Supporting information

In Tandem or Alone: a Remarkably Selective Transfer Hydrogenation of Alkenes Catalyzed by Ruthenium Olefin Metathesis Catalysts

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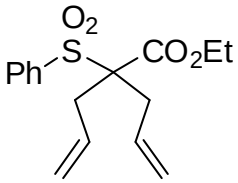
1. General information

All reactions were carried out in a pressure flask equipped with rotaflo stopcock under argon atmosphere using anhydrous solvents. THF (Aldrich) was dried by heating over sodium benzophenone ketyl and distilled under argon. ^{1}H and ^{13}C NMR spectroscopic data were recorded on Varian Mercury 400 MHz or Agilent 400 MHz spectrometer at room temperature. NMR spectra were calibrated to the solvent residual signals of $CDCl_3$ or TMS. TLC was performed on Sigma Aldrich plates 0.75 mL/g pore volume with fluorescence indicator 254 nm. Column chromatography was carried out using Fluka silica gel (pore size 60 Å, 230-400 mesh size, 40-63 μm partial mesh size) and mixture of distilled ethyl acetate and cyclohexane as an eluent. Calibrating curves and all GC analysis were determined using Clarus 680 spectrometer equipped with a FID detector. MS (ESI) spectra were recorded on SYNAPT G2-S HDMS (Waters). Unless otherwise stated, all chemicals were purchased from Aldrich, Across, TCI or Alfa Aesar and were used without further purification.

2. Synthesis of model substrates

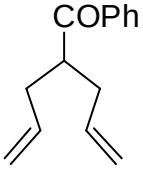
Dienes **1a**, **1b** and **1d** were commercially available or were synthesized by alkylation reaction of corresponding C-H acids following the described procedures. Diene **1c** was prepared by Krapcho decarboxylation reaction. Diene **4l** was synthesized by Steglich esterification reaction. Olefins **3g**, **3h**, **3i** and **3l** were commercially available and were used in transfer hydrogenation reaction without further purification. Cyclic olefins **3a**-**3e** and **3j**-**3k** were synthesized from corresponding dienes by ring closing metathesis reaction according to literature.

Synthesis of dienes 1b, 1c and 1d



1b

Ethyl 1,1-diallyl-1-(phenylsulfonyl)acetate (1b). Compound was prepared according to the literature. Analyses were in accordance with previously reported.[1]

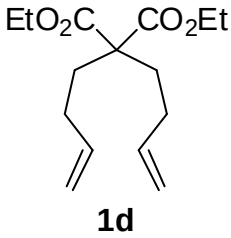


1c

2-allyl-1-phenylpent-4-en-1-one (1c). Commercially available ethyl 2,2-diallylbenzoylacetate (8.17 g, 30 mmol), LiCl (2.54 g, 60 mmol) and distilled water (50 μl) and DMSO (30 mL) were placed in a microwave tube. The tube

was sealed and the reaction mixture was heated using microwave irritation at 180 °C for 2 h. After reaction was completed (TLC monitoring) the reaction mixture was poured into brine (400 ml) and extracted with DCM (7x). Collected organic layers were washed with brine, dried over $MgSO_4$, filtered and evaporated. The crude product was purified using column chromatography to afford ketone **1c** (3.15 g, 52%). Analyses were in accordance with previously reported.[2]

NMR (400 MHz, $CDCl_3$) δ = 8.00-7.91 (m, 2H), 7.62-7.53 (m, 1H), 7.51-7.43 (m, 2H), 5.74 (ddt, *J* = 17.0, 10.1, 7.0 Hz, 2H), 5.14-4.88 (m, 4H), 3.72-3.43 (m, 1H), 2.61-2.46 (m, 2H), 2.37-2.23 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.9, 137.2, 135.5, 133.1, 128.8, 128.4, 117.1, 45.7, 35.9.

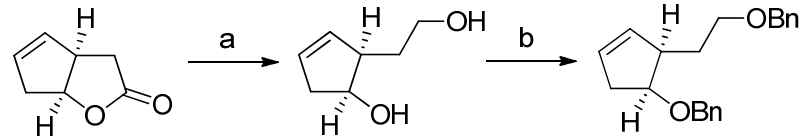


1d

Diethyl 2,2-di(but-3-en-1-yl)malonate (1d). Compound **1d** was prepared according to procedure reported for synthesis of **7m** starting from diethyl malonate (1.60 g, 10 mmol), NaH (0.69 g, 30 mmol) and homoallylbromide (2.84 g, 21 mmol). Crude product was purified to afford ester **1d** (1.50 g, 56%). Analyses were in accordance with previously reported.[3]

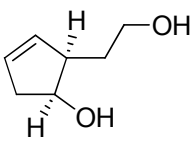
^1H NMR (400 MHz, $CDCl_3$) δ = 5.90-5.65 (m, 2H), 5.17-4.82 (m, 4H), 4.18 (q, *J* = 7.1 Hz, 4H), 2.12-1.84 (m, 8H), 1.24 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.6, 137.7, 115.2, 61.3, 57.1, 31.7, 28.5, 14.2.

Synthesis of 3f



Grieco lactone **4f** **3f**

Scheme. 1. Synthesis of **3f**. Reaction conditions: a) $LiAlH_4$, Et_2O, 48 h, RT; b) NaH, BnBr, THF, 4 h, 50 °C.

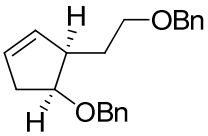


4f

(1*S*,2*R*)-2-(2-hydroxyethyl)cyclopent-3-enol (4f). To a suspension of $LiAlH_4$ (1.52 g, 40 mmol) in anhydrous diethyl ether (25 mL) a solution of commercially available Grieco lactone ((1*S*,5*R*)-2-oxabicyclo[3.3.0]oct-6-en-3-one) (1.24 g, 10 mmol) was added dropwise at 0 °C. Reaction mixture was left stirring for 2 h at room temperature. After full conversion of substrate was observed

(TLC monitoring) the reaction mixture was cooled down to 0 °C and a solution of Na_2SO_4 was added dropwise (CAUTION: extremely exothermic reaction). The granular solid (formed in 10 min) was filtered off and rinsed with ether (ca. 50 mL). The filtrate was washed with brine and organic layer was separated, dried over $MgSO_4$, filtered and evaporated to obtain crude diol **4f** (0.97 g, 75%) that was spectrally pure and was used in next step without further purification.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.78-5.65 (m, 1H), 5.58-5.49 (m, 1H), 4.44 (td, *J* = 6.1, 2.3 Hz, 1H), 3.85-3.73 (m, 1H), 3.65 (m, 1H), 3.45 (s, 2H), 2.76-2.67 (m, 1H), 2.59 (dd, *J* = 6.2, 2.6 Hz, 1H), 2.39-2.26 (m, 1H), 1.93-1.69 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 133.0, 128.1, 72.2, 61.8, 49.5, 41.7, 30.2.



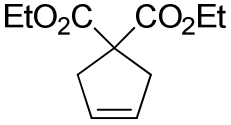
3f

(1*S*,2*R*)-1-benzyloxy-2-(2-benzyloxyethyl)cyclopent-3-en (3f). To a solution of diol **4f** (0.94 g, 7.3 mmol) in 25 mL of anhydrous THF NaH (0.70 g, 29.2 mmol) was carefully added at 0 °C. The suspension was stirred for 1 h at room temperature and then benzyl bromide (5.00 g, 29.2 mmol) was added dropwise over 5 min. The reaction mixture was stirred at 50 °C for 4 h. Excess of NaH was quenched with MeOH and reaction mixture was diluted with water (50 mL). Aqueous layer was extracted with TBME (3x), collected organic layers were combined, washed with brine and distilled water, dried over $MgSO_4$, filtered and evaporated to obtain crude product, that was purified using column chromatography to yield compound **3f** (1.60 g, 71%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55-7.10 (m, 10H), 5.90-5.56 (m, 2H), 4.52 (s, 2H), 4.50 (dd, *J* = 40.4, 11.9 Hz, 4H), 4.26-4.10 (m, 1H), 3.58 (t, *J* = 6.6 Hz, 2H), 3.00-2.76 (m, 1H), 2.62-2.37 (m, 2H), 2.16-1.98 (m, 1H), 1.89-1.66 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.8, 138.8, 133.7, 128.4, 128.3, 127.8, 127.6, 127.5, 127.5, 127.4, 80.1, 72.9, 71.4, 69.3, 44.9, 37.5, 28.4.

HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{21}H_{26}O_2Na$, 333.1830; found, 333.1840.

Synthesis of olefins 3a, 3b, 3c, 3d, 3e, 3j, 3k

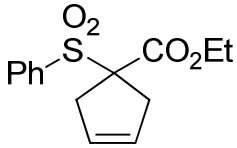


3a

Diethyl cyclopent-3-ene-1,1-dicarboxylate (3a). Diene **1a** (1.68 g, 7 mmol) was placed in a dry flask, degassed and diluted with anhydrous DCM (C=0.2M). **Gru-II** (5.94 mg, 0.007 mmol) was added and reaction

mixture was heated at 40 °C for 1 h. After that time solvent was removed under reduced pressure and then purification of crude product using column chromatography afforded spectrally pure ester **3a** (1.42 g, 95%). Analyses were in accordance with previously reported.[5]

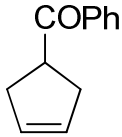
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.73-5.50 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 4H), 3.06-2.92 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.3, 127.9, 61.6, 58.9, 41.0, 14.2.



3b

Ethyl 1-(phenylsulfonyl)cyclopent-3-enecarboxylate (3b). Compound **3b** was prepared according to procedure reported for synthesis of **3a** starting from **1b** (1.29 g, 4.2 mmol), **Gru-II** (7.11 mg, 0.0084 mmol). Crude product was purified by column chromatography to afford ester **3b** (1.16 g, 99%). Analyses were in accordance with previously reported.[1]

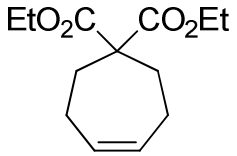
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91-7.83 (m, 2H), 7.72-7.63 (m, 1H), 7.58-7.50 (m, 2H), 5.72-5.54 (m, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.42-3.06 (m, 4H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.7, 136.8, 134.2, 130.1, 128.9, 127.7, 78.1, 62.8, 38.9, 13.9.



3c

1-benzoylcyclopent-3-en (3c). Compound **3c** was prepared according to procedure reported for synthesis of **3a** starting from **1c** (1.00 g, 5 mmol), **Gru-II** (21.2 mg, 0.025 mmol). Crude product was purified by column chromatography to afford ketone **3c** (0.85 g, 98%). Analyses were in accordance with previously reported.[6]

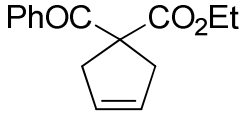
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03-7.94 (m, 2H), 7.61-7.52 (m, 1H), 7.51-7.43 (m, 2H), 5.82-5.58 (m, 2H), 4.08 (tt, *J* = 9.5, 6.3 Hz, 1H), 2.93-2.58 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 201.5, 136.6, 133.0, 129.0, 128.7, 128.7, 44.2, 36.4.



3d

Diethyl cyclohept-4-ene-1,1-dicarboxylate (3d). Compound **3d** was prepared according to procedure reported for synthesis of **3a** starting from **1d** (1.61 g, 6 mmol), **Gru-II** (25.5 mg 0.03 mmol). Crude product was purified by column chromatography to afford ester **3d** (1.41 g, 98%). Analyses were in accordance with previously reported.[3]

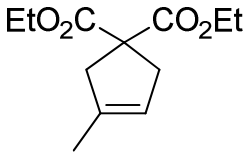
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.66 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 4H), 2.32-2.12 (m, 8H), 1.23 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.4, 131.0, 61.3, 58.1, 32.1, 24.6, 14.2.



3e

Ethyl 1-benzoylcyclopent-3-enecarboxylate (3e). Compound **3e** was prepared according to procedure reported for synthesis of **3a** starting from commercially available ethyl 2,2-allylbenzoylacetate (2.53 g, 9.3 mmol), **Gru-II** (7.9 mg, 0.0093 mmol). Crude product was purified by column chromatography to afford ketone **3e** (2.25 g, 99%). Analyses were in accordance with previously reported.[7]

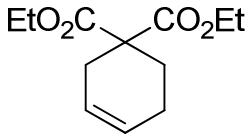
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91-7.80 (m, 2H), 7.60-7.47 (m, 1H), 7.46-7.36 (m, 2H), 5.66-5.55 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.32-3.03 (m, 4H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.9, 174.3, 135.0, 132.9, 128.9, 128.64, 127.7, 62.3, 61.7, 41.4, 13.8.



3j

Diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (3j). Compound was prepared according to the literature. Analyses were in accordance with previously reported. Analyses were in accordance with previously reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.39-5.25 (m, 1H), 4.40 (q, *J* = 7.1 Hz, 4H), 3.37-2.98 (m, 4H), 1.91 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.4, 137.5, 121.4, 61.5, 59.5, 44.7, 40,9, 15.1, 14.1.

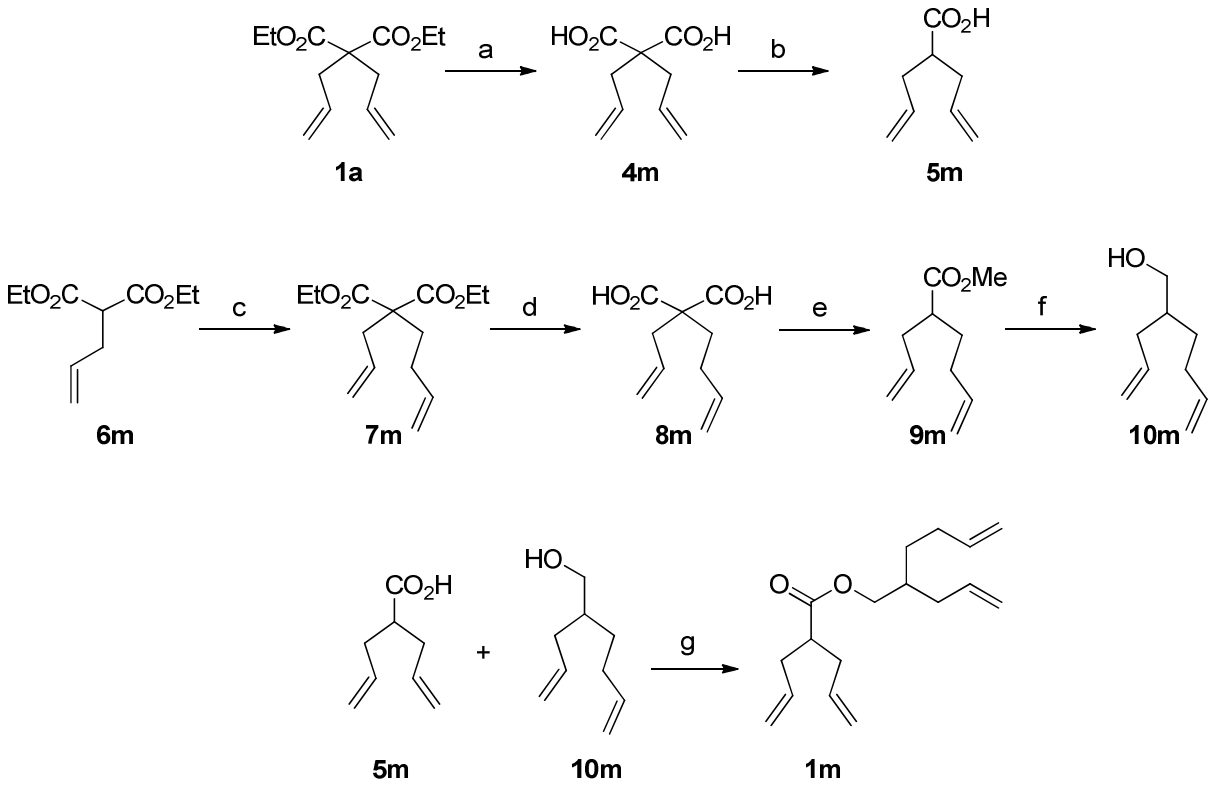


3k

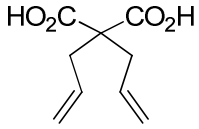
Diethyl cyclohex-3-ene-1,1-dicarboxylate (3k). Compound **3k** was prepared according to procedure reported for synthesis of **3a** starting from **7m** (1.53 g, 6 mmol), **Gru-II** (25.5 mg, 0.03 mmol). Crude product was purified by column chromatography to afford ester **3k** (1.00 g, 74%). Analyses were in accordance with previously reported.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.70-5.63 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 4H), 2.60-2.47 (m, 2H), 2.17-2.04 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.8, 126.2, 124.1, 61.4, 53.1, 30.5, 27.5, 22.4, 14.2.

Synthesis of tetraene 1m



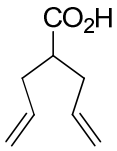
Scheme. 1. Synthesis of tetraene **1m**. Reaction conditions: a) KOH, EtOH/H_2O, 4 h, reflux; b) Δ, 140 °C MW irradiation, 3h; c) NaH, homoallyl bromide, DMF, 4 h, 50 °C; d) KOH, EtOH/H_2O, 4 h, reflux; e) 1. Δ, 140 °C MW irradiation 3 h; 2. MeOH, H^+, 12 h, reflux; f) $LiAlH_4$, Et_2O, 48 h; g) DMAP, EDCI, DCM, overnight, RT.



4m

2,2-diallylmalonic acid (4m). To commercially available diethyl diallylmalonate (4.81 g, 20 mmol) placed in a flask, 10 mL of 40% aqueous solution of KOH was poured and 5 mL of ethanol to make mixture homogenous. The reaction mixture was heated under reflux for 4 h. Solvent was removed under reduced pressure to dryness. Solid residue was diluted in distillated water and extracted with *n*-hexane. The alkaline layer was acidified with cold 10% HCl_{aq} and extracted with ether (3x). The combined ethereal extracts were dried over $MgSO_4$, filtered and evaporated. The residue solidified slowly and crystallization from cyclohexane afforded the pure acid **2m** (2.60 g, 70%). Analyses were in accordance with previously reported.[8]

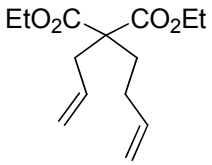
^{1}H NMR (400 MHz, CD_3OD) δ = 5.71 (ddt, *J* = 17.5, 10.2, 7.4 Hz, 2H), 5.19-5.06 (m, 4H), 2.67-2.56 (m, 4H); ^{13}C NMR (101 MHz, CD_3OD) δ = 174.3, 134.0, 119.2, 58.4, 37.8.



5m

2-allylpent-4-enoic acid (5m). Acid **4m** (2.12 g ,11.5 mmol) was placed in a flask and reaction was performed at 140 °C under microwave irritation for 3h under argon atmosphere. Crude product was purified by distillation under reduced pressure 69-71 °C / 0.4 mBar and spectrally pure acid **5m** (1.53 g, 95%) was obtained. Analyses were in accordance with previously reported.[9]

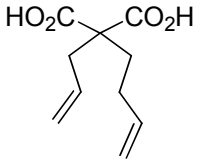
^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.82 (br, 1H), 5.89-5.68 (m, 2H), 5.22-4.92 (m, 4H), 2.66-2.47 (m, 1H), 2.47-2.34 (m, 2H), 2.34-2.21 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 181.7, 135.0, 117.5, 45.0, 35.6.



7m

Diethyl 2-allyl-2-homoallylmalonate (7m). Diethyl allylmalonate (5.00 g, 25 mmol) was placed in a dry flask, degassed and dissolved in anhydrous DMF. NaH (0.86 g, 37.5 mmol) was added to the solution and then the mixture was stirred for 0.5h at room temperature. Homoallylbromide (4.05 g, 30 mmol) was slowly added dropwise *via* syringe to the reaction mixture at room temperature. The reaction mixture was heated at 50 °C for 5 h. After the reaction was completed (TLC monitoring) the reaction mixture was cooled down and quenched with 100 mL of saturated aqueous solution of NH_4Cl. Organic layer was separated and aqueous layer was extracted with EtOAc (3x), combined extracts were washed with brine, dried over $MgSO_4$, filtered and evaporated to obtain crude product which was purified by filtration through silica gel pad to afford spectrally pure **7m** (5.54 g, 87%). Analyses were in accordance with previously reported.[5]

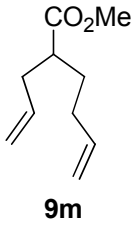
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.87-5.70 (m, 1H), 5.70-5.56 (m, 1H), 5.17-4.88 (m, 4H), 4.16 (q, *J* = 7.1 Hz, 4H), 2.73-2.58 (m, 2H), 2.03-1.87 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.1, 137.6, 132.4, 118.8, 114.9, 61.1, 57.1, 37.0, 31.5, 28.2, 14.0.



8m

2-allyl-2-homoallylmalonic acid (8m). Compound **8m** was prepared according to procedure reported for synthesis of **4m** starting from **7m** (6.36 g, 25 mmol), 13 mL of 40% KOH and 7mL of ethanol. Crude product **8m** (4.82 g, 97%) was spectrally pure and was used in next step without further purification. Analyses were in accordance with previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.86 (br, 2H), 6.04-5.47 (m, 2H), 5.35-4.80 (m, 4H), 2.71 (d, *J* = 7.4 Hz, 2H), 2.31-1.83 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 177.2, 137.0, 131.6, 120.1, 115.8, 57.7, 38.1, 32.4, 28.6.



