Supplementary Material (ESI) for Chemical Communications

A versatile, modular synthesis of monofunctionalized BODIPY dyes

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Supporting Info:

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C. ^{1}H NMR spectra were referenced to tetramethylsilane (0.00 ppm) as an internal standard. ^{13}C NMR spectra were referenced to the $CDCl_3$ (77.67 ppm) signal. Mass spectra were recorded on a Hewlett-Packard 5989A mass spectrometer (EI mode and CI mode). High-resolution mass data were obtained with a Kratos MS50TC instrument. Melting points were taken on a Reichert Thermovar and are uncorrected.
Absorption spectra where recorded on a Perkin Elmer Lambda 40. For the corrected steady-state emission spectra, a SPEX Fluorolog was used. Freshly prepared samples in 1-cm quartz cells were utilized to perform all UV–vis absorption and emission measurements. For the determination of the relative fluorescence quantum yields (Φ_f) in solution, only dilute solutions with an absorbance below 0.1 at the excitation wavelength of 500 nm were used. Rhodamine 6G in spectrograde ethanol (Fluka) was used as standard to determine the fluorescence quantum yields. All spectroscopic measurements were done at 20 °C.

General synthesis of 2-acyl-5-halopyrroles: 2-acetyl-5-chloropyrrole

CAUTION: This synthesis describes the preparation and handling of halogenated pyrroles. These compounds are highly unstable, and decompose rapidly and violently with the evolution of toxic gases. Always handle these compounds in a fume hood. Any remaining halopyrrole after reaction can be stabilized by the addition of a few drops of triethylamine to the reaction mixture just before evaporation.

A stirred solution of pyrrole (1.34 g, 1.4 ml, 20 mmol) in THF (100 ml) under nitrogen is cooled to -78 °C. A solution of NCS (2.67 g, 20 mmol) in THF (100 ml) is added dropwise over 15 minutes. The resulting solution is stirred at -78 °C for 30 minutes and then placed in the freezer for 14 h. The cooled solution is then brought to 0 °C and stirred at this temperature for 6 h. Next the acylating agent is added in a dropwise manner over 10 minutes and the resulting solution is left stirred at room temperature for 14 h. An aqueous solution of NaOAc (70 mmol in 200 ml H_2O) is added and the reaction is refluxed for 30 minutes. The mixture is extracted with diethyl ether (3 × 100 ml), washed with saturated $NaHCO_3$ (2 × 200 ml or until basic) and water (2 × 300 ml or until neutral). The solution is dried over $MgSO_4$, filtered and evaporated under reduced pressure until dryness. The residue is purified chromatographically (Silica, CH_2Cl_2/ethyl acetate; 9:1) to yield a colorless solid (1.258 g, 44 % yield). Mp 78-81°C.

^{1}H-NMR: 9.67 (s, br, 1H, NH), 6.84 (d, 1H, J = 3.66 Hz), 6.11 (d, 1H, J = 3.66 Hz), 2.42 (s, 3H); ^{13}C-NMR: 187.1, 131.4, 123.4, 117.6, 109.2, 24.9; LRMS (EI, 70 eV) m/z 143 (M+ 100), 145 (M^+ 31); HRMS: calcd. for C_6H_6ClNO 143.0138, found 143.0141.

Note: The acylating agent can be prepared as for any Vilsmeier reaction by mixing 22 mmol of a dimethylamide or a N-morpholinoylamide and 22 mmol of $POCl_3$ at 0 °C and stirring at room temperature until the Vilsmeier reagent has formed. After formation of the salt, it is dissolved in CH_2Cl_2 (50 ml) prior to addition.
In the case of trifluoroacetylation, the acylating agent constitutes of 20 mmol of trifluoroacetic acid anhydride in 50 ml of THF. The hydrolysis can then be replaced by stirring with water/$NaHCO_3$.

Condensation of selected pyrroles to corresponding BODIPY: 3-Chloro-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-sindacene **8b**

2-Acetyl-5-chloropyrrole (5 mmol, 670 mg) is dissolved in a mixture of 4 ml CH_2Cl_2 and 2ml pentane and stirred under nitrogen. 2,4-Dimethylpyrrole (620 µl, 5mmol, 1 equiv.) is added and the resulting solution is cooled to 0 °C in an ice bath, followed by the addition of $POCl_3$ (470 µl, 5mmol, 1 equiv.). The solution is stirred at room temperature for 6 h. During this period the mixture turns dark. Triethylamine (7 ml , 50 mmol) is added and the mixture is stirred for 10 minutes while being cooled to 0 °C. Borontrifluoride etherate (7 ml, 55 mmol) is added dropwise and the reaction mixture is than stirred at room temperature for 1 h. The orange solution is poured in diethyl ether (400 ml) and extracted with water (3 × 200 ml). The ethereal solution is dried over $MgSO_4$, filtered and concentrated *in vacuo*. The product is purified chromatographically (Silica, CH_2Cl_2/petroleum ether; 1:1, v/v) to yield brick-red crystals (964 mg, 72%). Mp 228-230 °C.

^{1}H-NMR: 7.03 (d, 1H, J = 3.63 Hz), 6.29 (d, 1H, J = 3.66 Hz), 6.17 (s, 1H), 2.58 (s, 3H), 2.50 (s, 3H), 2.40 (s, 3H);^{13}C-NMR: 160.8, 145.6, 140.3, 137.3, 134.2, 133.3, 124.0, 123.4, 115.3, 16.9, 15.8, 15.0; LRMS (EI, 70 eV) m/z 268 (M^+ 100); HRMS: calcd. for $C_{12}H_{12}BClF_2N_2$ 268.07501, found 268.07482.

3-Chloro-5,7-dimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8a**

Bright orange solid. Mp 162°C.^{1}H-NMR: 7.01 (s, 1H), 6.80 (d, 1H, J = 3.76 Hz), 6.23 (d, 1H, J = 3.76 Hz), 6.13 (s, 1H), 2.56 (s, 3H), 2.20 (s, 3H);^{13}C-NMR: 163.6, 145.9, 138.3, 136.4, 132.0, 126.7, 123.4, 121.7, 115.8, 15.2, 11.3; LRMS (EI, 70 eV) m/z 254 (M^+ 100); HRMS: calcd. for $C_{11}H_{10}BClF_2N_2$ 254.05936, found 254.06083.

3-Chloro-5-phenyl-8-methyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8c**

Purple solid. Mp 162-165°C.^{1}H-NMR: 7.91-7.88 (m, 2H), 7.48-7.45 (m, 3H), 7.35 (d, 1H, J = 3.21 Hz), 7.16 (d, 1H, J = 3.21 Hz), 6.67 (d, 1H, J = 3.21 Hz), 6.37 (d, 1H, J = 3.21 Hz), 2.55 (s, 3H);^{13}C-NMR: 160.3, 141.8, 133.9, 132.2, 130.0, 129.6; 129.5, 129.5, 129.0, 128.4, 126.5, 117.5, 15.5; LRMS (EI, 70 eV) m/z 316 (M^+ 100); HRMS: calcd. for $C_{16}H_{12}BClF_2N_2$ 316.07501, found 3.16.07492.

3-Chloro-5,6-cyclohexano-8-methyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8d**

Red solid. Mp 174-175°C.^{1}H-NMR: 6.96 (s, 2H), 6.27 (d, 1H, J = 3.66 Hz), 3.09 (t, 2H, J = 6.39 Hz), 2.58 (t, 2H, J = 6.39 Hz), 2.44 (s, 3H), 1.85 (m, 2H), 1.75 (m, 2H);^{13}C-NMR: 162.8, 139.2, 137.8, 135.7, 133.3, 131.9, 125.9, 124.0, 115.3, 25.1, 23.3, 22.6, 22.1, 15.1; LRMS (EI, 70 eV) m/z 294 (M^+ 100); HRMS: calcd. for $C_{14}H_{14}BClF_2N_2$ 294.09066, found 294.09051.

3-Chloro-5,7-dimethyl-8-phenyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8e**

Orange solid. Mp 137-140°C.^{1}H-NMR: 7.49-7.47 (m, 3H), 7.30 (d, 2H, J = 7.29 Hz), 6.31 (d, 1H, J = 3.66 Hz), 6.23 (d, 1H, J = 3.66 Hz), 6.14 (s, 1H), 2.63 (s, 3H), 1.51 (s, 3H);^{13}C-NMR: 162.7, 147.1, 141.8, 138.3, 133.8, .133.5, 133.2, 129.6, 128.9, 128.6, 127.3, 123.8, 115.7,

15.3, 15.0; LRMS (EI, 70 eV) m/z 330 (M^+ 100); HRMS: calcd. for $C_{17}H_{14}BClF_2N_2$ 330.09066, found 330.09052.

3-Bromo-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8f**

Bright orange solid. Mp 219-220°C.^{1}H-NMR: 6.99 (d, 1H, J = Hz), 6.40 (d, 1H, J = Hz), 6.18 (s, 1H), 2.58 (s, 3H), 2.50 (s, 3H), 2.41 (s, 3H); ^{13}C-NMR: 161.1, 160.8, 140.0, 135.0, 134.3, 124.1, 123.6, 119.1, 17.0, 15..8, 15.1 ; LRMS (EI, 70 eV) m/z 312 (M^+ 100); HRMS: calcd. for $C_{12}H_{12}BBrF_2N_2$ 312,02450, found 312.02444.

2-Chloro-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8g**

Orange solid. Mp 198-199°C.^{1}H-NMR: 7.44 (s, 1H), 6.92 (s, 1H), 6.21 (s, 1H), 2.58 (s, 3H), 2.52 (s, 3H), 2.43 (s, 3H); ^{13}C-NMR: 162.6, 147.1, 141.4, 135.0, 133.8, 132..9, 123.7, 120.4, 118.7, 17.1, 16.3, 15.2; LRMS (EI, 70 eV) m/z 268 (M^+ 100); HRMS: calcd. for $C_{12}H_{12}BClF_2N_2$ 268.07501, found 268.07547.

2-Bromo-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8h**

Bright orange solid. Mp 178-180°C.^{1}H-NMR: 7.48 (s, 1H), 7.02 (s, 1H), 6.22 (s, 1H), 2.58 (s, 3H), 2.53 (s, 3H), 2.43 (s, 3H);^{13}C-NMR: 162.6, 147.2, 141.1, 135.8, 134.9, 133.7, 123.8 123.1, 102.8, 17.0, 16.2, 15.1; LRMS (EI, 70 eV) m/z 312 (M^+ 100); HRMS: calcd. for $C_{12}H_{12}BBrlF_2N_2$ 312.02450, found 312.02453.

2-Bromo-5,6-dihydronaphtyl-8-methyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8i**

Purple solid. Mp 178-180°C.^{1}H-NMR: 8.66 (d, 1H, J = 7.53 Hz), 7.53 (s, 1H), 7.42-7.34 (m, 2H), 7.27 (sn 1H), 7.11 (s, 1H), 6.95 (s, 1H), 2.90 (t, 2H, J = 7.17 Hz), 2.70 (t, 2H, J = 7.17 Hz), 2.43 (s, 3H); ^{13}C-NMR: 157.2, 141.7, 139.5, 137.9, 136.8, 134.7, 133.7, 131.4, 129.2-129.0 (t), 129.0, 129.6, 127.6, 127.0, 126.0, 123.0, 103.6, 30.2, 22.2, 15.8; LRMS (EI, 70 eV) m/z 386 (M^+ 100); HRMS: calcd. for $C_{18}H_{14}BBrF_2N_2$ 386.04015, found 386.04007.

2-Iodo-5-phenyl-8-methyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8j**

Purple solid. Mp 123-125°C.^{1}H-NMR: 7.94-9.89 (m, 2H), 7.63 ‘s, 1H), 7.48-7.46 (m, 3H), 7.42 (d, 2H, J = 4.32 Hz), 7.26 (s, 1H), 6.72 (d, 1H, J = 4.32 Hz), 2.56 (s, 3H); ^{13}C-NMR: 161.7, 144.2, 142.6, 137.9, 135.7, 131.7, 131.0, 130.6, 130.5, 129.6, 129.59, 129.56, 128.5, 121.8, 16.1; LRMS (EI, 70 eV) m/z 408 (M^+ 100); HRMS: calcd. for $C_{16}H_{12}BF_2IN_2$ 408.01063, found 408.01072.

2-Iodo-5,7,8-Trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **8k**

Orange solid. Mp 176-178°C.^{1}H-NMR: 7.51 (s, 1H), 7.09 (s, 1H), 6.21 (s, 1H), 2.56 (s, 3H), 2.47 (s, 3H), 2.40 (s, 3H); ^{13}C-NMR: 162.4, 147.1, 140.9,140.7, 135.4, 134.7, 128.7, 123.9 ,17.1, 16.3, 15.2; LRMS (EI, 70 eV) m/z 360 (M^+ 100); HRMS: calcd. for $C_{12}H_{12}BF_2IN_2$ 360.01063, found 360.00963.

Sonogashira reaction: 3-Phenylethynyl-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **9a**

BODIPY **8b** (53.6 mg, 0.2 mmol) is dissolved in THF (2ml) and *i*Pr_2NEt (1ml) and purged with nitrogen. To the resulting solution is added phenylacetylene (29 µl, 0.26 mmol, 1.3 equivs.), followed by tetrakis(triphenylphosphine) palladium (11 mg, 0.02 mmol, 10 mol%) and CuI (3.8 mg, 0.02 mmol, 10 mol%). The mixture is refluxed for 3 h and cooled to room temperature after which the solvent is stripped. The product is purified by column (Silica, CH_2Cl_2/petroleum ether; 1:1, v/v) to yield **9a** as a purple crystalline solid (31 mg, 46%). Mp 202-204 °C.

^{1}H-NMR: 7.61 (d, 2H, J = 3.66 Hz), 7.33 (m, 3H), 7.04 (d, 1H, J = 3.66 Hz), 6.63 (d, 1H, J = 3.66 Hz), 6.18 (s, 1H), 2.62 (s, 3H), 2.53 (s, 3H), 2.41 (s, 3H); ^{13}C-NMR: 161.5, 145.7, 139.9, 135.6, 135.4, 132.4, 132.1, 129.5, 128.7, 123.8, 123.6, 123.2, 121.6, 98.3, 83.2, 17.3, 16.7, 15.6, LRMS (EI, 70 eV) m/z 334 (M^+ 100); HRMS: calcd. for $C_{20}H_{17}BF_2N_2$ 334.1453, found 334.14607.

2-Phenylethynyl-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **9b**

Red solid. Mp 191-192°C.^{1}H-NMR: 7.74 (s, 1H), 7.49 (m, 2H), 7.32 (m, 2H), 7.15 (s, 1H), 6.19 (s, 1H), 2.58 (s, 3H), 2.52 (s, 3H), 2.42 (s, 3H);^{13}C-NMR: 162.1, 146.7, 141.5, 139.9, 135.2, 133.7, 131.5, 128.4, 128.0, 124.7, 123.7, 123.6, 111.2, 90.4, 83.2, 17.1, 16.4, 15.2; LRMS (EI, 70 eV) m/z 334 (M^+ 100); HRMS: calcd. for $C_{20}H_{17}BF_2N_2$ 334.14529, found 334.14542.

3-Trimethylsilylethynyl-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **9c**

solid. Mp 241-243°C.^{1}H-NMR: 6.97 (d, 1H, J = 3.63 Hz), 6.56 (d, 1H, 3.66 Hz), 6.17 (s, 1H), 2.60 (s, 3H), 2.52 (s, 3H), 2.41 (s, 3H), 0.29 (s, 9H);^{13}C-NMR: 161.6, 145.5, 139.7, 135.0, 134.7 131.1, 123.5 ,122.7, 121.6, 104.1, 97.1, 16.2, 16.2, 15.1; LRMS (EI, 70 eV) m/z 330 (M^+ 100); HRMS: calcd. for $C_{17}H_{21}BF_2N_2Si$ 330.15351, found 330.15356.

2-Trimethylsilylethynyl-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **9d**

solid. Mp 213-214°C.^{1}H-NMR: 7.68 (s, 1H), 7.11 (s, 1H), 6.20 (s, 1H), 2.57 (s, 3H), 2.51 (s, 3H), 2.42 (s, 3H), 0.23 (s, 9H);^{13}C-NMR: 162.3, 146.7, 141.6, 140.3, 135.3, 133.3, 125.2, 123.8, 111.1, 98.7, 95.6, 17.1, 16.3, 15.1; LRMS (EI, 70 eV) m/z 330 (M^+ 100); HRMS: calcd. for $C_{17}H_{21}BF_2N_2Si$ 330.15351, found 330.15341.

Suzuki reaction: 3-(4-*t*-Butylphenyl)-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **10a**

BODIPY **8b** (53.6 mg, 0.2 mmol) is dissolved in toluene (1ml) and purged with nitrogen. To the solution is added 4-*t*-Butyl-benzeneboronic acid (46 mg, 0.26 mmol, 1.3 equivs.), followed by tetrakis(triphenylphosphine) palladium (11 mg, 0.02 mmol, 10 mol%) and Na_2CO_3 (1 ml of a 2M aquatic solution). The mixture is refluxed for 3 h, cooled to room

temperature and poured in diethyl ether (150 ml). The organic layer is dried over $MgSO_4$, filtered and evaporated to dryness. The crude product is purified by column (Silica, CH_2Cl_2/petroleum ether; 1:1, v/v) to yield **10a** as a dark red crystalline solid (68 mg, 93%). Mp 152-154 °C.

