

Supporting Information

Mesoporous Organosilica Grafted Pd Catalyst (MOG-Pd) For Efficient Base Free and Phosphine Free Synthesis of Tertiary Butyl Esters Via tertiary-Butoxycarbonylation Of Boronic Acid Derivatives Without Using Carbon Monoxide

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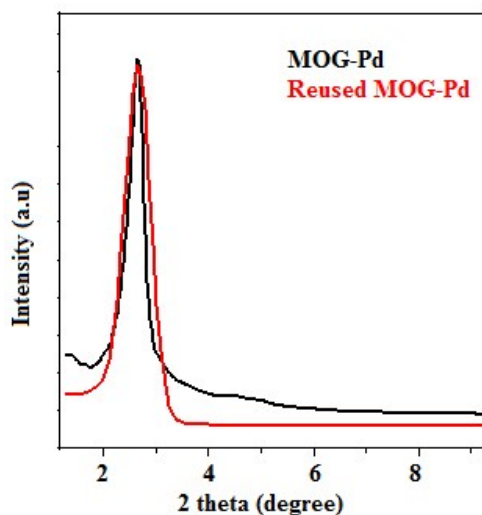


Fig S1: XRD pattern of the MOG-Pd and recycled MOG-Pd catalyst

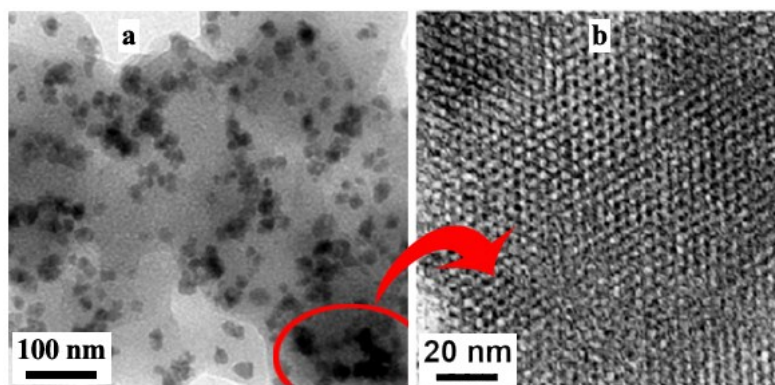


Fig S2: HR-TEM images of the recycled MOG-Pd catalyst

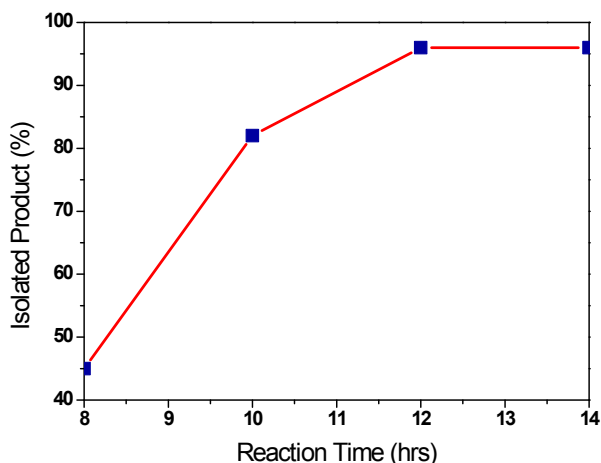


Fig S3: Effect of reaction time on MOG-Pd catalyzed tertiary butoxy carbonylation reaction
 Reaction condition: 1mmol A and 1.8 mmol B of model reaction, 25mg (6.44×10^{-3} mmol) MOG-Pd(II) catalyst, 10 mol % DABCO, 2 ml dioxane, 80 °C.

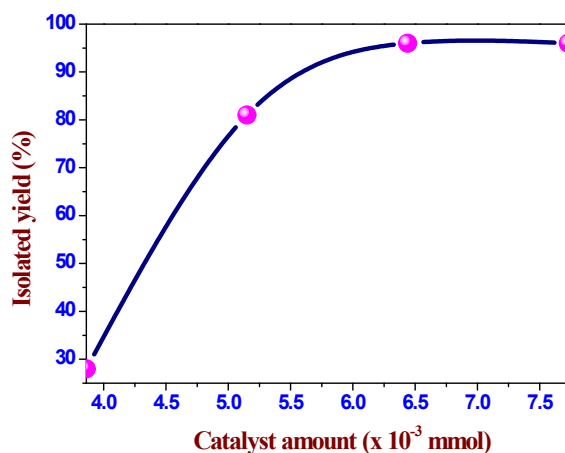


Fig S4: Effect of catalyst (MOG-Pd) amount on tertiary butoxy carbonylation reaction
 Reaction condition: 1mmol A and 1.8 mmol B of model reaction, 10 mol % DABCO, 2 ml dioxane, 80 °C, 12 h.

Characterization data and copies of NMR Spectra of compounds

***tert*-butyl picolinate (Table 3, entry 1)**

^1H NMR (400 MHz, 25°C, CDCl_3 , ppm): δ 8.72(1H, d, $J = 4.8$ Hz), 8.02(1H, d, $J = 7.9$ Hz), 7.78(1H, td, $J = 7.8, 1.7$ Hz), 7.40(1H, ddd, $J = 7.8, 4.8, 1.2$ Hz), 1.61(9H, s). ^{13}C NMR (100 MHz, 25°C, CDCl_3 , ppm): δ 164.3, 149.6, 149.6, 136.6, 126.4, 124.7, 82.2, 28.1.

***tert*-butyl nicotinate (Table 3, entry 2)**

^1H NMR (400 MHz, 25°C, CDCl_3 , ppm): δ 9.12(1H, s), 8.69 (1H, d, $J = 4.6$ Hz), 8.20(1H, d, $J = 8.1$ Hz), 7.32(1H, dd, $J = 8.0, 4.6$ Hz), 1.56(9H, s). ^{13}C NMR (100 MHz, 25°C, CDCl_3 , ppm): δ 164.4, 153.0, 150.8, 136.9, 127.4, 123.1, 81.8, 28.1.

***tert*-butyl isonicotinate (Table 3, entry 3)**

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 8.75(2H, s), 7.80(2H, d, $J = 5.29$ Hz), 1.61(9H, s). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 164.2, 150.5, 139.0, 122.9, 82.3, 28.1.

***tert*-butyl 5-cyanonicotinate (Table 3, entry 4)**

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 9.34(1H, d, $J = 1.9$ Hz), 8.98(1H, d, $J = 1.9$ Hz), 8.49(1H, t, $J = 1.9$ Hz), 1.62(9H, s). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 162.5, 154.8, 153.7, 140.2, 128.0, 115.8, 109.8, 83.7, 28.1.

***tert*-butyl 6-cyanonicotinate (Table 3, entry 5)**

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 9.23 (1H, d, $J = 1.43$ Hz), 8.37(1H, dd, $J = 7.8$, 1.9 Hz), 7.78(1H, d, $J = 7.8$ Hz), 1.62(9H, s). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 162.7, 151.9, 138.0, 136.5, 130.1, 127.8, 116.7, 83.4, 28.1.

***tert*-butyl 5-ethoxynicotinate (Table 3, entry 6)**

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 8.71(1H, d, $J = 1.6$ Hz), 8.38(1H, d, $J = 2.8$ Hz), 7.66(1H, dd, $J = 2.8$, 1.6 Hz), 4.08(2H, q, $J = 6.8$ Hz), 1.55(9H, s), 1.41(3H, t, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 164.5, 154.6, 142.8, 142.0, 128.1, 120.6, 82.1, 64.1, 28.1, 14.6.

***tert*-butyl 6-(benzyloxy)nicotinate (Table 3, entry 7)**

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 8.80(1H, d, $J = 2.0$ Hz), 8.23(1H, dd, $J = 8.7$, 2.0 Hz), 7.45(2H, m), 7.36(3H, m), 6.79(1H, d, $J = 8.7$ Hz), 5.43(2H, s), 1.58(9H, s). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 166.0, 164.7, 149.8, 139.7, 136.6, 128.6, 128.1, 121.5, 110.8, 81.2, 68.2, 28.1.

5-*tert*-butyl 2-methyl pyridine-2,5-dicarboxylate (Table 3, entry 8)

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 9.25(1H, d, $J = 1.3$ Hz), 8.38(1H, dd, $J = 8.1$, 1.9 Hz), 7.52(1H, d, $J = 8.1$ Hz), 4.04(3H, s), 1.62(9H, s). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 165.1, 163.5, 150.8, 150.4, 138.2, 130.4, 124.6, 82.9, 53.2, 28.1.

3-*tert*-butyl 5-ethyl pyridine-3,5-dicarboxylate (Table 3, entry 9)

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 9.32(1H, d, $J = 2.2$ Hz), 9.29(1H, d, $J = 2.2$ Hz), 8.79(1H, t, $J = 2.2$ Hz), 4.43(2H, q, $J = 7.4$ Hz), 1.61(9H, s), 1.41(3H, t, $J = 7.4$ Hz). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 164.6, 163.6, 154.1, 153.7, 137.7, 127.6, 126.1, 82.8, 61.7, 28.1, 14.3.

***tert*-butyl 5-allylnicotinate (Table 3, entry 10)**

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 9.01(1H, s), 8.58(1H, s), 8.10(1H, s), 5.93(1H, m), 5.13(2H, m), 3.45 (2H, t, $J = 6.6$ Hz), 1.60 (9H, s). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 164.3, 152.6, 148.2, 137.5, 135.5, 135.4, 127.8, 117.6, 82.3, 36.9, 28.1.

***tert*-butyl 6-(dimethylamino)nicotinate (Table 3, entry 11)**

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 8.76(1H, d, $J = 2.1$ Hz), 7.95(1H, dd, $J = 8.9$, 2.1 Hz), 6.44(1H, d, $J = 8.9$ Hz), 3.15(6H, s), 1.56(9H, s). ^{13}C NMR (100 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 165.6, 160.7, 151.0, 138.1, 115.3, 104.4, 80.3, 38.1, 28.1.

***tert*-butyl 2-phenylisonicotinate (Table 3, entry 12)**

^1H NMR (400 MHz, 25 $^\circ\text{C}$, CDCl_3 , ppm): δ 8.87(1H, d, $J = 4.6$ Hz), 8.25(1H, s), 8.12(2H, d, $J = 6.4$ Hz), 7.75(1H, dd, $J = 4.6$, 1.7 Hz), 7.52(3H, m), 1.60(9H, s). ^{13}C NMR (100 MHz,

25°C, CDCl₃, ppm): δ 163.8, 157.2, 150.7, 139.8, 137.9, 129.6, 129.0, 126.7, 121.1, 118.6, 82.2, 27.7.

***tert*-butyl quinoline-4-carboxylate (Table 3, entry 13)**

¹H NMR (400 MHz, 25°C, CDCl₃, ppm): δ 8.99(1H, d, *J* = 4.5 Hz), 8.71(1H, d, *J* = 8.5 Hz), 8.16(1H, d, *J* = 8.5 Hz), 7.81(1H, d, *J* = 4.5 Hz), 7.76(1H, m), 7.65(1H, m), 1.69(9H, s). ¹³C NMR (100 MHz, 25°C, CDCl₃, ppm): δ 165.8, 149.8, 149.2, 137.1, 136.2, 130.0, 129.6, 127.9, 125.6, 121.8, 83.0, 28.1.

***tert*-butyl 5-cyclopropylnicotinate (Table 3, entry 14)**

¹H NMR (400 MHz, 25°C, CDCl₃, ppm): δ 8.90(1H, s), 8.53(1H, s), 7.82(1H, s), 1.92(1H, m), 1.58(9H, s), 1.05(2H, m), 0.8(2H, m). ¹³C NMR (100 MHz, 25°C, CDCl₃, ppm): δ 164.6, 151.3, 147.6, 139.5, 133.5, 127.5, 82.1, 28.1, 12.9, 9.3.

***tert*-butyl 6-cyclopropylnicotinate (Table 3, entry 15)**

¹H NMR (400 MHz, 25°C, CDCl₃, ppm): δ 8.99(1H, s), 8.09(1H, m), 7.17(1H, d, *J* = 7.67 Hz), 2.10(1H, m), 1.58(9H, s), 1.10(4H, m). ¹³C NMR (100 MHz, 25°C, CDCl₃, ppm): δ 167.2, 164.6, 150.2, 137.1, 124.6, 120.8, 82.7, 28.1, 17.4, 11.2.

***tert*-butyl 2-methylbenzoate (Table 4, entry 1)**

¹H NMR (400 MHz, 25°C, CDCl₃, ppm): δ 7.82(1H, d, *J* = 7.5 Hz), 7.36(1H, t, *J* = 7.5 Hz), 7.22(2H, t, *J* = 7.6 Hz), 2.58(3H, s), 1.60(9H, s). ¹³C NMR (100 MHz, 25°C, CDCl₃, ppm): δ 167.3, 139.2, 131.6, 131.6, 131.4, 130.3, 125.7, 81.1, 28.3, 21.6.

***tert*-butyl 4-methoxybenzoate (Table 4, entry 2)**

¹H NMR (400 MHz, 25°C, CDCl₃, ppm): δ 7.94 (2H, d, *J* = 8.7 Hz), 6.88 (2H, d, *J* = 8.6 Hz), 3.82 (3H, s), 1.58 (9H, s). ¹³C NMR (100 MHz, 25°C, CDCl₃, ppm): δ 165.7, 163.0, 131.2, 124.5, 113.3, 80.4, 55.3, 28.3.

***tert*-butyl 3,4-dimethoxybenzoate (Table 4, entry 3)**

¹H NMR (400 MHz, 25°C, CDCl₃, ppm): δ 7.60 (1H, dd, *J* = 8.4, 2.0 Hz), 7.50 (1H, d, *J* = 2.0 Hz), 6.84 (1H, d, *J* = 8.4 Hz), 3.90 (s, 6H), 1.57 (9H, s). ¹³C NMR (100 MHz, 25°C, CDCl₃, ppm): δ (ppm) 165.7, 152.5, 148.5, 124.4, 123.2, 111.9, 110.1, 80.6, 55.94, 55.87, 28.3.

***tert*-butyl 2-fluorobenzoate (Table 4, entry 4)**

¹H NMR (400 MHz, 25°C, CDCl₃, ppm): δ 7.85(1H, td, *J* = 7.7, 1.8 Hz), 7.46(1H, m), 7.17(1H, td, *J* = 7.6, 1.0 Hz), 7.10(1H, dd, *J* = 10.1, 1.0 Hz), 1.59(9H, s). ¹³C NMR (100 MHz, 25°C, CDCl₃, ppm): δ 162.6, 162.1, 159.5, 132.7, 130.9, 122.6, 119.8, 115.4, 80.8, 27.2.

***tert*-butyl 4-fluorobenzoate (Table 4, entry 5)**

¹H NMR (400 MHz, 25°C, CDCl₃, ppm): δ 7.93(2H, m), 7.08(2H, t, *J* = 8.6 Hz), 1.58(9H, s). ¹³C NMR (100 MHz, 25°C, CDCl₃, ppm): δ 166.7, 164.3, 164.8, 131.8, 128.2, 115.2, 81.2, 28.1.

***tert*-butyl 2-chlorobenzoate (Table 4, entry 6)**

¹H NMR (400 MHz, 25^oC, CDCl₃, ppm): δ 7.73(1H, dd, *J* = 7.5, 1.7 Hz), 7.42(1H, dd, *J* = 7.9, 1.5 Hz), 7.36(1H, t, *J* = 7.9, 1.7 Hz), 7.29(1H, td, *J* = 7.5, 1.5 Hz), 1.61(9H, s). ¹³C NMR (100 MHz, 25^oC, CDCl₃, ppm): δ 165.3, 133.1, 132.2, 131.8, 130.9, 130.8, 126.5, 82.3, 28.2.

***tert*-butyl 4-chlorobenzoate (Table 4, entry 7)**

¹H NMR (400 MHz, 25^oC, CDCl₃, ppm): δ 7.92 (2H, d, *J* = 8.5 Hz), 7.38 (2H, d, *J* = 8.4 Hz), 1.58 (9H, s). ¹³C NMR (100 MHz, 25^oC, CDCl₃, ppm): δ 164.9, 138.8, 130.9, 130.4, 128.4, 81.5, 28.2.

***tert*-butyl 4-(trifluoromethyl)benzoate (Table 4, entry 8)**

¹H NMR (400 MHz, 25^oC, CDCl₃, ppm): δ 8.10 (2H, d, *J* = 8.1 Hz), 7.67 (2H, d, *J* = 8.0 Hz), 1.61 (9H, s). ¹³C NMR (100 MHz, 25^oC, CDCl₃, ppm): δ 164.5, 135.3, 133.9, 129.9, 125.2, 123.7, 82.0, 28.2.

***tert*-butyl 4-cyanobenzoate (Table 4, entry 9)**

¹H NMR (400 MHz, 25^oC, CDCl₃, ppm): δ 8.09 (2H, d, *J* = 8.0 Hz), 7.72(2H, d, *J* = 8.1 Hz), 1.60 (9H, s). ¹³C NMR (100 MHz, 25^oC, CDCl₃, ppm): δ 164.0, 135.8, 132.1, 130.0, 118.1, 115.8, 82.4, 28.2.

***tert*-butyl 4-biphenylbenzoate (Table 4, entry 10)**

¹H NMR (400 MHz, 25^oC, CDCl₃, ppm): δ 8.06 (2H, d, *J* = 8.4 Hz), 7.64 (4H, t, *J* = 7.6 Hz), 7.47 (2H, t, *J* = 7.4 Hz), 7.42-7.37 (1H, m), 1.62 (9H, s). ¹³C NMR (100 MHz, 25^oC, CDCl₃, ppm): δ 165.8, 145.2, 140.2, 130.8, 130.1, 128.9, 128.1, 127.4, 126.9, 81.0, 28.2.

