Supplementary Material

Copper(II)-catalyzed aerobic oxidation of hydrazides to azo intermediates and their Diels–Alder *versus* ene trapping

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General procedure for the *in situ* azo-generation-Diels-Alder reaction using diethyl hydrazinedicarboxylate with various dienes in chloroform (Table 2)

To a $CHCl_3$ (20 ml) solution of 2.30 mmol of appropriate diene, 10 mol% $CuCl_2$ and 20 mol% 2-ethyl-2-oxazoline was added 1.15 mmol of diethyl hydrazinedicarboxylate **1**. The resulting solution was stirred at room temperature in air and was monitored by TLC. The completion of the reaction was confirmed by the disappearance of the starting material. The solvent was removed by evaporation and the crude product was purified by silica gel chromatography (hexane: ethyl acetate, 4:1 v/v as the eluent).

Table 2 Entry 1

Using diethyl hydrazinedicarboxylate (203 mg, 1.15 mmol), cyclohexa-1,3-diene (185 mg, 2.31 mmol), $CuCl_2$ (16 mg, 0.12 mmol) and 2-ethyl-2-oxazoline (23 mg, 0.23 mmol), the reaction was stirred for 48 h, giving **4a** (186 mg, 63 %) and **5a** (66 mg, 23 %). The ratio of **4a** to **5a** was determined on the crude product by ^{1}H NMR using the signals at δ 6.70-6.45 to 5.94 (=C-H resonances in **4a** and **5a** respectively). Analytical and spectroscopic data were identical to those reported in the literature.[1,2]

Table 2, Entry 2

Using diethyl hydrazinedicarboxylate (201 mg, 1.14 mmol), freshly cracked cyclopentadiene (151 mg, 2.28 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (23 mg, 0.23 mmol), the reaction was stirred for 48 h giving **4b** as colorless oil (251 mg, 92 %); All other analytical and spectroscopic data were identical to those reported in the literature.[3]

Table2, Entry 3

Using diethyl hydrazinedicarboxylate (206 mg, 1.17 mmol), 2,3-dimethyl buta-1,3-diene (192 mg, 2.34 mmol), $CuCl_2$ (16 mg, 0.12 mmol) and 2-ethyl-2-oxazoline (23 mg, 0.23 mmol), the reaction was stirred for 40 h. Purification gave colorless oil of **4c** (270 mg, 90%): All other analytical and spectroscopic data were identical to those reported in the literature.[2]

Table 2, Entry 4

Using diethyl hydrazinedicarboxylate (206 mg, 1.17 mmol), hexa-2,4-diene (192 mg, 2.34 mmol), $CuCl_2$ (16 mg, 0.12 mmol) and 2-ethyl-2-oxazoline (24 mg, 0.24 mmol), the reaction was stirred for 48 h, giving **4d** (222 mg, 74%). Analytical and spectroscopic data were identical to those reported in the literature.[4]

Table 2, Entry 5

Using diethyl hydrazinedicarboxylate (209 mg, 1.19 mmol), 2-methyl buta-1,3-diene (163 mg, 2.39 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (22 mg, 0.23 mmol), the reaction was stirred for 48 h. Purification gave colorless oil **4e** (163 mg, 57%); analytical and spectroscopic data were identical to those reported in the literature.[5]

Table 2, Entry 6

Using diethyl hydrazinedicarboxylate (199 mg, 1.13 mmol), 9,10-dimethylanthracene (233 mg, 1.13 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (23 mg, 0.23 mmol), the reaction was stirred for 240 h, giving a white solid of **4f** (73 mg, 17%); m.p. 162 -163 °C (lit. 153 – 154 °C).[3] All other analytical and spectroscopic data were identical to those reported in the literature.[6]

Table 2, Entry 7

Using diethyl hydrazinedicarboxylate (200 mg, 1.14 mmol), 1,4-diphenyl buta-1,3-diene (234 mg, 1.14 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (23 mg, 0.23 mmol), the reaction was stirred for 360 h, giving a white solid of **4g** (86 mg, 20%); mp = 139 – 140 °C All other analytical and spectroscopic data were identical to those reported in the literature.[7]

General procedure for the *in situ* azo-generation-Diels-Alder reaction using 4-phenylurazole with various dienes in chloroform (Table 3)

To a $CHCl_3$ (20 ml) solution of the appropriate diene, 10% $CuCl_2$ and 20% 2-ethyl-2-oxazoline was added 4-phenylurazole **8**. The resulting solution was stirred at room temperature in air and was monitored by TLC. The completion of the reaction was confirmed by the disappearance of the starting material. The solvent was removed by evaporation and the crude product was purified by flash silica gel chromatography (hexane: ethyl acetate, 1:1 v/v as the eluent).

Table 3, Entry 1

Using 4-phenylurazole (197 mg, 1.12 mmol), cyclohexa-1,3-diene (179 mg, 2.24 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (22 mg, 0.22 mmol), the reaction was stirred for 6 h, giving a white solid of **10a** (334 mg, 94%); m.p. = 177-178 °C (lit. 172-174 °C). All other analytical and spectroscopic data were identical to those reported in the literature.[8,9]

Table 3, Entry 2

Using 4-phenylurazole (201 mg, 1.14 mmol), freshly cracked cyclopentadiene (151 mg, 2.28 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (23 mg, 0.23 mmol), the reaction was stirred for 5 h giving **10b** as a white solid (258 mg, 94 %); m.p. = 146-148 °C (lit. 133-134 °C). All other analytical and spectroscopic data were identical to those reported in the literature.[8]

Table 3, Entry 3

Using 4-phenylurazole (203 mg, 1.15 mmol), 2,3-dimethyl buta-1,3-diene (189 mg, 2.30 mmol), $CuCl_2$ (16 mg, 0.12 mmol) and 2-ethyl-2-oxazoline (23 mg, 0.23 mmol), the reaction was stirred for 8 h. Purification gave a white solid of **10c** (290 mg, 98%); m.p. = 172.5-174 °C (lit. 174-175.5 °C). All other analytical and spectroscopic data were identical to those reported in the literature.[8]

Table 3, Entry 4

Using 4-phenylurazole (199 mg, 1.13 mmol), hexa-2,4-diene (186 mg, 2.26 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (22 mg, 0.23 mmol), the reaction was stirred for 8 h, giving **10d** (270 mg, 93%); m.p. = 146-148 °C (lit. 135-136 °C). Analytical and spectroscopic data were identical to those reported in the literature.[10]

Table 3, Entry 5

Using 4-phenylurazole (201 mg, 1.14 mmol), 2-methyl buta-1,3-diene (155 mg, 2.28 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (22 mg, 0.23 mmol), the reaction was stirred for 8 h. Purification gave a white solid **10e** (266 mg, 96%); m p = 114-116 °C (lit. 110-112 °C). Analytical and spectroscopic data were identical to those reported in the literature.[8]

Table 3, Entry 6

Using 4-phenylurazole (197 mg, 1.12 mmol), 9,10-dimethylanthracene (231 mg, 1.12 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (22 mg, 0.22 mmol), the reaction was stirred for 3 h, giving a white solid of **10f** (408 mg, 96%); m.p. 237-239 °C. All other analytical and spectroscopic data were identical to those reported in the literature.[11,12]

Table 3, Entry 7

Using 4-phenylurazole (198 mg, 1.12 mmol), 1,4-diphenyl buta-1,3-diene (231 mg, 1.12 mmol), $CuCl_2$ (15 mg, 0.11 mmol) and 2-ethyl-2-oxazoline (22 mg, 0.22 mmol), the reaction was stirred for 24 h, giving a white solid of **10g** (403 mg, 94%); m.p. = 169-171 °C (lit. 160-161 °C). All other analytical and spectroscopic data were identical to those reported in the literature.[8]

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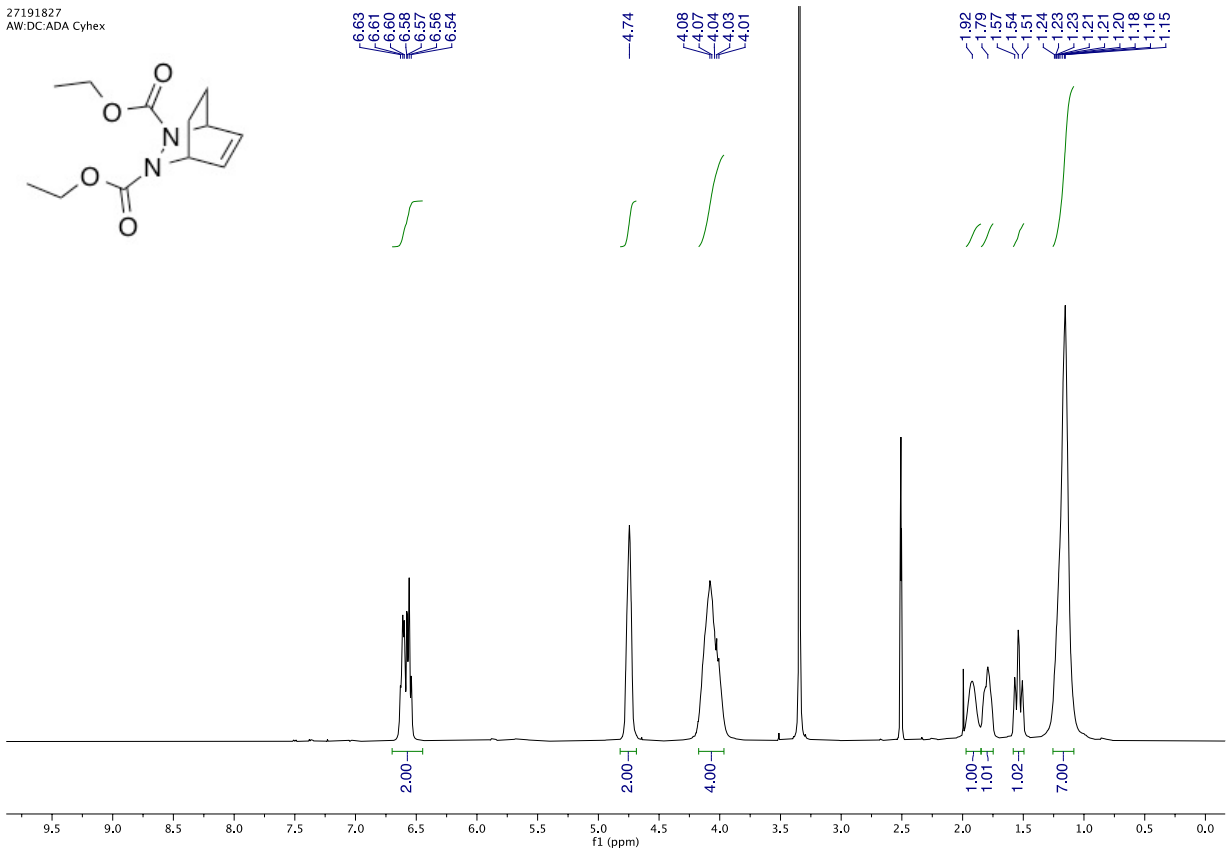
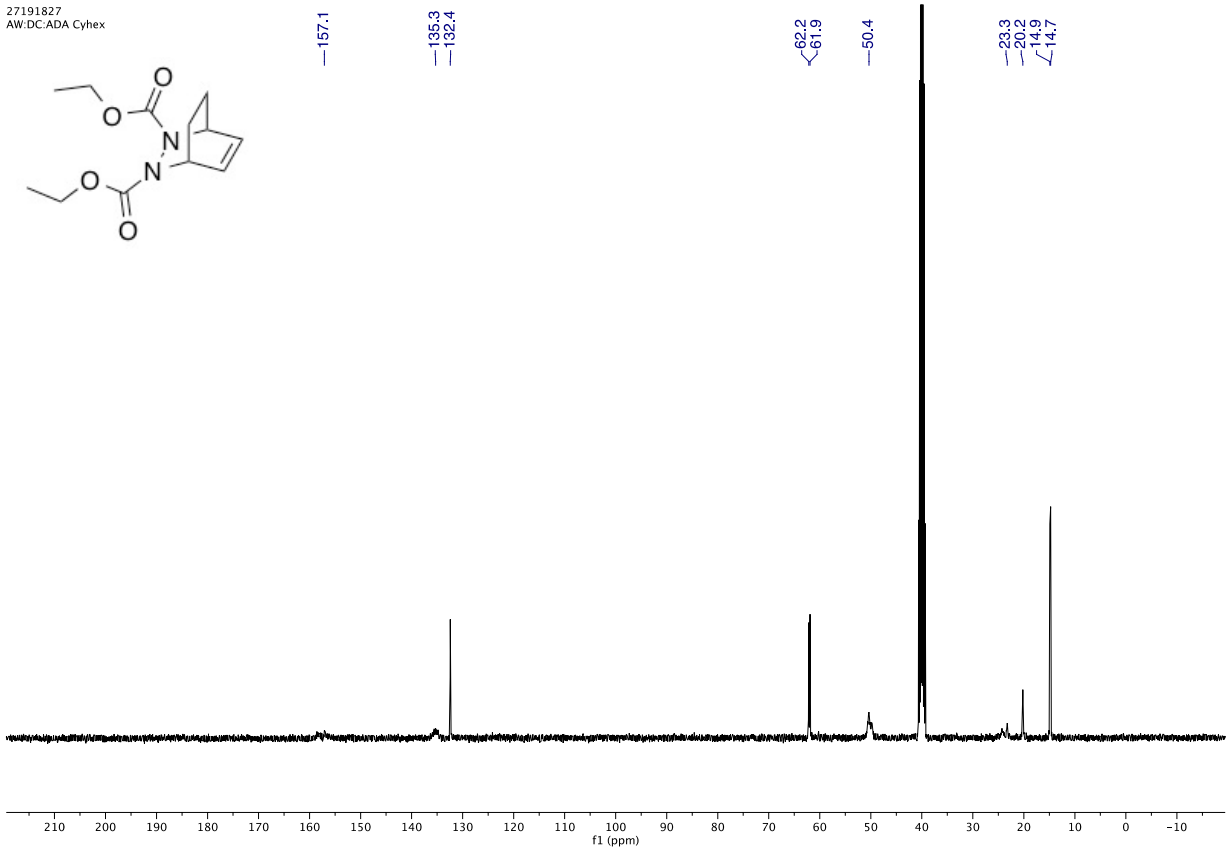
^{1}H and ^{13}C NMR spectra

4a at 25 °C (Table 2, Entry1)





