Supporting Information

Regioselective Arene C–H Alkylation Enabled by Organic Photoredox Catalysis

Natalie Holmberg-Douglas, Nicholas P.R. Onuska and David A. Nicewicz*

Department of Chemistry, University of North Carolina at Chapel Hill, New Venable Laboratories, Chapel Hill, NC 27599-3290, USA

E-mail: nicewicz@unc.edu

Table of Contents:

General Reagent Information: Commercially available reagents were purchased from Sigma-Aldrich, Fischer Scientific or TCI Corporation and were used without further purification. Solvents used in photochemical reactions were dried *via* distillation over compatible drying agent (typically calcium hydride or activated 4Å molecular sieves). Dry solvents were then degassed *via* freeze-pump-thaw (4 cycles or until no bubbling was visible during thawing). Solvents were then stored in a nitrogen filled glovebox (O_2 levels < 10 ppm) and dispensed within the glovebox.

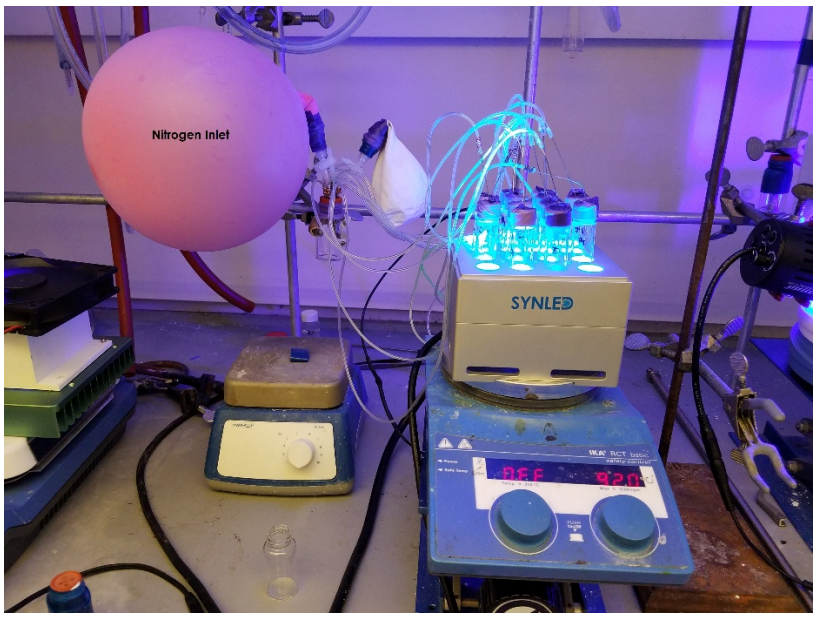
General Analytical Information: Proton and carbon (^{1}H and ^{13}C) magnetic resonance spectra were collected on a Bruker AVANCE III 600 CryoProbe (^{1} H NMR at 600 MHz and ^{13}C NMR at 151 MHz) spectrometer or Bruker AVANCE III 500 (^{1} H NMR at 500 MHz and ^{13}C NMR at 126 MHz) spectrometer. Unless otherwise noted, spectra are referenced to Chloroform-d (^{1} H NMR at 7.26 ppm and ^{13}C at 77.16 ppm) and reported as parts per million. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, ddddd = doublet of doublets of doublets of doublets of doublets, dt = doublet of triplets, ddt = doublet of doublets of triplets, td = triplet of doublets, tt = triplet of triplets, m = multiplet, q = quartet), coupling constants (Hz), and integration

High Resolution Mass Spectra (HRMS) were obtained via direct infusion using a Thermo LTQ FT mass spectrometer with positive mode electrospray ionization, via gas chromatography using an Exactive GC gas chromatographic system in positive mode chemical ionization, equipped with a Trace 1300 SSL injector and TriPlus RSH autosampler, or via liquid chromatography using Waters Acquity H-class liquid

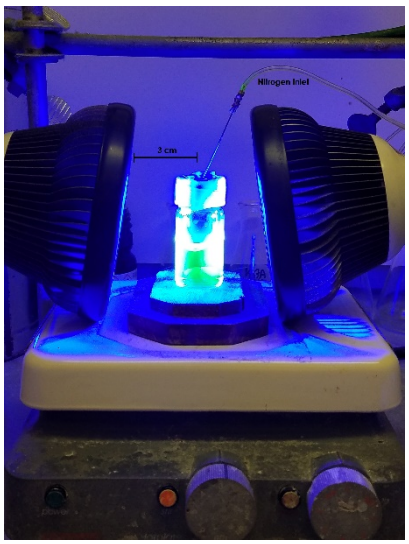
Electrochemical potentials were obtained with a standard set of conditions to main internal consistency. Cyclic voltammograms were collected with a Pine WaveNow Potentiostat. Data was analyzed using MATLAB by subtracting a background current prior to identifying the maximum current (Cp) and determining the potential (Ep/2) at half this value (Cp/2). The obtained value was referenced to Ag|AgCl and converted to SCE by subtracting 0.03 V. Samples were prepared with 0.1 mmol of analyte in 5 mL of 0.1 M tetra-(N)-butylammonium hexafluorophosphate in dry, degassed acetonitrile. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, 3.5 M NaCl silver-silver chloride reference electrode, and a scan rate of 100 mV/s. Reductions were measured by scanning potentials in the negative direction and oxidations in the positive direction.

Flash chromatography was performed using SiliaFlash P60 silica gel (40-63 μm) purchased from Silicycle.

General Photoreactor Configuration: All photochemical reactions were conducted using a SynLED Parallel Photoreactor, available for purchase from Sigma-Aldrich (item number: Z742680). The unit has bottom-lit LEDS (465-470 nm) with 130-140 lm intensity and a built-in cooling fan. The measured temperature range was 35 - 40°C. The reactor was fit to an IKA magnetic stirrer with round plate (item number: Z645052). Small stir bars are sometimes required for efficient stirring when using 2 dram vials. All reaction mixtures were kept under a positive pressure of nitrogen *via* an inlet needle which was routed to a standard Shlenk line, equip with a nitrogen source which feeds through a desiccant tube (Dririte/$CaCl_2$).

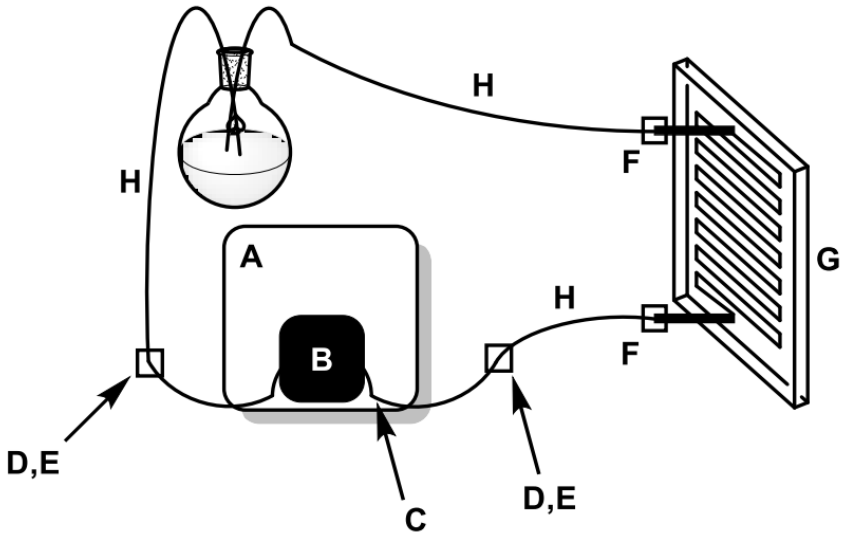


General Procedure for Photochemical Reactions: A flame-dried 2 dram borosilicate vial (purchased from Fisher Scientific, catalogue # 03-339-22D), equip with a stir bar, was charged with 3,6-Di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (0.05 equiv, 0.01 mmol). For solid/non-volatile substrates, the substrate (0.20 mmol) was then added. The vial was moved into a nitrogen filled glovebox (<10 ppm O_2) and acetonitrile (1.0 mL) and TFE (1.0 mL) were added via syringe. Ethyl diazoacetate (or other liquid diazo- compounds) was added via a microliter syringe (0.20 mmol, 1.0 equiv.). Vials were capped tightly with a Teflon lined phenolic resin septum cap (purchased through VWR international, Microliter Product # 15-0060K) and moved out of the glovebox. Prior to irradiation, vials were sealed with electrical tape to ensure maximal oxygen exclusion. The reaction vial was then placed into the reactor and equip with a nitrogen inlet needle. The reactions were irradiated for 18 hours unless otherwise noted. Following irradiation, the reaction mixture was concentrated under reduced pressure and the desired products were isolated *via* flash column chromatography (see substrate/product details for solvent information). *Unless otherwise noted, all reaction yields and regioisomer ratios are reported as the average of two separate trials (including chromatography)*. As regioisomers were extremely difficult to separate by conventional silica gel chromatography, NMR data for each regioisomer was determined from the mixture of compounds, utilizing 2-D NMR when required for peak assignments



General Procedure for Batch Reaction: A flame-dried 20 mL borosilicate vial (purchased from Chemglass Life Sciences, catalogue # CG-4904-01), equipped with a stir bar was charged with 3,6-Di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (0.05 equiv, 0.05 mmol). The vial was sealed with the PTFE faced septa and was then put under an inert atmosphere by evacuating under vacuum and refilling with nitrogen three times. A 1:1 mixture of MeCN and TFE was sparged to remove oxygen for fifteen minutes, then was transferred to the vial via cannula. Mesitylene (1.0 equiv., 1.0 mmol) and ethyldiazoacetate (1.0 equiv., 1.0 mmol) were added via microsyringe. Prior to irradiation, vials were sealed with electrical tape to ensure maximal oxygen exclusion. The reaction vial was then placed into the reactor and equip with a nitrogen inlet needle. The reactions were irradiated for 18 hours. Following irradiation, the reaction mixture was concentrated under reduced pressure and the desired products were isolated *via* flash column chromatography (see substrate/product details for solvent information). General Photoreactor Information: The photoreactor consists of two Par38 Royal Blue Aquarium LED lamps (Model #6851) angled towards the reaction wells for maximum LED exposure. The wells were placed on top of a stir plate for and the reactions were cooled with a fan. The measured temperature with cooling was 26 °C.

Large Scale Flow Synthesis of 1a:



A. Masterflex L/S Variable-Speed Drive (Cole-Parmer # EW-07528-30)

B. Masterflex L/S Rigid PTFE-Tubing Pump Head (Cole-Parmer # EW-77390-00)

C. Masterflex PTFE-tubing 4mm O.D. (Cole-Parmer # EW-77390-50)

D. 4MM PTFE Male NPT Compression Adapter (Cole-Parmer # WU-31321-62)

E. 1/8" O.D. to 1/8" PTFE Female NPT Compression Adapter (Cole-Parmer # EW31320-50)

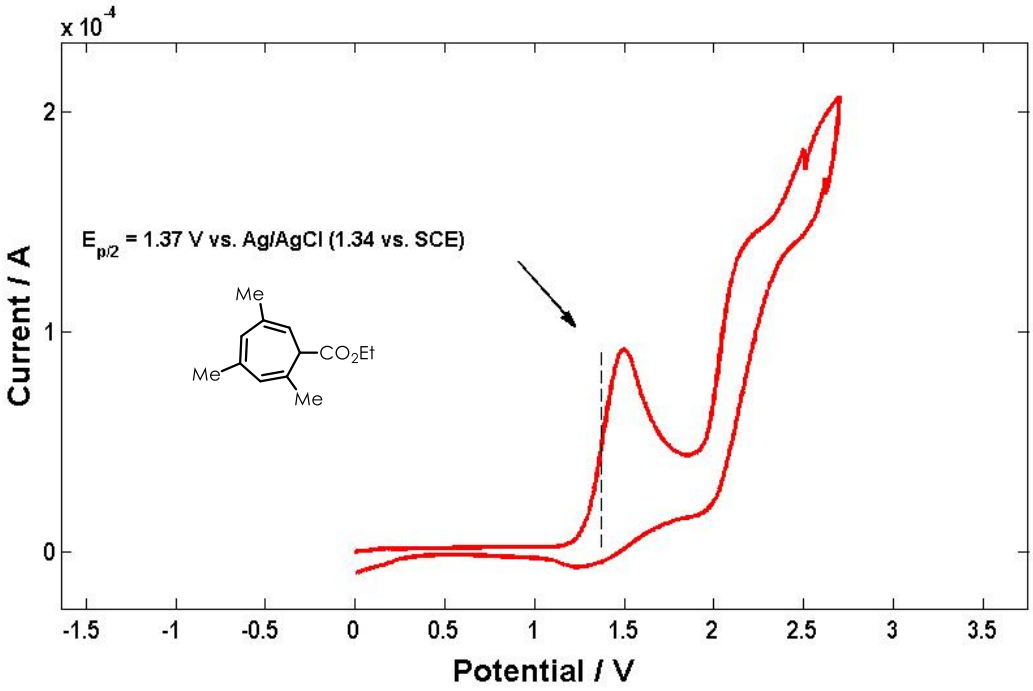
F. 1/4-28 flangeless fitting/ferrule for 1/8" O.D. tubing (Sigma-Aldrich SUPELCO # 58686)

G. Microreactor (Little Things Factory Gmbh # XXL-ST-02)

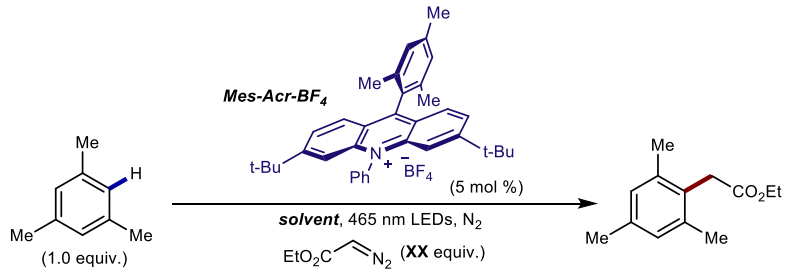
H. PTFE Tubing 1/16" I.D., 1/8" O.D. (Cole-Parmer # WU-06605-27)

A flame-dried, 100 mL pear flask was charged with 3,6-di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (143 mg, 0.05 Eq, 250 µmol) and degassed 1:1 MeCN:TFE (50 mL) . The resulting mixture was sparged with argon for five minutes. ethyl 2-diazoacetate (571 mg, 528 µL, 1.00 Eq, 5.00 mmol) followed by mesitylene (601 mg, 696 µL, 1.00 Eq, 5.00 mmol) were added via microsyringe. The flow cell was purged with 1:1 MeCN:TFE which was sparging with nitrogen prior to the introduction of the reaction mixture. Two 15W PAR38 blue LED floodlamps were positioned on either side of the microreactor (G). Tubing was introduced into the flask using a commercially available rubber septum which had been punctured. A nitrogen line was introduced into the headspace of the flask to ensure the complete exclusion of oxygen from the reaction mixture. The Masterflex L/S Variable-Speed Drive was set to 15 rpm and the occlusion bed of the pump head was adjusted as per the manufacturer's instructions. The floodlamps were then switched on and the reaction mixture was allowed to flow though the reactor for 18 hours. The temperature remained at ~35 ºC during the reaction, as measured at the center of the lamps, close to the flow cell using a conventional alcohol thermometer. Solvent was removed under reduced pressure and the resulting residue was purified via flash column chromatography (0->5% EtOAc/hexanes), yielding the desired product as a colorless oil (45%, 0.46 g).

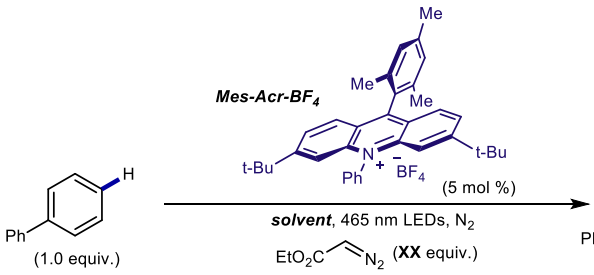
Electrochemical Data: Samples were prepared with 0.1 mmol of analyte in 5 mL of 0.1 M tetra-N-butylammonium hexafluorophosphate in dry, degassed acetonitrile. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, 3.5 M NaCl silver-silver chloride reference electrode, and a scan rate of 100 mV/s. Reductions were measured by scanning potentials in the negative direction and oxidations in the positive direction.


x 10^-4
2
1
0
Current / A
E_p/2 = 1.37 V vs. Ag/AgCl (1.34 vs. SCE)
Me
Me
Me
CO2Et
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
3
3.5
Potential / V

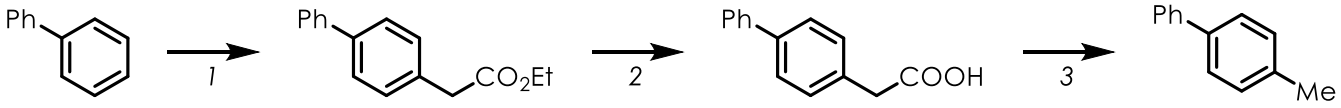
Optimization Data:



solvent (0.1 M)	*equiv. ethyl diaozacetate*	*yield*
MeOH	1.0	11%
MeCN	1.0	54%
DCE	1.0	31%
TFE	1.0	74%
TFE	2.0	31%
TFE	3.0	9.4%
TFE	4.0	<5%
TFE/MeCN	1.0	76%



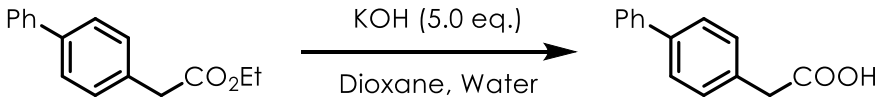
solvent	*equiv. ethyl diaozacetate*	*yield*
DCE/TFE (0.1 M), 1:1	1.0	56%
DCE/TFE (0.1 M), 1:2	1.0	36%
DCE/TFE (0.1 M), 2:1	1.0	21%
MeCN/TFE (0.1 M), 1:1	1.2	25%
MeCN/TFE (0.1 M), 1:1	1.4	16%
MeCN/TFE (0.1 M), 1:1	1.6	10%
MeCN/TFE (1:1), 1.25 eq. substrate	1.0	35%
MeCN/TFE (1:1), 1.50 eq. substrate	1.0	28%
MeCN/TFE (1:1), 1.75 eq. substrate	1.0	31%
MeCN/TFE (1:1), 2.00 eq. substrate	1.0	30%



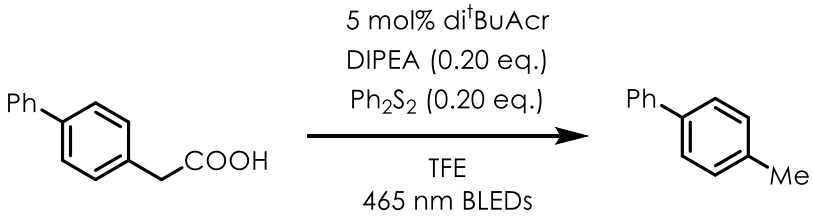
Procedure for Three Step Methylation:

1) Ethyl 2-([1,1'-biphenyl]-4-yl)acetate was prepared according to the general procedure (S3), 42% yield.

2) A 10 mL round bottom flask was charged with potassium hydroxide (47 mg, 5.0 eq., 0.832 mmol) and 0.10 mL water. Dioxane (1.6 mL) and ethyl 2-([1,1'-biphenyl]-4-yl)acetate (40.0



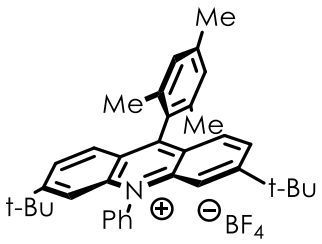
mg, 1.0 eq., 0.166 mmol) were added. This was heated at reflux for 18 hours. After, the solution was neutralized with 1 M HCl until pH ~7. The organics were extracted with diethyl ether (3 x 5 mL), washed once with brine, combined and dried over magnesium sulfate. This was filtered and concentrated to give the pure product, 2-([1,1'-biphenyl]-4-yl)acetic



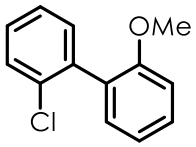
acid, as a white solid (27 mg, 76%). Spectral data matched that reported in the literature.[1]

3) The hydrodecarboxylation was performed according to the published procedure,[2] giving 4-methyl-1,1'-biphenyl as a white solid (70%). Spectral data matched that reported in the literature.[3]

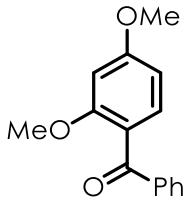
Catalyst and Substrate Synthesis:



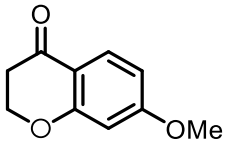
3,6-Di-tert-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate was prepared according to literature precedent. Spectral data matched that reported in the literature. [4]



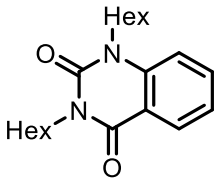
2-chloro-2'-methoxy-1,1'-biphenyl was prepared according to literature precedent. Spectral data matched that reported in the literature.[5]



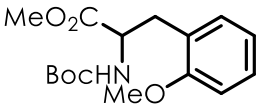
(2,4-dimethoxyphenyl)(phenyl)methanone was prepared according to literature precedent. Spectral data matched that reported in the literature.[4]



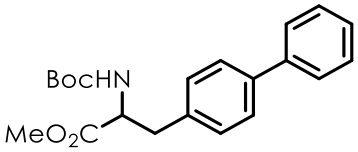
7-methoxychroman-4-one was prepared according to literature precedent. Spectral data matched that reported in the literature.[6]



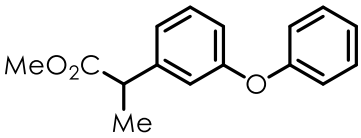
1,3-dihexanoylquinazoline-2,4(1H,3H)-dione was prepared according to literature precedent. Spectral data matched that reported in the literature.[5]



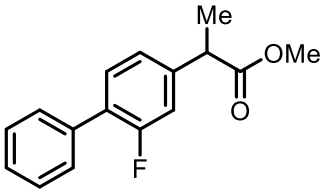
methyl 2-((tert-butoxycarbonyl)amino)-3-(2-methoxyphenyl)propanoate was prepared according to literature precedent. Spectral data matched that reported in the literature.[7]



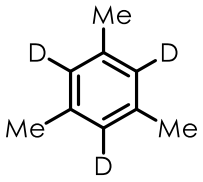
methyl 3-([1,1'-biphenyl]-4-yl)-2-((tert-butoxycarbonyl)amino) propanoate was prepared according to literature precedent. Spectral data matched that reported in the literature.[7]



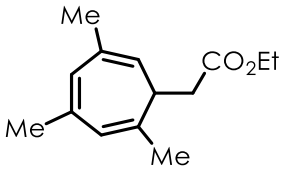
methyl 2-(3-phenoxyphenyl)propanoate was prepared according to literature precedent. Spectral data matched those previously reported in the literature.[8]



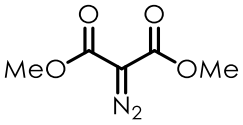
methyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate: A flame dried 25 mL RBF was charged with potassium carbonate (1.44 g, 5.1 Eq, 10.4 mmol), 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid (0.500 g, 1.00 Eq, 2.05 mmol) and DMF (5 mL). The reaction solution was cooled to 0 °C. Iodomethane (0.4 mL, 3.1 Eq., 6.36 mmol) was added dropwise over 5 minutes. The reaction was allowed to warm to room temperature while stirring overnight. After, the resulting reaction mixture was quenched with a saturated sodium bicarbonate solution. The organics were extracted with EtOAc (3x 15 mL), washed with brine (2x 30 mL) then a LiCl aqueous solution (2x 30 mL). The organics were combined, dried over magnesium sulfate, filtered and concentrated to give the crude mixture. This was purified via flash column chromatography with 5% EtOAc in Hexanes to give the pure product, a clear oil (0.3868 g, 73%). Spectral data matched that reported in the literature.[9]



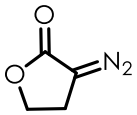
d_3-mesitylene was prepared according to literature precedent. Spectral data matched that reported in the literature. The final product was calculated to be 95.3% deuterated by using ^{1}H NMR integration of the methyl relative to residual aromatic protons with HMDSO as an internal standard.[10]



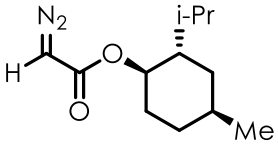
ethyl 2-(2,4,6-trimethylcyclohepta-2,4,6-trien-1-yl)acetate was prepared according to literature precedent. Spectral data matched that reported in the literature.[11]



dimethyl 2-diazomalonate was prepared according to literature precedent. Spectral data matched that reported in the literature.[12,13]

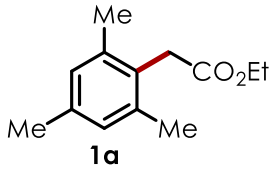


3-diazodihydrofuran-2(3H)-one was prepared according to literature precedent. Spectral data matched that reported in the literature.[14]



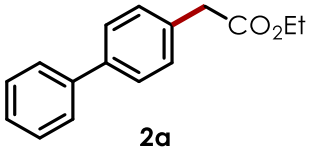
(-) Menthyl 2-diazoacetate was prepared according to literature precedent. Spectral data matched that reported in the literature.[15]

Procedure and Data for Product Synthesis:



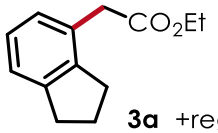
1a

Isolated by column chromatography (0-5% EtOAc in Hexanes) as a colorless oil, 76% yield. Spectral data matched reported literature values.[16]



2a

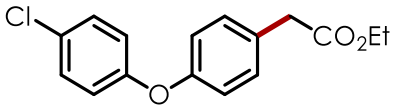
The desired product was isolated as a white solid, 42% yield, Spectral data matched reported literature values.[17]



3a +regioisomer

The desired product was isolated as a clear oil following flash column chromatography (3% EtOAc in hexanes) (24% yield) (NMR data for each individual isomer is not able to be reported due to overlapping signals. Regioisomeric ratio = 1:5 based on NMR ratios)

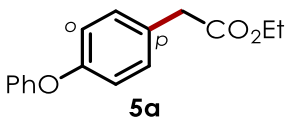
^{1}H NMR (500 MHz, Chloroform-*d*) □ 7.17 (d, *J* = 7.7 Hz, 1H), 7.15 (s, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.58 (s, 2H), 2.89 (q, *J* = 7.1 Hz, 4H), 2.10 – 2.00 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) □ 172.20, 144.84, 143.19, 131.94, 127.14, 125.39, 124.52, 60.94, 41.38, 32.90, 32.66, 25.62, 14.34.
^{13}C NMR (151 MHz, Chloroform-*d*) □ 172.07, 144.71, 143.06, 131.81, 127.01, 125.27, 124.39, 60.82, 41.27, 32.79, 32.54, 25.50, 14.23.
HRMS: Calculated (M+H): 205.1223; found: 205.1230



4a

The desired product was isolated as a clear oil following column chromatography (5% EtOAc in hexanes) as a clear oil (36% yield, n = 2). 4:1 ratio of para:ortho products. NMR characterization is given below for the major isomer.

^{1}H NMR (500 MHz, Chloroform-*d*) □ 7.31 – 7.25 (m, 5H), 6.99 – 6.93 (m, 4H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) □ 171.67, 155.93, 155.87, 130.74, 129.72, 129.40, 120.05, 119.49, 118.97, 60.97, 40.60, 14.22.
HRMS: Calculated (M+H): 291.0782; found: 291.0793

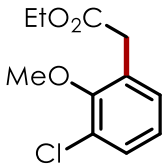


5a

Isolated by column chromatography (5% EtOAc in Hexanes) as a colorless oil, 29% yield (n=2), 5:1(para:ortho).

Para Isomer: **^{1}H NMR** (600 MHz, Chloroform-d) □ 1.25 – 1.29 (m, 3H), 3.59 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 6.94 – .96 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 7.09 (t J = 7.4 Hz, 1H), 7.21 – 7.27 (d, J = 8.1 Hz, 2H), 7.32 (t, J = 7.7, 5.5 Hz, 2H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 171.85, 157.26, 156.41, 130.70, 129.85, 123.38, 119.02, 119.01, 61.04, 40.74, 31.10, 14.33. **HRMS:** Calculated (M+H): 257.1172; found: 257.1151

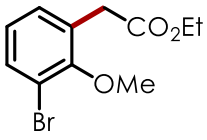
Ortho Isomer: **^{1}H NMR (600 MHz, Chloroform-d)** □ 1.17 (t, J = 7.1 Hz, 3H), 3.68 (s, 2H), 4.07 (q, J = 7.1 Hz, 2H), 6.88 (d, J = 8.1 Hz, 1H), 6.94 – 6.98 (app d, 1H), 7.09 (app t, 2H), 7.21 – 7.27 (m, 2H), 7.32 (3, 3H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 171.54, 157.44, 155.19, 131.61, 129.77, 129.04, 128.75, 126.19, 123.78, 123.14, 118.43, 60.91, 36.07, 14.27. **HRMS:** Calculated (M+H): 257.1172; found: 257.1151



6a

Isolated by column chromatography (10 to 30% EtOAc in Hexanes) as a colorless oil, 47% yield (n=2).

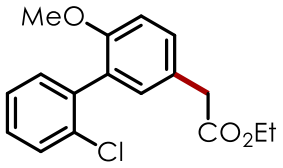
^{1}H NMR (600 MHz, Chloroform-d) □ 1.25 (d, J = 7.0 Hz, 3H), 3.52 (s, 2H), 3.89 (s, 3H), 4.15 (q, J = 7.1 Hz, 2H), 6.88 (d, J = 8.4 Hz, 1H), 7.14 (dd, J = 8.3, 2.1 Hz, 1H), 7.30 (d, J = 2.1 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 171.54, 154.20, 131.15, 128.69, 127.29, 122.43, 112.14, 77.37, 77.16, 61.14, 56.30, 40.28, 14.32. **HRMS:** Calculated (M+H): 229.0625; found: 229.0516



7a

Isolated by column chromatography (10% EtOAc in Hexanes) as a colorless oil, 33% yield (n=2).

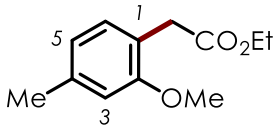
^{1}H NMR (600 MHz, Chloroform-d) □ 1.25 (t, J = 7.1 Hz, 4H), 3.52 (s, 2H), 3.88 (s, 3H), 4.15 (q, J = 7.1 Hz, 2H), 6.85 (d, J = 8.4 Hz, 1H), 7.19 (dd, J = 8.4, 2.2 Hz, 1H), 7.47 (d, J = 2.2 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 171.53, 155.07, 134.15, 129.45, 127.74, 111.96, 111.64, 61.13, 56.38, 40.15, 14.31. **HRMS:** Calculated (M+Na): 294.9940; found: 294.9951



8a

Isolated by column chromatography (10 % EtOAc in Hexanes) as a white solid, 55%. Spectra obtained as a mixture of rotational isomers.

^{1}H NMR (600 MHz, Chloroform-d) 1.28 (br app t, 3H), 3.63 (br s, 2H), 3.81 (br s, 3H), 4.14 – 4.26 (br app q, 2H), 6.98 (app d, J = 8.7, 3.8 Hz, 1H), 7.16 (s, 1H), 7.28 – 7.40 (m, 4H), 7.49 (app d, 1H). **^{13}C NMR (151 MHz, Chloroform-d)** 172.00, 156.84, 155.96, 137.84, 137.56, 134.05, 134.00, 132.03, 131.82, 131.79, 131.09, 130.16, 129.49, 129.43, 128.71, 128.66, 126.55, 126.03, 120.46, 111.17, 111.07, 60.98, 55.86, 55.76, 40.60, 31.11, 14.35. **HRMS:** Calculated (M+H); 305.0938, found: 305.0941



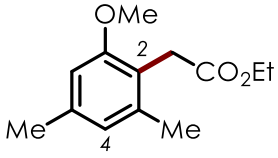
9a

The desired product was isolated as a mixture of three regioisomers following purification by column chromatography (7% EtOAc in hexane) as a clear oil , 57% yield (n = 2), 3.5:1.8:1.0 (***1:5:3***) (n=2).

*Regioisomer (1):***^{1}H NMR (500 MHz, Chloroform-*d*)** 7.06 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.69 (app. s, 1H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 3.58 (s, 2H), 2.35 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-d)** 172.27, 157.42, 138.60, 130.67, 125.21, 121.14, 111.51, 60.69, 55.45, 35.83, 21.73, 14.36. **HRMS:** Calculated (M+H): 209.1172; found: 209.1160

*Regioisomer (5):***^{1}H NMR (500 MHz, Chloroform-*d*)** 7.11 (d, *J* = 8.3 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.69 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.56 (s, 2H), 2.29 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** 172.02, 158.75, 138.32, 131.24, 120.18, 116.05, 111.22, 60.69, 55.29, 38.56, 20.05, 14.33. **HRMS:** Calculated (M+H): 209.1172; found: 209.1160

Regioisomer (3): **^{1}H NMR (500 MHz, Chloroform-*d*)** 7.15 (t, *J* = 7.9 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.70 (s, 2H), 2.29 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** 172.01, 157.74, 138.38, 127.80, 121.98, 111.22, 108.19, 60.89, 55.73, 32.09, 29.84, 14.29. **HRMS:** Calculated (M+H): 209.1172; found: 209.1160

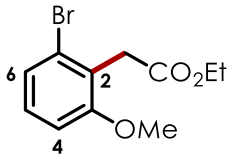


10a

The desired product was isolated as a mixture of two regioisomers following purification by column chromatography (3% EtOAc in hexane) as a clear oil , 48% yield (n = 2), 6.0:1.0 (***2:4***).

Regioisomer (2): **^{1}H NMR (500 MHz, Chloroform-*d*)** 6.64 (s, 1H), 6.57 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.65 (s, 2H), 2.31 (s, 3H), 2.25 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** 172.15, 157.69, 137.82 (d, *J* = 49.3 Hz), 123.41, 119.00, 113.55, 109.25, 60.61, 55.72, 31.84, 21.65, 19.78, 14.38. **HRMS:** Calculated (M+H): 223.1328; found: 223.1337

Regioisomer (4): **^{1}H NMR (500 MHz, Chloroform-*d*)** 6.61 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 3.61 (s, 2H), 2.31 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** 171.79, 158.18, 138.61, 124.17, 119.00, 60.79, 55.18, 34.90, 29.84, 20.75. **HRMS:** Calculated (M+H): 223.1328; found: 223.1337



11a

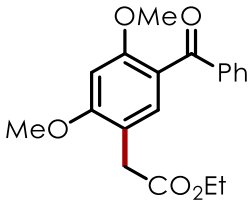
Isolated by column chromatography (10% EtOAc in Hexanes) as a colorless oil, 47% yield as a mixture of three regioisomers, 2.7:2.0:1.0 (**4:6:2**) (n=2)

Regioisomer (4): **^{1}H NMR (500 MHz, Chloroform-*d*)** □ 1.25 (t, 3H), 3.56 (s, 2H), 3.80 (s, 3H), 4.12 – 4.20 (q, 2H), 6.99 (s 1H), 7.05 (m, 2H).

Regioisomer (6): **^{1}H NMR (500 MHz, Chloroform-*d*)** □ 1.25 (t, 3H), 3.71 (s, 2H), 3.78 (s, 3H), 4.12 – 4.20 (q, 2H), 6.83 (dd, J = 8.5, 2.8 Hz, 1H), 7.04-7.20 (m, 2H).

Regioisomer (2): **^{1}H NMR (500 MHz, Chloroform-*d*)** □ 1.25 (t, 3H), 3.81 (3, 2H), 3.87 (s, 2H), 4.12 – 4.20 (q, 2H), 7.04-7.20 (m, 3H).

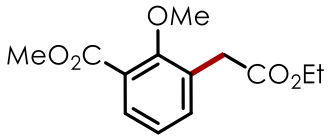
^{13}C NMR (126 MHz, Chloroform-*d*) □ 171.45, 171.07, 170.93, 159.32, 158.66, 158.24, 132.04, 131.90, 129.16, 126.45, 126.23, 125.30, 124.79, 123.90, 123.59, 122.39, 121.72, 118.09, 114.21, 113.75, 109.57, 77.16, 61.11, 60.89, 55.83, 55.66, 40.92, 35.71, 14.35, 14.34. **HRMS:** Calculated (M+H): 273.0120; found: 273.0128



12a

Isolated by column chromatography (20 to 30% EtOAc in Hexanes) as a white solid, 31% yield (n=2).