9m

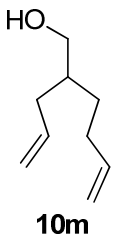
Methyl 2-allylhex-5-enoate (9m). 2-allylhex-5-enoic acid was prepared according to procedure reported for synthesis of **5m** starting from **8m** (4.96 g, 25mmol). Crude 2-allylhex-5-enoic acid (3.80 g, 98%) was dissolved in MeOH (100 mL), few drops of H_2SO_4 was added and the reaction mixture was heated to reflux for 4 h. After reaction was completed solvent was removed under reduced pressure and the residue was dissolved in EtOAc (100 mL), washed with saturated solution of $NaHCO_3$ and brine. Organic phase was dried over $MgSO_4$, filtered, evaporated to obtain crude ester **9m** (2.60 g, 62%) that was used in next step without further purification. Analyses were in accordance with previously reported.[11]

Analytical data of **2-allylhex-5-enoic acid**:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.71 (br, 1H), 5.86-5.67 (m, 2H), 5.17-4.92 (m, 4H), 2.56-2.43 (m, 1H), 2.43-2.34 (m, 1H), 2.31-2.20 (m, 1H), 2.16-2.01 (m, 2H), 1.82-1.69 (m, 1H), 1.64-1.54 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 182.2, 137.7, 135.1, 117.3, 115.5, 44.58, 36.2, 31.4, 30.6.

Analytical data of methyl ester **9m**:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.84-5.70 (m, 2H), 5.10-4.91 (m, 4H), 3.65 (s, 3H), 2.60-2.45 (m, 1H), 2.42-2.37 (m, 1H), 2.35-2.22 (m, 1H), 2.20-2.07 (m, 2H), 1.90-1.73 (m, 1H), 1.73-1.61 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.2, 137.4, 135.1, 116.5, 114.8, 50.9, 44.4, 36.2, 31.1, 30.6.

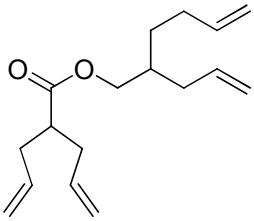


10m

2-allylhex-5-en-1-ol (10m). To a well stirred suspension of $LiAlH_4$ (228 mg, 6 mmol) in anhydrous diethyl ether (15 mL) ethereal solution of ester **9m** (252 mg, 1.5 mmol) was added dropwise at 0 °C. The reaction mixture was left stirring for 2 days. After reaction was completed the reaction mixture was cooled down to 0 °C and saturated solution of Na_2SO_4 was added dropwise (CAUTION: extremely exothermic reaction). The granular white solid was formed (in ca. 15 min), filtered off and rinsed with ether (50 mL). The filtrate was washed with brine, dried over $MgSO_4$, filtered and

evaporated to obtain spectrally pure alcohol **10m** (200 mg, 95%). Analyses were in accordance with previously reported.[12]

^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.00-5.64 (m, 2H), 5.18-4.85 (m, 4H), 3.55 (d, *J* = 5.5 Hz, 2H), 2.19-1.98 (m, 4H), 1.76-1.20 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 138.9, 137.0, 116.4, 114.7, 65.37, 39.9, 35.8, 31.2, 29.9.



1m

2-allylhex-5-en-1-yl 2-allylpent-4-enoate (1m). Solution of acid **5m** (617 mg, 4.4 mmol), DMAP (977 mg, 8 mmol) and alcohol **10m** (561 mg, 4 mmol) was dissolved in DCM. EDCI (1.92 g, 10 mmol) was added in one portion to ice-cooled reaction mixture and stirring was continued at room temperature overnight. Solvent was removed under reduced pressure and the residue was dissolved in EtOAc, washed with distilled water and saturated solution of $NaHCO_3$. Combined organic phases were dried over $MgSO_4$, filtered and evaporated to obtain crude product. Purification using column chromatography afforded spectrally pure ester **1m** (350 mg, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.91-5.64 (m, 4H), 5.19-4.89 (m, 8H), 3.99 (d, *J* = 5.5 Hz, 2H), 2.61-2.48 (m, 1H), 2.43-2.32 (m, 2H), 2.31-2.21 (m, 2H), 2.18-2.01 (m, 4H), 1.87-1.69 (m, 1H), 1.471.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.1, 138.6, 136.1, 135.4, 117.1, 116.9, 114.8, 66.3, 45.2, 36.8, 36.0, 35.7, 31.0, 30.1.

HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{17}H_{26}O_2Na$, 285.1830; found, 285.1837.

Elemental analysis calcd (%) for $C_{17}H_{26}O_2$ (262.19): C 77.82, H 9.99; found: C 77.70, H 9.89.

IR (film) cm^{-1} 3078, 2979, 2925, 2858, 1736,1641,1442, 1173, 993, 914.

3. General Procedures

Several general procedures of transfer hydrogenation and sequential ring closing metathesis/ transfer hydrogenation reactions were shown below. In every case RCM and transfer hydrogenation reactions were carried out at 40 °C and 80 °C respectively for appropriate period of time (see Tab. 2 and Tab. 3). Unless otherwise noted the obtained hydrogenation products were spectrally pure without further purification. In case of substrates **1d** and **3a** NaH was used instead of HCO_2Na.

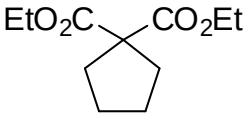
General Procedure of Transfer Hydrogenation Reaction

Procedure A. Olefin (1 mmol) was placed in a dry pressure ampoule, then it was degassed and diluted in 5mL of anhydrous THF. Catalyst was added to the resulting solution followed by addition of solid HCO_2Na (0.2mmol) and HCO_2H (50 mmol). Reaction mixture was stirred for appropriate period of time at 80 °C and then allowed to cool down to room temperature and poured into a saturated solution of $NaHCO_3$ (ca. 30 mL) to obtain neutral pH. Aqueous layer was extracted with organic solvent, the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and evaporated to obtain crude product.

General Procedure of Tandem Ring Closing Metathesis / Transfer Hydrogenation Reaction

Procedure B. Diene (1 mmol) was placed in a dry pressure ampoule, then it was degassed and diluted in 5mL of anhydrous THF. Catalyst was added to the resulting solution and the ring closing metathesis reaction was carried out for 0.5 h at 40 °C. Once the RCM reaction was completed, solid HCO_2Na (0.2 mmol) and HCO_2H (50 mmol) were added and the reaction was continued for appropriate period of time at 80 °C and then the solution was allowed to cool down to room temperature and poured into saturated solution of $NaHCO_3$ (ca. 30 mL) to obtain neutral pH. Aqueous layer was extracted with organic solvent, the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and evaporated to obtain crude product.

4. Transfer hydrogenation of selected olefins

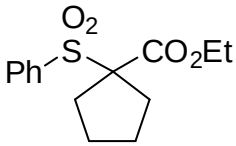


2a

Diethyl cyclopentane-1,1-dicarboxylate (2a). Spectrally pure product was synthesized according to general procedure A using **3a** as a starting material and NaH instead of HCO_2Na without further purification (212 mg, 99%). Analyses were in accordance with previously reported.[13]

Furthermore transfer hydrogenation reaction was also carried out in open flask. The reaction mixture was heated at 80 °C under inert atmosphere for 15 h. GC-FID analysis confirmed 90% starting material conversion to desired product. Duren was used as an internal standard. Reduction product was not isolated.

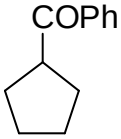
^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.20-4.12 (m, 4H), 2.21-2.11 (m, 4H), 1.71-1.62 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.7, 61.1, 60.4, 34.4, 25.4, 14.0.



2b

Ethyl 1-(phenylsulfonyl)cyclopentanecarboxylate (2b). Spectrally pure product was synthesized according to general procedure A without further purification (280 mg, 99%). Analyses were in accordance with previously reported.[14]

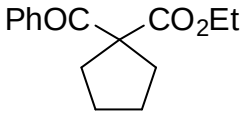
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92-7.80 (m, 2H), 7.73-7.61 (m, 1H), 7.58-7.48 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.53-2.32 (m, 4H), 1.92-1.78 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.0, 137.4, 134.0, 130.0, 128.8, 79.6, 62.5, 32.5, 25.4, 13.9.



2c

Benzoylcyclopentane (2c). Product was synthesized according to general procedure A and then purified by column chromatography to yield title compound as colorless oil (170 mg, 98%). Analyses were in accordance with previously reported.[15]

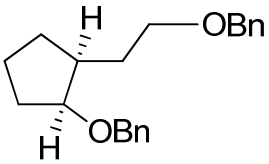
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03-7.93 (m, 2H), 7.60-7.50 (m, 1H), 7.50-7.42 (m, 2H), 3.72 (quint, *J* = 7.88 Hz, 1H), 2.06-1.85 (m, 4H), 1.83-1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.9, 137.0, 132.8, 128.6, 128.6, 46.5, 30.1, 26.4.



2e

Ethyl 1-benzoylcyclopentanecarboxylate (2e). Crude product was synthesized according to general procedure A using **3e** as starting material and NaH instead HCO_2Na. Purification by bulb-to-bulb distillation yielded title compound as colorless oil (202 mg, 98%). Analyses were in accordance with previously reported.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87-7.85 (m, 1H), 7.85-7.83 (m, 1H), 7.54-7.48 (m, 1H), 7.44-7.38 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.48-2.20 (m, 4H), 1.71 (m, 4H), 0.96 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.2, 174.9, 135.4, 132.8, 128.9, 128.5, 63.7, 61.4, 35.1, 26.4, 13.8.



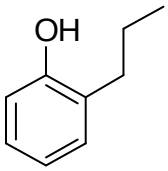
2f

(1S,2S)-1-benzyloxy-2-(benzyloxyethyl)cyclopentane (2f). Crude product was synthesized according to general procedure A and then purified by bulb-to-bulb distillation to yield **2f** (280 mg, 90%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48-7.19 (m, 10H), 4.52 (s, 2H), 4.48 (dd, *J* = 84.1, 12.1 Hz, 2H), 3.88-3.81 (m, 1H), 3.53 (t, *J* = 6.6 Hz, 3H), 2.12-1.44 (m, 9H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ = 139.5, 139.0, 128.4, 128.3, 127.7, 127.6, 127.5, 127.3, 81.7, 73.0, 70.6, 69.8, 41.8, 30.7, 29.5, 29.3, 22.0.

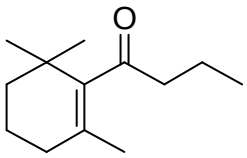
HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{21}H_{26}O_2Na$, 333.1830; found, 333.1840.



2g

2-Propylphenol (2g). Crude product was synthesized according to general procedure A and then purified by column chromatography to yield **2g** (101 mg, 74%) as colorless oil. Analyses were in accordance with previously reported.[17]

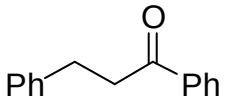
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23-7.03 (m, 2H), 6.89 (td, *J* = 7.4, 1.1 Hz, 1H), 6.77 (dd, *J* = 7.9, 1.1 Hz, 1H), 4.86 (s, 1H), 2.68-2.55 (m, 2H), 1.74-1.59 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5, 130.4, 128.5, 127.1, 120.8, 115.3, 32.1, 23.0, 14.1.



2h

1-(2,6,6-Trimethylcyclohex-1-en-1-yl)butan-1-one (2h). Spectrally pure product was synthesized according to general procedure A without further purification (161 mg, 83%). Analyses were in accordance with previously reported.[18]

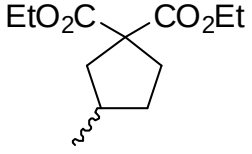
^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.50 (t, *J* = 7.4 Hz, 2H), 1.93 (t, *J* = 6.3 Hz, 2H), 1.69-1.59 (m, 4H), 1.53 (s, 3H), 1.45-1.39 (m, 2H), 1.04 (s, 6H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 212.0, 143.6, 128.7, 47.8, 39.0, 33.3, 31.2, 28.8, 20.95, 19.0, 16.7, 13.9.



2i

1,3-Diphenylpropan-1-one (2i). Crude product was synthesized according to general procedure A and then purified by crystallization to yield **2i** (191 mg, 91%) as white crystals. Analyses were in accordance with previously reported.[19]

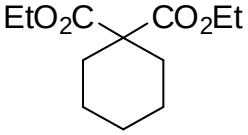
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02-7.92 (m, 2H), 7.60-7.52 (m, 1H), 7.50-7.41 (m, 2H), 7.35-7.17 (m, 5H), 3.34-3.27 (m, 2H), 3.12-3.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.3, 141.4, 136.9, 133.2, 128.7, 128.6, 128.5, 128.2, 126.3, 40.6, 30.2.



2j

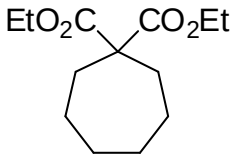
Diethyl 3-methylcyclopentane-1,1-dicarboxylate (2j). Crude product was synthesized according to general procedure A and then purified by bulb-to-bulb distillation (98 mg, 43%). Analyses were in accordance with previously reported.[20]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.16 (q, *J* = 7.1 Hz, 4H), 2.43 (dd, *J* = 13.3, 7.1 Hz, 1H), 2.35-2.25 (m, 1H), 2.19-2.08 (m, 1H), 2.07-1.97 (m, 1H), 1.88-1.78 (m, 1H), 1.65 (dd, *J* = 13.3, 10.1 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 6H), 1.00 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.8, 61.2, 60.4, 42.5, 34.4, 34.1, 34.0, 19.6, 14.0.



2k

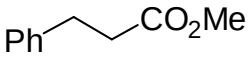
Diethyl cyclohexane-1,1-dicarboxylate (2k). Incomplete conversion was obtained and crude product was a mixture of substrate and hydrogenation product in ratio 50 : 50 and 20 : 80 when reaction was carried out 120 h and 336 h respectively (determined by NMR). Hydrogenation product was not isolated.



2d

Diethyl cycloheptane-1,1-dicarboxylate (2d). Spectrally pure product was synthesized according to general procedure A without further purification (228 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.14 (q, *J* = 7.1 Hz, 4H), 2.11-2.05 (m, 4H), 1.60-1.47 (m, 8H), 1.21 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.1, 61.2, 57.7, 33.8, 29.9, 23.9, 14.2.

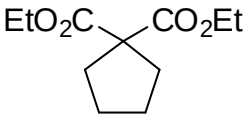


2l

Methyl 3-phenylpropanoate (2l). Crude product was synthesized according to general procedure A and then purified by column chromatography to yield **2l** (158 mg, 96%). Analyses were in accordance with previously reported.[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45-7.10 (m, 5H), 3.67 (s, 3H), 2.95 (t, *J* = 7.9 Hz, 2H), 2.63 (t, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.5, 140.6, 128.6, 128.4, 126.39, 51.8, 35.8, 31.1.

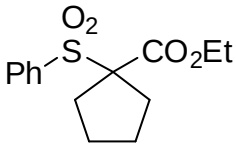
5. Sequential Ring Closing Metathesis / Transfer Hydrogenation Reaction of selected diens



2a

Diethyl cyclopentane-1,1-dicarboxylate (2a). Product was synthesized according to general procedure B using diene **1a** as a starting material and NaH instead of HCO_2Na. Spectrally pure product was isolated by extraction (214 mg, 99%). Analyses were in accordance with previously reported.[13]

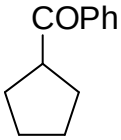
^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.20-4.12 (m, 4H), 2.21-2.11 (m, 4H), 1.71-1.62 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.7, 61.1, 60.4, 34.4, 25.4, 14.0.



2b

Ethyl 1-(phenylsulfonyl)cyclopentanecarboxylate (2b). Product was synthesized according to general procedure B using diene **1b** as a starting material. Purification by using column chromatography afforded spectrally pure product **2b** (273 mg, 97%). Analyses were in accordance with previously reported.[14]

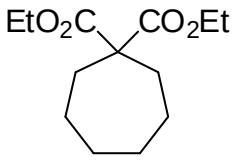
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.80 (m, 2H), 7.73-7.61 (m, 1H), 7.58-7.48 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.53-2.32 (m, 4H), 1.92-1.78 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.0, 137.4, 134.0, 130.0, 128.8, 79.6, 62.5, 32.5, 25.45, 13.9.



2c

Benzoylcyclopentane (2c). Product was synthesized according to general procedure B using **1c** as a starting material. Purification by using column chromatography afforded spectrally pure product **2c** (160 mg, 92%). Analyses were in accordance with previously reported.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03-7.93 (m, 2H), 7.60-7.50 (m, 1H), 7.50-7.42 (m, 2H), 3.72 (quint, *J* = 7.88 Hz, 1H), 2.06-1.85 (m, 4H), 1.83-1.54 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.9, 137.0, 132.8, 128.6, 128.6, 46.5, 30.1, 26.4.

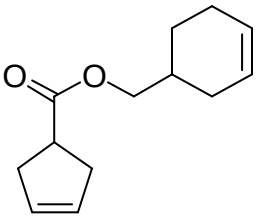


2d

Diethyl cycloheptane-1,1-dicarboxylate (2d). Product was synthesized according to general procedure B using **1c** as a starting material. Spectrally pure product was isolated by extraction (204 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.14 (q, *J* = 7.1 Hz, 4H), 2.11-2.05 (m, 4H), 1.60-1.47 (m, 8H), 1.21 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.1, 61.2, 57.7, 33.8, 29.9, 23.9, 14.2.

6. Ring Closing Metathesis and transfer hydrogenation reaction sequence of tetraene 1m



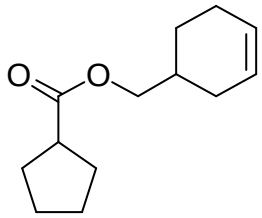
3m

Cyclohex-3-en-1-ylmethyl cyclopent-3-enecarboxylate (3m). Compound **3m** was prepared according to procedure reported for synthesis of **3a** starting from **1m** (64 mg, 0.243 mmol), **Gru-II** (6 mg,

0.0073 mmol). Crude product was purified by column chromatography to afford title ester **3l** (44 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.74-5.57 (m, 4H), 3.99 (d, *J* = 6.6 Hz, 2H), 3.25-3.04 (m, 1H), 2.75-2.57 (m, 4H), 2.16-2.02 (m, 3H), 2.02-1.89 (m, 1H), 1.82-1.70 (m, 2H), 1.39-1.18 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 176.2, 129.0, 127.0, 125.5, 68.8, 41.7, 36.3, 33.1, 28.2, 25.3, 24.4.

HRMS (ESI): *m*/*z* $[M+Na]^+$ calcd for $C_{13}H_{18}O_2Na$, 229.1204; found, 229.1215.



2m

Procedure A

Cyclohex-3-en-1-ylmethyl cyclopentanecarboxylate (2m). Compound **2m** was synthesized according to general procedure A using **3m** (20.6 mg 0.1 mmol), **Gru-II** (1.7 mg, 0.002 mmol), HCO_2Na (1.4 mg, 0.02 mmol), HCO_2H (189 µL, 5mmol) and durene (5.4 mg, 0.04 mmol) as internal standard. Crude product was isolated according to procedure A and was analyzed by GC-FID (92% GC yield).