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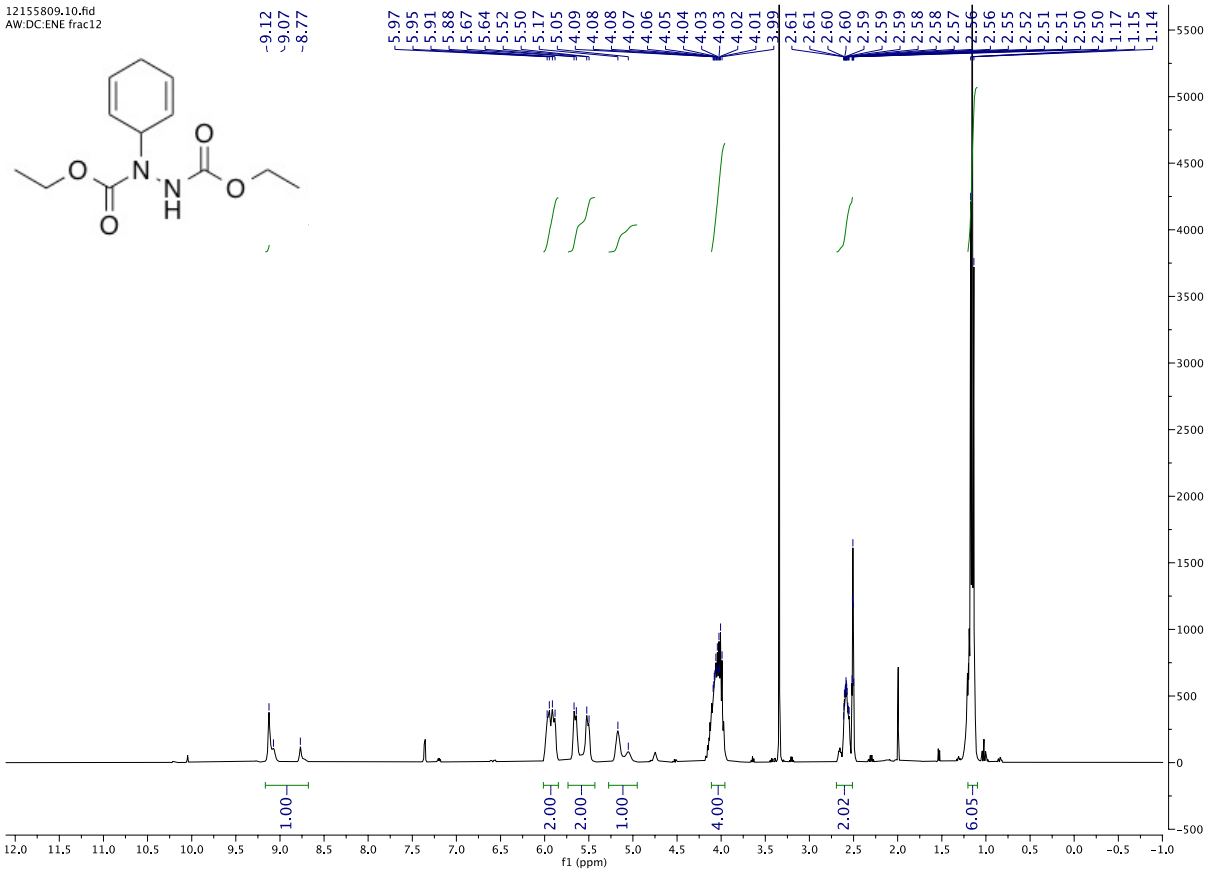
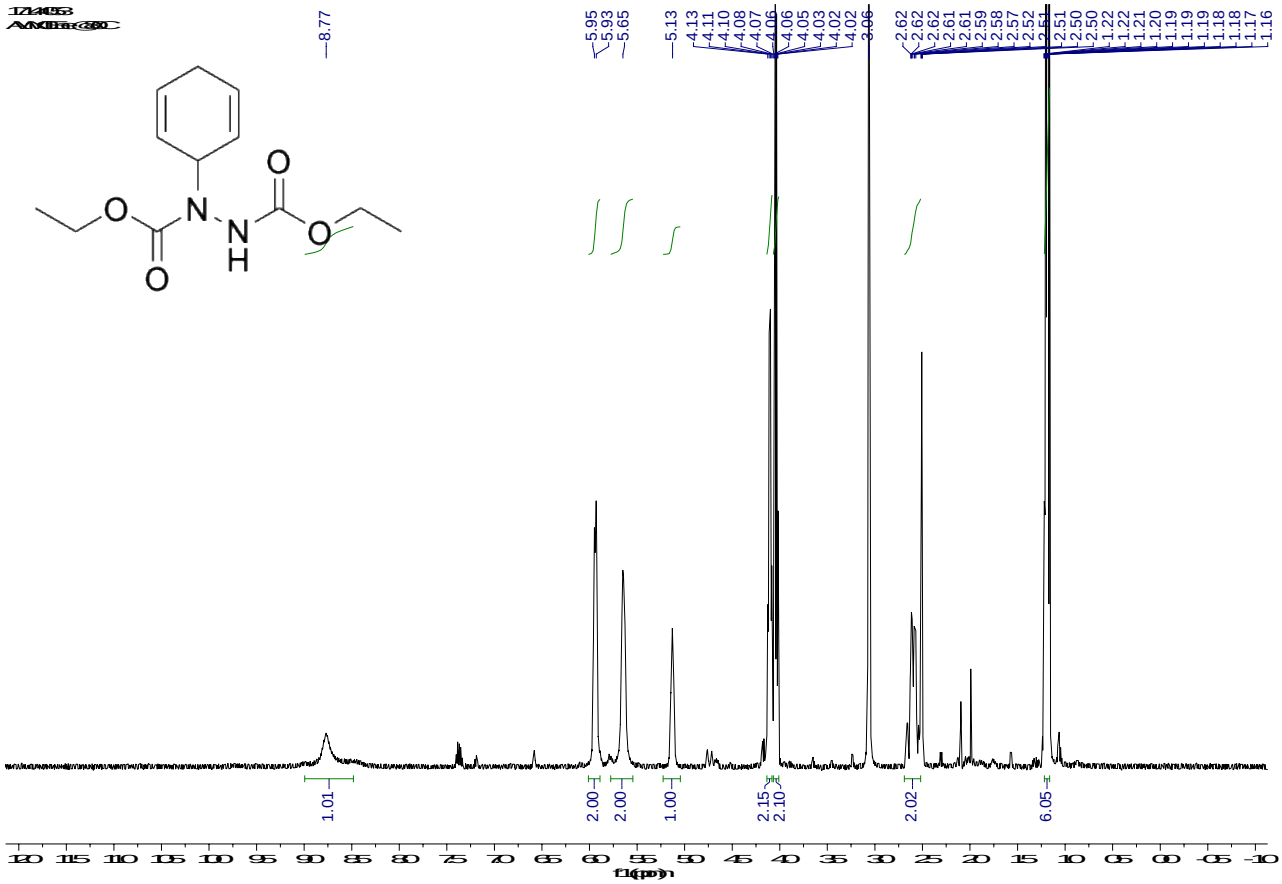
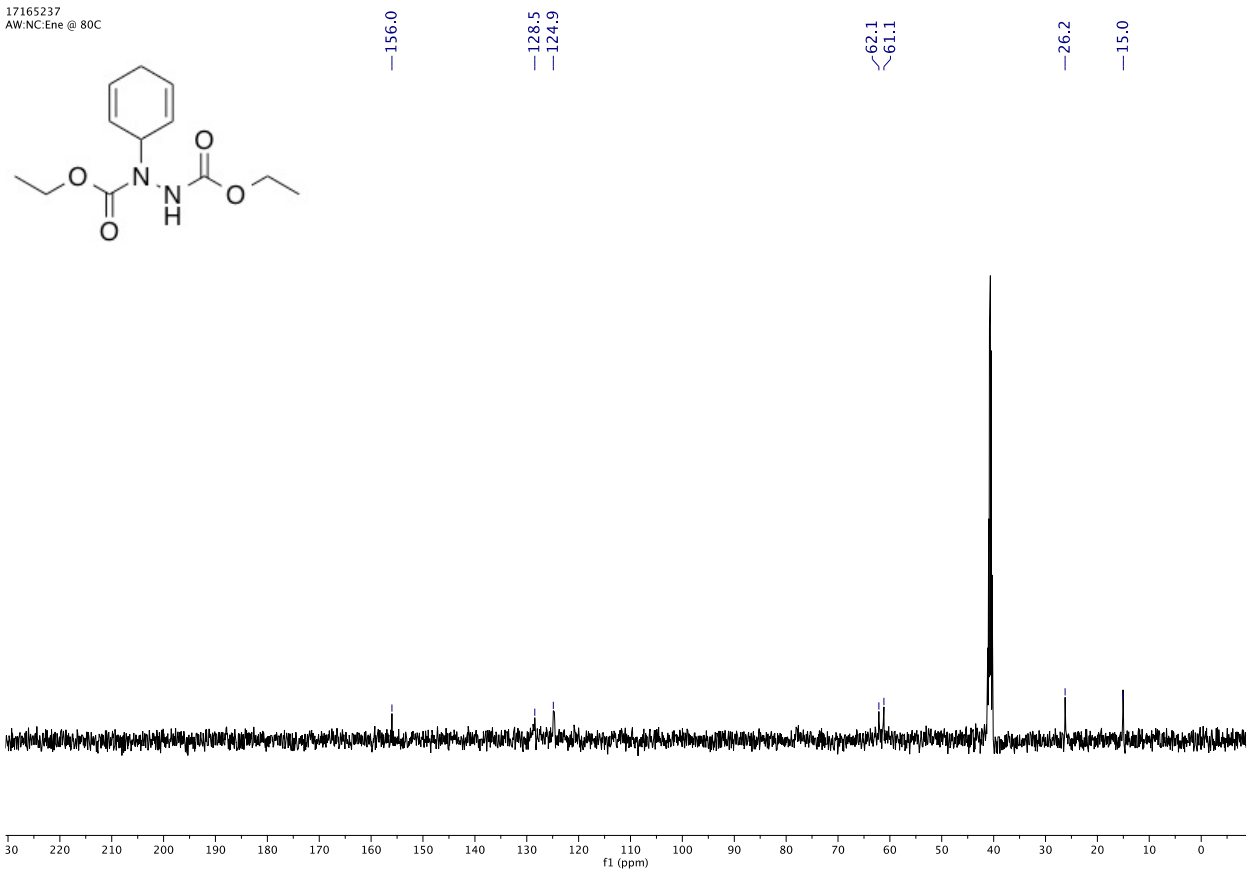


5a at 80 °C





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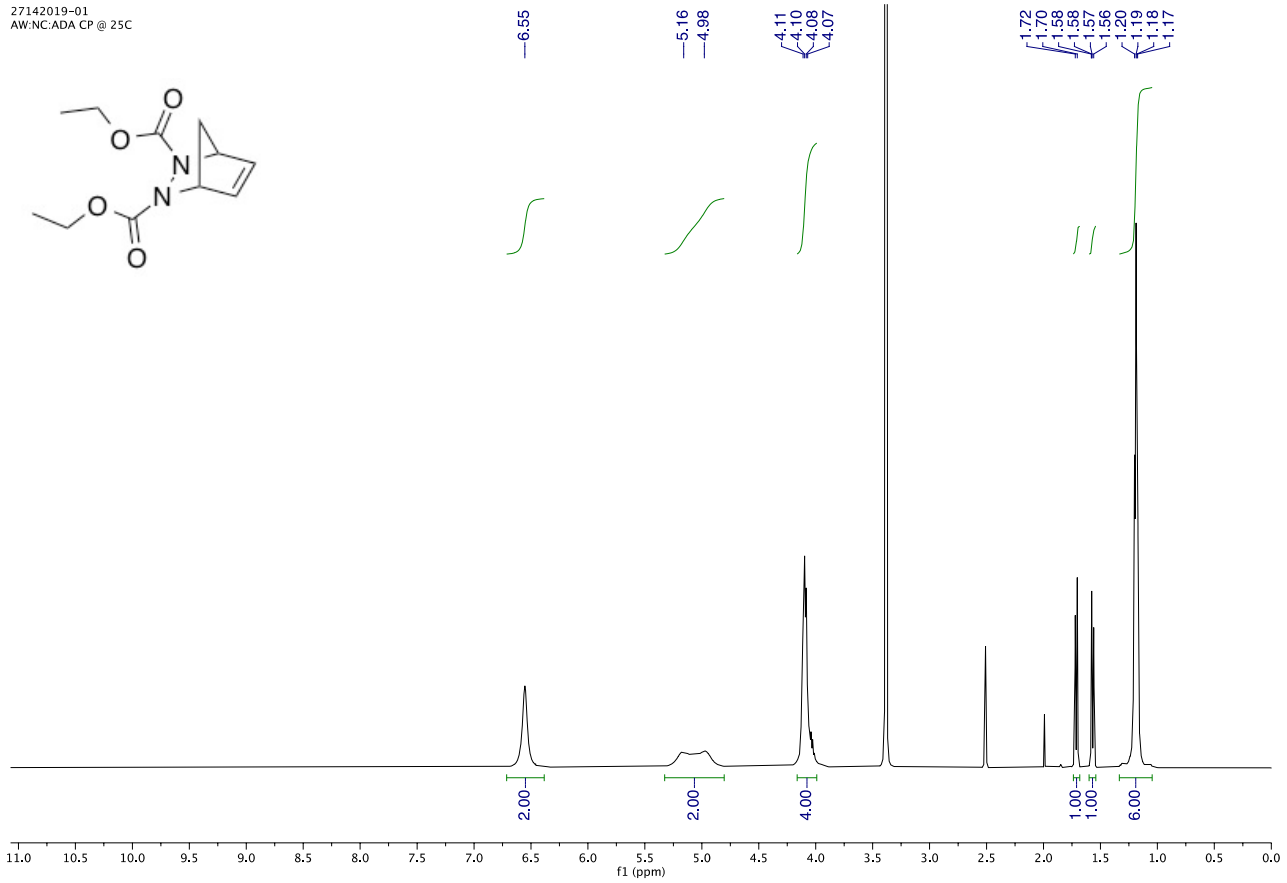

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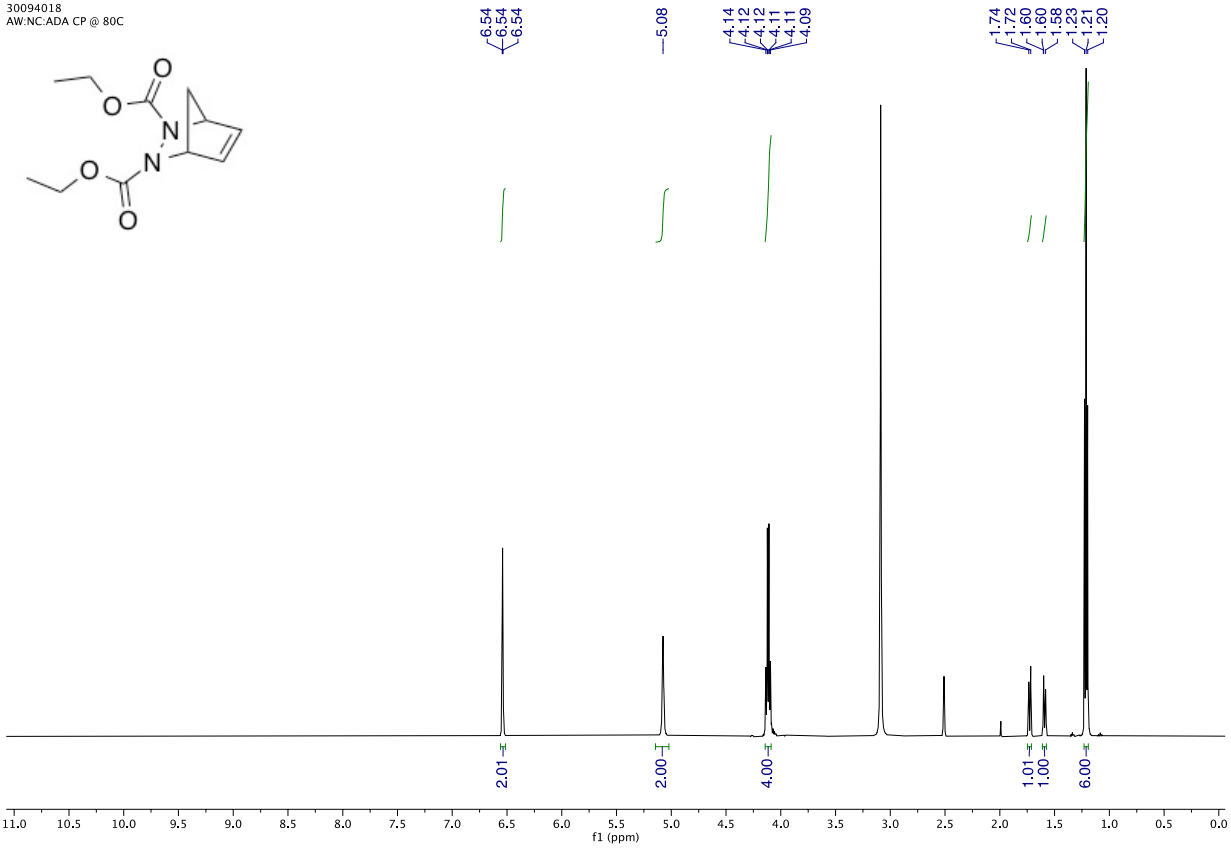

