

Supporting Information

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Rhodium-Catalyzed Synthesis of 2,3-Disubstituted Indoles from β,β -Disubstituted Styryl Azides**

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General. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 500 MHz or 300 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were obtained by peak matching. Melting points are reported uncorrected. Infrared spectroscopy was obtained using a diamond attenuated total reflectance (ATR) accessory. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on 60Å (40 – 60 μm) mesh silica gel (SiO_2). Medium pressure liquid chromatography (MPLC) was performed to force flow the indicated solvent system down columns that had been packed with 60Å (40 – 60 μm) mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Acetonitrile, Methanol, Toluene, THF, Et_2O , and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.¹ Metal salts were stored in a nitrogen atmosphere dry box.

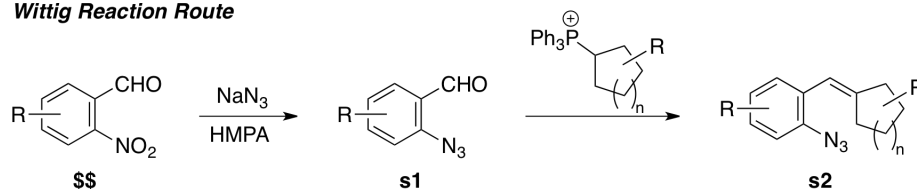
I. Preparation of Substrates using Wittig Reaction.

A. Routes to Substrates

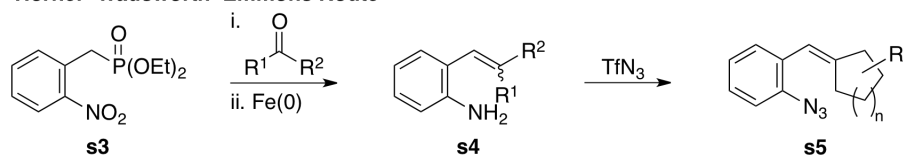
The styryl azides investigated in this study were synthesized by one three different routes (Scheme s1). The majority of the substrates were formed in two steps from commercially available *ortho*-nitro-substituted benzaldehydes starting by a nucleophilic aromatic substitution using NaN_3 , followed by a Wittig reaction. Alternatively the styryl azides were constructed from phosphonate **s3** using a Horner–Wadsworth–Emmons reaction of phosphonate **s3**, followed by an iron-mediated reduction to form aniline **s4**. Azidation then provided the required styryl azide. Finally styryl azides, **14b** and **14c**, were accessed from boronic acid **s5** and the corresponding vinyl triflate **s6**.

Scheme s1. Routes to Styryl Azides.

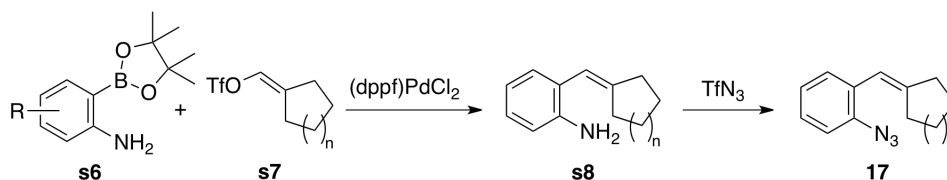
I. Wittig Reaction Route



II. Horner–Wadsworth–Emmons Route

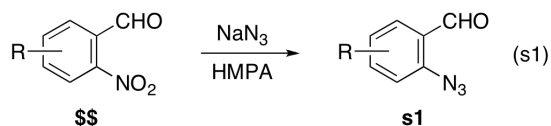


III. Suzuki Route



B. General Procedure for the Nucleophilic Substitution of 2-Nitrobenzaldehydes.

Following the procedure of Driver and co-workers,² the 2-azidobenzaldehydes were prepared. Yields were not optimized.

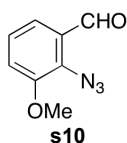


To a dry, stir bar-equipped scintillation vial were added 0.453 g of 2-nitro-benzaldehyde (3.0 mmol), 0.585 g of NaN_3 (9.0 mmol), and 9.0 mL of HMPA. The reaction was stirred overnight at room temperature, then was taken up in diethyl ether (100 mL) and washed with water (5×50 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo*. Purification with MPLC afford the 2-azido-benzaldehyde.

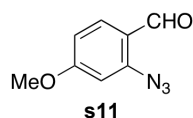
C. Synthesis of 2-Azidobenzaldehydes.



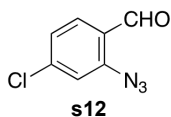
Benzaldehyde s9.² The general procedure was followed using 2.10 g of 2-nitrobenzaldehyde (13.9 mmol) and 2.92 g of NaN_3 (45.0 mmol, 3.3 eq) in 40 mL of HMPA. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow solid (1.70 g, 83%); mp 33 - 36 °C; The spectral data matched that reported by Driver and co-workers: ^1H NMR (500 MHz, CDCl_3) 10.25 (s, 1H), 7.79 (dd, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.54 (dt, $J = 1.5$ Hz, 8.0 Hz, 1H) 7.14 – 7.19 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 188.4 (CH), 142.8 (C), 135.4 (CH), 128.9 (CH), 126.9 (C), 124.8 (C), 119.1 (CH); IR (thin film): 2971, 2121, 1690, 1594, 1477, 1290, 1274 cm^{-1} .



Benzaldehyde s10. The general procedure was followed using 1.81 g of 2-nitro-3-methoxybenzaldehyde (10 mmol) and 1.31 g of NaN_3 (20 mmol) in 50 mL of HMPA at 50 °C. Purification of the reaction mixture using MPLC (1:30 EtOAc:hexanes) afforded the product as a white solid (1.61 g, 91%); mp 54 – 56 °C; ^1H NMR (500 MHz; CDCl_3) δ 10.15 (s, 1H), 7.82 (d, $J = 8.5$ Hz, 1H), 6.72 (dd, $J = 2.5$ Hz, 8.5 Hz, 1H), 6.67 (d, $J = 2.5$ Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.2 (CH), 165.3 (C), 144.9 (C), 131.1 (CH), 121.0 (C), 111.1 (CH), 103.9 (CH), 55.8 (CH_3); IR (thin film): 2359, 2341, 2110, 1723, 1264, 730, 703 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_8\text{H}_7\text{O}_2\text{N}_3$ (M^+) 177.05383, found 177.05529.

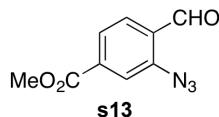


Benzaldehyde s11. The general procedure was followed using 1.81 g of 2-nitro-4-methoxybenzaldehyde (10 mmol) and 1.31 g of NaN_3 (20 mmol) in 50 mL of HMPA at 50 °C. Purification of the reaction mixture using MPLC (1:30 EtOAc: hexanes) afforded the product as a white solid (1.62 g, 92%); mp 73 – 75 °C; ^1H NMR (500 MHz; CDCl_3) δ 10.17 (s, 1H), 7.84 (d, $J = 9.0$ Hz, 1H), 6.74 (dd, $J = 2.5$ Hz, 9.0 Hz, 1H), 6.68 (d, $J = 2.5$ Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.2 (CH), 165.3 (C), 144.9 (C), 131.1 (CH), 121.1 (C), 111.1 (CH), 104.0 (CH), 55.8 (CH_3); IR (thin film): 3457, 3015, 2970, 2116, 1744, 1367, 1229, 750, 528 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_8\text{H}_7\text{O}_2\text{N}_3$ (M^+) 177.05383, found 177.05520.

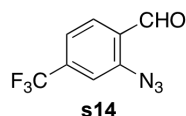


Benzaldehyde s12. The general procedure was followed using 1.85 g of 2-nitro-4-chlorobenzaldehyde (10 mmol) and 0.98 g of NaN_3 (15 mmol) in 50 mL of HMPA. Purification of the reaction mixture using MPLC (1:100 EtOAc:hexanes) afforded the product as a white solid (1.45 g, 80%); mp 91 – 93 °C; ^1H NMR (500 MHz; CDCl_3) δ 10.28 (s, 1H), 7.82 (d, $J = 8.5$ Hz, 1H), 7.26 (d, $J = 2.0$ Hz, 1H), 7.21 (dd, $J = 1.5$ Hz, 8.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.4 (CH), 144.0 (C), 141.7 (C), 130.2 (CH), 125.6 (CH), 125.4 (C),

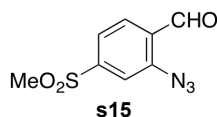
119.2 (CH); IR (thin film): 3455, 3016, 2969, 2123, 1739, 1366, 1216, 750, 528 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_7\text{H}_4\text{ON}_3\text{Cl}$ (M)⁺ 183.00134, found 183.00217.



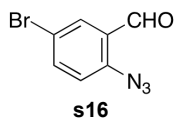
Benzaldehyde s13. The general procedure was followed using 2.09 g of methyl 4-formyl-3-nitrobenzoate (10 mmol) and 1.31 g of NaN_3 (20 mmol) in 50 mL of HMPA. Purification of the reaction mixture using MPLC (1:30 EtOAc: hexanes) afforded the product as a white solid (1.95 g, 95 %); mp 112 – 114 °C; ^1H NMR (500 MHz; CDCl_3) δ 10.38 (s, 1H), 7.94 – 7.92 (m, 2H), 7.85 – 7.83 (m, 1H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 188.1 (CH), 165.3 (C), 143.1 (C), 136.2 (C), 129.4 (C), 129.1 (CH), 125.6 (CH), 120.3 (C), 52.8 (CH₃); IR (thin film): 3458, 3015, 2970, 2122, 1738, 1366, 1216, 762, 527 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_9\text{H}_7\text{O}_3\text{N}_3$ (M)⁺ 205.04875, found 205.04990.



Benzaldehyde s14.³ The general procedure was followed using 2.69 g of 2-nitro-4-trifluoromethylbenzaldehyde (12.3 mmol) and 2.21 g of NaN_3 (34.0 mmol) in 50 mL of HMPA. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a yellow solid (2.49 g, 94%); mp 89 -91 °C; The spectral data matched that reported by Driver and co-workers:² ^1H NMR (500 MHz, CDCl_3) 10.38 (s, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.50 (s, 1H) 7.48 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 187.5 (CH), 143.5 (C), 136.8 (q, $J_{\text{CF}} = 31.4$ Hz, C), 129.8 (CH), 126.1 (C), 122.9 (q, $J_{\text{CF}} = 270.9$ Hz, C), 121.6 (q, $J_{\text{CF}} = 3.5$ Hz, CH) 116.3 (q, $J_{\text{CF}} = 36.3$ Hz, CH); ^{19}F NMR (CDCl_3 , 282 MHz) δ -61.10; IR (thin film): 2980, 2901, 2122, 1689, 1414, 1392, 1328, 1072, 750 cm^{-1} .

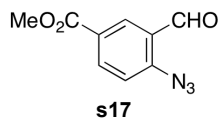


Benzaldehyde s15. The general procedure was followed using 2.29 g of 4-(methylsulfonyl)-2-nitrobenzaldehyde (10 mmol) and 1.31 g of NaN_3 (20 mmol) in 50 mL of HMPA. Purification of the reaction mixture using MPLC (1:10 EtOAc: hexanes) afforded the product as a white solid (1.96 g, 87%); mp 125 – 127 °C; ^1H NMR (500 MHz; CDCl_3) δ 10.40 (s, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.85 (s, 1H), 7.5 (d, $J = 8.0$ Hz, 1H), 3.12 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.3 (CH), 146.5 (C), 144.1 (C), 130.3 (CH), 129.8 (C), 132.3 (CH), 118.4 (CH), 44.2 (CH₃); IR (thin film): 3023, 2925, 2852, 2115, 1681, 1398, 1279, 1159, 1135 cm^{-1} .



Benzaldehyde s16.⁴ The general procedure was followed using 2.03 g of 2-nitro-5-bromobenzaldehyde (10 mmol) and 1.3 g of NaN_3 (20 mmol) in 40 mL of DMSO at 50 °C. Purification of the reaction mixture using MPLC (1:100 EtOAc:hexanes) afforded the product as a white solid (2.19 g, 97%); mp 94 – 96 °C; ^1H NMR (500 MHz; CDCl_3) δ 10.27 (s, 1H), 7.98 (d, $J = 2.5$ Hz, 1H), 7.70 (dd, $J = 2.5$ Hz, 8.5 Hz, 1H), 7.16 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.1 (CH), 141.9 (C), 138.0 (CH), 131.7 (CH), 128.0 (C), 120.8

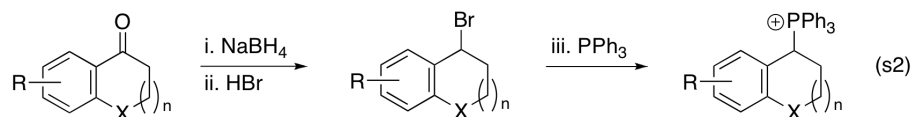
(CH), 118.3 (C); IR (thin film): 3457, 3005, 2970, 2130, 1725, 1368, 1214, 750, 527 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_7\text{H}_4\text{ON}_3\text{Br}$ (M^+) 224.95377, found 224.95459.



Benzaldehyde s17. The general procedure was followed using 2.09 g of methyl 3-formyl-4-nitrobenzoate (10 mmol) and 1.31 g of NaN_3 (20 mmol) in 50 mL of HMPA. Purification of the reaction mixture using MPLC (1:30 EtOAc:hexanes) afforded the product as a white solid (1.97 g, 96%); mp 118 –110 $^\circ\text{C}$; ^1H NMR (500 MHz; CDCl_3) δ 10.31 (s, 1H), 8.49 (d, $J = 2.0$ Hz, 1H), 8.23 (dd, $J = 2.0$ Hz, 8.5 Hz, 1H), 7.31 (d, $J = 8.5$ Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.7 (CH), 165.4 (C), 146.8 (C), 136.0 (CH), 130.8 (CH), 127.0 (C), 127.6 (C), 119.2 (CH), 52.4 (CH_3); IR (thin film): 3458, 3015, 2970, 2122, 1738, 1366, 1216, 762, 527 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_9\text{H}_7\text{O}_3\text{N}_3$ (M^+) 205.04875, found 205.04980.

D. General Procedure for the Phosphonium Salt Synthesis.

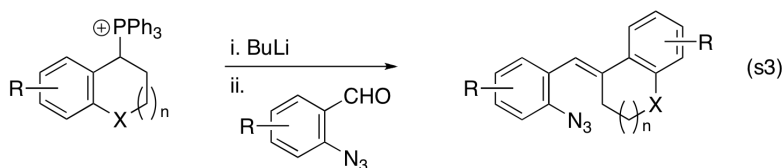
Unless otherwise noted, the phosphonium salt was synthesized from the corresponding cycloketone. Yields were not optimized.



To a solution of 2.92 g of α -tetralone (20 mmol) in 30 mL of EtOH was added 1.52 g of NaBH_4 (40 mmol). The mixture was monitored by thin layer chromatography. Once the starting material spot had disappeared, the mixture was concentrated *in vacuo*, and the resulting material was diluted with 50 mL of water. The resulting aqueous mixture was extracted with dichloromethane (3×10 mL). The organic phase (containing the alcohol) was treated with proportional HBr. The progress of the reaction was monitored by thin layer chromatography. Once the alcohol completely consumed, the mixture was diluted with 100 mL of water, then extracted with dichloromethane (3×20 mL). The resulting organic phase was dried over Na_2SO_4 . The mixture was filtered and the filtrate was concentrated *in vacuo* to afford bromide. To a solution of the bromide in 60 mL of PhMe was added 5.76 g of PPh_3 . The reaction mixture was heated to reflux. After 16h, the mixture was cooled down to room temperature, then filtrated. The solid was washed with diethyl ether (3×30 mL), and dried under high vacuum to afford phosphonium salt.

E. General Procedure for the Wittig Reaction of 2-Azidobenzaldehydes.

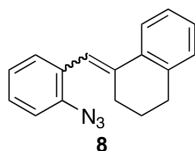
Following the procedure of Scott and co-workers,⁵ the 2-azidobenzaldehydes were prepared. Yields were not optimized.



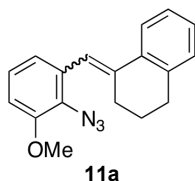
To a solution of 4.0 mmol of the phosphonium salt in 12 mL of THF at -78 $^\circ\text{C}$, was added 1.6 mL of *n*-BuLi (2.5 M in hexanes, 4.0 mmol) dropwise. After stirring 1h at -78 $^\circ\text{C}$, the mixture was warmed to room

temperature and stirred additional one hour. Then 0.647 g of 2-azidobenzaldehyde (4.4 mmol) was added and the mixture was stirred for 1 h at ambient temperature. The resulting mixture was diluted with 15 mL of water and extracted with CH₂Cl₂ (3 × 10 mL). The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated in *vacuo*. Purification of the reaction mixture using MPLC afforded the product.

E. Synthesis of Styryl Azides.

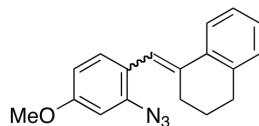


Styryl Azide 8. The general procedure was followed using 1.94 g of 2-azidobenzaldehyde **s9** (13.2 mmol), 6.85 g of the phosphonium salt (14.5 mmol), 5.8 mL of a 2.5 M solution of BuLi in hexanes in 50 mL of THF. Purification by MPLC (pure hexanes) afforded the product as a white powder, as an 84:16 mixture of *E*- and *Z*-isomers (2.24 g, 65%); R_f = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (*E*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.80 - 7.99 (m, 1H), 7.33 - 7.37 (m, 2H), 7.13 - 7.26 (m, 5H), 7.07 (s, 1H), 2.91 (t, *J* = 6.5 Hz, 2H), 2.71 (t, *J* = 6.0 Hz, 2H), 1.87 - 1.92 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 138.7 (C), 138.6 (C), 137.9 (C), 135.9 (C), 130.9 (CH), 130.1 (C), 129.2 (CH), 128.1 (CH), 127.6 (CH), 126.2 (CH), 124.7 (CH), 124.3 (CH), 118.7 (CH), 118.4 (CH); 30.4 (CH₂), 28.2 (CH₂), 23.8 (CH₂); Selected spectral data for the minor (*Z*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.13 - 7.26 (m, 5H), 7.07 - 7.08 (m, 1H), 6.95 - 6.98 (m, 1H), 6.85 - 6.88 (m, 1H), 6.47 (s, 1H), 2.95 (t, *J* = 6.5 Hz, 2H), 2.63 (t, *J* = 6.5 Hz, 2H), 2.05 - 2.10 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 139.8 (C), 138.7 (C), 138.0 (C), 134.7 (C), 131.3 (CH), 130.1 (C), 128.9 (CH), 128.0 (CH), 127.6 (CH), 124.7 (CH), 124.5 (CH), 119.9 (CH), 118.5 (CH), 35.0 (CH₂), 29.7 (CH₂), 24.2 (CH₂); Selected spectral data for the mixture: δ IR (thin film): 2117, 2083, 1486, 1445, 756, 745 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₇H₁₅N₃ (*M* - N₂)⁺ 261.12660, found 261.12679.



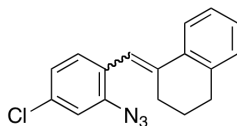
Styryl Azide 11a. The general procedure was followed using 0.58 g of 2-azido-3-methoxybenzaldehyde **s10** (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:50 EtOAc:hexanes) afforded the product as a white powder, as a 76:24 mixture of *E*- and *Z*-isomers (0.63 g, 72%). Selected spectral data for the major (*E*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.76 - 7.74 (m, 1H), 7.23 - 7.21 (m, 2H), 7.14 - 7.04 (m, 3H), 6.93 - 6.90 (m, 1H), 6.84 - 6.82 (m, 1H), 3.93 (s, 3H), 2.88 (t, *J* = 6.5 Hz, 2H), 2.66 (dt, *J* = 1.5 Hz, 6.0 Hz, 2H), 1.86 (pent, *J* = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 153.9 (C), 138.5 (C), 137.8 (C), 135.9 (C), 131.8 (C), 129.2 (CH), 127.6 (CH), 126.9 (C), 126.2 (CH), 124.6 (CH), 124.6 (CH), 122.8 (CH), 119.4 (CH), 110.2 (CH), 56.1 (CH₃), 30.3 (CH₂), 28.2 (CH₂), 23.7 (CH₂); Selected spectral data for the minor (*Z*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.27 - 7.25 (m, 1H), 7.14 - 7.04 (m, 3H), 6.88 - 6.85 (m, 1H), 6.75 - 6.71 (m, 2H), 6.41 (s, 1H), 3.91 (s, 3H), 2.92 (t, *J* = 6.5 Hz, 2H), 2.60 (dt, *J* = 1.5 Hz, 6.0 Hz, 2H), 2.04 (pent, *J* = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 153.9 (C), 139.5 (C), 138.8 (C), 134.8 (C), 132.5 (C), 129.0 (CH), 128.8 (CH), 127.5 (CH), 125.7 (CH), 125.0 (C), 124.8 (CH), 123.1 (CH), 120.5 (CH), 109.9 (CH), 56.0 (CH₃), 34.9 (CH₂), 29.7 (CH₂), 24.2 (CH₂); Selected

spectral data for the mixture: δ IR (thin film): 2933, 2103, 1756, 1450, 1262, 1087, 737 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{ON}$ ($\text{M}-\text{N}_2$)⁺ 263.13102, found 163.132000.



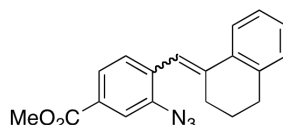
11b

Styryl Azide 11b. The general procedure was followed using 0.58 g of 2-azido-4-methoxybenzaldehyde **s11** (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:50 EtOAc: hexanes) afforded the product as a white powder, as an 83:17 mixture of *E*- and *Z*-isomers (0.37 g, 43%). Selected spectral data for the major (*E*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.74 – 7.72 (m, 1H), 7.26 (d, $J = 8.5$ Hz, 1H), 7.23 – 7.19 (m, 2H), 7.14 – 7.12 (m, 1H), 6.97 (s, 1H), 6.74 – 6.71 (m, 2H), 3.87 (s, 3H), 2.87 (t, $J = 6.5$ Hz, 2H), 2.67 (dt, $J = 1.5$ Hz, 6.0 Hz, 2H), 1.87 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.5 (C), 139.6 (C), 137.7 (C), 137.5 (C), 136.1 (C), 131.7 (CH), 129.1 (CH), 127.4 (CH), 126.2 (CH), 124.5 (CH), 122.8 (C), 118.3 (CH), 110.0 (CH), 104.2 (CH), 55.5 (CH_3), 30.3 (CH_2), 28.1 (CH_2), 23.7 (CH_2); Selected spectral data for the minor (*Z*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.23 – 7.19 (m, 1H), 7.10 – 7.05 (m, 3H), 6.86 (t, $J = 6.5$ Hz, 1H), 6.69 (d, $J = 2.5$ Hz, 1H), 6.51 (dd, $J = 2.5$ Hz, 8.5 Hz, 1H), 6.33 (s, 1H), 3.83 (s, 3H), 2.91 (t, $J = 6.5$ Hz, 2H), 2.57 (dt, $J = 1.5$ Hz, 6.0 Hz, 2H), 2.03 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.5 (C), 138.7 (C), 134.9 (C), 132.7 (C), 132.0 (CH), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.5 (C), 124.7 (CH), 123.1 (C), 119.4 (CH), 110.6 (CH), 104.0 (CH), 55.4 (CH_3), 34.9 (CH_2), 29.7 (CH_2), 24.2 (CH_2); Selected spectral data for the mixture: δ IR (thin film): 2935, 2101, 1753, 1436, 1266, 1084, 739 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{ON}_3$ (M)⁺ 291.13717, found 291.13649.



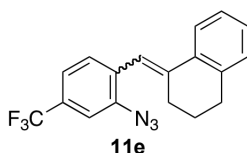
11c

Styryl Azide 11c. The general procedure was followed using 0.60 g of 2-azido-4-chlorobenzaldehyde **s12** (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a white powder, as an 82:18 mixture of *E*- and *Z*-isomers (0.49 g, 55%). Selected spectral data for the major (*E*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.71 – 7.70 (m, 1H), 7.26 – 7.20 (m, 3H), 7.16 (d, $J = 2.0$ Hz, 1H), 7.13 – 7.12 (m, 2H), 6.91 (s, 1H), 2.86 (t, $J = 6.5$ Hz, 2H), 2.62 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 1.85 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.8 (C), 139.3 (C), 137.9 (C), 135.6 (C), 133.3 (C), 131.8 (CH), 129.2 (CH), 128.6 (C), 127.8 (CH), 126.3 (CH), 124.6 (CH), 124.6 (CH), 118.6 (CH), 117.6 (CH), 30.3 (CH_2), 28.2 (CH_2), 23.7 (CH_2); Selected spectral data for the minor (*Z*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.23 – 7.19 (m, 1H), 7.11 – 7.09 (m, 1H), 7.04 (d, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.88 (dd, $J = 2.0$ Hz, 8.5 Hz, 1H), 6.84 (t, $J = 6.0$ Hz, 1H), 6.27 (s, 1H), 2.89 (t, $J = 6.5$ Hz, 2H), 2.56 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 2.03 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 140.6 (C), 139.2 (C), 139.0 (C), 134.4 (C), 133.2 (C), 132.3 (CH), 129.1 (C), 129.0 (CH), 128.8 (CH), 124.8 (CH), 124.8 (CH), 124.6 (CH), 118.7 (CH), 118.6 (CH), 34.9 (CH_2), 29.7 (CH_2), 24.1 (CH_2); Selected spectral data for the mixture: δ IR (thin film): 2931, 2109, 1738, 1486, 1286, 756 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{Cl}$ (M)⁺ 295.08762, found 295.08889.



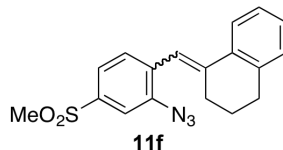
11d

Styryl Azide 11d. The general procedure was followed using 0.68 g of methyl 3-azido-4-formylbenzoate **s13** (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:50 EtOAc: hexanes) afforded the product as a white powder, as an 83:17 mixture of *E*- and *Z*-isomers (0.39 g, 41%). Selected spectral data for the major (*E*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 1.5$ Hz, 1H), 7.80 (dd, $J = 1.5$ Hz, 8.0 Hz, 1H), 7.73 (dd, $J = 3.5$ Hz, 5.5 Hz, 1H), 7.39 (d, $J = 3.0$ Hz, 1H), 7.22 (dd, $J = 3.5$ Hz, 5.5 Hz, 2H), 7.14 – 7.12 (m, 1H), 7.00 (s, 1H), 3.95 (s, 3H), 2.87 (t, $J = 6.5$ Hz, 2H), 2.67 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 1.86 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.2 (C), 140.4 (C), 139.1 (C), 138.1 (C), 135.5 (C), 134.6 (C), 130.7 (CH), 129.6 (C), 129.2 (CH), 128.0 (CH), 126.3 (CH), 125.4 (CH), 124.7 (CH), 119.4 (CH), 117.9 (CH), 52.4 (CH_3), 30.2 (CH_2), 28.3 (CH_2), 23.7 (CH_2); Selected spectral data for the minor (*Z*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, $J = 1.5$ Hz, 1H), 7.55 (dd, $J = 3.0$ Hz, 8.0 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.14 – 7.12 (m, 2H), 6.94 (d, $J = 8.5$ Hz, 1H), 6.80 (t, $J = 8.5$ Hz, 1H), 6.35 (s, 1H), 3.92 (s, 3H), 2.90 (t, $J = 6.5$ Hz, 2H), 2.59 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 2.03 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.2 (C), 141.1 (C), 139.0 (C), 138.3 (C), 135.5 (C), 134.2 (C), 131.2 (CH), 129.2 (CH), 129.0 (CH), 128.8 (CH), 128.8 (C), 125.4 (CH), 124.8 (CH), 119.6 (CH), 119.0 (CH), 52.3 (CH_3), 34.9 (CH_2), 29.6 (CH_2), 24.0 (CH_2); Selected spectral data for the mixture: δ IR (thin film): 3456, 3015, 2970, 2116, 1739, 1436, 1367, 1228, 1092, 748, 527 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2\text{N}_3$ (M) $^+$ 319.13208, found 319.13140.

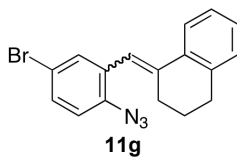


11e

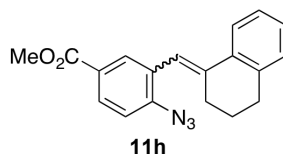
Styryl Azide 11e. The general procedure was followed using 0.95 g of 2-azidobenzaldehyde **s14** (4.4 mmol), 1.89 g of the phosphonium salt (4.0 mmol), 1.8 mL of a 2.5 M solution of BuLi in hexanes in 20 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow powder, as a 87:13 mixture of *E*- and *Z*-isomers (1.81 g, 81%). Selected spectral data for the major (*E*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.75 – 7.77 (m, 1H), 7.40 – 7.46 (m, 3H), 7.24 – 7.28 (m, 2H), 7.14 – 7.18 (m, 1H), 7.02 (s, 1H), 2.91 (m, $J = 6.5$ Hz, 2H), 2.67 – 2.69 (m, 2H), 1.89 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 140.5 (C), 139.4 (C), 133.6 (C), 131.3 (CH), 130.1 (q, $J_{\text{CF}} = 32.6$ Hz, C), 129.3 (CH), 129.0 (C), 128.1 (CH), 126.3 (CH), 124.7 (CH), 123.8 (q, $J_{\text{CF}} = 270.8$ Hz, C), 121.0 (q, $J_{\text{CF}} = 3.5$ Hz, CH), 117.4 (CH), 115.3 (q, $J_{\text{CF}} = 3.8$ Hz, CH), 30.2 (CH_2), 28.2 (CH_2), 23.7 (CH_2) one overlapping aromatic carbon signal; Selected spectral data for the minor (*Z*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.46 (m, 1H), 7.24 – 7.28 (m, 1H), 7.14 – 7.18 (m, 3H), 6.99 (d, $J = 8.0$ Hz, 1H), 6.86 – 6.89 (m, 1H), 6.37 (s, 1H), 2.95 (t, $J = 6.5$ Hz, 2H), 2.62 – 2.64 (m, 2H), 2.01 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.9 (C), 139.1 (C), 138.8 (C), 134.3 (C), 134.1 (C), 138.1 (CH), 135.3 (CH), 131.8 (CH), 129.0 (CH), 128.8 (CH), 124.9 (CH), 118.5 (CH), 115.5 (q, $J_{\text{CF}} = 3.8$ Hz, CH), 34.9 (CH_2), 29.6 (CH_2), 24.0 (CH_2); ^{19}F NMR (CDCl_3 , 282 MHz) δ –63.12; Selected spectral data for the mixture: IR (thin film): 2111, 1739, 1328, 1273, 1123, 913, 745 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{14}\text{N}_3\text{F}_3$ (M) $^+$ 329.11398, found 329.11303.



Styryl Azide 11f. The general procedure was followed using 0.74 g of 2-azido-4-(methylsulfonyl)benzaldehyde **s15** (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:20 EtOAc: hexanes) afforded the product as a white powder as one isomer (0.47 g, 46%): ^1H NMR (500 MHz, CDCl_3) δ 7.73 (d, $J = 1.5$ Hz, 2H), 7.68 (dd, $J = 1.5$ Hz, 8.0 Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.25 – 7.22 (m, 2H), 7.15 – 7.13 (m, 1H), 6.98 (s, 1H), 3.11 (s, 3H), 2.88 (t, $J = 6.5$ Hz, 2H), 2.66 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 1.87 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.5 (C), 140.1 (C), 139.7 (C), 138.2 (C), 135.5 (C), 135.1 (C), 131.7 (CH), 129.3 (CH), 128.3 (CH), 126.3 (CH), 124.7 (CH), 123.0 (CH), 117.2 (CH), 117.1 (CH), 44.6 (CH_3), 30.1 (CH_2), 28.3 (CH_2), 23.7 (CH_2); IR (thin film): 3454, 3026, 2969, 2116, 1738, 1366, 1206, 738, 536 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{NS}$ ($\text{M}-\text{N}_2$) $^+$ 311.09800, found 311.09698.

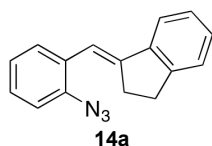


Styryl Azide 11g. The general procedure was followed using 0.75 g of 2-azido-5-bromobenzaldehyde **s16** (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a white powder, as an 83:17 mixture of *E*- and *Z*-isomers (0.62 g, 61%). Selected spectral data for the major (*E*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.73 – 7.71 (m, 1H), 7.45 (d, $J = 2.5$ Hz, 1H), 7.42 (dd, $J = 2.5$ Hz, 8.5 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.17 – 7.14 (m, 1H), 7.05 (d, $J = 8.5$ Hz, 1H), 6.92 (s, 1H), 2.88 (t, $J = 6.5$ Hz, 2H), 2.66 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 1.87 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.9 (C), 138.0 (C), 137.8 (C), 135.4 (C), 133.4 (CH), 131.9 (C), 130.7 (CH), 129.2 (CH), 128.0 (C), 127.9 (CH), 126.2 (CH), 124.8 (CH), 120.0 (CH), 117.4 (CH), 30.3 (CH_2), 28.1 (CH_2), 23.7 (CH_2); Selected spectral data for the minor (*Z*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.34 (dd, $J = 2.0$ Hz, 8.5 Hz, 1H), 7.27 (d, $J = 2.0$ Hz, 1H), 7.17 – 7.14 (m, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.90 – 6.87 (m, 1H), 6.28 (s, 1H), 2.92 (t, $J = 6.5$ Hz, 2H), 2.59 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 2.04 (pent, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.1 (C), 138.9 (C), 137.2 (C), 134.0 (C), 133.7 (CH), 132.6 (C), 129.0 (CH), 128.6 (CH), 128.0 (C), 124.8 (CH), 124.8 (CH), 120.1 (CH), 118.3 (CH), 117.2 (CH), 35.0 (CH_2), 29.7 (CH_2), 24.1 (CH_2); Selected spectral data for the mixture: δ IR (thin film): 3457, 3015, 2970, 2122, 1755, 1369, 1215, 747, 516 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{Br}$ (M) $^+$ 339.03710, found 339.03776.

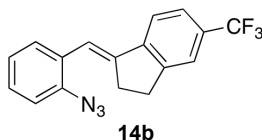


Styryl Azide 11h. The general procedure was followed using 0.68 g of methyl 3-azido-4-formylbenzoate **s17** (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:50 EtOAc: hexanes) afforded the product as a white powder, as an 87:13 mixture of *E*- and *Z*-isomers (0.38 g, 40%). Selected spectral data for the major (*E*) isomer: ^1H NMR (500 MHz,

CDCl₃) δ 8.03 (d, *J* = 1.5 Hz, 1H), 7.98 (dd, *J* = 1.5 Hz, 8.0 Hz, 1H), 7.74 (dd, *J* = 3.5 Hz, 5.5 Hz, 1H), 7.23 – 7.20 (m, 3H), 7.15 – 7.14 (m, 1H), 6.98 (s, 1H), 3.94 (s, 3H), 2.87 (t, *J* = 6.5 Hz, 2H), 2.69 (dt, *J* = 1.5 Hz, 6.5 Hz, 2H), 1.86 (pent, *J* = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.5 (C), 143.2 (C), 139.6 (C), 138.0 (C), 135.6 (C), 132.2 (CH), 129.9 (C), 129.3 (CH), 129.2 (CH), 127.8 (CH), 126.2 (CH), 126.1 (C), 124.6 (CH), 118.2 (CH), 117.7 (CH), 52.1 (CH₃), 30.3 (CH₂), 28.2 (CH₂), 23.7 (CH₂); Selected spectral data for the minor (*Z*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.92 (dd, *J* = 3.0, 8.5 Hz, 1H), 7.83 (d, *J* = 3.0 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.13 – 7.10 (m, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.80 (t, *J* = 6.5 Hz, 1H), 6.33 (s, 1H), 3.82 (s, 3H), 2.92 (t, *J* = 6.5 Hz, 2H), 2.60 (dt, *J* = 1.5 Hz, 6.5 Hz, 2H), 2.05 (pent, *J* = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.3 (C), 142.6 (C), 140.9 (C), 138.9 (C), 135.5 (C), 134.2 (C), 132.7 (CH), 130.8 (CH), 129.0 (CH), 128.4 (CH), 126.4 (CH), 126.1 (C), 124.8 (CH), 118.7 (CH), 118.4 (CH), 52.0 (CH₃), 35.0 (CH₂), 29.7 (CH₂), 24.1 (CH₂); Selected spectral data for the mixture: δ IR (thin film): 3024, 2969, 2121, 1753, 1372, 1292, 762, 528 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₉H₁₇ON (M)⁺ 291.12593, found 291.12443.

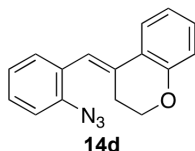


Styryl Azide 14a. The general procedure was followed using 0.92 g of 2-azidobenzaldehyde **s9** (6.54 mmol), 2.40 g of the phosphonium salt (5.24 mmol), 2.3 mL of a 2.5 M solution of BuLi in hexanes in 15 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow powder, as an 82:18 mixture of *E*- and *Z*-isomers (0.24 g, 19%): R_f = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (*E*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.67 (m, 1H), 7.54 (dd, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.10 – 7.35 (m, 7H), 3.00 – 3.08 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 146.0 (C), 145.6 (C), 142.4 (C), 137.8 (C), 130.0 (C), 128.9 (CH), 128.5 (CH), 127.6 (CH), 126.8 (CH), 125.3 (CH), 124.5 (CH), 120.7 (CH), 118.4 (CH), 113.4 (CH), 30.8 (CH₂), 30.7 (CH₂); Selected spectral data for the minor (*Z*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.10 – 7.35 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.92 – 6.95 (m, 1H), 6.47 (s, 1H), 3.00 – 3.08 (m, 2H), 2.94 – 2.97 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 149.0 (C), 145.0 (C), 139.4 (C), 138.0 (C), 130.8 (CH), 130.1 (C), 129.0 (CH), 128.5 (CH), 125.9 (CH), 125.4 (CH), 124.7 (CH), 124.2 (CH), 118.7 (CH), 116.8 (CH), 33.9 (CH₂), 30.2 (CH₂); Selected spectral data for the mixture: IR (thin film): 2117, 2084, 1570, 1483, 1277, 1264, 749 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₆H₁₃N₃ (M)⁺ 247.11095, found 247.11013.



Styryl Azide 14b. The general procedure was followed using 0.76 g of 2-azidobenzaldehyde **s9** (5.18 mmol), 2.48 g of the phosphonium salt (4.70 mmol), 2.1 mL of a 2.5 M solution of BuLi in hexanes in 15 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow oil, as a 72:28 mixture of *E*- and *Z*-isomers (0.52 g, 35%): R_f = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (*E*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.51 – 7.54 (m, 2H), 7.30 – 7.39 (m, 2H), 7.11 – 7.23 (m, 3H), 3.18 – 3.24 (m, 2H), 3.05 – 3.08 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 144.3 (C), 143.7 (C), 143.5 (C), 143.3 (C), 138.0 (C), 129.4 (C), 128.9 (CH), 128.1 (CH), 127.1 (CH), 125.1 (q, *J*_{CF} = 4.0 Hz, CH), 124.6 (CH), 124.2 (q, *J*_{CF} = 271.9, C), 123.9 (CH), 118.4 (CH), 115.0 (CH), 30.4 (CH₂), 29.6 (CH₂); Selected spectral data for the minor (*Z*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.39 (m,

2H), 7.11 – 7.23 (m, 2H), 7.13 (dd, $J = 0.5$ Hz, 7.5 Hz, 1H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.57 (s, 1H), 3.18 – 3.24 (m, 2H), 2.99 – 3.30 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.5 (C), 141.3 (C), 138.1 (C), 130.5 (CH), 129.5 (C), 128.8 (CH), 127.5 (C), 127.4 (CH), 127.2 (C), 126.3 (CH), 125.1 (q, $J_{CF} = 4.0$ Hz, CH), 124.8 (CH), 118.8 (CH), 118.5 (CH), 33.5 (CH_2), 28.8 (CH_2); ^{19}F NMR (CDCl_3 , 282 MHz) δ -63.12; Selected spectral data for the mixture: IR (thin film): 2124, 2083, 1595, 1318, 1160, 1118, 750 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{12}\text{N}_3\text{F}_3$ (M) $^+$ 315.09833, found 315.09885.

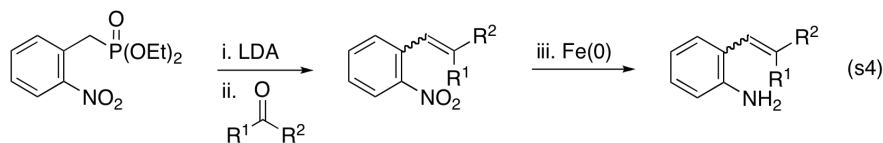


Styryl Azide 14d. The general procedure was followed using 0.65 g of 2-azidobenzaldehyde **s9** (4.42 mmol), 1.87 g of the phosphonium salt (3.95 mmol), 1.73 mL of a 2.5 M solution of BuLi in hexanes in 20 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a white powder, as an 83:17 mixture of *E*- and *Z*-isomers (0.28 g, 27%): $R_f = 0.45$ (18:82 EtOAc: hexane). Selected spectral data for the major (*E*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.70 (dd, $J = 1.5$ Hz, 8.0 Hz, 1H), 7.32 – 7.35 (m, 1H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.19 – 7.22 (m, 2H), 7.14 – 7.17 (m, 1H), 7.08 (s, 1H), 6.95 – 6.98 (m, 1H), 6.83 – 6.85 (m, 1H), 4.20 (t, $J = 6.0$ Hz, 2H), 2.80 – 2.83 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.9 (C), 138.7 (C), 132.1 (C), 130.9 (CH), 129.5 (CH), 128.8 (C), 128.3 (CH), 124.8 (CH), 124.3 (CH), 122.4 (C), 120.9 (CH), 118.4 (CH), 117.5 (CH), 117.0 (CH), 66.2 (CH_2), 26.9 (CH_2); Selected spectral data for the minor (*Z*) isomer: ^1H NMR (500 MHz, CDCl_3): δ 7.38 (d, $J = 7.5$ Hz, 1H), 7.29 – 7.30 (m, 1H), 7.09 – 7.11 (m, 1H), 7.00 – 7.04 (m, 2H), 6.84 (dd, $J = 1.0$ Hz, 8.0 Hz, 1H), 6.65 – 6.58 (m, 1H), 6.29 (s, 1H), 4.38 (t, 5.5 Hz, 2H), 2.71- 2.73 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) 154.9 (C) 138.1 (C), 132.5 (C), 131.1 (CH), 129.7 (CH), 128.53 (CH), 128.50 (CH), 124.7 (CH), 120.6 (C), 120.0 (CH), 119.3 (CH), 118.6 (CH), 117.1 (CH), 67.4 (CH_2), 33.3 (CH_2); Selected spectral data for the mixture: δ IR (thin film): 2117, 2091, 1603, 1572, 1468, 1450, 1281, 1049, 749 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{13}\text{ON}_3$ (M) $^+$ 263.10587, found 263.10672.

II. Preparation of Substrates using a Horner–Wadsworth–Emmons Reaction.

A. General Procedure for the Horner–Wadsworth–Emmons Reaction and Fe-Mediated Nitro-Group Reduction

2-Amino substituted styrenes were synthesized via a two-step procedure of Horner-Wadsworth-Emmons reaction followed by nitro-group reduction. Yields were not optimized.

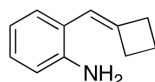


To a -78 °C solution of LDA (4.4 mmol) in 10 mL of THF was added dropwise *ortho*-nitrobenzylphosphonate in 3 mL of THF. After an additional hour, a solution of the ketone in 5 mL of THF was added slowly to the mixture at -78 °C. The reaction mixture was allowed to warm to ambient temperature slowly. After 1h, 10 mL water was added to quench the reaction. The resulting mixture was taken up by dichloromethane and separated. The aqueous phase was washed with 3×5 mL dichloromethane. The resulting organic phase was washed with

20 mL of brine and dried over Na_2SO_4 . After filtration, the filtrate was concentrated *in vacuo* to produce 2-nitrostyrene, which was submitted to the subsequent Fe-mediated nitro-group reduction without further purification.

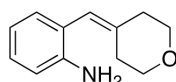
To a solution of nitro-substituted styrene (prepared from 4.0 mmol of *ortho*-nitrobenzylphosphonate) in 20 mL of AcOH and 20 mL of EtOH was added 1.8 g of Fe powder (32 mmol). The resultant mixture was allowed to reflux at 80 °C overnight. After cooled down to ambient temperature, the resulting mixture was filtrated with a pad of Celite. The filtrate was diluted with 50 mL of water and washed with 3 × 10 mL dichloromethane. The resulting organic phase was washed with 40 mL of brine and dried over Na_2SO_4 . After filtration, the filtrate was concentrated *in vacuo*. Purification of the reaction mixture using MPLC afforded the product

B. Synthesis of *ortho*-Amino-Substituted Styrenes.



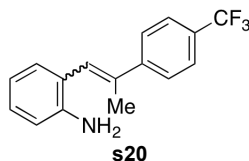
s18

Styrene s18. The general procedure of Horner–Wadsworth–Emmons reaction was followed using 1.09 g of *ortho*-nitrobenzylphosphonate⁶ (4.0 mmol), 0.45 mL of cyclobutanone (6.0 mmol) and LDA (4.4 mmol) in 6 mL of THF. After work-up, the representative pathway of nitro-group reduction was followed by using 1.79 g of Fe (32.0 mmol), in 20.0 mL of AcOH and 20.0 mL of EtOH. Purification by MPLC (1:100 – 20:80 EtOAc: hexanes) afforded the product as a light yellow oil (0.25 g, 39% two steps): ¹H NMR (500 MHz, CDCl_3) δ 7.16 – 7.19 (m, 1H), 7.07 – 7.11 (m, 1H), 6.72 (d, J = 8.0 Hz, 1H), 6.79 – 6.83 (m, 1H), 6.11 (s, 1H), 3.71 (s, 2H), 2.92 – 2.99 (m, 4H), 2.10 – 2.16 (m, 2H); ¹³C NMR (125 MHz, CDCl_3) δ 145.2 (C), 143.5 (C), 128.2 (CH), 127.3 (CH), 123.4 (C), 118.5 (CH), 115.8 (CH), 115.7 (CH), 32.6 (CH_2), 32.3 (CH_2), 18.2 (CH_2); IR (thin film): 3451, 3366, 2948, 1614, 1488 1297, 1263, 744 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{13}\text{N}$ (M)⁺ 159.10480, found 159.10560.



s19

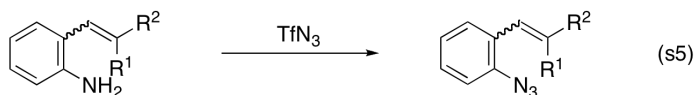
Styrene s19. The general procedure of Horner–Wadsworth–Emmons reaction was followed using 1.09 g of *ortho*-nitrobenzylphosphonate⁶ (4.0 mmol), 0.55 mL of tetrahydro-4*H*-pyran-4-one (6.0 mmol) and LDA (4.4 mmol) in 6 mL of THF. After work-up, the representative pathway of nitro-group reduction was followed by using 1.79 g of Fe (32.0 mmol), in 20.0 mL of AcOH and 20.0 mL of EtOH. Purification by MPLC (1:100 – 20:80 EtOAc: hexanes) afforded the product as a light yellow oil (0.50 g, 66% two steps): ¹H NMR (500 MHz, CDCl_3) 7.07 (t, J = 8.0 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.69 – 6.75 (m, 2H), 6.14 (s, 1H), 3.80 (t, J = 5.5 Hz, 2H), 3.69 (s, 2H), 3.66 (t, J = 5.5 Hz, 2H), 2.43 (t, J = 5.5 Hz, 2H), 2.36 (t, J = 5.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl_3) δ 144.2 (C), 139.8 (C), 130.1 (CH), 127.9 (CH), 122.9 (C), 119.6 (CH), 118.1 (CH), 115.1 (CH), 69.7 (CH_2), 69.0 (CH_2), 37.0 (CH_2), 31.0 (CH_2); IR (thin film): 3459, 3355, 1613, 1489, 1452, 1229, 1093, 995, 746 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{ON}$ (M)⁺ 189.11537, found 189.11613.



Styrene s20. The general procedure of Horner–Wadsworth–Emmons reaction was followed using 1.09 g of *ortho*-nitrobenzylphosphonate⁶ (4.0 mmol), 0.83 g of 4-acetylbenzotrifluoride (4.4 mmol) and LDA (4.4 mmol) in 6 mL of THF. After work-up, the representative pathway of nitro-group reduction was followed by using 1.79 g of Fe (32.0 mmol), in 20.0 mL of AcOH and 20.0 mL of EtOH. Purification by MPLC (1:100 – 20:80 EtOAc: hexanes) afforded the crude product as a brown oil (0.34 g, 31% two steps). The aniline was carried on to the azidation reaction without further purification.

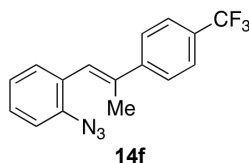
C. General Procedure for the Azidation Reaction.

Following the procedure of Tor and co-workers,⁷ the aniline group was transformed into an azide (s5). Yields were not optimized.

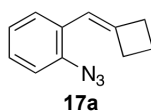


To a solution of aniline (3 mmol) in 5 mL of CH₂Cl₂ was added subsequently 24 mg of CuSO₄, 1.2 mL of Et₃N, freshly prepared triflyl azide (9 mmol) in 15 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was allowed to react at room temperature overnight. Then, the reaction mixture was taken up by 15 mL dichloromethane, neutralized with a saturated aq. soln. of NaHCO₃ and washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated *in vacuo*. Purification of the reaction mixture using MPLC afforded the product.

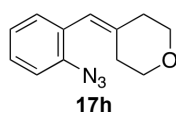
D. Synthesis of Styryl Azides.



Styryl Azide 14f. The general procedure for azidation was followed using 0.31 g of aniline **s20** (1.1 mmol), 0.01 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 3.0 mmol of Tf₂O), and 0.4 mL of Et₃N (3.0 mmol) in 4 mL CH₂Cl₂, 2 mL of MeOH and 1 mL of H₂O. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow solid (0.22 g, 66%): mp 62 - 65 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.20 (m, 1H), 7.12 (dd, *J* = 1.0 Hz, 8.0 Hz, 1H), 6.80 – 6.83 (m, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 2.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 145.3 (C), 138.6 (C), 138.1 (C), 131.1 (CH), 129.076 (q, *J*_{CF} = 32.6 Hz, C), 129.075 (C), 128.7 (CH), 128.1 (CH), 125.2 (q, *J*_{CF} = 3.5 Hz, CH), 124.3 (CH), 124.2 (q, *J*_{CF} = 271 Hz, C), 123.5 (CH), 118.2 (CH), 23.0 (CH₃); ¹⁹F NMR (CDCl₃, 282 MHz) δ –63.04; IR (thin film): 2122, 1615, 1482, 1323, 1123, 738 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₆H₁₂N₃F₃ (M)⁺ 303.09833, found 303.09697.



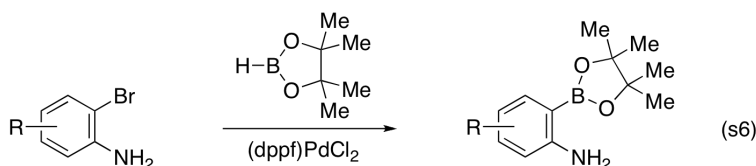
Styryl Azide 17a. The general procedure for azidation was followed using 0.23 g of aniline **s18** (1.44 mmol), 0.02 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 4.5 mmol of Tf₂O), and 0.6 mL of Et₃N (4.5 mmol) in 6 mL CH₂Cl₂, 3 mL of MeOH and 2 mL of H₂O. Purification by MPLC (100% hexanes) afforded the product as a light yellow oil (0.14 g, 54%): ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.35 (s, 1H), 3.01 – 3.04 (m, 2H), 2.92 – 2.95 (m, 2H), 2.12 – 2.16 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 146.5 (C), 136.5 (C), 129.5 (C), 127.9 (CH), 127.1 (CH), 124.5 (CH), 118.3 (CH), 115.1 (CH), 32.9 (CH₂), 32.7 (CH₂), 18.4 (CH₂); IR (thin film): 2951, 2113, 1482, 1285, 1099, 743, 665 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₁H₁₁N₃ (M)⁺ 185.09530, found 185.09451.



Styryl Azide 17h. The general procedure for azidation was followed using 0.43 g of aniline **s19** (2.28 mmol), 0.02 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 9.0 mmol of Tf₂O), and 1.3 mL of Et₃N (9.0 mmol) in 6 mL CH₂Cl₂, 3 mL of MeOH and 2 mL of H₂O. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow oil (0.31 g, 63%): ¹H NMR (500 MHz, CDCl₃) 7.22 – 7.25 (m, 1H), 7.10 – 7.15 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.24 (s, 1H), 3.77 (t, *J* = 5.5 Hz, 2H), 3.64 (t, *J* = 5.5 Hz, 2H), 2.37 – 2.41 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 139.3 (C), 138.1 (C), 130.8 (CH), 129.1 (C), 128.0 (CH), 124.3 (CH), 119.3 (CH), 118.4 (CH), 69.4 (CH₂), 68.6 (CH₂), 37.2 (CH₂), 30.9 (CH₂); IR (thin film): 2115, 2082, 1482, 1279, 1230, 1097, 997, 748, 665 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₂H₁₃ON₃ (M)⁺ 215.10587, found 215.10709.

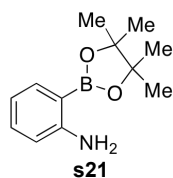
III. Preparation of Substrates using a Suzuki Reaction.

General Procedure for the Arylboronic Acid Pinacol Ester Syntheses.

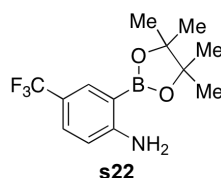


To a mixture of 0.85 g of 2-bromo-aniline (5.0 mmol), 2.09 mL of Et₃N (20.0 mmol), 0.185 g of (dppf)PdCl₂ (0.25 mmol) in 15 mL 1,4-dioxane, was added dropwise 2.20 mL 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 mmol). The resultant mixture was heated to 100 °C. After 12h, the mixture was cooled to room temperature and diluted with 20 mL of NH₄Cl. The resulting aqueous phase was extracted with an additional 2 × 20 mL of CH₂Cl₂. The combined organic phases were washed with 1 × 30 mL of brine. The resulting organic phase was dried over Na₂SO₄, and was concentrated *in vacuo*. Purification via MPLC afforded the product.

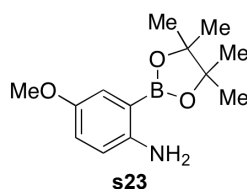
A. Syntheses of Arylboronic Acid Pinacol Esters.



Aniline s21.⁸ The general procedure was followed using 3.4 g of 2-bromo-aniline (20.0 mmol), 8.7 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (60.0 mmol), 0.82 g of (dppf)PdCl₂ (1.0 mmol), and 8.4 mL of Et₃N (80.0 mmol) in 100 mL of 1, 4-dioxane. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow solid (3.02 g, 69%): mp 62 -64 °C; The spectral data matched that reported by Driver and co-workers:⁸ ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.0 Hz, 1H), 6.70 (t, *J* = 7.0 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.76 (s, 2H), 1.36 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 153.7 (C), 136.8 (CH), 132.8 (CH), 116.9 (CH), 114.8 (CH), 83.5 (C), 25.0 (CH₃); IR (thin film): 3486, 3380, 1624, 1605, 1352, 1311, 1244, 1135, 1086, 847, 758, 654 cm⁻¹.

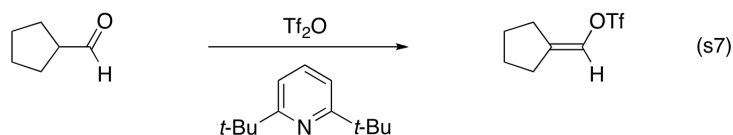


Aniline s22.⁸ The general procedure was followed using 2.65 g of 2-bromo-4-(trifluoromethyl)aniline (10.0 mmol), 4.4 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30.0 mmol), 0.41 g of (dppf)PdCl₂ (0.5 mmol), and 4.2 mL of Et₃N (40.0 mmol) in 50 mL of 1, 4-dioxane. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a brown solid (1.81 g, 63%): mp 107 -109 °C. The spectral data matched that reported by Driver and co-workers:⁸ ¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 6.59 (d, *J* = 8.5 Hz, 1H), 5.08 (s, 2H), 1.35 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 156.1 (C), 134.3 (q, *J*_{CF} = 3.8 Hz, CH), 129.5 (q, *J*_{CF} = 3.8 Hz, CH), 125.0 (q, *J*_{CF} = 268.8 Hz, C), 118.5 (q, *J*_{CF} = 32.5 Hz, C), 84.0 (C), 114.2 (CH), 24.9 (CH₃); ¹⁹F NMR (CDCl₃, 282 MHz) δ -61.64; IR (thin film): 3472, 3375, 1625, 1370, 1304, 1256, 1140, 1097, 1072, 832.9 cm⁻¹.



Aniline s23.⁸ The general procedure was followed using 2.02 g of 2-bromo-4-methoxyaniline (10.0 mmol), 4.4 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30.0 mmol), 0.41 g of (dppf)PdCl₂ (0.5 mmol), and 4.2 mL of Et₃N (40.0 mmol) in 50 mL of 1, 4-dioxane. Purification by MPLC (5:100 – 10:90 EtOAc: hexanes) afforded the product as a brown liquid (1.52 g, 61%). The spectral data matched that reported by Driver and co-workers:⁸ ¹H NMR (500 MHz, CDCl₃) δ 7.15 (d, *J* = 3.5 Hz, 1H), 6.85 (dd, *J* = 3.0 Hz, 8.5 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 1H), 4.48 (s, 2H), 3.76 (s, 3H), 1.34 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 151.3 (C), 147.9 (C), 120.7 (CH), 119.5 (CH), 116.5 (CH), 83.6 (C), 56.0 (CH₃), 25.0 (CH₃); IR (thin film): 3456, 3366, 1494, 1421, 1359, 1304, 1226, 1037, 855, 829, 750 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₃H₂₀O₃NB (M)⁺ 249.1536, found 249.1540.

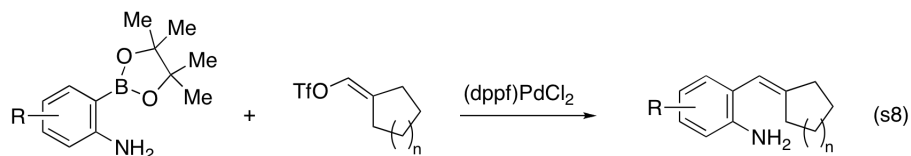
B. General Procedure for the Triflate Formation.



To a mixture of 10.0 mmol of cyclopentanecarboxaldehyde and 2.65 mL 2,6-di-*tert*-butylpyridine (12.0 mmol) in 40 mL of 1,2-dichloroethane was added 1.85 mL of triflic anhydride (11.0 mmol). The resultant mixture was heated to 70 °C. After 2h, the mixture was cooled to room temperature and diluted with 40 mL CH₂Cl₂. The resulting aqueous phase was extracted with an additional 2 × 30 mL of CH₂Cl₂. The combined organic phases were washed with 1 × 30 mL of brine. The resulting organic phase was dried over Na₂SO₄, and was concentrated *in vacuo* to afford crude triflate.

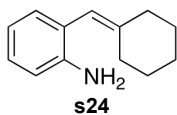
C. General Procedure for the Suzuki Reaction.

Following the procedure of Driver and co-workers,⁸ was aniline **s6** treated with vinyl triflate **s7** in the presence of (dppf)PdCl₂ to produce the desired aniline (s8). Yields were not optimized.



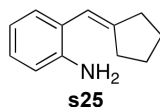
To a mixture of 0.919 g of boronic ether **s6** (3.2 mmol), 0.261 g of (dppf)PdCl₂ (0.32 mmol) in 40 mL 1,4-dioxane was added 8 mL of a 3M solution of NaOH in water followed by 1.36 g of crude triflate **s7** (5.12 mmol). The resultant mixture was heated to 80 °C. After 12 h, the mixture was cooled to room temperature and filtrated through a pad of Celite. The filtrate was diluted with 20 mL saturated NH₄Cl and extracted with an additional 2 × 30 mL of CH₂Cl₂. The combined organic phases were washed with 1 × 30 mL of brine. The resulting organic phase was dried over Na₂SO₄, and was concentrated *in vacuo*. Purification via MPLC afforded the product.

D. Synthesis of Anilines.

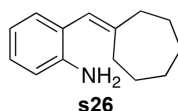


Aniline s24. The general procedure was followed using 1.10 g of boronic ester **s6** (5.0 mmol), crude vinyl triflate (derived from 10.0 mmol of cyclohexanecarboxaldehyde), 0.82 g of (dppf)PdCl₂ (1.0 mmol), and 1.8 g of NaOH (45.0 mmol) in 75 mL of 1,4-dioxane and 15 mL of water. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow oil (0.74 g, 79%): ¹H NMR (500 MHz, CDCl₃) δ 7.09 (t, *J* = 6.0 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.05 (s, 1H), 3.70 (s, 2H), 2.33 (t, *J* = 6.0 Hz, 2H), 2.24 (t, *J* = 6.0 Hz, 2H), 1.56 – 1.70 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 145.4 (C), 144.3 (C), 130.3 (CH), 127.5 (CH), 124.0 (C), 118.0 (CH), 117.8 (CH), 115.0 (CH), 37.2 (CH₂), 30.0

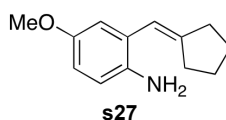
(CH₂), 28.9 (CH₂), 28.1 (CH₂), 26.8 (CH₂); IR (thin film): 3466, 3368, 1161, 1489, 1448, 1297, 1265, 745 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₃H₁₇N (M)⁺ 187.13610, found 187.13596.



Aniline s25. The general procedure was followed using 2.19 g of boronic ester **s6** (10.0 mmol), crude vinyl triflate (derived from 15.0 mmol of cyclopentanecarboxaldehyde), 0.82 g of (dppf)PdCl₂ (1.0 mmol), and 3.6 g of NaOH (90.0 mmol) in 100 mL of 1, 4-dioxane and 30 mL of water. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow oil (1.54 g, 89%): ¹H NMR (500 MHz, CDCl₃) δ 7.16 (d, *J* = 7.5 Hz, 1H), 7.05 (dt, *J* = 1.5 Hz, 7.5 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.23 (s, 1H), 3.67 (s, 2H), 2.49 (s, 2H), 2.39 (s, 2H), 1.70 – 1.73 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 148.6 (C), 143.7 (C), 129.1 (CH), 127.3 (CH), 124.9 (C), 118.2 (CH), 115.7 (CH), 115.2 (CH), 34.6 (CH₂), 30.7 (CH₂), 26.7 (CH₂), 25.8 (CH₂); IR (thin film): 3452, 3368, 1613, 1488, 1453, 1295, 1263, 1155, 871, 744 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₂H₁₅N (M)⁺ 173.1164, found 173.1204.



Aniline s26. The general procedure was followed using 0.76 g of boronic ester **s6** (3.5 mmol), crude vinyl triflate (derived from 10.0 mmol of cycloheptanecarboxaldehyde), 0.25 g of (dppf)PdCl₂ (0.3 mmol), and 1.2 g of NaOH (30.0 mmol) in 40 mL of 1, 4-dioxane and 10 mL of water. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow oil (0.25 g, 35%): ¹H NMR (500 MHz, CDCl₃) δ 7.07 (dt, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.74 (dt, *J* = 1.0 Hz, 7.5 Hz, 1H), 6.71 (dd, *J* = 1.5 Hz, 7.5 Hz, 1H), 6.10 (s, 1H), 3.68 (s, 2H), 2.43 – 2.45 (m, 2H), 2.31 – 2.33 (m, 2H), 1.68 – 1.72 (m, 2H), 1.52 – 1.62 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 147.5 (C), 144.0 (C), 130.0 (CH), 127.4 (CH), 124.5 (C), 121.0 (CH), 118.0 (CH), 114.9 (CH), 37.8 (CH₂), 31.2 (CH₂), 29.9 (CH₂), 29.5 (CH₂), 29.37 (CH₂), 27.3 (CH₂); IR (thin film): 3464, 3372, 2918, 2849, 1611, 1489, 1451, 745 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₄H₁₉N (M)⁺ 201.15175 found 201.15198



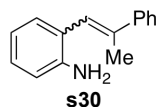
Aniline s27. The general procedure was followed using 1.69 g of boronic ester **s6** (6.8 mmol), crude vinyl triflate (derived from 10.0 mmol of cyclopentanecarboxaldehyde), 0.57 g of (dppf)PdCl₂ (0.68 mmol), and 1.44 g of NaOH (36.0 mmol) in 40 mL of 1, 4-dioxane and 12 mL of water. Purification by MPLC (2:100 – 20:80 EtOAc: hexanes) afforded the product as a brown oil (0.97 g, 70%): ¹H NMR (500 MHz, CDCl₃) δ 6.77 (d, *J* = 1.8 Hz, 1H), 6.64 – 6.64 (m, 2H), 6.23 (t, *J* = 2.3 Hz, 1H), 3.75 (s, 3H), 3.44 (s, 2H), 2.48 (ddd, *J* = 7.7, 5.5, 1.9 Hz, 2H), 2.42-2.40 (m, 2H), 1.71 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 152.4 (C), 148.8 (C), 137.5 (C), 126.2 (C), 116.4 (CH), 115.9 (CH), 114.6 (CH), 112.9 (CH), 55.8 (CH₃), 34.7 (CH₂), 30.8 (CH₂), 26.7 (CH₂), 25.8 (CH₂); IR (thin film): 3437, 3357, 2947, 1604, 1494, 1281, 1040, 904, 813 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₃H₁₇ON (M)⁺ 203.13102, found 203.13075.



Aniline s28. The general procedure was followed using 1.44 g of boronic ester **s6** (5.8 mmol), crude vinyl triflate (derived from 9.0 mmol of cyclohexanecarboxaldehyde), 0.57 g of (dppf)PdCl₂ (0.68 mmol), and 1.20 g of NaOH (30.0 mmol) in 40 mL of 1, 4-dioxane and 10 mL of water. Purification by MPLC (2:100 – 20:80 EtOAc: hexanes) afforded the product as a brown oil (0.21 g, 17%): ¹H NMR (500 MHz, CDCl₃): 6.60 – 6.68 (m, 3H), 6.01 (s, 1H), 3.74 (s, 3H), 3.13 (s, 2H), 2.29 (t, *J* = 6.0 Hz, 2H), 2.21 (t, *J* = 6.5 Hz, 2H), 1.52 – 1.66 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 152.2 (C), 145.6 (C), 138.0 (C), 125.3 (C), 117.7 (CH), 116.1 (CH), 115.7 (CH), 113.1 (CH), 55.8 (CH₃), 37.2 (CH₂), 30.0 (CH₂), 28.8 (CH₂), 28.0 (CH₂), 26.7 (CH₂); IR (thin film): 3438, 3358, 1494, 1276, 1216, 1159, 1039, 811 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₄H₁₉ON (M)⁺ 217.1467, found 217.1466.



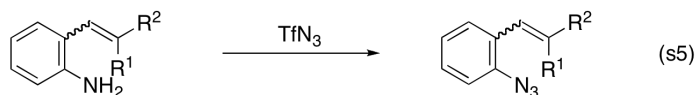
Aniline s29. The general procedure was followed using 3.01 g of boronic ester **s6** (10.5 mmol), crude vinyl triflate (derived from 15.0 mmol corresponding aldehyde), 0.87 g of (dppf)PdCl₂ (1.05 mmol), and 3.60 g of NaOH (90.0 mmol) in 110 mL of 1, 4-dioxane and 30 mL of water. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a brown liquid (1.82 g, 62%): ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.5 Hz, 1H), 7.26 (s, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.98 (s, 1H), 4.01 (s, 2H), 2.32 (t, *J* = 5.5 Hz, 2H), 2.18 (t, *J* = 6.5 Hz, 2H), 1.54 – 1.71 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 147.3 (C), 147.1 (C), 127.3 (q, *J*_{CF} = 3.8 Hz, CH), 125.1 (q, *J*_{CF} = 268.8 Hz, C), 124.6 (q, *J*_{CF} = 3.8 Hz, CH), 123.3 (C), 119.5 (q, *J*_{CF} = 31.3 Hz, C), 116.4 (CH), 114.1 (CH), 37.1 (CH₂), 30.0 (CH₂), 28.8 (CH₂), 28.0 (CH₂), 26.6 (CH₂); ¹⁹F NMR (CDCl₃, 282 MHz) δ – 61.47; IR (thin film): 3492, 3398, 1620, 1323, 1142, 1103, 1071, 820 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₄H₁₆NF₃ (M)⁺ 255.1235, found 255.1239.



Aniline s30. The general procedure was followed using 1.75 g of boronic ester **s6** (8.0 mmol), crude vinyl triflate (derived from 15.0 mmol corresponding aldehyde), 0.66 g of (dppf)PdCl₂ (0.8 mmol), and 3.60 g of NaOH (90.0 mmol) in 110 mL of 1,4-dioxane and 30 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow oil, as a 69:31 mixture of *Z*- and *E*-isomers (1.41 g, 84%): *R*_f = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (*Z*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.11 – 7.23 (m, 5H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.72 – 6.76 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.52 (t, *J* = 7.5 Hz, 1H), 6.41 (s, 1H), 3.70 (br, 2H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 144.0 (C), 141.2 (C), 139.5 (C), 130.0 (CH), 128.1 (CH), 127.5 (CH), 127.0 (CH), 123.98 (C), 123.1 (CH), 118.3 (CH), 115.3 (CH), 25.7 (CH₃) one overlapping aromatic C not distinguishable; Selected spectral data for the minor (*E*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.57 – 7.58 (m, 2H), 7.38 – 7.41 (m, 2H), 7.31 – 7.34 (m, 1H), 7.11- 7.23 (m, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.72 – 6.76 (m, 2H), 3.70 (br s, 2H), 2.17 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 144.4 (C), 142.9 (C), 139.1 (C), 130.5 (CH), 128.4 (CH), 128.1 (CH), 127.4 (CH), 124.01 (C), 123.9 (CH), 123.5 (CH), 118.2 (CH), 115.2 (CH), 17.2 (CH₃); Selected spectral data for the mixture: δ IR (thin film): 3464, 3374, 1613, 1489, 1454, 1275, 1264 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₅H₁₅N (M)⁺ 209.12045, found 209.12206.

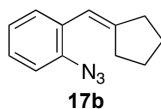
E. General Procedure for Styryl Azides Syntheses.

Following the procedure of Tor and co-workers,⁷ the aniline group was transformed into an azide (s5). Yields were not optimized.

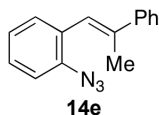


To a solution of aniline (3 mmol) in 5 mL of CH₂Cl₂ was added subsequently 24 mg of CuSO₄, 1.2 mL of Et₃N, freshly prepared triflyl azide (9 mmol) in 15 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was allowed to react at room temperature overnight. Then, the reaction mixture was taken up by 15 mL dichloromethane, neutralized with a saturated aq. soln. of NaHCO₃ and washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated *in vacuo*. Purification of the reaction mixture using MPLC afforded the product.

F. Synthesis of Styryl Azides.

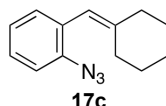


Styryl Azide 17b. The general procedure for azidation was followed using 0.95 g of aniline **s39** (5.5 mmol), 0.05 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 18.0 mmol of Tf₂O), and 2.5 mL of Et₃N (18.0 mmol) in 6 mL of CH₂Cl₂, 4 mL of MeOH and 2 mL of H₂O. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow oil, as a 72:28 mixture of *Z*- and *E*-isomers (0.68 g, 62%): Selected spectral data for the major (*Z*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.32 (m, 6H), 7.13 – 7.15 (d, *J* = 8.5 Hz, 1H), 6.80 – 6.84 (m, 2H), 6.62 (s, 1H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.5 (C), 140.3 (C), 137.9 (C), 131.2 (CH), 129.8 (C), 128.4 (CH), 127.7 (CH), 127.1 (CH), 124.2 (CH), 121.9 (CH), 118.1 (CH), 26.5 (CH₃); Selected spectral data for the minor (*E*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.64 (dd, *J* = 1.0 Hz, 8.5 Hz, 2H), 7.36 – 7.47 (m, 5H), 7.18 (dd, *J* = 2.0 Hz, 6.0 Hz, 2H), 6.92 (s, 1H), 2.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.3 (C), 138.7 (C), 138.5 (C), 130.8 (CH), 130.2 (C), 128.5 (CH), 128.2 (CH), 127.5 (CH), 126.1 (CH), 124.4 (CH), 123.1 (CH), 118.5 (CH), 17.5 (CH₃); Selected spectral data for the mixture: δ IR (thin film): 2116, 2083, 1479, 1443, 1278, 759 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₂H₁₃N₃ (M)⁺ 199.1109, found 199.1112.

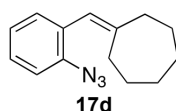


Styryl Azide 14e.⁹ The general procedure for azidation was followed using 0.65 g of aniline **s30** (3.1 mmol), 0.02 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 9.0 mmol of Tf₂O), and 1.3 mL of Et₃N (9.0 mmol) in 4 mL of CH₂Cl₂, 2 mL of MeOH and 1 mL of H₂O. Purification by MPLC (1:100 – 20:80 EtOAc: hexanes) afforded the product as a light yellow oil, as a 72:28 mixture of *Z*- and *E*-isomers (0.59 g, 81%): Selected spectral data for the major (*Z*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.32 (m, 6H), 7.13 – 7.15 (d, *J* = 8.5 Hz, 1H), 6.80 – 6.84 (m, 2H), 6.62 (s, 1H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.5 (C), 140.3 (C), 137.9 (C), 131.2 (CH), 129.8 (C), 128.4 (CH), 127.7 (CH), 127.1 (CH), 124.2 (CH), 121.9 (CH), 118.1 (CH), 26.5 (CH₃) one overlapping aromatic C not distinguishable; Selected spectral data for the minor (*E*) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.64 (dd, *J* = 1.0 Hz, 8.5 Hz, 2H), 7.36 – 7.47 (m, 5H), 7.18 (dd, *J* = 2.0

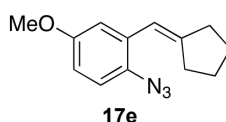
Hz, 6.0 Hz, 2H), 6.92 (s, 1H), 2.72 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.3 (C), 138.7 (C), 138.5 (C), 130.8 (CH), 130.2 (C), 128.5 (CH), 128.2 (CH), 127.5 (CH), 126.1 (CH), 124.4 (CH), 123.1 (CH), 118.5 (CH), 17.5 (CH_3); Selected spectral data for the mixture: δ IR (thin film): 2116, 2083, 1479, 1443, 1278, 759 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3$ (M^+) 235.11095, found 235.11230.



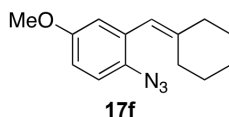
Styryl Azide 17c. The general procedure for azidation was followed using 1.42 g of aniline **s39** (7.6 mmol), 0.06 g of CuSO_4 , freshly prepared dichloromethane solution of TfN_3 (from 22.8 mmol of Tf_2O), and 3.2 mL of Et_3N (22.8 mmol) in 10 mL of CH_2Cl_2 , 5 mL of MeOH and 3 mL of H_2O . Purification by MPLC (100% hexane) afforded the product as a light yellow oil (1.36 g, 84%): ^1H NMR (500 MHz, CDCl_3) δ 7.23 – 7.27 (m, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 7.13 (dd, $J = 1.0$ Hz, 8.0 Hz, 1H), 7.07 – 7.10 (m, 1H), 6.14 (s, 1H), 2.30 (t, $J = 5.5$ Hz, 2H), 2.25 (t, $J = 5.5$ Hz, 2H), 1.55 – 1.68 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.0 (C), 138.0 (C), 131.0 (CH), 130.2 (C), 127.5 (CH), 124.3 (CH), 118.3 (CH), 117.3 (CH), 37.5 (CH_2), 29.8 (CH_2), 28.6 (CH_2), 27.9 (CH_2), 26.7 (CH_2); IR (thin film): 2112, 2080, 1482, 1444, 1281, 836, 746, 836, 746, 725, 671 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{N}_3$ (M^+) 213.12660, found 213.12686.



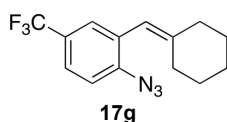
Styryl Azide 17d. The general procedure for azidation was followed using 0.21 g of aniline **s39** (1.1 mmol), 0.01 g of CuSO_4 , freshly prepared dichloromethane solution of TfN_3 (from 3.0 mmol of Tf_2O), and 0.4 mL of Et_3N (3.0 mmol) in 4 mL of CH_2Cl_2 , 2 mL of MeOH and 1 mL of H_2O . Purification by MPLC (100% hexane) afforded the product as a light yellow oil (0.18 g, 76%): ^1H NMR (500 MHz, CDCl_3) δ 7.19 – 7.26 (m, 2H), 7.08 – 7.14 (m, 2H), 6.25 (s, 1H), 2.45 (t, $J = 6.0$ Hz, 2H), 2.37 (t, $J = 6.0$ Hz, 2H), 1.58 – 1.70 (m, 8H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.8 (C), 137.8 (C), 130.6 (CH), 127.4 (CH), 124.3 (CH), 120.6 (CH), 118.3 (CH), 38.3 (CH_2), 31.3 (CH_2), 29.8 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 27.3 (CH_2) one overlapping aromatic C not distinguishable; IR (thin film): 2919, 2113, 2079, 1572, 1480, 1443, 1281, 1085, 746 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{N}_3$ (M^+) 227.14225 found 227.14169.



Styryl Azide 17e. The general procedure for azidation was followed using 0.97 g of aniline **s39** (4.8 mmol), 0.02 g of CuSO_4 , freshly prepared dichloromethane solution of TfN_3 (from 14.4 mmol of Tf_2O), and 2.0 mL of Et_3N (14.4 mmol) in 6 mL CH_2Cl_2 , 3 mL of MeOH and 2 mL of H_2O . Purification by MPLC (100% hexane) afforded the product as a light yellow oil (0.80 g, 73%): ^1H NMR (500 MHz, CDCl_3) δ 7.04 (d, $J = 8.7$ Hz, 1H), 6.93 (d, $J = 2.8$ Hz, 1H), 6.77 (dd, $J = 8.7, 2.9$ Hz, 1H), 6.43 (s, 1H), 3.80 (s, 3H), 2.46 – 2.52 (m, 4H), 1.71 – 1.78 (m, 2H), 1.71 – 1.66 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.4 (C), 149.3 (C), 131.6 (C), 129.8 (C), 119.1 (CH), 115.3 (CH), 114.6 (CH), 112.5 (CH), 55.5 (CH_3), 35.5 (CH_2), 31.2 (CH_2), 27.0 (CH_2), 25.6 (CH_2); IR (thin film): 2953, 2115, 2080, 1480, 1446, 744 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{ON}_3$ (M^+) 229.12152, found 229.12192.



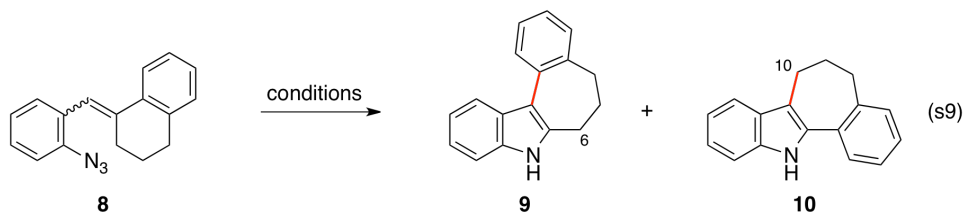
Styryl Azide 17f. The general procedure for azidation was followed using 0.21 g of aniline **s39** (1.0 mmol), 0.01 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 3.0 mmol of Tf₂O), and 1.3 mL of Et₃N (3.0 mmol) in 3 mL of CH₂Cl₂, 2 mL of MeOH and 1 mL of H₂O. Purification by MPLC (100% hexane) afforded the product as a light yellow oil (0.41 g, 43%): ¹H NMR (500 MHz, CDCl₃) δ 7.04 (d, *J* = 9.0 Hz, 1H), 6.80 (dd, *J* = 3.0 Hz, 8.5 Hz, 1H), 6.72 (d, *J* = 3.0 Hz, 1H), 6.12 (s, 1H), 3.79 (s, 3H), 2.26 – 2.31 (m, 4H), 1.56 – 1.67 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 156.3 (C), 145.3 (C), 131.3 (C), 130.6 (C), 119.3 (CH), 117.4 (CH), 116.4 (CH), 112.8 (CH), 55.5 (CH₃), 37.4 (CH₂), 29.9 (CH₂), 28.6 (CH₂), 27.8 (CH₂), 26.6 (CH₂); IR (thin film): 2106, 2084, 1486, 1284, 1239, 1165, 1035, 798, 732 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₄H₁₇ON₃ (M)⁺ 243.1372, found 243.1372.



Styryl Azide 17g. The general procedure for azidation was followed using 1.60 g of aniline **s39** (6.3 mmol), 0.04 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 18.8 mmol of Tf₂O), and 2.6 mL of Et₃N (18.8 mmol) in 8 mL of CH₂Cl₂, 4 mL of MeOH and 3 mL of H₂O. Purification by MPLC (100% hexane) afforded the product as a light yellow oil (0.04 g, 3%): ¹H NMR (500 MHz, CDCl₃) δ 7.49 (dd, *J* = 8.5 Hz, 2.0 Hz, 1H), 7.40 (s, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 6.11 (s, 1H), 2.30 (t, *J* = 5.5 Hz, 2H), 2.22 (t, *J* = 5.5 Hz, 2H), 1.54 – 1.70 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 146.7 (C), 141.5 (C), 130.6 (C), 128.2 (q, *J*_{CF} = 3.6 Hz, CH), 126.4 (q, *J*_{CF} = 31.4 Hz, C), 124.4 (q, *J*_{CF} = 3.4 Hz, CH), 124.0 (q, *J*_{CF} = 270.1 Hz, C), 118.5 (CH), 116.3 (CH), 37.4 (CH₂), 29.8 (CH₂), 28.5 (CH₂), 27.8 (CH₂), 26.5 (CH₂); ¹⁹F NMR (CDCl₃, 282 MHz) δ -61.62; IR (thin film): 2929, 2120, 2088, 1329, 1289, 1106, 817 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₄H₁₄NF₃ (M - N₂)⁺ 255.1000, found 255.1000.

IV. Development of Rhodium-Catalyzed Migration Reaction.

A. General Procedure for the Screening of Catalysts to Promote the Migration.



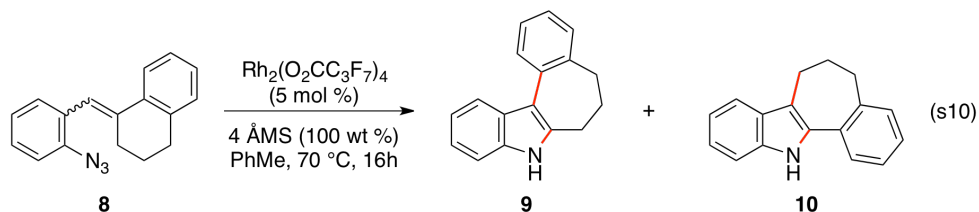
To a mixture of 0.026 g of aryl azide **8** (0.1 mmol), 0-100 % w/w of crushed 4 Å mol sieves, and metal salt (0 – 5 mol %) in Schlenk tube was added 0.50 mL of solvent. The resulting mixture was heated and, after 16 h, the heterogenous mixture was filtered through a short pad of Al₂O₃. The filtrate was concentrated *in vacuo*. The resulting solid (oil) was dissolved in 1.5 mL of CDCl₃ and 0.007 mL of dibromomethane (0.1 mmol) was added. The areas of the C–H peak on the carbon 6 position in **9** and carbon 10 in **10** were compared to the area of CH₂Br₂ to derive a yield.

Table s1. Optimization of Migration Process^{a,b}

Entry	metal salt	Mol %	solvent	wt %, 4 Å MS	T (°C)	yield, % ^c	6 : 7
1	none	n.a.	xylenes	0	170		xx:xx
2	Rh ₂ (O ₂ CCH ₃) ₄	5	PhMe	100	70	8	n.a.
3	Rh ₂ (O ₂ CCF ₃) ₄	5	PhMe	100	70	86	100:0
4	Rh ₂ (O ₂ CC ₃ F ₇) ₄	5	PhMe	100	70	95	100:0
5	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	PhMe	100	70	93	96:4
6	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	3	PhMe	100	70	80 ^d	96:4
7	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	3	PhMe	100	60	88 ^e	96:4
8	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	PhMe	100	80	95	96:4
9	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	DCE	100	60	74 ^f	96:4
10	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	DCE	100	70	94	98:2
11	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	DCE	100	80	88	96:4
12	Rh ₂ (esp) ₂	5	PhMe	100	70	98	>98:2
13	RhCl ₃	5	PhMe	100	70	0	n.a.
14	(Ph ₃ P) ₃ RuCl	5	PhMe	100	70	trace	n.a.
15	Cu(OTf) ₂	5	PhMe	100	70	0	n.a.
16	Ru(TPFP)CO	5	IPAC	0		48	100:0

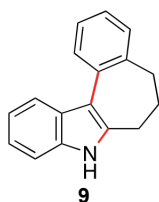
^a Reaction performed in conical vial. ^b 16 hour reaction time. ^c Isolated yield after Al₂O₃ chromatography.

B. Optimized General Procedure.



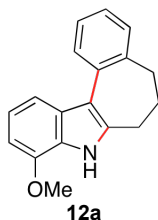
To a mixture of 0.026 g of aryl azide **5** (0.1 mmol), 100 % w/w of crushed 4 Å mol sieves, and metal salt (Rh₂(esp)₄ or Rh₂(hpfb)₄, 5 mol %) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 70 °C for 16 h, then, the heterogenous mixture was filtered through a short pad of Al₂O₃. The filtrate was concentrated *in vacuo* to afford analytically pure indole. In some cases, purification by MPLC is required.

C. Effect of Aryl Azide Substitution on Rhodium-Catalyzed Migration Selectivity.

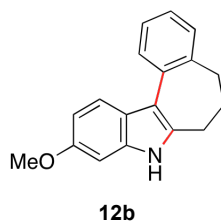


Indole 9. The general procedure was followed using 0.027 g of styryl azide **8** (0.102 mmol) and 0.005 g of Rh₂(hpfb)₄ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound **9** (0.025, 95%). mp 125 – 127 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.94 – 7.96 (m, 2H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.34 –

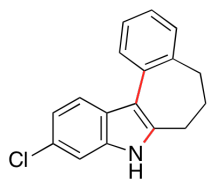
7.40 (m, 2H), 7.30 (d, $J = 7.5$ Hz, 1H), 7.18 – 7.24 (m, 3H), 2.94 (t, $J = 7.5$ Hz, 2H), 2.76 – 2.78 (m, 2H), 2.23 – 2.29 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.0 (C), 136.9 (C), 135.7 (C), 135.1 (C), 129.3 (CH), 127.9 (CH), 127.3 (C), 126.3 (CH), 125.3 (CH), 121.6 (CH), 120.1 (CH), 119.2 (CH), 112.8 (C), 110.6 (CH), 33.5 (CH_2), 30.1 (CH_2), 26.5 (CH_2); IR (thin film): 3396, 1599, 1492, 1459, 1275, 906, 745 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{N}$ (M) $^+$ 233.12054, found 233.11957.



Indoles 12a. The general procedure was followed using 0.0291 g of styryl azide **11a** (0.100 mmol) and 0.0053 g of $\text{Rh}_2(\text{hpfb})_4$ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **12a** (0.0252 g, 96%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 8.31 (br, 1H), 7.88 (dd, $J = 1.0$ Hz, 7.5 Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.38 (dt, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.30 (dd, $J = 1.0$ Hz, 7.5 Hz, 1H), 7.21 (dt, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 4.02 (s, 3H), 2.97 (t, $J = 7.5$ Hz, 2H), 2.79 – 2.76 (m, 2H), 2.30 – 2.25 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.0 (C), 145.8 (C), 141.0 (C), 136.5 (C), 135.4 (C), 129.3 (CH), 128.6 (C), 128.0 (CH), 126.3 (CH), 125.2 (CH), 120.5 (CH), 113.3 (C), 112.2 (CH), 101.8 (CH), 55.4 (CH_3), 33.6 (CH_2), 30.2 (CH_2), 26.4 (CH_2); IR (thin film): 3443, 2941, 1497, 1264, 733 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{ON}$ (M) $^+$ 263.13102, found 263.13028.

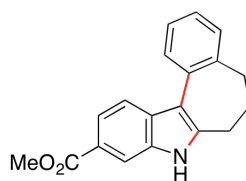


Indoles 12b. The general procedure was followed using 0.0291 g of styryl azide **11b** (0.100 mmol) and 0.0053 g of $\text{Rh}_2(\text{hpfb})_4$ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **12b** (0.0254 g, 97%) as a white solid; mp 164 – 166 $^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 7.85 – 7.83 (m, 2H), 7.81 (d, $J = 7.5$ Hz, 1H), 7.35 (dt, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.27 (dd, $J = 1.0$ Hz, 7.5 Hz, 1H), 7.21 (dt, $J = 1.0$ Hz, 7.5 Hz, 1H), 6.85 (dd, $J = 2.5$ Hz, 8.5 Hz, 1H), 6.82 (d, $J = 1.5$ Hz, 1H), 3.85 (s, 3H), 2.91 (t, $J = 7.5$ Hz, 2H), 2.77 – 2.75 (m, 2H), 2.23 – 2.17 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 156.0 (C), 141.1 (C), 136.6 (C), 135.6 (C), 135.0 (C), 129.3 (CH), 127.8 (CH), 126.3 (CH), 125.2 (CH), 121.7 (C), 120.0 (CH), 112.5 (C), 109.3 (CH), 94.7 (CH), 55.8 (CH_3), 33.7 (CH_2), 29.5 (CH_2), 26.8 (CH_2); IR (thin film): 3399, 2937, 1461, 1264, 738 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{ON}$ (M) $^+$ 263.13102, found 263.13140.



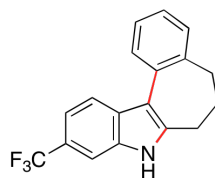
12c

Indoles 12c. The general procedure was followed using 0.0295 g of styryl azide **11c** (0.100 mmol) and 0.0053 g of $\text{Rh}_2(\text{hpfb})_4$ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **12c** (0.0264 g, 99%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.92 (br, 1H), 7.82 (d, $J = 8.5$ Hz, 1H), 7.79 (dd, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.37 (dt, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.21 (dt, $J = 1.5$ Hz, 6.5 Hz, 1H), 7.14 (dd, $J = 2.0$ Hz, 6.5 Hz, 1H), 2.91 (t, $J = 7.5$ Hz, 2H), 2.78 – 2.74 (m, 2H), 2.26 – 2.21 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 141.1 (C), 137.5 (C), 136.1 (C), 134.5 (C), 129.4 (CH), 127.8 (CH), 127.3 (C), 126.4 (CH), 126.0 (C), 125.6 (CH), 120.7 (CH), 120.1 (CH), 112.9 (C), 110.5 (CH), 33.5 (CH_2), 29.8 (CH_2), 26.6 (CH_2); IR (thin film): 3401, 2929, 1462, 1275, 749 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{17}\text{H}_{14}\text{NCl}$ (M) $^+$ 267.08147, found 267.08182.



12d

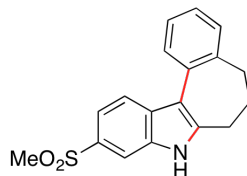
Indoles 12d. The general procedure was followed using 0.0319 g of styryl azide **11d** (0.100 mmol) and 0.0053 g of $\text{Rh}_2(\text{esp})_2$ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **12d** (0.0274 g, 94%) as a white solid; mp 203 – 205 $^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3) δ 8.55 (br, 1H), 8.11 (d, $J = 1.5$ Hz, 1H), 7.91 (d, $J = 8.5$ Hz, 1H), 7.85 (dd, $J = 1.5$ Hz, 8.5 Hz, 1H), 7.79 (dd, $J = 1.0$ Hz, 8.0 Hz, 1H), 7.37 (dt, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.20 (dt, $J = 1.5$ Hz, 7.5 Hz, 1H), 3.96 (s, 3H), 2.97 (t, $J = 7.5$ Hz, 2H), 2.75 – 2.72 (m, 2H), 2.30 – 2.25 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.4 (C), 140.9 (C), 140.8 (C), 135.0 (C), 134.5 (C), 130.9 (C), 129.4 (CH), 127.9 (CH), 126.4 (CH), 125.7 (CH), 122.9 (C), 121.3 (CH), 118.6 (CH), 113.5 (C), 112.9 (CH), 52.0 (CH_3), 33.3 (CH_2), 30.2 (CH_2), 26.4 (CH_2); IR (thin film): 3656, 2950, 1690, 1503, 1217, 1062, 911 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2\text{N}$ (M) $^+$ 291.12593, found 291.12553.