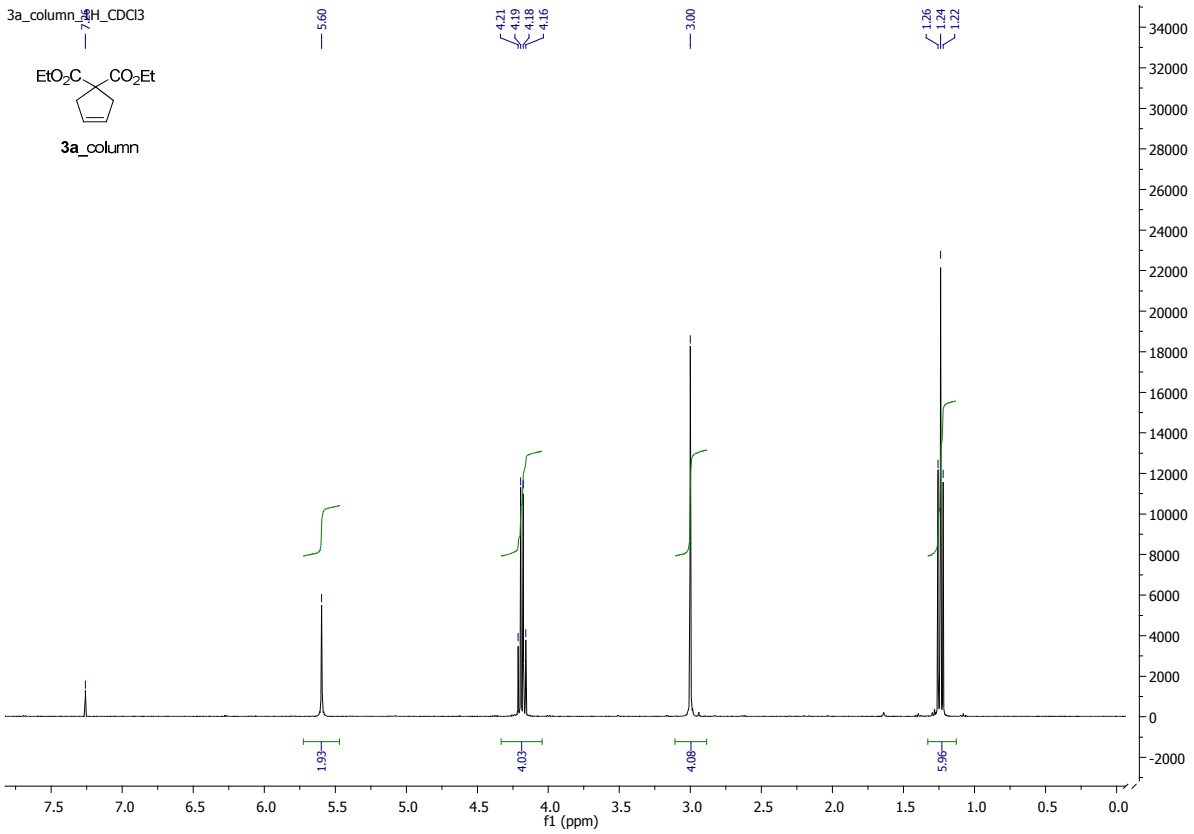
Procedure B

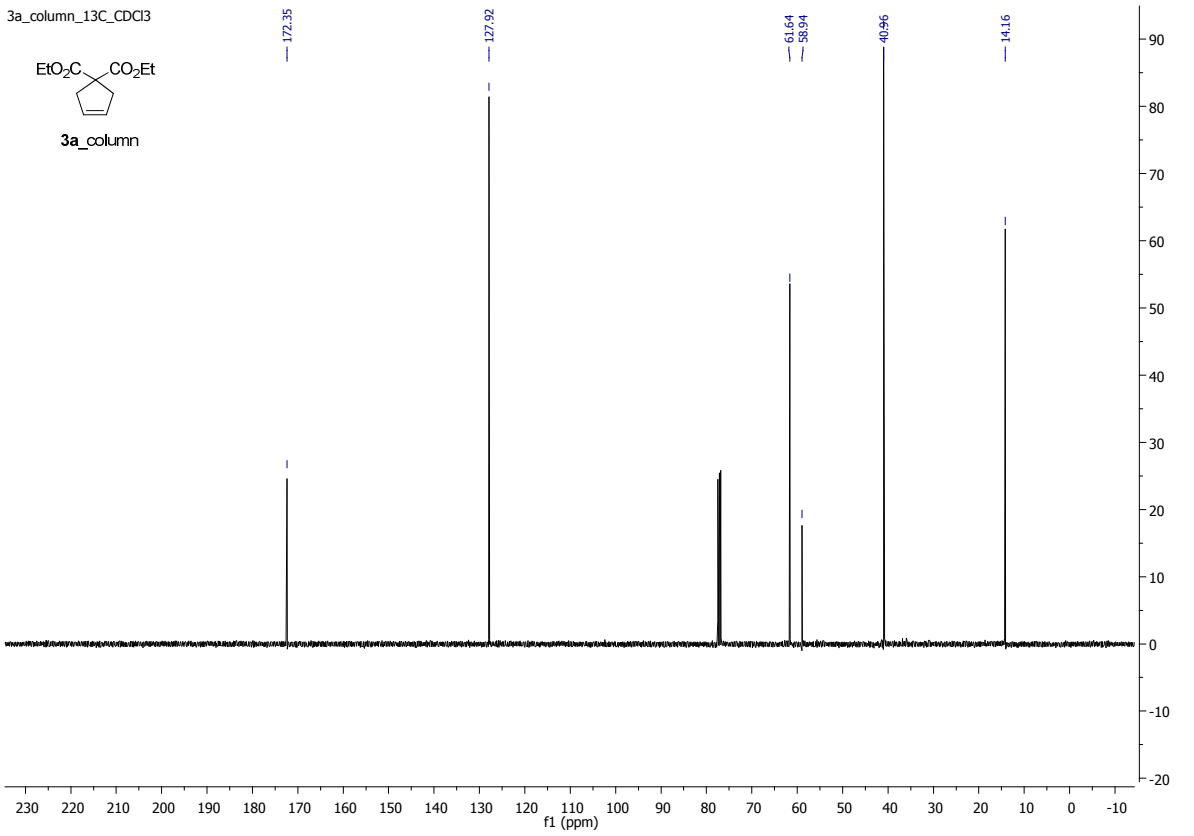
Compound **2m** was synthesized according to general procedure B using **1m** (20.6 mg 0.1 mmol), **Gru-II** (1.7 mg, 0.002 mmol). RCM reaction was carried out for 0.5 h at 40 °C. Then second portion of **Gru-II** (1.7 mg, 0.002 mmol), HCO_2Na (1.36 mg, 0.02 mmol), HCO_2H (189 µL, 5 mmol) and durene (5.4 mg, 0.04 mmol) as internal standard were added and reaction mixture was stirred for 4 h at 80 °C. Crude product was isolated according to procedure B and was analyzed by GC-FID (90% GC yield).

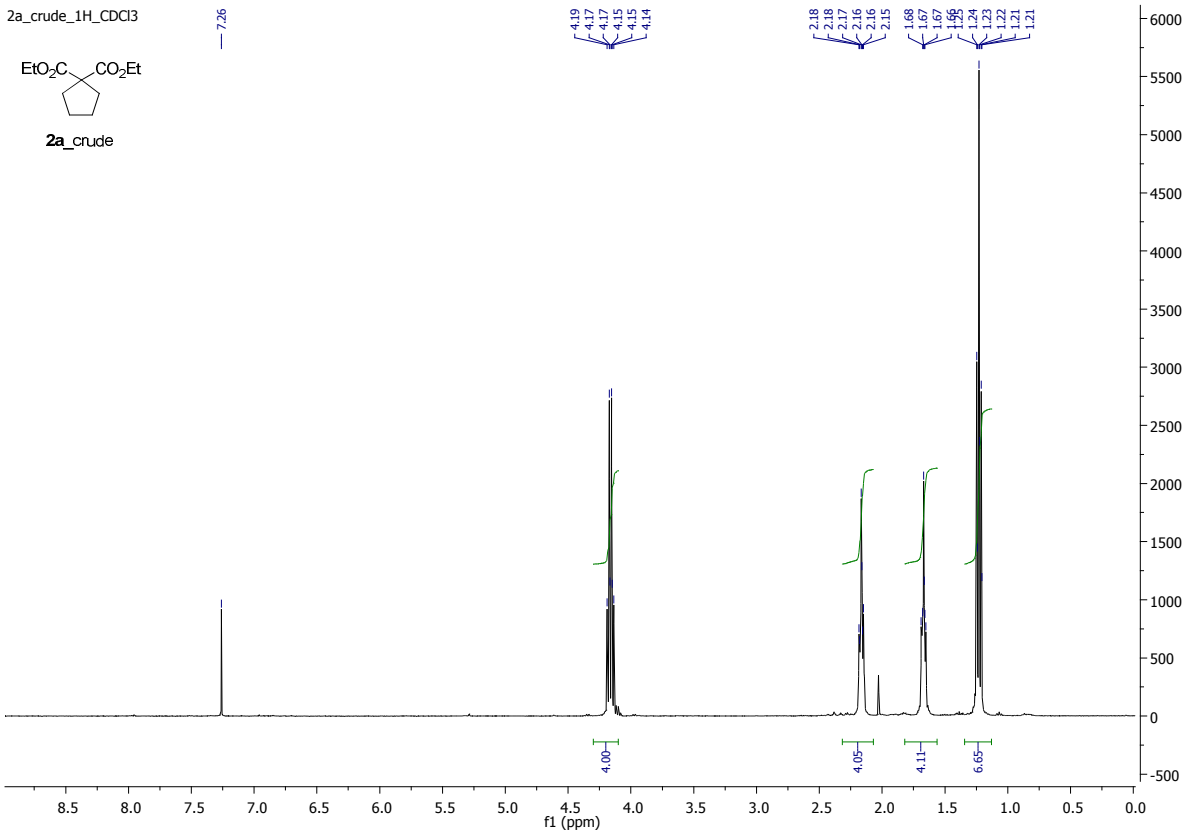
7. Evidence of ruthenium hydride species

Grubbs second generation catalyst (17 mg, 0.02 mmol) was placed in dry NMR tube and diluted with THF-d_8 (0.5mL) followed by addition of formic acid (15µL, 0.4 mmol). Then the tube was closed and reaction mixture was heated at 50 °C for 4h. After that time the reaction mixture was cooled down to room temperature and NMR spectrum was measured. A new signal with chemical shift -6.86 ppm appeared. This chemical shift is in the range characteristic for ruthenium hydride species.[22]

