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Supporting Information

Tricyclic 2-Benzazepines Obtained *via* an Unexpected Cyclization Involving Nitrilium Ylides

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General Information

All nitriles were distilled and stored over activated molecular sieves 4Å. NMR spectrum were recorded using Bruker Avance III spectrometer in $CDCl_3$ (^1H: 400.13 MHz; ^{13}C: 100.61 MHz; ^{19}F 376.50 MHz); chemical shifts are reported as parts per million (δ, ppm); the residual solvent peak ($CHCl_3$) was used as internal standard: 7.26 for ^1H and 77.16 ppm for ^{13}C; multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, m = multiplet, dd = doublet of doublets, dq = doublet of quartets, dqd = doublet of quartet of doublets, ddd = doublet/doublets of doublets; coupling constants, *J*, are reported in Hz. Mass spectra were recorded using Bruker microTOF spectrometer (ionization by electrospray, positive ions detection). Melting points were determined in open capillary tubes on Stuart SMP50 Automatic Melting Point Apparatus. Analytical thin-layer chromatography was carried out on UV-254 silica gel plates using appropriate eluents. Compounds were visualized with short-wavelength UV light. Flash column chromatography was performed using silica gel Merk grade 60 (0.040−0.063 mm) 230−400 mesh. HPLC was performed using ECOM ECS28 P instrument and YMC-Pack SIL-06 (20×250 mm) column eluting with hexane–acetone; gradient: 2–5 % B (0–5 min), 5–35 % B (5–40 min), 35–70 % B (40–50 min).

Preparation of (*E*)-3-arylidene-4-diazopyrrolidine-2,5-diones 5

To a stirred solution/suspension of appropriate benzylidene succinimide (3 mmol) in DCM (20 mL) were added 4-nosyl azide (685 mg, 3 mmol) and DBU (456 μL, 3 mmol) and the mixture was stirred at ambient temperature for 1–2 hours (controlled by TLC). The resulting mixture was subjected to flash column chromatography on silica gel eluting with DCM to afford pure diazo compound **5**.

(*E*)-3-Benzylidene-1-(2-chlorophenyl)-4-diazopyrrolidine-2,5-dione (5p)

Yield: 715 mg (74%). Orange solid; m.p. 142.2–143.1 °C (decomp). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H, =CH), 7.62 – 7.57 (m, 1H), 7.52 – 7.34 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 163.4, 133.3, 133.0, 130.9, 130.5, 130.4, 129.7, 129.7, 129.1, 128.8, 128.6, 127.8, 116.6, 60.3 ($C=N_2$). HRMS (ESI), *m/z* calcd for $C_{17}H_{10}ClN_3NaO_2$ $[M+Na]^+$ 346.0359 found 346.0362.

(*E*)-1-Cyclopropyl-3-diazo-4-(4-fluorobenzylidene)pyrrolidine-2,5-dione (5q)

Yield: 742 mg (91%). Orange solid; m.p. 123.6–124.8 °C (decomp). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H, =CH), 7.33 – 7.26 (m, 2H), 7.17 – 7.10 (m, 2H), 2.85 – 2.62 (m, 1H), 1.04 – 1.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 165.4, 163.1 (d, J = 251.6 Hz), 130.8 (d, J = 8.5 Hz), 129.6, 129.6, 126.0, 116.8, 116.0 (d, J = 22.0 Hz), 59.3 ($C=N_2$), 22.4, 5.4. ^{19}F (377 MHz, $CDCl_3$) δ -110.08. HRMS (ESI), *m/z* calcd for $C_{14}H_{10}FN_3NaO_2$ $[M+Na]^+$ 294.0655 found 294.0657.

General Procedure for the Preparation of 2-Benzazepines 7 and Maleimide-fused Indanes 8

Diazo compound **5** (0.5 mmol) was dissolved in corresponding nitrile (2 mL) followed by addition of $Rh_2(esp)_2$ (1.9 mg, 2.5 μmol, 0.5 mol %). The reaction mixture was stirred at 25 °C for 0.5–24 hours (controlled by TLC). After evaporation of the nitrile (as much as possible) the crude material was purified by column chromatography on silica gel eluting with *n*-hexane–acetone (gradient from 10:1 to 2.5:1) to afford azepines **7** and maleimide-fused indanes **8**.

5-Methyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7a)

Yield: 106 mg (70%). Pale yellow solid; m.p. 193.1–194.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.69 (m, 2H), 7.60 – 7.39 (m, 8H), 4.33 – 4.25 (m, 1H), 2.52 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 170.1, 165. 9, 138.8, 134.5, 133.6, 132.4, 131.8, 131.5, 130.3, 129.7, 129.1, 129.0, 128.7, 126.4, 59.0, 27.4. HRMS (ESI), *m/z* calcd for $C_{19}H_{14}N_2NaO_2$ $[M+Na]^+$ 325.0953 found 325.0950.

5,7-Dimethyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7b)

Yield: 112 mg (71%). Pale yellow solid; m.p. 229.4–230.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.1 Hz, 1H, =CH), 7.60 – 7.39 (m, 8H), 4.29 – 4.26 (m, 1H, CH), 2.55 – 2.49 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 169.9, 166.0, 139.6, 138.8, 133.7, 131.9, 131.8, 131.5, 131.2, 131.1, 130.2, 129.1, 128.6, 126.5, 59.1, 27.4, 21.7. HRMS (ESI), *m/z* calcd for $C_{20}H_{16}N_2NaO_2$ $[M+Na]^+$ 339.1110 found 386.1104.

9-Methoxy-5-methyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7c)

Yield: 111 mg (67%). Pale orange solid; m.p. 183.5–184.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.1 Hz, 1H, =CH), 7.53 – 7.45 (m, 6H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 4.24 (p, *J* = 1.6 Hz, 1H, CH), 3.96 (s, 3H, OCH_3), 2.51 (d, *J* = 1.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 169.8, 166.0, 157.9, 139.9, 131.9, 130.9, 130.2, 129.1, 128.8, 128.6, 126.5, 124.1, 121.4, 111.5, 59.1, 56.0, 27.5. HRMS (ESI), *m/z* calcd for $C_{20}H_{16}N_2NaO_3$ $[M+Na]^+$ 355.1059 found 355.1050.

7-Methoxy-5-methyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7d)

Yield: 85 mg (51%). Yellow solid; m.p. 175.8–177.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.0 Hz, 1H, =CH), 7.54 – 7.42 (m, 6H), 7.24 (d, *J* = 2.6 Hz, 1H), 7.12 (dd, *J* = 8.6, 2.6 Hz, 1H), 4.28 (p, *J* = 1.6 Hz, 1H, CH), 3.94 (s, 3H, OCH_3), 2.51 (d, *J* = 1.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 169.3, 166.1, 159.6, 140.5, 133.6, 133.5, 131.9, 129.3, 129.1, 128.6, 127.4, 126.5, 116.2, 115.2, 59.2, 55.7, 27.5. HRMS (ESI), *m/z* calcd for $C_{20}H_{17}N_2NaO_3$ $[M+H]^+$ 333.1239 found 333.1234.

9-Fluoro-5-methyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7e)

Yield: 133 mg (83%). Yellow solid; m.p. 106.2–107.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, *J* = 2.0 Hz, 1H, =CH), 7.61 – 7.43 (m, 7H), 7.30 (ddd, *J* = 9.3, 8.0, 1.2 Hz, 1H), 4.32 (p, *J* = 1.6 Hz, 1H, CH), 3.94 (s, 3H, OCH_3), 2.53 (d, *J* = 1.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 169.1 (d, *J* = 2.2 Hz), 165.5, 160.4 (d, *J* = 254.3 Hz), 140.1, 133.3, 131.7, 130.5 (d, *J* = 9.2 Hz), 129.2, 128.8, 125.9 (d, *J* = 7.4 Hz), 125.9, 125.4 (d, *J* = 3.6 Hz), 123.3 (d, *J* = 14.4 Hz), 116.8 (d, *J* = 21.6 Hz), 58.9, 27.5. ^{19}F (377 MHz, $CDCl_3$) δ -112.52. HRMS (ESI), *m/z* calcd for $C_{19}H_{13}FN_2NaO_2$ $[M+Na]^+$ 343.0859 found 343.0853.

6-Fluoro-5-methyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7f')

Retention time – 30.8–32.6 min Yield: 62 mg (39%). Yellow solid; m.p. 161.7–162.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.74 (d, *J* = 2.1 Hz, 1H, =CH), 7.59 – 7.36 (m, 7H), 7.24 (ddd, *J* = 10.5, 8.2, 1.2 Hz, 1H), 4.27 (p, *J* = 1.6 Hz, 1H, CH), 2.51 (dd, *J* = 4.1, 1.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 166.6 (d, *J* = 1.9 Hz), 165.7, 160.9 (d, *J* = 253.0 Hz), 136.4, 136.3, 134.4, 132.4 (d, *J* = 2.7 Hz), 131.7, 131.6 (d, *J* = 9.7 Hz), 129.2, 128.8, 127.0 (d, *J* = 3.0 Hz), 126.4, 116.9 (d, *J* = 23.6 Hz), 59.0, 26.9 (d, *J* = 7.7 Hz). ^{19}F (377 MHz, $CDCl_3$) δ -104.12. HRMS (ESI), *m/z* calcd for $C_{19}H_{14}FN_2O_2$ $[M+H]^+$ 321.1039 found 321.1030.

8-Fluoro-5-methyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7f'')

Retention time – 33.3–35.9 min. Yield: 66 mg (41%). Yellow solid; m.p. 119.0–120.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.69 (d, *J* = 2.2 Hz, 1H, =CH), 7.55 – 7.41 (m, 5H), 7.31 – 7.17 (m, 2H), 4.29 (p, *J* = 1.7 Hz, 1H, CH), 2.51 (d, *J* = 1.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 169.2, 165.6, 162.5 (d, *J* = 253.9 Hz), 137.0 (d, *J* = 8.3 Hz), 135.1 (d, *J* = 3.5 Hz), 133.4, 132.4, 132.3 (d, *J* = 1.9 Hz), 131.7, 129.2, 128.8, 126.4, 117.5 (d, *J* = 21.9 Hz), 116.5 (d, *J* = 21.6 Hz), 58.9, 27.4. ^{19}F (377 MHz, $CDCl_3$) δ -108.22. HRMS (ESI), *m/z* calcd for $C_{19}H_{14}FN_2O_2$ $[M+H]^+$ 321.1039 found 321.1031.

7-Fluoro-5-methyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7g)

Yield: 139 mg (87%). White solid; m.p. 192.9–193.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.1 Hz, 1H, =CH), 7.62 – 7.43 (m, 7H), 7.29 (td, *J* = 8.2, 2.6 Hz, 1H), 4.30 (p, *J* = 1.8 Hz, 1H, CH), 2.51 (d, *J* = 1.7 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 168.5 (d, *J* = 1.8 Hz), 165.8, 161.7 (d, *J* = 253.9 Hz), 140.9 (d, *J* = 7.2 Hz), 133.9 (d, *J* = 8.5 Hz), 132.6, 131.7, 131.6 (d, *J* = 1.9 Hz), 130.9 (d, *J* = 3.3 Hz), 129.2, 128.7, 126.4, 118.1 (d, *J* = 21.9 Hz), 116.7 (d, *J* = 22.6 Hz), 59.0, 27.3. ^{19}F (377 MHz, $CDCl_3$) δ -107.95. HRMS (ESI), *m/z* calcd for $C_{19}H_{13}FN_2NaO_2$ $[M+Na]^+$ 343.0859 found 343.0851.

7-Chloro-5-methyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7h)

Yield: 130 mg (77%). Pale yellow solid; m.p. 183.7–184.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H, =CH), 7.56 – 7.42 (m, 7H), 4.31 (p, *J* = 1.9 Hz, 1H, CH), 2.52 (d,

J = 1.5 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 168.6, 165.7, 140.1, 135.1, 132.9, 132.8, 132.5, 132.5, 131.7, 130.6, 129.8, 129.2, 128.7, 126.4, 59.0, 27.3. HRMS (ESI), *m/z* calcd for $C_{19}H_{13}ClN_2NaO_2$ $[M+Na]^+$ 359.0563 found 359.0558.

5-Methyl-2-phenyl-7-(trifluoromethyl)benzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7i)

Yield: 117 mg (63%). Pale yellow solid; m.p. 169.5–171.0 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.87 – 7.69 (m, 3H), 7.59 – 7.41 (m, 5H), 4.34 (p, *J* = 1.9 Hz, 1H, CH), 2.57 (d, *J* = 1.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 168.9, 165.5, 139.2, 137.7, 134.8, 132.1, 132.0 (q, *J* = 33.2 Hz), 131.9, 131.6, 129.2, 128.8, 126.7 (q, *J* = 3.5 Hz), 126.5 (q, *J* = 3.8 Hz), 126.4 (q, *J* = 273.0 Hz), 126.3, 58.9, 27.2. ^{19}F (377 MHz, $CDCl_3$) δ -62.89. HRMS (ESI), *m/z* calcd for $C_{20}H_{14}F_3N_2O_2$ $[M+H]^+$ 371.1007 found 371.1002.

5-Methyl-2-(p-tolyl)benzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7j)

Yield: 104 mg (66%). Pale yellow solid; m.p. 182.0–183.1 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.59 – 7.50 (m, 3H), 7.35 – 7.31 (m, 4H), 4.28 (p, *J* = 1.7 Hz, 1H, CH), 2.53 (d, *J* = 1.6 Hz, 3H, CH_3), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 169.9, 166.0, 138.8, 138.7, 134.6, 133.4, 132.5, 131.5, 130.2, 129.8, 129.7, 129.2, 128.9, 126.2, 59.1, 27.4, 21.3. HRMS (ESI), *m/z* calcd for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1290 found 317.1285.

2-(4-Methoxyphenyl)-5-methylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7k)

Yield: 125 mg (75%). Pale yellow solid; m.p. 162.7–164.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 2H), 7.59 – 7.51 (m, 3H), 7.40 – 7.35 (m, 2H), 7.06 – 7.00 (m, 2H), 4.28 (p, *J* = 1.6 Hz, 1H, CH), 3.86 (s, 3H, OCH_3), 2.53 (d, *J* = 1.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 169.9, 166.2, 159.6, 138.8, 134.6, 133.4, 132.5, 131.5, 130.2, 129.7, 128.9, 127.6, 124.4, 114.5, 59.0, 55.5, 27.4. HRMS (ESI), *m/z* calcd for $C_{20}H_{16}N_2NaO_3$ $[M+Na]^+$ 355.1058 found 355.1053.

2-Benzyl-5-methylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7l)

Yield: 131 mg (87%). Pale yellow solid; m.p. 131.5–132.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 1H, =CH), 7.57 – 7.46 (m, 5H), 7.38 – 7.29 (m, 3H), 4.85 (s, 2H, CH_2), 4.16 (p, *J* = 1.6 Hz, 1H, CH), 2.50 (d, *J* = 1.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 169.8, 166.6, 138.7, 135.6, 134.5, 132.8, 132.6, 131.4, 130.1, 129.7, 128.9, 128.8, 128.7, 127.9, 59.1, 42.6, 27.3. HRMS (ESI), *m/z* calcd for $C_{20}H_{16}N_2NaO_2$ $[M+Na]^+$ 339.1109 found 339.1104.

2-(4-Chlorophenyl)-5-methylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7m)

Yield: 84 mg (50%). Pale yellow solid; m.p. 165.3–166.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.60 – 7.43 (m, 7H), 4.29 (p, *J* = 1.7 Hz, 1H, CH), 2.53 (d, *J* = 1.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 170.1, 165.6, 138.8, 134.4, 134.4, 133.9, 132.0, 131.6, 130.3, 130.3, 129.8, 129.3,

129.1, 127.6, 59.0, 27.4. HRMS (ESI), *m/z* calcd for $C_{19}H_{13}ClN_2NaO_2$ $[M+Na]^+$ 359.0563 found 359.0559.

2-(4-Fluorophenyl)-5-methylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7n)

Yield: 118 mg (74%). Pale orange solid; m.p. 165.9–167.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H), 7.61 – 7.50 (m, 3H), 7.49 – 7.43 (m, 2H), 7.24 – 7.17 (m, 2H), 4.29 (p, *J* = 1.7 Hz, 1H, CH), 2.53 (d, *J* = 1.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.67, 170.09, 165.81, 162.23 (d, *J* = 248.8 Hz), 138.8, 134.4, 133.8, 132.1, 131.5, 130.3, 129.8, 129.1, 128.3 (d, *J* = 8.8 Hz), 127.7 (d, *J* = 3.3 Hz), 116.2 (d, *J* = 23.1 Hz), 59.0, 27.4. ^{19}F (377 MHz, $CDCl_3$) δ -112.20. HRMS (ESI), *m/z* calcd for $C_{19}H_{13}FN_2NaO_2$ $[M+Na]^+$ 343.0858 found 343.0858.

5-Methyl-2-(4-(trifluoromethyl)phenyl)benzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7o)

Yield: 26 mg (14%). Pale yellow solid; m.p. 176.4–177.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 4H), 7.69 – 7.64 (m, 2H), 7.61 – 7.54 (m, 3H), 4.32 (p, *J* = 1.7 Hz, 1H, CH), 2.54 (d, *J* = 1.6 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 170.2, 165.4, 138.8, 134.9, 134.3, 134.3, 131.8, 131.6, 130.4, 130.3 (q, *J* = 33.0 Hz), 129.8, 129.2, 126.9 (q, *J* = 272.4 Hz), 126.6, 126.3 (q, *J* = 3.9 Hz), 59.0, 27.4. ^{19}F (377 MHz, $CDCl_3$) δ -62.73. HRMS (ESI), *m/z* calcd for $C_{20}H_{14}F_3N_2O_2$ $[M+Na]^+$ 393.0826 found 393.0829.

2-(2-Chlorophenyl)-5-methylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7p)

Yield: 68 mg (45%). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$, as mixture of rotamers) δ 7.82 – 7.76 (m, 2.27H), 7.63 – 7.50 (m, 4.73H), 7.47 – 7.40 (m, 3.12H), 4.39 (p, *J* = 1.8 Hz, 0.67H), 4.32 (p, *J* = 1.8 Hz, 0.33H), 2.53 (d, *J* = 1.6 Hz, 3.38H). ^{13}C NMR (101 MHz, $CDCl_3$, as mixture of rotomers) δ 173.1, 173.1, 170.1, 169.8, 165.3, 165.1, 139.0, 138.9, 134.4, 134.4, 133.9, 132.9, 132.4, 132.2, 131.6, 131.5, 130.8, 130.8, 130.6, 130.4, 130.3, 130.2, 130.2, 129.9, 129.8, 129.8, 129.7, 129.1, 129.1, 127.8, 127.7, 59.5, 59.3, 27.4, 27.3. HRMS (ESI), *m/z* calcd for $C_{19}H_{13}ClN_2NaO_2$ $[M+Na]^+$ 359.0563 found 359.0558.

2-Cyclopropyl-7-fluoro-5-methylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7q)

Yield: 97 mg (68%). Beige solid; m.p. 142.7–143.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.2 Hz, 1H, =CH), 7.53 (dd, *J* = 8.7, 5.6 Hz, 1H), 7.42 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.26 (ddd, *J* = 8.7, 7.7, 2.7 Hz, 1H), 4.06 (p, *J* = 1.7 Hz, 1H, CH), 2.85 – 2.76 (m, 1H), 2.46 (d, *J* = 1.6 Hz, 3H, CH_3), 1.17 – 1.13 (m, 1H), 1.08 – 1.02 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 168.4 (d, *J* = 1.8 Hz), 167.3, 161.6 (d, *J* = 253.4 Hz), 140.8 (d, *J* = 7.1 Hz), 133.8 (d, *J* = 8.3 Hz), 131.8 (d, *J* = 2.0 Hz), 131.3, 130.9 (d, *J* = 3.3 Hz), 117.9 (d, *J* = 21.9 Hz), 116.6 (d, *J* = 22.6 Hz), 58.6, 27.3, 22.6, 5.0 (d, *J* = 16.2 Hz). ^{19}F (377 MHz, $CDCl_3$) δ -108.38. HRMS (ESI), *m/z* calcd for $C_{16}H_{13}FN_2NaO_2$ $[M+Na]^+$ 307.0858 found 307.0853.

5-Ethyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7r)

Yield: 117 mg (74%). White solid; m.p. 170.1–171.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.62 – 7.41 (m, 8H), 4.30 – 4.23 (m, 1H, CH), 2.91 (dq, *J* = 14.9, 7.4 Hz, 1H, CH_2), 2.80 (dqd, *J* = 15.1, 7.5, 1.8 Hz, 1H, CH_2), 1.03 (t, *J* = 7.4 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 173.8, 166.0, 138.3, 135.1, 133.5, 132.9, 131.9, 131.3, 130.0, 129.3, 129.1, 128.9, 128.6, 126.5, 58.9, 33.4, 11.9. HRMS (ESI), *m/z* calcd for $C_{20}H_{16}N_2NaO_2$ $[M+Na]^+$ 339.1109 found 339.1104.

5-Isopropyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7s)

Yield: 114 mg (69%). Pale yellow solid; m.p. 181.8–183.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 2H), 7.58 – 7.41 (m, 8H), 4.21 (s, 1H, CH), 3.16 (hept, *J* = 6.8 Hz, 1H), 1.36 (d, *J* = 6.5 Hz, 3H, CH_3), 0.83 (d, *J* = 6.9 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.6, 173.9, 166.1, 139.2, 135.4, 133.5, 133.4, 131.9, 130.9, 129.7, 129.1, 128.8, 128.8, 128.6, 126.5, 58.9, 37.4, 21.6, 20.5. HRMS (ESI), *m/z* calcd for $C_{21}H_{18}N_2NaO_2$ $[M+Na]^+$ 353.1265 found 353.1260.

5-Cyclopropyl-2-phenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7t)

Yield: 115 mg (70%). Pale yellow solid; m.p. 171.5–172.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 1H), 7.76 (d, *J* = 2.1 Hz, 1H, =CH), 7.59 – 7.41 (m, 8H), 4.21 (d, *J* = 2.0 Hz, 1H, CH), 1.95 – 1.86 (m, 1H), 1.45 – 1.35 (m, 1H), 1.17 – 1.10 (m, 2H), 0.87 – 0.79 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 172.9, 166.0, 139.8, 134.5, 133.5, 132.6, 131.9, 131.0, 130.0, 129.9, 129.1, 128.9, 128.6, 126.4, 58.6, 19.7, 12.6, 7.9. HRMS (ESI), *m/z* calcd for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ 329.1290 found 329.1285.

2,5-Diphenylbenzo[*e*]pyrrolo[3,4-*b*]azepine-1,3(2*H*,3a*H*)-dione (7u)

Yield: 114 mg (63%). White solid; m.p. 188.0–189.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.1 Hz, 1H, =CH), 7.70 – 7.61 (m, 2H), 7.55 – 7.36 (m, 12H), 4.44 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 170.9, 165.8, 140.4, 137.2, 136.6, 133.6, 133.4, 132.8, 131.9, 130.7, 130.6, 130.5, 130.0, 129.1, 128.6, 128.2, 128.1, 126.4, 59.5. HRMS (ESI), *m/z* calcd for $C_{24}H_{17}N_2O_2$ $[M+H]^+$ 365.1290 found 365.1289.

6-Methoxy-2-phenylindeno[1,2-*c*]pyrrole-1,3(2*H*,8*H*)-dione (8v')

Retention time – 25.9–28.4 min. Yield: 47 mg (32%). Yellow solid, m.p. 181.2–182.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.44 – 7.36 (m, 3H), 7.20 (d, *J* = 2.3 Hz, 1H), 7.02 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.91 (s, 3H, OMe), 3.81 (d, *J* = 1.1 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 164.7, 161.1, 151.4, 150.8, 145.8, 132.2, 129.0, 127.6, 127.3, 126.5, 123.7, 113.8, 111.7, 55.7, 33.5. HRMS (ESI), *m/z* calcd for $C_{18}H_{14}NO_3$ $[M+H]^+$ 292.0974 found 292.0977.

4-Methoxy-2-phenylindeno[1,2-*c*]pyrrole-1,3(2*H*,8*H*)-dione (8v'')

Retention time – 29.5–31.0 min. Yield: 13 mg (9%). Yellow solid, 175.0–176.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 5H), 7.41 – 7.35 (m, 1H), 7.26 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 4.02 (s, 3H, OMe), 3.86 (s, 2H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 163.6, 154.9, 150.8, 150.2, 147.4, 132.3, 130.9, 128.9, 127.6, 126.7, 123.9, 118.0, 110.0, 56.0, 33.7. HRMS (ESI), *m/z* calcd for $C_{18}H_{13}NNaO_3$ $[M+Na]^+$ 314.0793 found 314.0794.

General Procedure for Hydrogenation of 2-Benzazepines 7

Corresponding 2-benzazepine **7** (0.2 mmol) was dissolved in MeOH (5 mL) and solution was stirred for 10 min under inert atmosphere. Palladium on activated charcoal (42 mg, 0.04 mmol, 20 mol. %) (10% w/w) was added, and reaction was stirred under H_2 atmosphere overnight at room temperature. Then the mixture was filtered through celite pad and after evaporation of the solvent the crude material was purified by flash column chromatography on silica gel eluting with DCM to afford compounds **10**.

5-methyl-2-phenyl-5,10-dihydrobenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,4H)-dione (10a)

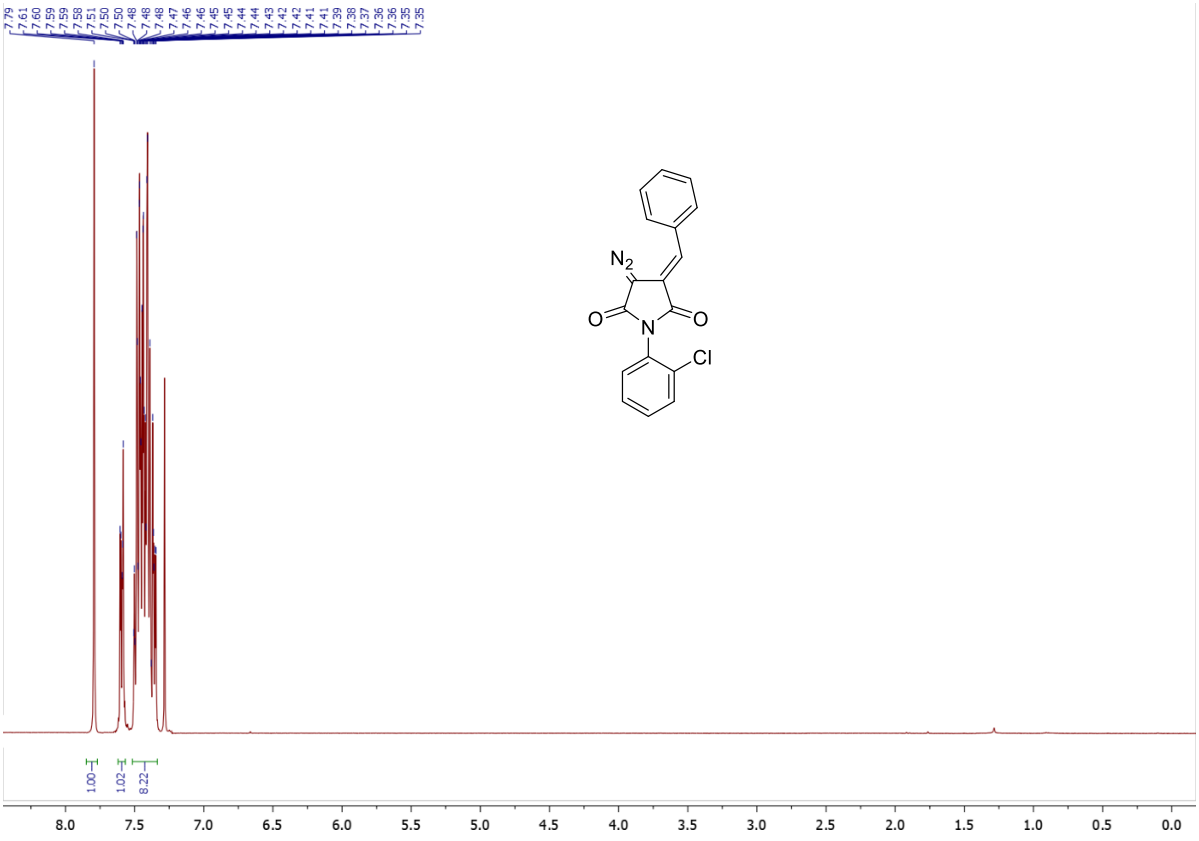
Yield: 16 mg (27%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.38 – 7.26 (m, 7H), 5.42 (d, *J* = 4.5 Hz, 1H, NH), 5.06 (qd, *J* = 7.0, 4.4 Hz, 1H, CH), 4.07 (d, *J* = 17.4 Hz, 1H, CH_2), 3.82 (d, *J* = 17.4 Hz, 1H, CH_2), 1.77 (d, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 166.1, 144.2, 138.7, 138.5, 132.1, 129.8, 128.9, 128.8, 127.6, 127.1, 126.2, 125.8, 97.5, 52.1, 27.0, 20.0. HRMS (ESI), *m/z* calcd for $C_{19}H_{16}N_2NaO_2$ $[M+Na]^+$ 327.1109 found 327.1104.

