Supplementary Information (SI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

A metal-free or metal e-waste catalysed alkyne hydration-condensation-decarboxylation cascade reaction in water gives access to (fused) carbocycles

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Experimental Section.

- General.

Glassware was dried in an oven at 175 °C before use. Reactions were performed in 5 to 100 ml round-bottomed flasks equipped with a magnetic stirrer and closed with a rubber septum part to sample out if necessary. Reagents and solvents were obtained from commercial sources and were used without further purification otherwise indicated. The 1,3-dicarbonyl compounds and alkynes for the synthesis of the starting alkynyl β-ketoesters were commercially available. Products were characterised by GC-MS, ^{1}H- and ^{13}C-NMR, and DEPT, and compared with commercial products if possible, or the given literature. Gas chromatographic analyses were performed in an instrument equipped with a 25 μm capillary column of 5% phenylmethylsilicone. *N*-dodecane was used as an external standard. GC-MS analyses were performed on a spectrometer equipped with the same column as the GC and operated under the same conditions. ^{1}H, ^{13}C, and DEPT measurements were recorded in a 300 MHz or 400 MHz instrument using $CDCl_3$ or CD_2Cl_2 as a solvent, containing TMS as an internal standard. Ultra-pressure liquid chromatography coupled to high-resolution massspectroscopy (UPLC-HRMS) was performed using the electrosprayionization technique without previous column separation and TOFMS ES+ as a mass analyzer

- Reaction procedures.

General procedure for the synthesis of the starting alkynyl β-ketoesters ***1, 6-14*** *(Figure S1):* The corresponding 1,3-dicarbonyl compound (1 equiv.) and alkyne compound (1.1 equiv.) were placed on a round-bottomed flask with potassium carbonate (4.5 eq.), acetone (0.5 M) and a magnetic stiring bar. The flask was sealed, heated to 50 °C and allowed to stir overnight. For the workup, a diluted solution of HCl was added till neutral or slightly acidic pH, the aqueous phase was extracted 4 times with AcOEt, the phases were collected, dried with $MgSO_4$, centrifugated and the organic solution was concentrated under reduced pressure (at this point, the excess of alkyne compound was removed). For all the reactions, the 1,3-dicarbonyl compound was fully converted to desired compound with >99% yield and selectivity, and the product was not further purified for compounds **1, 6** and **8**. Compound **7** was synthesized under the same general procedure, but using only 1.0 eq. of alkyne compound, which was slowly added (4 h) with a perfusor pump, in order to favor the mono-addition compound over di-addition compound, and the product was purified (to separate the di-addition compound), and so for compounds **9** and **10** (in order to remove the alkyne, which could not be removed by distillation under reduced pressure).

*Procedure for the synthesis of the starting alkynyl β-ketoester **15**:* This compound was synthesized by transesterification of **1** following a reported procedure.[S1] Briefly, **1** (6 mmol), 3-buten-1-ol (6 mmol) and lithium perchlorate (1.2 mmol) in toluene (25 mL) were heated to 100 °C for 18 h in a round-bottomed flask equipped with a Dean-Stark distillation condenser to remove the ethanol formed. The reaction mixture was cooled, filtered, concentrated under reduced pressure and purified by chromatogaphy (n-hexane-ethyl acetate, 9:1) to afford 2-(pent-2-yn-1-yl)-2-(pent-4-enoyl)cyclopentan-1-one **15** as a pale yellow liquid.

*General procedure for the synthesis of the starting bromo alkynyls 2-bromohex-3-yne (**27**) and 1-bromohex-3-yne (**28**).* Following a reported procedure,[S2] CBr_4 (5.1 g, 15.3 mmol) and PPh_3 (4.0 g, 15.3 mmol) were added in several portions to a stirred solution of hex-3-yn-2-ol or hex-3-yn-1-ol (1 g, 10.2 mmol), respectively, in CH_2Cl_2 (30 mL) at 0 °C. The mixture was stirred at ambient temperature for 1 h and at reflux temperature for 2 h. The solvent was evaporated and the residue suspended in pentane, which was also evaporated. The remaining white solid was suspended in pentane/Et_2O (90:10), the suspension was filtered and the solid carefully rinsed with the same solvent. The combined filtrates were evaporated and the residue was purified by flash chromatography (pentane/Et_2O, 100/0 to 95/5) to give products **27** and **28** as a colorless oil (91 and 80% isolated yield, respectively).

*Procedure for the synthesis of the starting alkenyl β-ketoester **S1**:* The compound was synthesized under the same general procedure for alkynyl β-ketoesters but, first, *cis*-1-chloropent-2-ene was synthesized from commerically available *cis*-pent-2-en-1-ol by chlorination with $SOCl_2$.

General procedure for the cascade ester-assisted alkyne hydration-condensation-decarboxylation reaction of alkynyl β-ketoesters with H_2SO_4 or Amberlyst 15: The reaction was carried out by adding the starting β-ketoester (0-5-1 mmol) to a two-necked round-bottomed flask equipped with a magnetic stir bar and containing either H_2SO_4 50% in water (1 ml, 10 equiv.) or wet Amberlyst 15 (0.1 equiv., 100 wt%) and toluene (0.5 M), and the mixture was placed in either a pre-heated oil bath or a steel block at 120 °C, and allowed to magnetically stir under reflux for 4-20 h. Then, the reaction was allowed to cool down to room temperature, it was diluted with brine and extracted 3-4 times with AcOEt, dried with $MgSO_4$, centrifugated, concetrated under reduced pressure and the crude was purified when needed by flash column chromatography (8:2 *n*-hexane: AcOEt gradient).

Procedure for the reuses of Amberlyst 15 for the the cascade ester-assisted alkyne hydration-condensation-decarboxylation reaction of compound ***4:*** The reaction was carried out following the described general procedure with Amberlsyt 15. The washing between uses was made only with toluene (5 times between each new use). For each new use, 4 extra equivalents of water were added to compensate the possible water loss from the wet Amberlyst.

- Computational studies.

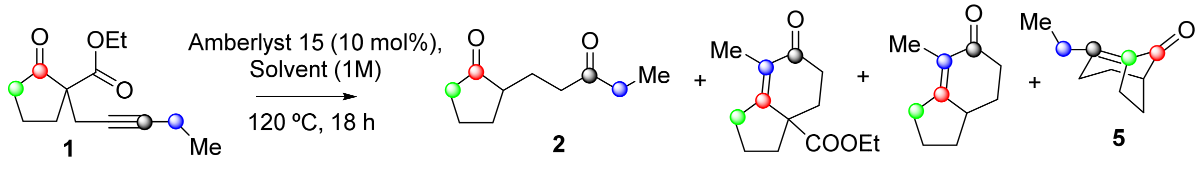
DFT electronic structure calculations were performed using Gaussian 09 software with the B3LYP coupled with the 6-31G(d,p) basis set. Geometries of reactants, intermediates, and products were optimized by calculating vibration frequences to confirm that it is an energy minimum. To obtain the Natural Population Analysis (NPA) charges, a Natural Bond Orbital (NBO) analysis was performed on the optimized structures.

Supplementary Tables.

Table S1. Literature precedents for representative proton-catalyzed alkyne hydration reactions and the work here shown.

Entry	Catalyst	Reaction conditions	Comments	Ref.
1	HCl in water (0.3 M)	140 °C, water as a solvent with a surfactant	Acid-catalyzed hydration of alkynes in microemulsions.	S3
2	Hierarchically porous poly(ionic liquid)s solid acid (10 wt%)	40-90 °C, CF_3CH_2OH as a solvent	Hydration of different alkynes using hierarchically. Amberlyst works poorly as a catalyst.	S4
3	Polyphenylene-based solid acid (300 wt%)	120 °C, neat water	Solid acid catalyst for the hydration of phenylacetylene and 1-octyne. The solid has to be prepared. Amberlyst works poorly as a catalyst.	S5
4	Sulfonated carbon (10 wt%)	100 °C, neat water	Solic acid catalyzed of phenylacetylene, to give 21% yield. Not other alkynes tested. The solid has to be prepared.	S6
5	p-Toluene sulfonic acid (PTSA, 100 mol%)	25-100 °C, AcOH as a solvent	Catalyzed hydration of alkynes using a combination of p-toluenesulfonic acid and acetic acid.	S7
6	CF_3SO_3H (20 mol%)	25-70 °C, CF_3CH_2OH as a solvent	Markovnikov-type alkyne hydration using 20 mol% of CF_3SO_3H.	S8
7	Sulfuric acid (18 mol%)	Microdoplets, milliseconds	Hydration of phenylacetylenes with limited scaling-up	S9
8	Bronsted acidic ionic liquids (BAILs, 20-100 mol%)	25-60 °C	BAILs act as solvent and catalysts for aromatic alkynes.	S10
9	*L*-cysteine (20-40 mol%)	70-80 °C, pH= 9.5, EtOH as a solvent	Organocatalytic hydration of activated alkynes.	S11

10	Selectfluor (1.2 equivalents)	60 ^oC, MeOH solvent	One-pot synthesis of fluorinated β-keto-imidates via functionalized hydration of alkynes.	S12
11	AcOH (solvent)	60 ^oC, air, AcOH/EtOH solvent	Transformation of alkynes to carbonyls using a remote OH group, employing HOAc and EtOH as solvents.	S13
12	p-Toluene sulfonic acid (PTSA, >20 mol%)	65-100 ^oC, EtOH or water solvent	PTSA-catalyzed hydration of unsymmetrical arylalkynes	S14
13	I_2 (2 equivalent)	25 ^oC, Acetonitrile as a solvent	Iodine-mediated hydration of alkynes, involving α-iodo intermediates and 5-exo-dig neighboring group participation.	S15
14	Superheated water	200 ^oC	Hydration of alkynes using microwave irradiation in superheated water	S16
15	Sulfuric acid (0.5-8.0 equivalents) in an ionic liquid	40 ^oC, neat water	Catalyzed hydration of alkynes in very short time (30 min)	S17
16	Zeolite H-Beta (50 wt%)	100 ^oC, neat water	Hydration of various alkynes under solvent-free conditions, however, propargylic aryl carbinols undergo Meyer–Schuster rearrangements.	S18
17	Critical water	295 ^oC, microwaves, 77 bar	Phenylacetylene to acetophenone near critical water regimen	S19
18	Overheated water	200 ^oC, microwaves,	Only for arylalkynes with activating electron donor groups	S16
19	Overheated water	290 ^oC, few minutes	Rupe rearrangement and decarboxylation reactions	S20



1 2 3 4 5

Table S2. Results for the Amberlyst-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **1**. Reaction conditions: **1** (1 mmol), solvent (1 mL), Amberlyst 15 (10 mol%), 120 ºC, 18 h. Combined GC and ^{1}H-NMR results. Mass balances are completed with **Int-1** and **Int-2**.

Entry	Solvent	Conv. 1 (%)	Yield (%)			
			2	3	4	5
1	Toluene (0.5M) (72 h)	>99	6	33	0	13
2	Toluene (0.5M) + 4 eq. H_2O	82	7	49	0	0
3	H_2O:toluene (1:1)	>99	12	67	0	0
4	EtOH:toluene (1:1) + 4 eq. H_2O	>99	12	76	0	0
5	EtOH:H_2O (10:1)	0	0	0	0	0
6	EtOH:H_2O (5:1) (0.8 M)	11	11	0	0	0
7	EtOH:H_2O (5:1) (0.8 M) - 11 eq. H_2O	4	4	0	0	0
8	EtOH:H_2O (5:1) (0.8 M)	97	33	26	25	0
9	Non-dry toluene (0.5 M)	>99	12	69	0	0
10	Non-dry 1,4-dioxane (0.5 M)	5	5	0	0	0
11	Non-dry 1-butanol (0.5 M)	0	0	0	0	0
12	EtOH (0.5 M)	0	0	0	0	0
13	Dry toluene (0.5 M)	>99	8	57	0	0
14	Dry 1,4-dioxane (0.5 M)	>99	9	55	0	0
15	Dry octane (0.5 M)	>99	7	65	0	0
16	Dry DMSO (0.5 M)	0	0	0	0	0

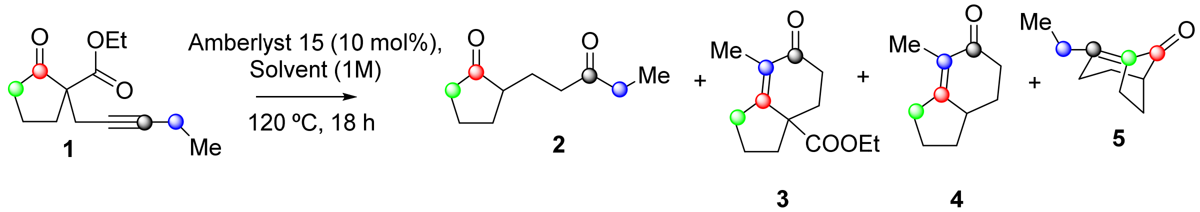


Table S3. Results for the alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **1** catalyzed by different metal sources, including RAM contacts from the Institute´s e-waste. Reaction conditions: **1** (1 mmol), solvent (1 mL), metal catalyst (0.6 mol%), 120 ºC, 18 h. Combined GC and ^{1}H-NMR results. Mass balances are completed with **Int-1** and **Int-2**.

Entry	Catalytic system	Conv (%)	2 (%)	4 (%)
1	H_2SO_4 (1.8 eq)	>99	-	67
2	AuCl (0.6% mol) + H_2SO_4 (1.8 eq)	>99	-	91
3	$CuCl_2$ (0.6% mol) + H_2SO_4 (1.8 eq)	>99	-	60
4	$NiCl_2$ (0.6% mol) + H_2SO_4 (1.8 eq)	>99	-	60
5	AuCl (0.6% mol)	>99	80	20
6	$CuCl_2$ (9.4% mol)	76	26	-
7	$NiCl_2$ (1.5% mol)	79	21	-

Supplementary Figures.

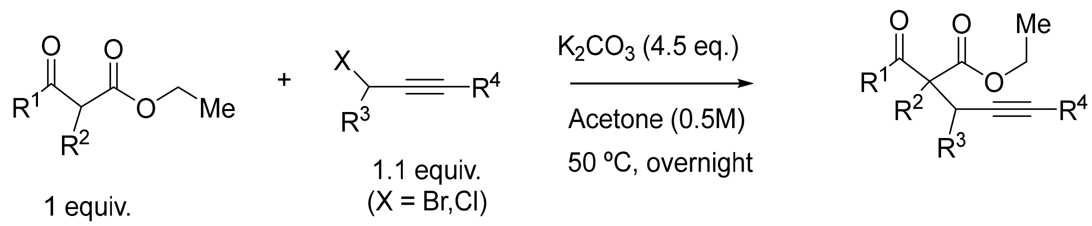


Figure S1. General reaction conditions for the synthesis of the starting alkynyl β-ketoesters.

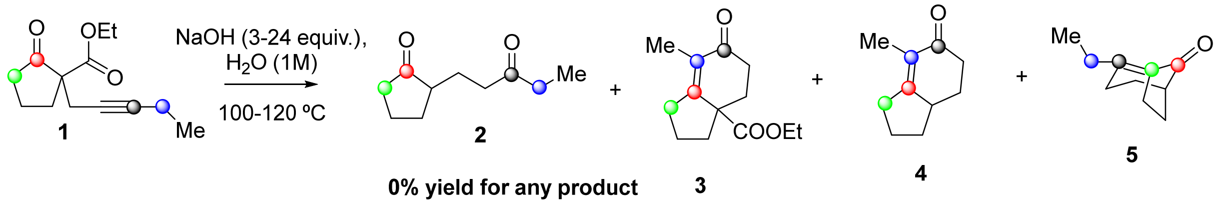
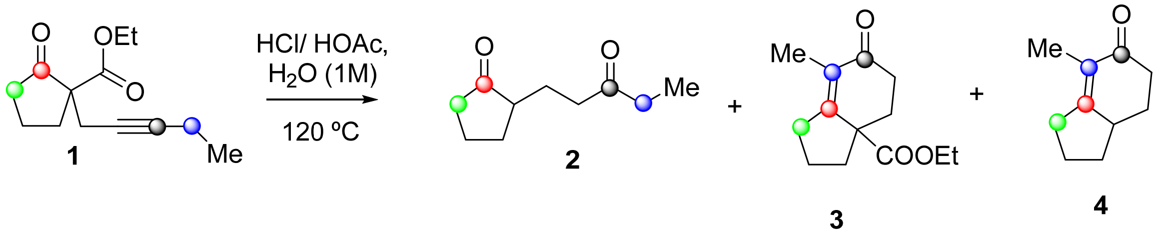
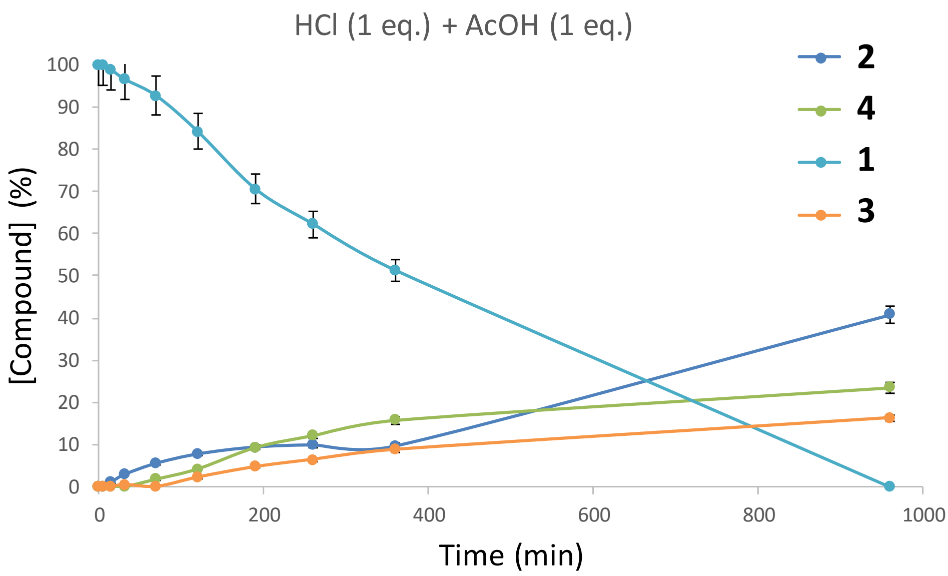


Figure S2. Results for the NaOH-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **1**. Reaction conditions: **1** (1 mmol), water (1 mL), NaOH, 120 ºC. Combined GC and ^{1}H-NMR results. The reaction was carried out by duplicate.





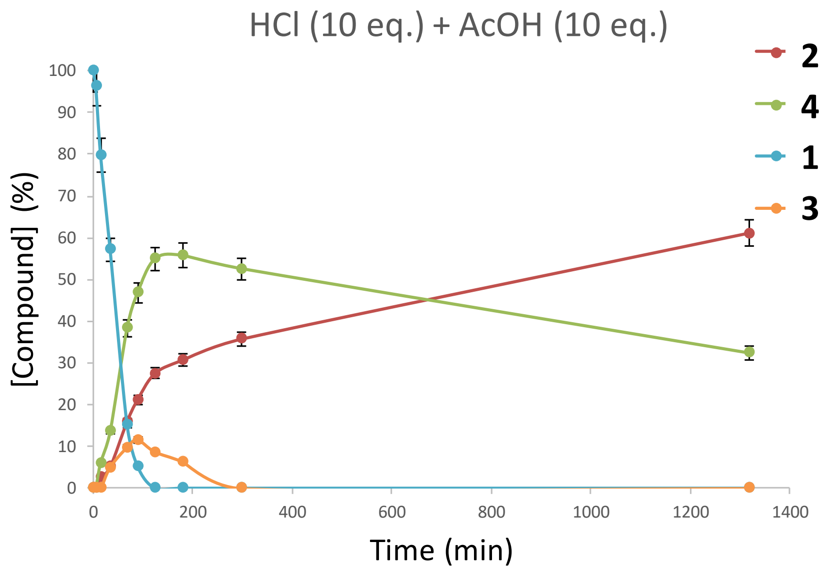
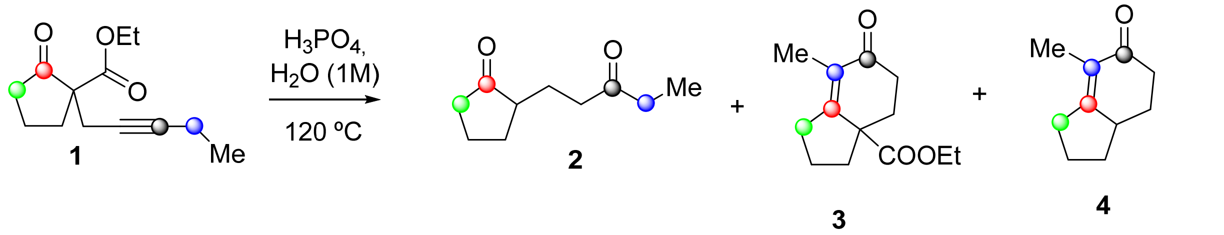


Figure S3. Kinetics for the H$^+$-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **1**. Reaction conditions: **1** (1 mmol), water (1 mL), HCl/HOAc, 120 ºC. Combined GC and ^{1}H-NMR results. Error bars account for a 5% uncertainty. Lines are a guide to the eye.



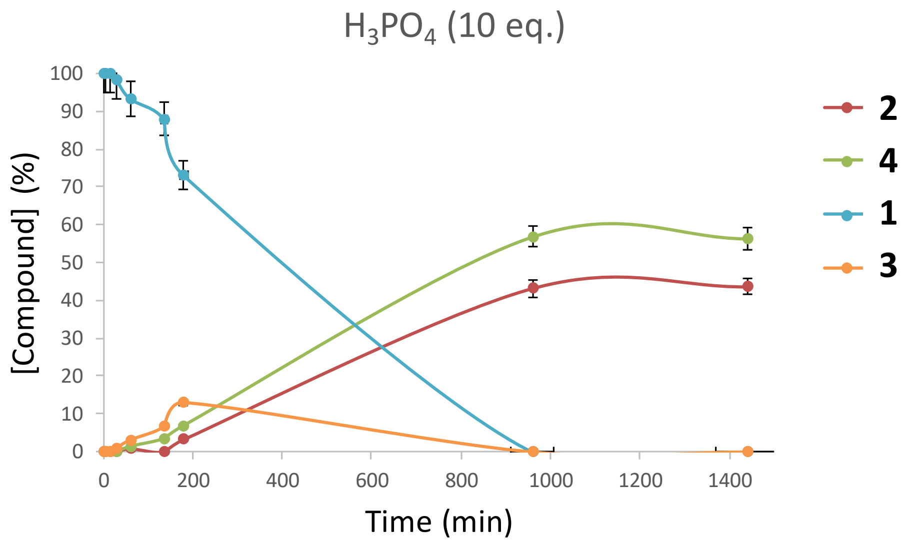
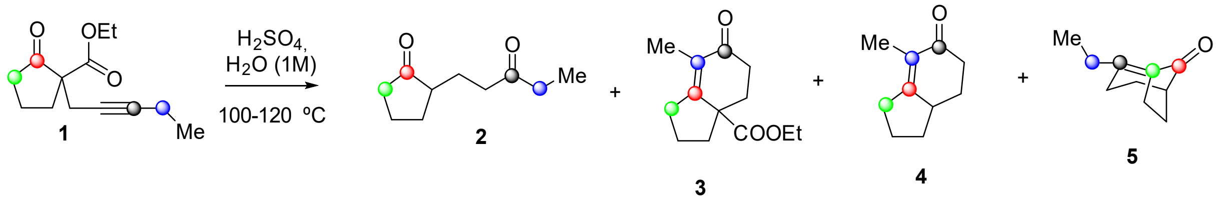


Figure S4. Kinetics for the H+-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **1**. Reaction conditions: **1** (1 mmol), water (1 mL), H_3PO_4 (10 equiv.), 120 ºC. Combined GC and ^{1}H-NMR results. Error bars account for a 5% uncertainty. Lines are a guide to the eye.



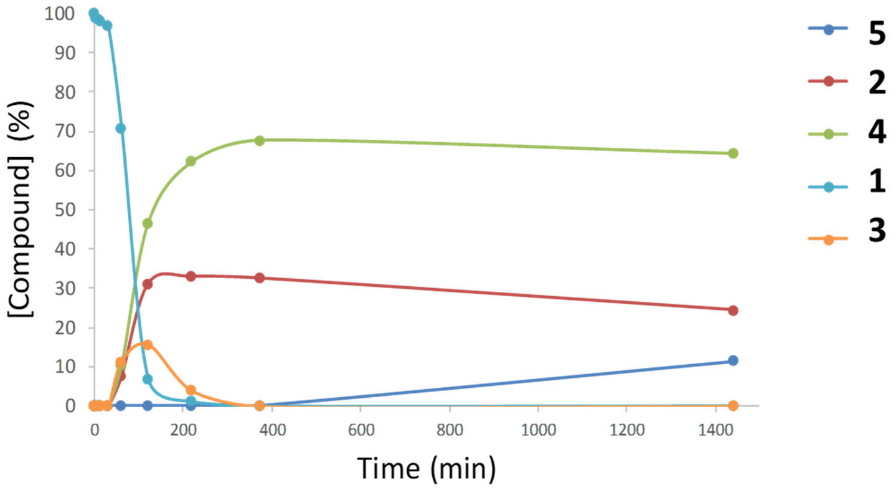


Figure S5. Kinetics for the H^+-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **1**. Reaction conditions: **1** (1 mmol), water (1 mL), H_2SO_4 (10 equiv.), 100 °C. Combined GC and ^1H-NMR results. Error bars account for a 5% uncertainty. Lines are a guide to the eye.

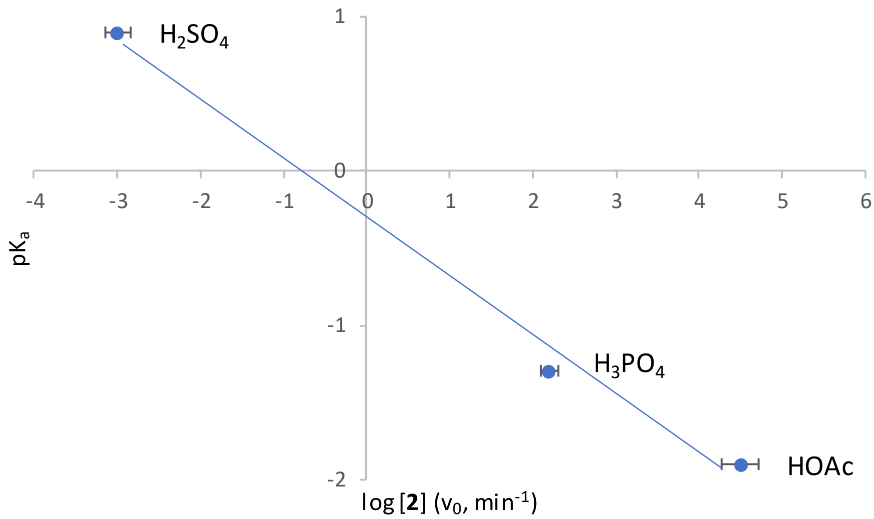
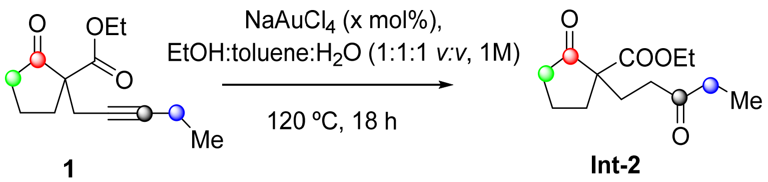
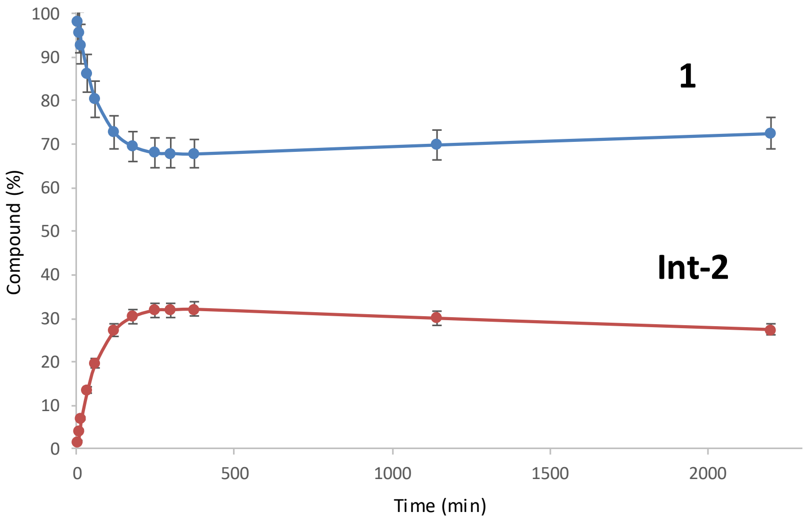


Figure S6. Plot representing the formation of the ketone product **2** (as a logarithm of the initial rate to match the pK_a, taken from a linear regression in the linear interval up to 10% yield) vs the acidity strength of the soluble acid catalyst. Reaction conditions: **1** (1 mmol), water (1 mL), soluble acid catalyst (10 equiv.) , 120 ^{o}C. Error bars account for a 5% uncertainty. The line is a guide to the eye.



Au mol%	conv. 1 (%)	yield Int-2 (%)
0.5	0	0
5	0	0
10	36	36



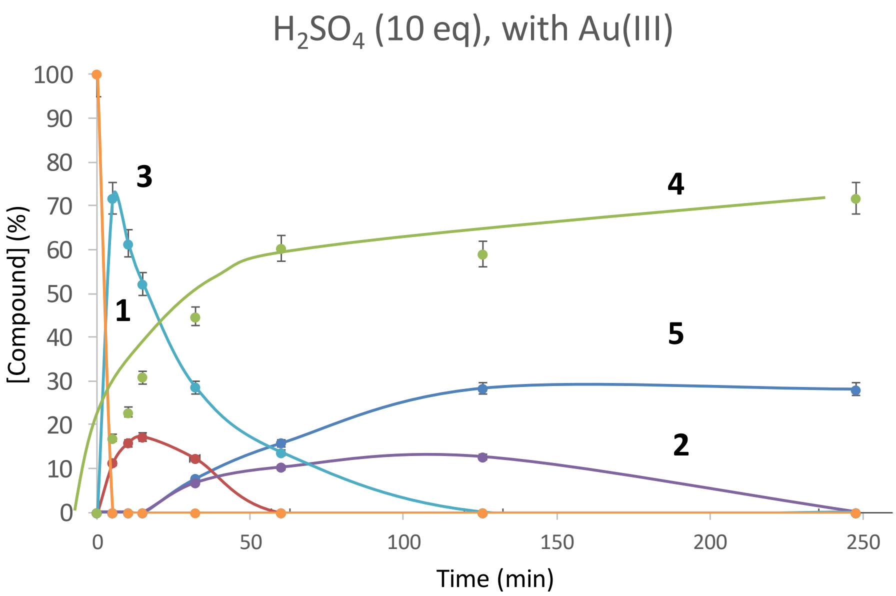


Figure S7. Results and kinetics for the Au-catalyzed ester-assisted alkyne hydration reaction of the β-ketoester **1** (top) and the same reaction plus H_2SO_4 (10 equivalenys). Reaction conditions: **1** (1 mmol), solvent combination (1 mL), $NaAuCl_4$ ($AuPPh_3Cl$ was also tested with similar results), 120 ºC, 18 h. Combined GC and ^{1}H-NMR results. The reactions were carried out by duplicate. Error bars account for a 5% uncertainty. Lines are a guide to the eye.

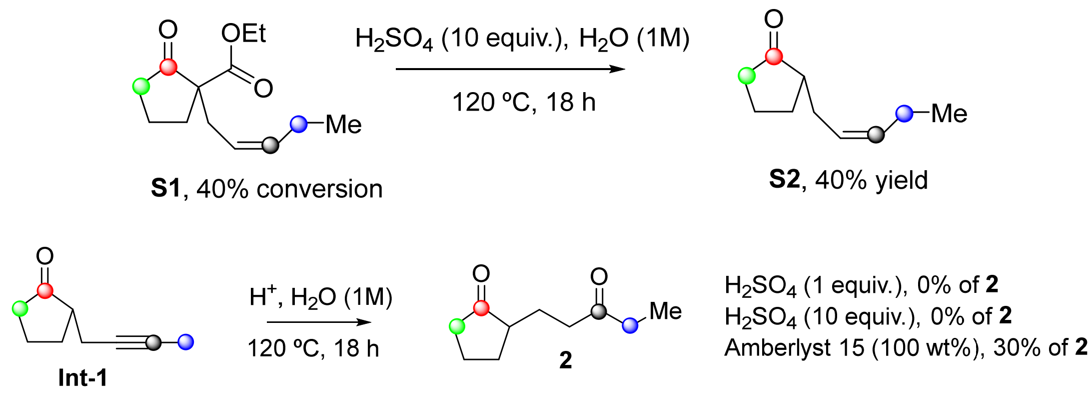


Figure S8. Top: Results for the H^+-catalyzed reaction of the β-ketoester **S1**. Reaction conditions: **S1** (1 mmol), H_2SO_4 (10 equivalents) in water (1 mL), 120 ºC, 18 h. Bottom: Results for the H^+–mediated alkyne hydration–condensation–decarboxylation cascade reaction of the alkyne **Int-1**, under the optimized reaction conditions. Combined GC and ^{1}H-NMR results. The reactions were carried out by duplicate.

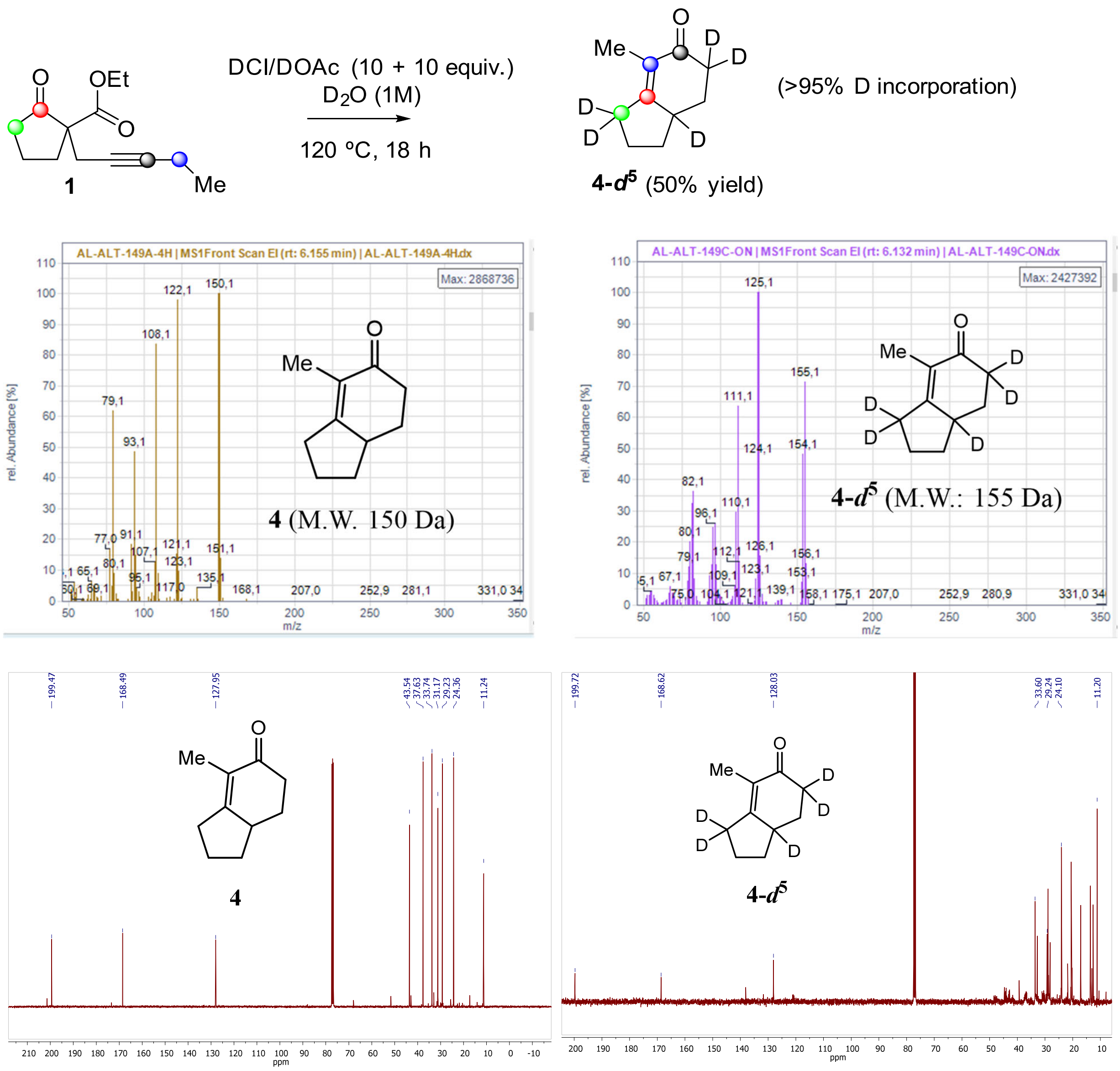
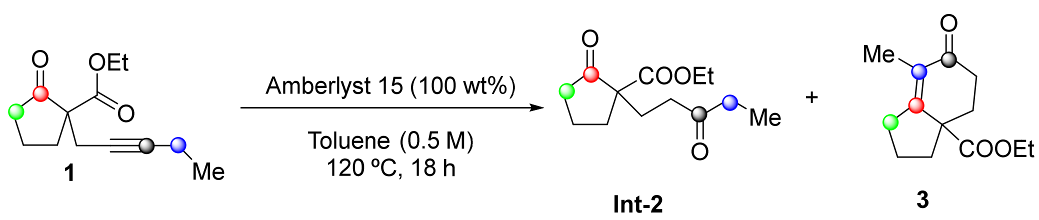
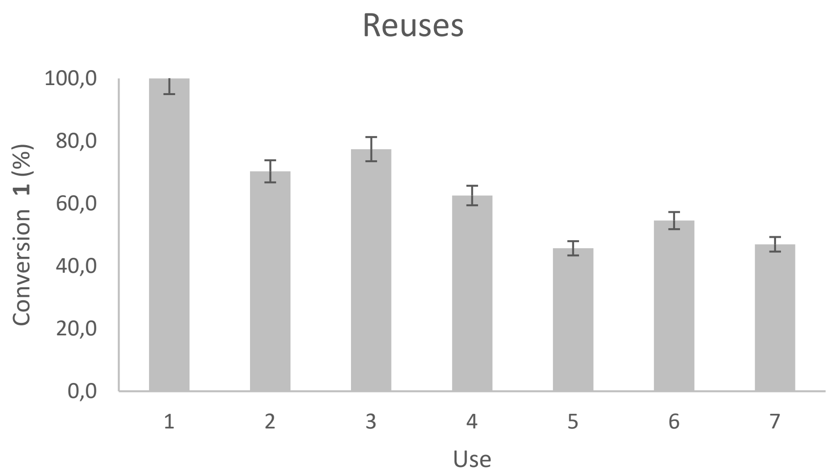


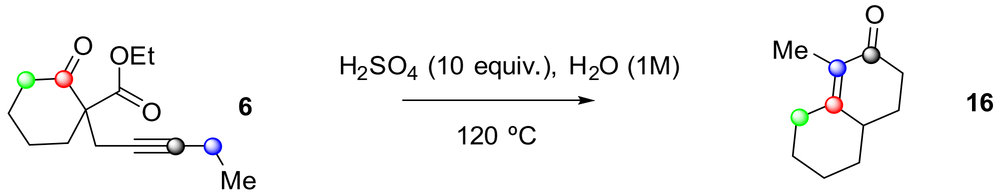
Figure S9. Results for the deuteration experiment. Reaction conditions and results: **1** (1 mmol), D_2O (1 mL), DCl/DOAc (10 + 10 equiv.) , 120 °C, 18 h (top), together with the gas chromatography coupled to mass spectrometry measuremements (GC-MS, middle) and the ^{13}C nuclear magnetic resonance (^{13}C-NMR, bottom) of the of product **4** after the non-(left) and isotopically labelled (right) experiment. Combined GC and ^{1}H-NMR results. The reaction was carried out by duplicate.





Use	Sel Int-2 (%)	Sel 3 (%)	Sel 4 (%)
1	27.9	39.2	9.0
2	35.6	28.8	8.5
3	46.8	22.1	3.3
4	46.6	30.2	7.0
5	34.1	29.7	5.8
6	39.2	33.8	5.9
7	34.5	18.5	7.1

Figure S10. Reuses of the Amberlyst 15 catalyst for the reaction of β-ketoester **1** and the selectivities obtained for each compound. Reaction conditions: **1** (1 mmol), toluene (0.5 M), Amberlyst 15 (10 mol%), water (4 eq.), 120 ºC, 18 h. Error bars account for a 5% uncertainty.



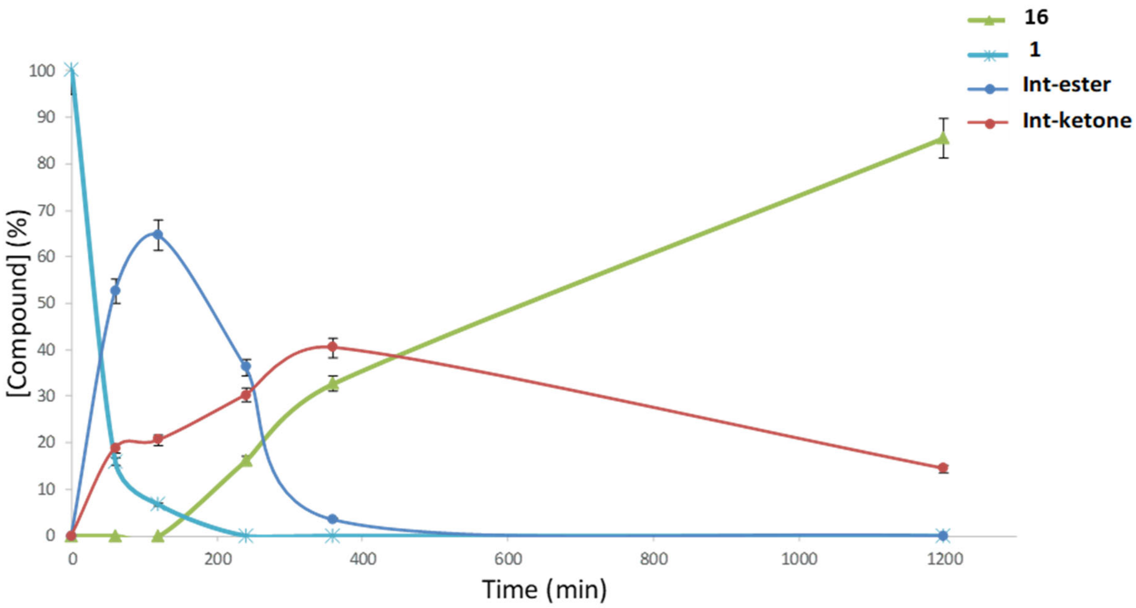
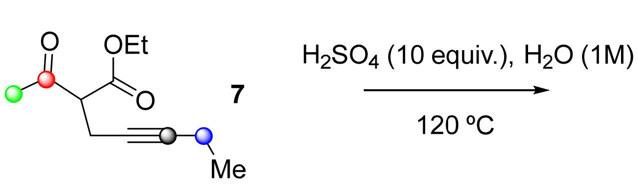


Figure S11. Kinetics for the H^+-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **6**. Reaction conditions: **6** (1 mmol), water (1 mL), H_2SO_4 (10 equiv.), 120 °C. Combined GC and ^{1}H-NMR results. Error bars account for a 5% uncertainty. Lines are a guide to the eye.



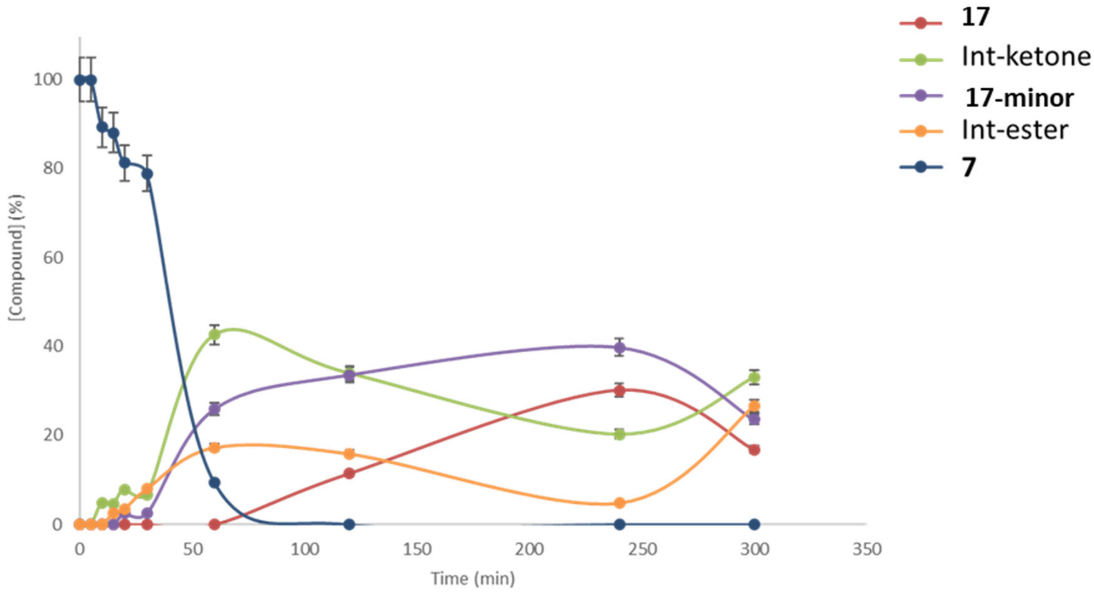


Figure S12. Kinetics for the H$^+$-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **7**. Reaction conditions: **7** (1 mmol), water (1 mL), H_2SO_4 (10 equiv.), 120 °C. Combined GC and ^{1}H-NMR results. Error bars account for a 5% uncertainty. Lines are a guide to the eye.

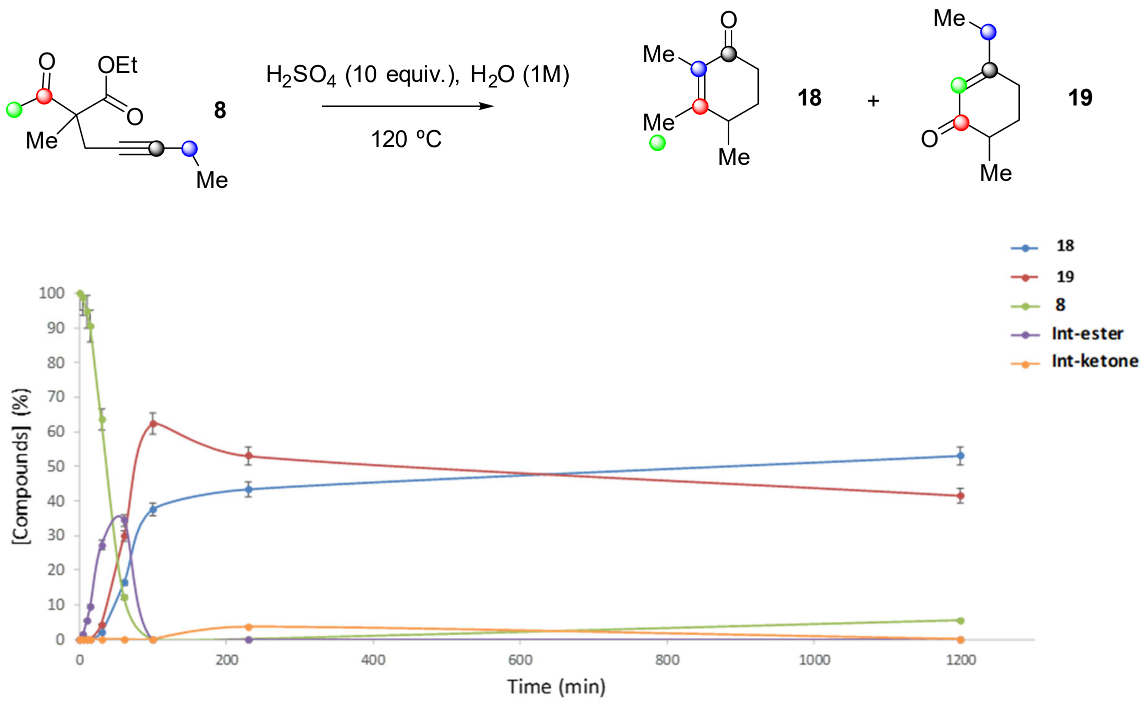


Figure S13. Kinetics for the H^+-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoester **8**. Reaction conditions: **8** (1 mmol), water (1 mL), H_2SO_4 (10 equiv.), 120 °C. Combined GC and ^1H-NMR results. Error bars account for a 5% uncertainty. Lines are a guide to the eye.

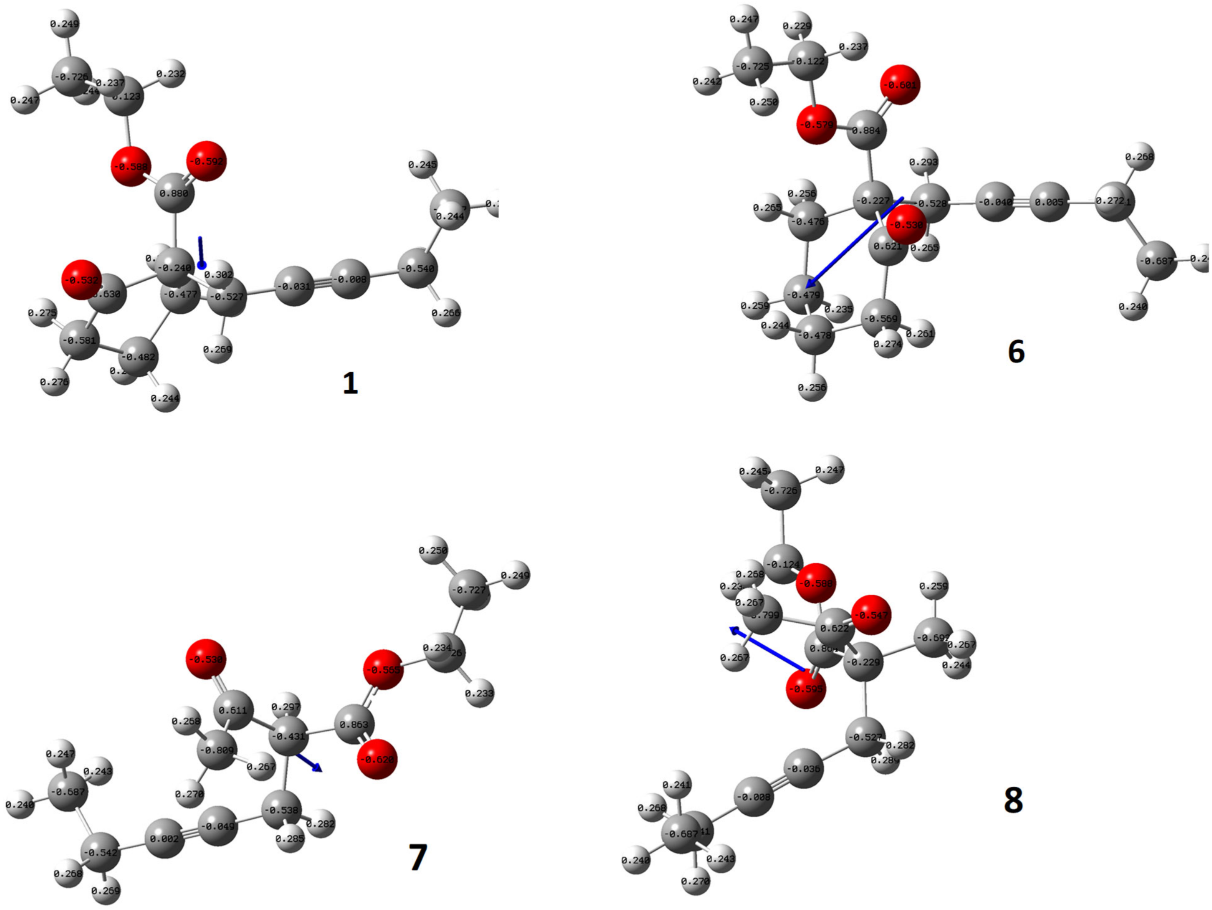


Figure S14. Optimized structures by density-functional calculations (DFT) of the starting materials **1** and **6-8**. Colour code: Carbon atoms in grey, hydrogen atoms in white, oxygen atoms in red.