^{1}H NMR (600 MHz, Chloroform-d) □ 1.23 – 1.26 (t, 3H), 3.55 (s, 2H), 3.72 (s, 3H), 3.90 (s, 3H), 4.14 (q, J = 7.2 Hz, 2H), 6.49 (s, 1H), 7.29 (s, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.75 – 7.80 (d, J = 7.1 Hz, 2H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 195.51, 171.76, 161.17, 159.31, 138.97, 133.39, 132.43, 129.83, 129.80, 128.11, 120.46, 115.37, 95.30, 60.79, 55.96, 55.83, 35.32, 14.35. **HRMS:** Calculated (M+H): 329.1383; found: 329.1395

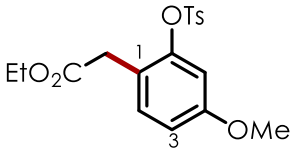


13a

The desired product was isolated as a single regioisomer following purification by column chromatography as a white solid (15% EtOAc in hexanes -> 20% EtOAc in hexanes), 63% yield (n = 2)

^{1}H NMR (500 MHz, Chloroform-*d*) □ 1.25 (d, J = 1.6 Hz, 4H), 3.63 (s, 2H), 3.88 (d, J = 2.8 Hz, 6H), 4.16 (q, J = 7.2 Hz, 2H), 6.89 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 2.2 Hz, 1H), 7.98 (dd, J = 8.6, 2.2 Hz, 1H). **^{13}C**

NMR □ 171.47, 166.95, 161.44, 132.64, 131.07, 123.37, 122.44, 109.98, 77.16, 60.91, 55.84, 52.05, 36.12, 29.85, 14.36. **HRMS:** Calculated (M+H): 253.1070; found : 253.1071

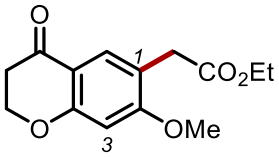


14a

The desired product was isolated as a mixture of two regioisomers following purification by column chromatography (15% EtOAc/in hexanes) as clear oil, 33% yield (n = 2), 2.3:1.0 (**1:3**) (n=2).

Regioisomer 1: **^{1}H NMR (500 MHz, Chloroform-d)** □ 7.72 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.55 (d, *J* = 2.3 Hz, 1H), 6.44 (dd, *J* = 8.2, 2.3 Hz, 1H), 4.21 – 4.10 (m, 2H), 3.70 (s, 3H), 3.54 (s, 2H), 2.44 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-d)**: □ 171.36, 158.08, 149.61, 145.36, 131.98, 131.03, 129.74, 128.61, 122.17, 113.76, 105.50, 60.76, 55.65, 35.47, 21.74, 14.20 **HRMS:** Calculated (M+H): 365.1053; found: 365.106

Regioisomer 3: **^{1}H NMR (500 MHz, Chloroform-d)**: δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 1H), 6.78 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.60 (d, *J* = 2.6 Hz, 1H), 4.17 – 4.03 (m, 2H), 3.70 (s, 3H), 3.41 (s, 2H), 2.45 (s, 3H), 1.29 – 1.13 (m, 3H).f**^{13}C NMR (126 MHz, Chloroform-d)**: δ 171.28, 159.69, 148.81, 145.93, 133.13, 132.75, 130.22, 128.87, 120.15, 113.53, 108.49, 61.28, 55.85, 35.25, 22.09, 14.51. **HRMS:** Calculated (M+H): 365.1053; found: 365.1063

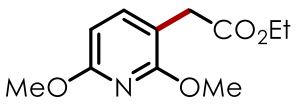


15a

Isolated by column chromatography (30% EtOAc in Hexanes) as a white solid, 50% yield, 3.8:1 (***1:3***) (n=2).

Regioisomer 1: **^{1}H NMR (600 MHz, Chloroform-d)** □ 1.25 (t, J = 7.1 Hz, 3H), 2.75 (t, 2H), 3.54 (s, 2H), 3.84 (s, 3H), 4.15 (q, 2H), 4.52 (t, 2H), 6.39 (s, 1H), 7.70 (s, 1H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 190.54, 171.57, 164.06, 163.55, 129.49, 118.05, 114.67, 99.05, 67.60, 60.89, 56.06, 37.49, 35.57, 14.37. **HRMS:** Calculated (M+H): 287.0889; found: 287.0898

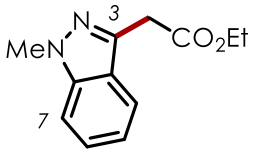
Regioisomer 3: **^{1}H NMR (600 MHz, Chloroform-d)** □ 1.25 (app t, 3H), 2.75 (app t, 2H), 3.66 (s, 2H), 3.88 (s, 3H), 4.15 (app q, 2H), 4.52 (app t, 2H), 6.63 (d, J = 8.9 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 191.17, 171.60, 163.44, 160.96, 128.07, 115.79, 110.96, 104.81, 67.53, 60.82, 56.16, 37.59, 28.74, 14.40. **HRMS:** Calculated (M+H): 287.0889; found: 287.0898



16a

The desired product was isolated as clear oil following purification by column chromatography (5% EtOAc in hexanes), 21% yield(n=2).

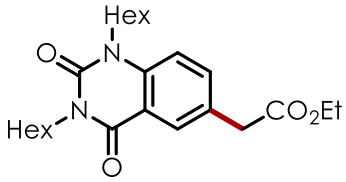
^{1}H NMR (500 MHz, Chloroform-*d*) □ 7.40 (d, *J* = 7.9 Hz, 1H), 6.29 (d, *J* = 7.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 3.52 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** □ 171.88, 162.40, 160.64, 141.93, 108.03, 100.44, 60.87, 53.71, 53.53, 34.65, 14.36. **HRMS:** Calculated (M+H): 226.1073; found: 226.1077



17a

The desired product was isolated as a mixture of regioisomers following purification by column chromatography (15% EtOAc in hexanes -> 20% EtOAc in hexanes) as a white solid, 23% yield (n =2), 10:1 (**3:7**). Spectral data for minor isomer is not reported due to the low concentration of this product in the obtained mixture (some signals corresponding to this product are visible in proton NMR data and were used to determine the ratio of regioisomers).

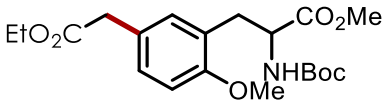
Regioisomer 3: **^{1}H NMR (500 MHz, Chloroform-*d*)**: □ 7.71 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.32 (m, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.04 (s, 3H), 4.00 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, Chloroform-*d*)** □ 170.54, 137.88, 126.52, 122.97, 120.65, 120.43, 109.15, 61.27, 35.50, 33.76, 29.84, 14.33. **HRMS:** Calculated (M+H): 219.1128; found: 219.1138



18a

Isolated by column chromatography (0 to 10% EtOAc in Hexanes) as a colorless oil, 13% yield (n=2).

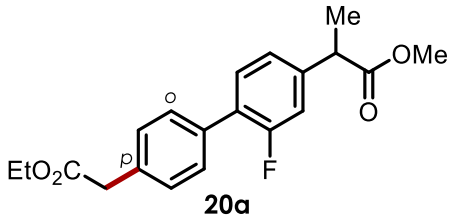
^{1}H NMR (600 MHz, Chloroform-d) □ 0.87 – 0.90 (m, 6H), 1.26 (d, J = 7.1 Hz, 3H), 1.30 – 1.37 (m, 12H), 1.65 – 1.73 (m, 5H), 3.67 (s, 2H), 4.05 – 4.11 (m, 4H), 4.15 – 4.18 (m, 2H), 7.14 (d, J = 8.6 Hz, 1H), 7.60 (dd, J = 8.6, 2.3 Hz, 1H), 8.11 (d, J = 2.2 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 171.31, 161.68, 150.77, 138.99, 136.12, 129.70, 128.83, 115.89, 114.02, 61.30, 43.95, 42.11, 40.38, 31.67, 31.61, 27.91, 27.42, 26.80, 26.62, 22.73, 22.72, 14.34, 14.22, 14.17. **HRMS:** Calculated (M+H): 445.2333; found: 445.2322



19a

Isolated by column chromatography (20% EtOAc in Hexanes) as a clear oil , 37% yield (n=2).

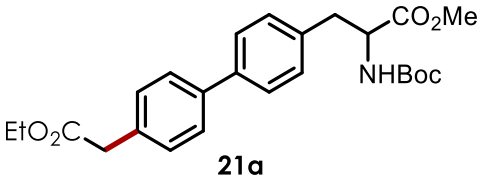
^{1}H NMR (600 MHz, Chloroform-d) □ 1.25 (t, J = 7.1 Hz, 3H), 1.38 (s, 9H), 3.04 (dd, J = 6.7, 3.1 Hz, 1H), 3.51 (s, 2H), 3.70 (s, 3H), 3.81 (s, 3H), 4.13 (q, J = 7.1 Hz, 2H), 4.48 (q, J = 7.3 Hz, 1H), 5.23 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 8.3 Hz, 1H), 7.00 (d, J = 2.3 Hz, 1H), 7.14 (d, J = 2.3 Hz, 1H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 172.97, 171.94, 156.84, 155.38, 132.20, 129.27, 126.30, 124.93, 110.60, 79.70, 60.95, 55.55, 54.22, 52.22, 40.56, 32.88, 28.41, 14.34. **HRMS:** Calculated (M+Na): 418.1836; found: 418.1847



20a

Isolated by column chromatography (10% EtOAc in Hexanes) as a white solid , 28% yield (n=2), 7.2:1 (**p:o**). Spectral data for minor isomer is not reported due to the low concentration of this product in the obtained mixture (some signals corresponding to this product are visible in proton NME data and were used to determine the ratio of regioisomers).

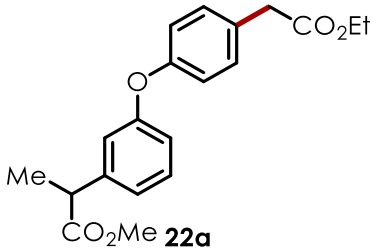
^{1}H NMR (600 MHz, Chloroform-*d*) □ 7.51 – 7.47 (m, 2H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.14 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.11 (dd, *J* = 11.5, 1.8 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.76 (q, *J* = 7.1 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 2H), 1.53 (d, *J* = 7.1 Hz, 3H), 1.27 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (151 MHz, Chloroform-*d*)** □ 174.58, 171.66, 159.81 (d, *J* = 248.3 Hz), 141.91 (d, *J* = 7.7 Hz), 134.38, 133.72, 130.87 (d, *J* = 3.9 Hz), 129.51, 129.23 (d, *J* = 2.8 Hz), 127.57 (d, *J* = 13.7 Hz), 123.67 (d, *J* = 3.3 Hz), 115.37 (d, *J* = 23.6 Hz), 61.11, 52.39, 45.03, 41.23, 18.57, 14.33. **HRMS:** Calculated (M+Na): 367.1316; found: 367.1332



21a

Isolated by column chromatography (20% EtOAc in Hexanes) as a white solid, 17% yield.

^{1}H NMR (600 MHz, Chloroform-d) □ 1.26 (t, J = 7.3 Hz, 3H), 1.42 (s, 9H), 3.05 – 3.20 (m, 2H), 3.65 (s, 2H), 3.74 (s, 3H), 4.17 (d, J = 7.1 Hz, 2H), 4.62 (q, J = 6.6 Hz, 1H), 5.01 (d, J = 8.5 Hz, 1H), 7.19 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.48 – 7.59 (m, 4H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 172.49, 171.75, 155.23, 139.66, 139.62, 135.17, 133.30, 129.87, 129.82, 127.29, 127.29, 80.12, 61.10, 54.49, 52.44, 41.17, 38.11, 28.44, 14.35. **HRMS:** Calculated (M+Na): 464.2043; found: 464.2057

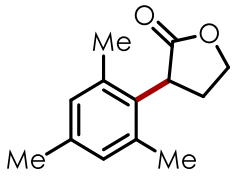


22a

Isolated by column chromatography (4% EtOAc in Hexanes) as a white semisolid in a 2:1 mixture of para/ortho isomers, 32% yield (n=2). NMR data is reported for the mixture of isomers – some trace impurities are present

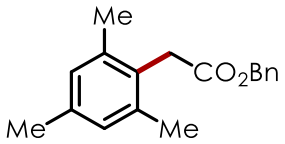
^{1}H NMR (600 MHz, Chloroform-*d*): □ 7.39 – 7.17 (m, 6H), 7.15 – 6.95 (m, 7H), 6.92 – 6.88 (m, 1H), 6.87 – 6.78 (m, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.10 (dq, *J* = 9.5, 7.1 Hz, 1H), 3.73 – 3.63 (m, 8H), 3.61 (s, 2H), 1.50 (d, *J* = 7.1 Hz, 3H), 1.45 (d, *J* = 7.2 Hz, 1H), 1.28 (dd, *J* = 8.8, 5.5 Hz, 3H), 1.19 (td, *J* = 7.2, 3.1 Hz, 2H).
^{13}C NMR (151 MHz, Chloroform-*d*): □ 174.79, 174.72, 171.84, 171.51, 157.53, 157.44, 156.17, 155.04, 142.60, 142.52, 141.42, 141.39, 130.72, 129.96, 129.90, 129.86, 129.79, 126.12, 125.04, 123.82, 123.13,

122.87, 122.42, 122.21, 119.05, 118.26, 118.21, 117.43, 61.05, 60.94, 52.25, 45.37, 45.15, 40.74, 36.04, 35.72, 18.63, 18.57, 14.32, 14.26.
HRMS: Calculated (M+Na): 365.1359; found: 365.1367



1b

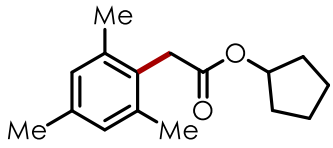
Isolated by column chromatography (10% EtOAc in Hexanes) as a colorless oil, 61% yield (n=2). Spectral data matched reported literature values.[18]



1c

Isolated by column chromatography (0-5% EtOAc in Hexanes) as a colorless oil, 44% yield (n=2).

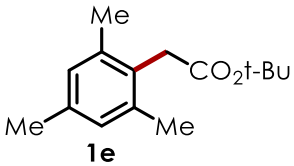
^{1}H NMR (600 MHz, Chloroform-d) □ 2.27 (s, 3H), 2.28 (s, 6H), 3.71 (s, 2H), 5.13 (s, 2H), 6.87 (s, 2H), 7.30 – 7.39 (m, 5H). **^{13}C NMR (151 MHz, Chloroform-d)** □ 171.48, 137.13, 136.66, 136.13, 129.03, 128.63, 128.58, 128.25, 128.15, 66.56, 53.58, 35.15, 22.29, 20.37. **HRMS:** Calculated (M+Na): 291.1355; found: 291.1365



1d

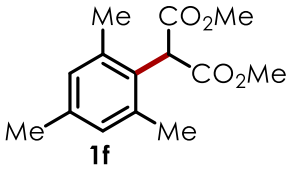
Isolated by column chromatography (0-5% EtOAc in Hexanes) as a colorless oil, 39% yield (n=2).

^{1}H NMR (600 MHz, Chloroform-d) □ 1.26 – 1.32 (m, 2H), 1.57 (m, 2H), 1.66 (m, 4H), 1.79 – 1.85 (m, 2H), 2.26 (s, 3H), 2.29 (s, 6H), 3.60 (s, 2H), 5.16 (dt, J = 6.0, 3.4 Hz, 1H), 6.86 (s, 2H). **^{13}C NMR (151 MHz, Chloroform-d)**) □ 171.43, 137.06, 136.41, 128.99, 128.94, 77.43, 35.50, 32.76, 23.80, 21.03, 20.35. **HRMS:** Calculated (M+H): 269.1511; found: 269.1515



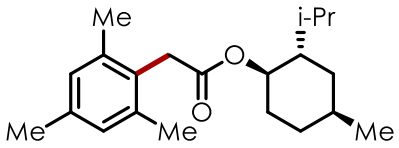
1e

Isolated by column chromatography (0-5% EtOAc in Hexanes) as a colorless oil, 57% yield (n=2). Spectral data matched reported literature values.[19]



1f

Isolated by column chromatography (0-10% EtOAc in Hexanes) as a colorless oil, 19% yield (n=2). Spectral data matched reported literature values.[20]



1g

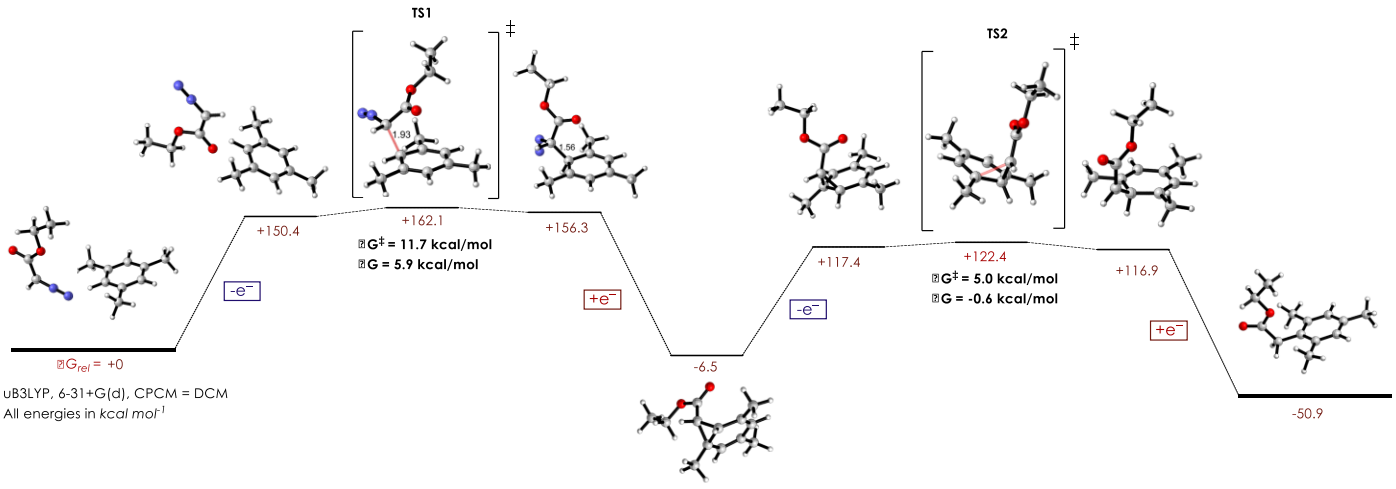
Isolated by column chromatography (0-2.5% EtOAc in Hexanes, stained with CAM) as a colorless oil, 45% yield (n=2).

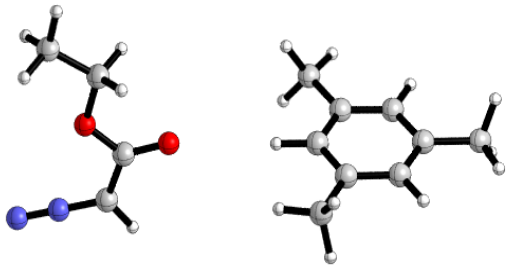
^{1}H NMR (600 MHz, Chloroform-d) □ 0.70 (d, J = 7.0 Hz, 3H), 0.84 (d, J = 7.1 Hz, 3H), 0.89 (d, J = 6.6 Hz, 3H), 0.91 – 1.07 (m, 3H), 1.32 (t, J = 11.6 Hz, 1H), 1.46 (dd, J = 16.8, 10.5 Hz, 1H), 1.65 (dt, J = 13.8, 7.6 Hz, 2H), 1.74 (d, J = 2.5 Hz, 1H), 1.98 (d, J = 11.4 Hz, 1H), 2.27 (d, J = 15.2 Hz, 9H), 3.63 (d, J = 3.0 Hz, 2H), 4.67 (td, J = 10.9, 4.4 Hz, 1H), 6.85 (s, 2H).**^{13}C NMR (151 MHz, Chloroform-d)** □ 171.19, 137.02, 136.39, 129.00, 128.90, 74.54, 47.17, 40.91, 35.46, 34.35, 31.48, 26.26, 23.42, 22.17, 21.03, 20.87, 20.32, 16.32. **HRMS:** Calculated(M+Na): 339.2294; found: 339.2164

Computational Details

All computations were performed using the Gaussian 9 software package at the UB3LYP level of theory using the 6-31+G(d) basis set with solvation in dichloromethane evaluated in a self-consistent reaction field (SCRF) with the PCM model. All obtained geometries were verified as minima by ensuring that they possess no negative vibrational frequencies. Transition states were calculated using the QST2 method. All transition states were verified as local maxima by ensuring that they possessed one negative vibrational mode, and confirming that this vibrational mode corresponds to the bond forming/bond breaking event in question. Transition states were confirmed using IRC calculations, which resulted in optimized product and starting material geometries which matched those submitted in the QST2 calculation. Free energies at 298.15 K were calculated using scaled vibrational frequencies. In cases where rotational isomers may exist, verification of the minimized geometry was accomplished by conducting a scan of dihedral angles corresponding to the proposed rotamers and comparing these energies to those of the previously optimized geometry.

Cartesian coordinates, thermally corrected free energies, and entropy values for all optimized geometries are given below. The complete computed reaction pathway is illustrated below for reference. All values of Gibbs free energy are given in kcal/mol, relative to the starting structure (neutral ethyl diazoacetate and mesitylene). Images were generated using the CYLview program.

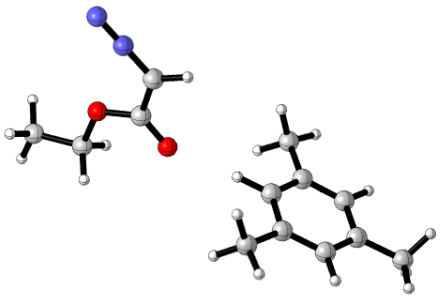




EE + Thermal Free Energy Correction: -765.961078 Hartree

Entropy = 178.382 cal mol^{-1} K^{-1}

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	C				-2.8314	0.6297	-1.0443
2	C	1.3979453			-4.2293	0.6308	-1.0331
3	C	1.4070432	121.494371		-4.9567	-0.007	-0.0114
4	C	1.3979455	118.474882	-0.0264526	-4.2494	-0.652	1.0074
5	C	1.4068836	121.50354	-0.0043475	-2.8428	-0.6729	1.0264
6	C	1.3982139	118.575327	0.0239836	-2.1504	-0.0291	-0.0037
7	H	1.0891737	119.315148	-179.975486	-4.7686	1.1367	-1.8328
8	H	1.0893248	119.303927	-179.980573	-4.799	-1.1504	1.805
9	H	1.0891301	119.382134	179.991935	-1.0613	-0.037	-0.0019
10	C	1.5131722	120.34408	179.909472	-6.4697	0.0121	-0.0239
11	H	1.0974324	111.316676	58.7053679	-6.8668	-0.4393	-0.942
12	H	1.0949723	111.373904	179.137364	-6.8828	-0.5389	0.8274
13	H	1.0975553	111.30313	-60.4865316	-6.8559	1.0385	0.0206
14	C	1.5132252	120.289995	-179.903435	-2.105	-1.3813	2.1416
15	H	1.0948338	111.386738	-179.269218	-1.0203	-1.296	2.0199
16	H	1.0974698	111.318552	-58.820444	-2.3679	-0.964	3.122
17	H	1.0975728	111.293648	60.3435463	-2.3572	-2.4491	2.171
18	C	1.5131921	121.115363	-179.915883	-2.0577	1.32	-2.1464
19	H	1.0975477	111.305651	119.589115	-1.4155	2.1146	-1.7454
20	H	1.0973677	111.332443	-121.226278	-1.4025	0.6163	-2.6753
21	H	1.0950701	111.379665	-0.7843466	-2.7299	1.772	-2.8833
22	C	5.8080126	116.677148	-161.532206	3.4085	-1.5376	-0.7494
23	H	1.0812335	66.8278606	75.0517232	2.7133	-2.2822	-1.1118
24	N	1.3085539	176.129169	-108.744412	4.6836	-1.7983	-0.8853
25	N	1.1361286	179.815074	2.4982451	5.7915	-2.0214	-1.0018
26	C	1.4528567	55.3678731	-104.672843	2.9646	-0.2973	-0.1367
27	O	1.2264522	122.871675	0.2591099	1.7804	-0.0133	0.0089
28	O	1.3488259	112.842776	-179.705781	3.9882	0.4931	0.2465
29	C	1.4556175	117.088947	-179.988084	3.6473	1.762	0.873
30	H	1.0939604	108.312402	59.425263	3.0578	1.5546	1.7709
31	H	1.0937974	108.334889	-58.2063726	3.0304	2.3355	0.1752
32	C	1.5161178	107.49944	-179.408067	4.9461	2.473	1.1989
33	H	1.0957083	109.187348	-179.906547	4.721	3.434	1.6747
34	H	1.0951741	111.138892	-60.5499745	5.5569	1.8826	1.8901
35	H	1.0951996	111.129048	60.7354875	5.5283	2.6671	0.2918

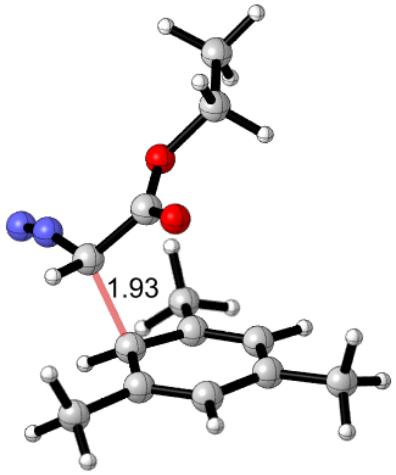


EE + Thermal Free Energy Correction: -765.721331 Hartree

Entropy = 168.135 cal mol^{-1} K^{-1}

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	C				2.4923	-0.3682	-1.1956
2	C	1.3770628			3.8691	-0.3422	-1.2025
3	C	1.4425676	121.49107		4.6224	-0.0073	-0.0187
4	C	1.4172257	119.833028	0.0867703	3.9424	0.3022	1.1856
5	C	1.3795927	120.526324	-0.0536421	2.5638	0.2871	1.2357
6	C	1.4255578	117.31832	-0.0432968	1.8381	-0.0513	0.0307
7	H	1.0864864	120.370938	179.949901	4.4184	-0.5763	-2.1102
8	H	1.0854367	119.064372	179.91617	4.5216	0.5511	2.0692
9	H	1.0897462	119.104039	-179.964942	0.7491	-0.0636	0.0691
10	C	1.4855863	118.907732	-179.793059	6.1061	0.0078	-0.092
11	H	1.1006635	109.84654	59.5459508	6.4355	0.7372	-0.8476
12	H	1.0911833	112.616357	-178.541665	6.5711	0.2487	0.8653
13	H	1.0998057	110.078575	-56.1597082	6.4767	-0.9662	-0.4435
14	C	1.4955955	122.904211	179.96908	1.7924	0.604	2.4772
15	H	1.0981272	110.358564	-121.235198	1.1557	-0.2453	2.7586
16	H	1.0921543	111.746441	0.1028779	2.4525	0.8438	3.3136
17	H	1.0980545	110.40585	121.471736	1.1172	1.4521	2.3024
18	C	1.5038114	122.832704	179.967373	1.6772	-0.7123	-2.4116
19	H	1.0965233	110.639557	121.204285	1.0382	-1.5815	-2.2153
20	H	1.0965571	110.620908	-120.327047	1.0152	0.1194	-2.6808
21	H	1.0927596	111.32077	0.4059232	2.3172	-0.9376	-3.2682
22	C	4.8995908	116.186916	155.822942	-2.7522	1.622	-0.337
23	H	1.0810984	60.8476395	-83.2998258	-1.9288	2.3115	-0.461
24	N	1.309962	176.368218	-29.2728119	-3.9593	2.1007	-0.5095
25	N	1.1353217	179.865642	129.331106	-5.0065	2.5132	-0.6584
26	C	1.4509076	61.5765857	99.8849116	-2.5512	0.2264	0.0051
27	O	1.2286856	122.888926	3.2527502	-1.4381	-0.2651	0.1757
28	O	1.3460335	112.988167	-176.74778	-3.7042	-0.4597	0.1131
29	C	1.4563057	117.291715	179.972746	-3.6111	-1.8726	0.4535
30	H	1.0937992	108.280538	59.1070736	-3.099	-1.9606	1.416
31	H	1.0938441	108.290227	-58.5105672	-3.0072	-2.3707	-0.3105
32	C	1.5160303	107.449337	-179.693563	-5.0234	-2.421	0.5084

33	H	1.095701	109.186871	-179.995096	-4.9865	-3.486	0.7633
34	H	1.0951558	111.138836	-60.6303961	-5.6177	-1.906	1.2706
35	H	1.0951245	111.127185	60.6428809	-5.5252	-2.3168	-0.4594

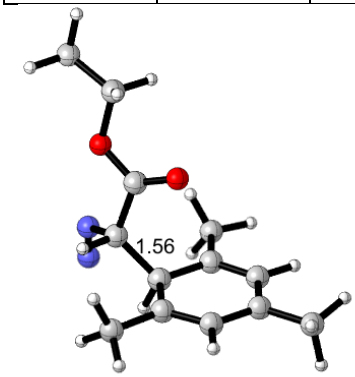


EE + Thermal Free Energy Correction: --765.702786

Entropy = 147.572 cal mol^{-1} K^{-1}

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	C				2.1384	0.8982	-0.4187
2	C	1.3782901			2.6678	-0.3689	-0.5365
3	C	1.4148372	121.888552		2.2408	-1.4369	0.2874
4	C	1.4171957	119.106886	-2.9265527	1.2858	-1.1844	1.3036
5	C	1.3785091	122.055699	2.6816757	0.7177	0.059	1.4811
6	C	1.4622644	118.84203	-3.6913651	1.0494	1.1222	0.5311
7	H	1.0871799	119.355436	178.256309	3.4582	-0.5511	-1.2604
8	H	1.0873544	118.608076	-174.538812	1.0303	-1.9886	1.9894
9	H	1.0930193	114.443933	150.558225	1.0141	2.1316	0.9489
10	C	1.4982058	120.25809	177.960282	2.8083	-2.8104	0.0975
11	H	1.0950725	111.571765	34.9095902	3.8619	-2.7733	-0.1987
12	H	1.0937144	112.013148	157.485179	2.7123	-3.4219	0.9992
13	H	1.1003018	109.647116	-83.2239554	2.2682	-3.3253	-0.7111
14	C	1.5038322	121.660613	-176.79262	-0.2412	0.3354	2.6061
15	H	1.0983805	111.383155	-100.239516	-1.283	0.3136	2.2588
16	H	1.0936006	111.002108	18.9477031	-0.1497	-0.4183	3.3932
17	H	1.0964852	111.639009	139.834488	-0.067	1.3215	3.0528
18	C	1.5039584	121.565671	177.662869	2.634	2.0401	-1.2627
19	H	1.1006897	111.61391	94.2721226	2.0222	2.1702	-2.1684
20	H	1.095809	111.909943	-145.200286	2.6189	2.9895	-0.7157
21	H	1.093566	110.979263	-24.1772342	3.6566	1.8588	-1.6052
22	C	1.9335286	103.333808	-108.290364	-0.4905	1.3814	-0.6091
23	H	1.0886907	101.162199	-36.5698147	-0.0477	1.9274	-1.4404
24	N	1.3800972	110.683841	-151.605865	-1.4217	2.193	0.0064
25	N	1.1370628	161.108199	-0.7233826	-1.93	2.8509	0.7821

26	C	1.5249687	109.35231	81.5879116	-1.0311	0.0236	-1.0446
27	O	1.2082218	120.258876	-73.0879192	-0.4323	-0.6371	-1.8599
28	O	1.327982	111.965179	105.680491	-2.1547	-0.2904	-0.4102
29	C	1.4759505	116.938925	178.769945	-2.7894	-1.5735	-0.7697
30	H	1.0931441	107.257652	62.7270371	-2.0872	-2.3682	-0.5045
31	H	1.0927286	107.291673	-54.0000946	-2.9288	-1.5745	-1.8535
32	C	1.5131756	107.542564	-175.598121	-4.0952	-1.6649	-0.0106
33	H	1.0954346	108.865925	179.76595	-4.5876	-2.6097	-0.2653
34	H	1.0947563	111.532573	-61.1059669	-3.9327	-1.6482	1.0719
35	H	1.0945203	111.317803	60.7483004	-4.7704	-0.8468	-0.2804

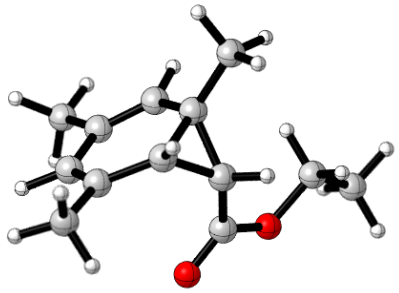


EE + Thermal Free Energy Correction: --765.712026 Hartree

Entropy = 147.378 cal mol^{-1} K^{-1}

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	C				1.6479	0.5892	-1.238
2	C	1.3708142			2.7071	-0.2731	-1.1211
3	C	1.4158383	121.85199		3.0417	-0.8827	0.1122
4	C	1.413806	120.229357	-0.0488609	2.2787	-0.6105	1.2709
5	C	1.3718338	121.955306	1.3702504	1.1859	0.2183	1.2425
6	C	1.5025677	119.961947	1.083929	0.8202	0.9291	-0.0309
7	H	1.0862827	119.518834	-178.193455	3.3186	-0.4909	-1.9921
8	H	1.0859286	118.64706	-179.619014	2.5619	-1.0872	2.2046
9	H	1.1130014	104.448605	111.325704	1.0501	1.9992	0.1711
10	C	1.4925473	119.646978	-178.324561	4.2281	-1.7848	0.192
11	H	1.100867	108.645619	82.462328	5.1316	-1.168	0.3151
12	H	1.0926745	112.030757	-158.816714	4.1714	-2.4618	1.0478
13	H	1.0941356	111.471796	-35.0561817	4.3581	-2.3581	-0.7308
14	C	1.496324	120.292139	-179.064093	0.4173	0.4971	2.4957
15	H	1.0963693	112.041879	-123.332071	-0.643	0.2372	2.3945
16	H	1.0918031	110.838964	-2.5903042	0.8251	-0.069	3.3355
17	H	1.0974565	110.564152	117.885674	0.4564	1.5658	2.7422
18	C	1.4995111	120.437607	178.2209	1.3459	1.2479	-2.5508
19	H	1.0992346	110.781767	97.6158932	0.555	0.7045	-3.087
20	H	1.0953388	112.055191	-142.355645	1.0069	2.2817	-2.4239
21	H	1.0927318	110.572982	-20.8910516	2.2292	1.2449	-3.1941

22	C	1.5610366	111.661109	-137.410945	-0.7052	0.939	-0.3624
23	H	1.0931429	109.844002	-32.0626706	-0.8583	1.2612	-1.3957
24	N	1.5437928	113.812007	-144.464601	-1.5025	2.0165	0.4035
25	N	1.1671294	124.337793	18.6878311	-1.0244	2.9515	0.9128
26	C	1.5314808	113.845812	87.5967374	-1.3782	-0.4295	-0.222
27	O	1.2168458	121.83863	-13.4689257	-0.7317	-1.4553	-0.1196
28	O	1.3233494	111.916182	168.971355	-2.6972	-0.3396	-0.2804
29	C	1.4683383	117.24089	177.452528	-3.4598	-1.5927	-0.2156
30	H	1.0928997	107.678784	57.537024	-3.1893	-2.0981	0.7149
31	H	1.0929828	107.597761	-59.7815607	-3.1487	-2.2129	-1.0601
32	C	1.5140109	107.381807	178.89096	-4.929	-1.2315	-0.2723
33	H	1.0955715	108.920624	179.935119	-5.5229	-2.151	-0.2267
34	H	1.0947462	111.173836	-60.8302306	-5.2131	-0.5969	0.5733
35	H	1.0948158	111.176612	60.7088653	-5.1727	-0.7113	-1.2043