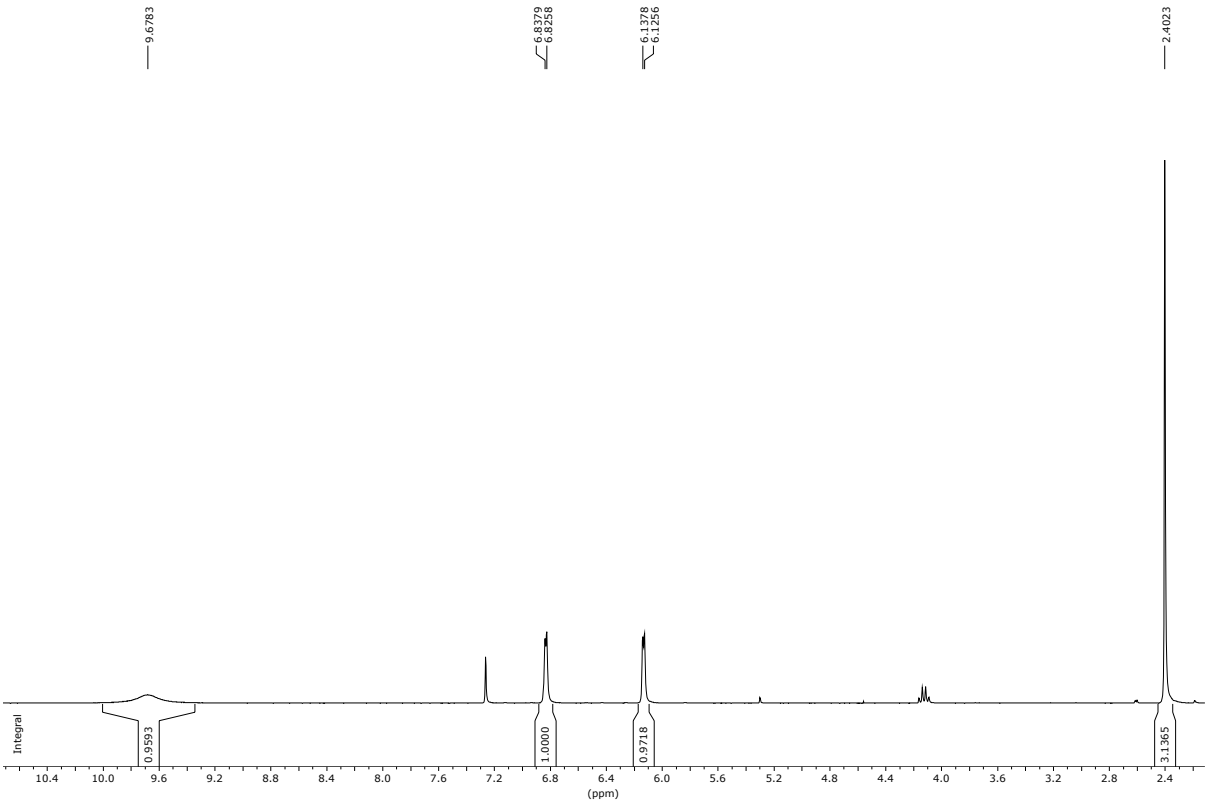
^{1}H-NMR: 7.82(d, 2H, J = 8.22 Hz), 7.45 (d, 2H, J = 8.22 Hz), 7.16 (d, 1H, J = 3.66 Hz), 6.54 (d, 1H, J = 3.66 Hz), 6.10 (s, 1H), 2.53 (s, 6H), 2.38 (s, 3H), 1.35 (s, 9H); ^{13}C-NMR: 158.0, 154.9, 151.8, 143.4, 140.6, 136.1, 133.3, 130.4, 128.9, 125.3, 125.2, 122.5, 118.2, 34.8, 31.4, 16.7, 16.4, 15.0; LRMS (EI, 70 eV) m/z 366 (M^+ 100); HRMS: calcd. for $C_{22}H_{25}N_2BF_2$ 366.2078, found 366.20892.

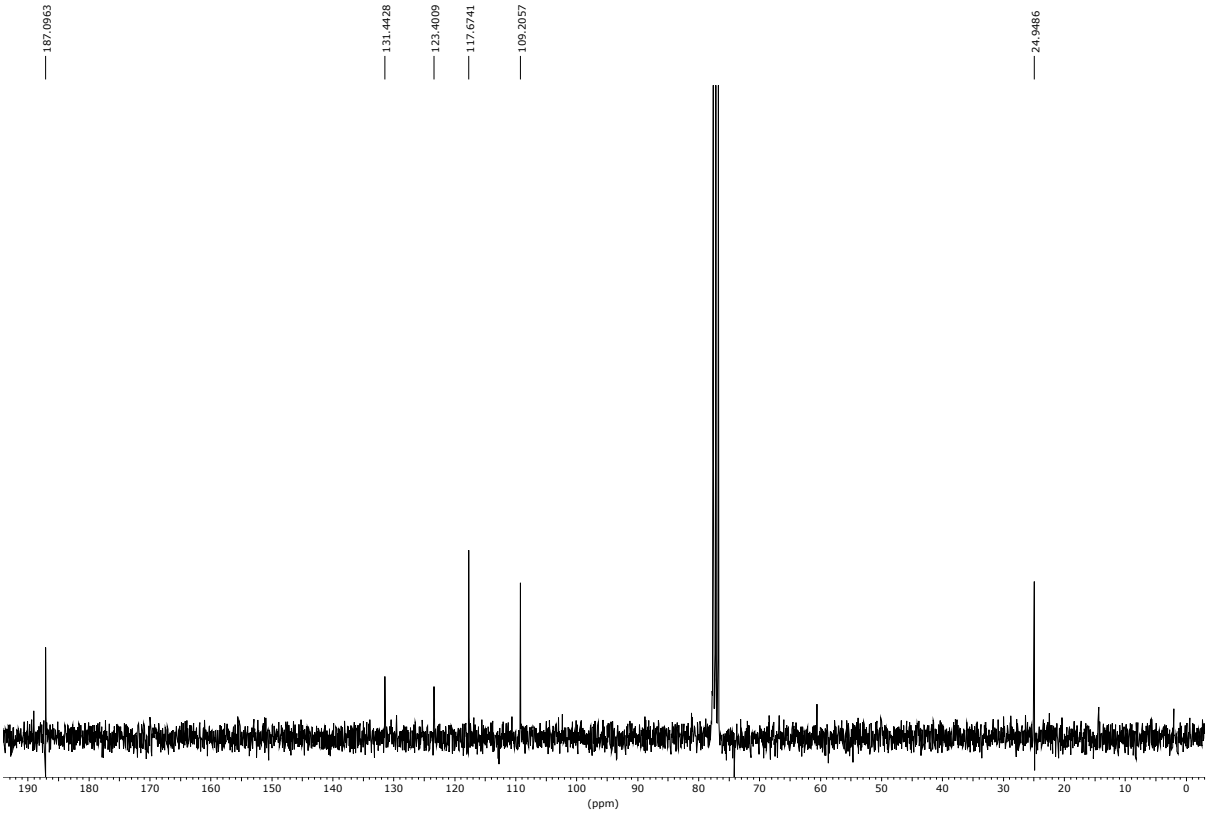
2-(4-*t*-Butylphenyl)-5,7,8-trimethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene **10b**

Red solid. Mp 166-168°C.^{1}H-NMR:7.91 (s, 1H), 7.49 (d, 2H, J = 8.2 Hz), 7.39 (d, 2H, J = 8.2 Hz), 7.26 (s, 1H), 6.15 (s, 1H), 2.58 (s, 6H), 2.42 (s, 3H), 1.34 (s, 9H);^{13}C-NMR: 160.0, 149.8, 145.2, 141.6, 135.6, 134.9, 134.3, 1341.4, 130.8, 125.7, 125.0, 122.7, 119.2, 34.5, 31.3, 16.9, 16.5, 14.9; LRMS (EI, 70 eV) m/z 366 (M^+ 100); HRMS: calcd. for $C_{22}H_{25}BF_2N_2$ 366,20789, found 366.20801.