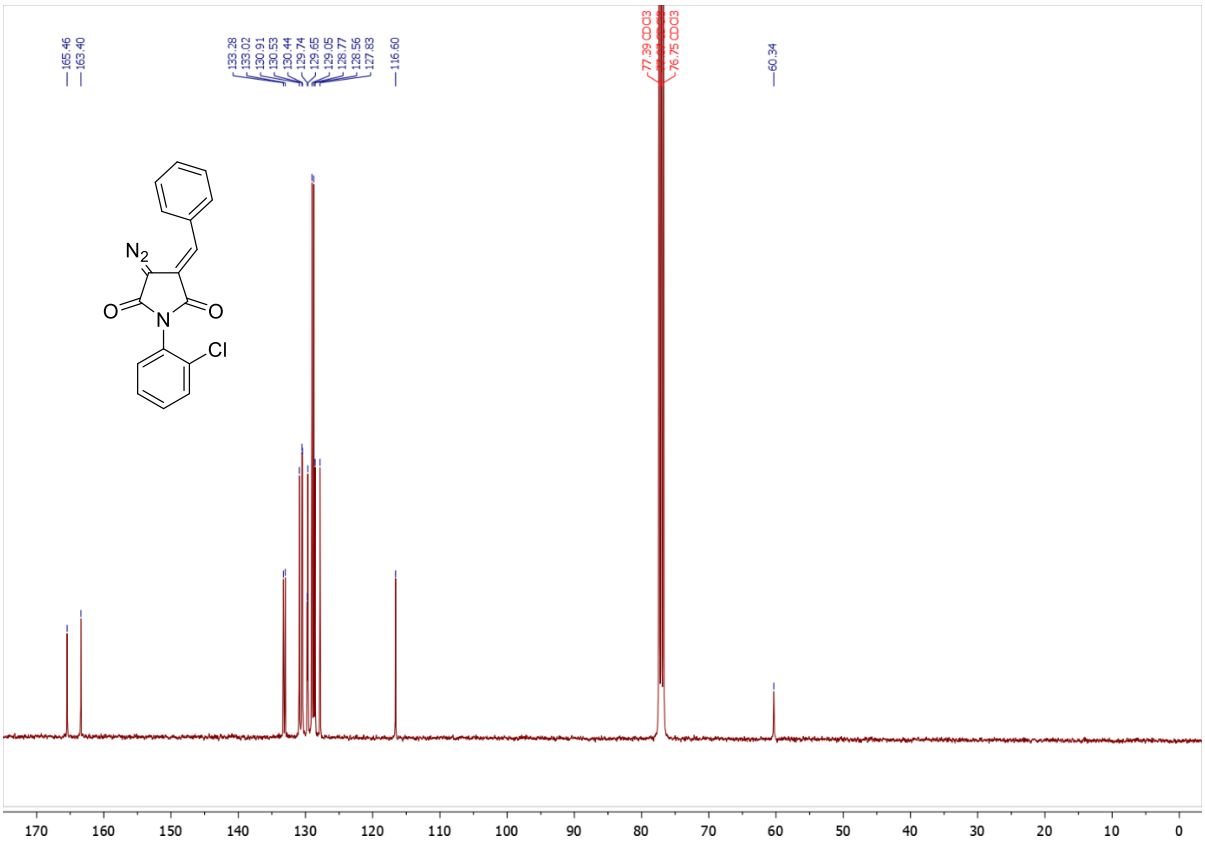
5-ethyl-2-phenyl-5,10-dihydrobenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,4H)-dione (10b)

Yield: 15 mg (24%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) 7.44 (tt, *J* = 7.6, 2.0 Hz, 2H), 7.39 – 7.24 (m, 6H), 7.19 (dd, *J* = 7.2, 1.8 Hz, 1H), 5.70 (d, *J* = 4.1 Hz, 1H, NH), 4.45 (q, *J* = 7.2 Hz, 1H, CH), 3.98 – 3.85 (m, 2H, CH_2), 2.15 (p, *J* = 7.4 Hz, 2H, $CH_3C\underline{H_2}$), 1.06 (t, *J* = 7.4 Hz, 2H, $C\underline{H_3}CH_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 166.2, 143.8, 137.9, 137.8, 132.1, 130.3, 128.9, 128.7, 128.6, 127.4, 127.1, 125.8, 96.9, 28.0, 27.4, 11.3. HRMS (ESI), *m/z* calcd for $C_{20}H_{18}N_2NaO_2$ $[M+Na]^+$ 341.1265 found 341.1260.

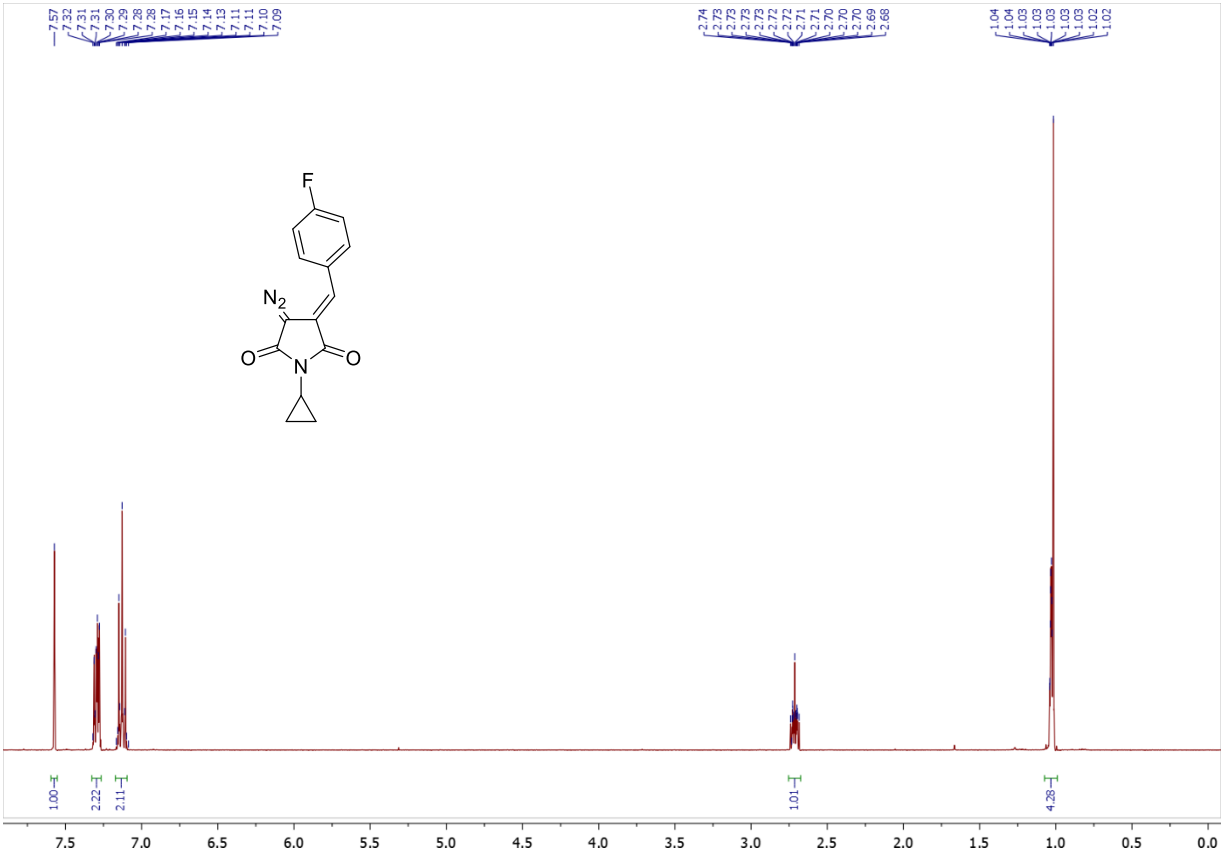
NMR Spectra

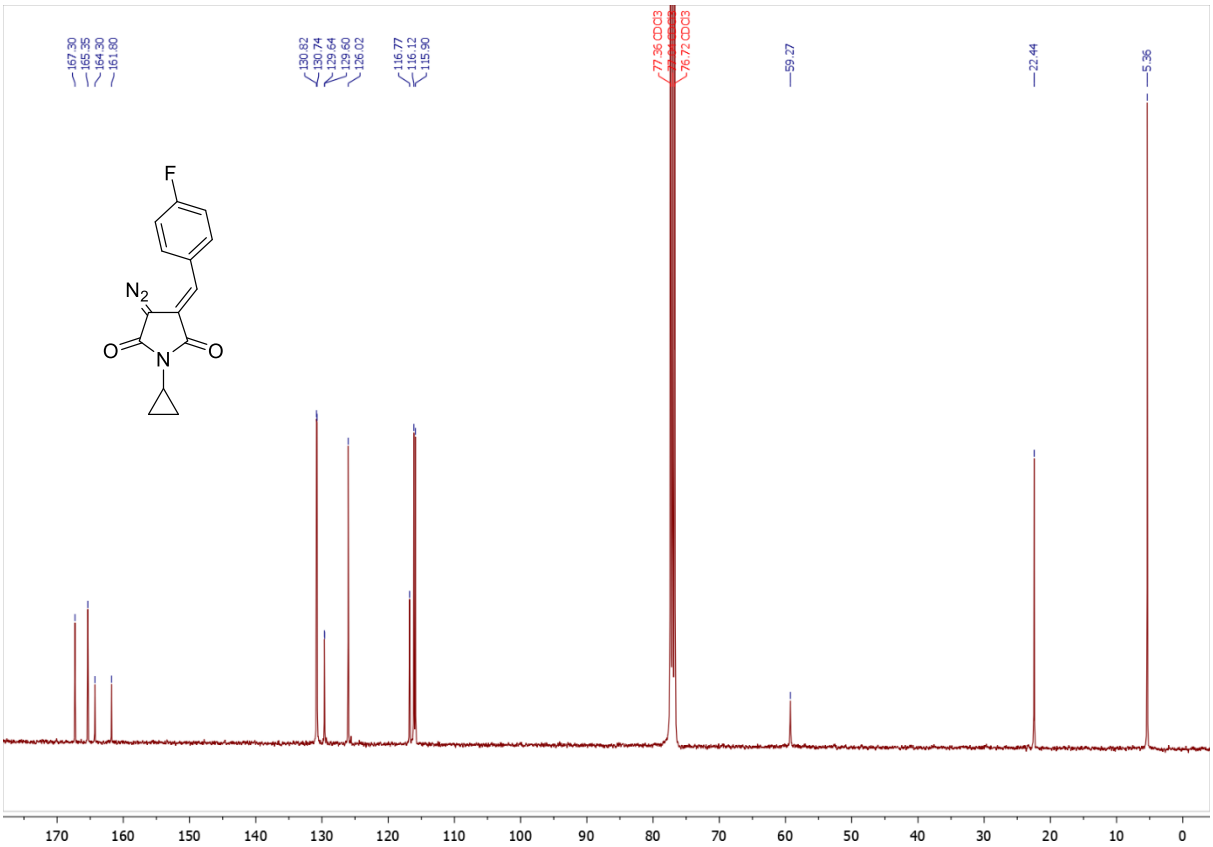
(*E*)-3-benzylidene-1-(2-chlorophenyl)-4-diazopyrrolidine-2,5-dione (5p)

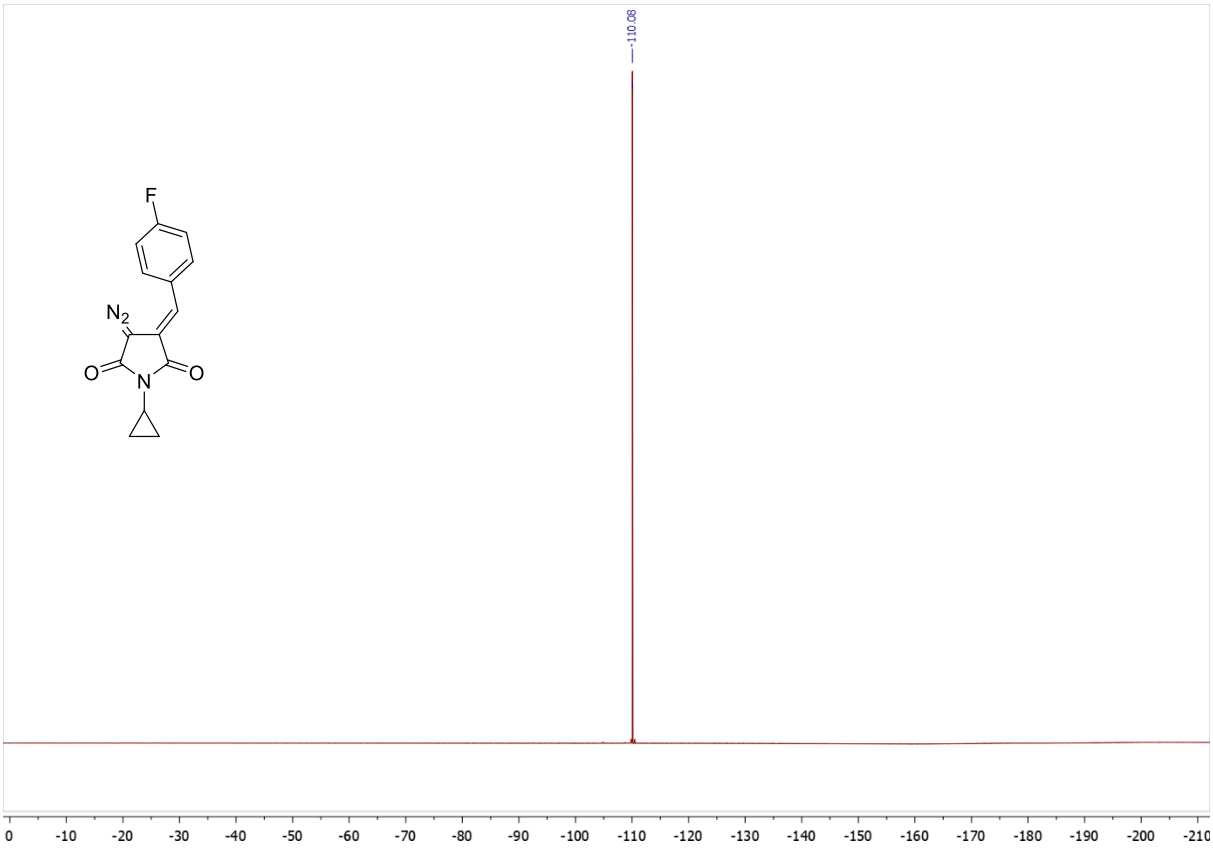




(*E*)-1-cyclopropyl-3-diazo-4-(4-fluorobenzylidene)pyrrolidine-2,5-dione (5q)



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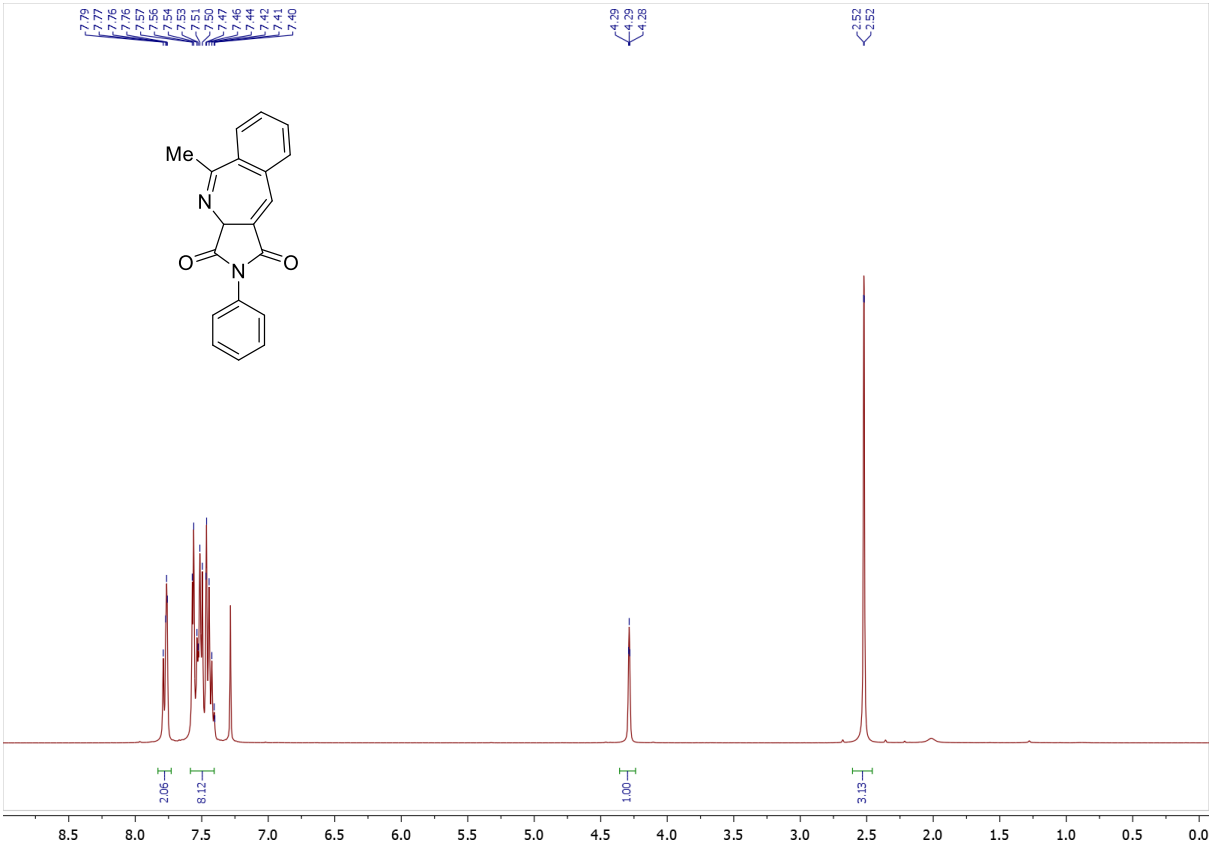
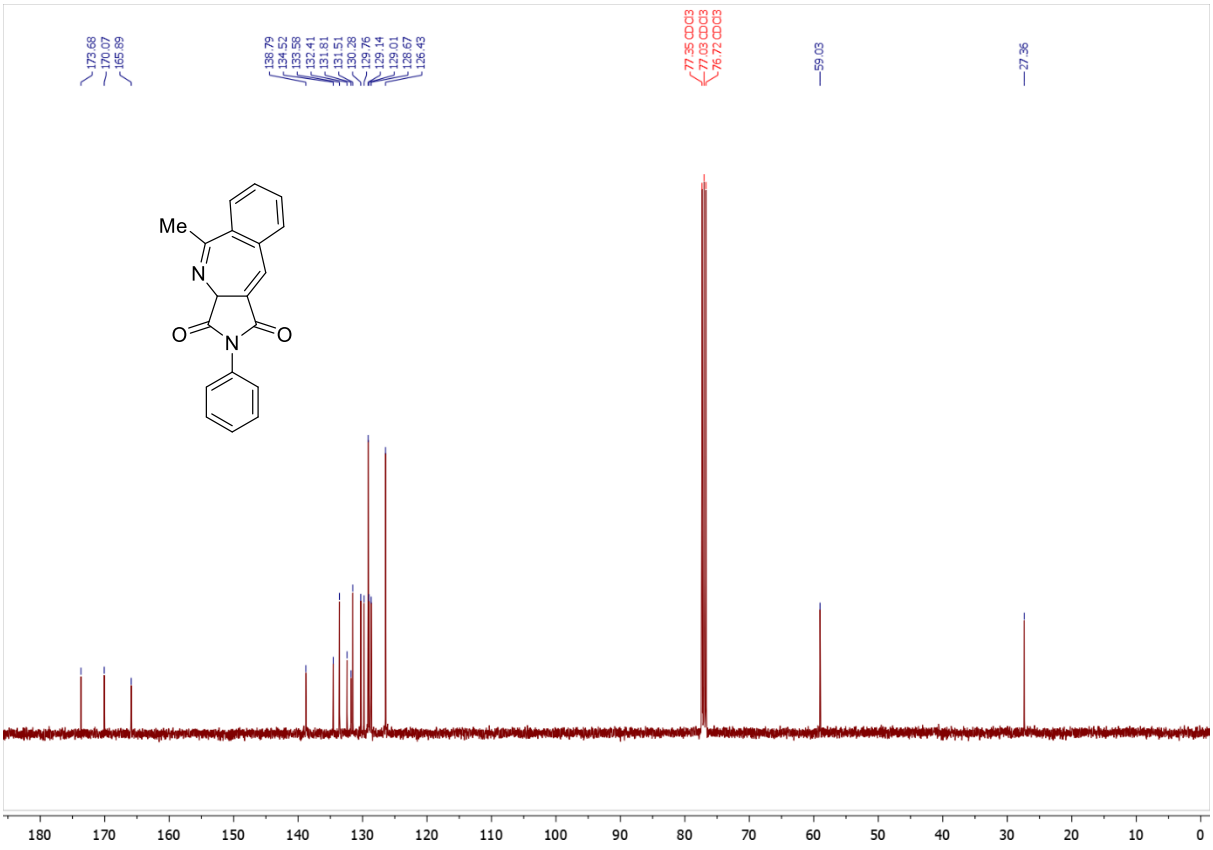
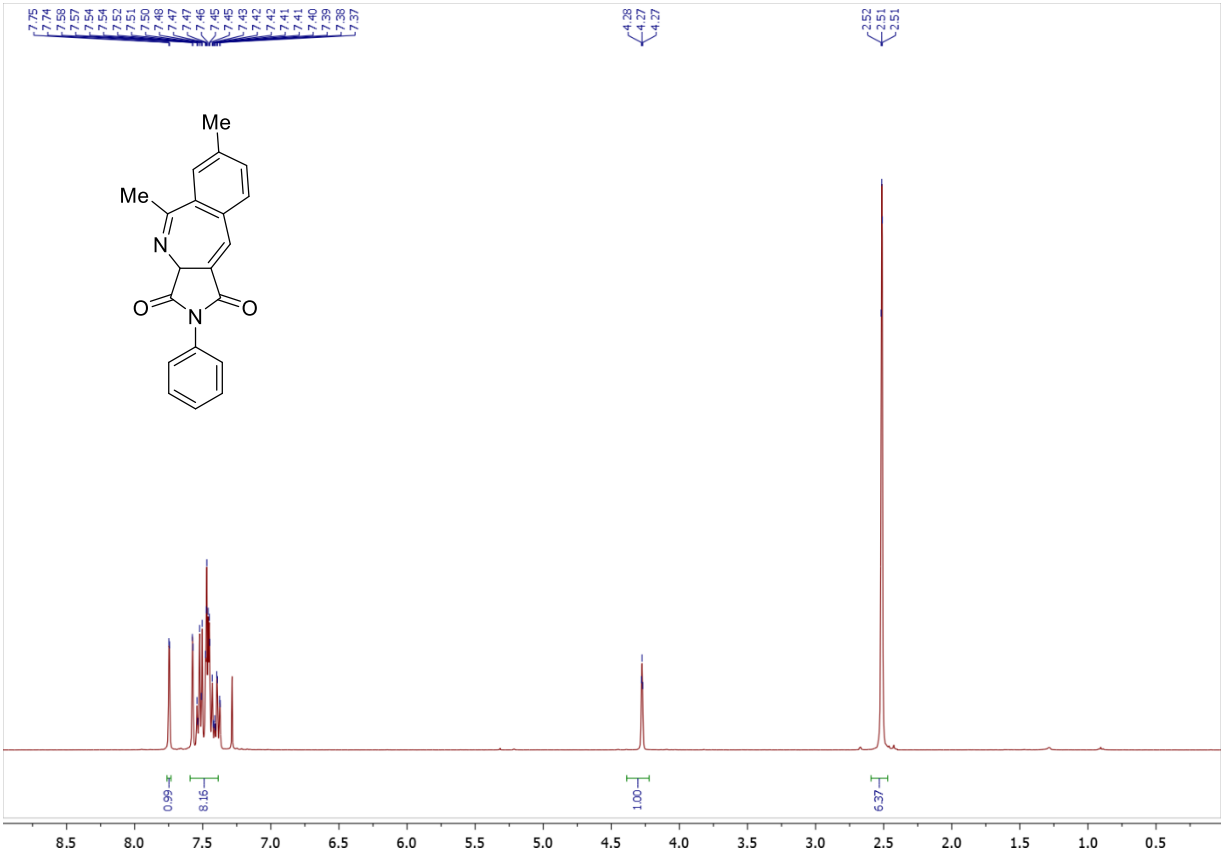
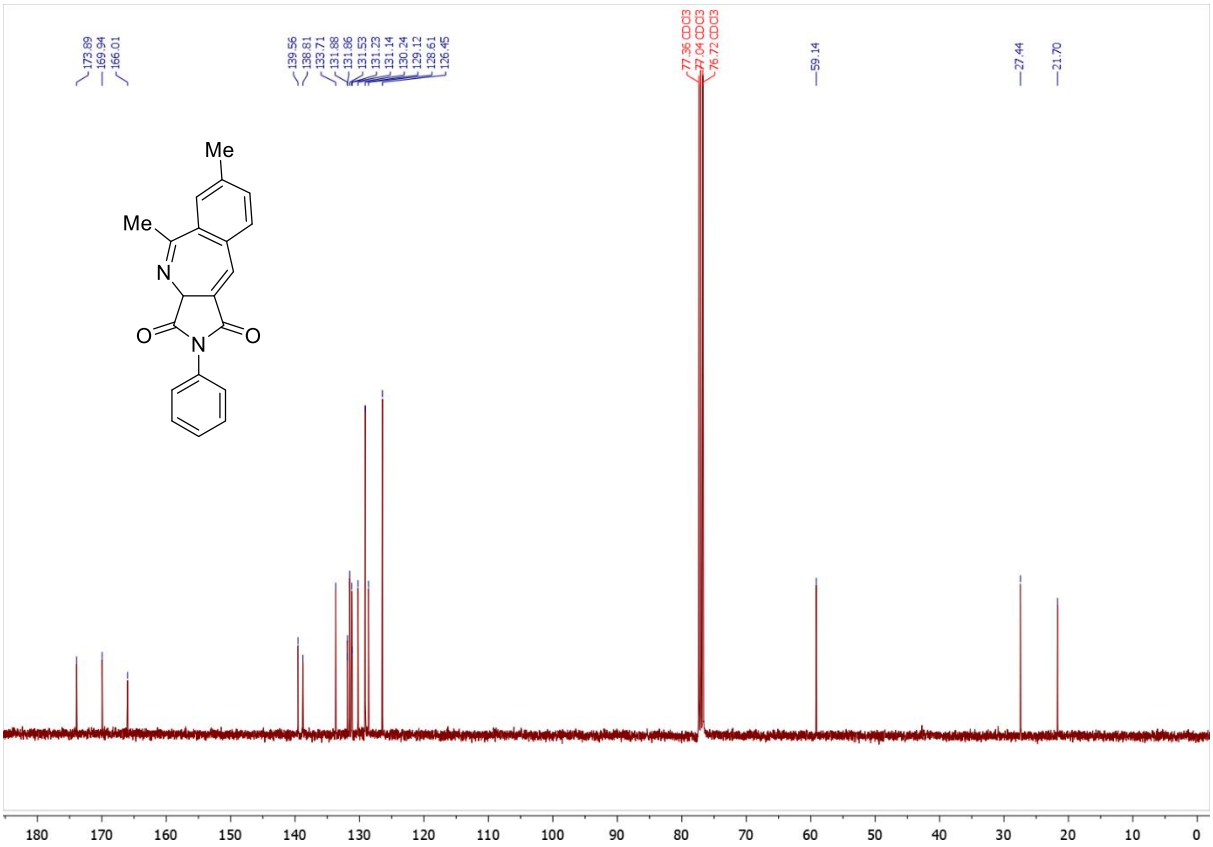
5-methyl-2-phenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7a)



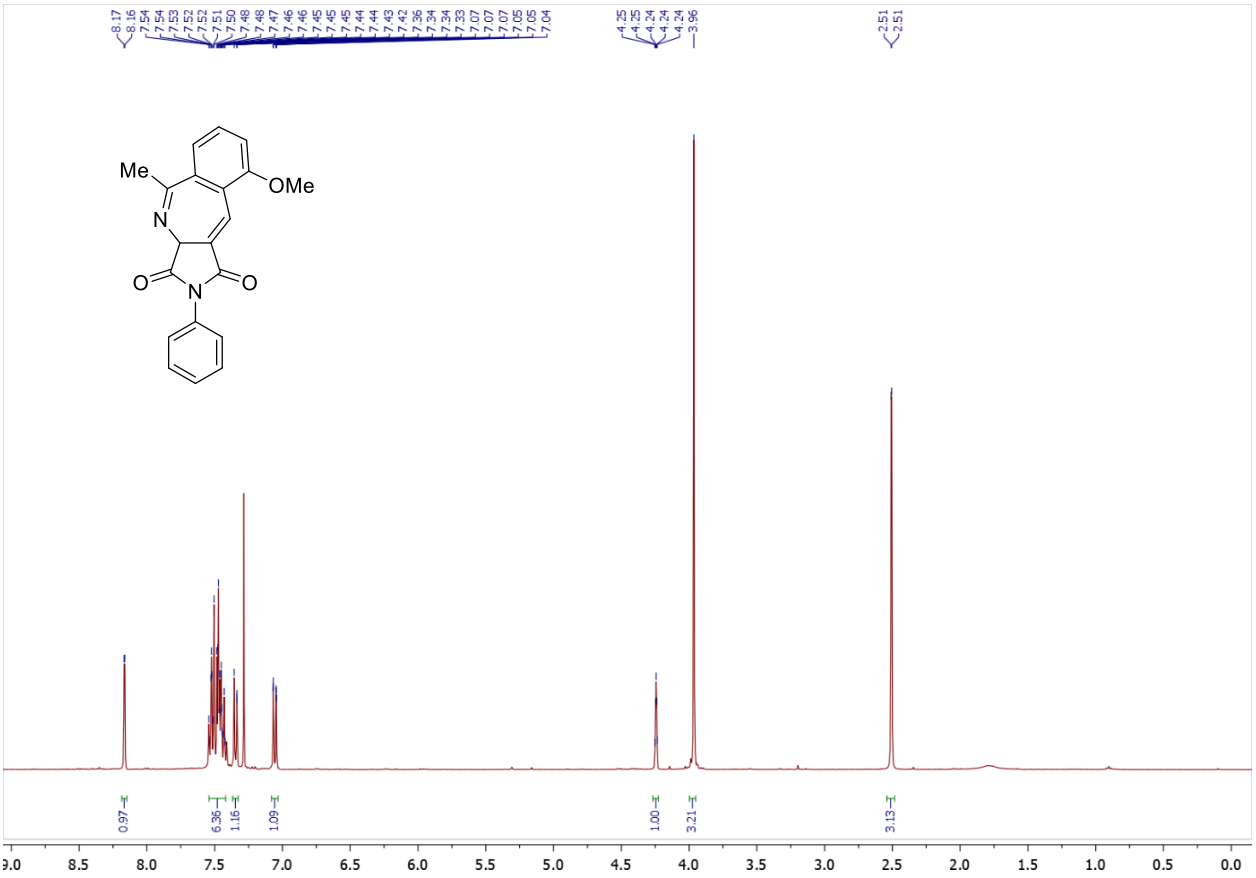


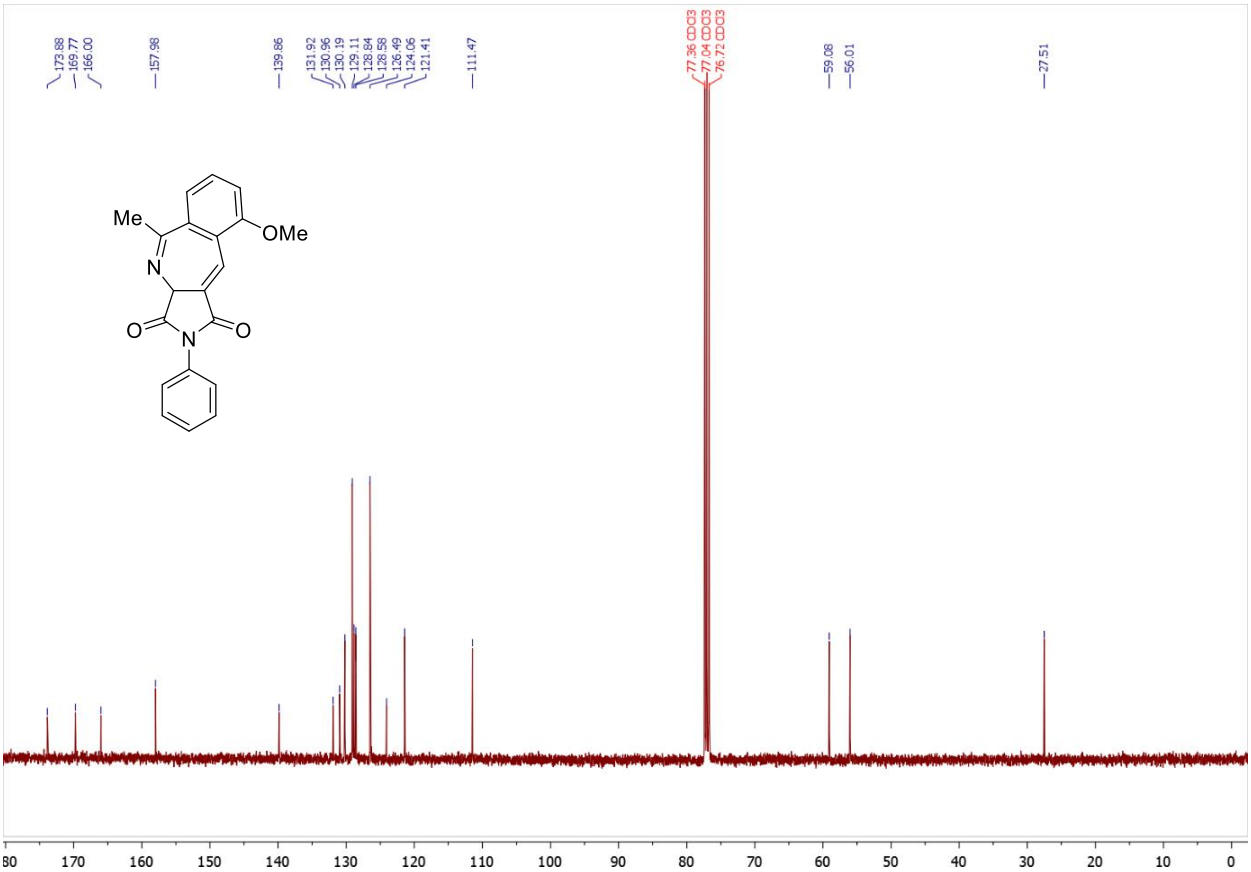
5,7-dimethyl-2-phenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7b)