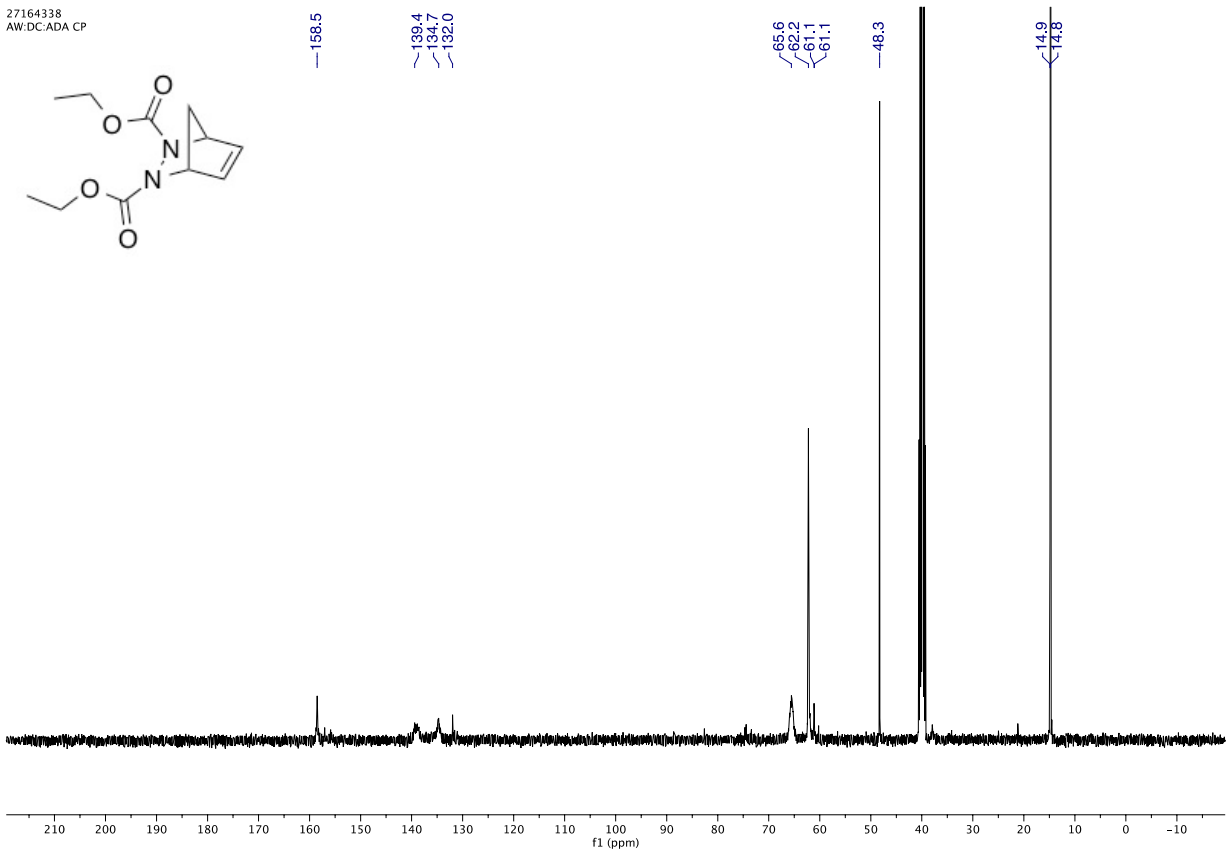

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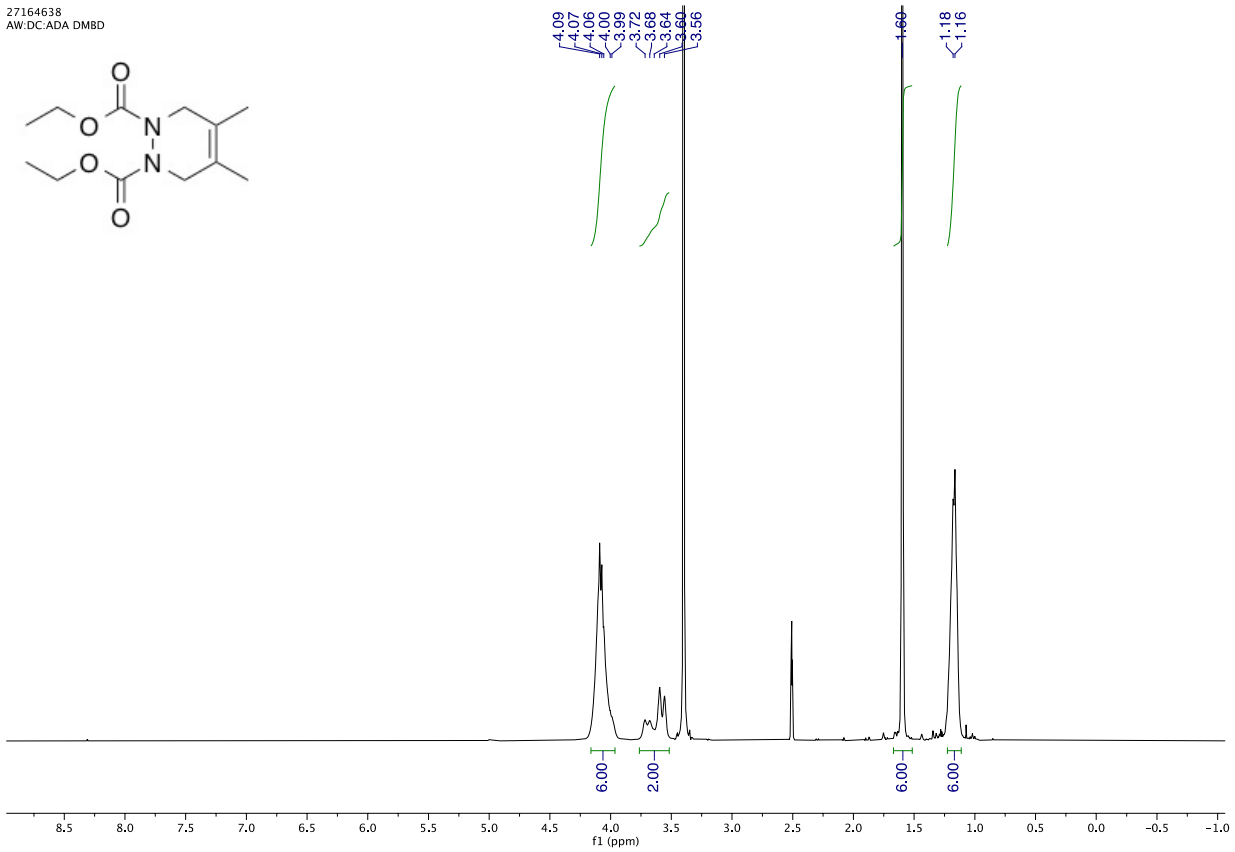

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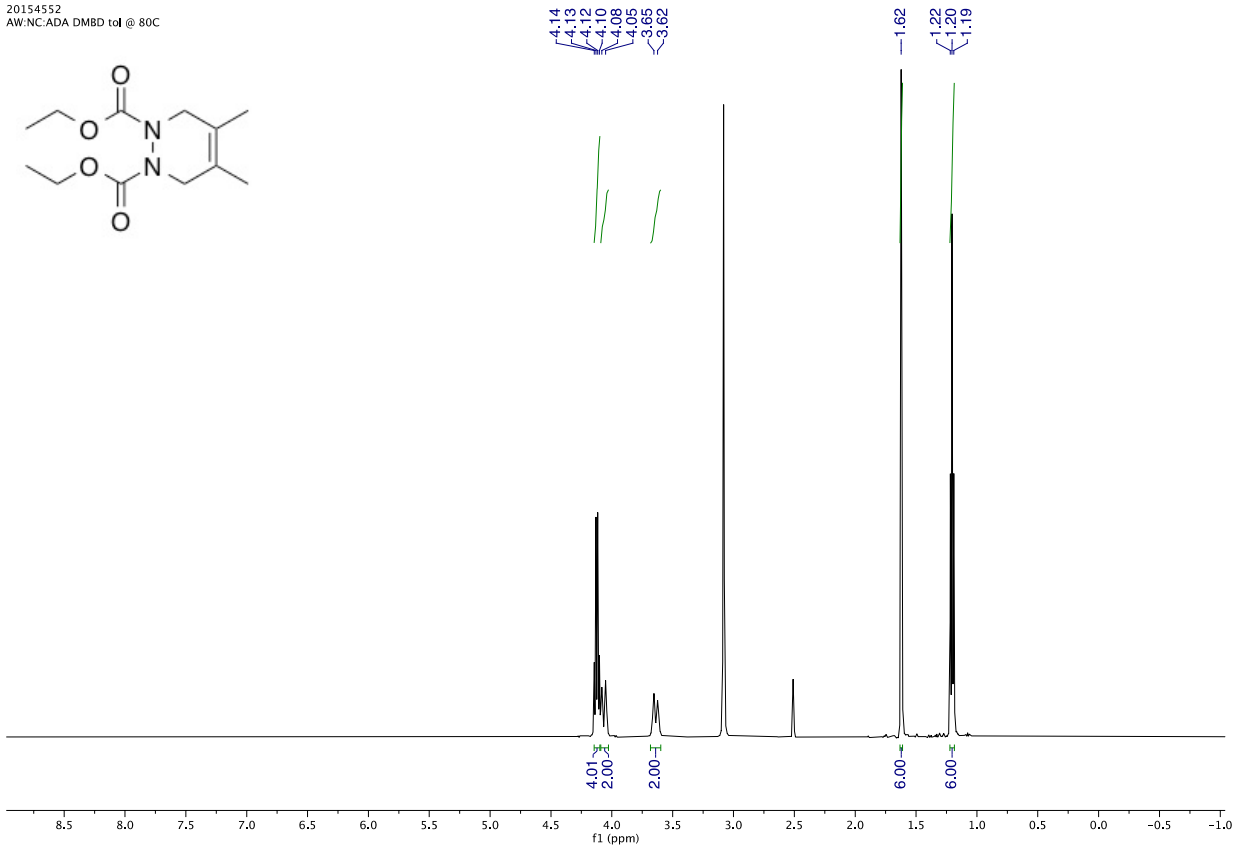