***tert*-butyl 1-napthoate (Table 4, entry 11)**

¹H NMR (400 MHz, 25^oC, CDCl₃, ppm): δ 8.86 (1H, d, *J* = 8.8 Hz), 8.08 (1H, dd, *J* = 7.4, 1.4 Hz), 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.62-7.47 (3H, m), 1.68 (9H, s). ¹³C NMR (100 MHz, 25^oC, CDCl₃, ppm): δ 167.2, 133.8, 132.6, 131.2, 129.6, 129.4, 128.5, 127.4, 126.1, 125.8, 124.5, 81.5, 28.3.

***tert*-butyl 2-napthoate (Table 4, entry 12)**

¹H NMR (400 MHz, 25^oC, CDCl₃, ppm): δ 8.57 (1H, s), 8.06 (1H, dd, *J* = 8.4, 1.8 Hz), 7.95 (1H, d, *J* = 8.1 Hz), 7.86 (2H, d, *J* = 8.8 Hz), 7.60-7.51 (2H, m), 1.63 (9H, s). ¹³C NMR (100 MHz, 25^oC, CDCl₃, ppm): δ 166.0, 135.3, 132.5, 130.7, 129.4, 127.9, 127.9, 127.7, 126.6, 125.3, 81.1, 28.2.

***tert*-butyl 2-thiophenoate (Table 4, entry 13)**

¹H NMR (400 MHz, 25^oC, CDCl₃, ppm): δ 7.72 (1H, d, *J* = 4.0 Hz), 7.49 (1H, d, *J* = 5.2 Hz), 7.07 (1H, t, *J* = 4.4 Hz), 1.58 (9H, s). ¹³C NMR (100 MHz, 25^oC, CDCl₃, ppm): δ 161.6, 135.9, 132.7, 131.6, 127.6, 81.7, 28.3.

Table 3, entry 1

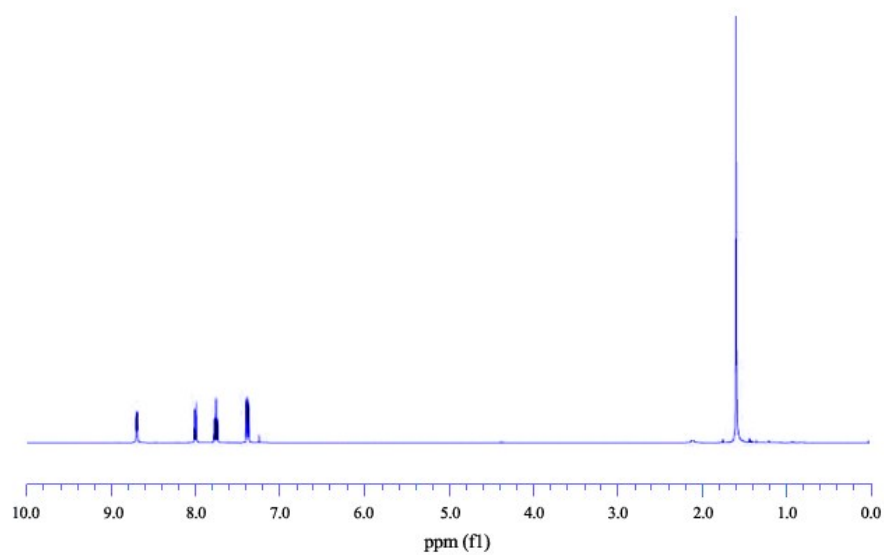


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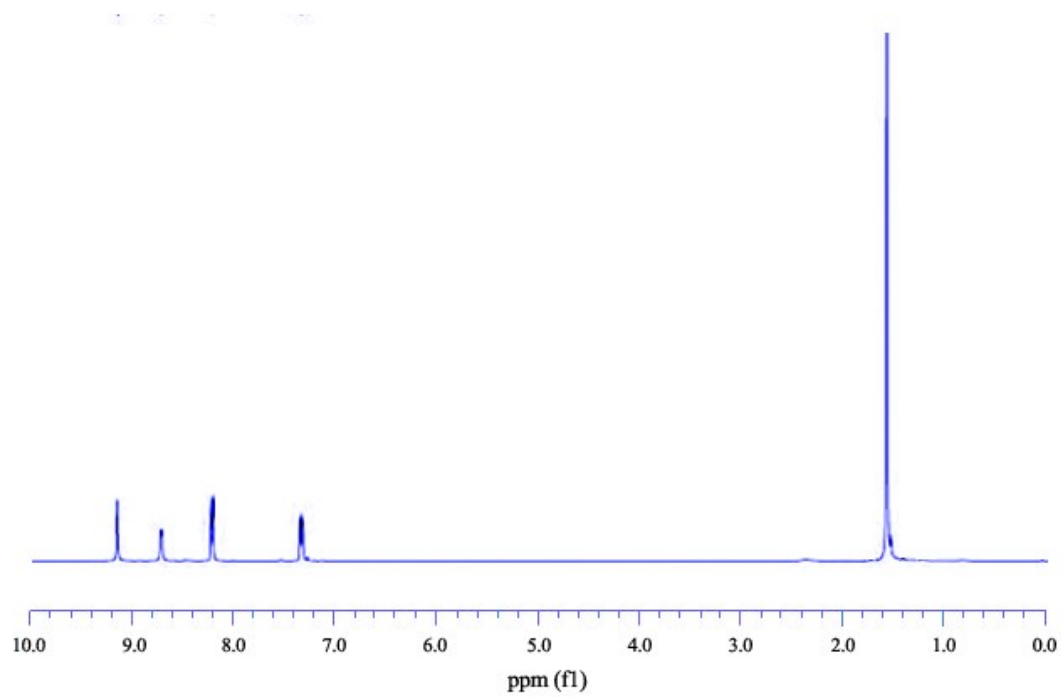


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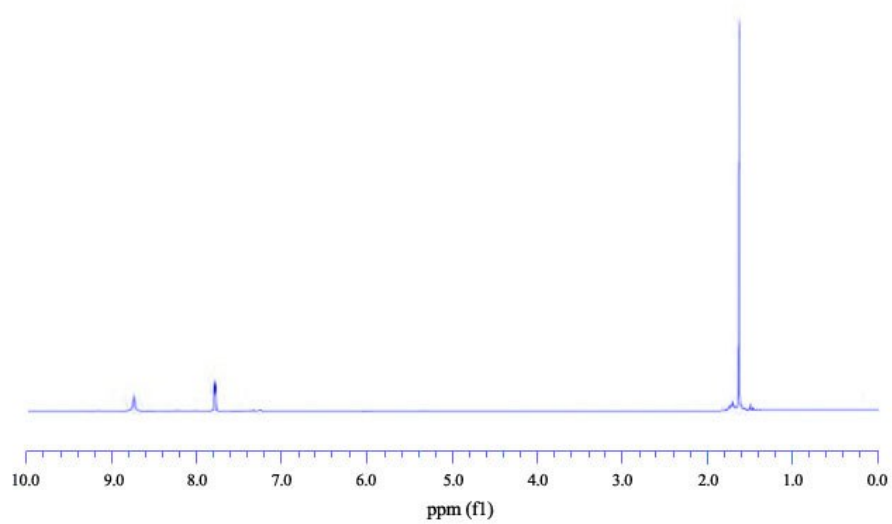


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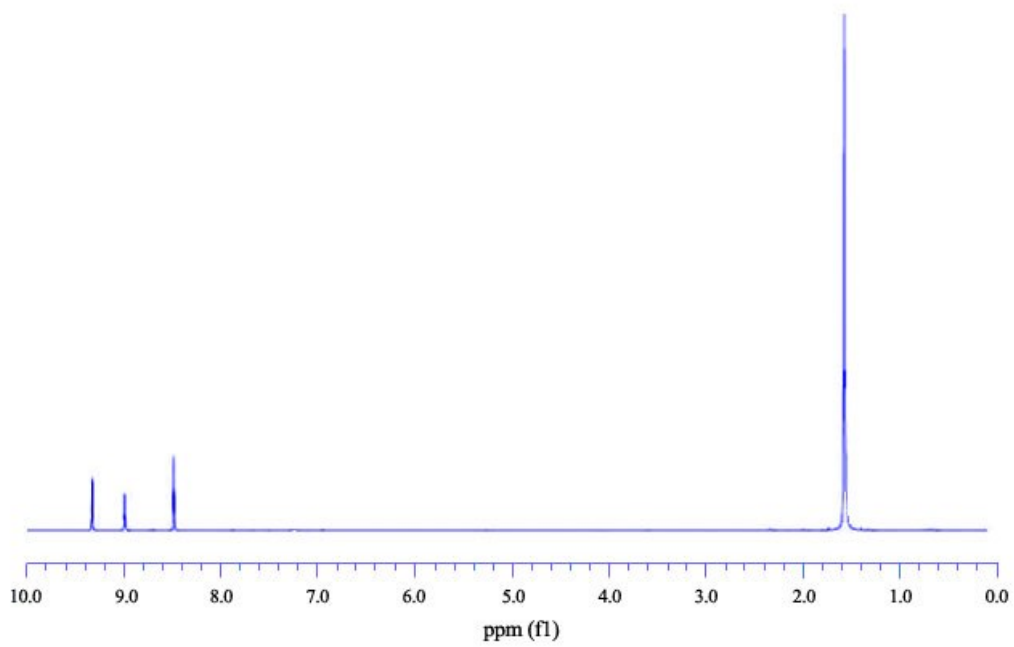


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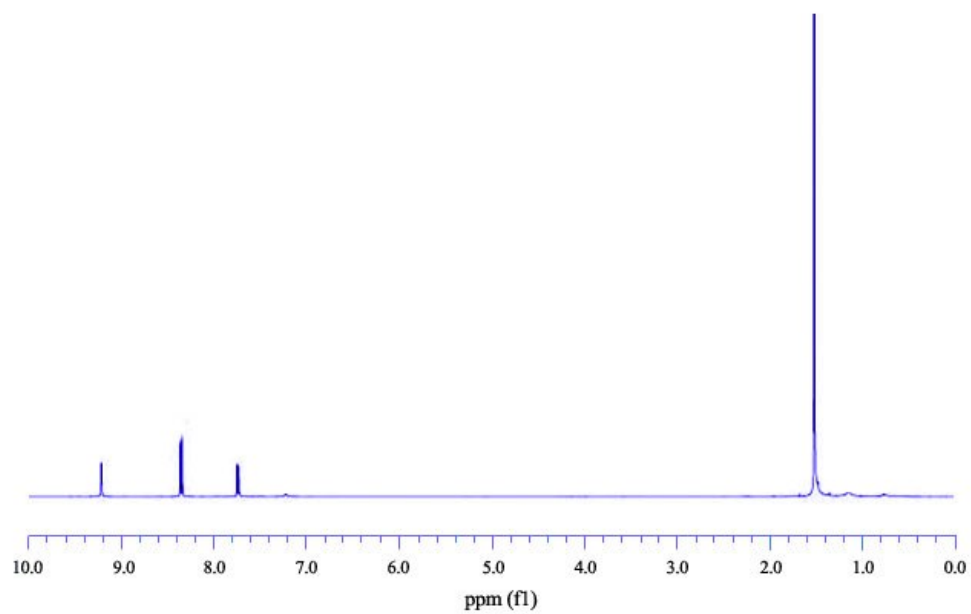


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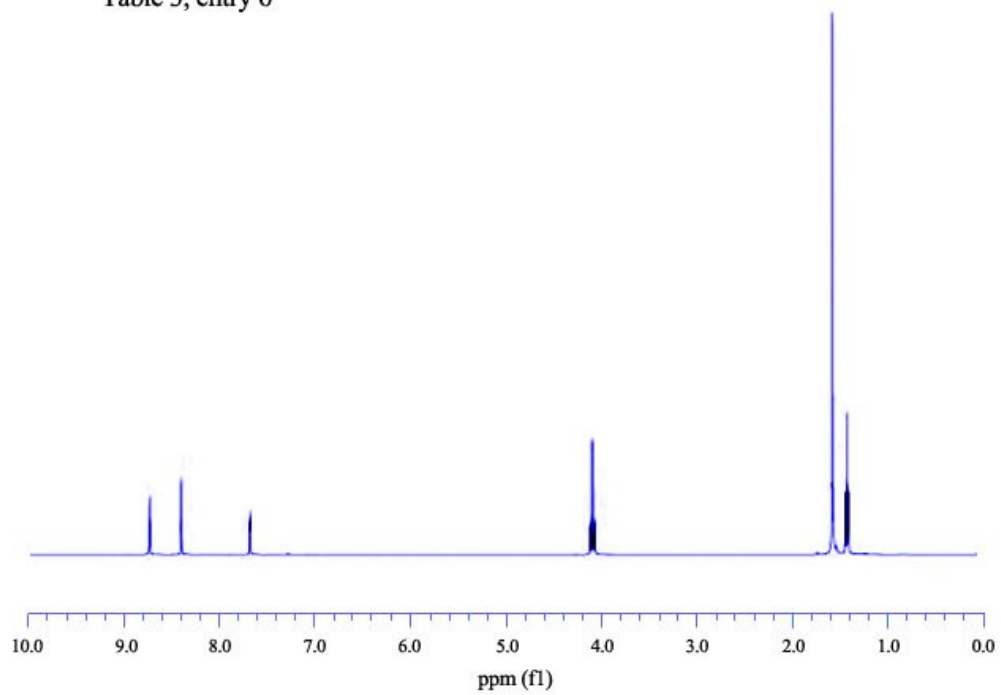


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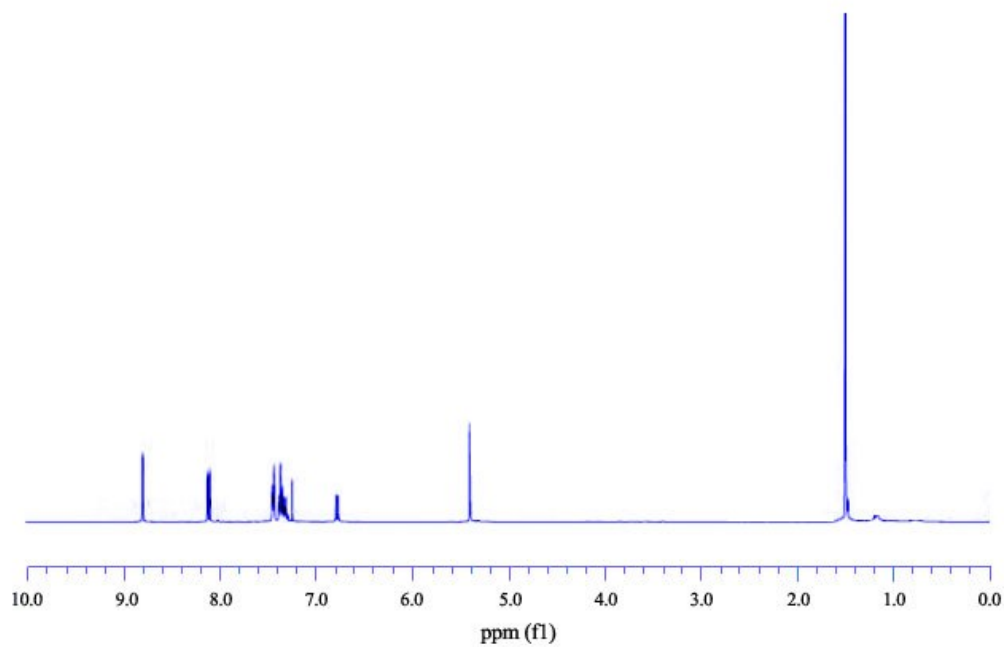


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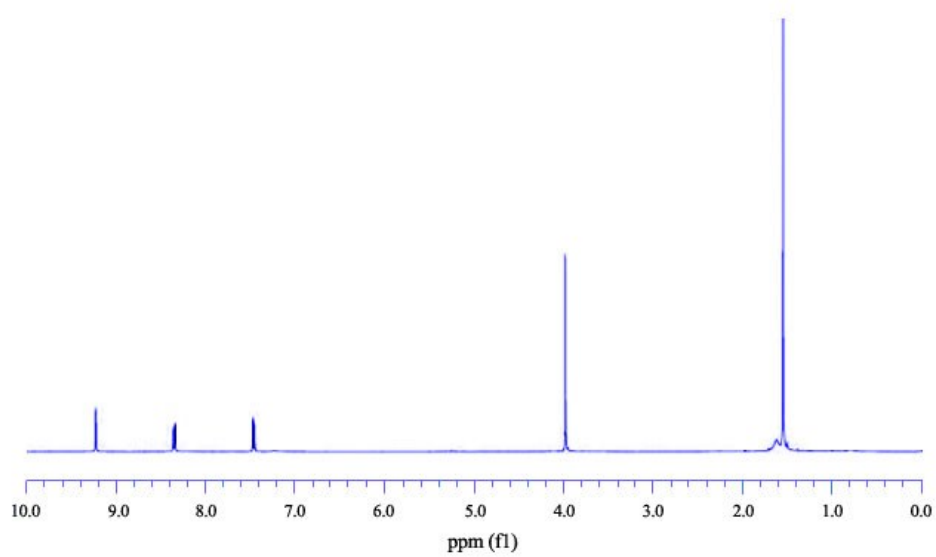


