Supporting Information

Brønsted Acid-Promoted Synthesis of Highly Functionalized Tetrahydrocarbazoles from Diethyl (*E*)-5-diazo-4-oxohex-2-enedioate

Vemula Arunkumar and Rengarajan Balamurugan*

School of Chemistry, University of Hyderabad, Gachibowli, Hyderabad-500046, India

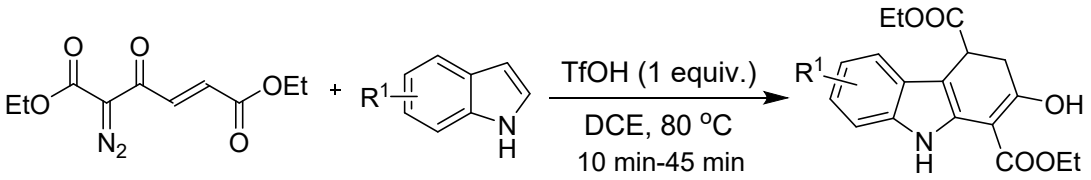
bala@uohyd.ac.in

Table of contents

1. General information:

All Chemicals and solvents were purchased from various commercial sources (Alfa, Sigma-Aldrich, Avra, TCI, BLD) and used without further purification. Starting materials were prepared by following known literature procedures. All the reactions were carried out under N_2 atmosphere with dry solvents using over dried glassware. Dichloromethane, dichloroethane, acetonitrile were dried over CaH_2 and freshly distilled before use. THF and toluene were dried over sodium and freshly distilled before use. ^1H and ^{13}C spectra were recorded on 400 and 500 MHz spectrometers using solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded using a FT-IR spectrometer reported in cm^{-1}. High-resolution mass spectra (HRMS) were recorded using ESI-Q-TOF technique. Single crystal X-ray diffraction data were collected in Bruker D8-Quest, diffractometers. Melting points were determined by using a melting range apparatus and are uncorrected. For TLC, silica gel plates 60 F254 were used and compounds were visualized by UV light and/or by treatment with seebach solution (phosphomolybdic acid (2.5 g), $Ce(SO_4)_2$ (1 g), conc. H_2SO_4 (6 mL) and H_2O (94 mL)) followed by heating. Column chromatography was performed on silica gel (100-200 mesh) using ethyl acetate and hexanes and chloroform/ethyl acetate mixture as eluent.

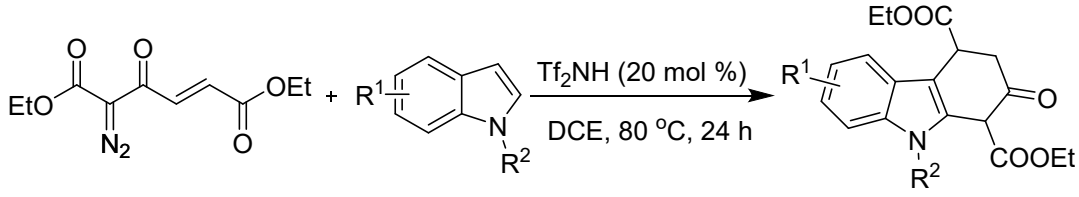
2. General procedure for the TfOH-promoted synthesis of tetrahydrocarbazoles from indole and diethyl (*E*)-5-diazo-4-oxohex-2-enedioate



1 **2** **3a-3t**

To a solution of diethyl (*E*)-5-diazo-4-oxohex-2-enedioate[1] (**1**) (0.100 g, 0.416 mmol) and indole (**2a**) (0.049 g, 0.42 mmol) in dry DCE (3 mL) in a sealed tube, TfOH (37 µL, 0.42 mmol) was added under nitrogen atmosphere. Then reaction mixture was heated at 80˚C. The progress of the reaction was monitored by TLC. After 45 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. Then it was extracted using ethyl acetate (3 x 10 mL). The combined organic layers were washed with saturated aqueous brine solution and dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure. The crude product was purified by column chromatography to get 0.103 g (75%) of the pure diethyl 2-hydroxy-4,9-dihydro-3H-carbazole-1,4-dicarboxylate **3a**. Yellow solid; m.p. = 86-87 ˚C; R_f = 0.56 in 20% EtOAc/hexanes; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.97 (br s, 1H), 8.84 (br s, 1H), 7.63 – 7.54 (m, 1H), 7.37 – 7.29 (m, 1H), 7.17 – 7.10 (m, 2H), 4.57 – 4.45 (m, 2H), 4.22 – 4.01 (m, 3H), 3.15 (dd, *J* = 17.5, 3.3 Hz, 1H), 3.08 (dd, *J* = 17.6, 8.3 Hz, 1H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

3. General procedure for the Tf_2NH-catalyzed synthesis of tetrahydrocarbazoles from indole and diethyl (*E*)-5-diazo-4-oxohex-2-enedioate



1 **4** **5a-5t**

To a solution of diethyl (*E*)-5-diazo-4-oxohex-2-enedioate[1] (**1**) (0.100 g, 0.416 mmol) and N-methylindole (**4**) (0.055 g, 0.42 mmol) in dry DCE (3 mL) in a sealed tube, Tf_2NH (0.023 g, 0.082 mmol) was added under nitrogen atmosphere. Then reaction mixture was heated at 80˚C. The progress of the

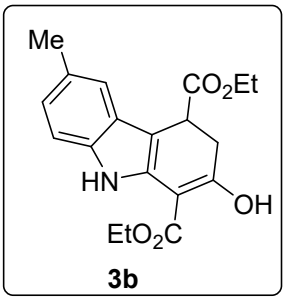
reaction was monitored by TLC. After 24 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. Then it was extracted using ethyl acetate (3 x 10 mL). The combined organic layers were washed with saturated aqueous brine solution and dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure. The crude product was purified by column chromatography to get 0.105 g (73%) of the pure **5a** as an inseparable mixture of keto and enol forms. Keto/enol forms = 94:6; dr of keto form = 1:0.68; Yellow solid; m.p. = 109-110 ˚C; R_f = 0.45 in 2% $CHCl_3$/EtOAc; **Major isomer :** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 1H), 7.34 – 7.29 (m, 1H), 7.30 – 7.26 (m, 1H), 7.20 –7.15 (m, 1H), 4.66 (s, 1H), 4.43 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.29 – 4.19 (m, 2H), 4.15 – 4.04 (m, 2H), 3.63 (s, 3H), 3.15 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.95 (dd, *J* = 14.2, 1.8 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). **Minor isomer:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 1H), 7.34 – 7.29 (m, 1H), 7.30 – 7.26 (m, 1H), 7.20 – 7.15 (m, 1H), 4.65 (s, 1H), 4.31 (dd, *J* = 6.8, 3.6 Hz, 1H), 4.29 – 4.19 (m, 2H), 4.14 – 4.05 (m, 2H), 3.63 (s, 3H), 3.25 (dd, *J* = 15.0, 3.7 Hz, 1H), 2.79 (dd, *J* = 15.0, 6.8 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

Compounds **5b-5t** were synthesized using the above procedure.

The compounds of **3a, 3c, 3d, 3e, 3f, 3j, 3l, 5a, 5c and 5d** are already reported in literature.[1]

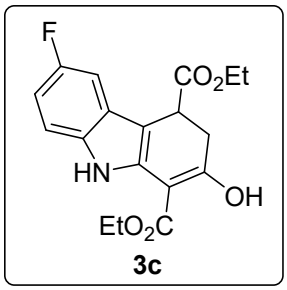
4. Characterization of Products 3b-3p

Diethyl 2-hydroxy-6-methyl-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3b): Yield (0.062 g, 43%); Yellow solid; m.p. = 82-83 ˚C; R_f = 0.51 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.03 (s, 1H), 8.74 (s, 1H), 7.36 (d, *J* = 0.5 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 6.95 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.13 – 4.06 (m, 2H), 3.12 (dd, *J* = 17.5, 3.6 Hz, 1H), 3.07 (dd, *J* = 17.5, 8.2 Hz, 1H), 2.47 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 172.9, 169.4, 134.0, 130.4, 129.3, 126.5, 122.2, 117.7, 110.4, 99.4, 94.5, 61.4, 60.9, 36.1, 32.4, 21.6, 14.5, 14.1. IR (neat, cm^{-1}): υ 3489, 2991, 2985, 1725, 1648, 1597, 1446, 1305, 1227, 1145, 1078, 859. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{22}NO_5$ $(M + H)^+$ 344.1492, found 344.1496.



3b

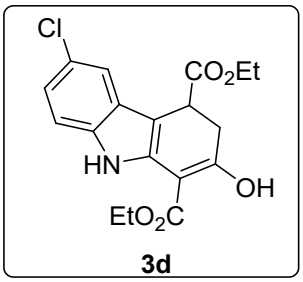
Diethyl 6-fluoro-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3c): Yield (0.074 g, 51%);



3c

Yellow solid; R_f = 0.51 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.03 (s, 1H), 8.80 (s, 1H), 7.21-7.16 (m, 2H), 6.81 (td, *J* = 9.0, 2.5 Hz, 1H), 4.46 (dq, *J* = 7.1, 1.6 Hz, 2H), 4.13 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.10 – 4.03 (m, 1H), 4.01 (dd, *J* = 8.6, 3.1 Hz, 1H), 3.11 (dd, *J* = 17.6, 3.1 Hz, 1H), 3.03 (dd, *J* = 17.6, 8.6 Hz, 1H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

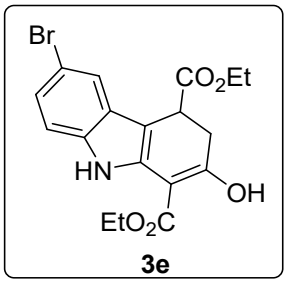
Diethyl 6-chloro-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3d): Yield (0.072 g, 48%);



3d

Yellow solid; m.p. = 142-143 ˚C; R_f = 0.48 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.04, (s, 1H), 8.85 (s, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.24 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.08 – 7.03 (m, 1H), 4.53 – 4.47 (m, 2H), 4.20 – 4.02 (m, 2H), 4.05 (dd, *J* = 8.7, 3.2 Hz, 1H), 3.15 (dd, *J* = 17.6, 3.1 Hz, 1H), 3.07 (dd, *J* = 17.6, 8.6 Hz, 1H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

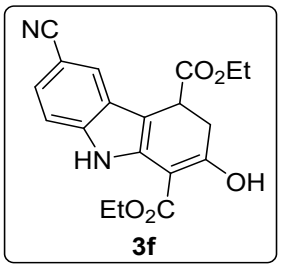
Diethyl 6-bromo-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3e): Yield (0.084 g, 20% EtOAc/hexanes; ^{1}H 1H), 7.67 – 7.66 (m, 1H), (m, 2H), 4.01 (dd, *J* = 8.8, *J* = 17.7, 8.7 Hz, 1H),



3e

49%); Yellow solid; m.p. = 152-153 ˚C; R_f = 0.42 in NMR (500 MHz, $CDCl_3$): δ 13.05 (s, 1H), 8.84 (s, 7.17 – 7.13 (m, 2H), 4.50 – 4.44 (m, 2H), 4.18 – 4.05 3.1 Hz, 1H), 3.12 (dd, *J* = 17.7, 3.1 Hz, 1H), 3.03 (dd, 1.47 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

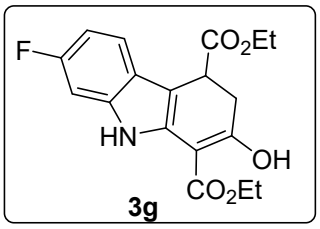
Diethyl 6-cyano-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3f): Yield (0.038 g, 26%);



3f

Yellow solid; m.p. = 188-189 ˚C; R_f = 0.37 in 30% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.16 (s, 1H), 9.08 (s, 1H), 7.91 (t, *J* = 0.5 Hz, 1H), 7.39 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.5 Hz, 1H), 4.56 – 4.50 (m, 2H), 4.22 – 4.05 (m, 3H), 3.19 (dd, *J* = 17.7, 2.9 Hz, 1H), 3.10 (dd, *J* = 17.7, 8.8 Hz, 1H), 1.52 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).

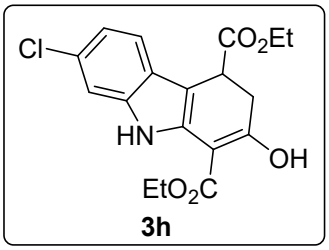
Diethyl 7-fluoro-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3g): Yield (0.062 g, 43%);



3g

Yellow solid; m.p. = 102-105 ˚C; R_f = 0.51 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.02 (s, 1H), 8.82 (s, 1H), 7.52 – 7.44 (m, 1H), 7.09 – 6.99 (m, 1H), 6.92 – 6.86 (m, 1H), 4.52 – 4.46 (m, 2H), 4.19 – 4.12 (m, 1H), 4.12 – 4.04 (m, 2H), 3.16 – 3.10 (m, 1H), 3.10 – 3.03 (m, 1H), 1.52 - 1.47 (m, 3H), 1.26 – 1.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.5, 172.7, 169.3, 159.5 (d, *J* = 235.0 Hz), 135.5 (d, *J* = 11.3 Hz), 130.6, 122.9, 118.5 (d, *J* = 8.5 Hz), 108.5 (d, *J* = 23.7 Hz), 99.7, 97.3 (d, *J* = 26.2 Hz), 94.3, 61.5, 61.0, 36.0, 32.2, 14.5, 14.1. IR (neat, cm^{-1}): υ 3469, 2981, 1719, 1647, 1625, 1587, 1221, 1133, 1078, 837, 758. HRMS (ESI-Q-TOF) m/z calcd for $C_{18}H_{19}FNO_5$ $(M + H)^+$ 348.1242, found 348.1241.

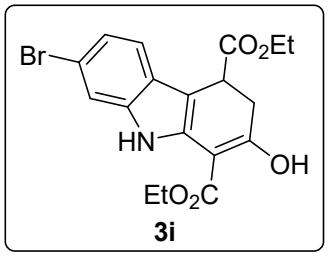
Diethyl 7-chloro-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3h): Yield (0.080 g, 53%);



3h

Yellow solid; m.p. = 92-94 ˚C; R_f = 0.48 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.06 (s, 1H), 8.83 (s, 1H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.09 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.48 (dq, *J* = 7.1, 1.0 Hz, 2H), 4.15 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.11 – 4.04 (m, 2H), 3.14 (dd, *J* = 17.6, 3.2 Hz, 1H), 3.06 (dd, *J* = 17.6, 8.6 Hz, 1H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.2, 172.6, 169.3, 136.0, 131.1, 126.3, 124.9, 120.7, 118.7, 110.7, 99.8, 94.1, 61.6, 61.1, 35.9, 32.2, 14.5, 14.1. IR (neat, cm^{-1}): υ 3472, 2983, 1722, 1647, 1595, 1468, 1330, 1223, 1079, 855. HRMS (ESI-Q-TOF) m/z calcd for $C_{18}H_{19}ClNO_5$ $(M + H)^+$ 364.0946, found 364.0946.

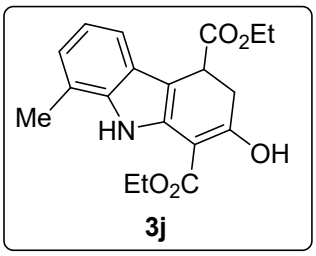
Diethyl 7-bromo-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3i): Yield (0.079 g, 46%);



3i

Brown solid; m.p. = 124-125 ˚C; R_f = 0.36 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.07 (s, 1H), 8.82 (s, 1H), 7.49 (d, *J* = 1.5 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.49 (qd, *J* = 7.1, 1.1 Hz, 2H), 4.18 – 4.11 (m, 1H), 4.11 – 4.03 (m, 2H), 3.14 (dd, *J* = 17.6, 3.2 Hz, 1H), 3.07 (dd, *J* = 17.6, 8.6 Hz, 1H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.2, 172.6, 169.2, 136.4, 131.1, 125.2, 123.3, 119.1, 113.8, 113.7, 99.8, 94.1, 61.6, 61.1, 35.8, 32.2, 14.5, 14.1. IR (neat, cm^{-1}): υ 3471, 2980, 1714, 1646, 1591, 1465, 1365, 1218, 1077, 852; HRMS (ESI-Q-TOF) m/z calcd for $C_{18}H_{19}BrNO_5$ $(M + H)^+$ 408.0441, found 408.0433.

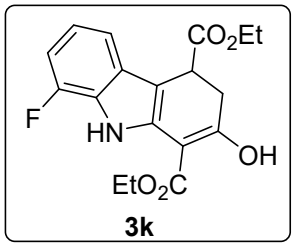
Diethyl 2-hydroxy-8-methyl-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3j): Yield (0.075 g, 52%);



3j

Yellow solid; m.p. = 80-83 ˚C; R_f = 0.45 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.95 (s, 1H), 8.79 (s, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.20 – 4.13 (m, 1H), 4.13 – 4.03 (m, 2H), 3.14 (dd, *J* = 17.5, 3.5 Hz, 1H), 3.08 (dd, *J* = 17.5, 8.3 Hz, 1H), 2.49 (s, 3H), 1.53 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).

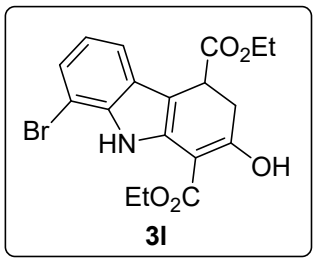
Diethyl 8-fluoro-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3k): Yield (0.056 g, 39%);



3k

Yellow solid; m.p. = 108-109 ˚C; R_f = 0.38 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.05 (s, 1H), 8.92 (s, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.03 – 6.97 (m, 1H), 6.81 (ddd, *J* = 11.0, 7.5, 0.5 Hz, 1H), 4.49 (dq, *J* = 7.1, 1.7 Hz, 2H), 4.17 – 4.09 (m, 1H), 4.09 – 4.02 (m, 2H), 3.13 (dd, *J* = 17.6, 3.3 Hz, 1H), 3.06 (dd, *J* = 17.6, 8.4 Hz, 1H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.4, 172.6, 169.4, 149.2 (d, *J* = 241.2 Hz), 131.1, 129.8 (d, *J* = 5.0 Hz), 120.3 (d, *J* = 6.2 Hz), 113.8 (d, *J* = 3.7 Hz), 105.7 (d, *J* = 16.2 Hz), 100.5 (d, *J* = 2.5 Hz), 94.2, 61.7, 61.1, 36.0, 32.3, 14.4, 14.1. IR (neat, cm^{-1}): υ 3480, 2989, 1727, 1645, 1562, 120, 1094, 1028, 776; HRMS (ESI-Q-TOF) m/z calcd for $C_{18}H_{19}FNO_5$ $(M + H)^+$ 348.1242, found 348.1244.

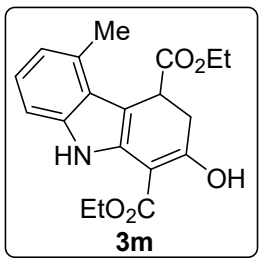
Diethyl 8-bromo-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3l): Yield (0.081 g, 48%);



3l

Yellow solid; m.p. = 108-109 ˚C; R_f = 0.38 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.99 (s, 1H), 9.04 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.25 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 4.49 (dq, *J* = 7.1, 1.5 Hz, 2H), 4.19 – 4.12 (m, 1H), 4.11 – 4.04 (m, 2H), 3.15 (dd, *J* = 17.6, 3.3 Hz, 1H), 3.08 (dd, *J* = 17.6, 8.6 Hz, 1H), 1.56 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

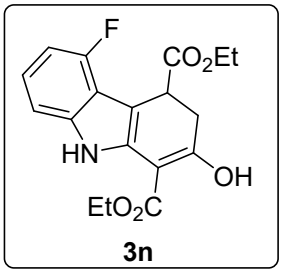
Diethyl 2-hydroxy-5-methyl-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3m): Yield (0.065 g, 45%); Yellow solid; m.p. = 80-85 ˚C; R_f = 0.42 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.98 (s, 1H), 8.82 (s, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.00 – 6.95 (m, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 4.46 (dq, *J* = 7.1, 1.0 Hz, 2H), 4.28 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.17 – 4.08 (m, 1H), 4.04 – 3.96 (m, 1H), 3.11 (dd, *J* = 17.1, 8.0 Hz, 1H), 3.02 (dd, *J* = 17.1, 1.7 Hz, 1H), 2.71 (s, 3H), 1.47 (t, *J* = 7.1 Hz,



3m

3H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.8, 172.9, 169.5, 135.6, 130.2, 129.2, 125.2, 121.6, 120.8, 108.7, 100.7, 94.5, 61.4, 61.0, 36.8, 33.3, 19.7, 14.5, 14.0. IR (neat, cm^{-1}): υ 3348, 2979, 1722, 1644, 1578, 1462, 1266, 1077, 970, 776. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{22}NO_5$ $(M + H)^+$ 344.1492, found 344.1492.

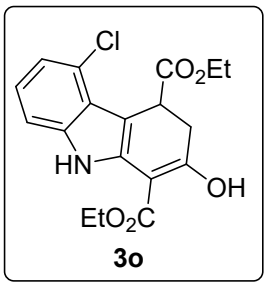
Diethyl 5-fluoro-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3n): Yield (0.060 g, 42%);



3n

Yellow solid; m.p. = 98-99 ˚C; R_f = 0.62 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.01 (s, 1H), 8.86 (s, 1H), 7.09 (d, J = 8.1 Hz, 1H), 6.98 (td, J = 8.0, 5.0 Hz, 1H), 6.75 (dd, J = 10.8, 7.9 Hz, 1H), 4.51 – 4.45 (m, 2H), 4.23 (t, J = 5.7 Hz, 1H), 4.18 – 4.10 (m, 1H), 4.08 – 4.00 (m, 1H), 3.11 (d, J = 5.6 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.0, 173.0, 169.2, 156.1 (d, J = 245.0 Hz), 138.1 (d, J = 11.2 Hz), 130.4, 121.0 (d, J = 7.5 Hz), 115.5 (d, J = 20.0 Hz), 109.0, 106.9 (d, J = 3.7 Hz), 105.3 (d, J = 18.7 Hz), 98.3, 94.3, 61.6, 61.0, 36.3, 32.8, 14.5, 14.0. IR (neat, cm^{-1}): υ 3414, 2980, 1720, 1634, 1595, 1368, 1078, 859, 730. HRMS (ESI-Q-TOF) m/z calcd for $C_{18}H_{19}FNO_5$ $(M + H)^+$ 348.1242, found 348.1241.

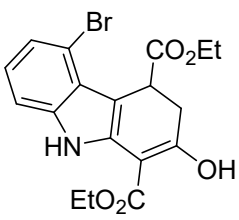
Diethyl 5-chloro-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3o): Yield (0.090 g, 60%);



3o

Brown solid; m.p. = 138-139 ˚C; R_f = 0.57 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.06 (s, 1H), 8.95 (s, 1H), 7.23 (dd, J = 8.0, 0.9 Hz, 1H), 7.07 (dd, J = 7.7, 0.9 Hz, 1H), 7.02 – 6.98 (m, 1H), 4.62 (dd, J = 8.4, 2.2 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.22 – 4.14 (m, 1H), 4.11 – 4.03 (m, 1H), 3.18 (dd, J = 17.5, 8.4 Hz, 1H), 3.12 (dd, J = 17.5, 2.2 Hz, 1H), 1.50 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 173.1, 169.1, 136.7, 131.6, 124.7, 123.9, 121.1, 120.8, 109.5, 100.4, 94.5, 61.6, 61.0, 35.8, 33.1, 14.5, 14.0. IR (neat, cm^{-1}): υ 3411, 2983, 2358, 1723, 1648, 1596, 1429, 1367, 1229, 1077, 941. HRMS (ESI-Q-TOF) m/z calcd for $C_{18}H_{19}ClNO_5$ $(M + H)^+$ 364.0946, found 364.0944.

Diethyl 5-bromo-2-hydroxy-4,9-dihydro-3*H*-carbazole-1,4-dicarboxylate (3p): Yield (0.104 g, 62%);



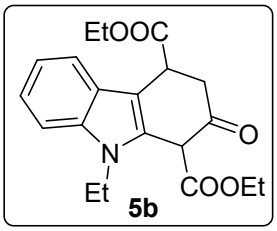
3p

Yellow solid; m.p. = 139-140 ˚C; R_f = 0.62 in 20% EtOAc/hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 13.04 (s, 1H), 8.96 (s, 1H), 7.28 (s, 1H), 7.27 – 7.24 (m, 1H), 6.94

(t, J = 7.9 Hz, 1H), 4.75 (dd, J = 8.0, 2.6 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.24 – 4.15 (m, 1H), 4.11 – 4.04 (m, J = 10.8, 7.1 Hz, 1H), 3.18 (dd, J = 17.5, 8.0 Hz, 1H), 3.13 (dd, J = 17.5, 2.7 Hz, 1H), 1.50 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2, 173.1, 169.3, 136.6, 131.8, 125.2, 124.2, 121.4, 112.6, 110.1, 101.1, 94.5, 61.7, 61.1, 35.5, 33.1, 14.5, 14.1. IR (neat, cm^{-1}): υ 3414, 2977, 2352, 1724, 1646, 1594, 1225, 1076, 858, 770. HRMS (ESI-Q-TOF) m/z calcd for $C_{18}H_{19}BrNO_5$ $(M + H)^+$ 408.0441, found 408.0446.

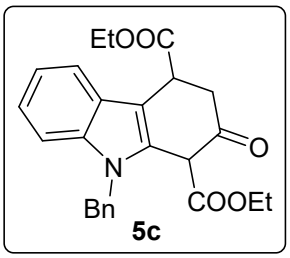
5. Characterization of Products 5b-5t:

Diethyl 9-ethyl-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate (5b): Yield (0.106 g, 71%); dr = 1:0.79; Keto/enol forms = 98:2; Yellow solid; m.p. = 85-86 ˚C; R_f = 0.6 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (t, J = 7.5 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.29 – 7.23 (m, 1H), 7.20 – 7.13 (m, 1H), 4.65 (s, 1H), 4.43 (dd, J = 6.7, 2.1 Hz, 1H), 4.29 – 4.16 (m, 2H), 4.23 – 4.17 (m, 4H), 3.19 (dd, J = 14.2, 6.7 Hz, 1H), 2.93 (dd, J = 14.2, 2.1 Hz, 1H), 1.34 – 1.17 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.8, 173.0, 167.0, 136.8, 130.2, 125.7, 122.5, 120.02, 119.9, 109.6, 107.7, 62.6, 61.4, 55.0, 39.9, 38.9, 38.2, 15.1, 14.9, 14.1. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (t, J = 7.5 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.26 (m, 1H), 7.20 – 7.13 (m, 1H), 4.63 (s, 1H), 4.31 (dd, J = 6.8, 3.6 Hz, 1H), 4.29 – 4.16 (m, 2H), 4.23 – 4.17 (m, 4H), 3.26 (dd, J = 15.1, 3.5 Hz, 1H), 2.77 (dd, J = 15.1, 6.8 Hz, 1H), 1.34 – 1.17 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.4, 172.2, 167.0, 136.7, 130.1, 125.5, 122.5, 120.0, 119.4, 109.6, 107.8, 62.3, 61.4, 54.5, 40.6, 38.4, 38.3, 15.1, 14.9, 14.1. IR (neat, cm^{-1}): υ 2980, 2925, 1722, 1619, 1495, 1332, 1250, 1152, 1027, 854, 733. HRMS (ESI-Q-TOF) m/z calcd for $C_{20}H_{24}NO_5$ $(M + H)^+$ 358.1649, found 358.1648.



5b

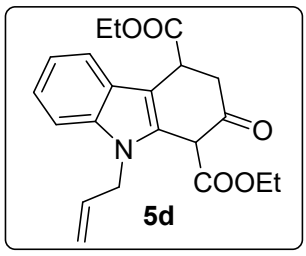
Diethyl 9-benzyl-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate (5c): Yield (0.098 g, 56%); dr = 1:0.59; Keto/enol forms = 96:4; Yellow gum; m.p. = 109-110 ˚C; R_f = 0.74 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 – 7.74 (m, 1H), 7.31 – 7.25 (m, 6H), 6.95 – 6.92 (m, 2H), 5.43 – 5.19 (m 2H), 4.60 (s, 1H), 4.51 (dd, J = 6.8, 2.0 Hz, 1H), 4.20 – 4.09 (m, 2H), 3.86 – 3.79 (m, 2H), 3.32 – 3.24 (m, 1H), 2.97 (dd, J = 14.3, 1.7 Hz, 1H), 1.20 (t, J = 7.5 Hz, 3H), 1.10 (t, J = 7.0 Hz, 3H). **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 – 7.74 (m, 1H),



5c

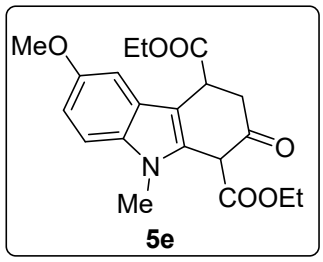
7.31 – 7.25 (m, 6H), 6.95 – 6.92 (m, 2H), 5.43 – 5.19 (m 2H), 4.53 (s, 1H), 4.35 (dd, *J* = 6.8, 3.6 Hz, 1H), 4.20 – 4.09 (m, 2H), 3.86 – 3.79 (m, 2H), 3.32 – 3.24 (m, 1H), 2.28 (dd, *J* = 15.2, 6.9 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.5 Hz, 3H).

Diethyl 9-allyl-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate (5d): Yield (0.078 g, 51%); dr = 1:0.55; Keto/enol forms = 97:3; Yellow gum; R_f = 0.57 in 2% $CHCl_3$/EtOAc; ^{1}H NMR (500 MHz, $CDCl_3$): **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 5.91 – 5.81 (m, 1H), 5.17 – 5.10 (m, 1H), 4.83 (dd, *J* = 17.1, 1.0 Hz, 1H), 4.72 – 4.68 (m, 1H), 4.65 – 4.61 (m, 2H), 4.44 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.26 – 4.10 (m, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.21 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.93 (dd, *J* = 14.3, 2.0 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.20 – 7.14 (m, 1H), 5.91 – 5.81 (m, 1H), 5.17 – 5.10 (m, 1H), 4.90 (dd, *J* = 17.1, 1.0 Hz, 1H), 4.72 – 4.68 (m, 1H), 4.65 – 4.61 (m, 2H), 4.32 (dd, *J* = 6.7, 3.6 Hz, 1H), 4.26 – 4.10 (m, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.27 (dd, *J* = 15.1, 3.6 Hz, 1H),2.77 (dd, *J* = 15.1, 6.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H).



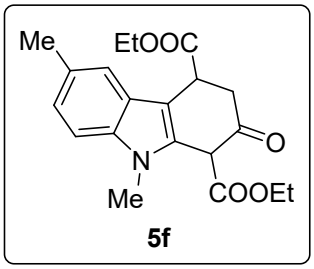
5d

Diethyl 6-Methoxy-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5e): Yield (0.066 g, 43%); dr = 1:0.58; Keto/enol forms = 93:7; Yellow solid; m.p. = 112-113 ˚C; R_f = 0.71 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.97 – 6.92 (m, 1H), 4.65 (s, 1H), 4.40 (d, *J* = 5.1 Hz, 1H), 4.31 – 4.20 (m, 2H), 4.18 – 4.06 (m, 2H), 3.89 (s, 3H), 3.62 (s, 3H), 3.16 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.98 – 2.94 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 173.0, 166.8, 154.4, 133.3, 131.3, 125.5, 112.7, 110.2, 107.2, 101.0, 62.6, 61.4, 55.9, 54.8, 40.0, 38.9, 30.0, 14.1. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.19 (m, 1H), 7.16 (d, *J* = 2.1 Hz, 1H), 6.97 – 6.92 (m, 1H), 4.65 (s, 1H), 4.40 (d, *J* = 5.1 Hz, 1H), 4.31 – 4.20 (m, 2H), 4.18 – 4.06 (m, 2H), 3.89 (s, 3H), 3.62 (s, 3H), 3.26 (dd, *J* = 15.0, 3.4 Hz, 1H), 2.80 (dd, *J* = 15.0, 6.8 Hz, 1H), 1.29 (t, *J* = 6.9 Hz, 3H), 1.24 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 172.2, 166.9, 154.5, 133.21, 131.2, 125.7, 112.7, 110.2, 107.2, 101.0, 62.2, 61.4, 55.9, 54.5, 40.7, 38.4, 29.9, 14.1. IR (neat, cm^{-1}): υ 2980, 2457, 1723, 1583, 1469, 1367, 1178, 1095, 969, 855, 734. HRMS (ESI-Q-TOF) m/z calcd for $C_{20}H_{24}NO_6$ $(M + H)^+$ 374.1598, found 374.1595.



