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SUPPORTING INFORMATION

Structure and Photoreactivity of Stable Zwitterionic Group 6 Metal Allenyls

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Experimental General.

Flame-dried glassware was used for moisture-sensitive reactions and anhydrous solvents were taken from a Pure Solvent PS-MD-5 apparatus. Silica gel (Merck: 230-400 mesh) was used as stationary phases for purification of crude reaction mixtures by flash column chromatography. NMR spectra were recorded at 25 ºC in $CDCl_3$ on a 300 MHz (300 MHz for ^1H, 75 MHz for ^{13}C) and 500 MHz (500 MHz for ^1H, 126 MHz for ^{13}C) and 700 MHz (700 MHz for ^1H, 176 MHz for ^{13}C) spectrometers. Chemical shifts are given in ppm relative to $CDCl_3$ (^1H, 7.27 ppm and ^{13}C, 77.00 ppm). IR spectra were taken on a MIR (8000-400 cm^{-1}) spectrometer as solid films by slow evaporation of the solvent using the attenuated total reflectance (ATR) technique. HRMS experiments were conducted on an Accurate Mass Q-TOF system. Commercially available reagents were used without further purification. Compounds **2a**,[1] **2b**,[2] **2c**[1] and **2d**[3] were prepared following reported procedures.

General procedure for the synthesis of compounds 3:

Under argon atmosphere, a solution of the corresponding alkynyl carbene **2** and 1,3-bis-(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IMes), 1,3-bis-(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (IPr) or 1,3-bis-(2,4,6-trimethylphenyl)-imidazolin-2-ylidene in pentane (previously distilled and degassed)

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was stirred at room temperature. The reaction was accompanied by a color change from red to yellow and the subsequent formation of a yellow precipitate. The solvent was decanted and the obtained yellow solid washed with pentane and dried in vacuum.

Compounds **3** are perfectly stable in the solid state at room temperature and in solution in Et_2O, THF and hexanes, but dissociate to some extent to the starting components in CH_2Cl_2 and CH_3CN solution. Samples in $CDCl_3$ solution are stable for their NMR analysis, although they slowly revert to some extent to the starting reagents if the solution is left to stand at rt.

Synthesis of 3a: From a solution of alkynyl carbene **2a** (74 mg, 0.30 mmol) and 1,3-bis-(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (100 mg, 0.33 mmol) in 10 mL pentane. **3a** (178 mg, 91%), was obtained after 2 h at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (s, 2H, NC*H*=C*H*N), 7.04–6.99 (m, 2H, CH_{arom}), 6.98–6.83 (m, 7H, CH_{arom}), 2.64-2.48 (m, 1H, OCH_2CH$_3$), 2.26 (s, 6H, CH_3), 2.23 (s, 12H, CH_3), 2.03-1.90 (m, 1H, OCH_2CH$_3$), 0.73 (t, *J* = 6.9 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 226.5 (CO), 220.8 (CO), 201.3 (C), 151.1 (C), 140.9 (C), 137.2 (C), 135.5 (C), 134.9 (C), 132.2 (C), 130.0 (CH), 129.5 (CH), 127.7 (CH), 127.2 (CH), 126.0 (CH), 122.7 (CH), 84.9 (C), 67.8 (CH_2), 21.3 (CH_3), 18.9 (CH_3), 15.5 (CH_3). IR (ATR): ν 3429, 2040, 1960, 1907, 1868, 1486, 1450, 668 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{37}H_{34}CrN_2O_6$ [M+H]$^+$ 655.2061; found 655.2015.

Synthesis of 3b: From a solution of alkynyl carbene **2b** (37 mg, 0.08 mmol) and 1,3-bis-(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (29 mg, 0.10 mmol) in 3 mL pentane. **3b** (55 mg, 89%) was obtained after 1 h at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10-6.82 (m, 6H, 4CH_{arom}, NC*H*=C*H*N), 4.06 (s, 5H, FcC*H*), 3.89-3.75 (m, 2H, FcC*H*), 3.64-3.52 (m, 2H, FcC*H*), 3.18-3.01 (m, 1H, OCH_2CH$_3$), 2.34-2.10 (m, 18H, CH_3), 1.51–1.36 (m, 1H, OCH_2CH$_3$), 0.91 (t, *J* = 6.9 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (500 MHz, $CDCl_3$): δ 226.7 (CO), 221.0 (CO), 199.3 (C), 155.8 (C), 152.5 (C), 140.9 (C), 130.1 (C), 129.4 (CH), 122.5 (CH), 88.9 (C), 79.3 (C), 69.6 (CH), 69.2 (CH), 67.7 (CH_2), 66.7 (CH), 66.0 (CH), 21.5 (CH_3), 18.7 (CH_3), 18.6 (CH_3), 16.0 (CH_3). IR (ATR): ν 3431, 2038, 1953, 1907, 1860, 1482, 1448, 668 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{41}H_{39}CrFeN_2O_6$ [M+H]$^+$ 763.1559; found 763.1580.

Synthesis of 3c: From a solution of alkynyl carbene **2c** (35 mg, 0.07 mmol) and 1,3-bis-(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (29 mg, 0.09 mmol) in 3

mL pentane. **3c** (58 mg, 100%) was obtained after 1 h at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (s, 2H, NC*H*=C*H*N), 7.08-6.90 (m, 6H, CH_{arom}), 6.90-6.83 (m, 4H, CH_{arom}), 2.57-2.43 (m, 1H, OCH_2CH$_3$), 2.28-2.21 (m, 18H, CH_3), 1.95-1.83 (m, 1H, OCH_2CH$_3$), 0.74 (t, J = 7.0 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 206.7 (CO), 201.7 (CO), 140.9 (C), 137.0 (C), 135.5 (C), 134.9 (C), 132.2 (C), 130.3 (CH), 130.0 (CH), 129.5 (CH), 127.8 (CH), 127.1 (CH), 126.1 (CH), 122.7 (CH), 85.4 (C), 67.6 (CH_2), 21.3 (CH_3), 19.1 (CH_3), 18.9 (CH_3), 15.5 (CH_3). IR (ATR): ν 3435, 2051, 1961, 1904, 1857, 1486, 1451, 589 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{37}H_{35}N_2O_6W$ $[M+H]^+$ 787.2076; found 787.2053.

Synthesis of 3d: From a solution of alkynyl carbene **2a** (20 mg, 0.06 mmol) and 1,3-bis-(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (25 mg, 0.64 mmol) in 3 mL pentane. **3d** (46 mg, 81%) was obtained after 2 h at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (t, J = 7.5 Hz, 2H, CH_{arom}), 7.26–7.16 (m, 4H, CH_{arom}), 7.11 (s, 2H, NC*H*=C*H*N), 6.96–6.79 (m, 5H, CH_{arom}), 2.97–2.85 (m, 2H, 2C*H*(CH$_3$)$_2$), 2.80–2.66 (m, 2H, 2C*H*(CH$_3$)$_2$), 2.64–2.54 (m, 1H, OCH_2CH$_3$), 2.01–1.93 (m, 1H, OCH_2CH$_3$), 1.43 (d, J = 6.3 Hz, 6H, CH(CH_3)$_2$), 1.27 (d, J = 6.3 Hz, 6H, CH(CH_3)$_2$), 1.17 (d, J = 6.5 Hz, 6H, CH(CH_3)$_2$), 1.09 (d, J = 6.5 Hz, 6H, CH(CH_3)$_2$), 0.74 (t, J = 6.6 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 226.6 (CO), 220.8 (CO), 202.4 (C), 165.2 (C), 151.5 (C), 146.3 (C), 145.2 (C), 137.1 (C), 133.3 (C), 131.6 (CH), 129.1 (CH), 127.9 (CH), 126.2 (CH), 125.2 (CH), 124.7 (CH), 124.1 (CH), 85.1 (C), 68.2 (CH_2), 29.6 (CH), 29.4 (CH), 26.5 (CH_3), 25.6 (CH_3), 22.8 (2xCH_3), 15.7 (CH_3). IR (ATR): ν 3437, 2970, 2039, 1909, 1868, 1455, 668 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{43}H_{47}CrN_2O_6$ $[M+H]^+$ 740.2917; found 740.2897.

Synthesis of 3e: From a solution of alkynyl carbene **2c** (35 mg, 0.07 mmol) and 1,3-bis-(2,6-diisopropylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (37 mg, 0.09 mmol) in 3 mL pentane. **3e** (61 mg, 97%) was obtained after 1 h at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.34 (m, 3H, CH_{arom}), 7.25–7.18 (m, 3H, CH_{arom}), 7.12 (s, 2H, NC*H*=C*H*N), 6.90 (s, 5H, CH_{arom}), 2.89 (dt, J = 13.4, 6.7 Hz, 2H, 2C*H*(CH$_3$)$_2$), 2.74 (dt, J = 13.5, 6.7 Hz, 2H, 2C*H*(CH$_3$)$_2$), 2.53 (m, 1H, OCH_2CH$_3$), 1.92 (m, 1H, OCH_2CH$_3$), 1.43 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.34 (d, J = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.20 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.11 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.73 (t, J = 7.0 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 209.1 (C), 206.7 (CO), 201.9 (CO), 155.3 (C), 146.2 (C), 145.1 (C), 136.9 (C), 133.2 (C), 131.6 (CH), 128.8 (CH),

128.0 (CH), 126.3 (CH), 125.2 (CH), 124.6 (CH), 124.0 (CH), 85.9 (C), 67.9 (CH_2), 29.7 (CH), 29.4 (CH), 26.5 (CH_3), 25.6 (CH_3), 23.1 (CH_3), 23.0 (CH_3), 15.6 (CH_3). IR (ATR): ν 3435, 2050, 1955, 1905, 1456, 590 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{43}H_{47}N_2O_6W$ $[M+H]^+$ 871.2945; found 871.2935.

Synthesis of 3f: From a solution of alkynyl carbene **2a** (20 mg, 0.06 mmol) and 1,3-bis-(2,4,6-trimethylphenyl)-imidazolin-2-ylidene (25 mg, 0.08 mmol) in 3 mL pentane. **3f** (53 mg, 100%), was obtained after 4 h at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03–6.96 (m, 2H, CH_{arom}), 6.94–6.87 (m, 3H, CH_{arom}), 6.84 (s, 2H, CH_{arom}), 6.76 (s, 2H, CH_{arom}), 4.37–4.20 (m, 2H, NCH_2), 4.01–3.84 (m, 2H, NCH_2), 2.62–2.52 (m, 1H, OCH_2CH$_3$), 2.46 (s, 6H, CH_3), 2.36 (s, 6H, CH_3), 2.22 (s, 6H, CH_3), 2.04–1.91 (m, 1H, OCH_2CH$_3$), 0.73 (t, J = 6.9 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 226.1 (CO), 220.4 (CO), 198.6 (C), 157.1 (C), 139.7 (C), 136.6 (C), 136.6 (C), 134.8 (C), 133.6 (C), 130.1 (CH), 129.9 (CH), 128.2 (CH), 127.6 (CH), 126.1 (CH), 85.7 (C), 69.1 (CH_2), 50.4 (NCH_2), 21.2 (CH_3), 19.0 (CH_3), 18.9 (CH_3), 15.5 (CH_3). IR (ATR): ν 3434, 2042, 1965, 1965, 1853, 1517, 1458, 666 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{37}H_{37}CrN_2O_6$ $[M+H]^+$ 257.2218; found 257.2192.

Synthesis of 3g: From a solution of alkynyl carbene **2d** (30 mg, 0.08 mmol) and 1,3-bis(2,4,6-trimethylphenyl)-1,3-dihydro-2*H*-imidazol-2-ylidene (25 mg, 0.09 mmol) in 3 mL pentane. **3g** (54mg, 100%), was obtained as light brown solid after 7 h at room temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22–7.16 (m, 1H, CH_{arom}), 7.11 (s, 2H, NCH=CHN), 7.04–7.00 (m, 1H, CH_{arom}), 6.98–6.93 (m, 2H, CH_{arom}), 6.89 (s, 4H, CH_{arom}), 3.01 (s, 1H, C≡CH), 2.60–2.49 (m, 1H, OCH_2CH$_3$), 2.27 (s, 11H, CH_3), 2.22 (s, 7H, CH_3), 2.01–1.92 (m, 1H, OCH_2CH$_3$), 0.75 (t, J = 7.0 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 226.4 (CO) 220.7 (CO), 170.9 (C), 169.4 (C), 161.6 (C), 156.1 (C), 141.1 (C), 137.3 (C), 135.6 (C), 134.8 (C), 132.2 (C), 130.2 (CH), 130.0 (CH), 129.7 (CH), 129.6 (CH), 128.6 (CH), 128.3 (CH), 122.8 (CH), 121.1 (C), 90.3 (C), 83.9 (C), 68.2 (CH_2), 21.4 (CH_3), 18.9 (CH_3), 18.9 (CH_3), 15.5 (CH_3). IR (ATR): ν 3428, 2038, 1907, 1869, 1486, 1421, 895 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{39}H_{35}CrN_2O_6$ $[M+H]^+$ 679.1895; found 679.1870.

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Photochemical reactions: general procedure: All photochemical reactions were conducted by using a 450-W medium-pressure mercury lamp fitted with a Pyrex filter. The samples were solved in diethyl ether (2 10^{-3}M) and degassed (vacuum-Ar, four cycles) in a rubber septum-sealed Pyrex tube filled with argon. The solvent was pure but not treated to exhaustive dryness. After 15 h irradiation, the solvent was removed under reduced pressure and the residue was dissolved in 10 mL of a mixture of hexane/AcOEt (9:1). The solution was filtered through a short pad of celite, the solvent removed under reduced pressure and the residue purified by column chromatography on silica gel.

Compound 4a: Following the general procedure from **3a** (50 mg, 0.08 mmol) in 40 mL of diethyl ether. After chromatography (AcOEt/MeOH, 10:1) **4a** (24 mg, 65%) was obtained as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.87–6.76 (m, 9H, C*H*$_{arom}$), 6.75 (s, 2H, NC*H*=C*H*N), 3.56 (s, 2H, CH_2), 2.86 (q, *J* = 7.0 Hz, 2H, OCH_2CH$_3$), 2.22 (s, 6H, CH_3), 2.18 (s, 12H, CH_3), 0.88 (t, *J* = 7.0 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 181.7 (CO), 154.6 (C), 140.0 (C), 138.5 (C), 135.2 (C), 134.4 (C), 131.3 (CH), 129.5 (CH), 127.4 (CH), 124.5 (CH), 119.9 (CH), 88.6 (C), 72.4 (CH_2), 65.1 (CH_2), 21.3 (CH_3), 19.0 (CH_3), 15.5 (CH_3). IR (film): 3020, 2969, 2922, 1560, 1483, 1443, 1107, 850, 737, 705 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{32}H_{37}N_2O_2$ $[M+H]^+$ 481.2850; found 481.2843. When the reaction is carried out in the same conditions but in the presence of added water (0.5 mL) the yield of **4a** increases up to 85%.

Compound 4b: Following the general procedure from **3b** (30 mg, 0.04 mmol) in 20 mL of diethyl ether. **4b** (12 mg, 52%) was obtained by crystallization of the crude product in hexane as orange solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.84 (s, 2H, NC*H*=C*H*N), 6.83 (s, 4H, C*H*$_{arom}$), 4.46 (s, 2H, CH_2), 3.97 (s, 5H, Cp-C*H*), 3.64 (d, *J* = 10.8 Hz, 4H, Cp-C*H*), 3.10 (q, *J* = 7.0 Hz, 2H, OCH_2CH$_3$), 2.25 (s, 18H, CH_3), 1.08 (t, *J* = 7.0 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 181.9 (C), 154.7 (C), 139.6 (C), 138.0 (C), 133.6 (C), 129.1 (CH), 119.7 (CH), 90.8 (C), 71.3 (CH_2), 68.9 (CH), 67.0 (CH), 65.1 (CH), 65.0 (CH_2), 20.9 (CH_3), 18.8 (CH_3), 15.6 (CH_3). IR (ATR): ν 1643, 1543, 1487, 1440, 1100, 852 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{36}H_{41}FeN_2O_2$ $[M+H]^+$ 589.2517; found 589.2527.

Compound 4c: Following the general procedure from **3d (**50mg, 0.071 mmol) in 40 of diethyl ether. After chromatography (AcOEt/MeOH, 10:1) **4a** (30 mg, 75%) was obtained as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.24 (m, 2H, C*H*$_{arom}$), 7.12

(m, 4H, CH_{arom}), 6.92–6.80 (m, 5H, 3CH_{arom}, NC*H*=C*H*N), 6.69–6.63 (m, 2H, CH_{arom}), 3.43 (s, 2H, CH_2), 2.99 (h, 4H, 2C*H*$(CH_3)_2$), 2.58 (q, *J* = 7.0 Hz, 2H, OCH_2CH_3), 1.32 (d, *J* = 6.7 Hz, 12H, CH(C$H_3)_2$), 1.14 (d, *J* = 6.8 Hz, 12H, CH(C$H_3)_2$), 0.80 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 181.8 (CO), 155.9 (C), 145.6 (C), 139.3 (C), 134.4 (C), 131.7 (CH), 129.2 (CH), 127.7 (CH), 124.3 (CH), 123.9 (CH), 120.4 (CH), 86.9 (C), 72.0 (CH_2), 64.5 (OCH_2), 28.7 (CH), 25.9 (CH_3), 22.9 (CH_3), 15.1 (CH_3). IR (ATR): ν 3065, 2964, 2926, 2866, 1728, 1570, 1452, 1365, 1261, 1102, 1024, 802, 749, 703 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{38}H_{49}N_2O_2$ $[M+H]^+$ 565.3789; found 565.3774.

Synthesis of 4a-*d*$_2$: Following the general photochemical procedure, a solution of **3a** (40 mg, 0.06 mmol) in 20 mL of diethyl ether with 0.5 mL of D_2O was irradiated for 15 h. After work-up and column chromatography on silicagel (AcOEt/MeOH, 10:1), **4a-*d*$_2$** (25 mg, 85%) was obtained as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90–6.72 (m, 10H, CH_{arom}, NC*H*=C*D*N), 2.86 (q, *J* = 7.0 Hz, 2H, OCH_2CH_3), 2.22 (s, 6H, CH_3), 2.18 (s, 12H, CH_3), 0.88 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 181.4 (CO), 154.1 (C), 139.7 (C), 138.1 (C), 134.8 (C), 134.0 (C), 131.0 (CH), 129.1 (CH), 127.0 (CH), 124.2 (CH), 119.5 (CH), 88.2 (C), 64.9 (CH_2), 21.3 (CH_3), 19.0 (CH_3), 15.4 (CH_3). IR (film): 3020, 2100, 1732, 1643, 1435, 1308, 1157, 850 cm^{-1}. $C_{32}H_{37}D_2N_2O_2$ $[M+H]^+$ 485.3132; found 485.3145.

Synthesis of 10: Following the general photochemical procedure, a solution of **3a** (80 mg, 0.11 mmol) and methyl fumarate (19 mg, 0.12 mmol) in 40 mL diethyl ether was irradiated for 15 h. After work-up, the residue was purified by column chromatography on silicagel (AcOEt/MeOH, 10:1), yielding **10** (20 mg, 30%, yellow oil) together with **4a** (8 mg, 13%). **Compound 10**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92–6.72 (m, 9H, CH_{arom}), 6.70 (s, 2H, NC*H*=C*H*N), 4.33 (d, *J* = 2.2 Hz, 1H, C*H*), 3.66 (s, 3H, CO_2CH_3), 3.47–3.36 (m, 1H, OCH_2CH_3), 3.34 (s, 3H, CO_2CH_3), 3.11–2.98 (m, 1H, OCH_2CH_3), 2.65 (dt, *J* = 12.2, 2.5 Hz, 1H, C*H*CH_2), 2.39 (dd, *J* = 17.5, 12.3 Hz, 1H, CHCH_2), 2.22 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 1.32 (dd, *J* = 17.2, 2.4 Hz, 1H, CHCH_2), 0.90 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 181.9 (CO), 174.3 (CO), 173.6 (CO), 154.3 (C), 139.2 (C), 138.2 (C), 135.4 (C), 134.4 (C), 134.0 (C), 132.5 (CH), 129.6 (CH), 128.7 (CH), 127.2 (CH), 124.9 (CH), 119.4 (CH), 87.0 (C), 64.3 (CH_2), 51.37 (CH), 51.2 (CH), 44.6 (CH) 29.1 (CH_2), 20.8 (CH_3), 18.7 (CH_3), 18.1 (CH_3), 14.9 (CH_3). IR (film): 2856, 1726, 1643, 1560, 1487, 1437, 1307,

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1157, 850 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{38}H_{45}N_2O_6$ $[M+H]^+$ 625.3283; found 625.3272.

Synthesis of 10-*d*$_2$: Following the general photochemical procedure, a solution of **3a** (20 mg, 0.031mmol) and methyl fumarate (6 mg, 0.037 mmol) in 20 mL of diethyl ether with 0.3 mL of D_2O was irradiated for 15 h. After work-up and column chromatography on silicagel (AcOEt/MeOH, 10:1), **10-*d*$_2$** (9 mg, 47%) was obtained as yellow oil, accompanied by **4a-*d*$_2$** (5 mg, 33%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91–6.70 (m, 11H, $CH_{arom,}$ NC*H*=C*H*N), 3.66 (s, 3H, CO_2CH_3), 3.40 (m, 1H, OCH_2CH_3), 3.33 (s, 3H, CO_2CH_3), 3.11–2.98 (m, 1H, OCH_2CH_3), 2.88 (m, 1H), 2.69–2.59 (m, 1H, $CHCH_2$), 2.39 (d, *J* = 12.5 Hz, 1H, $CHCH_2$), 2.23 (s, 6H, CH_3), 2.20 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 0.89 (t, *J* = 6.8 Hz, 3H, OCH_2CH_3). IR (film): 2856, 1738, 1557, 1488, 1446, 1427, 1117, 850 cm^{-1}. ESI-HRMS *m/z*: calcd for $C_{38}H_{43}D_2N_2O_6$ $[M+H]^+$ 627.3398; found 627.3410; calcd for $C_{38}H_{41}D_4N_2O_6$ $[M+H]^+$ 627.3523; found 627.3498.