12e

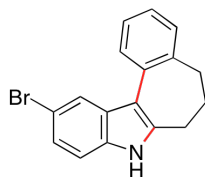
Indole 12e. The general procedure was followed using 0.046 g of styryl azide **11e** (0.140 mmol) and 0.007 g of $\text{Rh}_2(\text{hpfb})_4$ (0.007 mmol) in 0.6 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **12e** (0.038 g, 90%). ^1H NMR (500 MHz, CDCl_3): 8.18 (s, 1H), 7.98 (d, $J = 8.5$ Hz, 1H), 7.80 (d, $J = 7.5$ Hz, 1H), 7.06 (s, 1H), 7.38 – 7.42 (m, 2H), 7.31 – 7.32 (m, 1H), 7.22 – 7.26 (m, 1H), 2.95 (t, 7.5 Hz, 2H), 2.73 – 2.76 (m, 2H), 2.24 – 2.30 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): 141.0 (C), 139.7 (C), 134.6 (C), 134.3 (C), 129.6 (C), 129.5 (CH), 127.9 (CH), 126.5 (CH), 125.8 (CH), 125.3 (q, $J = 269.9$ Hz, C), 123.5 (q, $J = 31.8$ Hz, C), 119.4 (CH), 116.8 (q, $J = 3.5$ Hz, CH), 113.2 (C), 108.1 (q, $J = 4.8$ Hz, CH), 33.3 (CH_2), 30.1 (CH_2), 26.4 (CH_2); ^{19}F

NMR (CDCl₃, 282 MHz) ; IR (thin film): 3401, 2940, 1740, 1728, 1333, 1217, 1111, 1057 cm⁻¹. HRMS (EI) m/z calcd for C₁₈H₁₄NF₃ (M)⁺ 301.10783, found 301.10748.



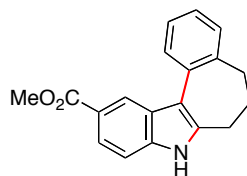
12f

Indoles 12f. The general procedure was followed using 0.0339 g of styryl azide **11f** (0.100 mmol) and 0.0053 g of Rh₂(hpfb)₄ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound **12f** (0.0295 g, 95%) as a white solid; mp 159 – 161 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.23 (br, 1H), 8.11 (d, *J* = 1.0 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 1.0 Hz, 8.5 Hz, 1H), 7.36 (dt, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.21 (dt, *J* = 1.0 Hz, 7.5 Hz, 1H), 3.13 (s, 3H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.71 (t, *J* = 6.0 Hz, 2H), 2.29 – 2.24 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 142.4 (C), 140.9 (C), 134.5 (C), 134.1 (C), 132.0 (C), 131.0 (C), 129.1 (CH), 127.8 (CH), 126.5 (CH), 126.0 (CH), 119.6 (CH), 118.2 (CH), 113.4 (C), 111.0 (CH), 45.3 (CH₃), 33.2 (CH₂), 30.2 (CH₂), 26.2 (CH₂); IR (thin film): 3351, 2928, 1498, 1265, 1141, 740 cm⁻¹. HRMS (EI) m/z calcd for C₁₈H₁₇O₂NS (M)⁺ 311.09800, found 311.09821.



12g

Indoles 12g. The general procedure was followed using 0.0340 g of styryl azide **11g** (0.100 mmol) and 0.0053 g of Rh₂(hpfb)₄ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound **12g** (0.0295 g, 95%) as a white solid; mp 146 – 148 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 1.5 Hz, 1H), 8.00 (br, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.37 (dt, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.21 (dt, *J* = 1.0 Hz, 6.5 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.74 – 2.72 (m, 2H), 2.27 – 2.22 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 140.9 (C), 138.2 (C), 134.4 (C), 134.3 (C), 129.4 (CH), 129.0 (C), 127.8 (CH), 126.5 (CH), 125.7 (CH), 124.3 (CH), 121.6 (CH), 113.5 (C), 112.6 (C), 111.9 (CH), 33.4 (CH₂), 30.1 (CH₂), 26.4 (CH₂); IR (thin film): 3411, 2936, 1469, 1264, 740 cm⁻¹. HRMS (EI) m/z calcd for C₁₇H₁₄NBr (M)⁺ 313.02891, found 313.03030.

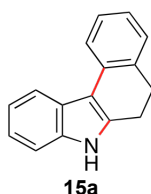


12h

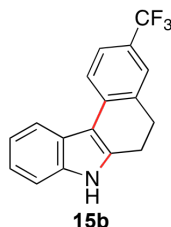
Indole 12h. The general procedure was followed using 0.0319 g of styryl azide **11h** (0.100 mmol) and 0.0053 g of Rh₂(esp)₂ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound **12h** (0.0276 g, 95%) as a white solid; mp 244 – 246 °C. ¹H NMR (500 MHz, acetone-*d*₆) δ 10.65 (br, 1H), 8.57 (s, 1H), 7.82 (dd, *J* = 1.0 Hz, 8.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.37 (dt, *J* = 1.5 Hz,

7.5 Hz, 1H), 7.28 (d, $J = 7.5$ Hz, 1H), 7.17 (dt, $J = 1.5$ Hz, 7.5 Hz, 1H), 3.87 (s, 3H), 3.04 (t, $J = 7.5$ Hz, 2H), 2.74 – 2.72 (m, 2H), 2.24 – 2.19 (m, 2H); ^{13}C NMR (125 MHz, acetone- d_6) δ 167.5 (C), 141.2 (C), 139.3 (C), 139.0 (C), 134.6 (C), 129.3 (CH), 127.7 (CH), 126.8 (C), 126.3 (CH), 125.4 (CH), 122.4 (CH), 121.6 (C), 121.2 (CH), 112.9 (C), 110.6 (CH), 51.0 (CH₃), 33.3 (CH₂), 29.6 (CH₂), 26.1 (CH₂); IR (thin film): 3643, 2951, 1737, 1231, 1062, 913, 857 cm^{-1} . HRMS (EI) m/z calcd for C₁₉H₁₇O₂N (M)⁺ 291.12593, found 291.12504.

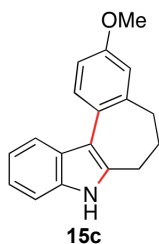
D. Effect of Migrating Group Identity on Rhodium-Catalyzed Migration Selectivity.



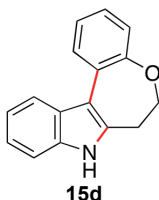
Indole 15a.¹⁰ The general procedure was followed using 0.041 g of styryl azide **14a** (0.17 mmol) and 0.006 g of Rh₂(esp)₄ (0.008 mmol) in 0.7 mL of PhMe. Filtration by Al₂O₃ afforded a 98:2 mixture of compound **12a** and **12b**; Purification by MPLC (10:100 EtOAc: hexanes) afforded compound **15a** as a white powder (0.032 g, 88%); Indole **15a** was previously reported by Katritzky and Wang:¹⁰ ^1H NMR (500 MHz, CDCl₃) δ 8.05 (d, $J = 7.5$ Hz, 1H), 7.95 (s, 1H), 7.88 (d, $J = 7.5$ Hz, 1H), 7.31 – 7.36 (m, 2H), 7.19 – 7.27 (m, 3H), 7.09 – 7.12 (m, 1H), 3.05 – 3.08 (t, $J = 7.5$ Hz, 2H), 2.93 – 2.96 (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl₃): δ 137.2 (C), 136.2 (C), 133.9 (C), 133.3 (C), 128.0 (CH), 127.0 (CH), 125.0 (C), 124.3 (CH), 122.3 (CH), 121.5 (CH), 120.6 (CH), 119.5 (CH), 111.1 (CH), 110.8 (C), 29.5 (CH₂), 22.5 (CH₂); IR (thin film): 3396, 1601, 1497, 1456, 1255, 908, 767, 731 cm^{-1} .



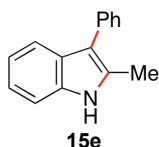
Indole 15b. The general procedure was followed using 0.050 g of styryl azide **14b** (0.16 mmol) and 0.006 g of Rh₂(esp)₄ (0.008 mmol) in 0.6 mL of PhMe. Filtration by Al₂O₃ afforded a 95:5 mixture of compound **15b** and **16b**; Purification by MPLC (10:100 EtOAc: hexanes) afforded compound **15b** as a light yellow powder (0.031 g, 78%); mp 227 – 230 °C; ^1H NMR (500 MHz, DMSO) δ 8.03 (d, $J = 7.5$ Hz, 1H), 7.93 – 7.95 (m, 1H), 7.37 – 7.45 (m, 3H), 7.11 – 7.13 (m, 2H), 3.10 (t, $J = 7.5$ Hz, 2H), 2.98 (t, $J = 8.0$ Hz, 2H), *N-H* peak not available; ^{13}C NMR (125 MHz, DMSO) δ 139.2 (C), 136.9 (C), 136.4 (C), 131.6 (C), 127.53 (CH), 127.49 (q, $J_{CF} = 27.8$ Hz, C), 126.0 (CH), 125.3 (q, $J_{CF} = 272.0$ Hz, C), 124.6, 121.5 (CH), 120.9 (q, $J_{CF} = 5.5$ Hz, CH), 120.6 (CH), 119.1 (CH), 112.2 (CH), 108.3 (C), 25.5 (CH₂), 21.5 (CH₂); IR (thin film): 3406, 1601, 1557, 1452, 1311, 1162, 1108, 749 cm^{-1} . HRMS (EI) m/z calcd for C₁₇H₁₂NF₃ (M)⁺ 287.09218, found 287.09182.



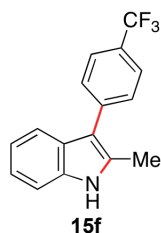
Indole 15c. The general procedure was followed using 0.041 g of styryl azide **14c** (0.141 mmol) and 0.005 g of $\text{Rh}_2(\text{esp})_4$ (0.007 mmol) in 0.5 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **15c** (0.034 g, 92%). ^1H NMR (500 MHz, CDCl_3) δ 7.99 (s, 1H), 7.56 (d, $J = 7.5$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.23 (t, $J = 7.5$ Hz, 1H), 7.15 (t, $J = 7.5$ Hz, 1H), 6.82 – 6.85 (m, 2H), 3.86 (s, 3H), 3.11 (t, $J = 7.0$ Hz, 2H), 2.89 – 2.91 (m, 2H), 2.15 – 2.19 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.7 (C), 144.0 (C), 136.1 (C), 132.7 (C), 130.2 (C), 126.4 (CH), 124.6 (C), 122.4 (CH), 119.5 (CH), 118.4 (CH), 115.5 (CH), 113.1 (C), 111.5 (CH), 110.5 (CH), 55.3 (CH_3), 35.6 (CH_2), 26.7 (CH_2), 26.0 (CH_2); IR (thin film): 3414, 2926, 2834, 1605, 1461, 1433, 1260, 1243, 1033, 810, 735 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{ON}$ (M) $^+$ 263.13102, found 263.13192.



Indole 15d. The general procedure was followed using 0.052 g of styryl azide **14d** (0.198 mmol) and 0.008 g of $\text{Rh}_2(\text{esp})_4$ (0.010 mmol) in 0.7 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **15d** (0.044 g, 94%). mp 175 – 177 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 8.14 (d, $J = 7.5$ Hz, 1H), 8.10 (d, $J = 7.5$ Hz, 1H), 8.04 (s, 1H), 7.31 – 7.32 (m, 1H), 7.12 – 7.26 (m, 5H), 4.39 (t, $J = 6.0$ Hz, 2H), 3.32 (t, $J = 6.0$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 158.7 (C), 136.5 (C), 134.8 (C), 128.4 (CH), 127.3 (C), 127.0 (C), 125.9 (CH), 123.8 (CH), 122.1 (CH), 121.1 (CH), 120.3 (CH), 120.2 (CH), 110.6 (CH), 109.7 (C), 70.0 (CH_2), 31.0 (CH_2); IR (thin film): 3348, 1492, 1459, 1441, 1196, 905, 748 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{13}\text{ON}$ (M) $^+$ 235.09972, found 235.10055.



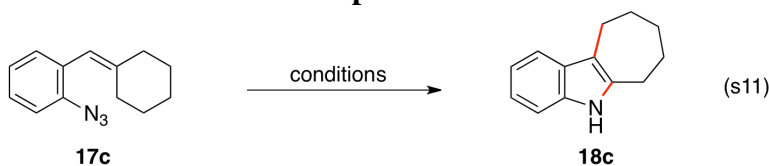
Indole 15e.¹¹ The general procedure was followed using 0.044 g of styryl azide **14e** (0.187 mmol) and 0.007 g of $\text{Rh}_2(\text{esp})_4$ (0.009 mmol) in 0.6 mL of PhMe (reaction is set up at 80 $^\circ\text{C}$). Filtration by Al_2O_3 afforded analytically pure compound **15e** (0.035 g, 91%). Spectral data for **15e** matched that reported by Tan and Hartwig:¹¹ ^1H NMR (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.53 – 7.55 (m, 2H), 7.47 – 7.50 (m, 2H), 7.31 – 7.35 (m, 2H), 7.17 – 7.20 (m, 1H), 7.12 – 7.15 (m, 1H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.5 (C), 135.3 (C), 131.4 (C), 129.5 (CH), 128.5 (CH), 127.9 (C), 125.8 (CH), 121.6 (CH), 120.0 (CH), 118.8 (CH), 114.6 (C), 110.3 (CH), 12.6 (CH_3); IR (thin film): 3401, 1603, 1496, 1459, 1258, 908, 748, 702 cm^{-1} .



Indole 15f.¹² The general procedure was followed using 0.036 g of styryl azide **14f** (0.117 mmol) and 0.005 g of $\text{Rh}_2(\text{esp})_4$ (0.006 mmol) in 0.5 mL of PhMe (reaction is set up at 80 °C). Filtration by Al_2O_3 afforded analytically pure compound **15f** (0.030 g, 93%). Indole **15f** was previously reported by Chiba and co-workers.¹² Spectral data for **15f**: ^1H NMR (500 MHz, CDCl_3) δ 8.02 (s, 1H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.66 (d, $J = 7.5$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.22 (dt, $J = 1.0$ Hz, 8.0 Hz, 1H), 7.16 (dt, $J = 1.0$ Hz, 7.5 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.4 (C), 135.3 (C), 132.2 (C), 129.4 (CH), 127.7 (q, $J_{\text{CF}} = 32.8$ Hz, C), 127.5 (C), 125.5 (q, $J_{\text{CF}} = 3.5$ Hz, CH), 124.5 (q, $J_{\text{CF}} = 269.9$ Hz, C), 122.0 (CH), 120.4 (CH), 118.5 (CH), 113.4 (C), 110.5 (CH), 12.6 (CH_3); IR (thin film): 3397, 1615, 1459, 1234, 1163, 1109, 1068, 747 cm^{-1} .

E. Effect of Ring Size on Rhodium-Catalyzed Migration.

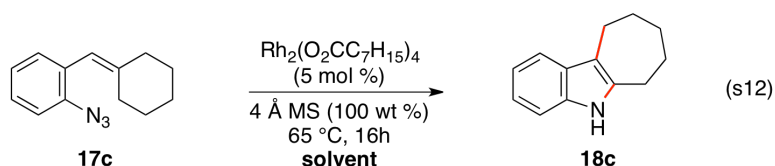
1. General Procedure for the Optimization of Conditions to Promote the Migration.



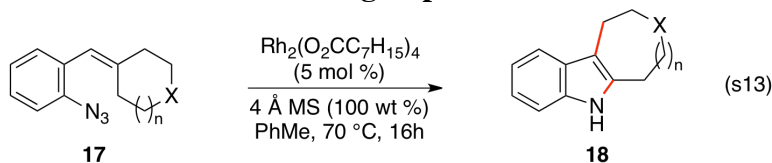
To a mixture of 0.1 mmol of aryl azide **17c** (0.1 mmol), 0-100 % w/w of crushed 4 Å mol sieves, and metal salt (0 – 5 mol %) in Schlenk tube was added 0.50 mL of solvent. The resulting mixture was heated and, after 16 h, the heterogenous mixture was filtered through a short pad of Al_2O_3 . The filtrate was concentrated *in vacuo*. The resulting solid (oil) was dissolved in 1.5 mL of CDCl_3 and 0.007 mL of dibromomethane (0.1 mmol) was added. The areas of the C–H peak on the carbon 13 position in **17c** and carbon 13 in **18c** were compared to the area of CH_2Br_2 to derive a yield.

Table s2. Optimization of Migration Process

entry	metal salt	mol %	wt %, 4 Å MS	temp (°C)	yield, % ^a
1	None	n.a.	0	150	>95
2	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	100	55	33
3	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	100	65	63
4	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	0	65	53
5	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	3	100	65	39
6	Rh ₂ (O ₂ CC ₇ H ₁₅) ₄	5	100	80	90
7	[Ir(cod)OMe] ₂	5	100	80	0
8	Rh ₂ (esp) ₂	5	100	80	20
9	RhCl(PPh ₃) ₃	5	100	80	0
10	Rh ₂ (O ₂ CC ₃ F ₇) ₄	5	100	80	66
11	RhCl ₃	5	100	80	0
12	Rh ₂ (O ₂ CCH ₃) ₄	5	100	80	0
13	Rh ₂ (O ₂ CCF ₃) ₄	5	100	80	34
14	RuCl ₃ .xH ₂ O	5	100	65	trace
15	RuCl ₃ .xH ₂ O	5	0	65	trace
16	Rh octanoate	5	100	65(40h)	90
17	Co TPP	5	100	65	0
18	Ag(OTf)	5	100	65	0
19	Cu(OTf) ₂	5	100	65	0
20	Rh octanoate (cyclopentane)	5	100	75	59
21	ZnI ₂	10	100	65	0
22	FeBr ₂	20	100	65	0
23	AuCl	10	100	65	0

^a Isolated yield after Al₂O₃ chromatography.**2. Optimization of Solvent.**

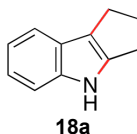
Solvent	PhMe	1,2-DCE	1,4-dioxane	DME	DMF
Yield, % ^a	63%	66%	0	0	0

^a Isolated yield after Al₂O₃ chromatography.**3. Optimized Procedure for Ring Expansion.**

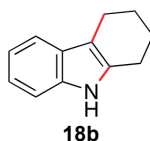
To a mixture of 0.026 g of aryl azide **17** (0.1 mmol), 100 % w/w of crushed 4 Å mol sieves, and metal salt (Rh₂(O₂CC₇H₁₅)₄, 5 mol %) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at

80 °C for 16 h, then, the heterogenous mixture was filtered through a short pad of Al₂O₃. The filtrate was concentrated *in vacuo* to afford analytically pure indole.

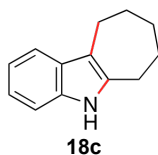
4. Scope and Limitations of Ring Expansion.



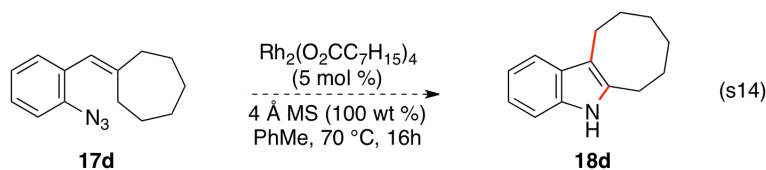
Indole 18a.¹¹ The general procedure was followed using 0.035 g of styryl azide **17a** (0.189 mmol) and 0.007 g of Rh₂(O₂CC₇H₁₅)₄ (0.009 mmol) in 0.6 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound **18a** (0.029 g, 98%). Indole **18a** was previously reported by Tan and Hartwig.¹¹ mp 58 - 61 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.74 (s, 1H), 7.47 – 7.49 (m, 1H), 7.29 – 7.31 (m, 1H), 7.12 – 7.14 (m, 2H), 2.86 -2.89 (m, 4H), 2.56 – 2.59 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 143.8 (C), 141.0 (C), 124.8 (C), 120.5 (CH), 119.8 (C), 119.5 (CH), 118.5 (CH), 111.4 (CH), 28.7 (CH₂), 25.9 (CH₂), 24.5 (CH₂); IR (thin film): 3400, 2951, 2853, 1467, 1313, 913, 736 cm⁻¹.



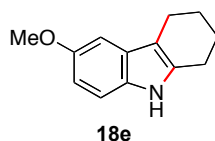
Indole 18b.¹³ The general procedure was followed using 0.055 g of styryl azide **17b** (0.276 mmol) and 0.011 g of Rh₂(O₂CC₇H₁₅)₄ (0.014 mmol) in 0.7 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound **18b** (0.044 g, 93%). The spectral data for **18b** matched that reported by Leogane and Lebel:¹³ ¹H NMR (500 MHz, CDCl₃) δ 7.64 (s, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.08 – 7.15 (m, 2H), 2.73 (t, *J* = 6.0 Hz, 4H), 1.87 – 1.96 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 135.7 (C), 134.1 (C), 127.9 (C), 121.0 (CH), 119.1 (CH), 117.7 (CH), 110.4 (CH), 110.2 (C), 23.34 (CH₂), 23.26 (CH₂), 21.0 (CH₂) one overlapping aliphatic C not distinguishable; IR (thin film): 3397, 1667, 1603, 1497, 1456, 1276, 911, 749 cm⁻¹.



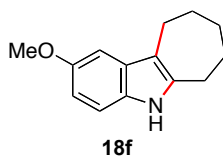
Indole 18c.¹⁴ The general procedure was followed using 0.051 g of styryl azide **17c** (0.239 mmol) and 0.009 g of Rh₂(O₂CC₇H₁₅)₄ (0.012 mmol) in 0.6 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound **18c** (0.041 g, 93%). The spectral data for **18c** matched that reported by Banwell and co-workers:¹⁴ mp 140 - 142 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (s, 1H), 7.15 – 7.53 (m, 1H), 7.26 – 7.27 (m, 1H), 7.11 – 7.15 (m, 2H), 2.82 -2.87 (m, 4H), 1.91 – 1.94 (m, 2H), 1.81 – 1.83 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 137.5 (C), 134.3 (C), 129.3 (C), 120.6 (CH), 119.1 (CH), 117.7 (CH), 113.8 (C), 110.3 (CH), 31.9 (CH₂), 29.6 (CH₂), 28.8 (CH₂), 27.6 (CH₂), 24.7 (CH₂); IR (thin film): 3391, 2914, 2844, 1465, 1438, 913, 743 cm⁻¹.



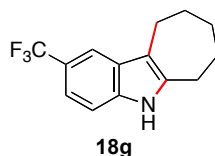
Indole 18d. The general procedure was followed using 0.046 g of styryl azide **17d** (0.203 mmol) and 0.008 g of $\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4$ (0.010 mmol) in 0.6 mL of PhMe. Analysis of the reaction progress using ^1H NMR spectroscopy revealed that 18% of indole **18d** formed and 35% starting of aryl azide **17d** remained.



Indole 18e. The general procedure was followed using 0.061 g of styryl azide **17e** (0.266 mmol) and 0.010 g of $\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4$ (0.013 mmol) in 0.7 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **18e** (0.054 g, 100%). Spectral data for **18e**: ^1H NMR (500 MHz, CDCl_3) δ 7.56 (s, 1H), 7.16 (d, $J = 9.0$ Hz, 1H), 6.97(d, $J = 2.5$ Hz, 1H), 6.81 (dd, $J = 2.5$ Hz, 9.0 Hz, 1H), 3.89 (s, 3H), 2.70 – 2.72 (m, 4H), 1.89 – 1.95 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.9 (C), 135.2 (C), 130.8 (C), 128.2 (C), 111.0 (CH), 110.5 (CH), 110.0 (C), 100.4 (CH), 56.0 (CH_3), 23.38 (CH_2), 23.27 (CH_2), 21.0 (CH_2) one overlapping aliphatic carbon signal not distinguishable; IR (thin film): 3281, 2936, 1659, 1492, 1274, 1214, 1030, 732 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{ON}$ (M) $^+$ 201.11537, found 201.11616.

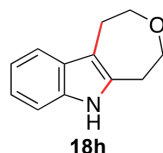


Indole 18f. The general procedure was followed using 0.045 g of styryl azide **17f** (0.201 mmol) and 0.008 g of $\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4$ (0.010 mmol) in 0.5 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **18e** (0.039 g, 100%). mp 42 - 46 $^\circ\text{C}$; Spectral data for **18f**: ^1H NMR (500 MHz, CDCl_3) δ 7.58 (s, 1H), 7.14 (d, $J = 8.5$ Hz, 1H), 6.97(d, $J = 2.5$ Hz, 1H), 6.79 (dd, $J = 2.5$ Hz, 8.5 Hz, 1H), 3.89 (s, 3H), 2.79 – 2.81(m, 4H), 1.90 – 1.92 (m, 2H), 1.79 – 1.81 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.9 (C), 138.6 (C), 129.6 (C), 129.4 (C), 113.6 (C), 110.9 (CH), 110.4 (CH), 100.1 (CH), 56.0 (CH_3), 31.9 (CH_2), 29.7 (CH_2), 28.8 (CH_2), 27.6 (CH_2), 24.8 (CH_2); IR (thin film): 3401, 2916, 1625, 1483, 1452, 913, 745 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{ON}$ (M) $^+$ 215.13102, found 215.13248.



Indole 18g. The general procedure was followed using 0.027 g of styryl azide **17g** (0.009 mmol) and 0.004 g of $\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4$ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **18g** (0.021 g, 88%). Spectral data for **18g**: ^1H NMR (500 MHz, CDCl_3) δ 7.89 (s, 1H), 7.76 (s, 1H), 7.29 – 7.34 (m, 2H), 2.82 – 2.86 (m, 4H), 1.90 – 1.94 (m, 2H), 1.76 – 1.82 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.3 (C), 135.6 (C), 128.7 (C), 125.6 (q, $J_{\text{CF}} = 270.1$ Hz, C), 121.4 (q, $J_{\text{CF}} = 31.3$ Hz, C), 117.4 (q, $J_{\text{CF}} = 3.6$ Hz, CH), 115.4 (q, $J_{\text{CF}} = 3.5$ Hz, CH), 114.7 (C), 110.2 (CH), 31.6 (CH_2), 29.6 (CH_2), 28.5 (CH_2), 27.4 (CH_2), 24.6 (CH_2);

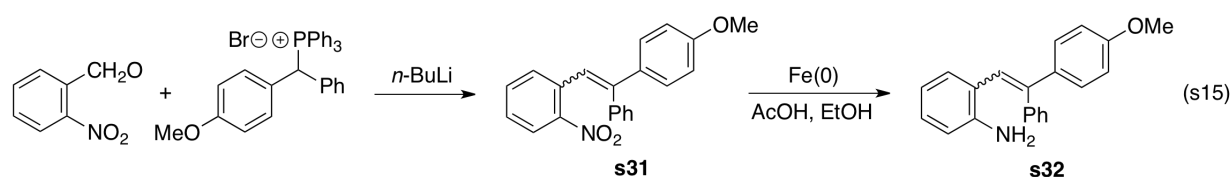
^{19}F NMR (CDCl_3 , 282 MHz) δ -60.66; IR (thin film): 3474, 3419, 2921, 1626, 1463, 1327, 1108, 1050, 763 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{N}$ (M) $^+$ 253.10783, found 253.10944.



Indole 18h. The general procedure was followed using 0.057 g of styryl azide **17h** (0.265 mmol) and 0.010 g of $\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15})_4$ (0.013 mmol) in 0.6 mL of PhMe. Filtration by Al_2O_3 afforded analytically pure compound **18h** (0.048 g, 97%). mp 116 - 119 $^\circ\text{C}$; Spectral data for **18h**: ^1H NMR (500 MHz, CDCl_3) δ 7.85 (s, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.12 - 7.18 (m, 2H), 3.97 - 4.02 (m, 4H), 3.00 - 3.03 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.5 (C), 134.8 (C), 128.9 (C), 121.2 (CH), 119.4 (CH), 117.8 (CH), 112.4 (C), 110.4 (CH), 73.1 (CH_2), 70.7 (CH_2), 32.2 (CH_2), 27.6 (CH_2); IR (thin film): 3400, 3294, 2936, 1464, 1113, 913 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{13}\text{ON}$ (M) $^+$ 187.09972, found 187.10060.

V. Mechanistic Experiments

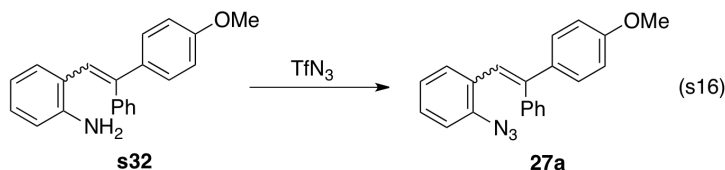
A. Synthesis of Aryl Azides 27.



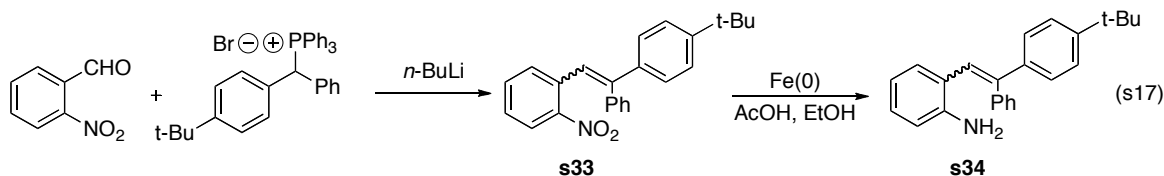
Styrene s31. To a solution of 10.4 g of the phosphonium salt (19.3 mmol) in 100 mL of THF at -78 $^\circ\text{C}$, was added 8.5 mL of n -BuLi (2.5 M in hexanes, 21.2 mmol) dropwise. After stirring for 1 h at -78 $^\circ\text{C}$, the mixture was warmed to room temperature and stirred additional half an hour. Then 2.65 g of 2-nitrobenzaldehyde (17.5 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH_2Cl_2 (3×30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na_2SO_4 . The mixture was filtered and the filtrate was concentrated *in vacuo* to afford styrene **s31**, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

Aniline s32. To a solution of nitro-substituted styrene **s31** in 40 mL of AcOH and 40 mL of EtOH was added 8.6 g of Fe powder (154.4 mmol). The resultant mixture was heated to reflux at 80 $^\circ\text{C}$. After 16 h, the reaction mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 80 mL of water and washed with 3×30 mL of dichloromethane. The resulting organic phase was washed with 50 mL of brine and dried over Na_2SO_4 . The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. Purification by MPLC (10:1 hexanes:EtOAc) afforded the product as a yellow viscous oil as an 67:33 mixture of *E*- and *Z*-isomers (1.37 g, 24%, two steps): Spectral data for the major (*E*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.29 - 7.39 (m, 4H), 7.17 - 7.19 (m, 1H), 7.10 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 7.5 Hz, 1H), 6.74 - 6.80 (m, 4H), 6.53 (t, J = 7.5 Hz, 1H), 3.80 (s, 3H), *N-H peak not observed*; ^{13}C NMR (125 MHz, CDCl_3) δ 144.5 (C), 143.8 (C), 143.6 (C), 132.3 (C), 131.7 (CH), 130.4 (CH), 128.25 (CH), 128.19 (CH), 127.9 (CH), 127.6 (CH), 123.93 (C), 123.90 (C), 123.8 (CH), 118.3 (CH), 115.5 (CH), 113.6 (CH), 55.2 (CH_3); Selected spectral data for the minor (*Z*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.29 - 7.39 (m, 4H), 7.24 - 7.26 (m, 3H), 6.96 - 7.02 (m, 3H), 6.64 - 6.66 (m, 3H),

6.50 (t, $J = 7.5$ Hz, 1H), 3.84 (s, 3H), *N-H* peak not available; ^{13}C NMR (125 MHz, CDCl_3) δ 144.6 (C), 140.3 (C), 136.0 (C), 130.51 (CH), 130.43 (CH), 129.3 (CH), 127.8 (CH), 127.4 (CH), 122.8 (CH), 118.2 (CH), 115.4 (CH), 55.4 (CH_3) these are the only visible peaks; IR (thin film): 3462, 3375, 1739, 1605, 1508, 1242, 1176, 1031, 749 cm^{-1} .



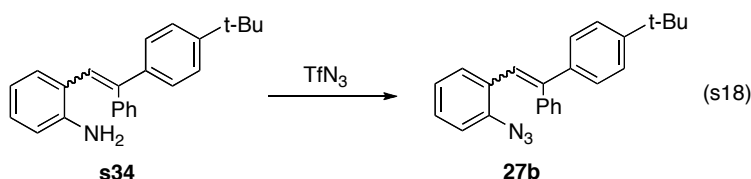
Aryl Azide 27a. To a solution of 0.82 g of aniline **s32** (2.7 mmol) in 5 mL of CH_2Cl_2 was added subsequently 24 mg of CuSO_4 , 1.2 mL of Et_3N , freshly prepared triflyl azide (9 mmol) in 15 mL of CH_2Cl_2 , 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h., the reaction mixture was diluted with 15 mL of CH_2Cl_2 , and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO_3 . Once pH 7 was reached, the resulting mixture was washed with 3×10 mL of CH_2Cl_2 . The resulting organic phase was washed with 20 mL of brine and dried over Na_2SO_4 . After filtration, the filtrate was concentrated *in vacuo*. Purification by MPLC (10:1 hexane:EtOAc) afforded the product as a yellow viscous oil as an 69:31 mixture of *E*- and *Z*-isomers (0.42 g, 48%): Selected spectral data for the major (*E*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.27 – 7.36 (m, 4H), 7.12 – 7.17 (m, 2H), 7.08 (d, $J = 9.0$ Hz, 2H), 6.87 – 6.88 (m, 2H), 6.80 – 6.83 (m, 3H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0 (C), 143.8 (C), 143.5 (C), 138.6 (C), 132.2 (C), 129.8 (C), 131.8 (CH), 130.7 (CH), 129.2 (CH), 128.37 (CH), 128.18 (CH), 128.11 (CH), 127.7 (CH), 124.1 (CH), 118.2 (CH), 113.8 (CH), 55.2 (CH_3); Selected spectral data for the minor (*Z*) isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.27 – 7.36 (m, 5H), 7.12 – 7.17 (m, 4H), 6.95 – 6.96 (m, 3H), 6.77 – 6.78 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.5 (C), 143.7 (C), 140.2 (C), 138.5 (C), 135.8 (C), 129.7 (C), 130.72 (CH), 130.58 (CH), 127.94 (CH), 127.82 (CH), 127.4 (CH), 124.0 (CH), 122.5 (CH), 121.3 (CH), 118.1 (CH), 113.6 (CH), 55.4 (CH_3); IR (thin film): 2117, 2085, 1738, 1604, 1509, 1289, 1246, 1176, 1034, 751 cm^{-1} .



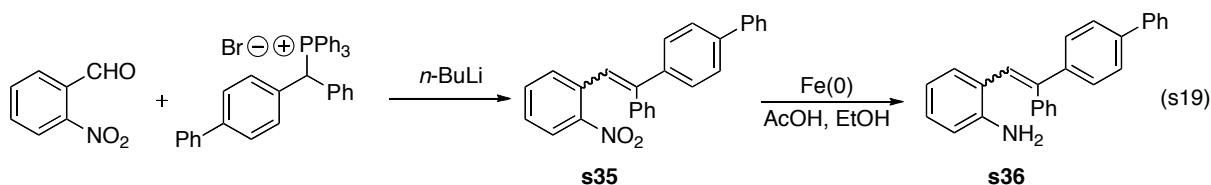
Styrene s33. To a solution of 10.8 g of the phosphonium salt (19.1 mmol) in 60 mL of THF at -78 $^\circ\text{C}$, was added 8.4 mL of *n*-BuLi (2.5 M in hexanes, 21.01 mmol) dropwise. After stirring for 1 h at -78 $^\circ\text{C}$, the mixture was warmed to room temperature and stirred additional half an hour. Then 2.69 g of 2-nitrobenzaldehyde (19.1 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH_2Cl_2 (3×30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na_2SO_4 . The mixture was filtered and the filtrate was concentrated *in vacuo* to afford styrene **s35**, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

Aniline s34. To a solution of nitro-substituted styrene **s33** in 40 mL of AcOH and 40 mL of EtOH was added 8.6 g of Fe powder (152.8 mmol). The resultant mixture was heated to reflux at 80 $^\circ\text{C}$. After 16 h, the reaction mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 80 mL of water and washed with 3×30 mL of dichloromethane. The resulting organic phase was washed with 50 mL of brine and dried over Na_2SO_4 . The resulting mixture was

filtered, and the filtrate was concentrated *in vacuo*. Purification by MPLC (10:1 hexanes:EtOAc) afforded the product as a yellow solid (1.5 g, 24%, two steps); Spectral data for the major isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.39 (m, 2H), 7.31 – 7.33 (m, 2H), 7.25 – 7.27 (m, 3H), 7.19 – 7.21 (m, 2H), 6.97 – 7.00 (m, 1H), 6.84 (s, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 1H), 6.51 (t, $J = 7.5$ Hz, 1H), 3.74 (br, 2H), 1.37 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 150.8 (C), 144.7 (C), 143.9 (C), 140.4 (C), 140.2 (C), 130.53 (CH), 130.43 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 125.2 (CH), 123.7 (CH), 118.2 (CH), 115.4 (CH), 34.6 (C), 31.4 (CH_3); IR (thin film): 3379, 1617, 1246, 905, 726, 701, 649 cm^{-1} .



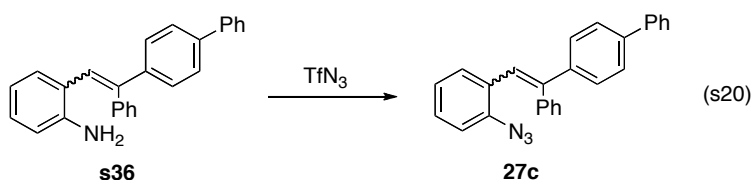
Aryl Azide 27b. To a solution of 1.2 g of aniline **s34** (3.8 mmol) in 5 mL of CH_2Cl_2 was added subsequently 32 mg of CuSO_4 , 1.6 mL of Et_3N , freshly prepared triflyl azide (12 mmol) in 15 mL of CH_2Cl_2 , 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 15 mL of CH_2Cl_2 , and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO_3 . Once pH 7 was reached, the resulting mixture was washed with 3×10 mL of CH_2Cl_2 . The resulting organic phase was washed with 20 mL of brine and dried over Na_2SO_4 . After filtration, the filtrate was concentrated *in vacuo*. Purification by MPLC (100:1 hexane:EtOAc) afforded the product as a yellow solid as an 1:1 mixture of *E*- and *Z*-isomers (0.88 g, 66%): Spectral data for *E*- and *Z*- isomers: ^1H NMR (500 MHz, CDCl_3) δ 7.27 – 7.36 (m, 14H), 7.11 – 7.17 (m, 6H), 7.06 – 7.07 (m, 2H), 7.02 (s, 2H), 6.76 – 6.82 (m, 4H), 1.33 – 1.34 (m, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ 150.9 (C), 143.4 (C), 140.1 (C), 138.6 (C), 136.8 (C), 130.78 (CH), 130.73 (CH), 130.56 (CH), 130.1 (CH), 129.70 (C), 129.63 (C), 128.35 (CH), 128.15 (CH), 128.08 (CH), 127.93 (CH), 127.90 (CH), 127.67 (CH), 127.55 (CH), 127.39 (CH), 125.20 (CH), 125.14 (CH), 124.01 (CH), 123.98 (CH), 122.7 (CH), 122.3 (CH), 118.1 (CH), 34.6 (CH_3), 31.4 (CH_3) *only distinguishable peaks*; IR (thin film): 2117, 2085, 1796, 1730, 1287, 908, 733 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{N}_3$ (M^+) 353.18920, found 353.19017.



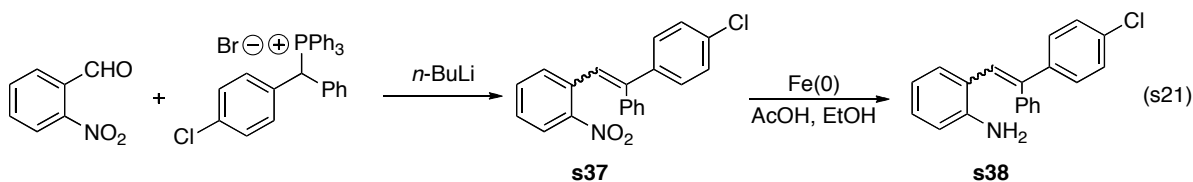
Styrene s35. To a solution of 9.6 g of the phosphonium salt (16.4 mmol) in 60 mL of THF at -78 $^\circ\text{C}$, was added 7.2 mL of *n*-BuLi (2.5 M in hexanes, 18.1 mmol) dropwise. After stirring for 1 h at -78 $^\circ\text{C}$, the mixture was warmed to room temperature and stirred additional half an hour. Then 2.48 g of 2-nitrobenzaldehyde (16.4 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH_2Cl_2 (3×30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na_2SO_4 . The mixture was filtered and the filtrate was concentrated *in vacuo* to afford styrene **s35**, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

Aniline s36. To a solution of nitro-substituted styrene **s35** in 30 mL of AcOH and 30 mL of EtOH was added 7.3 g of Fe powder (131.2 mmol). The resultant mixture was heated to reflux at 80 $^\circ\text{C}$. After 16 h, the reaction

mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 70 mL of water and washed with 3 × 30 mL of dichloromethane. The resulting organic phase was washed with 50 mL of brine and dried over Na₂SO₄. The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. Purification by MPLC (10:1 hexanes:EtOAc) afforded the product as a yellow solid (602 mg, 11%, two steps); Spectral data for the major isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.70 (m, 4H), 7.47 – 7.56 (m, 5H), 7.41 – 7.43 (m, 1H), 7.27 – 7.34 (m, 4H), 7.03 – 7.07 (m, 1H), 6.95 (s, 1H), 6.86 (d, J = 7.5 Hz, 1H), 6.70 – 6.71 (m, 1H), 6.56 – 6.60 (m, 1H), 3.92 (br, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 144.8 (C), 143.7 (C), 142.4 (C), 140.8 (C), 140.5 (C), 131.1 (CH), 130.63 (CH), 130.48 (CH), 128.9 (CH), 128.6 (CH), 128.38 (CH), 128.20 (CH), 127.6 (CH), 127.12 (CH), 127.01 (CH), 124.4 (CH), 123.7 (C), 118.3 (CH), 115.6 (CH); IR (thin film): 3457, 1739, 1486, 1454, 1366, 1216, 905 cm⁻¹.

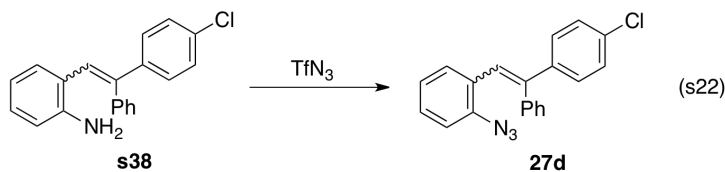


Aryl Azide 27c. To a solution of 0.55 g of aniline **s36** (1.6 mmol) in 5 mL of CH₂Cl₂ was added subsequently 16 mg of CuSO₄, 0.8 mL of Et₃N, freshly prepared triflyl azide (6 mmol) in 15 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 15 mL of CH₂Cl₂, and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO₃. Once pH 7 was reached, the resulting mixture was washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated *in vacuo*. Purification by MPLC (100:1 hexane:EtOAc) afforded the product as a pale solid (0.26 g, 43%). Spectral data for *E*- and *Z* isomer mixture: ¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.66 (m, 4H), 7.54 – 7.59 (m, 4H), 7.10 – 7.49 (m, 25H), 7.06 (s, 1H), 6.91 – 6.93 (m, 1H), 6.78 – 6.84 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.8 (C), 143.7 (C), 143.2 (C), 142.1 (C), 140.7 (C), 140.6 (C), 140.56 (C), 140.1 (C), 140.0 (C), 139.0 (C), 138.7 (C), 131.1 (CH), 130.84 (CH), 130.76 (CH), 130.6 (CH), 129.53, 129.46, 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.6 (CH), 127.4 (CH), 127.4 (CH), 127.1 (CH), 126.99 (CH), 126.94 (CH), 124.2 (CH), 124.1 (CH), 123.3 (CH), 123.0 (CH), 118.2 (CH), 118.2 (CH) *only distinguishable peaks*; IR (thin film): 2117, 2085, 1738, 1604, 1509, 1289, 1246, 1176, 1034, 751 cm⁻¹. HRMS (EI) *m/z* calcd for C₂₆H₁₉N₃ (M)⁺ 373.15790, found 373.15891.

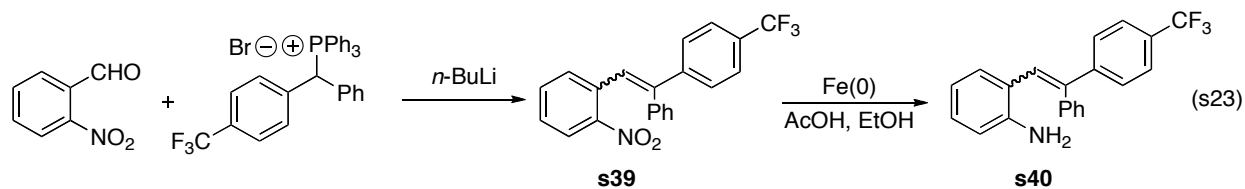


Styrene s37. To a solution of 8.5 g of the phosphonium salt (15.7 mmol) in 50 mL of THF at -78 °C, was added 6.9 mL of *n*-BuLi (2.5 M in hexanes, 17.3 mmol) dropwise. After stirring for 1 h at -78 °C, the mixture was warmed to room temperature and stirred additional half an hour. Then 2.4 g of 2-nitrobenzaldehyde (15.7 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH₂Cl₂ (3 × 30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na₂SO₄. The mixture was filtered and the filtrate was concentrated *in vacuo* to afford styrene **s37**, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

Aniline s38. To a solution of nitro-substituted styrene **s37** in 40 mL of AcOH and 40 mL of EtOH was added 7.1 g of Fe powder (125.6 mmol). The resultant mixture was heated to reflux at 80 °C. After 16 h, the reaction mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 80 mL of water and washed with 3 × 30 mL of dichloromethane. The resulting organic phase was washed with 50 mL of brine and dried over Na₂SO₄. The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. Purification by MPLC (10:1 hexanes:EtOAc) afforded the product as a pale solid (1024 mg, 21%, two steps); Spectral data for the major isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.12 – 7.36 (m, 9H), 6.98 – 7.04 (m, 1H), 6.81 – 6.84 (m, 1H), 6.77 – 6.78 (m, 1H), 6.66 – 6.68 (m, 1H), 6.50 – 6.56 (m, 1H), 3.76 (br, 2H); spectral data for both the *E*- and *Z*-isomer: ¹³C NMR (125 MHz, CDCl₃) δ 144.74 (C), 144.71 (C), 143.9 (C), 143.02 (C), 142.96 (C), 141.9 (C), 139.6 (C), 138.5 (C), 133.5 (C), 133.2 (C), 131.9 (CH), 130.45 (CH), 130.35 (CH), 130.29 (CH), 129.4 (CH), 128.52 (CH), 128.38 (CH), 128.36 (CH), 128.30 (CH), 128.13 (CH), 127.9 (CH), 127.6 (CH), 125.0 (CH), 124.8 (CH), 118.34 (CH), 118.28 (CH), 115.59 (CH), 115.54 (CH); IR (thin film): 3463, 3378, 1614, 1485, 1089, 728 cm⁻¹.

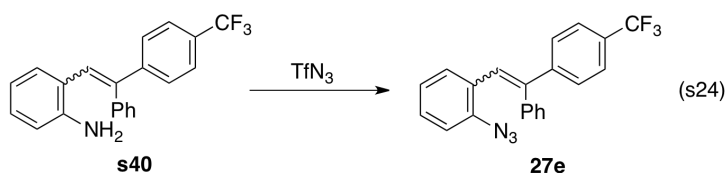


Aryl Azide 27d. To a solution of 0.90 g of aniline **s38** (3.0 mmol) in 5 mL of CH₂Cl₂ was added subsequently 24 mg of CuSO₄, 1.2 mL of Et₃N, freshly prepared triflyl azide (9 mmol) in 15 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 15 mL of CH₂Cl₂, and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO₃. Once pH 7 was reached, the resulting mixture was washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated *in vacuo*. Purification by MPLC (100:1 hexane:EtOAc) afforded the product as a yellow viscous oil (0.44 g, 45%): Spectral data for the mixture: ¹H NMR (500 MHz, CDCl₃) δ 7.10 – 7.37 (m, 22H), 6.96 – 7.04 (m, 2H), 6.75 – 6.84 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 143.0 (C), 142.7 (C), 141.6 (C), 139.6 (C), 138.78 (C), 138.74 (C), 138.5 (C), 133.7 (C), 133.4 (C), 132.0 (CH), 130.7 (CH), 130.51 (CH), 130.41 (CH), 130.1 (CH), 129.25 (CH), 129.17 (CH), 128.69 (CH), 128.55 (CH), 128.41 (CH), 128.36 (CH), 128.31 (CH), 128.0 (CH), 127.7 (CH), 126.6 (CH), 125.6 (CH), 124.24 (CH), 124.09 (CH), 123.8 (CH), 123.4 (CH), 118.30 (CH), 118.27 (CH), 118.18 (CH); IR (thin film): 2117, 2085, 1738, 1604, 1509, 1289, 1246, 1176, 1034, 751 cm⁻¹. HRMS (EI) *m/z* calcd for C₂₀H₁₄N₃Cl (M)⁺ 331.08762, found 331.08665.



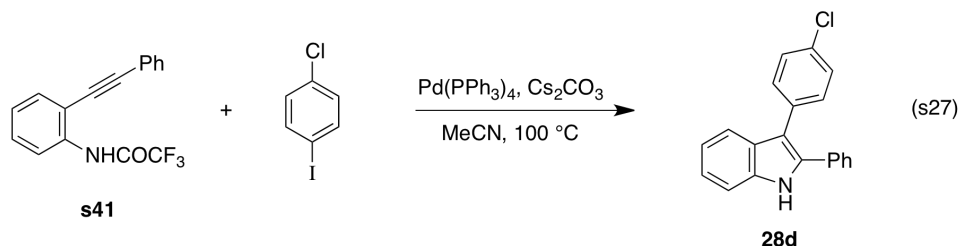
Styrene s39. To a solution of 3.46 g of the phosphonium salt (6 mmol) in 60 mL of THF at $-78\text{ }^{\circ}\text{C}$, was added 2.4 mL of *n*-BuLi (2.5 M in hexanes, 6 mmol) dropwise. After stirring for 1 h at $-78\text{ }^{\circ}\text{C}$, the mixture was warmed to room temperature and stirred additional half an hour. Then 0.91 g of 2-nitrobenzaldehyde (6 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH_2Cl_2 ($3 \times 30\text{ mL}$). The resulting organic phase was washed with 60 mL of brine and dried over Na_2SO_4 . The mixture was filtered and the filtrate was concentrated *in vacuo* to afford styrene **s31**, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

Aniline s40. To a solution of nitro-substituted styrene **s39** in 15 mL of AcOH and 15 mL of EtOH was added 2.7 g of Fe powder (48 mmol). The resultant mixture was heated to reflux at $80\text{ }^{\circ}\text{C}$. After 16 h, the reaction mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 20 mL of water and washed with $3 \times 10\text{ mL}$ of dichloromethane. The resulting organic phase was washed with 20 mL of brine and dried over Na_2SO_4 . The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. Purification by MPLC (10:1 hexanes:EtOAc) afforded the product as a yellow solid (190 mg, 12%, two steps); $^1\text{H NMR}$ (500 MHz; CDCl_3) δ 7.69 (d, $J = 8.5\text{ Hz}$, 2.4H), 7.61 (d, $J = 8.0\text{ Hz}$, 1.6H), 7.57 (d, $J = 8.5\text{ Hz}$, 2.4H), 7.45 (s, 4H), 7.42 (d, $J = 8.0\text{ Hz}$, 1.6H), 7.38 – 7.37 (m, 3.6H), 7.30 – 7.29 (m, 2.4H), 7.11 (t, $J = 7.5\text{ Hz}$, 2H), 7.01 (d, $J = 8.0\text{ Hz}$, 2H); 6.92 (d, $J = 8.0\text{ Hz}$, 1.2H), 6.84 (d, $J = 8.0\text{ Hz}$, 0.8H), 6.74 (dd, $J = 8.0, 3.5\text{ Hz}$, 2H), 6.62 (t, $J = 8.0\text{ Hz}$, 2H), 3.83 (br, 4H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 147.2 (C), 145.1 (C), 145.0 (C), 144.1 (C), 142.9 (C), 142.8 (C), 142.8 (C), 139.5 (C), 131.1 (CH), 130.6 (CH), 130.5 (CH), 130.4 (CH), 128.7 (CH), 128.6 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.2 (CH), 128.0 (CH), 126.4 (CH), 125.9 (CH), 125.3 (q, $J_{\text{CF}} = 3.5\text{ Hz}$, CF_3), 123.4 (C), 123.3 (C), 123.2 (C), 123.0 (C), 118.4 (CH), 118.4 (CH), 115.8 (CH), 115.7 (CH); *only distinguishable peaks*. HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{16}\text{F}_3\text{N}$ (M) $^+$ 339.12348, found 339.12435.

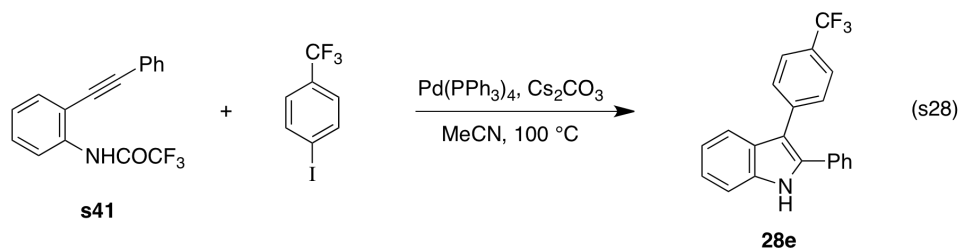


Aryl Azide 27e. To a solution of 0.17 g of aniline **s40** (0.5 mmol) in 5 mL of CH_2Cl_2 was added subsequently 6 mg of CuSO_4 , 0.3 mL of Et_3N , freshly prepared triflyl azide (2 mmol) in 5 mL of CH_2Cl_2 , 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 10 mL of CH_2Cl_2 , and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO_3 . Once pH 7 was reached, the resulting mixture was washed with $3 \times 10\text{ mL}$ of CH_2Cl_2 . The resulting organic phase was washed with 20 mL of brine and dried over Na_2SO_4 . After filtration, the filtrate was concentrated *in vacuo*. Purification by MPLC (100:1 hexane:EtOAc) afforded the product as a yellow viscous oil (0.076 g, 42%); $^1\text{H NMR}$ (500 MHz; CDCl_3) δ 7.59 (d, $J = 8.0\text{ Hz}$, 2.4H), 7.54 (d, $J = 8.0\text{ Hz}$, 1.6H), 7.46 (s, 2.4H), 7.44 (s, 1.6H), 7.36 – 7.28 (m, 8H), 7.23 – 7.10 (m, 8H), 6.81 – 6.77 (m, 4H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 146.7 (C), 144.0 (C), 142.8 (C), 142.4 (C), 139.3 (C), 138.9 (C), 131.0 (CH), 130.7 (CH), 130.5 (CH),

128.81 (CH), 128.76 (CH), 128.3 (CH), 127.8 (CH), 127.23 (CH), 127.18 (CH), 126.99 (CH), 122.8 (CH), 120.6 (CH), 119.8 (CH), 114.6 (C), 111.0 (CH); IR (thin film): 3415, 1770, 1455, 1248, 903, 725, 698, 649 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{26}\text{H}_{19}\text{N}$ (M)⁺ 345.15175, found 345.25258.

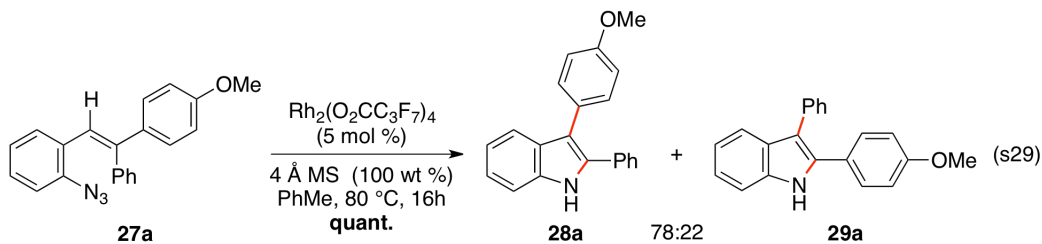


Indole 28d.¹⁵ To a solution of 0.59 g of acetylene (2.0 mmol) in 15 mL of MeCN was added subsequently 1.43 g of Cs_2CO_3 , 0.1 mol of $\text{Pd}(\text{PPh}_3)_4$ (5 mol %), 1.05 g of 1-chloro-4-iodobenzene (4.4 mmol). The resulting mixture was stirred at 100 °C until complete conversion (2h). After this time, the reaction mixture was cooled to room temperature, diluted with 30 mL of water and extracted with CH_2Cl_2 (3 \times 20 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na_2SO_4 . Purification by MPLC (30:1 hexane:EtOAc) afforded the product **28d** as a yellow solid (0.53 g, 88%). The spectral data matched that reported by Cacchi and co-workers:¹⁵ ^1H NMR (500 MHz, CDCl_3) δ 8.23 (br, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.34 -7.45 (m, 10H), 7.29 (t, J = 7.5 Hz, 1H), 7.20 – 7.23 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 135.9 (C), 134.4 (C), 133.7 (C), 132.4 (C), 132.1 (C), 131.4 (CH), 128.88 (CH), 128.84 (CH), 128.5 (C), 128.3 (CH), 128.0 (CH), 122.9 (CH), 120.7 (CH), 119.5 (CH), 113.8 (C), 111.1 (CH); IR (thin film): 3411, 1770, 1601, 1500, 1248, 1091, 1014, 905, 728 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{NCl}$ (M)⁺ 303.08147, found 303.08070.

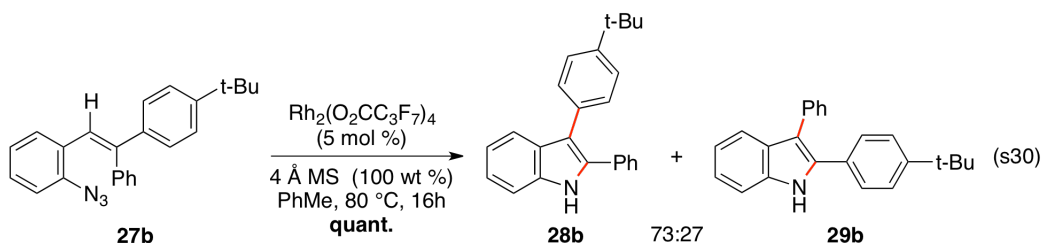


Indole 28e.¹⁶ To a solution of 0.59 g of acetylene (2.0 mmol) in 15 mL of MeCN was added subsequently 1.43 g of Cs_2CO_3 , 0.1 mol of $\text{Pd}(\text{PPh}_3)_4$ (5 mol %), 0.97 g of 4-trifluoromethyliodobenzene (4.4 mmol). The resulting mixture was stirred at 100 °C until complete conversion (2h). After this time, the reaction mixture was cooled to room temperature, diluted with 30 mL of water and extracted with CH_2Cl_2 (3 \times 20 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na_2SO_4 . Purification by MPLC (30:1 hexane:EtOAc) afforded the product **28e** as a yellow solid (0.63 g, 94%). The spectral data matched that reported by Wang and co-workers:¹⁶ ^1H NMR (500 MHz, CDCl_3) δ 8.29 (br, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.36 – 7.47 (m, 6H), 7.29 – 7.32 (m, 1H), 7.20 – 7.24 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 139.1 (C), 136.0 (C), 135.0 (C), 132.2 (C), 130.2 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 128.1 (d, J_{CF} = 38.5 Hz, CH), 125.5 (d, J_{CF} = 3.6 Hz, CH), 124.5 (d, J_{CF} = 270.0 Hz, C), 123.1 (C), 121.3 (C), 120.9 (CH), 119.3 (CH), 113.6 (C), 111.2 (CH); IR (thin film): 3405, 1614, 1448, 1321, 1108, 1065, 905, 850 cm^{-1} . HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{14}\text{NF}_3$ (M)⁺ 337.10783, found 337.10868.

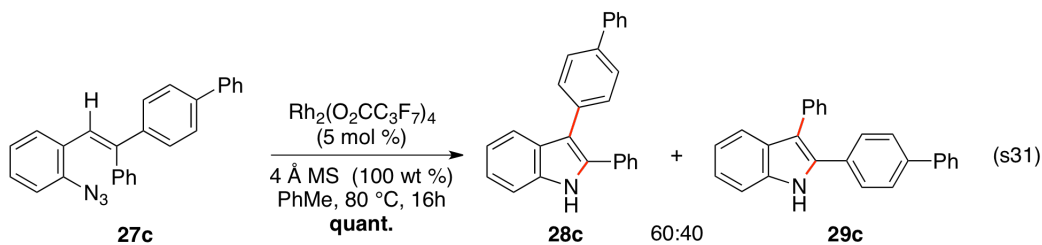
C. Intramolecular Competition Experiments.



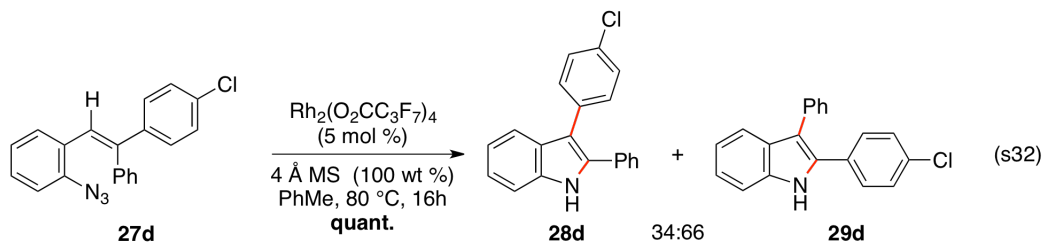
To a mixture of 0.023 g of aryl azide **27a** (0.07 mmol), 0.023 g of crushed 4 Å mol sieves, and 0.004 g of $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ (0.004 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al_2O_3 . The filtrate was concentrated *in vacuo* to afford 0.021 g of a mixture of **28a** and **29a** (78:22). The resulting solid was dissolved in 1.5 mL of CDCl_3 . The areas of the C–H peak on the methoxy position were compared to derive a ratio (78:22). The products were identified by comparison with published ^1H NMR spectra of **28a**.¹⁷



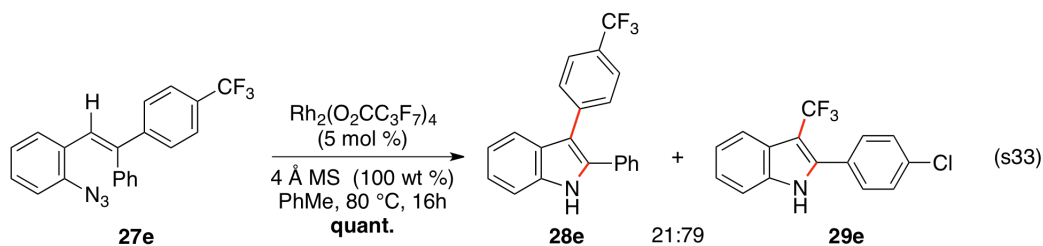
To a mixture of 0.058 g of aryl azide **27b** (0.16 mmol), 0.058 g of crushed 4 Å mol sieves, and 0.009 g of $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ (0.008 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al_2O_3 . The filtrate was concentrated *in vacuo* to afford 0.053 g of a mixture of **28b** and **29b** (73:27). The resulting solid was dissolved in 1.5 mL of CDCl_3 . The areas of the C–H peak on the aromatic region were compared to derive a ratio (73:27). The products were identified by comparison with ^1H NMR spectra of **28b**.



To a mixture of 0.060 g of aryl azide **27c** (0.16 mmol), 0.060 g of crushed 4 Å mol sieves, and 0.009 g of $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ (0.008 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al_2O_3 . The filtrate was concentrated *in vacuo* to afford 0.054 g of a mixture of **28c** and **29c** (60:40). The resulting solid was dissolved in 1.5 mL of CDCl_3 . The areas of the C–H peak on the aromatic region were compared to derive a ratio (60:40). The products were identified by comparison with ^1H NMR spectra of **28c**.



To a mixture of 0.043 g of aryl azide **27d** (0.13 mmol), 0.043 g of crushed 4 Å mol sieves, and 0.007 g of $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ (0.006 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al_2O_3 . The filtrate was concentrated *in vacuo* to afford 0.039 g of a mixture of **28d** and **29d** (34:66). The resulting solid was dissolved in 1.5 mL of CDCl_3 . The areas of the C–H peak on the aromatic region were compared to derive a ratio (34:66). The products were identified by comparison with ^1H NMR spectra of **28d**.



To a mixture of 0.040 g of aryl azide **27e** (0.11 mmol), 0.040 g of crushed 4 Å mol sieves, and 0.006 g of $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ (0.005 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al_2O_3 . The filtrate was concentrated *in vacuo* to afford 0.032 g of a mixture of **28e** and **29e** (21:79). The resulting solid was dissolved in 1.5 mL of CDCl_3 . The areas of the C–H peak on the aromatic region were compared to derive a ratio (21:79). The products were identified by comparison with ^1H NMR spectra of **28e**.

D. Correlation of Product Ratio with Hammett Plot.

The log of the product ratios were correlated with Hammett σ -values to ascertain the existence of any linear free energy relationships.

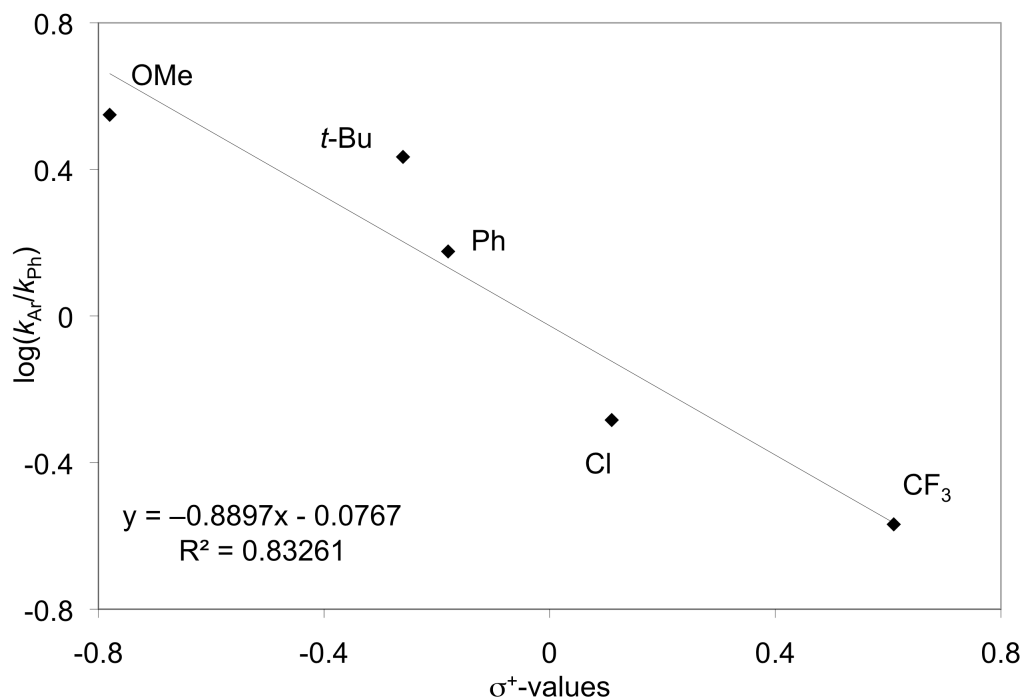


Figure s1. Correlation of Product Ratios with Hammett σ^+ -Values.

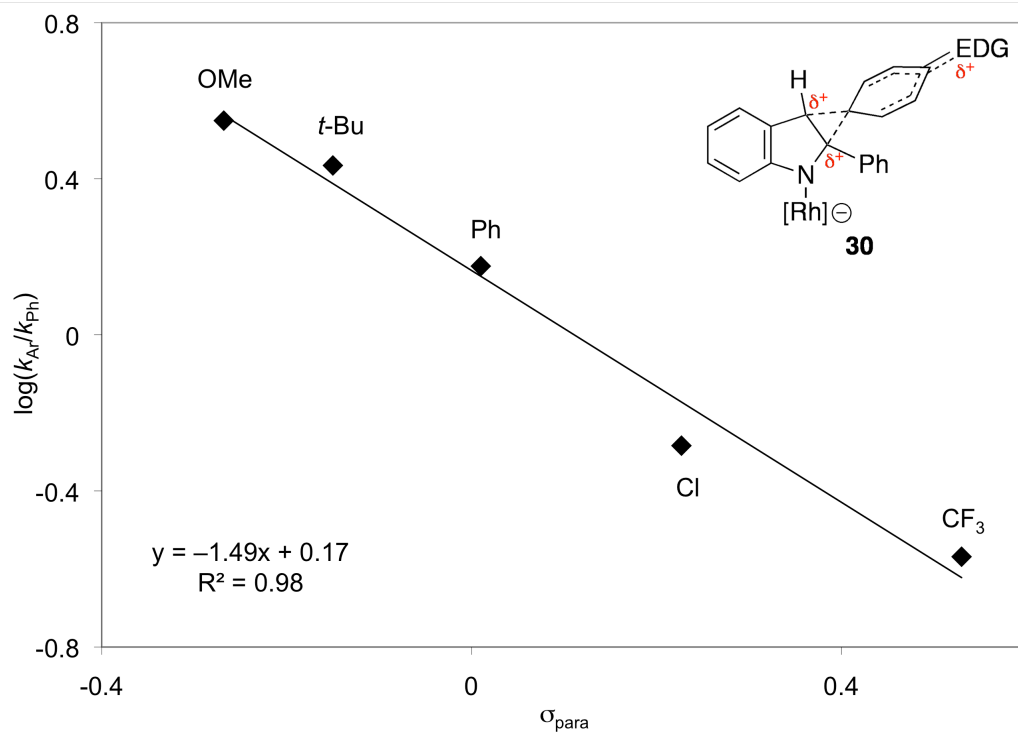
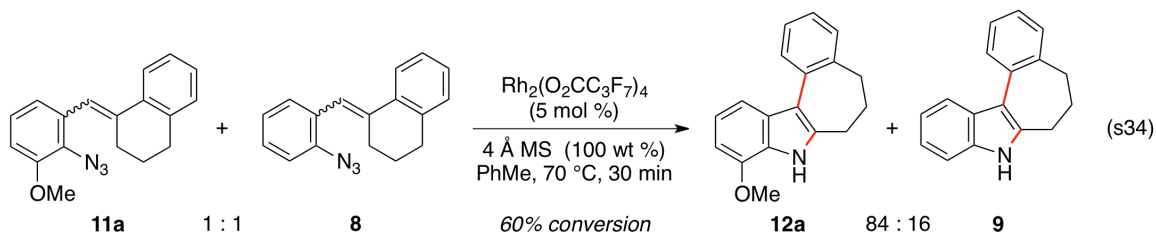


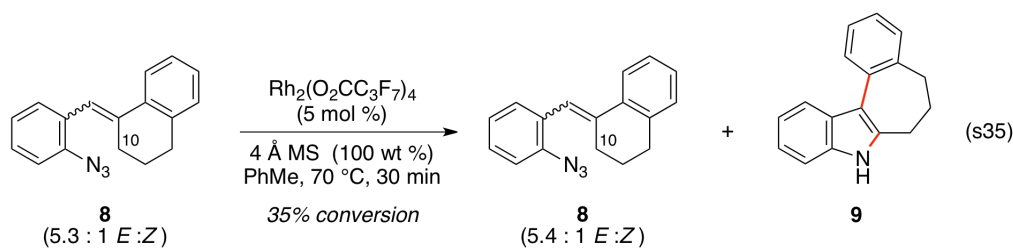
Figure s2. Correlation of Product Ratios with Hammett σ_{para} -Values.

D. Intermolecular Competition Experiment.



To a mixture of 0.013 g of styryl azide **11a** (0.05 mmol) and 0.0145 g of styryl azide **8** (0.05 mmol), 100 % w/w of crushed 4 Å mol sieves, and $\text{Rh}_2(\text{hpfb})_4$ (5 mol %) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 70 °C. After 30 min, the heterogenous mixture was filtered through a short pad of Al_2O_3 . The filtrate was concentrated *in vacuo* to afford analytically pure indoles. Analysis of the ^1H NMR spectrum showed 98% conversion of the styryl azide **11a** into **12a** and 23% conversion of the styryl azide **8** into indole **9**. ^1H NMR (500 MHz, CDCl_3) δ 4.02 (s, 3 H) vs 3.94 (s, 0.0734 H) vs 7.07 – 7.08 (m, 0.774 H) = **12a** vs **11a** vs **8**.

D. Examination of Rates of Reaction of *E*- and *Z*-Isomers.



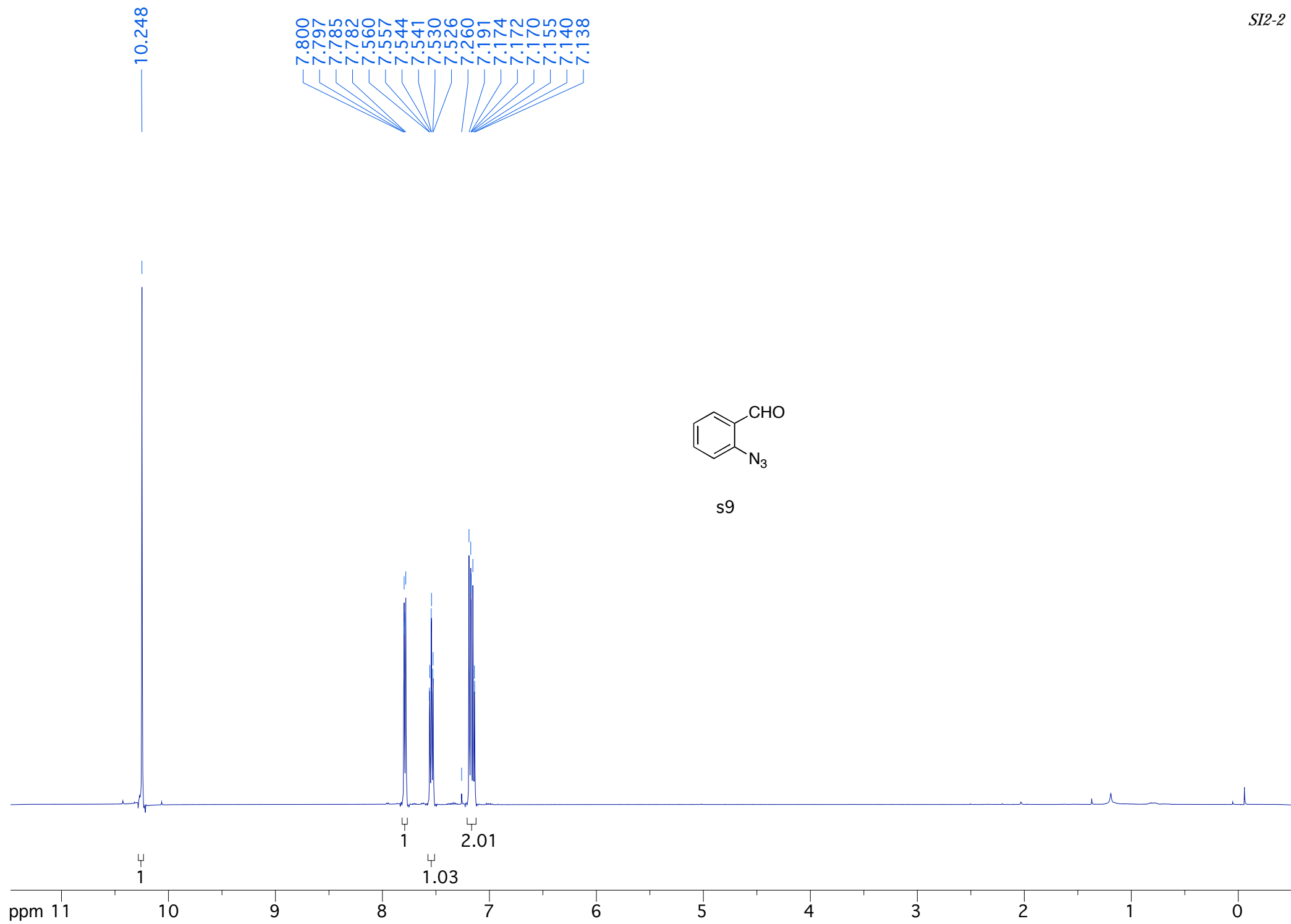
To a mixture of 0.043 g of aryl azide **8** (0.16 mmol), 0.043 g of crushed 4 Å mol sieves, and 0.009 g of $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ (0.008 mol) in Schlenk tube was added 0.60 mL of PhMe. The resulting mixture was heated at 70 °C, after 30 min, the heterogenous mixture was filtered through a short pad of Al_2O_3 . The filtrate was concentrated *in vacuo*. The resulting solid (oil) was dissolved in 1.5 mL of CDCl_3 . The areas of the C–H peak on the carbon **9** in starting material aryl azide **8** was compared to derive a *E:Z* ratio.

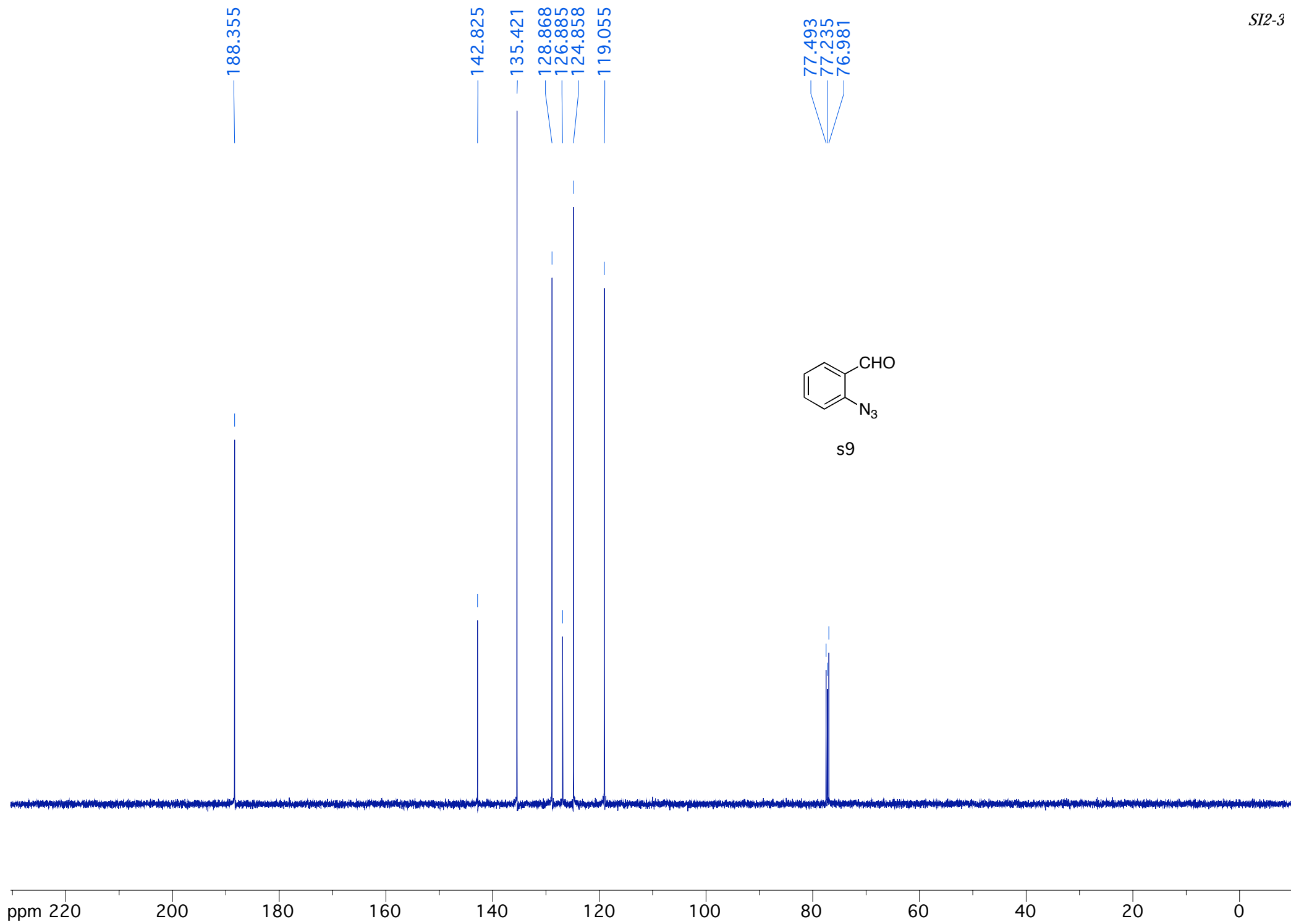
VI. References.

