Transition Metal-free [2,3]-sigmatropic rearrangement in the reaction of sulfur ylides with allenoates

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SUPPORTING INFORMATION

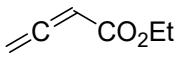
Contents

General Techniques. All reactions were carried out under non special conditions, opened flask and did not require anhydrous conditions, unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials, unless otherwise stated. All solutions used in workup procedures were saturated unless otherwise noted. All reagents were purchased at sigma-aldrich at ACS Reagent quality. *Tert*-butanol was purchased at sigma-aldrich (ACS Reagent ≥ 99%) and did not require further distillation. Allenoates were freshly prepared according to reported procedures in literature. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (60F-254) using UV light as visualizing agent and potassium permanganate solution and heat as developing agents. Silica gel (60, particle size 0.040-0.063 mm) was used for flash column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on 0.25, 0.50 or 1 mm silica gel plates (60F-254). Many products were purified using a Biotage® equipment (Isolera prime) and commercial silica-gel cartridge SFAR-DUO 10g (60 μM particle size). Many products were purified using flash column chromatography, using silica gel 60 (0.040-0.063 mm), 230-400 mesh ASTM.

NMR spectra were recorded on a Bruker 500 MHz or 400 MHz instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; band, several overlapping signals; b, broad. ^{1}H-NMR assignments were undertaken based on bidimentional NMR experiments of COSY, HSQC, HMBC and NOESY experiments. High resolution mass spectra (HRMS) were recorded on a mass spectrometer under fast atom bombardment (FAB) conditions. For crystal-structure determination, all measurements were made on a Rigaku Oxford Diffraction SuperNova area-detector diffractometer using Cu *Kα* radiation (λ = 1.54184 Å) from a micro-focus X-ray source and an Oxford Instruments Cryojet XL cooler.

List of Synthesized Allenoates:

Freshly prepared allenoates were synthesized following procedures described in literature.[1]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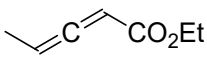
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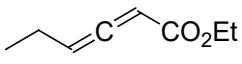
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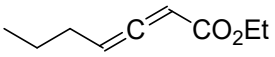
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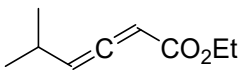
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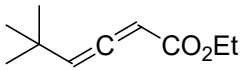
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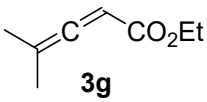
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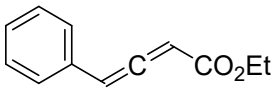
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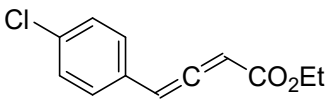
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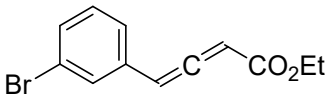
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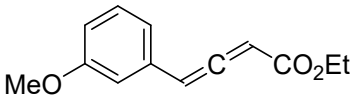
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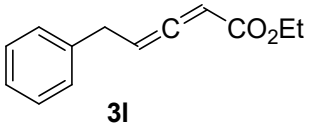
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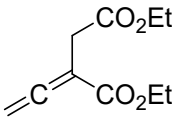
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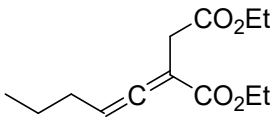
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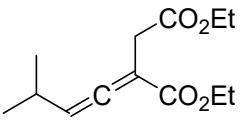
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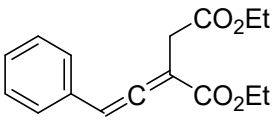
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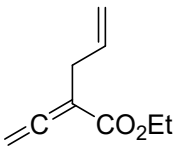
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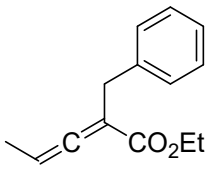
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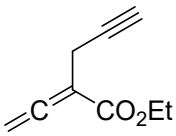
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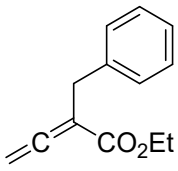
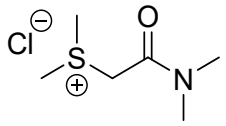

5h

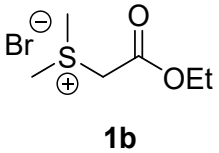
Syntheses of Stabilized Sulfonium Salts: Sulfonium salts were prepared using reported procedures,[2] consisting typically in mixing the corresponding sulfide (excess) to dimethylchloroacetamide and allowing to crystallize over a period of several days at room

[1] a) Z. Huang, X. Yang, F. Yang, T. Lu, Q. Zhou. *Org. Lett.* **2017**, *19*, 3524-3527; b) M. G. Sankar, M. Garcia-Castro, C. Golz, C. Strohmann, K. Kumar. *Angew. Chem. Int. Ed.* **2016**, *55*, 1-6.
[2] M. Valpuesta-Fernandez, P. Durate-Lanes, F. J. Lopez-Herrera. *Tetrahedron* **1990**, *46*, 7911-7922

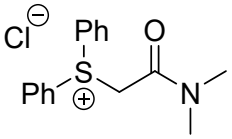
temperature. Finally, white crystals were filtered and dried at high vacuum. With exception of sulfonium salt **1c**, which reaction required previous work-up using extraction with water and ulterior lyophilization process.