An exhaustive ESI-MS analysis also revealed the presence of **10-*d*$_4$** due to the easy interchange of the NHC vinylic protons with the solvent. This fact was also appreciated by a careful integration of the aromatic region in the ^{1}H-NMR spectrum of **10-*d***.[4]

Reaction with nitrostyrene: Following the general photochemical procedure, a solution of **3a** (25 mg, 0.04 mmol) and nitrostyrene (10 mg, 0.07 mmol) in 20 mL of diethyl ether was irradiated for 15 h. After work-up, **t**he analysis by ^{1}H NMR of the reaction crude (15 mg, 70%), showed the presence of **11** (single diastereoisomer) accompanied by a small amount of **4a** (ratio **11:4a** 10:1). Compound **11** (viscous oil) decomposes in chromatography but can be obtained as a solid from Et_2O.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 – 7.00 (m, 3H), 6.91 – 6.72 (m, 13H), 4.59 (dd, *J* = 15.0, 12.4 Hz, 1H), 3.90 (d, *J* = 2.1 Hz, 1H), 3.54 (dd, *J* = 15.0, 3.7 Hz, 1H), 3.47–3.36 (m, 1H), 3.29–3.19 (m, 1H), 2.92–2.79 (m, 1H), 2.25 (s, 6H), 2.22 (s, 6H), 2.15 (s, 6H), 0.89 (t, *J* = 6.1 Hz, 3H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 181.9 (CO), 154.4 (C), 141.7 (C), 139.5 (C), 139.3 (C), 138.6 (C), 135.5 (C), 133.9 (C), 132.6 (CH), 129.7 (CH), 129.2 (CH), 128.9 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.0 (C), 126.4 (CH), 125.2 (CH), 119.7 (CH), 86.9 (C), 80.8 (CH), 74.5 (CH_2), 65.0 (CH_2), 46.2 (CH), 20.9 (CH_3), 18.8 (CH_3), 18.1 (CH_3), 14.8 (CH_3).

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Crystallographic data

X-ray data for compound 3a

The structure shows two independent molecules and half Et_2O molecule in the asymmetric unit. The chromium center presents an octahedral coordination mode and the cumulene C1=C2=C3 moiety shows C1-C2 bond distances (1.288(8) and 1.310(8) Å), considerably shorter than C2-C3 bond distances (1.328(8) and 1.352(8) Å). The cumulene bond angles for both independent molecules are different (164.6(7)º and 171.6(6)º), values within the range found for the structurally related complexes **1**.[5]

3a·0.25(CH$_3$CH$_2$)$_2$O:$(C_{37}H_{34}CrN_2O_6)\cdot 0.25(C_4H_{10}O)$, M_r = 673.19, 0.12 x 0.10 x 0.04 mm size, Triclinic, P-1, a = 11.6599(11), b = 16.1539(14), c = 19.2369(18) Å, α = 86.011(7), β = 88.184(8), γ = 85.019(7), V = 3599.7(6) Å^3, Z = 4, ϱ_{calcd} = 1.242 g cm^{-3}, μ = 0.365, Mo Kα, λ = 0.71073 Å, T = 120(2) K, $2\theta_{max}$ = 52.74, 30853/146999 reflns. collected/independent (R_{int} = 0.0970), Patterson primary solution and refinement on F^2 (SHELXS-97 and SHELXL-97)[6] 890 parameters, hydrogen atoms refined as *rigid* methyls, others *riding*, half diethyl ether solvent molecule refined with thermal parameters restrained to be equal, $R_1[I > 2\sigma(I)]$ = 0.1010, wR_2(all data) = 0.2850, $\Delta\rho_{max}$ = 1.16 eÅ^{-3}.

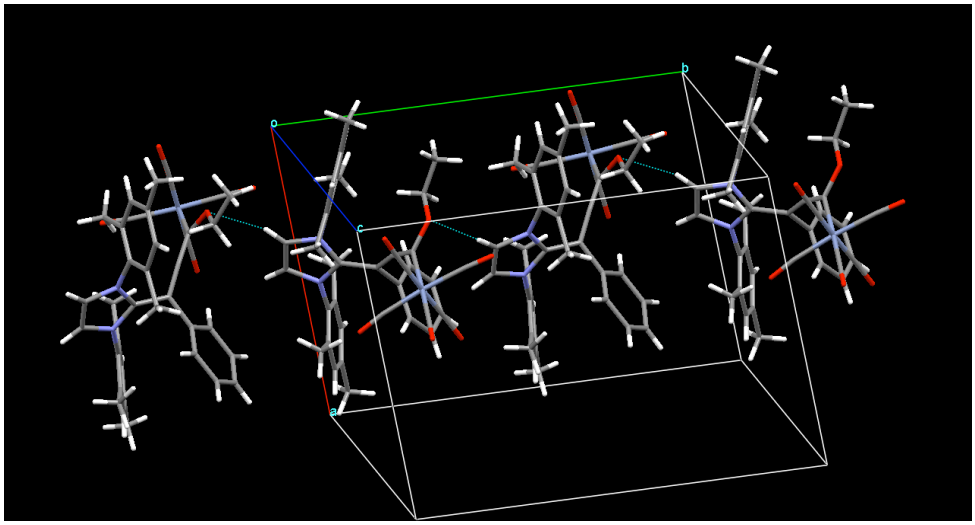

Figure 1. Packing view showing linear chains through C-H··O bonds for compound **3a**.

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X-ray data for compound 4a: ($C_{76}H_{90}Fe_2N_4O_5$), M_r = 1251.22, 0.27 x 0.17 x 0.04 mm size, Triclinic, P-1, a = 10.7606(10), b = 12.5977(12), c = 12.7837(12) Å, α = 89.969(2)°, β = 75.748(2), γ = 85.623(2), V = 1674.4(3) Å^3, Z = 1, ϱ_{calcd} = 1.241 g cm^{-3}, μ = 0.487, Mo Kα, λ = 0.71073 Å, T = 293(2) K, $2\theta_{max}$ = 50.00, 12955/5745 reflns. collected/independent (R_{int} = 0.0607), direct primary solution and refinement on F^2 379 parameters,[6] $R_1[I > 2\sigma(I)]$ = 0.0585, wR_2(all data) = 0.1655, $\Delta\rho_{max}$ = 0.973 eÅ^{-3}.

Computational Details:

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[7] They were performed using the three-parameter exchange functional of Becke in conjunction with the gradient corrected correlation functional of Lee, Yang, and Parr[8] (u)B3LYP using the double-ζ valence plus polarization basis set def2-SVP [9] for all atoms This protocol is designated (u)B3LYP/def2-SVP. Zero point vibrational energy (ZPVE) corrections have been computed at the same level and have not been corrected. Reactants and products were characterized by frequency calculations[10] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[11]

Cartesian coordinates (in Å) and total energies (in a. u., non corrected zero-point vibrational energies included) of all the stationary points discussed in the text. All calculations have been performed at the (u)B3LYP/def2-SVP + ΔZPVE level of theory.

3a **E =** -3033.558854

C	4.671888	1.150948	0.295996
C	3.682920	0.860885	-0.662693
C	3.868104	-0.115841	-1.658480
C	5.059643	-0.851330	-1.632470
C	6.051474	-0.629472	-0.668957
C	5.842221	0.383646	0.276043
N	2.488019	1.674821	-0.700608

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C	1.218858	1.378384	-0.268759
N	0.437981	2.439315	-0.651521
C	1.218072	3.378480	-1.313406
C	2.487309	2.908899	-1.342406
C	0.786959	0.214328	0.483908
C	-0.524461	-0.085468	0.590408
C	-1.726259	-0.548744	0.836051
Cr	-2.379757	-2.181222	-0.538609
C	-1.006466	-3.281392	0.183508
O	-0.187509	-3.971878	0.604423
C	-0.967997	2.687277	-0.413214
C	-1.389909	3.138976	0.849219
C	-2.741164	3.482446	0.998457
C	-3.655907	3.387603	-0.055036
C	-3.188732	2.937918	-1.298579
C	-1.851973	2.589834	-1.508010
C	-0.460203	3.214635	2.032595
C	-5.107672	3.757710	0.123771
C	-1.389095	2.123287	-2.866282
C	2.834764	-0.361096	-2.727490
C	7.303647	-1.469823	-0.634743
C	4.500639	2.261875	1.301755
C	1.786495	-0.578558	1.298314
C	2.265876	-1.825304	0.867421
C	3.108902	-2.588192	1.678976
C	3.489750	-2.117381	2.938998
C	3.012138	-0.882326	3.386476
C	2.164395	-0.124118	2.574017
O	-2.370825	-0.025573	1.927647
C	-3.788151	0.038827	1.990128

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C	-4.170332	0.481958	3.390613
C	-1.194285	-1.602892	-1.879207
O	-0.462198	-1.299139	-2.723573
C	-3.708752	-0.972990	-1.148421
O	-4.510615	-0.236315	-1.529299
C	-3.536836	-2.948173	0.768227
O	-4.224872	-3.505084	1.505555
C	-2.964746	-3.513918	-1.699371
O	-3.329508	-4.332646	-2.429927
H	-4.160573	0.756804	1.237737
H	-4.233973	-0.939676	1.763742
H	-5.265825	0.552959	3.481706
H	-3.805893	-0.239032	4.138808
H	-3.737580	1.467043	3.625837
H	0.787339	4.300964	-1.689512
H	3.396414	3.322241	-1.767742
H	-3.084687	3.832070	1.976137
H	-3.890574	2.841949	-2.131151
H	5.215295	-1.619473	-2.395117
H	-0.828566	3.938364	2.773919
H	0.562336	3.506434	1.749308
H	-0.404020	2.229339	2.525142
H	-5.337912	4.011593	1.168764
H	-5.765546	2.927214	-0.179837
H	-5.377400	4.625821	-0.501251
H	-0.789431	1.203909	-2.802945
H	-0.770178	2.883275	-3.373361
H	-2.251105	1.915868	-3.515251
H	2.591394	0.563922	-3.276076
H	1.886669	-0.739537	-2.316390

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H	3.196100	-1.097895	-3.458153
H	7.185009	-2.315246	0.065254
H	8.174079	-0.887599	-0.295447
H	7.536014	-1.893386	-1.623229
H	4.500253	3.253086	0.817465
H	5.318399	2.251200	2.035596
H	3.552691	2.169218	1.852075
H	1.765446	0.824206	2.943716
H	3.286782	-0.513861	4.378586
H	4.144168	-2.717804	3.576298
H	3.459577	-3.561806	1.327614
H	1.961129	-2.209790	-0.107167
H	6.613891	0.587715	1.023683

3a(T_1) E = -3033.501377

C	-1.679009	-1.078779	-2.121993
C	-1.502187	-0.867964	-0.742055
C	-2.089218	-1.779079	0.150644
C	-2.852040	-2.849836	-0.322319
C	-3.037213	-3.035088	-1.695005
C	-2.443547	-2.147472	-2.595627
C	-0.654279	0.308029	-0.311978
C	0.727346	0.235983	-0.385391
C	1.960138	-0.379022	-0.377246
O	2.927718	0.527952	-0.683860
C	4.289005	0.218908	-0.954779
C	4.547437	0.200998	-2.454138
C	-1.249000	1.574298	-0.054076
N	-2.592920	1.904370	0.088063
C	-2.710874	3.277117	0.302264

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C	-1.466105	3.805126	0.313787
N	-0.560697	2.769232	0.110152
C	-3.744549	1.048551	0.218416
C	-4.589650	0.861187	-0.890862
C	-5.743506	0.087965	-0.712407
C	-6.073800	-0.479567	0.524939
C	-5.222261	-0.240971	1.611842
C	-4.056109	0.523402	1.487580
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C	-3.166135	0.771819	2.680000
C	-7.301498	-1.343462	0.676429
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C	1.480080	3.501270	-1.039455
C	2.819164	3.901515	-0.953547
C	3.542268	3.820393	0.241968
C	2.890966	3.320041	1.378794
C	1.551479	2.922144	1.352400
C	0.737060	3.560347	-2.349526
C	4.987650	4.248732	0.314963
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Cr	2.254035	-2.396672	0.376185
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O	2.611119	-5.111393	1.669809
C	0.958479	-3.151742	-0.812767
O	0.258844	-3.702562	-1.538432
C	0.969433	-1.952352	1.698168
O	0.223832	-1.686341	2.537780
C	3.596700	-1.705239	1.525796
O	4.404066	-1.309577	2.246581
C	3.543863	-2.851875	-0.944909

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O	4.311854	-3.188598	-1.735388
H	4.874567	1.017947	-0.472373
H	4.577363	-0.731605	-0.491309
H	5.619880	0.040465	-2.650528
H	3.987143	-0.610075	-2.942739
H	4.248197	1.156545	-2.912073
H	-1.125807	4.825979	0.458104
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H	3.310595	4.285530	-1.852247
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H	5.158105	4.947646	1.150045
H	0.615016	1.331849	2.482973
H	-0.059219	2.937932	2.813279
H	1.534690	2.491423	3.468278
H	-2.989982	1.848039	2.839381
H	-2.176290	0.302227	2.556135
H	-3.616209	0.363337	3.595620
H	-7.070486	-2.395868	0.435252
H	-8.108164	-1.024932	-0.001373
H	-7.688831	-1.322313	1.706303
H	-4.278864	2.585023	-2.175778
H	-5.014467	1.180895	-2.983441
H	-3.280311	1.180251	-2.585820
H	-1.197306	-0.398124	-2.828617

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H	-2.563994	-2.294036	-3.672217
H	-3.628627	-3.877933	-2.061733
H	-3.298920	-3.548304	0.389916
H	-1.943716	-1.654007	1.223233
H	-6.403969	-0.072922	-1.569260

3c E = -2055.564117

C	-1.252844	2.873183	-1.605269
C	-0.157971	2.994072	-0.725373
C	-0.219693	3.779875	0.439425
C	-1.424366	4.439644	0.716235
C	-2.540750	4.334732	-0.118812
C	-2.432417	3.545664	-1.271655
N	1.096819	2.371748	-1.098692
C	1.740575	1.319495	-0.509963
N	2.919807	1.163335	-1.187571
C	2.996467	2.108893	-2.202045
C	1.866432	2.856424	-2.145574
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C	-0.090706	0.301095	0.692057
C	-1.373883	0.088018	0.929581
W	-2.351782	-1.656917	-0.206207
C	-3.591774	-2.226753	1.384638
O	-4.295717	-2.594759	2.227220
C	3.957309	0.174248	-0.986154
C	5.215953	0.608684	-0.525744
C	6.222736	-0.352502	-0.373050
C	6.012439	-1.704448	-0.668461
C	4.754104	-2.086232	-1.149831
C	3.709274	-1.170898	-1.324368

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C	5.517389	2.056427	-0.218591
C	7.098996	-2.727997	-0.452812
C	2.380747	-1.631810	-1.859269
C	0.942391	3.911473	1.389265
C	-3.836024	5.036317	0.206052
C	-1.178137	2.070681	-2.879913
C	2.186689	-0.025276	1.629696
C	3.149617	0.818069	2.212890
C	3.979723	0.364411	3.240961
C	3.862775	-0.946526	3.710630
C	2.904714	-1.793347	3.144294
C	2.074523	-1.338501	2.117716
O	-1.970201	1.030297	1.735814
C	-3.240604	0.773197	2.317246
C	-3.630273	1.986001	3.141735
C	-3.320892	-3.166730	-1.243932
O	-3.866674	-4.009663	-1.828720
C	-0.931495	-3.029606	0.464093
O	-0.136322	-3.800642	0.810462
C	-1.225241	-1.422184	-1.935408
O	-0.624899	-1.342880	-2.930315
C	-3.735687	-0.269329	-0.945510
O	-4.496407	0.492404	-1.376558
H	-3.989743	0.573054	1.533001
H	-3.188847	-0.121703	2.960545
H	-4.603799	1.815701	3.627783
H	-2.880826	2.181431	3.924538
H	-3.708063	2.883492	2.509490
H	1.535320	3.696546	-2.747419
H	3.845952	2.146611	-2.876259

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H	-1.486209	5.053646	1.618899
H	-3.297207	3.439537	-1.932193
H	4.573616	-3.133711	-1.406725
H	0.829937	4.804468	2.020282
H	1.906870	3.988072	0.863176
H	0.996978	3.035700	2.056468
H	-3.742419	5.672346	1.098262
H	-4.641534	4.306723	0.393665
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H	-0.589076	1.152600	-2.764370
H	-0.721969	2.654051	-3.698845
H	-2.185183	1.780752	-3.210053
H	1.969801	-0.945902	-2.613764
H	1.628530	-1.705801	-1.058347
H	2.468757	-2.625118	-2.320114
H	6.974163	-3.227459	0.523714
H	8.098795	-2.268971	-0.462141
H	7.072338	-3.513468	-1.223528
H	5.839264	2.602917	-1.122117
H	6.334762	2.132601	0.512669
H	4.648252	2.591552	0.187767
H	3.235219	1.854223	1.878068
H	4.712610	1.043713	3.684776
H	4.508118	-1.303447	4.517303
H	2.798550	-2.820225	3.503524
H	1.329326	-2.010274	1.692322
H	7.201227	-0.030493	-0.005584

3c(T_1) E = -2055.532391

C	-1.706484	3.310790	-0.867920

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C	-0.724651	2.967220	0.088123
C	-0.975540	3.099489	1.471374
C	-2.249021	3.524199	1.870737
C	-3.257129	3.843762	0.954802
C	-2.955527	3.744044	-0.406732
N	0.596195	2.624019	-0.384012
C	1.359408	1.495281	-0.136222
N	2.593558	1.752795	-0.709192
C	2.590961	3.019907	-1.278444
C	1.363006	3.553235	-1.082522
C	0.996336	0.323659	0.600426
C	-0.263014	-0.314533	0.455832
C	-0.938972	-1.188839	1.284528
W	-1.981465	-1.272189	-0.588834
C	-3.245667	-2.761773	0.270234
O	-3.981452	-3.576818	0.631988
C	3.659770	0.809408	-0.936538
C	4.922081	1.050359	-0.362279
C	5.951112	0.135679	-0.627312
C	5.758738	-0.985738	-1.439485
C	4.497097	-1.168239	-2.022709
C	3.434868	-0.286218	-1.799056
C	5.211568	2.266871	0.483903
C	6.866924	-1.982220	-1.674068
C	2.114855	-0.499537	-2.493803
C	0.070308	2.832975	2.521622
C	-4.635212	4.242759	1.416202
C	-1.454981	3.278116	-2.357107
C	2.025640	-0.289229	1.490784
C	2.834616	0.482606	2.350351

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C	3.765795	-0.109781	3.205942
C	3.917813	-1.498851	3.229800
C	3.125261	-2.284122	2.384888
C	2.195521	-1.689519	1.533093
O	-0.708204	-1.469861	2.563525
C	-1.599562	-2.388764	3.205943
C	-1.206117	-2.498823	4.664731
C	-3.362650	-1.831521	-2.081927
O	-4.123581	-2.133056	-2.918132
C	-0.693110	-2.813512	-1.233829
O	-0.002304	-3.662571	-1.599951
C	-1.440687	-0.242635	-2.368357
O	-1.201581	0.214836	-3.409035
C	-3.396267	0.157596	0.060030
O	-4.246068	0.863603	0.391520
H	-2.635227	-2.024528	3.091668
H	-1.533205	-3.366634	2.697767
H	-1.867877	-3.210295	5.182791
H	-0.168052	-2.851487	4.763212
H	-1.285174	-1.522019	5.166590
H	0.962900	4.523759	-1.354715
H	3.462201	3.413989	-1.791760
H	-2.450342	3.621261	2.941438
H	-3.722467	3.997994	-1.144106
H	4.332745	-2.022582	-2.685614
H	-0.207801	3.314930	3.469860
H	1.056583	3.219808	2.222452
H	0.187103	1.754268	2.708513
H	-4.619729	4.661693	2.433653
H	-5.299252	3.361313	1.428626

H	-5.090408	4.985636	0.743162
H	-0.705378	2.534517	-2.649444
H	-1.110216	4.260829	-2.724208
H	-2.383074	3.043505	-2.897642
H	1.777496	0.411390	-3.013853
H	1.315971	-0.769726	-1.787559
H	2.193014	-1.302787	-3.239377
H	6.730714	-2.875886	-1.040490
H	7.853489	-1.557124	-1.436688
H	6.884175	-2.328227	-2.719483
H	5.540936	3.117686	-0.138581
H	6.020976	2.057475	1.198065
H	4.334410	2.601311	1.052422
H	2.714730	1.567214	2.368467
H	4.367787	0.519386	3.867654
H	4.644199	-1.965332	3.900189
H	3.236563	-3.371936	2.385505
H	1.592980	-2.317226	0.874004
H	6.932363	0.308389	-0.175901

5(S_0) E = -2414.907121

C	4.037795	-0.279245	1.400461
C	2.746567	0.259129	1.243826
C	2.423411	1.425689	1.964323
C	3.360363	2.040877	2.799893
C	4.640742	1.498645	2.939309
C	4.970755	0.333159	2.238032
C	1.735221	-0.425214	0.383591
C	1.673954	-1.760335	0.218099
C	1.480891	-3.025053	-0.072043

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O	0.622444	-3.713351	0.745707
C	0.576172	-5.134017	0.747203
C	1.696726	-5.749303	1.570358
C	0.731401	0.374746	-0.318402
N	-0.588360	0.073468	-0.458437
C	-1.198580	1.030969	-1.247193
C	-0.246571	1.941080	-1.587769
N	0.941458	1.526651	-1.014367
C	-1.280628	-1.088489	0.093596
C	2.237434	2.153365	-1.258423
Cr	2.368167	-3.572099	-2.055097
C	0.543818	-3.660729	-2.548113
O	-0.585781	-3.669856	-2.786045
C	2.469401	-5.453076	-1.761418
O	2.603320	-6.595448	-1.693343
C	3.027271	-3.972162	-3.751465
O	3.428431	-4.211447	-4.808249
C	4.064286	-3.386844	-1.219583
O	5.072198	-3.254242	-0.678953
C	2.433882	-1.766437	-2.584338
O	2.501579	-0.674698	-2.964145
H	-0.402916	-5.381073	1.188558
H	0.579039	-5.515537	-0.284821
H	1.604453	-6.847227	1.584199
H	2.681184	-5.495285	1.149730
H	1.661697	-5.381465	2.607922
H	-2.253654	0.981246	-1.499545
H	-0.309308	2.836627	-2.198873
H	1.416076	1.847536	1.892181
H	3.082143	2.941048	3.354789