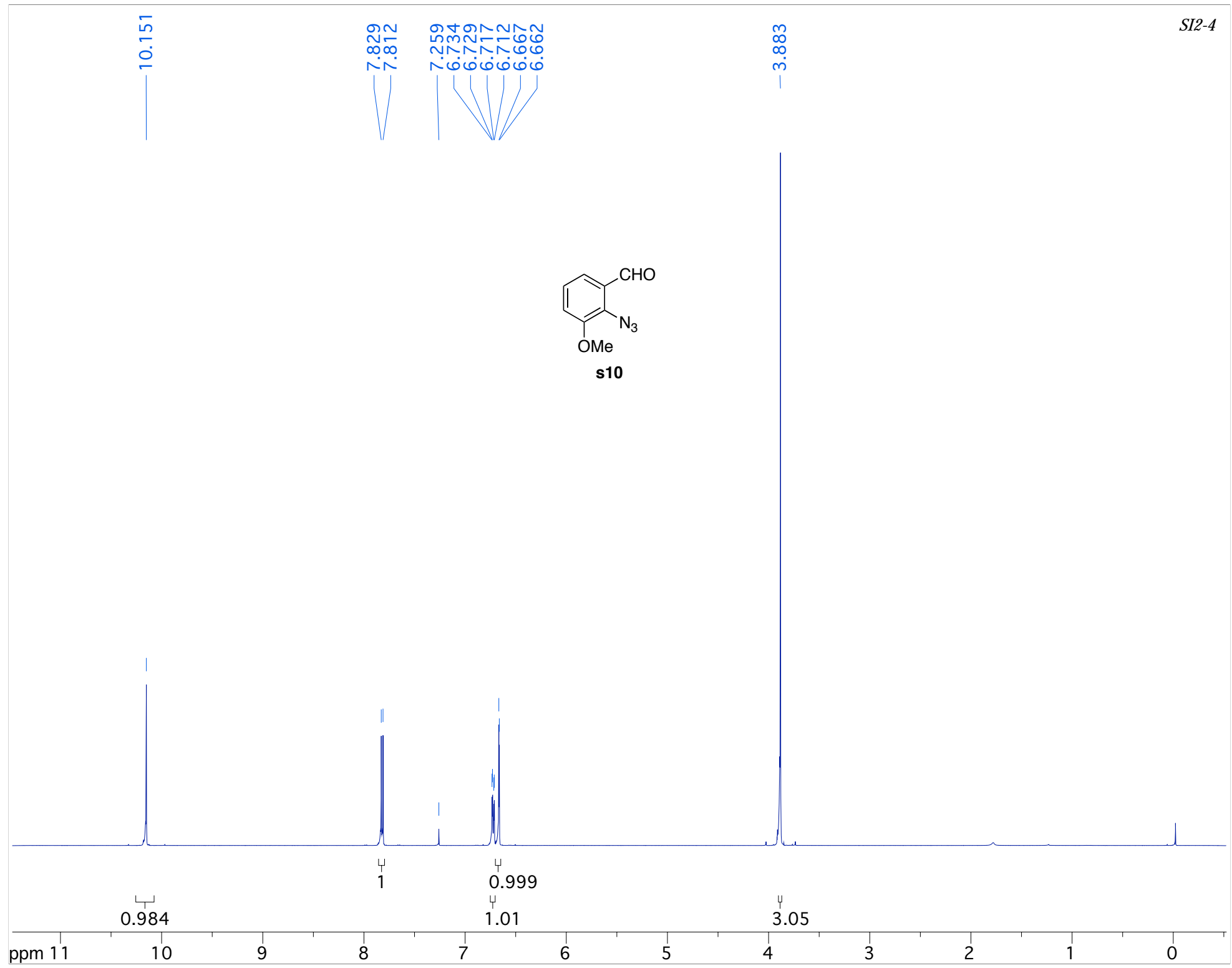
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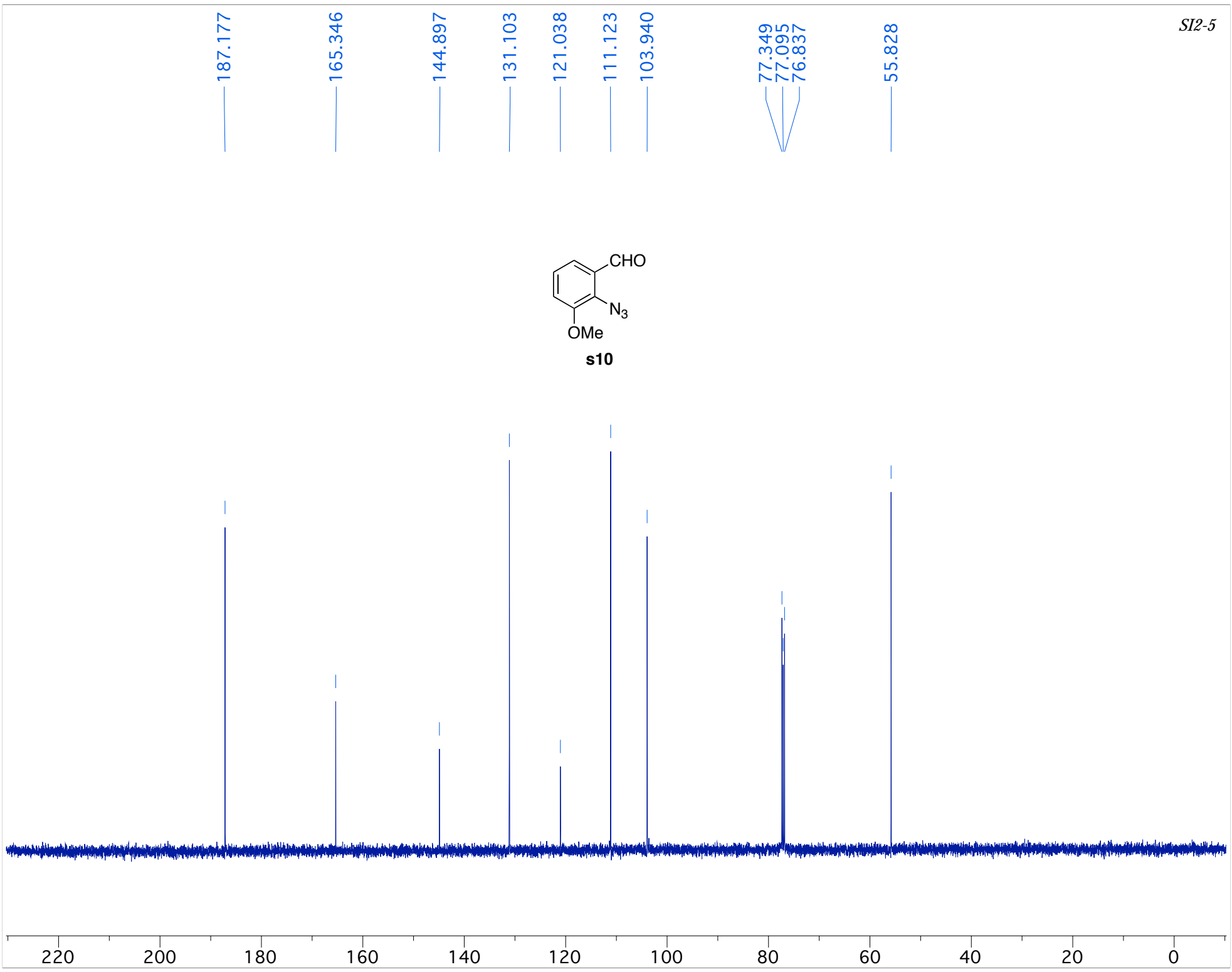
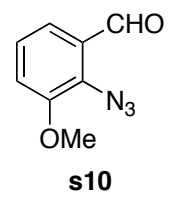
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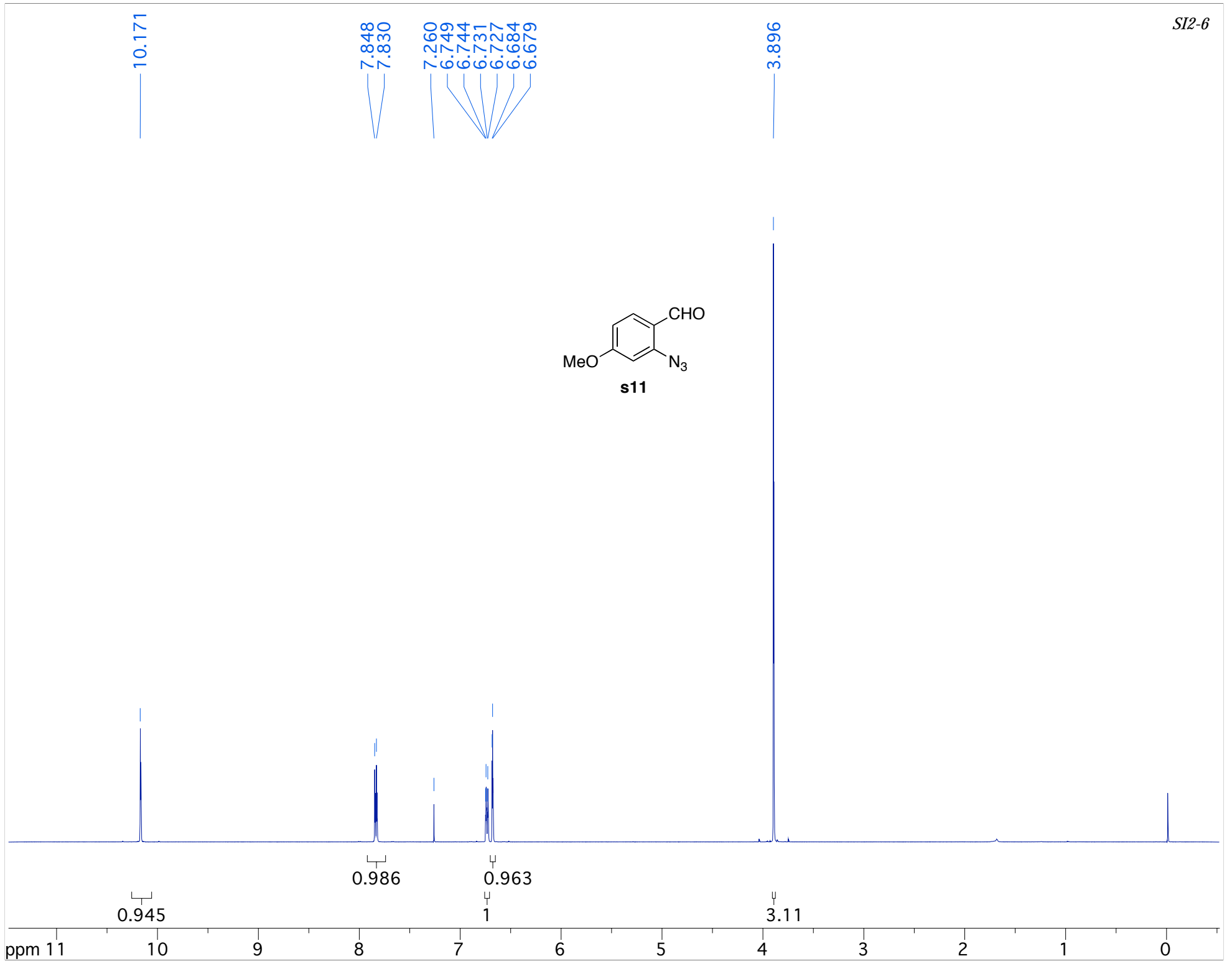
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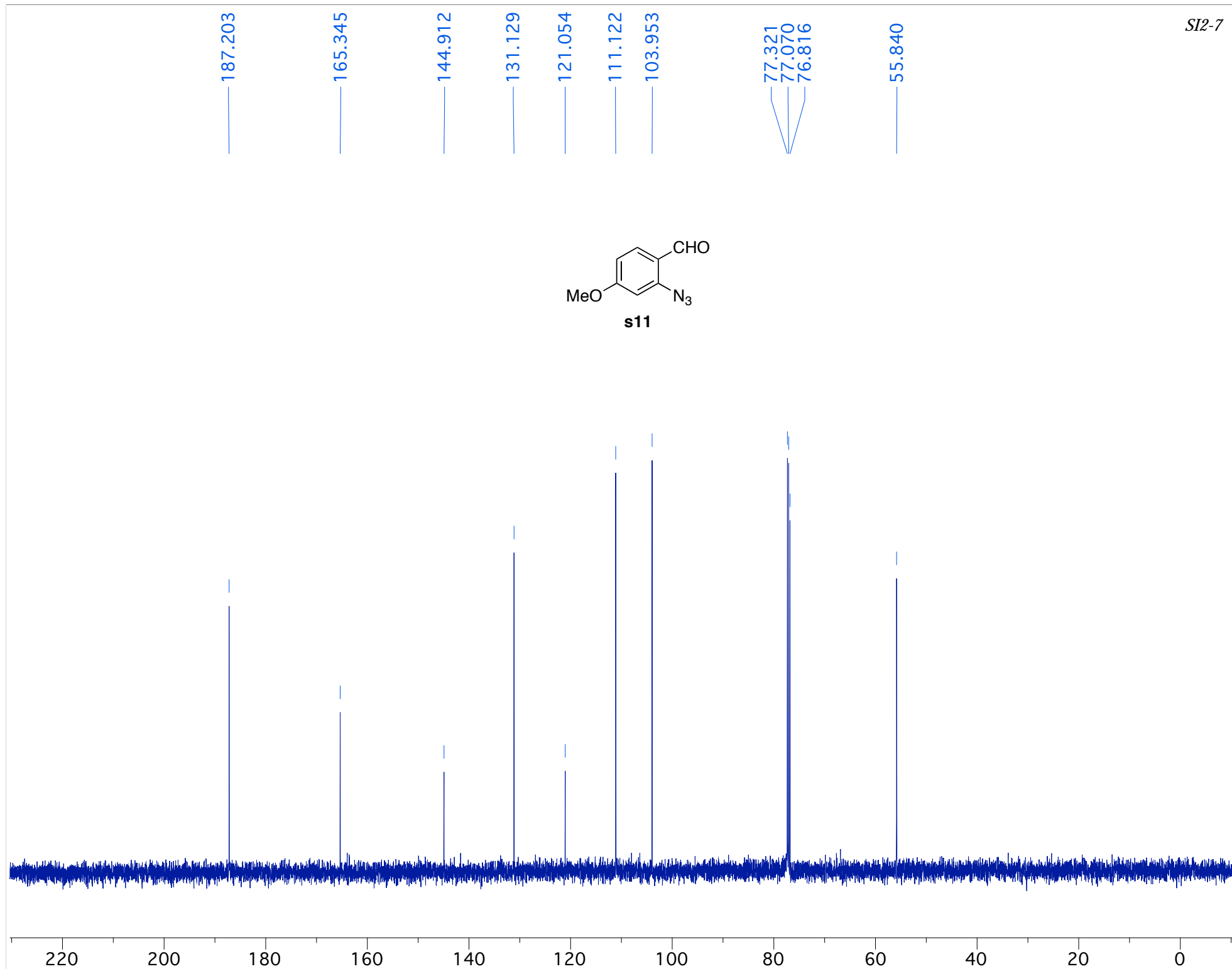


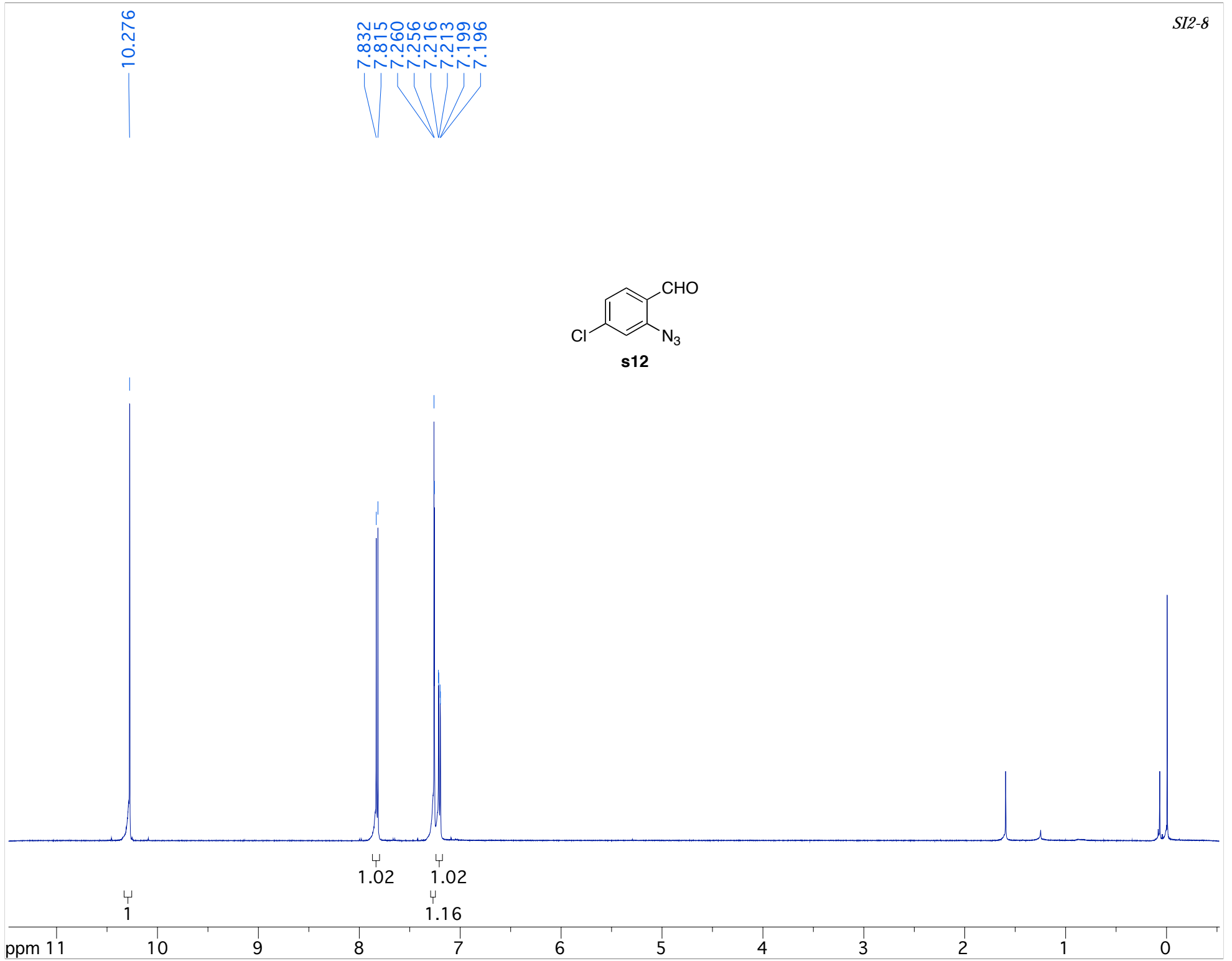
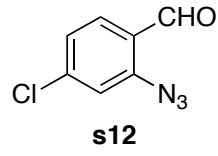


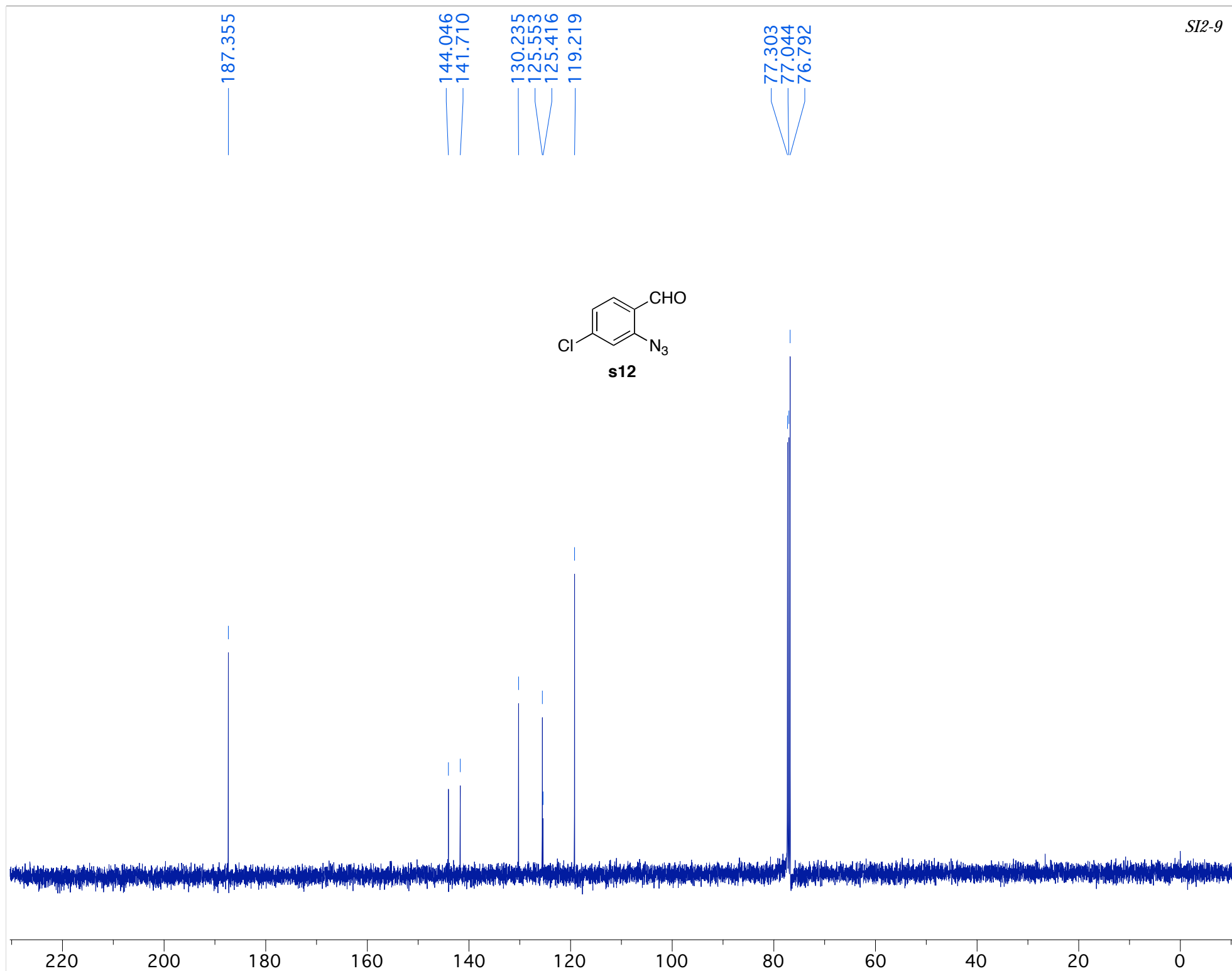


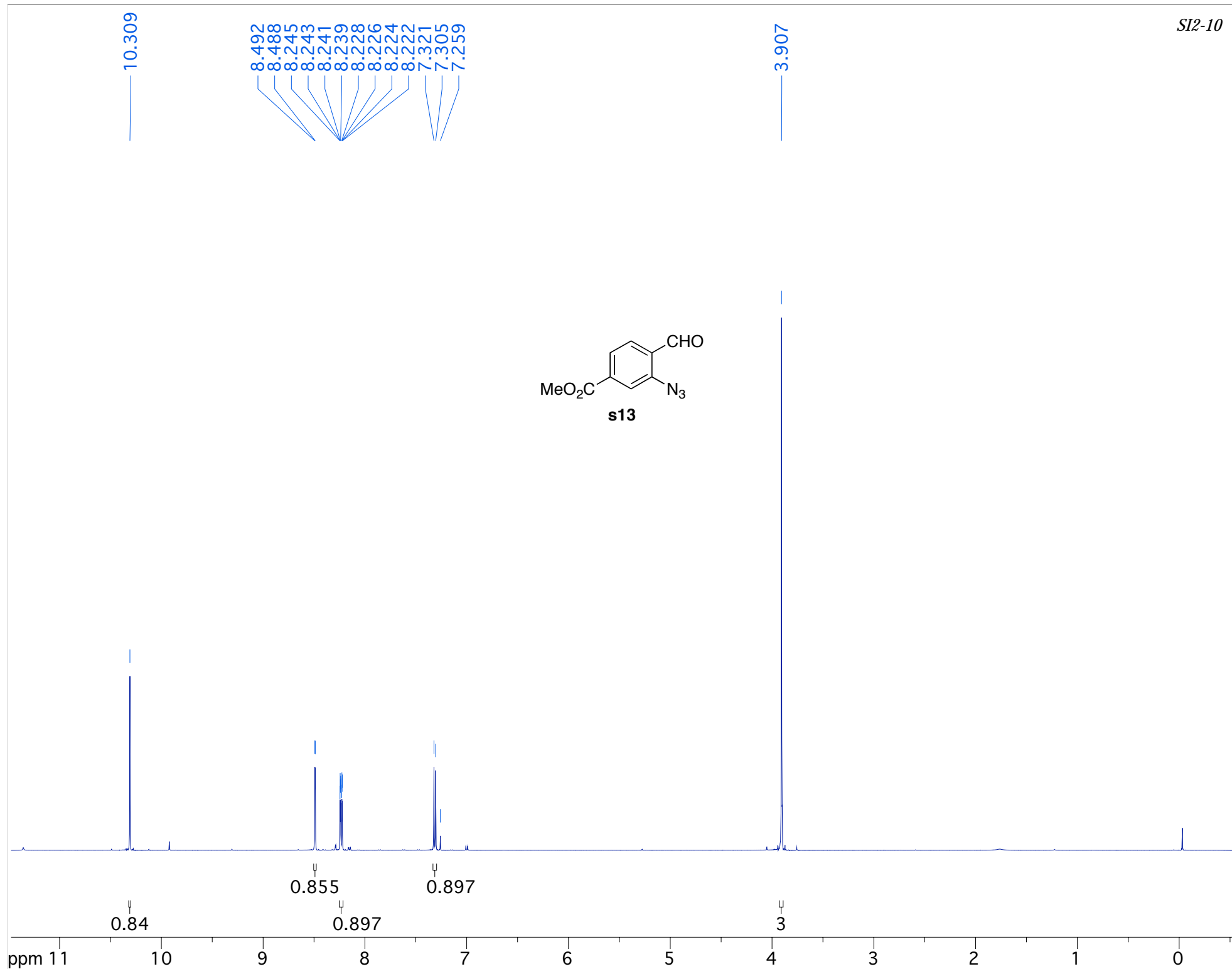


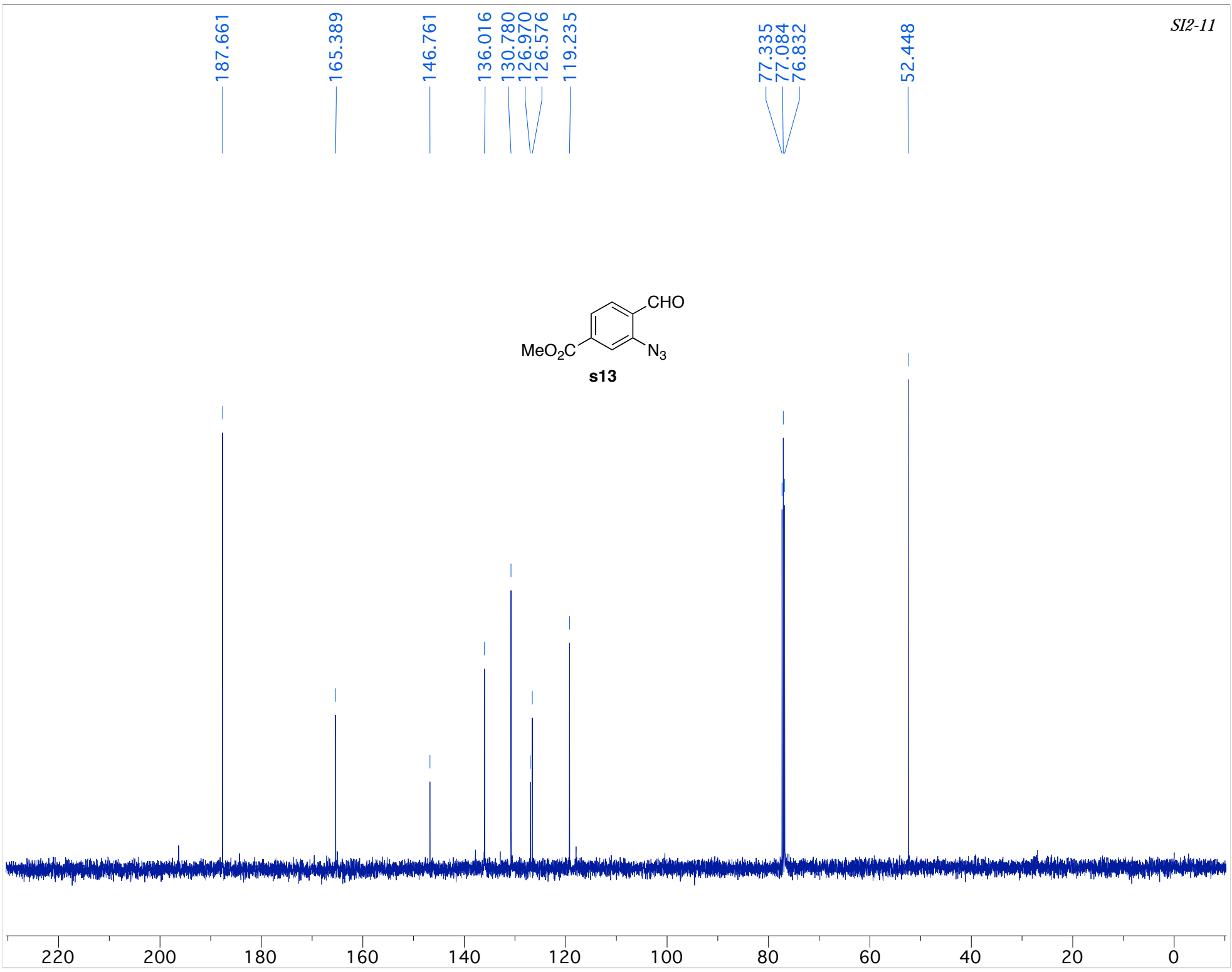
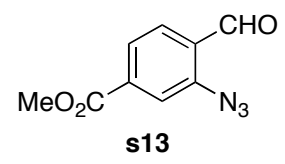


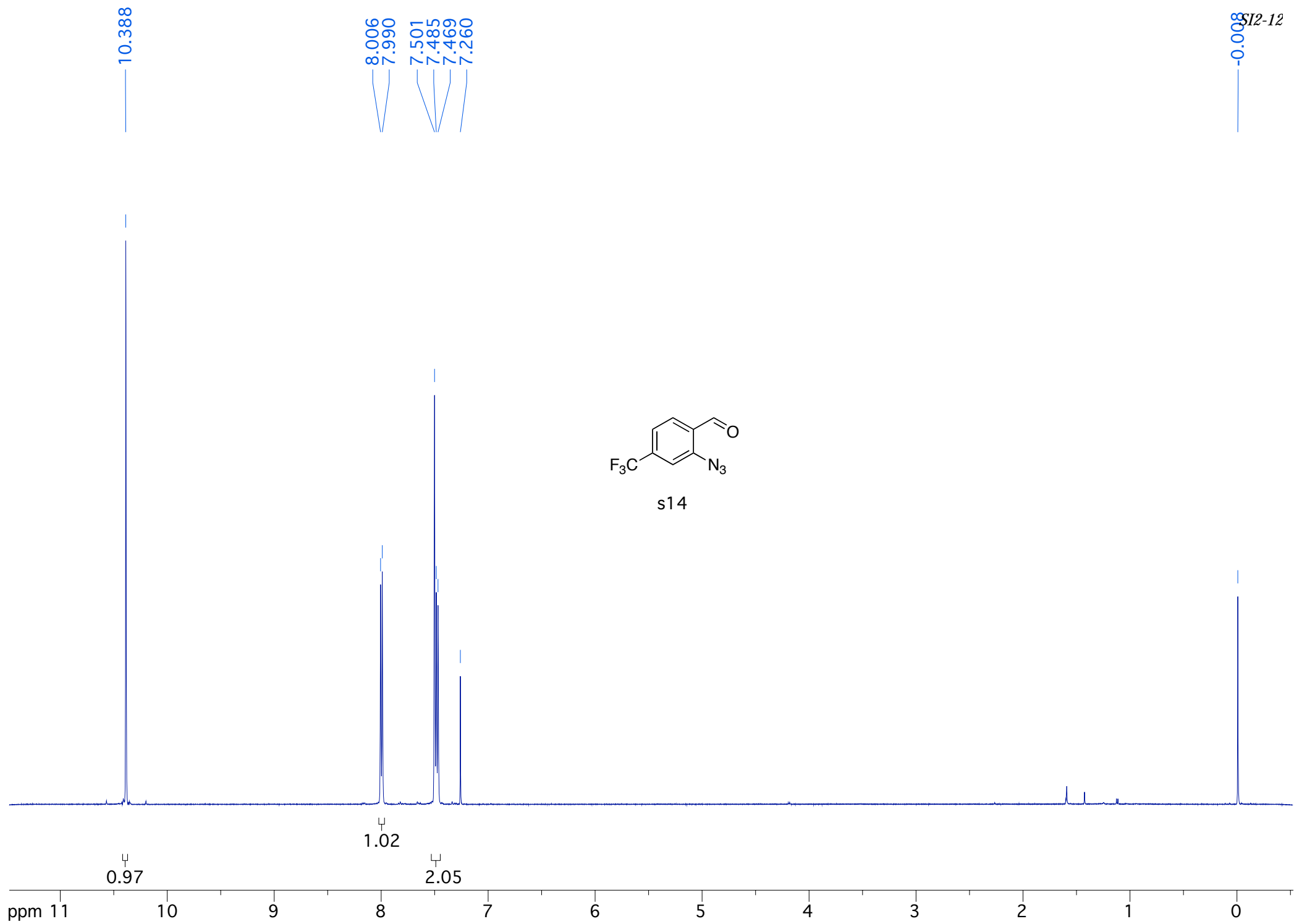


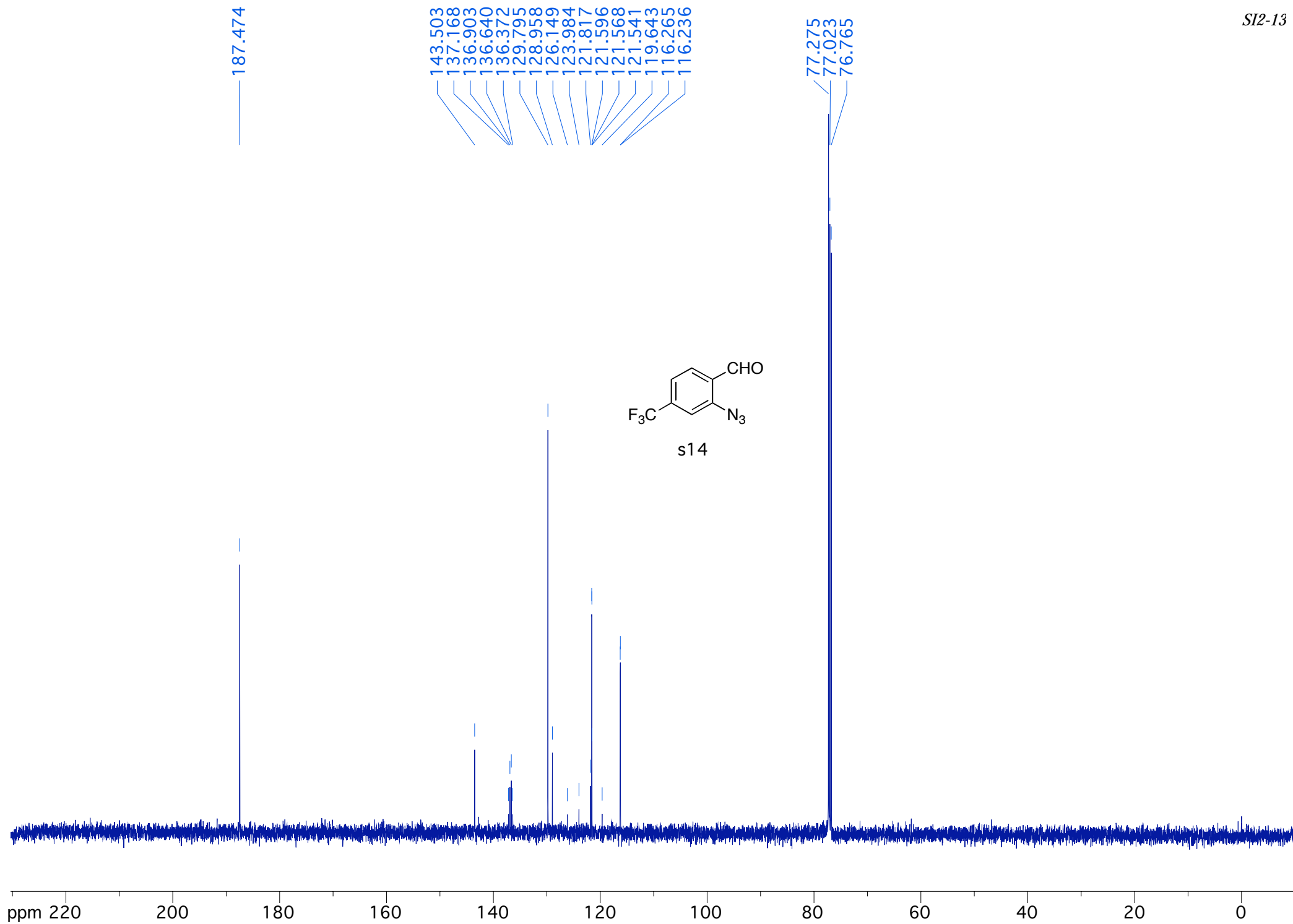


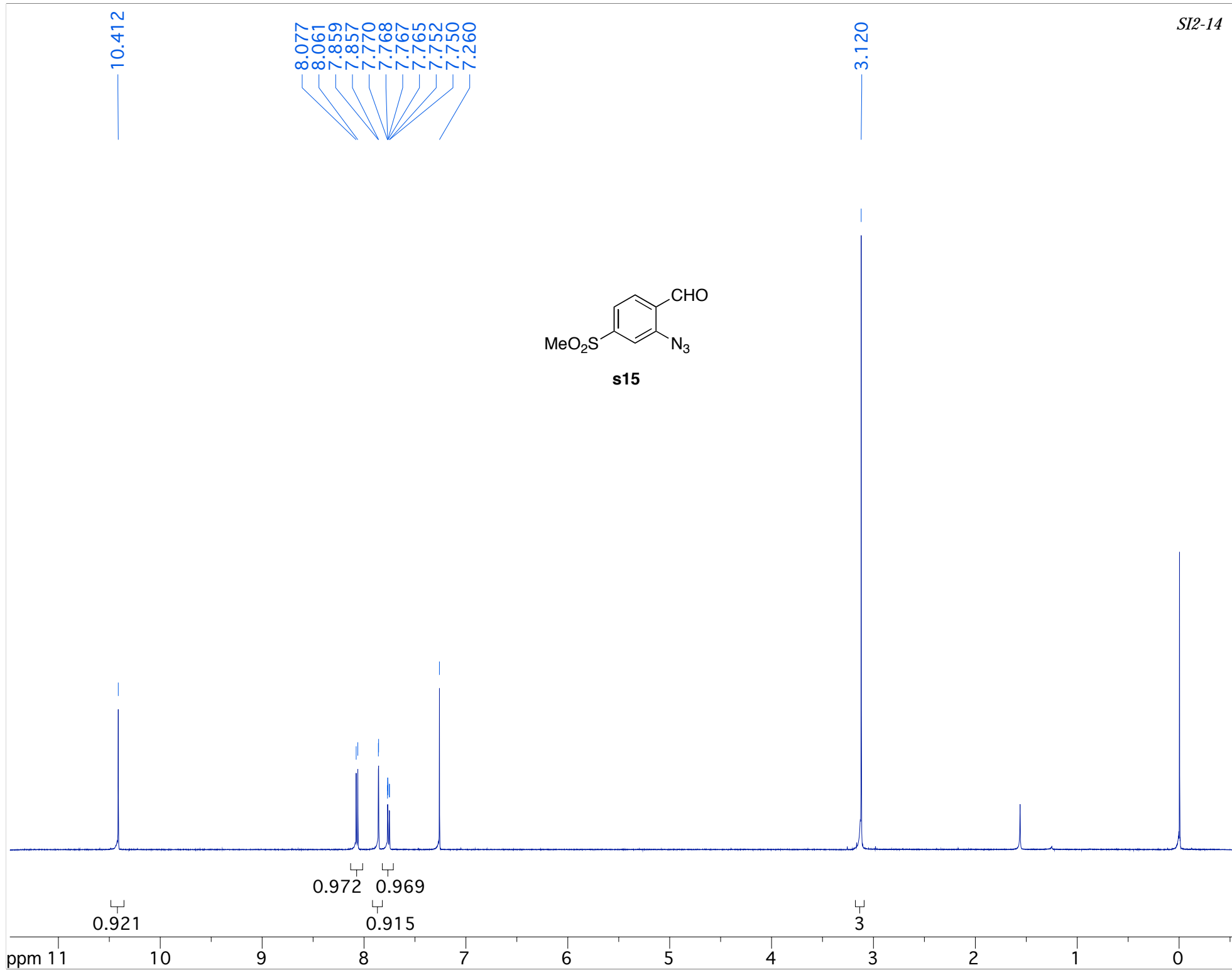


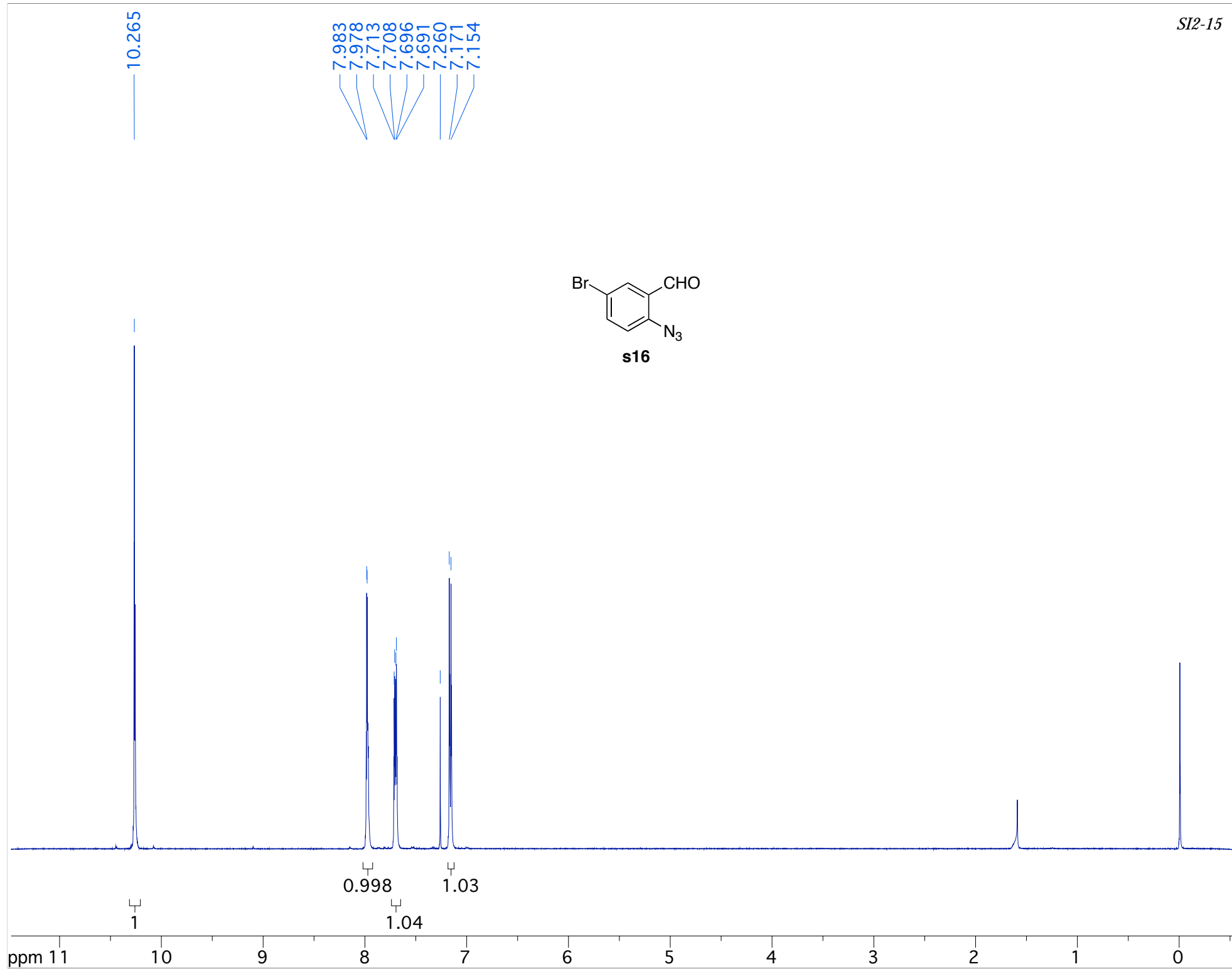


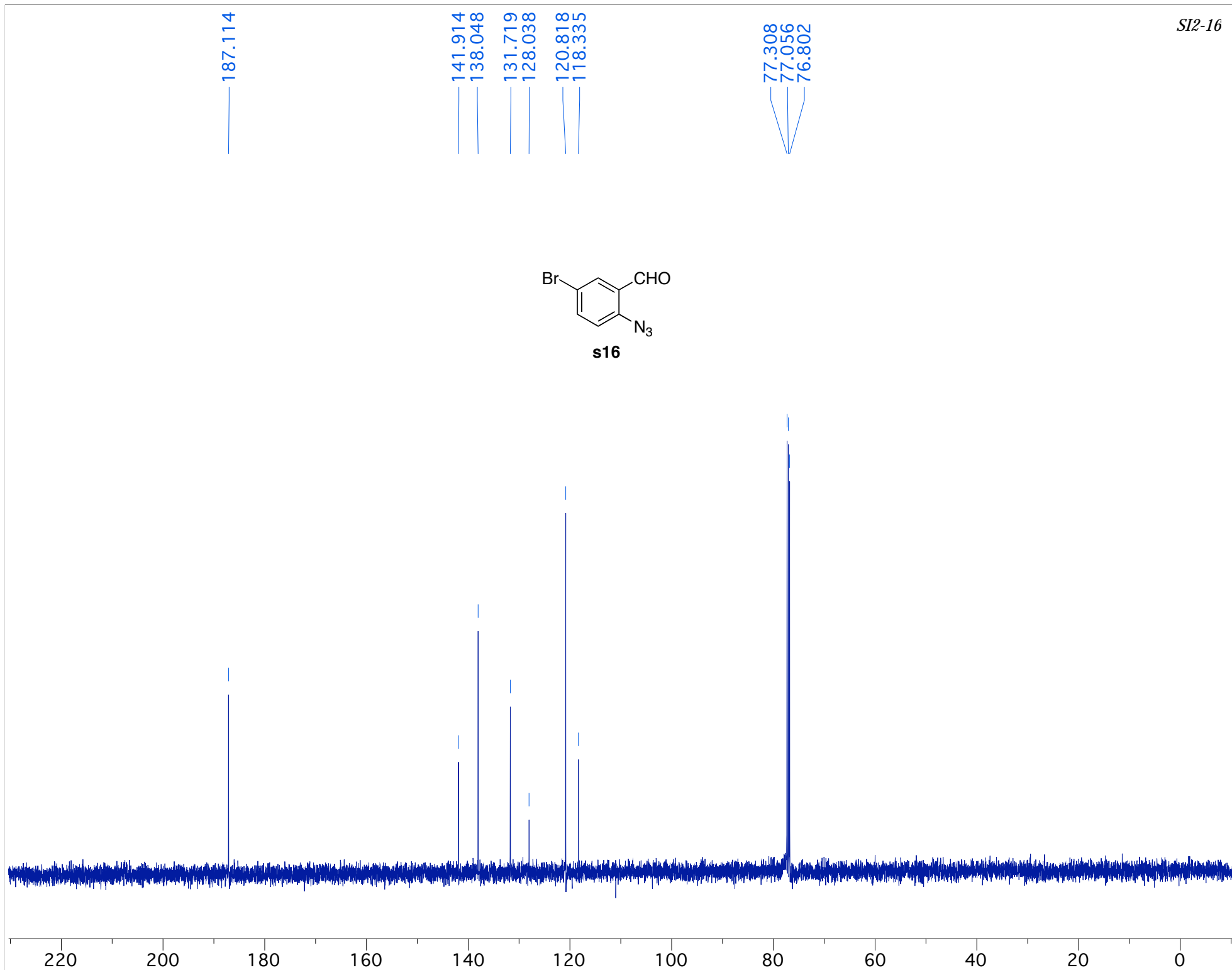


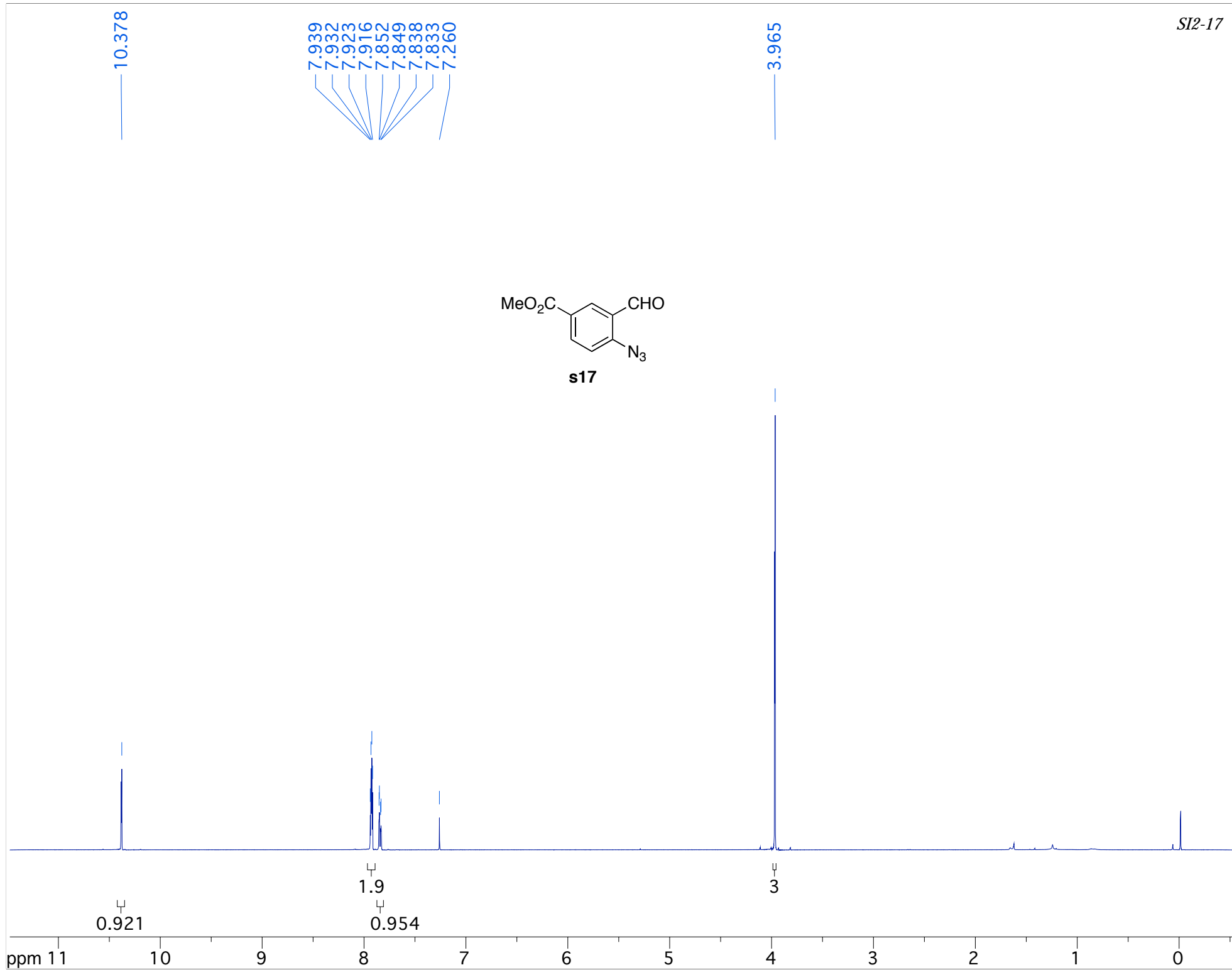


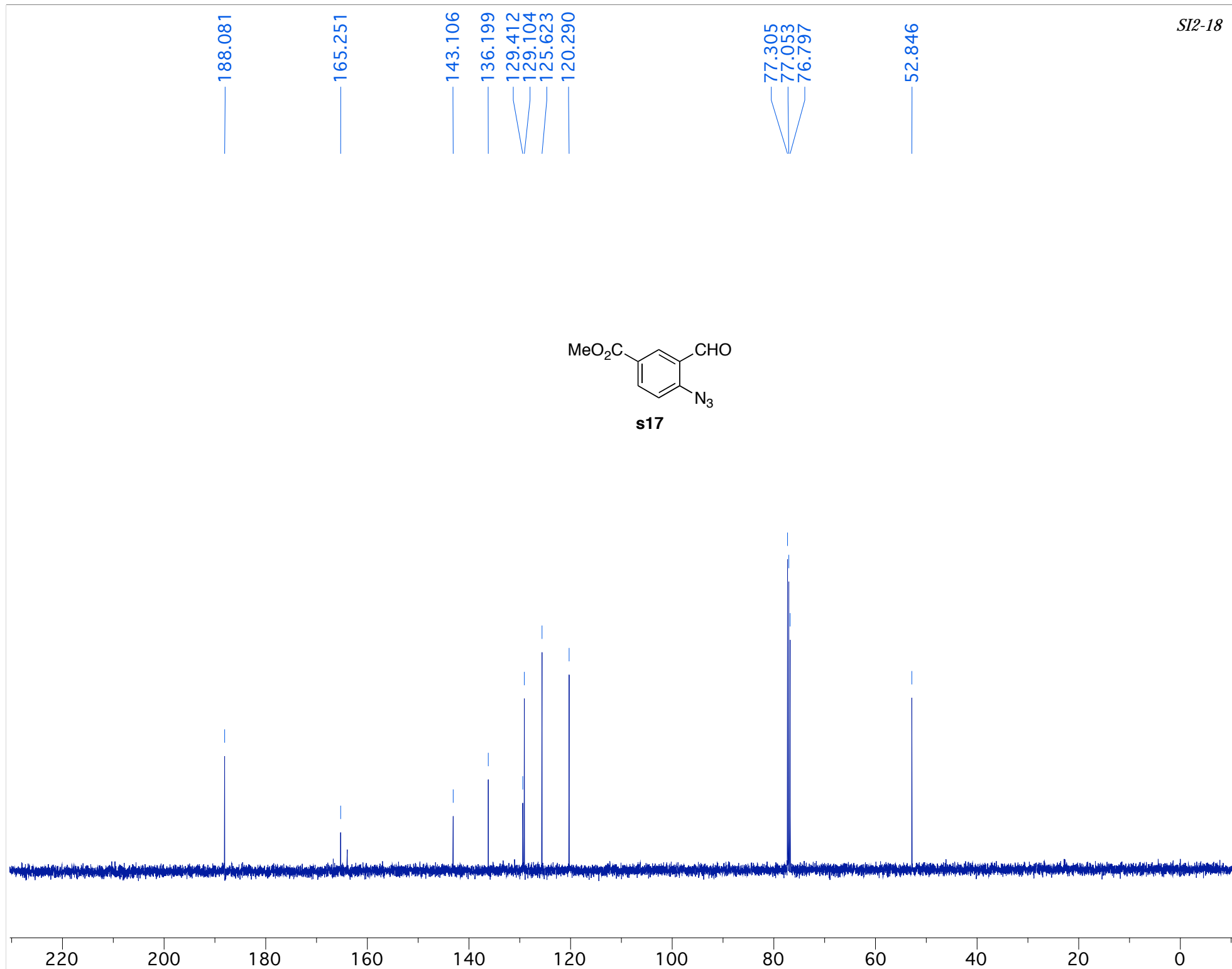






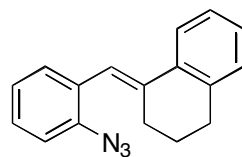




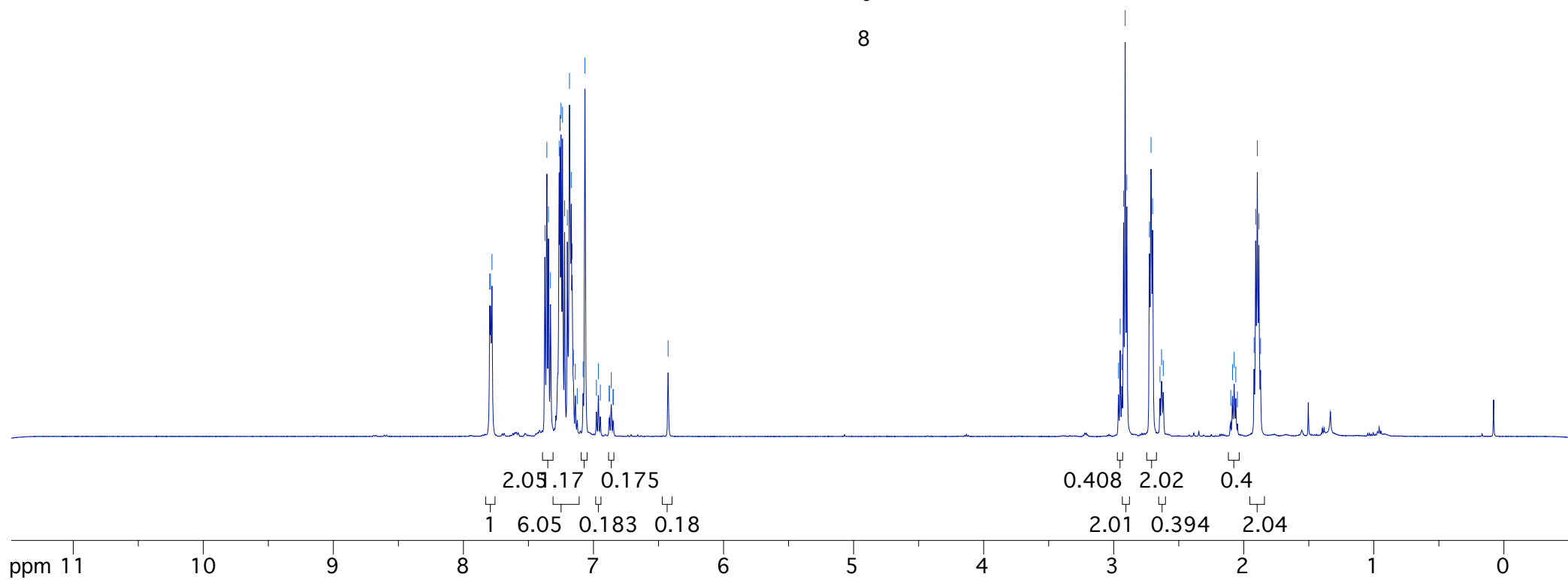


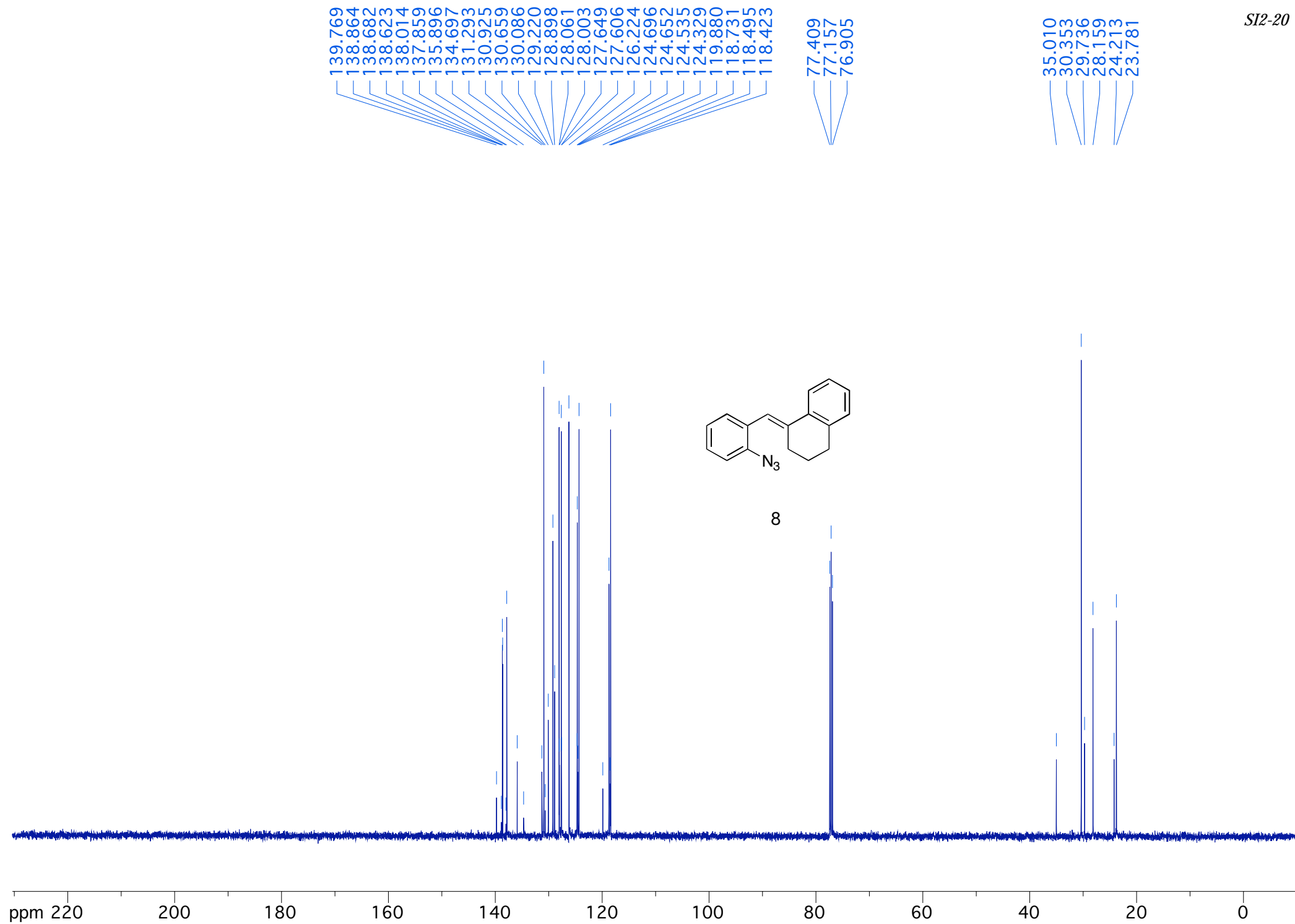
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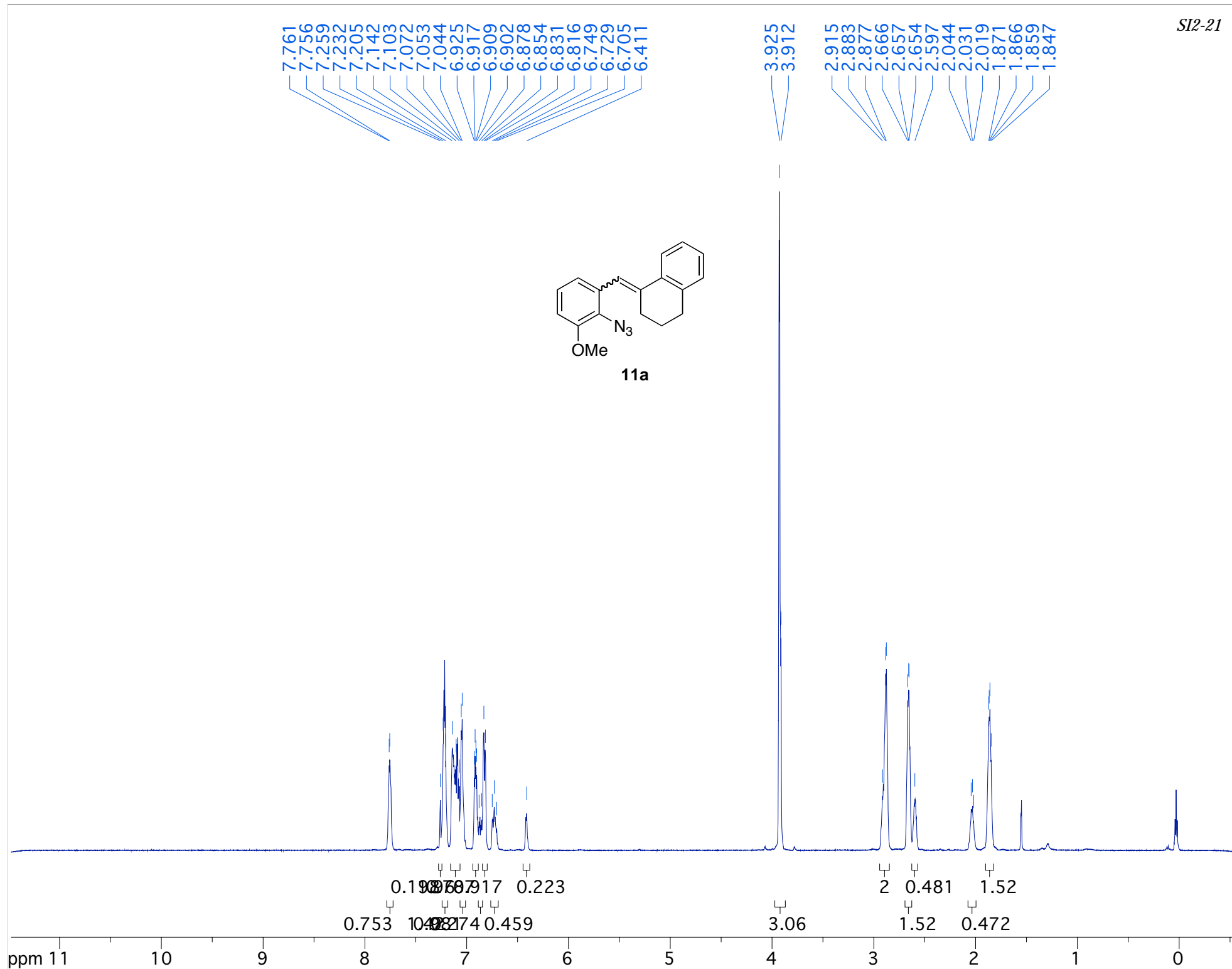
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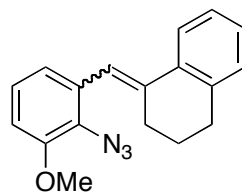


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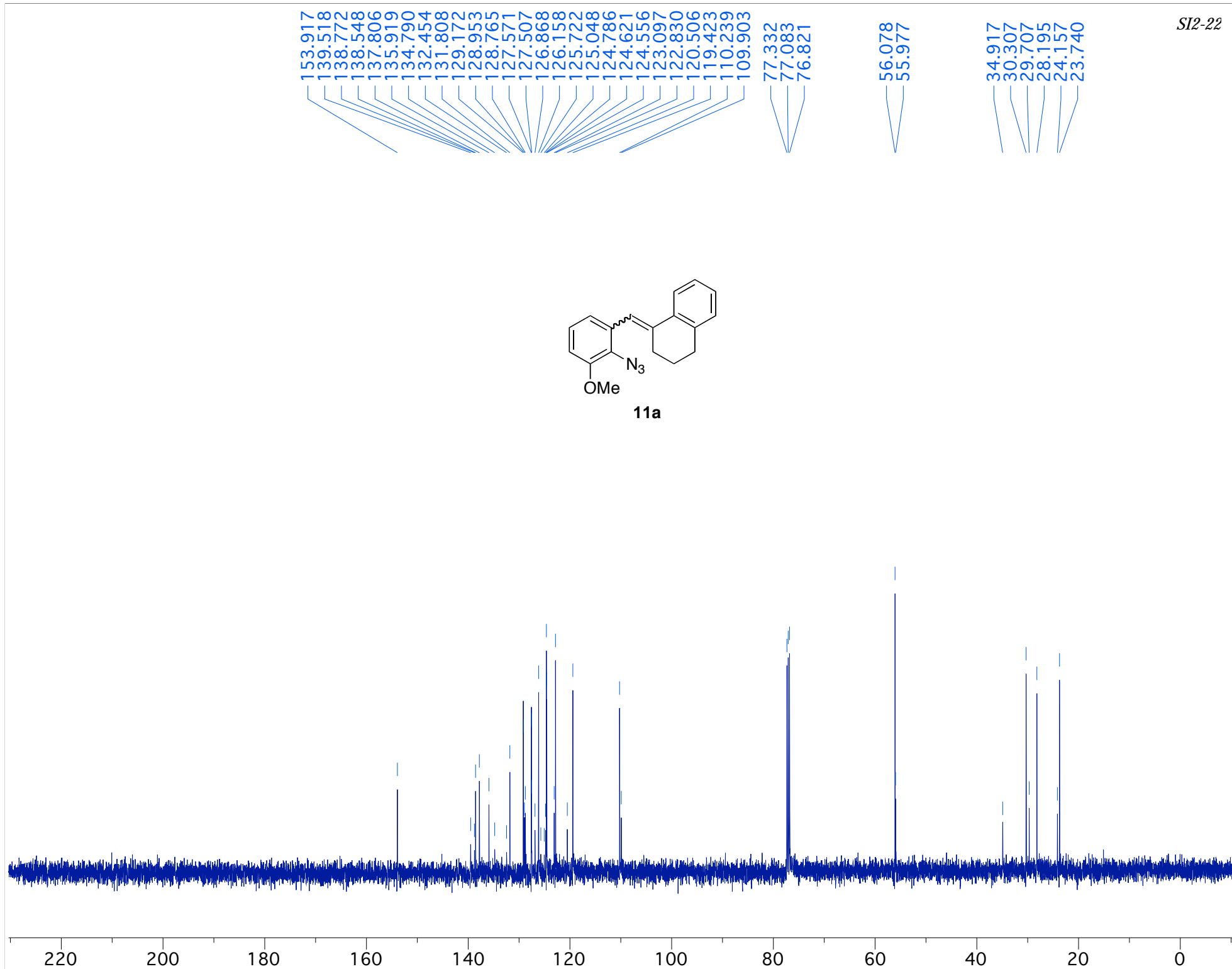


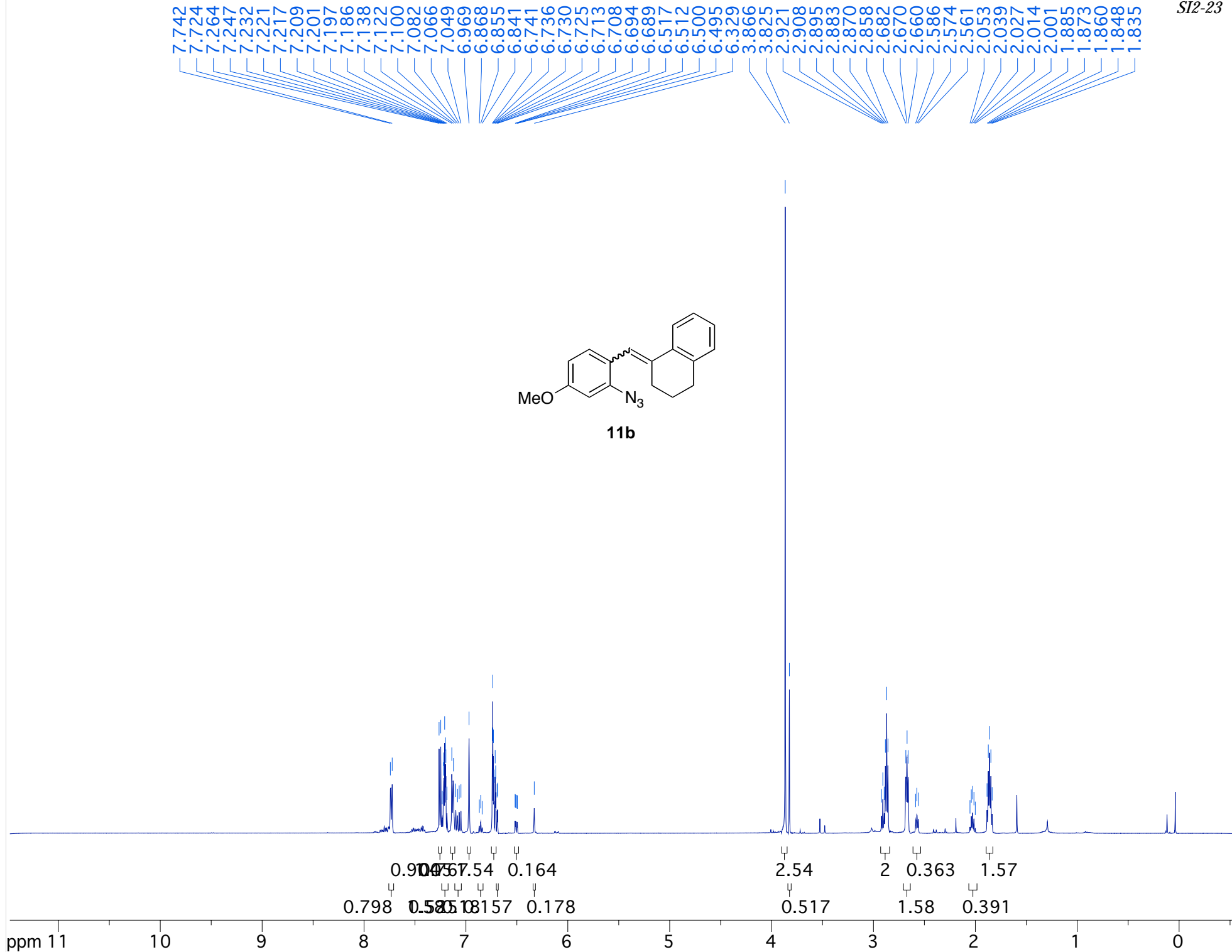


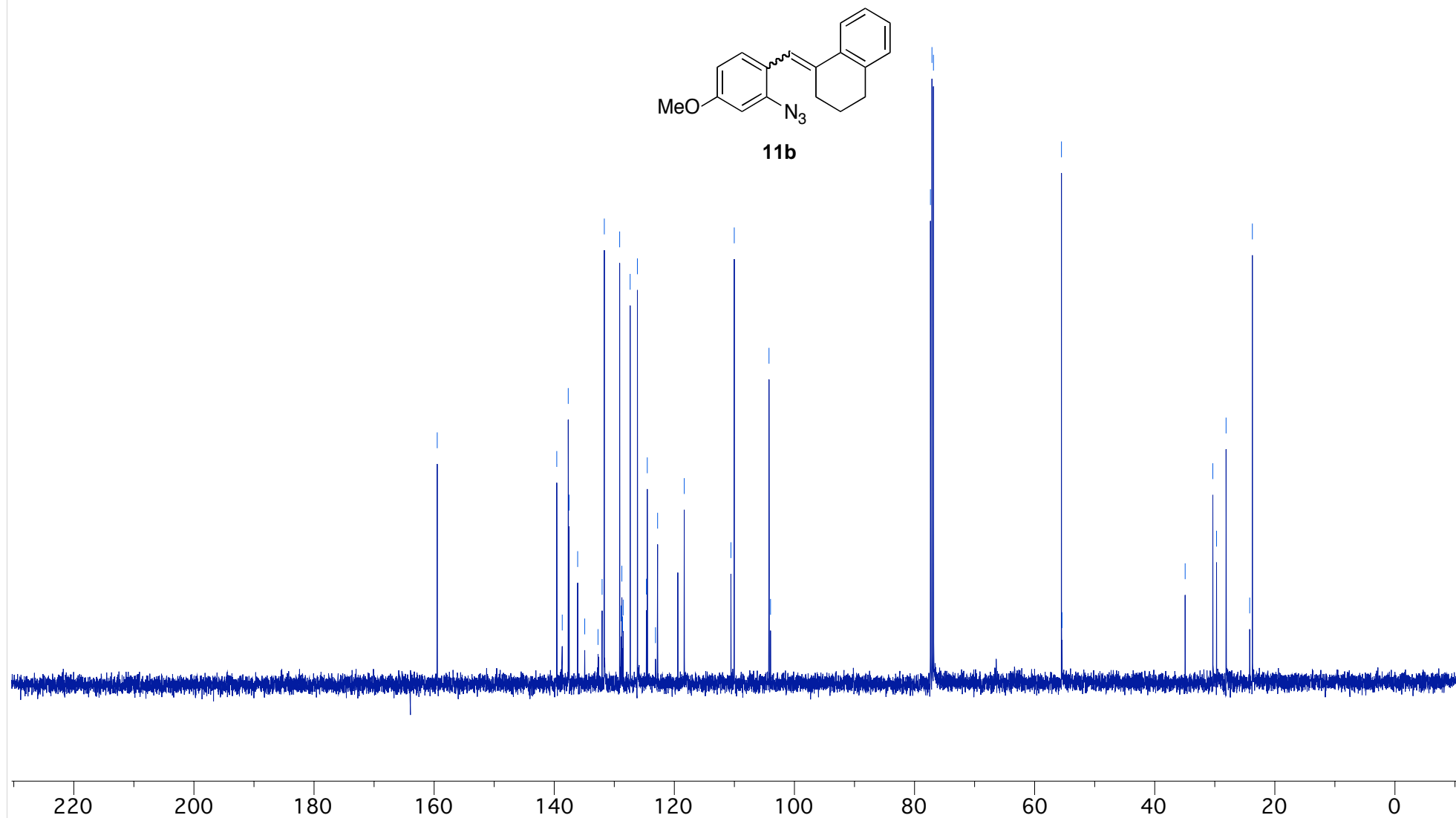


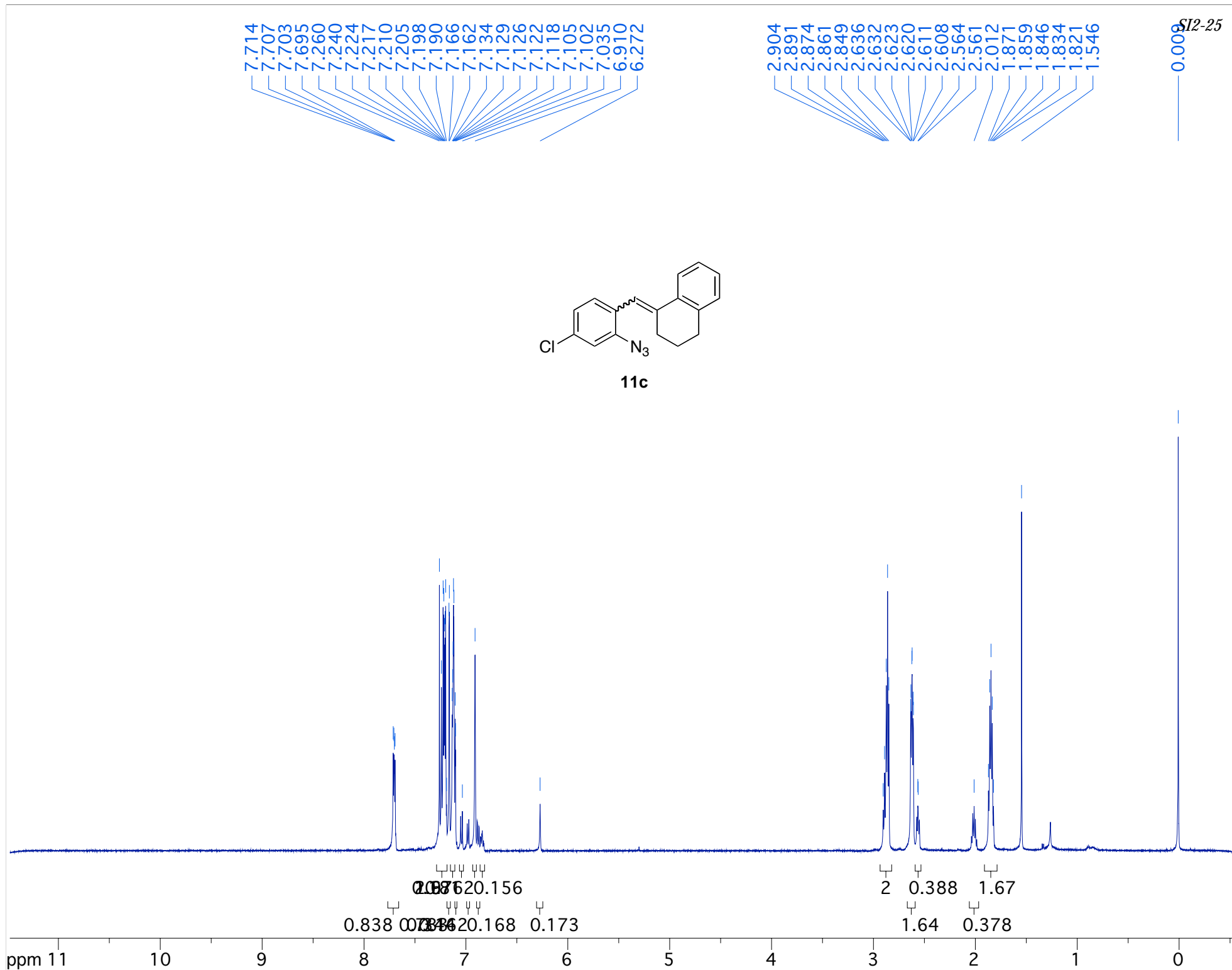


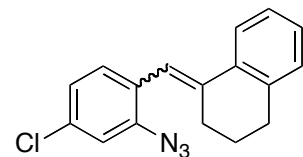
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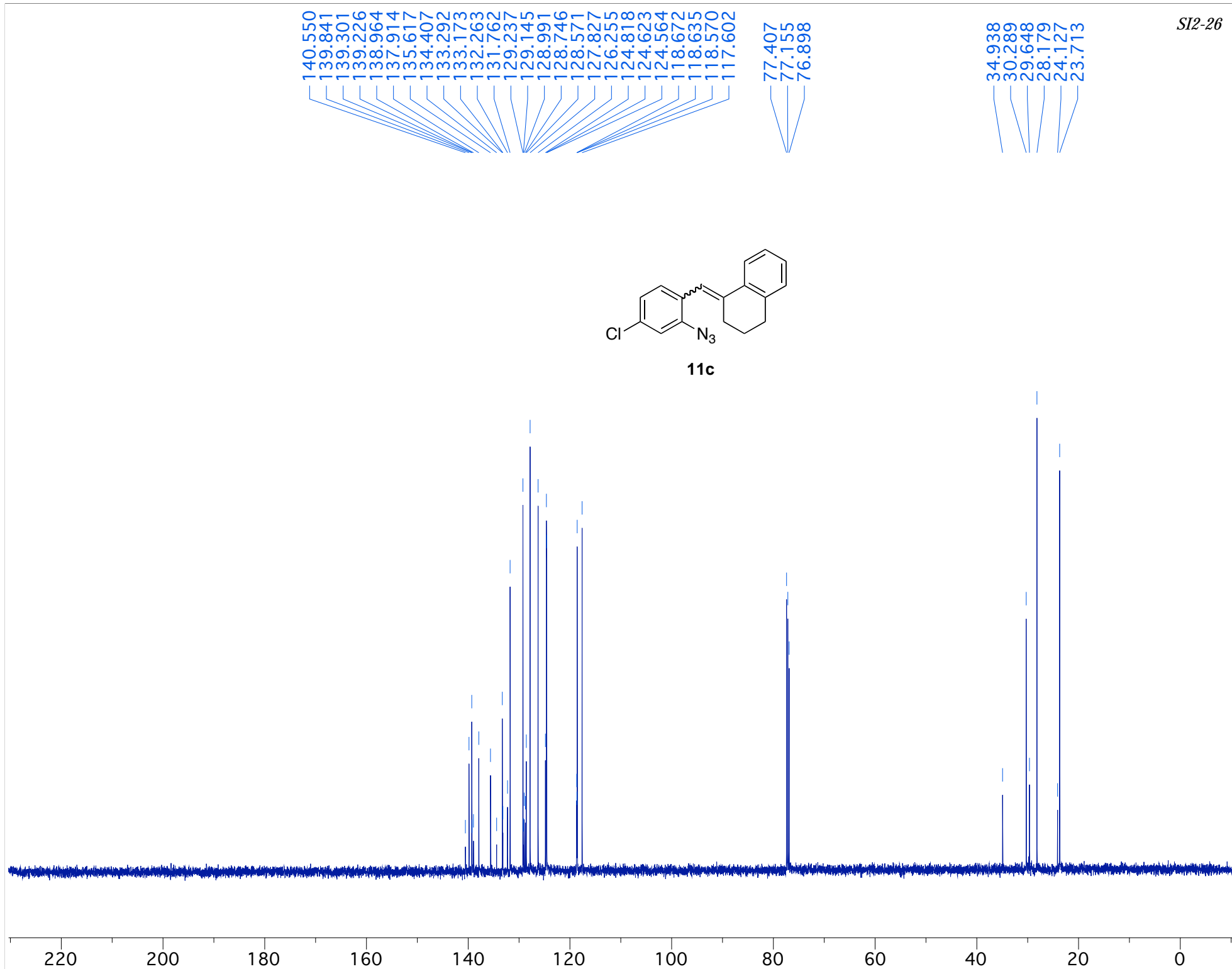


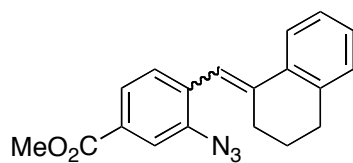




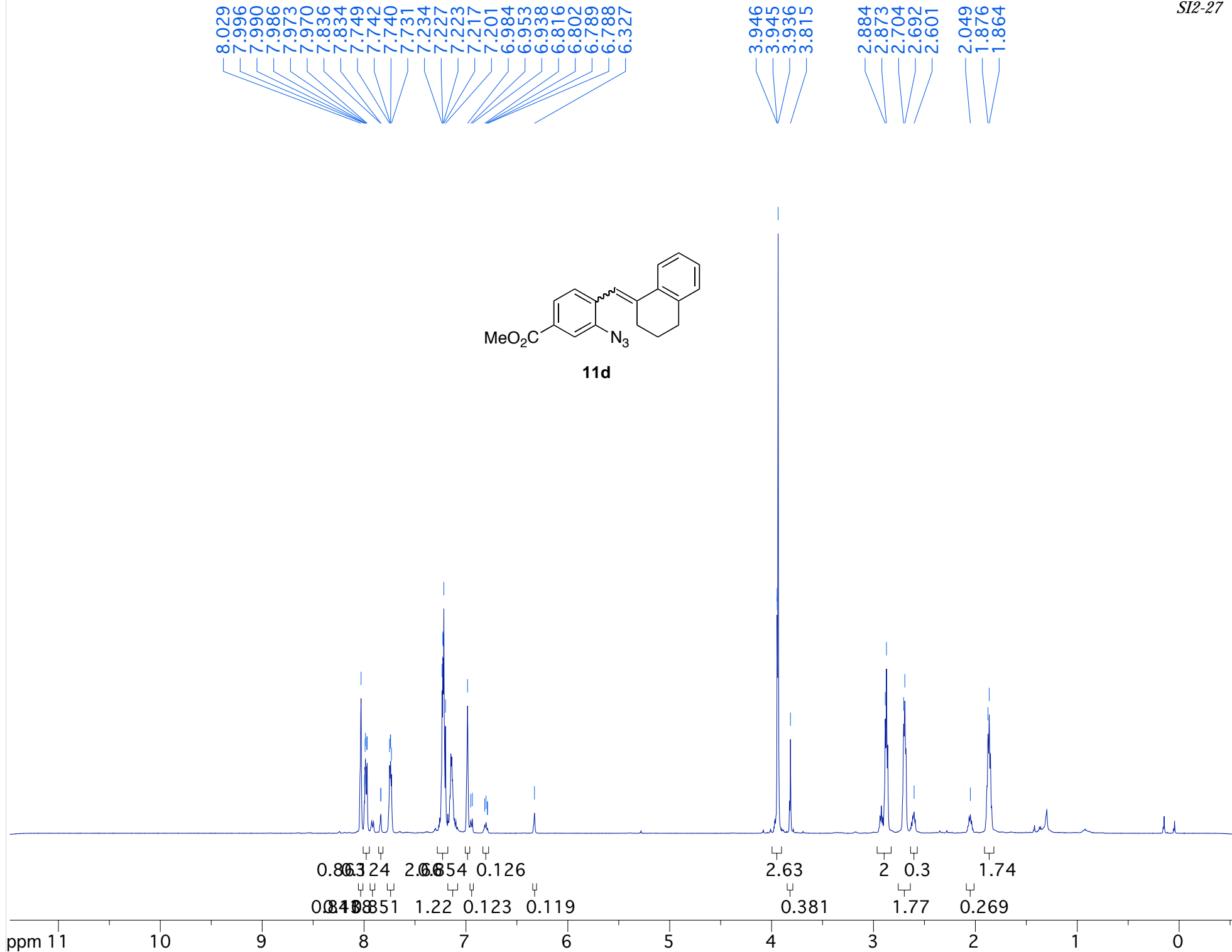


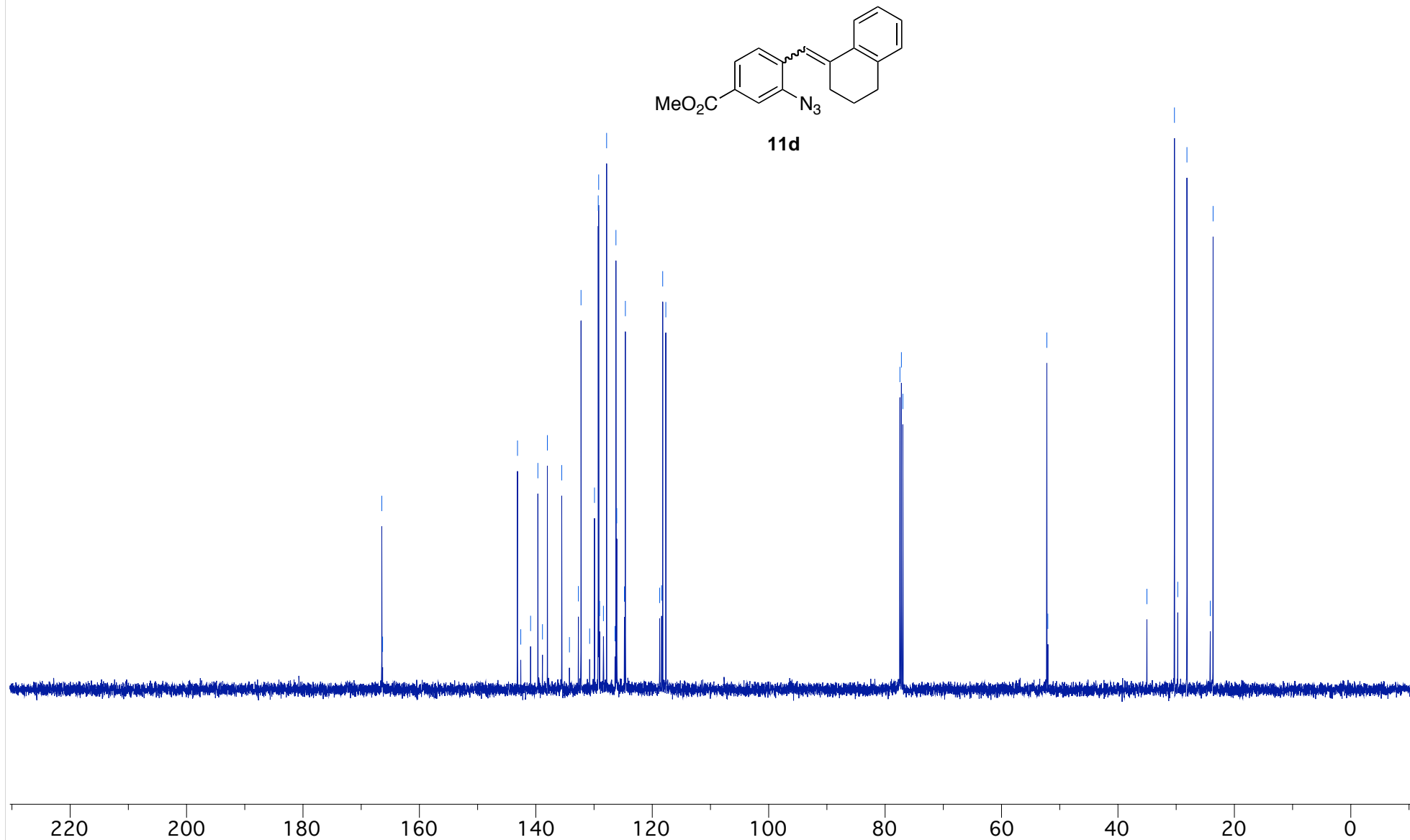
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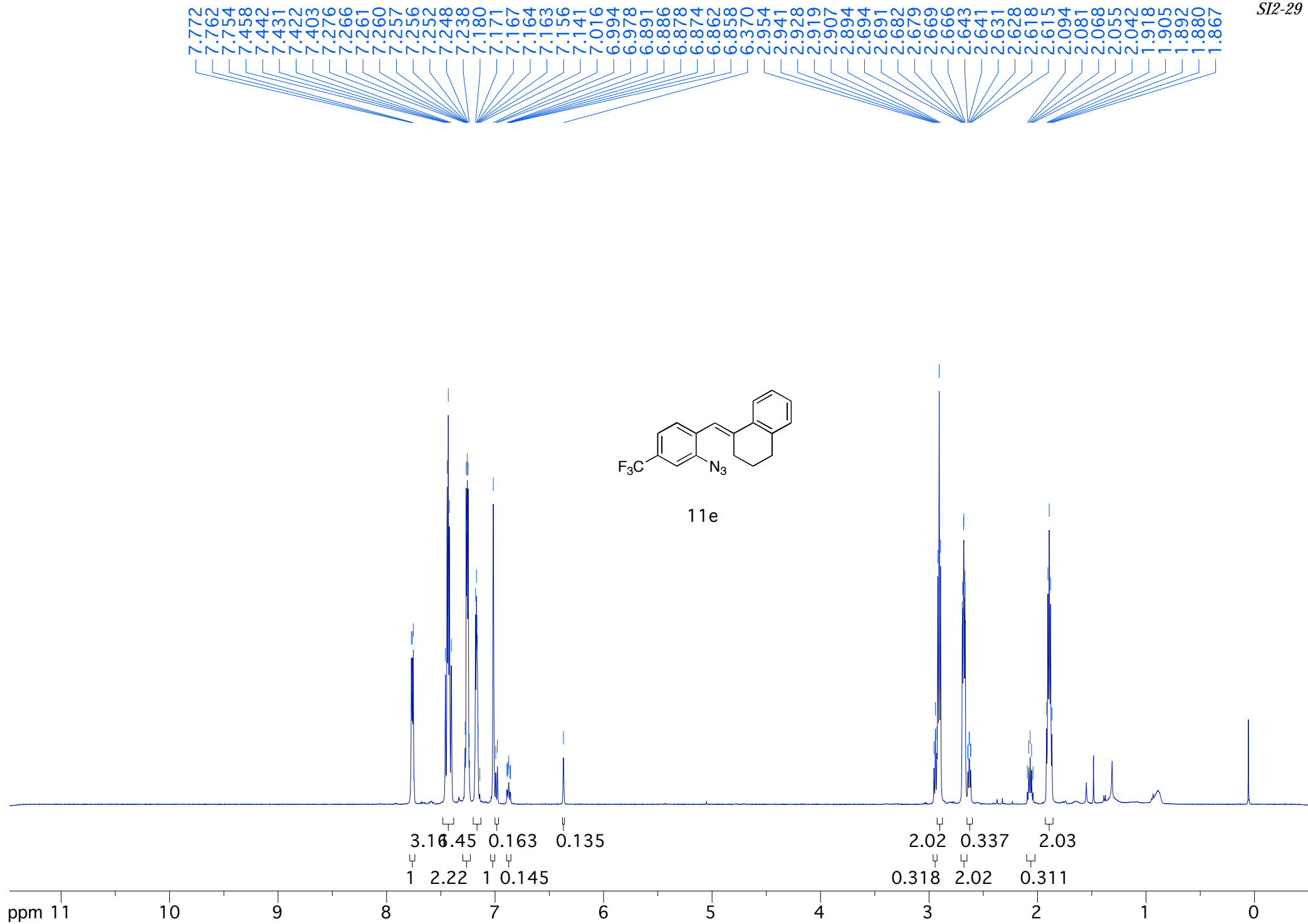




11d

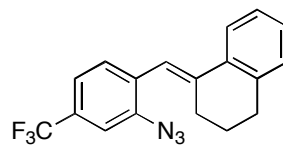




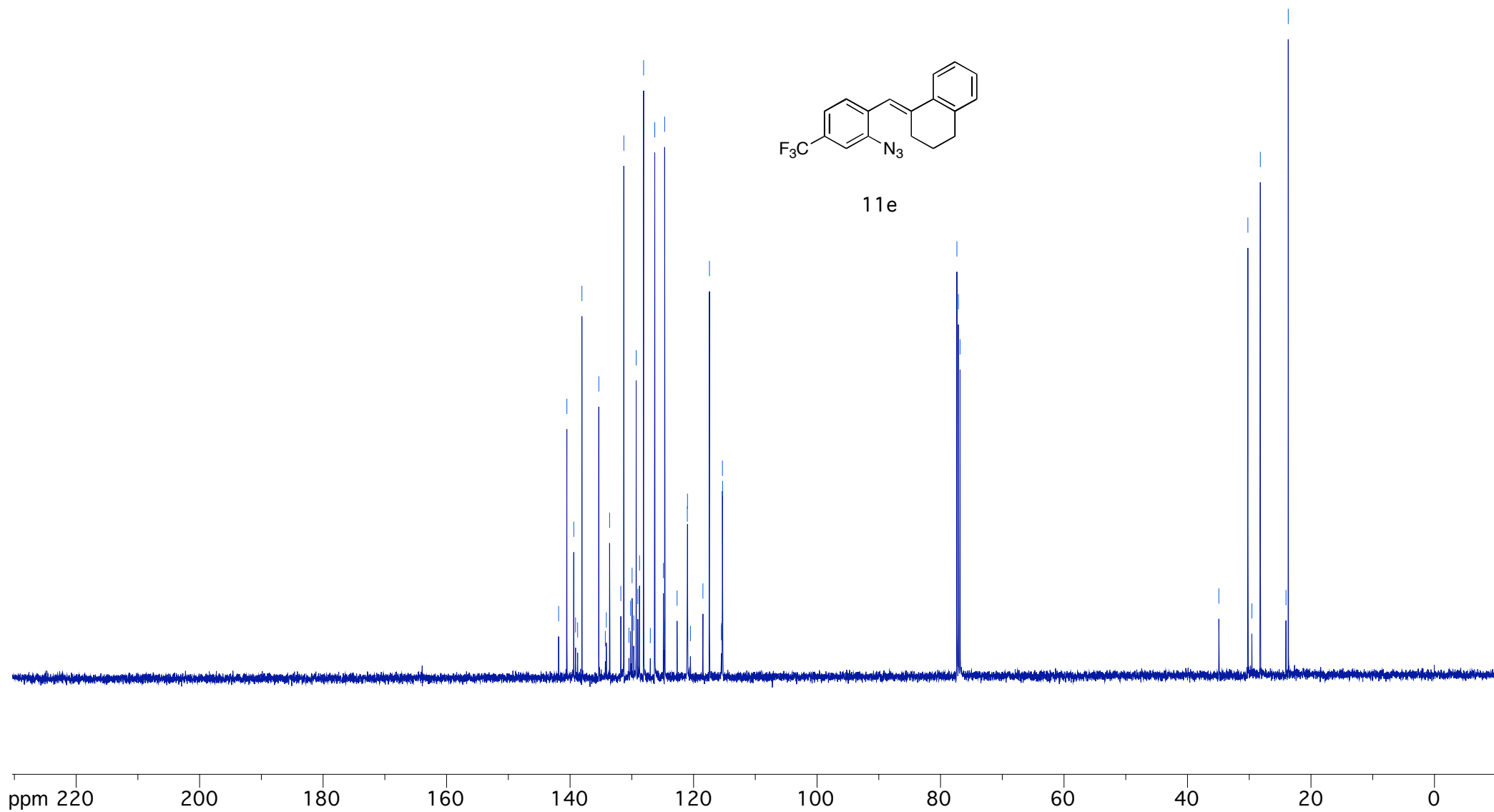


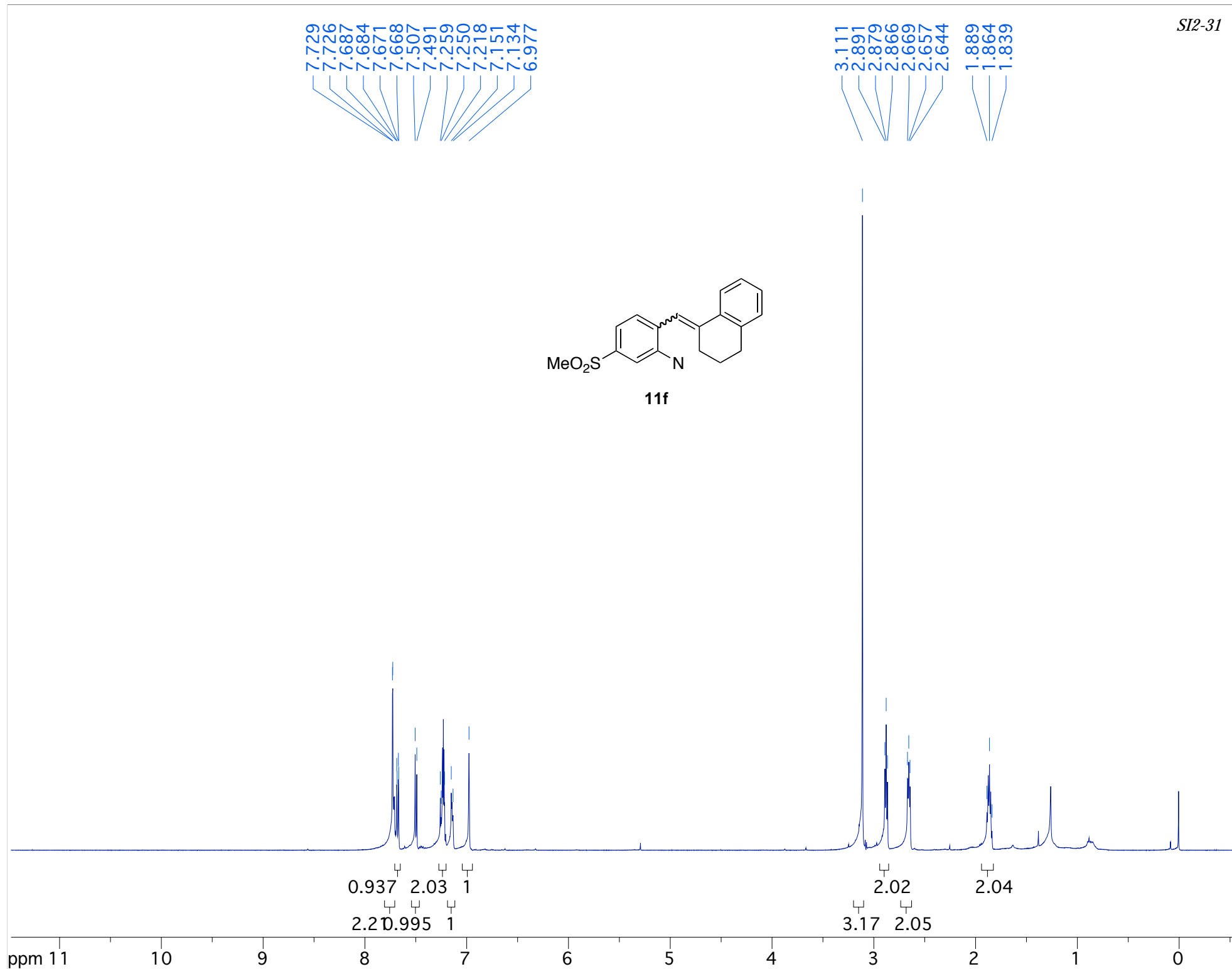
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134.294
134.128
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131.779
131.293
130.471
130.217
129.956
129.692
129.291
129.032
128.751
128.090
127.004
126.283
124.888
124.835
124.682
122.669
121.009
120.982
120.509
118.484
117.427
115.501
115.474
115.323
115.295
77.348
77.096
76.838

