Supporting Information

Synthesis of polycyclic allenoates using cesium carbonate as catalyst

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General remarks:

All reactions were performed in flamed glassware under an Ar atmosphere. Commercial reagents were distilled prior to use; CH_2Cl_2, THF and Et_2O were purified using a Dry Solvent Station GT S100 and toluene was distilled from Na.

Commercially available *n*-butyllithium was indicated to be 1.6 M solution in hexanes and dosed before use. ^{1}H NMR spectra were recorded on at 300 and 500 MHz using the solvent residual peak as internal standard[1]. Splitting patterns were reported as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

HRMS data were recorded on a microTOF spectrometer equipped with an orthogonal electrospray (ESI) interface.

Thin layer chromatography was performed using TLC Silica gel 60 F254 glass plates. Merck Geduran ® 40-63 μm silica gel was used for column chromatography.

Infrared spectra are reported in frequency of absorption.

Melting points were recorded with a SMP3 Stuart Scientific microscope in open capillary tubes and are uncorrected.

Keto-alkynes **1a-l** were prepared following literature procedure.[2]

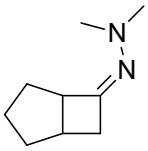
[1] Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512–7515

[2] (a) Schäfer, C.; Miesch, M.; Miesch, L. *Chem. – Eur. J.* **2012**, *18*, 8028–8031. (b) Schäfer, C.; Miesch, M.; Miesch, L. *Org. Biomol. Chem.* **2012**, *10*, 3253–3257. (c) Corominas, A.; Montaña, A. M.; *Synthetic Commun.*; **2013**, *43*, 2062-2072

Experimental procedure and characterization data for Dimethylhydrazone

In a solution of bicyclo[3.2.0]heptanone (3.63 g, 30.4 mmol, 1 equiv) in benzene (75 mL) was added *N,N*-dimethylhydrazine (2.8 mL, 45.6 mmol, 1.5 equiv) and 5 drops of trifluoroacetic acid. The reaction mixture was heated to reflux in a Dean-Stark for 16 h. The reaction mixture was cooled to rt, diluted with Et_2O (150 mL) and H_2O was added (20 mL). The aqueous phase was extracted with Et_2O (3×30 mL). The combined organic phases were washed with a satd aq soln of NaCl (20 mL), dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuum (15 mbar, 25 °C). The pure product (3.91 g, 25.7 mmol, 84%) was obtained by distillation under reduced pressure (76 °C, 10 mbar).

2-(bicyclo[3.2.0]heptan-6-ylidene)-1,1-dimethylhydrazine

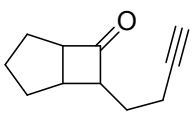


colorless oil, 84%

^{1}H NMR ($CDCl_3$, 300 MHz) : δ = 3.42-3.47 (m, 1H), 3.05 (ddd, 1H, *J*=17.3, 9.0, 1.8 Hz), 2.67-2.80 (m, 1H), 2.56 (s, 6H), 2.38 (dt, 1H, *J*=17.7, 3.8 Hz), 1.47-1.95 (m, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 75 MHz) : 162.5, 52.5, 46.9, 39.4, 33.0, 32.1, 32.0, 24.6 ppm. **IR** (neat) : υ = 2817 (NCH_3), 2774 (NCH_3), 1664 (C=N) cm^{-1}. **Anal.** : calc.: %C 71.00; %H : 10.59 ; found: volatile.

Experimental procedure and characterization data for Keto-Alkyne 1k

2-(Bicyclo[3.2.0]heptan-6-ylidene)-1,1-dimethylhydrazine (1.46 g, 9.62 mmol, 1 equiv) was dissolved in dry THF (30 mL) and cooled to -5 °C, then the *n*-BuLi solution (conc = 1.55 M, 7.8 mL, 1.5 equiv) was added dropwise. The resulting mixture was stirred for 1 h at -5 °C and the 4-iodobutyne (2.16 g, 12.0 mmol, 1.5 equiv) was added. After 1 h, the mixture was warmed and stirred at rt for 6 h and hydrolyzed with an aq soln of 10% HCl (15 mL) and stirred overnight. The aqueous phase was extracted with EtOAc (5×30 mL). The combined organic layers were washed successively with a satd aq soln of $NaHCO_3$ (30 mL), a satd aq soln of $Na_2S_2O_3$ (30 mL), and a satd aq soln of NaCl (30 mL), dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuum (15 mbar, 25 °C). The crude product was purified by column chromatography (petroleum ether/EtOAc 100/0 to 84/16) to afford the title compound as a colorless oil (0.92 g, 5.68 mmol, 59%).



1k
colorless oil, 59%

7-(but-3-yn-1-yl)bicyclo[3.2.0]heptan-6-one **1k**

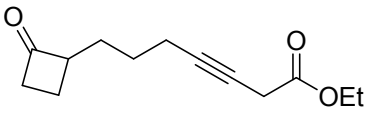
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.43-3.47 (m, 1H), 2.72-2.76 (m, 1H), 2.52 (dd, 1H, *J* = 11.7, 6.9 Hz), 2.27 (td, 2H, *J* = 7.1, 2.6 Hz), 1.96-2.00 (m, 1H), 1.93 (t, 1H, *J* = 2.7 Hz), 1.82-1.90 (m, 3H), 1.67-1.75 (m, 2H), 1.52-1.65 (m, 2H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 216.7, 83.5, 69.3, 62.8, 62.1, 36.5, 33.1, 29.6, 28.5, 25.5, 16.6

ppm. **IR** (neat): υ = 3289, 2942, 2861, 1764 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 185.0931; found: 185.0927. $\mathbf{R}_f$: 0.81 (petroleum ether/EtOAc 80/20).

Experimental procedure and characterization data for 3-Alkynoates

General procedure for the synthesis of 3-Alkynoates:

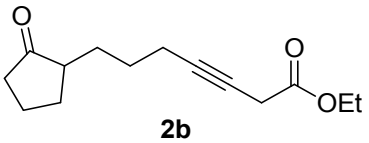
Alkynyl ketone (1 equiv) was dissolved in dry MeCN (conc = 0.25 $mmol.mL^{-1}$). Ethyl diazoacetate (1.1 equiv) and CuI (10 mol %) were added. The resulting mixture was stirred for 4 h and concentrated in vacuum (15 mbar, 25 °C). The crude product was purified by column chromatography to afford the title compound (petroleum ether/EtOAc 100/0 to 80/20).



2a
Colorless oil, 99%

Ethyl 7-(2-oxocyclobutyl)hept-3-ynoate **2a**

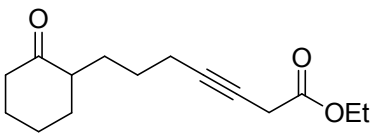
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.15 (q, 2H, *J* = 7.0 Hz), 3.24-3.30 (m, 1H), 3.20 (t, 2H, *J* = 2.4 Hz), 3.0 (dddd, 1H, *J* = 17.8, 10.6, 7.3, 3.2 Hz), 2.89 (dddd, 1H, *J* = 17.7, 9.7, 5.2, 2.8 Hz), 2.10-2.20 (m, 3H), 1.72-1.79 (m, 1H), 1.51-1.67 (m, 4H), 1.24 (t, 3H, *J* = 7.1 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 212.2, 169.2, 83.3, 72.4, 61.7, 60.3, 44.8, 28 .9, 26.4, 26.3, 18.9 (C_g), 17.2, 14.4 ppm. **IR** (neat): υ = 2934, 2861, 1774, 1738, 1177 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 245.1154; found: 245.1162. $\mathbf{R}_f$: 0.50 (petroleum ether/EtOAc 80/20).



2b
colorless oil, 93%

Ethyl 7-(2-oxocyclopentyl)hept-3-ynoate **2b**

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.17 (q, 2H, *J* = 7.2 Hz), 3.23 (t, 2H, *J* = 2.5 Hz), 2.29 (dd, 1H, *J* = 17.9, 9.1 Hz), 2.18-2.24 (m, 3H), 2.10 (dd, 1H, *J* = 18.8, 9.8 Hz), 1.97-2.06 (m, 2H), 1.74-1.86 (m, 2H), 1.47-1.59 (m, 3H), 1.29-1.38 (m, 1H), 1.27 (t, 3H, *J* = 7.1 Hz) ppm .**^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 221.5, 169.2, 83.5, 72.2, 61.7, 49.1, 38.4, 29.9, 29.3, 27.0, 26.4, 21.0, 19.1, 14.4 ppm. **IR** (neat): υ = 2941, 2870, 1732, 1157 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 259.1310; found: 259.1299. $\mathbf{R}_f$: 0.41 (petroleum ether/EtOAc 80/20).

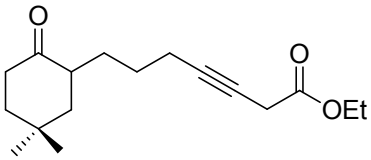


2c
colorless oil, 99%

Ethyl 7-(2-oxocyclohexyl)hept-3-ynoate **2c**

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.14 (q, 2H, *J* = 7.1 Hz), 3.20 (t, 2H, *J* = 2.4 Hz), 2.33-2.37 (m, 1H), 2.24-2.29 (m, 2H), 2.14-2.19 (m, 2H), 2.05-2.10 (m, 1H), 1.97-2.02 (m, 1H), 1.78-1.85 (m, 2H), 1.61-1.66 (m, 2H), 1.44-1.50 (m, 2H), 1.27-1.39 (m, 2H), 1.24 (t,

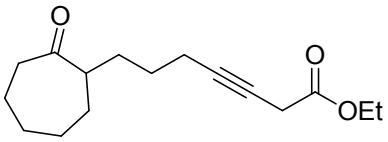
3H, *J* = 7.2 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 213.5, 169.2, 83.7, 72.0, 61.7, 50.6, 42.3, 34.2, 29.0, 28.3, 26.6, 26.4, 25.2, 19.2, 14.4 ppm. **IR** (neat): υ = 2932, 2861, 1706, 1177 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 273.1467; found: 273.1476. $\mathbf{R}_f$: 0.46 (petroleum ether/EtOAc 80/20).



2d
colorless oil, 99%

Ethyl 7-(5,5-dimethyl-2-oxocyclohexyl)hept-3-ynoate **2d**

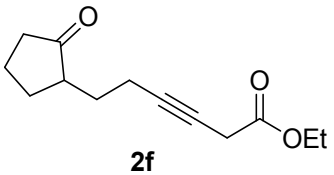
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.18 (q, 2H, *J* = 7.2 Hz), 3.23 (t, 2H, *J* = 2.4 Hz), 2.37-2.49 (m, 2H), 2.17-2.25 (m, 3H), 1.75-1.86 (m, 2H), 1.69-1.73 (m, 1H), 1.55-1.67 (m, 2H), 1.47-1.53 (m, 2H), 1.27 (t, 3H, *J* = 7.1 Hz), 1.21-1.24 (m, 1H), 1.20 (s, 3H), 0.99 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ= 213.8, 169.3, 83.9, 72.0, 61.8, 47.1, 46.0, 40.4, 38.8, 31.8, 31.1, 28.7, 26.6, 26.4, 24.9, 19.3, 14.5 ppm. **IR** (neat): υ = 2926, 2865, 1740, 1709, 1176 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc : 301.1780; found : 301.1769. $\mathbf{R}_f$: 0.42 (petroleum ether/EtOAc).



2e
colorless oil, 99%

Ethyl 7-(2-oxocycloheptyl)hept-3-ynoate **2e**

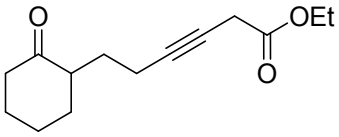
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.13 (q, 2H, *J* = 7.2 Hz), 3.18 (t, 2H, *J* = 2.4 Hz), 2.44 (tt, 2H, *J* = 11.2, 3.5 Hz), 2.35-2.39 (m, 1H), 2.12-2.15 (m, 2H), 1.78-1.82 (m, 4H), 1.65-1.70 (m, 1H), 1.51-1.59 (m, 1H), 1.36-1.49 (m, 3H), 1.25-1.33 (m, 3H), 1.23 (t, 3H, *J* = 7.1 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 216.4, 169.2, 83.5, 72.0, 61.7, 52.0, 42.9, 31.7, 31.6, 29.8, 28.7, 26.6, 26.3, 24.8, 19.1, 14.4 ppm. **IR** (neat): υ = 2927, 2854, 1739, 1698, 1161 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 287.1623; found: 287.1628. $\mathbf{R}_f$: 0.50 (petroleum ether/EtOAc).



2f
colorless oil, 96%

Ethyl 6-(2-oxocyclopentyl)hex-3-ynoate **2f**

^{1}H NMR ($CDCl_3$, 500 MHz): 4.16 (q, 2H, *J* = 7.2 Hz), 3.21 (t, 2H, *J* = 2.5 Hz), 2.18-2.37 (m, 5H), 2.10 (ddd, 1H, *J* = 18.6, 10.5, 8.1 Hz), 1.94-2.02 (m, 2H), 1.74-1.82 (m, 1H), 1.39-1.53 (m, 2H), 1.25 (t, 3H, *J* = 7.2 Hz,) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): 221.3, 169.1, 83.0, 72.6, 61.7, 48.4, 38.4, 29.7, 28.9, 26.4, 21.0, 17.4, 14.4 ppm. **IR** (neat): υ = 2960, 2868, 1731, 1157 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 245.1154; found: 245.1168. $\mathbf{R}_f$: 0.54 (petroleum ether/EtOAc 80/20).

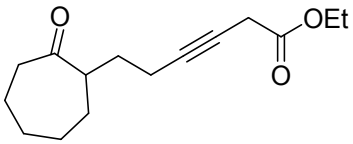


2g
colorless oil, 92%

Ethyl 6-(2-oxocyclohexyl)hex-3-ynoate **2g**

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.18 (q, 2H, *J* = 7.2 Hz), 3.23 (t, 2H, *J* = 2.3 Hz), 2.50 (m, 1H, *J* = 6.2 Hz), 2.30-2.40 (m, 2H), 2.24-2.28 (m, 2H), 2.11-2.15 (m, 1H), 1.98-2.01 (m, 2H), 1.85-1.88 (m, 1H), 1.63-1.72 (m, 2H), 1.32-1.39 (m, 2H), 1.28 (t, 3H, *J* = 7.2 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 213.3, 169.3, 83.6, 72.3, 61.8, 49.5, 42.6, 34.3, 28.7, 28.4, 26.5, 25.5,

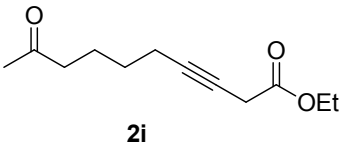
16.8, 14.5 ppm. **IR** (neat): υ = 2931, 2860, 1740, 1707, 1178 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 259.1310; found: 259.1318. $\mathbf{R}_f$: 0.31 (petroleum ether/EtOAc 90/10).



2h
colorless oil, 97%

Ethyl 6-(2-oxocycloheptyl)hex-3-ynoate **2h**

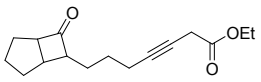
^{1}H NMR ($CDCl_3$, 500 MHz): 4.18 (q, 2H, *J* = 7.2 Hz), 3.23 (t, 2H, *J* = 2.5 Hz), 2.71-2.76 (m, 1H), 2.43-2.51 (m, 2H), 2.20 (tt, 2H, *J* = 7.1, 2.5 Hz), 1.80-1.96 (m, 5H), 1.61-1.71 (m, 1H), 1.40-1.53 (m, 2H), 1.26-1.34 (m, 5H) ppm.**^{13}C NMR** ($CDCl_3$, 125 MHz): 216.1, 169.2, 83.3, 72.6, 61.8, 50.8, 43.4, 31.6, 31.0, 29.4, 29.0, 26.4, 24.4, 17.0, 14.5 ppm. **IR** (neat): υ = 2926, 2854, 1740, 1698, 1162 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 273.1467; found: 273.1435. $\mathbf{R}_f$: 0.56 (petroleum ether/EtOAc 80/20).



2i
Colorless oil, 98%

Ethyl 9-oxodec-3-ynoate **2i**

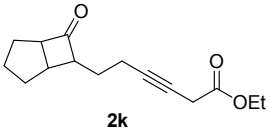
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.14 (q, 2H, *J*=7.2 Hz), 3.20 (t, 2H, *J*=2.2 Hz), 2.42 (t, 2H, *J* = 7.1 Hz), 2.18 (tt, 2H, *J*=7.1, 2.2 Hz), 2.11 (s, 3H), 1.65 (qt, 2H, *J*=7.4 Hz), 1.47 (qt, 2H, *J*=7.4 Hz), 1.24 (t, 3H, *J*=7.2 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 209.1, 169.2, 83.4, 72.2, 61.7, 43.4, 30.1, 28.3, 26.3, 23.2, 18.8, 14.4 ppm. **IR** (ATR): υ = 1740, 1713, 1178 cm^{-1}. **ESI-HRMS:** $[M+Na]^+$ calc : 233.1148; found: 233.1157. $\mathbf{R}_f$ **:** 0.24 (PE/AcOEt 90/10).



2j
colorless oil, 96%

Ethyl 7-(7-oxobicyclo[3.2.0]heptan-6-yl)hept-3-ynoate **2j**

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.18 (q, 2H, *J* = 7.1 Hz), 3.46 (ddd, 1H, *J* = 8.6, 6.7, 2.5 Hz), 3.23 (t, 2H, *J* = 2.5 Hz), 2.48-2.62 (m, 2H), 2.18-2.24 (m, 2H), 2.01 (d, 1H, *J* = 7.6 Hz), 1.55-1.87 (m, 9H), 1.27 (t, 3H, *J* = 7.2 Hz,) ppm. **^{13}C NMR** ($CDCl_3$, 75 MHz): δ = 217.5, 169.3, 83.4, 72.4, 63.9, 62.1, 61.8, 36.8, 33.3, 29.8, 29.1, 26.5, 26.4, 25.6, 19.0, 14.5 ppm. **IR** (neat): υ = 2937, 2861, 1767, 1741, 1171 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 285.1467; found: 285.1447. $\mathbf{R}_f$: 0.63 (petroleum ether/EtOAc 80/20).



2k
colorless oil, 57%

Ethyl 6-(7-oxobicyclo[3.2.0]heptan-6-yl)hex-3-ynoate **2k**

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 4.16 (q, 2H, *J* = 7.1 Hz), 3.46 (ddd, 1H, *J* = 9.9, 6.5, 2.9 Hz), 3.21 (t, 2H, *J* = 2.4 Hz), 2.73-2.77 (m, 1H), 2.54 (dd, 1H, *J* = 11.6, 6.9 Hz), 2.29 (tt, 2H, *J* = 7.1, 2.5 Hz), 1.98-2.02 (m, 1H), 1.83-1.90 (m, 3H), 1.68-1.75 (m, 2H), 1.56-1.66 (m, 2H), 1.26 (t, 3H, *J* = 7.2 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 217.2, 169.1, 82.8, 72.8, 63.1, 62.1, 61.8, 36.6, 33.2, 29.7, 28.8, 26.4, 25.5, 17.1, 14.4 ppm. **IR** (neat): υ = 2940, 2860, 1766, 1740, 1178 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 271.1310; found: 271.1308. $\mathbf{R}_f$: 0.31 (petroleum ether/EtOAc 90/10).

Experimental procedure and characterization data for Polycyclic Allenoates

Procedure A: reaction with TBAF

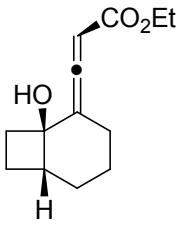
3-Alkynoate (1 equiv) was dissolved in dry THF (conc = 0.1 mmol.mL^{-1}) and TBAF (1 M soln in THF, 1.1 equiv) was added. The resulting mixture was stirred for 5 min at 25 °C and diluted with Et_2O (25 mL) and washed with a satd aq soln of NH_4Cl (10 mL). The aqueous phase was extracted with Et_2O (3×15 mL). The combined organic phases were washed with a satd aq soln of NaCl, dried (anhydrous Na_2SO_4), filtered, and concentrated under vacuum (25 °C, 15 mbar). The crude product was purified by column chromatography to afford the desired compound (petroleum ether/EtOAc 100/0 to 78/22).

Procedure B: reaction with Cs_2CO_3

3-Alkynoate (1 equiv) was dissolved in dry THF (conc = 0.1 mmol.mL^{-1}) and Cs_2CO_3 (10 mol %) was added. The resulting mixture was stirred overnight at 25 °C and diluted with Et_2O (25 mL) and washed with a satd aq soln of NH_4Cl (15 mL). The aqueous phase was extracted with Et_2O (3×15 mL). The combined organic phases were washed with a satd aq soln of NaCl (20 mL), dried (anhydrous Na_2SO_4), filtered, and concentrated under vacuum (25 °C, 15 mbar). The crude product was purified by column chromatography to afford the desired compound (petroleum ether/EtOAc 100/0 to 78/22).

Procedure C: "one-pot" reaction

Alkynyl ketone (1 equiv) was dissolved in dry MeCN (conc = 0.2 mmol.mL^{-1}). Ethyl diazoacetate (1.5 equiv) and Cs_2CO_4 (10 mol %) was added. The resulting mixture was stirred for 5 min at 25 °C, and the CuI (20% mol) was added. After 5 h of stirring, Cs_3CO_3 (10 mol %) was added and the reaction mixture was stirred overnight, diluted with Et_2O (20 mL) and washed with a satd aq soln of NH_4Cl (15 mL). The aqueous phase was extracted with Et_2O (3×15 mL). The combined organic phases were washed with a sad aq soln of NaCl (20 mL), dried (anhydrous Na_2SO_4), filtered and concentrated under vacuum (25 °C, 15 mbar). The crude product was purified by column chromatography to afford the desired compound (petroleum ether/EtOAc 100/0 to 78/22).

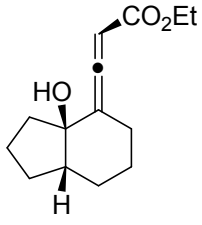


4b
yellowish oil, 28%
relative configuration

Cis, *Cis* Ethyl 3-(1-hydroxybicyclo[4.2.0]octan-2-ylidene)acrylate **4b**

This compound was synthesized according to method B.

^{1}H NMR ($CDCl_3$, 600 MHz): δ = 5.62 (t, 1H, *J* = 2.2 Hz), 4.17 (q, 2H, *J* = 7.2 Hz), 2.51-2.56 (m, 1H), 2.19-2.23 (m, 1H), 2.08 (sl, 1H), 1.89-1.96 (m, 2H), 1.63-1.76 (m, 4H), 1.49-1.69 (m, 3H), 1.33-1.47 (m, 4H), 1.28 (t, 3H, *J* = 7.2 Hz) ppm **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 209.6, 166.8, 111.7, 89.7, 72.2, 61.3, 42.8, 34.4, 26.4, 24.5, 21.7, 16.0, 14.6 ppm. . **IR** (neat): υ = 3380, 2927, 2858, 1955, 1697, 1151 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 245.1154; found: 245.1134. $\mathbf{R}_f$: 0.17 (petroleum ether/EtOAc 80/20).

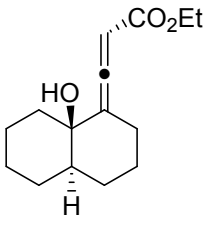


5b
yellowish oil
relative configuration

Cis, Cis Ethyl 3-(3a-hydroxyhexahydro-1H-inden-4(2H)-ylidene)acrylate **5b**

This compound was synthesized according to method B (87%) or method C (65%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.61 (dd, 1H, *J* = 2.8, 1.3 Hz), 4.11-4.20 (m, 2H), 2.58 (sl, 1H), 2.41-2.46 (m, 1H), 2.11-2.17 (m, 1H), 1.95-2.00 (m, 3H), 1.60-1.84 (m, 5H), 1.48-1.53 (m, 1H), 1.36-1.41 (m, 1H), 1.25 (t, 3H, *J* = 7.1 Hz), 1.21-1.23 (m, 1H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.8, 167.0, 113.3, 89.6, 79.9, 61.0, 48.9, 36.1, 28.9, 28.7, 28.6, 24.8, 20.8, 14.5 ppm. **IR** (neat): υ = 3391, 2930, 2869, 1957, 1695, 1149 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 259.1310; found: 259.1329. $\mathbf{R}_f$: 0.28 (petroleum ether/EtOAc 80/20).

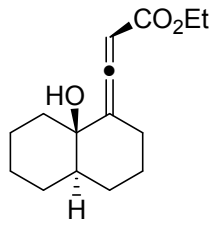


3a
white solid
relative configuration

Trans, *Trans* - Ethyl 3-(8a-hydroxyoctahydronaphthalen-1(2H)-ylidene)acrylate **3a**

This compound was synthesized according to method A (19%) or method C (5%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.53 (d, 1H, *J* = 4.0 Hz), δ_A=4.19 δ_B=4.13 (ABX_3, 2H, J_{AX}=7.0 Hz, J_{BX}=7.0 Hz, J_{AB}=8.5 Hz), 2.48 (tt, 1H, *J* = 12.8, 4.5 Hz), 2.28 (dt, 1H, *J* = 13.4, 2.2 Hz), 1.84-1.87 (m, 1H), 1.47-1.72 (m, 9H), 1.37-1.42 (m, 3H), 1.31-1.33 (m, 1H), 1.28 (t, 3H, *J* = 7.2 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.5, 166.7, 113.7, 88.9, 71.0, 60.9, 45.9, 37.1, 28.9, 28.4, 27.4, 26.9, 26.2, 21.9, 14.6 ppm. **IR** (neat): υ = 3456, 2929, 2855, 1957, 1697, 1149 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc : 273.1467; found : 273.1464. **Pf:** 61.5 – 62.3 °C. $\mathbf{R}_f$: 0.60 (petroleum ether/EtOAc 80/20).

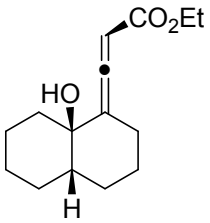


3b
white solid
relative configuration

Trans, *Cis* - Ethyl 3-(8a-hydroxyoctahydronaphthalen-1(2H)-ylidene)acrylate **3b**

This compound was synthesized according to method A (69%), method B (83%) or method C (63%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.59 (d, 1H, *J* = 3.6 Hz), 4.12-4.21 (m, 2H), 2.60 (tt, 1H, *J* = 13.4, 4.1 Hz), 2.21-2.24 (m, 1H), 1.94 (sl, 1H), 1.81-1.84 (m, 1H), 1.64-1.72 (m, 3H), 1.39-1.58 (m, 5H), 1.30-1.37 (m, 3H), 1.26 (t, 3H, *J* = 7.2 Hz), 1.21-1.24 (m, 1H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.2, 166.1, 114.2, 88.9, 70.8, 61.0, 45.8, 37.3, 28.8, 28.3, 27.3, 26.7, 26.4, 21.8, 14.6 ppm. **IR** (neat): υ = 3494, 2928, 2854, 1957, 1695, 1212 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 273.1467; found: 273.1464. **Pf**: 103.6 – 104.8 °C. $\mathbf{R}_f$: 0.53 (petroleum ether/EtOAc 80/20).

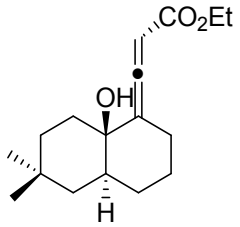


3c
white solid
relative configuration

Cis, *Cis* - Ethyl 3-(8a-hydroxyoctahydronaphthalen-1(2H)-ylidene)acrylate **3c**

This compound was synthesized according to method A (9%), method B (16%) or method C (11%).

^{1}H NMR ($CDCl_3$, 600 MHz, T=333 K): δ = 5.63 (t, 1H, *J* = 2.1 Hz), 4.19 (qd, 2H, *J* = 7.1, 0.6 Hz), 2.52-2.57 (m, 1H), 2.21-2.25 (m, 1H), 1.89-1.97 (m, 2H), 1.65-1.76 (m, 5H), 1.51-1.60 (m, 3H), 1.33-1.48 (m, 4H), 1.28 (t, 3H, *J* = 7.2 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 200 MHz, T=333K): δ = 208.0, 169.9, 113.1, 89.6, 72.8, 61.0, 44.0, 36.3, 36.2, 28.4, 28.3, 28.0, 23.9, 23.7, 14.6 ppm. **IR** (neat): υ = 3392, 2929, 2859, 1956, 1697, 1156 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 273.1467; found: 273.1483. **Pf**: 89.6 – 91.0°C. $\mathbf{R}_f$: 0.37 (petroleum ether/EtOAc 80/20).

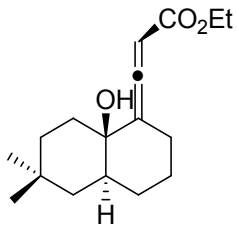


6a
colorless oil
relative configuration

Trans, *Trans* - Ethyl 3-(8a-hydroxy-6,6-dimethyloctahydronaphthalen-1(2H)-ylidene)acrylate **6a**

This compound was synthesized according to method C (5%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.52 (d, 1H, *J* = 4.0 Hz), δ_A=4.23 δ_B=4.11 (ABX_3, 2H, J_{AX}=7.5 Hz, J_{BX}=7.0 Hz, J_{AB}=4.0 Hz), 2.47 (tt, 1H, *J* = 13.1, 4.4 Hz), 2.28 (dt, 1H, *J* = 13.1, 2.8 Hz), 1.84-1.88 (m, 1H), 1.47-1.88 (m, 6H), 1.33-1.35 (m, 3H), 1.27 (t, 3H, *J* = 7.2 Hz), 1.20-1.25 (m, 1H), 1.04 (ddd, 1H, *J* = 13.3, 3.6, 2.5 Hz), 0.92 (s, 3H), 0.90 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.4, 166.7, 113.4, 88.9, 70.8, 60.9, 41.9, 41.6, 34.5, 33.4, 33.1, 30.9, 28.2, 27.4, 26.8, 24.8, 14.6 ppm. **IR** (neat): υ = 3466, 2929, 2857, 1958, 1697, 1148 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 301.1780; found: 301.1785. $\mathbf{R}_f$: 0.65 (petroleum ether/EtOAc 80/20).

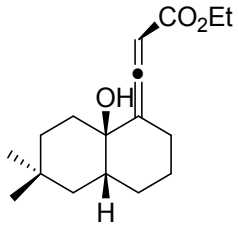


6b
white solid
relative configuration

Trans, *Cis* - Ethyl 3-(8a-hydroxy-6,6-dimethyloctahydronaphthalen-1(2H)-ylidene)acrylate **6b**

This compound was synthesized according to method B (77%) or method C (51%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.60 (d, 1H, *J* = 3.6 Hz), 4.10-4.19 (m, 2H), 2.59 (tt, 1H, *J* = 13.4, 3.8 Hz), 2.29 (sl, 1H), 2.22 (dt, 1H, *J* = 13.2, 2.6 Hz), 1.81-1.85 (m, 1H), 1.36-1.64 (m, 7H), 1.26-1.30 (m, 1H), 1.24 (t, 3H, *J* = 7.1 Hz), 1.13-1.17 (m, 1H), 0.98 (dt, 1H, *J* = 12.4, 2.0 Hz), 0.89 (s, 3H), 0.87 (s, 3H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.1, 167.1, 114.0, 88.8, 70.6, 61.0, 41.8, 41.4, 34.5, 33.5, 33.1, 30.9, 28.1, 27.3, 26.7, 25.0, 14.6 ppm. **IR** (neat): υ = 3400, 2931, 2856, 1958, 1696, 1154 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 301.1780; found: 301.1726. **Pf :** 102.6 – 103.4 °C. $\mathbf{R}_f$: 0.60 (petroleum ether/EtOAc 80/20).

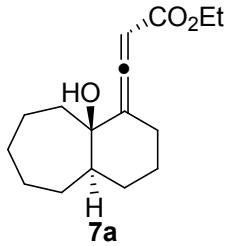


6c
white solid
relative configuration

Cis, *Cis* - Ethyl 3-(8a-hydroxy-6,6-dimethyloctahydronaphthalen-1(2H)-ylidene)acrylate **6c**

This compound was synthesized according to method B (16%) or method C (2%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.64 (d, 1H, *J* = 3.9 Hz), δ_A=4.19 δ_B=4.17 (ABX_3, 2H, J_{AX}=7.5 Hz, J_{BX}=7.0 Hz, J_{AB}=3.5 Hz), 2.58-2.65 (m, 1H), 2.51 (sl, 1H), 2.22 (d, 1H, *J* = 13.1 Hz), 2.14 (tt, 1H, *J* = 12.9, 5.1 Hz), 1.98-2.00 (m, 1H), 1.67-1.78 (m, 2H), 1.49-1.60 (m, 2H), 1.40 (t, 1H, *J* = 13.7 Hz), 1.27 (t, 3H, *J* = 7.2 Hz), 1.20-1.24 (m, 3H), 1.04 (dd, 1H, *J* = 13.3, 3.0 Hz), 0.96 (s, 3H), 0.89 (s, 3H) ppm **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 208.6, 167.3, 109.1, 88.9, 73.2, 61.2, 41.4, 38.1, 37.6, 35.4, 33.1, 31.0, 27.2, 26.7, 24.9, 20.5, 14.6 ppm. **IR** (neat): υ = 3392, 2934, 2864, 1956, 1697, 1160 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 301.1780; found: 301.1814. **Pf**: 76.1-78.8°C. $\mathbf{R}_f$: 0.38 (petroleum ether/EtOAc 80/20).

