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# Controlled Oxidation of Pyrroles: Synthesis of Highly Functionalized $\gamma$ -Lactams

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## General Experimental

### Nuclear Magnetic Resonance Spectroscopy

Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) nuclear magnetic resonance spectra were obtained on a Varian Mercury 2000 spectrometer operating at 300 MHz and 75 MHz respectively where samples were dissolved in deuterated chloroform ( $\text{CDCl}_3$ ). Chemical shifts were recorded as  $\delta$  values in parts per million (ppm) and referenced to the solvent used (In the case of  $\text{CDCl}_3$ , chemical shifts respectively appear at 7.26 ppm and 77.23 ppm for  $^1\text{H}$  and  $^{13}\text{C}$  spectra). Coupling constants were recorded as  $J$  values in Hz. The following abbreviations were used to describe  $^1\text{H}$  spectra peak splitting patterns; s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, t = triplet, dt = doublet of triplets, q = quartets, dq = doublet of quartets, bs = broad singlet, m = multiplet and ad = apparent doublet.

### Infrared Spectroscopy

Infrared spectra were obtained on a Shimadzu FTIR 8400s spectrometer, using NaCl plates. Liquids and solids were recorded as thin films from either  $\text{CDCl}_3$  or  $\text{CH}_2\text{Cl}_2$  in  $\text{cm}^{-1}$ .

### Mass Spectrometry

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Mass spectrometry and High-Resolution mass spectrometry was performed on a Kratos Concept ISQ mass instrument using electron impact mass spectrometry or by LSIMS with *m*-nitrobenzoic acid as the matrix.

Analytical analyses were performed by The Central Science Laboratory at the University of Tasmania. The molecular ion and mass fragments are quoted, with relative intensities of the peaks referenced to the most intense taken as 100%.

### **Column Chromatography**

Merck flash grade silica (32-63  $\mu\text{m}$ ) was used for column and flash chromatography.

### **Thin Layer Chromatography (TLC)**

Merck silica gel 60 F254 aluminium backed sheets were used for analytical thin layer chromatography. TLC plates were visualised under a 254 nm UV lamp and/or by treatment with a phosphomolybdic acid (37.5 g), ceric sulfate (7.5 g), sulfuric acid (37.5 ml), water (720 ml) dip or a potassium permanganate dip (3 g  $\text{KMnO}_4$ , 20 g  $\text{K}_2\text{CO}_3$ , 5 ml 5% aqueous NaOH, 300 ml water), followed by heating.

### **Solvents and Reagents**

All solvents and reagents were purified by standard laboratory procedures.<sup>1</sup>

Pyrrole analogues **4a**, **4b** and the Dess-Martin periodinane (**5**) were obtained from Oakwood chemicals, while pyrrole analogue **4h** was obtained from SAFC. Pyrrole analogues **4e**, **4f**, **4g** and **4i** were synthesized according to the general procedure of Smith et al.<sup>2</sup> Pyrrole analogues **4c** and **4d** were synthesized according to the general procedure of Banik et al.<sup>3</sup> Pyrrole analogue **9a** and **9b** was synthesized according to the general procedure of Brttian et al.<sup>4</sup>

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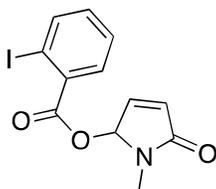
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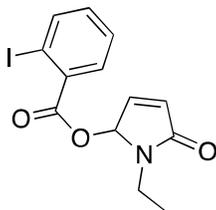
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#### General experimental for oxidation of pyrroles 4.

To a solution of the Dess-Martin periodinane (2.5 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (0.1M) at 0°C was slowly added *N*-alkyl pyrrole (1 equiv). The reaction mixture was allowed to stir at 0°C for 2 hours before quenching with H<sub>2</sub>O and solid Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>. The resulting solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 5 mL) and the combined organic extracts were washed with a solution of saturated NaHCO<sub>3</sub> (3 x 10 mL) before drying on Na<sub>2</sub>SO<sub>4</sub> and filtered. Solvent was evaporated under reduced pressure to yield the crude product, before purification by flash chromatography.



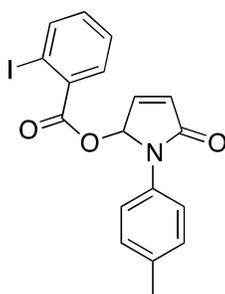
**(6a).** From **4a** following the general method in 81% yield as a yellow oil after purification with 40% ethyl acetate: hexanes. IR (thin film): 3094, 2926, 1718, 1582, 1244, 1014 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.01 (s, 3H), 6.30 (d, *J* = 6 Hz, 1H), 6.65 (ad, 1H), 7.09 (dd, *J* = 6.0, 1.8 Hz, 1H), 7.18 (td, *J* = 7.8, 1.8 Hz, 1H), 7.40 (td, *J* = 8.1, 1.2 Hz, 1H), 7.80 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.00 (dd, *J* = 8.1, 1.2 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 27.3, 85.4, 94.6, 128.3, 130.5, 131.5, 133.64, 133.68, 141.9, 165.9, 170.1; MS (+EI): *m/z* 343 (M<sup>+</sup>, 1); HRMS (+EI): *m/z* for C<sub>12</sub>H<sub>10</sub>INO<sub>3</sub> calc. 342.97053, found 342.97024.



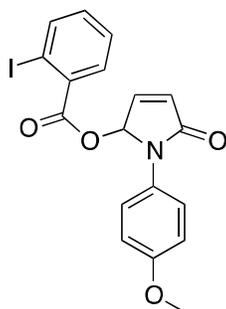
**(6b).** From **4b** following the general method in 83% yield as a yellow semisolid after purification with 40% ethyl acetate: hexanes. IR(thin film): 3094, 2974,

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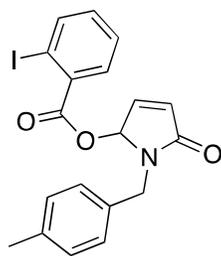
1723, 1582, 1223, 1014  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.20 (t,  $J = 7.2$  Hz, 3H), 3.31 (dq,  $J = 14.2, 7.1$  Hz, 1H), 3.69 (dq,  $J = 14.2, 7.1$  Hz, 1H), 6.28 (d,  $J = 6$  Hz, 1H), 6.76 (d,  $J = 1.5$  Hz, 1H), 7.09 (dd,  $J = 6, 1.8$  Hz), 7.18 (td,  $J = 7.2, 1.5$  Hz, 1H), 7.41 (td,  $J = 7.5, 1.2$  Hz, 1H), 7.80 (dd,  $J = 7.8, 1.8$  Hz, 1H), 8.01 (dd,  $J = 7.8, 0.9$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.0, 35.3, 83.7, 94.6, 128.3, 130.5, 131.5, 133.5, 133.6, 141.9, 165.8, 169.8; MS (+EI):  $m/z$  357 ( $\text{M}^+$ , 100), 230 (47); HRMS (+EI):  $m/z$  for  $\text{C}_{13}\text{H}_{12}\text{INO}_3$  calc. 356.9861, found 356.9935.



(**6c**). From **4c** following a modified general method, where extraction was preformed with ethyl acetate (3 x 10 mL) before the combined organic extracts were washed with a solution of saturated  $\text{NaHCO}_3$  (3 x 10 mL), dried on  $\text{Na}_2\text{SO}_4$  and filtered. Compound isolated in an 88% yield as a yellow oil after purification with 30% ethyl: hexanes. IR (thin film): 2923, 1718, 1581, 1516, 1387, 1205, 1014  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.32 (s, 3H), 6.42 (d,  $J = 6$  Hz, 1H), 7.11 - 7.17 (m, 1H), 7.19 (d,  $J = 8.3$  Hz, 2H), 7.22 - 7.28 (m, 2H), 7.34 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.41 (d,  $J = 8.5$  Hz, 2H), 7.62 (dd,  $J = 7.8, 1.7$  Hz, 1H), 7.98 (dd,  $J = 7.9, 1.2$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.2, 84.3, 94.6, 122.6, 128.2, 130.1, 130.8, 131.5, 133.3, 133.6, 136.0, 141.7, 141.8, 165.6, 168.8; MS (+EI):  $m/z$  419 ( $\text{M}^+$ , 12), 172 (100); HRMS (+EI):  $m/z$  for  $\text{C}_{18}\text{H}_{14}\text{INO}_3$  calc. 419.00184, found 419.00271.



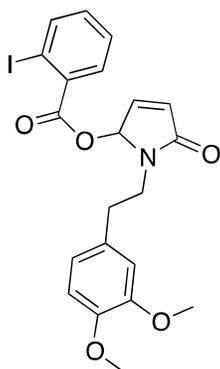
**(6d).** From **4d** following a modified general method, where extraction was preformed with ethyl acetate (3 x 10 mL) before the combined organic extracts were washed with a solution of saturated NaHCO<sub>3</sub> (3 x 10 mL), dried on Na<sub>2</sub>SO<sub>4</sub> and filtered. Compound isolated in a 93% yield as a yellow oil after purification with 30% ethyl: hexanes. IR (thin film): 2932, 1715, 1582, 1513, 1393, 1248, 1209, 1014 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.72 (s, 3H), 6.36 (d, *J* = 5.9 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 2H), 7.08 (td, *J* = 7.8, 1.7 Hz, 1H), 7.12 – 7.19 (m, 2H), 7.24 – 7.29 (m, 1H), 7.32 (d, *J* = 9.0 Hz, 2H), 7.56 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.91 (dd, *J* = 7.9, 1.2 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 55.7, 84.7, 94.6, 114.8, 125.5, 128.3, 130.8, 131.5, 133.6, 141.8, 141.9, 158.1, 165.6, 169.0, 170.4; MS (+EI): *m/z* 435 (M<sup>+</sup>, 18), 188 (100); HRMS (+EI): *m/z* for C<sub>18</sub>H<sub>14</sub>INO<sub>4</sub> calc. 434.99675, found 435.99791.



