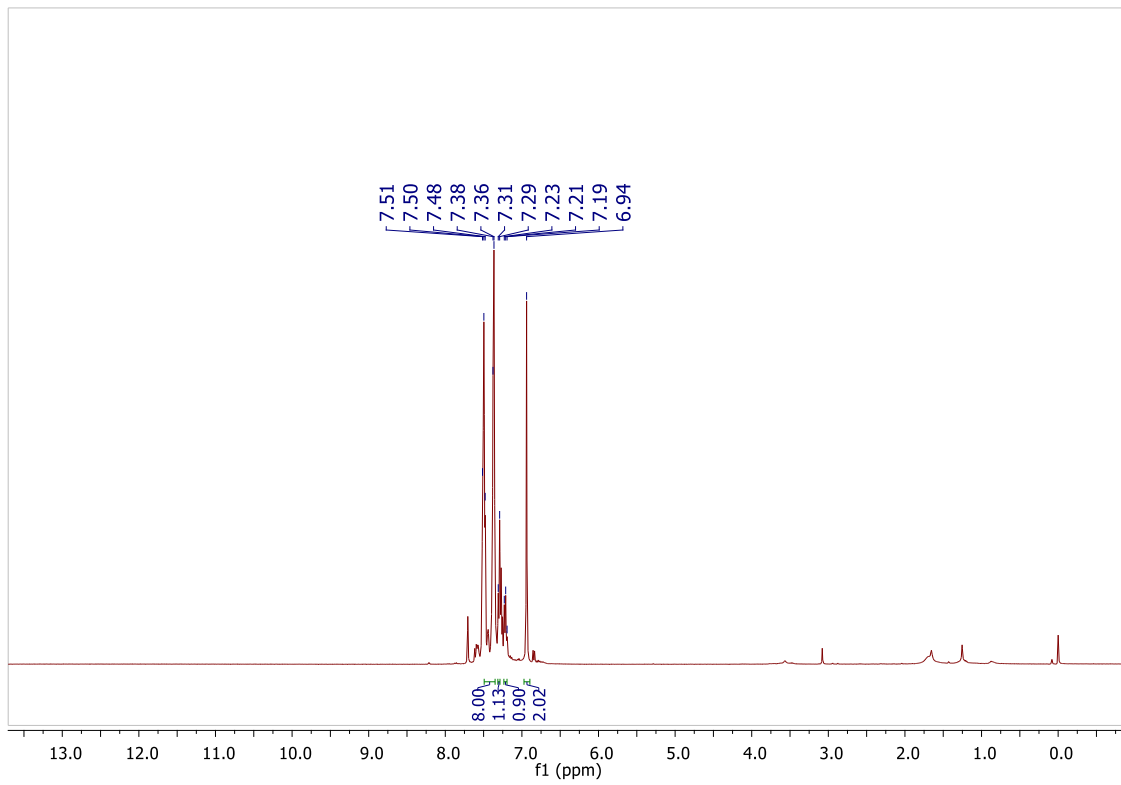
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