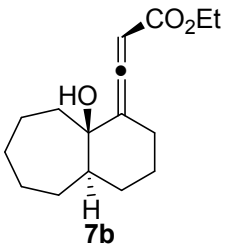


7a
colorless oil
relative configuration

Trans, *Trans* - Ethyl 3-(9a-hydroxydecahydro-1H-benzo[7]annulen-1-ylidene)acrylate **7a**

This compound was synthesized according to method C (12%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.53 (d, 1H, *J* = 3.8 Hz), δ_A = 4.19 δ_B=4.15 (ABX_3, 2H, J_{AX}=7.0 Hz, J_{BX}=7.0 Hz, J_{AB}=3.5 Hz), 2.44 (tt, 1H, *J* = 13.0, 4.3 Hz), 2.23-2.27 (m, 1H), 1.88-1.93 (m, 1H), 1.81-1.86 (m, 1H), 1.71-1.78 (m, 2H), 1.62-1.70 (m, 4H), 1.53-1.57 (m, 1H), 1.44-1.52 (m, 6H), 1.27 (t, 3H, *J* = 7.1 Hz), 1.20-1.24 (m, 1H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.5, 166.8, 114.5, 88.7, 74.0, 60.9, 49.3, 41.3, 30.3, 30.1, 28.6, 27.7, 27.6, 26.9, 21.2, 14.6 ppm. **IR** (neat): υ = 3460, 2924, 2856, 1957, 1696, 1149 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 287.1623; found: 287.1589. $\mathbf{R}_f$: 0.57 (petroleum ether/EtOAc 80/20).

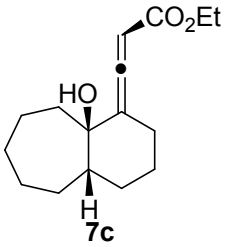


7b
white solid
relative configuration

Trans, *Cis* - Ethyl 3-(9a-hydroxydecahydro-1H-benzo[7]annulen-1-ylidene)acrylate **7b**

This compound was synthesized according to method B (81%) or method C (59%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.54 (d, 1H, *J* = 3.6 Hz), δ_A=4.18 δ_B=4.11 (ABX_3, 2H, J_{AX}=7.5 Hz, J_{BX}=7.5 Hz, J_{AB}=4.0 Hz), 2.52 (tt, 1H, *J* = 13.5, 4.2 Hz), 2.36 (sl, 1H), 2.17 (dt, 1H, *J* = 13.0, 2.2 Hz), 1.63-1.80 (m, 7H), 1.48-1.52 (m, 2H), 1.29-1.39 (m, 5H), 1.22 (t, 3H, *J* = 7.1 Hz,), 1.13-1.18 (m, 1H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.2, 167.1, 115.2, 88.6, 73.4, 61.0, 49.4, 40.9, 30.3, 29.8, 27.9, 27.4, 27.2, 26.8, 20.9, 14.6 ppm. **IR** (neat): υ = 3392, 2924, 2857, 1956, 1694, 1152 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 287.1623; found: 287.1589. **Pf :** 88.6 – 89.2 °C. $\mathbf{R}_f$: 0.50 (petroleum ether/EtOAc 80/20).

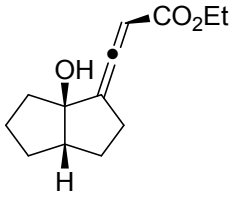


7c
colorless oil
relative configuration

Cis, *Cis* - Ethyl 3-(9a-hydroxydecahydro-1H-benzo[7]annulen-1-ylidene)acrylate **7c**

This compound was synthesized according to method B (12%) or method C (4%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.64 (dd, 1H, *J* = 2.0, 2.0 Hz), 4.17 (q, 2H, *J* = 7.1 Hz), 2.47-2.53 (m, 1H), 2.20-2.25 (m, 1H), 1.85-1.91 (m, 3H), 1.69-1.81 (m, 5H), 1.54-1.62 (m, 3H), 1.31-1.52 (m, 5H), 1.27 (t, 3H, *J* = 7.1 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 208.0, 167.0, 115.0, 89.5, 75.1, 61.1, 46.4, 40.8, 29.9, 29.4, 29.0, 28.5, 26.8, 23.8, 21.3, 14.6 ppm. **IR** (neat): υ = 3400, 2923, 2856, 1955, 1696, 1146 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 287.1623; found: 287.1612. $\mathbf{R}_f$: 0.38 (petroleum ether/EtOAc 80/20).

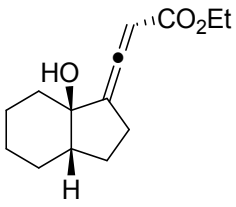


8b
colorless oil
relative configuration

Cis, *Cis* - Ethyl 3-(6a-hydroxyhexahydropentalen-1(2H)-ylidene)acrylate **8b**

This compound was synthesized according to method B (65%) or method C (64%).

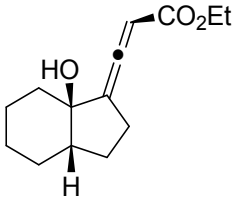
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.67 (t, 1H, *J* = 3.5 Hz), 4.16 (q, 2H, *J* = 7.2 Hz), 2.93 (sl, 1H), 2.71-2.78 (m, 1H), 2.52-2.59 (m, 1H), 2.35-2.41 (m, 1H), 2.07-2.16 (m, 1H), 1.95-2.05 (m, 1H), 1.86-1.93 (m, 2H), 1.73-1.81 (m, 1H), 1.57-1.65 (m, 1H), 1.33-1.45 (m, 2H), 1.25 (t, 3H, *J* = 7.1 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 206.6, 166.9, 117.2, 92.5, 91.1, 61.3, 52.6, 40.5, 32.0, 31.4, 30.8, 25.5, 14.6 ppm. **IR** (neat): υ = 3390, 2951, 2867, 1959, 1695, 1154 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc : 245.1154; found : 245.1133. $\mathbf{R}_f$: 0.26 (petroleum ether/EtOAc 80/20).



9a
yellow solid
relative configuration

Cis, *Trans* - Ethyl 3-(7a-hydroxyoctahydro-1H-inden-1-ylidene)acrylate **9a**
This compound was synthesized according to method C (22%).

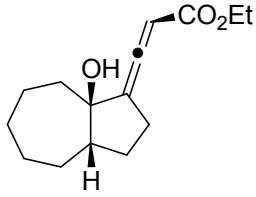
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.64 (t, 1H, *J* = 4.2 Hz), δ_A=4.18 δ_B=4.05 (ABX_3, 2H, J_{AX}=7.5 Hz, J_{BX}=7.0 Hz, J_{AB}=7.5 Hz), 2.65-2.76 (m, 2H), 2.08-2.16 (m, 1H), 1.86-1.95 (m, 3H), 1.53-1.64 (m, 4H), 1.43-1.50 (m, 2H), 1.41 (t, 3H, *J* = 7.2 Hz), 1.13-1.22 (m, 2H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.3, 166.4, 112.7, 91.2, 83.8, 61.0, 47.6, 34.8, 28.9, 28.4, 26.7, 24.6, 23.4, 14.5 ppm. **IR** (neat): υ = 3401, 2927, 2852, 1960, 1696, 1148 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 259.1310; found: 259.1314. **Pf :** 69.8 – 71.6 °C. **Rf**: 0.36 (petroleum ether/EtOAc 80/20).



9b
yellowish oil
relative configuration

Cis, *Cis* - Ethyl 3-(7a-hydroxyoctahydro-1H-inden-1-ylidene)acrylate **9b**
This compound was synthesized according to method B (87%) or method C (73%).

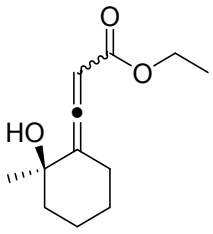
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.66 (t, 1H, *J* = 4.1 Hz), 4.14 (q, 2H, *J* = 7.1 Hz), 3.14 (sl, 1H), 2.74-2.81 (m, 1H), 2.55-2.63 (m, 1H), 2.11-2.18 (m, 1H), 1.91-1.97 (m, 1H), 1.86-1.90 (m, 1H), 1.50-1.63 (m, 4H), 1.42 (ttd, 1H, *J* = 9.2, 2.8, 2.8 Hz), 1.24 (t, 3H, *J* = 7.2 Hz), 1.11-1.22 (m, 2H), 1.00-1.07 (m, 1H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.1, 167.0, 113.6, 91.1, 83.3, 61.1, 47.2, 34.3, 28.7, 28.4, 26.7, 24.4, 23.9, 14.5 ppm. **IR** (neat): υ = 3374, 2928, 2854, 1960, 1696, 1153 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc : 259.1310; found : 259.1332. $\mathbf{R}_f$: 0.29 (petroleum ether/EtOAc 80/20).



10b
colorless oil
relative configuration

Cis, *Cis* - Ethyl 3-(8a-hydroxyoctahydroazulen-1(2H)-ylidene)acrylate **10b**
This compound was synthesized according to method B (62%) or method C (53%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.67 (t, 1H, *J* = 3.8 Hz), 4.16 (q, 2H, *J* = 7.1 Hz), 2.71-2.78 (m, 1H), 2.50-2.57 (m, 1H), 2.29 (sl, 1H), 2.12-2.22 (m, 2H), 1.91-1.95 (m, 1H), 1.75-1.82 (m, 2H), 1.66-1.72 (m, 2H), 1.54-1.59 (m, 2H), 1.29-1.45 (m, 4H), 1.26 (t, 3H, *J* = 7.2 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.4, 166.8, 118.3, 91.3, 86.5, 61.2, 52.9, 39.1, 33.4, 32.2, 31.2, 29.3, 29.1, 23.3, 14.6 ppm. **IR** (neat) : υ = 3370, 2921, 2851, 1958, 1696, 1155 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 273.1467; found: 273.1493. $\mathbf{R}_f$: 0.37 (petroleum ether/EtOAc 80/20).

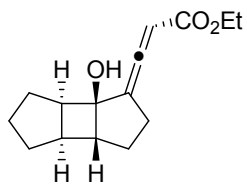


11
yellowish oil, 81%
relative configuration
trans/*cis* : 1:1

Ethyl 3-(2-hydroxy-2-methylcyclohexylidene)acrylate **11**

This compound was synthesized according method B (81%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.61 (s, 1H, *J*=2.7, 1.3 Hz), 5.59 (dd, 1H, *J*=2.7, 1.3 Hz), 4.12-4.19 (m, 4H), 2.88 (sl, 1H), 2.48-2.54 (m, 1H), 2.39-2.45 (m, 1H), 2.19-2.29 (m, 4H), 1.66-1.81 (m, 6H), 1.51-1.58 (m, 4H), 1.37 (s, 3H), 1.33 (s, 3H), 1.24-1.29 (m, 6H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 207.1, 207.0, 167.4, 166.7, 114.6, 113.9, 89.4, 89.2, 70.3, 69.9, 61.2, 61.0, 40.7, 40.6, 28.5, 28.3, 28.0, 27.9, 26.7, 26.6, 22.4, 22.3, 14.5 ppm. **ESI-HRMS:** $[M+Na]^+$ calc : 233.1148; found : 233.1159. **IR** (ATR): υ = 3411, 1960, 1697, 1162 (C-O) cm^{-1}. **R_f:** 0.37 (PE/AcOEt 80/20).

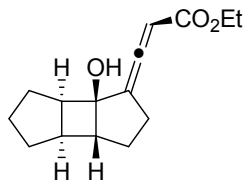


12a
yellowish oil
relative configuration

Cis, *Trans* - ethyl 3-(6b-hydroxyhexahydrocyclobuta[1,2:3,4]di[5]annulen-1(2H,3bH,6bH)-ylidene)acrylate **12a**

This compound was synthesized according to method C (32%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.67 (dd, 1H, *J* = 5.1, 2.0 Hz), 4.11-4.20 (m, 2H), 2.76-2.84 (m, 1H), 2.66-2.72 (m, 2H), 2.46 (sl, 1H), 1.99-2.13 (m, 4H), 1.74-1.80 (m, 2H), 1.68 (dd, 1H, *J* = 12.2, 7.0 Hz), 1.59-1.63 (m, 1H), 1.37-1.51 (m, 2H), 1.25 (t, 3H, *J* = 7.2 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 204.6, 166.7, 118.8, 91.7, 80.7, 61.2, 52.8, 47.4, 37.3, 33.3, 31.4, 30.2, 27.1, 25.9, 14.6 ppm. **IR** (neat): υ = 3367, 2940, 2852, 1959, 1696, 1161 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc : 271.1305; found : 271.1307. **R_f**: 0.59 (petroleum ether/EtOAc 80/20).

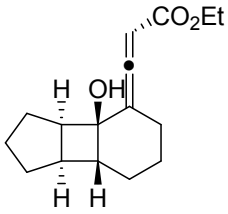


12b
yellowish solid
relative configuration

Cis, *Cis* - ethyl 3-(6b-hydroxyhexahydrocyclobuta[1,2:3,4]di[5] annulen-1(2H,3bH,6bH)-ylidene)acrylate **12b**

This compound was synthesized according to method C (61%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.76 (dd, 1H, *J* = 5.0, 1.8 Hz), δ_A=4.17 δ_B=4.15 (ABX_3, 2H, J_{AX}=7.5 Hz, J_{BX}=7.0 Hz, J_{AB}=5.5 Hz), 2.87-2.95 (m, 1H), 2.77 (dd, 1H, *J* = 8.3, 5.5 Hz), 2.67 (dd, 1H, *J* = 15.4, 7.3 Hz), 2.04-2.06 (m, 2H), 1.92-2.02 (m, 2H), 1.65-1.79 (m, 3H), 1.56-1.51 (m, 2H), 1.40-1.49 (m, 2H), 1.25 (t, 3H, *J* = 7.1 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 204.7, 166.8, 117.6, 92.0, 80.9, 61.1, 52.4, 47.9, 37.3, 33.2, 31.5, 30.4, 27.1, 25.9, 14.6 ppm. **IR** (neat): υ = 3413, 2940, 2853, 1961, 1698, 1155 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 271.1305; found: 271.1311. **Pf**: 59.7 – 61.8°C. **R_f**: 0.52 (petroleum ether/EtOAc 80/20).

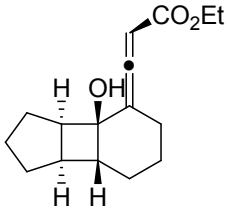


13a
yellowish oil
relative configuration

Cis, *Trans* - ethyl 3-(3b-hydroxyhexahydro-1H-cyclopenta[3,4] cyclobuta[1,2]benzen-4(2H,3bH,7bH)-ylidene)acrylate **13a**

This compound was synthesized according to method C (21%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.52 (dd, 1H, *J* = 4.1, 0.6 Hz), δ_A=4.21 δ_B=4.13 (ABX_3, 2H, J_{AX}=7.5 Hz, J_{BX}=7.0 Hz, J_{AB}=7.0 Hz), 2.72 (tt, 1H, *J* = 8.1, 2.1 Hz), 2.33-2.38 (m, 1H), 2.21-2.30 (m, 2H), 192-1.96 (m, 1H), 1.85-1.90 (m, 1H), 1.73-1.78 (m, 3H), 1.61-1.68 (m, 3H), 1.47-1.53 (m, 2H), 1.39-1.45 (m, 2H), 1.25 (t, 3H, *J* = 7.1 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 210.5, 166.4, 112.2, 89.6, 70.3, 61.0, 47.7, 46.3, 37.0, 31.5, 26.8, 26.3, 25.6, 24.7, 21.4, 14.6 ppm. **IR** (neat): υ = 3401, 2937, 2851, 1955, 1694, 1146 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc : 285.1467; found : 285.1447. $\mathbf{R}_f$: 0.56 (petroleum ether/EtOAc 80/20).



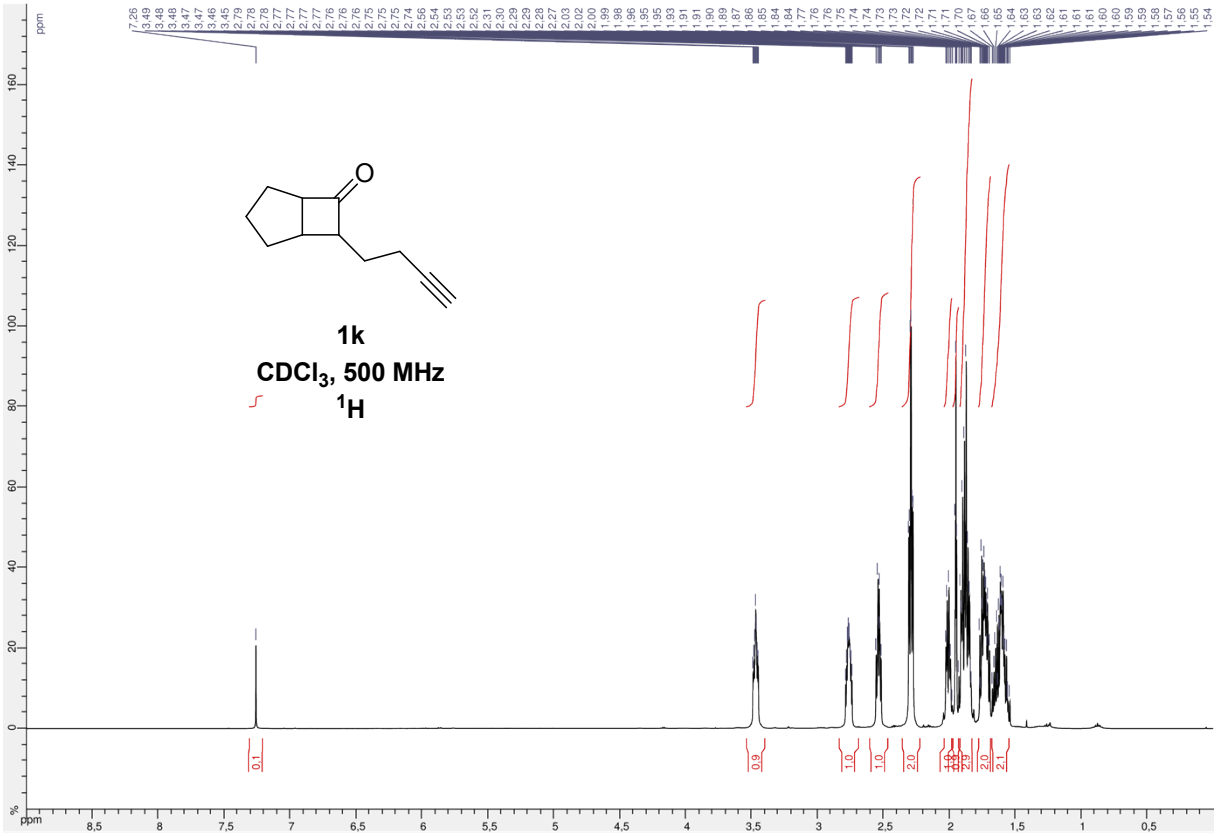
13b
white solid
relative configuration

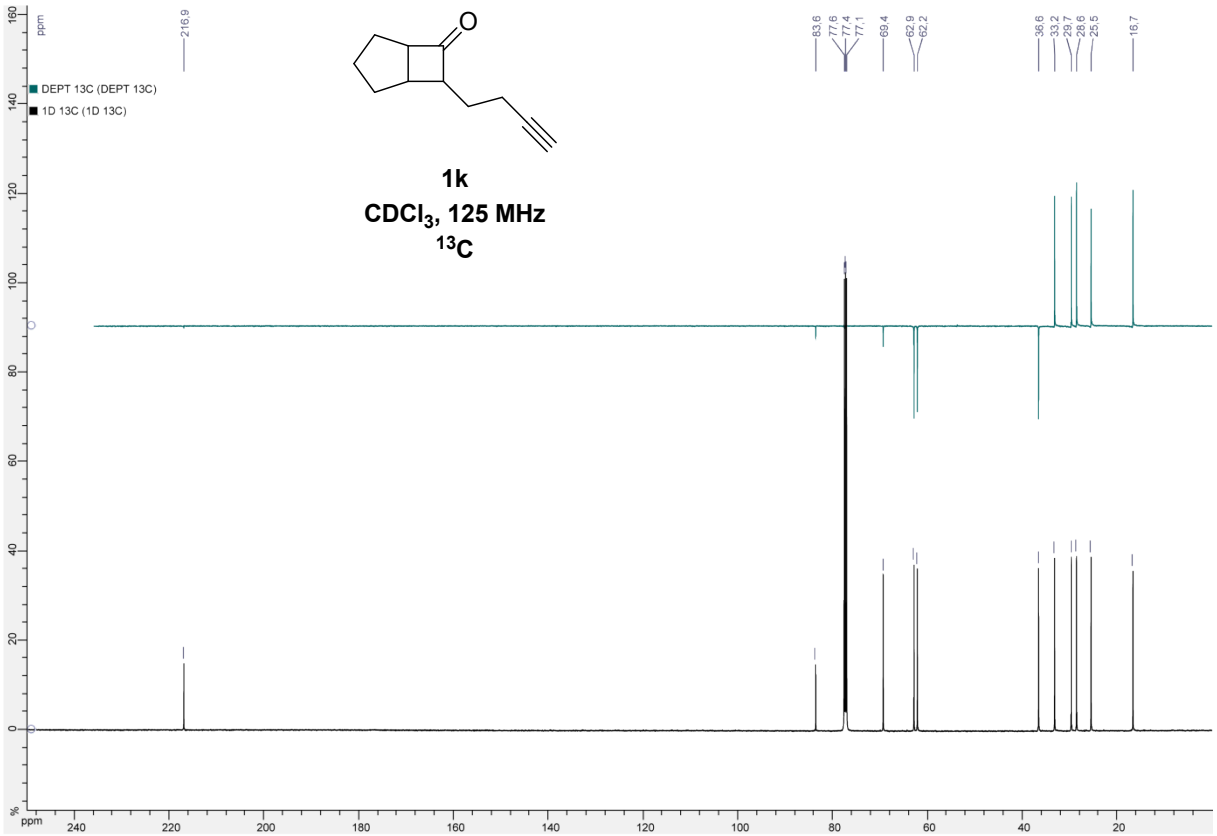
Cis, *Trans* - ethyl 3-(3b-hydroxyhexahydro-1H-cyclopenta[3,4] cyclobuta[1,2]benzen-4(2H,3bH,7bH)-ylidene)acrylate **13b**

This compound was synthesized according to method B (60%) or method C (44%).

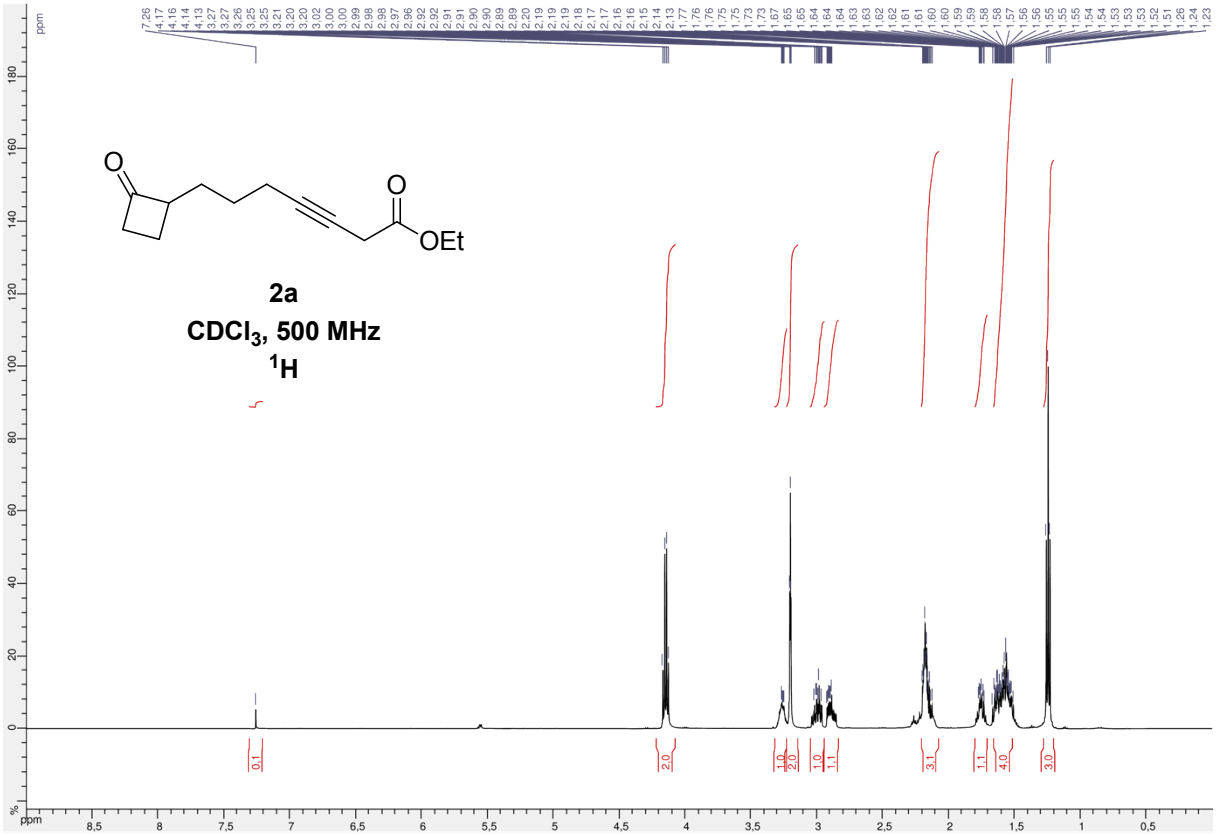
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 5.67 (t, 1H, *J* = 2.4 Hz), 4.14 (q, 2H, *J* = 7.0 Hz), 2.63 (tt, 1H, *J* = 8.3, 1.7 Hz), 2.33-2.36 (m, 2H), 2.10-2.19 (m, 2H), 1.93-2.00 (m, 2H), 1.36-1.84 (m, 9H), 1.24 (t, 3H, *J* = 7.1 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 210.0, 167.0, 113.5, 90.0, 69.9, 61.2, 48.2, 45.0, 36.5, 31.6, 26.7, 26.2, 25.8, 24.6, 21.0, 14.5 ppm. **IR** (neat): υ = 3378, 2934, 2850, 1953, 1697, 1147 cm^{-1}. **HRMS** (m/z): $[M+Na]^+$ calc: 285.1467; found: 285.1456. **Pf:** 49.6 – 53.8 °C. $\mathbf{R}_f$: 0.44 (petroleum ether/EtOAc 80/20).

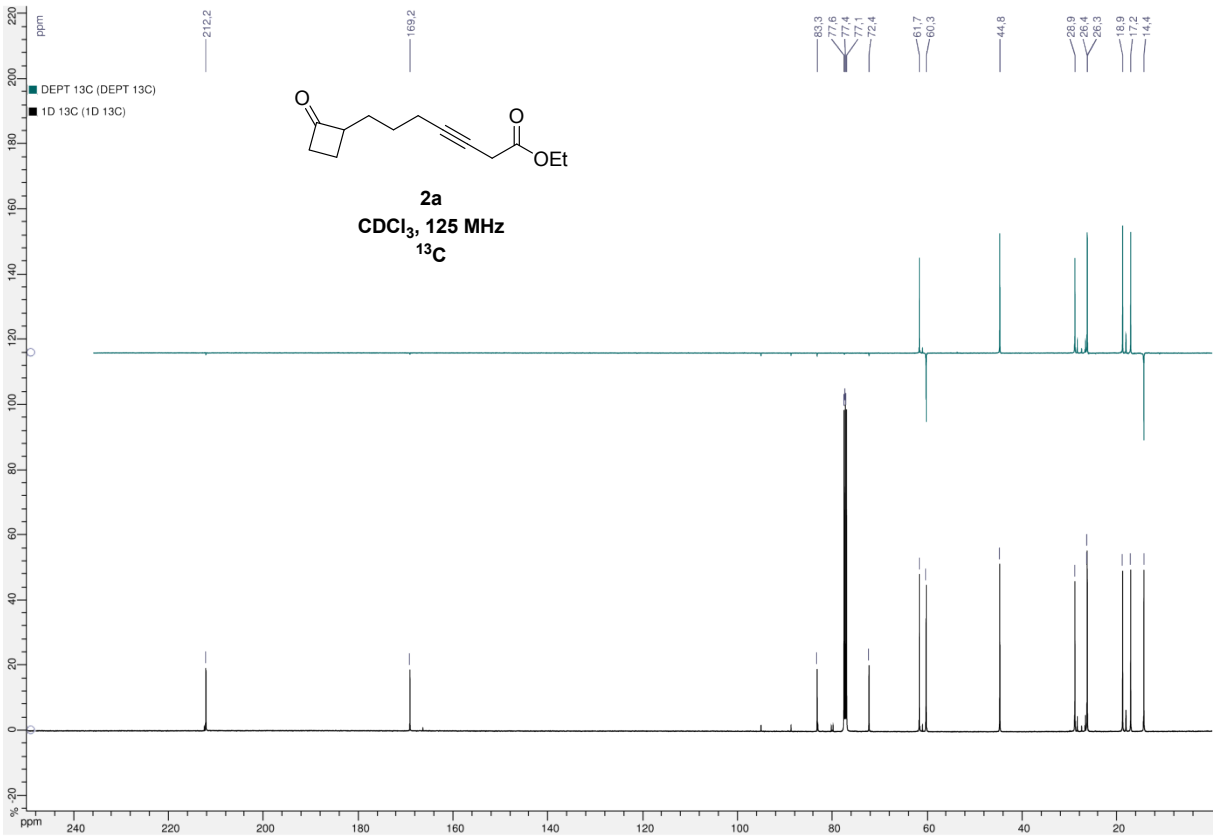
^{1}H and ^{13}C spectra for Keto-Alkyne 1k