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H	5.374280	1.976562	3.593369
H	5.967966	-0.102852	2.340327
H	4.305597	-1.187503	0.857551
H	-1.294014	-1.910652	-0.635220
H	-2.309006	-0.792912	0.343219
H	-0.761291	-1.443380	0.991145
H	2.581760	2.706267	-0.373907
H	2.131117	2.837388	-2.109709
H	2.971497	1.379568	-1.513769

5(T_1) E = -2414.851163

C	4.481553	0.421678	-0.221606
C	3.248261	0.579177	0.452344
C	3.098212	1.716632	1.279895
C	4.122050	2.655978	1.414006
C	5.333734	2.483653	0.737055
C	5.504554	1.356391	-0.076315
C	2.182741	-0.428475	0.311333
C	2.417694	-1.730239	-0.135514
C	1.851972	-2.863701	-0.649548
O	0.475099	-2.846712	-0.655575
C	-0.285178	-3.801515	-1.393130
C	-1.755396	-3.566882	-1.097359
C	0.813245	-0.063900	0.619576
N	-0.028254	-0.711189	1.474978
C	-1.263215	-0.094191	1.466172
C	-1.182196	0.966752	0.615082
N	0.098017	0.975133	0.092806
C	0.333976	-1.853880	2.303438

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C	0.587819	1.893084	-0.924944
Cr	3.252376	-4.403479	-1.169847
C	2.328627	-4.864480	-2.763478
O	1.816132	-5.172468	-3.748998
C	2.209671	-5.617407	-0.148933
O	1.588096	-6.352752	0.485469
C	4.508429	-5.752337	-1.538188
O	5.273928	-6.585072	-1.766355
C	4.228696	-3.957106	0.414475
O	4.834699	-3.729083	1.364293
C	4.262517	-3.120090	-2.158393
O	4.881360	-2.353226	-2.752816
H	-0.082553	-3.676069	-2.469263
H	0.011732	-4.823736	-1.114941
H	-2.374125	-4.263511	-1.684383
H	-1.979186	-3.730015	-0.030903
H	-2.051163	-2.538778	-1.359442
H	-2.092138	-0.451429	2.070218
H	-1.927194	1.705743	0.334362
H	2.176451	1.853443	1.853379
H	3.977683	3.521347	2.066861
H	6.137461	3.215895	0.845525
H	6.445878	1.206810	-0.611851
H	4.622358	-0.440969	-0.874827
H	0.208446	-2.786498	1.737990
H	-0.305188	-1.858811	3.196344
H	1.386106	-1.760095	2.602131
H	1.160338	2.717242	-0.473604
H	-0.268921	2.294948	-1.481623
H	1.249179	1.348279	-1.611733

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TS1 **E =** -2567.493888

C	1.192794	1.437657	-2.097647
C	1.574149	1.122932	-0.773856
C	2.077968	2.166391	0.035629
C	2.195545	3.463410	-0.465265
C	1.827057	3.754082	-1.783328
C	1.322283	2.732675	-2.596208
C	1.518085	-0.274592	-0.288562
C	0.366590	-0.998771	-0.517874
O	0.734619	-2.684019	-0.746149
C	2.724161	-0.867416	0.381691
N	3.957908	-0.138134	0.376956
C	4.598065	-0.320899	1.591673
C	3.782470	-1.041002	2.408434
N	2.629841	-1.351678	1.725042
C	4.680456	0.179795	-0.836341
C	1.587205	-2.217048	2.227152
C	-1.010656	-0.865128	-0.638008
O	-1.487570	-1.934142	-1.387252
C	-2.850631	-2.097969	-1.772083
C	-2.957747	-3.376216	-2.582742
Cr	-2.205268	0.497871	0.580526
C	-3.187169	1.537433	1.785367
O	-3.792081	2.169906	2.538383
C	-1.726811	2.044010	-0.443834
O	-1.525426	3.003922	-1.040742
C	-0.729106	0.763817	1.745227
O	0.106888	0.964239	2.513114
C	-2.675908	-1.090815	1.503039

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O	-2.952474	-2.063683	2.056184
C	-3.791695	0.432078	-0.459366
O	-4.798348	0.484521	-1.019735
O	3.055754	-2.778134	-1.798749
H	-3.488663	-2.148155	-0.877053
H	-3.165210	-1.227864	-2.368063
H	-3.998426	-3.525197	-2.909471
H	-2.320088	-3.332687	-3.479889
H	-2.661360	-4.252849	-1.984649
H	3.930011	-1.335669	3.445075
H	5.580334	0.100588	1.790864
H	0.798806	0.643571	-2.736484
H	1.021205	2.949395	-3.624473
H	1.922338	4.771261	-2.171024
H	2.571028	4.258856	0.184167
H	2.351290	1.957079	1.070427
H	5.457538	0.925219	-0.613623
H	4.001183	0.616560	-1.580213
H	5.169021	-0.714781	-1.273147
H	1.706970	-2.322115	3.313966
H	1.626613	-3.214334	1.757073
H	0.594995	-1.789659	2.027221
H	-0.102482	-2.900338	-1.222041
H	1.546970	-2.795192	-1.342619
H	3.240608	-2.173716	-2.532872
H	3.195993	-2.217608	-0.978797

6(T_1) **E =** -2490.665467

C	-3.110459	1.004718	1.820103

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C	-2.818435	0.745794	0.450600
C	-3.727221	-0.100854	-0.238331
C	-4.834369	-0.659368	0.395276
C	-5.097665	-0.393361	1.746908
C	-4.219775	0.444318	2.448696
C	-1.735060	1.455929	-0.234030
C	-1.048880	0.976867	-1.370486
O	-0.523047	1.962159	-2.178734
C	-1.454823	2.851730	0.185464
N	-0.305944	3.209291	0.955951
C	-0.586149	4.372257	1.656116
C	-1.890353	4.696357	1.466228
N	-2.476181	3.733715	0.646696
C	1.023016	2.771375	0.611524
C	-3.644051	3.997226	-0.157584
C	-0.792229	-0.381537	-1.777538
O	-0.354146	-0.286226	-3.112638
C	-0.296549	-1.393139	-3.978610
C	-0.335298	-0.882844	-5.411886
Cr	-0.129379	-2.092349	-0.502829
C	1.535019	-1.302176	-0.911470
O	2.540374	-0.804776	-1.192759
C	0.150222	-3.410968	-1.814037
O	0.361205	-4.321360	-2.502455
C	0.572022	-3.355160	0.650739
O	1.025830	-4.141137	1.377609
C	-1.912145	-2.760022	-0.384601
O	-2.947269	-3.265935	-0.369149
C	-0.262282	-1.017515	1.071827
O	-0.211868	-0.488104	2.094082

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H	0.628107	-1.971985	-3.810028
H	-1.147064	-2.068765	-3.785732
H	-0.277076	-1.724745	-6.121169
H	-1.265406	-0.324790	-5.604953
H	0.513599	-0.208252	-5.610517
H	0.158488	4.849505	2.291650
H	-2.475627	5.499054	1.911327
H	-3.546582	-0.305550	-1.295257
H	-5.500040	-1.317105	-0.171998
H	-5.967224	-0.833311	2.243602
H	-4.398616	0.656156	3.508217
H	-2.430965	1.637185	2.392896
H	-4.381882	4.561638	0.434844
H	-4.102920	3.045524	-0.462059
H	-3.403934	4.573349	-1.077359
H	1.717390	3.033836	1.424989
H	1.382072	3.220169	-0.335869
H	1.035815	1.679414	0.486793
H	-0.082526	1.473931	-2.895565

6(S_0) E = -2490.731584

C	-3.422718	0.788339	1.710957
C	-3.026623	0.764433	0.349064
C	-3.850979	0.018279	-0.530124
C	-5.004835	-0.622677	-0.087283
C	-5.393516	-0.557733	1.258373
C	-4.584012	0.150118	2.152241
C	-1.814842	1.453018	-0.121774
C	-1.079743	0.963498	-1.310757
O	-0.990422	1.951325	-2.304223

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C	-1.437370	2.693288	0.405345
N	-0.156825	3.240565	0.419215
C	-0.191018	4.512489	0.968645
C	-1.471771	4.788911	1.310584
N	-2.251955	3.689247	0.957737
C	1.056394	2.516272	0.105043
C	-3.688437	3.749465	0.812499
C	-0.516392	-0.257047	-1.549497
O	-0.006141	-0.293551	-2.902230
C	-0.853195	-0.941024	-3.828831
C	-0.103883	-1.126071	-5.139056
Cr	0.127152	-1.950297	-0.303444
C	1.740690	-0.985126	-0.333185
O	2.718843	-0.365633	-0.375808
C	0.731725	-2.905007	-1.813946
O	1.147129	-3.531300	-2.695650
C	0.742151	-3.351011	0.737904
O	1.133706	-4.229615	1.394670
C	-1.614109	-2.660304	-0.553191
O	-2.655318	-3.116826	-0.754158
C	-0.344400	-1.081036	1.317032
O	-0.535231	-0.627779	2.363052
H	-1.172679	-1.920923	-3.428894
H	-1.777973	-0.347117	-3.988560
H	-0.749235	-1.607390	-5.892797
H	0.231610	-0.155592	-5.541421
H	0.783364	-1.758923	-4.983435
H	0.712451	5.103404	1.091383
H	-1.904627	5.674294	1.767577
H	-3.559636	-0.053630	-1.579447

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H	-5.609058	-1.189282	-0.802505
H	-6.295835	-1.069312	1.605136
H	-4.843742	0.185612	3.215497
H	-2.777139	1.286344	2.438432
H	-4.006813	4.801393	0.865078
H	-4.216678	3.166935	1.584828
H	-3.977906	3.332422	-0.164574
H	1.917771	3.142623	0.378003
H	1.106116	2.270699	-0.964625
H	1.100665	1.577228	0.673484
H	-0.414993	1.524170	-2.967869

7(S_0) E = -2490.763726

C	-1.737206	-2.421603	-0.320098
C	-1.342959	-1.211793	-0.935009
C	-0.955782	-1.289456	-2.293534
C	-0.957140	-2.497969	-2.989803
C	-1.361541	-3.681745	-2.360152
C	-1.755971	-3.631664	-1.020369
C	-1.369269	0.068510	-0.180607
C	-0.224858	1.007595	-0.151055
O	-0.397354	2.187892	0.210471
C	-2.556956	0.414228	0.497799
N	-2.724842	1.125749	1.675994
C	-4.073255	1.238068	1.972163
C	-4.773029	0.594768	1.006699
N	-3.854052	0.098021	0.091320
C	-1.675083	1.521209	2.600947
C	-4.221386	-0.413850	-1.211095
C	1.138663	0.550199	-0.555598

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O	1.968729	1.636563	-0.950471
C	1.596509	2.290818	-2.135671
C	2.595584	3.406580	-2.401613
Cr	2.268135	-0.550462	1.133816
C	2.111414	1.113661	2.037475
O	2.013970	2.106179	2.617775
C	3.834432	0.058122	0.231859
O	4.817867	0.379377	-0.277725
C	3.328999	-1.310416	2.433771
O	3.999262	-1.783748	3.261430
C	2.258251	-2.093903	0.044609
O	2.258686	-3.038008	-0.623421
C	0.756428	-1.207308	2.029891
O	-0.124168	-1.652871	2.643588
H	1.590125	1.575822	-2.990925
H	0.575019	2.708895	-2.050944
H	2.357346	3.939261	-3.338011
H	2.580497	4.130237	-1.571367
H	3.616825	2.999304	-2.475737
H	-4.415938	1.754186	2.864297
H	-5.842748	0.454652	0.881000
H	-0.664343	-0.372082	-2.809758
H	-0.646490	-2.515980	-4.039036
H	-1.359256	-4.629933	-2.905062
H	-2.057817	-4.548161	-0.503876
H	-2.004174	-2.406146	0.739164
H	-5.272083	-0.153567	-1.407246
H	-4.096706	-1.505564	-1.283372
H	-3.586618	0.046166	-1.982033
H	-2.151139	1.921677	3.507087

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H	-1.018349	2.263865	2.126234
H	-1.069853	0.645203	2.871526
H	1.112108	-0.205236	-1.353345

TS2 E = -2490.728118

C	4.917982	1.717477	1.480200
C	3.546884	1.380966	1.340798
C	2.656762	2.003170	2.254699
C	3.108916	2.875583	3.240737
C	4.473347	3.178974	3.368696
C	5.371545	2.588187	2.474594
C	3.076845	0.451595	0.305103
C	1.718549	0.555845	-0.324566
O	1.140049	-0.542794	-0.678283
C	3.859477	-0.652127	-0.064873
N	3.925066	-1.258378	-1.312545
C	4.781779	-2.344695	-1.267750
C	5.286345	-2.428568	-0.011640
N	4.718107	-1.404745	0.738461
C	3.299403	-0.752998	-2.517179
C	4.747614	-1.351817	2.182552
C	1.095421	1.783195	-0.555133
C	-1.372909	-0.718379	-1.884052
O	-1.296649	-1.353625	-2.841780
Cr	-1.552368	0.332781	-0.288446
C	-0.892199	-1.175143	0.725011
O	-0.578843	-2.086798	1.348799
C	-1.431979	1.417493	1.272002
O	-1.401781	2.055253	2.235147

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C	-3.273566	-0.168540	0.023432
O	-4.376377	-0.485935	0.224857
C	-2.210804	1.807866	-1.271230
O	-2.685136	2.696010	-1.841623
H	1.590909	1.782299	2.177020
H	5.637350	1.303300	0.767617
H	6.439824	2.822289	2.536447
H	2.383779	3.325115	3.926815
H	4.824266	3.867249	4.142948
H	2.225518	-0.992294	-2.519286
H	3.817133	-1.177748	-3.390230
H	3.390924	0.344152	-2.534152
H	5.413831	-0.559174	2.561237
H	5.080393	-2.327023	2.568026
H	3.735804	-1.139012	2.559740
H	5.989737	-3.134457	0.420802
H	4.973461	-2.957534	-2.144049
H	0.294441	1.779324	-1.309090
O	1.757534	3.001722	-0.409065
C	0.946790	4.079531	-0.017413
H	0.468789	3.877790	0.961940
H	0.119561	4.227707	-0.745798
C	1.804994	5.332547	0.055950
H	2.278930	5.530895	-0.919292
H	2.604498	5.207283	0.802862
H	1.195905	6.208719	0.334309

8 E = -2490.761461

C	-0.308605	1.514464	1.537776
C	-1.634783	1.674651	1.052731

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C	-2.027185	3.004643	0.746974
C	-1.154078	4.087979	0.883206
C	0.149245	3.898302	1.349650
C	0.556884	2.595320	1.678664
C	-2.561498	0.540888	0.910333
C	-2.562746	-0.586976	1.902526
O	-2.892931	-1.795491	1.483613
Cr	-1.625667	-3.266275	0.570630
C	-0.958874	-2.088282	-0.760267
O	-0.502621	-1.459614	-1.617105
C	-3.468521	0.499244	-0.158008
N	-3.292925	0.998233	-1.452910
C	-4.415896	0.714757	-2.222601
C	-5.288606	0.031585	-1.443385
N	-4.730053	-0.088652	-0.180714
C	-2.050511	1.491417	-2.002283
C	-5.441178	-0.583238	0.980664
C	-2.281759	-0.331487	3.218928
O	-2.094204	-1.340204	4.156034
C	-3.252184	-2.047573	4.561148
C	-4.129722	-1.243583	5.518228
C	-3.123096	-3.650545	-0.538929
O	-4.029820	-3.879625	-1.214647
C	-2.296132	-4.446761	1.916580
O	-2.687912	-5.178472	2.715772
C	-0.191732	-2.749219	1.730080
O	0.704133	-2.455090	2.388520
C	-0.628420	-4.626100	-0.161311
O	0.004222	-5.487433	-0.626237
H	-3.828524	-2.364281	3.675739

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H	-2.890234	-2.962380	5.062221
H	-3.563052	-0.948650	6.417625
H	-4.491431	-0.324512	5.029073
H	-5.007945	-1.831780	5.837384
H	-6.266437	-0.380007	-1.676576
H	-4.478684	1.002549	-3.268047
H	0.033279	0.512842	1.803184
H	1.573239	2.419423	2.045642
H	0.831925	4.744833	1.466191
H	-1.507679	5.095759	0.639881
H	-3.054977	3.187051	0.419773
H	-1.892907	2.562068	-1.788296
H	-2.058274	1.332798	-3.090789
H	-1.208927	0.932699	-1.572229
H	-6.505828	-0.684913	0.724294
H	-5.332301	0.133038	1.809433
H	-5.011773	-1.541144	1.309787
H	-2.084364	0.678008	3.589919

9 E = -880.684895

C	-0.080243	-0.931091	0.187987
N	1.003702	-1.742156	0.445590
C	0.572717	-2.949695	0.971666
C	-0.783490	-2.905677	1.027963
N	-1.180393	-1.662864	0.564293
O	-1.480860	2.952145	-0.351258
C	-1.886131	4.298964	-0.473861
C	-0.790495	5.240048	-0.969253
C	-0.057659	0.397413	-0.326519
C	-1.077819	0.756898	-1.285808

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C	-1.364910	2.241612	-1.563039
H	-2.776630	4.370857	-1.133525
H	-1.149015	6.282407	-0.949954
H	-0.485933	5.014836	-2.003736
H	0.100697	5.164278	-0.327256
H	-2.206112	4.605214	0.535903
H	-2.314686	2.260294	-2.130463
H	-0.583288	2.673011	-2.219178
C	1.007243	1.322049	0.137862
C	3.057467	3.067723	1.061049
C	1.326485	1.428858	1.509440
C	1.761140	2.113799	-0.755237
C	2.758539	2.979729	-0.303029
C	2.337517	2.278603	1.964002
H	3.843377	3.739825	1.414911
H	2.552896	2.337966	3.034809
H	3.320380	3.579281	-1.025050
H	0.749921	0.846211	2.233529
H	1.572403	2.030195	-1.828141
H	1.266298	-3.738626	1.247389
H	-1.500178	-3.647756	1.367203
O	-1.777893	-0.071060	-1.888003
C	2.377281	-1.447900	0.079920
H	2.927774	-2.394053	-0.013598
H	2.869871	-0.807060	0.826844
H	2.392642	-0.922206	-0.884054
C	-2.544902	-1.171437	0.583762
H	-2.543092	-0.129520	0.938785
H	-3.135765	-1.795611	1.267513
H	-2.965613	-1.170322	-0.432289

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Molecular orbitals HOMO (left) and LUMO (right) of **3a** calculated at the B3LYP/6-31+G(d)&LANL2DZ level (isosurface value 0.04).

