

Electronic Supplementary Information

Tetranuclear Zn_2Ln_2 Coordination Clusters as catalysts in Petasis Borono-Mannich Multicomponent Reaction

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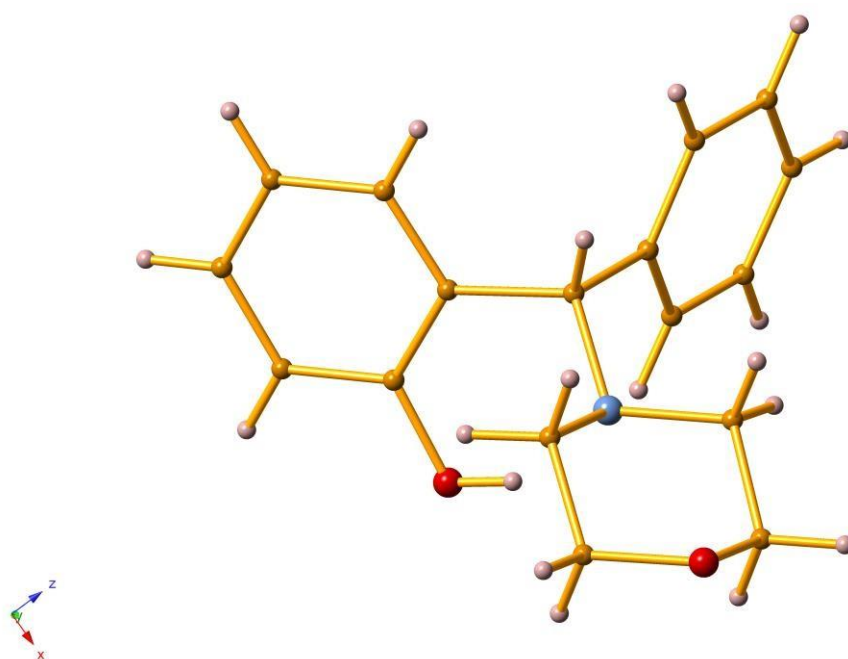
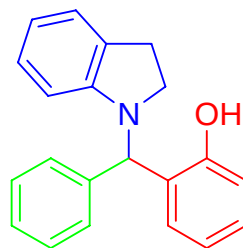


Figure S1. The crystal structure of compound **4aba**

Products

Synthesis of Compound **4aa**

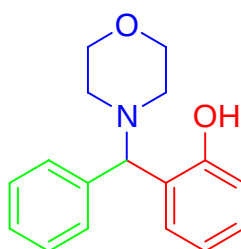


Salicylaldehyde (61 mg, 0.5 mmol), indoline (59 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4aaa** (289 mg, 0.96 mmol, 96%).

¹H NMR (CDCl₃, 500 MHz): δ = 11.03 (s, 1H), 7.54 – 7.48 (m, 1H), 7.46 – 7.39 (m, 2H), 7.32 – 7.26 (m, 3H), 7.19 – 7.15 (m, 1H), 7.14 – 7.11 (m, 1H), 6.99 – 6.92 (m, 3H), 6.90 (dd, J = 5.2 Hz, 3.8 Hz, 1H), 6.83 – 6.78 (m, 2H), 6.49 (d, J = 6.0 Hz, 1H), 5.34 (s, 1H), 3.21 (m, 1H), 3.01 (m, 1H), 2.93 (m, 1H).

¹³C NMR (CDCl₃, 126 MHz): δ = 156.22, 151.08, 139.54, 132.12, 128.50, 128.02, 127.37, 124.60, 121.08, 119.79, 117.02, 111.76, 69.98, 53.00, 28.51.

Synthesis of Compound **4aba**

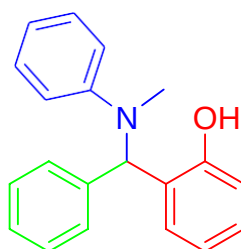


Salicylaldehyde (61 mg, 0.5 mmol), morpholine (43 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4aba** (255 mg, 0.95 mmol, 95%).

¹H NMR (CDCl₃, 500 MHz): δ = 10.36 (s, 1H), 7.43 – 7.38 (m, 2H), 7.46 – 7.39 (m, 2H), 7.28 – 7.24 (m, 3H), 7.19 – 7.16 (m, 1H), 7.01 – 6.96 (m, 1H), 6.74 – 6.69 (m, 2H), 4.64 (s, 1H), 3.60 (t, J = 5.2, 4H), 2.34 – 2.26 (m, 4H).

¹³C NMR (DMSO-d₆, 126 MHz): δ = 155.74, 147.70, 128.90, 128.88, 128.82, 128.58, 128.47, 128.14, 127.53, 127.36, 119.65, 116.31, 66.69, 52.50.

Synthesis of Compound **4aca**

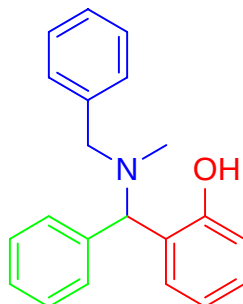


Salicylaldehyde (61 mg, 0.5 mmol), N-methylaniline (53 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4aca** (271 mg, 0.94 mmol, 94%).

¹H NMR (CDCl₃, 500 MHz): δ = 9.79 (s, 1H), 7.24 – 7.12 (m, 8H), 7.03 – 6.94 (m, 2H), 6.96 – 6.89 (m, 3H), 6.79 – 6.74 (m, 1H), 5.86 (s, 1H), 2.83 (s, 3H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 157.63, 149.45, 142.71, 131.90, 128.14, 26.88, 123.99, 121.72, 119.60, 117.33, 114.66, 68.55, 37.50.

Synthesis of Compound **4ada**

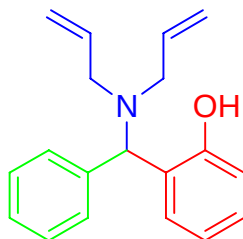


Salicylaldehyde (61 mg, 0.5 mmol), N-benzylmethylamine (60 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4ada** (282 mg, 0.93 mmol, 93%).

^1H NMR (CDCl_3 , 500 MHz): δ = 12.31 (s, 1H), 7.50 – 7.54 (m, 2H), 7.33 – 7.23 (m, 8H), 7.16 – 7.10 (m, 1H), 6.93 – 6.84 (m, 2H), 6.73 – 6.68 (m, 1H), 4.72 (s, 1H), 3.58 (s, 2H), 2.19 (s, 3H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 156.94, 138.79, 136.90, 129.25, 129.10, 128.94, 128.76, 128.63, 128.55, 128.02, 127.51, 125.24, 122.58, 118.83, 117.21, 75.53, 59.65, 38.92.

Synthesis of Compound **4aea**

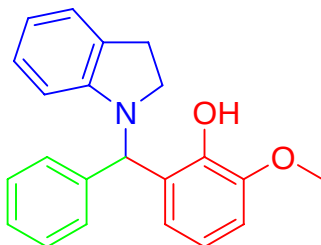


Salicylaldehyde (61 mg, 0.5 mmol), diallylamine (48 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4aea** (251 mg, 0.90 mmol, 90%).

^1H NMR (CDCl_3 , 500 MHz): δ = 12.08 (s, 1H), 7.43 – 7.37 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 7.13 – 7.09 (m, 1H), 6.86 – 6.78 (m, 2H), 6.69 (t, J = 6.2, 1H), 5.91 – 5.83 (m, 2H), 5.25 – 5.18 (m, 2H), 5.16 – 5.08 (m, 2H), 5.06 (s, 1H), 3.38 – 3.32 (m, 2H), 3.07 – 3.02 (m, 2H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 143.32, 133.50, 130.18, 129.53, 128.36, 127.83, 126.76, 121.28, 119.48, 118.41, 116.12, 71.39, 56.22.

Synthesis of Compound **4baa**

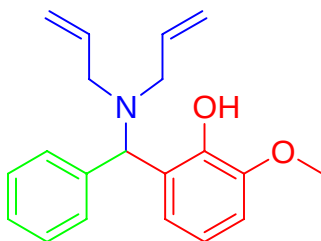


2-methoxybenzaldehyde (68 mg, 0.5 mmol), indoline (59 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4baa** (314 mg, 0.95 mmol, 95%).

^1H NMR (CDCl_3 , 500 MHz): δ = 7.56 (s, 1H), 7.44 – 7.36 (m, 2H), 7.31 – 7.24 (m, 3H), 7.10 (dd, J = 4.5, J = 3.6, 1H), 6.95 – 6.90 (m, 1H), 6.82 – 6.75 (m, 3H), 6.72 – 6.68 (m, 1H), 6.33 (d, J = 4.8 Hz), 5.72 (s, 1H), 3.90 (s, 3H), 3.21– 3.14 (m, 2H), 2.95 (t, J = 6.2 Hz, 2H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 151.78, 147.15, 144.31, 140.67, 130.87, 128.55, 128.41, 127.32, 127.19, 124.22, 121.14, 120.65, 119.42, 118.70, 109.88, 109.53, 63.54, 55.98, 52.32, 28.43.

Synthesis of Compound **4bea**

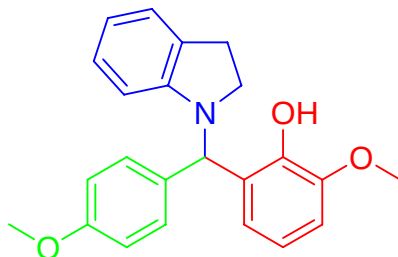


2-methoxybenzaldehyde (68 mg, 0.5 mmol), indoline (59 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4bea** (287 mg, 0.93 mmol, 93%).

^1H NMR (CDCl_3 , 500 MHz): δ = 12.32 (s, 1H), 7.48 – 7.37 (m, 4H), 6.58 – 6.52 (m, 1H), 6.51 – 6.44 (m, 3H), 5.86 – 6.77 (m, 2H), 5.24 – 5.12 (m, 5H), 3.78 (s, 3H), 3.44 – 3.38 (m, 2H), 3.24 – 2.17 (m, 2H).

¹³C NMR (CDCl₃, 126 MHz): δ = 148.68, 144.39, 142.91, 134.23, 129.35, 128.49, 127.98, 126.99, 123.60, 121.15, 118.47, 110.72, 73.03, 58.13, 52.28.

Synthesis of Compound **4bab**

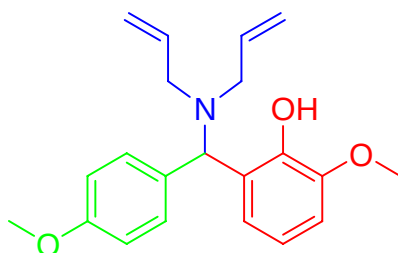


2-methoxybenzaldehyde (68 mg, 0.5 mmol), indoline (59 mg, 0.5 mmol), 4-Methoxyphenylboronic acid (76 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4bab** (354 mg, 0.98 mmol, 98%).

¹H NMR (CDCl₃, 500 MHz): δ = 7.36 – 7.28 (m, 2H), 7.13 – 7.08 (m, 1H), 7.05 – 6.99 (m, 1H), 6.96 – 6.88 (m, 3H), 6.87 – 6.82 (m, 2H), 6.80 – 6.74 (m, 1H), 6.36 (d, J = 4.8 Hz, 1H), 5.64 (s, 1H), 3.90 (s, 3H), 3.81 (s, 3H), 3.21 – 3.14 (m, 2H), 2.95 (t, J = 5.2 Hz, 2H).

¹³C NMR (CDCl₃, 126 MHz): δ = 158.61, 151.92, 147.43, 144.20, 132.39, 130.89, 129.80, 126.81, 124.21, 120.76, 119.26, 118.39, 113.27, 109.69, 109.46, 63.58, 55.96, 55.20.

Synthesis of Compound **4beb**

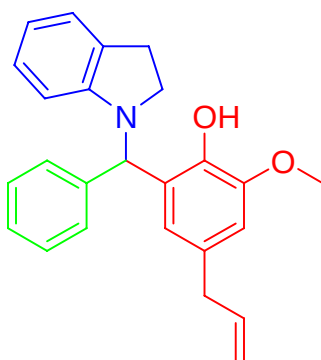


2-methoxybenzaldehyde (68 mg, 0.5 mmol), diallylamine (48 mg, 0.5 mmol), 4-Methoxyphenylboronic acid (76 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4beb** (315 mg, 0.93 mmol, 93%).

¹H NMR (CDCl₃, 500 MHz): δ = 12.45 (s, 1H), 7.34 – 7.27 (m, 2H), 6.88 – 6.80 (m, 2H), 6.77 – 6.72 (m, 1H), 6.65 (t, 1H), 6.46 – 6.39 (m, 1H), 5.91 – 5.84 (m, 2H), 5.22 – 5.15 (m, 3H), 5.02 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.37 – 3.31 (m, 2H), 3.06 – 2.99 (m, 2H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 159.30, 148.30, 146.97, 135.50, 130.61, 130.18, 125.51, 121.20, 119.35, 118.41, 113.93, 113.56, 110.68, 69.24, 55.20, 52.27.

Synthesis of Compound **4caa**

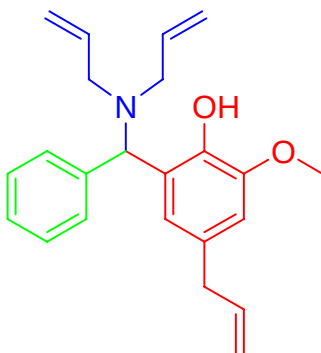


5-Allyl-2-hydroxy-3-methoxybenzaldehyde (96 mg, 0.5 mmol), indoline (59 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4caa** (322 mg, 0.87 mmol, 87%).

^1H NMR (CDCl_3 , 500 MHz): δ = 7.45 (dd, J = 6.4 Hz, 4.5 Hz, 2H), 7.31 – 7.24 (m, 3H), 7.20 – 7.15 (m, 1H), 7.13 – 7.06 (m, 3H), 6.95 – 6.88 (m, 1H), 6.55 – 6.48 (m, 2H), 5.91 – 5.86 (m, 1H), 5.65 (s, 1H), 5.02 – 4.94 (m, 2H), 3.88 (s, 3H), 3.29 – 3.23 (m, 2H), 3.20 – 3.08 (m, 3H), 2.94 – 2.87 (m, 2H).

^{13}C NMR (CDCl_3 , 126 MHz): δ = 151.87, 147.13, 142.58, 140.72, 137.81, 131.06, 128.54, 128.40, 128.16, 127.30, 127.19, 124.19, 120.88, 119.56, 118.82, 115.47, 110.34, 109.75, 64.13, 56.04, 52.45, 39.95, 28.45.