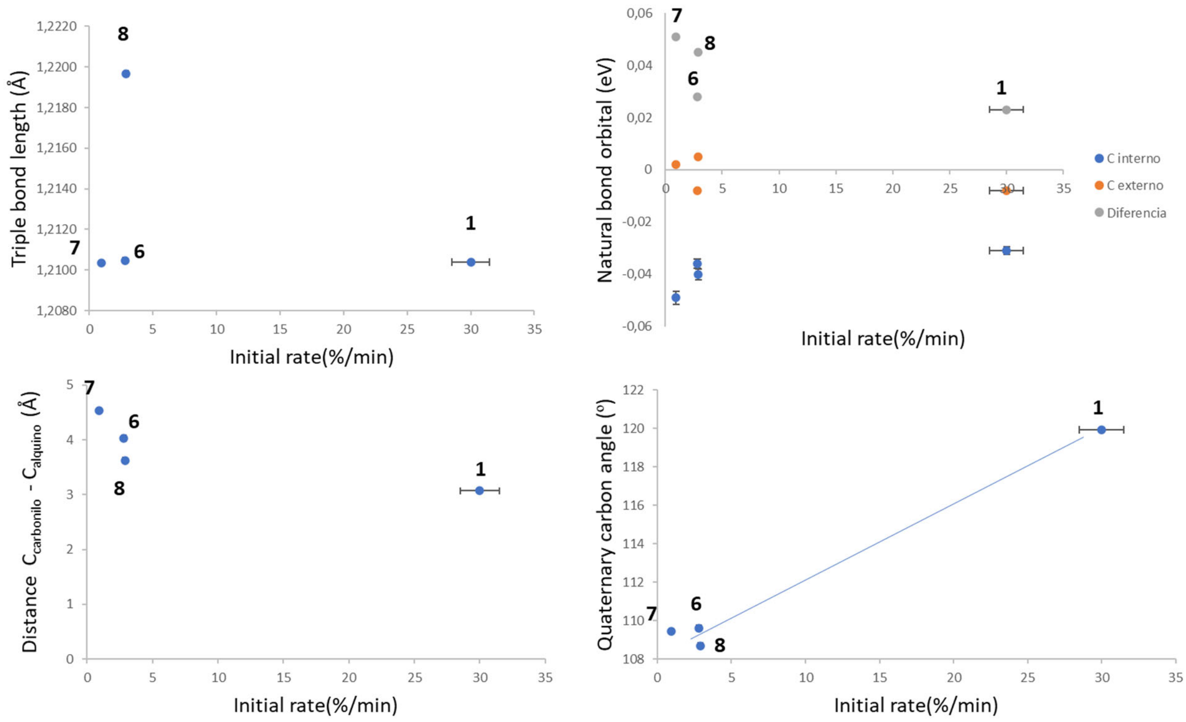


Figure S15. Plots from different parameters of the starting materials **1, 6-8**, calculated by density-functional calculations (DFT)**,** vs the initial reaction rate during the H^+-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoestesrs. Reaction conditions: β-ketoesters (1 mmol), water (1 mL), H_2SO_4 (10 equiv.), 120 °C. Error bars account for a 5% uncertainty. The line is a guide to the eye.

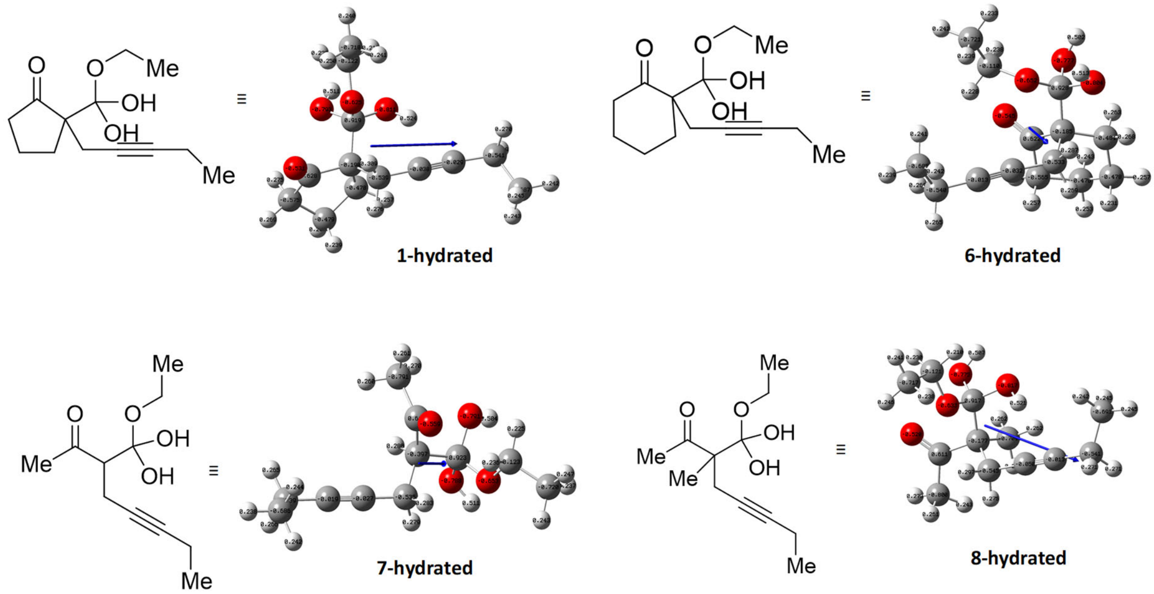


Figure S16. Optimized structures by density-functional calculations (DFT) of the expected hydrate intermediates during the ester-assisted hydration reaction of the starting materials **1** and **6-8**. Colour code: Carbon atoms in grey, hydrogen atoms in white, oxygen atoms in red.

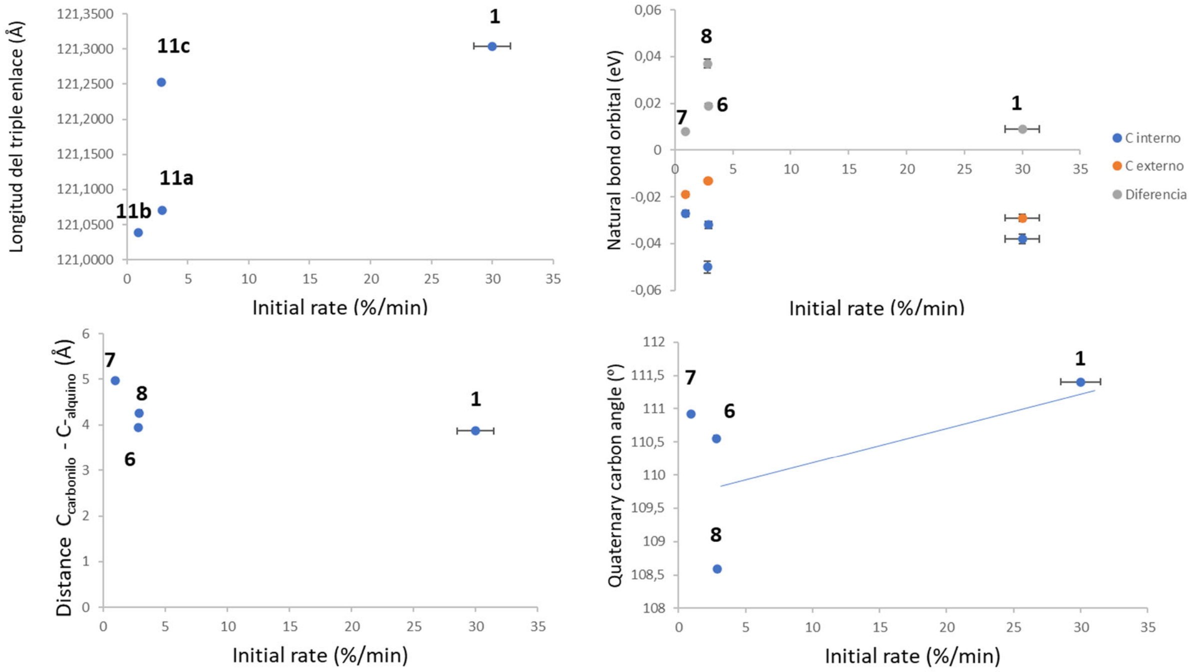
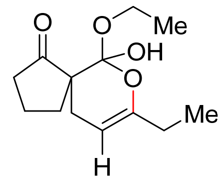
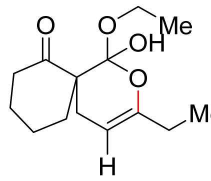


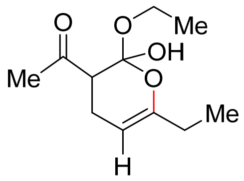
Figure S17. Plots from different parameters of the expected hydrate intermediates during the ester-assisted hydration reaction of the starting materials **1, 6-8**, calculated by density-functional calculations (DFT)**,** vs the initial reaction rate during the H^+-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoestesrs. Reaction conditions: β-ketoesters (1 mmol), water (1 mL), H_2SO_4 (10 equiv.), 120 °C. Error bars account for a 5% uncertainty. The lines are a guide to the eye.



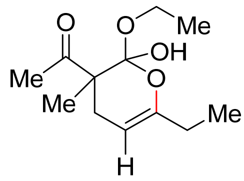
1-hydroalkoxylated



6-hydroalkoxylated



7-hydroalkoxylated



8-hydroalkoxylated

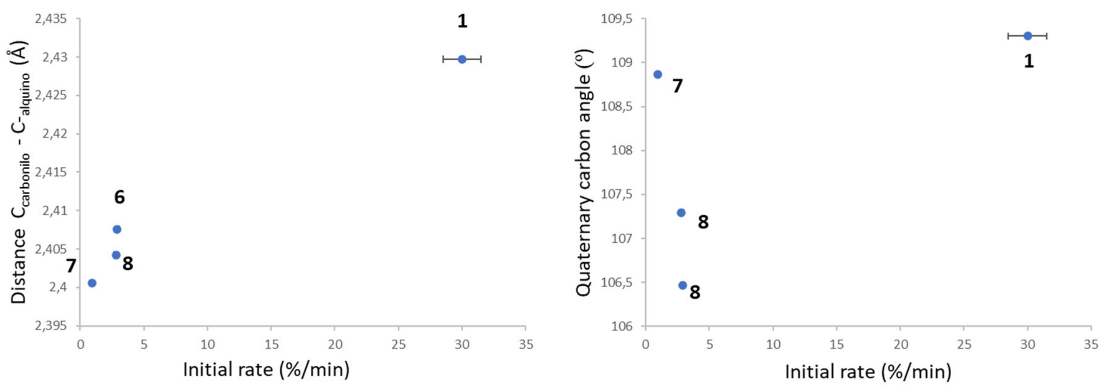


Figure S18. Plots from different parameters of the expected hydroalkoxylated intermediates during the ester-assisted hydration reaction of the starting materials **1, 6-8**, calculated by density-functional calculations (DFT), vs the initial reaction rate during the H^+-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoestesrs. Reaction conditions: β-ketoesters (1 mmol), water (1 mL), H_2SO_4 (10 equiv.), 120 °C. Error bars account for a 5% uncertainty. The line is a guide to the eye.

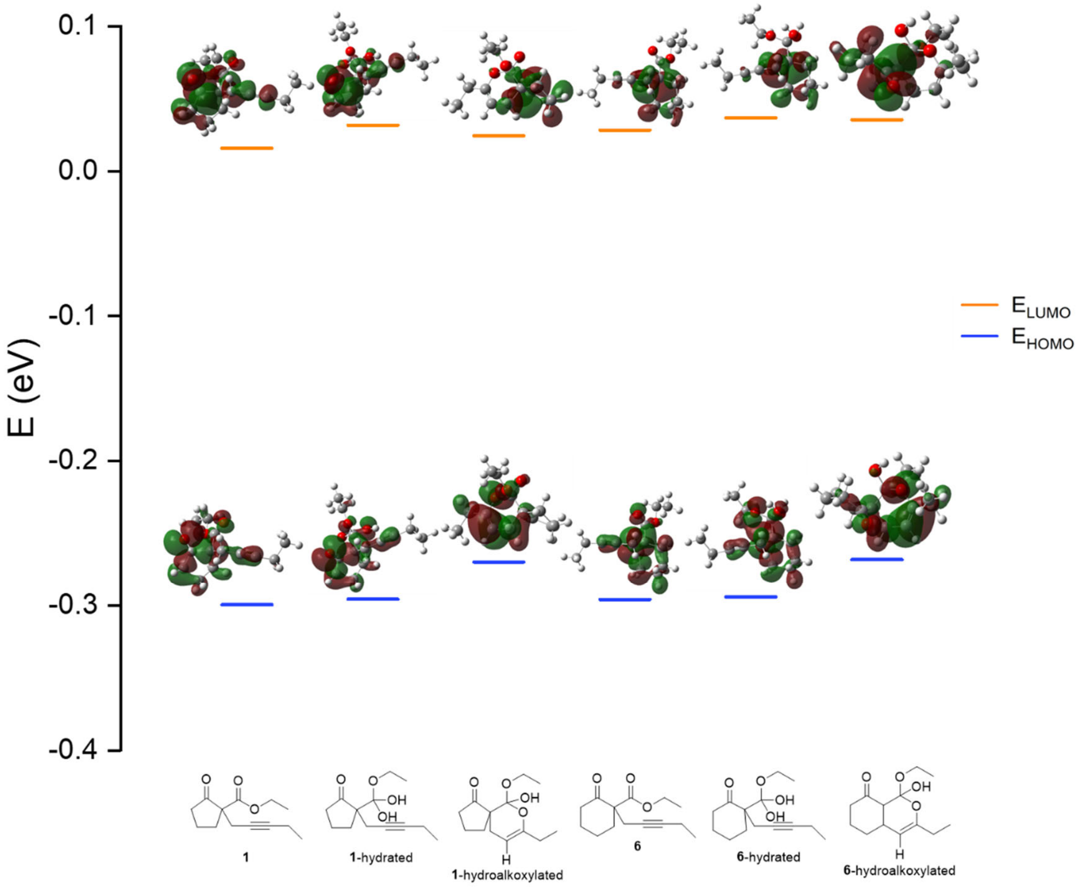


Figure S19. Computed relative energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) after density-functional calculations (DFT) of the starting materials **1** and **6**, and the corresponding hydrated and hydroalkoxylated intermediates during the ester-assisted hydration reaction. The HOMO and LUMO orbitals are represented in the structures. Colour code: Carbon atoms in grey, hydrogen atoms in white, oxygen atoms in red.

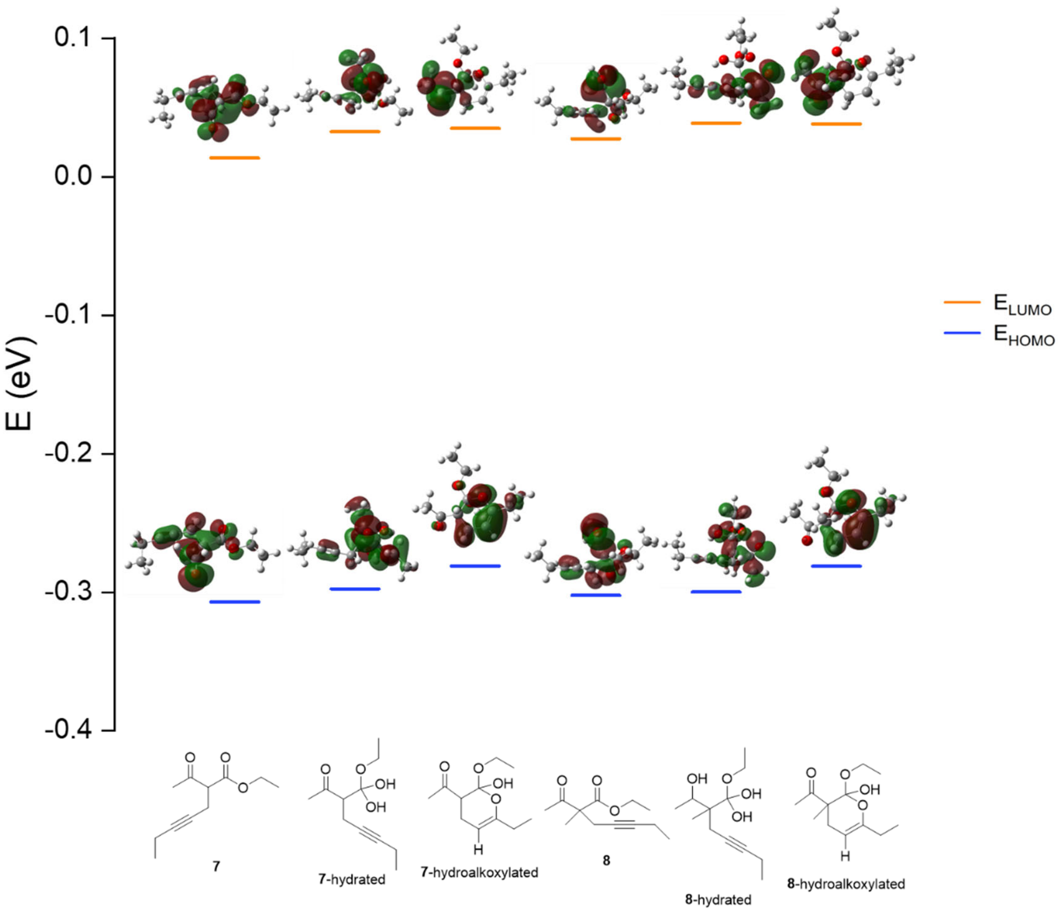


Figure S20. Computed relative energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) after density-functional calculations (DFT) of the starting materials **7** and **8**, and the corresponding hydrated and hydroalkoxylated intermediates during the ester-assisted hydration reaction.

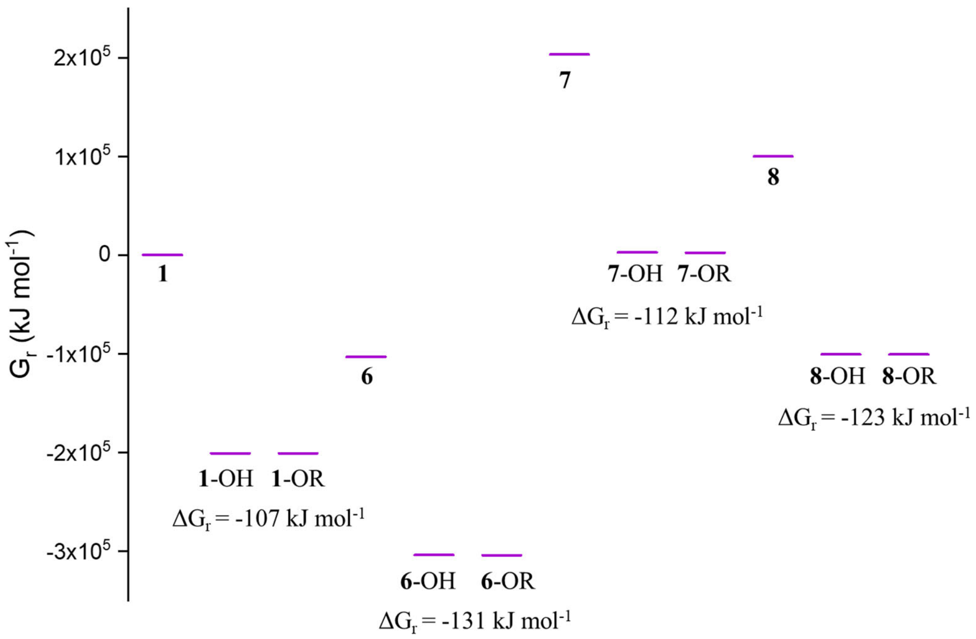
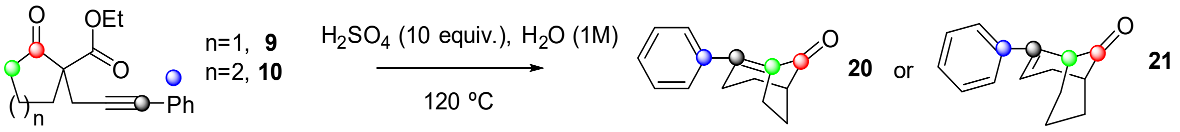
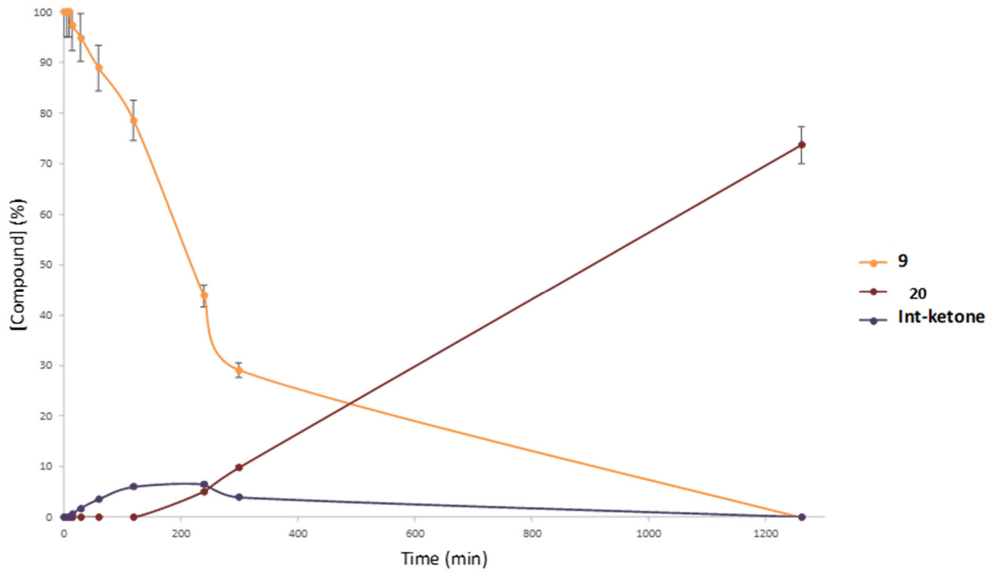


Figure S21. Computed relative Gibbs free energies of the starting materials **1, 6-8**, and the corresponding hydrated (-OH) and hydroalkoxylated (-OR) intermediates during the ester-assisted hydration reaction.





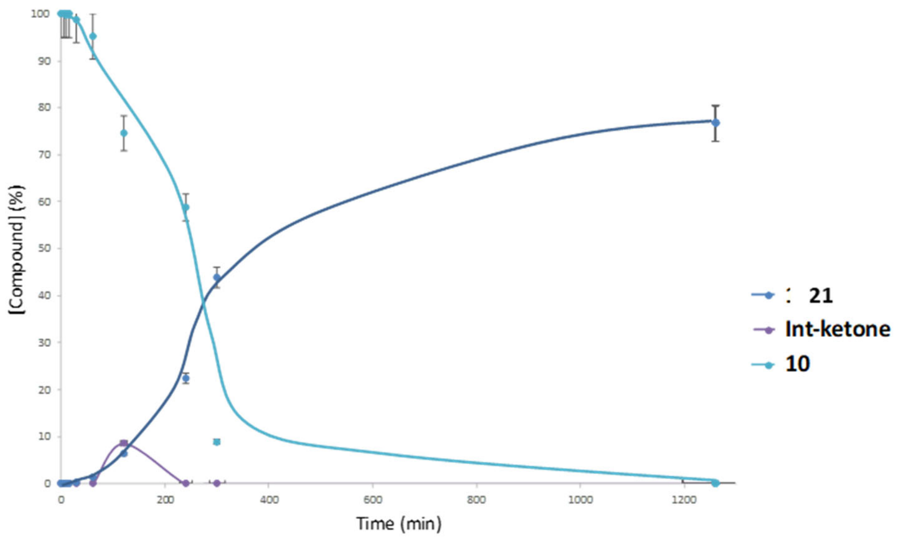
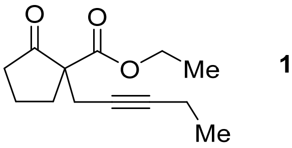


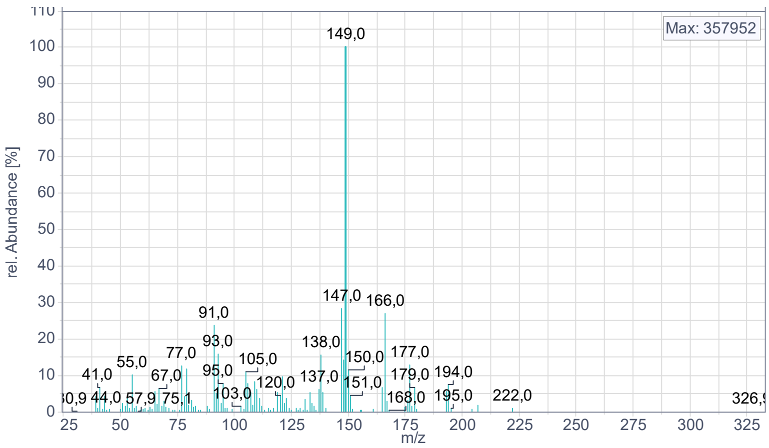
Figure S22. Kinetics for the H^+-catalyzed alkyne hydration-condensation-decarboxylation cascade reaction of the β-ketoesters **9** or **10**. Reaction conditions: **9** or **10** (1 mmol), water (1 mL), H_2SO_4 (10 equiv.), 120 ºC. Combined GC and ^1H-NMR results. Error bars account for a 5% uncertainty. Lines are a guide to the eye.

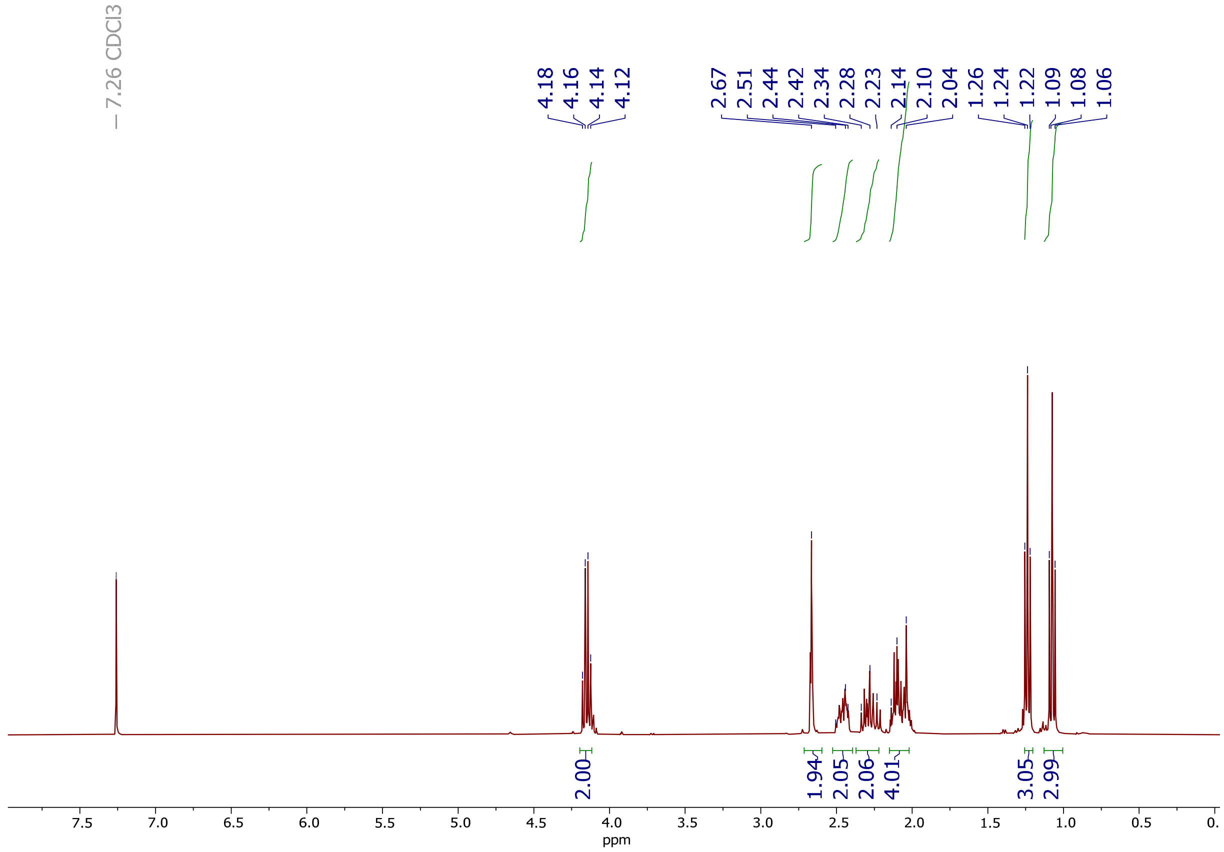
Compound characterization with copies of the spectra.

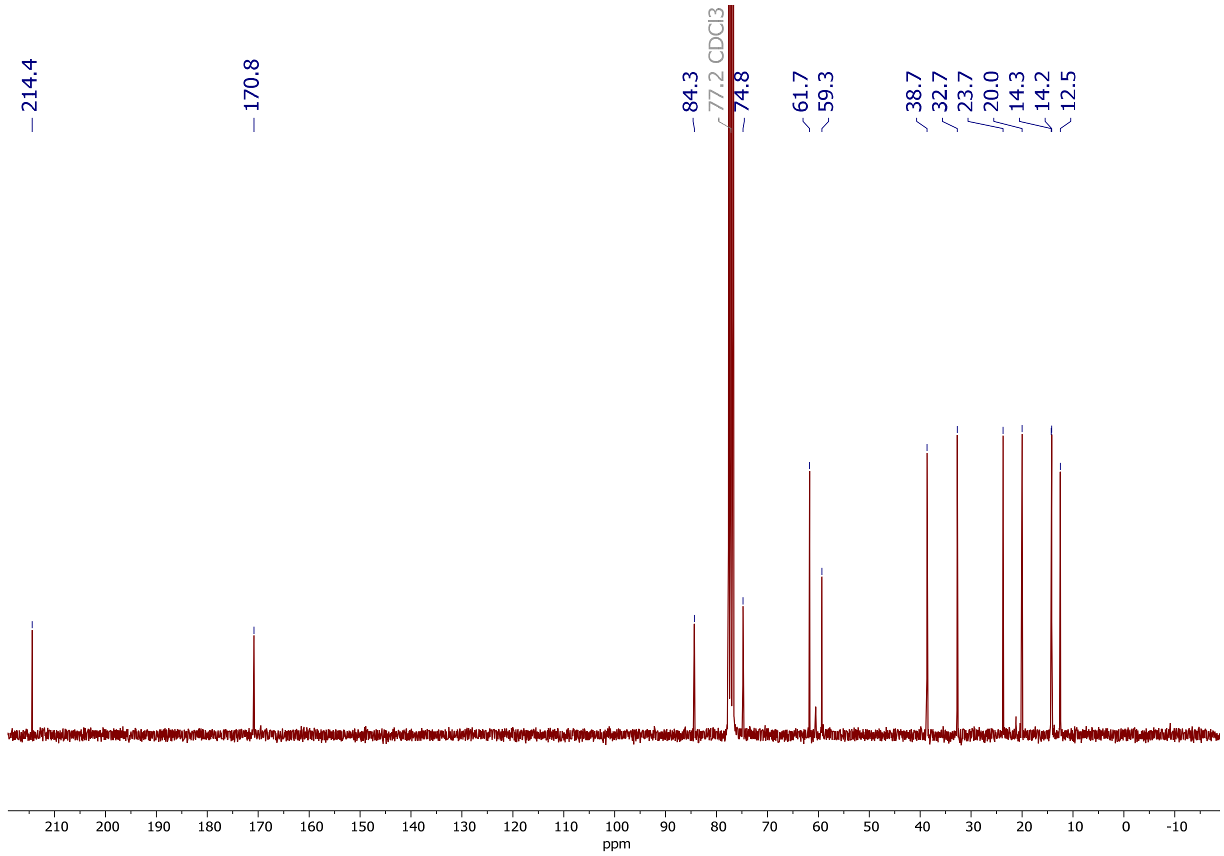


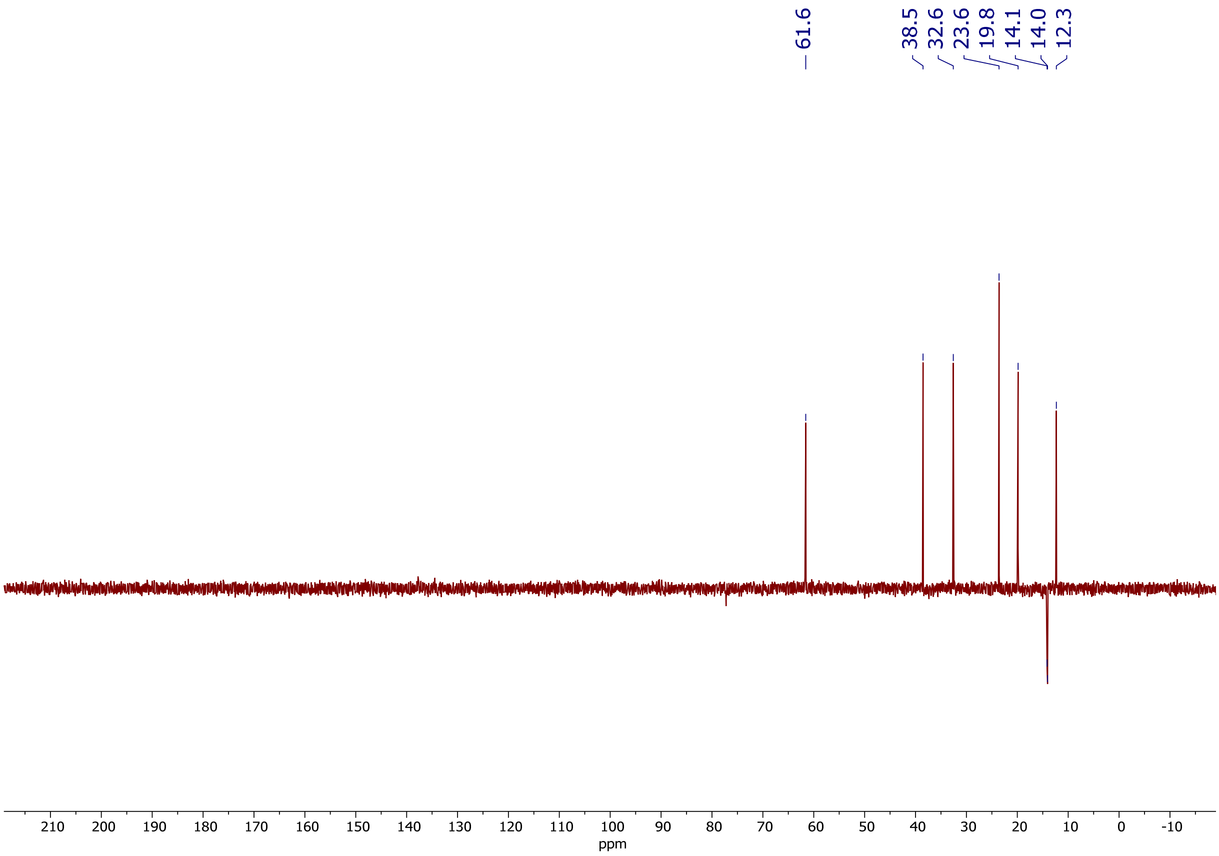
1

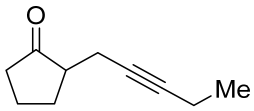
Ethyl 2-oxo-1-(pent-2-yn-1-yl)cyclopentane-1-carboxylate **1**. **GC-MS; m/z, (relative intensity):** 222 (M+•, 1), 195 (1), 194 (7), 177 (13), 166 (27), 150 (12), 149 (100), 148 (14), 147 (28), 138 (15), 121 (9), 105 (11), 93 (16), 91 (24), 79 (12), 77 (13), 55 (10). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 4.15 (q, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 2.4 Hz, 2H), 2.52 – 2.40 (m, 2H), 2.36 – 2.20 (m, 2H), 2.17 – 1.97 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 214.4 (C), 170.8 (C), 84.3 (C), 74.8 (C), 61.7 (CH_2), 59.3 (C), 38.7 (CH_2), 32.7 (CH_2), 23.7 (CH_2), 20.0 (CH_2), 14.3 (CH_3), 14.2 (CH_3), 12.5 (CH_2). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{13}H_{19}O_3$: 223.1329] found: 223.1334.




7.26 CDCl3
4.18
4.16
4.14
4.12
2.67
2.51
2.44
2.42
2.34
2.28
2.23
2.14
2.10
2.04
1.26
1.24
1.22
1.09
1.08
1.06
2.00
1.94
2.05
2.06
4.01
3.05
2.99
ppm

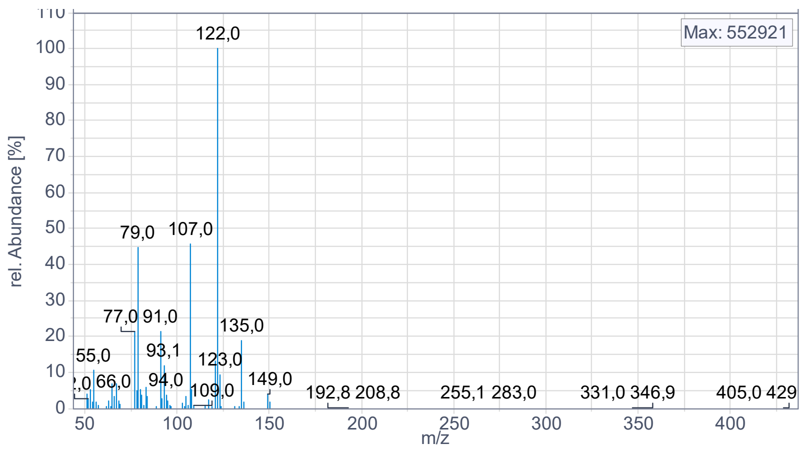

214.4
170.8
84.3
77.2 CDCl3
74.8
61.7
59.3
38.7
32.7
23.7
20.0
14.3
14.2
12.5
ppm

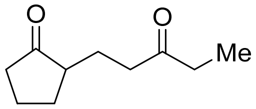




Int-1

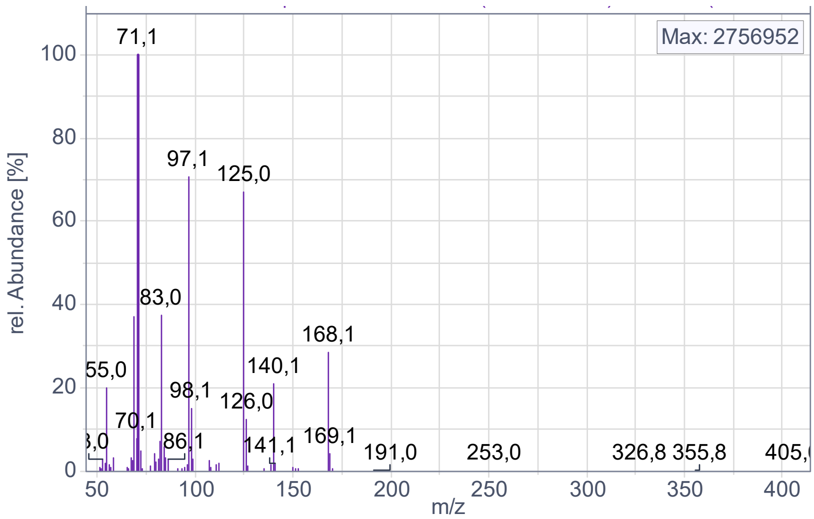
2-(Pent-2-yn-1-yl)cyclopentan-1-one **Int-1**. **GC-MS; m/z, (relative intensity):** 150 (M+•, 1), 135 (19), 123 (9), 122 (100), 121 (13), 107 (46), 93 (12), 91 (21), 79 (45), 77 (21), 55 (11).

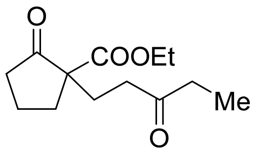




2

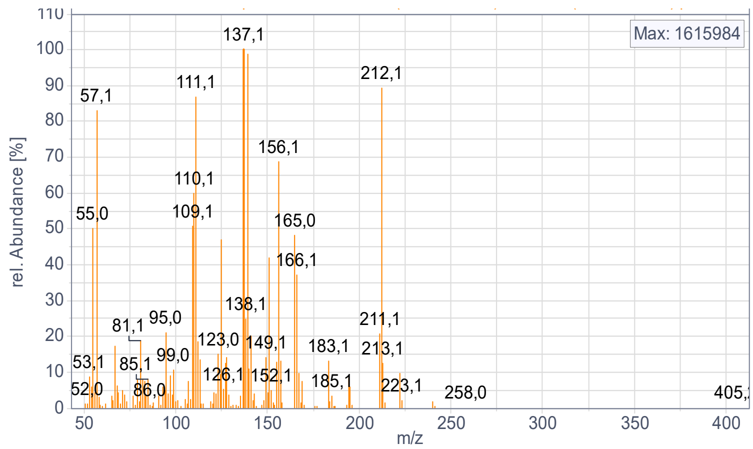
2-(3-Oxopentyl)cyclopentan-1-one **2**. **GC-MS; m/z, (relative intensity):** 168 (M+•, 28), 140 (21), 125 (67), 98 (15), 97 (71), 83 (38), 71 (100), 69 (37), 55 (20).

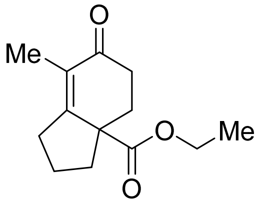


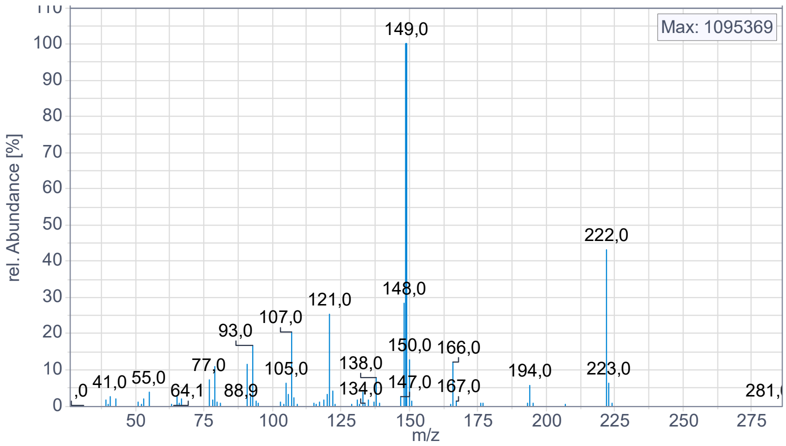


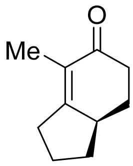
Int-2

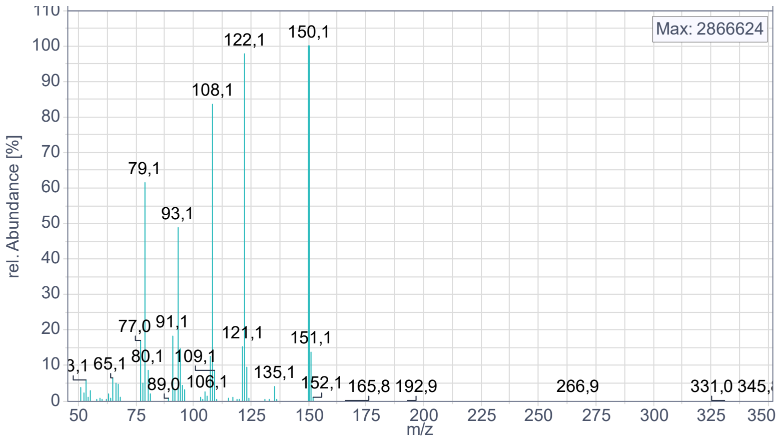
Ethyl 2-*oxo*-1-(3-oxopentyl)cyclopentane-1-carboxylate **Int-2**. **GC-MS; m/z, (relative intensity):** 240 (M+•, 2), 222 (10), 213 (13), 212 (89), 211 (21), 194 (8), 183 (13), 167 (10), 166 (37), 165 (48), 156 (69), 151 (42), 149 (14), 141 (20), 140 (11), 139 (99), 138 (25), 137 (100), 128 (14), 127 (13), 125 (47), 124 (9), 123 (15), 113 (13), 112 (19), 111 (87), 110 (60), 109 (51), 99 (11), 97 (9), 95 (21), 85 (8), 83 (7), 82 (8), 81 (19), 79 (8), 67 (17), 57 (83), 55 (50).

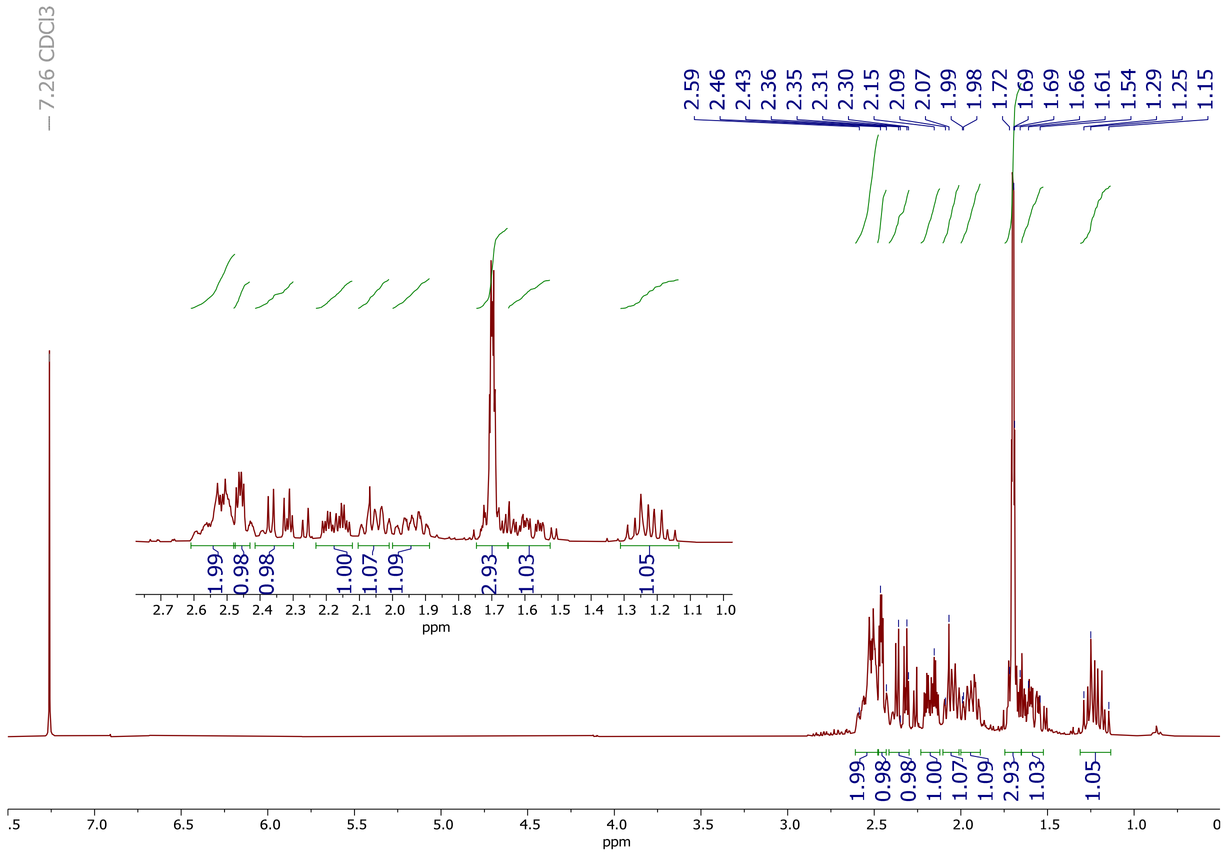


 **3** Ethyl 7-methyl-6-*oxo*-1,2,3,4,5,6-hexahydro-3*aH*-indene-3*a*-carboxylate **3**. **GC-MS; m/z, (relative intensity):** 222 (M+•, 43), 166 (12), 150 (13), 149 (100), 148 (28), 138 (8), 121 (26), 107 (20), 93 (17), 91 (12), 79 (11). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 4.22 – 4.03 (m, 2H), 2.60 – 2.48 (m, 3H), 2.47 – 2.32 (m, 2H), 1.87 –1.75 (m, 2H), 1.72 (t, *J* = 1.5 Hz, 3H), 1.61 – 1.48 (m, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 198.6 (C), 174.0 (C), 163.8 (C), 129.3 (C), 61.3 (CH_2), 55.0 (C), 39.2 (CH_2), 34.8 (CH_2), 33.0 (CH_2), 30.9 (CH_2), 22.6 (CH_2), 14.2 (CH_3), 11.5 (CH_3). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{13}H_{19}O_3$: 223.1329] found: 223.1336.