NMR-Spectra

2-acetyl-5-chloropyrrole





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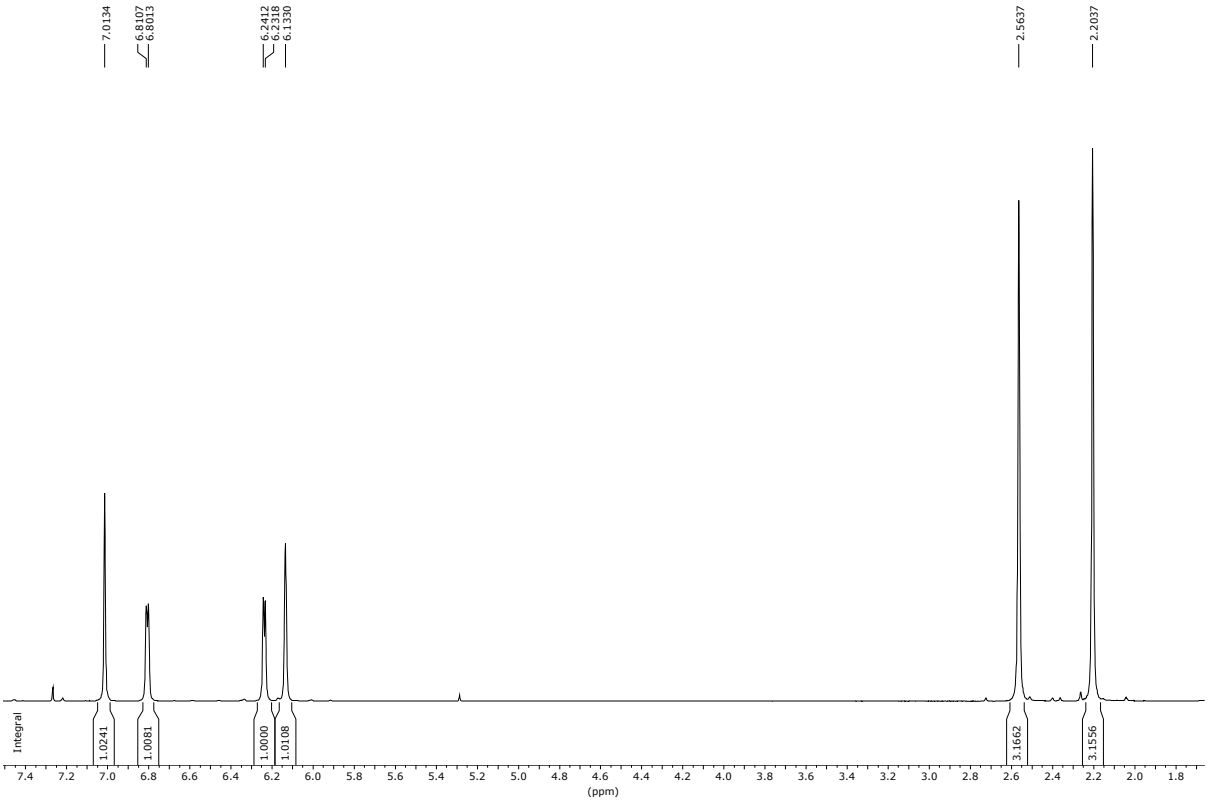
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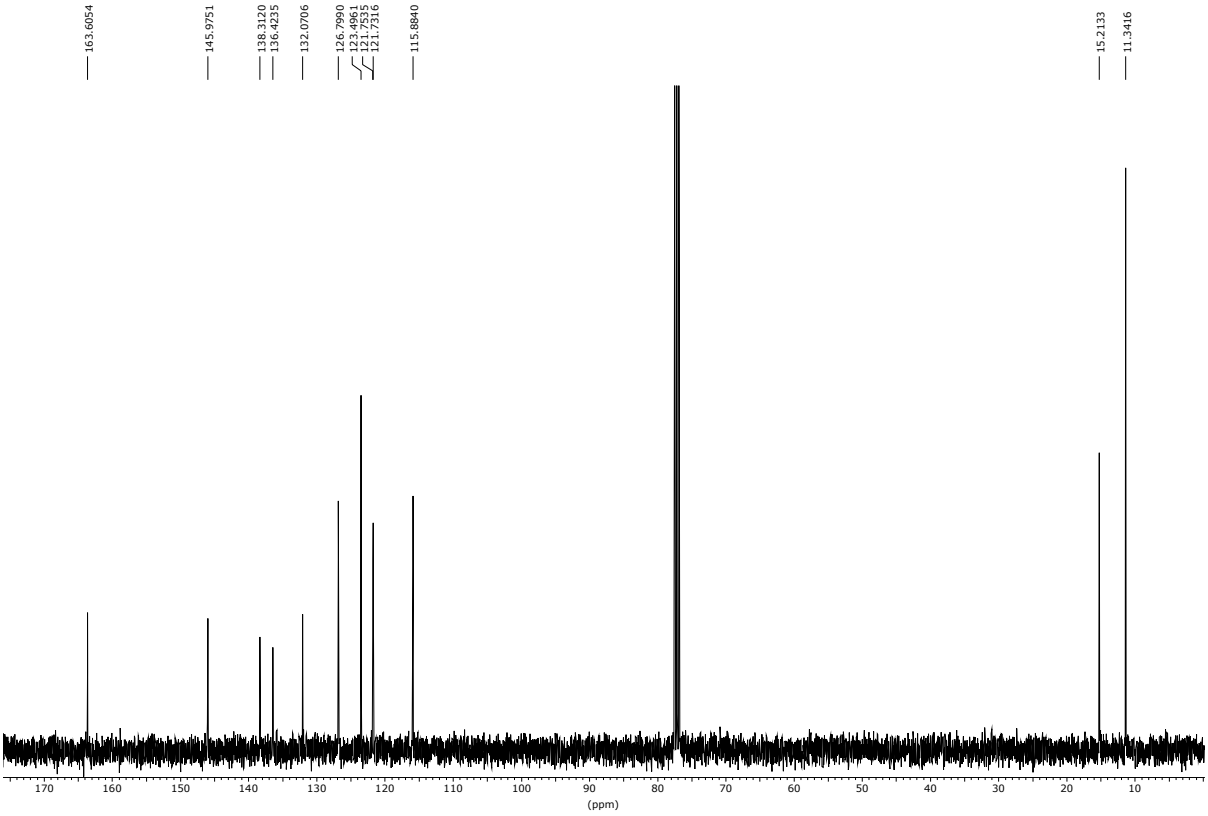
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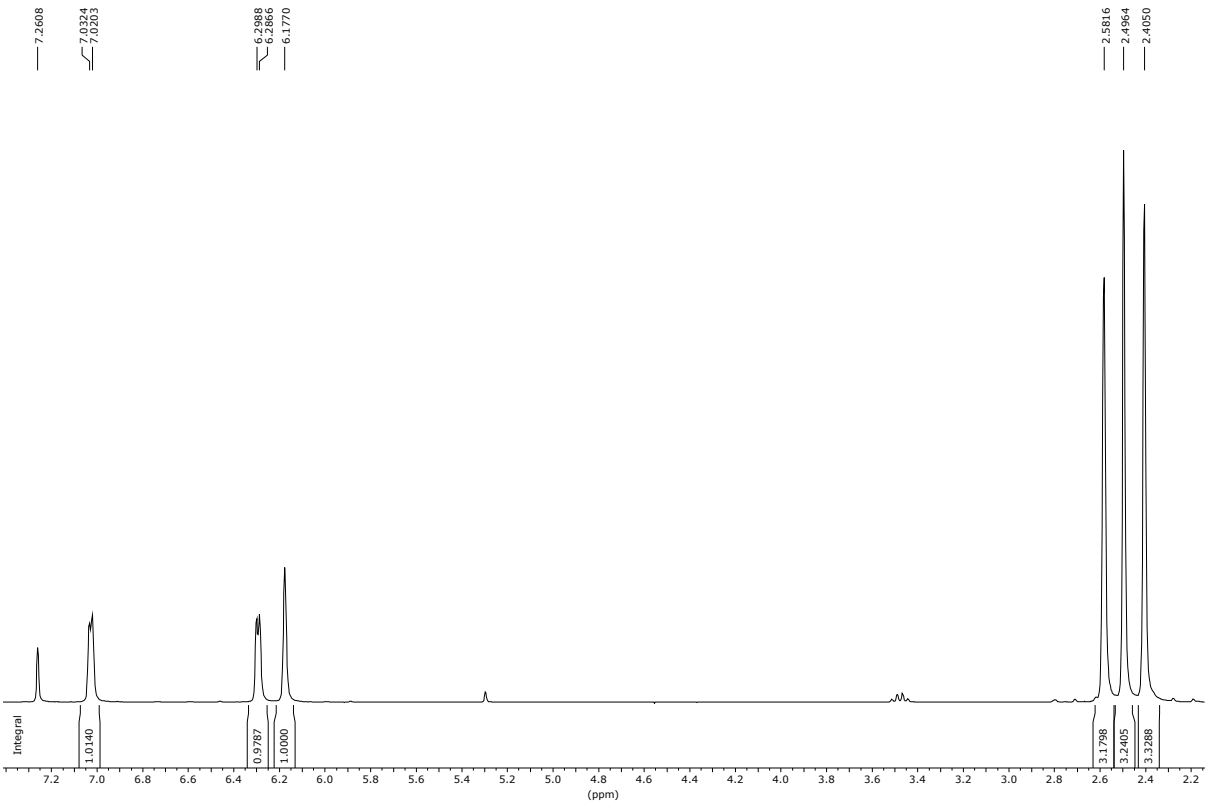
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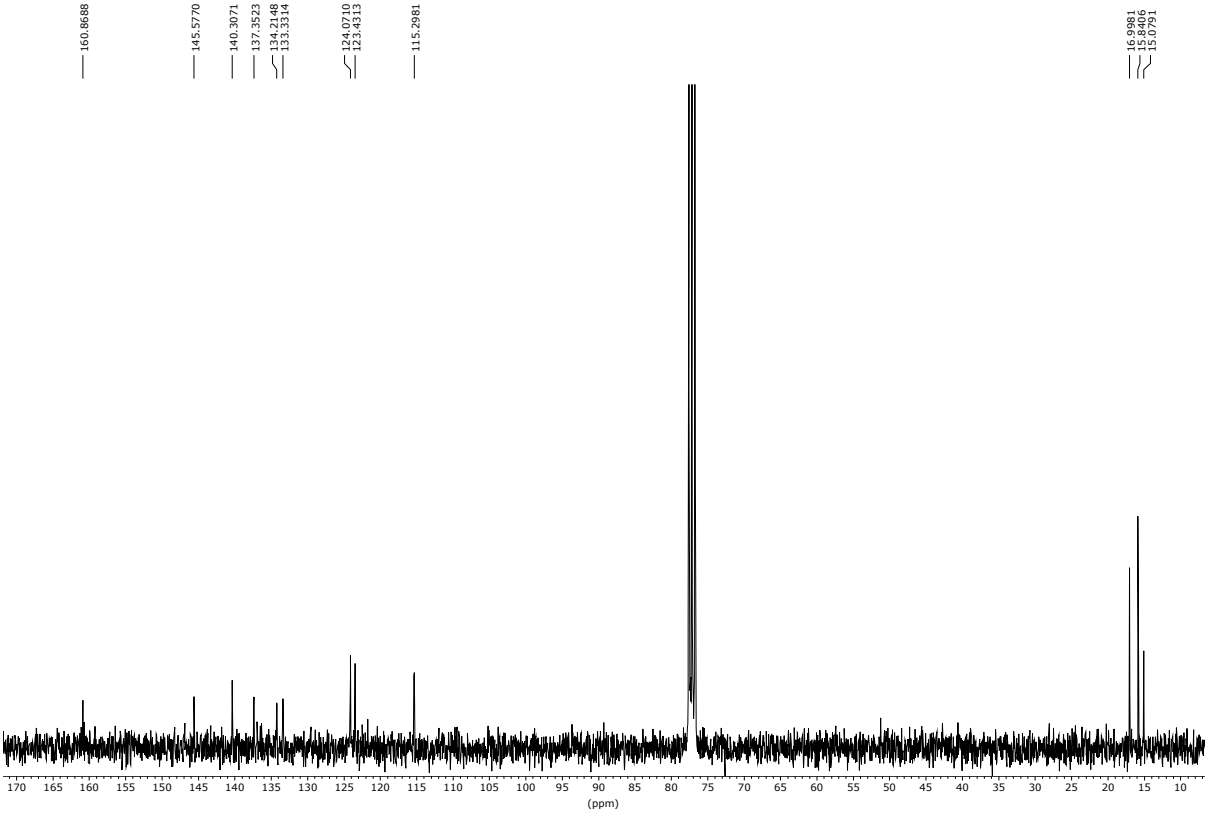
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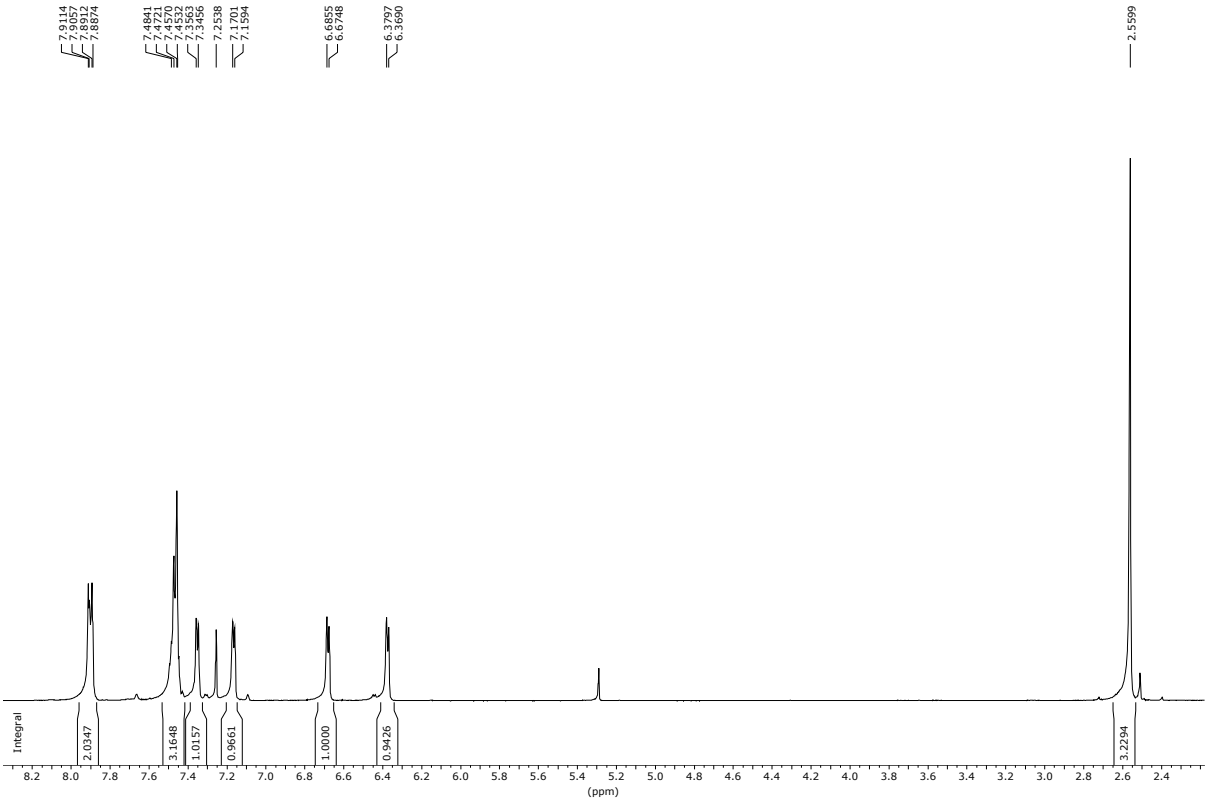
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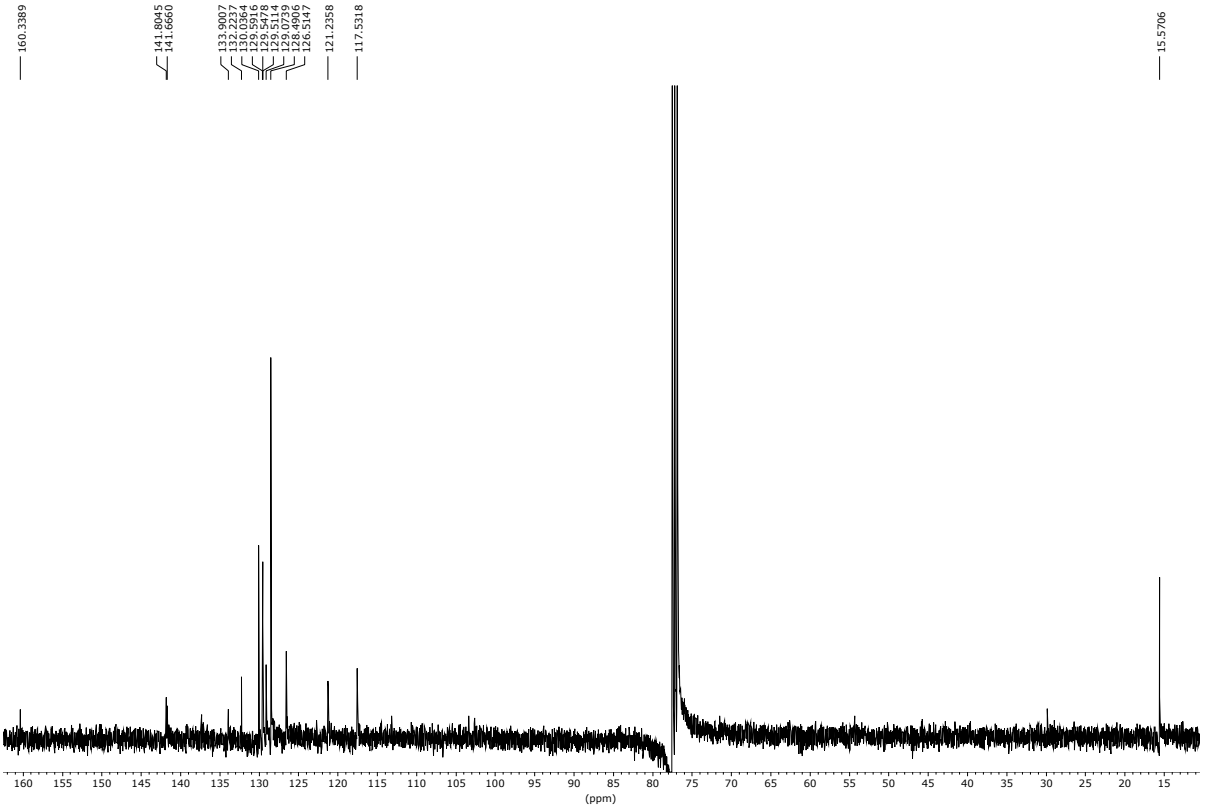
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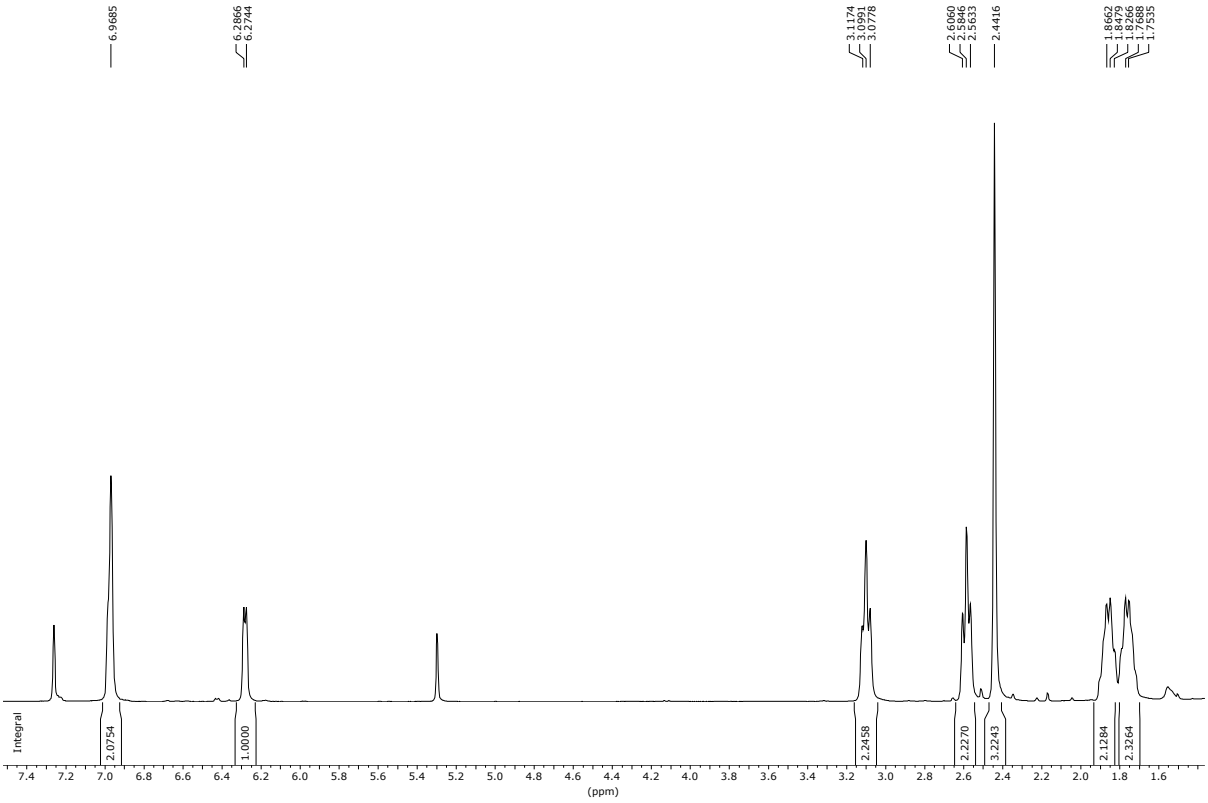
8d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1.8296
1.7688
1.7535
Integral
2.0754
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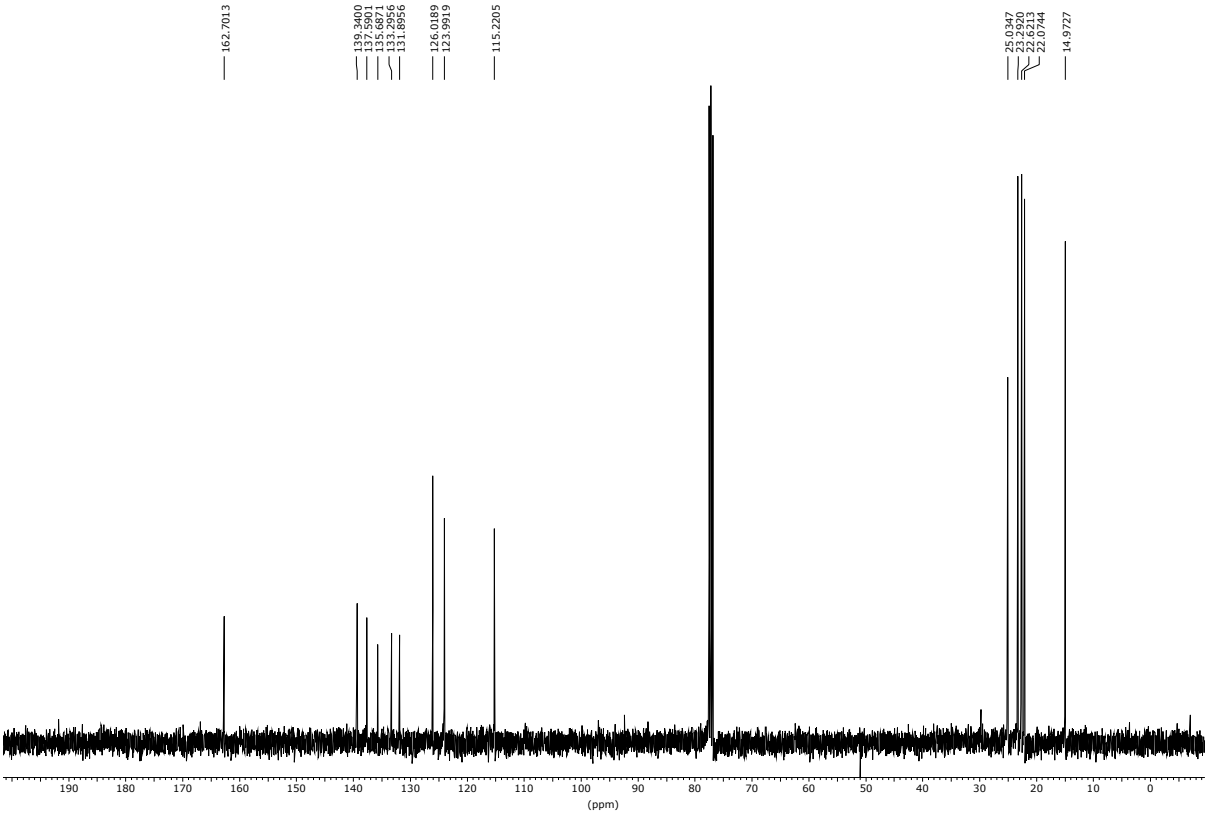
2.2458
2.2270
3.2243
2.1284
2.3264
(ppm)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133.2956
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25.0347
23.2970
22.4211
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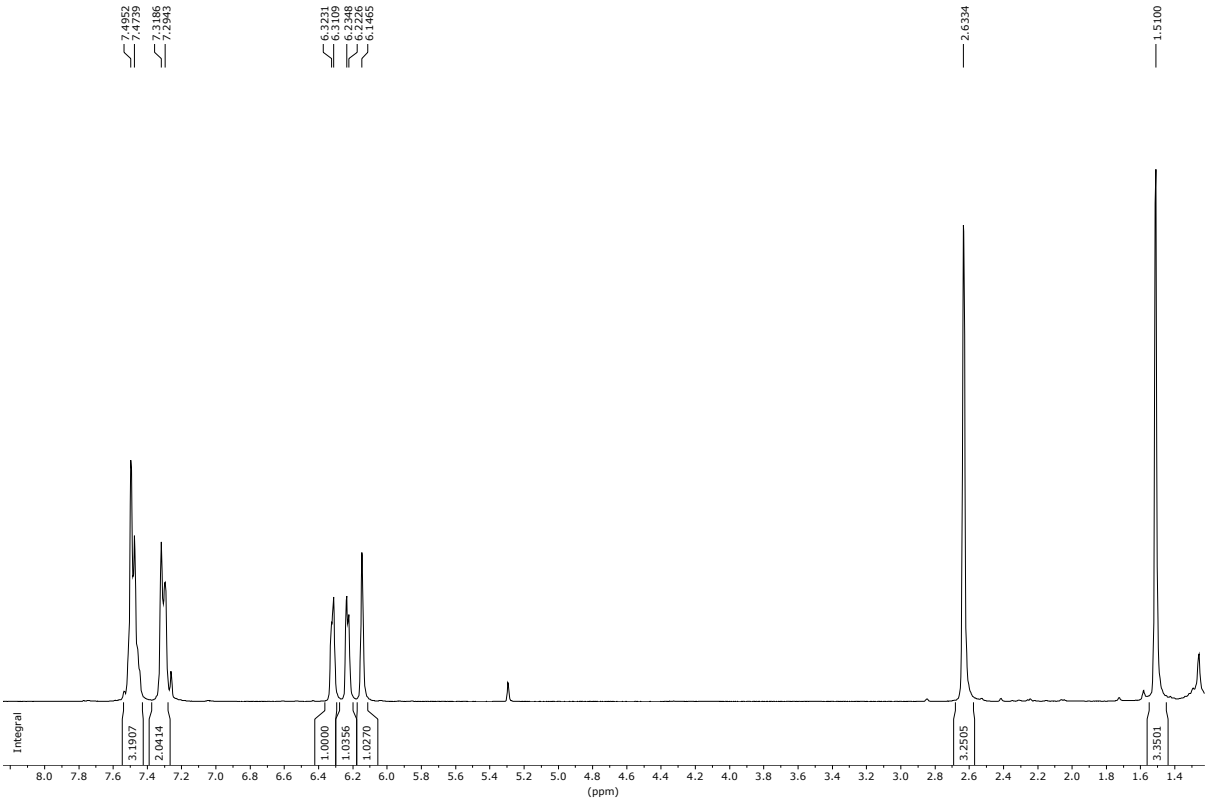
14.9727
(ppm)