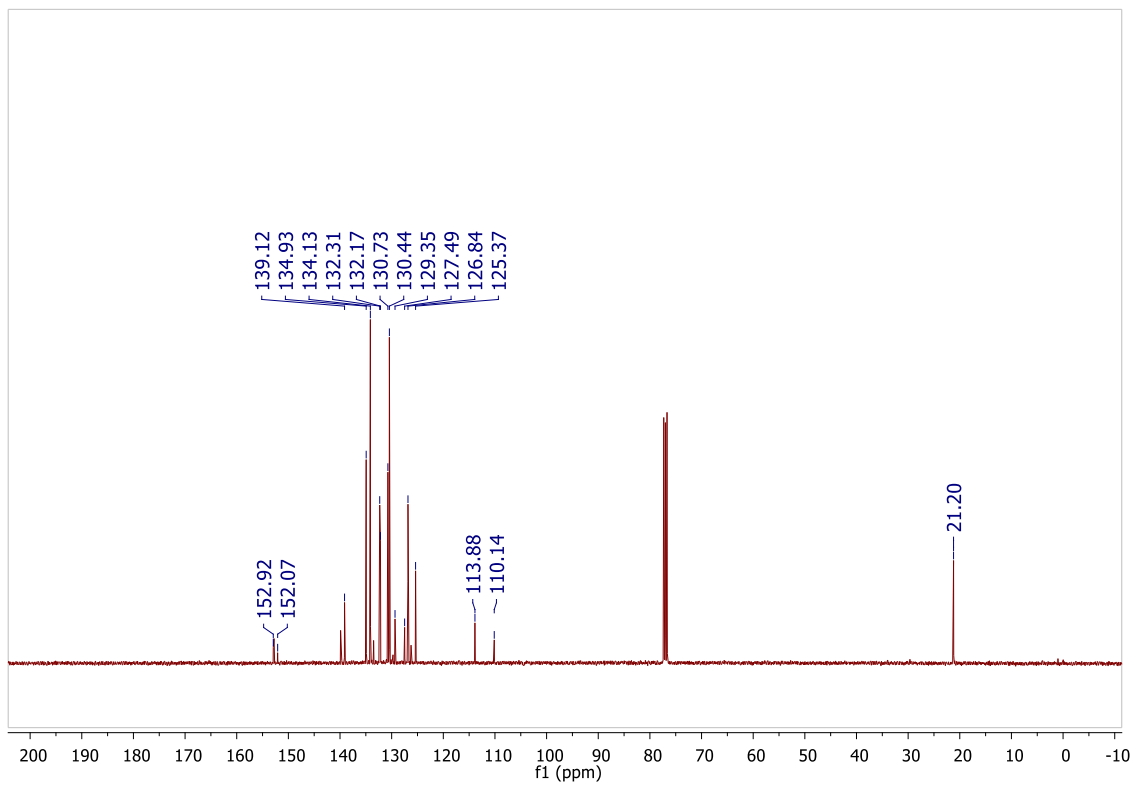
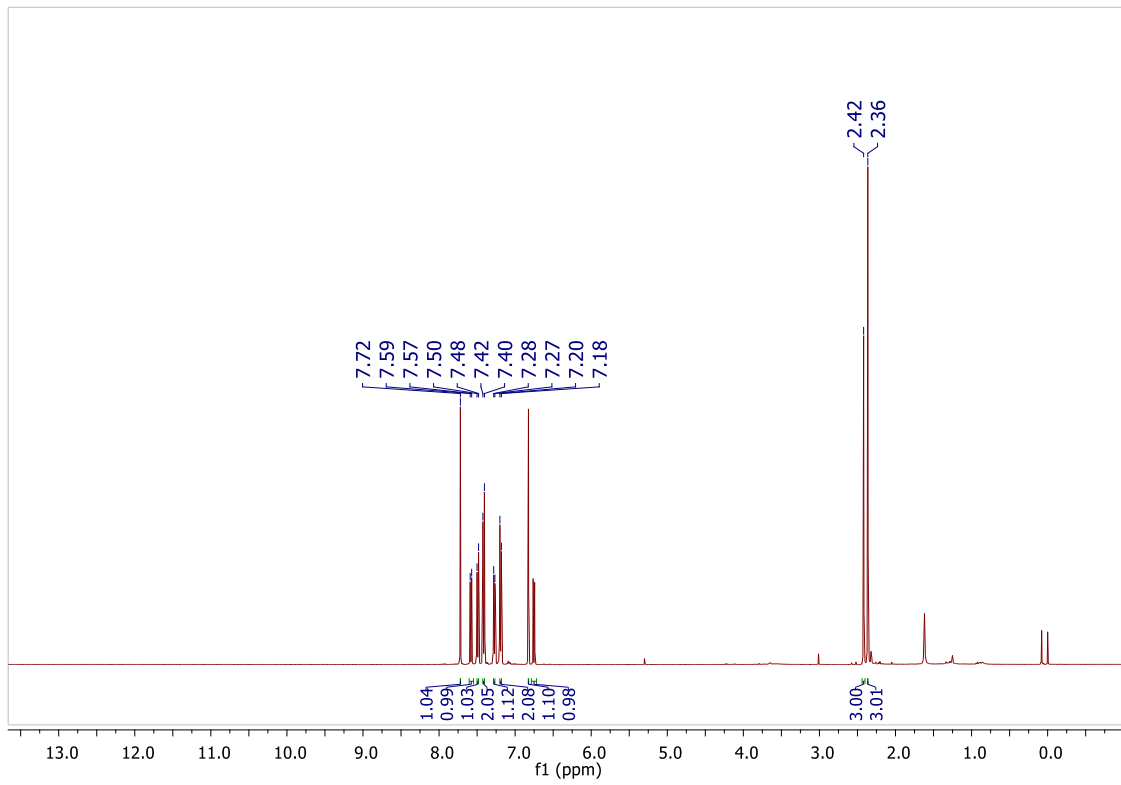