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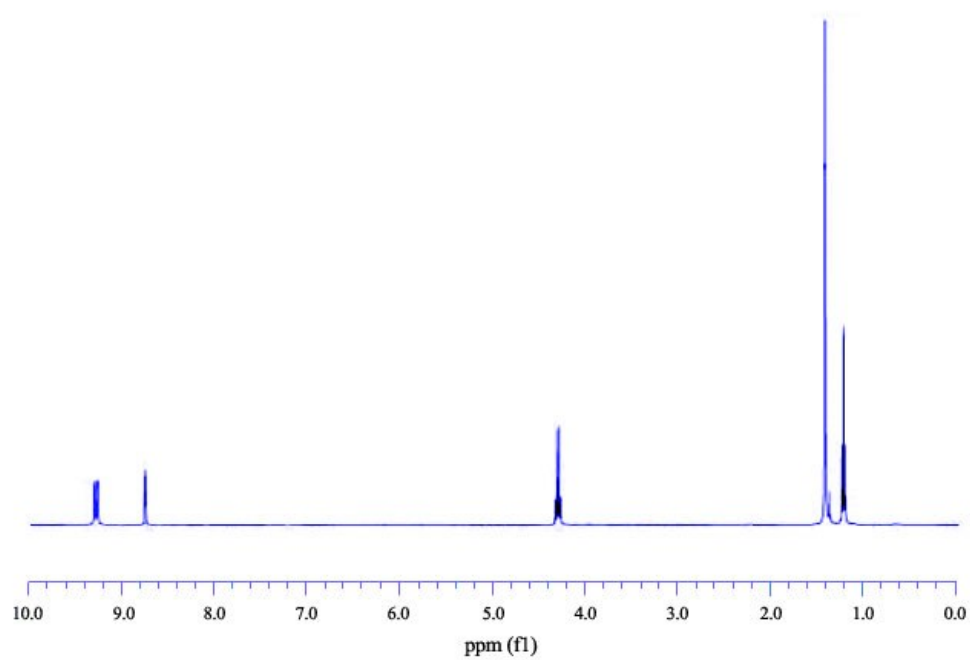


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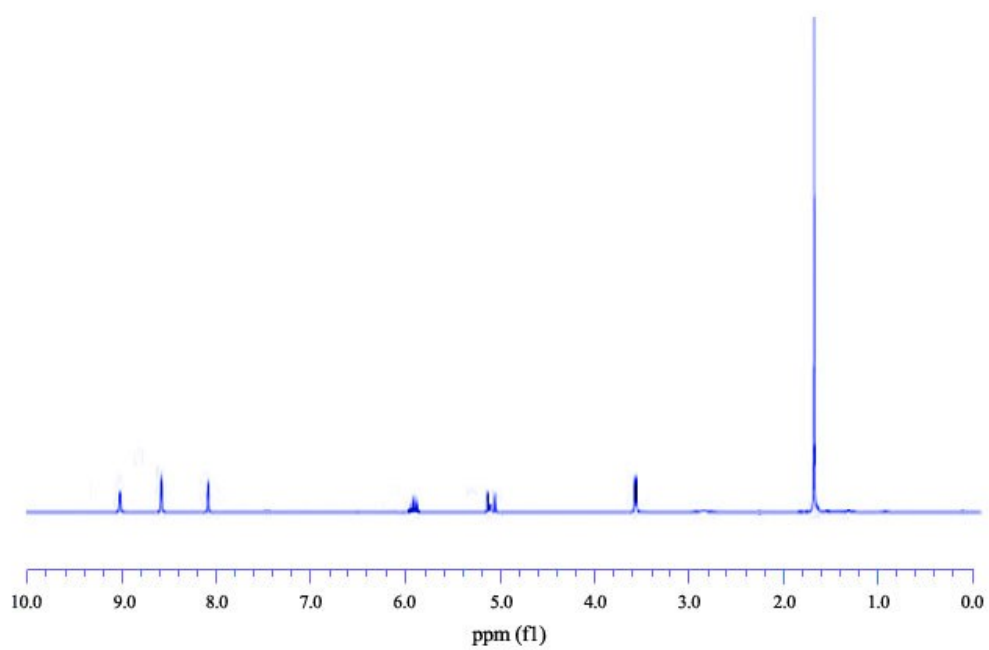


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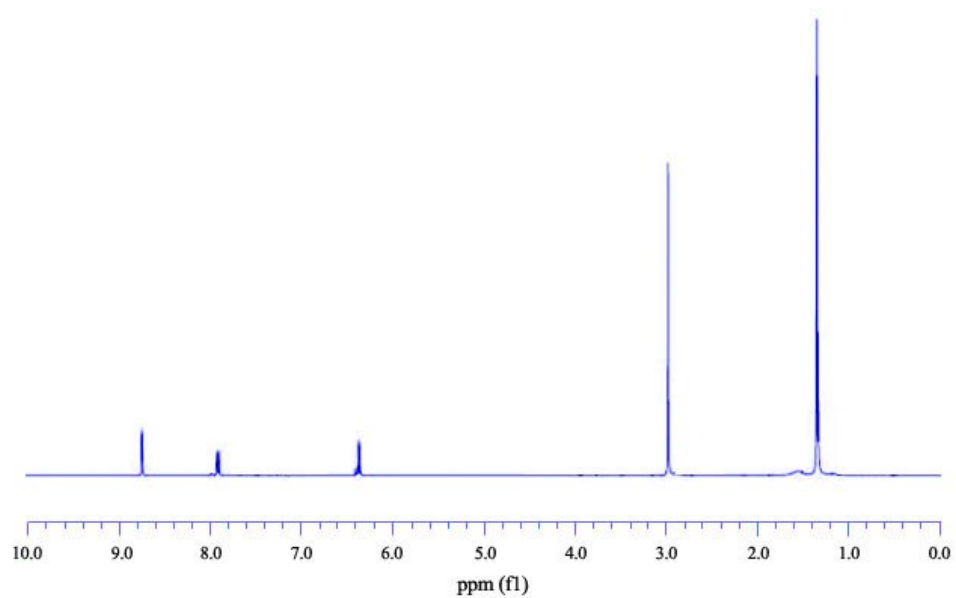


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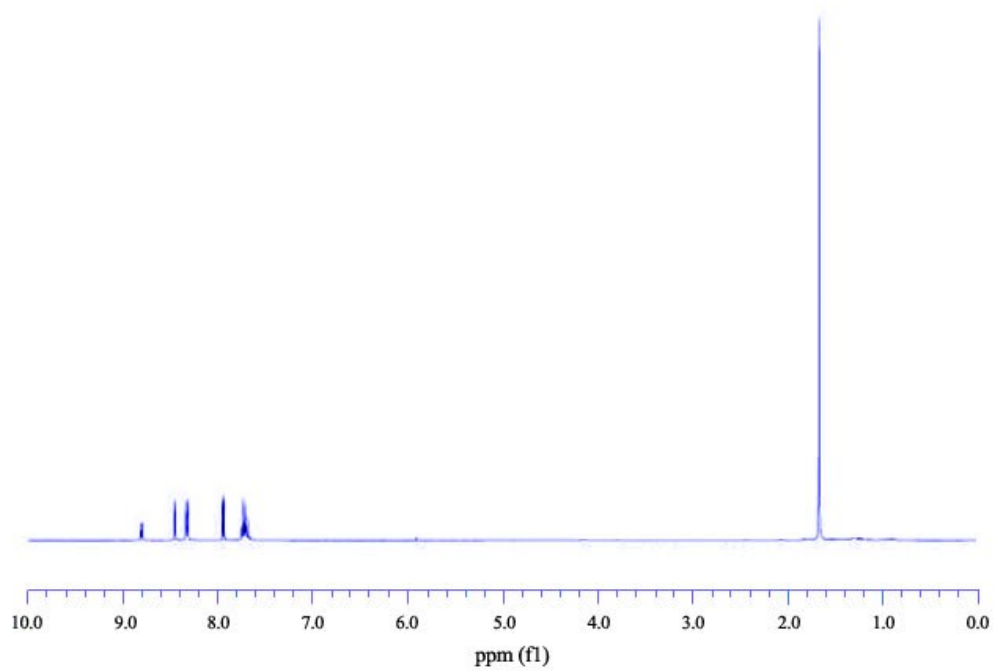


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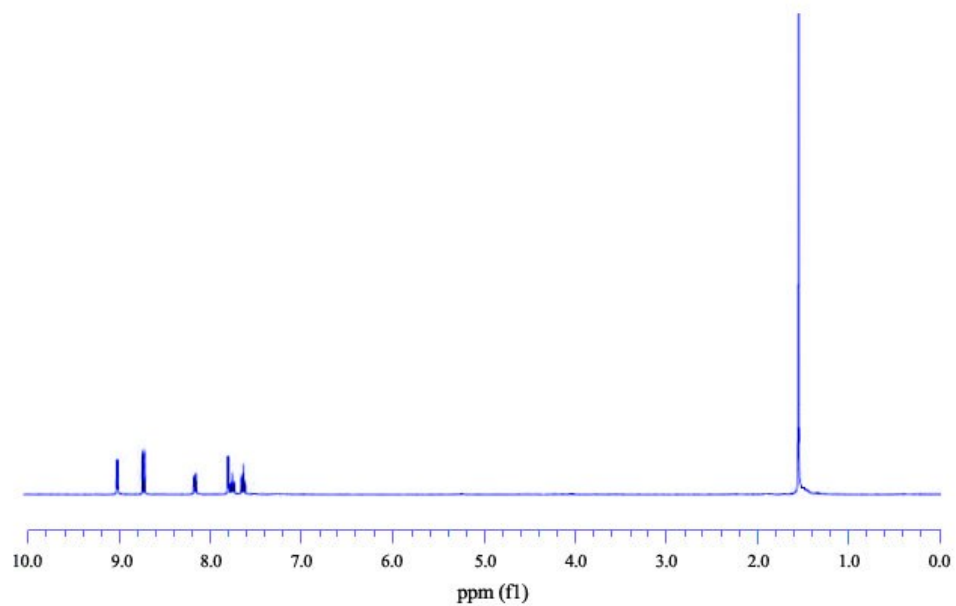


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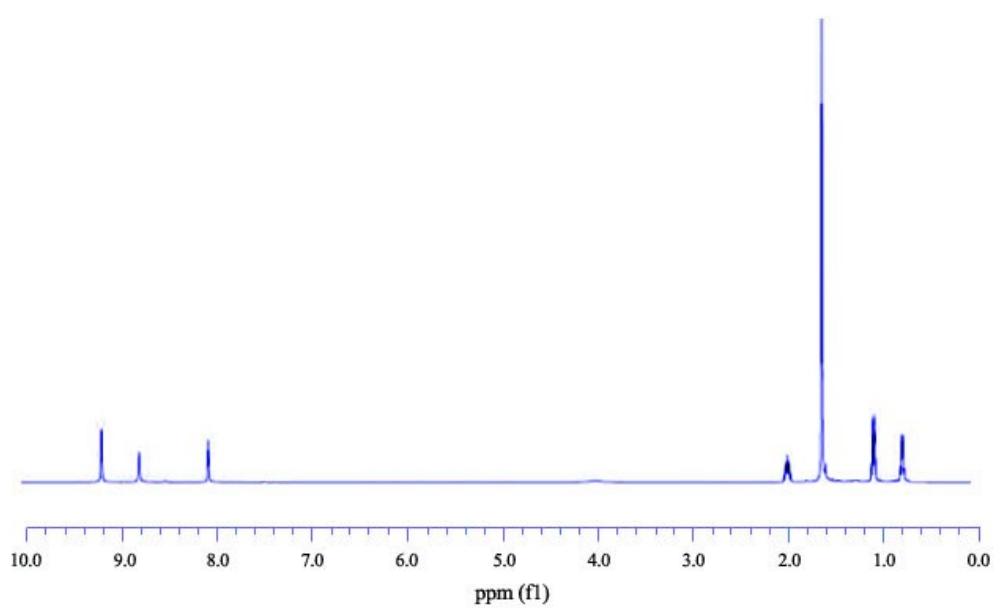


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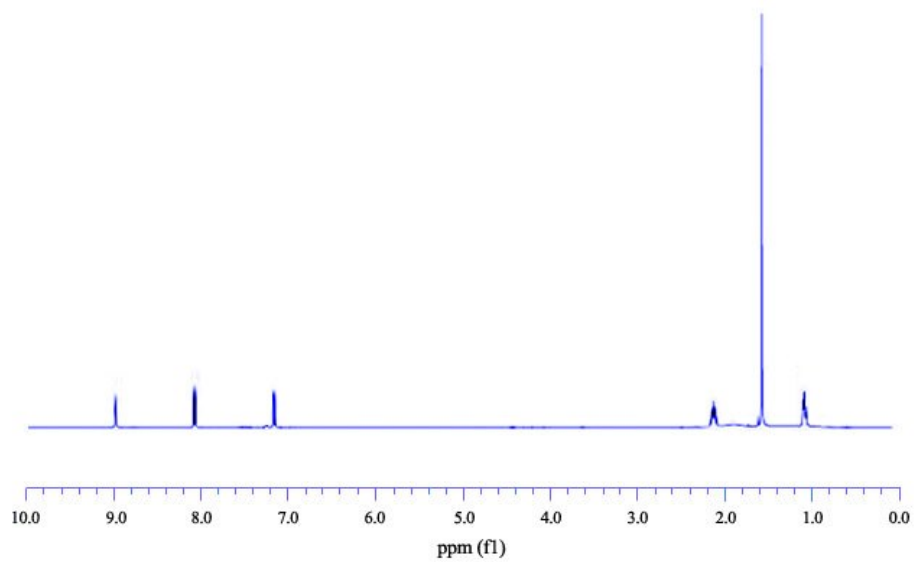


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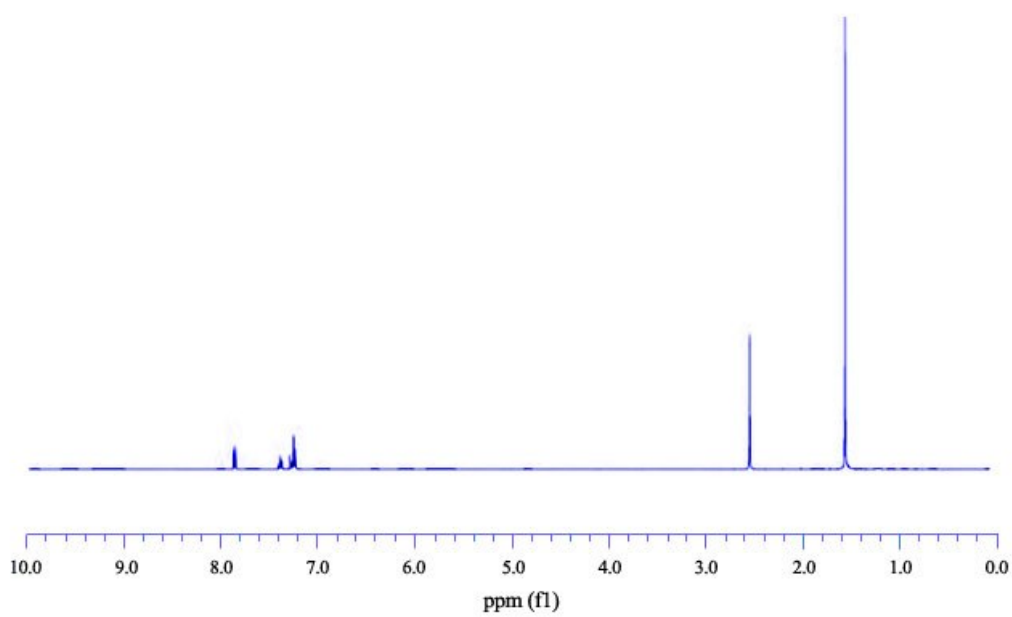


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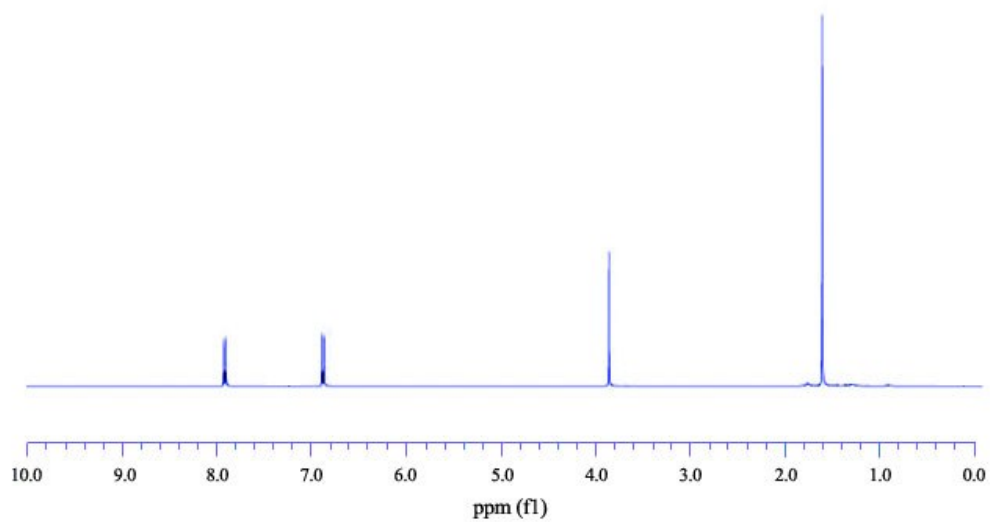