8. NMR spectra



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CO2Et
2a_crude
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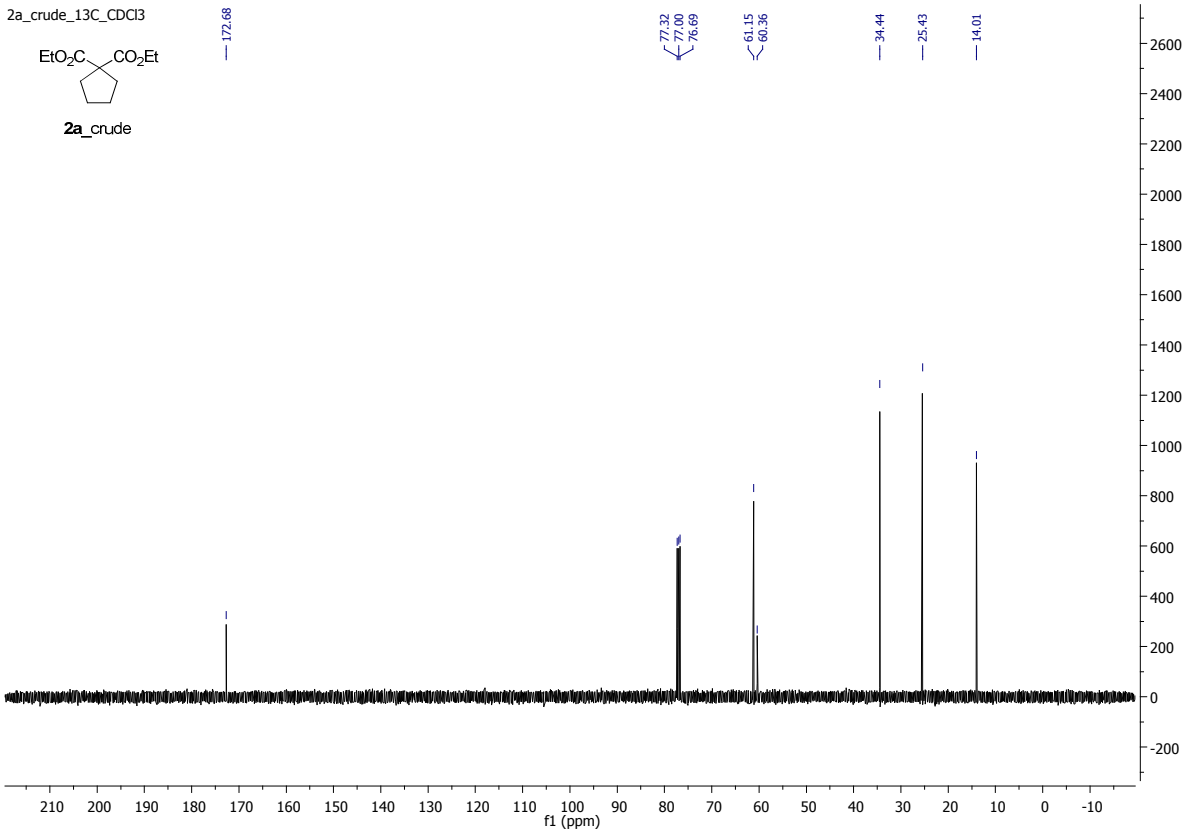
4.19
4.17
4.17
4.15
4.15
4.14
2.18
2.18
2.17
2.16
2.16
2.15
1.68
1.67
1.67
1.24
1.23
1.22
1.21
1.21
4.00
4.05
4.11
6.65
f1 (ppm)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CO2Et
2a_crude
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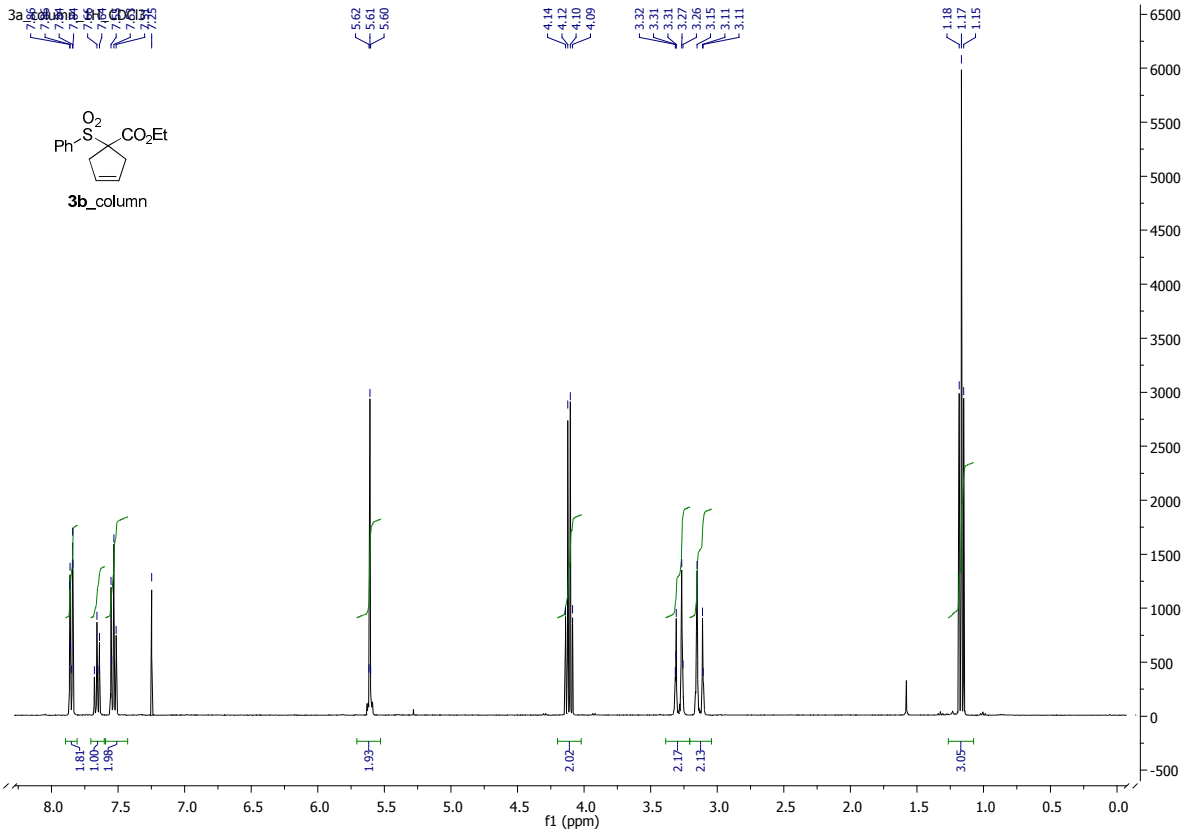
76.69
61.15
60.36
34.44
25.43
14.01
f1 (ppm)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3.31
3.31
3.27
3.26
3.15
3.11
3.11
1.18
1.17
1.15
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1.00
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1.93
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2.13
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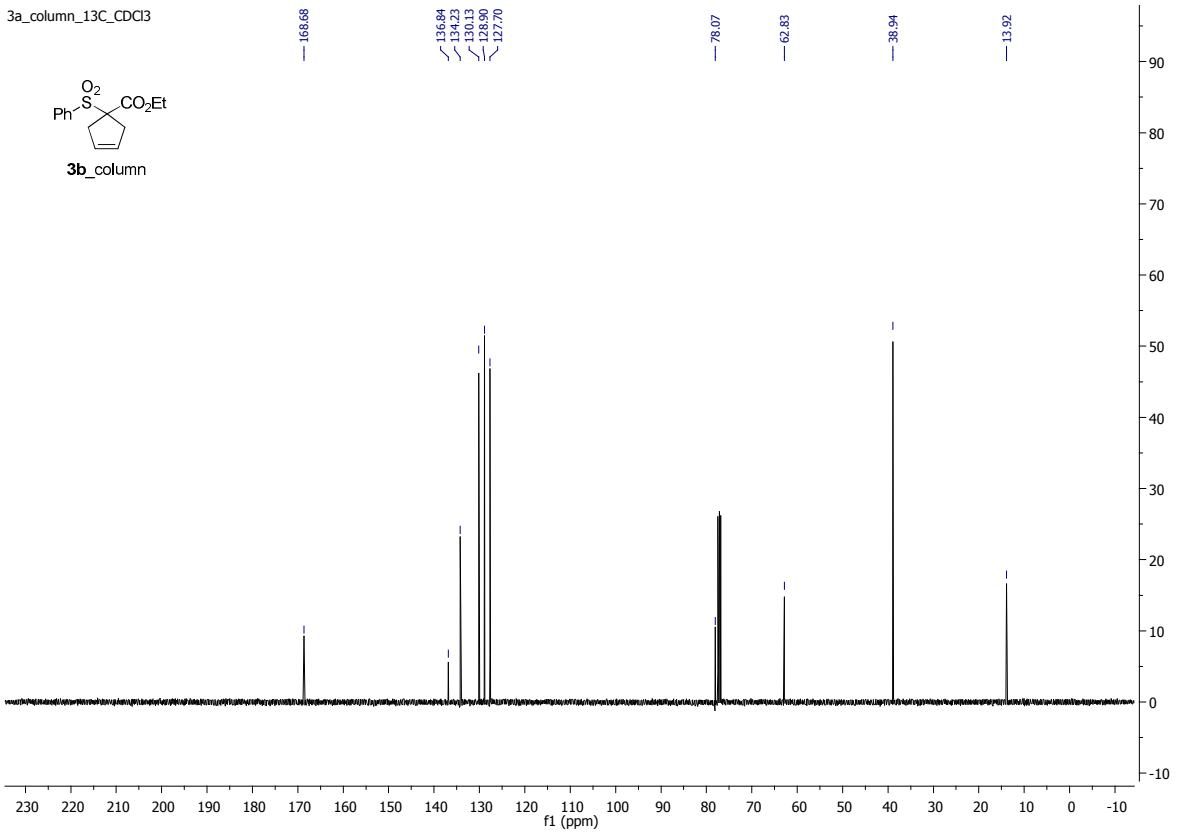
f1 (ppm)
3b_column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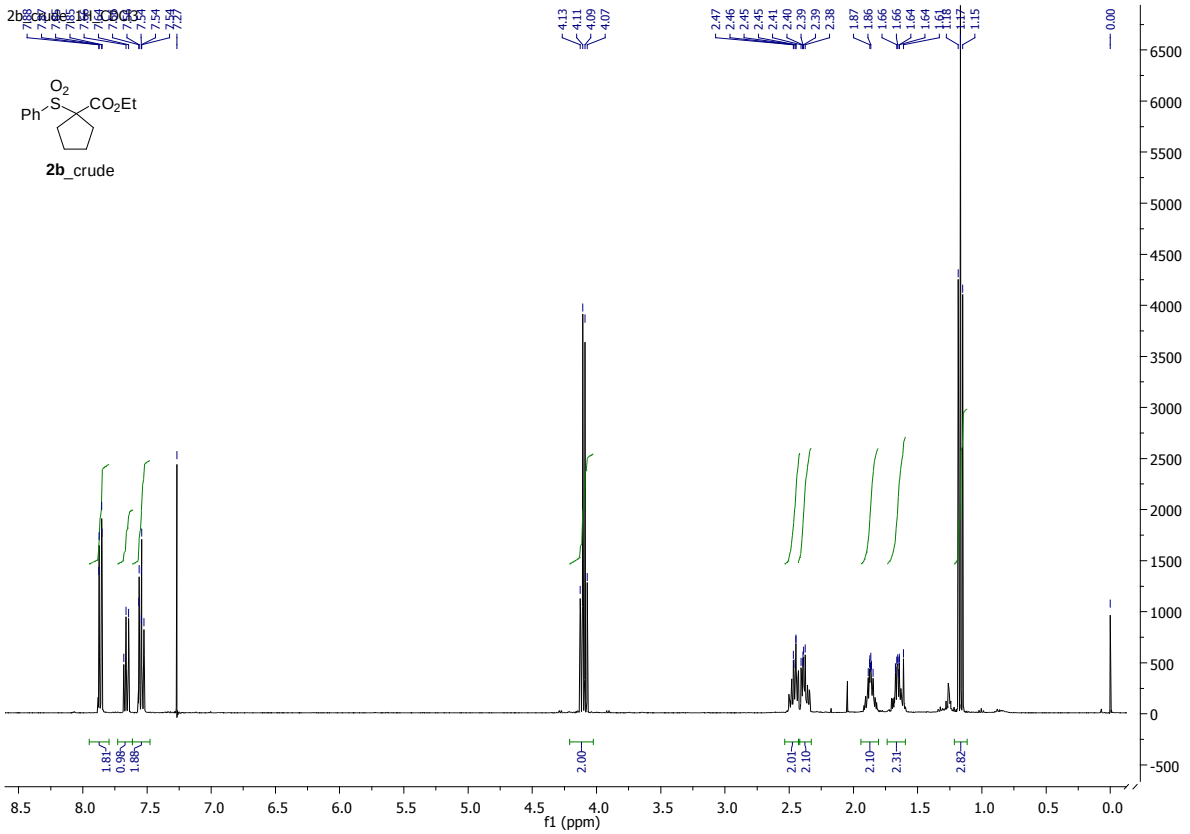
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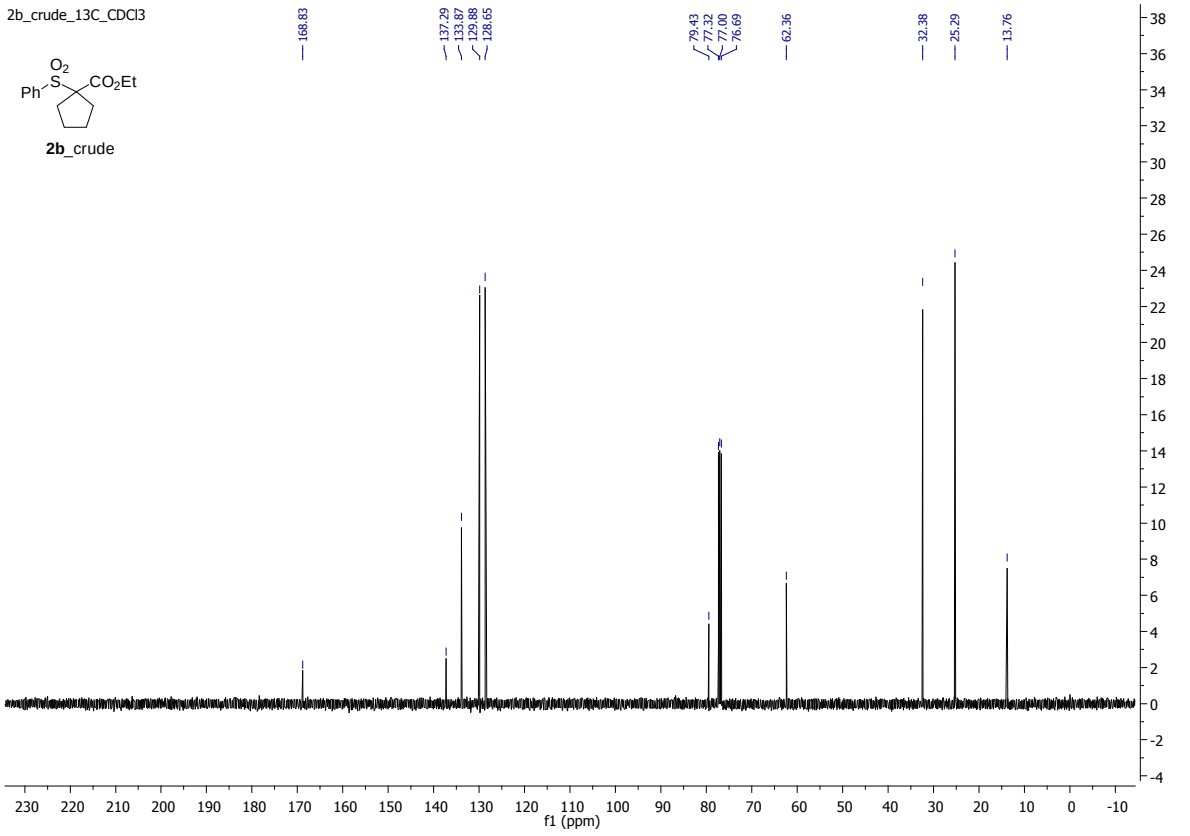
2.39
2.38
1.87
1.86
1.66
1.64
1.18
1.17
1.15
0.00
1.81
0.98
1.88
2.00
2.01
2.10
2.10
2.31
2.82
f1 (ppm)
O2
S
Ph
CO2Et
2b_crude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129.88
128.65
79.43
77.32
77.00
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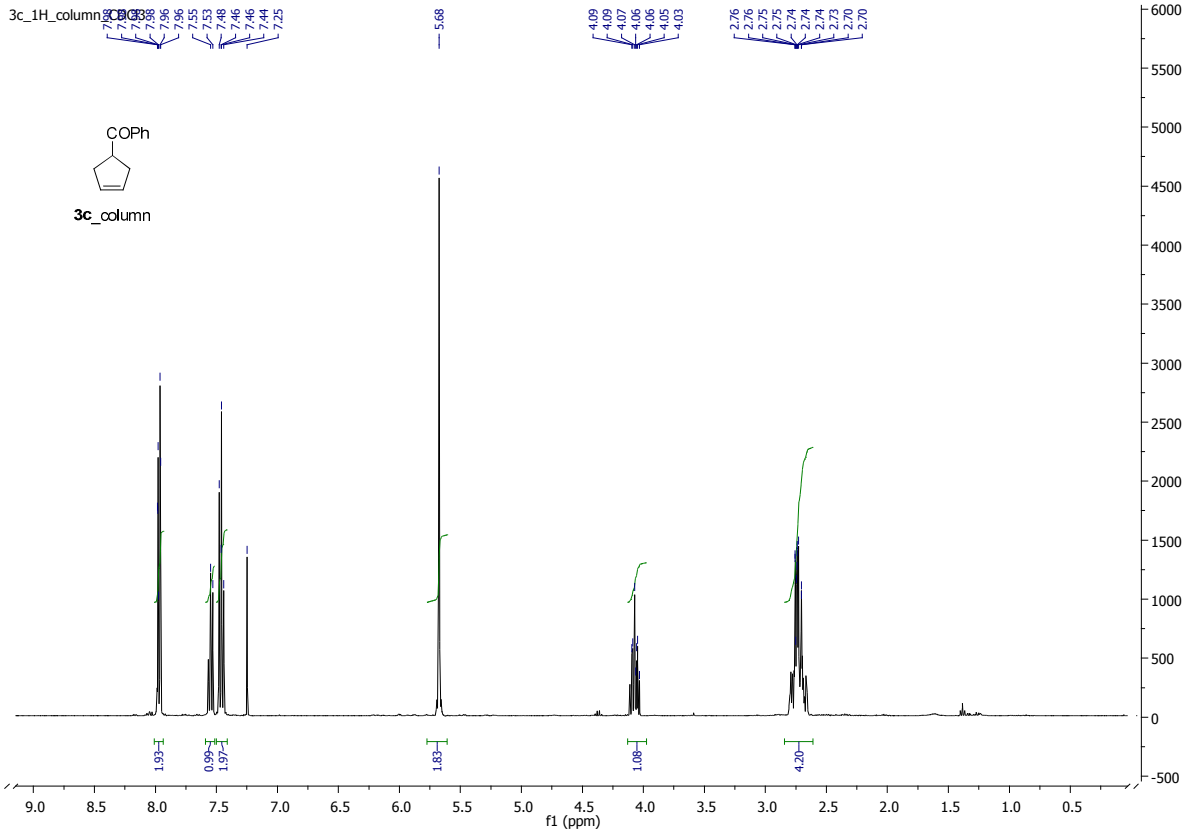
62.36
32.38
25.29
13.76
f1 (ppm)
O2
S
Ph
CO2Et
2b_crude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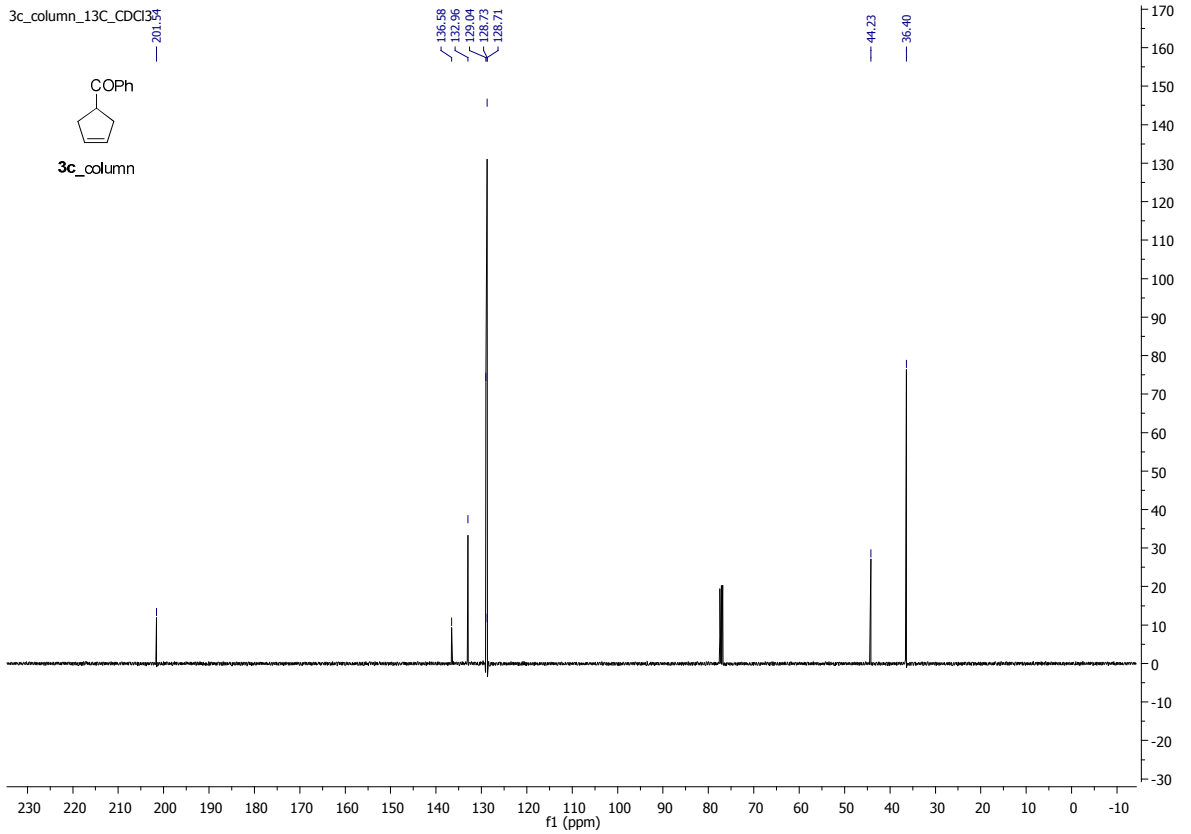