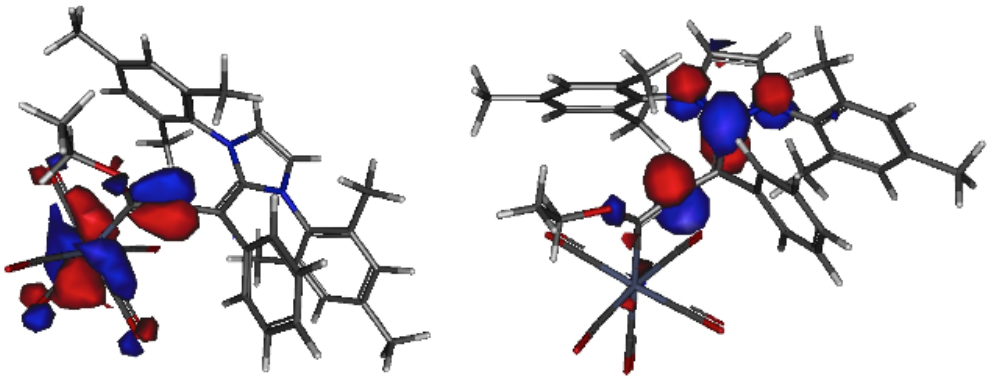

Figure 2

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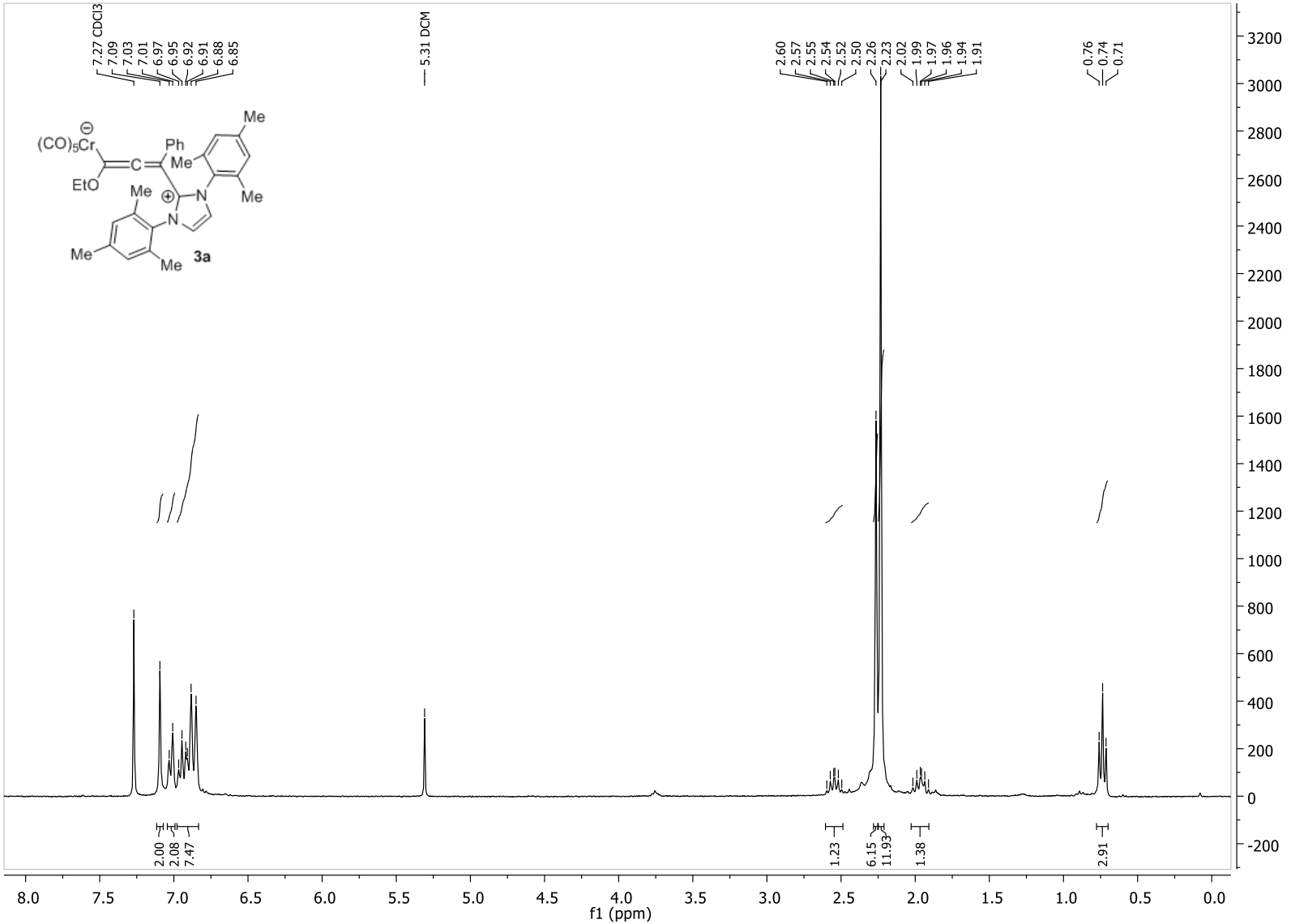

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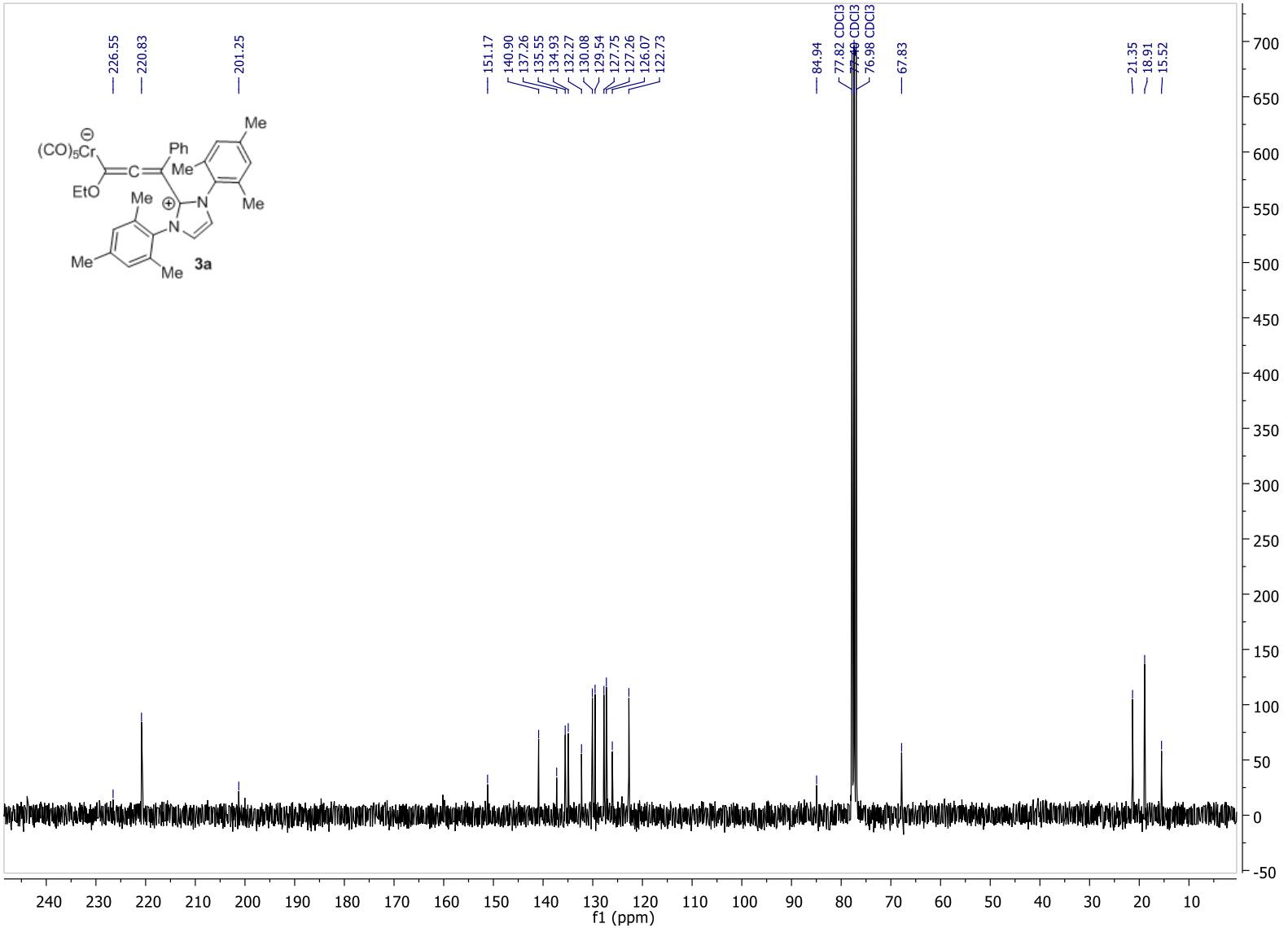

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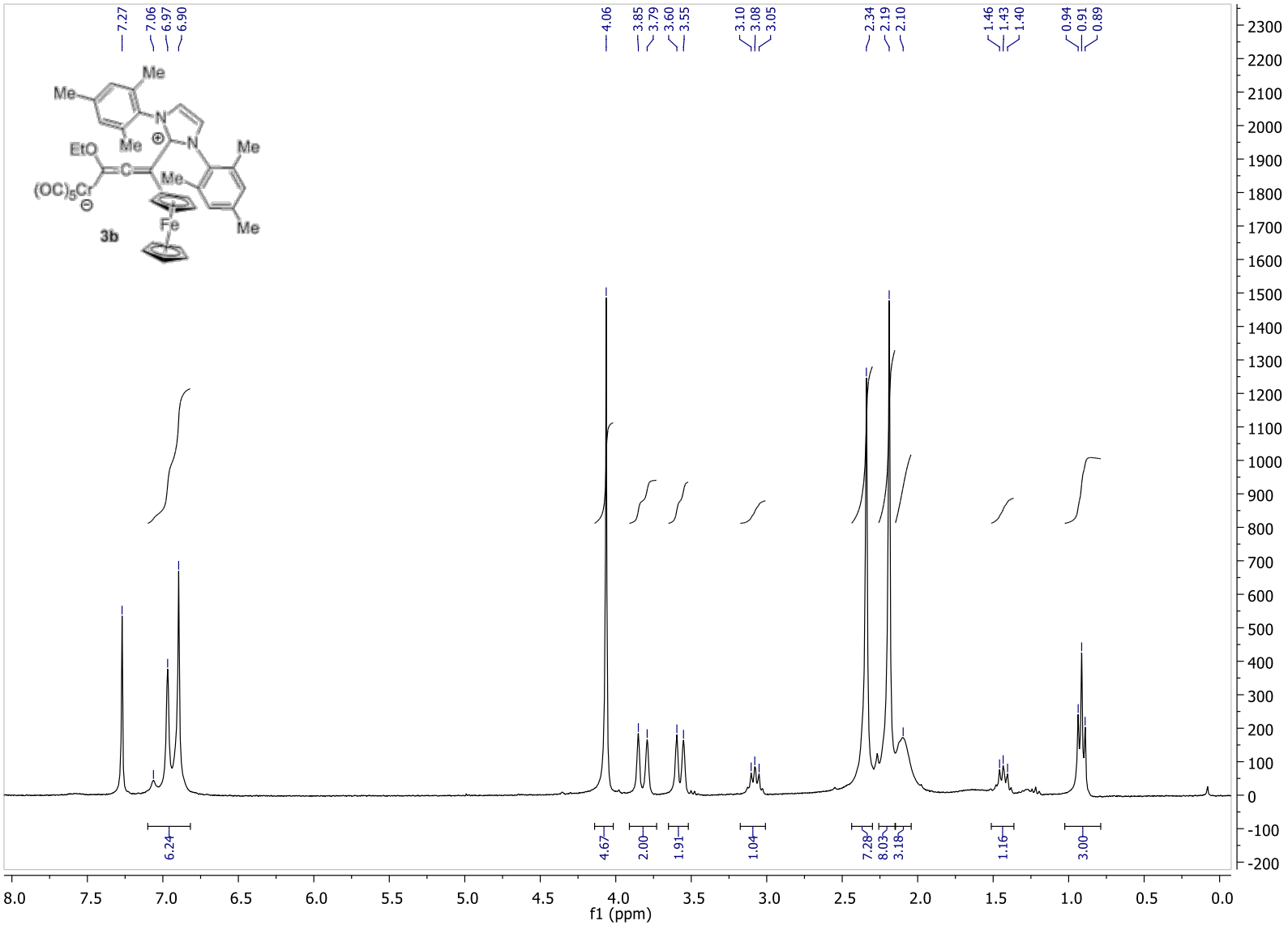

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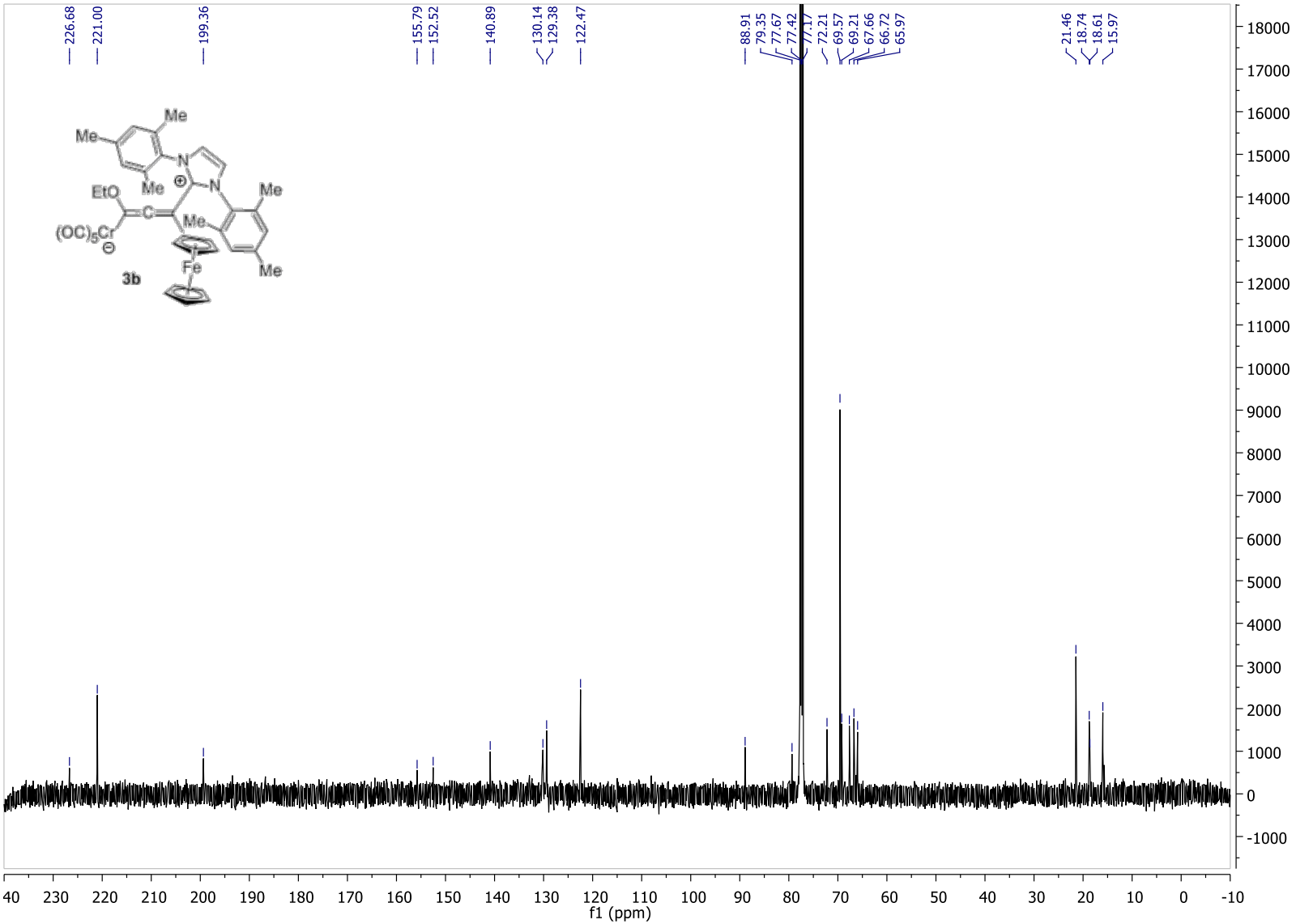

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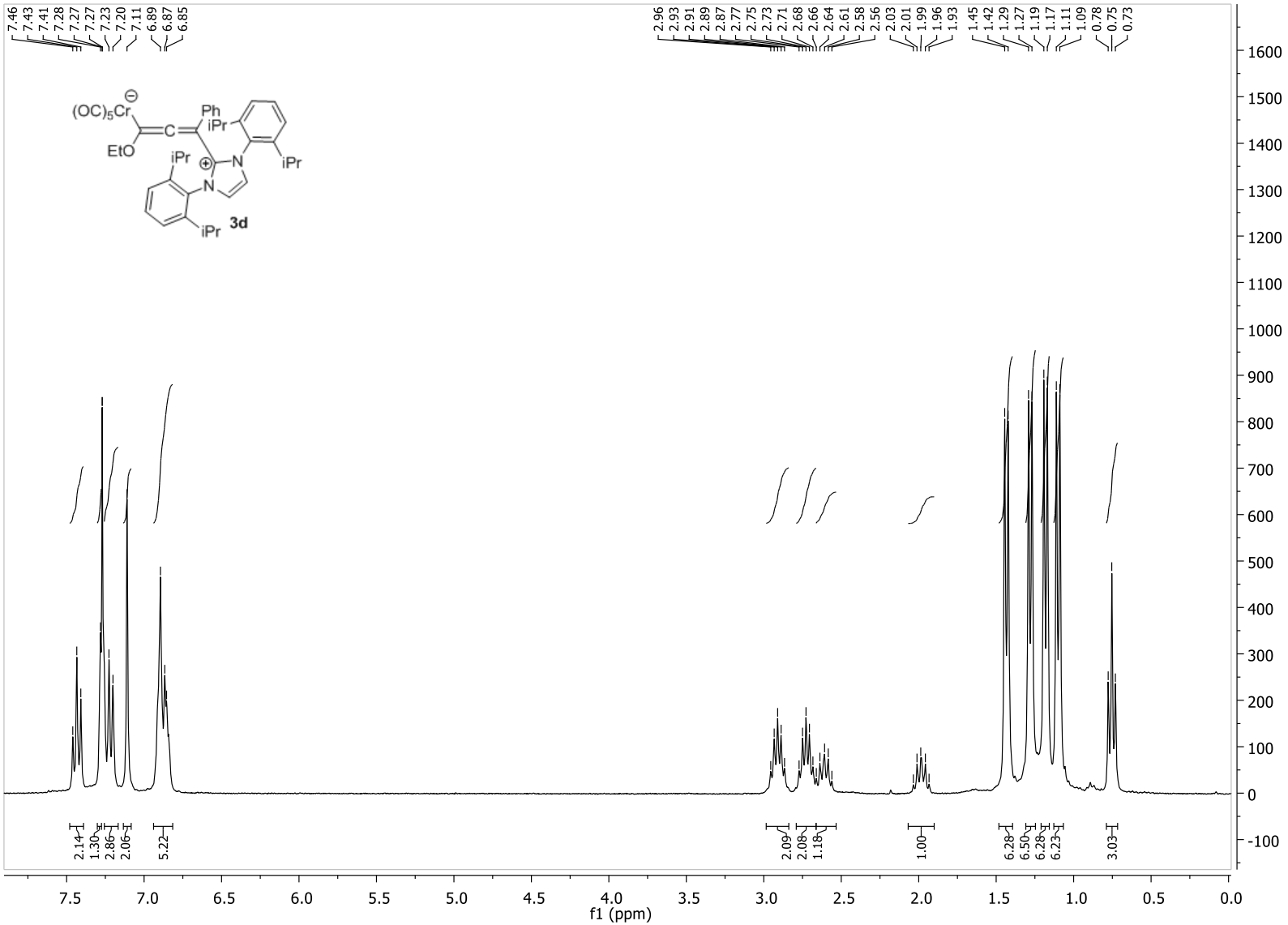

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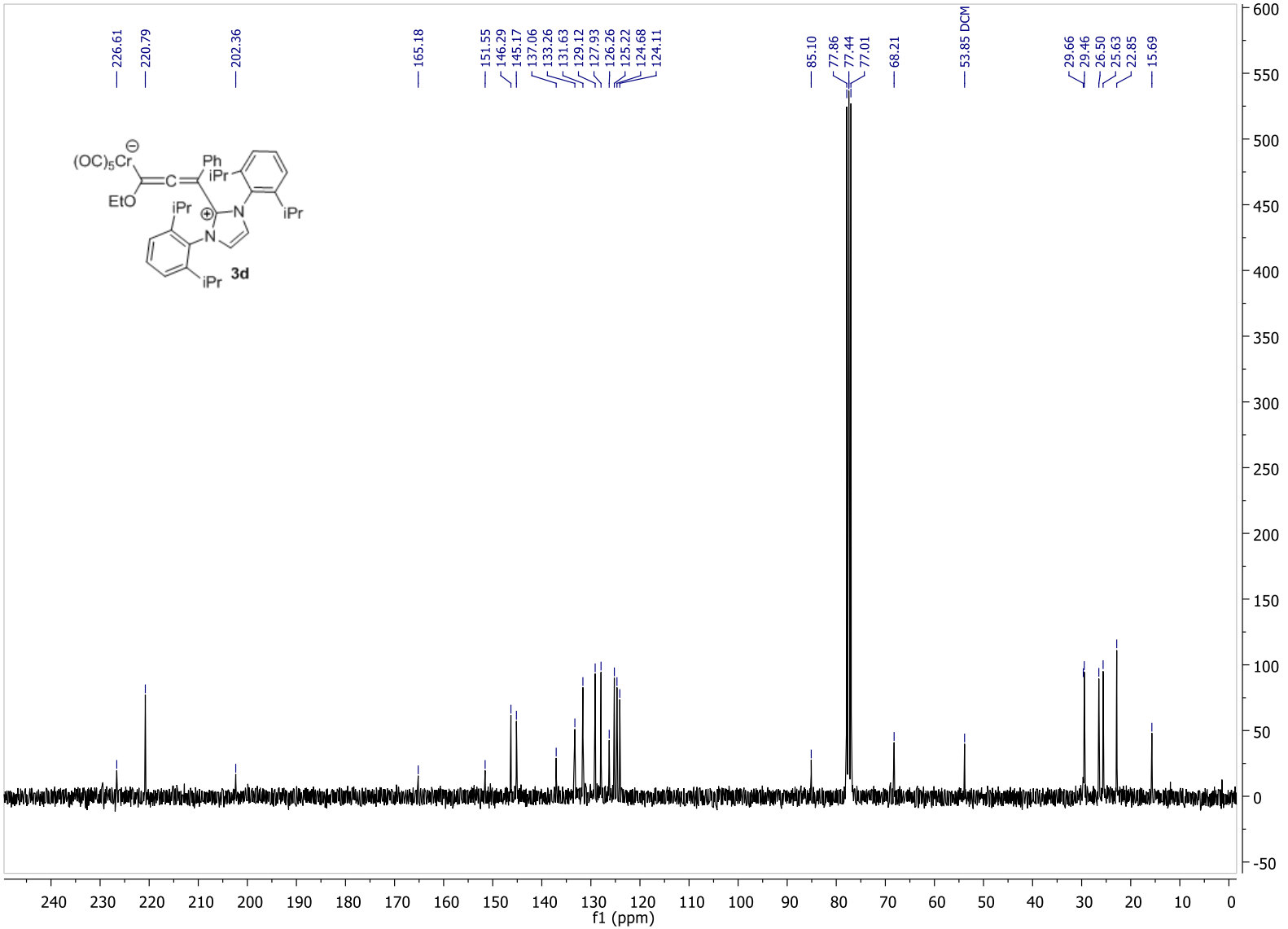