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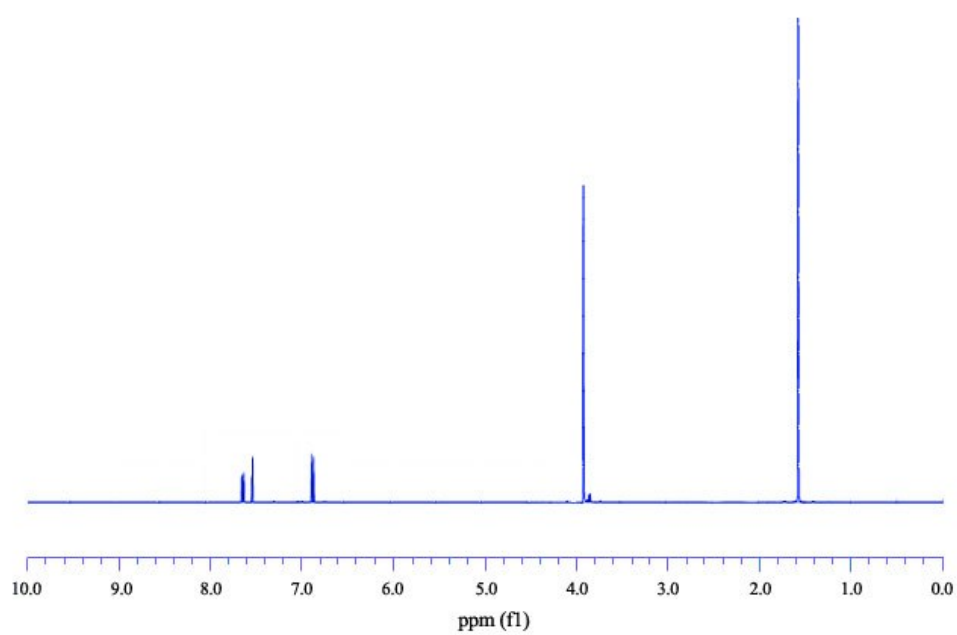


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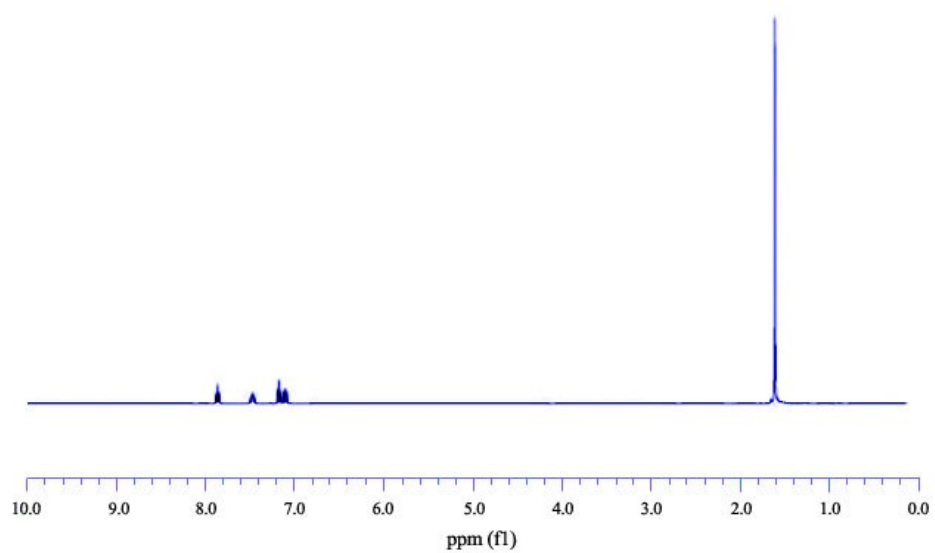


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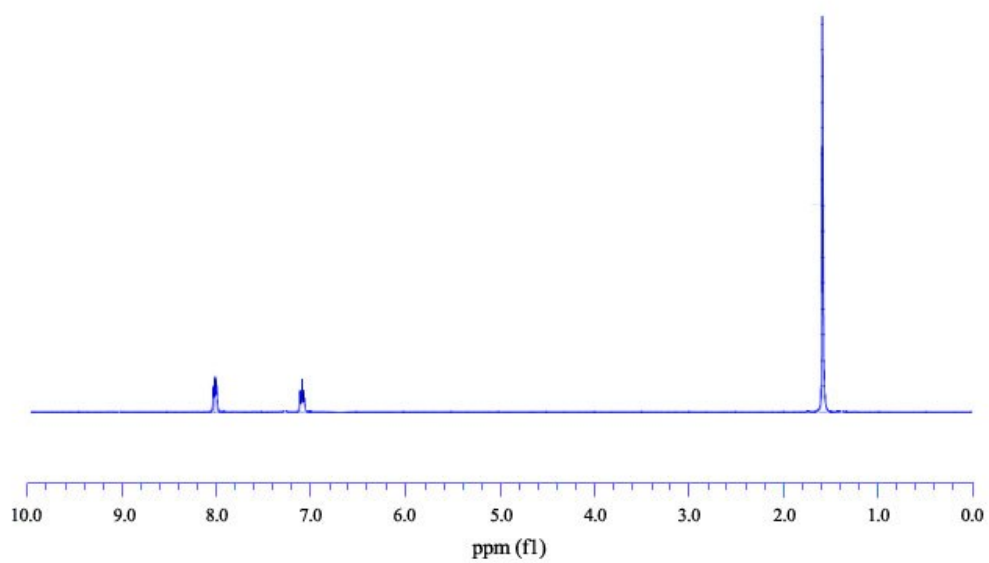


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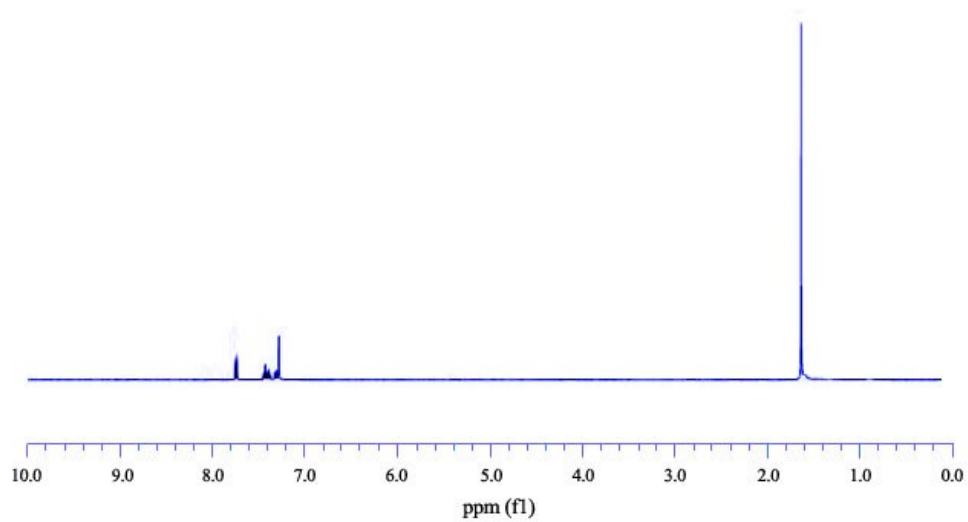


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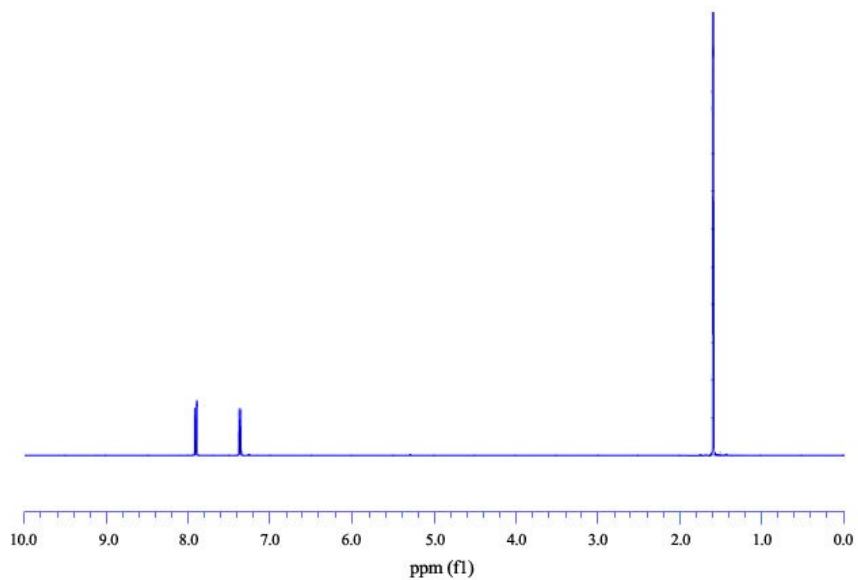


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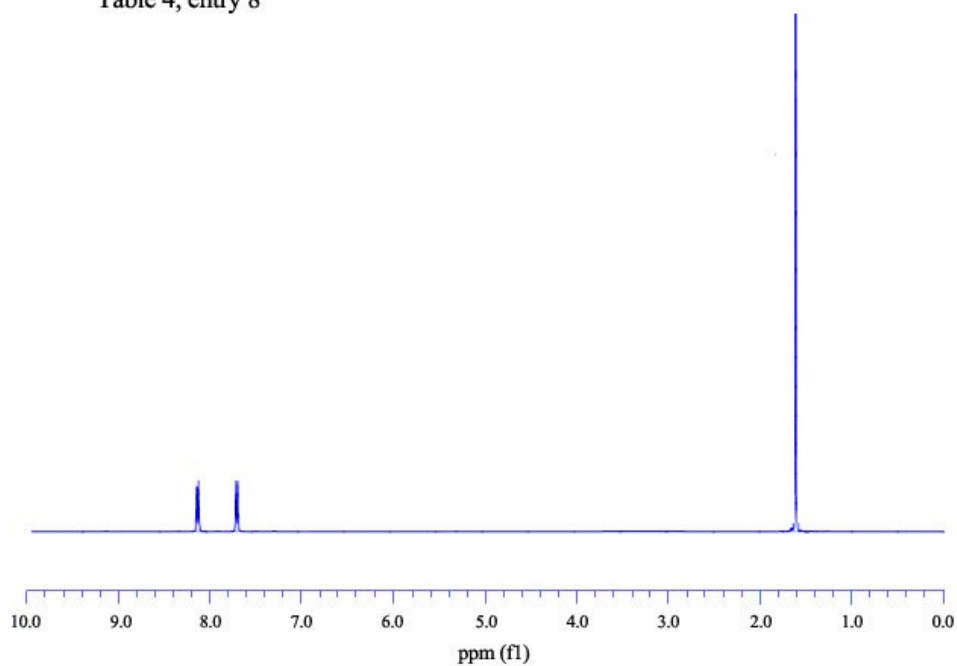


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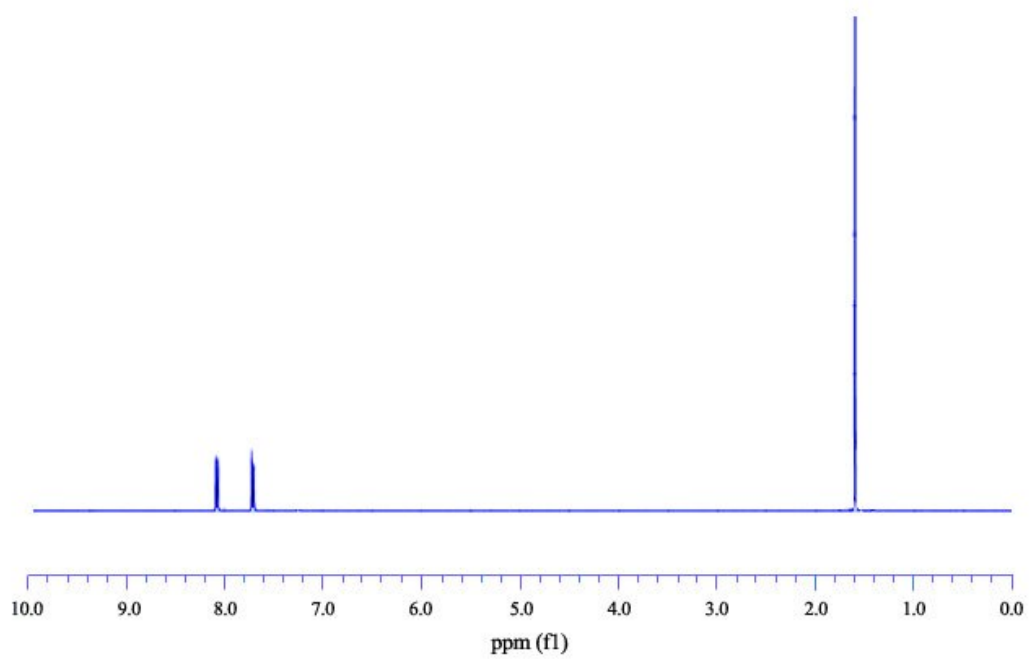


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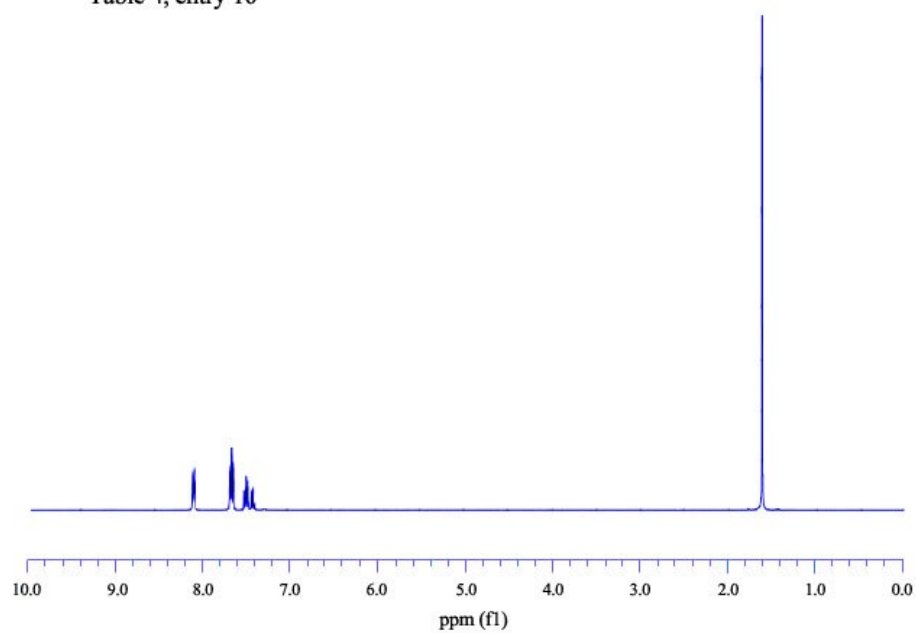


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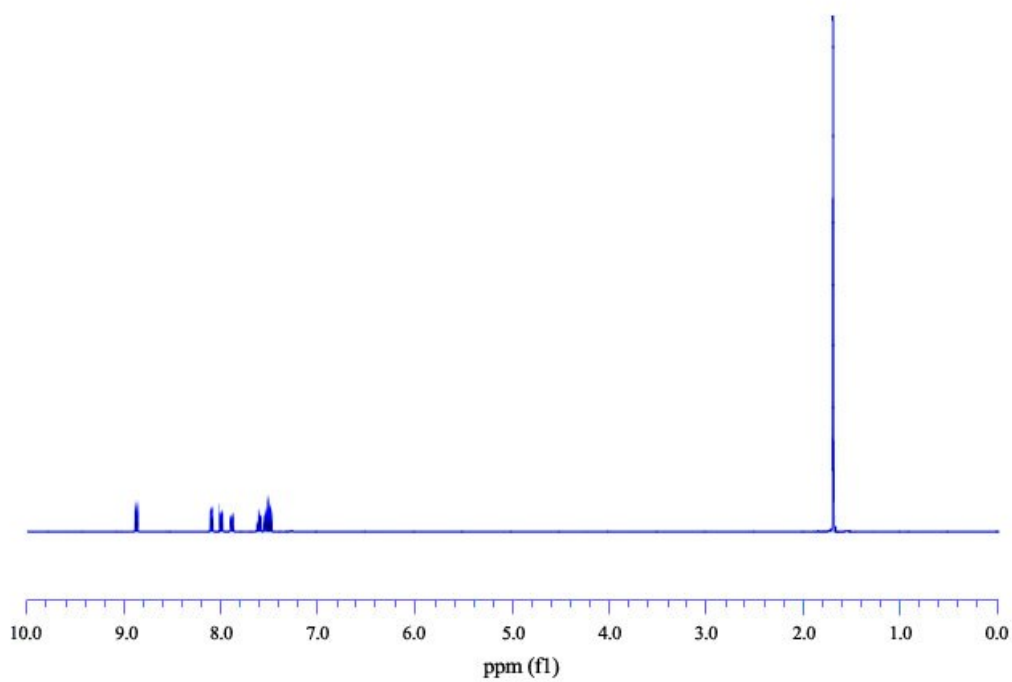