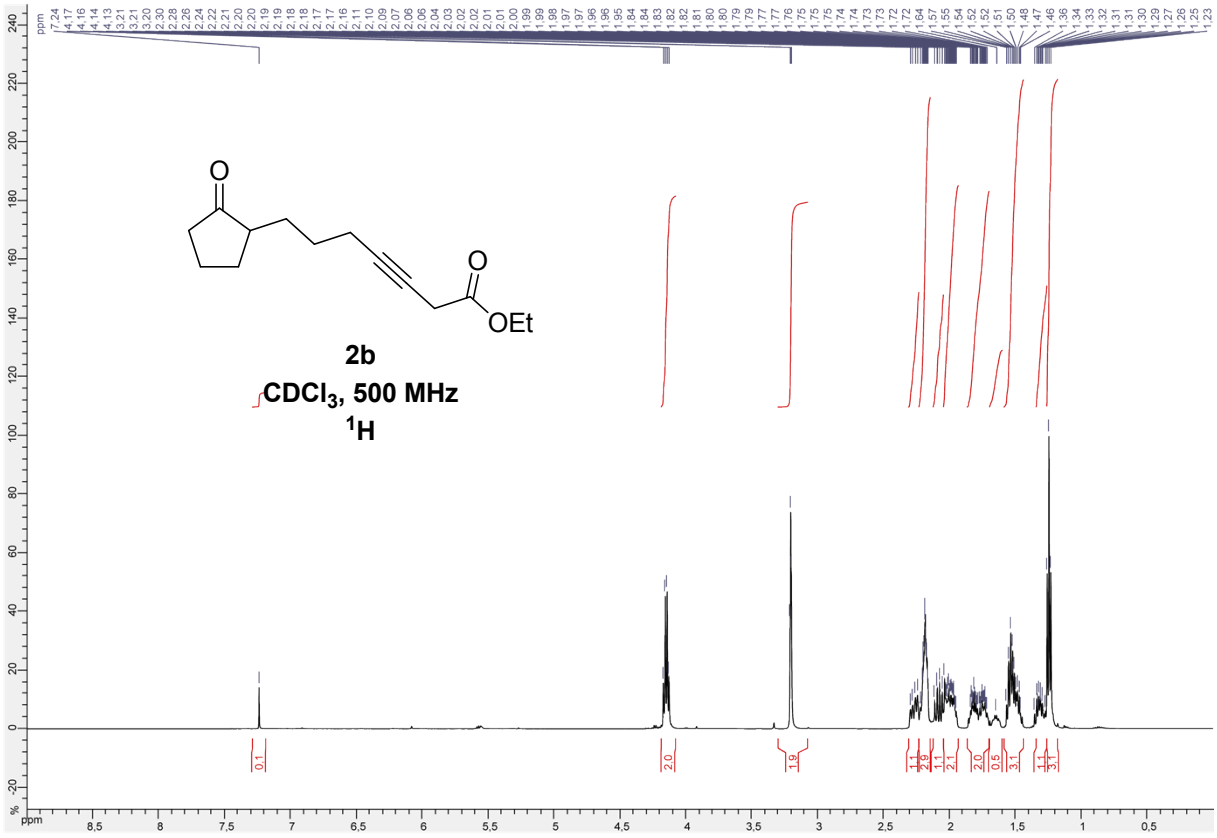


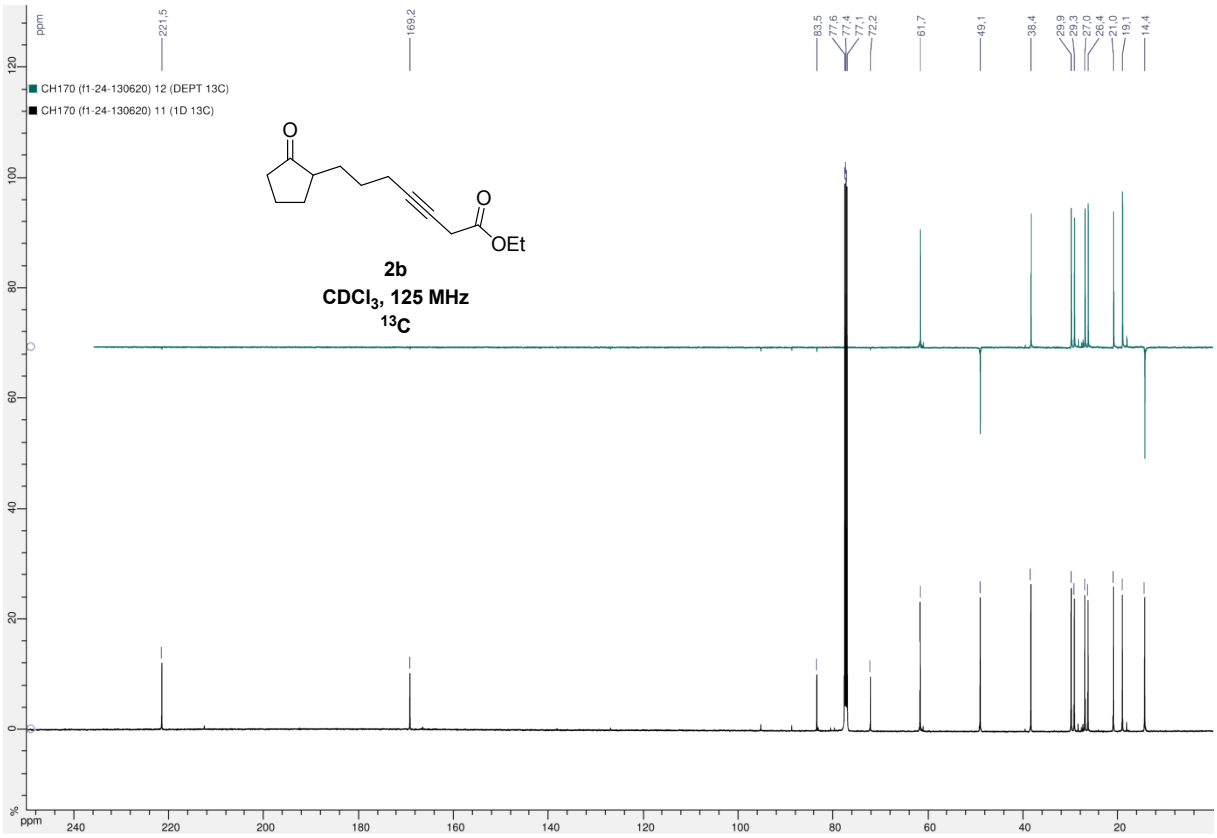


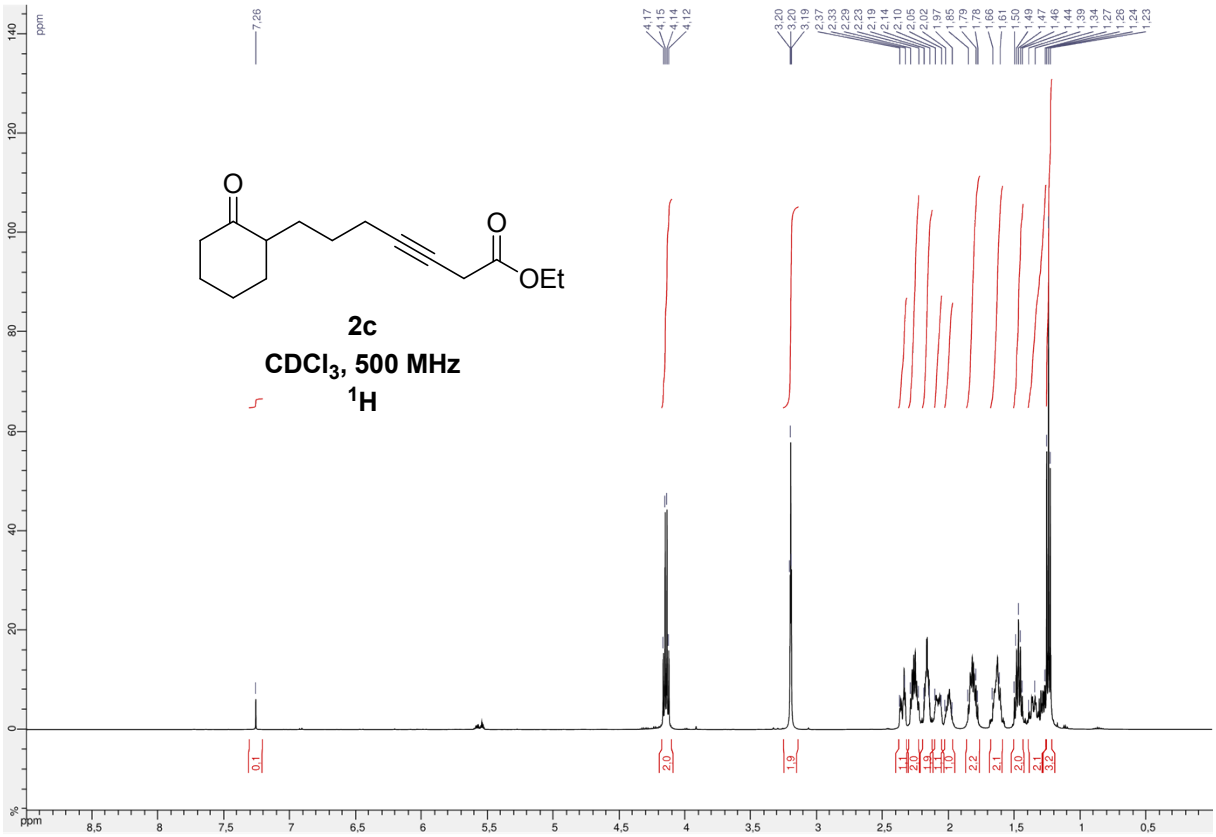
^{1}H and ^{13}C spectra for 3-Alkynoate 2a-2k

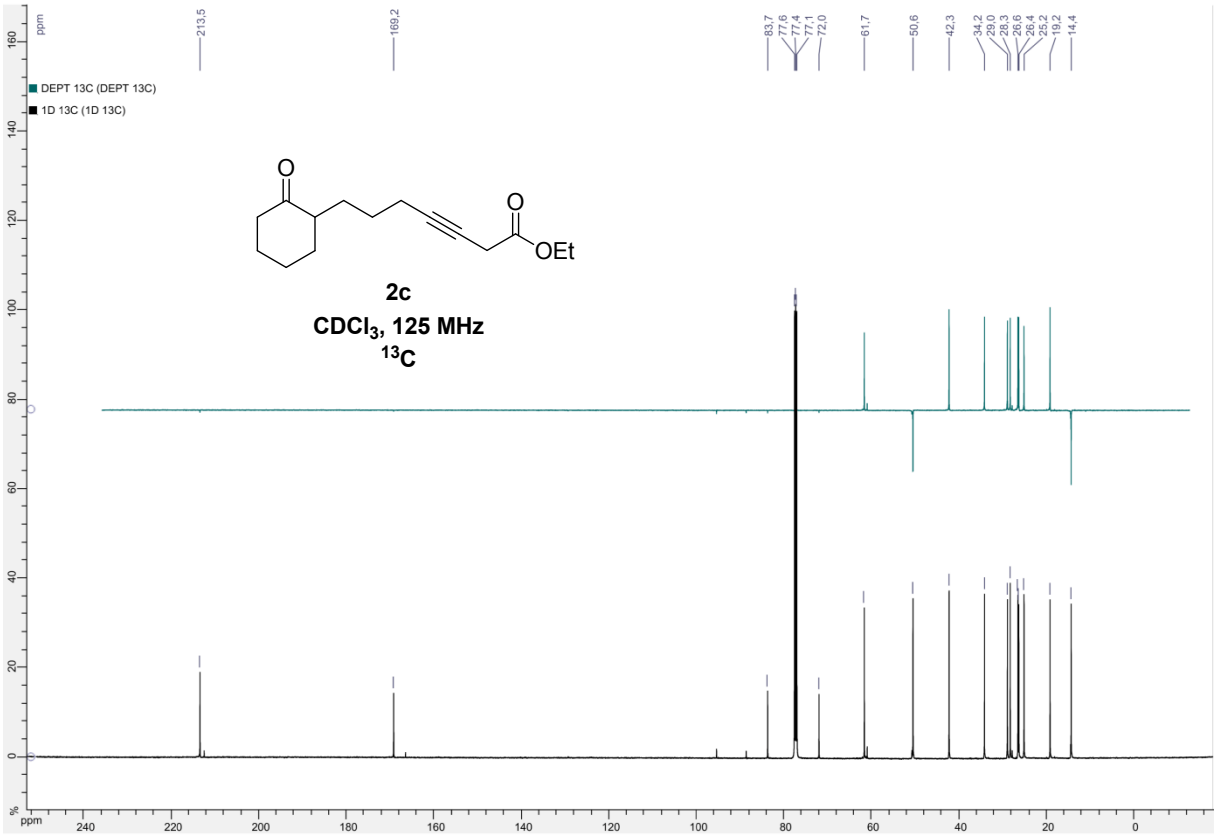


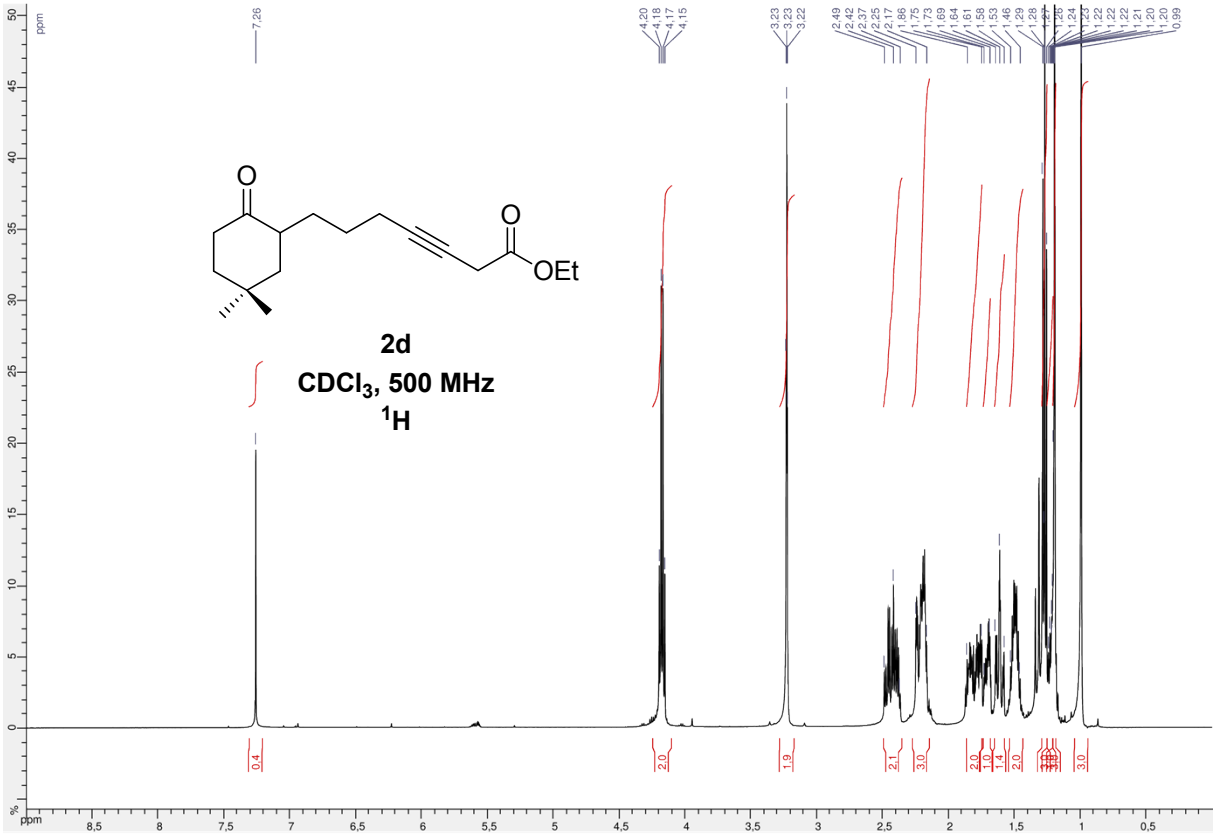


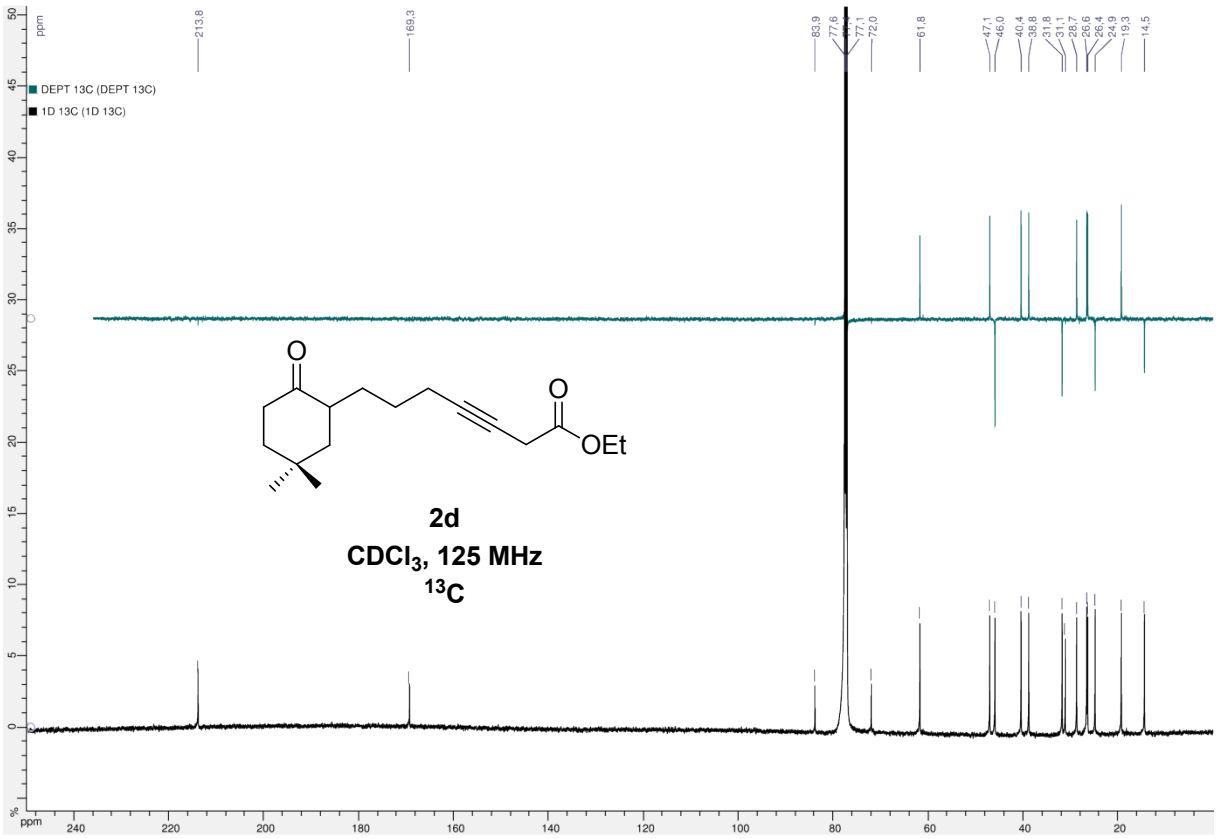

O
O
OEt
2b
CDCl3, 500 MHz
1H

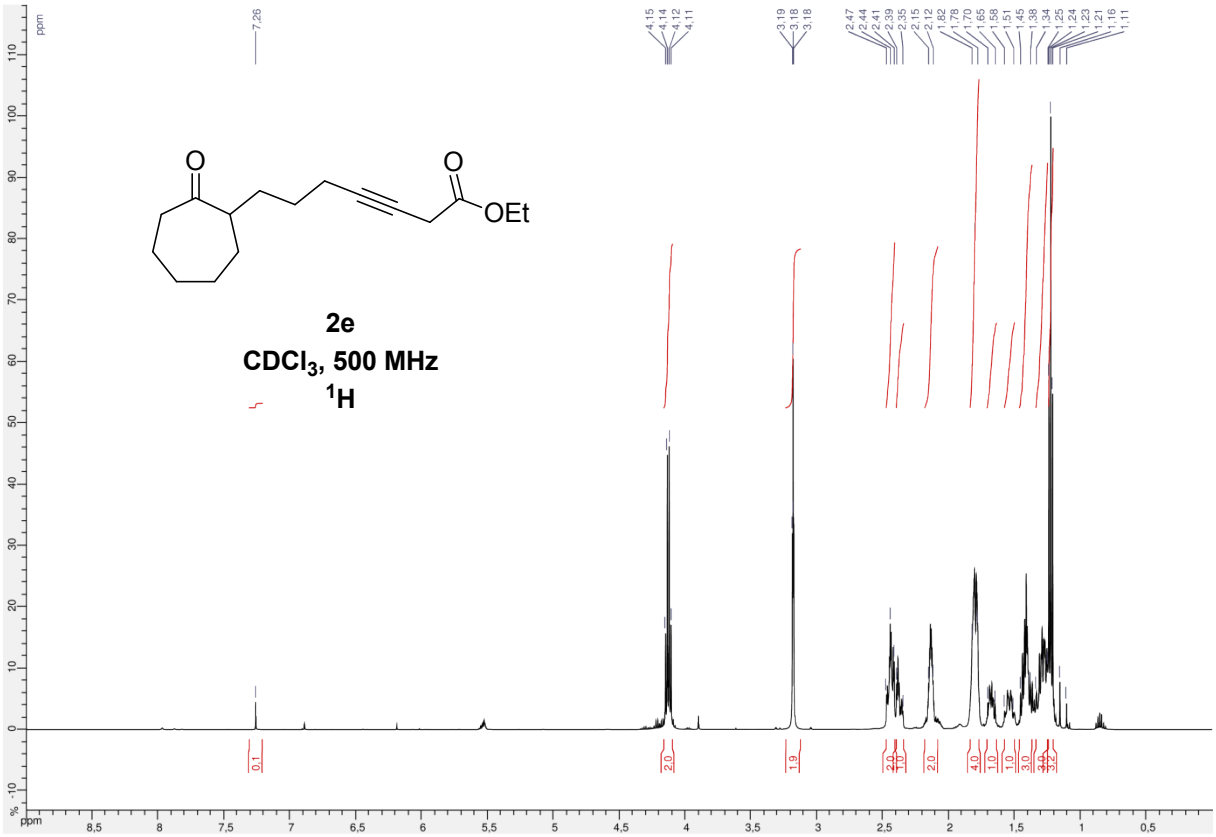

CH170 (f1-24-130620) 12 (DEPT 13C)
CH170 (f1-24-130620) 11 (1D 13C)
O
O
OEt
2b
CDCl3, 125 MHz
13C

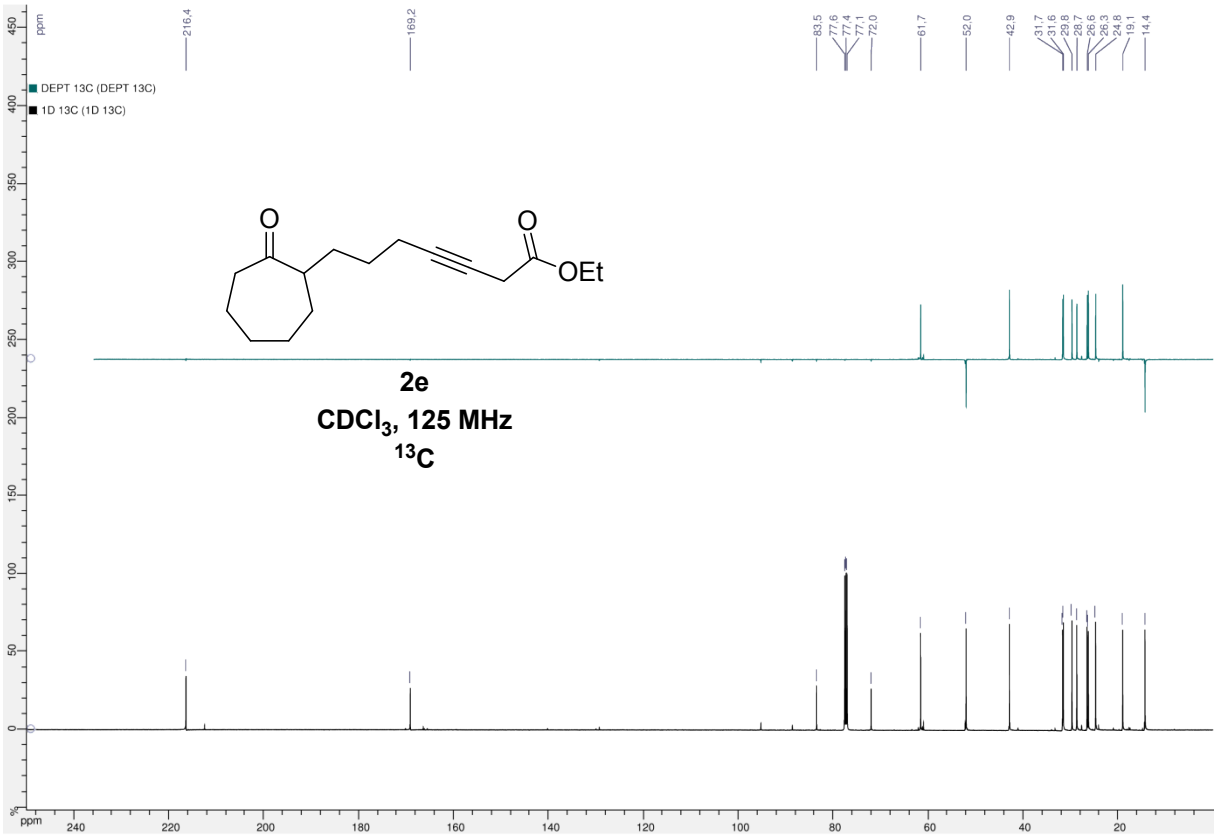

O
O
OEt
2c
CDCl3, 500 MHz
1H

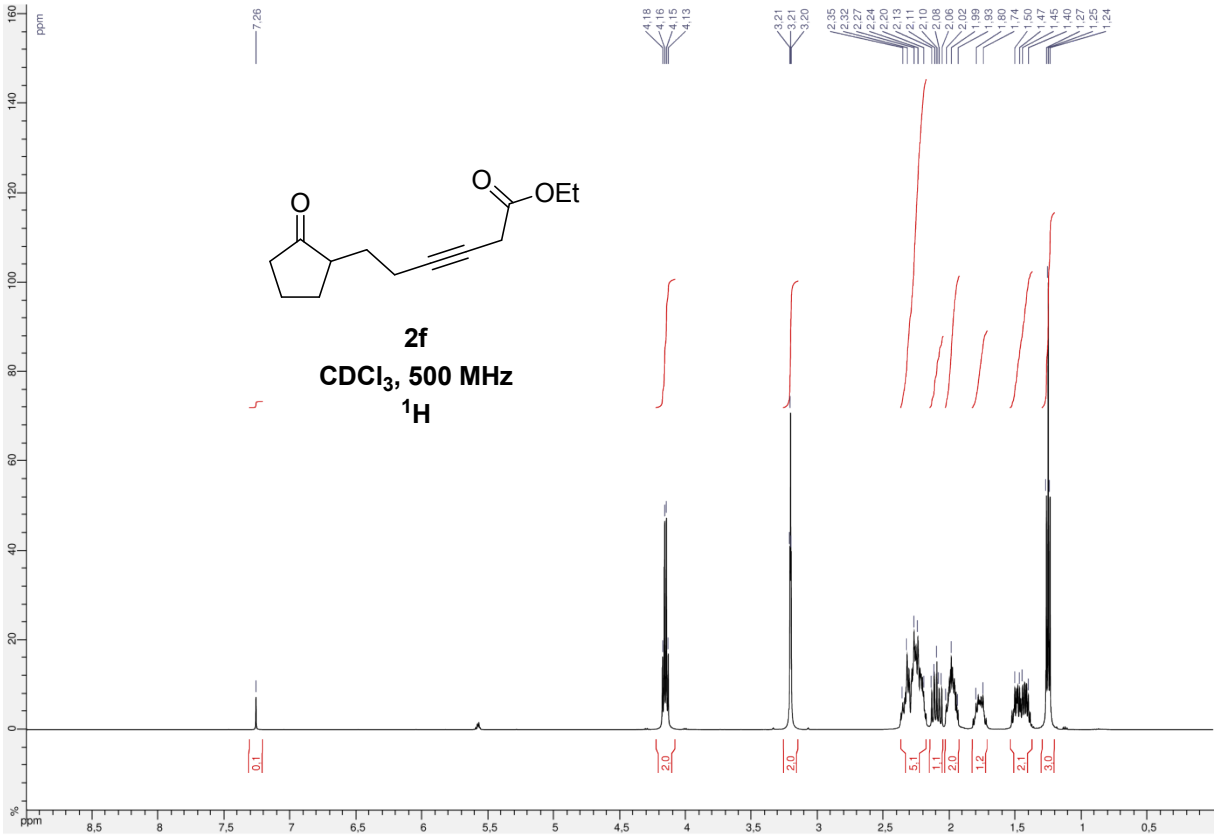

DEPT 13C (DEPT 13C)
1D 13C (1D 13C)
O
O
OEt
2c
CDCl3, 125 MHz
13C

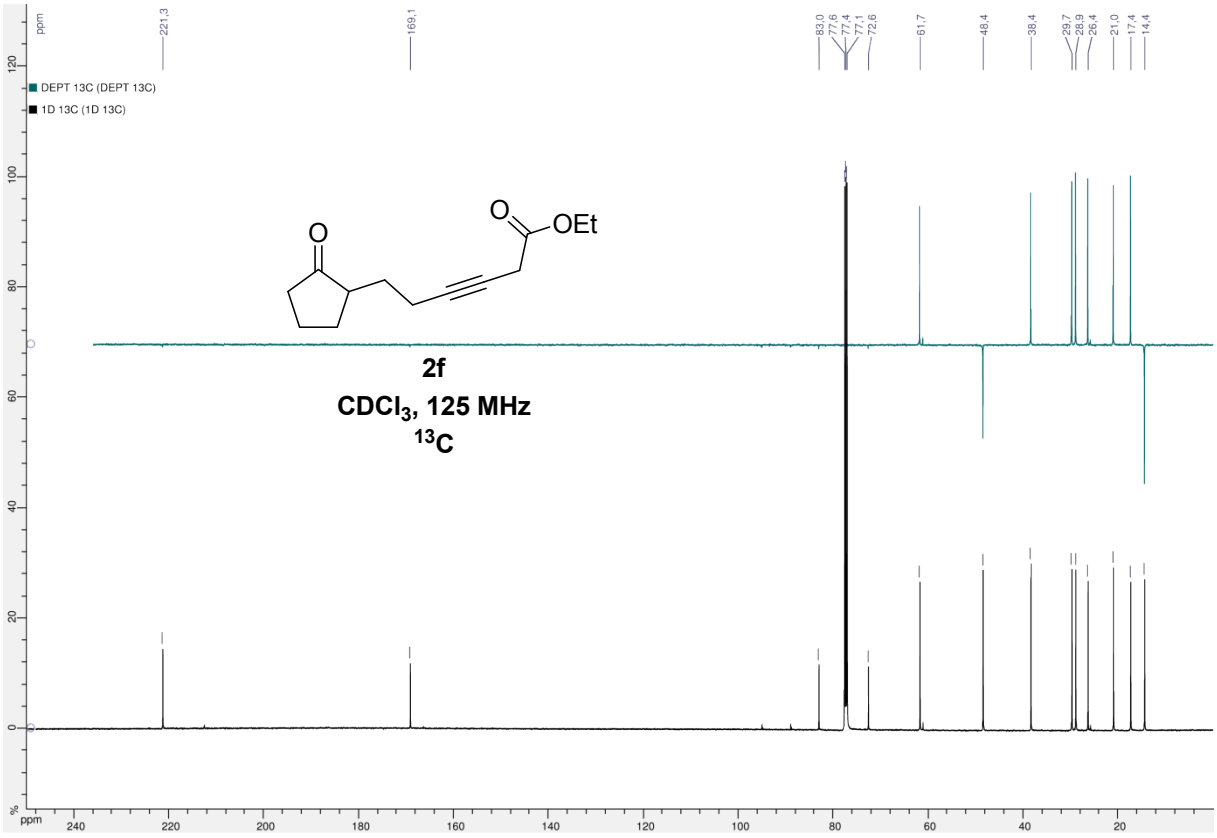

O
O
OEt
2d
CDCl3, 500 MHz
1H

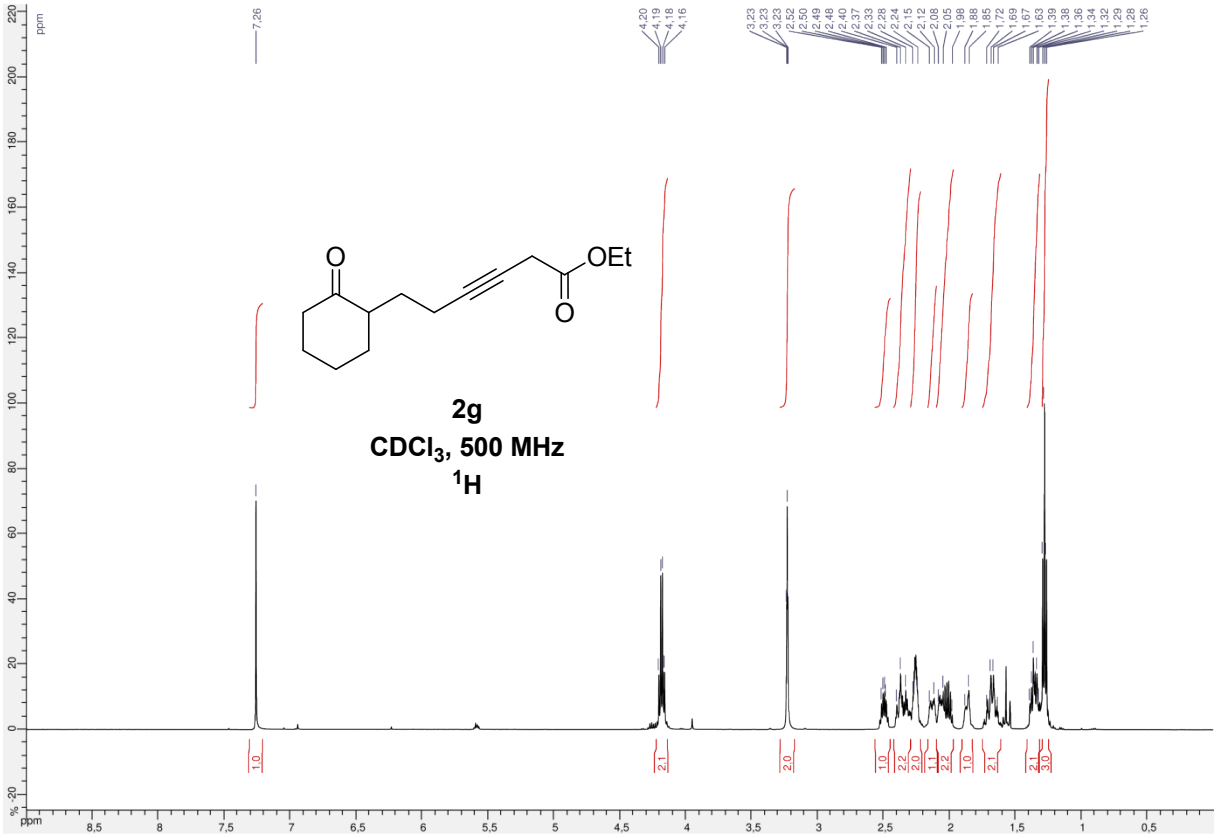

DEPT 13C (DEPT 13C)
1D 13C (1D 13C)
O
O
OEt
2d
CDCl3, 125 MHz
13C

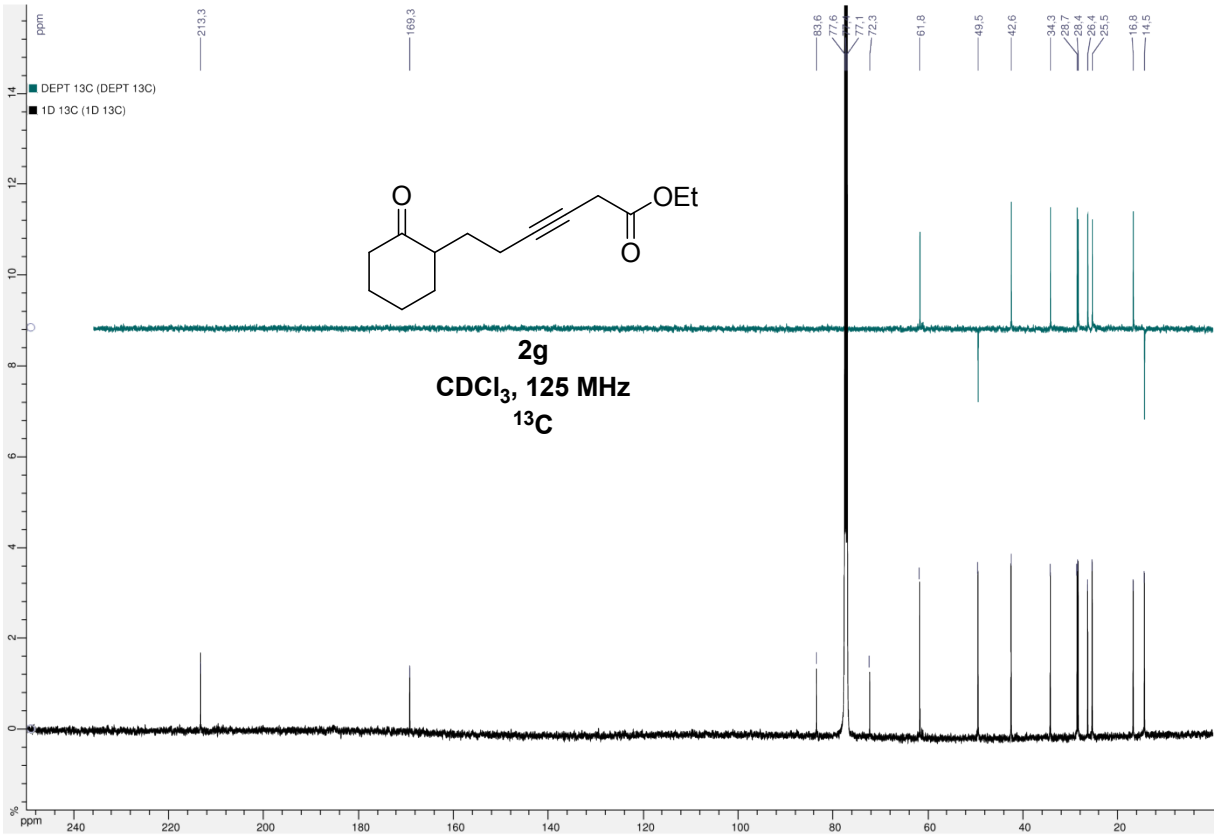

7.26
4.15
4.14
4.12
4.11
3.19
3.18
3.18
2.47
2.44
2.41
2.39
2.35
2.15
2.12
1.82
1.78
1.70
1.65
1.58
1.51
1.45
1.38
1.34
1.25
1.24
1.23
1.21
1.16
1.11
O
O
OEt
2e
CDCl3, 500 MHz
1H
ppm