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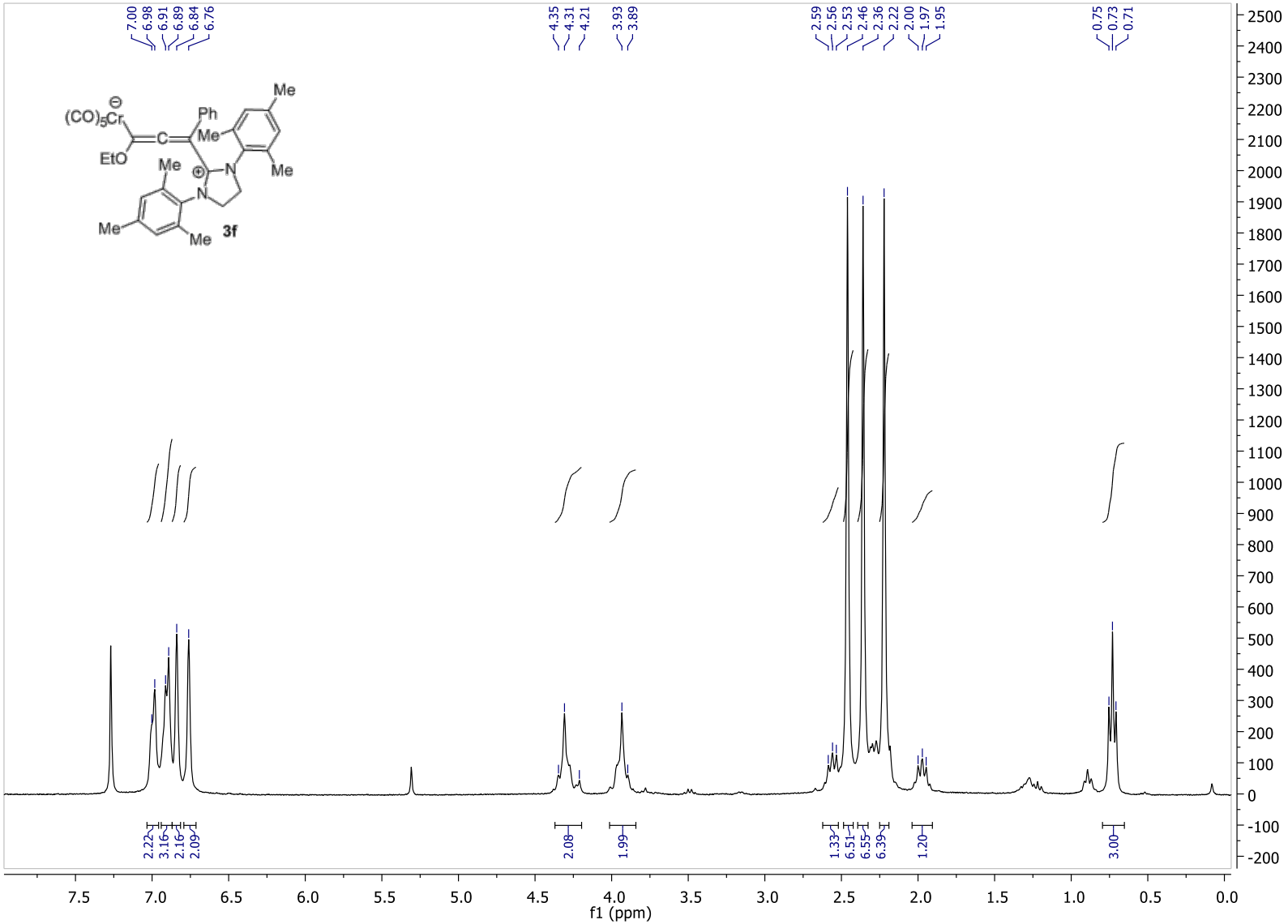

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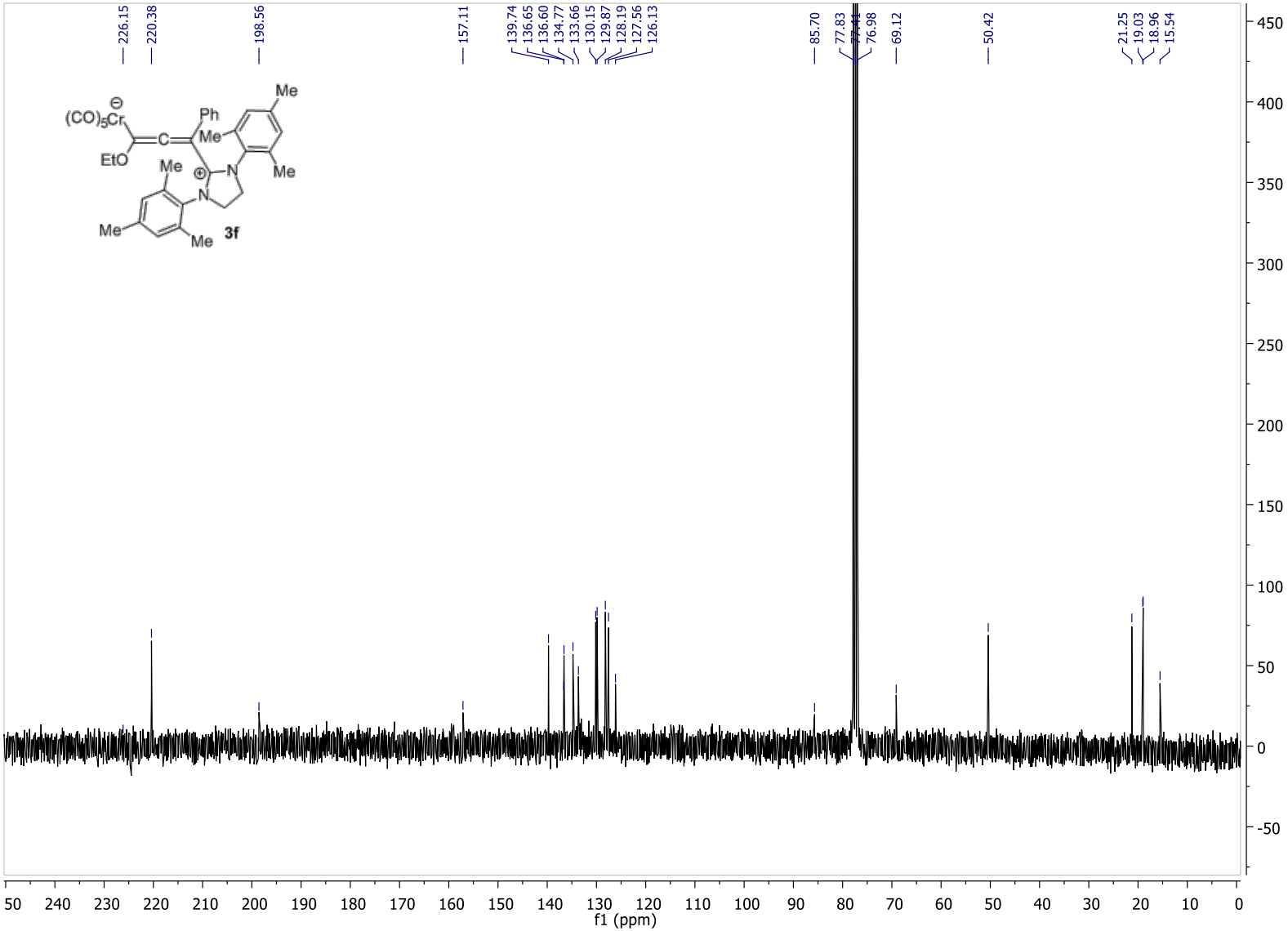

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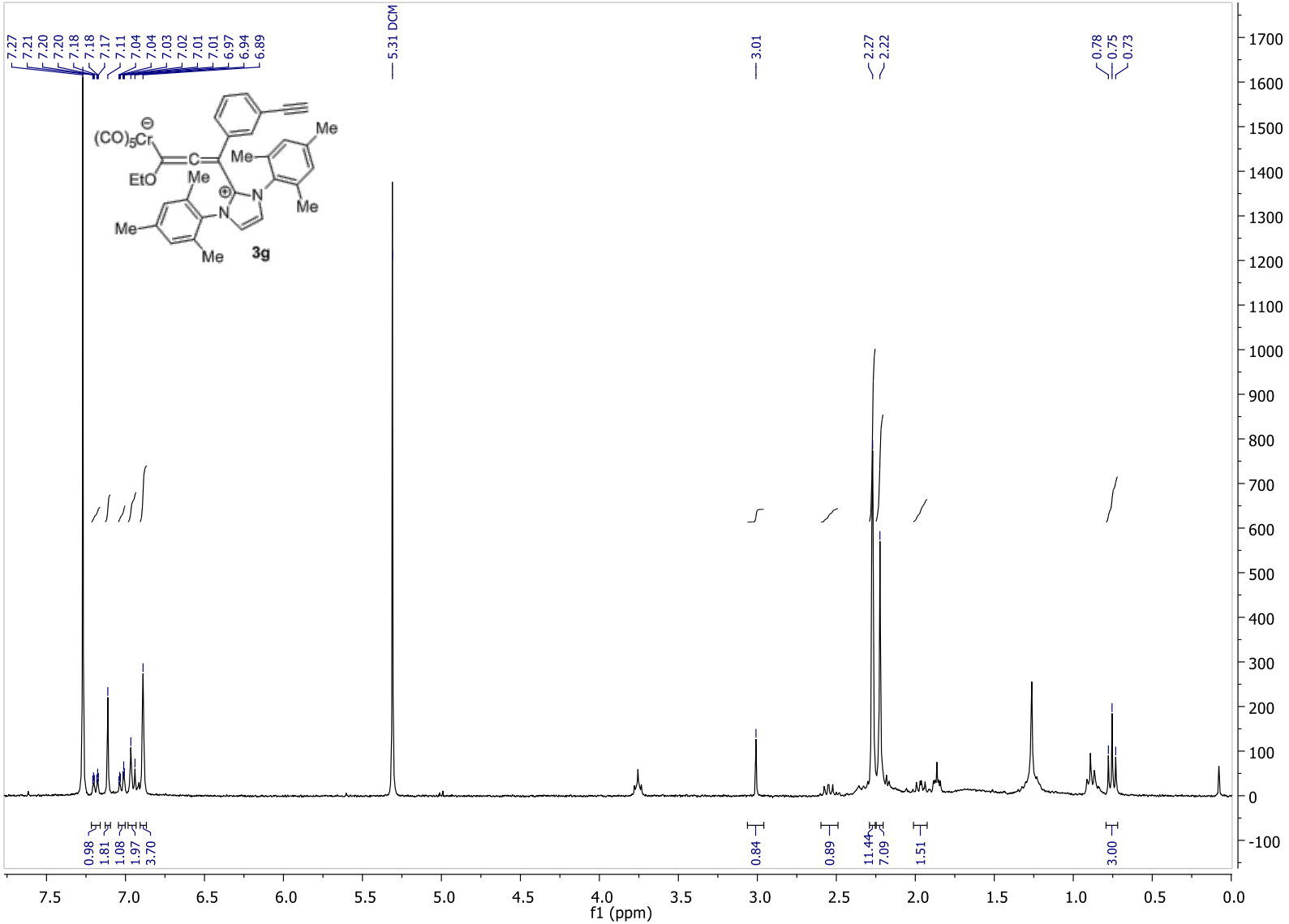

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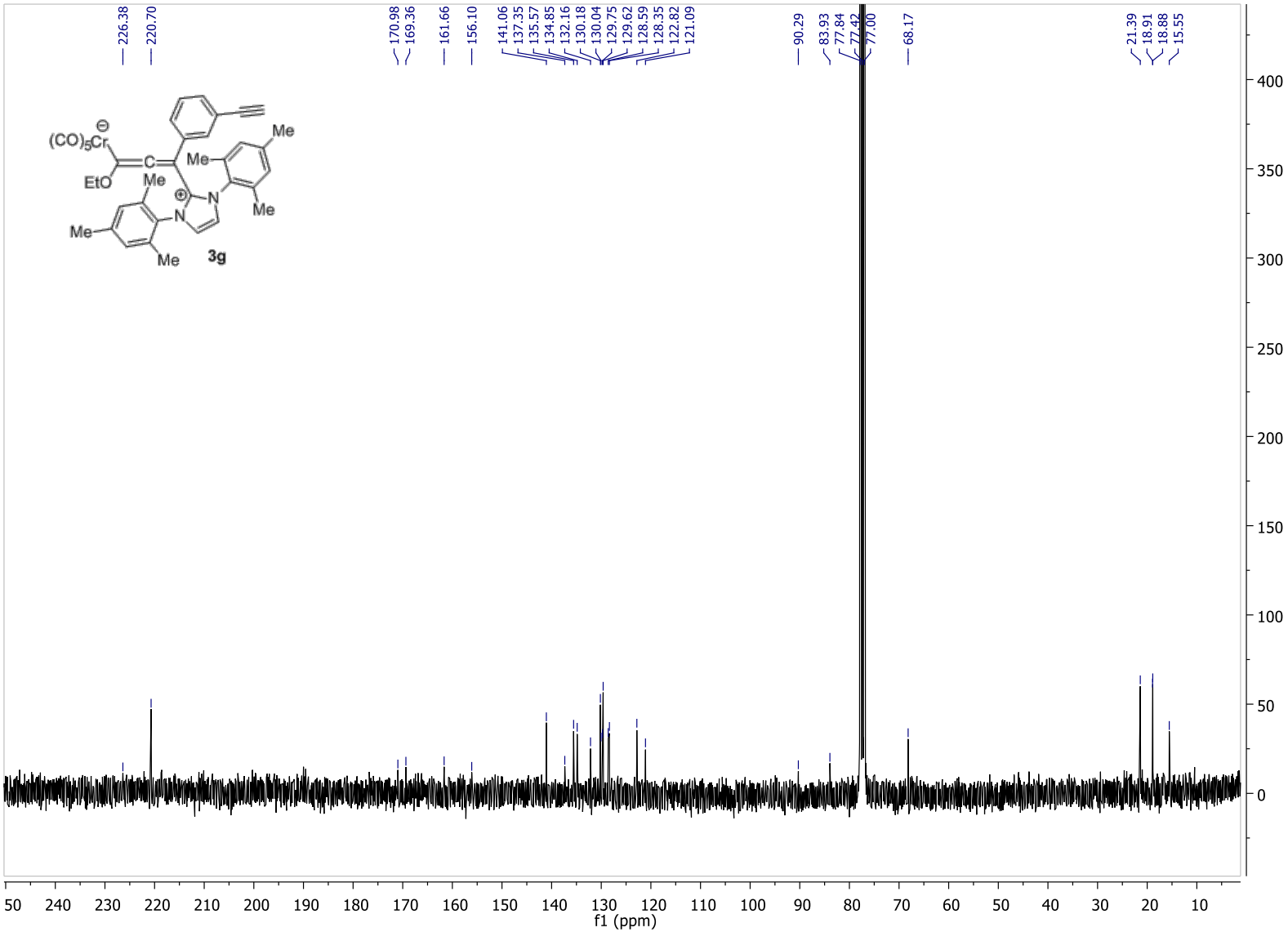

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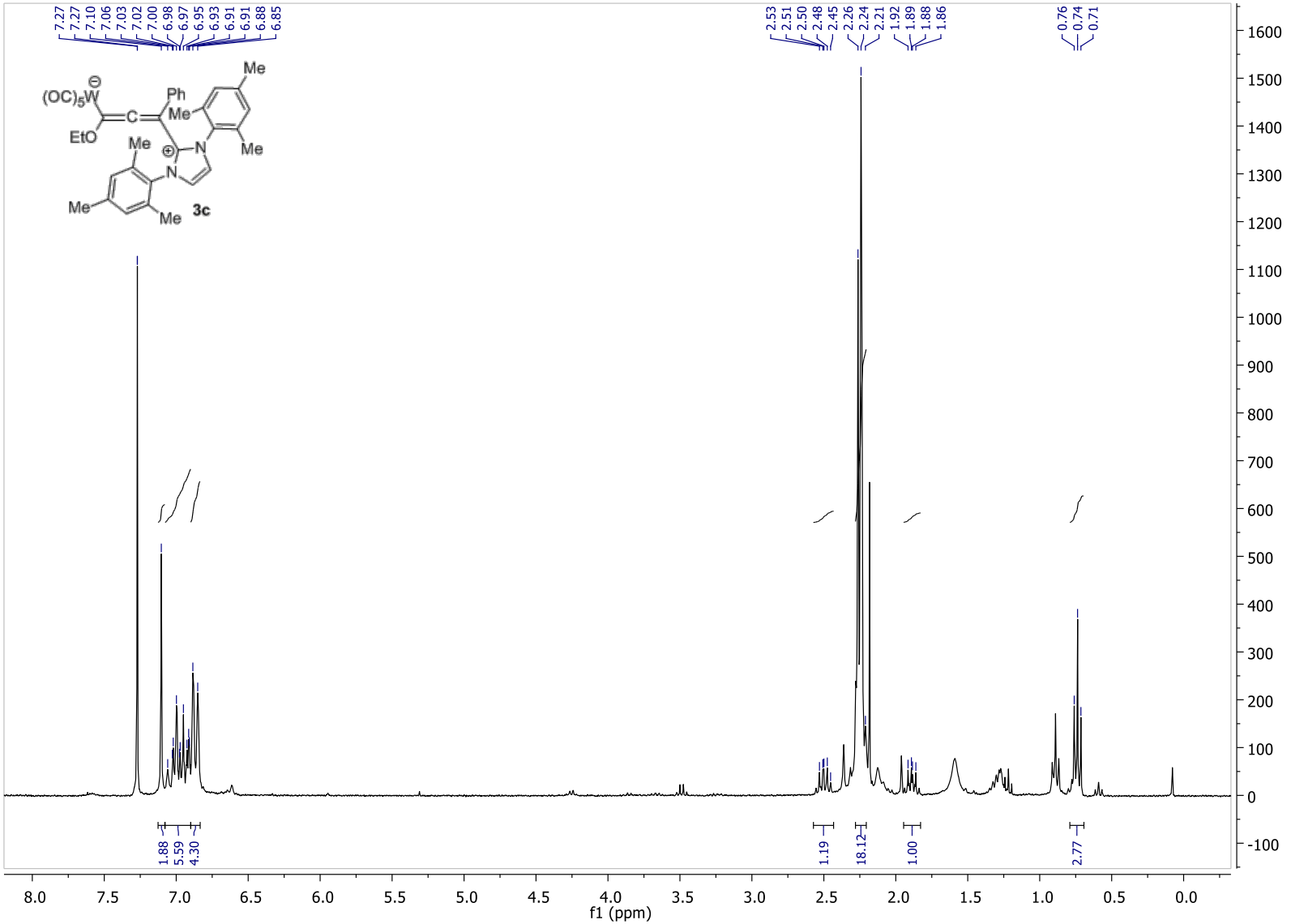

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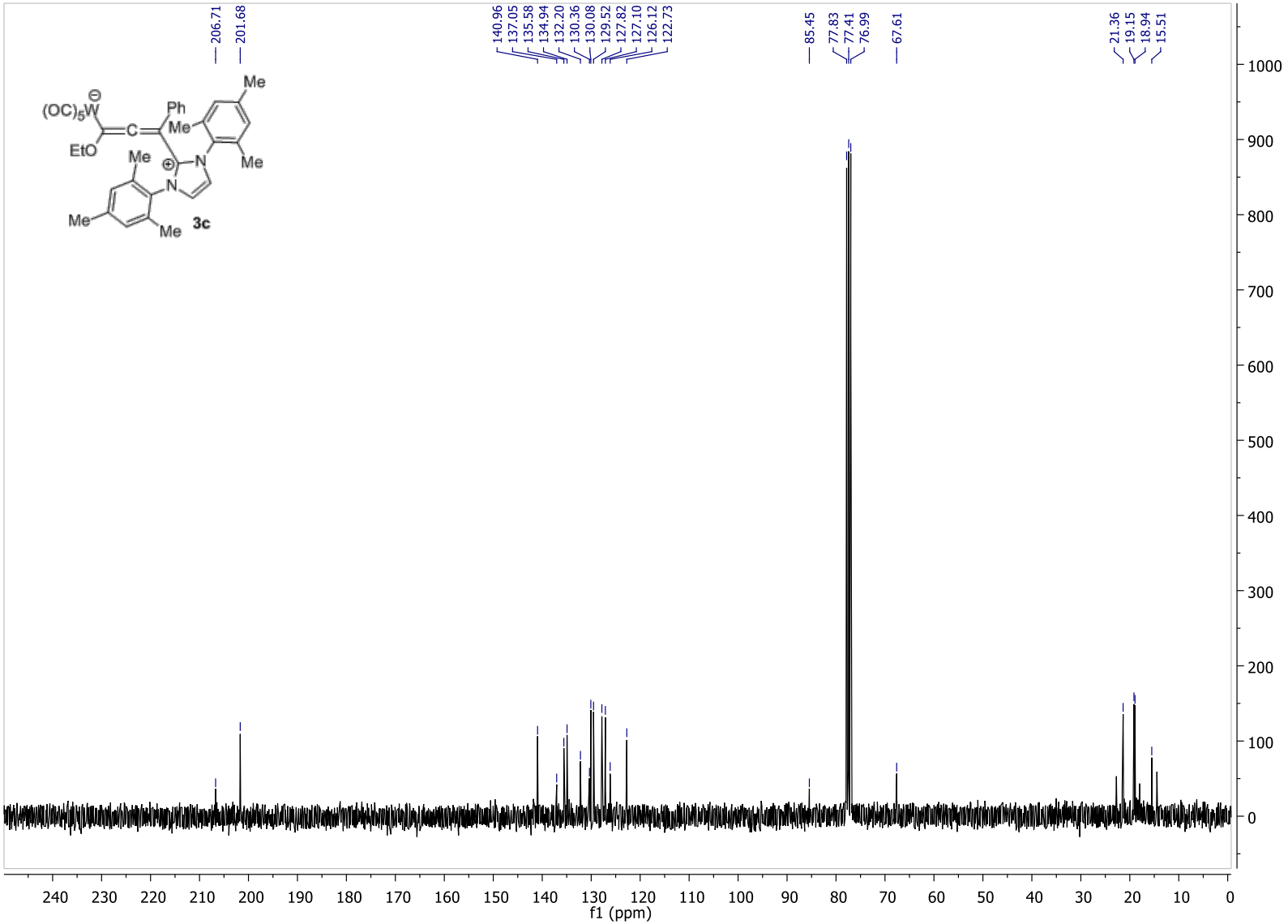