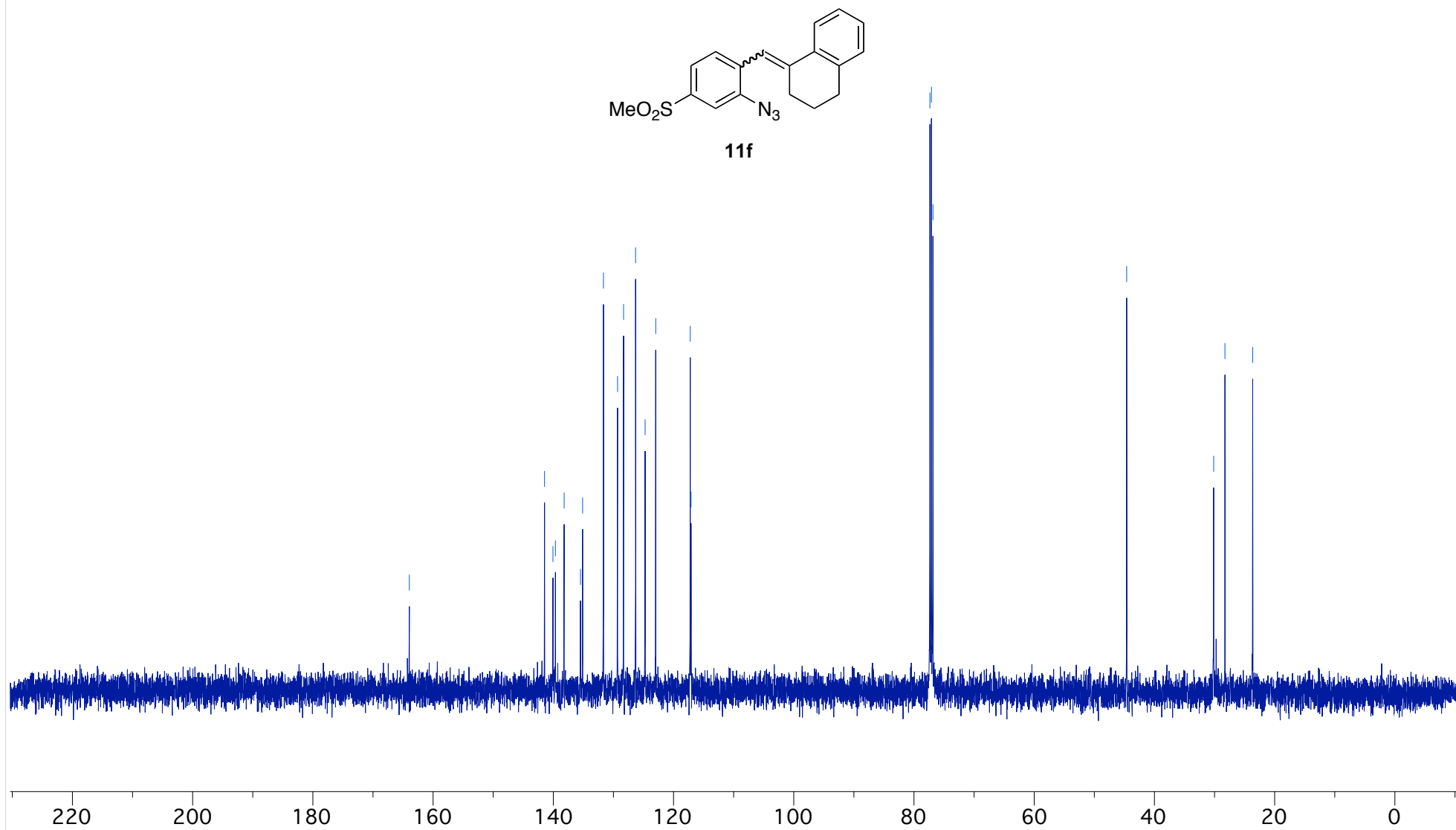
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29.569
28.207
24.049
23.683

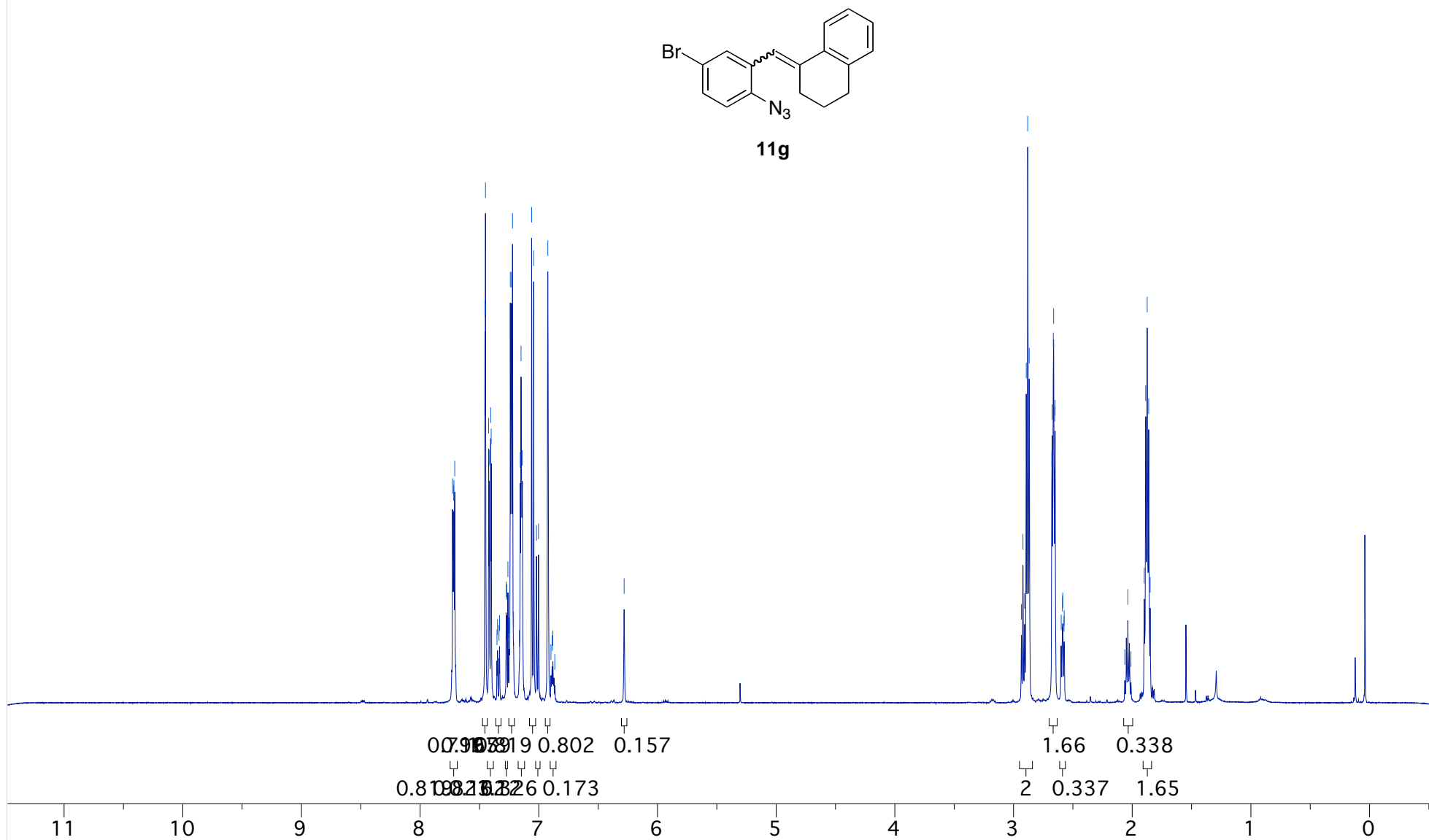


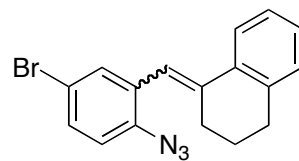
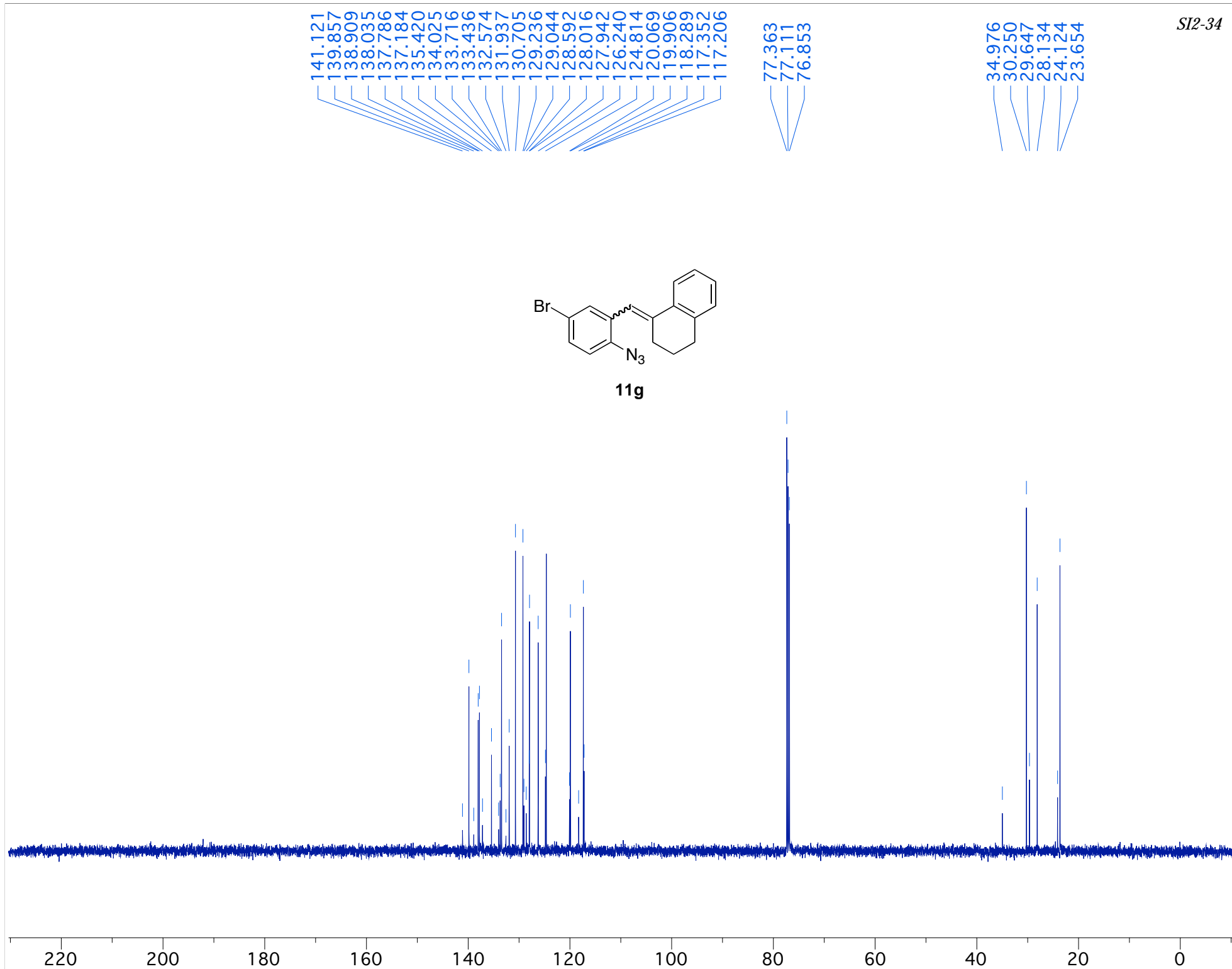
11e

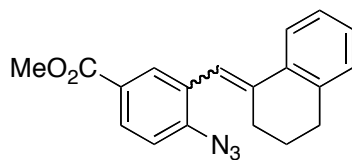




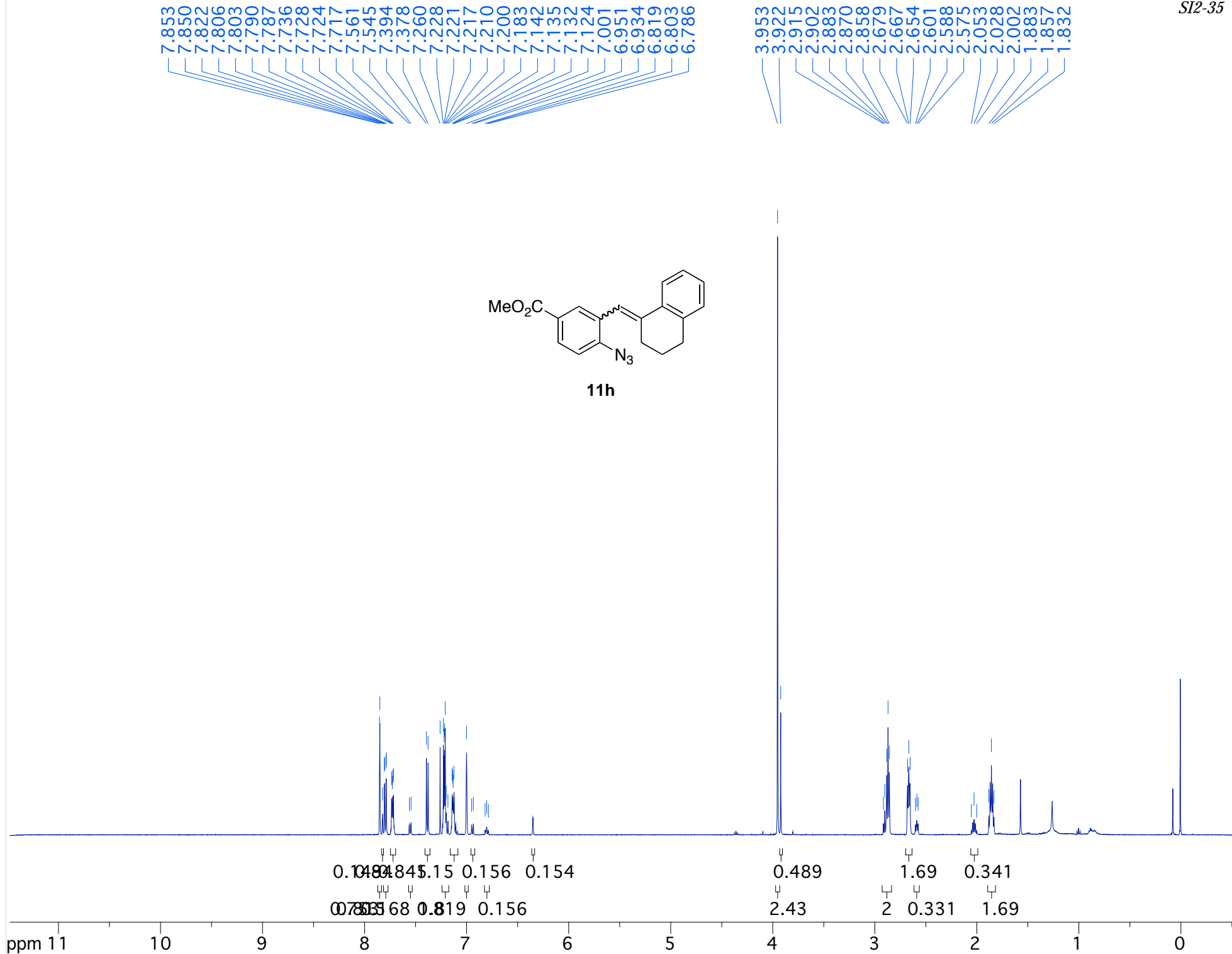


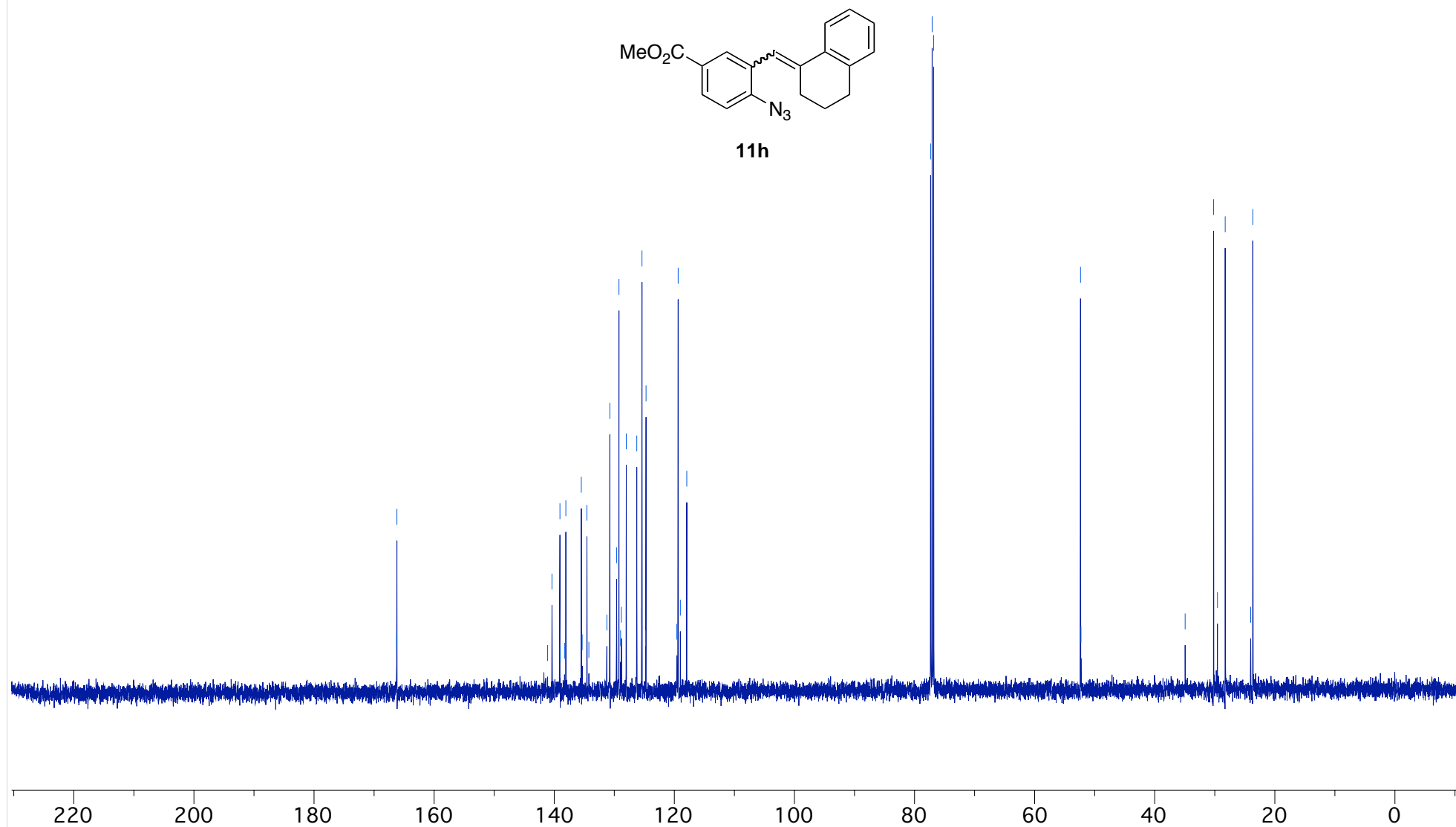


**11g**



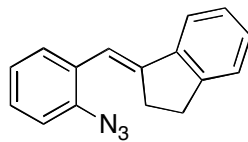
11h



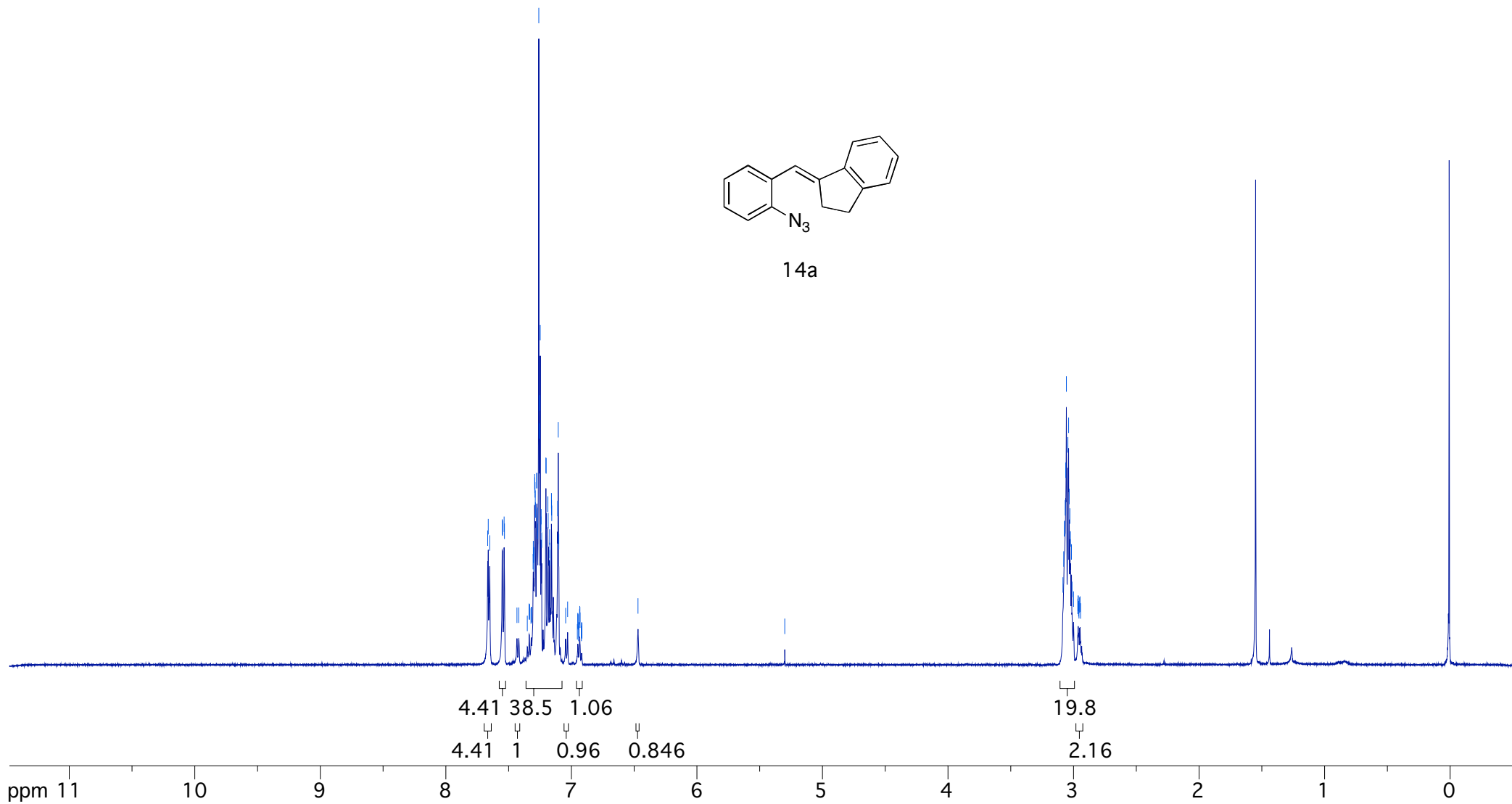


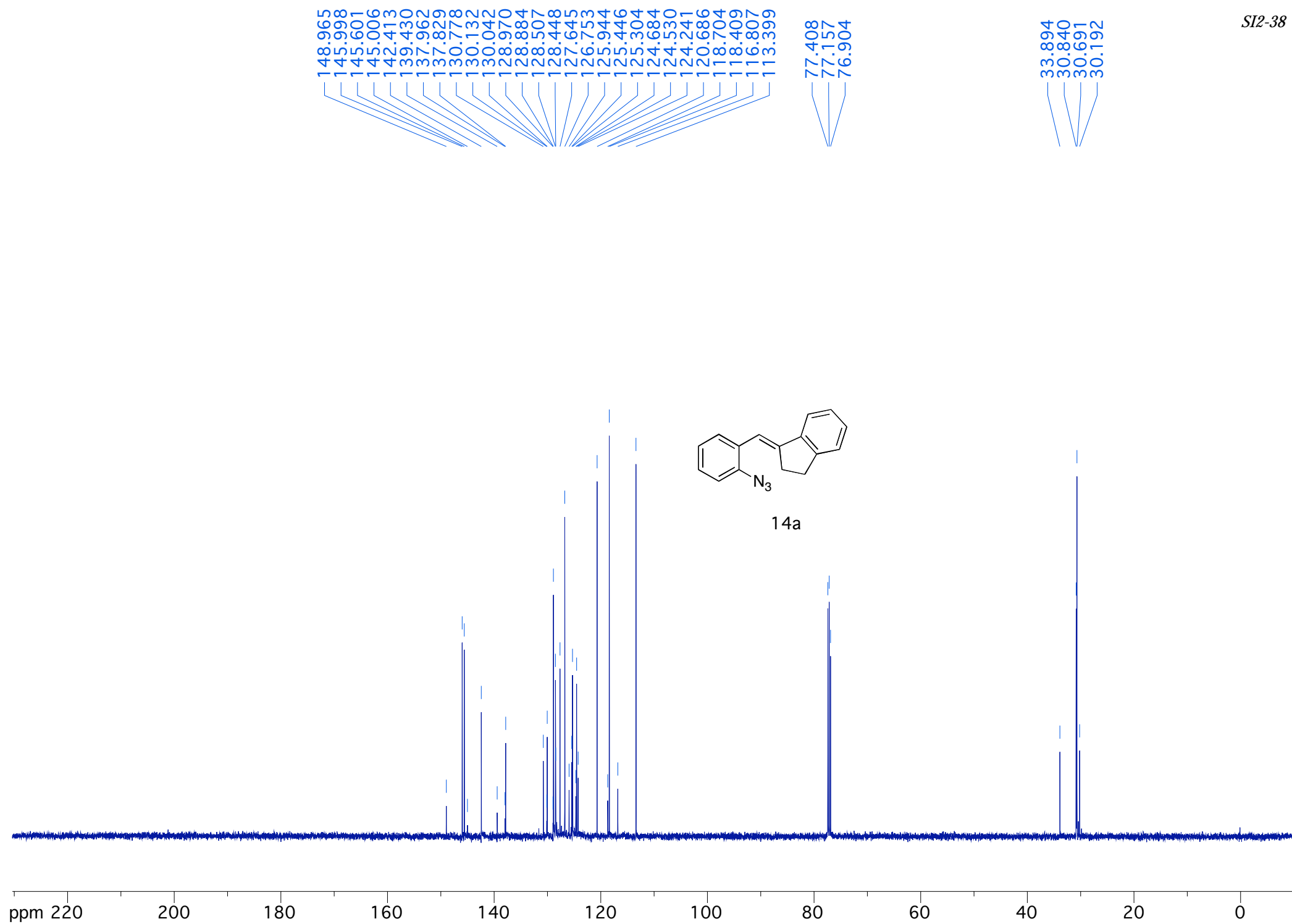
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7.337
7.335
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7.320
7.319
7.317
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7.303
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7.290
7.288
7.286
7.277
7.275
7.271
7.269
7.260
7.256
7.254
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7.241
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7.203
7.201
7.188
7.187
7.185
7.173
7.172
7.171
7.159
7.158
7.156
7.109
7.105
7.100
7.046
7.030
6.952
6.949
6.948
6.947
6.943
6.939
6.934
6.933
6.932
6.931
6.920
6.919
6.918
6.916
6.469
5.500
3.084
3.078
3.073
3.072
3.066
3.062
3.057
3.045
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3.034
3.029
3.024
3.017
3.011
3.006
2.964
2.962

SI2-37



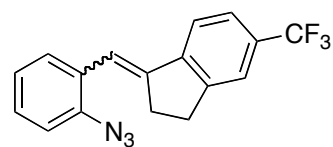
14a



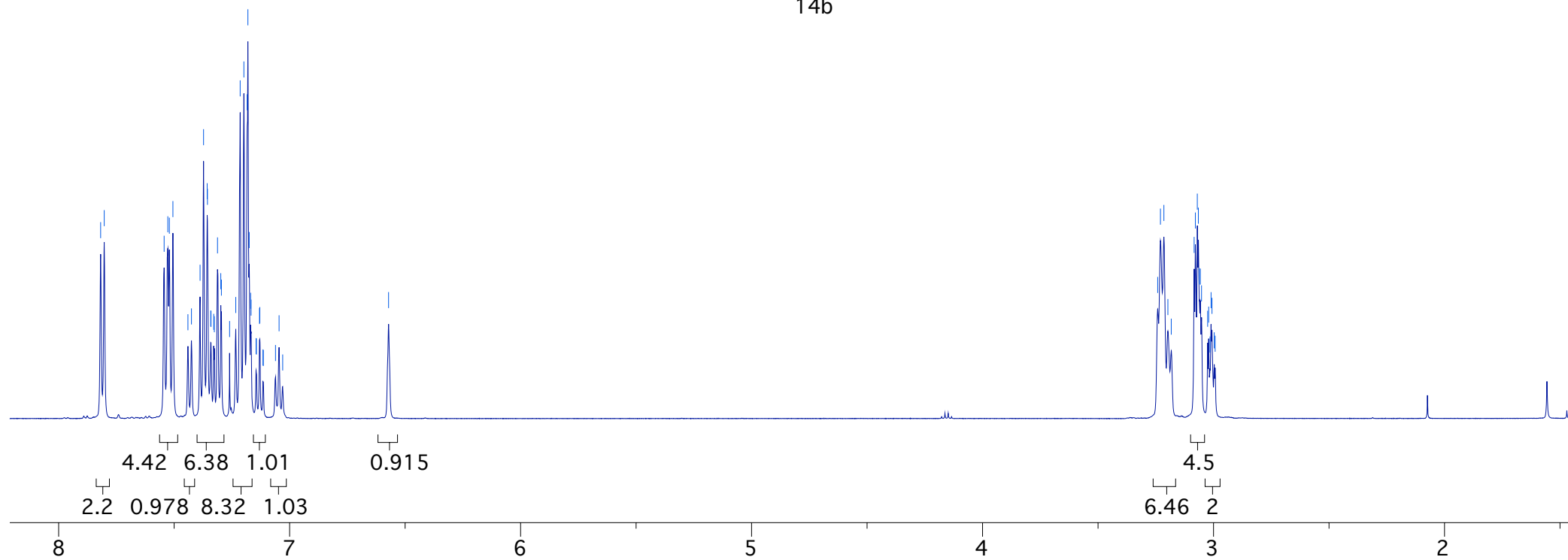


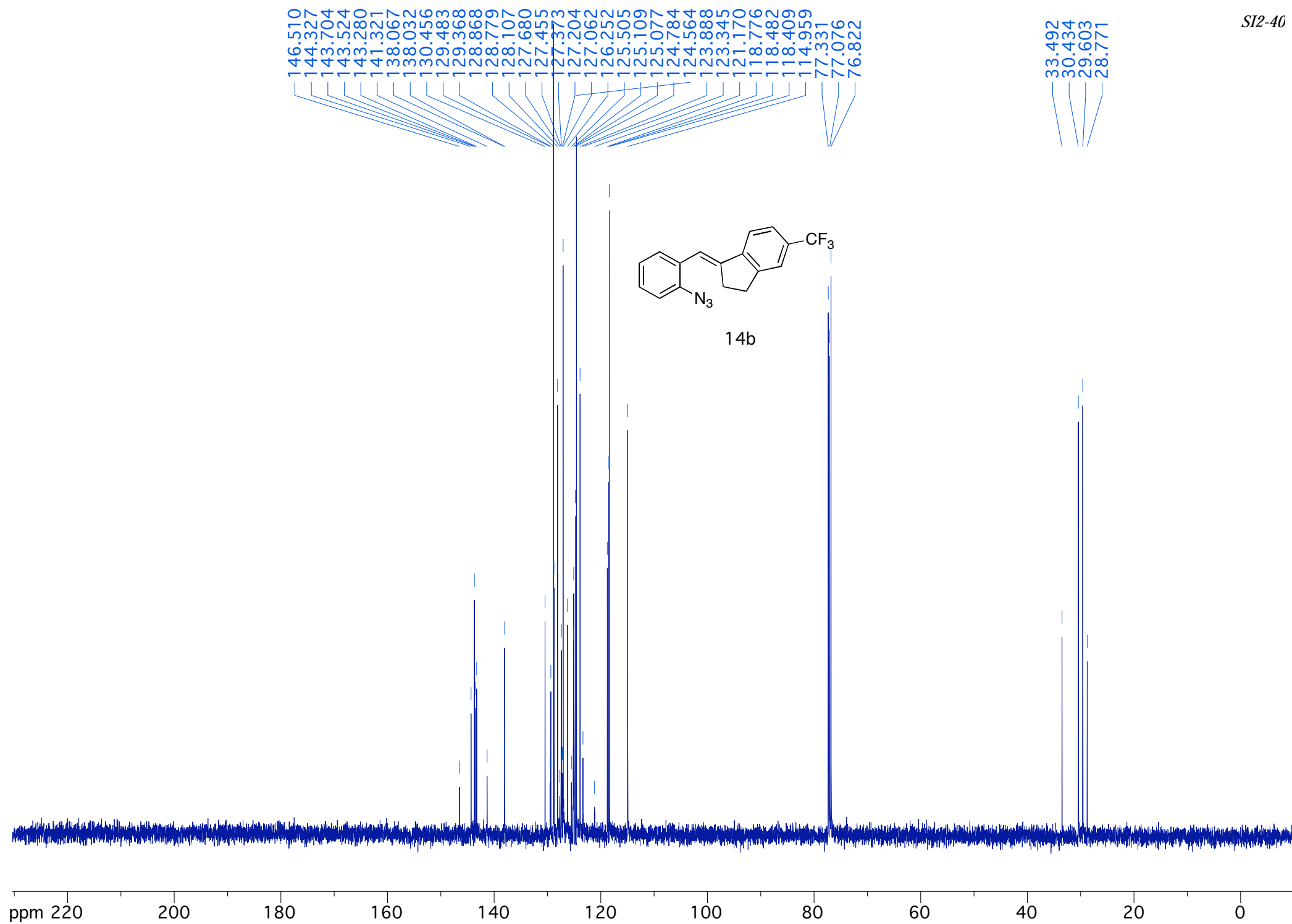
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7.543
7.527
7.521
7.505
7.440
7.425
7.388
7.373
7.357
7.356
7.341
7.340
7.329
7.326
7.312
7.298
7.295
7.260
7.233
7.214
7.198
7.184
7.181
7.175
7.169
7.167
7.145
7.144
7.130
7.129
7.115
7.114
7.061
7.046
7.030
6.572

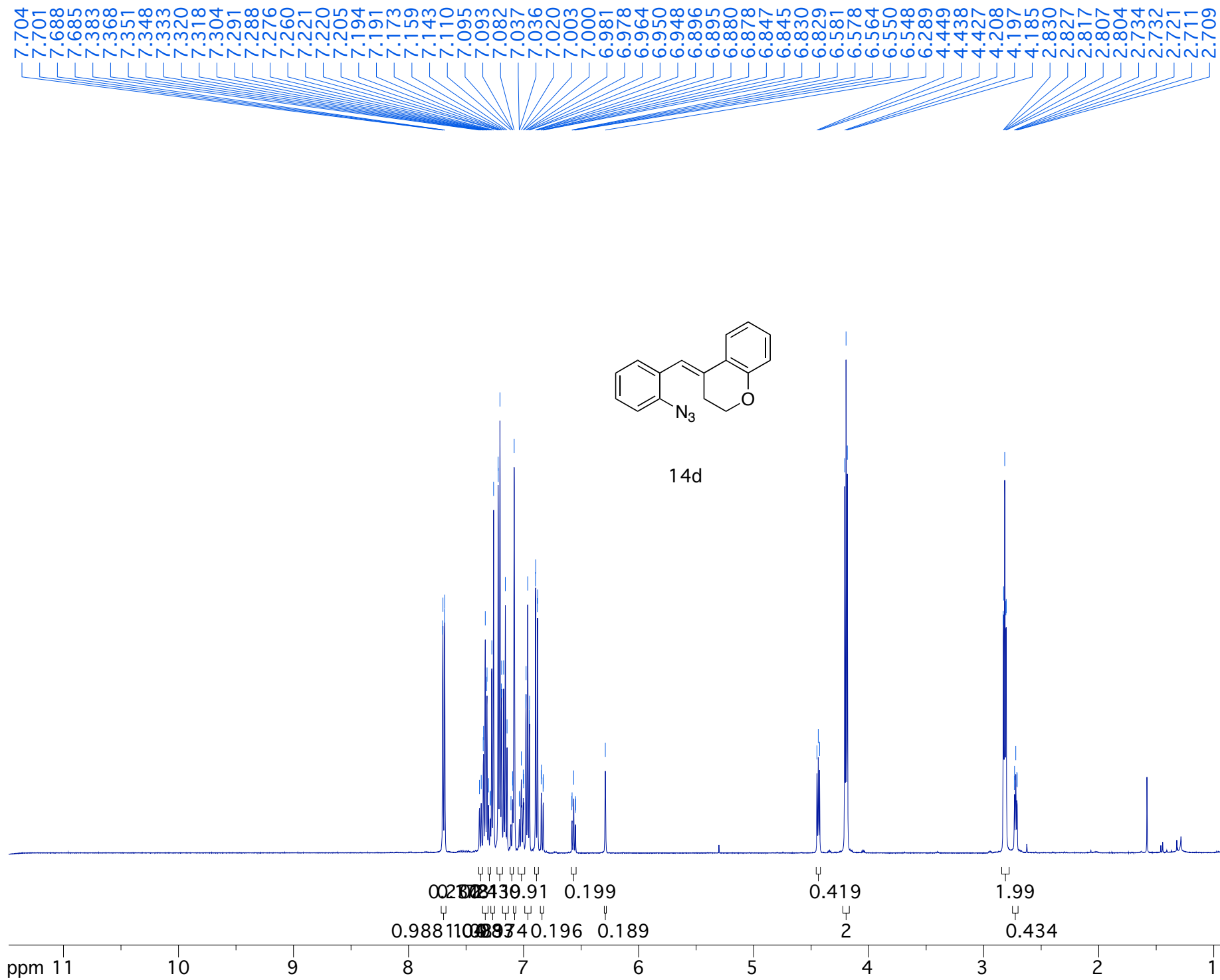
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3.230
3.215
3.198
3.183
3.084
3.079
3.070
3.066
3.061
3.057
3.052
3.025
3.021
3.015
3.011
3.007
3.007
2.997
2.993



14b







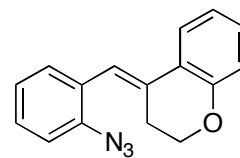
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154.882
138.699
138.080
132.483
132.129
131.058
130.925
129.662
129.470
128.810
128.526
128.503
128.340
124.757
124.727
124.315
122.405
120.877
120.598
119.981
119.334
118.613
118.424
117.483
117.061
116.984

77.349
77.098
76.846

67.432
66.228

33.320

26.930

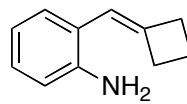


14d

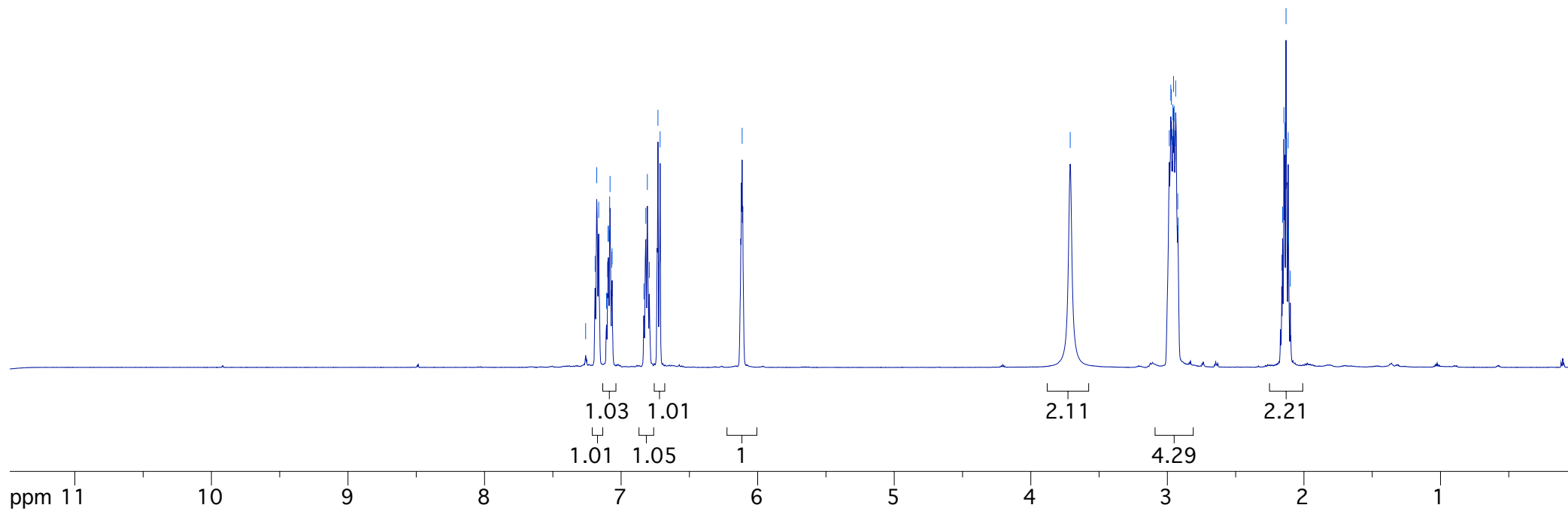
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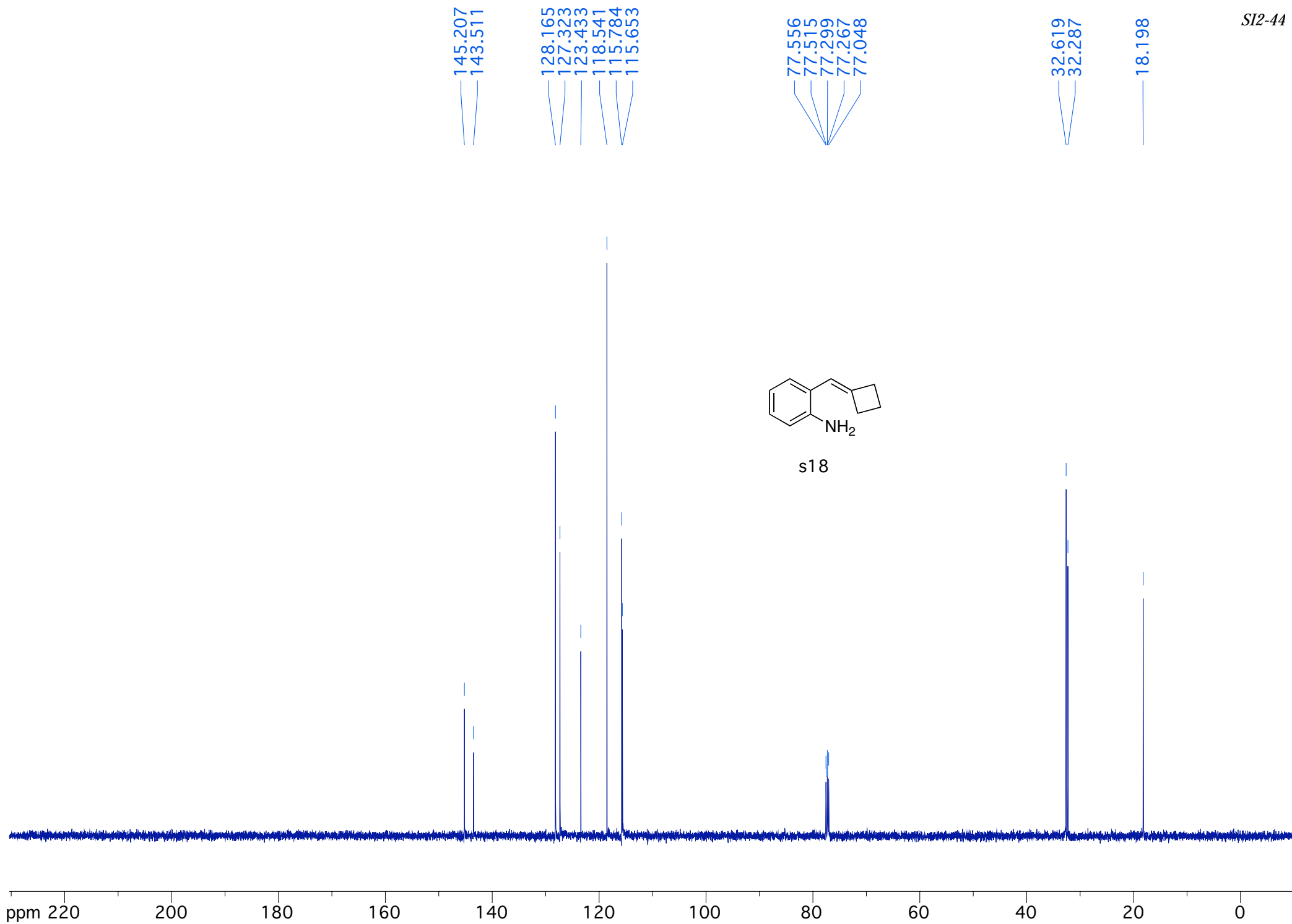
7.260
7.190
7.178
7.164
7.107
7.099
7.096
7.093
7.084
7.081
7.069
7.066
6.833
6.819
6.808
6.793
6.730
6.714
6.114

3.711
2.986
2.975
2.970
2.965
2.959
2.955
2.950
2.944
2.939
2.924
2.921
2.162
2.156
2.147
2.141
2.131
2.127
2.115
2.113
2.100



s18

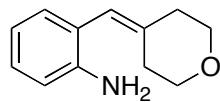




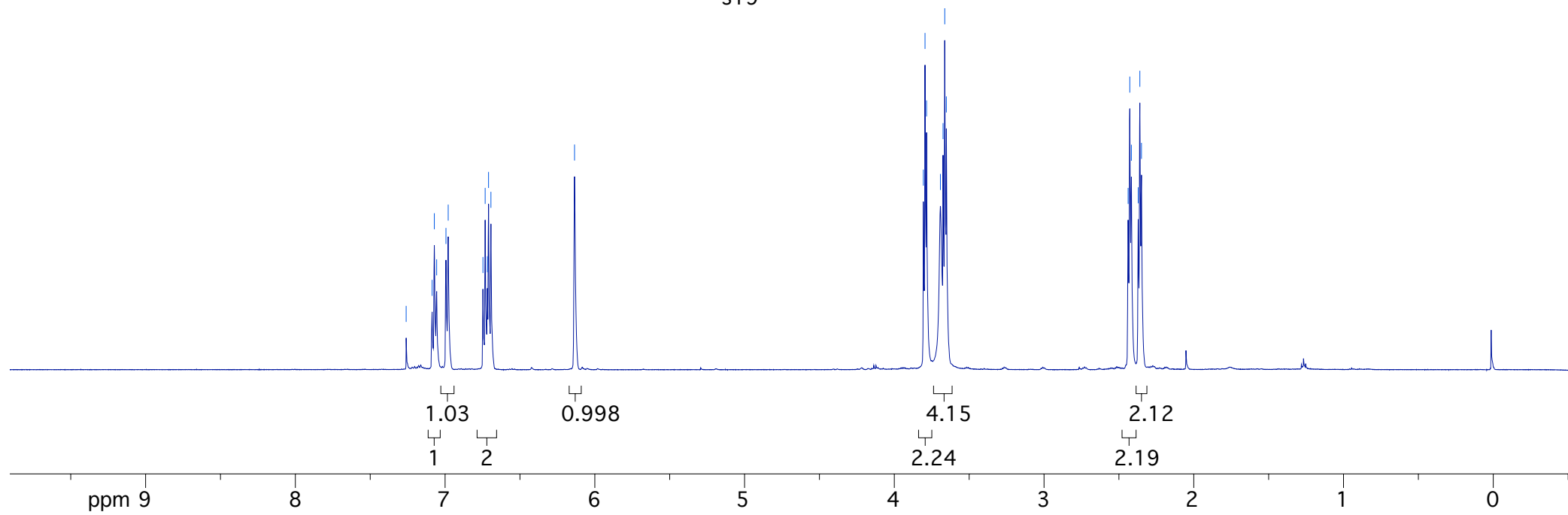
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7.056
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6.979
6.747
6.732
6.718
6.710
6.694
6.136

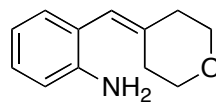
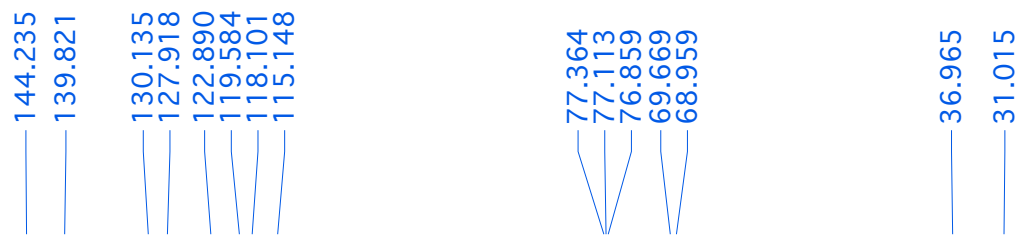
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3.652

2.438
2.427
2.417
2.371
2.360
2.349

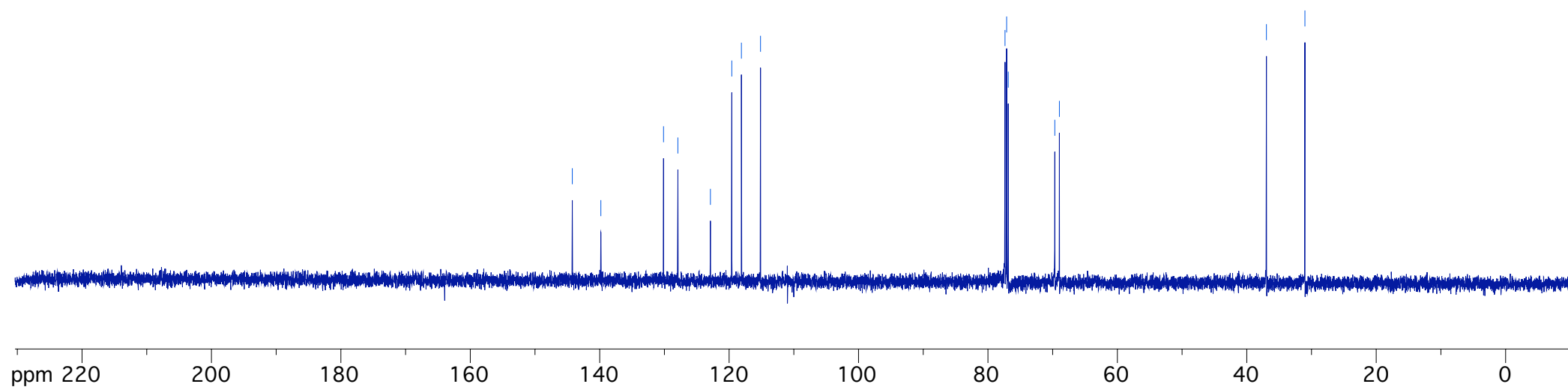


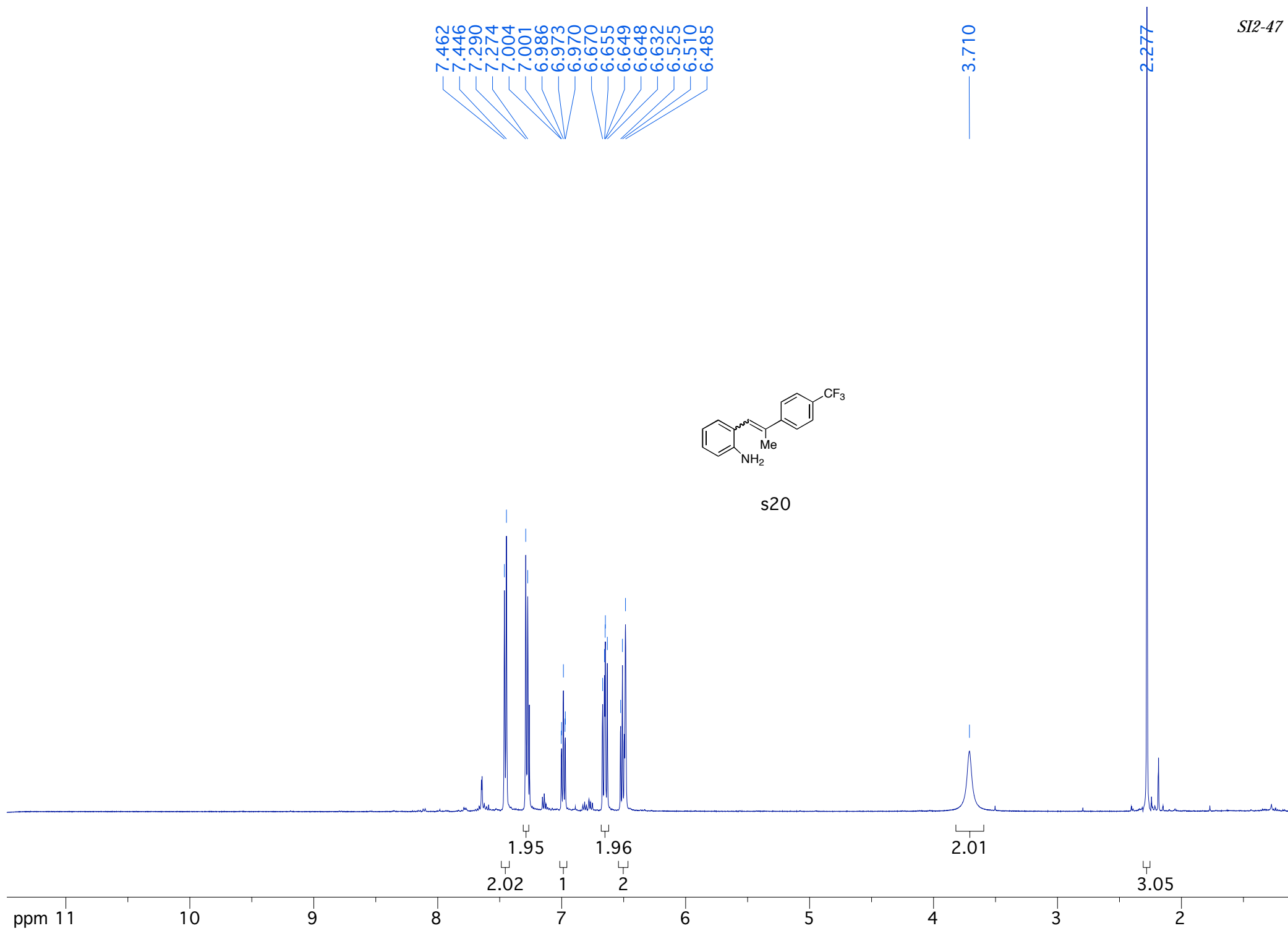
s19

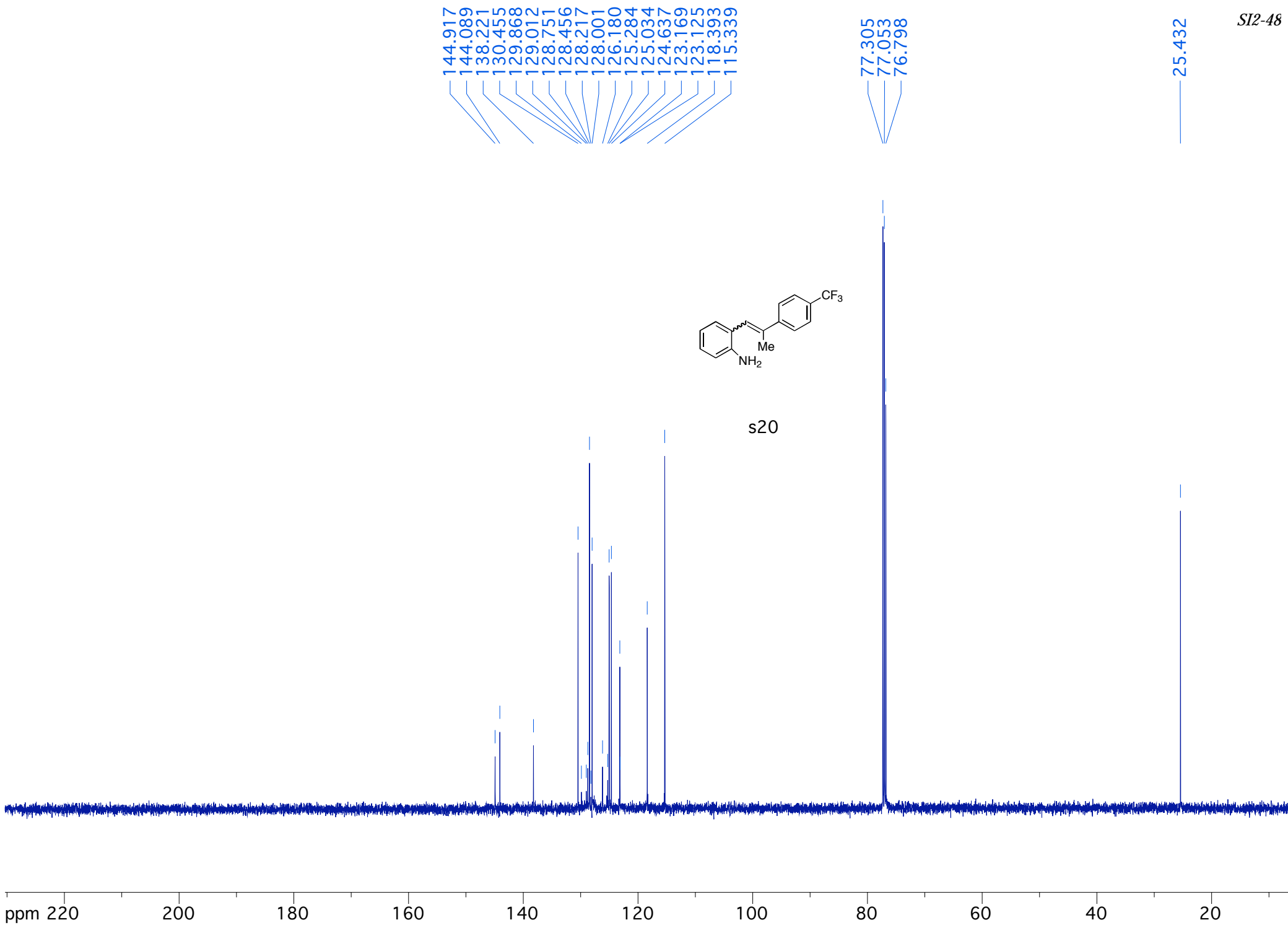




s19

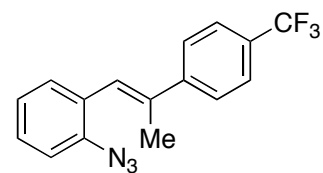




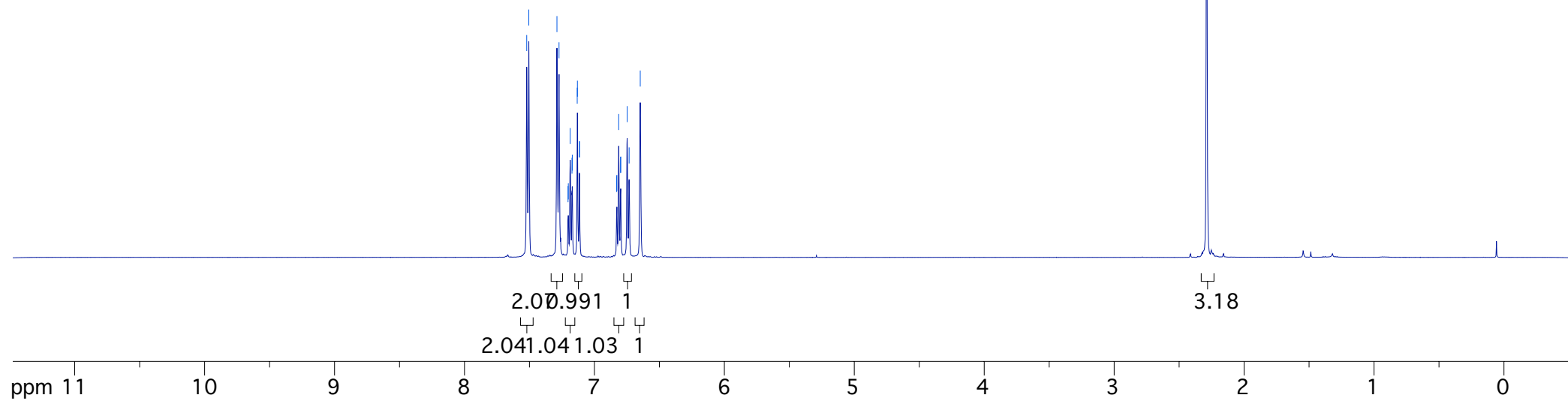


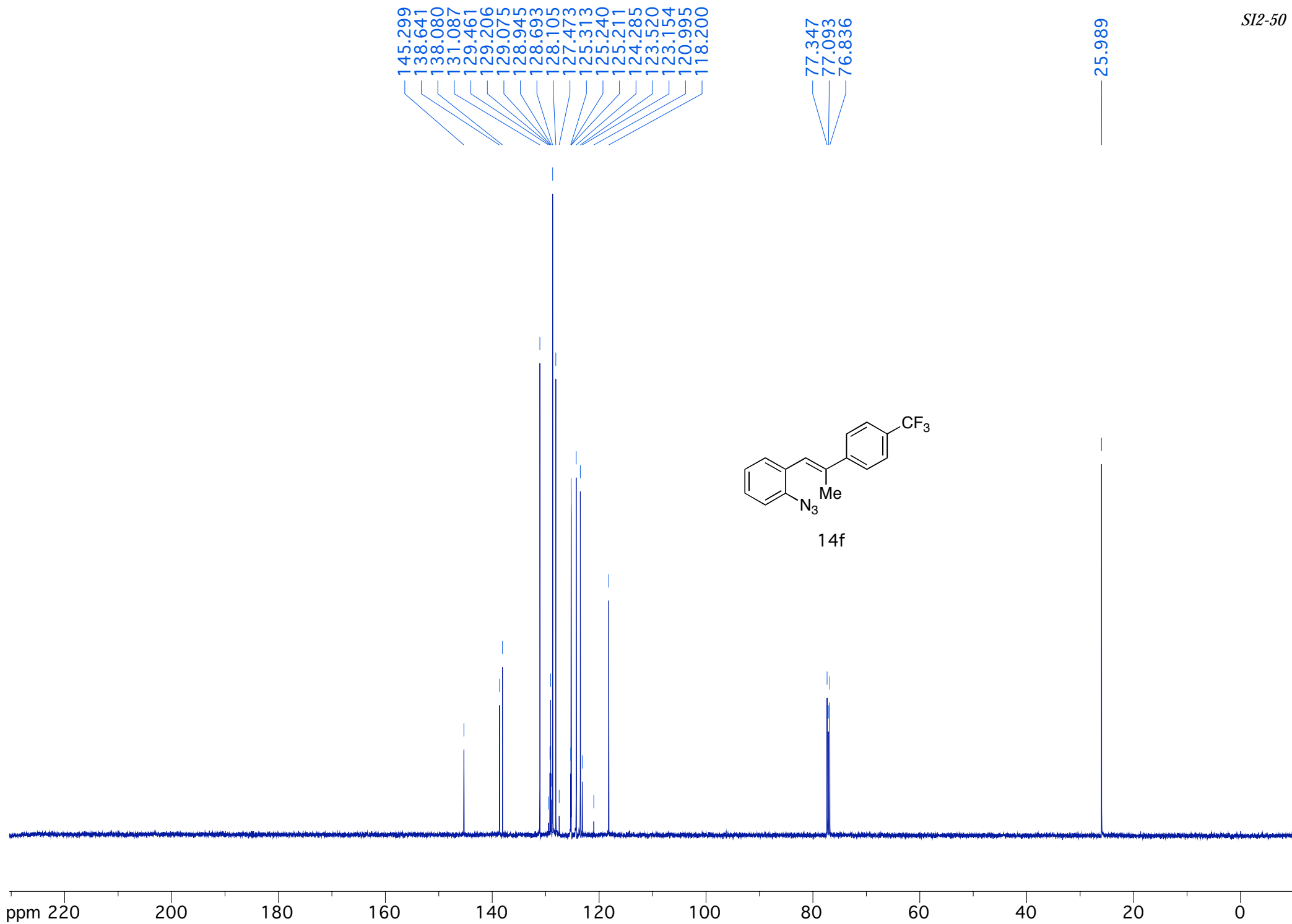
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7.272
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7.201
7.187
7.173
7.170
7.132
7.131
7.116
7.115
6.829
6.827
6.813
6.799
6.797
6.748
6.733
6.647

2.290



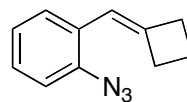
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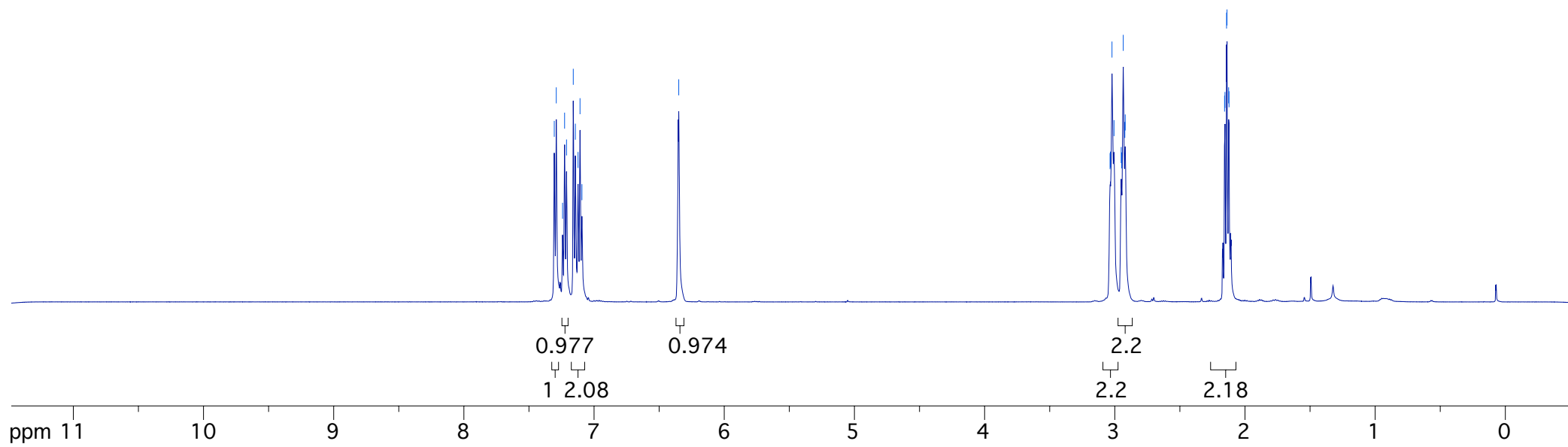


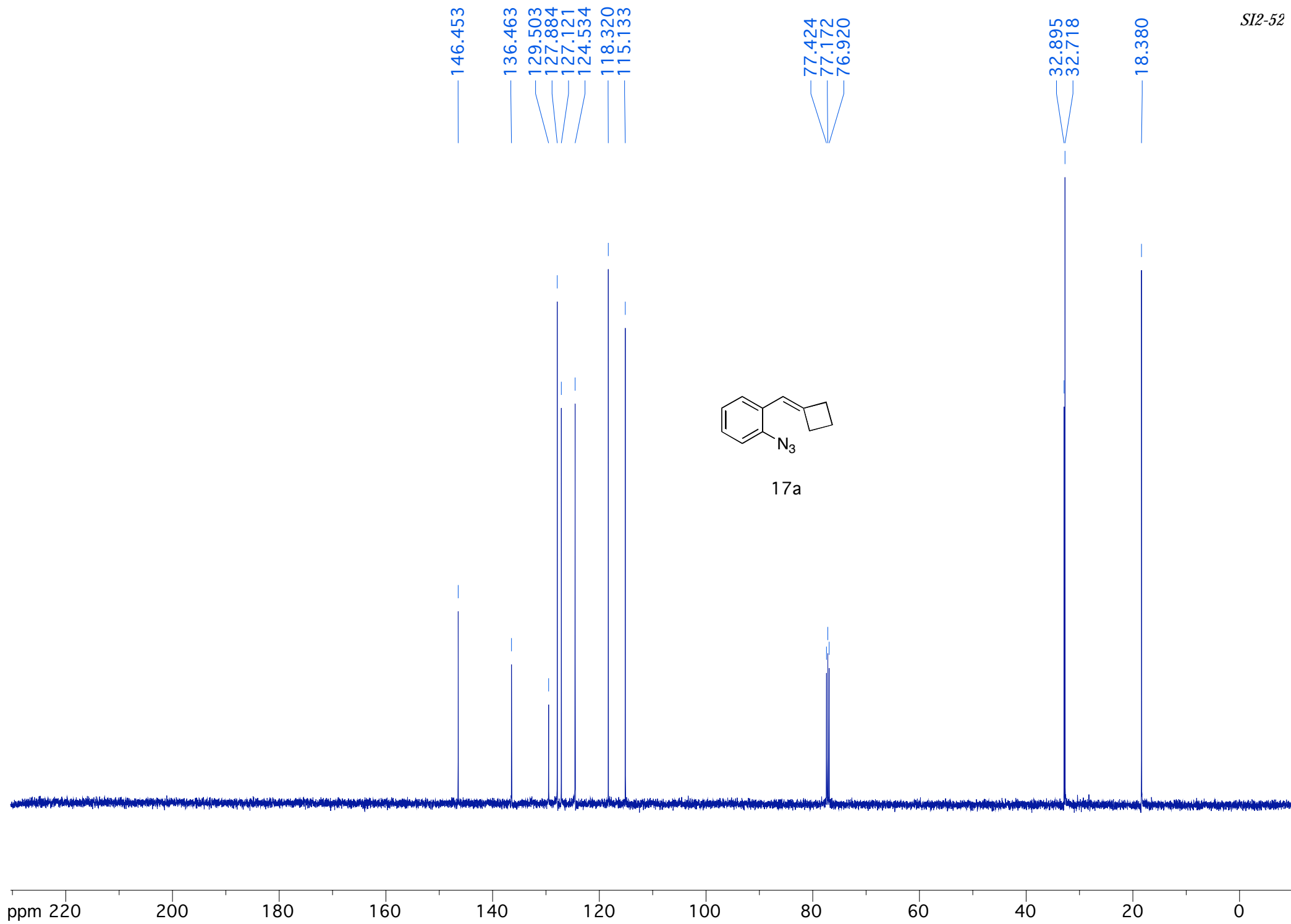
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7.290
7.242
7.226
7.211
7.160
7.144
7.123
7.108
7.093
6.349

3.036
3.034
3.022
3.006
2.951
2.948
2.935
2.923
2.920
2.157
2.154
2.142
2.138
2.126
2.122



17a

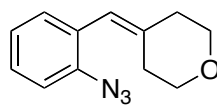




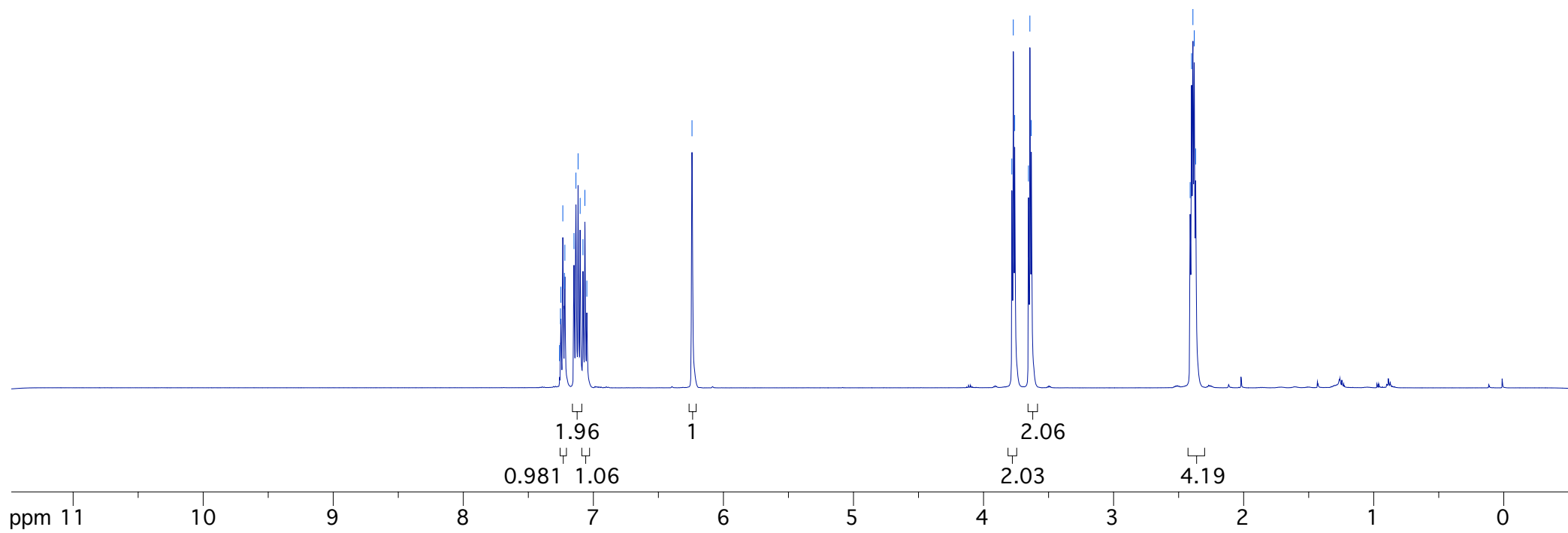
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7.235
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7.134
7.118
7.102
7.080
7.065
7.050
6.242

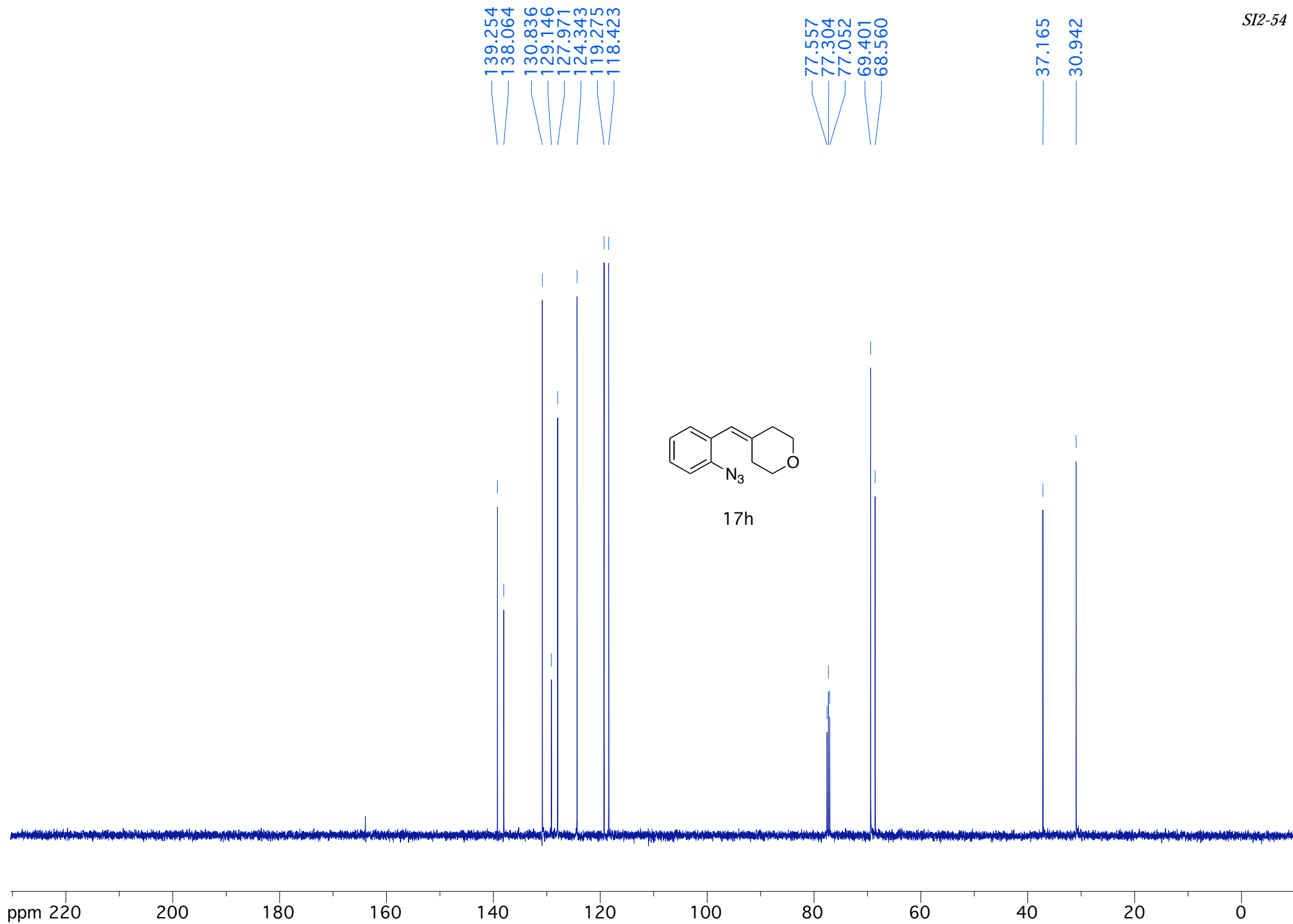
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3.633

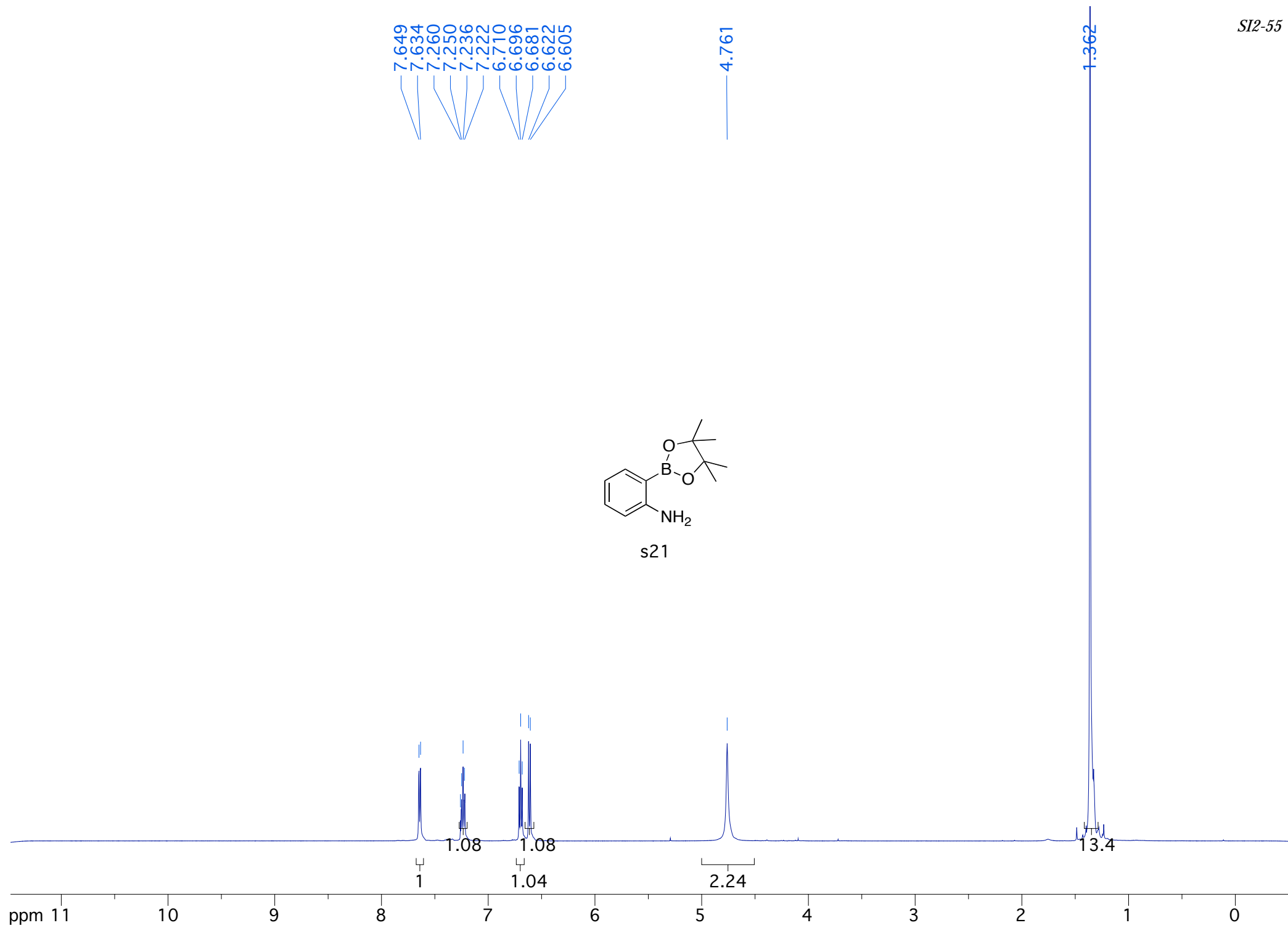
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2.369

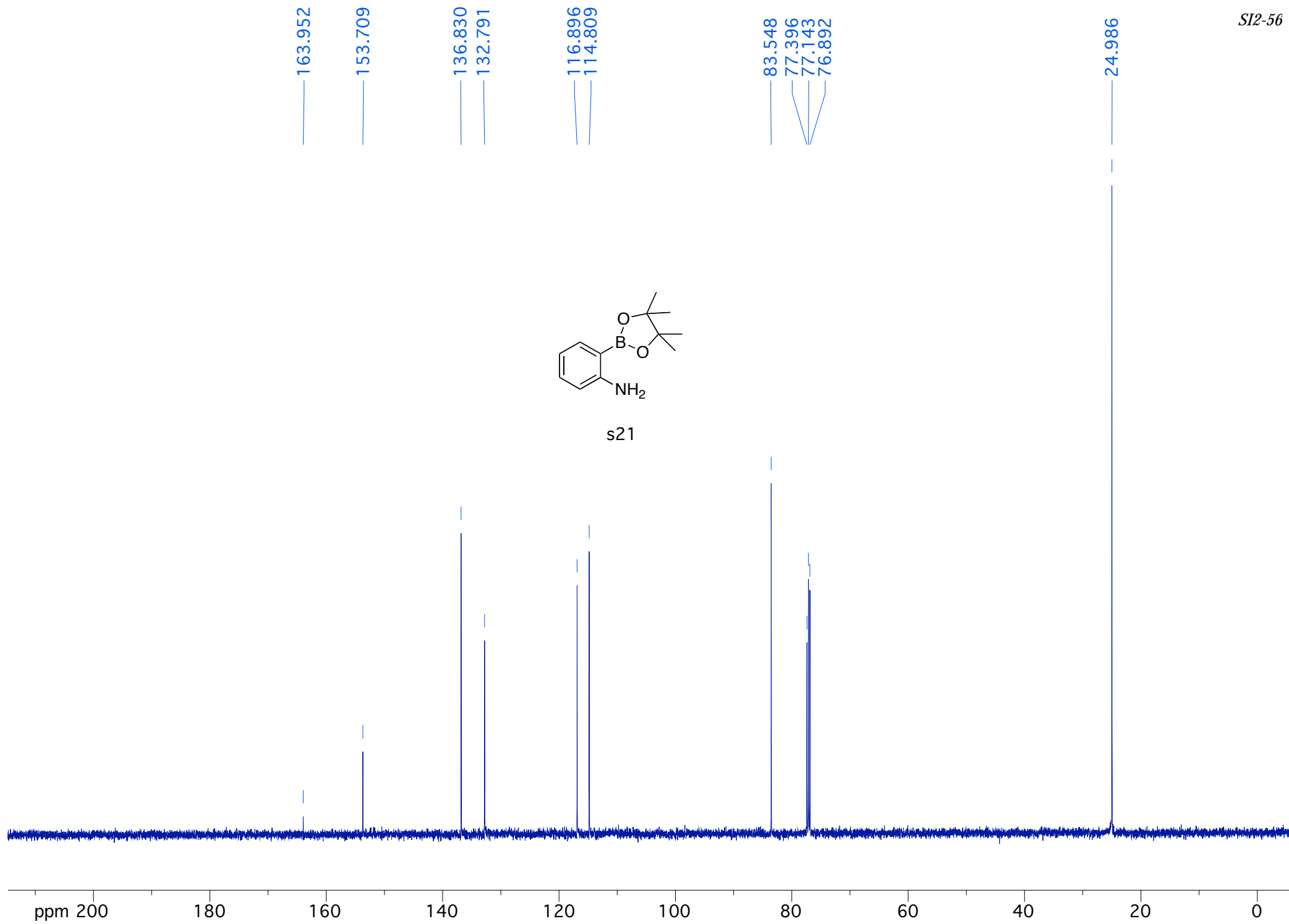


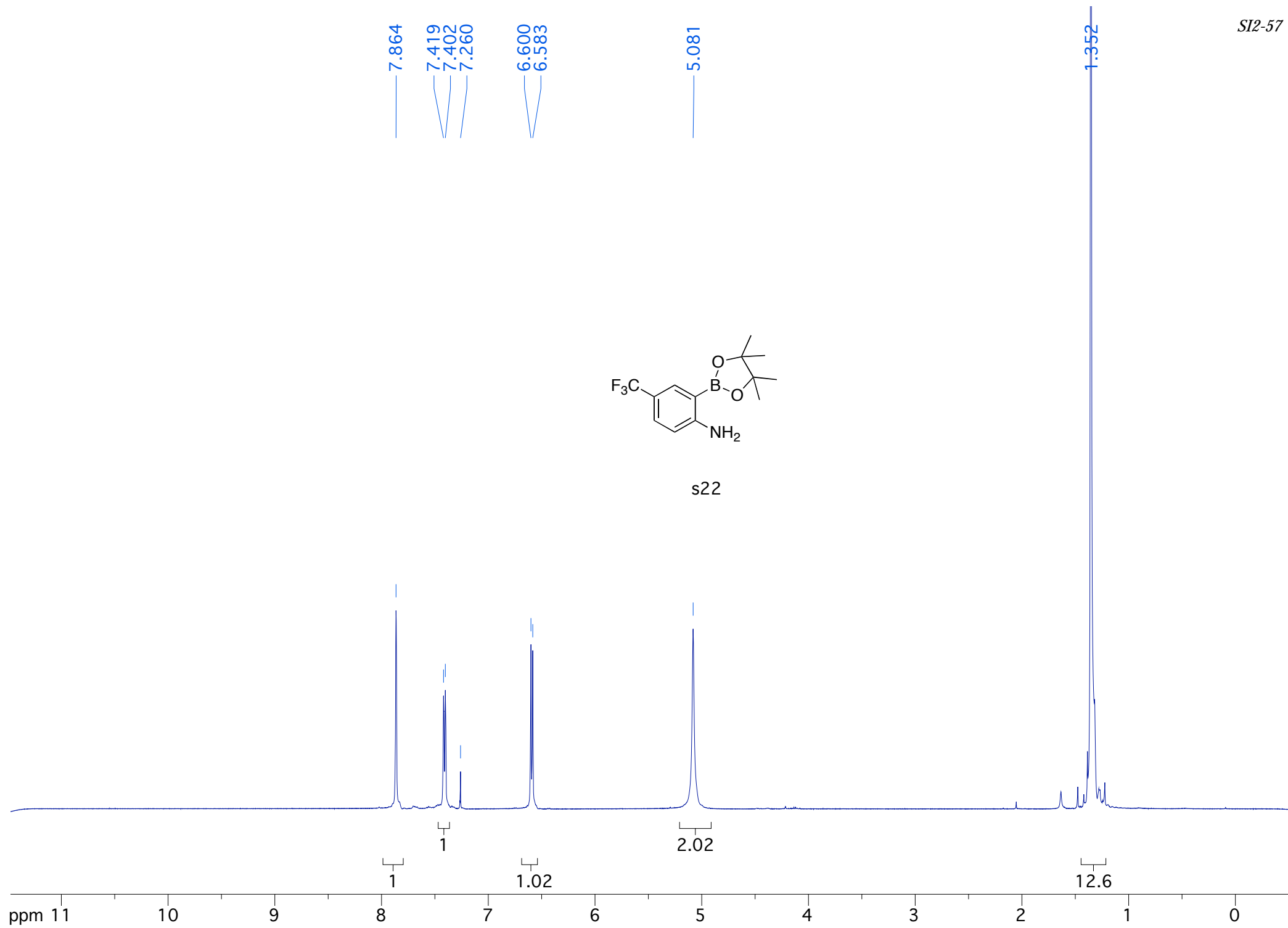
17h

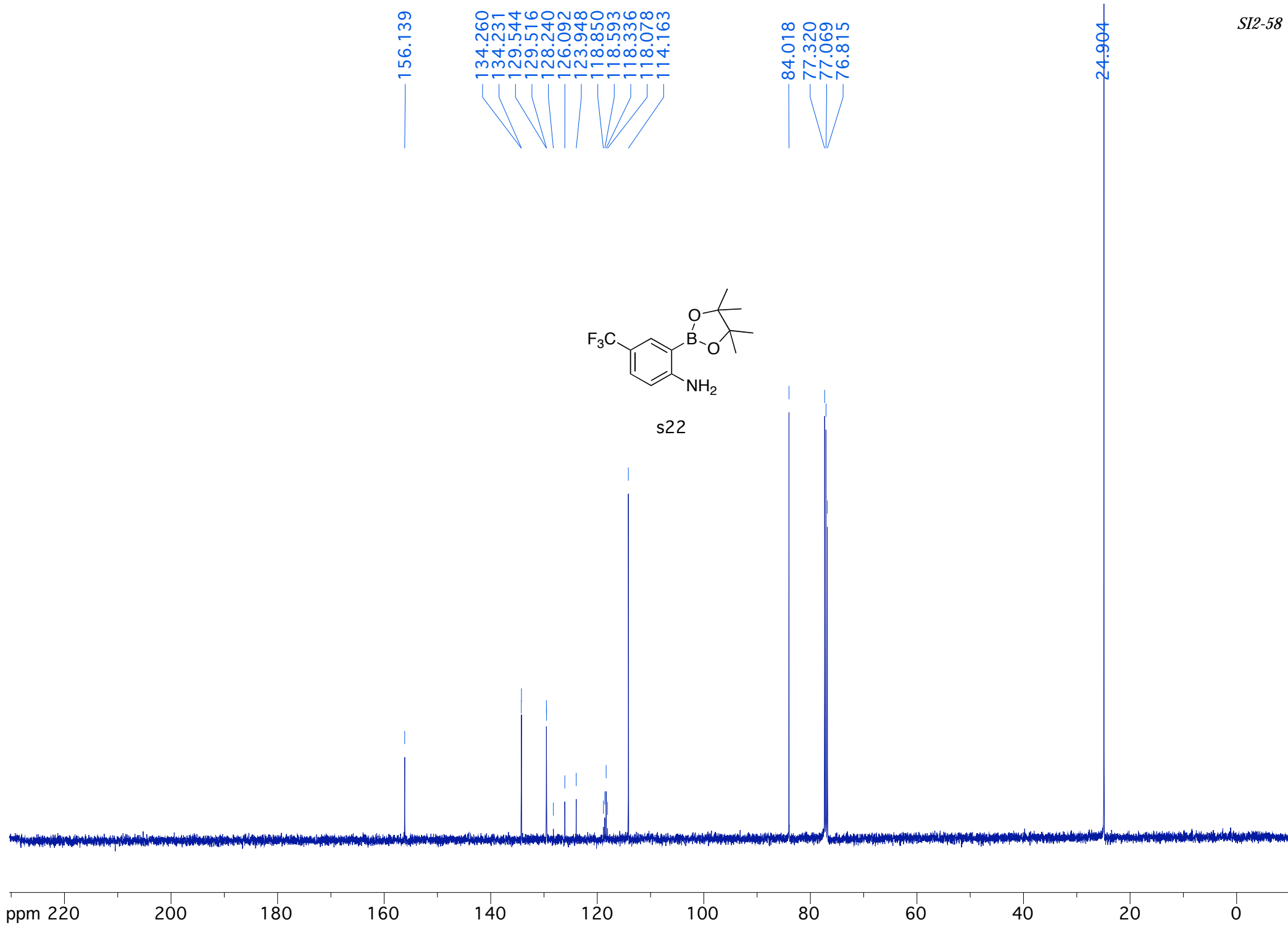


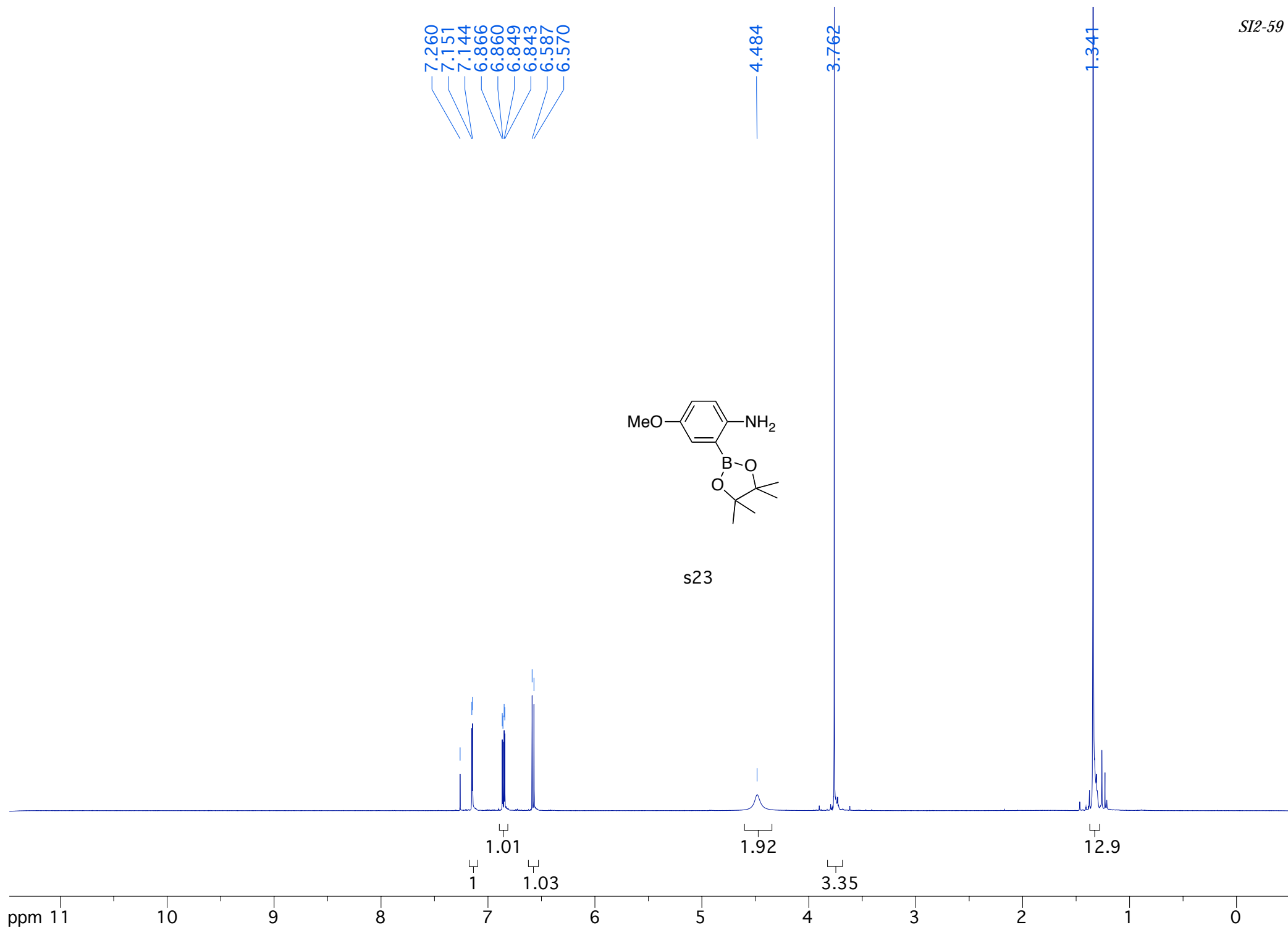


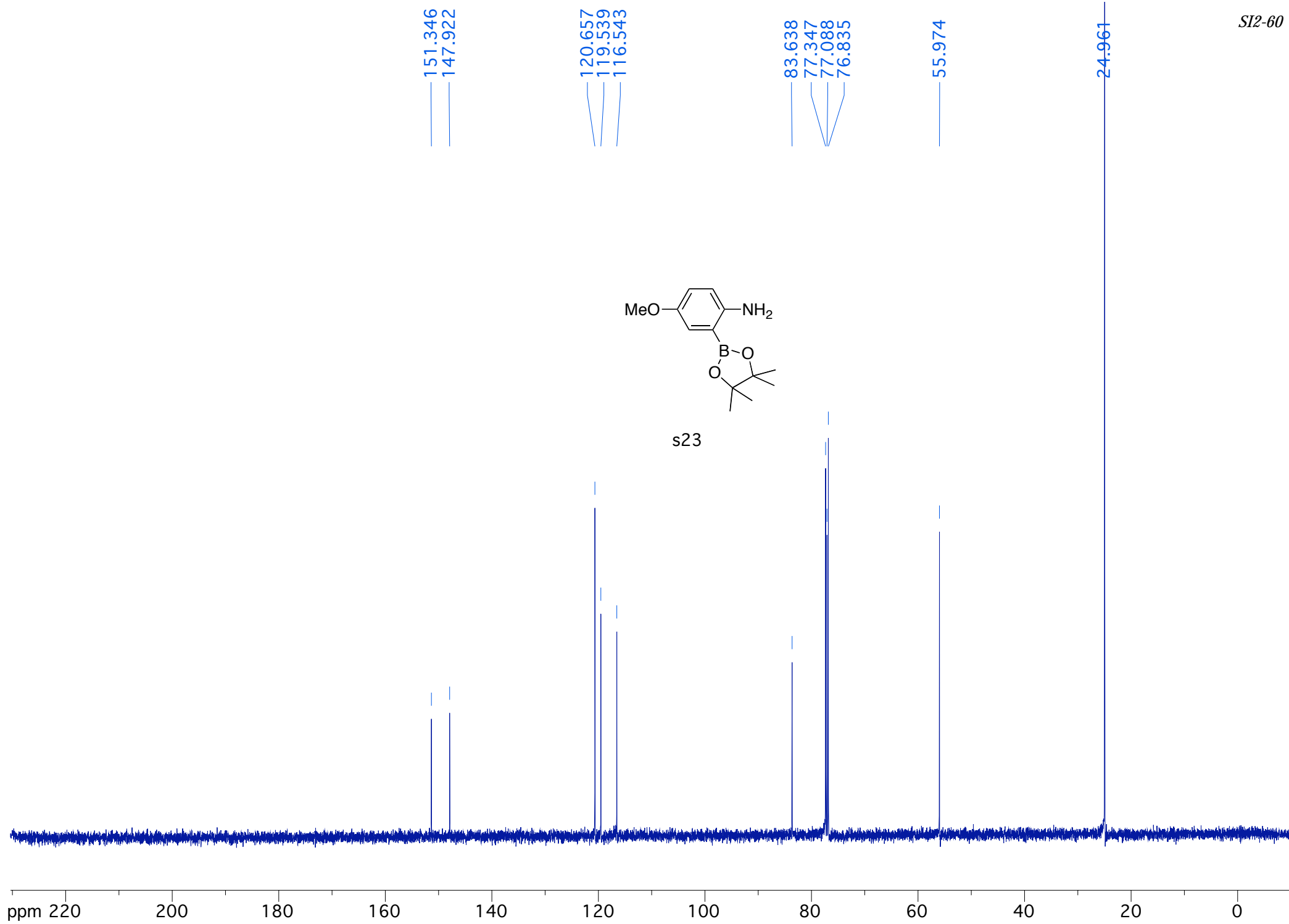








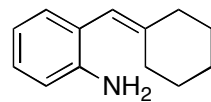




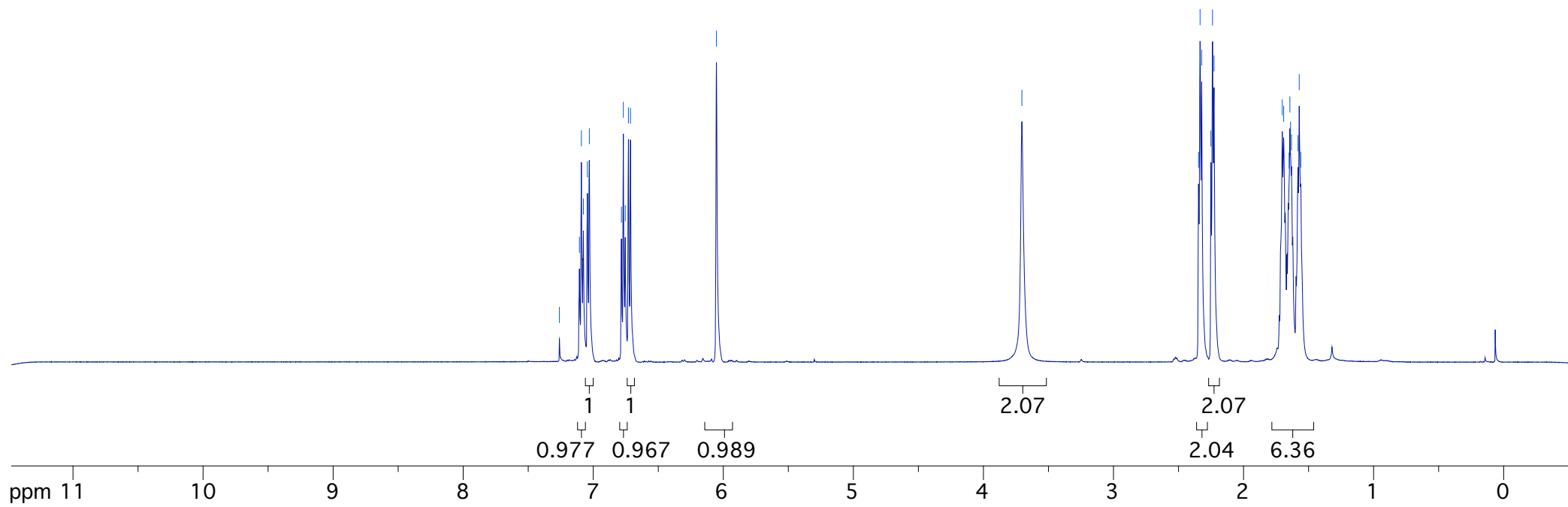
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7.076
7.045
7.030
6.783
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6.754
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6.714
6.053