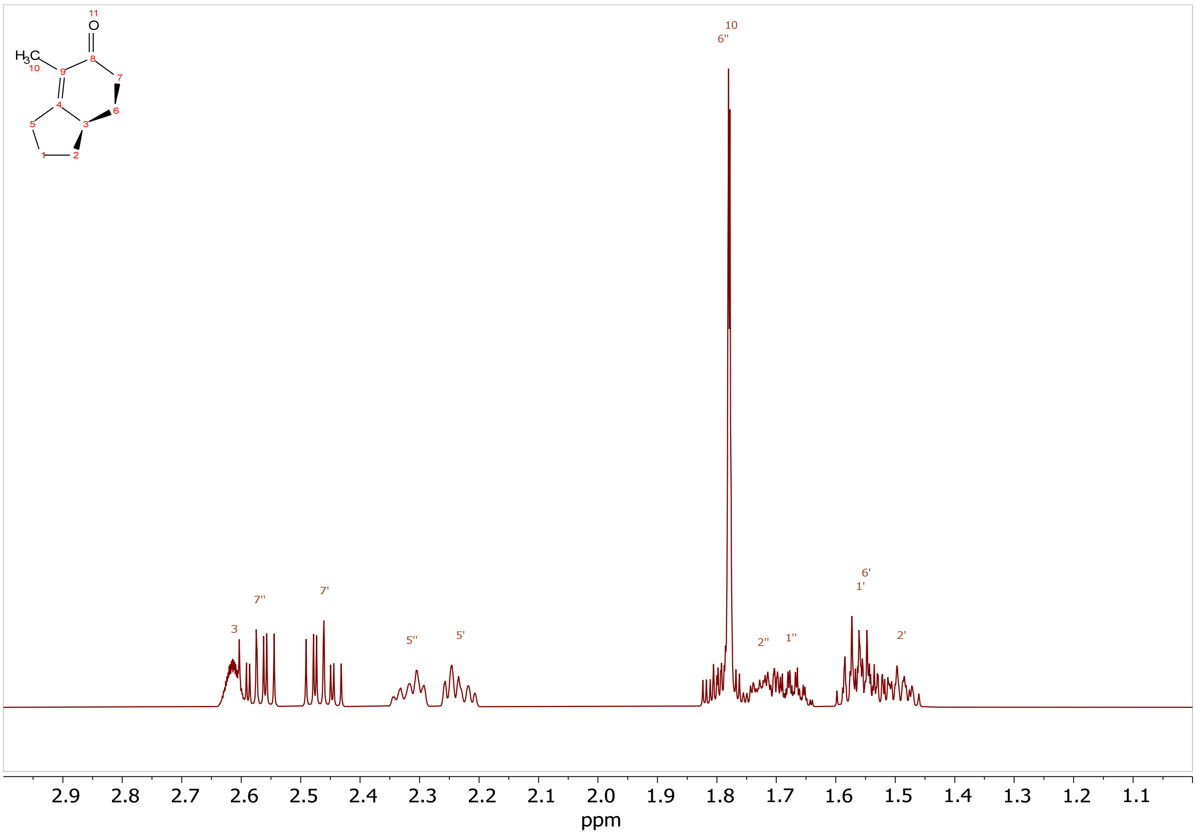


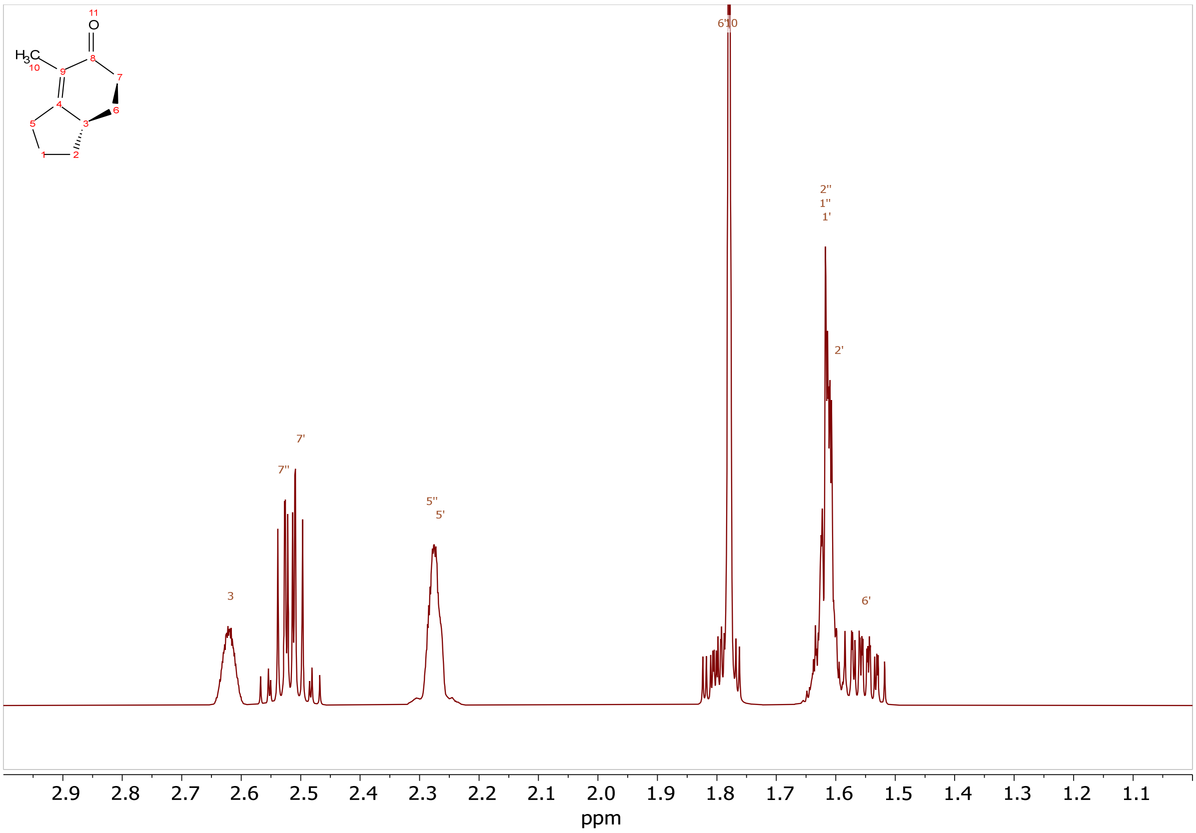
 **4** 4-Methyl-1,2,3,6,7,7*a*-hexahydro-5*H*-inden-5-one **4**. **GC-MS; m/z, (relative intensity):** 150 (M+•, 100), 123 (10), 122 (98), 108 (83), 94 (15), 93 (49), 91 (18), 79 (62), 77 (17). **^{1}H NMR (300 MHz, $CDCl_3$) δ** 2.62 – 2.48 (m, 2H), 2.46 (dd, *J* = 4.6, 2.4 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.18 (ddd, *J* = 12.6, 4.6, 2.4 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.99 – 1.88 (m, 1H), 1.70 (dt, *J* = 2.6, 1.4 Hz, 3H), 1.65 (s, 2H), 1.29i – 1.12 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 199.6 (C), 168.7 (C), 128.1 (C), 43.7 (CH), 37.8 (CH_2), 33.9 (CH_2), 31.3 (CH_2), 29.4 (CH_2), 24.5 (CH_2), 11.4 (CH_3). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{10}H_{15}O$: 151.1123] found: 151.1121.



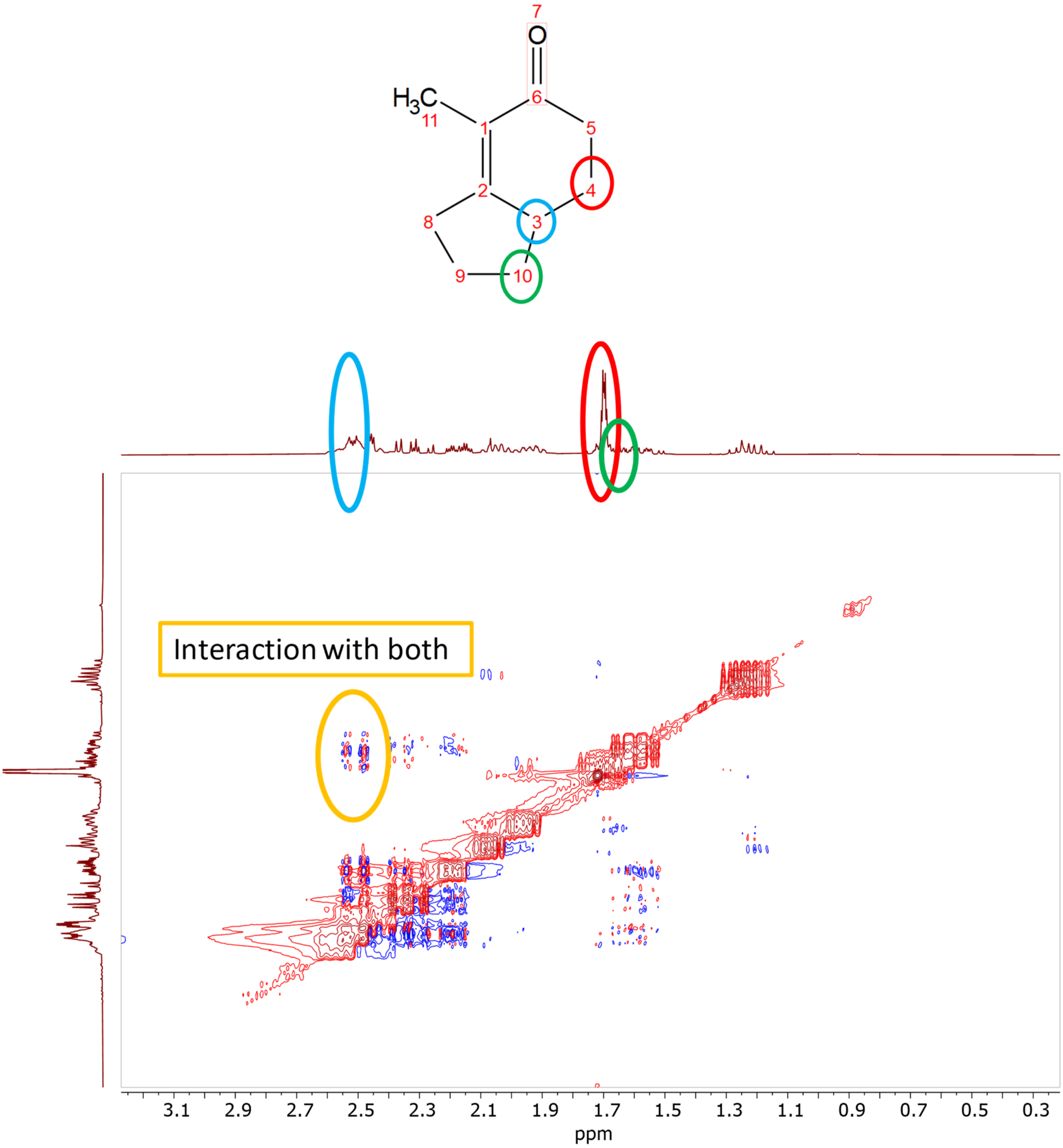


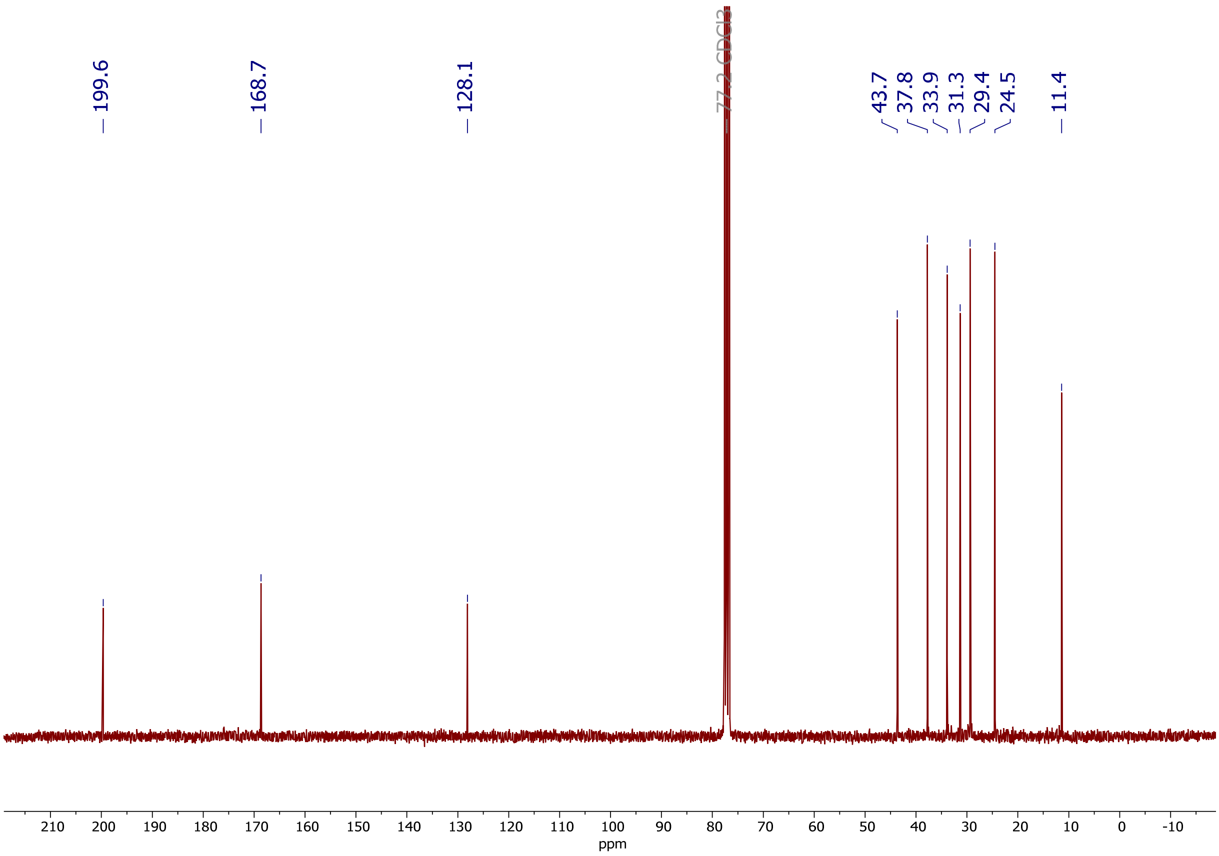
Simulated:

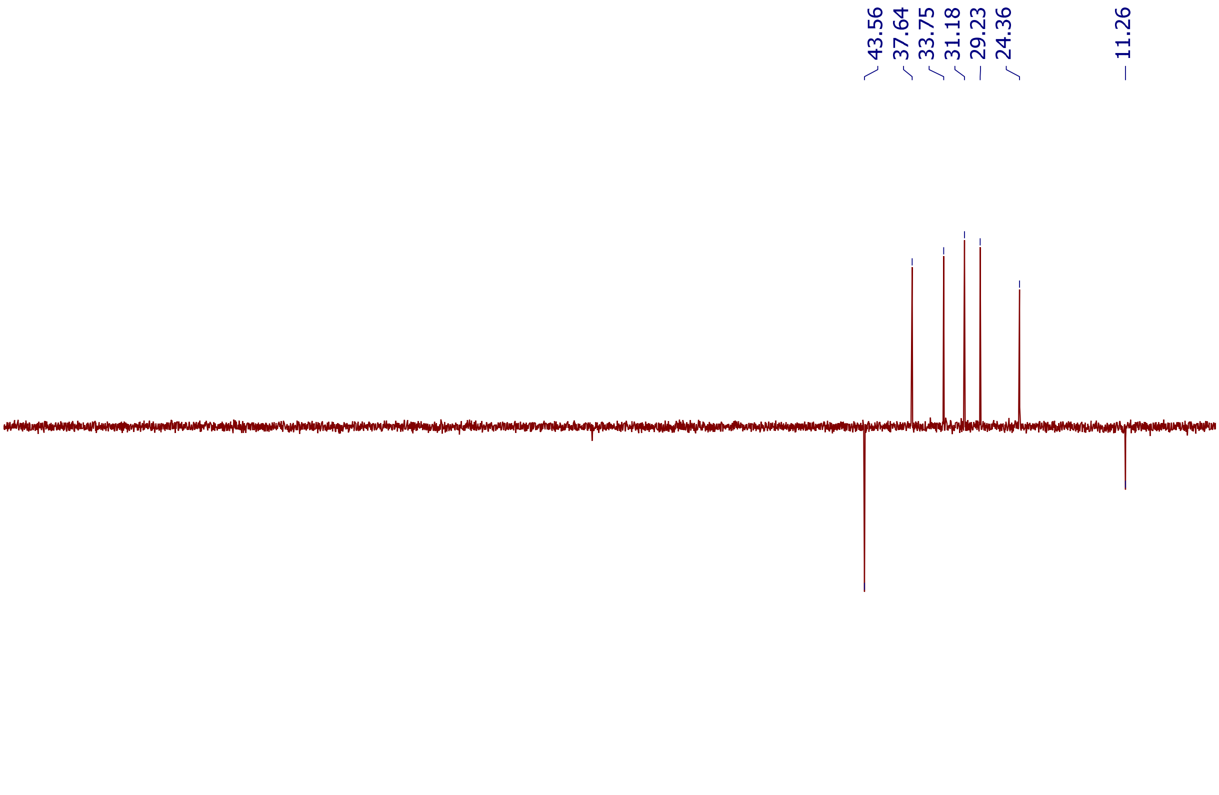


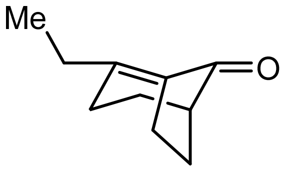


Experimental 2D nuclear overhauser enhancement spectrum (NOESY):



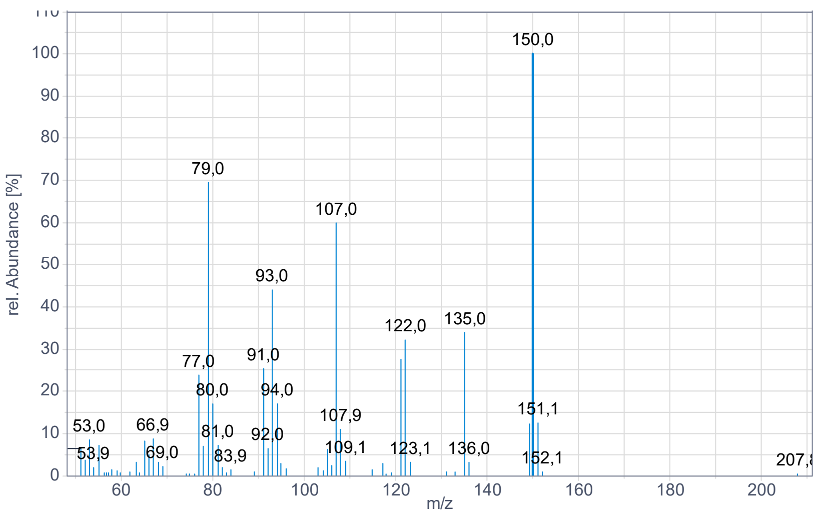

199.6
168.7
128.1
77.2 CDCl3
43.7
37.8
33.9
31.3
29.4
24.5
11.4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

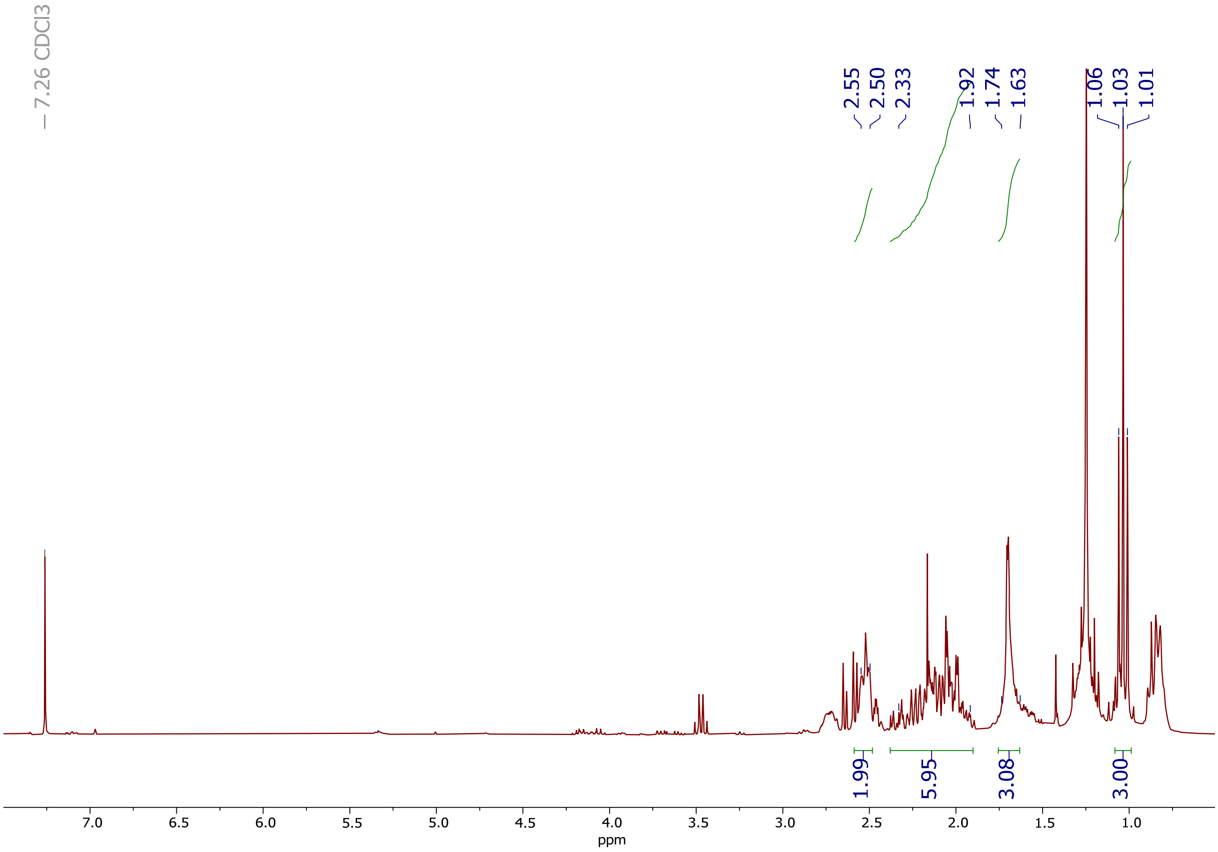

43.56
37.64
33.75
31.18
29.23
24.36
11.26
50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
ppm

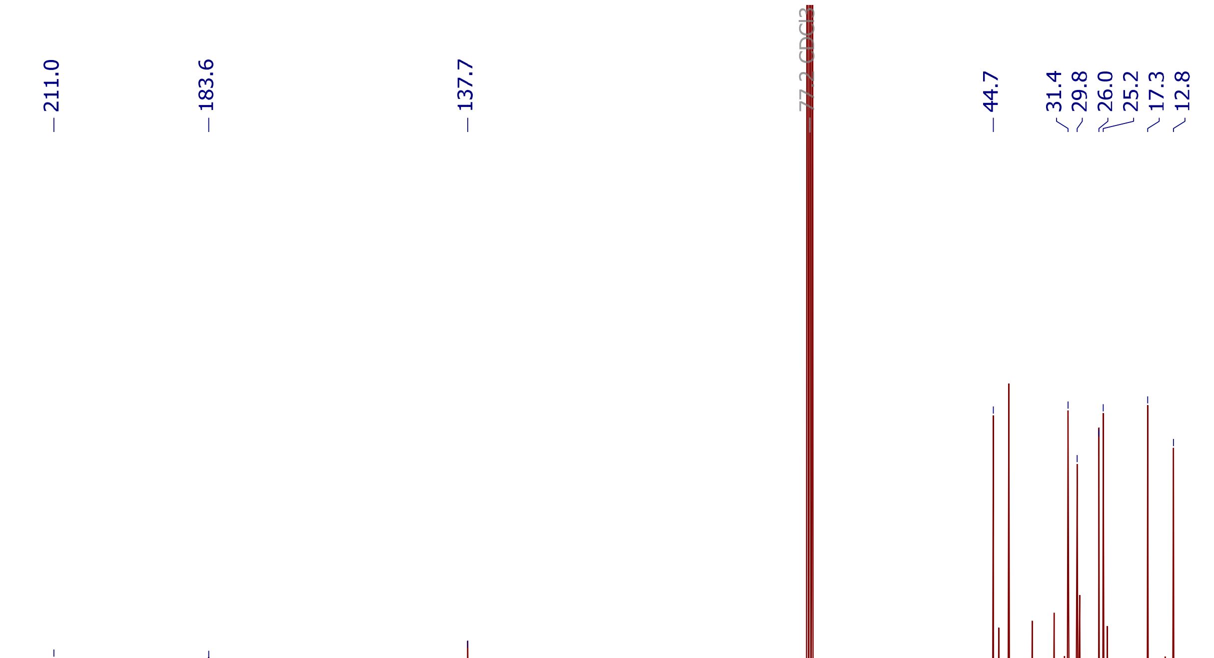


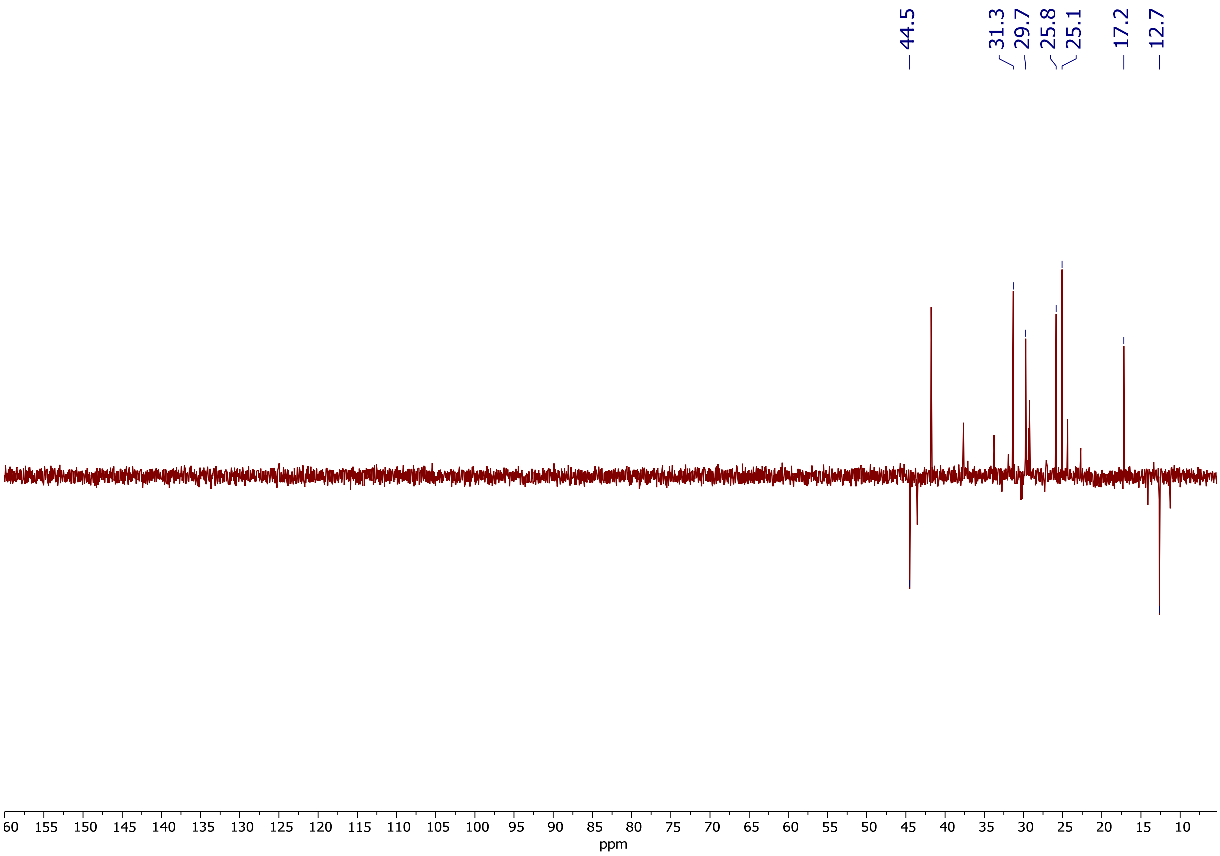
5

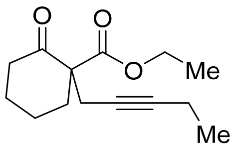
2-Ethylbicyclo[3.2.1]oct-1-en-8-one **5**. **GC-MS; m/z, (relative intensity):** 150 (M+•, 100), 149 (12), 135 (34), 122 (32), 121 (28), 107 (60), 93 (44), 91 (25), 79 (69), 77 (24), 53 (9). **^{1}H NMR (300 MHz, $CDCl_3$) δ** 2.55 – 2.50 (m, 2H), 2.33 – 1.92 (m, 6H), 1.74 – 1.63 (m, 3H), 1.03 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 211.0 (C), 183.6 (C), 137.7 (C), 44.7 (CH), 31.4 (CH_2), 29.8 (CH_2), 26.0 (CH_2), 25.2 (CH_2), 17.3(CH_2), 12.8 (CH_3).




7.26 CDCl3
2.55
2.50
2.33
1.92
1.74
1.63
1.06
1.03
1.01
1.99
5.95
3.08
3.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

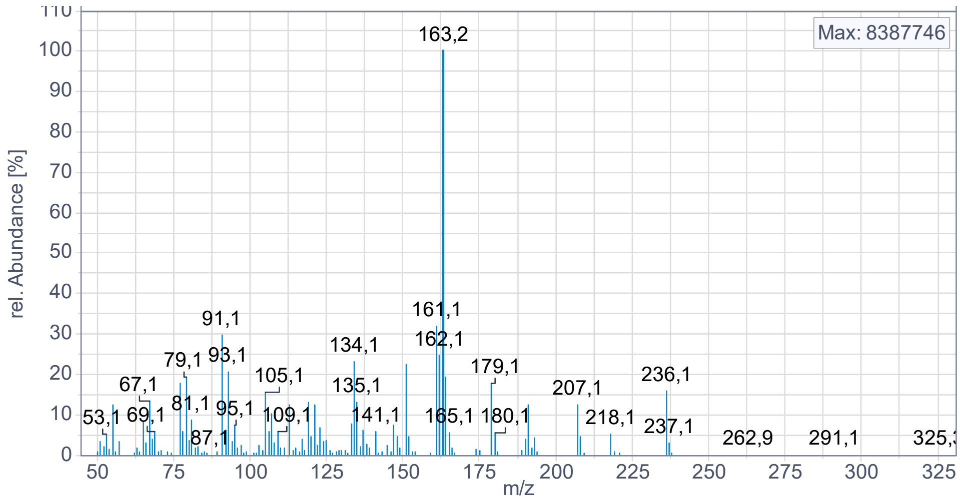

211.0
183.6
137.7
77.2 CDCl3
44.7
31.4
29.8
26.0
25.2
17.3
12.8
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

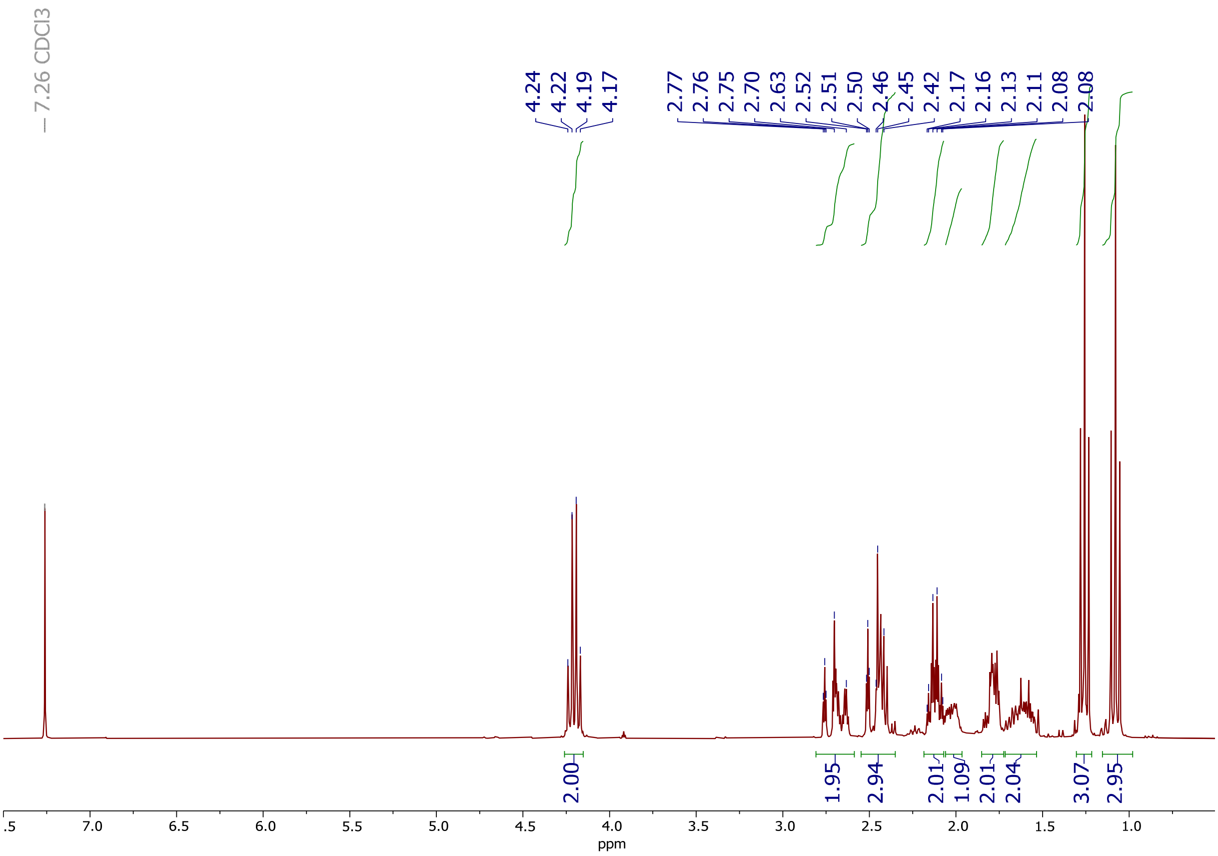


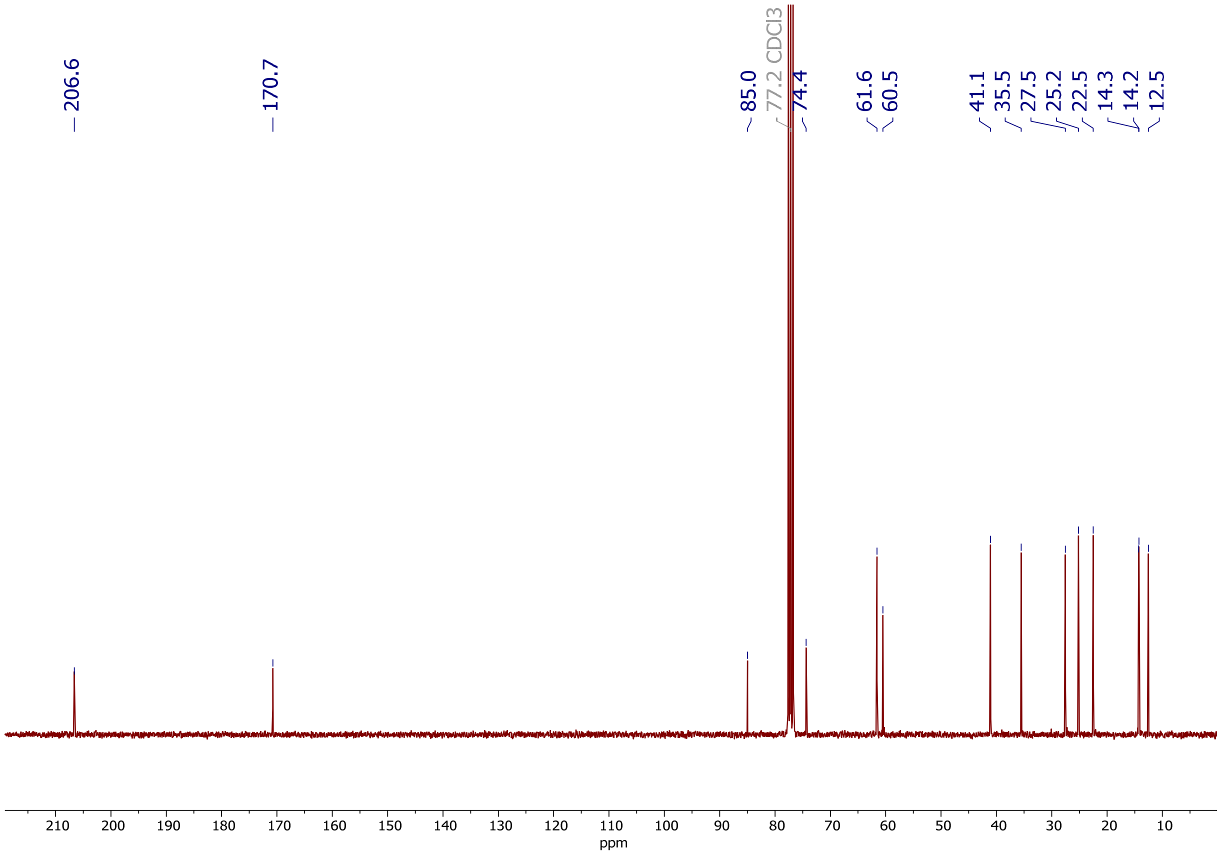


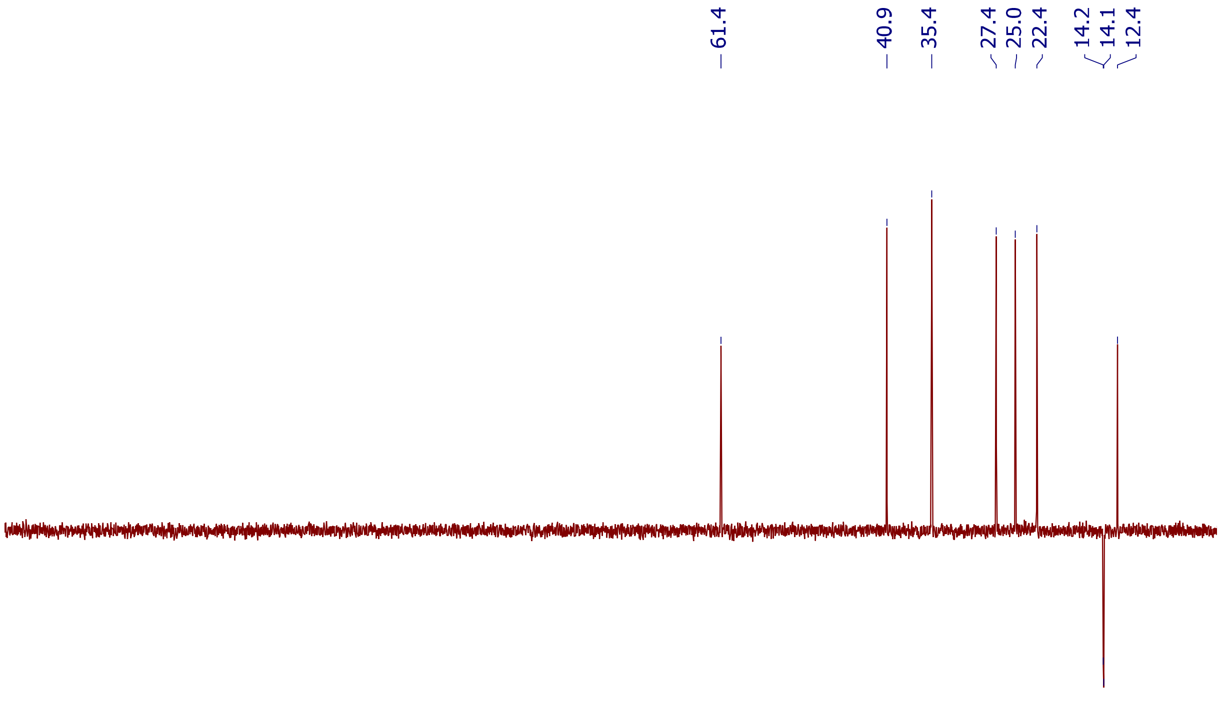
6

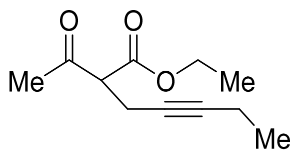
Ethyl 2-*oxo*-1-(pent-2-yn-1-yl)cyclohexane-1-carboxylate **6**. **GC-MS; m/z, (relative intensity):** 236 (M+•, 16), 207 (13), 191 (13), 179 (18), 164 (19), 163 (100), 162 (25), 161 (32), 151 (23), 134 (23), 119 (13), 118 (1), 113 (13), 105 (16), 93 (21), 91 (30), 79 (19), 67 (13). **^{1}H NMR (300 MHz, $CDCl_3$) δ** 4.20 (q, *J* = 7.2 Hz, 2H), 2.80 – 2.58 (m, 2H), 2.55 – 2.31 (m, 3H), 2.12 (qt, *J* = 7.5, 2.4 Hz, 2H), 2.07 – 1.96 (m, 1H), 1.79 (ddt, *J* = 10.0, 6.6, 3.5 Hz, 2H), 1.72 – 1.51 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 206.6 (C), 170.7 (C), 85.0 (C), 74.4 (C), 61.6 (CH2), 60.5 (C), 41.1 (CH_2), 35.5 (CH_2), 27.5 (CH_2), 25.2 (CH_2), 22.5 (CH_2), 14.3 (CH_3), 14.2 (CH_3), 12.5 (CH_2). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{14}H_{21}O_3$: 237.1492] found: 237.1495.


Max: 8387746
rel. Abundance [%]
m/z
163,2
161,1
162,1
91,1
93,1
134,1
79,1
179,1
105,1
67,1
135,1
236,1
207,1
81,1
95,1
53,1
69,1
109,1
141,1
165,1
180,1
218,1
237,1
87,1
262,9
291,1


7.26 CDCl3
4.24
4.22
4.19
4.17
2.77
2.76
2.75
2.70
2.63
2.52
2.51
2.50
2.46
2.45
2.42
2.17
2.16
2.13
2.11
2.08
2.08
2.00
1.95
2.94
2.01
1.09
2.01
2.04
3.07
2.95
ppm

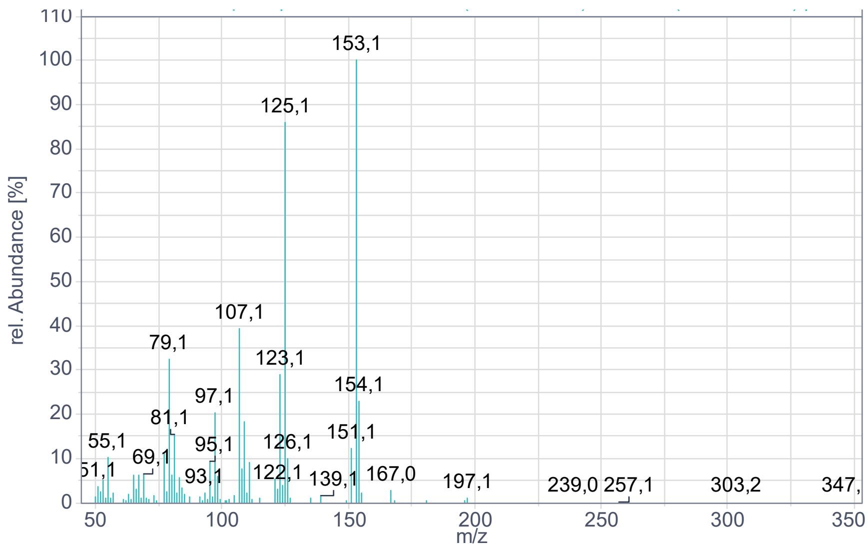

206.6
170.7
85.0
77.2 CDCl3
74.4
61.6
60.5
41.1
35.5
27.5
25.2
22.5
14.3
14.2
12.5
ppm

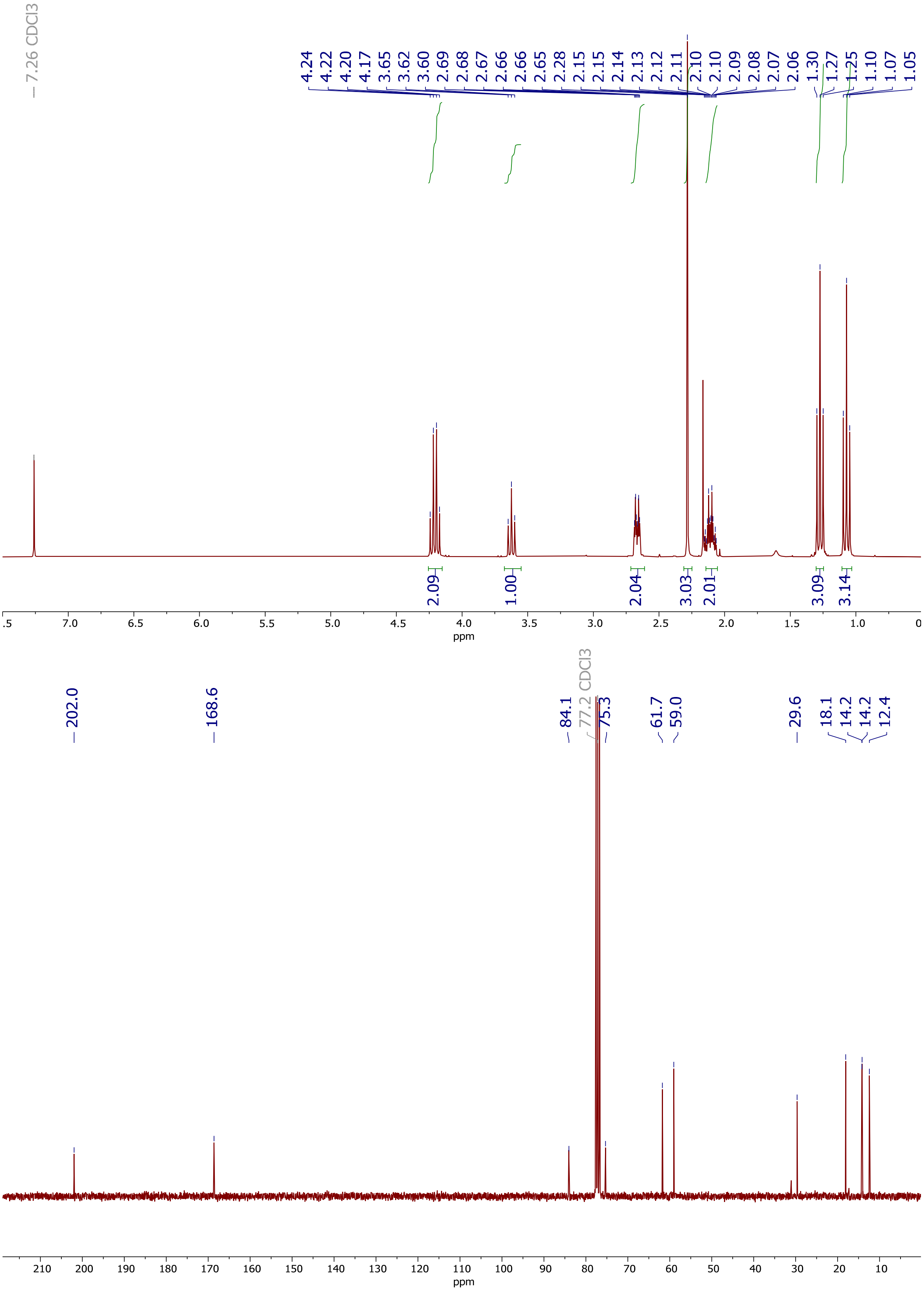

61.4
40.9
35.4
27.4
25.0
22.4
14.2
14.1
12.4
ppm

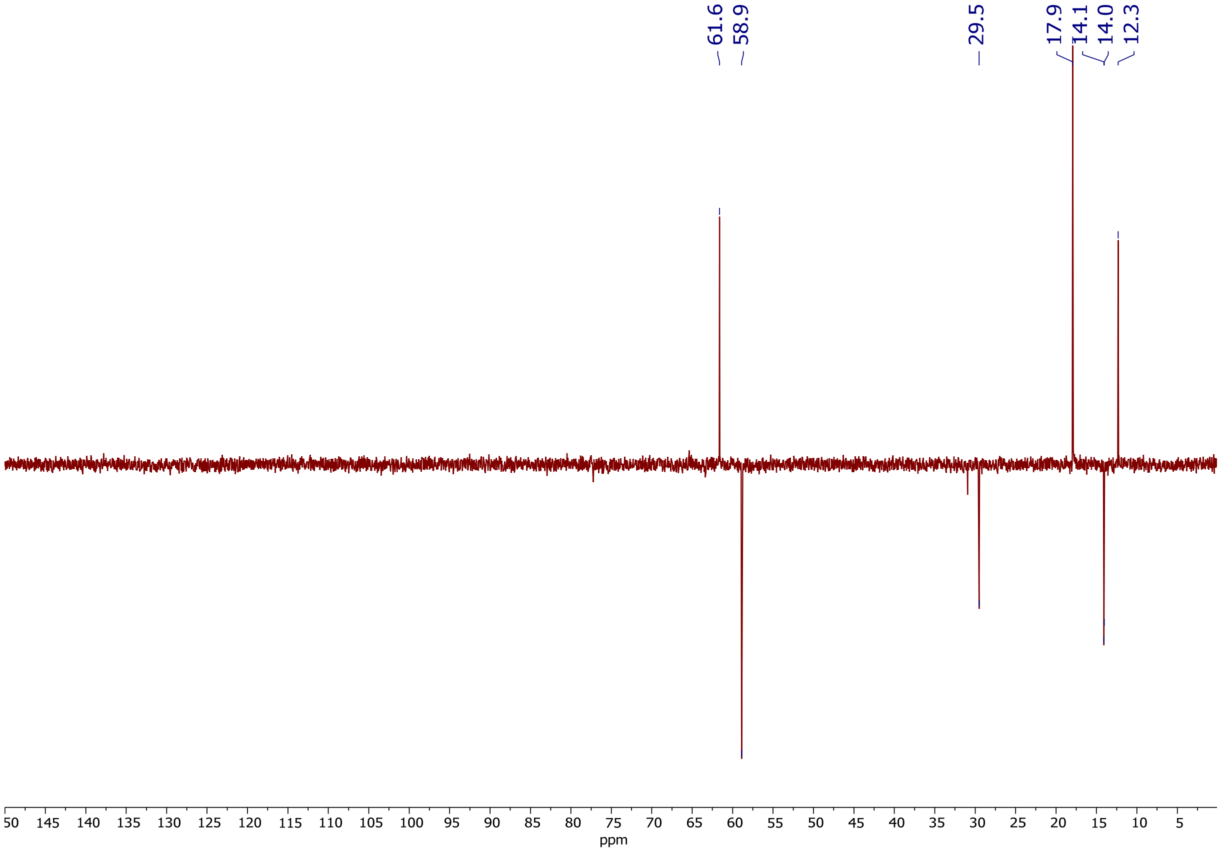


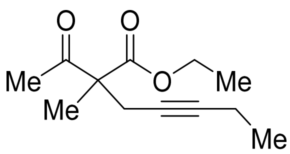
7

Ethyl 2-acetylhept-4-ynoate **7**. **GC-MS; m/z, (relative intensity):** 197 (M+•, 1), 154 (23), 153 (100), 151 (12), 125 (86), 123 (29), 111 (9), 109 (18), 107 (39), 97 (20), 95 (9), 81 (15), 79 (32), 77 (11), 55 (10). **^{1}H NMR (300 MHz, $CDCl_3$) δ** 4.21 (q, *J* = 7.2 Hz, 2H), 3.62 (t, *J* = 7.5 Hz, 1H), 2.67 (dtd, *J* = 7.5, 2.4, 0.8 Hz, 2H), 2.28 (s, 3H), 2.11 (qt, *J* = 7.3, 2.3 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 202.0 (C), 168.6 (C), 84.1 (C), 75.3 (C), 61.7 (CH_2), 59.0 (CH), 29.6 (CH_3), 18.1 (CH_2), 14.2 (CH_3), 14.1 (CH_3), 12.4 (CH_2). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{11}H_{17}O_3$: 197.1176] found: 197.1182.