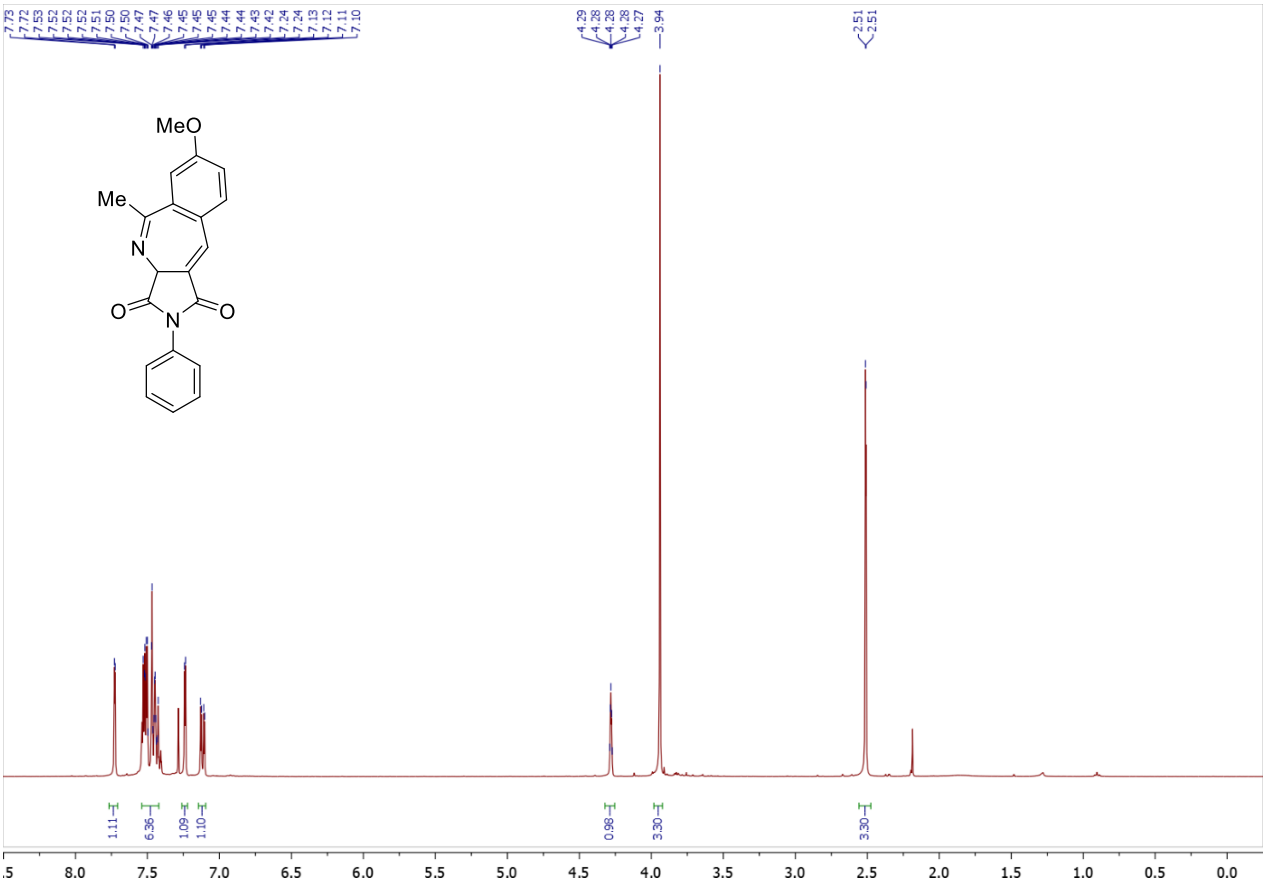


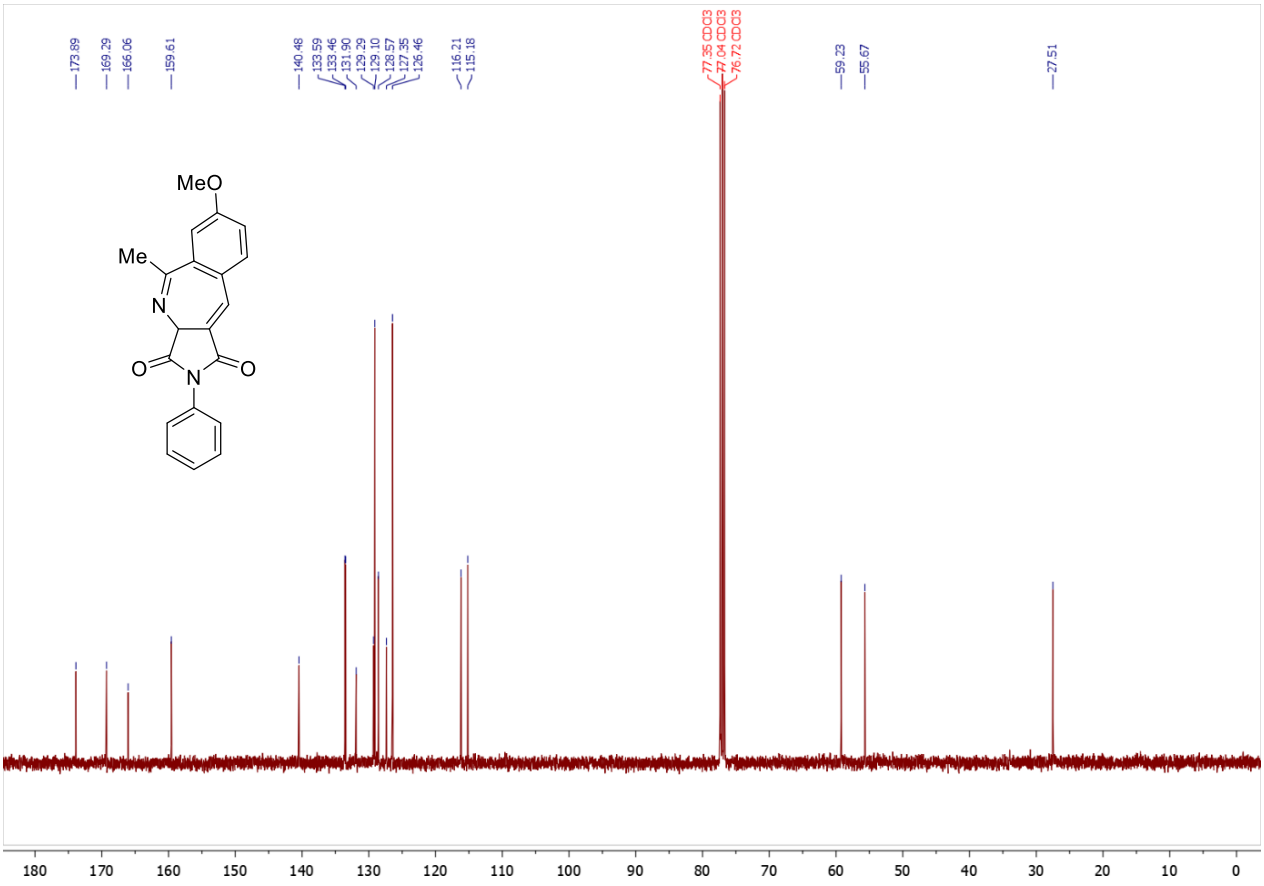
9-methoxy-5-methyl-2-phenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7c)



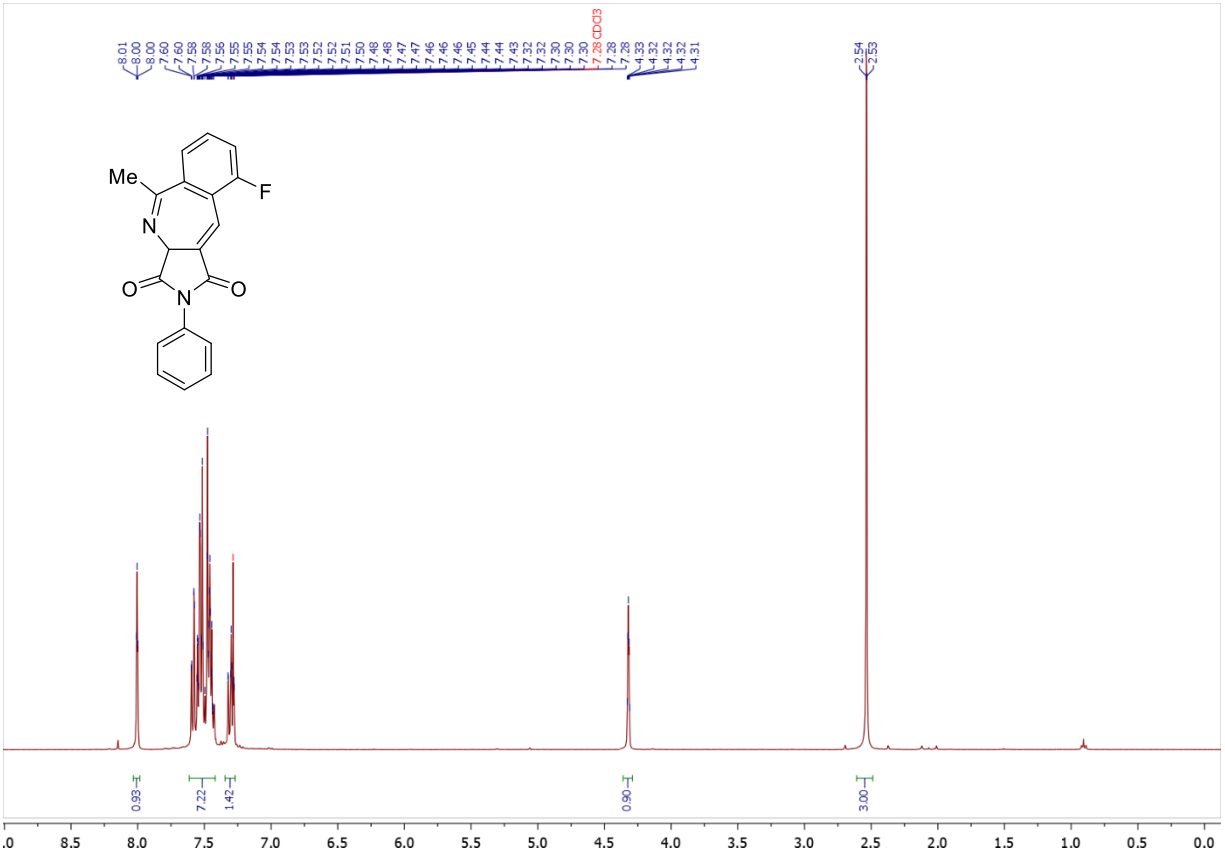


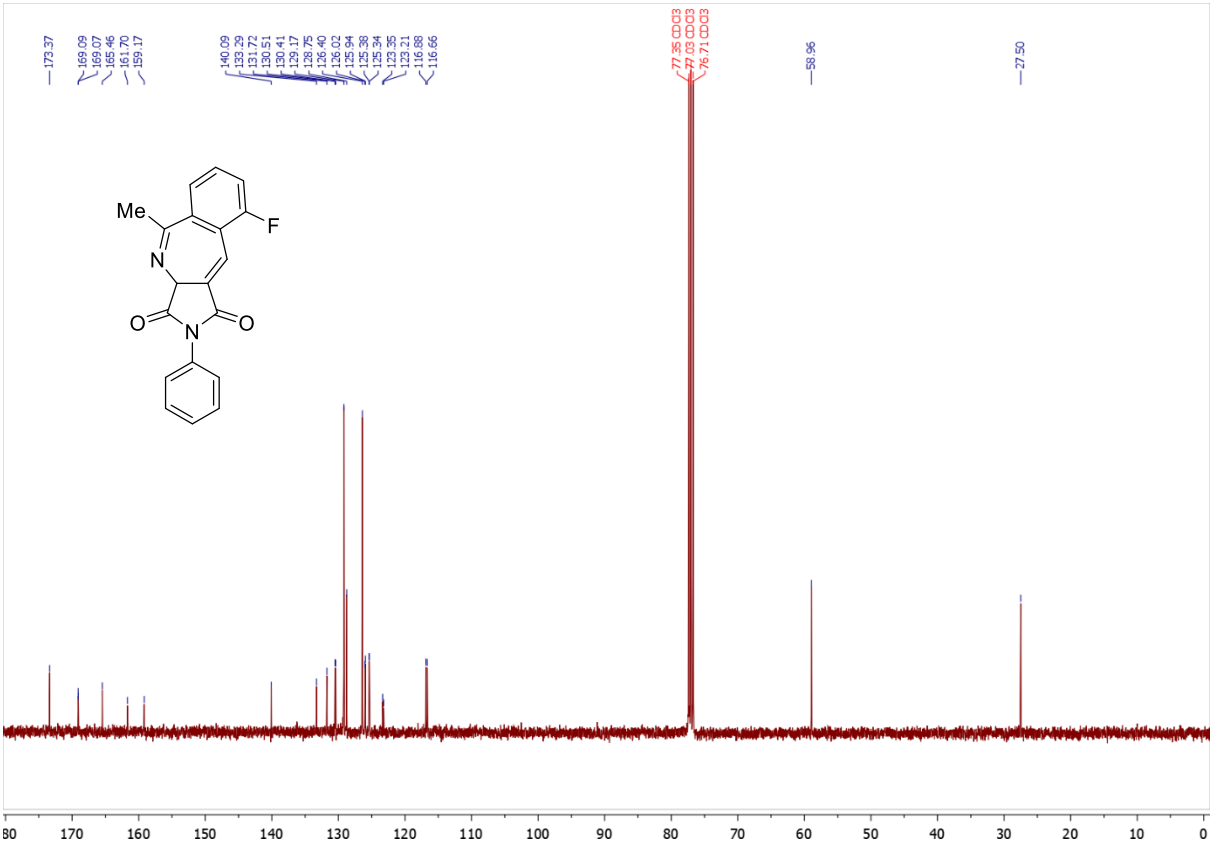
7-methoxy-5-methyl-2-phenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7d)

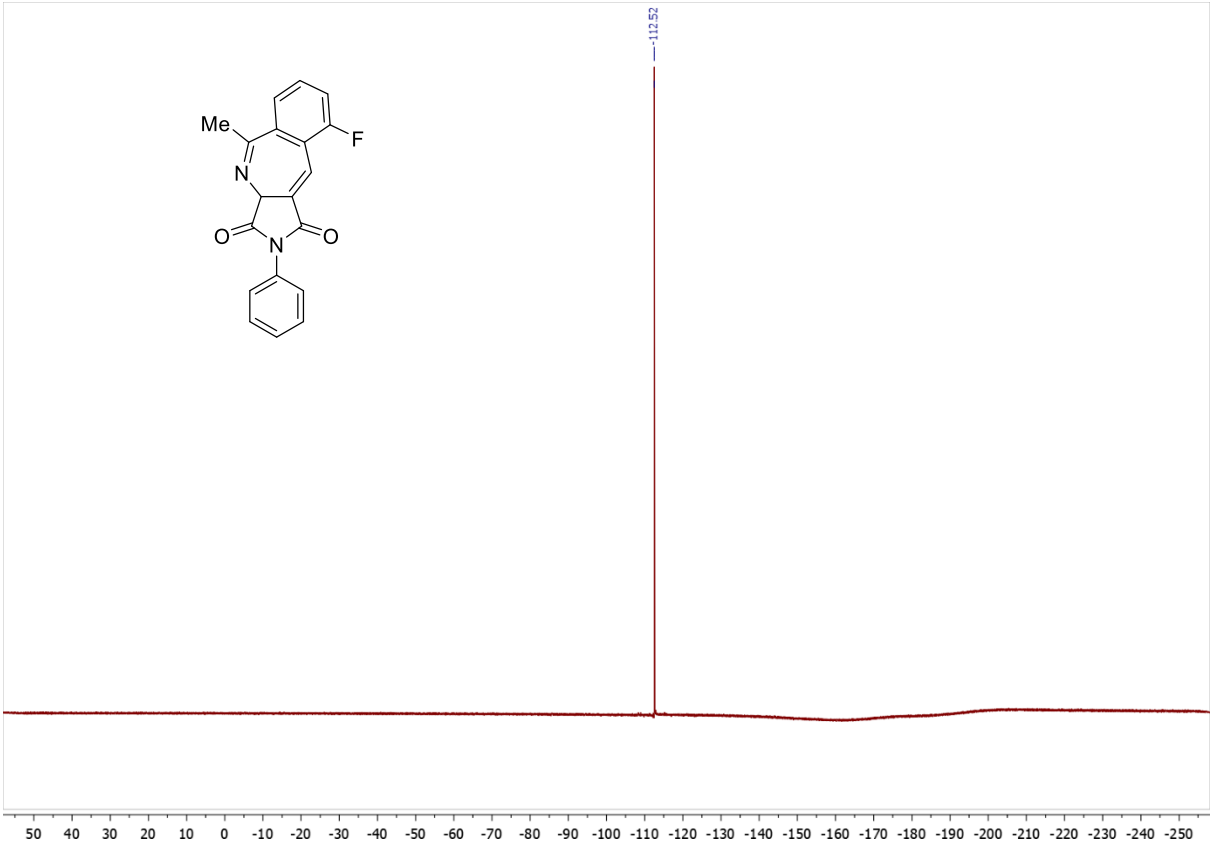




9-fluoro-5-methyl-2-phenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7e)



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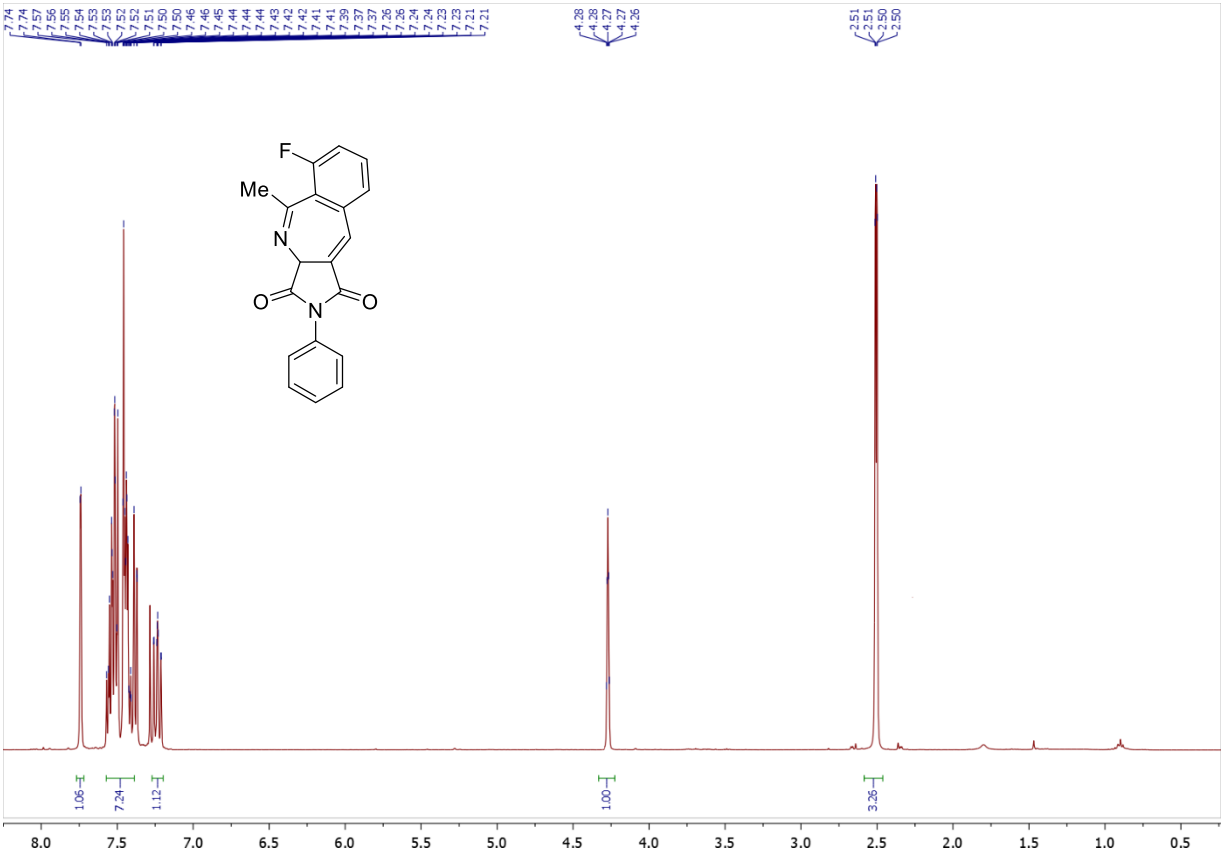

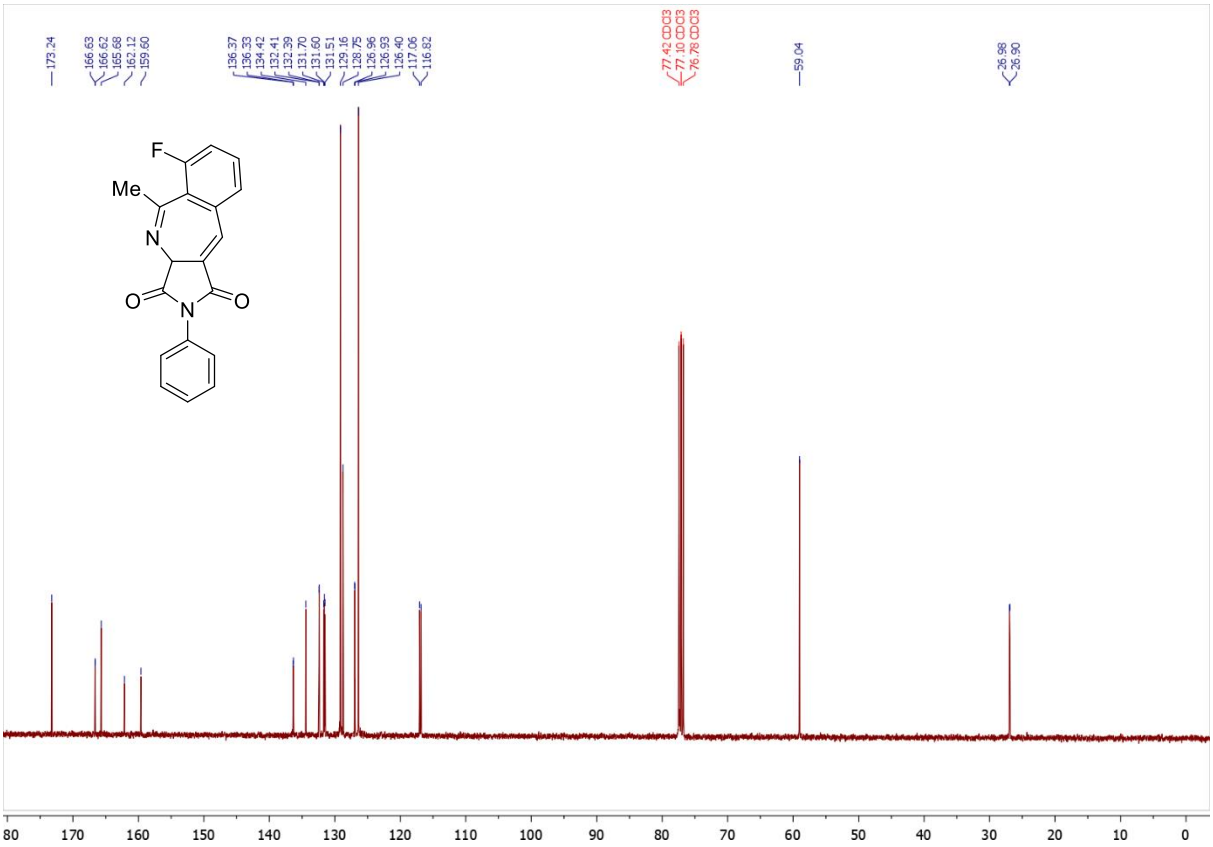

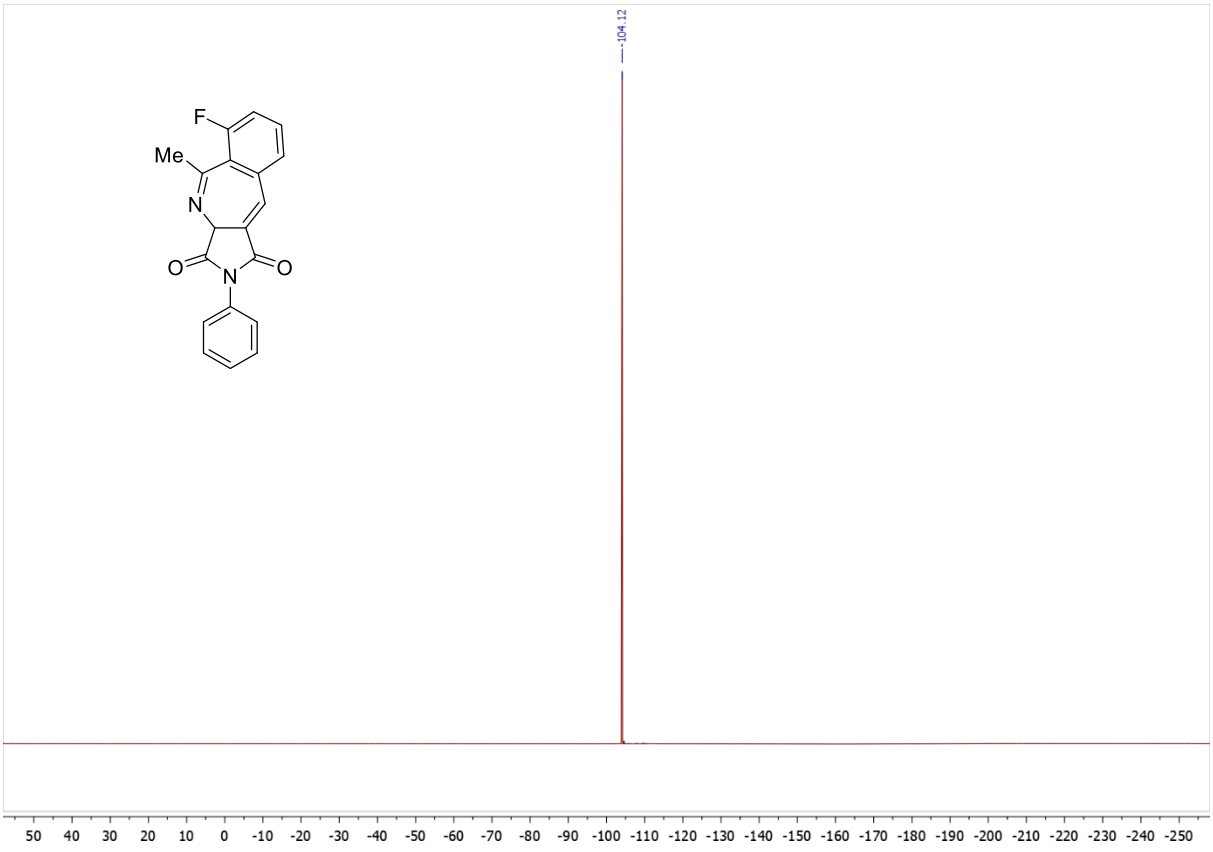
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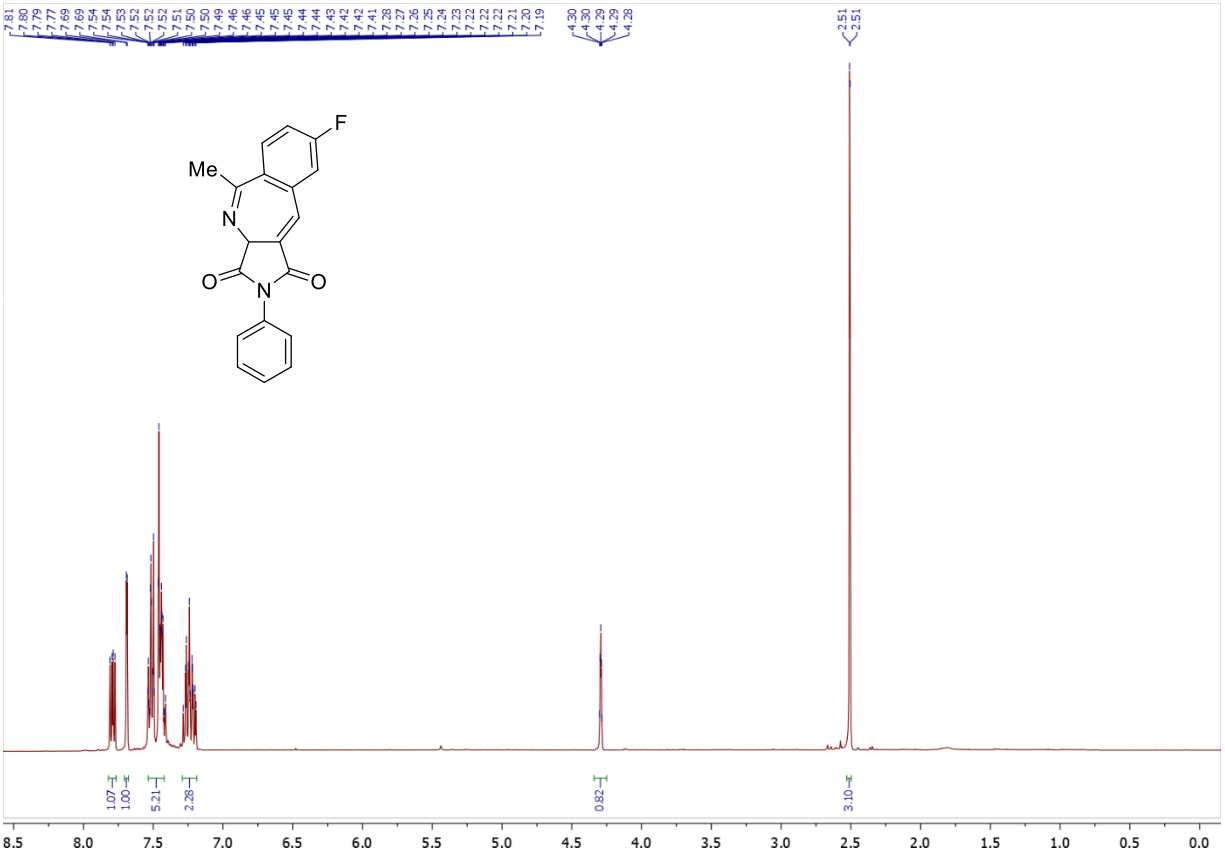