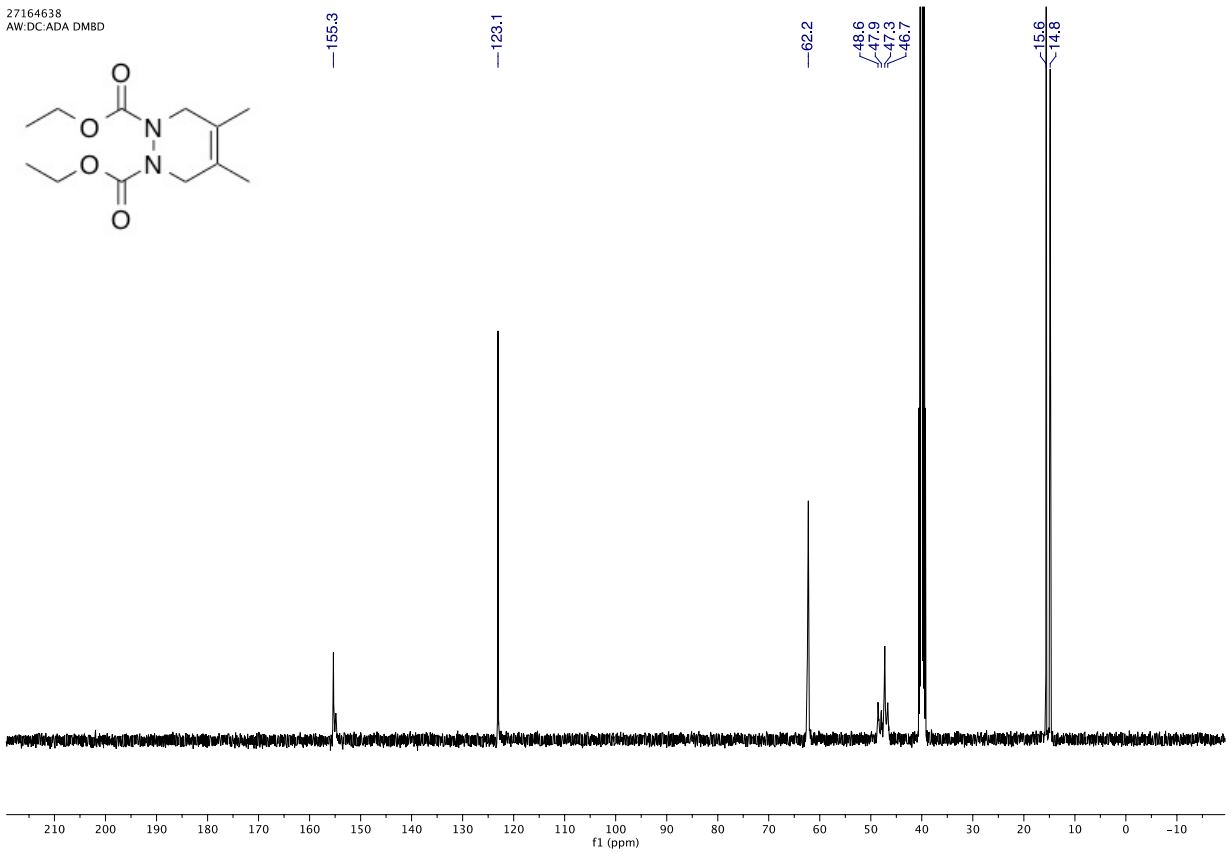

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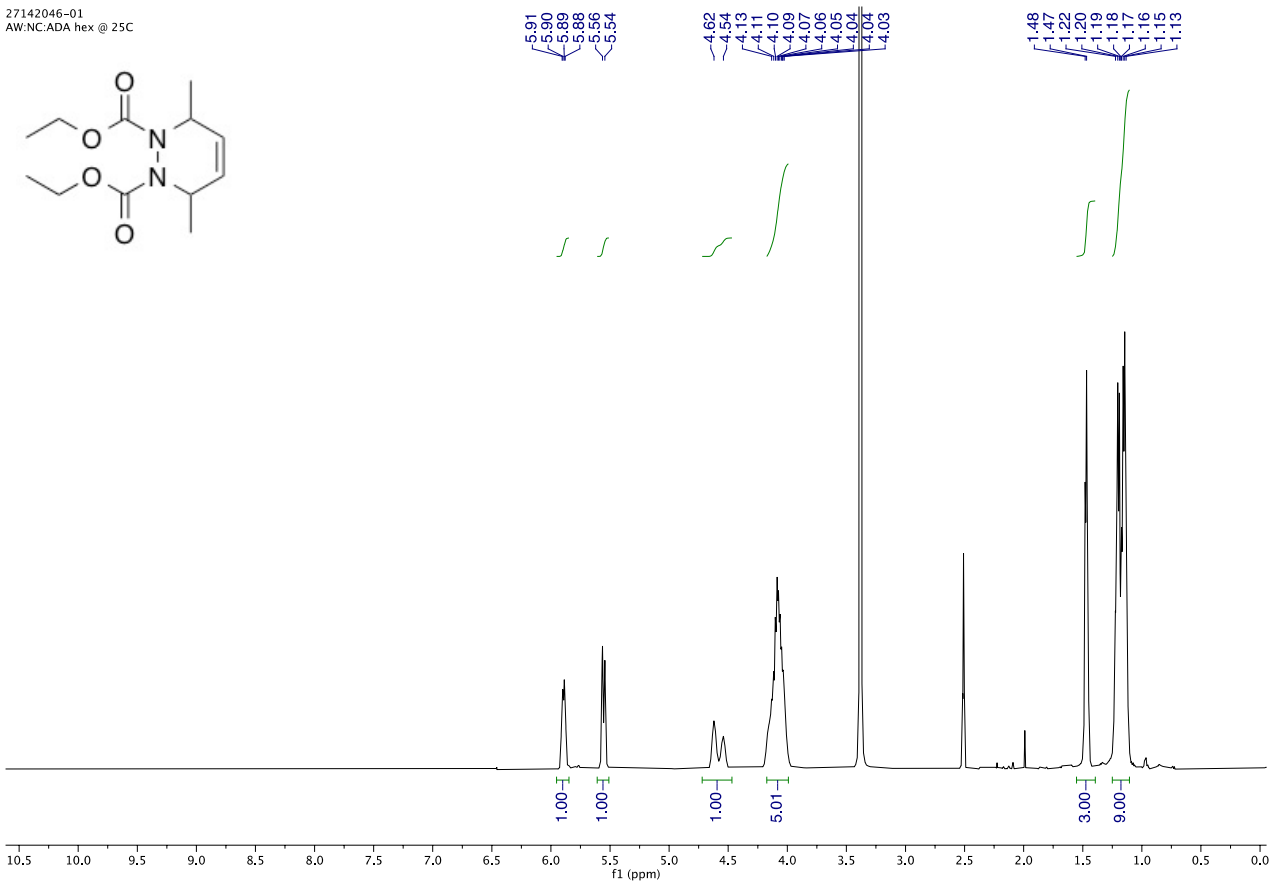

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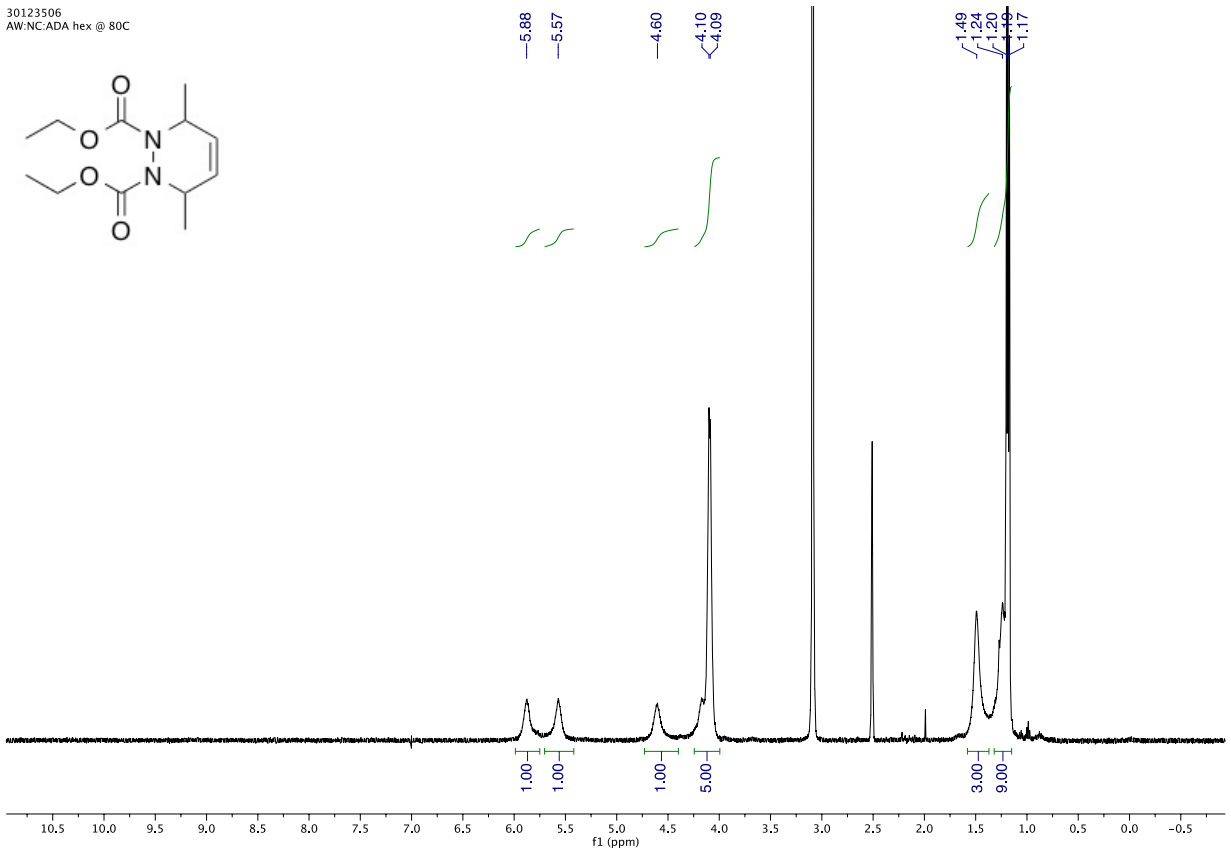

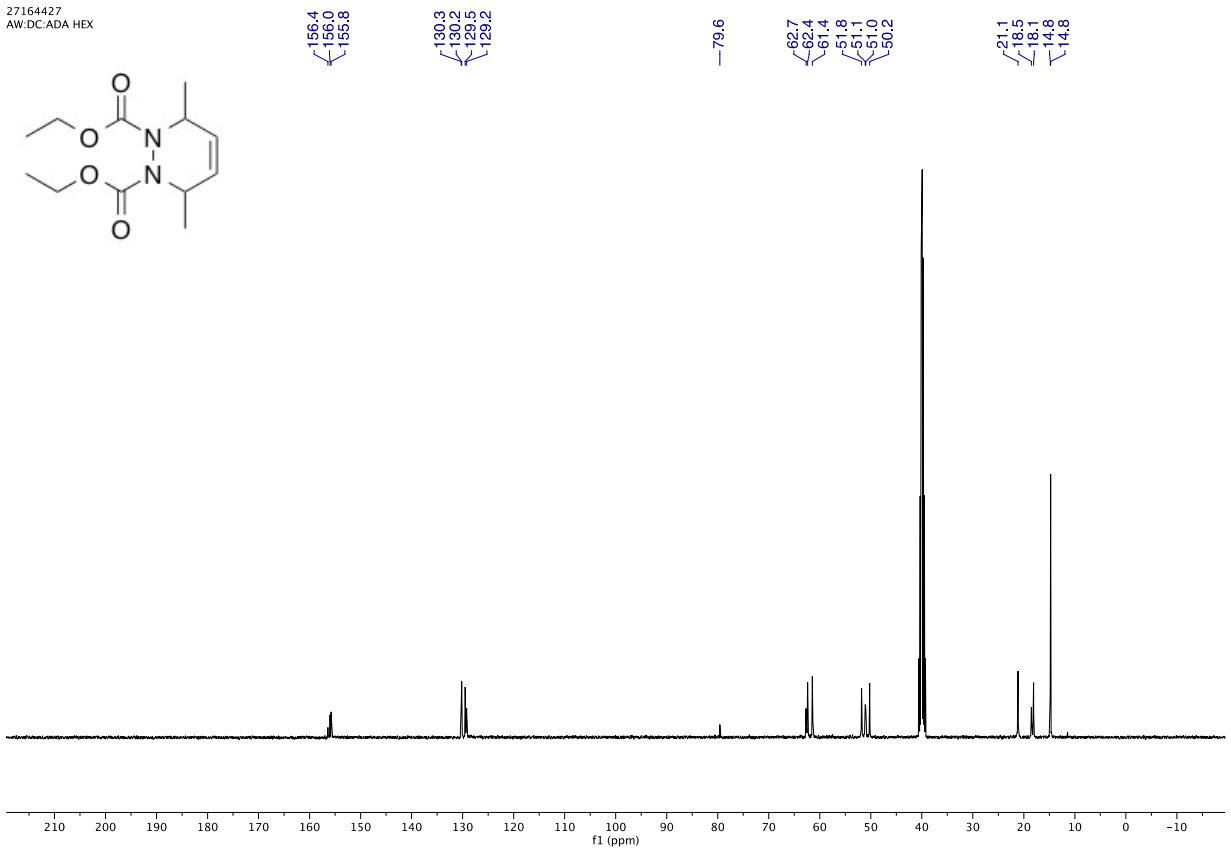

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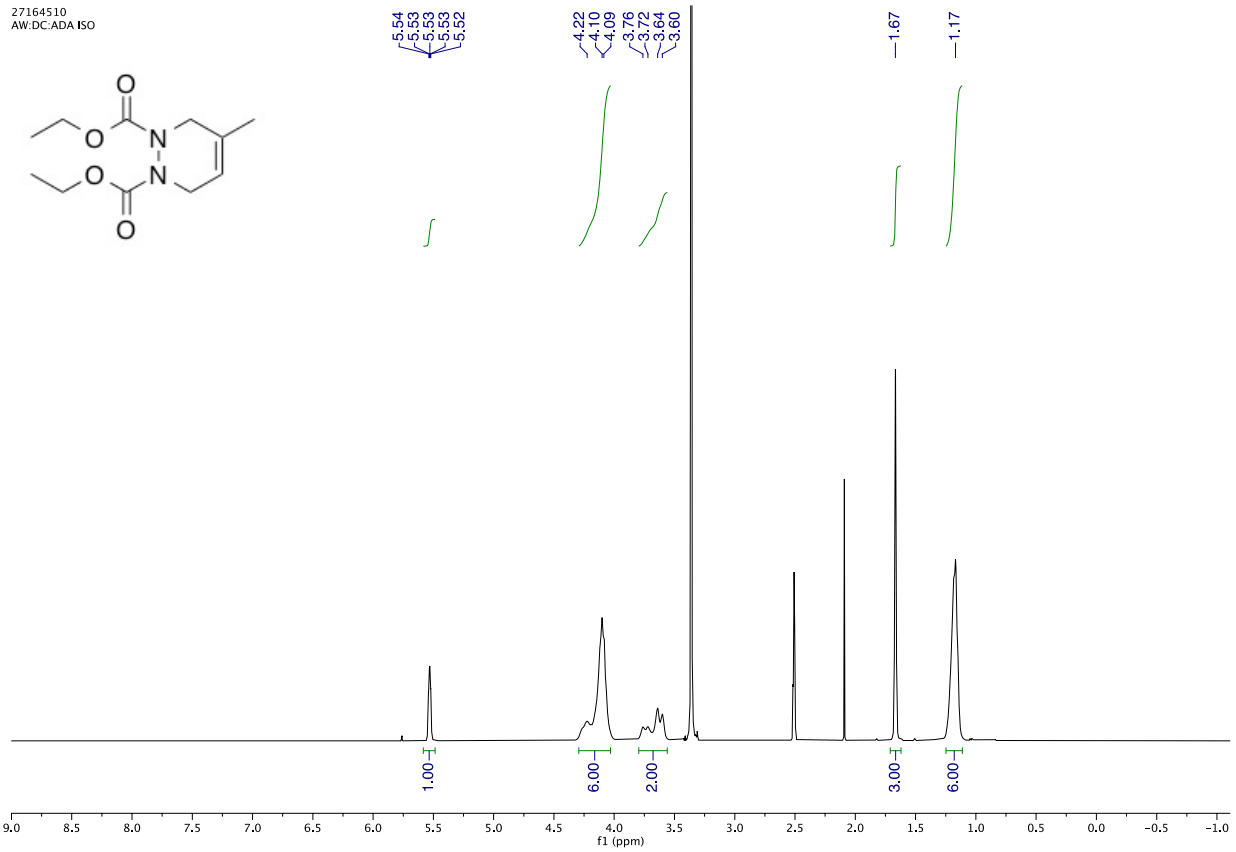

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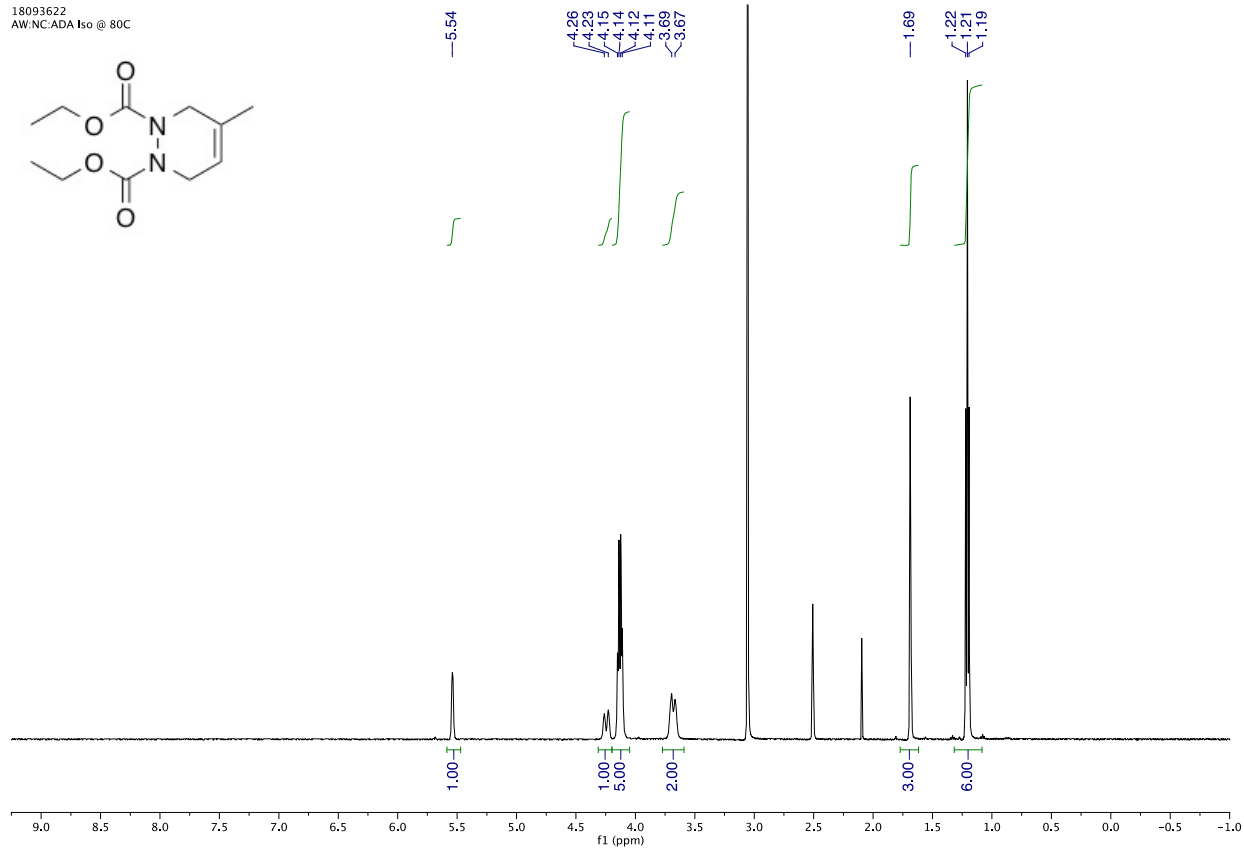