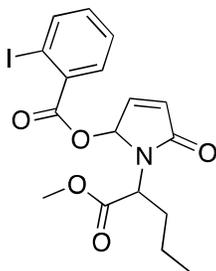
**(6e).** From **4e** following the general method in 93% yield as a brown semisolid after purification with 50% ethyl acetate: hexanes. IR (thin film): 2924, 1718, 1582, 1244, 1014 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.27 (s, 3H), 4.44 (d, *J* = 15

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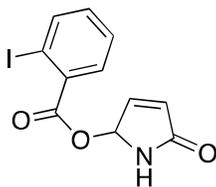
Hz, 1H), 4.77 (d,  $J = 15$  Hz, 1H), 6.35 (d,  $J = 6$  Hz, 1H), 6.64 (d,  $J = 1.5$  Hz, 1H), 7.06 (s, 1H), 7.08-7.10 (m, 2H), 7.15-7.18 (m, 2H), 7.32 (td,  $J = 7.8, 1.2$  Hz, 1H), 7.44 (dd,  $J = 7.8, 1.8$  Hz, 1H), 7.99 (dd,  $J = 7.8, 1.2$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 44.1, 83.9, 94.6, 128.1, 128.4, 129.6, 130.2, 131.5, 133.5, 133.8, 137.5, 141.8, 142.3, 165.5, 170.0; MS (+EI):  $m/z$  433 ( $\text{M}^+$ , 2), 248 (47), 202 (17); HRMS (+EI):  $m/z$  for  $\text{C}_{19}\text{H}_{16}\text{INO}_3$ , calc. 433.01748, found 433.01876.



**(6f).** From **4f** following the general method in 96% yield as brown oil after purification with 50% ethyl acetate: hexanes. IR(thin film): 2938, 2833, 1715, 1582, 1263, 1014  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.84 (ddd,  $J = 13.5, 8.9, 6.4$  Hz, 1H), 2.94 (ddd,  $J = 13.7, 9.0, 6.2$  Hz, 1H), 3.44 (ddd,  $J = 14.2, 8.9, 6.2$  Hz, 1H), 3.83 (s, 2H), 3.84 (s, 3H), 3.92 (ddd,  $J = 14.3, 9.0, 6.4$  Hz, 1H), 6.30 (dd,  $J = 5.9, 0.7$  Hz, 1H), 6.63 (d,  $J = 1.7$  Hz, 1H), 7.05 (dd,  $J = 5.9, 1.8$  Hz, 1H), 7.20 (ddd,  $J = 7.9, 7.4, 1.7$  Hz, 1H), 7.41 (ddd,  $J = 7.8, 7.5, 1.2$  Hz, 1H), 7.77 (ddd,  $J = 7.8, 1.5, 0.3$  Hz, 1H), 8.03 (ddd,  $J = 8.1, 1.2, 0.3$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  34.3, 42.1, 56.0, 56.1, 84.0, 94.6, 111.4, 112.1, 120.9, 128.3, 130.4, 130.9, 131.5, 133.7, 142.0, 142.1, 147.8, 149.1, 165.8, 170.1; MS (+EI):  $m/z$  493 ( $\text{M}^+$ , 7), 261 (32), 248 (19); HRMS (+EI):  $m/z$  for  $\text{C}_{21}\text{H}_{20}\text{INO}_5$ , calc. 493.03861, found 493.03919.



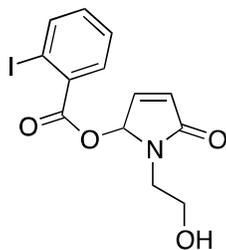
**(6g)**. From **4g** following the general method in 86% yield as a brown oil in a 1:1 mixture of diastereomers, after purification with 30% ethyl acetate: hexanes.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.83 (t,  $J = 7.3$  Hz, 3H), 0.92 (t,  $J = 7.2$  Hz, 3H), 1.39 (dddd,  $J = 20.7, 13.9, 9.8, 5.0$  Hz, 4H), 1.78-2.09 (m, 4H), 3.61 (s, 3H), 3.73 (s, 3H), 4.59 (dd,  $J = 9.4, 6.3$  Hz, 1H), 4.80 (dd,  $J = 10.7, 5.2$  Hz, 1H), 6.33 (dd,  $J = 6.0, 2.2$  Hz, 1H), 6.75-6.81 (m, 1H), 7.08 (d,  $J = 1.6$  Hz, 1H), 7.14-7.23 (m, 3H), 7.41 (ddd,  $J = 5.4, 4.5, 2.2$  Hz, 2H), 7.80 (ddd,  $J = 9.6, 7.8, 1.7$  Hz, 2H), 8.03 (dd,  $J = 7.9, 2.9$  Hz, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.6, 13.7, 19.6, 19.7, 30.7, 31.9, 52.5, 52.6, 54.2, 54.3, 83.3, 84.8, 94.7, 94.7, 128.2, 128.8, 129.1, 129.8, 131.3, 131.5, 133.2, 133.6, 141.9, 142.0, 142.9, 143.6, 165.3, 165.5, 170.5, 171.3, 171.5, 171.7; MS (+EI):  $m/z$  443 ( $\text{M}^+$ , 7), 248 (14), 212 (17); HRMS (+EI):  $m/z$  for  $\text{C}_{17}\text{H}_{18}\text{INO}_5$ , calc. 443.02296, found 443.02342.



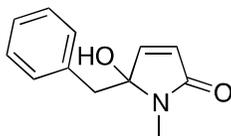
**(6h)**. From **4h** following the general method in 56% yield as a brown oil without need for further purification. IR (thin film): 3246, 3103, 1719, 1582, 1247, 1015  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.28-6.33 (m, 1H), 6.54-6.57 (m, 1H), 6.67 (bs, 1H), 7.11-7.23 (m, 2H), 7.43 (td,  $J = 7.4, 3.9$  Hz, 1H), 7.83 (dd,  $J = 7.8, 1.7$  Hz, 1H), 8.03 (dd,  $J = 7.4, 0.6$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  81.3, 94.7, 128.3, 130.4,

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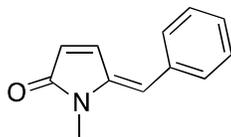
131.7, 133.8, 142.0, 144.2, 166.4, 171.9; MS (+EI):  $m/z$  329 (M+, 100), 230(88);  
HRMS (+EI):  $m/z$  for C<sub>11</sub>H<sub>8</sub>INO<sub>3</sub>, calc. 329.9548, found 329.9622.



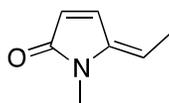
**(10).** From **9** following a modified general method, where 1 equiv of Dess-Martin was used instead of 2.5 equiv, in 61% yield as a colourless oil after purification with 60% ethyl acetate: hexanes. IR (thin film): 3403, 2935, 2879, 1681, 1582, 1413, 1245, 1089 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.05 (bs, 1H), 3.42-3.51 (m, 1H), 3.70-3.80 (m, 3H), 6.28 (d,  $J$  = 6 Hz, 1H), 6.83 (s, 1H), 7.10-7.18 (m, 2H), 7.39 (dt,  $J$  = 7.8, 1.2 Hz, 1H), 7.79 (dd,  $J$  = 7.8, 1.2 Hz, 1H), 7.97 (dd,  $J$  = 8.1, 1.2 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 43.5, 61.1, 84.8, 94.4, 128.1, 129.9, 131.3, 133.3, 133.5, 141.6, 142.5, 165.7, 170.9; MS (+EI):  $m/z$  395 (M+Na, 75), 270 (10); HRMS (+EI):  $m/z$  for C<sub>13</sub>H<sub>12</sub>INNaO<sub>4</sub> calc. 395.9709, found 395.9704.



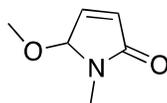
**(12)** From **11a** following the general method in 35% yield after purification with 100% ethyl acetate. IR (thin film): 3314, 3027, 2925, 1701, 1596 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.88 (d,  $J$  = 13.7 Hz, 1H), 2.90 (s, 1H), 3.24 (d,  $J$  = 13.7 Hz, 1H), 5.86 (d,  $J$  = 6.0 Hz, 1H), 6.81 (d,  $J$  = 6.0 Hz, 1H), 7.13 (dd,  $J$  = 7.6, 1.9 Hz, 2H), 7.21-7.30 (m, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 23.8, 42.1, 92.0, 126.9, 127.3, 128.5, 130.2, 134.9, 149.2, 169.6; MS (+EI):  $m/z$  226 (M+Na, 100), 204 (22), 186 (18); HRMS (+EI):  $m/z$  for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>Na, calc. 226.0844, found 226.0839.