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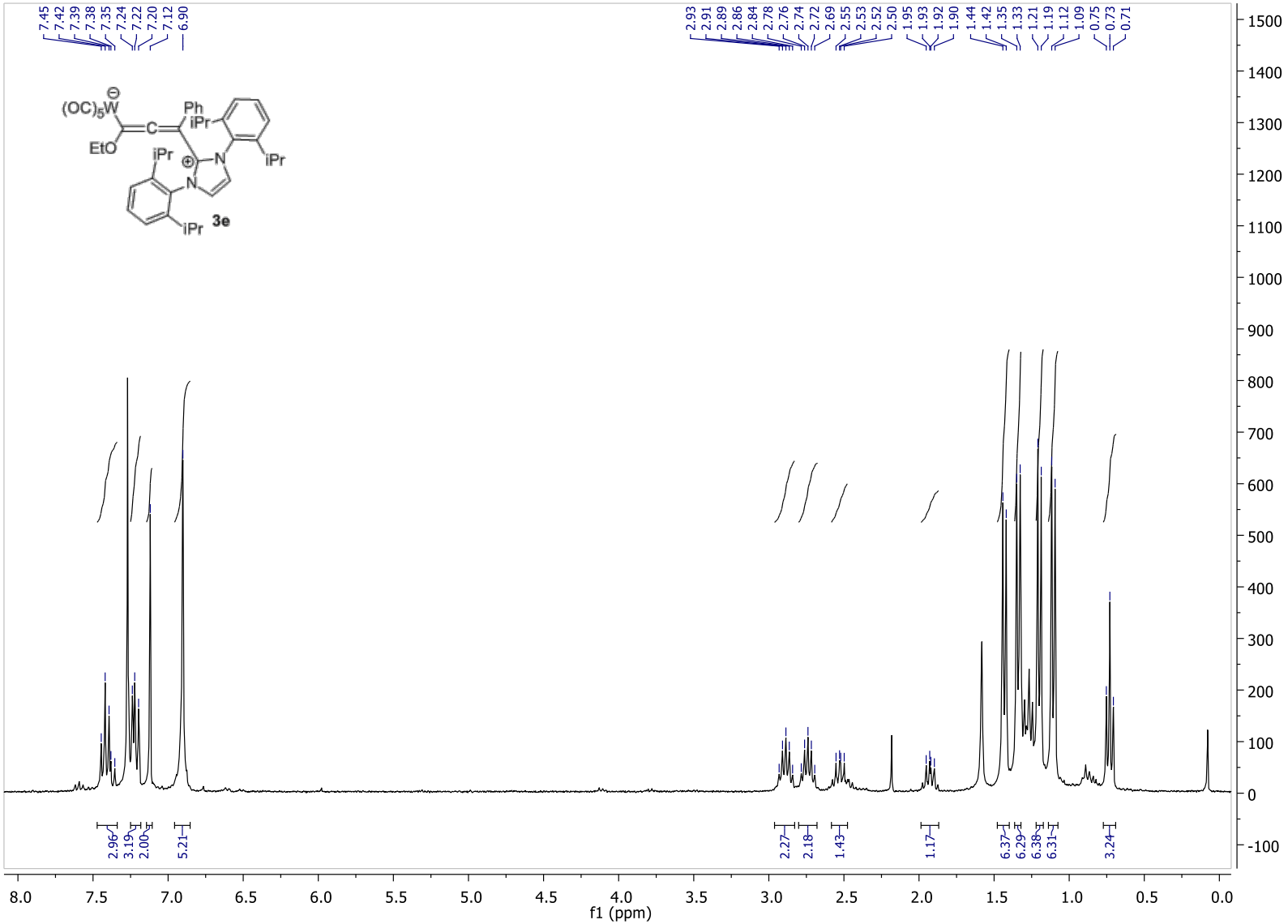

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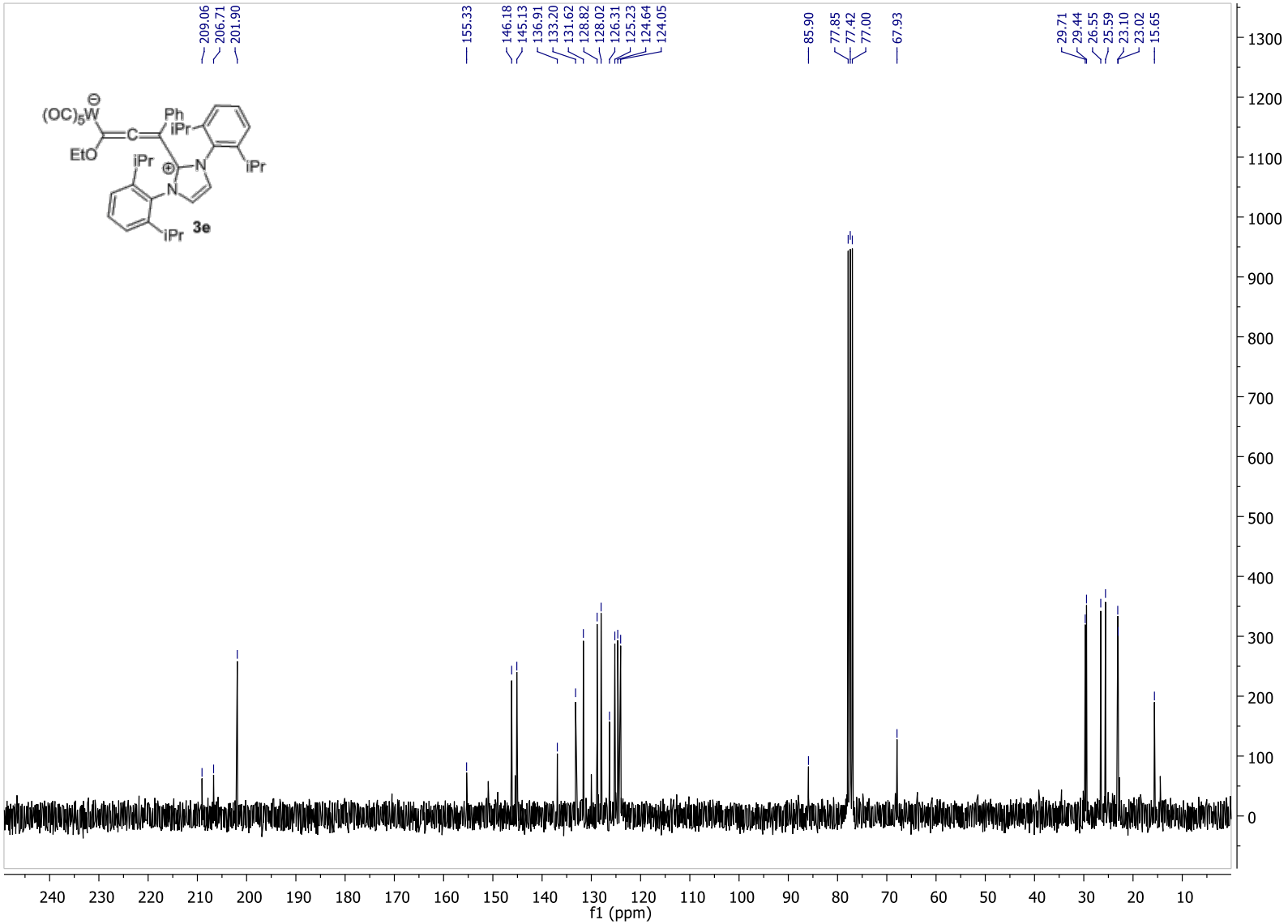

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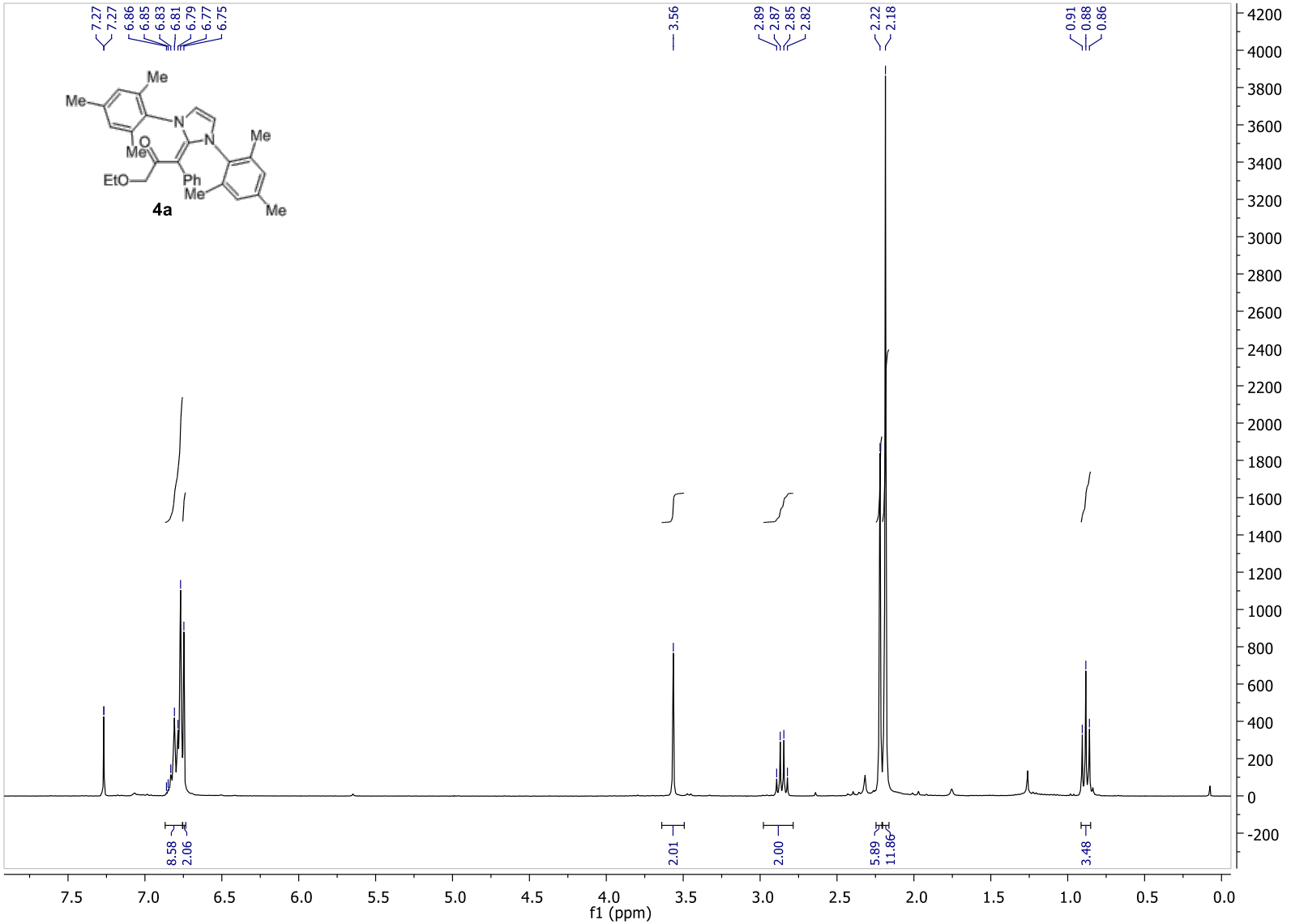

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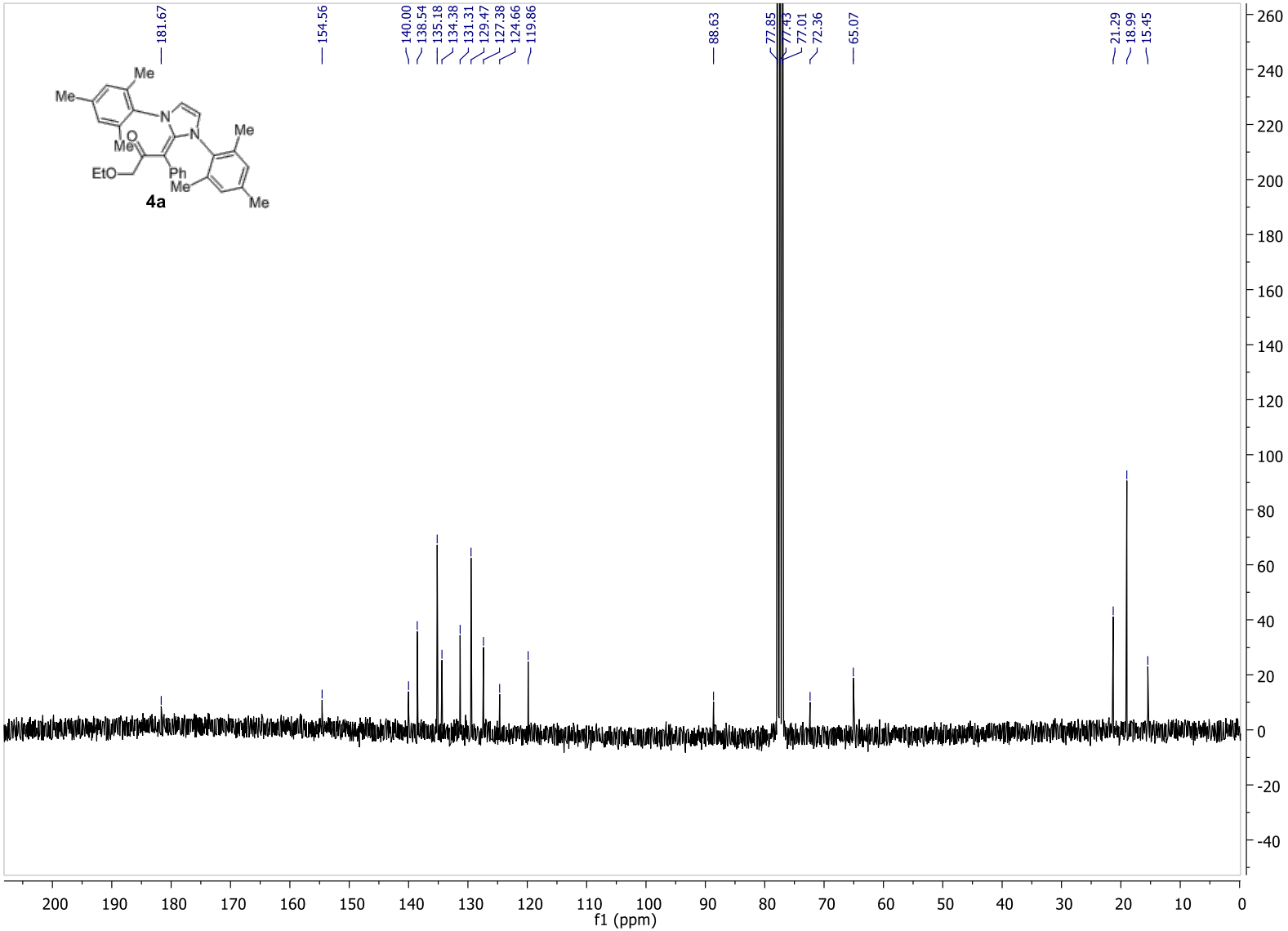

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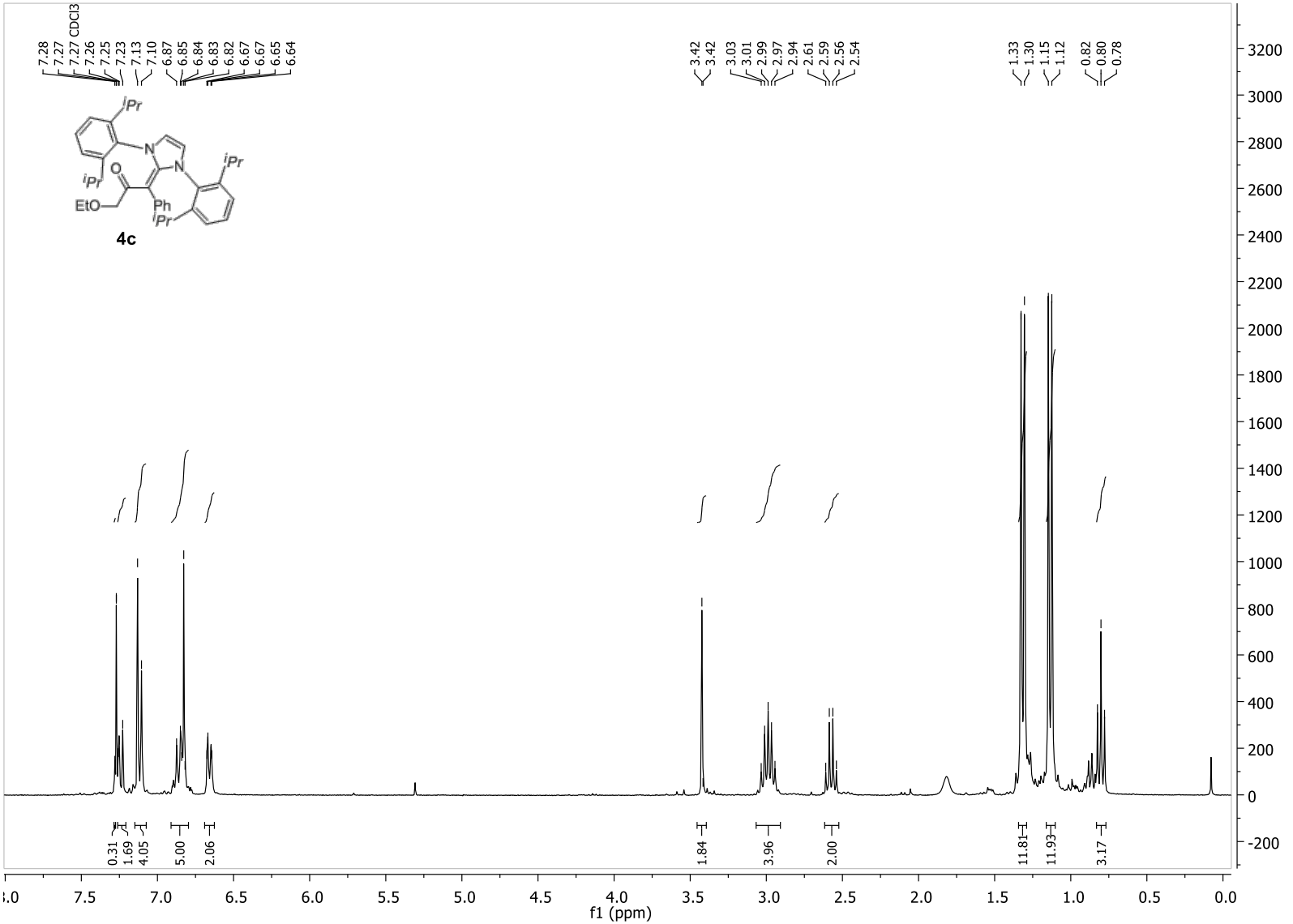

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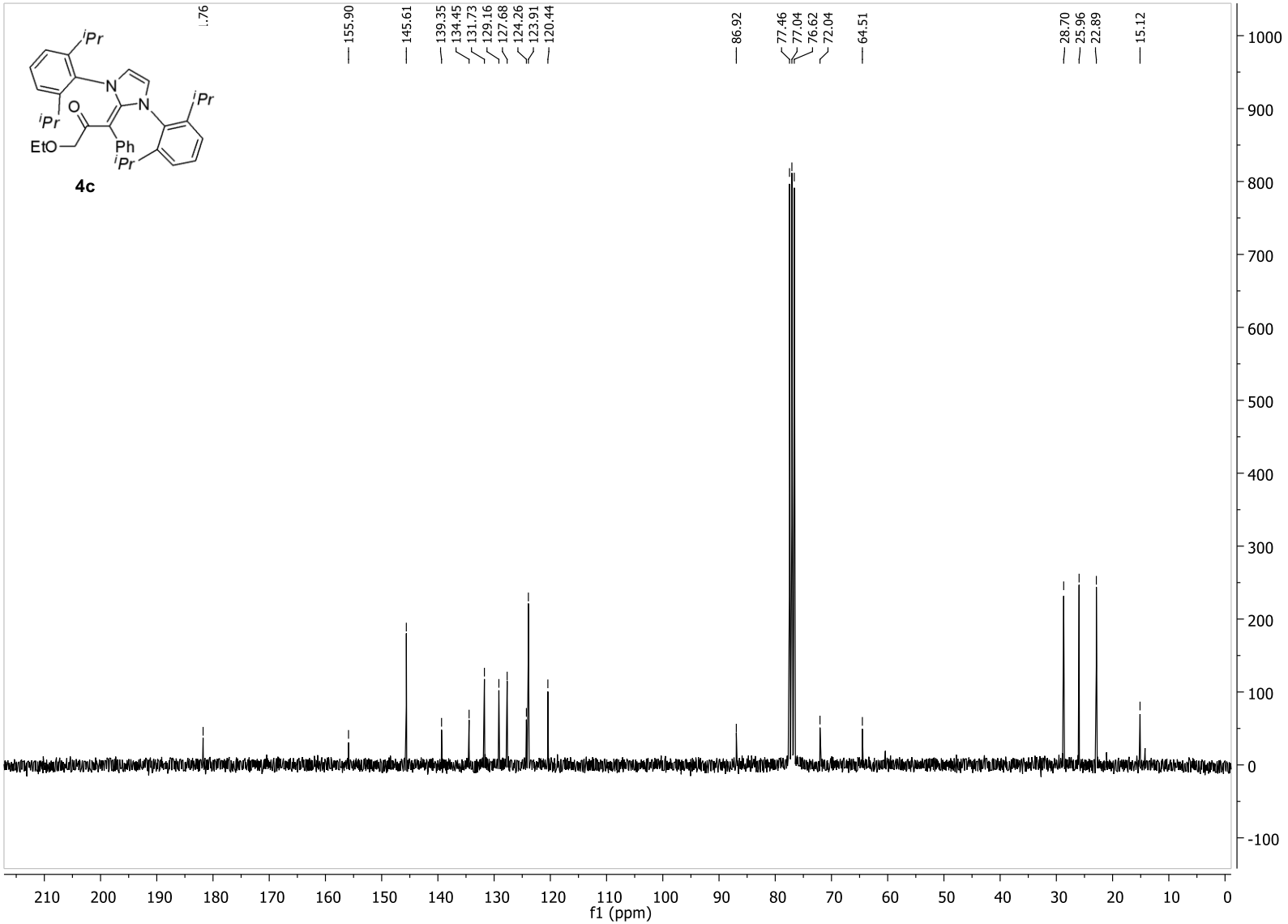