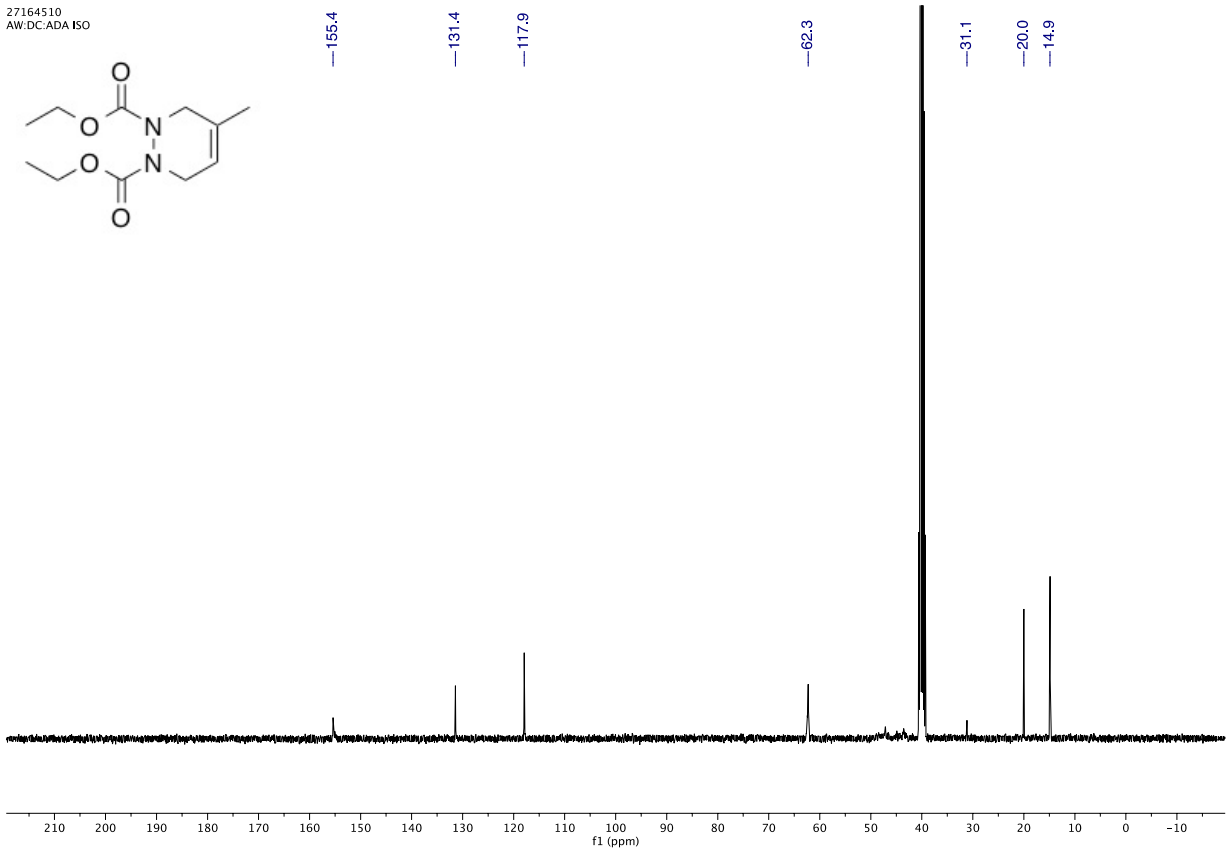

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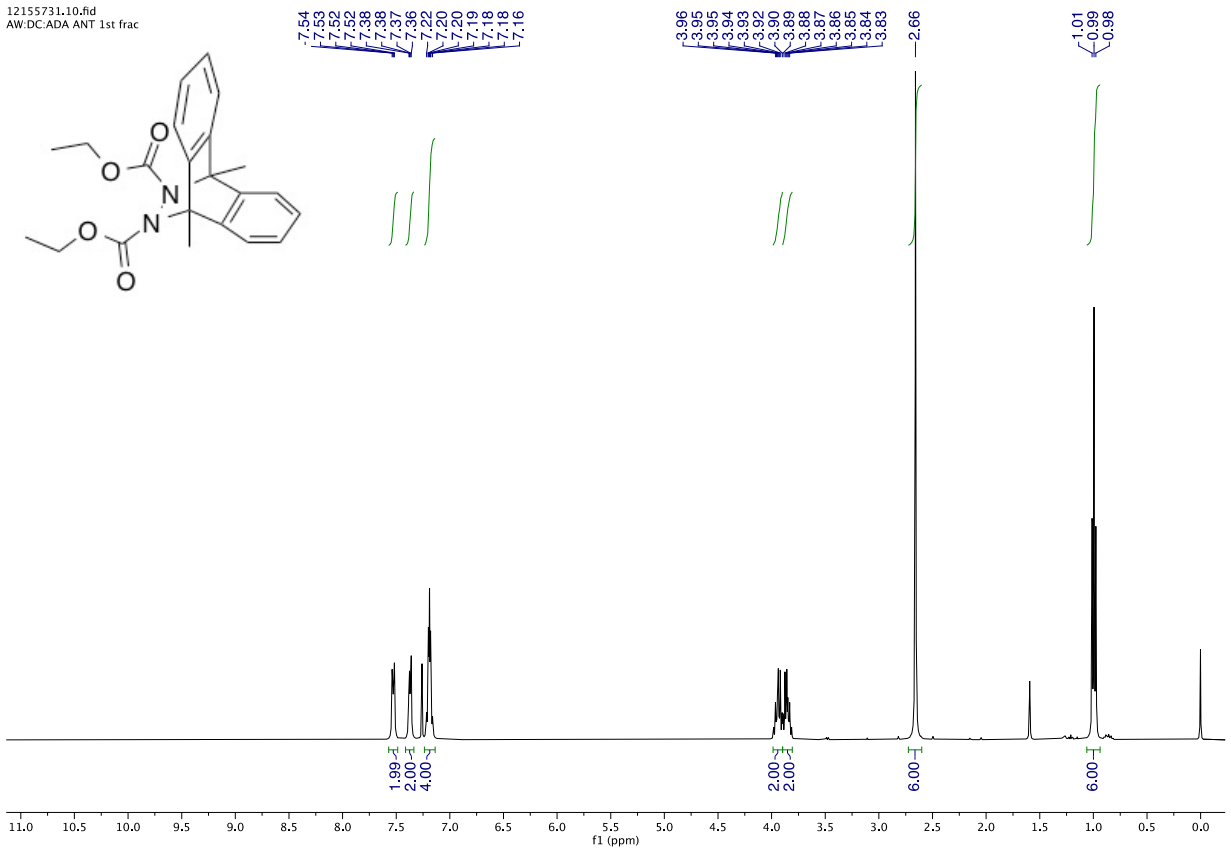

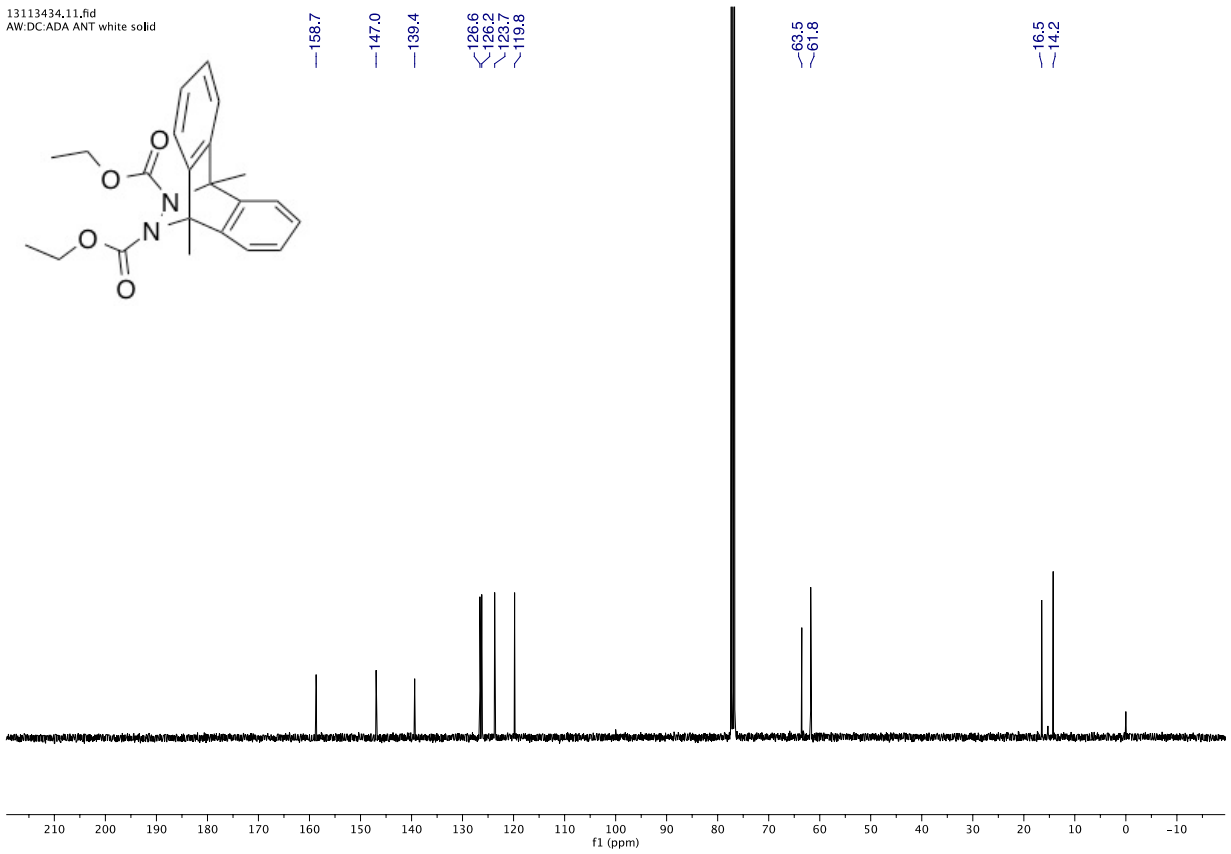

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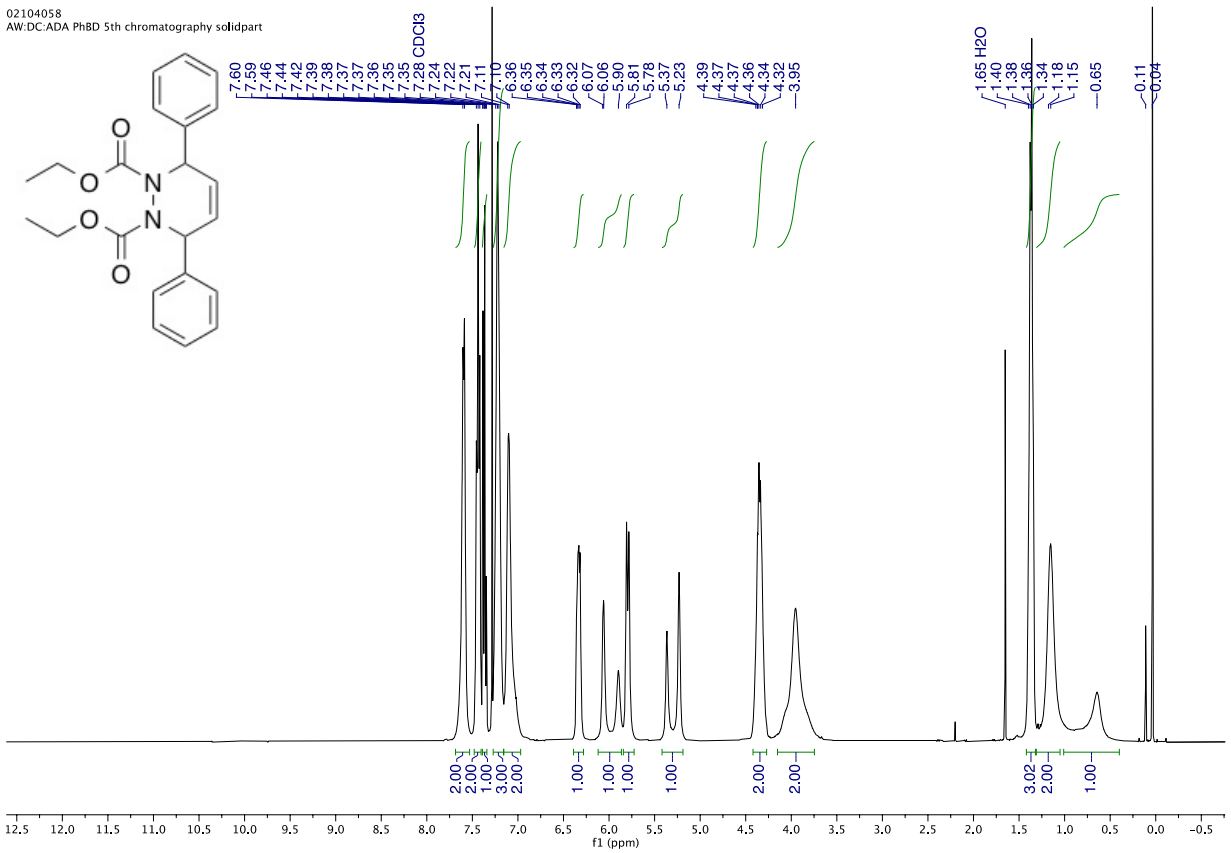

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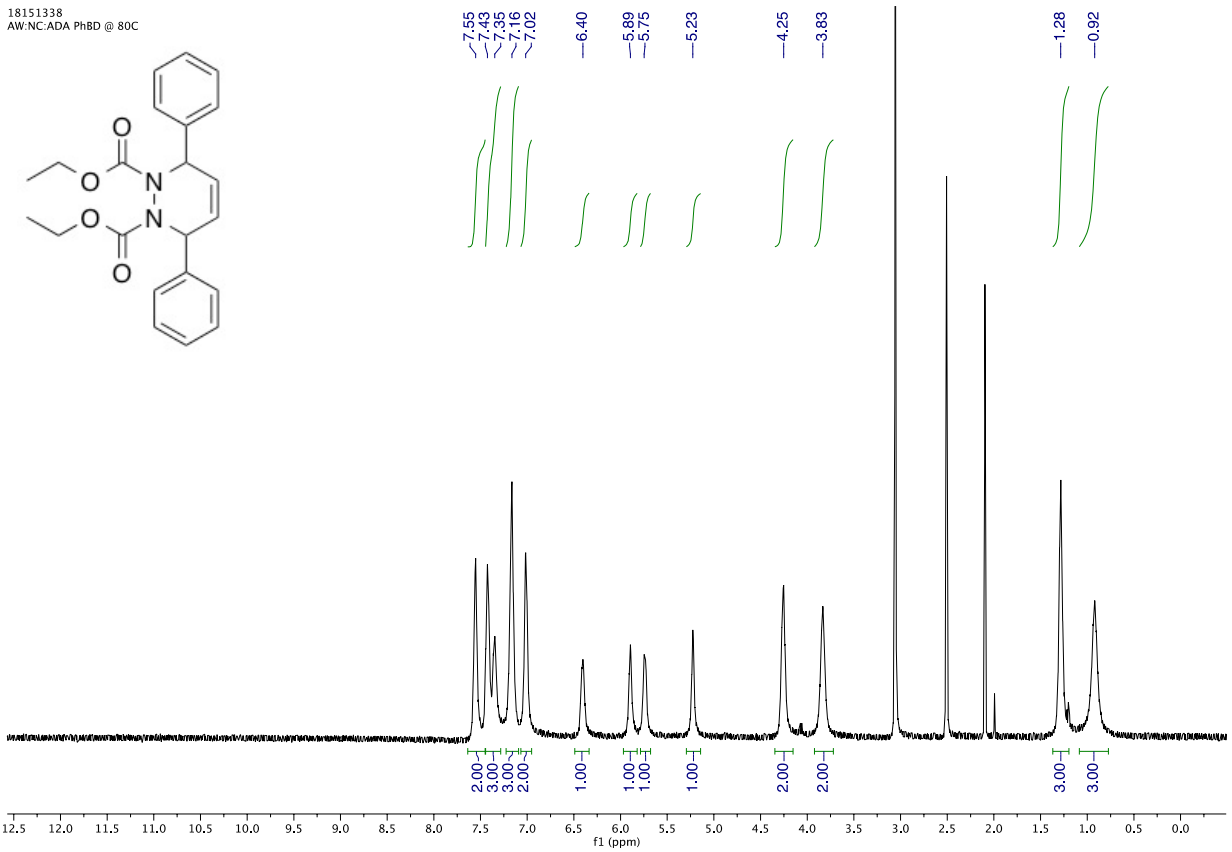