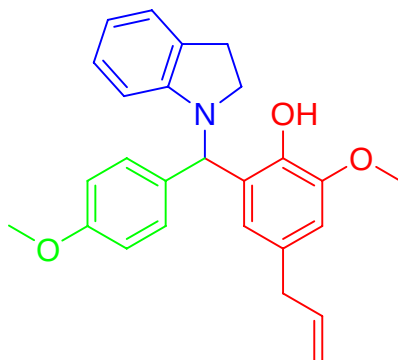
Synthesis of Compound **4cea**



5-Allyl-2-hydroxy-3-methoxybenzaldehyde (96 mg, 0.5 mmol), diallylamine (48 mg, 0.5 mmol), benzene boronic acid (61 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4cea** (293 mg, 0.84 mmol, 84%).

¹H NMR (CDCl₃, 500 MHz): δ = 12.08 (s, 1H), 7.44 – 7.38 (m, 2H), 7.32 – 7.24 (m, 3H), 6.59 (d, 1H), 6.31 (d, 1H), 5.89 – 5.81 (m, 3H), 5.22 – 5.17 (m, 2H), 5.13 – 5.09 (m, 2H), 5.00 – 4.94 (m, 3H), 3.88 (s, 3H), 3.44 – 3.39 (m, 2H), 3.19 – 3.14 (m, 2H), 3.10 – 3.05 (m, 2H).
¹³C NMR (CDCl₃, 126 MHz): δ = 148.19, 144.87, 137.80, 133.29, 129.24, 127.91, 123.71, 122.48, 120.92, 119.38, 110.09, 70.39, 55.91, 52.28.

Synthesis of Compound **4cab**

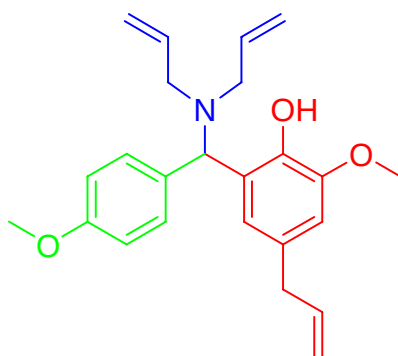


5-Allyl-2-hydroxy-3-methoxybenzaldehyde (96 mg, 0.5 mmol), indoline (59 mg, 0.5 mmol), 4-Methoxyphenylboronic acid (76 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4cab** (357 mg, 0.89 mmol, 89%).

¹H NMR (CDCl₃, 500 MHz): δ = 7.90 (s, 1H), 7.34 – 7.28 (m, 2H), 7.10 – 7.04 (m, 2H), 6.95 – 6.91 (m, 1H), 6.88 – 6.82 (m, 2H), 6.66 – 6.56 (m, 4H), 6.35 – 6.30 (m, 1H), 5.94 – 5.90 (m, 1H), 5.54 (s, 1H), 5.05 – 4.94 (m, 2H), 3.87 (m, 3H), 3.80 (m, 3H), 3.28 – 3.24 (m, 2H), 3.11 – 3.05 (m, 3H), 2.98 (t, J = 4.6 Hz, 2H).

¹³C NMR (CDCl₃, 126 MHz): δ = 158.86, 151.68, 146.99, 142.72, 137.83, 132.72, 131.14, 129.75, 129.46, 127.20, 124.20, 121.37, 120.63, 119.03, 115.54, 113.94, 113.81, 110.33, 110.03, 64.11, 55.11, 52.70, 40.32, 28.53.

Synthesis of Compound **4ceb**

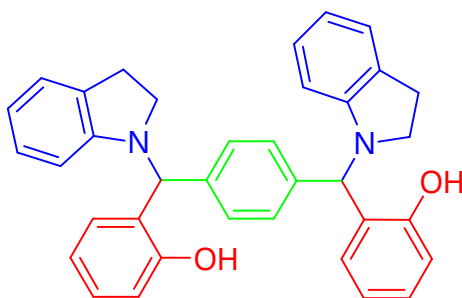


5-Allyl-2-hydroxy-3-methoxybenzaldehyde (96 mg, 0.5 mmol), diallylamine (48 mg, 0.5 mmol), 4-Methoxyphenylboronic acid (76 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4ceb** (326 mg, 0.86 mmol, 86%).

¹H NMR (CDCl₃, 500 MHz): δ = 9.98 (s, 1H), 7.33 (dd, J = 6.2 Hz, 4.5 Hz, 2H), 6.85 – 6.79 (m, 2H), 6.64 (t, J = 4.8 Hz, 1H), 6.59 – 6.54 (m, 1H), 5.85 – 5.79 (m, 3H), 5.14 – 5.08 (m, 2H), 5.04 – 4.94 (m, 5H), 3.71 (s, 3H), 3.69 (s, 3H), 3.32 (s, 2H), 3.20 – 3.14 (m, 2H), 3.09 – 3.02 (m, 3H).

¹³C NMR (CDCl₃, 126 MHz): δ = 158.76, 148.08, 143.29, 138.45, 134.66, 133.60, 130.29, 129.64, 127.87, 127.63, 120.13, 118.59, 115.93, 114.40, 111.32, 65.70, 56.01, 55.36, 52.23.

Synthesis of Compound **4aac**

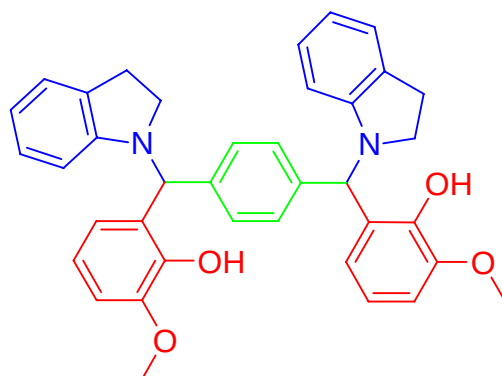


Salicylaldehyde (122 mg, 1.0 mmol), indoline (118 mg, 1.0 mmol), benzene 1, 4-diboronic acid (83 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4aac** (482 mg, 0.92 mmol, 92%).

¹H NMR (CDCl₃, 500 MHz): δ = 9.99 (s, 2H), 7.43 (s, 3H), 7.21 – 7.17 (m, 2H), 7.15 – 7.10 (m, 2H), 6.98 – 6.93 (m, 3H), 6.91 – 6.87 (m, 2H), 6.85 – 6.80 (m, 3H), 6.44 – 6.40 (m, 2H), 5.31 (s, 2H), 3.17 – 3.13 (m, 2H), 3.07 – 3.02 (m, 2H), 2.93 – 2.86 (m, 4H).

¹³C NMR (CDCl₃, 126 MHz): δ = 156.24, 151.01, 150.99, 139.38, 139.37, 132.10, 129.30, 129.26, 128.92, 128.47, 127.36, 126.19, 126.13, 124.63, 121.30, 120.06, 117.73, 117.10, 112.06, 69.84, 69.81, 53.57, 53.52, 28.51.

Synthesis of Compound **4bac**

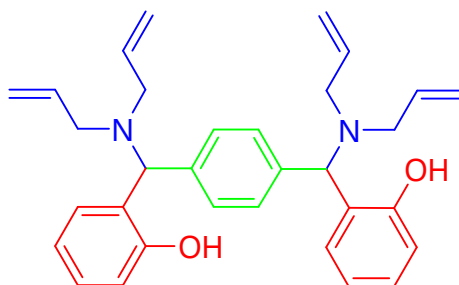


2-methoxybenzaldehyde (136 mg, 1.0 mmol), indoline (118 mg, 1.0 mmol), benzene 1, 4-diboronic acid (83 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4bac** (555 mg, 0.95 mmol, 95%).

¹H NMR (CDCl₃, 500 MHz): δ = 7.35 (s, 4H), 7.08 (d, 2H), 6.92 (t, 2H), 6.79 – 6.72 (m, 6H), 6.69 (t, 2H), 6.30 (d, 2H), 5.69 (d, 2H), 3.89 (s, 6H), 3.18 – 3.12 (m, 4H), 2.92 (t, 4H).

¹³C NMR (CDCl₃, 126 MHz): δ = 151.78, 147.15, 144.31, 140.67, 130.87, 128.55, 128.41, 127.32, 127.19, 124.22, 121.14, 120.65, 119.42, 118.70, 109.88, 109.53, 63.54, 55.98, 52.32, 28.43.

Synthesis of Compound **4aec**

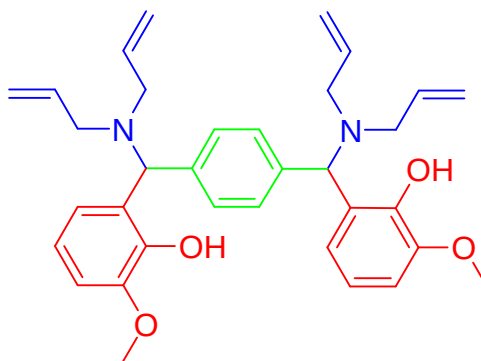


Salicylaldehyde (122 mg, 1.0 mmol), diallylamine (96 mg, 1.0 mmol), benzene 1, 4-diboronic acid (83 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4aec** (413 mg, 0.86 mmol, 86%).

¹H NMR (CDCl₃, 500 MHz): δ = 11.97 (s, 2H), 7.40 (s, 4H), 7.14 – 7.10 (m, 2H), 6.84 – 6.79 (m, 4H), 6.70 – 6.65 (m, 2H), 5.88 – 5.81 (m, 4H), 5.22 – 5.16 (m, 4H), 5.13 – 5.08 (m, 4H), 5.00 (m, 2H), 3.34 – 3.29 (m, 4H), 3.07 – 2.97 (m, 4H).

¹³C NMR (CDCl₃, 126 MHz): δ = 157.43, 137.73, 133.28, 129.64, 129.20, 128.64, 124.80, 119.46, 119.04, 116.92, 69.99, 51.91.

Synthesis of Compound **4bec**

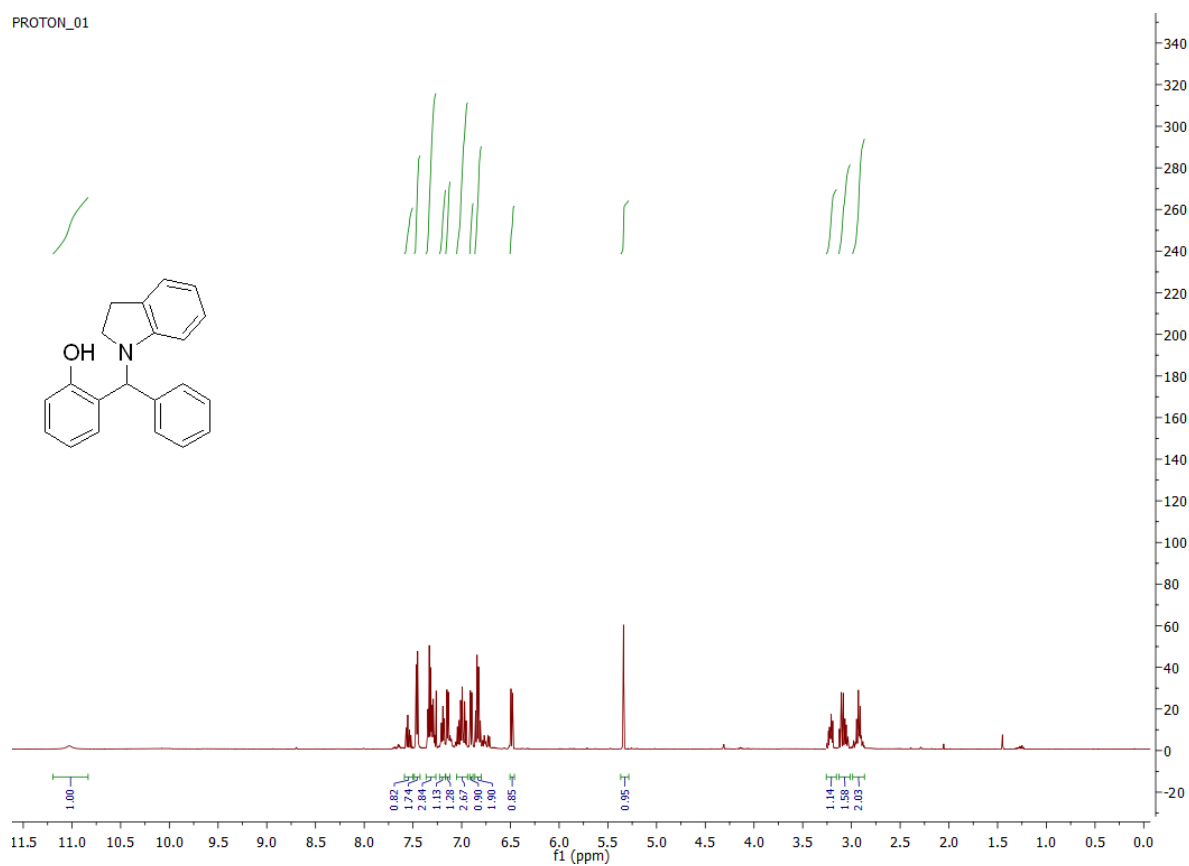


2-methoxybenzaldehyde (136 mg, 1.0 mmol), diallylamine (96 mg, 1.0 mmol), benzene 1, 4-diboronic acid (83 mg, 0.5 mmol), 1.0 mol% **5Dy**, 5 mL DME, rt, 16 h. The crude product was purified by column chromatography with silica (10% ethyl acetate in hexanes) to afford the title compound **4bec** (475 mg, 0.88 mmol, 88%).