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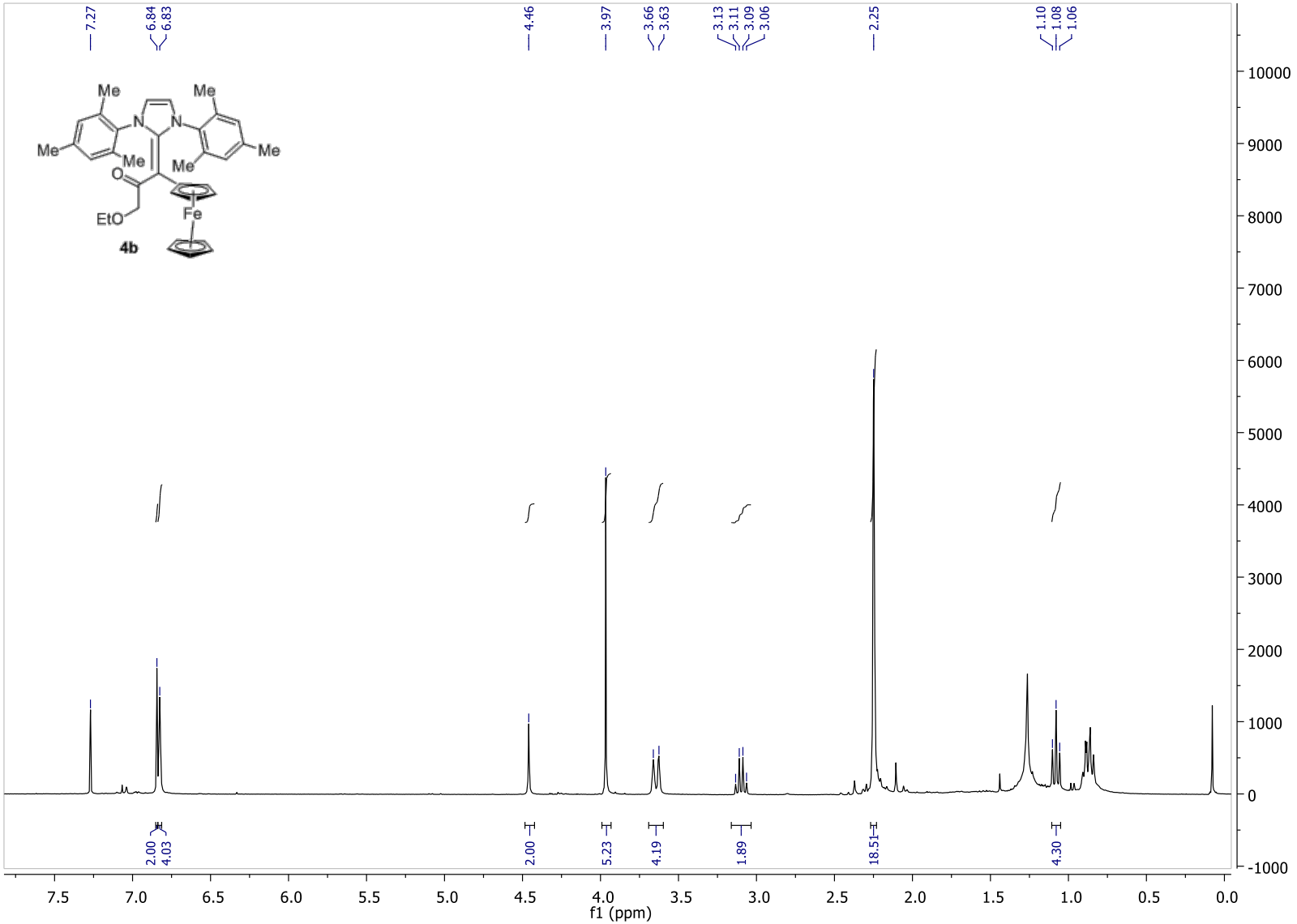

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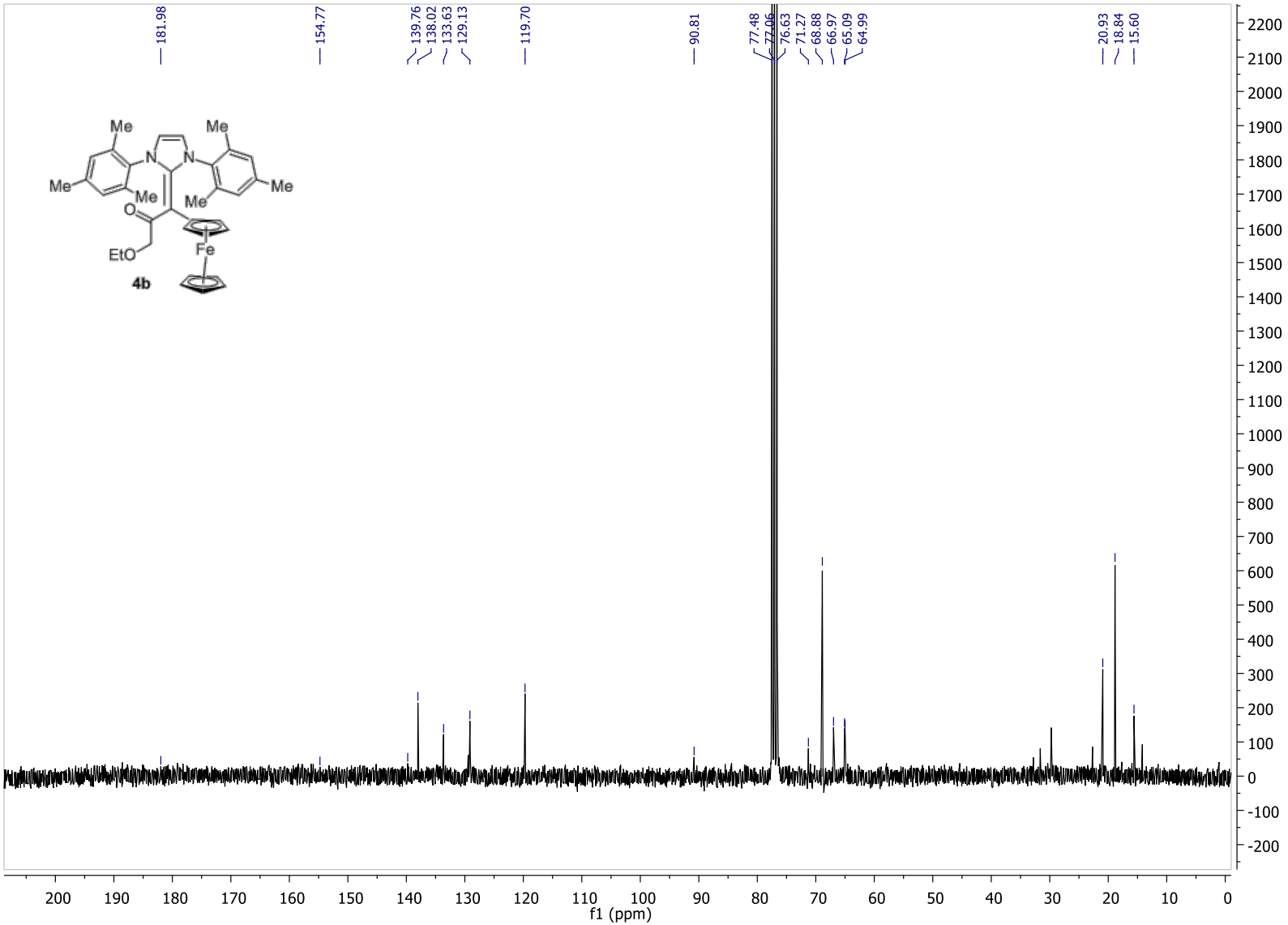

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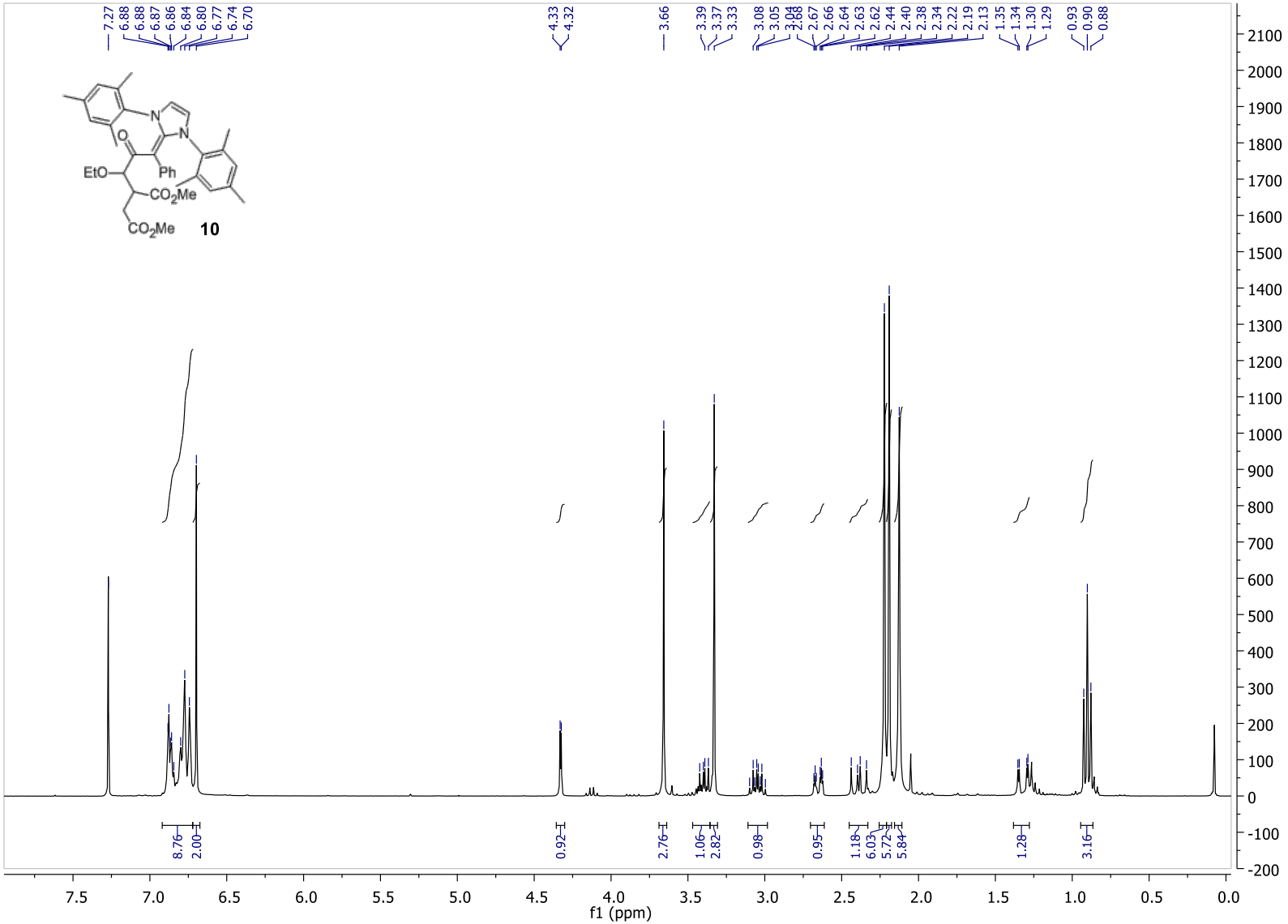

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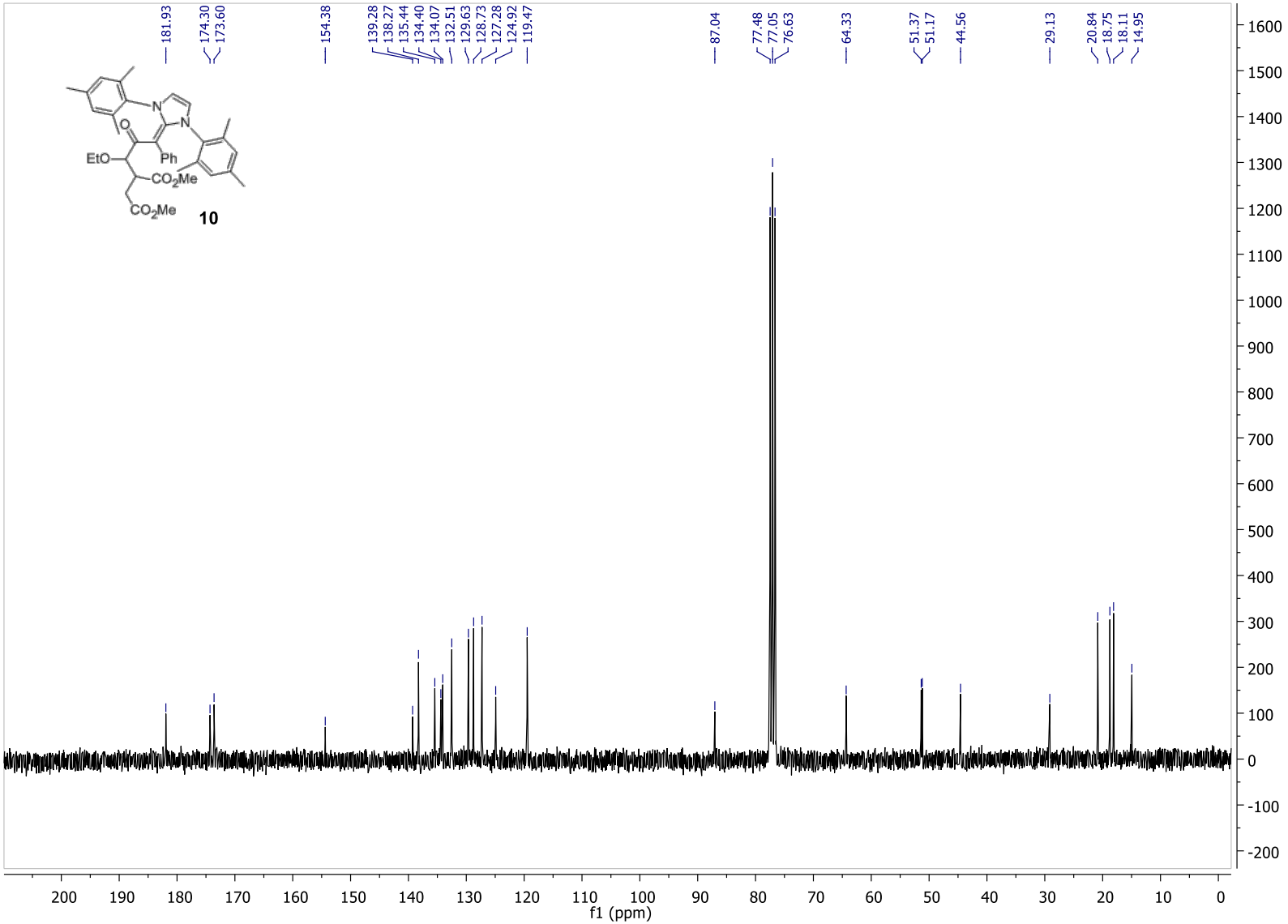

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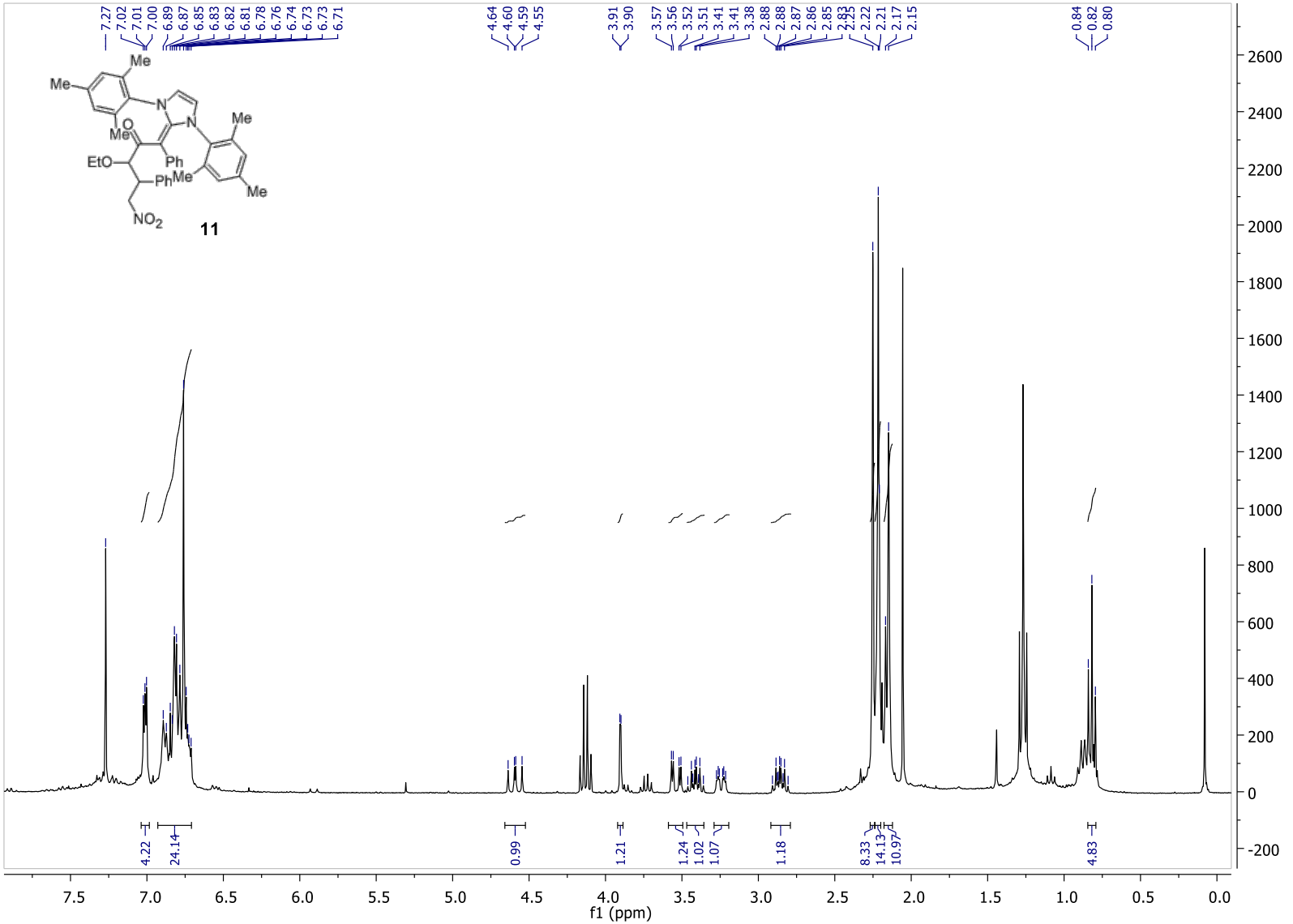

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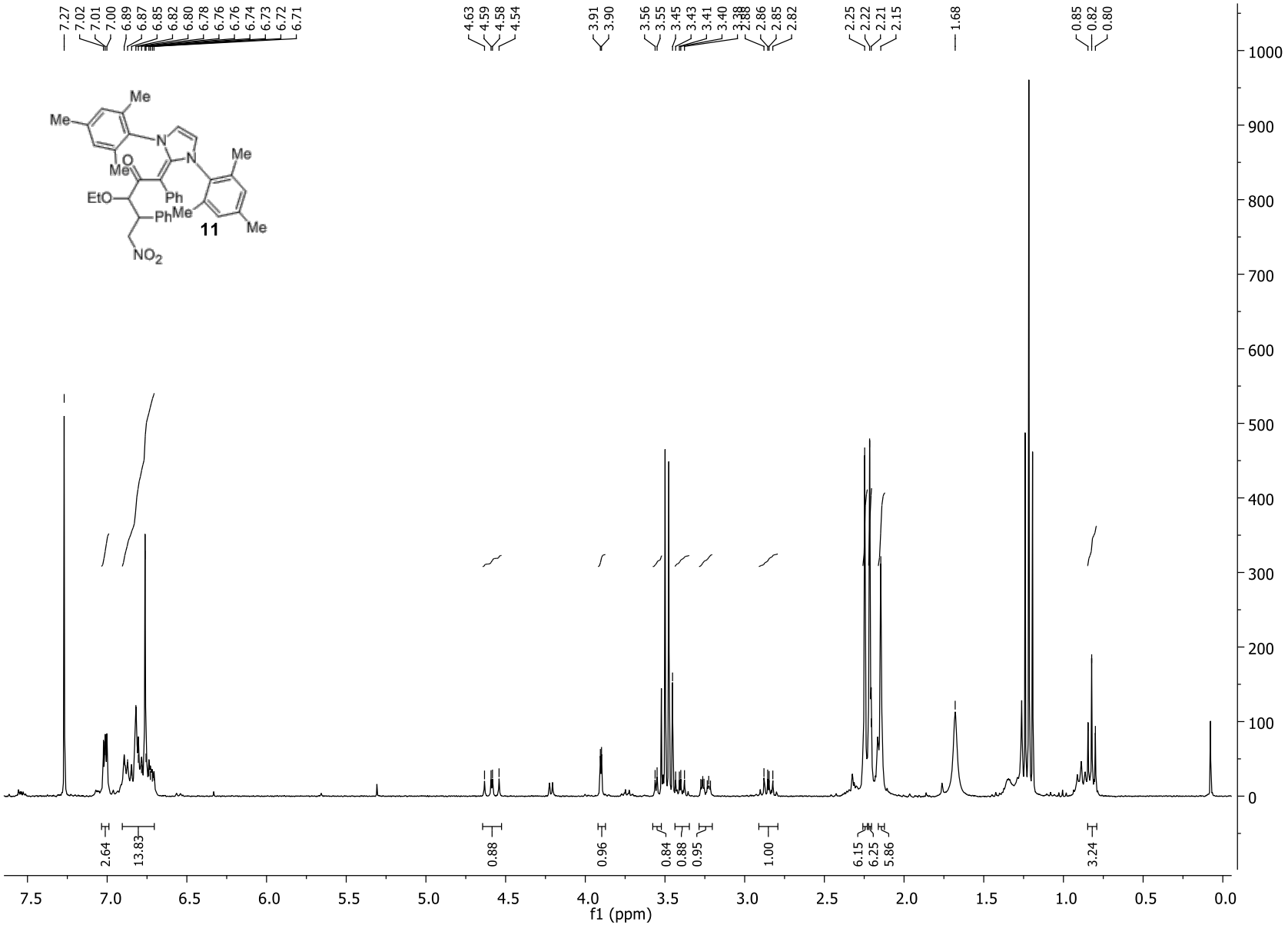