EE + Thermal Free Energy Correction: -656.428463

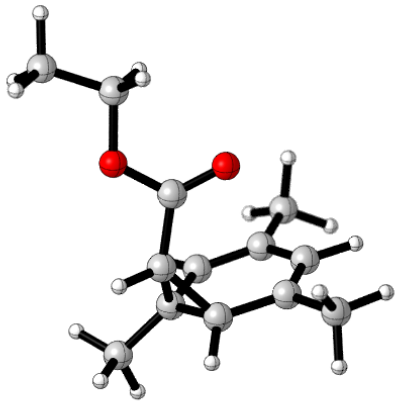
Entropy = 127.753 cal mol^{-1} K^{-1}

For N_2, EE + Thermal Free Energy Correction: -109.543015

Entropy = 45.784 cal mol^{-1} K^{-1}

Tag	**Symbol**	**Bond**	**Angle**	**Dihedral**	**X**	**Y**	**Z**
1	C				2.1905	-0.7204	0.0888
2	C	1.3525966			2.2677	0.5113	0.6424
3	C	1.4615547	122.846152		1.3637	1.6012	0.2804
4	C	1.3548539	120.088711	-1.788194	0.4192	1.4122	-0.6724
5	C	1.4851548	123.329038	3.4302192	0.1875	0.1082	-1.3444
6	C	1.4852258	120.260168	-3.2268858	1.112	-1.0386	-0.8815
7	H	1.0889539	119.468635	179.738405	3.0612	0.7293	1.3556
8	H	1.0895722	119.932408	-173.20021	-0.1791	2.2541	-1.0194
9	H	1.0900808	114.413831	149.247678	1.3879	-1.7751	-1.6363
10	C	1.509532	117.760416	-178.668935	1.5724	2.9389	0.948
11	H	1.0982662	111.031353	55.3588229	2.6001	3.297	0.8004
12	H	1.094916	111.623671	176.255425	0.8856	3.6966	0.5568
13	H	1.0983309	110.980213	-63.1548997	1.4162	2.8657	2.0327
14	C	1.5209846	115.401952	-145.402935	-0.2243	0.1916	-2.8062

15	H	1.0975011	111.098753	-61.2730536	-1.173	0.7317	-2.9192
16	H	1.0967084	110.462096	58.3347218	0.5367	0.7244	-3.3891
17	H	1.0956239	111.37854	178.37953	-0.3497	-0.8052	-3.2433
18	C	1.5044539	122.991908	174.406424	3.1923	-1.8078	0.3669
19	H	1.0989178	110.995181	120.1863	2.7056	-2.6874	0.8108
20	H	1.0995094	110.927495	-121.570459	3.669	-2.1498	-0.563
21	H	1.0948878	111.642399	-0.7679511	3.9779	-1.4681	1.0497
22	C	1.5156268	123.979928	-64.8982979	-0.3621	-1.0671	-0.5303
23	H	1.0892036	114.175788	-150.099083	-0.9486	-1.7672	-1.1238
24	C	1.4995738	123.737229	-7.7752192	-0.8875	-0.9427	0.8687
25	O	1.2183937	124.877458	-26.6670589	-0.2761	-1.2609	1.8734
26	O	1.354157	117.450139	156.1843	-2.1562	-0.4946	1.0215
27	C	1.4536881	122.205117	-3.0785448	-2.9726	-0.0798	-0.1075
28	H	1.0946165	109.085583	61.5345772	-3.1129	-0.932	-0.78
29	H	1.0929866	109.007277	-57.4688897	-2.456	0.7188	-0.646
30	C	1.5174417	107.260242	-178.082453	-4.3002	0.4001	0.4491
31	H	1.0958492	109.364314	-179.812425	-4.9463	0.7192	-0.3765
32	H	1.0951225	111.00383	-60.3047524	-4.8092	-0.4008	0.9957
33	H	1.0951823	110.942782	60.7002415	-4.1572	1.2506	1.1241

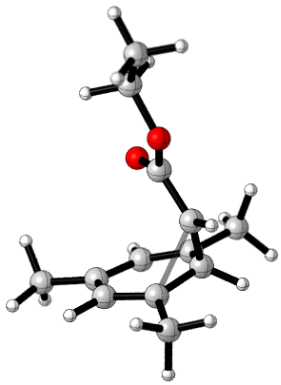


EE + Thermal Free Energy Correction: -656.230901

Entropy = 133.065 cal mol^{-1} K^{-1}

Tag	**Symbol**	**Bond**	**Angle**	**Dihedral**	**X**	**Y**	**Z**
1	C				1.8941	-0.0233	1.176
2	C	1.3946688			2.0964	1.0763	0.3423
3	C	1.4128173	122.747468		1.696	1.0921	-1.0125
4	C	1.3982269	118.927461	-1.6664998	1.1021	-0.0513	-1.5556
5	C	1.459282	124.010155	1.8448254	0.828	-1.2674	-0.797
6	C	1.4691442	120.40021	-1.2226164	1.2171	-1.2251	0.6703
7	H	1.0865283	118.484438	179.333836	2.5907	1.953	0.7517
8	H	1.08777	118.84834	-175.720788	0.8586	-0.0631	-2.6157
9	H	1.088291	115.23433	150.20038	1.5219	-2.1601	1.1364

10	C	1.5012273	120.094224	179.174387	1.9267	2.3155	-1.8514
11	H	1.0951268	110.941141	43.2447311	2.9251	2.7291	-1.6741
12	H	1.0927781	111.75603	165.247959	1.8116	2.1034	-2.9172
13	H	1.0983077	109.766756	-74.8858559	1.202	3.0946	-1.5792
14	C	1.5226179	116.210583	-148.523152	0.8967	-2.5748	-1.5744
15	H	1.0951883	110.533715	-60.0044425	0.1696	-2.5734	-2.3934
16	H	1.0948268	110.154693	60.0615119	1.898	-2.711	-1.9957
17	H	1.0936384	110.902889	179.833738	0.6806	-3.4272	-0.9242
18	C	1.4879317	121.606068	176.867612	2.3871	-0.0387	2.5798
19	H	1.0987035	109.910317	124.147916	1.5536	-0.2395	3.2669
20	H	1.0991138	109.869229	-119.48827	3.0998	-0.8642	2.7164
21	H	1.0916727	112.351543	2.2139842	2.8684	0.8999	2.8611
22	C	1.5272754	120.8033	-68.355421	-0.2677	-1.1948	0.3139
23	H	1.0855813	114.824127	-151.310307	-0.7824	-2.1442	0.4244
24	C	1.501354	123.707093	-5.6907103	-1.1598	-0.0127	0.5606
25	O	1.218747	125.6598	-2.2768204	-0.8267	1.0287	1.099
26	O	1.3363185	109.615121	178.513059	-2.3908	-0.2787	0.1138
27	C	1.4624684	117.177679	179.128878	-3.4045	0.7606	0.2901
28	H	1.0934216	107.923763	59.9677402	-3.0676	1.6533	-0.2439
29	H	1.0934734	107.882002	-57.3376583	-3.4659	0.9922	1.357
30	C	1.5149553	107.516129	-178.687772	-4.7101	0.2217	-0.2577
31	H	1.0956175	109.054239	-179.977962	-5.4893	0.9826	-0.1383
32	H	1.0950336	111.178115	-60.6915326	-4.6238	-0.0166	-1.323
33	H	1.0949806	111.155181	60.736236	-5.0236	-0.6781	0.2818

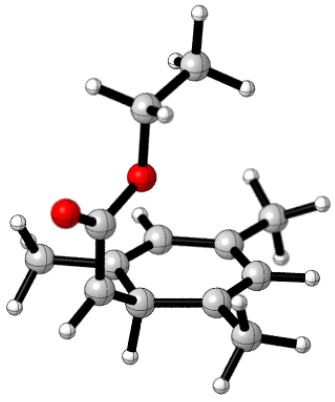


EE + Thermal Free Energy Correction: -656.222938

Entropy = 132.556 cal mol^{-1} K^{-1}

Tag	**Symbol**	**Bond**	**Angle**	**Dihedral**	**X**	**Y**	**Z**
1	C				1.6035	-0.7726	-1.1515
2	C	1.3692158			2.1361	-1.1817	0.0417
3	C	1.4247543	121.9435191		2.0987	-0.3601	1.2051
4	C	1.4050636	120.0638744	-6.4743177	1.6272	0.9607	1.1192

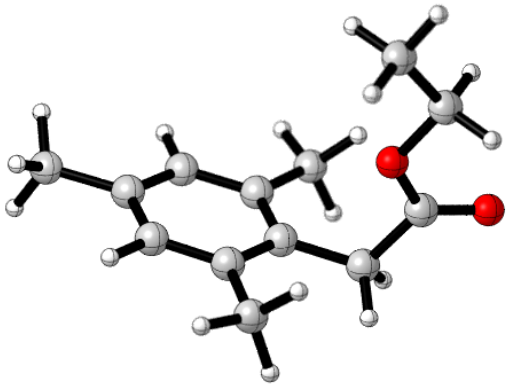
5	C	1.4008963	121.9421731	-1.1497609	1.2058	1.5198	-0.0942
6	C	1.4956469	117.8850954	11.204704	1.0259	0.6027	-1.2619
7	H	1.0866137	119.4918209	-179.9916417	2.5567	-2.1801	0.1255
8	H	1.0873379	118.945785	-174.5297238	1.69	1.6	1.9965
9	H	1.0955779	113.7072362	-147.9972727	1.2444	1.0713	-2.2278
10	C	1.4958718	119.2322297	174.2787556	2.5817	-0.9154	2.5074
11	H	1.0962927	111.0867943	45.4073486	3.5325	-1.4464	2.3814
12	H	1.0925622	112.4391578	168.1845407	2.6988	-0.1438	3.272
13	H	1.0999133	109.2018966	-71.8499715	1.856	-1.6548	2.8768
14	C	1.50542	120.7784982	-161.702642	1.0967	3.0123	-0.258
15	H	1.0947865	111.9317423	-48.9636677	0.5448	3.4749	0.5666
16	H	1.098747	108.3570029	69.3059031	2.1105	3.4359	-0.2538
17	H	1.0930608	112.8121631	-172.1171816	0.6285	3.3019	-1.2023
18	C	1.4927853	123.1308698	-175.8086415	1.5467	-1.645	-2.3615
19	H	1.099006	110.2473848	119.8649172	0.5041	-1.7895	-2.6776
20	H	1.098427	110.9038332	-122.2562258	2.0697	-1.1774	-3.2067
21	H	1.0922489	111.8147255	-0.6256521	1.987	-2.627	-2.1749
22	C	1.5154833	83.9386751	102.9223311	-0.4485	0.7452	-0.9417
23	H	1.0838058	117.263299	82.0760457	-0.9556	1.6257	-1.3188
24	C	1.4774941	125.9917766	-100.6179356	-1.2763	-0.2343	-0.208
25	O	1.2205815	125.0596943	-0.6001977	-0.8768	-1.301	0.2306
26	O	1.3380262	109.409345	-179.9852086	-2.5294	0.2251	-0.1131
27	C	1.4657003	116.9864859	178.1345787	-3.5068	-0.6412	0.5521
28	H	1.0940538	107.6060106	60.5788102	-3.1615	-0.8033	1.5775
29	H	1.0940279	107.6652947	-56.0016734	-3.5053	-1.6038	0.0322
30	C	1.5140262	107.6218226	-177.7590228	-4.8507	0.0535	0.4921
31	H	1.0955601	109.0614991	-179.9011877	-5.6005	-0.5746	0.9856
32	H	1.094702	111.3091417	-60.6476376	-4.8226	1.0193	1.0067
33	H	1.094561	111.2750525	60.8707807	-5.1686	0.2147	-0.5428



EE + Thermal Free Energy Correction: -656.231844 Hartree

Entropy = 136.631 cal mol^{-1} K^{-1}

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	C				-0.8735	-0.6706	-1.3578
2	C	1.3708583			-1.8882	0.2421	-1.2289
3	C	1.4162185	121.6639963		-2.4349	0.5724	0.0351
4	C	1.4171854	120.6482837	-0.0098826	-1.9439	-0.0376	1.2163
5	C	1.3704012	121.7166703	-0.2115535	-0.9348	-0.9642	1.1827
6	C	1.5061419	119.6986493	4.0158623	-0.3789	-1.4129	-0.1442
7	H	1.0861999	119.6139215	-176.8324931	-2.2789	0.7387	-2.1124
8	H	1.0862726	118.6466813	179.1363948	-2.3772	0.2503	2.1699
9	H	1.1110047	102.2652736	103.1235337	-0.8469	-2.4124	-0.2719
10	C	1.4919685	119.7734549	-178.7560946	-3.5575	1.5511	0.1239
11	H	1.1011149	108.4087832	91.1835968	-4.5073	0.9964	0.0725
12	H	1.0935964	111.7196864	-151.0245485	-3.5506	2.0896	1.0757
13	H	1.0930725	111.914575	-26.9792925	-3.5486	2.2588	-0.7091
14	C	1.4944602	121.8575981	179.3091334	-0.4043	-1.5982	2.4277
15	H	1.0922755	111.3377348	10.1773217	-1.0319	-1.3653	3.2908
16	H	1.0961886	111.2479653	132.2124217	-0.3307	-2.6865	2.319
17	H	1.098691	110.1599213	-109.8183473	0.6115	-1.2343	2.6347
18	C	1.4941082	121.8135206	-178.8810488	-0.2776	-1.0034	-2.6869
19	H	1.0988808	109.996802	107.8487683	0.7305	-0.5731	-2.7651
20	H	1.0960364	111.3641529	-134.1599697	-0.1672	-2.0863	-2.8151
21	H	1.0923951	111.3360823	-11.9241265	-0.8813	-0.6031	-3.5046
22	C	1.5130629	114.1756044	-143.2889863	1.1139	-1.6595	-0.1344
23	H	1.0829738	120.2924874	-113.7626901	1.5014	-2.6683	-0.2051
24	C	1.4563018	123.3369005	66.8528995	2.1003	-0.5943	-0.0196
25	O	1.2282202	122.8751251	179.4737741	3.3102	-0.805	-0.0031
26	O	1.3474081	112.8458741	-0.5373503	1.5418	0.629	0.0648
27	C	1.4585335	117.002264	-179.9978723	2.4494	1.7646	0.1831
28	H	1.0937831	108.0025783	58.281016	3.1123	1.7596	-0.6869
29	H	1.0938459	107.9834694	-58.8920249	3.0552	1.6205	1.0824
30	C	1.5151972	107.7930003	179.6949924	1.6091	3.0234	0.2548
31	H	1.0956504	109.057892	179.9898798	2.2718	3.8913	0.3444
32	H	1.0950955	111.1985588	-60.7619894	1.0034	3.1472	-0.6491
33	H	1.0950783	111.2109484	60.73248	0.9458	3.0079	1.126



EE + Thermal Free Energy Correction: -656.499163 Hartree

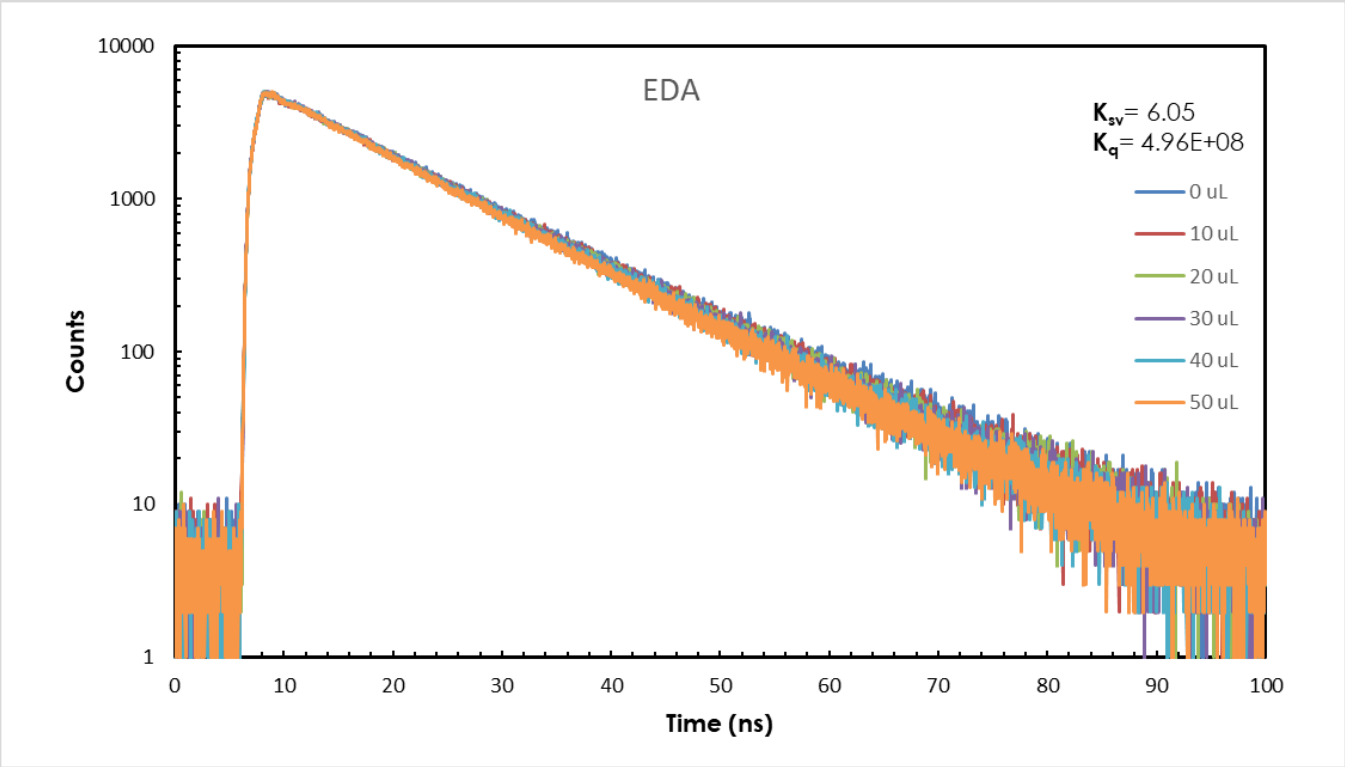
Entropy = 134.337 cal mol^{-1} K^{-1}

Tag	Symbol	Bond	Angle	Dihedral	X	Y	Z
1	C				1.0842	1.2883	-0.3026
2	C	1.4011245			2.2955	0.8641	-0.8647
3	C	1.3996053	121.9064235		2.924	-0.3195	-0.461
4	C	1.3994295	117.8058541	0.4188111	2.2981	-1.0864	0.5282
5	C	1.4020468	122.0623604	-0.3715496	1.0856	-0.6978	1.1152
6	C	1.4113239	119.234435	0.0681857	0.4716	0.5027	0.6985
7	H	1.0887802	118.8409328	179.7666483	2.7578	1.4748	-1.6385
8	H	1.0887323	119.158669	179.4725568	2.7634	-2.0157	0.8526
9	C	1.5123169	121.0808633	-178.3994892	4.2493	-0.7415	-1.0548
10	H	1.0987263	111.0978792	88.5846947	5.0896	-0.3177	-0.4878
11	H	1.0955362	111.4435719	-151.8846898	4.3653	-1.8308	-1.0418
12	H	1.0956613	111.442287	-30.9081029	4.3514	-0.3989	-2.0905
13	C	1.5149145	118.9508385	179.9119703	0.4689	-1.5829	2.1788
14	H	1.0944632	110.5808539	-2.9576164	1.0666	-2.4889	2.3194
15	H	1.0981282	111.9454729	116.6578467	0.41	-1.0759	3.1511
16	H	1.096597	111.9162079	-123.0135301	-0.5489	-1.8931	1.9135
17	C	1.5143287	119.2082199	-179.9565256	0.4571	2.5791	-0.7861
18	H	1.0974012	112.1449747	121.7522783	-0.5545	2.4245	-1.1824
19	H	1.0980552	111.9073463	-118.216056	0.373	3.3206	0.0194
20	H	1.094324	110.703263	1.6978704	1.0582	3.0262	-1.5838
21	C	1.5166364	120.8590637	-179.5297039	-0.8347	0.9635	1.3161
22	H	1.0962497	110.6450361	21.382819	-0.9851	0.4958	2.2961
23	C	1.5251944	117.0543302	-99.3675838	-2.1113	0.6796	0.5313
24	O	1.221144	123.3157415	-153.1760852	-3.1225	1.3574	0.6275
25	O	1.3406312	113.2218907	28.9257311	-2.0257	-0.4138	-0.2397
26	C	1.4562357	117.2129474	177.668561	-3.2151	-0.7957	-0.9881
27	H	1.0938847	108.2506226	58.2310132	-3.4974	0.0414	-1.6332
28	H	1.0940167	108.2695893	-59.1321229	-4.0264	-0.9726	-0.2758
29	C	1.5162621	107.5918196	179.5258777	-2.875	-2.0397	-1.7855

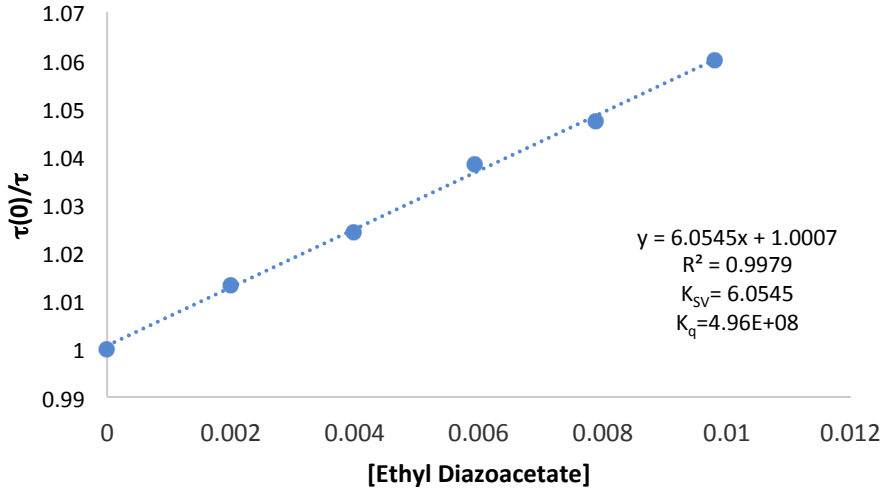
30	H	1.0958641	109.2751407	-179.9323576	-3.7534	-2.3513	-2.3619
31	H	1.0952966	111.1204562	-60.5238783	-2.0552	-1.8476	-2.486
32	H	1.0952769	111.1434126	60.6623744	-2.587	-2.8653	-1.1259
33	H	1.0939632	111.4227273	138.61141	-0.8308	2.0417	1.5011

Emission and Isotope Studies:

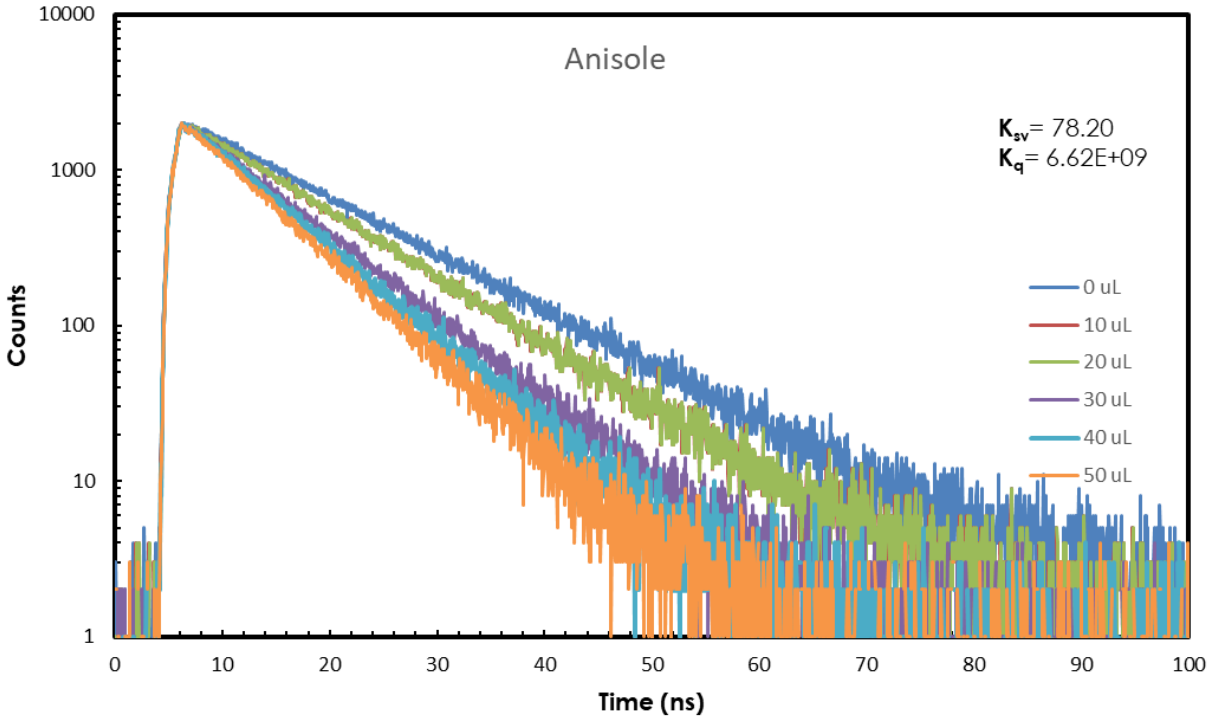
Emission lifetime and Stern-Volmer Experiments: Emission lifetime measurements were taken at ambient temperature using a Edinburgh FLS920 spectrometer and fit to single exponential according to the methods previously described by our laboratory.[21] The fluorescence of **Mes-Acr-Ph** in 1:1 MeCN:TFE was observed as a single exponential decay. Stern-Volmer analysis on the quenching of fluorescence lifetime was carried at a 1.5×10^{-6} M concentration of Mes-Acr-Ph. The quenching constant was determined with varying quencher concentrations in the range of 0-1.0×10^{-2} M. Bimolecular quenching constant, k_q, was determined from the corresponding Stern-Volmer Constant.



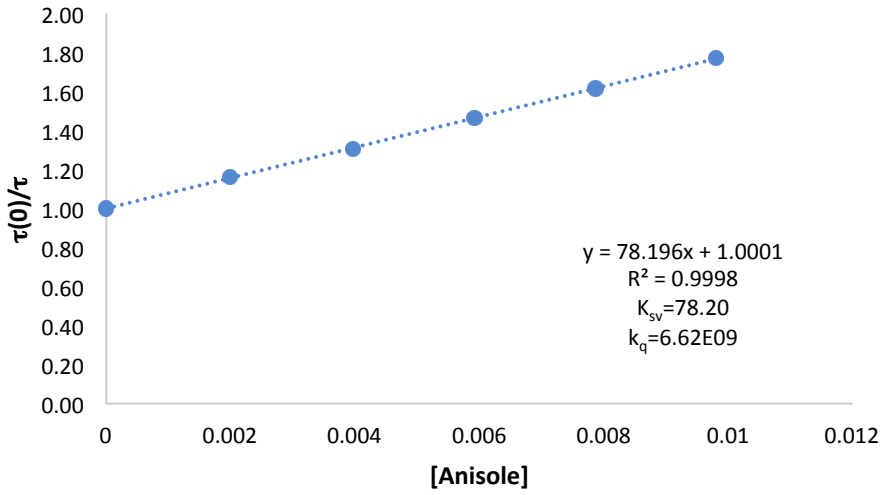
Fluorescence decay obtained by Time-Correlated Single Photon Counting of 3,6-Di-tert-butyl-9-mesityl-10-phenylacridinium tetrafluoroborate in 1:1 MeCN:TFE with quenching by ethyl diazoacetate 0-1.0×10^{-2} M.



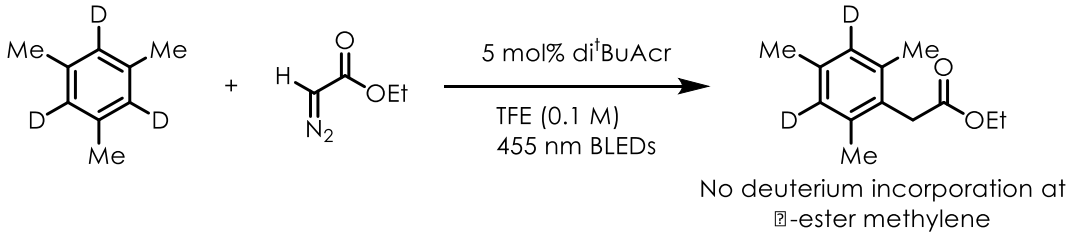
Stern-Volmer Analysis of the fluorescence quenching of 3,6-Di-tert-butyl-9-mesityl-10-phenylacridinium tetrafluoroborate in 1:1 MeCN:TFE with quenching by ethyl diazoacetate 0-1.0x10^{-2} M.



Fluorescence decay obtained by Time-Correlated Single Photon Counting of 3,6-Di-tert-butyl-9-mesityl-10-phenylacridinium tetrafluoroborate in 1:1 MeCN:TFE with quenching by anisole 0-1.0x10^{-2} M.

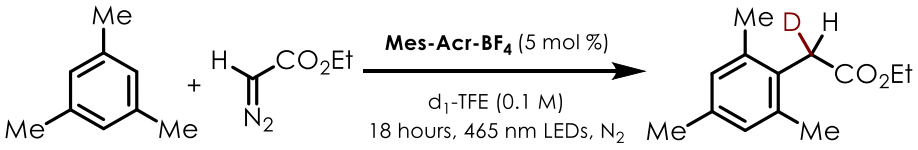


Stern-Volmer Analysis of the fluorescence quenching of 3,6-Di-tert-butyl-9-mesityl-10-phenylacridinium tetrafluoroborate in 1:1 MeCN:TFE with quenching by anisole 0-1.0x10^{-2} M.

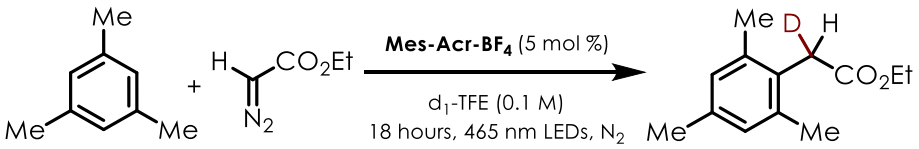


The reaction was prepared according to the general conditions with d_3-Mesitylene as the substrate. The reaction was analyzed by NMR and GCMS and showed no deuterium incorporation at the α-ester methylene.

Deuterium is incorporated from d_1- 2,2,2-trifluoroethanol

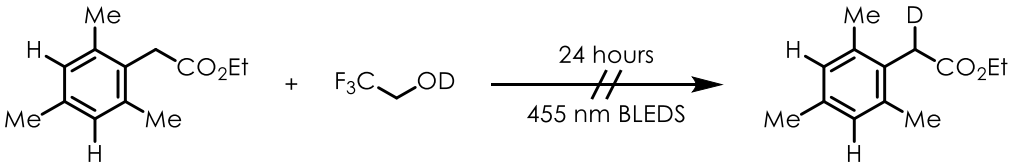


Deuterium is incorporated from d_1- 2,2,2-trifluoroethanol



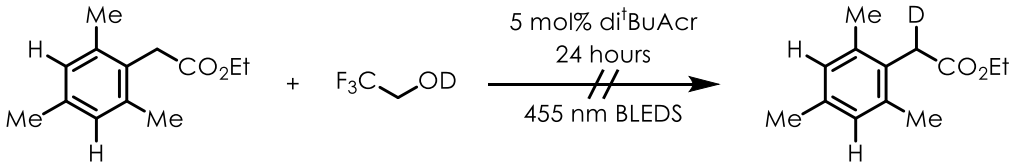
The reaction was prepared according to the general conditions using d_1-2,2,2 trifluoroethanol. The reaction was analyzed by NMR and GCMS. The major product observed was mono deuteration. Minor di- and non-deuterated product was observed, which is believed to be from enolate equilibration of the monodeuterated product in the last protonation step.

No Deuterium exchage from d_1 TFE occurs once product is formed



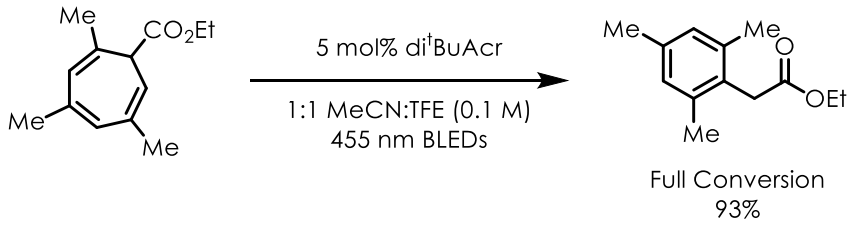
Ethyl 2-mesitylacetate (0.100 mmol, 20.6 mg) were added to a 2 dram vial equipped with a stir bar. The vial was moved to a nitrogen filled glovebox (<10 ppm O_2) and and 0.50 mL 2,2,2,-trifluoroethan-1-ol-d was added. The vial was capped tightly with a Teflon lined phenolic resin septum cap (purchased through VWR international, Microliter Product # 15-0060K) and moved out of the glovebox. Prior to irradiation, vials were sealed with electrical tape to ensure maximal oxygen exclusion. The reaction vial was then placed into the reactor and equip with a nitrogen inlet needle. The reactions were irradiated for 18 hours to mimic any heating throughout the reaction. The reaction was concentrated and analyzed by ^{1}H NMR which showed no deuterium incorporation.

No Deuterium exchage from d_1 TFE occurs once product is formed



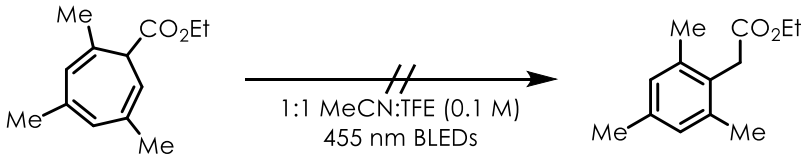
Ethyl 2-mesitylacetate (0.100 mmol, 20.6 mg) and 3,6-Di-tert-butyl-9-mesityl-10-phenylacridinium tetrafluoroborate (0.05 mmol, 2,9 mg) were added to a 2 dram vial equipped with a stir bar. The vial was moved to a nitrogen filled glovebox (<10 ppm O_2) and and 0.50 mL 2,2,2,-trifluoroethan-1-ol-d was added. The vial was capped tightly with a Teflon lined phenolic resin septum cap (purchased through VWR international, Microliter Product # 15-0060K) and moved out of the glovebox. Prior to irradiation, vials were sealed with electrical tape to ensure maximal oxygen exclusion. The reaction vial was then placed into the reactor and equip with a nitrogen inlet needle. The reaction were irradiated for 18 hour, then was concentrated and analyzed by ^{1}H NMR which showed no deuterium incorporation.

Full Conversion to the Desired Product When Subjecting the Intermediate Cycloheptatriene

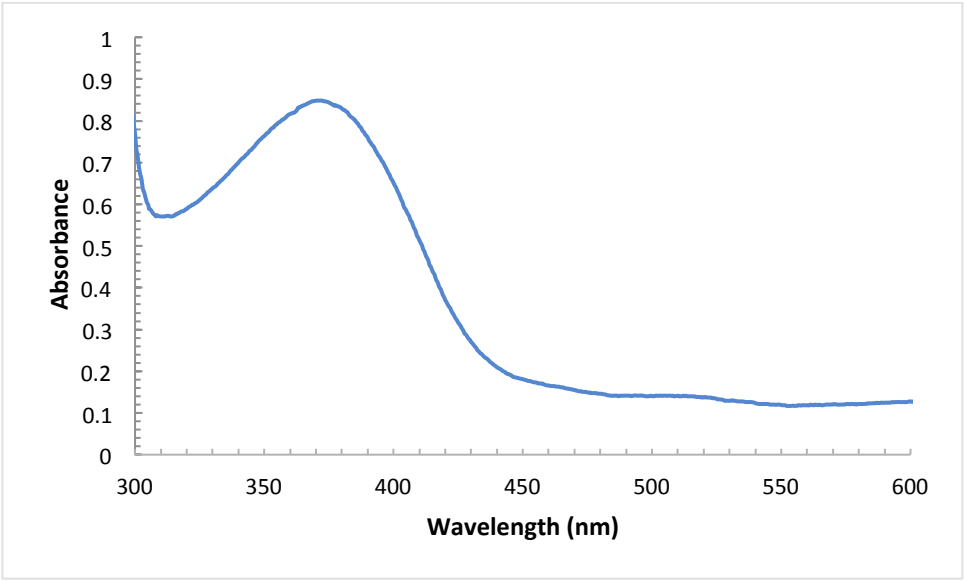


The reaction was prepared according to the general conditions with ethyl 2-(2,4,6-trimethylcyclohepta-2,4,6-trien-1-yl)acetate as the substrate. The reaction was analyzed by ^{1}H NMR which gave full conversion to the desired product. Spectra data matched those previously reported.