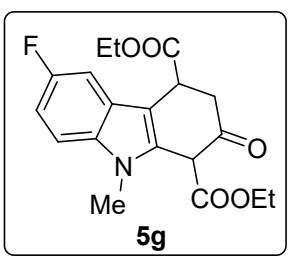
5e

Diethyl 6,9-dimethyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5f): Yield (0.078 g, 52%); dr = 1:0.67; Keto/enol forms = 94:6; Yellow solid; m.p. = 99-100 ˚C; R_f = 0.65 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.18 (dd, *J* = 8.3, 4.8 Hz, 1H), 7.10 – 7.06 (m, 1H), 4.63 (s, 1H), 4.38 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.27 – 4.17 (m, 2H), 4.14 – 4.02 (m, 2H), 3.58 (s, 3H), 3.13 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.94 – 2.90 (m, 1H), 2.46 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7, 173.0, 166.9, 136.4, 130.9, 129.3, 125.4, 124.1, 118.9, 109.0, 107.2, 62.5, 61.3, 54.8, 40.1, 38.9, 29.9, 21.4, 14.0. **Minor isomer:** ^{1}H NMR (500 MHz, $CDCl_3$): 7.47 (dd, *J* = 2.6, 1.6 Hz, 1H), 7.18 (dd, *J* = 8.3, 4.8 Hz, 1H), 7.10 – 7.06 (m, 1H), 4.63 (s, 1H), 4.38 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.27 – 4.17 (m, 2H), 4.14 – 4.02 (m, 2H), 4.61 (s, 3H), 3.21 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.75 (dd, *J* = 15.0, 6.8 Hz, 1H), 2.46 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7, 173.0, 166.9, 136.4, 130.9, 129.3, 125.4, 124.1, 118.9, 109.0, 107.2, 62.5, 61.3, 54.8, 40.1, 38.9, 29.9, 21.4, 14.0. IR (neat, cm^{-1}): υ 2929, 2134, 1720, 1651, 1444, 1368, 1297, 1147, 1029, 861, 792. HRMS (ESI-Q-TOF) m/z calcd for $C_{20}H_{24}NO_5$ $(M + H)^+$ 358.1649, found 358.1643



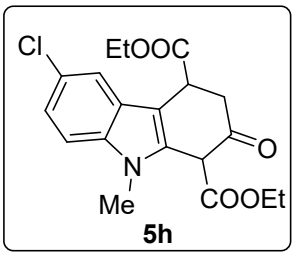
5f

Diethyl 6-Fluoro-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5g): Yield (0.075 g, 50%); dr = 1:0.72; Keto/enol forms = 91:9; Yellow gum; R_f = 0.75 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 1H), 7.22 (dt, *J* = 8.9, 4.5 Hz, 1H), 7.04 – 6.97 (m, 1H), 4.63 (s, 1H), 4.35 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.31 – 4.18 (m, 2H), 4.17 – 4.06 (m, 2H), 3.62 (s, 3H), 3.13 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.95 (dd, *J* = 14.3, 2.2 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 172.8, 166.7, 158.1 (d, *J* = 234.0 Hz), 134.6, 132.5, 125.5 (d, *J* = 10.0 Hz), 110.9 (d, *J* = 26.0 Hz), 110.1 (d, *J* = 10 Hz), 107.7, 104.3 (d, *J* = 24.0 Hz), 62.7, 61.5, 54.8, 39.9, 38.8, 30.1, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 2H), 7.22 (dt, *J* = 8.9, 4.5 Hz, 1H), 7.04 – 6.97 (m, 1H), 4.63 (s, 1H), 4.35 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.31 – 4.18 (m, 2H), 4.17 – 4.06 (m, 2H), 3.25 (dd, *J* = 15.3, 3.9 Hz, 1H), 2.78 (dd, *J* = 15.1, 6.8 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 172.0, 166.7, 158.1 (d, *J* = 234.0 Hz), 134.5, 132.3, 125.5 (d, *J* = 10.0 Hz), 110.9 (d, *J* = 26.0 Hz), 110.1 (d, *J* = 10 Hz), 107.7, 104.3 (d, *J* = 24.0 Hz), 62.4, 61.5, 40.5, 38.2, 30.1, 14.0. IR (neat, cm^{-1}): υ 2919, 2155, 1724, 1486, 1369, 1297, 1028, 855, 734. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{21}FNO_5$ $(M + H)^+$ 362.1398, found 362.1396.



5g

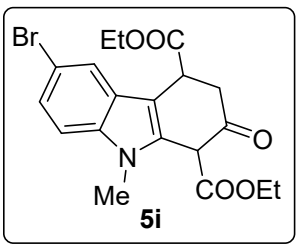
Diethyl 6-chloro-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5h): Yield



5h

(0.078 g, 50%); dr = 1:0.62; Keto/enol forms = 90:10; Yellow gum; R_f = 0.6 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 – 7.64 (m, 1H), 7.22 – 7.19 (m, 2H), 4.63 (s, 1H), 4.36 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.29 – 4.20 (m, 2H), 4.16 – 4.06 (m, 2H), 3.61 (s, 3H), 3.13 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.95 (dd, *J* = 14.3, 2.0 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 172.7, 166.6, 136.4, 132.3, 126.3, 125.9, 122.9, 118.8, 110.4, 107.4, 62.7, 61.6, 54.7, 39.8, 38.7, 30.1, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 – 7.64 (m, 1H), 7.22 - 7.19 (m, 2H), 4.63 (s, 1H), 4.36 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.29 – 4.20 (m, 2H), 4.16 – 4.06 (m, 2H), 3.62 (s, 3H), 1.31 – 1.25 (m, 3H), 3.25 (dd, *J* = 15.2, 3.7 Hz, 1H), 2.78 (dd, *J* = 15.1, 6.8 Hz, 1H), 1.28 (t, *J* = 7.3 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 171.9, 166.6, 136.3, 132.1, 126.1, 125.8, 122.9, 118.8, 110.4, 107.4, 62.4, 61.6, 54.3, 40.4, 38.1, 29.9, 14.0. IR (neat, cm^{-1}): υ 2989, 2919, 1724, 1588 1469, 1368, 1182, 1095, 860, 796. IR (neat, cm^{-1}): υ 2921, 2851, 1722, 1587, 1460, 1368, 1233, 1177, 1068, 843, 735. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{21}ClNO_5$ $(M + H)^+$ 378.1103, found 378.1103.

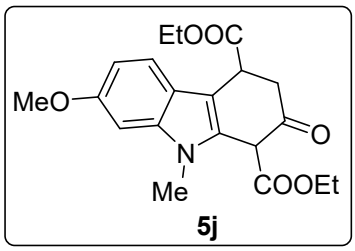
Diethyl 6-bromo-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5i): Yield



5i

(0.084 g, 48%); dr = 1:0.60; Keto/enol forms = 90:10; Brown gum; R_f = 0.64 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 1.8 Hz, 1H), 7.36 (dd, *J* = 3.1, 2.0 Hz, 1H), 7.21 (d, *J* = 4.7 Hz, 1H), 4.65 (s, 1H), 4.38 (dd, *J* = 6.8, 2.3 Hz, 1H), 4.32 – 4.21 (m, 2H), 4.22 – 4.06 (m, 2H), 3.63 (s, 3H), 3.15 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.98 (dd, *J* = 14.3, 2.2 Hz, 1H), 1.29 (t, *J* = 7.3 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 172.6, 166.5, 136.7, 132.2, 126.7, 125.4, 121.9, 113.3, 110.9, 107.3, 62.7, 61.5, 54.7, 39.8, 38.7, 30.0, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.37 (dd, *J* = 3.1, 2.0 Hz, 1H), 7.19 (d, *J* = 4.7 Hz, 1H), 4.64 (s, 1H), 4.38 (dd, *J* = 6.8, 2.3 Hz, 1H), 4.32 – 4.21 (m, 2H), 4.22 – 4.06 (m, 2H), 3.65 (s, 3H), 3.29 (dd, *J* = 15.2, 3.9 Hz, 1H), 2.80 (dd, *J* = 15.2, 6.9 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 172.0, 166.5, 136.6, 132.0, 126.9, 125.3, 121.9, 113.3, 110.9, 107.3, 62.4, 61.5, 54.3, 40.4, 38.1, 29.9, 14.0. IR (neat, cm^{-1}): υ 2989, 2916, 1725, 1610, 1579, 1468, 1368, 1190, 1096, 1022, 858, 794. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{21}BrNO_5$ $(M + H)^+$ 422.0598, found 422.0599.

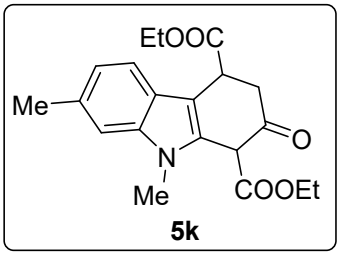
Diethyl 7-Methoxy-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5j): Yield



5j

(0.069 g, 45%); dr = 1:0.80; Keto/enol forms = 97:3; Brown gum; R_f = 0.4 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 2.8 Hz, 1H), 6.84 (dd, *J* = 4.5, 2.2 Hz, 1H), 6.76 (d, *J* = 2.2 Hz, 1H), 4.62 (s, 1H), 4.38 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.32 – 4.18 (m, 2H), 4.17 – 4.04 (m, 2H), 3.88 (s, 3H), 3.58 (s, 3H), 3.13 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.93 (dd, *J* = 14.2, 2.1 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 173.0, 167.0, 157.0, 138.9, 129.6, 120.0, 119.7, 109.7, 107.8, 93.1, 62.5, 61.4, 55.7, 54.8, 40.0, 39.0, 29.9, 14.1. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* = 2.8 Hz, 1H), 6.82 (dd, *J* = 4.5, 2.2 Hz, 1H), 6.77 (d, *J* = 2.2 Hz, 1H), 4.62 (s, 1H), 4.38 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.32 – 4.18 (m, 2H), 4.17 – 4.04 (m, 2H), 3.88 (s, 3H), 3.59 (s, 3H), 3.24 (dd, *J* = 15.0, 3.9 Hz, 1H), 2.78 (dd, *J* = 15.0, 6.8 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 172.2, 167.0, 157.0, 138.8, 129.4, 119.6, 109.7, 107.8, 93.1, 62.2, 61.4, 55.7, 54.4, 40.6, 38.4, 29.8, 14.1. IR (neat, cm^{-1}): υ 2922, 1730, 1623, 1494, 1377, 1227, 1031, 860. HRMS (ESI-Q-TOF) m/z calcd for $C_{20}H_{24}NO_6$ $(M + H)^+$ 374.1598, found 374.1596.

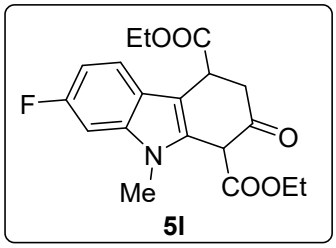
Diethyl 7-Methyl-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5k): Yield



5k

(0.074 g, 50%); dr = 1:0.72; Keto/enol forms = 96:4; Brown gum; R_f = 0.37 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 3.8 Hz, 1H), 7.10 (s, 1H), 7.01 (dd, *J* = 4.4, 0.9 Hz, 1H), 4.63 (s, 1H), 4.40 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.31 – 4.18 (m, 2H), 4.13 – 4.03 (m, 2H), 3.59 (s, 3H), 3.14 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.95 – 2.91 (m, 1H), 2.49 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 173.1, 166.9, 138.4, 132.5, 130.2, 123.1, 121.7, 118.9, 109.4, 107.6, 62.5, 61.4, 54.8, 40.0, 39.0, 29.8, 21.9, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 3.8 Hz, 1H), 7.11 (s, 1H), 7.00 (dd, *J* = 4.4, 0.9 Hz, 1H), 4.63 (s, 1H), 4.40 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.30 – 4.17 (m, 2H), 4.15 – 4.03 (m, 2H), 3.60 (s, 3H), 3.24 (dd, *J* = 15.0, 3.7 Hz, 1H), 2.78 (dd, *J* = 15.0, 6.8 Hz, 1H), 2.50 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 172.2, 166.9, 138.3, 132.5, 130.0, 123.2, 121.8, 118.9, 109.4, 107.6, 62.2, 61.4, 54.4, 40.7, 38.4, 29.8, 21.9, 14.0. IR (neat, cm^{-1}): υ 2921, 1730, 1590, 1468, 1371, 1178, 1031, 858, 754. HRMS (ESI-Q-TOF) m/z calcd for $C_{20}H_{24}NO_5$ $(M + H)^+$ 358.1649, found 358.1647.

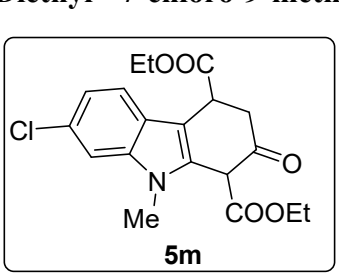
Diethyl 7-Fluoro-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5l): Yield



5l

(0.081 g, 54%); dr = 1:0.83; Keto/enol forms = 95:5; Brown gum; R_f = 0.45 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 1H), 7.00 (dd, *J* = 4.9, 2.2 Hz, 1H), 6.96 – 6.88 (m, 1H), 4.63 (s, 1H), 4.39 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.31 – 4.18 (m, 2H), 4.17 – 4.03 (m, 2H), 3.58 (s, 3H), 3.13 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.97 – 2.92 (m, 1H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2, 172.8, 166.8, 160.3 (d, *J* = 238.0 Hz), 138.1, 131.3, 121.7, 120.2 (d, *J* = 10.1 Hz), 108.8 (d, *J* = 6.0 Hz), 108.6 (d, *J* = 5.0 Hz), 108.0 (d, *J* = 6.0 Hz), 96.0 (d, *J* = 26.0 Hz), 62.7, 61.5, 54.7, 39.8, 38.9, 30.0, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 1H), 6.98 (dd, *J* = 4.9, 2.2 Hz, 1H), 6.96 – 6.88 (m, 1H), 4.63 (s, 1H), 4.39 (dd, *J* = 6.7, 2.2 Hz, 1H), 4.31 – 4.18 (m, 2H), 4.17 – 4.03 (m, 2H), 3.59 (s, 1H), 3.25 (dd, *J* = 15.1, 3.8 Hz, 1H), 2.79 (dd, *J* = 15.0, 6.8 Hz, 1H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 172.0, 166.8, 160.3 (d, *J* = 238.0 Hz), 138.3, 131.0, 121.9, 120.2 (d, *J* = 10.0 Hz), 108.8 (d, *J* = 6.0 Hz), 108.6 (d, *J* = 5.0 Hz), 108.0 (d, *J* = 6.0 Hz), 96.0 (d, *J* = 26.0 Hz), 62.4, 61.5, 54.7, 40.5, 38.3, 29.9, 14.0. IR (neat, cm^{-1}): υ 2980, 1722, 1623, 1576, 1470, 1360, 1234, 1175, 1028, 945, 828. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{21}FNO_5$ $(M + H)^+$ 362.1398, found 362.1397.

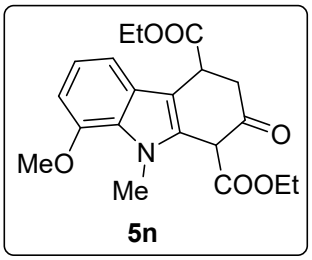
Diethyl 7-chloro-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5m): Yield



5m

(0.106 g, 68%); dr = 1:0.64; Keto/enol forms = 91:9; Brown gum; R_f = 0.8 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.36 – 7.22 (m, 1H), 7.13 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.62 (s, 1H), 4.38 (dd, *J* = 6.8, 2.2 Hz, 1H), 4.29 – 4.15 (m, 2H), 4.15 – 4.04 (m, 2H), 3.59 (s, 3H), 3.13 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.95 (dd, *J* = 14.3, 2.2 Hz, 1H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.0, 172.7, 166.6, 138.5, 131.7, 128.7, 123.7, 120.2, 118.6, 109.5, 108.0, 62.7, 61.5, 54.7, 39.8, 38.8, 30.0, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.36 – 7.22 (m, 1H), 7.13 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.62 (s, 1H), 4.38 (dd, *J* = 6.8, 2.2 Hz, 1H), 4.29 – 4.15 (m, 2H), 4.15 – 4.04 (m, 2H), 3.60 (s, 3H), 3.24 (dd, *J* = 15.1, 3.6 Hz, 1H), 2.78 (dd, *J* = 15.1, 6.8 Hz, 1H), 1.34 – 1.27 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 171.9, 166.6, 138.4, 131.5, 128.7, 123.9, 120.7, 118.6, 109.5, 108.1, 62.4, 61.5, 54.3, 40.5, 38.2, 29.9, 14.0. IR (neat, cm^{-1}): υ 2980, 1726, 1623, 1480, 1385, 1234, 1182, 1026, 863. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{21}ClNNaO_5$ $(M + Na)^+$ 400.0922, found 400.0922.

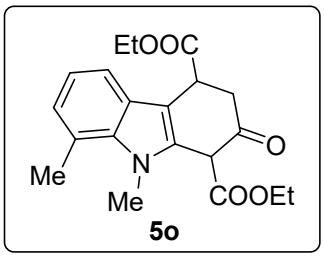
Diethyl 8-methoxy-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5n): Yield



5n

(0.088 g, 57%); dr = 1:0.56; Keto/enol forms = 95:5; Brown gum; R_f = 0.75 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7. 24 (m, 1H), 7.07 – 7.01 (m, 1H), 6.69 – 6.05 (m, 1H), 4.61 (s, 1H), 4.37 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.28 – 4.18 (m, 2H), 4.13 – 4.03 (m, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.12 (dd, *J* = 14.2, 6.7 Hz, 1H), 2.91 (dd, *J* = 14.2, 2.1 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 173.0, 166.8, 147.7, 131.4, 127.6, 127.3, 120.4, 111.9, 108.0, 103.5, 62.5, 61.4, 55.4, 55.0, 40.0, 38.9, 33.0, 14.1. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7. 24 (m, 1H), 7.07 – 7.01 (m, 1H), 6.69 – 6.05 (m, 1H), 4.60 (s, 1H), 4.37 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.28 – 4.18 (m, 2H), 4.13 – 4.03 (m, 2H), 3.92 (s, 3H), 3.90 (s, 3H), 3.20 (dd, *J* = 15.1, 3.4 Hz, 1H), 2.76 (dd, *J* = 15.0, 6.8 Hz, 1H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 172.2, 166.8, 147.7, 131.2, 127.4, 120.4, 111.9, 108.0, 103.5, 62.2, 61.4, 55.0, 54.4, 40.8, 38.3, 32.9, 14.1. IR (neat, cm^{-1}): υ 2986, 1728, 1581, 1458, 1496, 1370, 1251, 1094, 854, 777. HRMS (ESI-Q-TOF) m/z calcd for $C_{20}H_{24}NO_6$ $(M + H)^+$ 374.1598 found 374.1598.

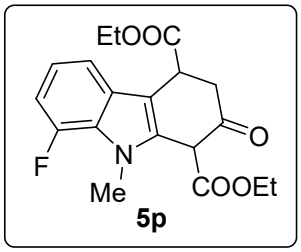
Diethyl 8,9-dimethyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5o): Yield (0.096 g,



5o

64%); dr = 1:0.60; Keto/enol forms = 94:6; Brown gum; R_f = 0.45 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.49 (m, 1H), 7.06 – 7.00 (m, 1H), 6.96 (t, *J* = 5.7 Hz, 1H), 4.63 (s, 1H), 4.39 (dd, *J* = 6.8, 2.1 Hz, 1H), 4.31 – 4.18 (m, 2H), 4.14 – 4.02 (m, 2H), 3.87 (s, 3H), 3.13 (dd, *J* = 14.2, 6.8 Hz, 1H), 2.92 (dd, *J* = 14.2, 1.8 Hz, 1H), 2.76 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 173.0, 166.9, 136.9, 131.5, 126.1, 125.6, 121.3, 120.1, 117.2, 108.0, 62.6, 61.4, 54.5, 40.8, 38.8, 33.0, 20.2, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 – 7.49 (m, 1H), 7.06 – 7.00 (m, 1H), 6.96 (t, *J* = 5.7 Hz, 1H), 4.62 (s, 1H), 4.39 (dd, *J* = 6.8, 2.1 Hz, 1H), 4.31 – 4.18 (m, 2H), 4.14 – 4.02 (m, 2H), 3.88 (s, 3H), 3.21 (dd, *J* = 15.0, 3.3 Hz, 1H), 2.77 (s, 3H), 2.80 – 2.72 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 173.0, 172.2, 166.9, 136.7, 131.3, 126.2, 125.6, 121.3, 120.2, 117.2, 108.0, 62.3, 61.4, 54.5, 40.0, 38.2, 32.9, 20.2, 14.0. IR (neat, cm^{-1}): υ 2986, 1729, 1580, 1455, 1368, 1186, 1080, 854, 744. HRMS (ESI-Q-TOF) m/z calcd for $C_{20}H_{24}NO_5$ $(M + H)^+$ 358.1649, found 358.1648.

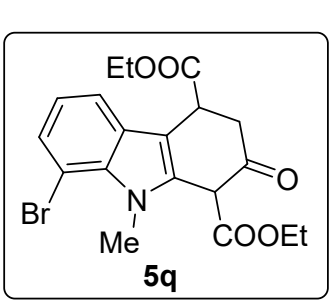
Diethyl 8-Fluoro-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5p): Yield



5p

(0.072 g, 48%); dr = 1:0.56; Keto/enol forms = 89:11; Yellow gum; R_f = 0.62 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.00 (t, J = 7.7 Hz, 1H), 4.65 (s, 1H), 4.40 (d, *J* = 6.5, 1.5 Hz, 1H), 4.33 – 4.21 (m, 2H), 4.15 – 4.08 (m, 2H), 4.01 (s, 3H), 3.15 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.96 (d, *J* = 7.1 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.0, 172.7, 166.6, 150.1 (d, *J* = 242.5 Hz), 132.3, 128.9 (d, *J* = 5.0 Hz), 125.9 (d, *J* = 8.7 Hz), 120.2 (dd, *J* = 6.2, 3.7 Hz), 114.9 (d, *J* = 3.4 Hz), 108.3 (dd, *J* = 17.5, 6.2 Hz). 62.7, 61.5, 54.7, 32.4, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H), 4.65 (s, 1H), 4.40 (d, *J* = 6.5, 1.5 Hz, 1H), 4.33 – 4.21 (m, 2H), 4.15 – 4.08 (m, 2H), 4.02 (s, 3H), 3.24 (dd, *J* = 15.5, 3.0 Hz, 1H), 2.79 (dd, *J* = 15.1, 7.0 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5, 171.9, 166.6, 150.1 (d, *J* = 242.5 Hz), 132.1, 129.1 (d, *J* = 5.0 Hz), 125.9 (d, *J* = 8.7 Hz), 120.2 (dd, *J* = 6.2, 3.7 Hz), 114.9 (d, *J* = 3.4 Hz), 108.3 (dd, *J* = 17.5, 6.2 Hz), 62.4, 61.4, 54.7, 40.5, 38.2, 32.3, 14.0. IR (neat, cm^{-1}): υ 2980, 1723, 1452, 1366, 1177, 1030, 873, 777. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{21}FNO_5$ $(M + H)^+$ 362.1398, found 362.1399.

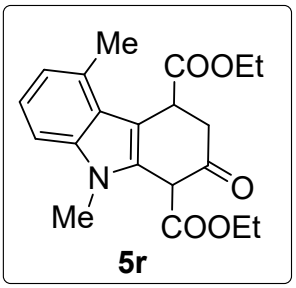
Diethyl 8-bromo-9-methyl-2-oxo-2,3,4,9-tetrhydro-1*H*-carbazole-1,4-dicarboxylate (5q): Yield



5q

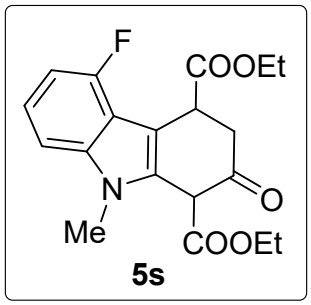
(0.067 g, 38%); dr = 1:0.61; Keto/enol forms = 90:10; Yellow gum; R_f = 0.57 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.97 – 6.91 (m, 1H), 4.64 (s, 1H), 4.40 (dd, *J* = 6.5, 2.0 Hz, 1H), 4.32 – 4.23 (m, 2H), 4.17– 4.06 (m, 2H), 3.85 (s, 3H), 3.15 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.96 (dd, *J* = 14.5, 2.0 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 172.3, 166.5, 134.7, 133.2, 128.0, 121.0, 118.5, 108.5, 103.9, 62.4, 61.3, 55.1, 39.8, 38.7, 32.7, 13.8. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 1H), 7.09 – 7.02 (m, 1H), 6.97 – 6.91 (m, 1H), 4.65 (s, 1H), 4.40 (dd, *J* = 6.5, 2.0 Hz, 1H), 4.32 – 4.23 (m, 2H), 4.17– 4.06 (m, 2H), 3.86 (s, 3H), 3.25 (dd, *J* = 15.0, 3.5 Hz, 1H), 2.80 (dd, *J* = 15.0, 6.5 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.9, 171.6, 166.3, 134.7, 133.2, 128.0, 121.0, 118.4, 108.5, 103.9, 62.2, 61.3, 54.6, 40.3, 38.1, 32.5, 13.8. IR (neat, cm^{-1}): υ 2979, 1723, 1636, 1463, 1369, 1233, 1174, 1093, 784, 724. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{21}BrNO_5$ $(M + H)^+$ 422.0598, found 422.0597.

Diethyl 5,9-dimethyl-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate (5r): Yield (0.074 g, 50%); dr = 1:0.61; Keto/enol forms = 89:11; Yellow solid; m.p. = 108-109 ˚C; R_f = 0.57 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 – 7.16 (m, 2H), 6.96 – 6.91 (m, 1H), 4.73 (s, 1H), 4.72 – 4.70 (m, 1H), 4.33 – 4.20 (m, 2H), 4.17 – 4.04 (m, 2H), 3.63 (s, 3H), 3.24 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.91 (dd, *J* = 14.2, 1.9 Hz, 1H), 2.78 (s, 3H), 1.32 (*t*, *J* = 7.1 Hz, 3H), 1.21 (*t*, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 173.6, 166.9, 138.1, 131.3, 130.6, 124.1, 122.6, 121.7, 108.5, 107.27, 62.6, 61.5, 55.1, 41.2, 40.4, 30.0, 19.9, 14.1, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 – 7.16 (m, 2H), 6.96 – 6.91 (m, 1H), 4.72 – 4.69 (m, 1H), 4.64 (dd, *J* = 6.4, 2.2 Hz, 1H), 4.33 – 4.20 (m, 2H), 4.17 – 4.04 (m, 2H), 3.63 (s, 3H), 3.13 (dd, *J* = 15.5, 1.9 Hz, 1H), 2.86 – 2.81 (m, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.1, 172.7, 166.7, 137.9, 131.1, 130.7, 124.2, 122.5, 121.7, 108.6, 107.3, 62.2, 61.5, 54.2, 42.3, 39.1, 29.8, 19.8, 14.2, 14.1. IR (neat, cm^{-1}): υ 2924, 1720, 1565, 1463, 1330, 1148, 1025, 855, 742. HRMS (ESI-Q-TOF) m/z calcd for $C_{20}H_{24}NO_5$ $(M + H)^+$ 358.1649, found 358.1648.



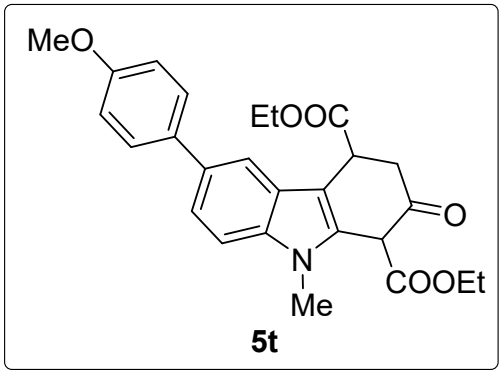
5r

Diethyl 5-fluoro-9-methyl-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate (5s): Yield (0.064 g, 43%); dr = 1:0.80; Keto/enol forms = 89:11; Yellow solid; m.p. = 110-111 ˚C; R_f = 0.74 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 – 7.13 (m, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.80 – 6.77 (m, 1H), 4.65 (s, 1H), 4.57 (dd, *J* = 6.9, 2.3 Hz, 1H), 4.30 – 4.20 (m, 2H), 4.19 – 4.07 (m, 2H), 3.62 (s, 3H), 3.24 – 3.17 (m, 1H), 2.91 (dd, *J* = 14.2, 2.3 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 173.2, 166.7, 156.6 (d, *J* = 246.0 Hz), 140.5, 131.16 (d, *J* = 38.0 Hz), 123.19 (d, *J* = 7.0 Hz), 114.3, 106.5, 105.33 (d, *J* = 19.0 Hz), 62.7, 61.4, 54.9, 40.6, 39.6, 30.3, 14.0. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 – 7.13 (m, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.83 – 6.77 (m, 1H), 4.62 (s, 1H), 4.45 (dd, *J* = 7.1, 3.6 Hz, 1H), 4.30 – 4.20 (m, 2H), 4.19 – 4.07 (m, 2H), 3.64 (s, 3H), 3.23 – 3.18 (m, 1H), 2.86 (dd, *J* = 15.2, 6.8 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 172.4, 166.5, 156.6 (d, *J* = 246.0 Hz), 140.5, 131.16 (d, *J* = 38.0 Hz), 123.19 (d, *J* = 7.0 Hz), 114.3, 106.5, 105.33 (d, *J* = 19.0 Hz), 62.4, 61.3, 54.3, 41.1, 38.8, 30.2, 14.0. IR (neat, cm^{-1}): υ 2980, 2160, 1721, 1630, 1567, 1465, 1367, 1236, 1174, 1090, 856. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{21}FNO_5$ $(M + H)^+$ 362.1398, found 362.1398.



5s

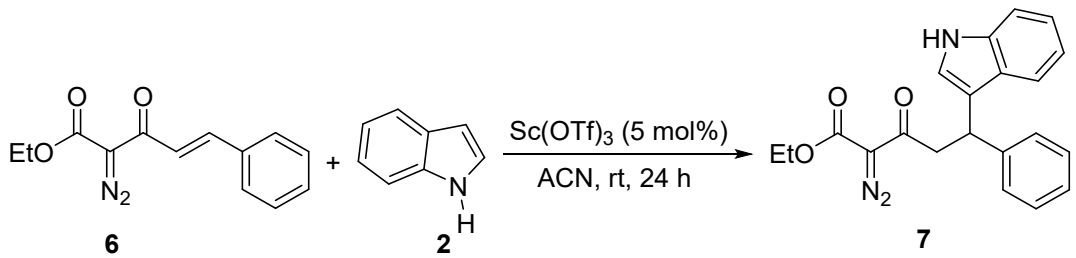
Diethyl 6-(4-methoxyphenyl)-9-mmethyl-2-oxo-2,3,4,9-tertrahydro-1*H*-carbazole-1,4-dicarboxylate (5t). Yield (0.075 g, 40%); dr = 1:0.81; Keto/enol forms = 92:8; Yellow gum; R_f = 0.57 in 2% $CHCl_3$/EtOAc; **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 1.5 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.50 (dd, *J* = 3.0, 1.8 Hz, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 4.69 (s, 1H), 4.48 (dd, *J* = 6.7, 2.1 Hz, 1H), 4.32 – 4.22 (m, 2H), 4.19 – 4.09 (m, 2H), 3.89 (s, 3H), 3.68 (s, 3H), 3.19 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.99 (dd, *J* = 14.2, 2.0 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.6, 173.0, 172.2, 166.8, 158.6, 137.1, 134.9, 133.4, 131.5, 128.3, 125.8, 122.2, 117.1, 114.2, 109.6, 108.0, 62.6, 61.5, 55.4, 54.4, 40.1, 38.9, 30.0, 14.1. **Minor isomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 1.5 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.52 (dd, *J* = 3.0, 1.8 Hz, 2H), 7.37 (d, *J* = 5.3 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 2H), 4.68 (s, 1H), 4.37 (dd, *J* = 6.7, 3.6 Hz, 1H), 4.32 – 4.22 (m, 2H), 4.19 – 4.09 (m, 2H), 3.89 (s, 3H), 3.68 (s, 3H), 3.29 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.83 (dd, *J* = 15.0, 6.8 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.0, 173.0, 172.2, 166.8, 158.6, 137.2, 134.9, 133.3, 131.4, 128.3, 125.6, 122.2, 117.1, 114.2, 109.6, 108.0, 62.3, 61.5, 55.4, 54.8, 40.8, 38.3, 29.9, 14.1. IR (neat, cm^{-1}): υ 2923, 1730, 1608, 1577, 1478, 1370, 1242, 1180, 1097, 801, 734. HRMS (ESI-Q-TOF) m/z calcd for $C_{26}H_{28}NO_6$ $(M + H)^+$ 450.1911, found 450.1911.



5t

6. Characterization of Products 7-15

Ethyl 2-diazo-5-(1*H*-indol-3-yl)-3-oxo-5-phenylpentanoate (7)[3]

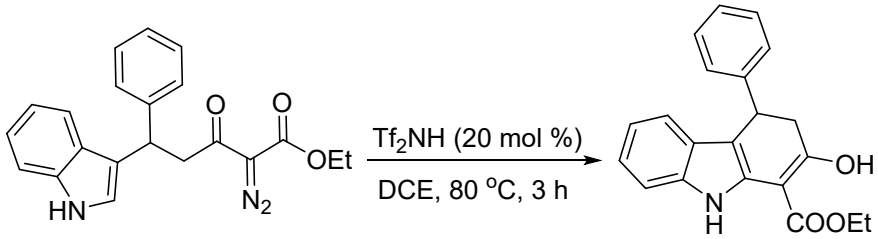


6 **2** **7**

A solution of diazoacetoacetate enone **6** (0.150 g, 0.614 mmol), indole **2** (0.108 g, 0.922 mmol), and $Sc(OTf)_3$ (0.015 g, 0.030 mmol) in acetonitrile (2 mL) was stirred at room temperature for 24 h. Then solvent was evaporated under reduced pressure and the obtained crude was purified by column

chromatography to get 0.118 g (53%) of Ethyl 2-diazo-5-(1*H*-indol-3-yl)-3-oxo-5-phenylpentanoate (**7**). Light yellow solid; R_f = 0.71 in 20% EtOAc/Hexanes; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.12 (m, 3H), 7.13 (s, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 4.99 (t, *J* = 7.5 Hz, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 3.71 (dd, *J* = 7.5, 3.4 Hz, 2H), 1.34 (t, *J* = 7.0 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 161.3, 144.0, 136.5, 128.3, 127.9, 126.7, 126.2, 122.1, 121.4, 119.5, 119.4, 119.0, 111.0, 77.2, 61.4, 46.0, 38.2, 14.3. IR (neat, cm^{-1}): υ 3401, 2950, 2136, 1711, 1646, 1456, 1372, 1206, 1042, 741. HRMS (ESI-Q-TOF) m/z calcd for $C_{21}H_{19}N_3NaO_3$ $(M+Na)^+$ 384.1319, found 384.1318.