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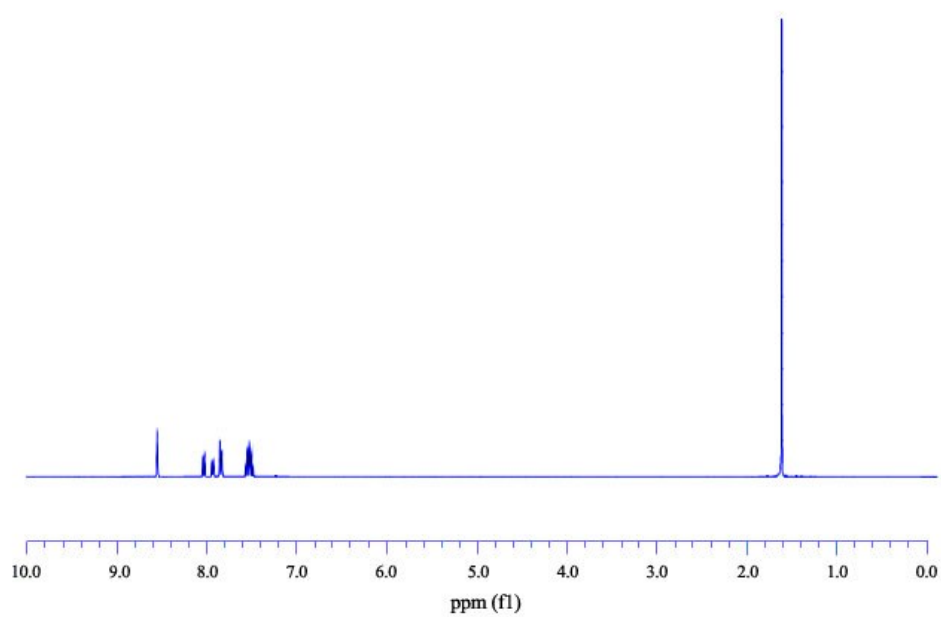


Table 4, entry 13

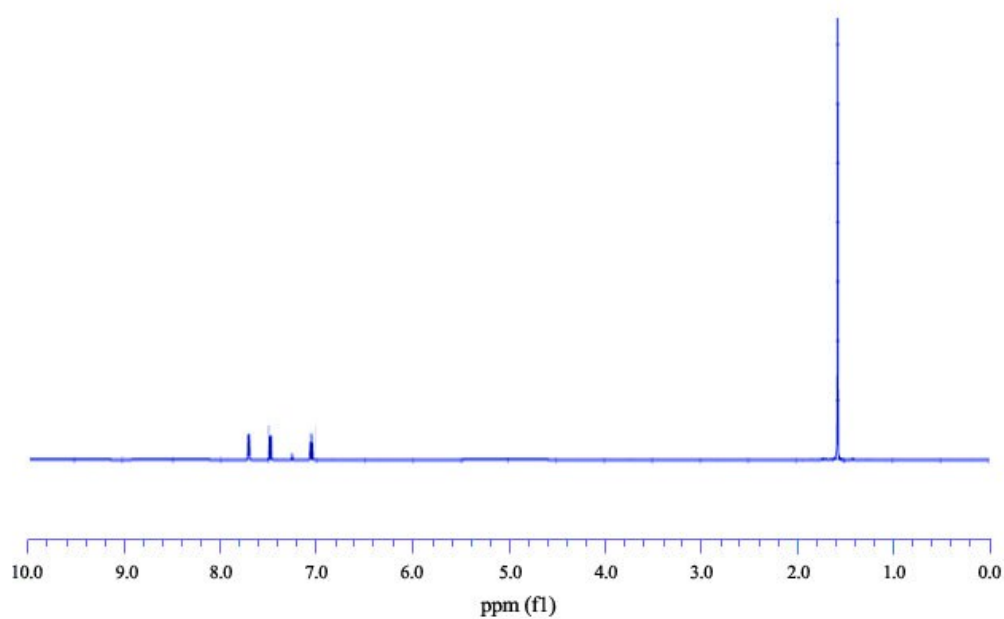


Table 3, entry 1

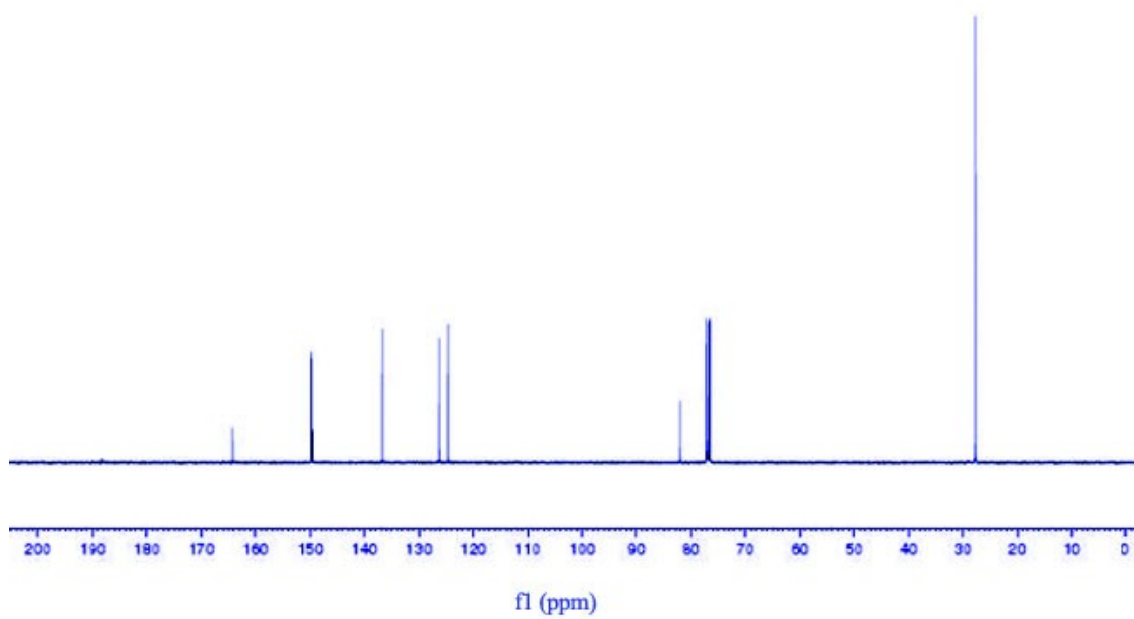


Table 3, entry 2

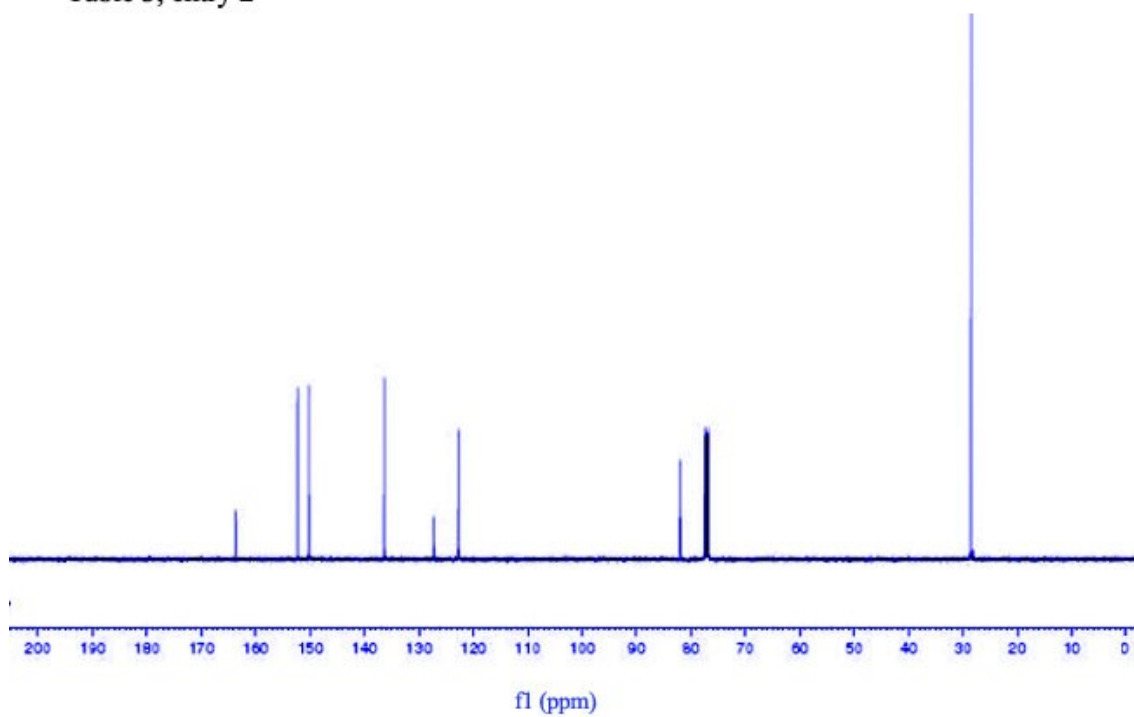


Table 3, entry 3

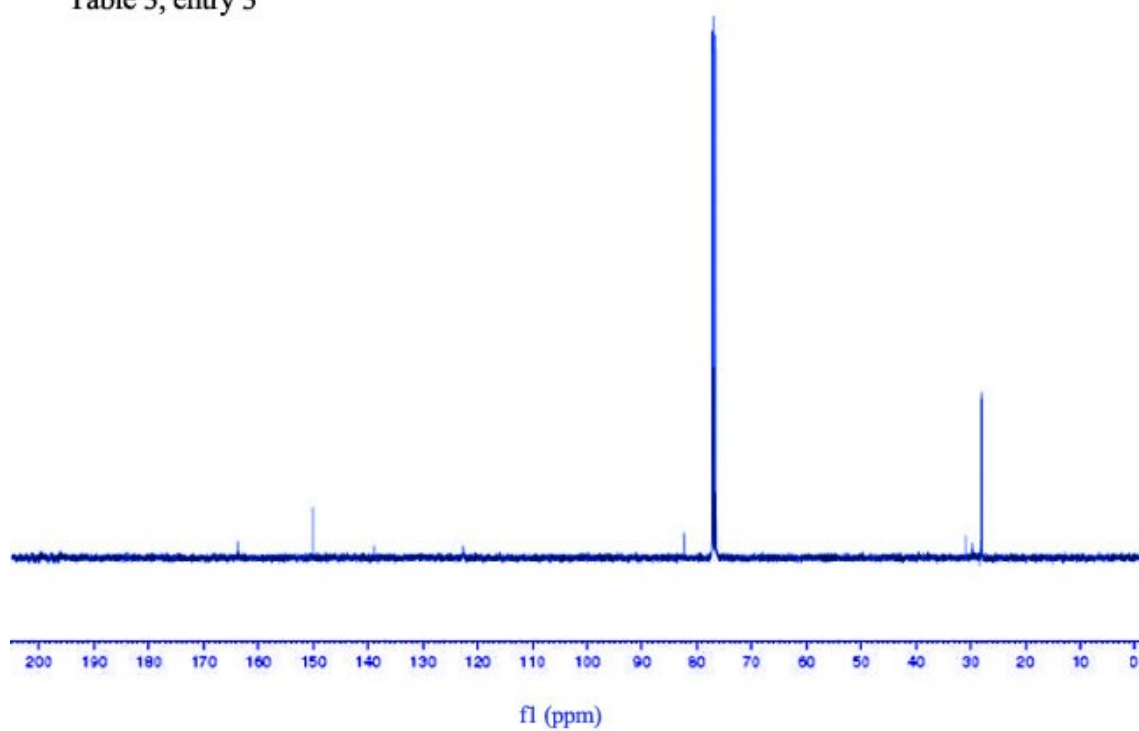


Table 3, entry 4

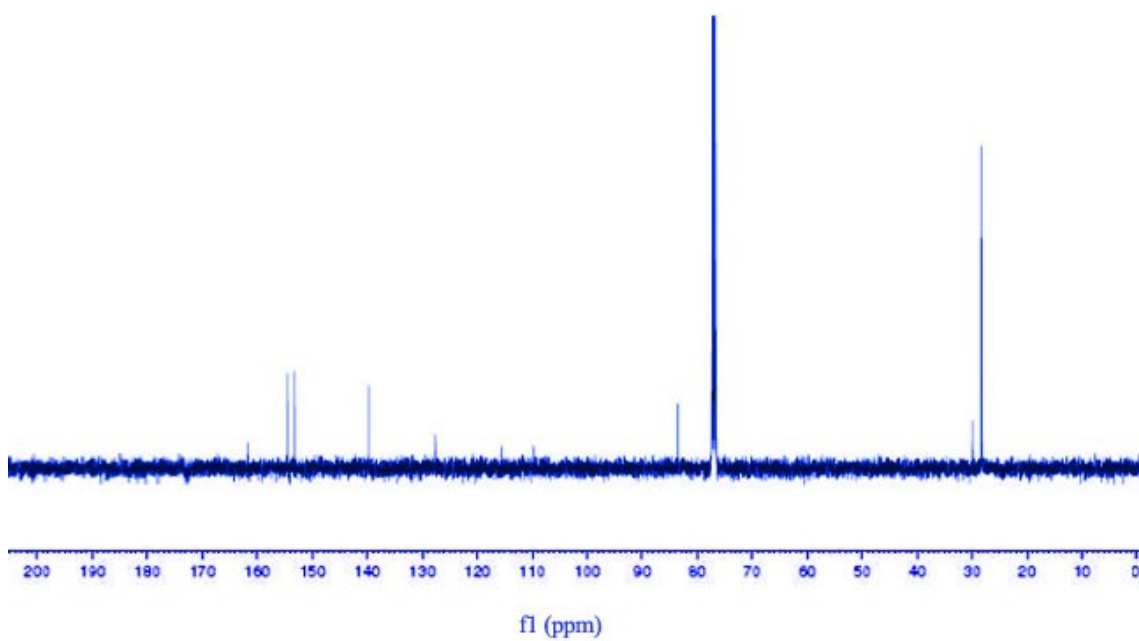


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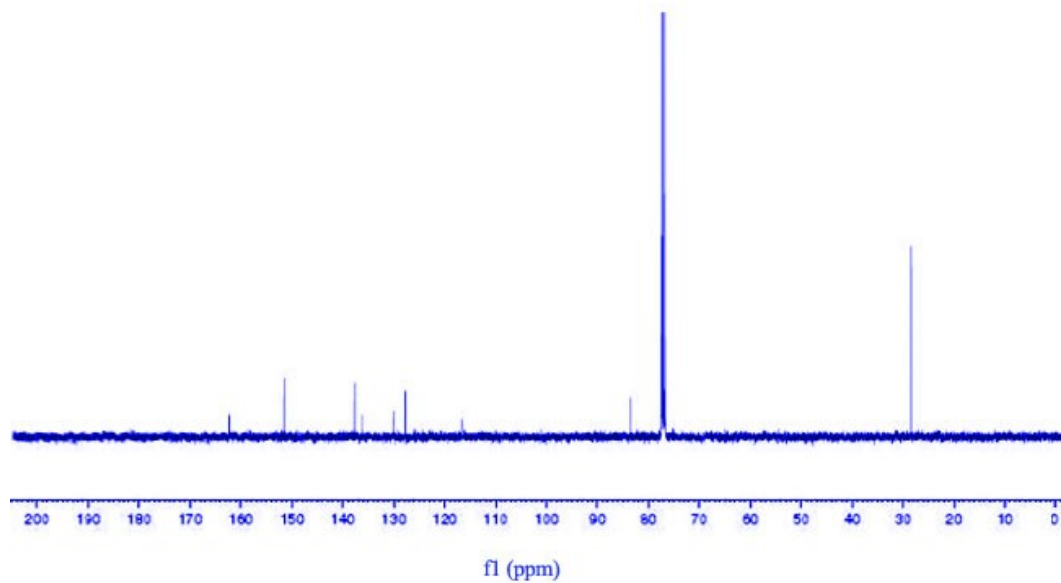


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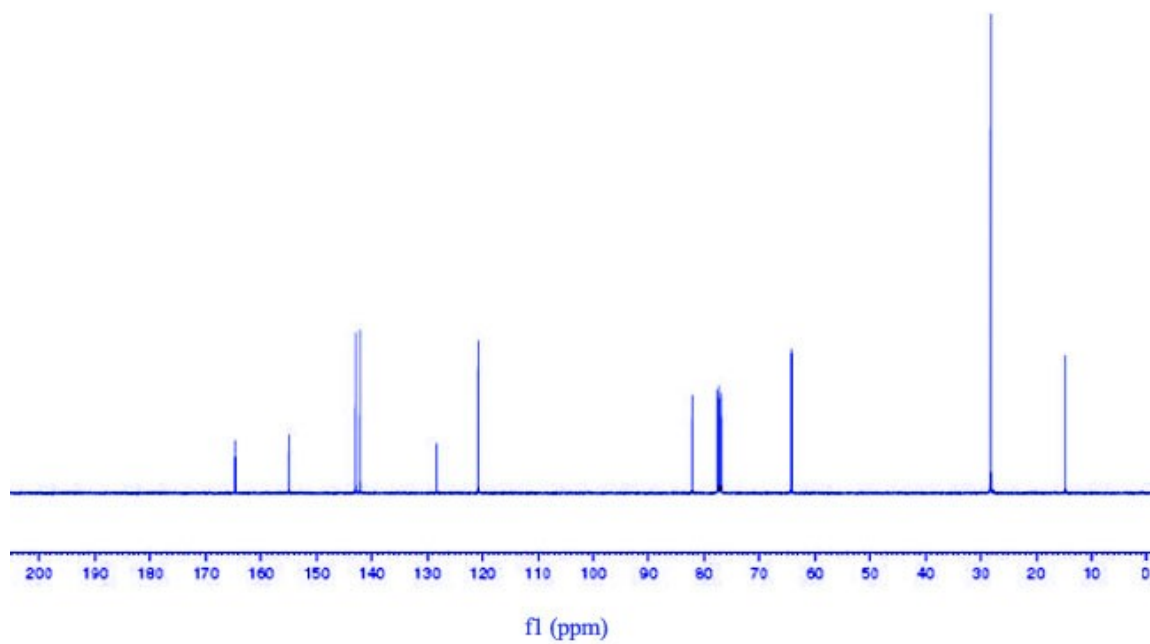