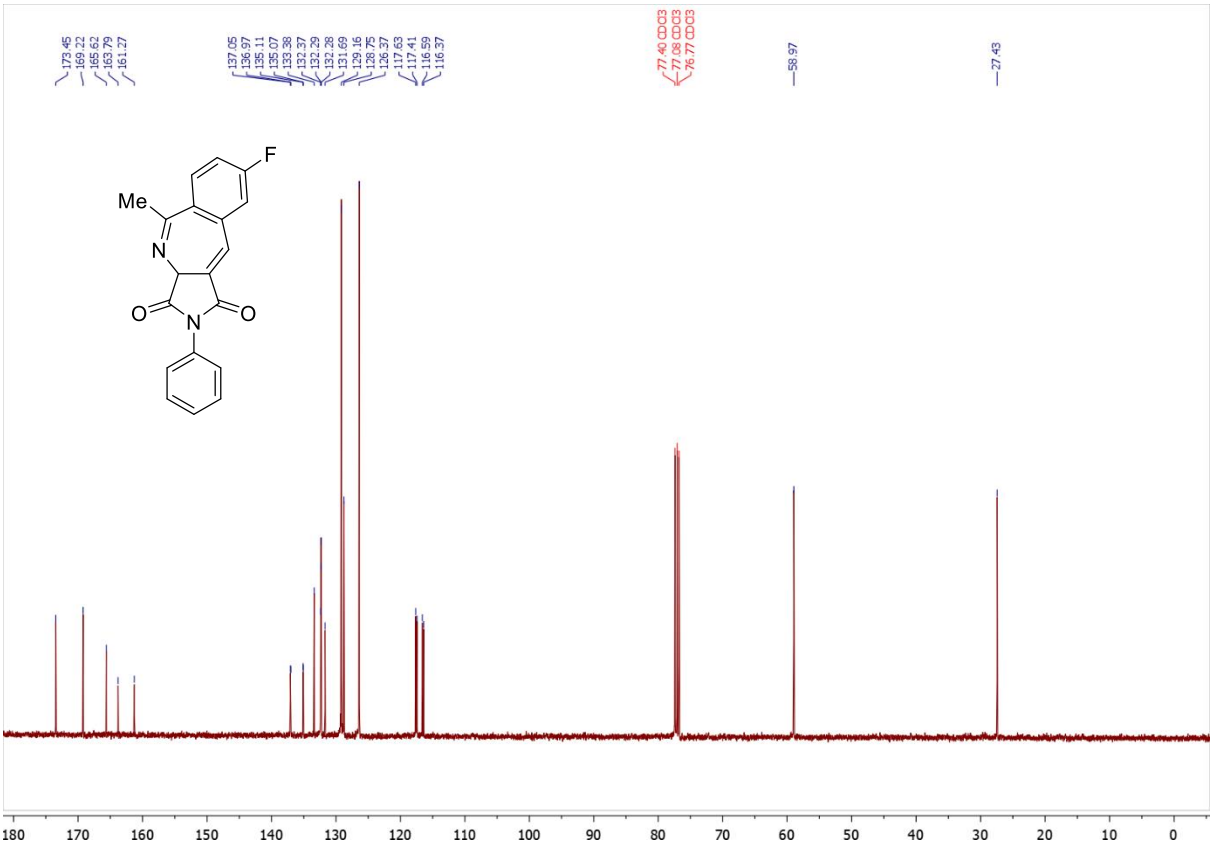

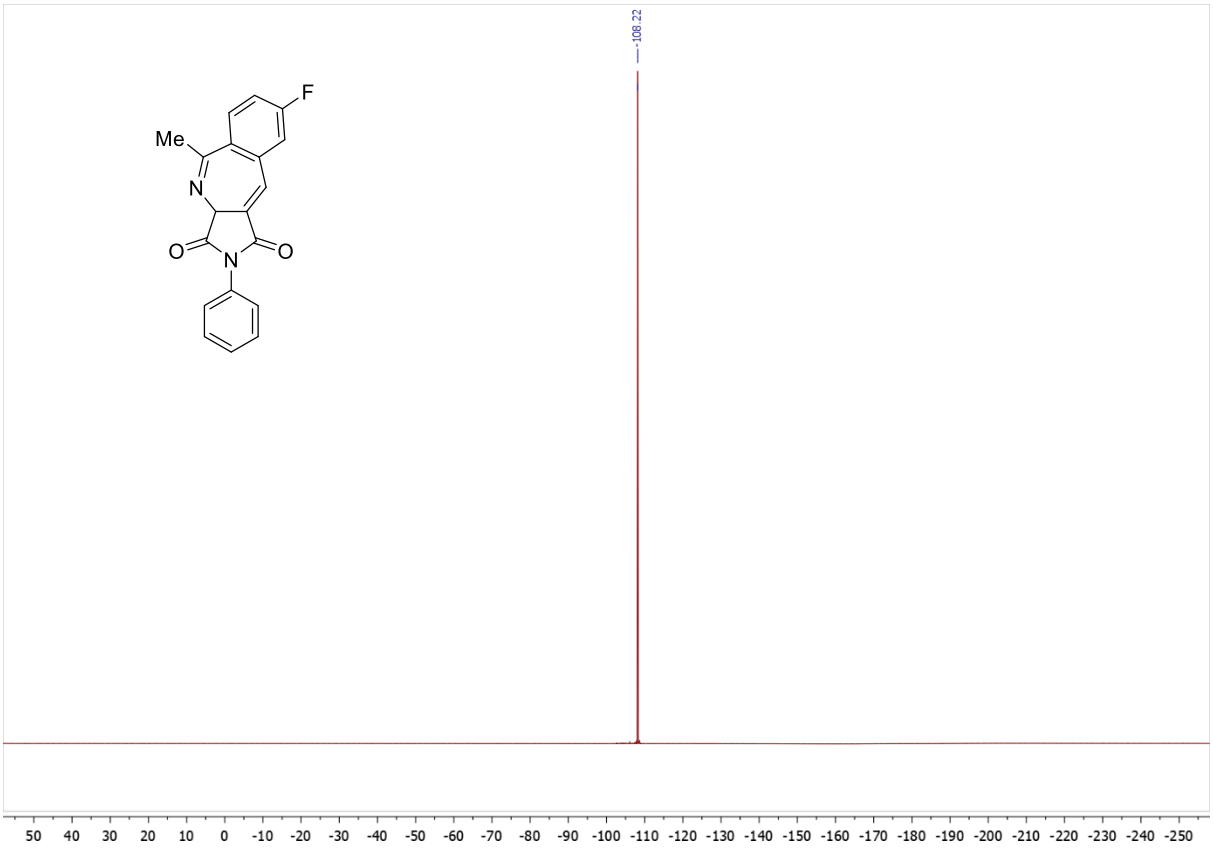
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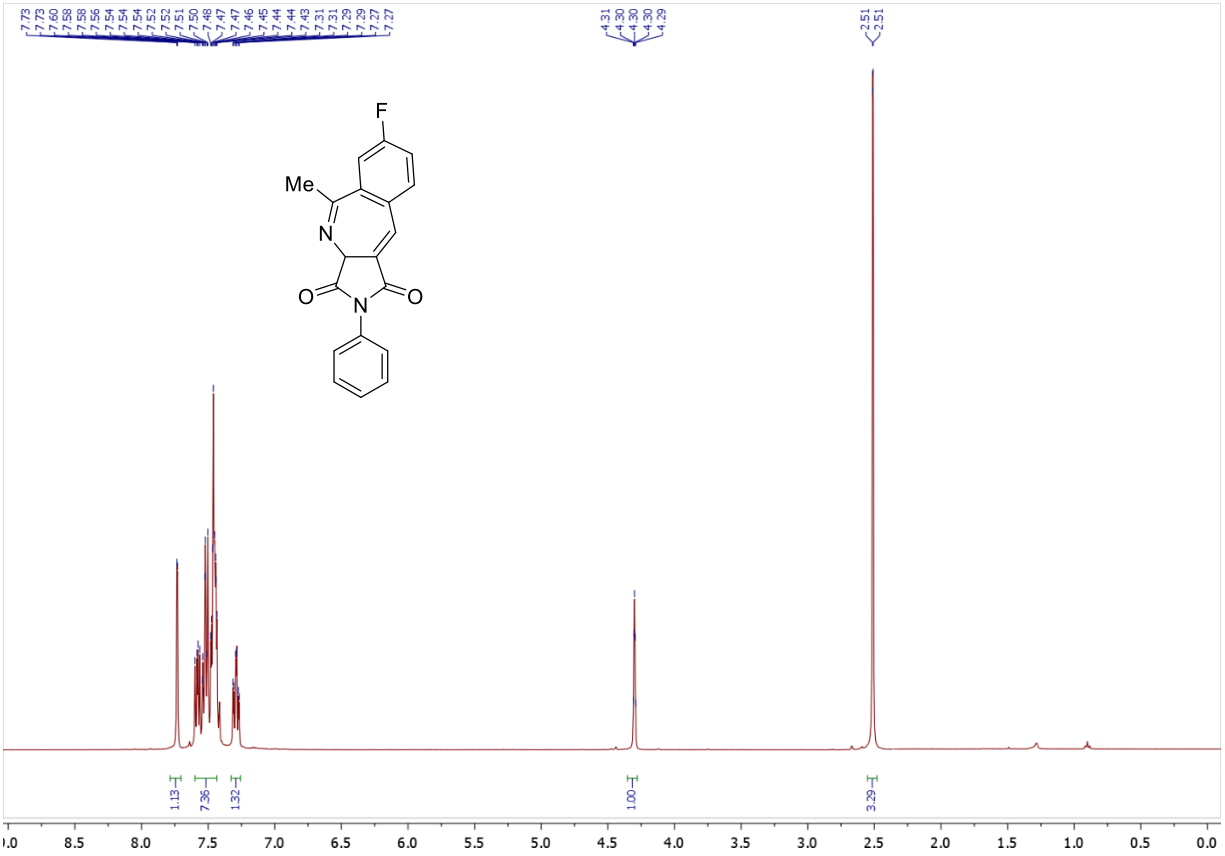

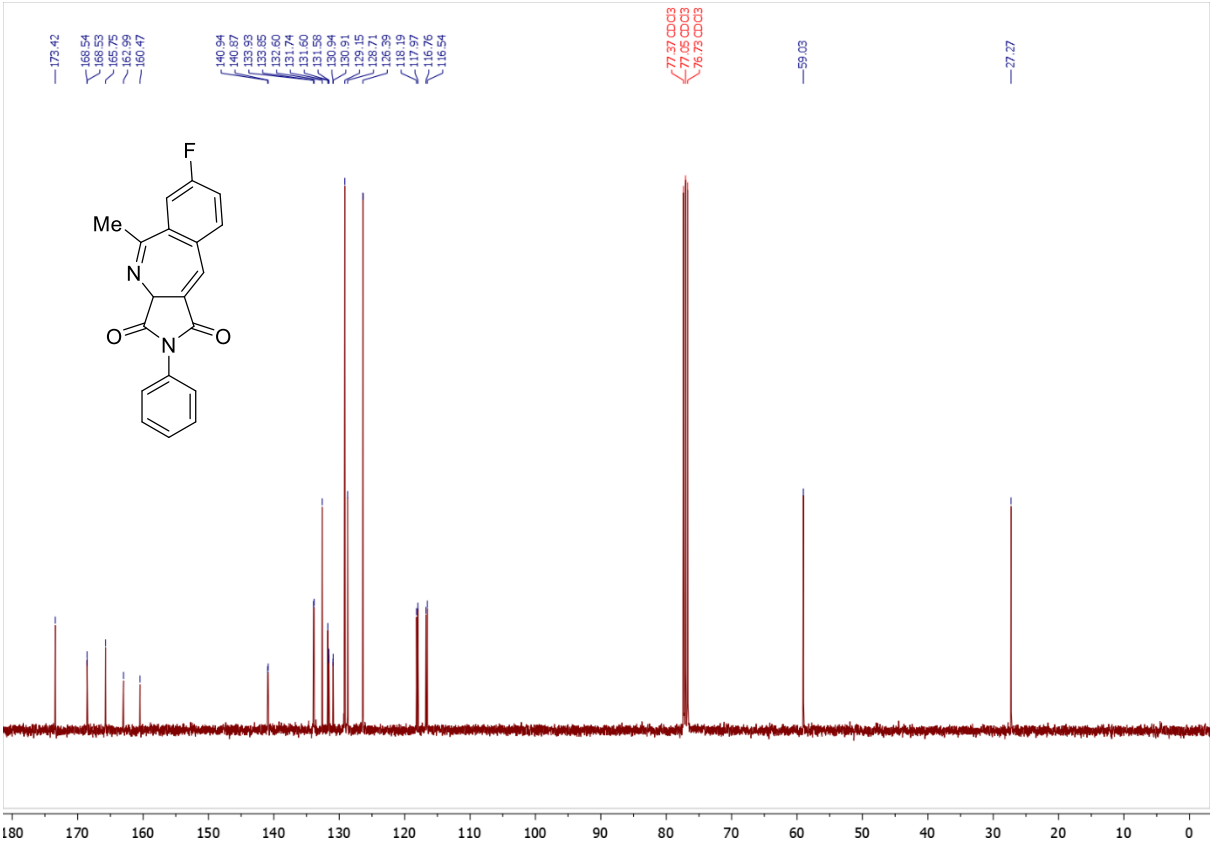

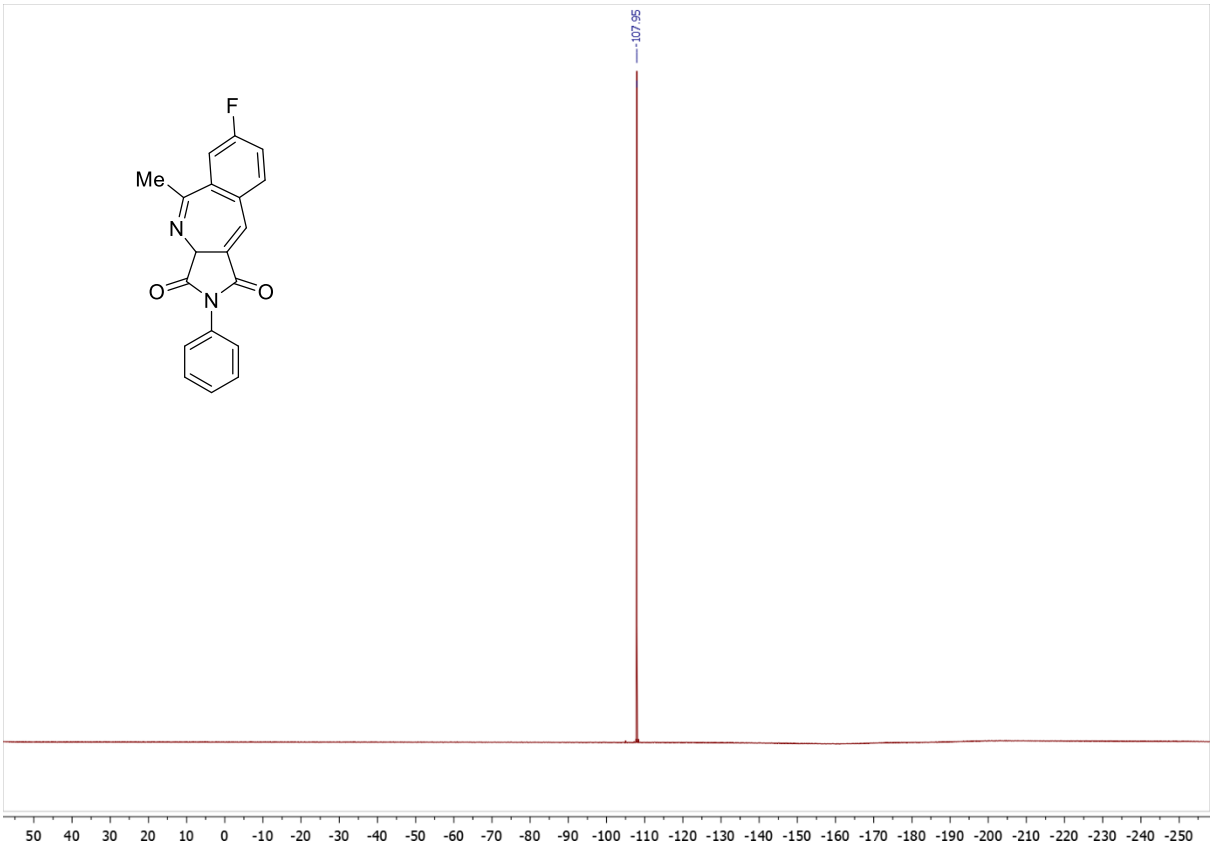
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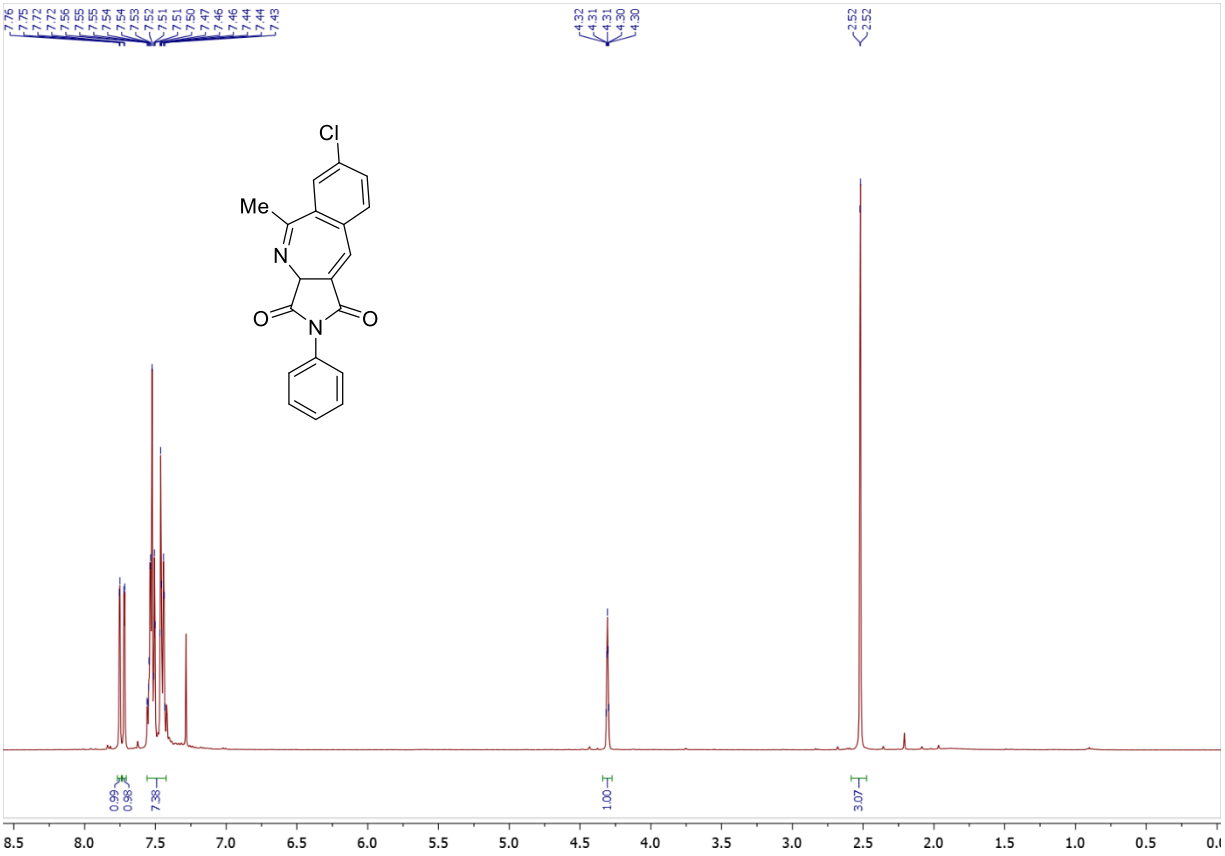
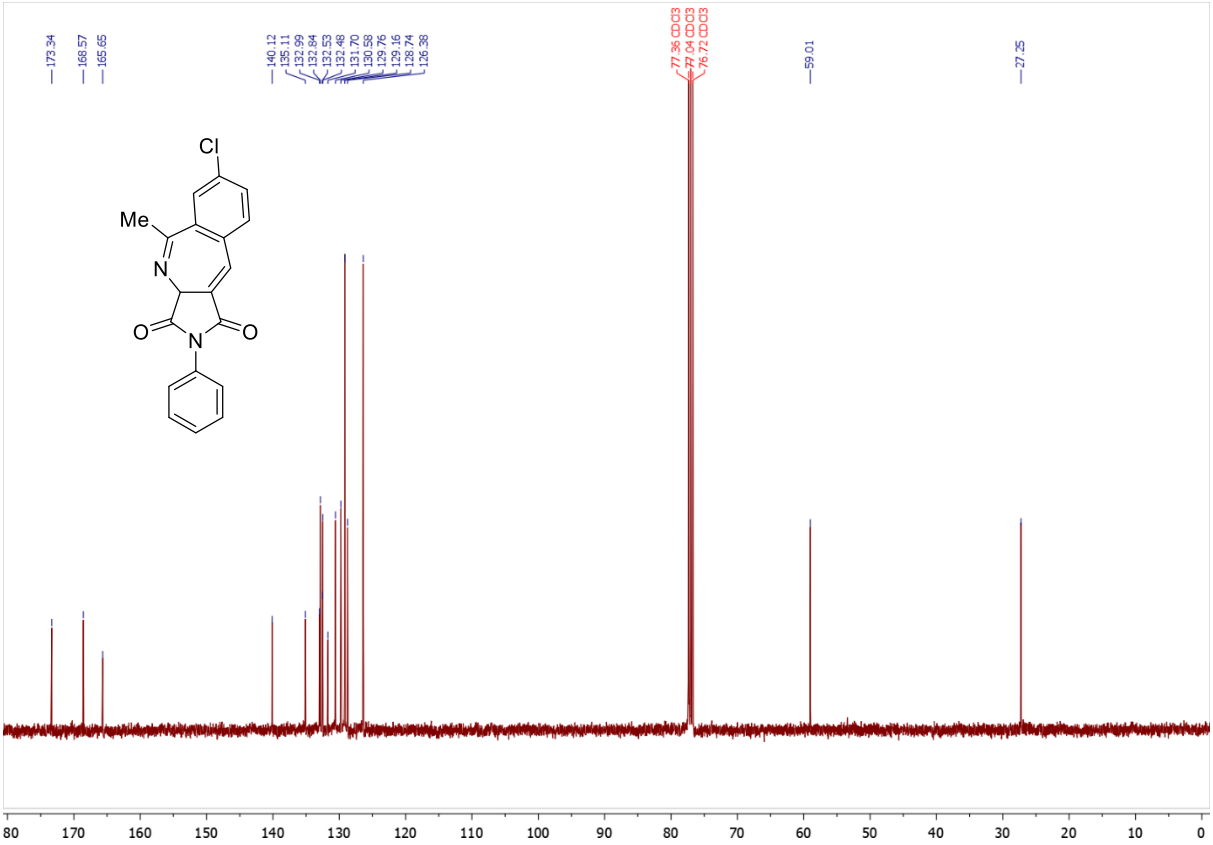
7-chloro-5-methyl-2-phenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7h)





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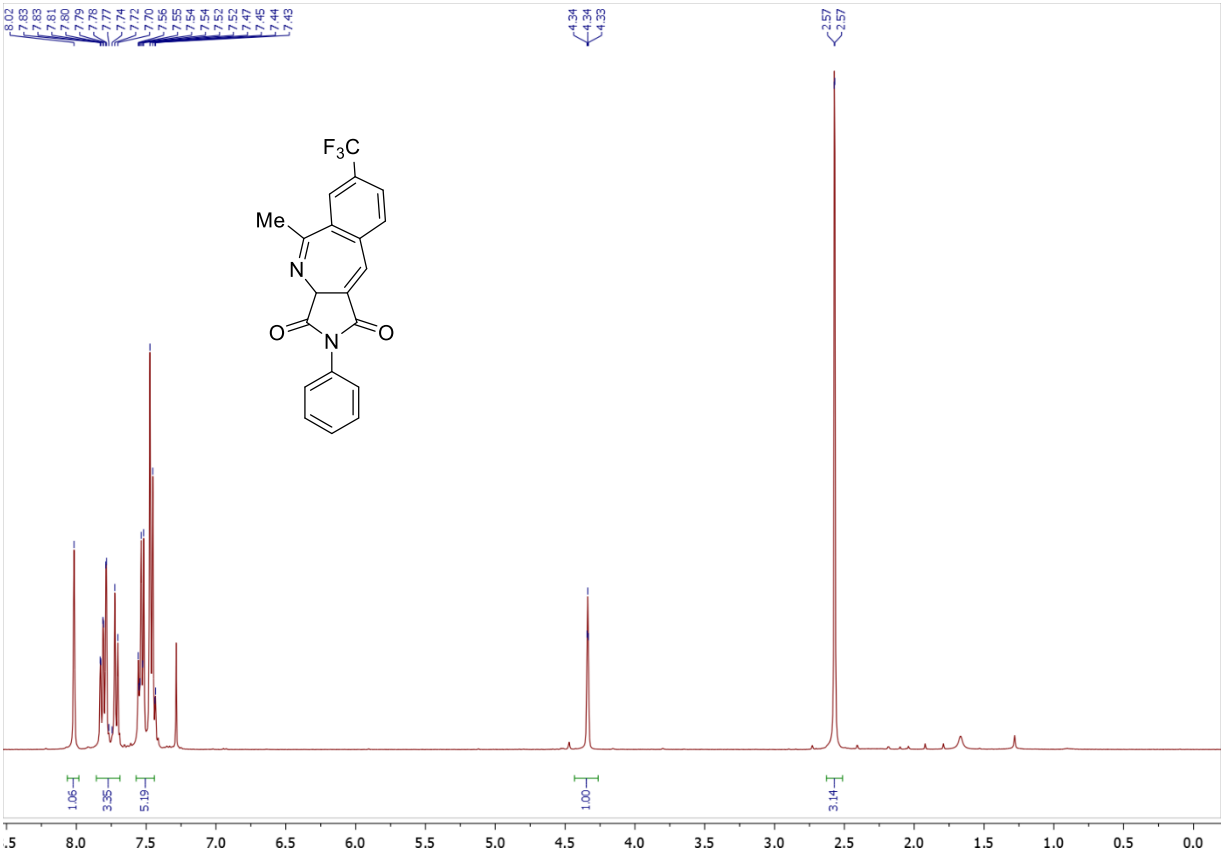