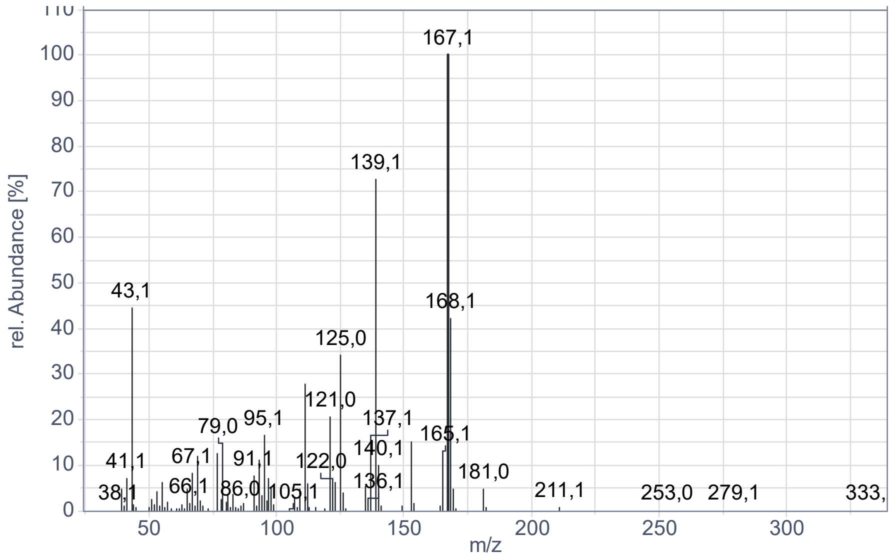

7.26 CDCl3
4.24
4.22
4.20
4.17
3.65
3.62
3.60
2.69
2.68
2.67
2.66
2.66
2.65
2.28
2.15
2.15
2.14
2.13
2.12
2.11
2.10
2.10
2.09
2.08
2.07
2.06
1.30
1.27
1.25
1.10
1.07
1.05
2.09
1.00
2.04
3.03
2.01
3.09
3.14
ppm
202.0
168.6
84.1
77.2 CDCl3
75.3
61.7
59.0
29.6
18.1
14.2
14.2
12.4
ppm

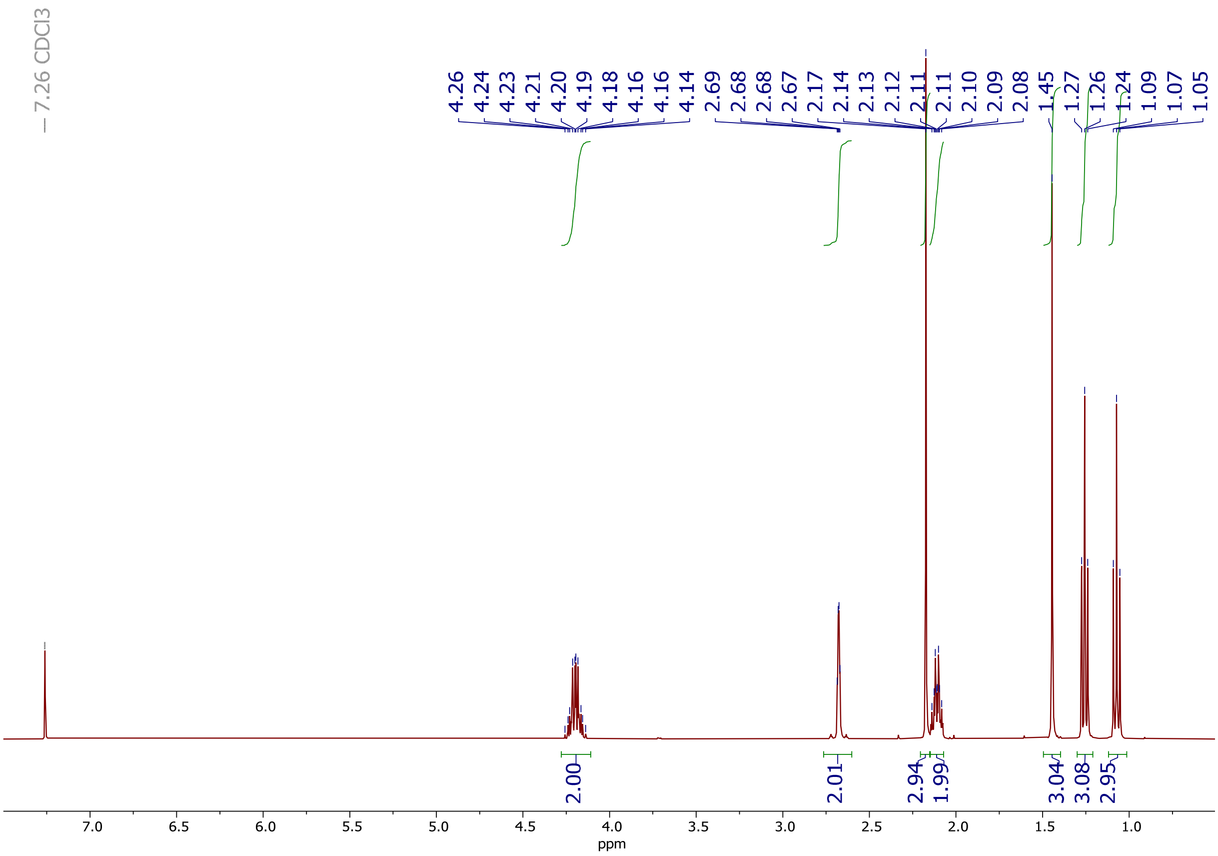


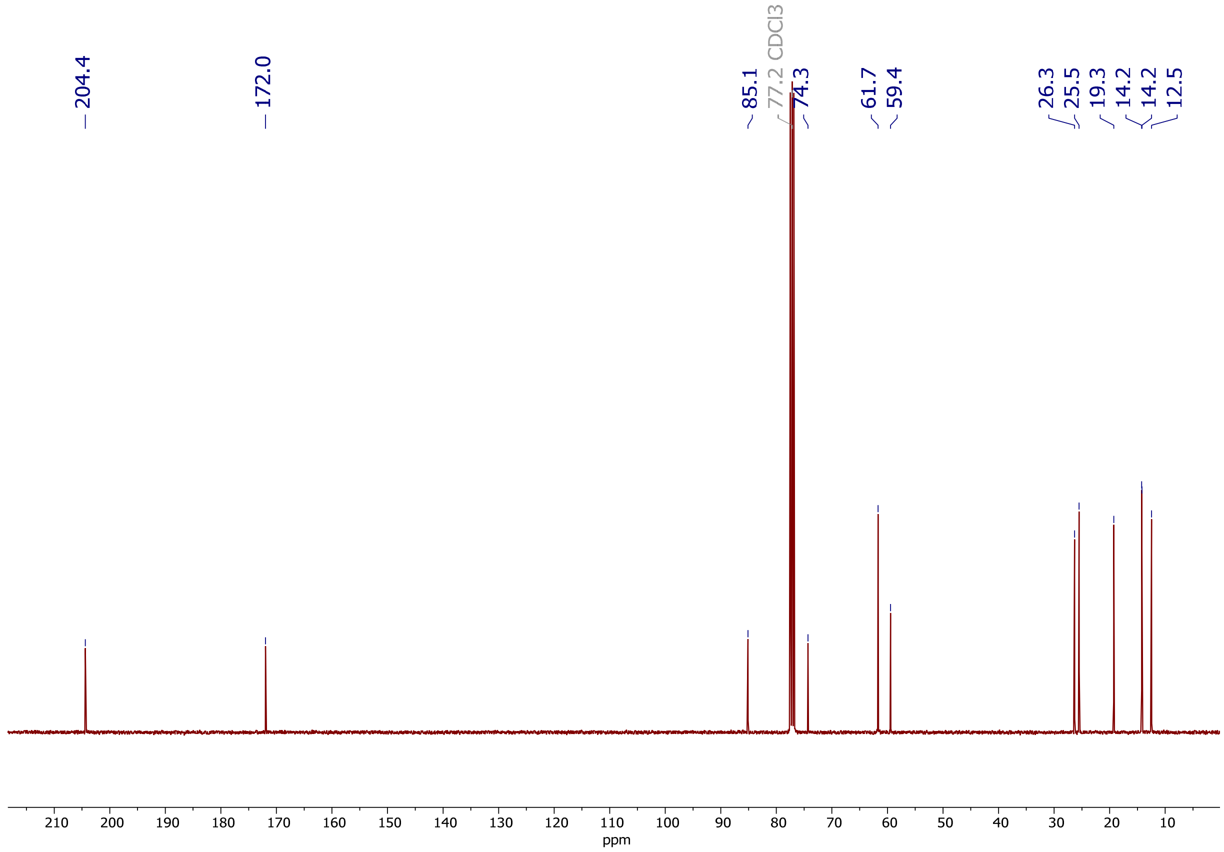


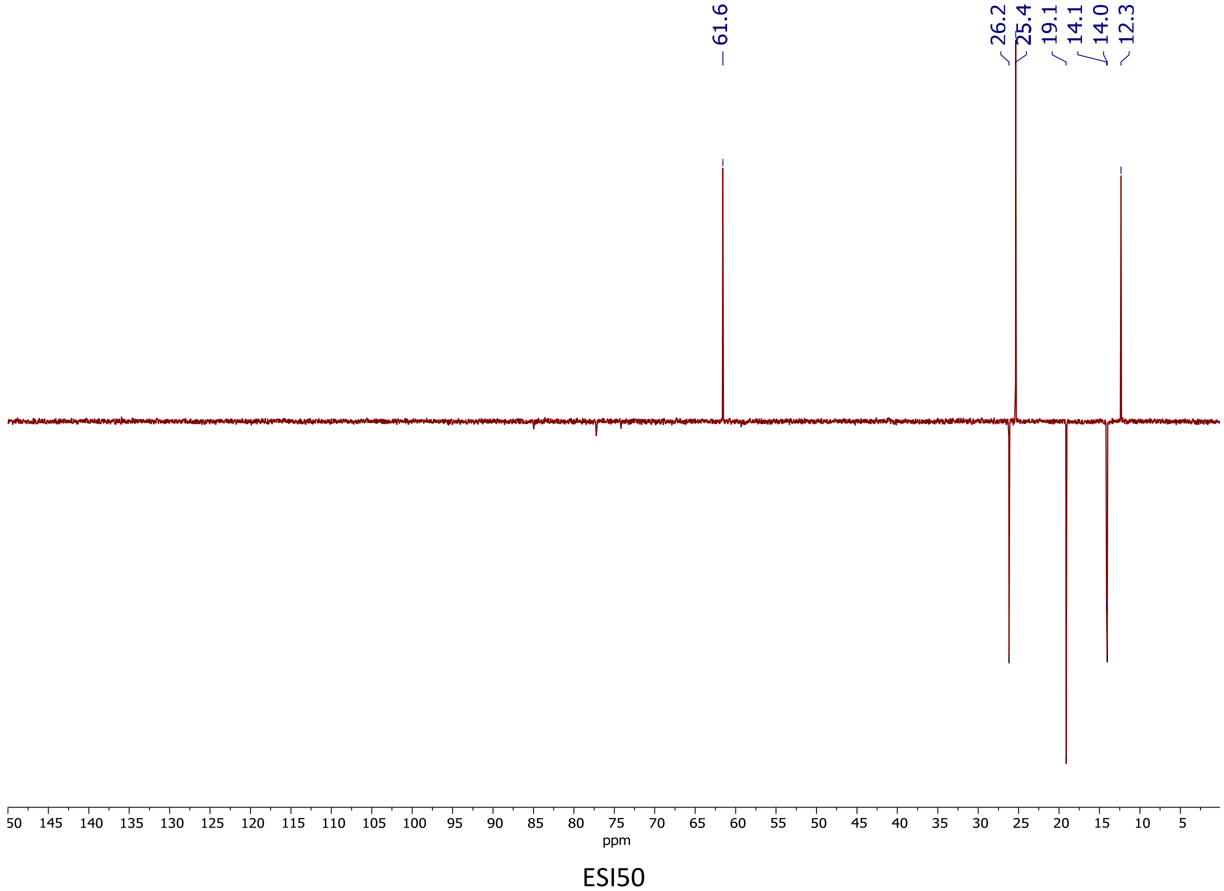
8

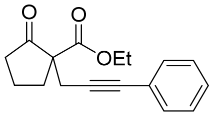
Ethyl 2-acetyl-2-methylhept-4-ynoate **8**. **GC-MS; m/z, (relative intensity):** 211 (M+•,1), 168 (42), 167 (100), 165 (13), 153 (15), 139 (73), 137 (17), 125 (34), 121 (21), 111 (28), 95 (17), 93 (11), 79 (15), 77 (12), 69 (12), 43 (45) . **^{1}H NMR (401 MHz, $CDCl_3$) δ** 4.20 (qd, *J* = 7.2, 4.9 Hz, 2H), 2.68 (q, *J* = 2.4 Hz, 2H), 2.17 (s, 3H), 2.11 (qt, *J* = 7.5, 2.5 Hz, 2H), 1.45 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 204.4 (C), 172.0 (C), 85.1 (C), 74.3 (C), 61.7 (CH), 59.4 (C), 26.3 (CH_2), 25.5 (CH), 19.3 (CH_2), 14.2 (CH_2), 14.2 (CH_2), 12.5 (CH_3). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{12}H_{19}O_3$: 211.1332] found: 211.1337.


167,1
139,1
43,1
168,1
125,0
121,0
79,0
95,1
137,1
165,1
41,1
67,1
91,1
122,0
140,1
181,0
38,1
66,1
86,0
105,1
136,1
211,1
253,0
279,1
333,
rel. Abundance [%]
m/z

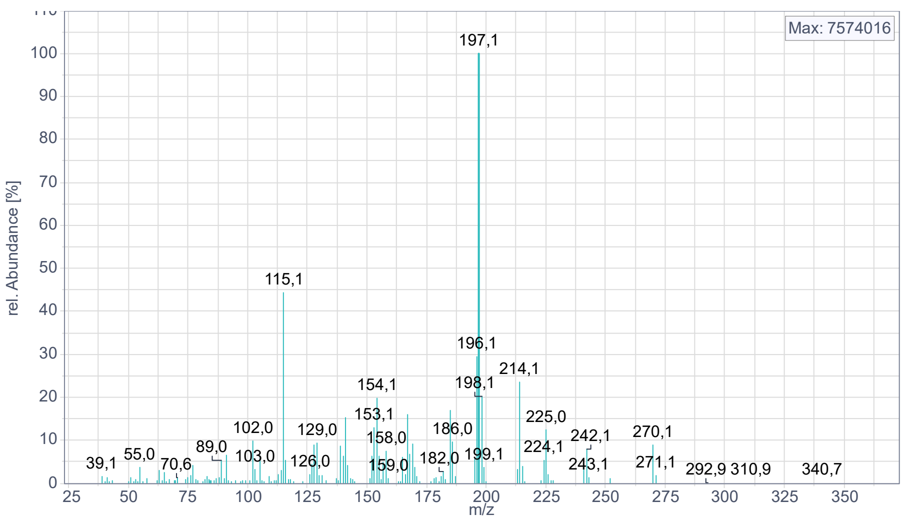

7.26 CDCl3
4.26
4.24
4.23
4.21
4.20
4.19
4.18
4.16
4.14
2.69
2.68
2.68
2.67
2.17
2.14
2.13
2.12
2.11
2.11
2.10
2.09
2.08
1.45
1.27
1.26
1.24
1.09
1.07
1.05
2.00
2.01
2.94
1.99
3.04
3.08
2.95
ppm

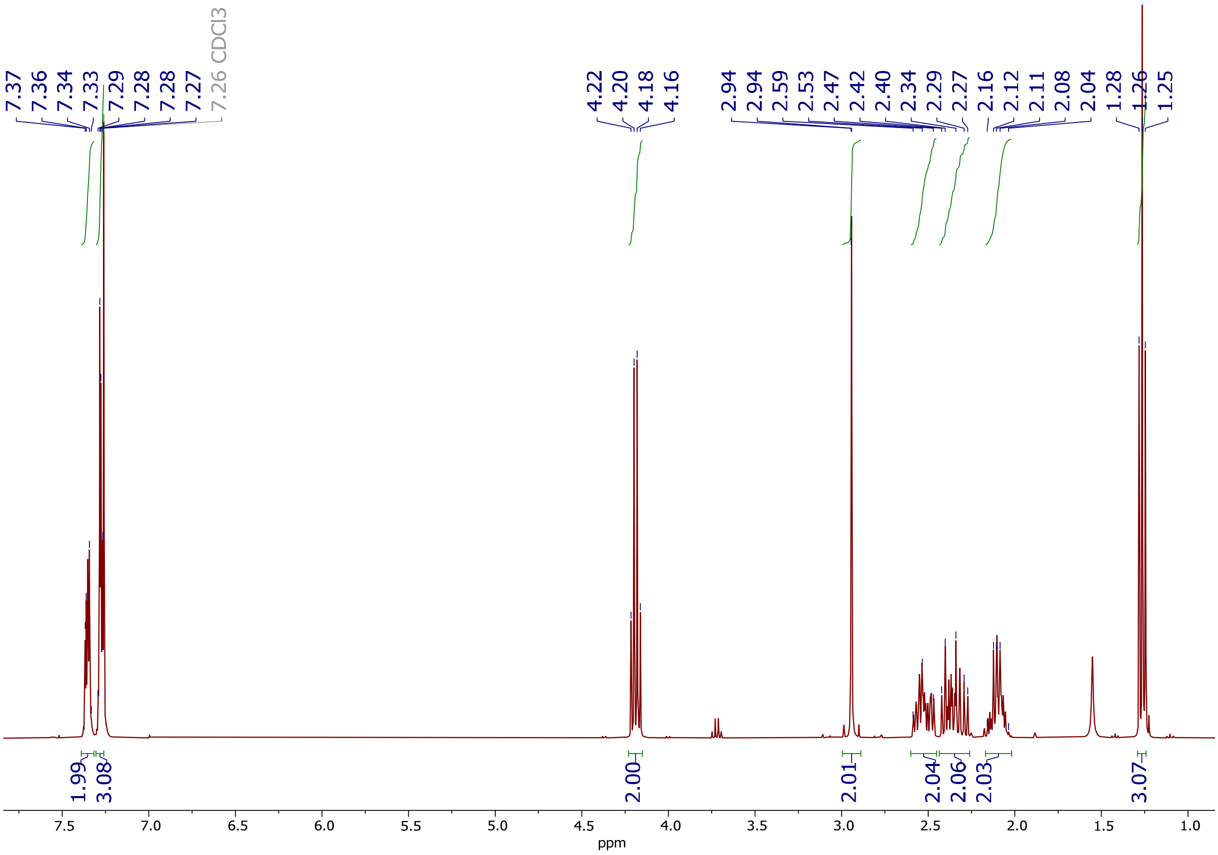

204.4
172.0
85.1
77.2 CDCl3
74.3
61.7
59.4
26.3
25.5
19.3
14.2
14.2
12.5
ppm

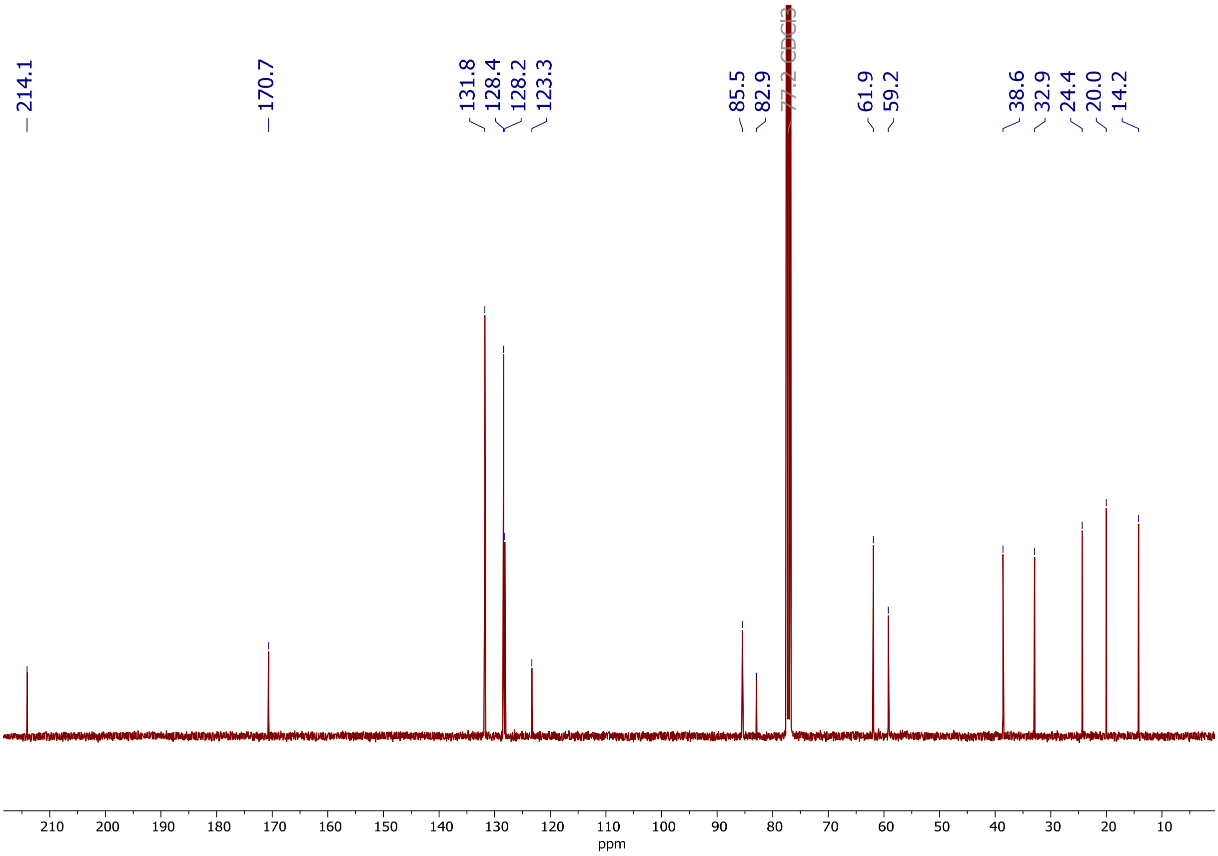

61.6
26.2
25.4
19.1
14.1
14.0
12.3
ppm

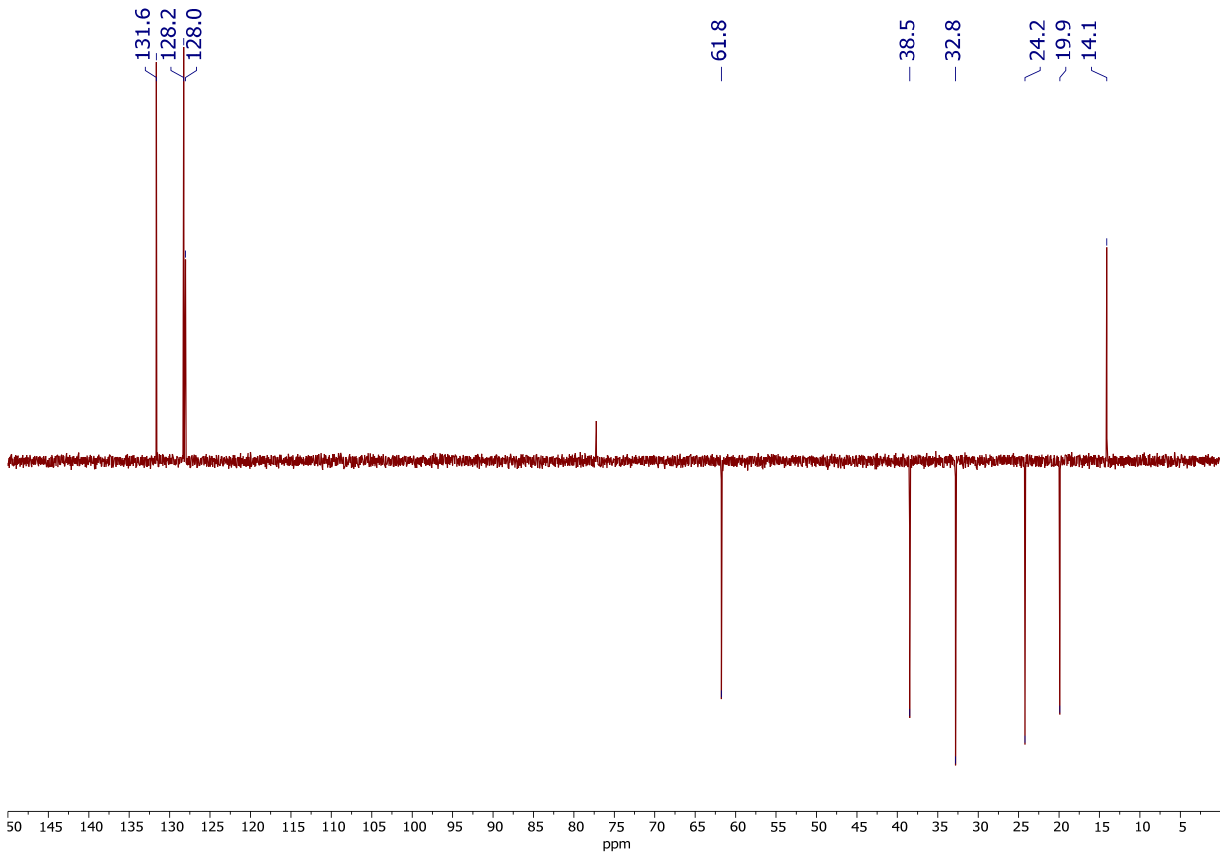
 **9**

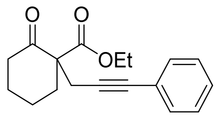
Ethyl 2-*oxo*-1-(3-phenylprop-2-yn-1-yl)cyclopentane-1-carboxylate **9**. **GC-MS; m/z, (relative intensity):** 270 (M+•, 9), 242 (9), 225 (12), 214 (23), 198 (20), 197 (100), 196 (30), 185 (17), 167 (16), 154 (20), 153 (13), 141 (15), 139 (9), 129 (9), 128 (9), 115 (44), 102 (10). **^{1}H NMR (401 MHz, $CDCl_3$) δ:** 7.36 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.31 – 7.24 (m, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.94 (d, *J* = 1.0 Hz, 2H), 2.65 – 2.45 (m, 2H), 2.44 – 2.24 (m, 2H), 2.19 – 2.02 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 214.1 (C), 170.7 (C), 131.8 (2CH), 128.4 (2CH), 128.2 (CH), 123.3 (C), 85.5 (C), 82.9 (C), 61.9 (CH_2), 59.2 (C), 38.6 (CH_2), 32.9 (CH_2), 24.4 (CH_2), 20.0 (CH_2), 14.2 (CH_3). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{17}H_{19}O_3$: 271.1329] found: 271.1336.




7.37
7.36
7.34
7.33
7.29
7.28
7.28
7.27
7.26 CDCl3
4.22
4.20
4.18
4.16
2.94
2.94
2.59
2.53
2.47
2.42
2.40
2.34
2.29
2.27
2.16
2.12
2.11
2.08
2.04
1.28
1.26
1.25
1.99
3.08
2.00
2.01
2.04
2.06
2.03
3.07
ppm

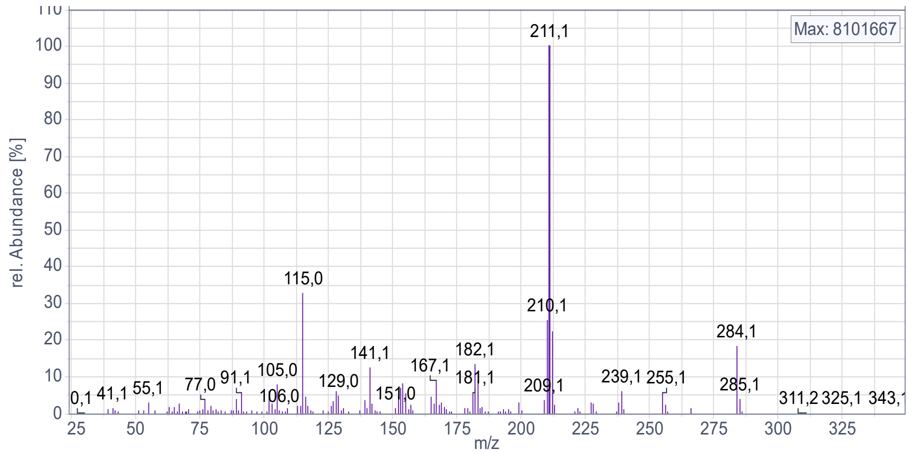

214.1
170.7
131.8
128.4
128.2
123.3
85.5
82.9
77.2 CDCl3
61.9
59.2
38.6
32.9
24.4
20.0
14.2
ppm





10

Ethyl 2-*oxo*-1-(3-phenylprop-2-yn-1-yl)cyclohexane-1-carboxylate **10**. **GC-MS; m/z, (relative intensity):** 284 (M+•, 18), 212 (22), 211 (100), 210 (25), 183 (9), 167 (9), 154 (8), 182 (13), 115 (33), 105 (8). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 7.34 – 7.31 (m, 2H), 7.24 – 7.21 (m, 3H), 4.20 (qd, *J* = 7.1, 1.7 Hz, 2H), 2.97 (d, *J* = 17.1 Hz, 1H), 2.76 – 2.69 (m, 1H), 2.71 (d, *J* = 17.1 Hz, 1H), 2.47 – 2.39 (m, 2H), 2.6 – 1.99 (m, 1H), 1.86 – 1.76 (m, 2H), 1.68 – 1.58 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ:** 206.2 (C), 170.5 (C), 131.6 (2CH), 128.2 (2CH), 127.8 (CH), 123.5 (C), 85.1 (C), 83.5 (C), 61.6 (CH_2), 60.4 (C), 40.9 (CH_2), 35.6 (CH_2), 27.4 (CH_2), 25.7 (CH_2), 22.4 (CH_2), 14.2 (CH_3). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{18}H_{21}O_3$: 285.1486] found: 285.1491.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rel. Abundance [%]
m/z
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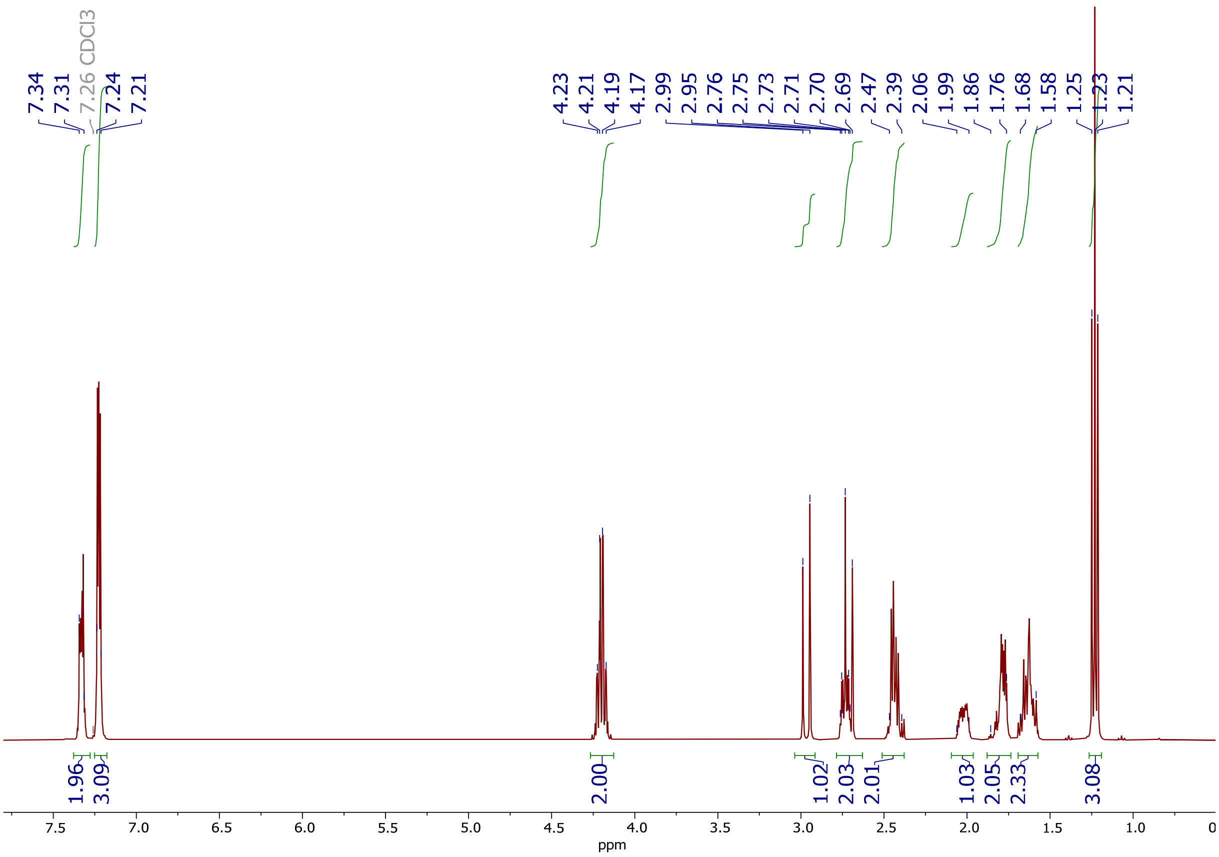
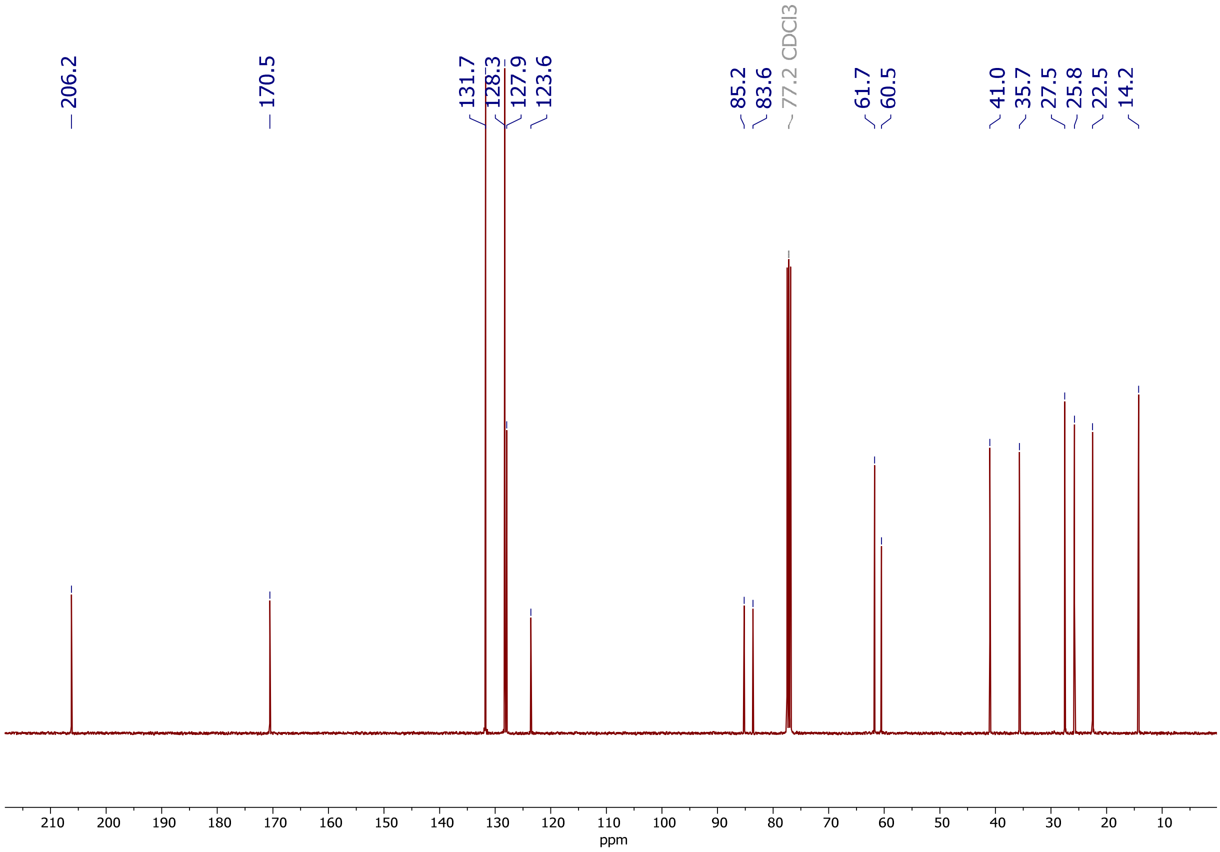
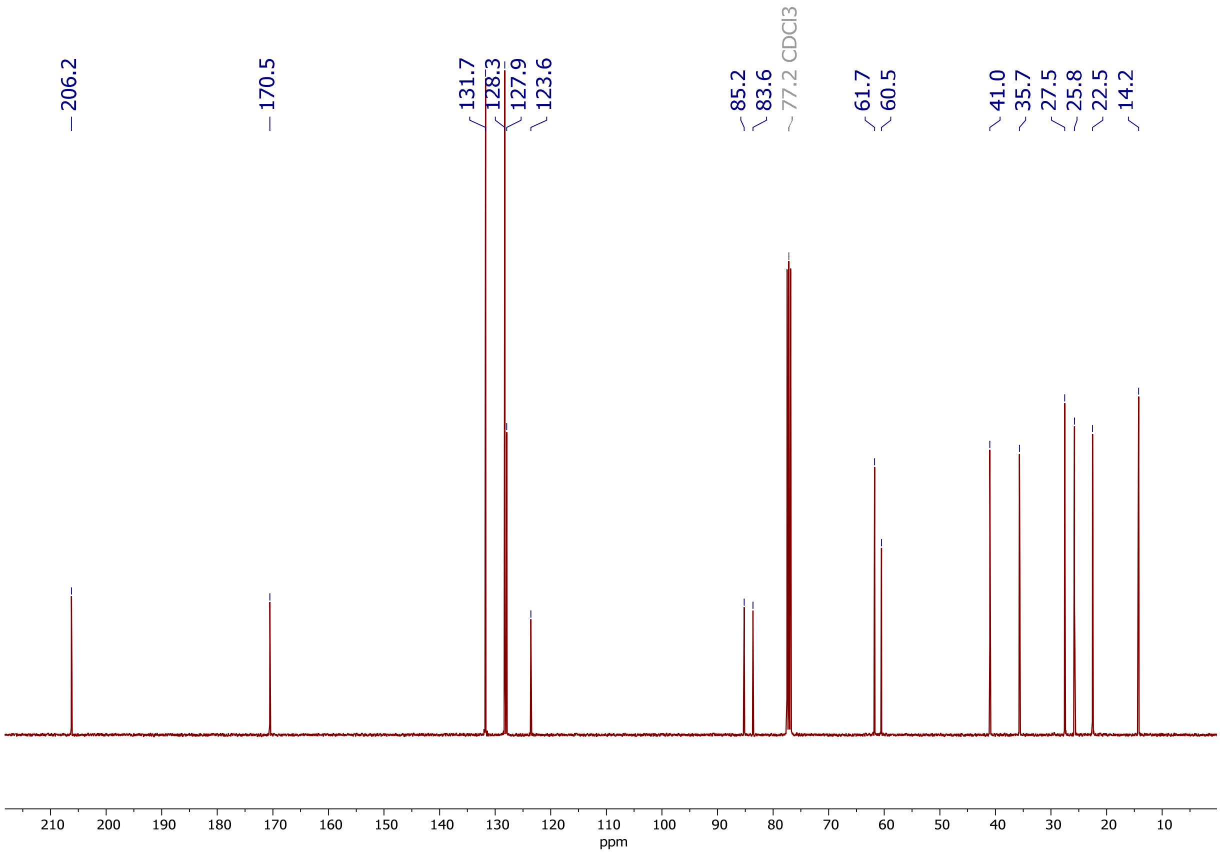
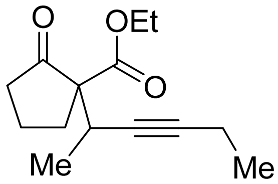
115,0
210,1
284,1
141,1
182,1
167,1
181,1
129,0
105,0
91,1
77,0
55,1
41,1
0,1
106,0
151,0
209,1
239,1
255,1
285,1
311,2
325,1


7.34
7.31
7.26 CDCl3
7.24
7.21
4.23
4.21
4.19
4.17
2.99
2.95
2.76
2.75
2.73
2.71
2.70
2.69
2.47
2.39
2.06
1.99
1.86
1.76
1.68
1.58
1.25
1.23
1.21
1.96
3.09
2.00
1.02
2.03
2.01
1.03
2.05
2.33
3.08
ppm

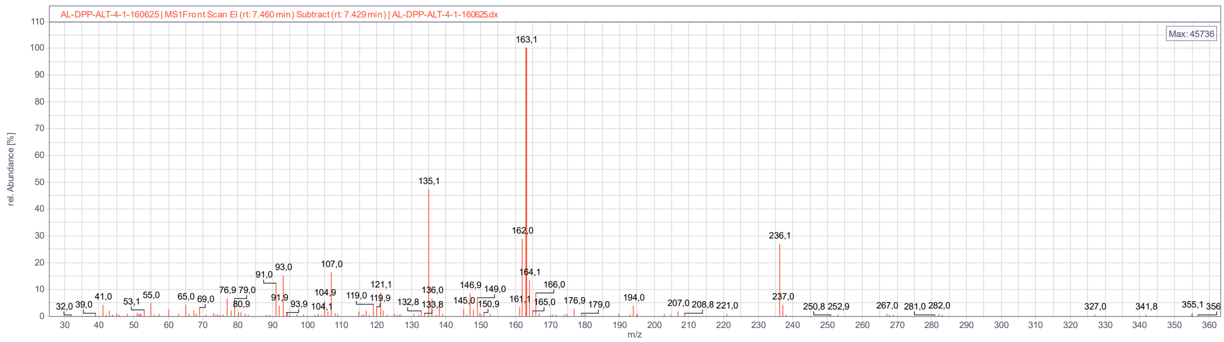

206.2
170.5
131.7
128.3
127.9
123.6
85.2
83.6
77.2 CDCl3
61.7
60.5
41.0
35.7
27.5
25.8
22.5
14.2
ppm

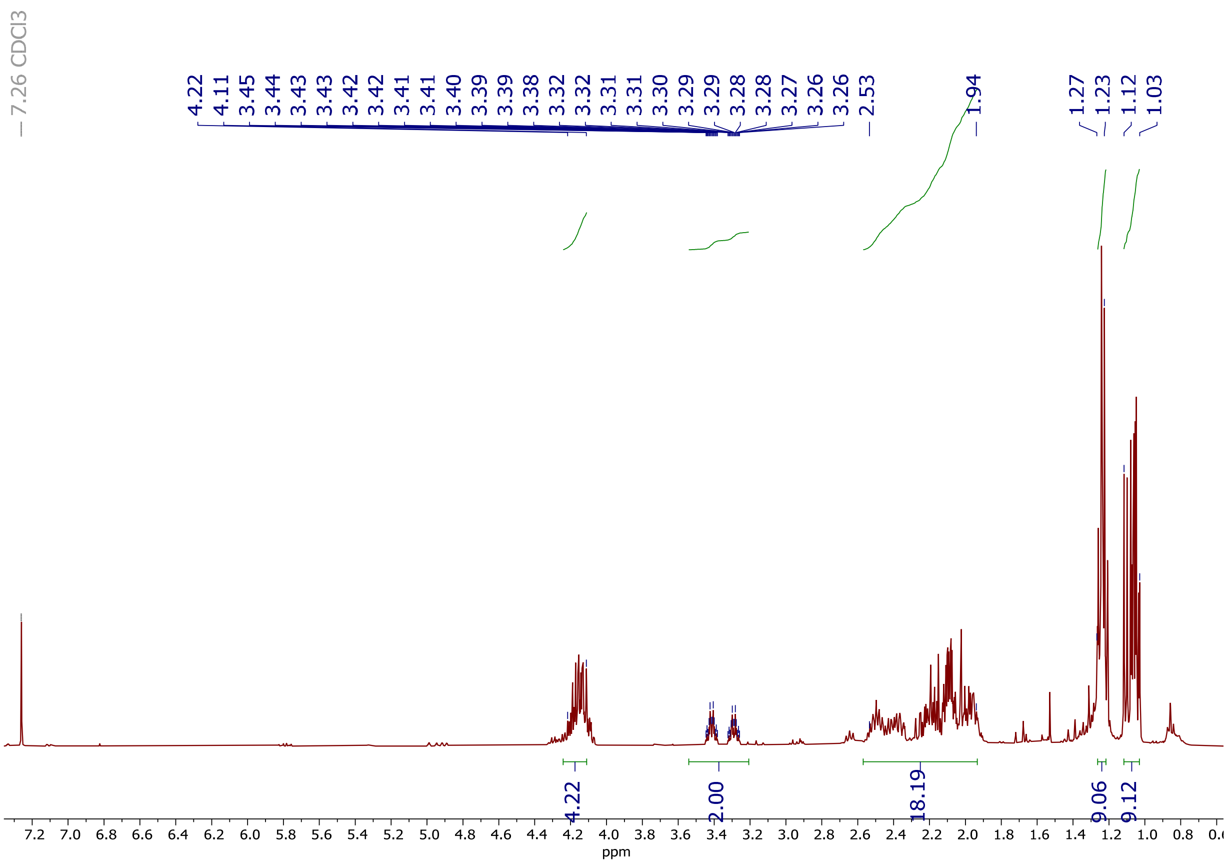

206.2
170.5
131.7
128.3
127.9
123.6
85.2
83.6
77.2 CDCl3
61.7
60.5
41.0
35.7
27.5
25.8
22.5
14.2
ppm

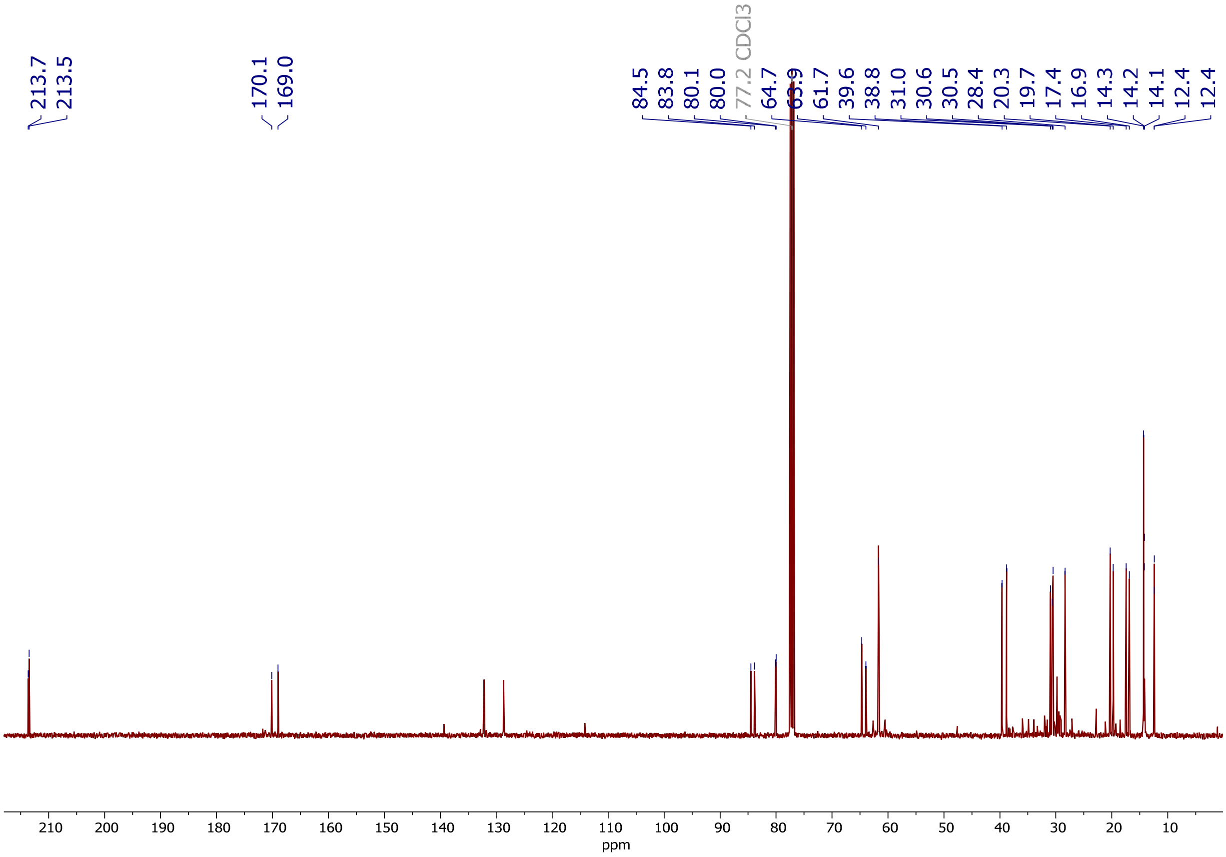


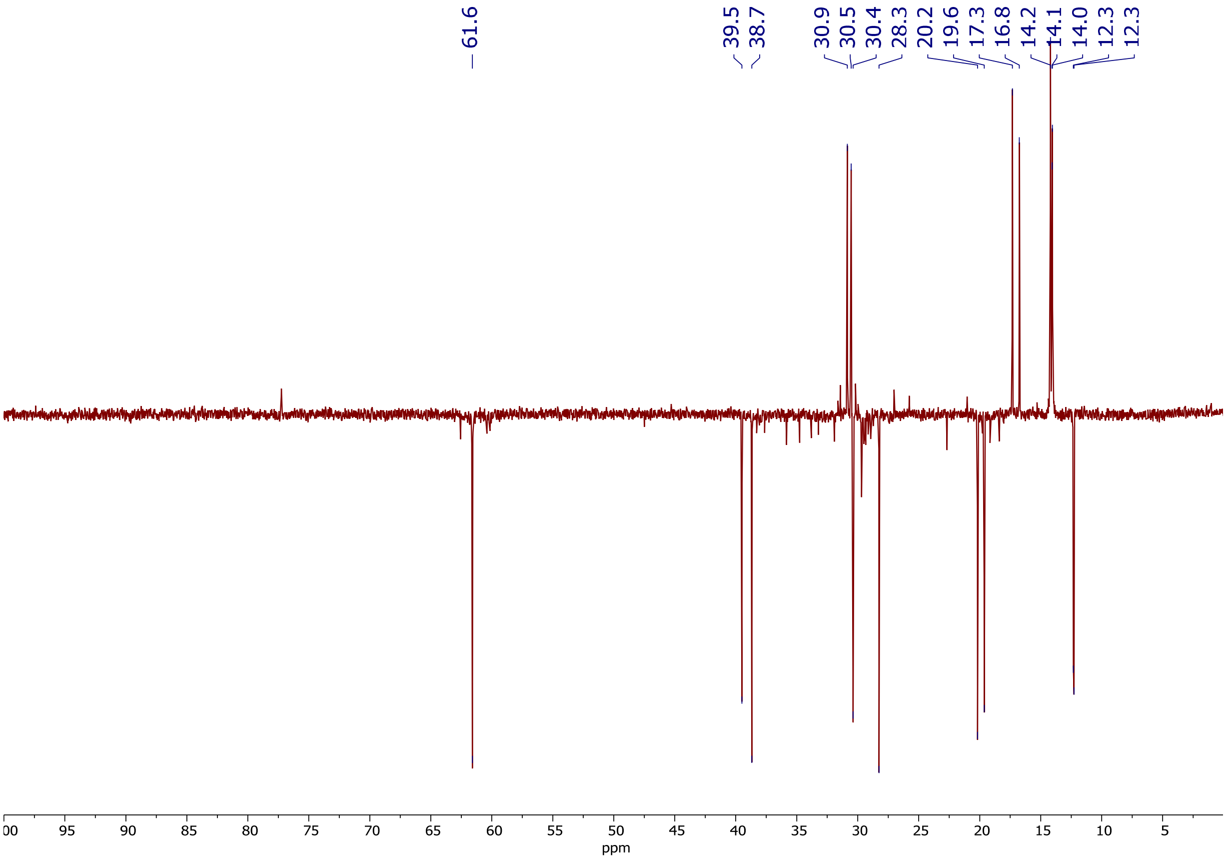
11

Ethyl 1-(hex-3-yn-2-yl)-2-oxocyclopentane-1-carboxylate **13** as a mixture of 2 proquiral compounds. **GC-MS; m/z, (relative intensity):** 236 (M+•, 27), 163 (100), 135 (47), 107 (16), 93 (15), 77 (7). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 4.22 – 4.11 (m, 4H), 3.41 (qt, *J* = 7.2, 2.4 Hz, 1H), 3.29 (qt, *J* = 7.6, 2.4 Hz, 1H), 2.53 – 1.94 (m, 16H), 1.27 – 1.23 (m, 9H), 1.12 – 1.03 (m, 9H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 213.7 (C), 213.5 (C), 170.1 (C), 169.0 (C), 84.5 (C), 83.8 (C), 80.1 (C), 80.0 (C), 64.7 (C), 63.9 (C), 61.7 (2xCH_2), 39.6 (CH_2), 38.8 (CH_2), 31.0 (CH), 30.6 (CH), 30.4 (2xCH_2), 20.3 (CH_2), 19.7 (CH_2), 17.4 (CH_3), 16.9 (CH_3), 14.3 (2xCH_3), 14.2 (CH_3), 14.1 (CH_3), 12.4 (CH_2), 12.3 (CH_2).