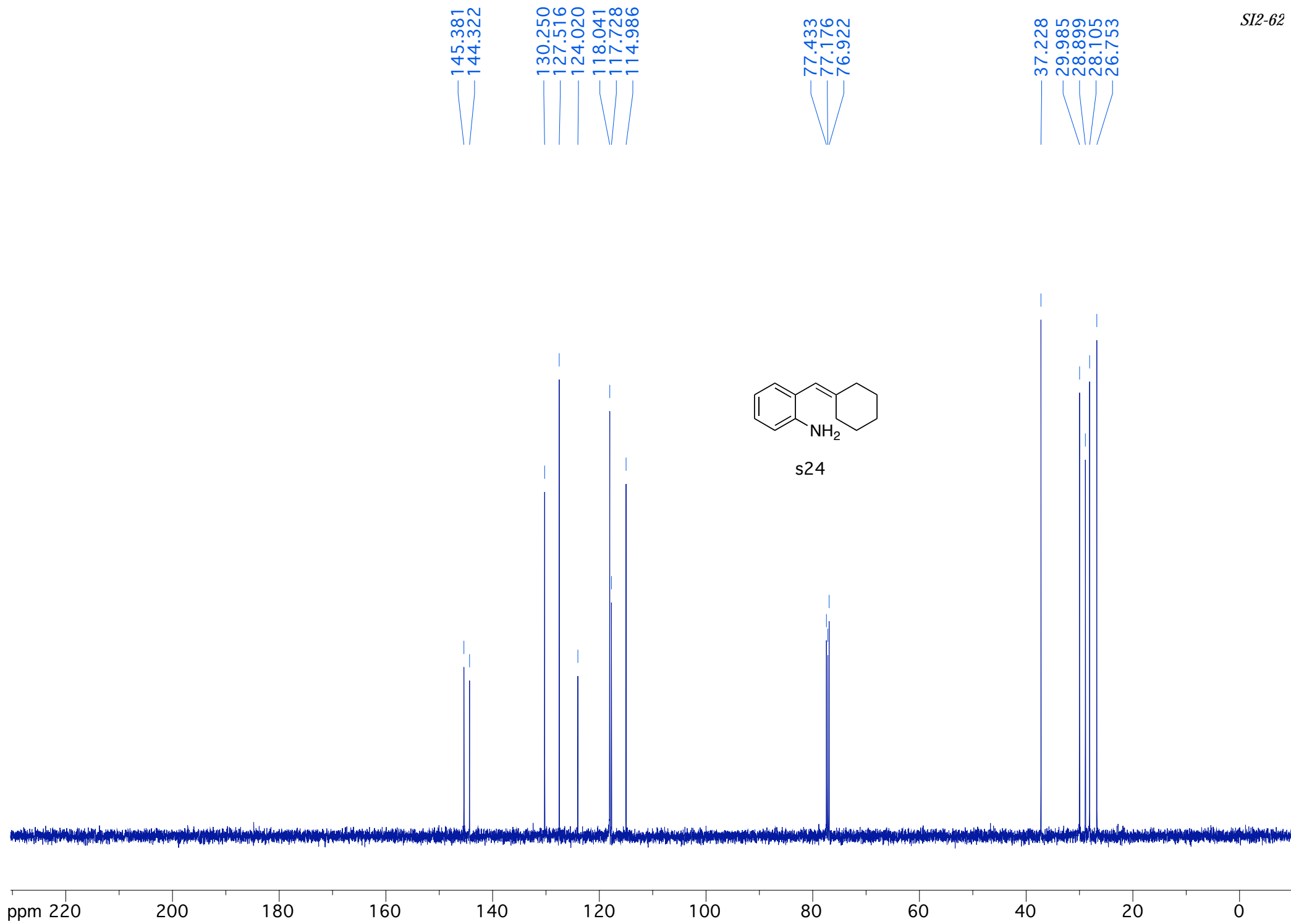
3.704

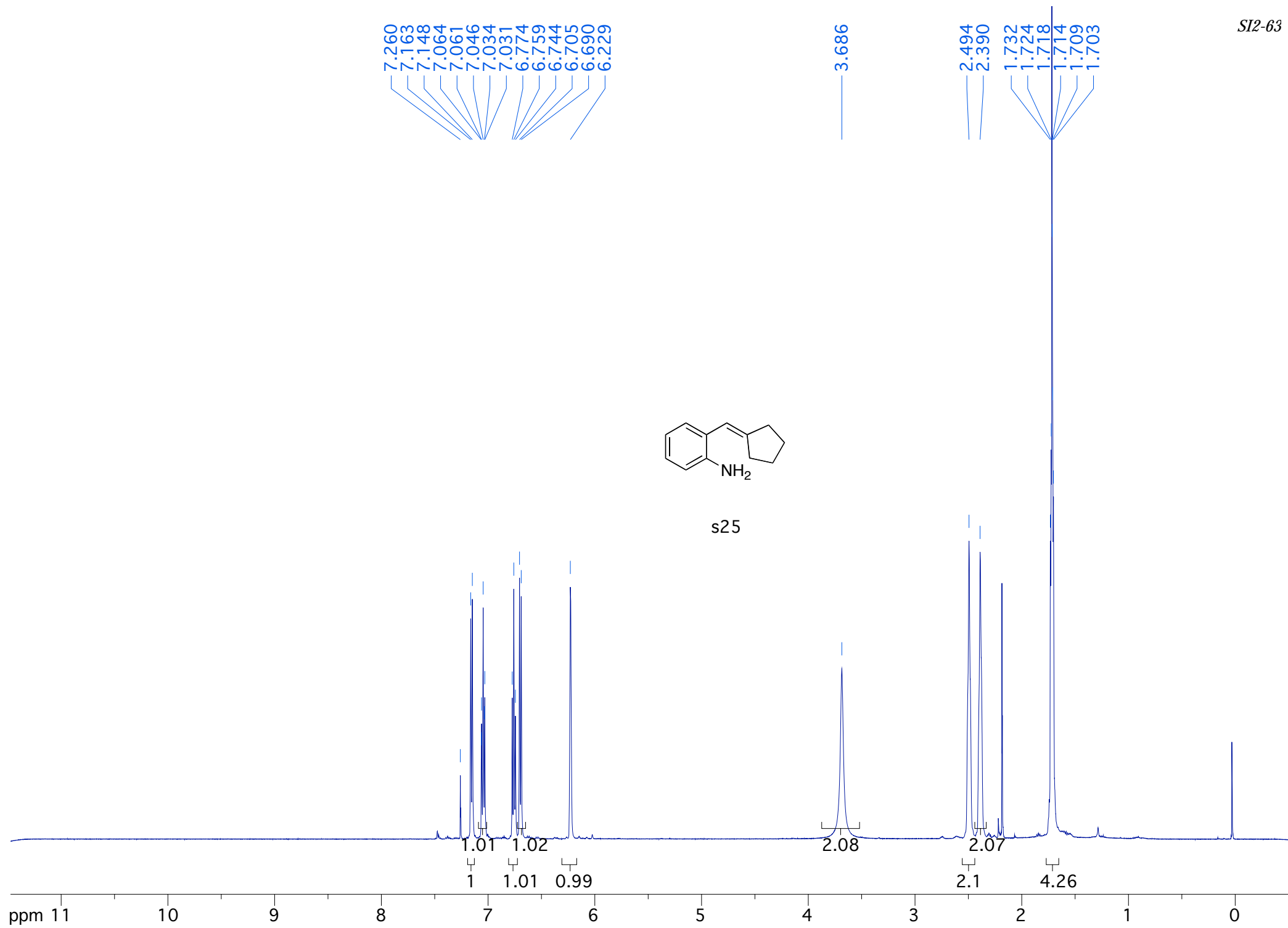
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2.322
2.251
2.239
2.227
1.702
1.692
1.650
1.644
1.639
1.632
1.581
1.572



s24





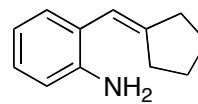


148.644
143.693

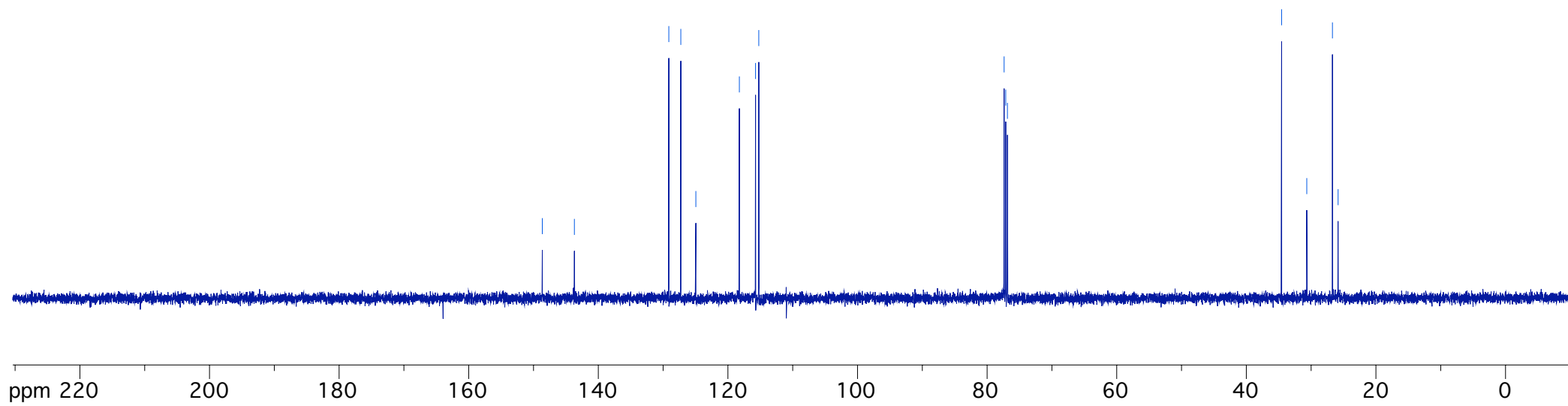
129.119
127.268
124.947
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115.736
115.236

77.378
77.126
76.867

34.555
30.671
26.710
25.836

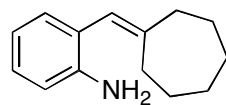


s25

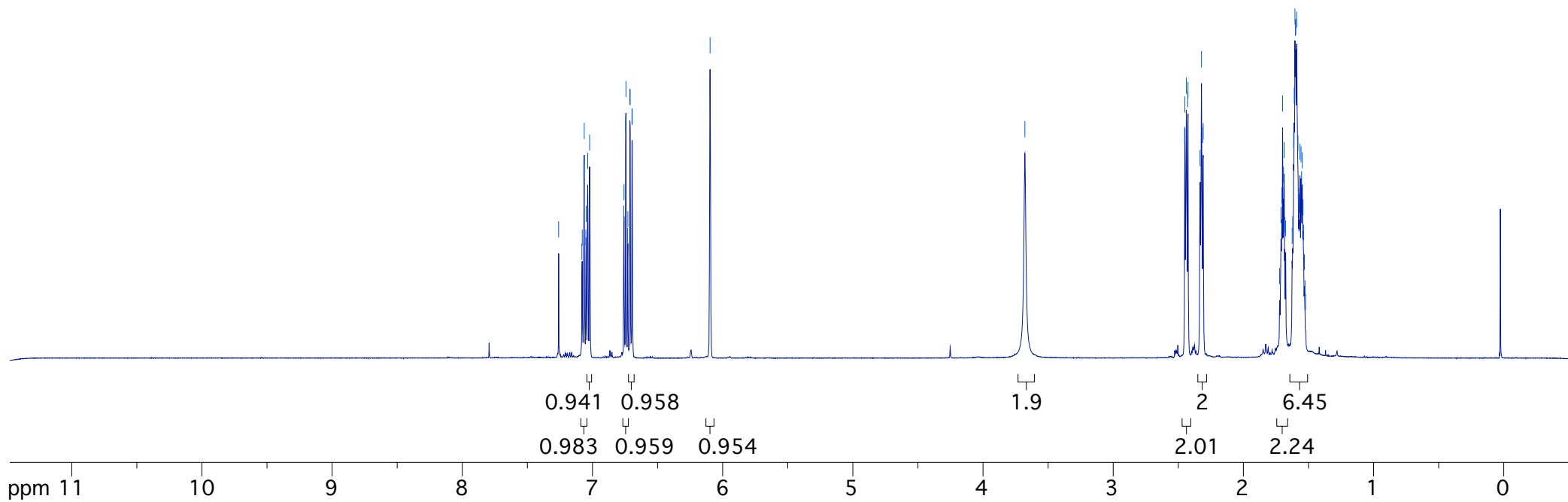


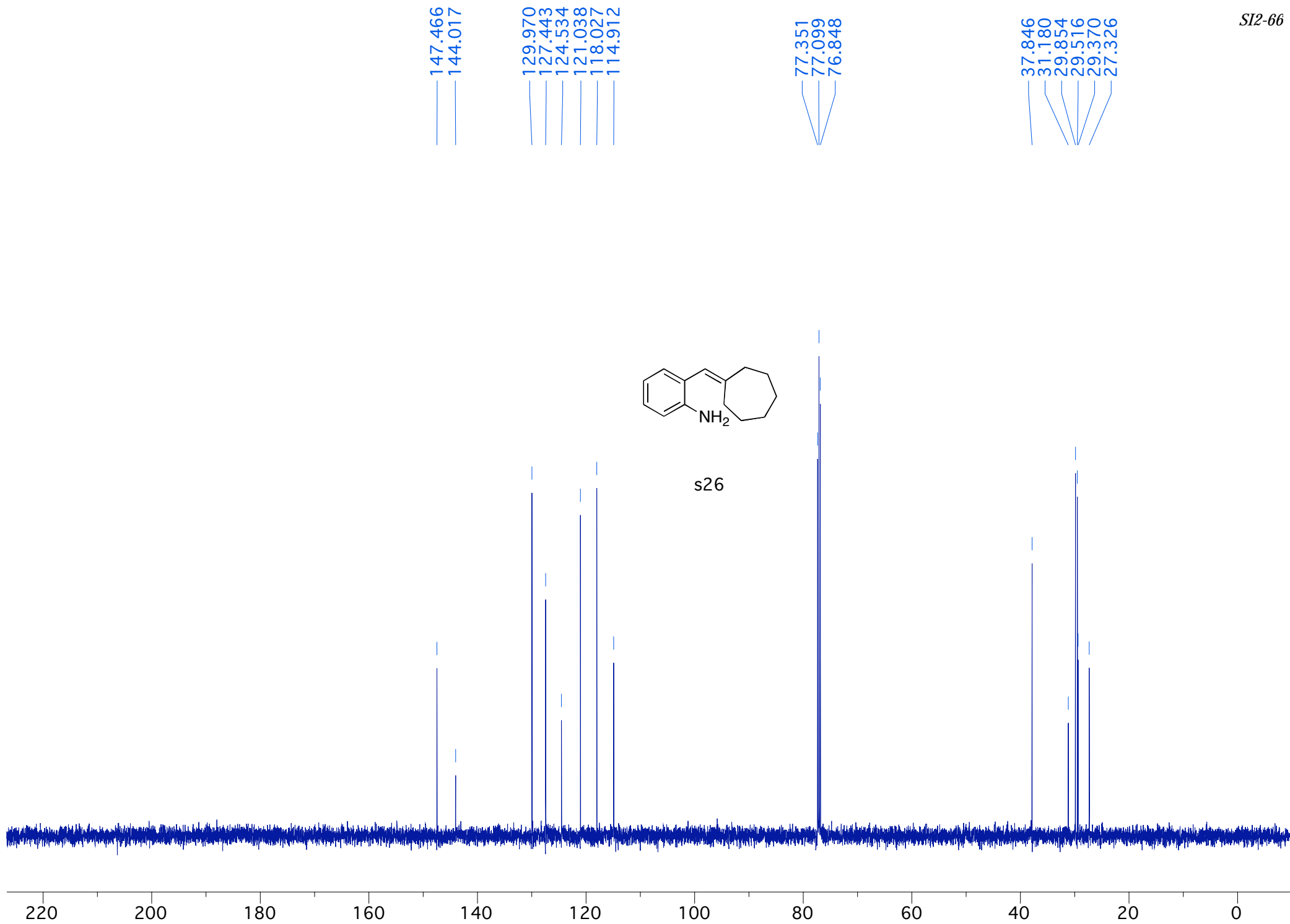
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7.022
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6.745
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6.728
6.713
6.710
6.697
6.695
6.097
3.678
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2.449
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2.425
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1.598
1.590
1.581
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1.522

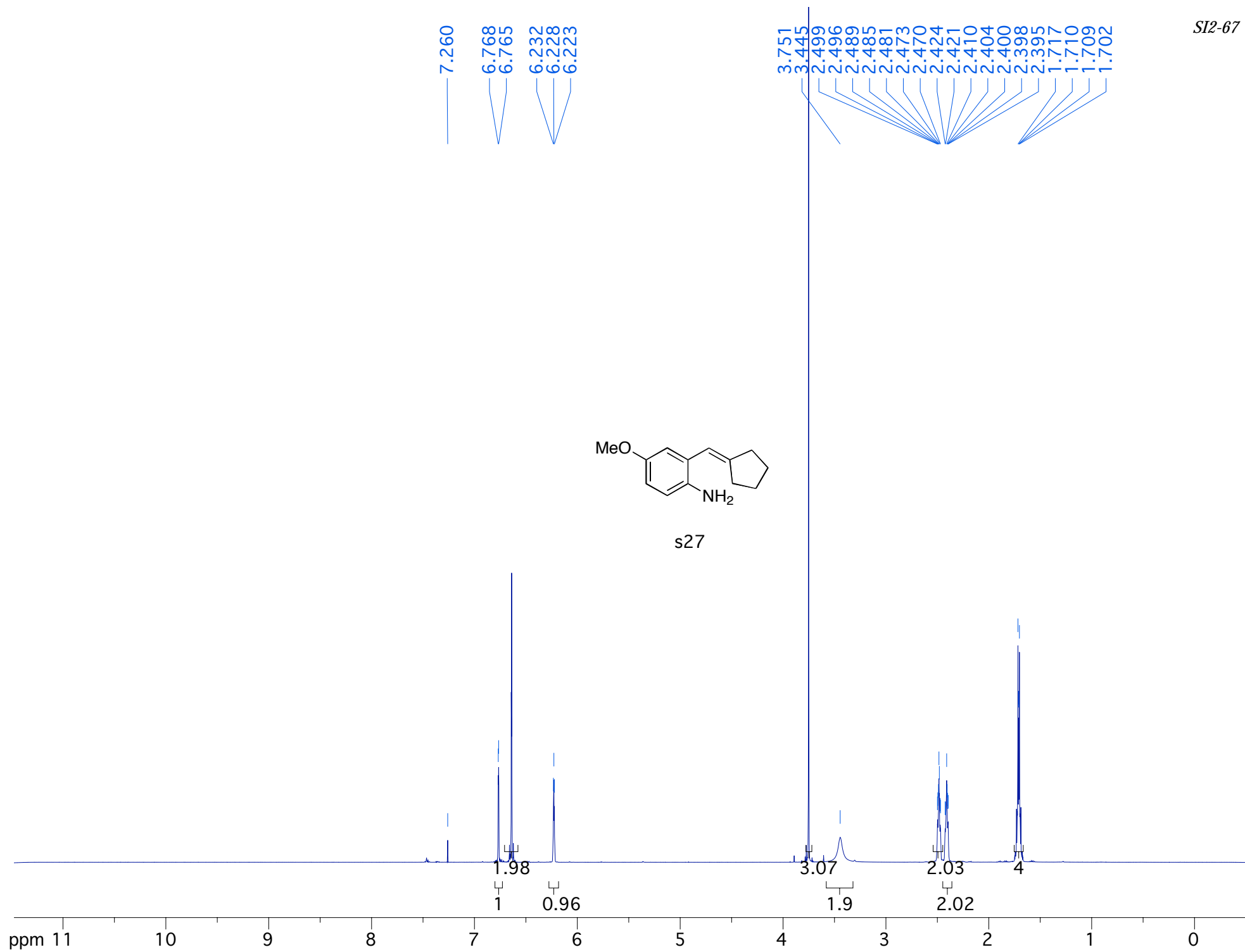
SI2-65

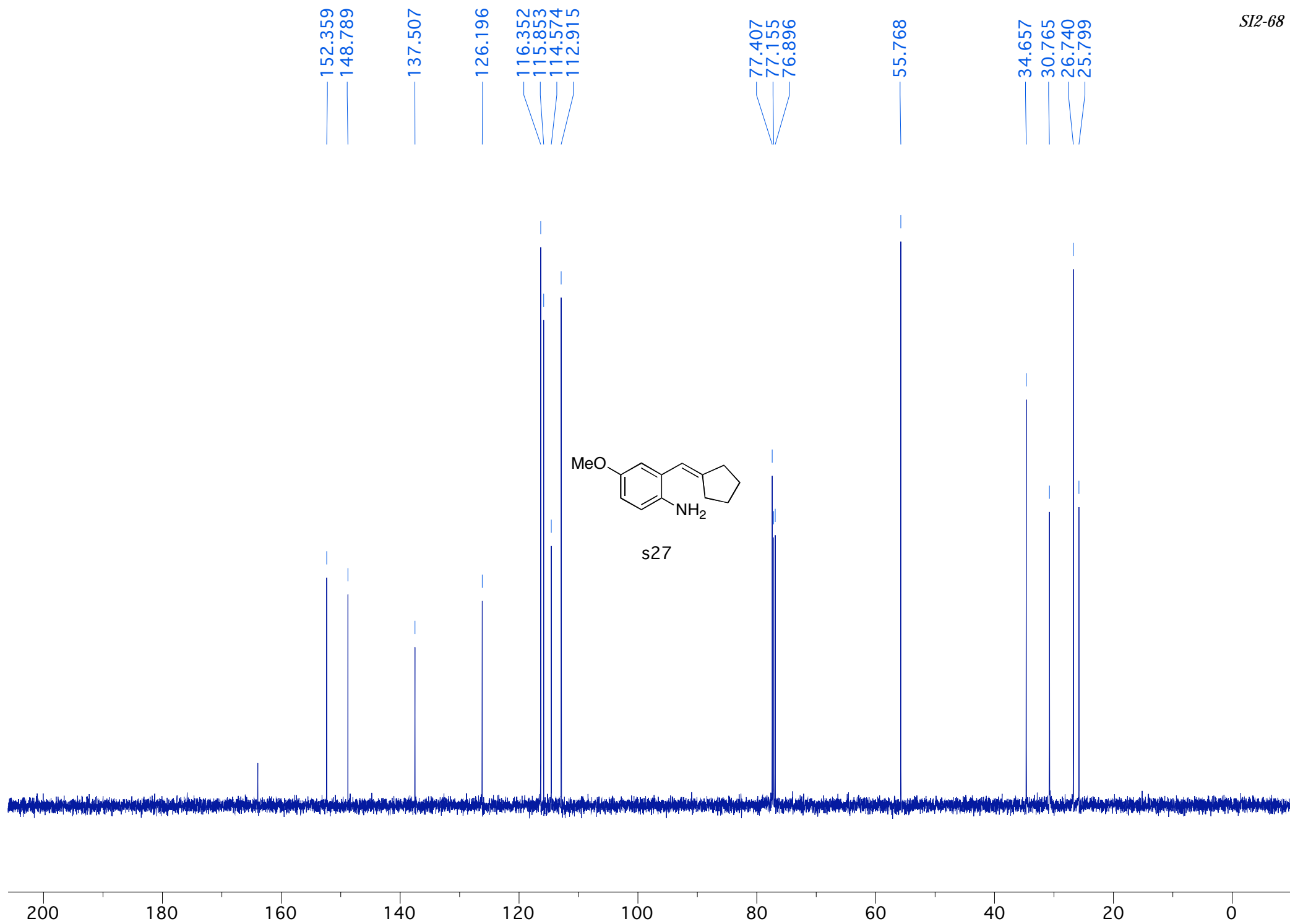


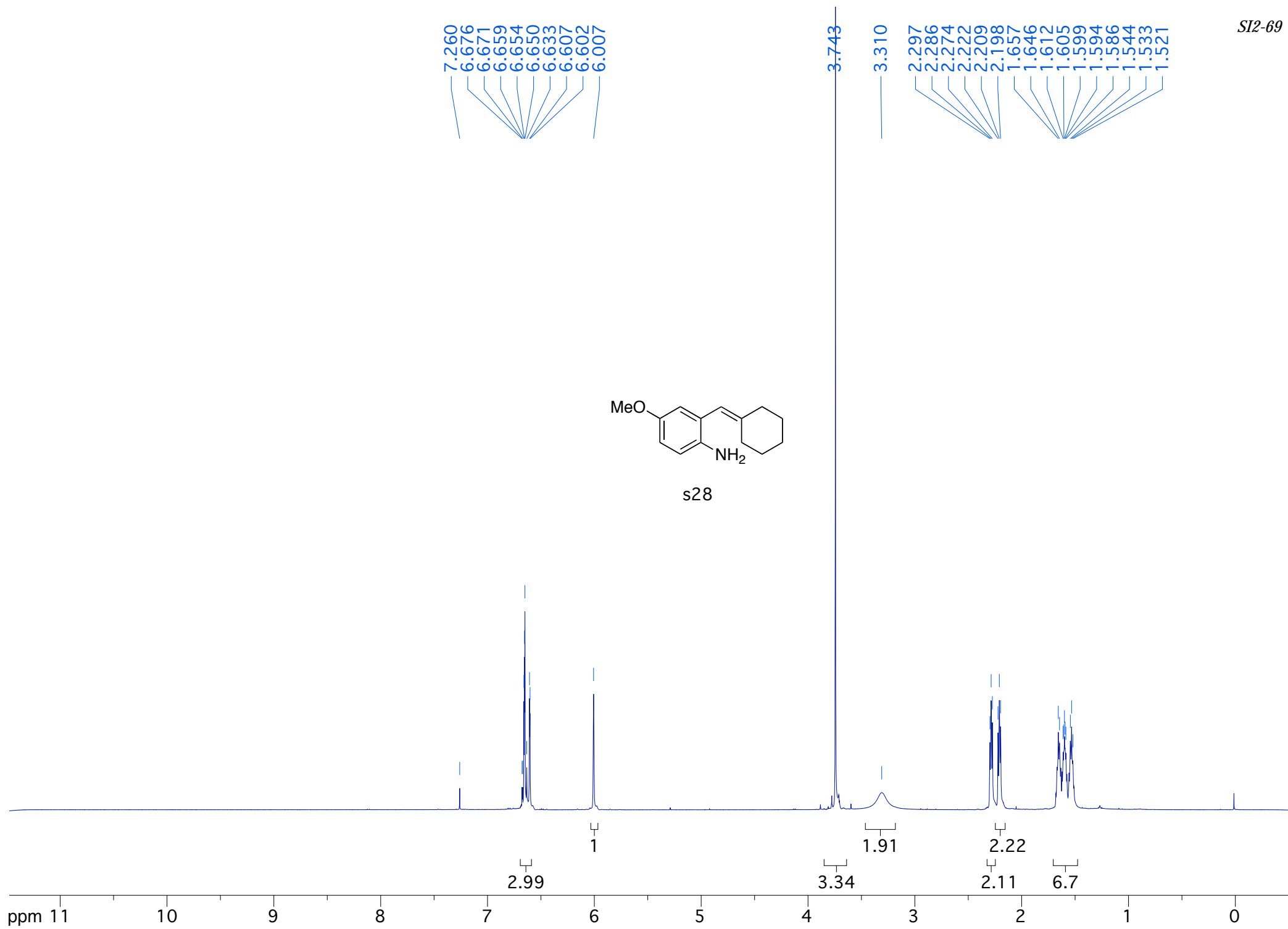
s26



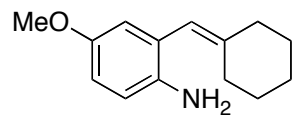




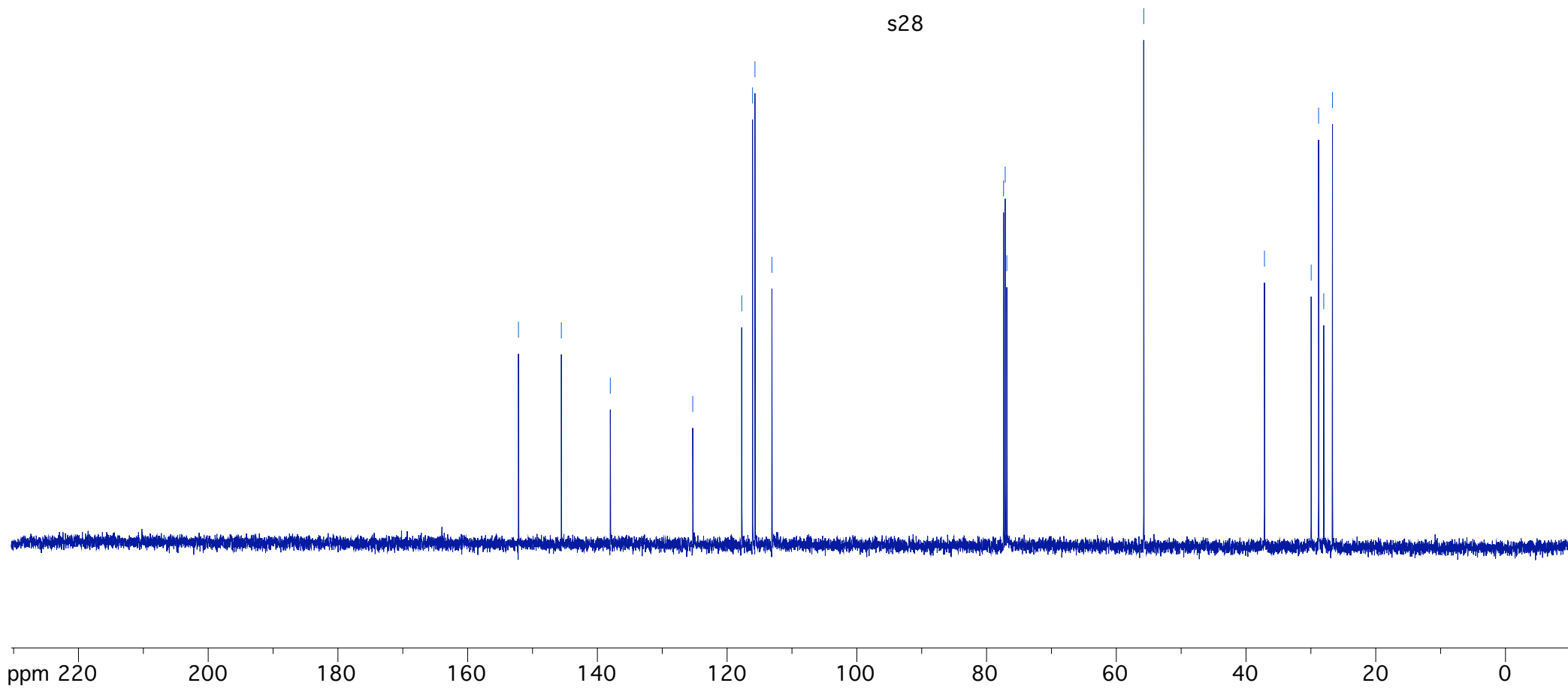




152.167
145.556
138.006
125.298
117.745
116.073
115.705
113.092
77.378
77.127
76.873
55.768
37.153
29.954
28.811
28.014
26.666



s28

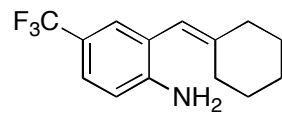


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7.302
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7.297
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7.260
6.704
6.688

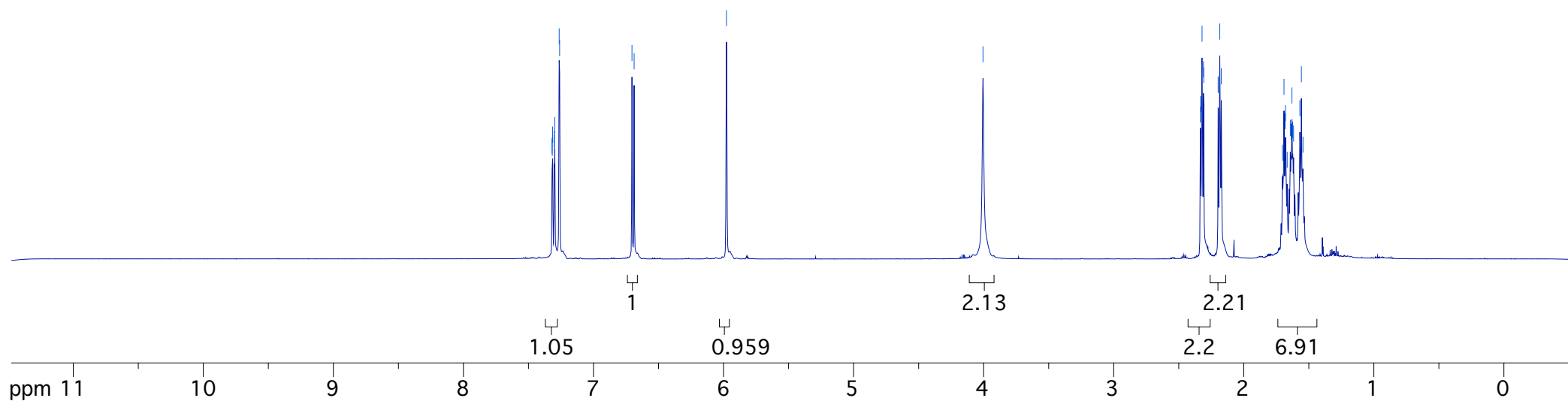
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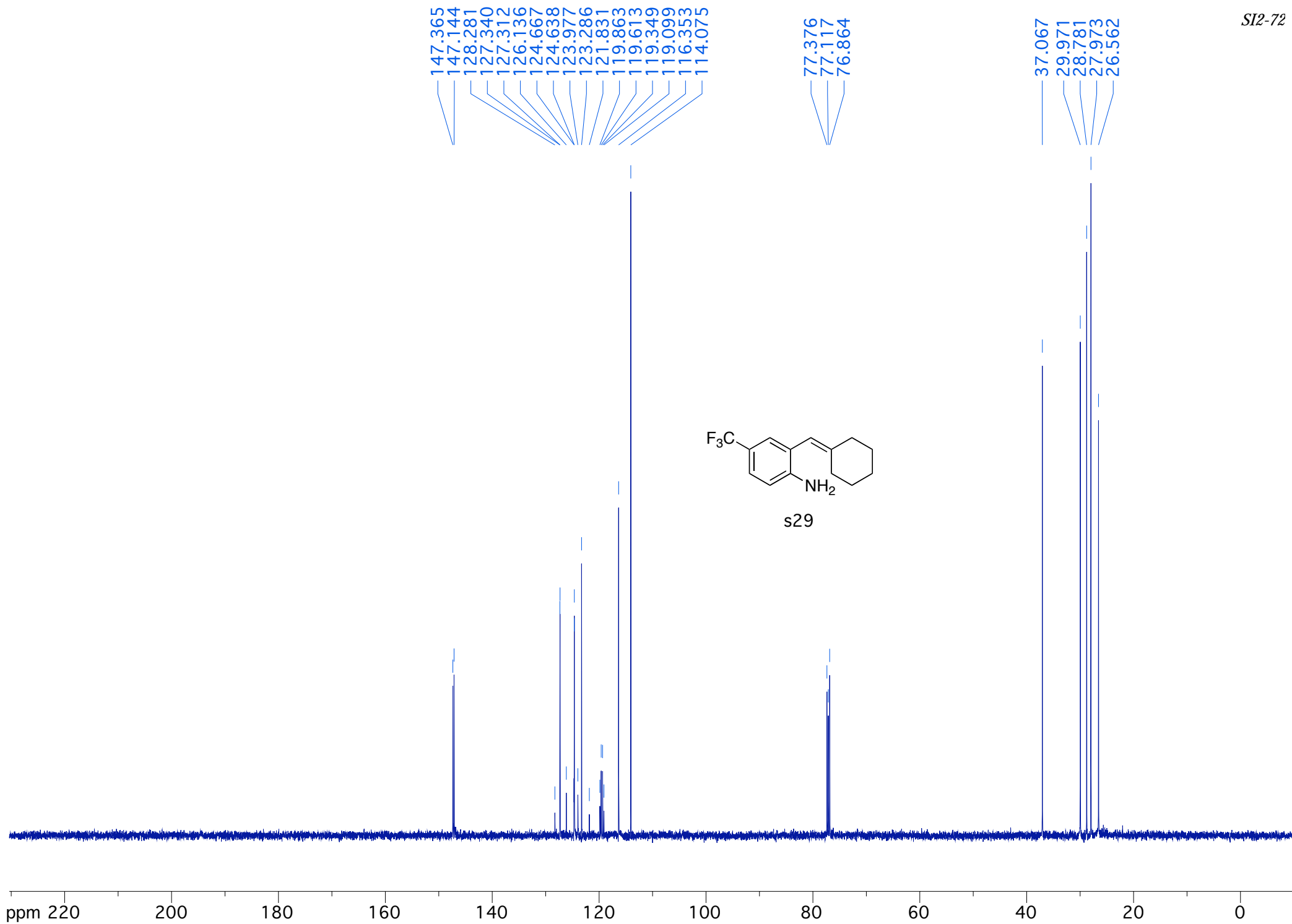
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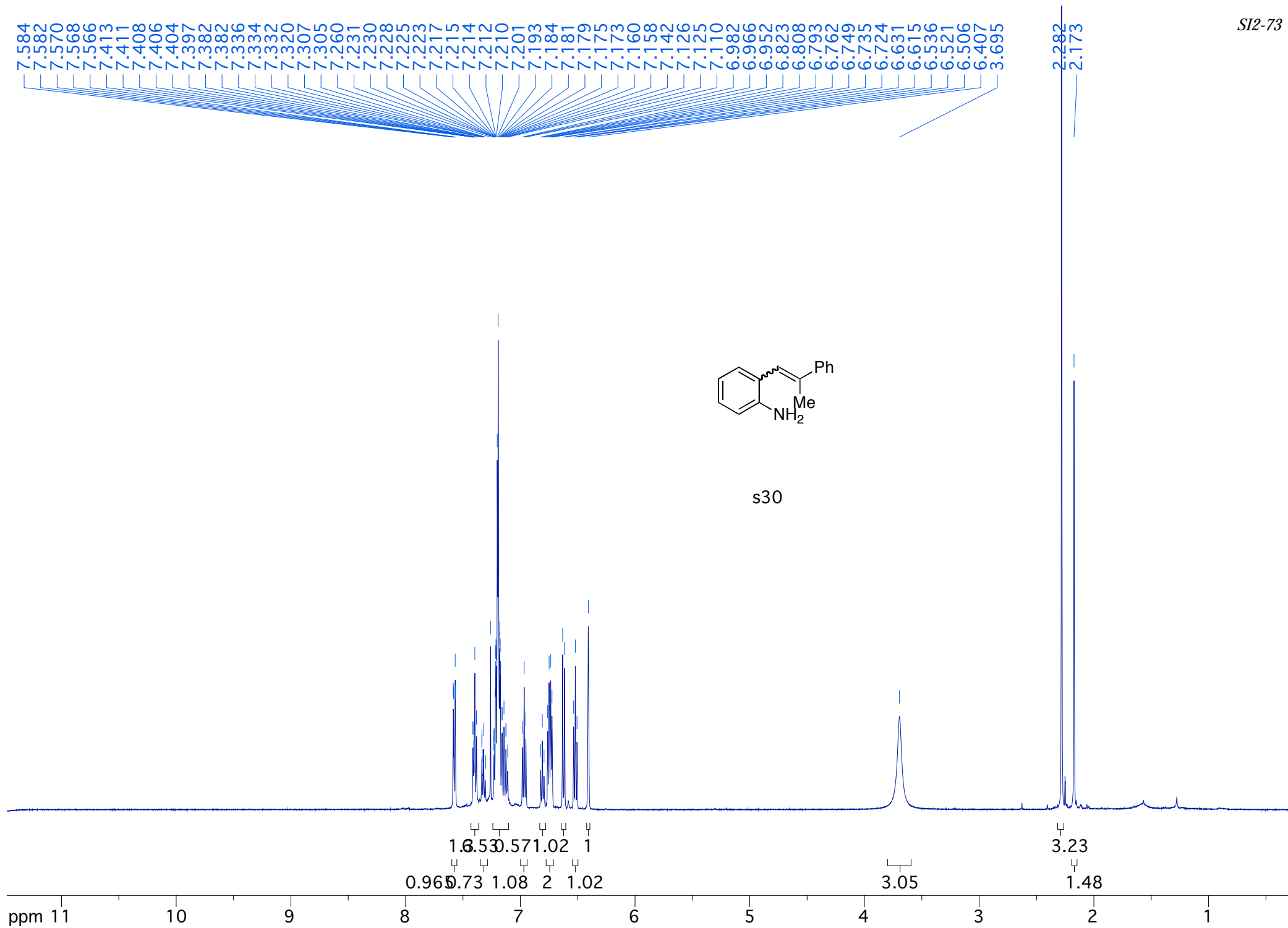
2.334
2.332
2.321
2.310
2.308
2.197
2.196
2.184
2.173
1.703
1.691
1.682
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1.636
1.630
1.624
1.617
1.569
1.557
1.545

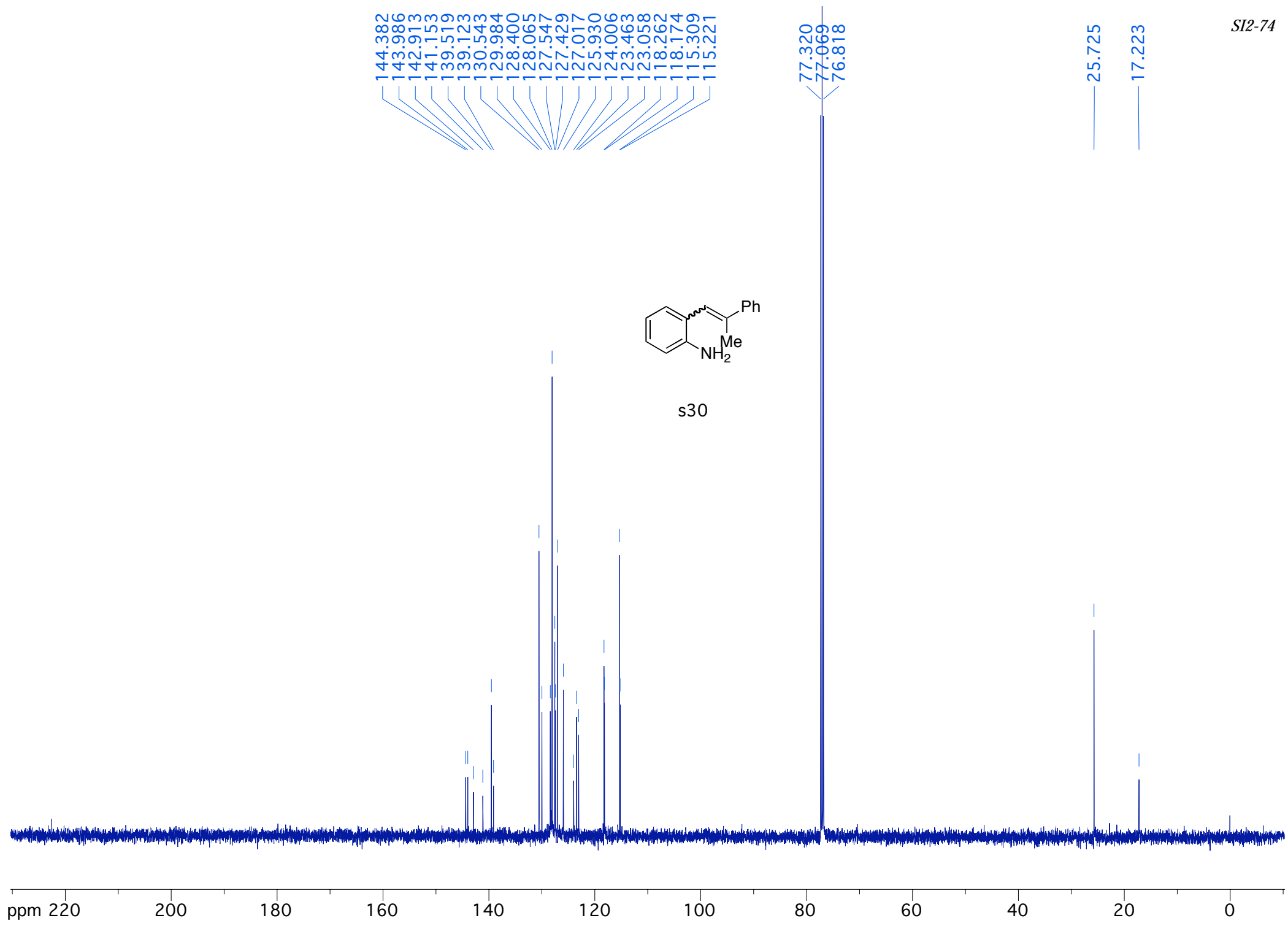


s29



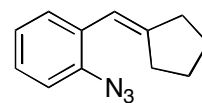




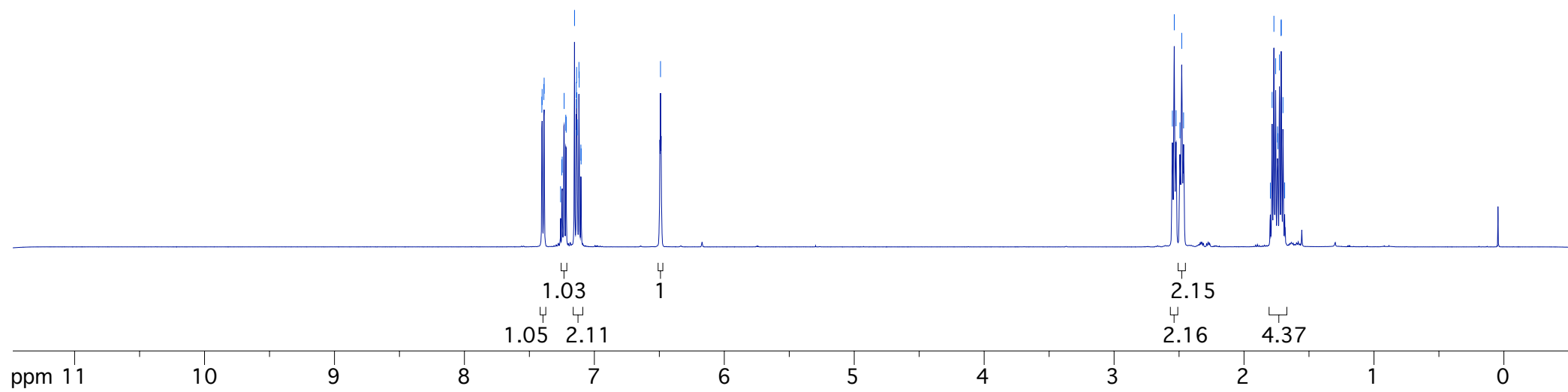


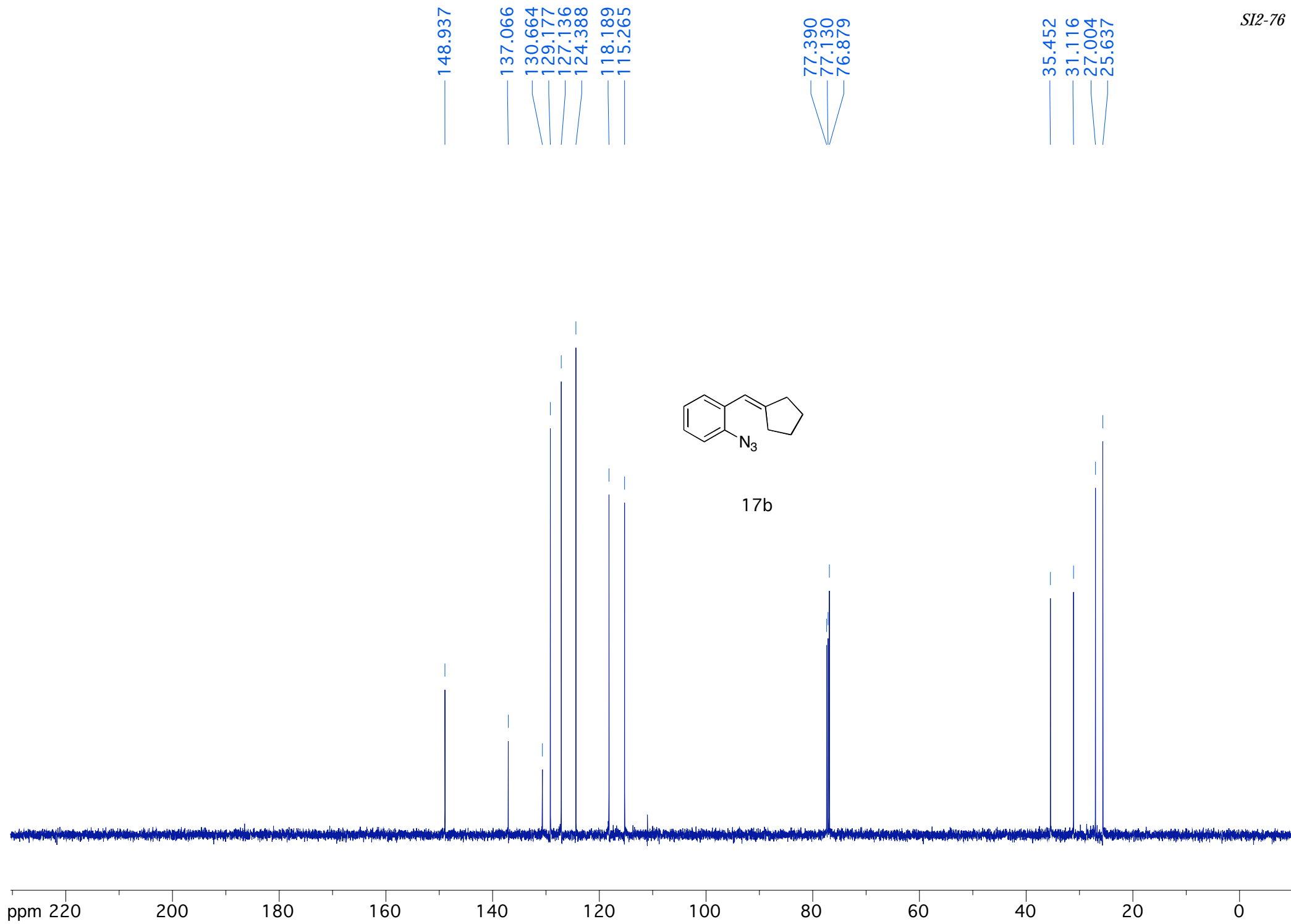
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7.250
7.247
7.233
7.220
7.217
7.153
7.139
7.136
7.134
7.132
7.119
7.117
7.104
7.102
6.491

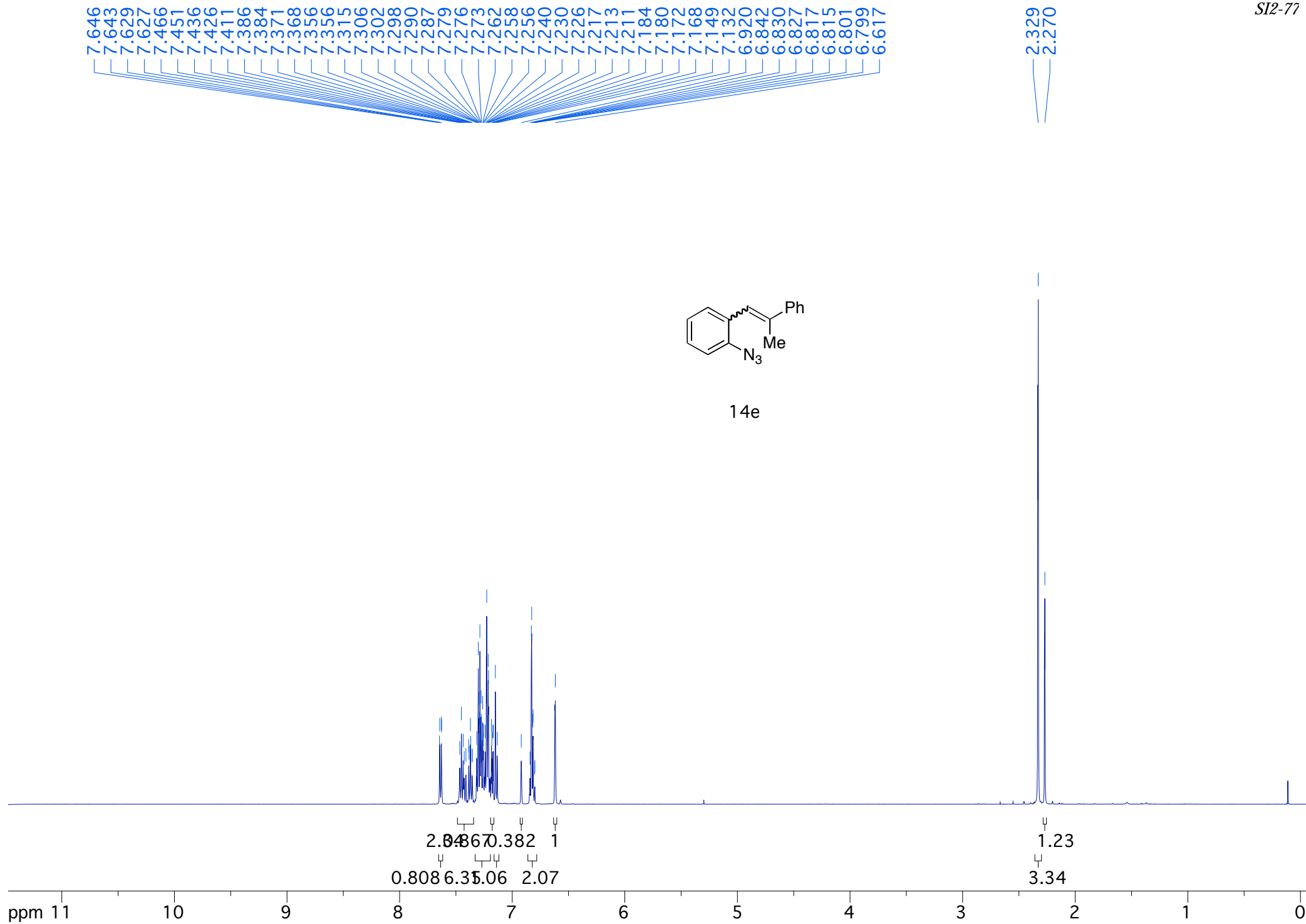
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1.714
1.700
1.687

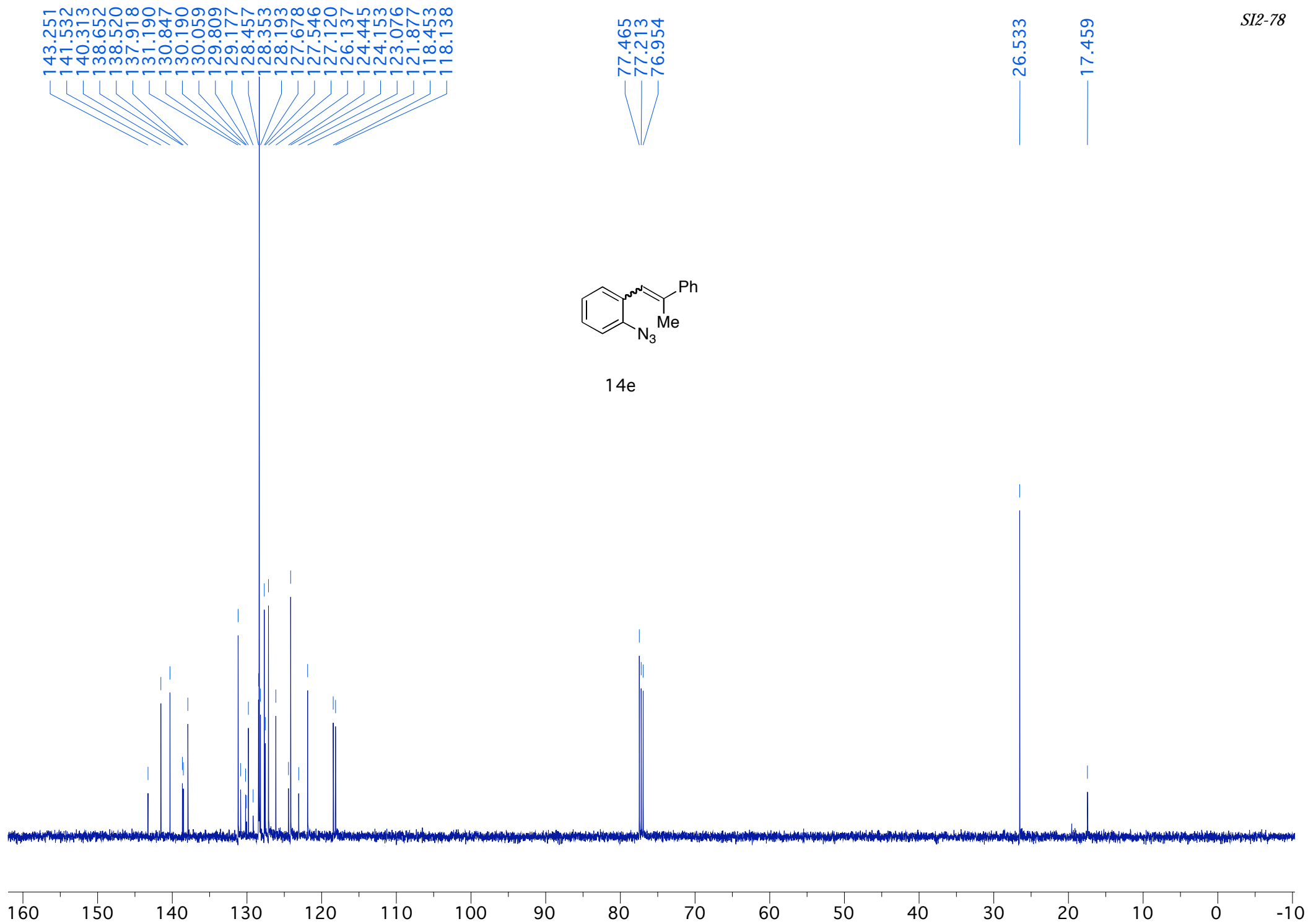


17b



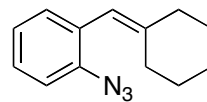




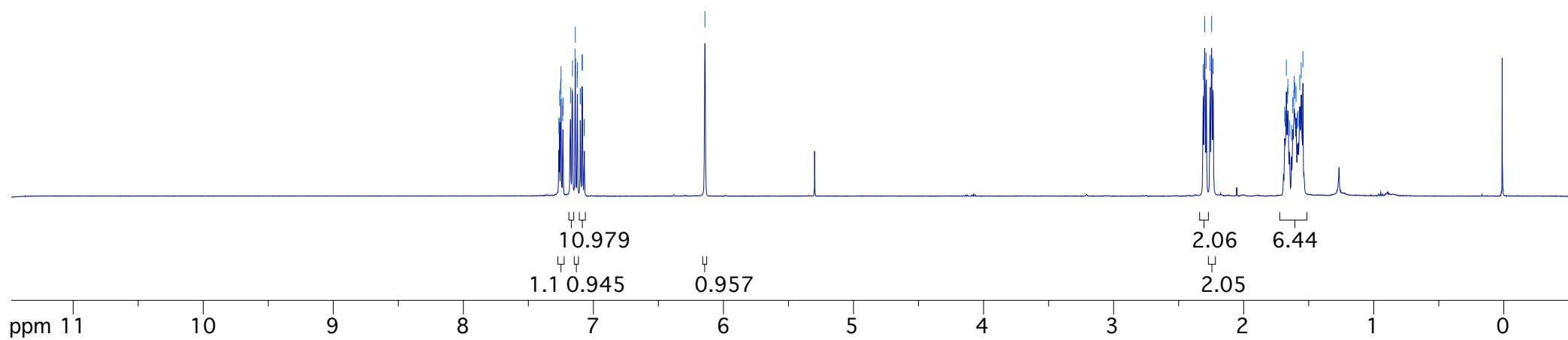


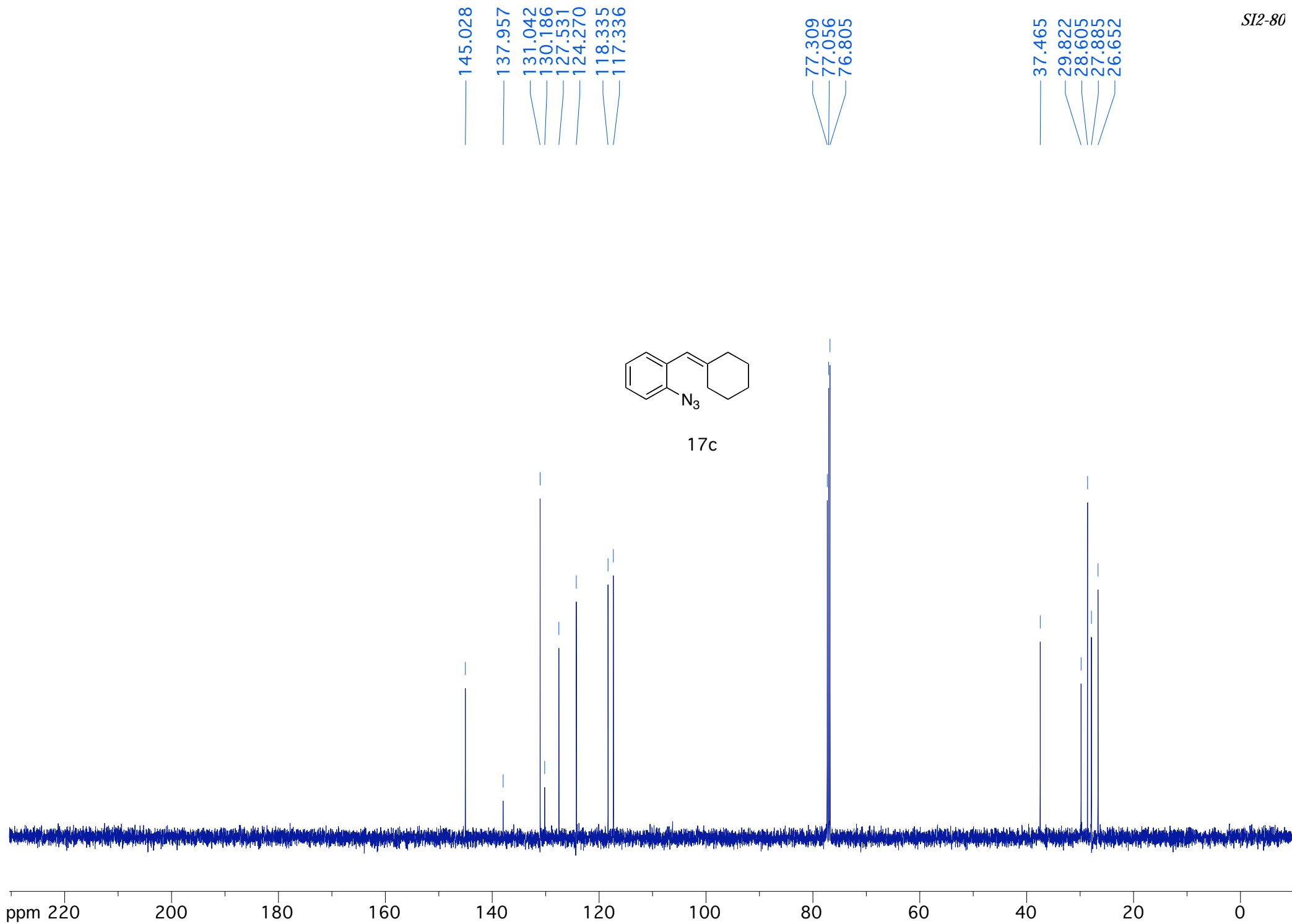
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7.252
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7.234
7.233
7.176
7.161
7.141
7.139
7.125
7.123
7.101
7.099
7.087
7.084
7.071
7.070
6.142

2.311
2.300
2.289
2.258
2.247
2.236
1.684
1.681
1.672
1.663
1.660
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1.581
1.569
1.558
1.545



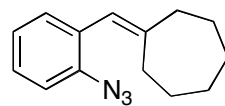
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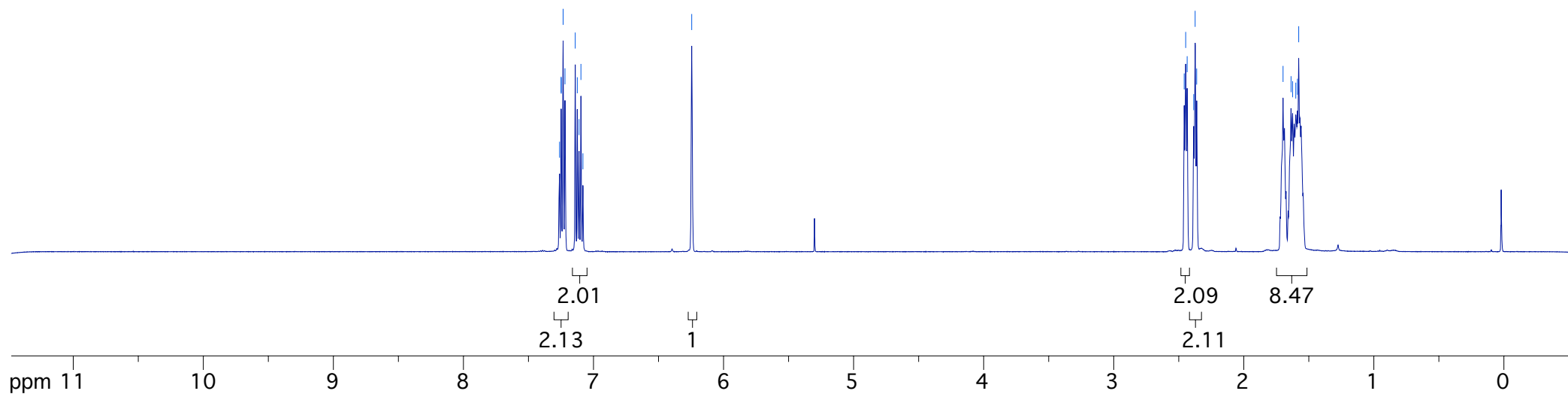


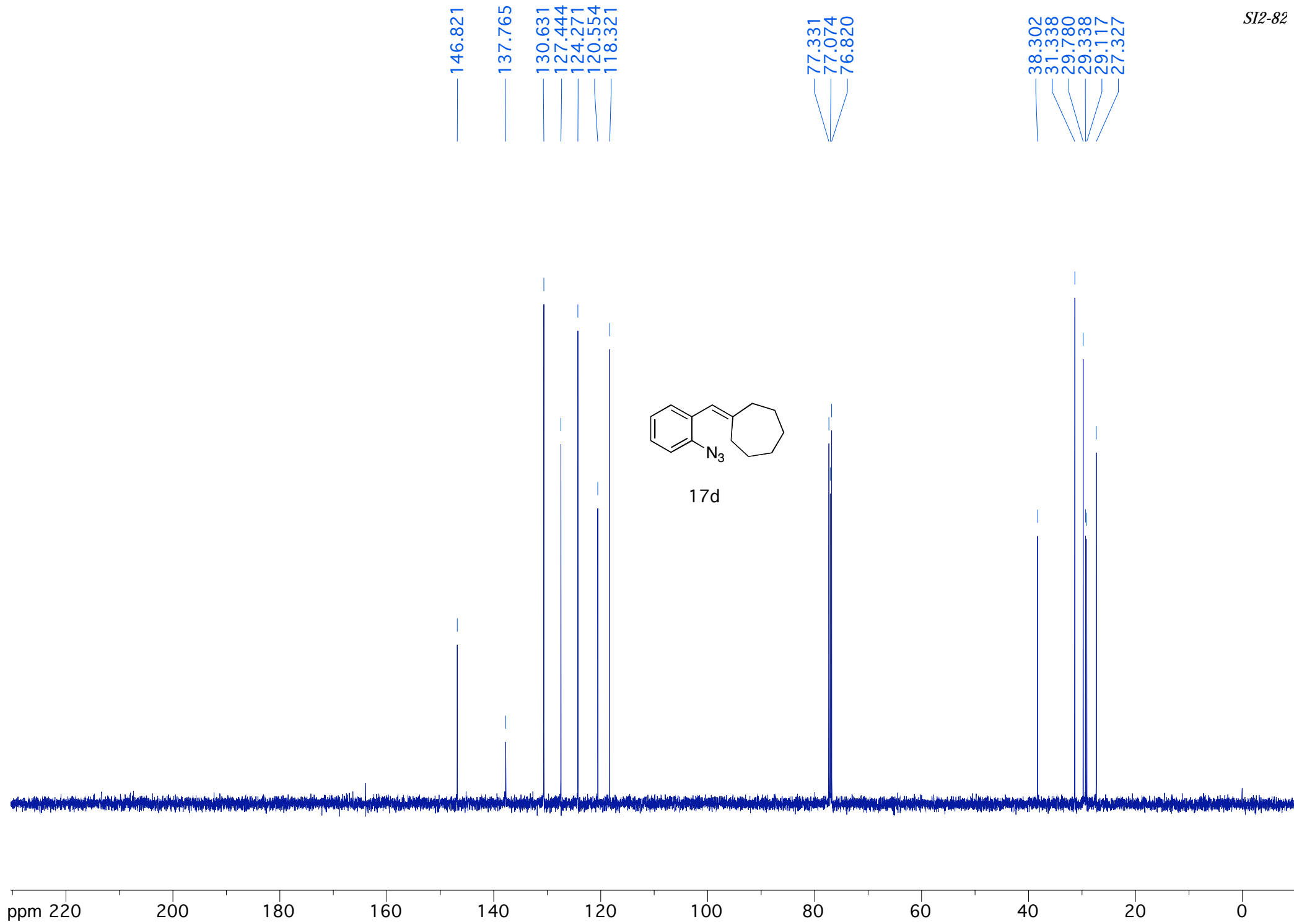
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7.248
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7.125
7.111
7.097
7.081
6.245

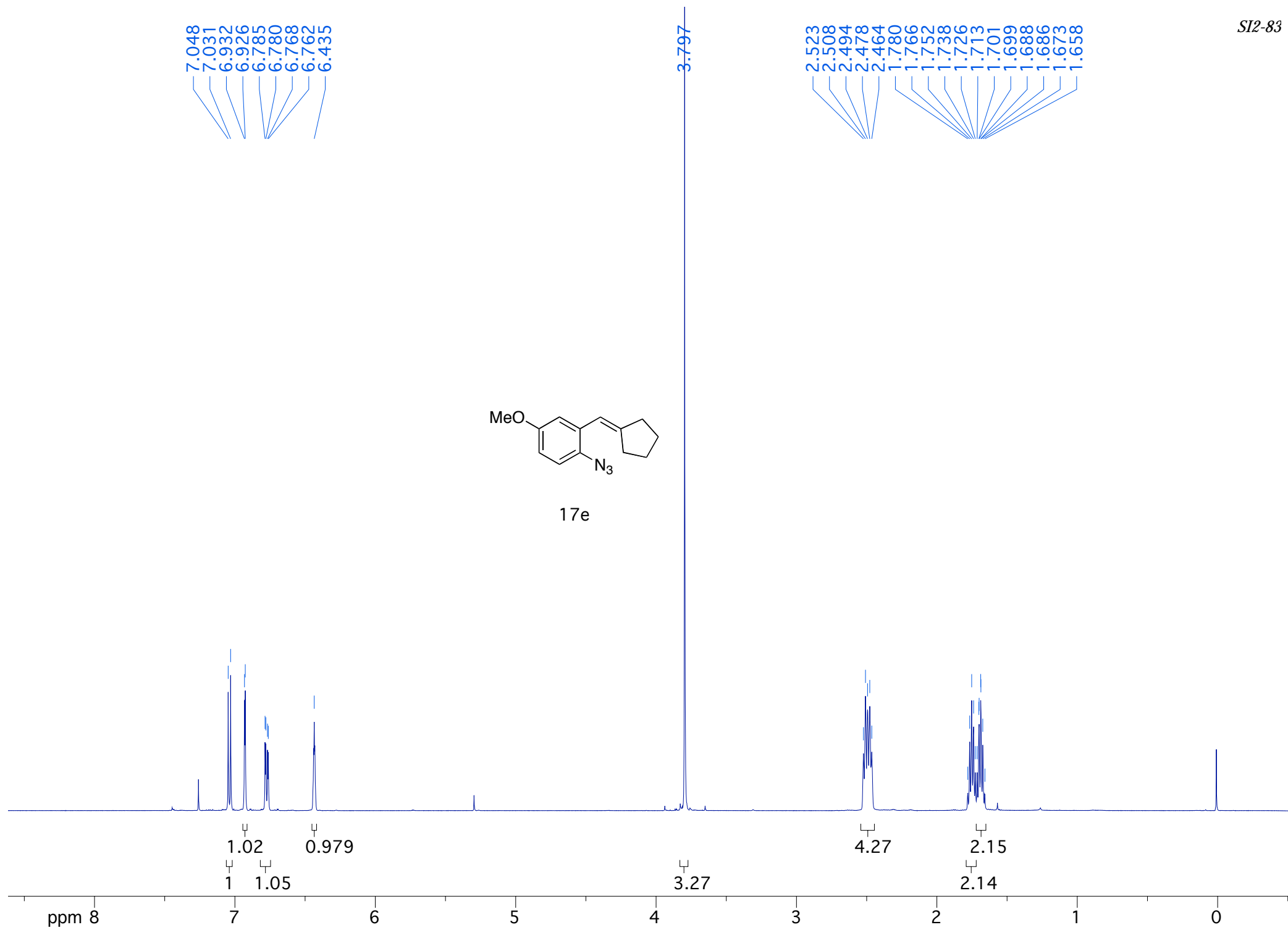
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1.587
1.578

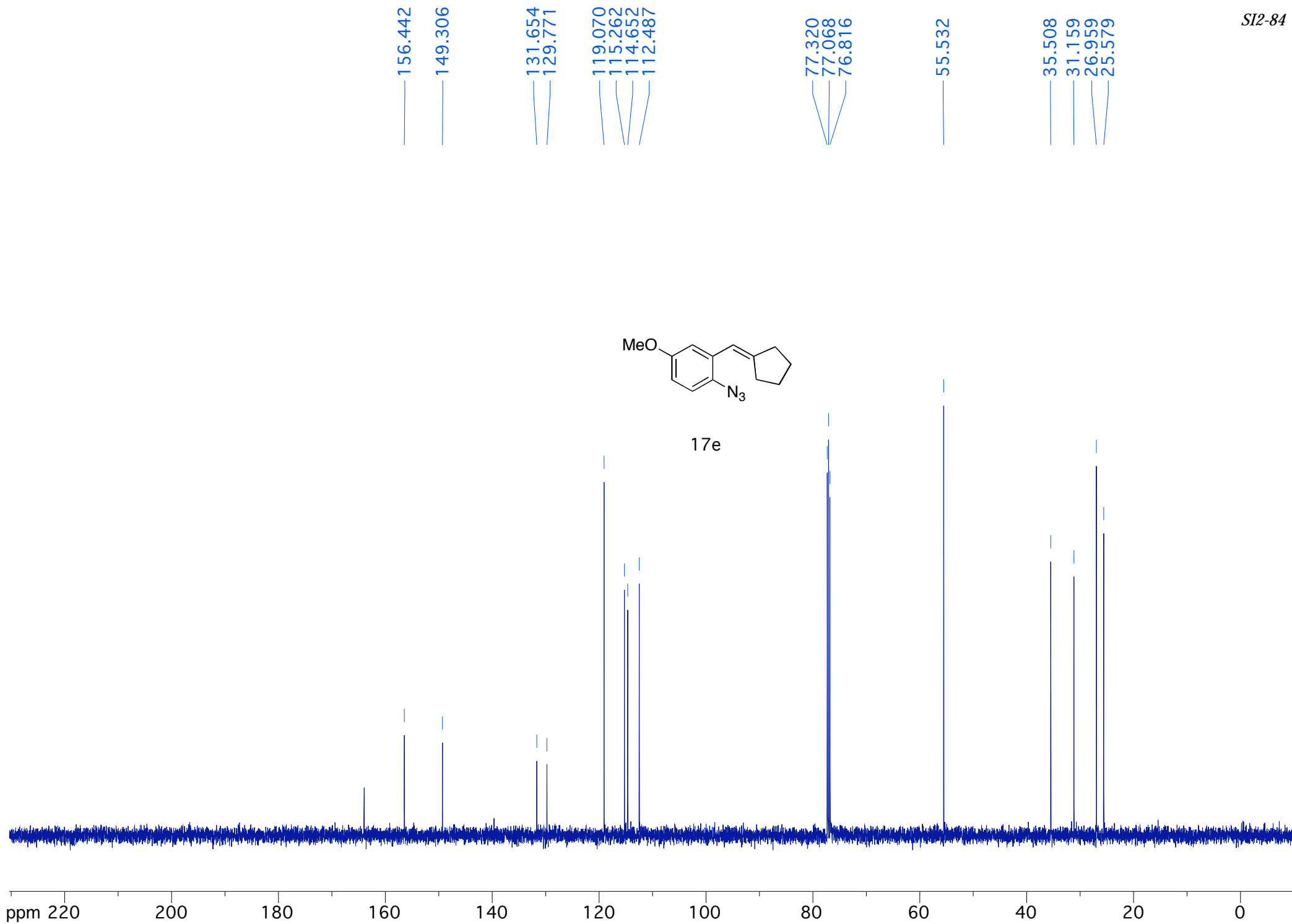


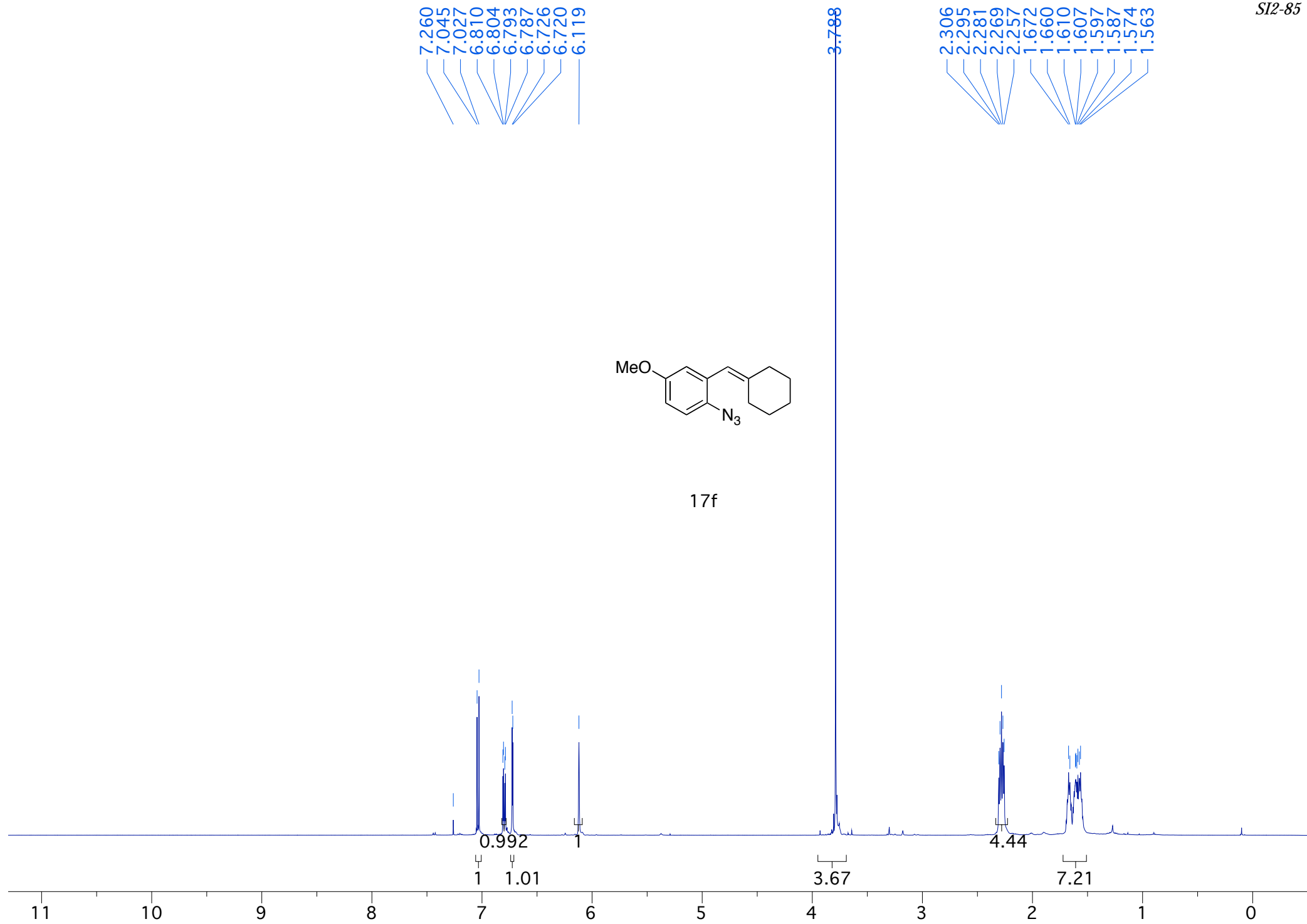
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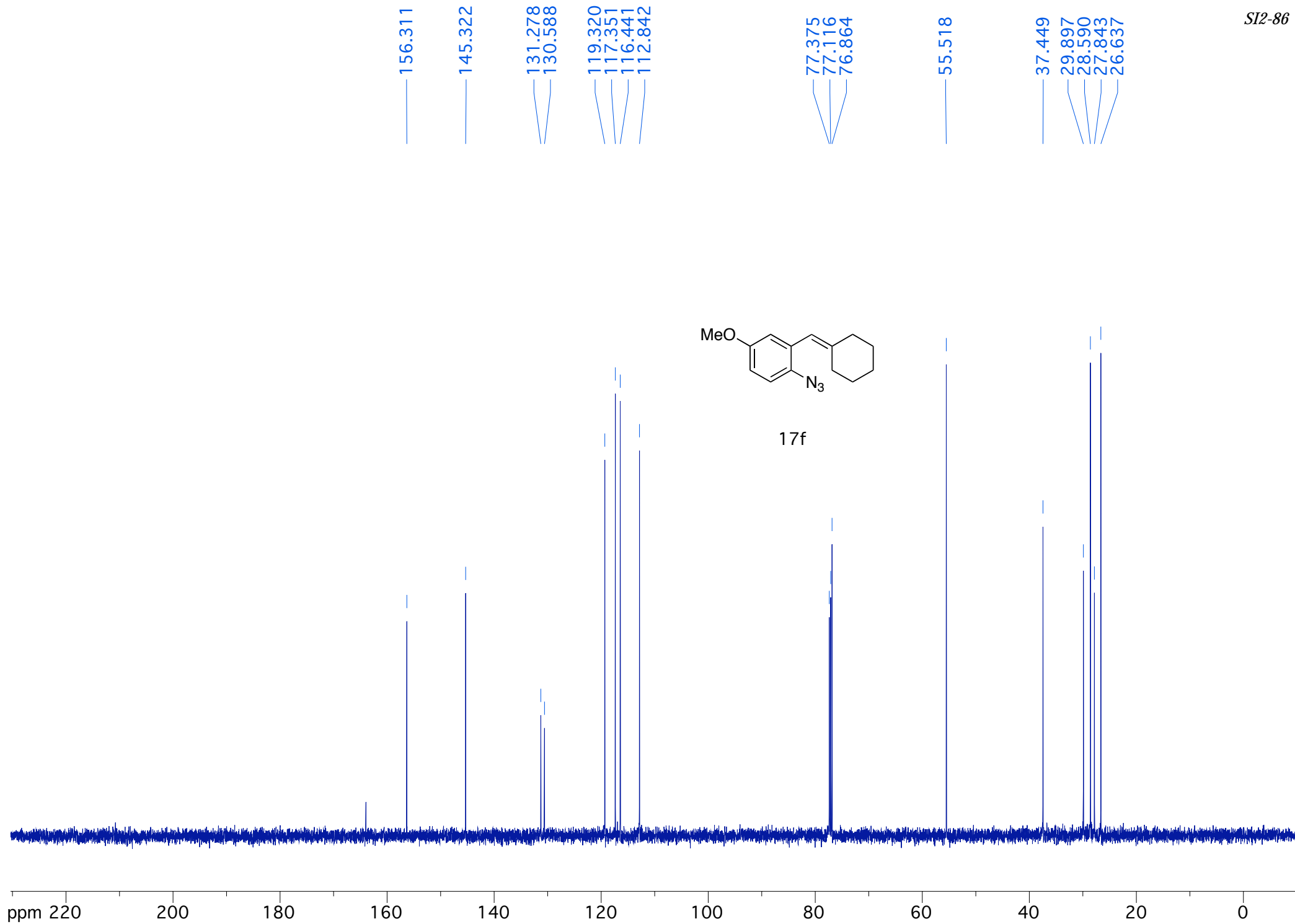