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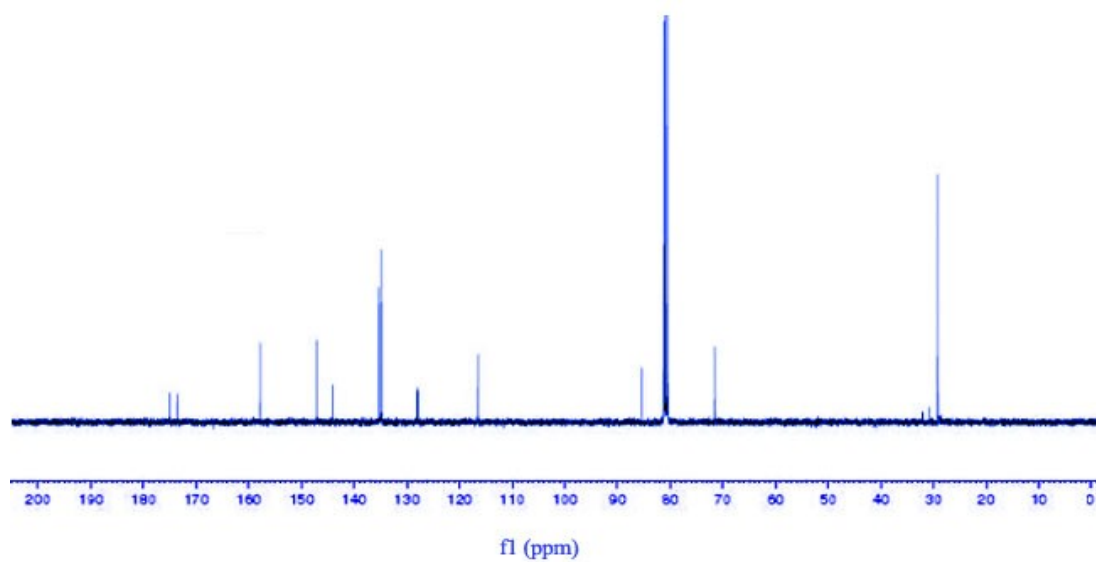


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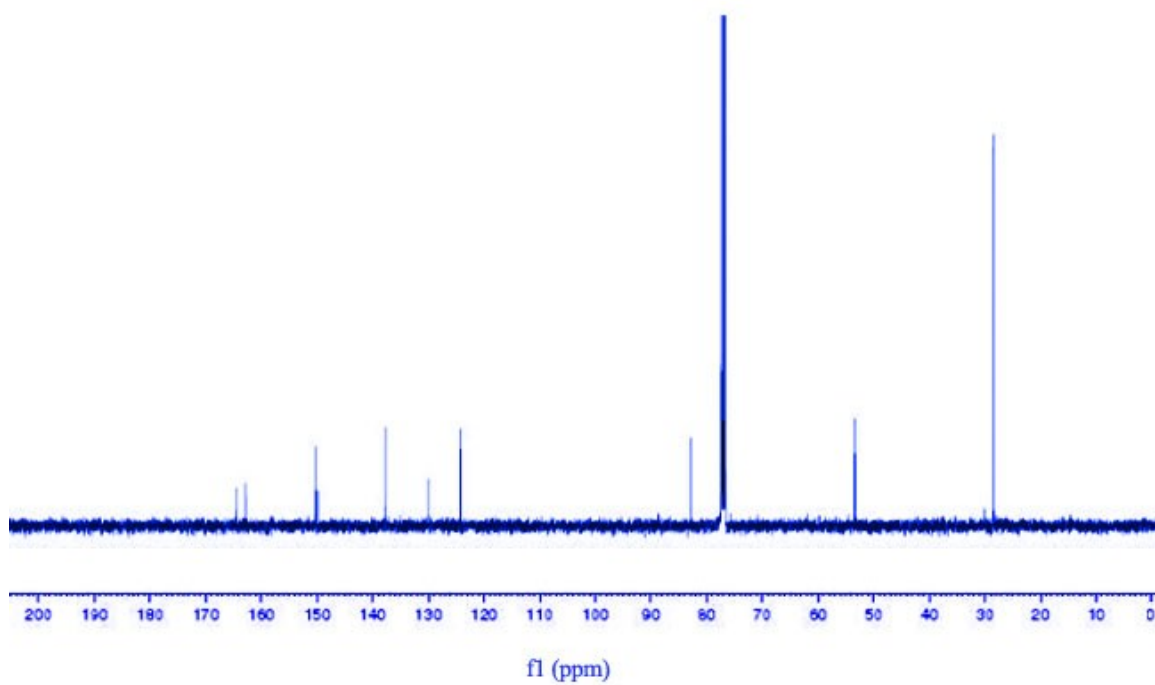


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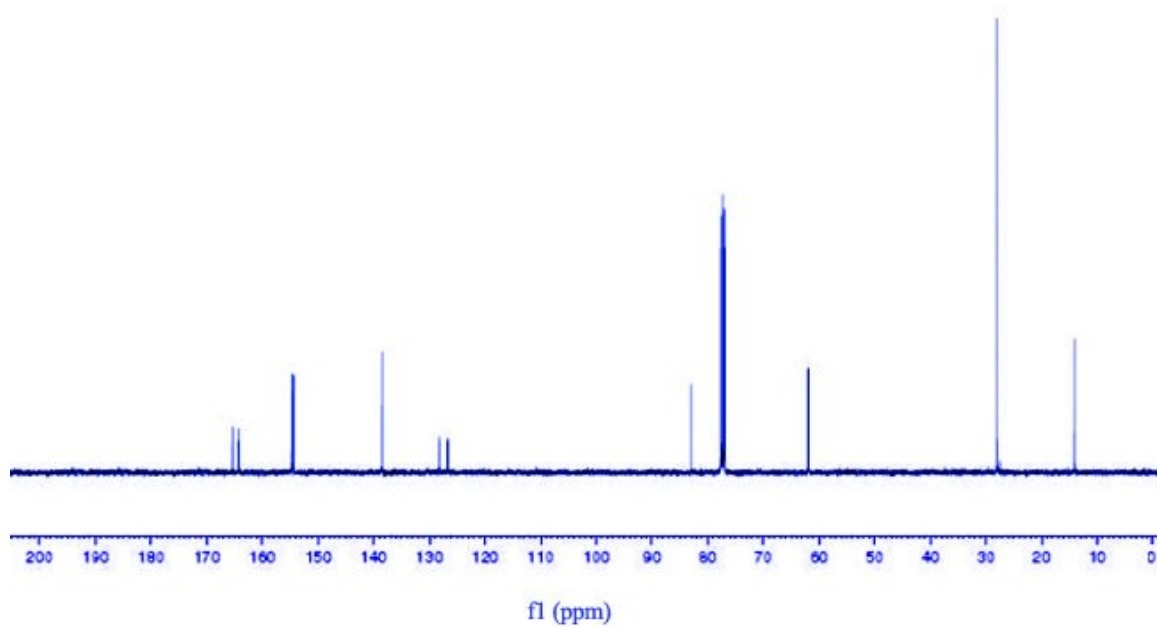


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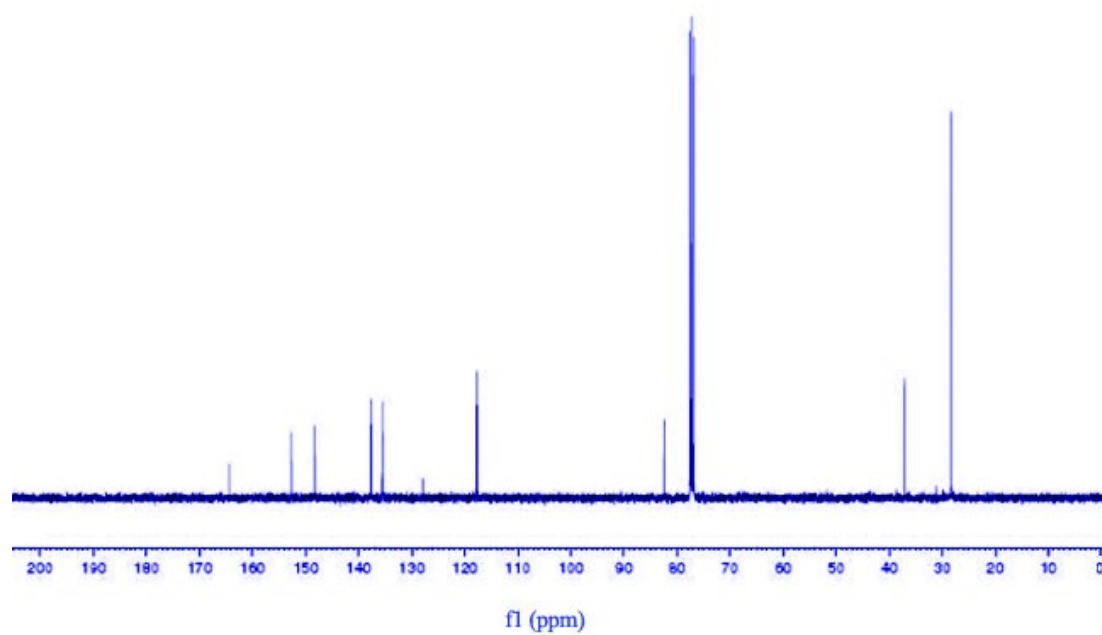


Table 3, entry 11

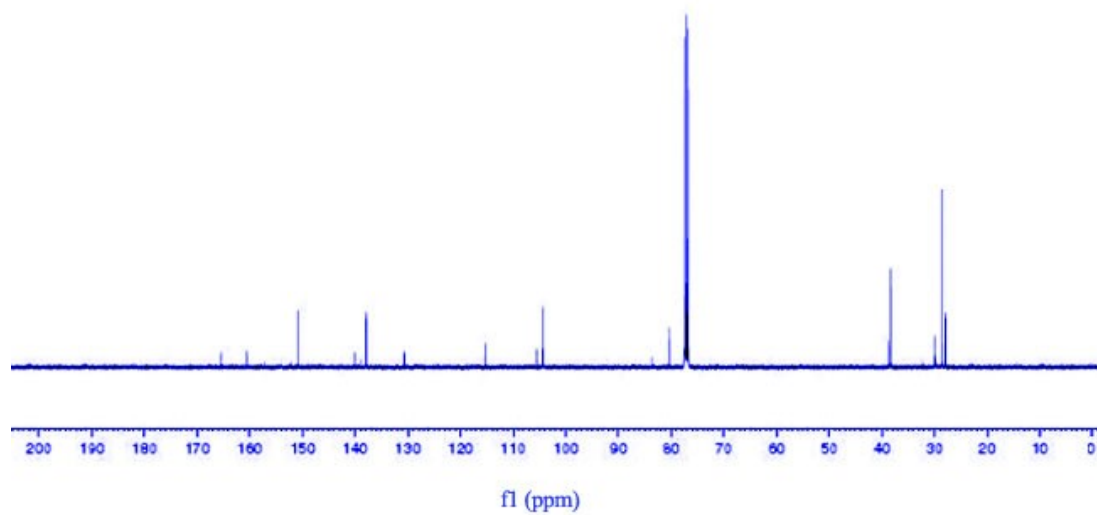


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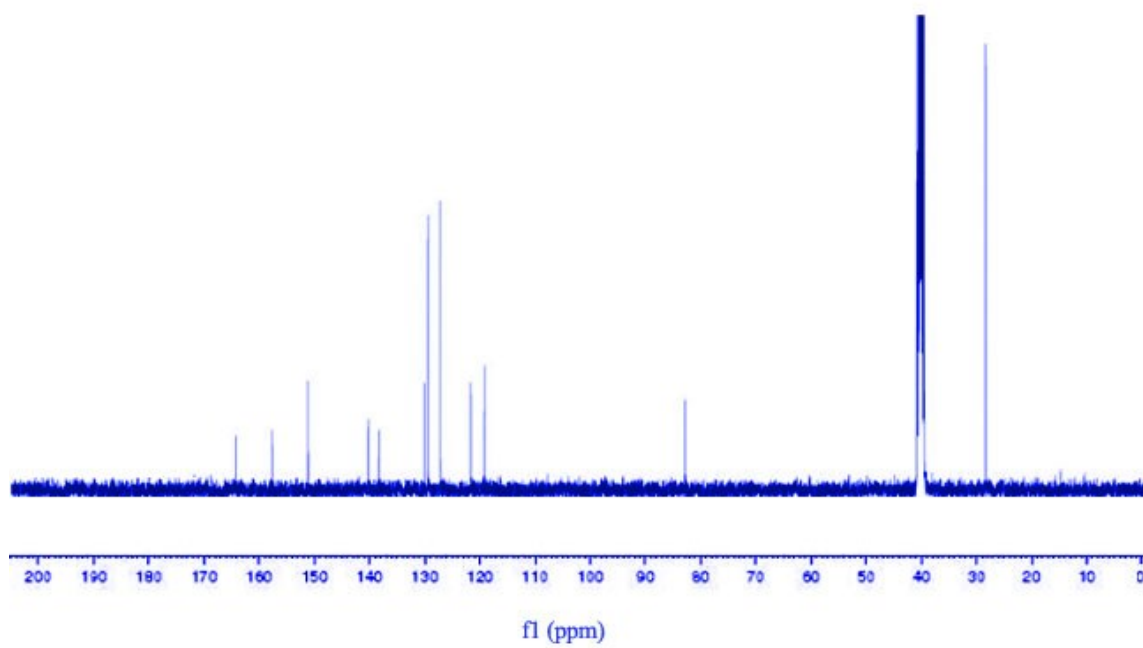


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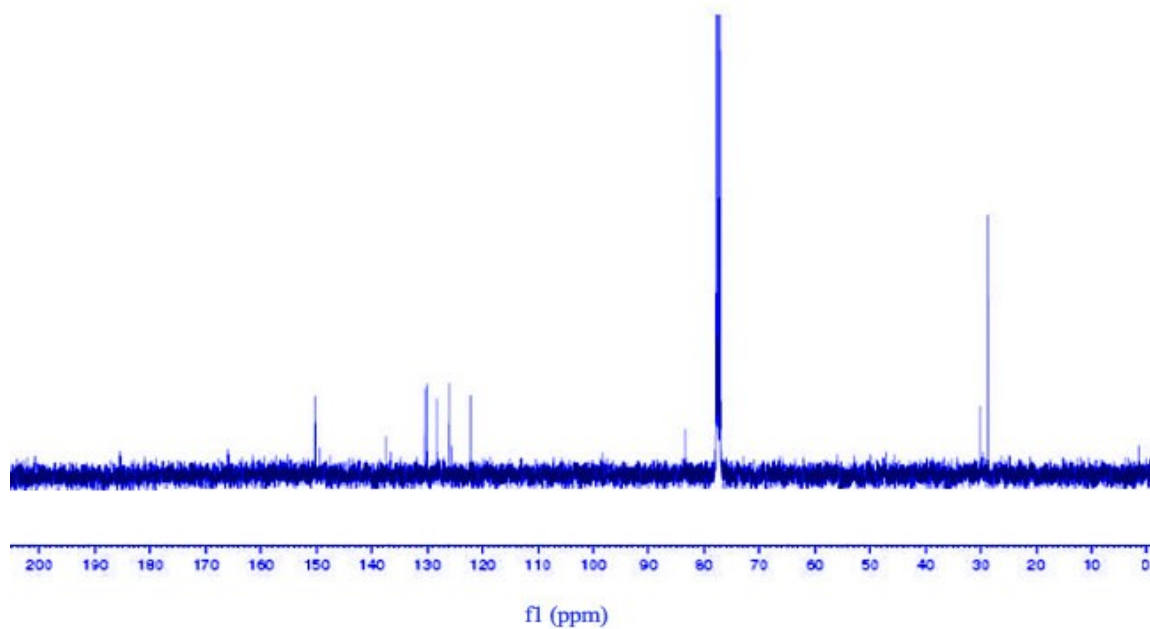


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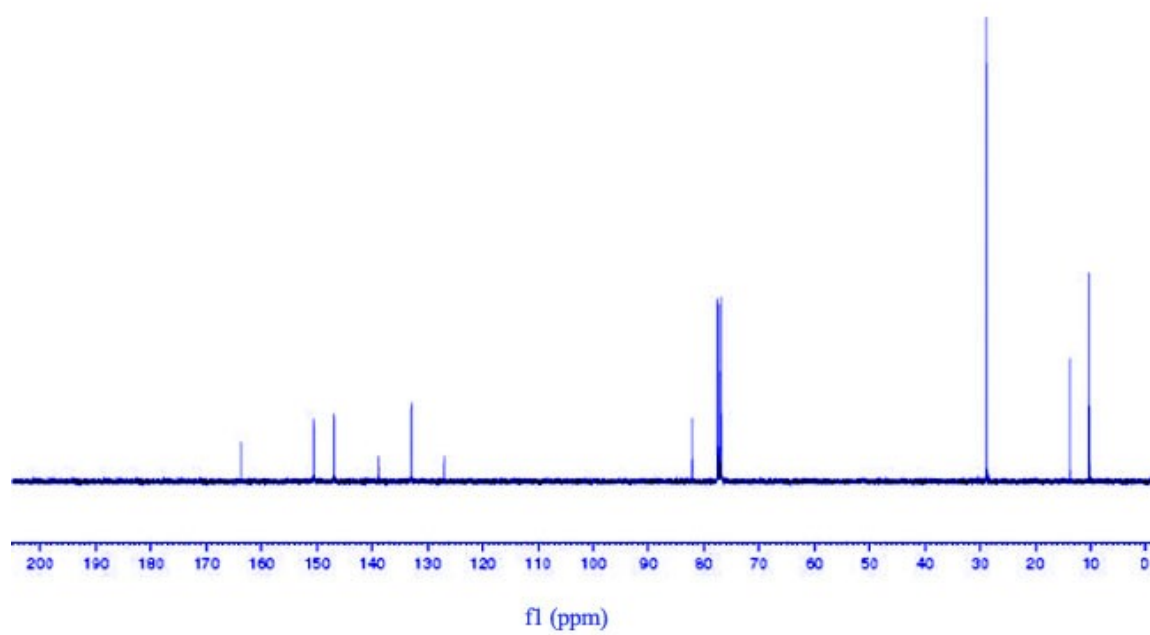