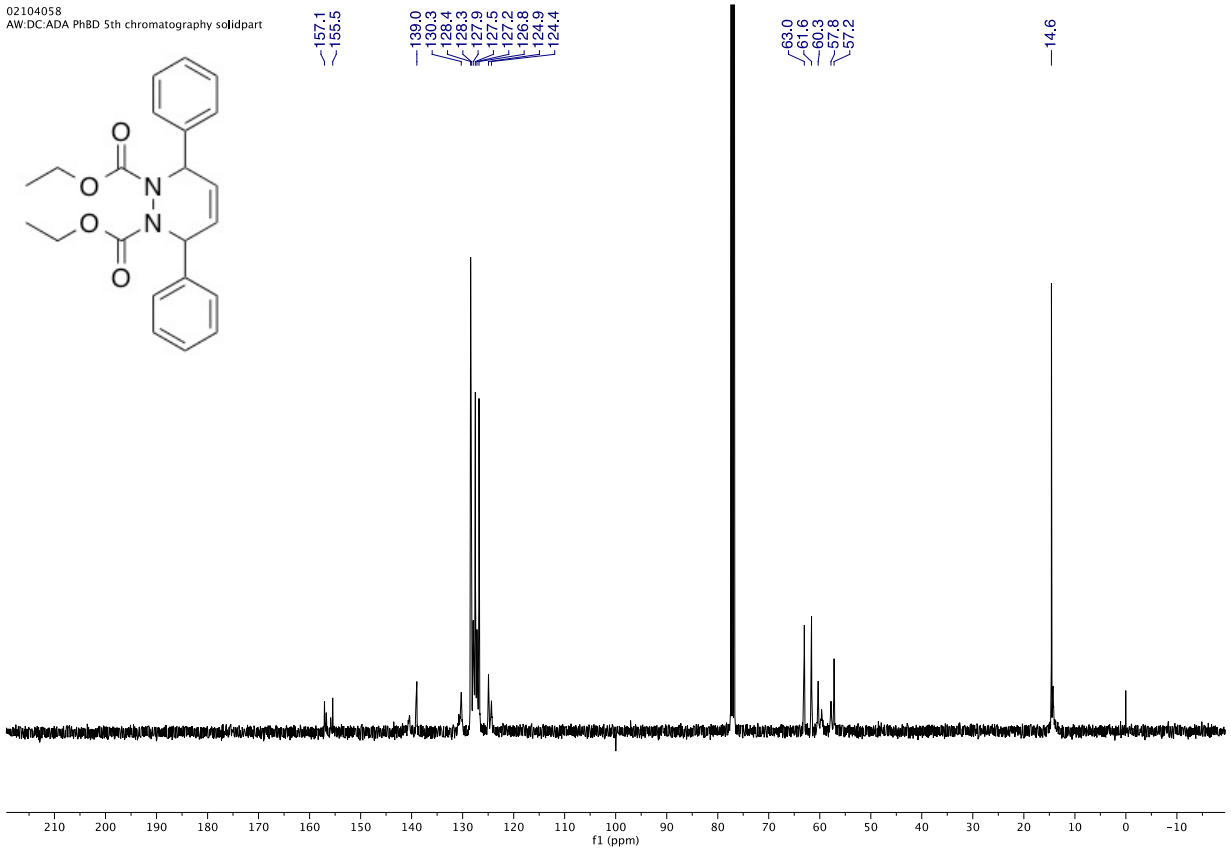

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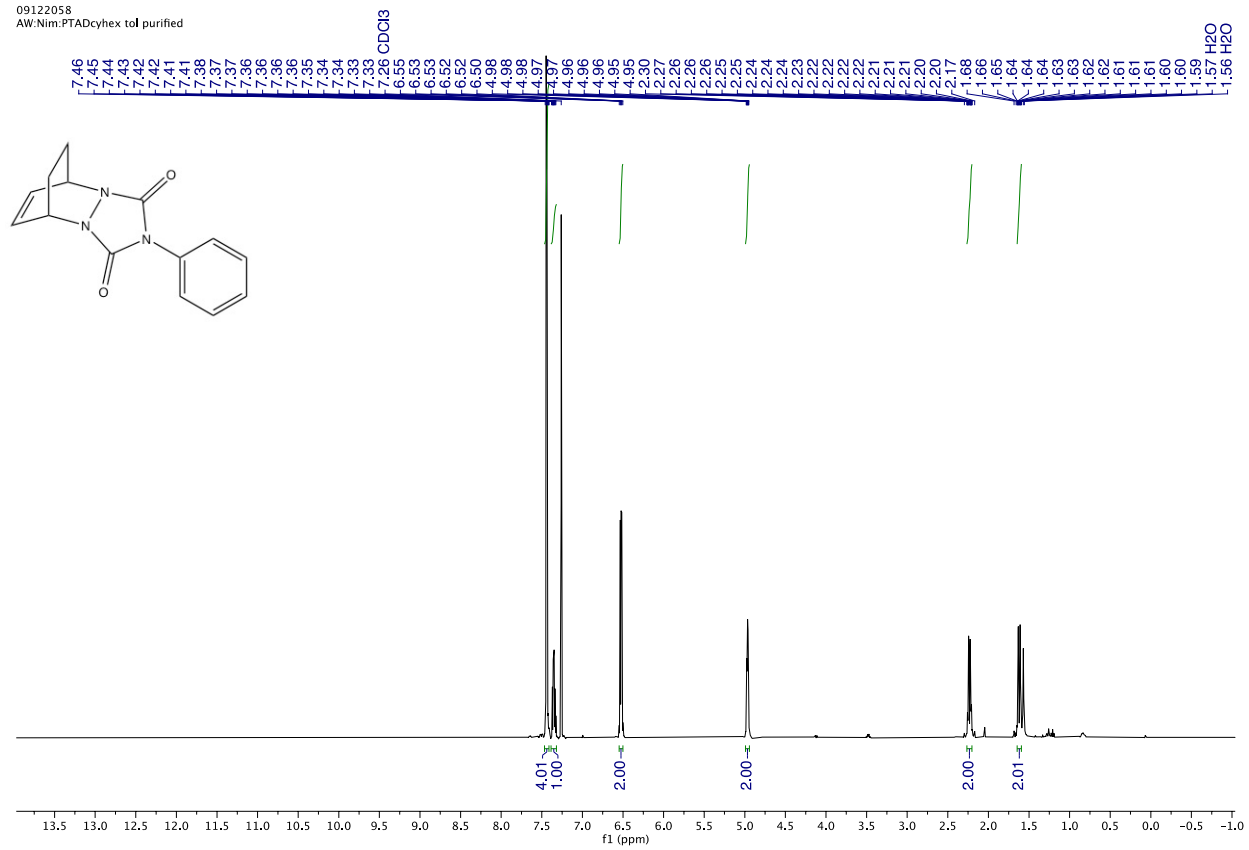

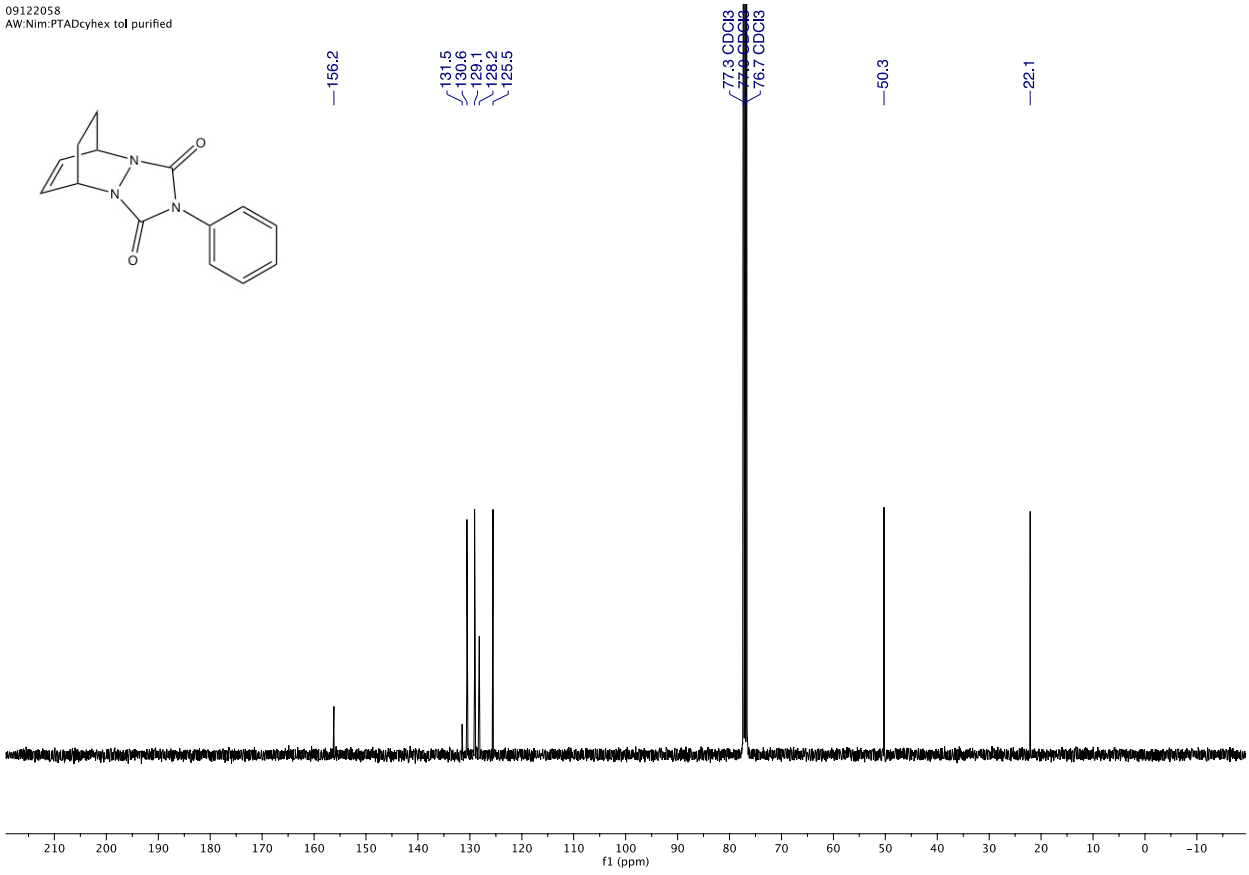

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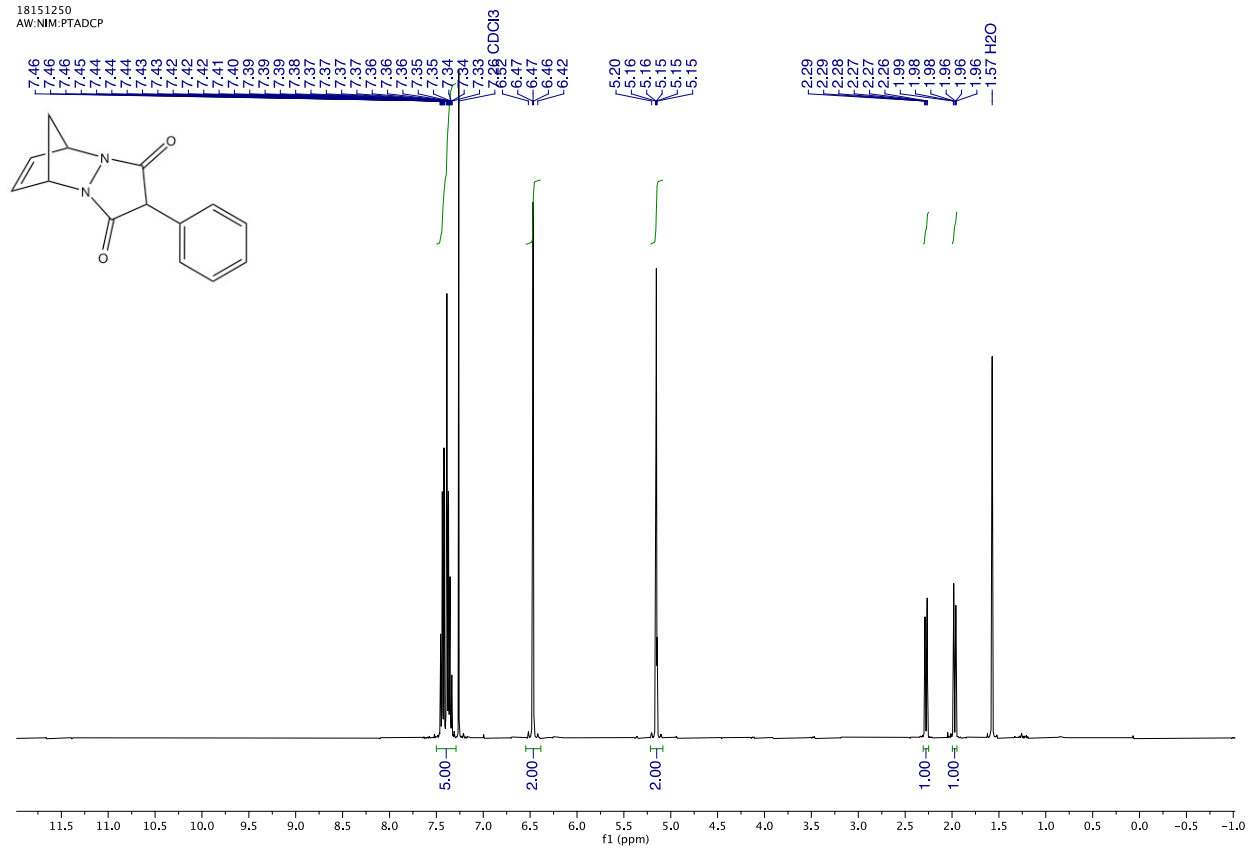