Without the Photoredox Catalyst, No Ring Opening is Observed

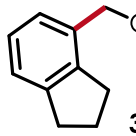


The reaction was prepared according to the general conditions with ethyl 2-(2,4,6-trimethylcyclohepta-2,4,6-trien-1-yl)acetate as the substrate and without 5 mol% di^{t}BuAcr. The reaction was analyzed by ^{1}H NMR which gave only returned starting material with no ethyl 2-mesitylacetate observed. Spectra data matched those previously reported.

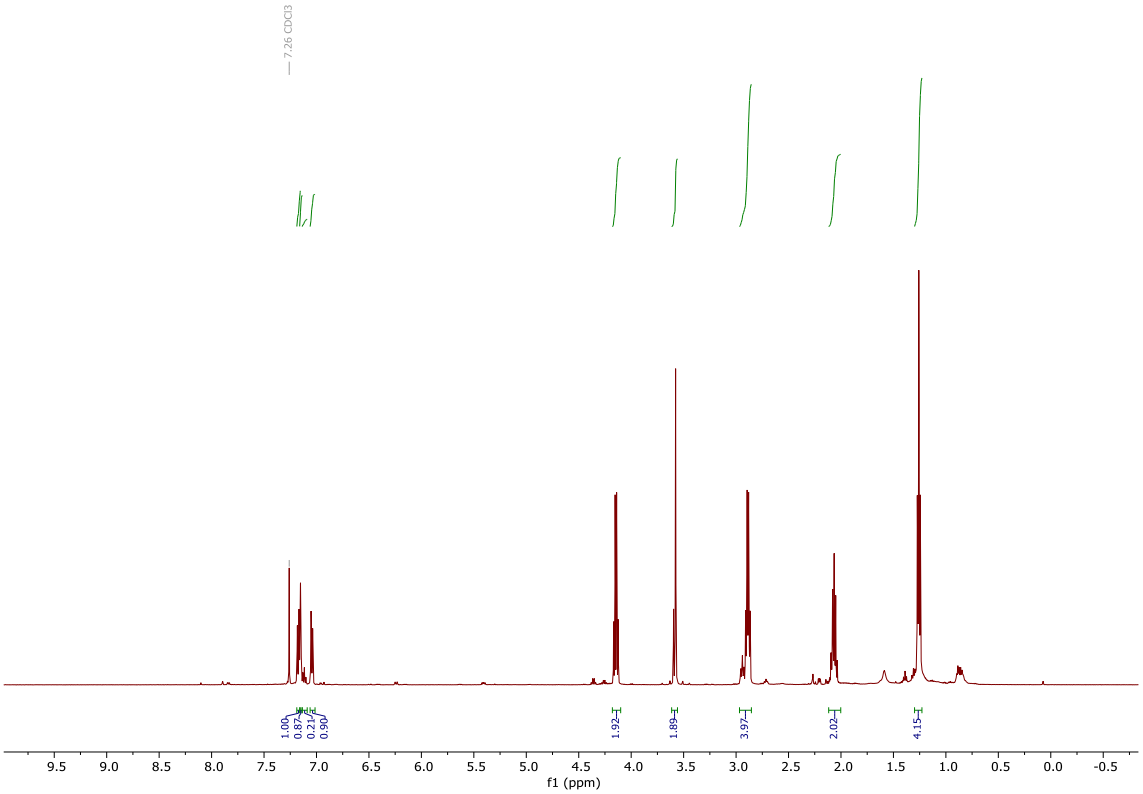


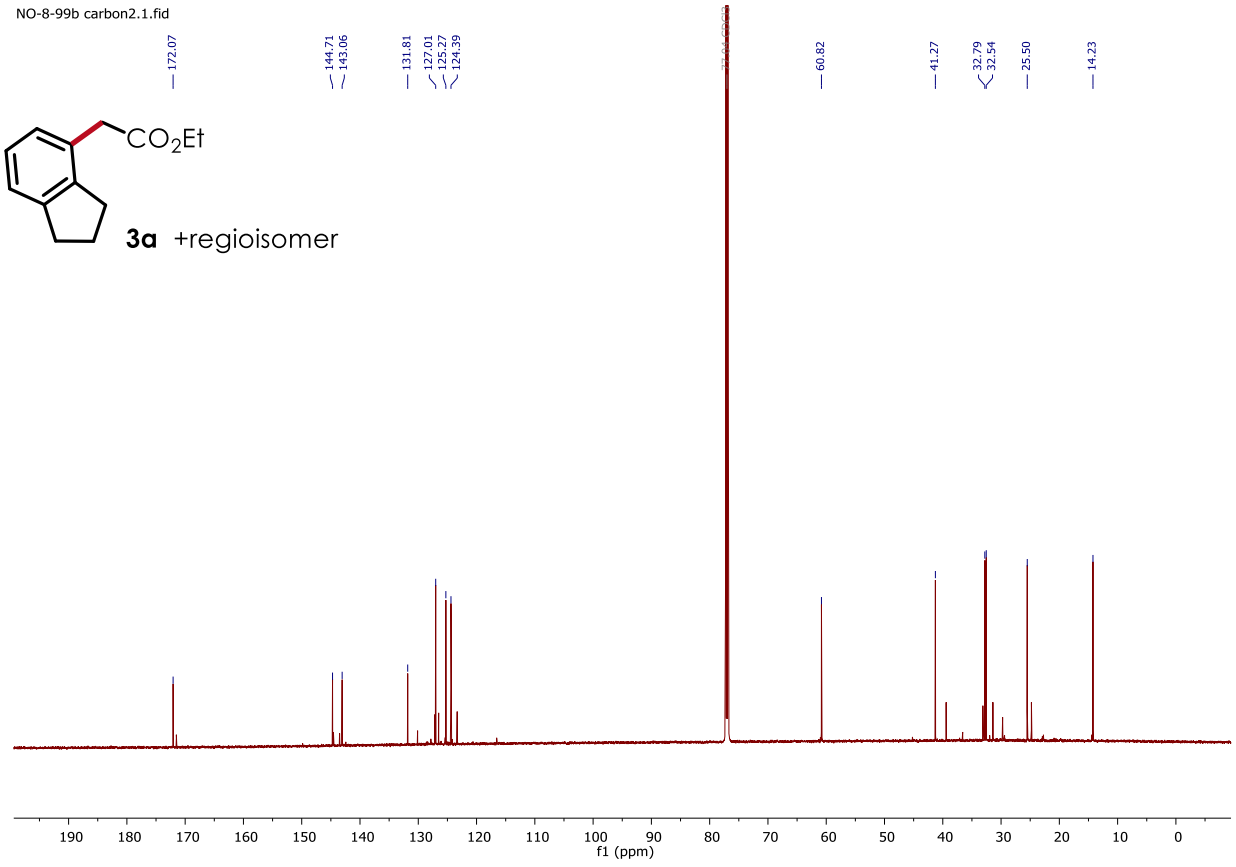
UV-Vis absorbance of a 0.5 mM solution of ethyl diazoacetate in 1:1 MeCN:TFE. λ_{max} =371 nm

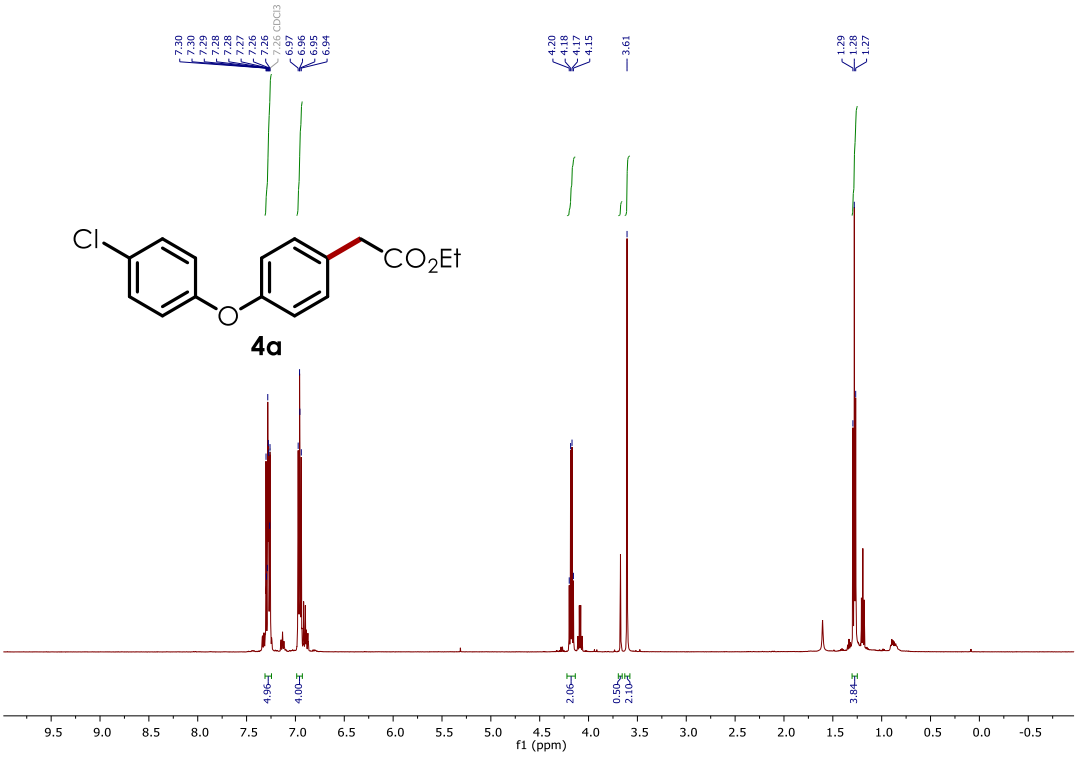
Spectral data:

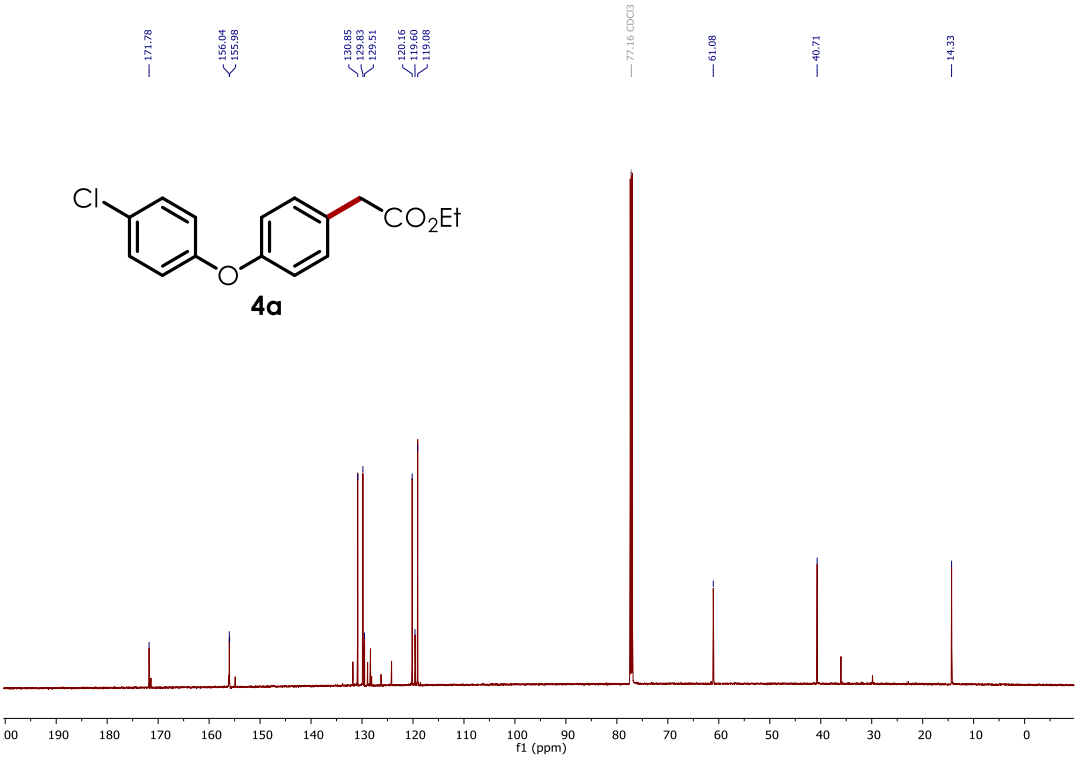


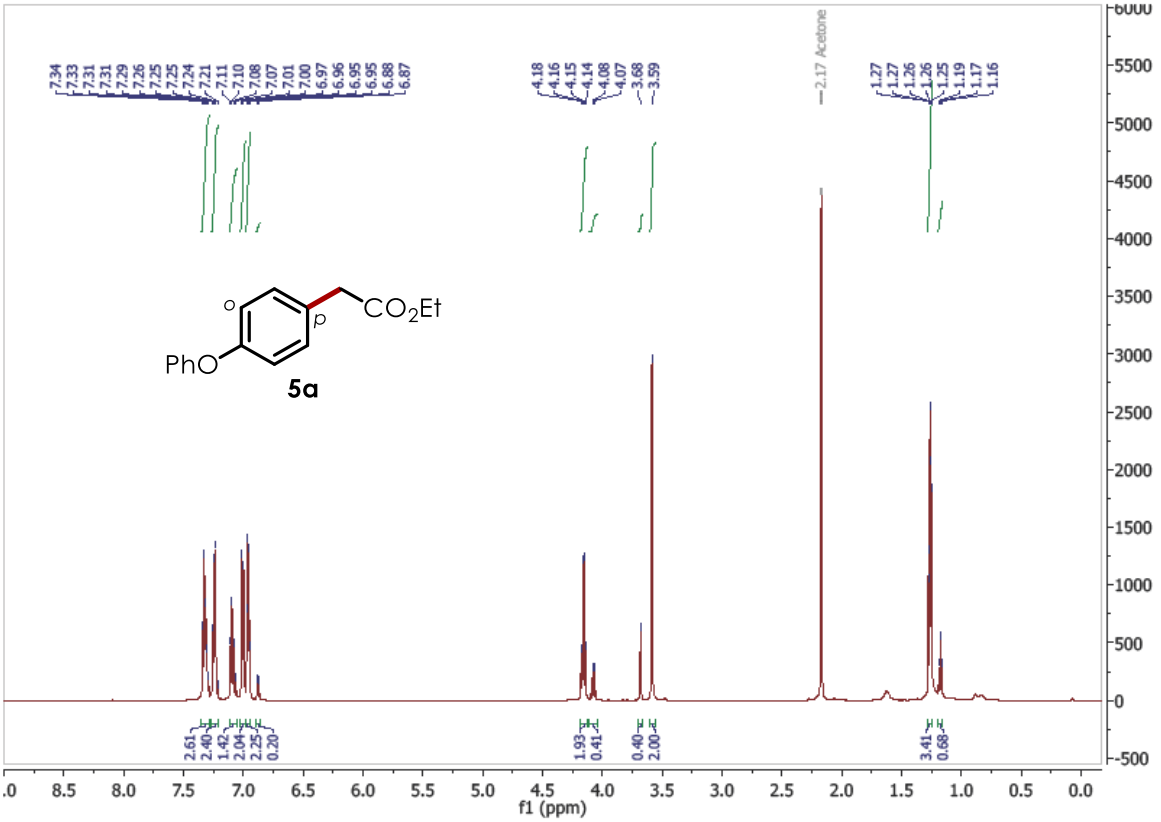
3a +regioisomer

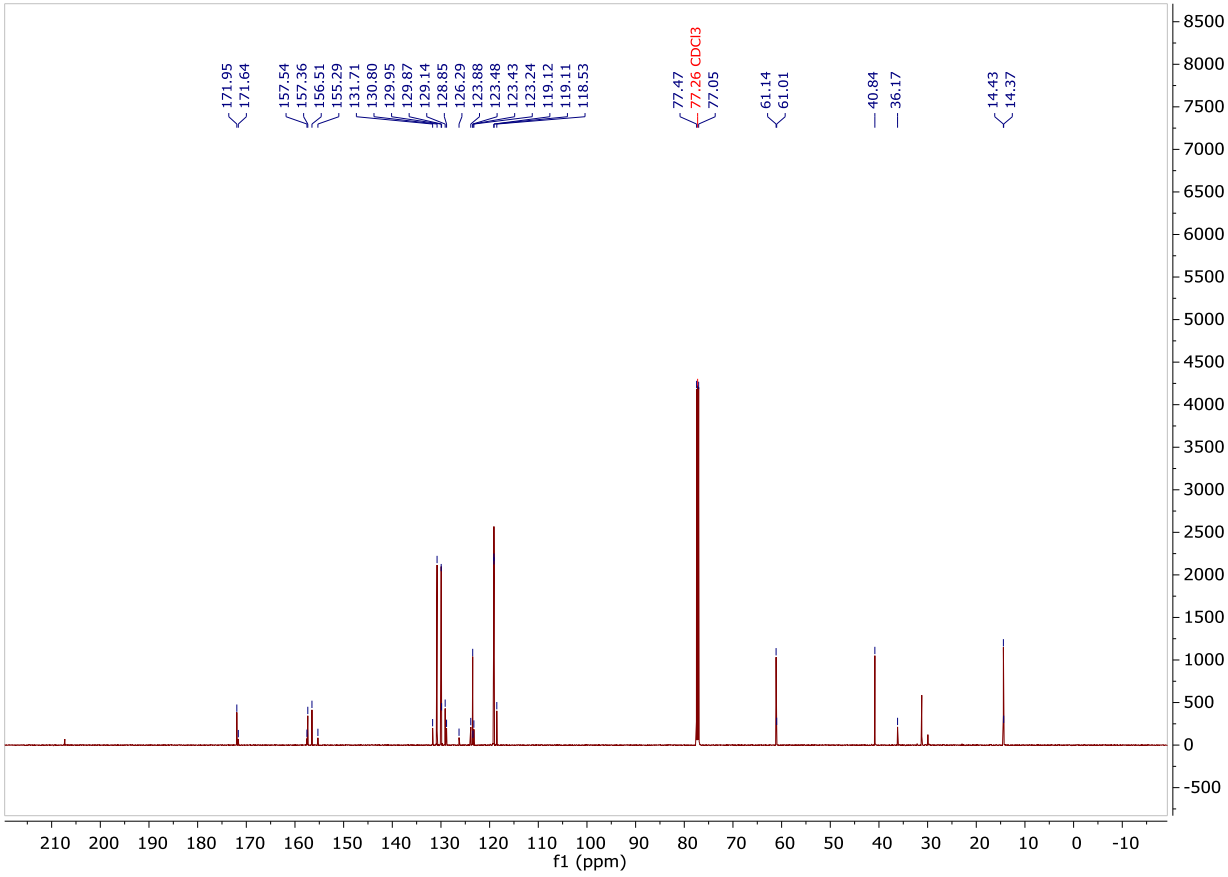

7.26 CDCl3
1.00
0.87
0.21
0.90
1.92
1.89
3.97
2.02
4.15
f1 (ppm)

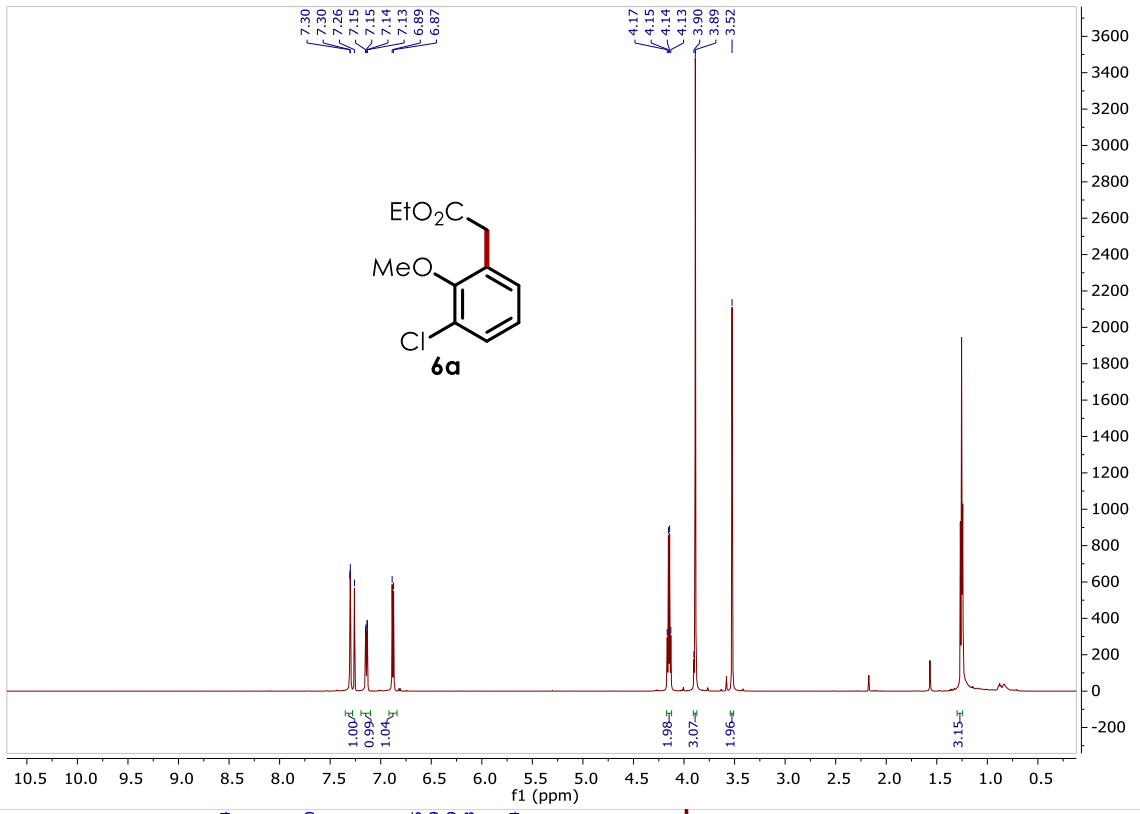

NO-8-99b carbon2.1.fid
172.07
144.71
143.06
131.81
127.01
125.27
124.39
77.16 CDCl3
60.82
41.27
32.79
32.54
25.50
14.23
CO2Et
3a +regioisomer
f1 (ppm)

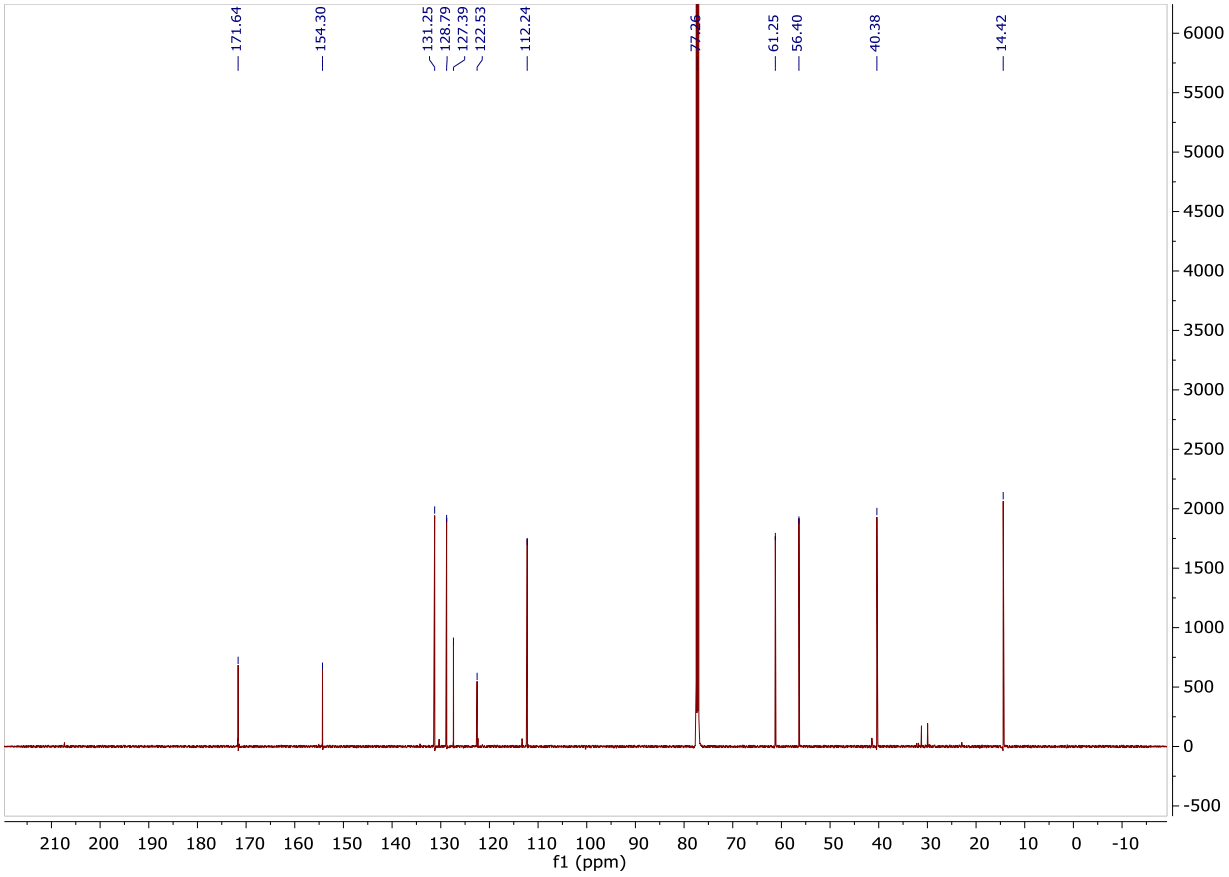

7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.26 CDCl3
6.97
6.96
6.95
6.94
4.20
4.18
4.17
4.15
3.61
1.29
1.28
1.27
Cl
CO2Et
O
4a
4.96
4.00
2.06
0.59
2.10
3.84
f1 (ppm)

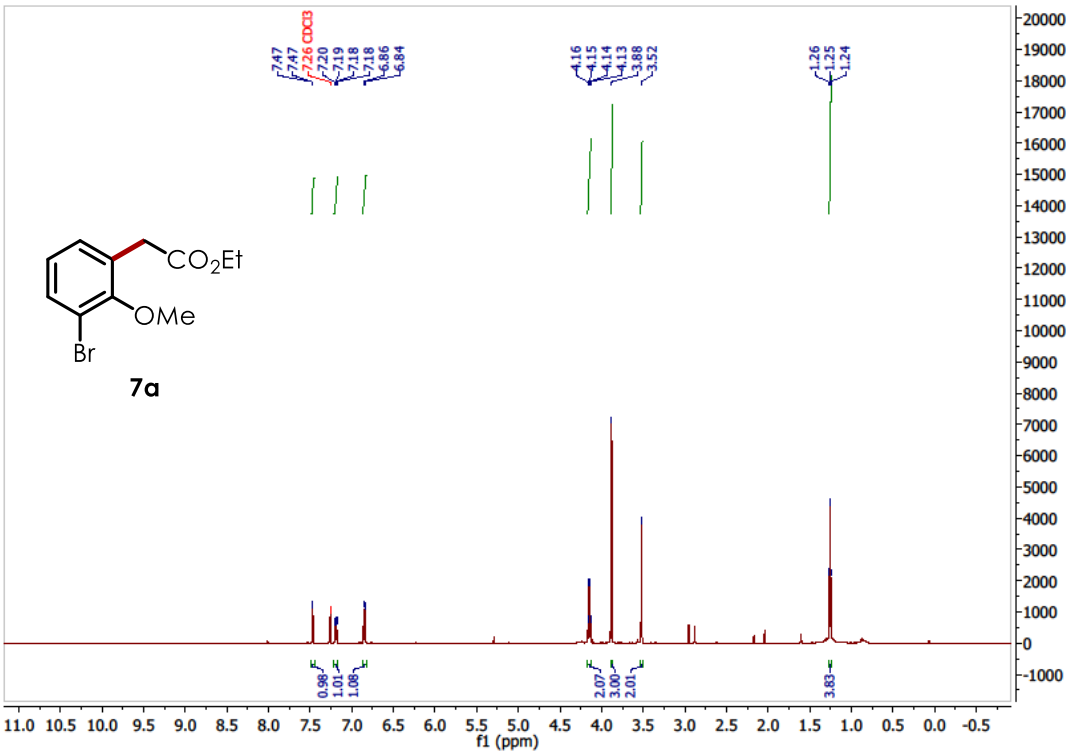

171.78
156.04
155.98
130.85
129.83
129.51
120.16
119.60
119.08
77.16 CDCl3
61.08
40.71
14.33
Cl
CO2Et
O
4a
f1 (ppm)

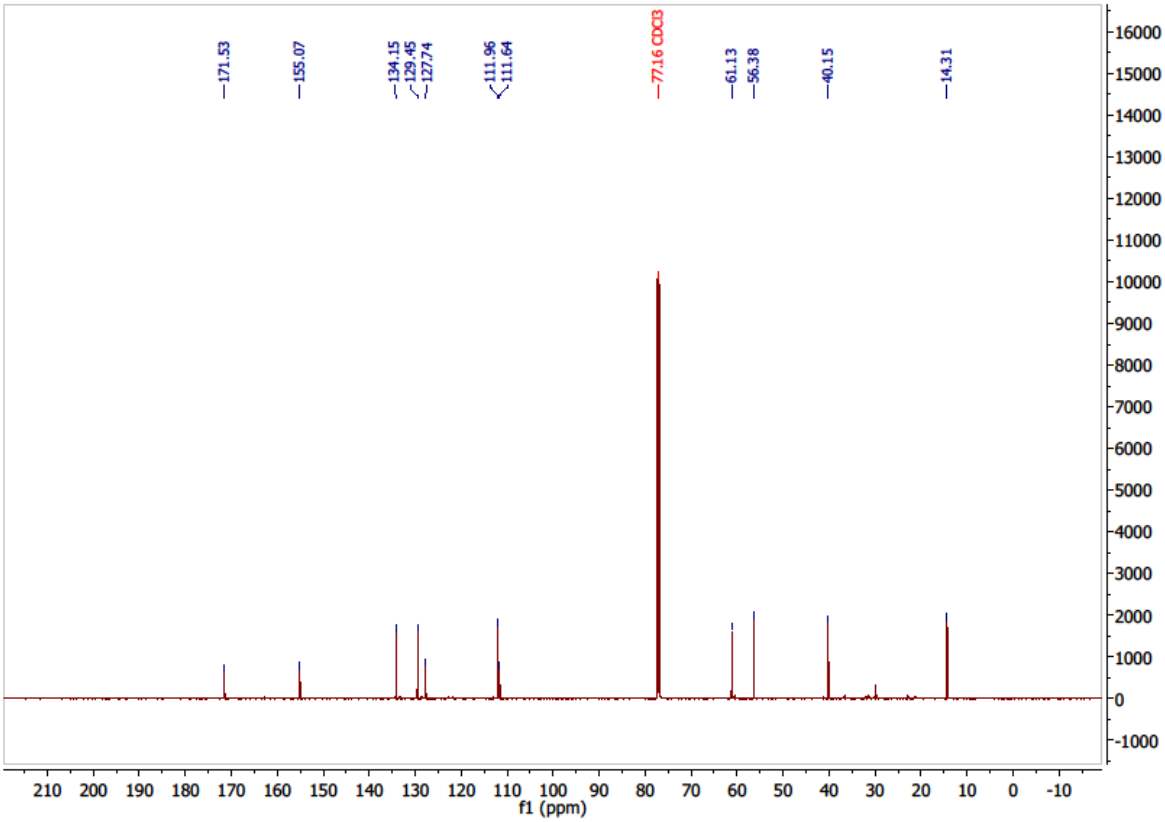

7.34
7.33
7.31
7.31
7.29
7.26
7.25
7.25
7.24
7.21
7.11
7.10
7.08
7.07
7.01
7.00
6.97
6.96
6.95
6.95
6.88
6.87
4.18
4.16
4.15
4.14
4.08
4.07
3.68
3.59
2.17 Acetone
1.27
1.27
1.26
1.26
1.25
1.19
1.17
1.16
o
p
CO2Et
PhO
5a
2.61
2.40
1.42
2.04
2.25
0.20
1.93
0.41
0.40
2.00
3.41
0.68
f1 (ppm)

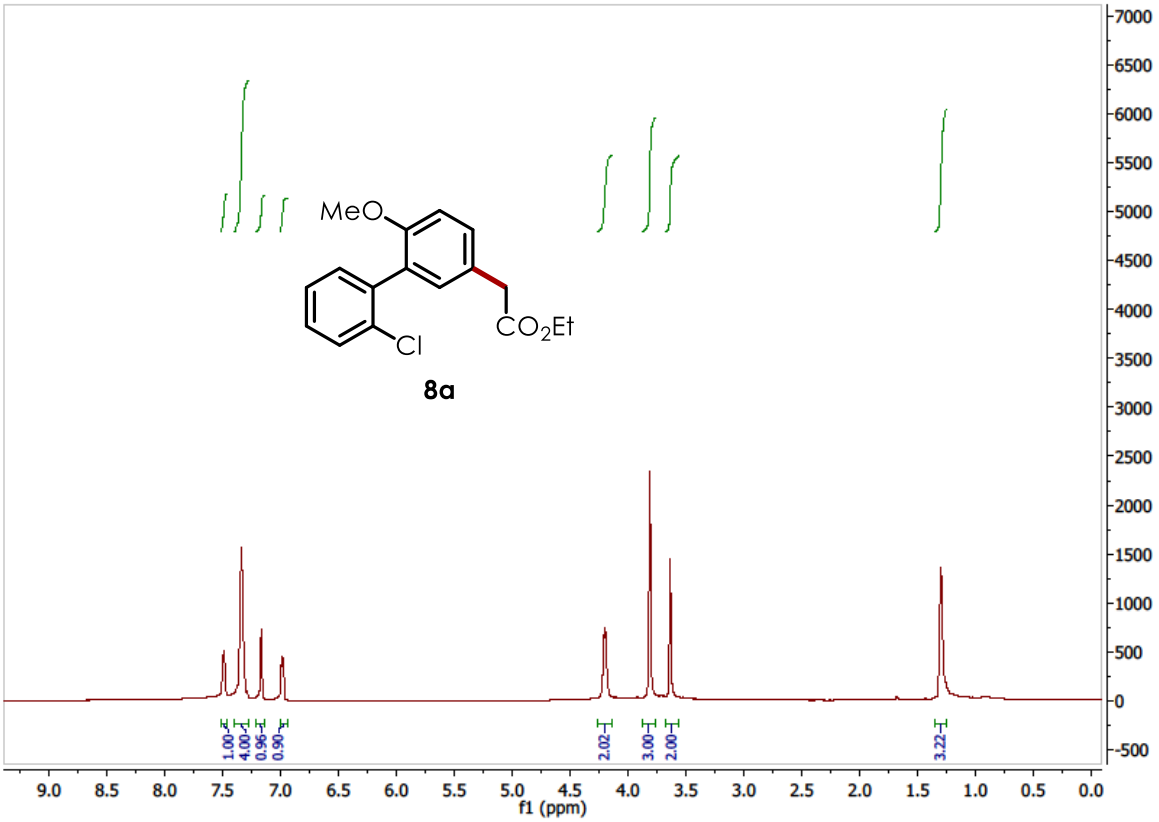

171.95
171.64
157.54
157.36
156.51
155.29
131.71
130.80
129.95
129.87
129.14
128.85
126.29
123.88
123.48
123.43
123.24
119.12
119.11
118.53
77.47
77.26 CDCl3
77.05
61.14
61.01
40.84
36.17
14.43
14.37
f1 (ppm)