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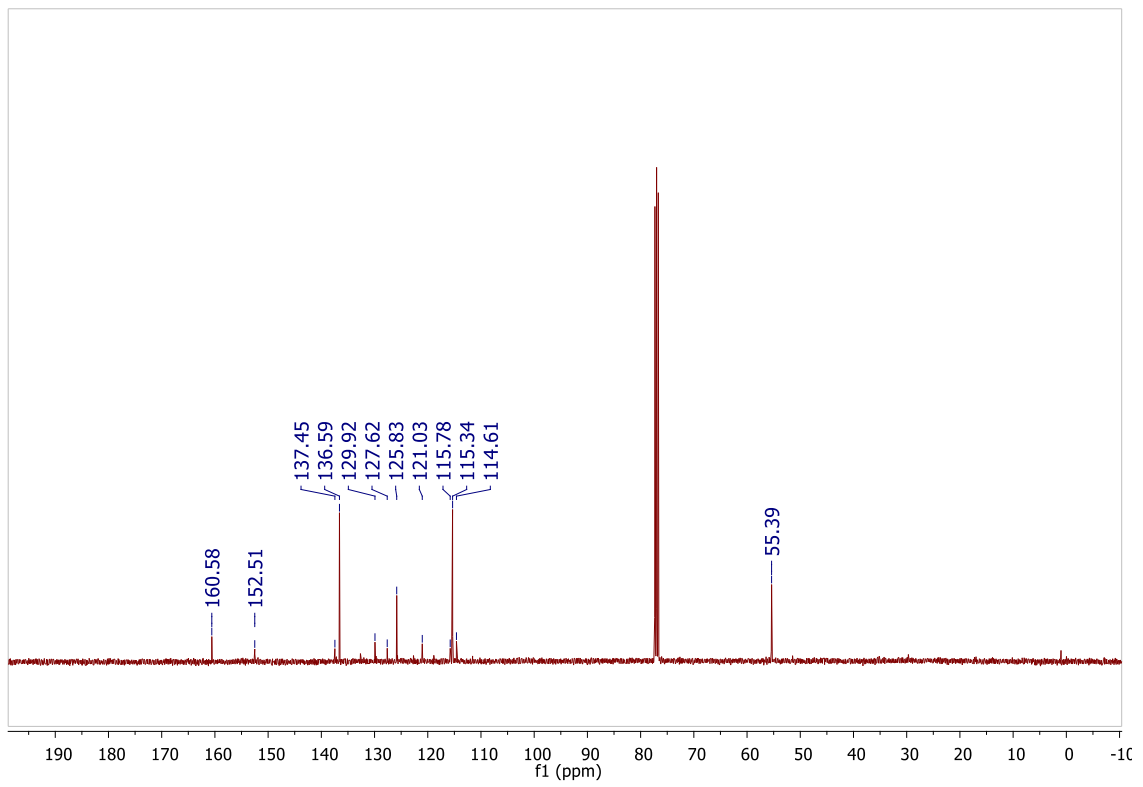
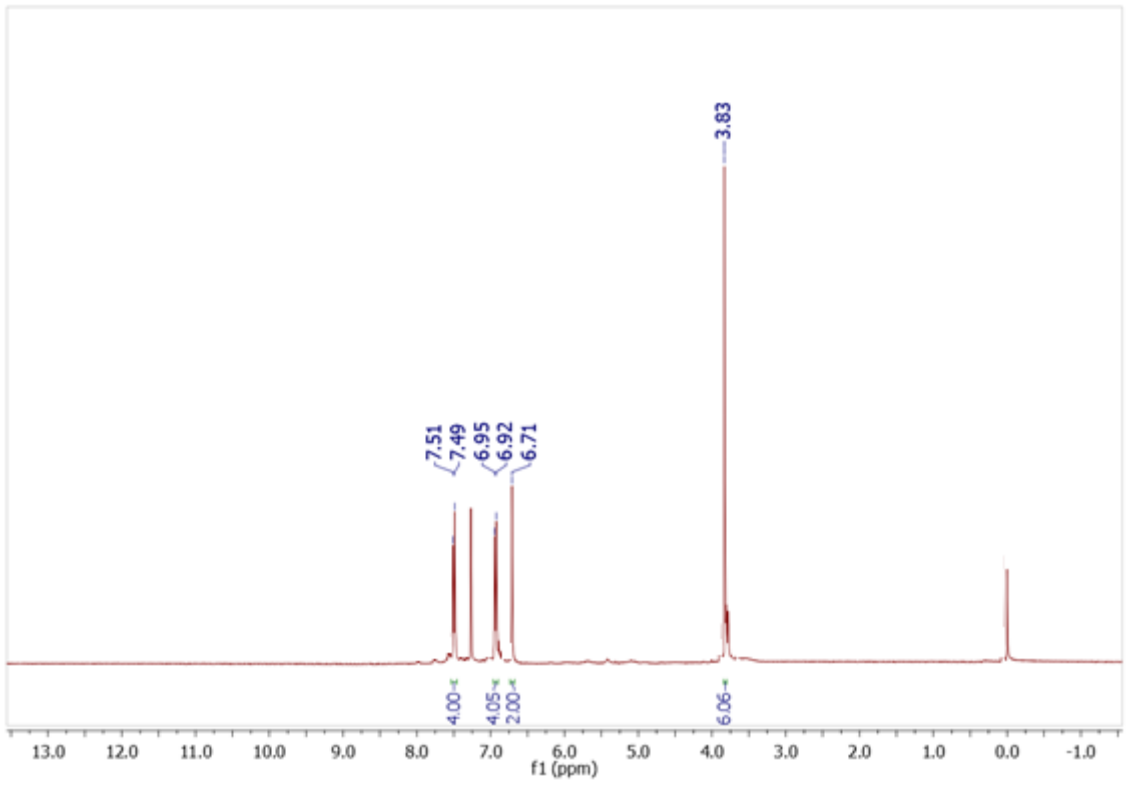