213.7
213.5
170.1
169.0
84.5
83.8
80.1
80.0
77.2 CDCl3
64.7
63.9
61.7
39.6
38.8
31.0
30.6
30.5
28.4
20.3
19.7
17.4
16.9
14.3
14.2
14.1
12.4
12.4
ppm


61.6
39.5
38.7
30.9
30.5
30.4
28.3
20.2
19.6
17.3
16.8
14.2
14.1
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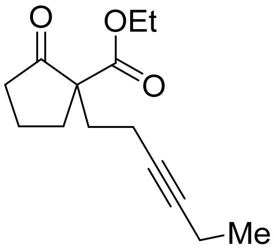
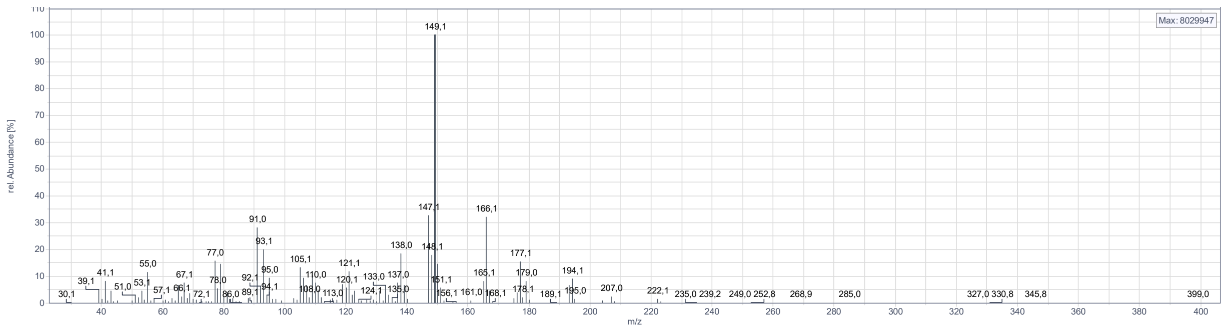
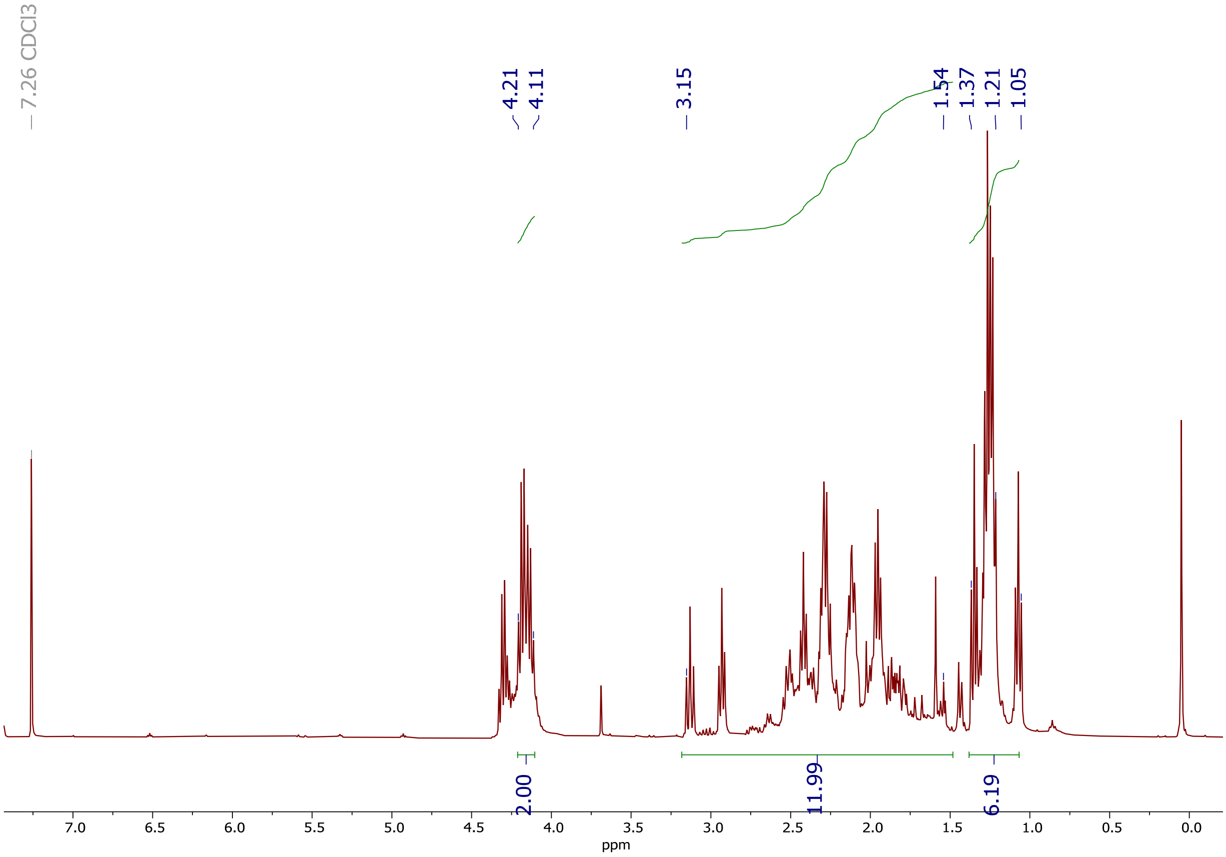
12.3
12.3
ppm

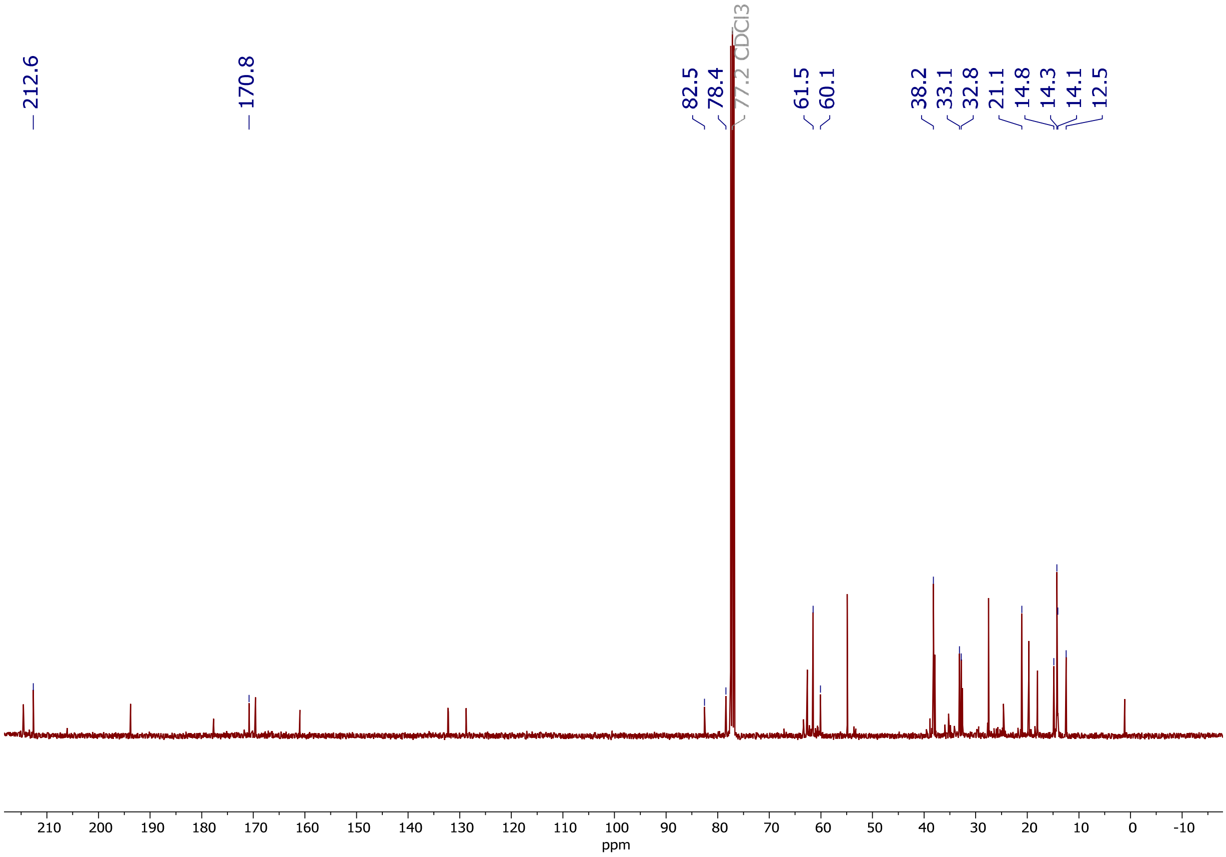


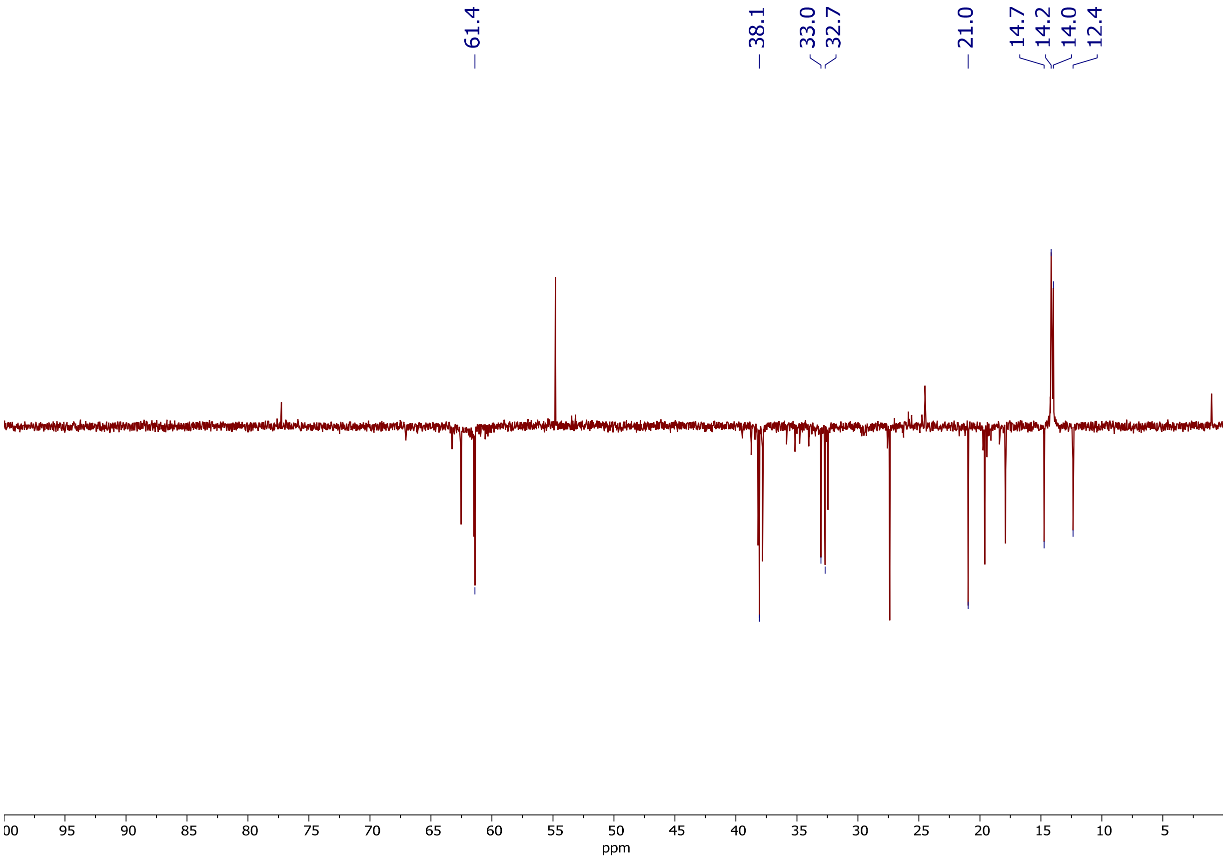
12

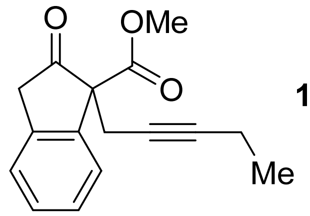
Ethyl 1-(hex-3-yn-1-yl)-2-oxocyclopentane-1-carboxylate **12. GC-MS; m/z, (relative intensity):** 236 (M+•, 1), 221 (1), 207 (2), 195 (9), 177 (15), 166 (32), 149 (100), 138 (18), 91 (29), 77 (15). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 4.21 – 4.11 (m, 2H), 3.15 – 1.54 (m, 12H), 1.21 – 1.05 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 212.6 (C), 170.8 (C), 82.5 (C), 78.4 (C), 61.5 (CH_2), 60.1 (C), 38.2 (CH_2), 33.1 (CH_2), 32.8 (CH_2), 21.1 (CH_2), 14.8 (CH_2), 14.3 (CH_3), 14.1 (CH_3), 12.5 (CH_2).





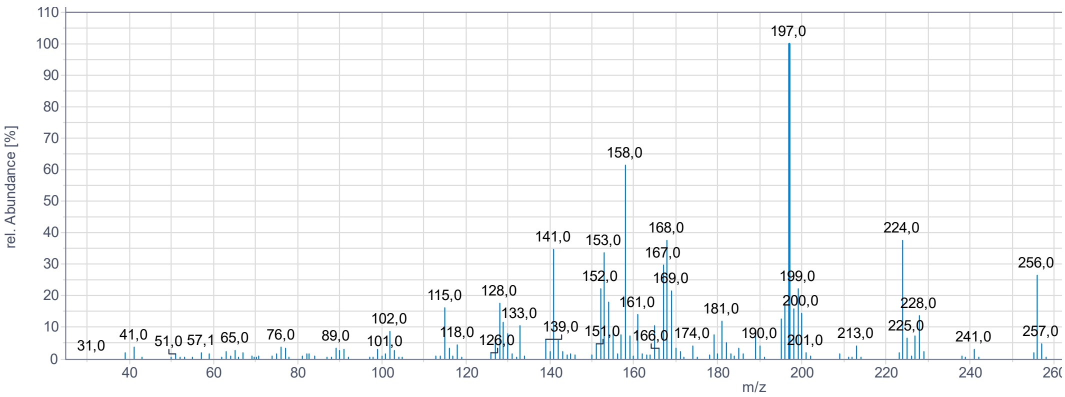

212.6
170.8
82.5
78.4
77.2 CDCl3
61.5
60.1
38.2
33.1
32.8
21.1
14.8
14.3
14.1
12.5
ppm

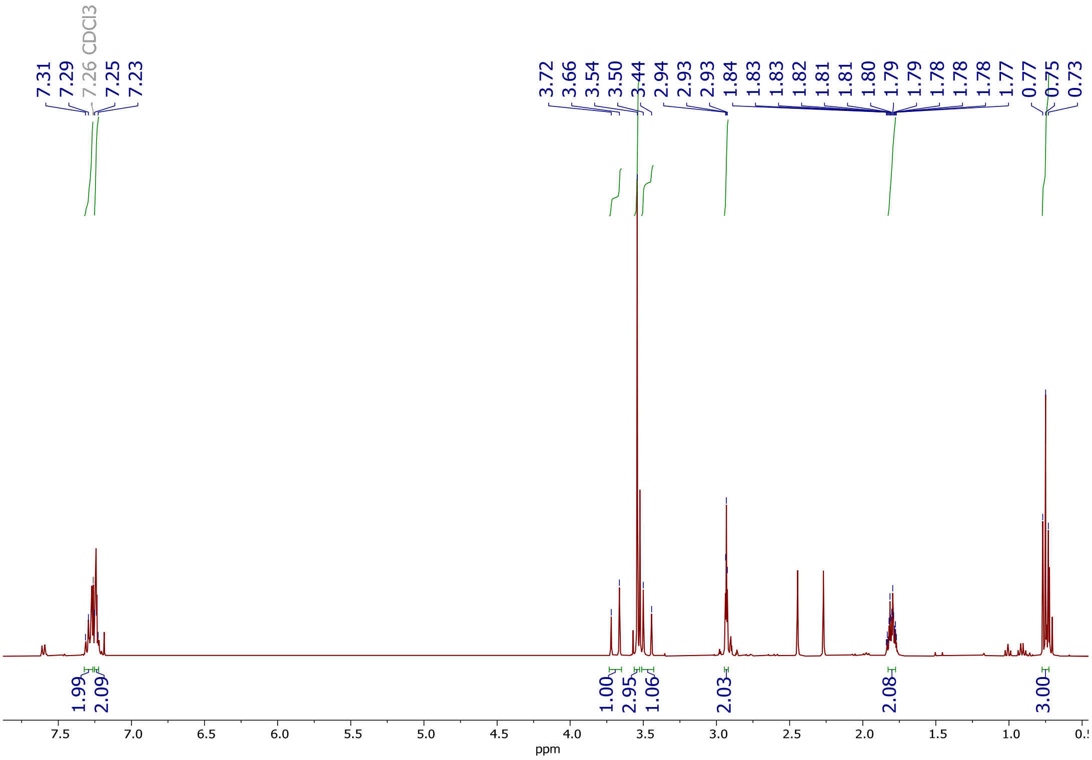

61.4
38.1
33.0
32.7
21.0
14.7
14.2
14.0
12.4
ppm

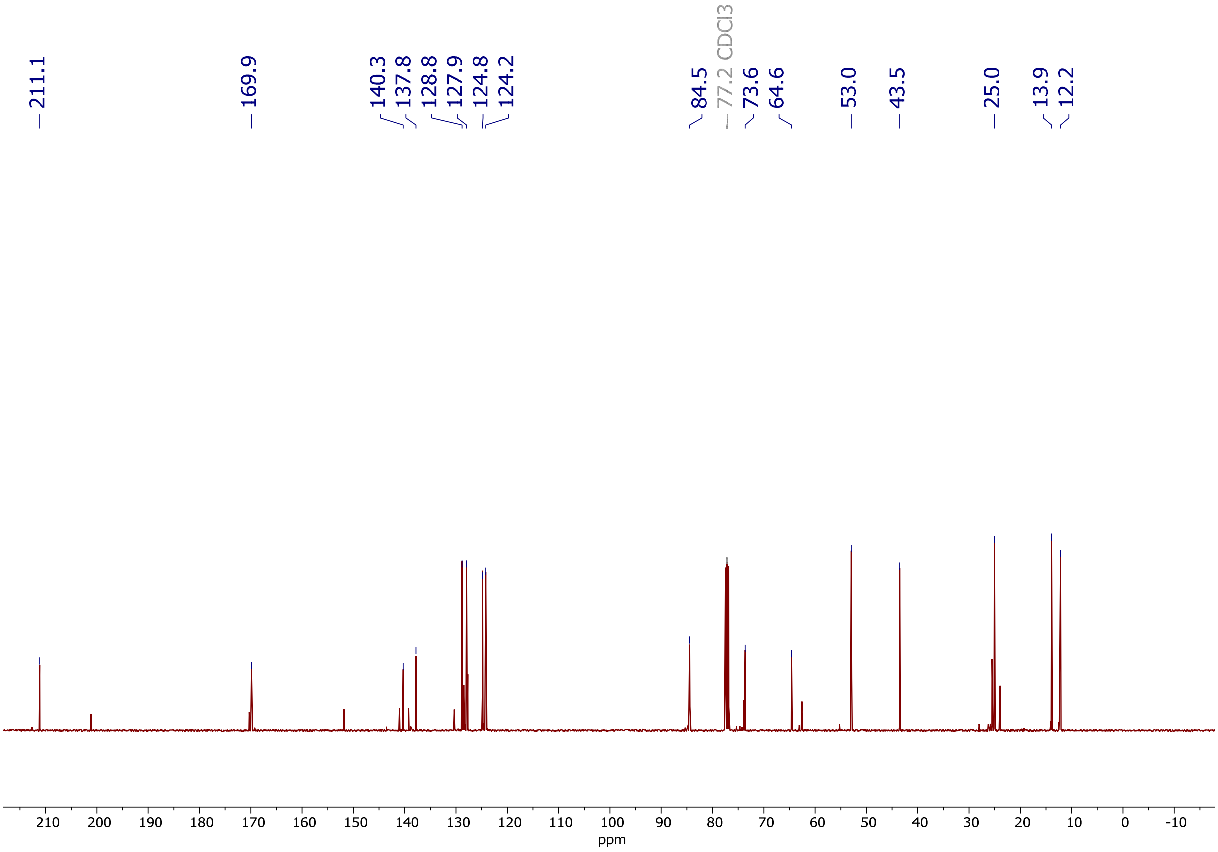


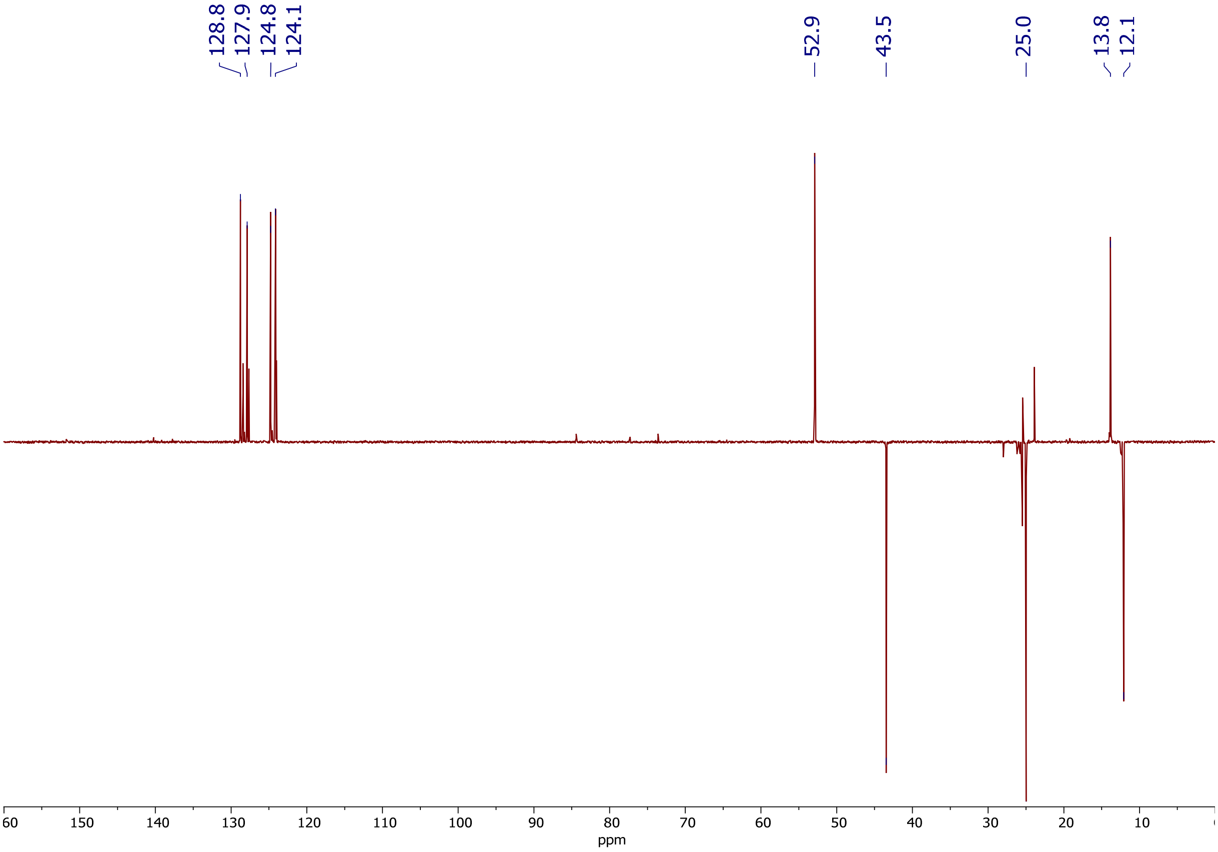
13

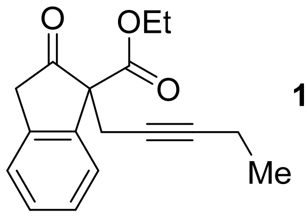
Methyl 2-*oxo*-1-(pent-2-yn-1-yl)-2,3-dihydro-1*H*-indene-1-carboxylate **13. GC-MS; m/z, (relative intensity):** 256 (M+•, 27), 224 (37), 197 (100), 168 (40), 158 (63), 153 (36), 141 (37), 128 (20), 115 (16), 102 (9). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 7.32 – 7.21 (m, 4H), 3.73 – 3.66 (d, *J* = 22.8 Hz, 1H), 3.54 (s, 3H), 3.47 (d, *J* = 22.8 Hz, 1H), 2.93 (t, *J* = 2.4 Hz, 2H), 1.80 (qt, *J* = 7.2, 2.4 Hz, 2H), 0.75 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 211.1 (C), 169.9 (C), 140.3 (C), 137.8 (C), 128.8 (CH), 127.9 (CH), 124.8 (CH), 124.2 (CH), 84.5 (C), 73.7 (C) , 64.6 (C), 53.0 (CH_3), 43.5 (CH_2), 25.0 (CH_2), 13.9 (CH_3), 12.2 (CH_2).





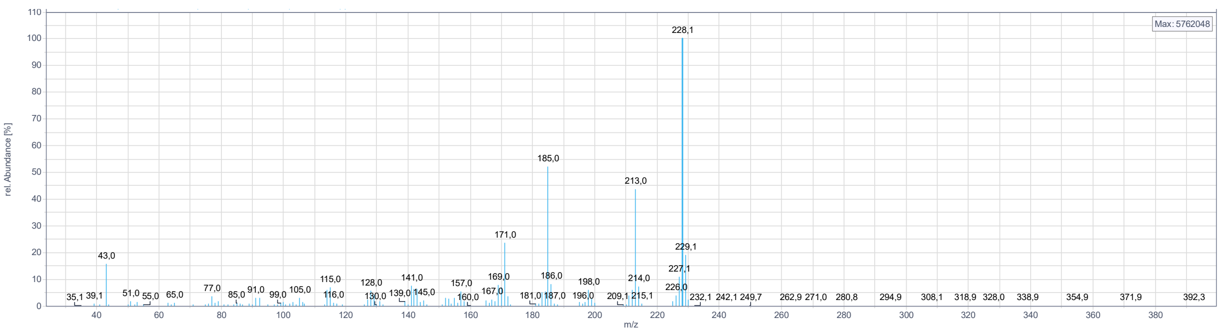

211.1
169.9
140.3
137.8
128.8
127.9
124.8
124.2
84.5
77.2 CDCl3
73.6
64.6
53.0
43.5
25.0
13.9
12.2
ppm

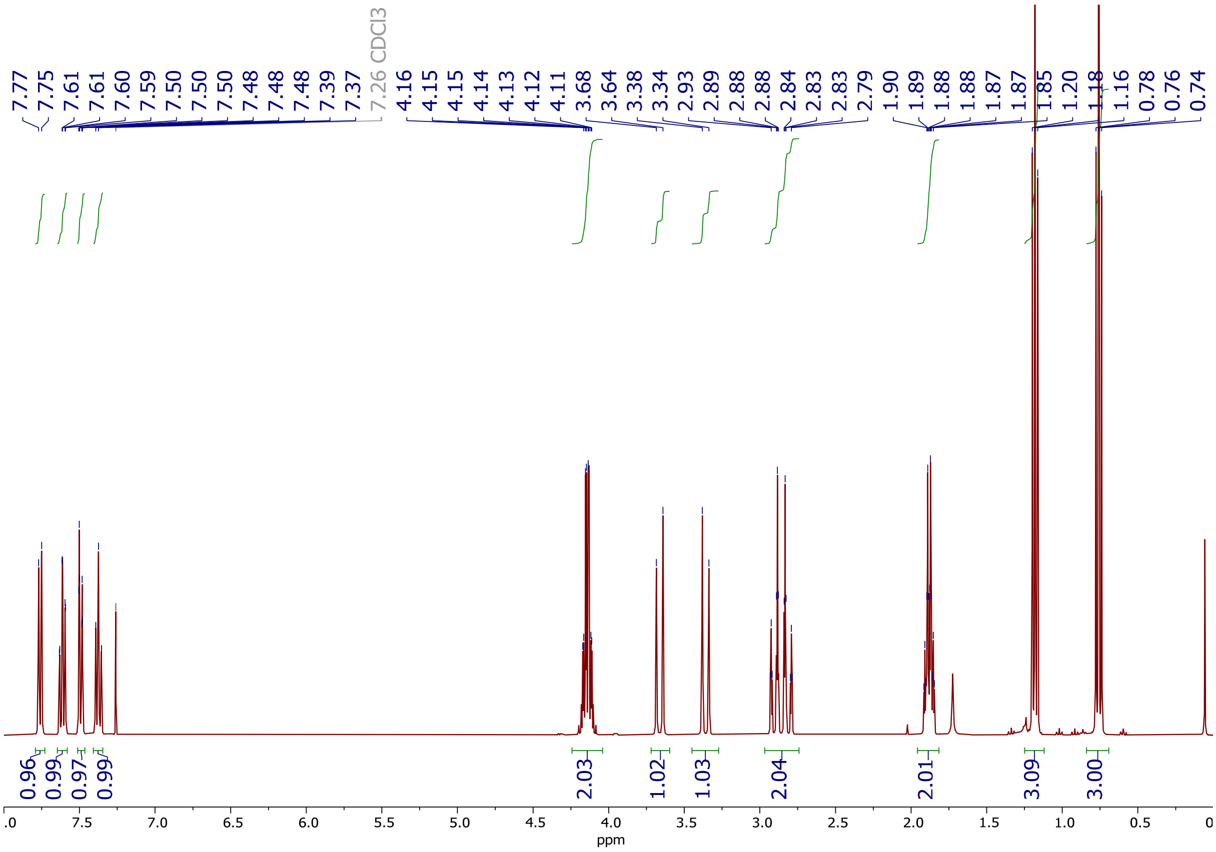

128.8
127.9
124.8
124.1
52.9
43.5
25.0
13.8
12.1
ppm

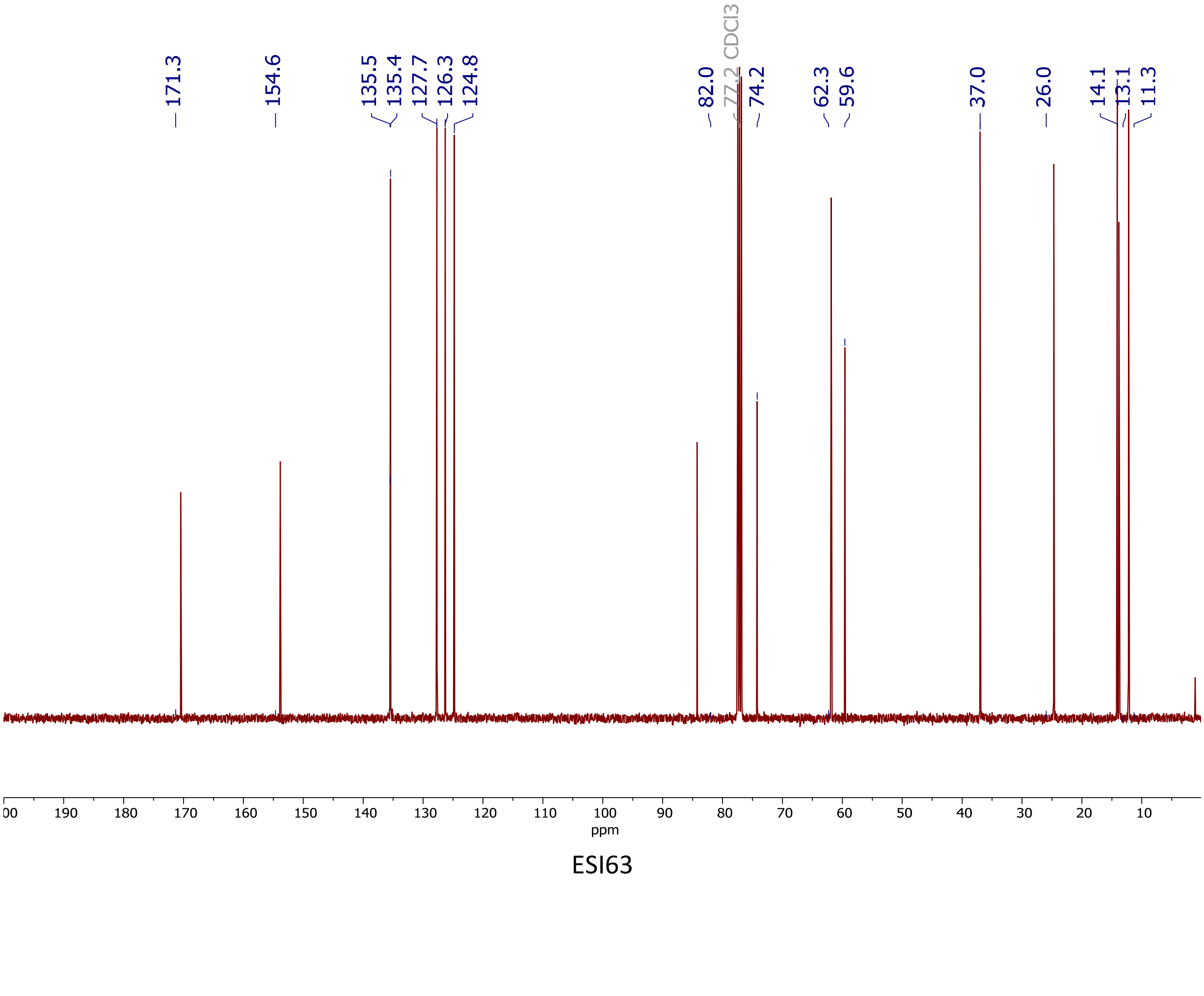


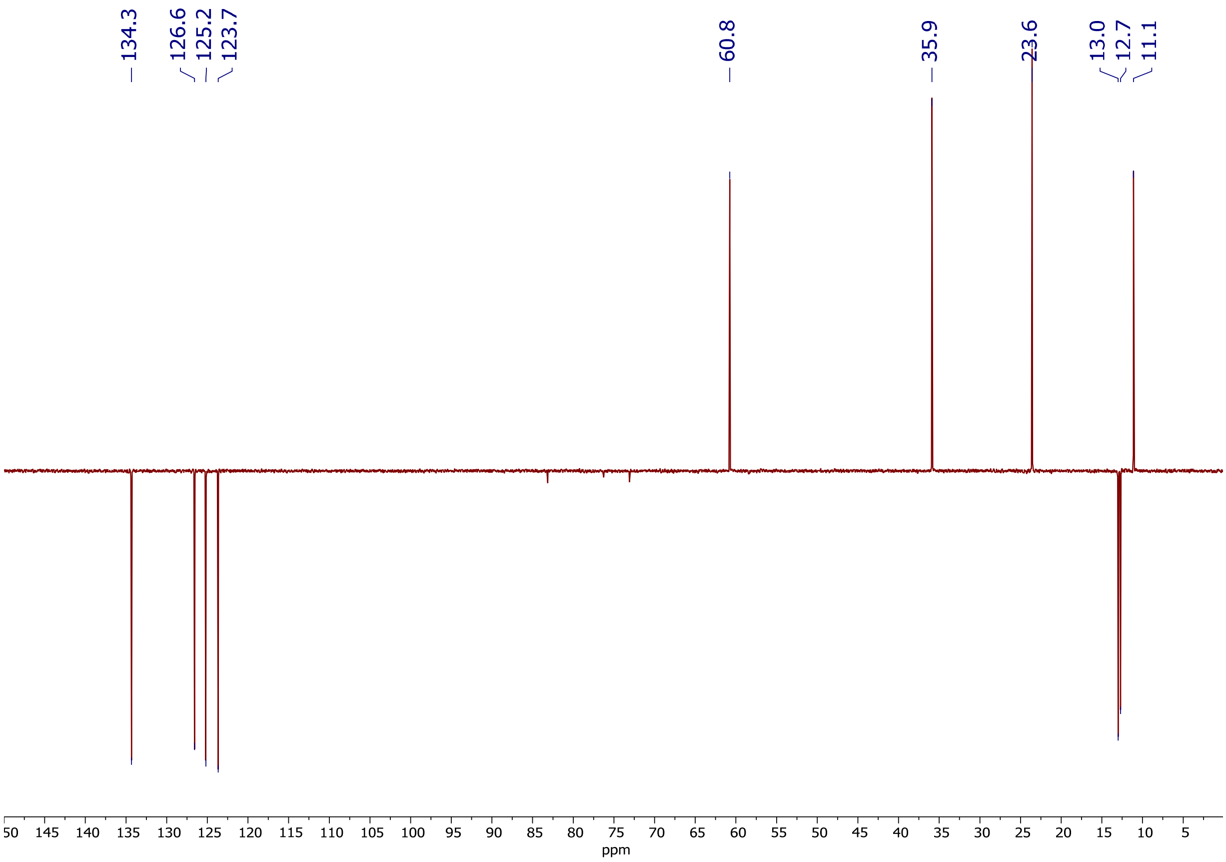
14

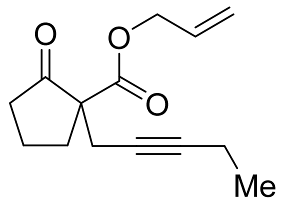
Ethyl 2-*oxo*-1-(pent-2-yn-1-yl)-2,3-dihydro-1*H*-indene-1-carboxylate **14. GC-MS; m/z, (relative intensity):** 270 (M+•, 1), 228 (100), 213 (43), 185 (52), 171 (24), 141 (7), 128 (4), 115 (6), 43 (15). **^{1}H NMR (401 MHz, CDCl$_3$) δ** 7.76 (d, *J* = 7.6 Hz, 1H), 7.61 (td, *J* = 7.6, 1.2 Hz, 1H), 7.49 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 4.14 (qd, *J* = 7.2, 2.4 Hz, 2H), 3.66 (d, *J* = 17.2 Hz, 1H), 3.36 (d, *J* = 17.2 Hz, 1H), 2.86 (qt, *J* = 16.4, 2.4 Hz, 2H), 1.88 (qt, *J* = 7.6, 2.4 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 205.2 (C), 171.3 (C), 154.6 (C), 135.5 (C), 135.4 (CH), 127.7 (CH), 126.3 (CH), 124.8 (CH), 82.0 (C), 74.2 (C) , 62.3 (C), 59.6 (CH$_2$), 37.0 (CH$_2$), 26.0 (CH$_2$), 14.1 (CH$_3$) 13.1 (CH$_3$), 11.3 (CH$_2$).





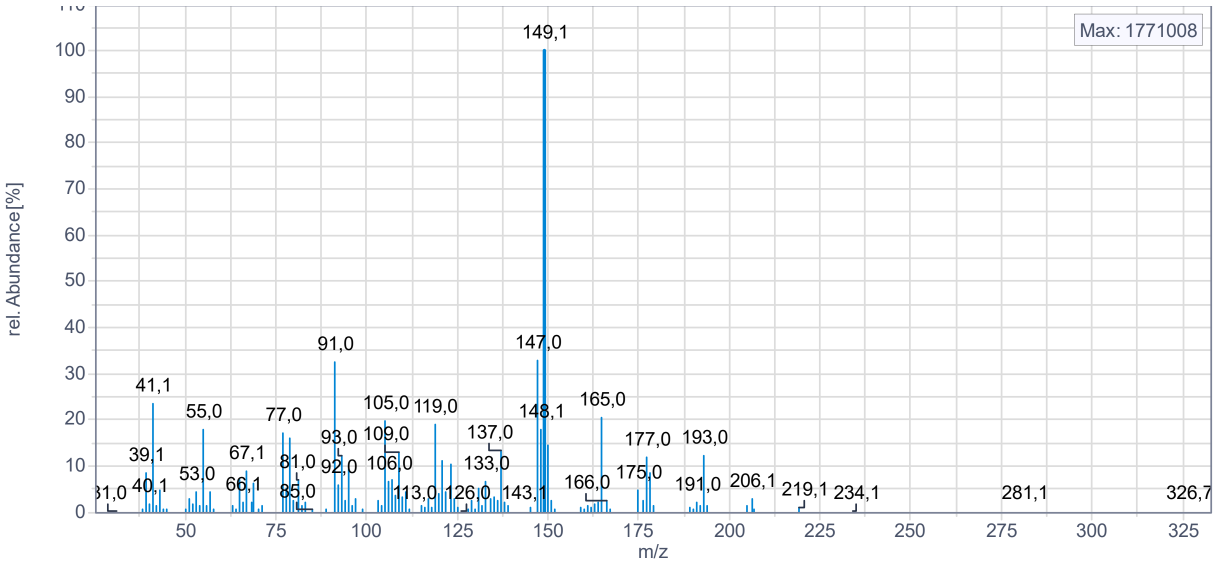


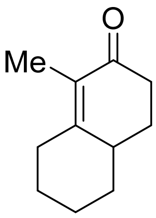




15

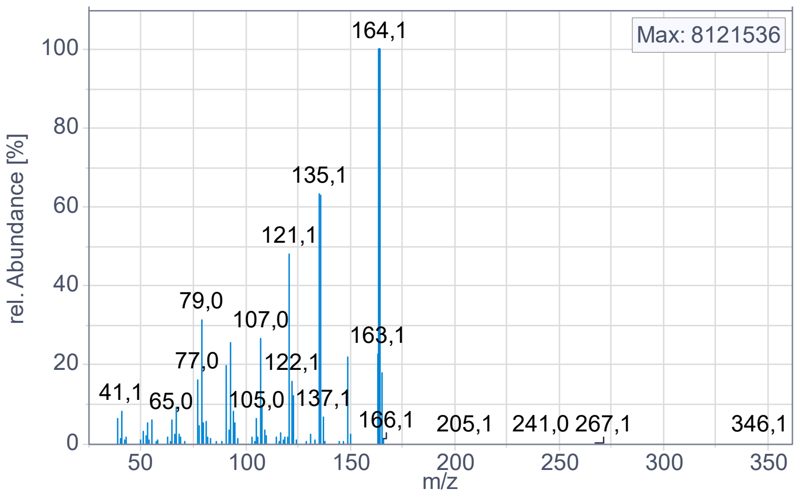
Allyl 2-oxo-1-(pent-2-yn-1-yl)cyclopentane-1-carboxylate **15. GC-MS; m/z, (relative intensity):** 234 (M+•, 1), 206 (3), 193 (11), 177 (10), 165 (20), 149 (100), 137 (12), 119 (18), 91 (32), 77 (16), 55 (16) 41 (23).

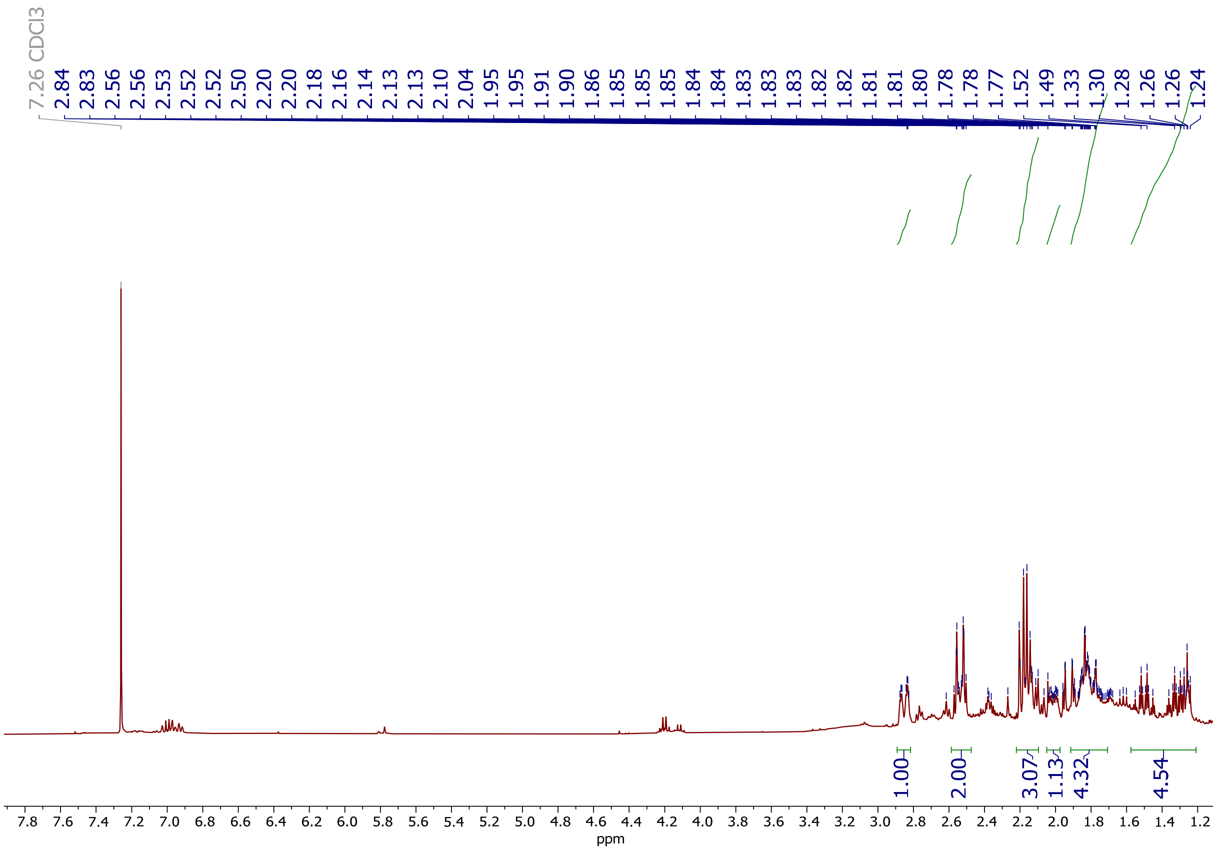


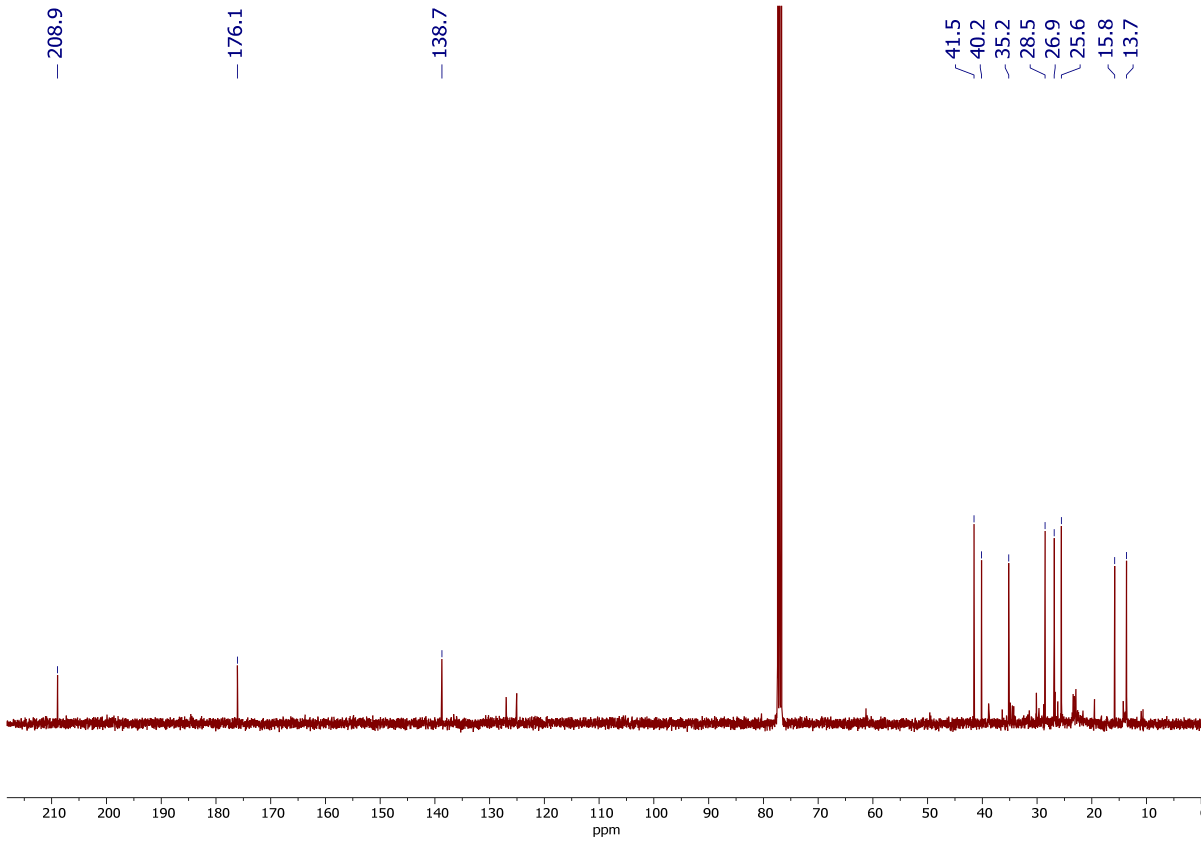


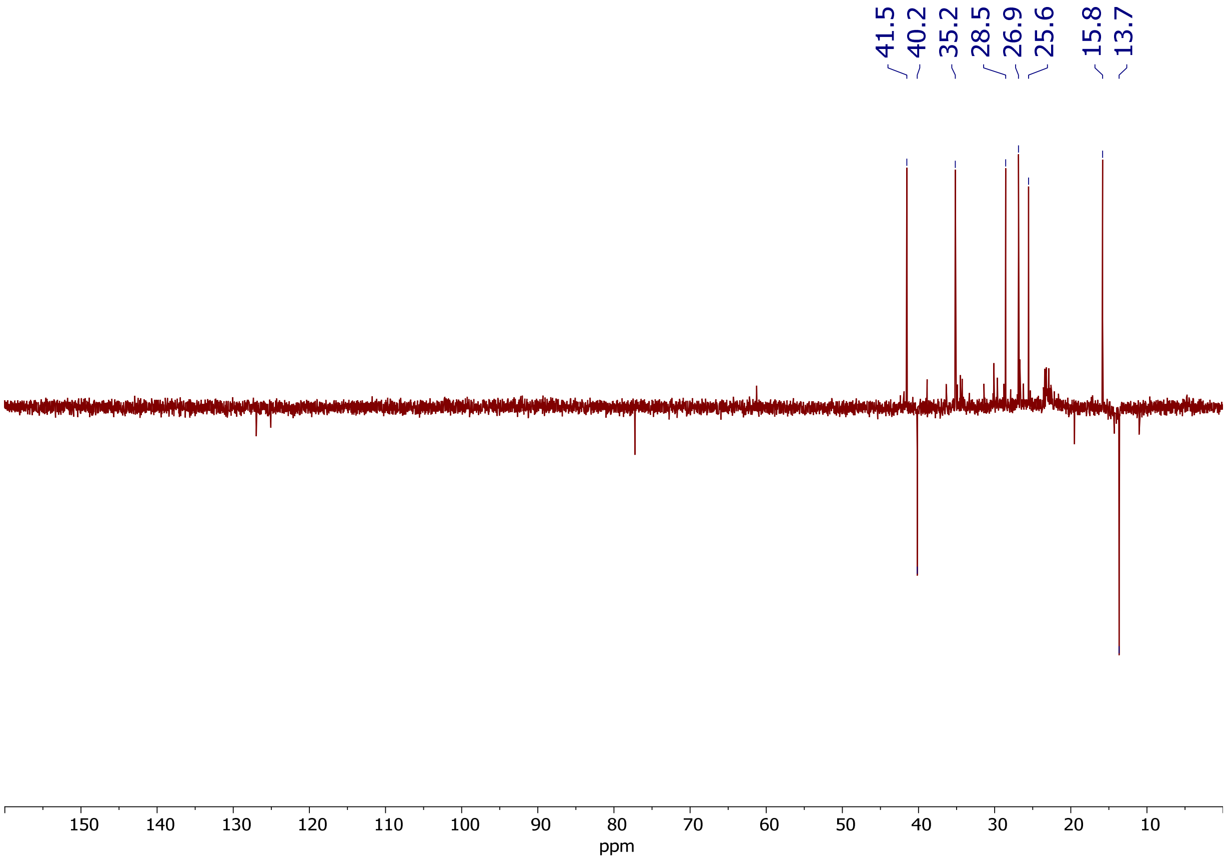
16

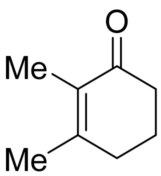
1-Methyl-4,4*a*,5,6,7,8-hexahydronaphthalen-2(3*H*)-one **16**. **GC-MS; m/z, (relative intensity):** 164 (M+•, 100), 135 (64), 136 (63), 121 (48), 79 (31), 107 (27), 93 (26), 163 (23), 149 (22), 91 (20), 165 (18), 77 (16), 122 (16), 123 (12). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 2.85 (ddt, *J* = 13.6, 4.0, 2.1 Hz, 1H), 2.58 – 2.49 (m, 2H), 2.22 – 2.11 (m, 3H), 2.06 – 1.97 (m, 1H), 1.92 – 1.75 (m, 4H), 1.55 – 1.21 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 208.9 (C), 176.1 (C), 138.7 (C), 41.5 (CH_2), 40.2 (CH), 35.2 (CH_2), 28.6 (CH_2), 26.9 (CH_2), 25.6 (CH_2), 15.8 (CH_2), 13.7 (CH_3).