8e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7.3186
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6.3231
6.3109
6.2348
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6.1465
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Integral
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1.0000
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1.0270
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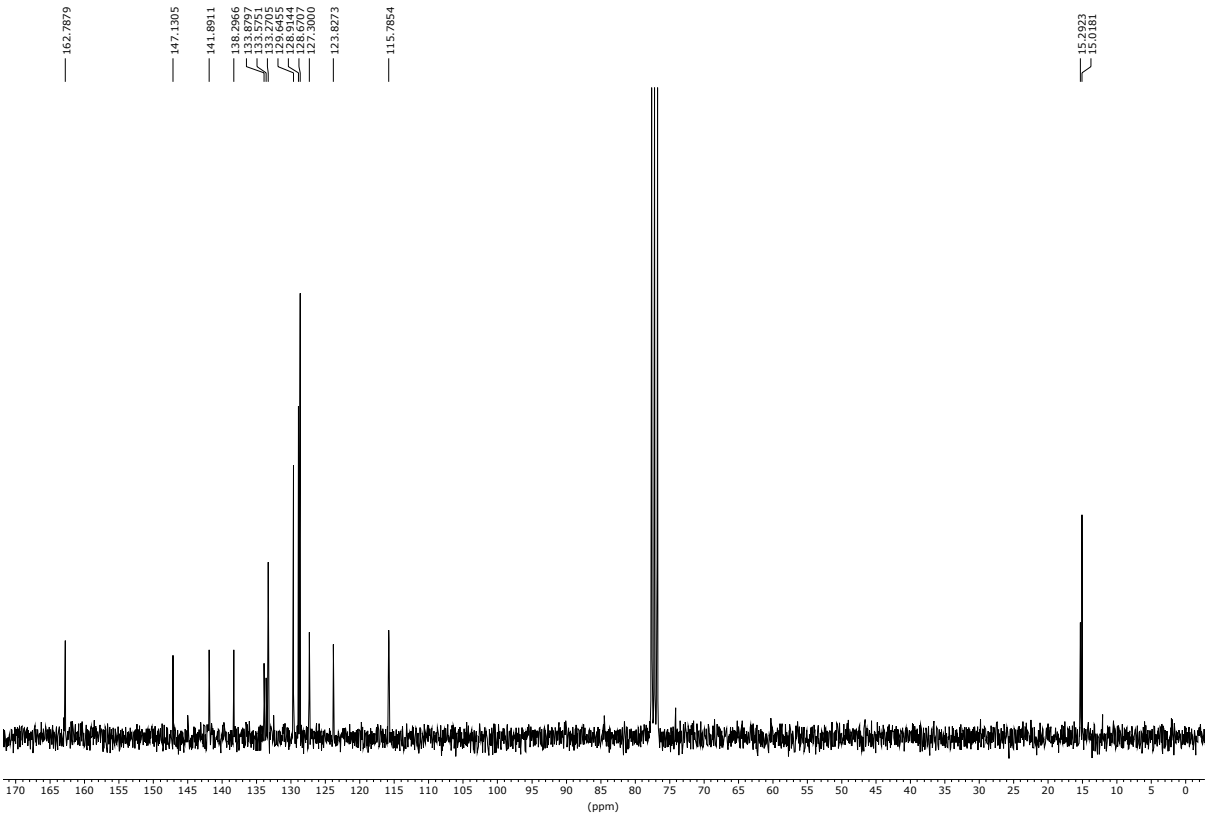
3.3501
(ppm)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141.8911
138.2966
133.8797
133.5751
133.2705
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129.3414
128.6707
127.3000
123.8273
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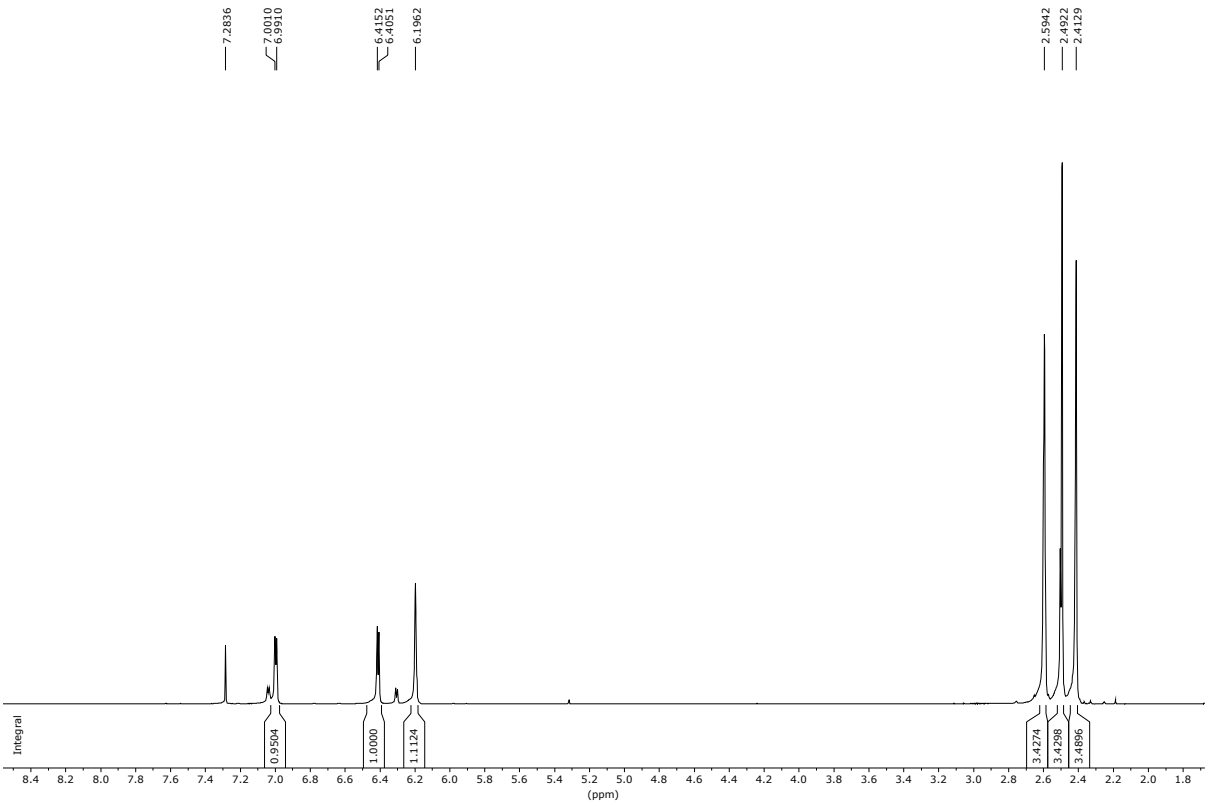
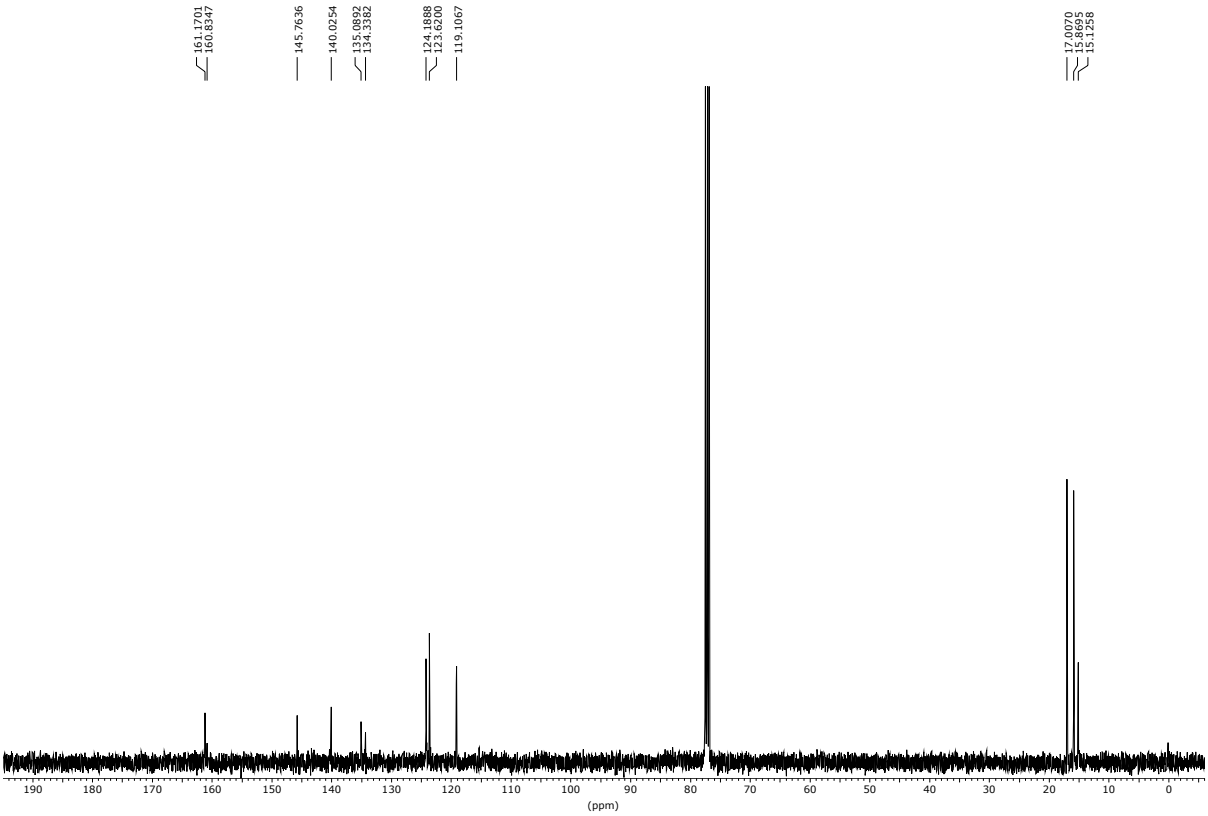
15.0181
(ppm)

8f


7.2836
7.0010
6.9910
6.4152
6.4051
6.1962
2.5942
2.4922
2.4129
Integral
0.9504
1.0000
1.1124
3.4274
3.4298
3.4896
(ppm)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160.8347
145.7636
140.0254
135.0892
134.3382
124.1888
123.6200
119.1067
17.0070
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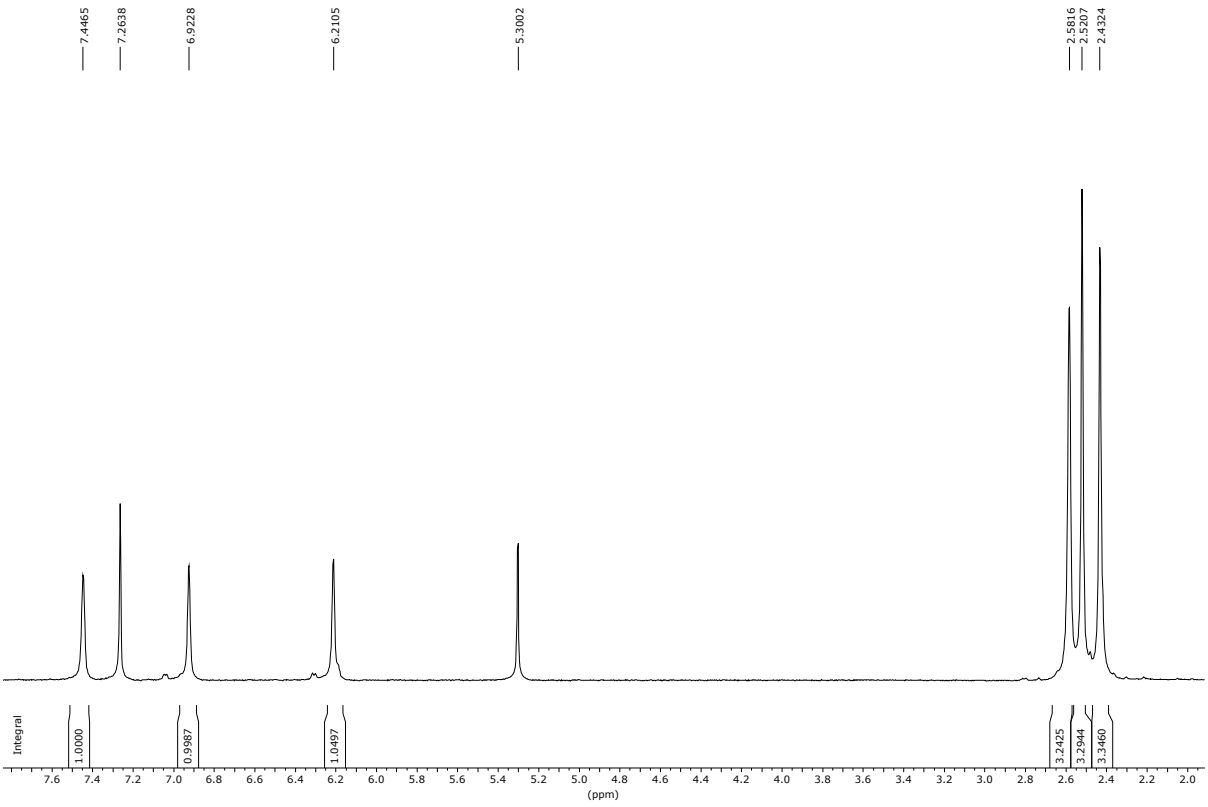
15.1258
(ppm)