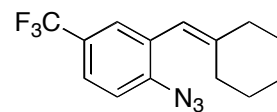




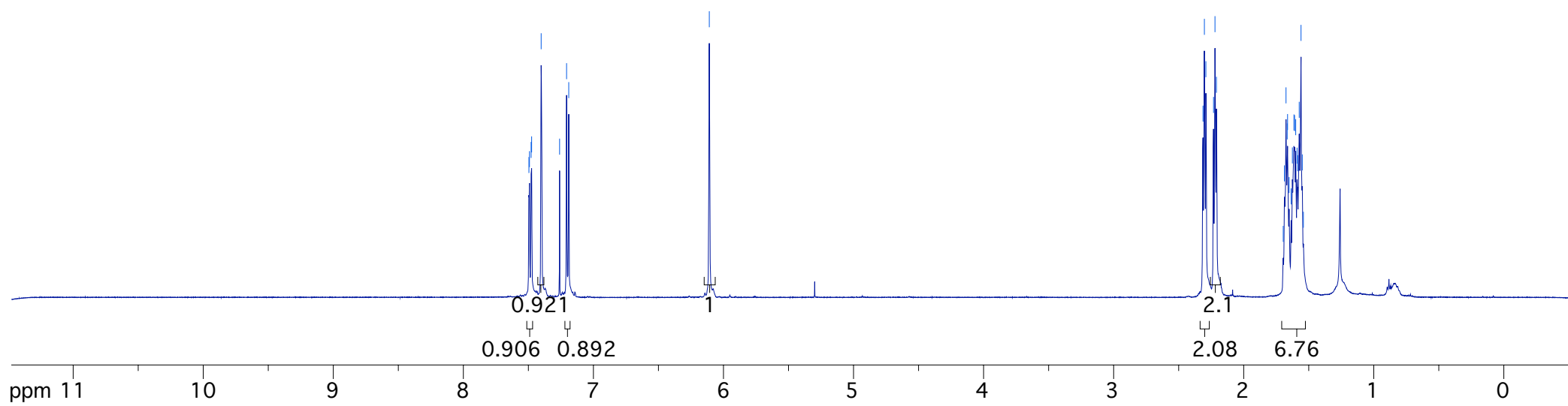
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7.190

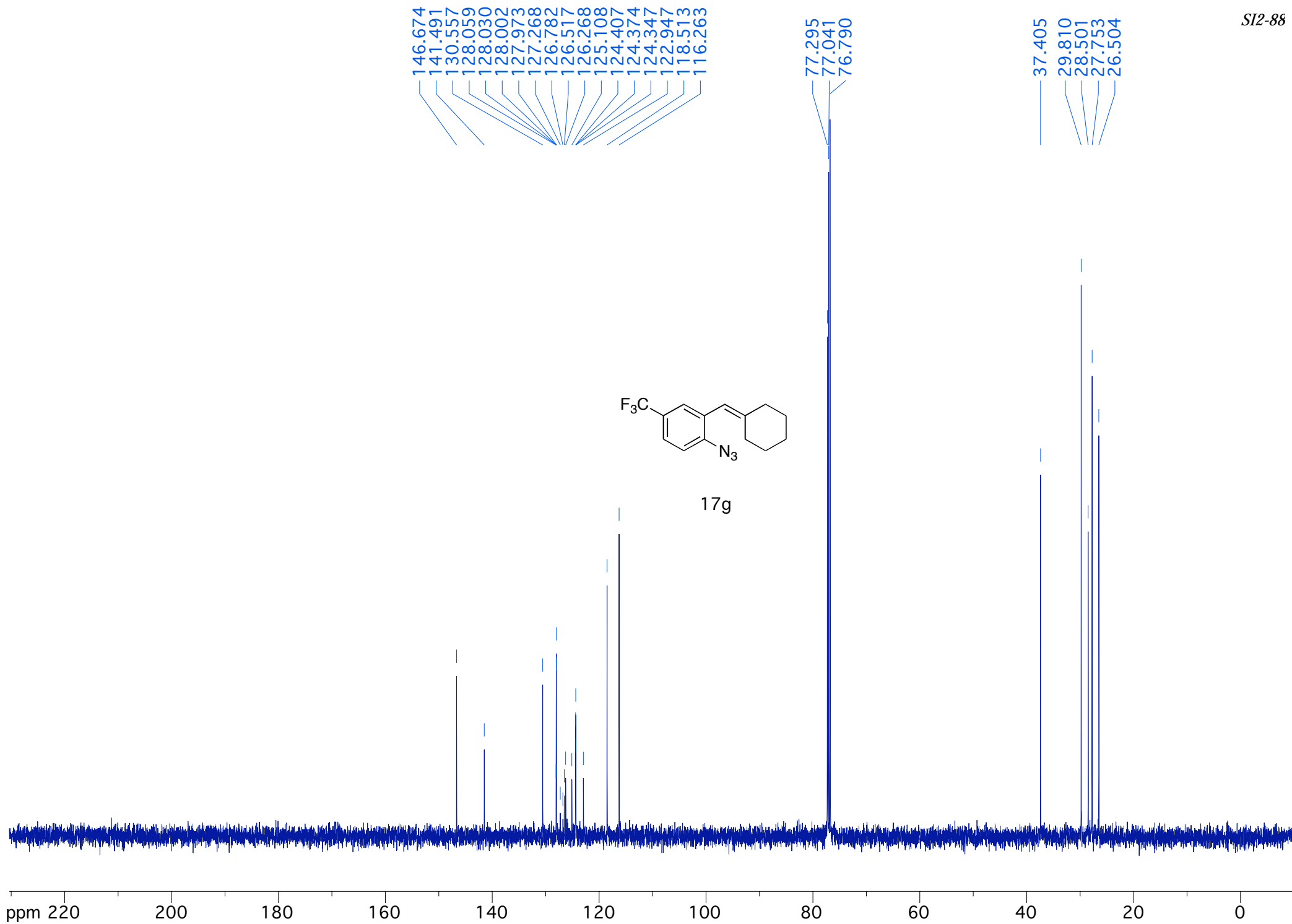
6.109

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1.663
1.651
1.635
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1.609
1.600
1.590
1.586
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1.550
1.541



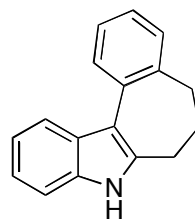
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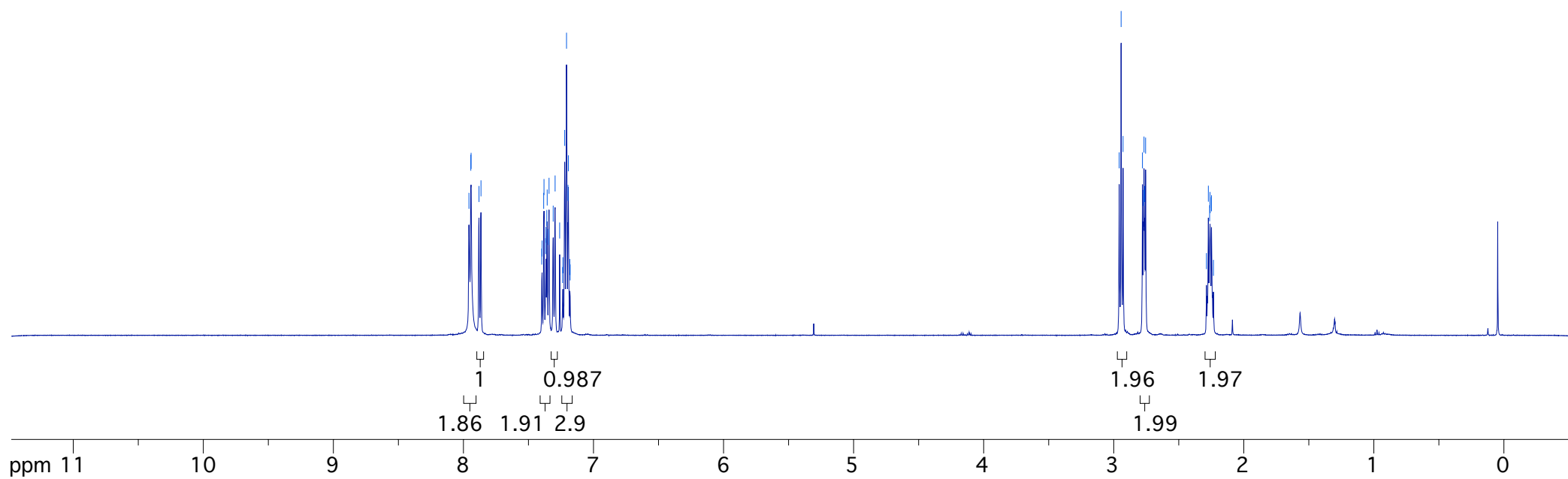


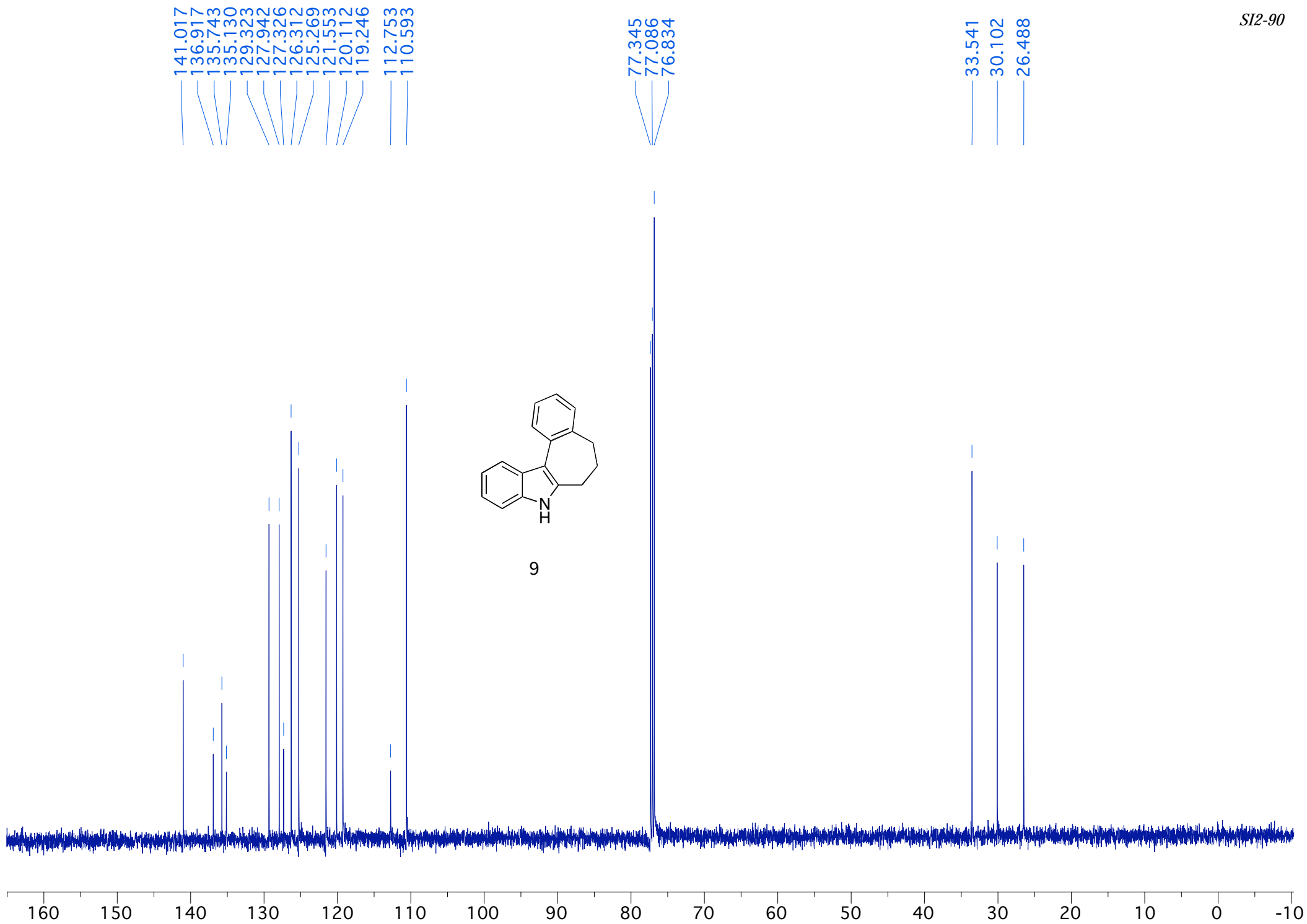
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7.380
7.368
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7.359
7.356
7.346
7.342
7.310
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7.235
7.221
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7.196
7.193
7.182
7.179

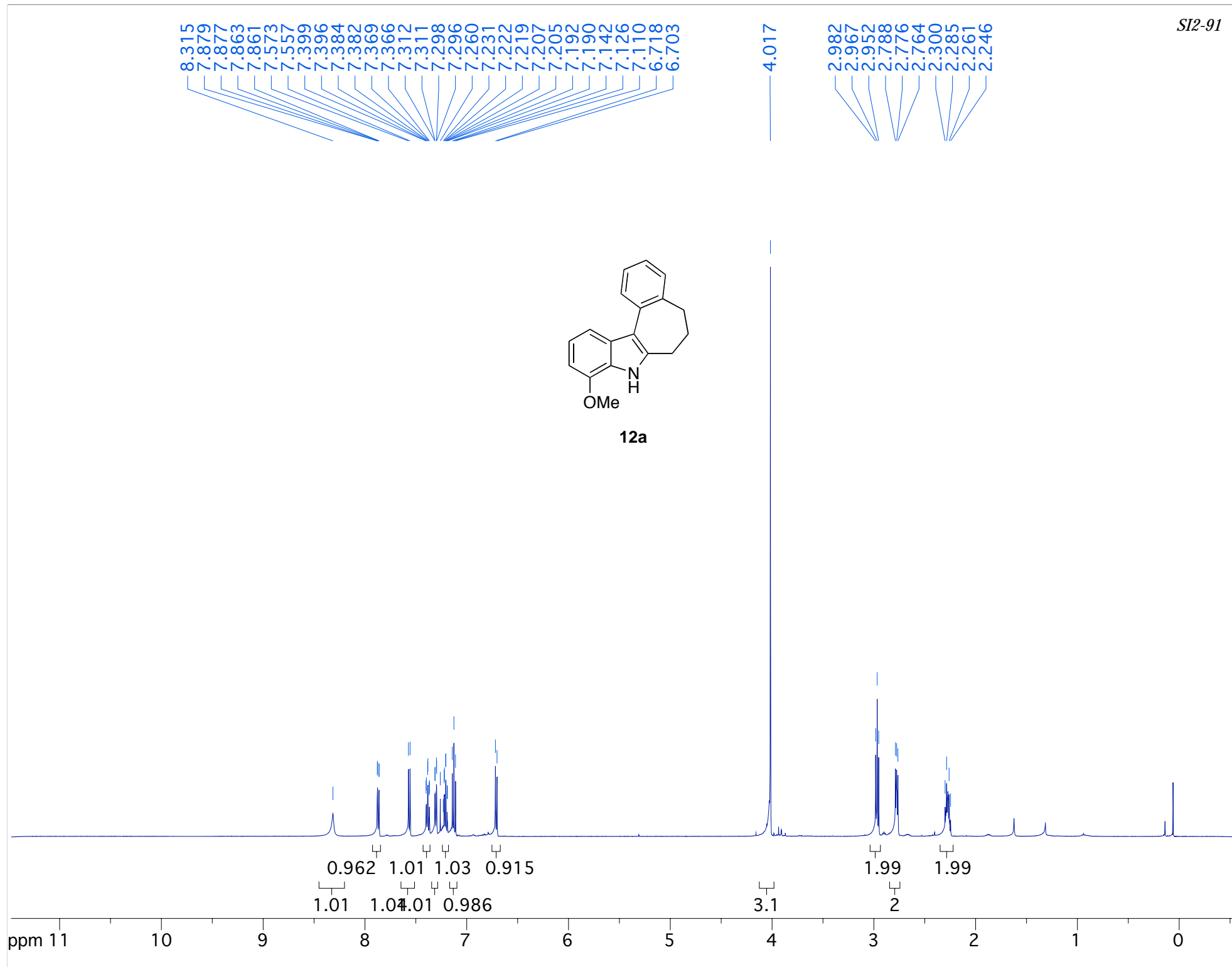
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2.928
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2.258
2.248
2.233

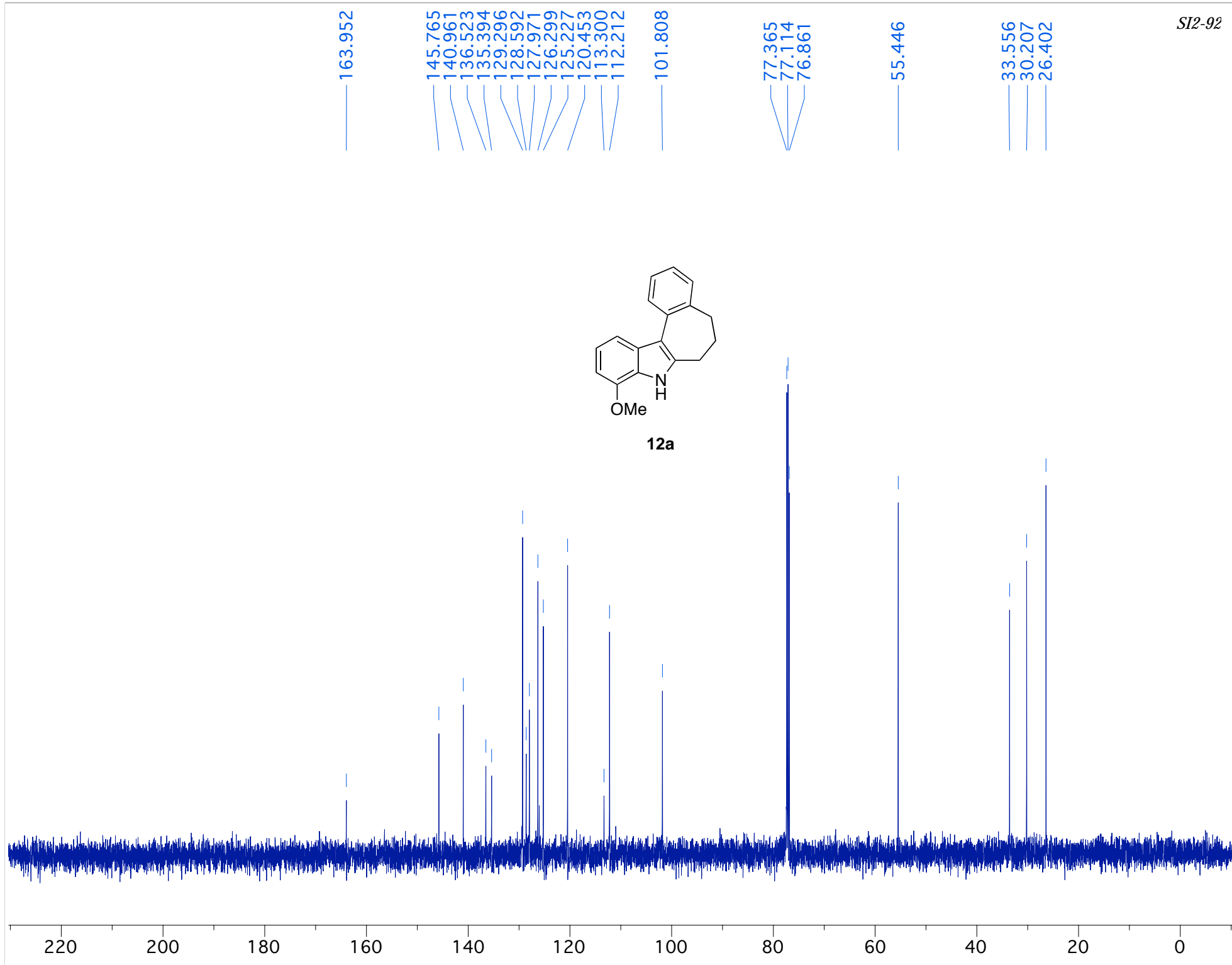


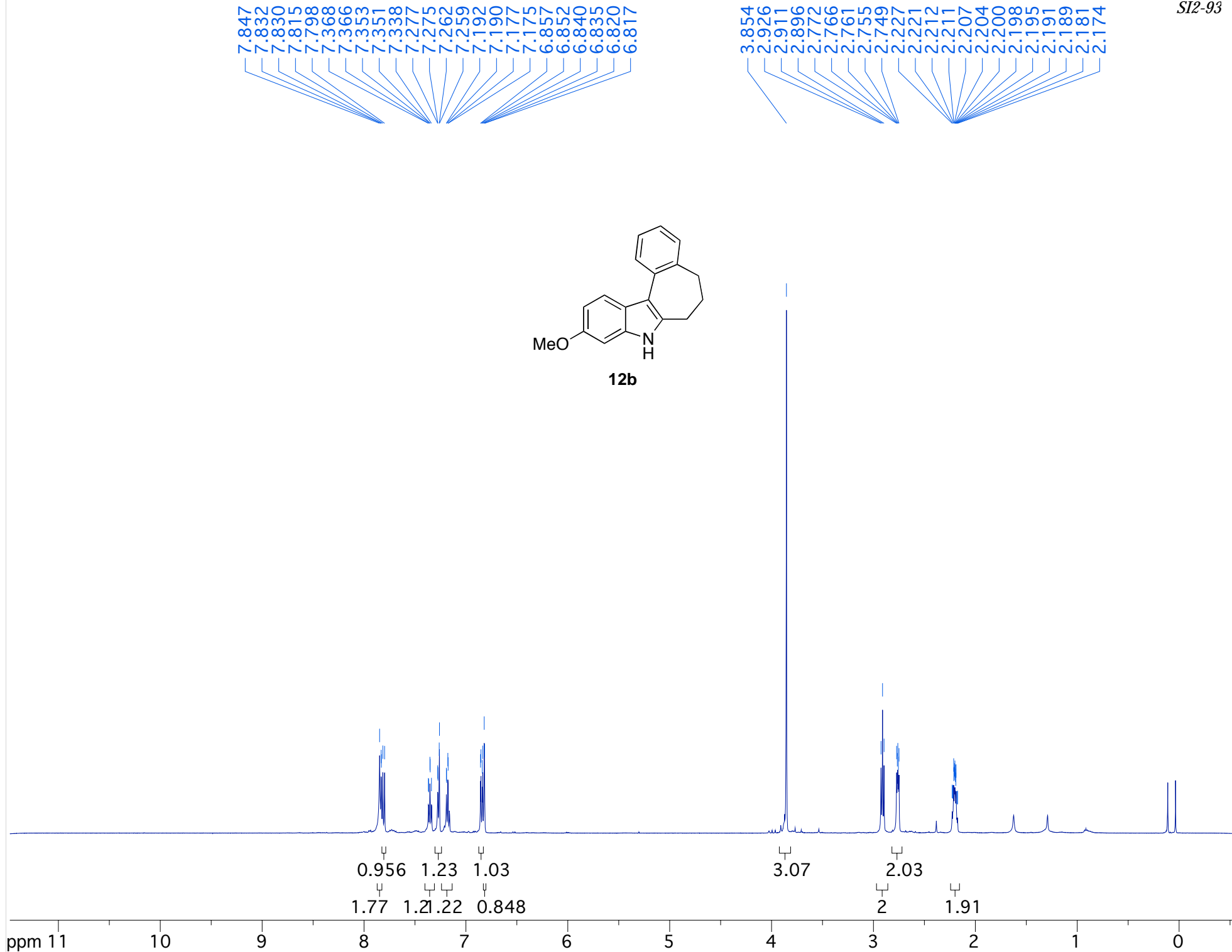
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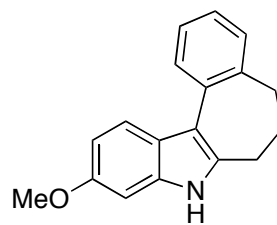




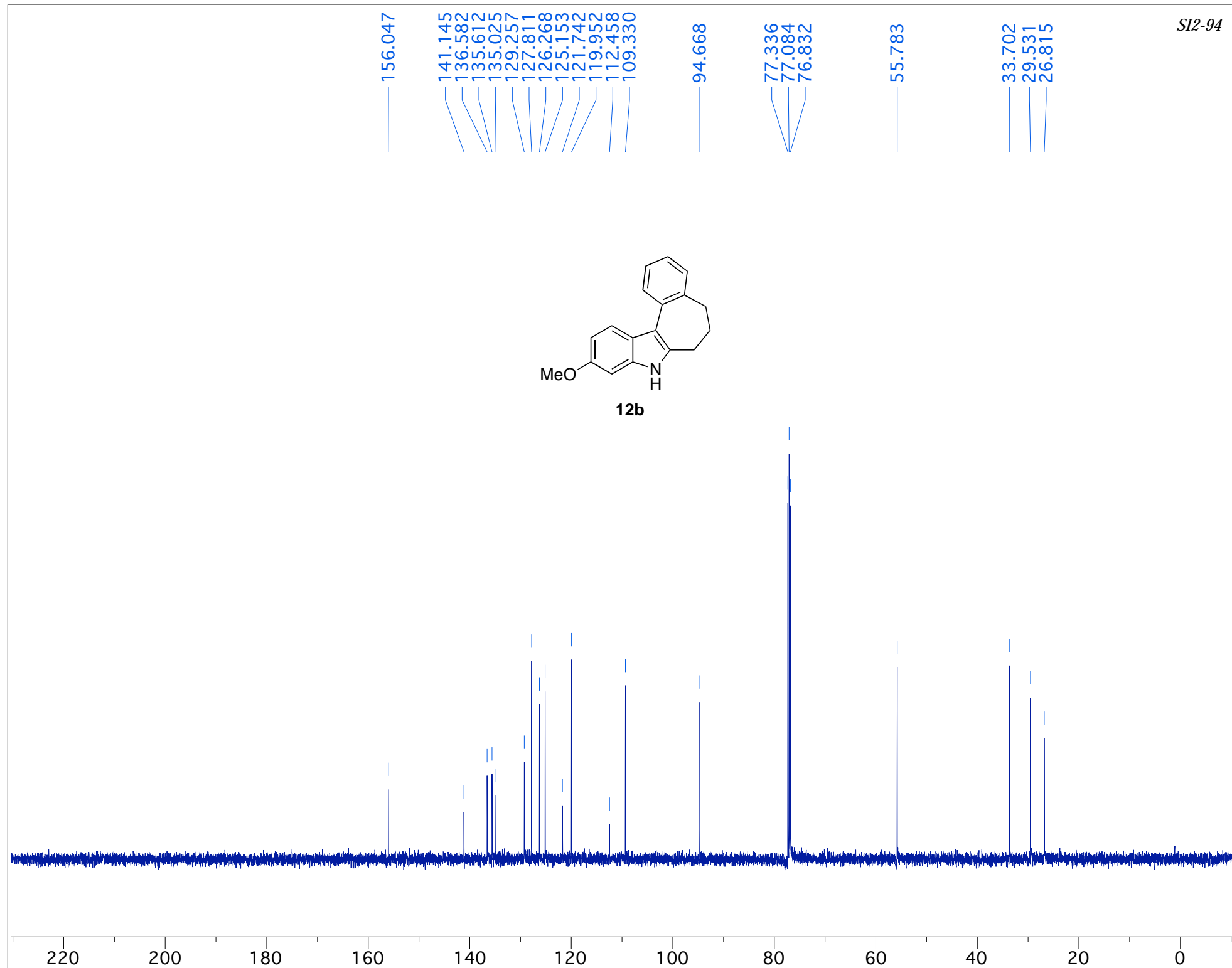




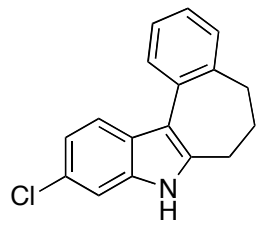




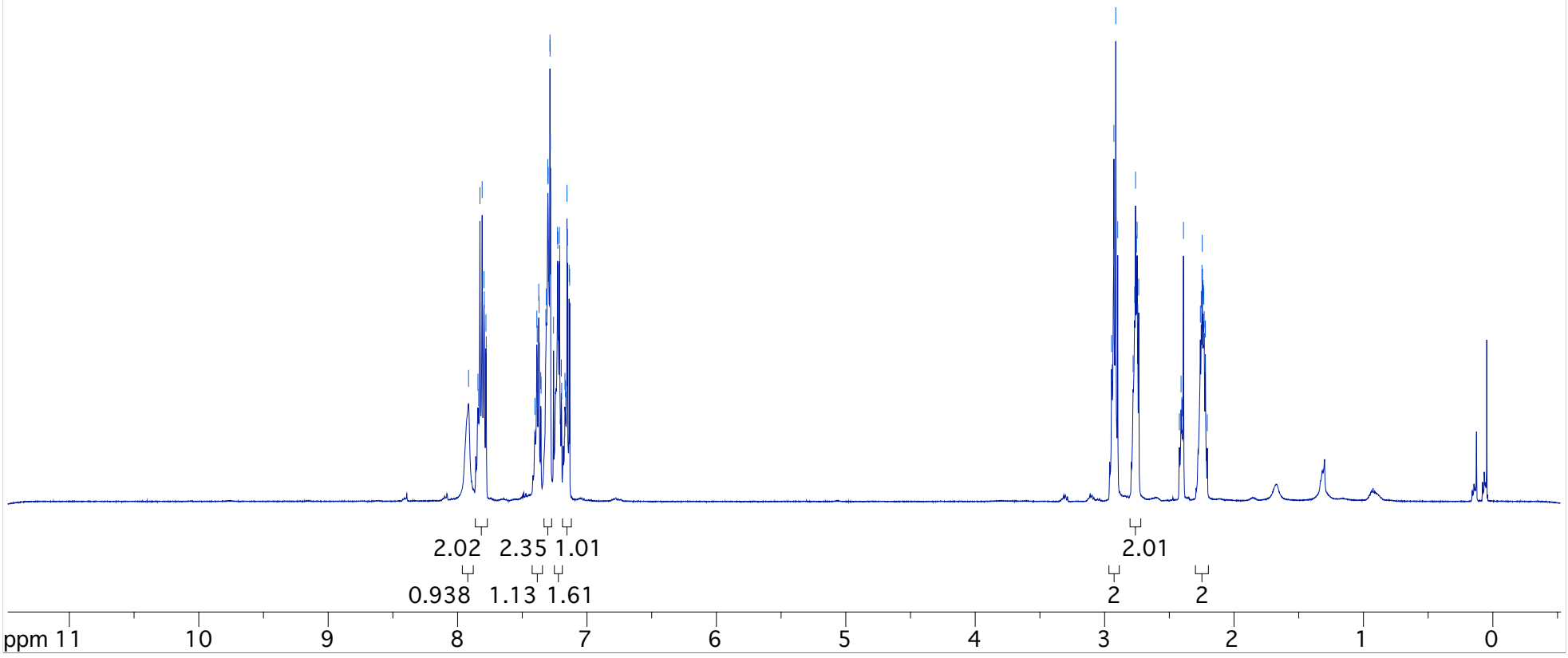
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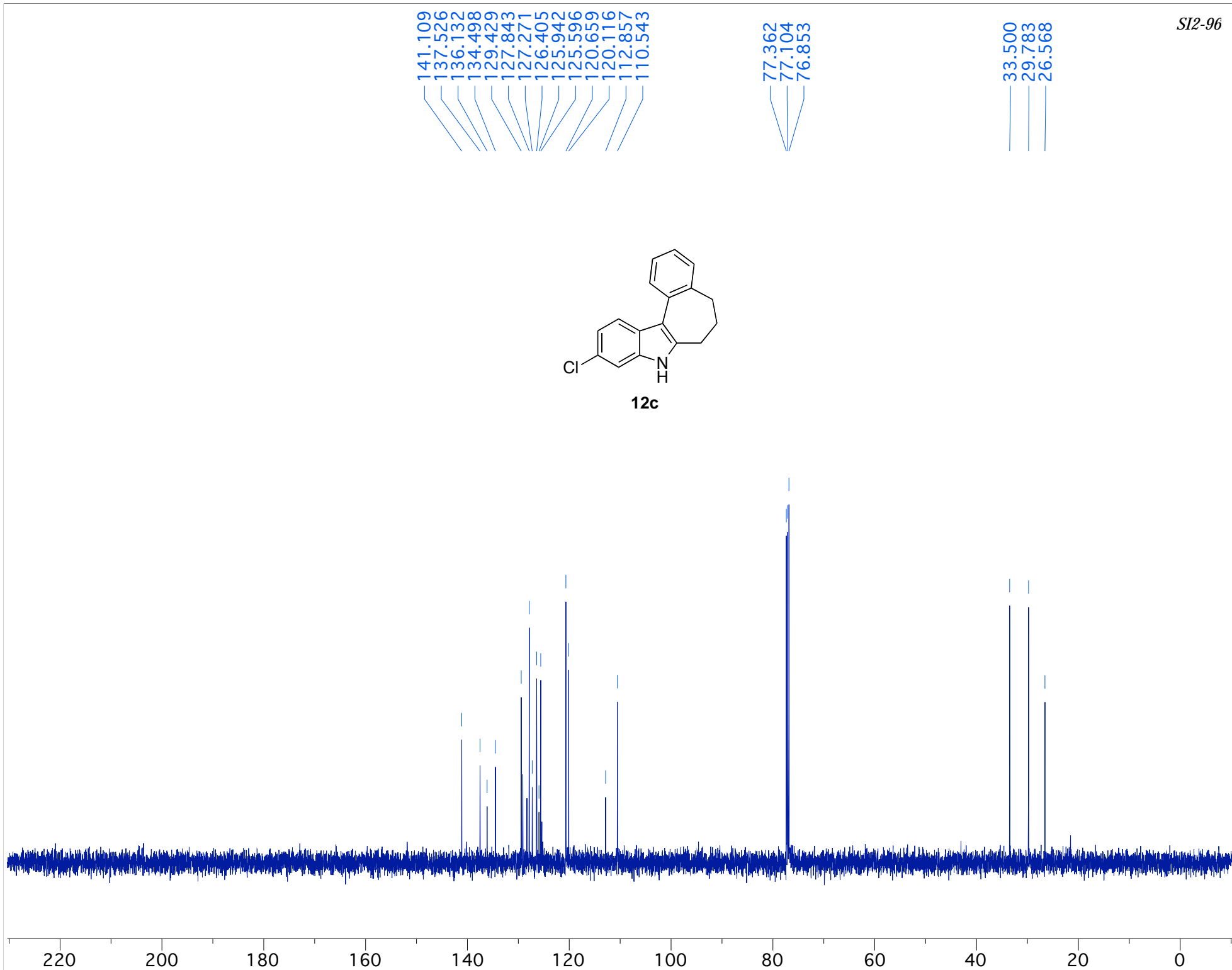
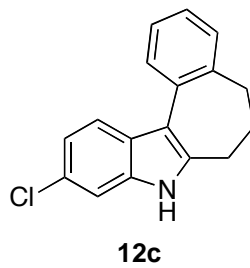


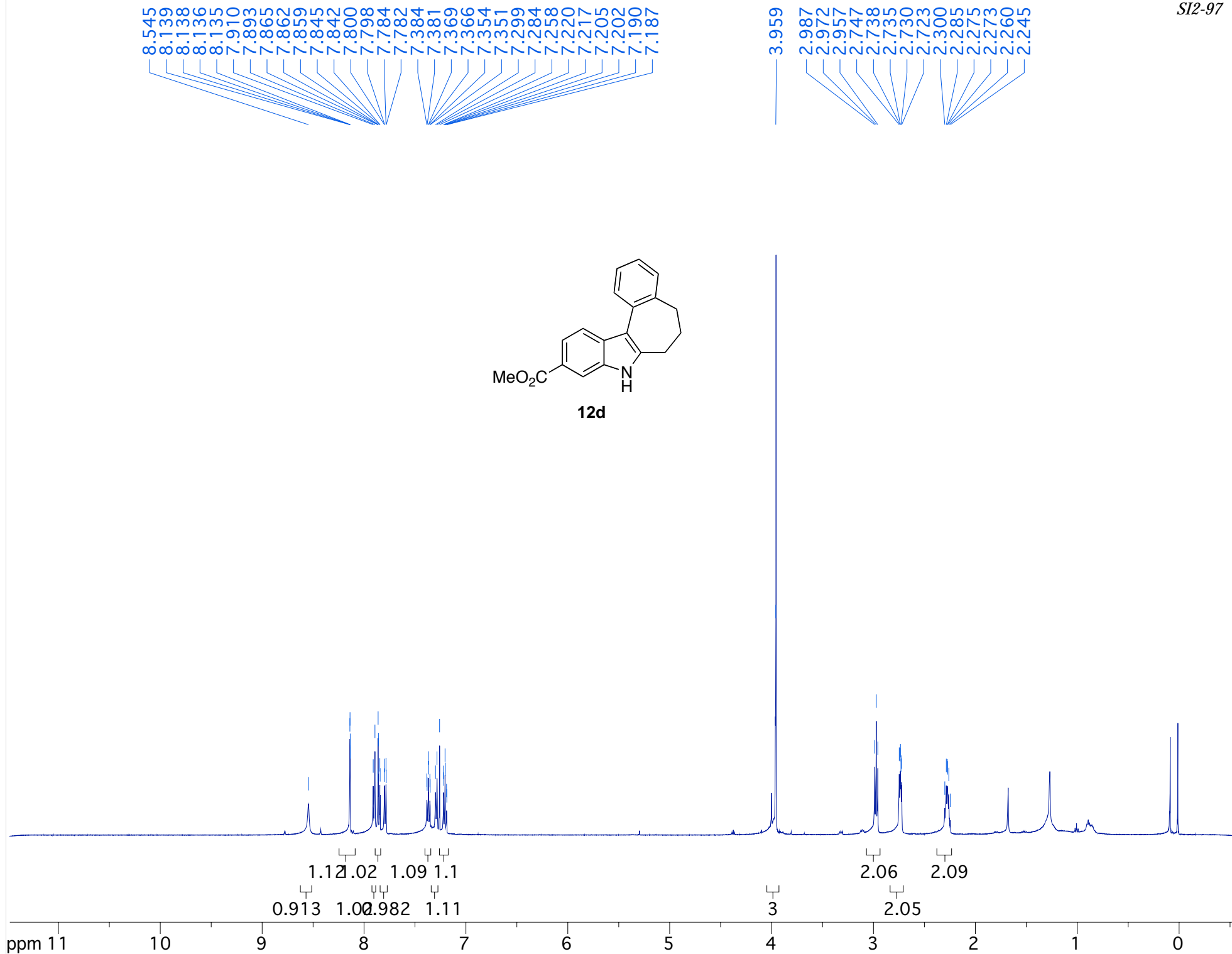
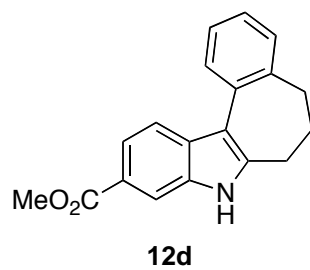
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7.781
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7.402
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7.380
7.373
7.370
7.358
7.355
7.318
7.314
7.302
7.302
7.301
7.296
7.292
7.286
7.286
7.283
7.282
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7.228
7.225
7.213
7.210
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7.196
7.170
7.167
7.163
7.163
7.155
7.151
7.138
7.134
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2.942
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2.914
2.899
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2.744
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2.422
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2.404
2.402
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2.260
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2.231
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2.220

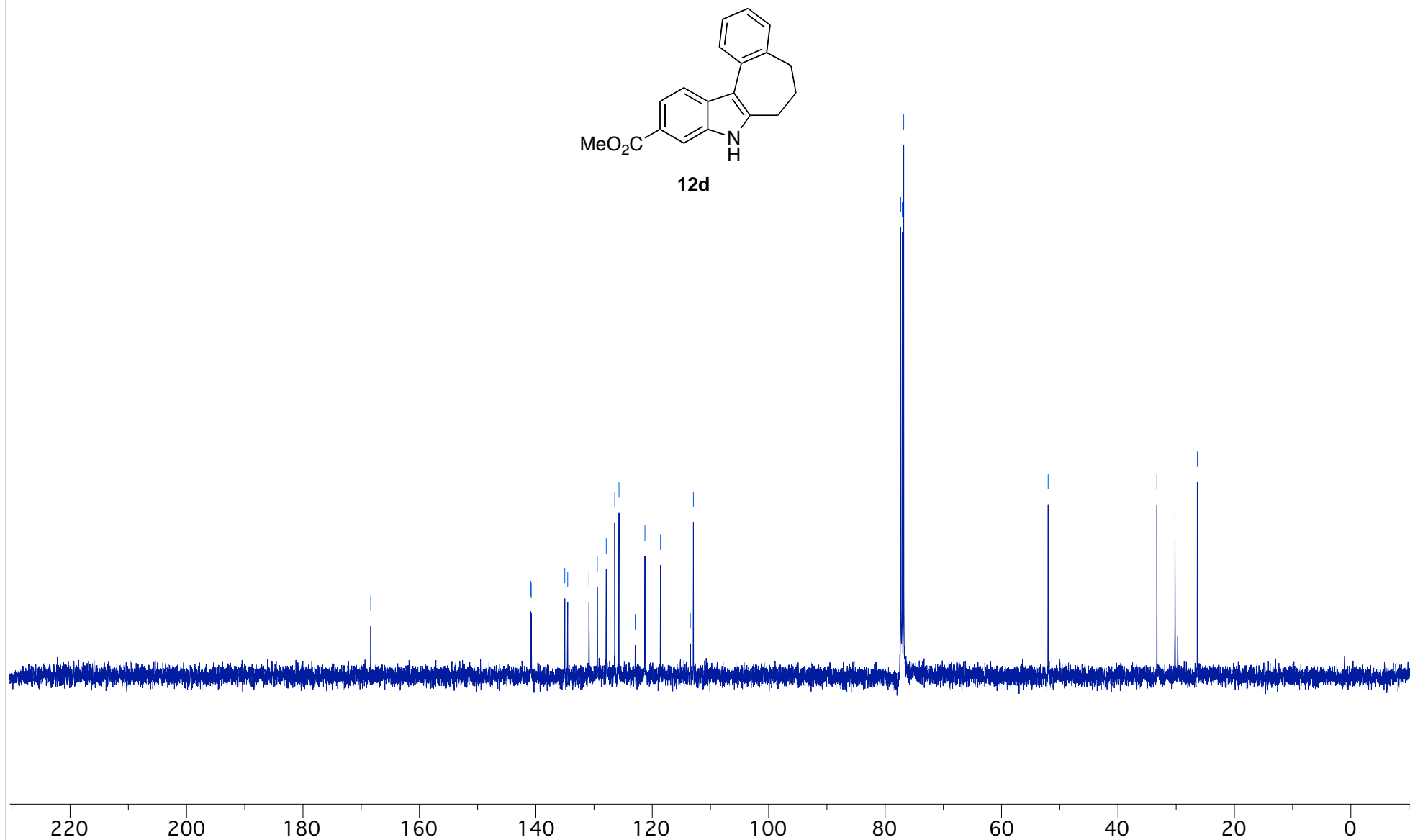


12c



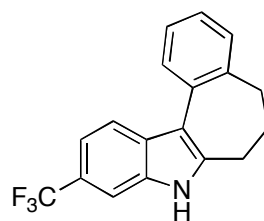




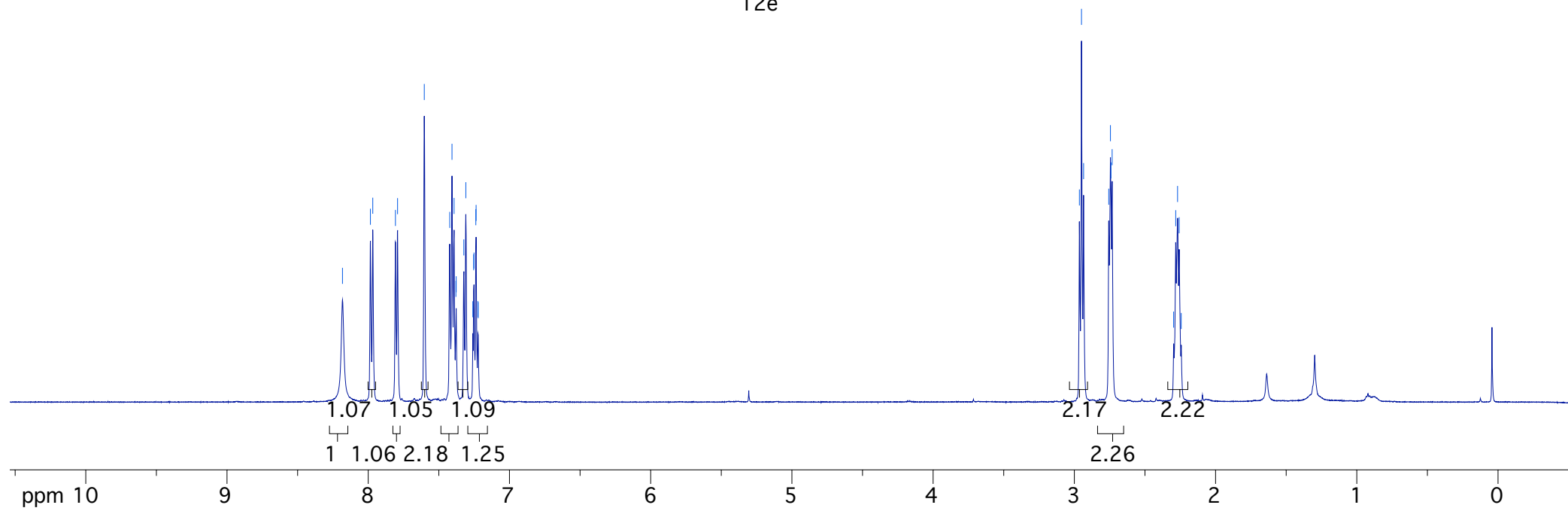


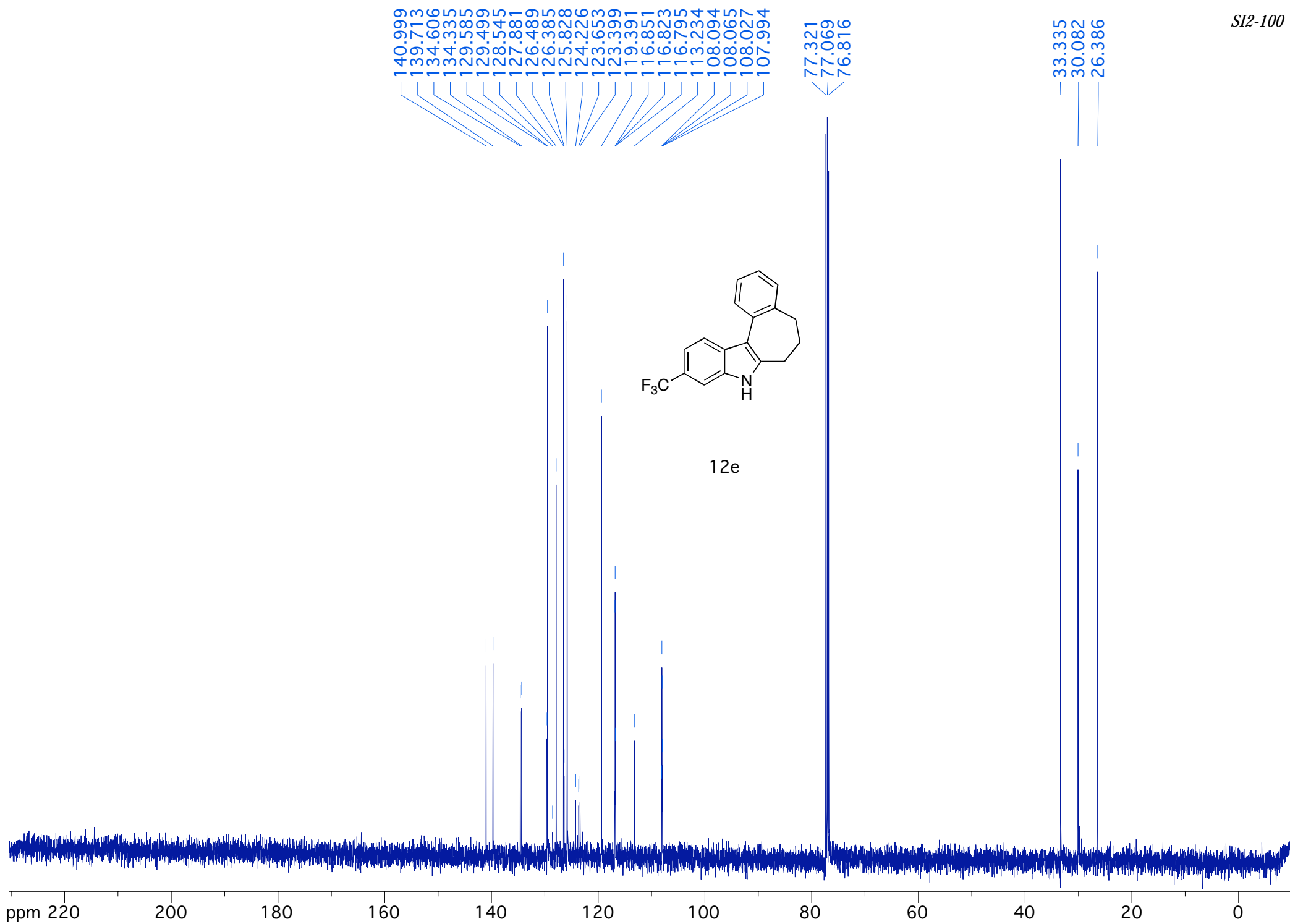
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7.259
7.253
7.251
7.238
7.236
7.223
7.221

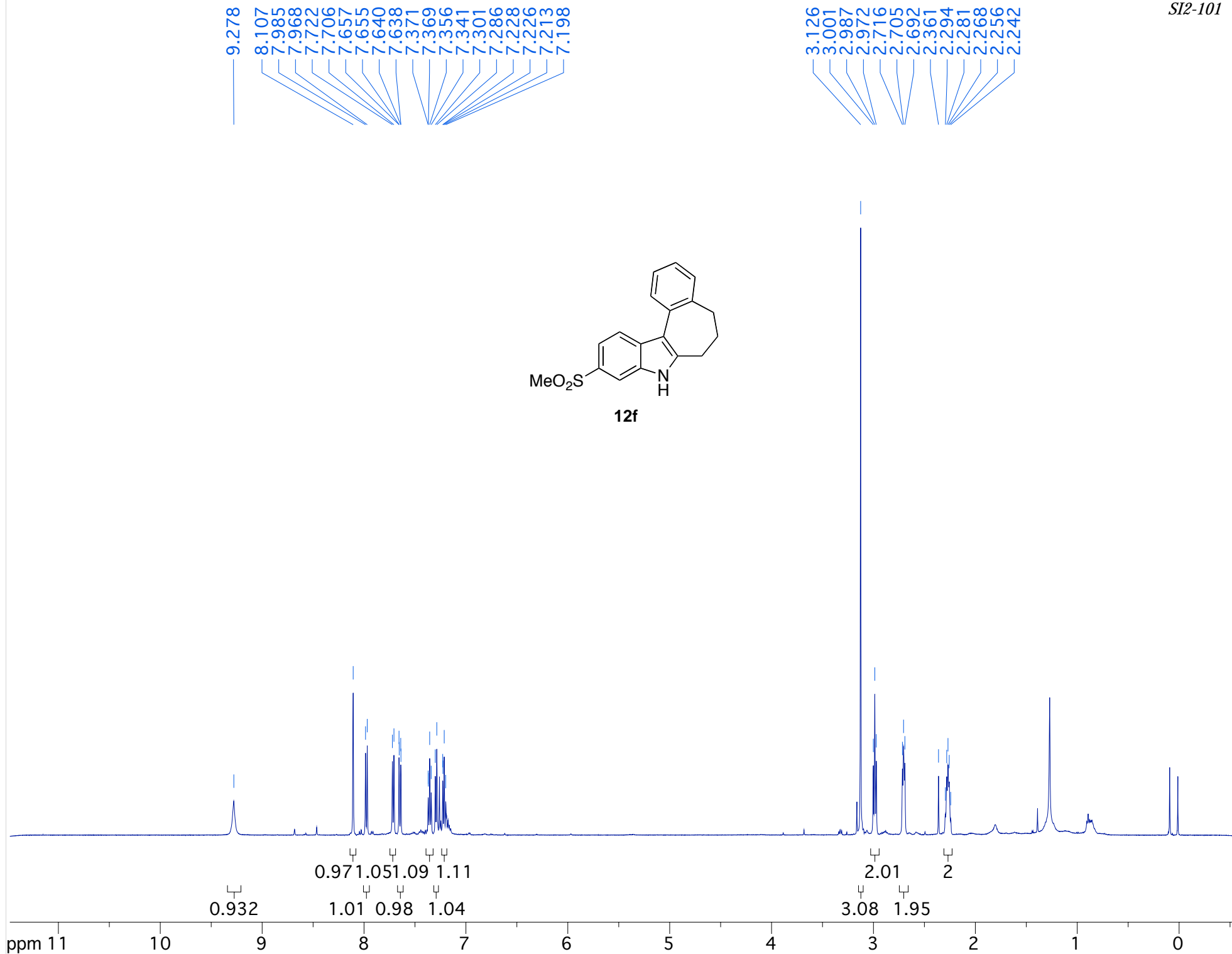
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2.741
2.732
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2.282
2.269
2.258
2.243

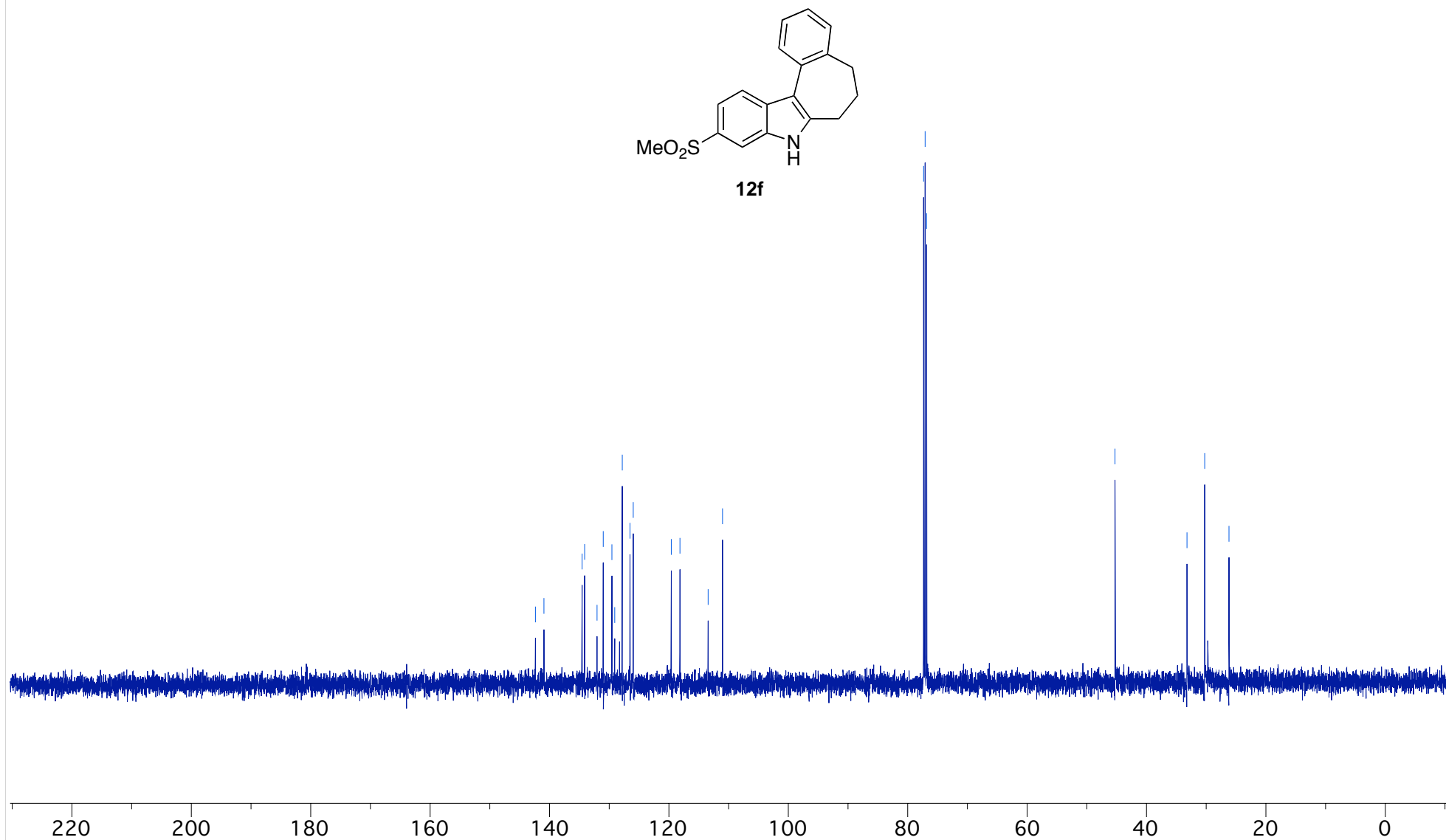


12e



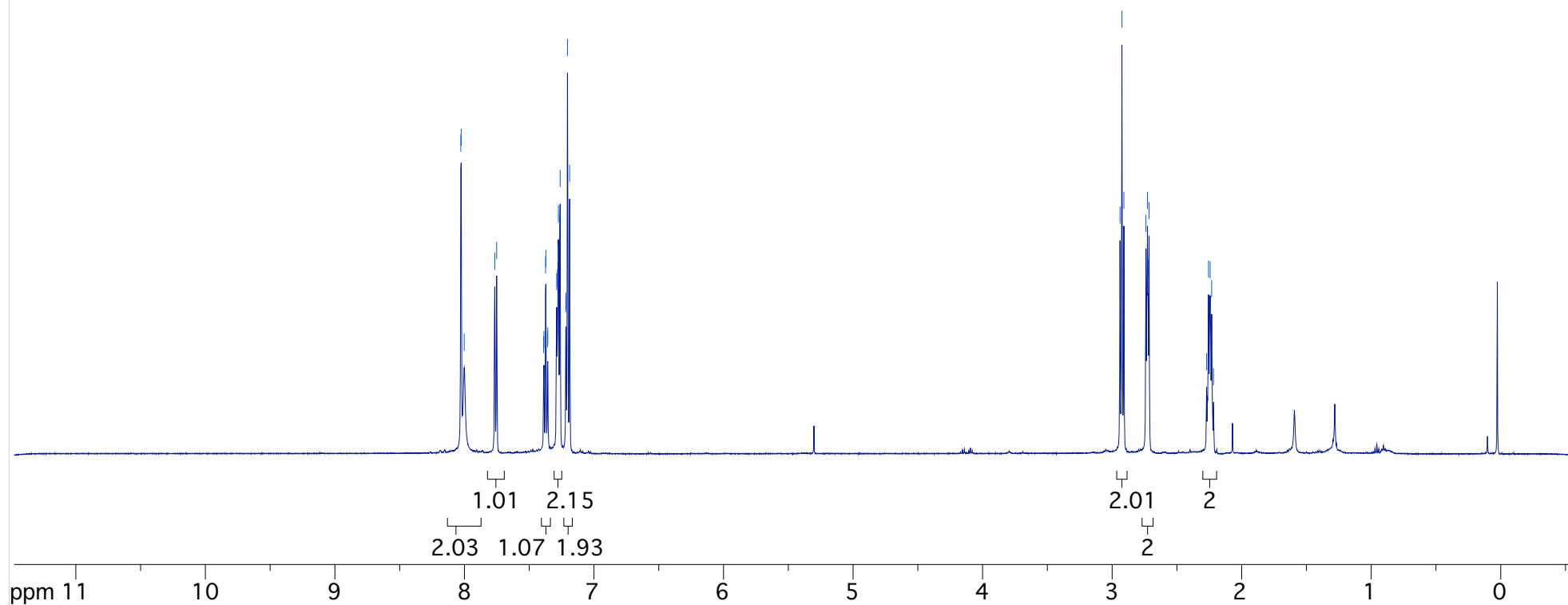
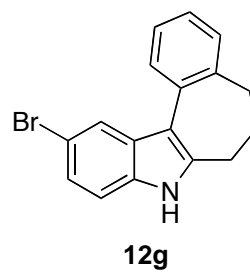


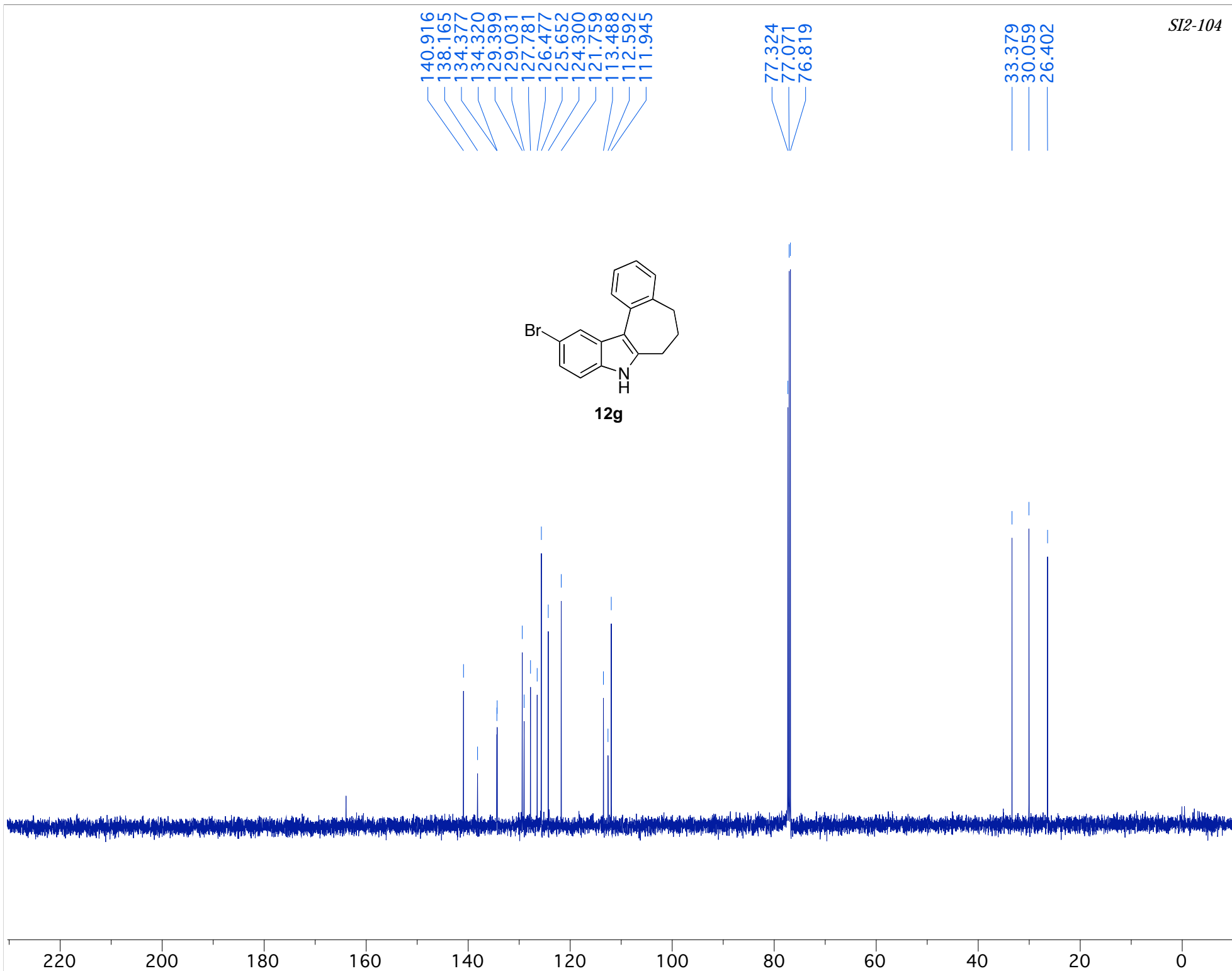


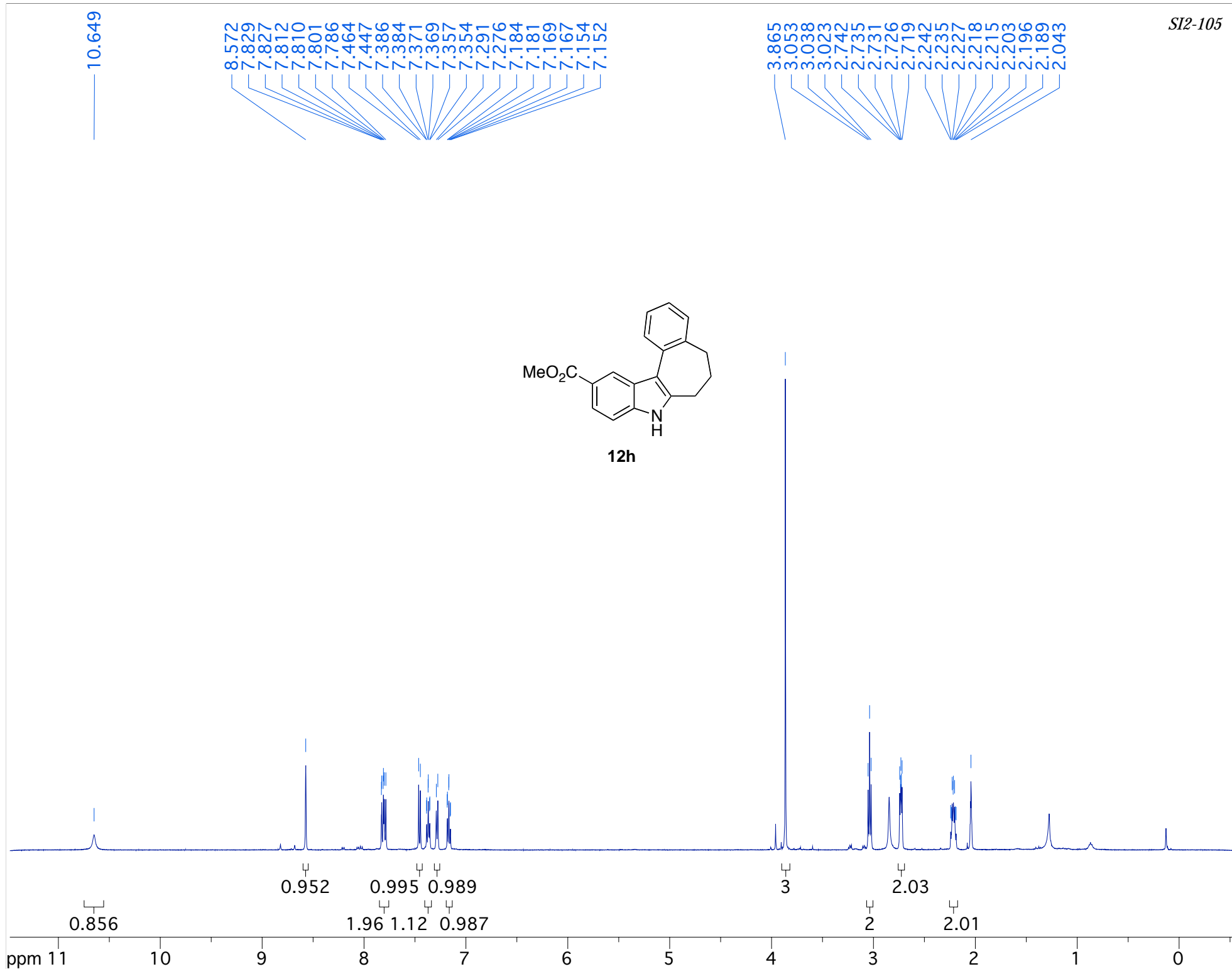


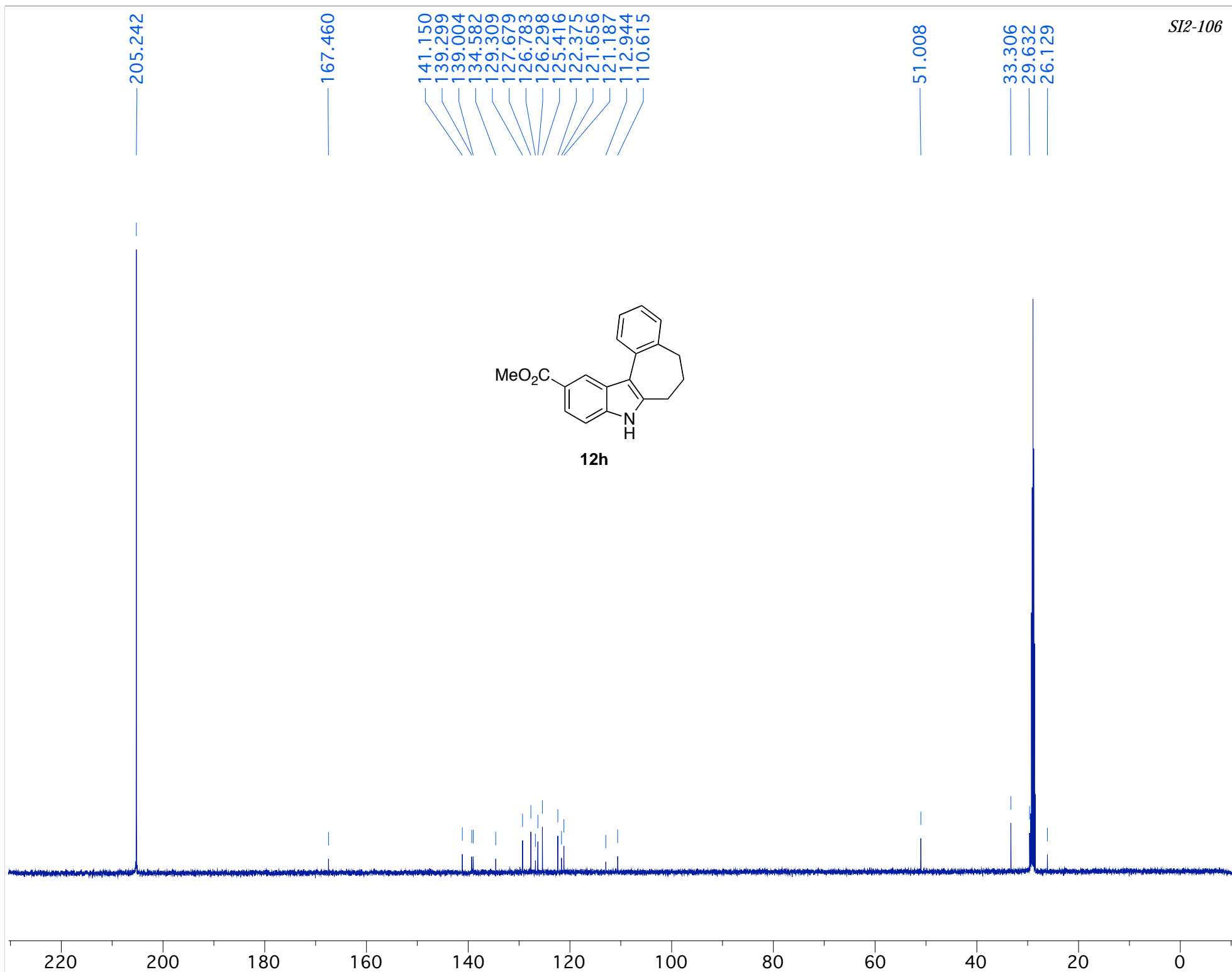
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7.374
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7.261
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7.205
7.188

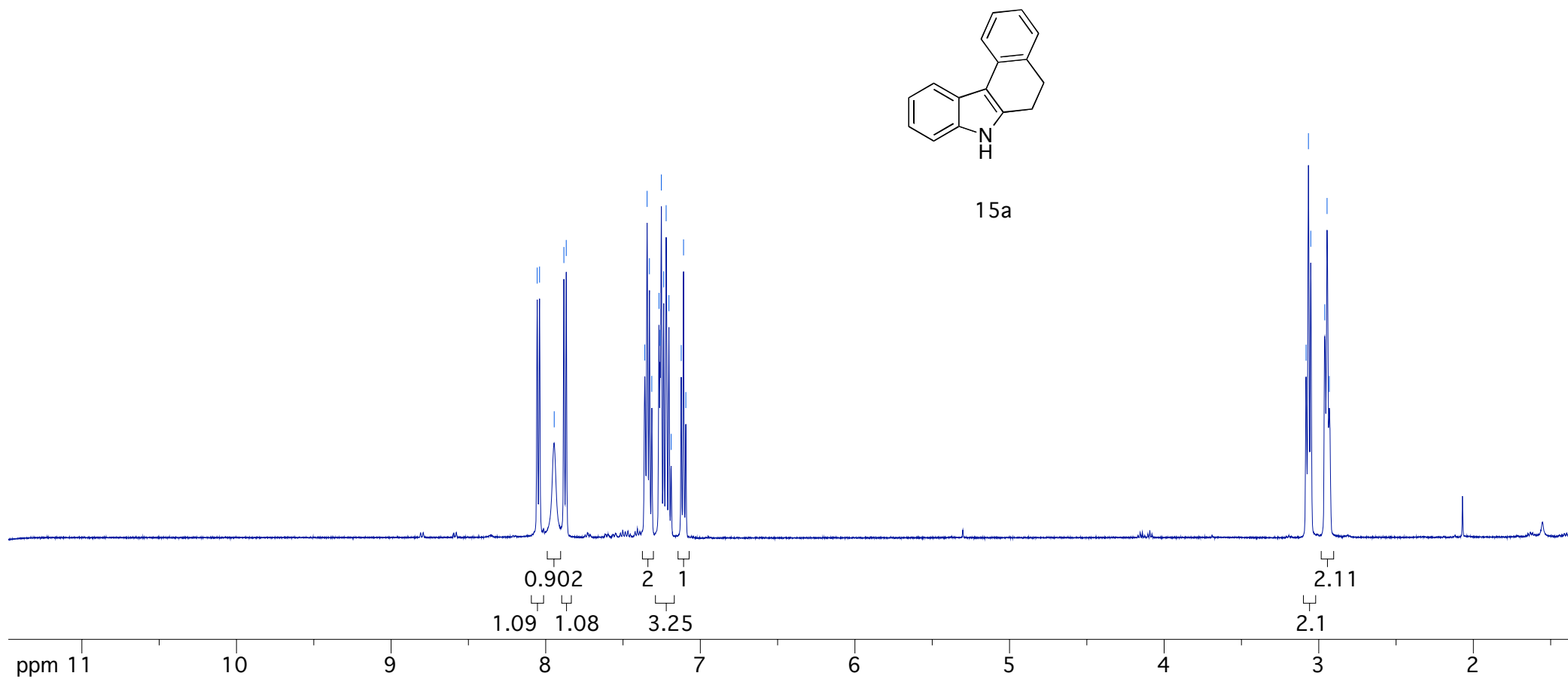
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2.739
2.727
2.723
2.715
2.271
2.256
2.244
2.232
2.217

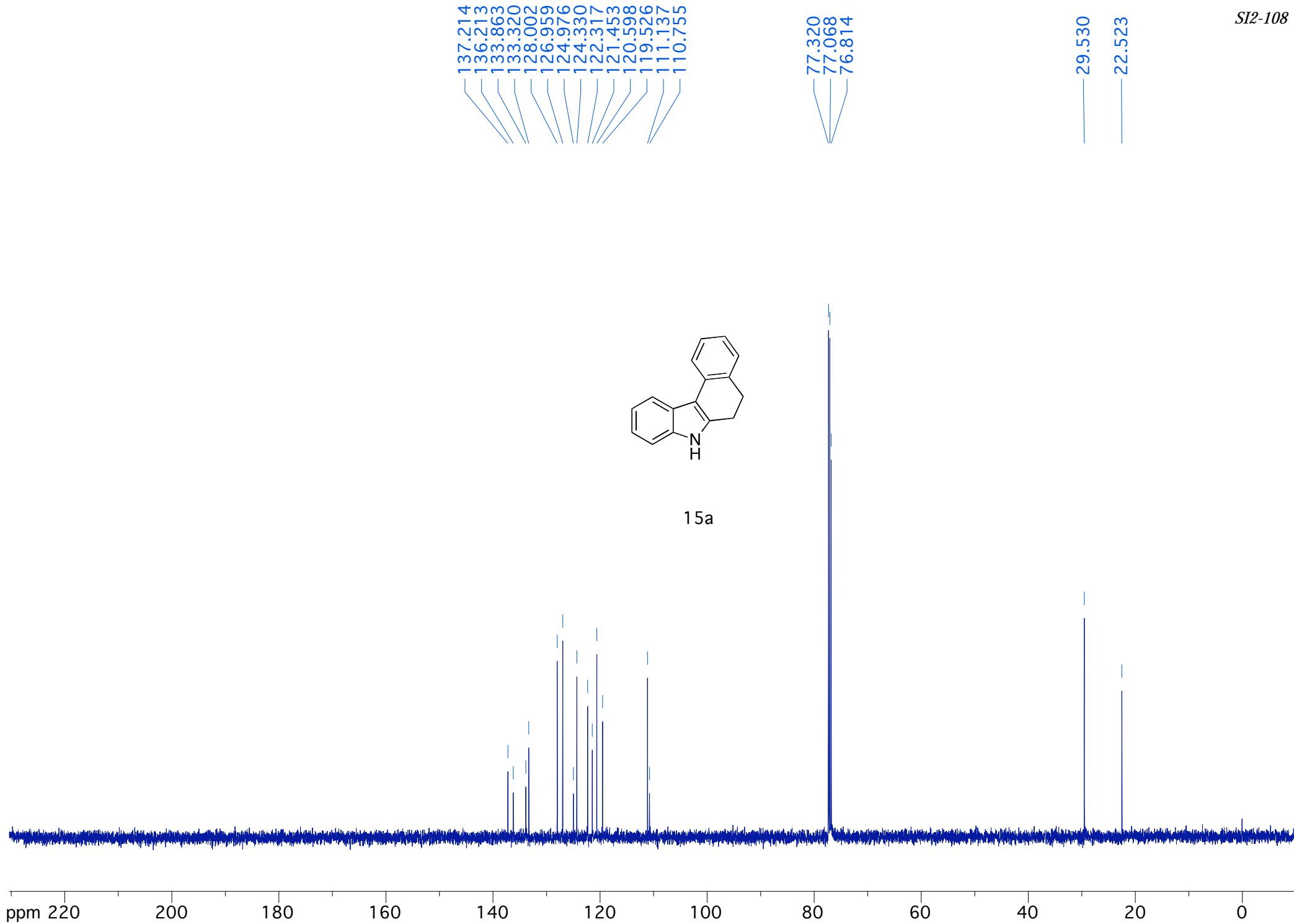






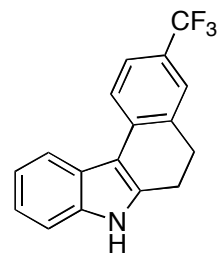




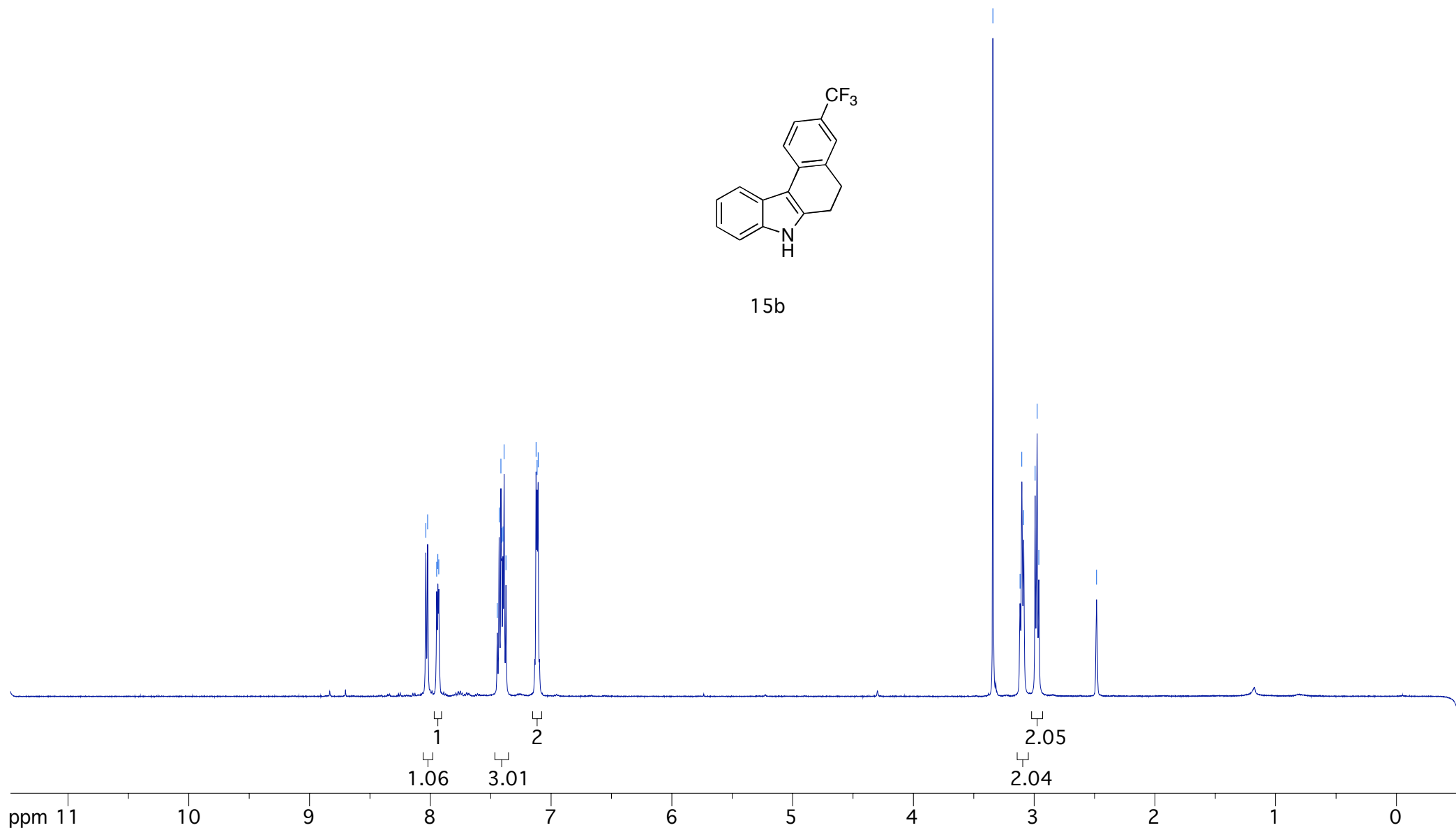


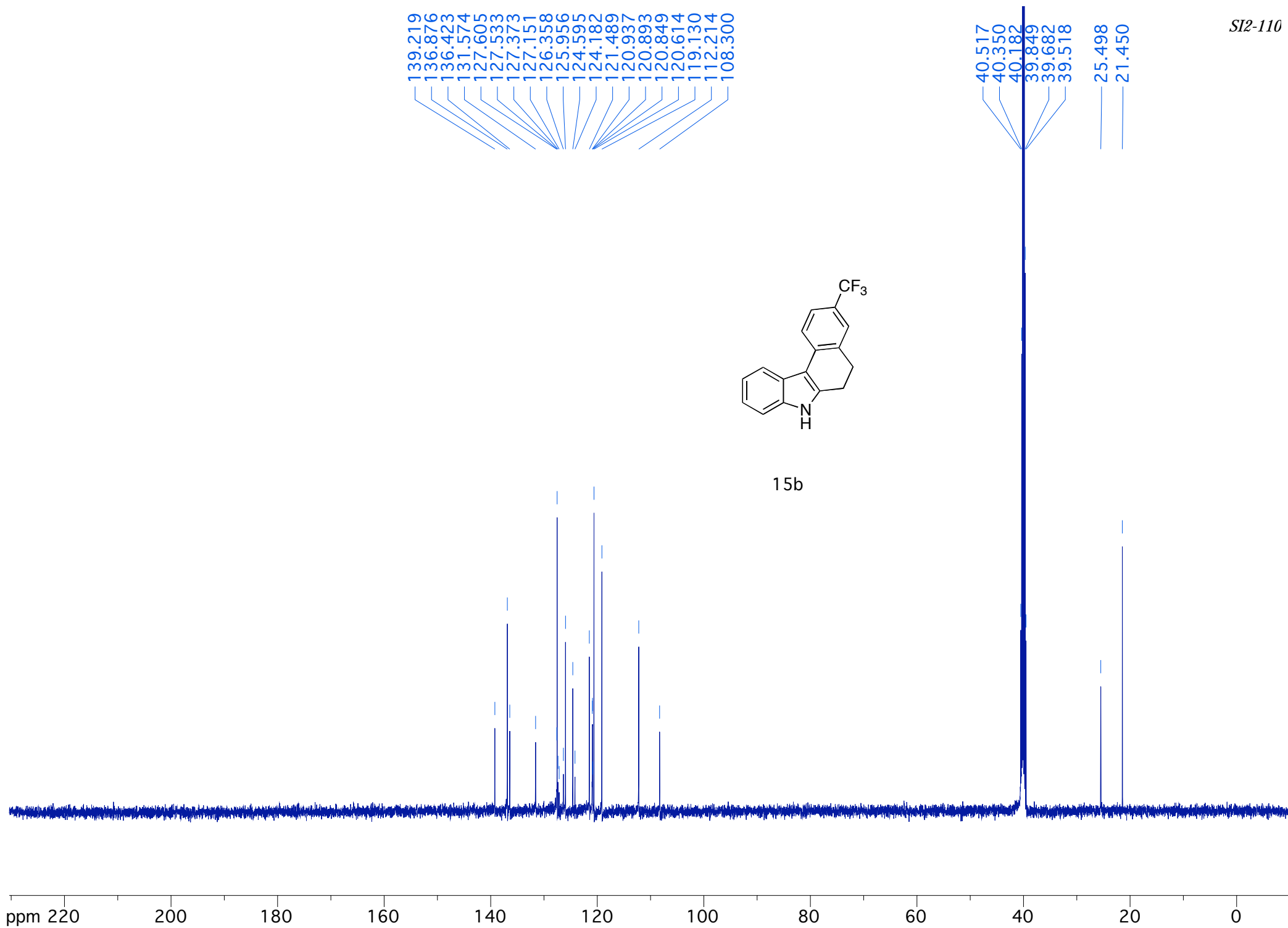
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7.416
7.409
7.398
7.389
7.374
7.125
7.116
7.107

3.342
3.117
3.102
3.087
2.992
2.976
2.962
2.484



15b



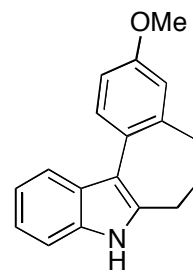


7.990
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7.555
7.486
7.470
7.370
7.354
7.260
7.240
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7.211
7.161
7.146
7.132
6.853
6.848
6.836
6.831
6.821
6.816

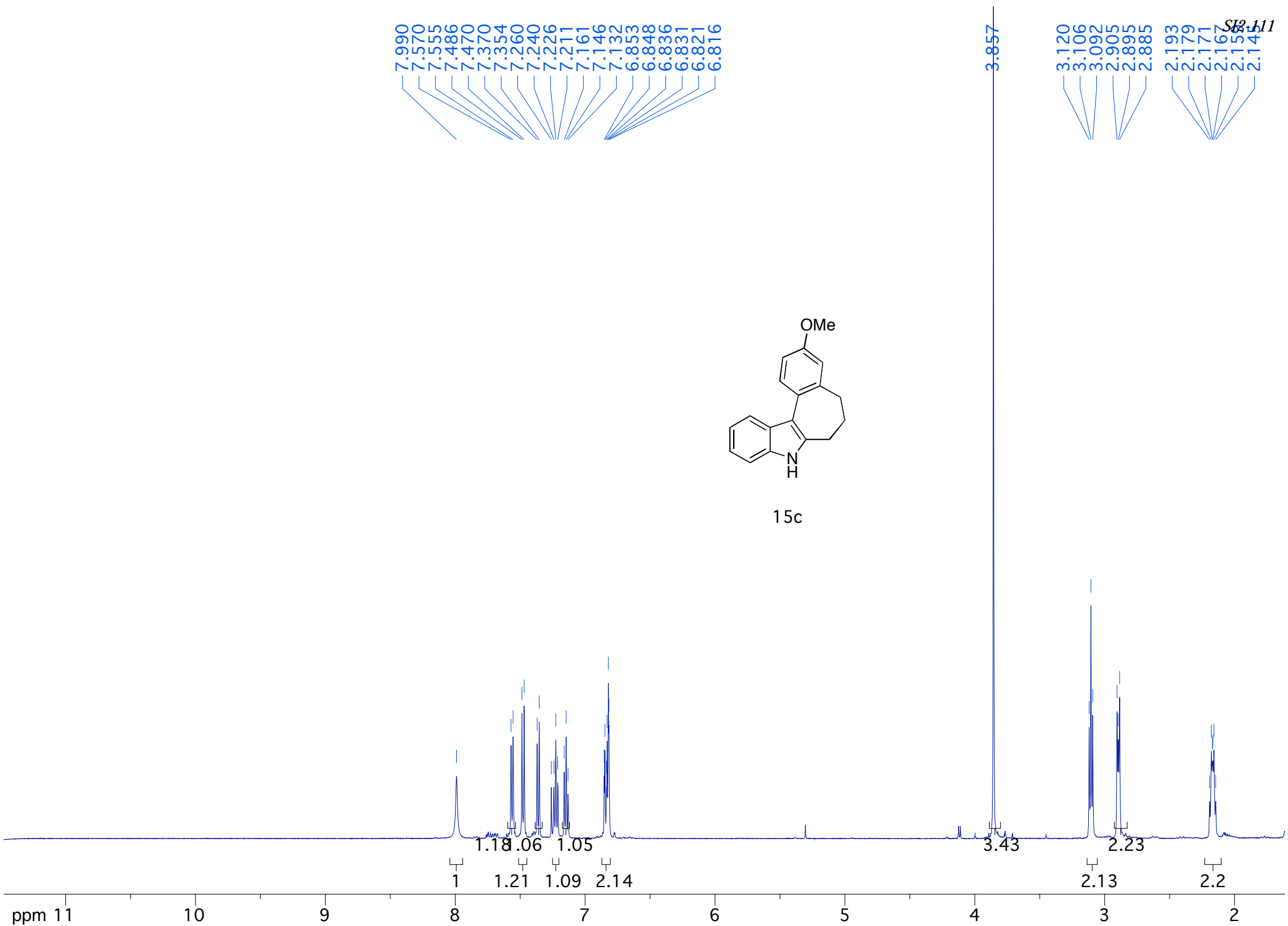
3.857

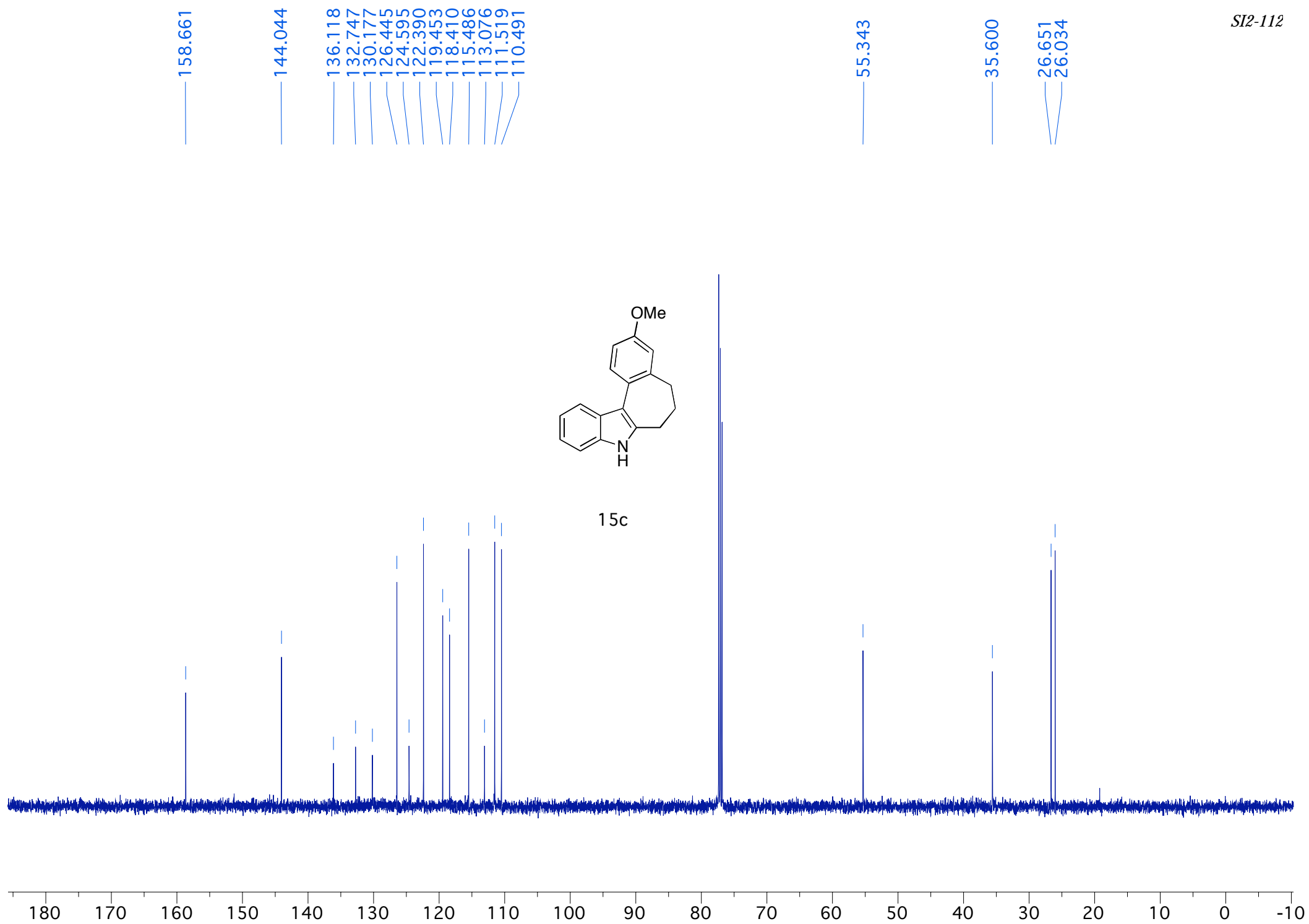
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3.106
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2.885
2.193
2.179
2.171
2.167
2.158
2.144