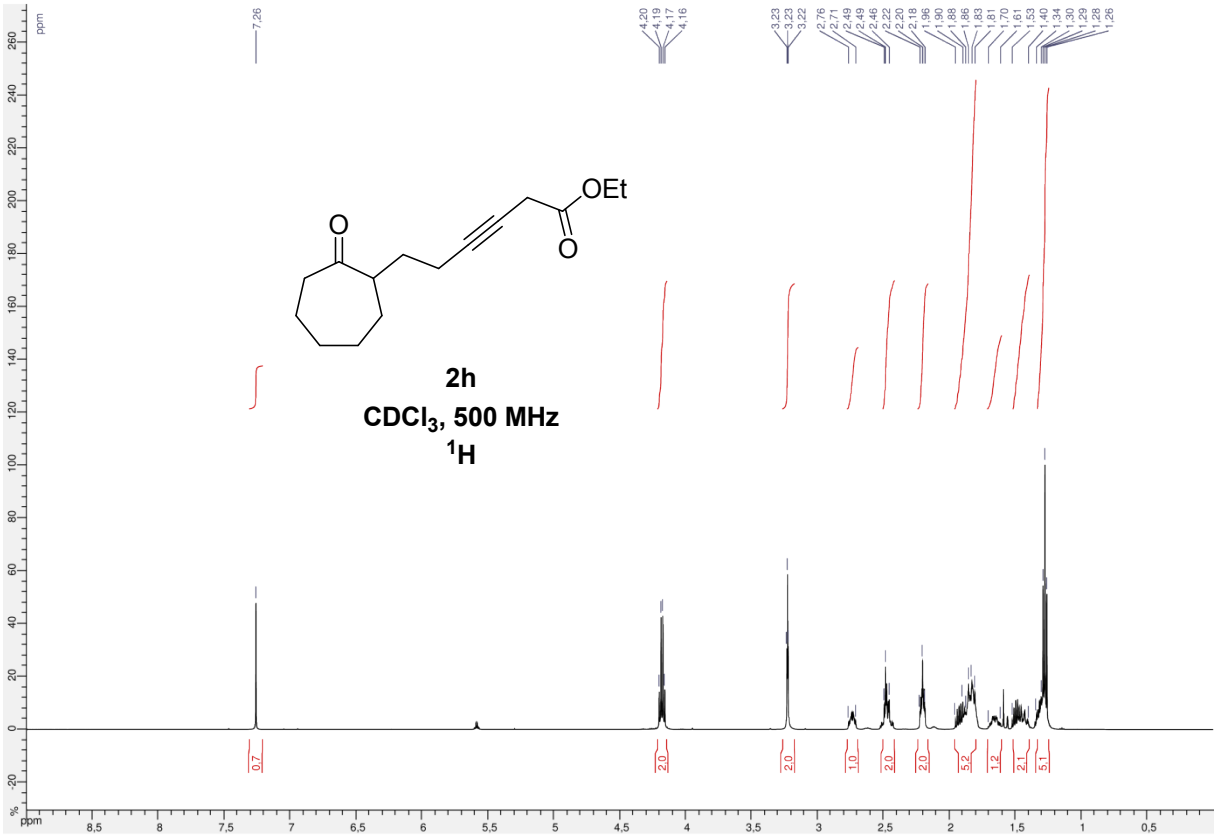

216.4
169.2
83.5
77.6
77.4
77.1
72.0
61.7
52.0
42.9
31.7
31.6
29.8
28.7
26.6
26.3
24.8
19.1
14.4
DEPT 13C (DEPT 13C)
1D 13C (1D 13C)
O
O
OEt
2e
CDCl3, 125 MHz
13C
ppm

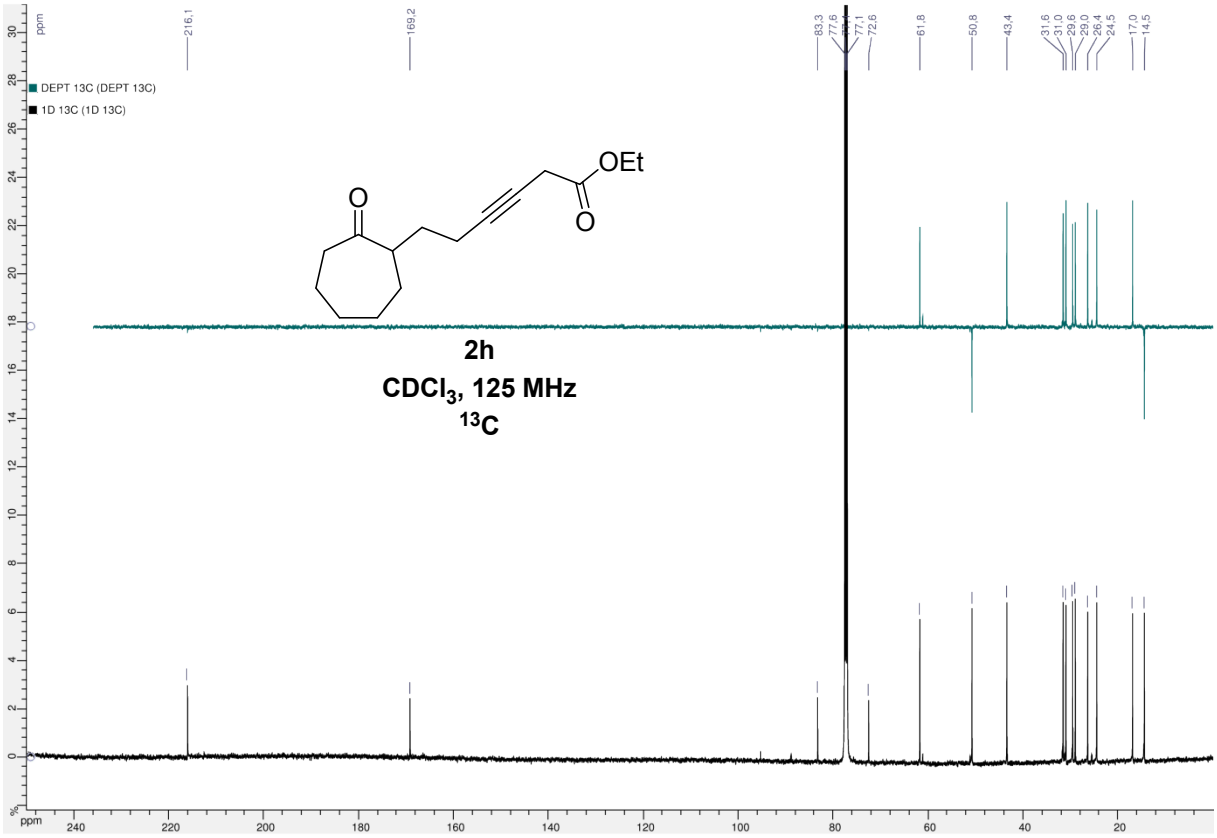

O
O
OEt
2f
CDCl3, 500 MHz
1H

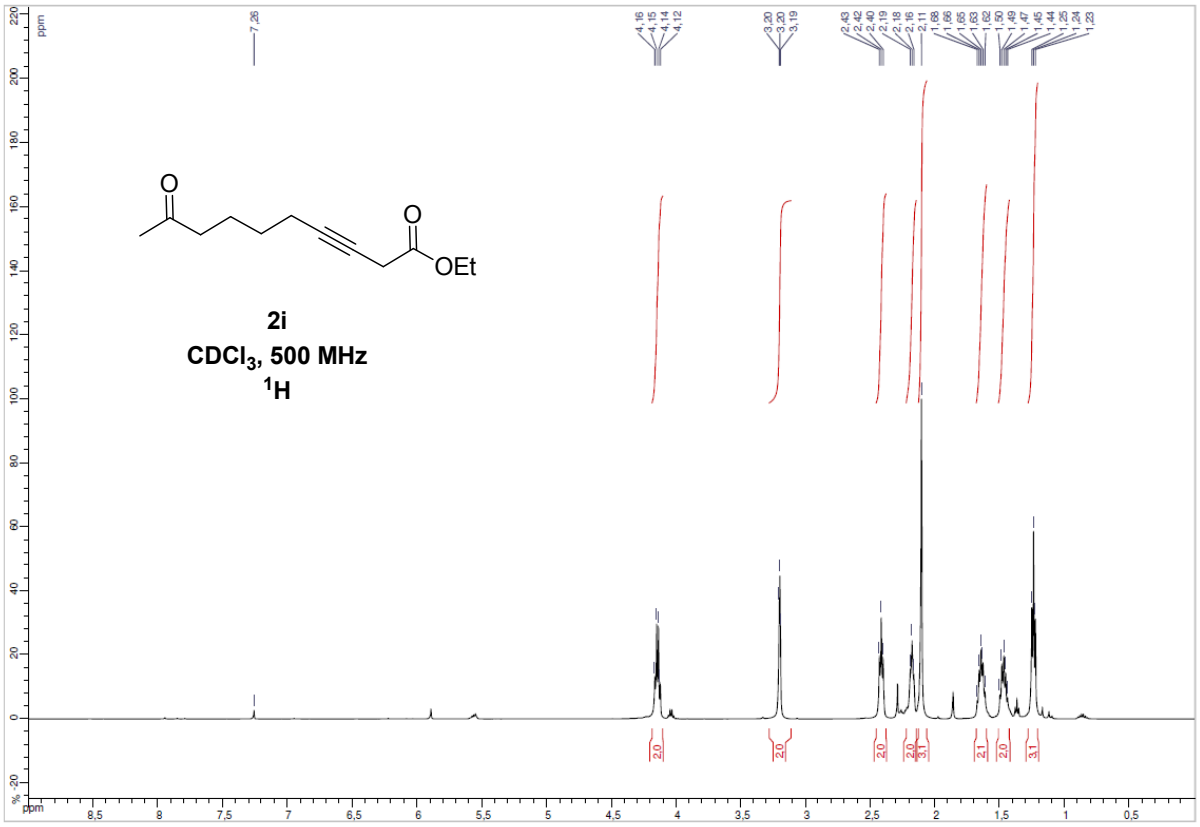

DEPT 13C (DEPT 13C)
1D 13C (1D 13C)
O
O
OEt
2f
CDCl3, 125 MHz
13C

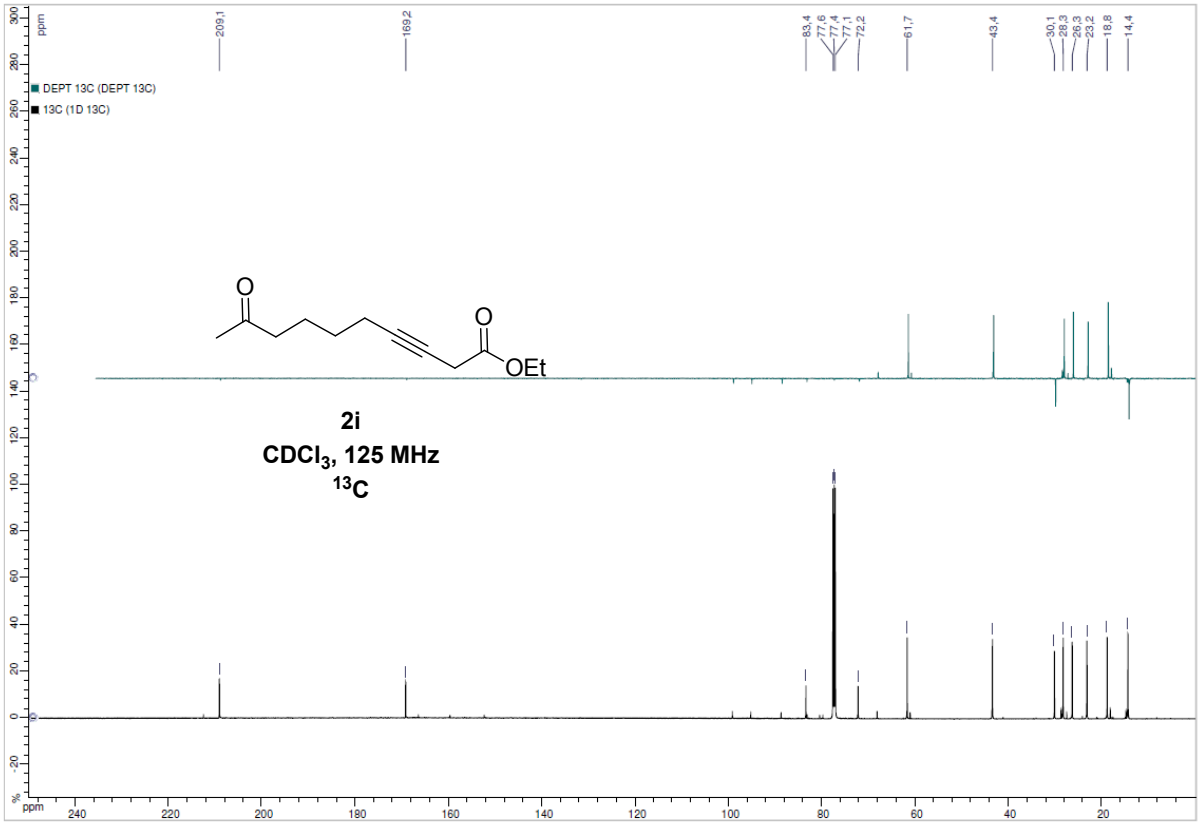

O
OEt
O
2g
CDCl3, 500 MHz
1H

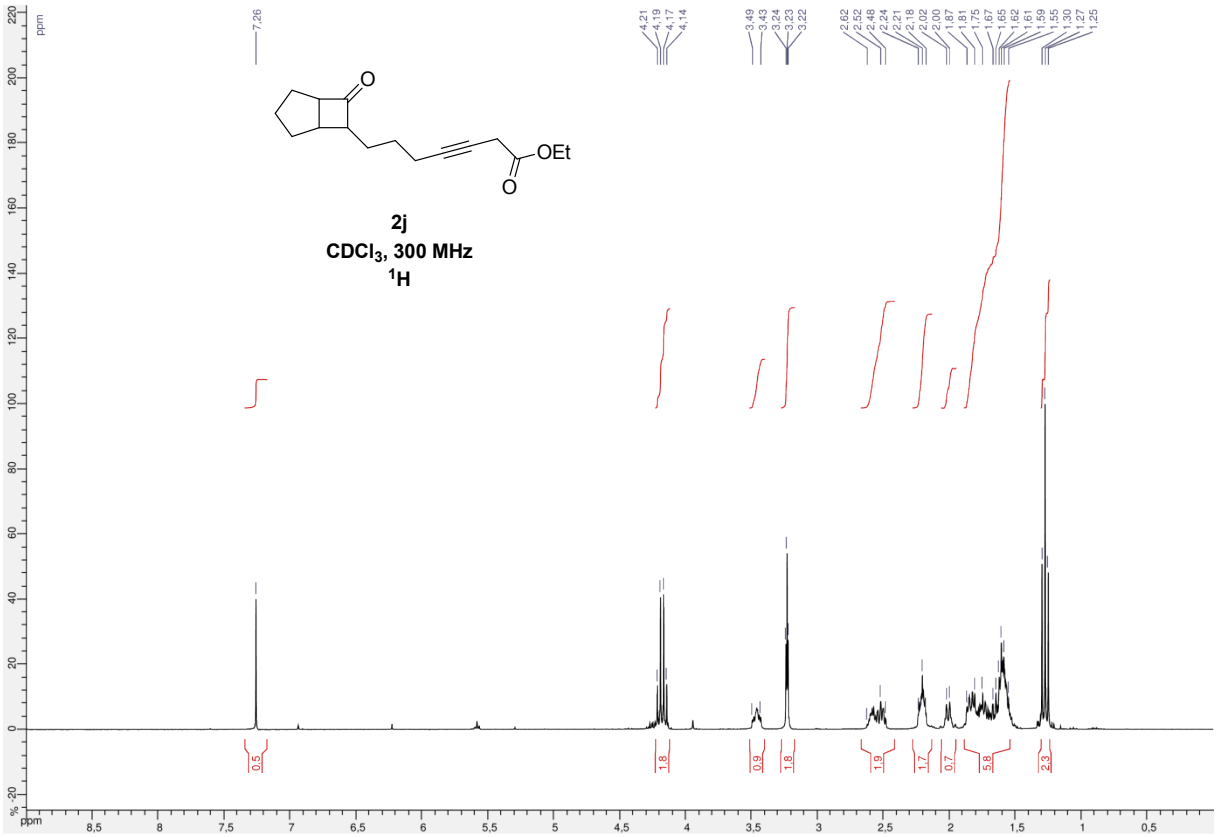

DEPT 13C (DEPT 13C)
1D 13C (1D 13C)
O
OEt
O
2g
CDCl3, 125 MHz
13C


OEt
O
O
2h
CDCl3, 500 MHz
1H

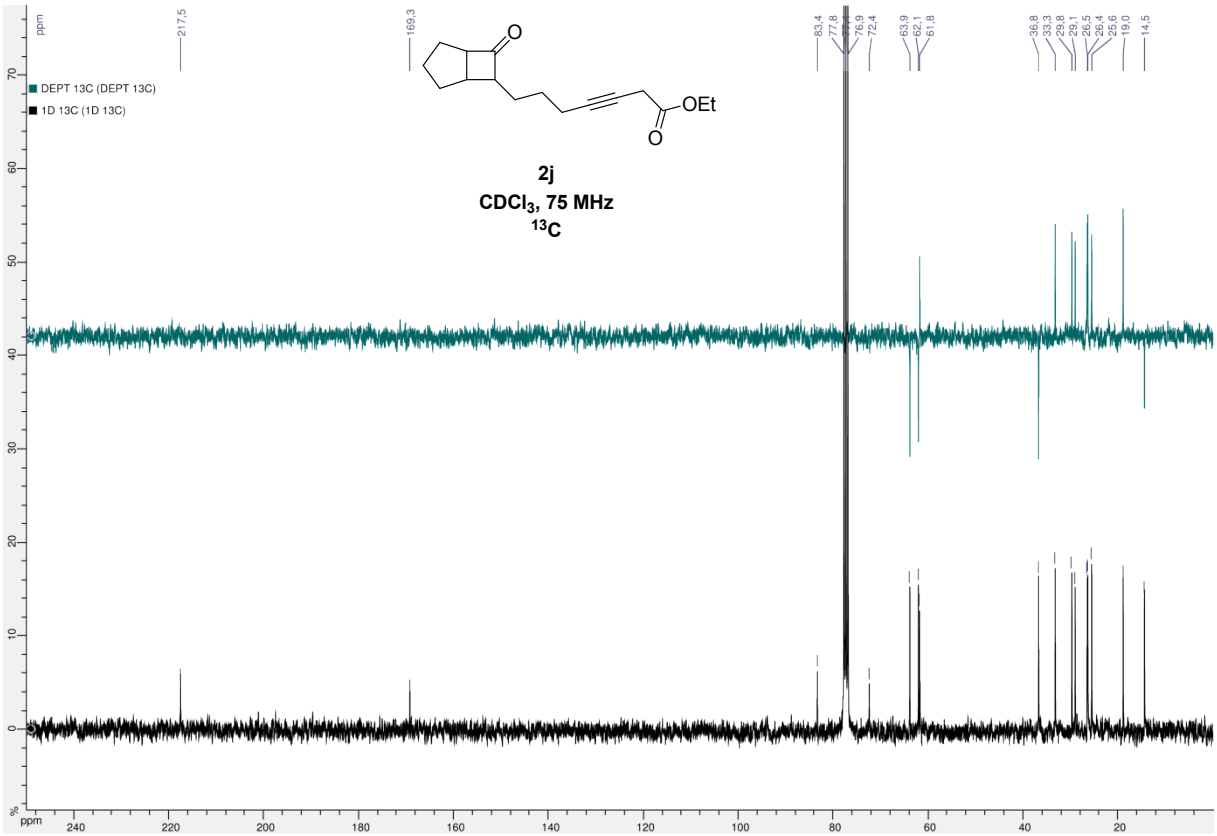

DEPT 13C (DEPT 13C)
1D 13C (1D 13C)
OEt
O
O
2h
CDCl3, 125 MHz
13C


7.26
4.16
4.15
4.14
4.12
3.20
3.20
3.19
2.43
2.42
2.40
2.19
2.18
2.16
2.11
1.66
1.65
1.63
1.62
1.50
1.49
1.47
1.45
1.44
1.25
1.24
1.23
O
O
OEt
2i
CDCl3, 500 MHz
1H
2.0
2.0
2.0
2.0
3.1
2.1
2.0
3.1

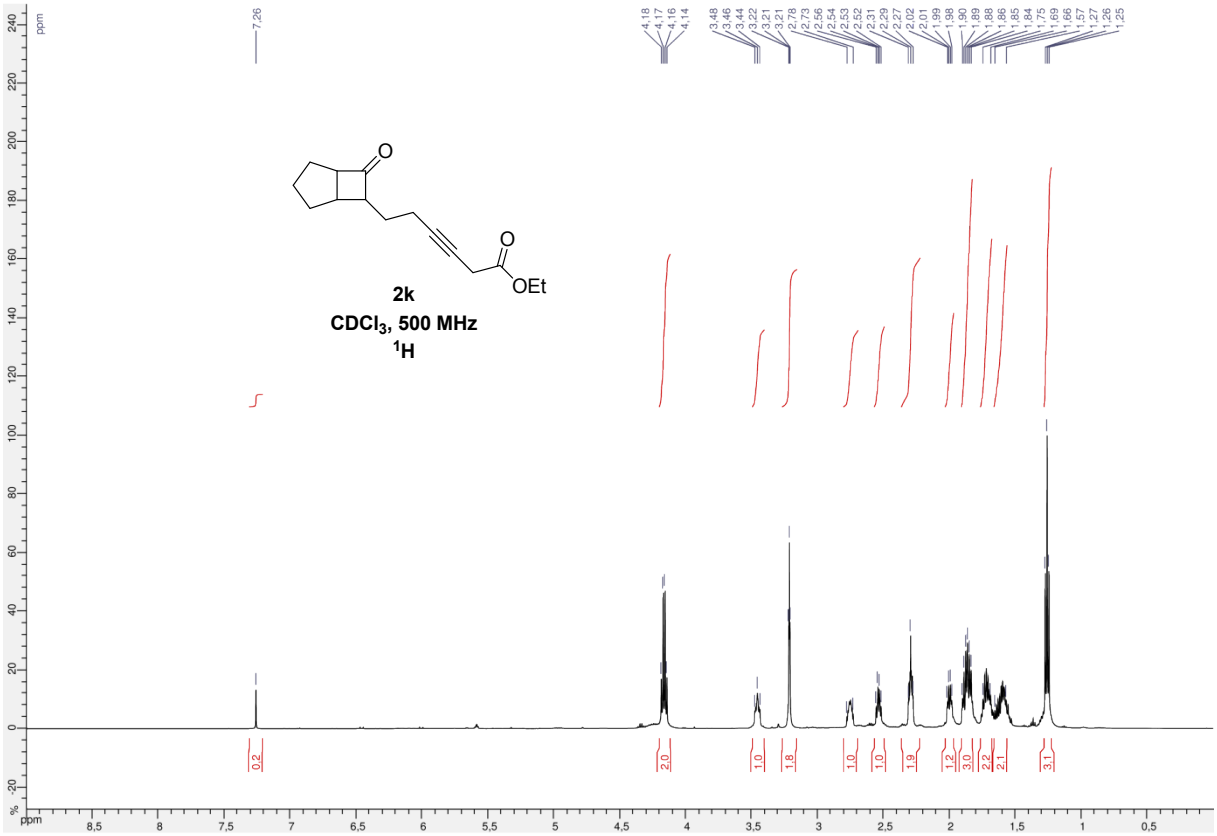

209.1
169.2
83.4
77.6
77.4
77.1
72.2
61.7
43.4
30.1
28.3
26.3
23.2
18.8
14.4
DEPT 13C (DEPT 13C)
13C (1D 13C)
O
O
OEt
2i
CDCl3, 125 MHz
13C