8g


7.4465
7.2638
6.9228
6.2105
5.3002
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Integral
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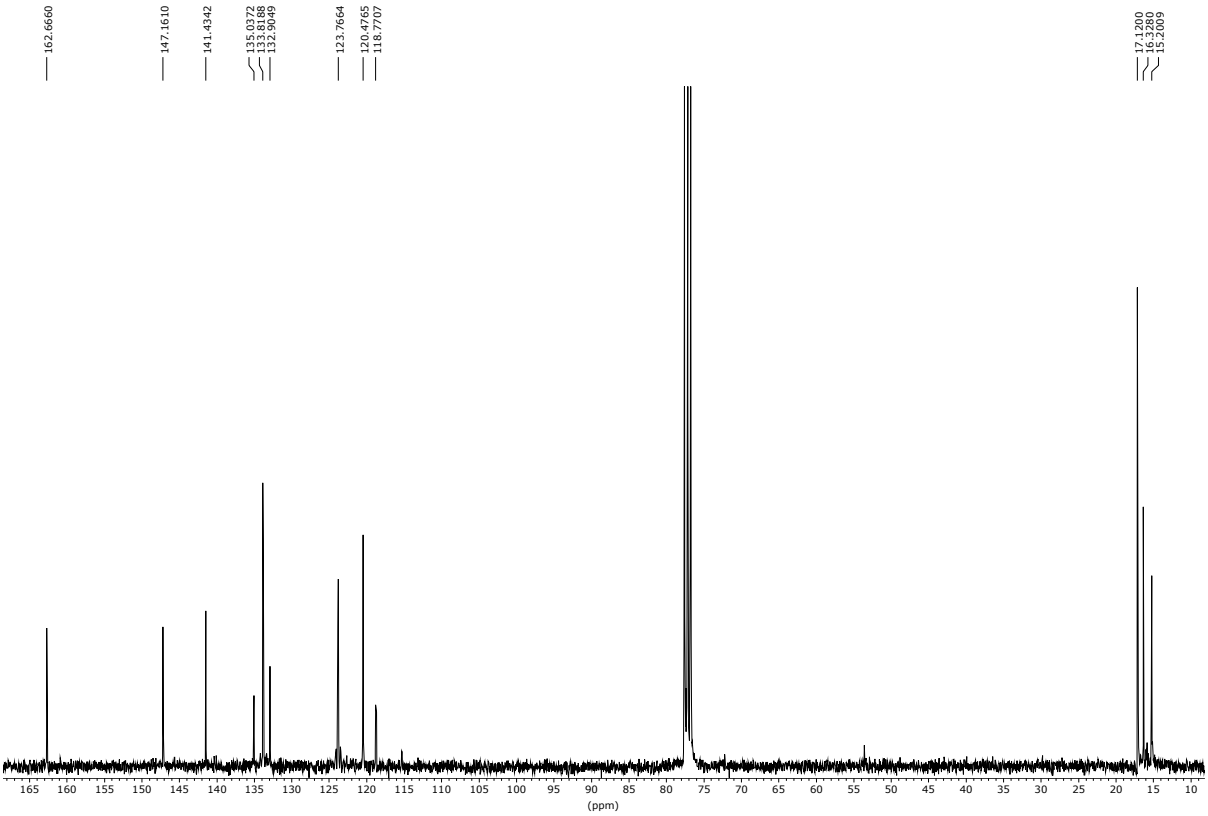
3.2425
3.2944
3.3460
(ppm)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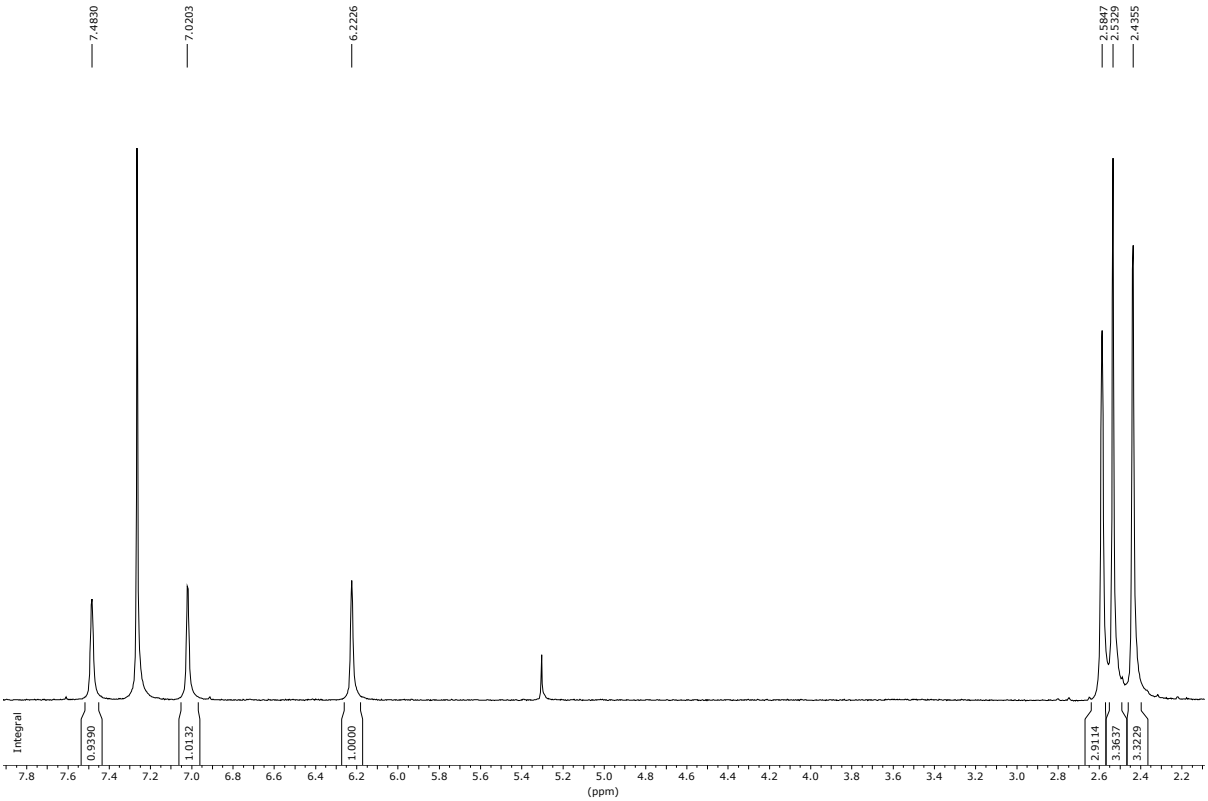
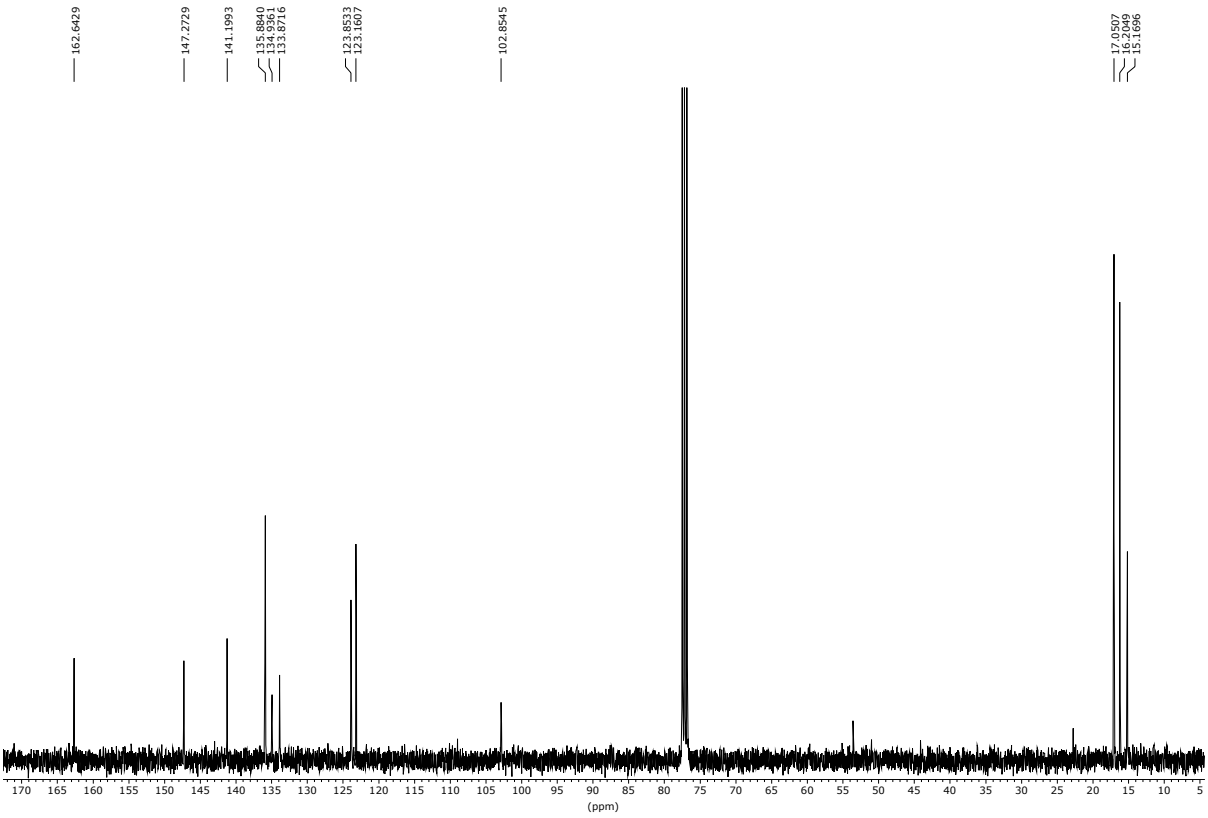
147.1610
141.4342
135.0272
133.8188
132.9049
123.7664
120.4765
118.7707
17.1200
16.3280
15.2009
(ppm)

8h


7.4830
7.0203
6.2226
2.5847
2.5329
2.4355
Integral
0.9390
1.0132
1.0000
2.9114
3.3637
3.3229
(ppm)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147.2729
141.1993
135.8840
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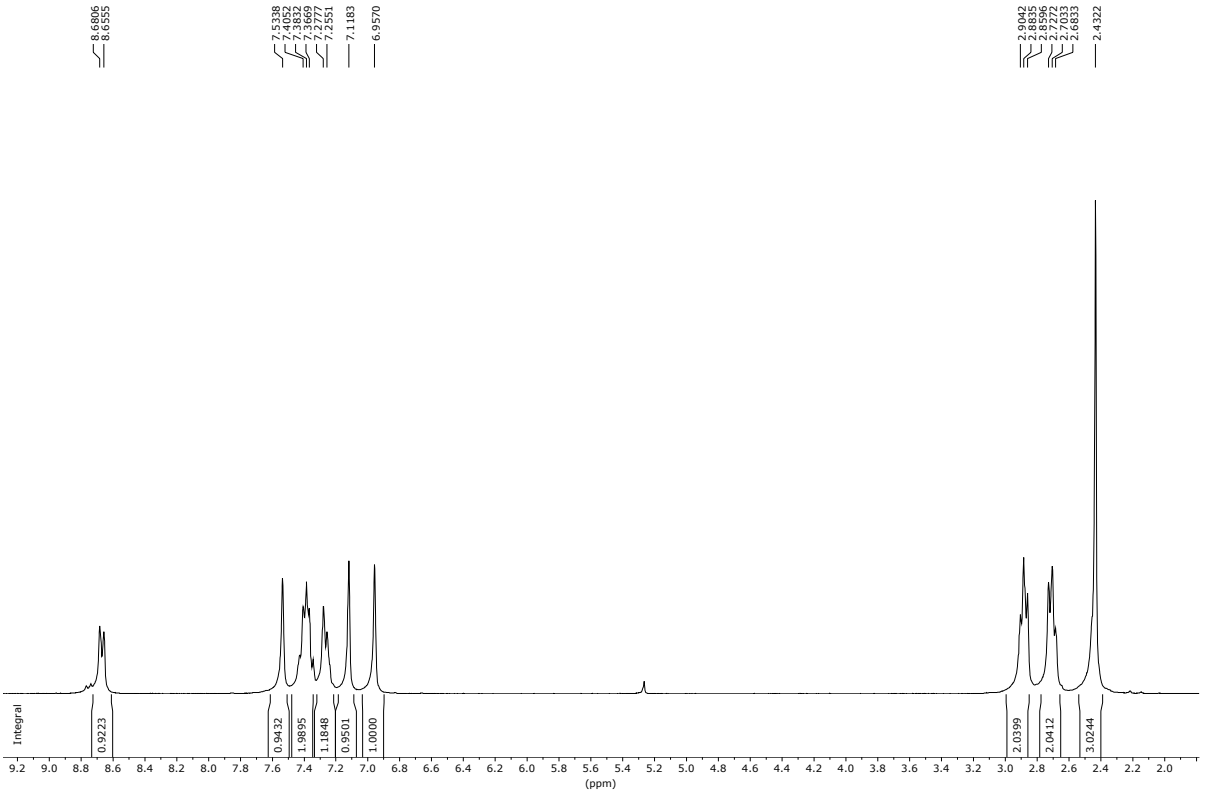
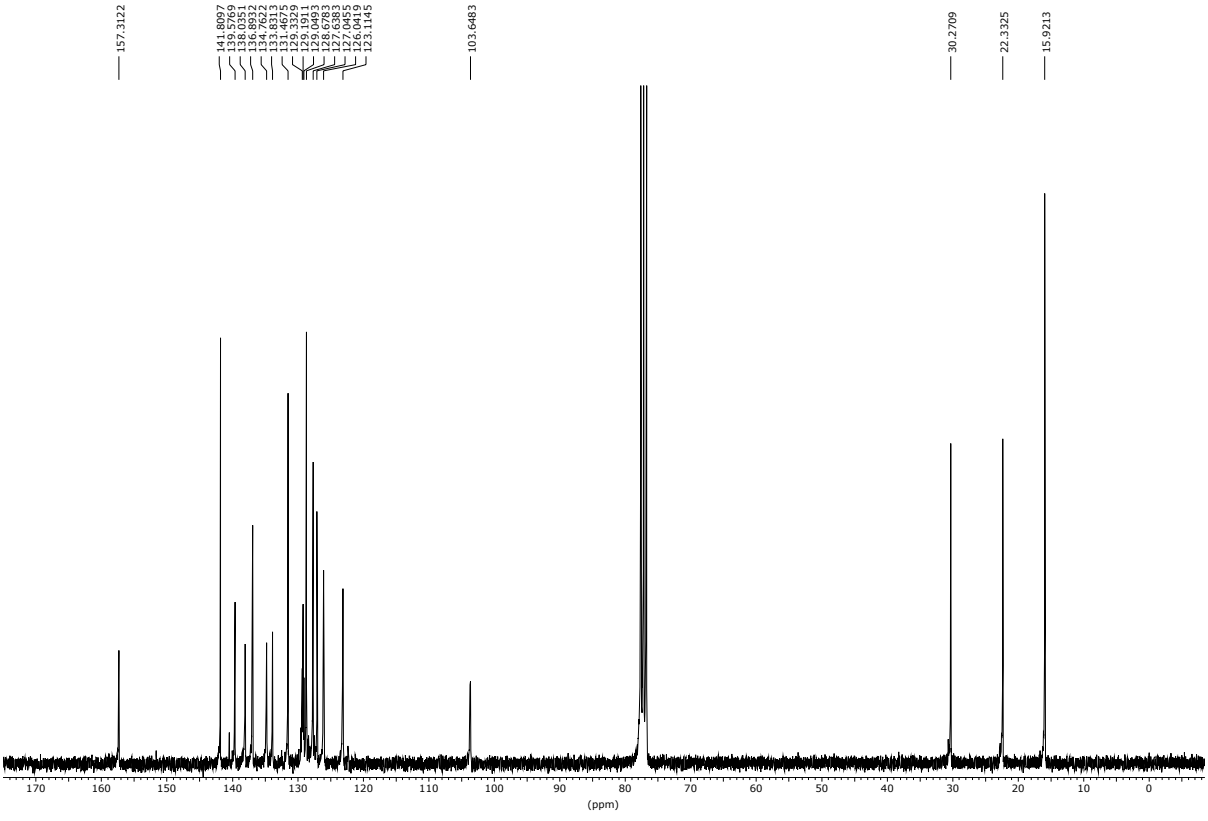
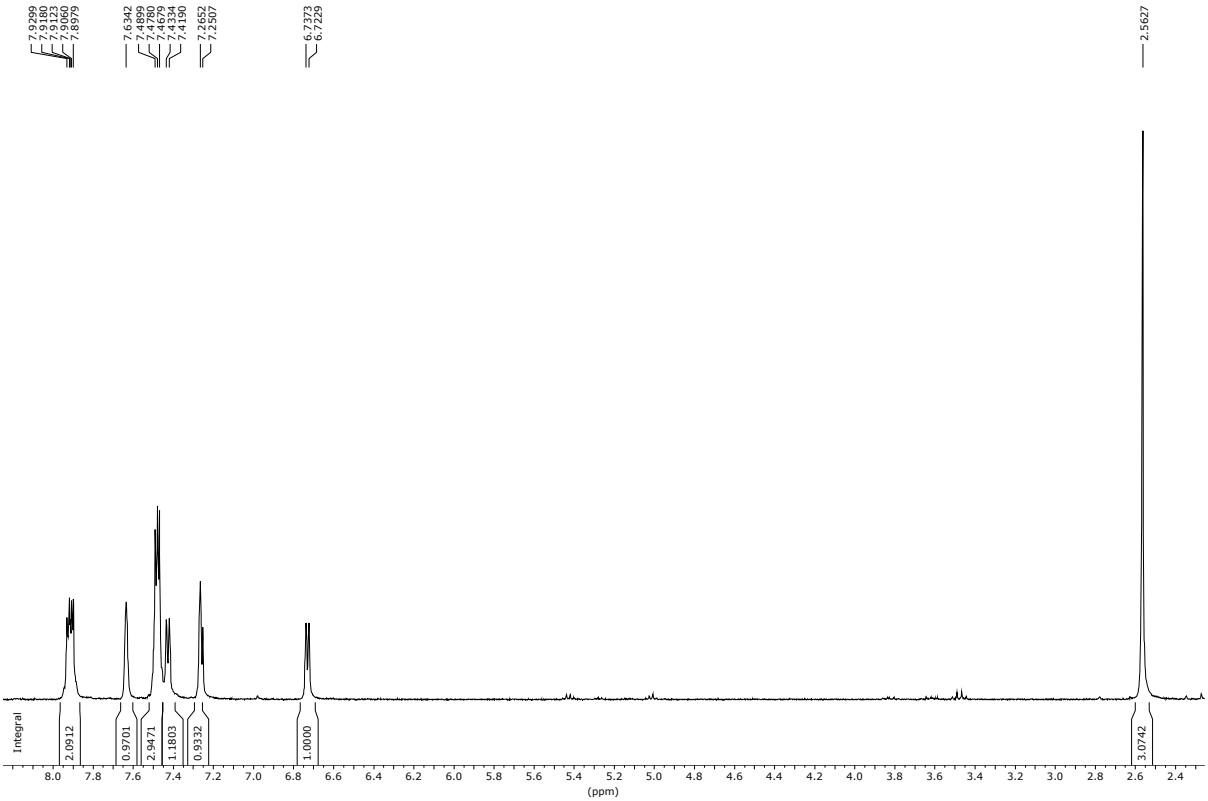
133.8716
123.8533
123.1607
102.8545
17.0507
16.2049
15.1696
(ppm)