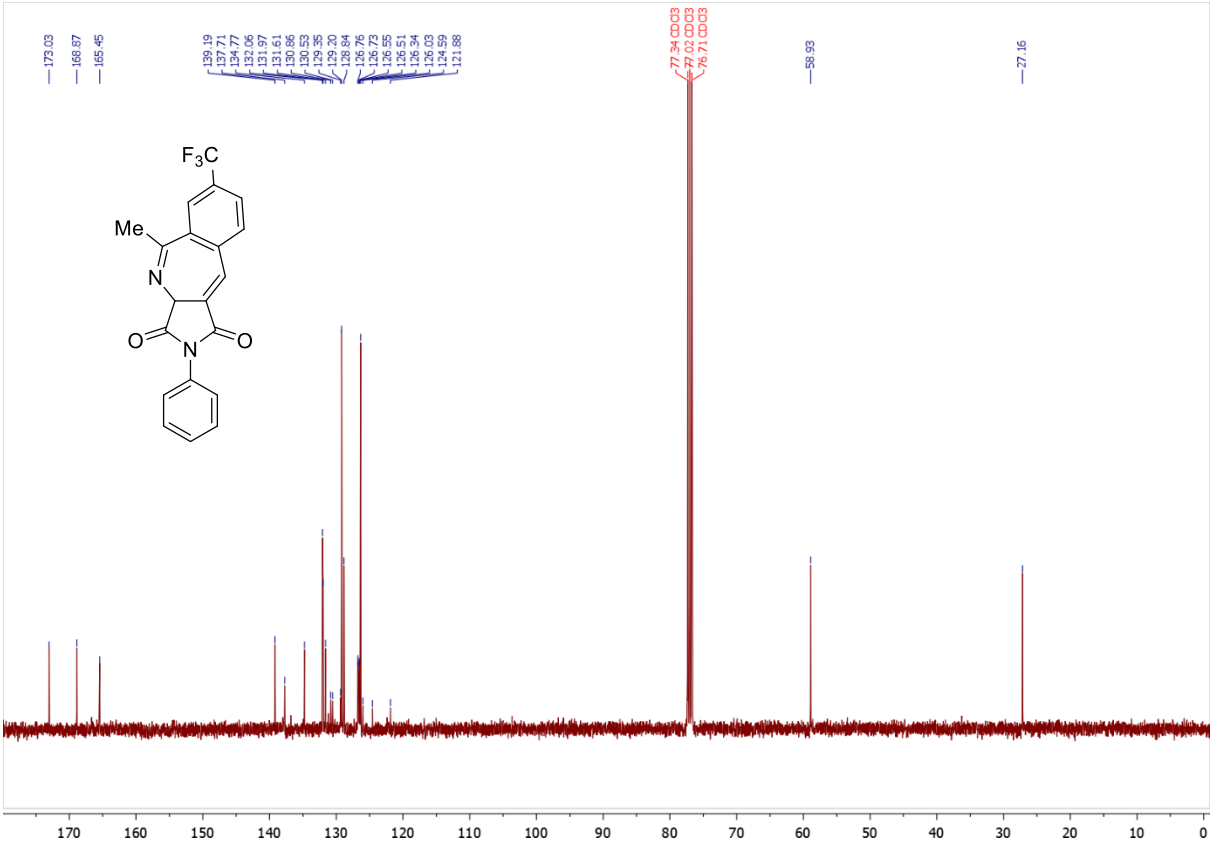

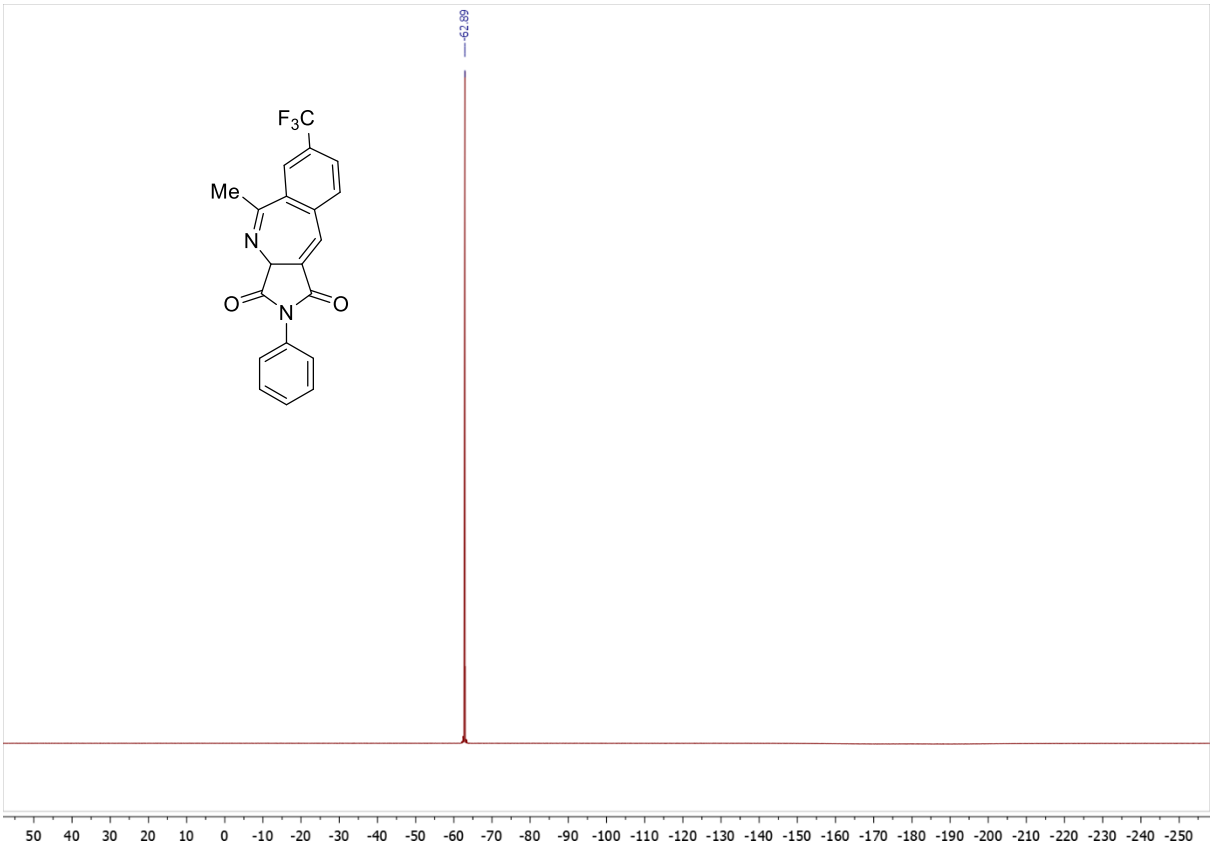
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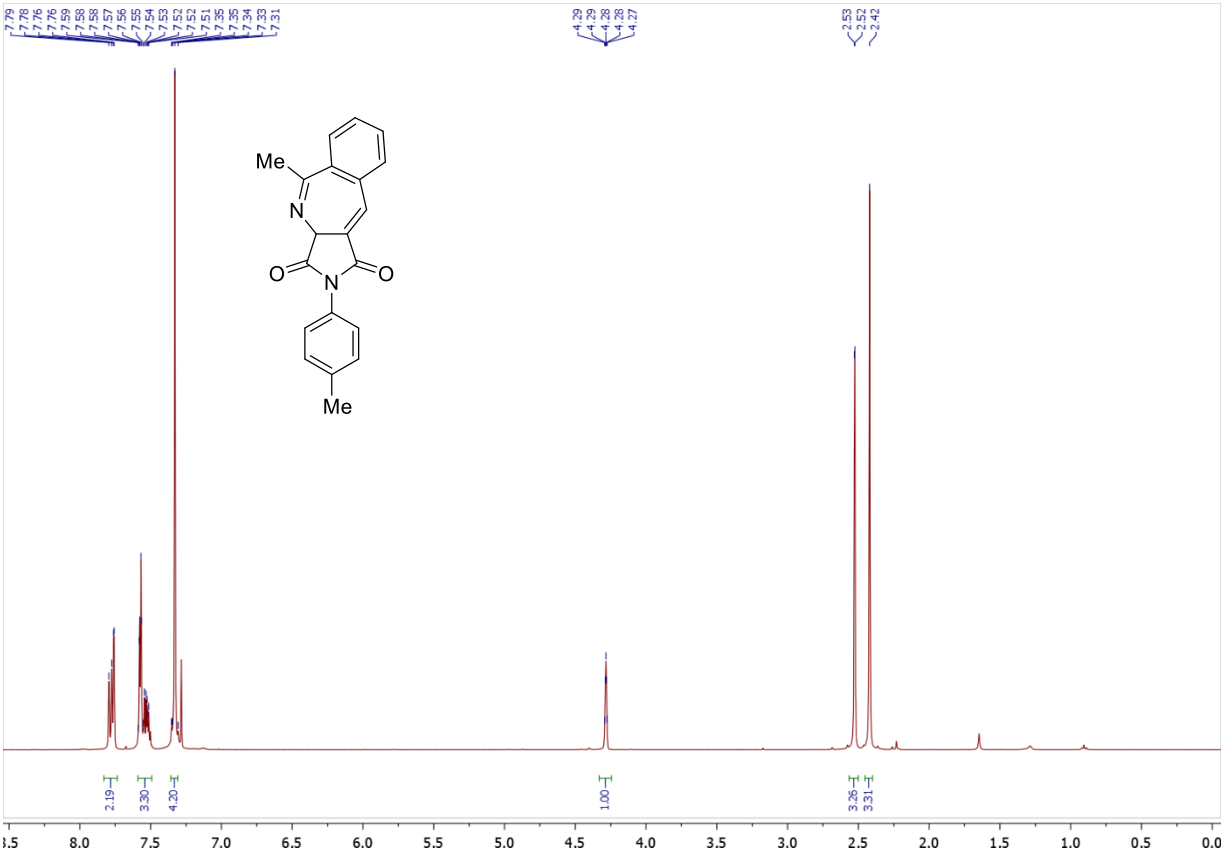
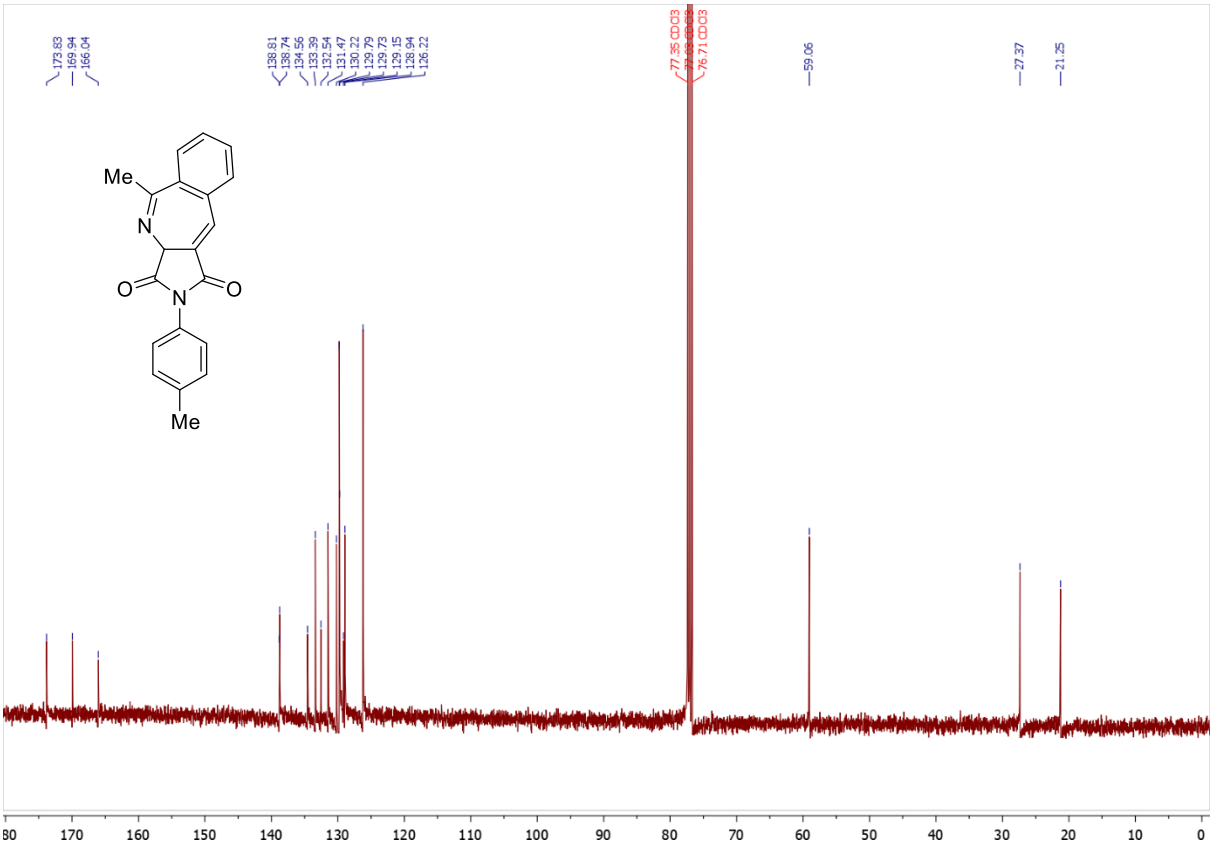
5-methyl-2-(p-tolyl)benzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7j)





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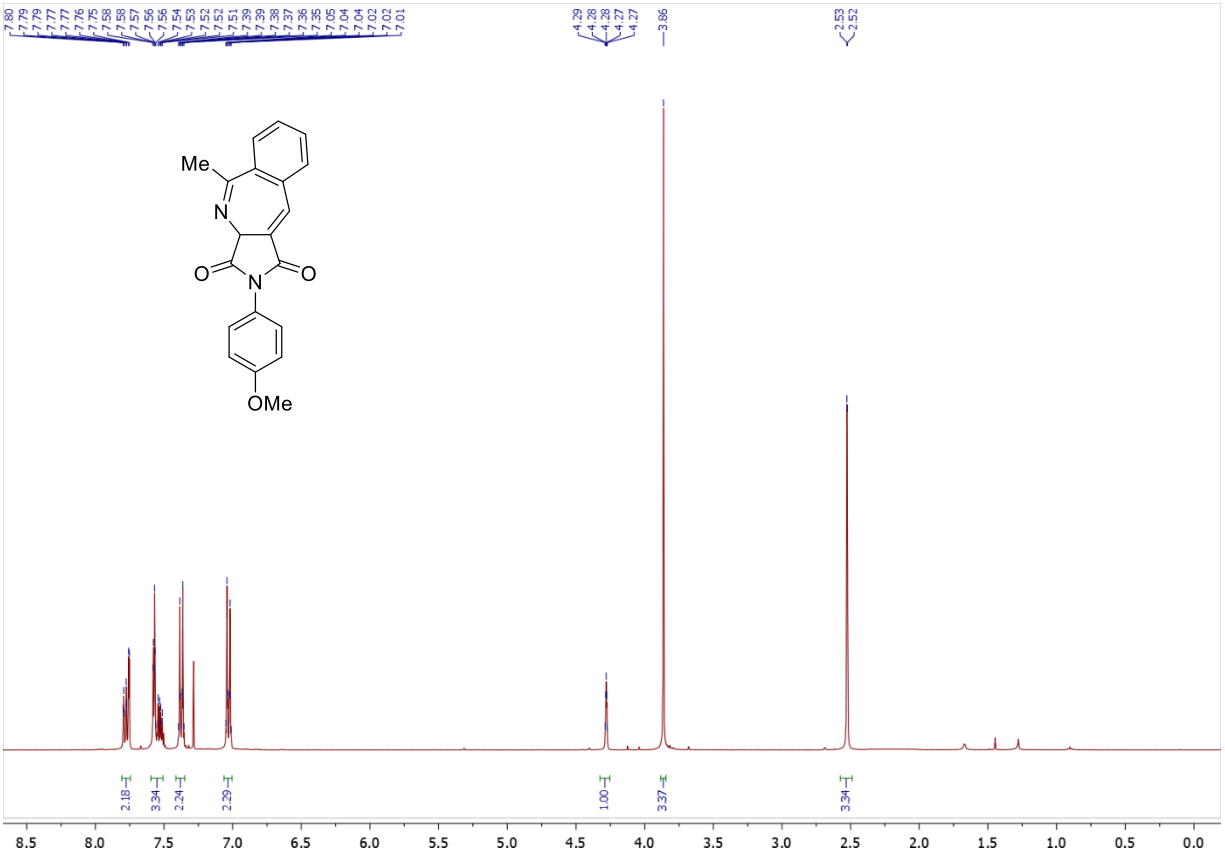
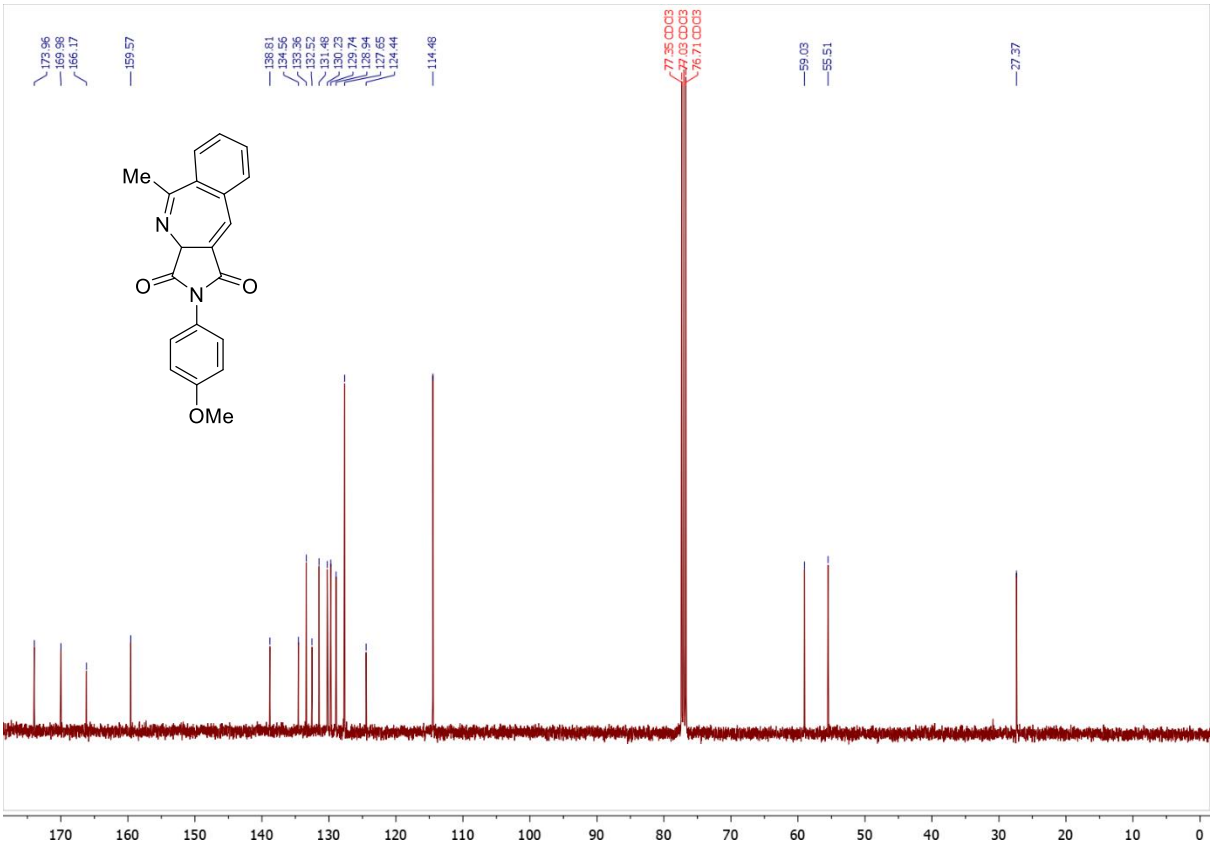
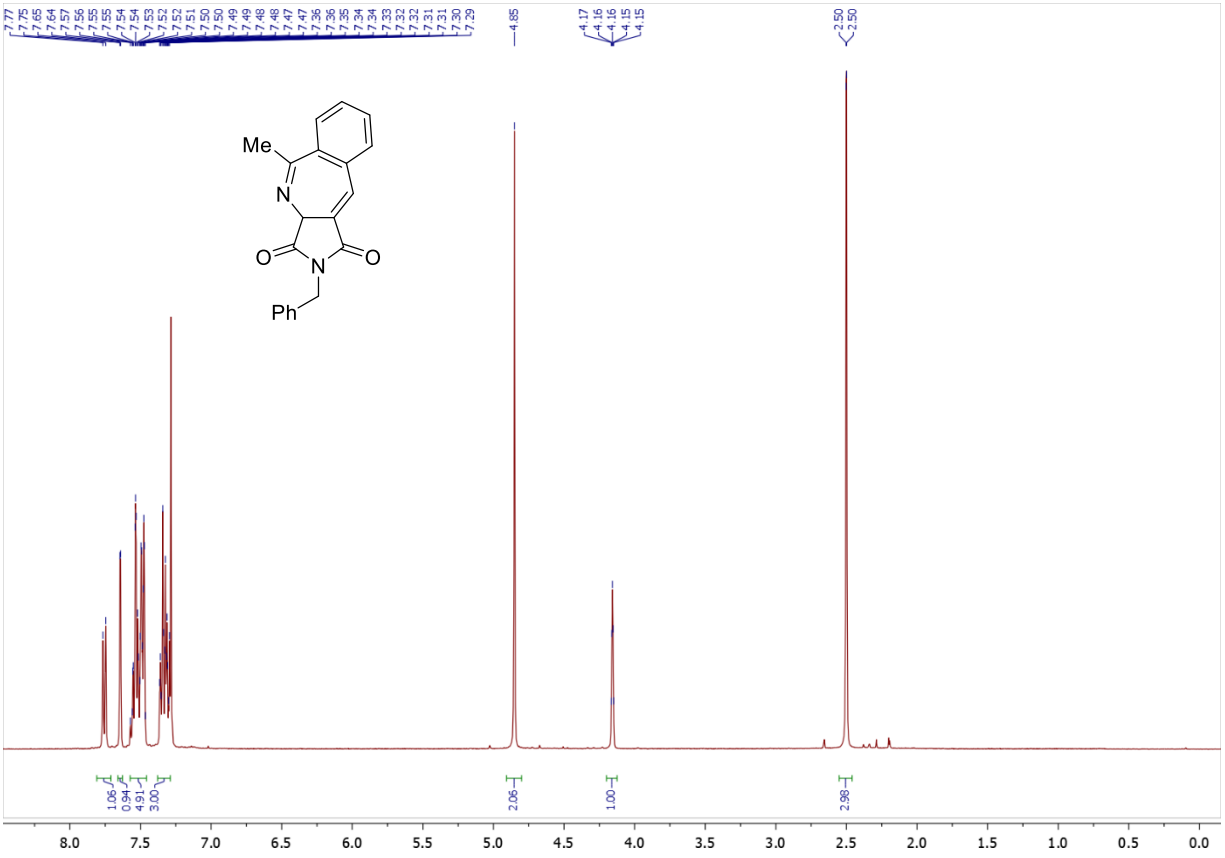
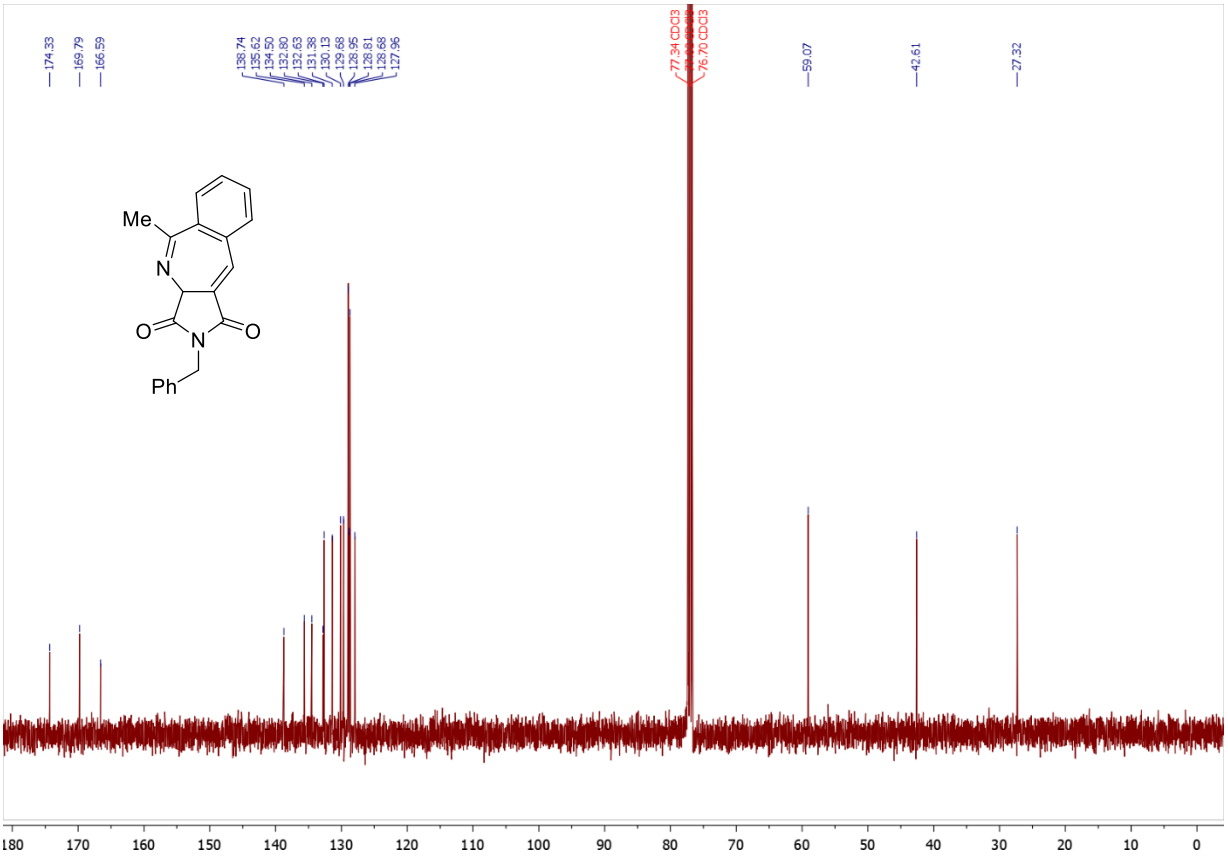


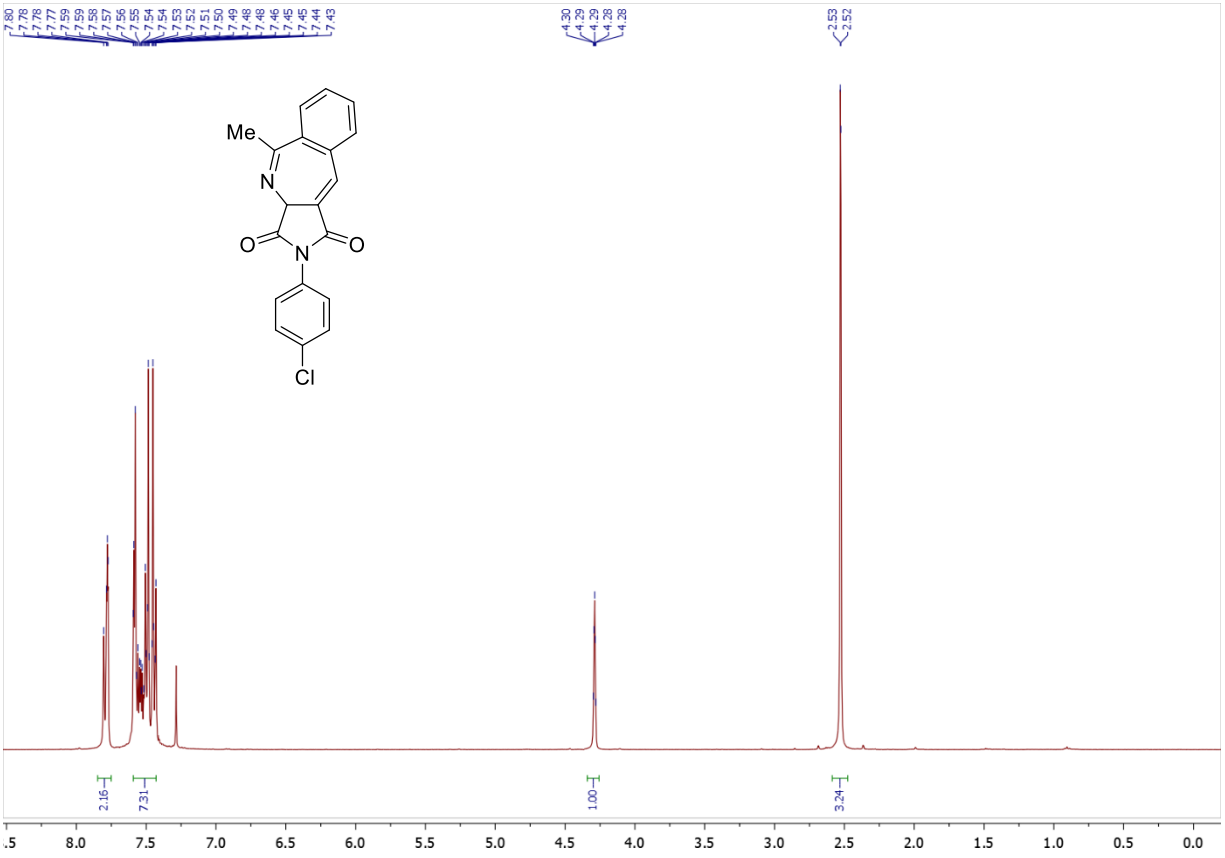


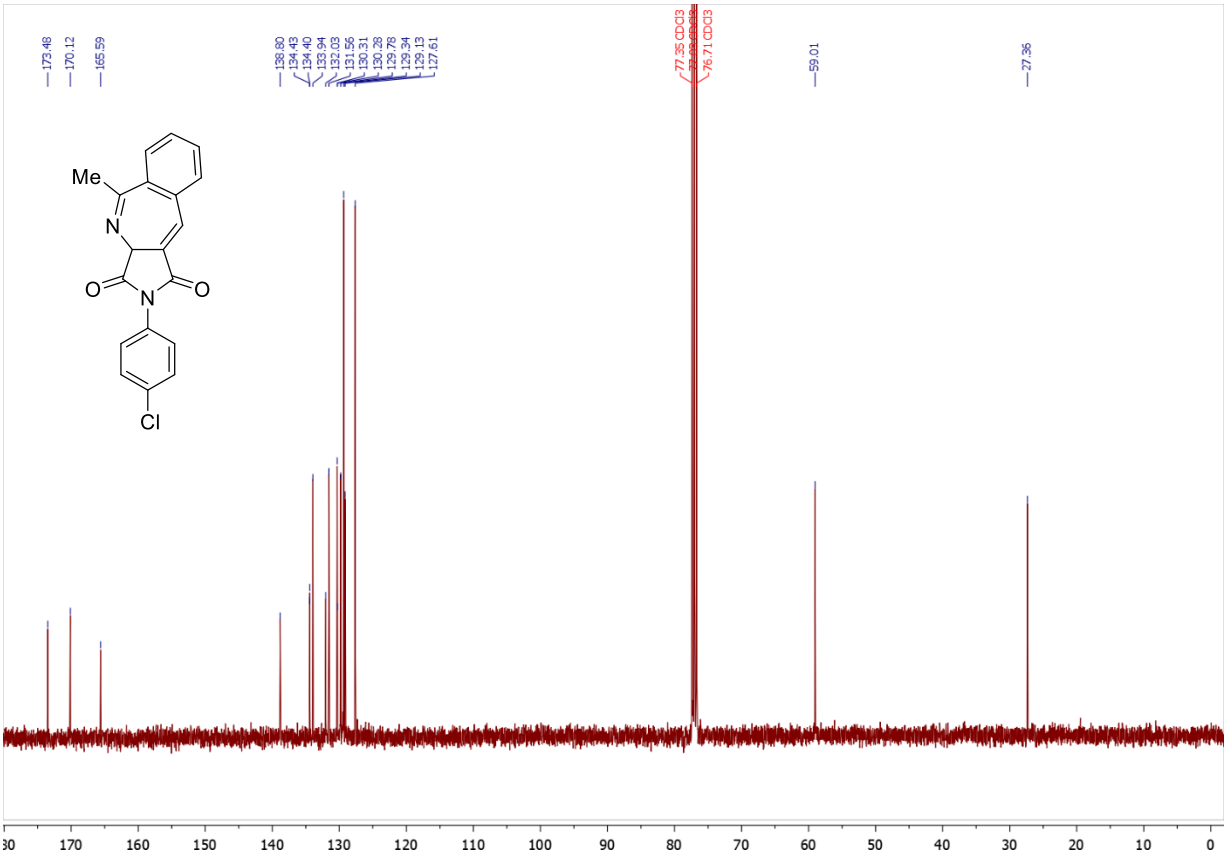
2-benzyl-5-methylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7l)