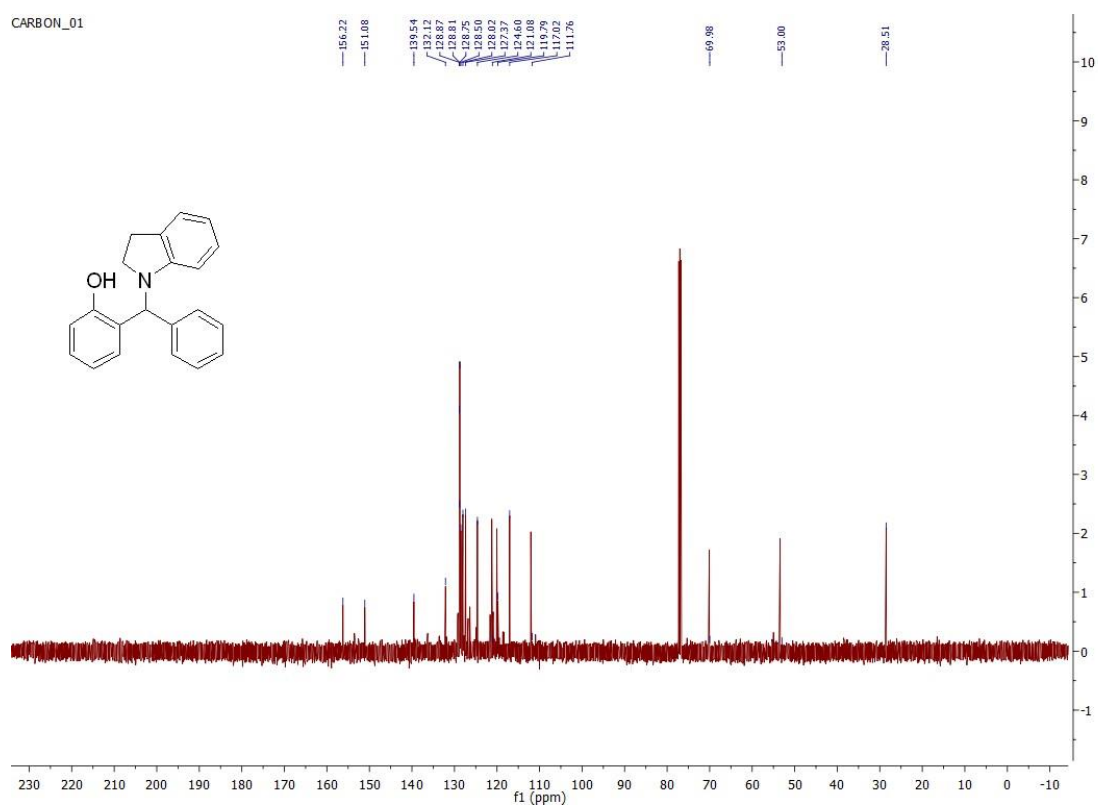
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¹³C NMR (CDCl₃, 126 MHz): δ = 148.21, 146.94, 141.78, 133.24, 129.74, 123.78, 121.16, 119.43, 110.64, 69.79, 55.92, 52.23.

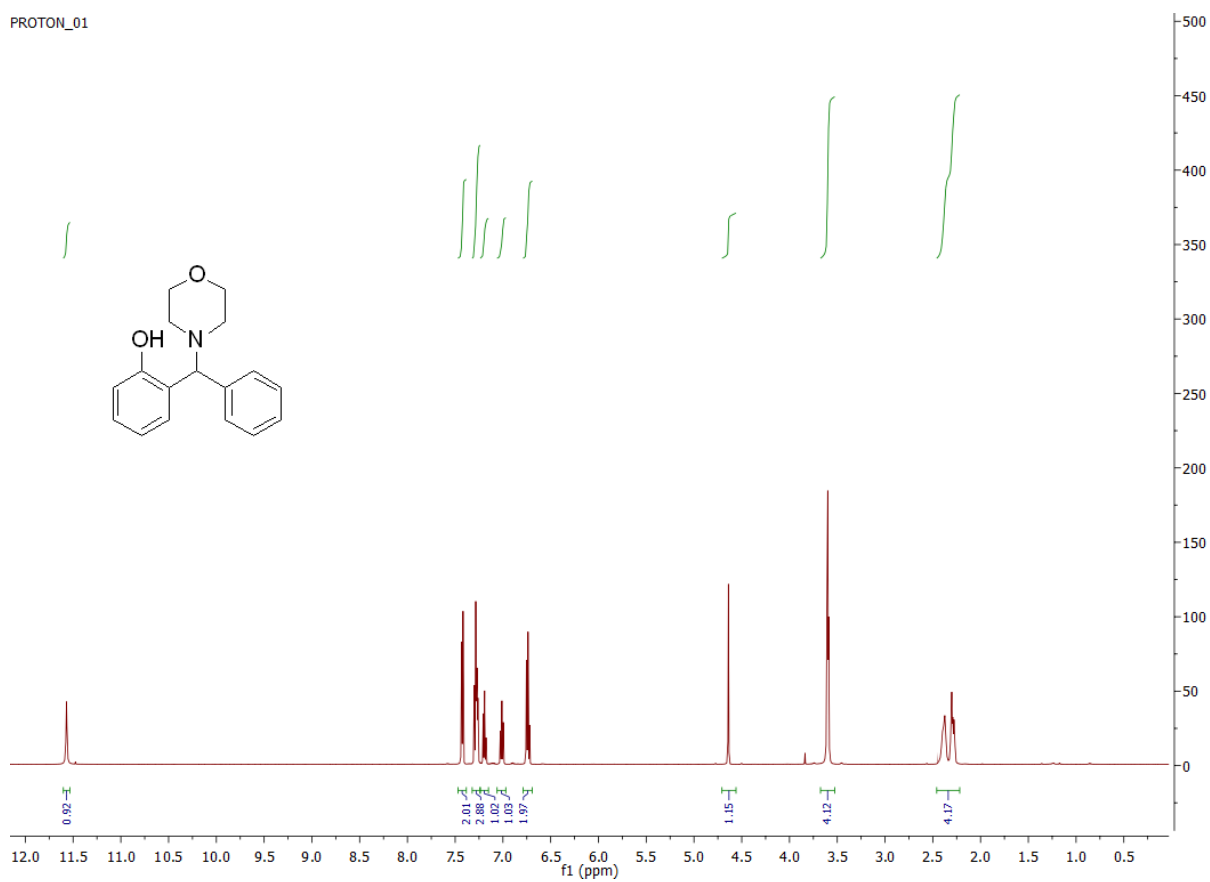
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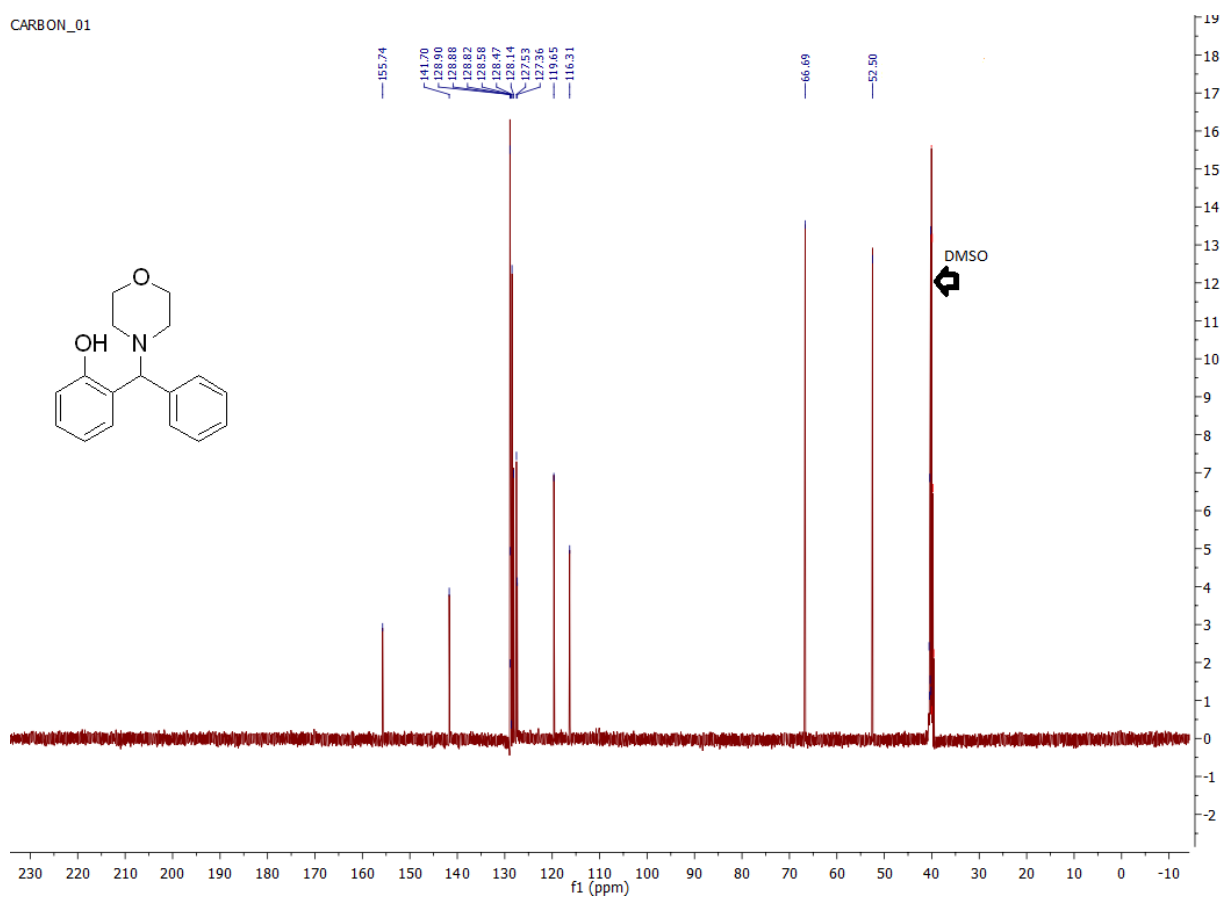
CARBON_01