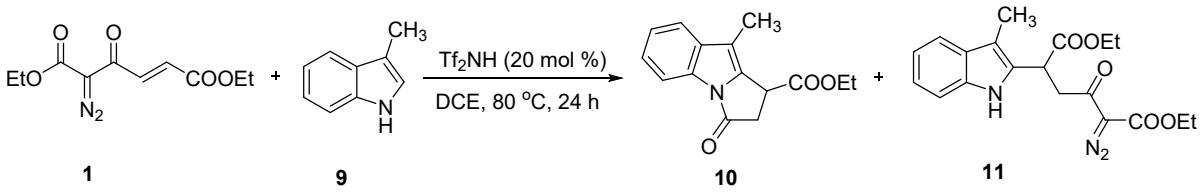
Ethyl 2-Hydroxy-4-phenyl-4,9-dihydro-3*H*-carbazole-1-carboxylate (8):



7 **8**

To a solution of ehyl 2-diazo-5-(1*H*-indol-3-yl)-3-oxo-5-phenylpentanoate (**7**) (0.050 g, 0.14 mmol) in dry DCE (1.5 mL), Tf_2NH (0.008 g, 0.03 mmol) was added under nitrogen atmosphere. Then reaction mixture was heated at 80 ˚C. The progress of the reaction was monitored by TLC. After 3h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution. Then it was extracted using ethyl acetate (3 x 10 mL). The combined organic layers were washed with saturated aqueous brine solution and dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure. The crude product was purified by column chromatography to get 0.015 g (33%) of the pure ethyl 2-Hydroxy-4-phenyl-4,9-dihydro-3*H*-carbazole-1-carboxylate (**8**). Yellow gum; R_f = 0.45 in 20% EtOAc/Hexanes; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.91 (s, 1H), 8.87 (s, 1H), 7.35 (dd, *J* = 10.2, 7.9 Hz, 2H), 7.32 – 7.29 (m, 3H), 7.27 – 7.23 (m, 1H), 7.07 (ddd, *J* = 8.1, 6.7, 1.6 Hz, 1H), 6.95 -6.91 (m, 2H), 4.54 (qd, *J* = 7.1, 1.1 Hz, 2H), 4.47 (t, *J* = 7.9 Hz, 1H), 3.22 (dd, *J* = 17.4, 8.3 Hz, 1H), 2.98 (dd, *J* = 17.4, 7.5 Hz, 1H), 1.55 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.7, 169.5, 144.0, 135.8, 130.0, 128.6, 127.6, 126.7, 126.2, 120.5, 119.6, 118.2, 110.6, 105.7, 95.2, 61.5, 39.5, 37.0, 14.5. IR (neat, cm^{-1}): υ 3484, 2937, 1646, 1591, 1308, 1248, 1219, 1065, 739. HRMS (ESI-Q-TOF) m/z calcd for $C_{21}H_{20}NO_3$ $(M + H)^+$ 338.1438, found 338.1435.

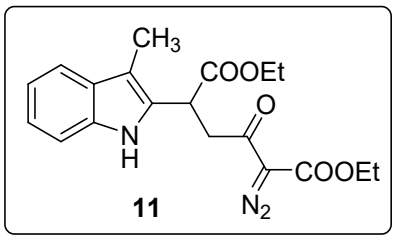
Synthesis of ethyl 9-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-a]indole-1-carboxylate (10):



1 **9** **10** **11**

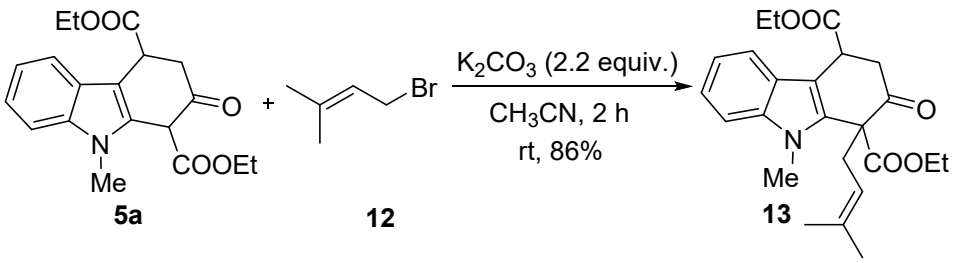
A solution of diethyl of (*E*)- 5-diazo-4-oxohex-2-enedioate **1** (0.050 g, 0.21 mmol) and 3-methyl indole **9** (0.027 g, 0.21 mmol) in dry DCE (1.5 mL), 20 mol% Tf_2NH (0.012 g, 0.043 mmol) was added under nitrogen atmosphere and stirred for 24h. The reaction mixture was quenched with a saturated $NaHCO_3$ solution. Then it was extracted using ethyl acetate. The combined organic layers were washed with saturated brine solution and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The obtained crude residue was purified by column chromatography by eluting with 10% EtOAc/hexane to afford the compounds **10** and **11**. Yield (0.022 g, 41%); Yellow solid; m.p. = 109-110 ˚C; R_f = 0.51 in 20% EtOAc/Hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 – 8.01 (m, 1H), 7.54 – 7.45 (m, 1H), 7.37 – 7.30 (m, 2H), 4.33 – 4.23 (m, 3H), 3.54 (dd, *J* = 18.2, 3.6 Hz, 1H), 3.28 (dd, *J* = 18.2, 9.2 Hz, 1H), 2.30 (t, *J* = 0.5 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 169.1, 135.9, 134.9, 130.2, 124.1, 124.0, 119.0, 113.7, 111.5, 62.0, 38.4, 37.8, 14.1, 8.4. IR (neat, cm^{-1}): υ 2979, 1736, 1454, 1376, 1310, 1215, 1102, 750. HRMS (ESI-Q-TOF) m/z calcd for $C_{15}H_{16}NO_3$ $(M + H)^+$ 258.1125, found 258.1133.

Diethyl2-diazo-5-(3-methyl-1*H*-indol-2-yl)-3-oxohexanedioate (11): Yield (0.010 g, 13%); Yellow solid; m.p. = 82-83 ˚C; R_f = 0.57 in 20% EtOAc/Hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.49 (dd, *J* = 9.2, 4.9 Hz, 1H), 4.32 – 4.21 (m, 3H), 4.15 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.71 (dd, *J* = 18.3, 9.2 Hz, 1H), 3.44 (dd, *J* = 18.3, 4.9 Hz, 1H), 2.33 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 190.3, 172.8, 161.1, 135.6, 129.6, 128.8, 121.9, 119.1, 118.5, 110.7, 108.9, 76.2, 61.6, 61.5, 42.8, 38.2, 14.3, 14.0, 8.4. IR (neat, cm^{-1}): υ 3351, 2970, 2136, 1712, 1648, 1467, 1306, 1207, 1028, 740. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{22}N_3O_5$ $(M + H)^+$ 372.1154, found 372.1154.



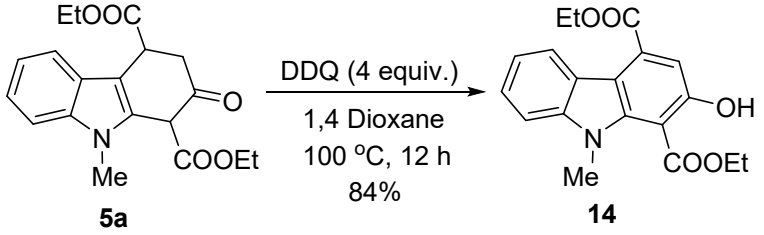
11

Synthesis of diethyl 9-methyl-1-(3-methylbut-2-en-1-yl)-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate (13).[1]



To a solution of diethyl 9-methyl-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate **5a** (0.030 g, 0.087 mmol) and prenyl bromide **12** (11 µL, 0.095 mmol) in dry acetonitrile (1 mL) taken in a 10 mL RB flask, K_2CO_3 (0.026 g, 0.19 mmol) was added. The reaction mixture was stirred for 2h at room temperature. Then, the reaction mixture was filtered. The crude residue was purified by column chromatography by eluting with 10% EtOAc/hexane to afford the compound **13**. Yield (0.030 g, 86%); Yellow gum; R_f = 0.37 in 20% EtOAc/Hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 4.70 – 4.66 (m, 1H), 4.62 – 4.52 (m, 1H), 4.33 (dd, *J* = 6.7, 2.9 Hz, 1H), 4.30 – 4.21 (m, 1H), 4.14 – 4.10 (m, 3H), 3.65 (s, 3H), 3.23 (dd, *J* = 15.0, 9.8 Hz, 1H), 3.08 (dd, *J* = 14.8, 2.9 Hz, 1H), 2.94 (d, *J* = 10.4 Hz, 1H), 2.72 (dd, *J* = 14.7, 6.8 Hz, 1H), 1.58 (s, 3H), 1.53 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.6, 172.2, 170.1, 138.4, 136.5, 133.6, 125.3, 122.3, 119.9, 119.4, 117.5, 109.2, 108.2, 62.1, 61.1, 60.8, 40.9, 38.1, 34.9, 30.5, 25.8, 17.8, 14.0, 13.8. IR (neat, cm^{-1}): υ 2922, 1735, 1468, 1367, 1226, 1135, 1025, 743. HRMS (ESI-Q-TOF) m/z calcd for $C_{24}H_{30}NO_5$ $(M + H)^+$ 412.2118, found 412.2118.

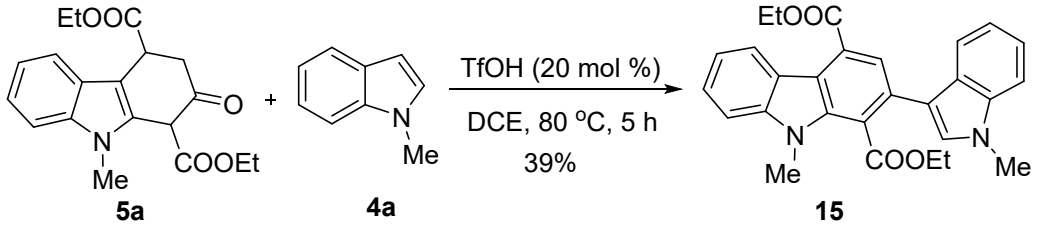
Synthesis of diethyl 2-hydroxy-9-methyl-9*H*-carbazole-1,4-dicarboxylate (14).[2]



A solution of diethyl 9-methyl-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate **5a** (0.025 g, 0.073 mmol) and DDQ (0.066 g, 0.29 mmol) in 1,4 dioxane (1 mL) taken in a sealed tube was stirred at 100 °C for 12 h. After completion of the reaction as monitored by TLC, it was brought to room

temperature. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography using a 20% ethyl acetate in hexanes to afford compound **14**. Yield (0.021 g, 84%); Yellow solid; m.p. = 99-100 ˚C; R_f = 0.28 in 20% EtOAc/Hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.20 (br s, 1H), 8.51 (d, *J* = 8.0 Hz, 1H), 7.45 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.32 (s, 1H), 7.26 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 4.55 (q, *J* = 7.0 Hz, 2H), 4.52 (q, *J* = 7.0 Hz, 2H), 3.75 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.46 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 167.2, 159.1, 143.3, 142.1, 131.4, 125.8, 123.5, 121.6, 120.6, 116.0, 111.0, 109.3, 101.2, 62.1, 61.6, 35.8, 14.3. IR (neat, cm^{-1}): υ 2979, 1720, 1662, 1568, 1373, 1273, 1196, 1094, 1017, 747. HRMS (ESI-Q-TOF) m/z calcd for $C_{19}H_{20}NO_5$ $(M + H)^+$ 342.1336, found 342.1336.

Synthesis of diethyl 9-methyl-2-(1-methyl-1*H*-indol-3-yl)-9H-carbazole-1,4-dicarboxylate (15).



A solution of 9-methyl-2-oxo-2,3,4,9-tetrahydro-1*H*-carbazole-1,4-dicarboxylate **5a** (0.025 g, 0.073 mmol) and N-methyl indole **4a** (0.010 g, 0.076 mmol) in dry DCE (1 mL) taken in a sealed tube, TfOH (1.3 μL, 0.015 mmol) was added under nitrogen atmosphere. The reaction mixture was heated at 80 ˚C for 5h. The reaction mixture was quenched with a saturated aqueous $NaHCO_3$ solution. Then it was extracted using ethyl acetate. The combined organic layers were washed with saturated aqueous brine solution and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure. The crude residue was purified by column chromatography by eluting with 10% EtOAc/hexanes to afford the compound **15**. Yield (0.013 g, 39%); Yellow solid; m.p. = 131-132 ˚C; R_f = 0.8 in 10% EtOAc/Hexanes; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.83 (t, *J* = 9.1 Hz, 1H), 7.99 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.22 (s, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 4.52 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.86 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.5, 167.7, 142.5, 138.0, 136.7, 129.9, 128.1, 127.8, 126.8, 126.3, 125.1, 124.3, 122.1, 121.1, 120.9, 120.2, 120.0, 119.8, 119.7, 113.9, 109.2, 108.4, 61.5, 61.2, 32.9, 30.7, 14.3, 13.6. IR (neat, cm^{-1}): υ 2923, 1716, 1590, 1466, 1392, 1230, 1080,

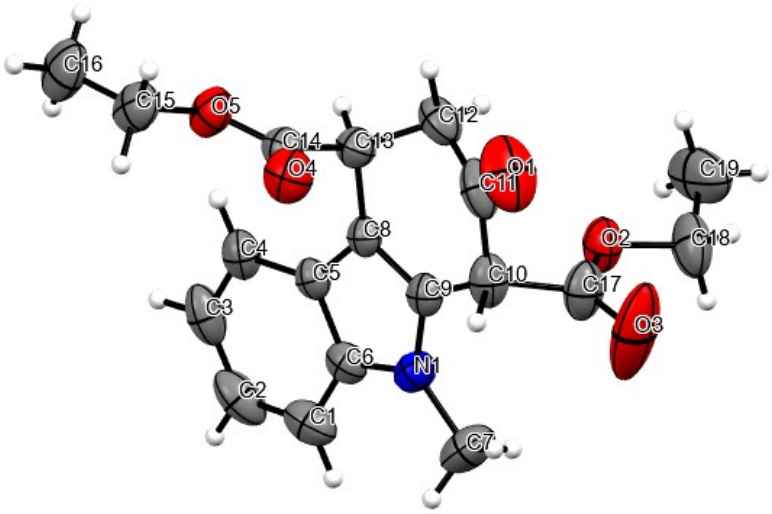
1055, 1018, 967, 858, 793. HRMS (ESI-Q-TOF) m/z calcd for $C_{28}H_{27}N_2O_4$ $(M + H)^+$ 455.1965, found 455.1965.

7. Crystal structure and Data of 5a, 10 and 15

The Rigaku Oxford Diffraction detector system [λ(Mo-Kα) = 0.71073 Å] at 288K, 296K, graphite monochromator with a ω scan width of 0.3o. The data were reduced using OLEX 2.1.27 and the structures were solved using SHELXT-97 and refined using the program SHELXL-2018/3. All non-hydrogen atoms were refined anisotropically.

Experimental: Single crystals of **5a**, **10** and **15** were obtained by slow evaporation method used for the crystal growth from the mixture of ethyl acetate/hexane at room temperature.

ORTEP-Drawing of compound 5a:

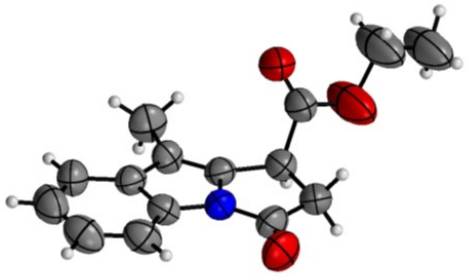


X-Ray Crystal Data for Compound 5a:

CCDC Number	2275329
Compound identification code	RB001A_0m_a
Empirical formula	C19 H21 N O5

Formula weight	343.37
Temperature	288 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a=8.4646(7) alpha= 90 b=21.096(2) beta=105.960(4) c=10.1483(10) gamma=90
Volume	1742.3(3)Å3
Z	4
Density (calculated)	1.309 g/cm3
Absorption coefficient	0.095 mm-1
F(000)	728.0
Reflections collected	4033
Independent reflections	2823
Completeness to theta = 27.539°	0.995
Refinement method	Full-matrix least-squares on F2
Max. and min. transmission	0.991 and 0.983
Goodness-of-fit on F2	1.058
R(reflections)	0.0676(2823)
wR2(reflections)	0.1976(4013)
Diffractometer	Xcalibur Gemini Eos CCD

ORTEP-Drawing of compound 10:

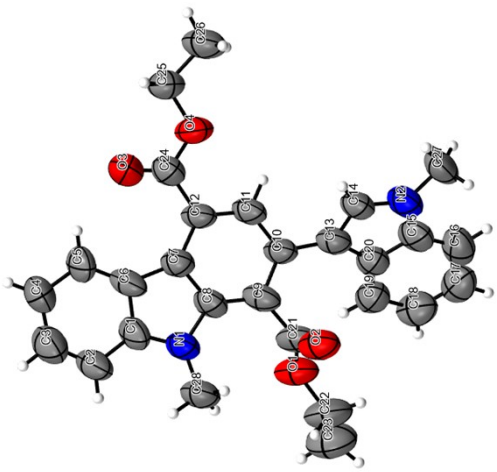


X-Ray Crystal Data for Compound 10:

CCDC Number	2275179
Compound identification code	rb47
Empirical formula	C15 H14 N O3
Formula weight	256.27
Temperature	296 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a=8.6191(4) alpha=81.898(4) b=8.8839(4) beta=73.226(3) c=9.3999(3) gamma=73.495(4)
Volume	659.38(5)Å3

Z	2
Density (calculated)	1.291 g/cm3
Absorption coefficient	0.090 mm-1
F(000)	470.0
Reflections collected	2904
Independent reflections	1563
Completeness to theta = 27.539°	0.970
Refinement method	Full-matrix least-squares on F2
Max. and min. transmission	0.987 and 0.983
Goodness-of-fit on F2	1.047
R(reflections)	0.0664(1563)
wR2(reflections)	0.2301(2817)
Diffractometer	Xcalibur Gemini Eos CCD

X-Ray Crystal Data for Compound 15:



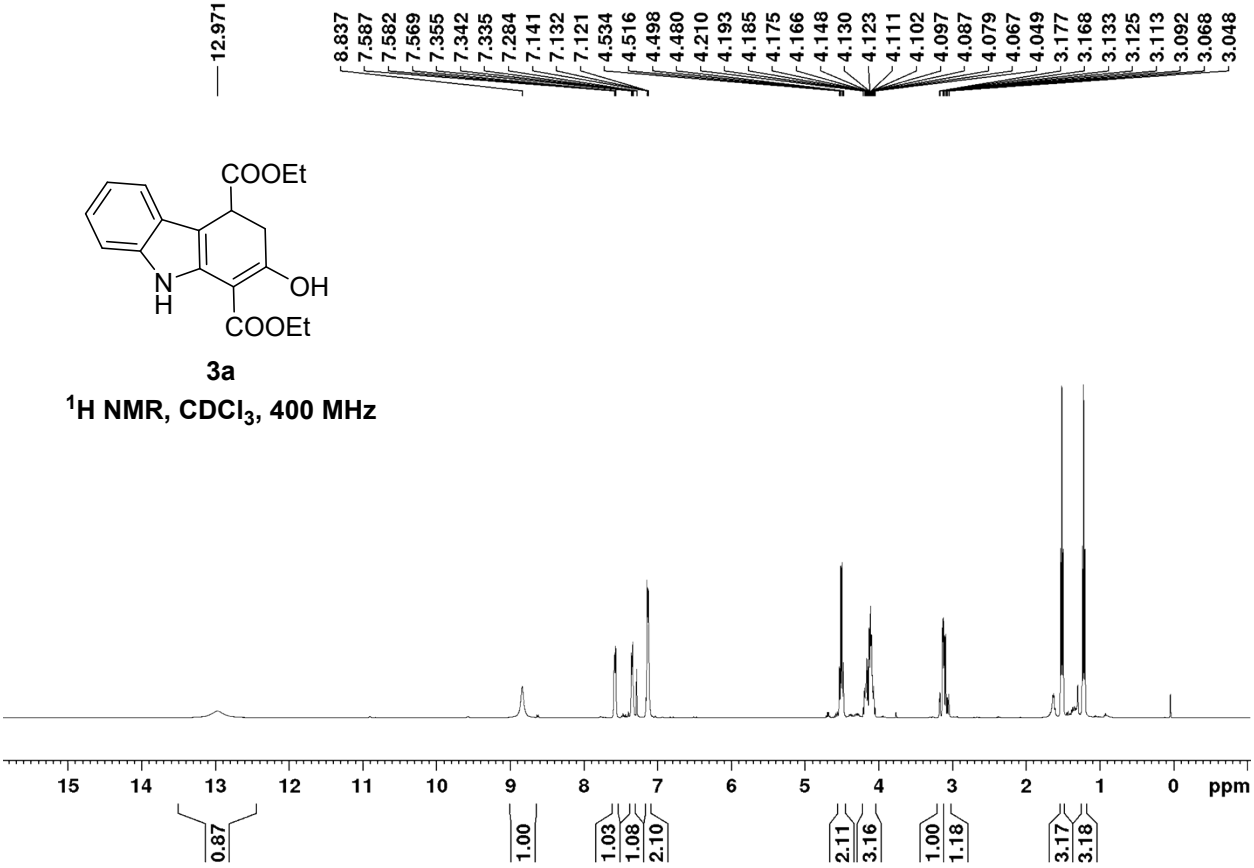
X-Ray Crystal Data for Compound 15:

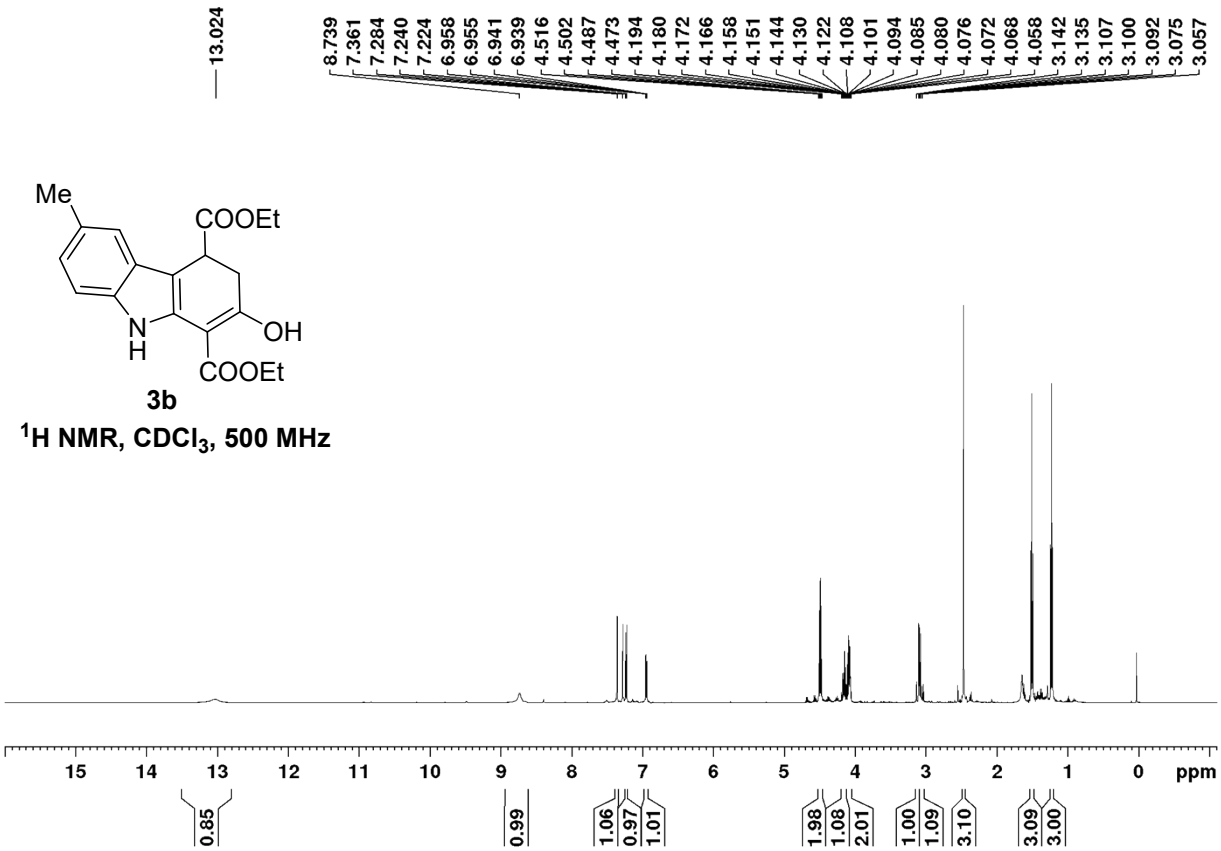
CCDC Number	2277539
Compound identification code	rb 54
Empirical formula	C29 H26 N O4
Formula weight	406.38
Temperature	296 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a=7.8862(5) alpha=109.715(9) b=12.8660(12) beta=97.202(7) c=12.9041(13) gamma=106.377(7)
Volume	1146.8(2)Å3
Z	2
Density (calculated)	1.311 g/cm3
Absorption coefficient	0.087 mm-1
F(000)	478.0
Reflections collected	3917
Independent reflections	1155
Completeness to theta = 27.539°	0.995
Refinement method	Full-matrix least-squares on F2
Max. and min. transmission	0.991 and 0.987
Goodness-of-fit on F2	1.208
R(reflections)	0.1775(1155)
wR2(reflections)	0.5960(3915)
Diffractometer	Xcalibur Gemini Eos CCD

8. References

1. S, Sakthivel, R. Balamurugan, *J. Org. Chem.* 2018, **83**, 12171.
2. E. Alvarez-Manzaneda, R. Chahboun, E. Cabrera, E. Alvarez, A. Haidour, J. M. Ramos, R. Alvarez-Manzaneda, Y. Charrah, Es-Samti, *Org. Biomol. Chem.* 2009, **7**, 5146.
3. C. S. Shanahan, P. Truong, S. M. Mason, J. S Leszczynski, M. P. Doyle, *Org. Lett.* 2013, **15**, 36

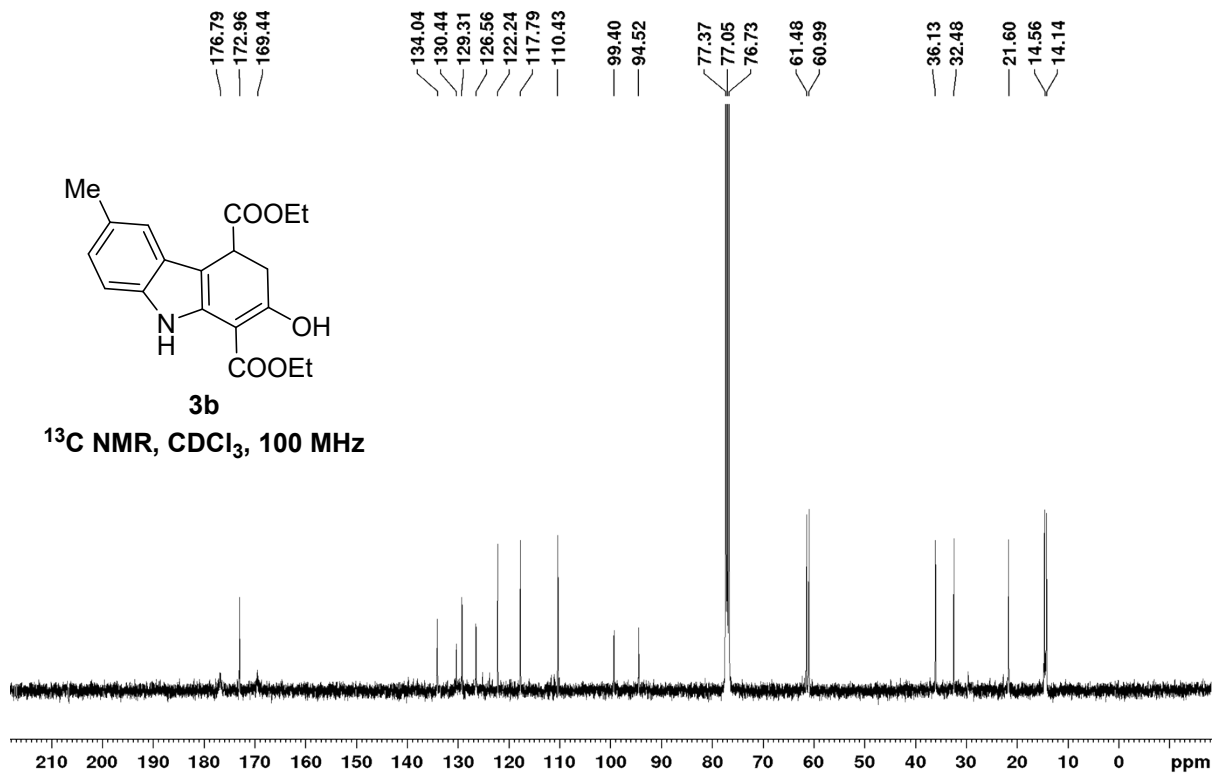
9. Copies of ^{1}H NMR and ^{13}C NMR Spectra of 3a- 3p