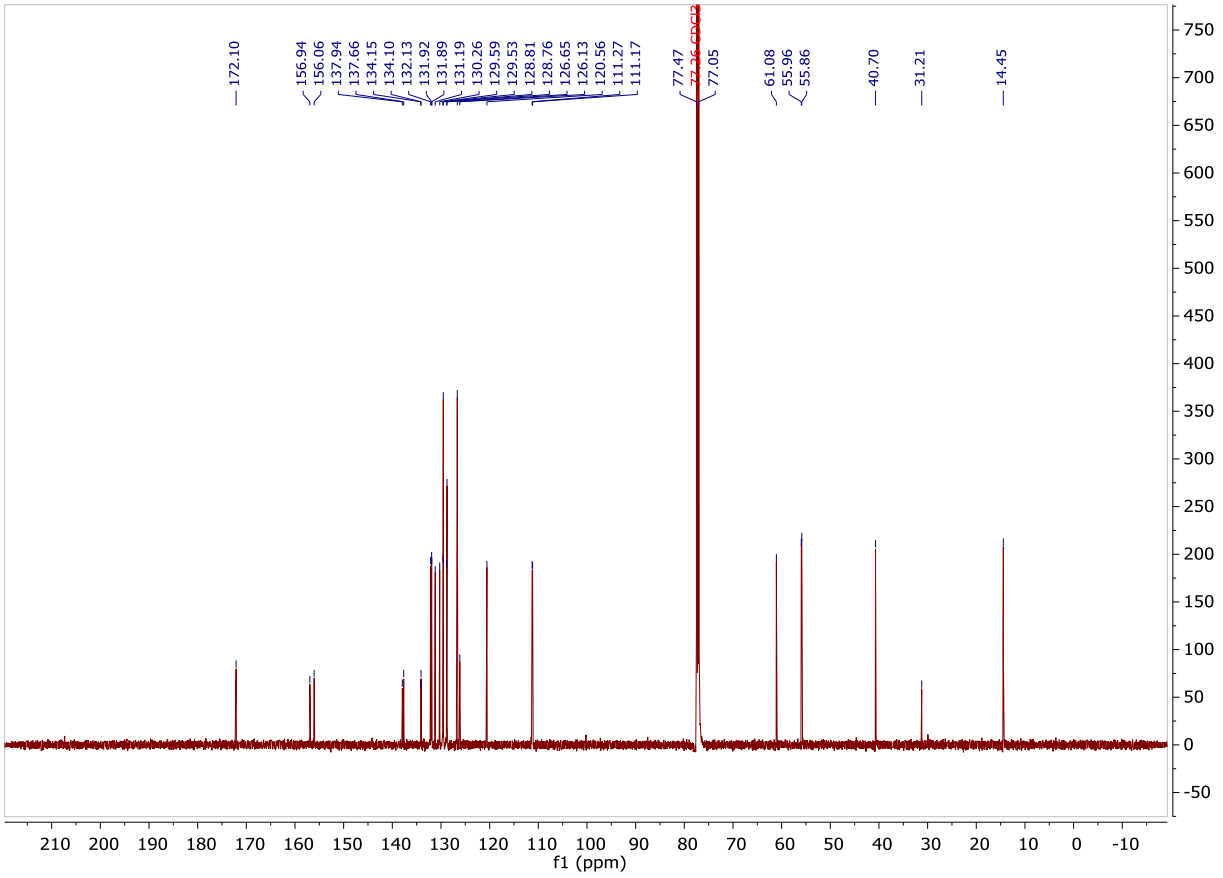

7.30
7.30
7.26
7.15
7.15
7.14
7.13
6.89
6.87
4.17
4.15
4.14
4.13
3.90
3.89
3.52
EtO2C
MeO
Cl
6a
1.00
0.99
1.04
1.98
3.07
1.96
3.15
f1 (ppm)

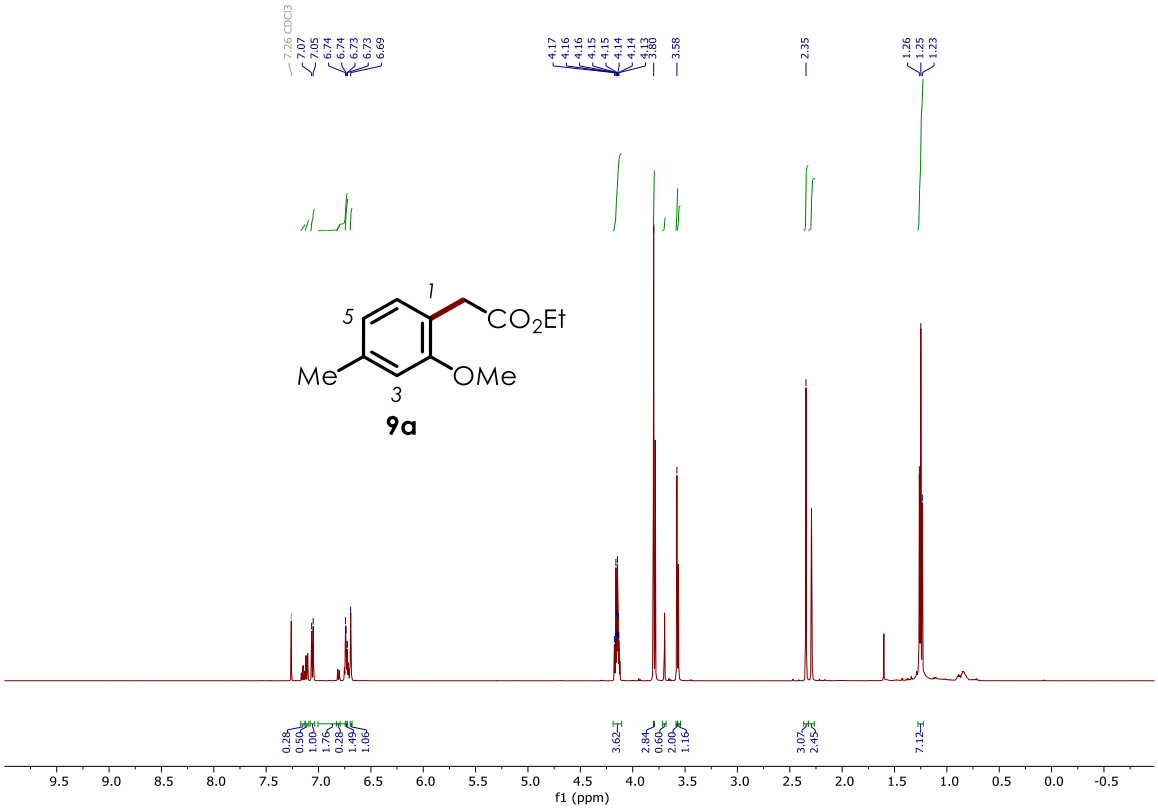

171.64
154.30
131.25
128.79
127.39
122.53
112.24
77.26
61.25
56.40
40.38
14.42
f1 (ppm)

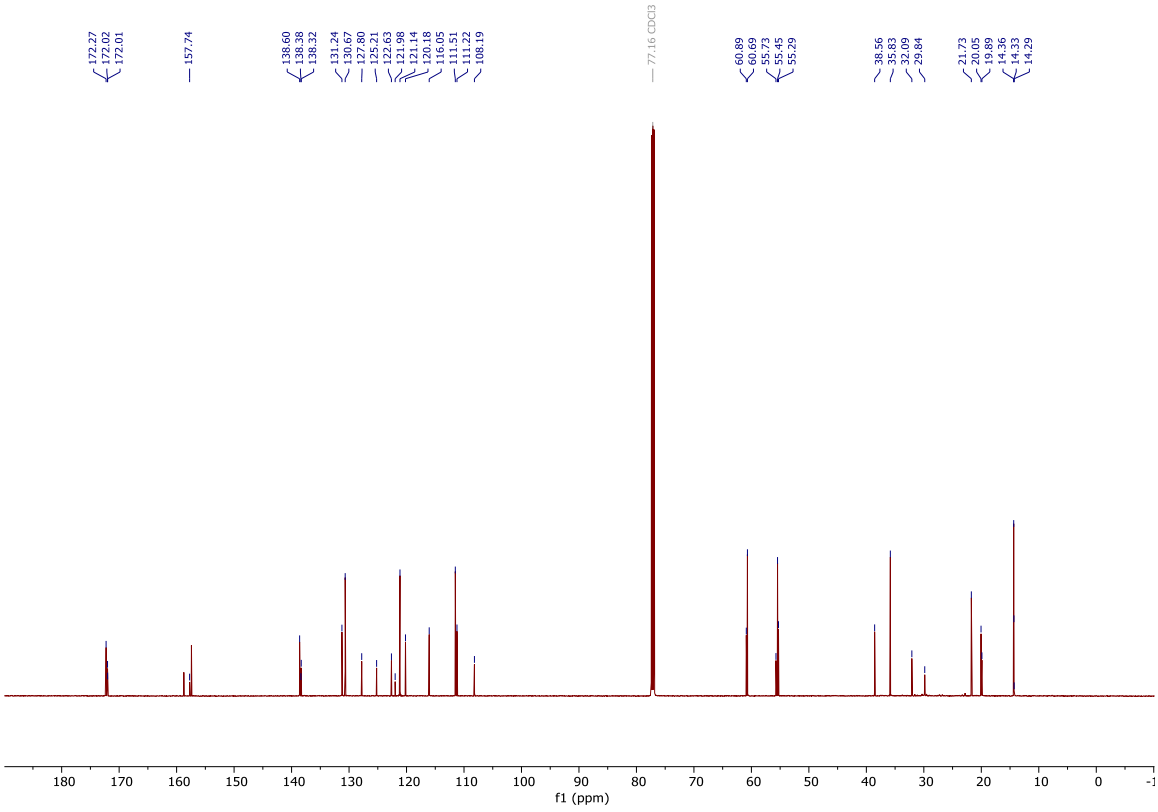

7.47
7.47
7.26 CDCl3
7.20
7.19
7.18
7.18
6.86
6.84
4.16
4.15
4.14
4.13
3.88
3.52
1.26
1.25
1.24
CO2Et
OMe
Br
7a
0.98
1.01
1.08
2.07
3.00
2.01
3.83
f1 (ppm)


171.53
155.07
134.15
129.45
127.74
111.96
111.64
77.16 CDCl3
61.13
56.38
40.15
14.31
f1 (ppm)

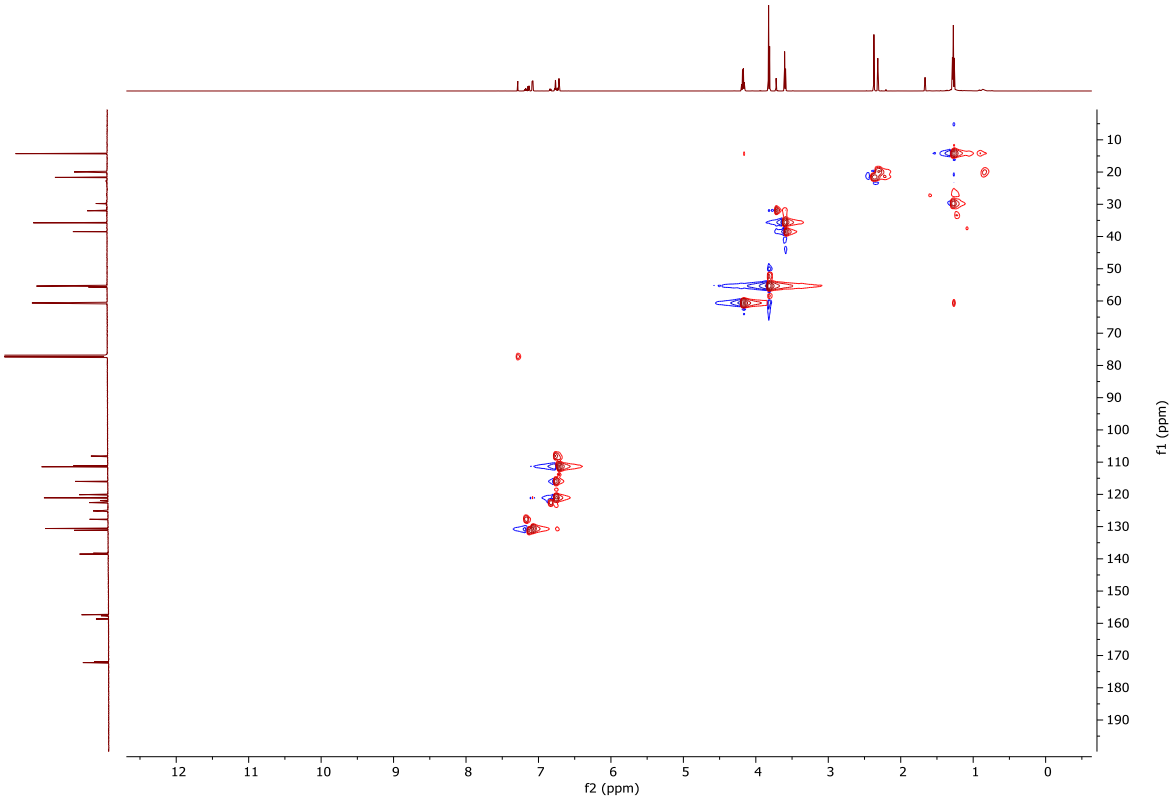

MeO
Cl
CO2Et
8a
1.00
4.00
0.96
0.90
2.02
3.00
2.00
3.22
f1 (ppm)


172.10
156.94
156.06
137.94
137.66
134.15
134.10
132.13
131.92
131.89
131.19
130.26
129.59
129.53
128.81
128.76
126.65
126.13
120.56
111.27
111.17
77.47
77.36 CDCl3
77.05
61.08
55.96
55.86
40.70
31.21
14.45
f1 (ppm)

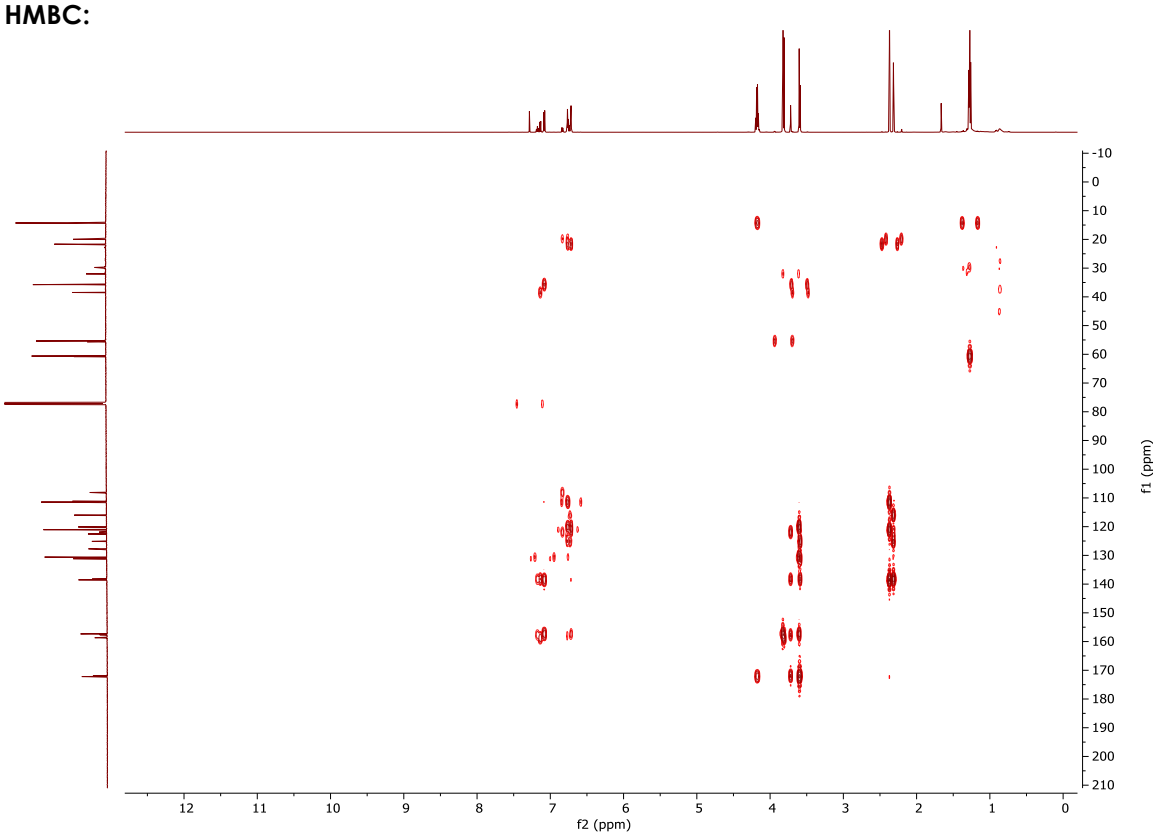

7.26 CDCl3
7.07
7.05
6.74
6.74
6.73
6.73
6.69
4.17
4.16
4.16
4.15
4.15
4.14
4.14
4.13
3.80
3.58
2.35
1.26
1.25
1.23
1
5
CO2Et
Me
OMe
3
9a
0.28
0.50
1.00
1.76
0.28
1.49
1.06
3.62
2.84
0.60
2.00
1.16
3.07
2.45
7.12
f1 (ppm)

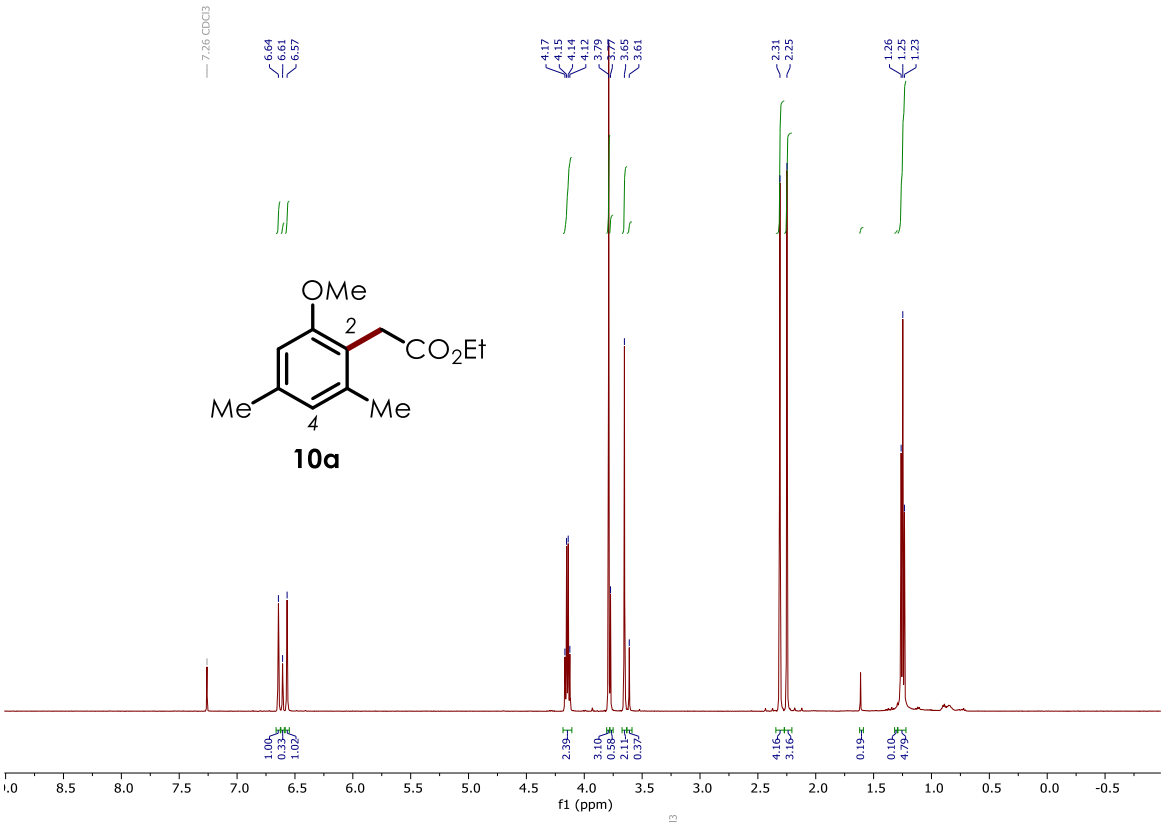

172.27
172.02
172.01
157.74
138.60
138.38
138.32
131.24
130.67
127.80
125.21
122.63
121.98
121.14
120.18
116.05
111.51
111.22
108.19
77.16 CDCl3
60.89
60.69
55.73
55.45
55.29
38.56
35.83
32.09
29.84
21.73
20.05
19.89
14.36
14.33
14.29
f1 (ppm)

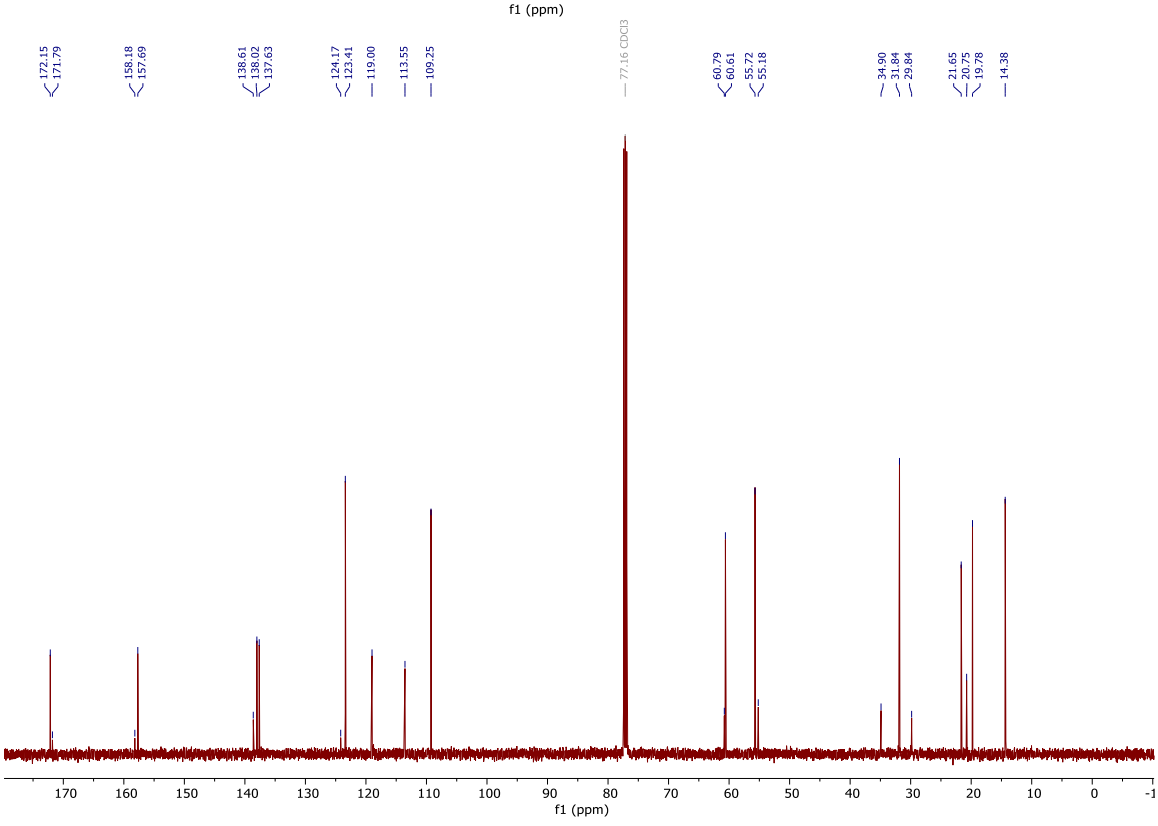
HSQC:

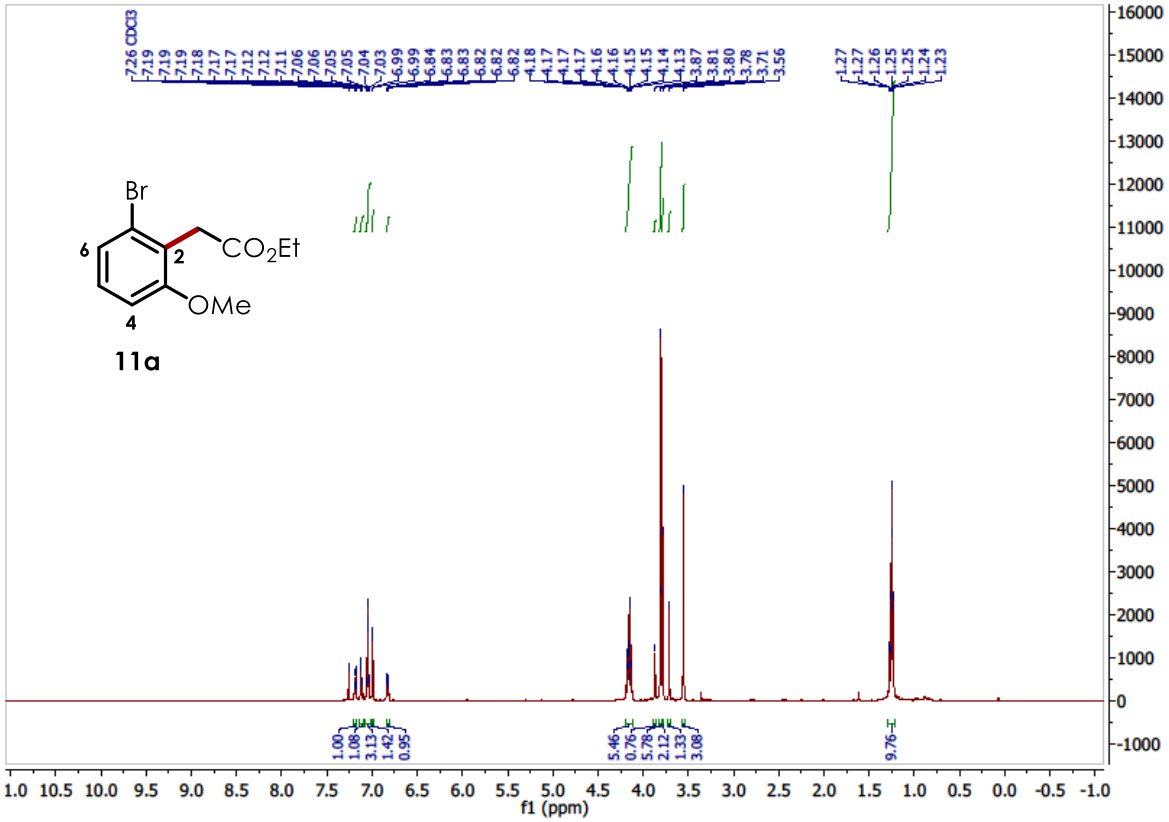


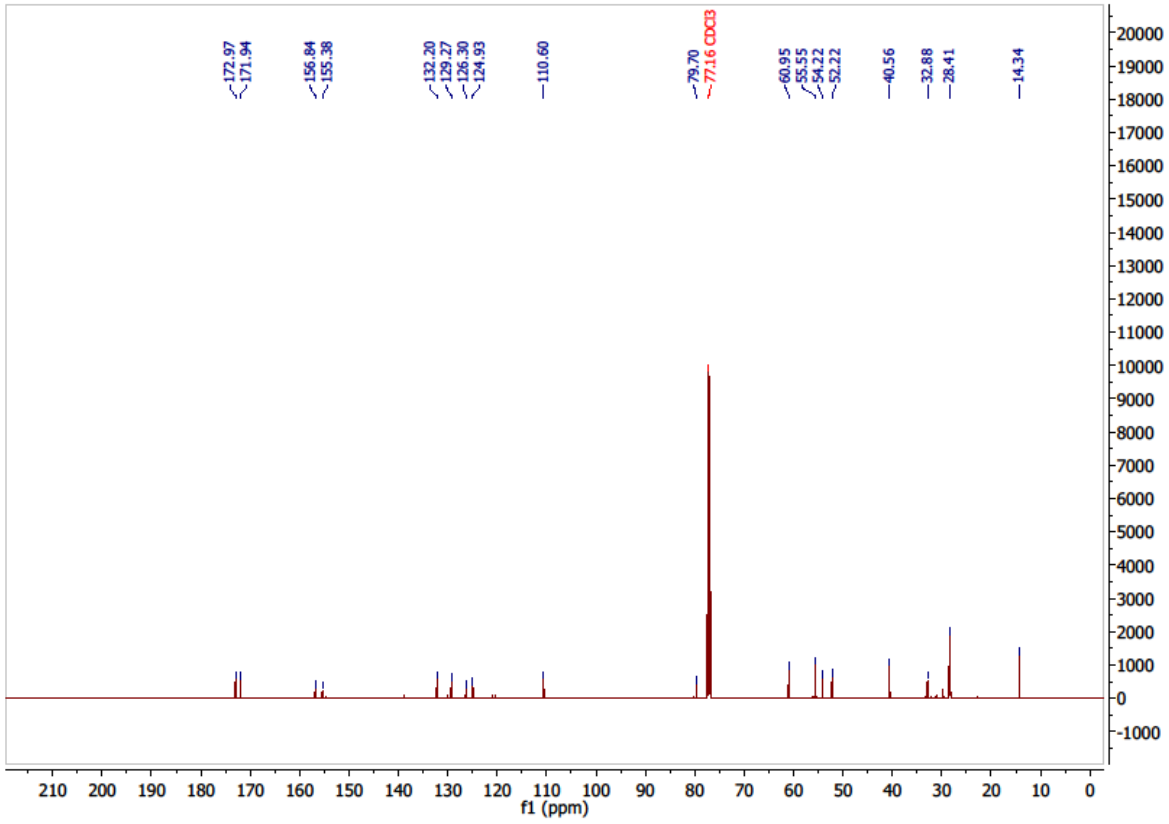
HMBC:

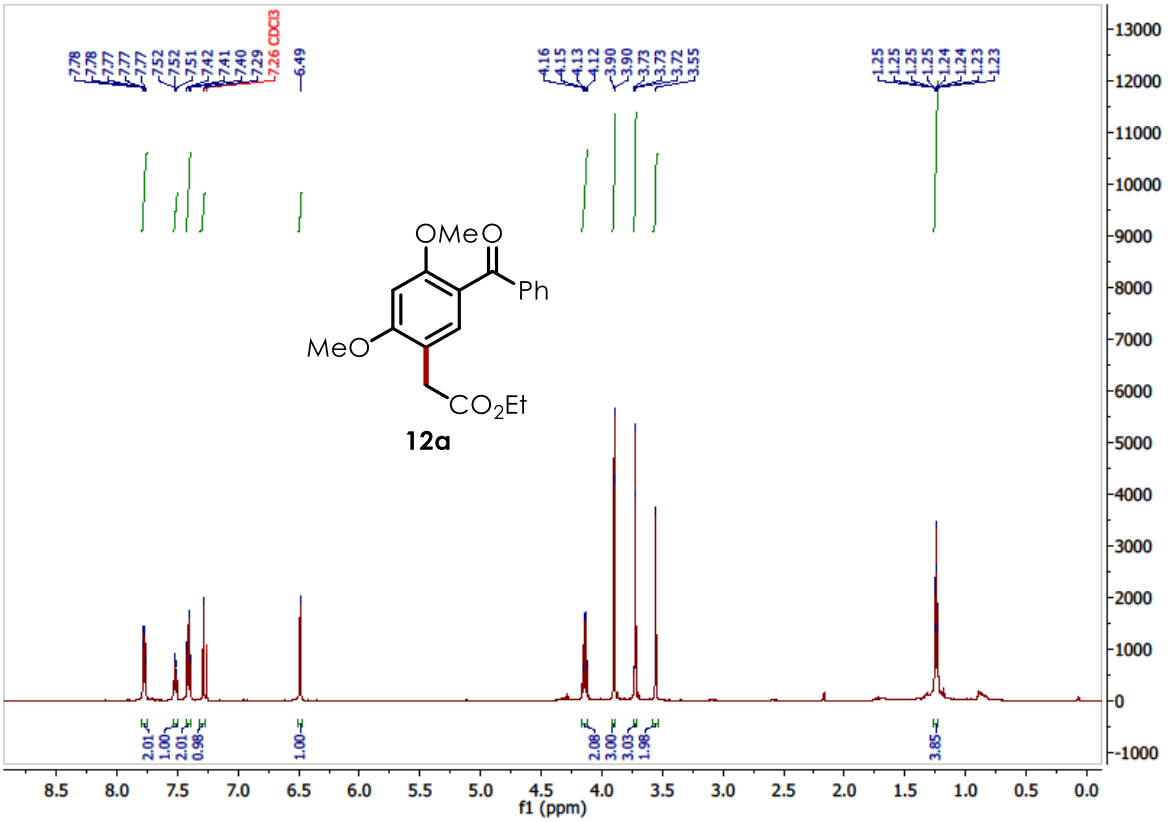


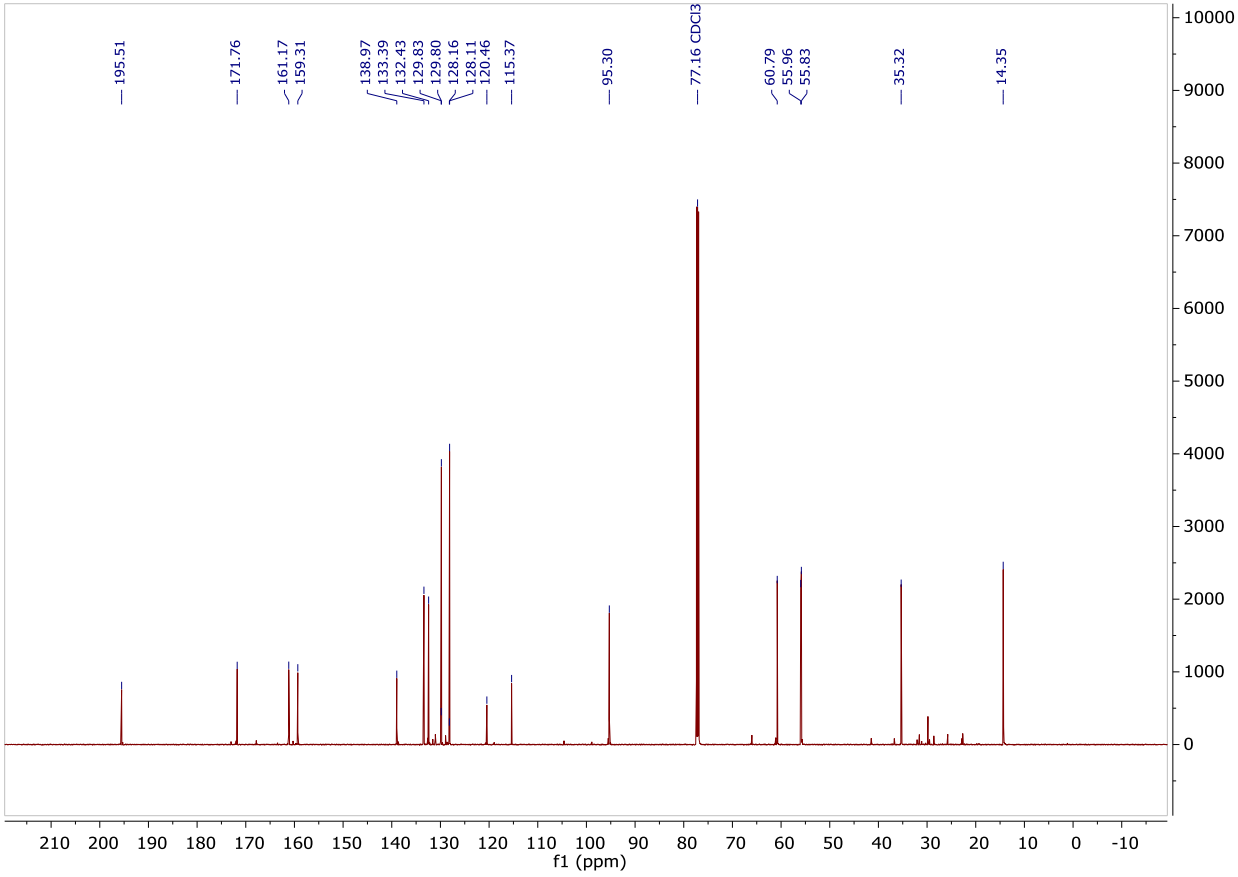

7.26 CDCl3
6.64
6.61
6.57
4.17
4.15
4.14
4.12
3.79
3.77
3.65
3.61
2.31
2.25
1.26
1.25
1.23
OMe
2
CO2Et
Me
Me
4
10a
1.00
0.33
1.02
2.39
3.10
0.58
2.11
0.37
4.16
3.16
0.19
0.10
4.79
f1 (ppm)

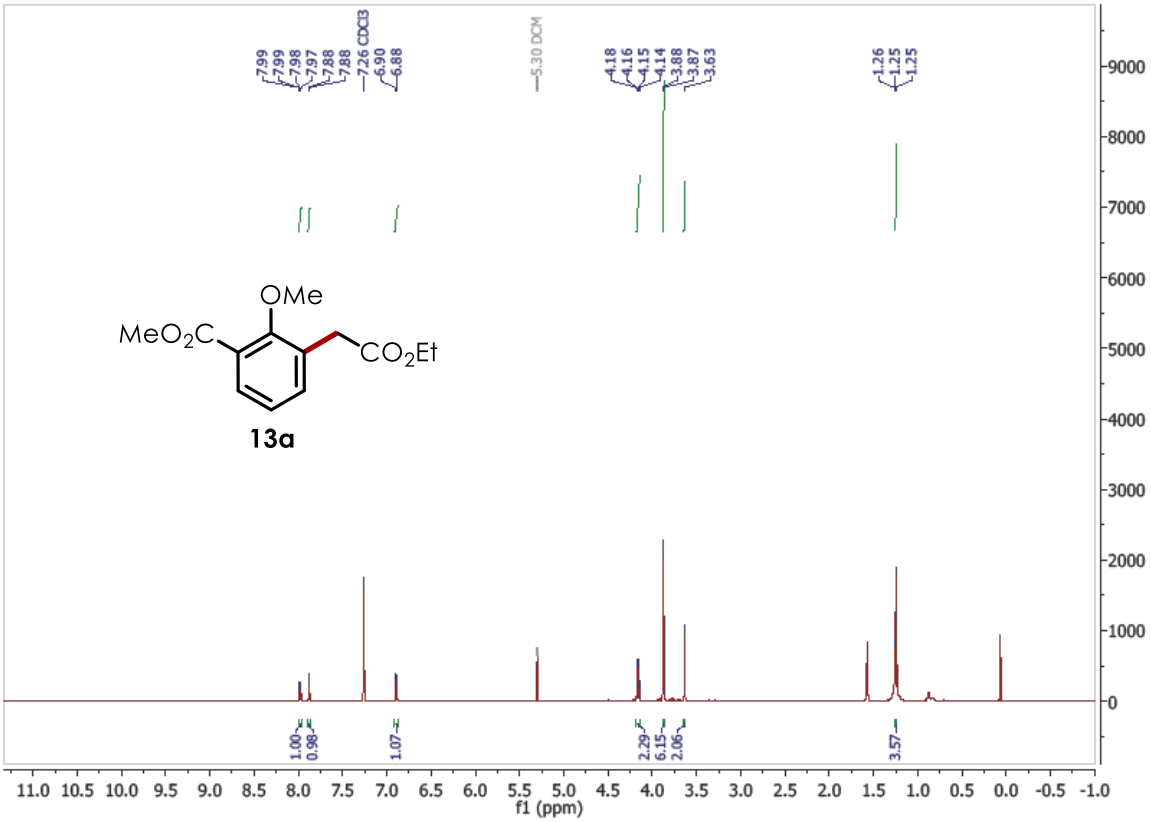

172.15
171.79
158.18
157.69
138.61
138.02
137.63
124.17
123.41
119.00
113.55
109.25
77.16 CDCl3
60.79
60.61
55.72
55.18
34.90
31.84
29.84
21.65
20.75
19.78
14.38
f1 (ppm)

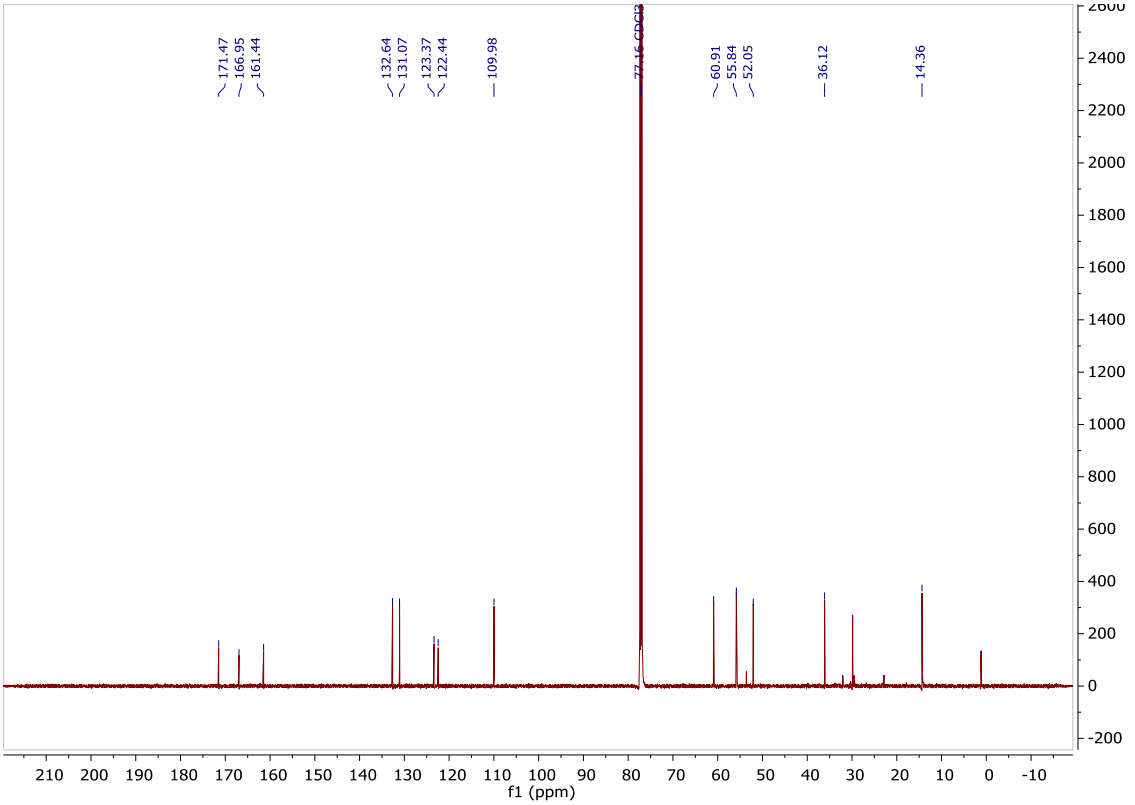

Br
6
2
CO2Et
OMe
4
11a
f1 (ppm)

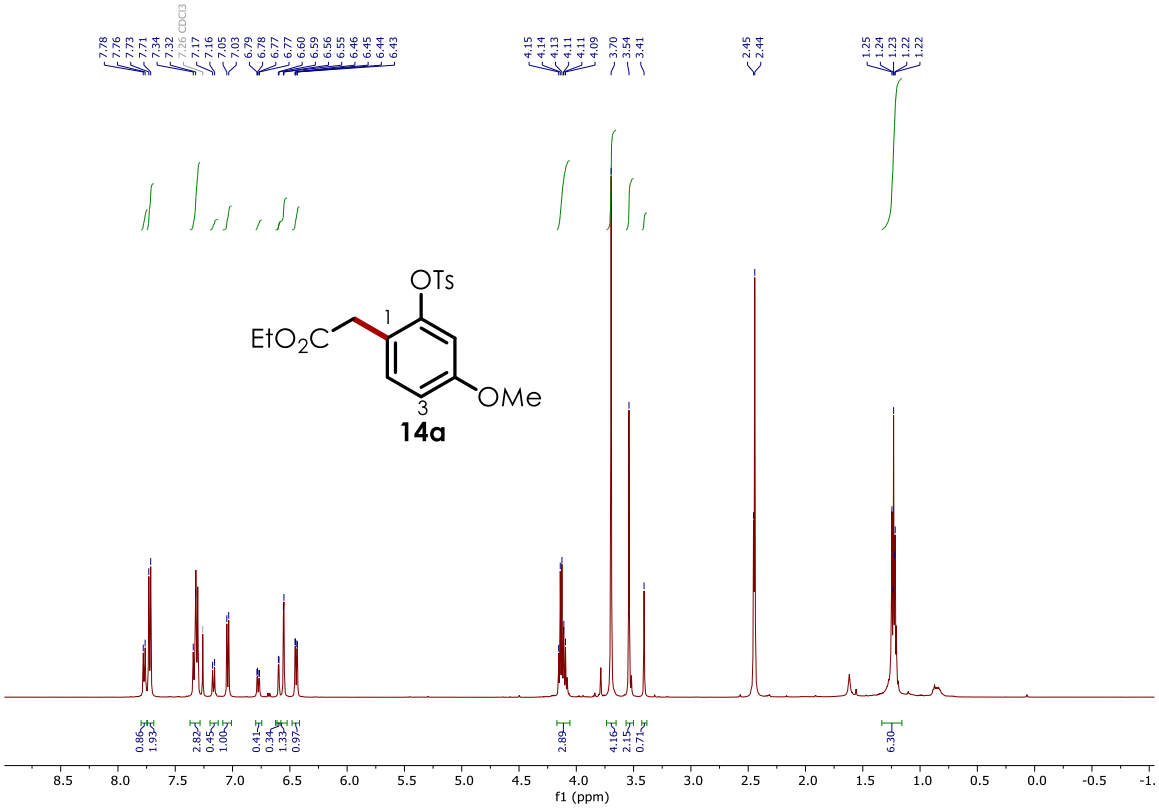

f1 (ppm)

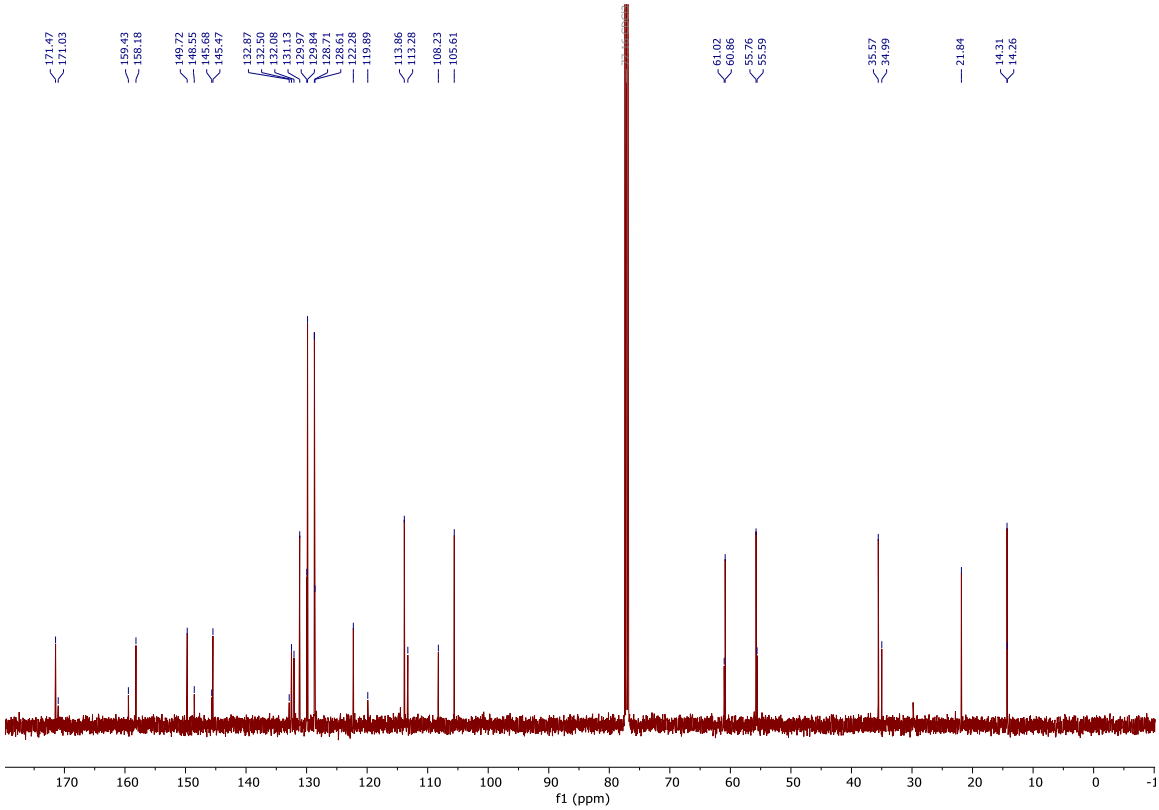

7.78
7.78
7.77
7.77
7.77
7.77
7.52
7.52
7.51
7.42
7.41
7.40
7.29
7.26 CDCl3
6.49
4.16
4.15
4.13
4.12
3.90
3.90
3.73
3.73
3.72
3.55
1.25
1.25
1.25
1.25
1.24
1.24
1.23
1.23
OMe
O
Ph
MeO
CO2Et
12a
2.01
1.00
2.01
0.98
1.00
2.08
3.00
3.03
1.98
3.85
f1 (ppm)

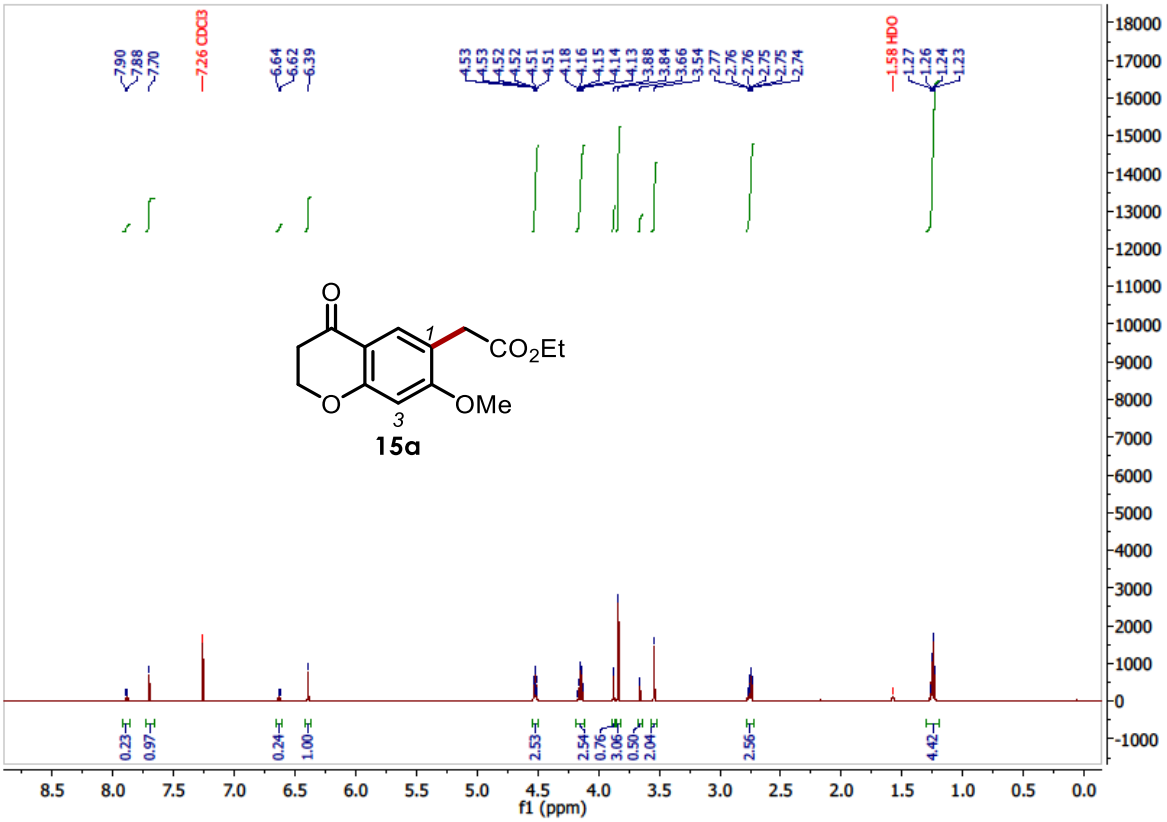

195.51
171.76
161.17
159.31
138.97
133.39
132.43
129.83
129.80
128.16
128.11
120.46
115.37
95.30
77.16 CDCl3
60.79
55.96
55.83
35.32
14.35
f1 (ppm)

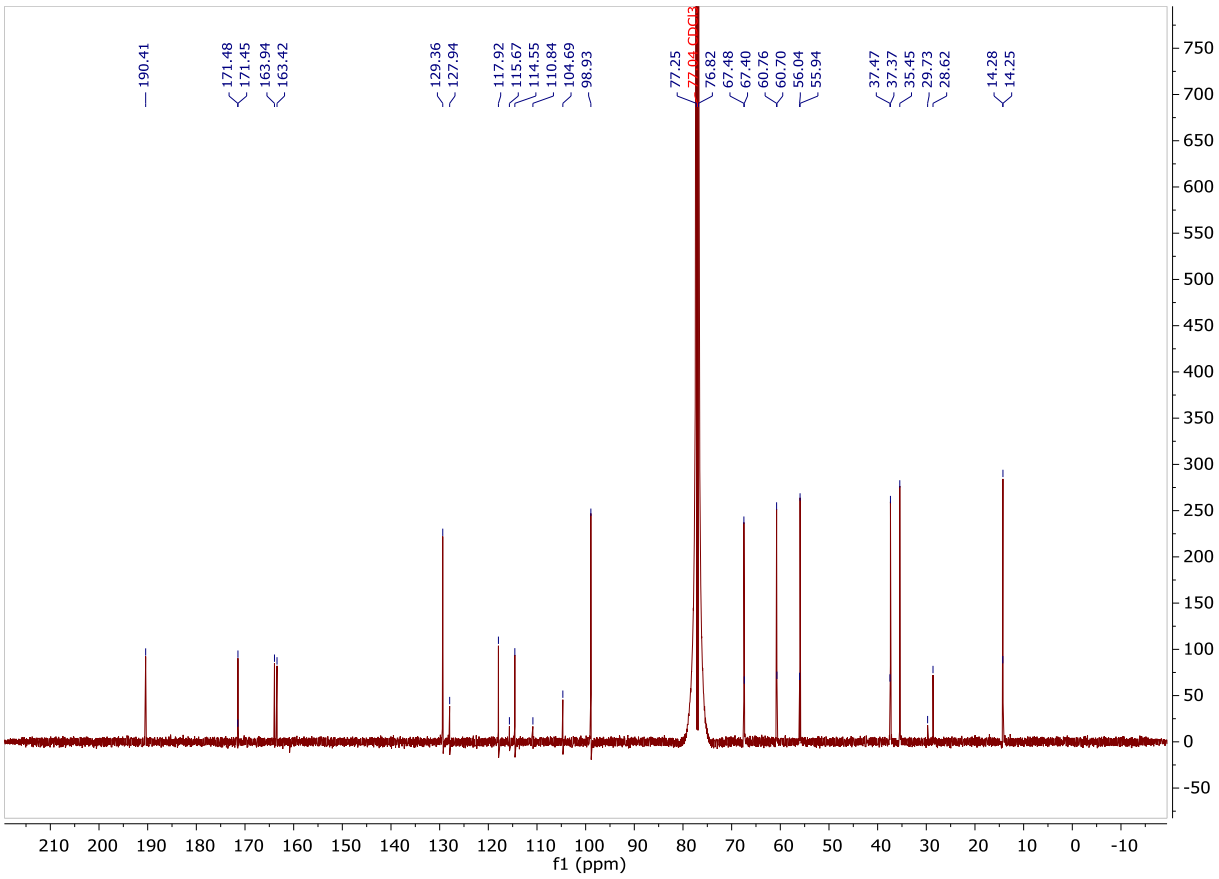

7.99
7.99
7.98
7.97
7.88
7.88
7.26 CDCl3
6.90
6.88
5.30 DCM
4.18
4.16
4.15
4.14
3.88
3.87
3.63
1.26
1.25
1.25
OMe
MeO2C
CO2Et
13a
1.00
0.98
1.07
2.29
6.15
2.06
3.57
f1 (ppm)

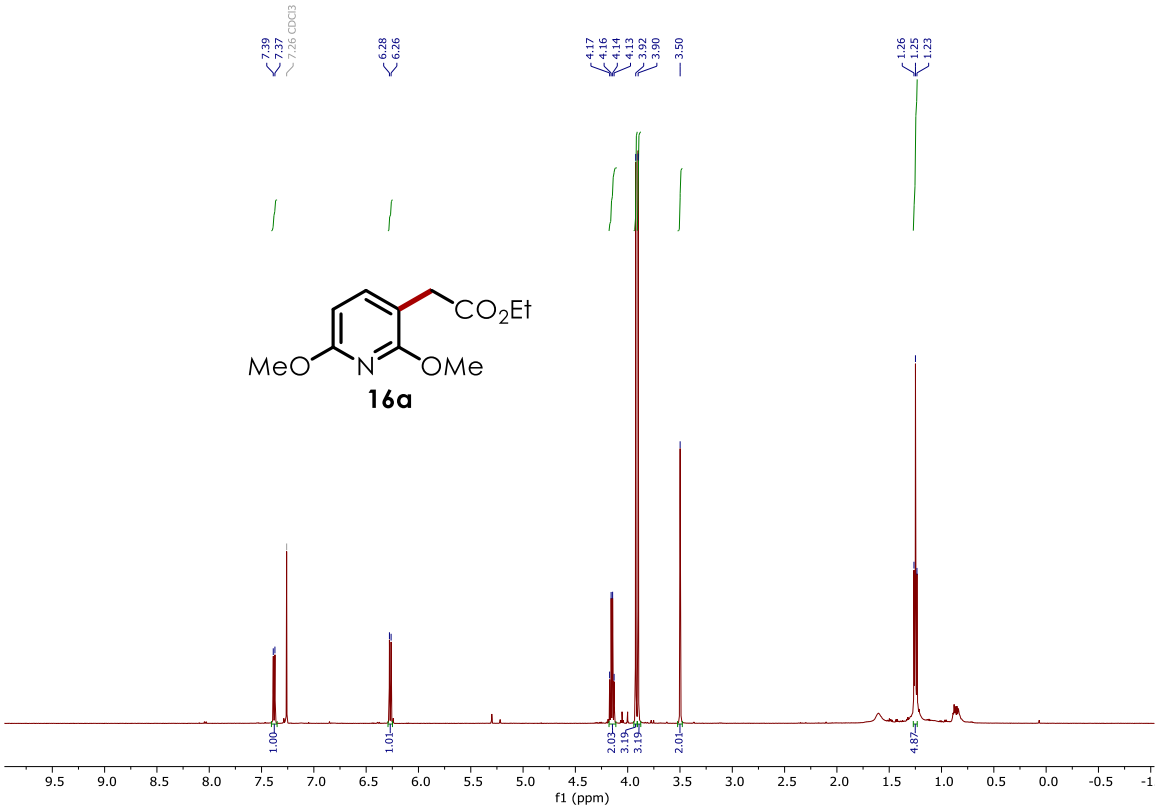

171.47
166.95
161.44
132.64
131.07
123.37
122.44
109.98
77.16 CDCl3
60.91
55.84
52.05
36.12
14.36
f1 (ppm)

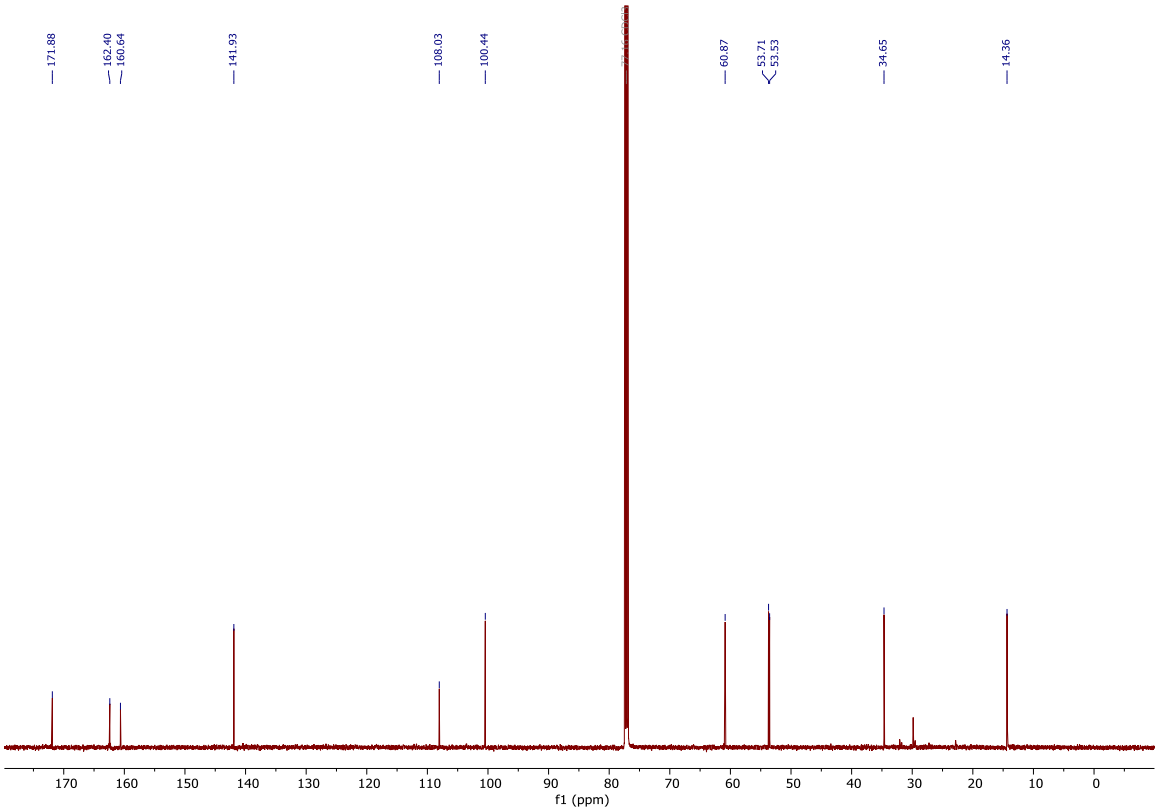

OTs
EtO2C
1
3
OMe
14a
f1 (ppm)

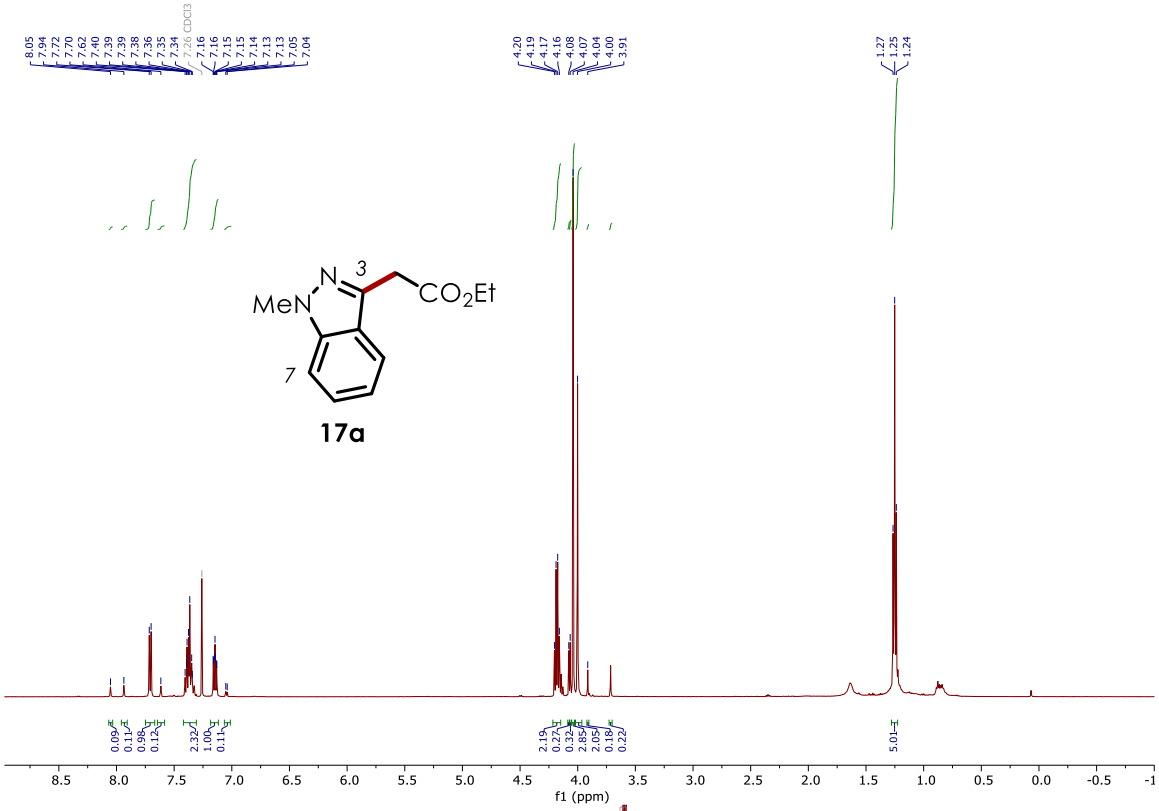

f1 (ppm)


7.90
7.88
7.70
7.26 CDCl3
6.64
6.62
6.39
4.53
4.53
4.52
4.52
4.51
4.51
4.18
4.16
4.15
4.14
4.13
3.88
3.84
3.66
3.54
2.77
2.76
2.76
2.75
2.75
2.74
1.58 HDO
1.27
1.26
1.24
1.23
O
O
1
CO2Et
OMe
3
15a
0.23
0.97
0.24
1.00
2.53
2.54
0.76
3.06
0.50
2.04
2.56
4.42
f1 (ppm)

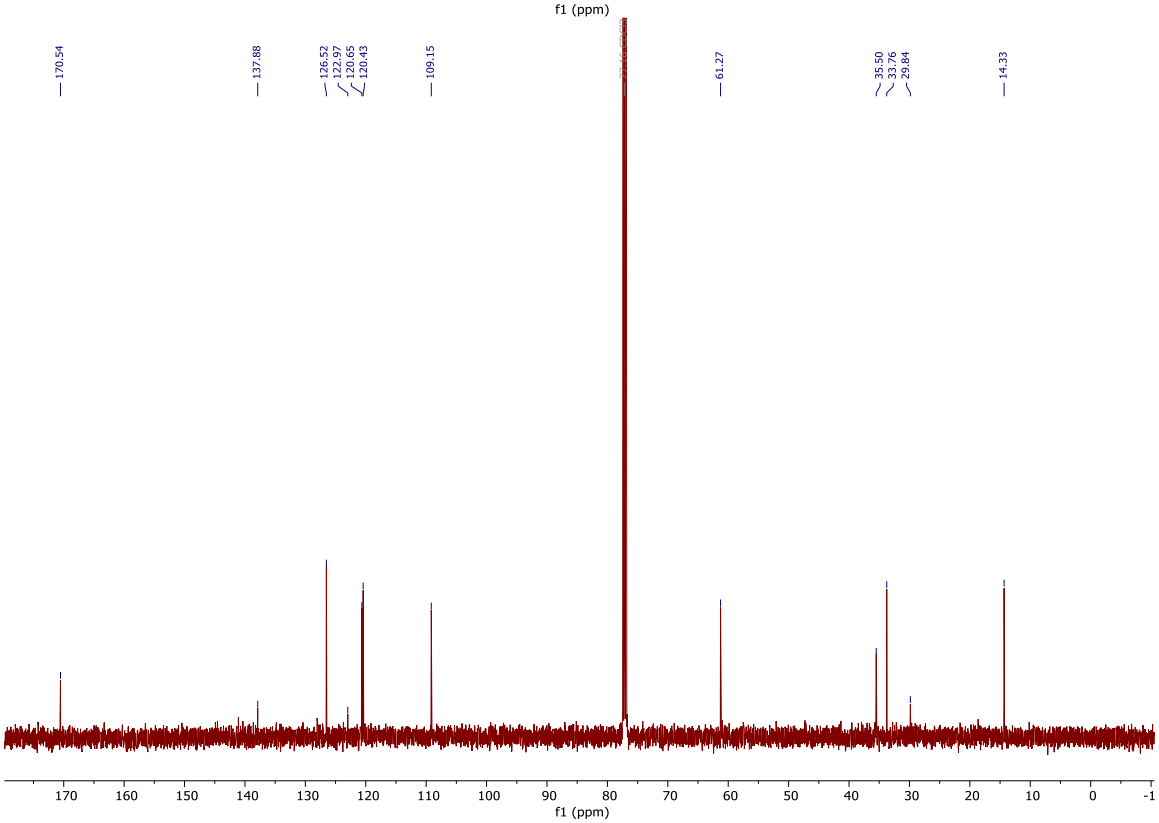

190.41
171.48
171.45
163.94
163.42
129.36
127.94
117.92
115.67
114.55
110.84
104.69
98.93
77.25
77.04 CDCl3
76.82
67.48
67.40
60.76
60.70
56.04
55.94
37.47
37.37
35.45
29.73
28.62
14.28
14.25
f1 (ppm)

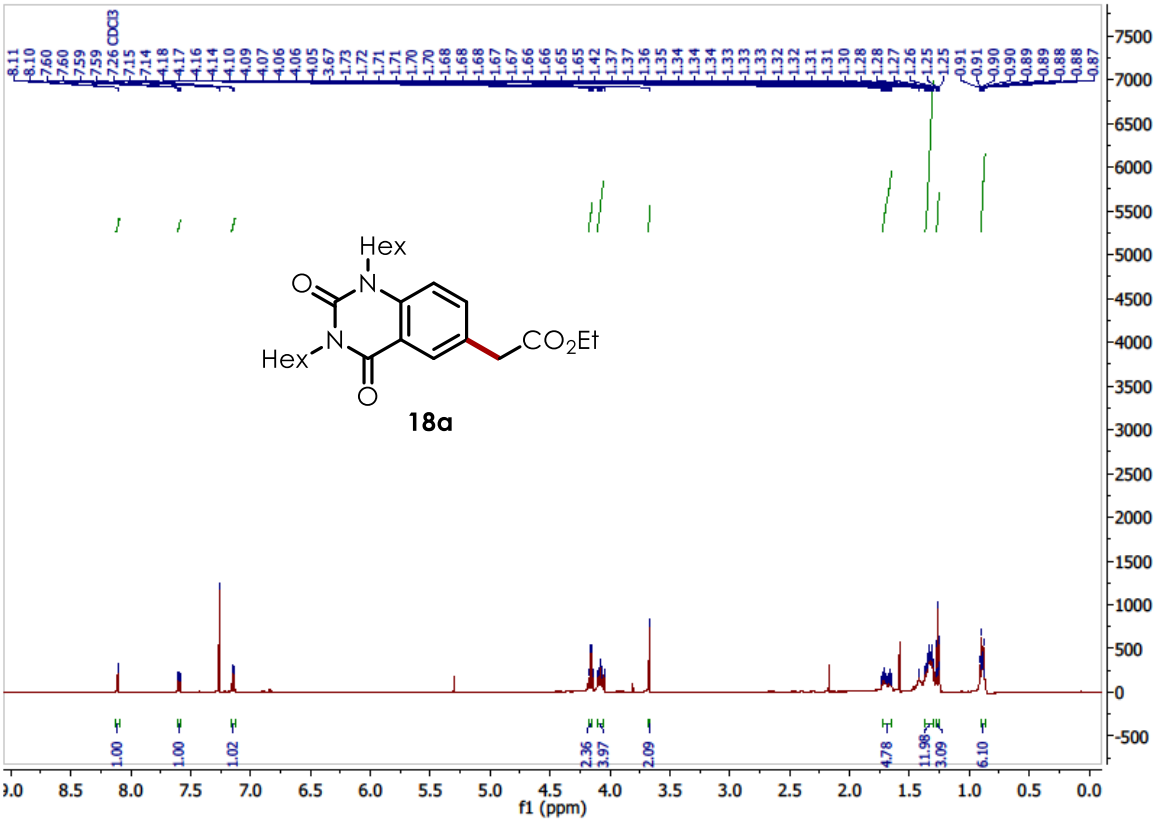

7.39
7.37
7.26 CDCl3
6.28
6.26
4.17
4.16
4.14
4.13
3.92
3.90
3.50
1.26
1.25
1.23
CO2Et
MeO
N
OMe
16a
1.00
1.01
2.03
3.19
3.19
2.01
4.87
f1 (ppm)