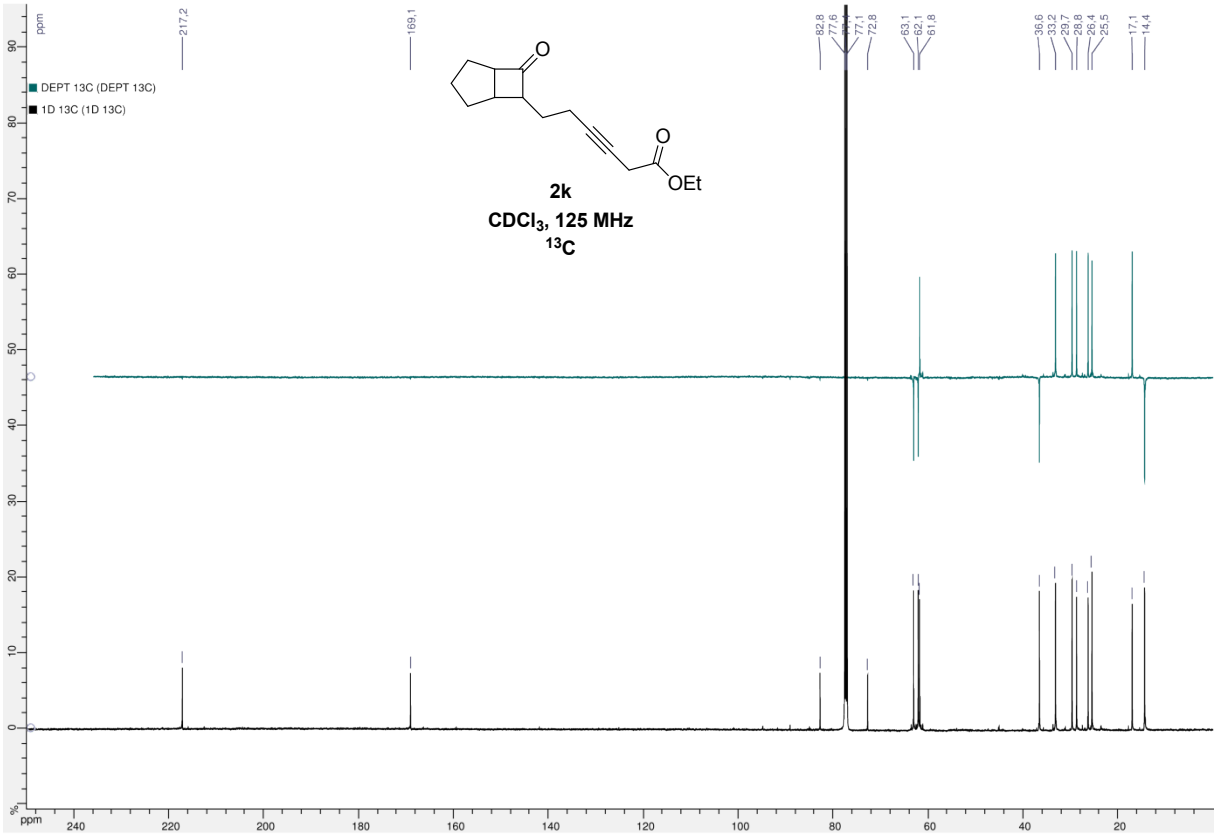


2j
$CDCl_3$, 300 MHz
^1H

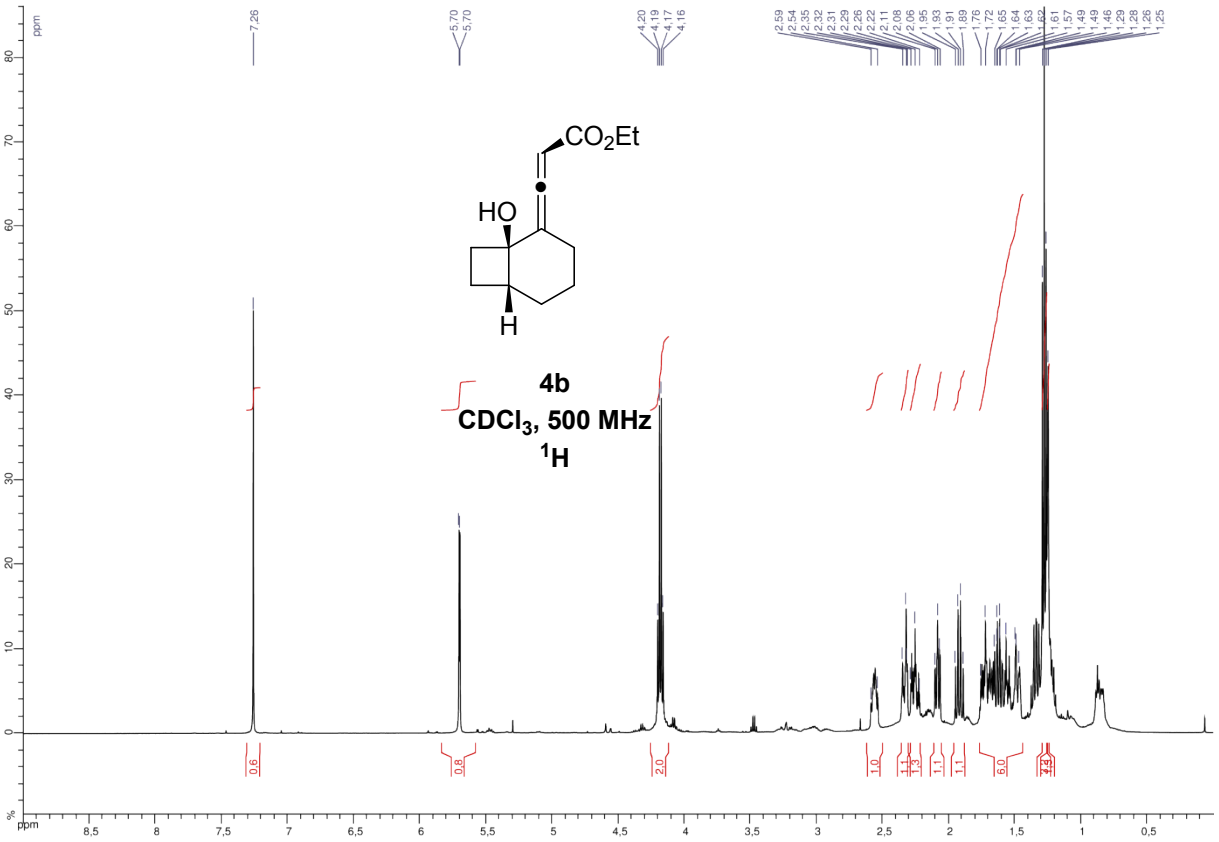


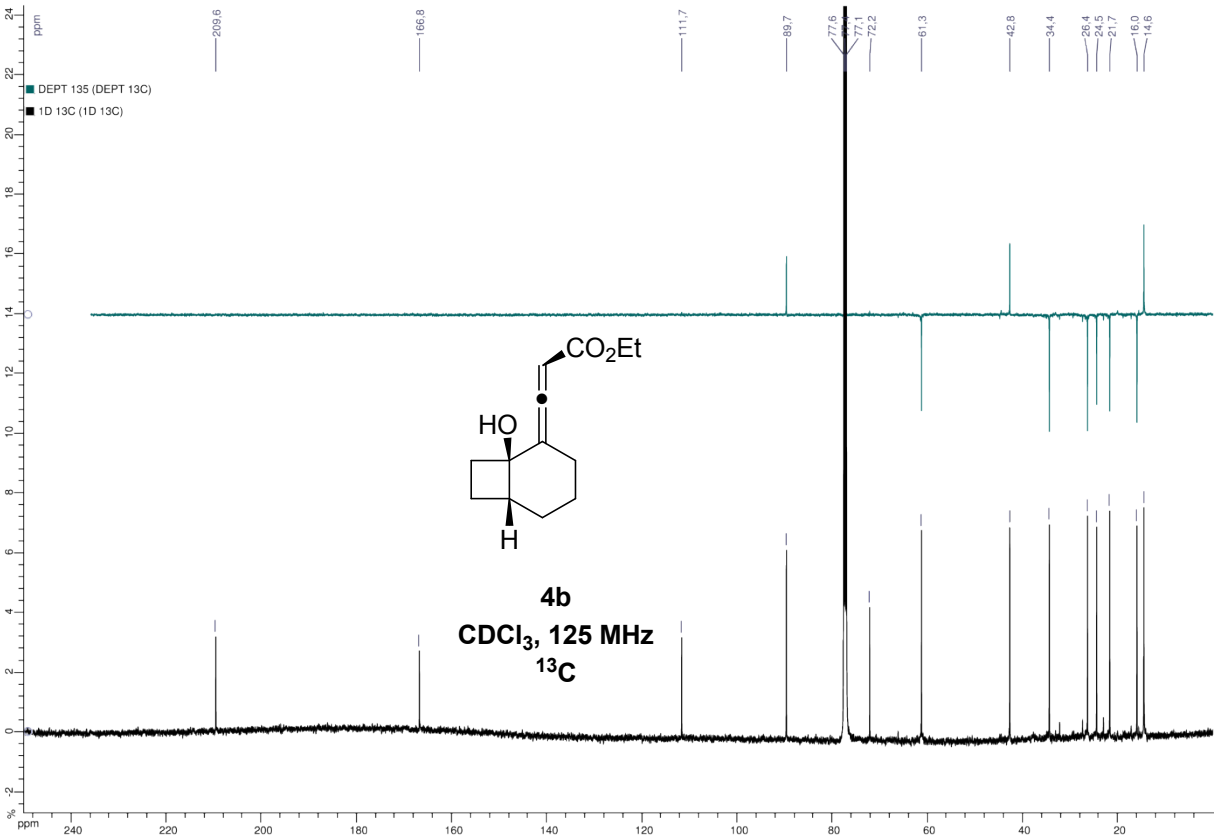
2j
$CDCl_3$, 75 MHz
^{13}C

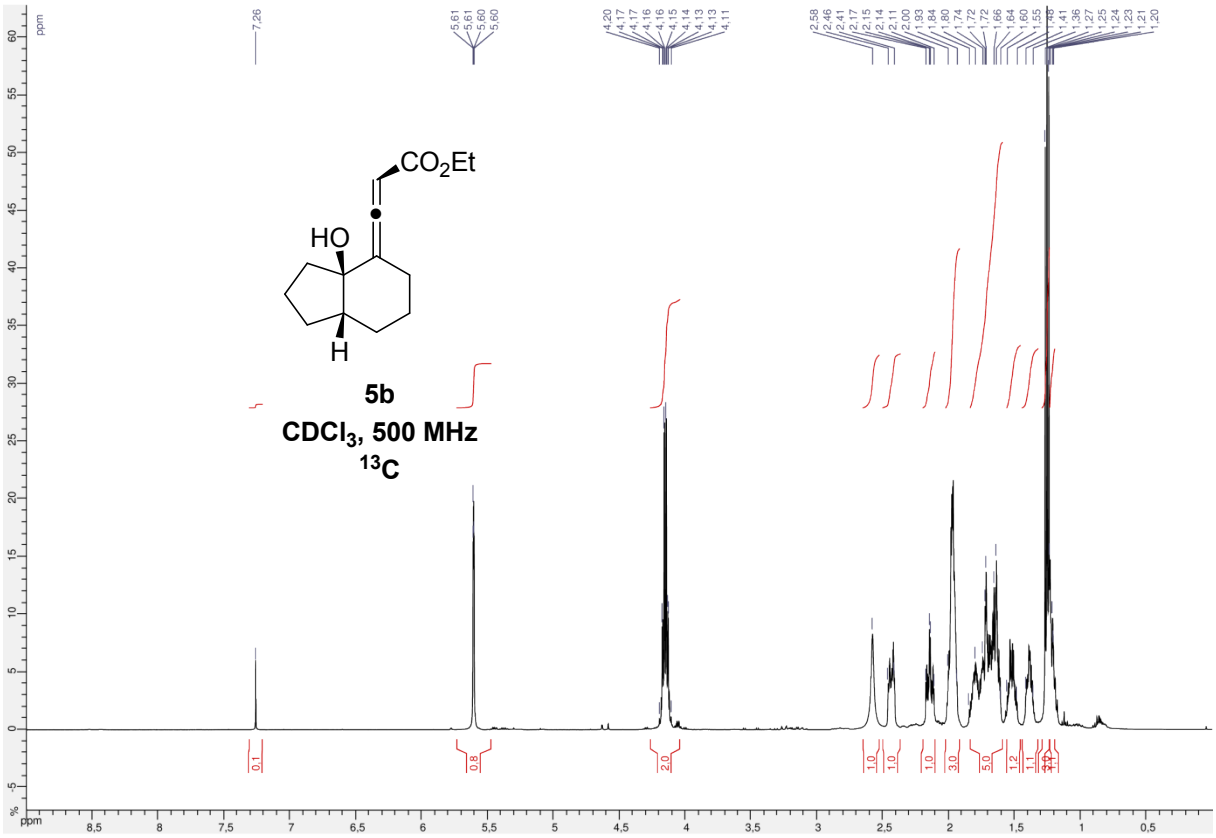

7.26
4.18
4.17
4.16
4.14
3.48
3.46
3.44
3.22
3.21
3.21
2.78
2.73
2.56
2.54
2.53
2.52
2.31
2.29
2.27
2.02
2.01
1.99
1.98
1.90
1.89
1.88
1.86
1.85
1.84
1.75
1.69
1.66
1.57
1.27
1.26
1.25
O
O
OEt
2k
CDCl3, 500 MHz
1H
0.2
2.0
1.0
1.8
1.0
1.0
1.9
1.2
3.0
2.2
2.1
3.1
ppm

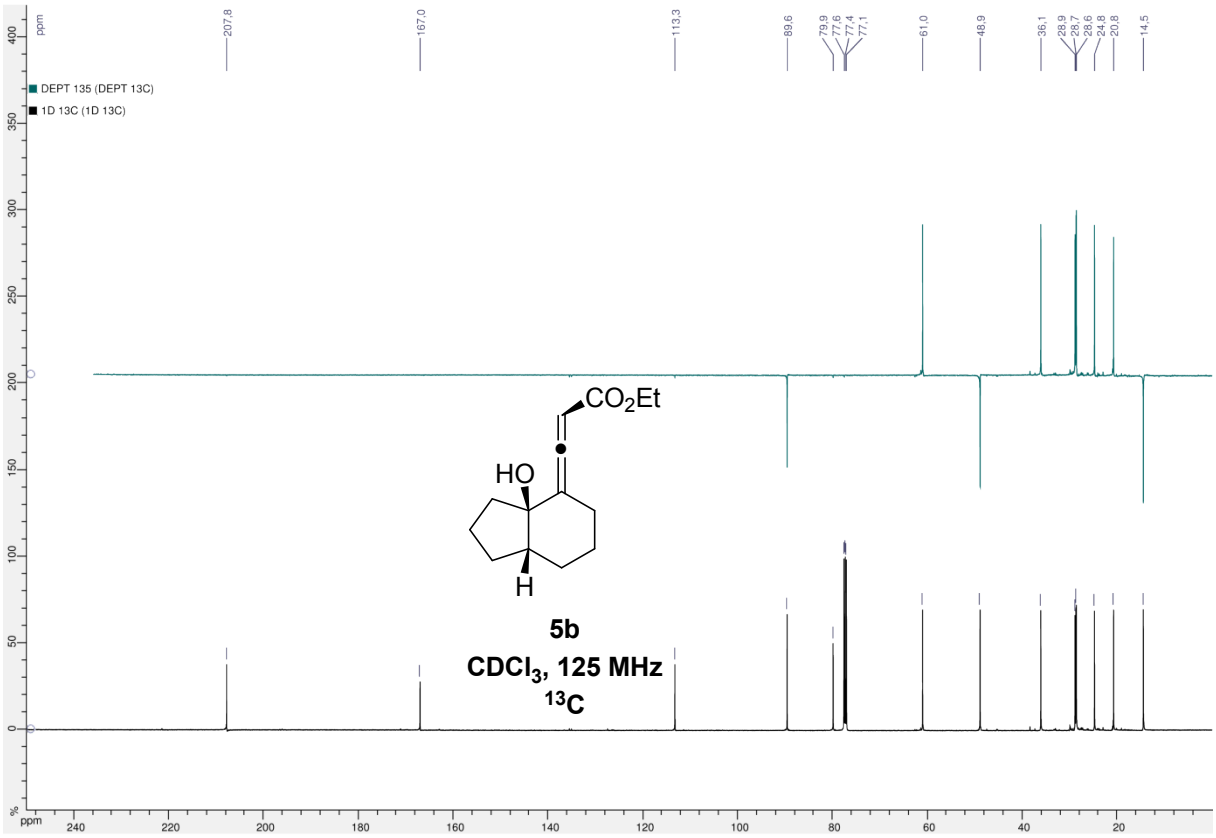

217.2
169.1
82.8
77.6
77.4
77.1
72.8
63.1
62.1
61.8
36.6
33.2
29.7
28.8
26.4
25.5
17.1
14.4
DEPT 13C (DEPT 13C)
1D 13C (1D 13C)
O
O
OEt
2k
CDCl3, 125 MHz
13C
ppm

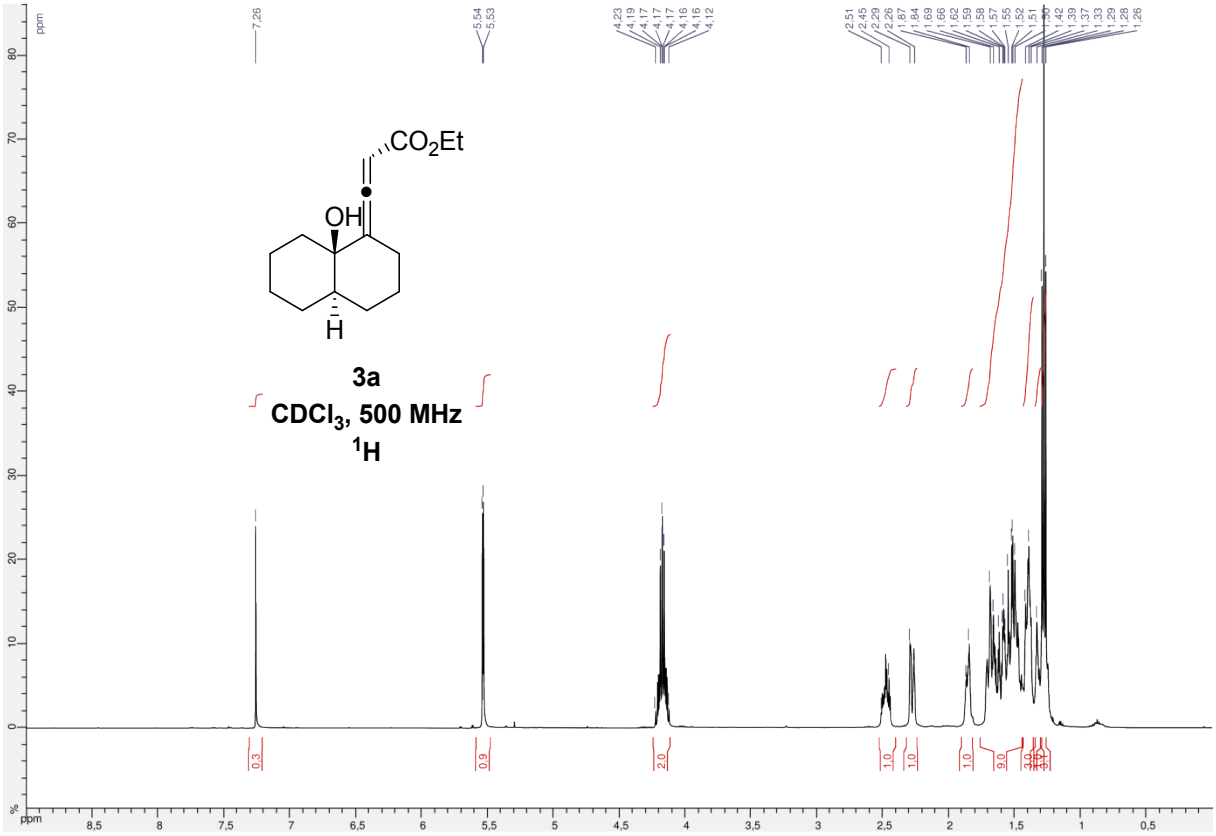
H and ^{13}C spectra for Polycyclic Allenoates 3 to 13