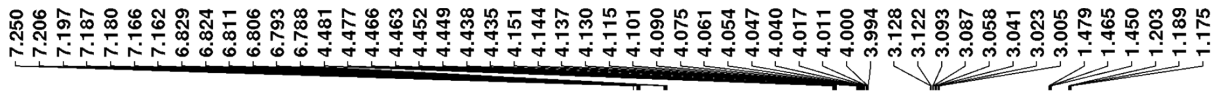
3b

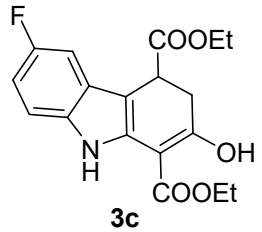
^{1}H NMR, $CDCl_3$, 500 MHz



3b

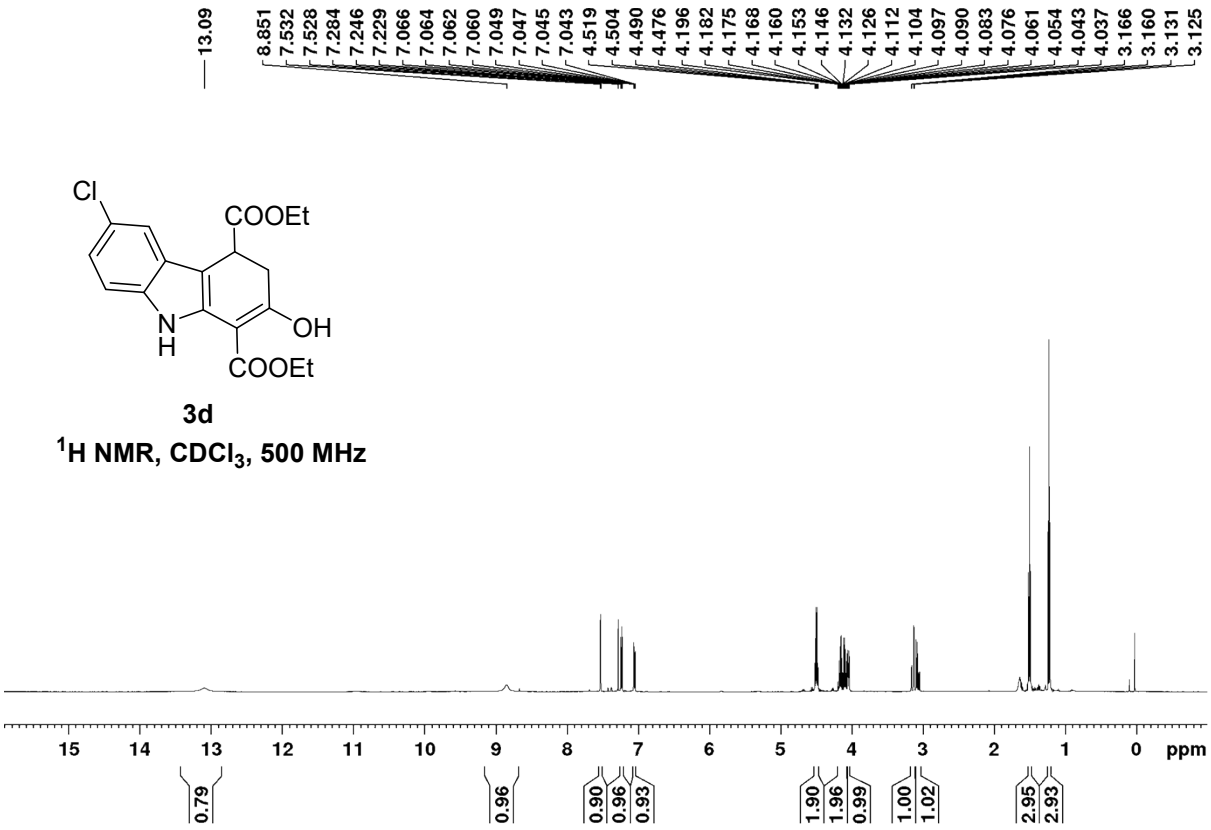
^{13}C NMR, $CDCl_3$, 100 MHz





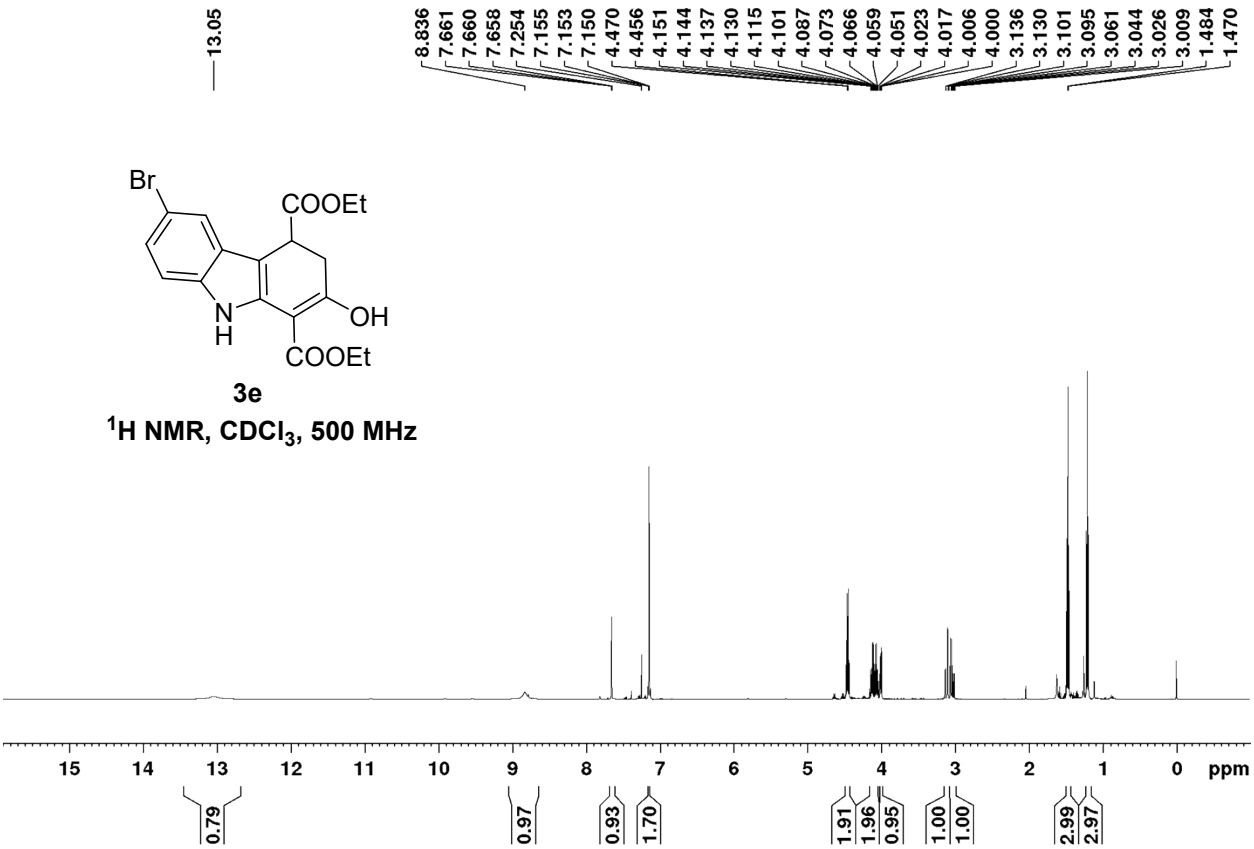
3c

^{1}H NMR, $CDCl_3$, 500 MHz



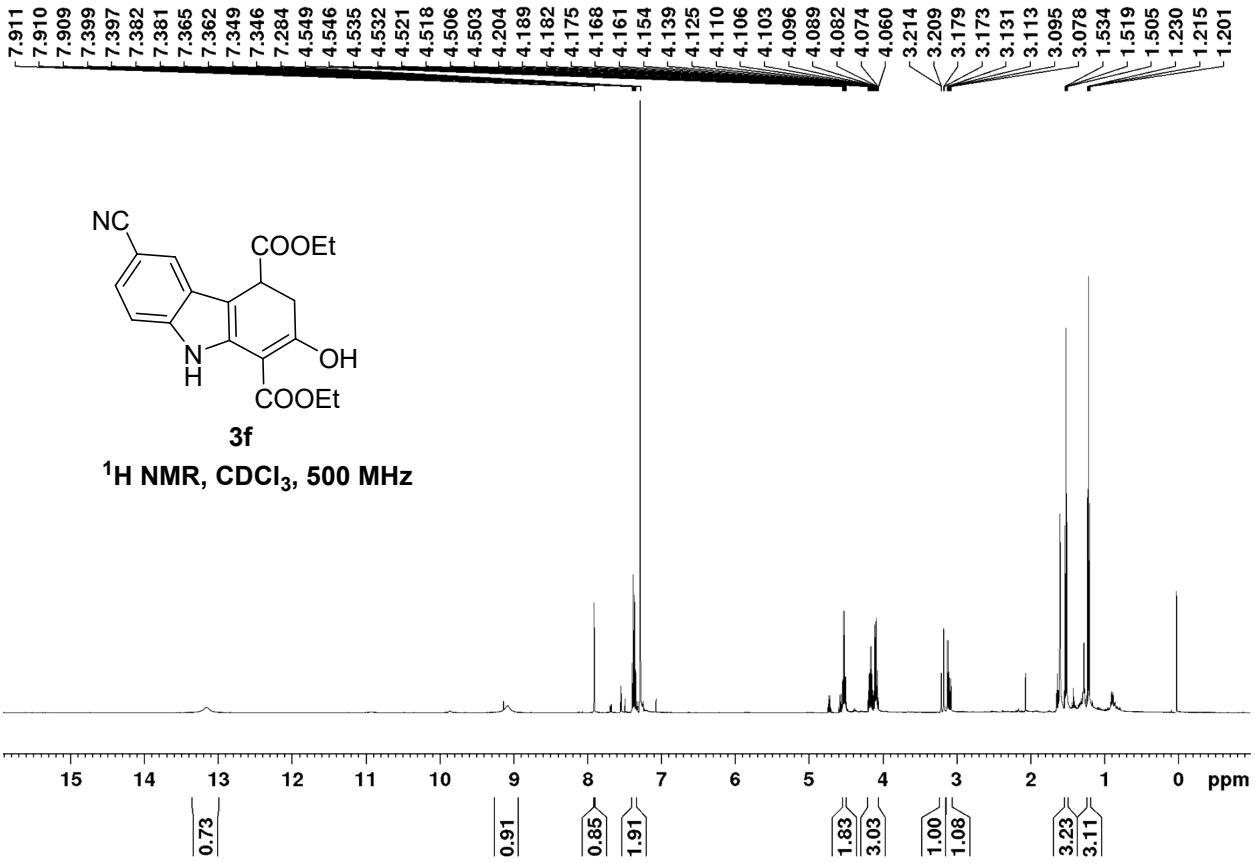
3d

^{1}H NMR, $CDCl_3$, 500 MHz



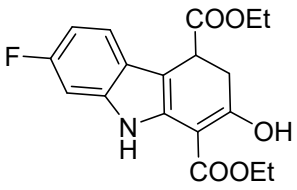
3e

^{1}H NMR, $CDCl_3$, 500 MHz



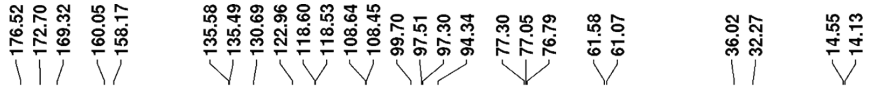
3f

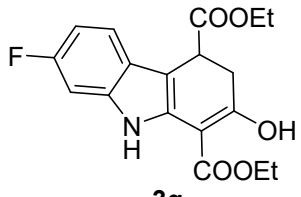
^{1}H NMR, $CDCl_3$, 500 MHz



3g

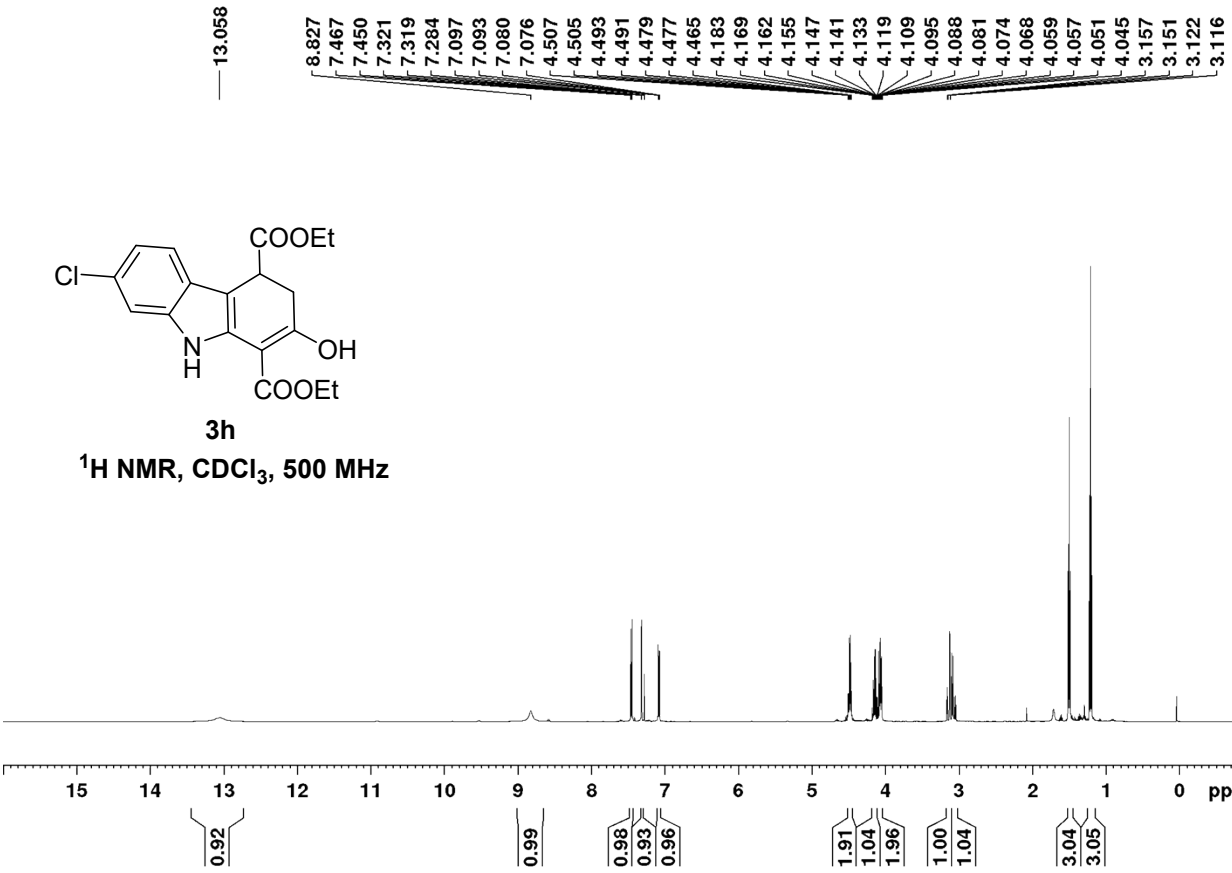
^{1}H NMR, $CDCl_3$, 500 MHz





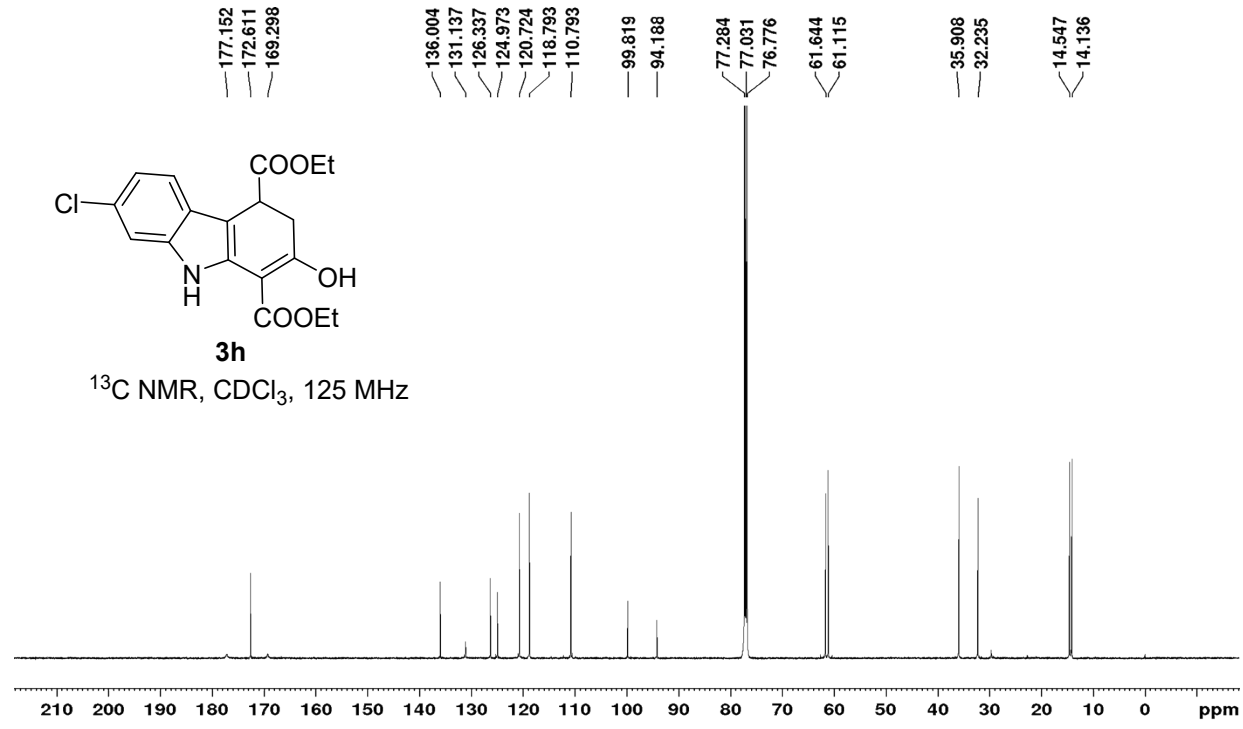
3g

^{13}C NMR, $CDCl_3$, 125 MHz



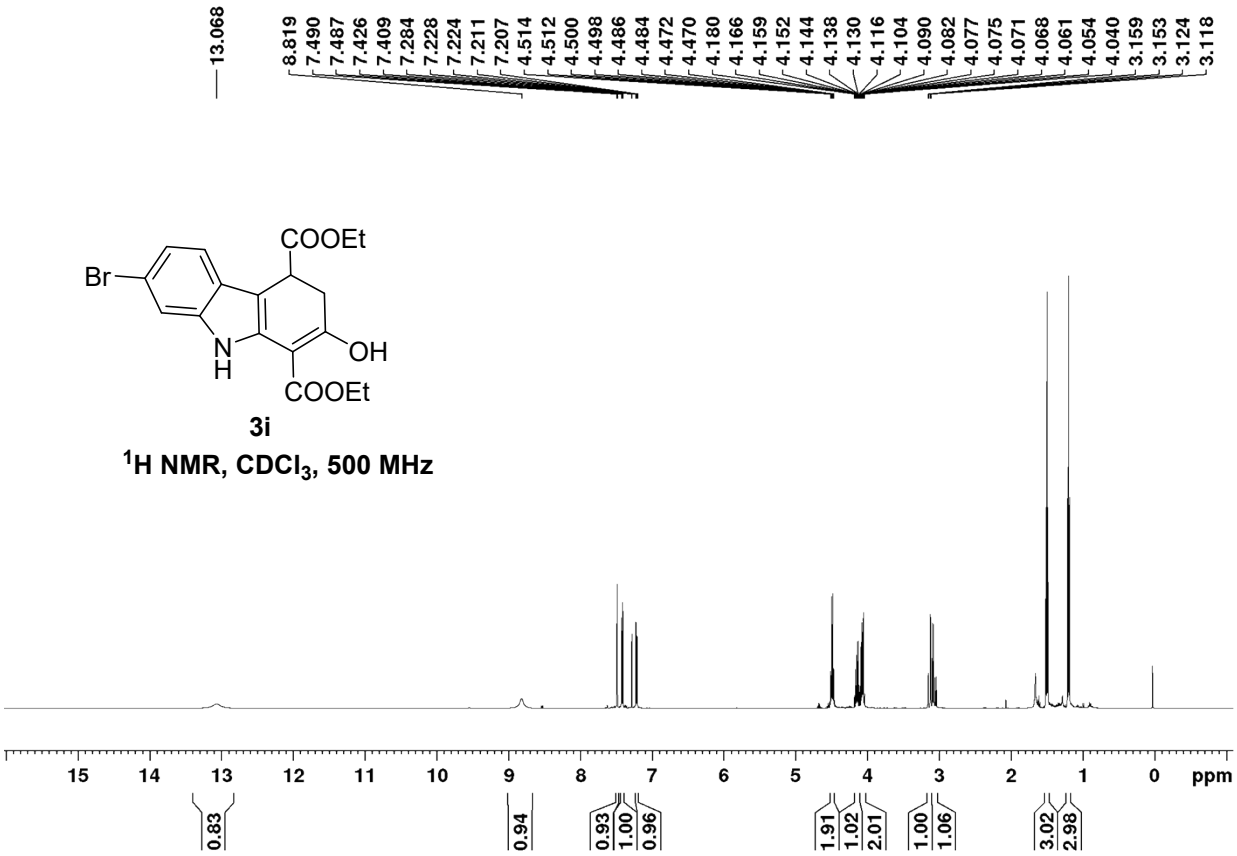
3h

^{1}H NMR, $CDCl_3$, 500 MHz



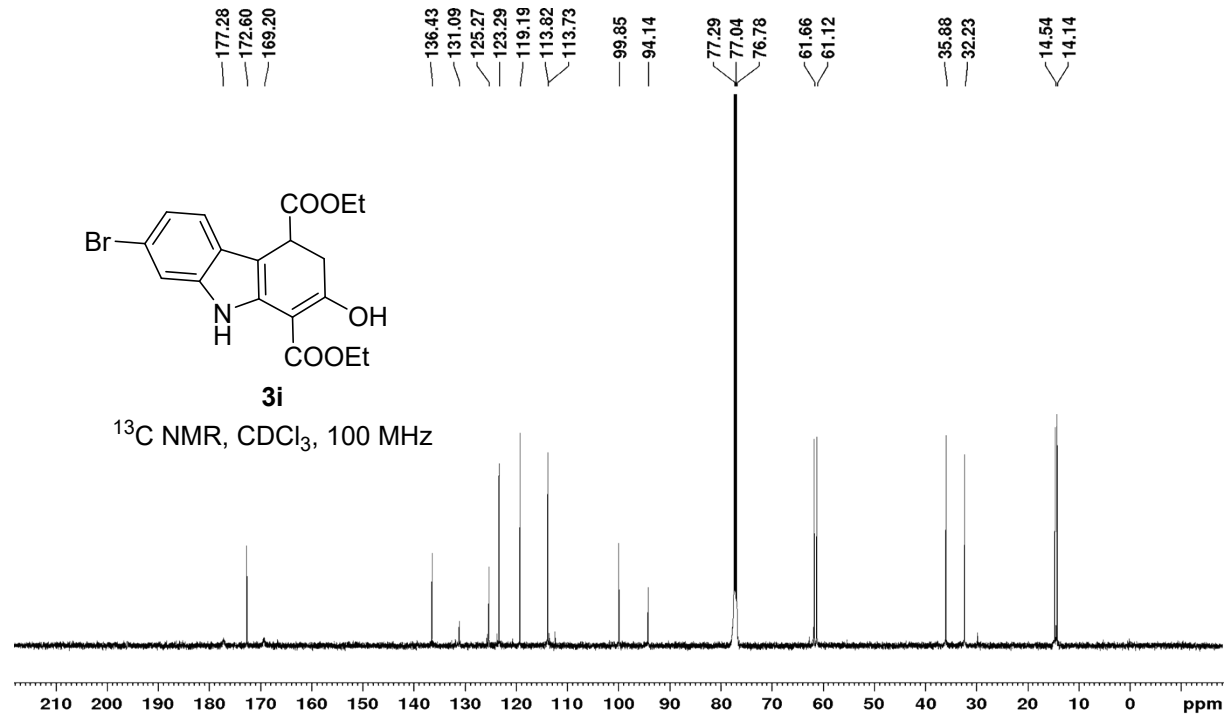
3h

^{13}C NMR, $CDCl_3$, 125 MHz



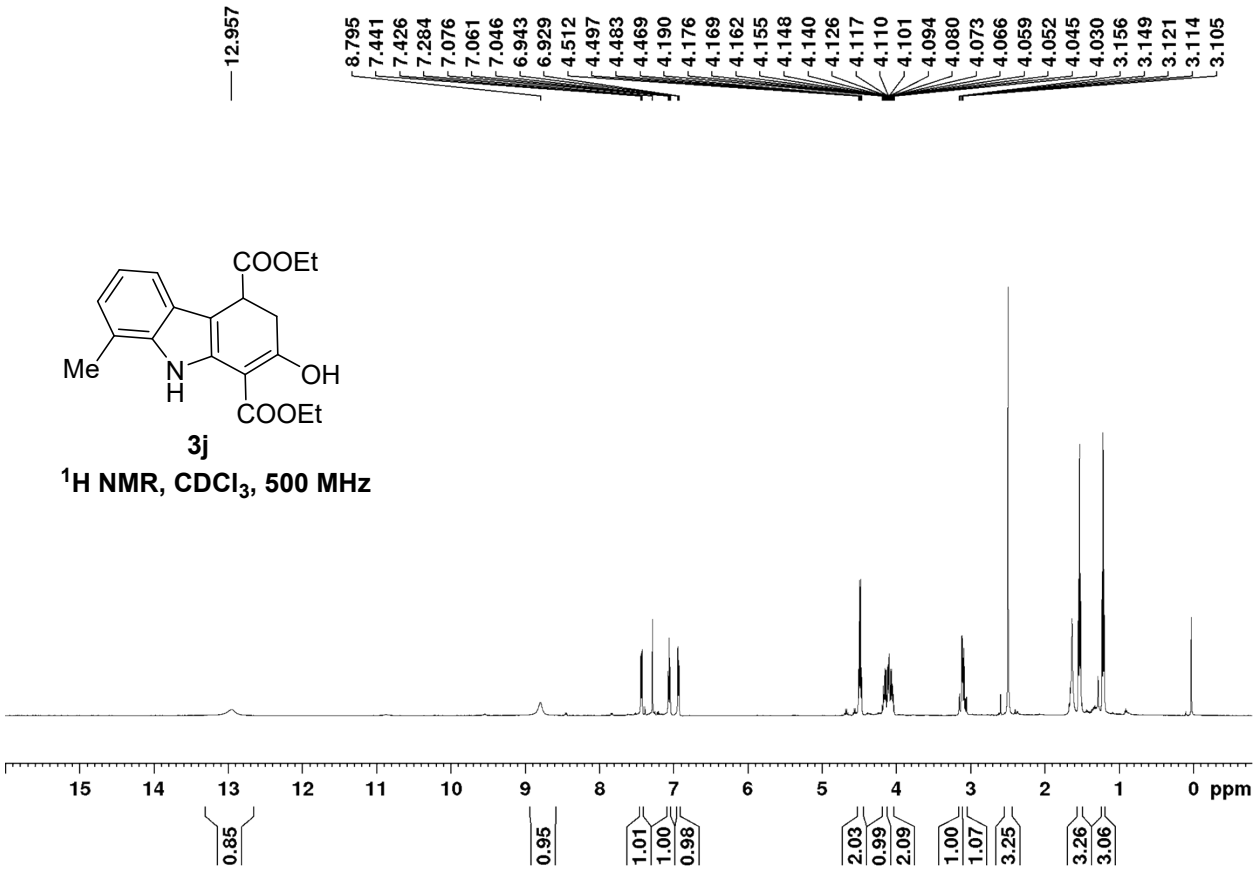
3i

^{1}H NMR, $CDCl_3$, 500 MHz



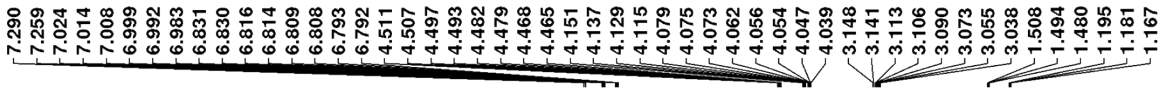
3i

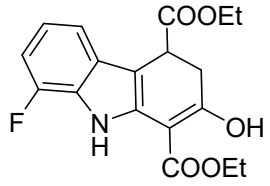
^{13}C NMR, $CDCl_3$, 100 MHz



3j

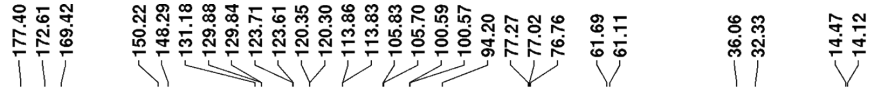
^{1}H NMR, $CDCl_3$, 500 MHz

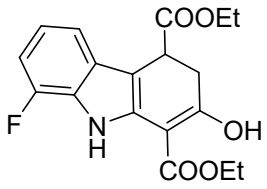




3k

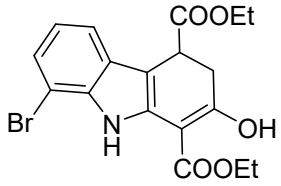
^{1}H NMR, $CDCl_3$, 500 MHz





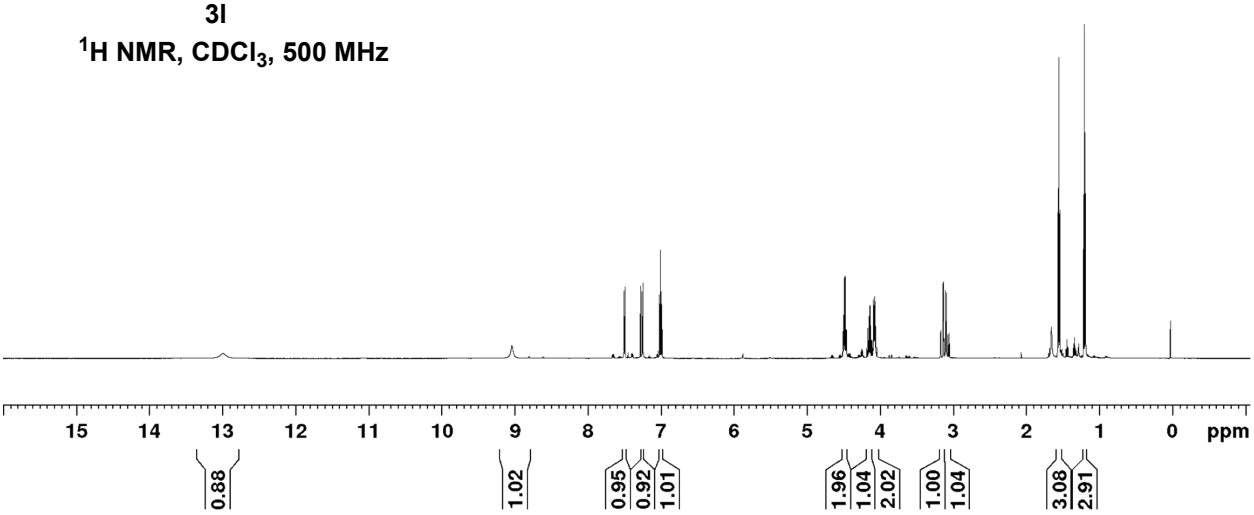
3k

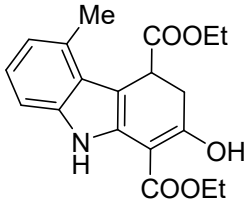
^{13}C NMR, $CDCl_3$, 125 MHz



3l

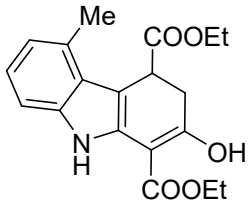
^{1}H NMR, $CDCl_3$, 500 MHz





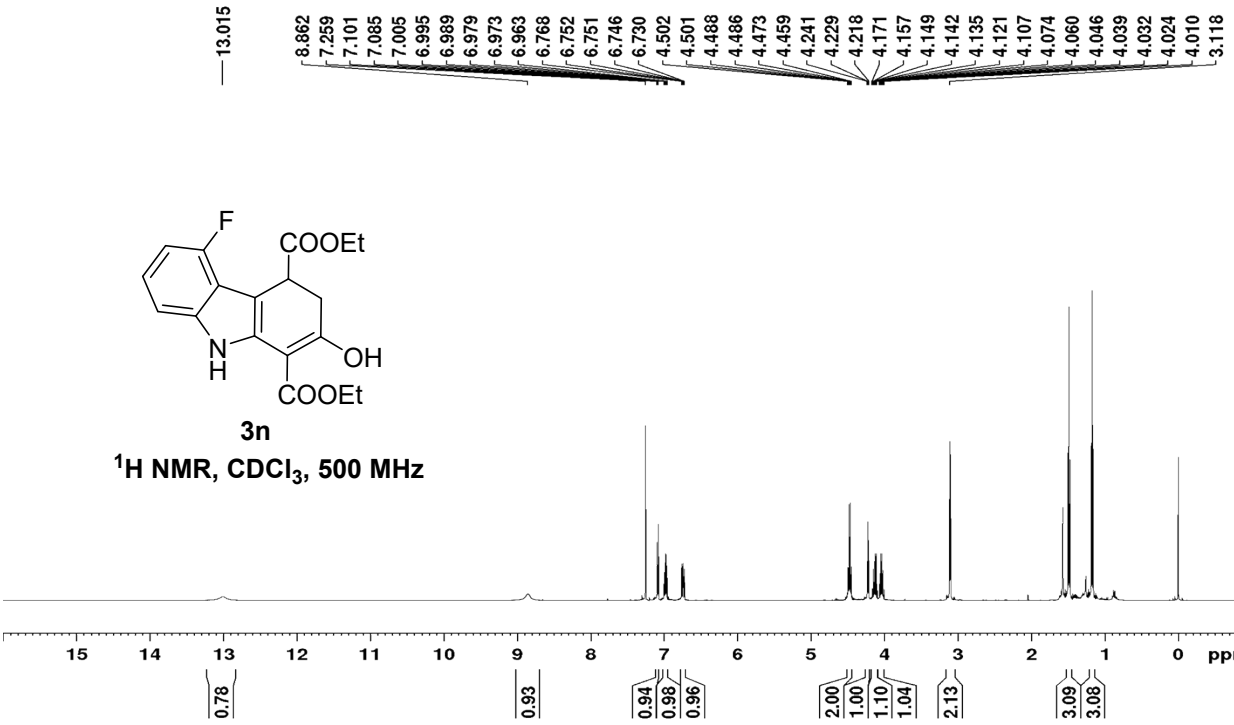
3m

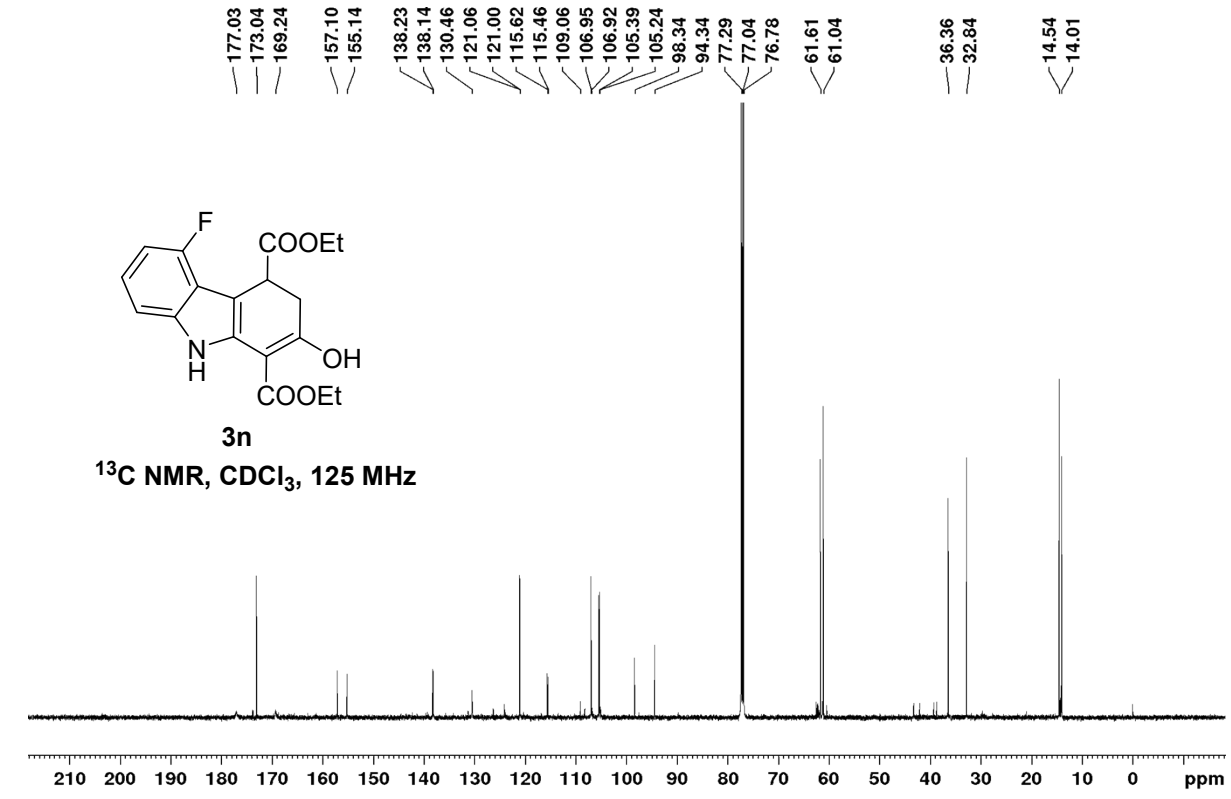
^{1}H NMR, $CDCl_3$, 500 MHz

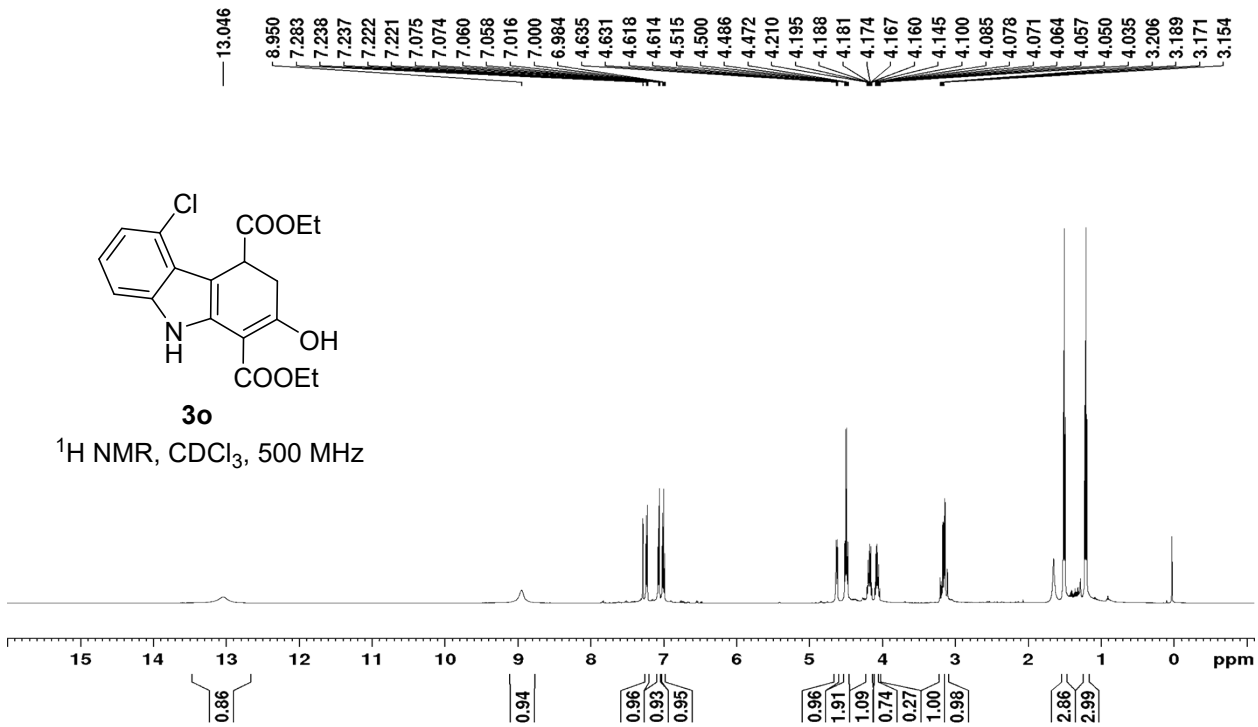


3m

^{13}C NMR, $CDCl_3$, 125 MHz

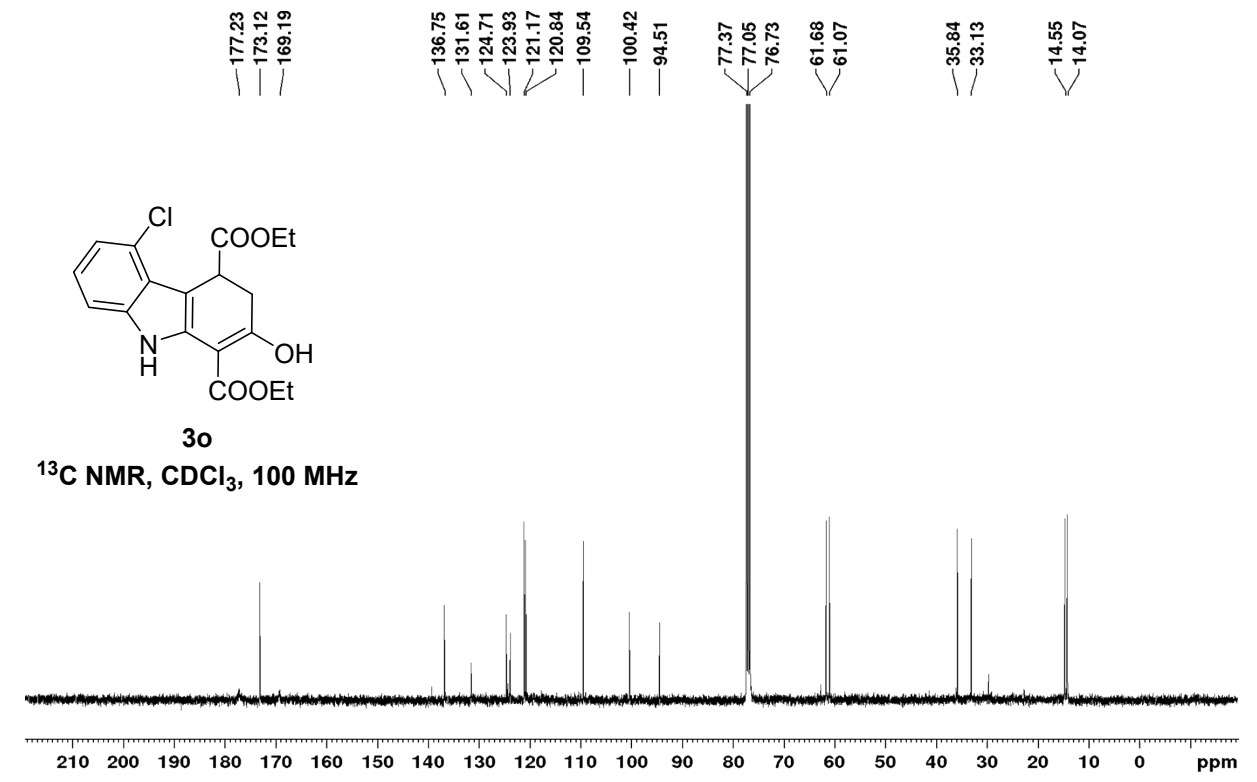

13.015
8.862
7.259
7.101
7.085
7.005
6.995
6.989
6.979
6.973
6.963
6.768
6.752
6.751
6.746
6.730
4.502
4.501
4.488
4.486
4.473
4.459
4.241
4.229
4.218
4.171
4.157
4.149
4.142
4.135
4.121
4.107
4.074
4.060
4.046
4.039
4.032
4.024
4.010
3.118
F
COOEt
N
H
OH
COOEt
3n
1H NMR, CDCl3, 500 MHz
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.78
0.93
0.94
0.98
0.96
2.00
1.00
1.10
1.04
2.13
3.09
3.08


177.03
173.04
169.24
157.10
155.14
138.23
138.14
130.46
121.06
121.00
115.62
115.46
109.06
106.95
106.92
105.39
105.24
98.34
94.34
77.29
77.04
76.78
61.61
61.04
36.36
32.84
14.54
14.01
F
COOEt
N
H
OH
COOEt
3n
13C NMR, CDCl3, 125 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