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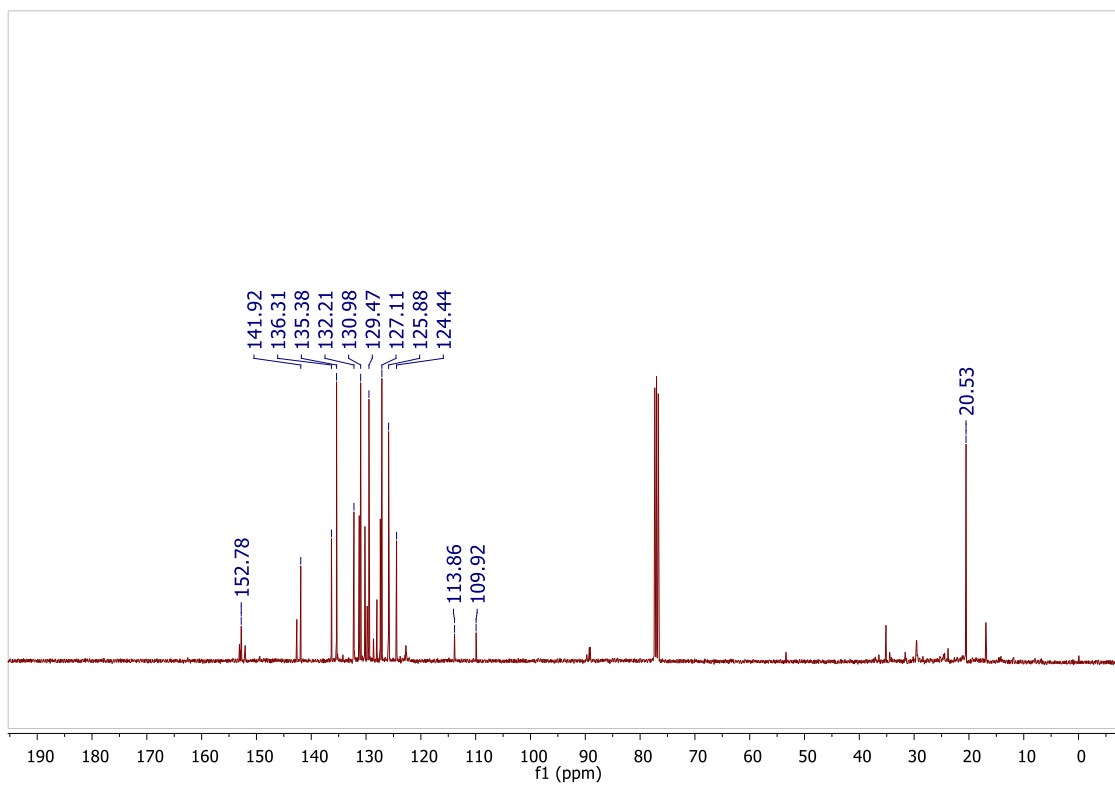