SI2-111



15c

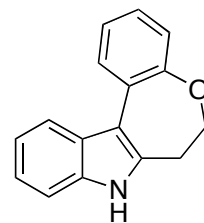




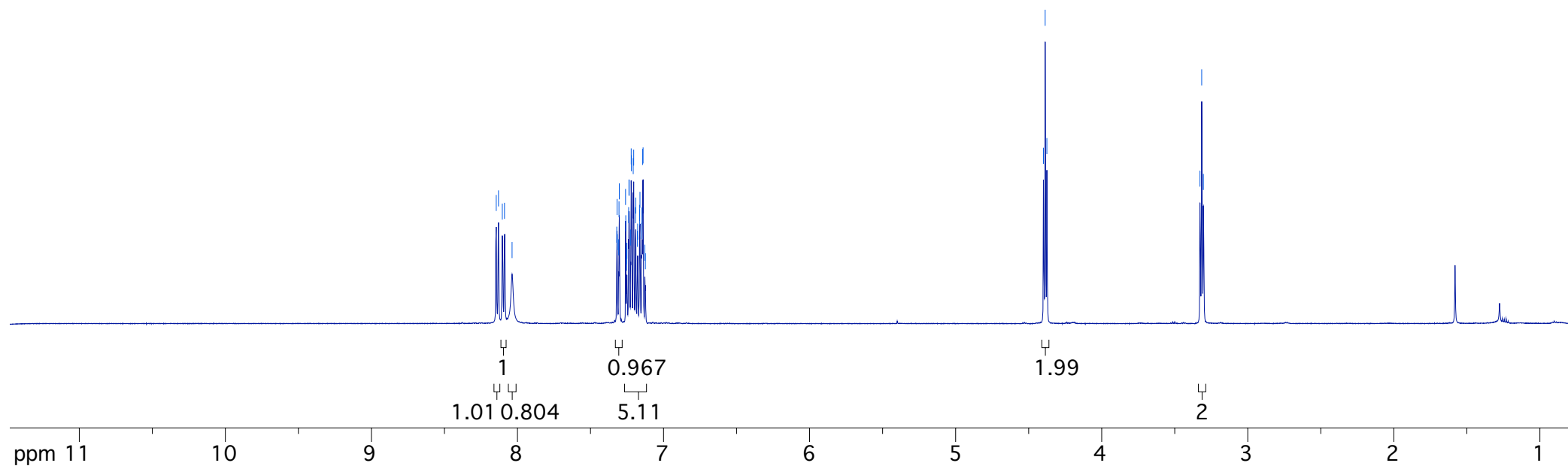
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8.089
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7.316
7.307
7.305
7.303
7.260
7.259
7.254
7.253
7.251
7.239
7.237
7.235
7.225
7.221
7.220
7.208
7.204
7.193
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7.179
7.177
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7.161
7.151
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7.140
7.128
7.124

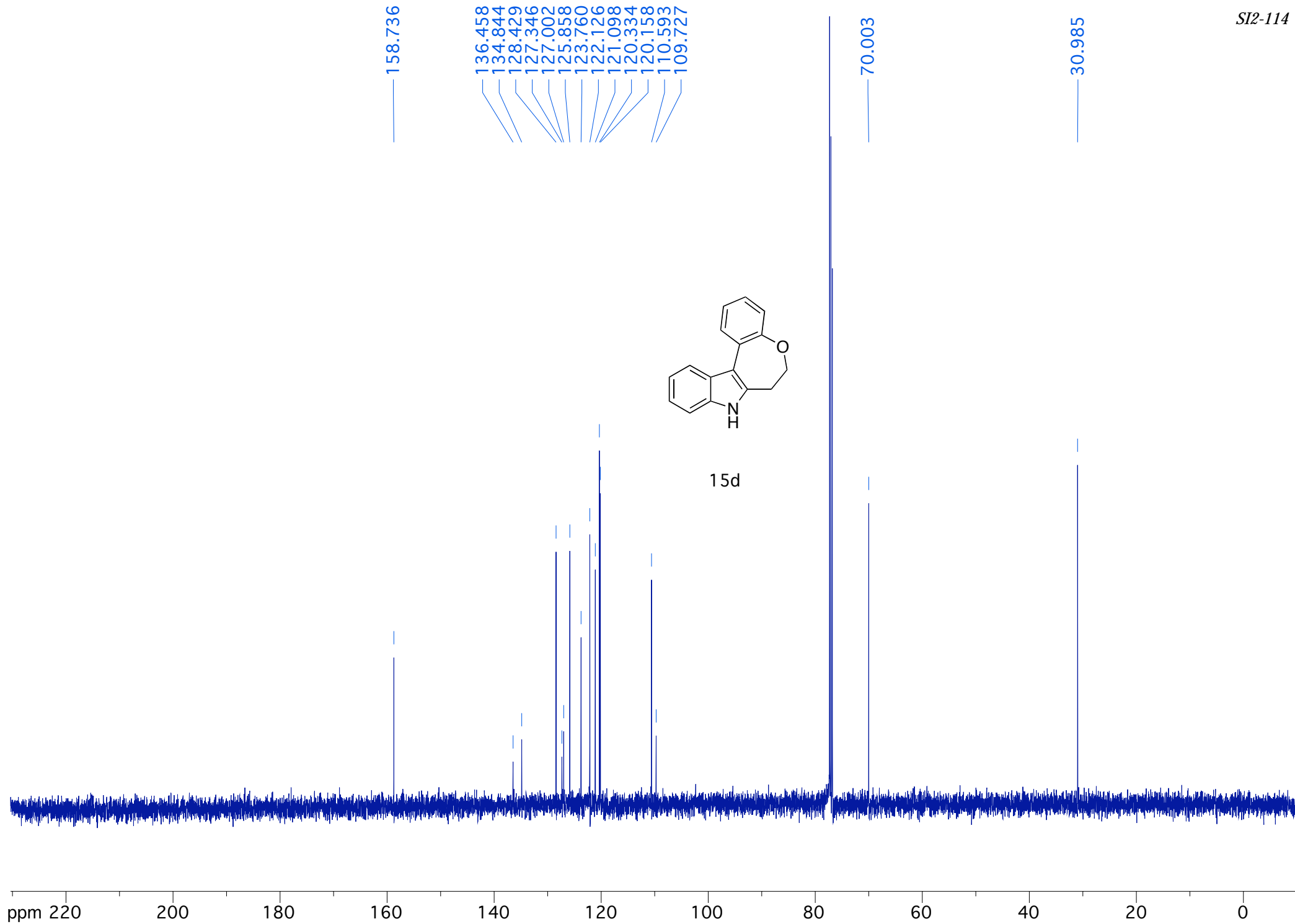
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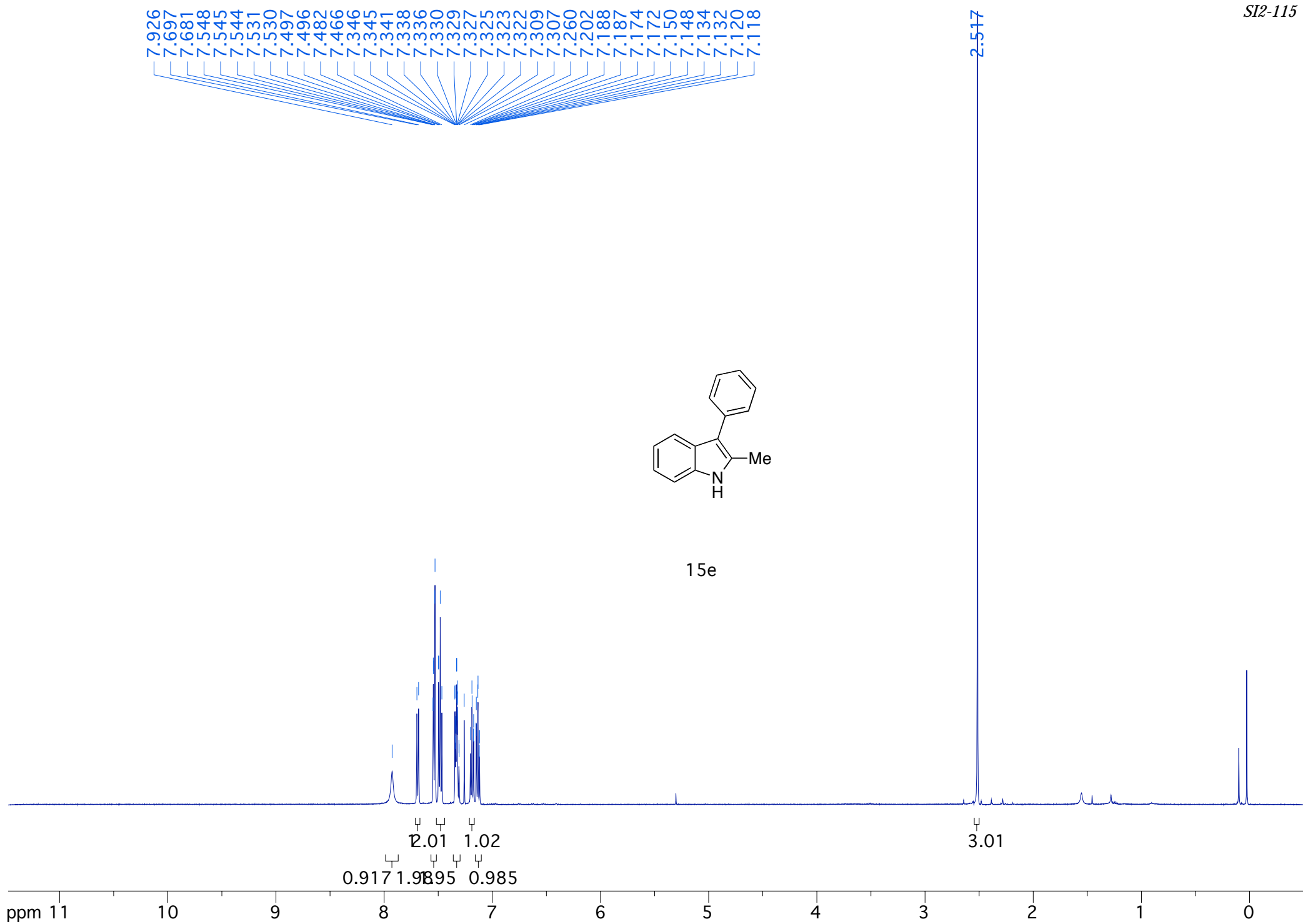
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15d



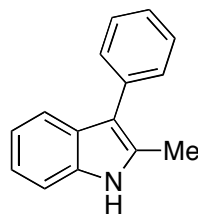




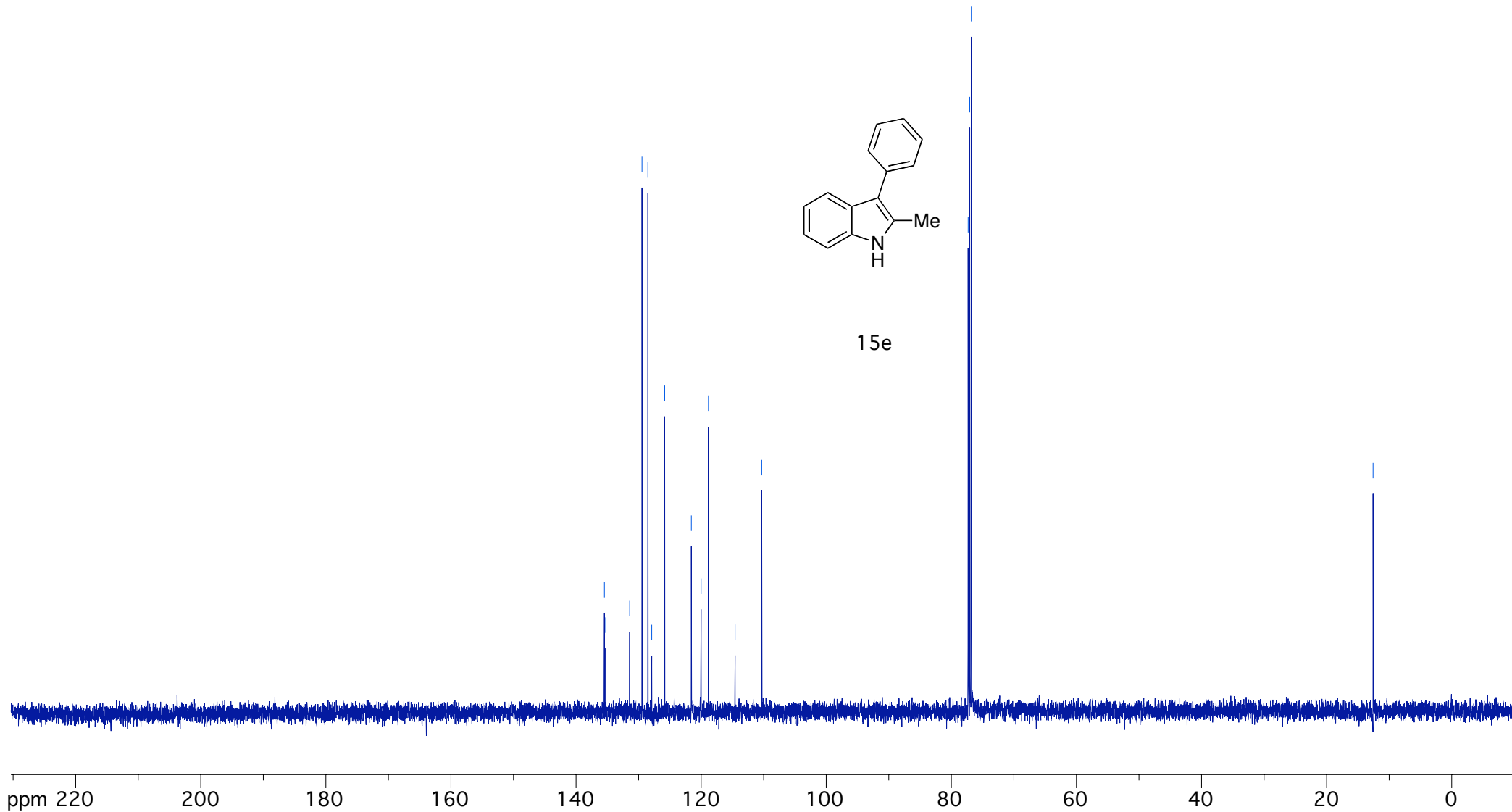
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125.828
121.568
120.006
118.835
114.574
110.314

77.314
77.056
76.805

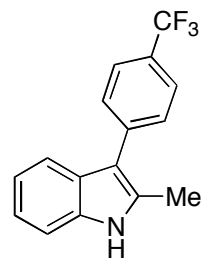
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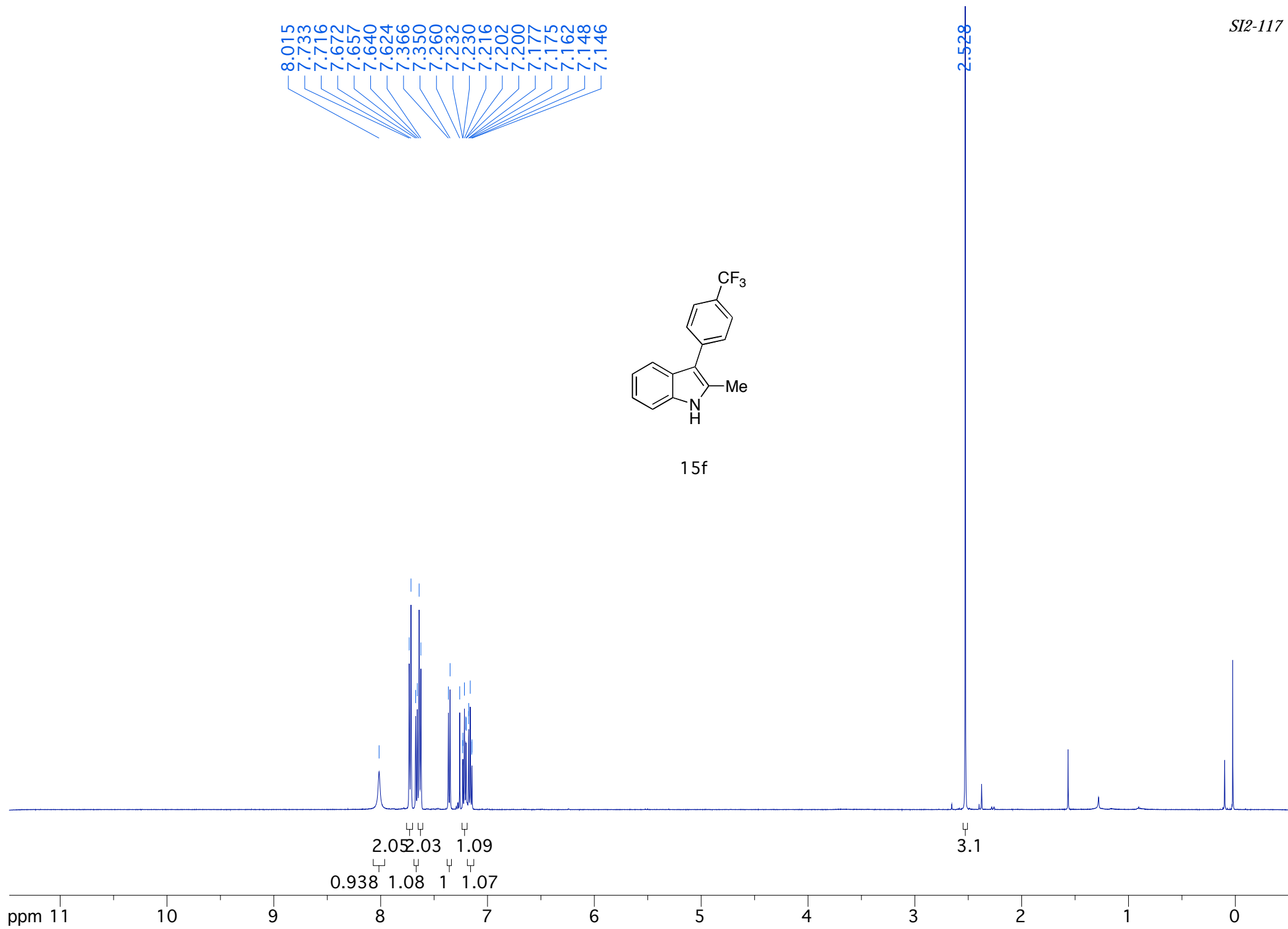
15e



8.015
7.733
7.716
7.672
7.657
7.640
7.624
7.366
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7.260
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7.202
7.200
7.177
7.175
7.162
7.148
7.146



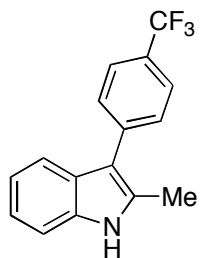
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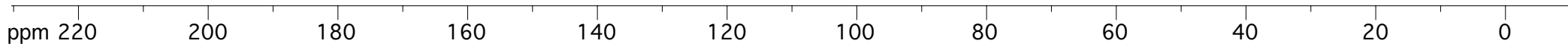
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127.590
127.486
125.623
125.475
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113.415
110.520

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77.053
76.794

12.615

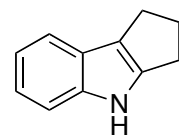


15f

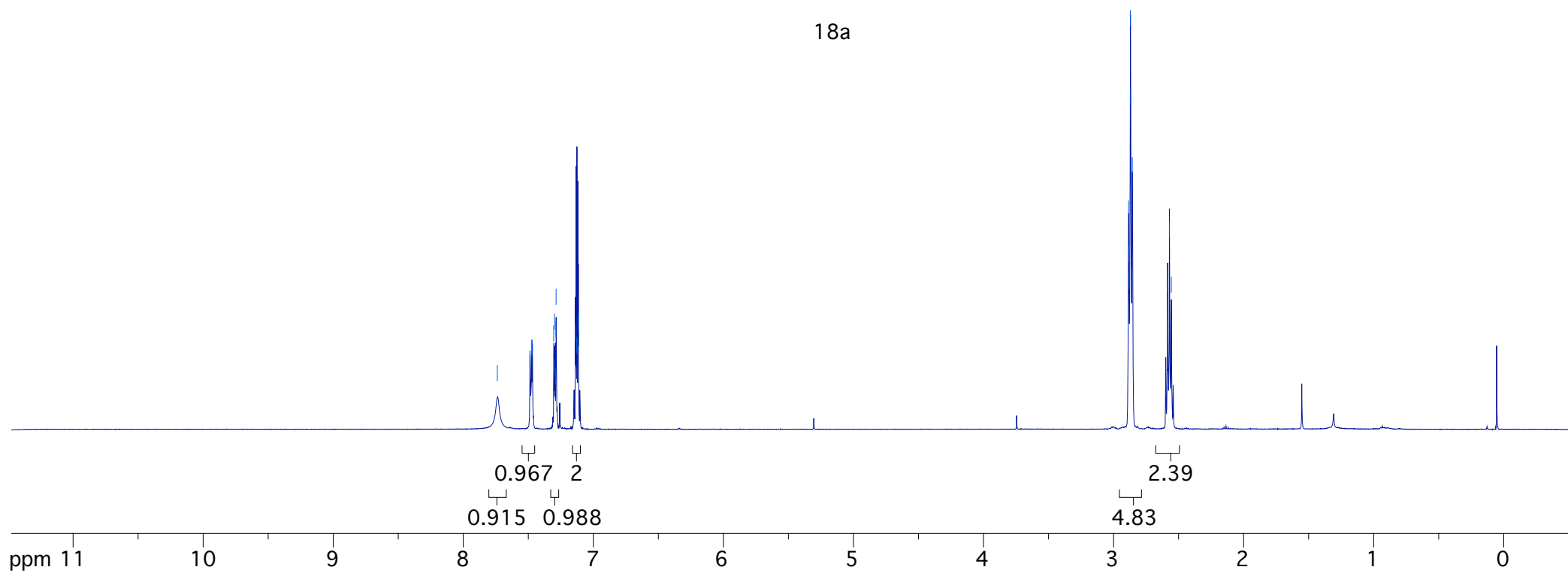


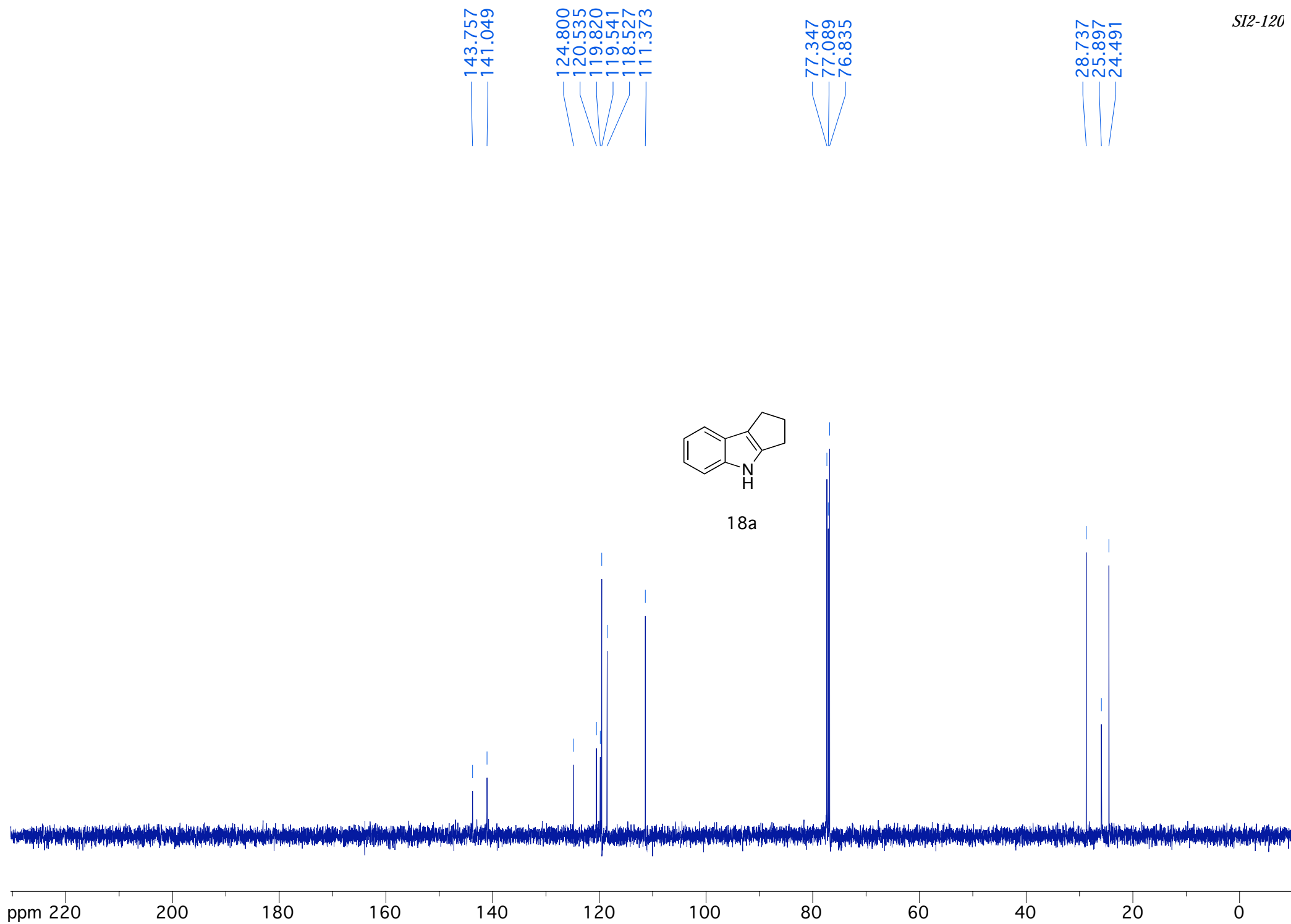
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7.470
7.306
7.304
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7.299
7.290
7.288
7.286
7.139
7.135
7.128
7.120
7.117

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2.585
2.583
2.571
2.556



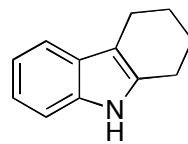
18a



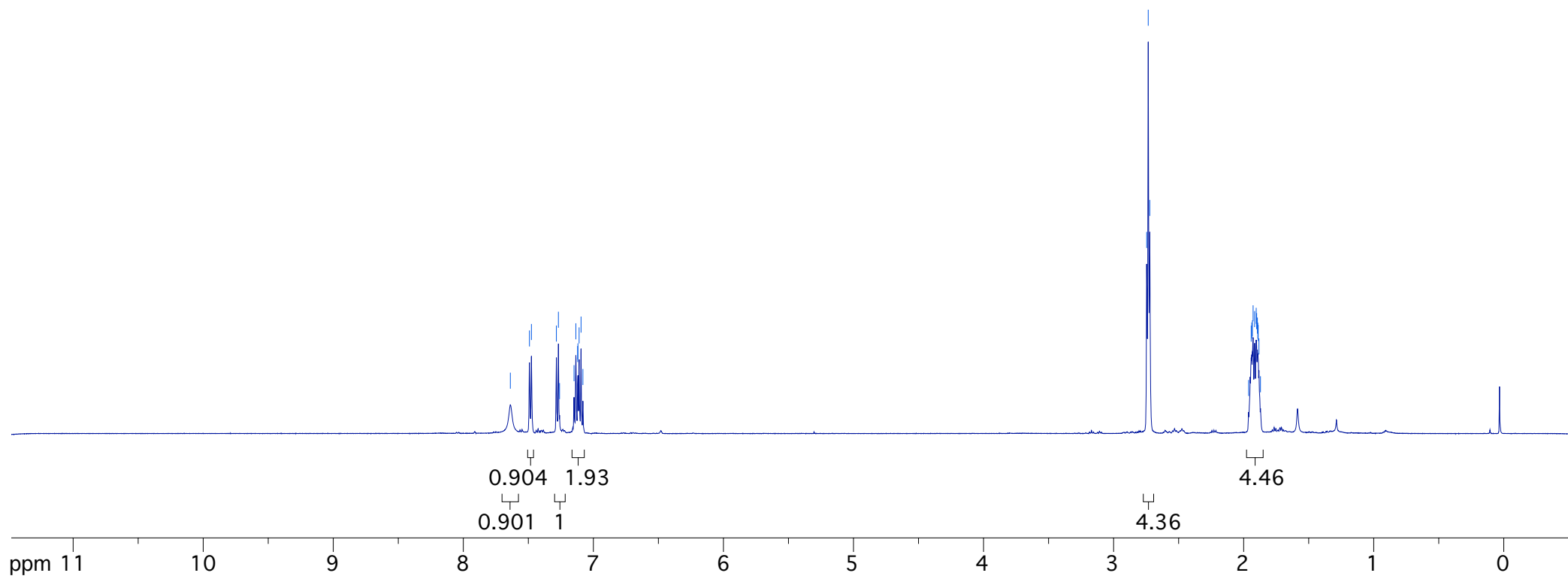


7.638
7.491
7.476
7.284
7.269
7.260
7.149
7.135
7.121
7.119
7.110
7.095
7.081

2.746
2.734
2.722
1.962
1.942
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1.882
1.871



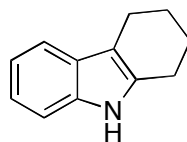
18b



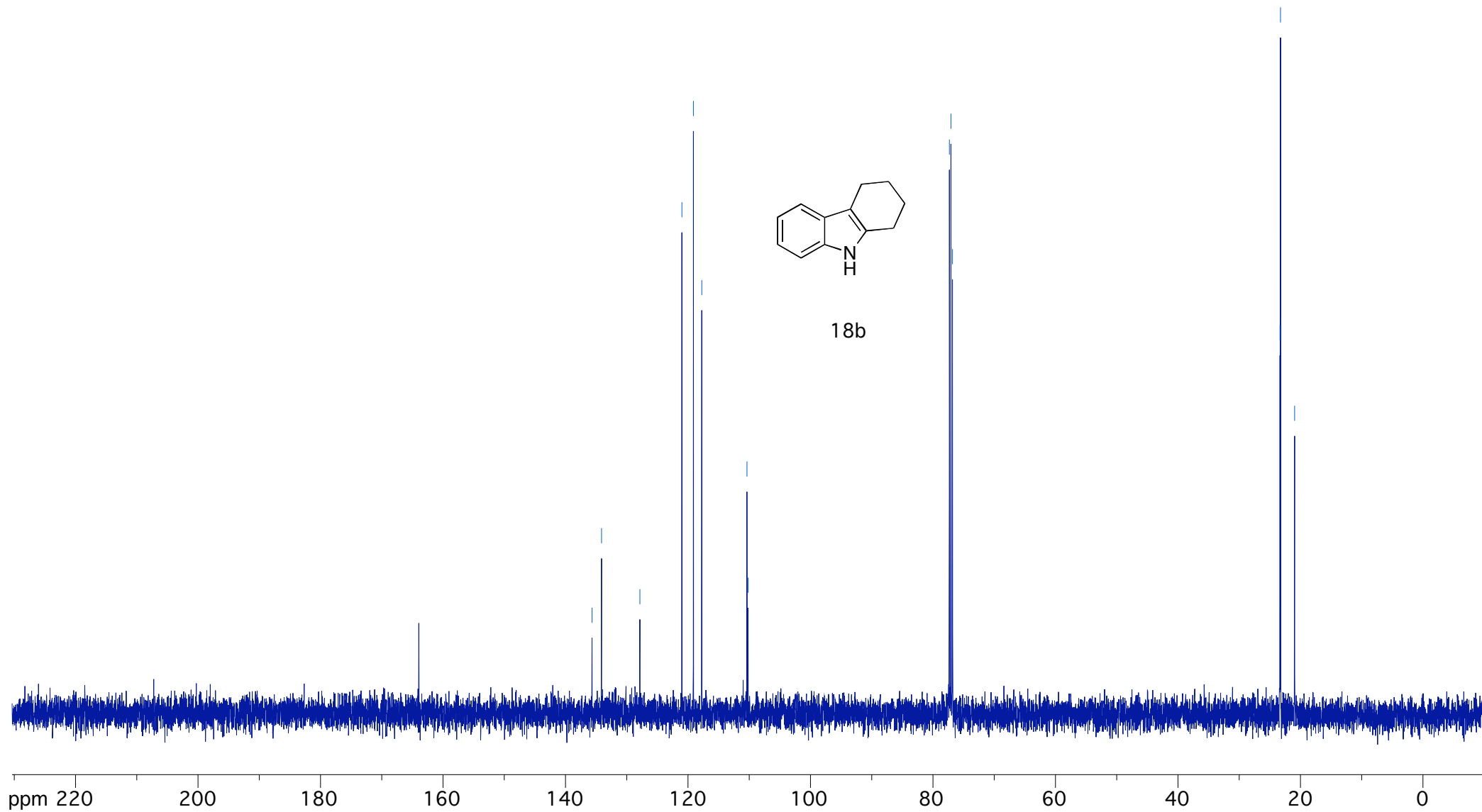
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110.195

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77.069
76.815

23.344
23.261
20.955

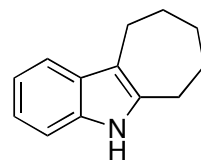


18b

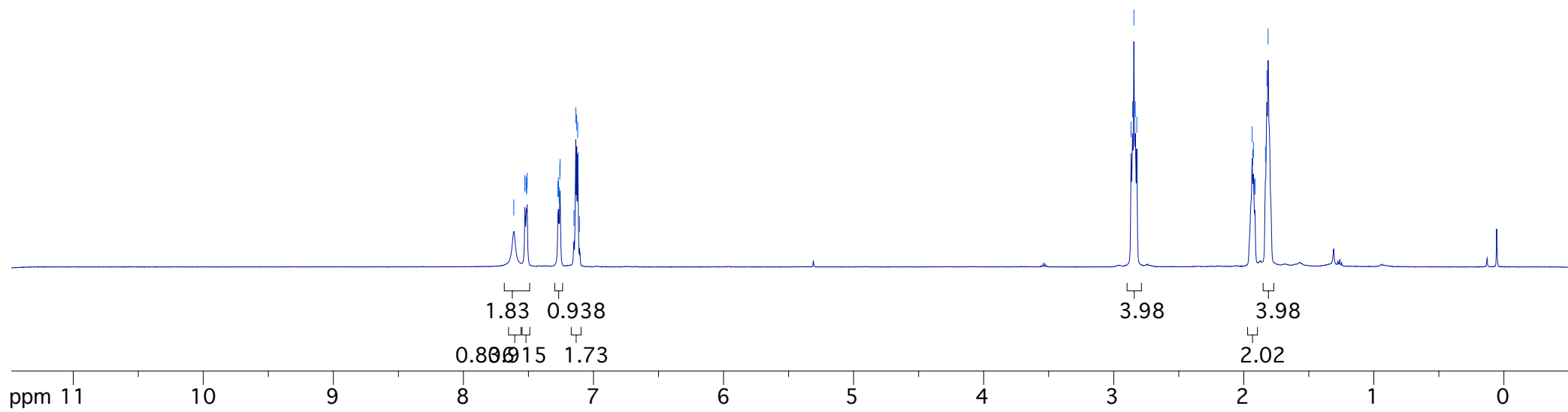


7.613
7.527
7.515
7.514
7.510
7.273
7.270
7.268
7.264
7.259
7.257
7.150
7.136
7.129
7.121
7.118
7.107

2.867
2.855
2.845
2.834
2.823
1.936
1.931
1.926
1.918
1.914
1.833
1.823
1.813



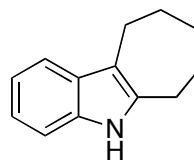
18c



137.478
134.275
129.310
120.643
119.056
117.690
113.753
110.256

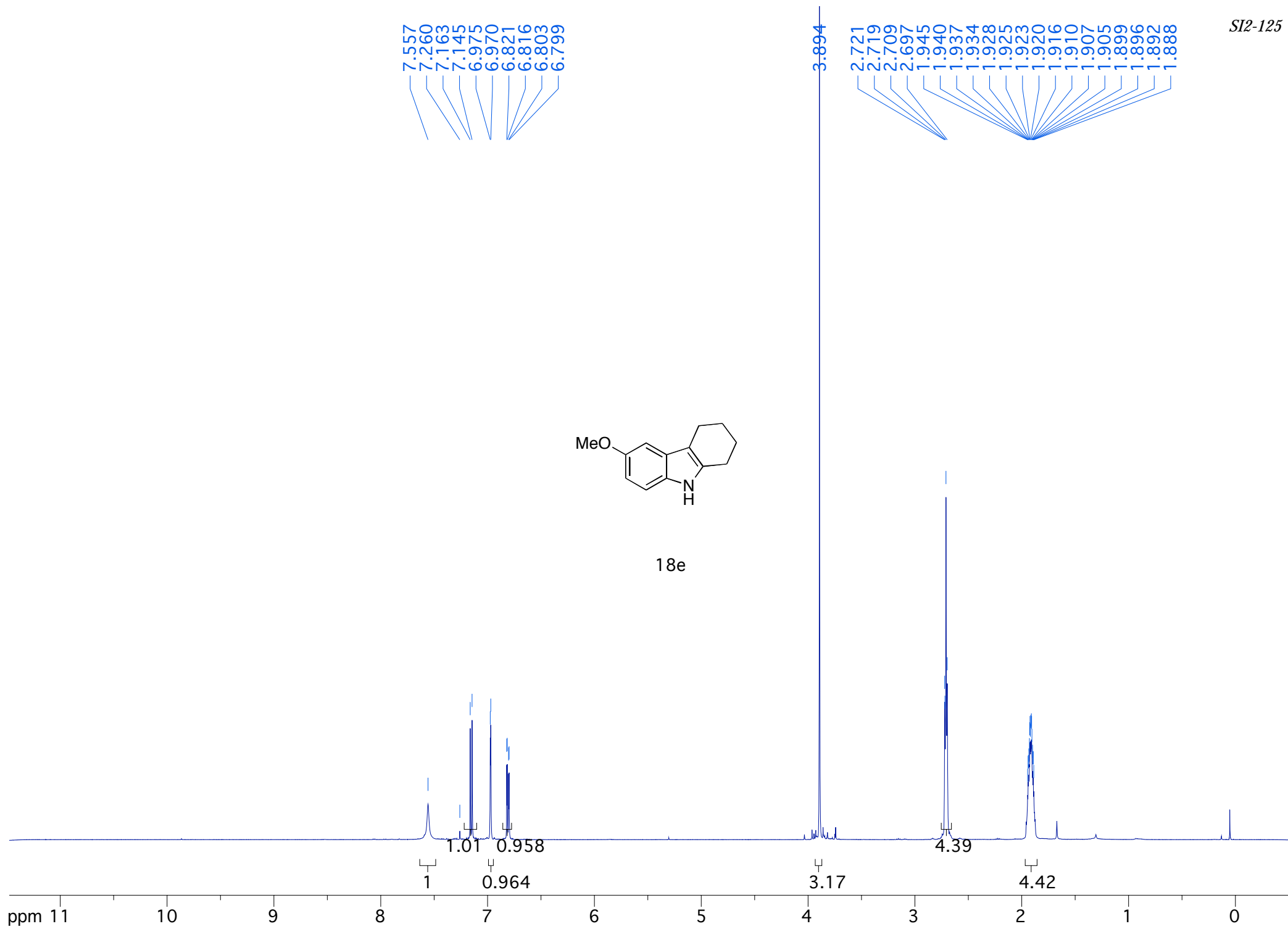
77.349
77.098
76.845

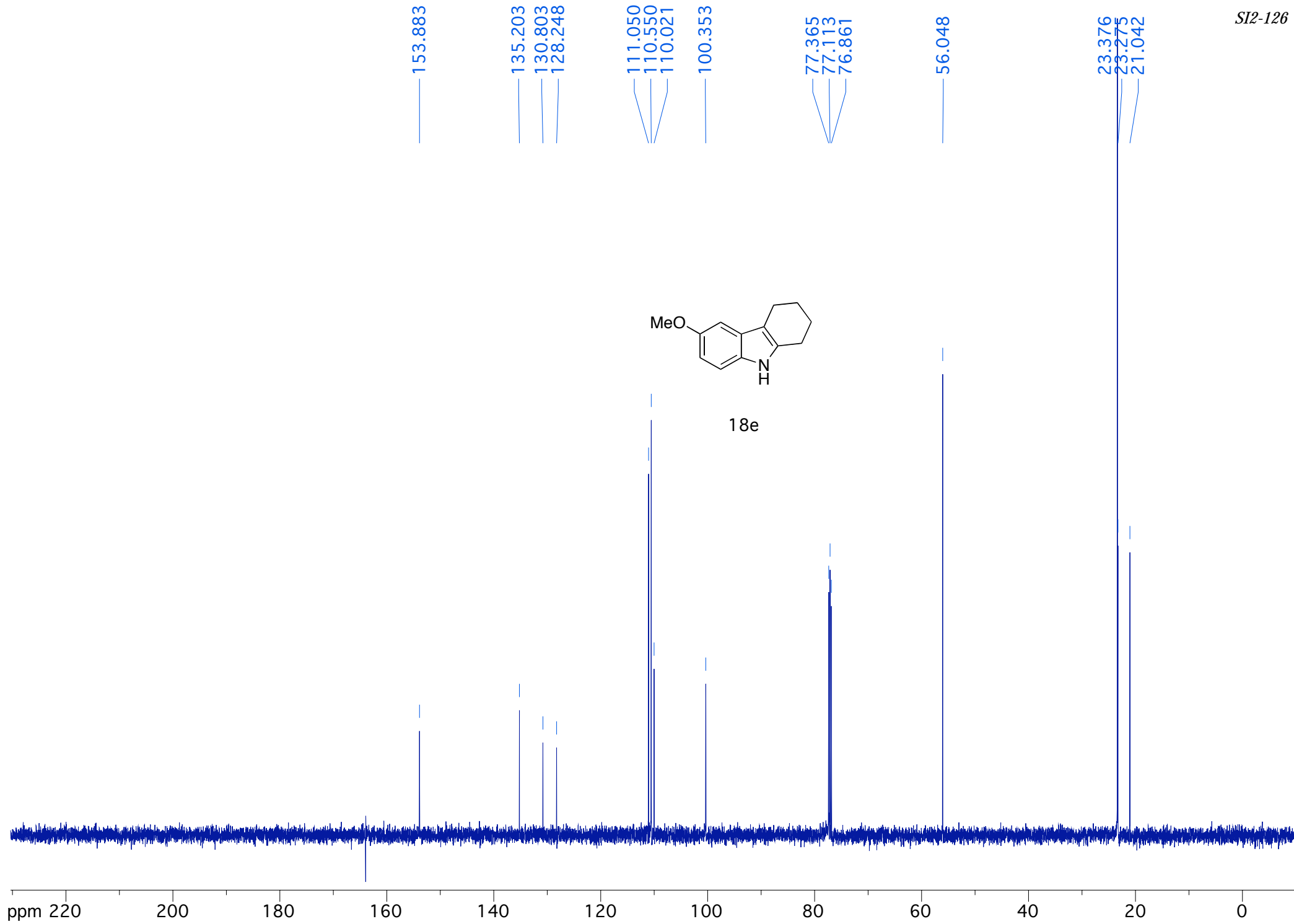
31.866
29.604
28.794
27.591
24.727

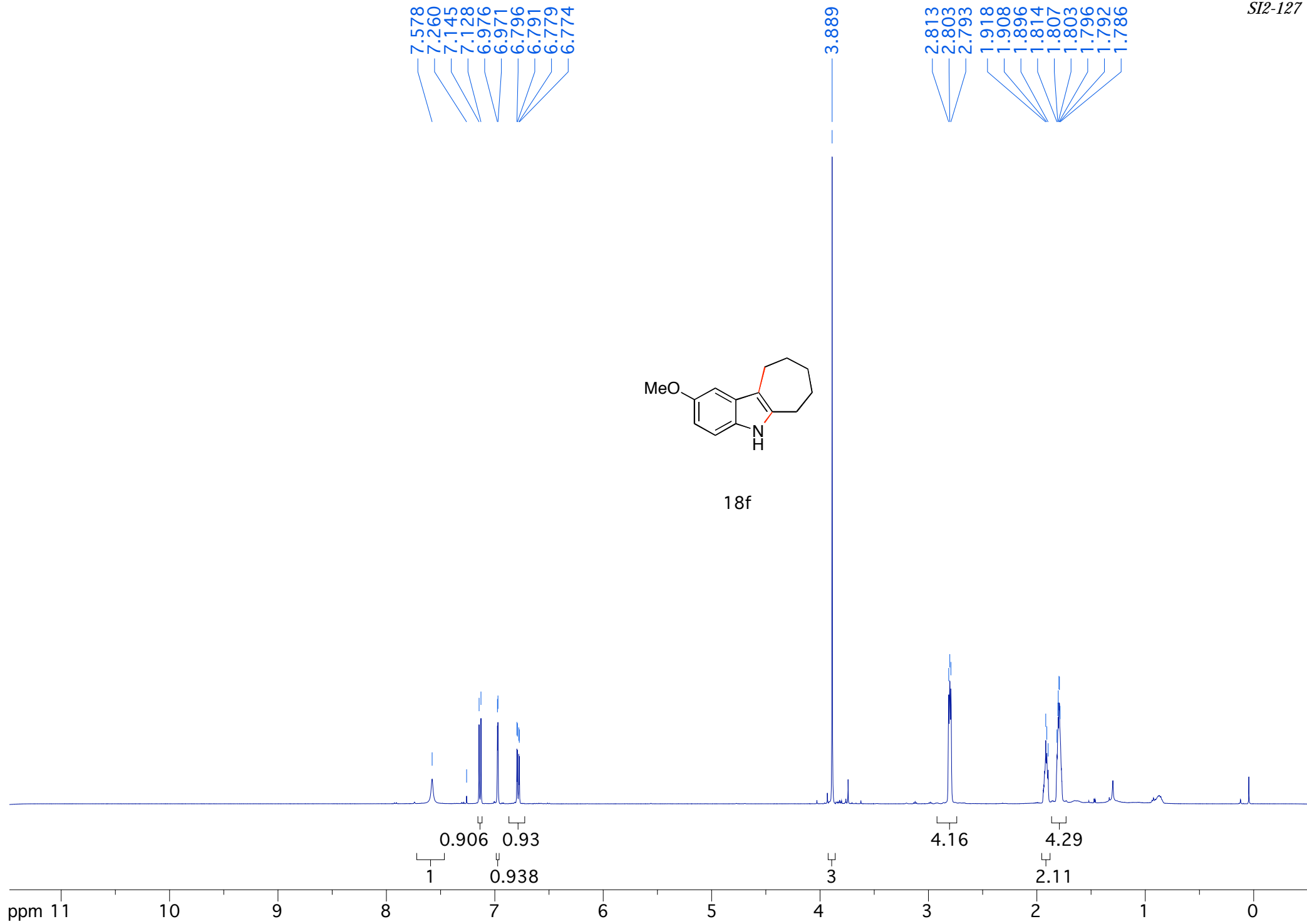


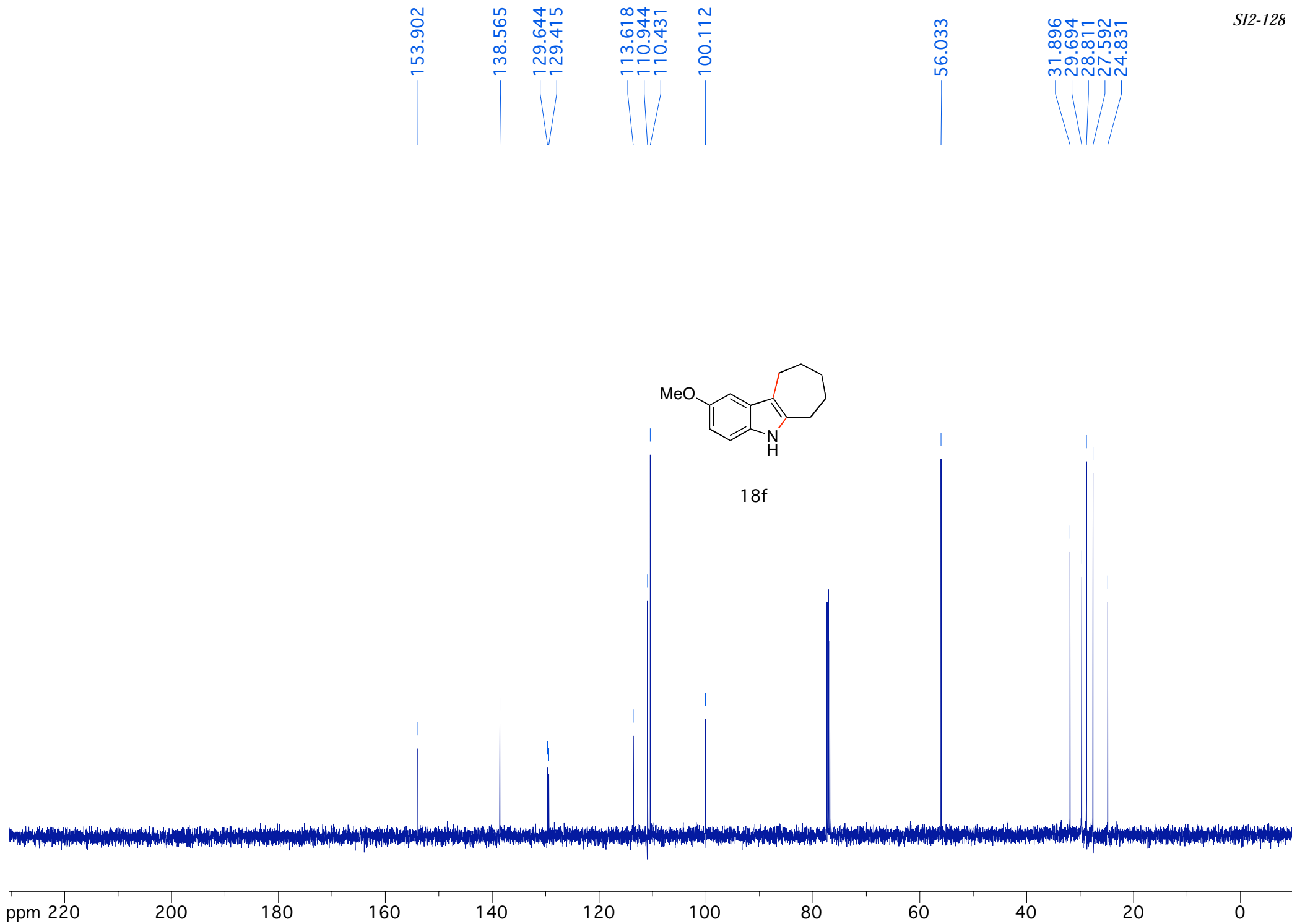
18c

ppm 220 200 180 160 140 120 100 80 60 40 20 0



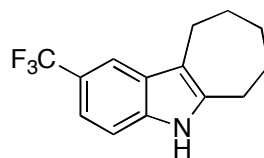




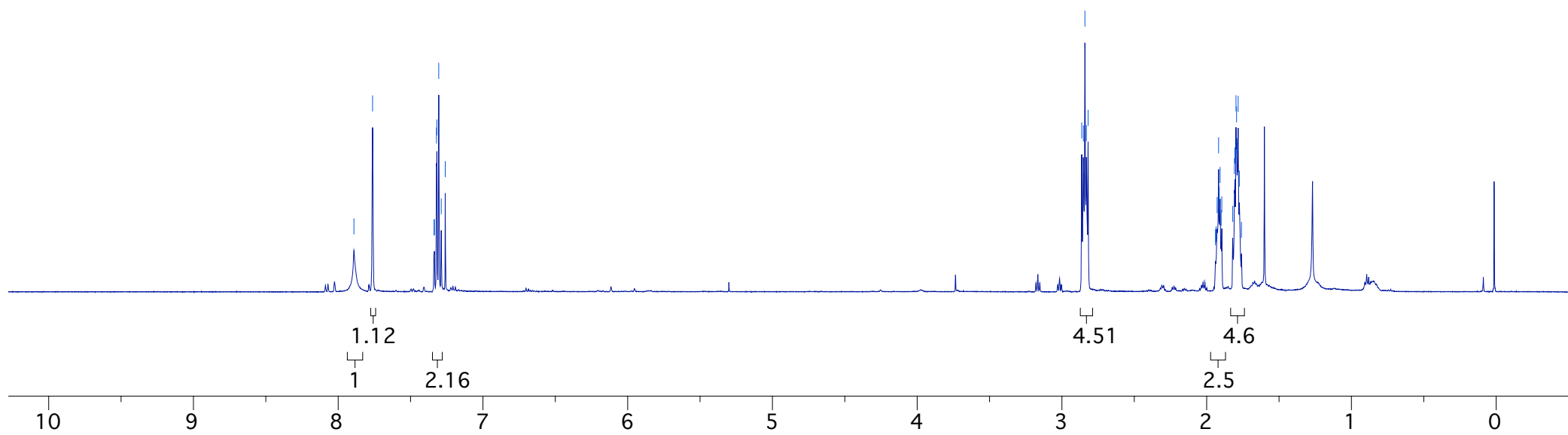


7.891
7.763
7.338
7.335
7.321
7.318
7.305
7.288
7.260

2.863
2.852
2.841
2.831
2.819
1.939
1.935
1.928
1.918
1.913
1.907
1.900
1.895
1.820
1.808
1.805
1.797
1.794
1.788
1.782
1.774
1.759



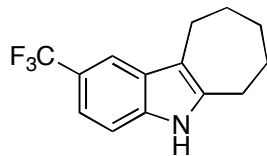
18g



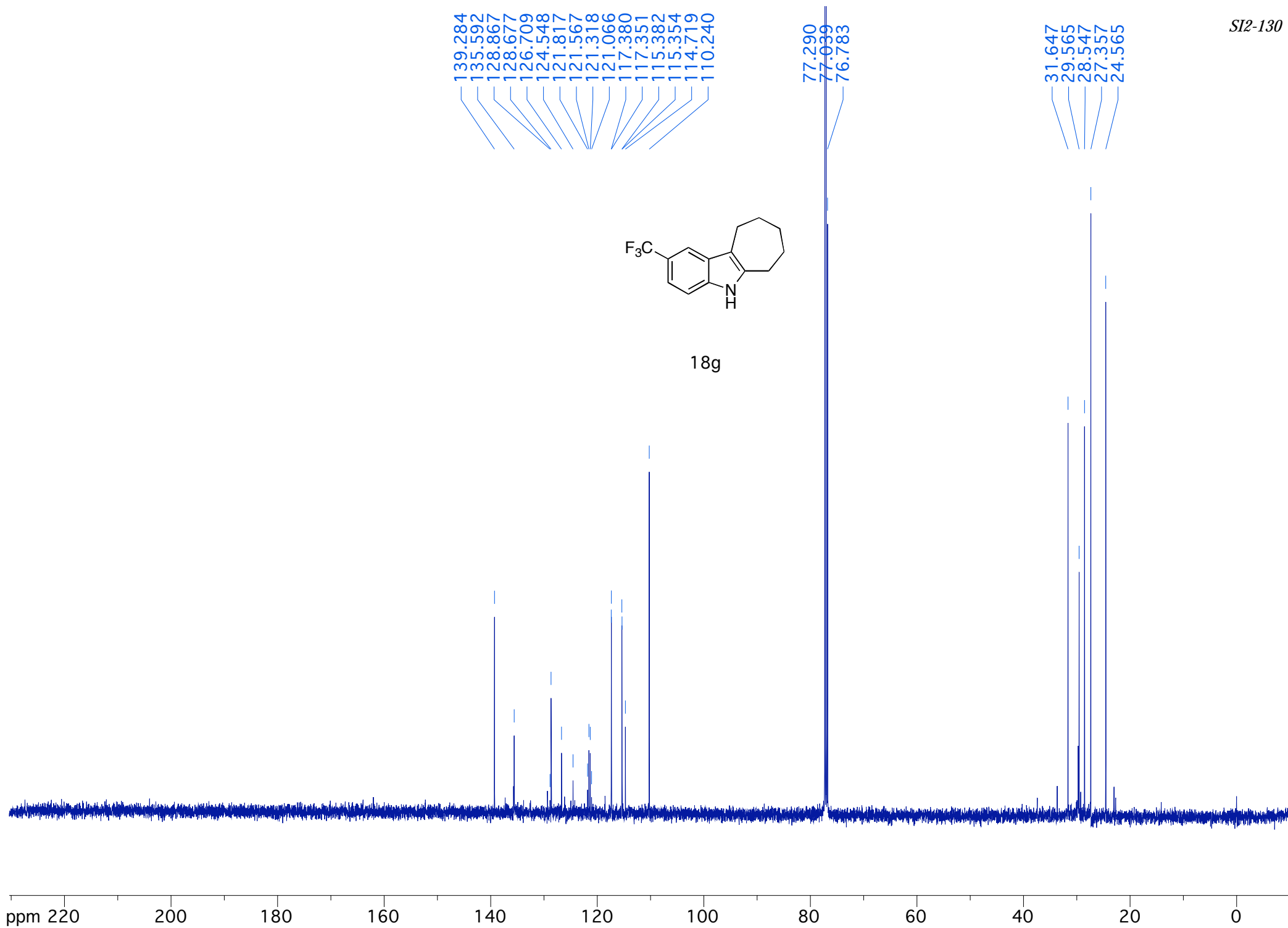
139.284
135.592
128.867
128.677
126.709
124.548
121.817
121.567
121.318
121.066
117.380
117.351
115.382
115.354
114.719
110.240

77.290
77.039
76.783

31.647
29.565
28.547
27.357
24.565



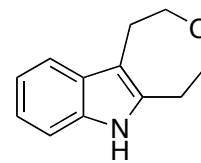
18g



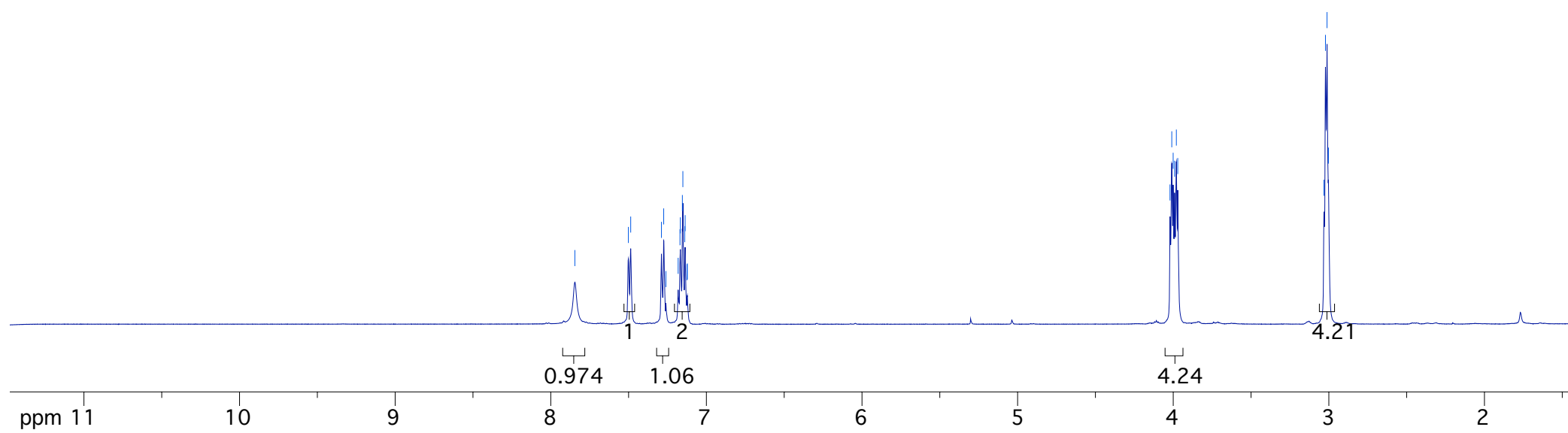
7.845
7.501
7.486
7.289
7.274
7.260
7.181
7.170
7.167
7.154
7.151
7.139
7.137
7.125

4.021
4.009
4.000
3.991
3.980
3.971

3.031
3.022
3.012
3.003



18h



135.494
134.760

128.942

121.243

119.380

117.789

112.371

110.433

77.366

77.114

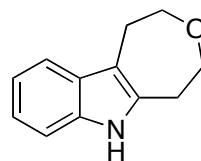
76.861

73.052

70.679

32.210

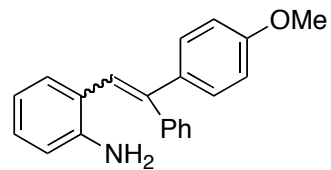
27.606



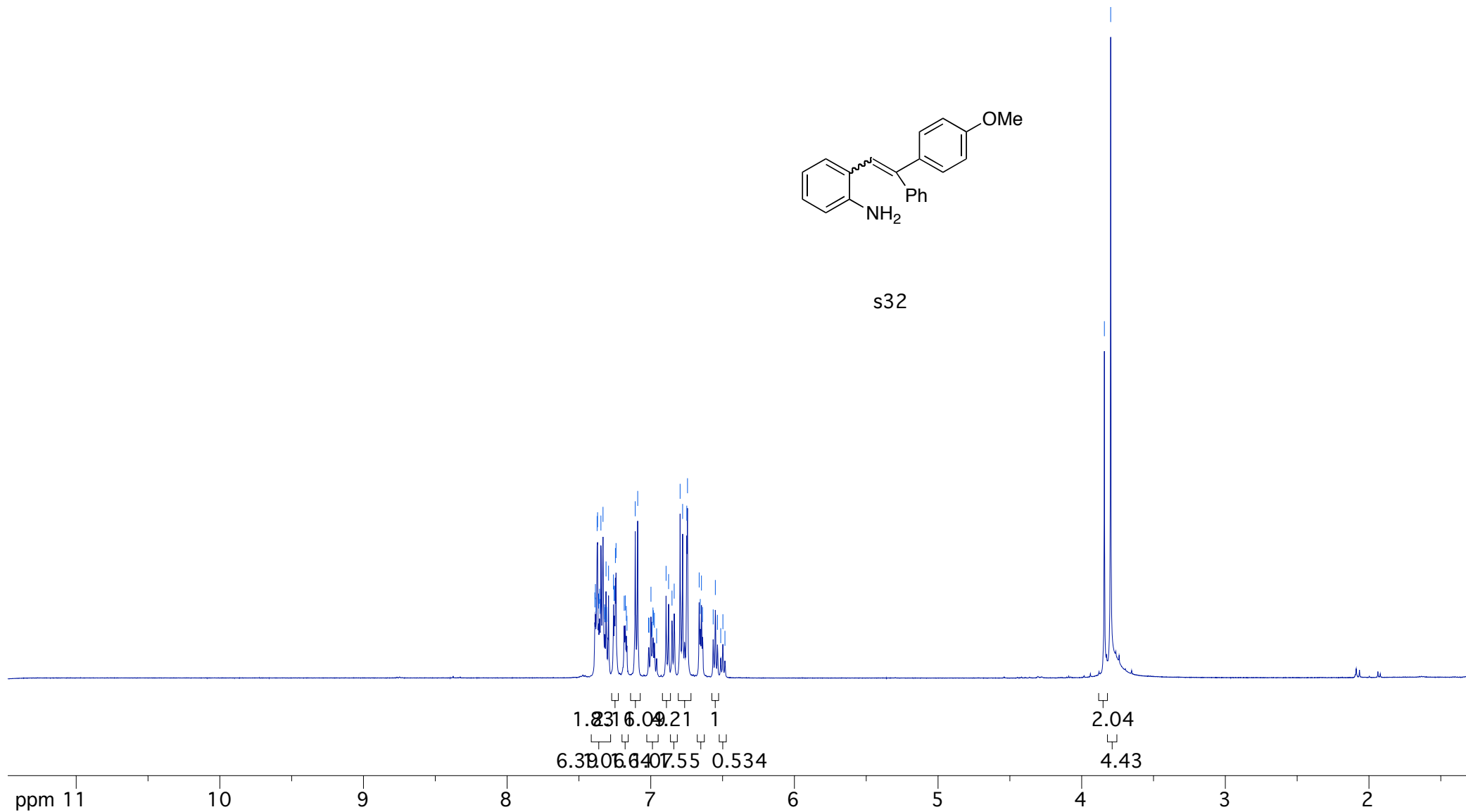
18h

ppm 220 200 180 160 140 120 100 80 60 40 20 0

7.389
7.385
7.381
7.373
7.370
7.364
7.357
7.354
7.347
7.332
7.321
7.319
7.311
7.307
7.294
7.260
7.255
7.253
7.246
7.242
7.185
7.178
7.170
7.166
7.108
7.091
7.015
7.013
6.999
6.990
6.985
6.982
6.975
6.959
6.893
6.876
6.852
6.837
6.796
6.778
6.749
6.744
6.663
6.655
6.647
6.640
6.566
6.551
6.536
6.513
6.498
6.484
3.842
3.798



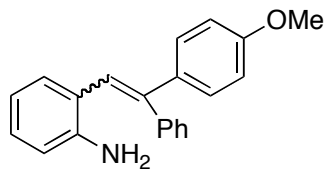
s32



159.382
158.898
144.632
144.530
143.795
143.645
140.254
136.009
132.277
131.703
130.509
130.426
130.382
129.282
128.252
128.193
127.928
127.841
127.621
127.352
123.904
123.834
122.802
118.262
118.189
115.528
115.426
113.629

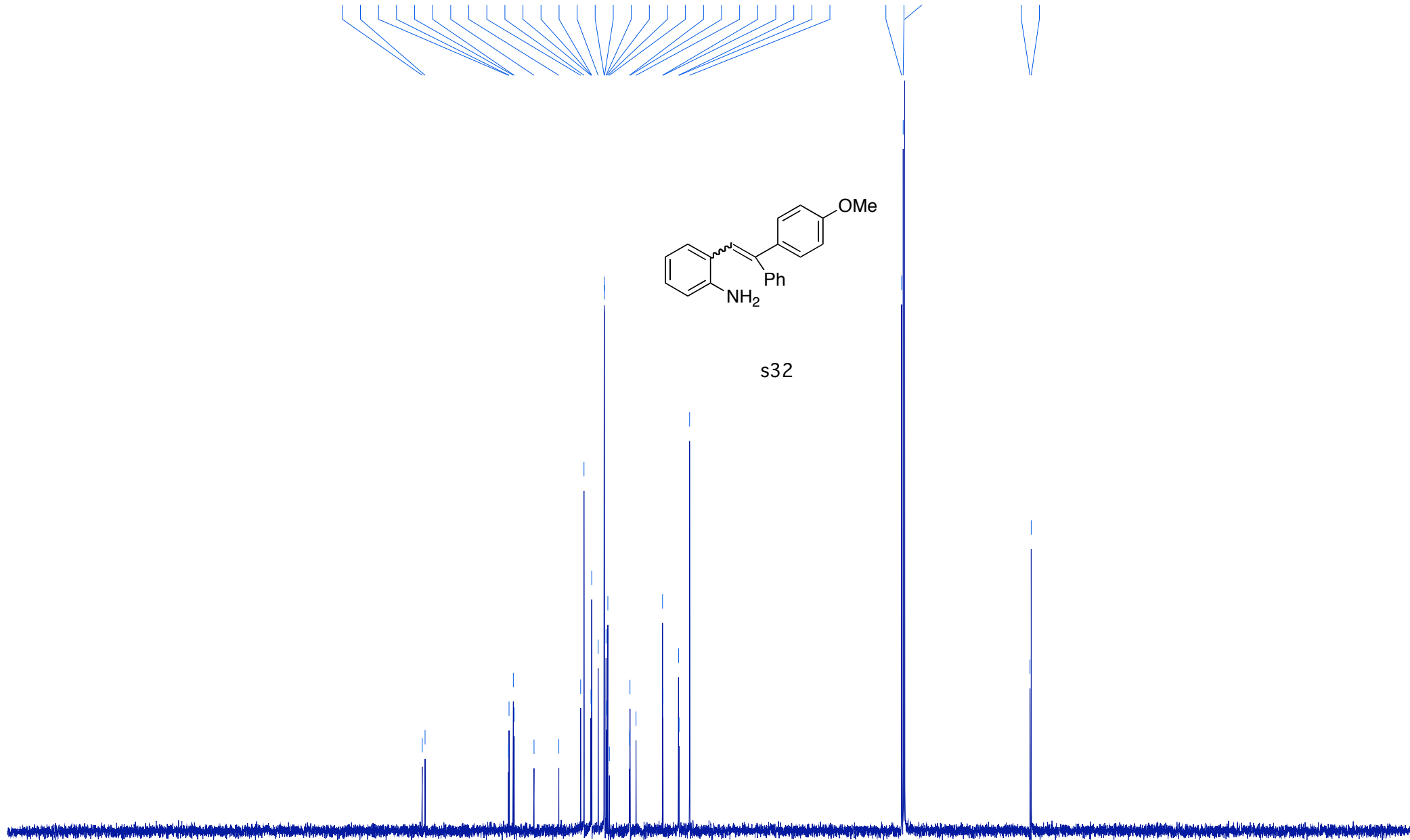
77.342
77.086
76.834

55.386
55.180



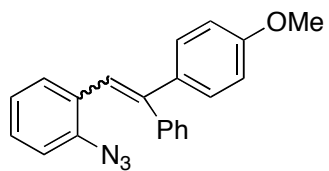
s32

ppm 220 200 180 160 140 120 100 80 60 40 20 0

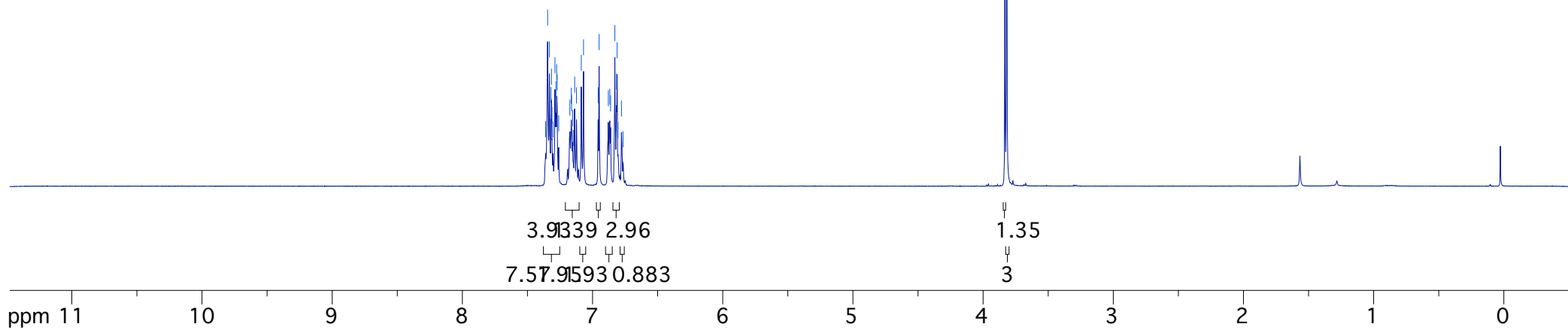


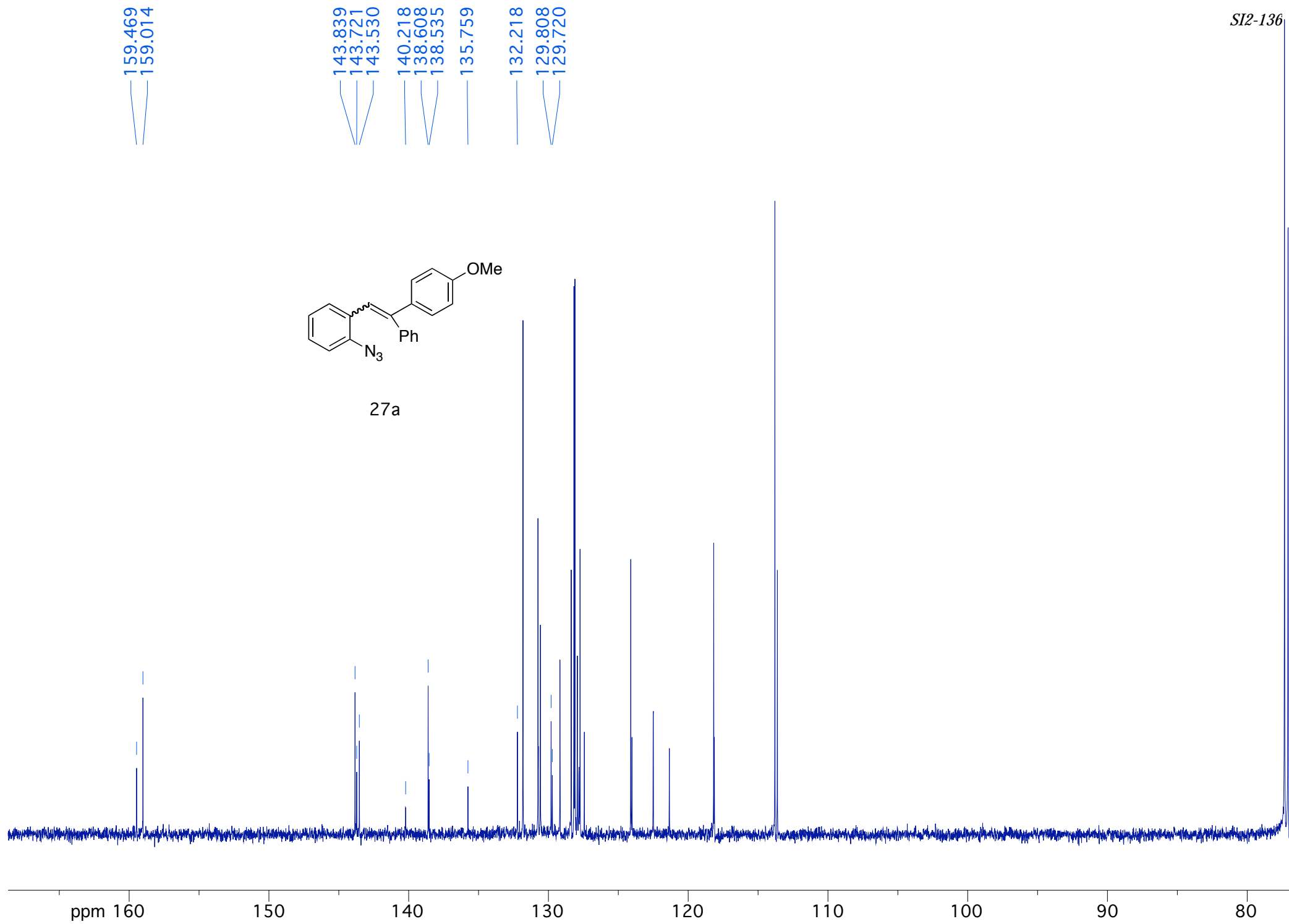
7.361
7.345
7.332
7.320
7.316
7.312
7.303
7.289
7.281
7.276
7.272
7.260
7.174
7.164
7.161
7.153
7.148
7.137
7.124
7.087
7.069
6.957
6.949
6.879
6.867
6.862
6.829
6.816
6.811
6.804
6.778
6.766

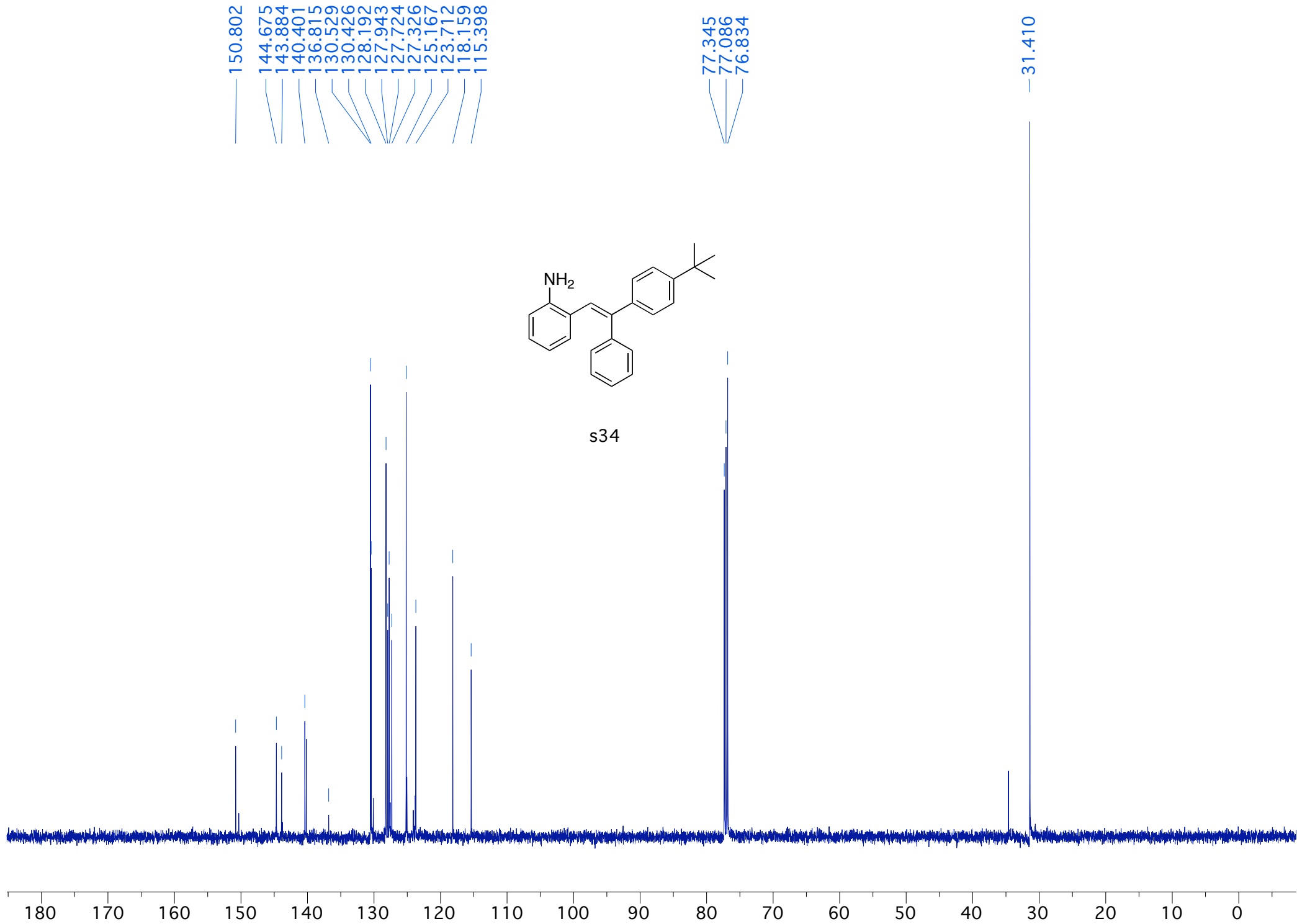
3.833
3.819

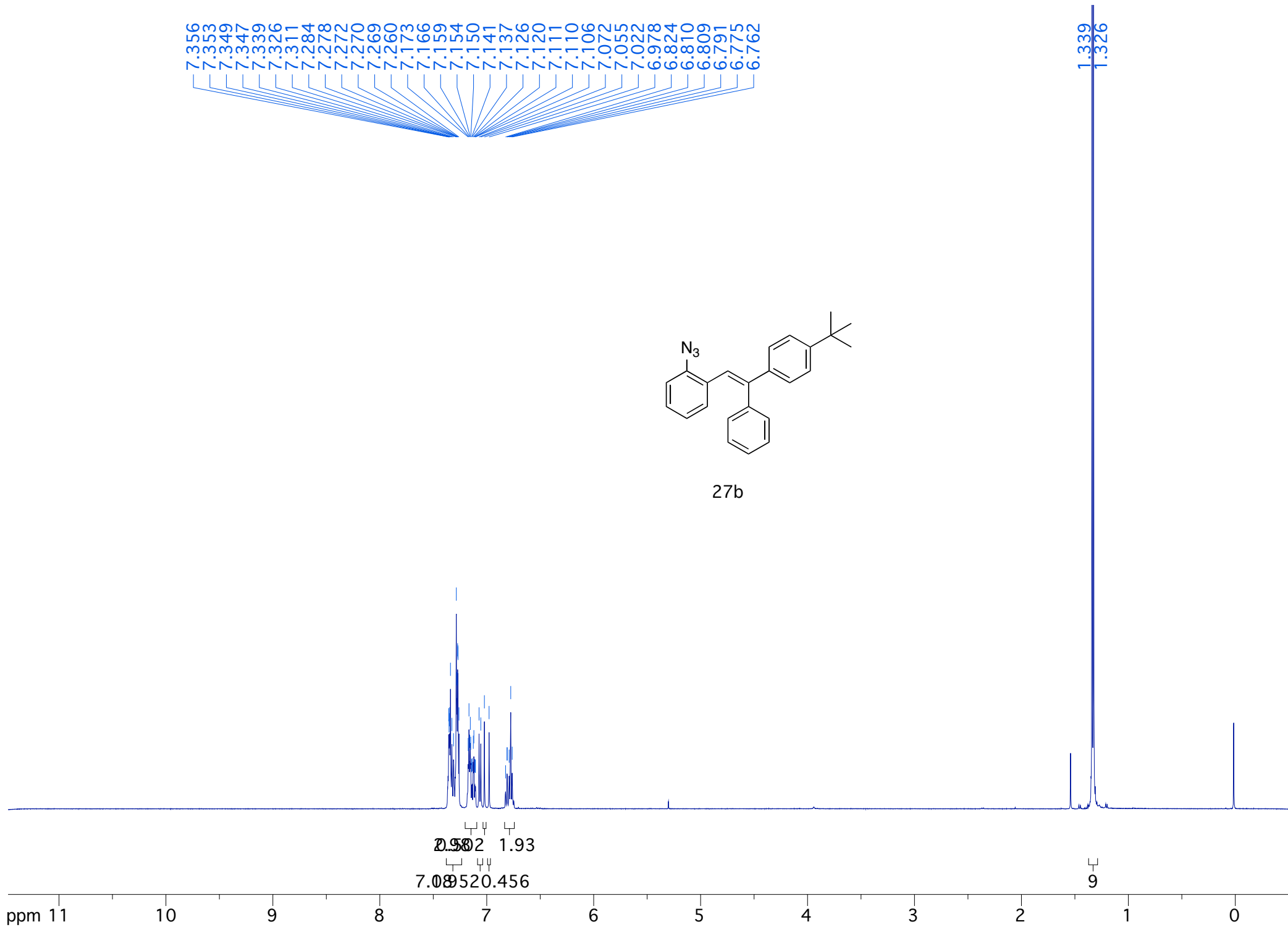


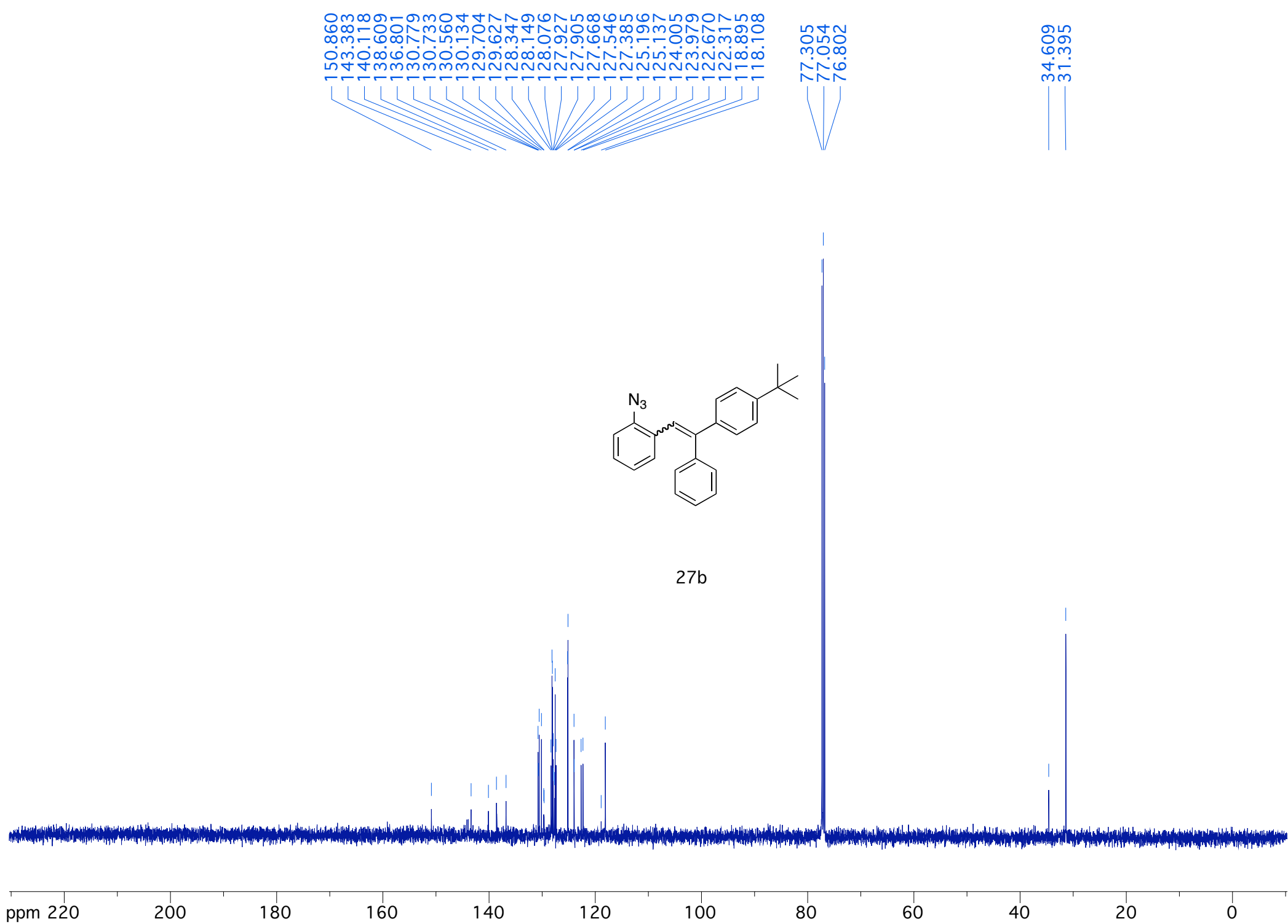
27a



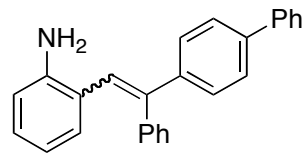








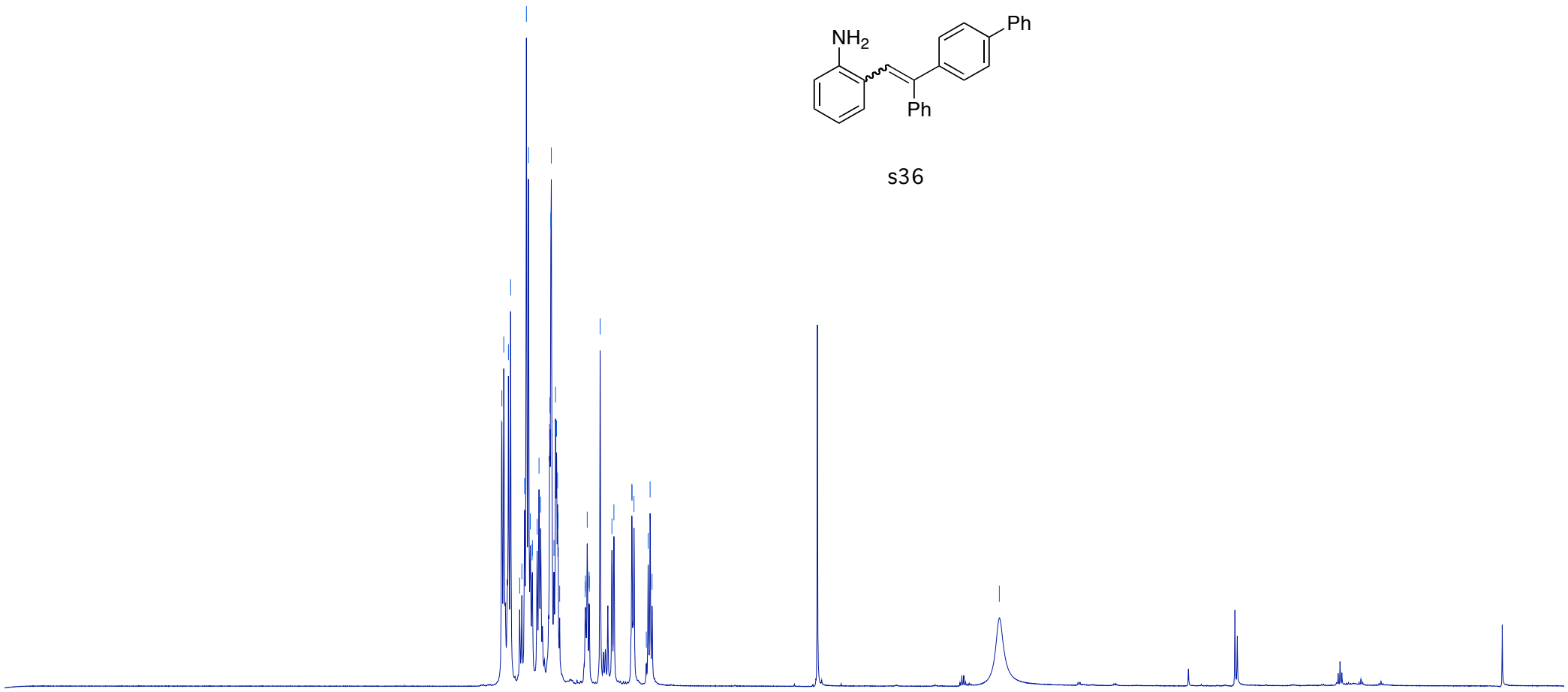
7.701
7.699
7.685
7.649
7.633
7.564
7.547
7.527
7.513
7.497
7.483
7.470
7.467
7.431
7.417
7.405
7.337
7.334
7.327
7.323
7.303
7.291
7.284
7.276
7.272
7.260
7.067
7.064
7.051
7.036
7.034
6.953
6.863
6.848
6.712
6.711
6.696
6.602
6.588
6.573
6.559
3.920



s36

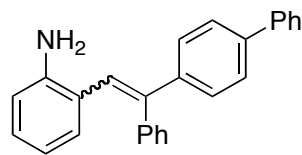
5.07
4.11
2.09
1.67
1.03
0.882
0.911
1.06
1.08
2

ppm 11 10 9 8 7 6 5 4 3 2 1 0

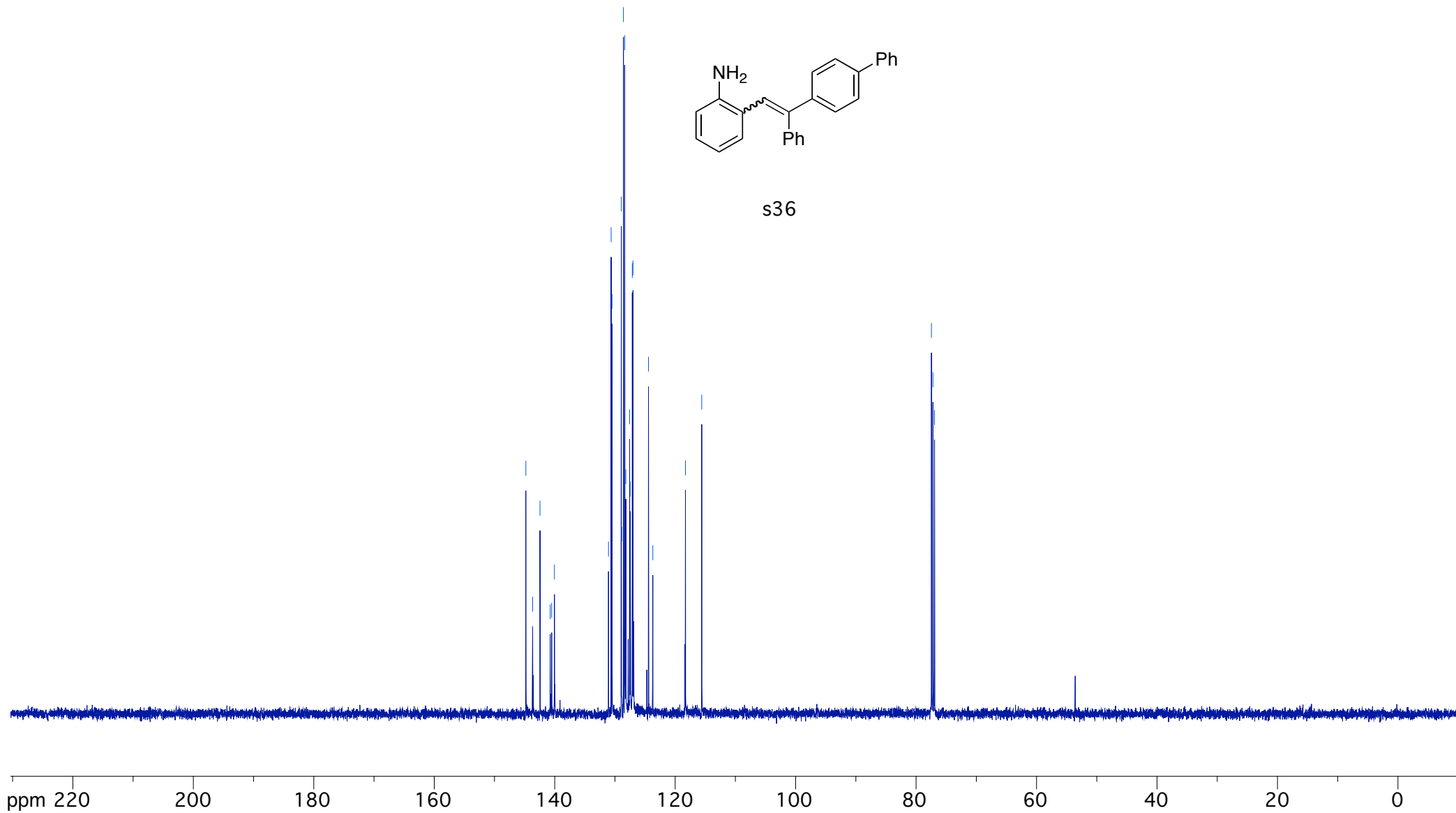


144.793
143.665
142.442
140.750
140.507
140.048
131.072
130.630
130.484
128.941
128.869
128.589
128.383
128.195
127.561
127.475
127.118
127.007
124.432
123.712
118.293
115.590