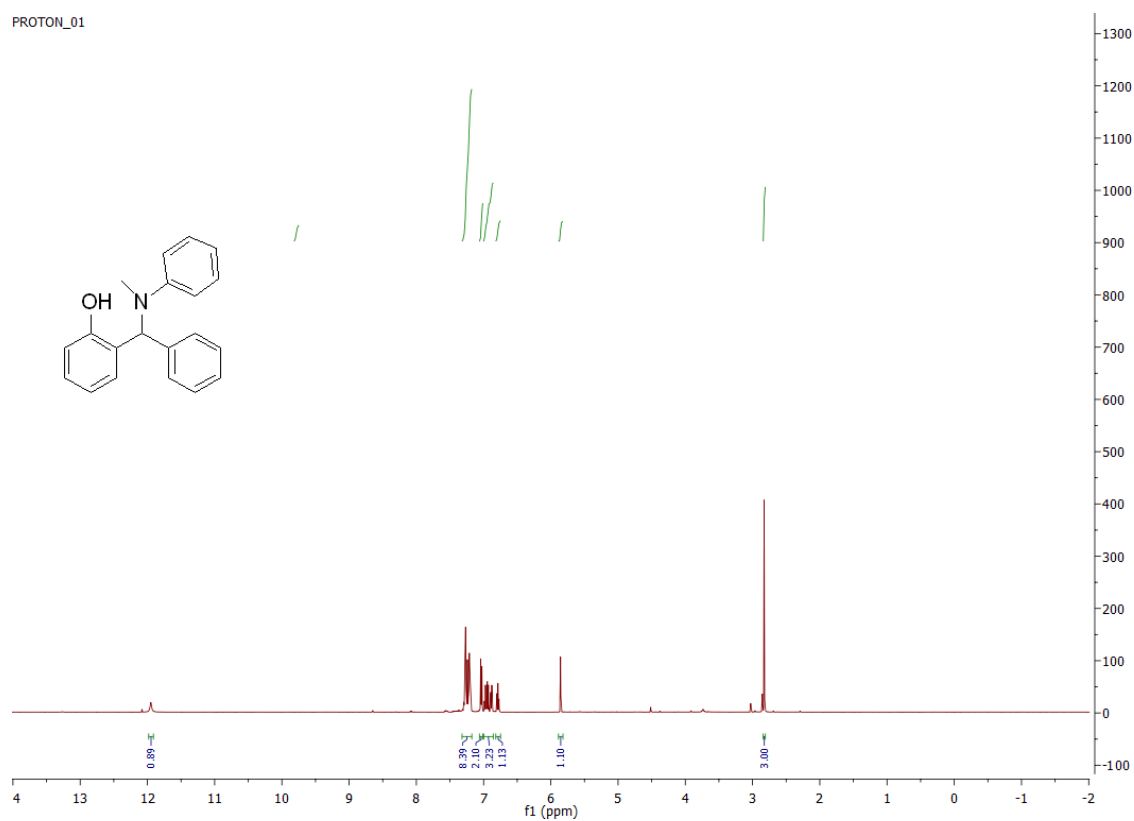
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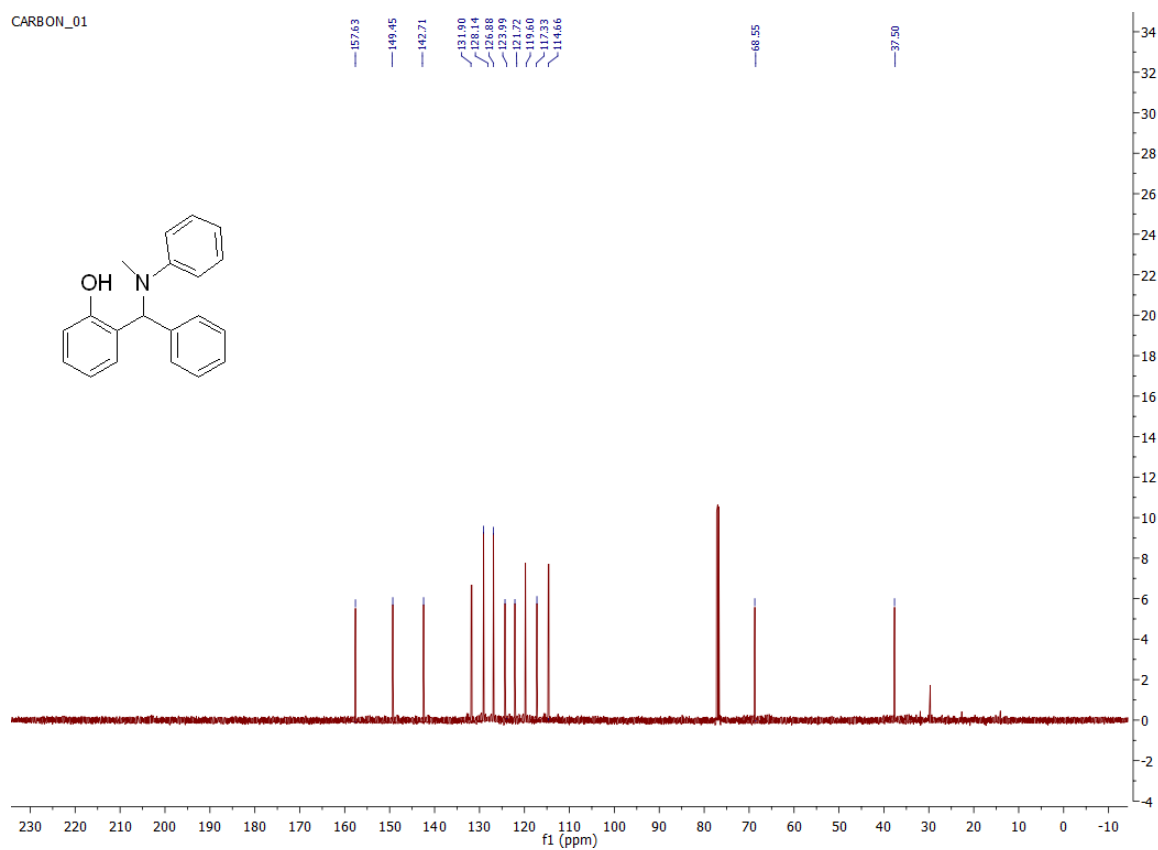
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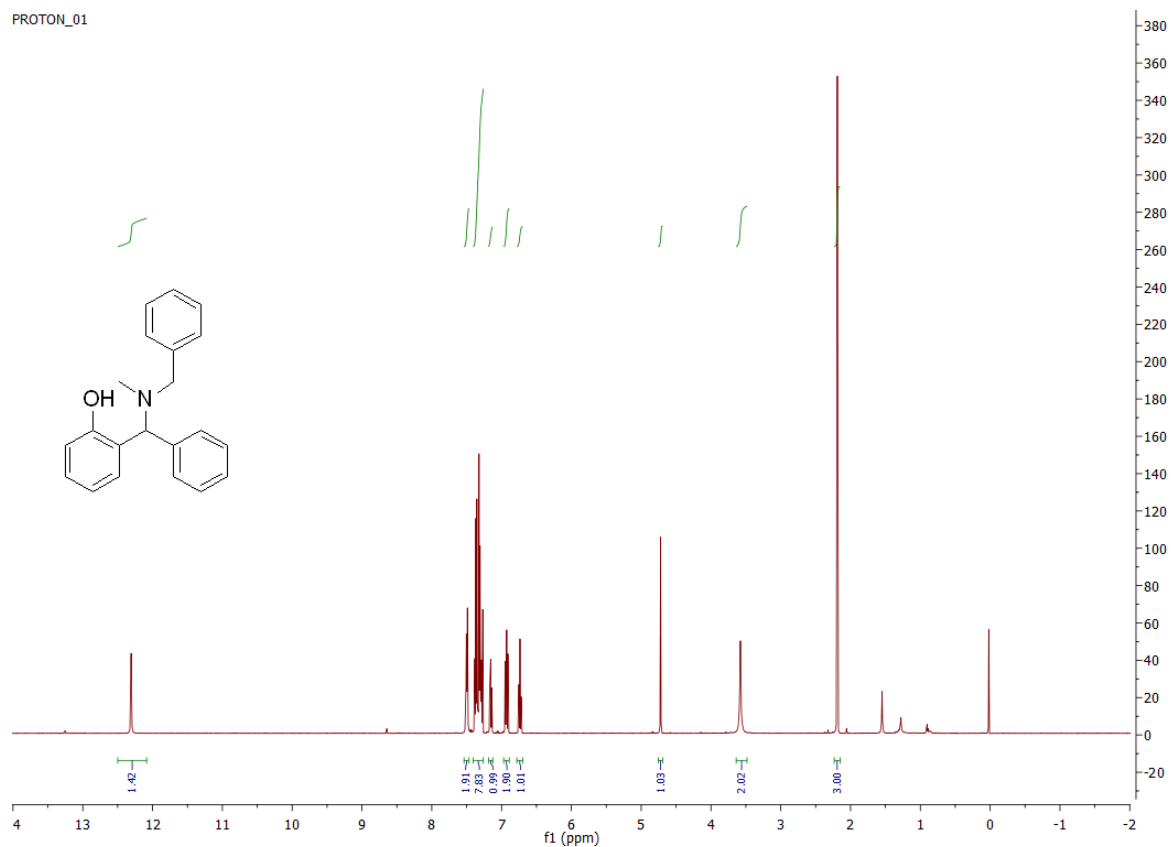
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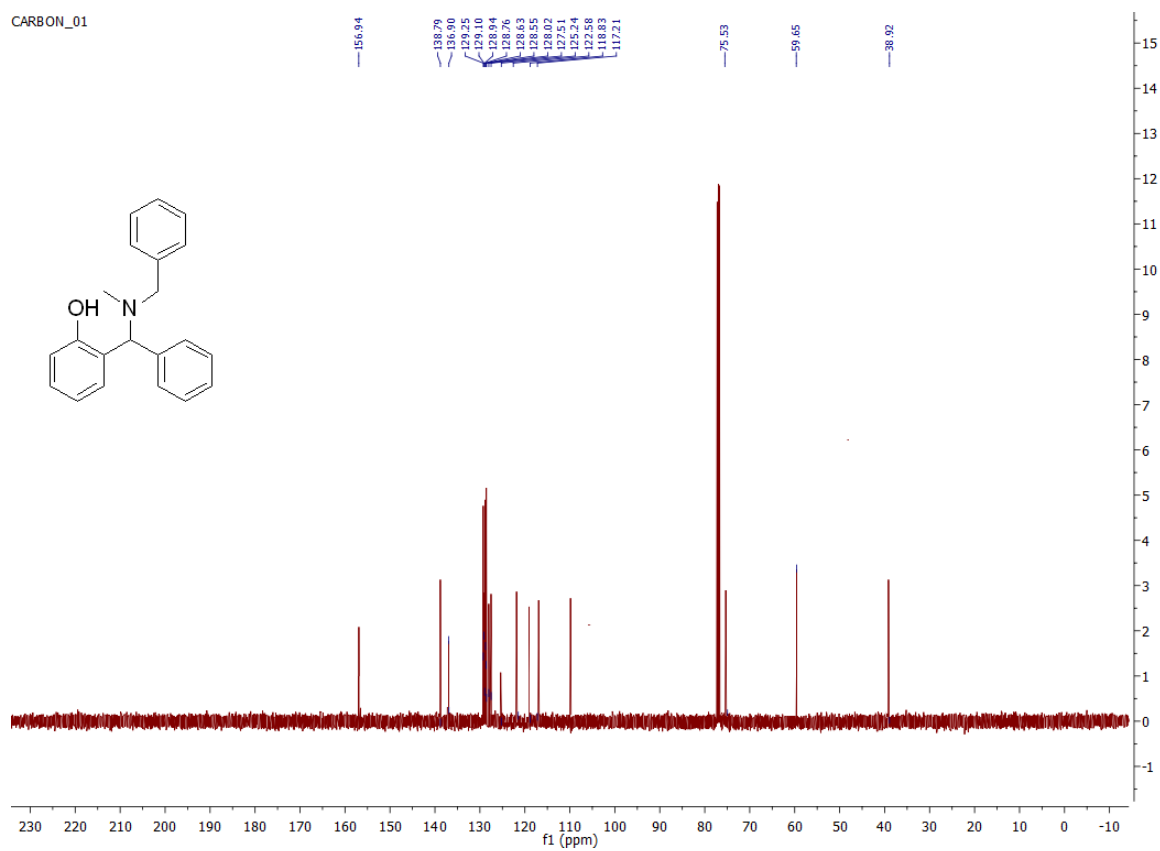
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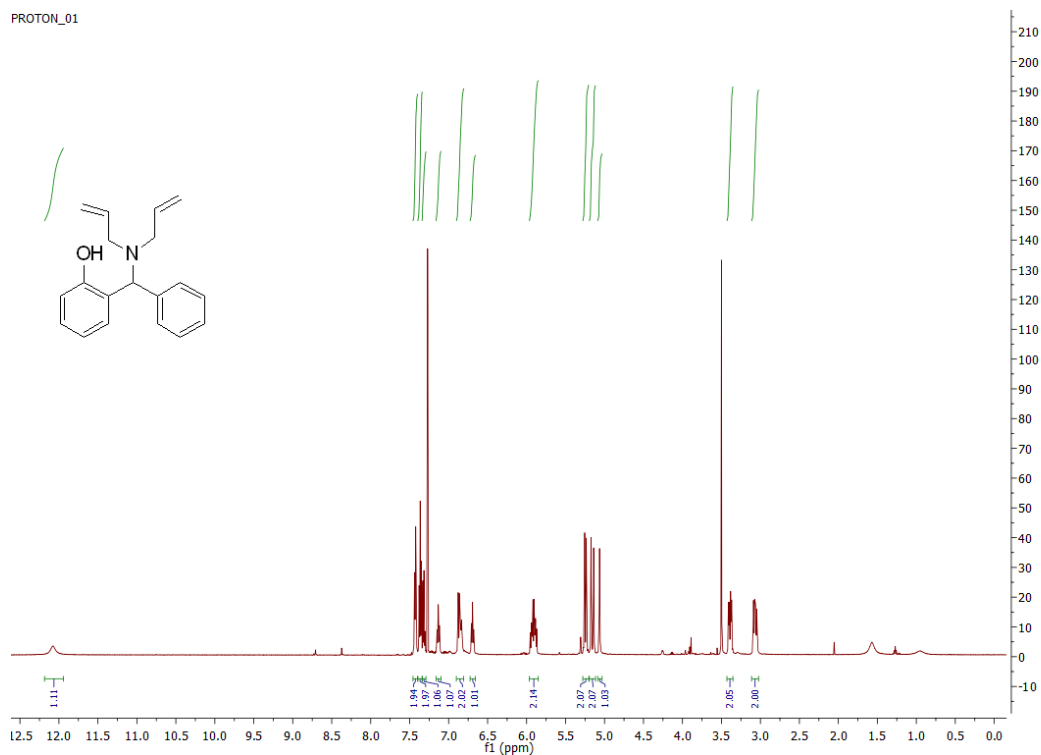
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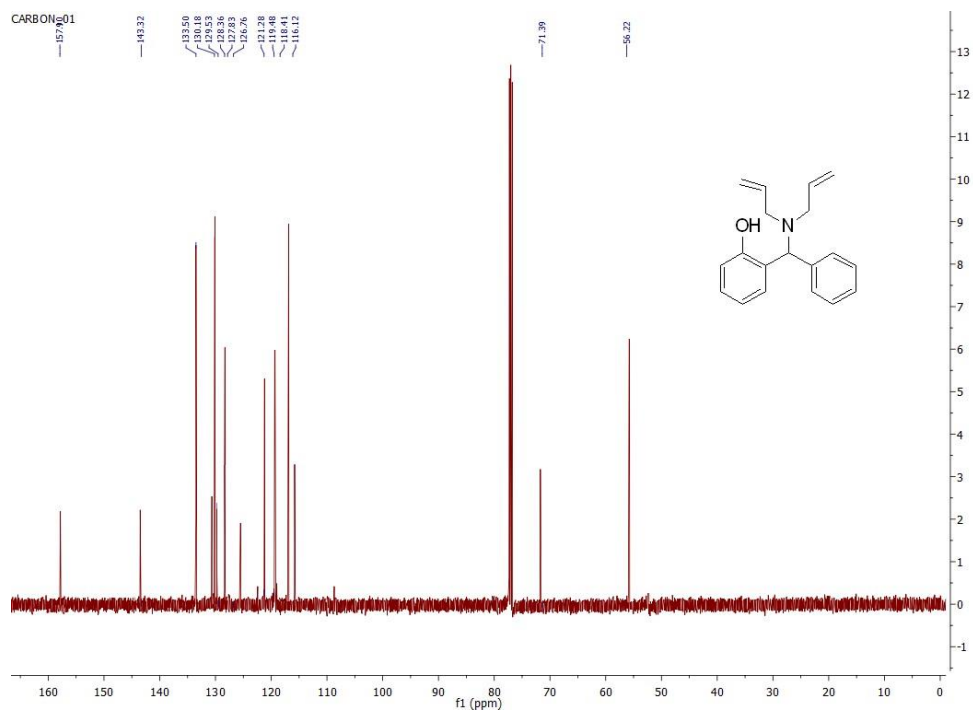
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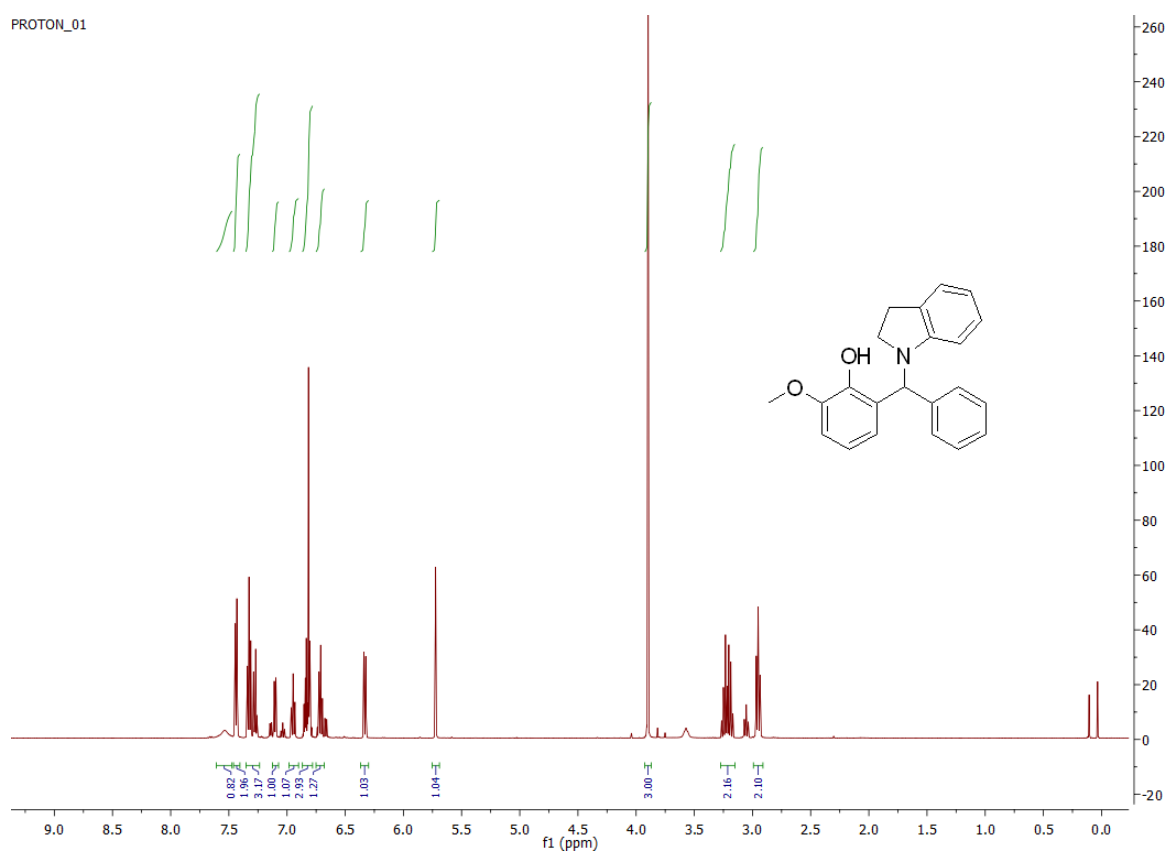