COPh
3c_column
f1 (ppm)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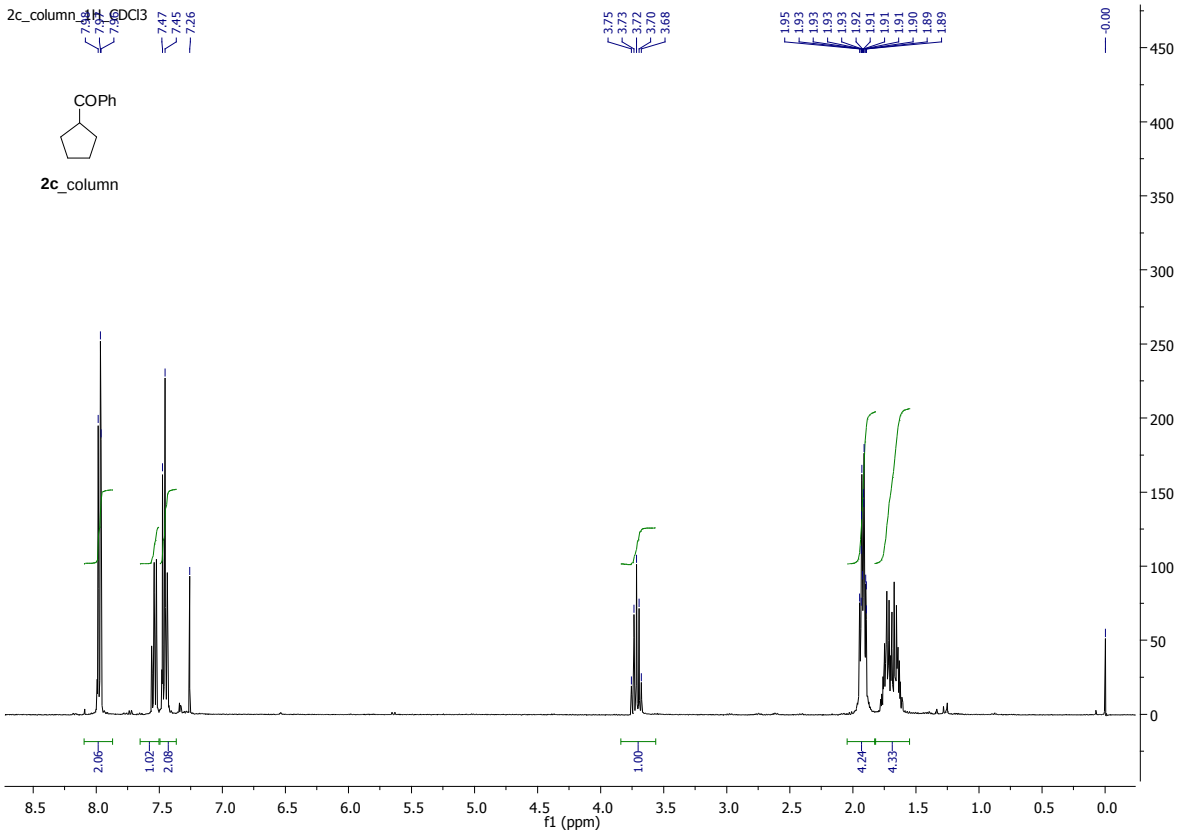
COPh
3c_column
f1 (ppm)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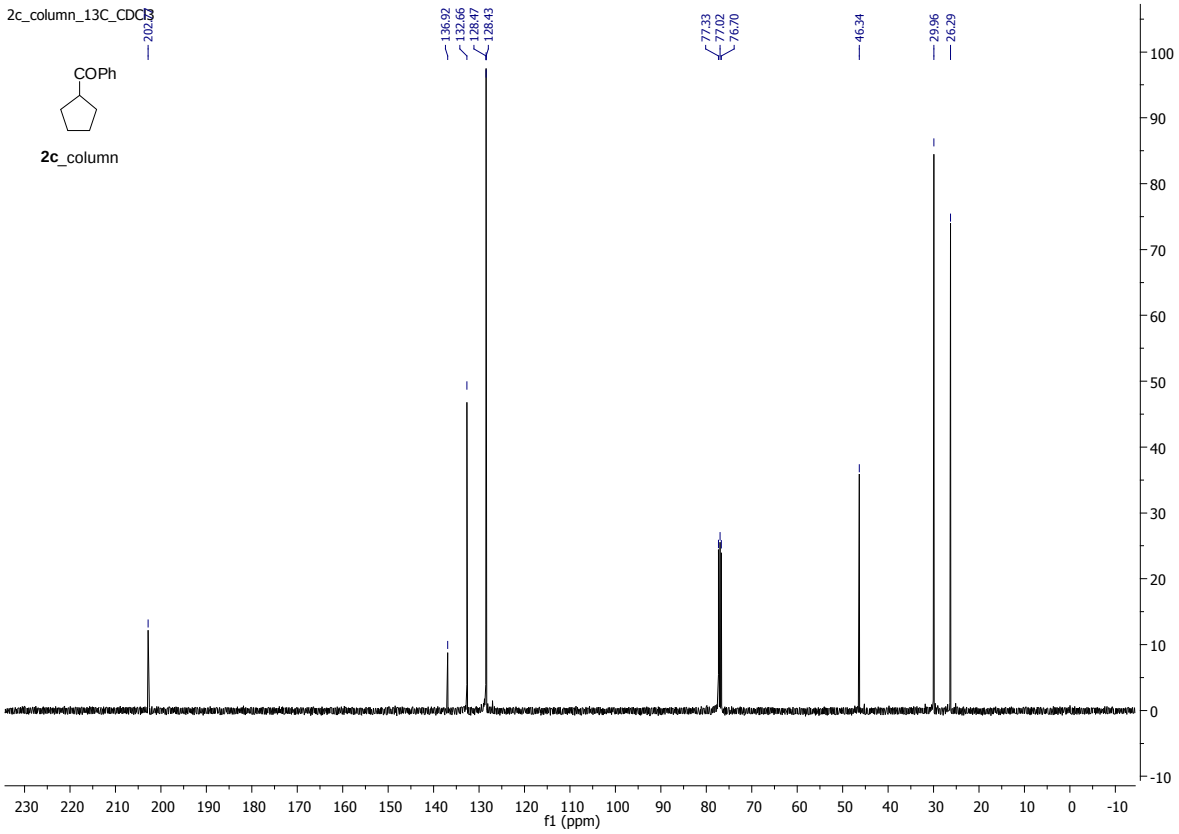
COPh
2c_column
f1 (ppm)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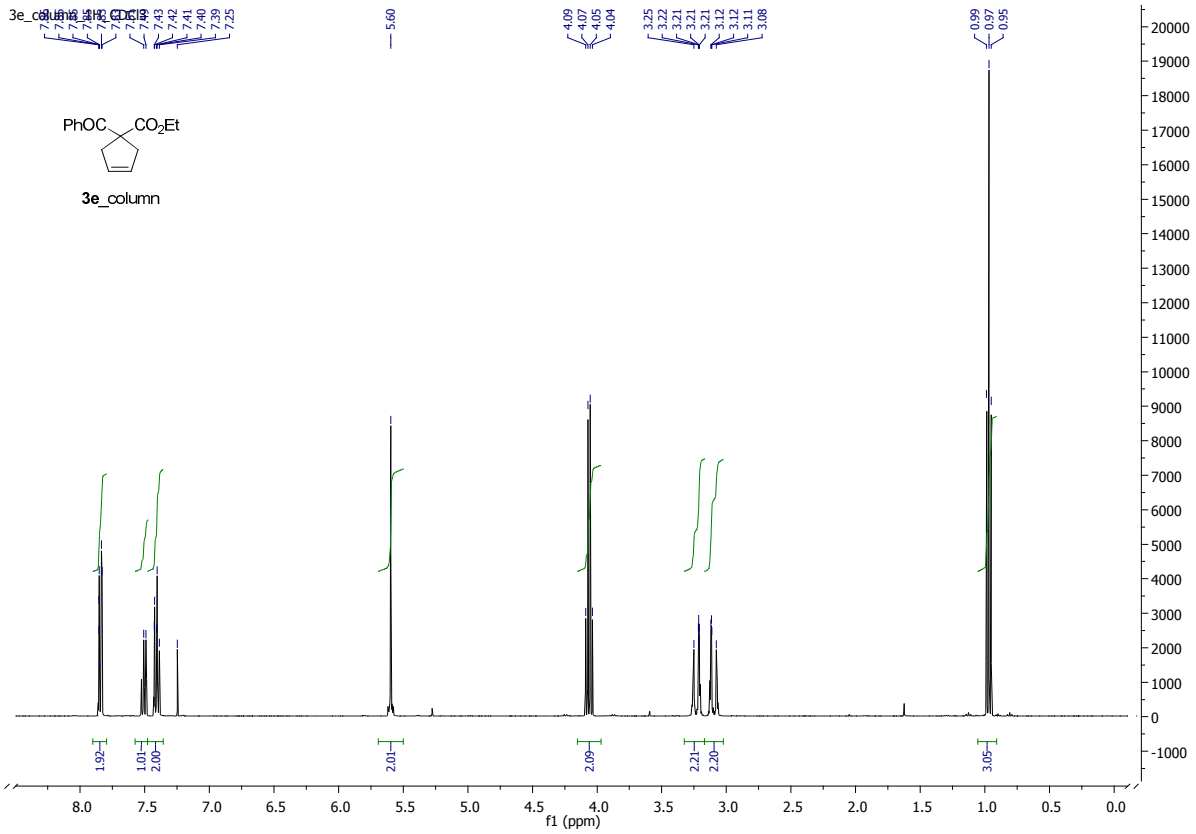
2c_column
f1 (ppm)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CO2Et
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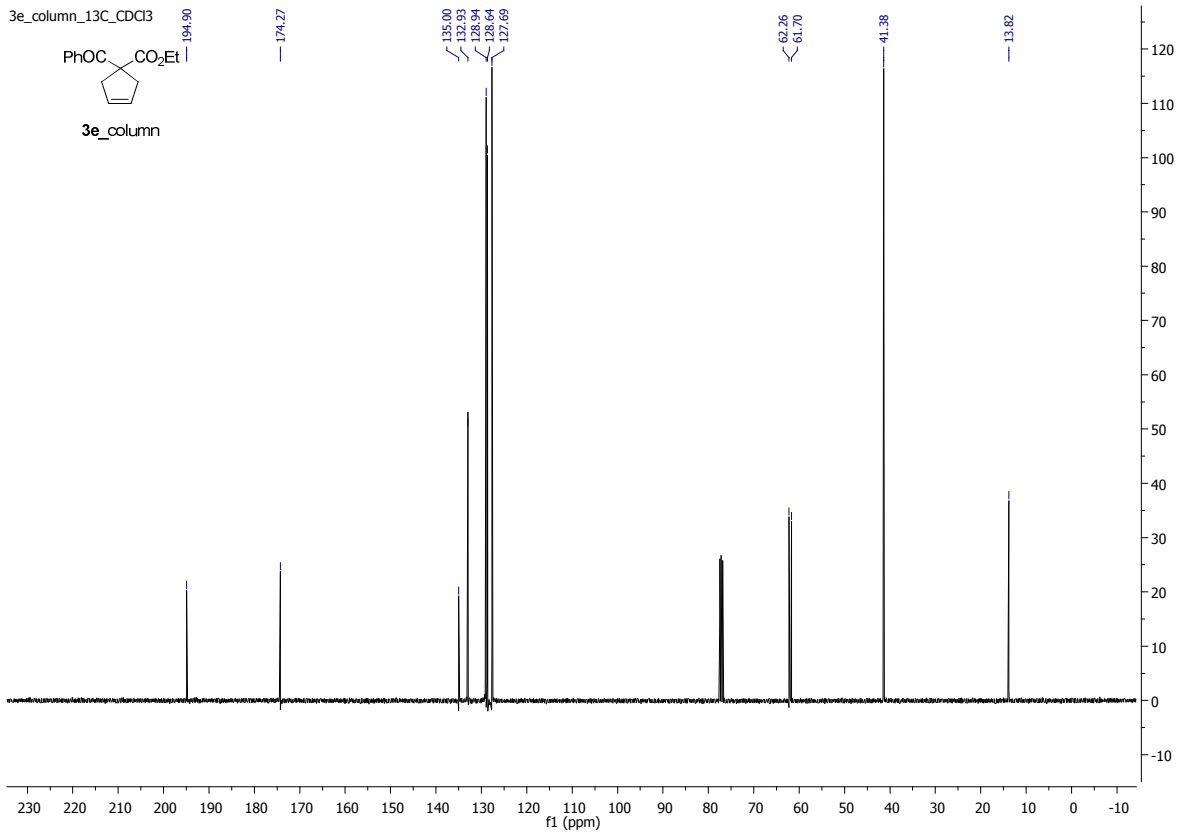
4.09
4.07
4.05
4.04
3.25
3.22
3.21
3.21
3.21
3.12
3.11
3.08
0.99
0.97
0.95
1.92
1.01
2.00
2.01
2.09
2.21
2.20
3.05
f1 (ppm)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CO2Et
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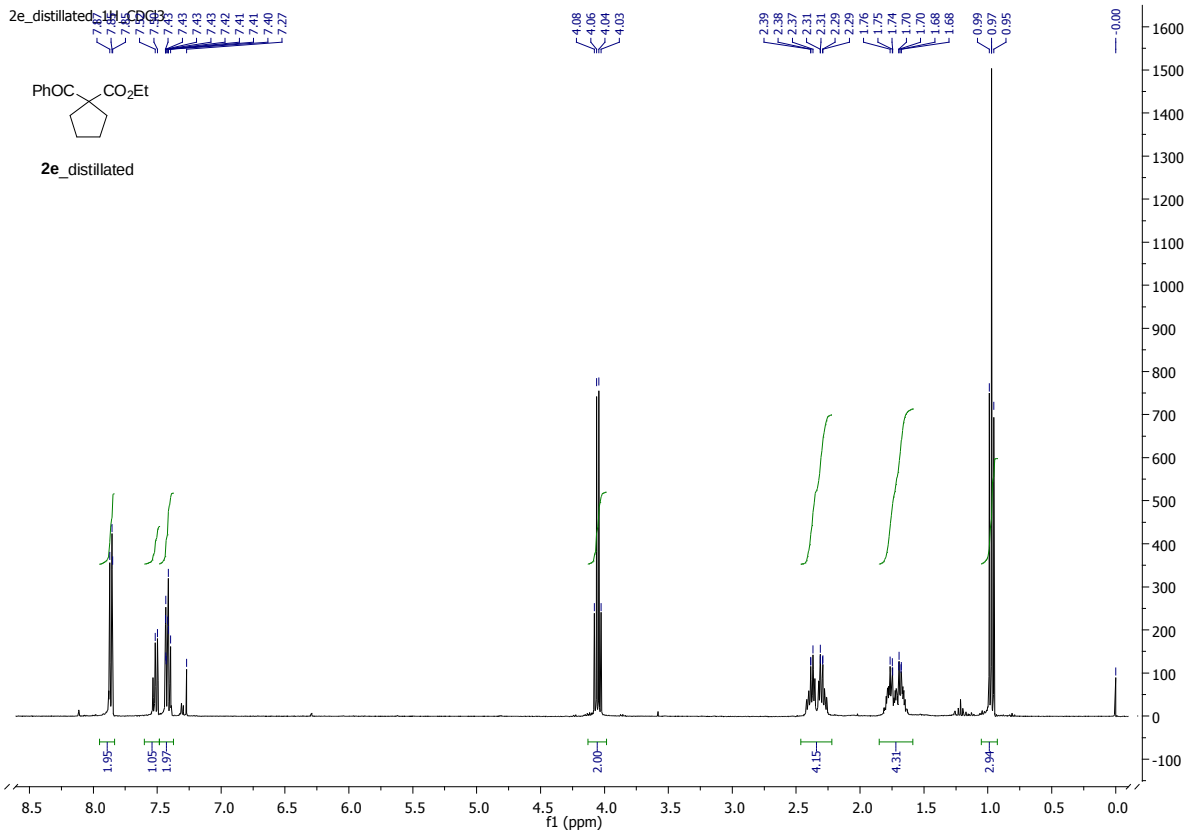
13.82
f1 (ppm)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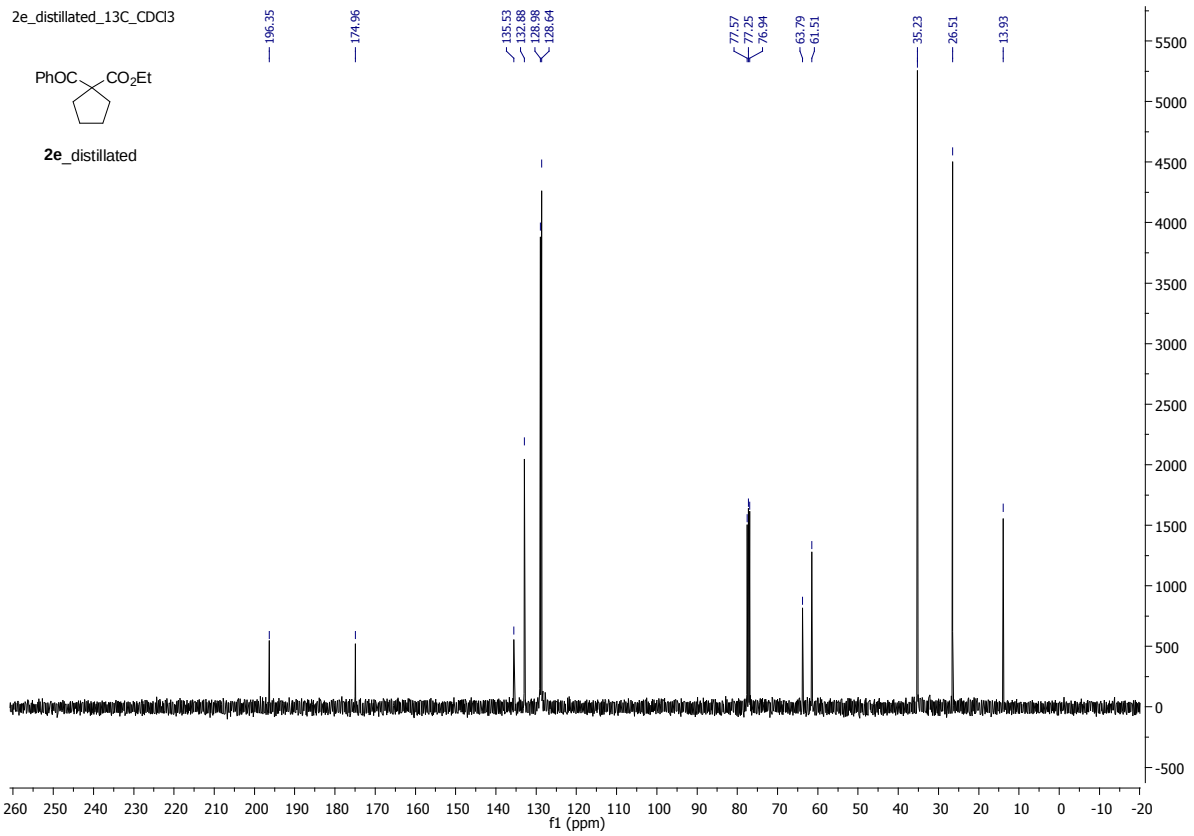
CO2Et
2e_distilled
f1 (ppm)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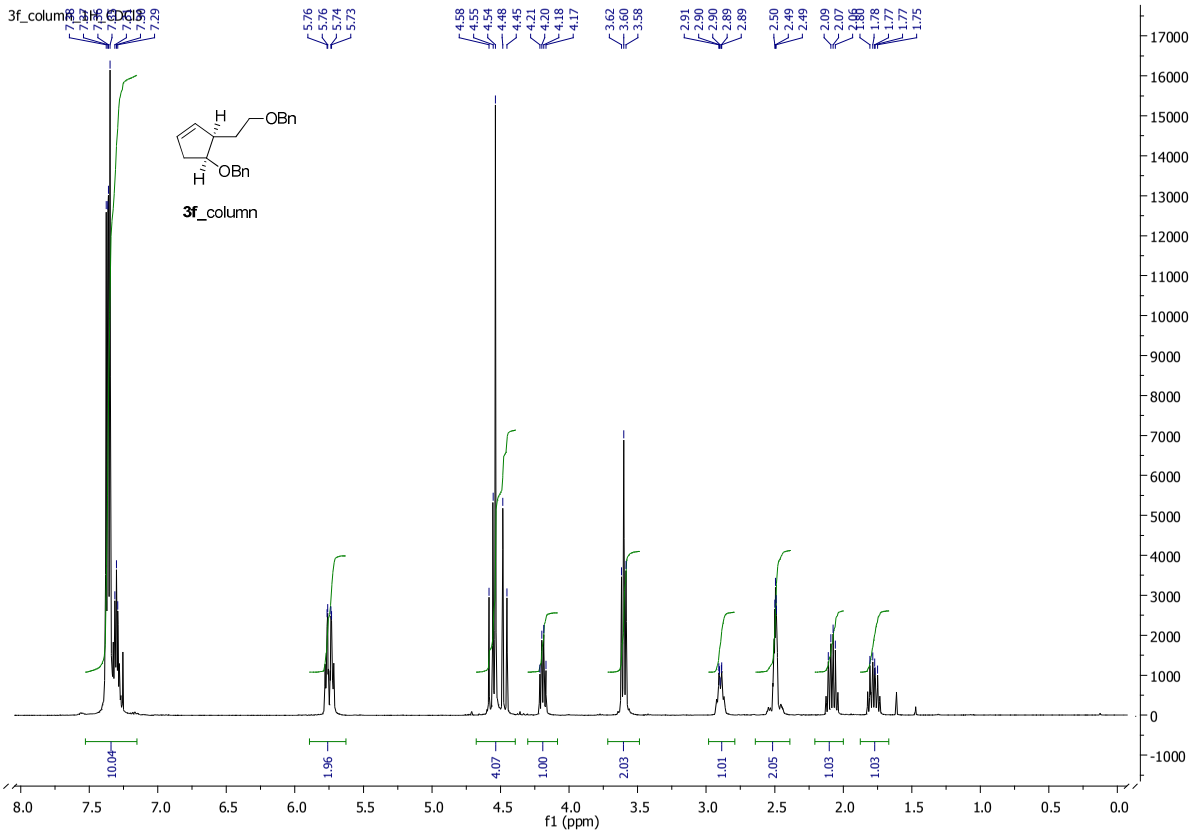
PhOC
CO2Et
2e_distilled
f1 (ppm)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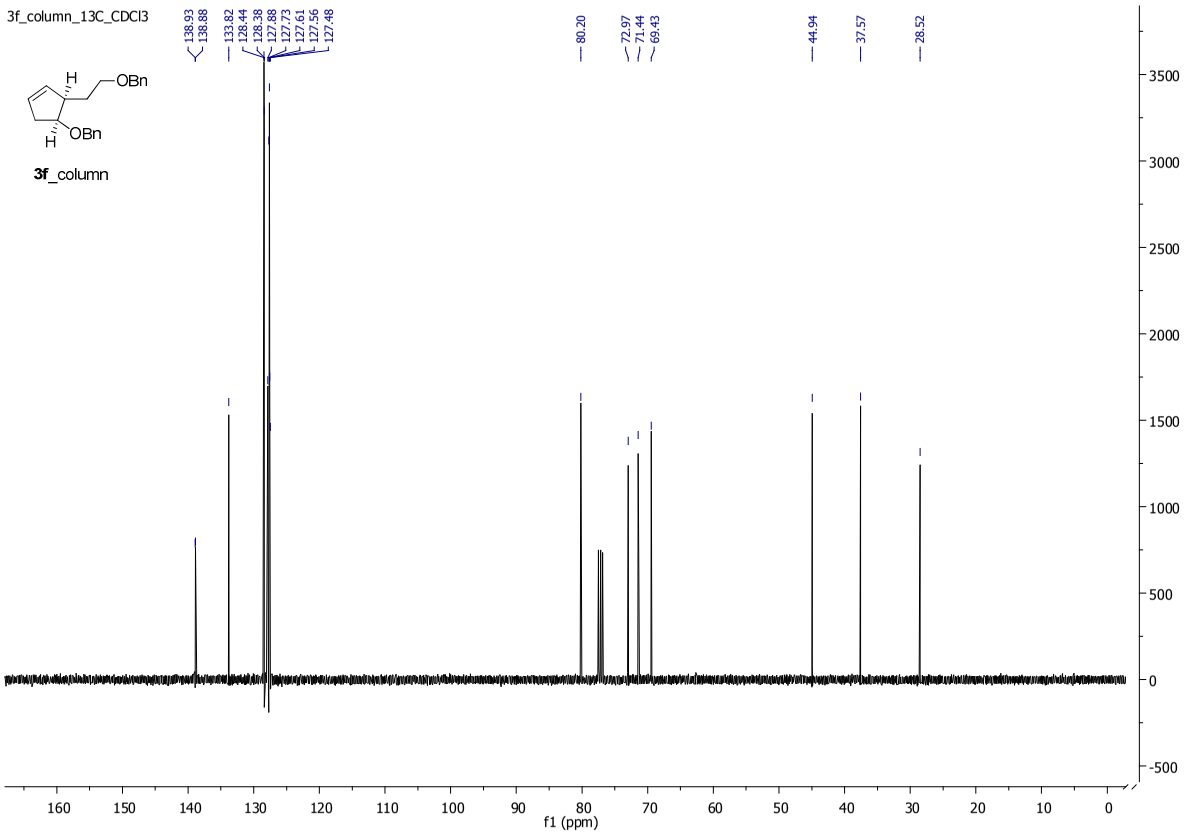
OBn
OBn
3f_column
f1 (ppm)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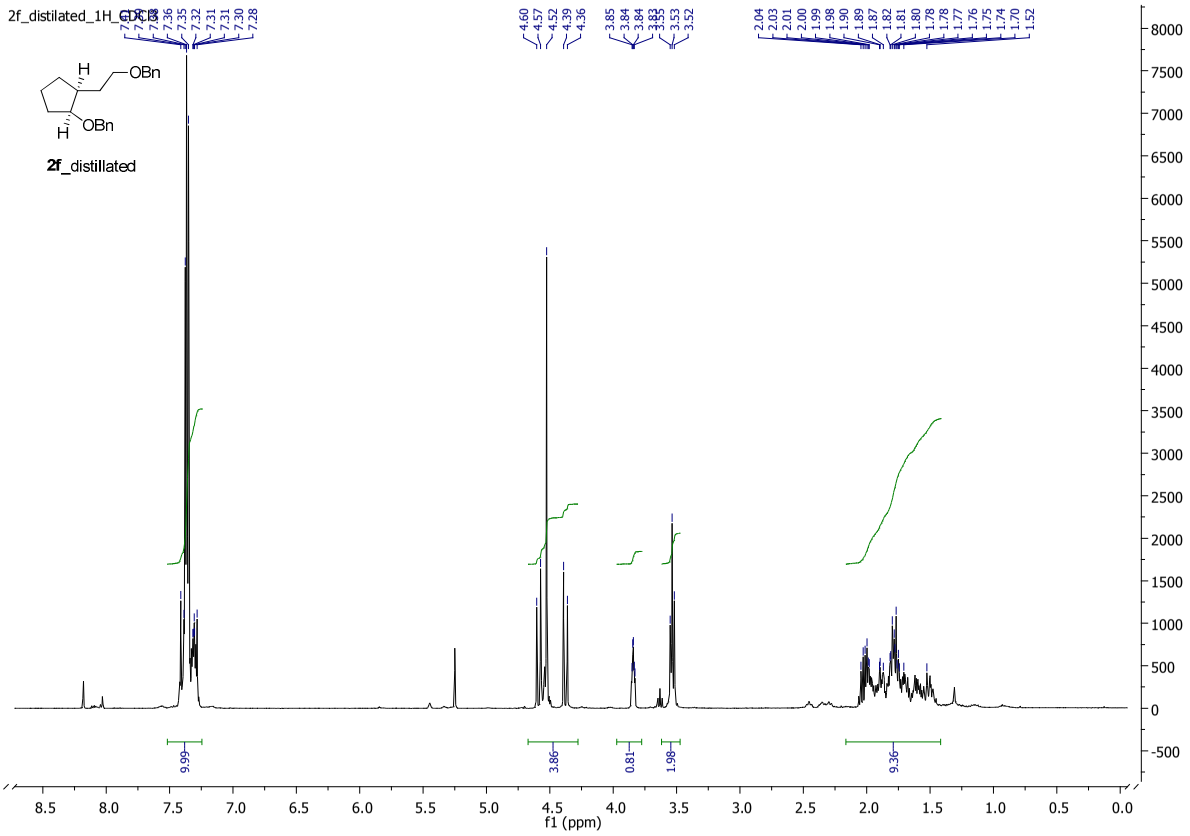
OBn
OBn
3f_column
f1 (ppm)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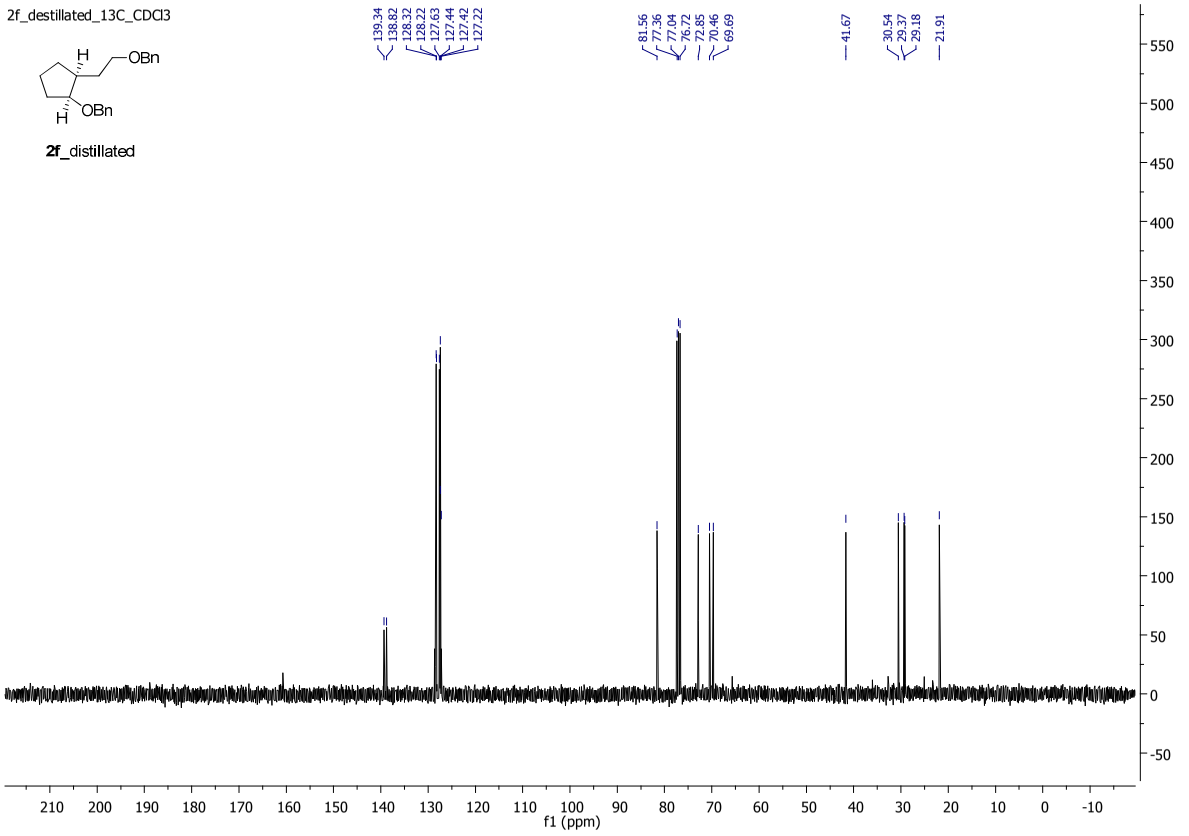
OBn
2f_distillated
f1 (ppm)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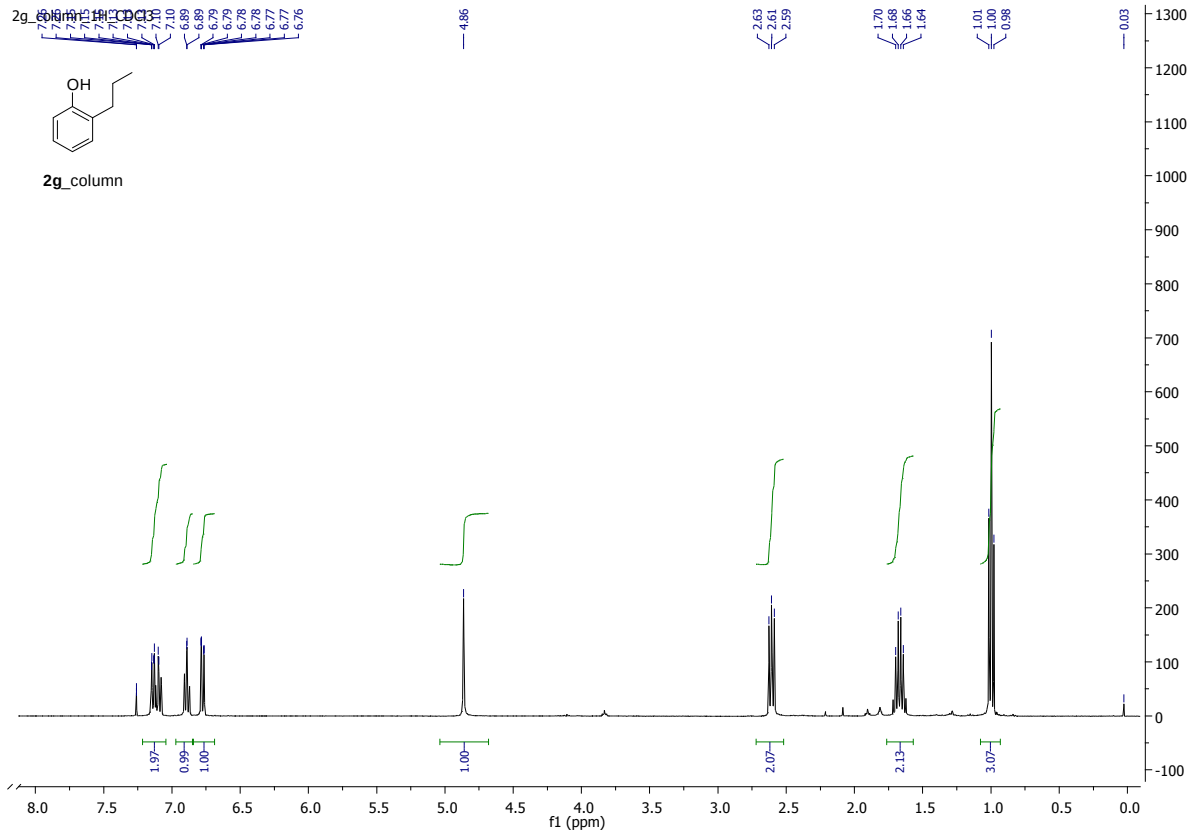
OBn
OBn