8i


8.6806
8.6555
7.5338
7.4052
7.3832
7.3669
7.2777
7.2551
7.1183
6.9570
2.9042
2.8845
2.8596
2.7272
2.7033
2.6833
2.4322
Integral
0.9223
0.9432
1.9895
1.1848
0.9501
1.0000
2.0399
2.0412
3.0244
(ppm)


157.3122
141.8097
139.5769
138.0351
136.8932
134.4922
133.8313
131.4675
129.3329
129.1911
129.0493
128.6783
127.6383
127.0455
126.0419
123.1145
103.6483
30.2709
22.3325
15.9213
(ppm)

8j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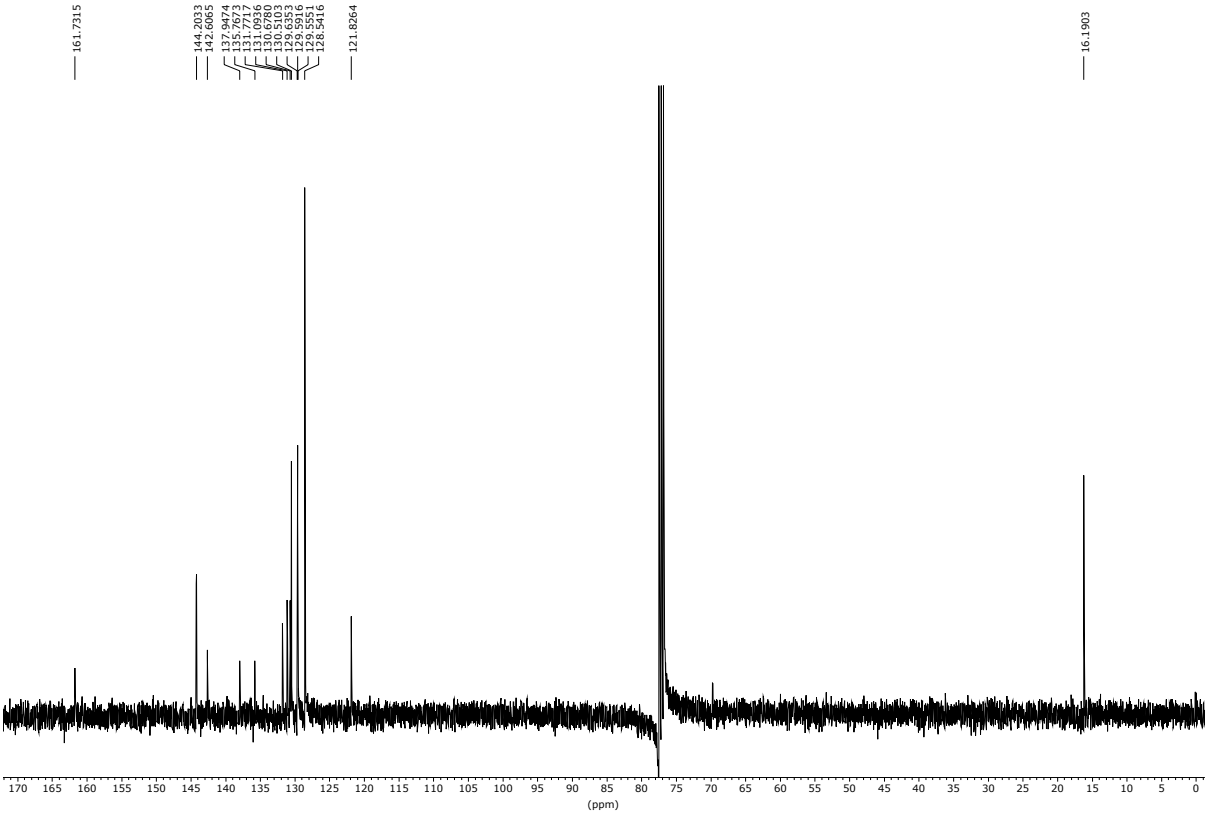
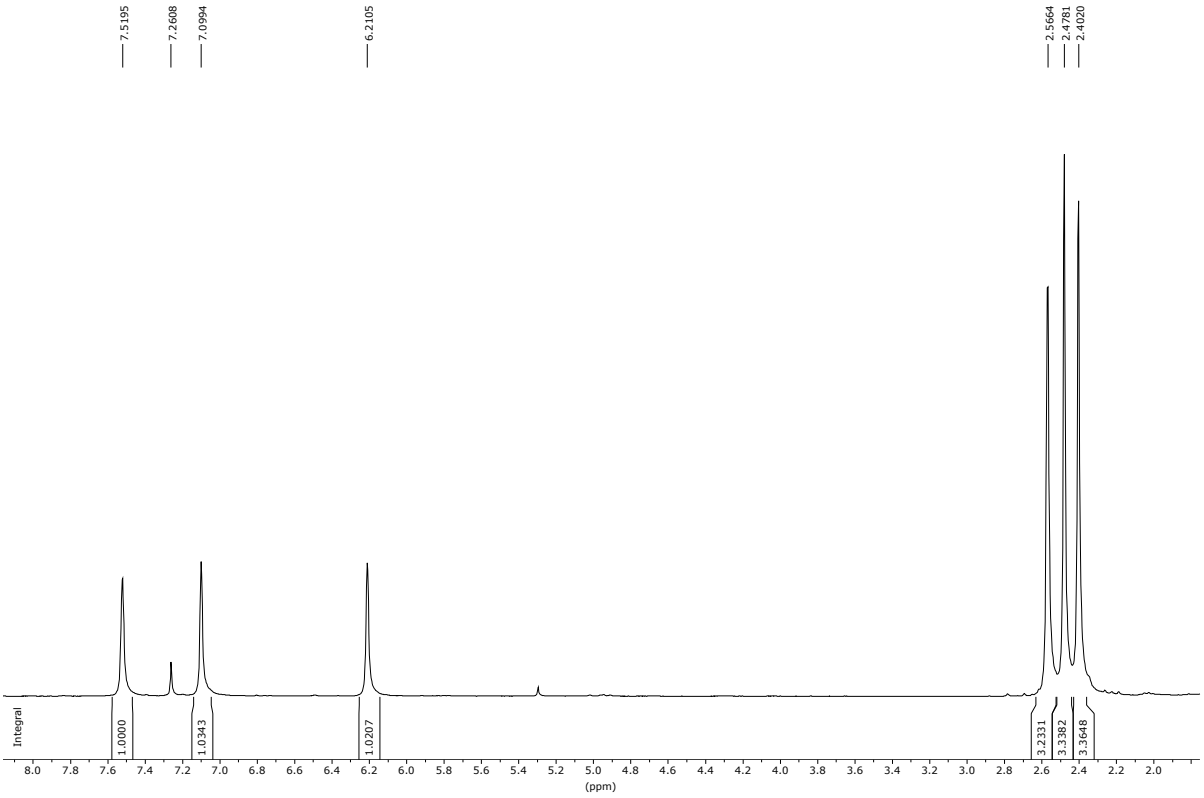
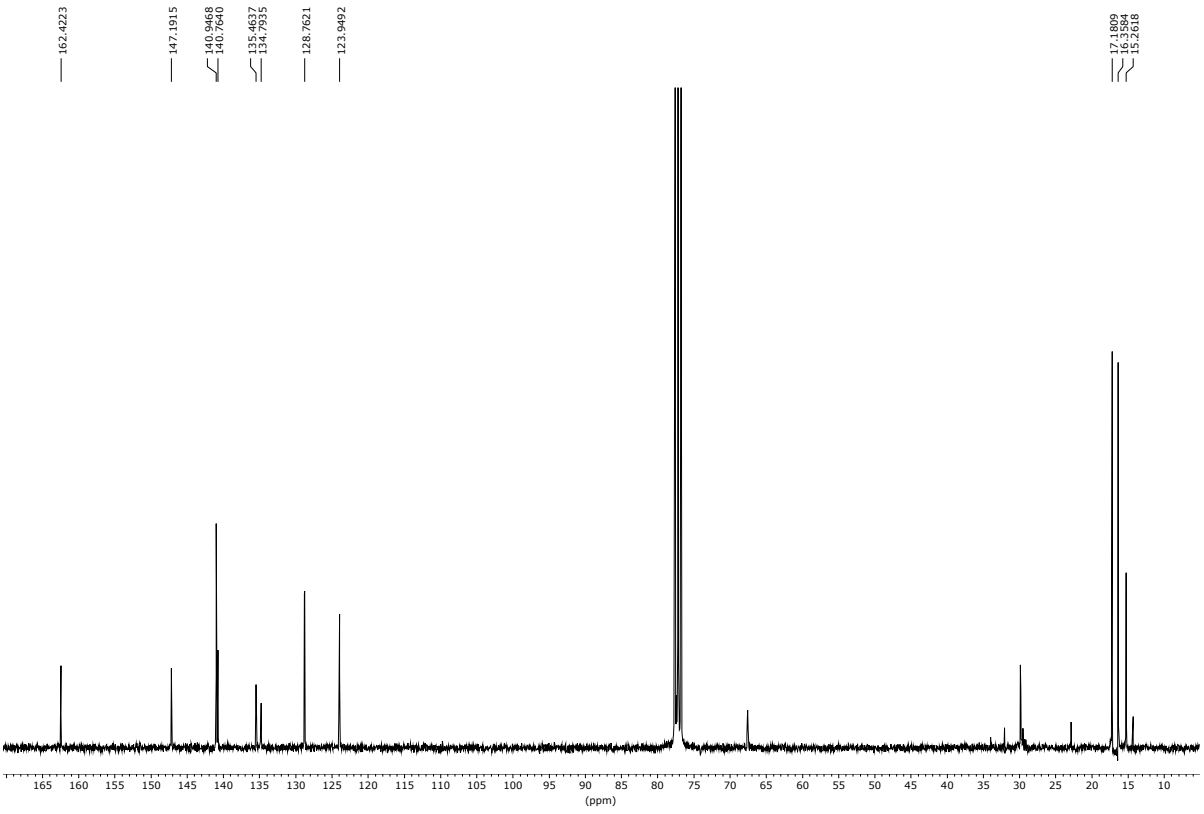
7.9180
7.9123
7.9060
7.8979
7.6342
7.4899
7.4780
7.4679
7.4334
7.4190
7.2652
7.2507
6.7373
6.7229
2.5627
Integral
2.0912
0.9701
2.9471
1.1803
0.9332
1.0000
3.0742
(ppm)


161.7315
144.2033
142.6065
137.9474
135.7973
133.7717
131.0936
130.6780
130.3153
129.9916
129.5551
128.9416
121.8264
16.1903
(ppm)

8k


7.5195
7.2608
7.0994
6.2105
2.5664
2.4781
2.4020
Integral
1.0000
1.0343
1.0207
3.2331
3.3382
3.3648
(ppm)


162.4223
147.1915
140.9468
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135.4637
134.7935
128.7621
123.9492
17.1809
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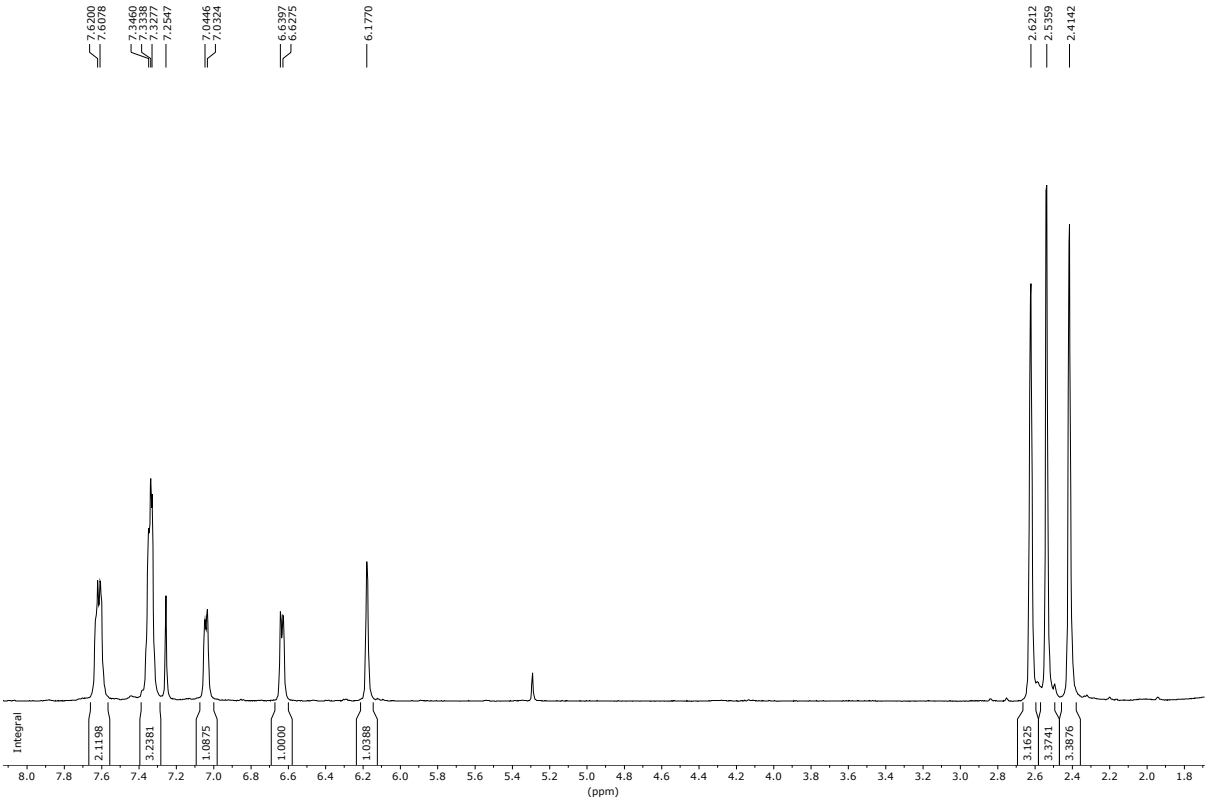
15.2618
(ppm)