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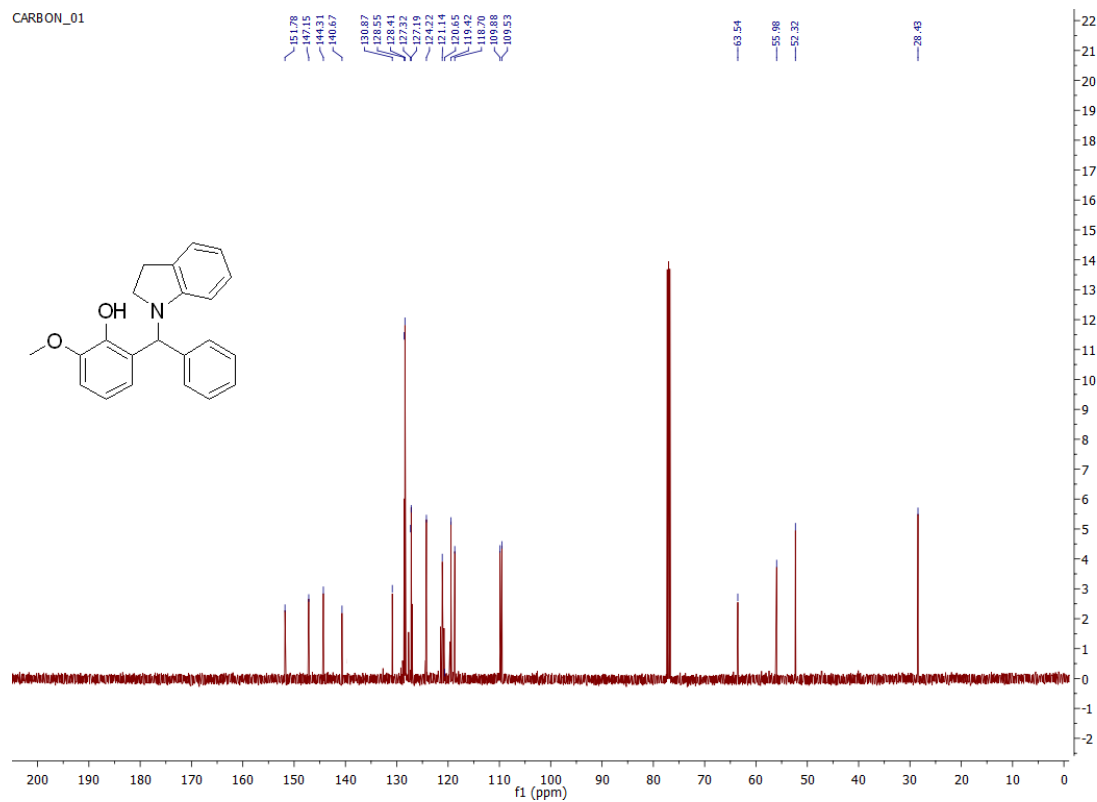
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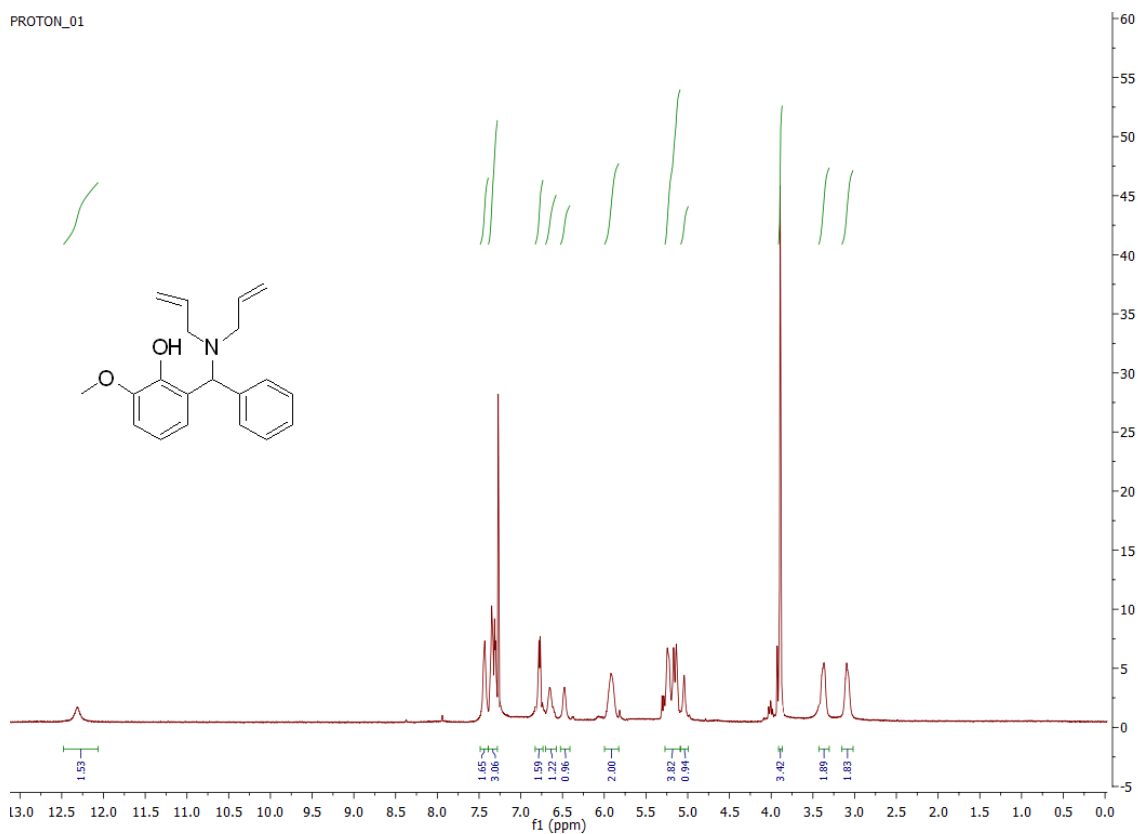
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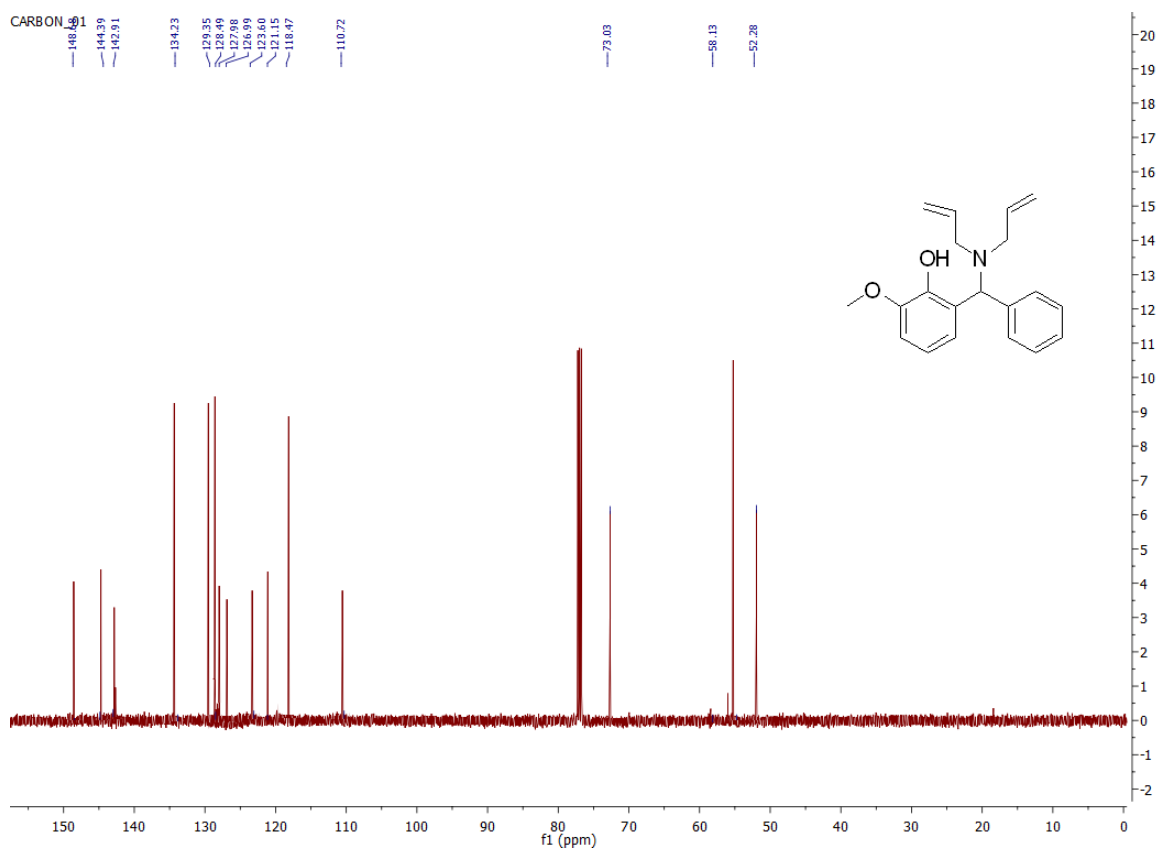
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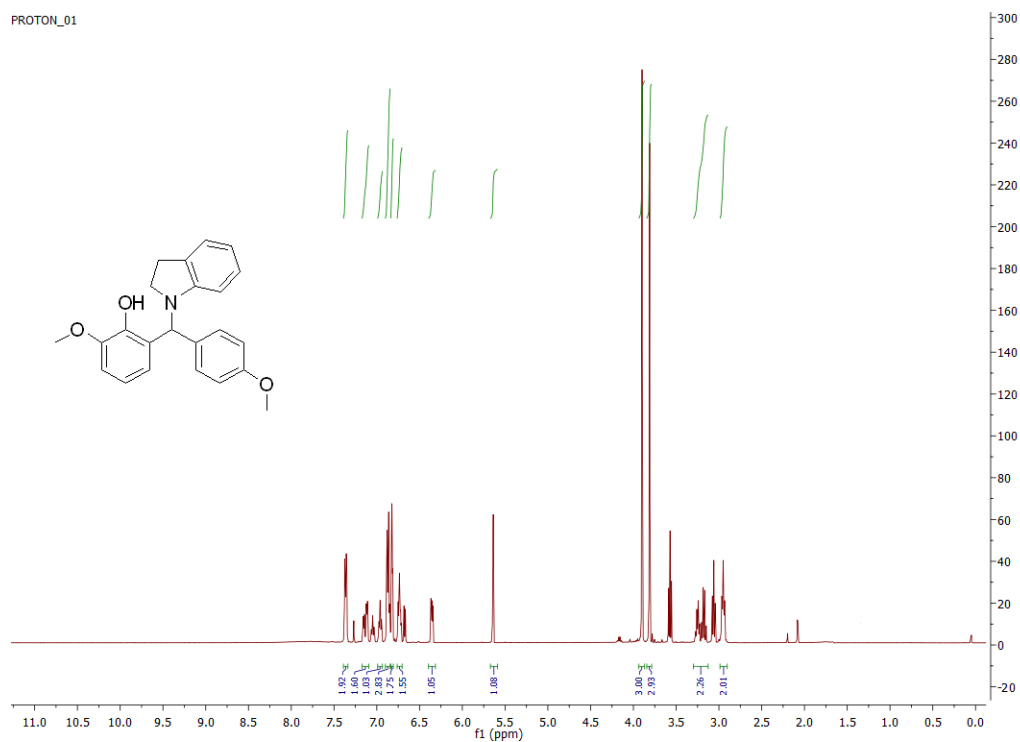
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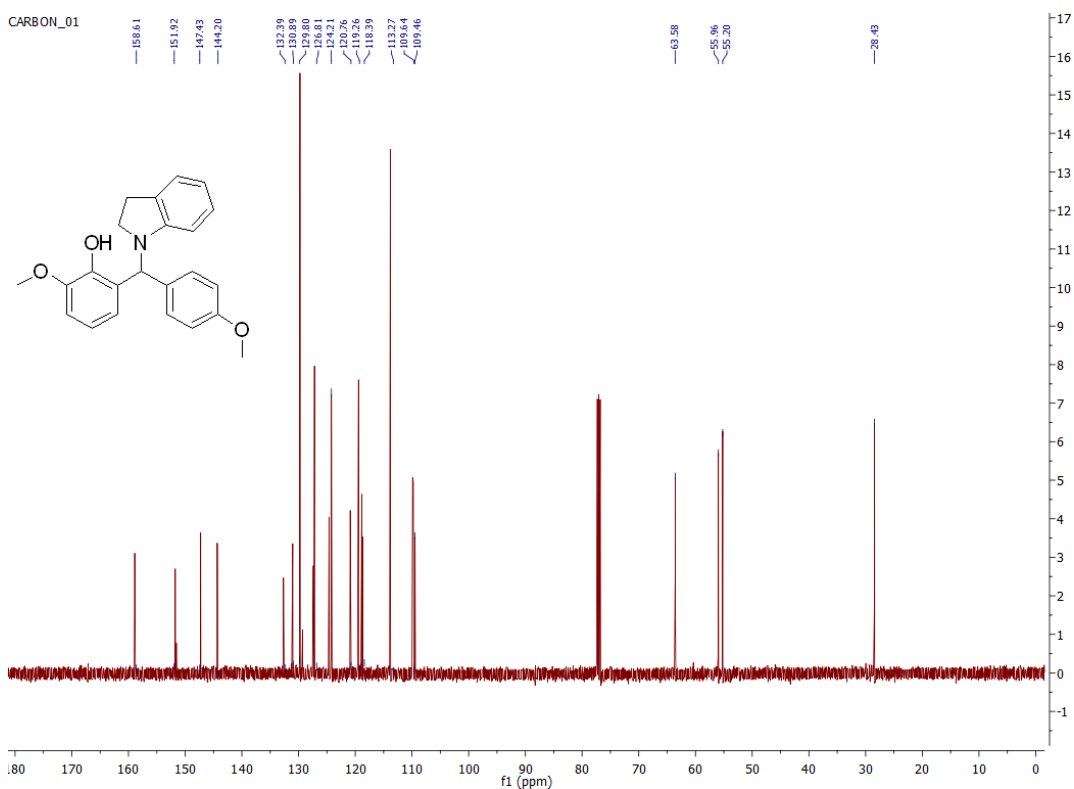
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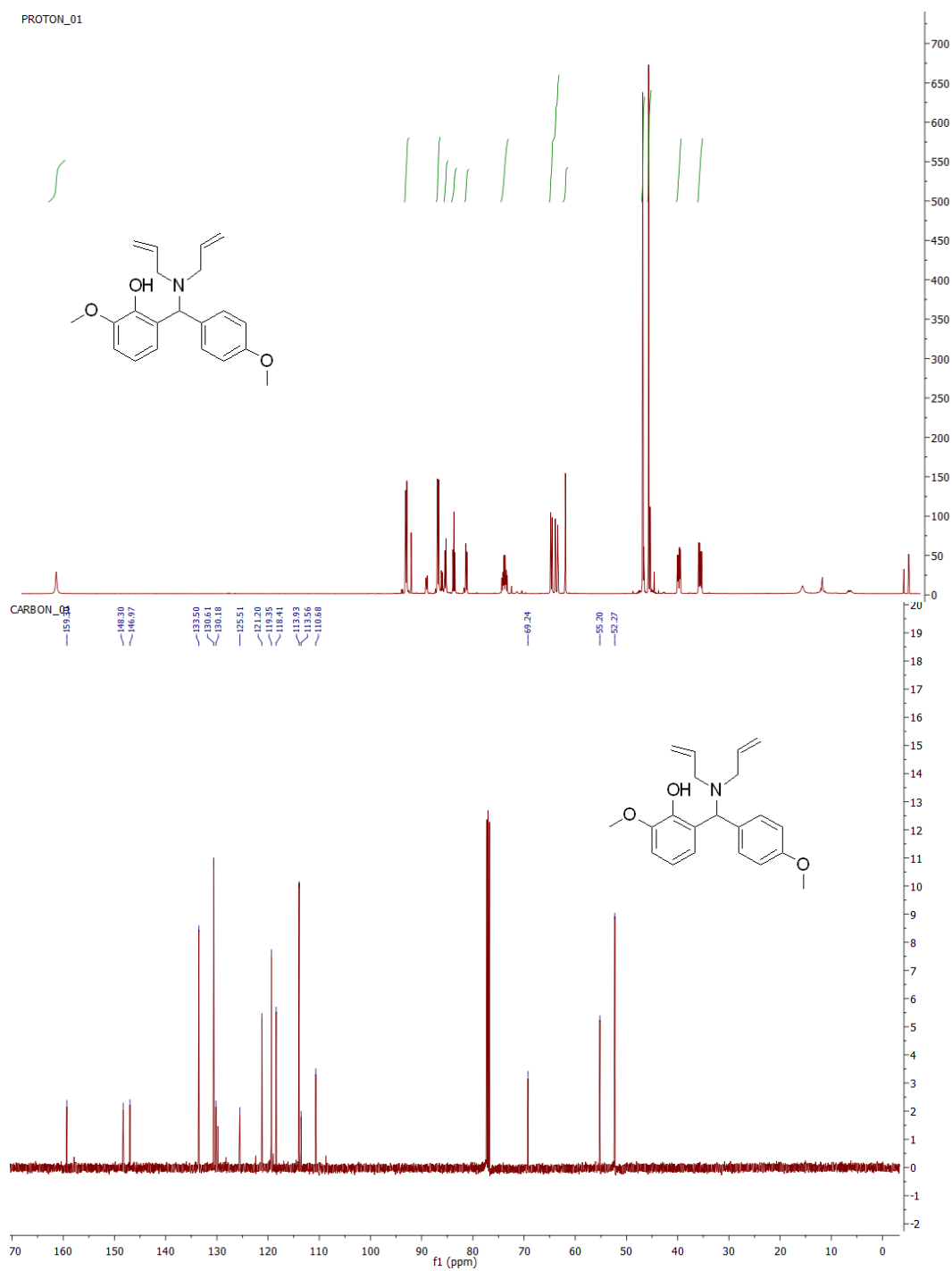
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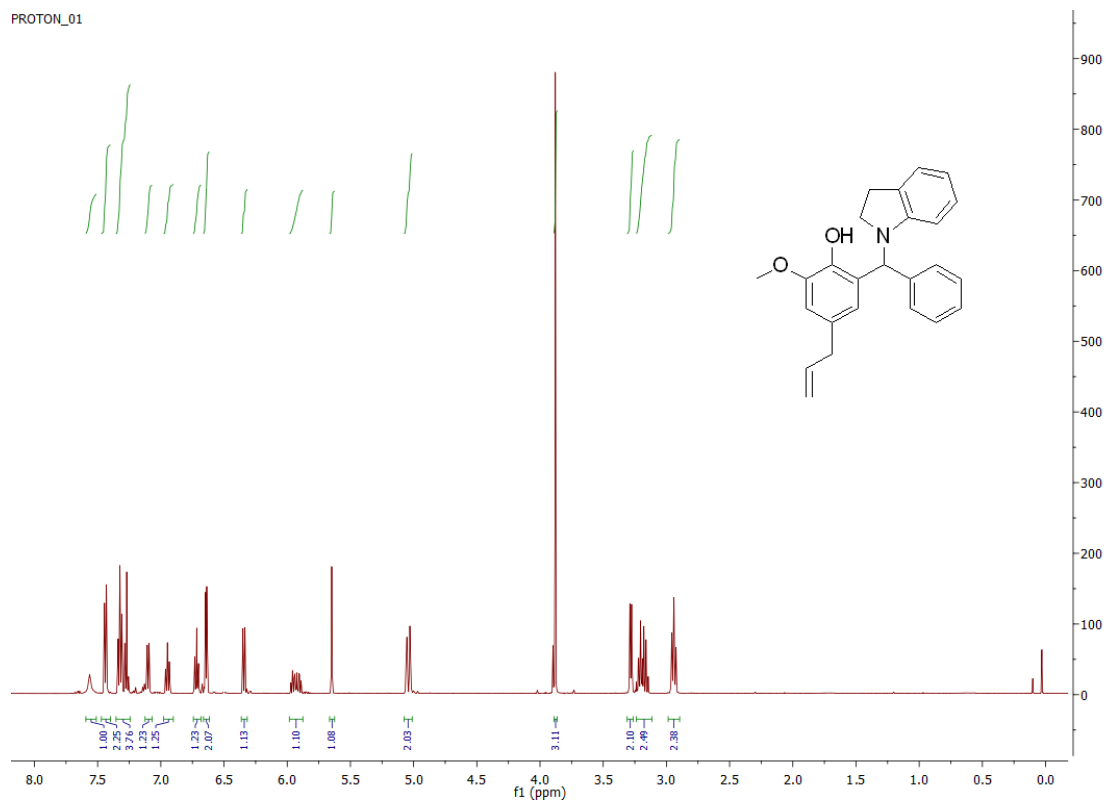