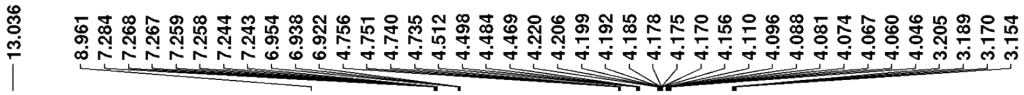
3o

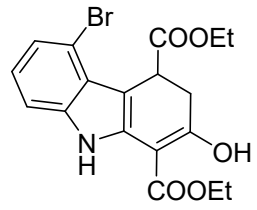
^{1}H NMR, $CDCl_3$, 500 MHz



3o

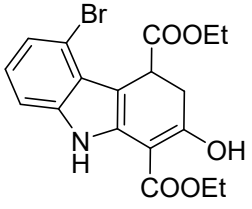
^{13}C NMR, $CDCl_3$, 100 MHz





3p

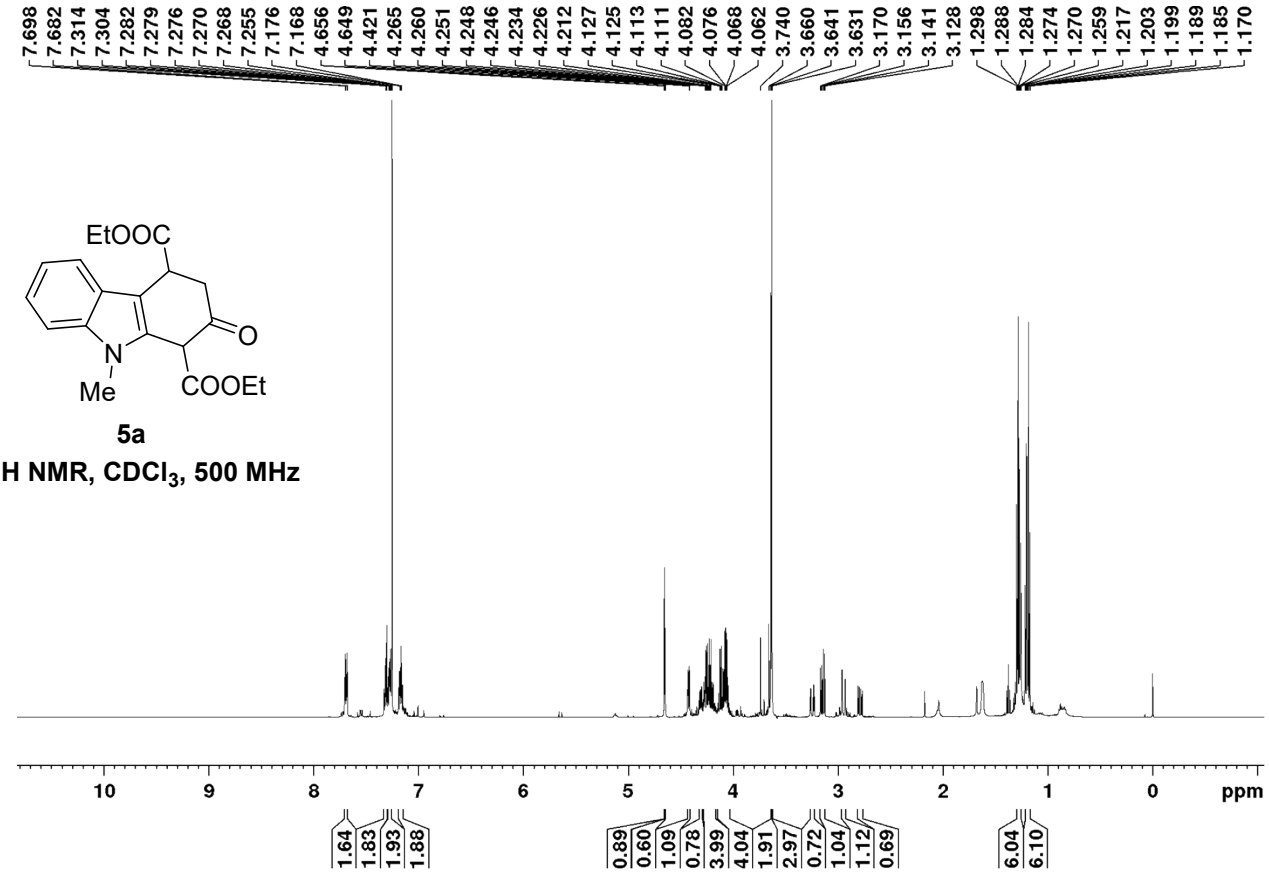
^{1}H NMR, $CDCl_3$, 500 MHz

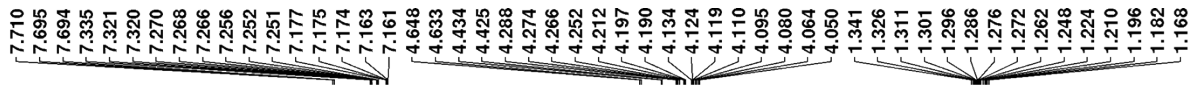


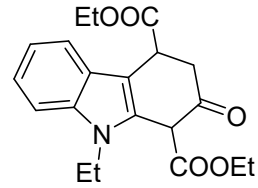
3p

^{13}C NMR, $CDCl_3$, 100 MHz

10. Copies of ^{1}H NMR and ^{13}C NMR Spectra of 5a- 5t

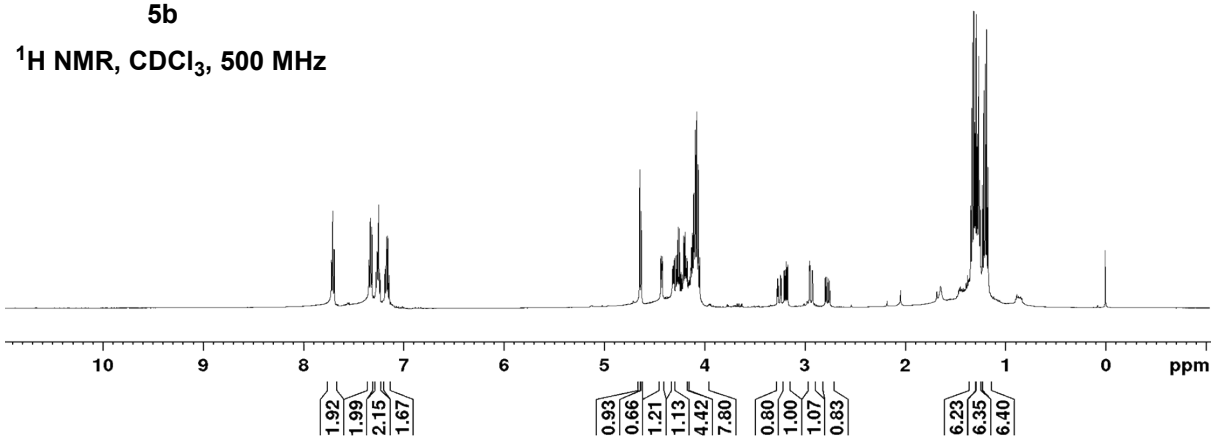


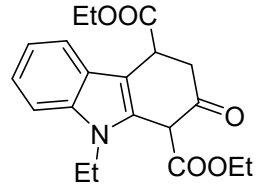




5b

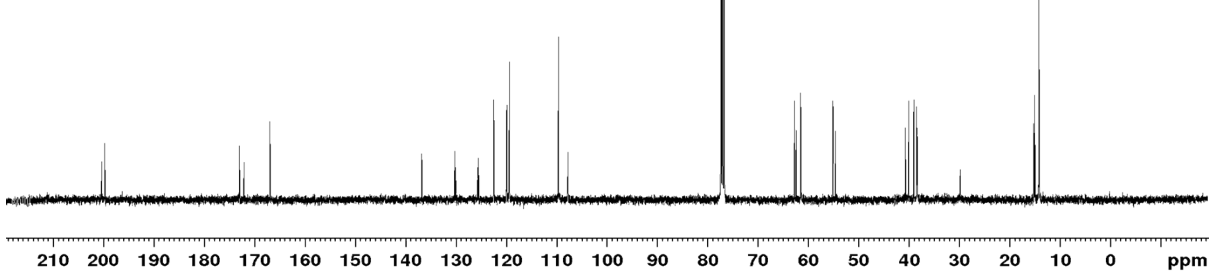
^{1}H NMR, $CDCl_3$, 500 MHz

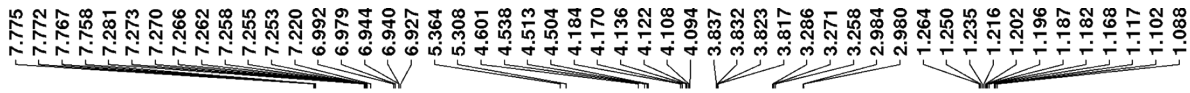


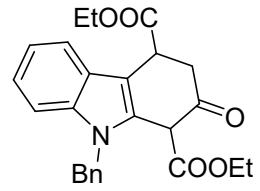


5b

^{13}C NMR, $CDCl_3$, 125 MHz

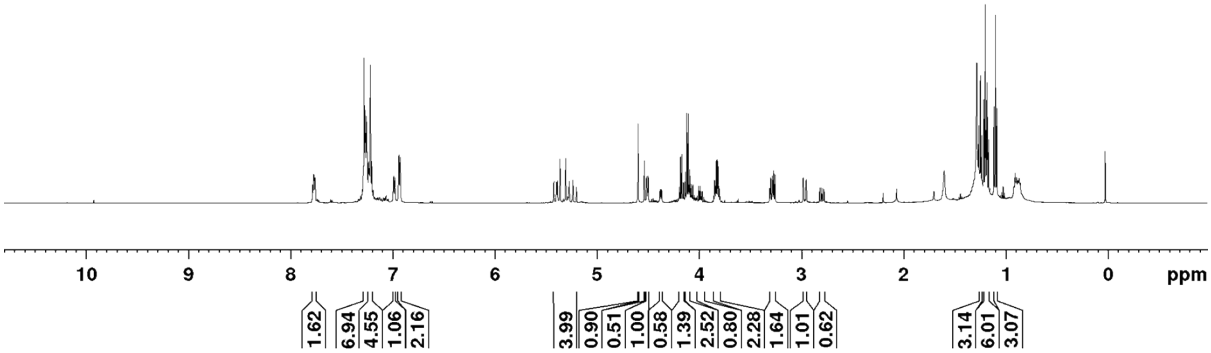


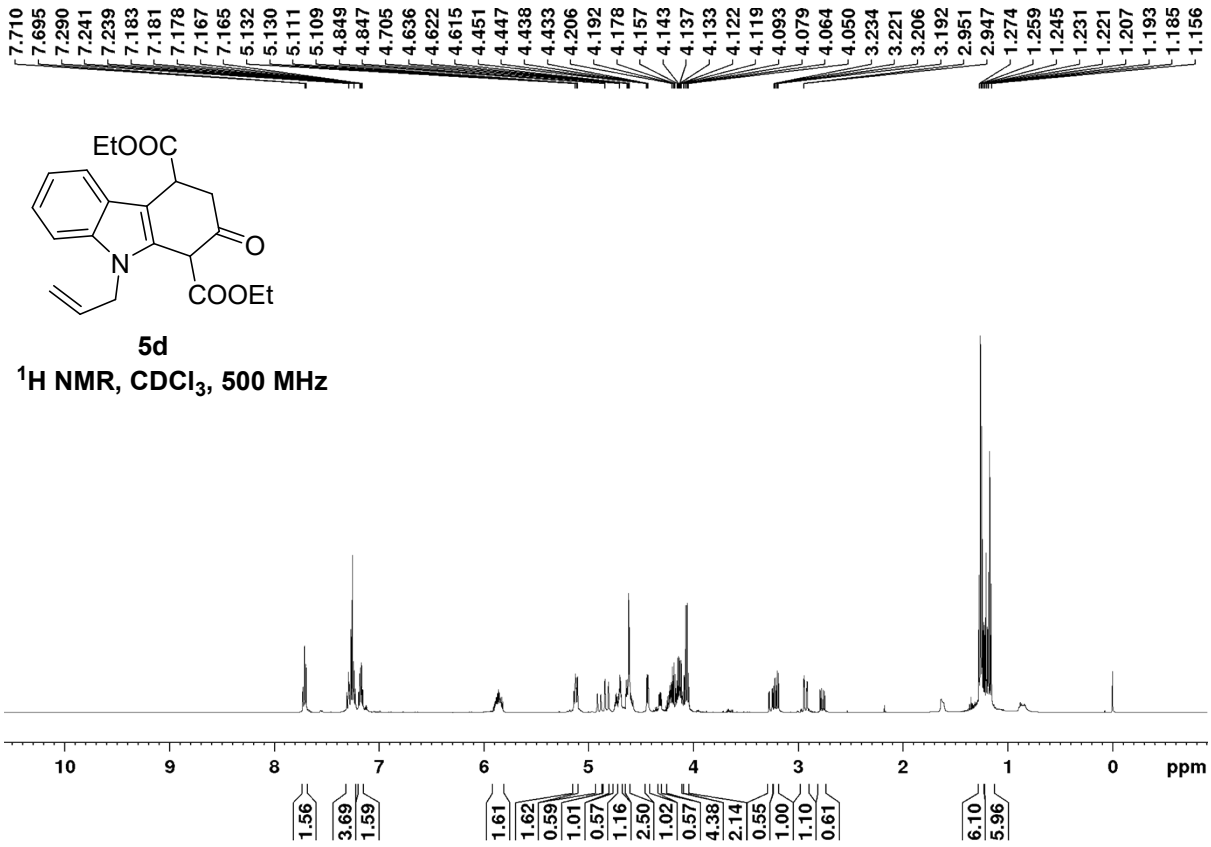




5c

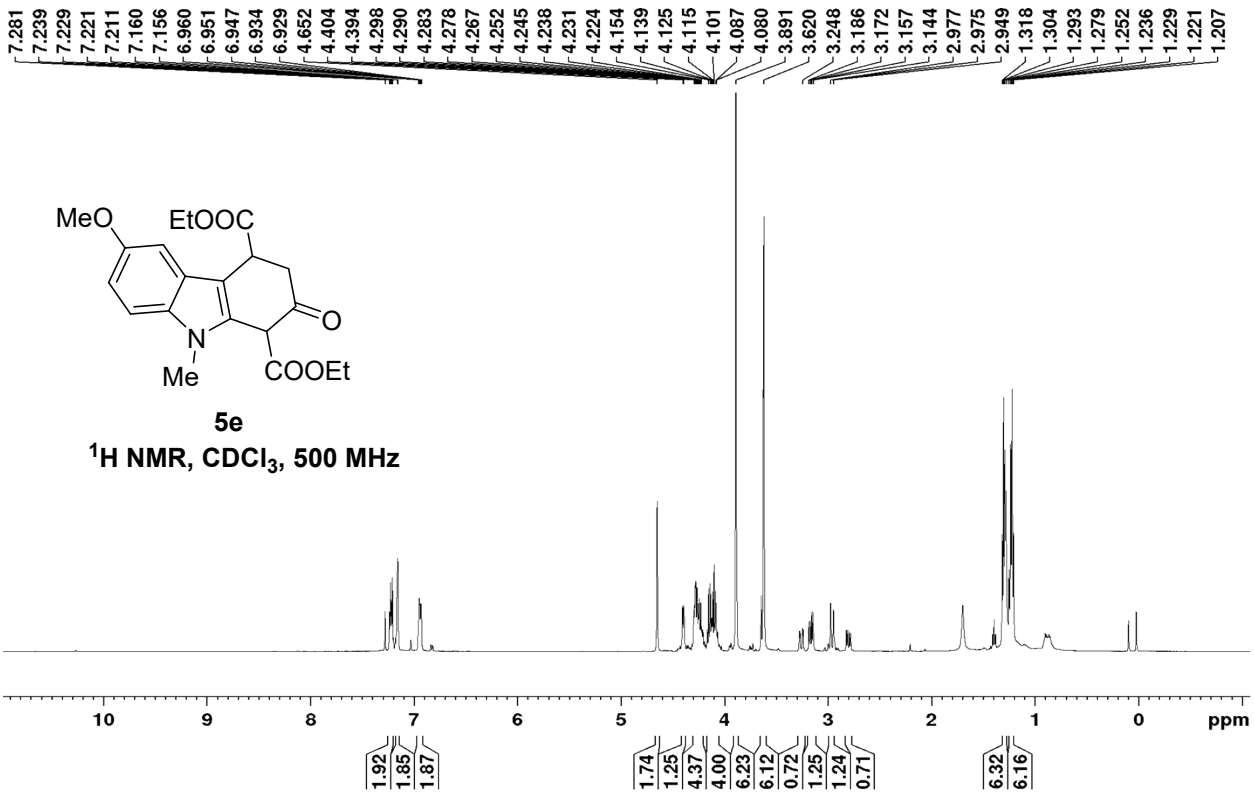
^{1}H NMR, $CDCl_3$, 500 MHz





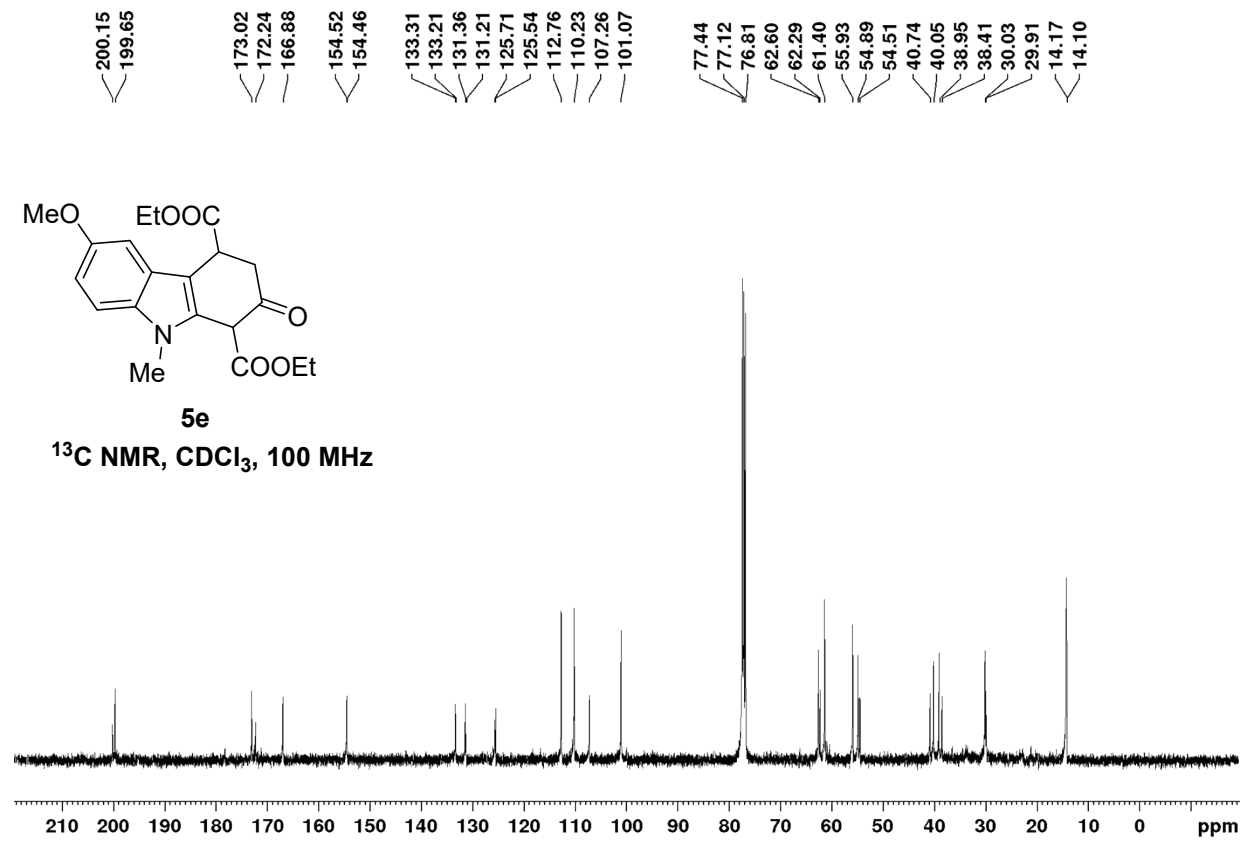
5d

^{1}H NMR, $CDCl_3$, 500 MHz



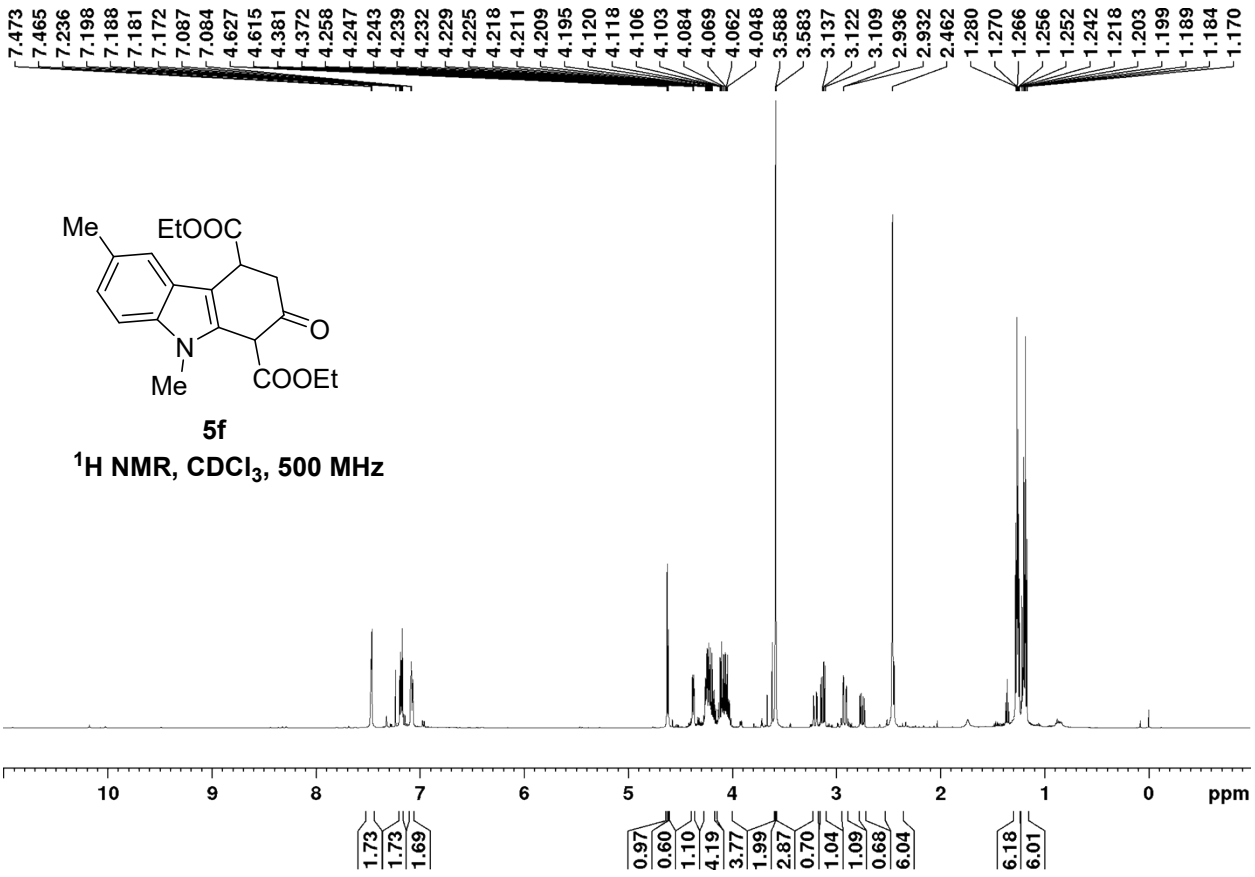
5e

^{1}H NMR, $CDCl_3$, 500 MHz



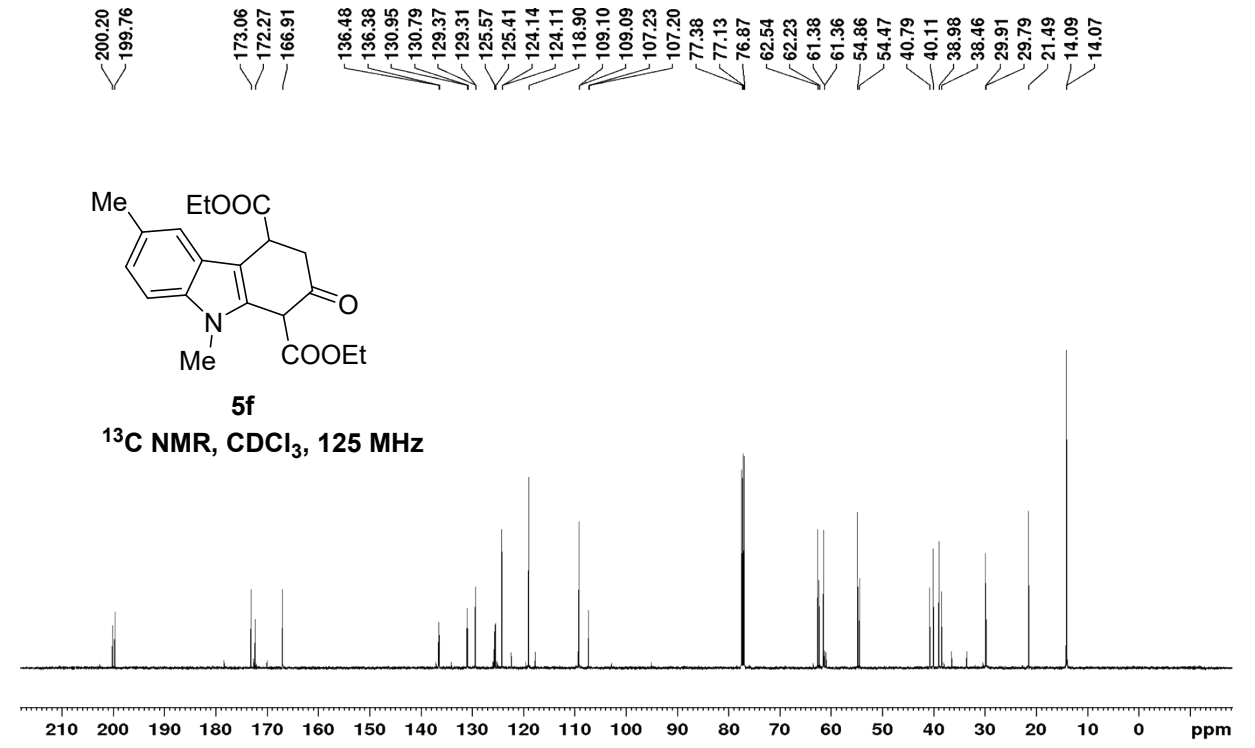
5e

^{13}C NMR, $CDCl_3$, 100 MHz



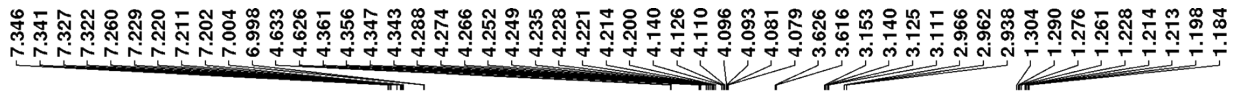
5f

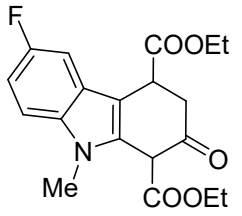
^{1}H NMR, $CDCl_3$, 500 MHz



5f

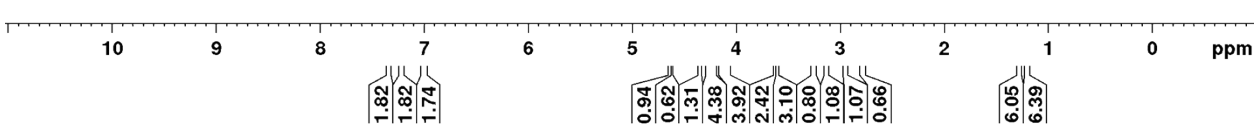
^{13}C NMR, $CDCl_3$, 125 MHz

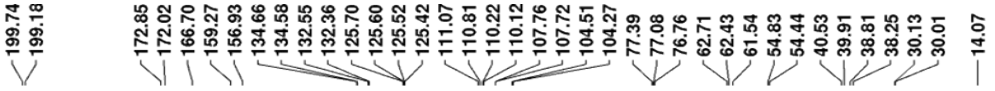


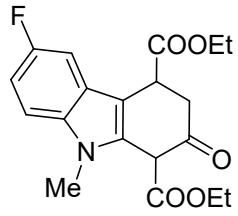


5g

^{1}H NMR, $CDCl_3$, 500 MHz

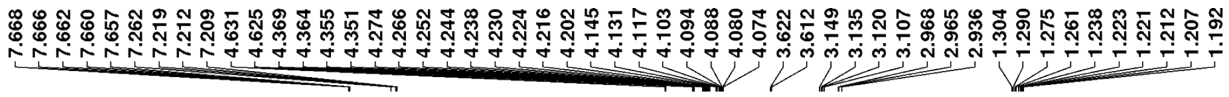


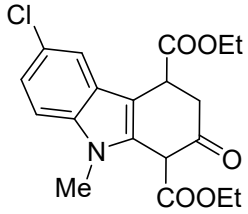




5g

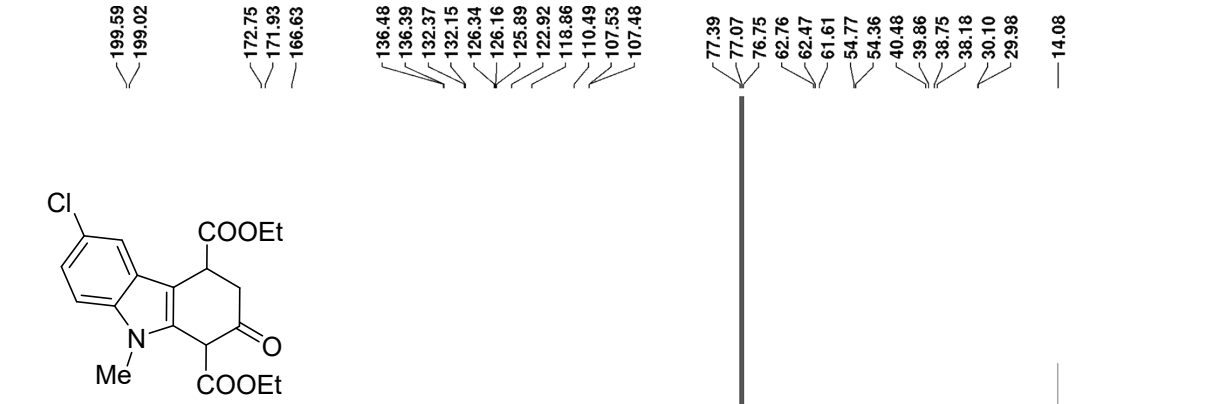
^{13}C NMR, $CDCl_3$, 100 MHz





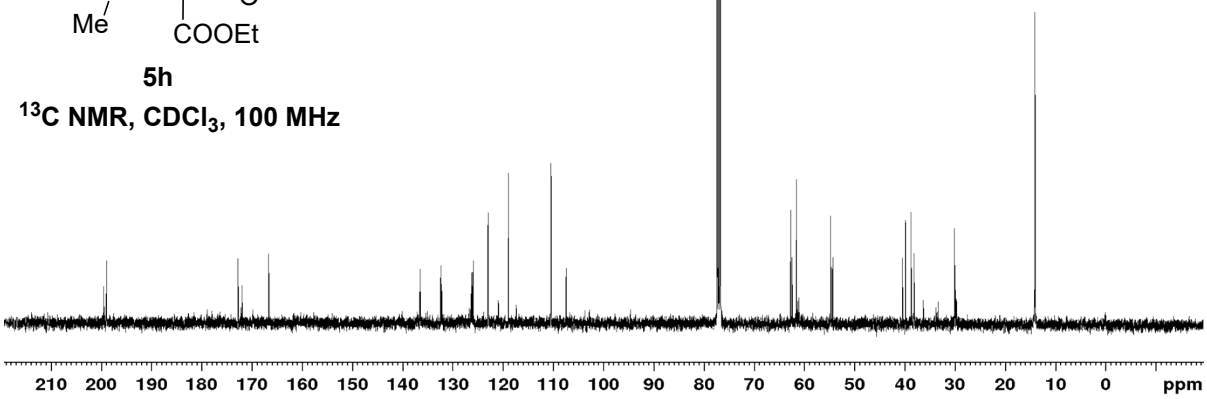
5h

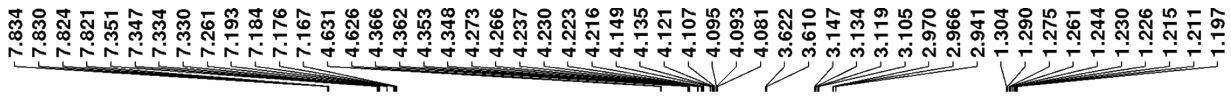
^{1}H NMR, $CDCl_3$, 500 MHz

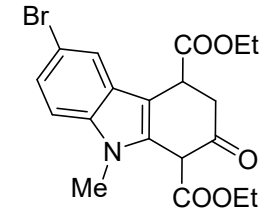


5h

^{13}C NMR, $CDCl_3$, 100 MHz

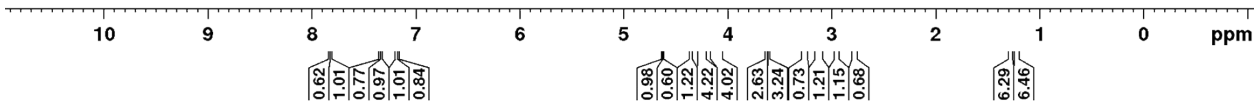


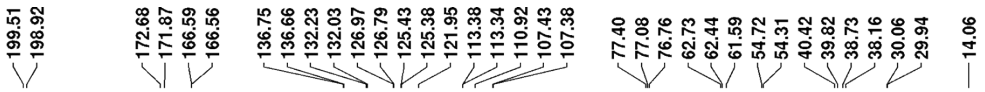


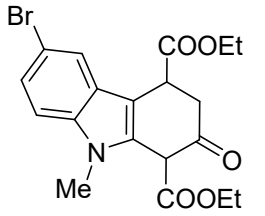


5i

^{1}H NMR, $CDCl_3$, 500 MHz

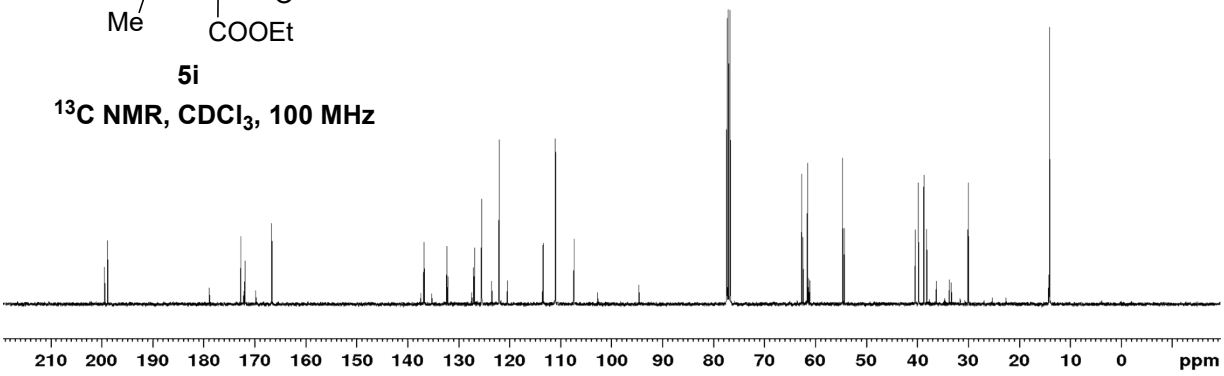


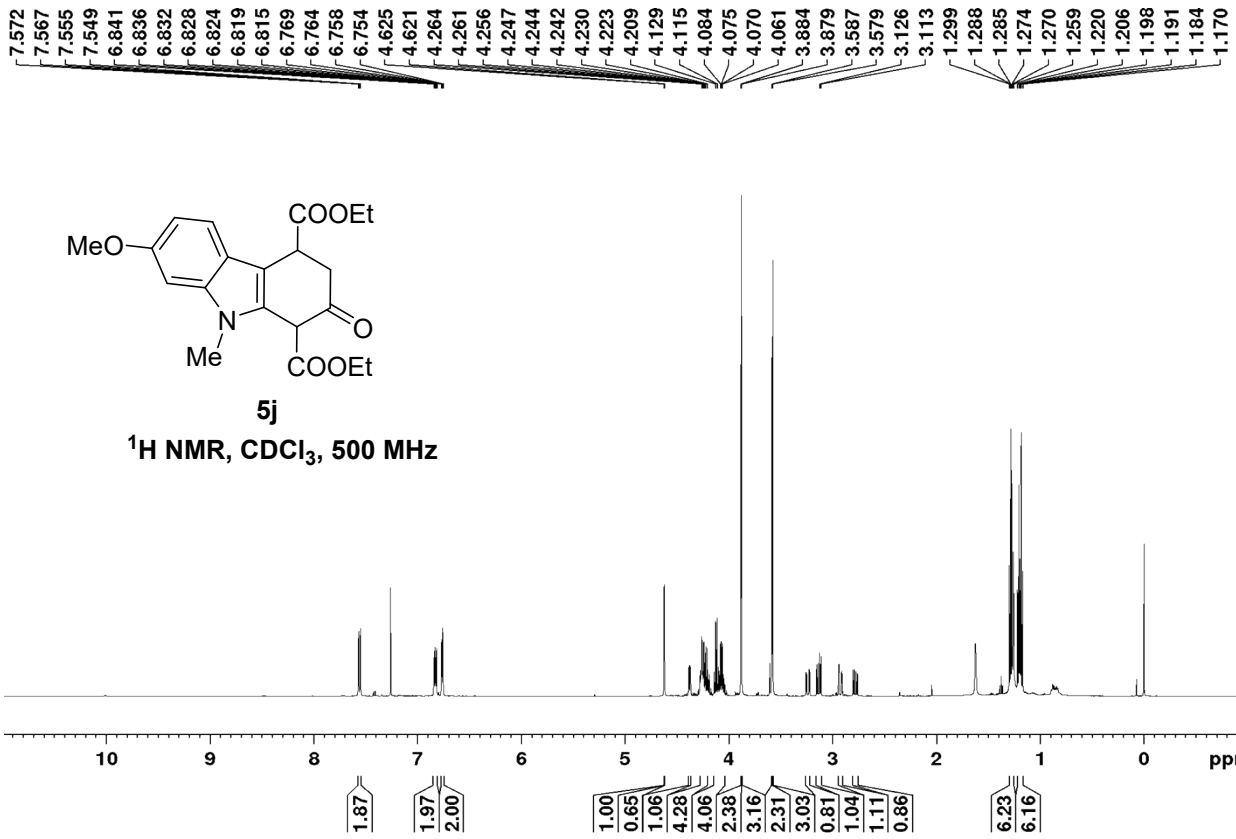




5i

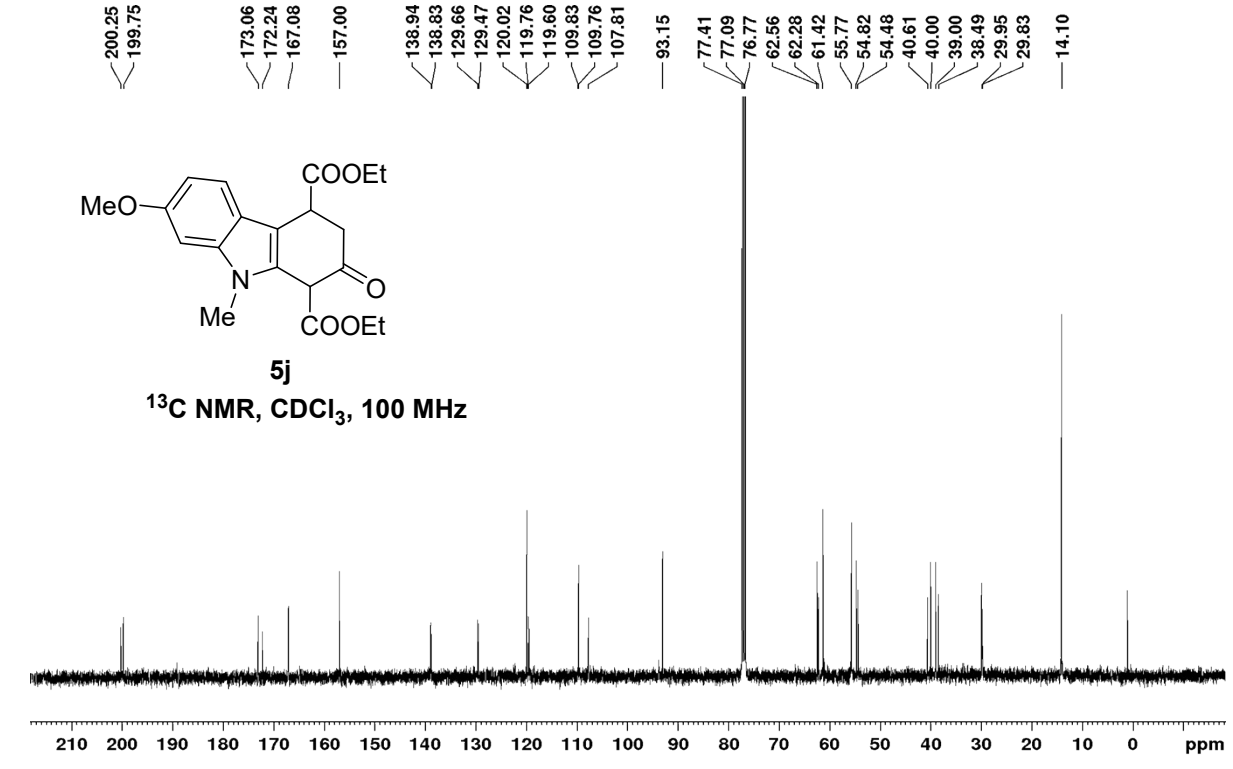
^{13}C NMR, $CDCl_3$, 100 MHz





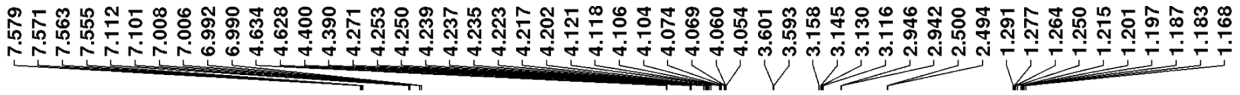
5j

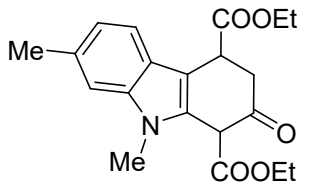
^{1}H NMR, $CDCl_3$, 500 MHz



5j

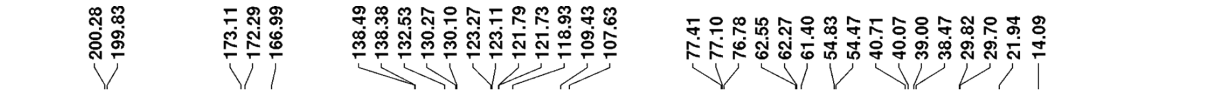
^{13}C NMR, $CDCl_3$, 100 MHz

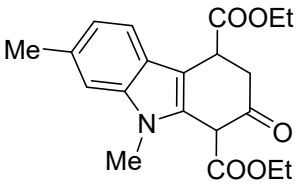




5k

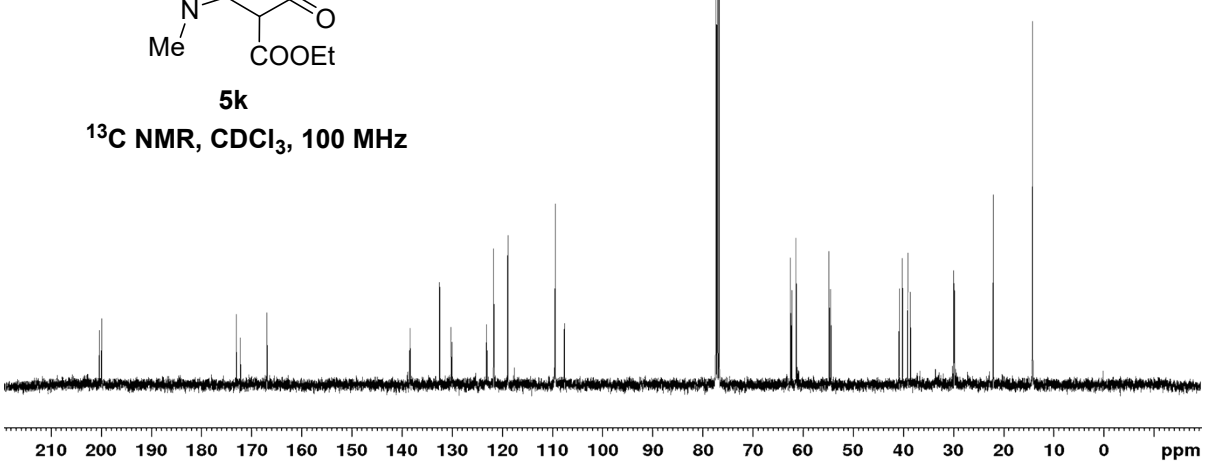
^{1}H NMR, $CDCl_3$, 500 MHz

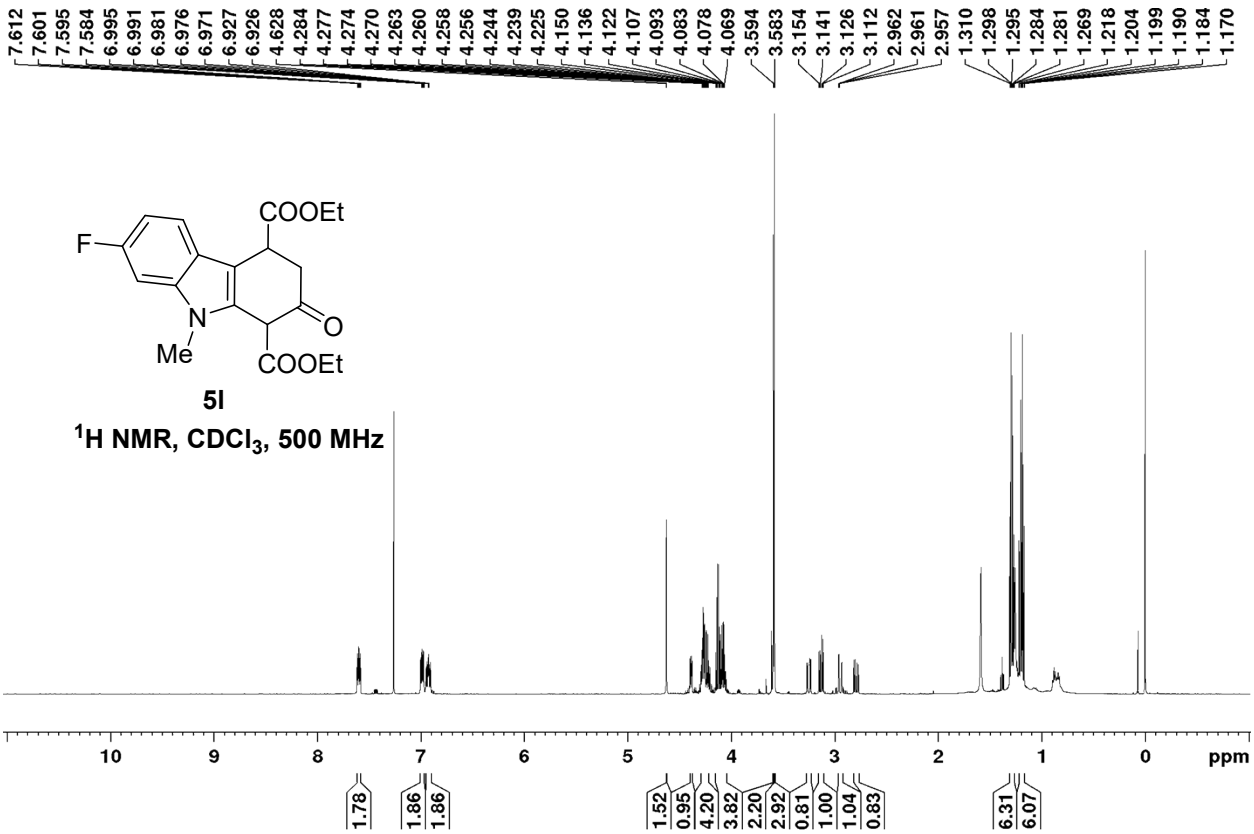




5k

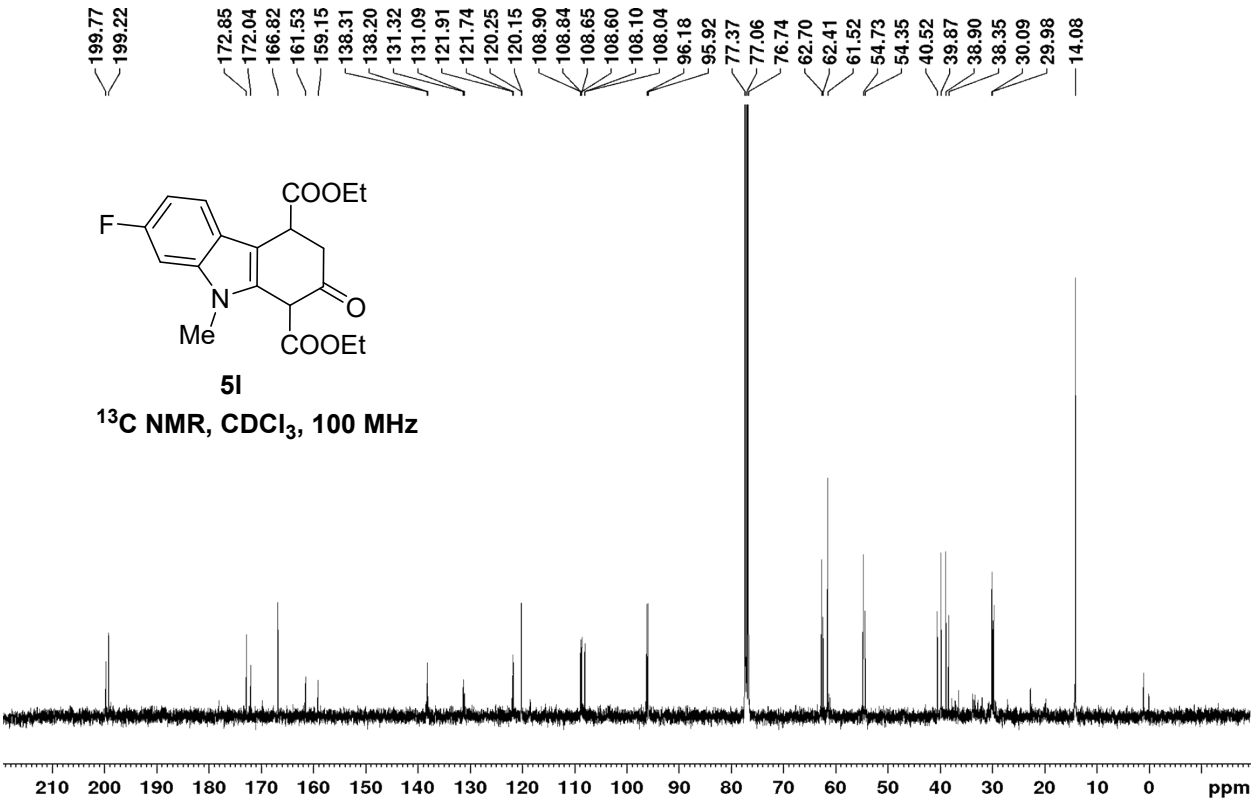
^{13}C NMR, $CDCl_3$, 100 MHz





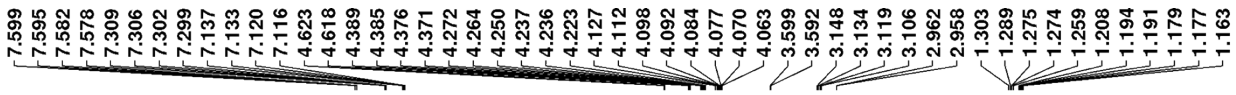
5l

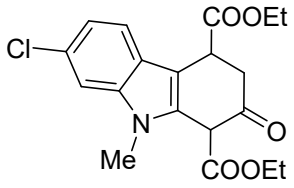
^{1}H NMR, $CDCl_3$, 500 MHz



5l

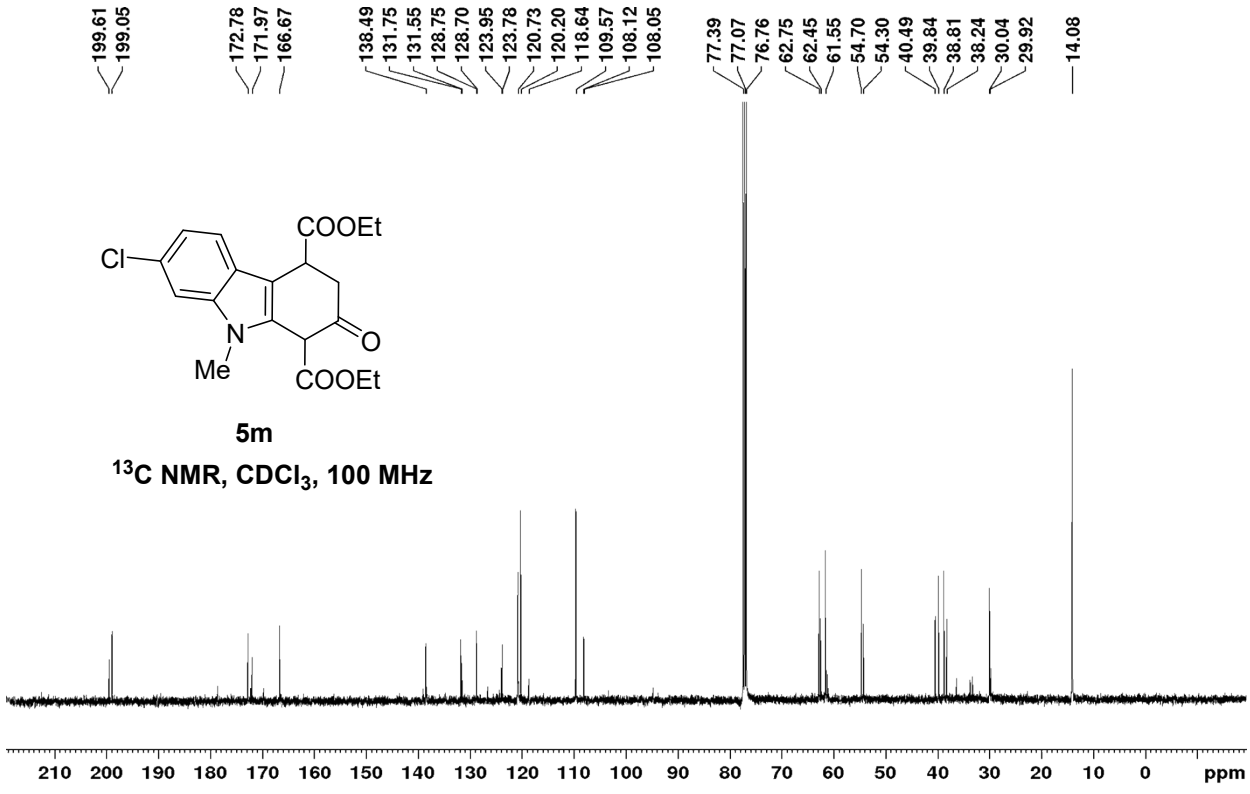
^{13}C NMR, $CDCl_3$, 100 MHz





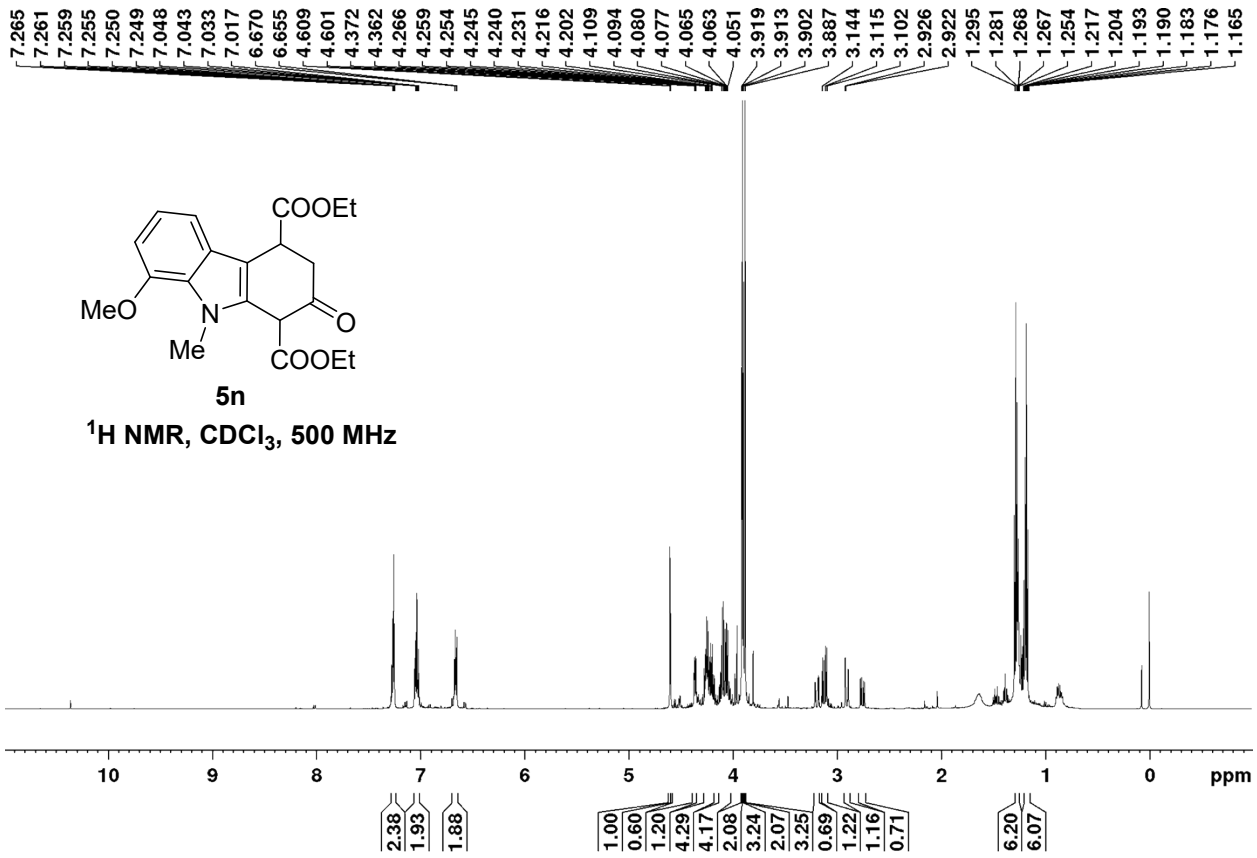
5m

^{1}H NMR, $CDCl_3$, 500 MHz



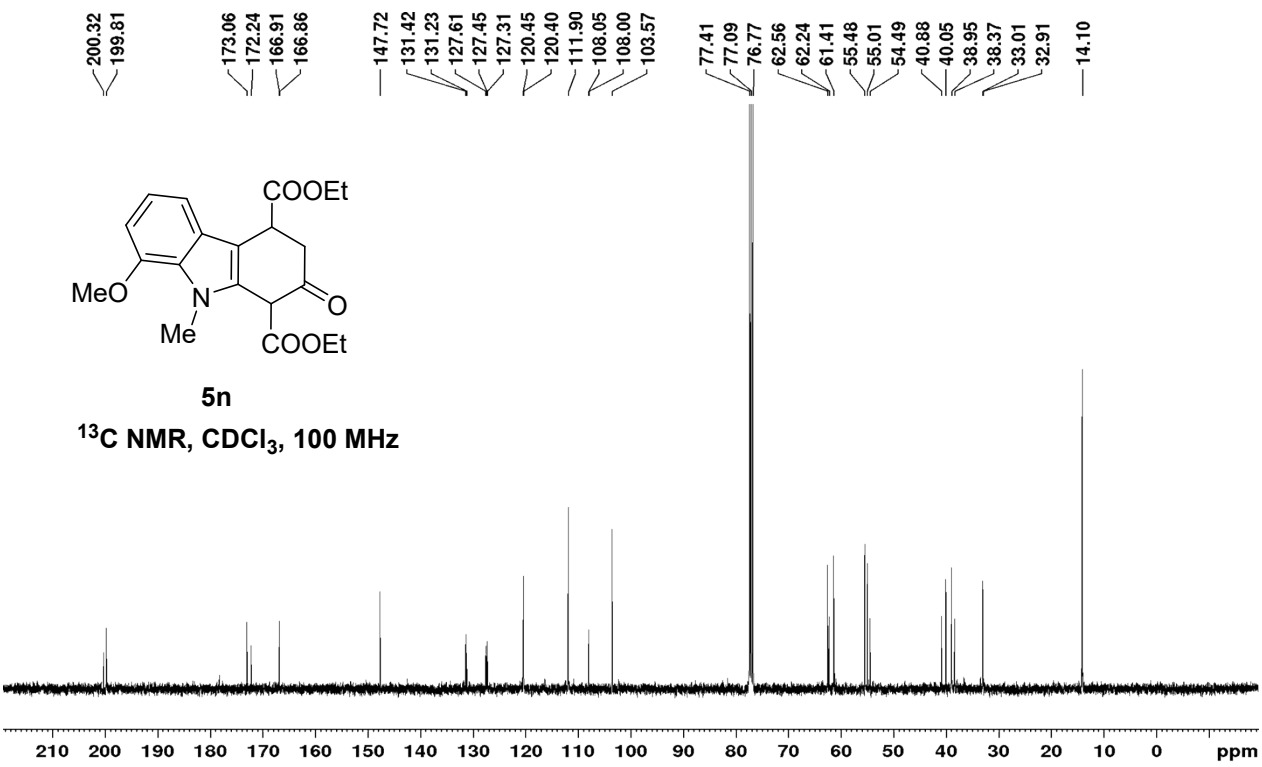
5m

^{13}C NMR, $CDCl_3$, 100 MHz



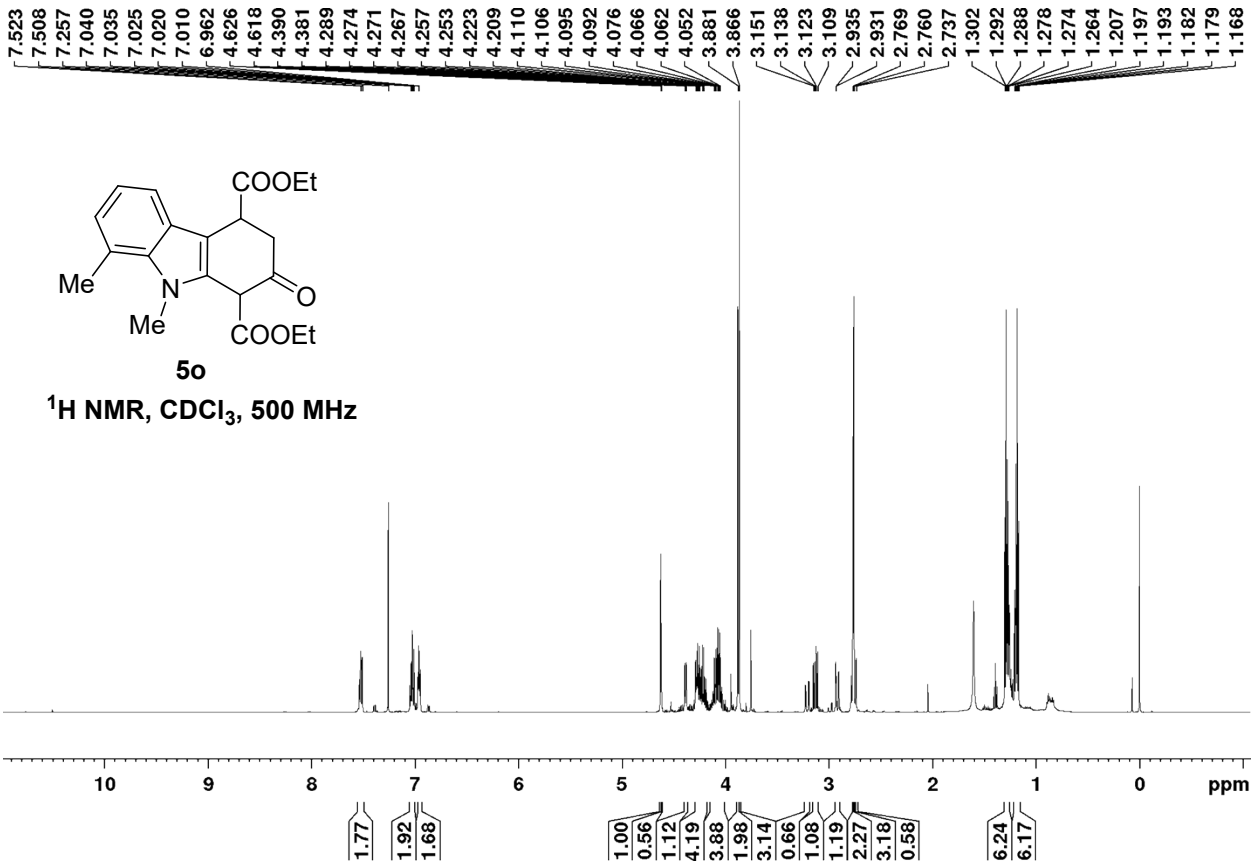
5n

^{1}H NMR, $CDCl_3$, 500 MHz



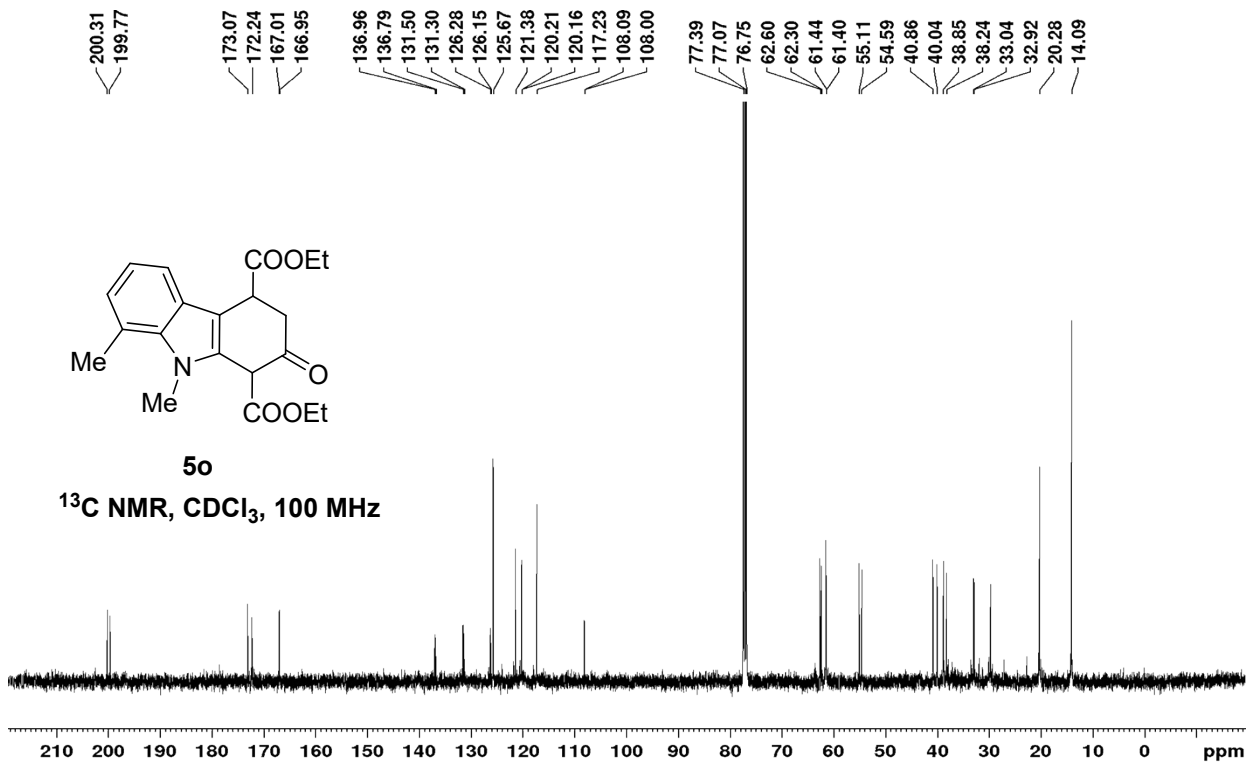
5n

^{13}C NMR, $CDCl_3$, 100 MHz



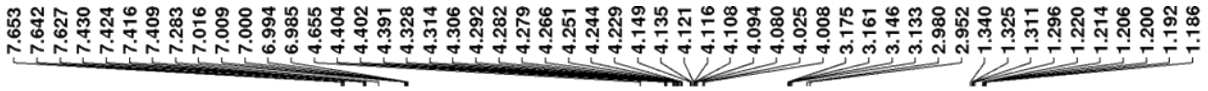
5o

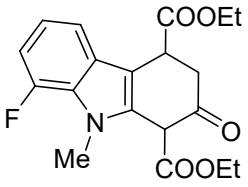
^{1}H NMR, $CDCl_3$, 500 MHz



5o

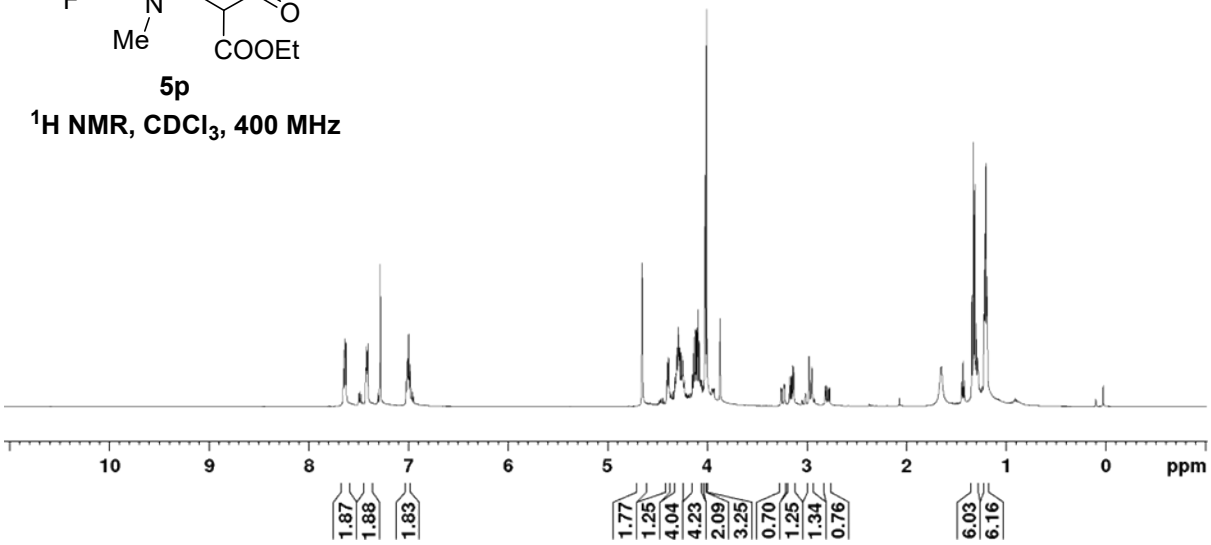
^{13}C NMR, $CDCl_3$, 100 MHz

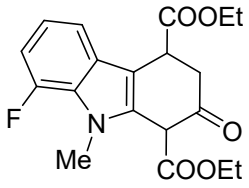




5p

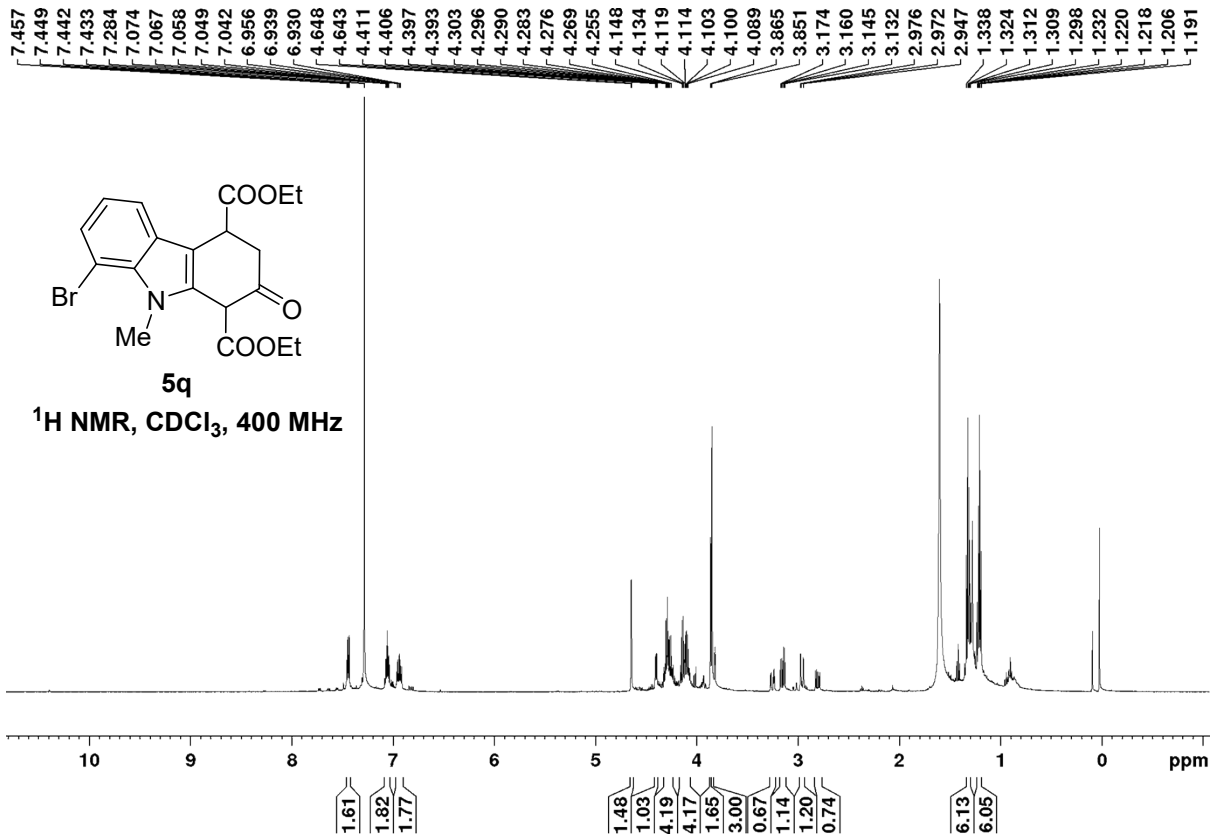
^{1}H NMR, $CDCl_3$, 400 MHz





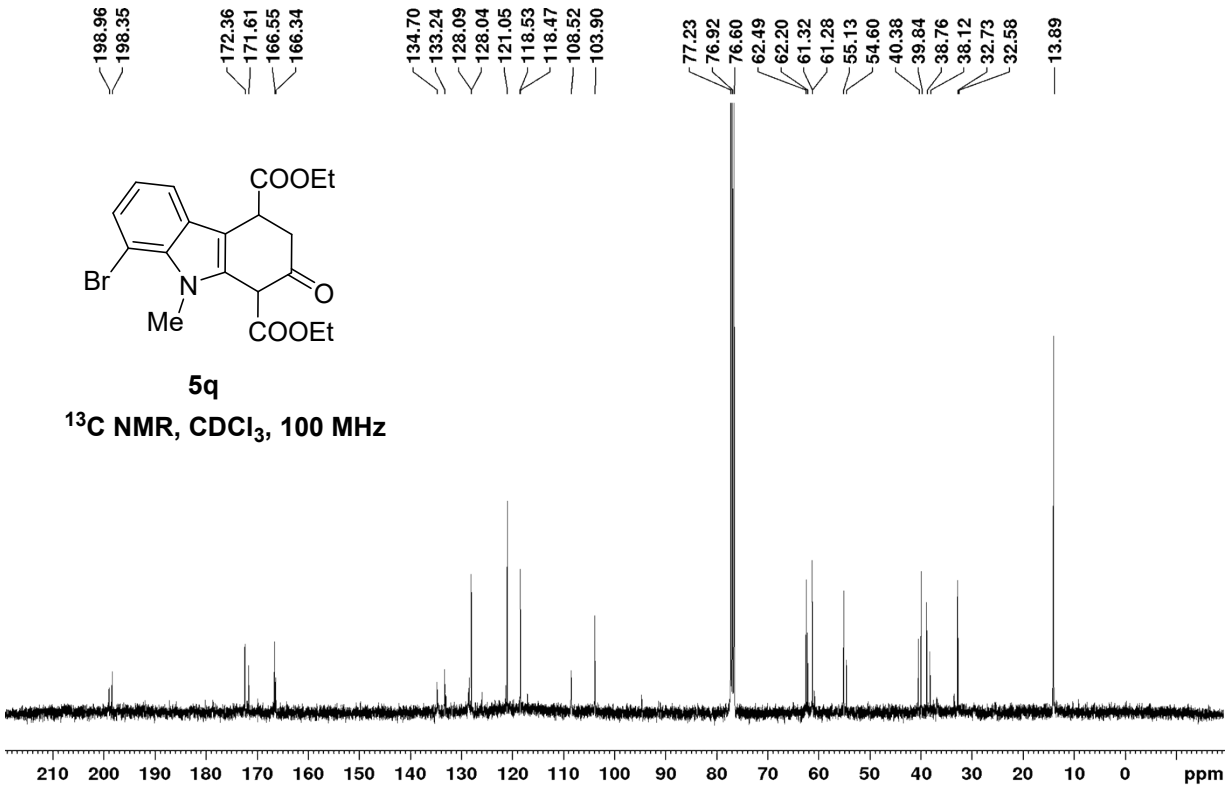
5p

^{13}C NMR, $CDCl_3$, 125 MHz



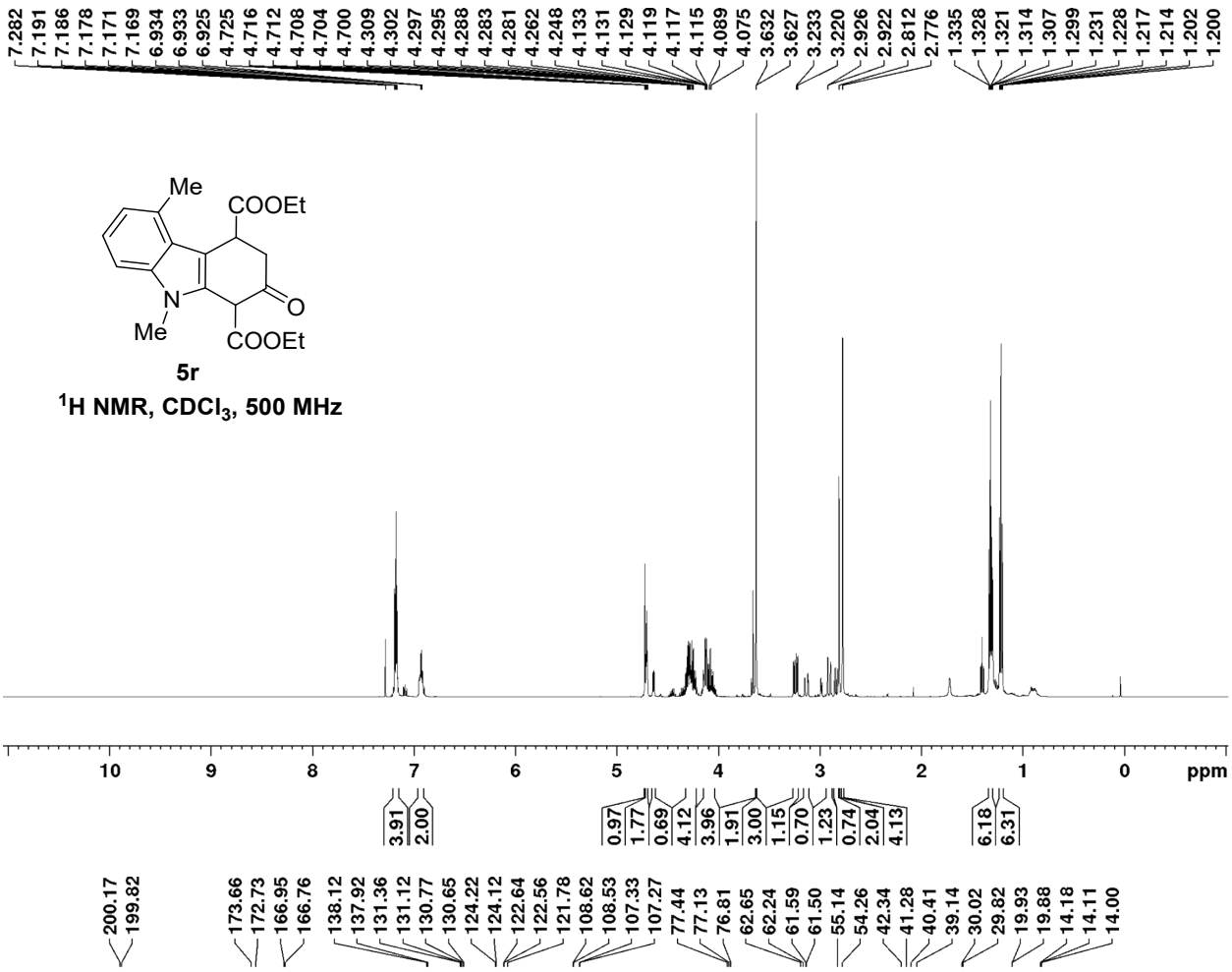
5q

^{1}H NMR, $CDCl_3$, 400 MHz



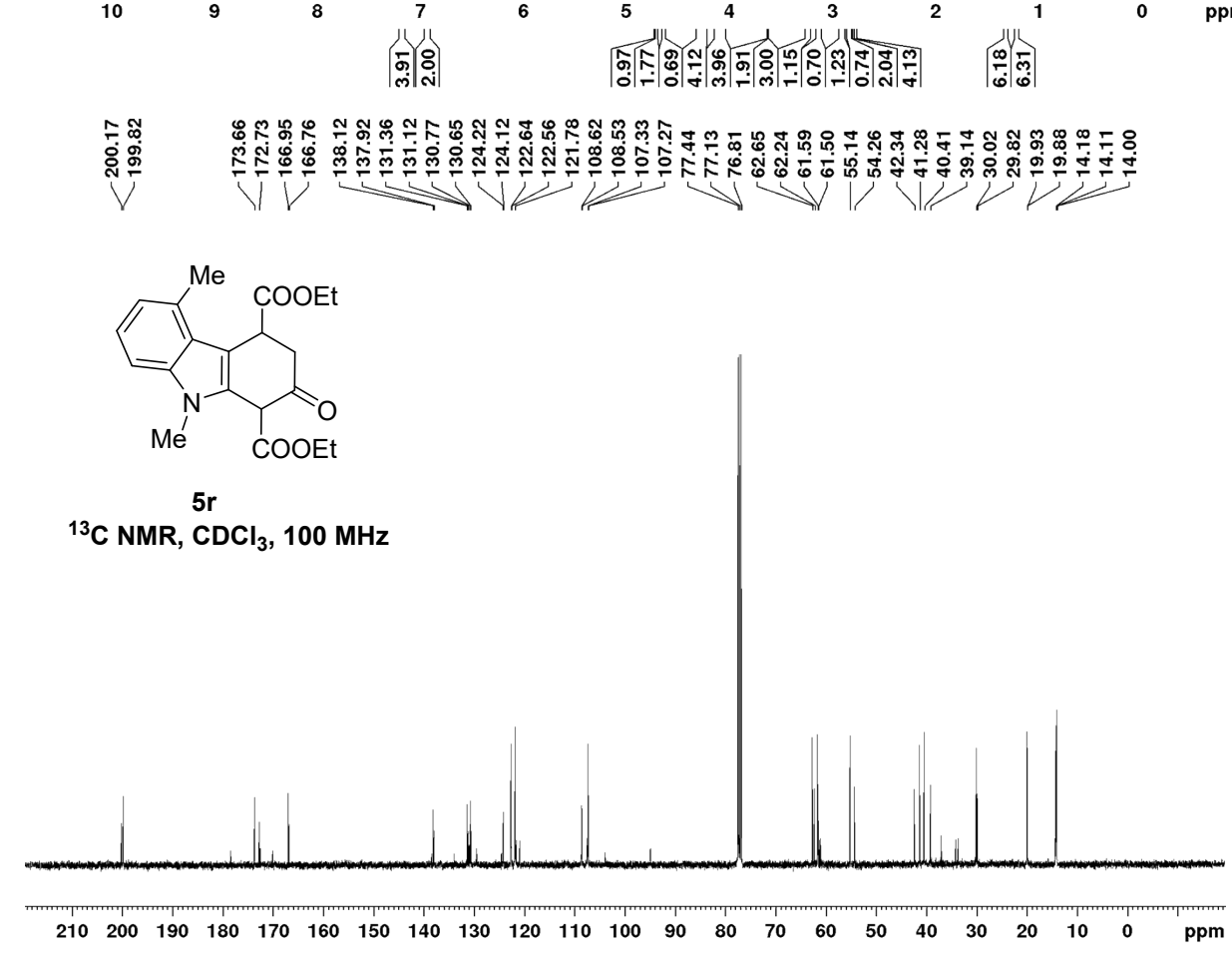
5q

^{13}C NMR, $CDCl_3$, 100 MHz



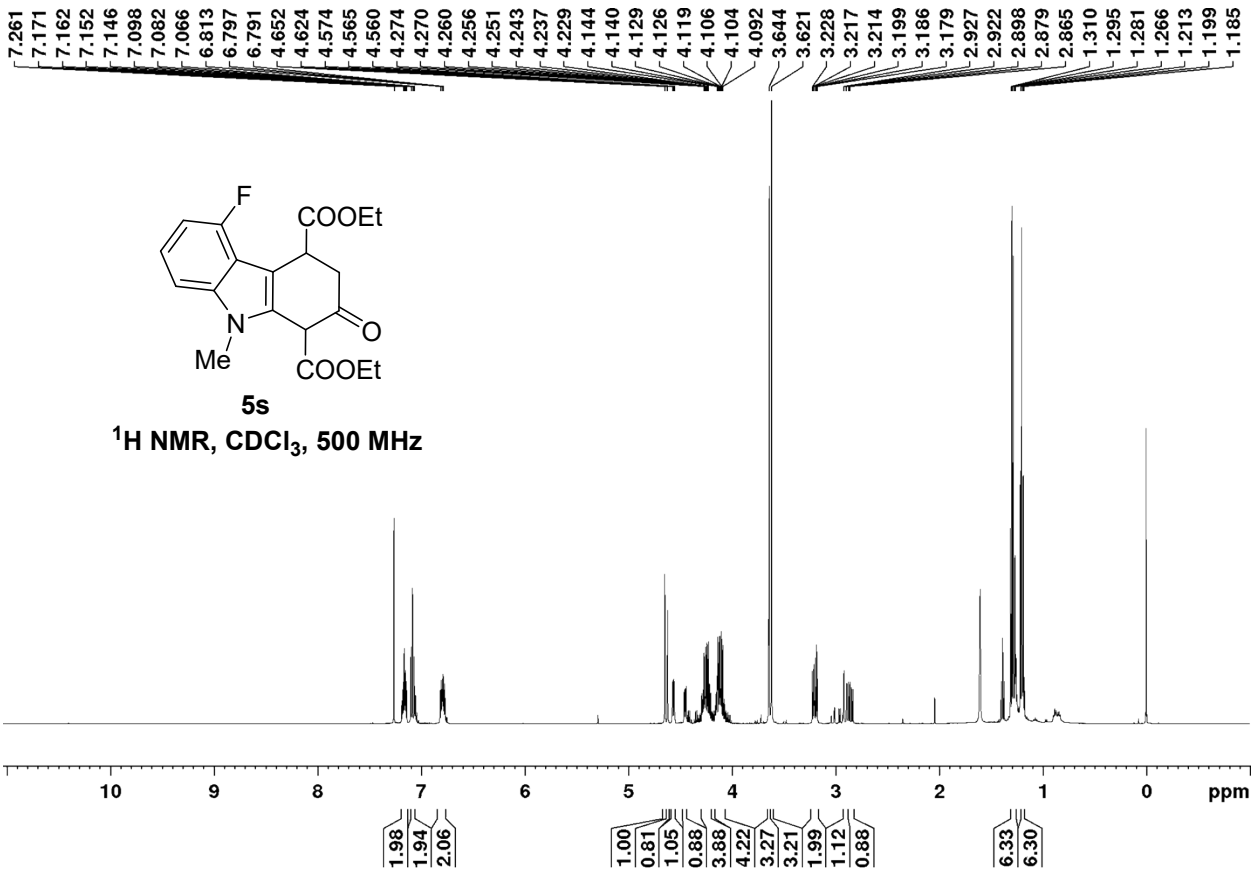
5r

^{1}H NMR, $CDCl_3$, 500 MHz



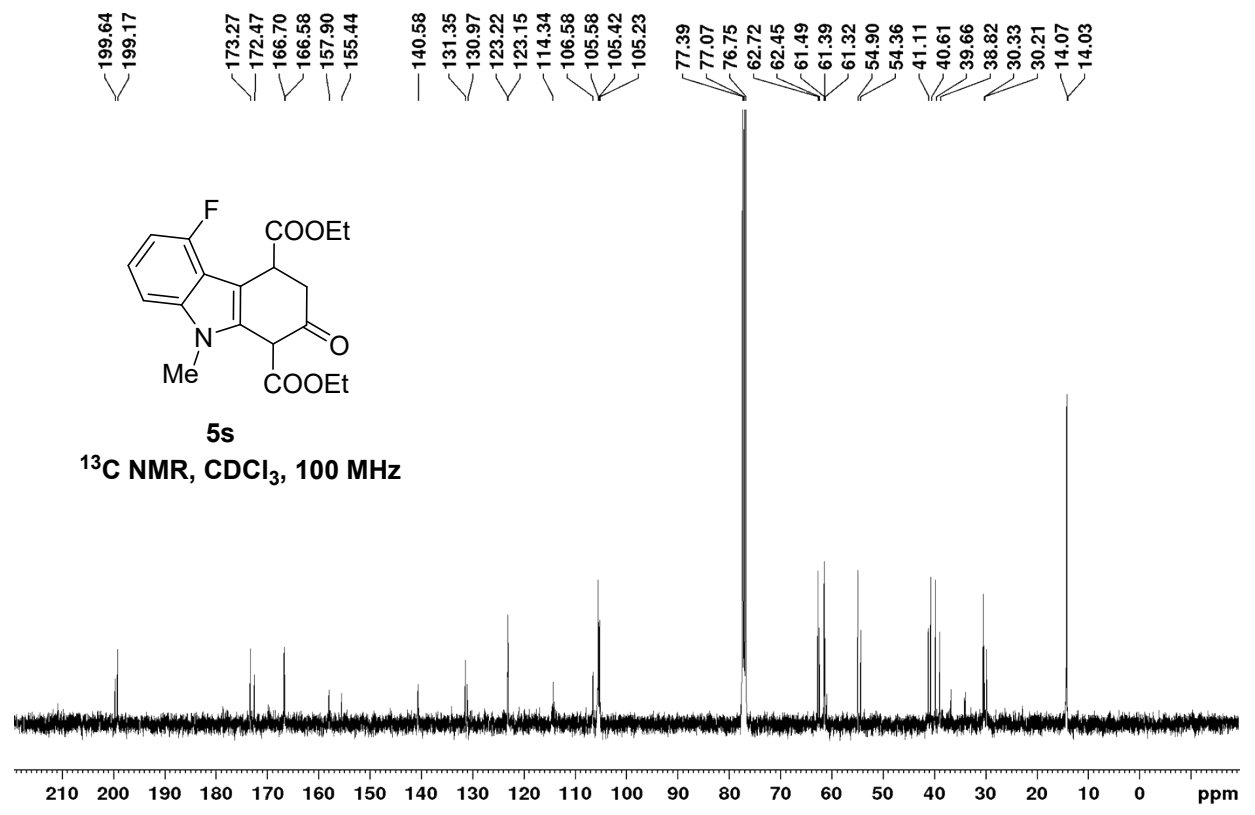
5r

^{13}C NMR, $CDCl_3$, 100 MHz



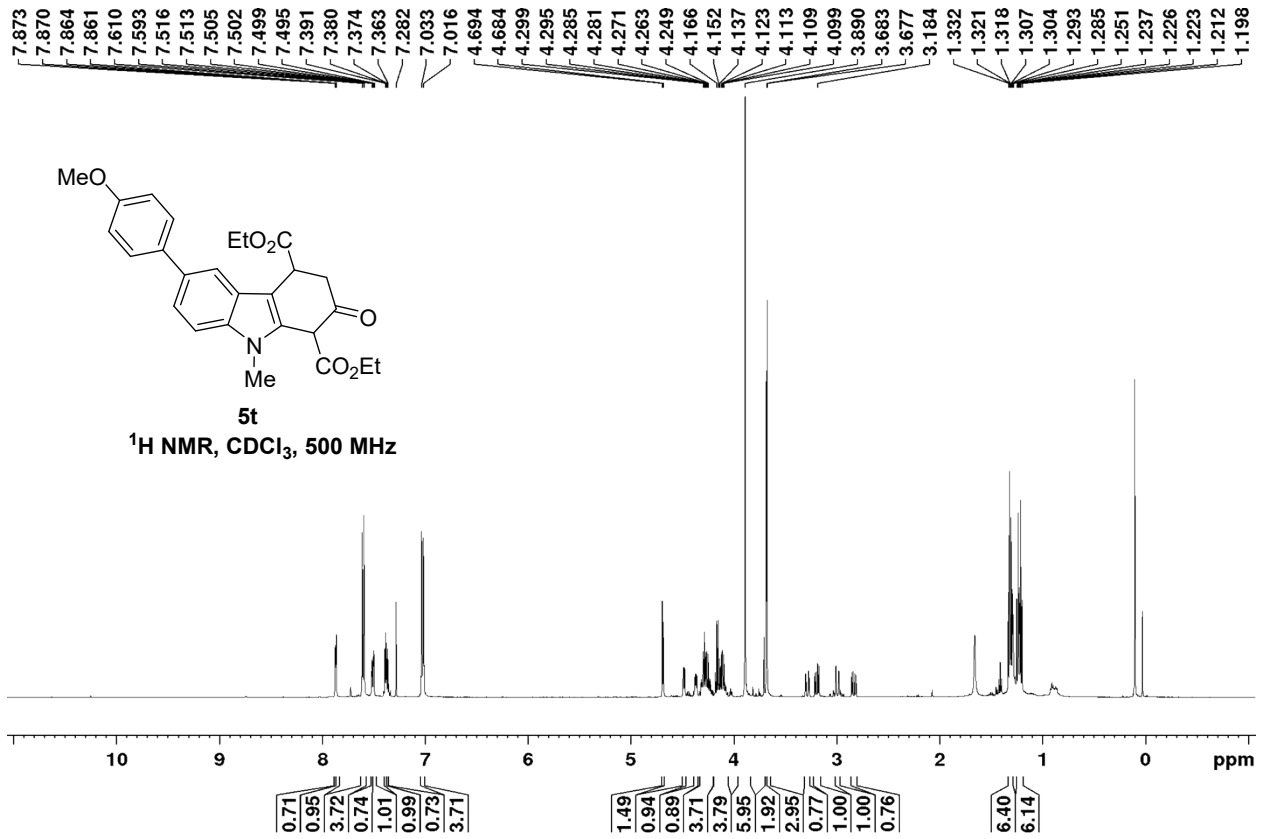
5s

^{1}H NMR, $CDCl_3$, 500 MHz



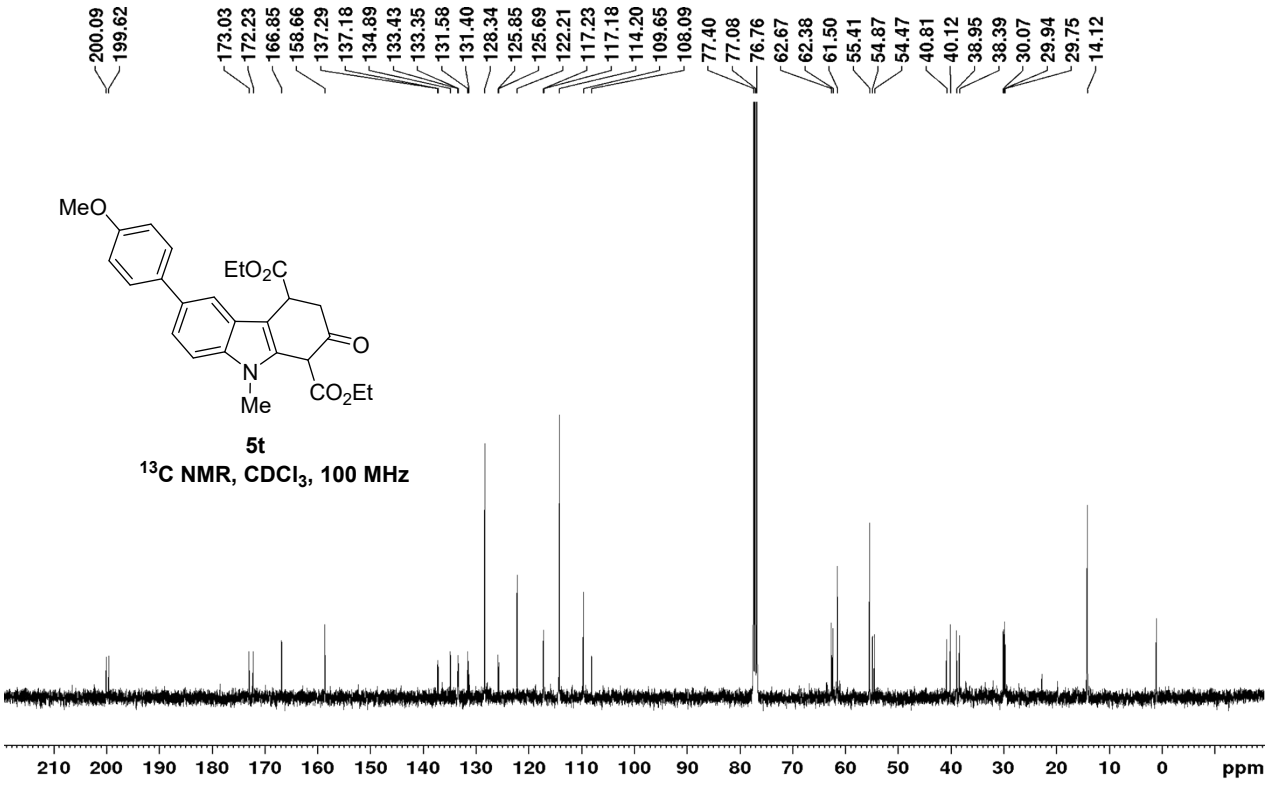
5s

^{13}C NMR, $CDCl_3$, 100 MHz



5t

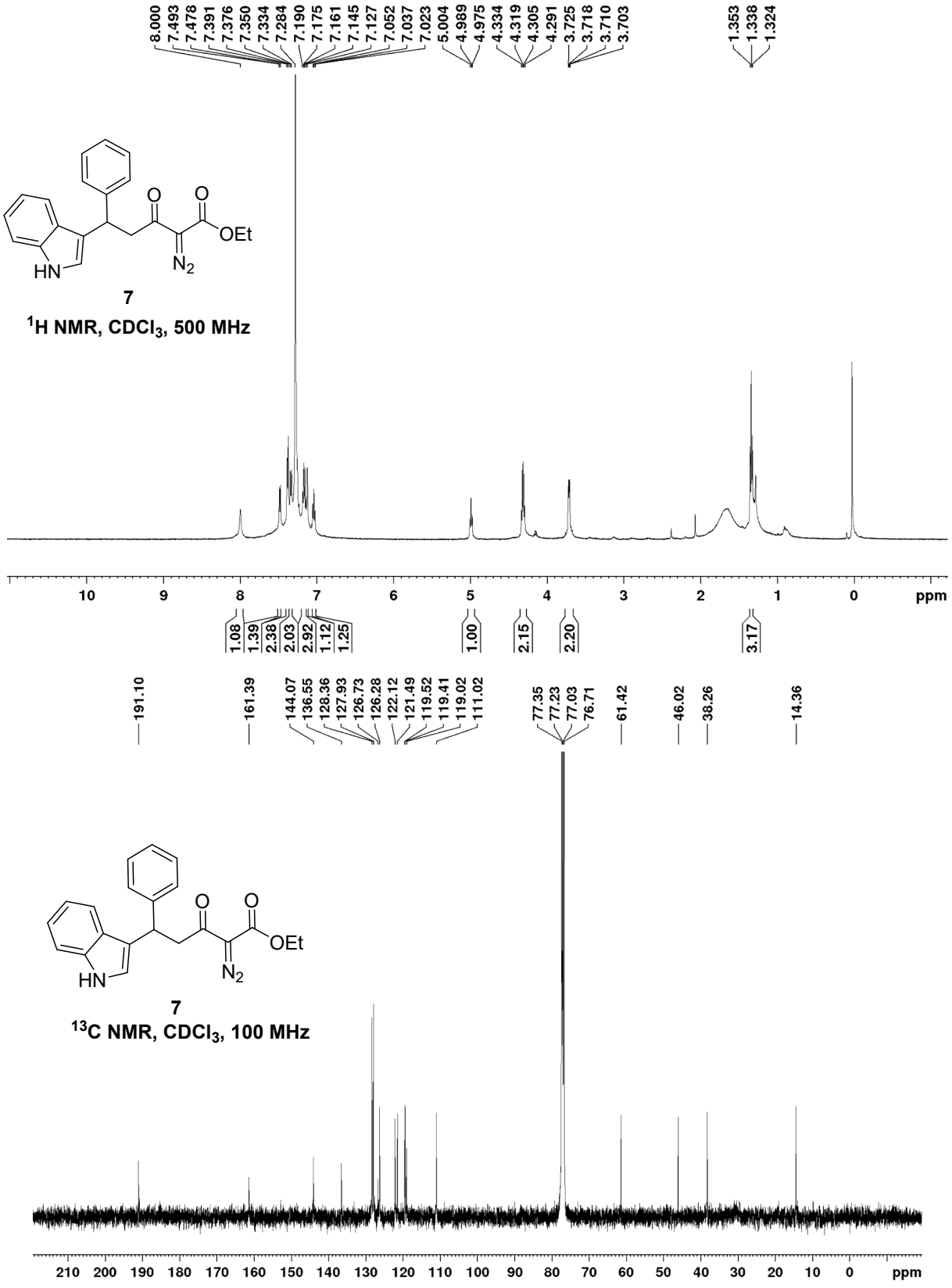
^{1}H NMR, $CDCl_3$, 500 MHz

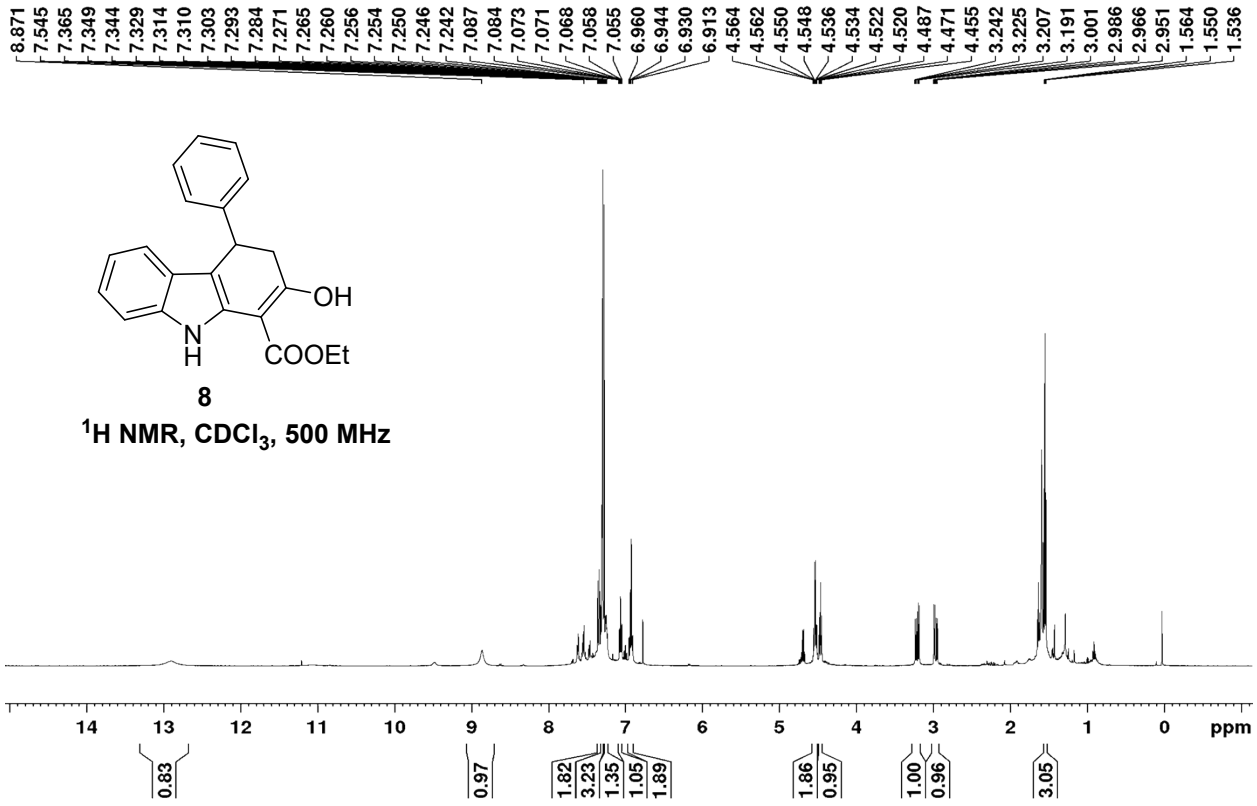


5t

^{13}C NMR, $CDCl_3$, 100 MHz

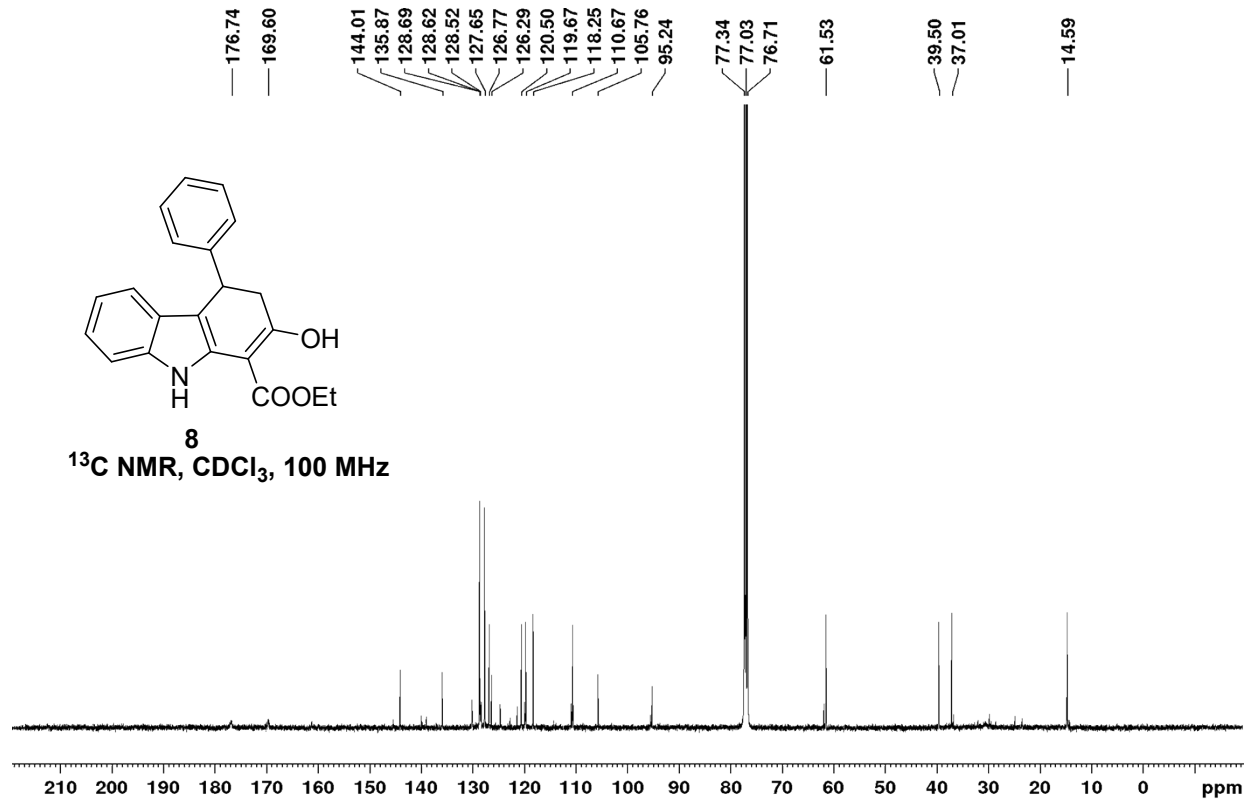
11. Copies of ^{1}H NMR and ^{13}C NMR Spectra of Compounds 7 to 15





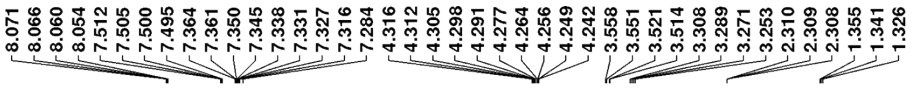
8

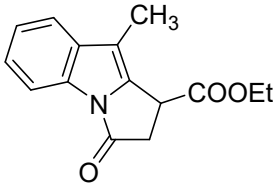
^{1}H NMR, $CDCl_3$, 500 MHz



8

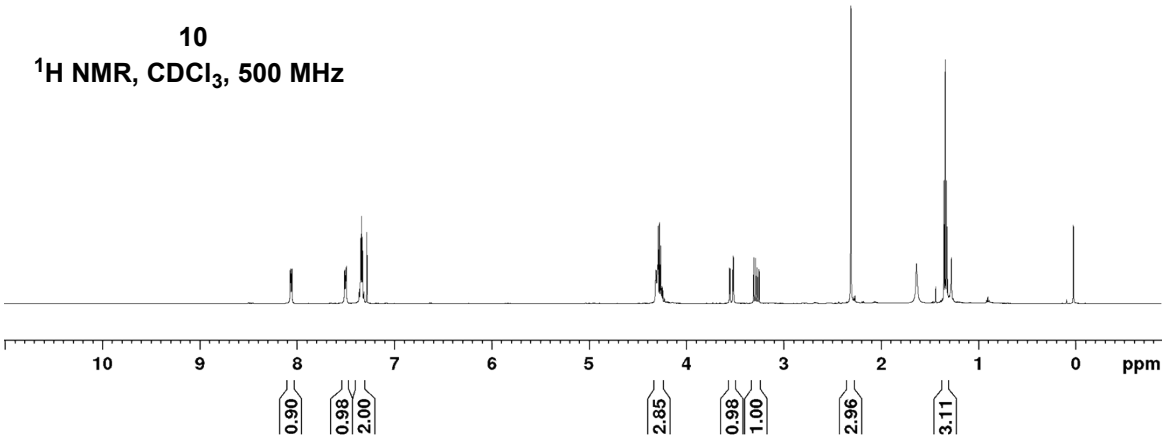
^{13}C NMR, $CDCl_3$, 100 MHz

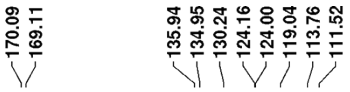


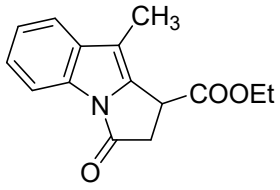


10

^{1}H NMR, $CDCl_3$, 500 MHz

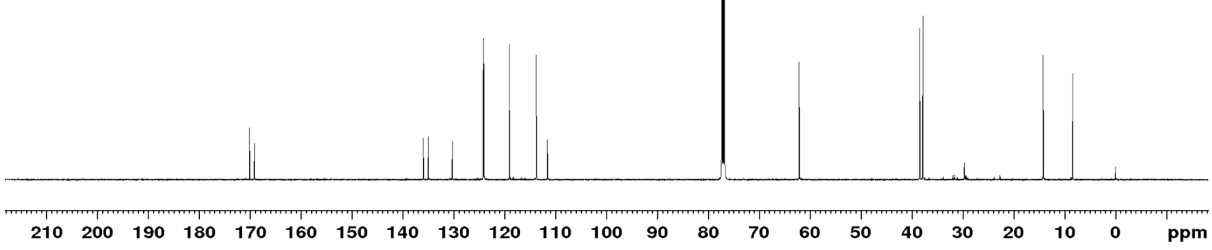


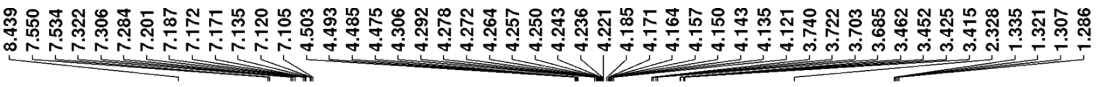


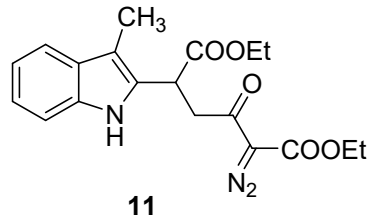


10

^{13}C NMR, $CDCl_3$, 125 MHz

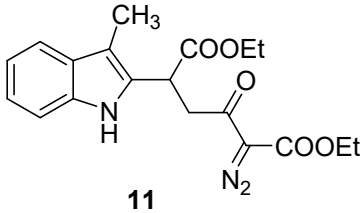






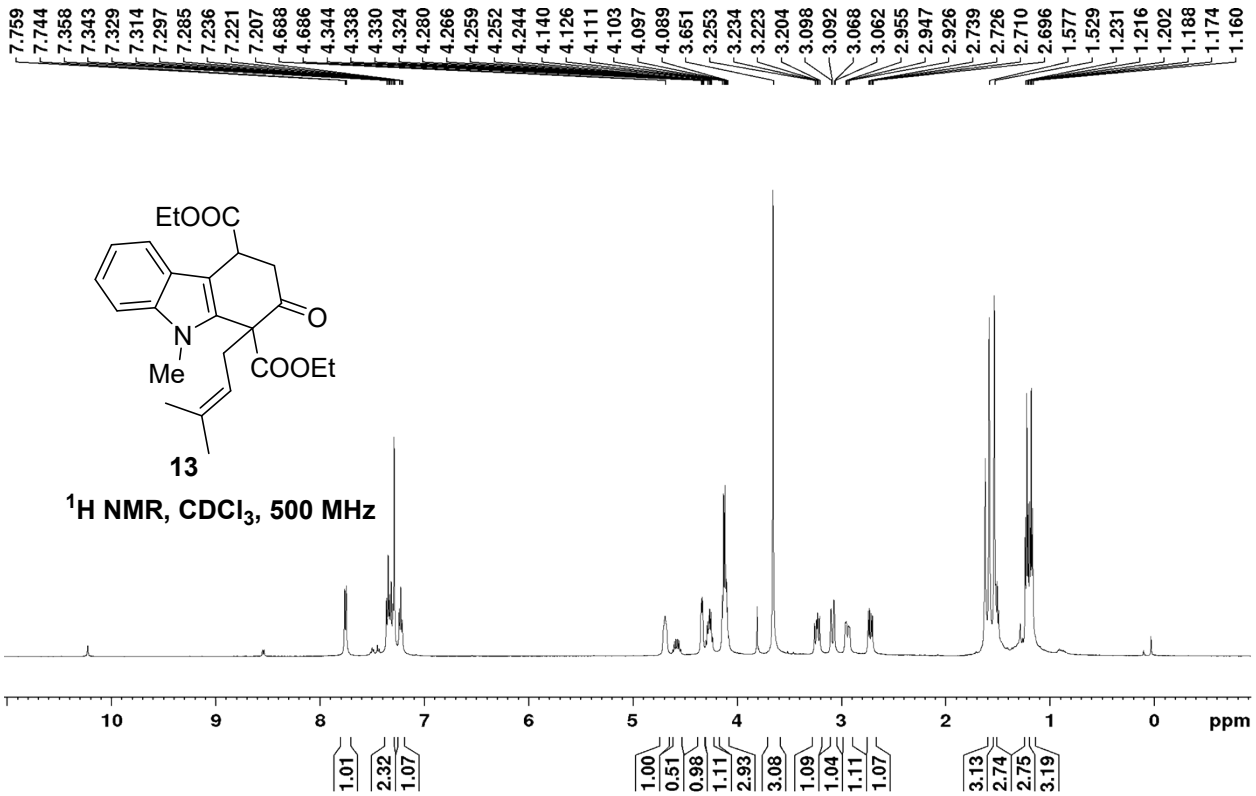
11

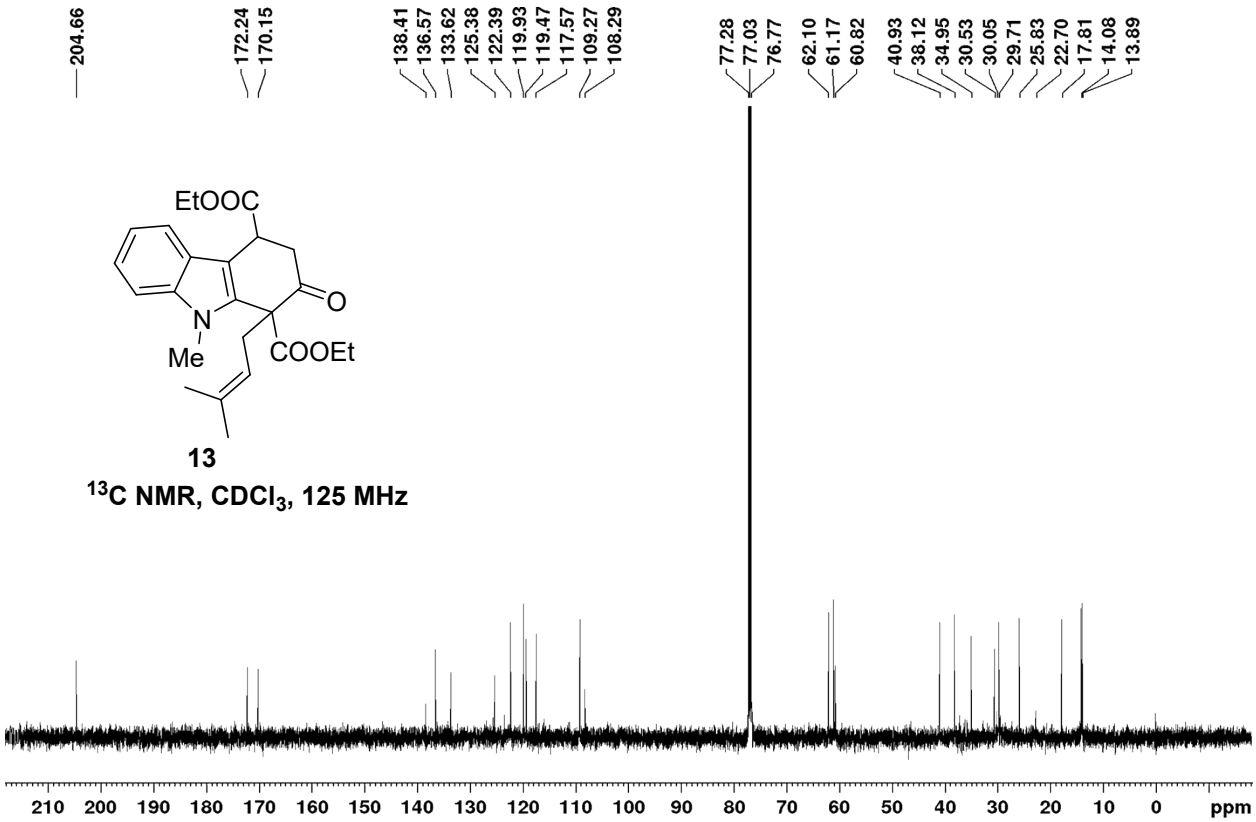
^{1}H NMR, $CDCl_3$, 500 MHz

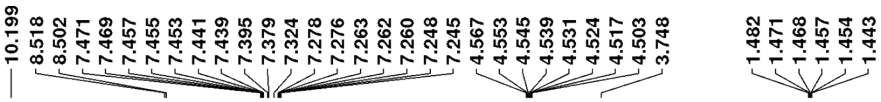


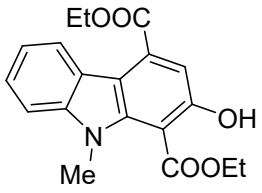
11

^{13}C NMR, $CDCl_3$, 125 MHz


7.759
7.744
7.358
7.343
7.329
7.314
7.297
7.285
7.236
7.221
7.207
4.688
4.686
4.344
4.338
4.330
4.324
4.280
4.266
4.259
4.252
4.244
4.140
4.126
4.111
4.103
4.097
4.089
3.651
3.253
3.234
3.223
3.204
3.098
3.092
3.068
3.062
2.955
2.947
2.926
2.739
2.726
2.710
2.696
1.577
1.529
1.231
1.216
1.202
1.188
1.174
1.160
EtOOC
O
N
Me
COOEt
13
1H NMR, CDCl3, 500 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
2.32
1.07
1.00
0.51
0.98
1.11
2.93
3.08
1.09
1.04
1.11
1.07
3.13
2.74
2.75
3.19

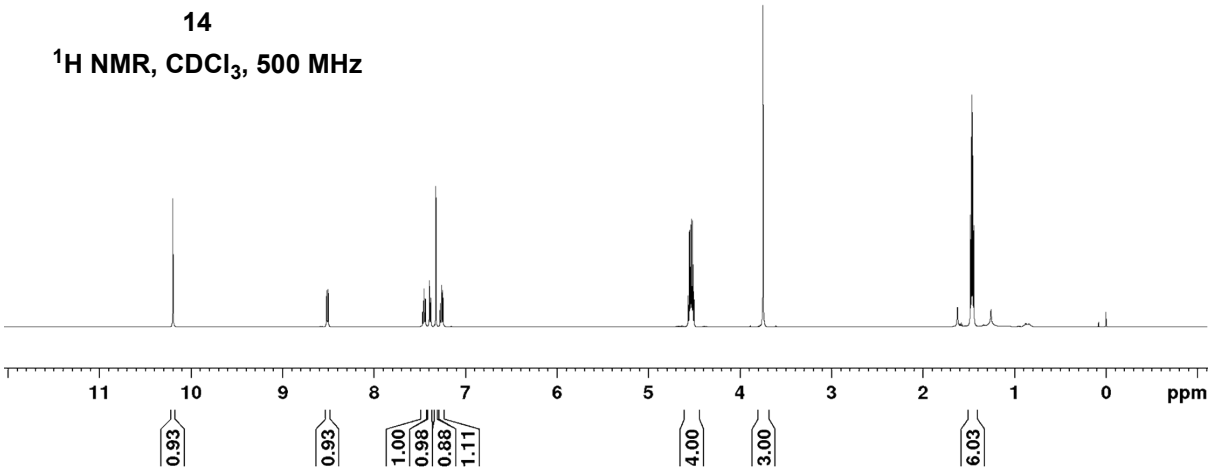

204.66
172.24
170.15
138.41
136.57
133.62
125.38
122.39
119.93
119.47
117.57
109.27
108.29
77.28
77.03
76.77
62.10
61.17
60.82
40.93
38.12
34.95
30.53
30.05
29.71
25.83
22.70
17.81
14.08
13.89
EtOOC
O
N
Me
COOEt
13
13C NMR, CDCl3, 125 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

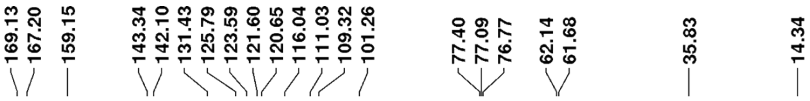


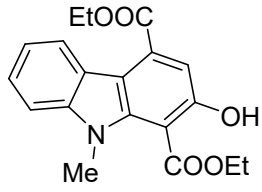


14

^{1}H NMR, $CDCl_3$, 500 MHz

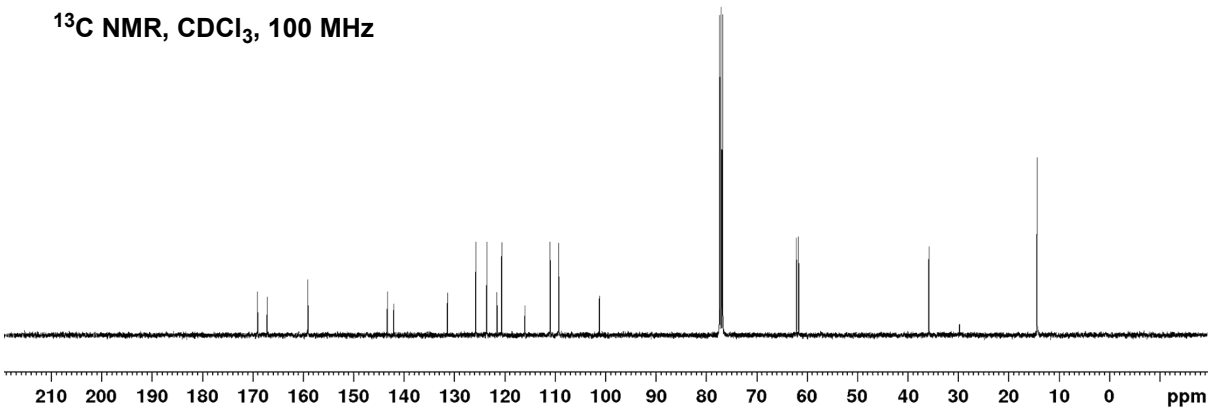


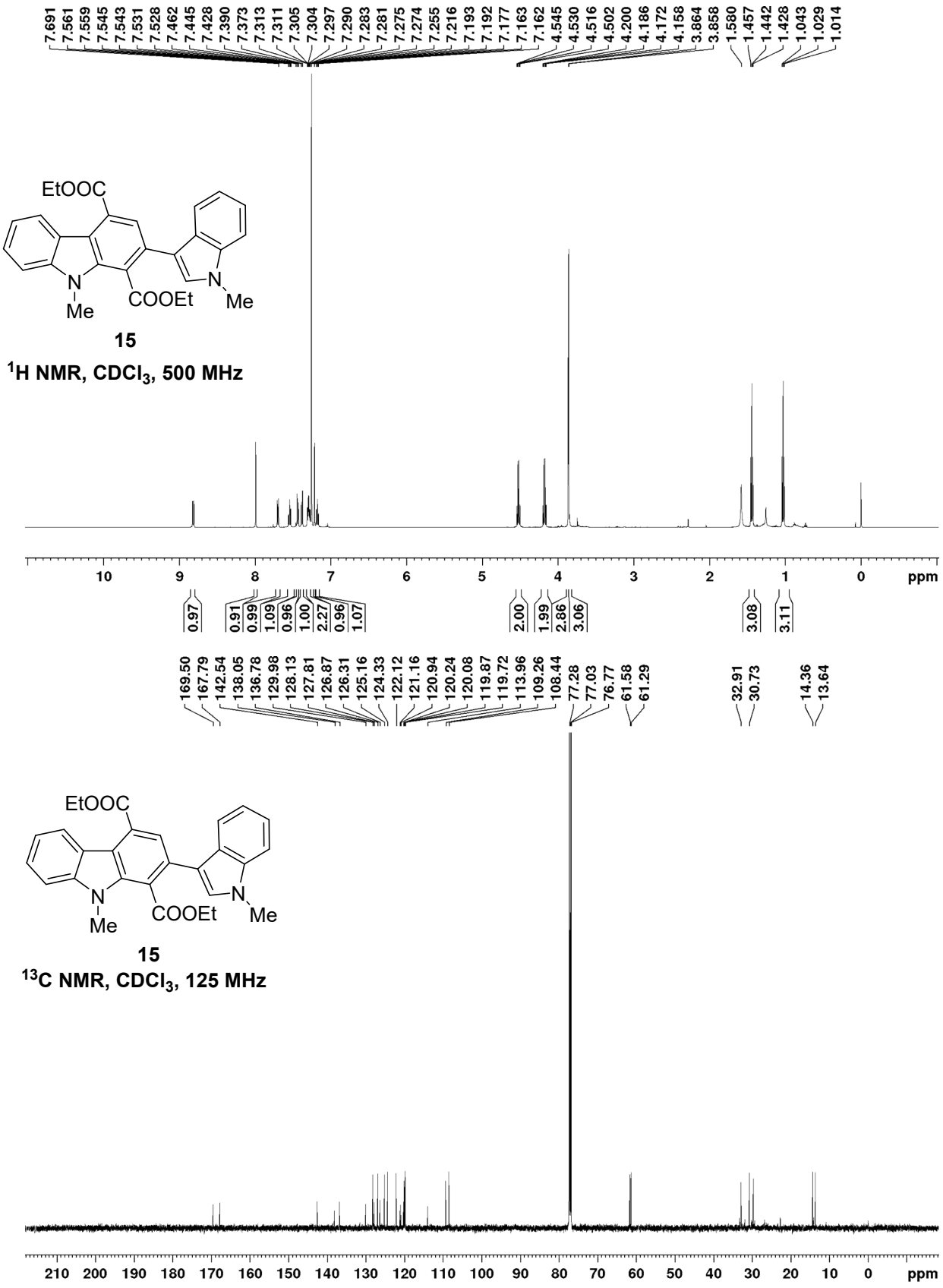




14

^{13}C NMR, $CDCl_3$, 100 MHz





15

^{1}H NMR, $CDCl_3$, 500 MHz

15

^{13}C NMR, $CDCl_3$, 125 MHz