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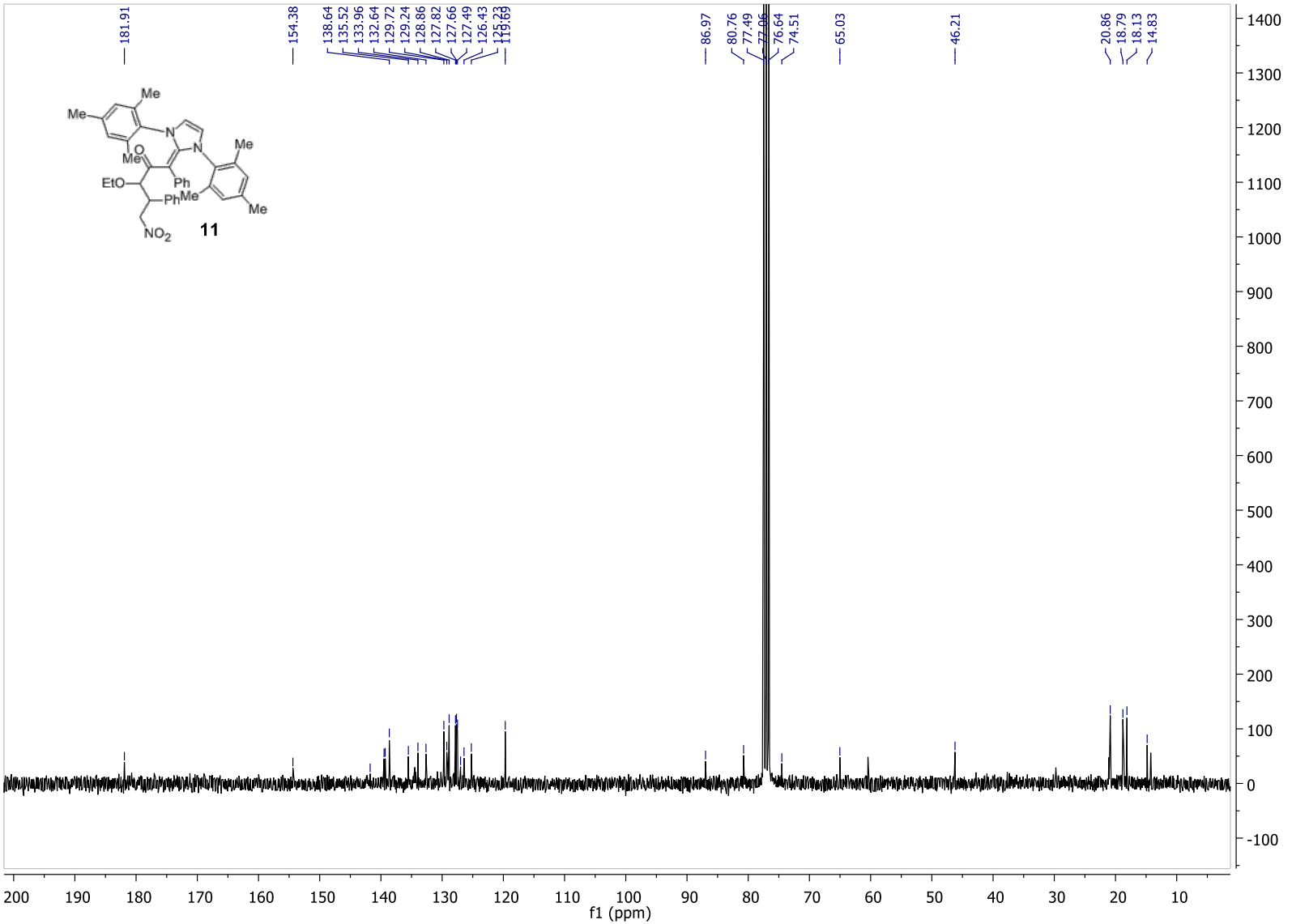

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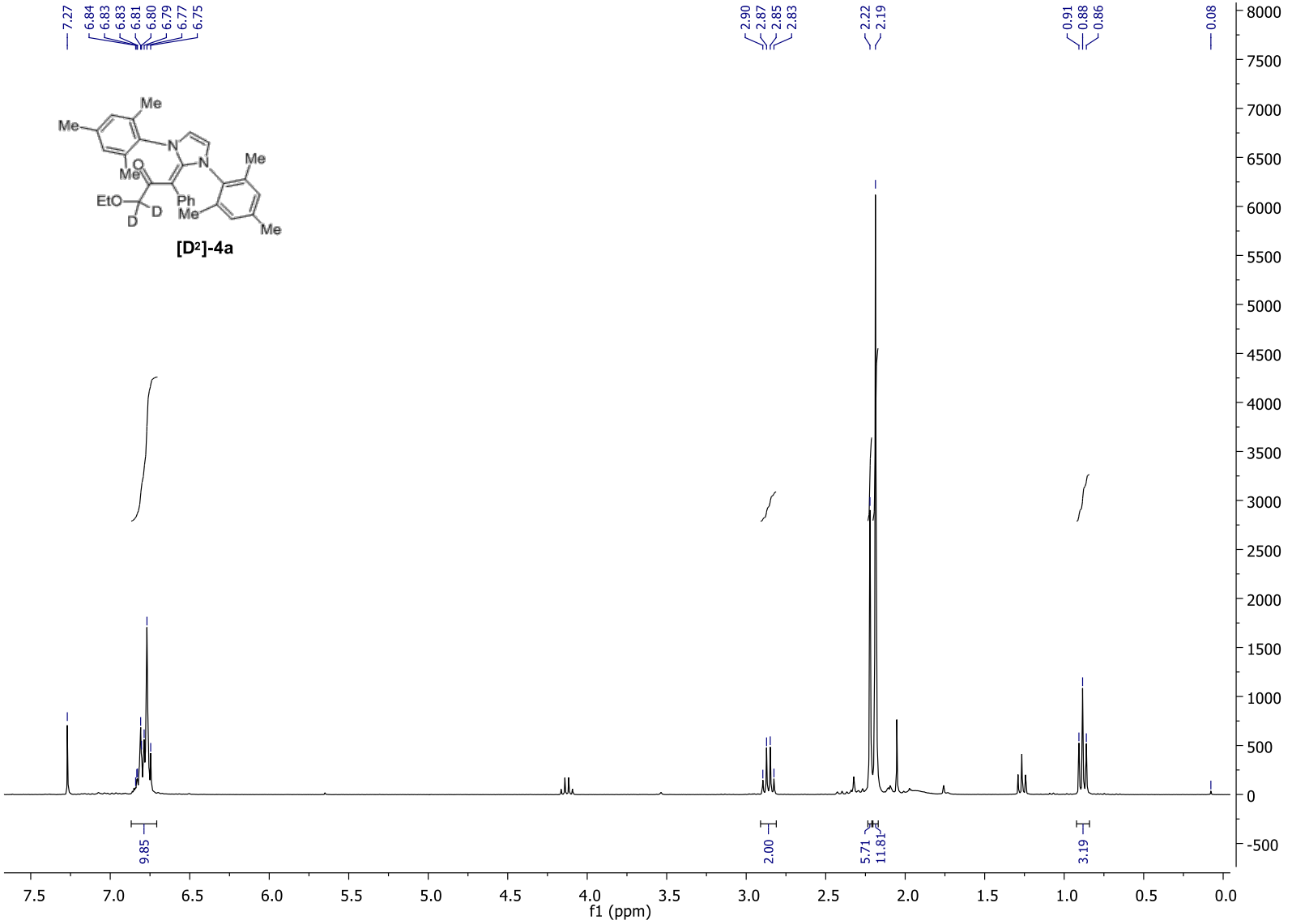

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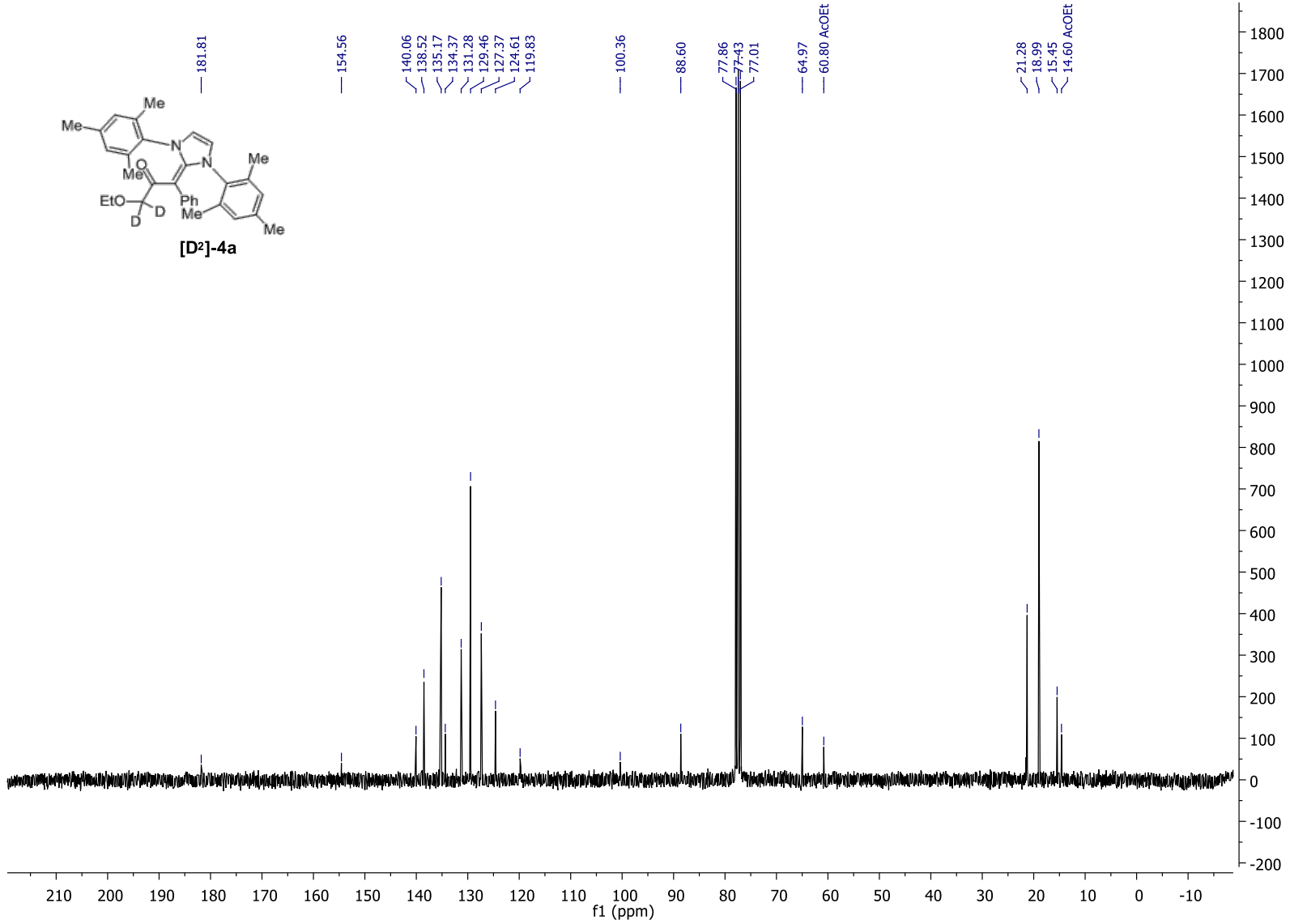

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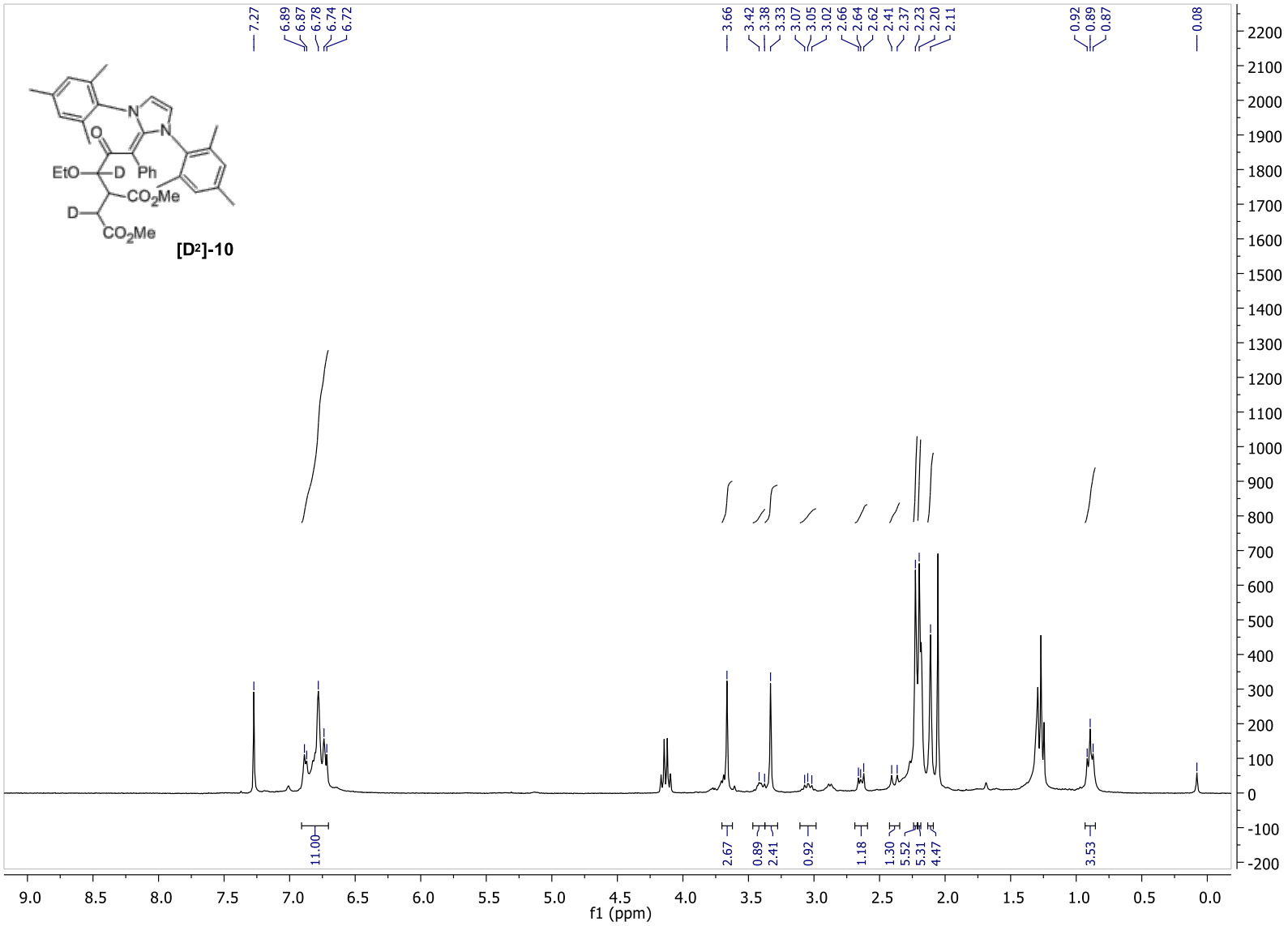

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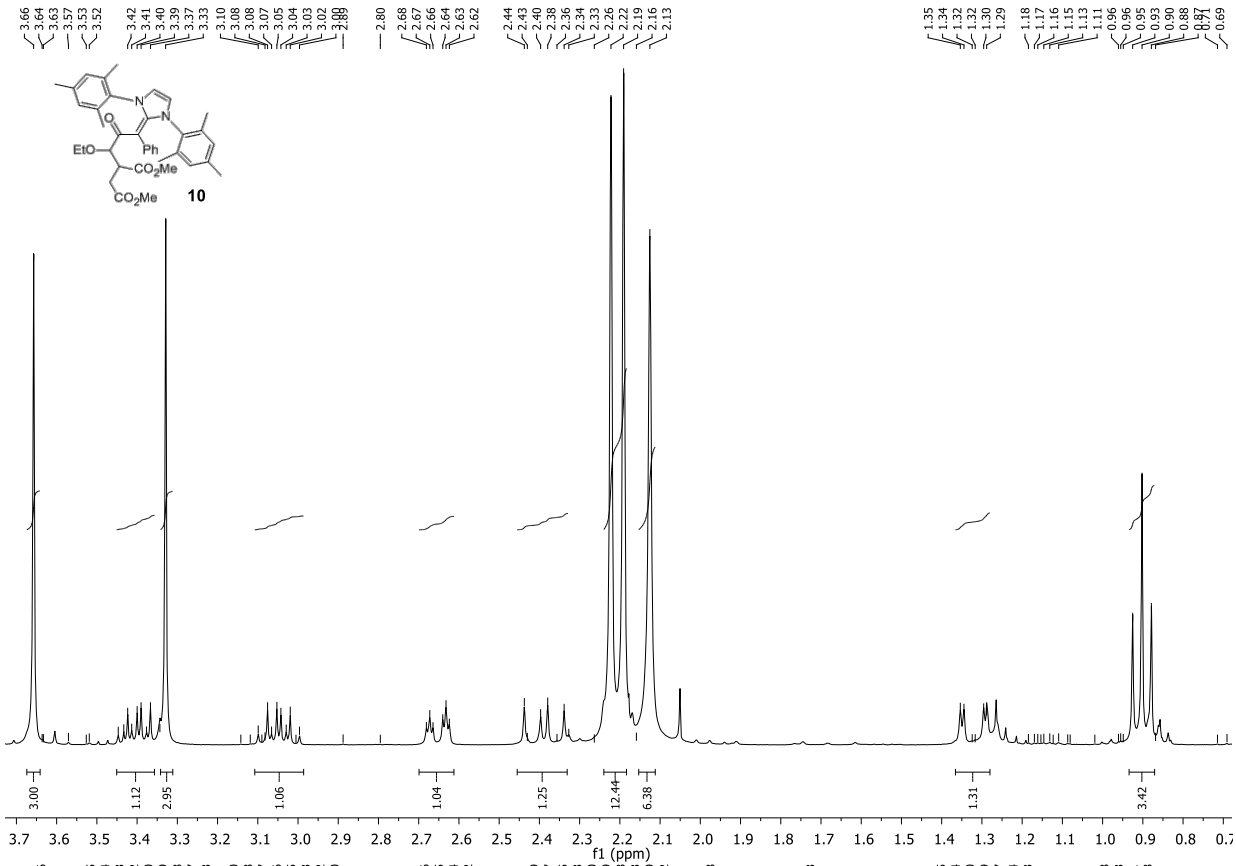

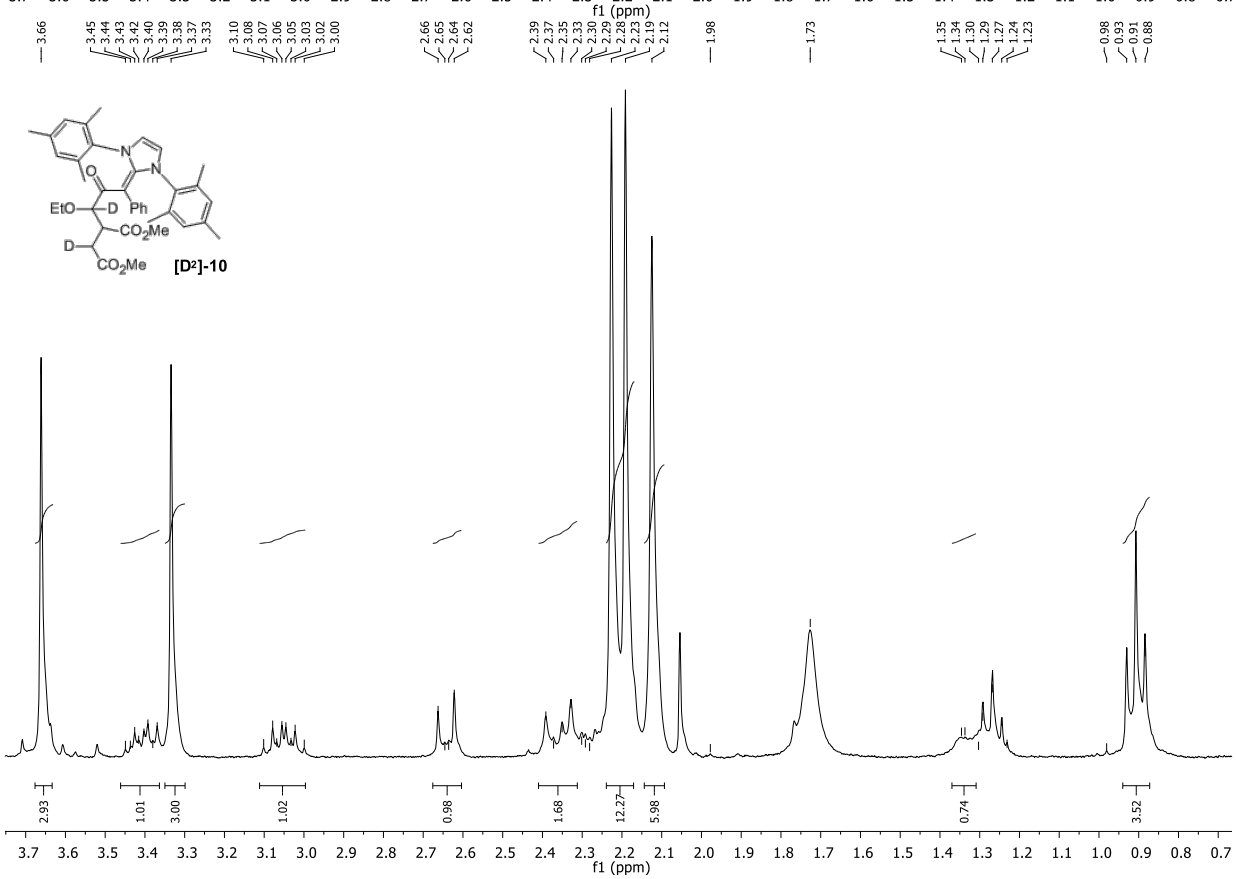

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