2f_distillated
f1 (ppm)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2g_column
4.86
2.63
2.61
2.59
1.70
1.68
1.66
1.64
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1.00
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0.03
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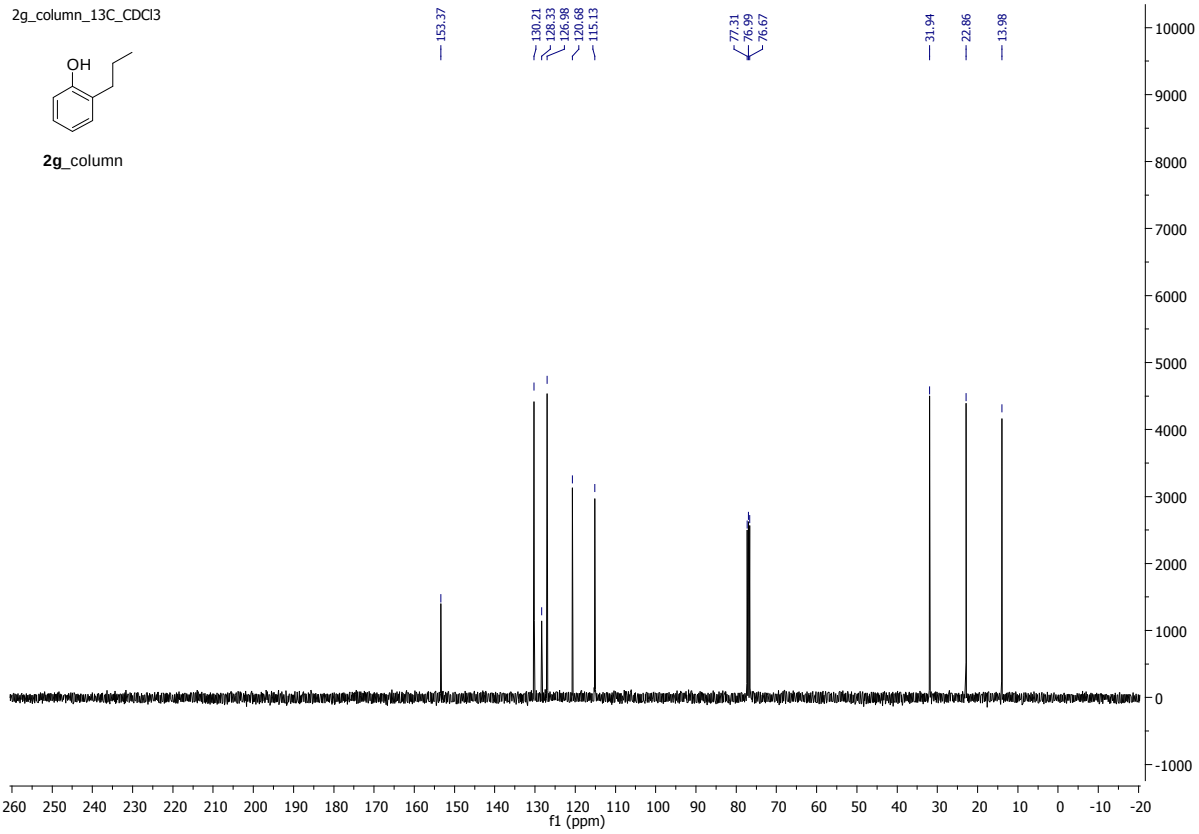
0.99
1.00
1.00
2.07
2.13
3.07
f1 (ppm)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OH
2g_column
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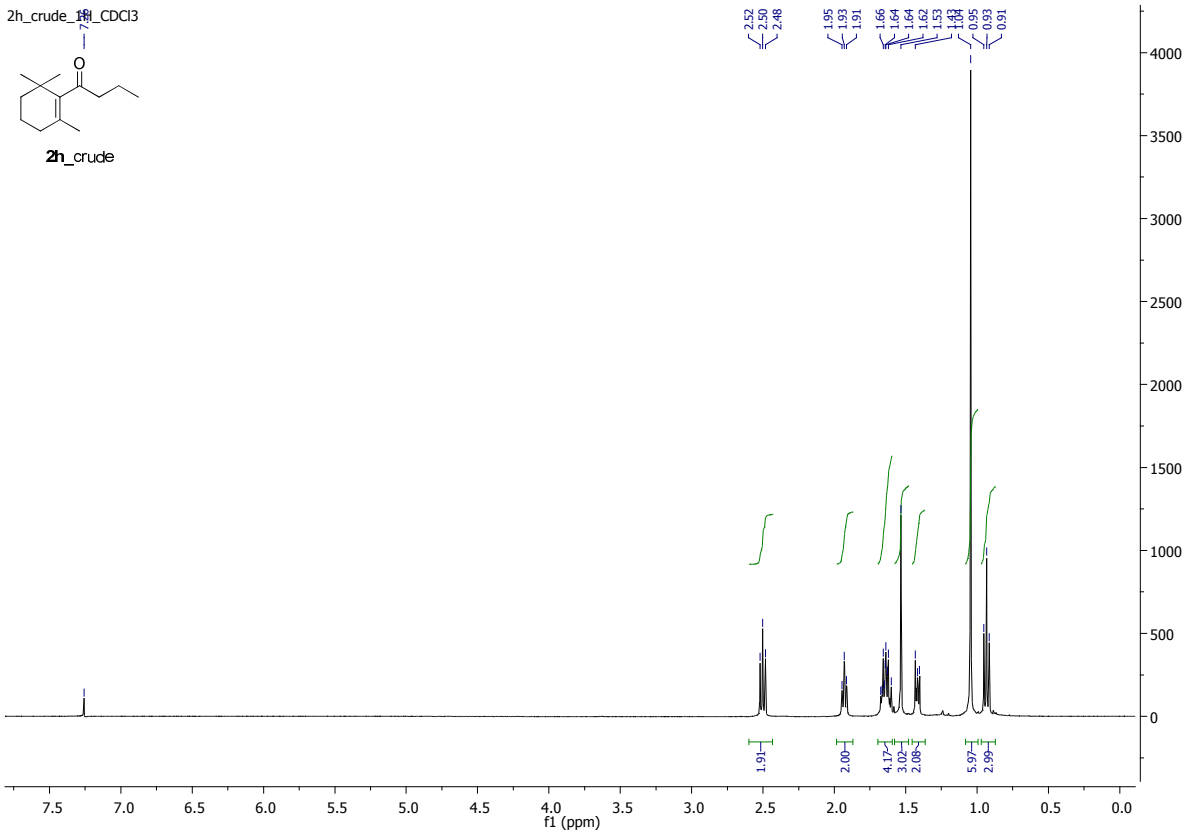
76.99
76.67
31.94
22.86
13.98
f1 (ppm)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1.66
1.64
1.64
1.62
1.53
1.43
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0.93
0.91
1.91
2.00
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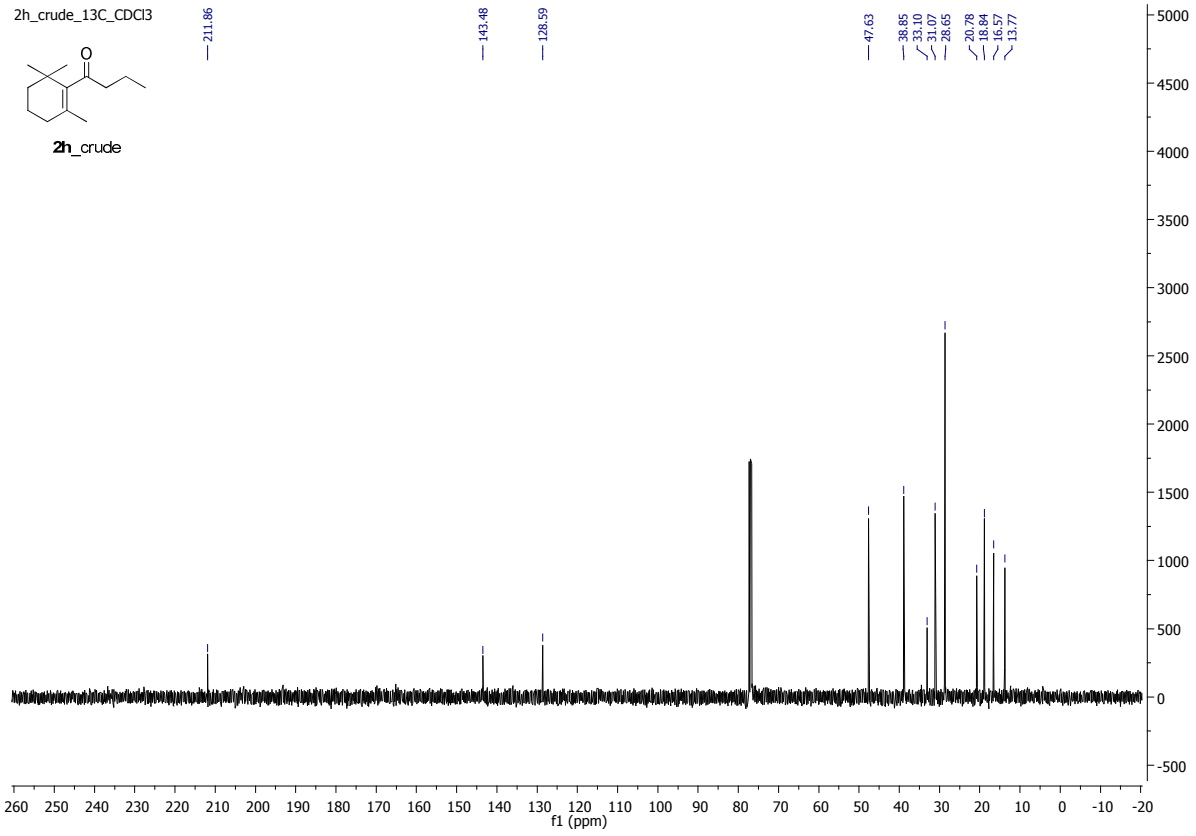
3.02
2.08
5.97
2.99
f1 (ppm)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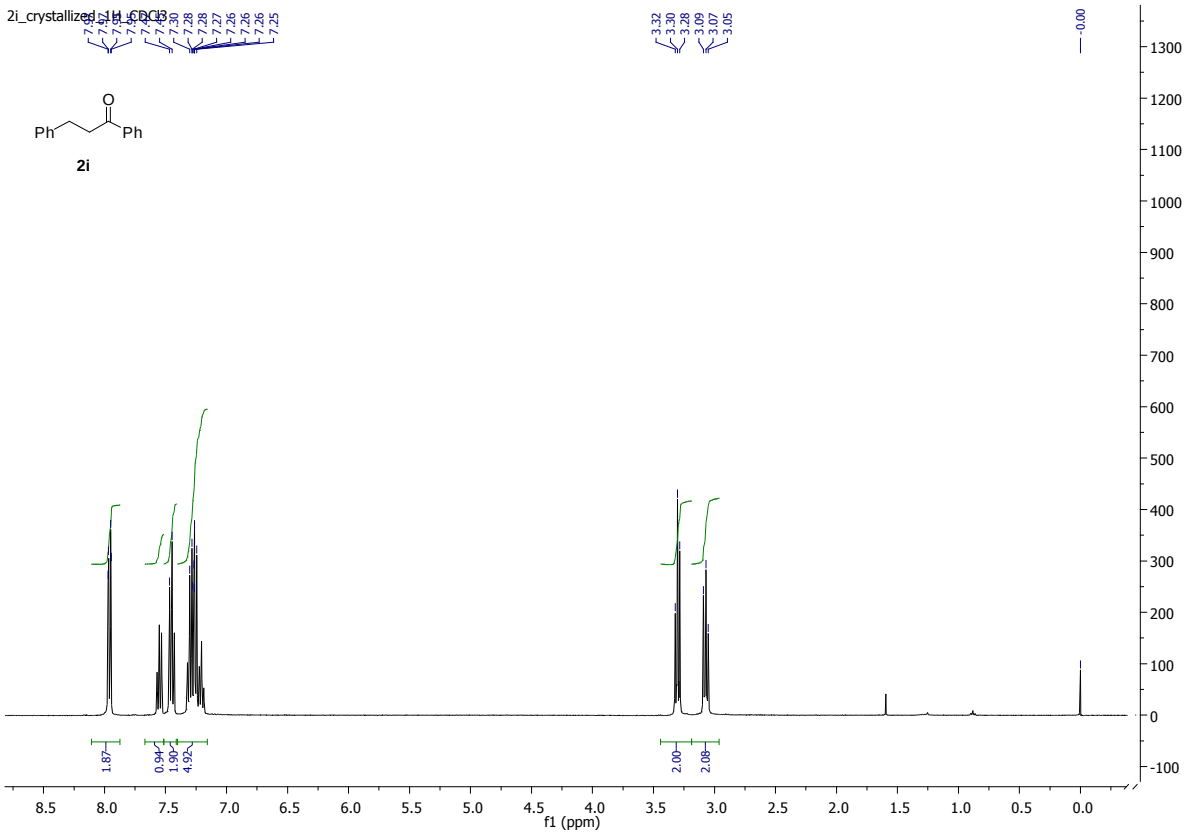
18.84
16.57
13.77
f1 (ppm)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7.30
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7.27
7.26
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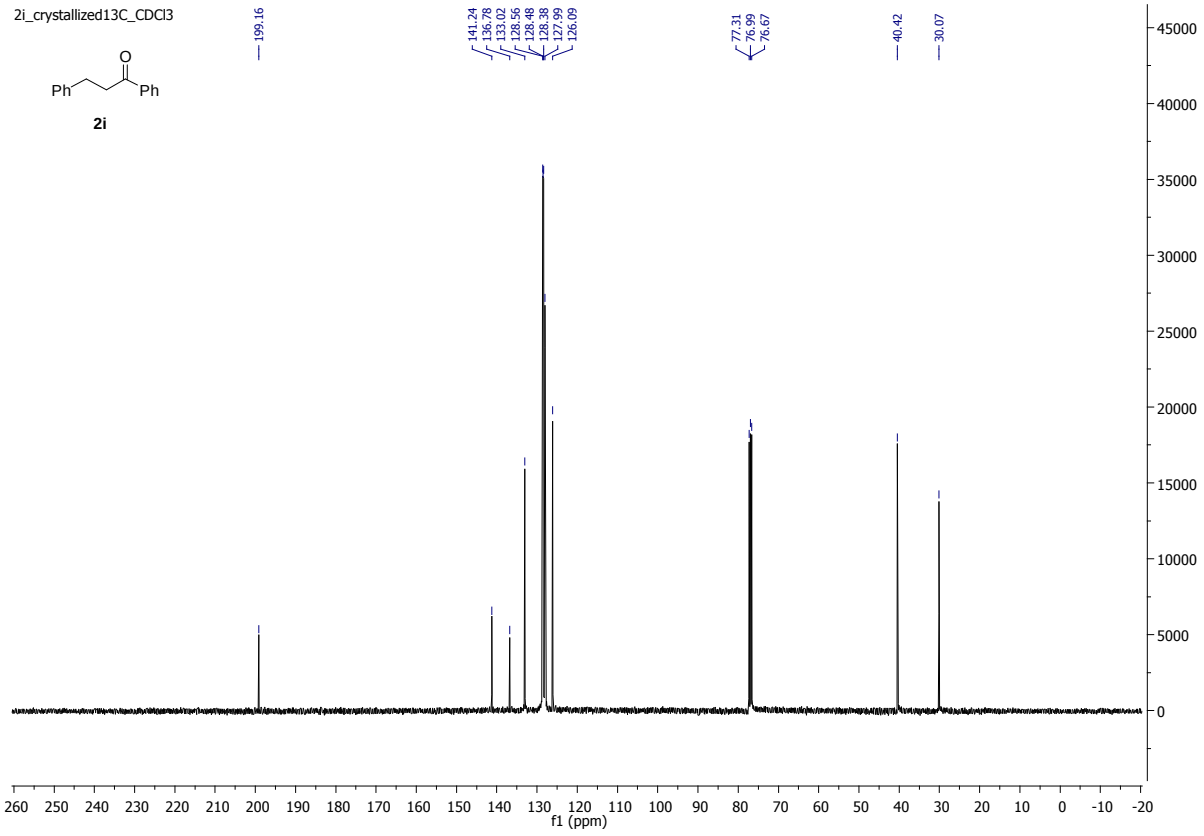
7.25
3.32
3.30
3.28
3.09
3.07
3.05
-0.00
O
Ph
Ph
2i
1.87
0.94
1.90
4.92
2.00
2.08
f1 (ppm)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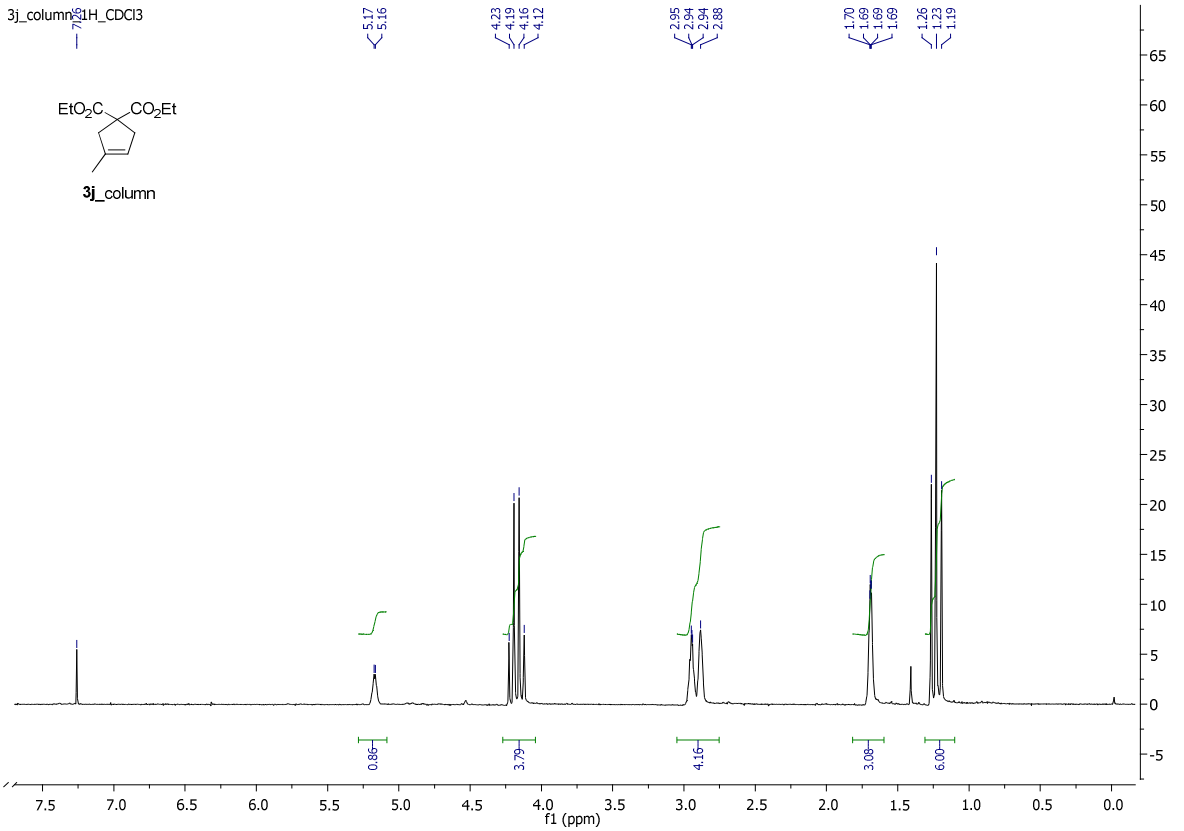
30.07
O
Ph
Ph
2i
f1 (ppm)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2.94
2.88
1.70
1.69
1.69
1.69
1.26
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EtO2C