Table 3, entry 15

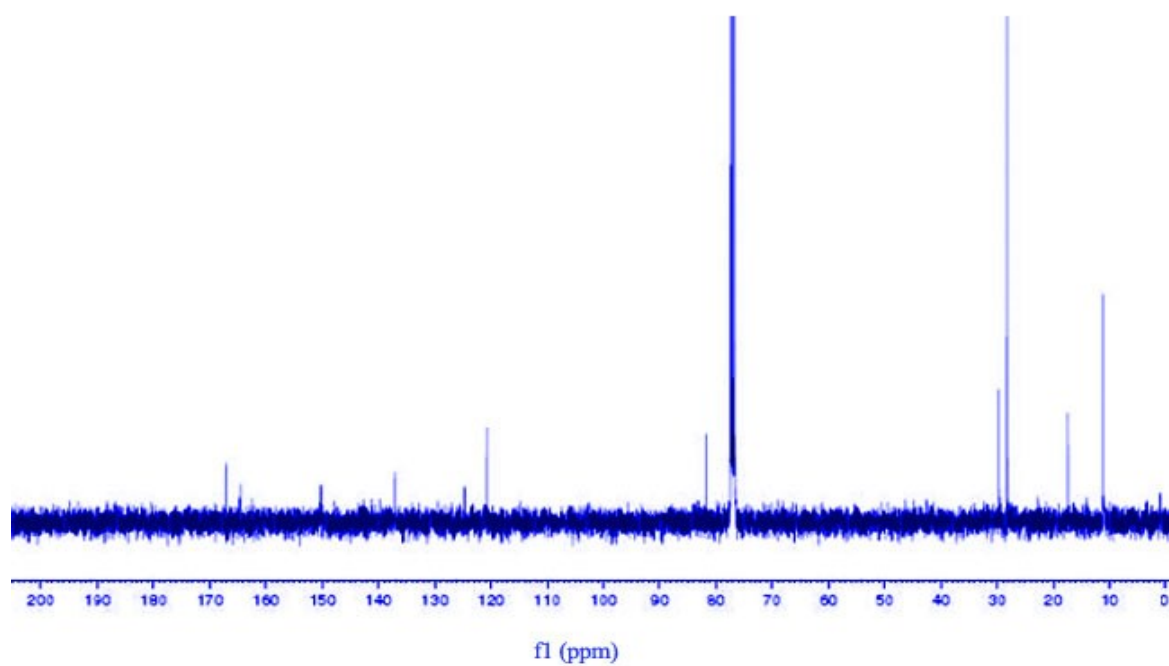


Table 4, entry 1

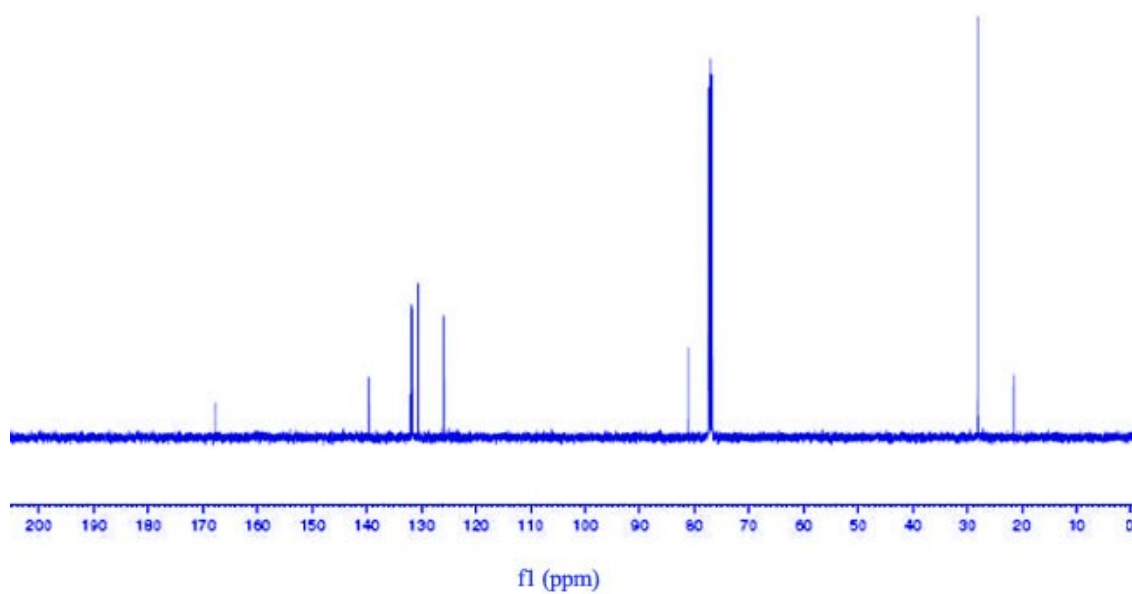


Table 4, entry 2

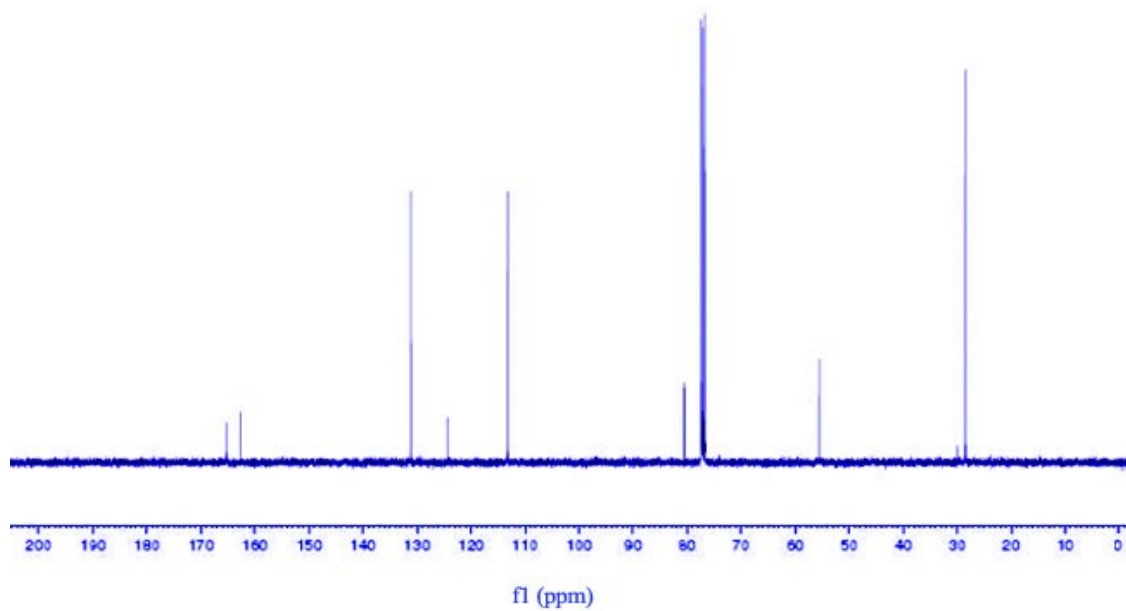


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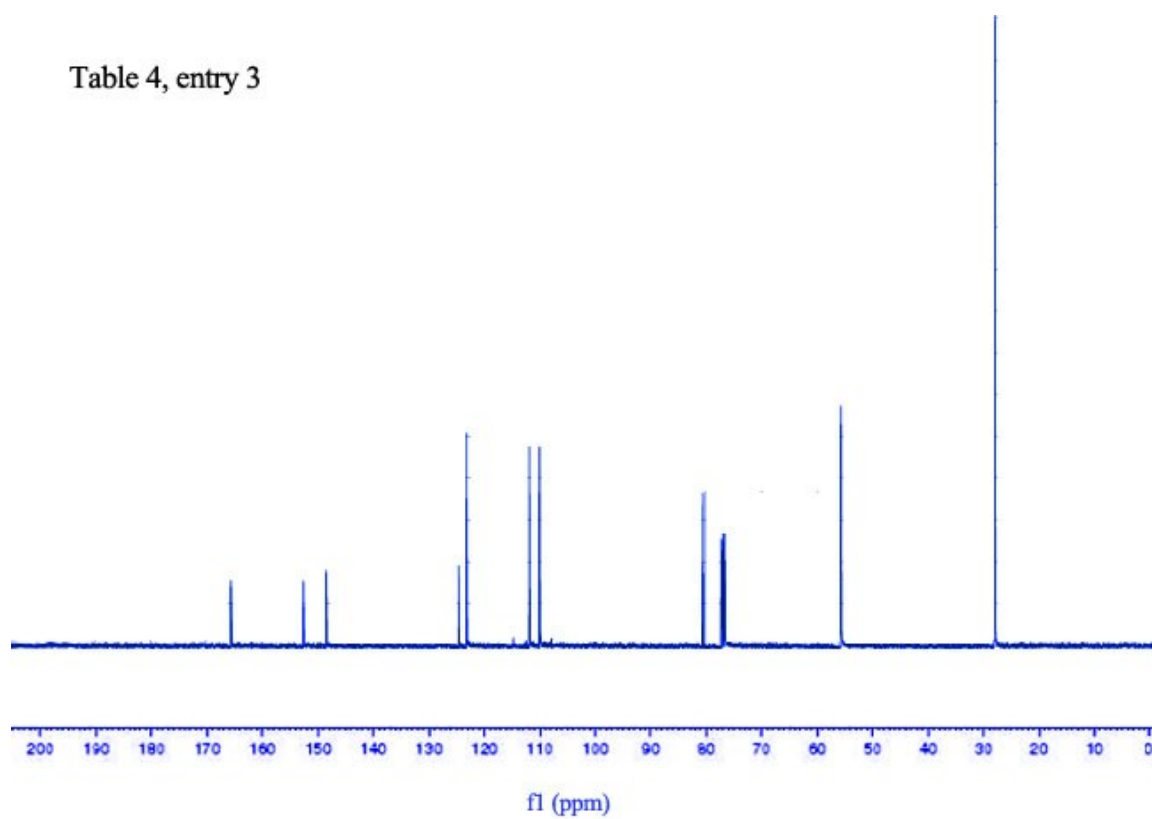


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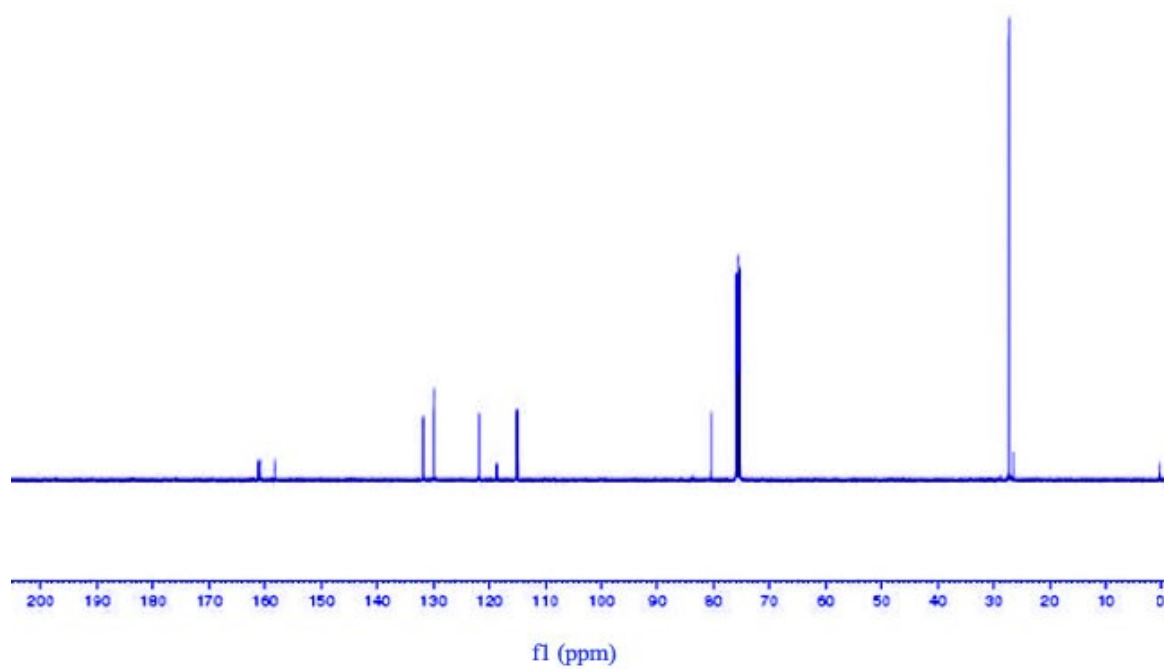


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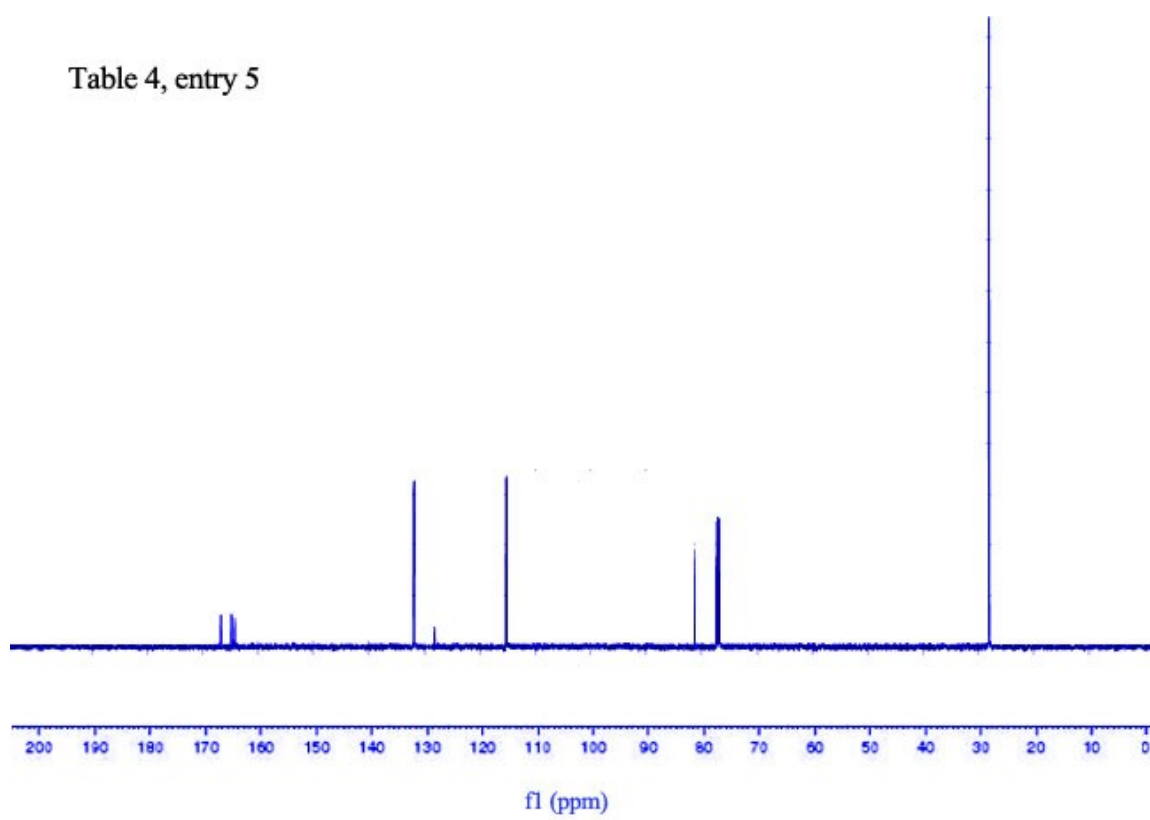


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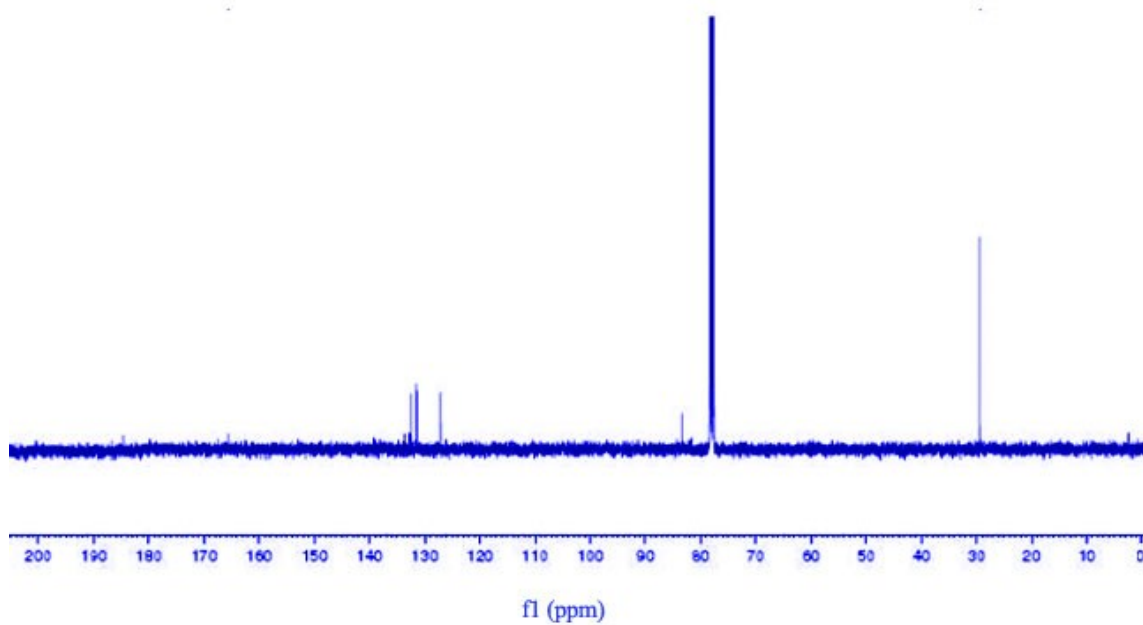