7.26 CDCl3
2.84
2.83
2.56
2.56
2.53
2.52
2.52
2.50
2.20
2.20
2.18
2.16
2.14
2.13
2.13
2.10
2.04
1.95
1.95
1.91
1.90
1.86
1.85
1.85
1.85
1.84
1.84
1.83
1.83
1.83
1.82
1.82
1.81
1.81
1.80
1.78
1.78
1.77
1.52
1.49
1.33
1.30
1.28
1.26
1.26
1.24
1.00
2.00
3.07
1.13
4.32
4.54
ppm

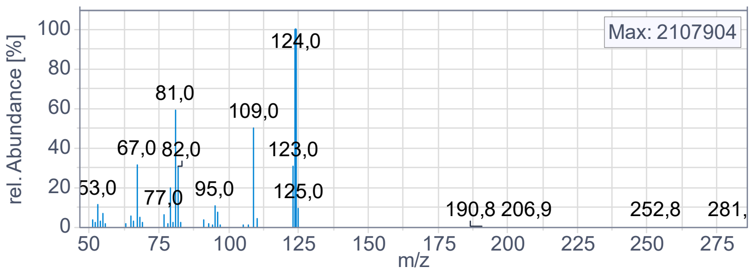

208.9
176.1
138.7
41.5
40.2
35.2
28.5
26.9
25.6
15.8
13.7
ppm

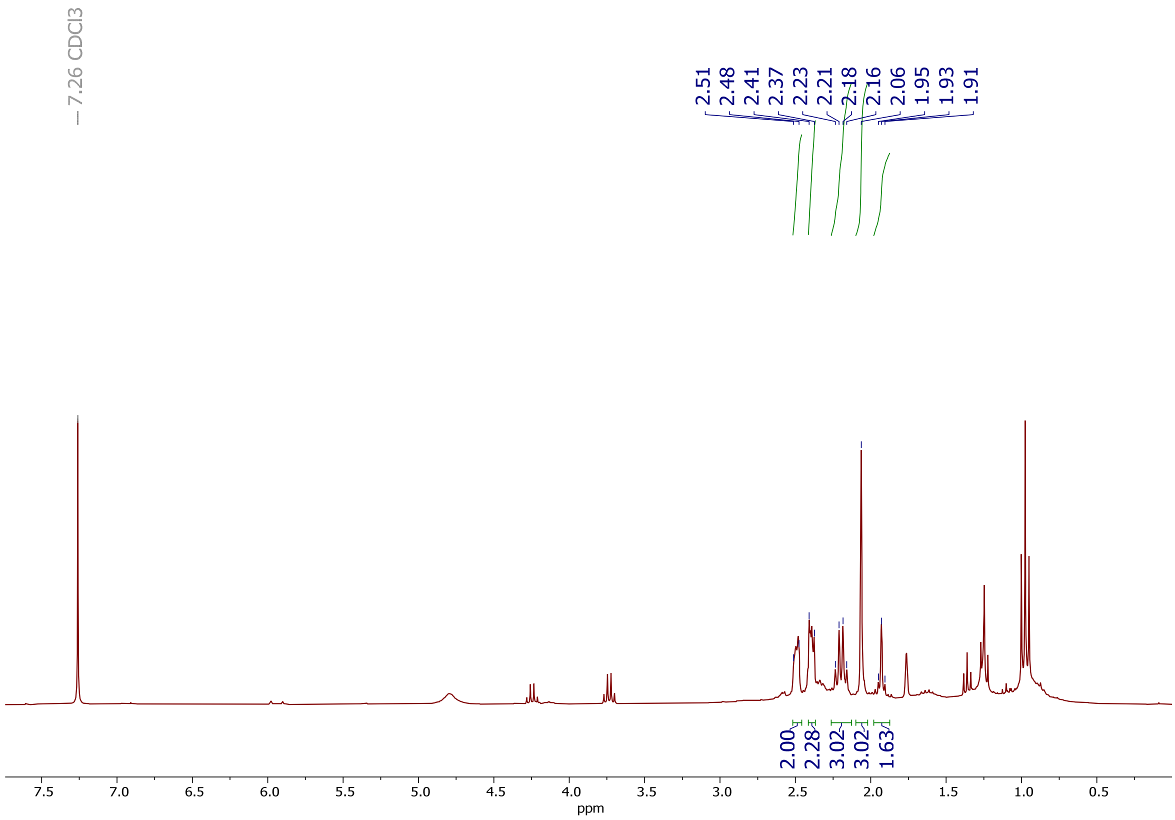


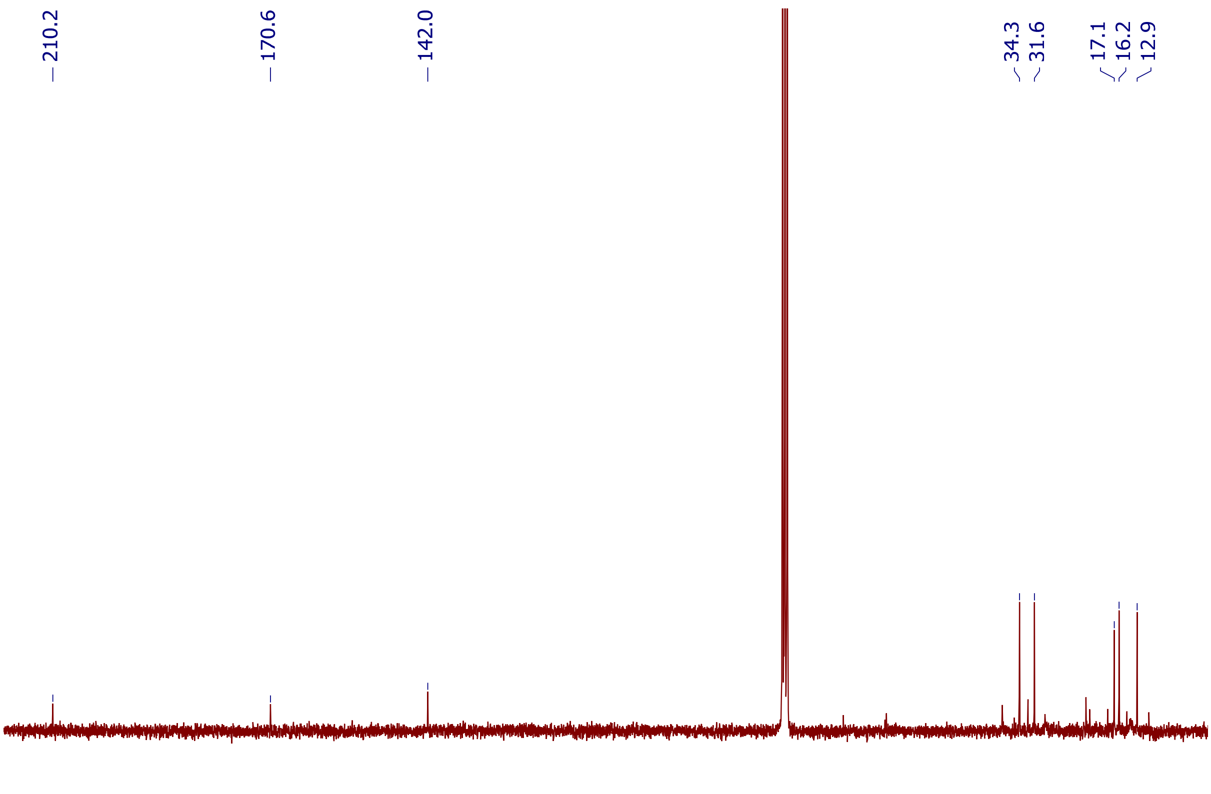


17

2,3-Dimethylcyclohex-2-en-1-one **17**. **GC-MS; m/z, (relative intensity):** 124 (M+•,100), 123 (31), 109 (50), 82 (31), 81 (59), 79 (19), 67 (32), 53 (11), 95 (11). **^{1}H NMR (300 MHz, $CDCl_3$) δ** 2.54 – 2.45 (m, 2H), 2.40 (td, *J* = 5.5, 3.1 Hz, 2H), 2.20 (q, *J* = 7.5 Hz, 3H), 2.06 (s, 3H), 1.94 (q, *J* = 6.6 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 210.2 (C), 170.6 (C), 142.0 (C), 34.4 (CH_2), 31.6 (CH_2), 17.1 (CH_3), 16.2 (CH_2), 12.9 (CH_3).




7.26 CDCl3
2.51
2.48
2.41
2.37
2.23
2.21
2.18
2.16
2.06
1.95
1.93
1.91
2.00
2.28
3.02
3.02
1.63
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


210.2
170.6
142.0
34.3
31.6
17.1
16.2
12.9
210
200
190
180
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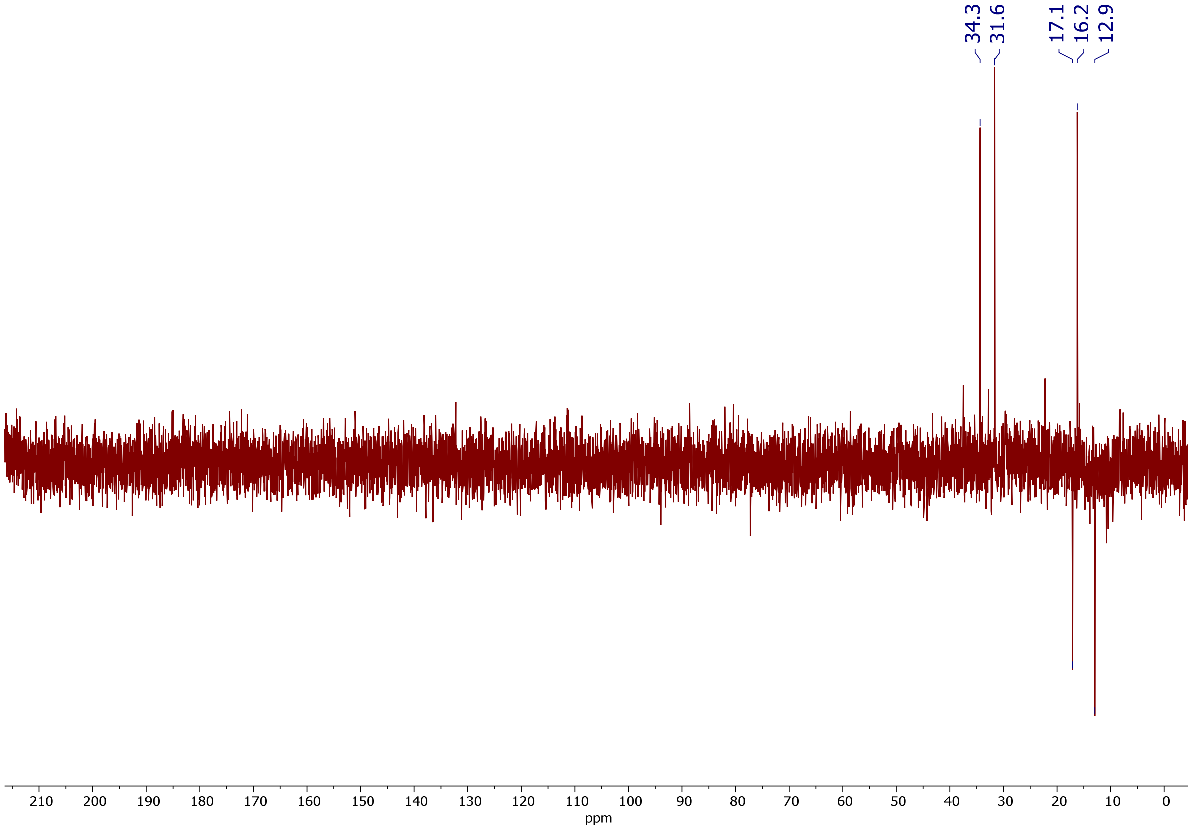
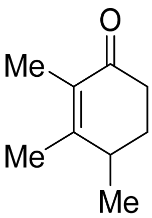
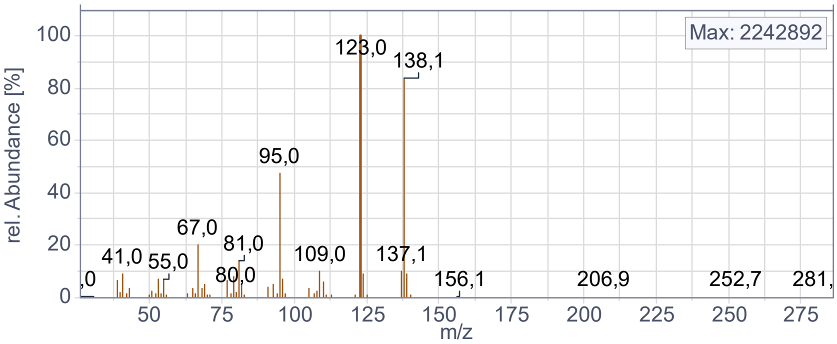
40
30
20
10
ppm

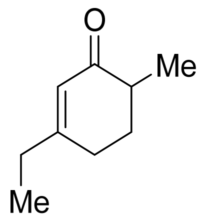




18

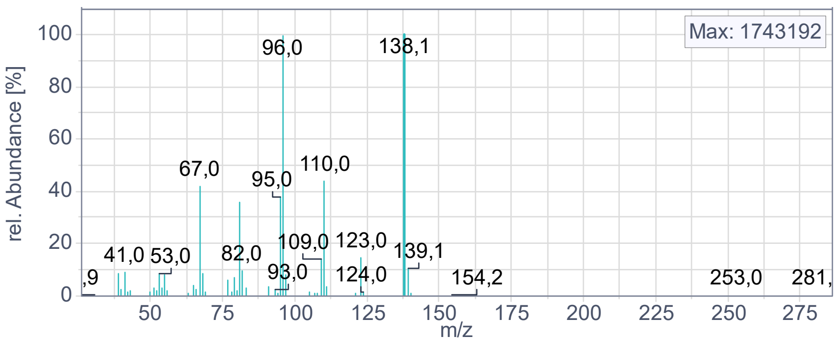
2,3,4-Trimethylcyclohex-2-en-1-one **15**. **GC-MS; m/z, (relative intensity):** 138 (M+•, 84), 123 (100), 95 (48), 67 (20), 81 (14), 109 (10), 137 (10), 124 (9). **^{1}H NMR (401 MHz, CDCl$_3$) δ** 2.57 – 2.28 (m, 4H), 1.92 – 1.90 (m, 3H), 1.75 (t, *J* = 1.2 Hz, 3H), 1.73 – 1.64 (m, 2H), 1.18 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 198.9(C), 159.3 (C), 130.5 (C), 35.7 (CH), 34.0 (CH$_2$), 30.6 (CH$_2$), 19.8 (CH$_3$), 17.8 (CH$_3$), 11.3 (CH$_3$). **HRMS (UPLC):** [M+H$^+$; calculated for $C_9H_{15}O$: 139.1117] found: 139.1116.

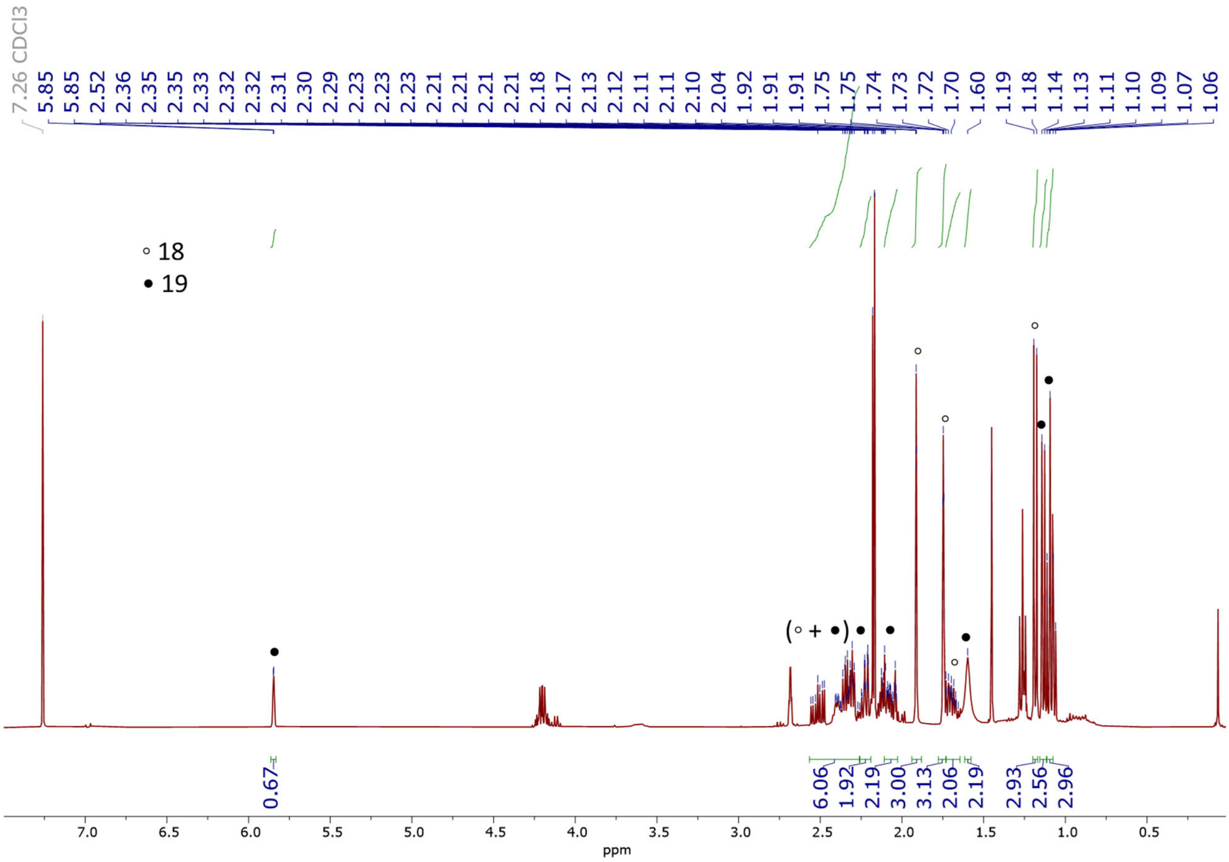




19

3-Ethyl-6-methylcyclohex-2-en-1-one **16**. **GC-MS; m/z, (relative intensity):** 138 (M+•, 100), 96 (100), 110 (44), 67 (42), 95 (38), 81 (36), 123 (14), 109 (14), 139 (11), 82 (9), 41 (9). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 5.85 (d, *J* = 1.2 Hz, 1H), 2.57 – 2.28 (m, 1H), 2.22 (dt, *J* = 7.5, 1.5 Hz, 2H), 2.13 – 2.02 (m, 2H), 1.61-1.57 (m, 2H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 202.5 (C), 166.7 (C), 124.1 (CH), 40.8 (CH), 30.9 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 15.1 (CH_3), 11.1 (CH_3). **HRMS (UPLC):** [M+H$^+$; calculated for $C_9H_{15}O$: 139.1117] found: 139.1116.





7.26 CDCl3
5.85
5.85
2.52
2.36
2.35
2.35
2.33
2.32
2.32
2.31
2.30
2.29
2.23
2.23
2.23
2.21
2.21
2.21
2.21
2.18
2.17
2.13
2.12
2.11
2.11
2.10
2.04
1.92
1.91
1.91
1.75
1.75
1.74
1.73
1.72
1.70
1.60
1.19
1.18
1.14
1.13
1.11
1.10
1.09
1.07
1.06
∘ 18
• 19
(∘ + •)
0.67
6.06
1.92
2.19
3.00
3.13
2.06
2.19
2.93
2.56
2.96
7.0
6.5
6.0
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4.5
4.0
3.5
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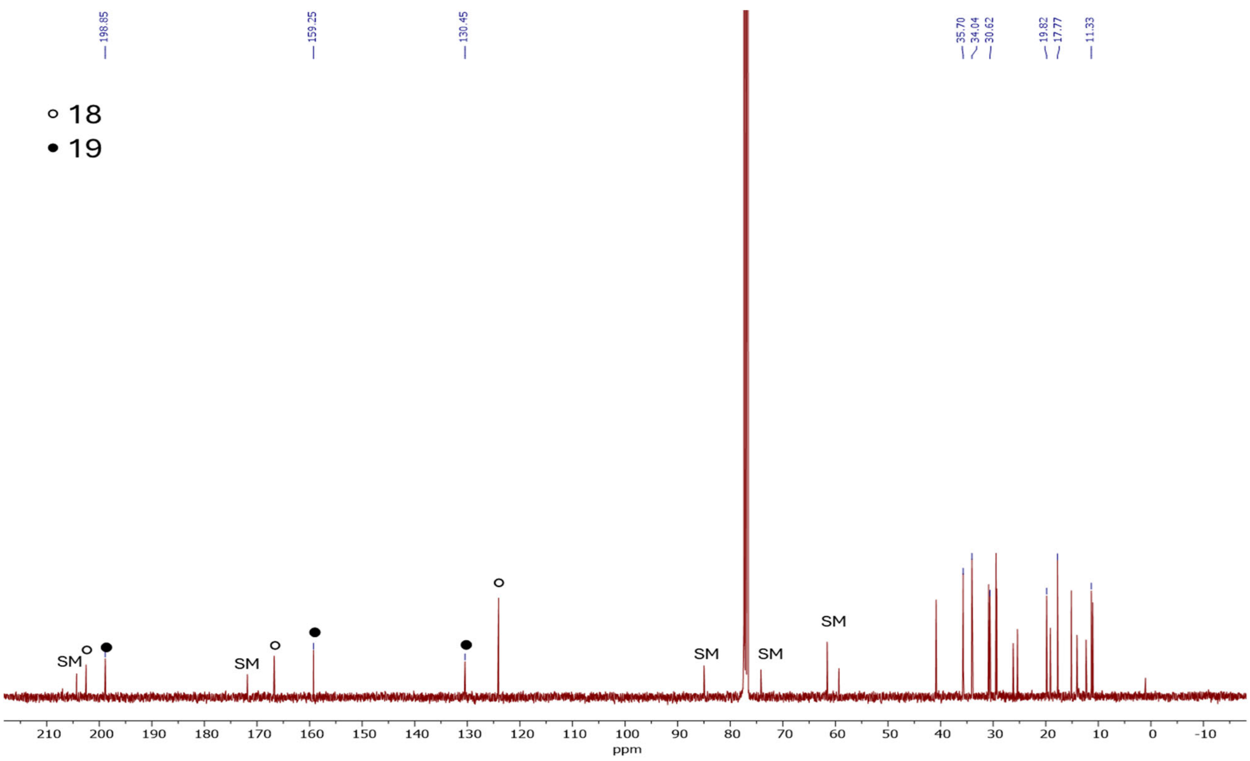
2.0
1.5
1.0
0.5
ppm



198.85
159.25
130.45
35.70
34.04
30.62
19.82
17.77
11.33
∘ 18
• 19
SM
SM
SM
SM
SM
210
200
190
180
170
160
150
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110
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90
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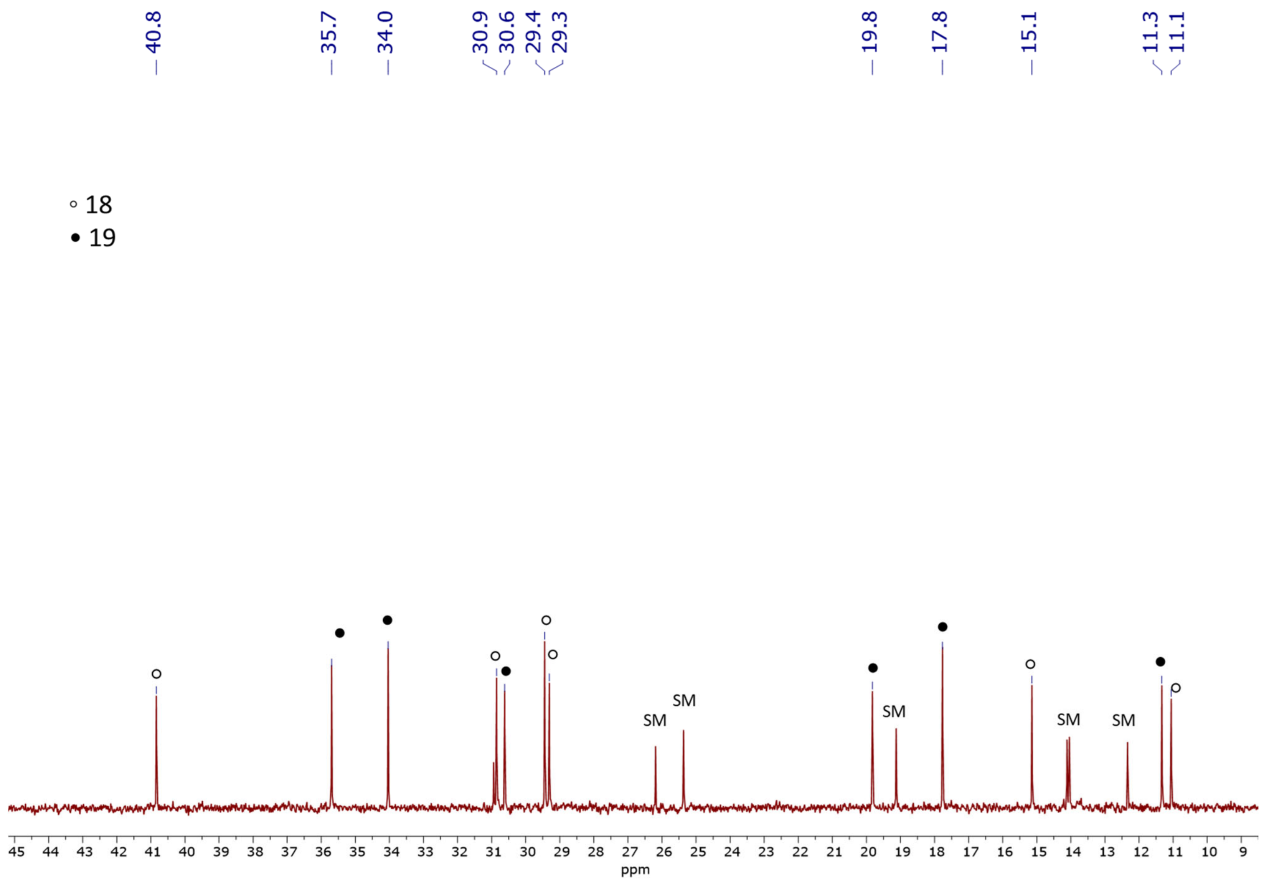
50
40
30
20
10
0
-10
ppm


40.8
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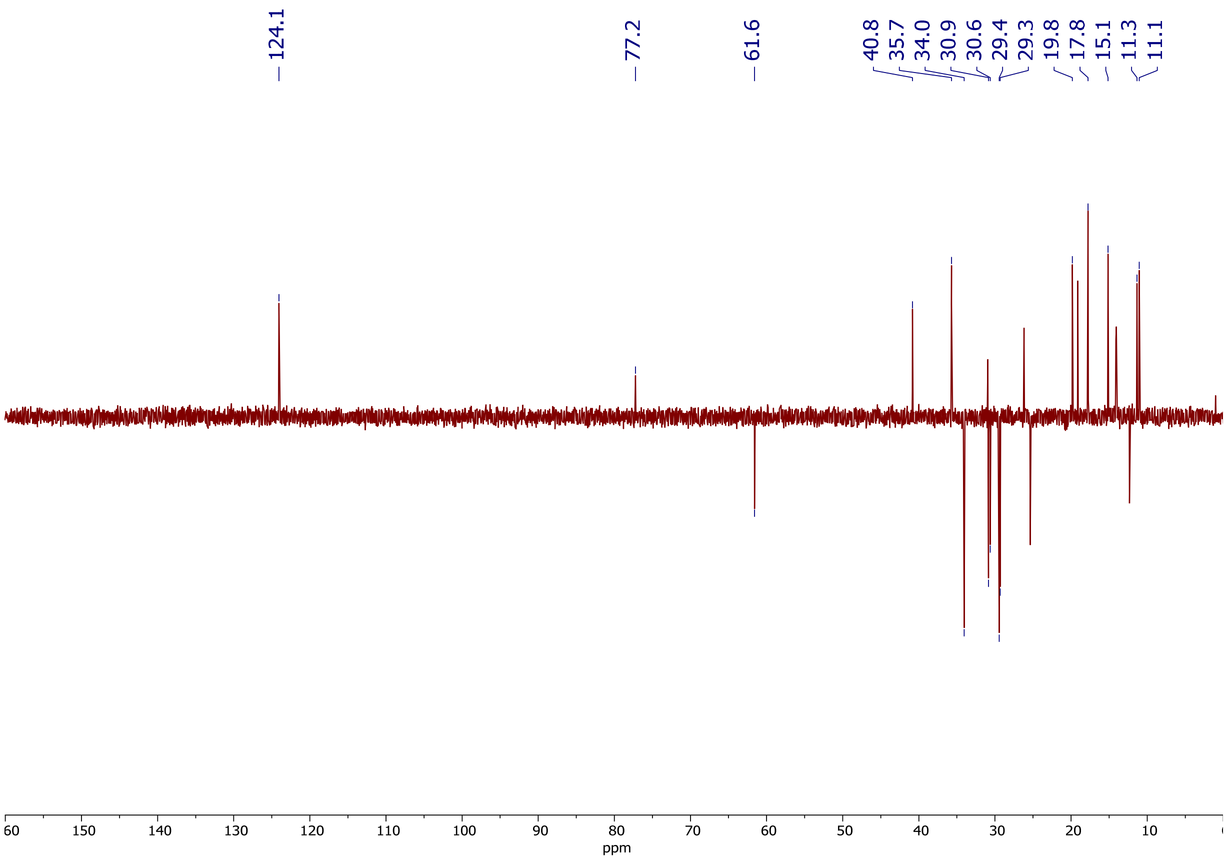
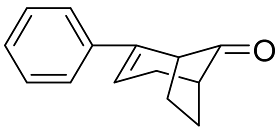
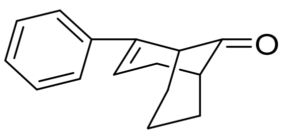
34.0
30.9
30.6
29.4
29.3
19.8
17.8
15.1
11.3
11.1
○ 18
● 19
SM
SM
SM
SM
SM
45 44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9
ppm





20

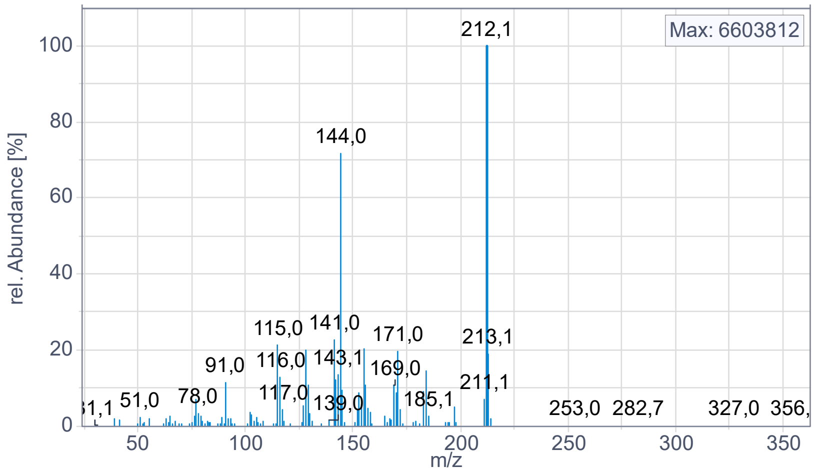
(1,5)-2-Phenylbicyclo[3.2.1]oct-2-en-8-one **20. GC-MS (m/z, relative intensity):** 198 (M+•, 26), 171 (30), 170 (100), 169 (17), 155 (26). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 7.33 – 7.02 (m, 5H), 6.01 – 5.90 (m, 1H), 4.05 (qd, *J* = 7.1, 1.7 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.54 (dtd, *J* = 11.0, 5.5, 2.5 Hz, 1H), 2.38 (dt, *J* = 13.1, 8.6 Hz, 1H), 1.95 (ddd, *J* = 9.3, 4.9, 3.2 Hz, 1H), 1.91 – 1.83 (m, 1H), 1.76 – 1.55 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 182.0 (C), 146.1 (C), 143.5 (C), 128.6 (2CH), 128.3 (2CH), 125.7 (CH), 125.7 (CH), 53.3 (CH), 47.7 (CH), 30.9 (CH_2), 29.3 (CH_2), 28.5 (CH_2). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{14}H_{15}O$: 199.1123] found: 199.1119.

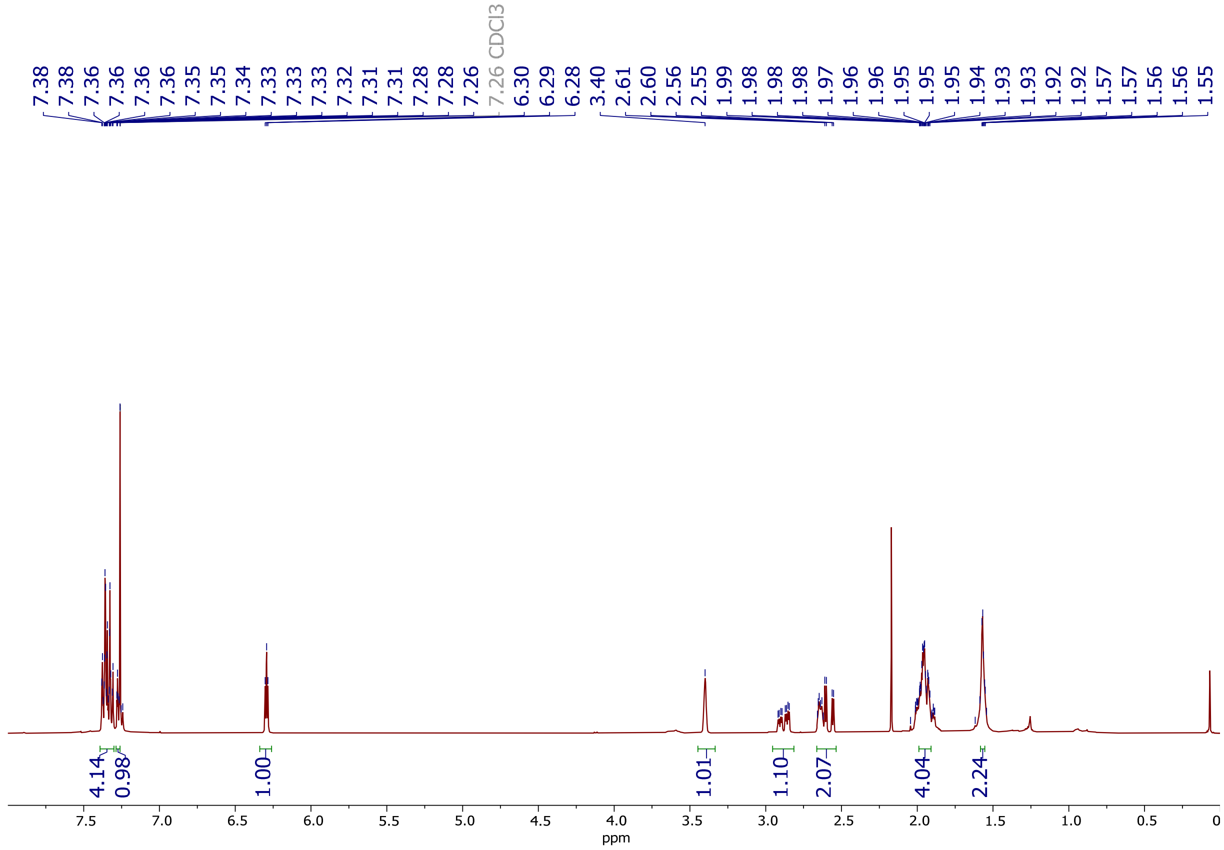


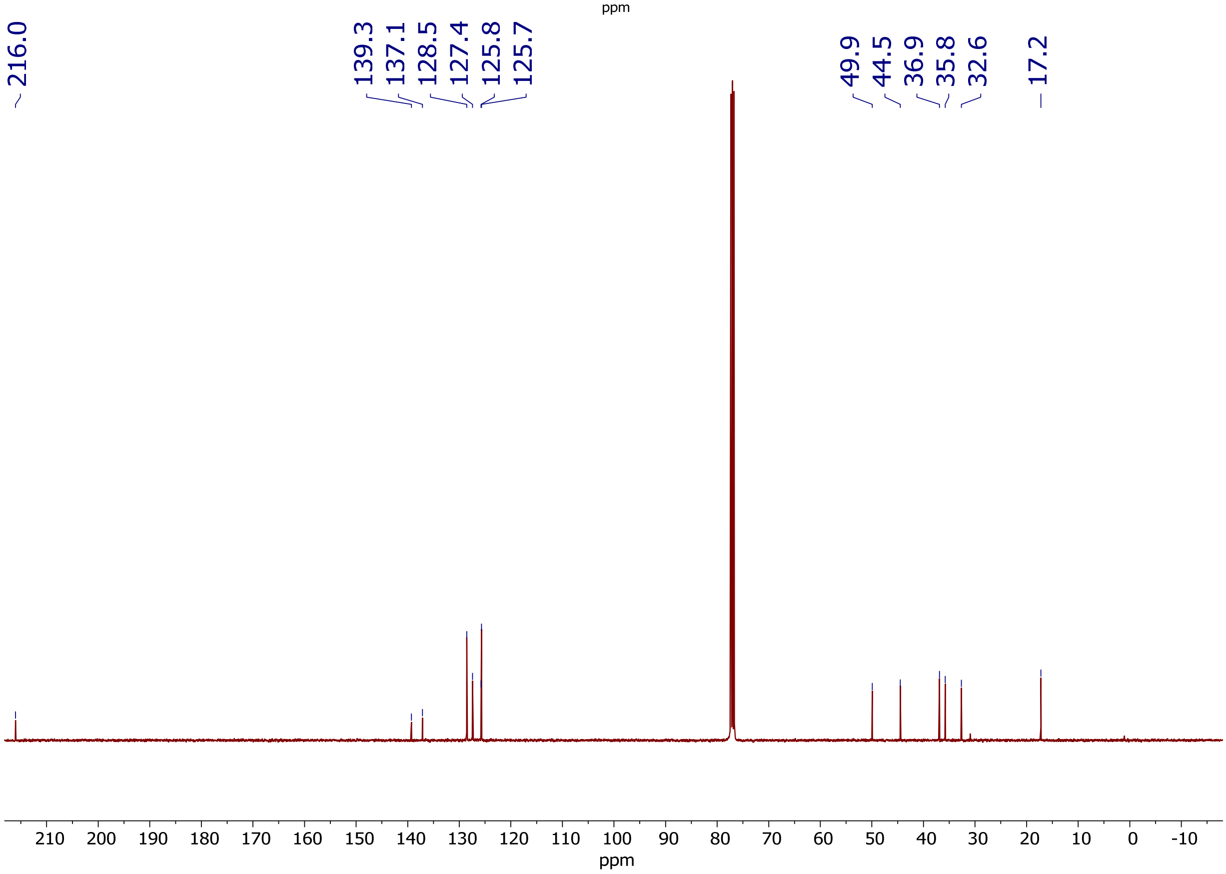
21

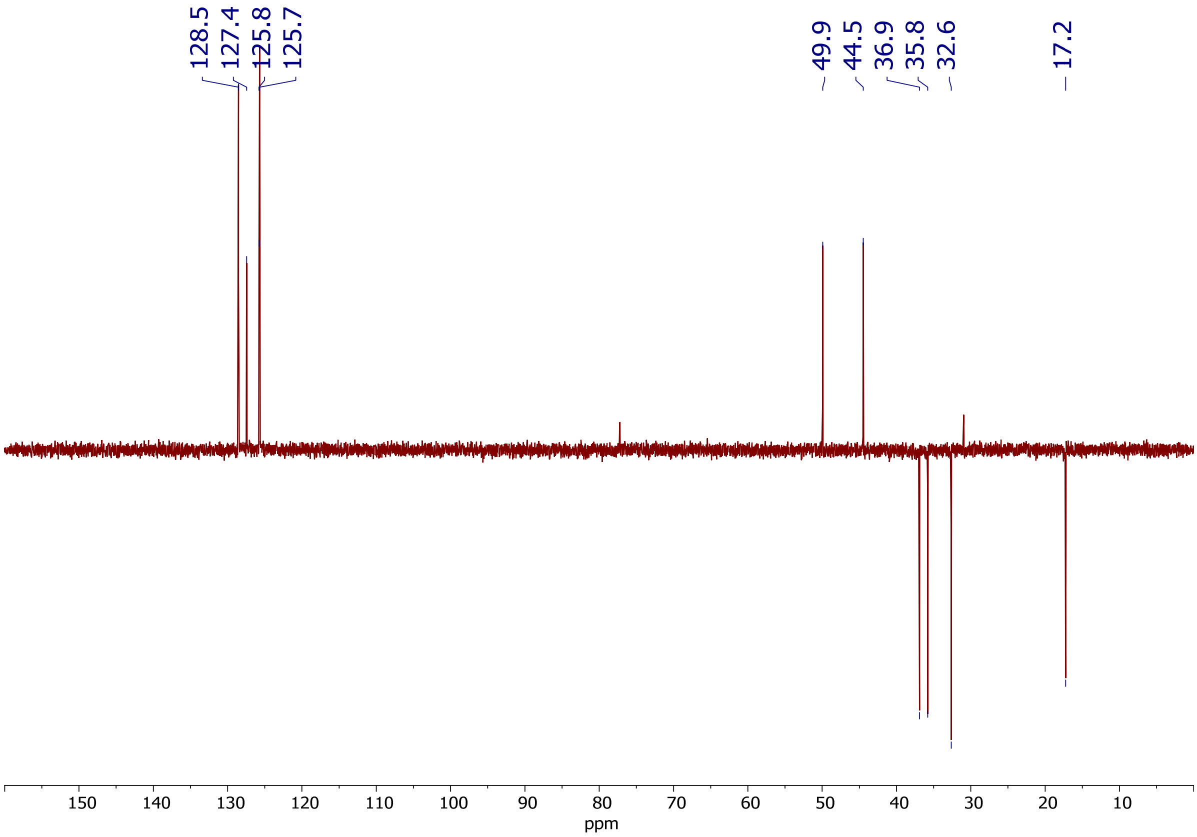
(1,5)-2-Phenylbicyclo[3.3.1]non-2-en-9-one **21**. **GC-MS (m/z, relative intensity):** 212 (M+•, 100), 211 (9), 185 (10), 171 (24), 169 (20), 149 (22), 144 (68), 143 (13), 141 (20), 140 (11), 139 (10), 130 (12), 129 (11), 116 (13), 115 (12), 91 (14), 78 (10), 51 (11). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 7.38 – 7.03 (m, 5H), 6.18 (t, *J* = 3.8 Hz, 1H), 3.31 (s, *J* = 2.1 Hz, 1H), 2.76 (ddd, *J* = 19.1, 7.4, 3.4 Hz, 1H), 2.58

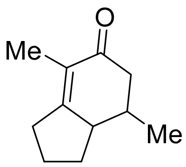
– 2.51 (m, 1H), 2.46 (dd, *J* = 19.1, 4.1 Hz, 1H), 2.20 – 1.94 (m, 1H), 1.92 – 1.76 (m, 5H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 216.2 (C), 139.3 (C), 137.1 (C), 128.6 (2CH), 127.5 (2CH), 125.8 (CH), 125.7 (CH), 49.9 (CH), 44.5 (CH), 36.9 (CH_2), 35.8 (CH_2), 32.7 (CH_2), 17.2 (CH_2). **HRMS (UPLC):** [M+H$^+$; calculated for $C_{15}H_{17}O$: 213.1279] found: 213.1268.