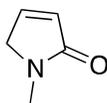
**(13a)** From **11a** following the general method. After the initial work up, the crude mixture (99.9 mg) was reacted under nitrogen with BF<sub>3</sub>.OEt<sub>2</sub> (86.2 mg, 0.60 mmol) and Et<sub>3</sub>SiH (72.8 mg, 0.63 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) for 20 hours. The reaction mixture was quenched with saturated K<sub>2</sub>CO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 5 mL). The organic fractions were collected, dried on Na<sub>2</sub>SO<sub>4</sub> and filtered before the solvent was removed under reduced pressure. The crude mixture was purified on silica with 40% ethyl acetate:hexanes to reveal **11a** as a brown semi solid in a 2 step 89% yield (74.1 mg, 0.40 mmol). IR (thin film): 3058, 2945, 1691, 1632, 1432, 1122, 801; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.21 (s, 3H), 6.27 (dd, *J* = 5.9, 1.7 Hz, 1H), 6.42 (s, 1H), 7.45 – 7.26 (m, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 25.6, 113.7, 125.7, 127.9, 128.8, 129.3, 133.9, 134.9, 141.1, 169.8; MS (+EI): *m/z* 185 (M<sup>+</sup>, 100), 156 (78), 129 (18), 115 (29); HRMS (+EI): *m/z* for C<sub>12</sub>H<sub>11</sub>NO, calc. 185.08406, found 185.08411.



**(13b)** Following the procedure of **13a**; from **11b** in 96% yield as an orange oil after purification with 30% ethyl acetate: hexanes. IR (thin film): 2978, 2890, 1643, 1434, 809 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.97 (d, *J* = 7.5 Hz, 3H), 3.09 (s, 3H), 5.45 (q, *J* = 7.5 Hz, 1H), 6.18 (d, *J* = 5.9 Hz, 1H), 7.25 (d, *J* = 5.9 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 13.1, 25.4, 109.7, 124.5, 131.8, 141.3, 170.2; MS (+EI): *m/z* 123 (M<sup>+</sup>, 100), 94 (49).

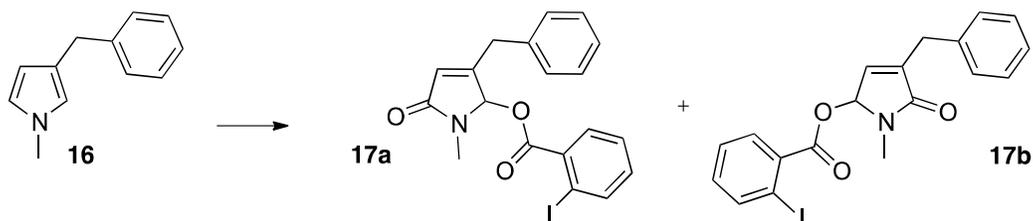


To a solution of **6a** (28.3 mg, 0.082 mmol) in MeOH (2 ml) at 0°C, was added TMSCl (32  $\mu$ L, 0.25 mmol). The reaction mixture was allowed to stir for 3 hours before removing the solvent under reduced pressure. The residue was taken up in ethyl acetate (10 mL) and washed with a 1:1 mixture of saturated NaHCO<sub>3</sub> and H<sub>2</sub>O (2 x 10 mL) followed by a solution of saturated NaCl (10 mL). The organic layer was dried on Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure to yield **14** (8.3 mg, 0.065 mmol, 79%) as a brown oil. No further purification was required. Spectra consistent with literature values.<sup>6</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.92 (s, 3H), 3.10 (s, 3H), 5.31 (s, 1H), 6.27 (d,  $J$  = 5.9 Hz, 1H), 6.84-6.89 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  26.3, 50.5, 89.8, 131.0, 143.4, 170.0; MS (+EI)  $m/z$  127 (M<sup>+</sup>, 50), 96 (100); HRMS (+EI)  $m/z$  for C<sub>6</sub>H<sub>9</sub>NO<sub>2</sub> calc. 127.06332, found 127.06285.

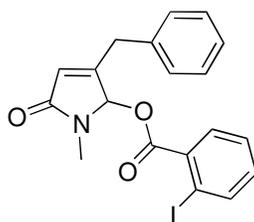


To a solution of **6a** (42.8 mg, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.2 mL) at 0°C was added triethylsilane (42  $\mu$ L, 30.5 mg, 0.26 mmol) followed by BF<sub>3</sub>.OEt<sub>2</sub> (35  $\mu$ L, 40.2 mg, 0.28 mmol). The mixture was allowed to warm to room temperature and left to stir for 20 hours before quenching with saturated K<sub>2</sub>CO<sub>3</sub> (5 ml). The organic layer was removed before extracting the aqueous layer with CHCl<sub>2</sub> (3 x 5 mL). The combined organic fractions were dried on Na<sub>2</sub>SO<sub>4</sub> and filtered before removing solvent under reduced pressure to yield **15** (9.4 mg, 78%) as brown oil. No further purification was required. Spectra consistent with literature

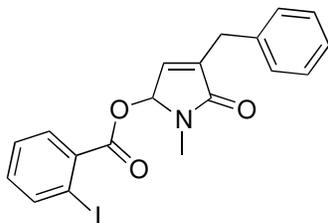
values.<sup>5</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.04 (s, 3H), 3.95-3.99 (m, 2H), 6.18 (dt, *J* = 6.0, 1.9 Hz, 1H), 7.04 (dt, *J* = 6.0, 1.7 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 29.2, 54.9, 128.6, 142.4, 173.3; MS (+EI) *m/z* 97 (M+, 100), 85 (8), 68 (55); HRMS (+EI) *m/z* for C<sub>5</sub>H<sub>7</sub>NO calc. 97.05276, found 97.05286.



(**17a**, **17b**) From **16** following the general method in a combined yield of 61%. Compounds were isolated on silica with 30% ethyl acetate: hexanes to reveal a 36% yield of **17a** and 25% yield of **17b**.

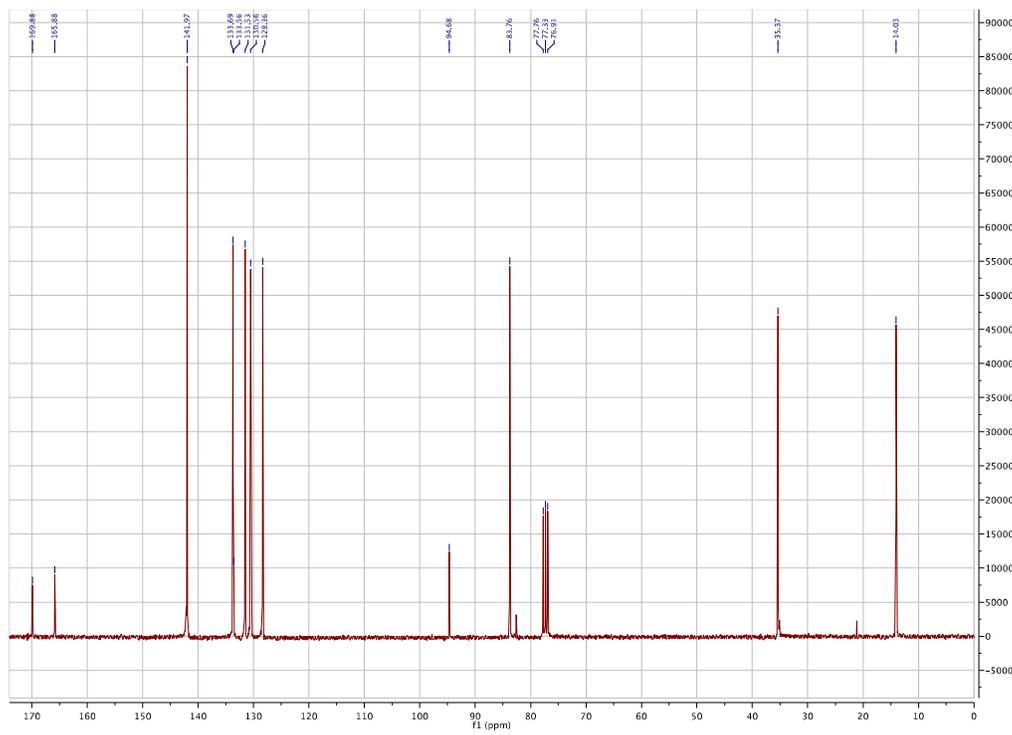
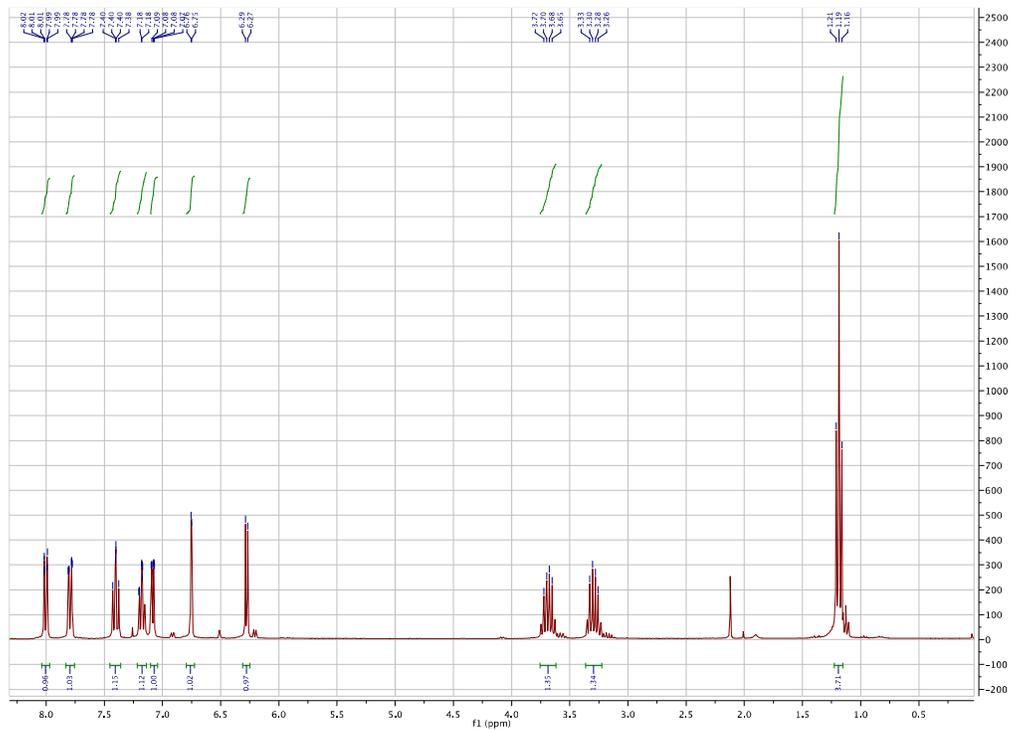
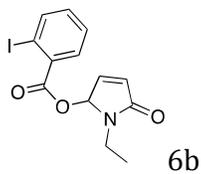