CO2Et
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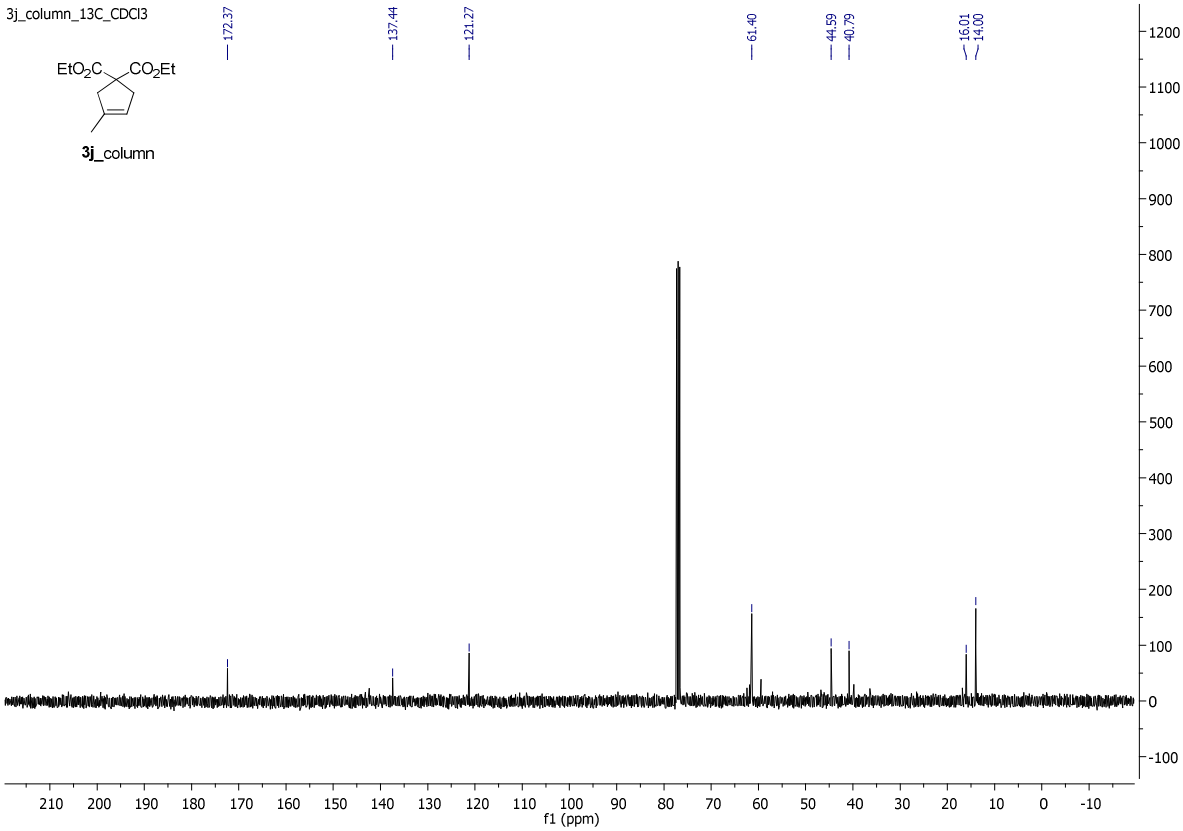
6.00
f1 (ppm)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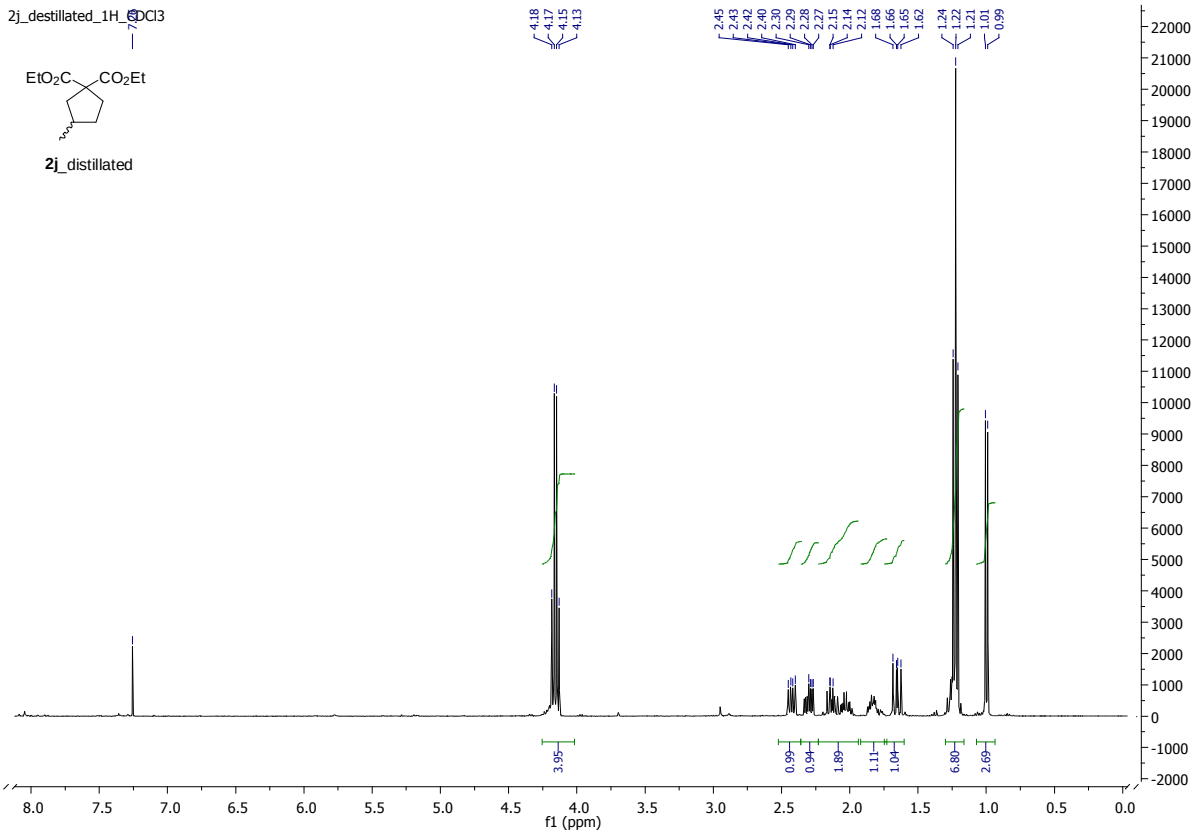
40.79
16.01
14.00
EtO2C
CO2Et
3j_column
f1 (ppm)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CO2Et
2j_distillated
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4.17
4.15
4.13
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2.29
2.28
2.27
2.15
2.14
2.12
1.68
1.66
1.65
1.62
1.24
1.22
1.21
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3.95
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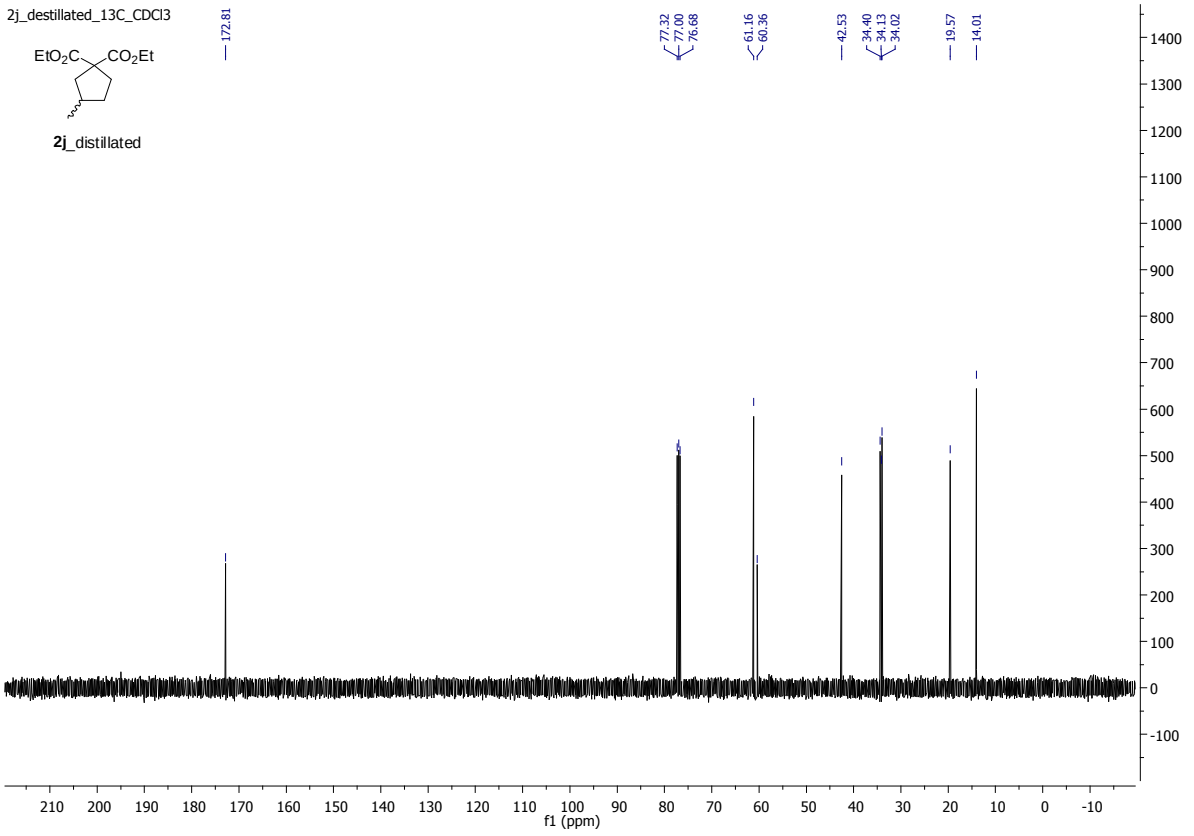
0.94
1.89
1.11
1.04
6.80
2.69
f1 (ppm)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CO2Et
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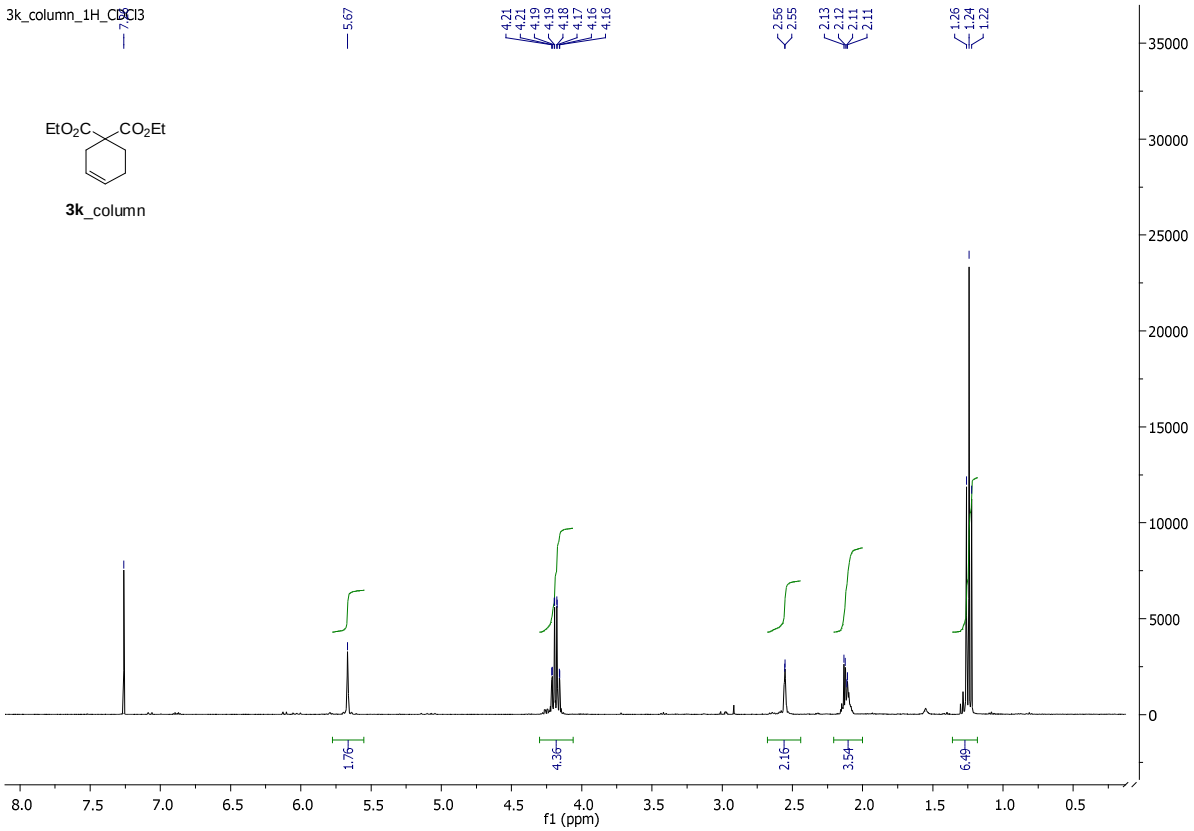
34.02
19.57
14.01
f1 (ppm)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5.67
4.21
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4.19
4.19
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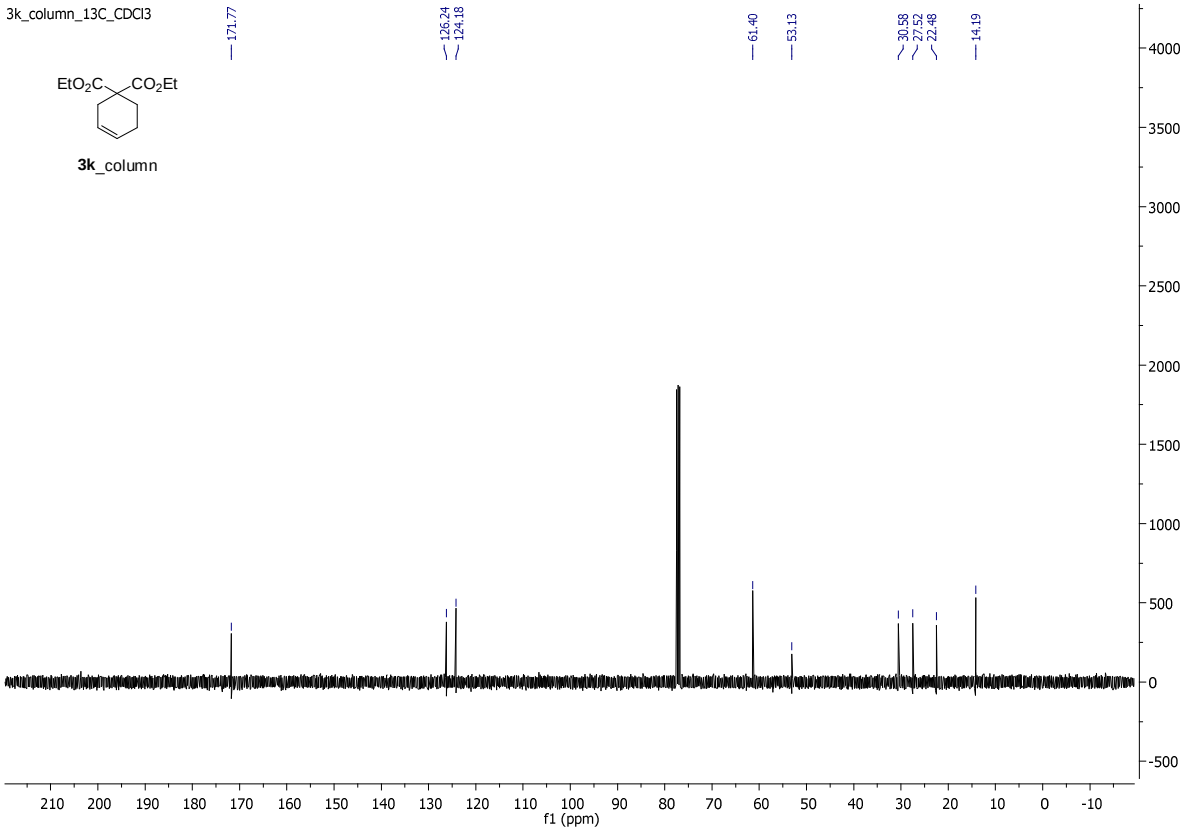
4.17
4.16
4.16
2.56
2.55
2.13
2.12
2.11
2.11
1.26
1.24
1.22
EtO2C
CO2Et
3k_column
1.76
4.36
2.16
3.54
6.49
f1 (ppm)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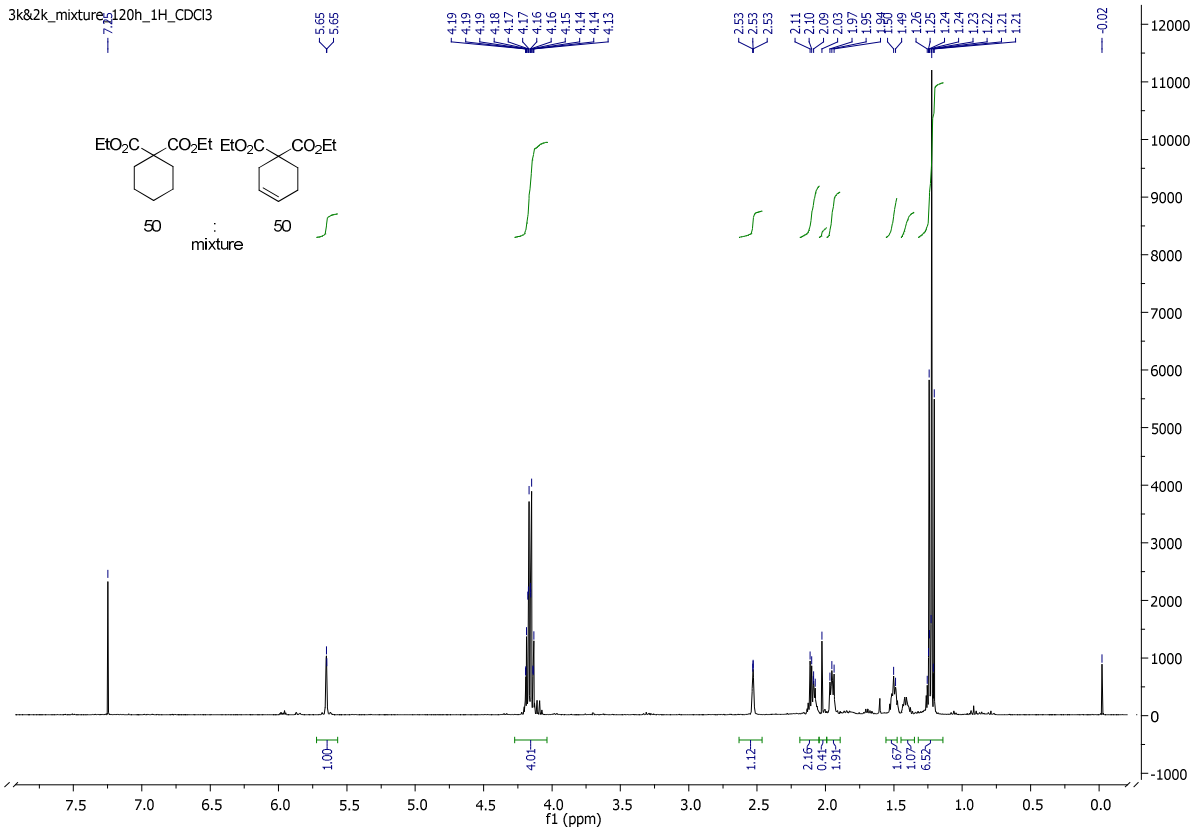
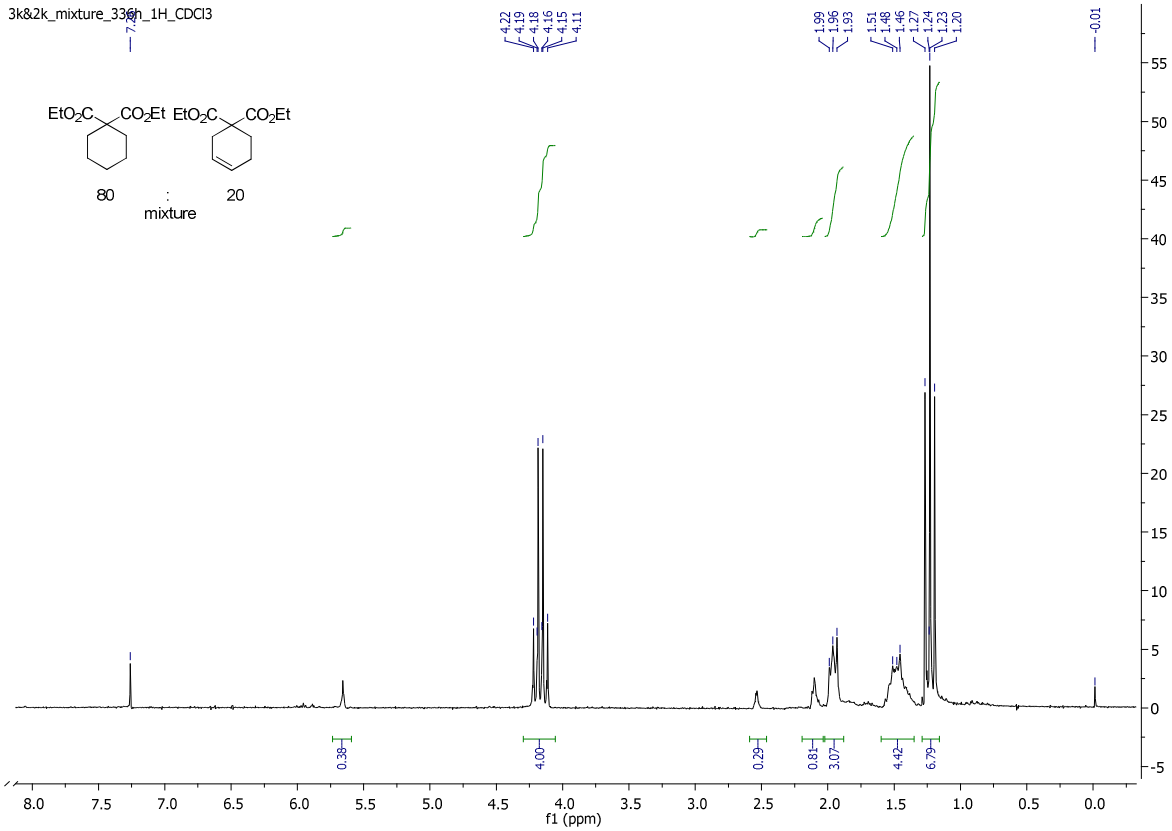
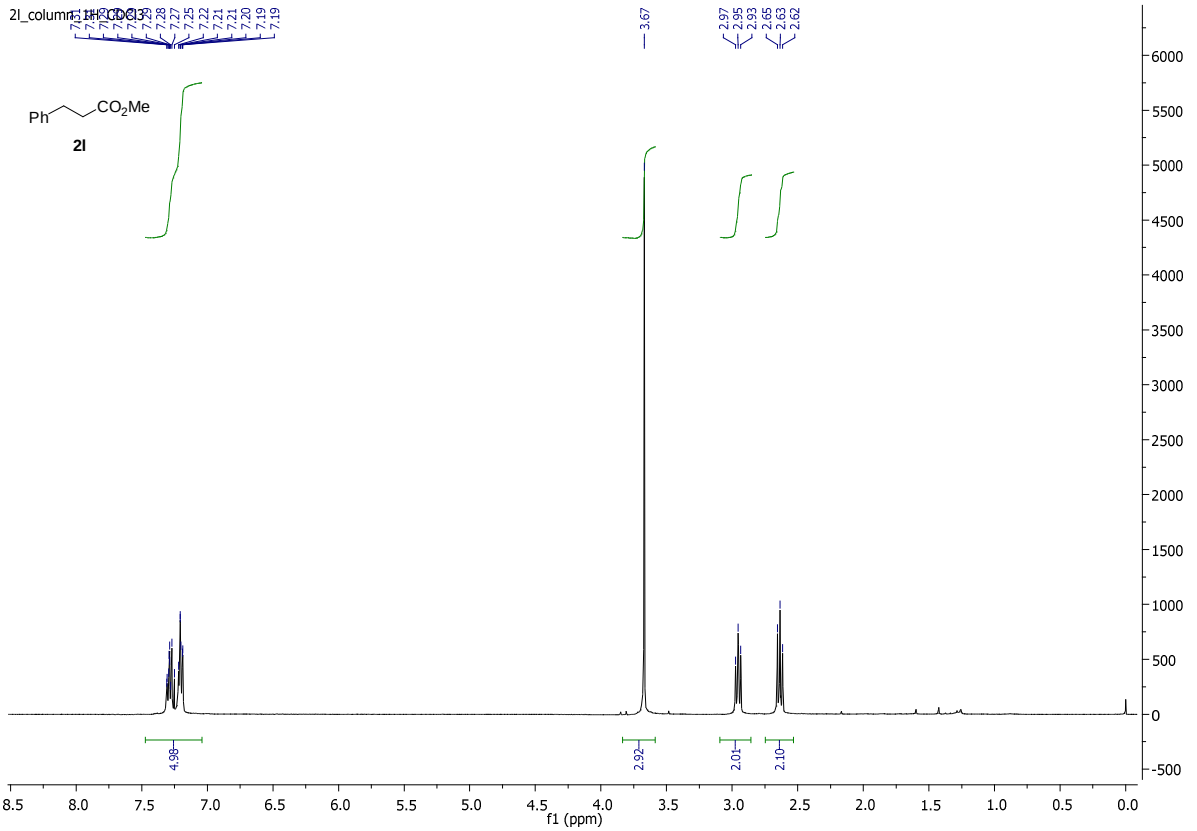
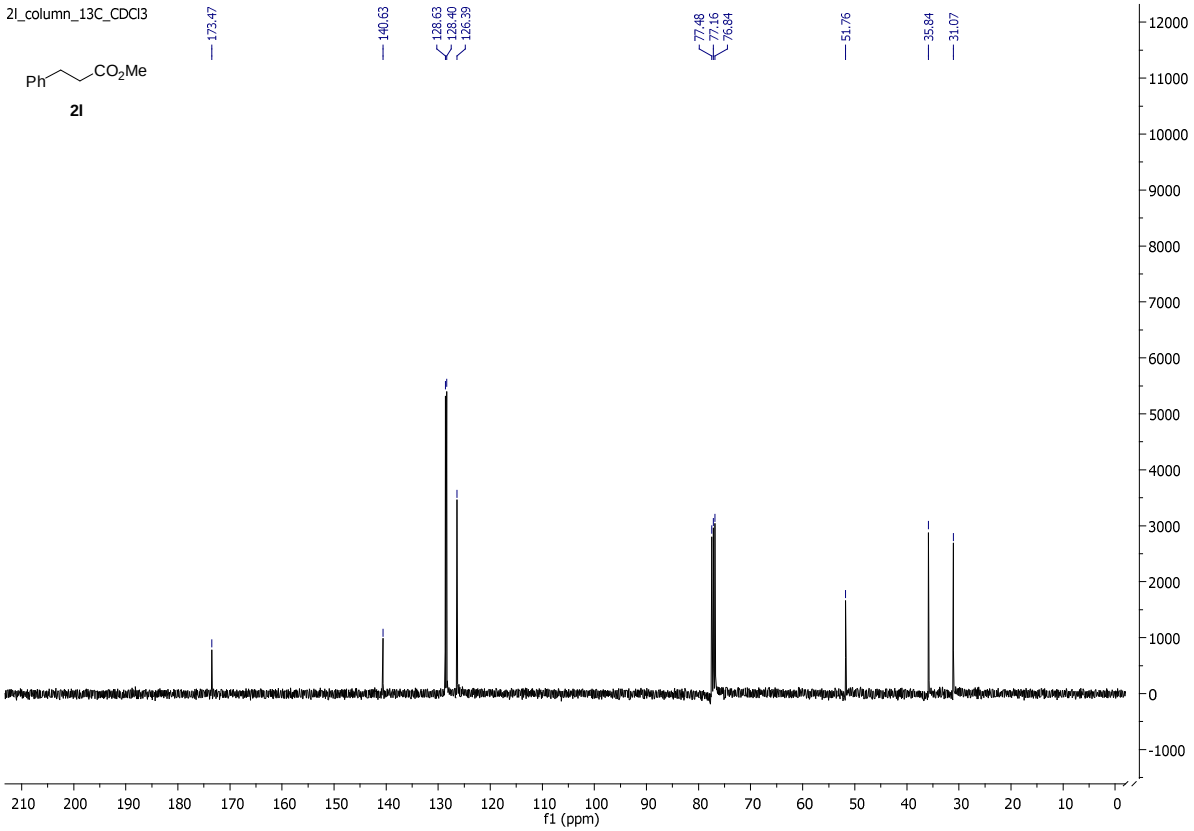
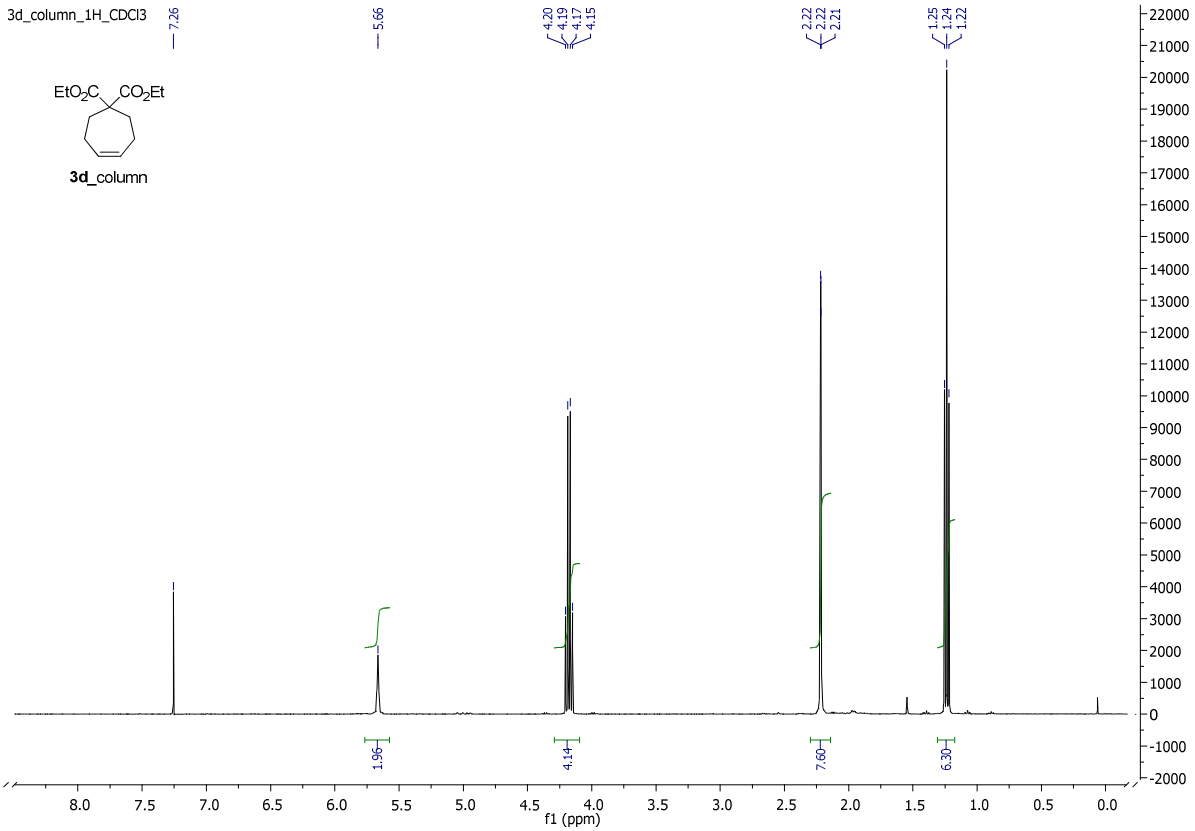
27.52
22.48
14.19
EtO2C
CO2Et
3k_column
f1 (ppm)