7.38 7.38 7.36 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.28 7.28 7.26
7.26 CDCl3
6.30 6.29 6.28 3.40 2.61 2.60 2.56 2.55 1.99 1.98 1.98 1.98 1.97 1.96 1.96 1.95 1.95 1.95 1.94 1.93 1.93 1.92 1.92 1.57 1.57 1.56 1.56 1.55
4.14 0.98 1.00 1.01 1.10 2.07 4.04 2.24
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
ppm

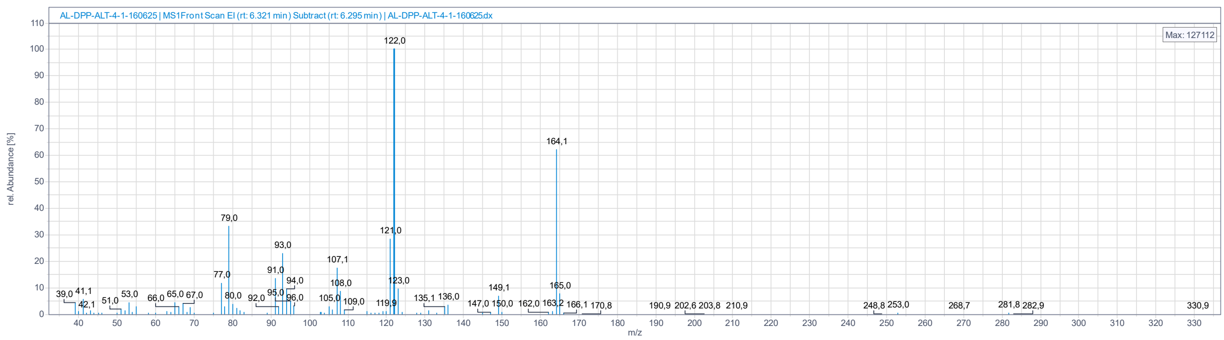

216.0
139.3 137.1 128.5 127.4 125.8 125.7
49.9 44.5 36.9 35.8 32.6 17.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

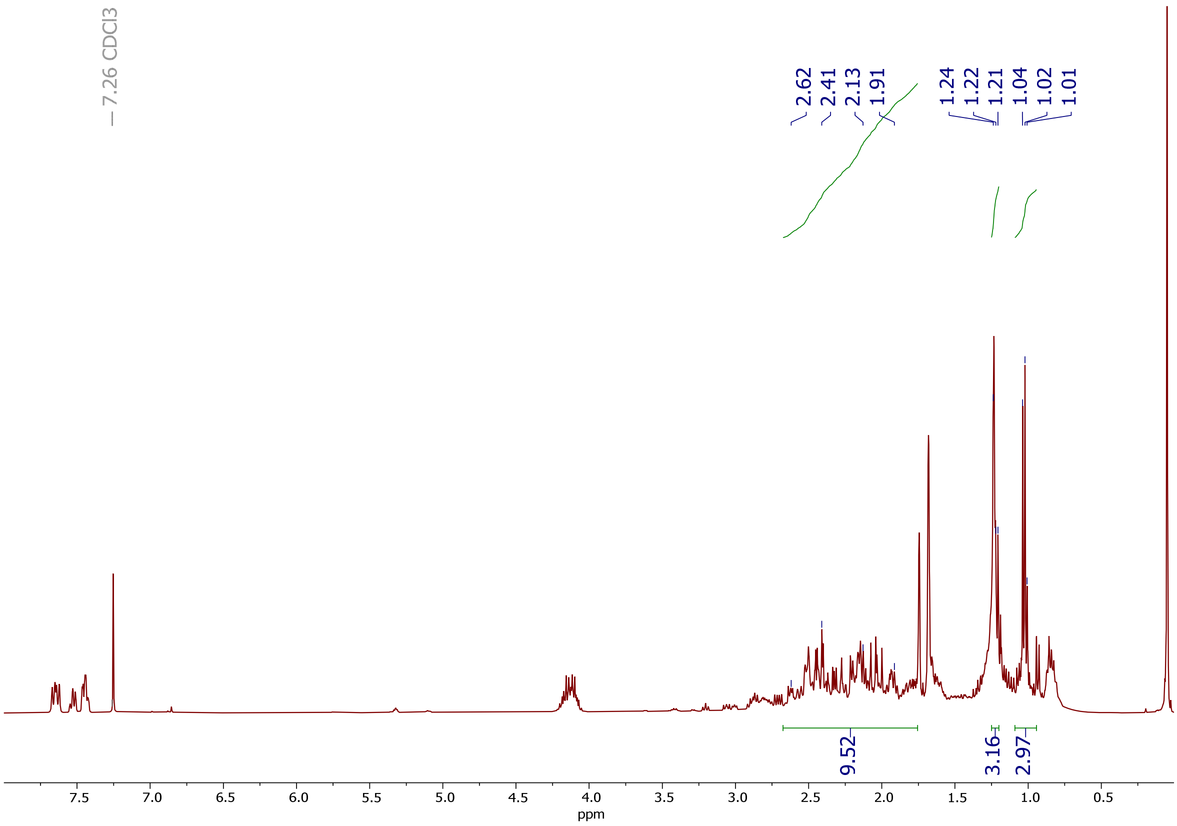


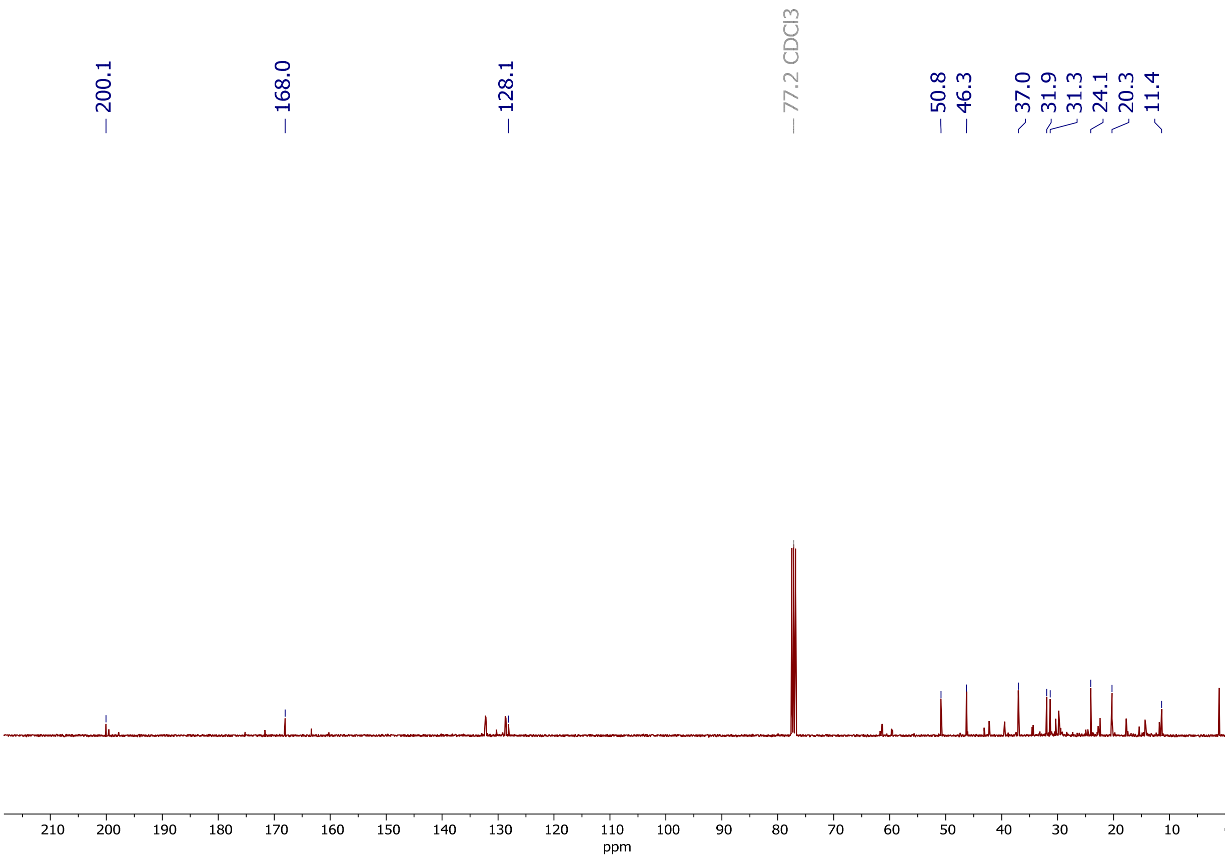


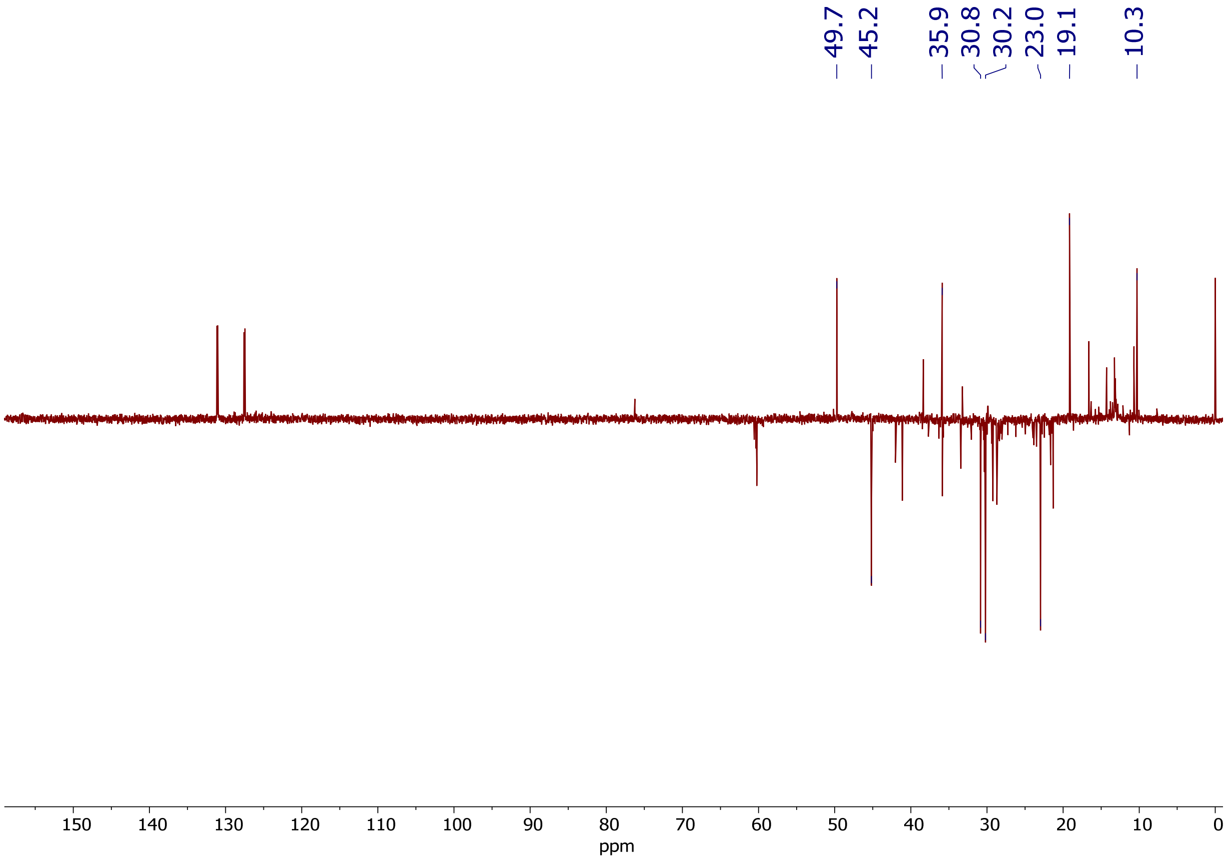
22

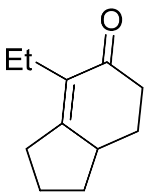
4,7a-dimethyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one **22**. **GC-MS; m/z, (relative intensity):** 164 (M+•, 62), 122 (100), 107 (18), 93 (24), 79 (33). **^{1}H NMR (401 MHz, CDCl$_3$) δ** 2.61-1.78 (m, 10H), 1.21 (s, 3H), 1.93 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$) δ** 200.1 (C), 168.0 (C), 132.3 (C), 49.7 (CH), 46.3 (CH$_2$), 37.0 (CH), 31.3 (CH$_2$), 29.8 (CH$_2$), 24.1 (CH$_2$), 20.3 (CH$_3$), 11.4 (CH$_3$).




7.26 CDCl3
2.62
2.41
2.13
1.91
1.24
1.22
1.21
1.04
1.02
1.01
9.52
3.16
2.97
ppm

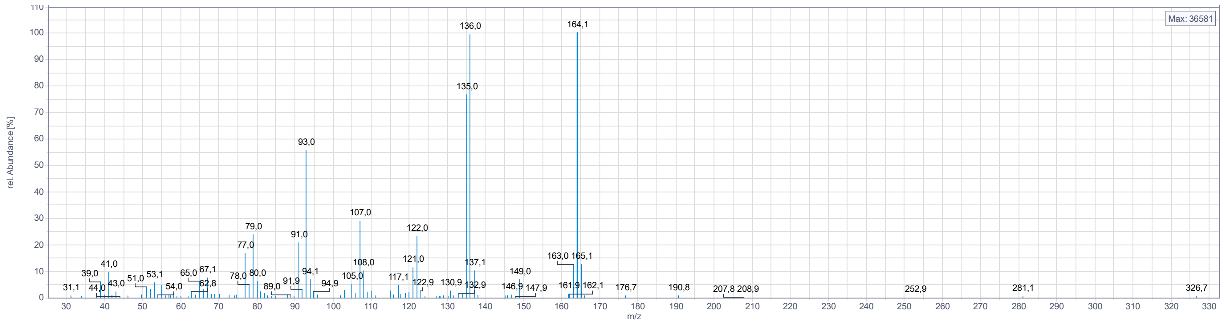

200.1
168.0
128.1
77.2 CDCl3
50.8
46.3
37.0
31.9
31.3
24.1
20.3
11.4
ppm

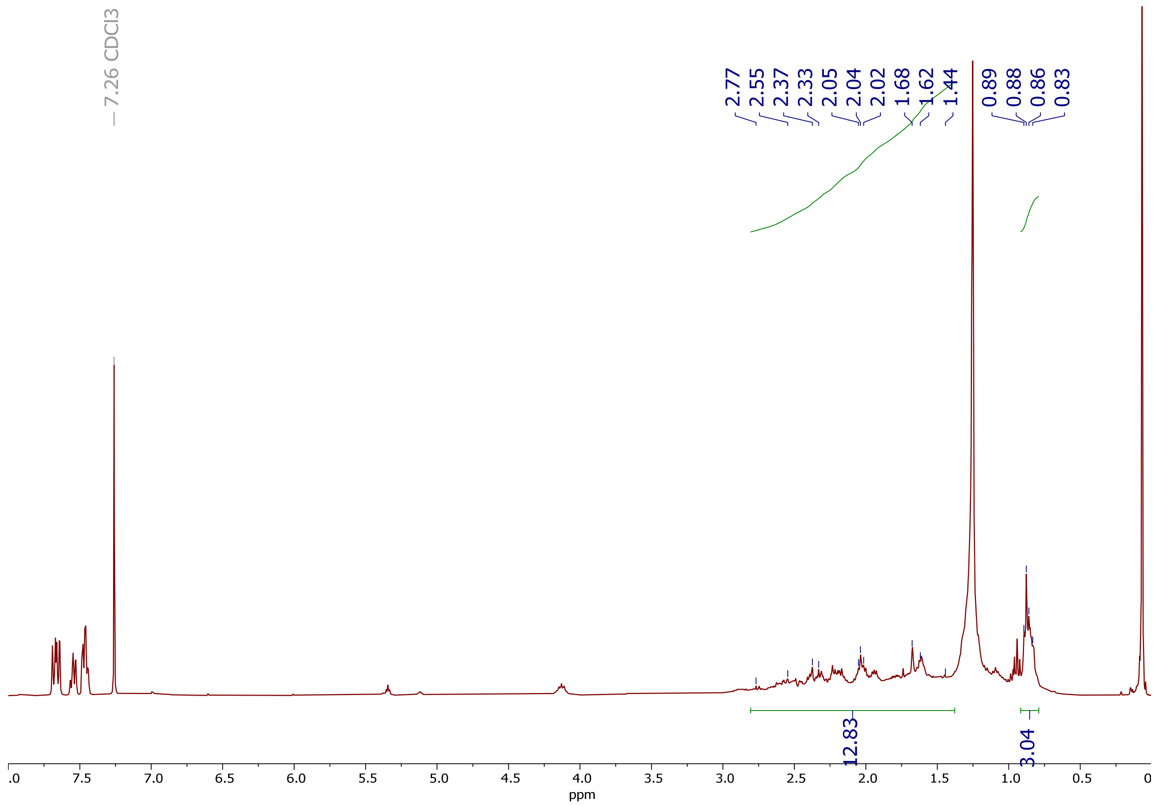


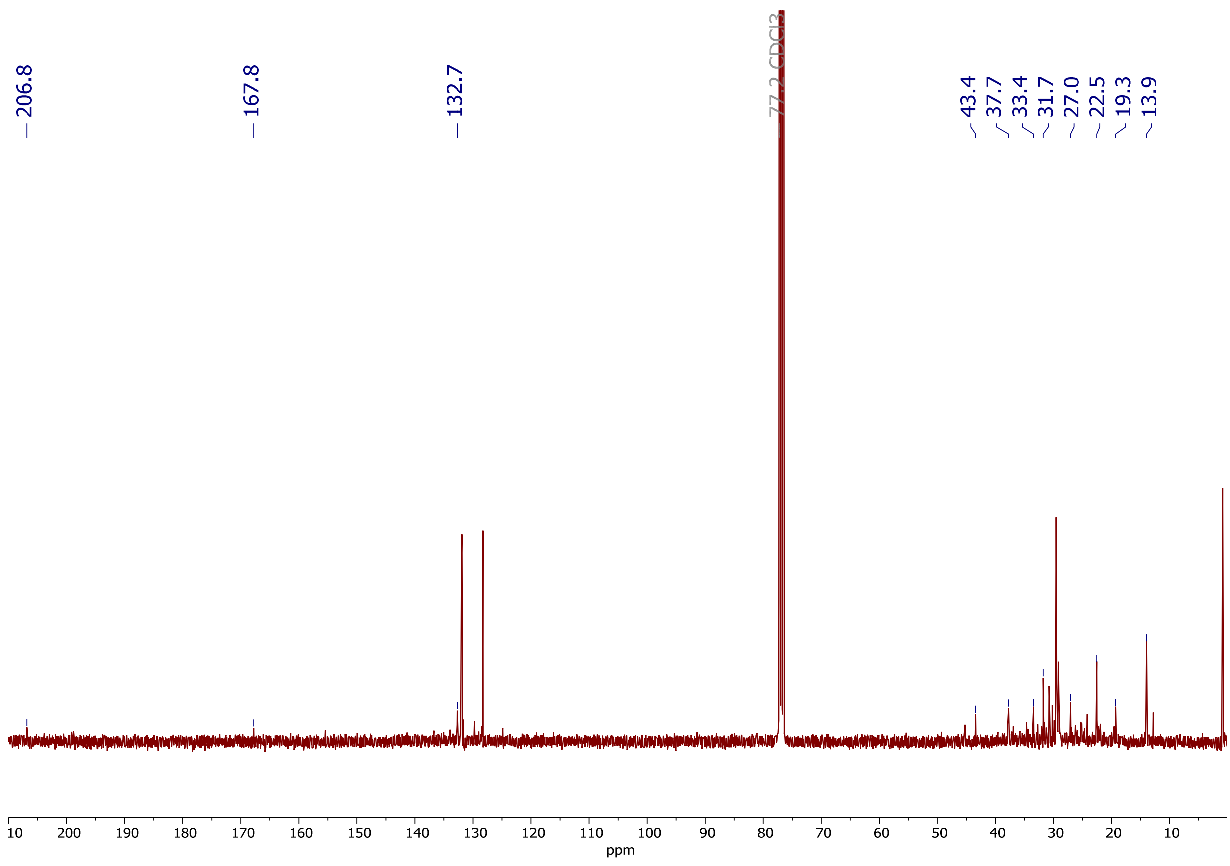


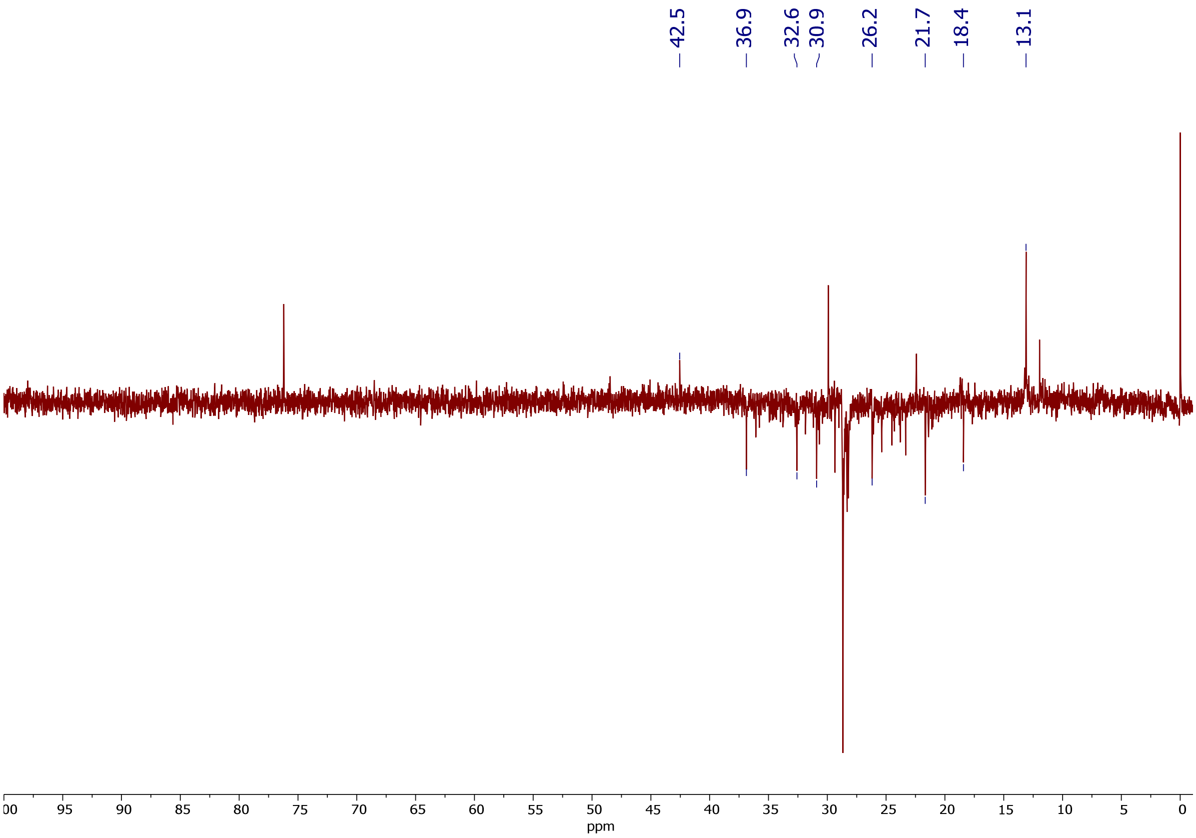
23

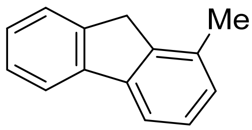
4-ethyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one **23**. **GC-MS; m/z, (relative intensity):** 164 (M+•, 100), 136 (100), 135 (76), 122 (23), 107 (28), 93 (55), 79 (23).). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 2.55-1.48 (m, 13H), 2.38 (t, J = 7.2 Hz, 3H) **^{13}C NMR (101 MHz, $CDCl_3$) δ** 206.9 (C), 167.8 (C), 132.7 (C), 43.4 (CH), 37.7 (CH_2), 33.4 (CH_2), 31.8 (CH_2), 27.0 (CH_2), 22.5 (CH_2), 19.3 (CH_2), 13.9 (CH_3).




7.26 CDCl3
2.77
2.55
2.37
2.33
2.05
2.04
2.02
1.68
1.62
1.44
0.89
0.88
0.86
0.83
12.83
3.04
ppm

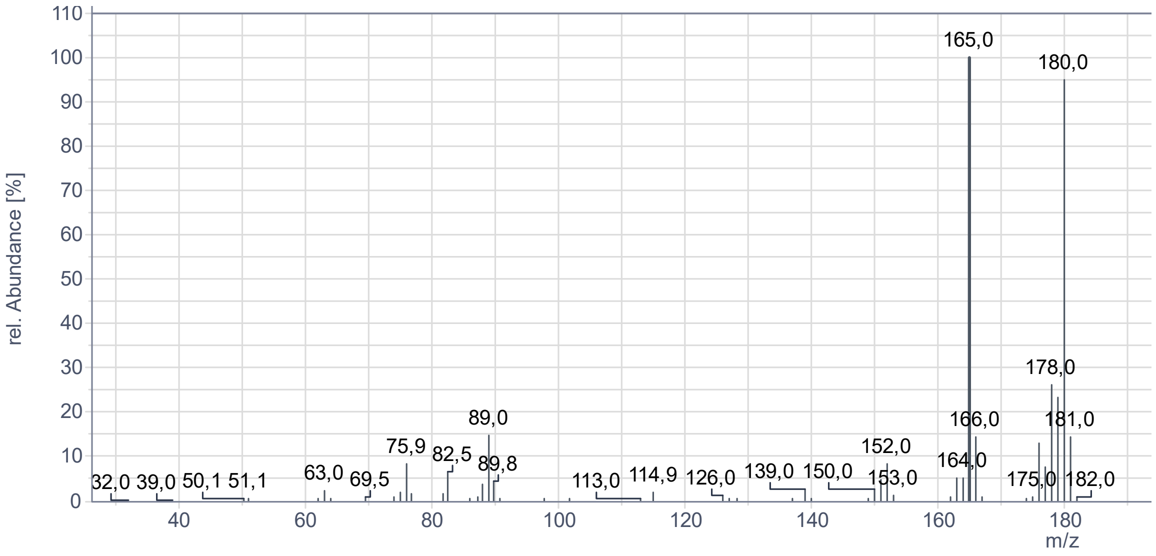

206.8
167.8
132.7
77.2 CDCl3
43.4
37.7
33.4
31.7
27.0
22.5
19.3
13.9
ppm



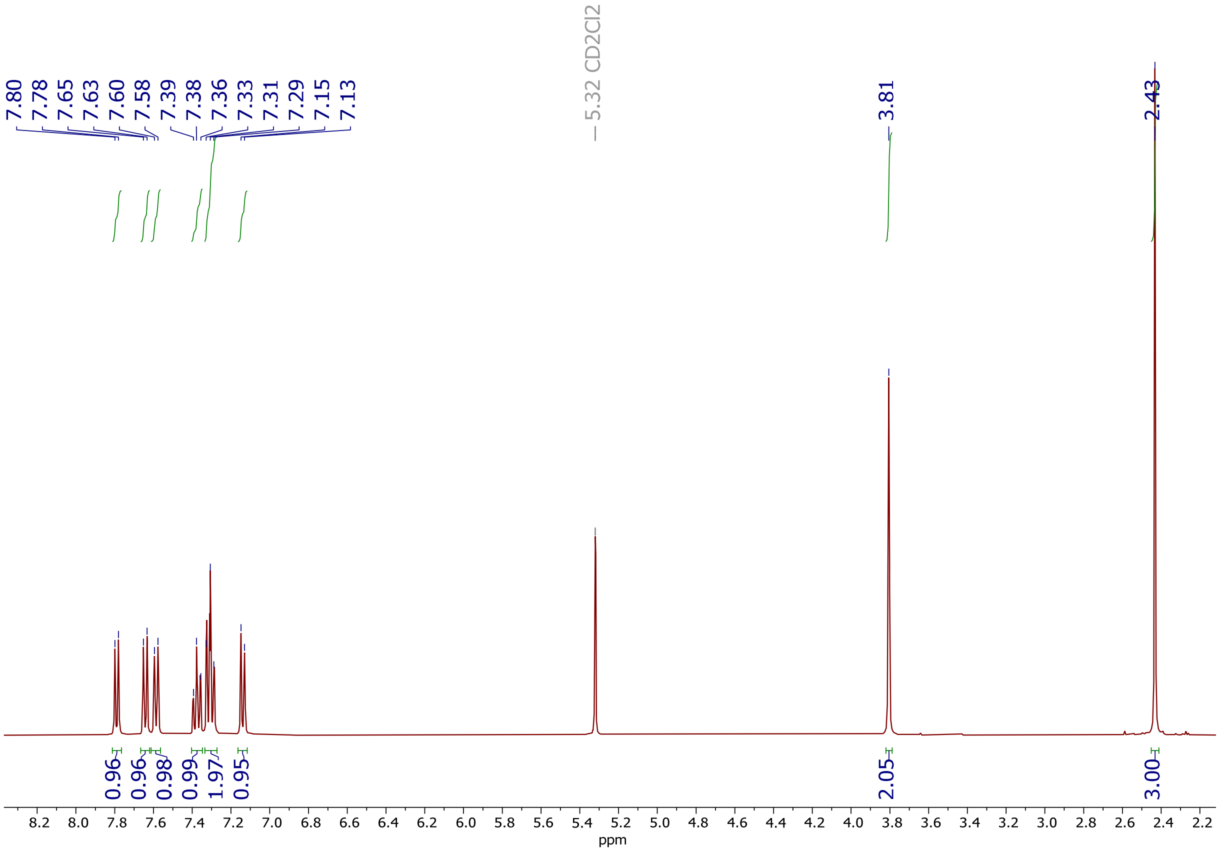


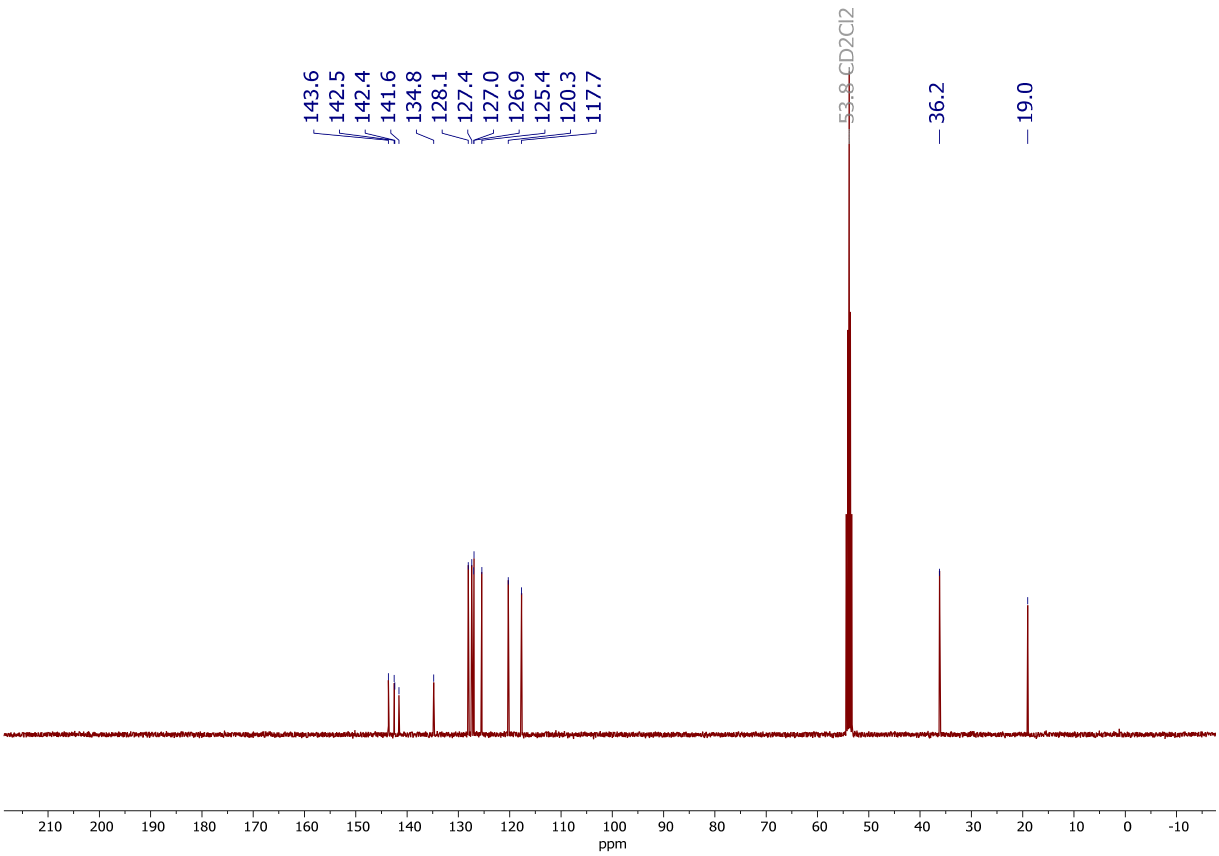
24

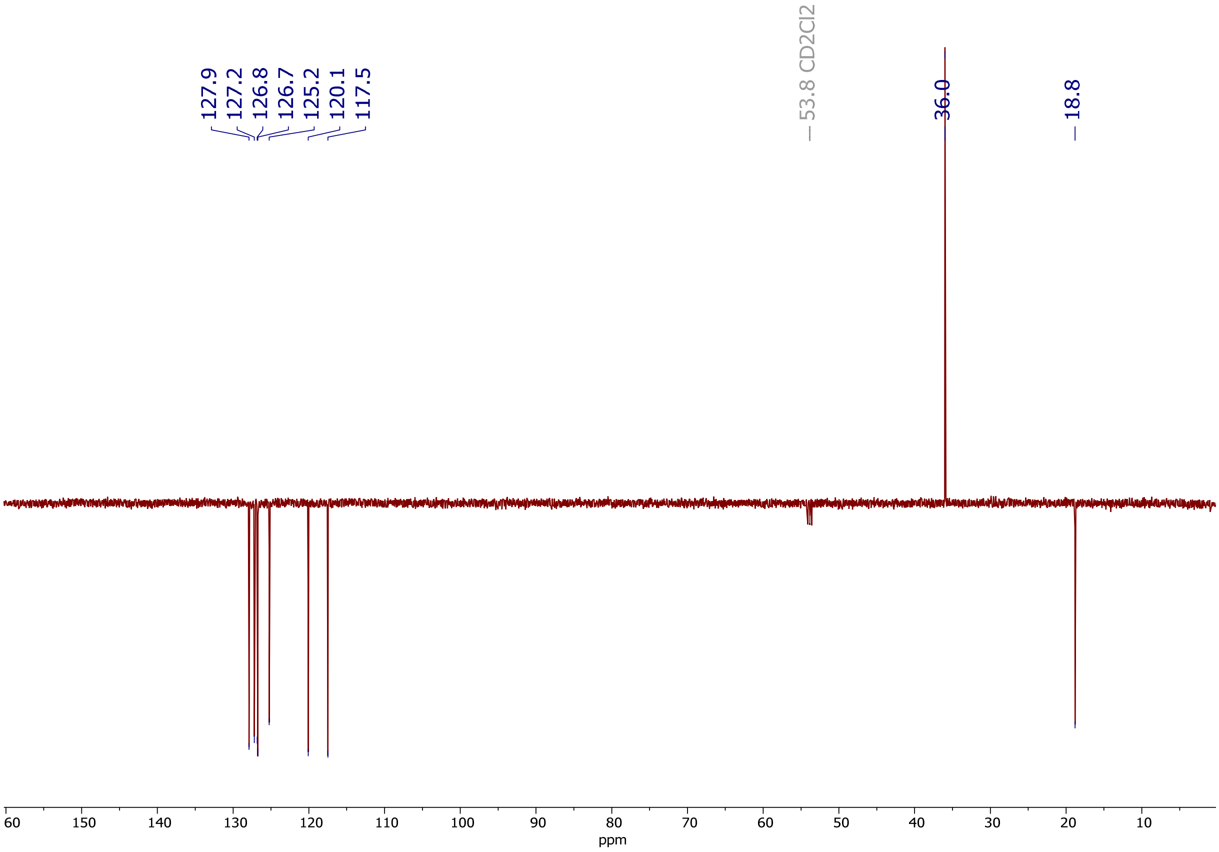
1-Methyl-9*H*-fluorene **24**. **GC-MS (m/z, relative intensity):** 180 (M+•, 95), 165 (100), 152 (100), 89 (15), 82 (10), 75 (11), 68 (5). **^{1}H NMR (401 MHz, CD_2Cl_2) δ** 7.79 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.59 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.37 (tdd, *J* = 6.8, 1.2, 0.6 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.14 (dt, J = 7.4, 0.8 Hz, 1H), 3.81 (s, 2H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, CD_2Cl_2) δ** 143.6 (C), 142.53 (C), 142.4 (C), 141.6 (C), 134.8 (C), 128.1 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 125.4 (CH), 120.3 (CH), 117.7 (CH), 36.2 (CH_2) , 19.0 (CH_3)

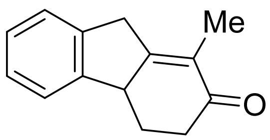


110
100
90
80
70
60
50
40
30
20
10
0
rel. Abundance [%]
165,0
180,0
178,0
166,0
181,0
89,0
152,0
75,9
82,5
89,8
164,0
63,0
139,0
150,0
32,0
39,0
50,1
51,1
69,5
113,0
114,9
126,0
153,0
175,0
182,0
40
60
80
100
120
140
160
180
m/z


7.80
7.78
7.65
7.63
7.60
7.58
7.39
7.38
7.36
7.33
7.31
7.29
7.15
7.13
5.32 CD2Cl2
3.81
2.43
0.96
0.96
0.98
0.99
1.97
0.95
2.05
3.00
ppm

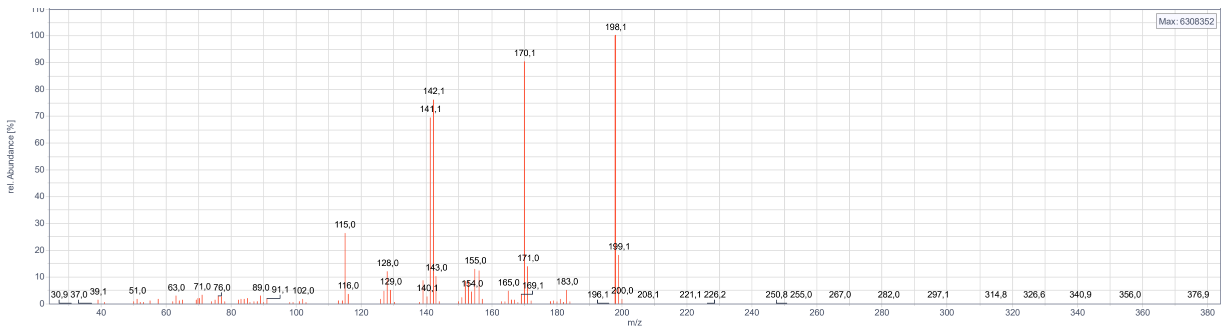

143.6
142.5
142.4
141.6
134.8
128.1
127.4
127.0
126.9
125.4
120.3
117.7
53.8 CD2Cl2
36.2
19.0
ppm

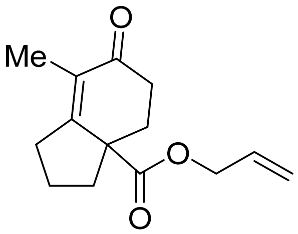




25

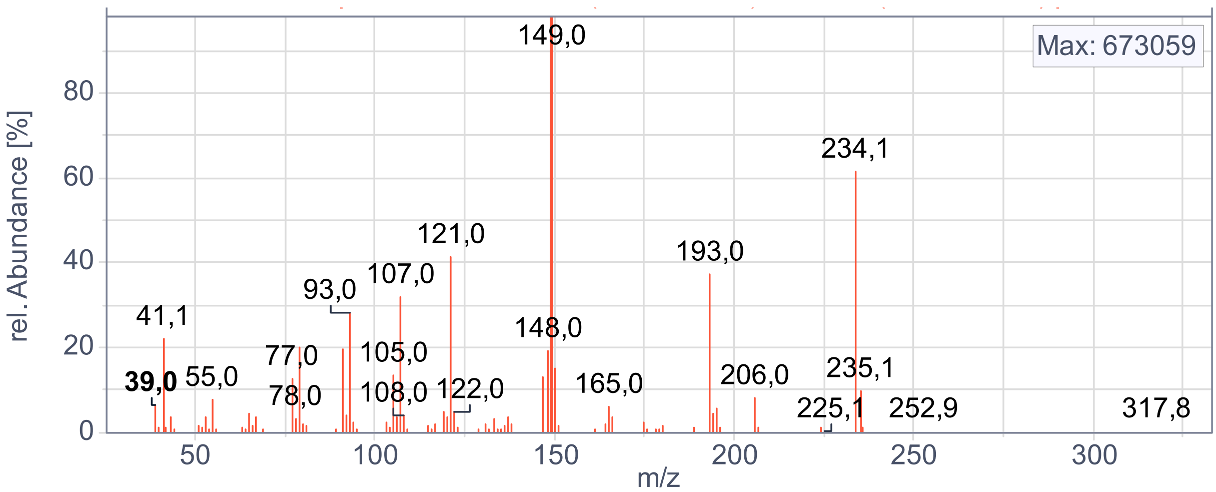
1-methyl-3,4,4a,9-tetrahydro-2*H*-fluoren-2-one **25**. **GC-MS (m/z, relative intensity):** 198 (M+•, 100), 170 (90), 142 (76), 115 (26).

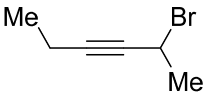




26

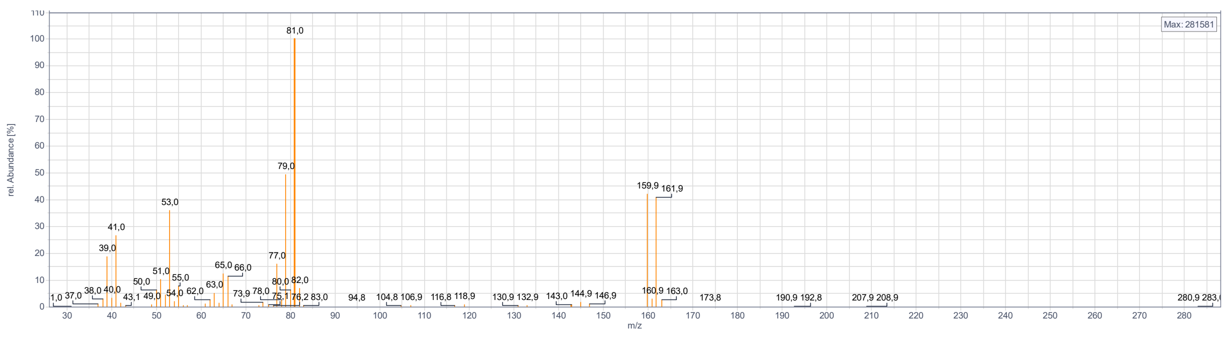
Allyl 7-methyl-6-oxo-1,2,3,4,5,6-hexahydro-3a*H*-indene-3a-carboxylate **26**. **GC-MS; m/z, (relative intensity):** 234 (M+•, 62), 193 (37), 150 (15), 149 (100), 148 (19), 147 (13), 121 (41), 107 (32), 105 (13), 93 (28), 91 (20), 79 (20), 77 (12), 41 (22).

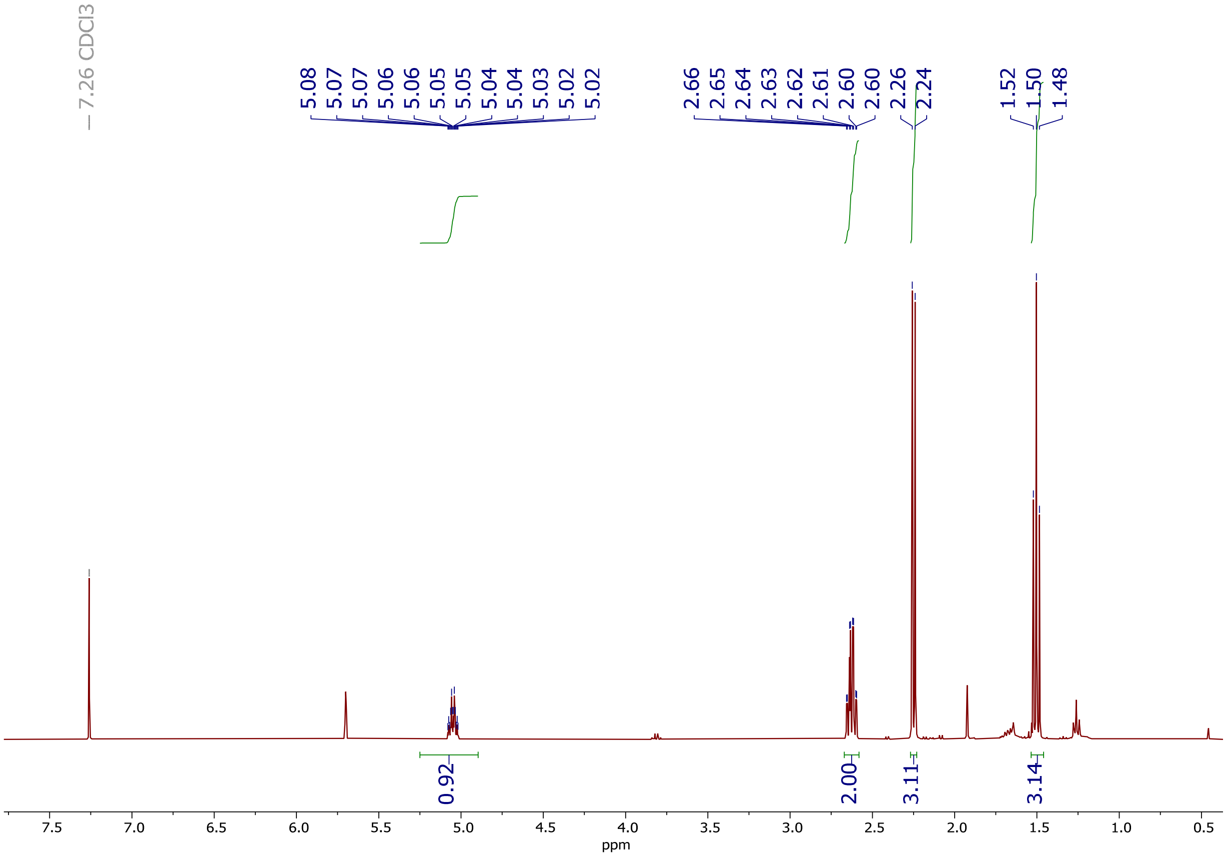




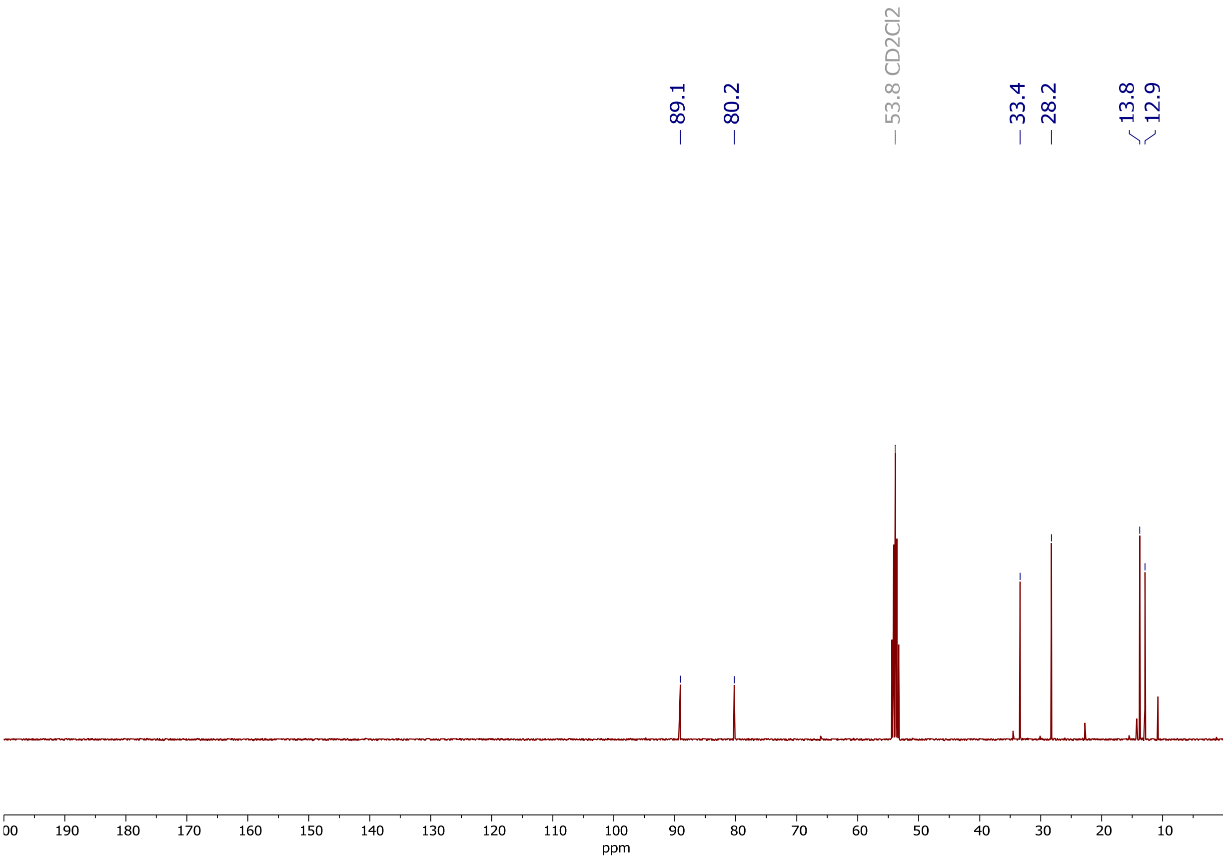
27

2-bromohex-3-yne **27. GC-MS; m/z, (relative intensity):** 162 (M+•, 45), 160 (45), 81 (100), 79 (48), 65 (12), 53 (35), 41 (26), 39 (19). **^{1}H NMR (401 MHz, $CDCl_3$) δ** 5.05 (qt, *J* = 6.8, 2.0 Hz, 1H), 2.63 (qt, *J* = 7.6, 2.0 Hz, 2H), 2.25 (d, *J* = 6.8 Hz, 3H), 1.50 (t, *J* = 7.6, 3H). **^{13}C NMR (101 MHz, CD_2Cl_2) δ** 89.1 (C), 80.2 (C), 33.4 (CH), 28.2 (CH_3), 13.8 (CH_3), 12.9 (CH_2).