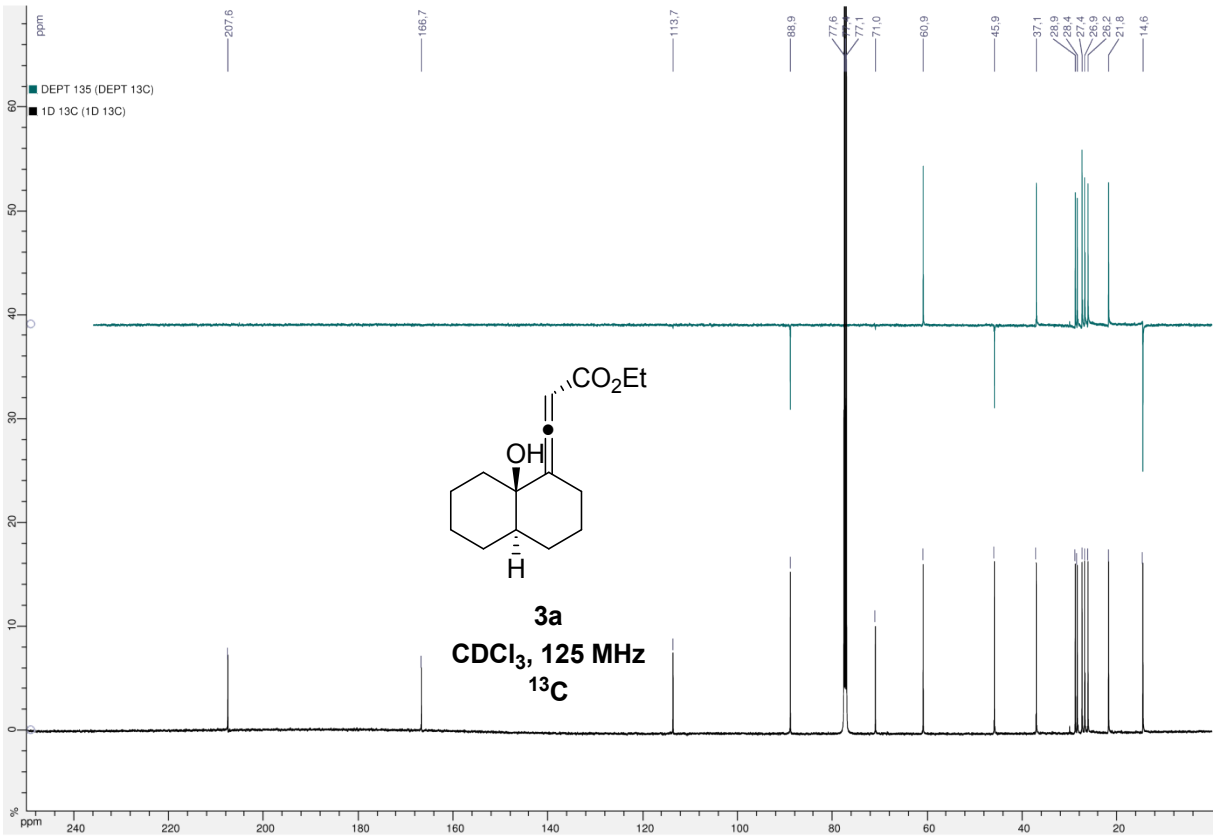


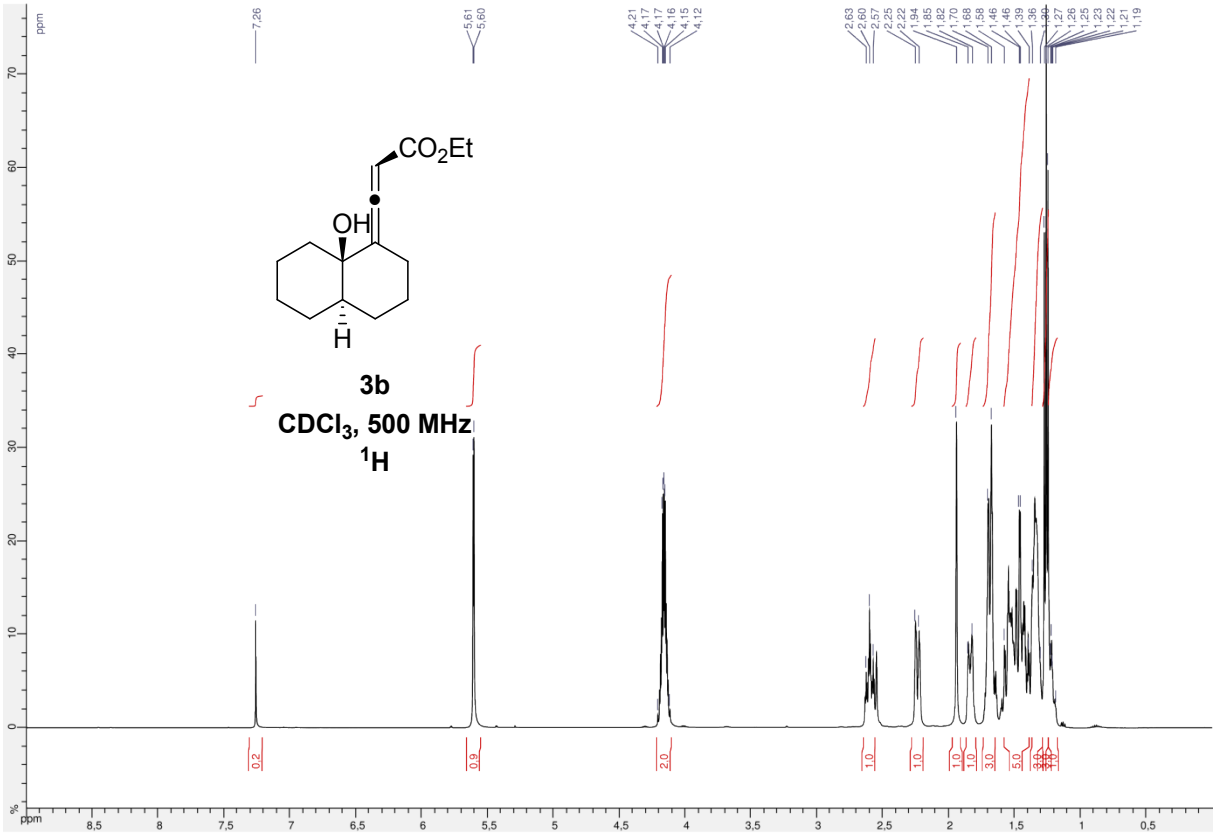


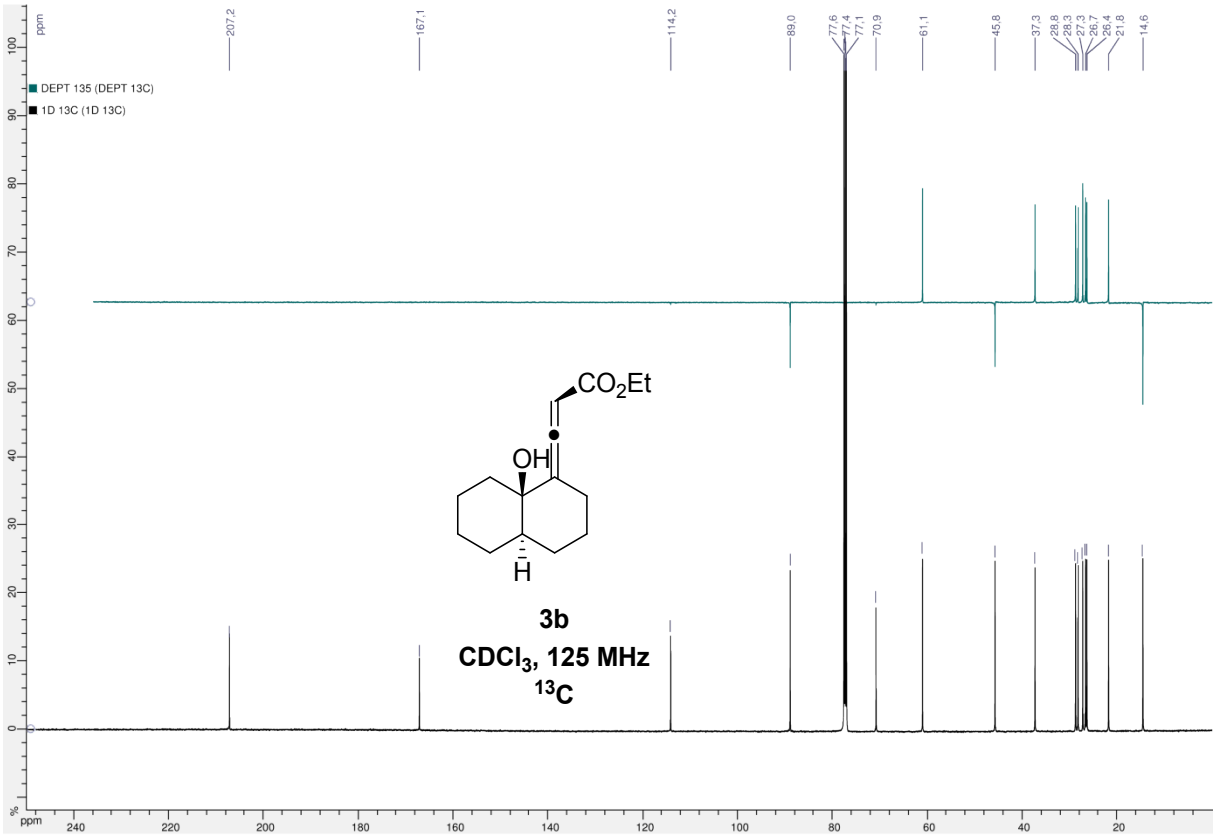

CO2Et
HO
H
5b
CDCl3, 500 MHz
13C

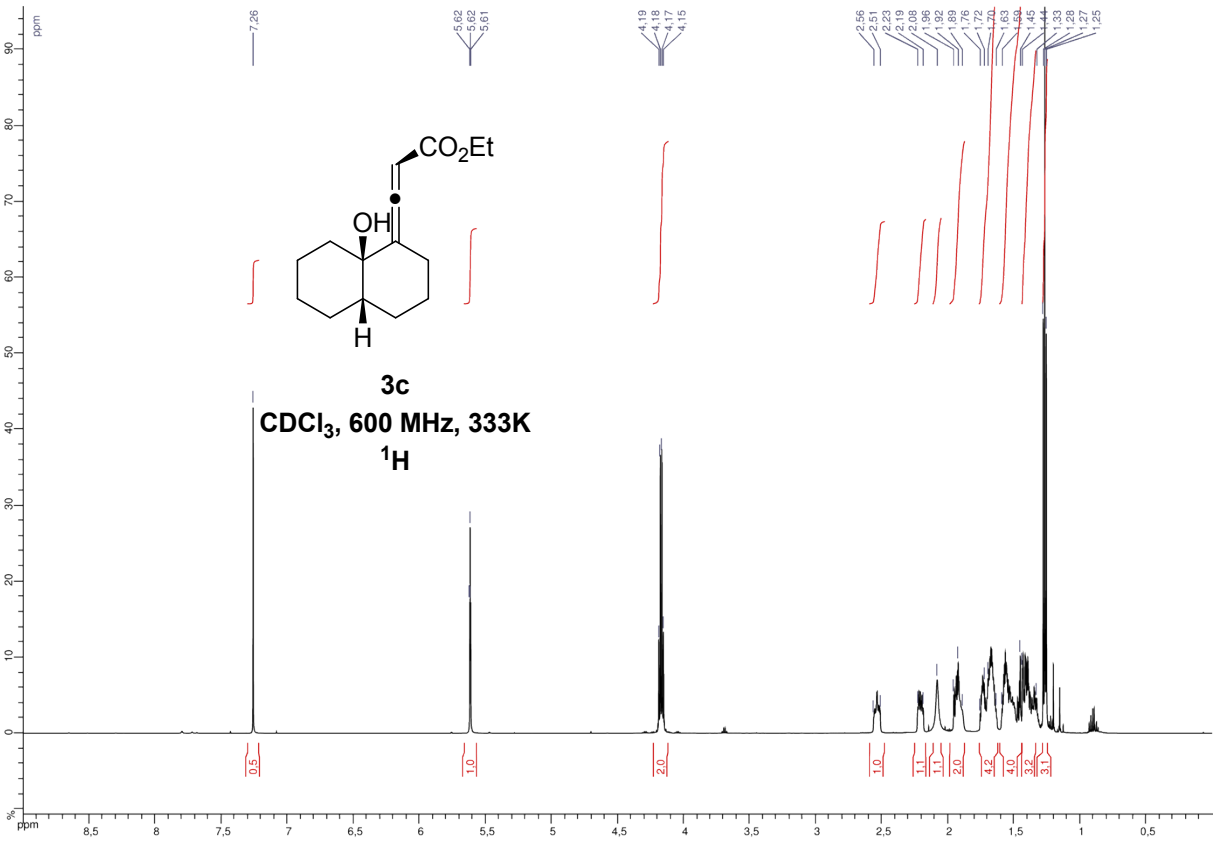

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
HO
H
5b
CDCl3, 125 MHz
13C

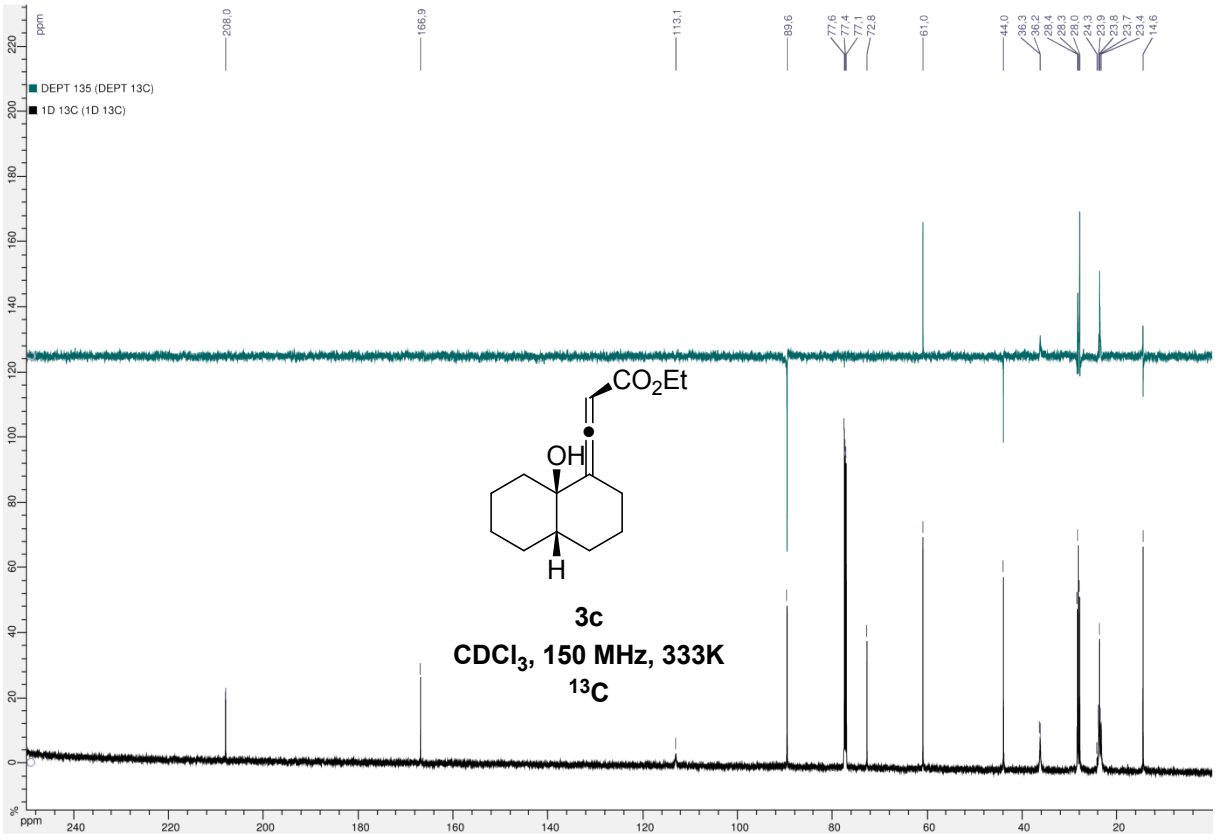

CO2Et
OH
H
3a
CDCl3, 500 MHz
1H

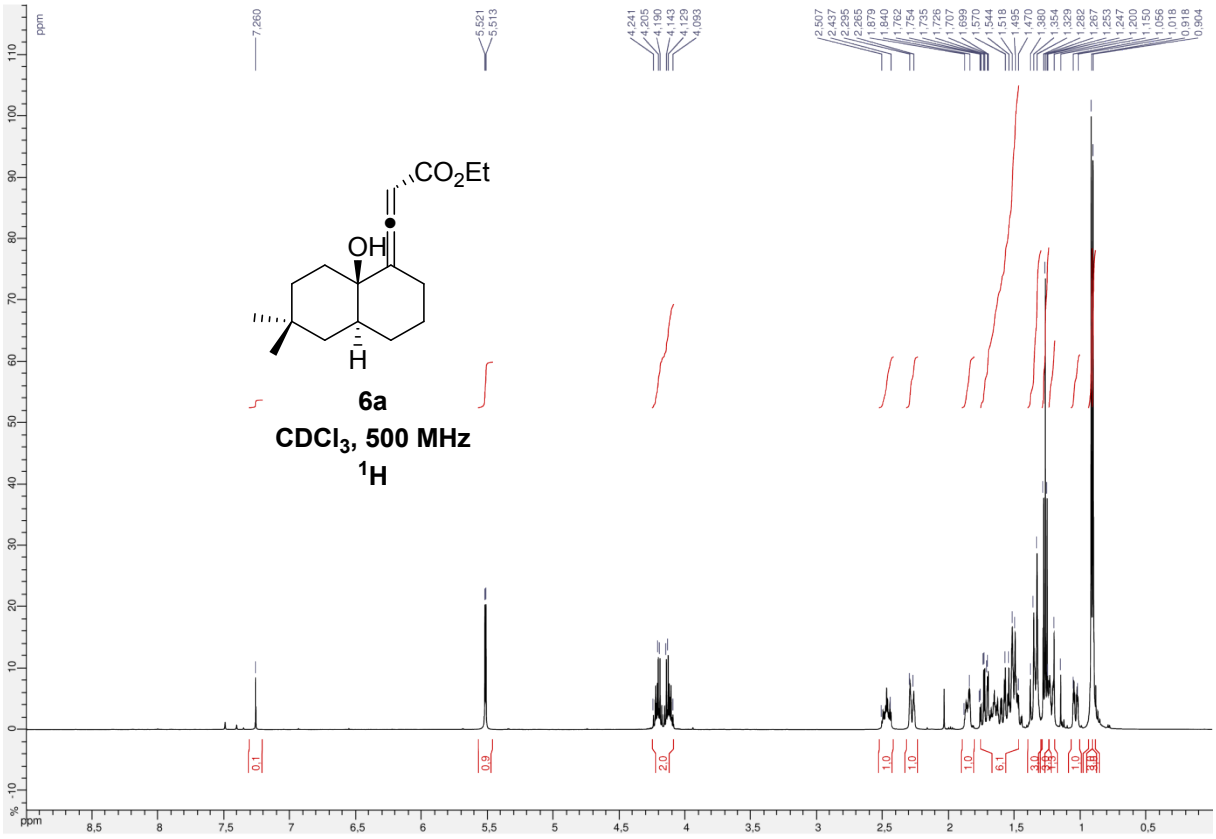

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
3a
CDCl3, 125 MHz
13C

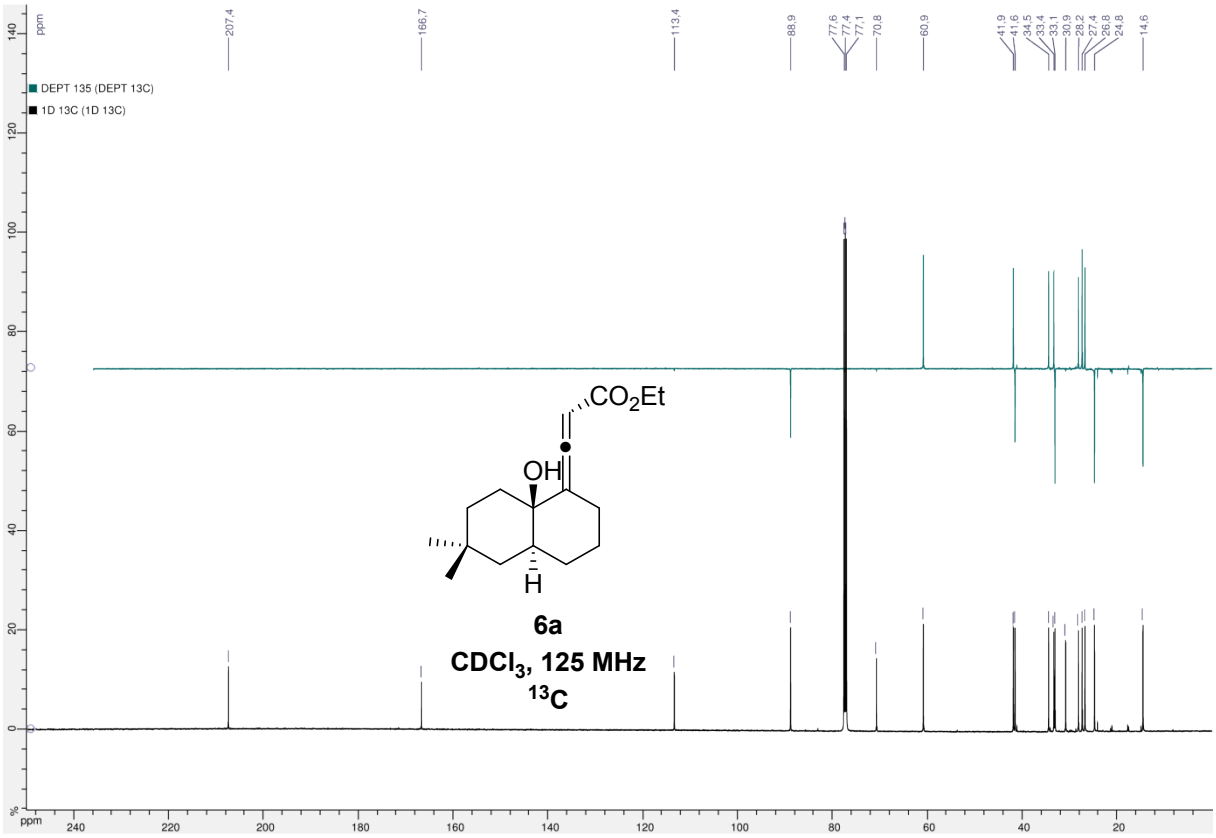

CO2Et
OH
H
3b
CDCl3, 500 MHz
1H

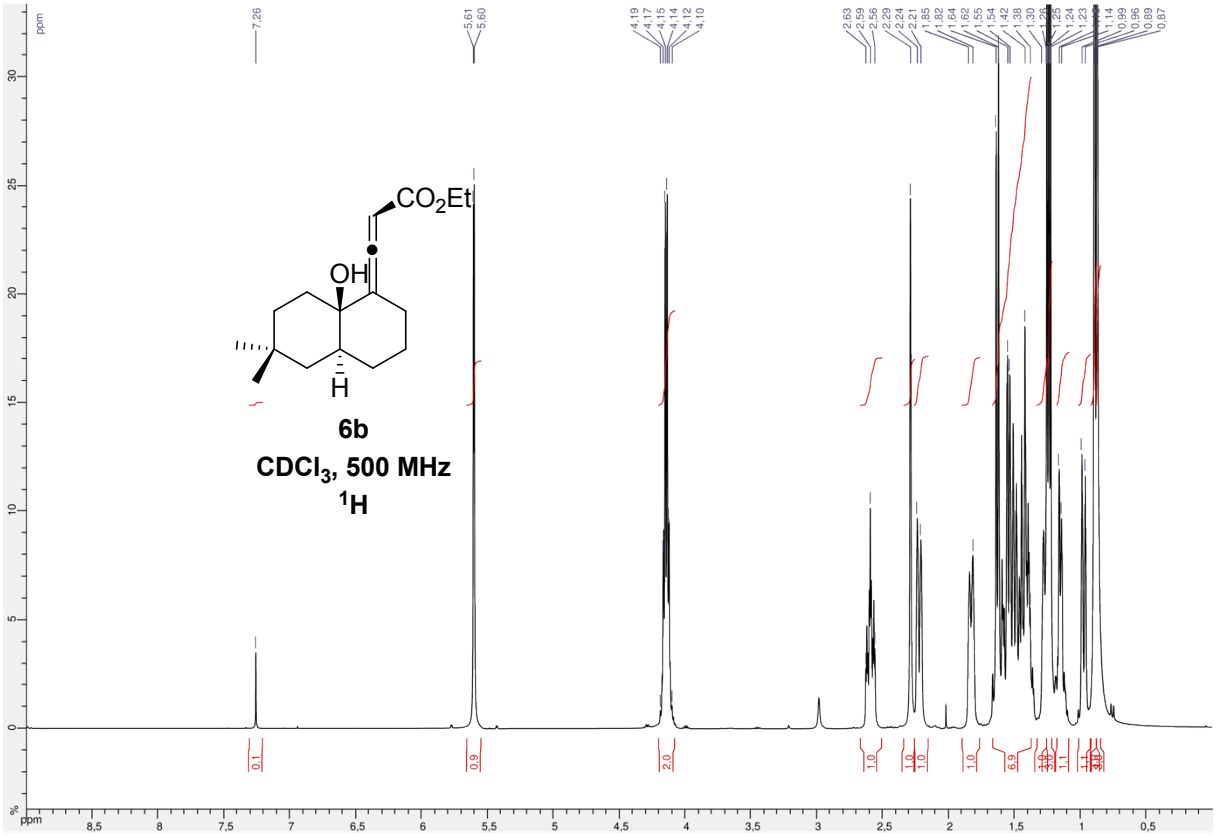

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
3b
CDCl3, 125 MHz
13C

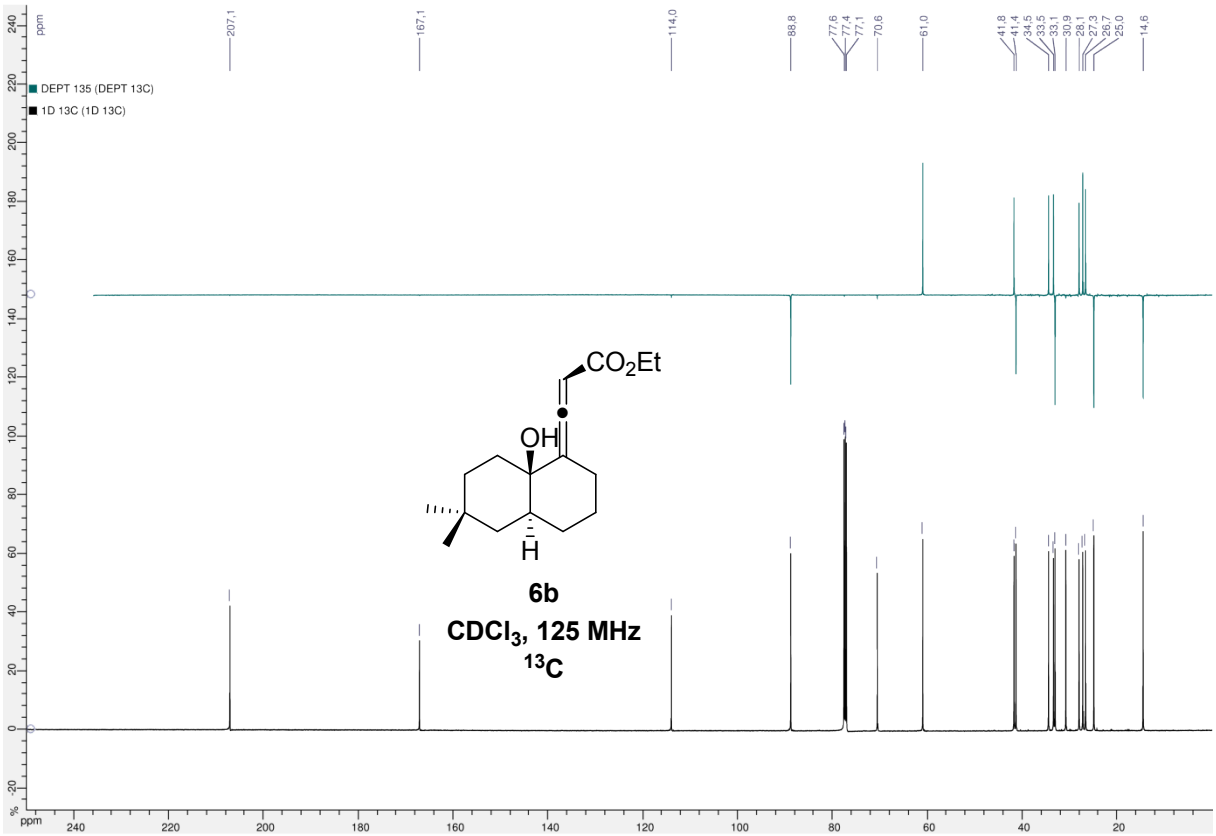

CO2Et
OH
H
3c
CDCl3, 600 MHz, 333K
1H

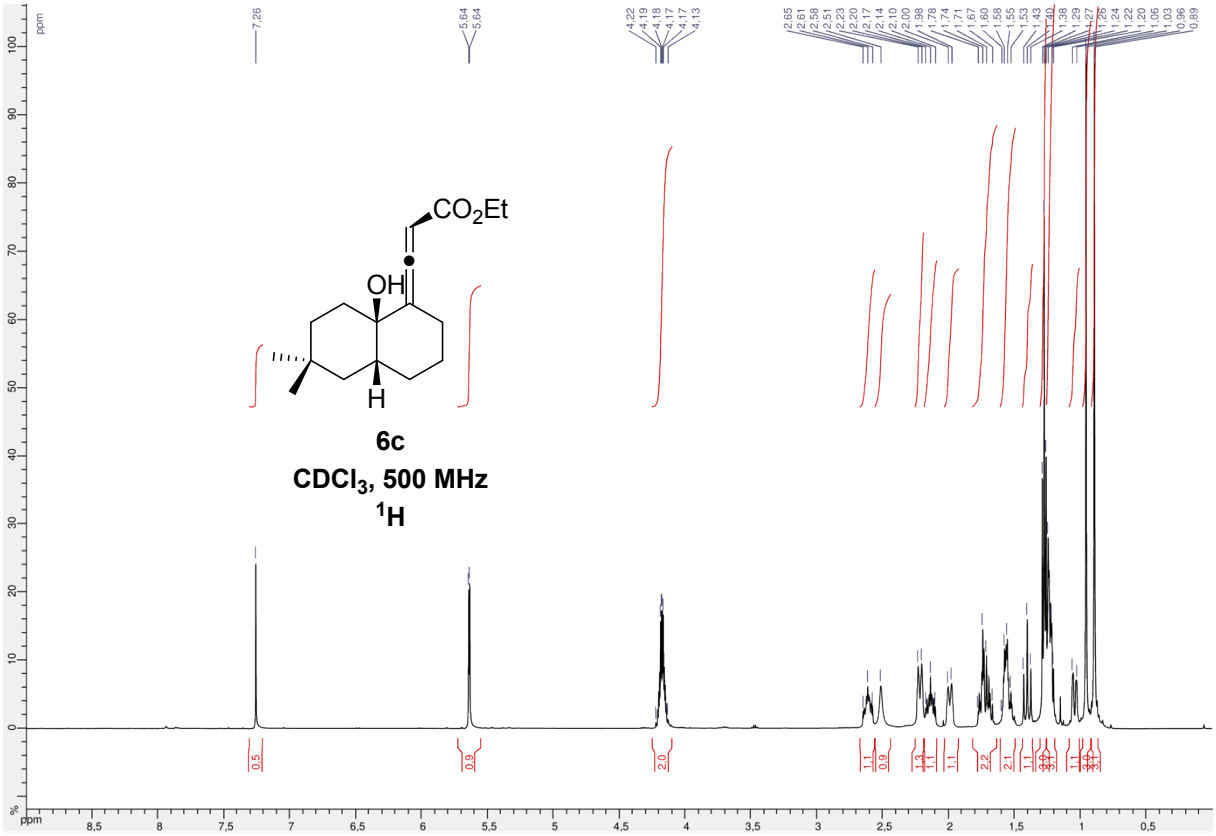

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
3c
CDCl3, 150 MHz, 333K
13C