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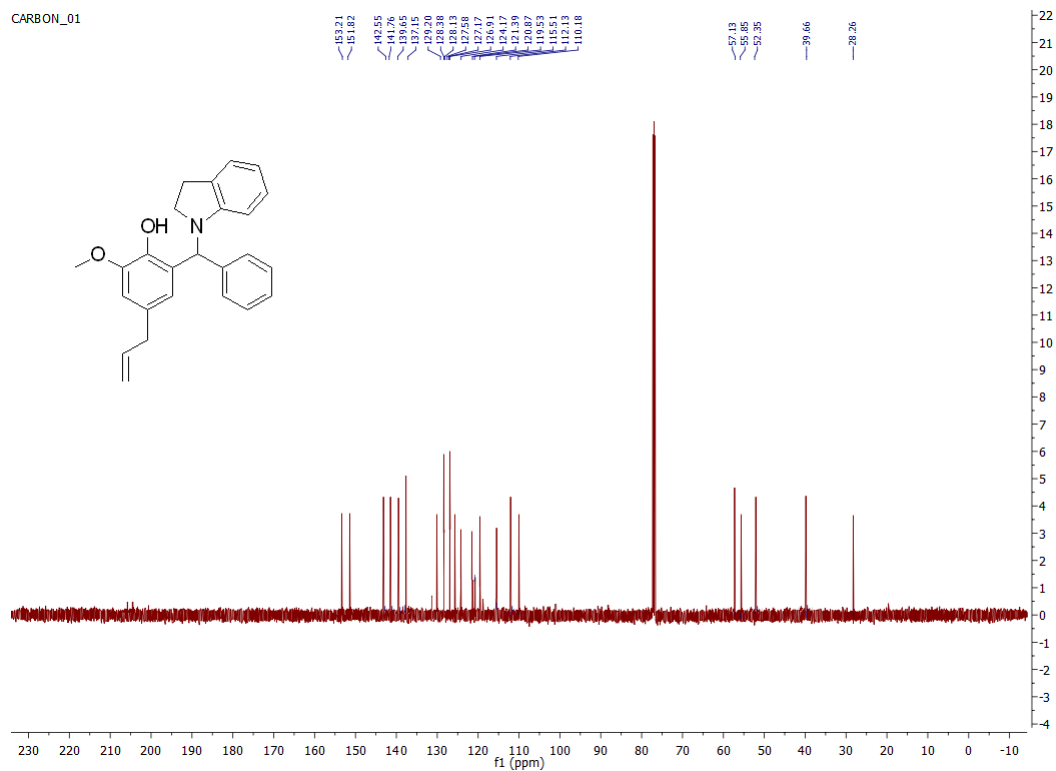
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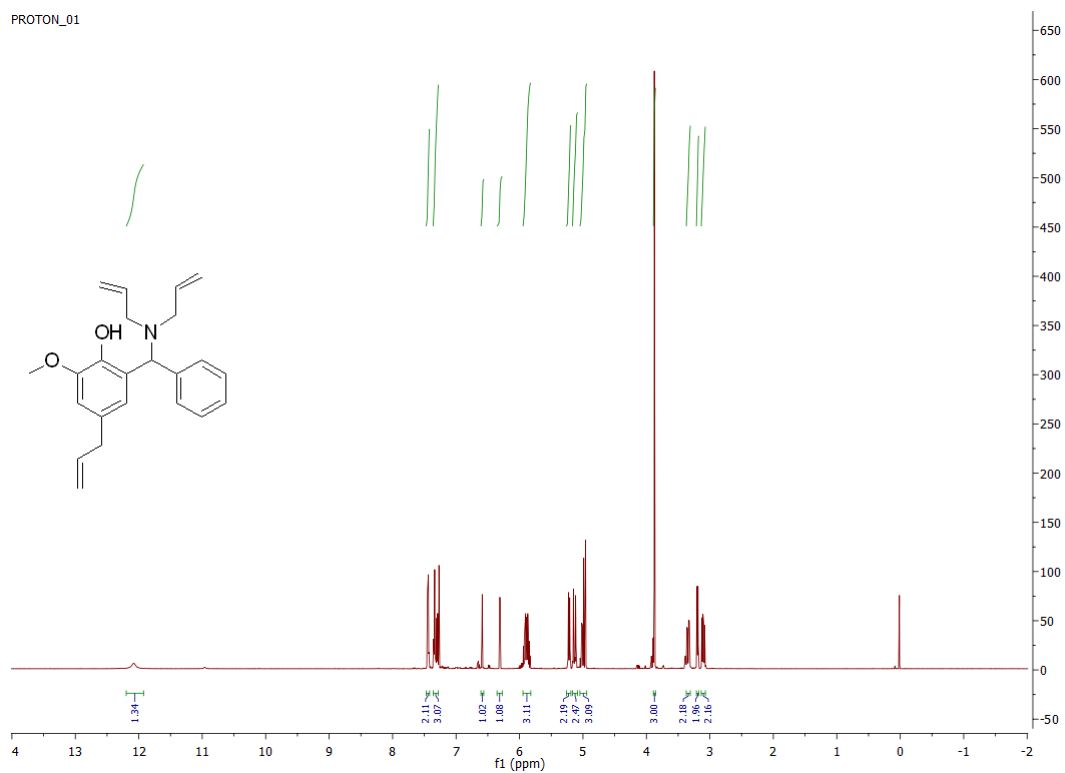
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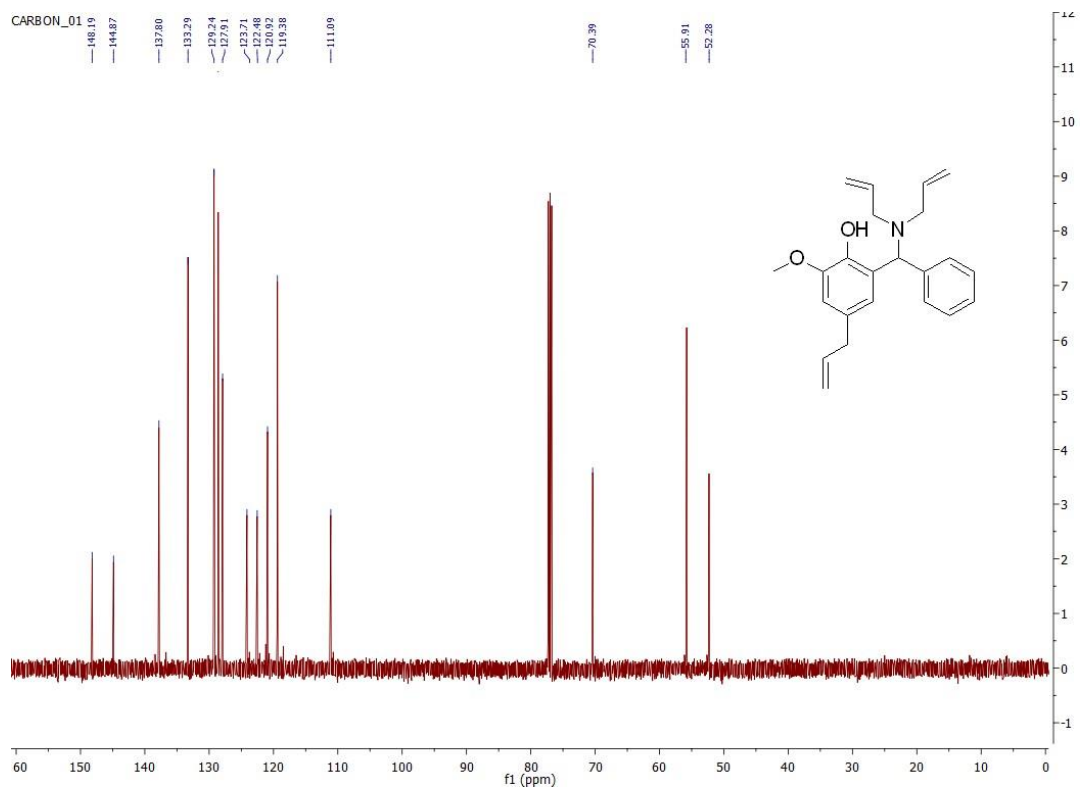
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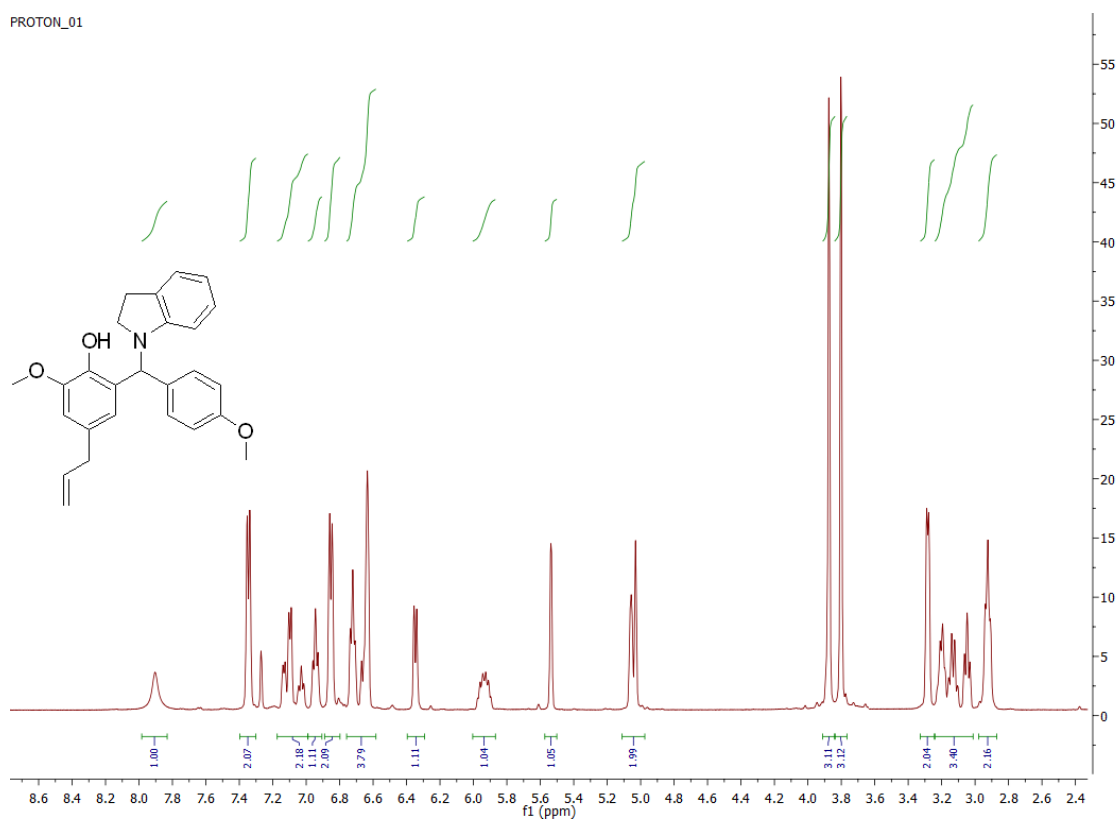
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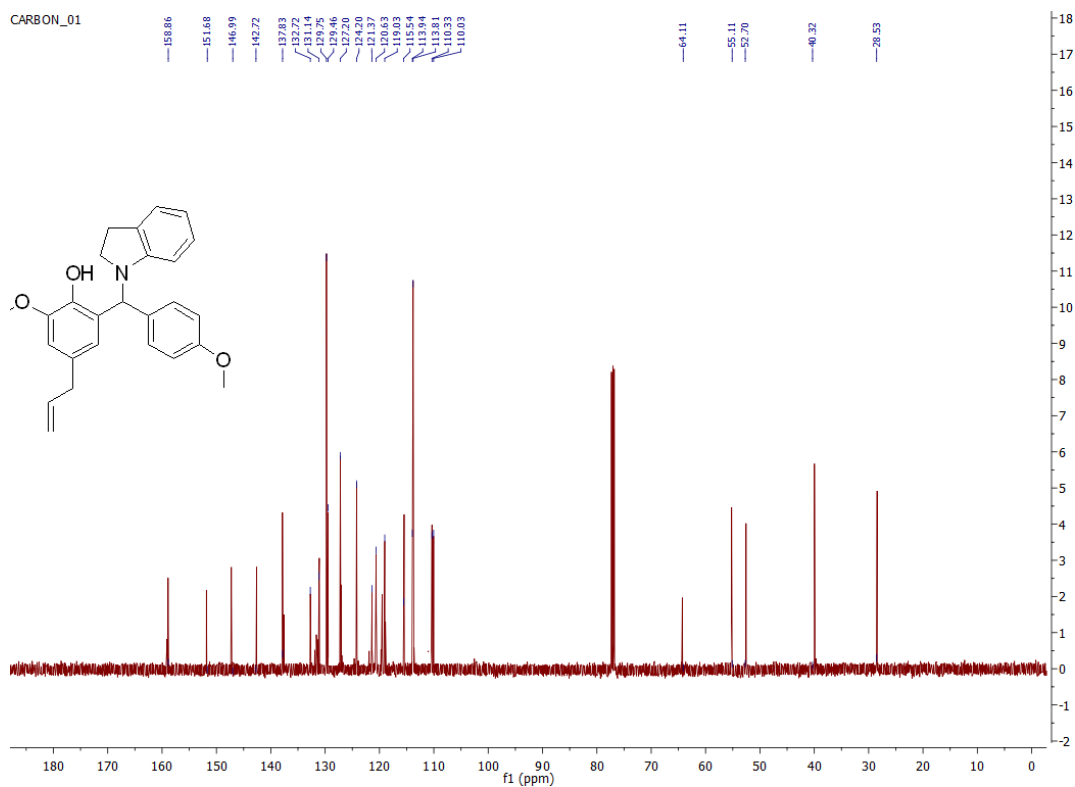
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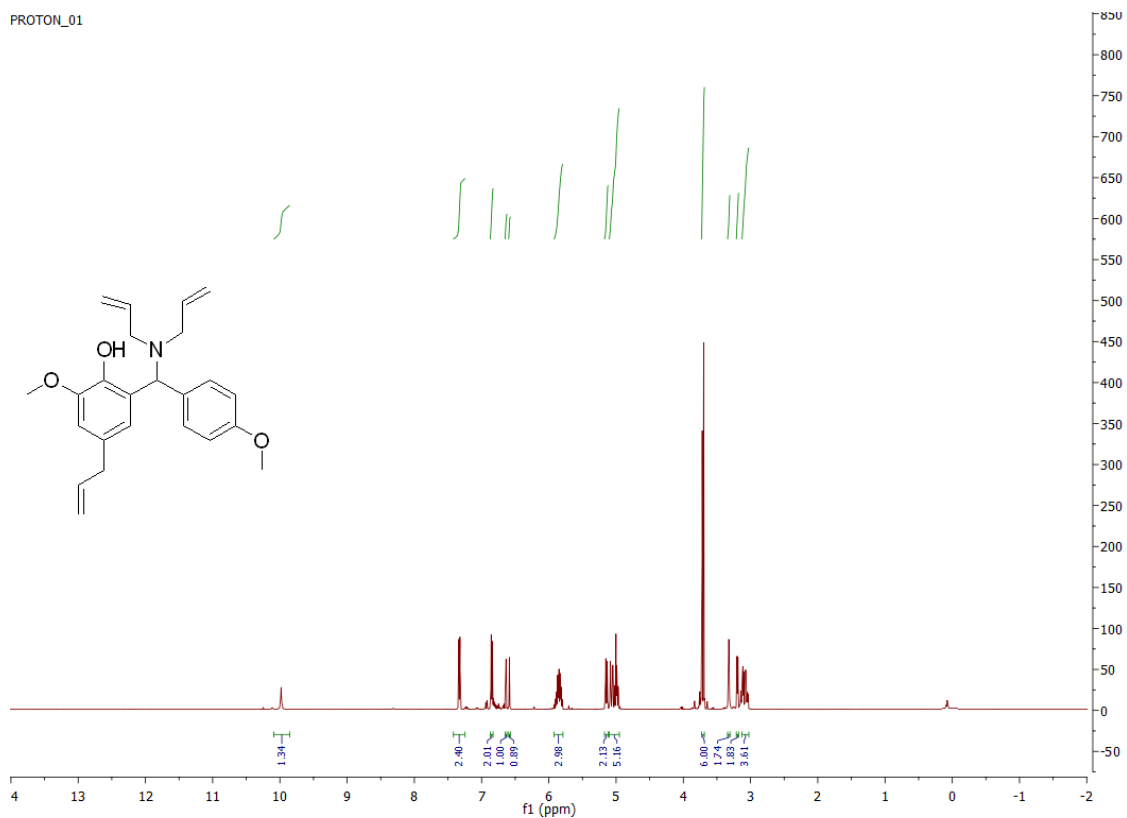