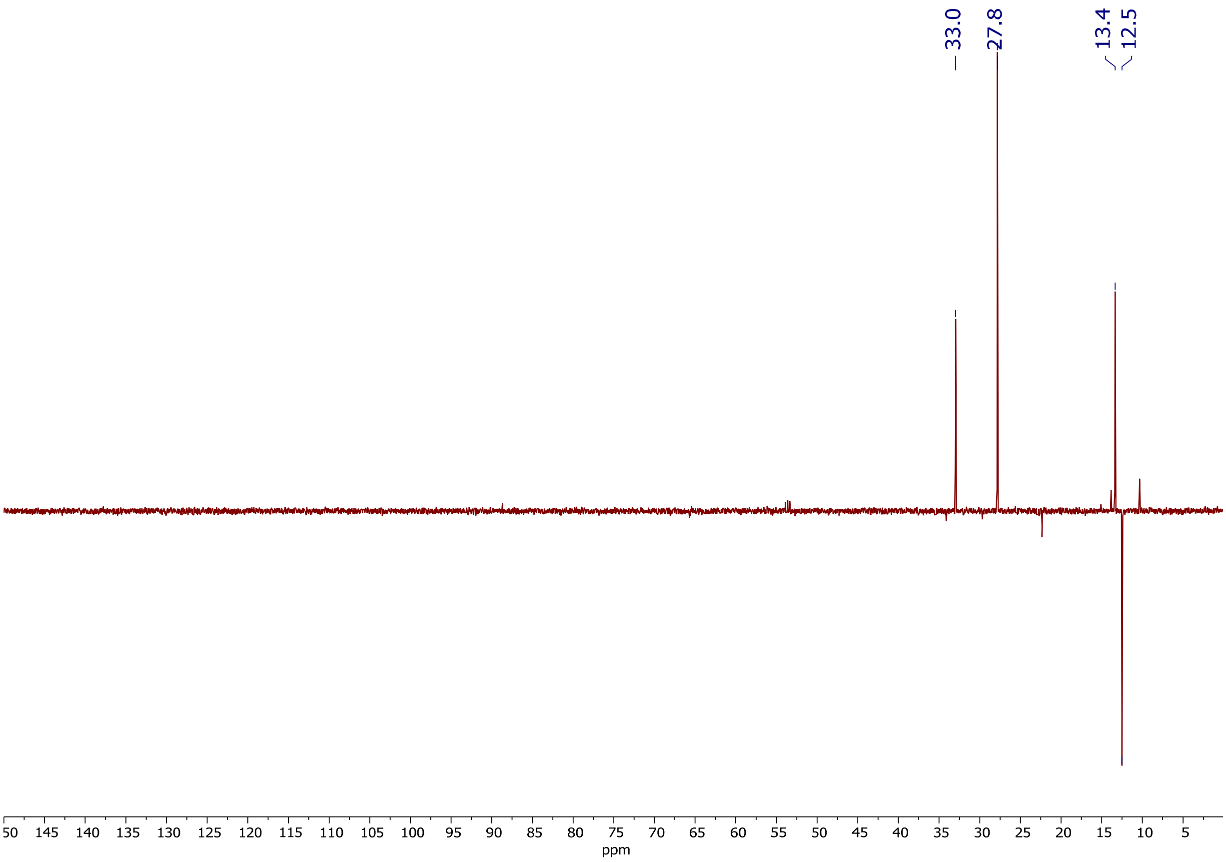


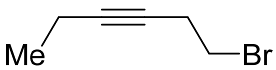


7.26 CDCl3
5.08
5.07
5.07
5.06
5.06
5.05
5.05
5.04
5.04
5.03
5.02
5.02
2.66
2.65
2.64
2.63
2.62
2.61
2.60
2.60
2.26
2.24
1.52
1.50
1.48
0.92
2.00
3.11
3.14
ppm



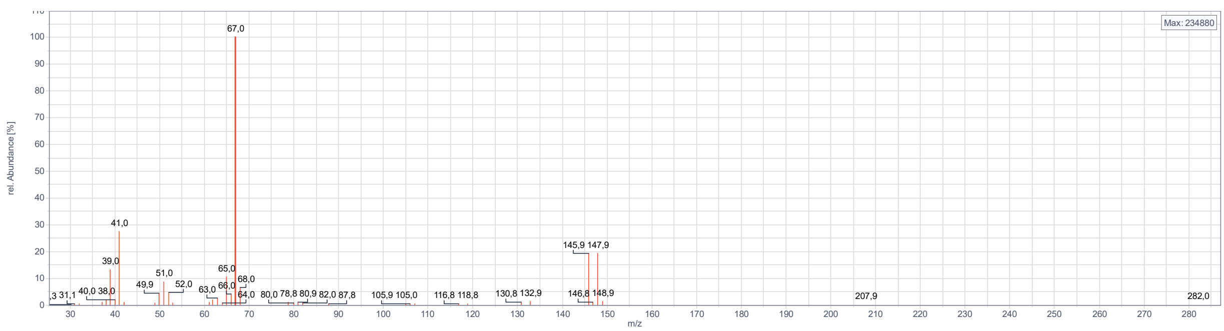
89.1
80.2
53.8 CD2Cl2
33.4
28.2
13.8
12.9
ppm

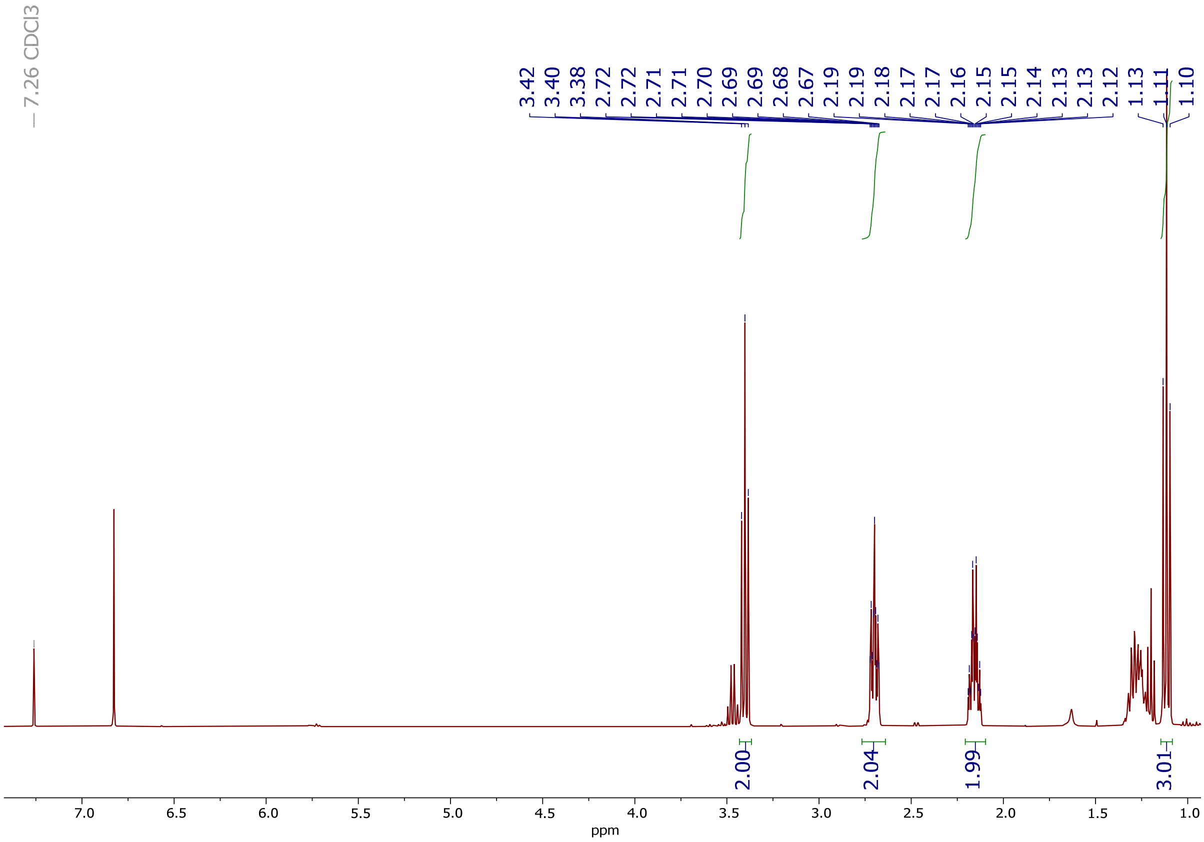


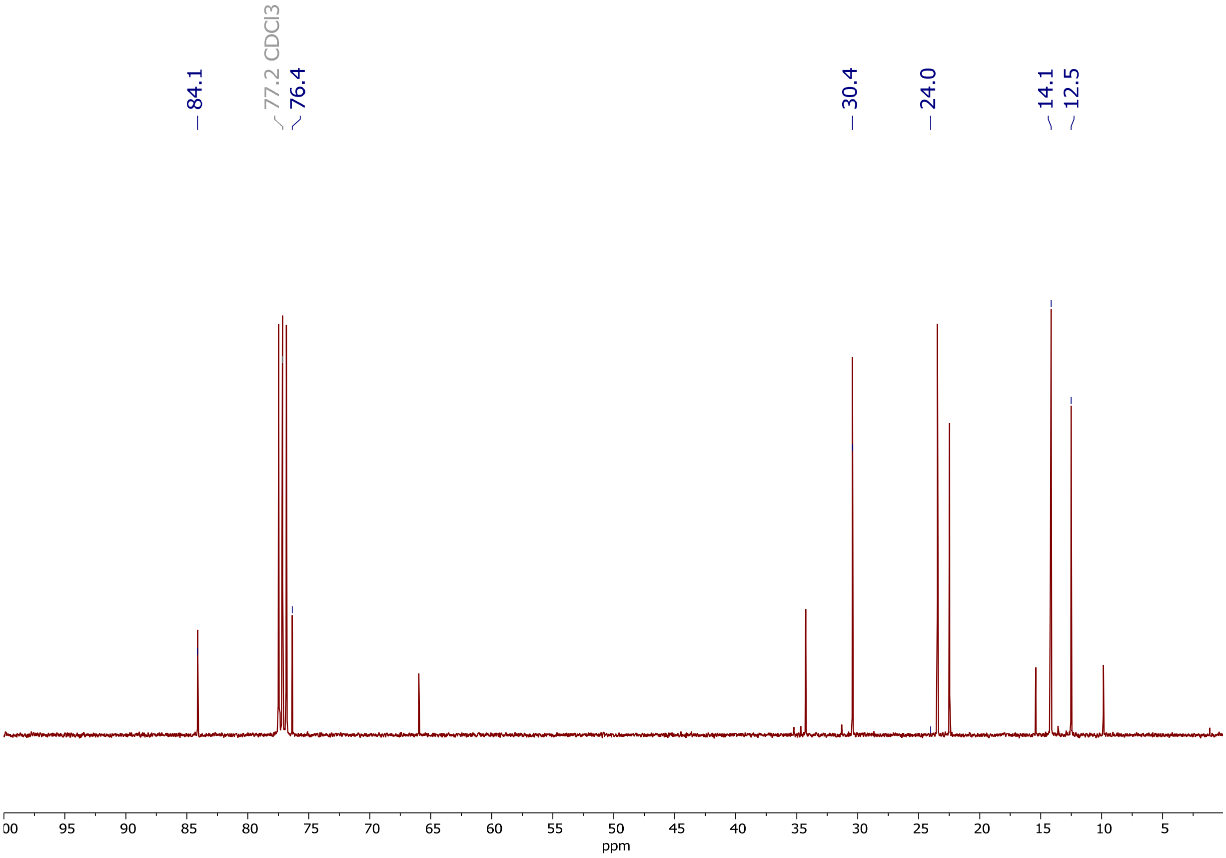


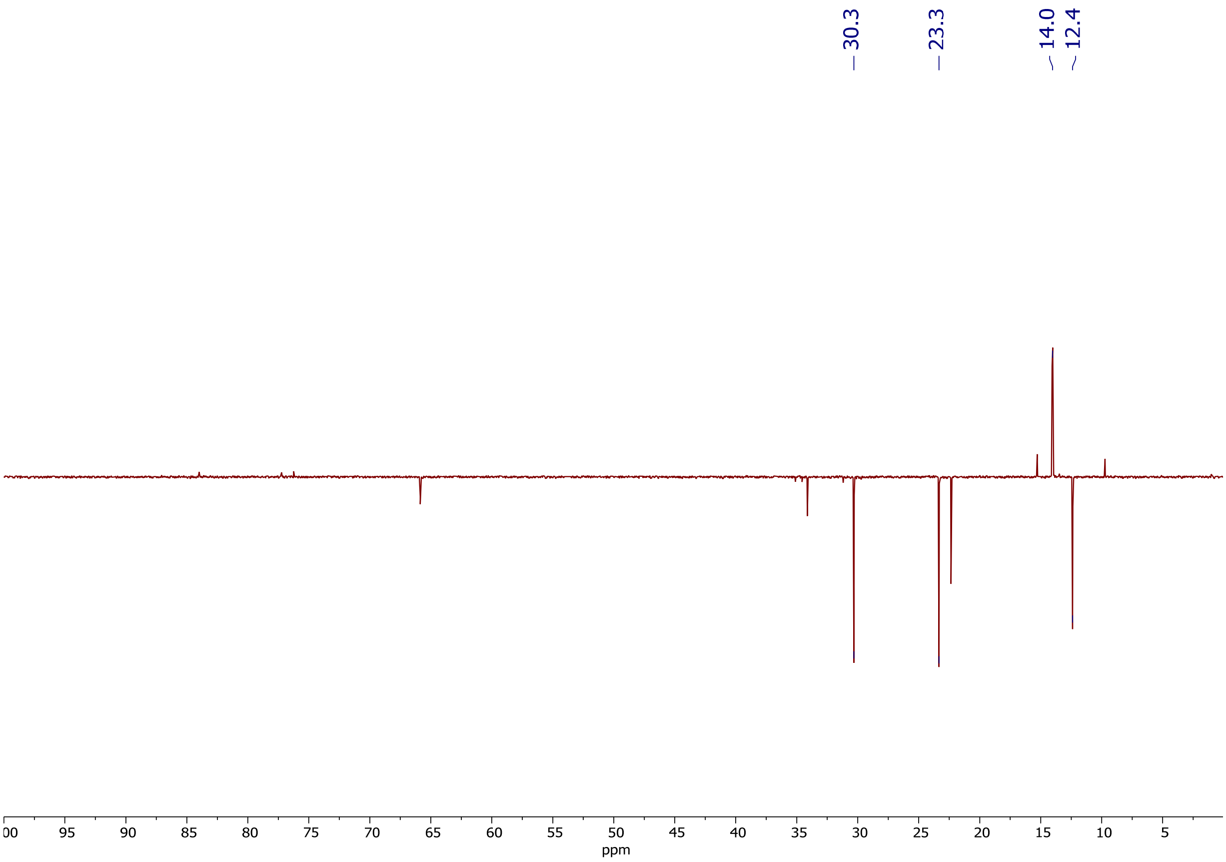
28

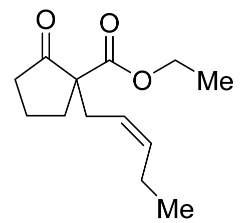
1-bromohex-3-yne **28. GC-MS; m/z, (relative intensity):** 162 (M+•, 1), 81 (100), 148-146 (20), 67 (100), 51 (8), 41 (27), 39 (13). **[1]H NMR (401 MHz, $CDCl_3$) δ** 3.40 (t, *J* = 7.6 Hz, 2H), 2.70 (tt, *J* = 7.6, 2.4 Hz, 2H), 2.16 (qt, *J* = 7.6, 2.4 Hz, 2H), 1.11 (t, *J* = 7.6, 3H). **[13]C NMR (101 MHz, CD_2Cl_2) δ** 84.1 (C), 76.4 (C), 30.4 (CH_2), 24.0 (CH_2), 14.1 (CH_3), 12.5 (CH_2).




7.26 CDCl3
3.42
3.40
3.38
2.72
2.72
2.71
2.71
2.70
2.69
2.69
2.68
2.67
2.19
2.19
2.18
2.17
2.17
2.16
2.15
2.15
2.14
2.13
2.13
2.12
1.13
1.11
1.10
2.00
2.04
1.99
3.01
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

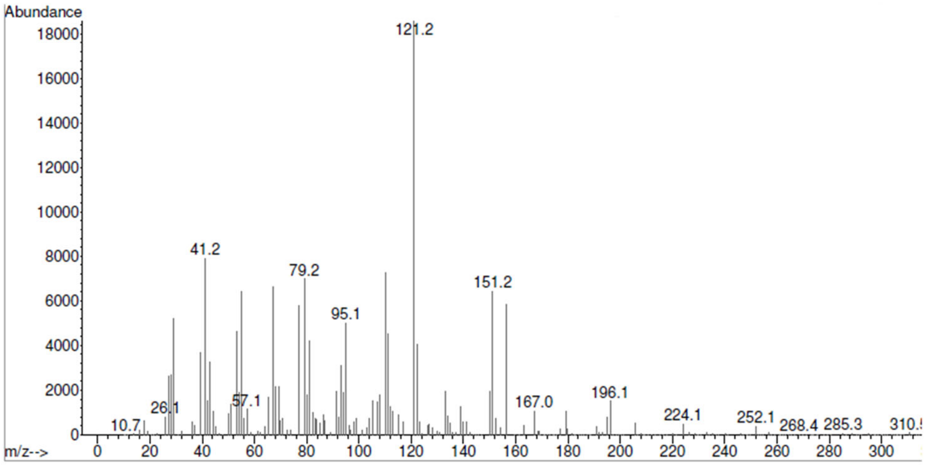

84.1
77.2 CDCl3
76.4
30.4
24.0
14.1
12.5
00
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
ppm



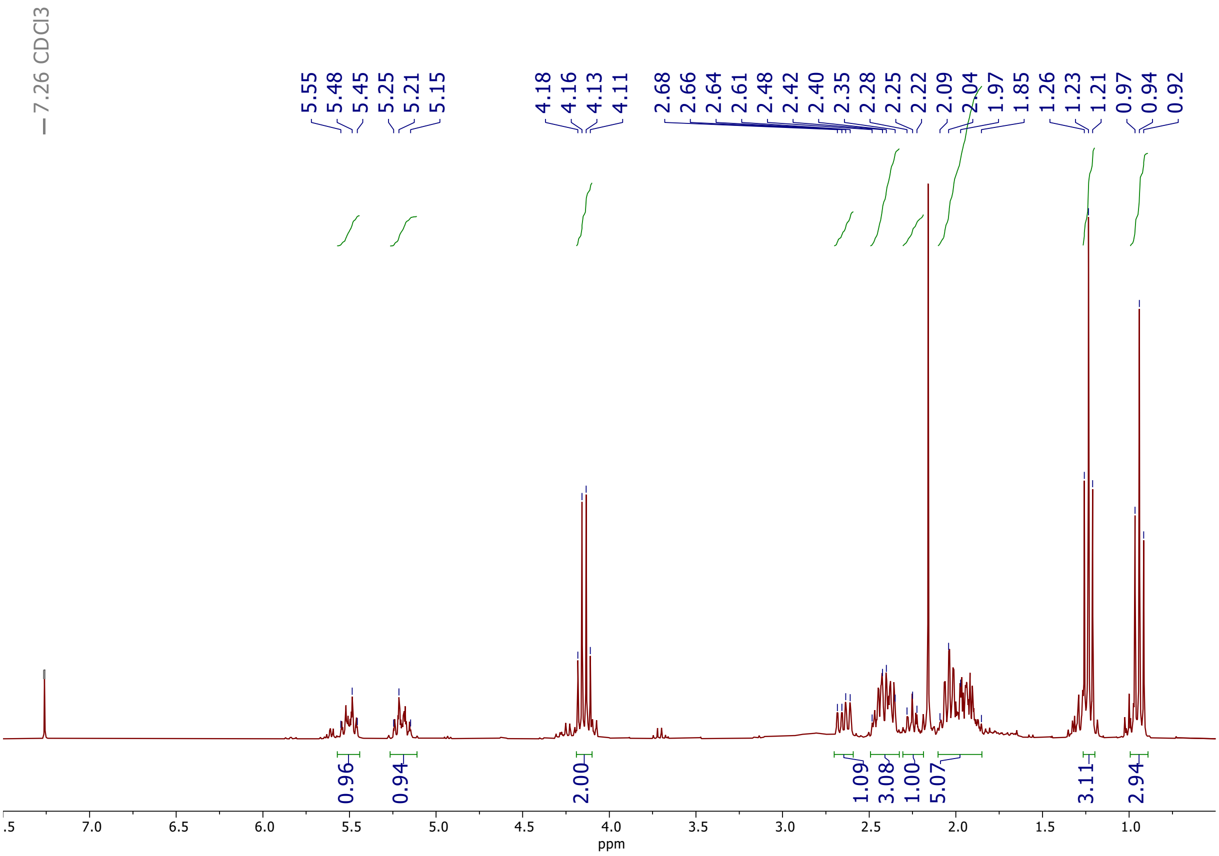


S1

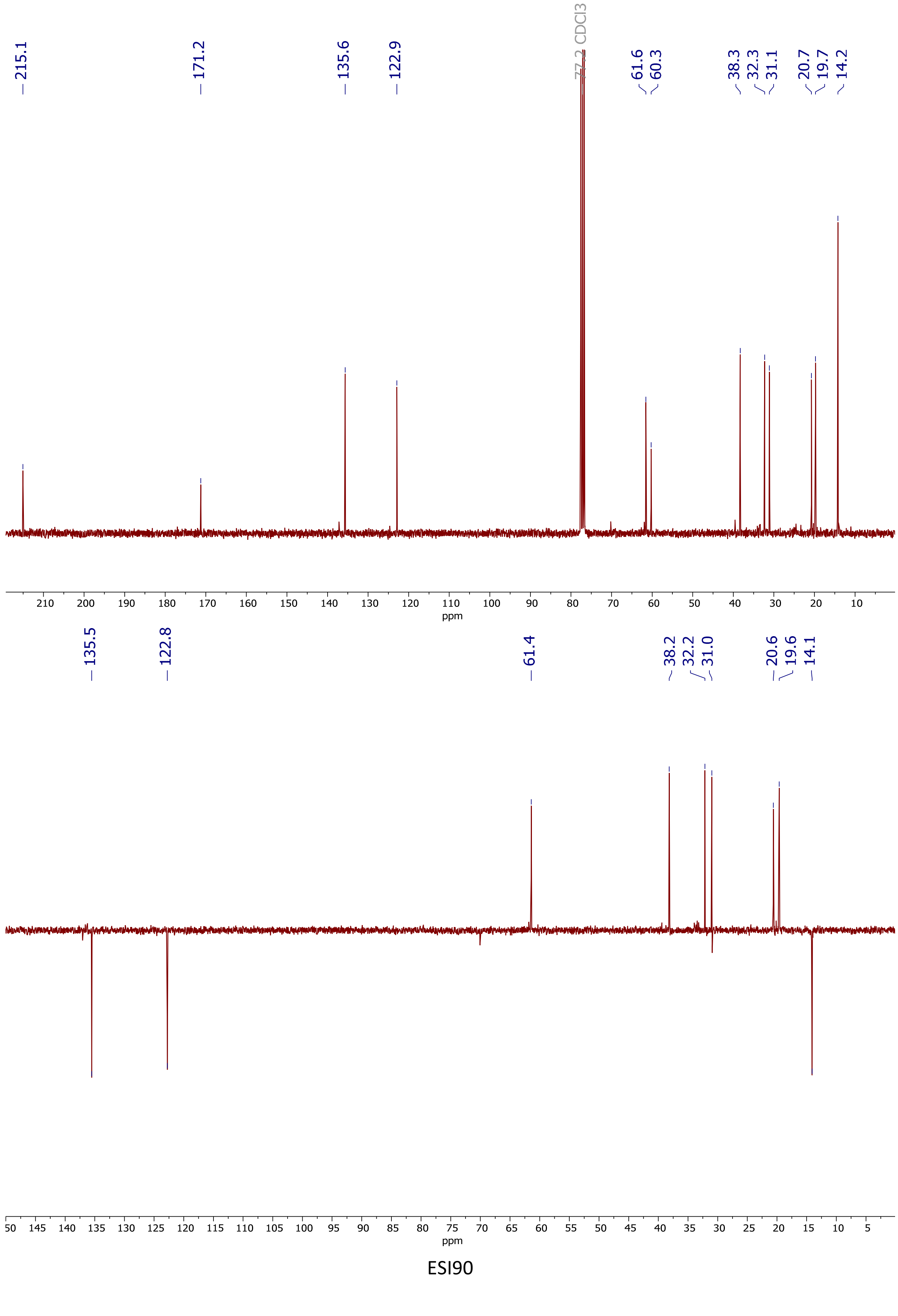
Ethyl (*Z*)-2-*oxo*-1-(pent-2-en-1-yl)cyclopentane-1-carboxylate **S1**. **GC-MS (m/z, relative intensity):** 224 (M+•, 12), 196 (11), 180 (14), 156 (39), 151 (34), 121 (100), 110 (19), 95 (29), 67 (24), 41 (45), 26 (26). **^{1}H NMR (300 MHz, $CDCl_3$) δ** 5.55 – 5.45 (m, 1H), 5.25 – 5.15 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.68 – 2.61 (m, 1H), 2.48 – 2.35 (m, 3H), 2.25 (td, *J* = 8.1, 2.1 Hz, 1H), 2.09 – 1.85 (m, 5H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$) δ** 215.1 (C), 171.2 (C), 135.6 (CH), 122.9 (CH), 61.6 (CH_2), 60.3 (C), 38.3 (CH_2), 32.3 (CH_2), 31.1 (CH_2), 20.7 (CH_2), 19.7 (CH_2), 14.2 (CH_3).

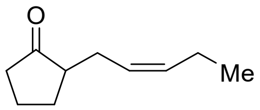


Abundance
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
m/z-->
121.2
41.2
79.2
151.2
95.1
26.1
57.1
10.7
167.0
196.1
224.1
252.1
268.4
285.3



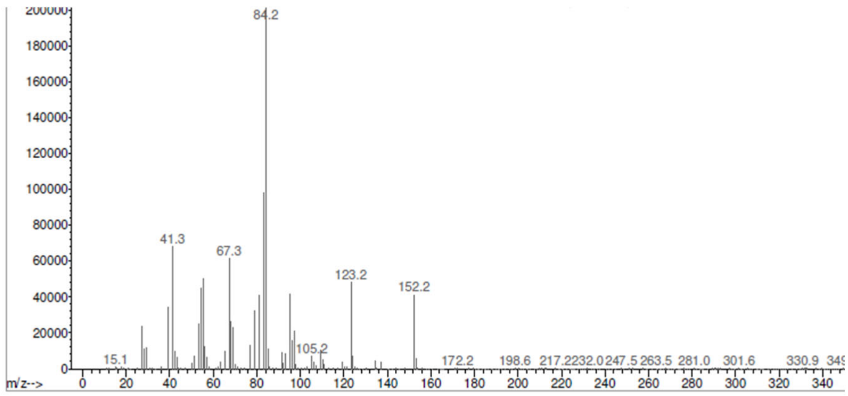
7.26 CDCl3
5.55
5.48
5.45
5.25
5.21
5.15
4.18
4.16
4.13
4.11
2.68
2.66
2.64
2.61
2.48
2.42
2.40
2.35
2.28
2.25
2.22
2.09
2.04
1.97
1.85
1.26
1.23
1.21
0.97
0.94
0.92
0.96
0.94
2.00
1.09
3.08
1.00
5.07
3.11
2.94
ppm

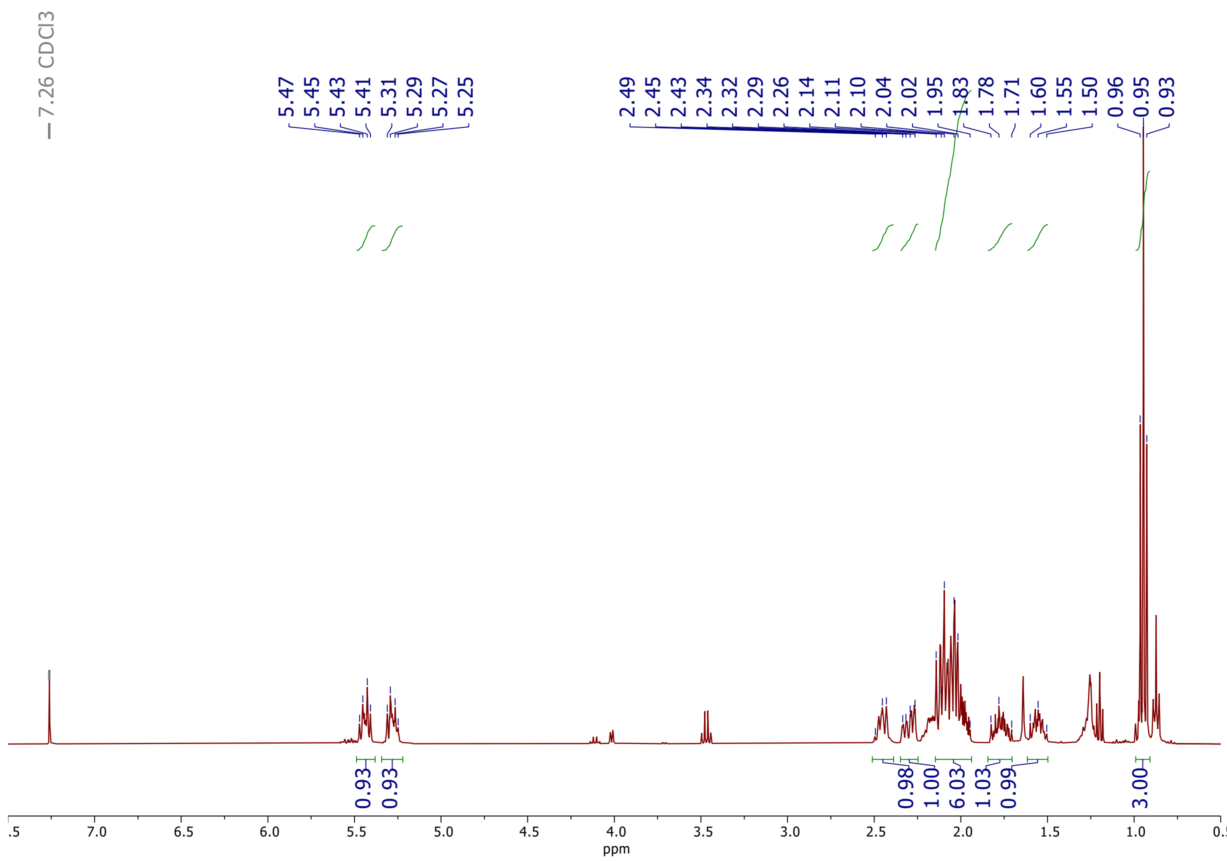

215.1
171.2
135.6
122.9
77.2 CDCl3
61.6
60.3
38.3
32.3
31.1
20.7
19.7
14.2
ppm
135.5
122.8
61.4
38.2
32.2
31.0
20.6
19.6
14.1
ppm

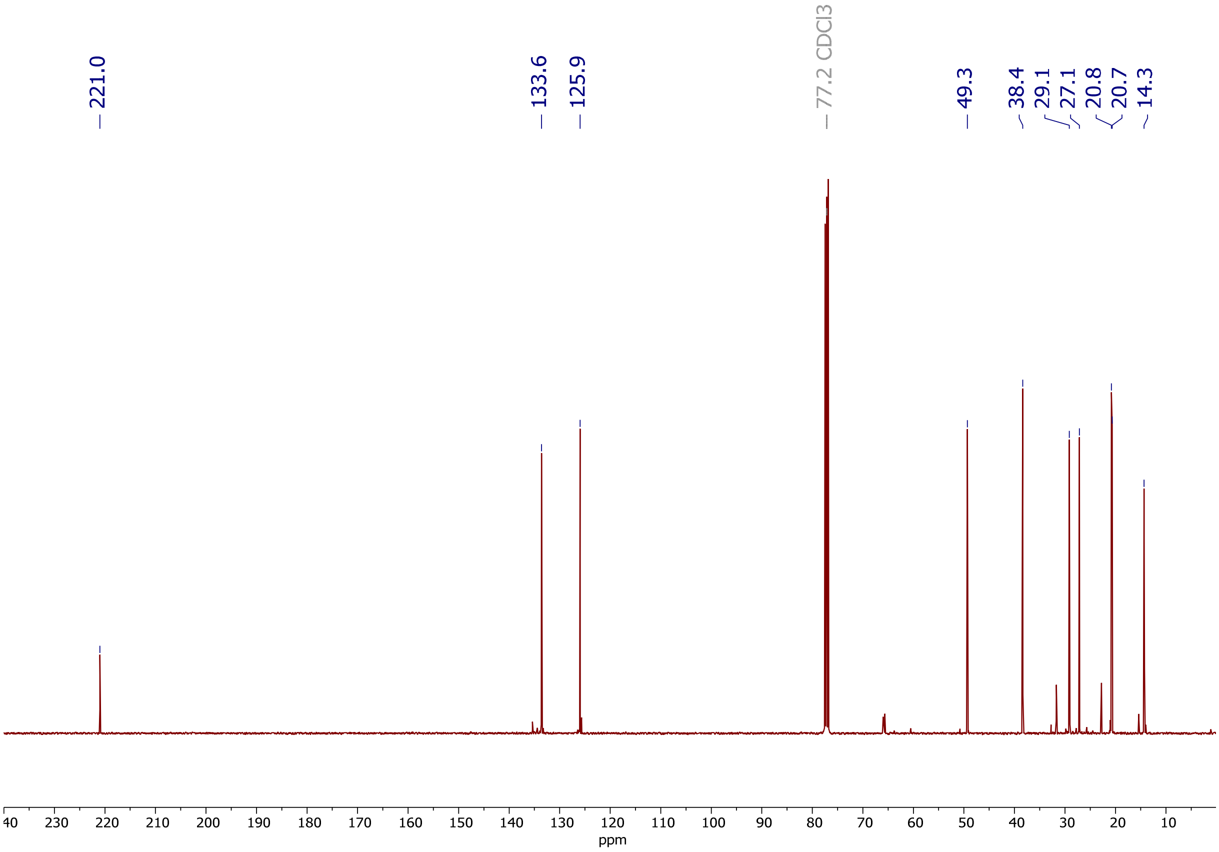


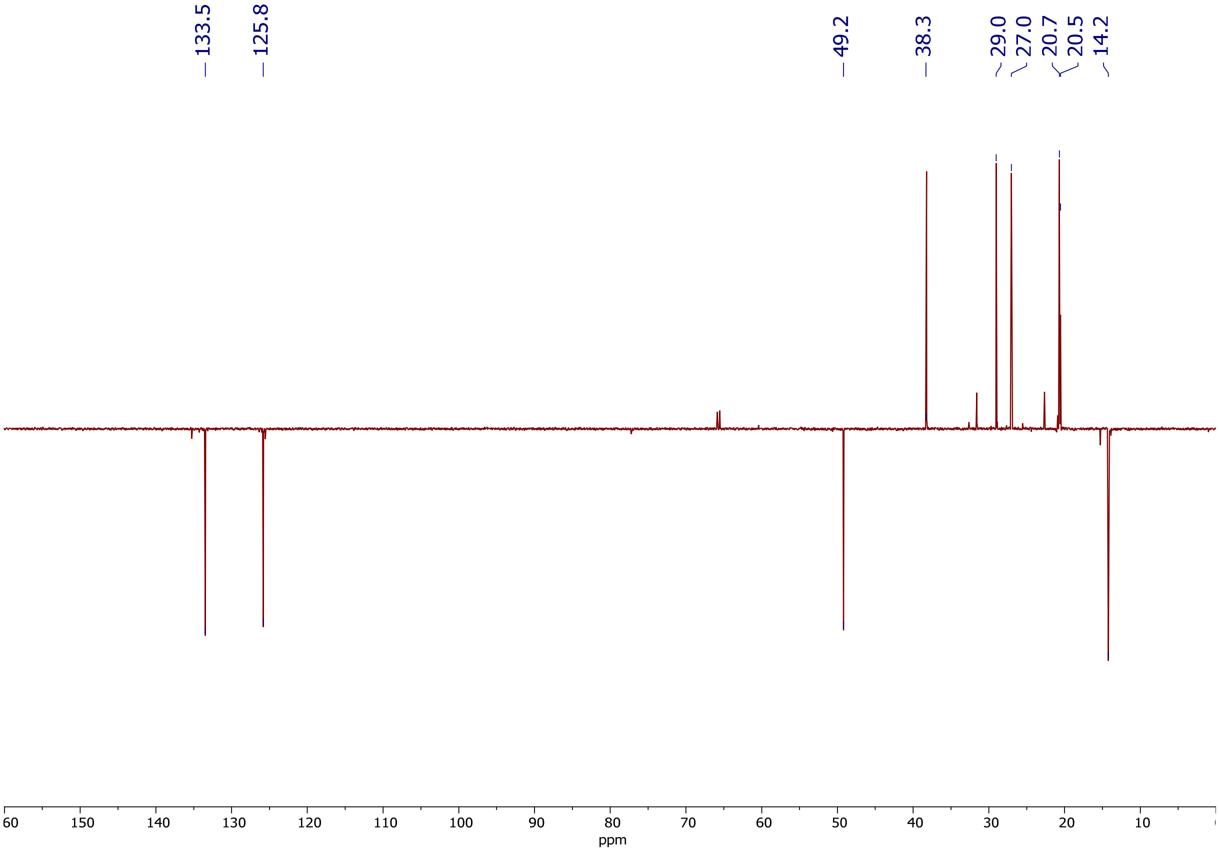
S2

(*Z*)-2-(pent-2-en-1-yl)cyclopentan-1-one **S2**. **GC-MS; m/z, (relative intensity):** 152 (M+•, 23), 123 (29), 105 (9), 95 (22), 84 (100), 67 (32), 41 (36). **^{1}H NMR (401 MHz, CDCl$_3$) δ** 5.47 – 5.41 (m, 1H), 5.31 – 5.25 (m, 1H), 2.49 – 2.43 (m, 1H), 2.30 (ddt, *J* = 18.4, 8.1, 1.6 Hz, 1H), 2.14 – 2.02 (m, 6H), 1.95 (ddd, *J* = 12.5, 6.4, 2.5 Hz, 1H), 1.83 – 1.71 (m, 1H), 1.60 – 1.50 (m, 1H), 0.95 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$) δ** 221.0 (C), 133.6 (CH), 125.9 (CH), 49.3 (CH), 38.4 (CH$_2$), 29.1 (CH$_2$), 27.1 (CH$_2$), 20.8 (CH$_2$), 20.7 (CH$_2$), 14.3 (CH$_3$).





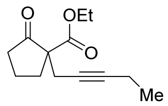

221.0
133.6
125.9
77.2 CDCl3
49.3
38.4
29.1
27.1
20.8
20.7
14.3
ppm


133.5
125.8
49.2
38.3
29.0
27.0
20.7
20.5
14.2
ppm

Computational details

Cartesian coordenates of the optimized structures

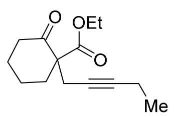
1



C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.526265
C	1.483720	0.000000	1.916370
C	2.168055	-0.799921	0.785106
C	1.421439	-0.396458	-0.509827
C	1.271954	-1.520564	-1.532427
O	1.500564	-1.429781	-2.716867
C	2.025517	0.861883	-1.202584
C	3.444299	0.735304	-1.529238
C	4.626586	0.643069	-1.771524
C	6.044049	0.523817	-2.120161
C	6.274108	0.129876	-3.590912
O	-0.925150	0.292249	-0.721673
O	0.792596	-2.642693	-0.947175
C	0.539057	-3.757674	-1.835757
C	-0.032867	-4.885961	-1.000165
H	1.667624	-0.439623	2.900196
H	1.866281	1.026702	1.944954
H	3.239460	-0.600667	0.706413
H	2.035851	-1.870526	0.961993

H	-0.598378	0.827573	1.915549
H	-0.486477	-0.933057	1.843123
H	-0.152268	-3.430351	-2.617829
H	1.478144	-4.039433	-2.321978
H	-0.240264	-5.750500	-1.638168
H	0.671395	-5.194857	-0.222259
H	-0.967163	-4.581929	-0.519809
H	1.439429	1.052309	-2.106703
H	1.882568	1.729635	-0.545007
H	6.551153	1.475117	-1.910756
H	6.517458	-0.218571	-1.463864
H	7.345190	0.050830	-3.802094
H	5.804966	-0.832344	-3.812951
H	5.843705	0.875856	-4.264528

6



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C	2.395981	-0.987857	0.119999
C	1.013166	-1.054660	-0.544006

O	-1.031389	0.023302	2.187753
C	-1.411198	-0.344926	-0.499736
O	-2.100834	0.372712	-1.190036
C	0.382441	1.424605	-0.521269
C	-0.253405	2.536733	0.182388
C	-0.761797	3.454165	0.784989
C	-1.382249	4.564925	1.508745
C	-0.362875	5.560209	2.092195
O	-1.777665	-1.580752	-0.109268
C	-3.117577	-1.987582	-0.472793
C	-3.356953	-3.356414	0.133141
H	1.209997	-0.108645	3.290625
H	1.821095	0.986594	2.044972
H	3.278990	-1.022682	2.109065
H	1.887144	-2.080201	1.915556
H	3.017774	-1.800100	-0.273752
H	2.909557	-0.055224	-0.146512
H	1.102630	-0.926616	-1.630002
H	0.587884	-2.049327	-0.377947
H	-3.821672	-1.240661	-0.095039
H	-3.199704	-1.998267	-1.564419
H	-4.365020	-3.701575	-0.116744
H	-2.639313	-4.087521	-0.250693
H	-3.264439	-3.319984	1.222010

H	1.470442	1.539945	-0.464451
H	0.113731	1.456715	-1.582807
H	-2.069396	5.094703	0.835959
H	-2.004733	4.159555	2.316945
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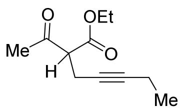
7 

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C	1.340918	3.519211	1.665571
C	0.758208	4.862470	1.697120
C	-0.385668	4.999716	2.719058
O	-1.020469	-0.009281	2.169384
C	1.986247	-1.391588	2.104092
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C	1.912962	-4.134072	4.498085

O	2.575581	-1.795671	1.120915
H	-1.001850	-0.236459	-0.360503
H	0.281676	0.996820	-0.358352
H	0.732989	-0.710761	-0.392868
H	1.162982	0.202214	3.280141
H	1.823408	-4.003803	2.324201
H	3.355451	-3.456497	3.010417
H	2.273454	-5.167169	4.513656
H	2.369150	-3.597716	5.334784
H	0.829493	-4.144393	4.644645
H	3.284248	1.014858	2.246498
H	2.646098	0.747852	0.639742
H	1.546328	5.591640	1.926557
H	0.389724	5.122155	0.696061
H	-0.789632	6.016589	2.703490
H	-1.196420	4.302222	2.492056
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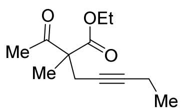
8



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C	-1.676667	1.561947	2.579988
C	-1.749009	2.468093	1.433360
C	-1.814081	3.255783	0.516530
C	-1.885448	4.215474	-0.587629
C	-0.535067	4.882143	-0.907862
C	-2.521361	-0.564603	1.506071
O	-3.603583	-0.051781	1.323905
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C	-3.281212	-2.547751	0.438027
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H	1.011663	0.198294	-0.356462
H	-0.329786	-0.978404	-0.362321
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H	-4.152826	-2.576722	1.098656
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H	-1.887824	-3.885443	-0.541480
H	-2.466813	-4.461932	1.032477
H	-2.115271	-0.560773	4.224359
H	-0.352585	-0.295654	4.159579
H	-1.054814	-1.754863	3.447205
H	-2.633134	1.585205	3.114059

H	-0.904843	1.915333	3.273964
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H	-2.626538	4.987593	-0.342356
H	-0.645554	5.590366	-1.734838
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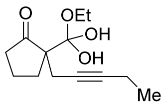
1-hydrated 

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C	1.181275	0.894786	-0.348399
C	3.510790	0.115771	0.330290
O	3.141062	-1.080416	-0.305624
C	2.506405	2.298899	1.246346
C	3.479970	2.438545	2.332802
C	4.282016	2.555298	3.235324
C	5.221428	2.755120	4.343311
C	4.757569	3.840225	5.332731
O	1.275950	1.612763	-1.317591
O	4.161802	0.998031	-0.535641

C	5.277935	0.470636	-1.261298
C	5.892866	1.614793	-2.047702
O	4.345945	-0.274634	1.395111
H	-0.533540	-0.851292	1.966741
H	-0.489640	0.909262	1.905334
H	1.686431	0.395191	2.911547
H	1.882322	-1.023305	1.887871
H	-0.917204	0.349971	-0.478703
H	0.229380	-1.003620	-0.382622
H	4.932218	-0.324603	-1.932456
H	6.005238	0.037132	-0.562174
H	6.742392	1.255581	-2.637326
H	6.245750	2.402622	-1.375775
H	5.155579	2.049619	-2.728114
H	4.572692	0.531047	1.892170
H	3.774157	-1.751503	-0.013839
H	2.844684	2.843389	0.360667
H	1.561169	2.759806	1.561985
H	5.360544	1.806954	4.878866
H	6.206930	3.022887	3.940645
H	5.488028	3.955869	6.139112
H	4.645559	4.804003	4.828670
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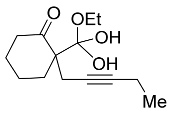
6-hydrated 

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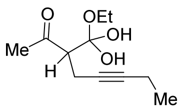
C	2.380052	1.031253	1.413831
C	2.357988	0.929333	-0.121576
C	0.923495	1.043496	-0.644380
C	-0.810129	-1.252754	2.043825
O	-0.104154	-2.402062	1.683110
C	-0.723162	1.291922	2.080618
C	-0.397958	1.715688	3.442893
C	-0.093168	2.118993	4.543002
C	0.246983	2.590256	5.887501
C	-0.755711	2.138382	6.964889
O	1.883504	-0.763557	2.904421
O	-1.189232	-1.230117	3.402953
C	-0.342401	-1.773053	4.433223
C	-1.251393	-2.330475	5.516930
O	-2.057306	-1.248774	1.373361
H	0.296402	-0.976371	4.822904
H	0.302586	-2.543704	4.008545
H	-0.650868	-2.713372	6.348861

H	-1.868870	-3.149230	5.133560
H	-1.917623	-1.553651	5.905140
H	-2.709906	-1.335069	2.084110
H	-0.775440	-3.084697	1.538893
H	-0.494856	2.119594	1.400114
H	-1.798925	1.110063	1.983262
H	1.251677	2.233856	6.150162
H	0.308922	3.686787	5.883105
H	-0.459054	2.519541	7.947096
H	-1.760414	2.507943	6.741323
H	-0.802703	1.047123	7.018977
H	3.381007	0.876057	1.824147
H	2.044265	2.031318	1.720790
H	2.996711	1.706090	-0.557015
H	2.784312	-0.036027	-0.424369
H	0.902501	0.908427	-1.732161
H	0.549602	2.059445	-0.460029
H	-1.029297	0.136403	-0.343464
H	0.309357	-0.998624	-0.326360

7-hydrated 

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C	1.329316	-2.376469	2.975539
C	1.275376	-3.529454	2.611188
C	1.185635	-4.932760	2.201057
C	-0.008122	-5.673097	2.831809
O	-1.032030	-0.025358	2.156939
C	1.848589	1.416560	2.631619
O	1.554937	2.283030	1.568407
O	1.337264	1.878607	3.861153
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H	2.124461	-0.316023	1.467697
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H	-0.247349	2.946197	3.043770
H	-0.707321	1.498453	3.952237
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H	3.372561	1.748398	3.726229
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H	1.112675	-4.988041	1.106706
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H	-0.032578	-6.714864	2.496877
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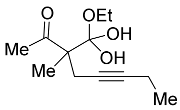
8-hydrated 

C	0.000000	0.000000	0.000000
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C	-2.195190	1.214868	1.671833
C	-3.556519	1.378394	2.190902
C	-4.688372	1.540156	2.594612
C	-6.058398	1.721825	3.082870
C	-6.254337	1.255719	4.537630
C	-2.095947	-1.327041	1.981031
C	-1.178768	0.176044	3.797160
O	-0.377008	-0.852424	4.296868

O	-2.391882	0.052098	4.514776
O	-0.621997	1.448784	3.980520
C	-0.075629	1.717011	5.276179
C	0.333774	3.179160	5.306856
H	0.953765	-0.406358	-0.339875
H	-0.824237	-0.563063	-0.443844
H	-0.071964	1.032958	-0.361052
H	-2.265863	1.092451	0.585465
H	-1.630091	2.134452	1.857009
H	-0.827625	1.505520	6.048375
H	0.785517	1.062250	5.446732
H	0.777035	3.428170	6.276364
H	1.071715	3.385803	4.526491
H	-0.530072	3.830868	5.144293
H	-0.843099	-1.184213	5.077511
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H	-6.333644	2.780895	2.996256
H	-6.747508	1.174657	2.426676
H	-7.294503	1.397973	4.845288
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H	-5.616152	1.824743	5.219967
H	-1.488429	-2.161249	2.338744
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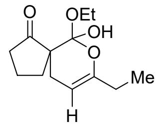
1-hydroalkoxylated 

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O	0.804751	1.047422	-0.551891
C	-0.749612	1.228976	2.099064
C	-1.490493	0.827980	3.378838
C	-1.211247	-0.673772	3.562711
C	-0.812790	-1.163709	2.151460
O	-0.807161	2.325128	1.579952
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O	0.457537	-1.248408	-0.390241
C	0.490341	-1.506494	-1.806394
C	1.079693	-2.892338	-1.996738
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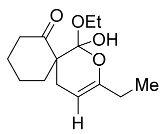
H	-2.072507	-1.217896	3.959650
H	-0.385389	-0.827283	4.265527
H	-0.249082	-2.098973	2.163832

H	-1.708804	-1.324003	1.542339
H	-2.554097	1.033658	3.207297
H	-1.183530	1.461343	4.217174
H	-0.524918	-1.444458	-2.210583
H	1.100869	-0.743761	-2.302238
H	1.122212	-3.139570	-3.062218
H	2.093520	-2.943699	-1.589101
H	0.468463	-3.646250	-1.492084
H	1.845479	-1.027340	1.972473
H	1.491160	0.245724	3.127468
H	3.257957	1.288880	1.723732
H	-1.418838	1.176127	-0.478637
H	2.917094	1.922862	-1.745606
H	2.040379	3.231452	-0.990752
H	4.497007	3.638143	-0.870137
H	3.852104	3.450361	0.765486
H	4.742088	2.121859	0.004647

6-hydroalkoxylated 

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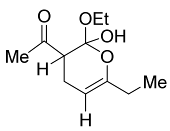
C	2.440466	-0.963177	1.383865
C	2.378548	-0.854641	-0.153362
C	0.941400	-1.016310	-0.661210
C	-0.772159	-1.220464	2.141608
O	-0.786559	-1.191599	3.568123
C	-1.149607	0.007289	4.178032
C	-1.144512	1.159880	3.507955
C	-0.726891	1.265876	2.069933
O	-2.067651	-1.143120	1.628281
C	-2.962116	-2.209615	1.973014
C	-4.316718	-1.881909	1.370765
O	-0.169381	-2.448501	1.836817
C	-1.472317	-0.193333	5.628854
C	-0.273088	-0.695890	6.450612
O	1.856004	0.793756	2.892366
H	3.439900	-0.744175	1.769121
H	2.163846	-1.981022	1.677663
H	3.037502	-1.607255	-0.601036
H	2.768754	0.125263	-0.460727
H	0.910605	-0.873674	-1.748208
H	0.590949	-2.033482	-0.461557
H	-1.028854	-0.146250	-0.339702
H	0.296963	1.010119	-0.315134
H	-2.573123	-3.154886	1.576153

H	-3.030235	-2.297691	3.064365
H	-5.034584	-2.674569	1.604027
H	-4.699401	-0.938576	1.770179
H	-4.244435	-1.790615	0.283218
H	-0.184622	-2.969339	2.653001
H	-1.603434	1.448998	1.434788
H	-0.054666	2.121456	1.947691
H	-1.437283	2.063287	4.032768
H	-1.830415	0.758734	6.033157
H	-2.299115	-0.911365	5.719468
H	-0.550425	-0.824510	7.501551
H	0.083500	-1.658232	6.073225
H	0.557345	0.014203	6.396604

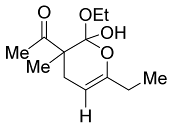
7-hydroalkoxylated



C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.341051
O	1.166419	0.000000	2.078601
C	2.367015	-0.397211	1.393268
C	2.483278	0.389763	0.062614
C	1.262293	0.065985	-0.814916
C	-1.210959	-0.000171	2.229873

C	-1.343531	-1.276751	3.076095
O	3.431476	-0.068780	2.198824
C	3.480984	-0.698170	3.497567
C	4.804417	-0.313802	4.132676
O	2.358020	-1.783210	1.197756
C	3.796846	0.065106	-0.670430
C	5.002505	0.913642	-0.332325
O	3.842890	-0.822749	-1.500467
H	2.480884	1.446742	0.349126
H	4.813688	1.955411	-0.620186
H	5.171543	0.903188	0.747751
H	5.878825	0.542307	-0.865324
H	2.635695	-0.346093	4.098096
H	3.394596	-1.781559	3.376989
H	4.882388	-0.756609	5.130566
H	5.643752	-0.673131	3.530267
H	4.888948	0.772487	4.231098
H	1.459904	-0.870822	-1.352454
H	1.167655	0.831549	-1.594737
H	-0.954438	-0.020509	-0.515924
H	1.552389	-2.018600	0.716214
H	-1.144620	0.868925	2.897880
H	-2.100913	0.141865	1.608846
H	-2.208616	-1.212458	3.742980

H	-1.472008	-2.157313	2.438177
H	-0.450174	-1.429612	3.686898

8-hydroalkoxylated 

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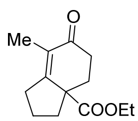
C	2.193682	1.112815	1.442600
C	2.362348	0.813859	-0.066942
C	1.080824	0.356029	-0.706958
C	3.600965	1.104971	2.106610
O	4.594254	0.949485	1.420006
C	1.542961	2.499135	1.648572
O	1.045248	0.240551	3.368758
C	0.175042	-0.685385	4.053974
C	0.198988	-0.320478	5.526880
O	1.871570	-1.269896	1.907959
C	-1.328111	-0.433580	-0.551429
C	-1.674559	-1.894896	-0.222677
C	3.738619	1.337235	3.598069
H	3.096949	2.144773	3.957009
H	3.428775	0.433099	4.129219

H	4.785122	1.552830	3.818908
H	-0.835456	-0.598877	3.641948
H	0.531023	-1.706289	3.888118
H	-0.470170	-0.982289	6.085639
H	1.206601	-0.422436	5.940193
H	-0.132642	0.710939	5.678059
H	3.165386	0.080003	-0.204276
H	2.730873	1.718497	-0.563987
H	1.024538	0.318989	-1.790198
H	1.869688	-1.509136	0.969981
H	-2.103969	0.222422	-0.134826
H	-1.324523	-0.275938	-1.634484
H	-2.668793	-2.152769	-0.599818
H	-0.951652	-2.580041	-0.677579
H	-1.664438	-2.061312	0.857600
H	2.234028	3.291116	1.342034
H	0.641529	2.584213	1.036620
H	1.260843	2.660241	2.689987

3

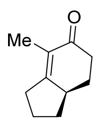


C	-0.016803	0.197229	0.242482

C	0.267278	0.052355	1.554257
C	1.631051	-0.369291	2.086490
C	2.364896	-1.245941	1.062119
C	2.404157	-0.543348	-0.299541
C	1.040237	-0.050333	-0.778413
C	-0.728421	0.147113	2.691553
C	0.037800	-0.310718	3.956810
C	1.255366	-1.087027	3.417680
C	2.525132	0.837881	2.434627
O	1.813435	1.927996	2.791380
C	2.586773	3.092115	3.178923
C	1.606919	4.192592	3.534831
O	0.832578	0.132049	-1.971316
C	-1.387811	0.575363	-0.260136
O	3.737701	0.810191	2.430362
H	0.370492	0.559811	4.528230
H	-0.578568	-0.921944	4.622016
H	0.971908	-2.118152	3.174159
H	2.091959	-1.135798	4.121105
H	-1.585398	-0.506086	2.479836
H	-1.134686	1.160127	2.792539
H	3.377413	-1.465938	1.410053
H	1.823533	-2.194969	0.975222
H	2.810390	-1.188243	-1.083742

H	3.069273	0.329444	-0.245413
H	-1.350938	0.727449	-1.339777
H	-2.123733	-0.210478	-0.048208
H	-1.750906	1.493476	0.214451
H	2.153920	5.093608	3.828830
H	0.970098	4.440667	2.681166
H	0.965868	3.893740	4.369231
H	3.230584	2.821538	4.021289
H	3.236507	3.371817	2.344476

4



C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.337000
C	1.277766	0.000000	2.116951
C	2.248768	-0.998349	1.500525
C	2.442171	-0.673690	0.025153
C	1.197275	0.000009	-0.625911
C	-1.186012	0.012781	2.250359
C	-0.640650	-0.517419	3.569827
C	0.864485	-0.482270	3.501201
O	1.304175	0.530078	-1.706125
C	-1.280479	0.000000	-0.775486

H	-0.994864	0.122690	4.408613
H	-0.995043	-1.558045	3.743816
H	1.271260	-1.502913	3.678936
H	1.264220	0.206720	4.278552
H	1.776495	0.994857	2.134200
H	-1.991657	-0.649228	1.861196
H	-1.639448	1.024363	2.349688
H	3.228208	-0.935155	2.025381
H	1.837897	-2.027615	1.603311
H	2.656267	-1.620473	-0.519399
H	3.284052	0.050887	-0.045518
H	-1.054777	0.000000	-1.865361
H	-1.868910	-0.909255	-0.519017
H	-1.869485	0.908812	-0.518774

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