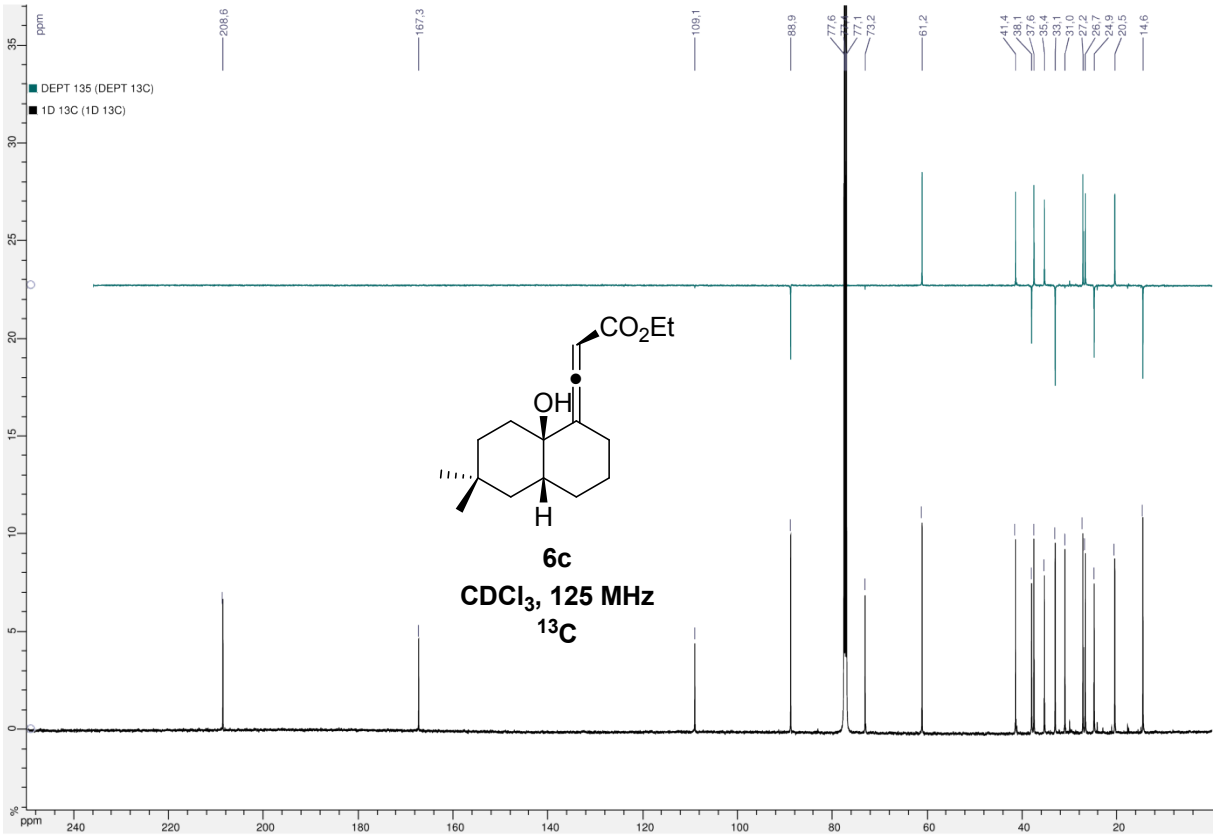

CO2Et
OH
H
6a
CDCl3, 500 MHz
1H

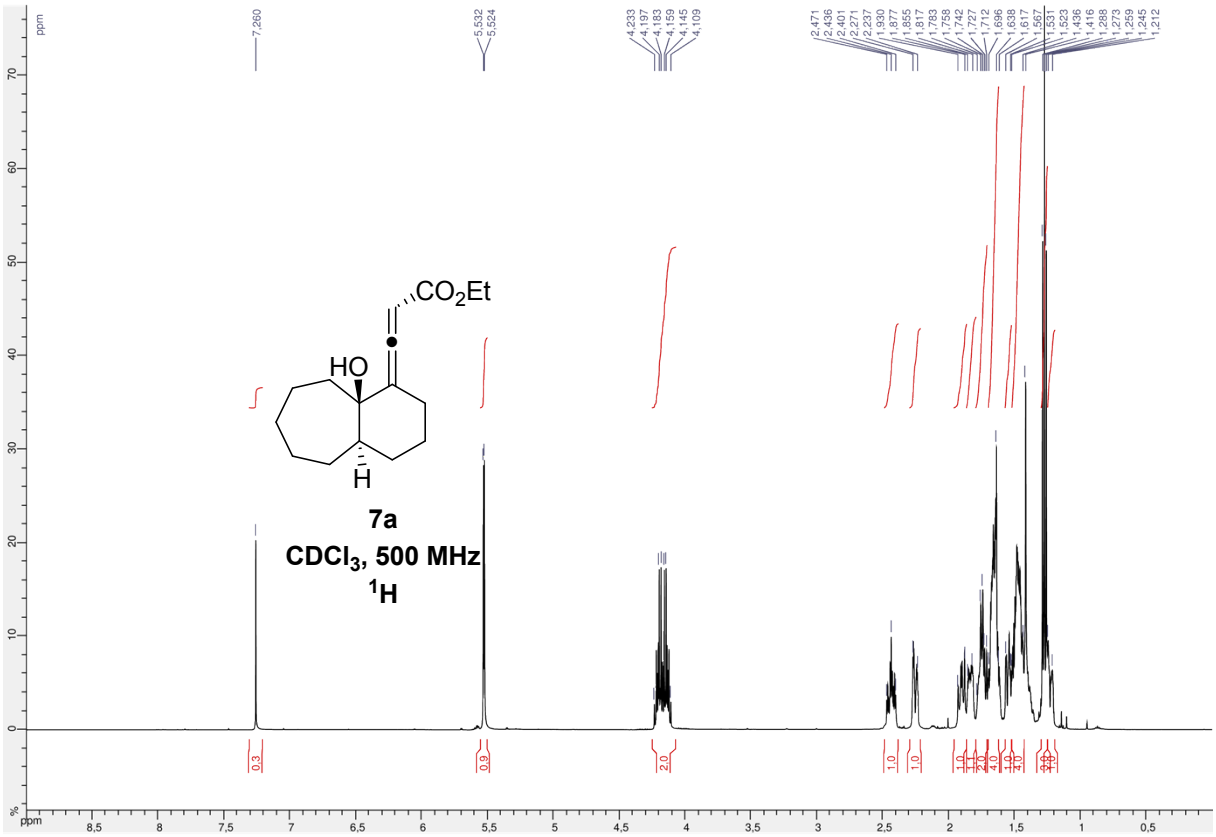

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
6a
CDCl3, 125 MHz
13C

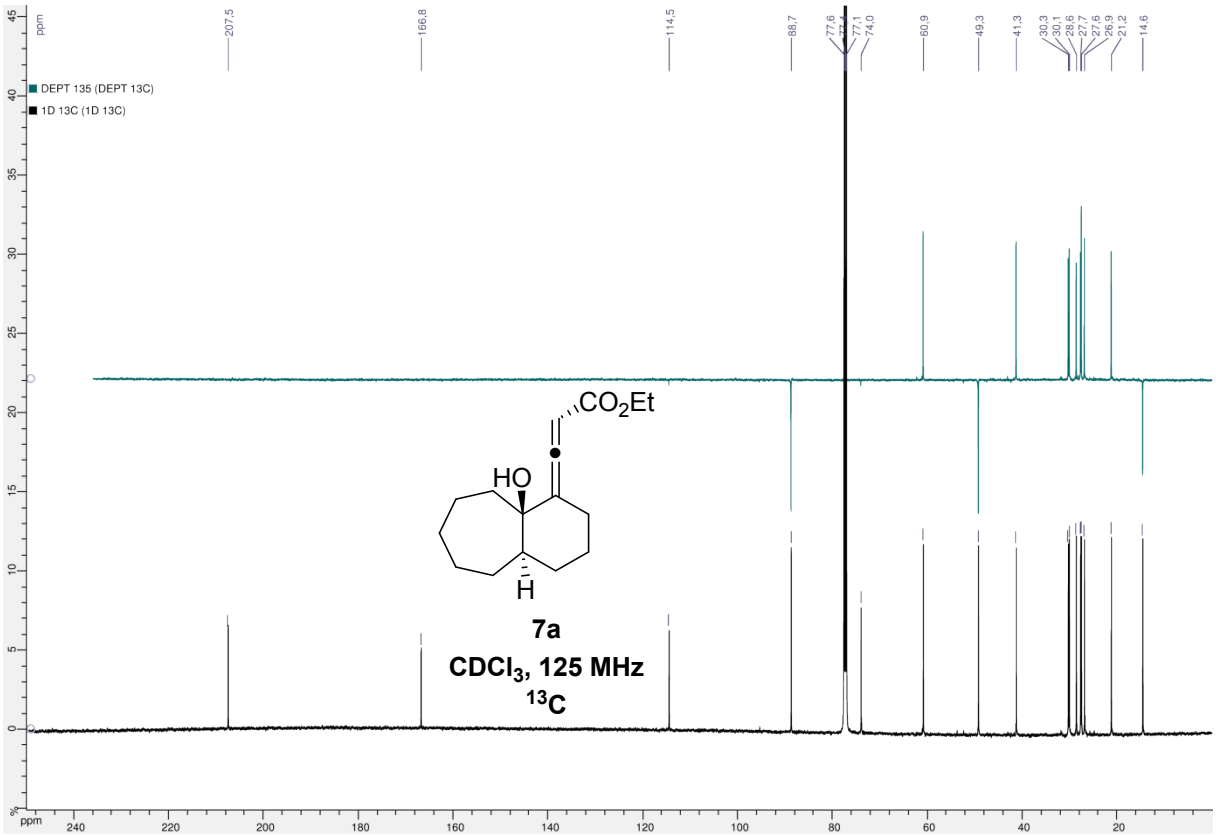

CO2Et
OH
H
6b
CDCl3, 500 MHz
1H

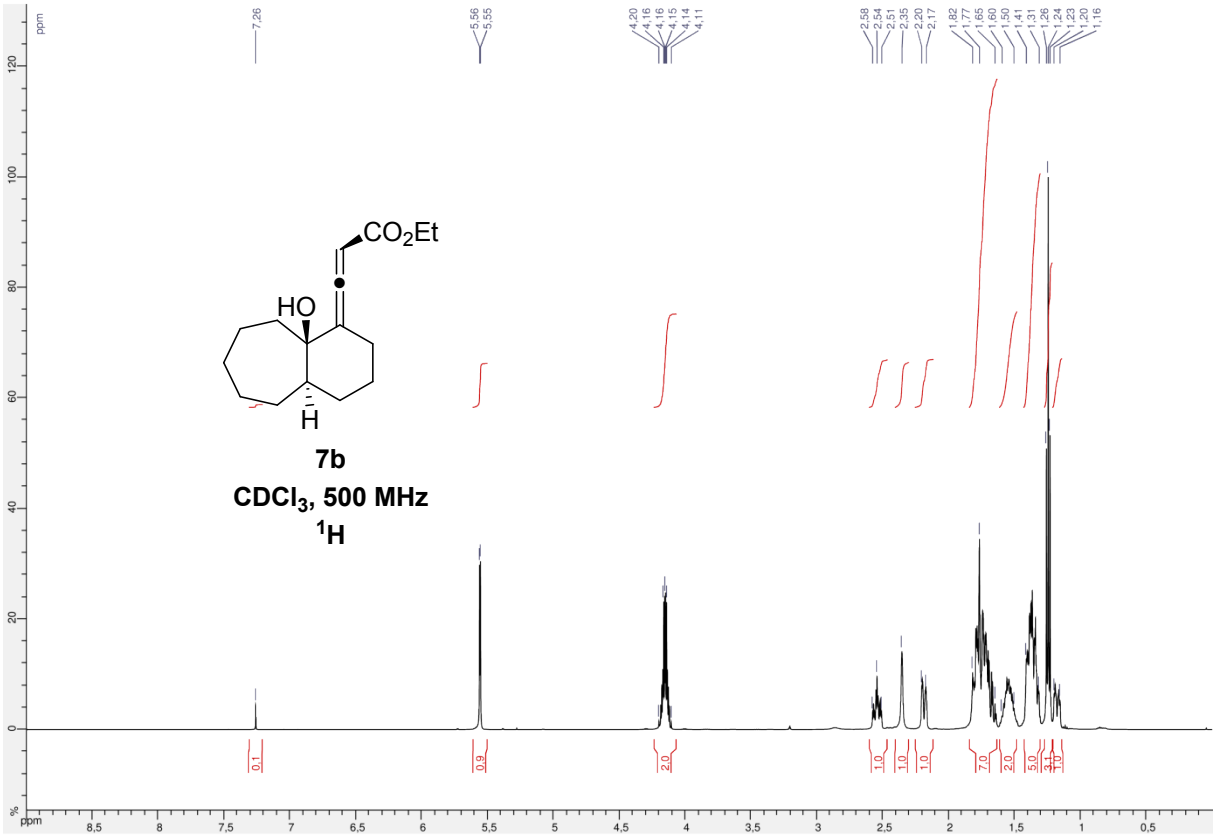

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
6b
CDCl3, 125 MHz
13C

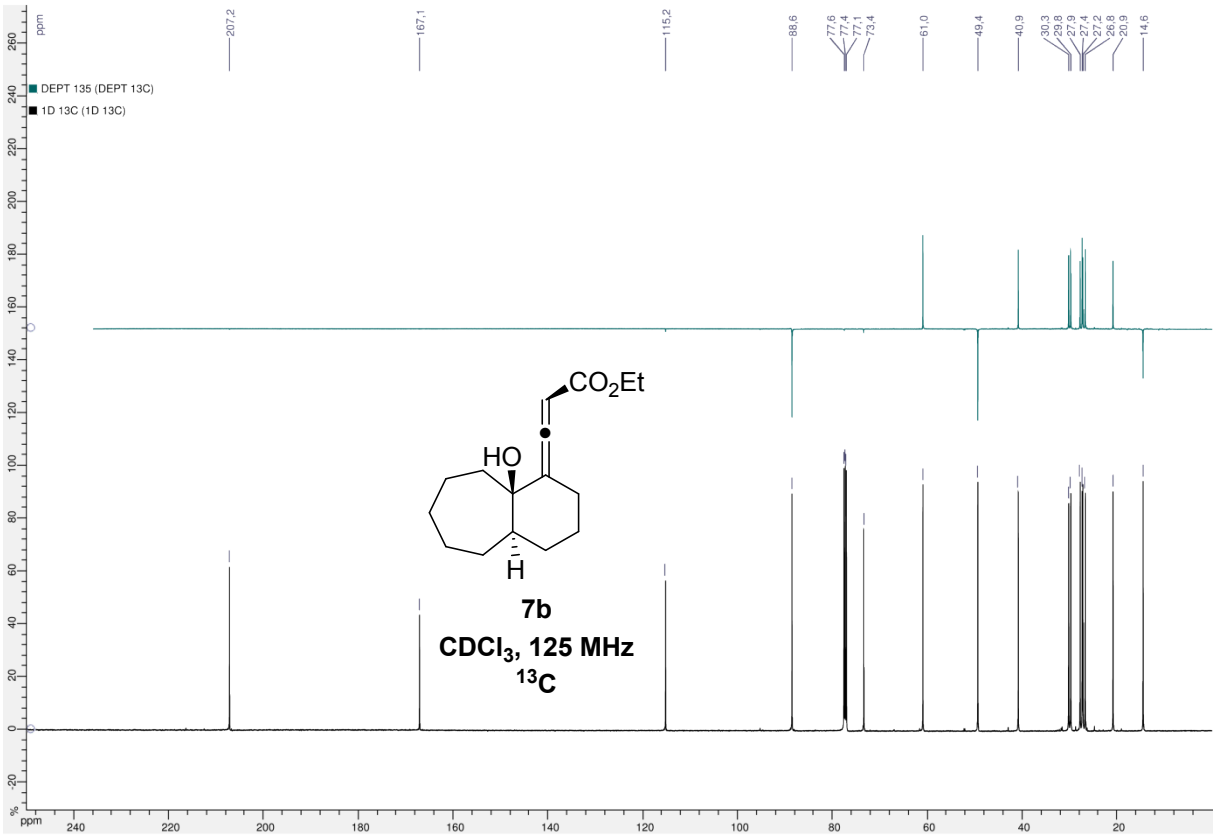

CO2Et
OH
H
6c
CDCl3, 500 MHz
1H

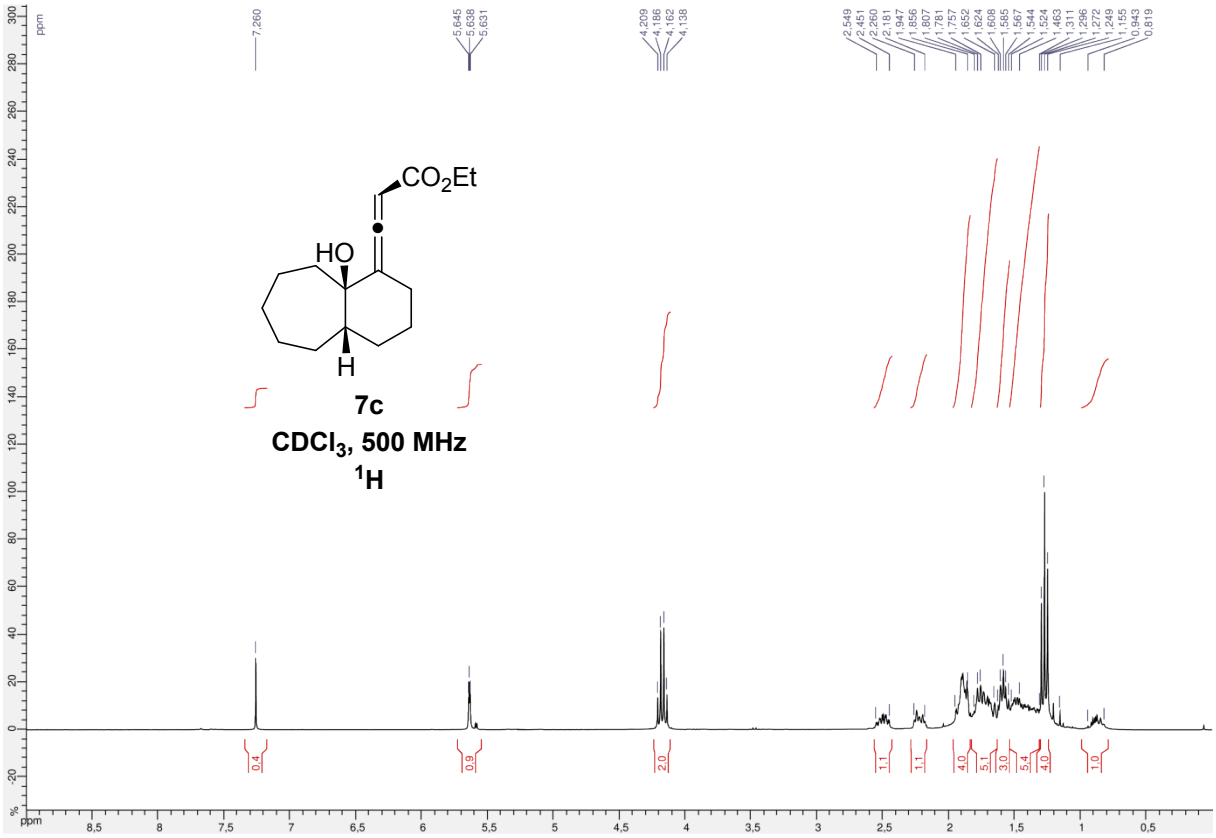

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
6c
CDCl3, 125 MHz
13C

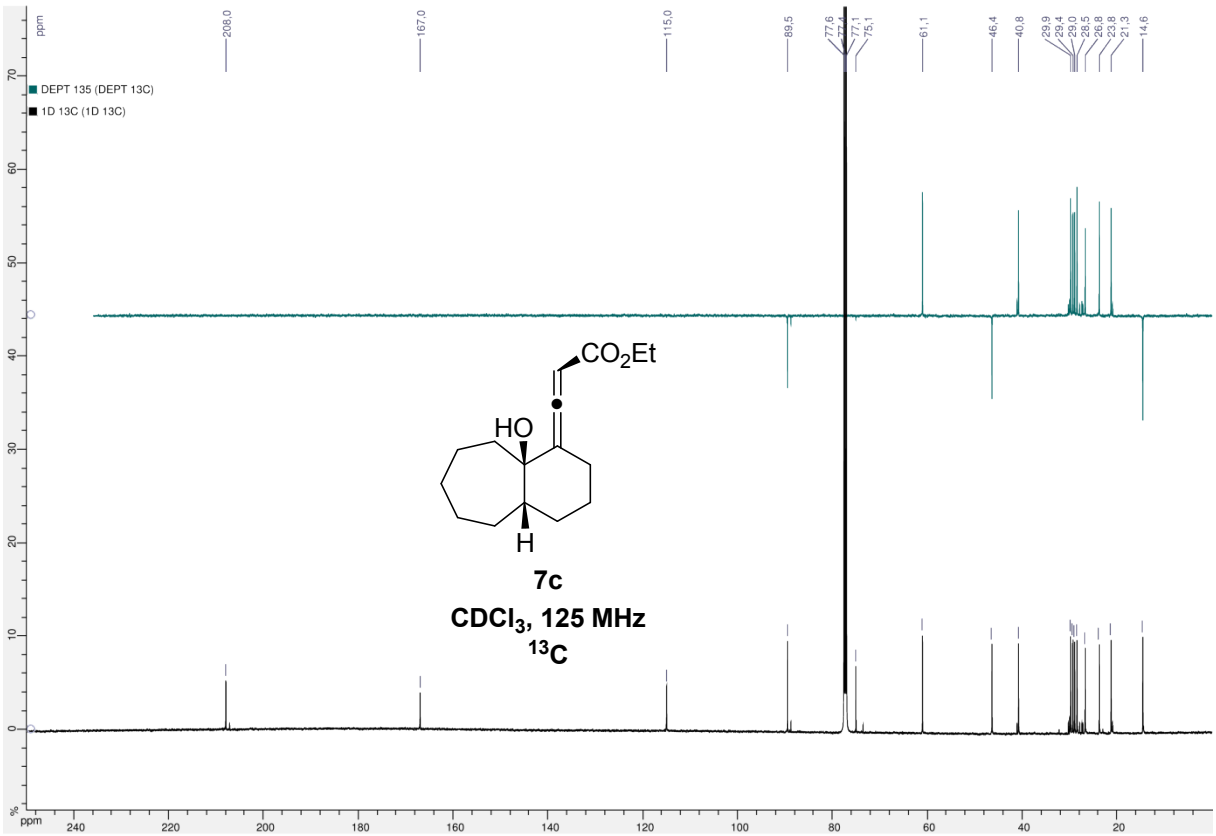

7,260
5,532
5,524
4,233
4,197
4,183
4,159
4,145
4,109
2,471
2,436
2,401
2,271
2,237
1,930
1,877
1,855
1,817
1,783
1,758
1,742
1,722
1,712
1,698
1,638
1,617
1,567
1,531
1,523
1,436
1,416
1,288
1,273
1,259
1,245
1,212
ppm
CO2Et
HO
H
7a
CDCl3, 500 MHz
1H

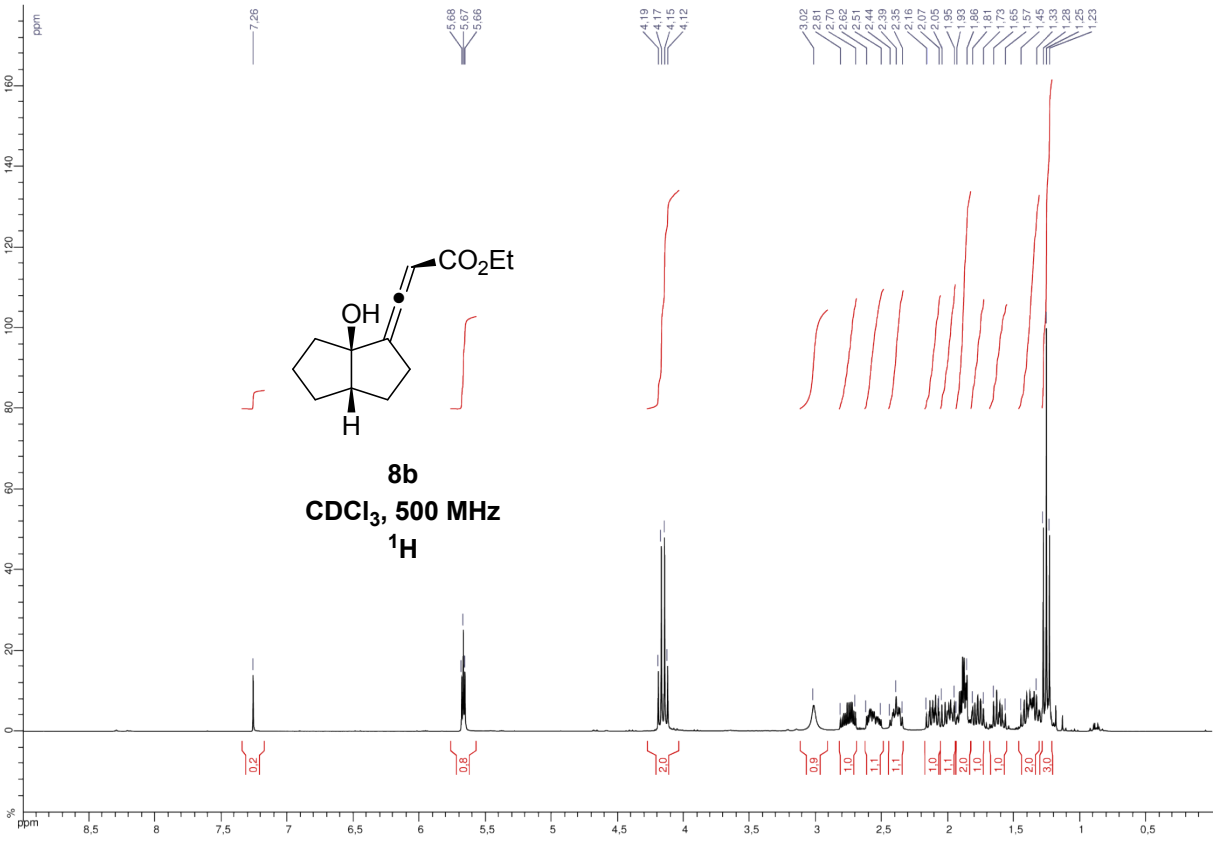

ppm
DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
207,5
166,8
114,5
88,7
77,6
77,4
77,1
74,0
60,9
49,3
41,3
30,3
30,1
28,6
27,7
27,6
26,9
21,2
14,6
CO2Et
HO
H
7a
CDCl3, 125 MHz
13C