IR (thin film): 3062, 2924, 1711, 1582, 1240, 1014 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 2.97 (s, 3H), 3.69 (dd, *J* = 31.7, 17.3 Hz, 2H), 5.89 (s, 1H), 6.66 (s, 1H), 7.33-7.15 (m, 6H), 7.41 (td, *J* = 7.6, 1.2 Hz, 1H), 7.67 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.2 Hz, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 27.3, 34.8, 84.8, 94.6, 125.2, 127.2, 128.2, 129.05, 129.08, 129.2, 131.3, 133.5, 136.0, 141.8, 157.3, 165.9, 170.2; MS (+EI) *m/z* 433 (M+, 5), 186 (100); HRMS (+EI) *m/z* for C<sub>19</sub>H<sub>16</sub>INO<sub>3</sub> calc. 433.01746, found 433.01784.

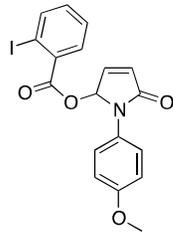


IR (thin film): 3062, 2925, 1712, 1581, 1242, 1013  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.05 (s, 3H), 3.64 (s, 2H), 6.49 (d,  $J = 3$  Hz, 1H), 6.54 (s, 1H), 7.18 (dt,  $J = 8.1, 1.5$  Hz, 1H), 7.21-7.26 (m, 5 H), 7.41 (t,  $J = 9$  Hz), 7.79 (dd,  $J = 9, 3$  Hz, 1H), 8.01 (d,  $J = 9$  Hz, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.6, 32.2, 84.2, 94.4, 126.8, 128.2, 128.8, 129.2, 131.4, 133.4, 133.8, 134.7, 137.3, 141.8, 143.1, 166.0, 170.2; MS (+EI)  $m/z$  433 ( $\text{M}^+$ , 10), 341 (4), 306 (3), 185 (100); HRMS (+EI)  $m/z$  for  $\text{C}_{19}\text{H}_{16}\text{INO}_3$  calc. 433.01746, found 433.01574.

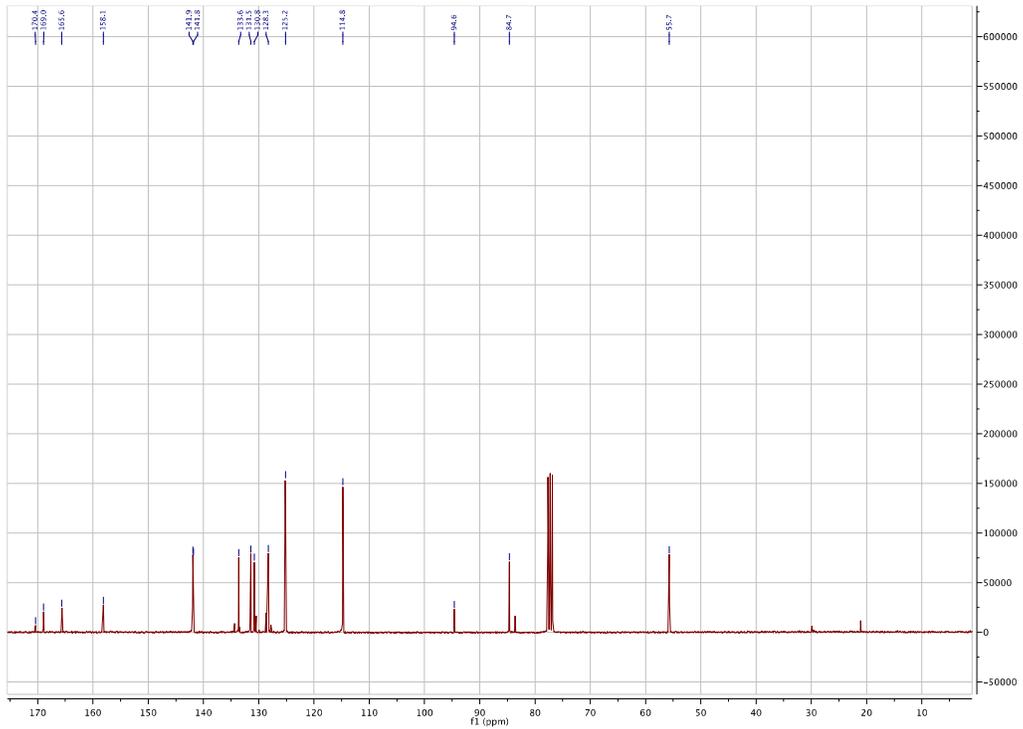
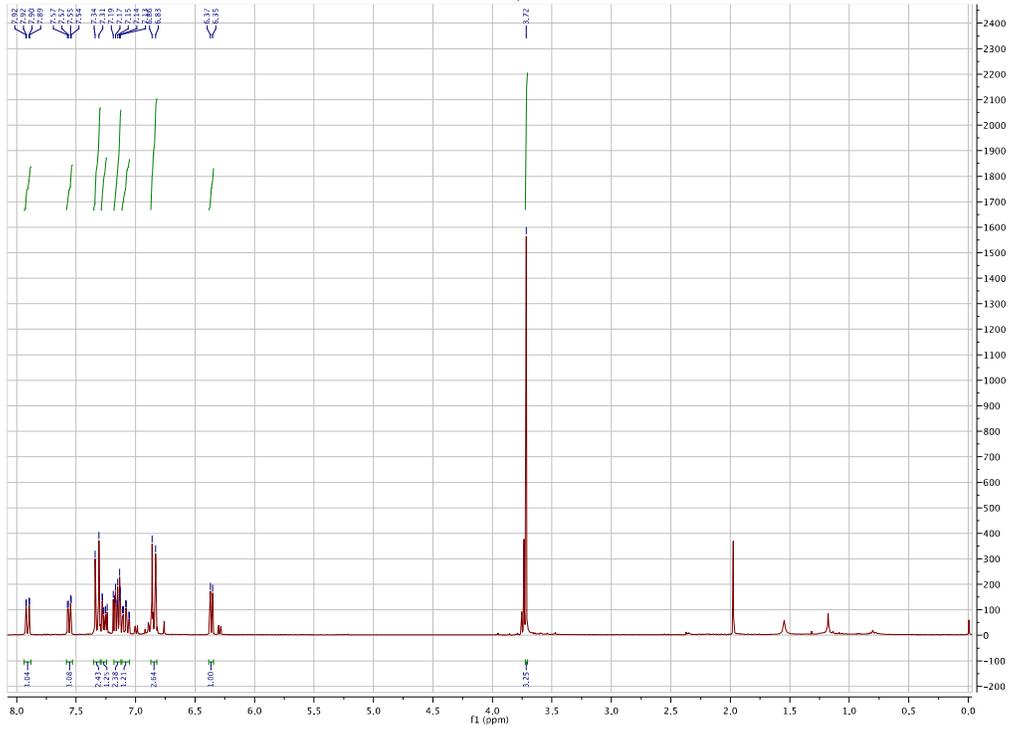


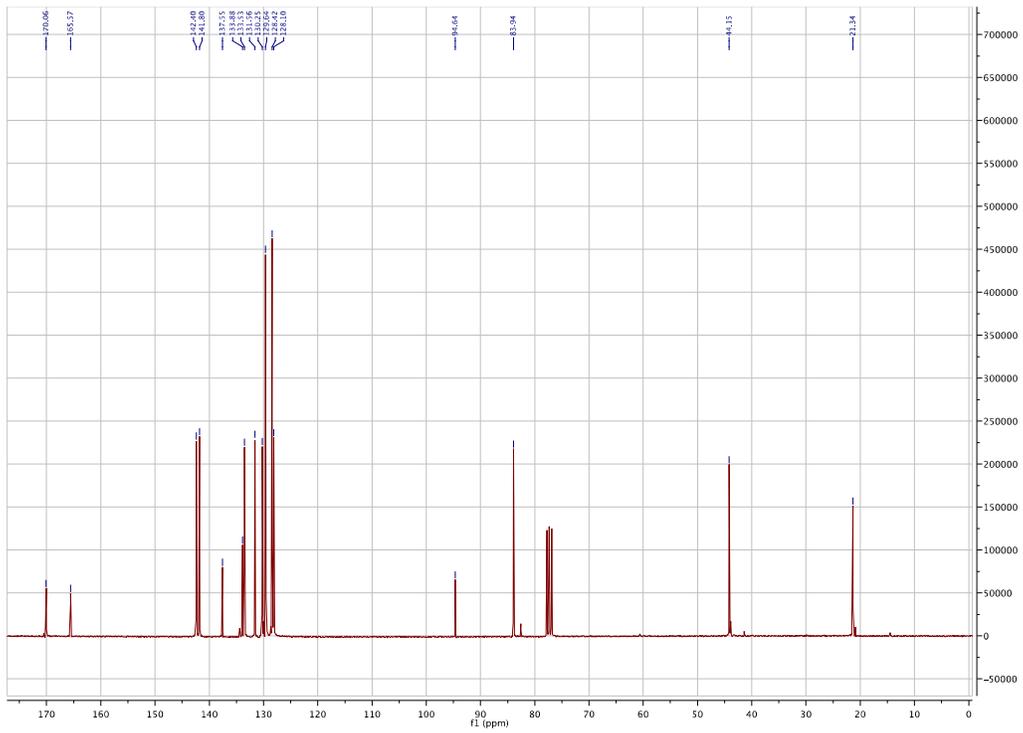
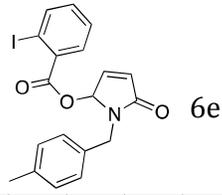


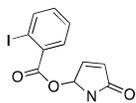




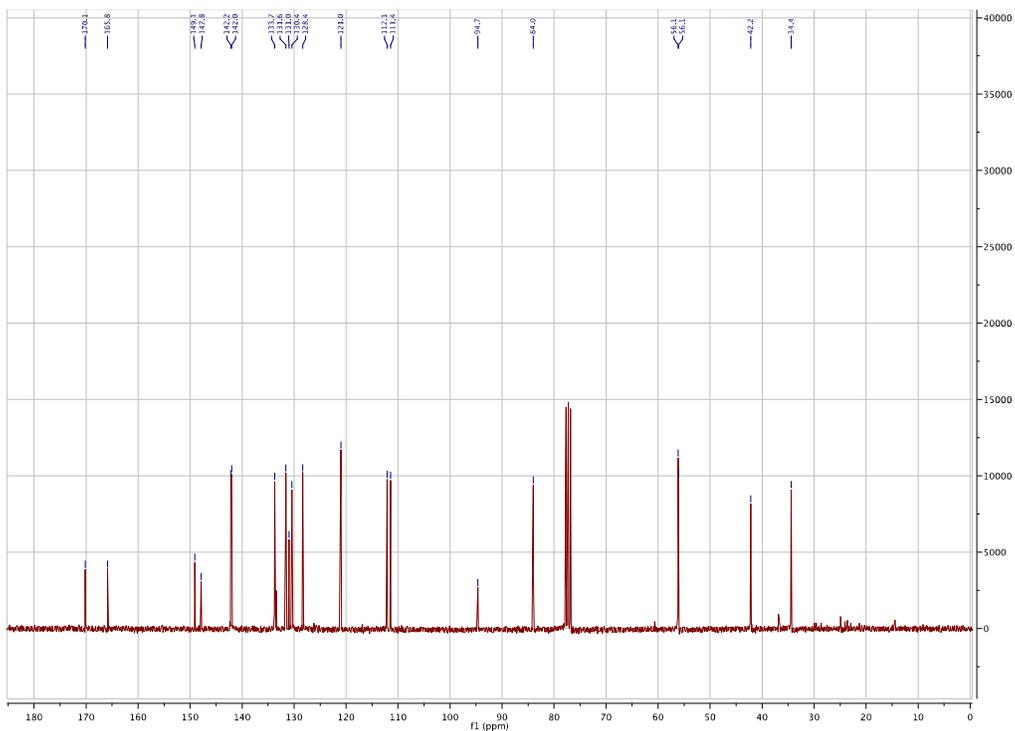
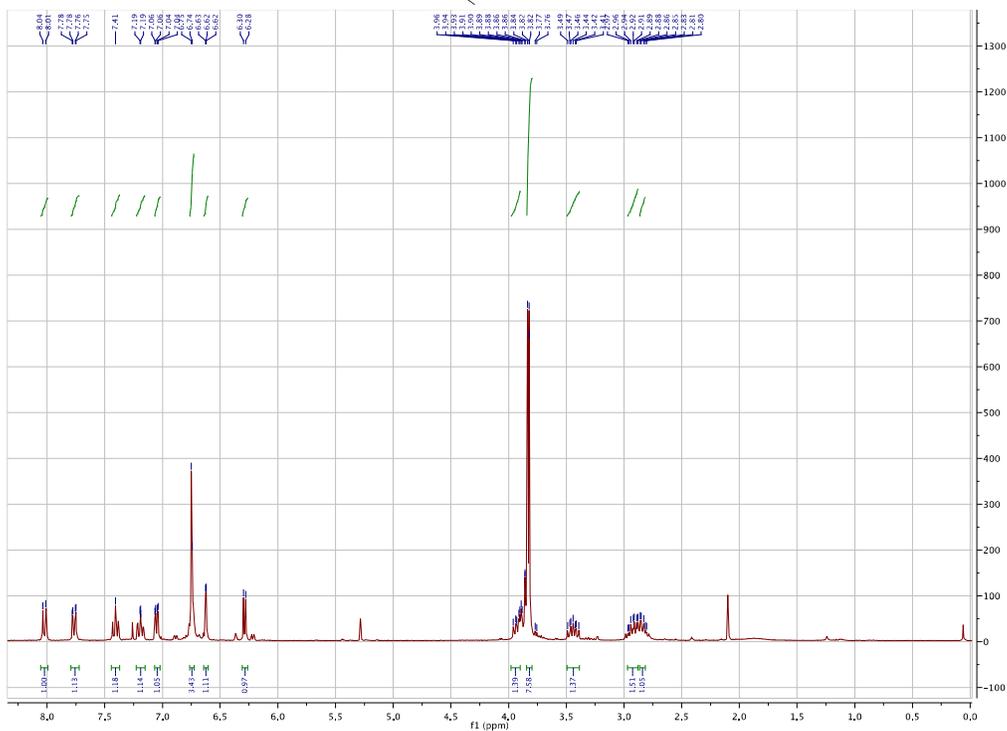
6d

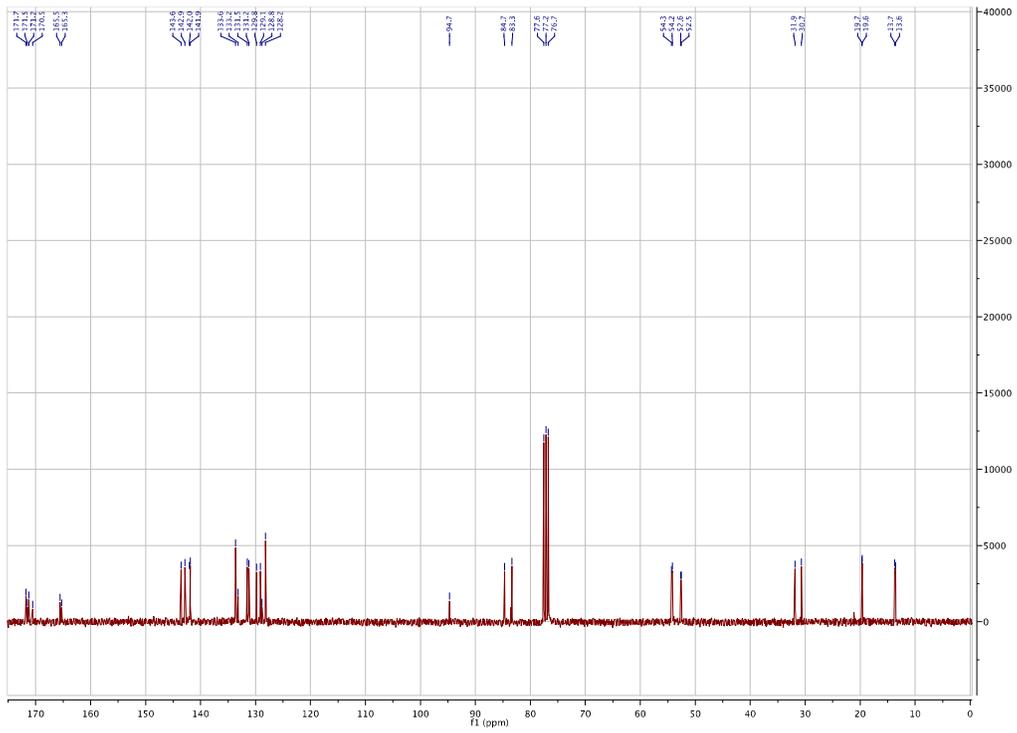
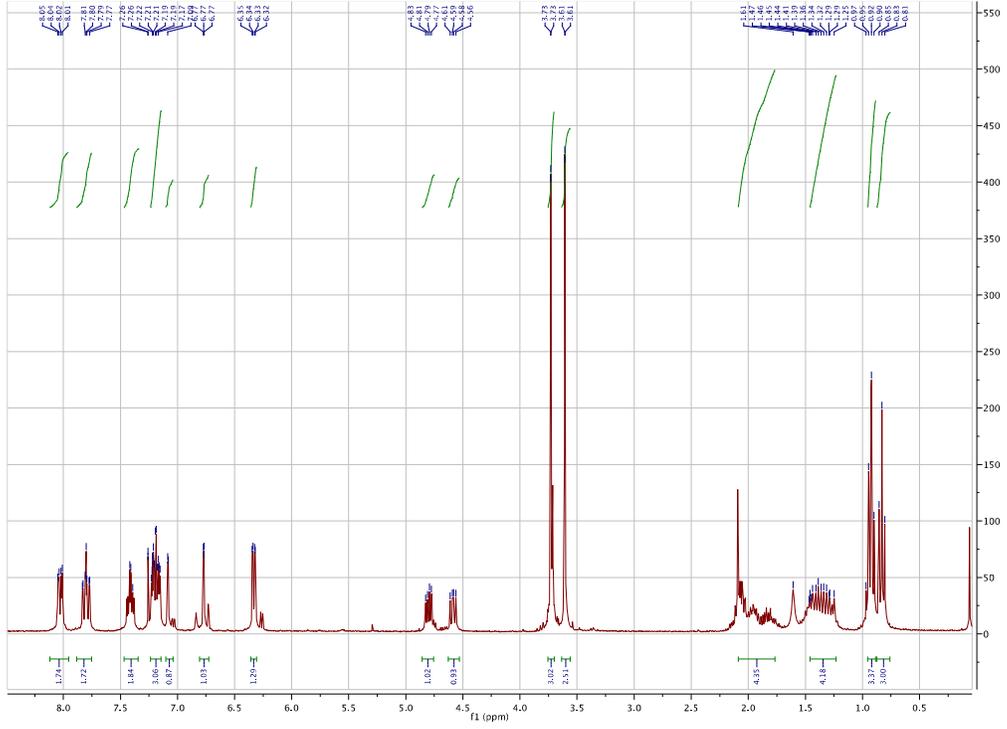
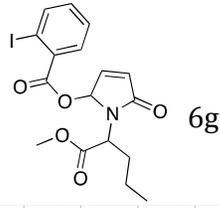


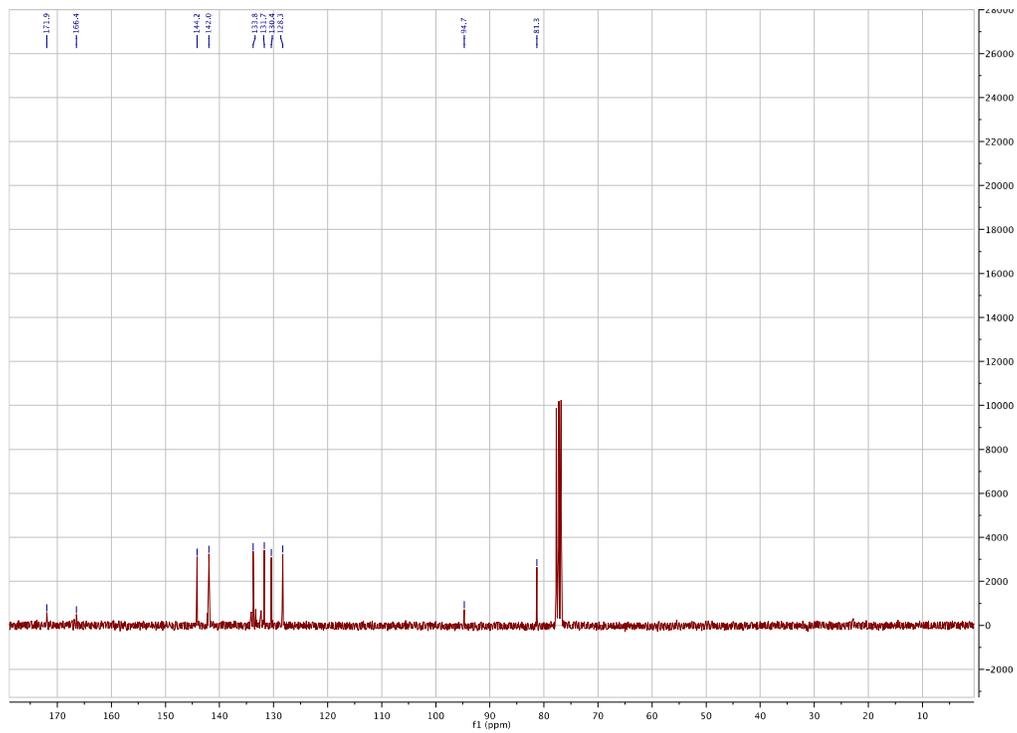
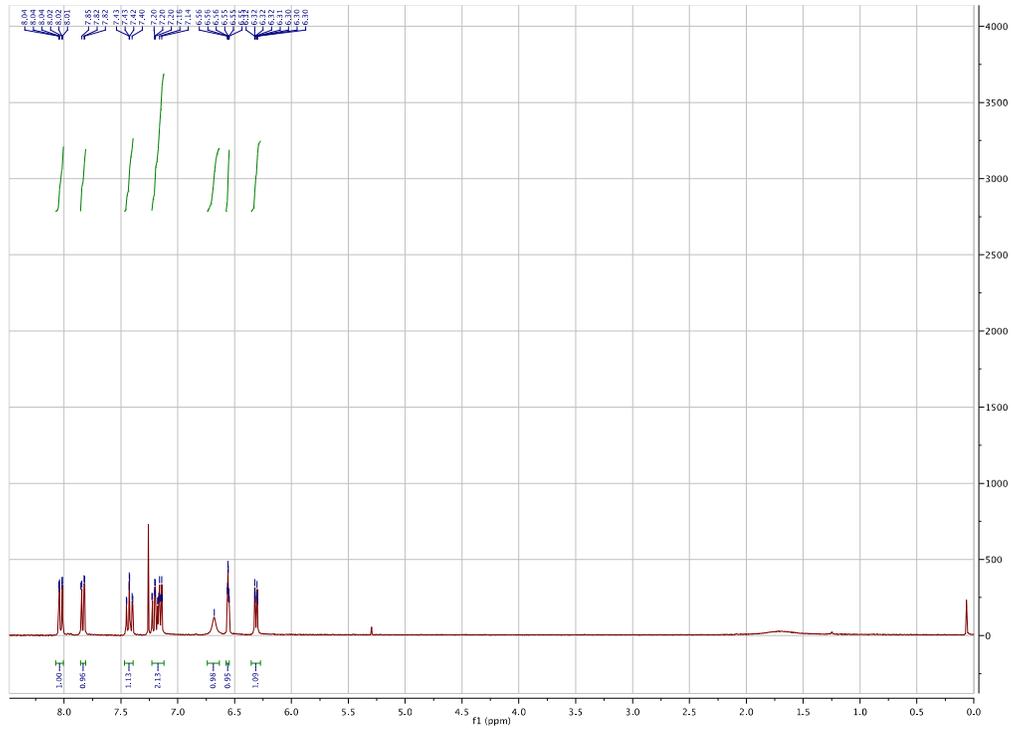
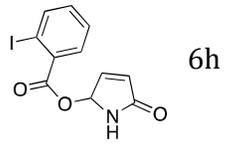




6f

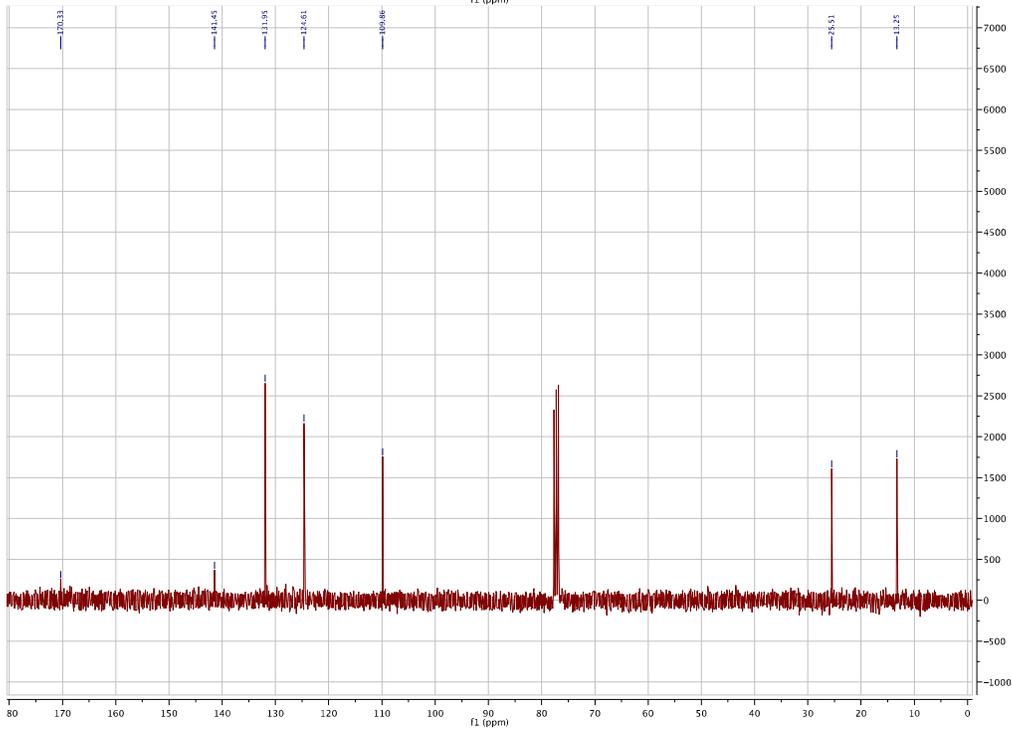
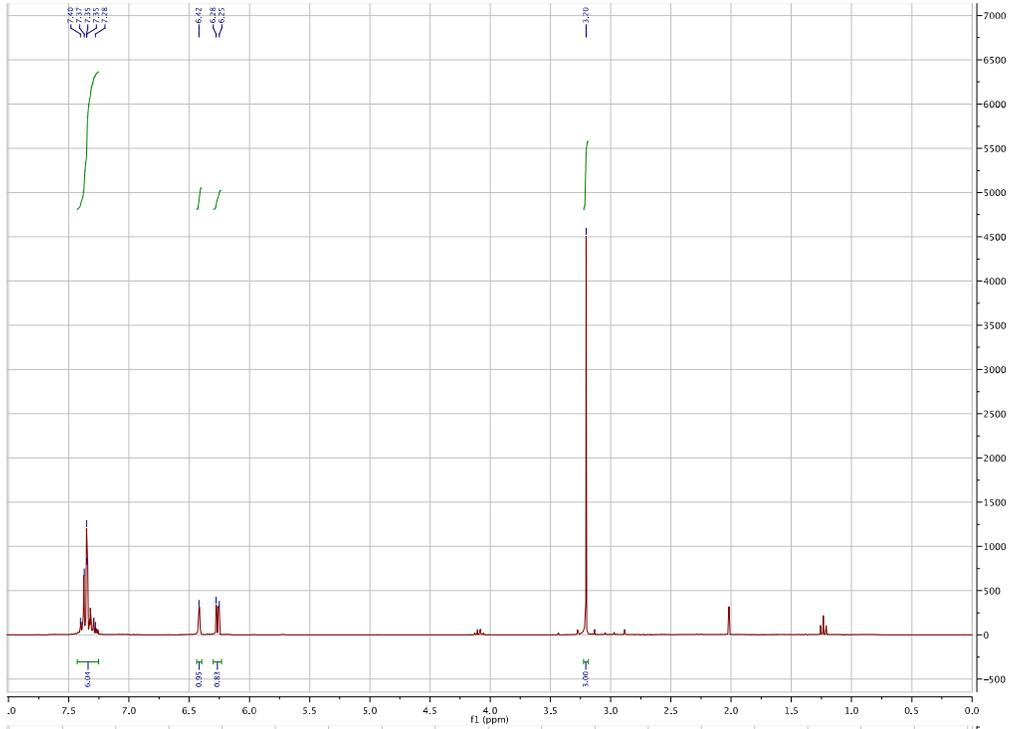
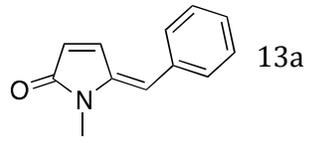


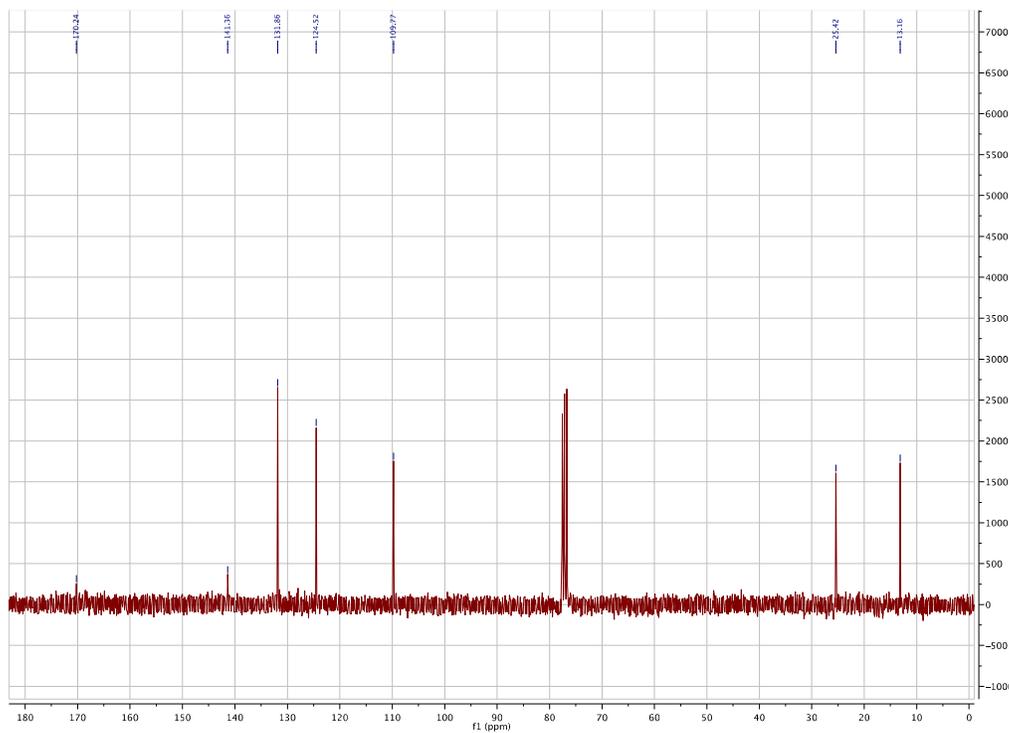
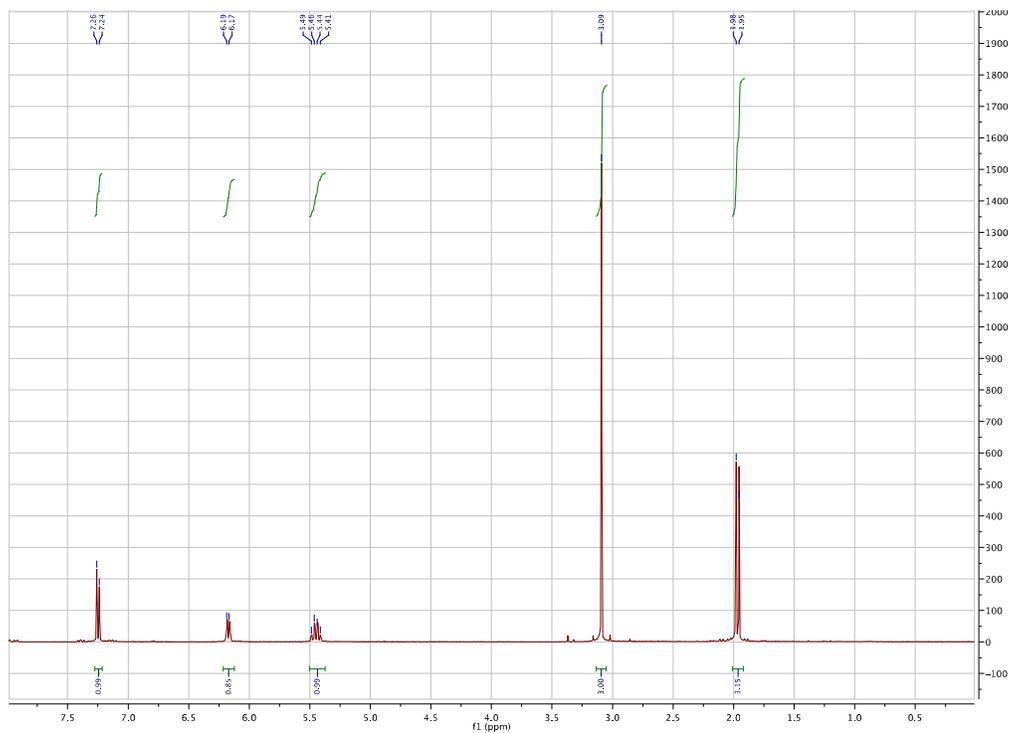
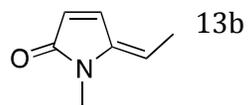