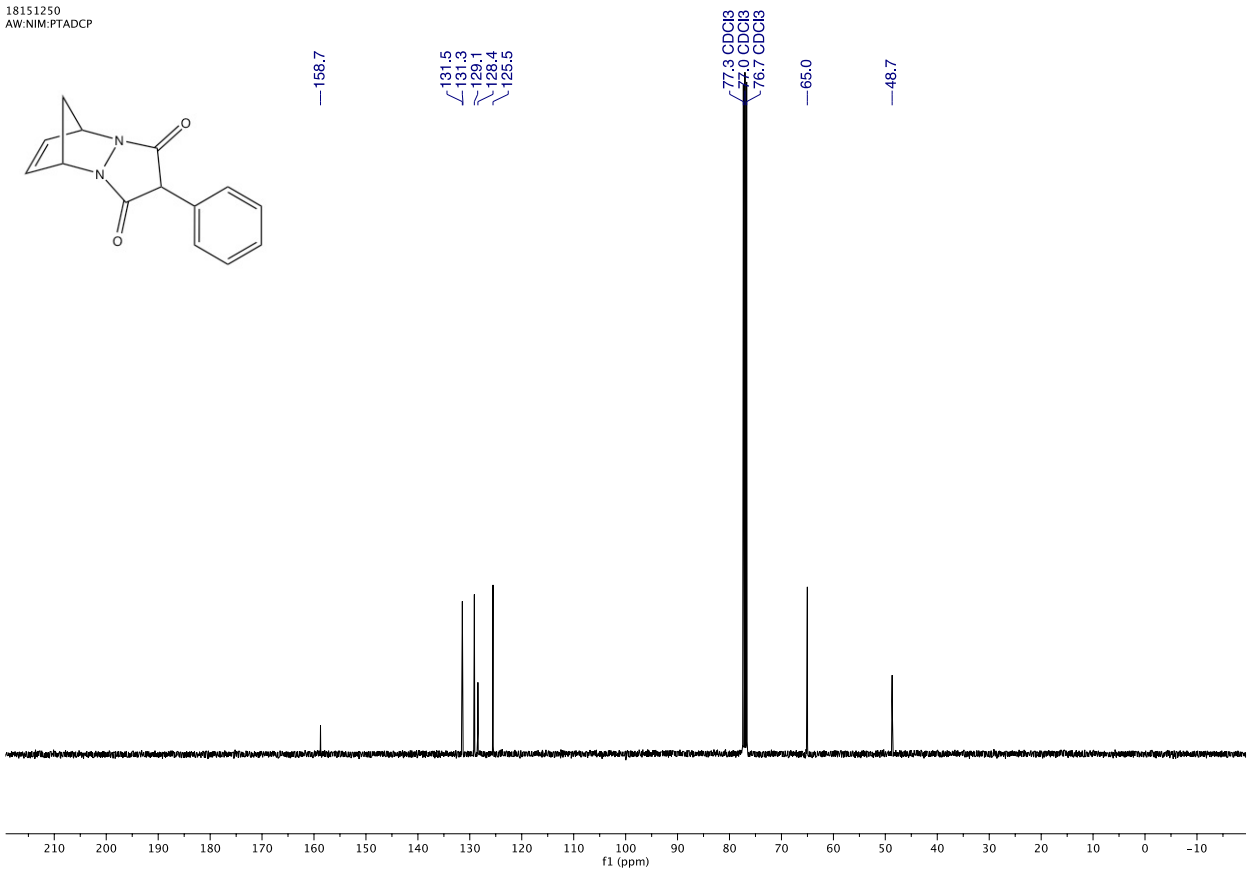

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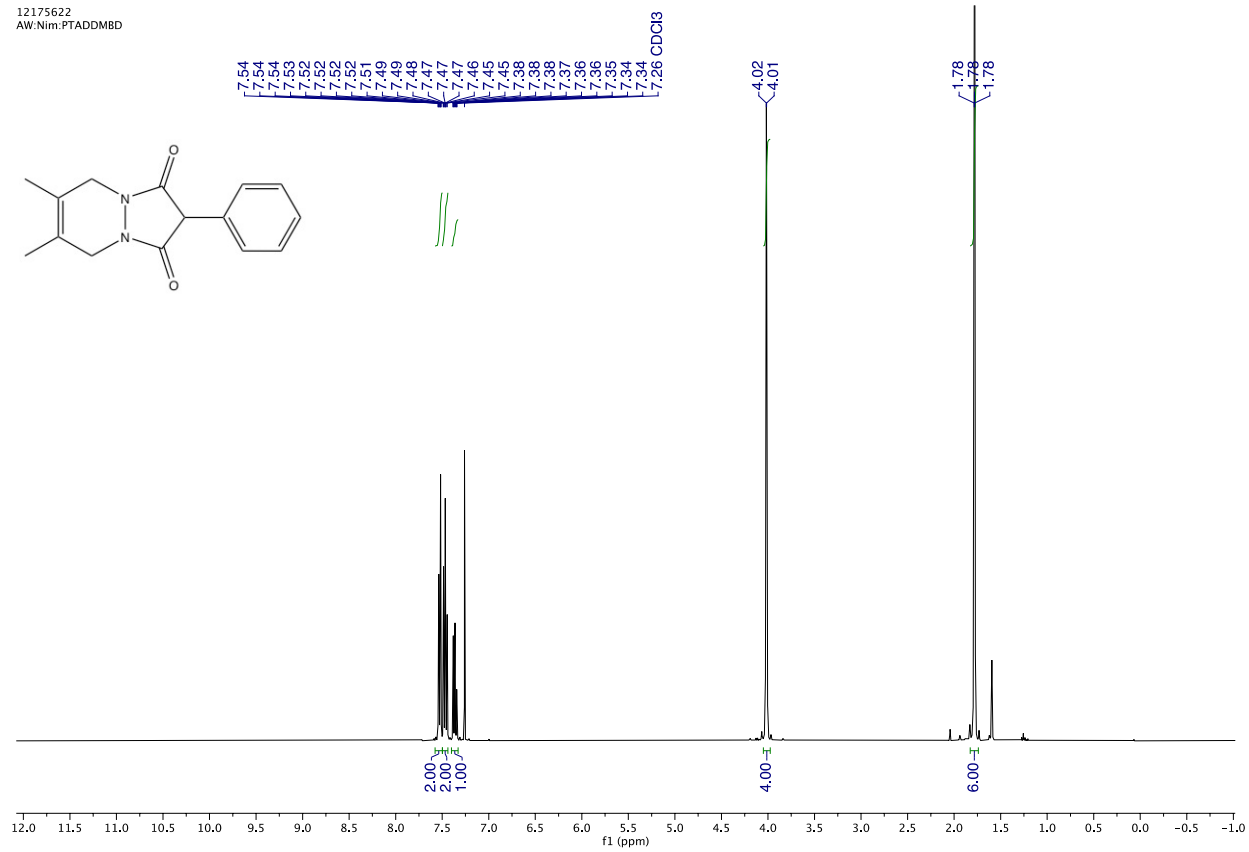

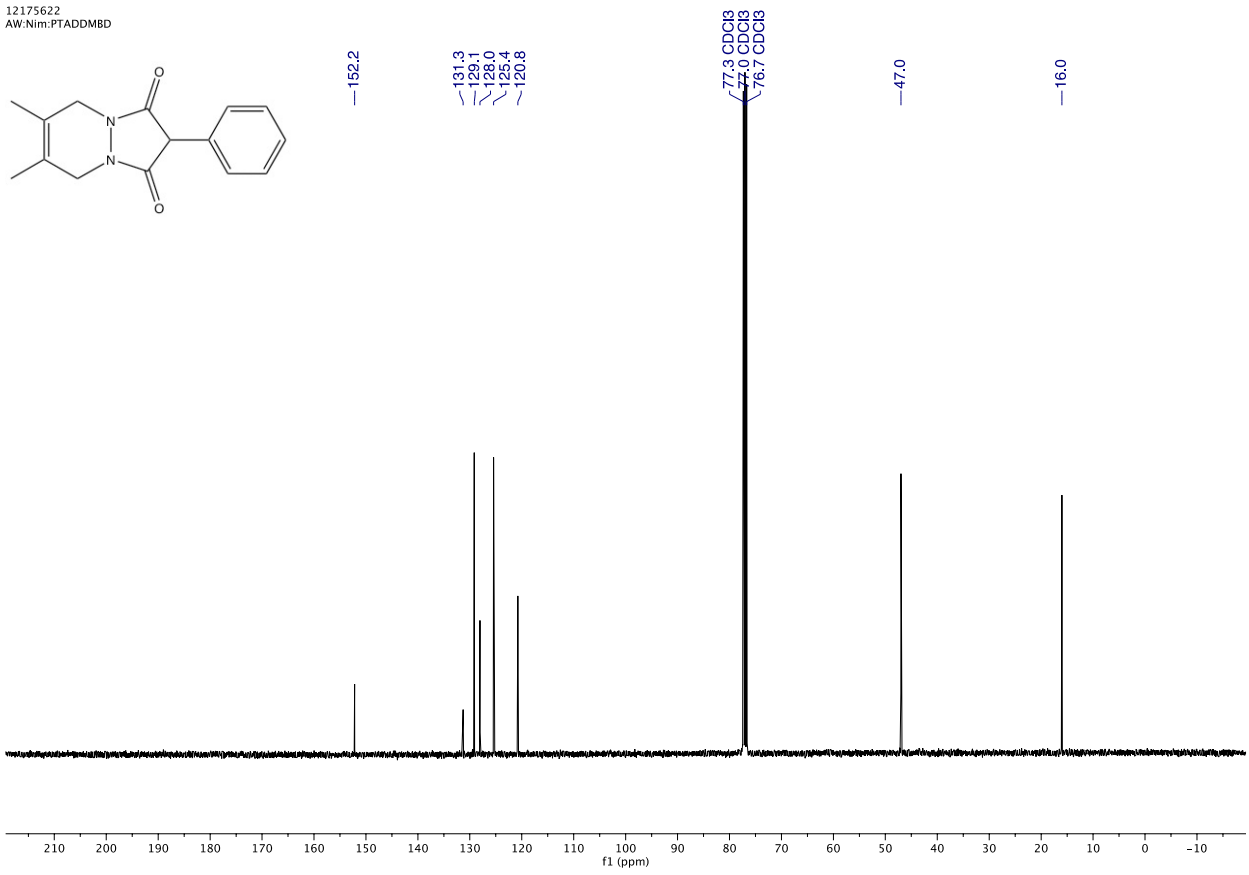

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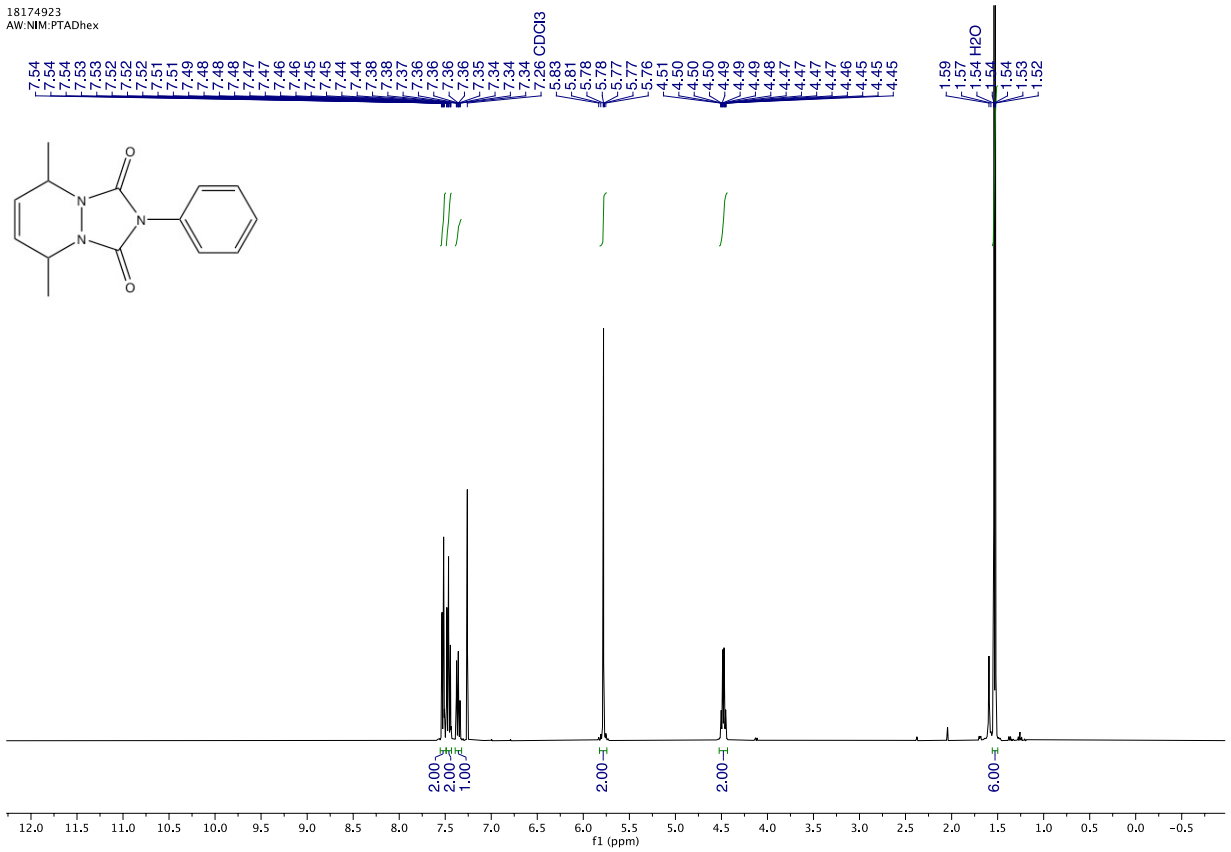