2-(4-chlorophenyl)-5-methylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7m)





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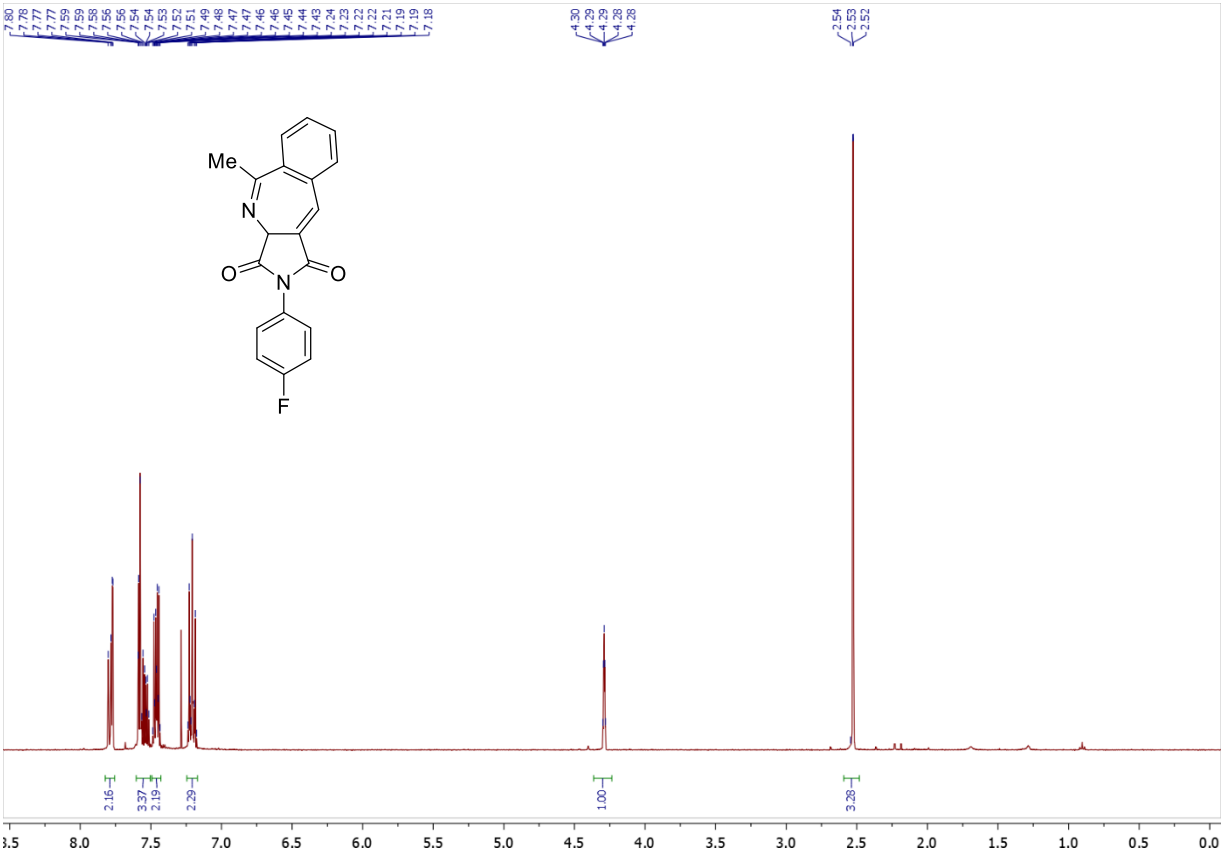

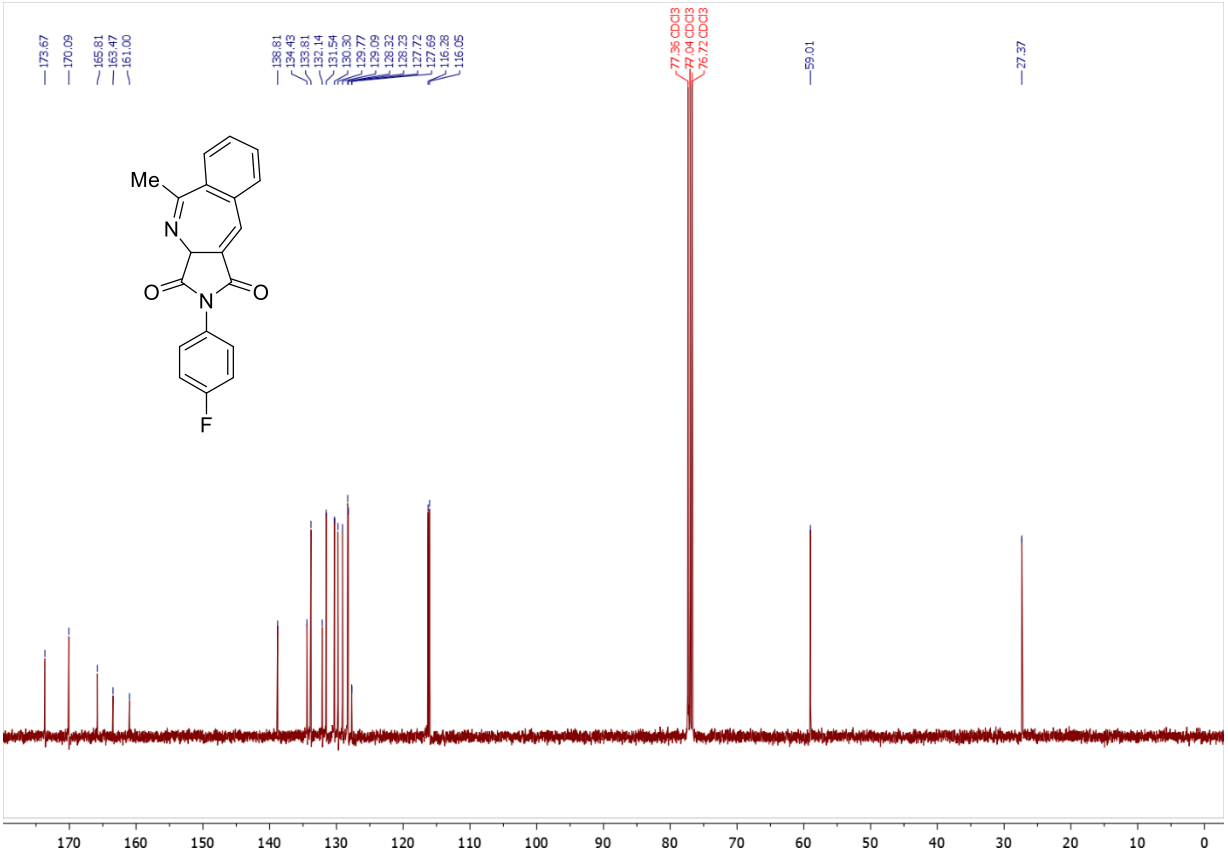

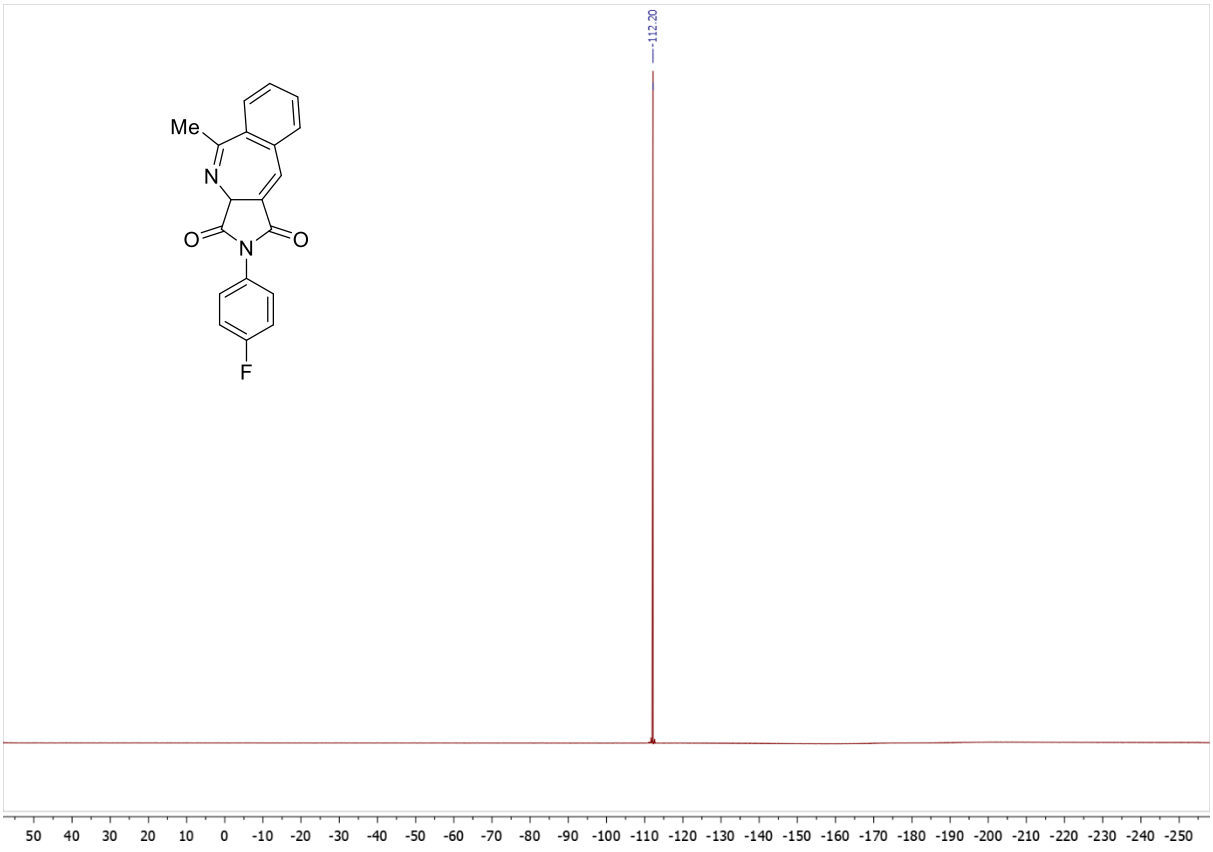
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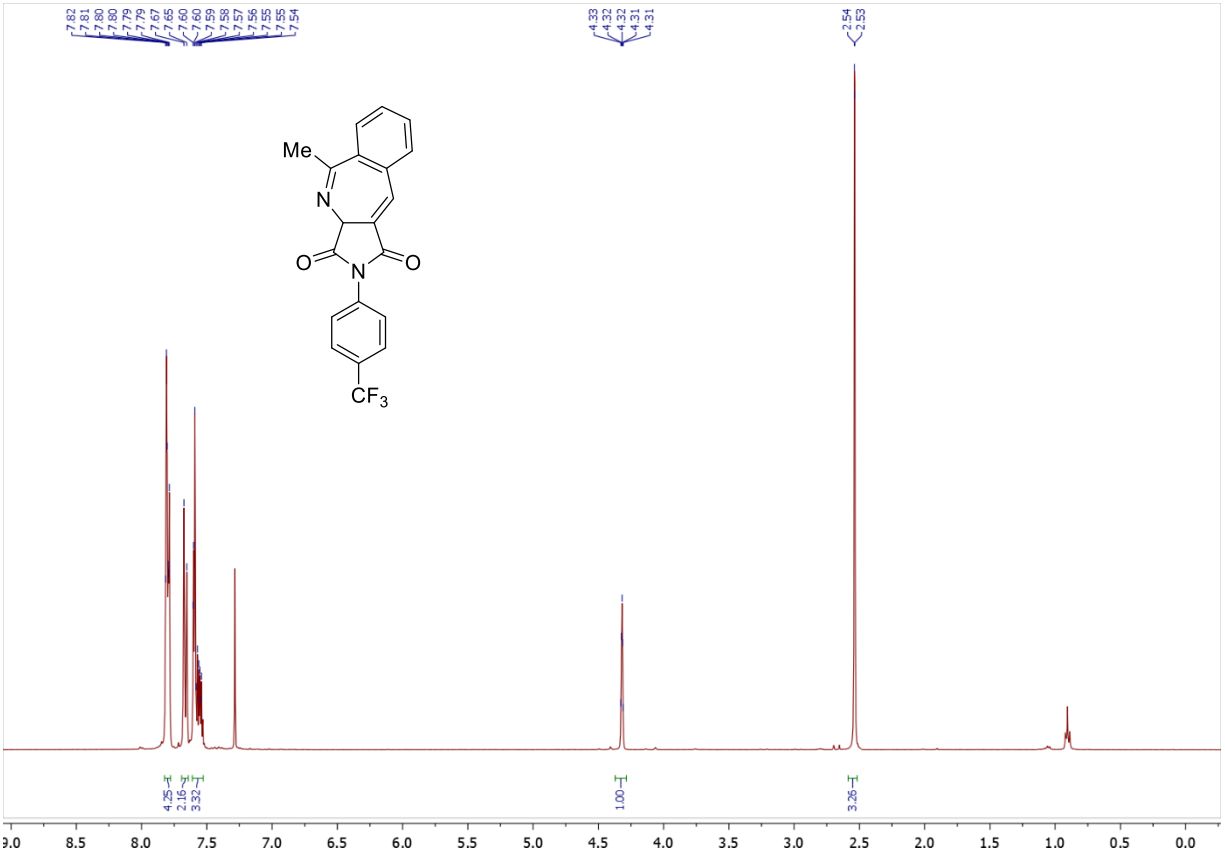

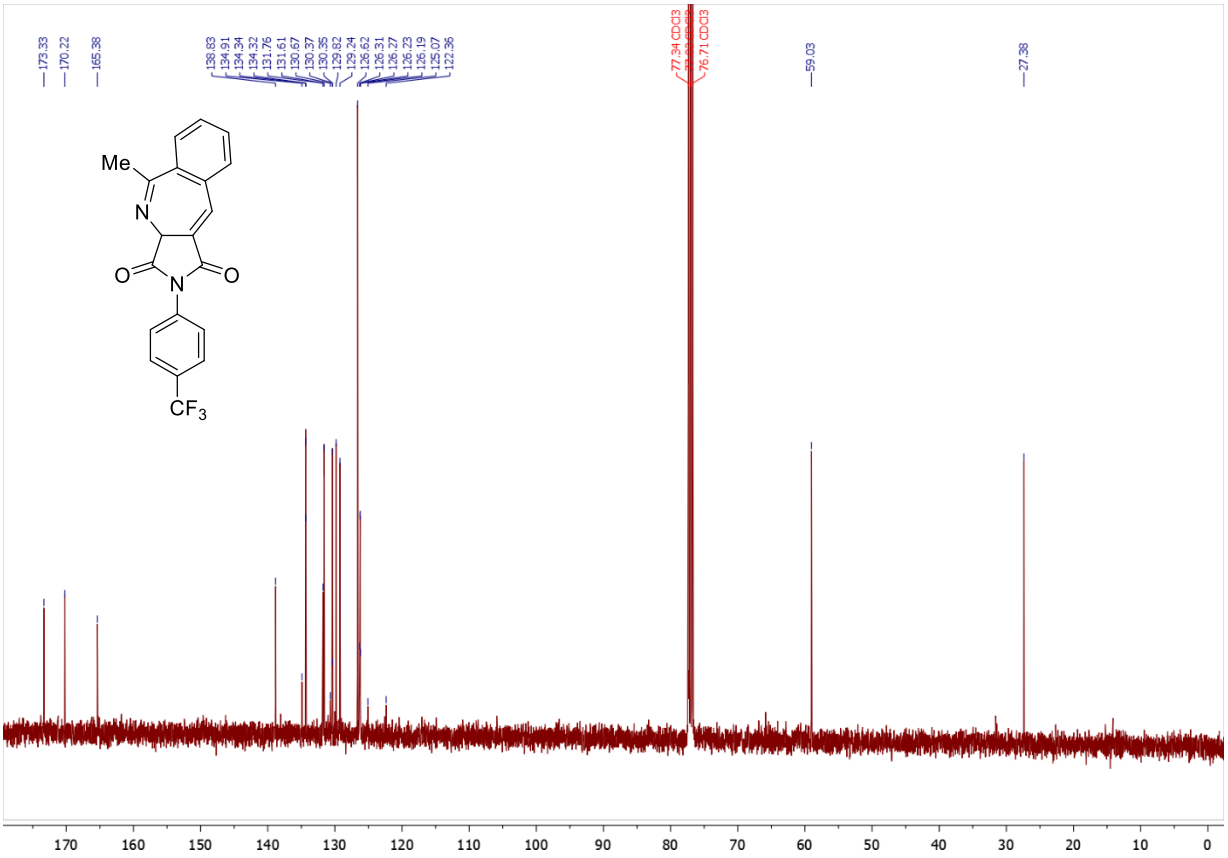

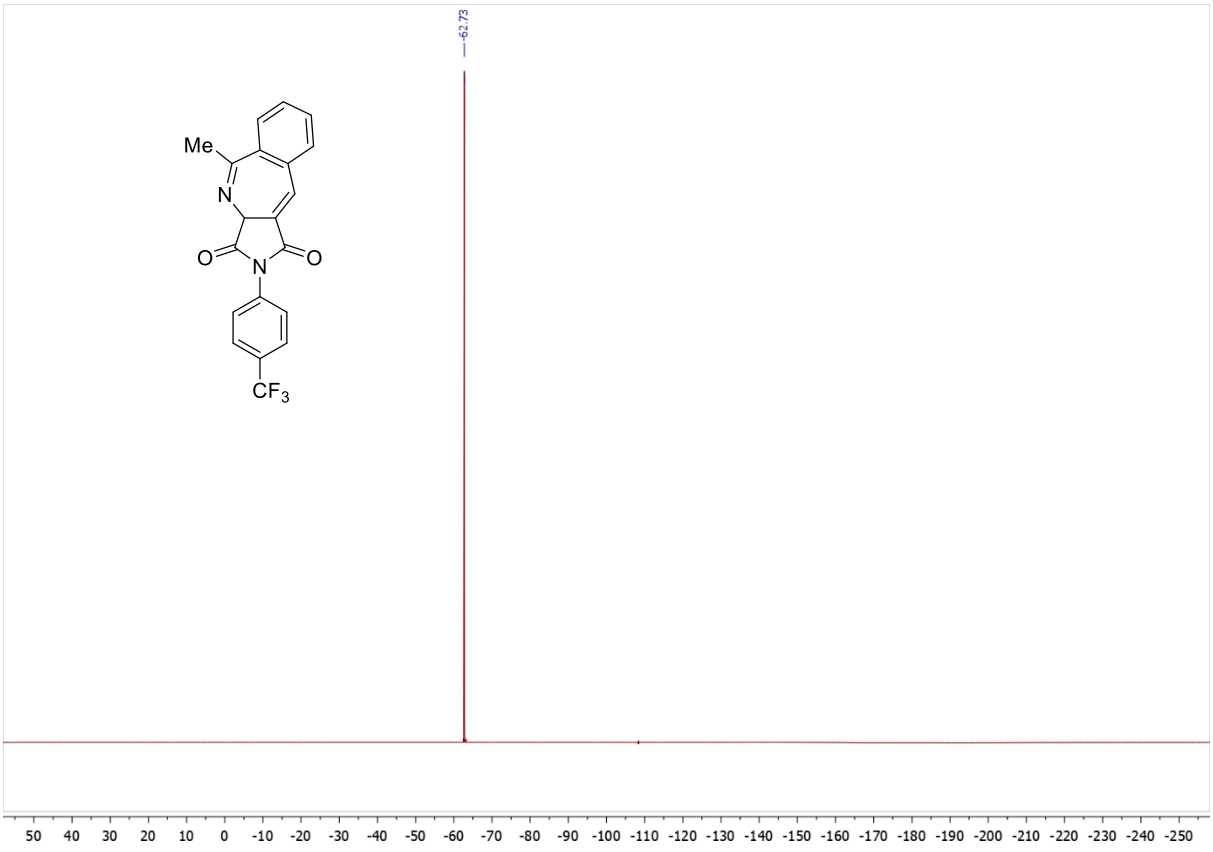
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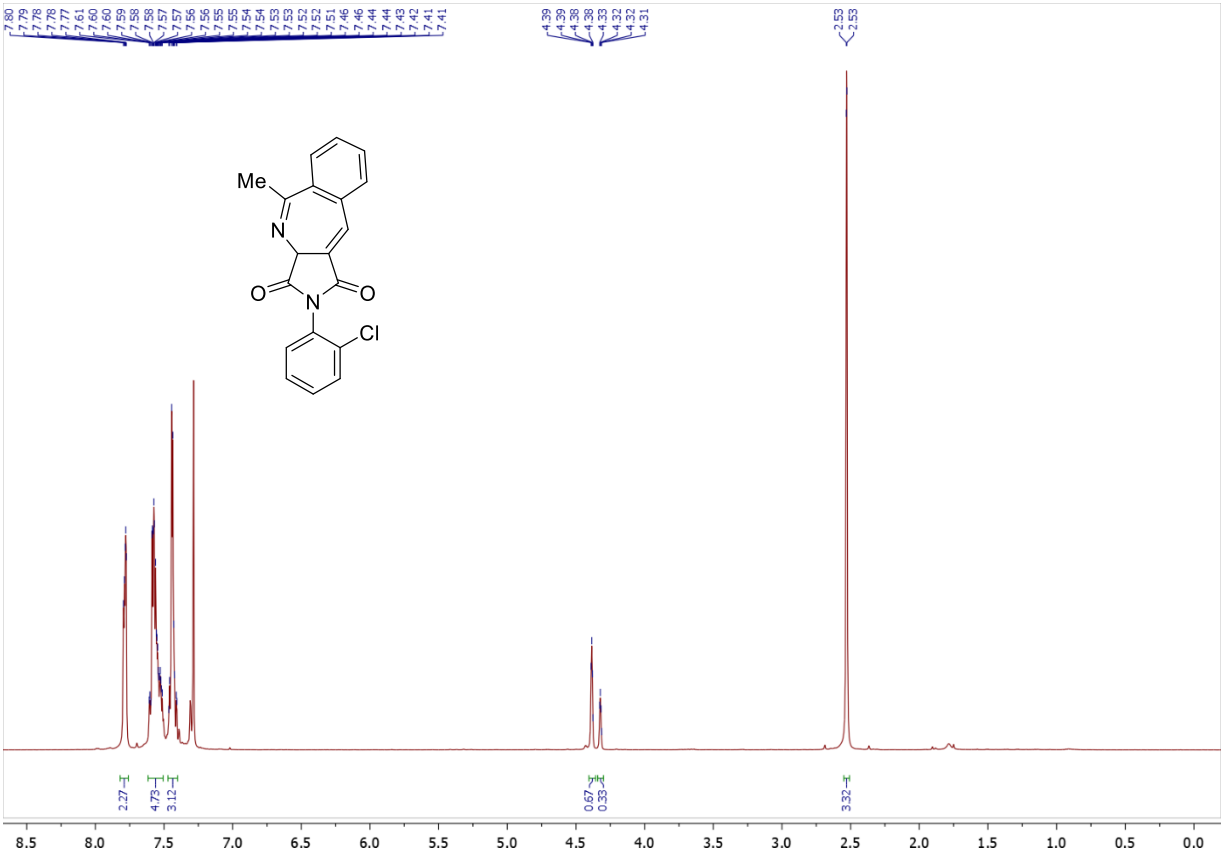
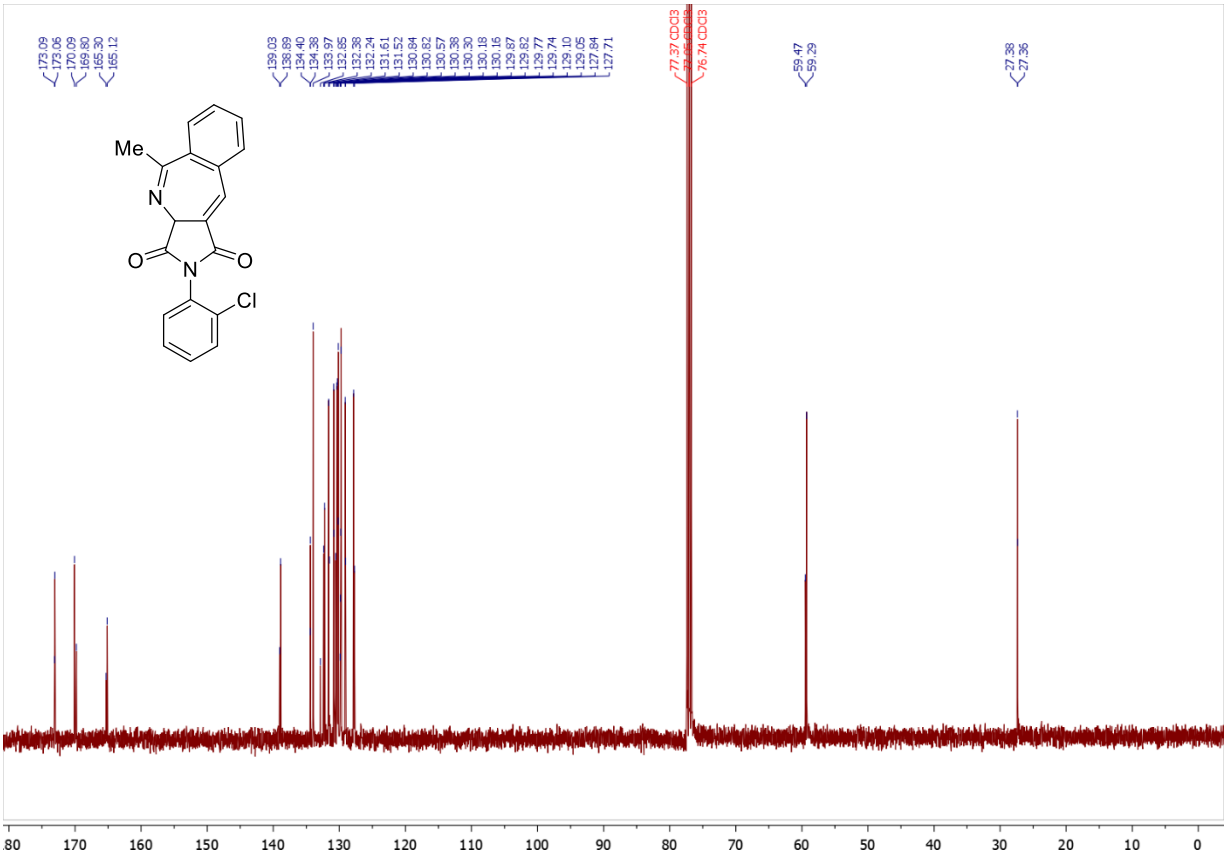
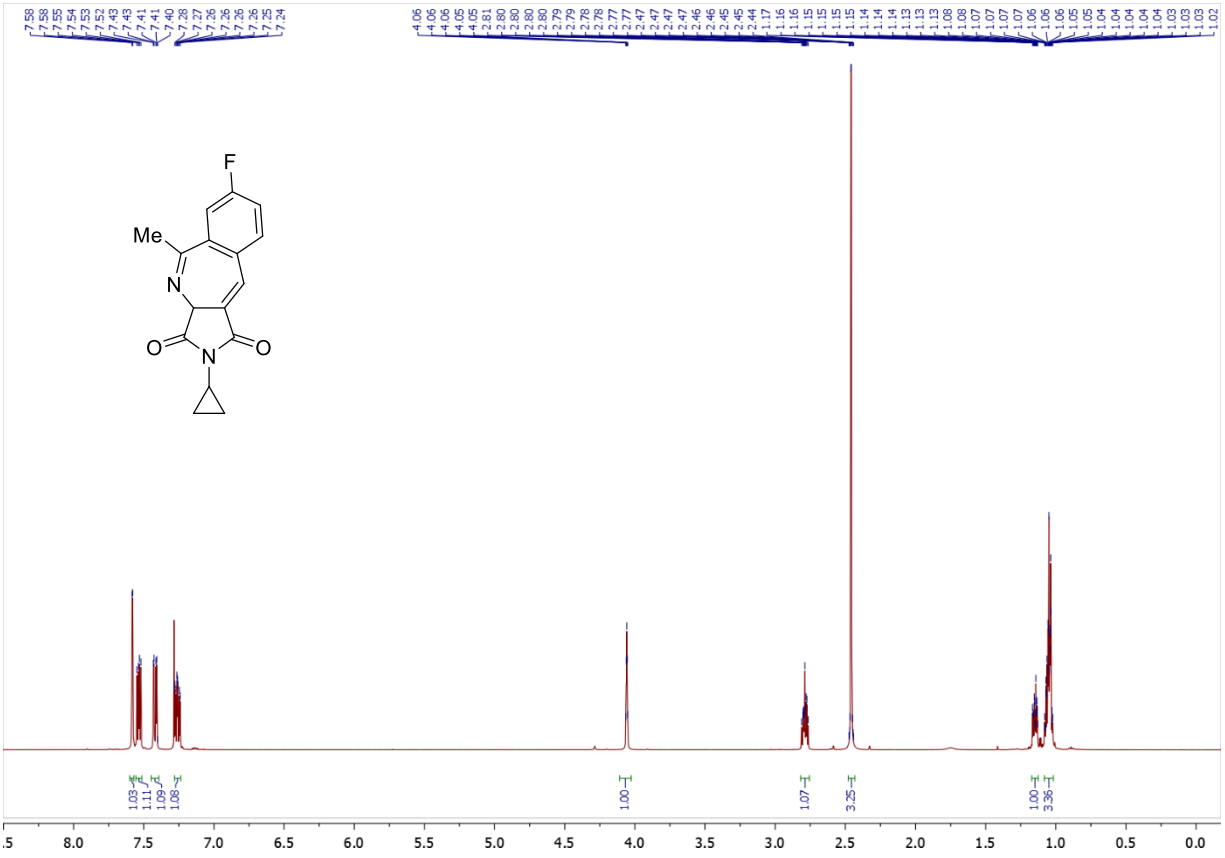
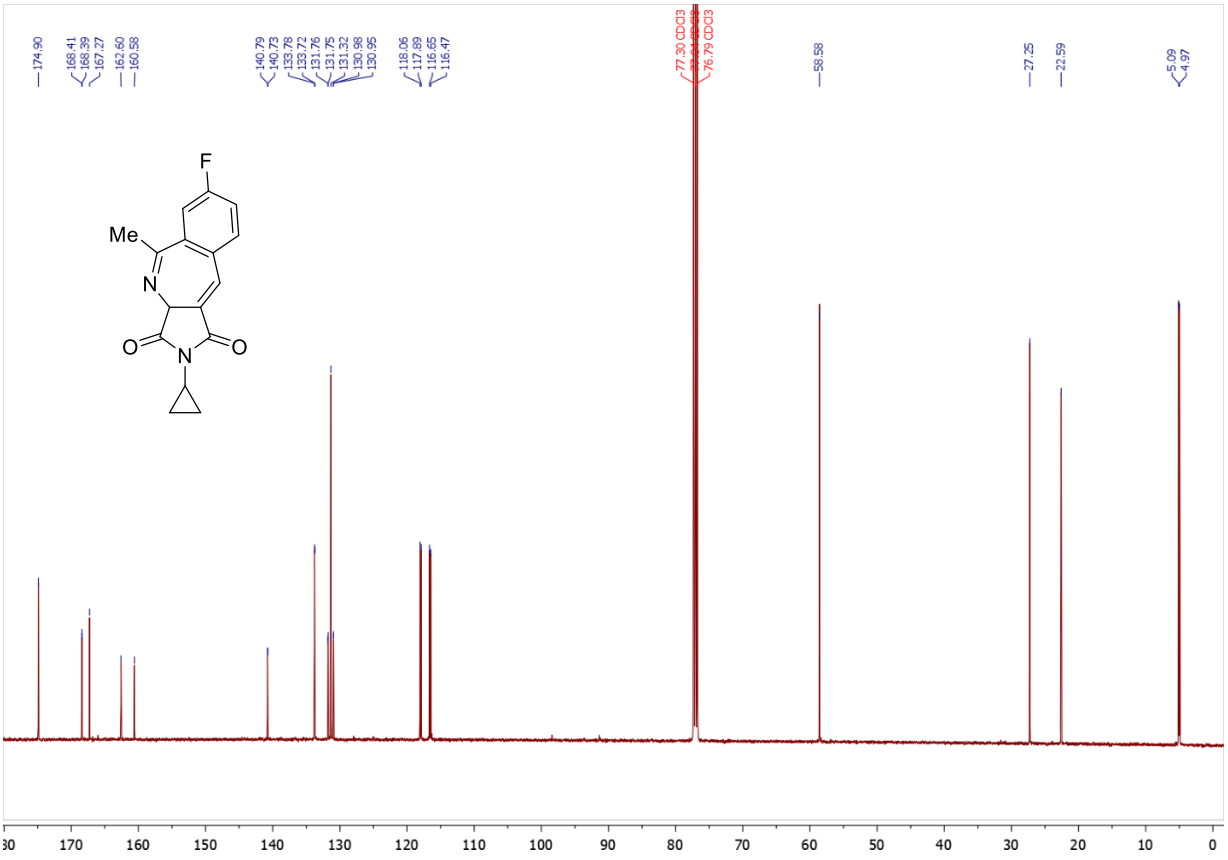
2-(2-chlorophenyl)-5-methylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7p)