9a


7.6200
7.6078
7.3460
7.3338
7.3277
7.2547
7.0446
7.0324
6.6397
6.6275
6.1770
2.6212
2.5359
2.4142
Integral
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3.2381
1.0875
1.0000
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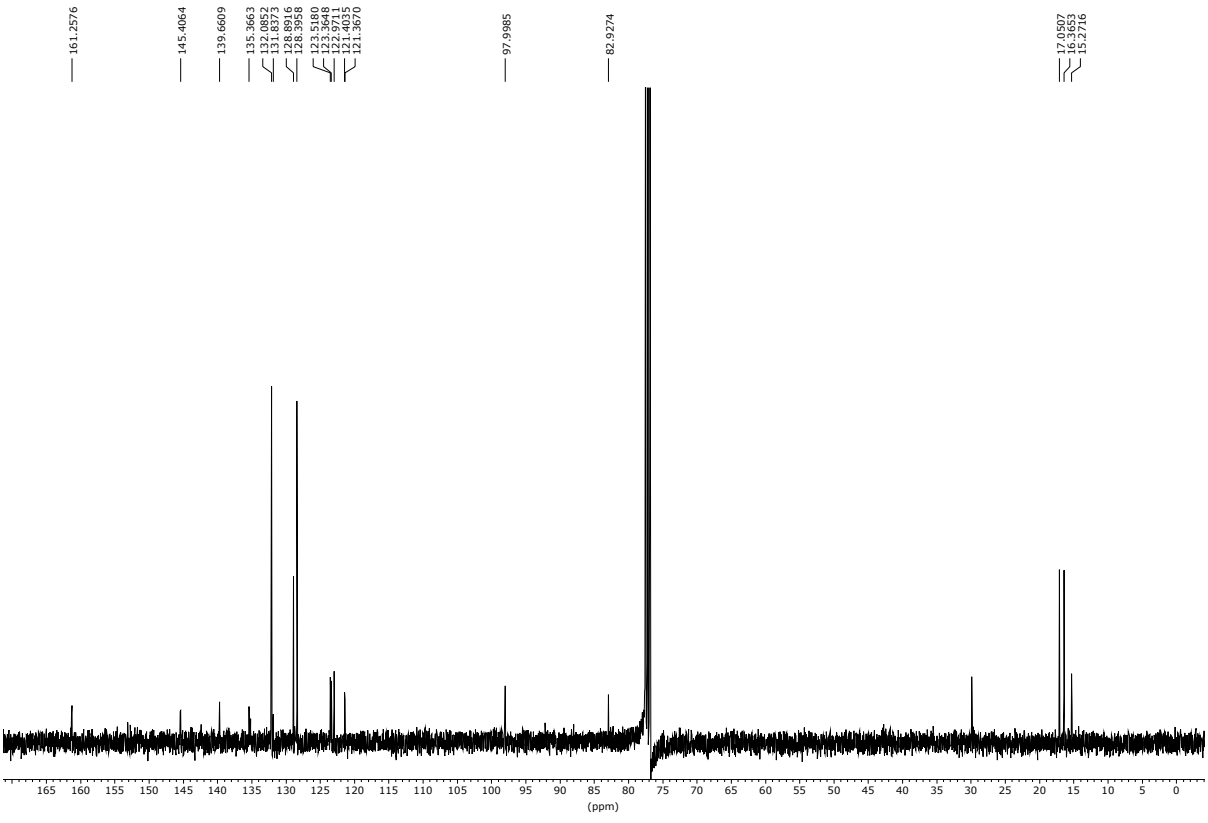
3.1625
3.3741
3.3876
(ppm)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145.4064
139.6609
135.3663
131.8852
131.8373
128.8916
128.3958
123.5180
123.3648
122.9711
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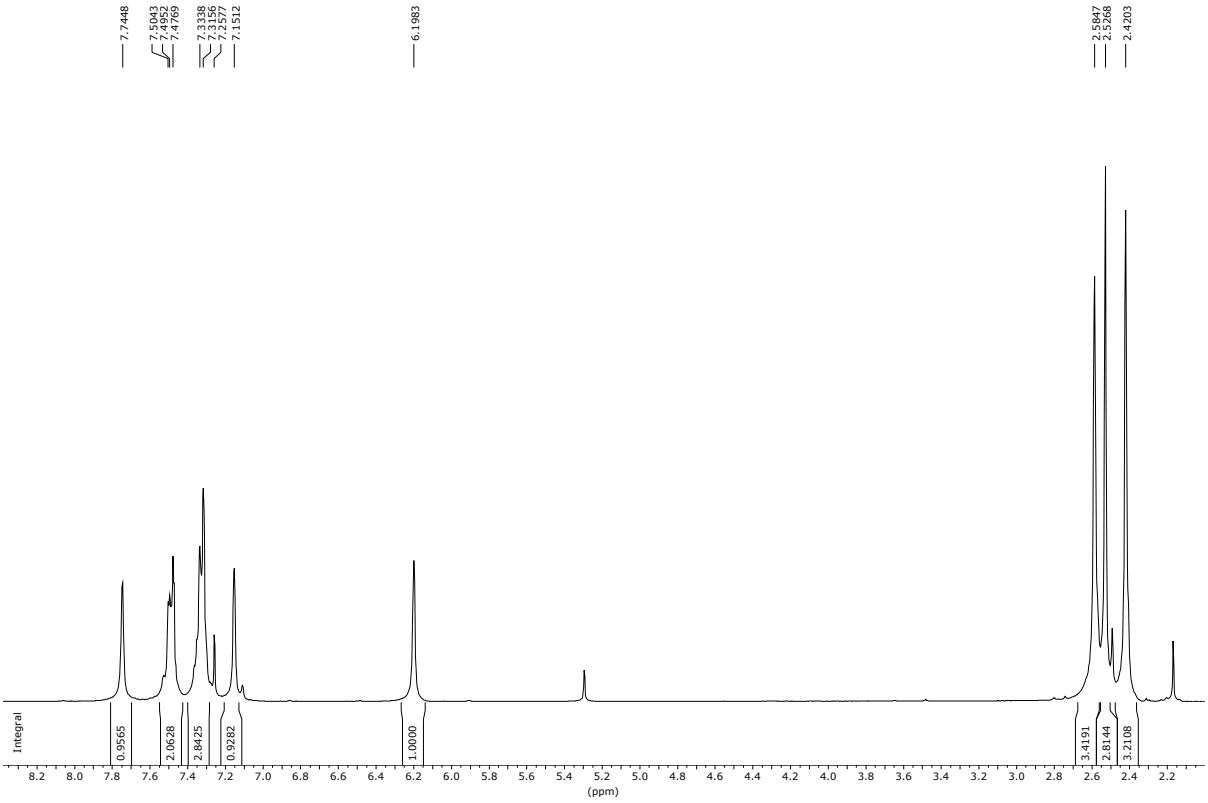
121.3670
97.9985
82.9274
17.0507
16.3653
15.2716
(ppm)

9b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7.5943
7.4952
7.4769
7.3338
7.3156
7.2577
7.1512
6.1983
2.5847
2.5268
2.4203
Integral
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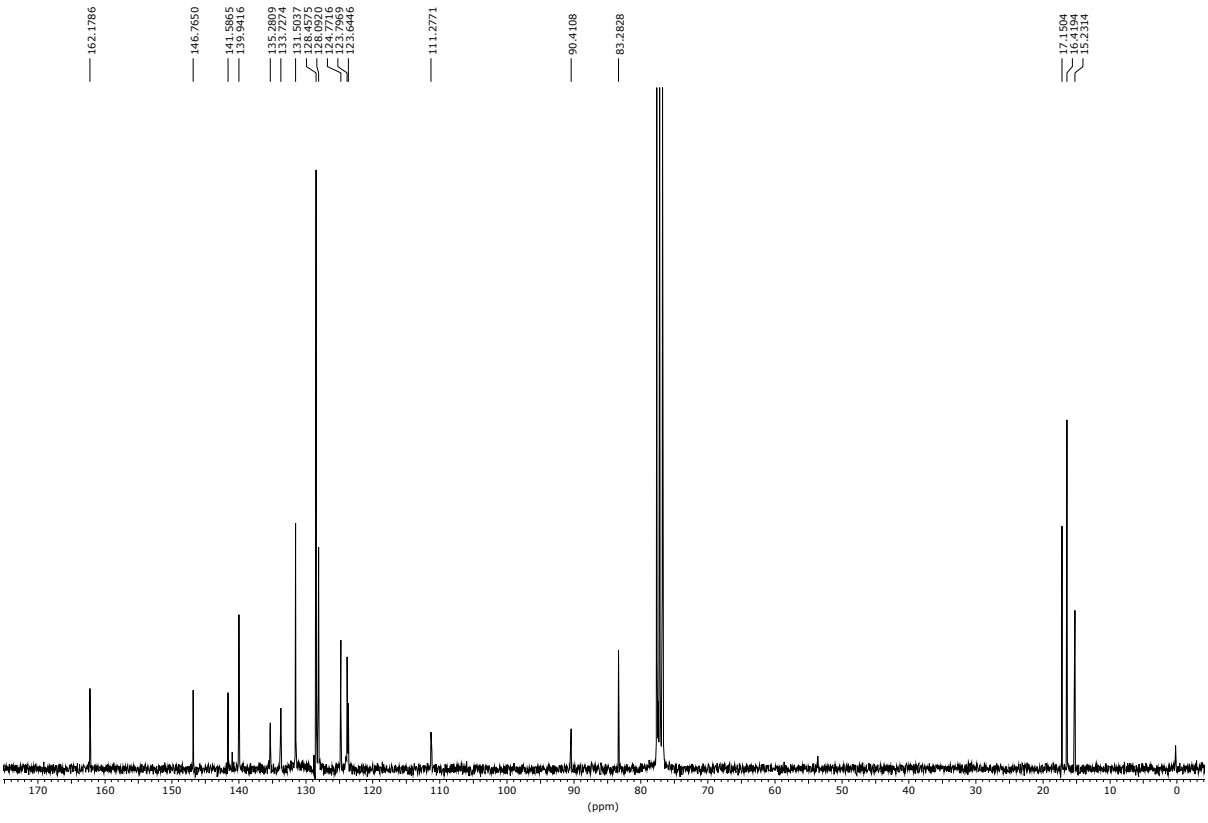
3.2108
(ppm)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139.9416
135.2809
133.7274
131.5037
128.4575
126.9910
124.7716
123.7969
123.6446
111.2771
90.4108
83.2828
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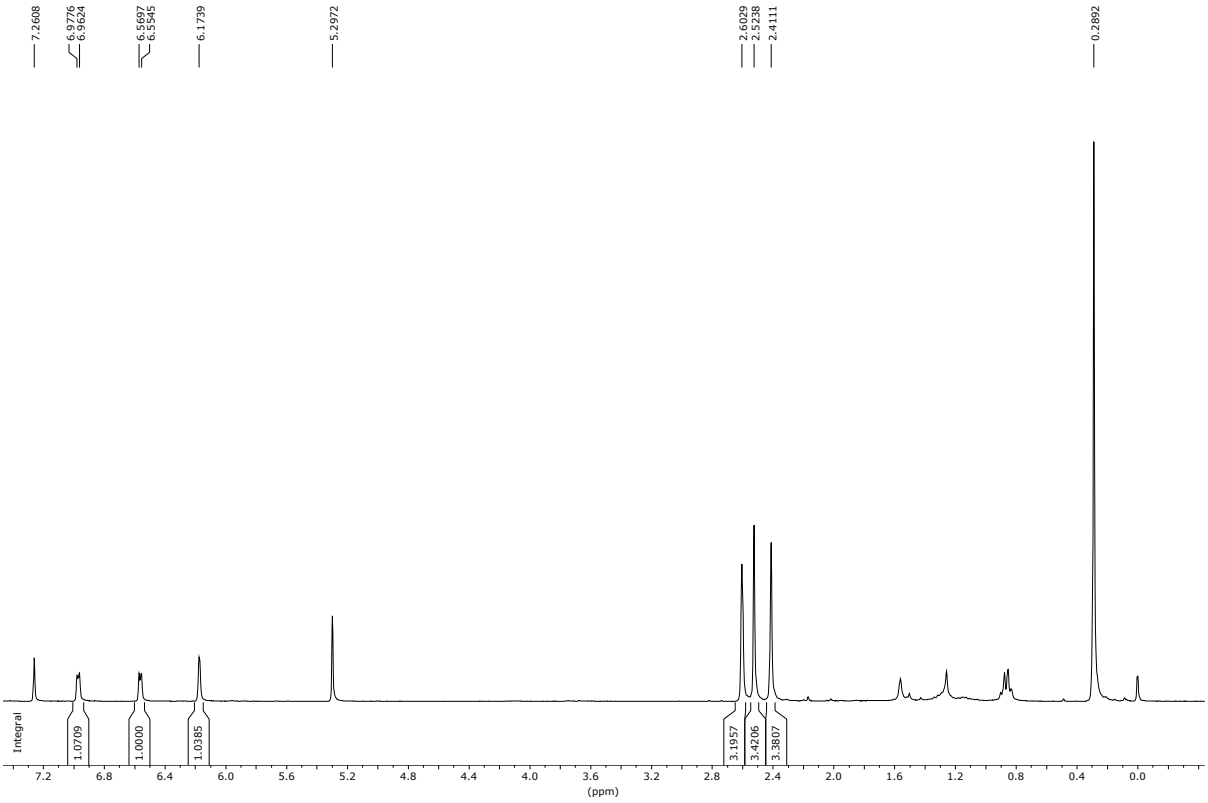
15.2314
(ppm)

9c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6.9624
6.5697
6.5545
6.1739
5.2972
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Integral
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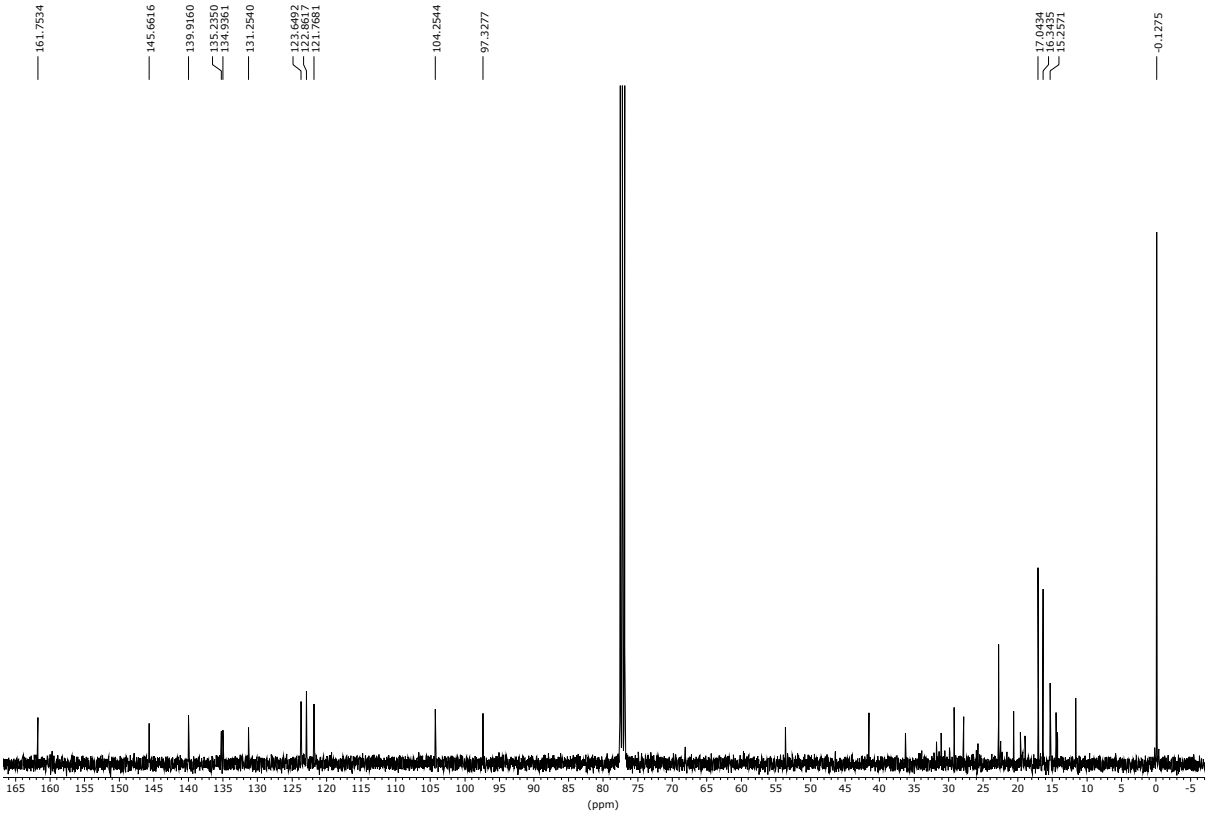
(ppm)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131.2540
123.6492
123.4657
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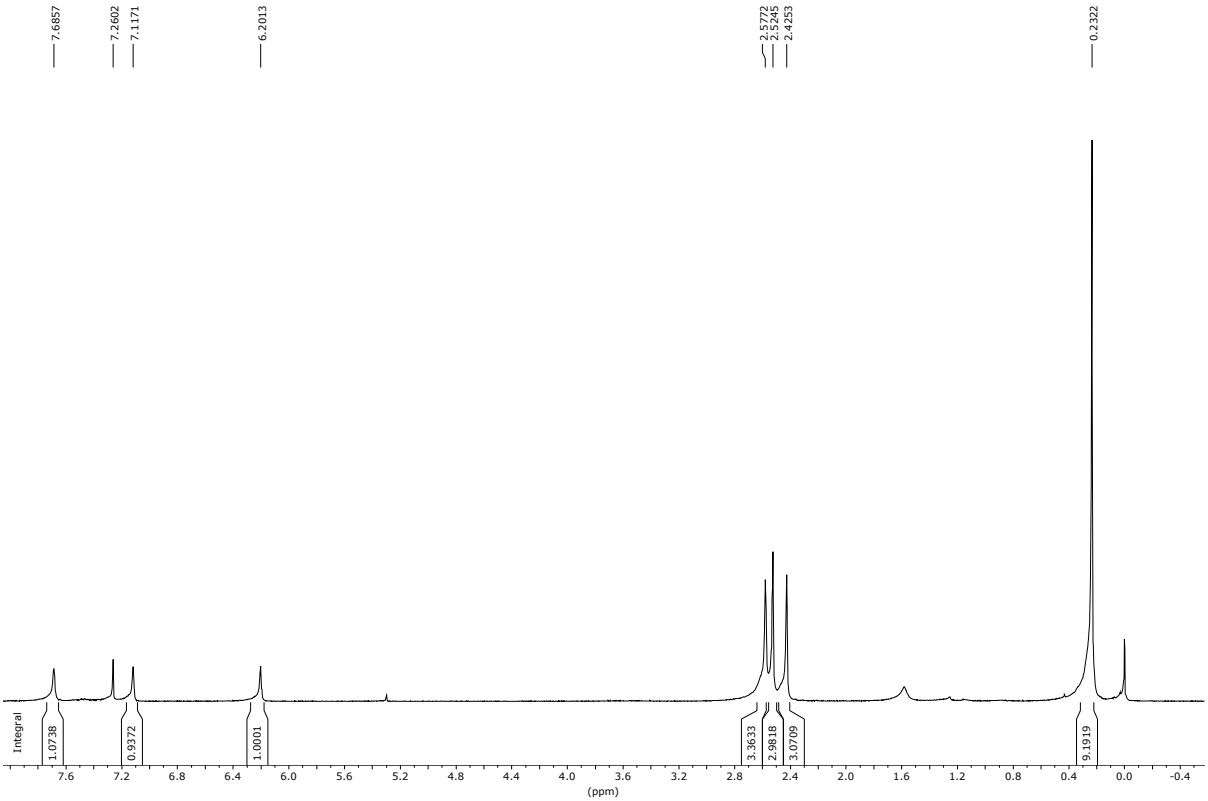
104.2544
97.3277
17.0434
16.3435
15.2571
-0.1275
(ppm)