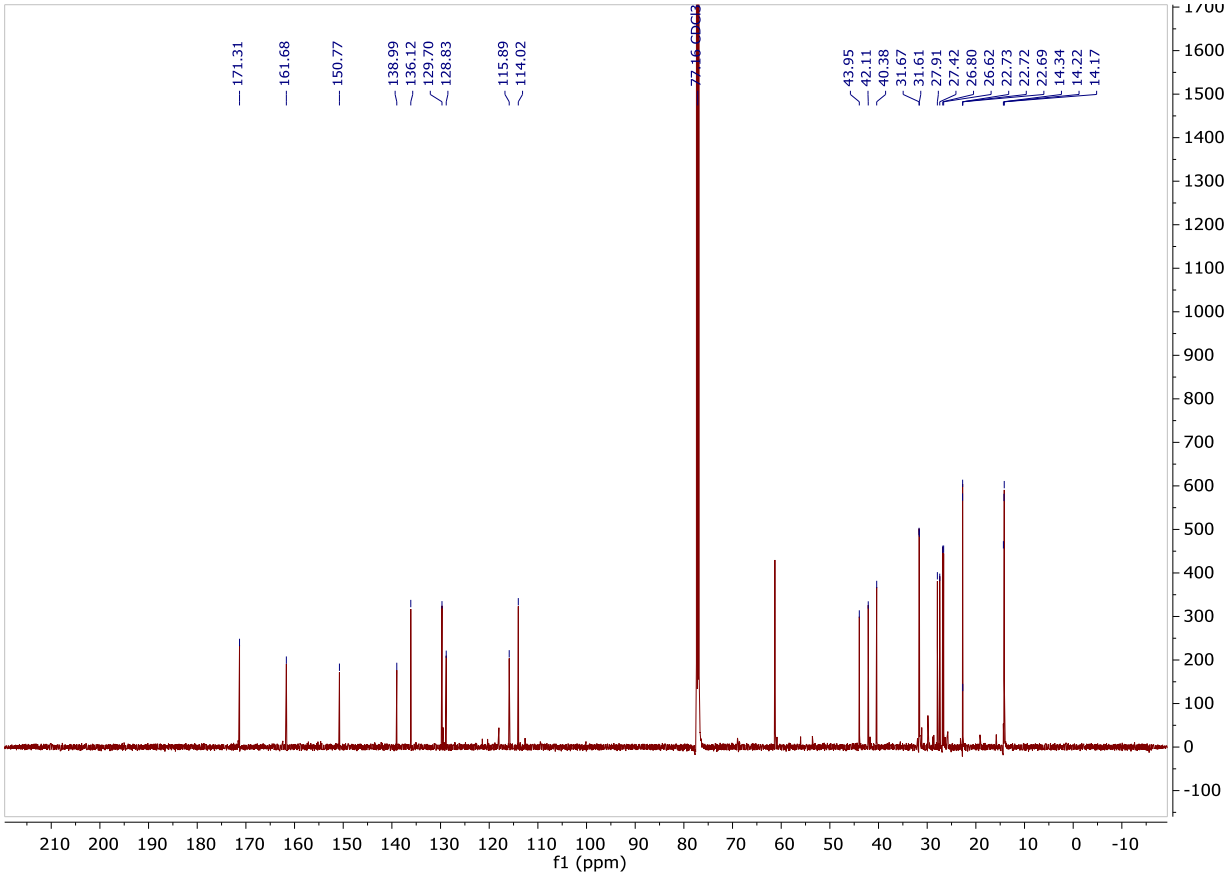

171.88
162.40
160.64
141.93
108.03
100.44
77.16
60.87
53.71
53.53
34.65
14.36
f1 (ppm)

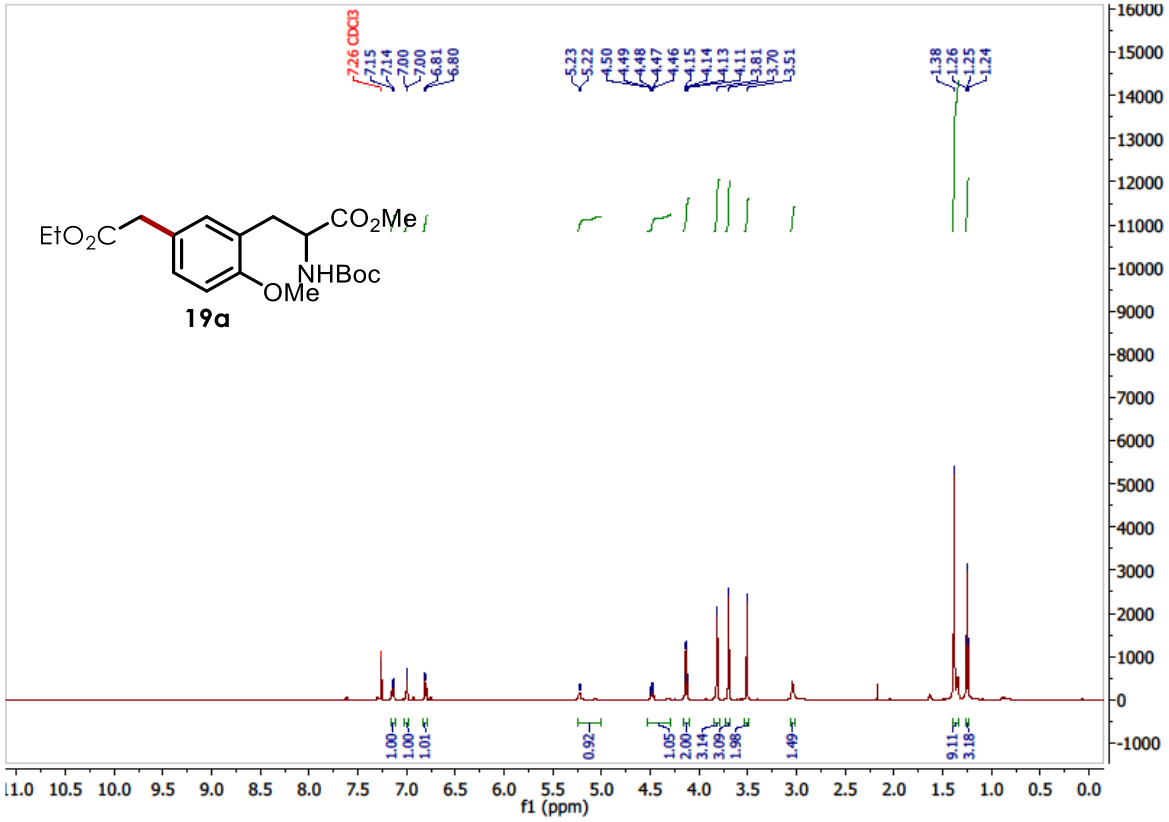

8.05
7.94
7.72
7.70
7.62
7.40
7.39
7.39
7.38
7.36
7.35
7.34
7.26 CDCl3
7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.05
7.04
4.20
4.19
4.17
4.16
4.08
4.07
4.04
4.00
3.91
1.27
1.25
1.24
MeN
N
3
CO2Et
7
0.09
0.11
0.98
0.12
2.32
1.00
0.11
2.19
0.27
0.32
2.85
2.05
0.19
0.22
5.01
f1 (ppm)

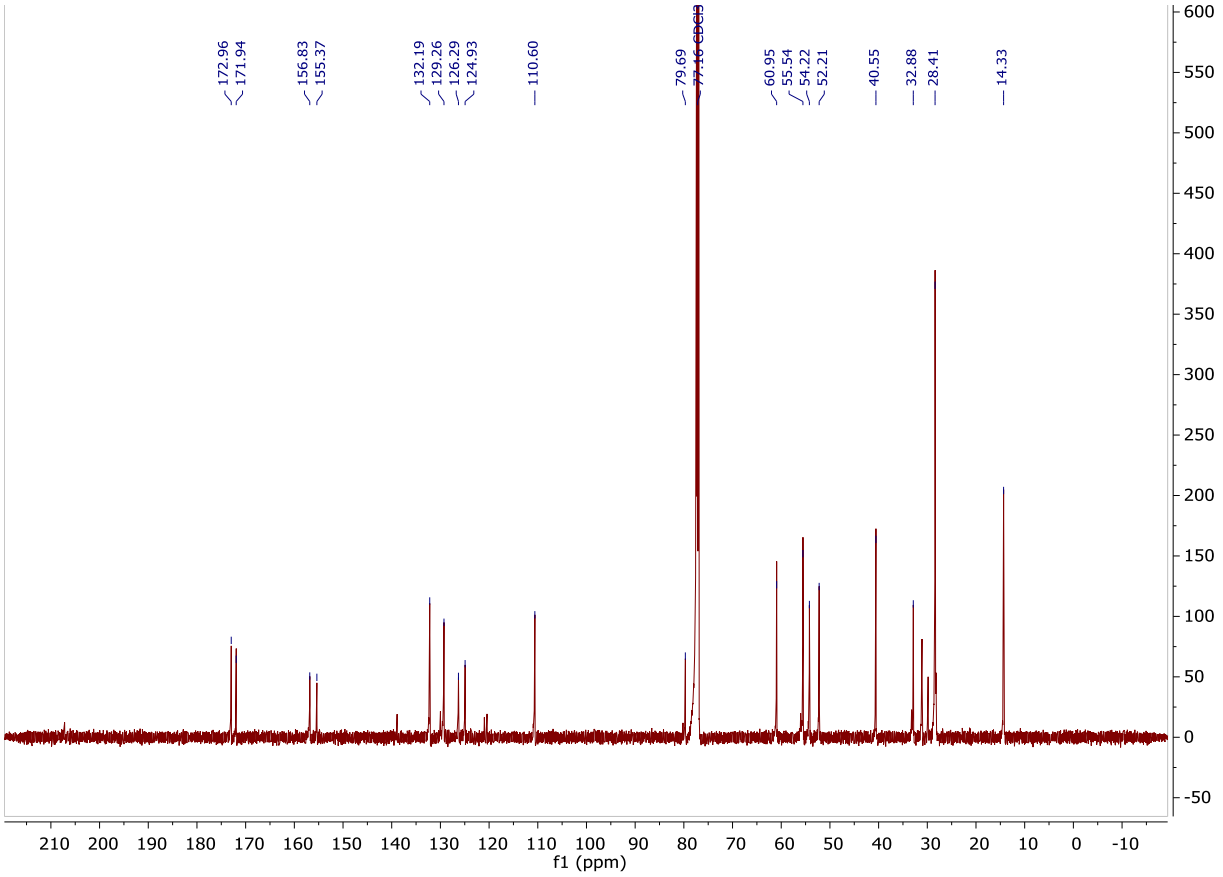
17a

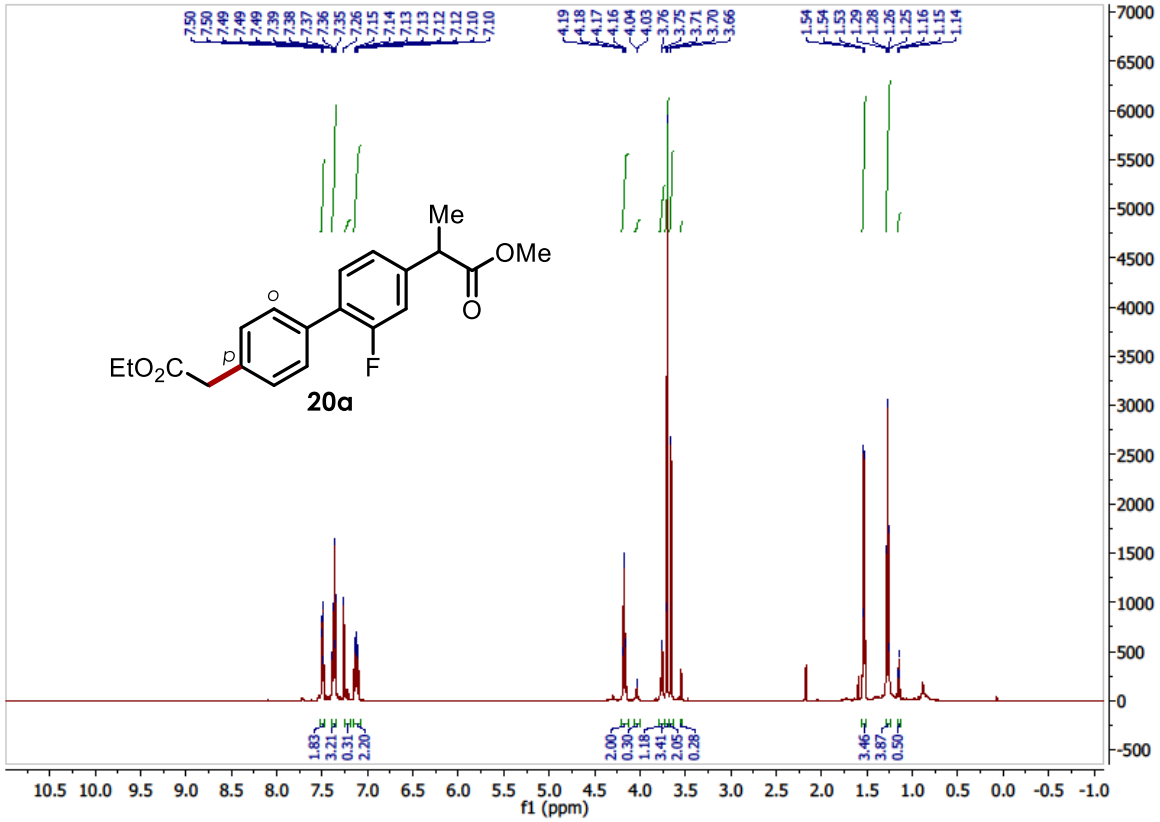

170.54
137.88
126.52
122.97
120.65
120.43
109.15
77.16
61.27
35.50
33.76
29.84
14.33
f1 (ppm)

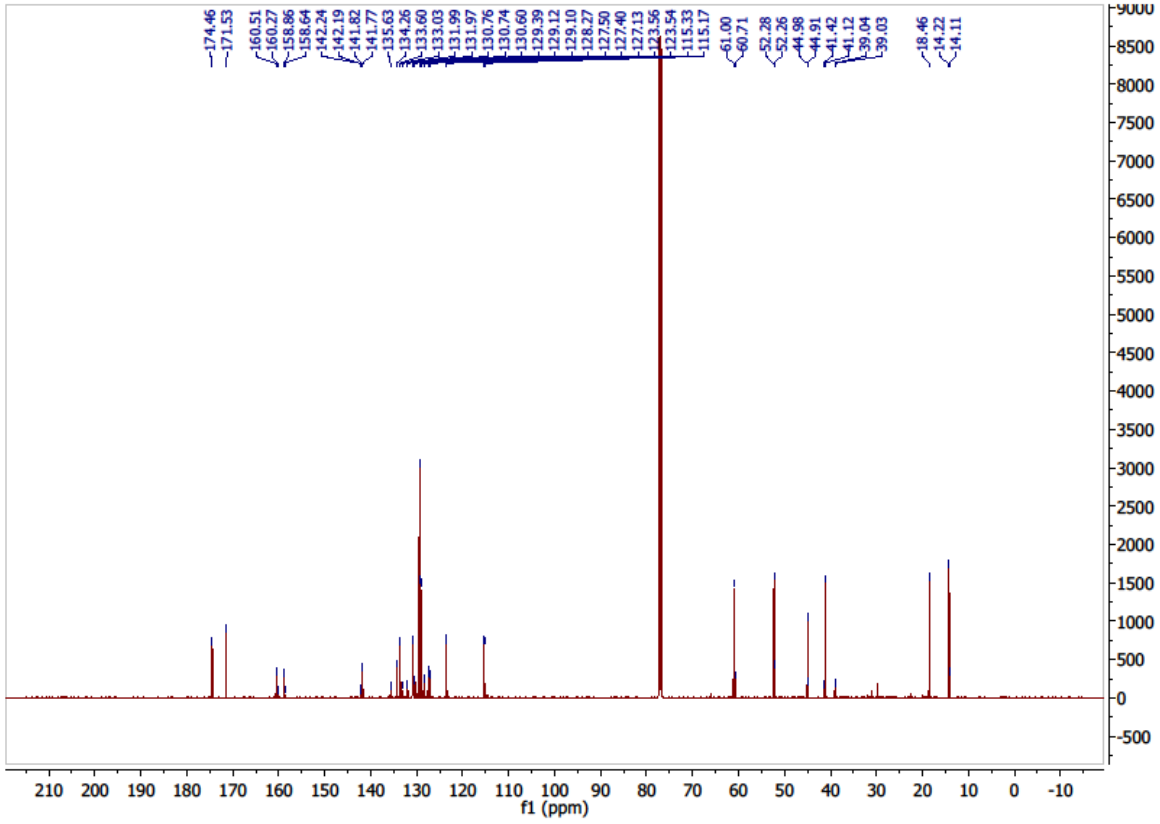

Hex
N
O
N
Hex
O
CO2Et
18a
f1 (ppm)


171.31
161.68
150.77
138.99
136.12
129.70
128.83
115.89
114.02
77.16 CDCl3
43.95
42.11
40.38
31.67
31.61
27.91
27.42
26.80
26.62
22.73
22.72
22.69
14.34
14.22
14.17
f1 (ppm)

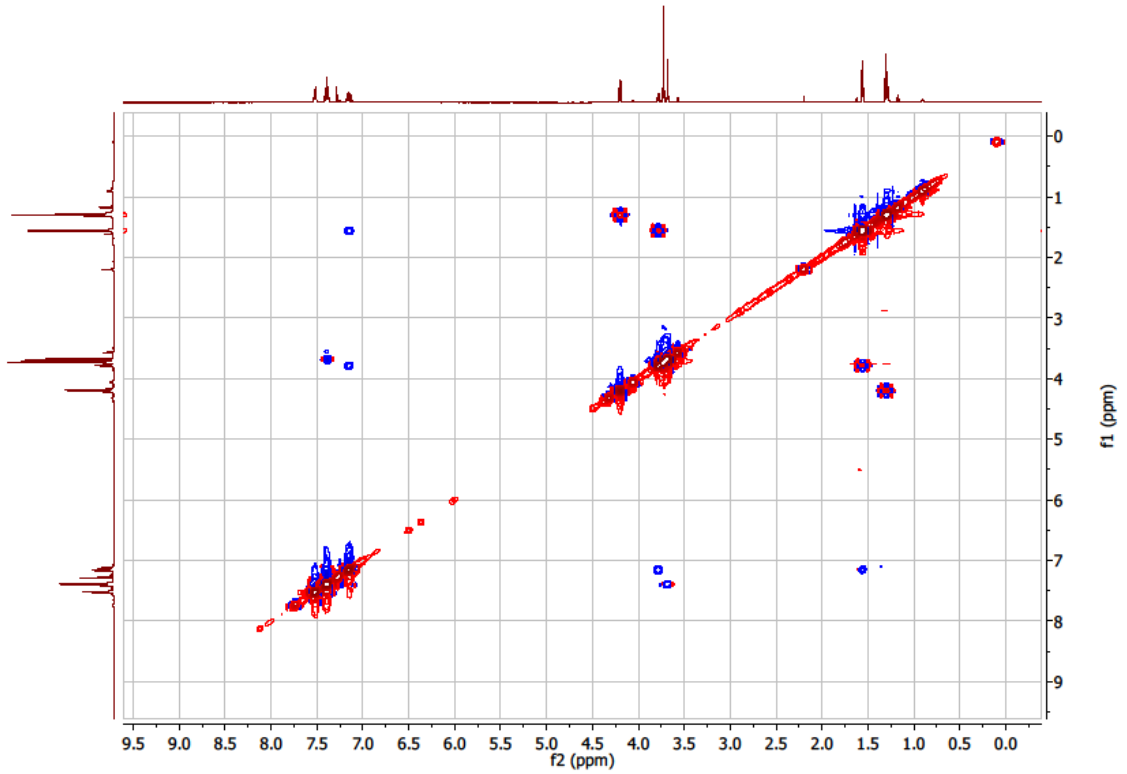

EtO2C
CO2Me
NHBoc
OMe
19a
f1 (ppm)


f1 (ppm)

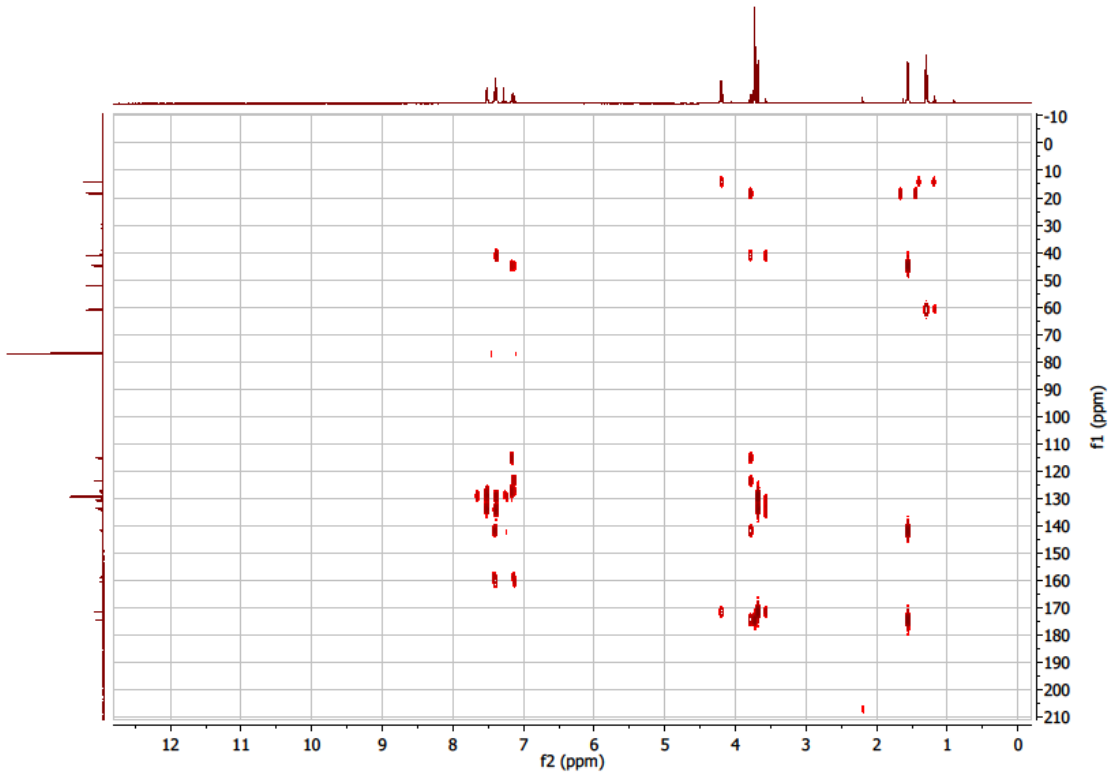

Me
OMe
O
o
p
EtO2C
F
20a
f1 (ppm)


f1 (ppm)

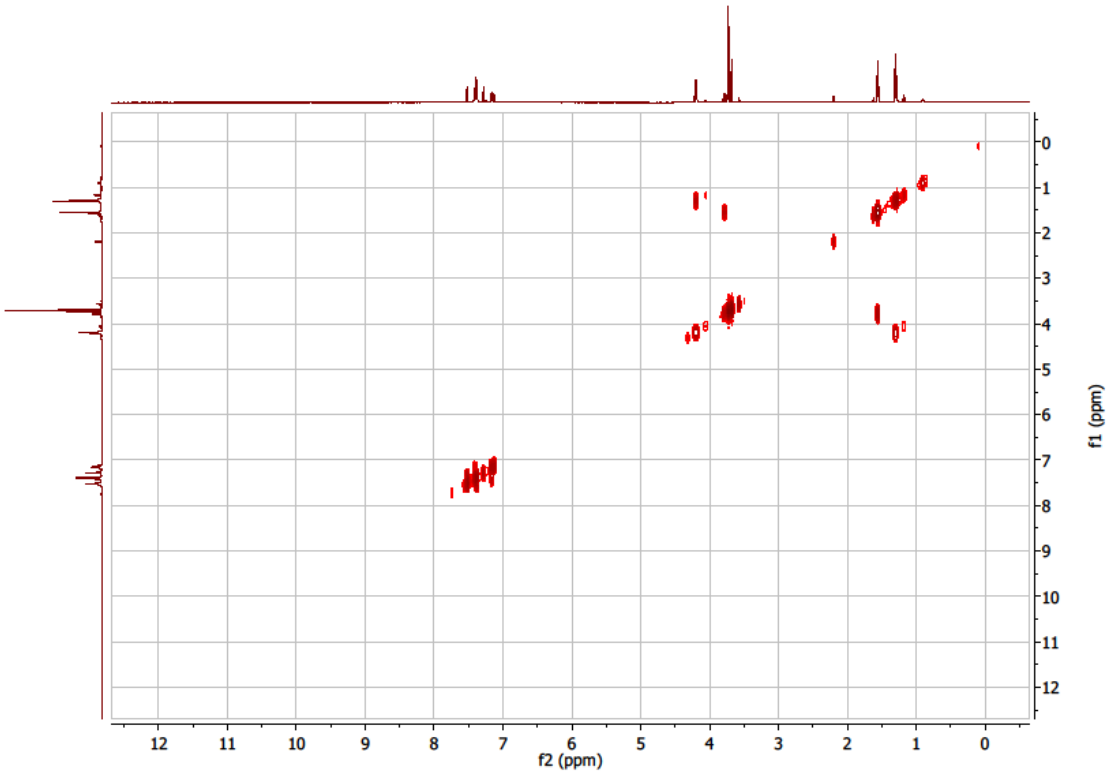
HSQC:



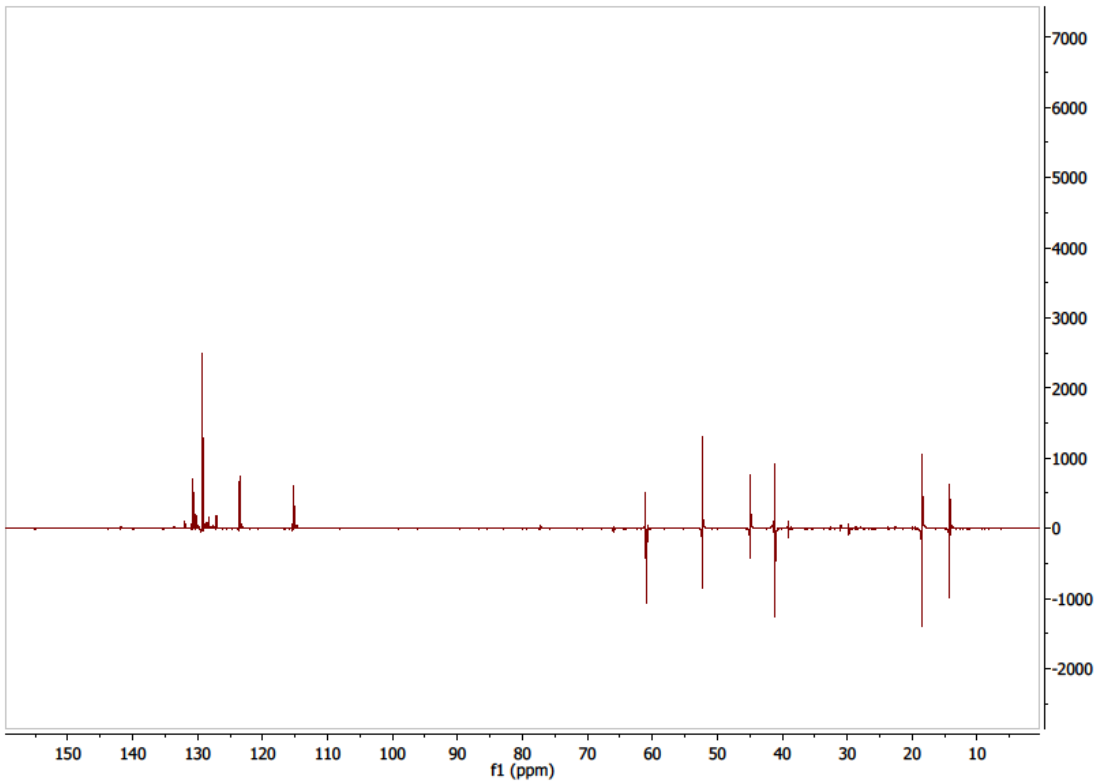
HMQC:

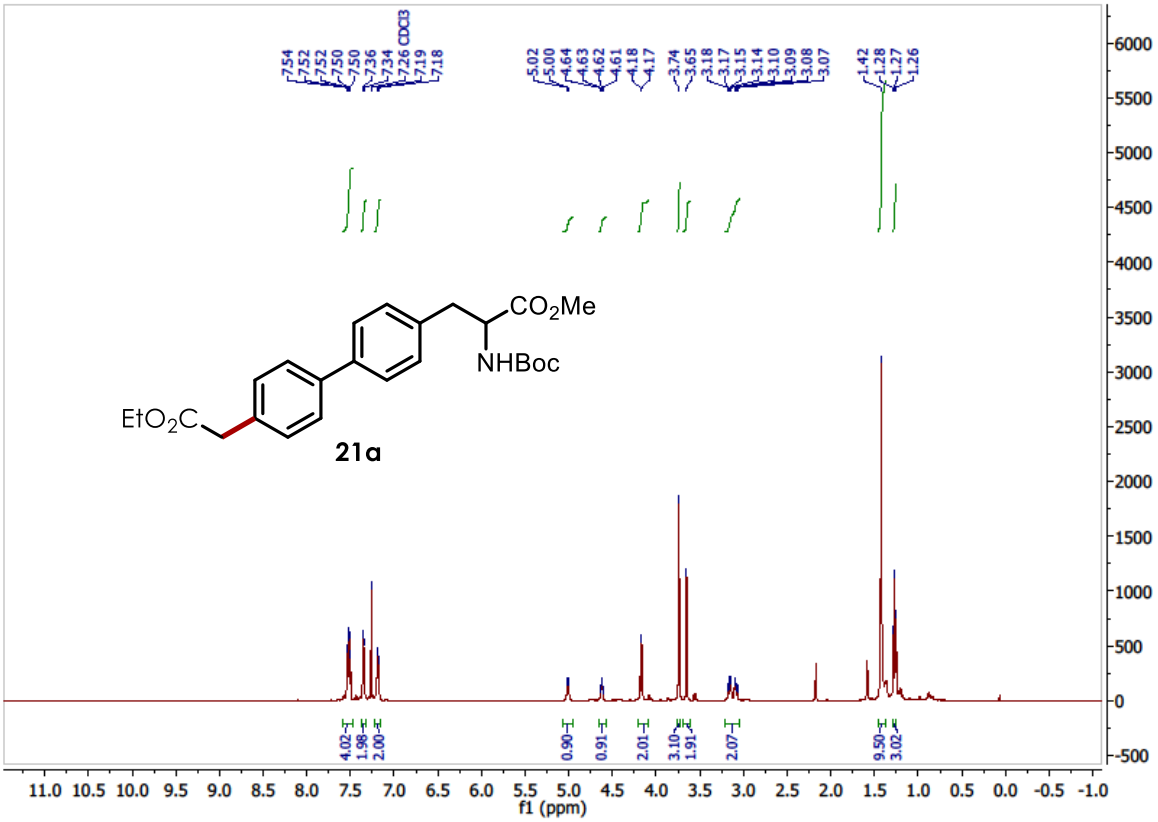


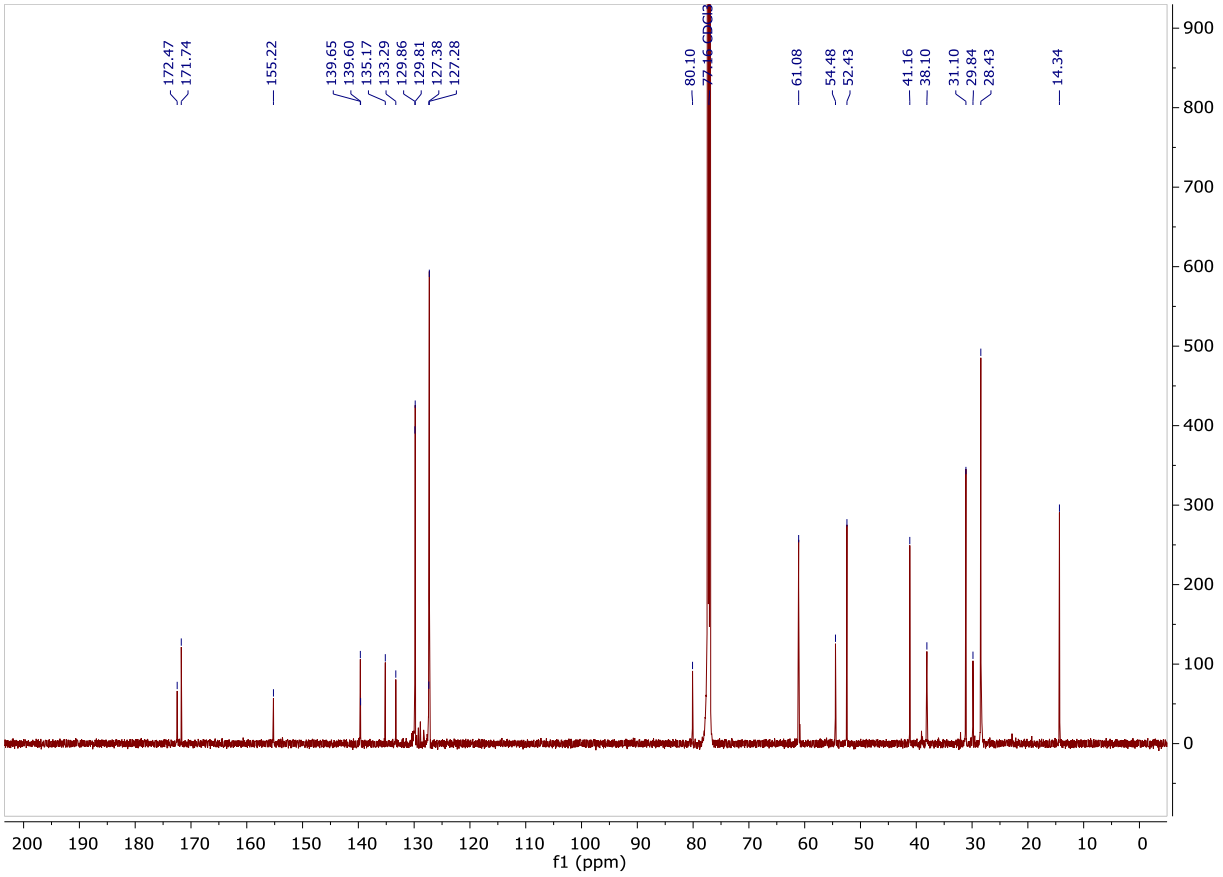
COSY:

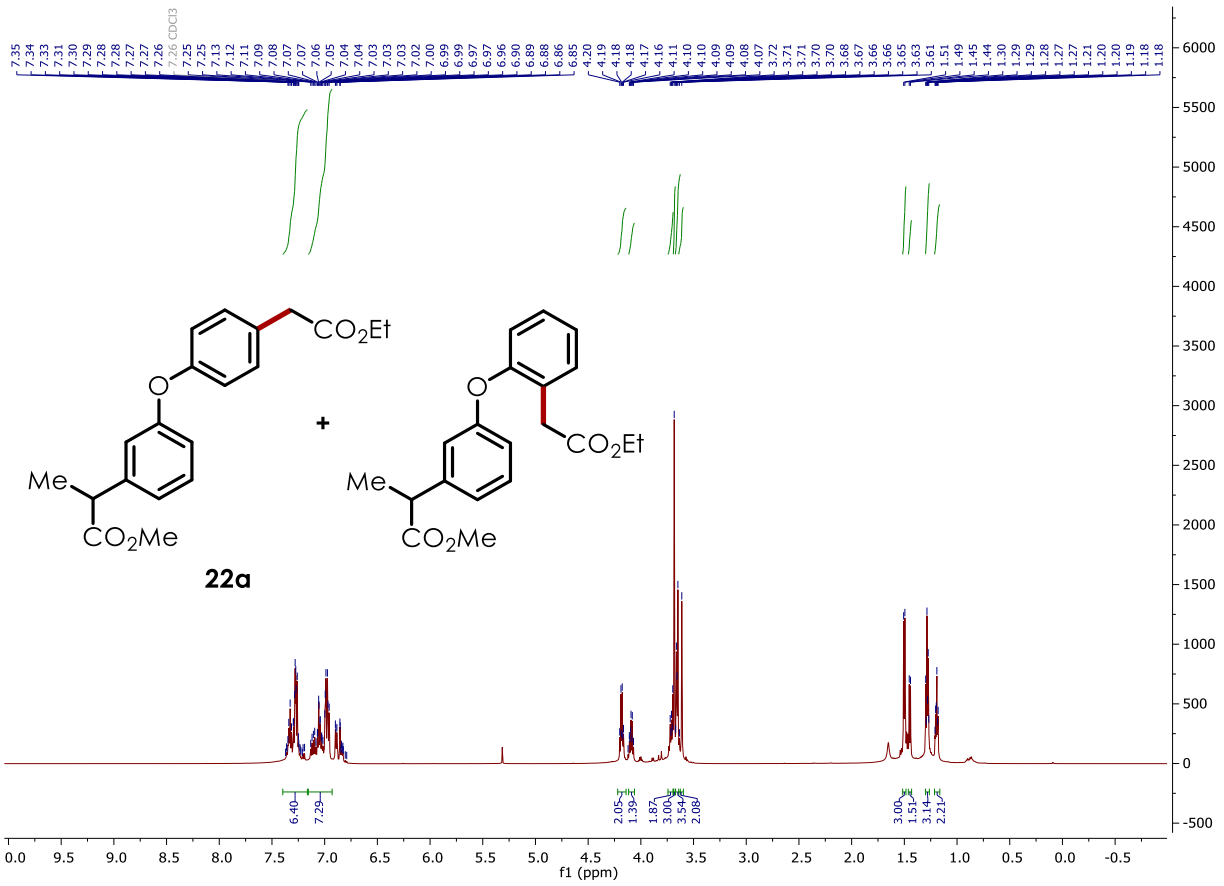


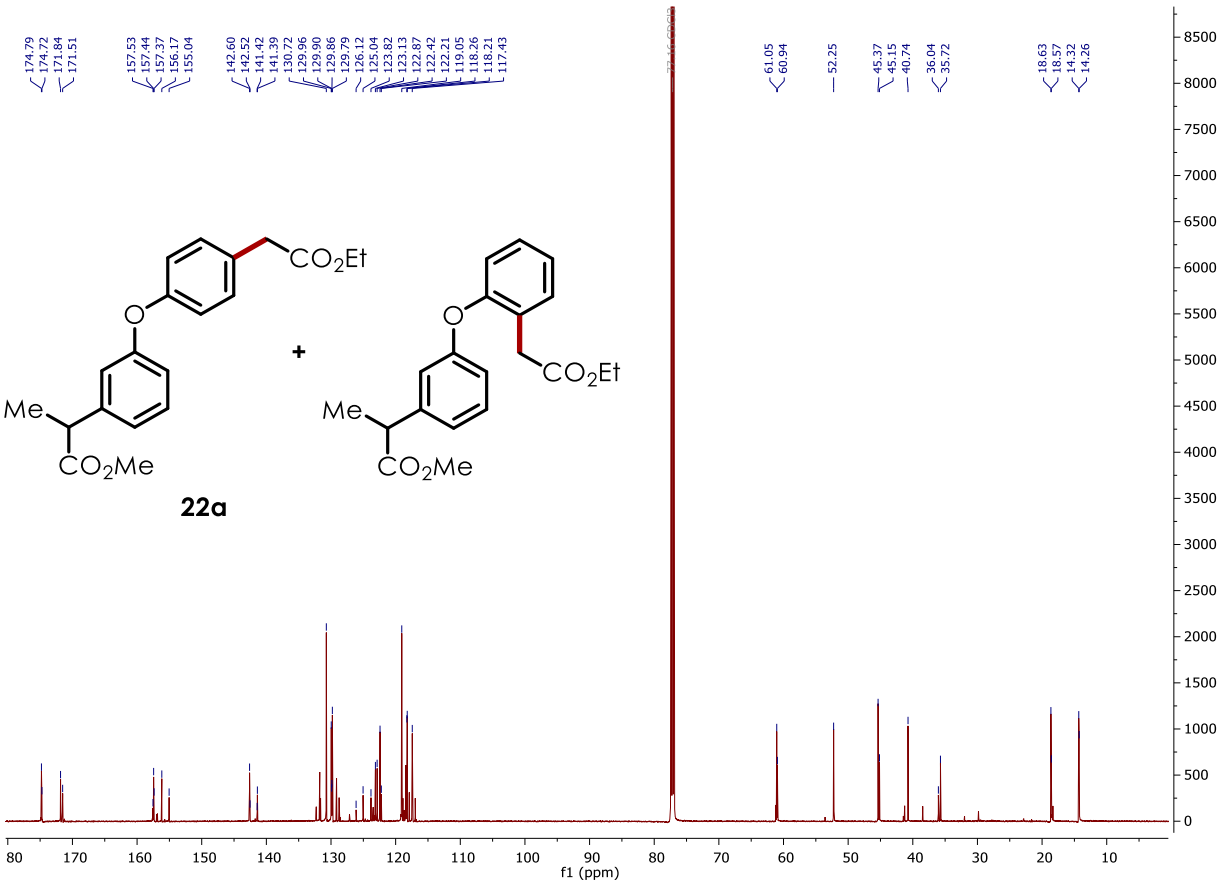
DEPT:

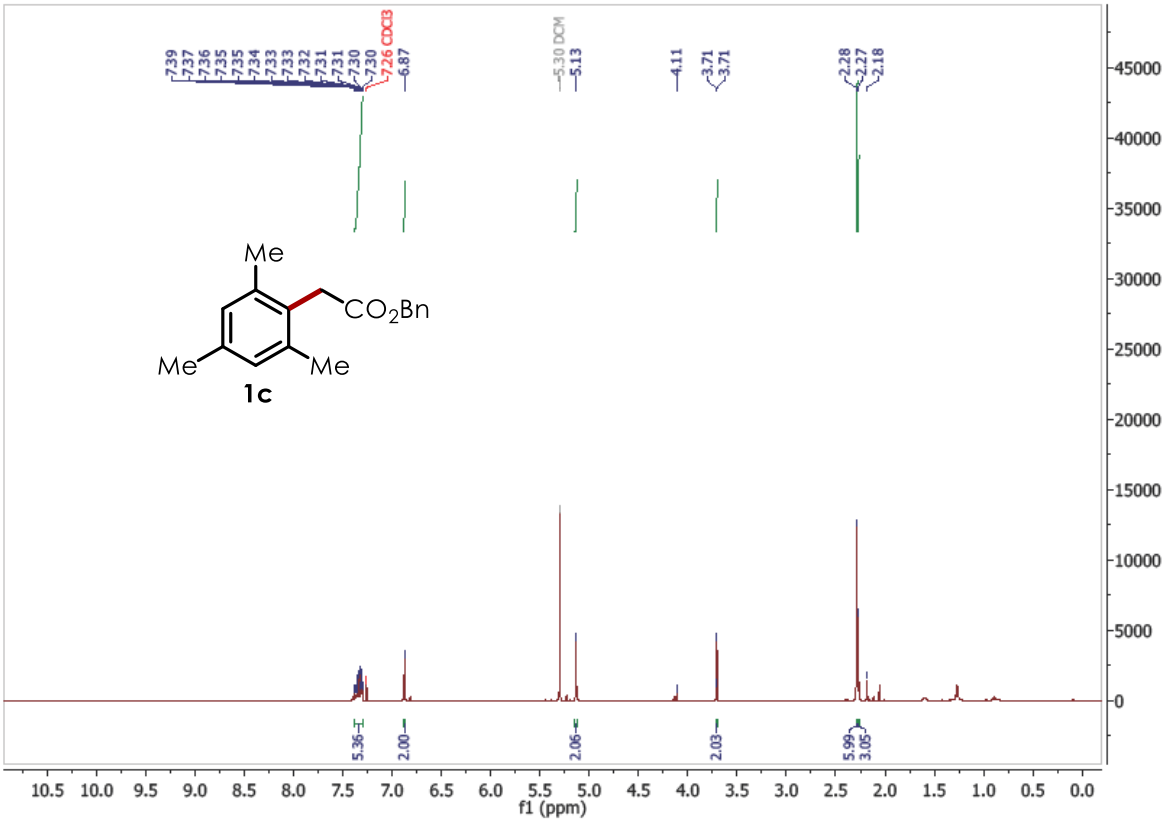


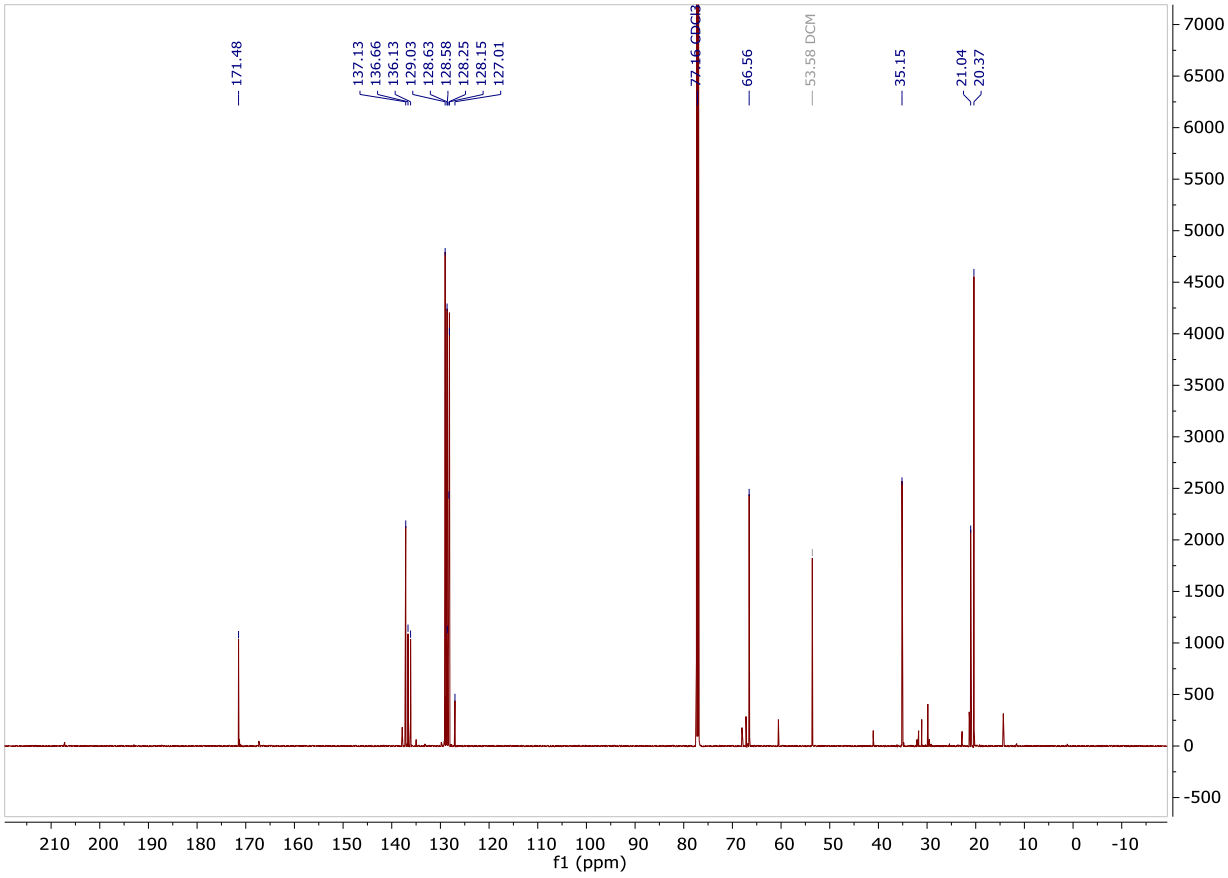

7.54
7.52
7.52
7.50
7.50
7.36
7.34
7.26 CDCl3
7.19
7.18
5.02
5.00
4.64
4.63
4.62
4.61
4.18
4.17
3.74
3.65
3.18
3.17
3.15
3.14
3.10
3.09
3.08
3.07
1.42
1.28
1.27
1.26
CO2Me
NHBoc
EtO2C
21a
4.02
1.98
2.00
0.90
0.91
2.01
3.10
1.91
2.07
9.50
3.02
f1 (ppm)

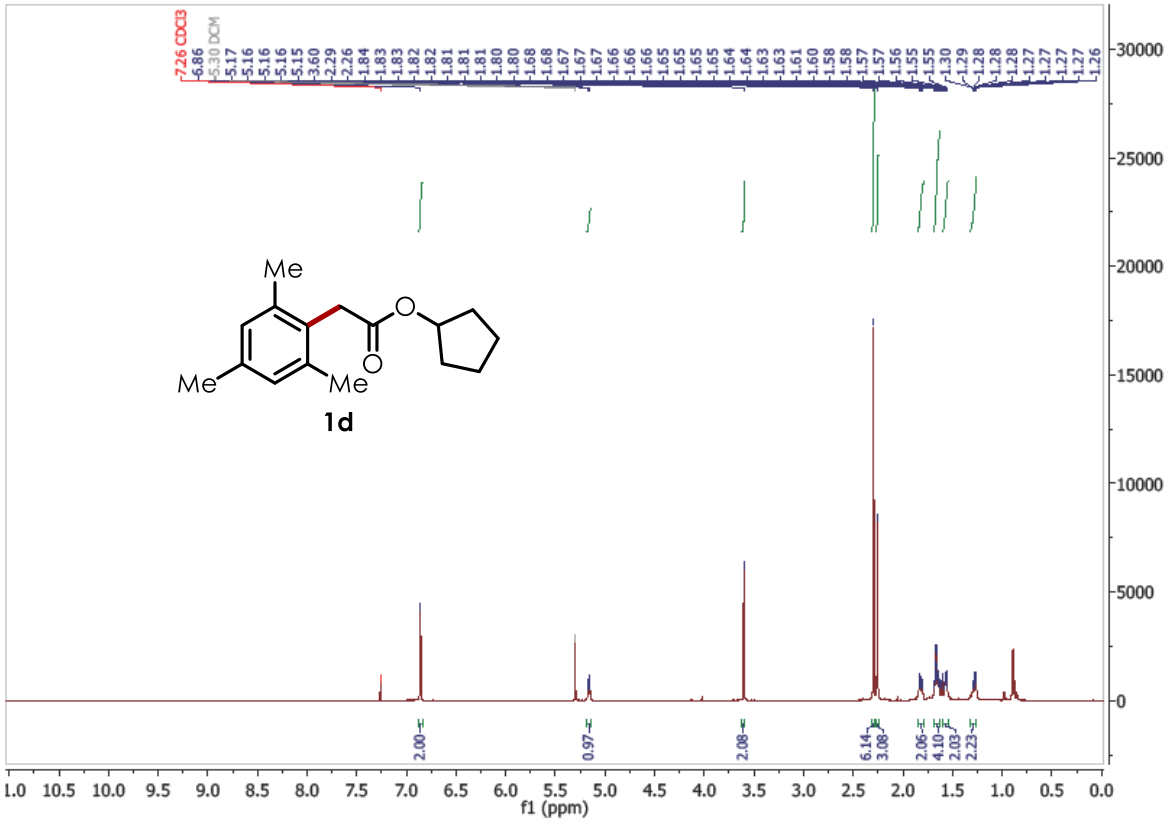

172.47
171.74
155.22
139.65
139.60
135.17
133.29
129.86
129.81
127.38
127.28
80.10
77.16 CDCl3
61.08
54.48
52.43
41.16
38.10
31.10
29.84
28.43
14.34
f1 (ppm)

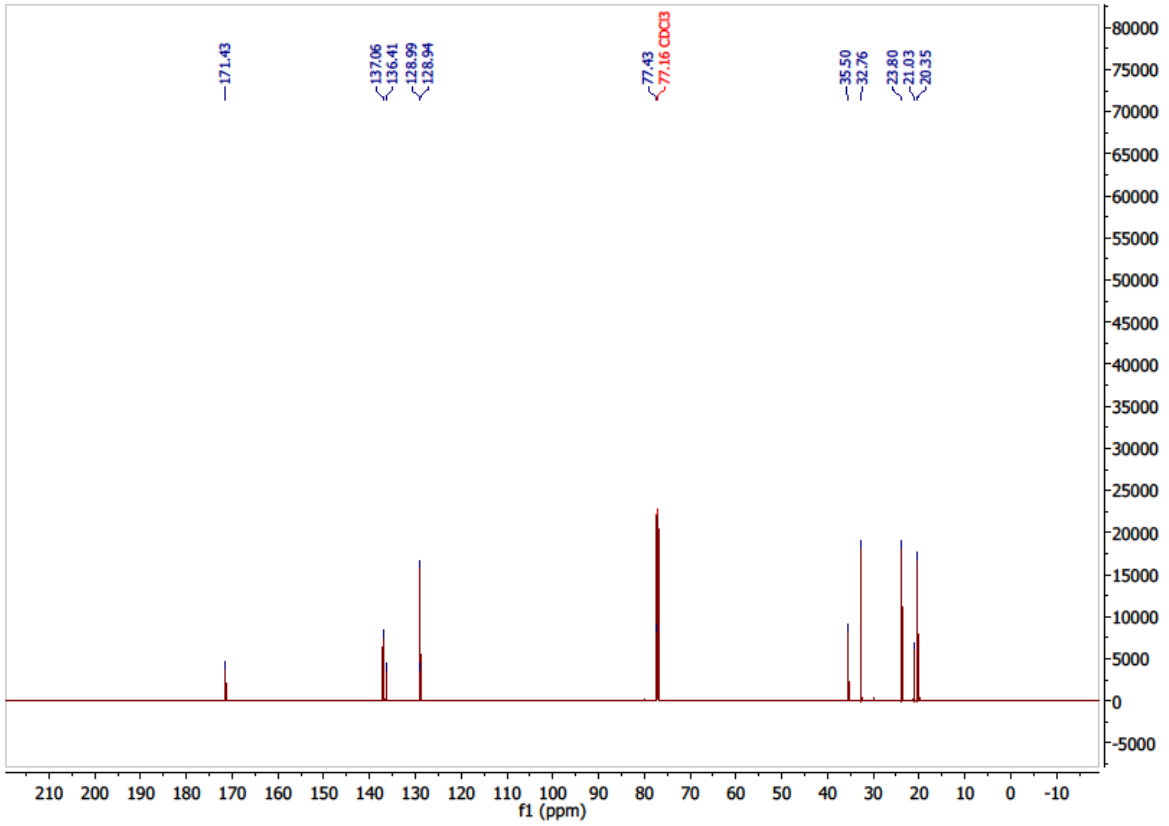

CO2Et
O
Me
CO2Me
+
22a
f1 (ppm)

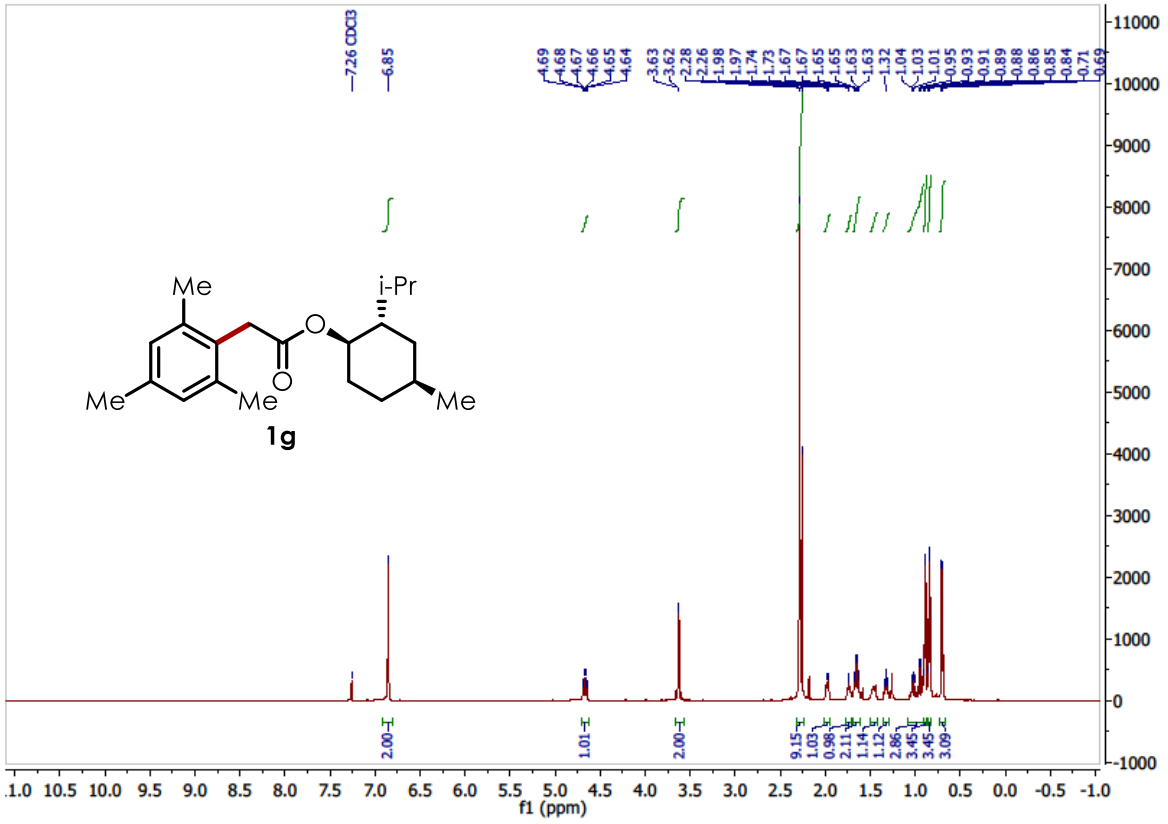

174.79
174.72
171.84
171.51
157.53
157.44
157.37
156.17
155.04
142.60
142.52
141.42
141.39
130.72
129.96
129.90
129.86
129.79
126.12
125.04
123.82
123.13
122.87
122.42
122.21
119.05
118.26
118.21
117.43
61.05
60.94
52.25
45.37
45.15
40.74
36.04
35.72
18.63
18.57
14.32
14.26
CO2Et
Me
CO2Me
+
CO2Et
Me
CO2Me
22a
f1 (ppm)


7.39
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.26 CDCl3
6.87
5.30 DCM
5.13
4.11
3.71
3.71
2.28
2.27
2.18
Me
CO2Bn
Me
Me
1c
5.36
2.00
2.06
2.03
5.99
3.05
f1 (ppm)


171.48
137.13
136.66
136.13
129.03
128.63
128.58
128.25
128.15
127.01
77.16 CDCl3
66.56
53.58 DCM
35.15
21.04
20.37
f1 (ppm)


Me
Me
Me
O
O
1d
f1 (ppm)


171.43
137.06
136.41
128.99
128.94
77.43
77.16 CDCl3
35.50
32.76
23.80
21.03
20.35
f1 (ppm)


7.26 CDCl3
6.85
4.69
4.68
4.67
4.66
4.65
4.64
3.63
3.62
2.28
2.26
1.98
1.97
1.74
1.73
1.67
1.67
1.65
1.65
1.63
1.63
1.32
1.04
1.03
1.01
0.95
0.93
0.91
0.89
0.88
0.86
0.85
0.84
0.71
0.69
Me
i-Pr
O
O
Me
Me
Me
1g
2.00
1.01
2.00
9.15
1.03
0.98
2.11
1.14
1.12
2.86
3.45
3.45
3.09
f1 (ppm)

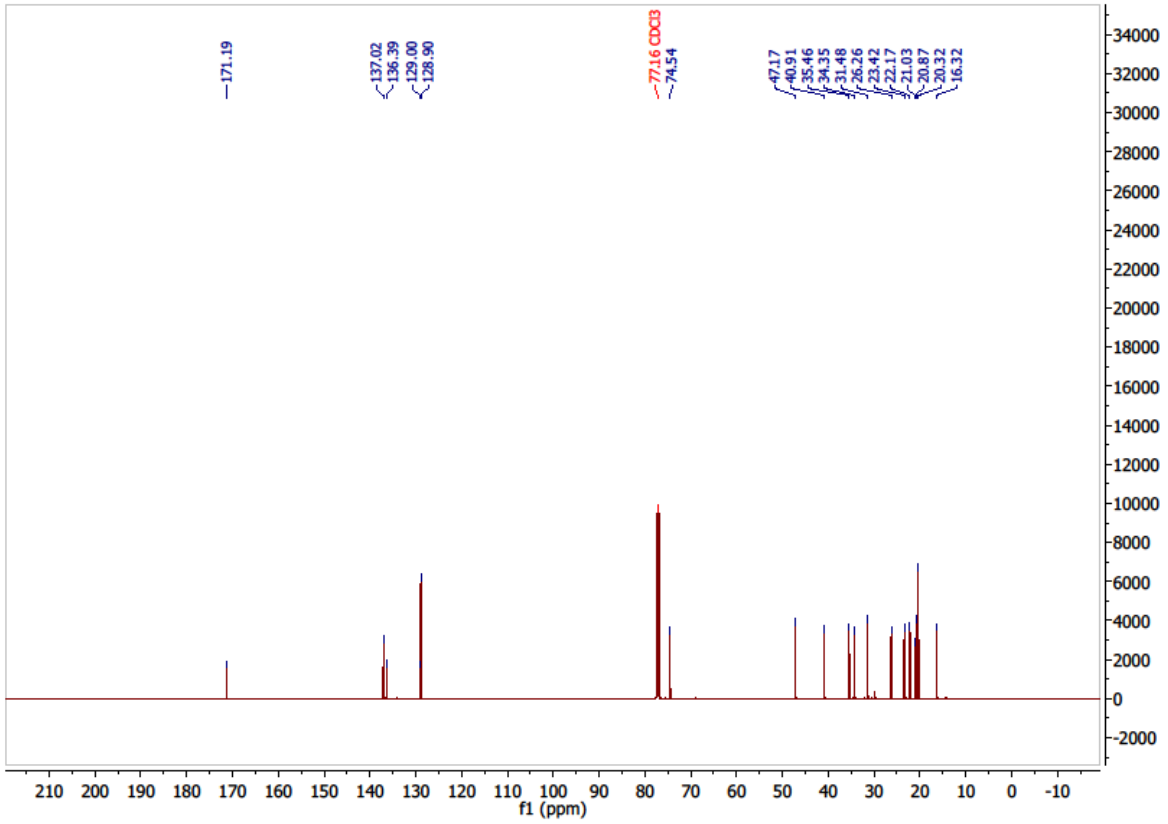
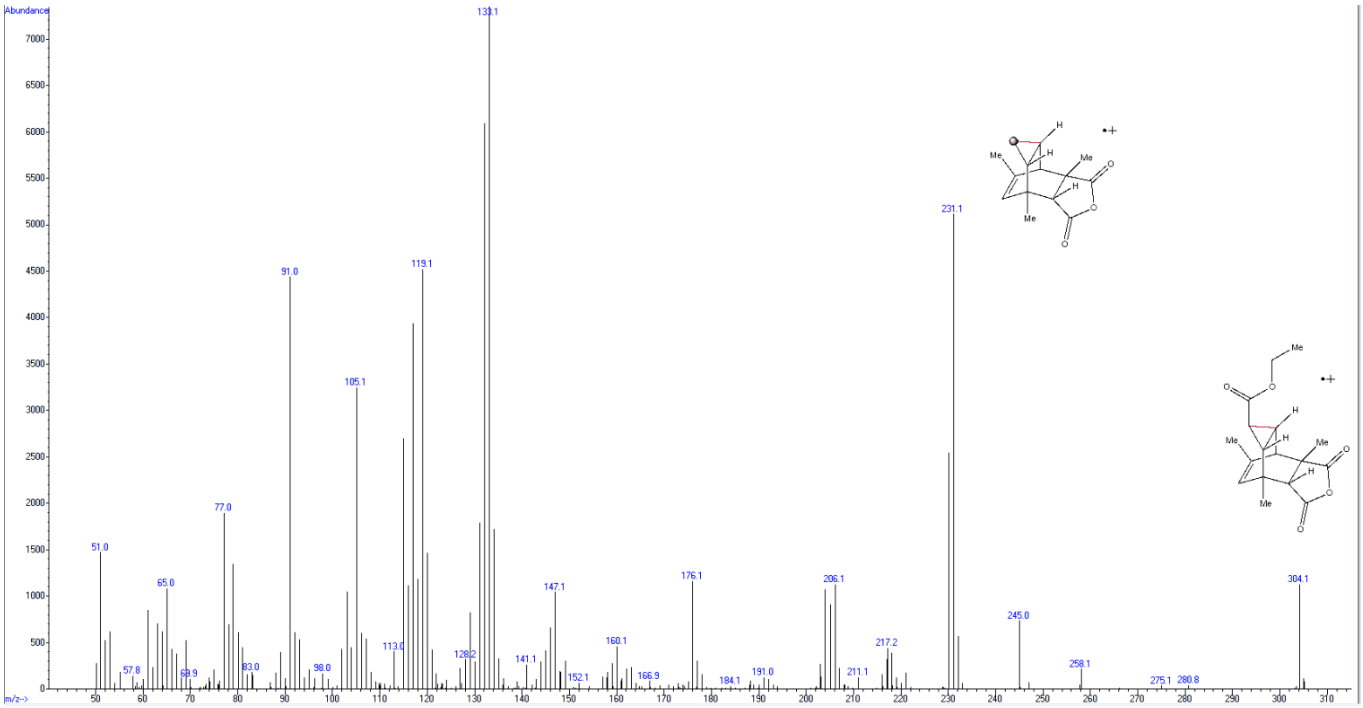

171.19
137.02
136.39
129.00
128.90
77.16 CDCl3
74.54
47.17
40.91
35.46
34.35
31.48
26.26
23.42
22.17
21.03
20.87
20.32
16.32
f1 (ppm)

Figure X: Mass spectrum from GC-MS trace of crude reaction mixture containing 1.0 eq. maleic anhydride



References:

(1) Crisóstomo, F. P.; Martín, T.; Carrillo, R. Ascorbic Acid as an Initiator for the Direct C□H Arylation of (Hetero)Arenes with Anilines Nitrosated In Situ. *Angewandte Chemie International Edition* **2014**, *53* (8), 2181–2185. https://doi.org/10.1002/anie.201309761.

(2) Griffin, J. D.; Zeller, M. A.; Nicewicz, D. A. Hydrodecarboxylation of Carboxylic and Malonic Acid Derivatives via Organic Photoredox Catalysis: Substrate Scope and Mechanistic Insight. *J. Am. Chem. Soc.* **2015**. https://doi.org/10.1021/jacs.5b07770.

(3) Hoshiya, N.; Shimoda, M.; Yoshikawa, H.; Yamashita, Y.; Shuto, S.; Arisawa, M. Sulfur Modification of Au via Treatment with Piranha Solution Provides Low-Pd Releasing and Recyclable Pd Material, SAPd. *Journal of the American Chemical Society* **2010**, *132* (21), 7270–7272. https://doi.org/10.1021/ja9100084.

(4) McManus, J. B.; Nicewicz, D. A. Direct C–H Cyanation of Arenes via Organic Photoredox Catalysis. *Journal of the American Chemical Society* **2017**, *139* (8), 2880–2883. https://doi.org/10.1021/jacs.6b12708.

(5) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. Site-Selective Arene C-H Amination via Photoredox Catalysis. *Science* **2015**, *349* (6254), 1326–1330. https://doi.org/10.1126/science.aac9895.

(6) Das, B.; THIRUPATHI, P.; RAVIKANTH, B.; KUMAR, R.; SARMA, A.; BASHA, S. Isolation, Synthesis, and Bioactivity of Homoisoflavonoids from Caesalpinia Pulcherrima. *Chem. Pharm. Bull.* **2009**, *57* (10), 1139–1141.

(7) Chen, W.; Huang, Z.; Tay, N. E. S.; Giglio, B.; Wang, M.; Wang, H.; Wu, Z.; Nicewicz, D. A.; Li, Z. Direct Arene C-H Fluorination with 18F– via Organic Photoredox Catalysis. *Science (New York, N.Y.)* **2019**, *in press*.

(8) Windsor, M. A.; Hermanson, D. J.; Kingsley, P. J.; Xu, S.; Crews, B. C.; Ho, W.; Keenan, C. M.; Banerjee, S.; Sharkey, K. A.; Marnett, L. J. Substrate-Selective Inhibition of Cyclooxygenase-2: Development and Evaluation of Achiral Profen Probes. *ACS Medicinal Chemistry Letters* **2012**, *3* (9), 759–763. https://doi.org/10.1021/ml3001616.

(9) Chen, Y.; Sun, J.; Huang, Z.; Liao, H.; Peng, S.; Lehmann, J.; Zhang, Y. Design, Synthesis and Evaluation of Tacrine–Flurbiprofen–Nitrate Trihybrids as Novel Anti-Alzheimer's Disease Agents. *Bioorganic & Medicinal Chemistry* **2013**, *21* (9), 2462–2470. https://doi.org/10.1016/j.bmc.2013.03.005.

(10) Lau, W.; Kochi, J. K. Kinetics and Mechanism of Aromatic Thallation. Identification and Proof of Competing Electrophilic and Electron-Transfer Pathways. *Journal of the American Chemical Society* **1984**, *106* (23), 7100–7112. https://doi.org/10.1021/ja00335a039.

(11) Mackay, W. D.; Johnson, J. S. Kinetic Separation and Asymmetric Reactions of Norcaradiene Cycloadducts: Facilitated Access via H_2O-Accelerated Cycloaddition. *Organic Letters* **2016**, *18* (3), 536–539. https://doi.org/10.1021/acs.orglett.5b03577.

(12) Racine, S.; Hegedüs, B.; Scopelliti, R.; Waser, J. Divergent Reactivity of Thioalkynes in Lewis Acid Catalyzed Annulations with Donor–Acceptor Cyclopropanes. *Chemistry – A European Journal* **2016**, *22* (34), 11997–12001. https://doi.org/10.1002/chem.201602755.

(13) de Nanteuil, F.; Waser, J. Catalytic [3+2] Annulation of Aminocyclopropanes for the Enantiospecific Synthesis of Cyclopentylamines. *Angewandte Chemie International Edition* **2011**, *50* (50), 12075–12079. https://doi.org/10.1002/anie.201106255.

(14) Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. Catalytic Z-Selective Olefin Cross-Metathesis for Natural Product Synthesis. *Nature* **2011**, *471* (7339), 461–466. https://doi.org/10.1038/nature09957.

(15) Toma, T.; Shimokawa, J.; Fukuyama, T. *N* , *N* '-Ditosylhydrazine: A Convenient Reagent for Facile Synthesis of Diazoacetates †. *Organic Letters* **2007**, *9* (16), 3195–3197. https://doi.org/10.1021/ol701432k.

(16) Zimmermann, B.; Dzik, W. I.; Himmler, T.; Goossen, L. J. Palladium-Catalyzed Cross-Coupling of Sterically Demanding Boronic Acids with α-Bromocarbonyl Compounds. *The Journal of Organic Chemistry* **2011**, *76* (19), 8107–8112. https://doi.org/10.1021/jo2014998.

(17) Kawamoto, T.; Sato, A.; Ryu, I. Cyanoborohydride-Promoted Radical Arylation of Benzene. *Organic Letters* **2014**, *16* (8), 2111–2113. https://doi.org/10.1021/ol500614q.

(18) Huang, Z.; Chen, Z.; Lim, L. H.; Quang, G. C. P.; Hirao, H.; Zhou, J. (Steve). Weak Arene C□H···O Hydrogen Bonding in Palladium-Catalyzed Arylation and Vinylation of Lactones. *Angewandte Chemie International Edition* **2013**, *52* (22), 5807–5812. https://doi.org/10.1002/anie.201300481.

(19) Jørgensen, M.; Lee, S.; Liu, X.; Wolkowski, J. P.; Hartwig, J. F. Efficient Synthesis of α-Aryl Esters by Room-Temperature Palladium-Catalyzed Coupling of Aryl Halides with Ester Enolates. *Journal of the American Chemical Society* **2002**, *124* (42), 12557–12565. https://doi.org/10.1021/ja027643u.
(20) Muehlebach, M.; Boeger, M.; Cederbaum, F.; Cornes, D.; Friedmann, A. A.; Glock, J.; Niderman, T.; Stoller, A.; Wagner, T. Aryldiones Incorporating a [1,4,5]Oxadiazepane Ring. Part I: Discovery of the Novel Cereal Herbicide Pinoxaden. *Bioorganic & Medicinal Chemistry* **2009**, *17* (12), 4241–4256. https://doi.org/10.1016/j.bmc.2008.12.062.
(21) Romero, N. A.; Nicewicz, D. A. Mechanistic Insight into the Photoredox Catalysis of Anti-Markovnikov Alkene Hydrofunctionalization Reactions. *J. Am. Chem. Soc.* **2014**, 10.1021/ja506228u. https://doi.org/10.1021/ja506228u.