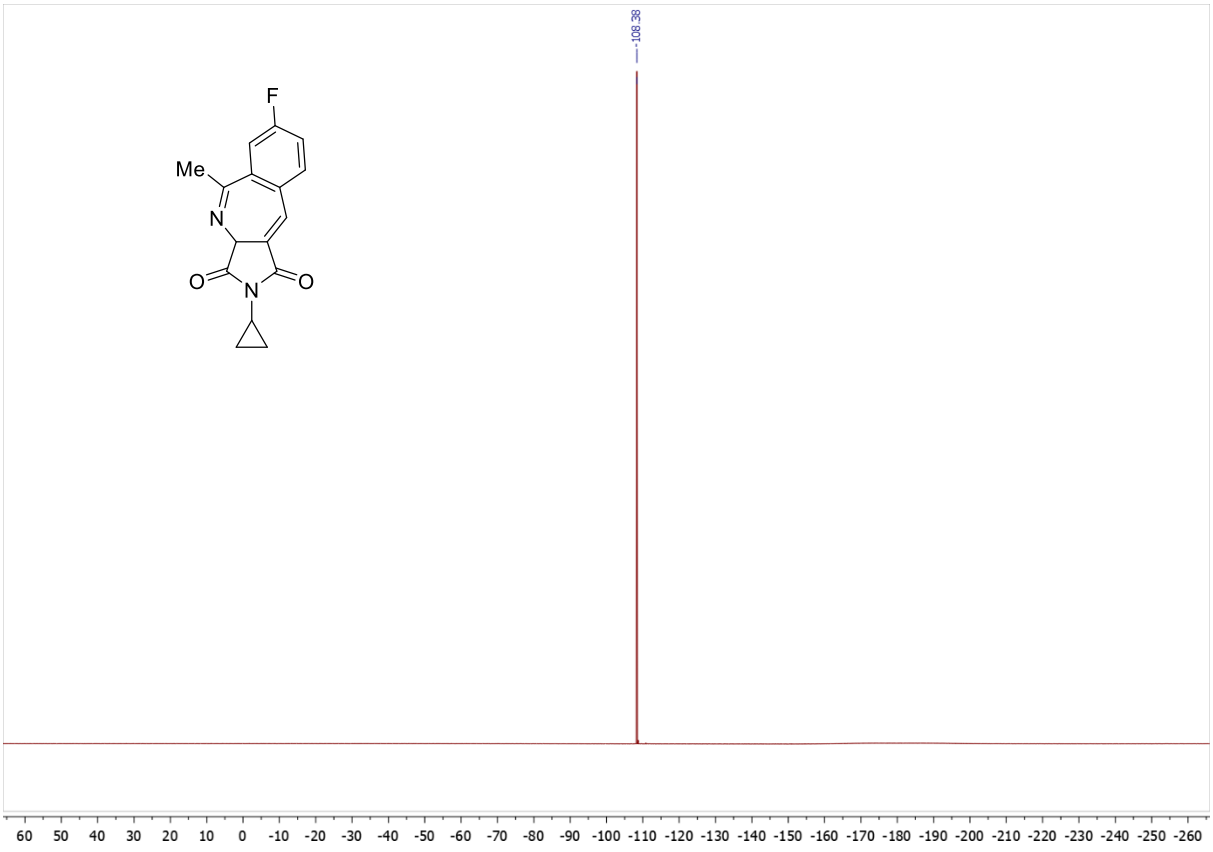




2-cyclopropyl-7-fluoro-5-methylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7q)



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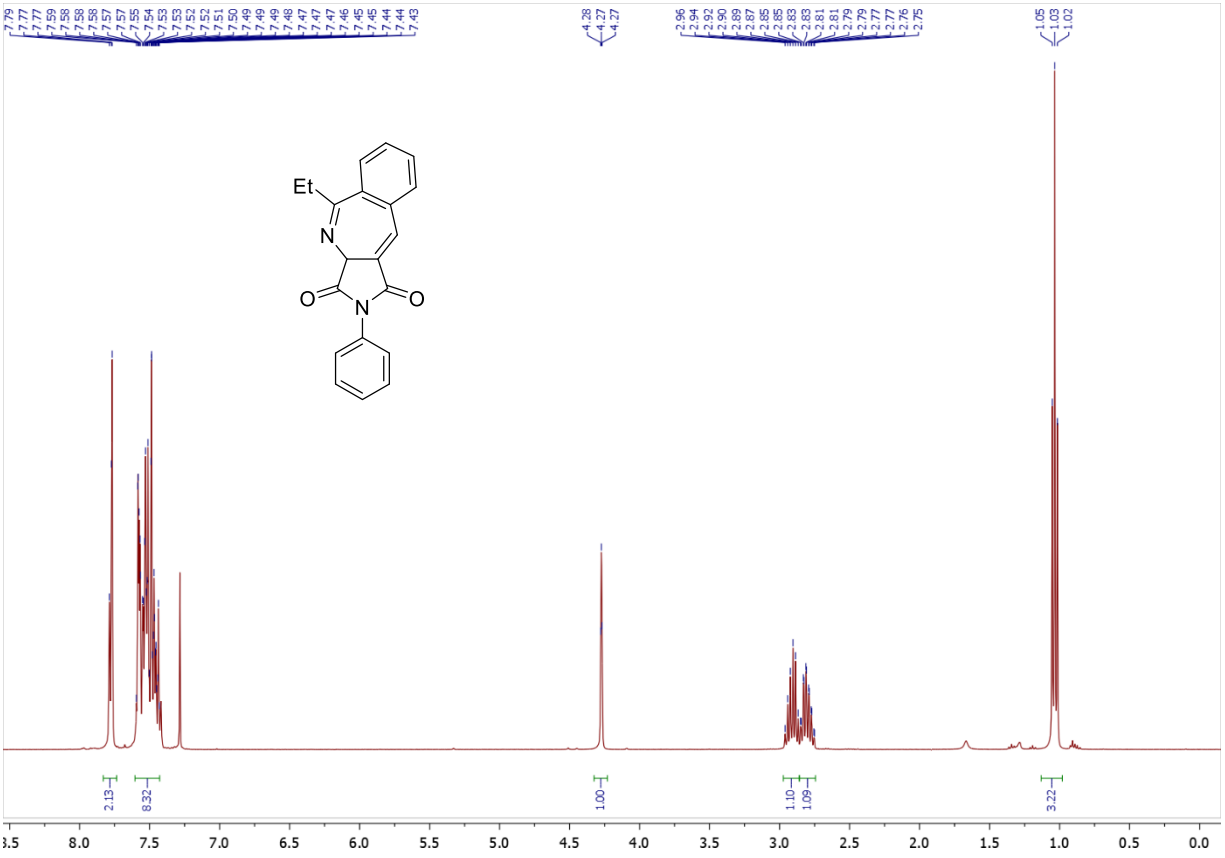
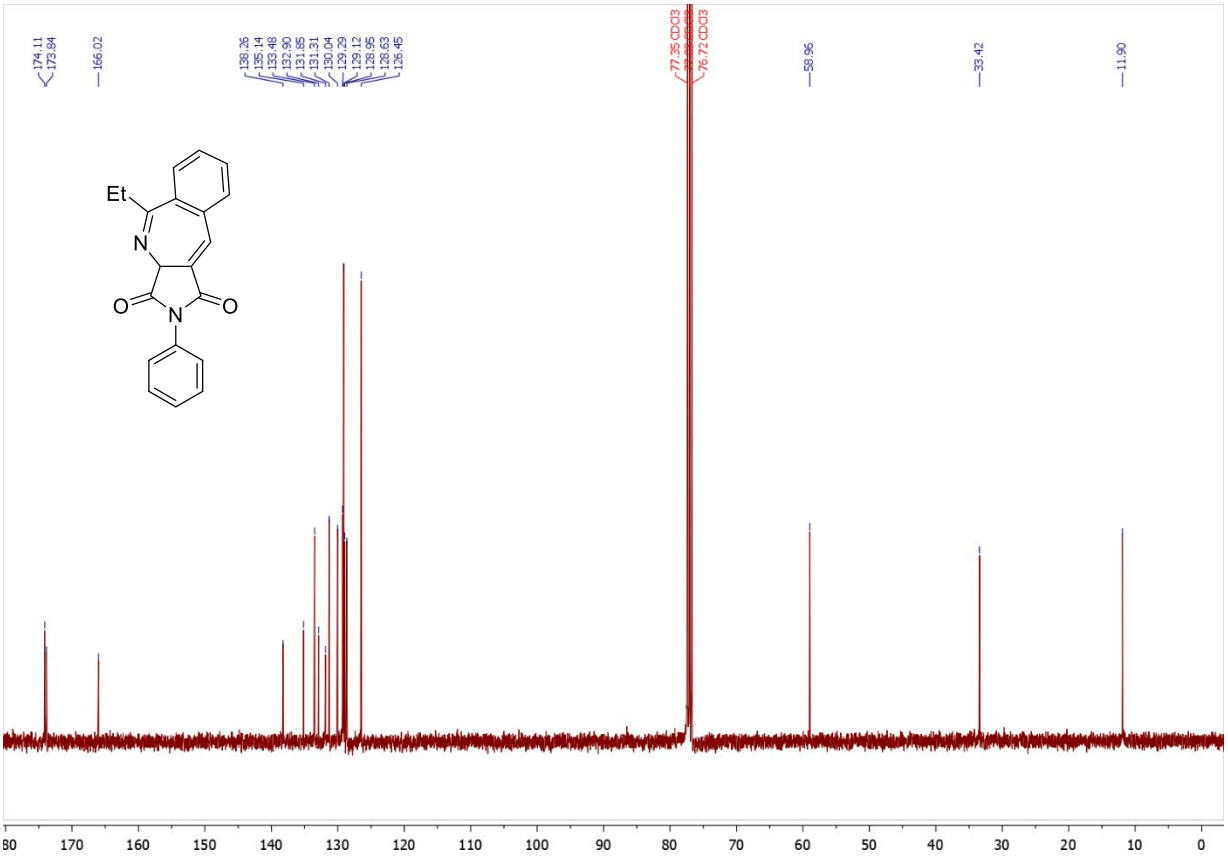
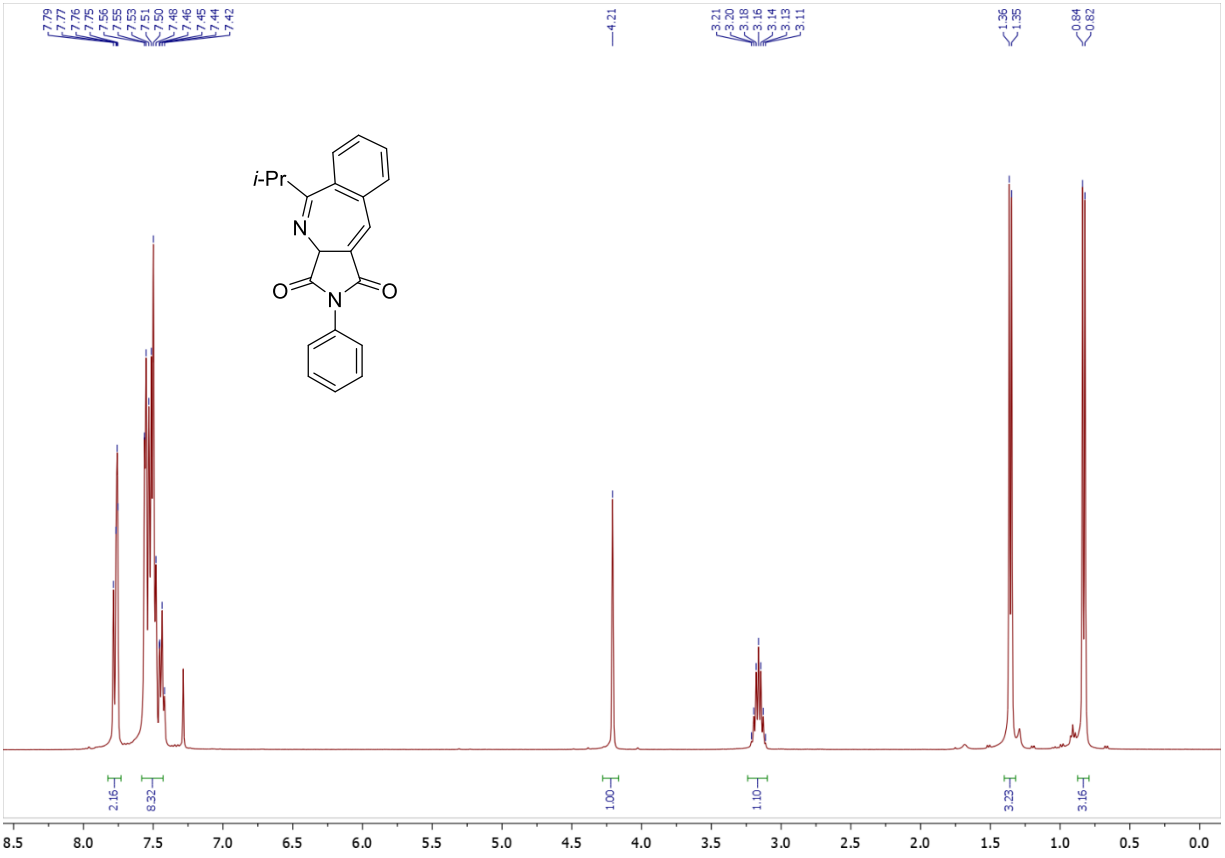
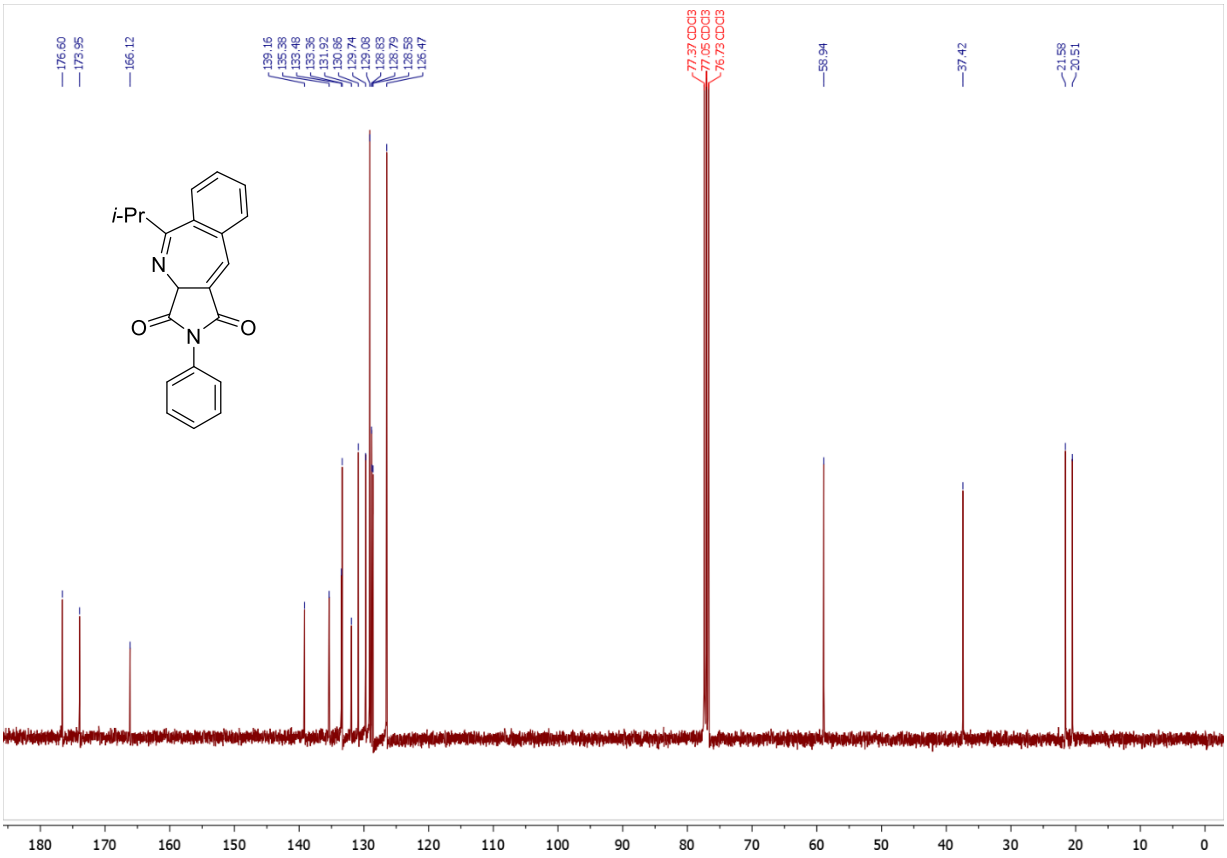
5-ethyl-2-phenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7r)





5-isopropyl-2-phenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7s)





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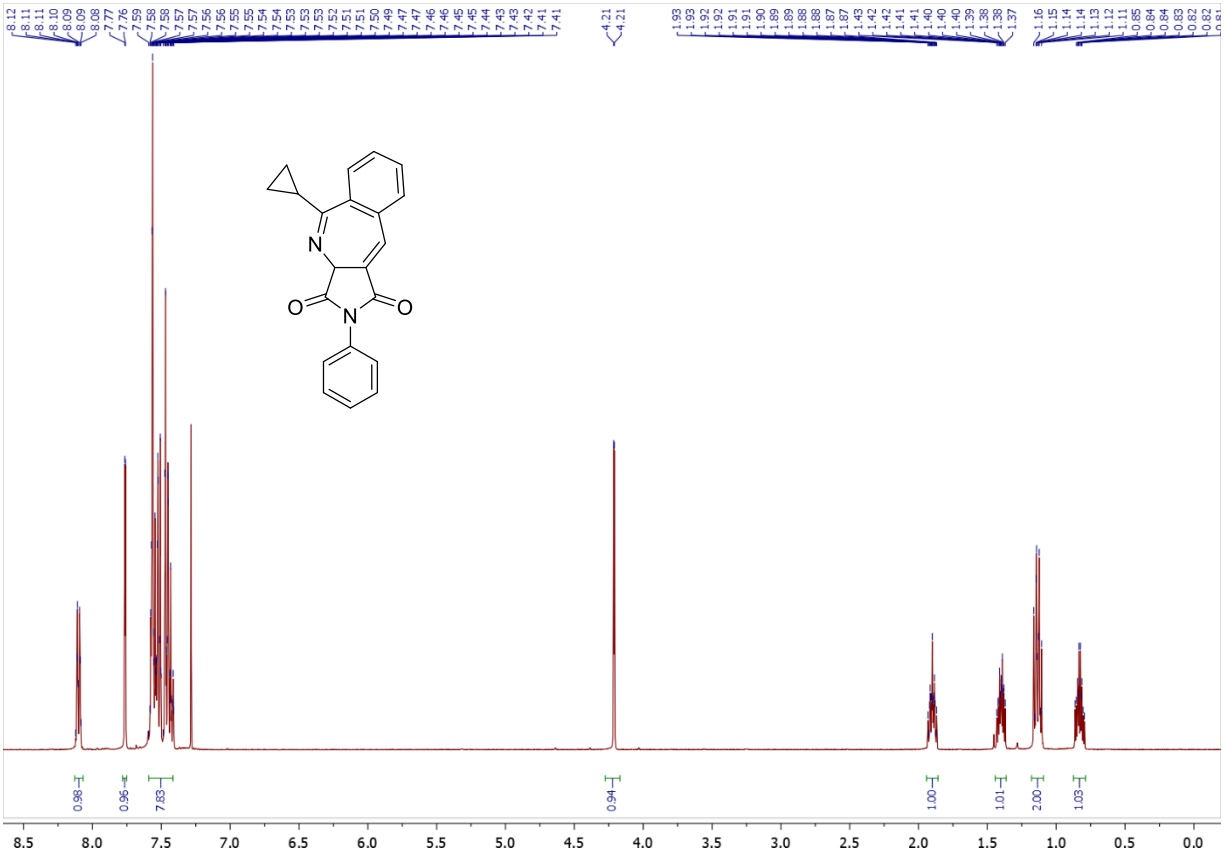
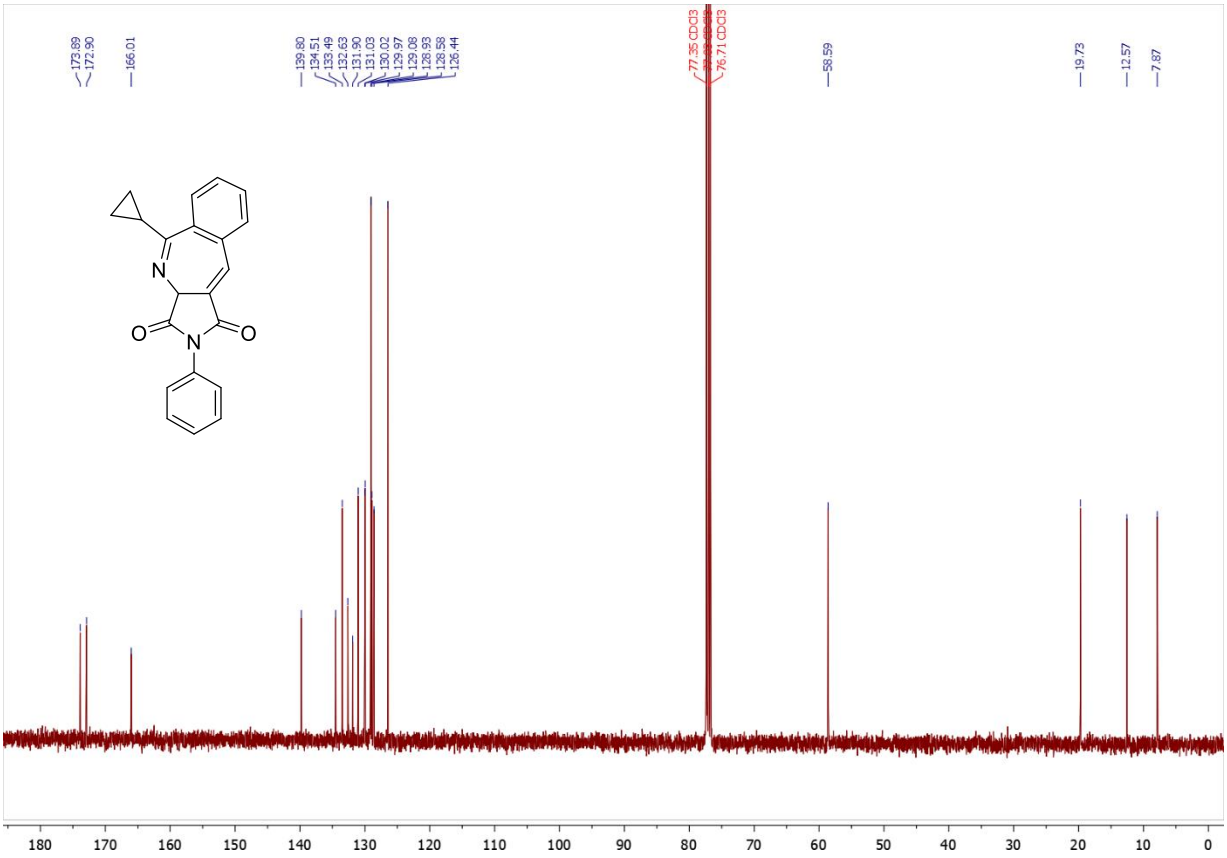
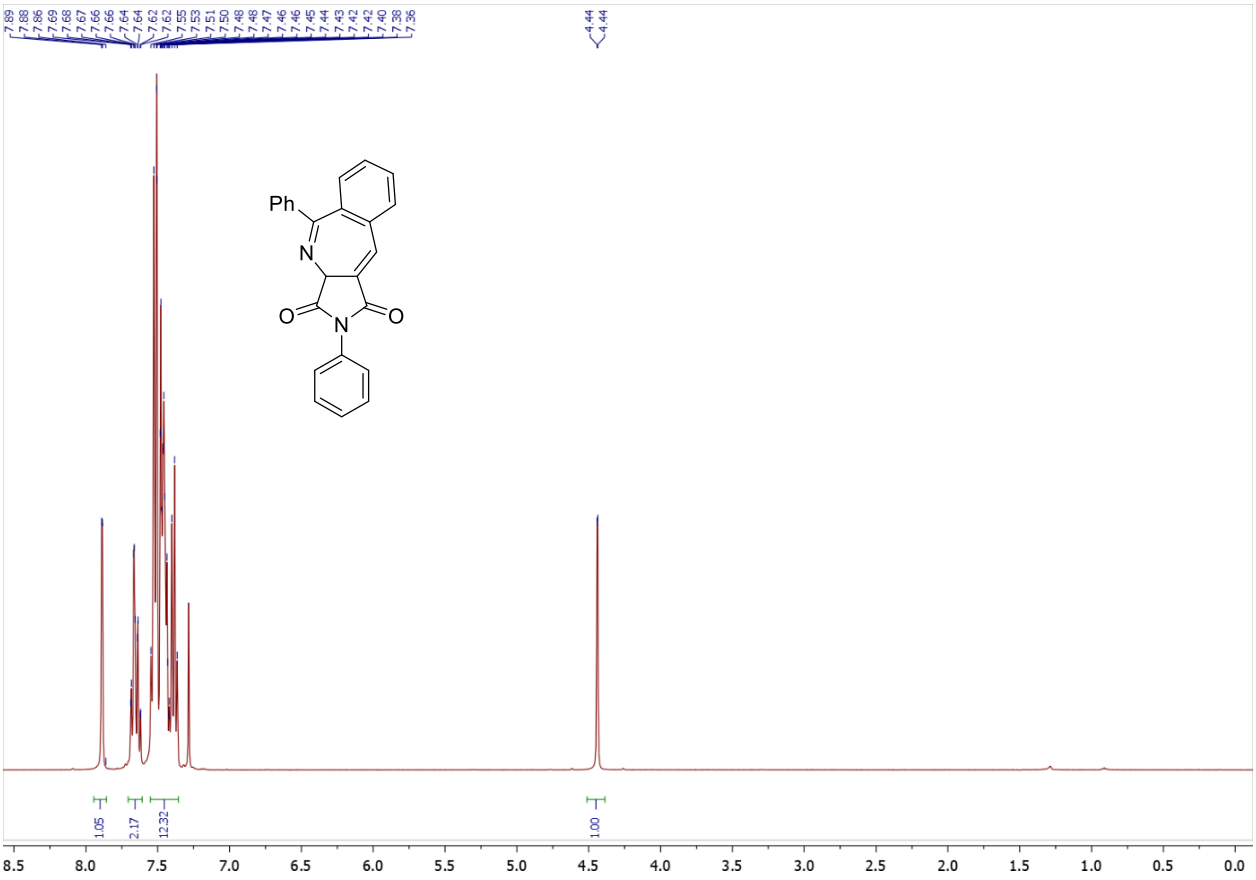
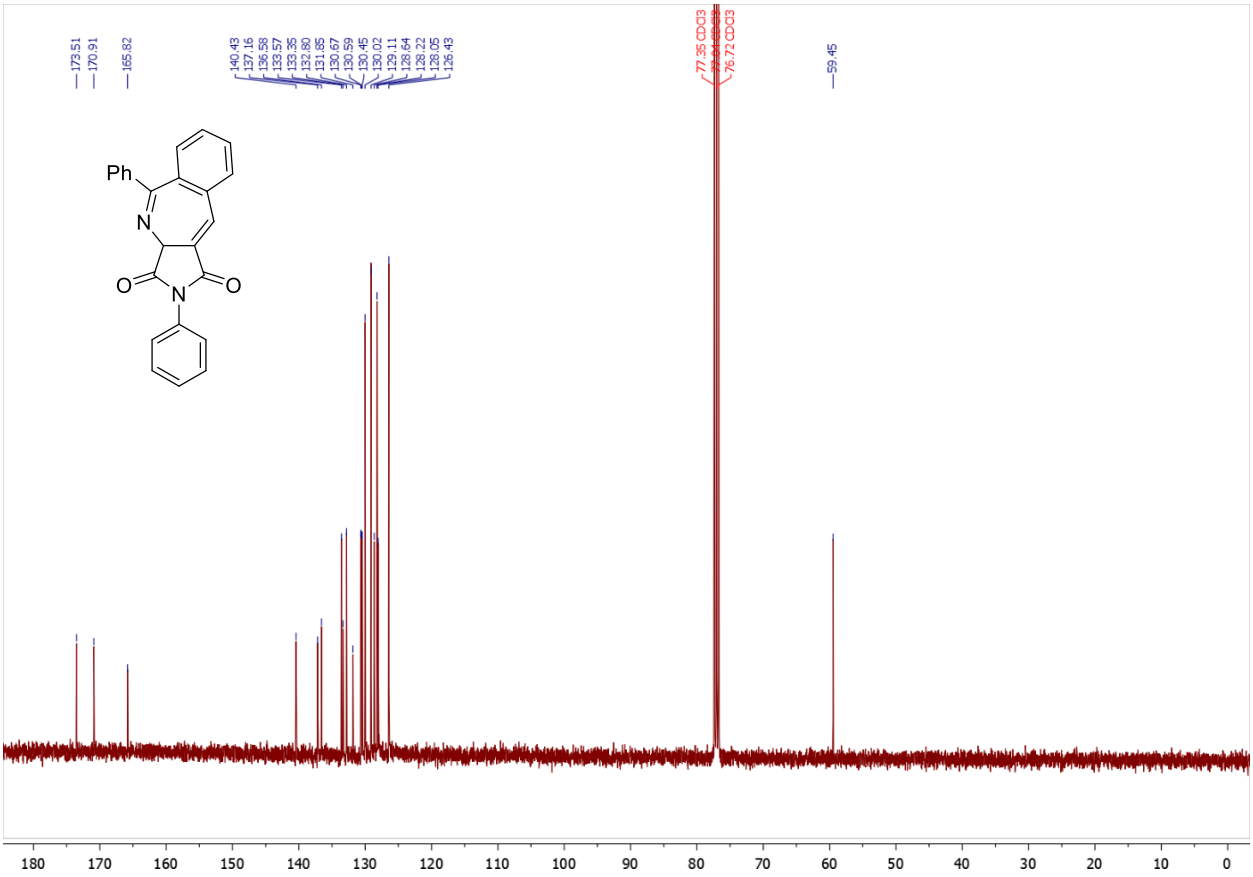