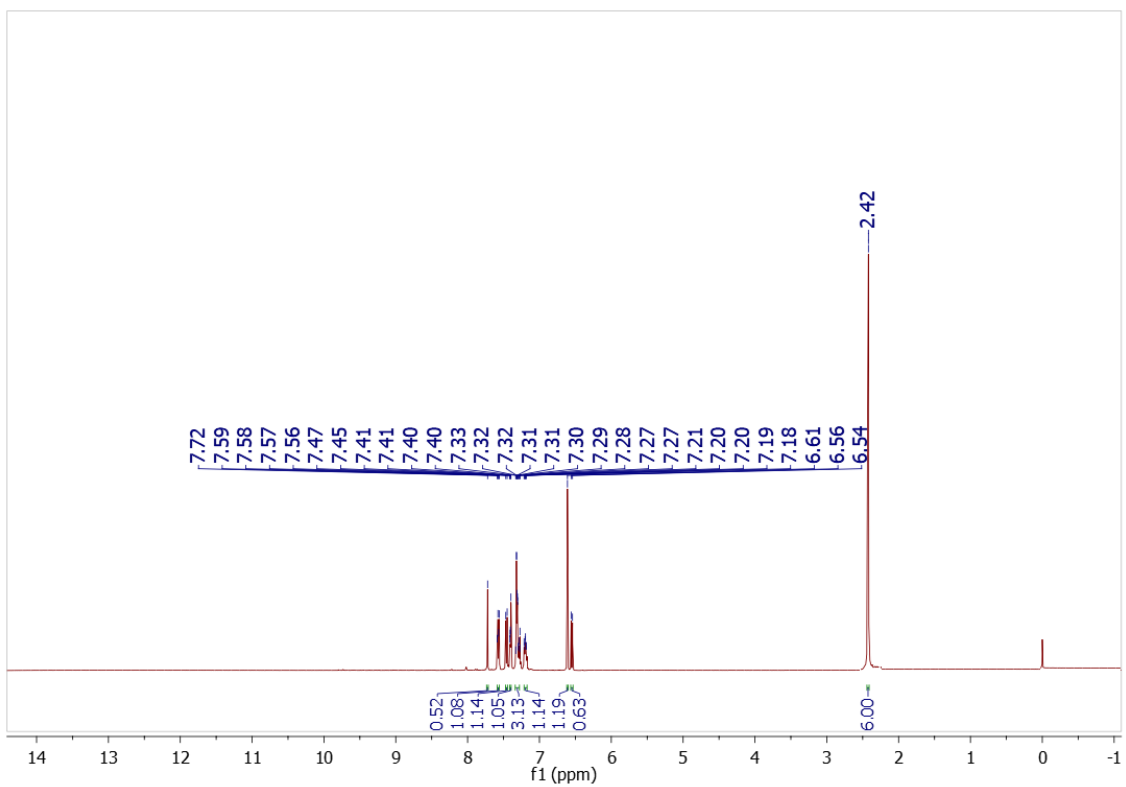
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