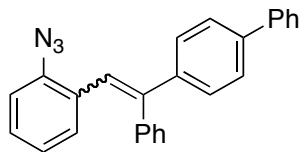
77.451
77.199
76.941



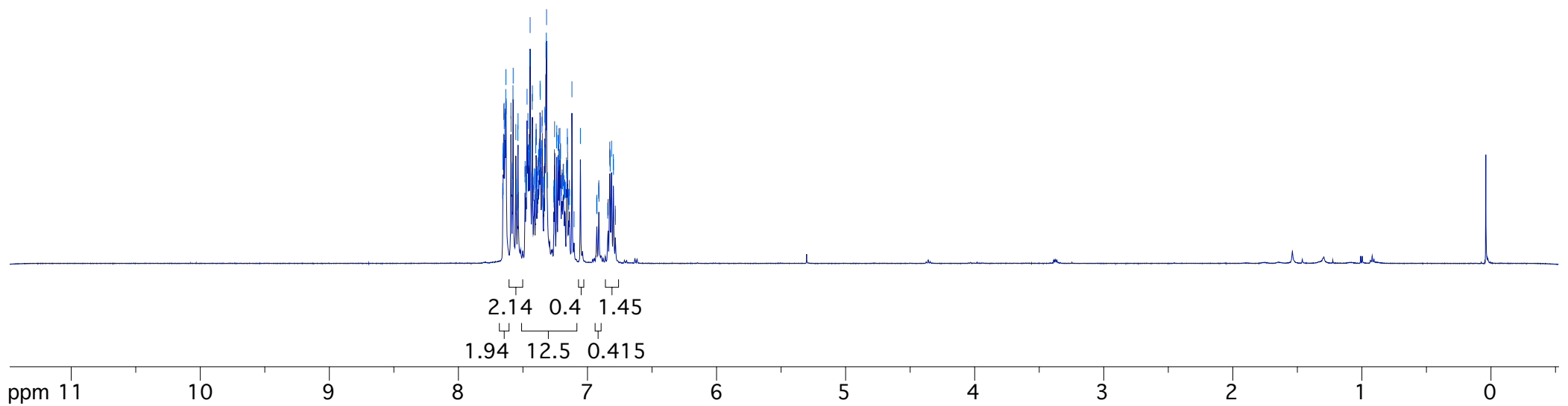
s36



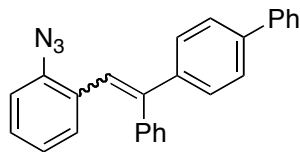
7.657
7.655
7.653
7.652
7.650
7.648
7.646
7.645
7.642
7.641
7.639
7.636
7.634
7.632
7.630
7.630
7.593
7.592
7.589
7.582
7.577
7.576
7.555
7.551
7.544
7.539
7.538
7.535
7.483
7.479
7.477
7.476
7.475
7.474
7.468
7.466
7.461
7.458
7.456
7.453
7.450
7.448
7.446
7.444
7.433
7.428
7.427
7.417
7.416
7.414
7.412
7.408
7.404
7.403
7.401
7.399
7.398
7.396
7.393
7.391
7.389
7.387
7.385
7.382
7.380
7.378
7.376
7.374
7.373
7.371
7.368
7.366
7.362
7.360
7.358
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7.353
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7.349
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7.343
7.339
7.337
7.335
7.332
7.330
7.328



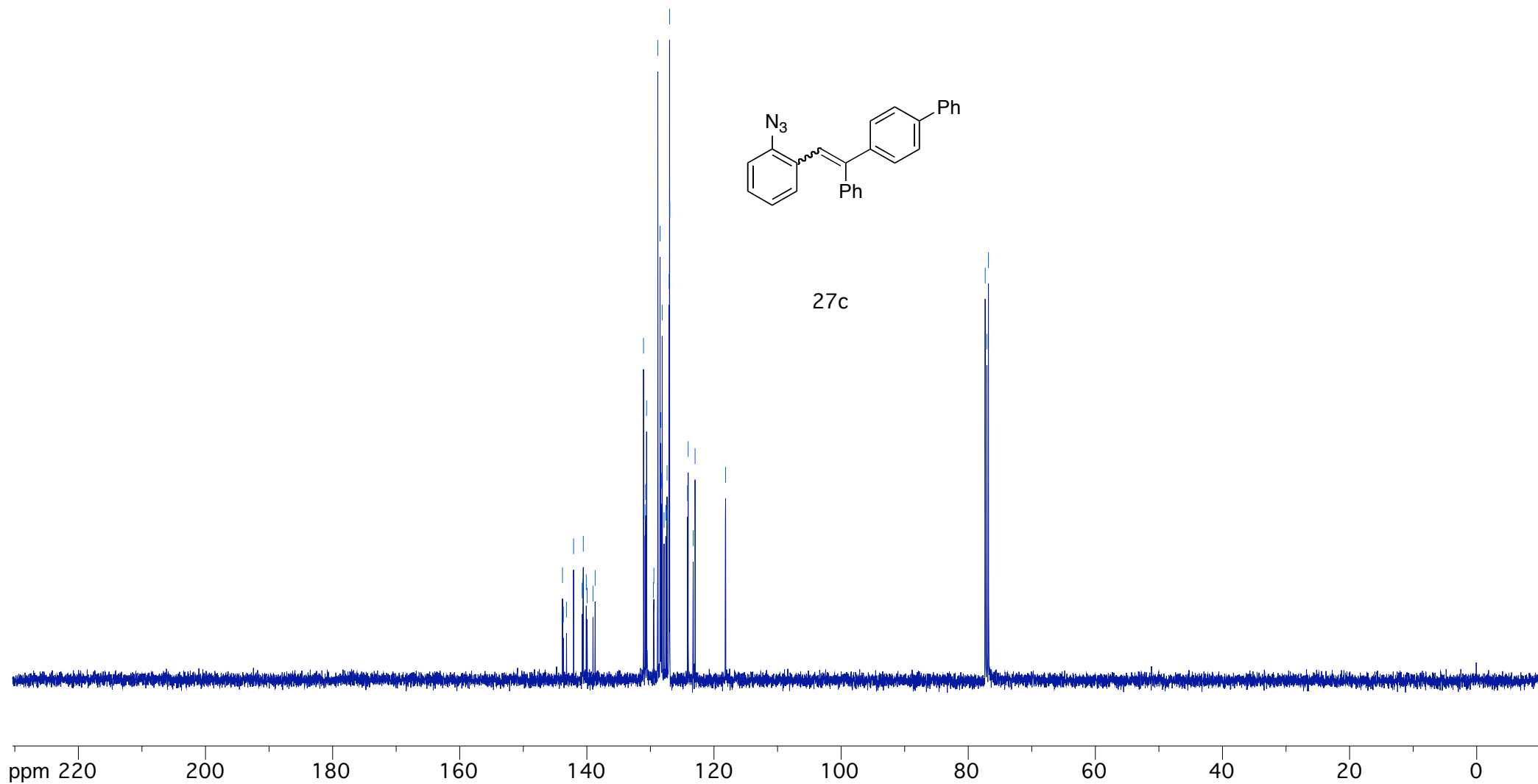
27c

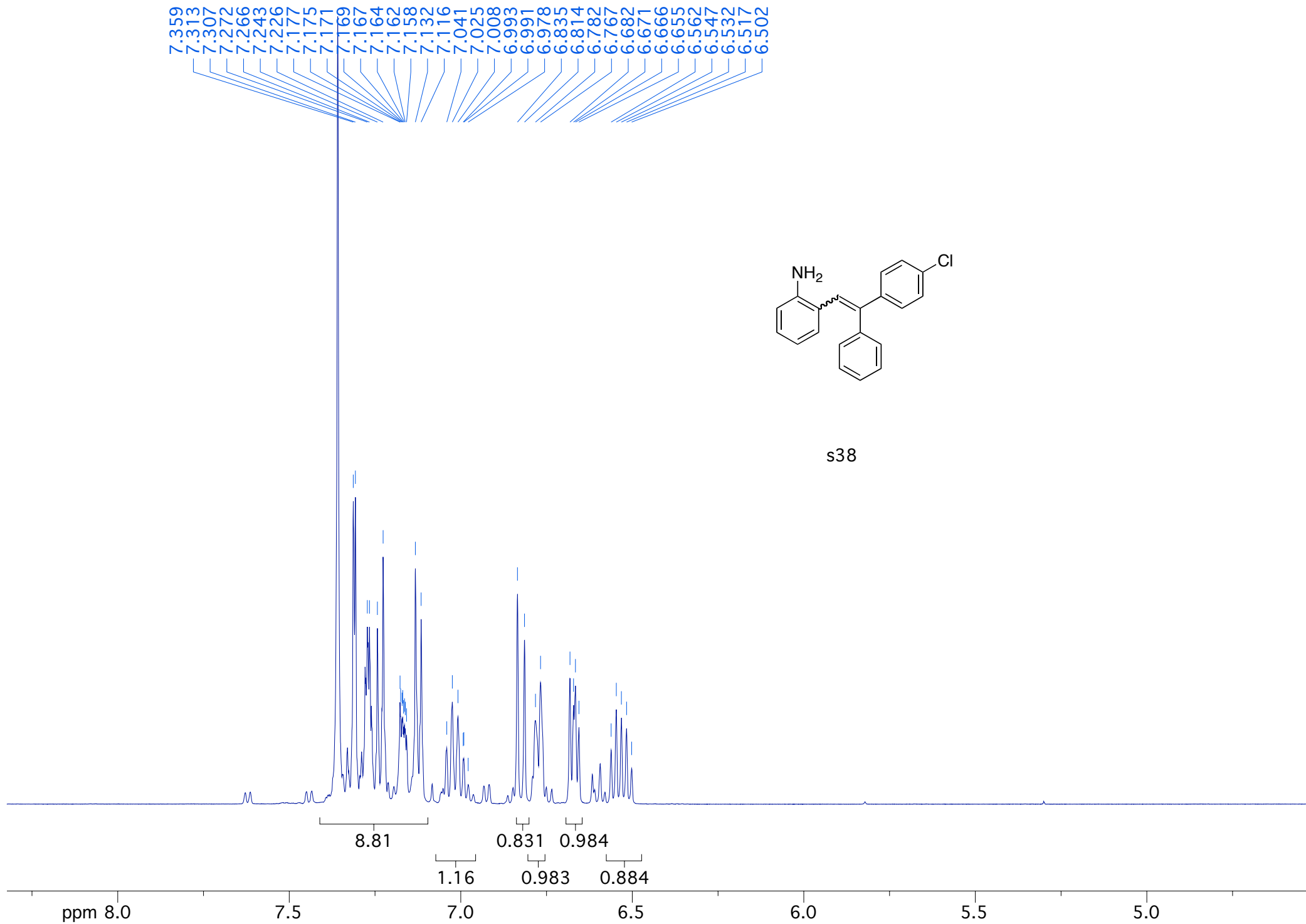


143.838
143.695
143.207
142.090
140.739
140.622
140.562
140.092
139.959
139.034
138.698
131.087
130.837
130.764
130.604
129.529
129.456
128.839
128.486
128.278
128.149
127.855
127.575
127.413
127.385
127.061
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126.944
124.167
124.065
123.272
122.977
118.174
77.331
77.075
76.820

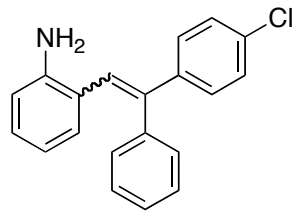


27c

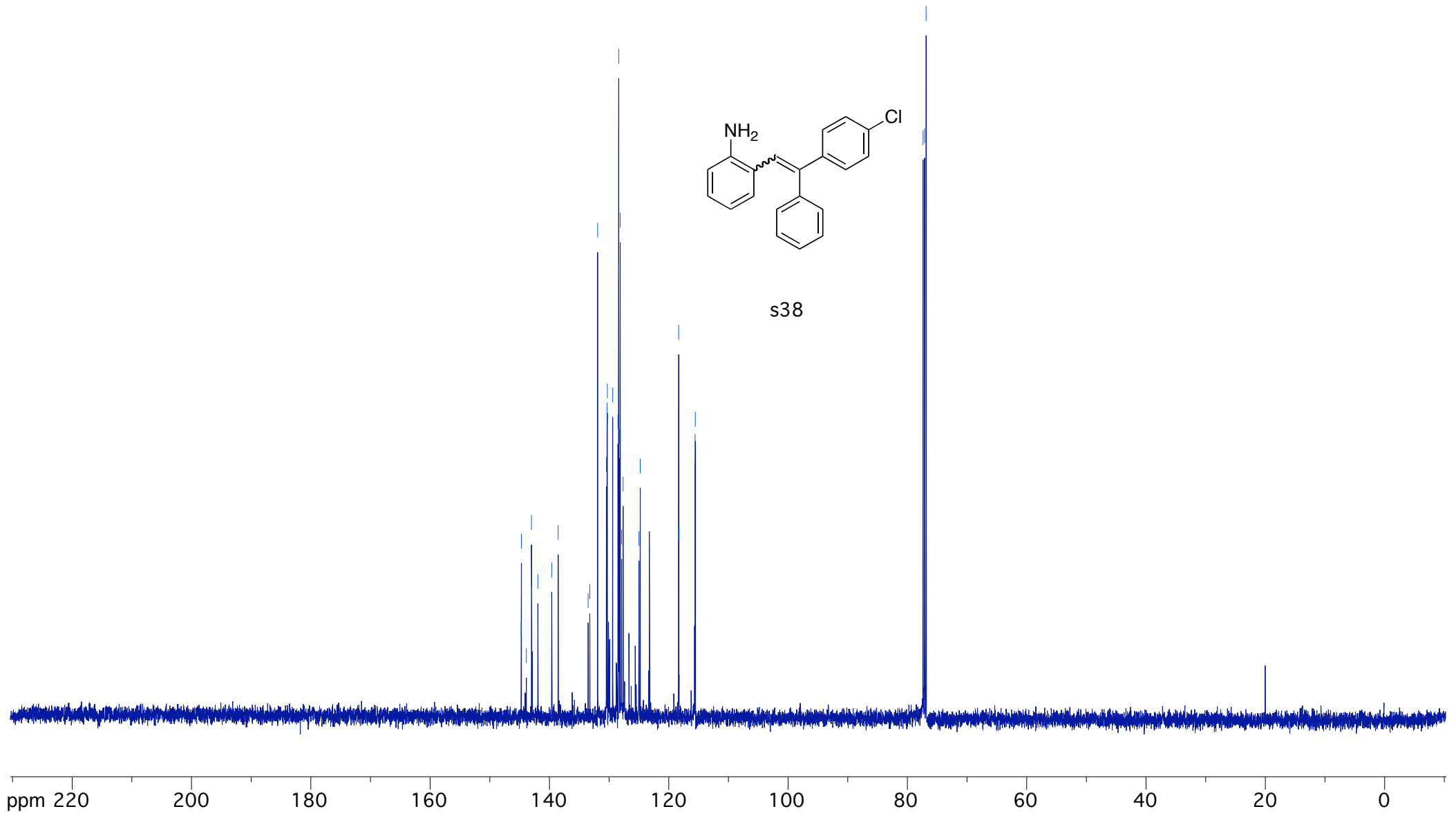




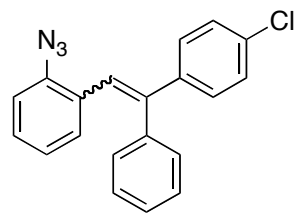
144.743
144.705
143.868
143.016
142.957
141.944
139.622
138.535
133.510
133.232
131.925
130.452
130.352
130.294
129.399
128.521
128.382
128.359
128.295
128.134
127.903
127.649
124.993
124.785
118.336
118.276
115.588
115.545
77.375
77.116
76.864



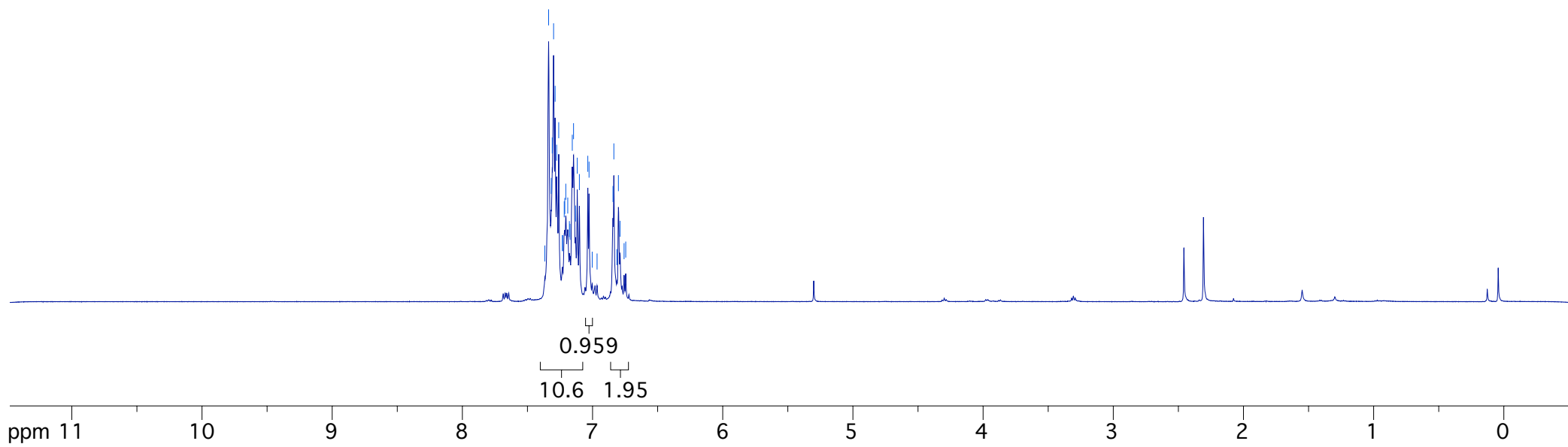
s38



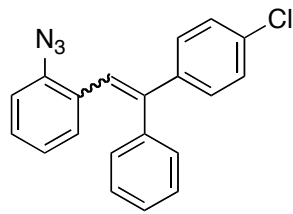
7.366
7.338
7.317
7.310
7.299
7.287
7.276
7.260
7.231
7.231
7.218
7.213
7.206
7.191
7.178
7.173
7.156
7.146
7.131
7.118
7.101
7.036
7.027
7.003
6.965
6.843
6.836
6.814
6.801
6.789
6.758
6.745



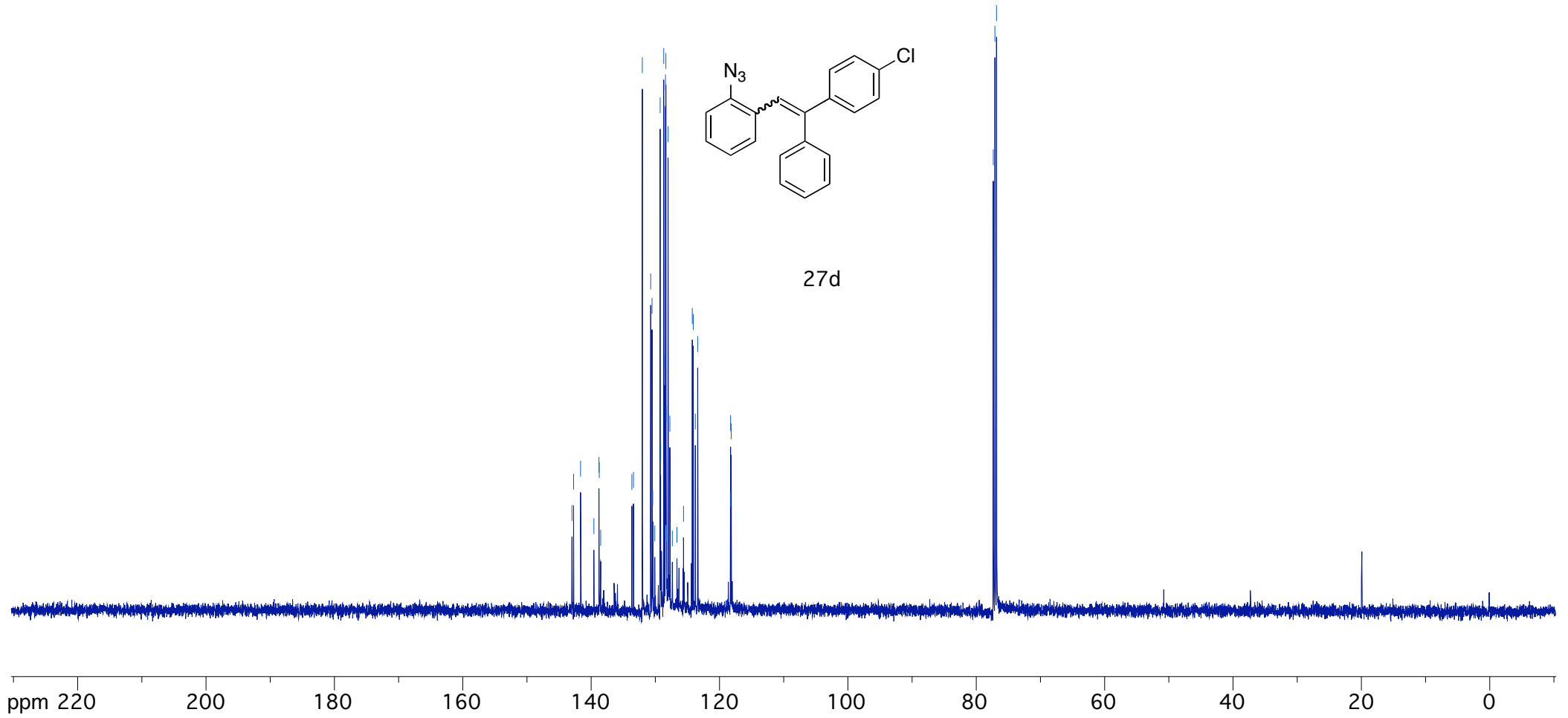
27d



142.988
142.736
141.649
139.575
138.785
138.740
138.513
133.657
133.407
132.027
130.723
130.511
130.411
130.088
129.250
129.172
128.692
128.553
128.413
128.356
128.313
128.267
128.012
127.736
127.356
126.636
125.607
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124.094
123.769
123.403
118.305
118.274
118.175
77.353
77.099
76.848

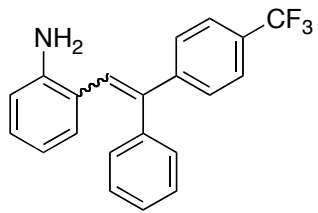


27d

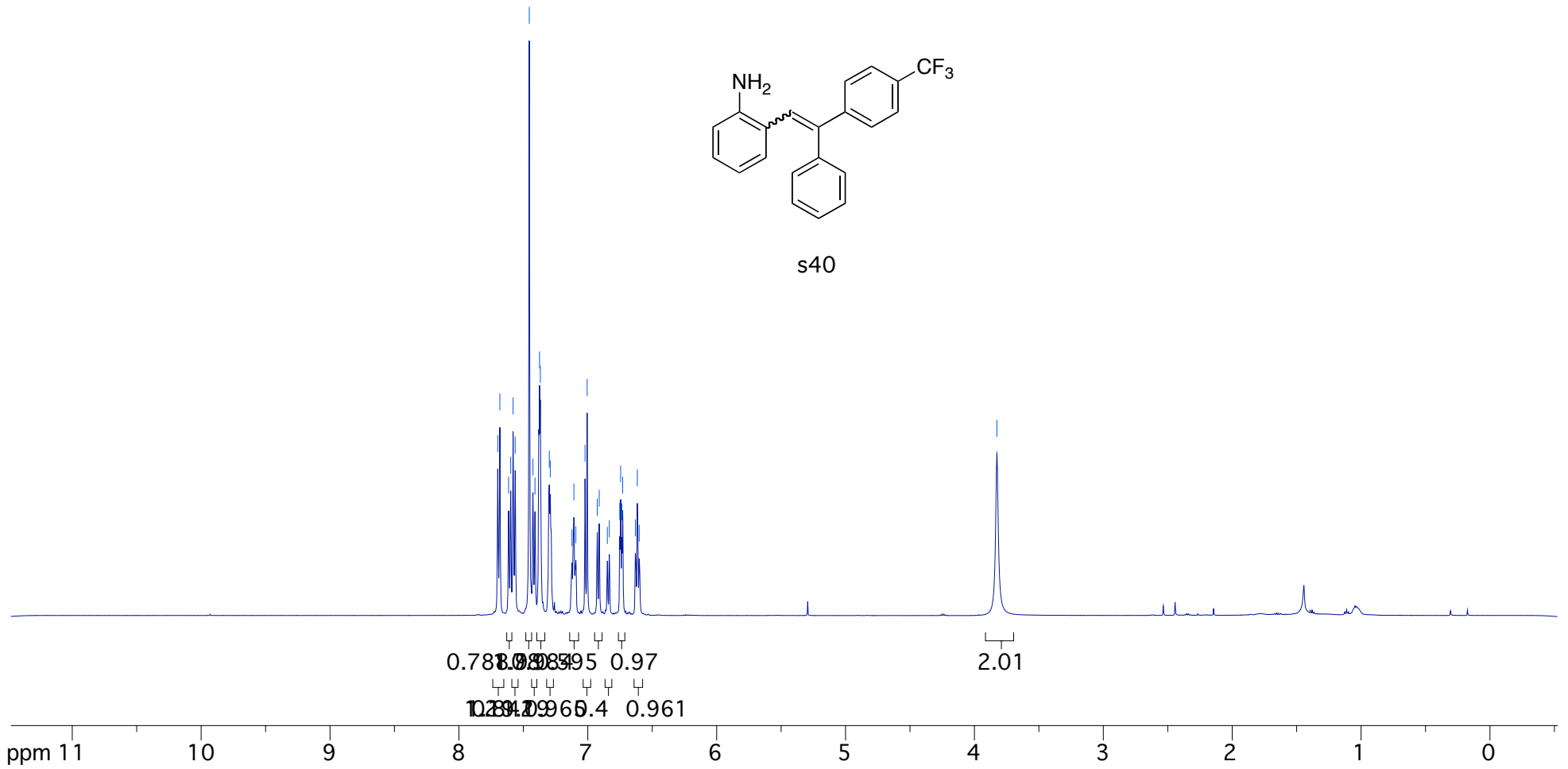


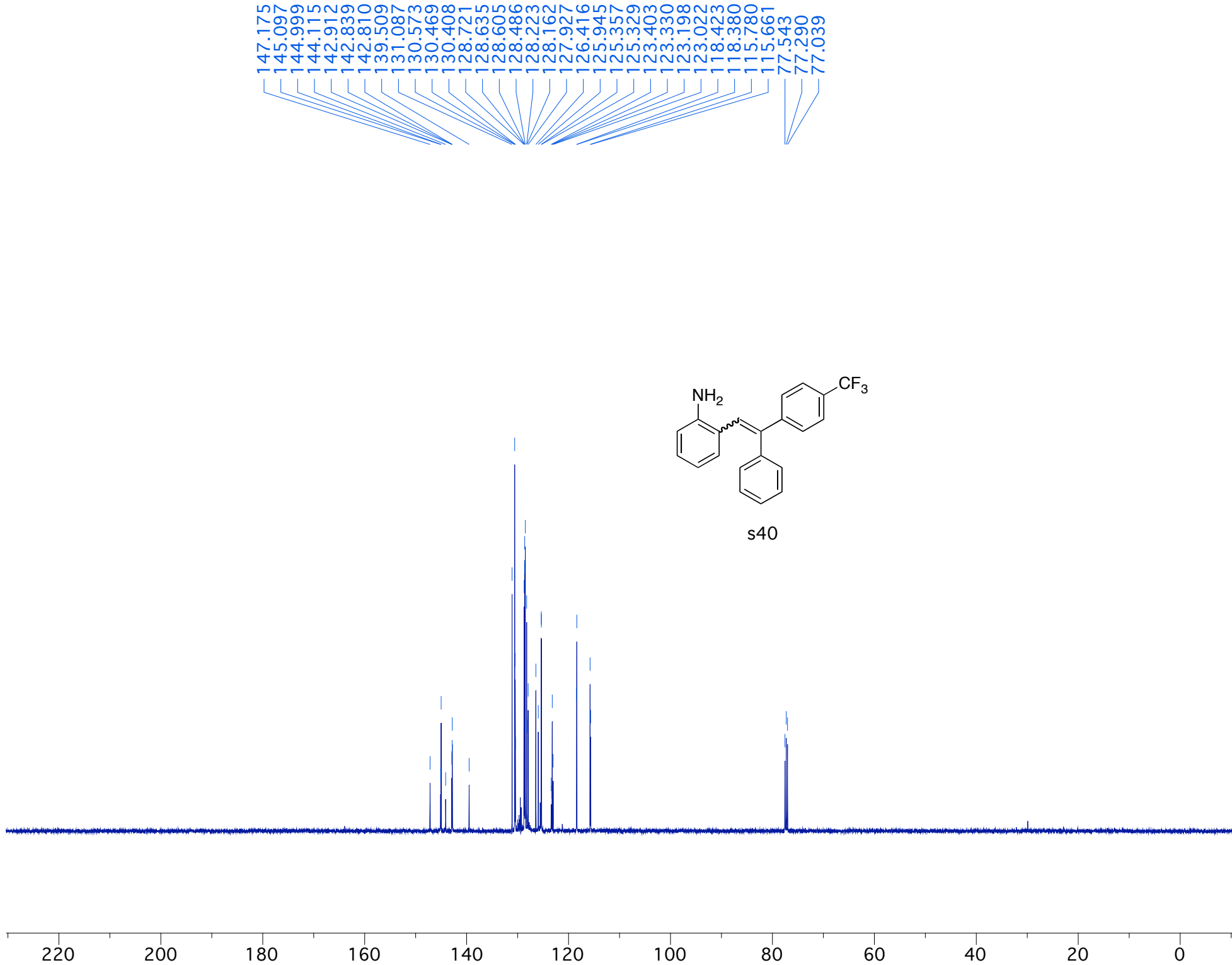
7.699
7.682
7.614
7.598
7.580
7.563
7.454
7.426
7.410
7.374
7.368
7.299
7.291
7.123
7.108
7.093
7.021
7.005
6.927
6.911
6.848
6.833
6.752
6.745
6.736
6.729
6.631
6.616
6.601

3.826

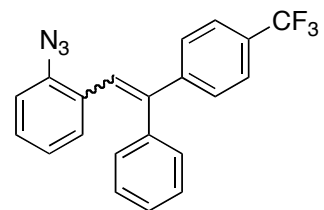


s40

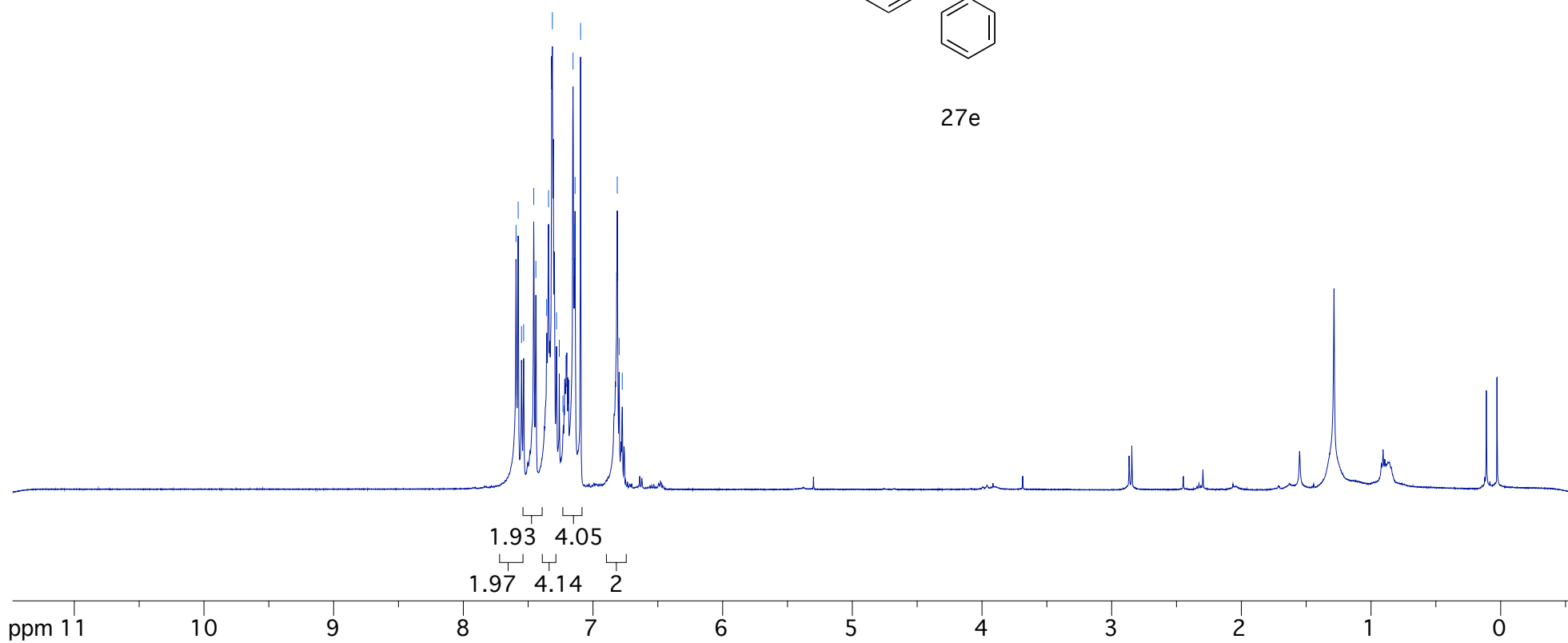


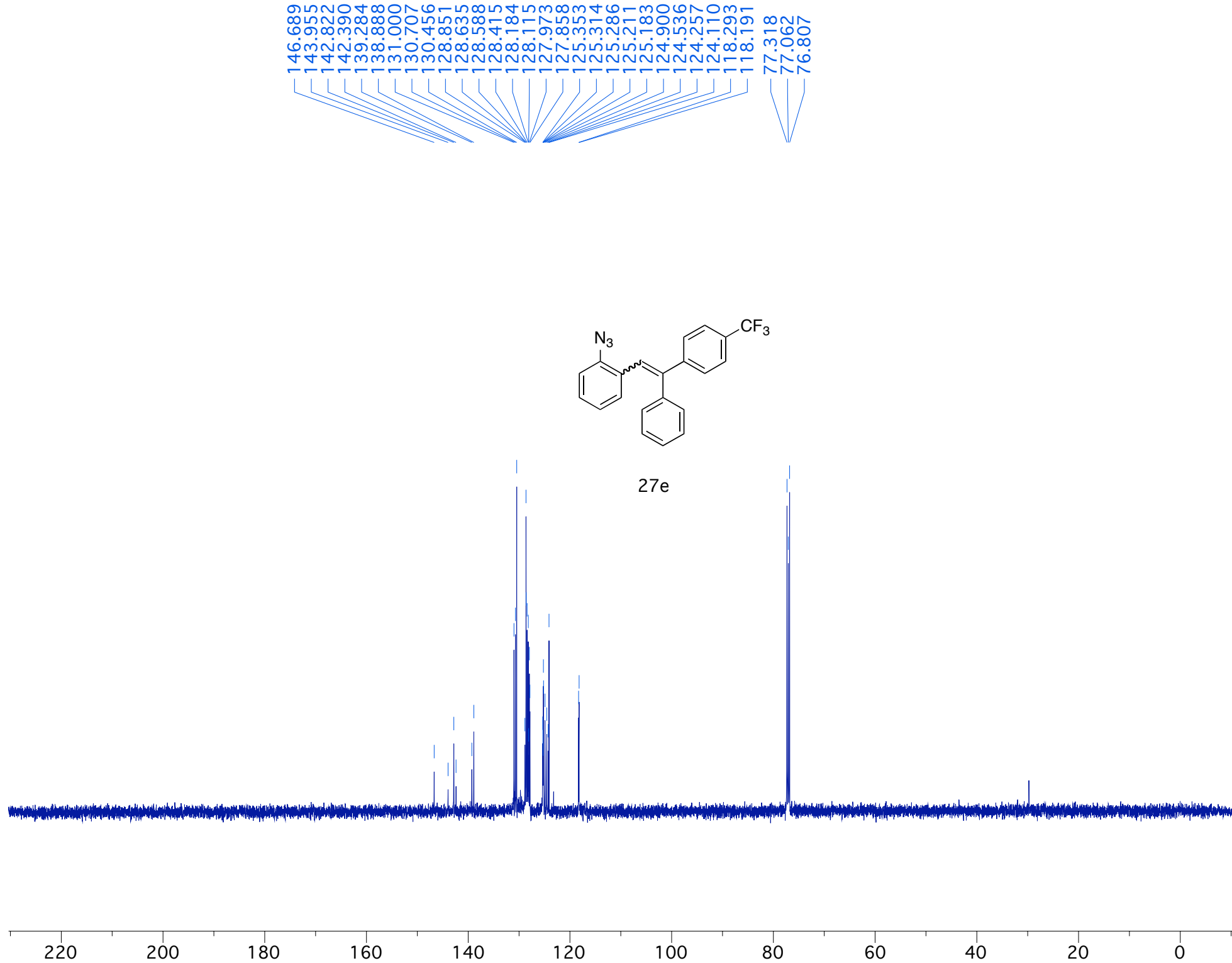


7.593
7.577
7.551
7.535
7.457
7.441
7.357
7.343
7.313
7.281
7.260
7.232
7.154
7.147
7.145
7.138
7.096
6.813
6.798
6.774

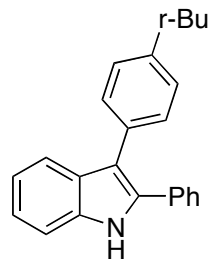


27e



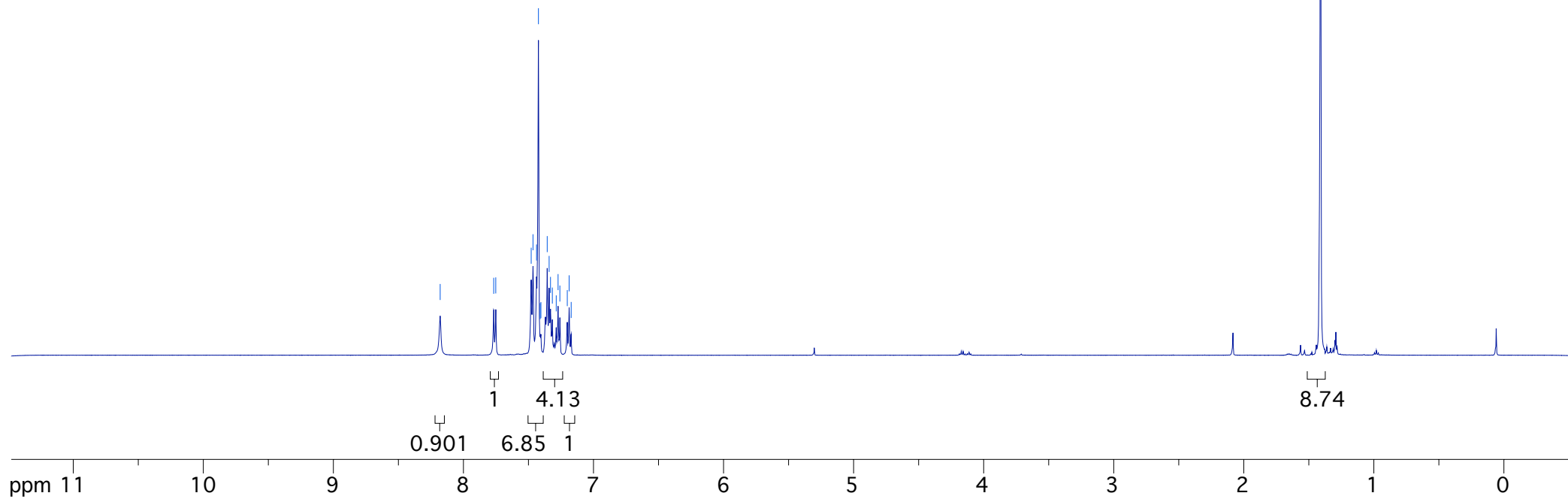


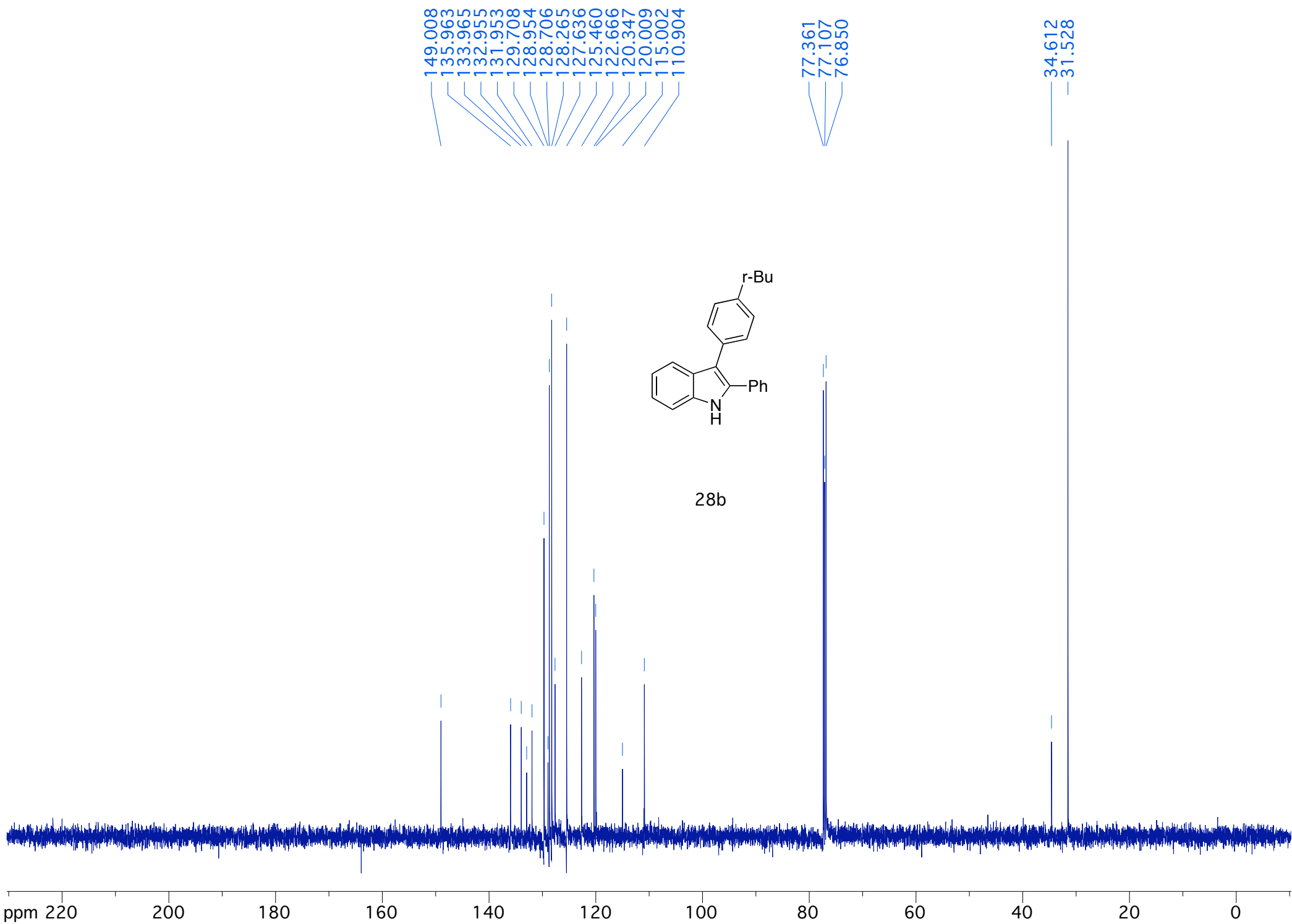
8.179
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7.751
7.479
7.465
7.438
7.423
7.410
7.404
7.356
7.341
7.330
7.316
7.286
7.272
7.258
7.201
7.187
7.172



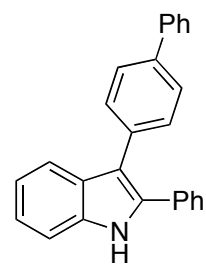
28b

1.409

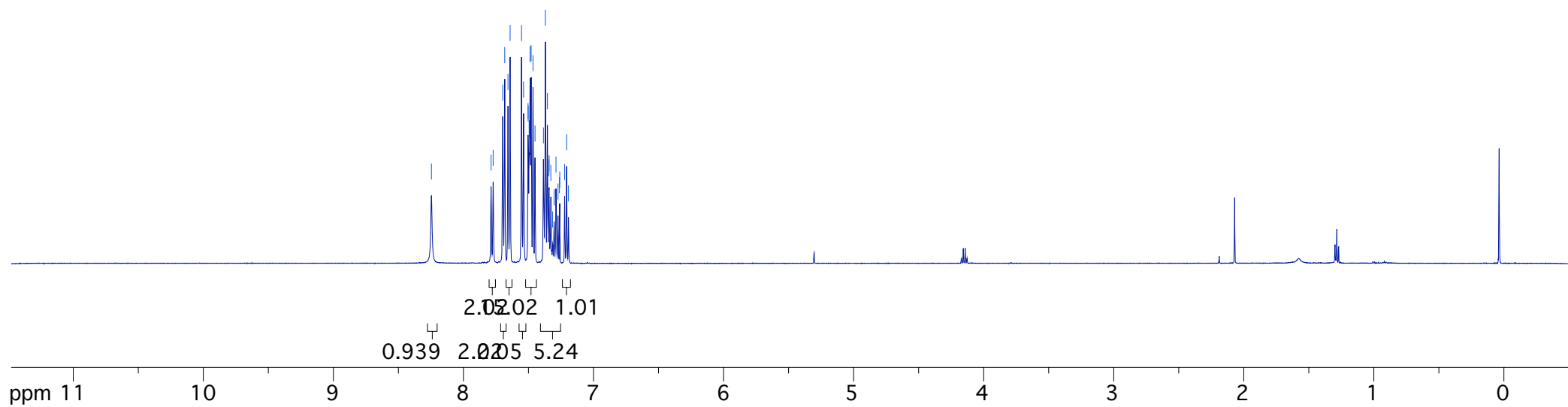


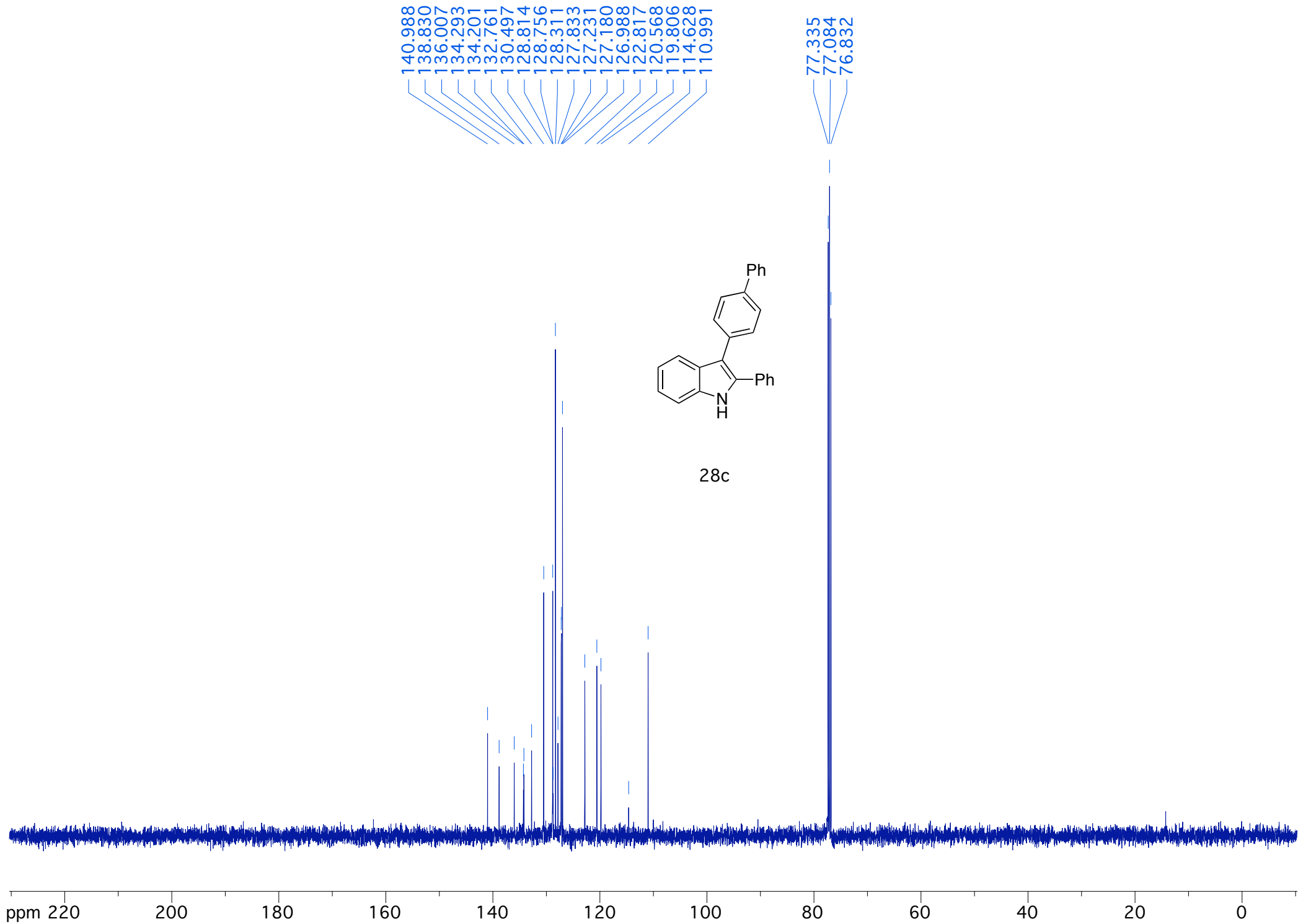


8.246
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7.682
7.657
7.641
7.553
7.538
7.503
7.502
7.495
7.493
7.487
7.479
7.465
7.449
7.385
7.370
7.354
7.343
7.343
7.341
7.328
7.315
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7.288
7.273
7.262
7.259
7.222
7.206
7.192

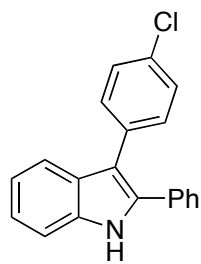


28c

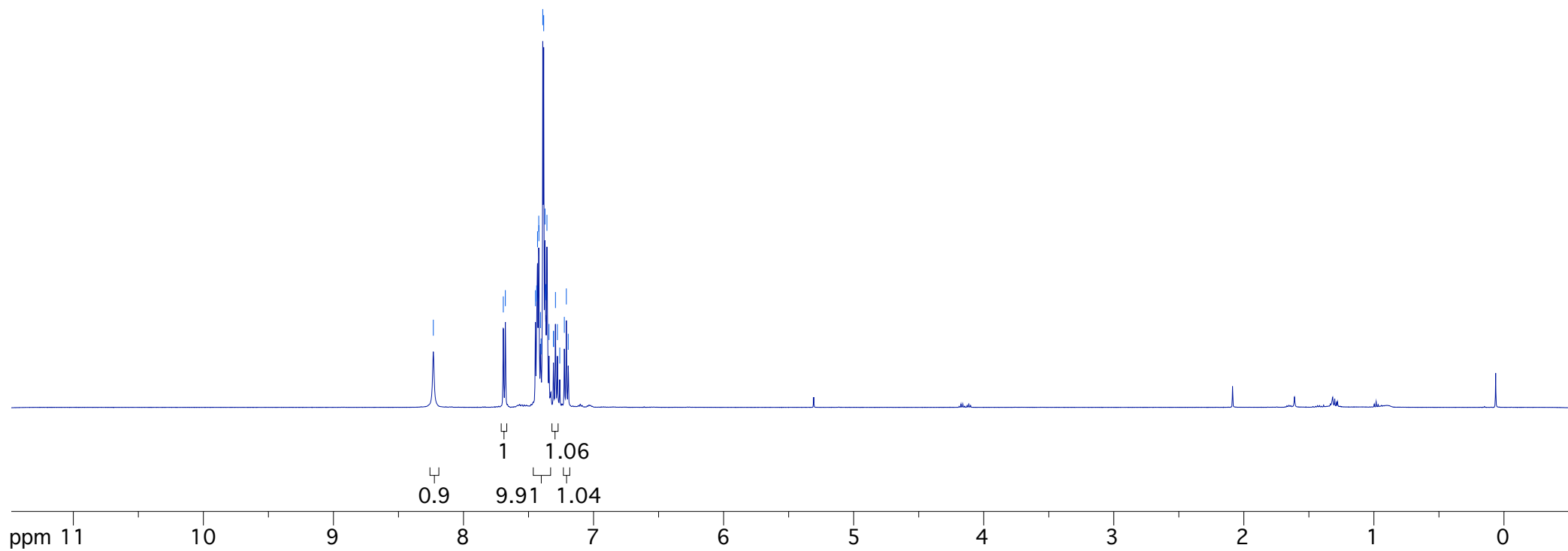


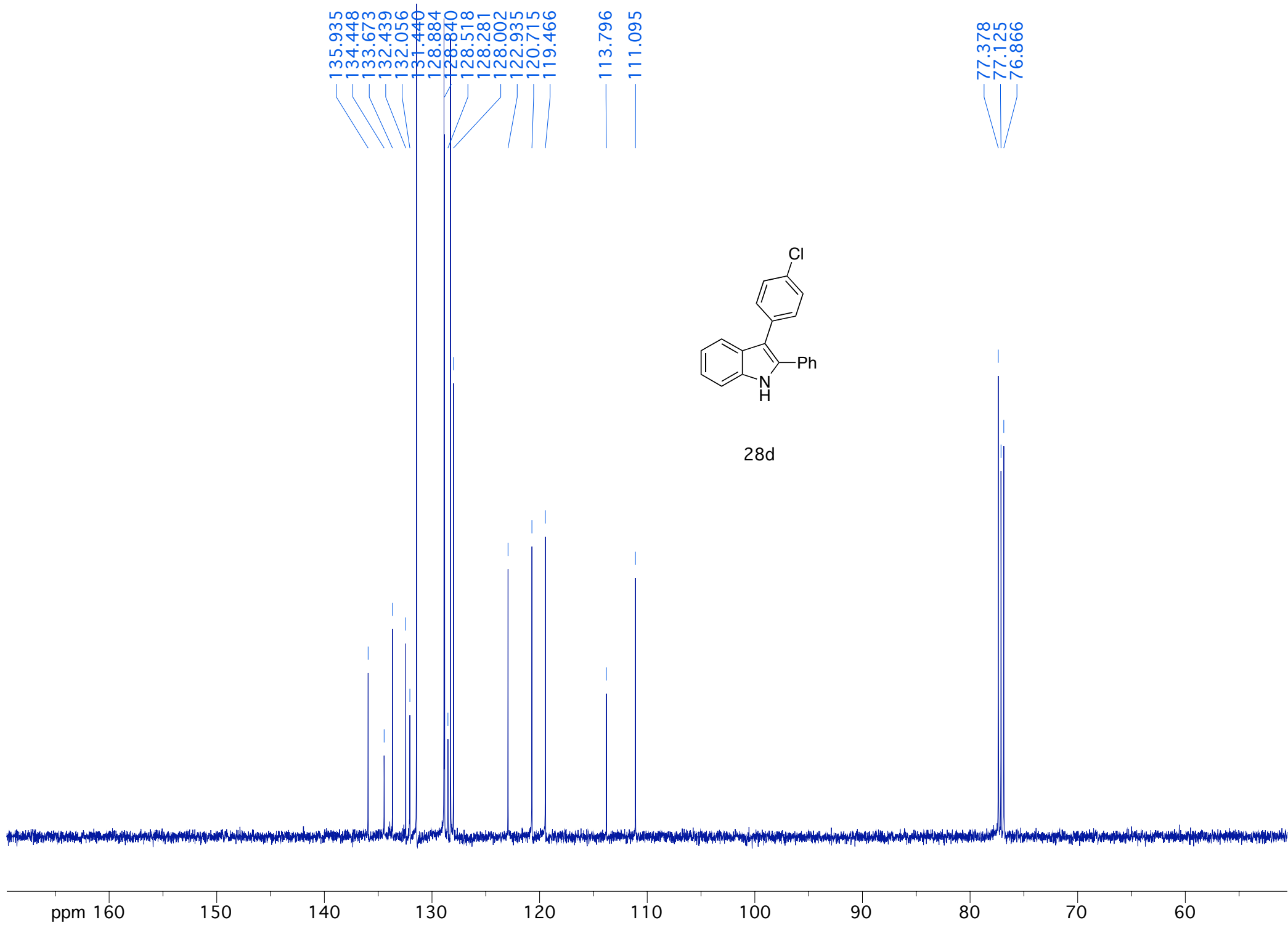


8.232
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7.431
7.421
7.420
7.408
7.404
7.391
7.383
7.373
7.367
7.358
7.343
7.308
7.307
7.293
7.278
7.260
7.225
7.209
7.195

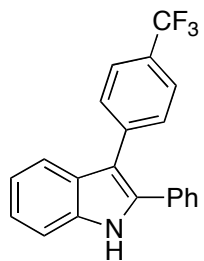


28d

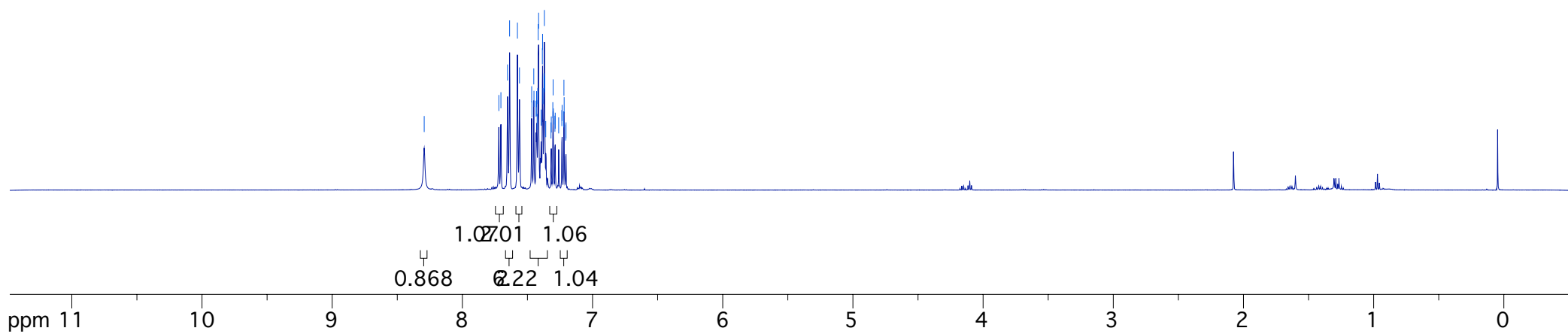


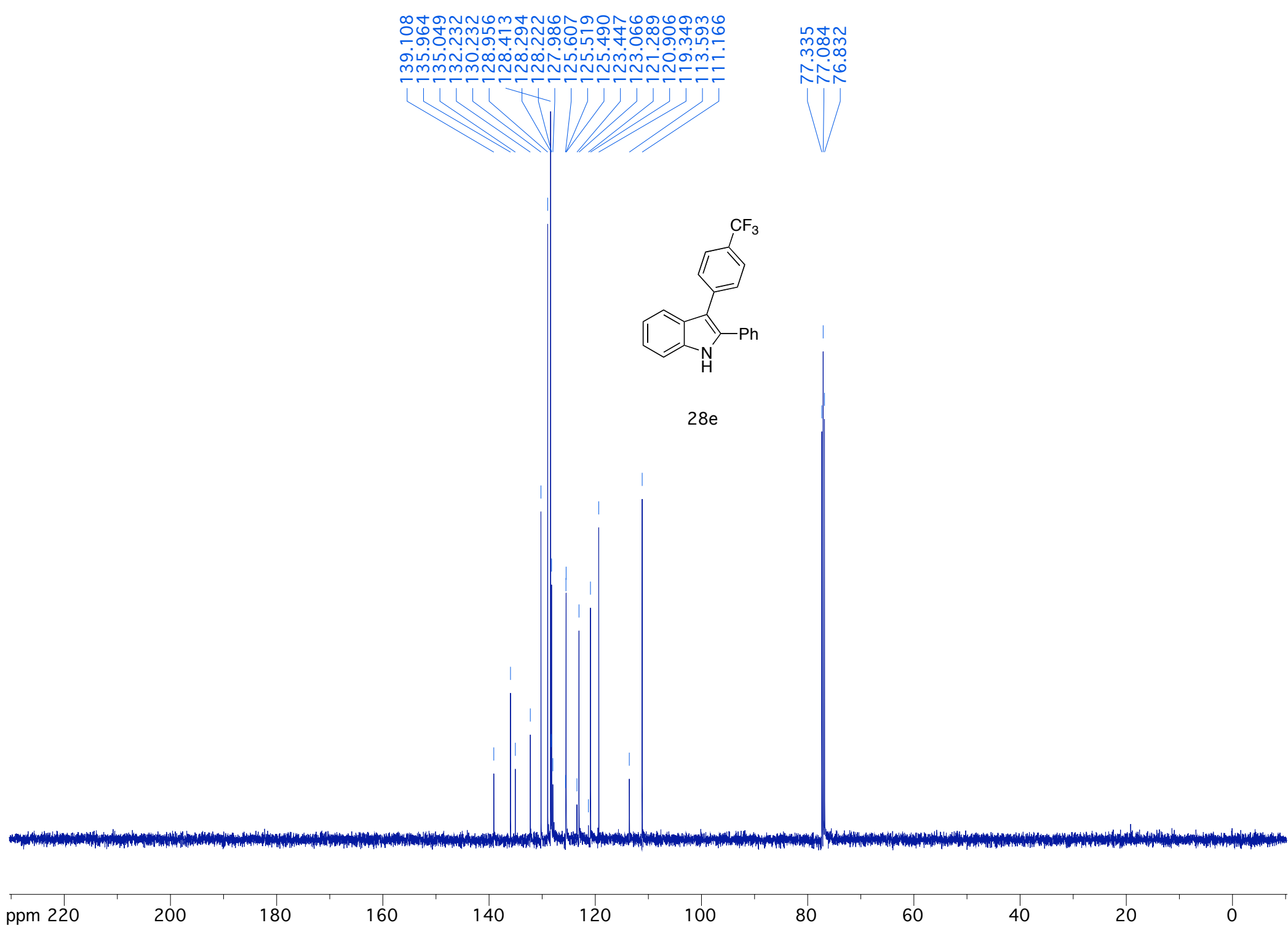


8.293
7.720
7.704
7.653
7.637
7.577
7.561
7.468
7.466
7.451
7.450
7.434
7.430
7.428
7.426
7.421
7.418
7.414
7.395
7.385
7.384
7.381
7.373
7.370
7.367
7.359
7.319
7.317
7.305
7.303
7.301
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7.287
7.260
7.236
7.234
7.222
7.220
7.218
7.206
7.204



28e

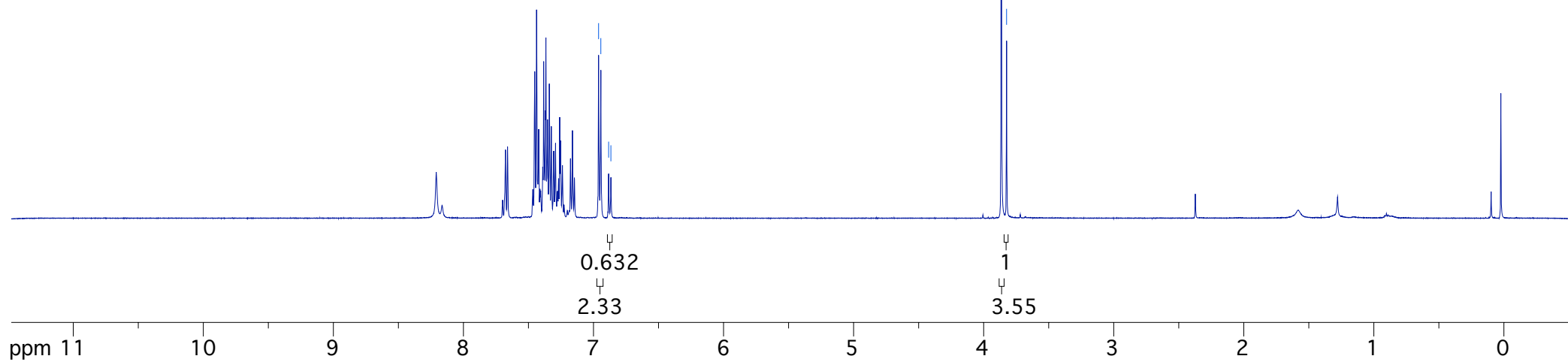
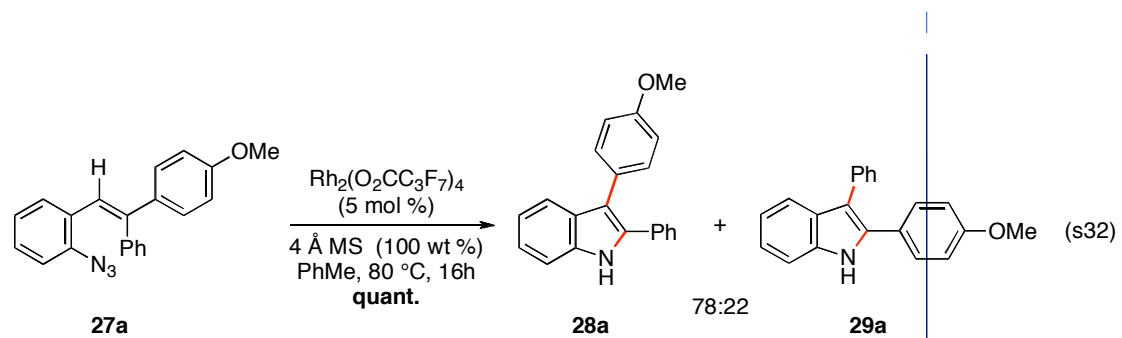




6.961
6.944
6.884
6.866

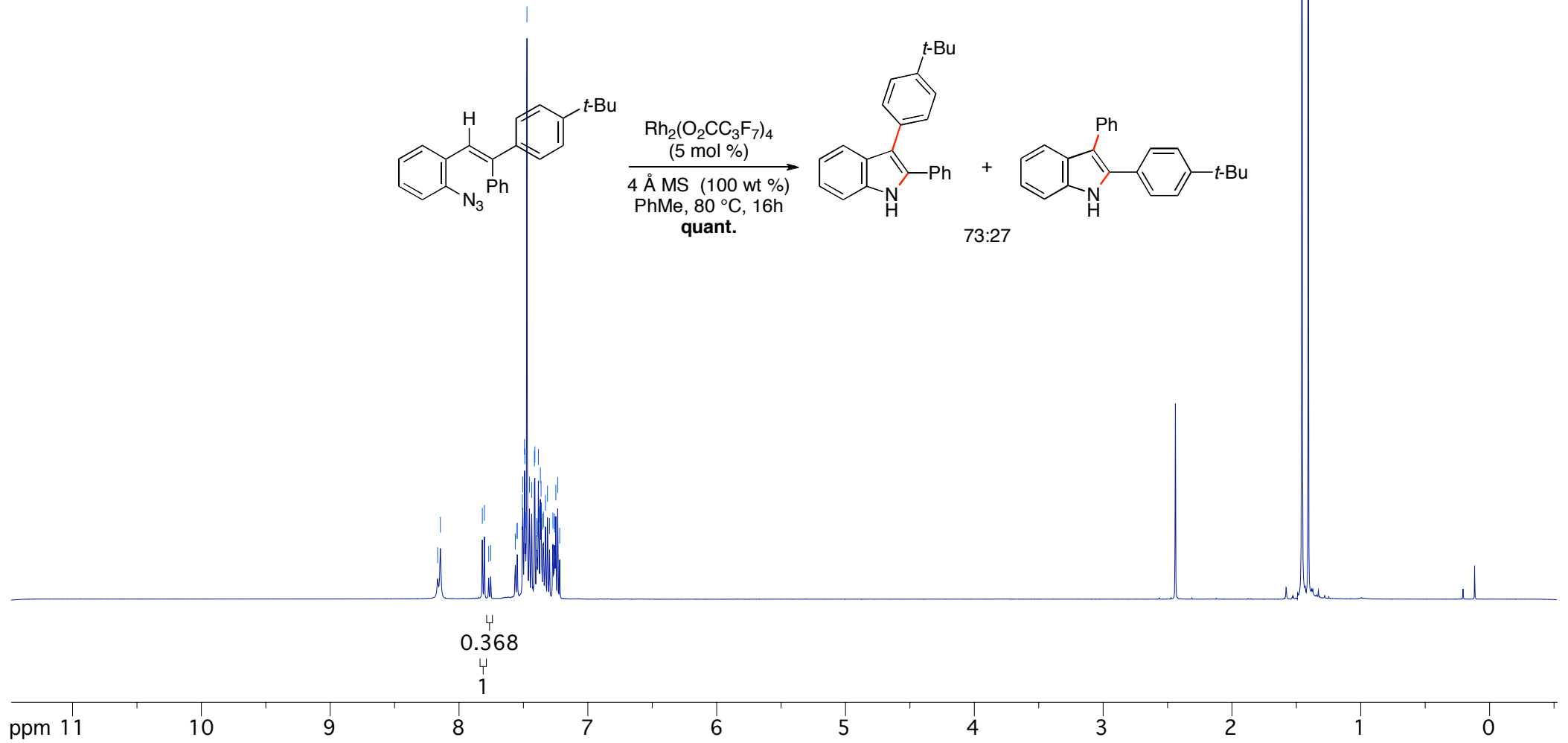
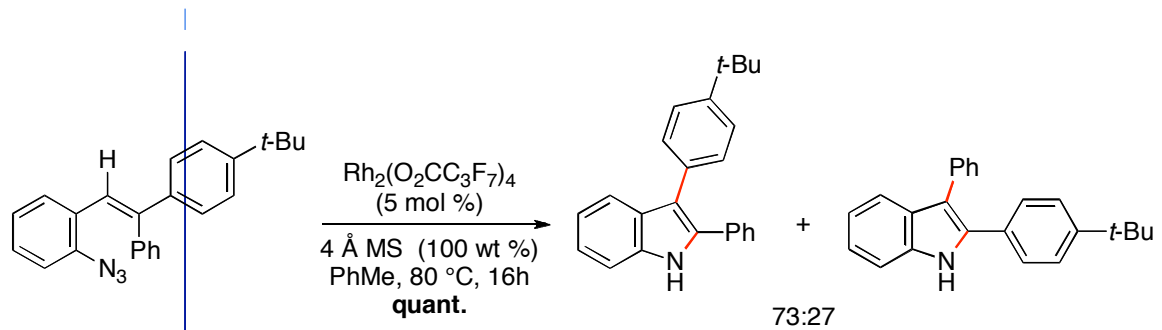
3.864
3.824

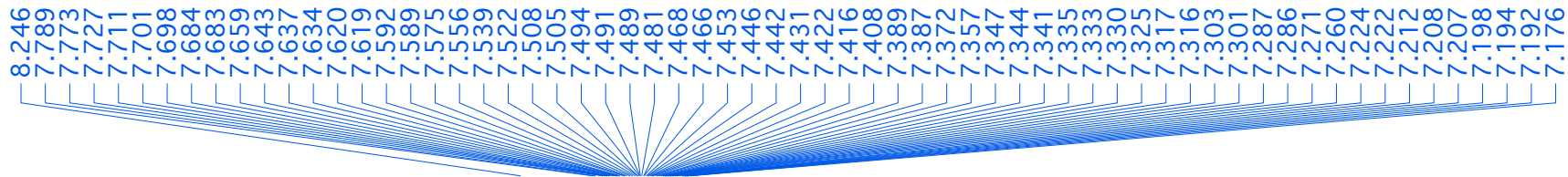
Intramolecular Competition Experiment



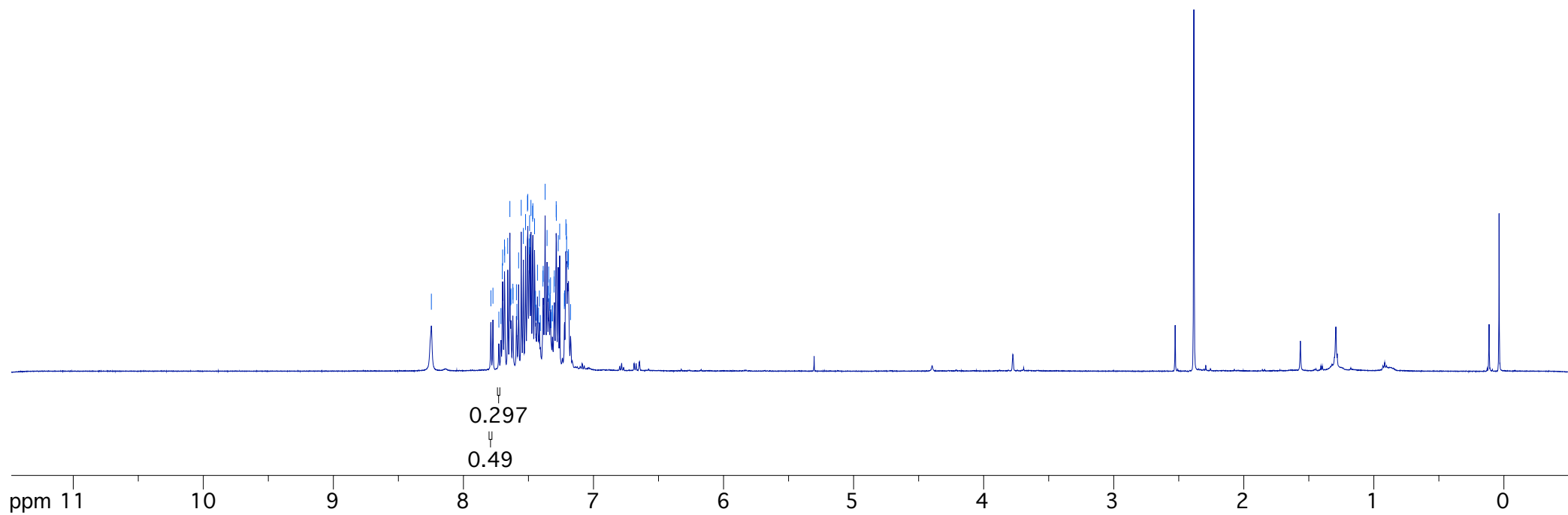
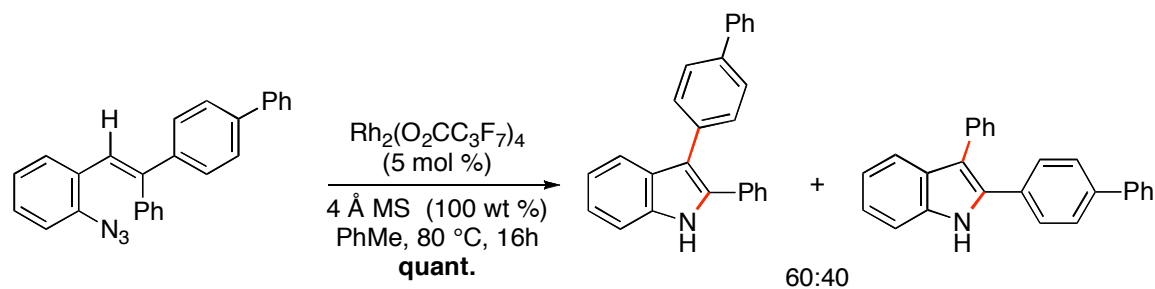
8.166
8.145
7.819
7.803
7.770
7.754
7.563
7.549
7.548
7.508
7.505
7.492
7.490
7.484
7.473
7.453
7.436
7.415
7.401
7.397
7.393
7.384
7.379
7.369
7.363
7.360
7.349
7.345
7.329
7.313
7.297
7.271
7.260
7.259
7.248
7.234
7.219

Intramolecular Competition Experiment



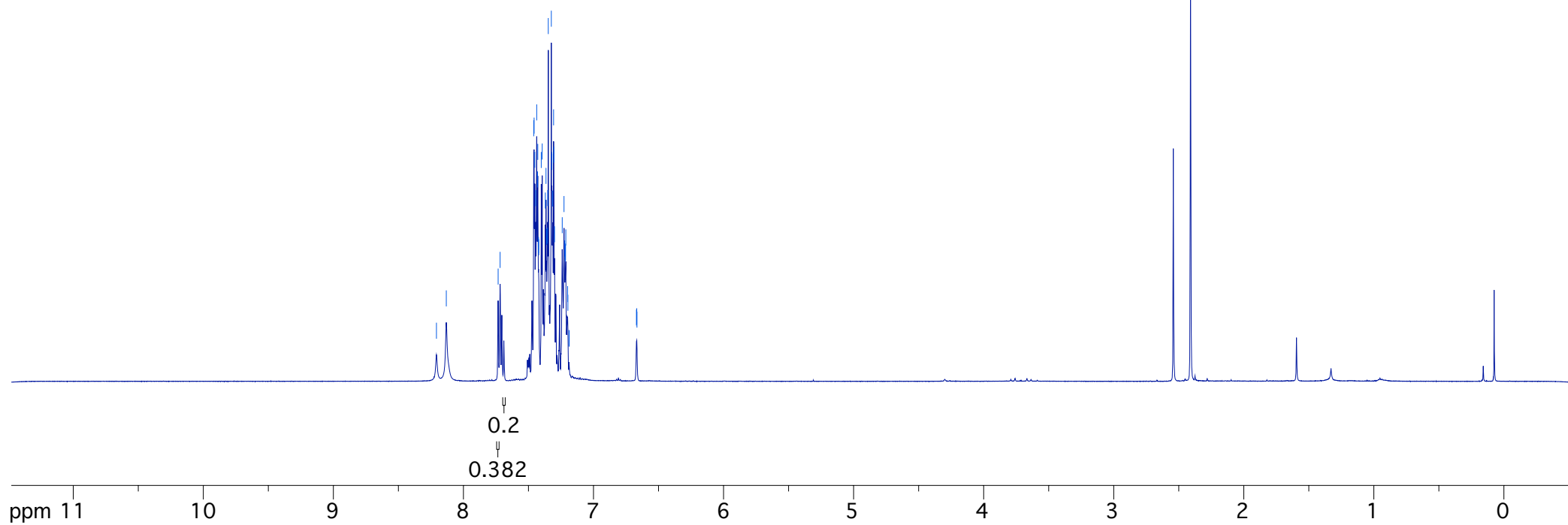
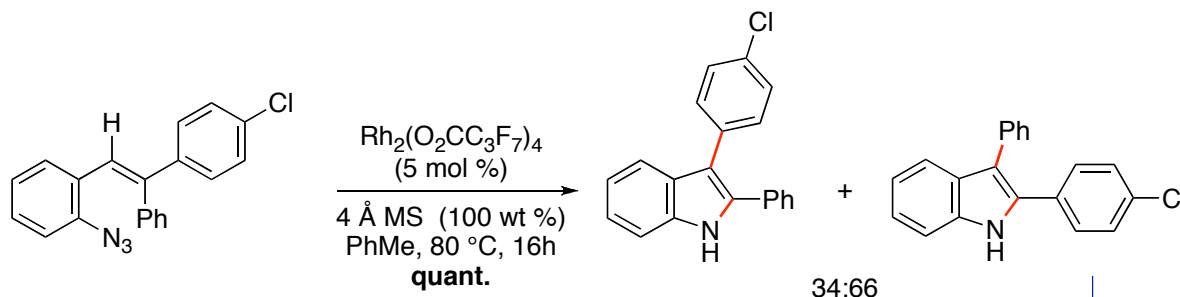


Intramolecular Competition Experiment



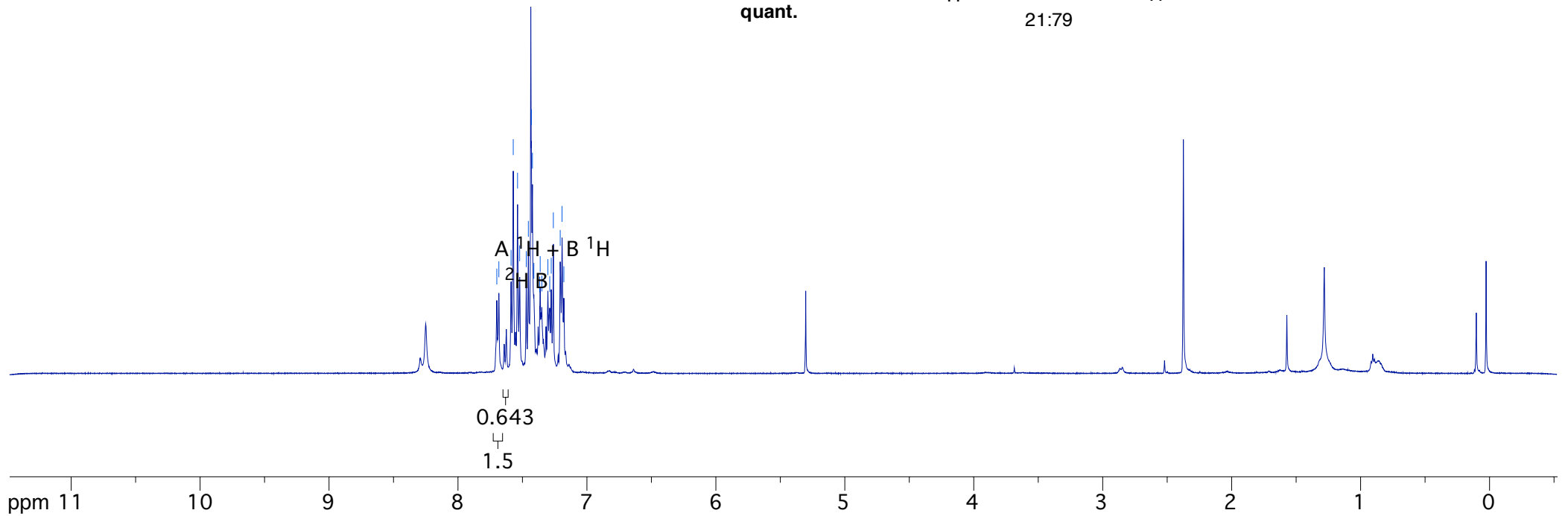
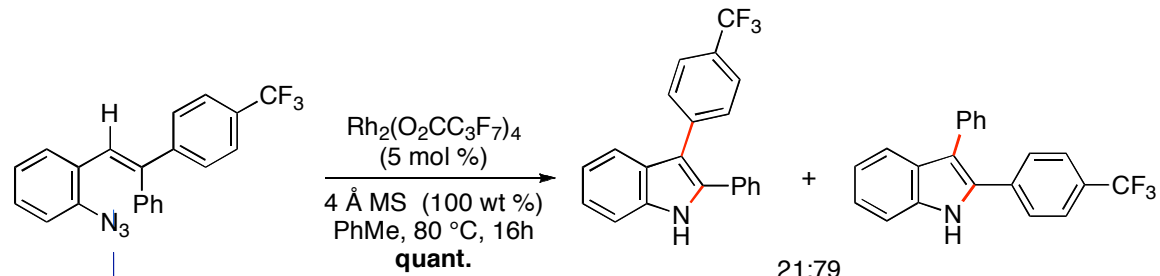
8.207
8.132
7.733
7.718
7.459
7.457
7.451
7.444
7.437
7.430
7.428
7.422
7.421
7.402
7.394
7.370
7.365
7.361
7.356
7.352
7.348
7.324
7.321
7.320
7.314
7.307
7.305
7.299
7.240
7.227
7.222
7.218
7.216
7.215
7.213
7.199
7.197
7.188
7.186
6.670
6.666

Intramolecular Competition Experiment



7.699
7.683
7.588
7.571
7.538
7.522
7.470
7.454
7.435
7.431
7.423
7.411
7.366
7.362
7.349
7.303
7.288
7.277
7.260
7.207
7.193
7.179

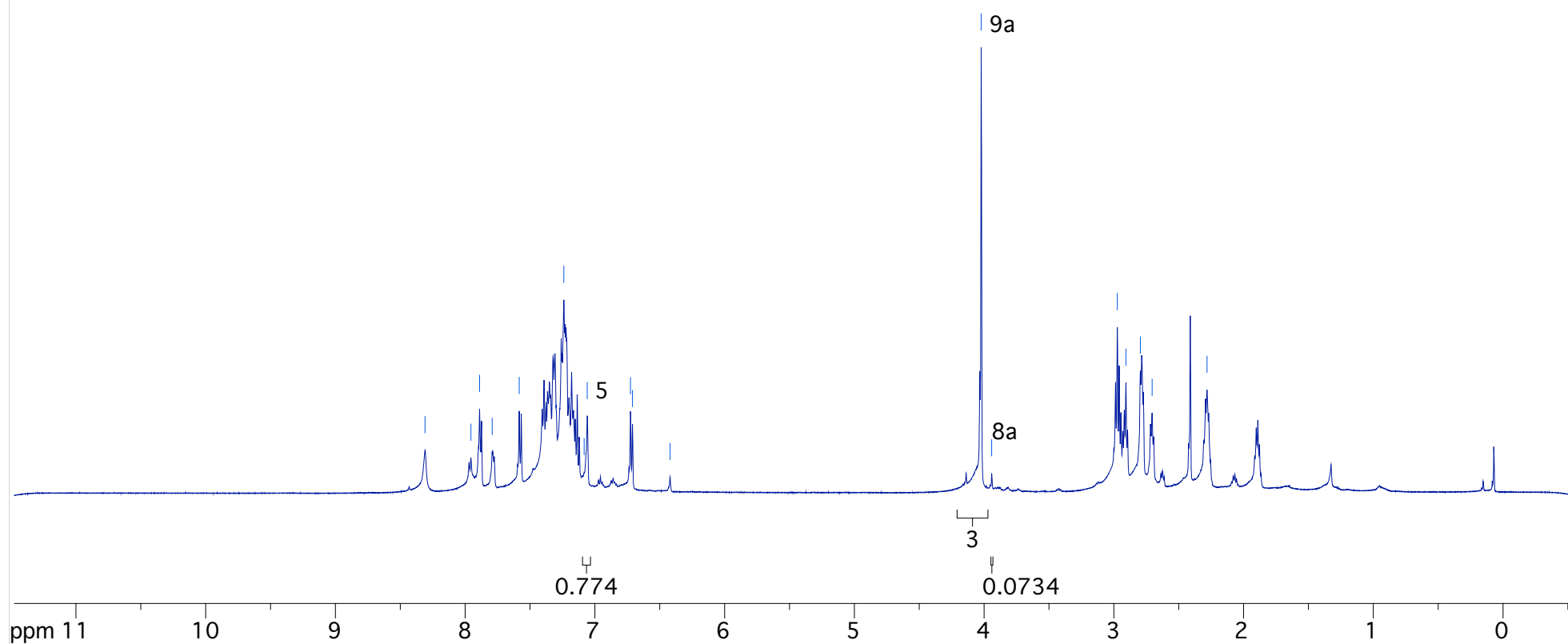
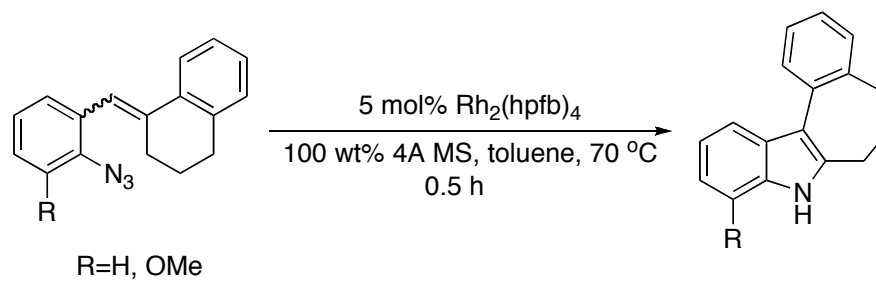
Intramolecular Competition Experiment





Intermolecular Competition Experiment

5 vs 8a



Examination of Rates of Reaction of E- and Z-Isomers