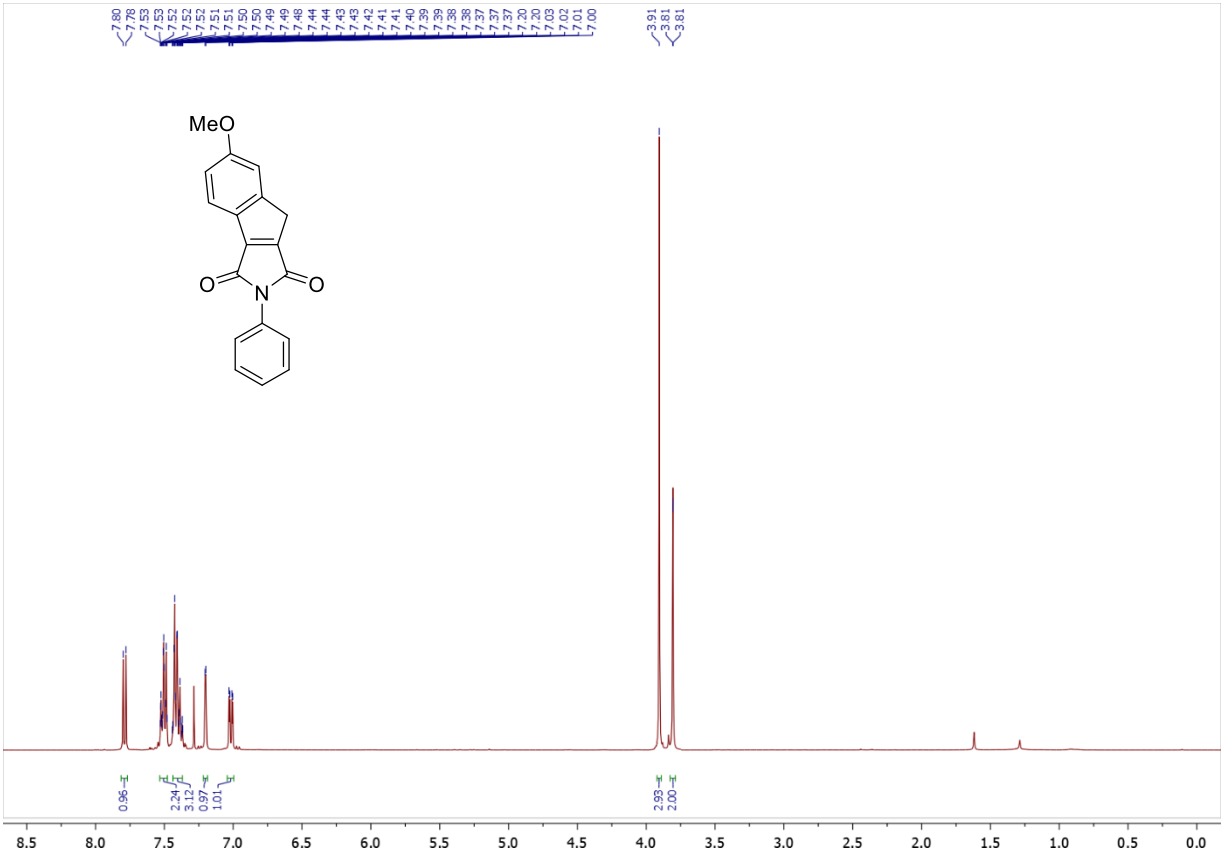


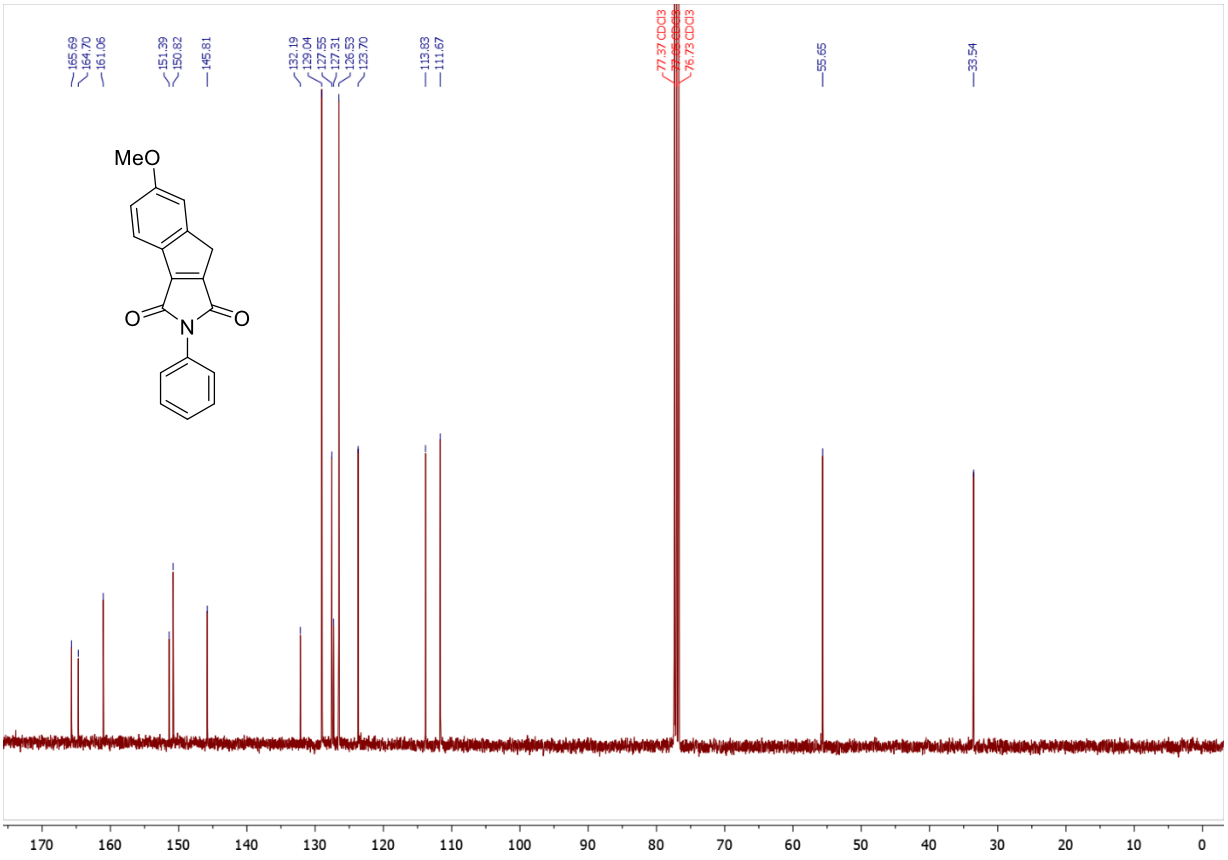
2,5-diphenylbenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,3aH)-dione (7u)



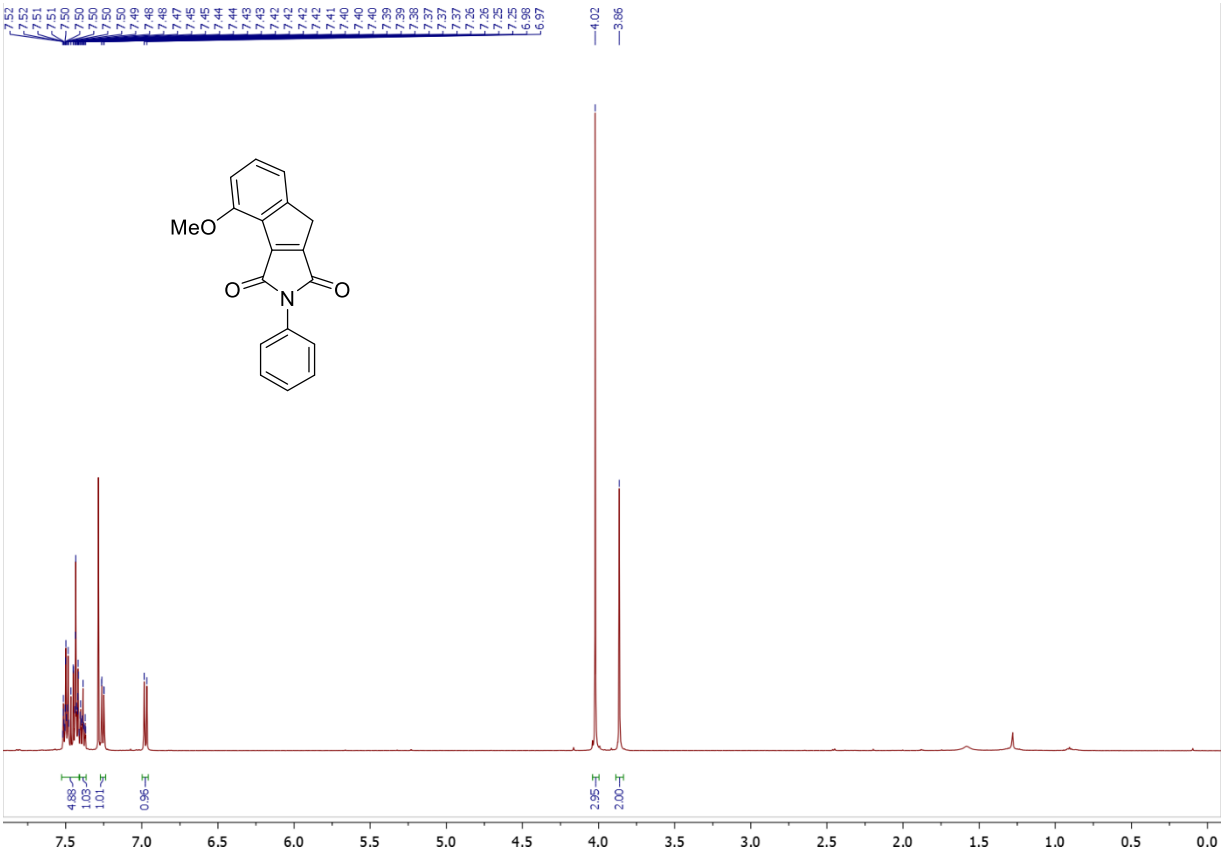


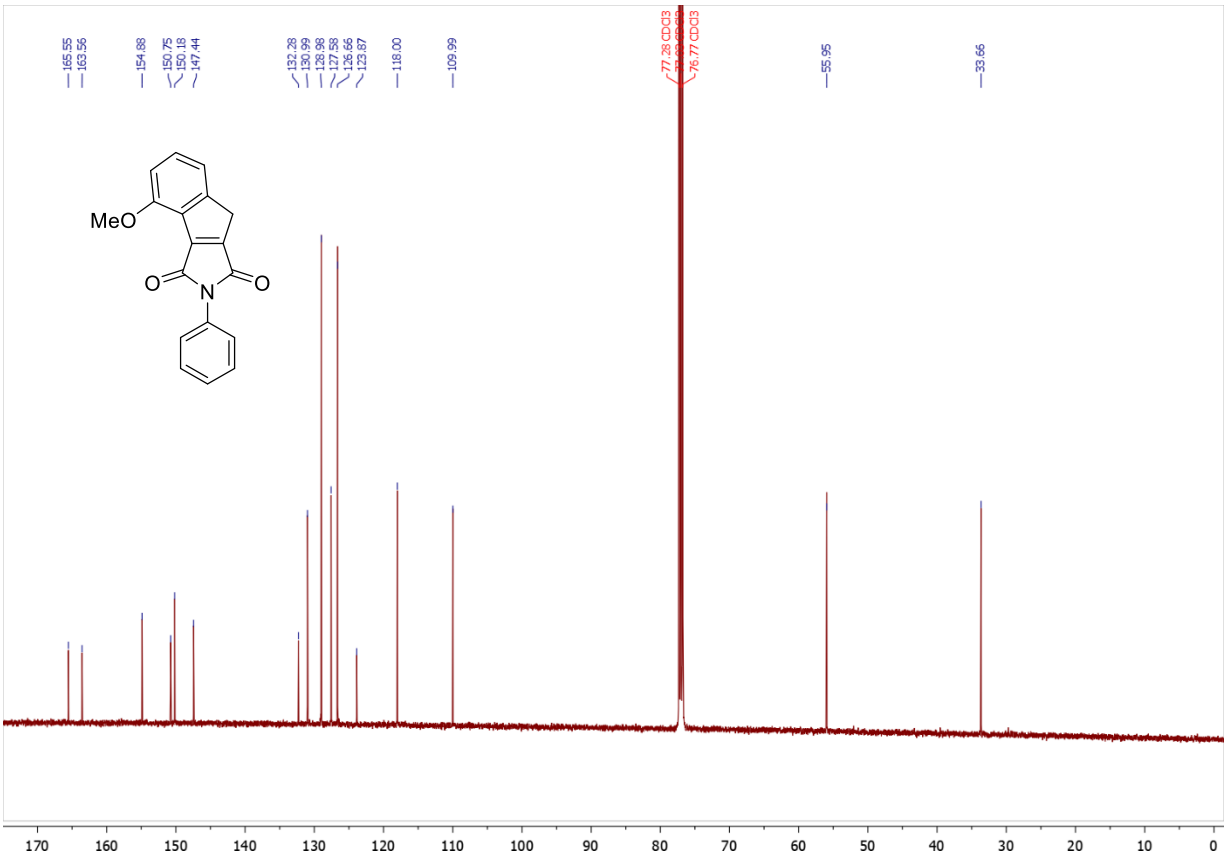
6-methoxy-2-phenylindeno[1,2-c]pyrrole-1,3(2H,8H)-dione (8v')



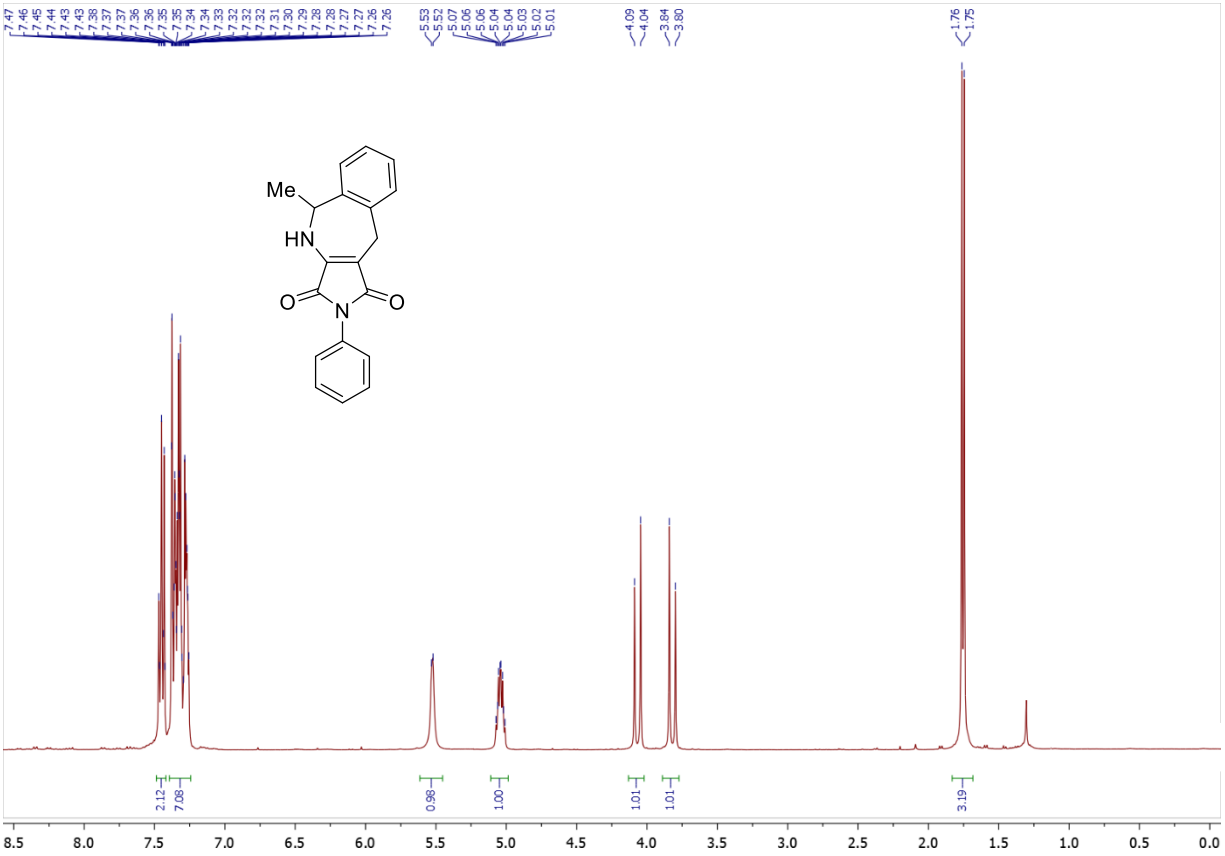


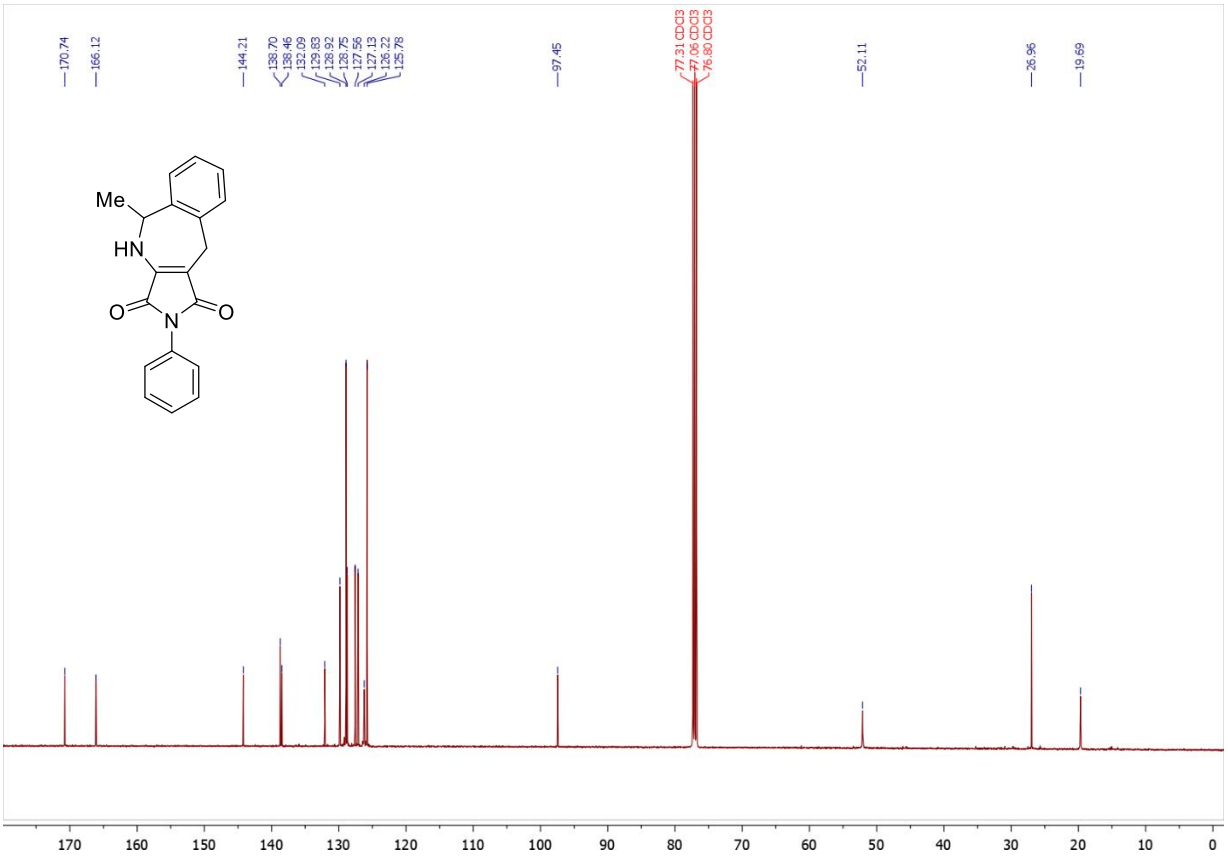
4-methoxy-2-phenylindeno[1,2-c]pyrrole-1,3(2H,8H)-dione (8v'')





5-methyl-2-phenyl-5,10-dihydrobenzo[e]pyrrolo[3,4-b]azepine-1,3(2H,4H)-dione (10a)





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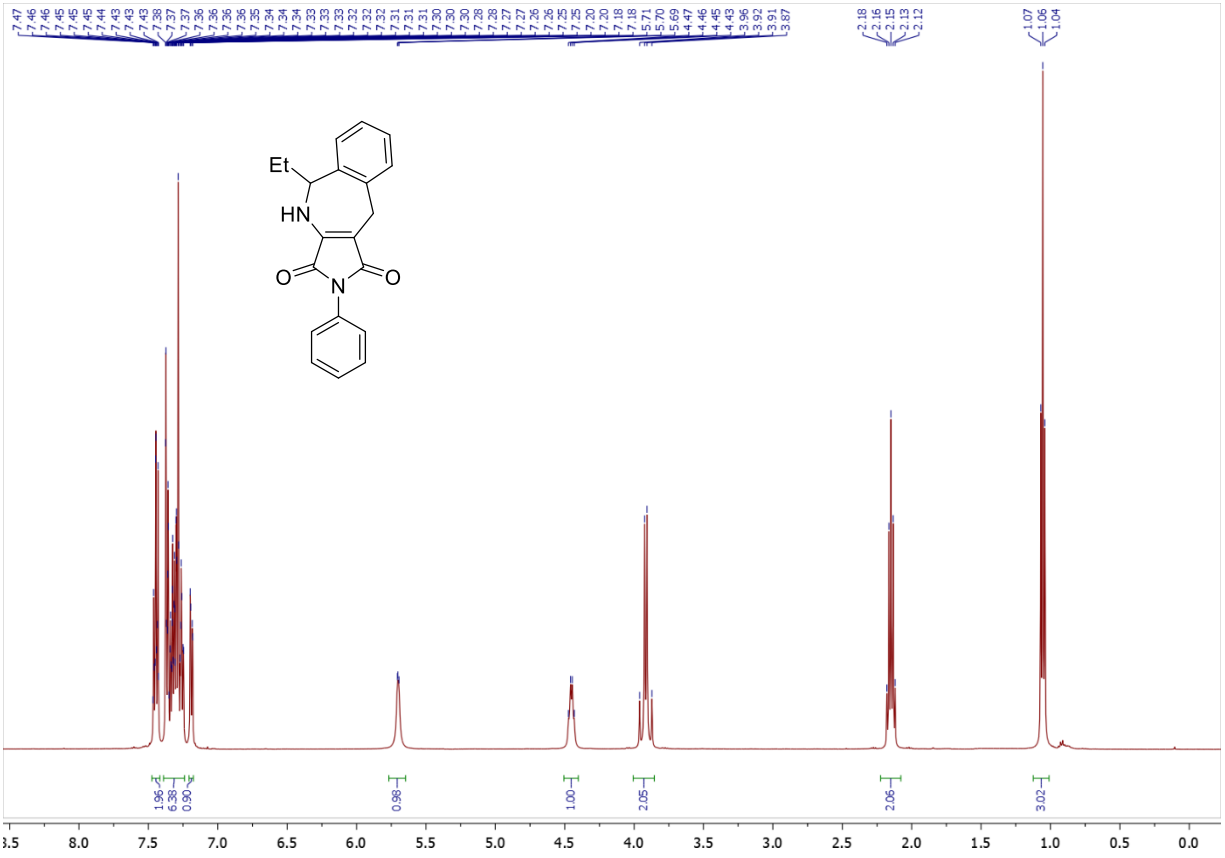

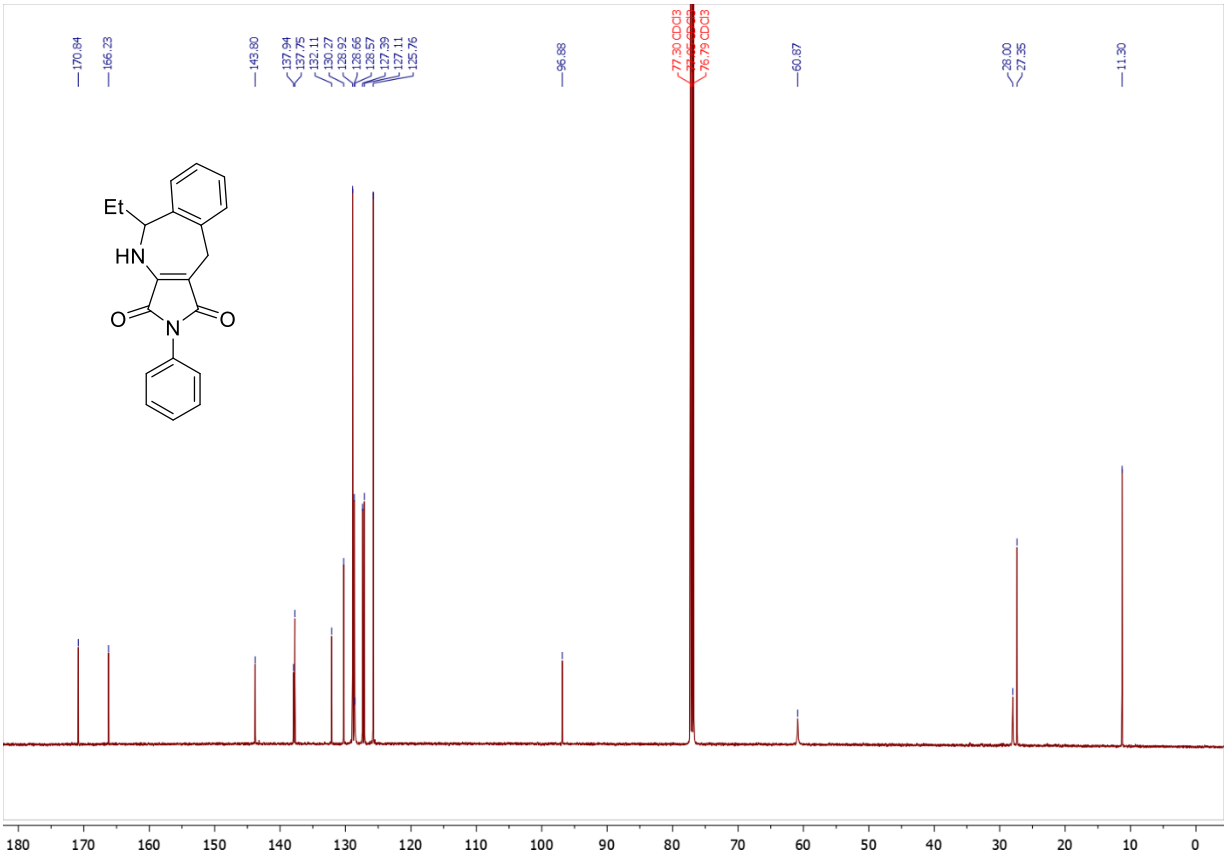

Crystallographic data for 7g

X-ray Single Crystal analysis was performed on Agilent Technologies "Xcalibur" diffractometer with monochromated CuKα radiation. The crystal was kept at 100 K during data collection. Using Olex2[2], the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimization. CCDC 2062898 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via **https://www.ccdc.cam.ac.uk/**.

Empirical Formula	$C_{19}H_{13}FN_2O_2$
Formula weight	320.31
Temperature, K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.5776(2)
b/Å	14.3577(2)
c/Å	11.1685(3)
α/Å	90
β/Å	115.979(3)
γ/Å	90
Volume/Å^3	1524.77(6)
Z	4
ρ_{calc}g/cm^3	1.395
μ/mm^{-1}	0.831
F(000)	664.0
Crystal size/mm^3	0.3 × 0.28 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.3 to 147.556
Index ranges	$-9 \le h \le 13$, $-17 \le k \le 15$, $-13 \le l \le 13$
Reflections collected	8152
Independent reflections	2927 [R_{int} = 0.0340, R_{sigma} = 0.0316]
Data/restraints/parameters	2927/0/218
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0337, wR_2 = 0.0816
Final R indexes [all data]	R_1 = 0.0388, wR_2 = 0.0853
Largest diff. peak/hole / e Å^{-3}	0.25/-0.23

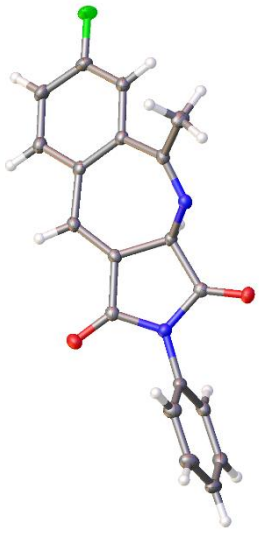

Figure 1. ORTEP representation of compound **7g** (thermal ellipsoids are shown at 50% probability)

References

1. Chupakhin, E. G.; Kantin, G. P.; Dar'in, D. V.; Krasavin, M. *Mendeleev Commun*. **2021**, 31, 36.
2. Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *Acta Cryst*. **2015**, A71, 59.
3. Sheldrick, G. M. *Acta Cryst*. **2015**, C71, 3.