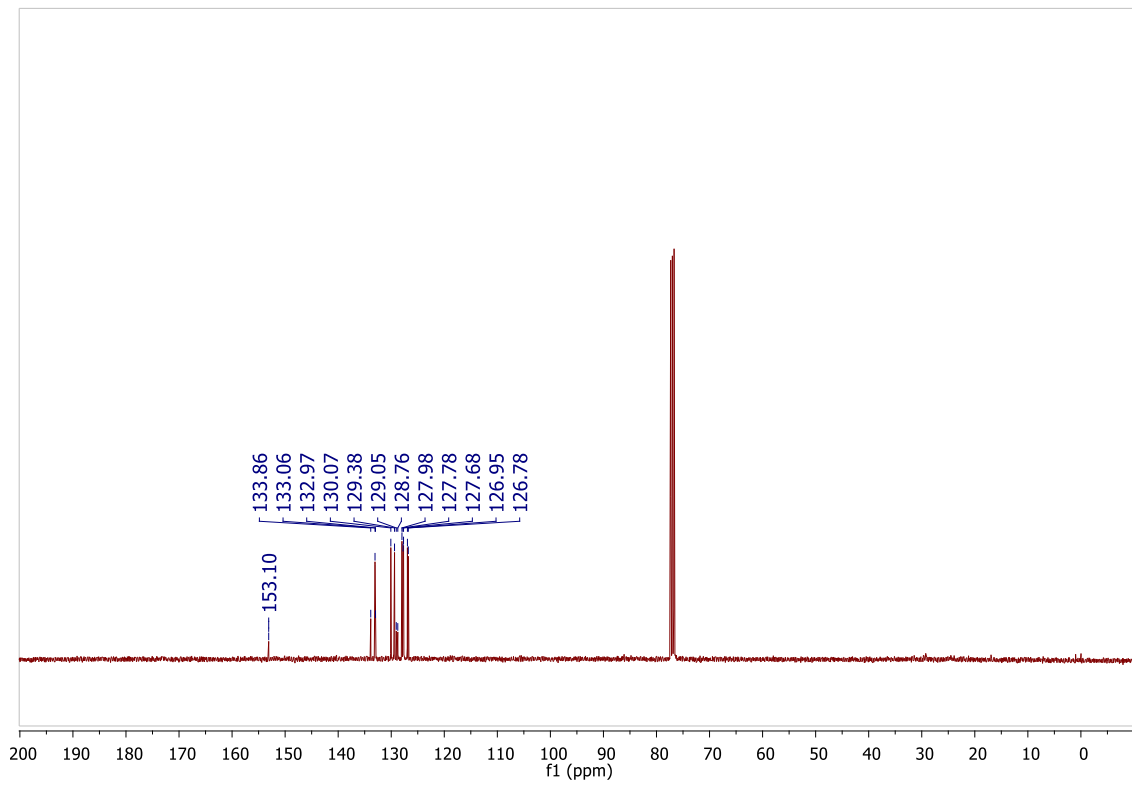
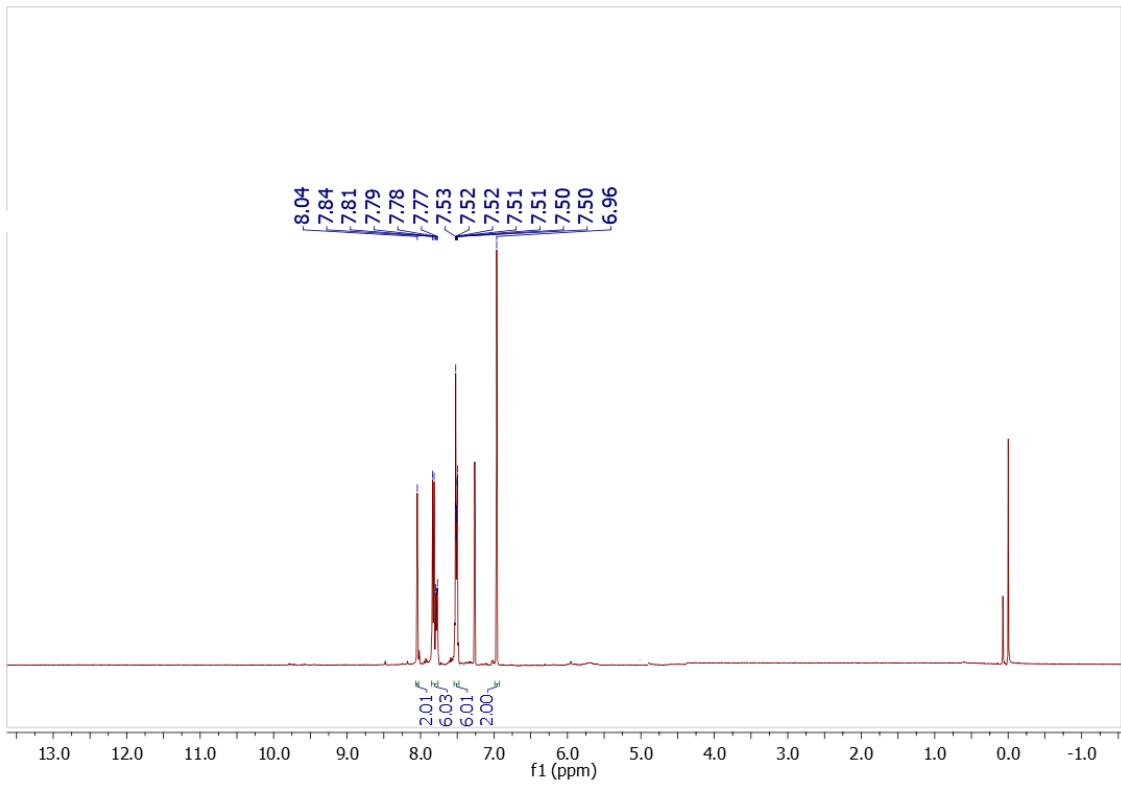
4c:



4d:



4e:



4f:

