SUPPORTING INFORMATION

Cyclopropanation vs. single-carbon insertion of pyrrole-2,3-diones with sulfonium ylides: synthesis of functionalized 2-azabicyclo[3.1.0]hexanes and pyridine-2,3-diones

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General information

^{1}H, ^{13}C NMR spectra were recorded on a Bruker Avance III HD spectrometer (at 400, 101 MHz, respectively) at 40 °C (313K) in $CDCl_3$ and DMSO-d_6 using the residual solvent peak ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm; DMSO-d_6: δH = 2.50 ppm; δC = 39.52 ppm) as internal standards. Splitting patterns of apparent multiplets were designated as s (singlet), d (doublet), t (triplet), q(quartet), m (multiplet), br (broadened). FT-IR spectra were recorded on a Perkin–Elmer Spectrum Two spectrometer from mulls in mineral oil. Melting points were measured with Mettler Toledo MP70 Melting Point apparatus. Thin-layer chromatography (TLC) was performed on silica gel 60 F254 plates (Merck); spots were visualized with UV light (254 nm / 365 nm) or iodine vapors. Flash column chromatography was performed on silica gel (Acros Organics, 35–70 μm). HPLC analyses were performed on Hitachi Chromaster equipped with PDA detector Hitachi Chromaster 5430 (NUCLEODUR C18 Gravity column 3 μm, 4 × 150 mm). The ee value was determined by HPLC on an Agilent 1260 instrument equipped with a diode array detector (254 nm); analysis conditions: Daicel CHIRALPAK IA-U column (100 x 3 mm, 1.6 um); mobile phase: hexane: isopropyl alcohol 50:50; flow rate 0.2 mL/min. HRMS were recorded on Bruker MicroTOF (ESI+). Elemental analyses were carried out on a Vario MICRO Cube analyzer. Thermal analysis was performed on NETZSCH Jupiter STA 449 F1. X-ray structural analyses were performed on an Xcalibur Ruby diffractometer using a Mo X-ray source (MoKα 0.71073 Å), by scanning at 295(2) K. All solvents and reagents were purchased from commercial vendors and were used as received. Solvent drying was performed by standard methods. MeCN was stored over 4Å molecular sieves.

Synthesis of starting materials

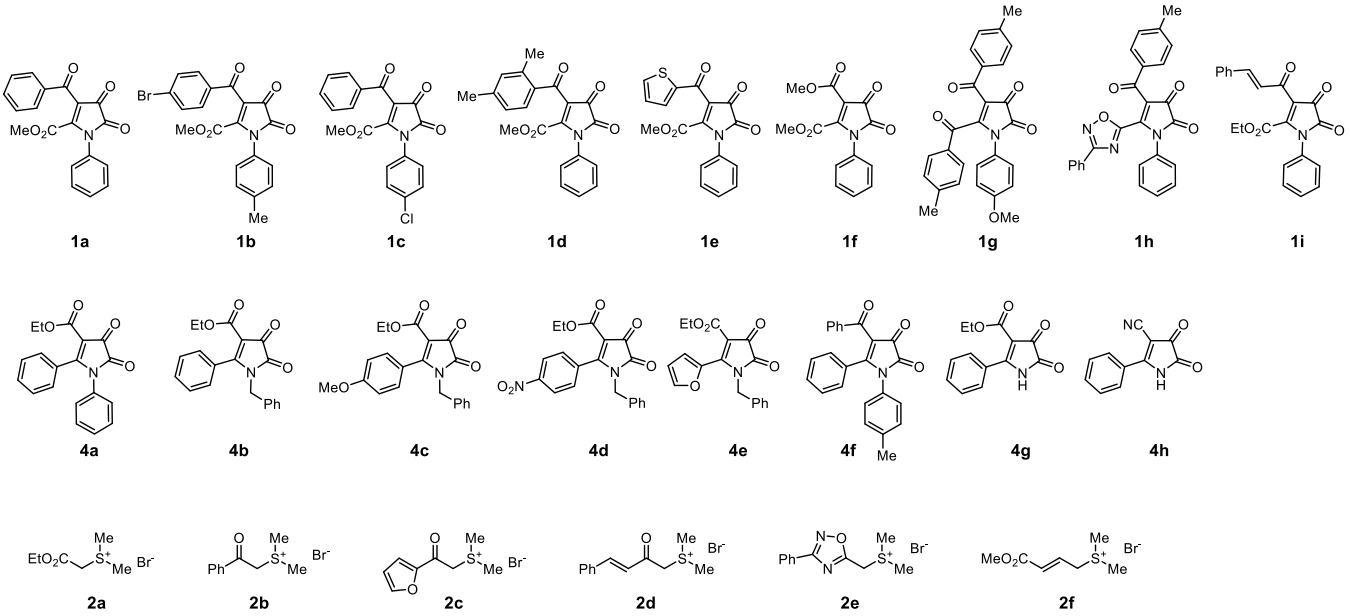
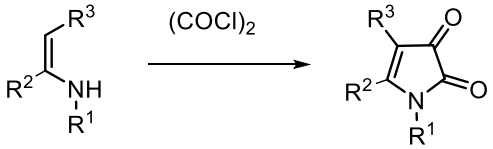


Figure S1. Numbering the pyrrole-2,3-diones **1**, **4** and sulfonium salts **2** used in the present study

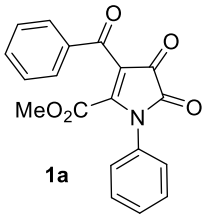
General procedure SM1 (synthesis of pyrrole-2,3-diones 1): oxalyl chloride (0.94 mL, 11 mmol) is added dropwise to corresponding enamine (10 mmol) in dry $CHCl_3$ (10 mL) and the mixture is refluxed for 1–2 h (**Scheme S1**). Warm hexanes (10 mL) are added to the reaction mixture. The formed crystalline product is filtered and washed with hexanes to give **1a–e**,**1h** [1,2]**, 1f** [3], **1g** [4], **1i** [5] as an orange-red powder.



Scheme S1. Synthesis of pyrrole-2,3-diones **1** and **4**

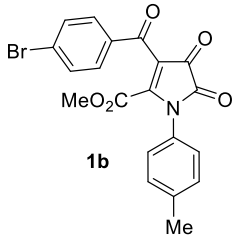
General procedure SM2 (synthesis of pyrrole-2,3-diones 4): a solution of oxalyl chloride (1.02 mL, 12 mmol) in dry Et_2O (10 mL) is added dropwise to the corresponding enamine (10 mmol) in dry Et_2O (30 mL) and the mixture is stirred at RT for 2-24 h (**Scheme S1**). The formed crystalline product is filtered and washed with hexanes to give **4a–e**, **4g** [6], **4f** [7], **4h** [8] as an orange-yellow powder.

Spectral data for pyrrole-2.3-diones **1** and **4**



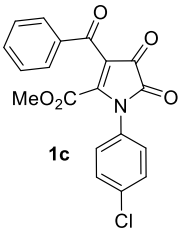
1a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.76 (m, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.43 (m, 5H), 7.40 – 7.28 (m, 2H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.6, 177.8, 166.5, 160.3, 155.4, 136.5, 134.0, 132.5, 130.0 (2C), 129.9, 129.8 (2C), 128.6 (2C), 126.2 (2C), 111.5, 53.9.



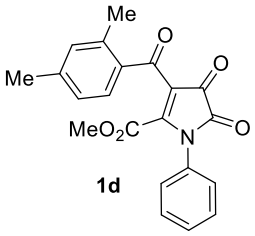
1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.4, 177.5, 167.7, 160.3, 155.6, 140.4, 135.2, 131.9 (2C), 131.3 (2C), 130.6 (2C), 129.6, 129.2, 126.1 (2C), 110.6, 54.0, 21.4.



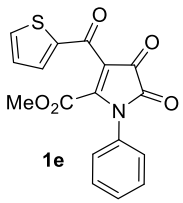
1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 8.1 Hz, 1H), 7.52 – 7.45 (m, 4H), 7.30 – 7.21 (m, 2H), 3.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.5, 177.6, 165.4, 160.1, 155.2, 136.4, 136.0, 134.1, 130.9, 130.3 (2C), 129.8 (2C), 128.6 (2C), 127.6 (2C), 112.0, 54.1.



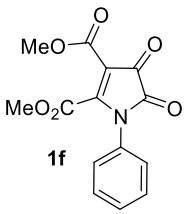
1d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (m, 3H), 7.41 – 7.35 (m, 1H), 7.35 – 7.24 (m, 2H), 7.14 – 6.98 (m, 2H), 3.72 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.1, 177.9, 165.7, 160.3, 155.4, 142.9, 138.7, 133.8, 132.5, 132.4, 130.7, 129.9 (2C), 129.8, 126.2 (2C), 126.1, 112.2, 53.8, 21.6, 20.5.



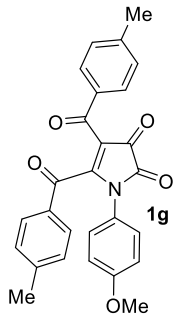
1e

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 3.9 Hz, 1H), 7.75 (d, *J* = 5.1 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.34 – 7.29 (m, 2H), 7.25 – 7.18 (m, 1H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.1, 176.3, 167.8, 160.4, 155.5, 143.3, 135.7, 135.6, 132.2, 130.0 (3C), 128.7, 126.4 (2C), 110.8, 54.0.

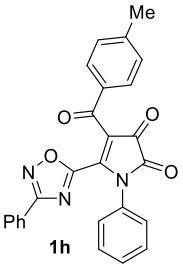


1f

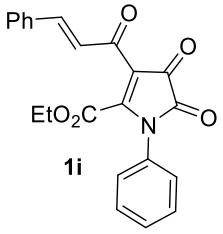
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.42 (m, 3H), 7.32 – 7.22 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.6, 166.7, 160.3, 159.8, 155.1, 132.1, 130.04, 130.01 (2C), 126.5 (2C), 102.1, 54.0, 52.4.



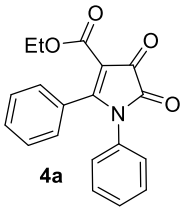
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.20 (m, 4H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 3.74 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.2, 185.2, 177.8, 174.9, 160.4, 156.7, 146.8, 144.7, 134.1, 132.0, 130.1 (2C), 130.1 (2C), 129.1 (2C), 129.0 (2C), 128.5 (2C), 126.9, 115.1, 115.0 (2C), 55.6, 22.1, 21.9.



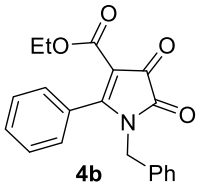
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.72 (m, 4H), 7.55 – 7.34 (m, 6H), 7.32 – 7.18 (m, 4H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.6, 178.8, 169.3, 166.0, 155.1, 155.0, 145.6, 134.0, 132.7, 132.1, 129.9, 129.9, 129.6, 129.1, 127.7, 127.1, 125.3, 116.5, 21.9.



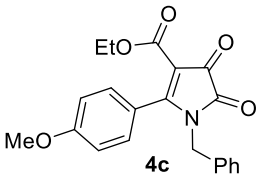
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 15.7 Hz, 1H), 7.72 – 7.62 (m, 3H), 7.53 – 7.45 (m, 3H), 7.45 – 7.39 (m, 3H), 7.36 – 7.30 (m, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.5, 178.7, 167.3, 160.0, 155.8, 145.1, 134.7, 131.9, 131.1, 130.1, 129.9 (2C), 129.11 (2C), 129.08 (2C), 126.8 (2C), 123.0, 109.7, 63.7, 13.8.



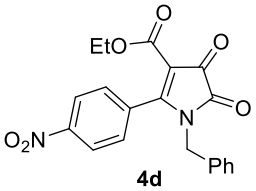
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 1H), 7.36 – 7.22 (m, 7H), 7.02 – 6.91 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.1, 175.7, 161.0, 156.8, 132.8, 132.1, 129.4 (2C), 129.3 (2C), 128.7, 128.2 (2C), 127.70 (2C), 127.68, 105.0, 60.9, 14.1.



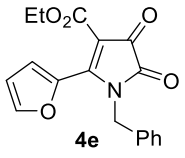
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.09 (m, 5H), 6.92 – 6.75 (m, 2H), 4.66 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.4, 177.8, 160.6, 157.9, 135.3, 131.7, 128.9 (2C), 128.5 (2C), 128.2, 128.1, 127.9 (2C), 127.6 (2C), 104.6, 60.5, 45.1, 14.0.



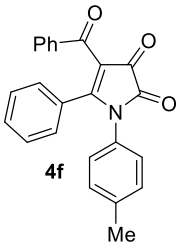
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 5H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.92 – 6.87 (m, 2H), 4.72 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.3, 177.9, 163.0, 161.2, 158.6, 135.6, 130.6 (2C), 128.9 (2C), 128.2, 127.5 (2C), 119.7, 114.1 (2C), 104.5, 60.6, 55.7, 45.3, 14.2.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.31 – 7.17 (m, 3H), 6.87 – 6.73 (m, 2H), 4.66 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 175.3, 160.2, 156.9, 149.5, 134.8, 134.2, 129.2 (2C), 129.2 (2C), 128.7, 127.4 (2C), 123.6 (2C), 104.9, 61.0, 45.3, 14.1.

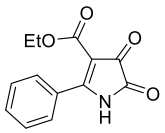


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.9, 0.7 Hz, 1H), 7.78 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.30 – 7.18 (m, 3H), 7.07 – 7.01 (m, 2H), 6.66 (dd, *J* = 3.9, 1.7 Hz, 1H), 5.16 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.7, 161.8, 160.7, 158.7, 148.3, 141.3, 135.9, 128.9 (2C), 128.1, 127.4, 126.7 (2C), 114.3, 102.3, 61.1, 46.6, 14.4.



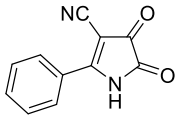
4f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.25 – 7.18 (m, 4H), 7.15 – 7.08 (m, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.5, 179.0, 173.9, 157.5, 138.8, 137.3, 133.5, 132.4, 130.4, 130.1 (2C), 129.7 (2C), 129.5 (2C), 128.6 (2C), 128.5 (2C), 128.4, 127.6, 127.2 (2C), 113.1, 21.2.



4g

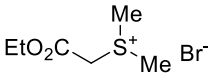
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.82 – 7.74 (m, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.5, 172.5, 161.5, 157.9, 134.3, 129.1 (2C), 129.0 (2C), 128.3, 104.1, 61.1, 14.2.



4h

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.21 (s, 1H), 8.14 – 8.06 (m, 2H), 7.92 – 7.81 (m, 1H), 7.77 – 7.67 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 178.9, 173.9, 159.2, 135.6, 129.6 (2C), 128.5 (2C), 126.3, 113.6, 81.9.

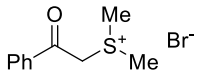
General procedure SM3 (synthesis of sulfonium salts): Me_2S (1.5 equiv.) is added to the solution of the corresponding alkyl bromides (1 equiv.) in acetone (1M solution) and the solution is stirred at RT for 2 days. The resulting precipitate is filtered, washed with acetone and dried to give sulfonium salts **2a–c** [9, 10], **2f** [11] as a white powder.



2a

Sulfonium salt **2a**: according to **GP SM3** from ethyl bromoacetate and dimethyl sulfide.

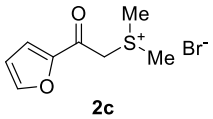
^{1}H NMR (400 MHz, DMSO-d_6) δ 4.76 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.06 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.5, 62.6, 44.3, 24.7, 13.7.



2b

Sulfonium salt **2b**: according to **GP SM3** from phenacyl bromide and dimethyl sulfide.

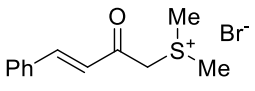
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 – 7.99 (m, 2H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.69 – 7.59 (m, 2H), 5.71 (s, 2H), 3.07 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 191.3, 134.8, 133.8, 129.0, 128.5, 52.7, 24.5.



2c

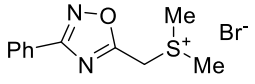
Sulfonium salt **2c**: according to **GP SM3** from 2-bromo-1-(furan-2-yl)ethan-1-one and dimethyl sulfide.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.73 (dd, *J* = 3.7, 0.7 Hz, 1H), 6.85 (dd, *J* = 3.7, 1.7 Hz, 1H), 5.39 (s, 2H), 3.06 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 178.3, 149.7, 149.5, 121.7, 113.2, 50.5.



2d

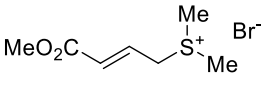
Sulfonium salt **2d**: $CuBr_2$ (2.669 g, 1.05 equiv.) is added to the solution of benzylideneacetone (1.661 g, 1 equiv.) in 20 mL EtOAc at room temperature. The resulting solution is stirred at RT for 2 days, filtered through Celite and washed with 10 mL EtOAc. Me_2S (1.25 mL, 1.5 equiv.) is added to the filtered EtOAc solution and the solution is stirred at RT for 2 days. The resulting precipitate is filtered, washed with EtOAc and dried. Brownish solid, 740 mg (23% in 2 steps).
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (d, *J* = 16.4 Hz, 1H), 7.82 – 7.75 (m, 2H), 7.54 – 7.40 (m, 3H), 7.03 (d, *J* = 16.4 Hz, 1H), 5.25 (s, 2H), 2.99 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 190.8, 146.6, 133.5, 131.3, 129.0 (2C), 128.7 (2C), 123.9, 52.6, 24.4.



2e

Sulfonium salt **2e**: Me_2S (111 µL, 1.5 equiv.) is added to the solution of 5-(bromomethyl)-3-phenyl-1,2,4-oxadiazole [12] (239 mg, 1 equiv.) in acetone (1 mL) and the solution is stirred at RT for 2 days. The resulting precipitate is filtered, washed with acetone and dried. Off-white solid, 168 mg (56%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 – 8.24 (m, 2H), 8.02 – 7.79 (m, 3H), 5.61 (s, 2H), 3.43 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.3, 168.0, 131.8, 129.2 (2C), 127.1 (2C), 125.4, 35.7, 25.0.



2f

Sulfonium salt **2f**: according to **GP SM3** from methyl (*E*)-4-bromobut-2-enoate and dimethyl sulfide

^{1}H NMR (400 MHz, DMSO-d_6) δ 6.40 (dt, *J* = 15.4, 7.6 Hz, 1H), 5.93 (dt, *J* = 15.5, 1.2 Hz, 1H), 3.96 (dd, *J* = 7.6, 1.3 Hz, 2H), 3.26 (s, 3H), 2.51 (s, 6H).**^{13}C NMR** (101 MHz, DMSO-d_6) δ 164.6, 134.1, 129.4, 51.7, 41.8, 23.8.

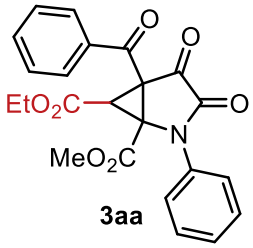
Synthesis of products 3, 4 and 6

General procedure A (cyclopropanation of pyrrole-2,3-diones): NEt_3 (1.1 equiv.) is added to the solution of the pyrrole-2,3-dione **1** (1 equiv.) and the sulfonium salt **2** (1.05 equiv.) in dry acetonitrile (1.5 mL / 0.3 mmol of **1**) and the mixture is stirred at room temperature for 30-60 min. The solvent is then evaporated under reduced pressure and the residue is purified by crystallization or flash column chromatography to afford the cyclopropane **3** (loading in the minimum volume of dichloromethane).

General procedure B (ring-expansion of pyrrole-2,3-diones): NEt_3 (1.1 equiv.) is added to the reaction vial containing a solution of the pyrrole-2,3-dione **4** (1 equiv.) and the sulfonium salt **2** (1.05 equiv.) in dry acetonitrile (1.5 mL / 0.3 mmol of **4**) and the mixture is stirred at room temperature for 30 min, then the vial is placed in a heating block preheated to 80 °C for 1-2 h (TLC or HPLC control). The solvent is then evaporated under reduced pressure and the residue is purified by crystallization to afford the pyridine-2,3-dione **5**. Alternatively, Boc_2O (2 equiv.) is added to the reaction vial at room temperature, followed by a catalytic amount of DMAP and the mixture is stirred overnight at RT. The solvent is then evaporated and the residue is purified by flash column chromatography (loading in the minimum volume of dichloromethane) to give *O*-Boc pyridine-2,3-dione **5-Boc**.

General procedure C (ring-opening of cyclopropanes **3**): concentrated H_2SO_4 (1 mL per 0.3 mmol of cyclopropane **3**) is added to the test tube containing cyclopropane **3** and the solution stirred at room temperature for 2 h. Ice water (20 mL) is added to the solution cooled in an ice-water bath and the resulting solution is extracted with ethyl acetate (30 mL). The water phase is washed with additional 10 mL of EtOAc and the combined EtOAc phase is washed with water (20 mL×3) until neutral medium is reached. EtOAc is evaporated under reduced pressure and the residue is recrystallized to afford pyridine-2,3-dione **6.**

6-Ethyl 1-methyl (1*R,5*S**,6*R**)-5-benzoyl-3,4-dioxo-2-phenyl-2-azabicyclo[3.1.0]hexane-1,6-dicarboxylate (3aa)**

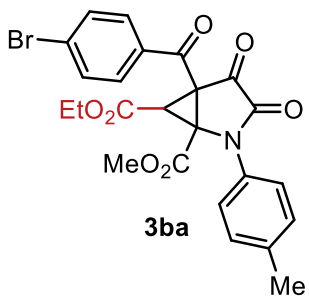


3aa

According to **GP A** from pyrrole-2,3-dione **1a** (0.3 mmol scale) and sulfonium salt **2a**. Isolation by flash column chromatography (PhMe/EtOAc 12/1) gave a white powder (110 mg, 87%). Running the reaction on the 2 mmol scale and isolating by crystallization from EtOH gave 708 mg (84%) of product **3aa**. Scale-up reaction (5 mmol scale) gave 1.925 g (91%) of product **3aa** after crystallization from EtOH. mp 159–161 °C, R_f = 0.6 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.61 – 7.49 (m, 4H), 7.48 – 7.41 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 1H), 3.58 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.6, 185.1, 165.4, 164.2, 156.7, 136.7, 135.0, 134.2, 129.7 (2C), 129.6 (2C), 129.3 (2C), 127.1, 120.1 (2C), 63.9, 54.8, 54.0, 46.8, 45.7, 13.9. **IR** (mineral oil), cm^{-1}: 1782, 1755, 1742, 1723, 1670, 1595, 1579. HRMS (ESI): m/z calcd for $C_{23}H_{19}NO_7$: 444.1054 [M+Na]+; found: 444.1055.

6-Ethyl 1-methyl (1*R,5*S**,6*R**)-5-(4-bromobenzoyl)-3,4-dioxo-2-(p-tolyl)-2-azabicyclo[3.1.0]hexane-1,6-dicarboxylate (3ba)**

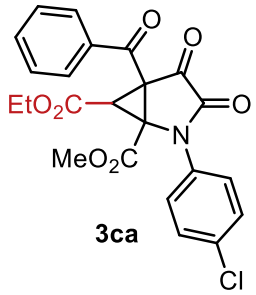


3ba

According to **GP A** from pyrrole-2,3-dione **1b** (0.5 mmol scale) and sulfonium salt **2a**. Isolation by crystallization from EtOH gave a white powder (188 mg, 73%). mp 213–215 °C, R_f = 0.67 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.63 (m, 4H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.18 (d, *J* = 7.2 Hz, 2H), 4.10 (s, 1H), 3.62 (s, 3H), 2.37 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.8, 185.0, 165.2, 164.2, 156.5, 137.2, 134.0, 133.1, 132.8 (2C), 131.1 (2C), 130.7, 130.2 (2C), 120.0 (2C), 64.0, 54.8, 54.1, 46.5, 45.8, 21.2, 14.0. **IR** (mineral oil), cm^{-1}: 1782, 1750, 1724, 1676, 1581, 1567, 1515. HRMS (ESI): m/z calcd for $C_{24}H_{20}BrNO_7$: 536.0315 [M+Na]+; found: 536.0314.

6-Ethyl 1-methyl (1*R,5*S**,6*R**)-5-benzoyl-2-(4-chlorophenyl)-3,4-dioxo-2-azabicyclo[3.1.0]hexane-1,6-dicarboxylate (3ca)**

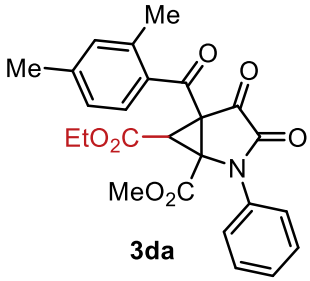


3ca

According to **GP A** from pyrrole-2,3-dione **1c** (0.3 mmol scale) and sulfonium salt **2a**. Isolation by crystallization from EtOH gave a white powder (113 mg, 82%). mp 167–169 °C, R_f = 0.6 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 2H), 7.72 – 7.62 (m, 1H), 7.57 – 7.49 (m, 4H), 7.47 – 7.37 (m, 2H), 4.18 (q, *J* = 6.8 Hz, 2H), 4.13 (s, 1H), 3.60 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.3, 184.6, 165.3, 164.0, 156.6, 135.2, 135.1, 134.1, 132.7, 129.7 (2C), 129.7 (2C), 129.4 (2C), 121.3 (2C), 64.0, 54.6, 54.1, 46.8, 45.5, 14.0. **IR** (mineral oil), cm^{-1}: 1781, 1758, 1751, 1721, 1673, 1595, 1580. HRMS (ESI): m/z calcd for $C_{23}H_{18}ClNO_7$: 478.0664 [M+Na]+; found: 478.0669.

6-Ethyl 1-methyl (1*R,5*S**,6*R**)-5-(2,4-dimethylbenzoyl)-3,4-dioxo-2-phenyl-2-azabicyclo[3.1.0]hexane-1,6-dicarboxylate (3da)**

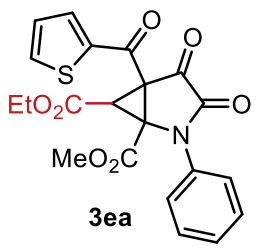


3da

According to **GP A** from pyrrole-2,3-dione **1d** (0.3 mmol scale) and sulfonium salt **2a**. Isolation by flash column chromatography (PhMe/EtOAc 15/1) gave a viscous pale-yellow oil (128 mg, 95%). R_f = 0.6 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.9 Hz, 3H), 7.45 – 7.36 (m, 2H), 7.25 (s, 1H), 4.27 (q, *J* = 6.9 Hz, 2H), 4.26 (s, 1H), 3.74 (s, 3H), 2.65 (s, 3H), 2.50 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.7, 185.6, 165.5, 164.3, 156.9, 144.7, 141.9, 136.8, 133.7, 131.4, 131.1, 129.5 (2C), 127.2, 127.0, 120.1 (2C), 63.7, 55.5, 54.0, 48.2, 45.9, 21.8, 21.7, 13.9. **IR** ($CHCl_3$), cm^{-1}: 1770, 1745, 1678, 1612, 1497. HRMS (ESI): m/z calcd for $C_{25}H_{23}NO_7$: 472.1367 [M+Na]+; found: 472.1365.

6-Ethyl 1-methyl (1*R,5*R**,6*R**)-3,4-dioxo-2-phenyl-5-(thiophene-2-carbonyl)-2-azabicyclo[3.1.0]hexane-1,6-dicarboxylate (3ea)**

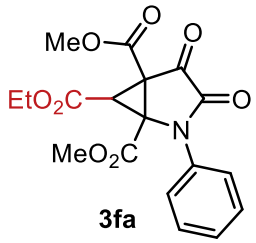


3ea

According to **GP A** from pyrrole-2,3-dione **1e** (0.3 mmol scale) and sulfonium salt **2a**. Isolation by crystallization from EtOH gave a pale-beige powder (83 mg, 64%). mp 134–135 °C, R_f = 0.5 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.64 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.20 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.19 (s, 1H), 4.17 (d, *J* = 7.1 Hz, 2H), 3.60 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.9, 178.5, 165.3, 164.0, 156.7, 141.2, 136.9, 136.6, 135.5, 129.6 (2C), 129.0, 127.1, 120.1 (2C), 63.9, 54.7, 54.0, 47.1, 45.8, 13.9. **IR** (mineral oil), cm^{-1}: 1776, 1756, 1742, 1715, 1661, 1589, 1516, 1496. HRMS (ESI): m/z calcd for $C_{21}H_{17}NO_7S$: 450.0618 [M+Na]+; found: 450.0618.

6-Ethyl 1,5-dimethyl (1*R,5*R**,6*R**)-3,4-dioxo-2-phenyl-2-azabicyclo[3.1.0]hexane-1,5,6-tricarboxylate (3fa)**

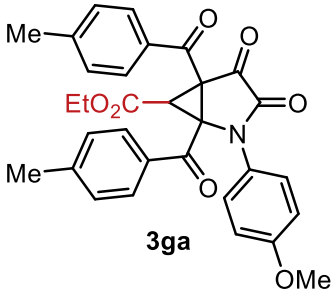


3fa

According to **GP A** from pyrrole-2,3-dione **1f** (0.3 mmol scale) and sulfonium salt **2a**. Isolation by flash column chromatography (PhMe/EtOAc 12/1) gave a white powder (83 mg, 73%). R_f = 0.5 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.38 – 7.31 (m, 2H), 7.25 – 7.19 (m, 1H), 4.09 (s, 1H), 4.05 (qd, *J* = 7.1, 1.1 Hz, 2H), 3.78 (s, 3H), 3.63 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.6, 164.9, 163.7, 162.7, 156.6, 136.5, 129.6, 127.2 (2C), 120.2 (2C), 63.8, 55.1, 54.2 (2C), 45.4, 41.9, 13.9. **IR** (mineral oil), cm^{-1}: 1776, 1746, 1724, 1596, 1497. HRMS (ESI): m/z calcd for $C_{18}H_{17}NO_8$: 398.0846 [M+Na]+; found: 398.0844.

Ethyl (1*R,5*S**,6*R**)-2-(4-methoxyphenyl)-1,5-bis(4-methylbenzoyl)-3,4-dioxo-2-azabicyclo[3.1.0]hexane-6-carboxylate (3ga)**

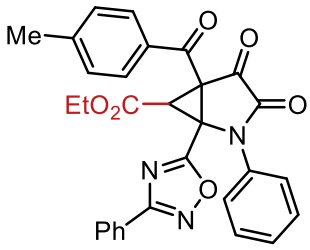


3ga

According to **GP A** from pyrrole-2,3-dione **1g** (0.5 mmol scale) and sulfonium salt **2a**. Isolation by crystallization from EtOH gave a yellow powder (199 mg, 76%). mp 178–180 °C, R_f = 0.7 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 9.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 9.1 Hz, 2H), 4.25 (s, 1H), 4.22 (qd, *J* = 7.1, 1.1 Hz, 2H), 3.71 (s, 3H), 2.45 (s, 3H), 2.33 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.4, 186.3, 185.3, 166.0, 158.2, 156.7, 146.5, 144.9, 132.9, 132.3, 130.6 (2C), 129.9 (2C), 129.3 (2C), 129.2, 128.9 (2C), 122.0 (2C), 114.6 (2C), 63.8, 60.0, 55.5, 49.8, 45.6, 22.0, 21.8, 14.0. **IR** (mineral oil), cm^{-1}: 1766, 1735, 1674, 1602, 1571, 1510. HRMS (ESI): m/z calcd for $C_{31}H_{27}NO_7$: 548,1680 [M+Na]+; found: 548.1675.

Ethyl (1*R,5*S**,6*R**)-5-(4-methylbenzoyl)-3,4-dioxo-2-phenyl-1-(3-phenyl-1,2,4-oxadiazol-5-yl)-2-azabicyclo[3.1.0]hexane-6-carboxylate (3ha)**

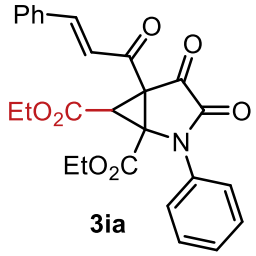


3ha

According to **GP A** from pyrrole-2,3-dione **1h** (0.3 mmol scale) and sulfonium salt **2a**. Isolation by crystallization from EtOH gave an off-white powder (134 mg, 85%). mp 188–190 °C, R_f = 0.8 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.51 – 7.45 (m, 1H), 7.44 – 7.37 (m, 4H), 7.31 – 7.21 (m, 3H), 4.51 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.5, 184.5, 170.9, 168.9, 165.2, 156.6, 146.5, 135.7, 131.9, 131.6, 130.0 (2C), 129.9 (2C), 129.8 (2C), 129.0 (2C), 127.7 (2C), 127.6, 125.8, 120.9 (2C), 64.2, 51.2, 47.4, 46.0, 22.0, 14.0. **IR** (mineral oil), cm^{-1}: 1778, 1762, 1727, 1680, 1600, 1525. HRMS (ESI): m/z calcd for $C_{30}H_{23}N_3O_6$: 544.1479 [M+Na]+; found: 544.1474.

Diethyl (1*R,5*S**,6*R**)-5-cinnamoyl-3,4-dioxo-2-phenyl-2-azabicyclo[3.1.0]hexane-1,6-dicarboxylate (3ia)**

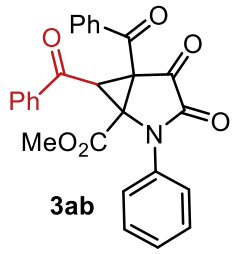


3ia

According to **GP A** from pyrrole-2,3-dione **1i** (1.0 mmol scale) and sulfonium salt **2a**. Isolation by recrystallization from EtOH/Me_2CO gave an off-white powder (359 mg, 78%). mp 169–171 °C, R_f = 0.64 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 15.9 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.57 – 7.51 (m, 2H), 7.49 – 7.37 (m, 5H), 7.33 – 7.25 (m, 1H), 7.14 (d, *J* = 15.9 Hz, 1H), 4.21 (s, 1H), 4.20 – 4.05 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.2, 185.2, 165.4, 163.1, 156.8, 147.7, 136.4, 133.8, 131.9, 129.5 (2C), 129.3 (2C), 129.2 (2C), 127.2, 122.6, 120.5 (2C), 63.7, 63.6, 56.4, 46.8 (2C), 13.9, 13.8. **IR** (mineral oil), cm^{-1}: 1778, 1741, 1726, 1684, 1646, 1604, 1574, 1495. Anal. Calcd for $C_{26}H_{23}NO_7$: C 67.67; H 5.02; N 3.04. Found: C 68.00; H 5.01; N 3.29.

Methyl (1*R,5*S**,6*R**)-5,6-dibenzoyl-3,4-dioxo-2-phenyl-2-azabicyclo[3.1.0]hexane-1-carboxylate (3ab)**

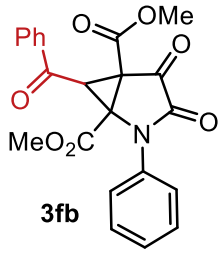


3ab

According to **GP A** from pyrrole-2,3-dione **1a** (0.3 mmol scale) and sulfonium salt **2b**. Isolation by crystallization from EtOH gave an off-white powder (105 mg, 77%). mp 184–186 °C, R_f = 0.1 (PhMe/EtOAc 4/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 7.92 – 7.82 (m, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.59 – 7.47 (m, 4H), 7.40 – 7.30 (m, 2H), 7.27 – 7.21 (m, 2H), 7.19 – 7.11 (m, 1H), 5.16 (s, 1H), 3.67 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.9, 187.0, 185.5, 164.8, 157.0, 136.7, 135.4, 135.0, 134.6, 134.3, 130.0 (2C), 129.5 (4C), 129.4 (2C), 129.3 (2C), 126.8, 120.3 (2C), 57.0, 54.2, 50.2, 48.2. **IR** (mineral oil), cm^{-1}: 1769, 1742, 1730, 1670, 1590, 1576, 1495. HRMS (ESI): m/z calcd for $C_{27}H_{19}NO_6$: 476.1105 [M+Na]+; found: 476.1104.

Dimethyl (1*R,5*R**,6*R**)-6-benzoyl-3,4-dioxo-2-phenyl-2-azabicyclo[3.1.0]hexane-1,5-dicarboxylate (3fb)**

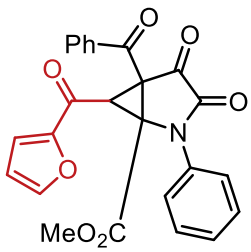


3fb

According to **GP A** from pyrrole-2,3-dione **1f** (0.3 mmol scale) and sulfonium salt **2b**. Isolation by crystallization from EtOH gave a white powder (95 mg, 78%). mp 190–192 °C, R_f = 0.35 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.18 (m, 4H), 7.13 (t, *J* = 7.2 Hz, 1H), 5.18 (s, 1H), 3.86 (s, 3H), 3.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.5, 183.9, 164.1, 163.2, 156.8, 136.4, 135.3, 134.7, 129.4 (2C), 129.4 (2C), 129.3 (2C), 126.9, 120.5 (2C), 57.5, 54.3, 54.1, 49.9, 43.0. **IR** (mineral oil), cm^{-1}: 1783, 1736, 1660, 1595, 1579, 1497. HRMS (ESI): m/z calcd for $C_{22}H_{17}NO_7$: 430.0897 [M+H]+; found: 430.0896.

Methyl (1*R,5*S**,6*R**)-5-benzoyl-6-(furan-2-carbonyl)-3,4-dioxo-2-phenyl-2-azabicyclo[3.1.0]hexane-1-carboxylate (3ac)**

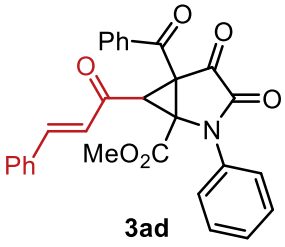


3ac

According to **GP A** from pyrrole-2,3-dione **1a** (0.3 mmol scale) and sulfonium salt **2c**. Isolation by crystallization from EtOH gave a pale-yellow powder (117 mg, 88%). mp 182–184 °C, R_f = 0.41 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.76 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.71 – 7.60 (m, 1H), 7.60 – 7.46 (m, 2H), 7.44 – 7.36 (m, 3H), 7.33 – 7.24 (m, 2H), 7.23 – 7.12 (m, 1H), 6.66 (dd, *J* = 3.7, 1.7 Hz, 1H), 5.04 (s, 1H), 3.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.9, 185.3, 177.9, 164.5, 156.8, 151.3, 148.8, 136.9, 135.0, 134.3, 129.9 (2C), 129.4 (2C), 129.3 (2C), 126.8, 120.8, 119.7 (2C), 113.9, 56.5, 54.1, 49.7, 47.8. **IR** (mineral oil), cm^{-1}: 1759, 1737, 1691, 1693, 11596, 1580, 1596, 1495. Anal. Calcd for $C_{25}H_{17}NO_7$: C 67.72; H 3.86; N 3.16. Found: C 67.82; H 4.03; N 3.18.

Methyl (1*R,5*S**,6*R**)-5-benzoyl-6-cinnamoyl-3,4-dioxo-2-phenyl-2-azabicyclo[3.1.0]hexane-1-carboxylate (3ad)**

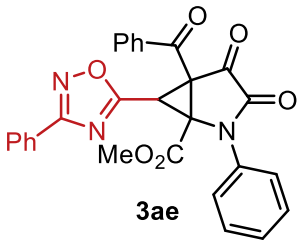


3ad

According to **GP A** from pyrrole-2,3-dione **1a** (0.3 mmol scale) and sulfonium salt **2d**. Isolation by crystallization from EtOH gave a beige powder (94 mg, 65%). mp 185–187 °C, R_f = 0.58 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 16.0 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.47 (tt, *J* = 14.3, 7.3 Hz, 7H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 16.0 Hz, 1H), 4.72 (s, 1H), 3.64 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.1, 187.0, 185.5, 164.8, 157.0, 148.1, 136.9, 135.0, 134.4, 133.6, 132.1, 129.9 (2C), 129.5 (2C), 129.4 (2C), 129.3 (2C), 129.2 (2C), 126.8, 123.6, 120.1 (2C), 56.8, 54.1, 51.5, 48.4. **IR** (mineral oil), cm^{-1}: 1759, 1732, 1691, 1660, 1590, 1572, 1495. Anal. Calcd for $C_{29}H_{21}NO_6$: C 72.64; H 4.41; N 2.92. Found: C 72.95; H 4.29; N 2.76.

Methyl (1*R,5*S**,6*R**)-5-benzoyl-3,4-dioxo-2-phenyl-6-(3-phenyl-1,2,4-oxadiazol-5-yl)-2-azabicyclo[3.1.0]hexane-1-carboxylate (3ae)**

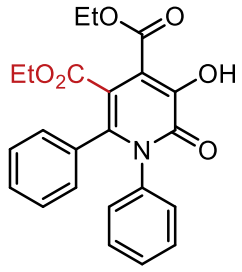


3ae

According to **GP A** from pyrrole-2,3-dione **1a** (0.3 mmol scale) and sulfonium salt **2e**. Isolation by crystallization from EtOH gave an off-white powder (105 mg, 71%). mp 195–197 °C, R_f = 0.62 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.79 (m, 4H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 2H), 7.50 – 7.33 (m, 7H), 7.30 – 7.18 (m, 1H), 4.76 (d, *J* = 1.2 Hz, 1H), 3.64 (d, *J* = 1.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.2, 184.2, 170.7, 168.9, 163.9, 156.7, 136.3, 135.3, 134.1, 132.0, 129.8 (2C), 129.7 (2C), 129.5 (2C), 129.1 (2C), 127.9 (2C), 127.4, 125.3, 120.0 (2C), 55.7, 54.2, 47.1, 38.1. **IR** (mineral oil), cm^{-1}: 1772, 1753, 1739, 1681, 1594, 1512. Anal. Calcd for $C_{28}H_{19}N_3O_6$: C 68.15; H 3.88; N 8.52. Found: C 68.27; H 4.03; N 8.51.

Diethyl 5-hydroxy-6-oxo-1,2-diphenyl-1,6-dihydropyridine-3,4-dicarboxylate (5aa)

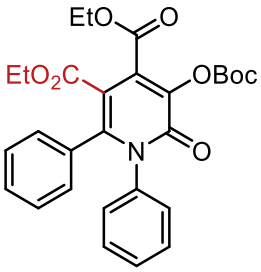


5aa

According to **GP B** from pyrrole-2,3-dione **4a** (0.3 mmol scale) and sulfonium salt **2a**. Isolation by crystallization from EtOH/H_2O gave an off-white powder (72 mg, 59%). Running the reaction on the 2 mmol scale and isolating by crystallization from EtOH gave 401 mg (49%) of product **5aa**. Scale-up reaction (4 mmol scale) gave 772 mg (47%) of product **5aa** after crystallization from EtOH/H_2O. mp 152–153 °C, R_f = 0.6 (Hexanes/EtOAc 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.28 – 7.08 (m, 6H), 7.07 – 7.03 (m, 2H), 6.98 (dt, *J* = 8.0, 1.1 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 165.9, 158.8, 147.6, 139.0, 137.6, 132.9, 130.6 (2C), 129.1 (2C), 128.85, 128.81 (2C), 128.76, 127.7 (2C), 114.9, 112.0, 62.5, 61.5, 14.1, 13.6. **IR** (mineral oil), cm^{-1}: 3215, 1722, 1645, 1615, 1592, 1551, 1489. HRMS (ESI): m/z calcd for $C_{23}H_{21}NO_6$: 408.1442 [M+H]+; found: 408.1440.

Diethyl 5-((*tert*-butoxycarbonyl)oxy)-6-oxo-1,2-diphenyl-1,6-dihydropyridine-3,4-dicarboxylate (5aa-Boc)

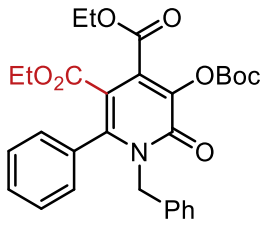


5aa-Boc

According to **GP B** from pyrrole-2,3-dione **4a** (0.3 mmol scale) and sulfonium salt **2a**. The product was converted to the *O*-Boc derivative and purified by flash column chromatography (Hexanes/EtOAc 5/1.5). Off-white powder (107 mg, 70%). mp 150–152 °C, R_f = 0.55 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.10 (m, 6H), 7.05 – 7.00 (m, 2H), 6.98 – 6.93 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 1.54 (s, 9H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7, 163.6, 157.7, 149.8, 149.0, 138.1, 137.5, 133.5, 133.4, 129.7 (2C), 129.1 (2C), 129.0 (2C), 128.95, 128.7, 127.8 (2C), 109.6, 84.6, 62.4, 61.5, 27.8 (3C), 14.2, 13.5. **IR** (mineral oil), cm^{-1}: 1768, 1737, 1677, 1621, 1592, 1544. Anal. Calcd for $C_{28}H_{29}NO_8$: C 66.26; H 5.76; N 2.76. Found: C 65.90; H 5.99; N 2.71.

Diethyl 1-benzyl-5-((*tert*-butoxycarbonyl)oxy)-6-oxo-2-phenyl-1,6-dihydropyridine-3,4-dicarboxylate (5ba-Boc)

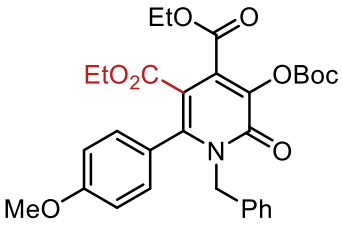


5ba-Boc

According to **GP B** from pyrrole-2,3-dione **4b** (0.3 mmol scale) and sulfonium salt **2a**. The product was converted to the *O*-Boc derivative and purified by flash column chromatography (Hexanes/EtOAc 5/1.5). Pale-yellow oil (135 mg, 86%). R_f = 0.25 (Hexanes/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.17 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.84 – 6.72 (m, 2H), 5.09 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.82 (q, *J* = 7.1 Hz, 2H), 1.57 (s, 9H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.5, 163.6, 158.0, 149.8, 149.0, 137.9, 136.0, 133.1, 132.9, 129.8, 129.1 (2C), 128.6 (2C), 128.2 (2C), 127.6, 127.0 (2C), 110.1, 84.7, 62.4, 61.5, 50.0, 27.8 (3C), 14.2, 13.5. **IR** ($CHCl_3$), cm^{-1}: 1769, 1738, 1669, 1617, 1542, 1496, 1475. Anal. Calcd for $C_{29}H_{31}NO_8$: C 66.78; H 5.99; N 2.69. Found: C 66.88; H 6.22; N 2.74.

Diethyl 1-benzyl-5-((*tert*-butoxycarbonyl)oxy)-2-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3,4-dicarboxylate (5ca-Boc)

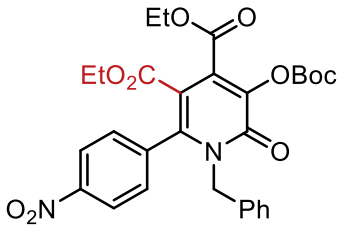


5ca-Boc

According to **GP B** from pyrrole-2,3-dione **4c** (0.3 mmol scale) and sulfonium salt **2a**. The product was converted to the *O*-Boc derivative and purified by flash column chromatography (Hexanes/EtOAc 5/1.5). Pale-beige powder (152 mg, 92%). mp 138–140 °C, R_f = 0.26 (Hexanes/EtOAc 5/1.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 3H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.86 – 6.74 (m, 4H), 5.10 (s, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.86 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.56 (s, 9H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.7, 163.6, 160.7, 158.0, 149.8, 148.8, 137.8, 136.1, 132.9, 130.5 (2C), 128.5 (2C), 127.5, 127.0 (2C), 125.0, 113.7 (2C), 110.5, 84.6, 62.4, 61.5, 55.5, 49.9, 27.8 (3C), 14.1, 13.6. **IR** (mineral oil), cm^{-1}: 1773, 1748, 1733, 1679, 1609, 1543, 1506. Anal. Calcd for $C_{30}H_{33}NO_9$: C 65.33; H 6.03; N 2.54. Found: C 65.65; H 6.18; N 2.59.

Diethyl 1-benzyl-5-((*tert*-butoxycarbonyl)oxy)-2-(4-nitrophenyl)-6-oxo-1,6-dihydropyridine-3,4-dicarboxylate (5da-Boc)

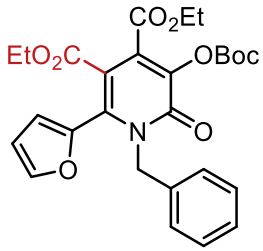


5da-Boc

According to **GP B** from pyrrole-2,3-dione **4d** (0.3 mmol scale) and sulfonium salt **2a**. The product was converted to the *O*-Boc derivative and purified by flash column chromatography (Hexanes/EtOAc 5/1.5). Pale-yellow powder (148 mg, 87%). mp 144–146 °C, R_f = 0.32 (Hexanes/EtOAc 5/1.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.0 Hz, 2H), 7.24 – 7.13 (m, 5H), 6.84 – 6.66 (m, 2H), 5.06 (s, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.87 (q, *J* = 7.1 Hz, 2H), 1.58 (d, *J* = 0.8 Hz, 9H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6, 163.3, 157.7, 149.7, 148.6, 146.9, 138.9, 138.4, 135.4, 133.2, 130.4 (2C), 128.9 (2C), 128.1, 126.7 (2C), 123.3 (2C), 109.6, 85.0, 62.6, 61.9, 50.0, 27.8 (3C), 14.2, 13.6. **IR** (mineral oil), cm^{-1}: 1765, 1736, 1668, 1614, 1603, 1542. Anal. Calcd for $C_{29}H_{30}N_2O_{10}$: C 61.48; H 5.34; N 4.94. Found: C 61.59; H 5.46; N 5.10.

Diethyl 1-benzyl-5-((tert-butoxycarbonyl)oxy)-2-(furan-2-yl)-6-oxo-1,6-dihydropyridine-3,4-dicarboxylate (5ea-Boc)

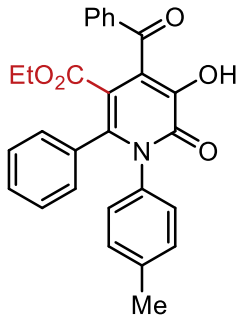


5ea-Boc

According to **GP B** from pyrrole-2,3-dione **4e** (0.3 mmol scale) and sulfonium salt **2a**. The product was converted to the *O*-Boc derivative and purified by flash column chromatography (Hexanes/EtOAc 5/1.5). Pale oil (144 mg, 94%). R_f = 0.25 (Hexanes/EtOAc 5/1.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.25 – 7.16 (m, 3H), 7.05 – 6.90 (m, 2H), 6.41 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.25 (d, *J* = 3.4 Hz, 1H), 5.17 (s, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 1.55 (s, 9H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.4, 163.1, 157.7, 149.5, 144.0, 143.5, 139.4, 137.9, 135.9, 132.5, 128.6 (2C), 127.7, 127.0 (2C), 114.1, 113.0, 111.4, 84.8, 62.5, 61.9, 50.0, 27.7 (3C), 14.1, 13.9. **IR** ($CHCl_3$), cm^{-1}: 1770, 1738, 1672, 1620, 1535. Anal. Calcd for $C_{27}H_{29}NO_9$: C 63.40; H 5.71; N 2.74. Found: C 63.80; H 5.55; N 2.67.

Ethyl 4-benzoyl-5-hydroxy-6-oxo-2-phenyl-1-(*p*-tolyl)-1,6-dihydropyridine-3-carboxylate (5fa)

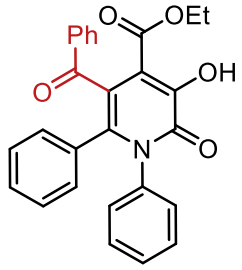


5fa

According to **GP B** from pyrrole-2,3-dione **4f** (2.0 mmol scale) and sulfonium salt **2a**. Isolation by crystallization from MeCN/H_2O gave an off-white powder (705 mg, 78%). mp 216–218 °C, R_f = 0.3 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.96 (m, 2H), 7.67 – 7.57 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.22 – 7.00 (m, 7H), 6.92 (t, *J* = 8.4 Hz, 3H), 3.72 (q, *J* = 7.2 Hz, 2H), 2.26 (s, 3H), 0.66 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.9, 165.2, 159.4, 142.2, 141.9, 138.8, 136.7, 134.9, 133.8, 133.4, 130.3 (2C), 129.8 (2C), 129.7 (2C), 128.8 (2C), 128.7, 128.4 (2C), 127.7 (2C), 124.5, 112.5, 61.4, 21.2, 13.2. **IR** (mineral oil), cm^{-1}: 3192, 1720, 1700, 1667, 1639, 1615, 1596, 1580, 1548, 1507, 1489. HRMS (ESI): m/z calcd for $C_{28}H_{23}NO_5$: 454.1649 [M+H]+; found: 454.1646.

Ethyl 5-benzoyl-3-hydroxy-2-oxo-1,6-diphenyl-1,2-dihydropyridine-4-carboxylate (5ab)

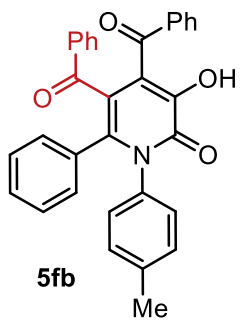


5ab

According to **GP B** from pyrrole-2,3-dione **4a** (1.0 mmol scale) and sulfonium salt **2b**. Isolation by crystallization from MeCN/H_2O gave a pale-beige powder (195 mg, 44%). mp 198–200 °C, R_f = 0.15 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.65 (d, *J* = 6.9 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.7 Hz, 2H), 7.24 – 7.12 (m, 3H), 7.02 (d, *J* = 7.0 Hz, 2H), 6.94 – 6.81 (m, 5H), 4.11 (q, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.7, 166.6, 158.5, 149.9, 138.3, 137.6, 137.0, 132.9, 131.9, 131.2 (2C), 129.1 (2C), 129.0 (2C), 128.9 (2C), 128.6, 128.6, 128.3 (2C), 127.5 (2C), 117.3, 114.2, 62.5, 13.3. **IR** (mineral oil), cm^{-1}: 3185, 1744, 1658, 1644, 1593, 1578, 1545. HRMS (ESI): m/z calcd for $C_{27}H_{21}NO_5$: 462.1312 [M+Na]+; found: 462.1314.

(5-Hydroxy-6-oxo-2-phenyl-1-(*p*-tolyl)-1,6-dihydropyridine-3,4-diyl)bis(phenylmethanone) (5fb)



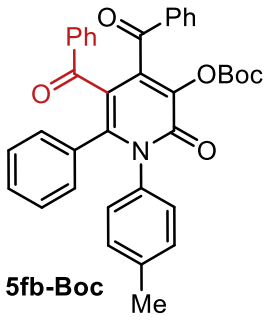
5fb

According to **GP B** from pyrrole-2,3-dione **4f** (0.3 mmol scale) and sulfonium salt **2b**. Isolation by crystallization from EtOH gave an off-white powder (93 mg, 64%). mp 258–260 °C, R_f = 0.28 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.1 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.41 (m, 4H), 7.31 – 7.20 (m, 1H), 7.15 – 7.09 (m, 3H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.93 – 6.82 (m, 5H), 2.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.2, 193.3, 159.6, 142.7, 138.9, 138.9, 138.5, 136.8, 134.8, 134.0, 132.6, 132.3, 131.3 (2C), 130.0 (2C), 129.9 (2C), 129.4 (2C), 128.7, 128.67 (2C), 128.4 (2C), 127.9 (2C), 127.7 (2C), 124.9, 120.2, 21.2. **IR** (mineral oil), cm^{-1}: 3228, 1670, 1639, 1615,

1593, 1578, 1510. HRMS (ESI): m/z calcd for $C_{32}H_{23}NO_4$: 486.1700 [M+H]+; found: 486.1702.

tert-Butyl (4,5-dibenzoyl-2-oxo-6-phenyl-1-(p-tolyl)-1,2-dihydropyridin-3-yl) carbonate (5fb-Boc)

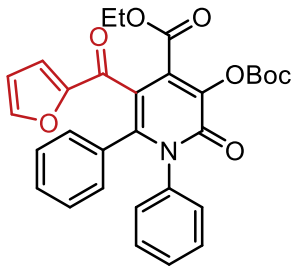


5fb-Boc

According to **GP B** from pyrrole-2,3-dione **4f** (0.3 mmol scale) and sulfonium salt **2b**. The product was converted to the *O*-Boc derivative and purified by flash column chromatography (Hexanes/EtOAc 5/2). Off-white foam (100 mg, 57%). mp 256–257 °C, R_f = 0.55 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.90 – 6.79 (m, 5H), 2.22 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.7, 192.3, 157.6, 149.3, 147.0, 139.6, 138.7, 138.4, 137.5, 136.4, 134.8, 134.1, 132.6, 132.4, 130.7 (2C), 129.9 (2C), 129.7 (2C), 129.3 (2C), 129.0, 128.7 (2C), 128.6 (2C), 127.8 (2C), 127.7 (2C), 118.0, 84.3, 27.6 (3C), 21.2. **IR** (mineral oil), cm^{-1}: 1768, 1675, 1615, 1597, 1580, 1532. Anal. Calcd for $C_{37}H_{31}NO_6$: C 75.88; H 5.34; N 2.39. Found: C 76.24; H 5.28; N 2.47.

Ethyl 3-((_tert_-butoxycarbonyl)oxy)-5-(furan-2-carbonyl)-2-oxo-1,6-diphenyl-1,2-dihydropyridine-4-carboxylate (5ac-Boc)

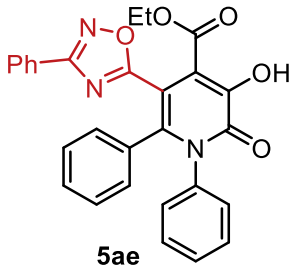


5ac-Boc

According to **GP B** from pyrrole-2,3-dione **4a** (0.3 mmol scale) and sulfonium salt **2c**. The product was converted to the *O*-Boc derivative and purified by flash column chromatography (Hexanes/EtOAc 5/3). Pale-beige powder (78 mg, 49%). mp 162–164 °C, R_f = 0.38 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.24 – 7.13 (m, 3H), 7.10 – 6.92 (m, 7H), 6.90 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.31 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.55 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 180.1, 163.0, 157.8, 152.9, 149.8, 146.7, 146.4, 139.0, 137.4, 132.5, 132.0, 130.3 (2C), 129.1, 129.03 (2C), 129.0 (2C), 128.7, 127.7 (2C), 119.0, 115.7, 112.5, 84.5, 62.5, 27.8 (3C), 13.8. **IR** (mineral oil), cm^{-1}: 1776, 1737, 1673, 1641, 1563, 1542. Anal. Calcd for $C_{30}H_{27}NO_8$: C 68.05; H 5.14; N 2.65. Found: C 68.38; H 5.37; N 2.88.

Ethyl 3-hydroxy-2-oxo-1,6-diphenyl-5-(3-phenyl-1,2,4-oxadiazol-5-yl)-1,2-dihydropyridine-4-carboxylate (5ae)

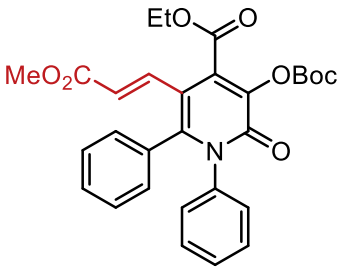


5ae

According to **GP B** from pyrrole-2,3-dione **4a** (0.3 mmol scale) and sulfonium salt **2e**. Isolation by crystallization from EtOH/H_2O gave an off-white powder (94 mg, 65%). mp 172–174 °C, R_f = 0.12 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.91 (d, *J* = 6.6 Hz, 2H), 7.55 – 7.35 (m, 3H), 7.32 – 7.13 (m, 3H), 7.05 (d, *J* = 5.5 Hz, 7H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 168.2, 166.5, 158.5, 150.3, 141.7, 137.5, 131.9, 131.3, 130.4 (2C), 129.2 (2C), 129.18, 129.0 (2C), 128.9, 128.8 (2C), 127.8 (2C), 127.4 (2C), 126.8, 114.2, 102.2, 62.8, 13.7. **IR** (mineral oil), cm^{-1}: 3268, 3186, 1744, 1655, 1630, 1594, 1574, 1559. Anal. Calcd for $C_{28}H_{21}N_3O_5$: C 70.14; H 4.41; N 8.76. Found: C 70.48; H 4.20; N 8.91.

Ethyl (_E_)-3-((_tert_-butoxycarbonyl)oxy)-5-(3-methoxy-3-oxoprop-1-en-1-yl)-2-oxo-1,6-diphenyl-1,2-dihydropyridine-4-carboxylate (5af-Boc)

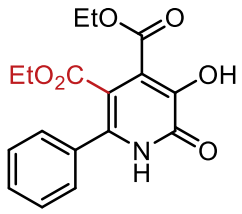


5af-Boc

According to **GP B** from pyrrole-2,3-dione **4a** (0.3 mmol scale) and sulfonium salt **2f**. The product was converted to the *O*-Boc derivative and purified by flash column chromatography (Hexanes/EtOAc 5/2). Pale-beige powder (100 mg, 64%). mp 144–146 °C, R_f = 0.15 (Hexanes/EtOAc 5/1.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 6H), 7.07 (d, *J* = 16.3 Hz, 1H), 7.01 – 6.95 (m, 4H), 5.81 (d, *J* = 16.3 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 1.54 (s, 9H), 1.39 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 164.1, 157.1, 149.9, 148.5, 139.0, 138.2, 137.7, 134.1, 132.4, 130.2 (2C), 129.4, 129.0 (2C), 128.9 (2C), 128.6, 128.4 (2C), 120.3, 109.4, 84.7, 62.7, 51.7, 27.7 (3C), 14.1. **IR** (mineral oil), cm^{-1}: 1769, 1737, 1711, 1679, 1625, 1609, 1521. Anal. Calcd for $C_{29}H_{29}NO_8$: C 67.04; H 5.63; N 2.70. Found: C 67.26; H 5.65; N 2.81.

Diethyl 5-hydroxy-6-oxo-2-phenyl-1,6-dihydropyridine-3,4-dicarboxylate (5ga)

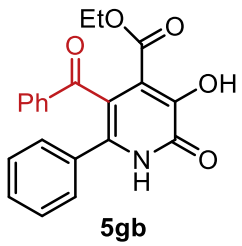


5ga

According to **GP B** from pyrrole-2,3-dione **4g** (0.3 mmol scale) and sulfonium salt **2a**. The reaction mixture was poured into 30 mL of water and formed precipitate was filtered off. White powder (59 mg, 88%). mp 200–202 °C, R_f = 0.35 (PhMe/EtOAc 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.80 (s, 1H), 7.64 – 7.23 (m, 5H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 165.6, 158.7, 146.9, 137.0, 133.1, 130.0, 128.8 (2C), 128.5 (2C), 118.3, 110.9, 62.5, 61.6, 14.1, 13.6. **IR** (mineral oil), cm^{-1}: 3150, 1742, 1717, 1642, 1620, 1599. Anal. Calcd for $C_{17}H_{17}NO_6$: C 61.63; H 5.17; N 4.23. Found: C 61.86; H 5.21; N 4.02.

Ethyl 5-benzoyl-3-hydroxy-2-oxo-6-phenyl-1,2-dihydropyridine-4-carboxylate (5gb)

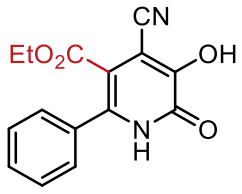


5gb

According to **GP B** from pyrrole-2,3-dione **4g** (0.3 mmol scale) and sulfonium salt **2b**. Isolation by crystallization from EtOH gave a white powder (70 mg, 64%). mp 225–227 °C, R_f = 0.3 (PhMe/EtOAc 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 9.72 (s, 1H), 7.66 (d, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.17 (m, 7H), 4.09 (q, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.6, 166.7, 158.7, 149.3, 137.8, 135.0, 133.2, 132.3, 129.9, 129.3 (2C), 129.0 (2C), 128.8 (2C), 128.5 (2C), 117.3, 116.6, 62.6, 13.3. **IR** (mineral oil), cm^{-1}: 3144, 1744, 1717, 1659, 1634, 1597. Anal. Calcd for $C_{21}H_{17}NO_5$: C 69.41; H 4.72; N 3.85. Found: C 69.58; H 4.96; N 3.92.

Ethyl 4-cyano-5-hydroxy-6-oxo-2-phenyl-1,6-dihydropyridine-3-carboxylate (5ha)

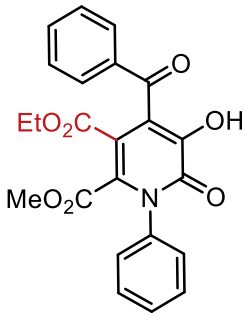


5ha

According to **GP B** from pyrrole-2,3-dione **4h** (0.3 mmol scale) and sulfonium salt **2a**. The reaction mixture was poured into 30 mL of water and formed precipitate was filtered off. Yellow powder (57 mg, 40%). mp 232–234 °C, R_f = 0.13 (EtOAc).

^{1}H NMR (400 MHz, DMSO) δ 12.55 (s, 1H), 11.79 (s, 1H), 7.51 – 7.41 (m, 3H), 7.40 – 7.27 (m, 2H), 3.94 (q, *J* = 7.1 Hz, 2H), 0.84 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 164.0, 157.0, 153.5, 139.6, 133.2, 129.2, 128.6 (2C), 128.0 (2C), 113.5, 107.2, 97.5, 60.9, 13.0. **IR** (mineral oil), cm^{-1}: 3264, 3184, 2233, 1726, 1659. Anal. Calcd for $C_{15}H_{12}N_2O_4$: C 63.38; H 4.26; N 9.85. Found: C 63.38; H 4.15; N 9.98.

3-Ethyl 2-methyl 4-benzoyl-5-hydroxy-6-oxo-1-phenyl-1,6-dihydropyridine-2,3-dicarboxylate (6aa)



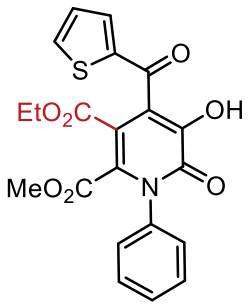
6aa

According to **GP C** from cyclopropane **3aa** (0.3 mmol scale). Isolation by recrystallization from MTBE/DCM gave an off-white powder, 102 mg (81%), mp 180–182 °C, R_f = 0.23 (PhMe/EtOAc 5/1).

Thermal method: a test tube containing 0.3 mmol of **3aa** is placed in an oil bath preheated to 180 °C and stirred for 1 h. The test tube is cooled to room temperature and the residue is crystallized from MTBE/DCM. Off-white powder, 88 mg (70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.57 – 7.45 (m, 5H), 7.34 (dd, *J* = 6.6, 3.0 Hz, 2H), 6.89 (s, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.49 (s, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 163.1, 162.0, 158.4, 143.0, 136.7, 136.5, 136.2, 134.0, 130.3, 129.6 (2C), 129.4 (2C), 128.9 (2C), 128.2 (2C), 124.5, 108.6, 62.3, 53.0, 13.3. **IR** (mineral oil), cm^{-1}: 3368, 1737, 1713, 1680, 1646, 1596, 1513. Anal. Calcd for $C_{23}H_{19}NO_7$: C 65.56; H 4.54; N 3.32. Found: C 65.78; H 4.70; N 3.45.

3-Ethyl 2-methyl 5-hydroxy-6-oxo-1-phenyl-4-(thiophene-2-carbonyl)-1,6-dihydropyridine-2,3-dicarboxylate (6ea)

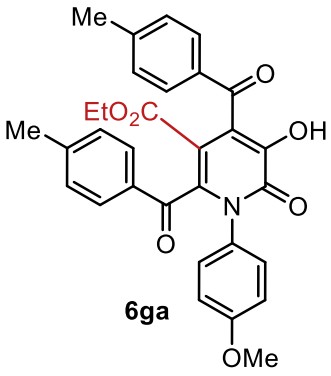


6ea

According to **GP C** from cyclopropane **3ea** (0.3 mmol scale). Isolation by recrystallization from EtOH gave an off-white powder, 97 mg (76%), mp 170–172 °C, R_f = 0.22 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.64 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.40 – 7.29 (m, 2H), 7.16 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.99 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.48 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 183.4, 163.0, 162.0, 158.5, 143.8, 143.3, 136.6, 136.2, 135.1, 134.6, 130.3, 129.6 (2C), 128.4, 128.2 (2C), 123.9, 108.5, 62.4, 53.1, 13.4. **IR** (mineral oil), cm^{-1}: 3296, 1751, 1715, 1657, 1643, 1612, 1594, 1541. Anal. Calcd for $C_{21}H_{17}NO_7S$: C 59.01; H 4.01; N 3.28; S 7.50. Found: C 59.32; H 4.07; N 3.48; S 7.63.

Ethyl 5-hydroxy-1-(4-methoxyphenyl)-2,4-bis(4-methylbenzoyl)-6-oxo-1,6-dihydropyridine-3-carboxylate (6ga)

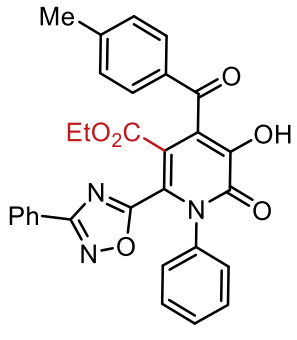


6ga

According to **GP C** from cyclopropane **3ga** (0.3 mmol scale). Isolation by recrystallization from EtOH gave an off-white powder, 133 mg (84%), mp 218–220 °C, R_f = 0.31 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12 – 6.46 (br. m, 4H), 6.82 (s, 1H), 3.84 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.7, 188.2, 163.3, 160.3, 159.3, 145.2, 144.9, 142.4, 142.3, 134.2, 134.2, 130.1 (2C), 129.6 (2C), 129.6 (2C), 129.5 (2C), 129.1 (2C), 128.1, 125.1, 114.5 (2C), 108.7, 62.1, 55.6, 21.9, 21.9, 13.0. **IR** (mineral oil), cm^{-1}: 3238, 1710, 1682, 1648, 1605, 1575, 1511. Anal. Calcd for $C_{31}H_{27}NO_7$: C 70.85; H 5.18; N 2.67. Found: C 71.07; H 4.99; N 2.49.

Ethyl 5-hydroxy-4-(4-methylbenzoyl)-6-oxo-1-phenyl-2-(3-phenyl-1,2,4-oxadiazol-5-yl)-1,6-dihydropyridine-3-carboxylate (6ha)



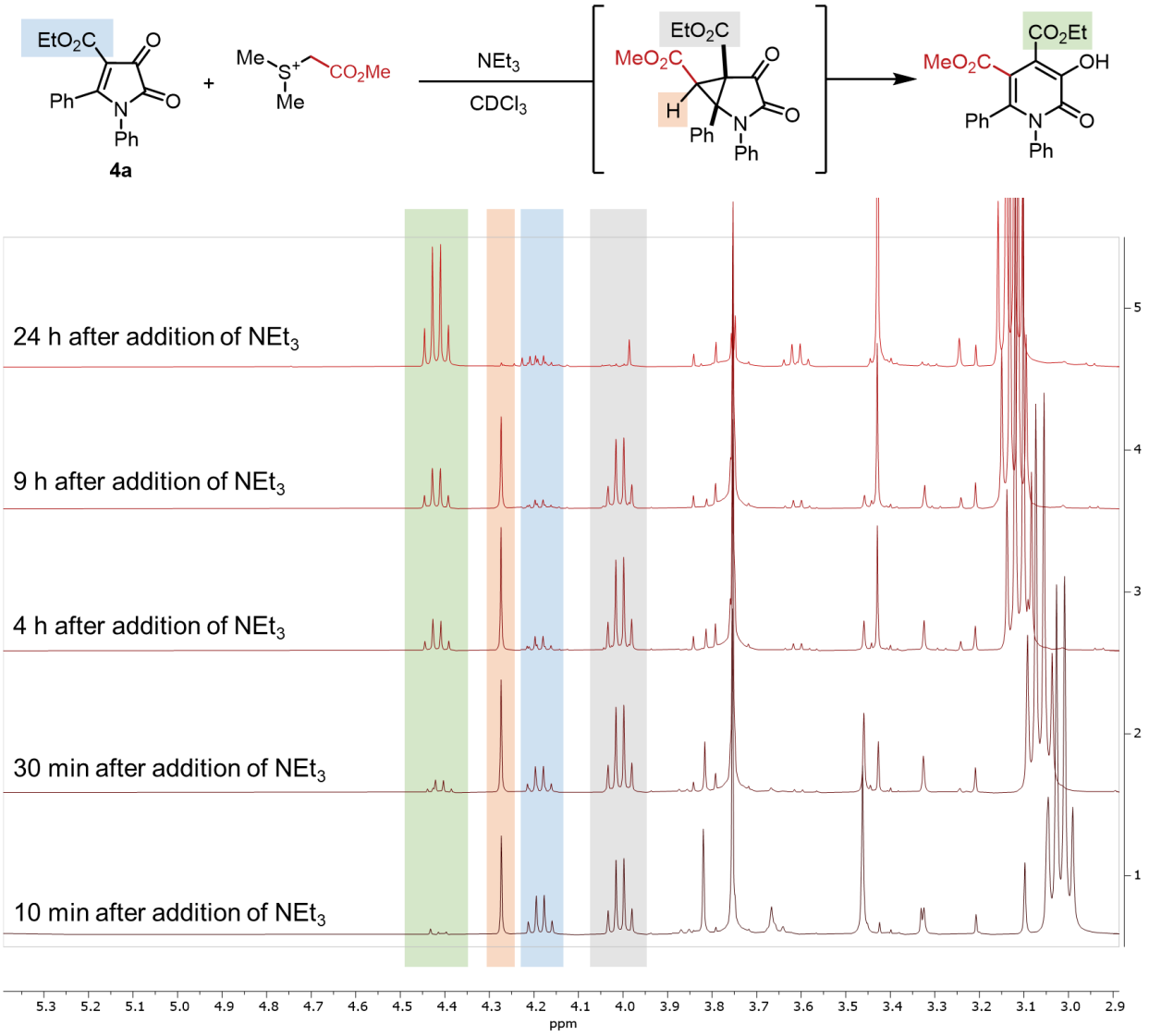
6ha

According to **GP C** from cyclopropane **3ha** (0.3 mmol scale). Isolation by recrystallization from EtOH gave an off-white powder, 149 mg (95%), mp 199–201 °C, R_f = 0.24 (PhMe/EtOAc 5/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.85 (m, 4H), 7.53 – 7.28 (m, 10H), 7.18 (s, 1H), 3.91 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.0, 169.0, 168.5, 162.6, 158.6, 145.2, 144.9, 136.0, 134.0, 131.6, 130.3, 129.7 (2C), 129.6 (4C), 129.0 (2C), 128.0 (2C), 127.5 (2C), 127.2, 126.1, 124.7, 115.1, 62.5, 22.0, 13.3. **IR** (mineral oil), cm^{-1}: 3264, 1724, 1682, 1649, 1623, 1592, 1526. Anal. Calcd for $C_{30}H_{23}N_3O_6$: C 69.09; H 4.45; N 8.06. Found: C 69.48; H 4.40; N 8.25.

NMR monitoring of cyclopropanation and ring expansion

NMR monitoring (**Scheme S2**) was performed on the reaction of pyrrole-2,3-dione **4a** with sulfonium salt derived from methyl bromoacetate (for spectra simplification).



Scheme S2. NMR monitoring of the reaction of **4a** and sulfonium ylide in $CDCl_3$

Thermal analysis of cyclopropane 3aa

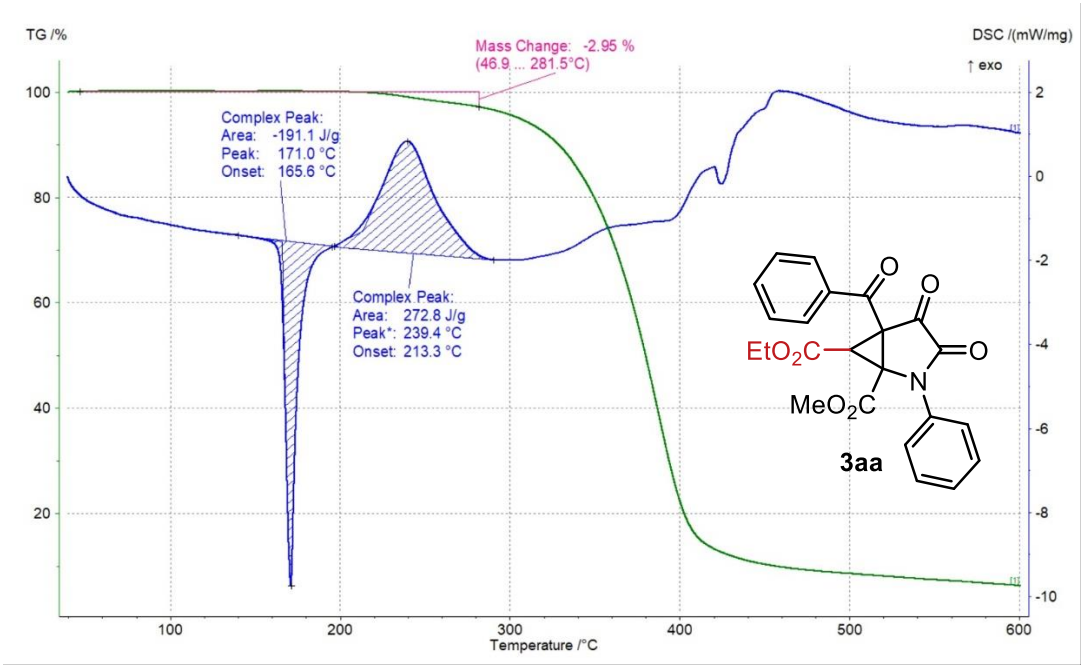


Figure S2. Thermal analysis of cyclopropane **3aa** (argon atmosphere)

Conditions for cyclopropane 3aa ring-opening reaction

The optimization reactions of the ring-opening of cyclopropanes **3** were tested on product **3aa** (0.03 mmol scale) at room temperature (solvents: DCM or HFIP) and monitored by TLC (**Fig. S3**, *note*: not all conditions are represented) – disappearance of **3aa** (R_f 0.6 PhMe/AcOEt 5/1) and formation of the product **6aa** (R_f ~0.3 PhMe/AcOEt 5/1 tailing spot). The following catalysts were tested – Lewis acids: $Sc(OTf)_3$, $Cu(OTf)_2$, $Y(OTf)_3$, $TiCl_4$, $Ni(ClO_4)_2 \cdot 6H_2O$, $BF_3 \cdot Et_2O$; Brønsted acids: TfOH, 4N HCl in 1,4-dioxane (as a solvent), AcOH; and bases: DBU, K_2CO_3.

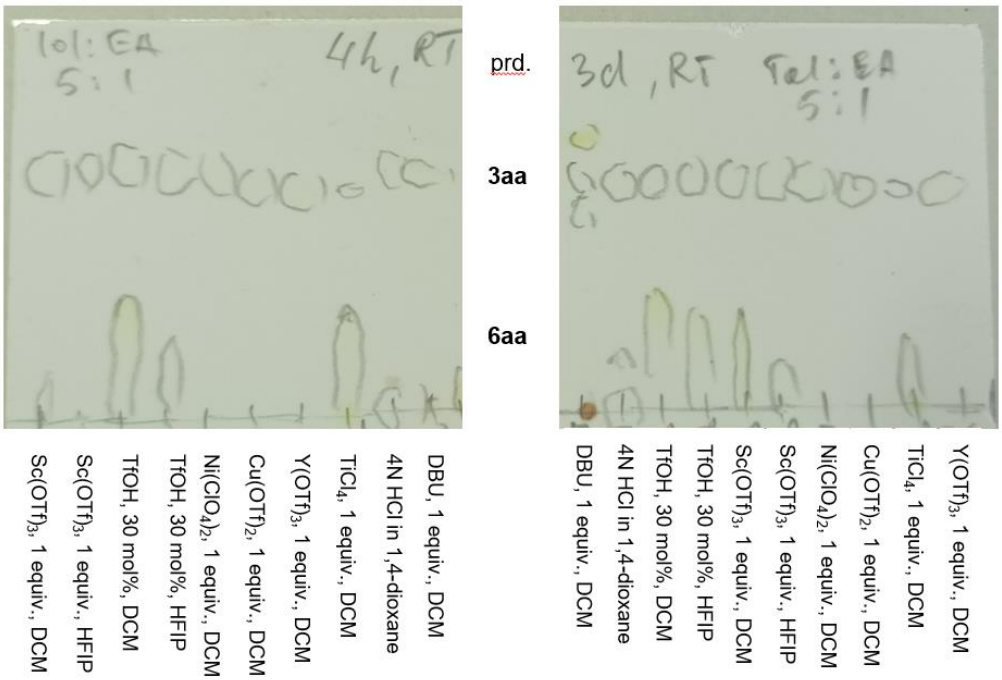
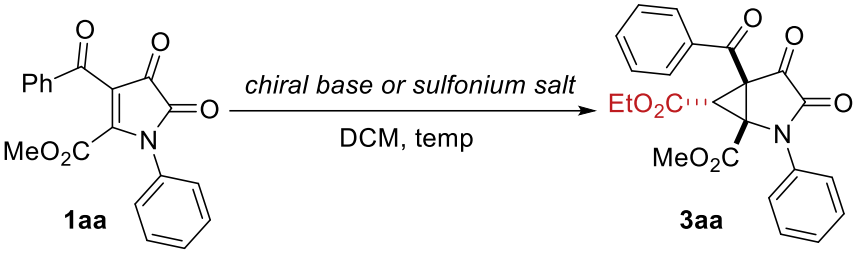


Figure S3. TLC of the optimization studies (**3aa**→**6aa**)

Attempts for an asymmetric synthesis of the cyclopropane 3aa

In order to carry out the asymmetric synthesis of **3aa** (**Scheme S3**), a number of conditions were tested (**Table S1**). The reaction of **1aa** with known chiral sulfonium salt **Y1** resulted in the highest ee (50%) among the tested conditions (*note*: the absolute configuration of major enantiomer of **3aa** is not known).

Procedure for the asymmetric synthesis of 3aa: to the cooled (dry-ice/acetone bath) DCM (2 mL) solution of pyrrole-2,3-dione **1aa** (1 equiv.) and sulfonium salt **Y1** (1 equiv.) under Ar atmosphere is added the solution of NEt_3 (1.1 equiv.) in 2 mL of DCM dropwise during 5 min. The mixture is stirred for 10 min and then warmed to RT. The solvent is then evaporated under reduced pressure and the residue is purified by flash column chromatography (PhMe/EtOAc 7/1) to afford the cyclopropane **3aa** (loading in the minimum volume of dichloromethane).



Scheme S3. Asymmetric synthesis of the cyclopropane **3aa**

Table S1

Entry	Chiral base / sulfonium salt	Conditions	ee, %	Yield, %
1	**C1 (commercial)** + **2a**	DCM (0.5M), RT	0	75
2	**C2 [13]** + **2a**	DCM (0.5M), RT	0	62
3	**C3 [14]** + **2a**	DCM (0.5M), RT	0	65
4	**Y1 [15]** + Et_3N	DCM (0.5M), RT	15	57
5	**Y1** + Et_3N	DCM (0.025M), –78 °C	50	60

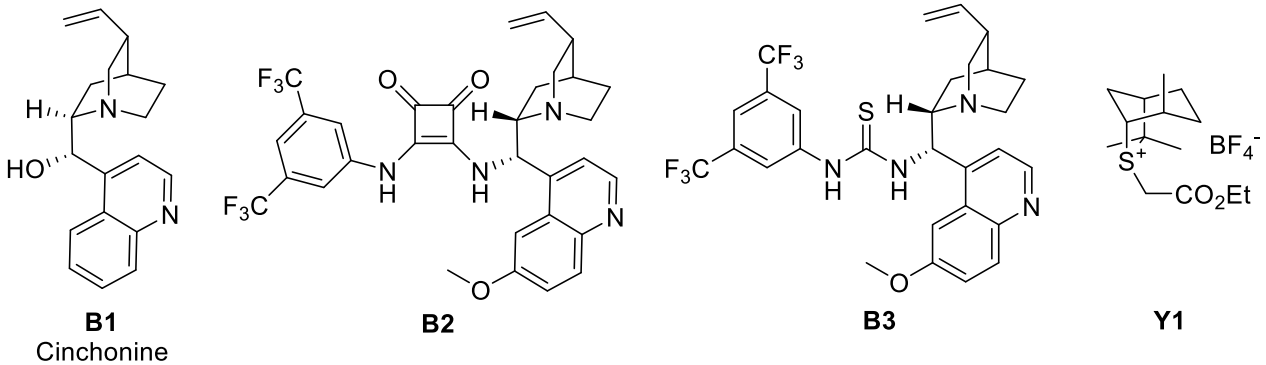
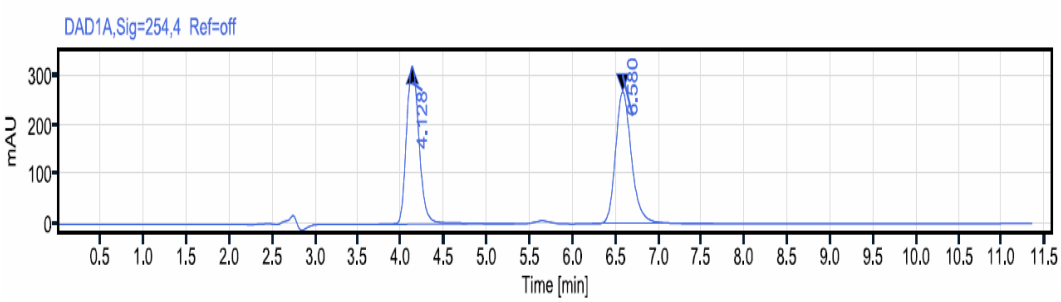
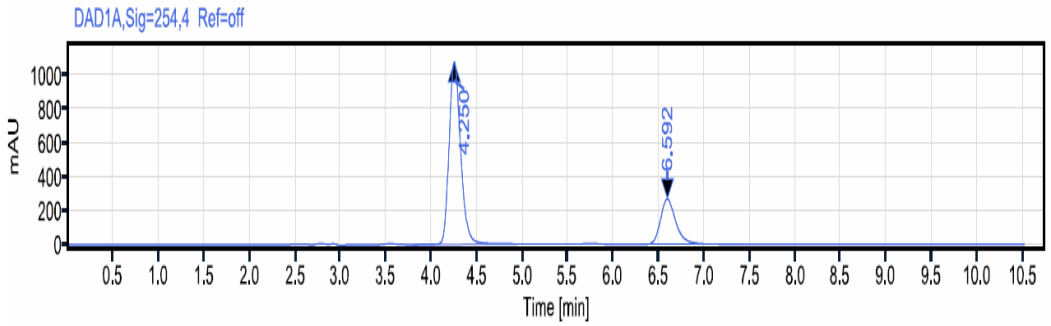


Figure S4. Tested chiral bases **B1–B3** and sulfonium salt **Y1**



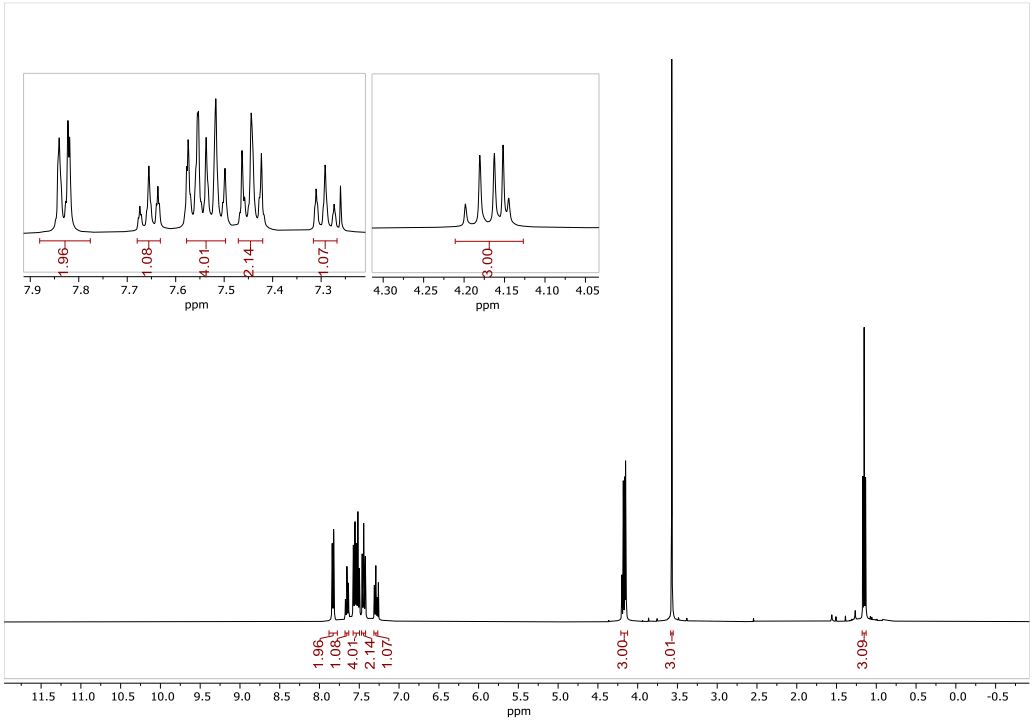
Signal:	DAD1A,Sig=254,4 Ref=off				
RT [min]	Type	Width [min]	Area	Height	Area %
4.128	MM m	1.67	3298.82	317.68	49.04
6.580	BM m	1.41	3428.56	264.89	50.96

Figure S5. Chromatogram of racemic **3aa**



Signal:	DAD1A,Sig=254,4 Ref=off				
RT [min]	Type	Width [min]	Area	Height	Area %
4.250	BM m	1.45	9574.40	1080.04	75.12
6.592	BM m	1.12	3171.26	268.86	24.88

Figure S6. Chromatogram of enantioenriched **3aa** (entry 5, **Table S1**)



^{1}H NMR of enantioenriched **3aa** ($CDCl_3$; single diastereomer)

Crystal structure determination

The unit cell parameters and the X-ray diffraction intensities were measured on a Xcalibur Ruby diffractometer. The empirical absorption correction was introduced by multi-scan method using SCALE3 ABSPACK algorithm [16]. Using the Olex2 [17], the structures were solved with the SHELXT [18] program and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms with the SHELXL program [19]. Hydrogen atoms bound to carbon were positioned geometrically and refined using a riding model. The hydrogen atoms of NH and OH groups were refined independently with isotropic displacement parameters.

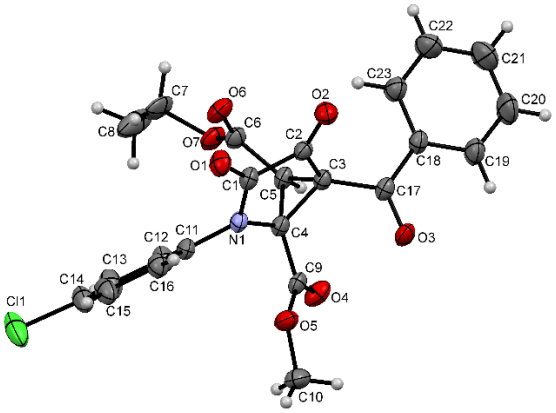


Figure S7. *Molecular structure of compound* ***3ca*** *showing 30% probability amplitude displacement ellipsoids (CCDC 2410200).*

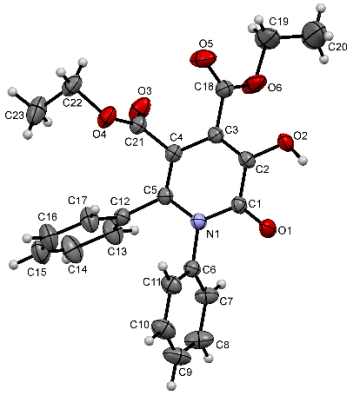


Figure S8. *Molecular structure of compound* ***5aa*** *showing 30% probability amplitude displacement ellipsoids (CCDC 2410198).*

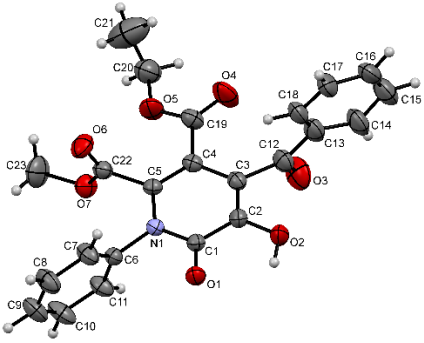


Figure S9. *Molecular structure of compound* ***6aa*** *showing 30% probability amplitude displacement ellipsoids (CCDC 2410199).*

Table S2. Crystal data and structure refinement for compounds **3ca**, **5aa**, **6aa**.

Compound	**3ca**	**5aa**	**6aa**
CCDC	2410200	2410198	2410199
Empirical formula	$C_{23}H_{18}ClNO_7$	$C_{23}H_{21}NO_6$	$C_{23}H_{19}NO_7$
Formula weight	455.83	407.41	421.39
Temperature, K	295(2)	295(2)	295(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	I2/a	Pbcn
a, Å	11.3507(19)	20.404(5)	13.3392(19)
b, Å	11.705(2)	9.4554(19)	16.5142(19)
c, Å	17.151(3)	22.554(3)	19.544(3)
α, °	90	90	90
β, °	94.734(14)	91.201(17)	90
γ, °	90	90	90
Volume, $Å^3$	2271.0(7)	4350.3(15)	4305.3(10)
Z	4	8	8
Density (calculated), g/cm^3	1.333	1.244	1.300
Absorption coefficient, mm^{-1}	0.212	0.091	0.097
F(000)	944.0	1712.0	1760.0
Crystal size, mm^3	0.6 × 0.5 × 0.06	0.35 × 0.25 × 0.04	0.5 × 0.35 × 0.2
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection, °	4.218 to 59.35	3.994 to 58.944	3.926 to 58.958
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 16, -20 ≤ l ≤ 23	-27 ≤ h ≤ 26, -12 ≤ k ≤ 12, -29 ≤ l ≤ 31	-8 ≤ h ≤ 17, -20 ≤ k ≤ 14, -17 ≤ l ≤ 24
Reflections collected	12632	11810	15135
Independent reflections	5480 [R_{int} = 0.0334, R_{sigma} = 0.0516]	5141 [R_{int} = 0.0456, R_{sigma} = 0.0632]	5264 [R_{int} = 0.0408, R_{sigma} = 0.0483]
Data/restraints/parameters	5480/41/311	5141/96/327	5264/244/362
Goodness-of-fit on F^2	1.023	1.038	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0608, wR_2 = 0.1485	R_1 = 0.0710, wR_2 = 0.1840	R_1 = 0.0608, wR_2 = 0.1482
Final R indexes [all data]	R_1 = 0.1094, wR_2 = 0.1912	R_1 = 0.1296, wR_2 = 0.2446	R_1 = 0.1202, wR_2 = 0.1935
Largest diff. peak/hole, $eÅ^{-3}$	0.33/-0.47	0.43/-0.27	0.25/-0.17

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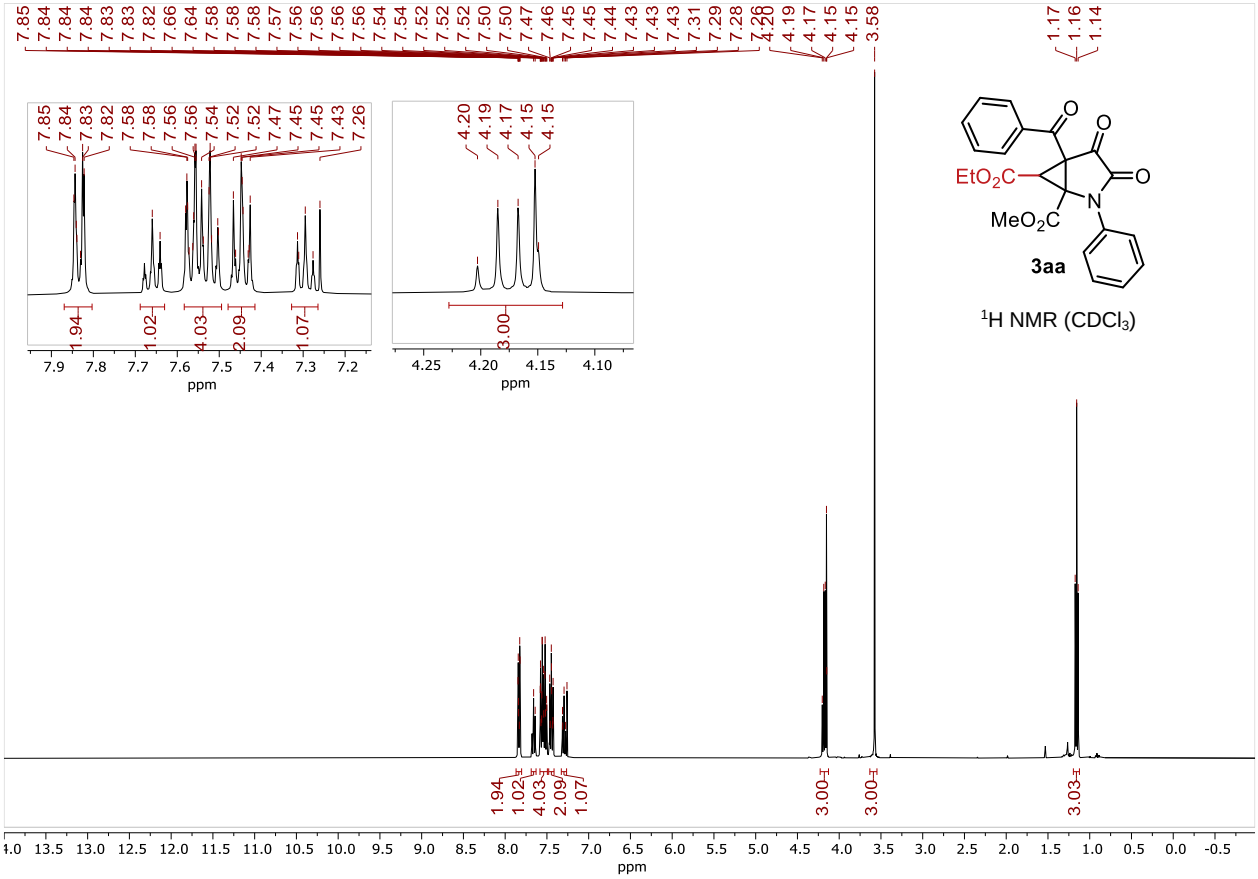
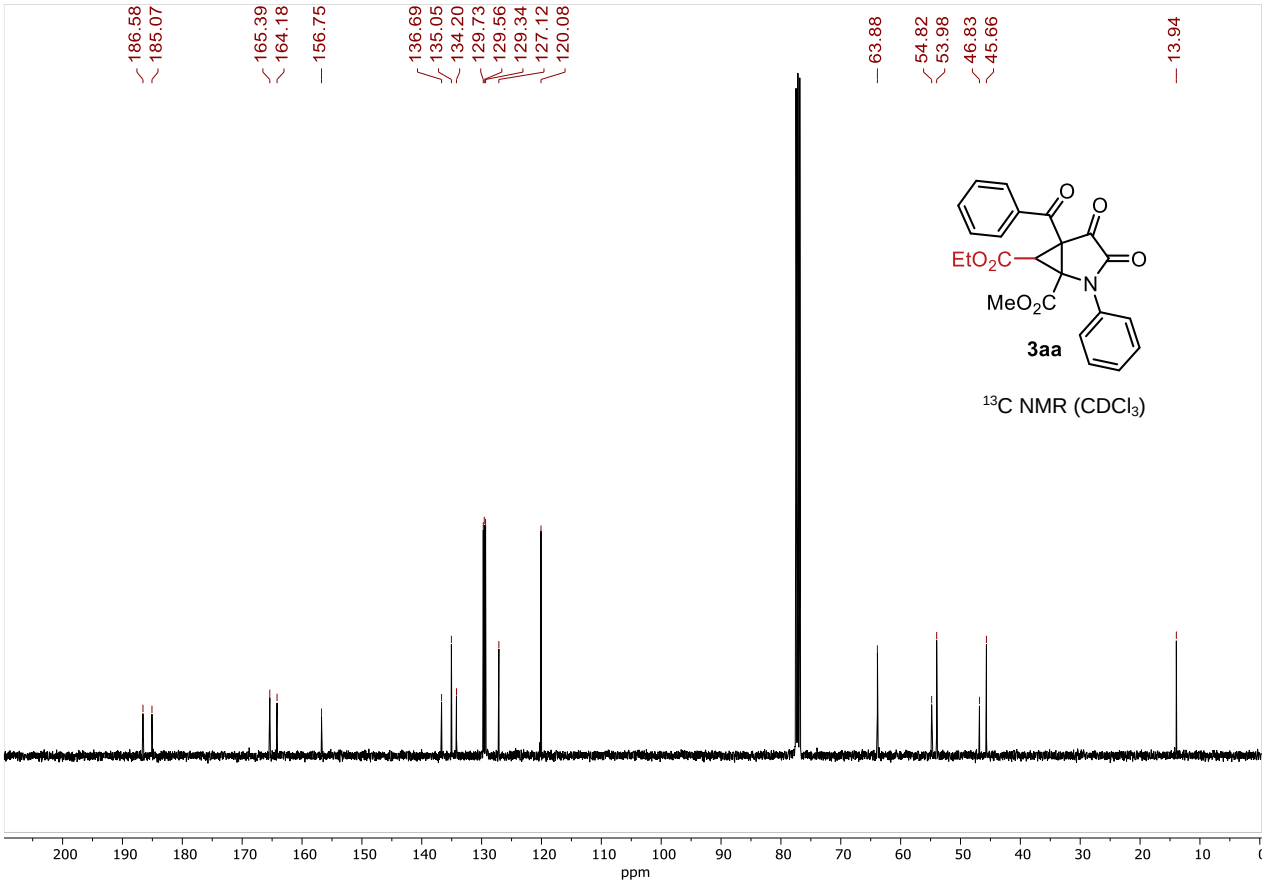
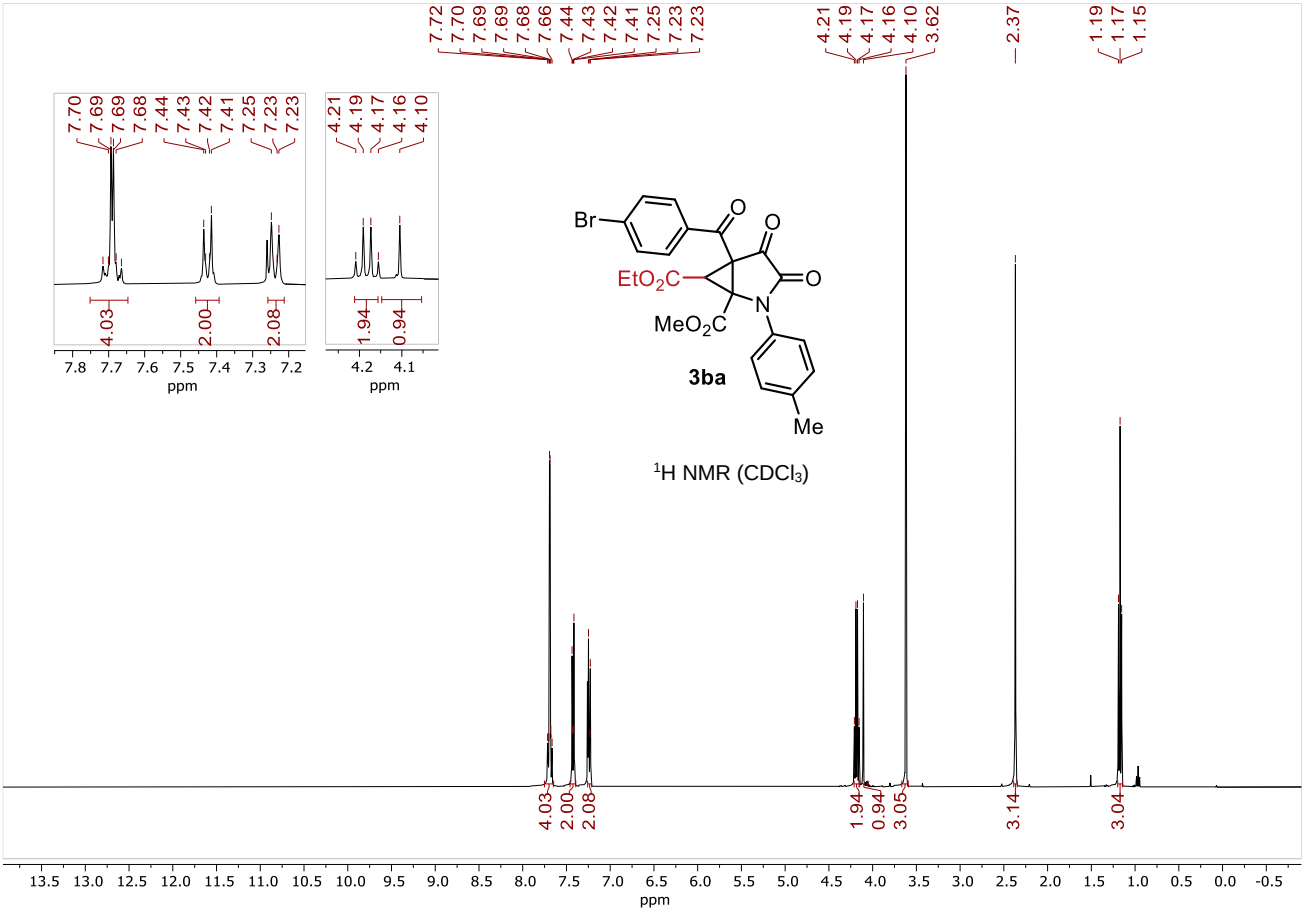
Copies of NMR spectra



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Me
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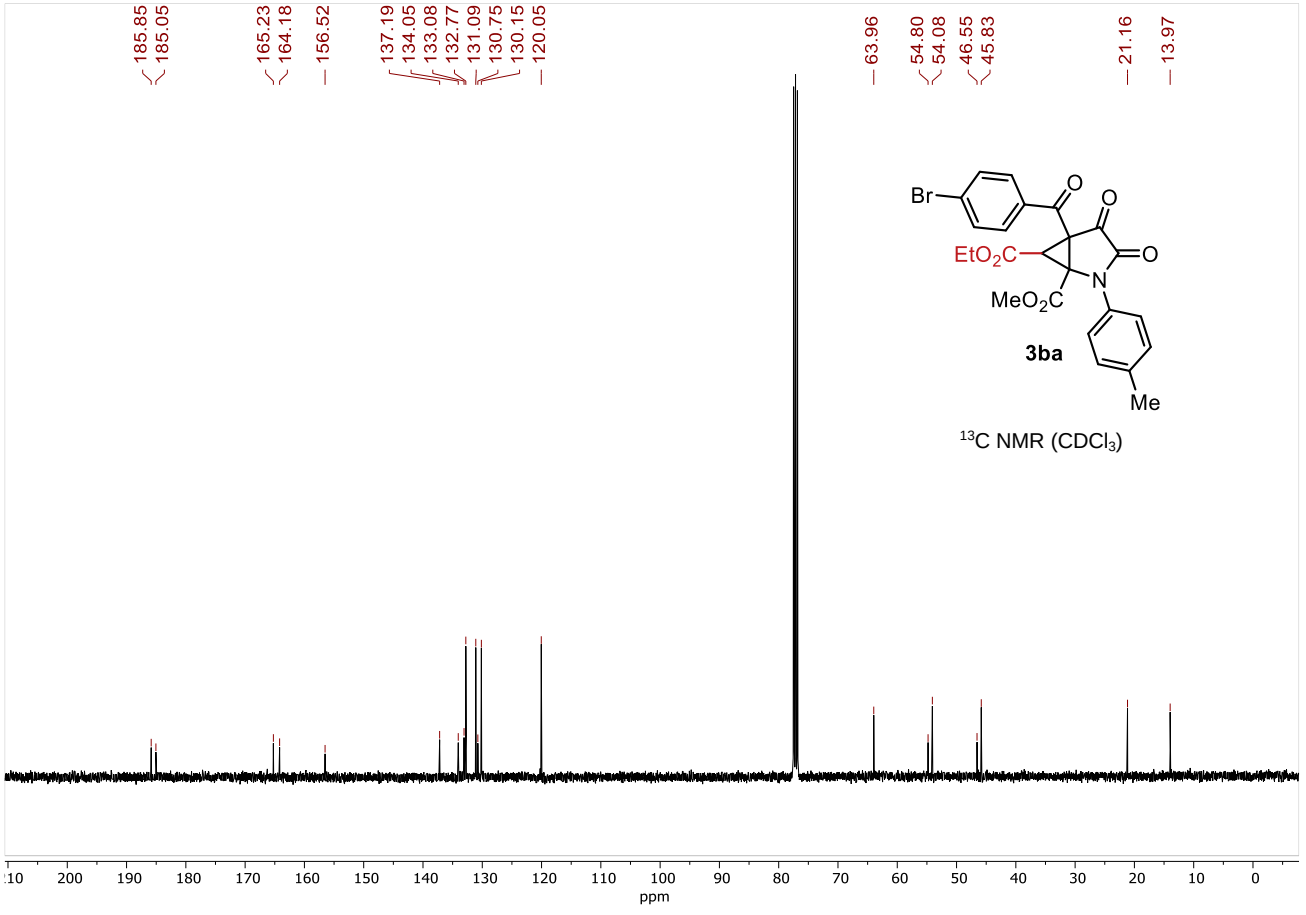
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3ba
Me
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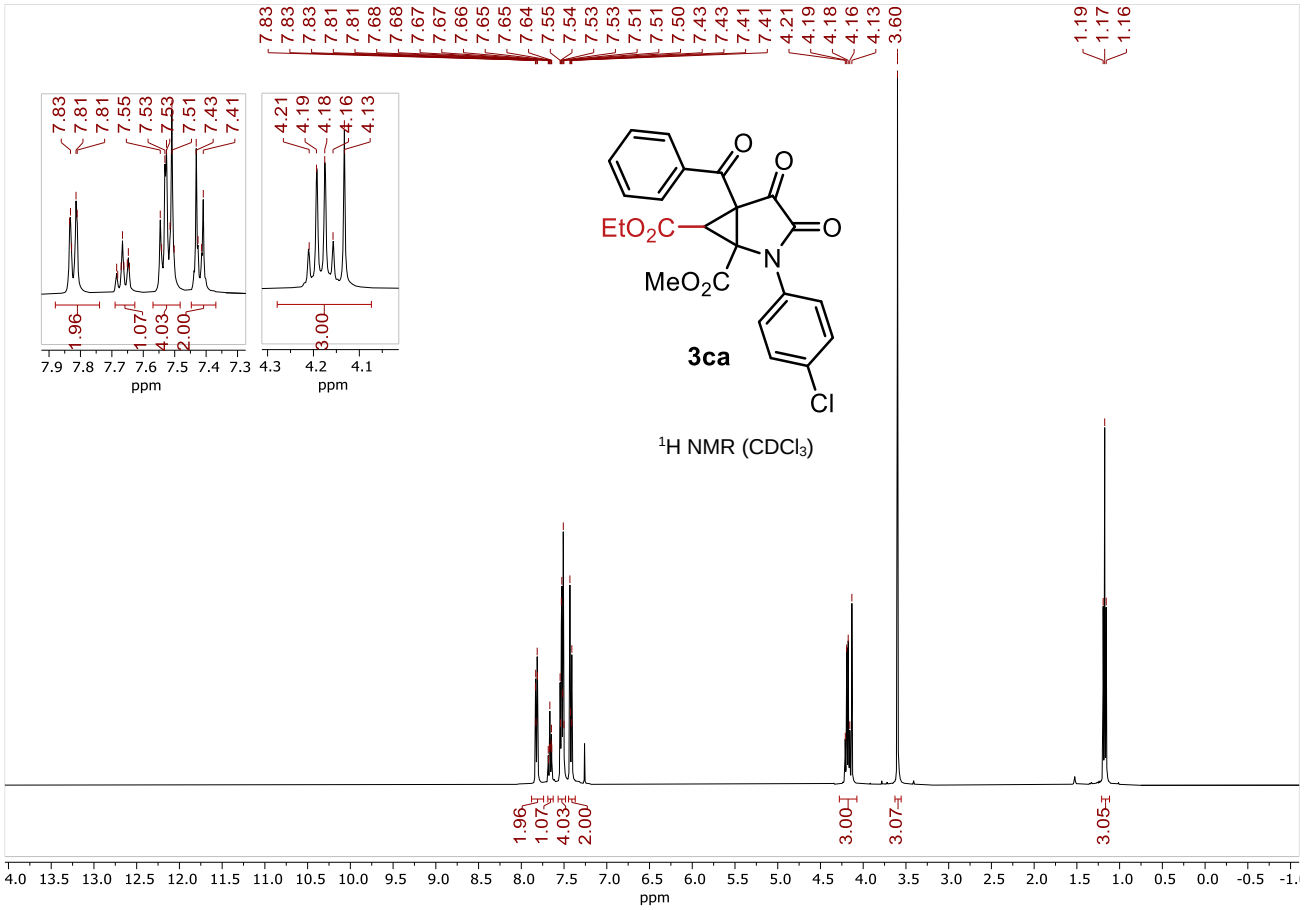
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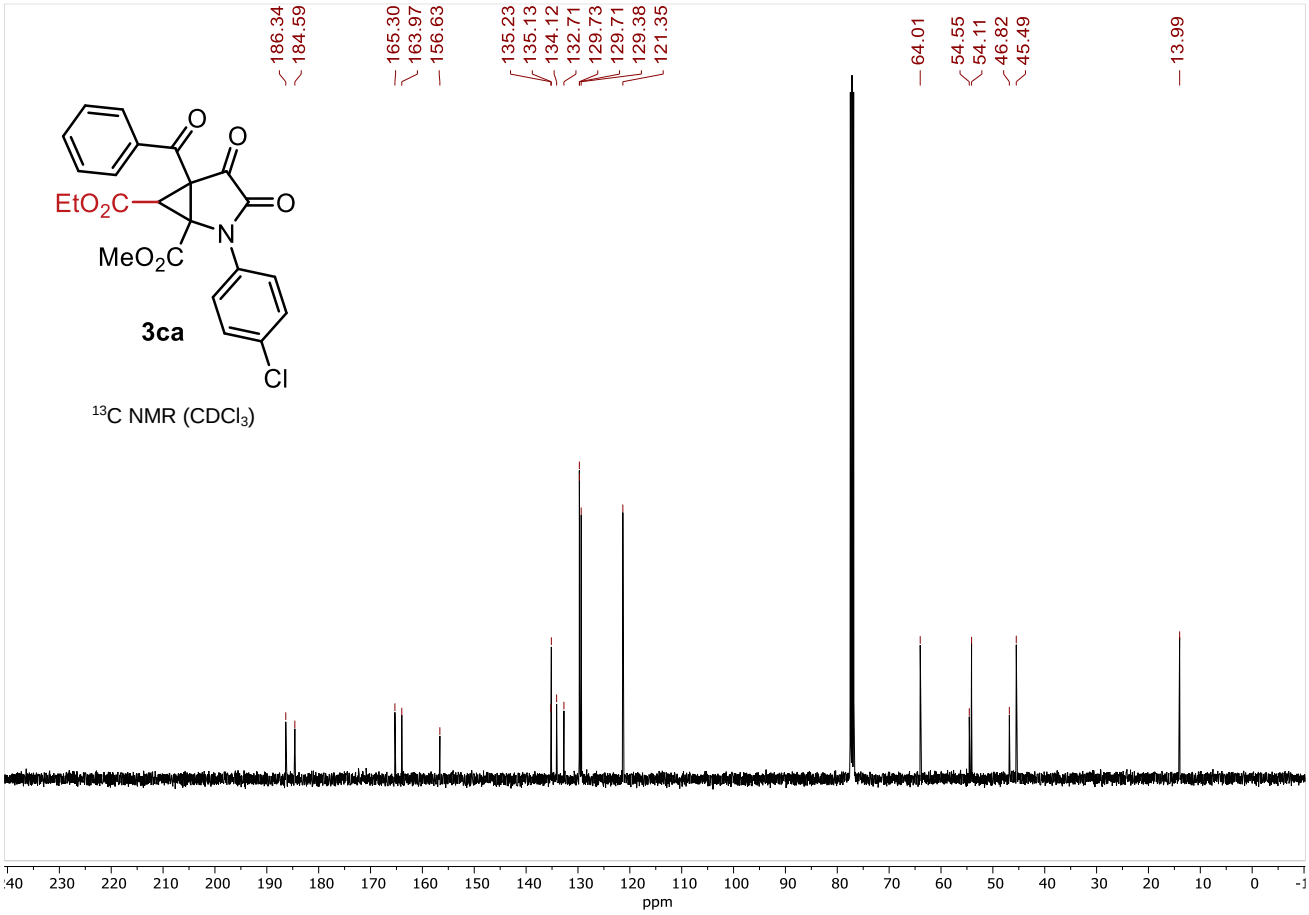
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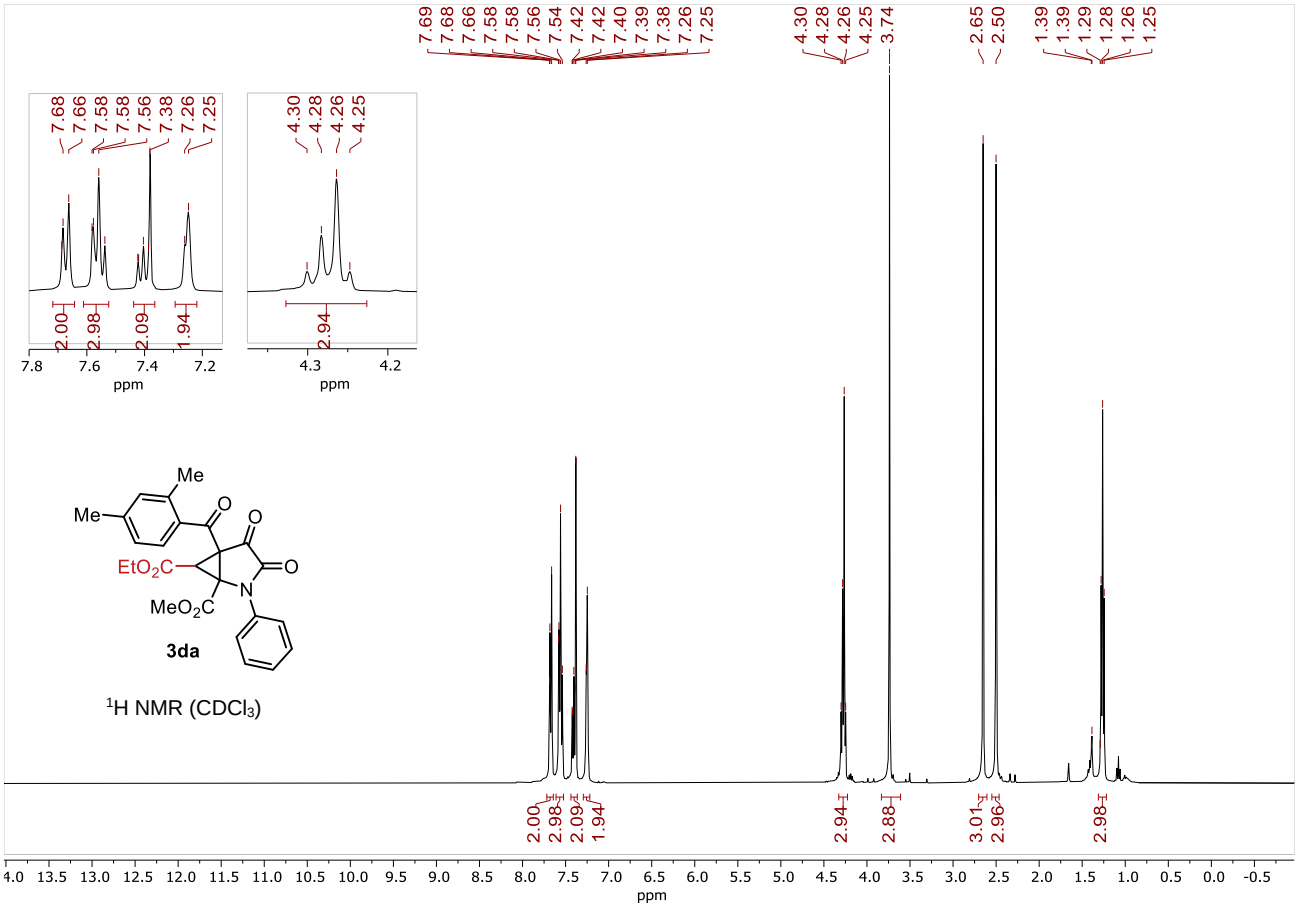
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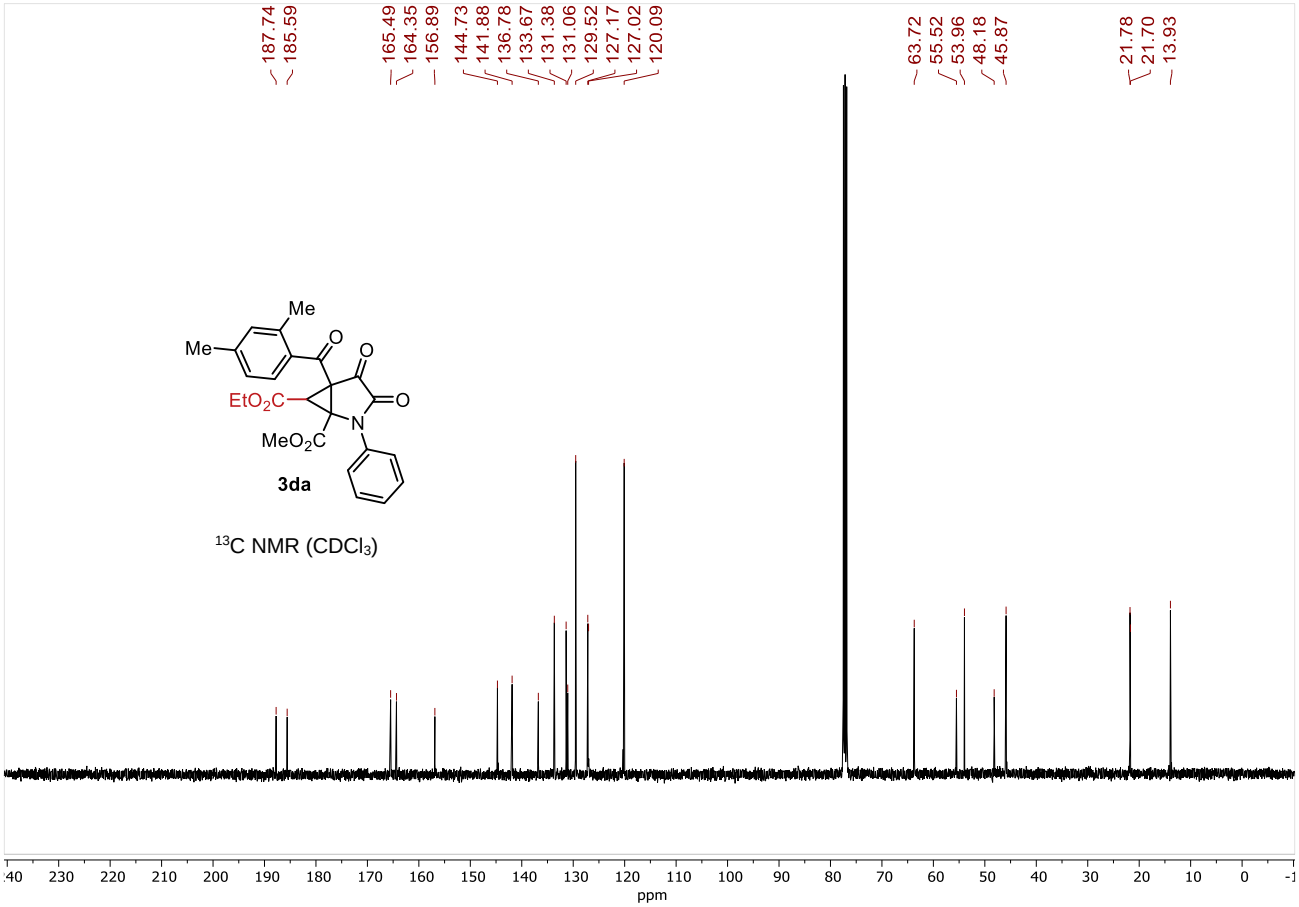
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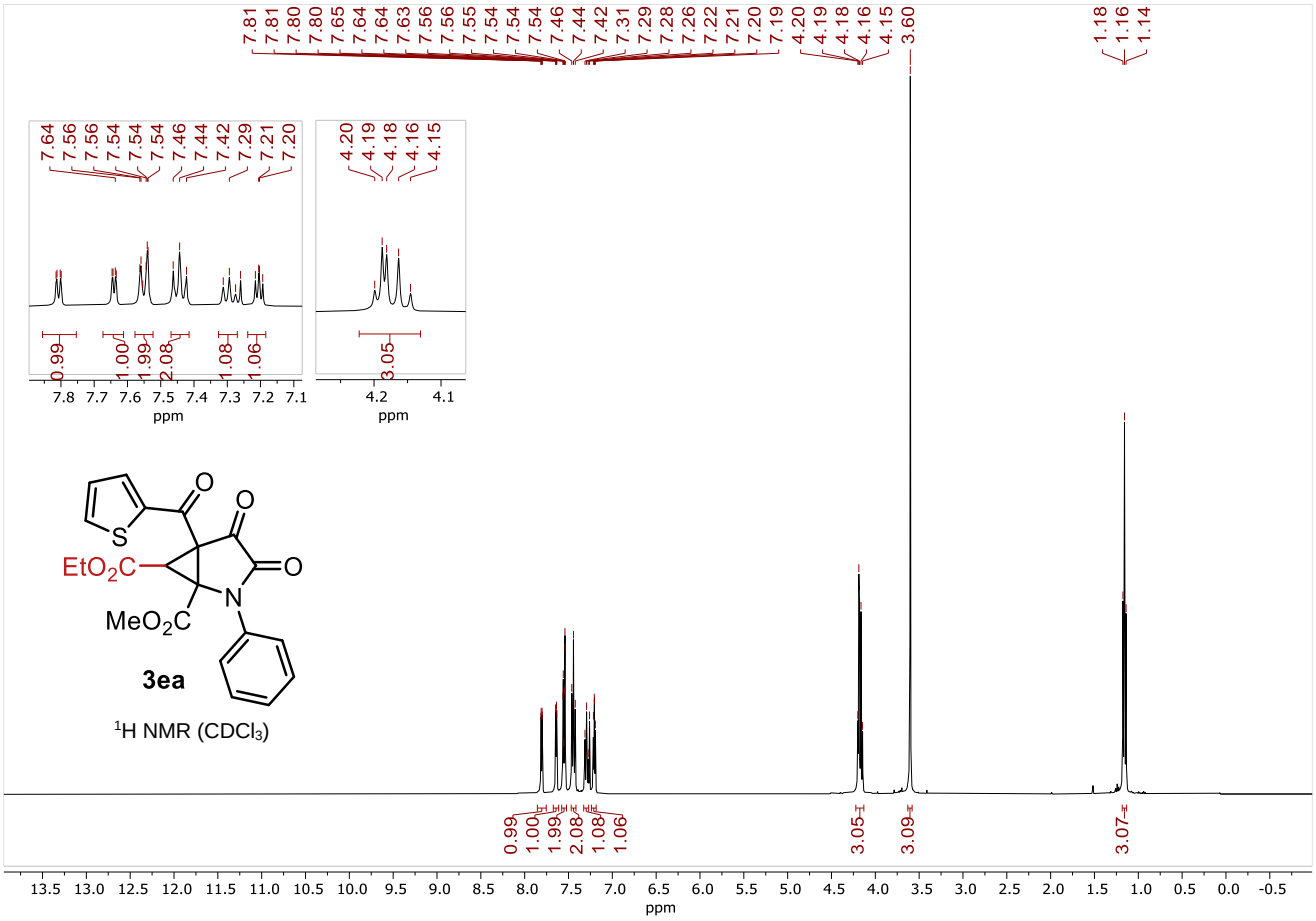
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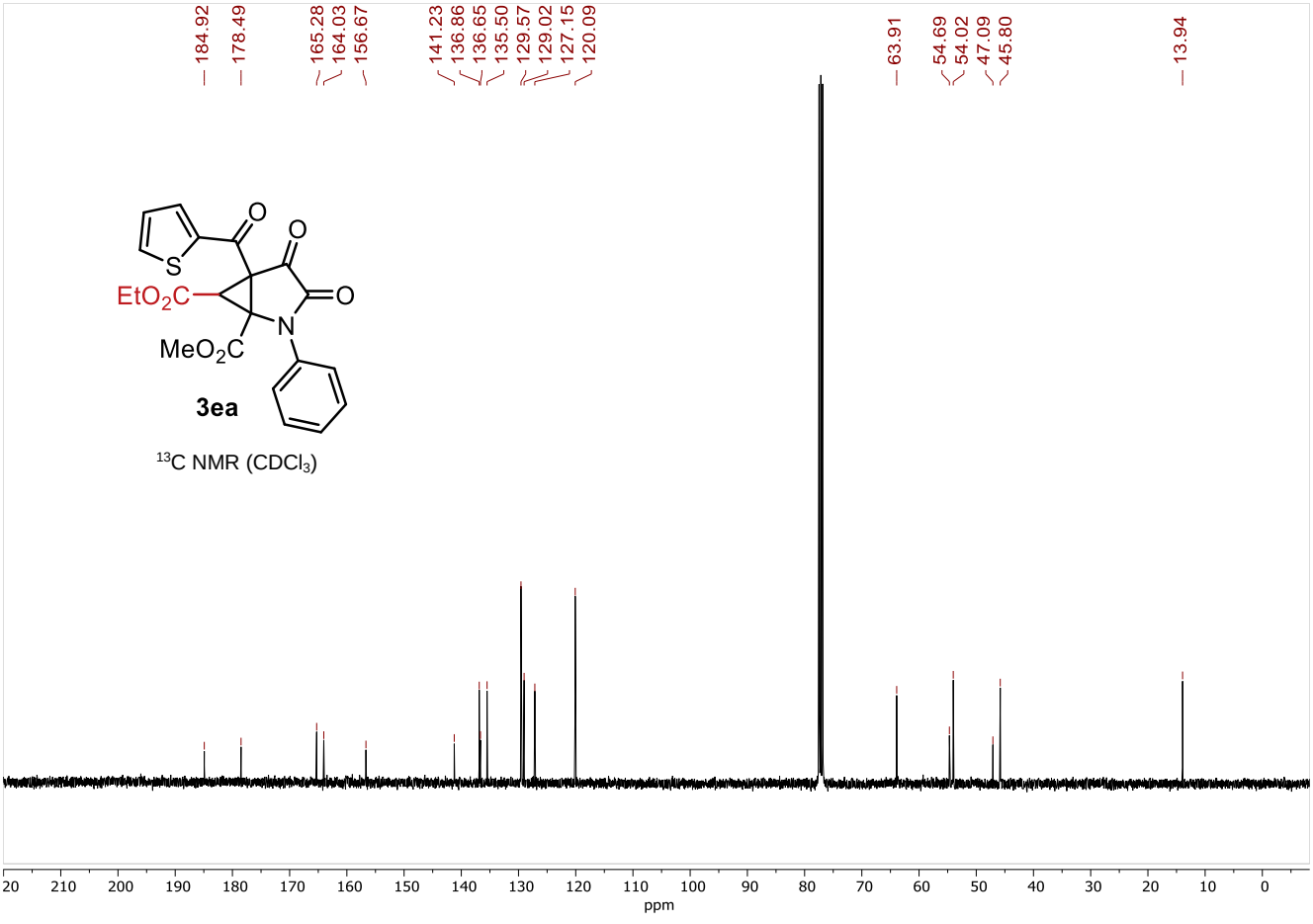
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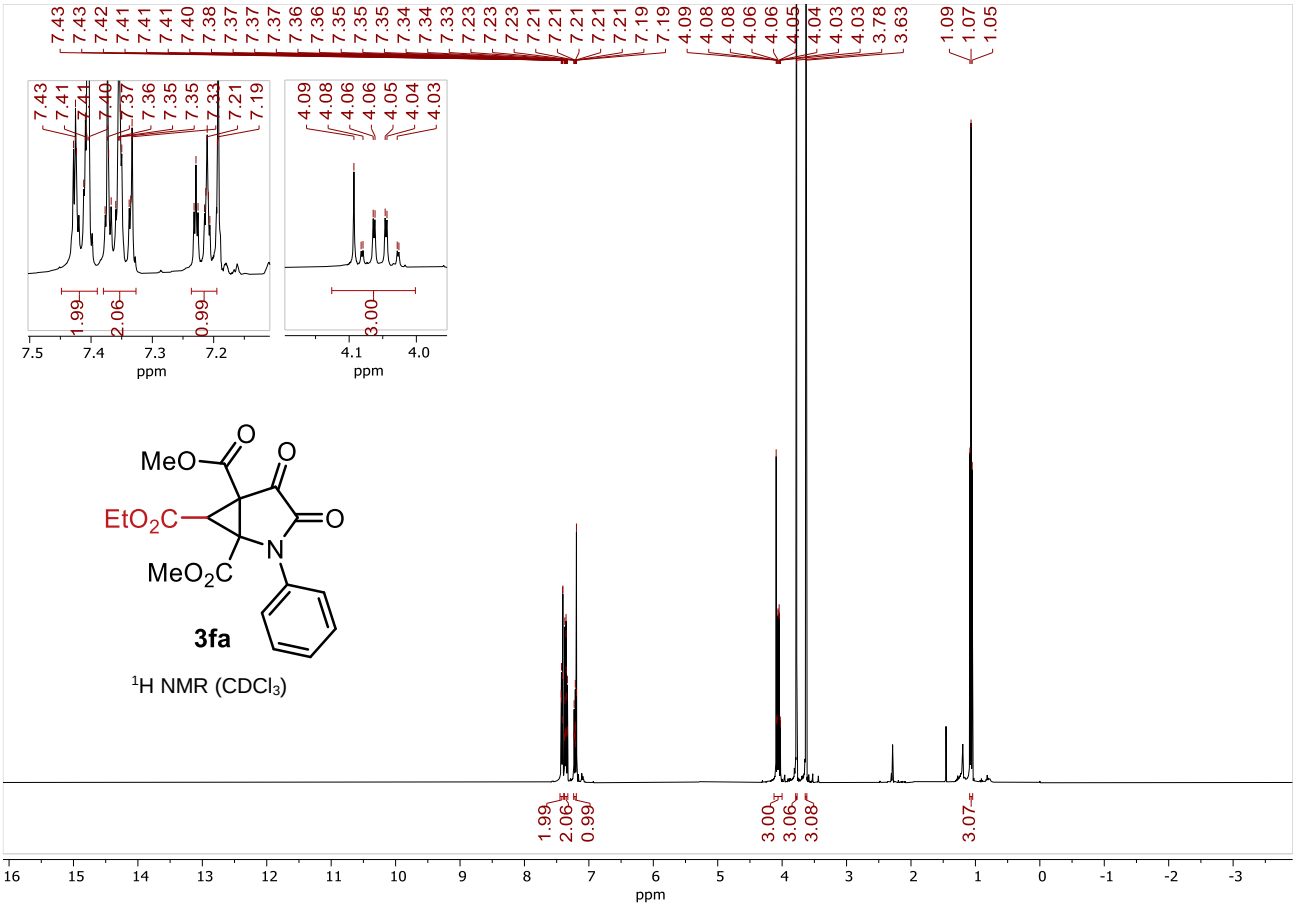
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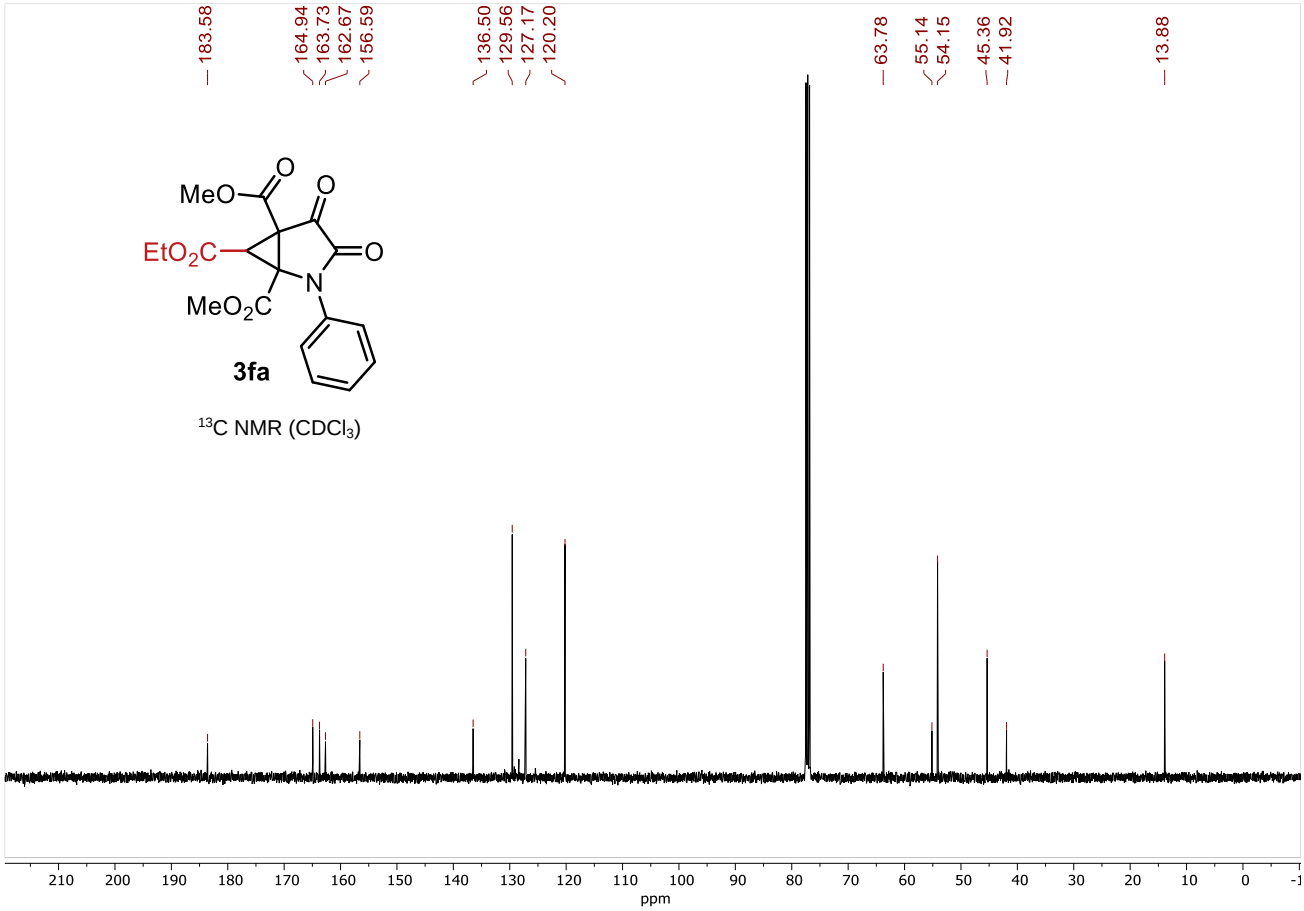
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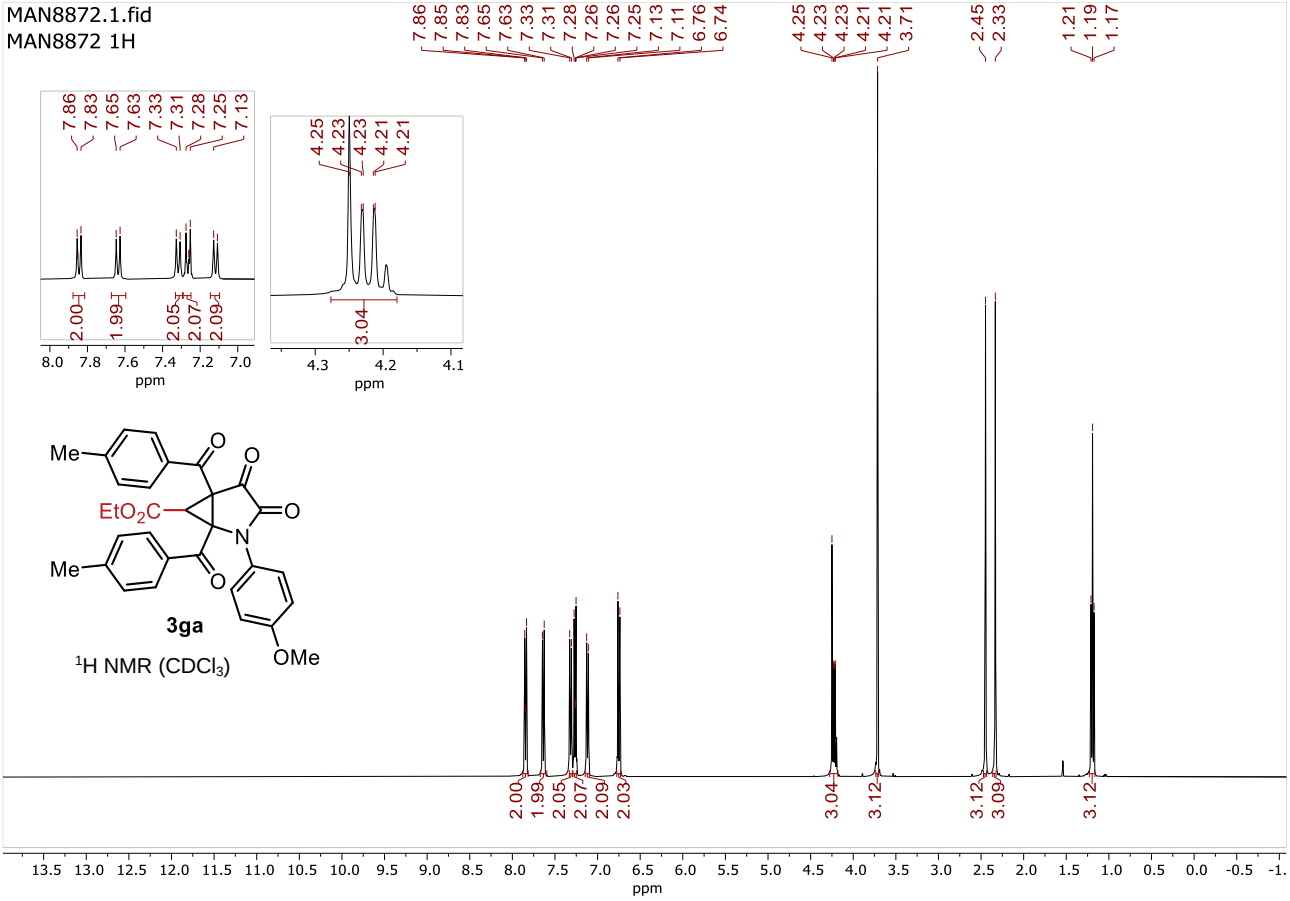
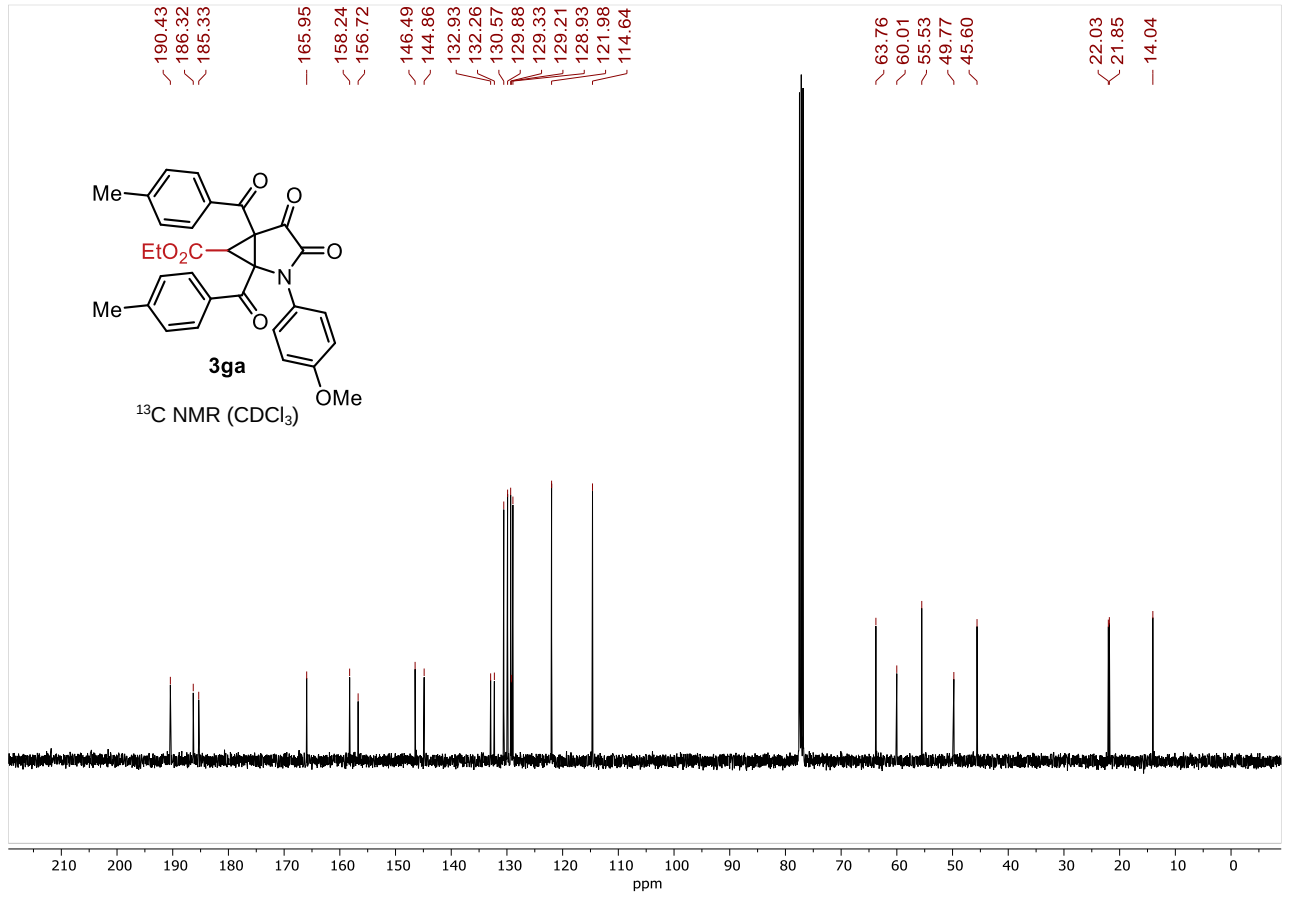

MAN8872.1.fid
MAN8872 1H
7.86 7.85 7.83 7.65 7.63 7.33 7.31 7.28 7.26 7.25 7.13 7.11 6.76 6.74
4.25 4.23 4.23 4.21 4.21 3.71
2.45 2.33
1.21 1.19 1.17
2.00 1.99 2.05 2.07 2.09 2.03
3.04
3.12
3.12 3.09
3.12
ppm
Me
EtO2C
Me
O
N
OMe
3ga
1H NMR (CDCl3)


190.43 186.32 185.33
165.95
158.24 156.72
146.49 144.86
132.93 132.26 130.57 129.88 129.33 129.21 128.93 121.98 114.64
63.76 60.01 55.53 49.77 45.60
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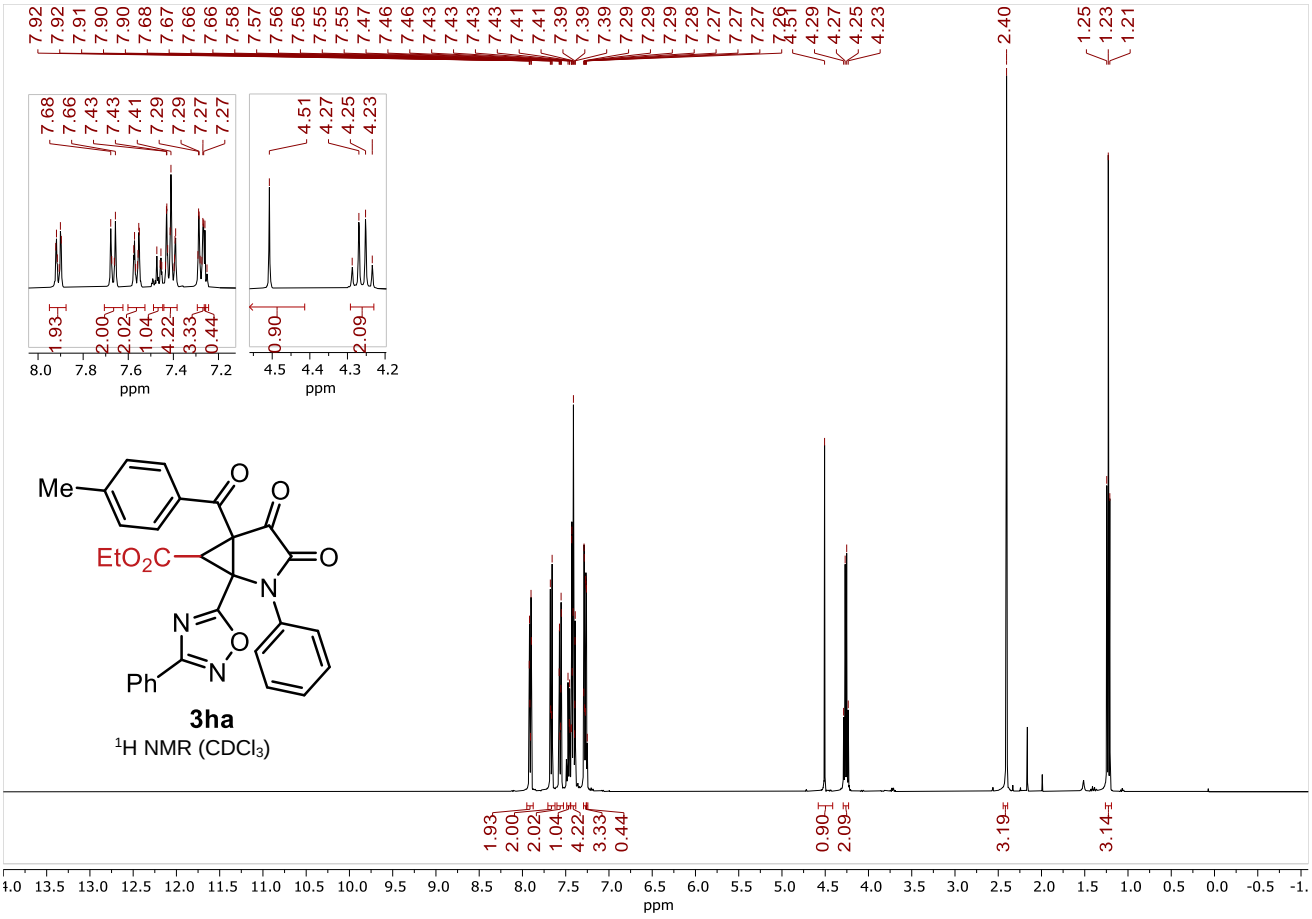
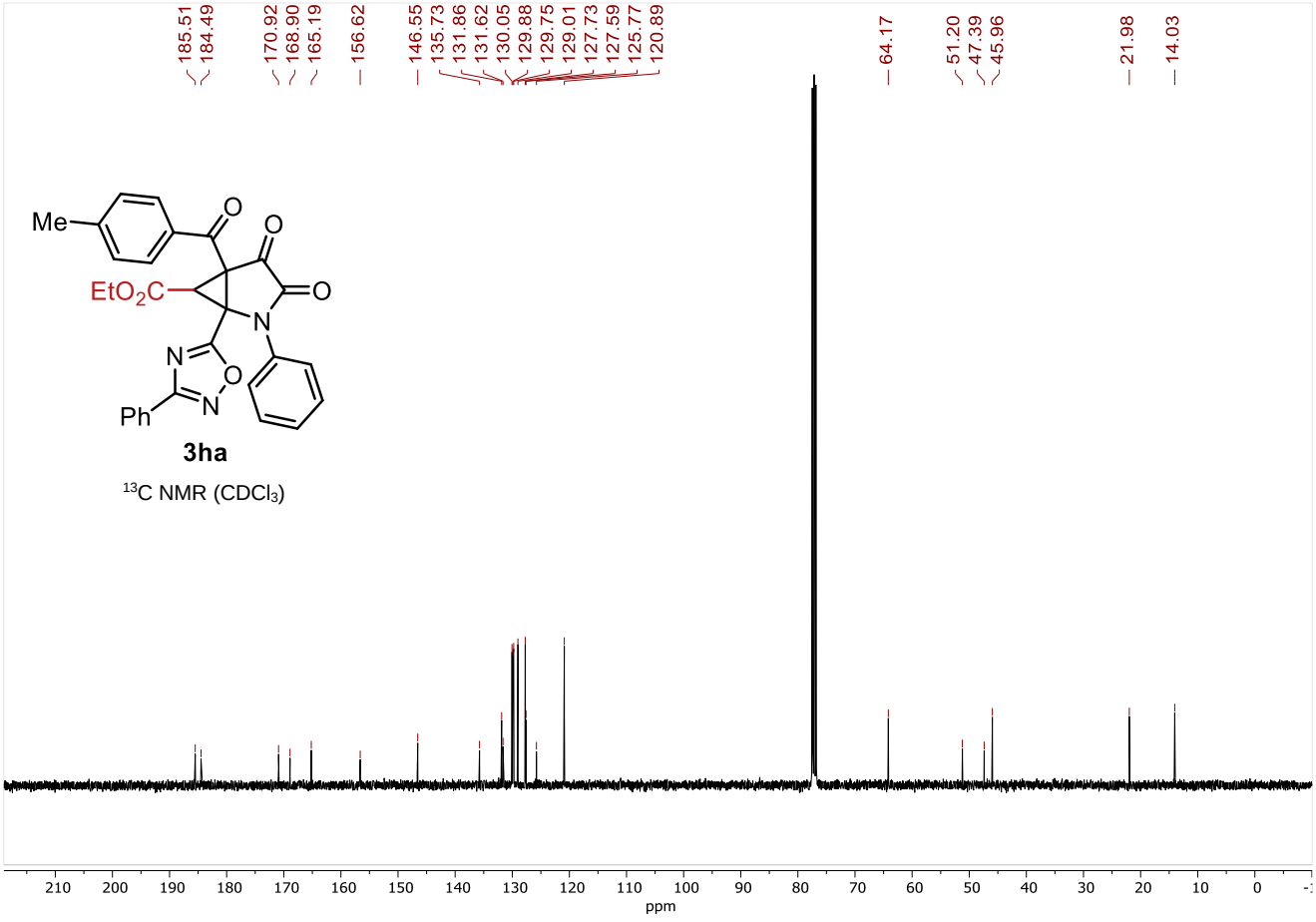
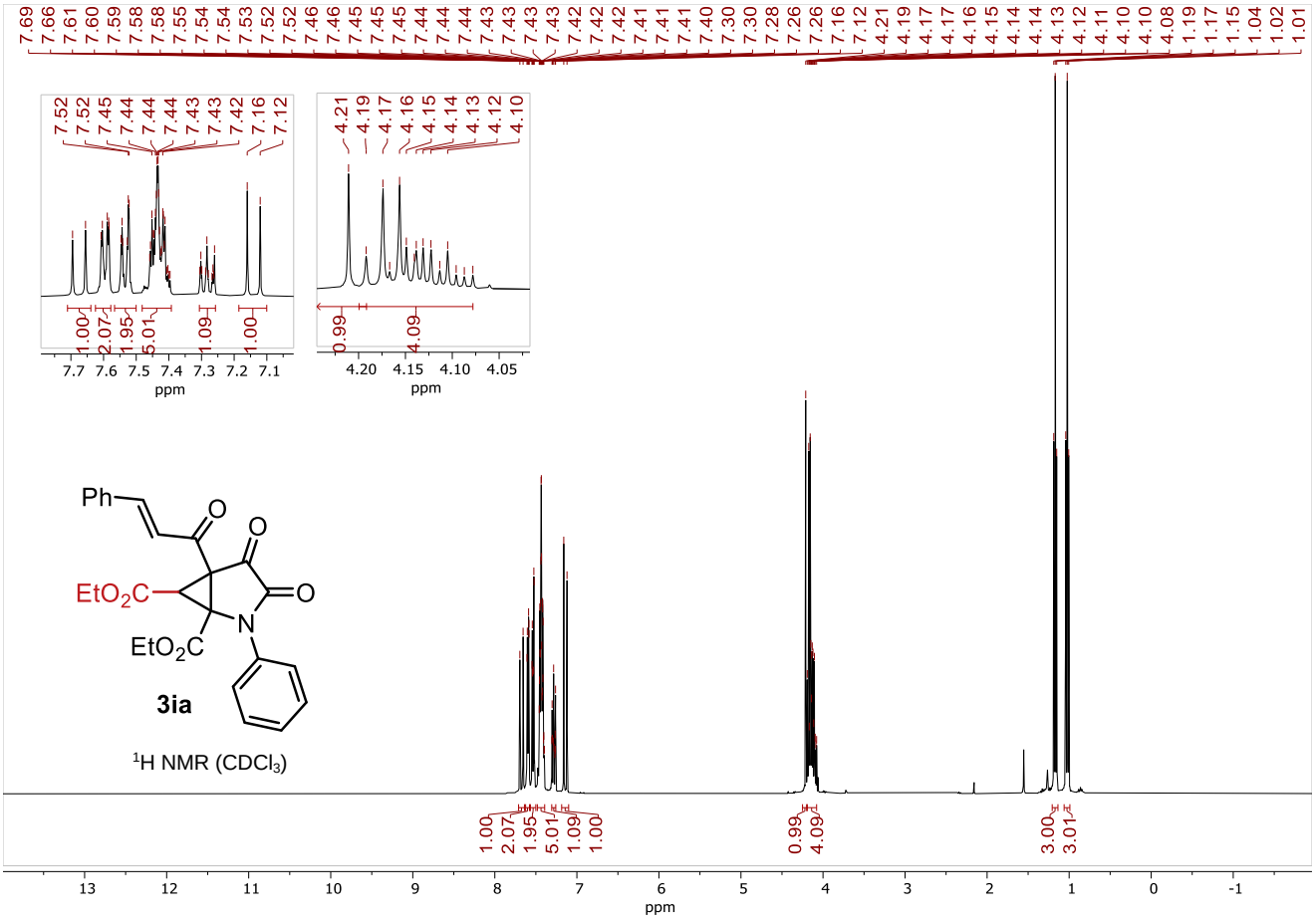
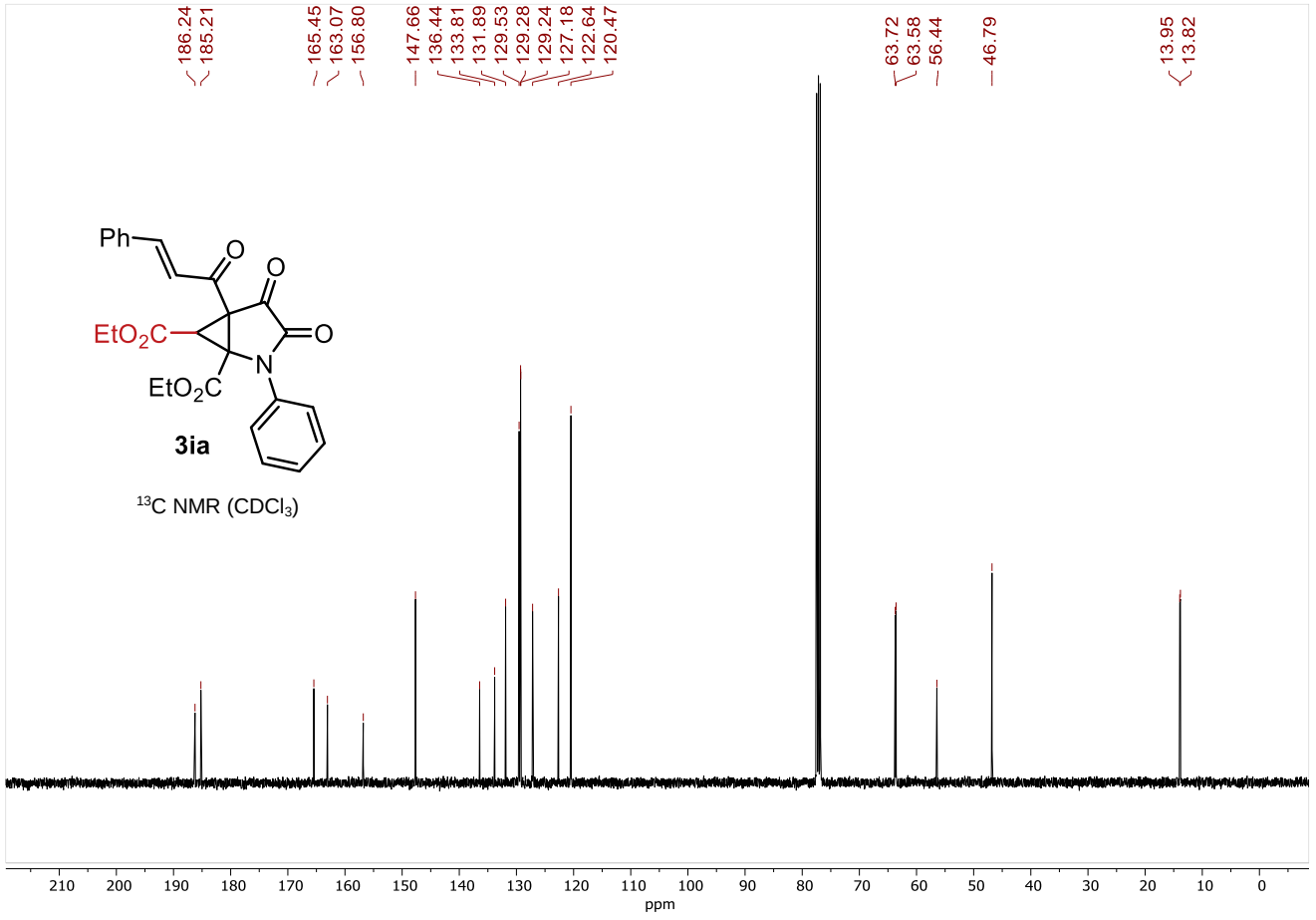
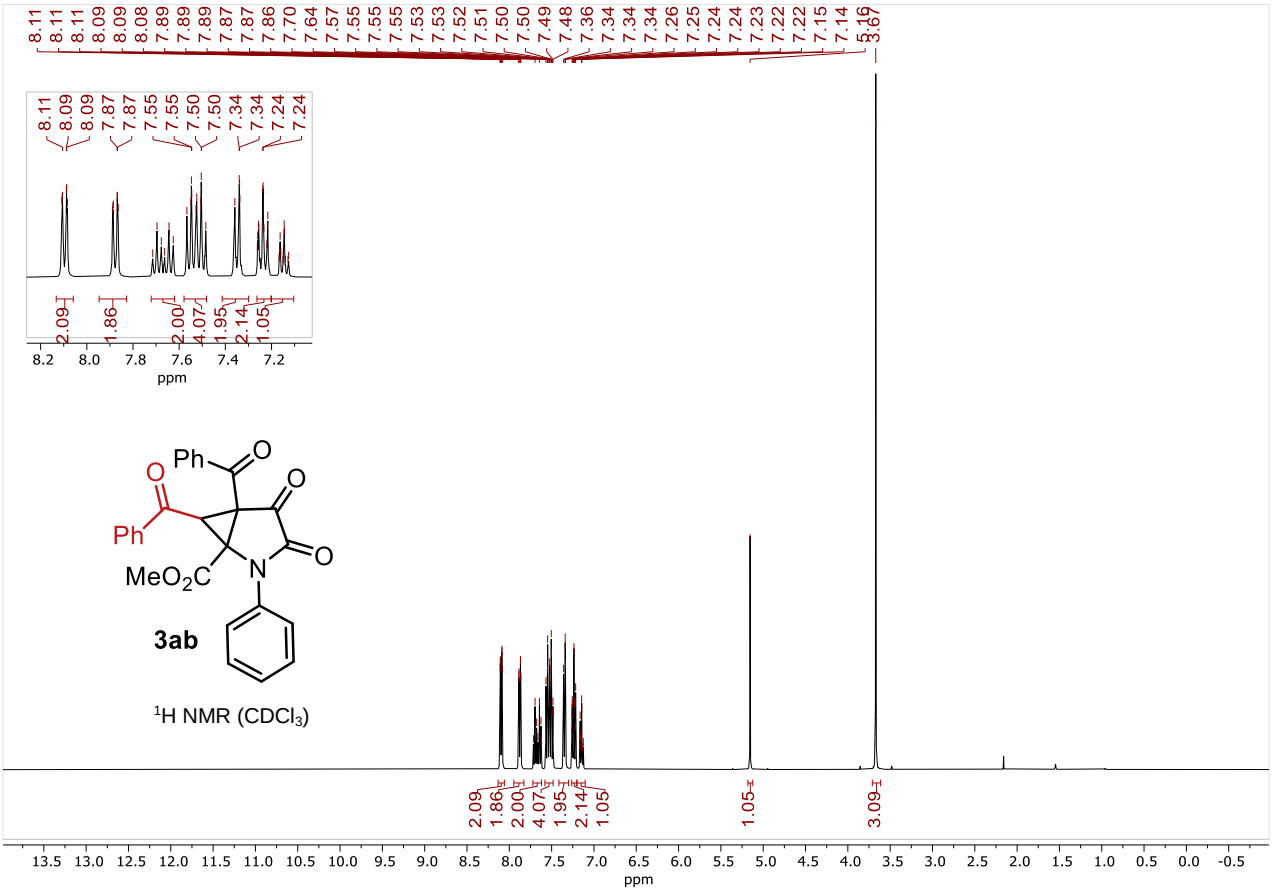
14.04
ppm
Me
EtO2C
Me
O
N
OMe
3ga
13C NMR (CDCl3)

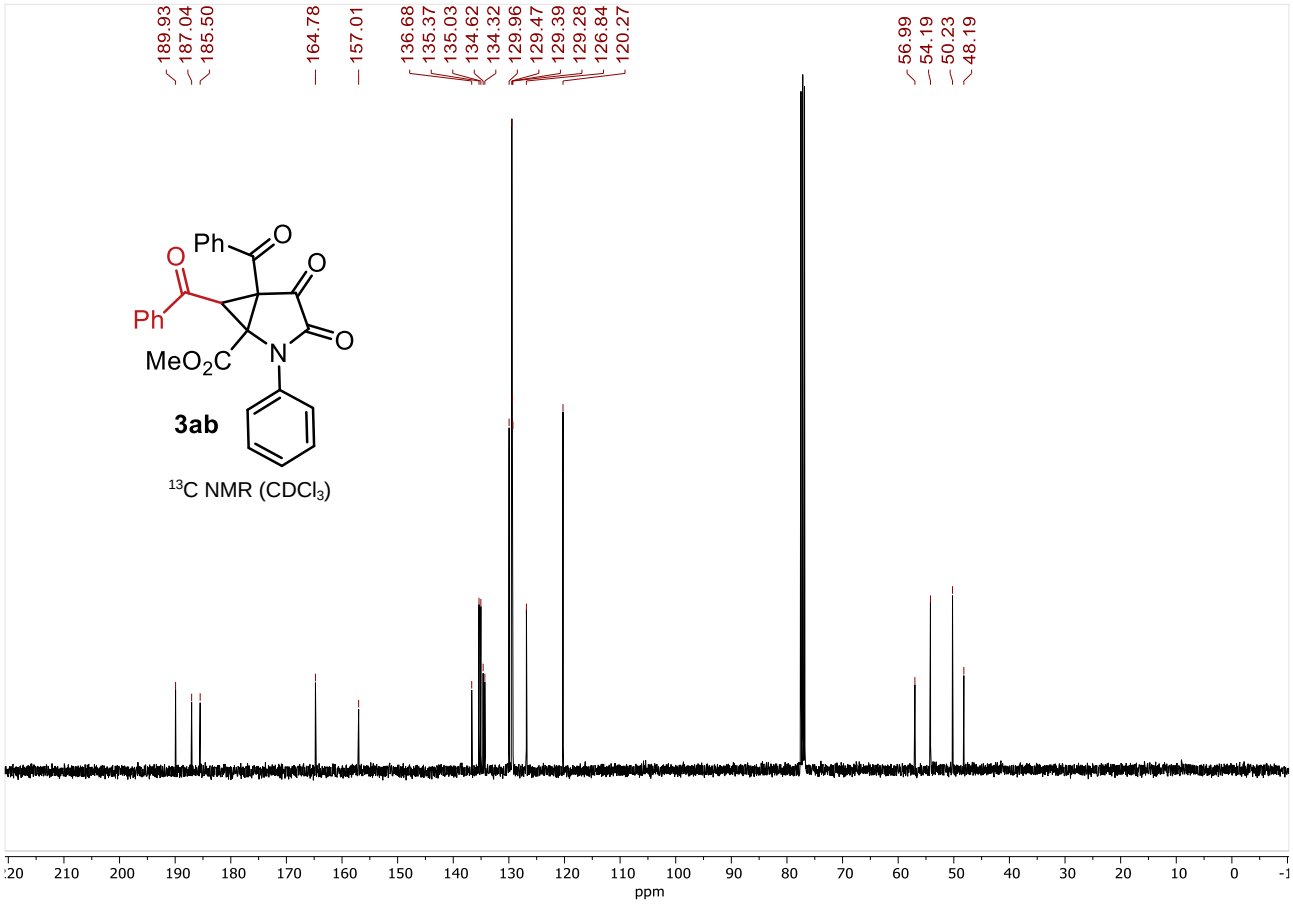

3ha
^{1}H NMR ($CDCl_3$)
ppm

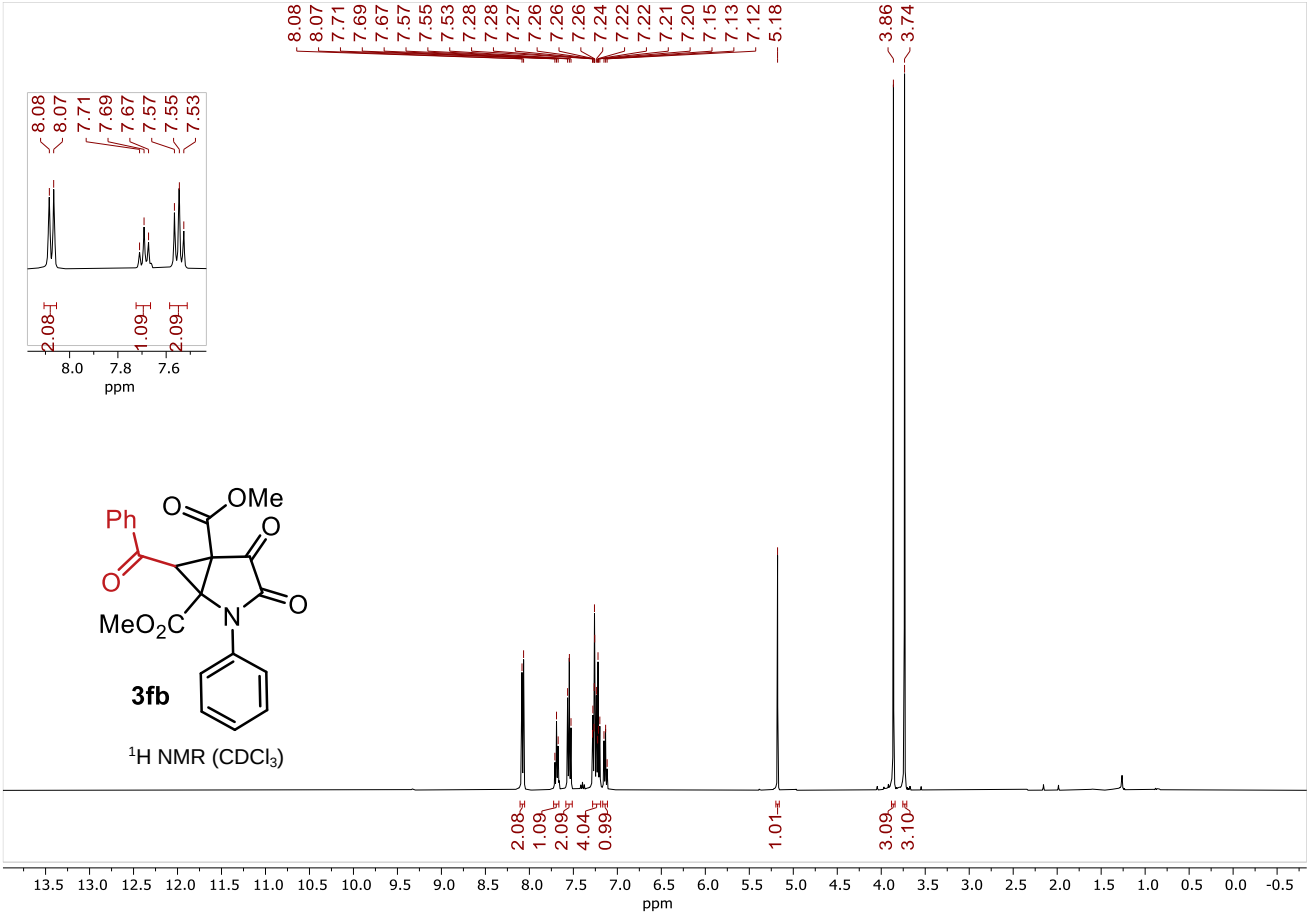

3ha
^{13}C NMR ($CDCl_3$)
ppm


Ph
EtO2C
EtO2C
3ia
1H NMR (CDCl3)
ppm


Ph
EtO2C
EtO2C
3ia
13C NMR (CDCl3)
ppm


3ab
^{1}H NMR ($CDCl_3$)
ppm


3ab
^{13}C NMR ($CDCl_3$)
ppm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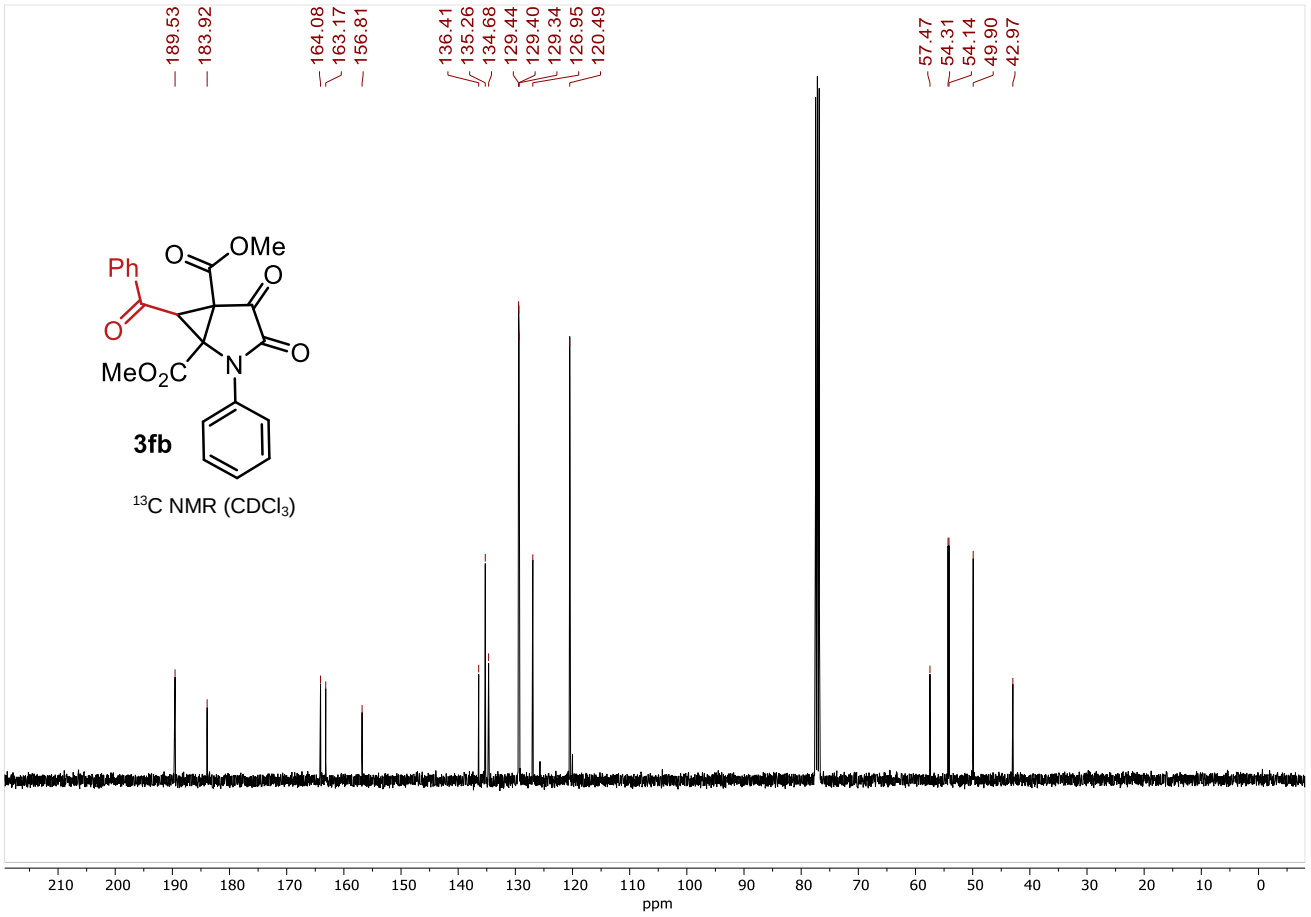
8.07
7.71
7.69
7.67
7.57
7.55
7.53
7.28
7.28
7.27
7.26
7.26
7.26
7.24
7.22
7.22
7.21
7.20
7.15
7.13
7.12
5.18
3.86
3.74
2.08
1.09
2.09
4.04
0.99
1.01
3.09
3.10
ppm
Ph
OMe
MeO2C
3fb
1H NMR (CDCl3)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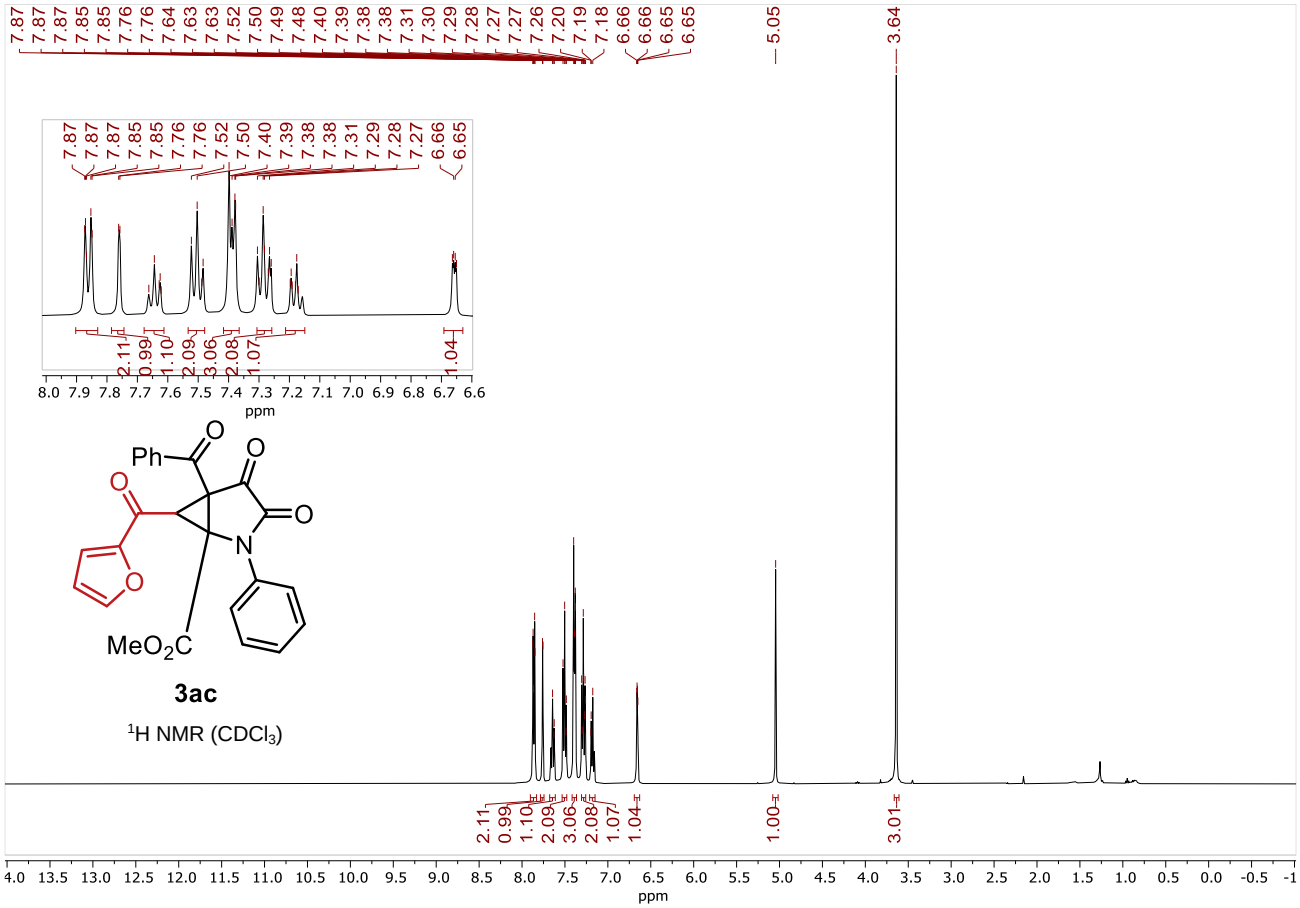
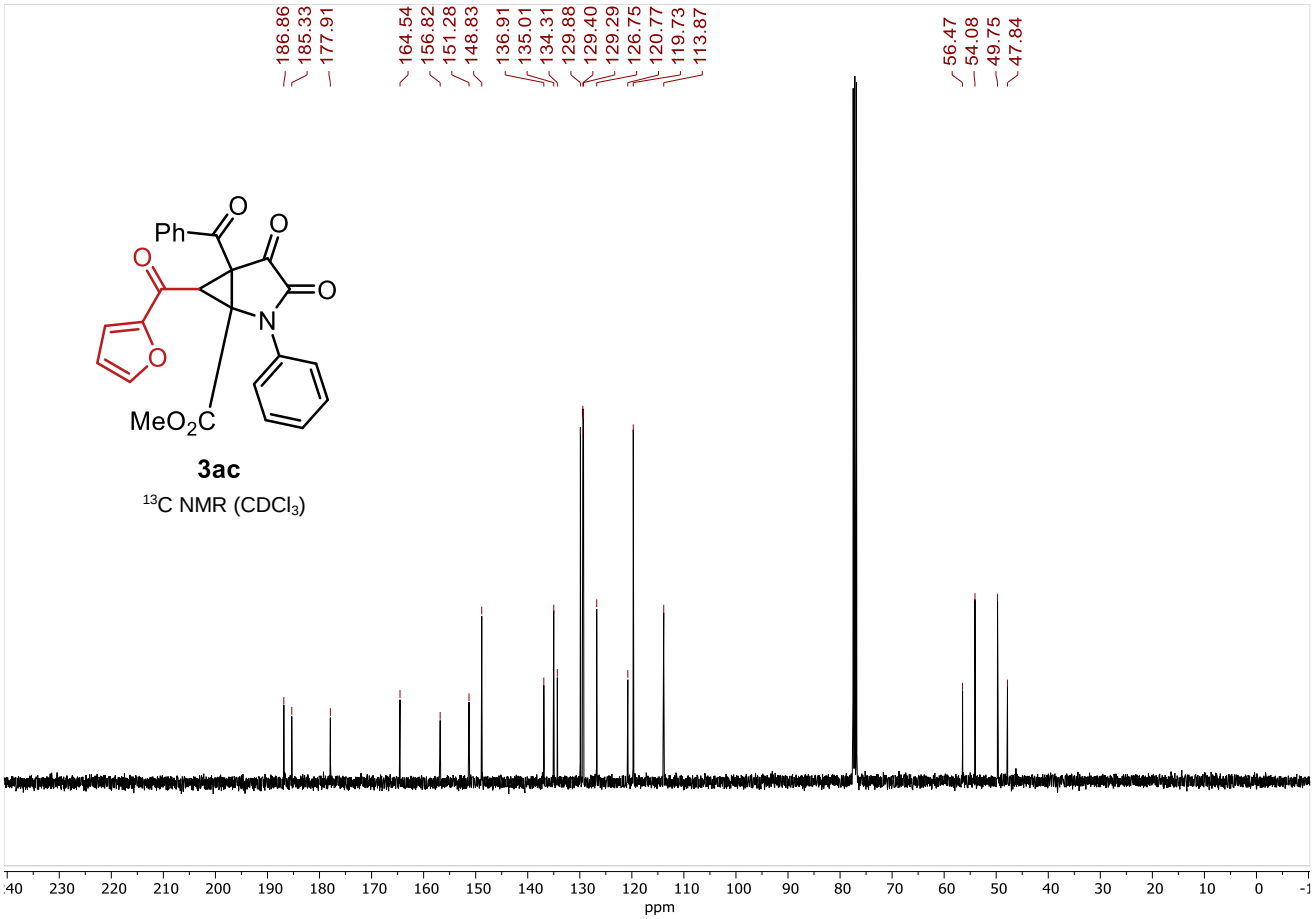
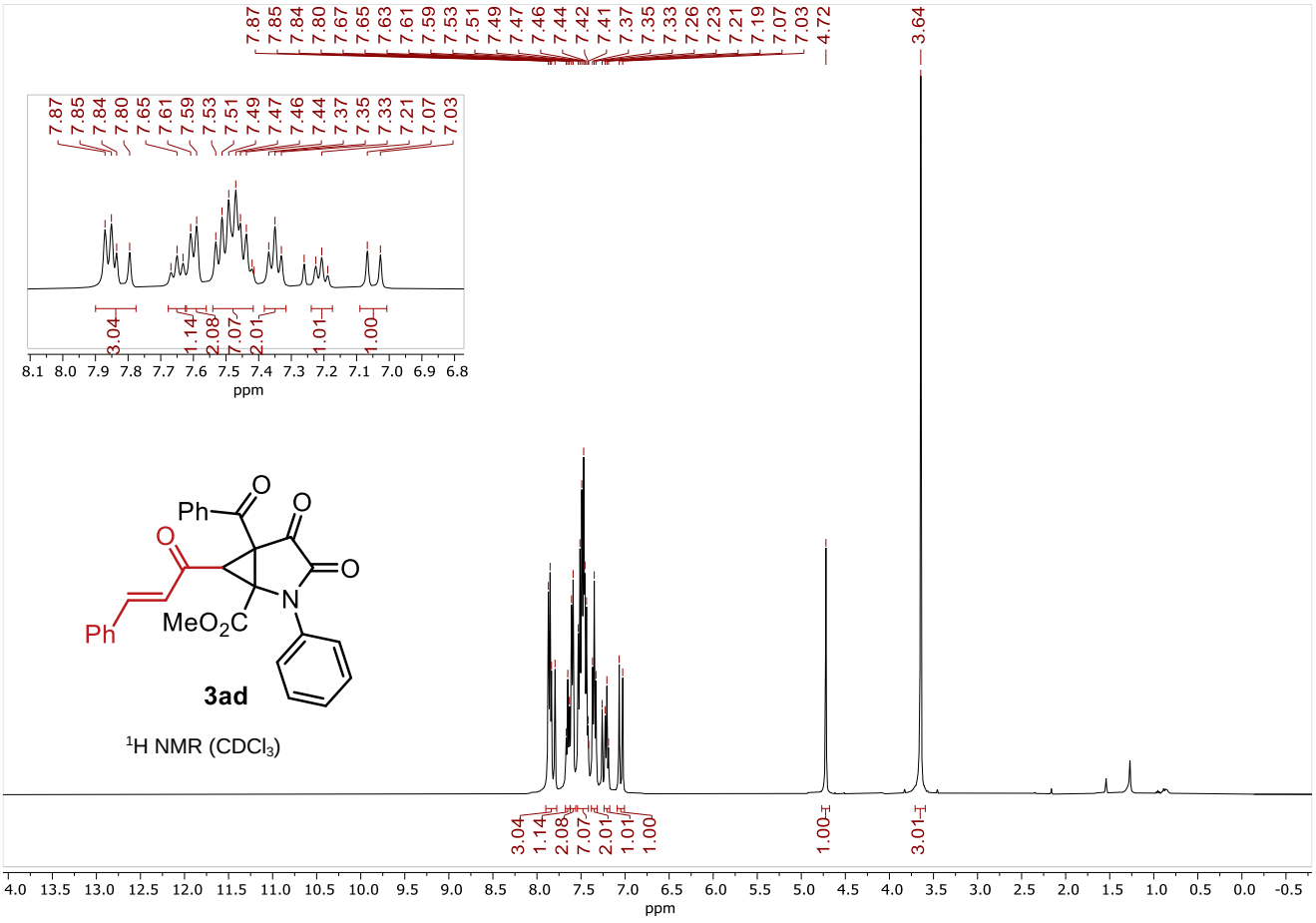
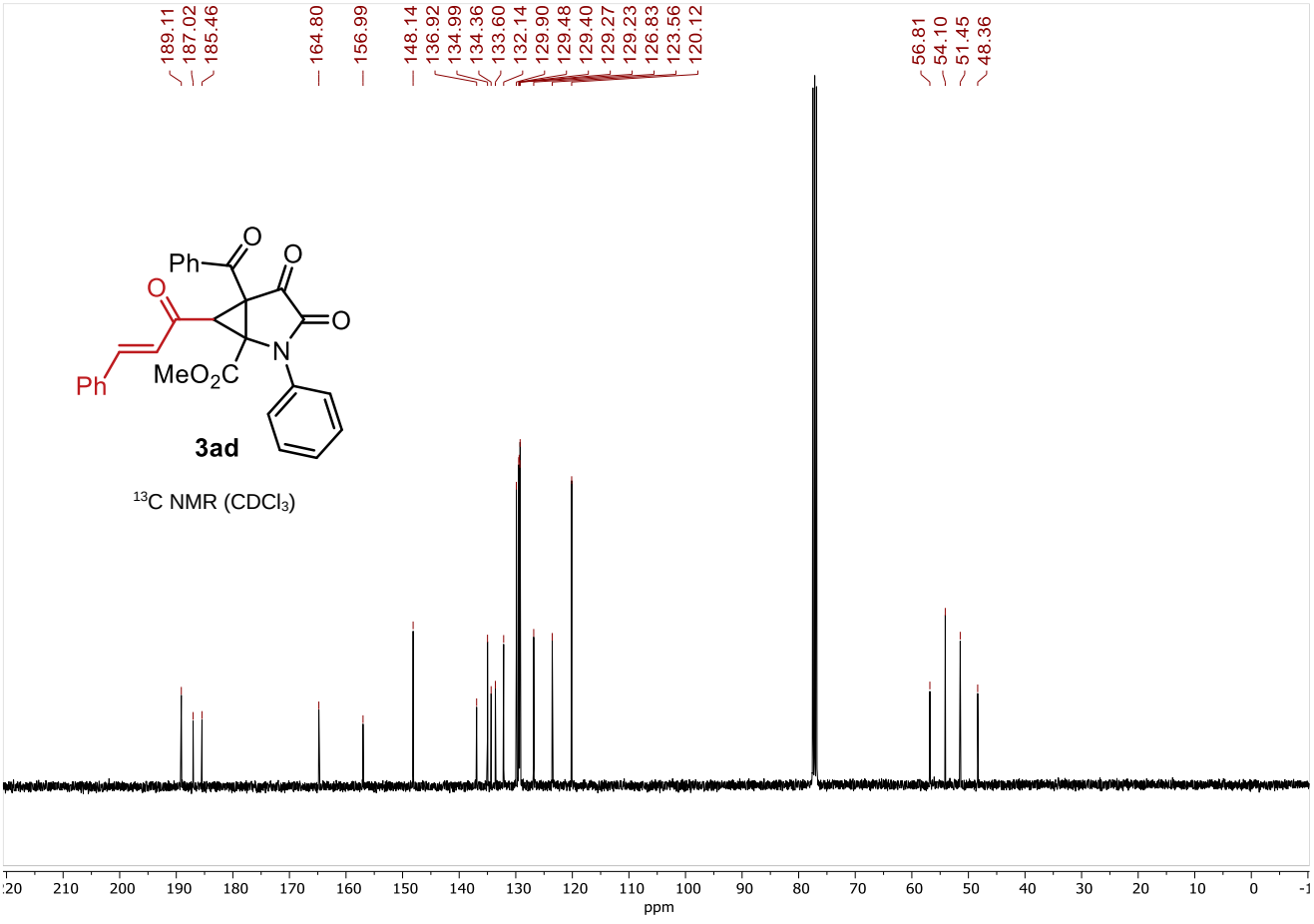
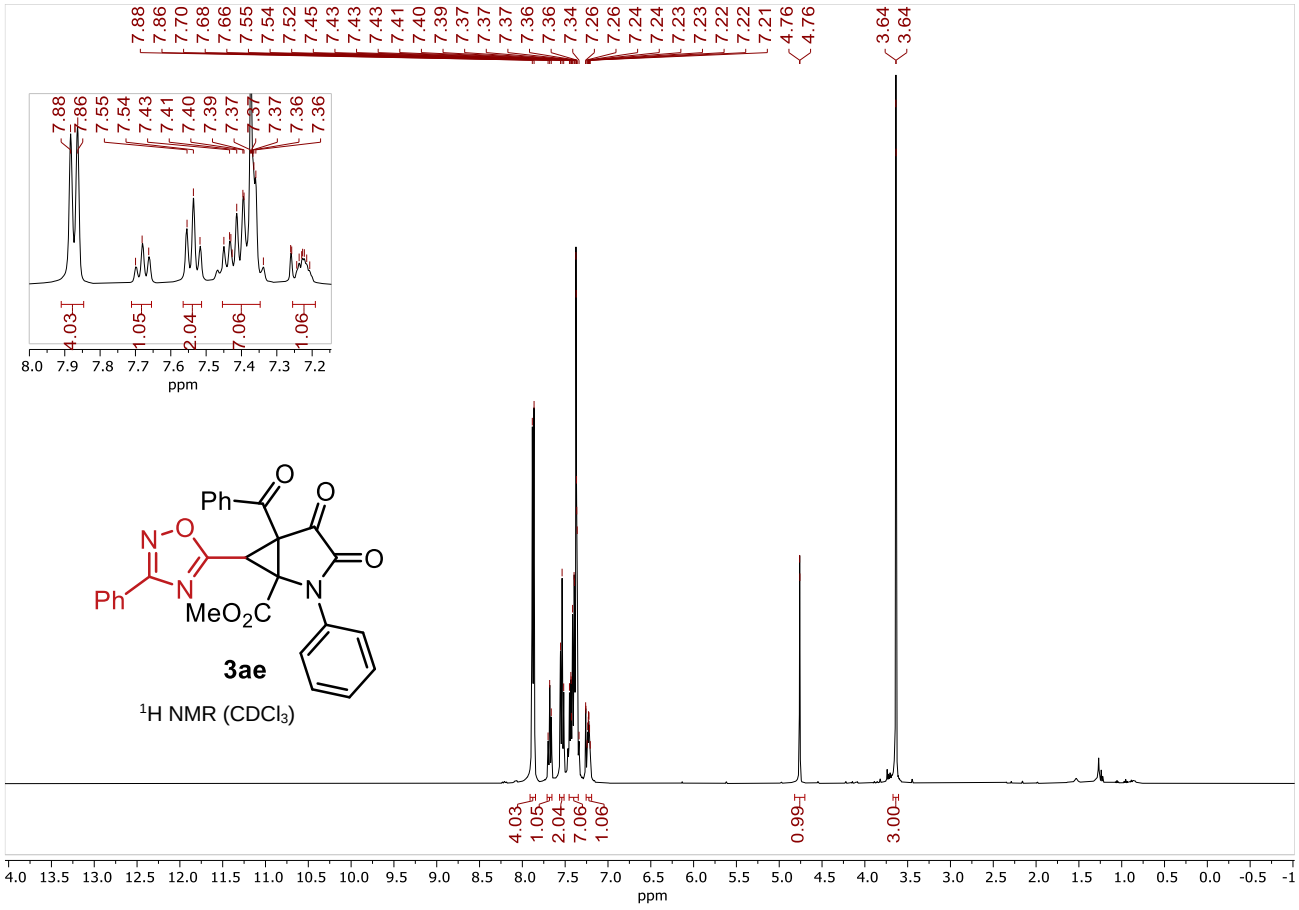
183.92
164.08
163.17
156.81
136.41
135.26
134.68
129.44
129.40
129.34
126.95
120.49
57.47
54.31
54.14
49.90
42.97
ppm
Ph
OMe
MeO2C
3fb
13C NMR (CDCl3)

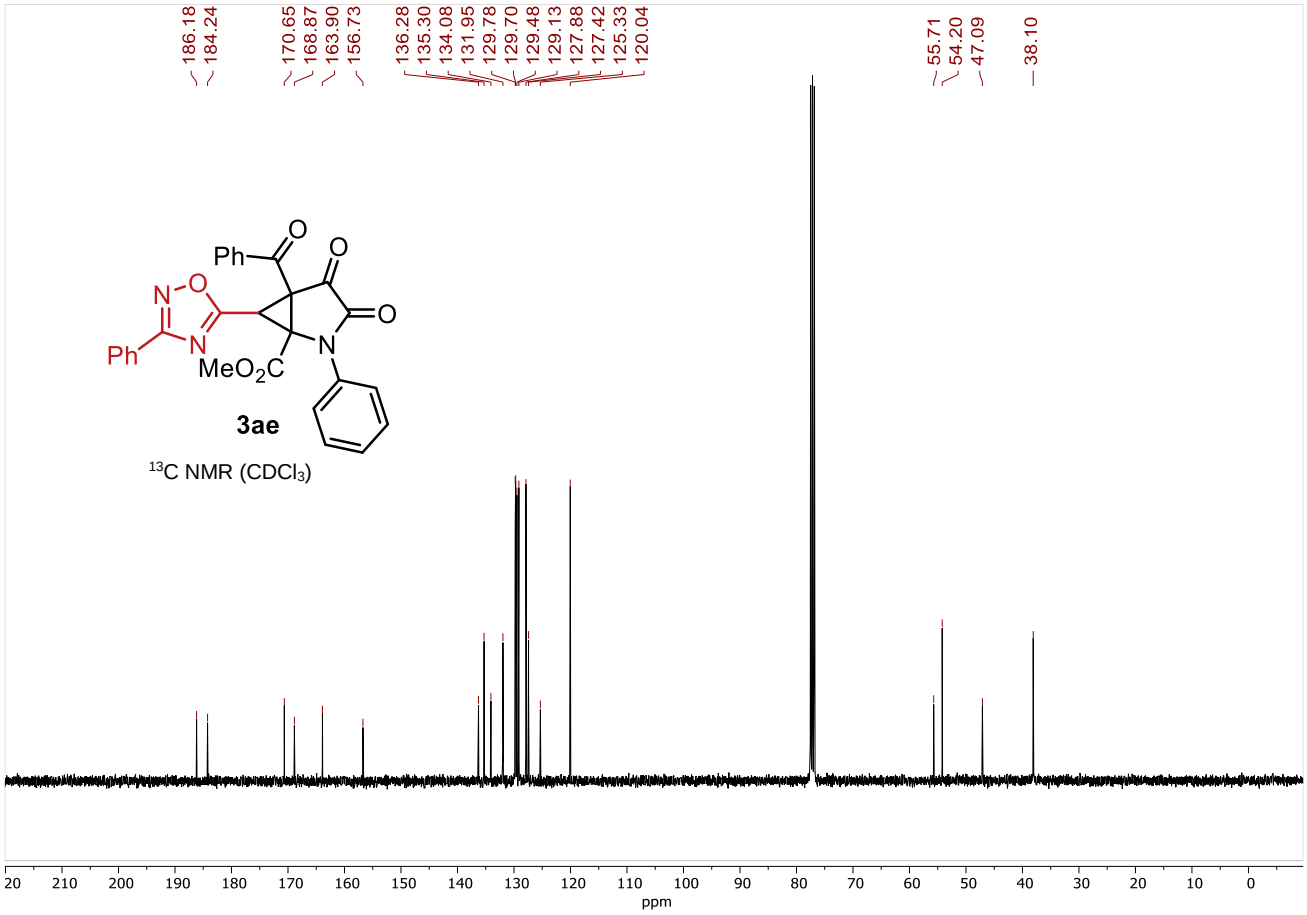

Ph
O
O
O
O
N
O
MeO2C
3ac
1H NMR (CDCl3)
ppm

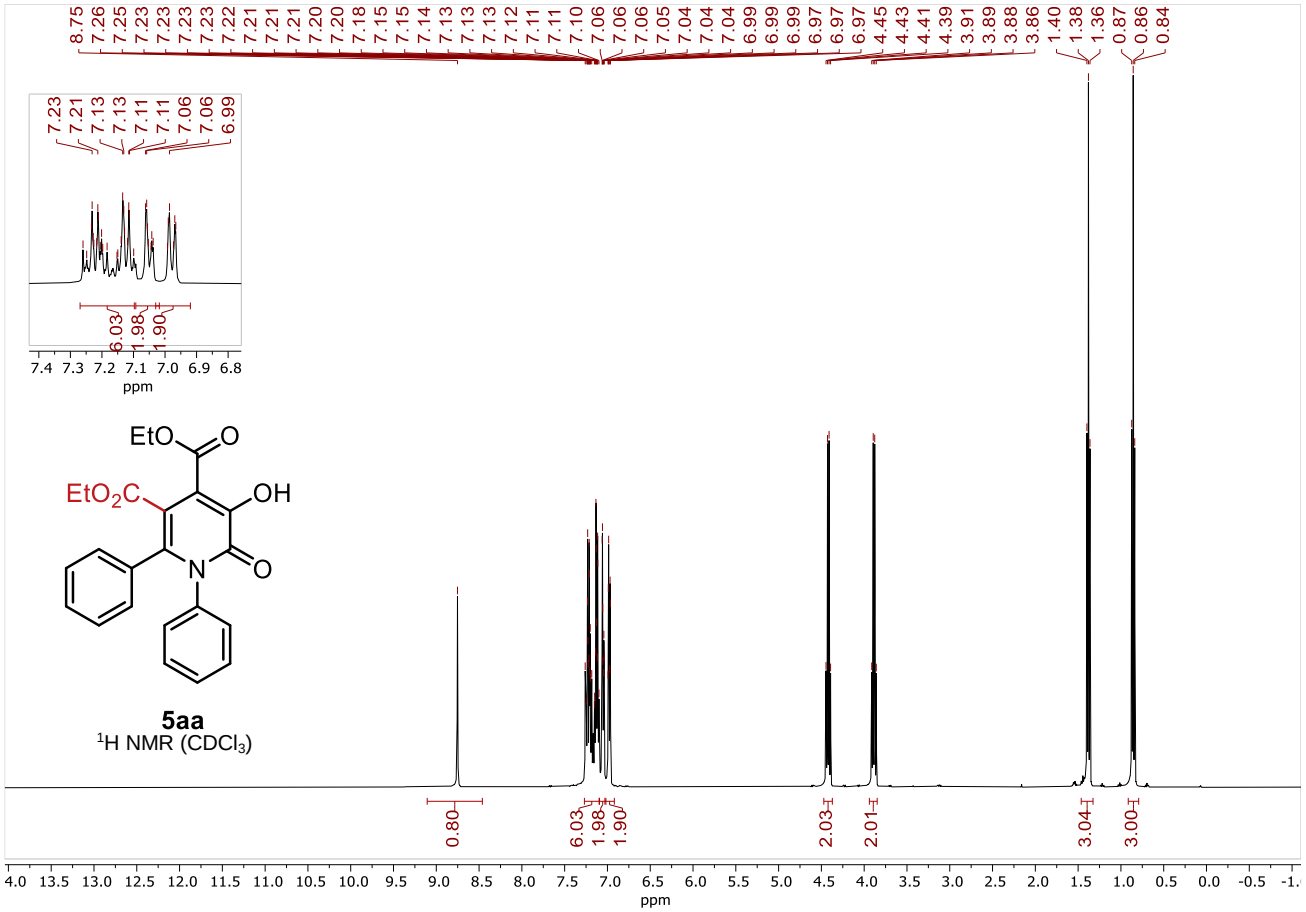

Ph
O
O
O
O
N
O
MeO2C
3ac
13C NMR (CDCl3)
ppm

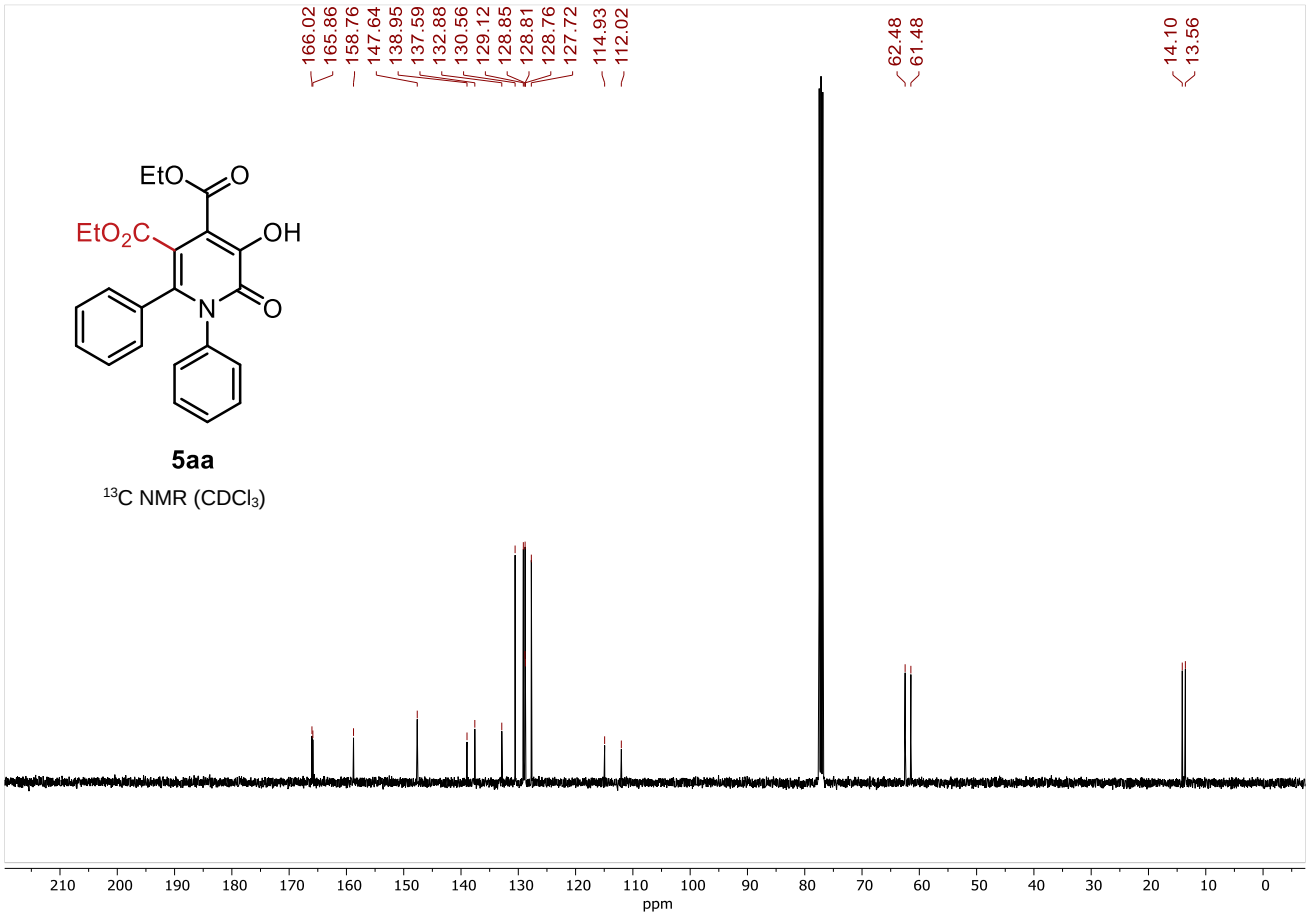

7.87 7.85 7.84 7.80 7.67 7.65 7.63 7.61 7.59 7.53 7.51 7.49 7.47 7.46 7.44 7.42 7.41 7.37 7.35 7.33 7.26 7.23 7.21 7.19 7.07 7.03 4.72 3.64
3.04 1.14 2.08 7.07 2.01 1.01 1.00 1.00 3.01
ppm
Ph
O
O
O
N
MeO2C
Ph
3ad
1H NMR (CDCl3)

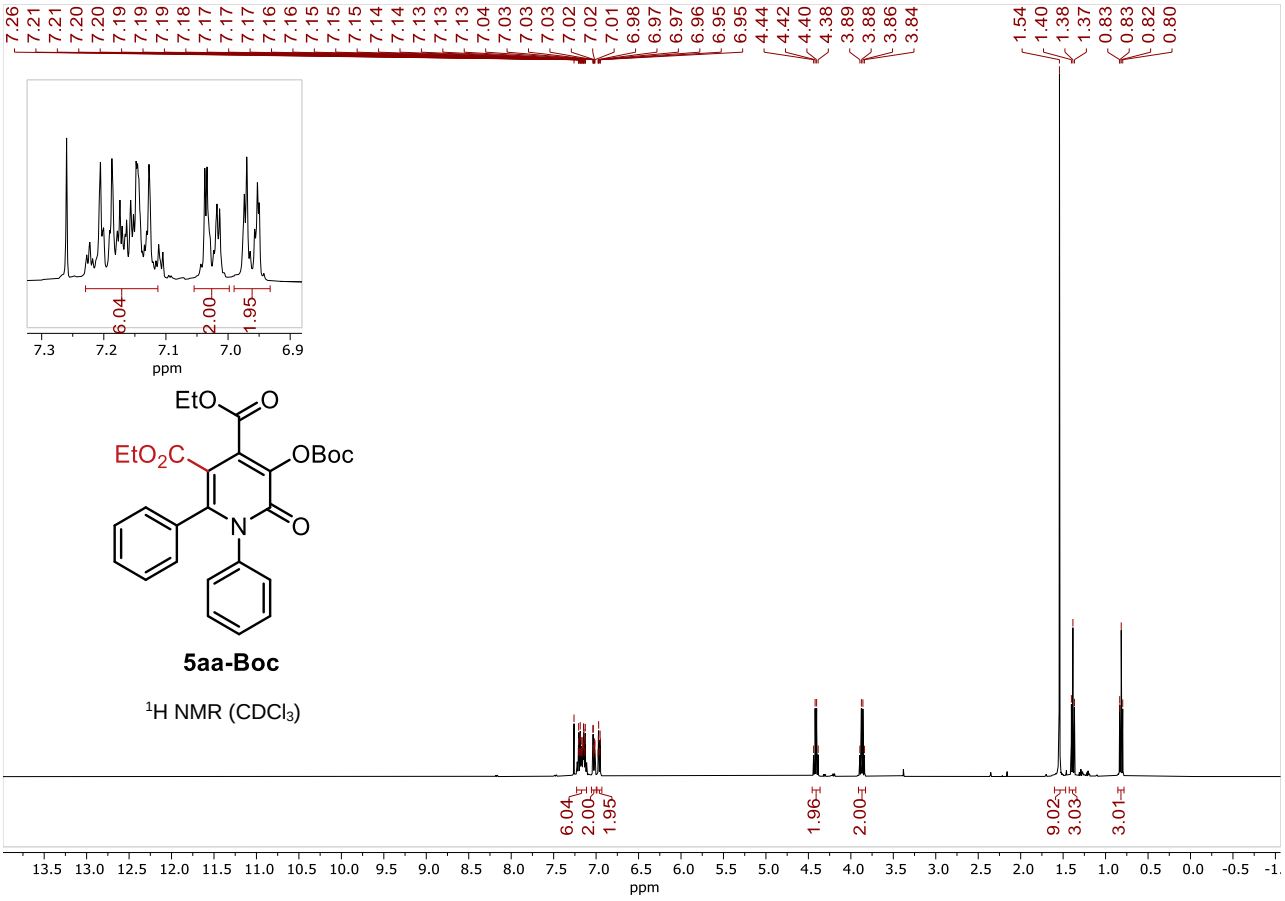

189.11 187.02 185.46 164.80 156.99 148.14 136.92 134.99 134.36 133.60 132.14 129.90 129.48 129.40 129.27 129.23 126.83 123.56 120.12 56.81 54.10 51.45 48.36
ppm
Ph
O
O
O
N
MeO2C
Ph
3ad
13C NMR (CDCl3)

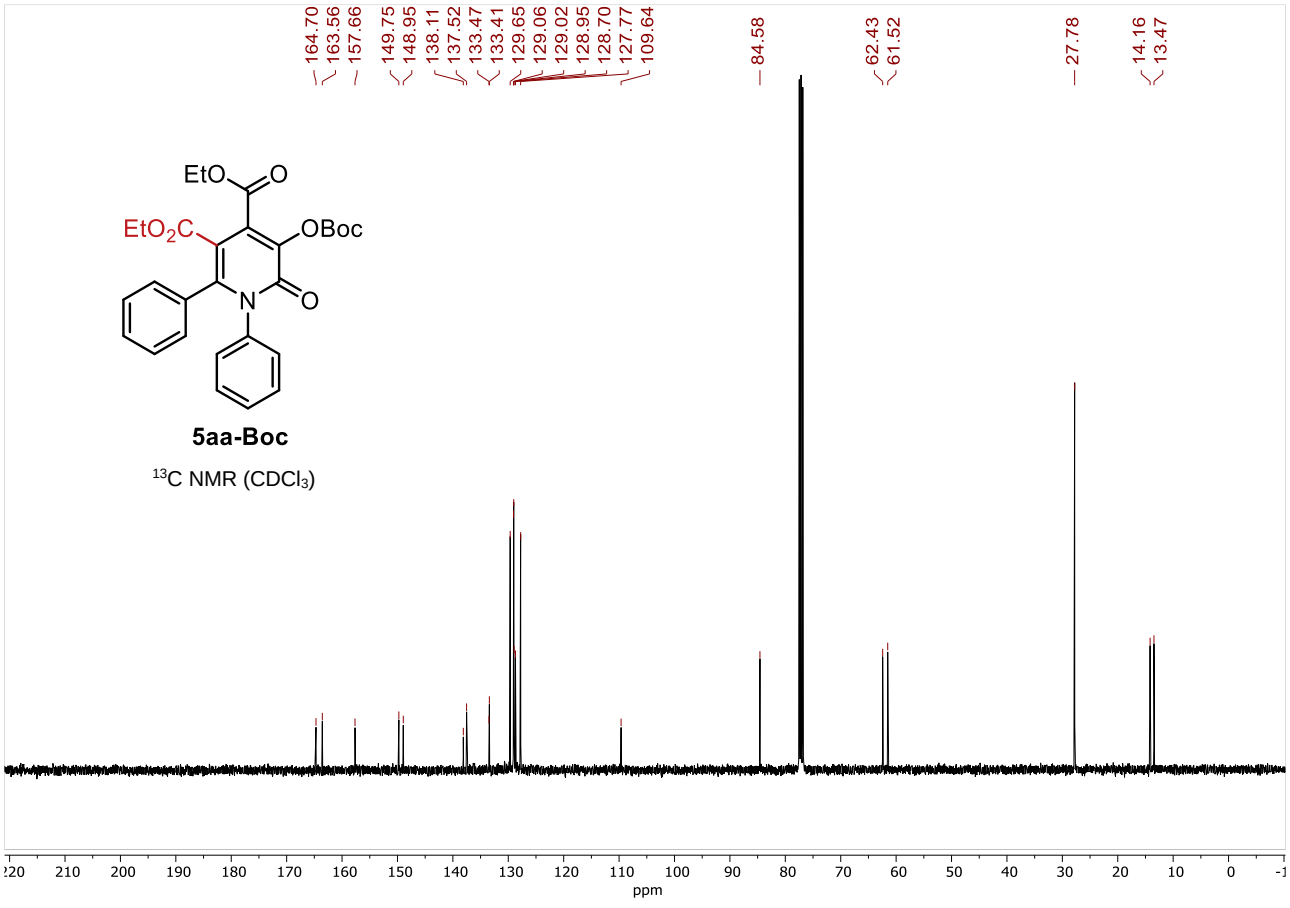

7.88 7.86 7.70 7.68 7.66 7.55 7.54 7.52 7.45 7.43 7.43 7.43 7.41 7.40 7.39 7.37 7.37 7.37 7.36 7.36 7.34 7.26 7.26 7.24 7.24 7.23 7.23 7.22 7.22 7.21 4.76 4.76 3.64 3.64
4.03 1.05 2.04 7.06 1.06
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
ppm
Ph
O
O
N
O
O
N
Ph
N
MeO2C
3ae
1H NMR (CDCl3)
4.03 1.05 2.04 7.06 1.06 0.99 3.00
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm

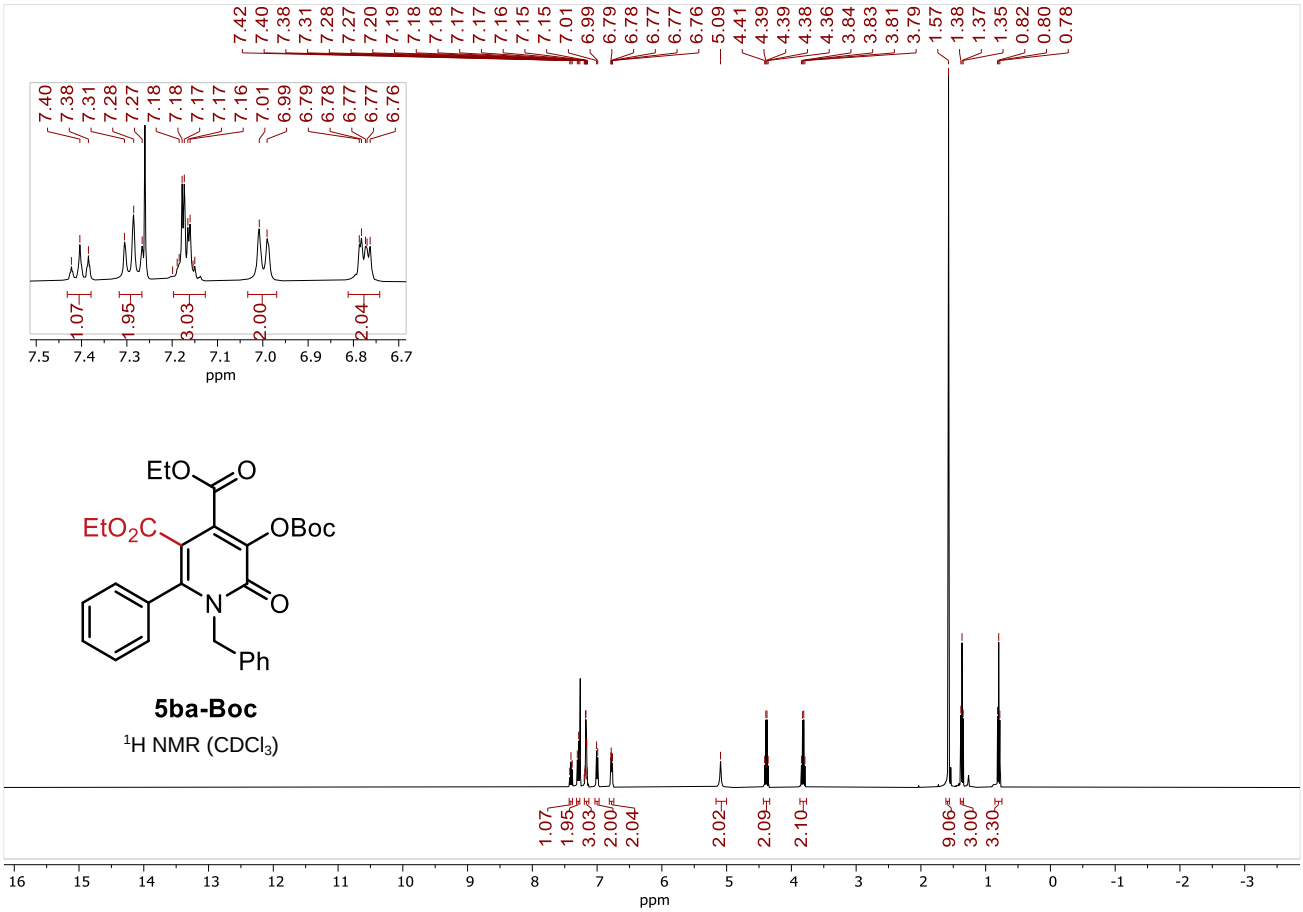

186.18 184.24 170.65 168.87 163.90 156.73 136.28 135.30 134.08 131.95 129.78 129.70 129.48 129.13 127.88 127.42 125.33 120.04 55.71 54.20 47.09 38.10
Ph
O
O
N
O
O
N
Ph
N
MeO2C
3ae
13C NMR (CDCl3)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


8.75 7.26 7.25 7.23 7.23 7.23 7.23 7.22 7.21 7.21 7.21 7.20 7.20 7.18 7.15 7.15 7.14 7.13 7.13 7.13 7.12 7.11 7.11 7.10 7.06 7.06 7.06 7.05 7.04 7.04 7.04 6.99 6.99 6.99 6.97 6.97 6.97 4.45 4.43 4.41 4.39 3.91 3.89 3.88 3.86 1.40 1.38 1.36 0.87 0.86 0.84
7.23 7.21 7.13 7.13 7.11 7.11 7.06 7.06 6.99
6.03 1.98 1.90
7.4 7.3 7.2 7.1 7.0 6.9 6.8
ppm
EtO
O
EtO2C
OH
N
O
5aa
1H NMR (CDCl3)
0.80 6.03 1.98 1.90 2.03 2.01 3.04 3.00
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


166.02 165.86 158.76 147.64 138.95 137.59 132.88 130.56 129.12 128.85 128.81 128.76 127.72 114.93 112.02
62.48 61.48
14.10 13.56
EtO
O
EtO2C
OH
N
O
5aa
13C NMR (CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


7.26 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.17 7.17 7.16 7.16 7.15 7.15 7.15 7.14 7.14 7.13 7.13 7.13 7.04 7.03 7.03 7.03 7.02 7.02 7.01 6.98 6.97 6.97 6.96 6.95 6.95 4.44 4.42 4.40 4.38 3.89 3.88 3.86 3.84 1.54 1.40 1.38 1.37 0.83 0.83 0.82 0.80
6.04 2.00 1.95
7.3 7.2 7.1 7.0 6.9
ppm
EtO
O
EtO2C
OBoc
N
O
5aa-Boc
1H NMR (CDCl3)
6.04 2.00 1.95 1.96 2.00 9.02 3.03 3.01
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


164.70 163.56 157.66 149.75 148.95 138.11 137.52 133.47 133.41 129.65 129.06 129.02 128.95 128.70 127.77 109.64 84.58 62.43 61.52 27.78 14.16 13.47
EtO
O
EtO2C
OBoc
N
O
5aa-Boc
13C NMR (CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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1.07 1.95 3.03 2.00 2.04
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
ppm
EtO
O
EtO2C
OBoc
N
O
Ph
5ba-Boc
1H NMR (CDCl3)
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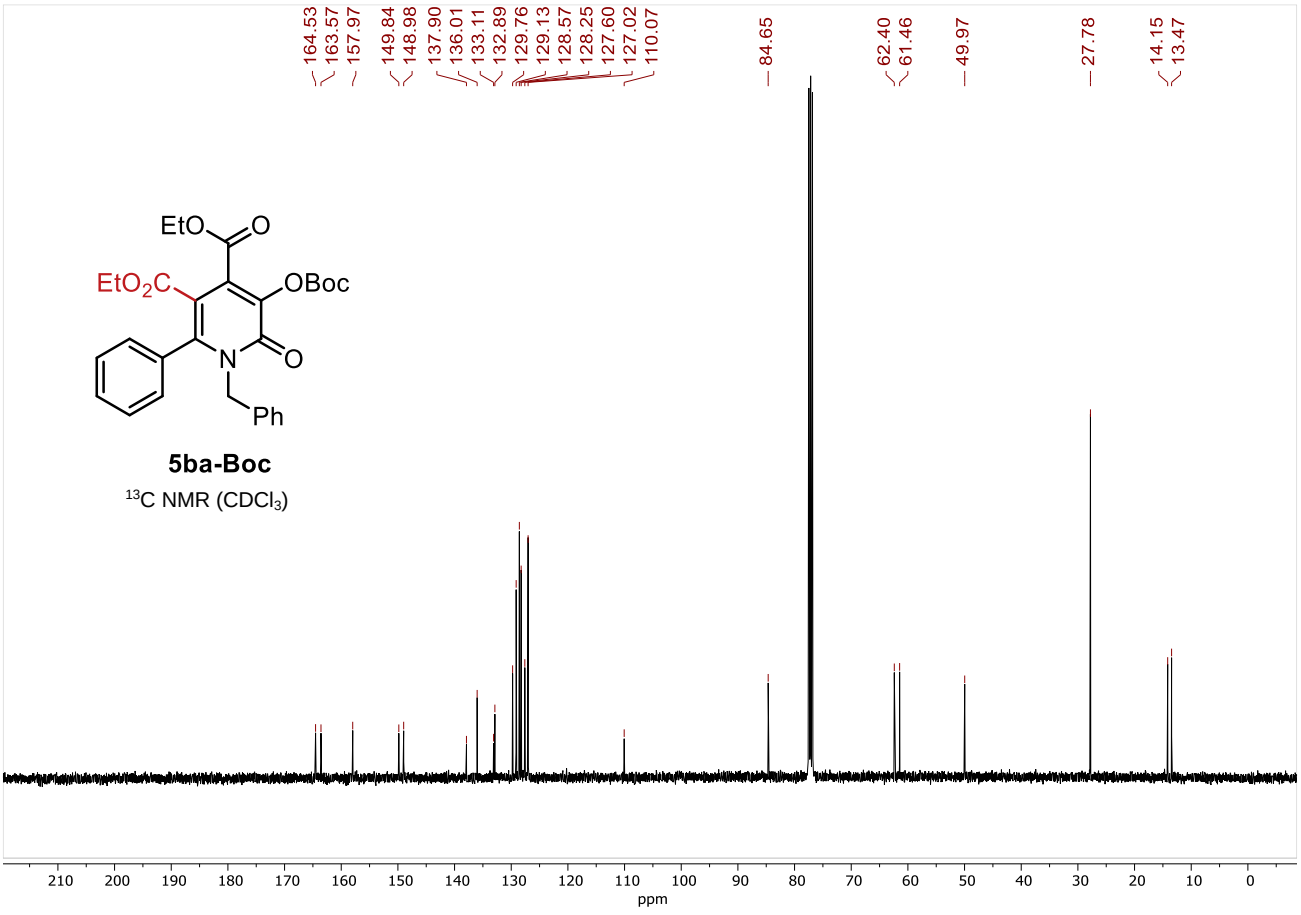
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm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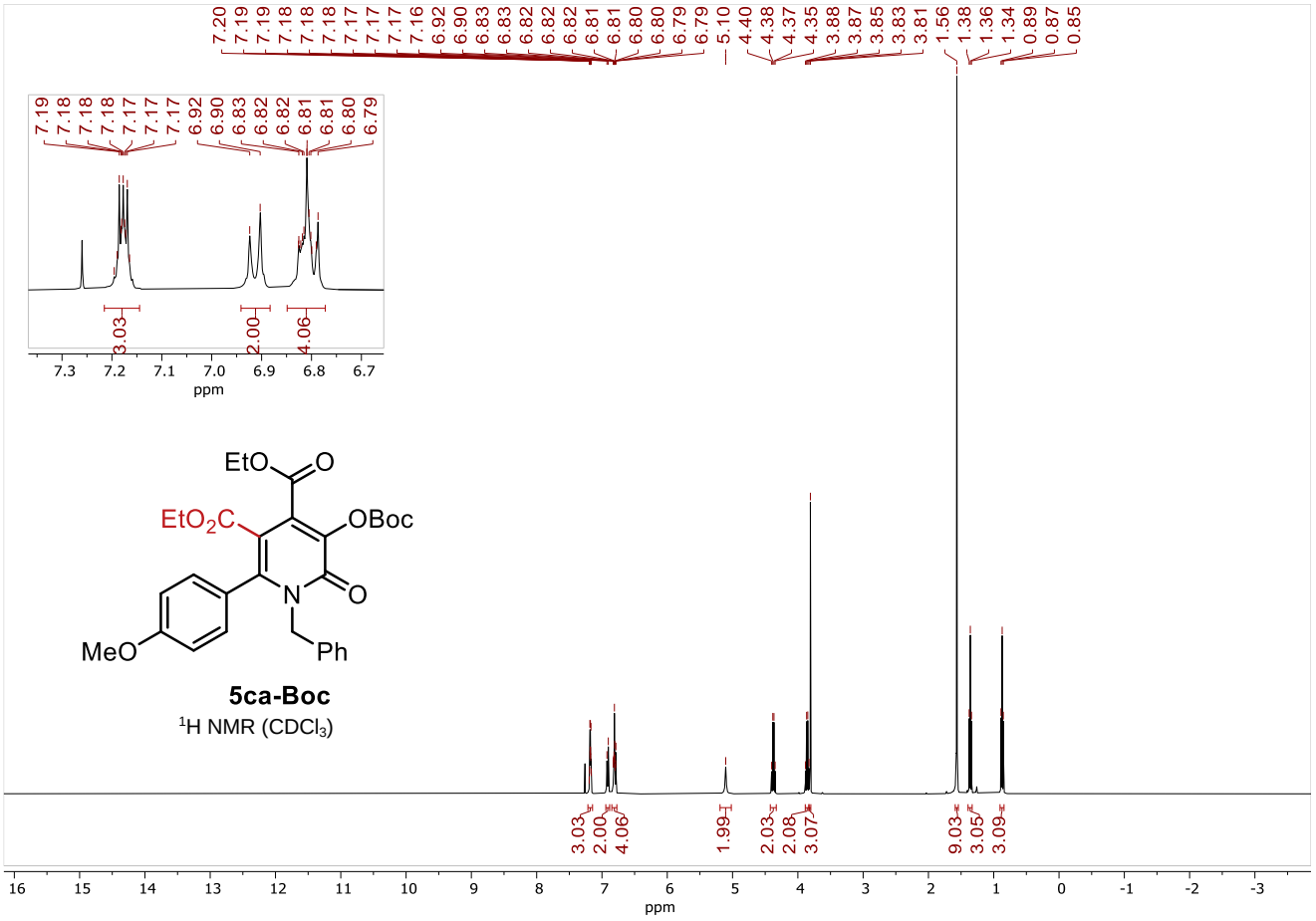
EtO
O
EtO2C
OBoc
N
O
Ph
5ba-Boc
13C NMR (CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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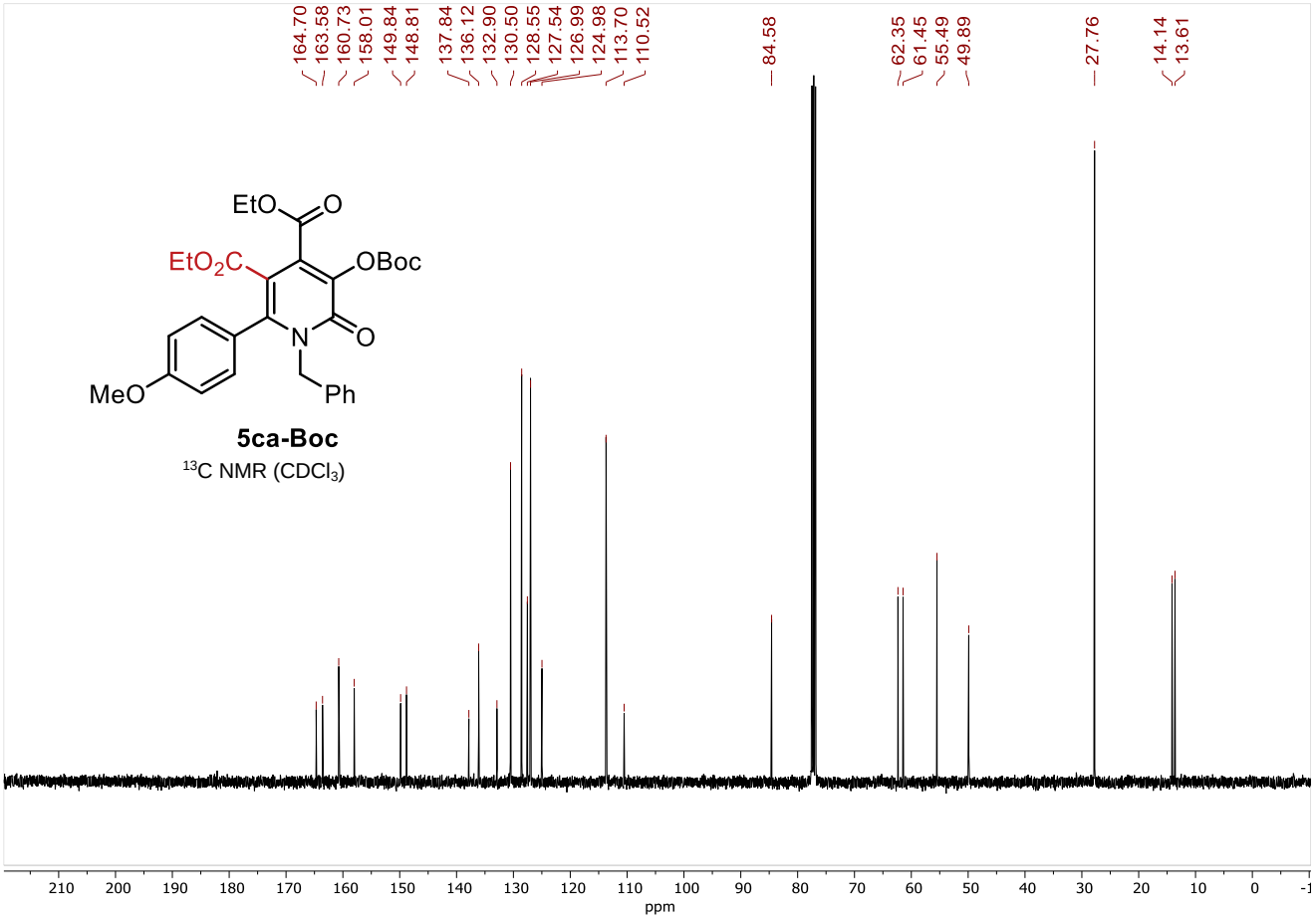
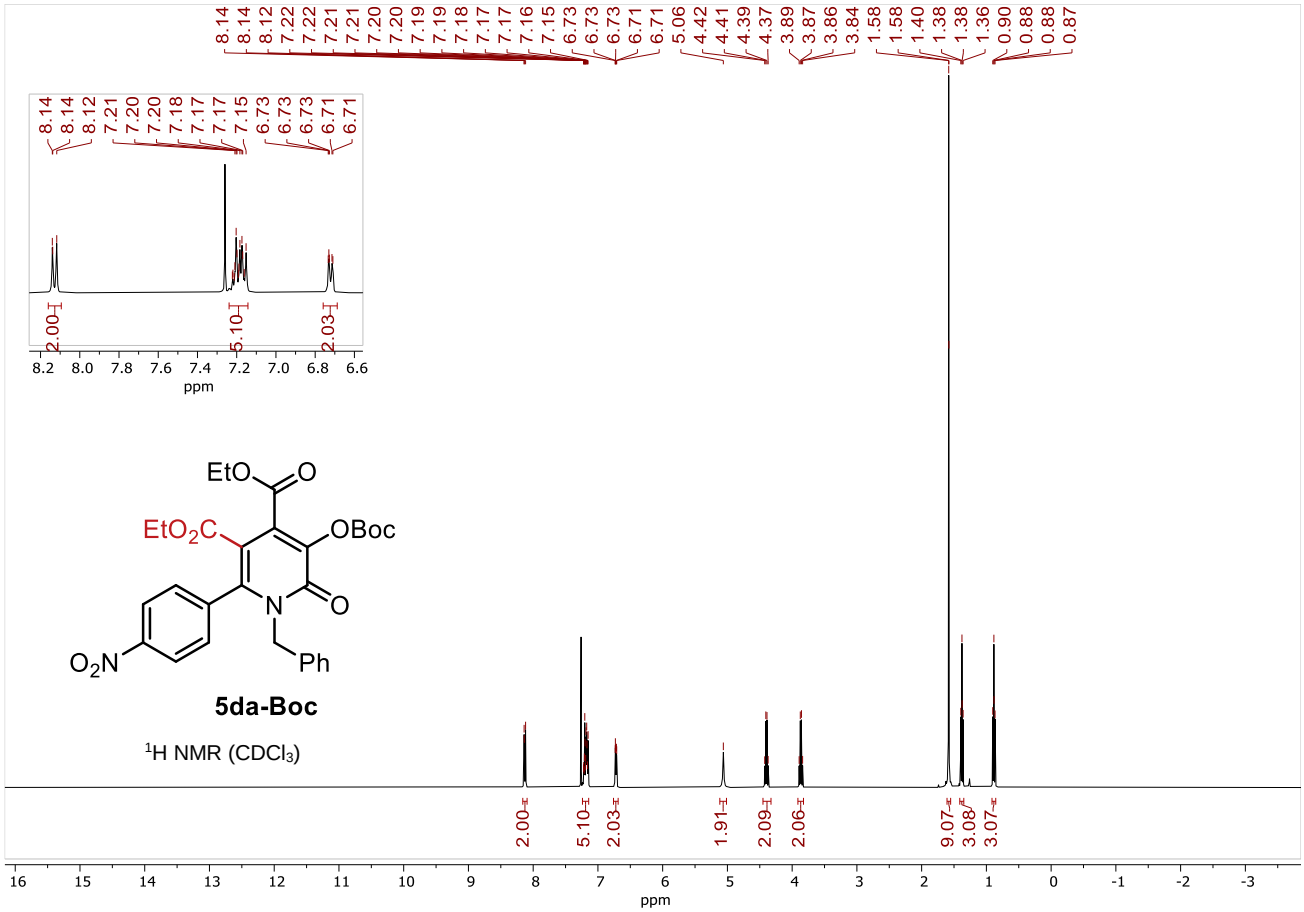
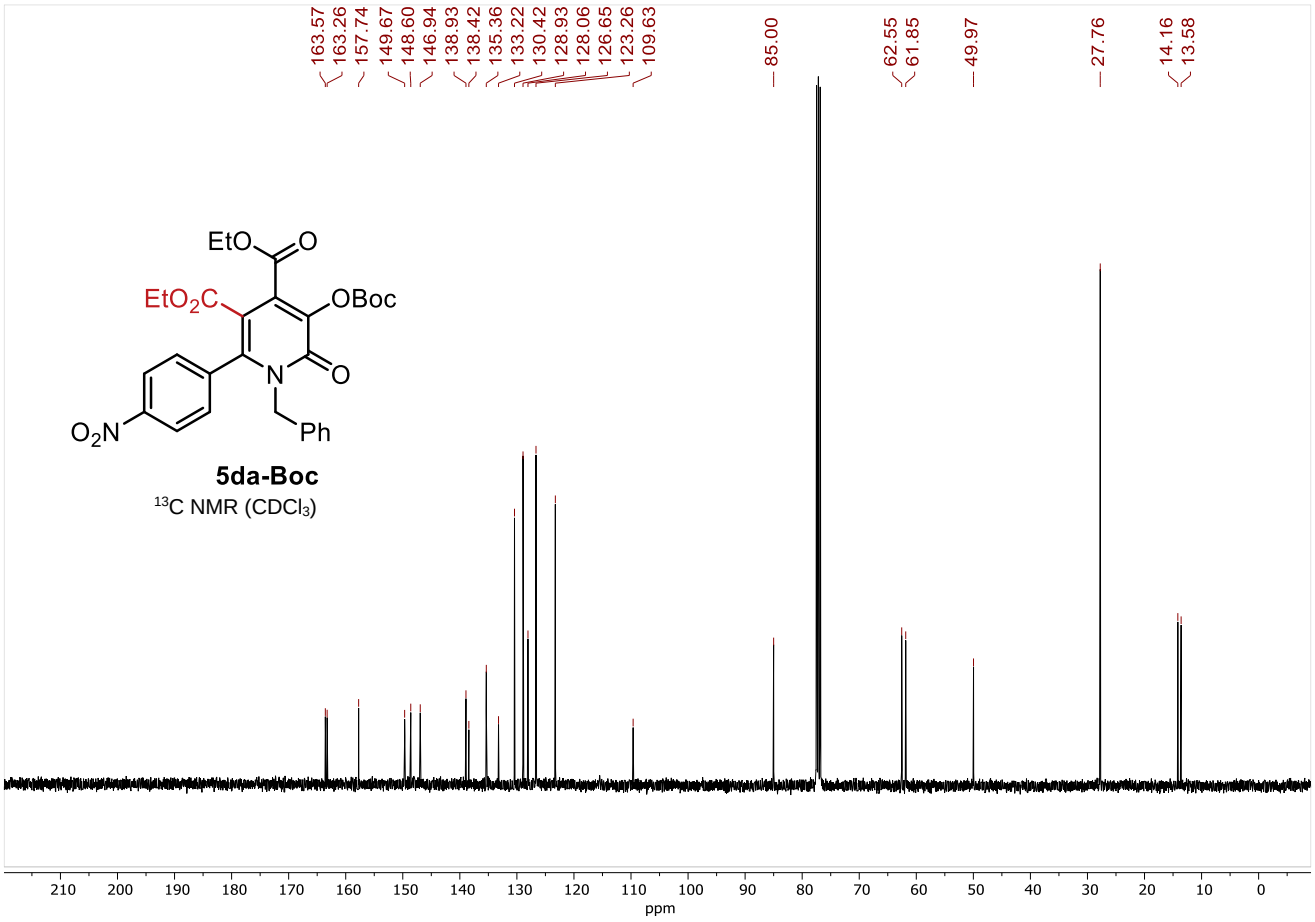
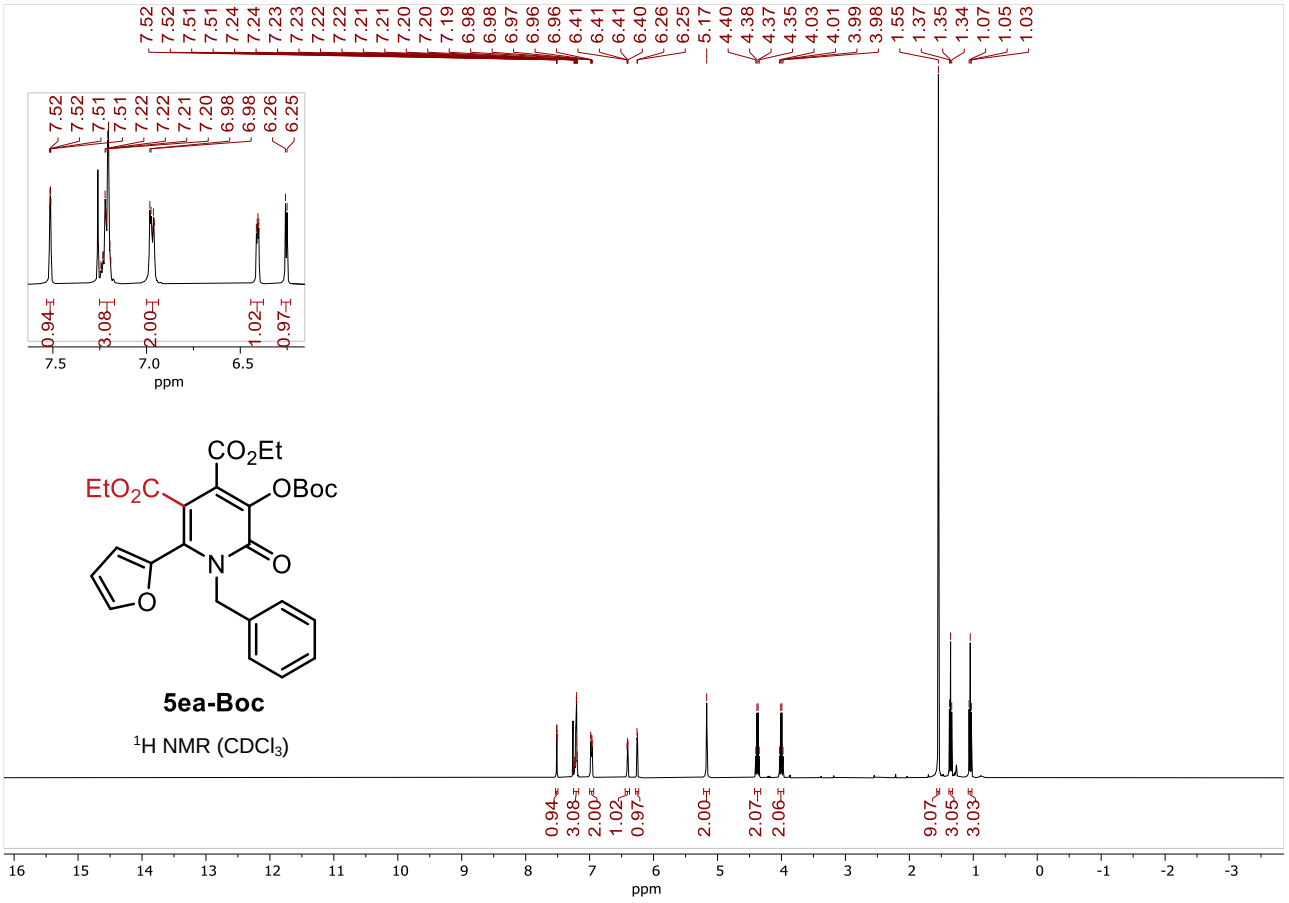
3.03 2.00 4.06
ppm
EtO
O
EtO2C
OBoc
N
O
MeO
Ph
5ca-Boc
1H NMR (CDCl3)
3.03 2.00 4.06 1.99 2.03 2.08 3.07 9.03 3.05 3.09
ppm


164.70 163.58 160.73 158.01 149.84 148.81 137.84 136.12 132.90 130.50 128.55 127.54 126.99 124.98 113.70 110.52 84.58 62.35 61.45 55.49 49.89 27.76 14.14 13.61
EtO
O
EtO2C
OBoc
N
O
MeO
Ph
5ca-Boc
13C NMR (CDCl3)
ppm


8.14 8.14 8.12 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.17 7.17 7.16 7.15 6.73 6.73 6.71 6.71 5.06 4.42 4.41 4.39 4.37 3.89 3.87 3.86 3.84 1.58 1.58 1.40 1.38 1.38 1.36 0.90 0.88 0.88 0.87
2.00 5.10 2.03
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
ppm
EtO
O
EtO2C
OBoc
N
O
O2N
Ph
5da-Boc
1H NMR (CDCl3)
2.00 5.10 2.03 1.91 2.09 2.06 9.07 3.08 3.07
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm


163.57 163.26 157.74 149.67 148.60 146.94 138.93 138.42 135.36 133.22 130.42 128.93 128.06 126.65 123.26 109.63
85.00
62.55 61.85
49.97
27.76
14.16 13.58
EtO
O
EtO2C
OBoc
N
O
O2N
Ph
5da-Boc
13C NMR (CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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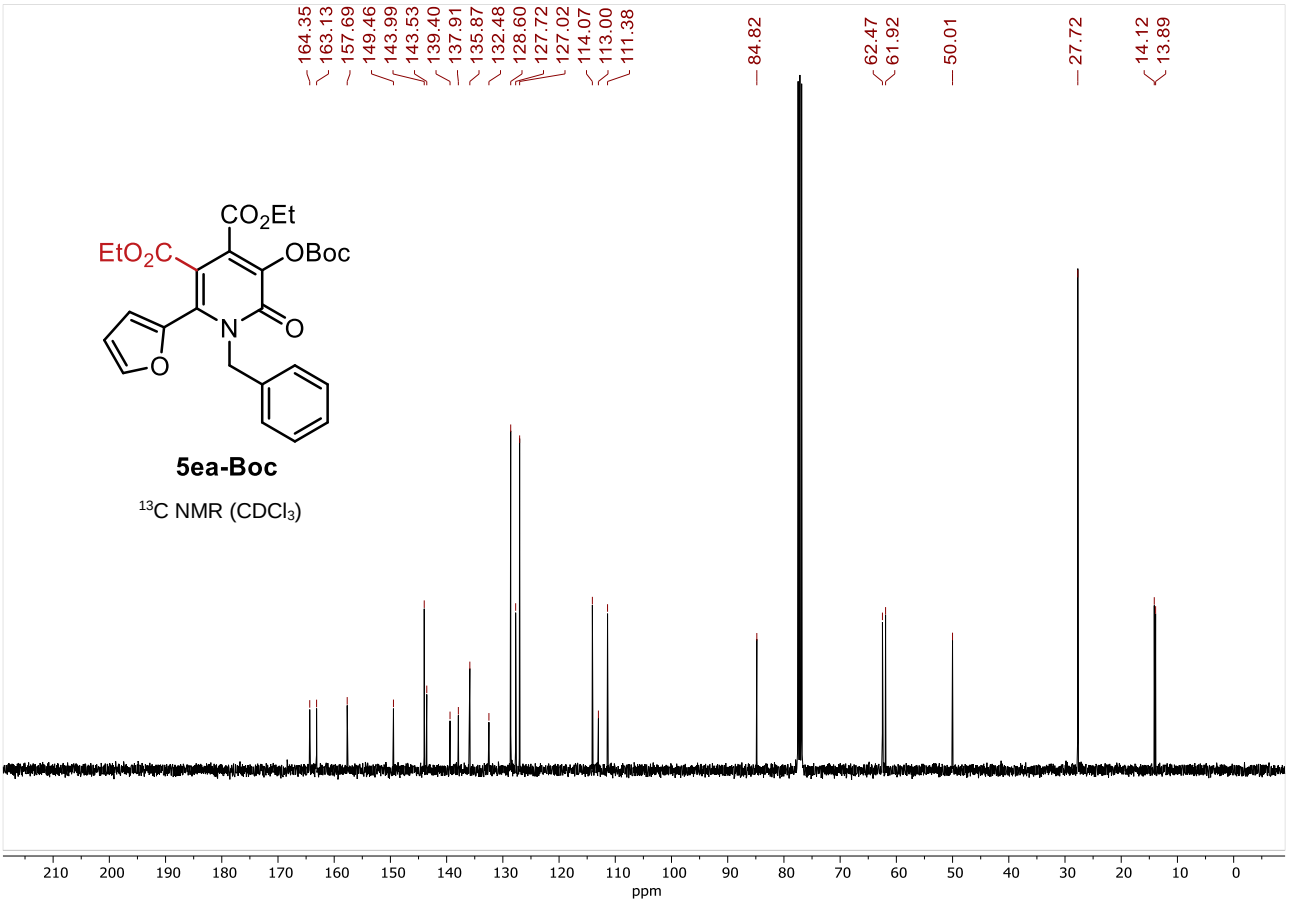
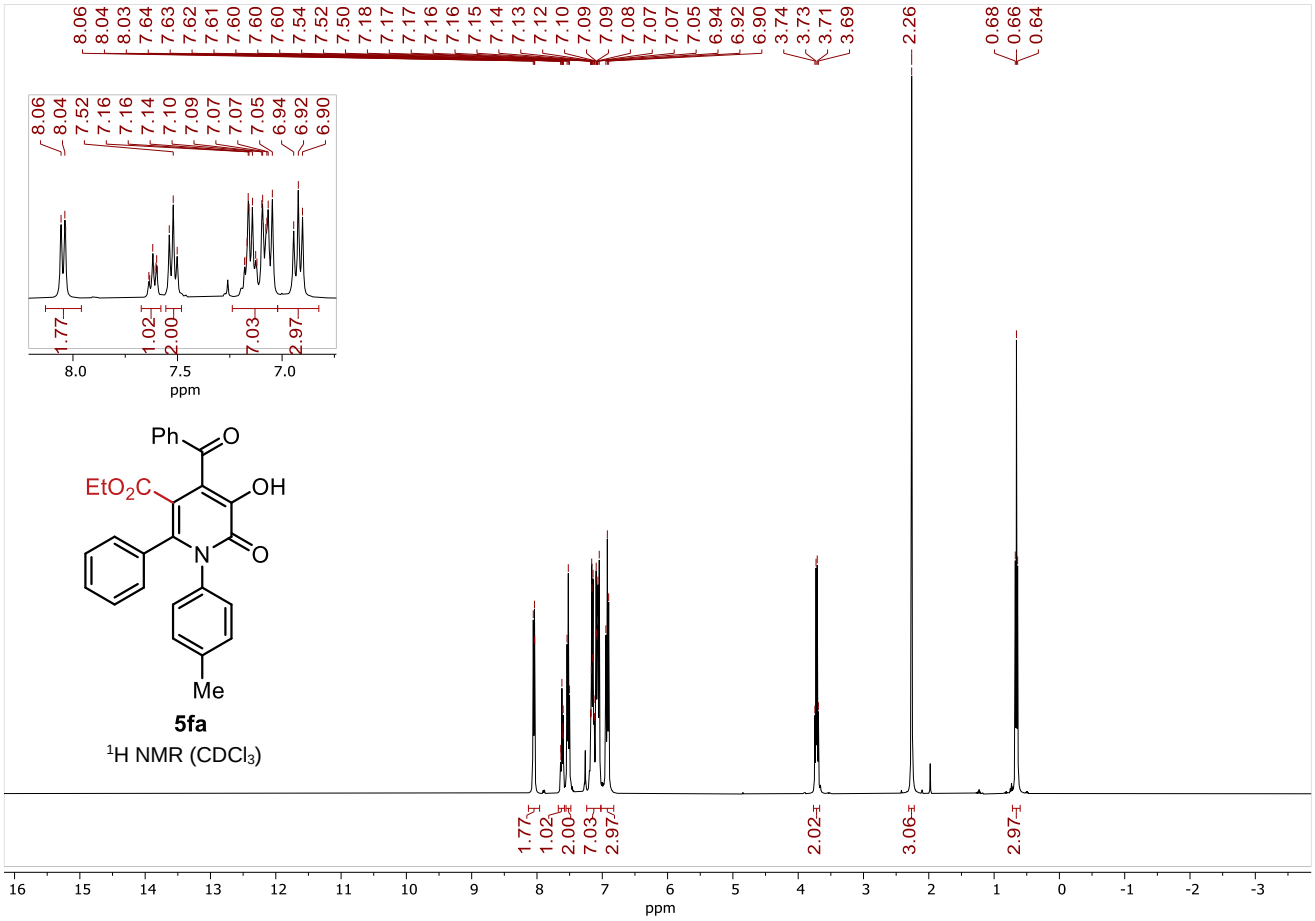
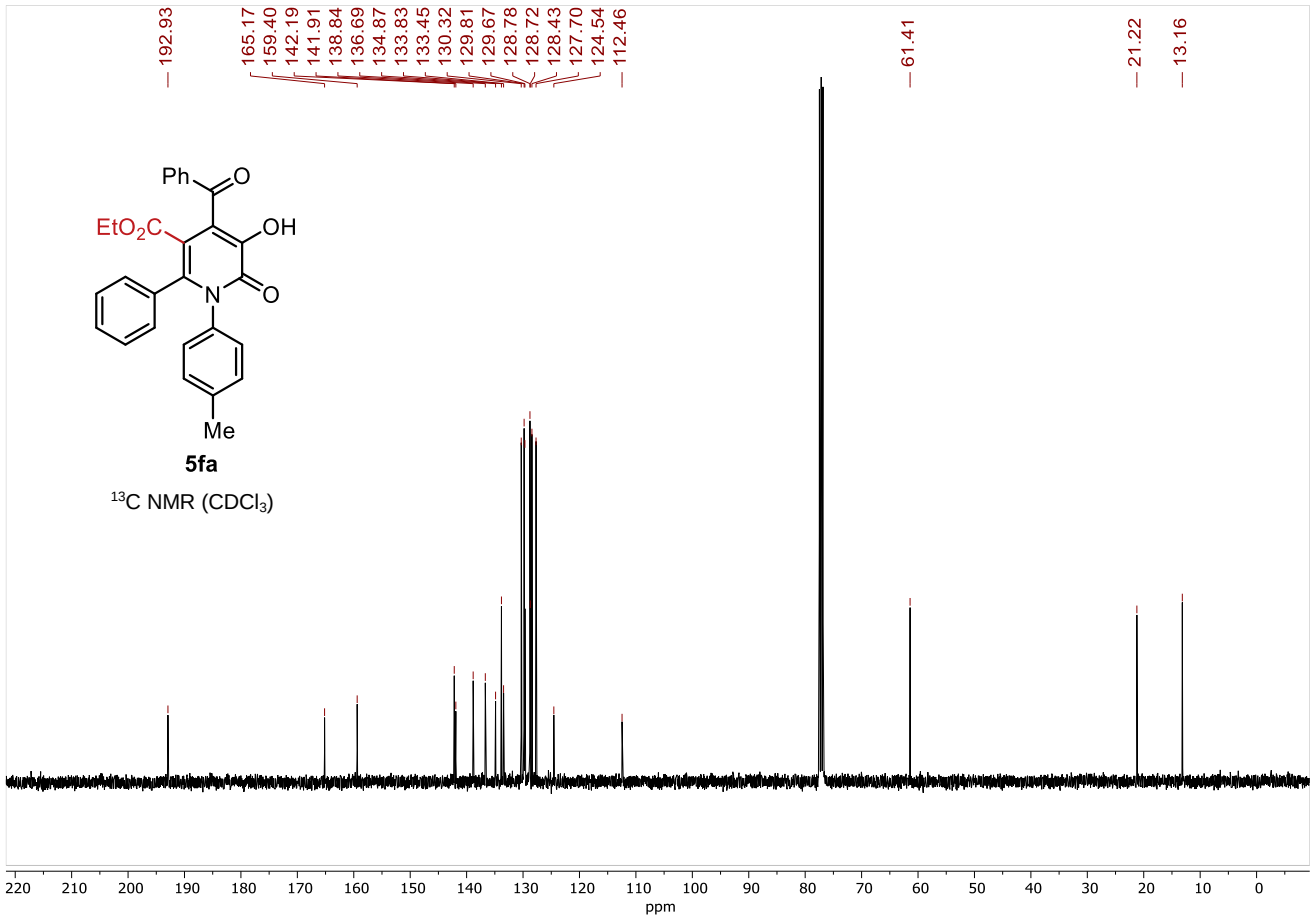
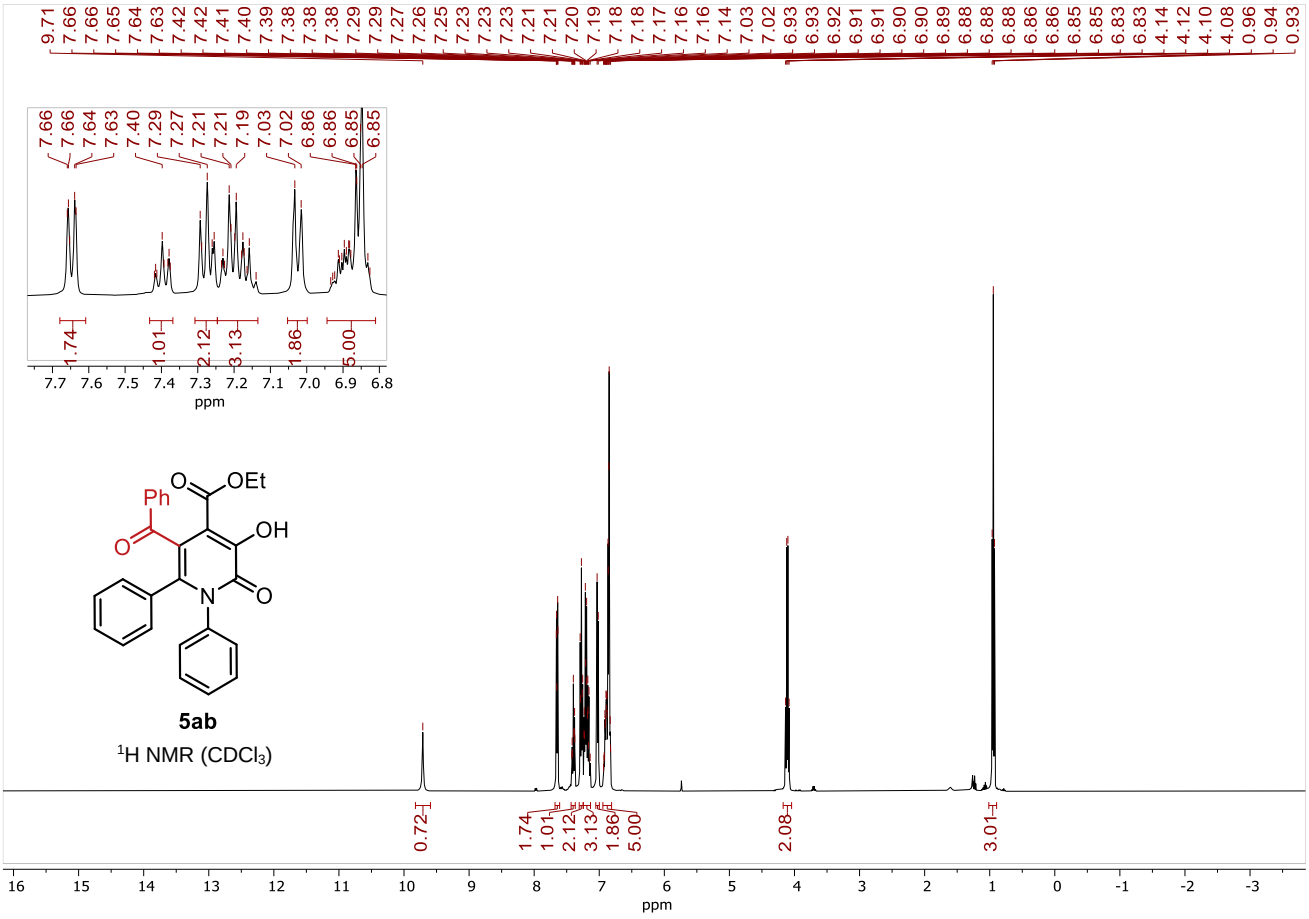
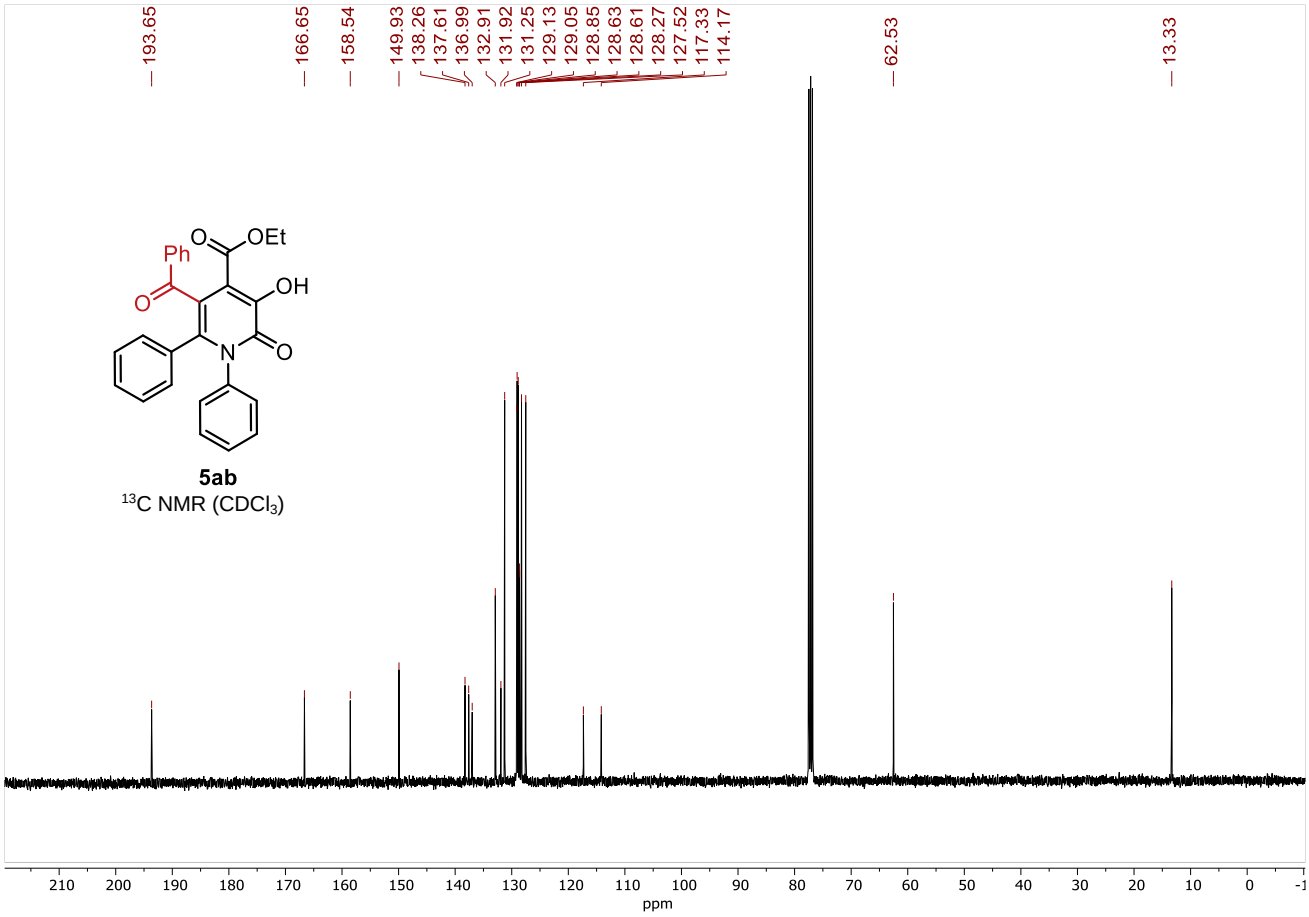
0.94 3.08 2.00 1.02 0.97
7.5 7.0 6.5
ppm
CO2Et
EtO2C
OBoc
N
O
O
5ea-Boc
1H NMR (CDCl3)
0.94 3.08 2.00 1.02 0.97 2.00 2.07 2.06 9.07 3.05 3.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

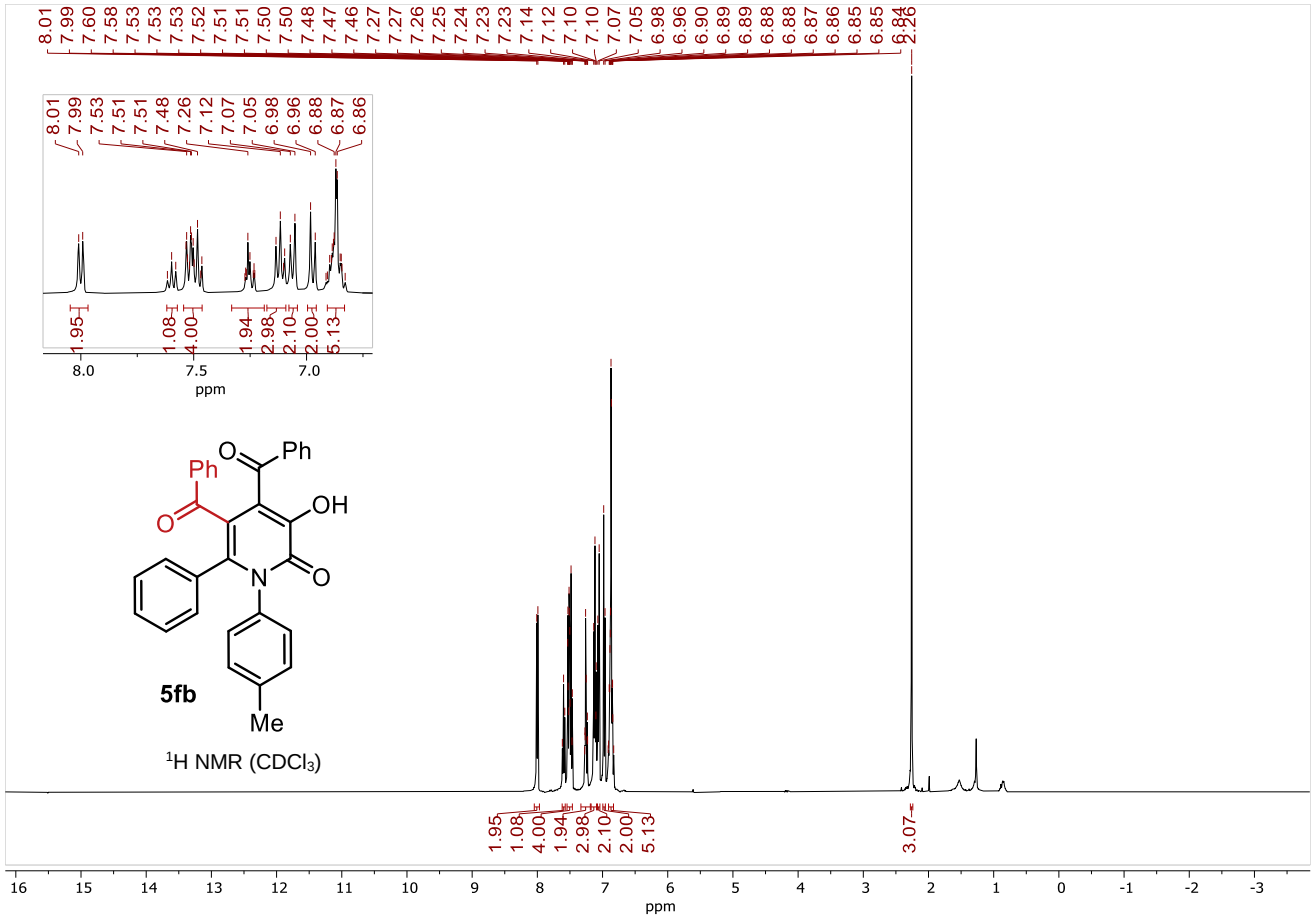

164.35 163.13 157.69 149.46 143.99 143.53 139.40 137.91 135.87 132.48 128.60 127.72 127.02 114.07 113.00 111.38 84.82 62.47 61.92 50.01 27.72 14.12 13.89
CO2Et
EtO2C
OBoc
N
O
O
5ea-Boc
13C NMR (CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

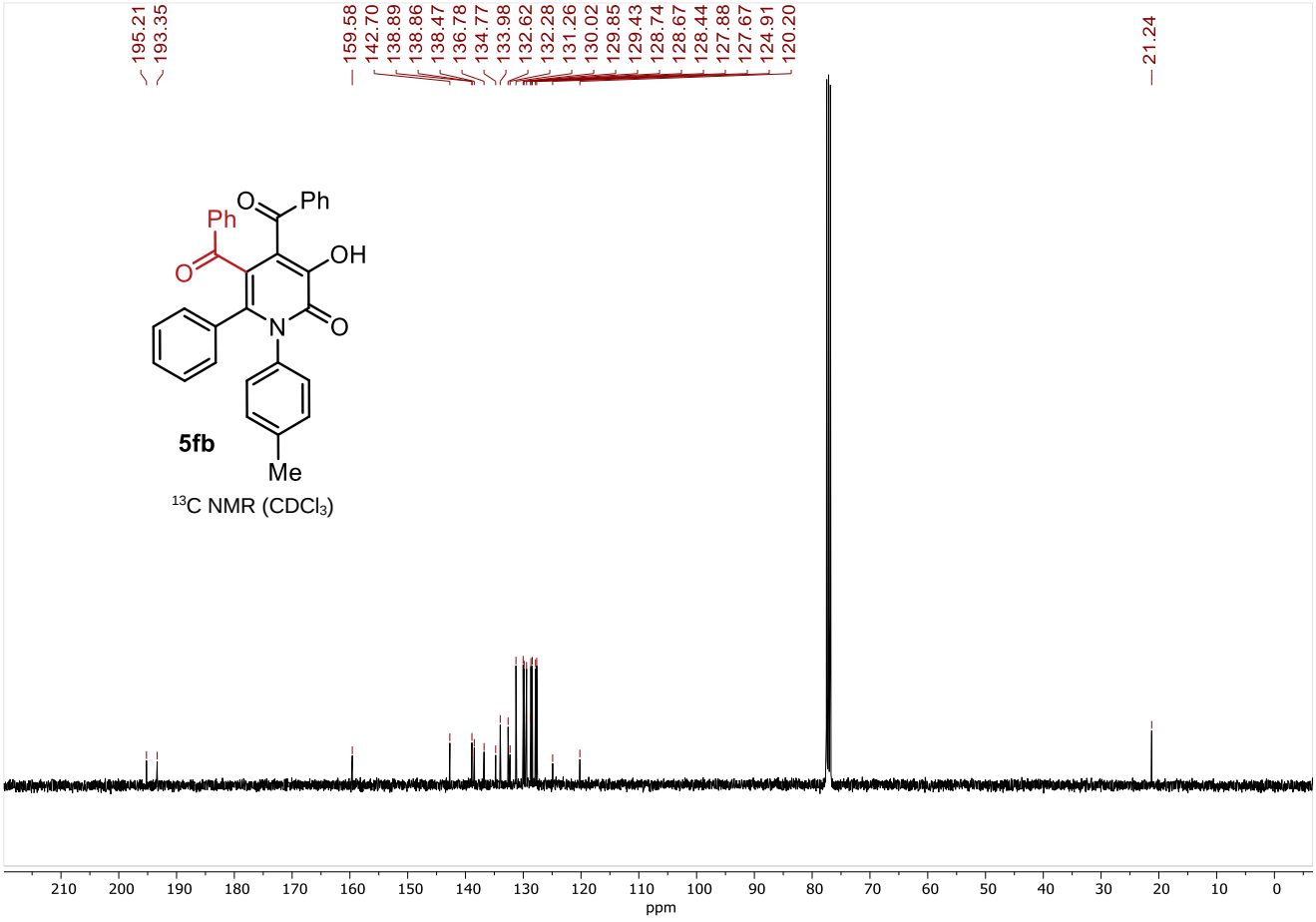

8.06 8.04 8.03 7.64 7.63 7.62 7.61 7.60 7.60 7.60 7.54 7.52 7.50 7.18 7.17 7.17 7.16 7.16 7.15 7.14 7.13 7.12 7.10 7.09 7.09 7.08 7.07 7.07 7.05 6.94 6.92 6.90 3.74 3.73 3.71 3.69 2.26 0.68 0.66 0.64
1.77 1.02 2.00 7.03 2.97
8.0 7.5 7.0
ppm
Ph O
EtO2C OH
N O
Me
5fa
1H NMR (CDCl3)
1.77 1.02 2.00 7.03 2.97 2.02 3.06 2.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

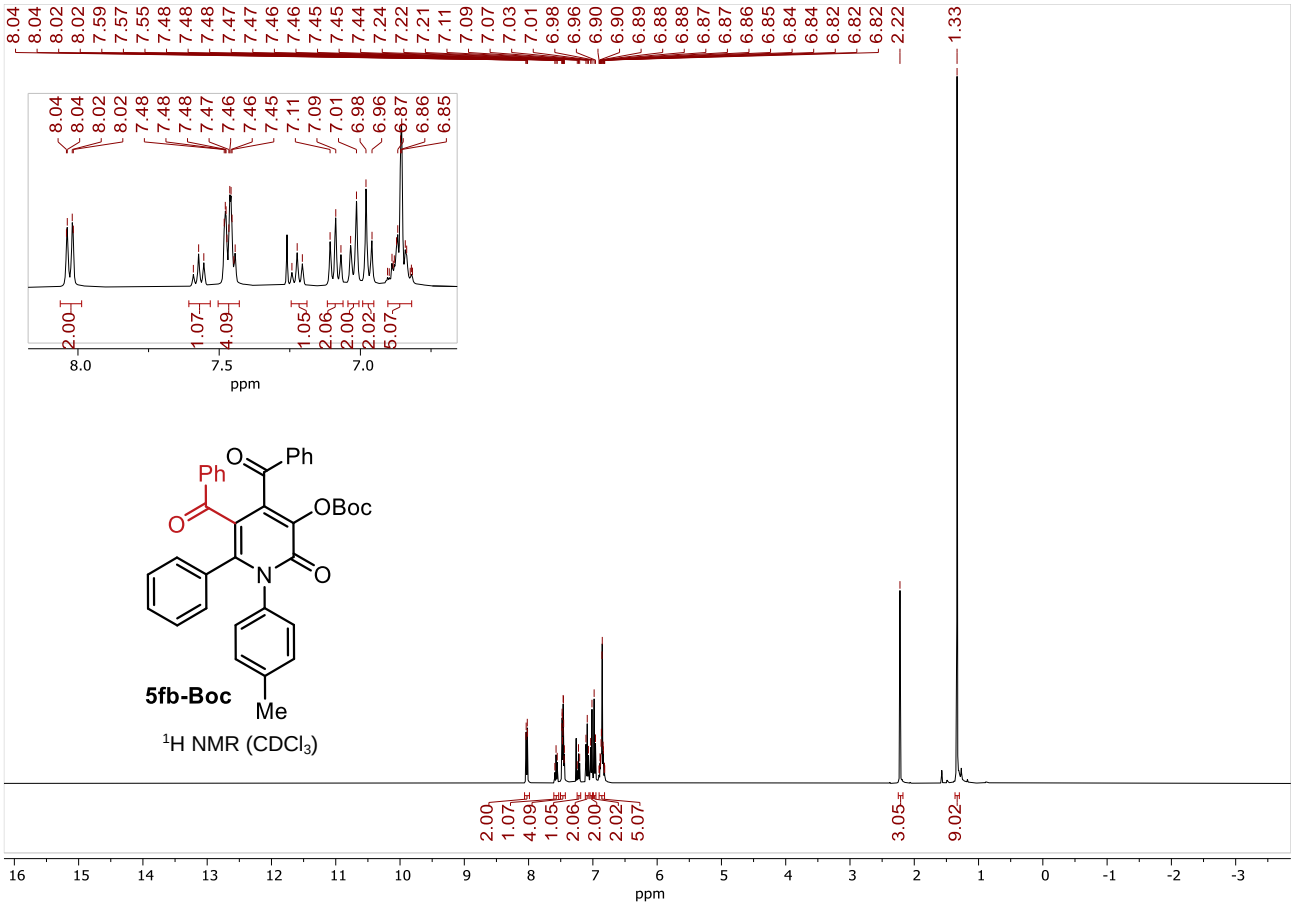

192.93 165.17 159.40 142.19 141.91 138.84 136.69 134.87 133.83 133.45 130.32 129.81 129.67 128.78 128.72 128.43 127.70 124.54 112.46 61.41 21.22 13.16
Ph O
EtO2C OH
N O
Me
5fa
13C NMR (CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

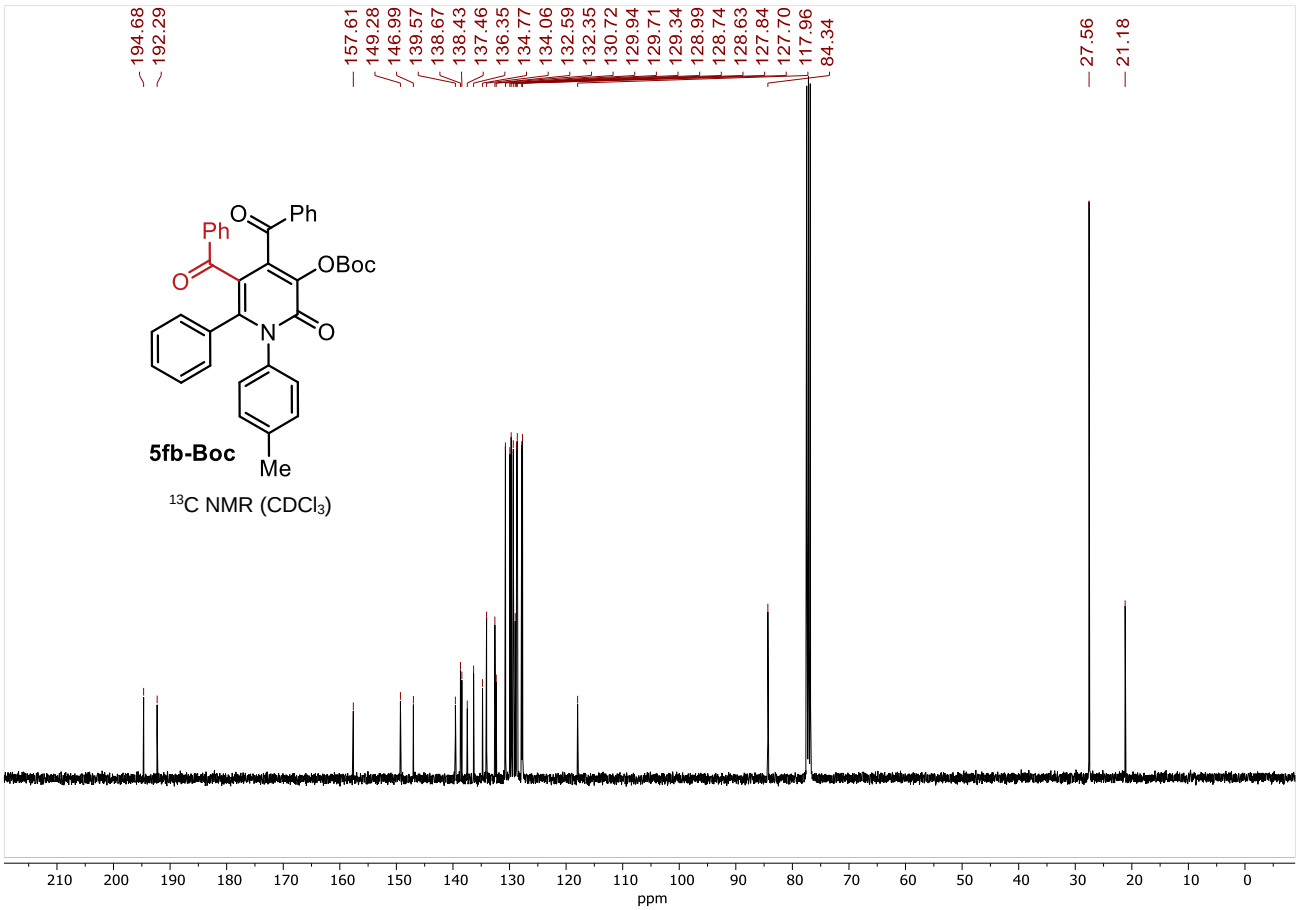

9.71 7.66 7.65 7.64 7.63 7.42 7.41 7.40 7.39 7.38 7.38 7.29 7.29 7.27 7.26 7.25 7.23 7.23 7.21 7.21 7.20 7.19 7.18 7.18 7.17 7.16 7.16 7.14 7.03 7.02 6.93 6.92 6.91 6.91 6.90 6.90 6.89 6.88 6.88 6.86 6.86 6.85 6.85 6.83 6.83 4.14 4.12 4.10 4.08 0.96 0.94 0.93
7.66 7.66 7.64 7.63 7.40 7.29 7.27 7.21 7.21 7.19 7.03 7.02 6.86 6.86 6.85 6.85
1.74 1.01 2.12 3.13 1.86 5.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
ppm
Ph
O
OEt
OH
O
N
O
5ab
1H NMR (CDCl3)
0.72 1.74 1.01 2.12 3.13 1.86 5.00 2.08 3.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

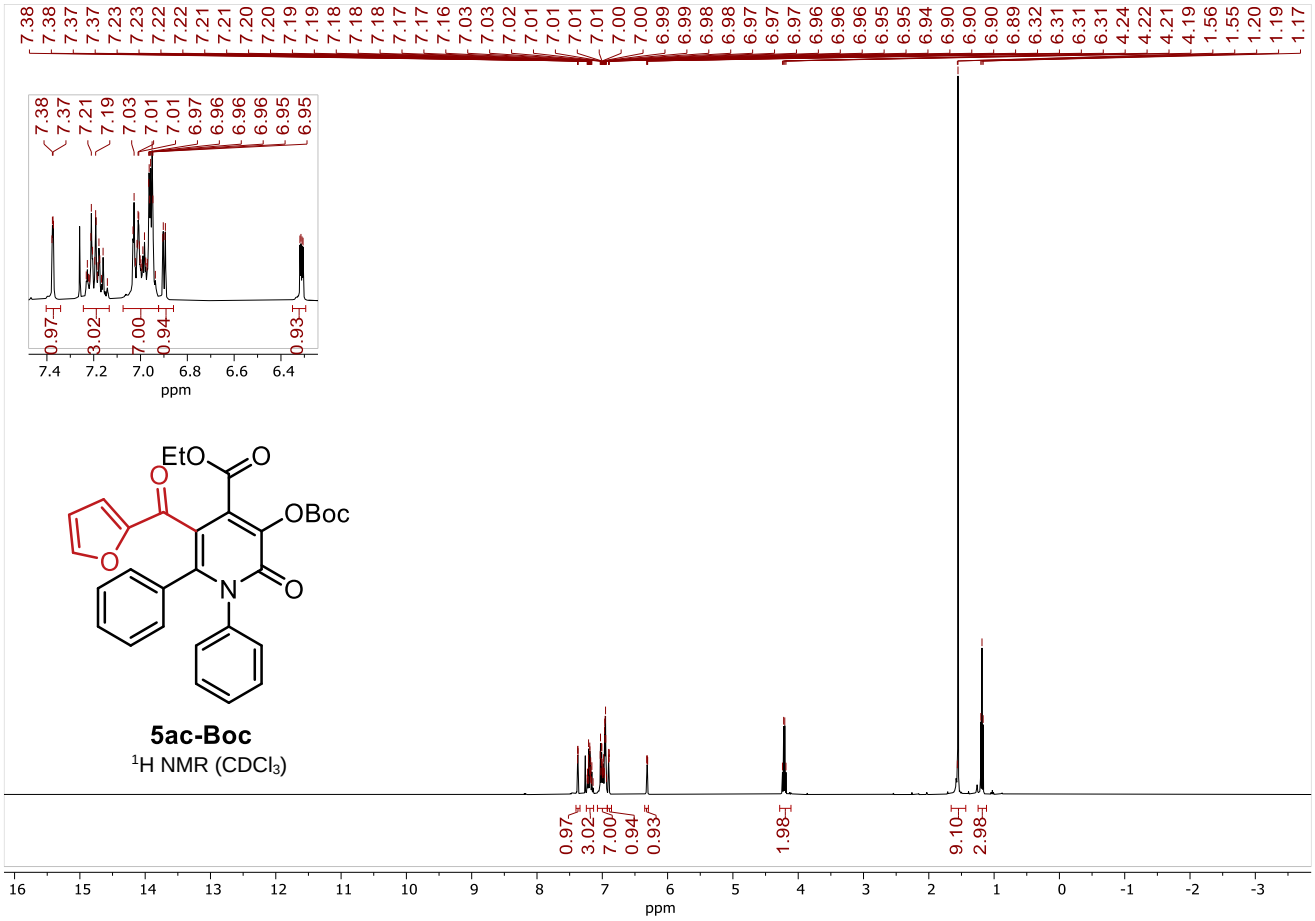

193.65 166.65 158.54 149.93 138.26 137.61 136.99 132.91 131.92 131.25 129.13 129.05 128.85 128.63 128.61 128.27 127.52 117.33 114.17 62.53 13.33
Ph
O
OEt
OH
O
N
O
5ab
13C NMR (CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm

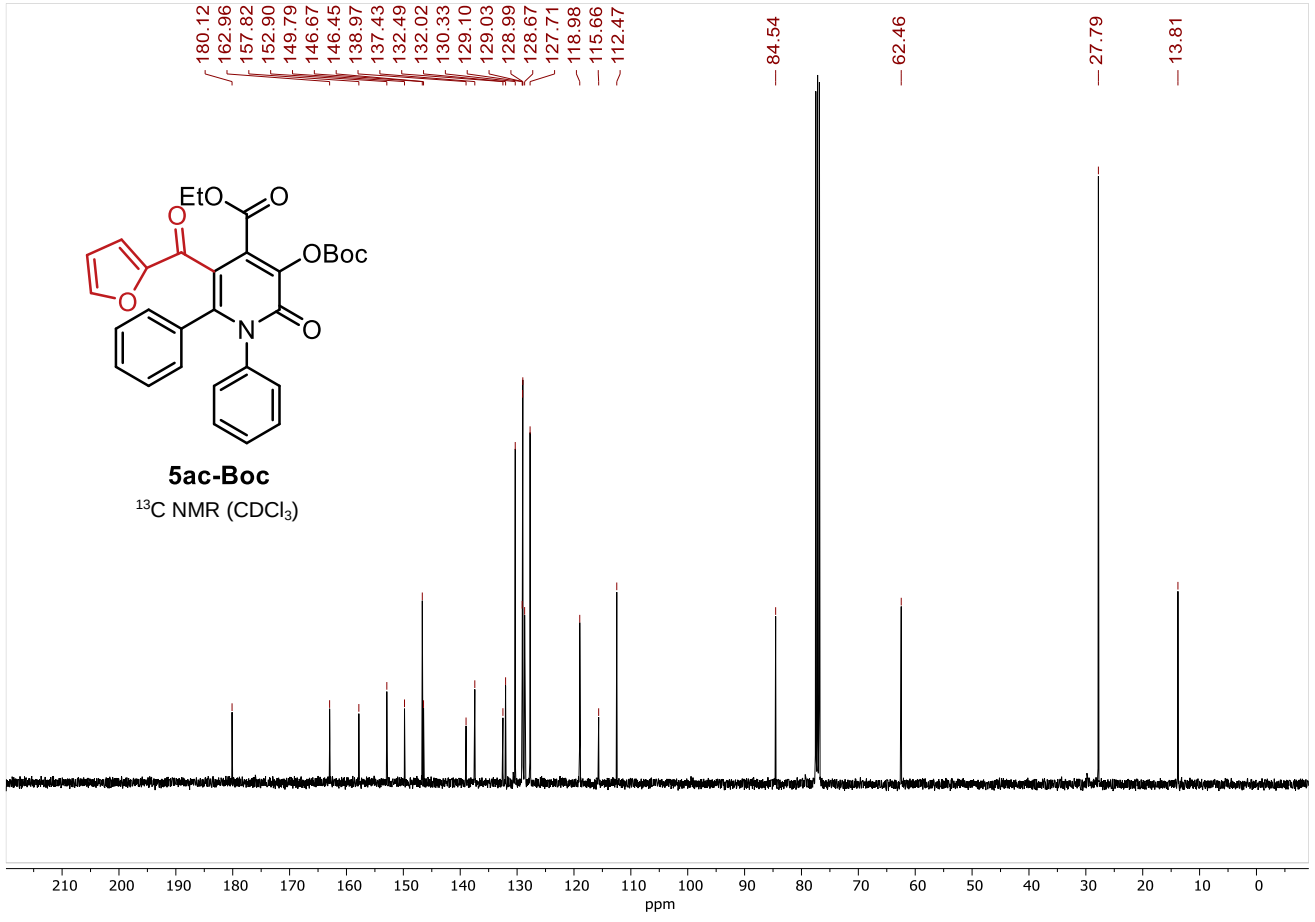

5fb
Me
^{1}H NMR ($CDCl_3$)
ppm

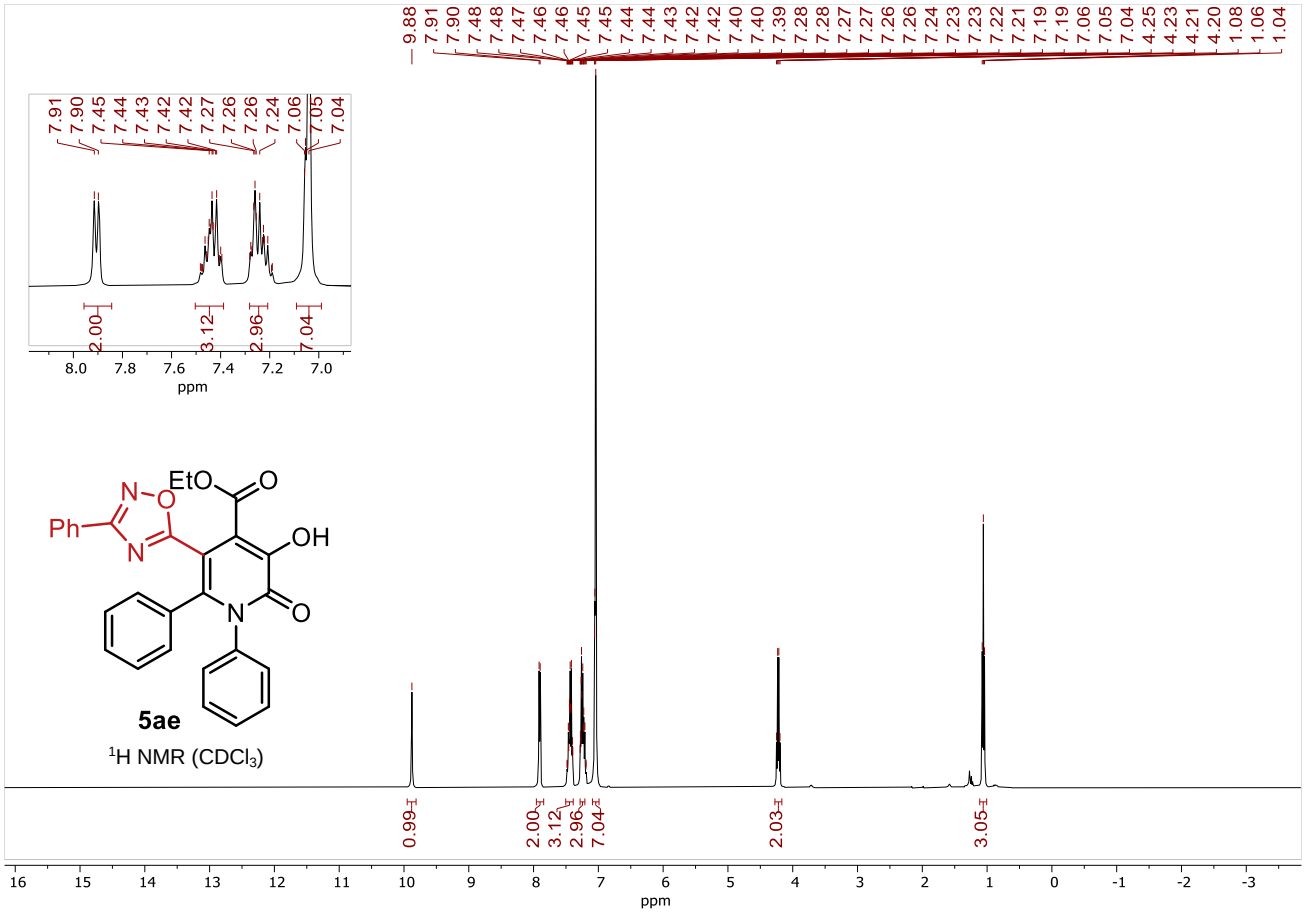

5fb
Me
^{13}C NMR ($CDCl_3$)
ppm

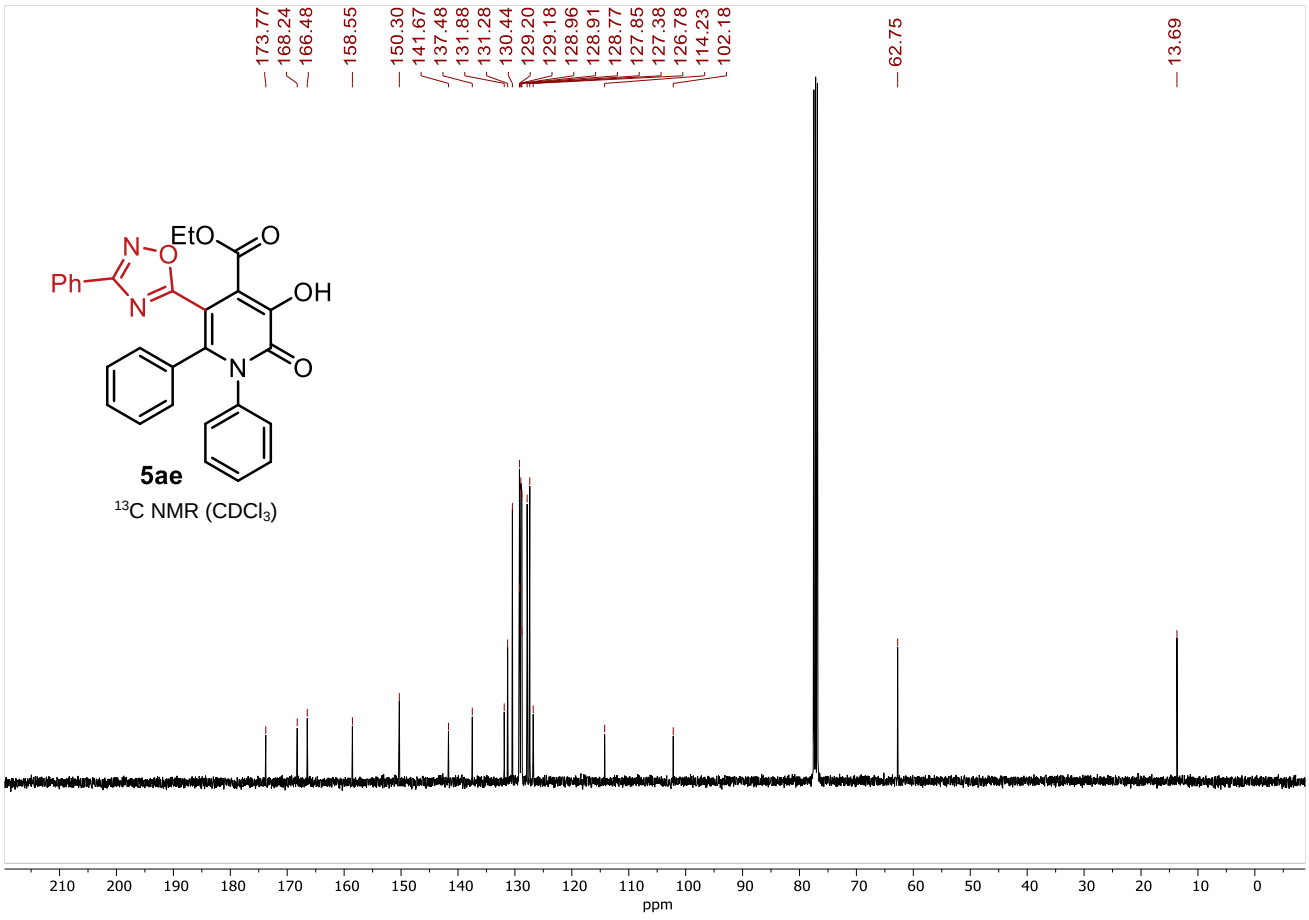

5fb-Boc
Me
Ph
OBoc
^{1}H NMR ($CDCl_3$)
ppm

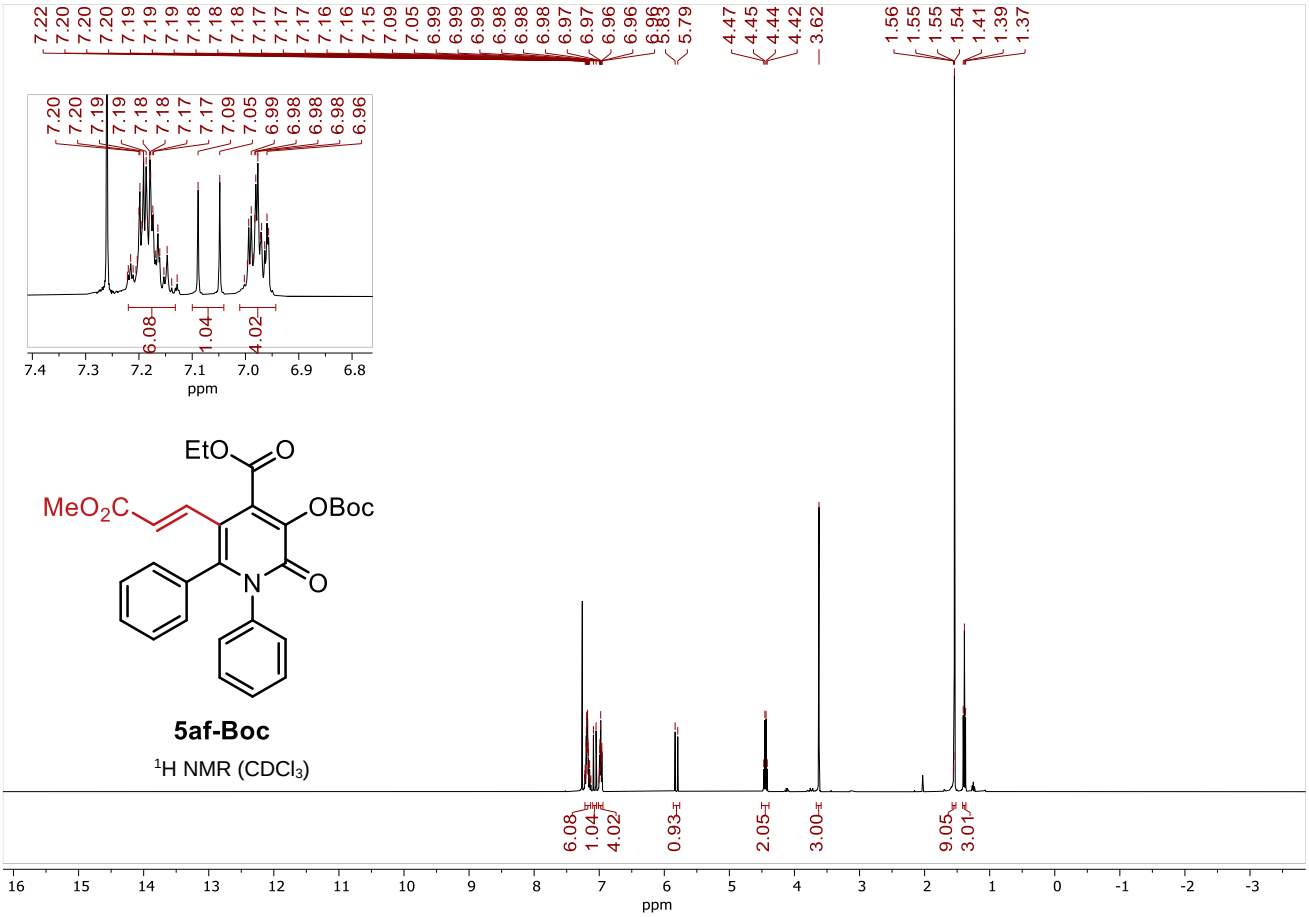

5fb-Boc
Me
Ph
OBoc
^{13}C NMR ($CDCl_3$)
ppm

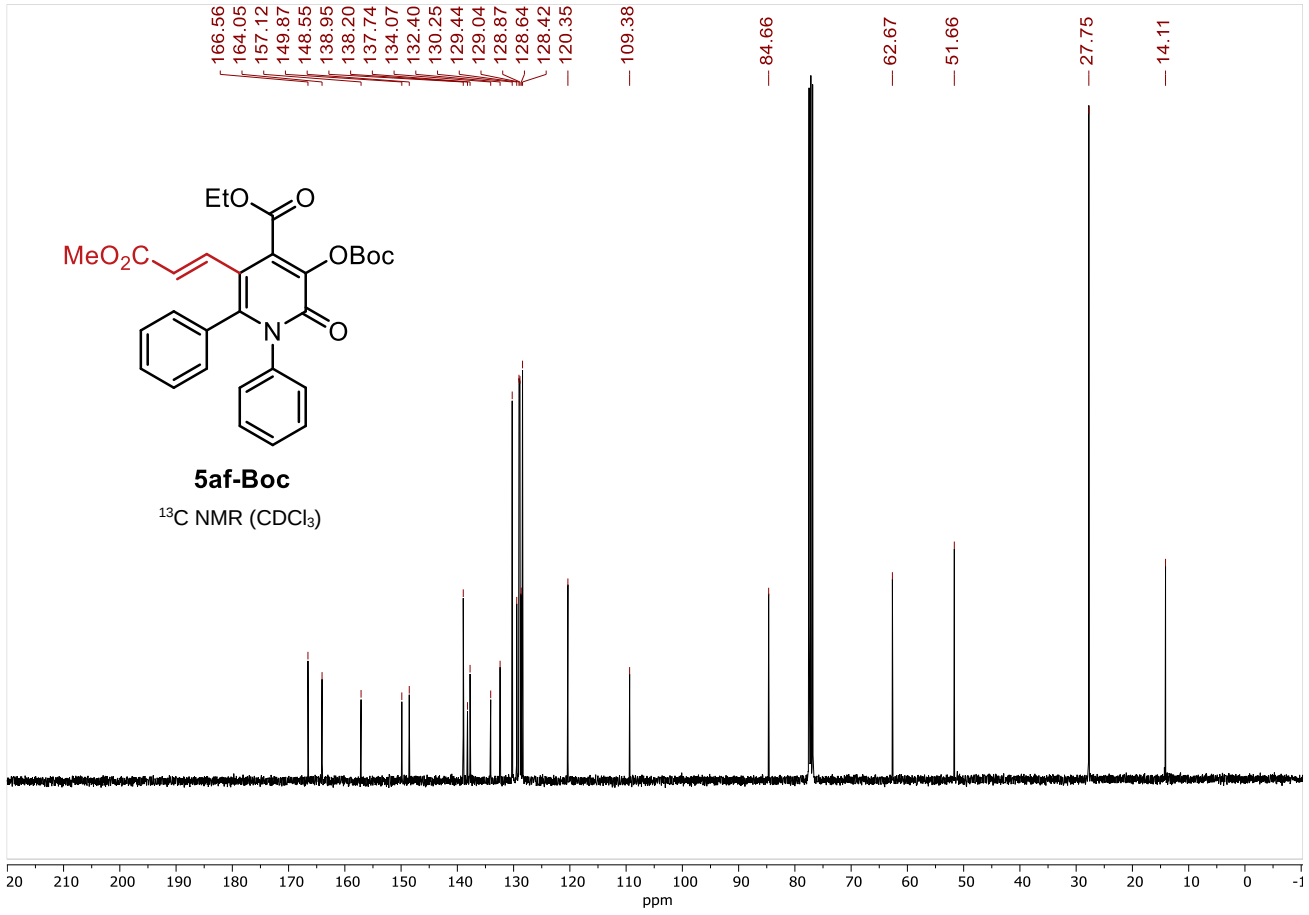

EtO
O
O
OBoc
O
N
O
5ac-Boc
1H NMR (CDCl3)
ppm

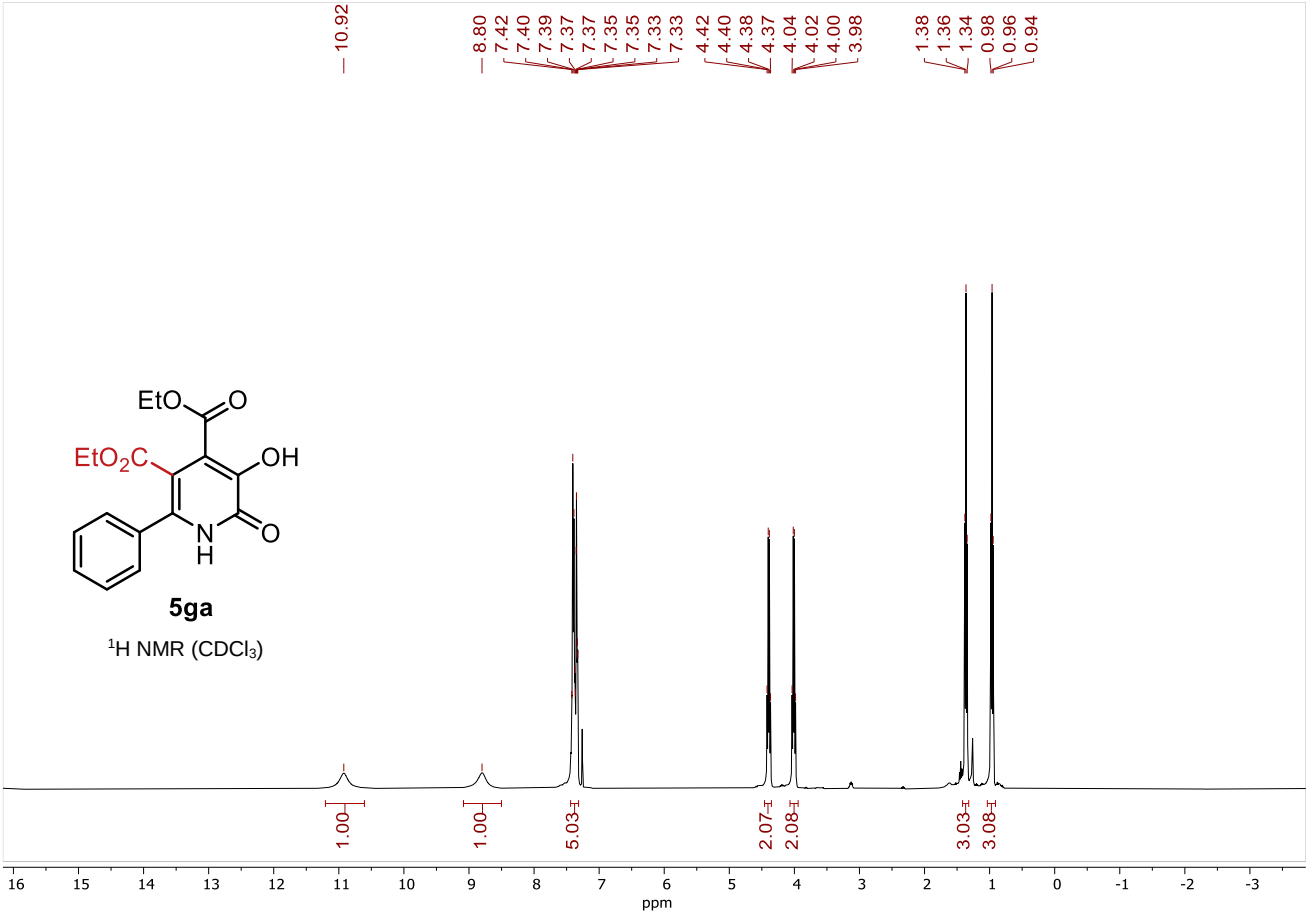

EtO
O
O
OBoc
O
N
O
5ac-Boc
13C NMR (CDCl3)
ppm

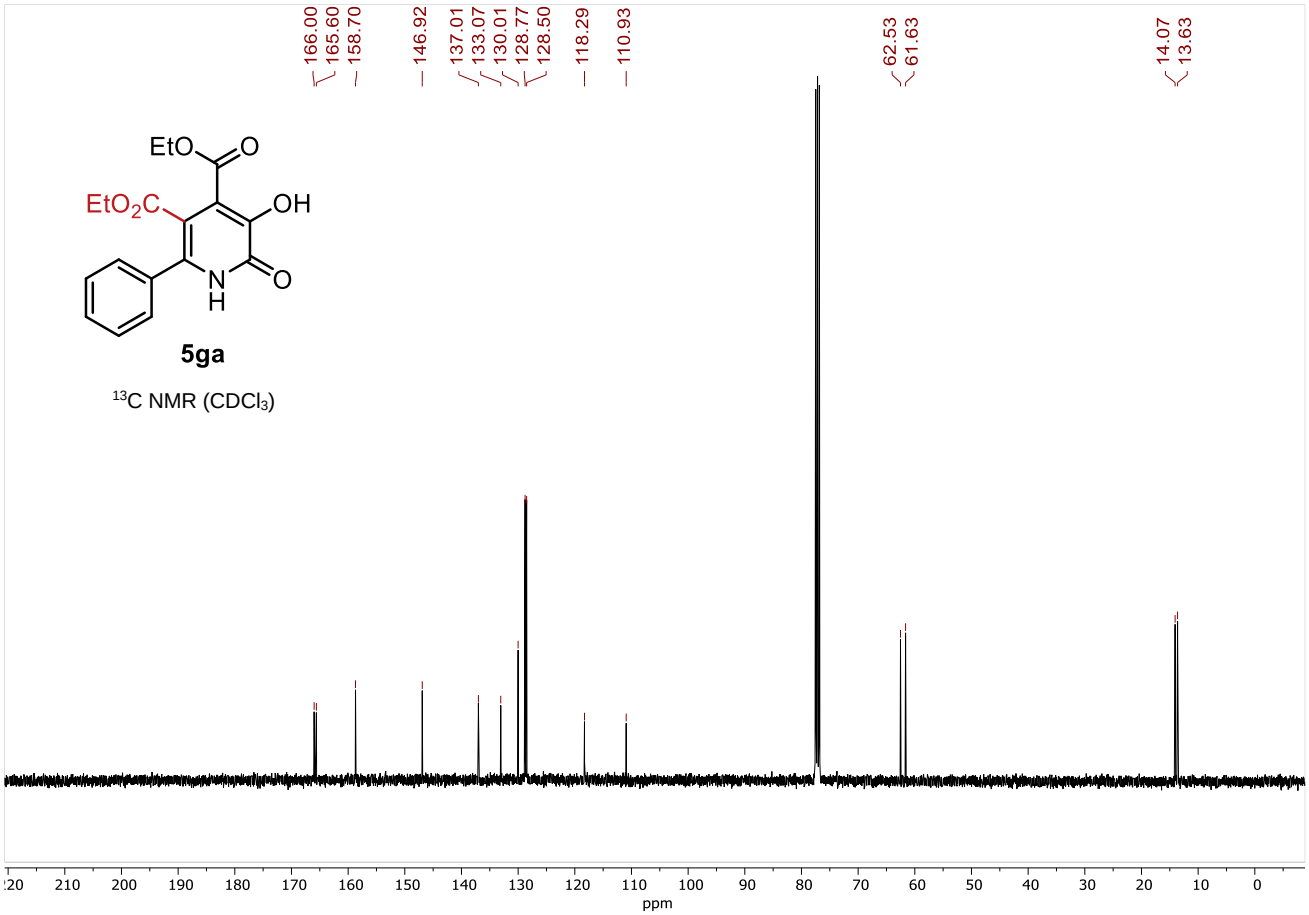

9.88
7.91
7.90
7.48
7.48
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.42
7.40
7.40
7.39
7.28
7.28
7.27
7.27
7.26
7.26
7.24
7.23
7.23
7.22
7.21
7.19
7.19
7.06
7.05
7.04
4.25
4.23
4.21
4.20
1.08
1.06
1.04
2.00
3.12
2.96
7.04
8.0
7.8
7.6
7.4
7.2
7.0
ppm
EtO
O
N
O
Ph
N
OH
O
N
5ae
1H NMR (CDCl3)
0.99
2.00
3.12
2.96
7.04
2.03
3.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm

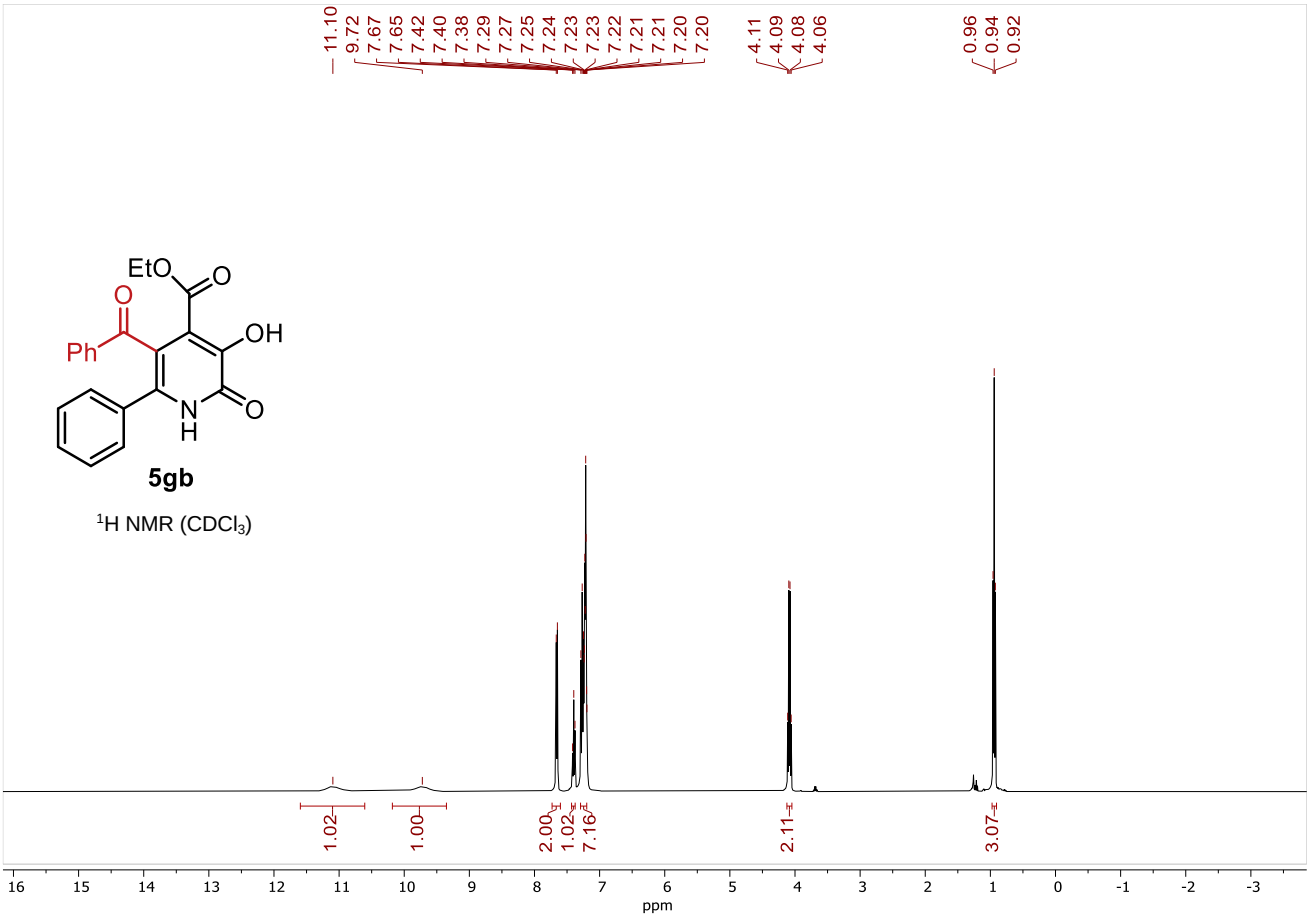

173.77
168.24
166.48
158.55
150.30
141.67
137.48
131.88
131.28
130.44
129.20
129.18
128.96
128.91
128.77
127.85
127.38
126.78
114.23
102.18
62.75
13.69
EtO
O
N
O
Ph
N
OH
O
N
5ae
13C NMR (CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

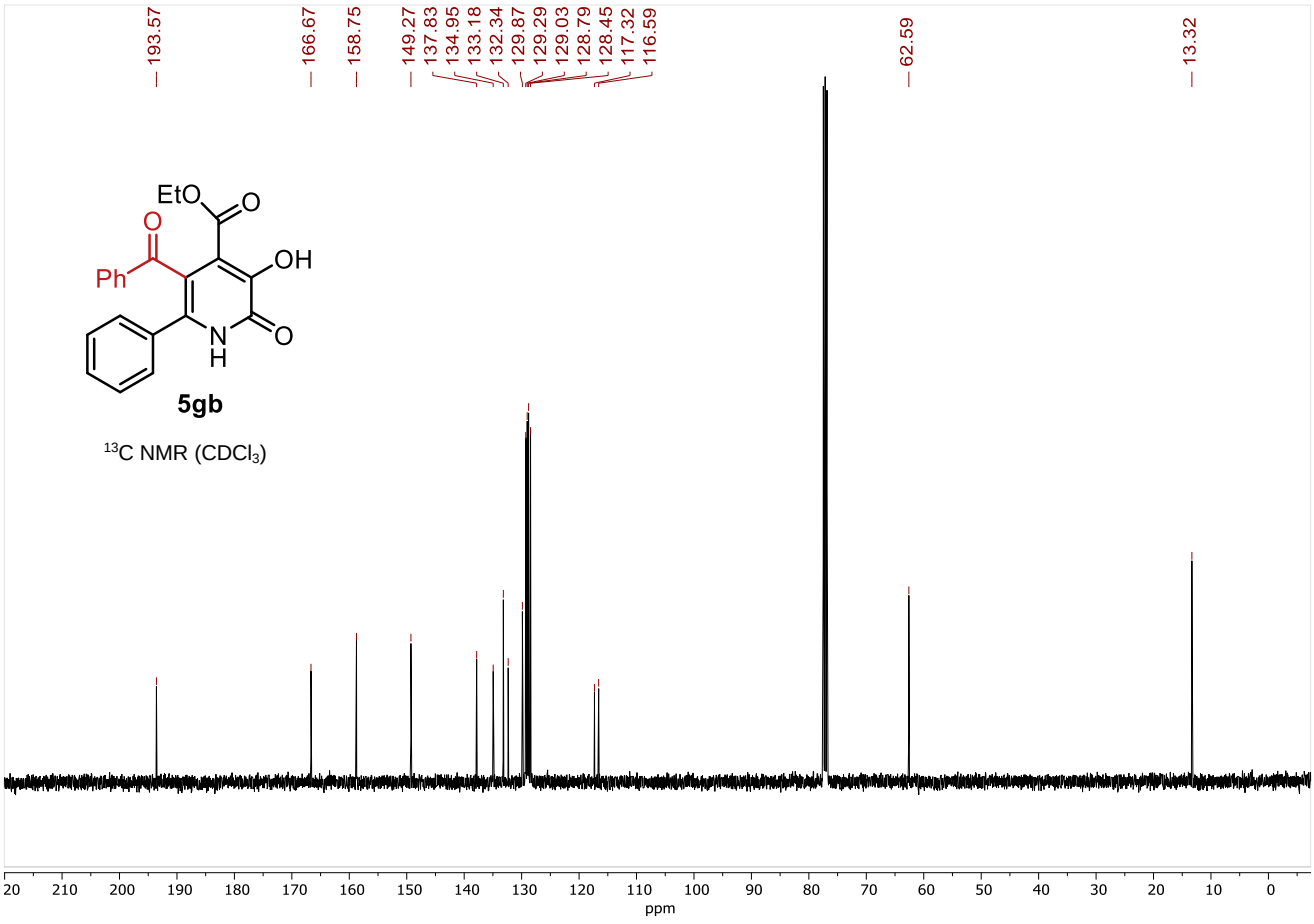

EtO
O
MeO2C
OBoc
N
O
5af-Boc
1H NMR (CDCl3)
ppm

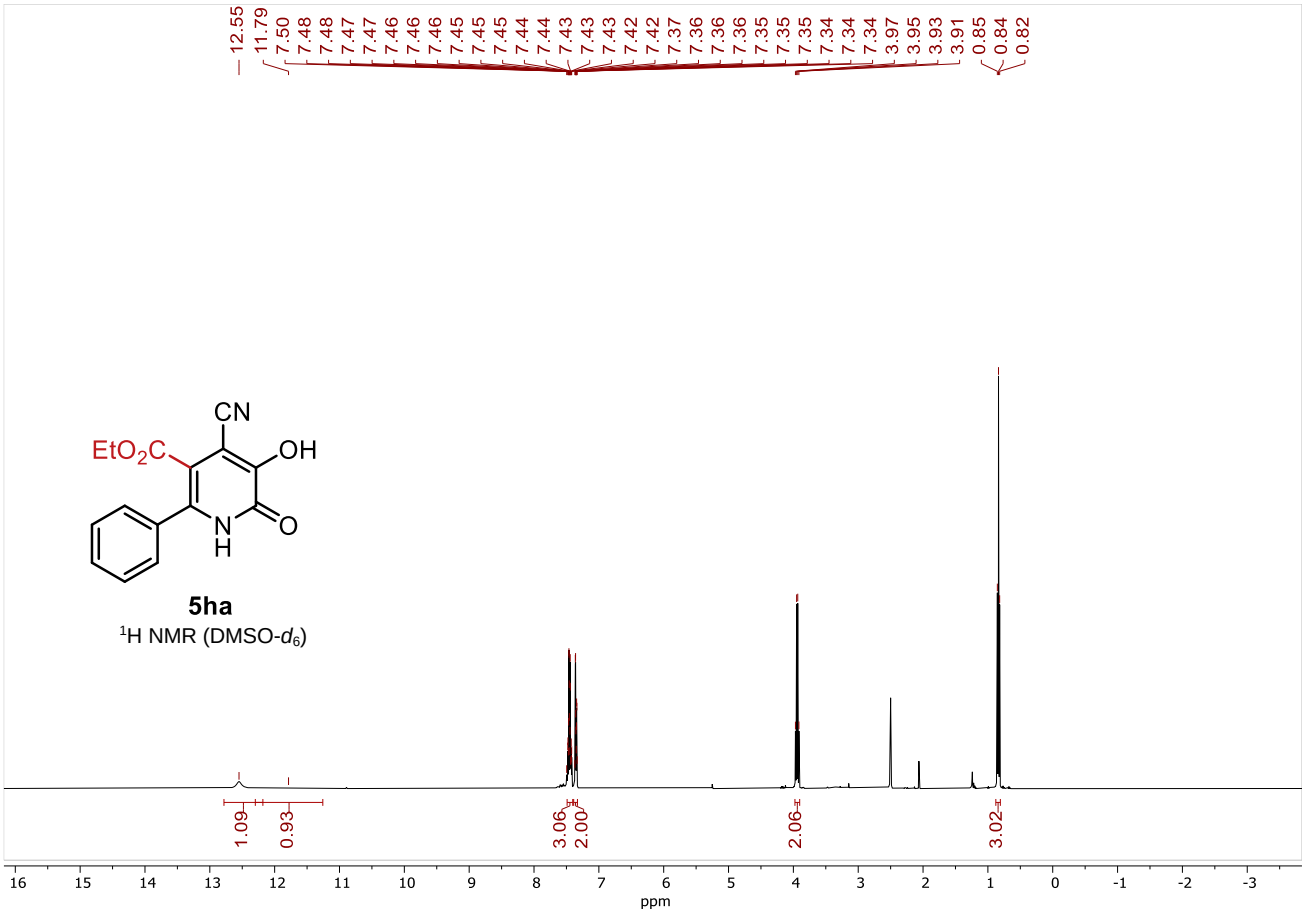

EtO
O
MeO2C
OBoc
N
O
5af-Boc
13C NMR (CDCl3)
ppm


10.92
8.80
7.42
7.40
7.39
7.37
7.37
7.35
7.35
7.33
7.33
4.42
4.40
4.38
4.37
4.04
4.02
4.00
3.98
1.38
1.36
1.34
0.98
0.96
0.94
EtO
O
EtO2C
OH
N
H
O
5ga
1H NMR (CDCl3)
1.00
1.00
5.03
2.07
2.08
3.03
3.08
ppm


166.00
165.60
158.70
146.92
137.01
133.07
130.01
128.77
128.50
118.29
110.93
62.53
61.63
14.07
13.63
EtO
O
EtO2C
OH
N
H
O
5ga
13C NMR (CDCl3)
ppm

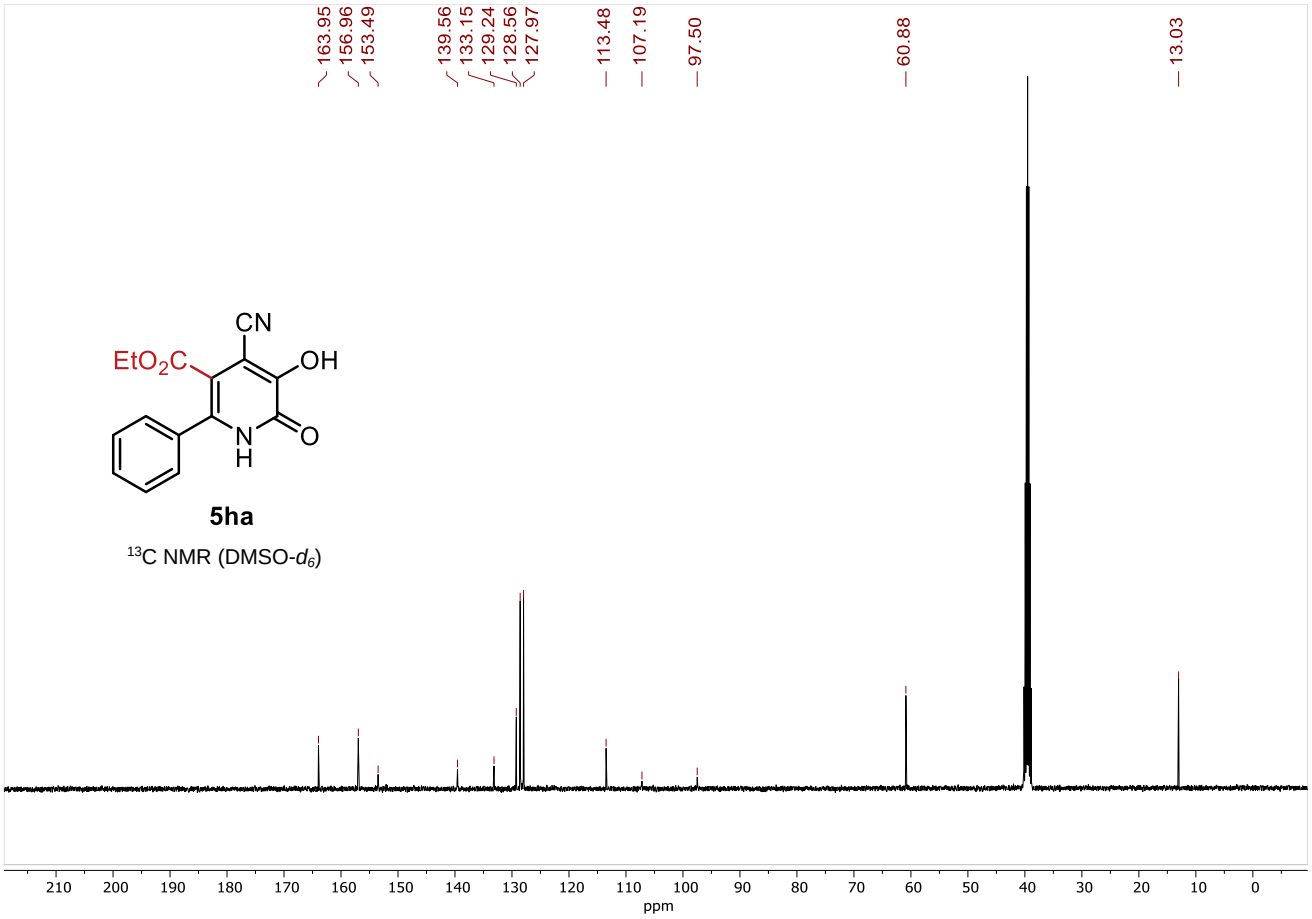

11.10
9.72
7.67
7.65
7.42
7.40
7.38
7.29
7.27
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.20
4.11
4.09
4.08
4.06
0.96
0.94
0.92
EtO
O
O
Ph
OH
N
H
O
5gb
1H NMR (CDCl3)
1.02
1.00
2.00
1.02
7.16
2.11
3.07
ppm


193.57
166.67
158.75
149.27
137.83
134.95
133.18
132.34
129.87
129.29
129.03
128.79
128.45
117.32
116.59
62.59
13.32
EtO
O
O
Ph
OH
N
H
O
5gb
13C NMR (CDCl3)
ppm



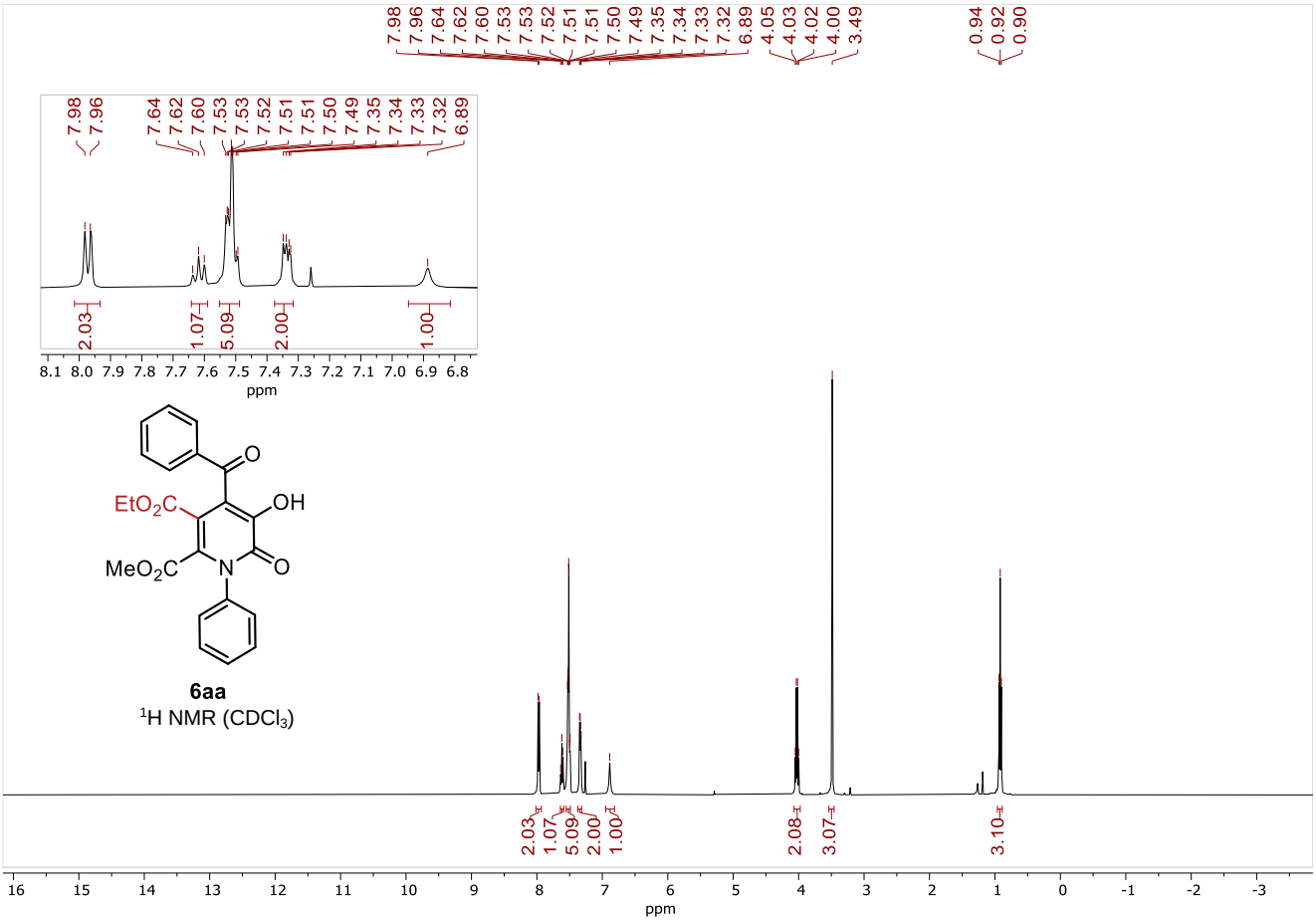
5ha

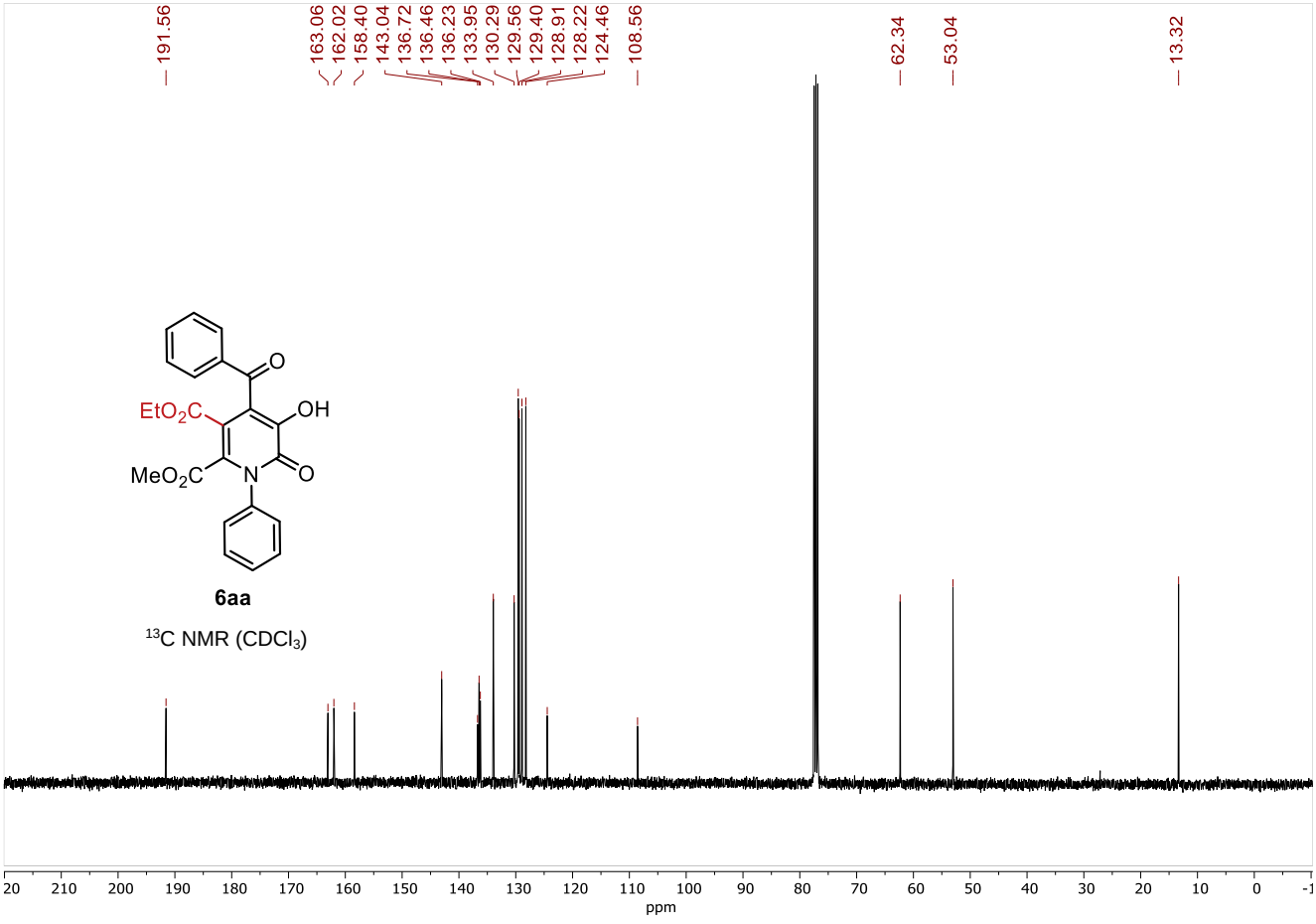
^{1}H NMR (DMSO-d_6)

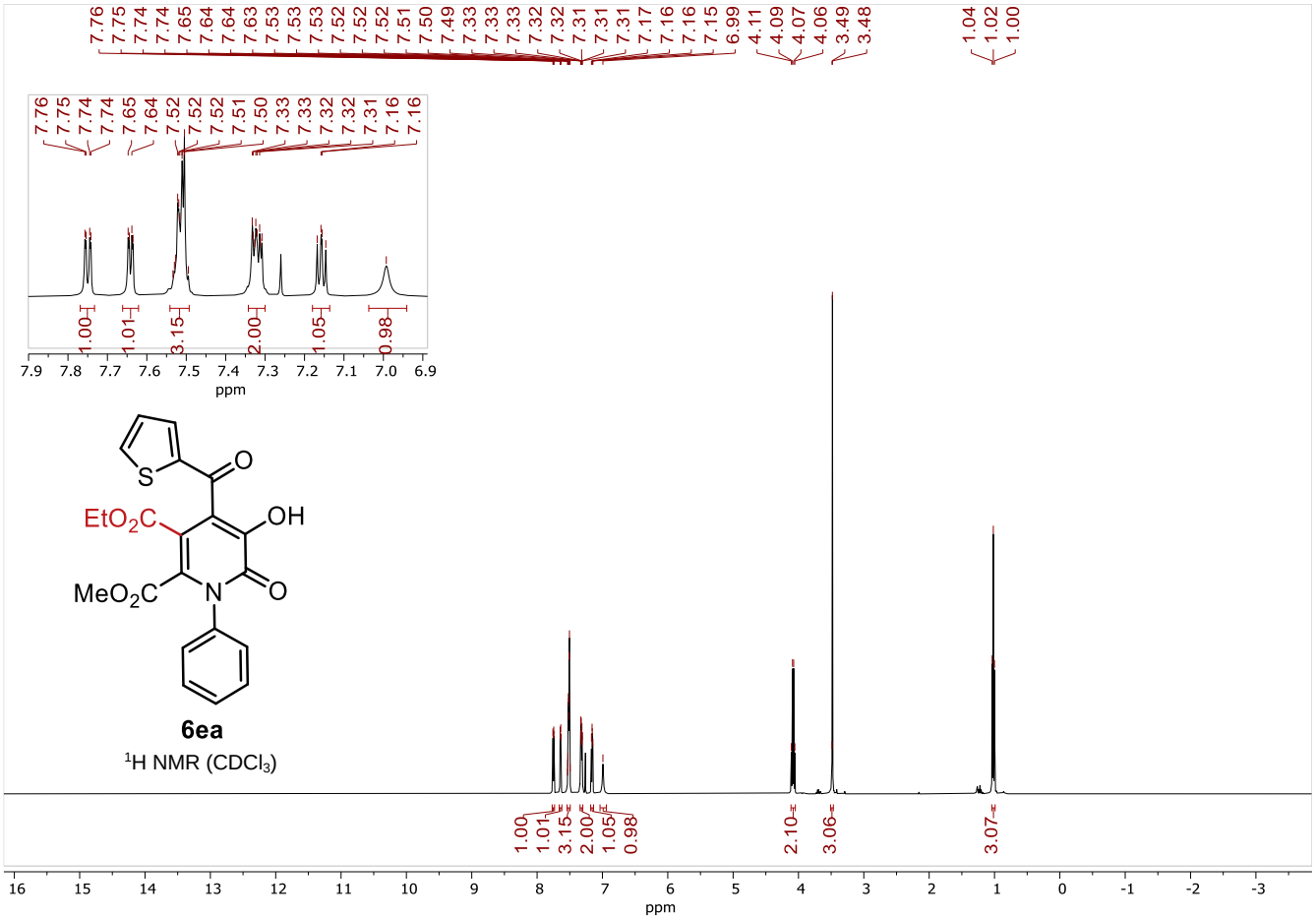


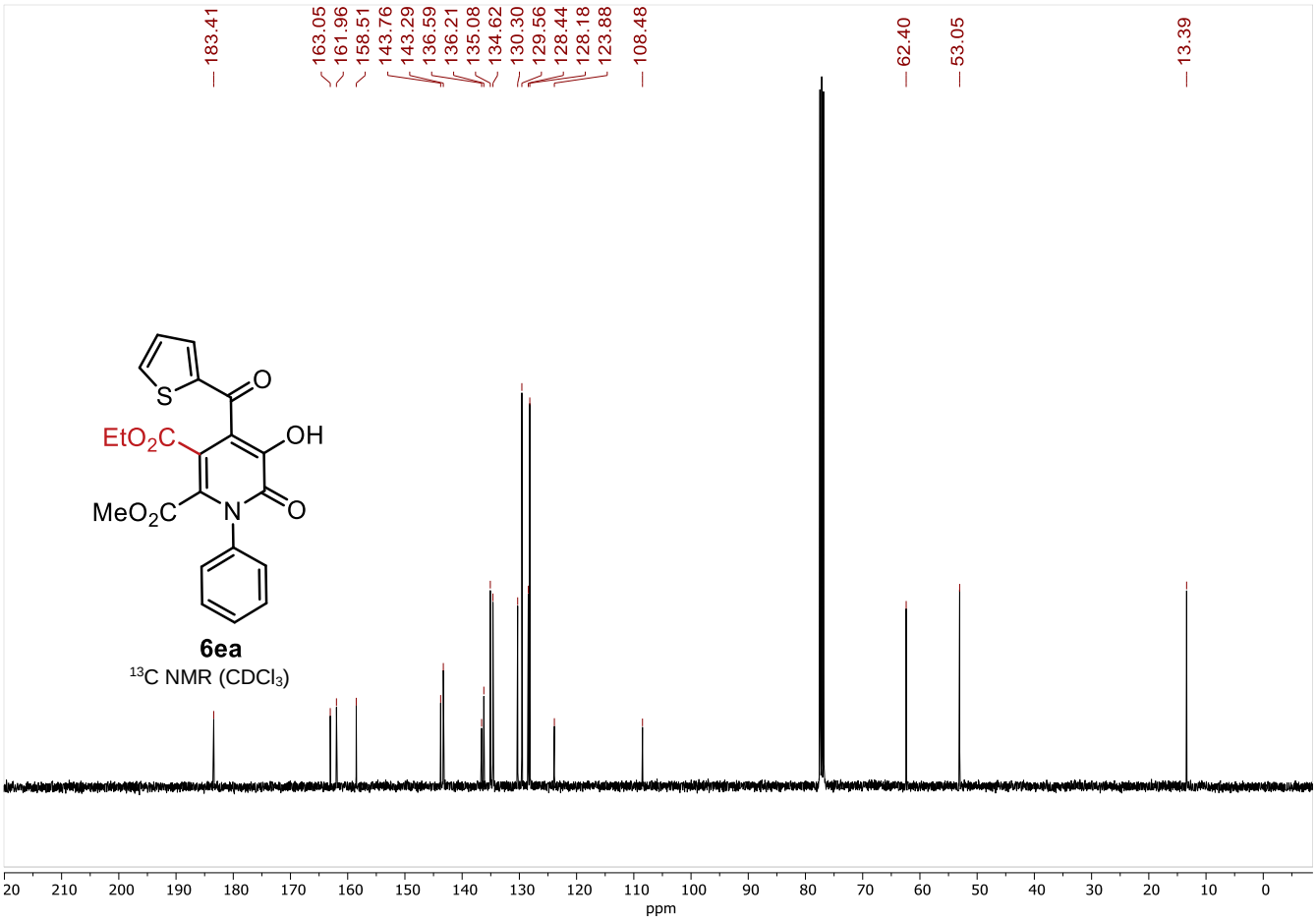
5ha

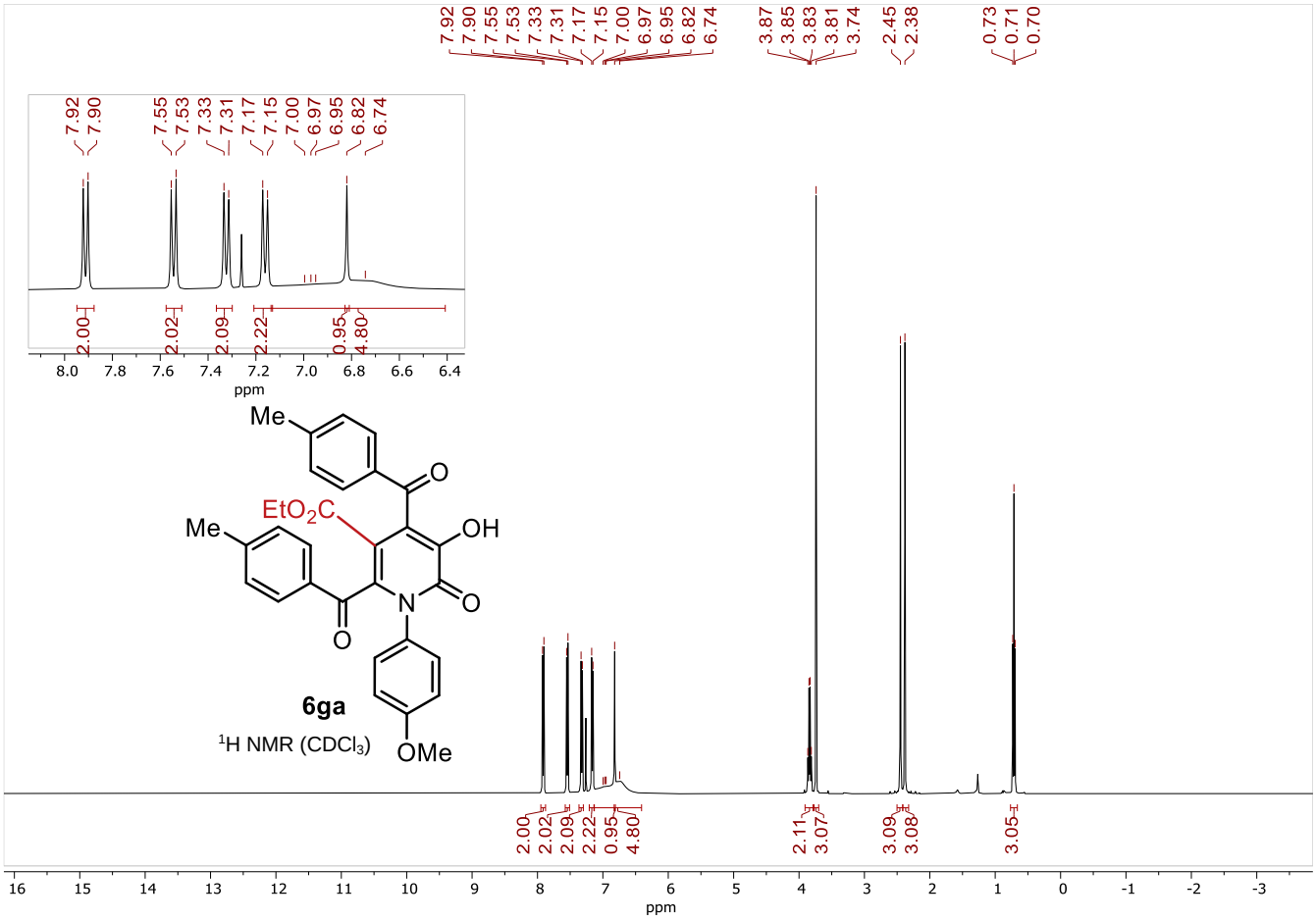
^{13}C NMR (DMSO-d_6)

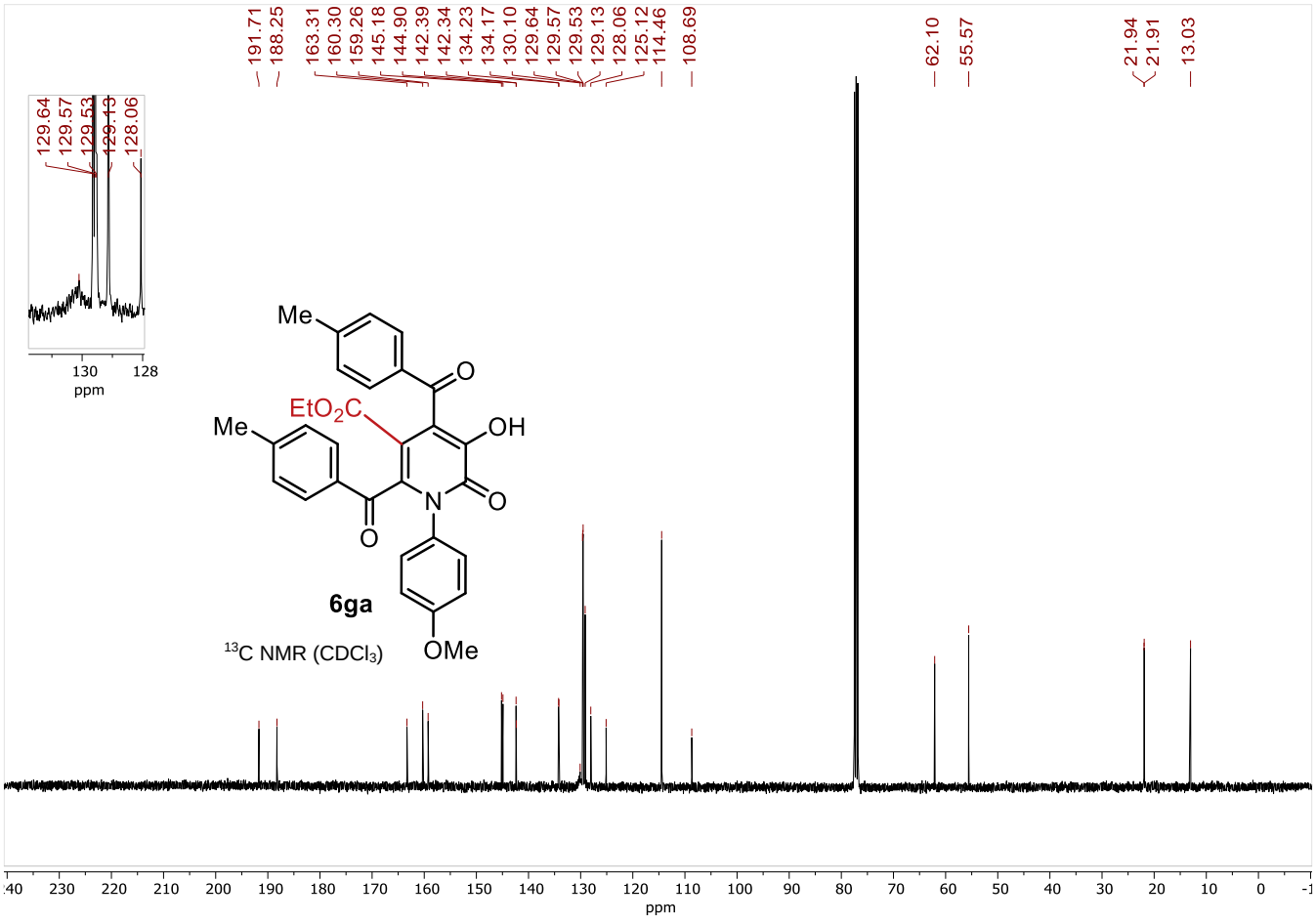

7.98 7.96 7.64 7.62 7.60 7.53 7.53 7.52 7.51 7.51 7.50 7.49 7.35 7.34 7.33 7.32 6.89 4.05 4.03 4.02 4.00 3.49 0.94 0.92 0.90
2.03 1.07 5.09 2.00 1.00
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
ppm
EtO2C
OH
MeO2C
N
O
6aa
1H NMR (CDCl3)
2.03 1.07 5.09 2.00 1.00 2.08 3.07 3.10
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
ppm

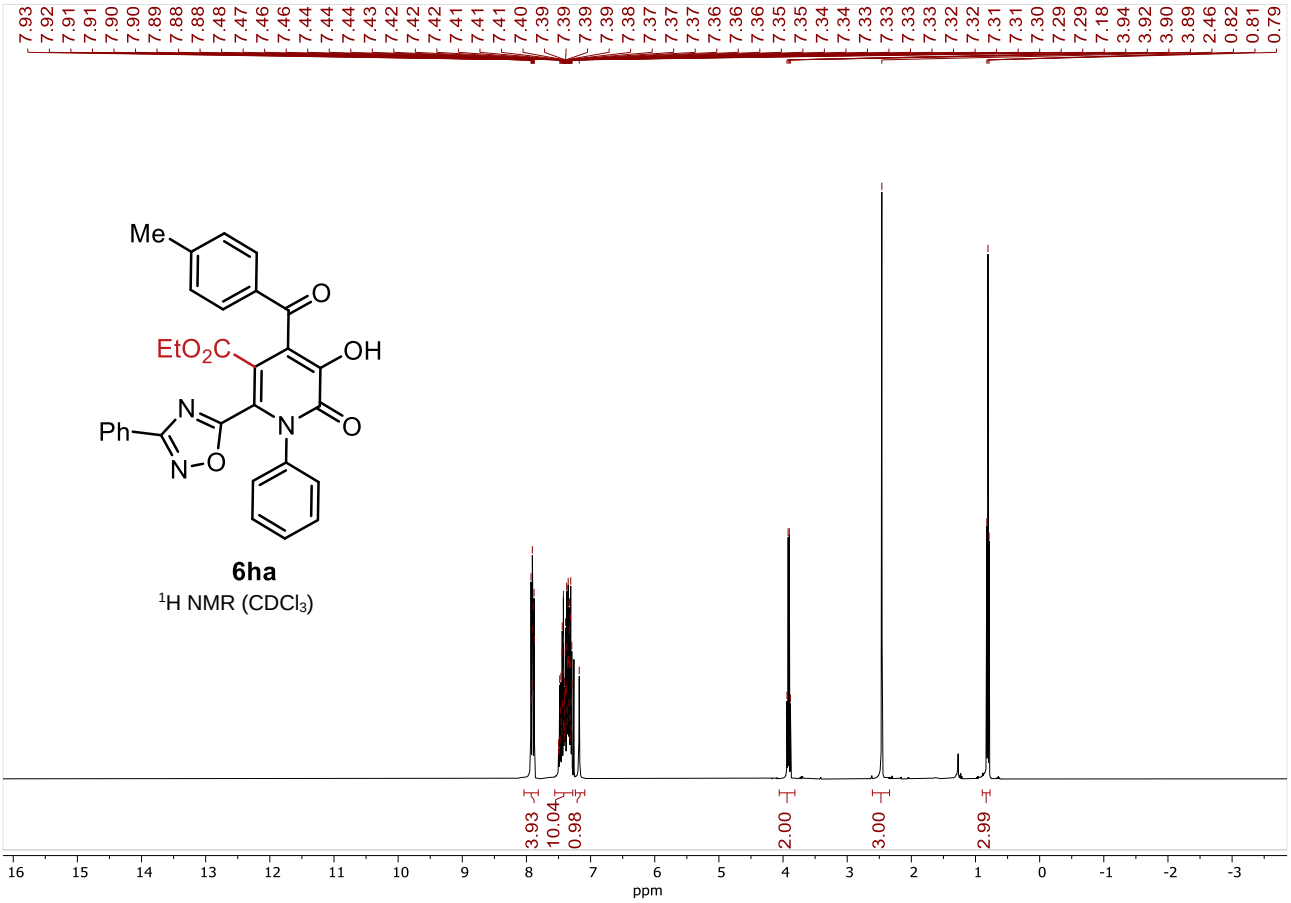

191.56
163.06 162.02 158.40 143.04 136.72 136.46 136.23 133.95 130.29 129.56 129.40 128.91 128.22 124.46
108.56
62.34
53.04
13.32
EtO2C
OH
MeO2C
N
O
6aa
13C NMR (CDCl3)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
ppm

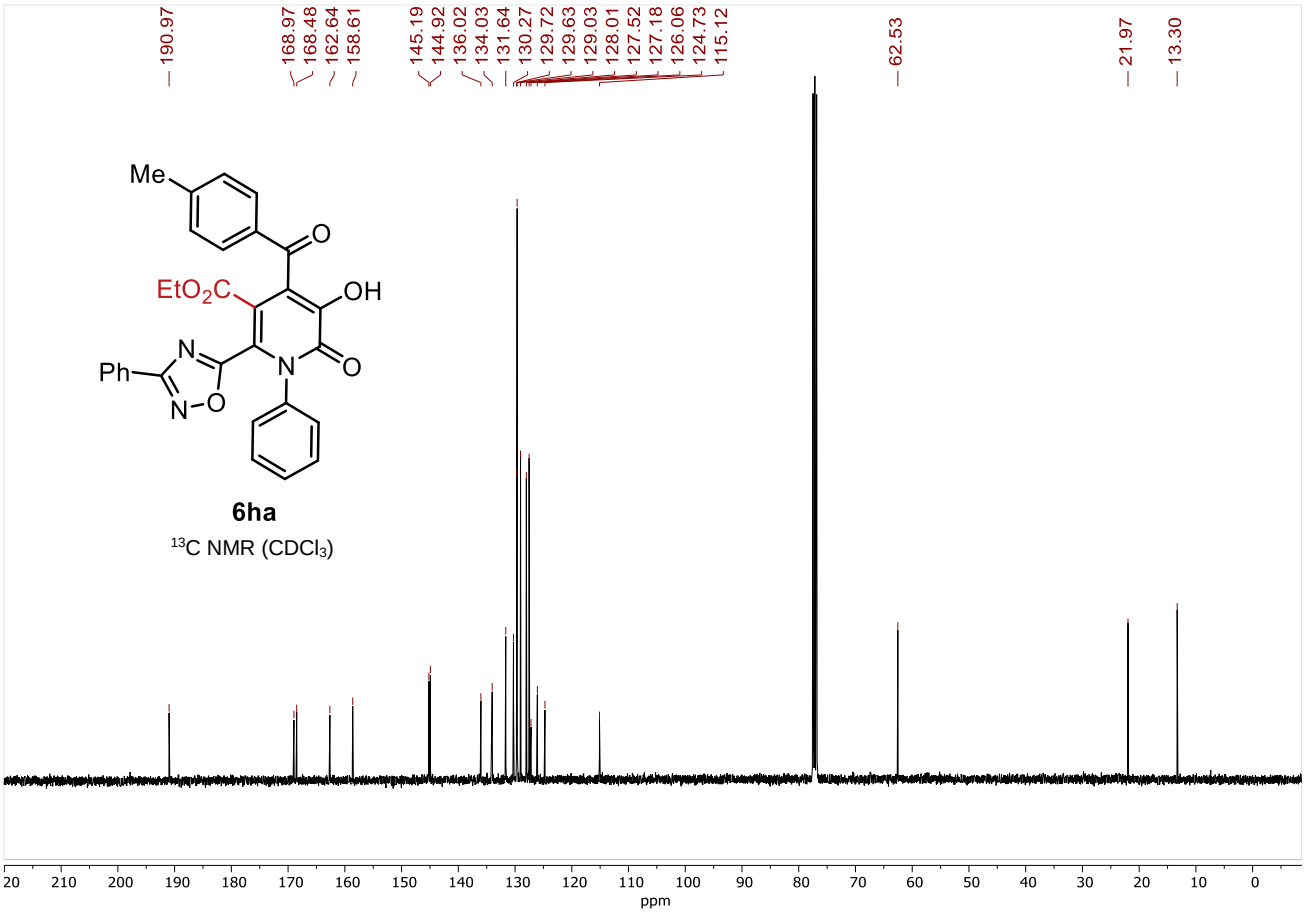

7.76 7.75 7.74 7.74 7.65 7.64 7.64 7.63 7.53 7.53 7.53 7.52 7.52 7.52 7.51 7.50 7.49 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.17 7.16 7.16 7.15 6.99 4.11 4.09 4.07 4.06 3.49 3.48 1.04 1.02 1.00
1.00 1.01 3.15 2.00 1.05 0.98
ppm
S
O
EtO2C
OH
MeO2C
N
O
6ea
1H NMR (CDCl3)
1.00 1.01 3.15 2.00 1.05 0.98 2.10 3.06 3.07
ppm


183.41
163.05 161.96 158.51 143.76 143.29 136.59 136.21 135.08 134.62 130.30 129.56 128.44 128.18 123.88 108.48
62.40 53.05 13.39
S
O
EtO2C
OH
MeO2C
N
O
6ea
13C NMR (CDCl3)
ppm


6ga
^{1}H NMR ($CDCl_3$)


6ga
^{13}C NMR ($CDCl_3$)


Me
O
EtO2C
OH
N
Ph
N
O
N
O
6ha
1H NMR (CDCl3)
3.93
10.04
0.98
2.00
3.00
2.99
ppm


Me
O
EtO2C
OH
N
Ph
N
O
N
O
6ha
13C NMR (CDCl3)
190.97
168.97
168.48
162.64
158.61
145.19
144.92
136.02
134.03
131.64
130.27
129.72
129.63
129.03
128.01
127.52
127.18
126.06
124.73
115.12
62.53
21.97
13.30
ppm