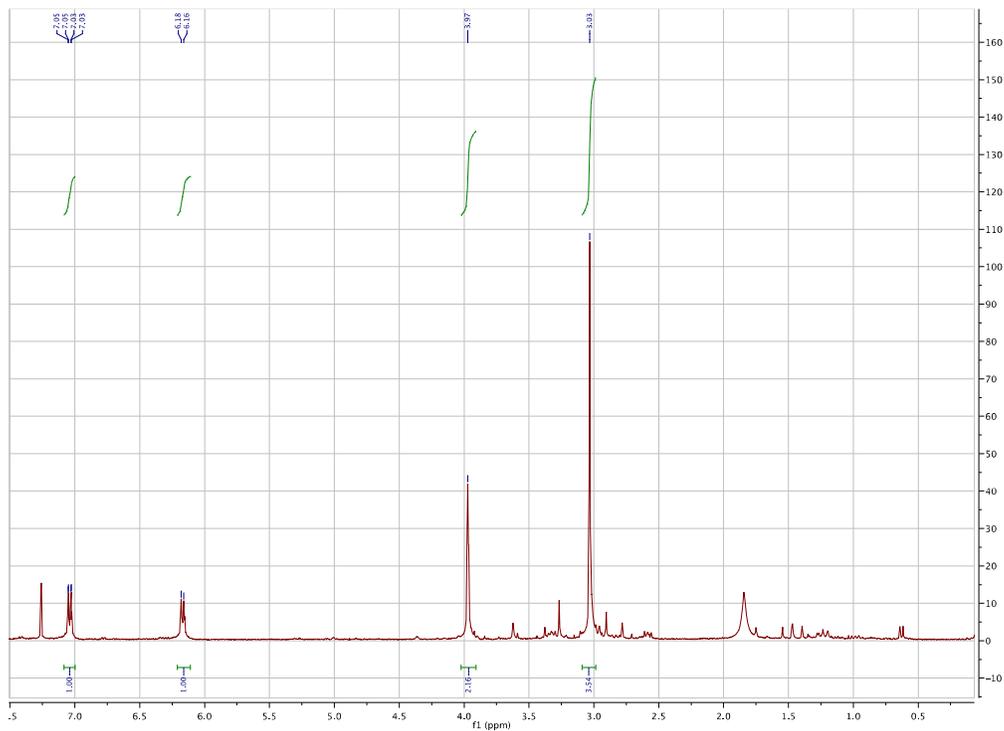
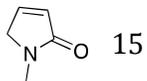
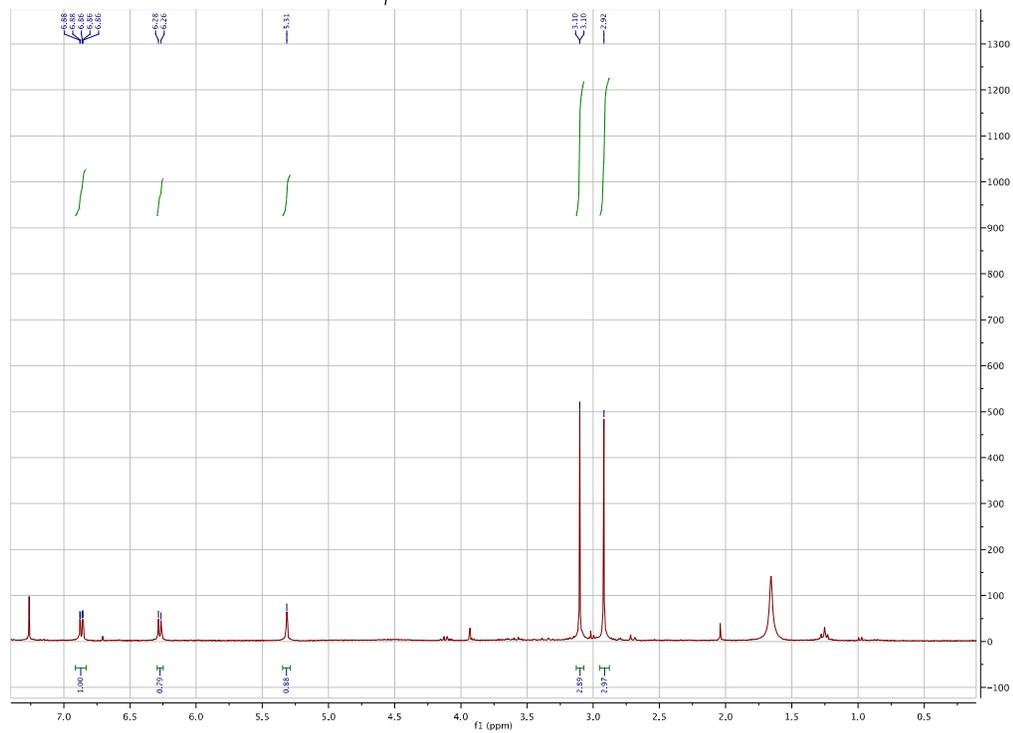
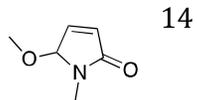


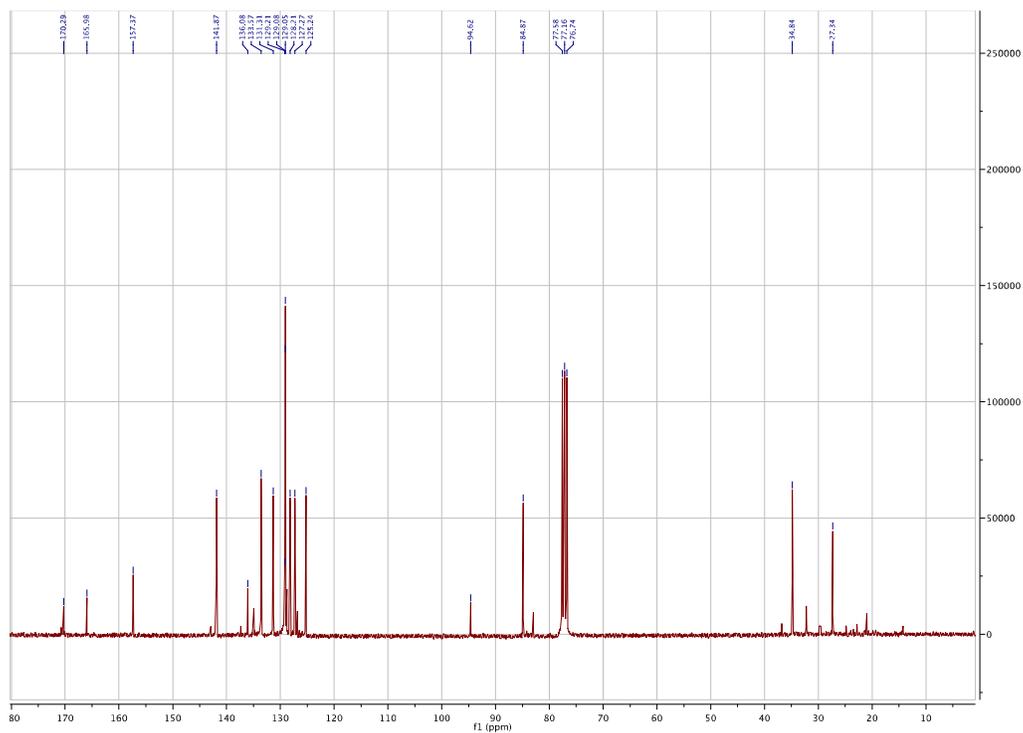
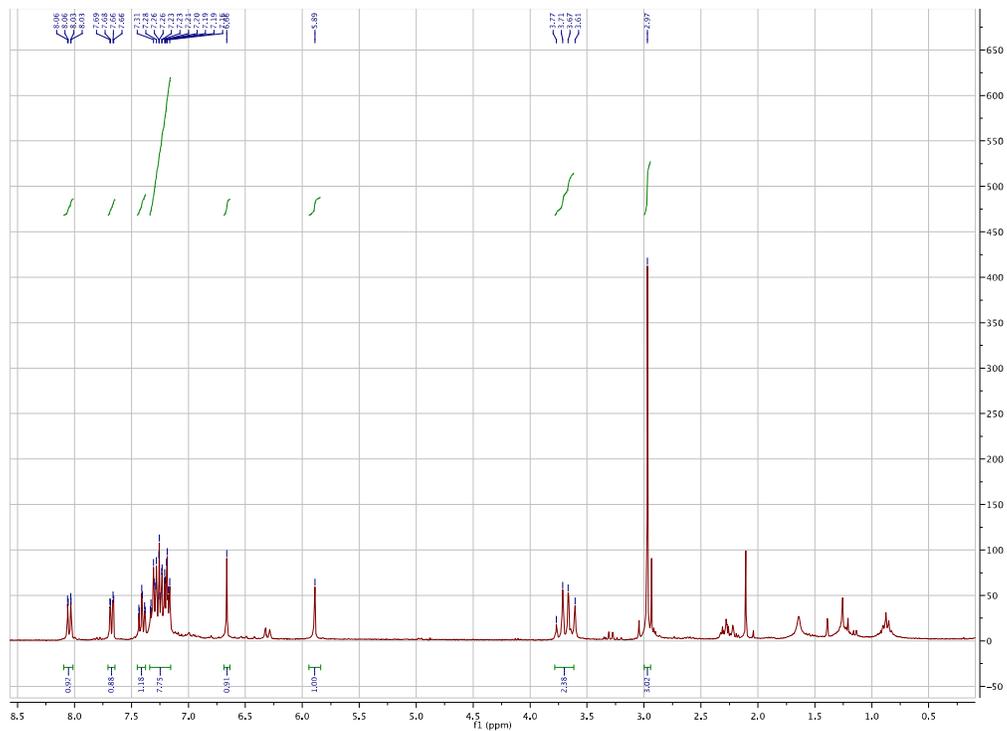
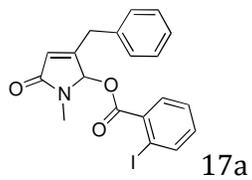


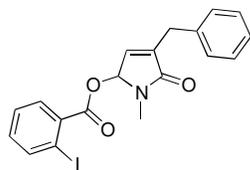












17b