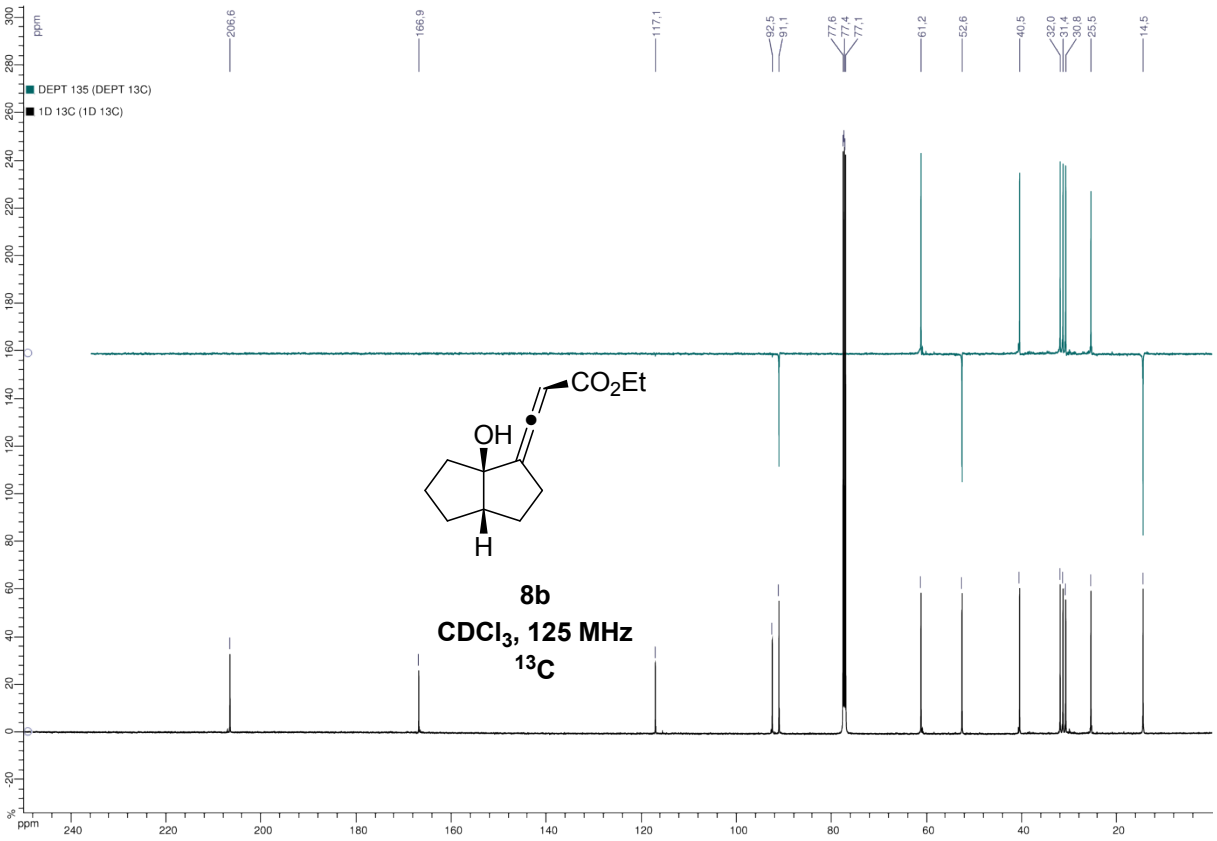

CO2Et
HO
H
7b
CDCl3, 500 MHz
1H

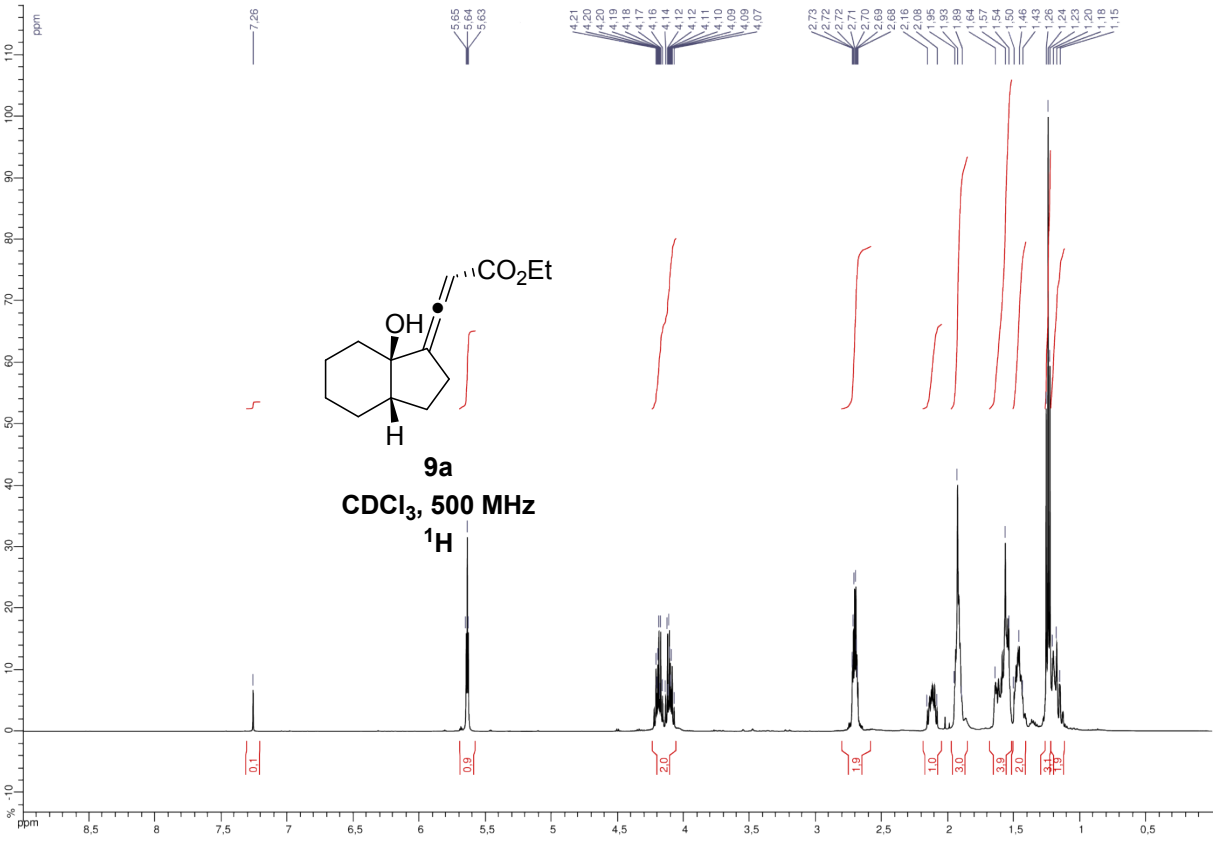

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
HO
H
7b
CDCl3, 125 MHz
13C

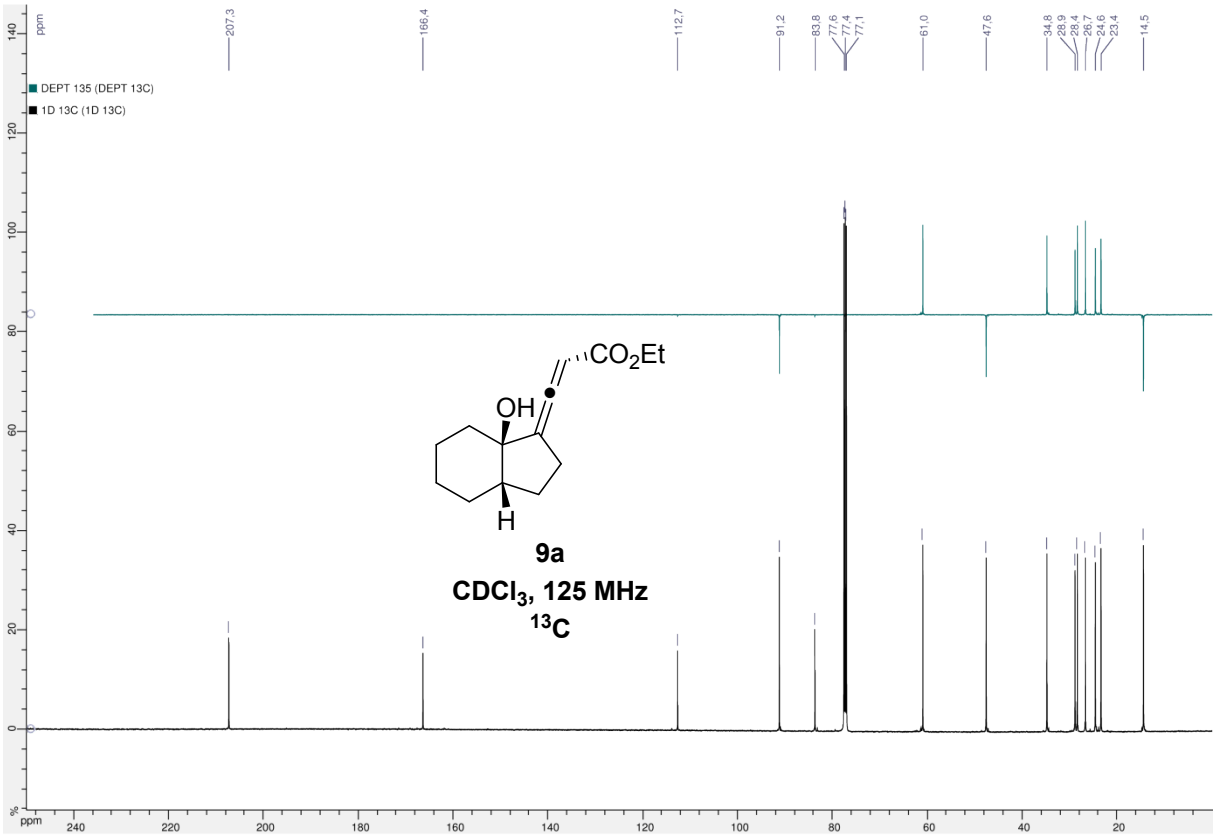

CO2Et
HO
H
7c
CDCl3, 500 MHz
1H

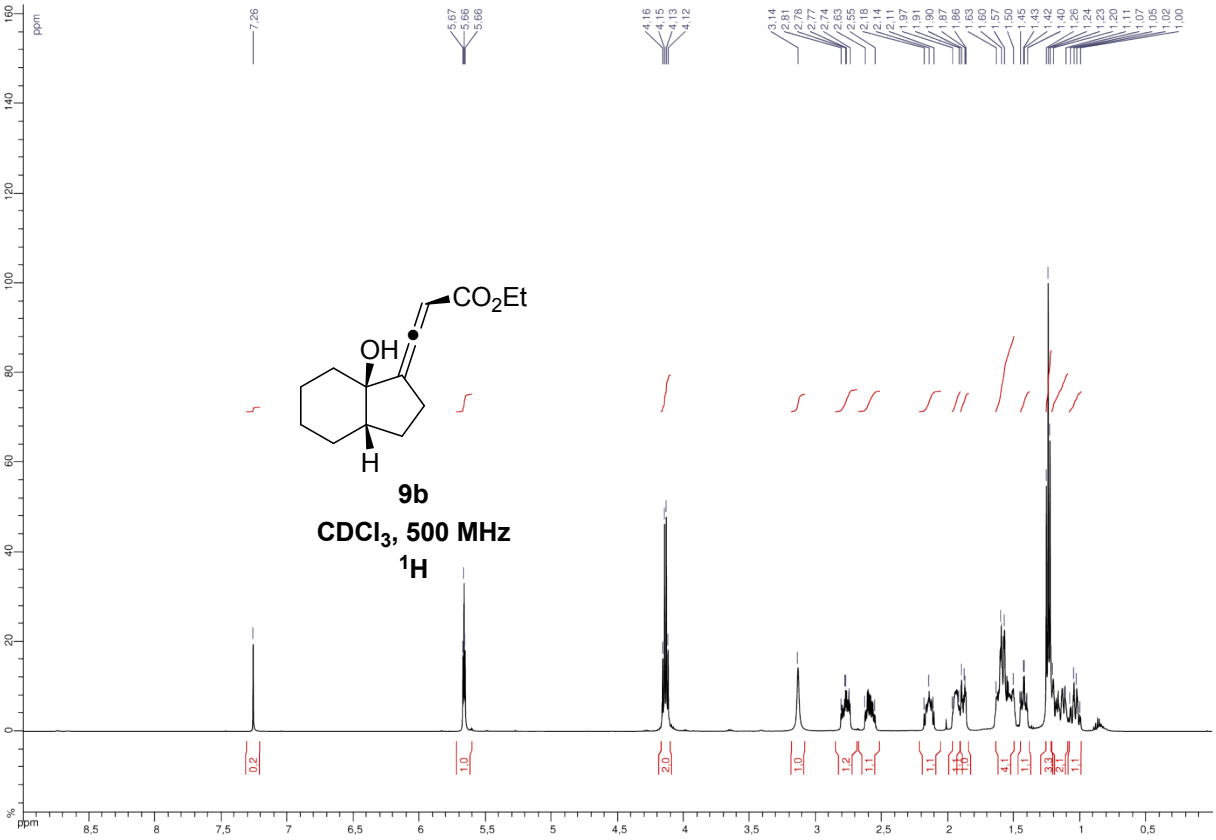

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
HO
H
7c
CDCl3, 125 MHz
13C

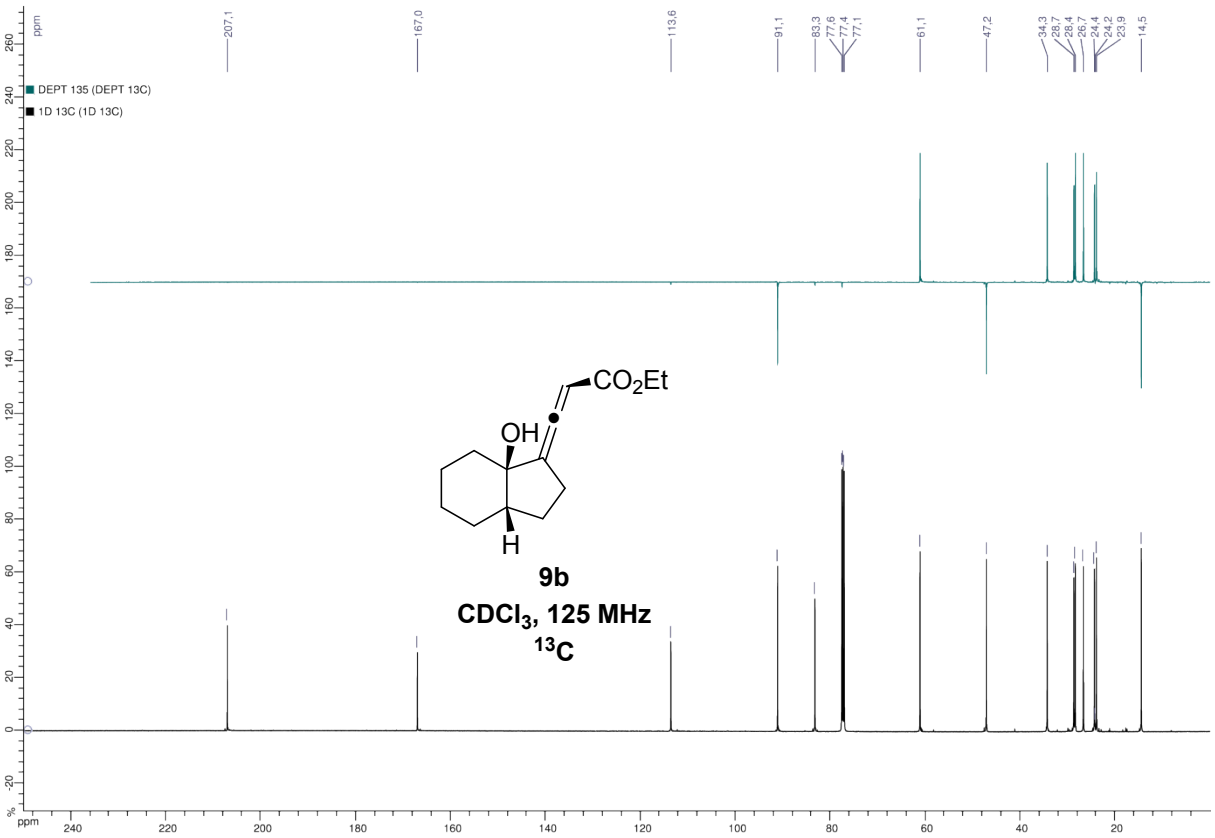

CO2Et
OH
H
8b
CDCl3, 500 MHz
1H

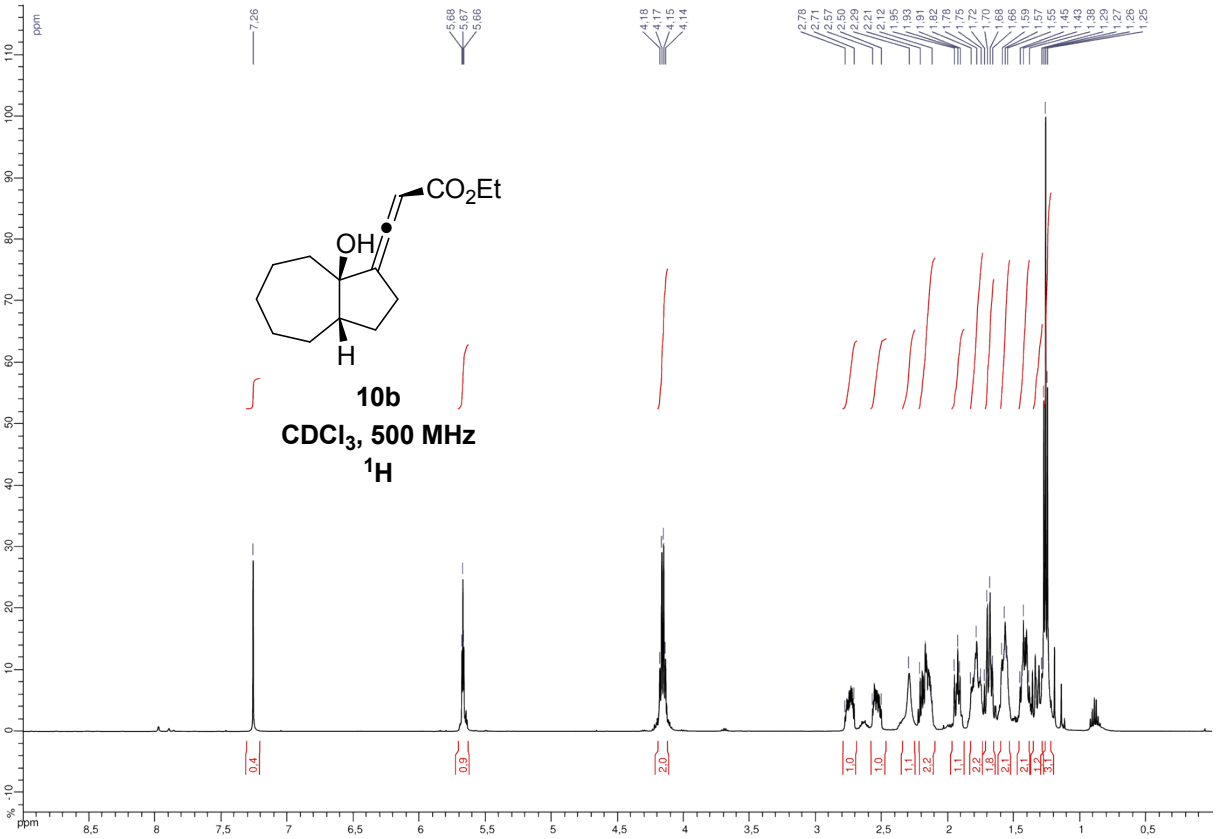

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
8b
CDCl3, 125 MHz
13C

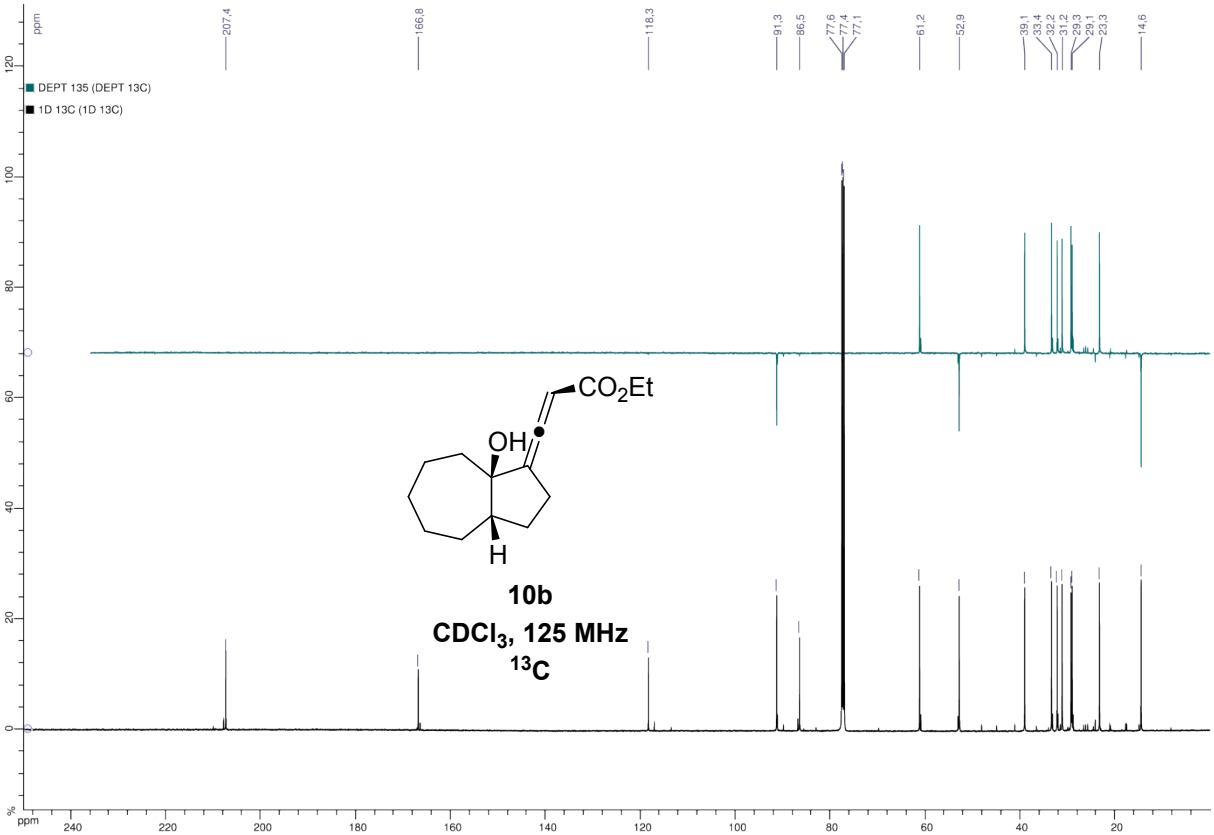

CO2Et
OH
H
9a
CDCl3, 500 MHz
1H

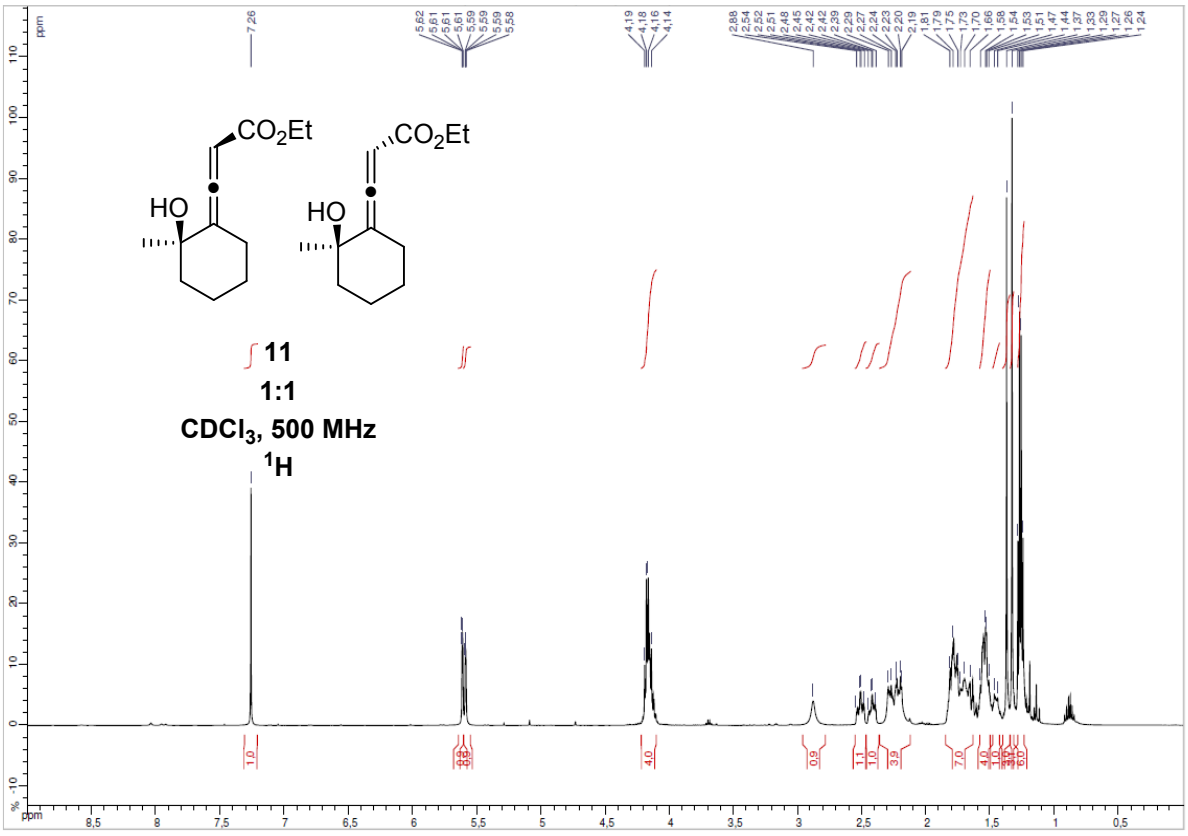

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
9a
CDCl3, 125 MHz
13C

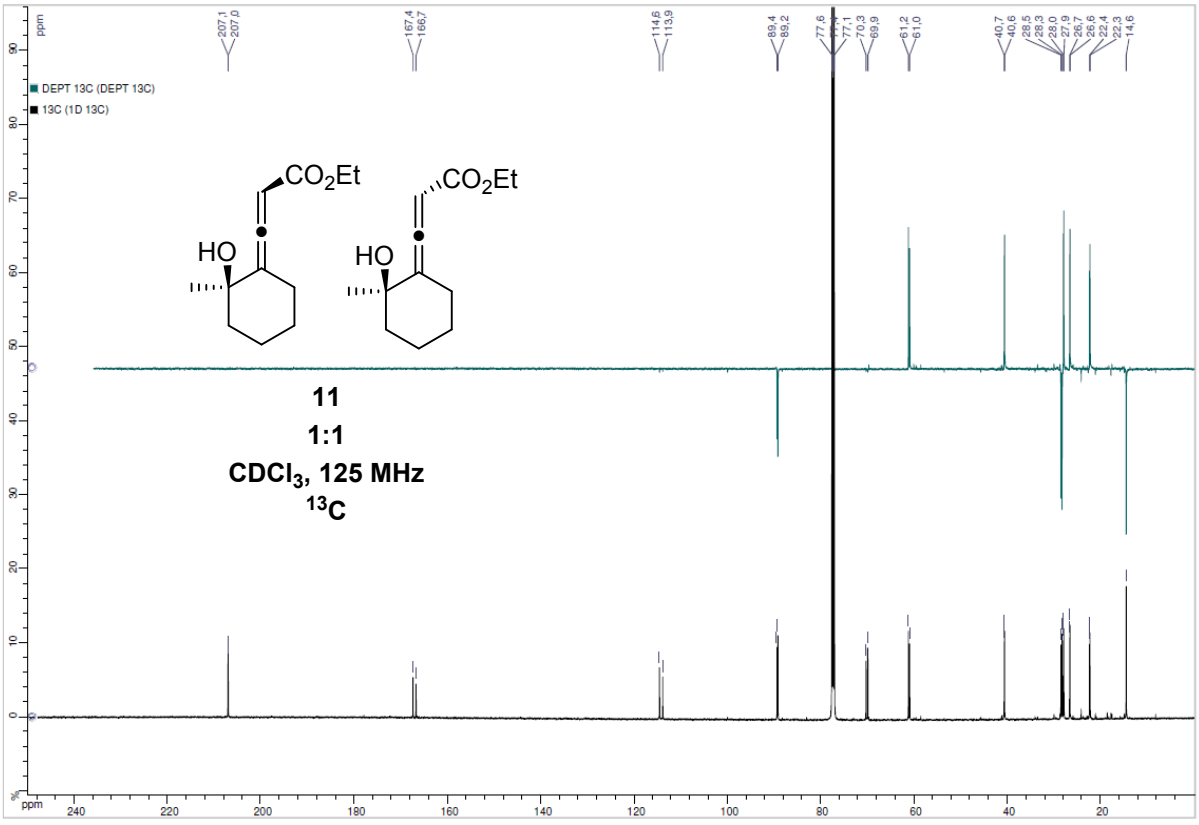

CO2Et
OH
H
9b
CDCl3, 500 MHz
1H

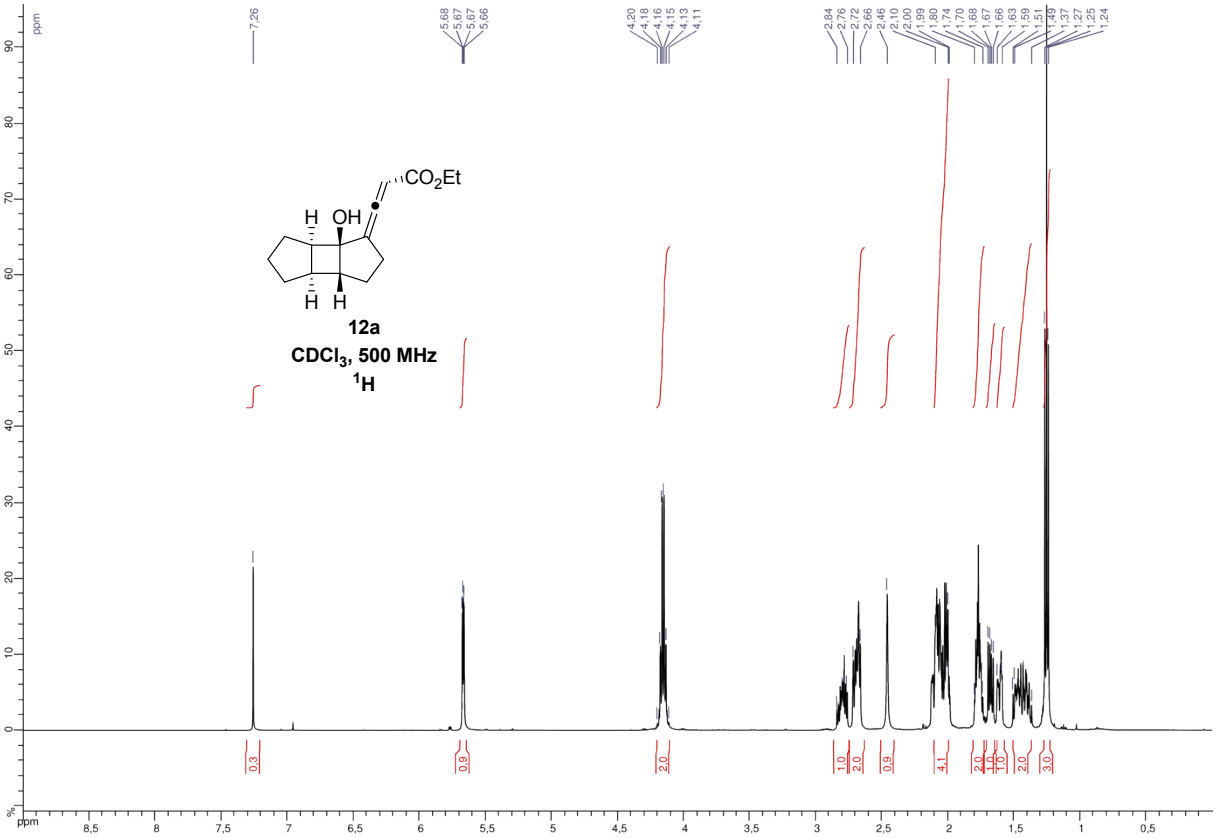

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
9b
CDCl3, 125 MHz
13C

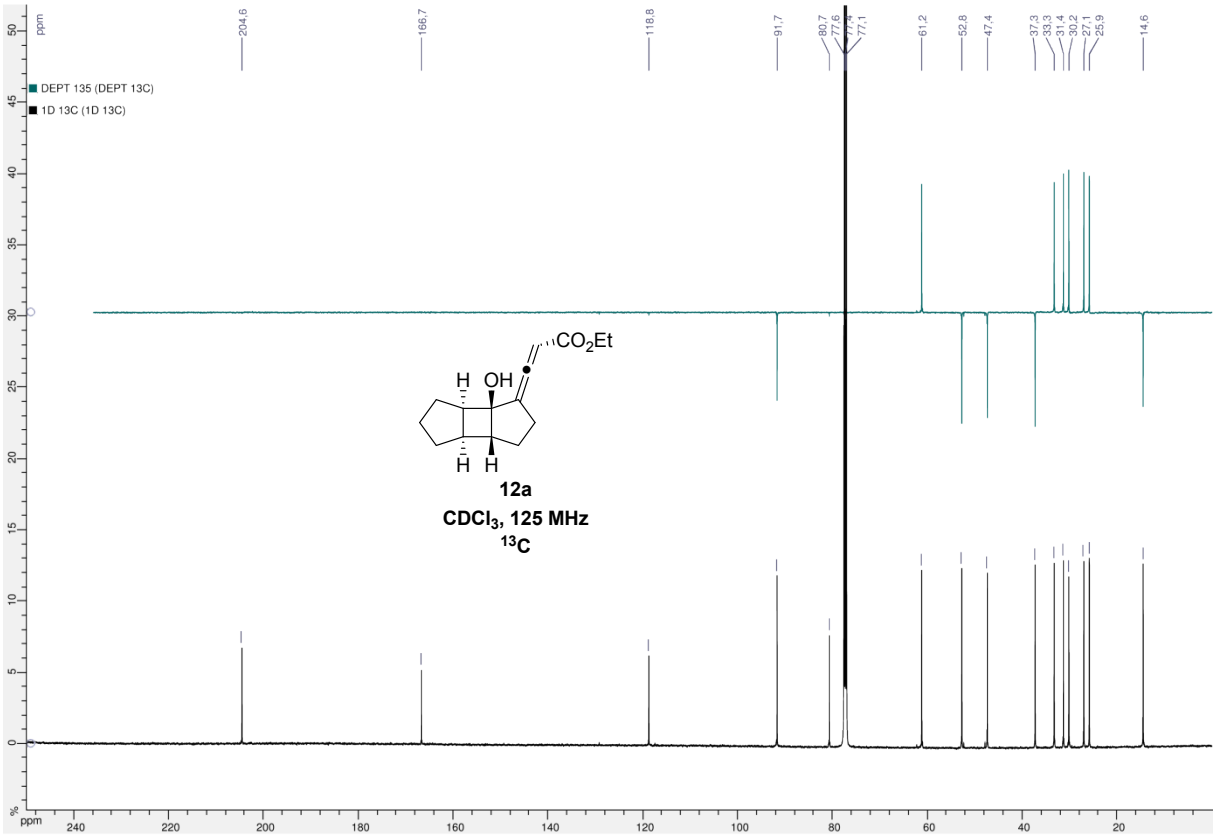

CO2Et
OH
H
10b
CDCl3, 500 MHz
1H

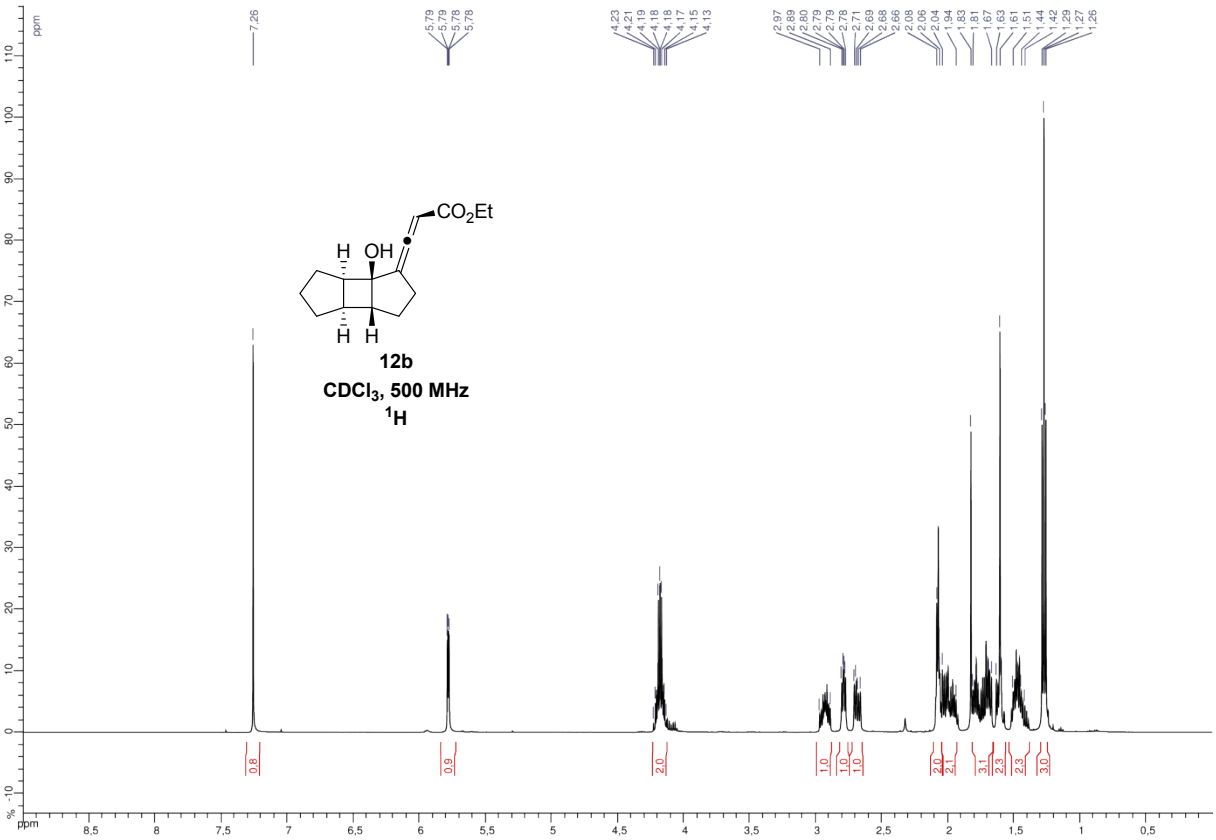

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
OH
H
10b
CDCl3, 125 MHz
13C

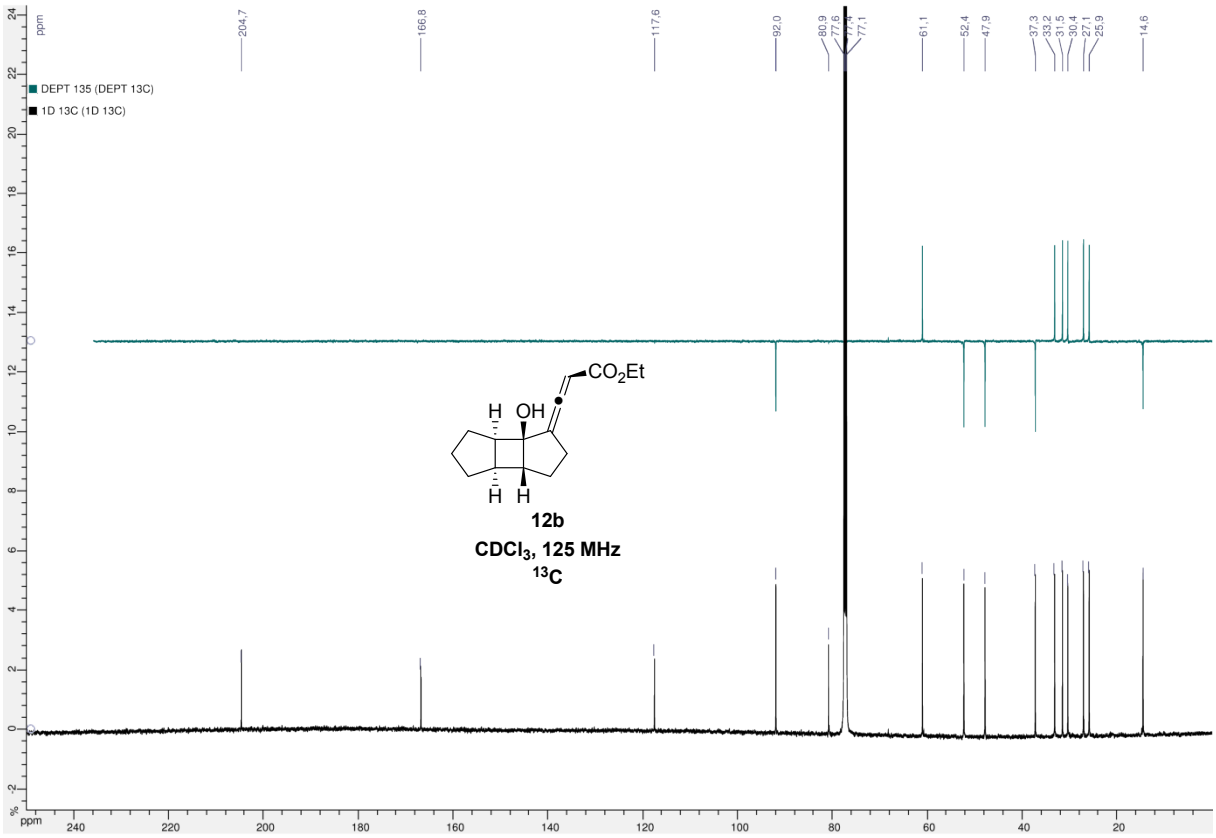

CO2Et
HO
CO2Et
HO
11
1:1
CDCl3, 500 MHz
1H

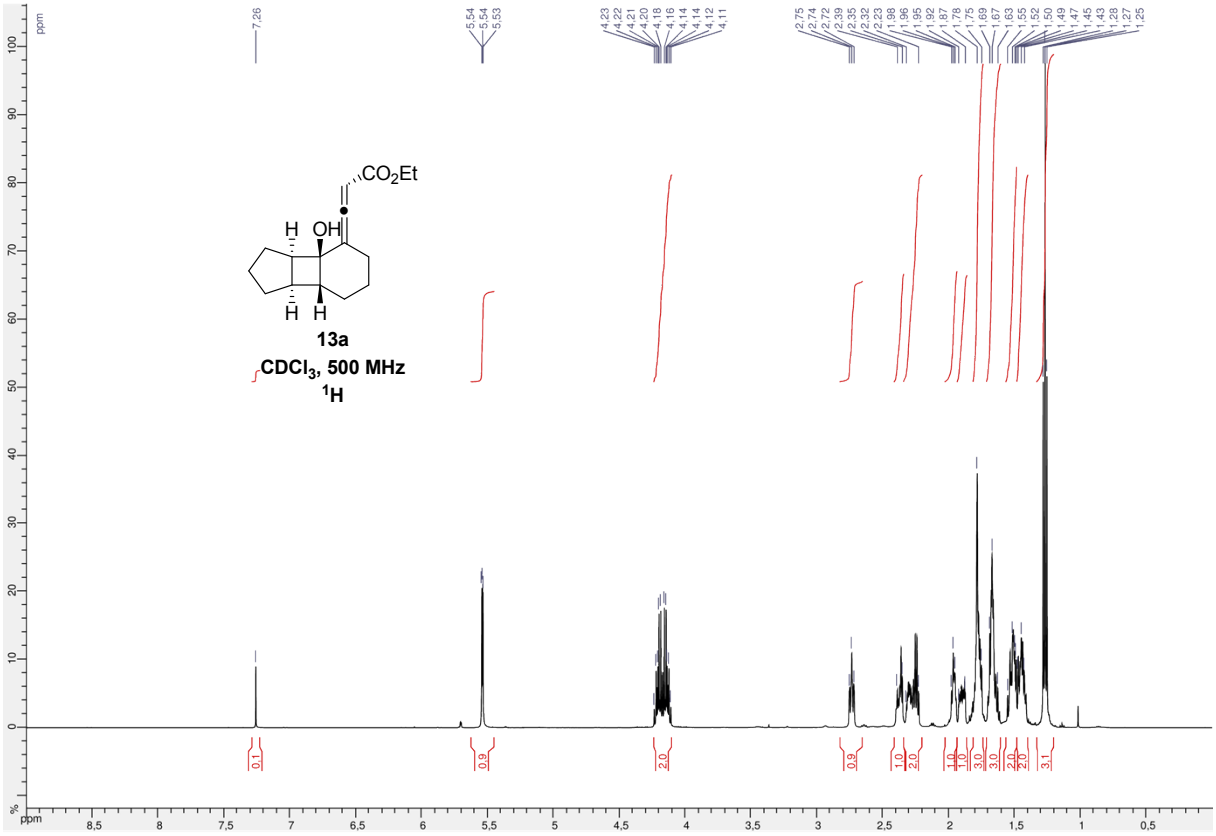

DEPT 13C (DEPT 13C)
13C (1D 13C)
CO2Et
HO
CO2Et
HO
11
1:1
CDCl3, 125 MHz
13C

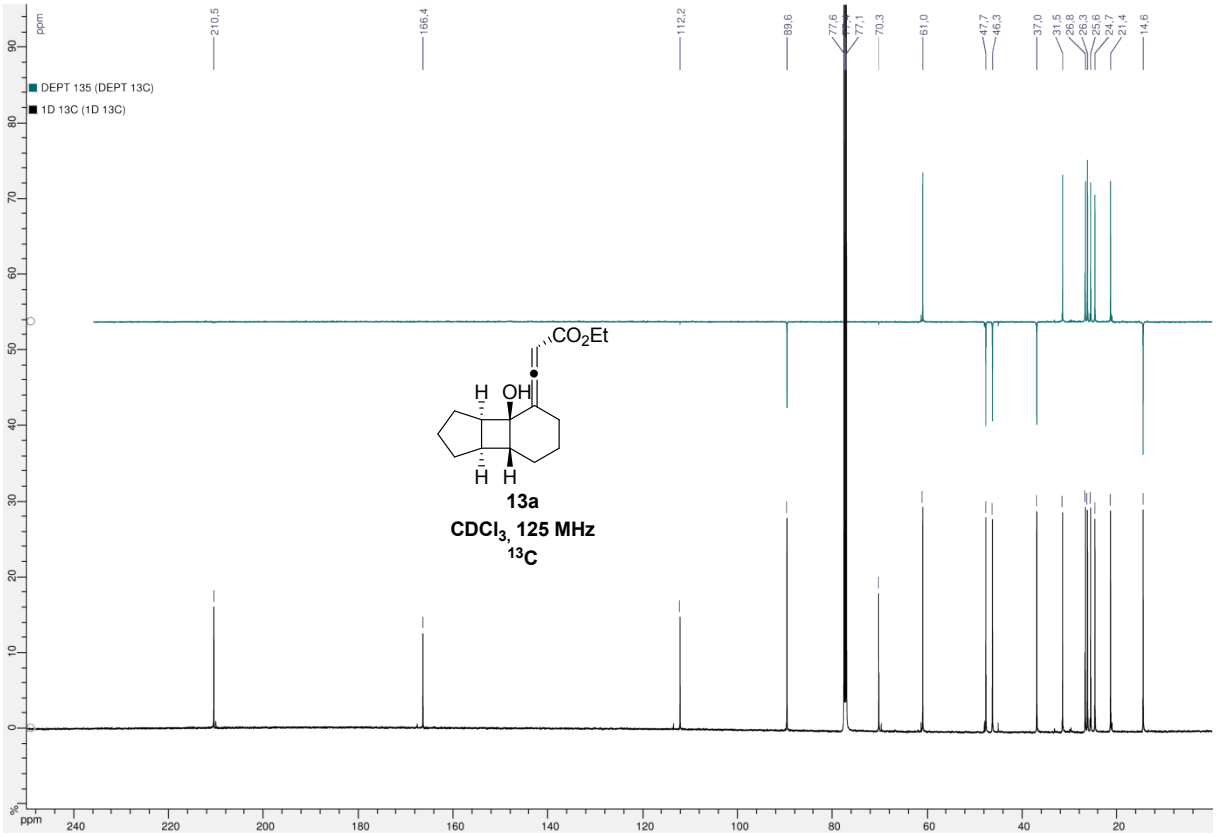

12a
CDCl3, 500 MHz
1H

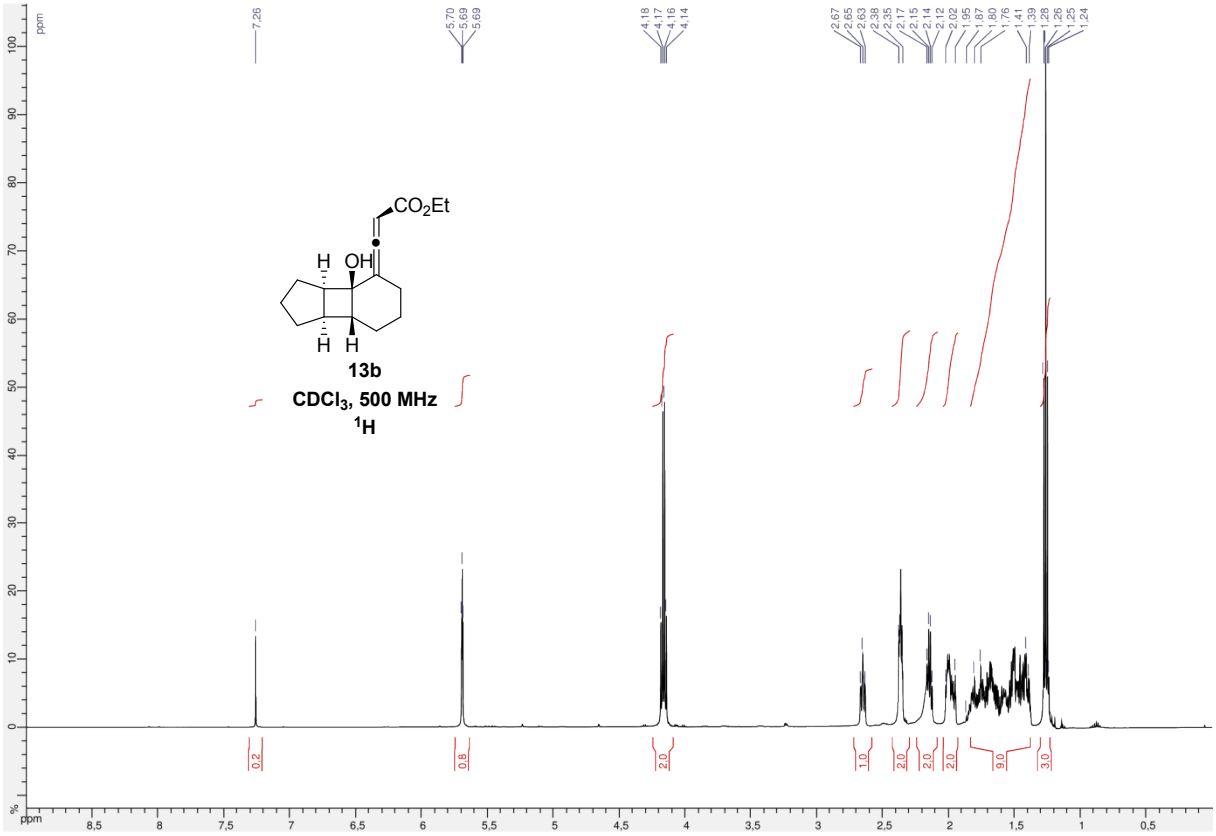

DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
12a
CDCl3, 125 MHz
13C

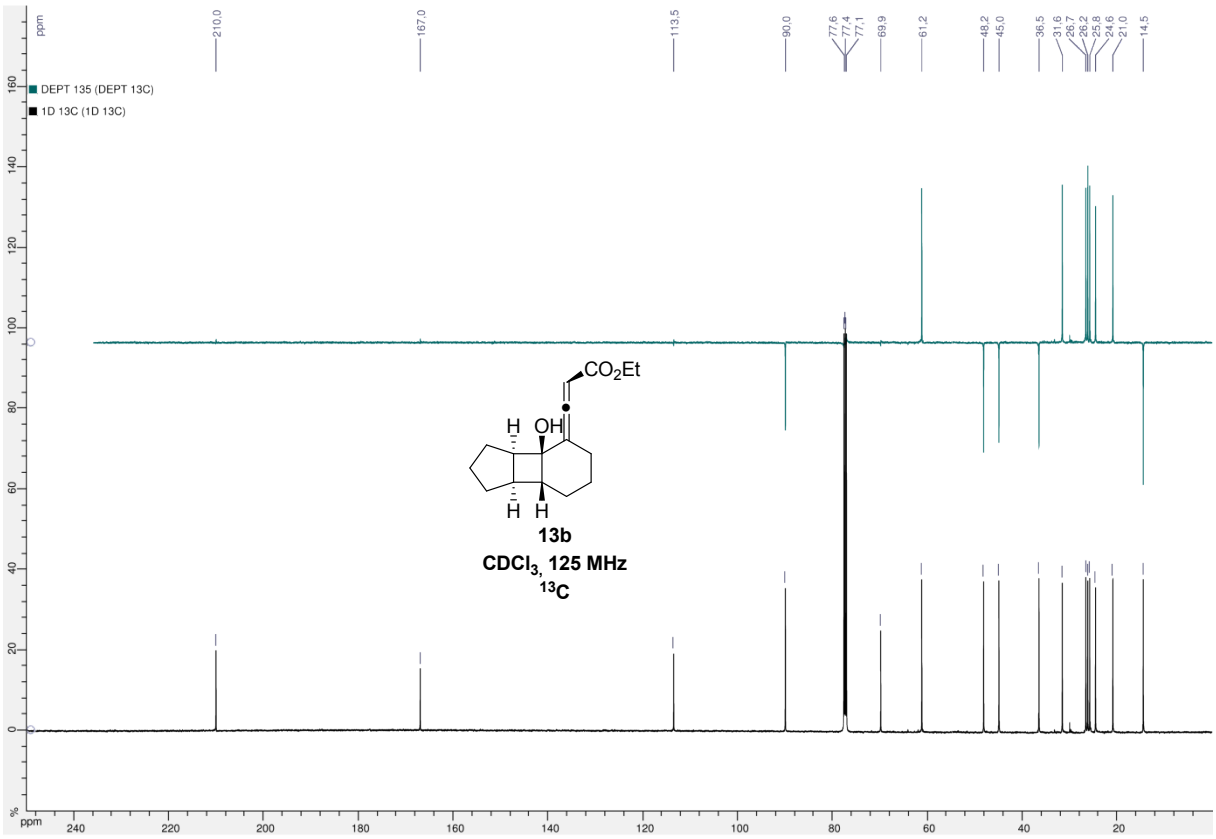

7.26
5.79
5.79
5.78
5.78
4.23
4.21
4.19
4.18
4.18
4.17
4.15
4.13
2.97
2.89
2.80
2.79
2.78
2.71
2.69
2.68
2.66
2.08
2.06
2.04
1.94
1.83
1.81
1.67
1.63
1.61
1.51
1.44
1.42
1.29
1.27
1.26
ppm
CO2Et
H OH
H H
12b
CDCl3, 500 MHz
1H
0.8
0.9
2.0
1.0
1.0
1.0
2.0
2.1
3.1
2.3
2.3
3.0


204.7
166.8
117.6
92.0
80.9
77.6
77.4
77.1
61.1
52.4
47.9
37.3
33.2
31.5
30.4
27.1
25.9
14.6
ppm
DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
H OH
H H
12b
CDCl3, 125 MHz
13C


CO2Et
H OH
H H
13a
CDCl3, 500 MHz
1H


DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
H OH
H H
13a
CDCl3, 125 MHz
13C


CO2Et
H OH
H H
13b
CDCl3, 500 MHz
1H


DEPT 135 (DEPT 13C)
1D 13C (1D 13C)
CO2Et
H OH
H H
13b
CDCl3, 125 MHz
13C