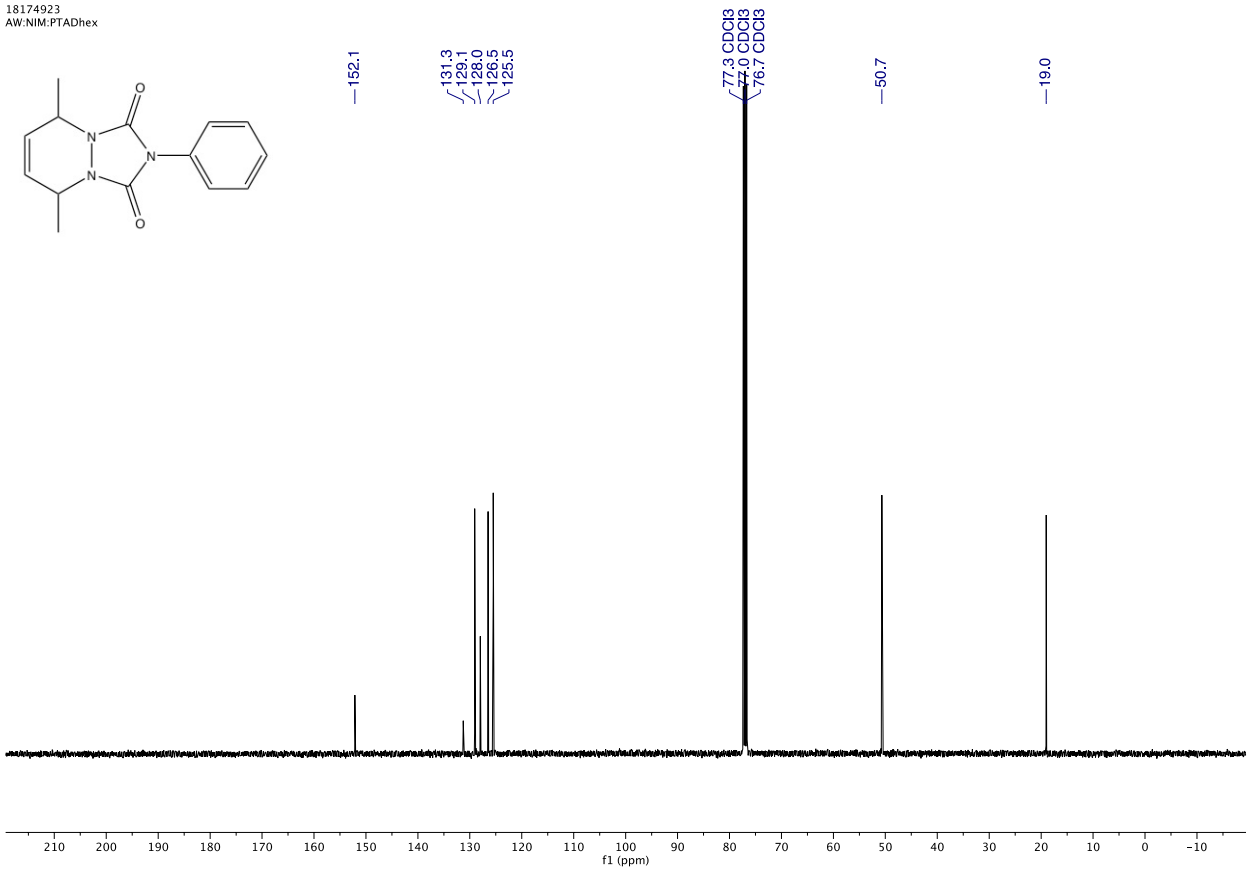

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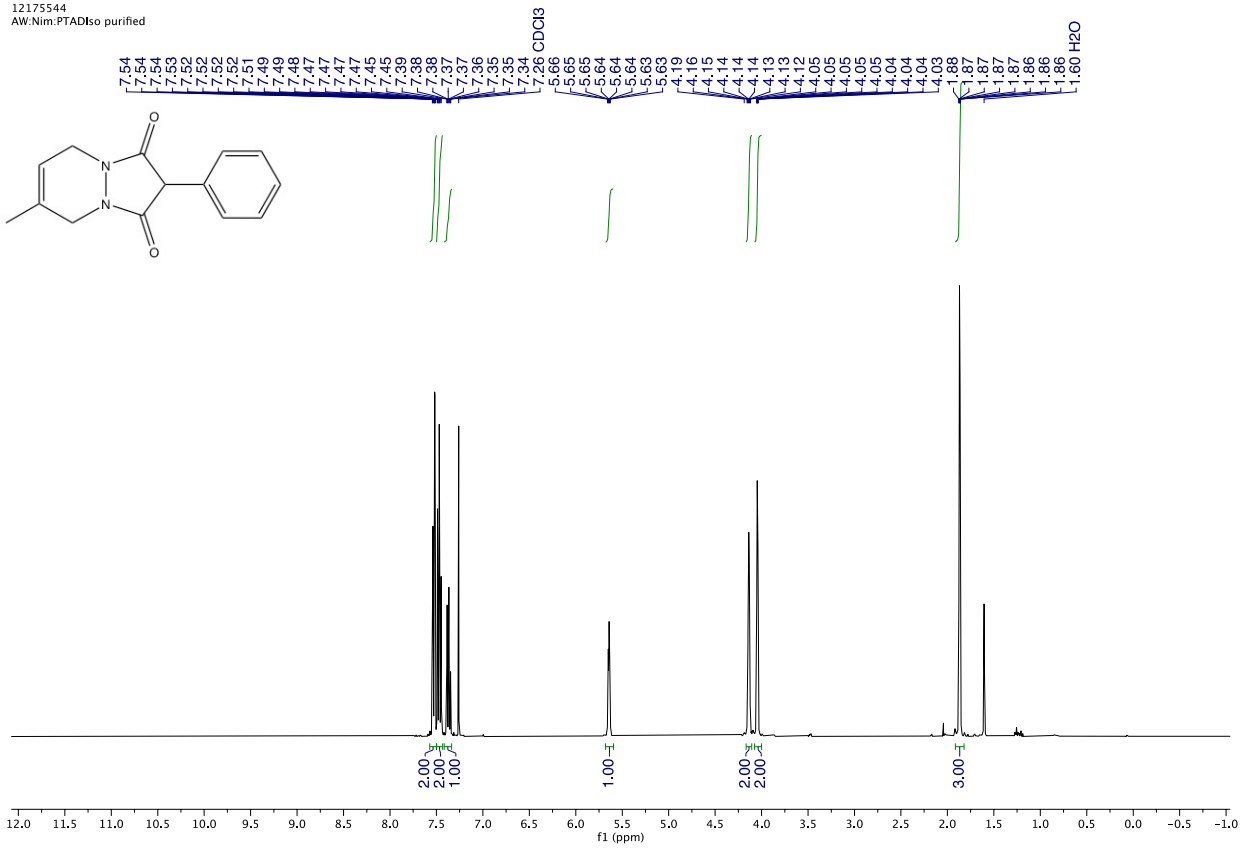

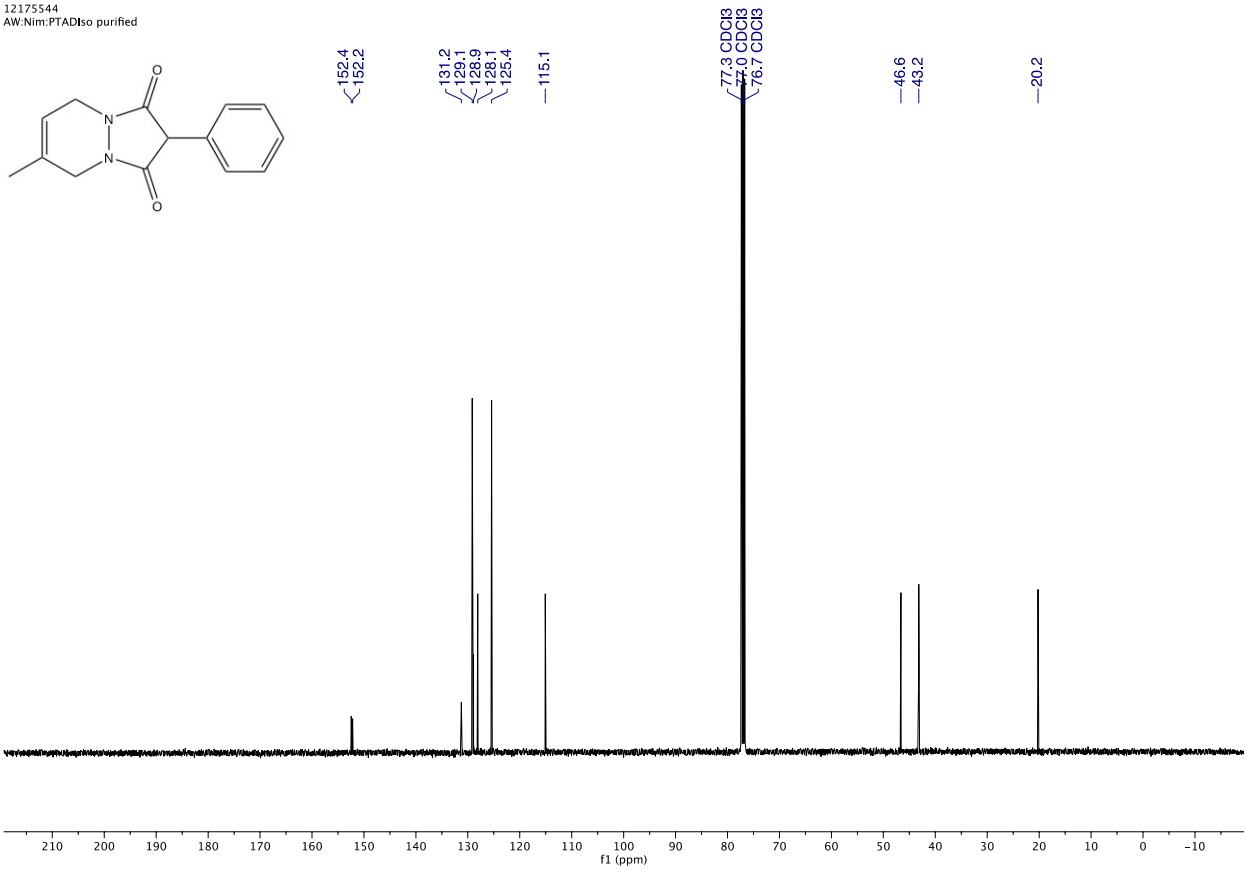

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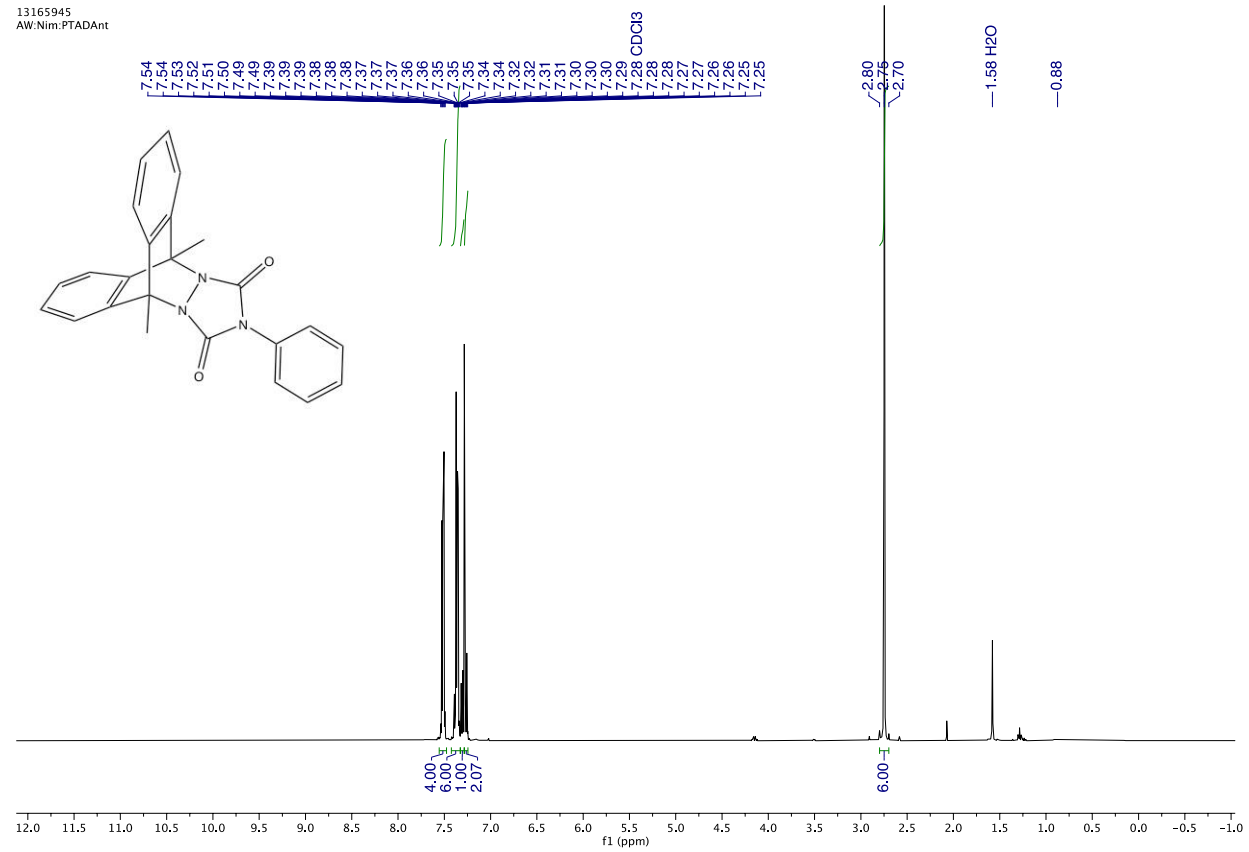

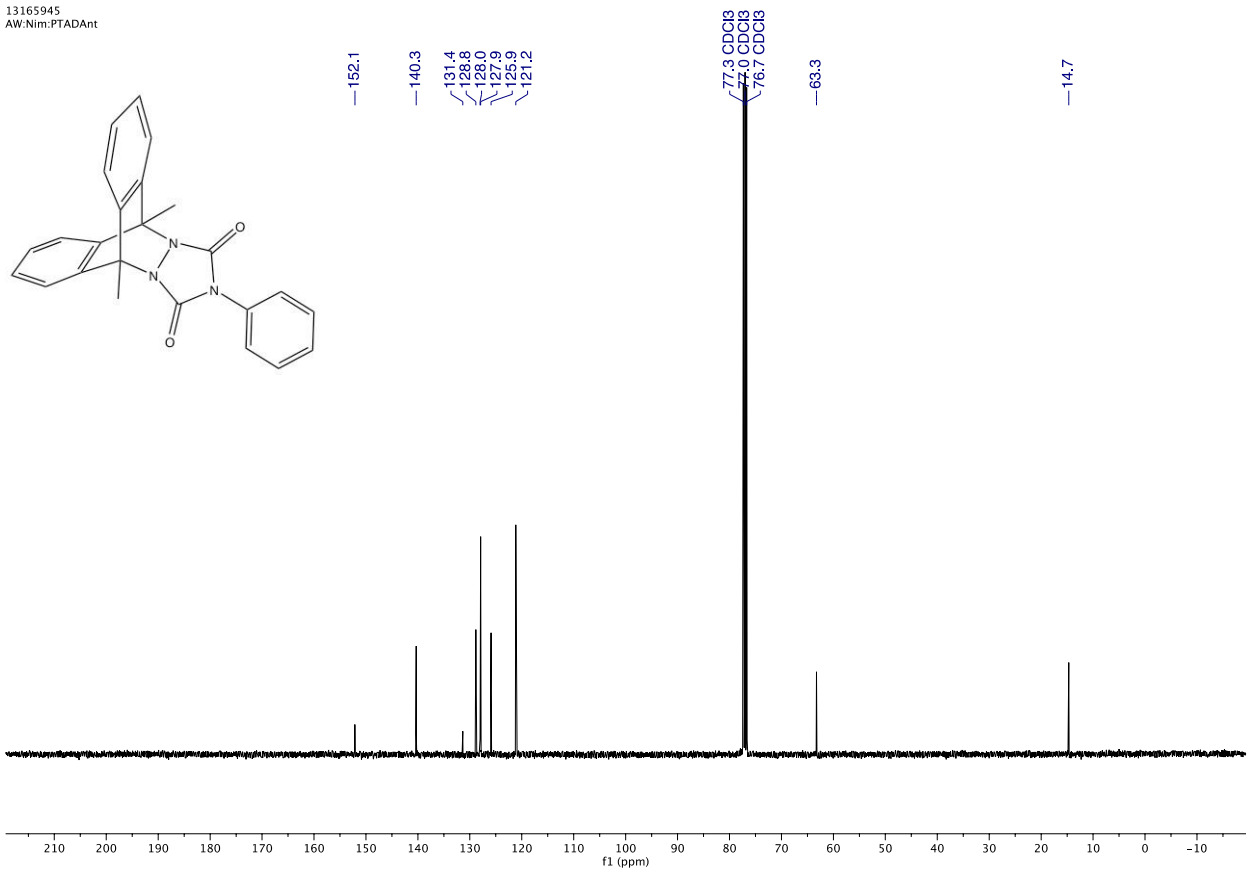

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