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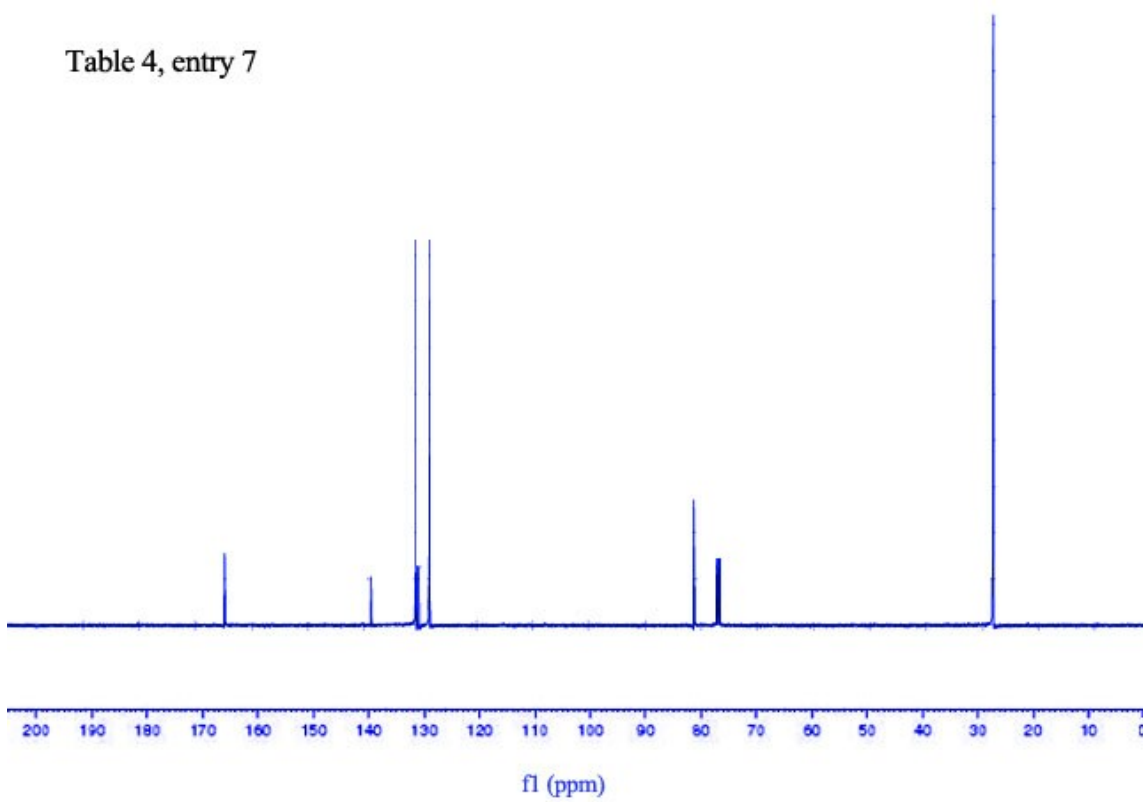


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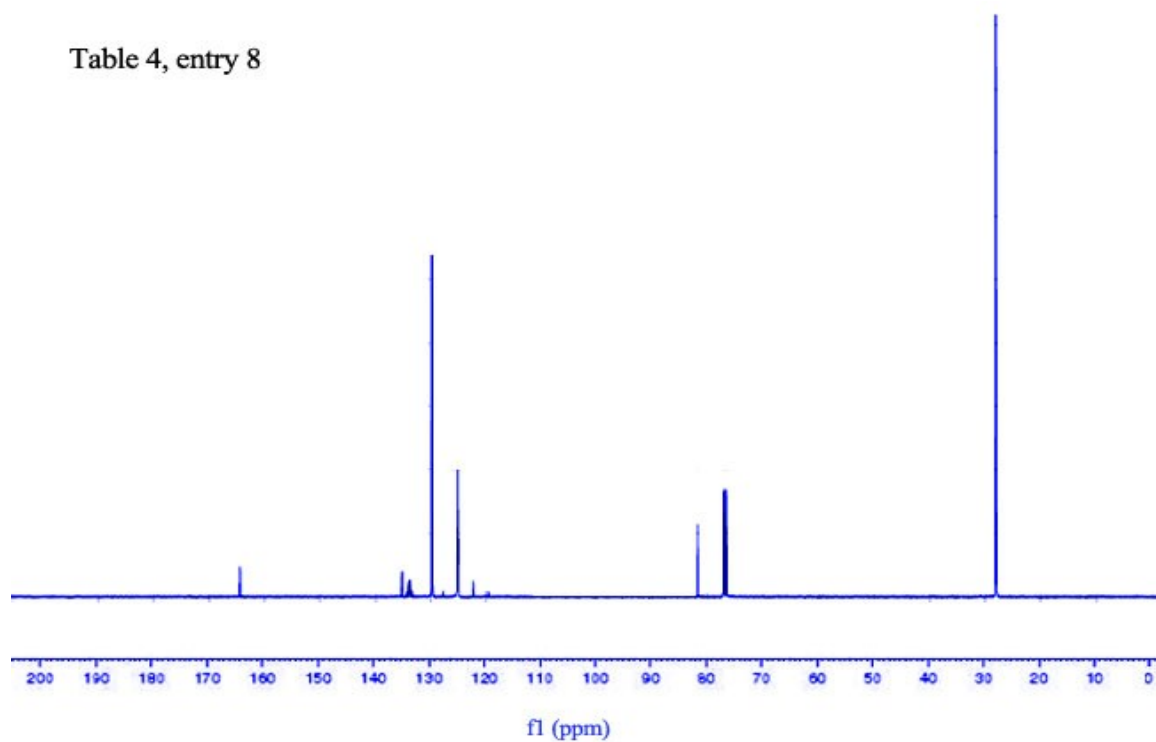


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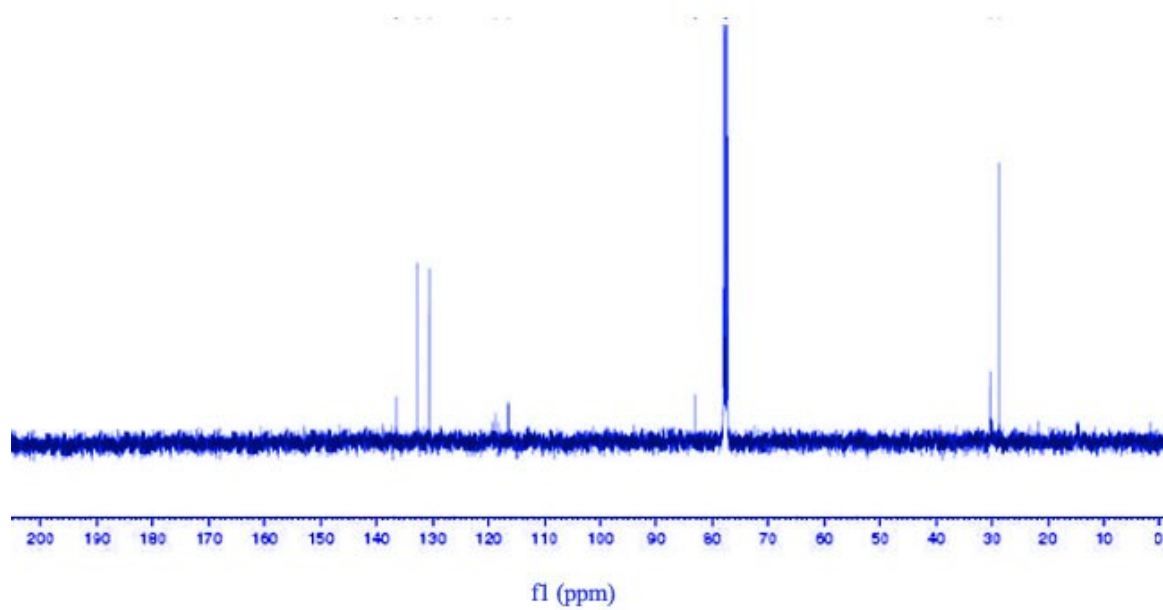


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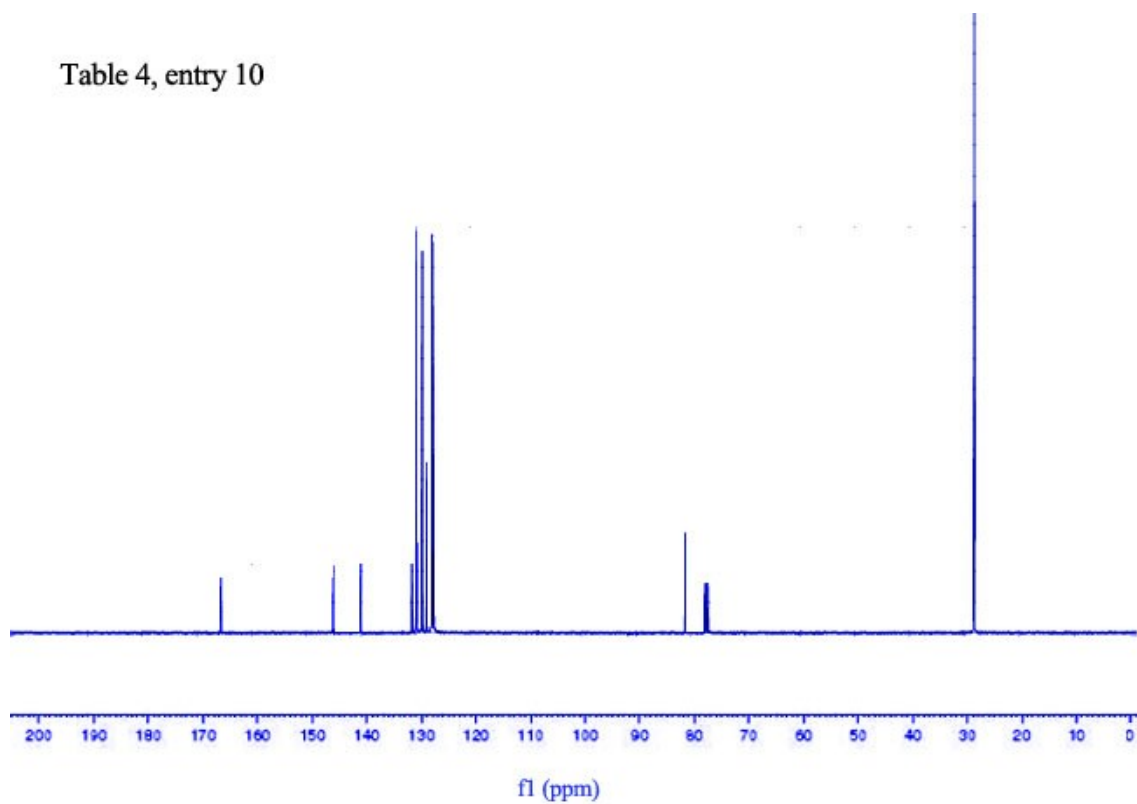


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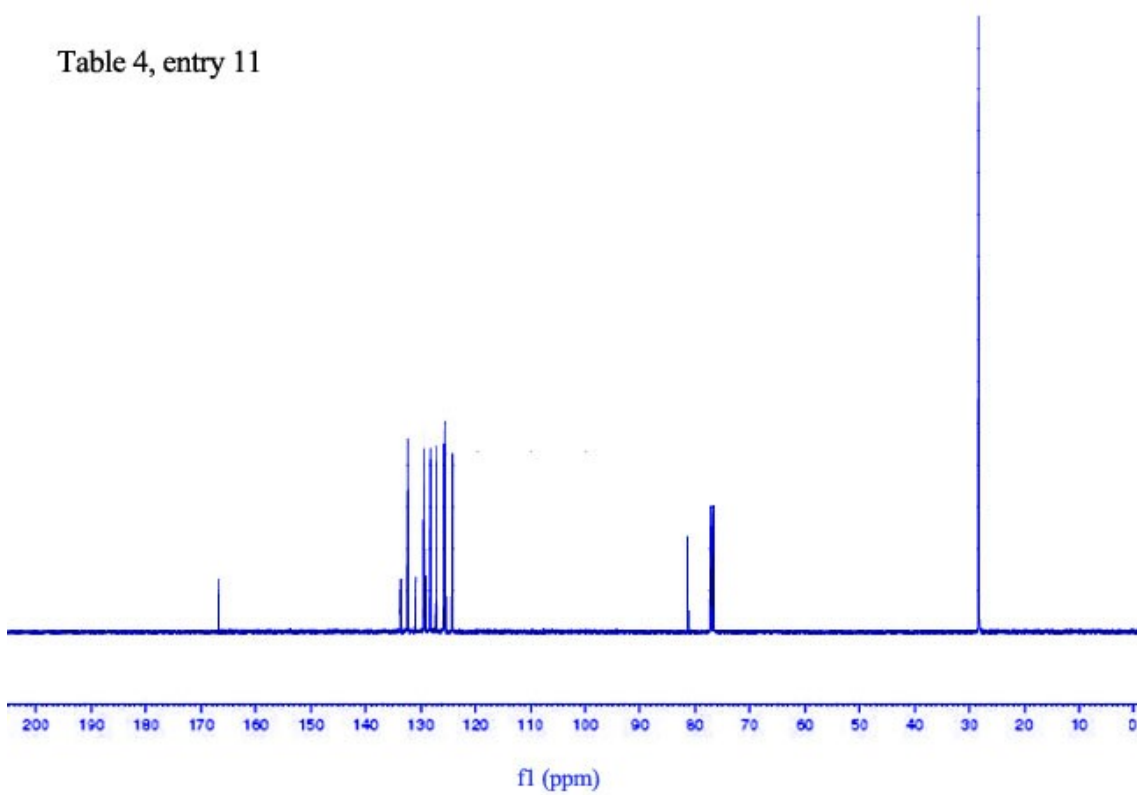


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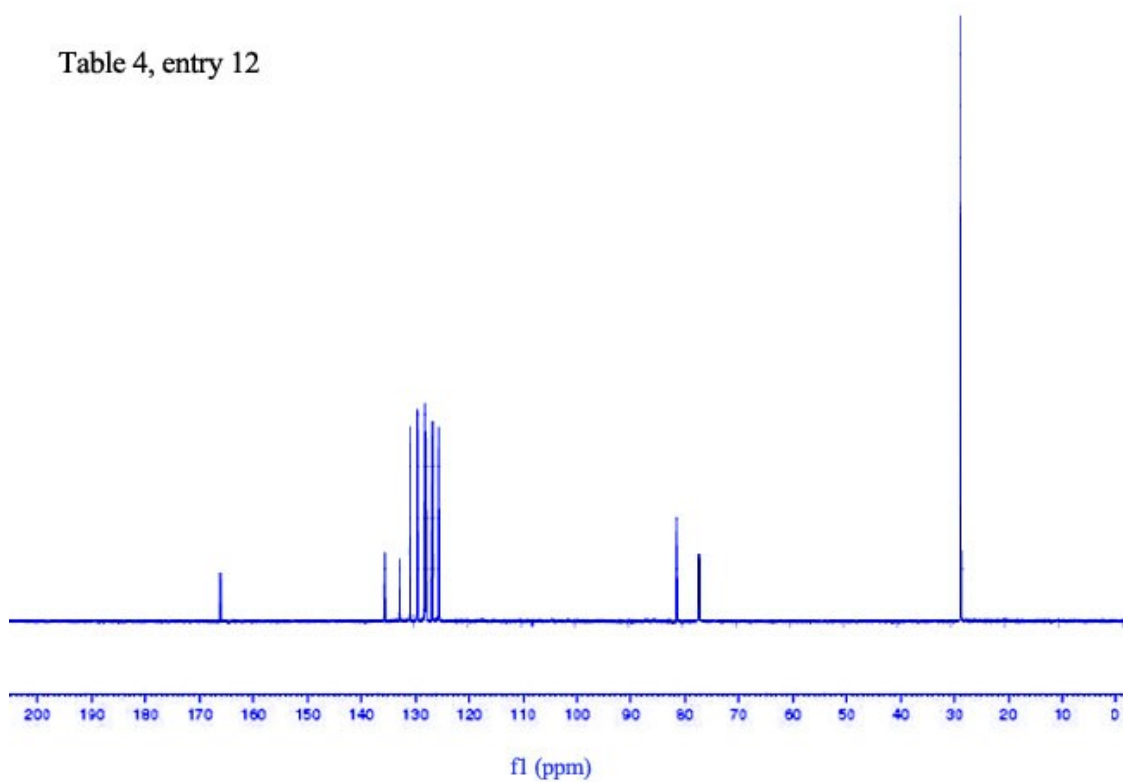


Table 4, entry 13