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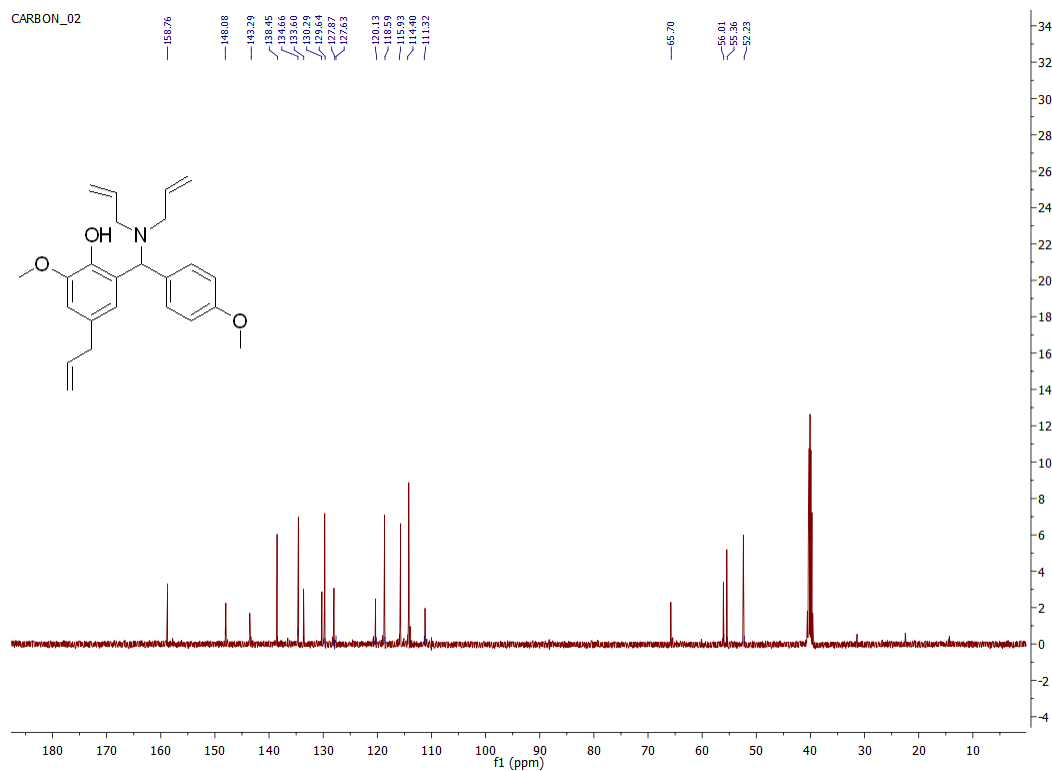
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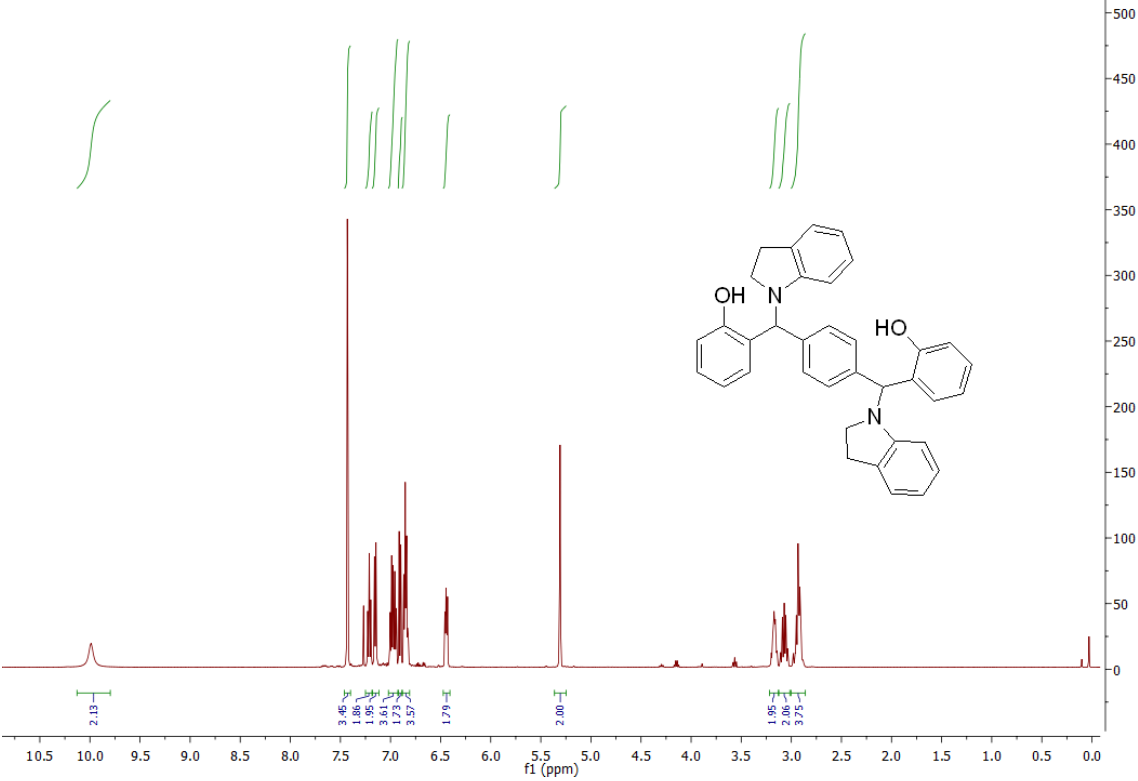
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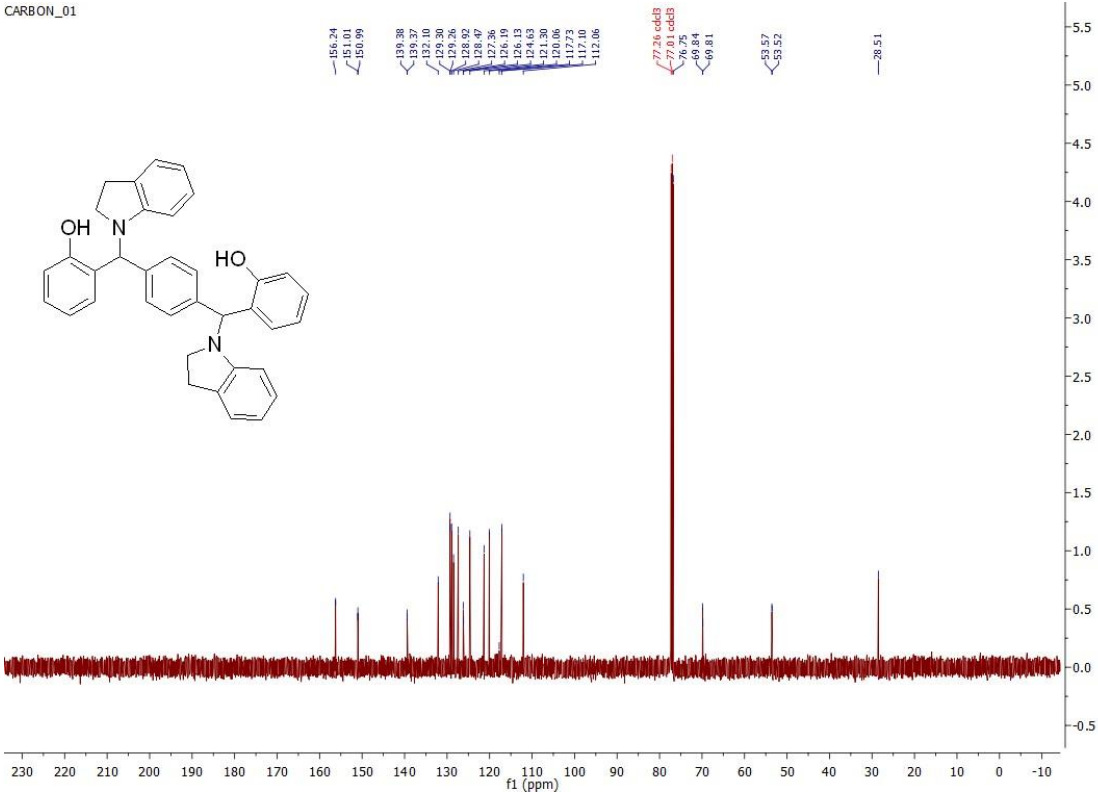
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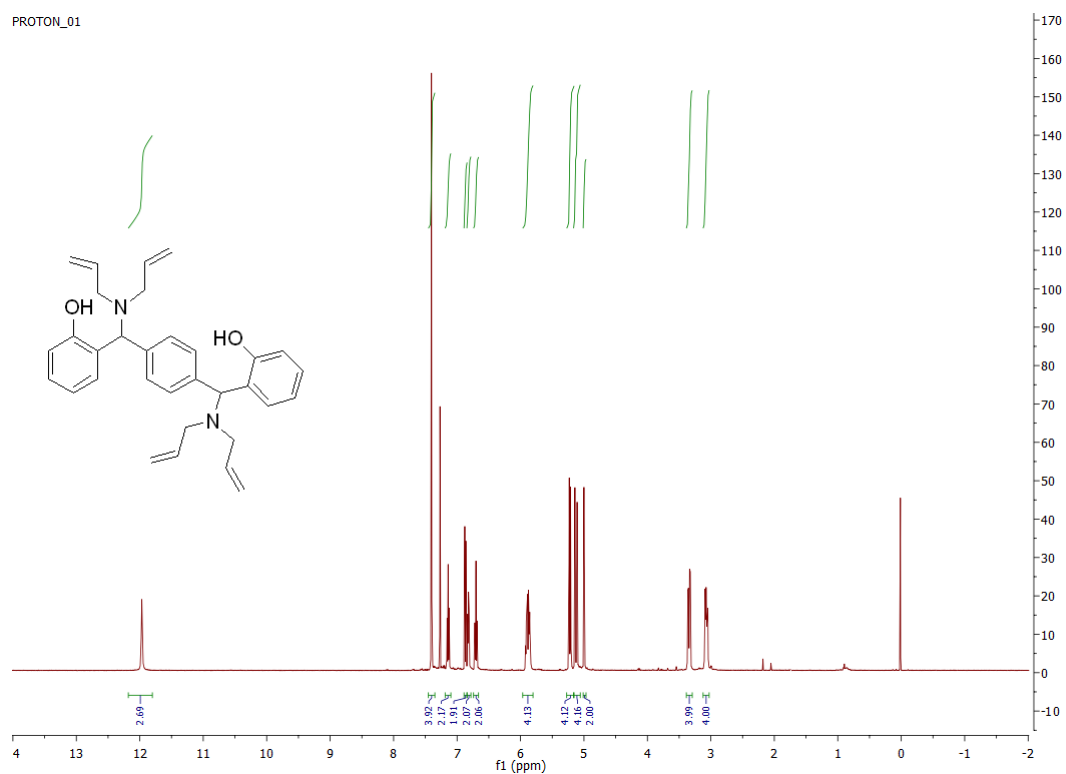
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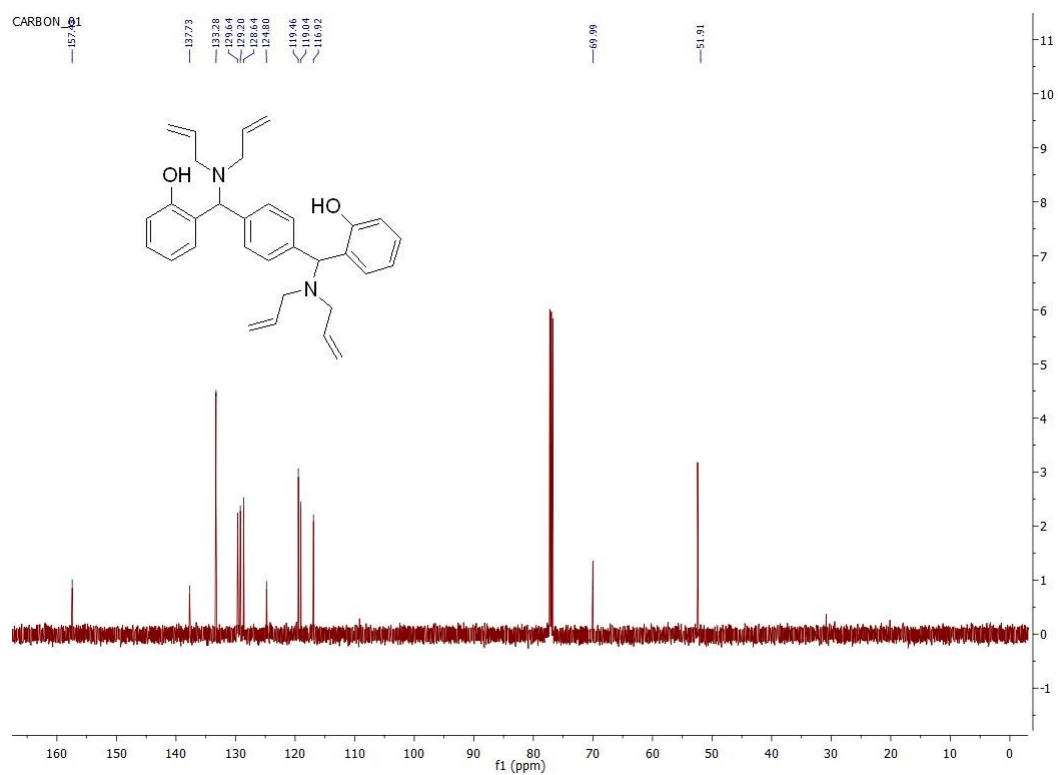
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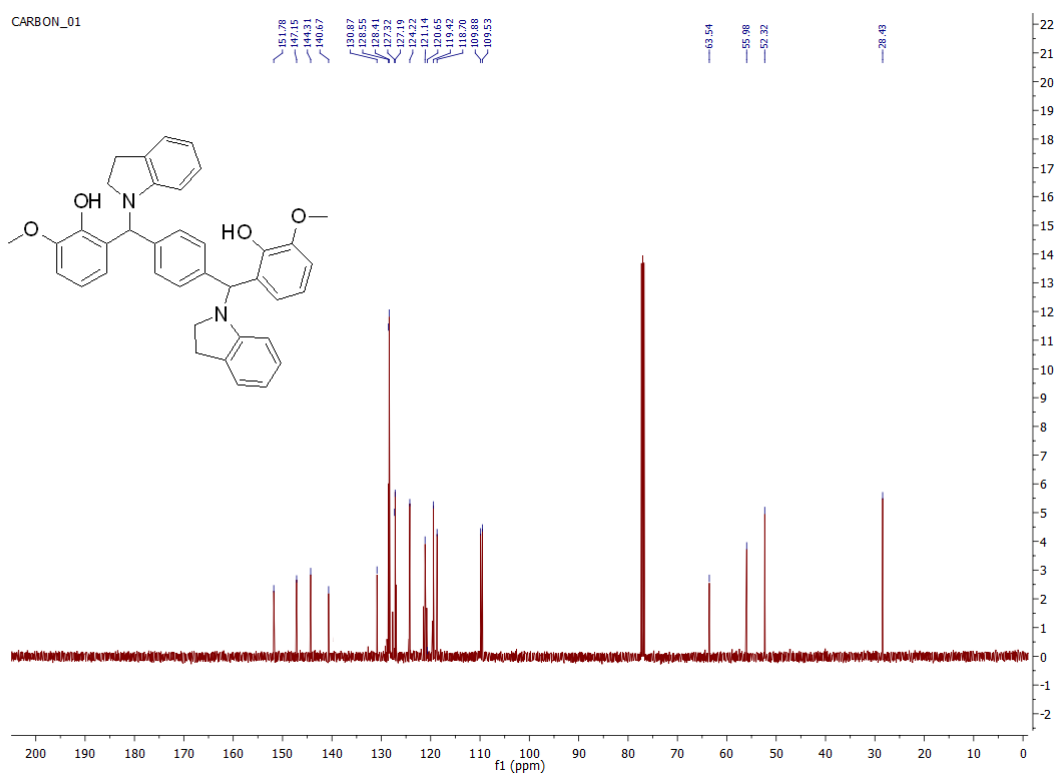
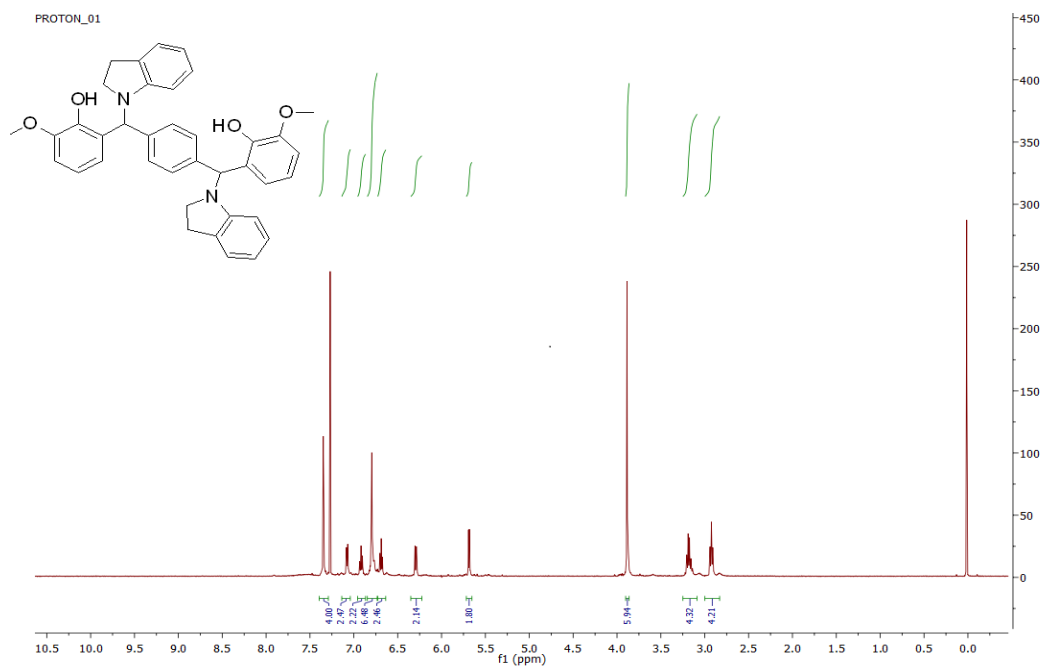