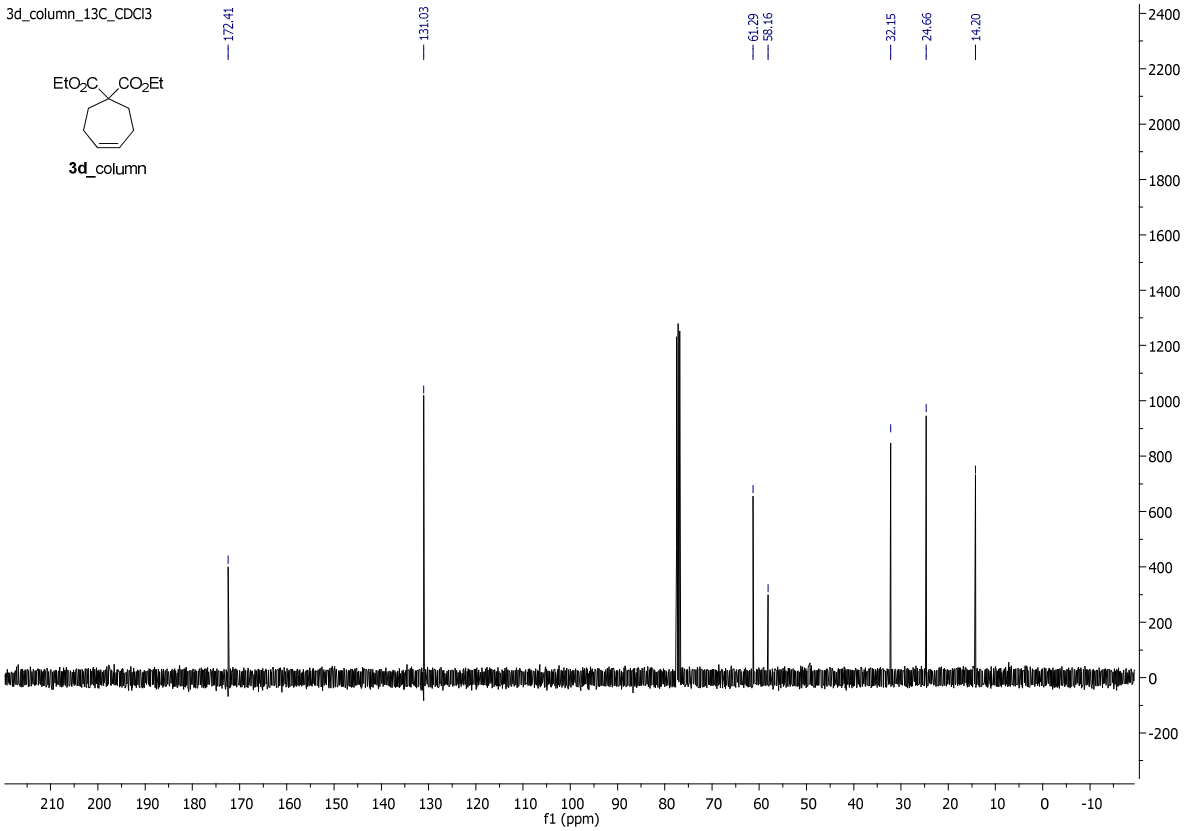

3k&2k_mixture_120h_1H_CDCl3
EtO2C CO2Et EtO2C CO2Et
50 : 50
mixture
f1 (ppm)

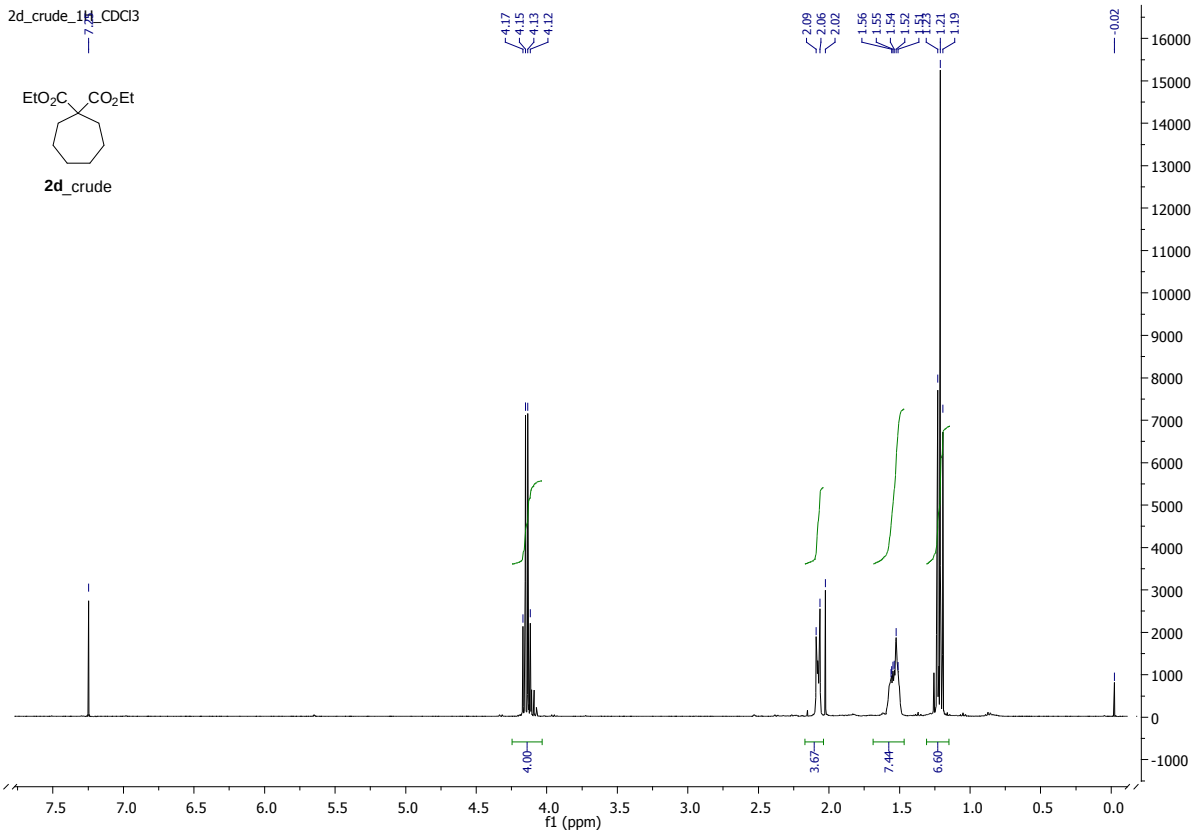

3k&2k_mixture_336h_1H_CDCl3
EtO2C CO2Et EtO2C CO2Et
80 : 20
mixture
f1 (ppm)

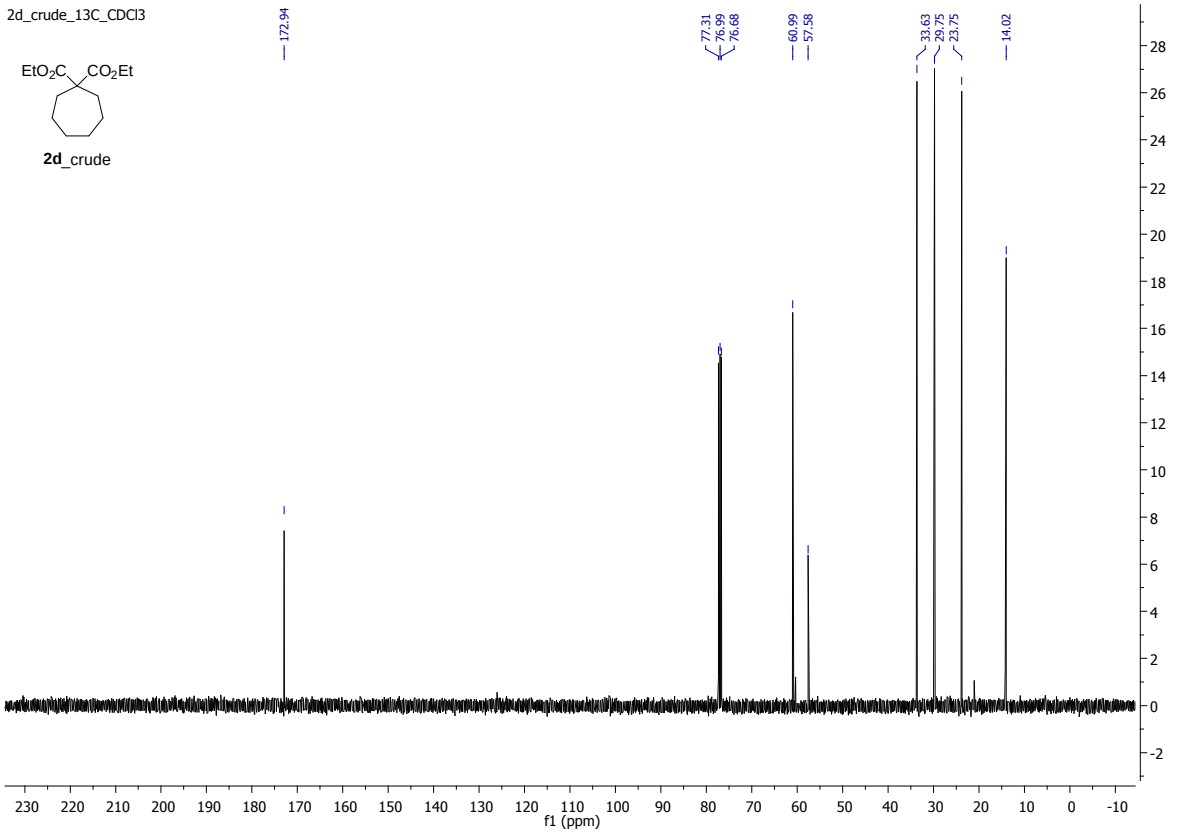

2l_column_1H_CDCl3
Ph
CO2Me
2l
7.31
7.30
7.29
7.28
7.27
7.25
7.22
7.21
7.21
7.20
7.19
7.19
3.67
2.97
2.95
2.93
2.65
2.63
2.62
4.98
2.92
2.01
2.10
f1 (ppm)


2l_column_13C_CDCl3
Ph
CO2Me
2l
173.47
140.63
128.63
128.40
126.39
77.48
77.16
76.84
51.76
35.84
31.07
f1 (ppm)


3d_column_1H_CDCl3
7.26
5.66
4.20
4.19
4.17
4.15
2.22
2.22
2.21
1.25
1.24
1.22
EtO2C
CO2Et
3d_column
1.96
4.14
7.60
6.30
f1 (ppm)


3d_column_13C_CDCl3
172.41
131.03
61.29
58.16
32.15
24.66
14.20
EtO2C
CO2Et
3d_column
f1 (ppm)


2d_crude_1H_CDCl3
EtO2C CO2Et
2d_crude
7.74
4.17
4.15
4.13
4.12
2.09
2.06
2.02
1.56
1.55
1.54
1.52
1.51
1.23
1.21
1.19
-0.02
4.00
3.67
7.44
6.60
f1 (ppm)


2d_crude_13C_CDCl3
EtO2C CO2Et
2d_crude
172.94
77.31
76.99
76.68
60.99
57.58
33.63
29.75
23.75
14.02
f1 (ppm)

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