9d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Integral
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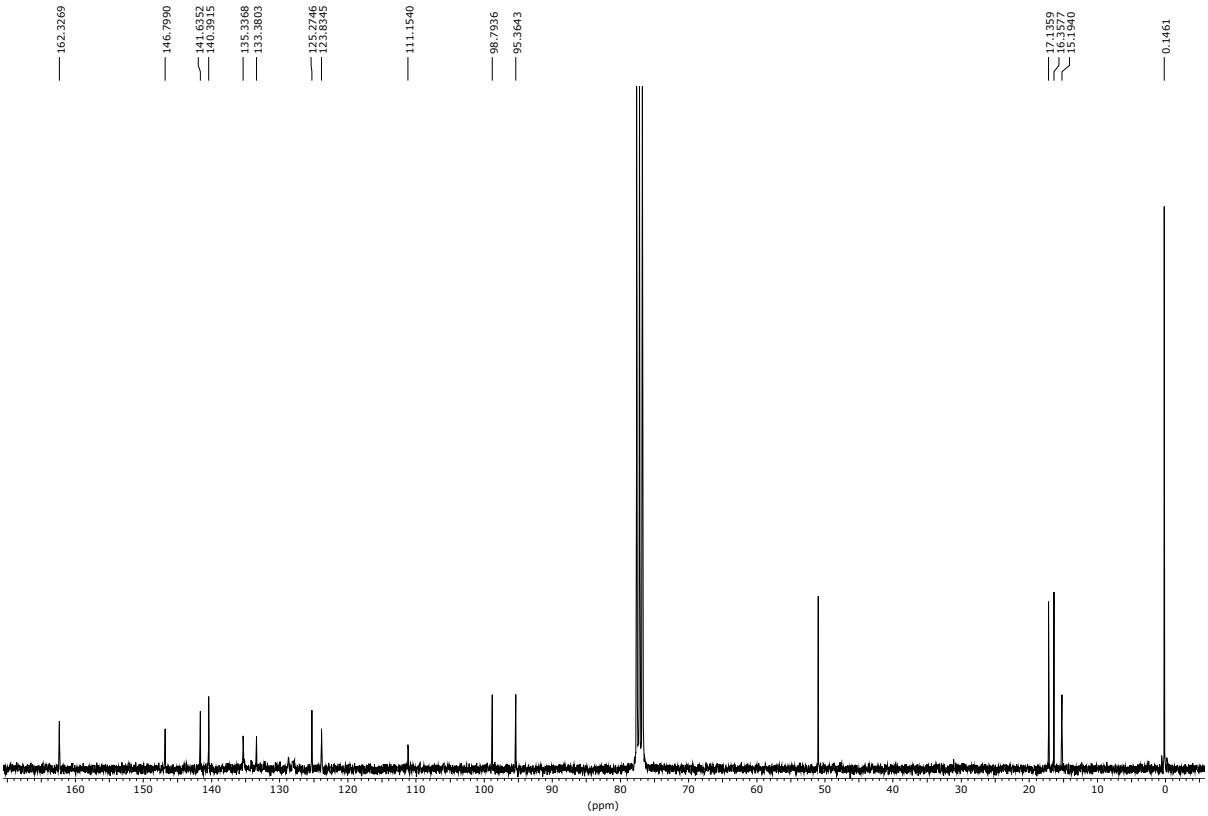
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140.3915
135.3368
133.3803
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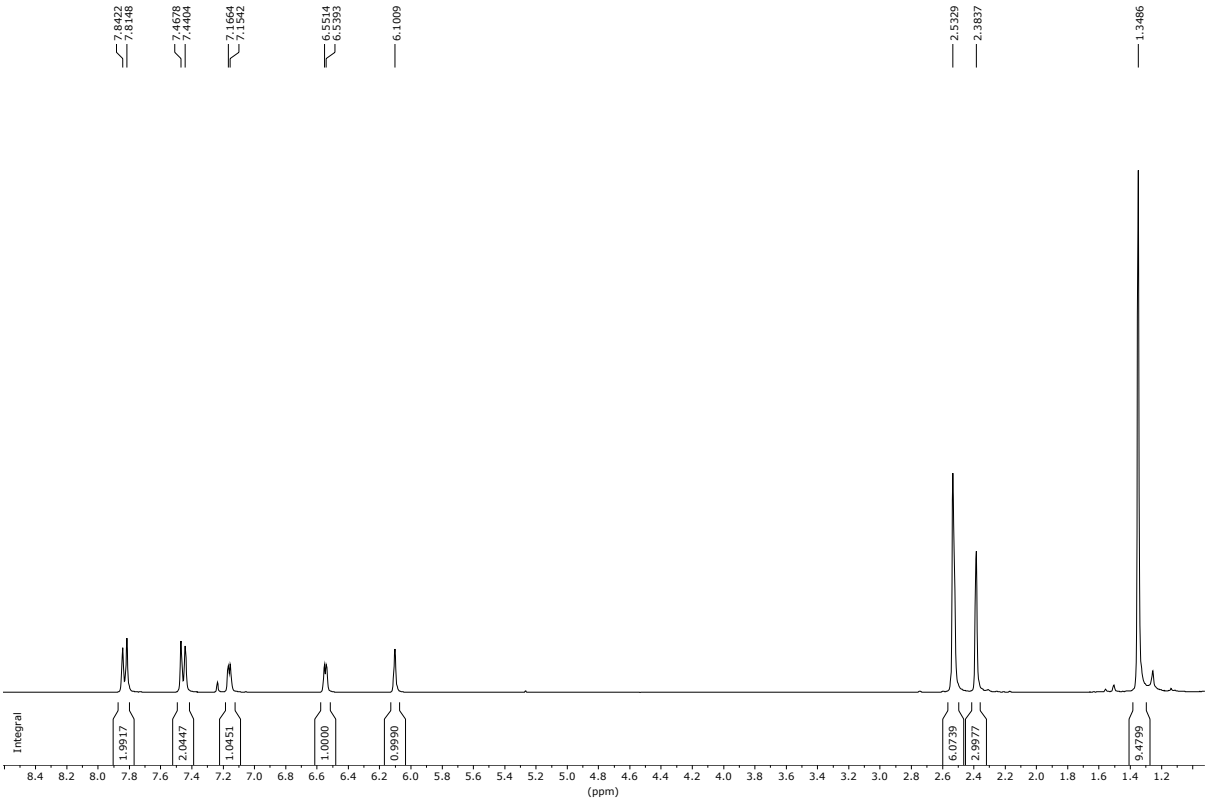
10a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7.4678
7.4404
7.1664
7.1542
6.5514
6.5393
6.1009
2.5329
2.3837
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Integral
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1.0451
1.0000
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6.0739
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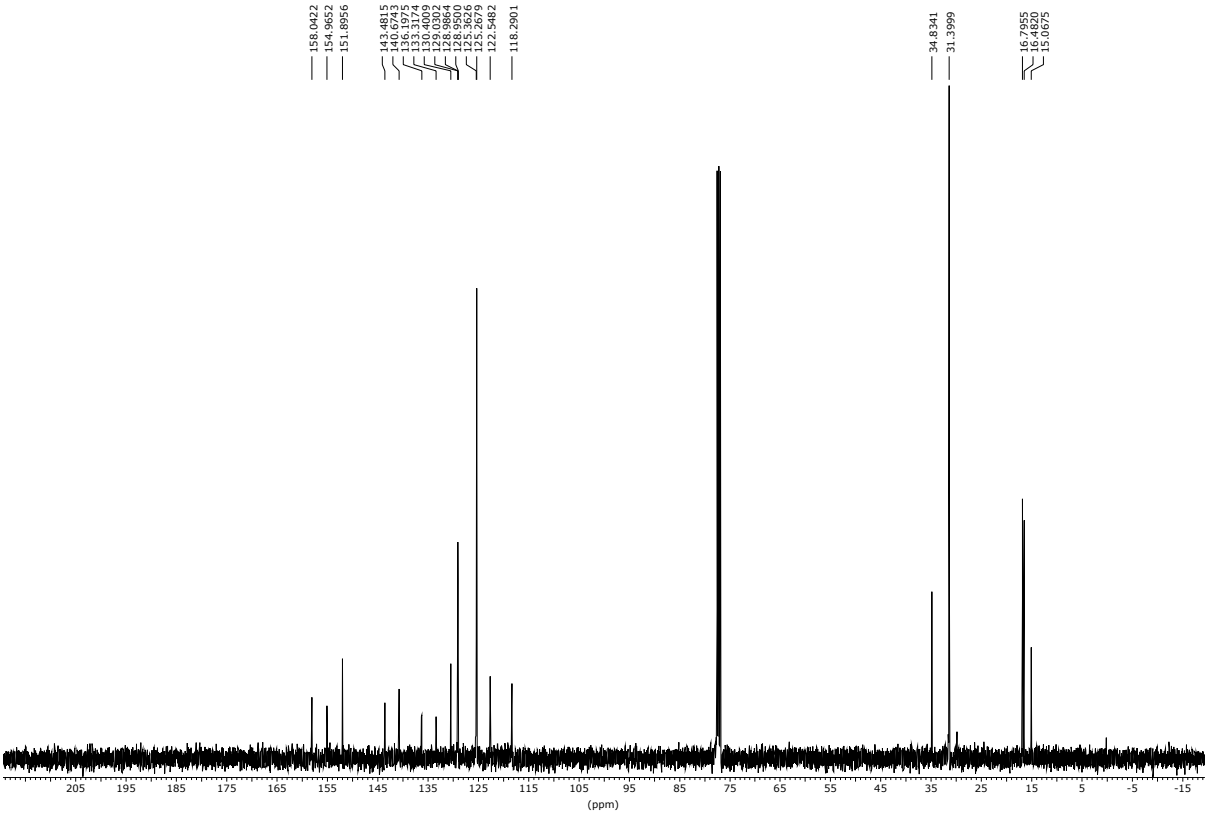
(ppm)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136.1975
133.3714
130.4009
129.0302
128.9864
128.9550
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125.2679
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118.2901
34.8341
31.3999
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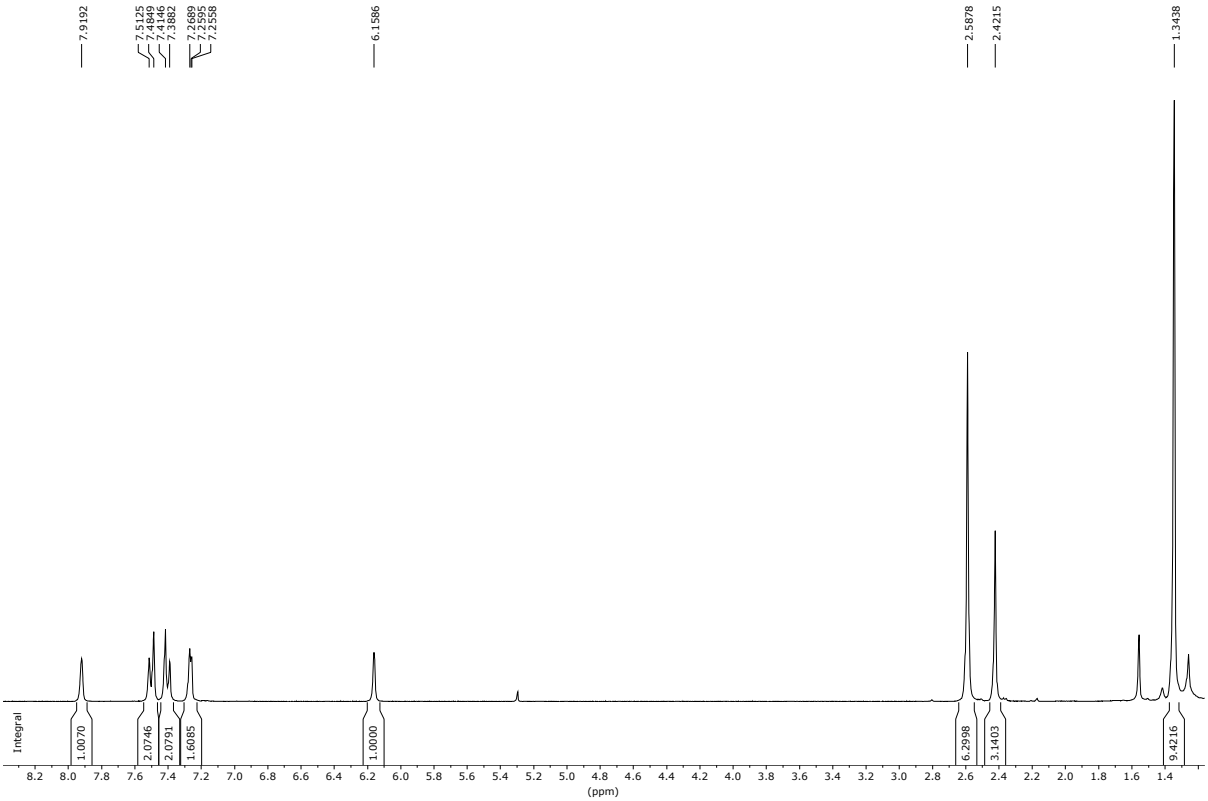
15.0675
(ppm)

10b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7.4146
7.3882
7.2689
7.2595
7.2558
6.1586
2.5878
2.4215
1.3438
Integral
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2.0746
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1.6085
1.0000
6.2998
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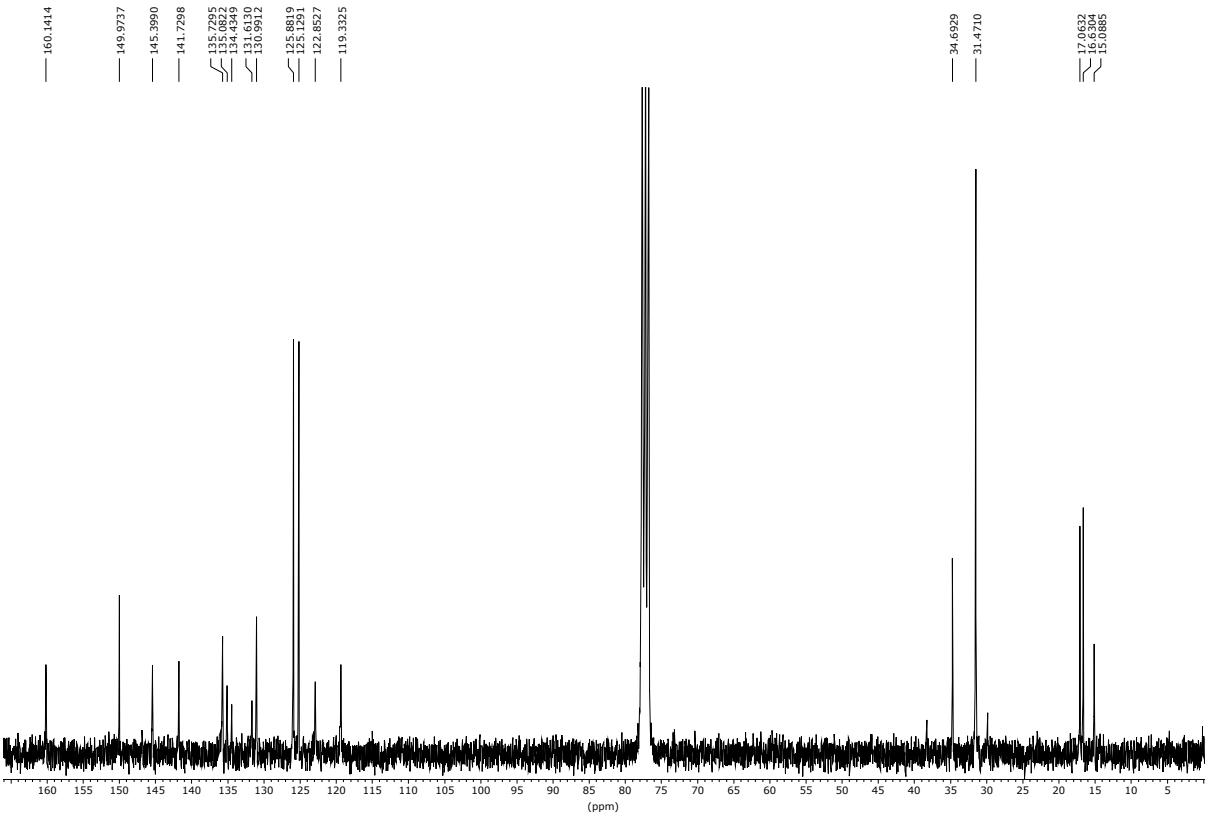
(ppm)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141.7298
135.7295
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130.9912
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122.8527
119.3325
34.6929
31.4710
17.0632
16.6304
15.0885
(ppm)