PROTON_01

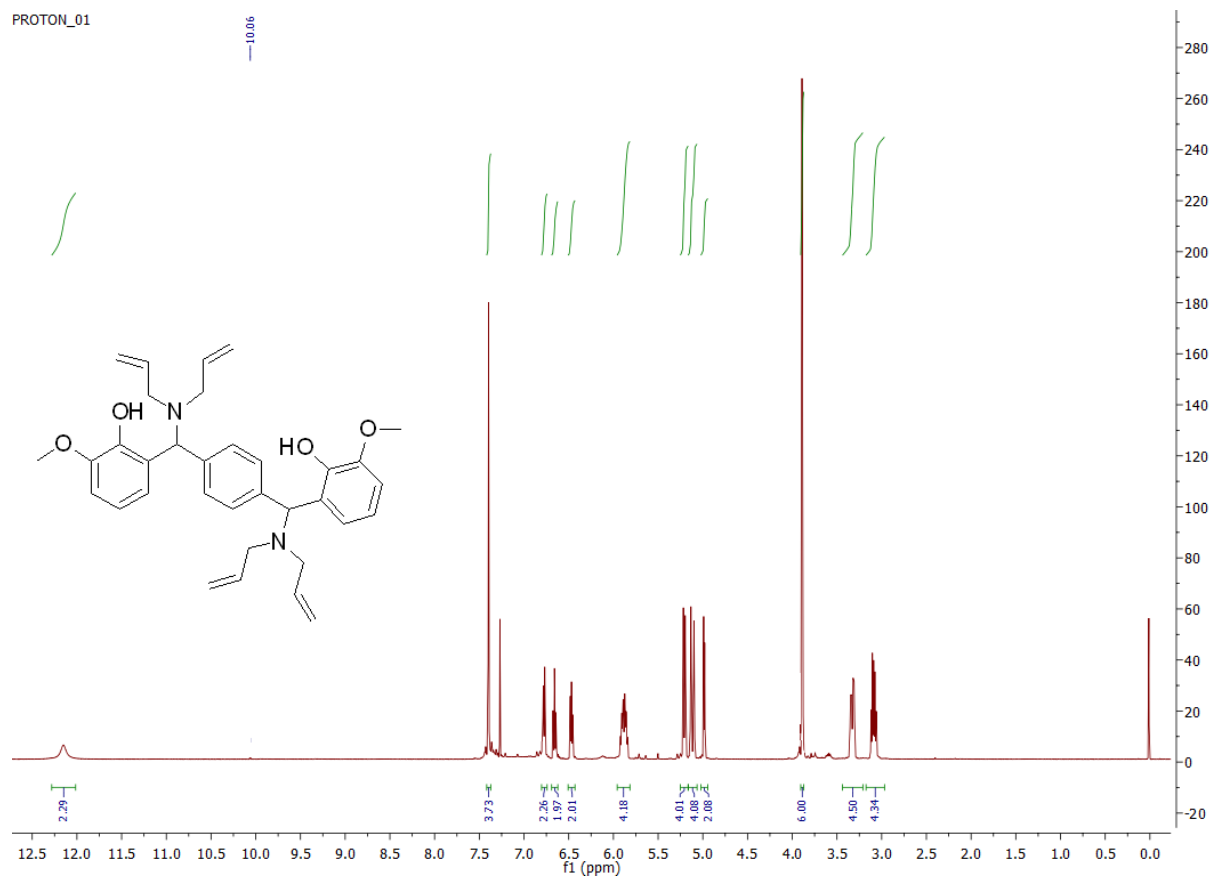


CARBON_01





PROTON_01



CARBON_01