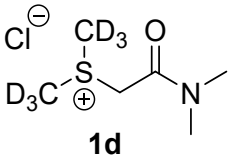
1a



1b

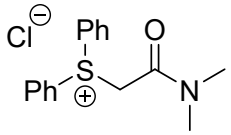


1c



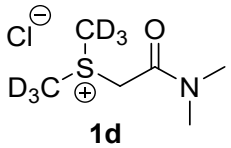
1d

Spectroscopic data of new sulfonium salts 1.



1c

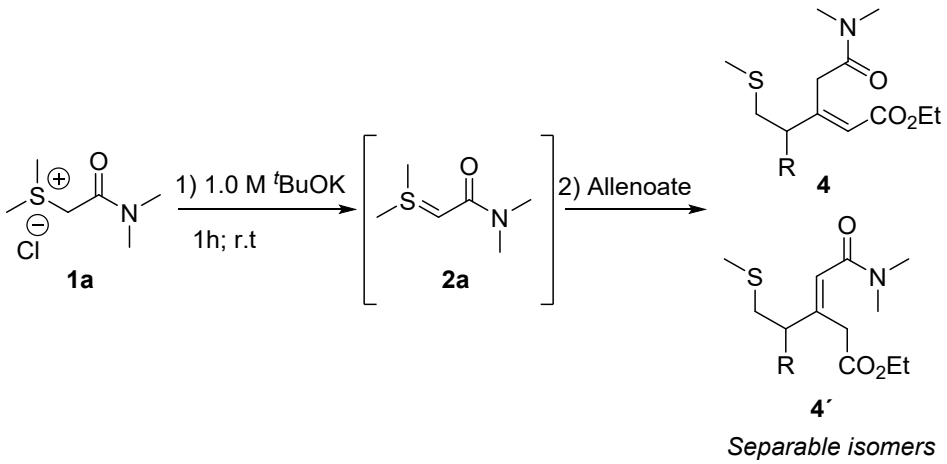
Colorless liquid. $C_{16}H_{18}ClNOS$; Elemental Analysis: 63.296 %C, 5.511 %H, 2.532 %N, 13.775 %S, 10.024 %O; 4.862 %Cl; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 2.93 (s, 3H, NC*H*$_3$), 3.03 (s, 3H, NC*H*$_3$), 4.02 (s, 2H, -SC*H*$_2$), 7.18 (m, 4H, Ph), 7.23 (m, 4H, Ph), 7.27 (m, 2H, Ph); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 36.0 (N*C*H$_3$), 37.7 (N*C*H$_3$), 41.0 (S*C*H$_2$), 127.0 (Ph), 129.2 (Ph), 131.0 (Ph), 135.8 (Ph), 166.8 (*C*=O).



1d

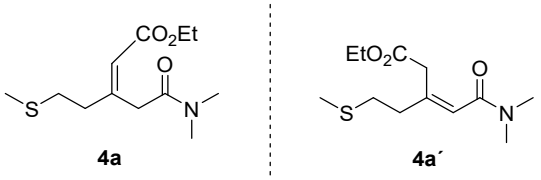
Hygroscopic white solid. $C_6H_8D_6ClNOS$; Elemental Analysis: 36.583 %C, 8.757 %H, 6.967 %N, 13.370 %S, 17.009 %O; 17.314 %Cl; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 2.90 (s, 3H, NC*H*$_3$), 3.10 (s, 3H, NC*H*$_3$), 5.57 (s, 2H, -SC*H*$_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 35.7 (N*C*H$_3$), 37.9 (N*C*H$_3$), 41.2 (S*C*H$_2$), 48.9 (S*C*D$_3$), 163.4 (*C*=O).

General Procedure for syntheses of compounds 4.



Sulfonium salt **1a** (scale of 100-400 mg, 1.0 equiv.) was solved in *tert*-butanol (10 – 40 mL, respectively). Then, a 1.0 molar solution of potassium *tert*-butoxide (1.0 equiv.) in ^{t}BuOH was added. Reaction was stirred at room temperature for 1 hour. Then, allenoate **3** (1.0 equiv.) was added and reaction was stirred between 1 hour (for most compounds) and 12 hours. Reactions were monitored by TLC. To work-up, a saturated solution of ammonium chloride was added and ethyl acetate was added for extraction (three times). Organic layers were sequentially washed with distilled water and a saturated solution of sodium chloride and then dried over anhydrous magnesium sulfate, filtered and evaporated in rotavapor to afford slightly yellow oils. Purification was done by flash column chromatography or using Isolera Prime Biotage® equipment using different gradient of ethyl acetate and hexanes.

Compounds 4a/4a´:

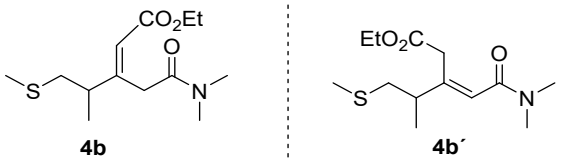


Following the general procedure with: Sulfonium salt **1a** (204 mg, 1.11 mmol, 1.0 eq.), allenoate **3a** (125 mg, 1.11 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.11 mL, 1.11 mmol, 1.0 eq.) in 18 mL of ^{t}BuOH, affording, after purification through Isolera Biotage® flash chromatography, 70 mg of compound **4a** as a colorless oil and 130 mg of compound **4a´** as a colorless oil. Overall yield: **69%**.

Compound **4a**: R_f = 0.22 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 260.13107; $[M + H]^+$ calculated for $C_{12}H_{22}NO_3S$ 260.13204; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.26 (t, *J* = 7.17 Hz, 3H, -OCH$_2$C*H$_3$*), 2.12 (s, 3H, SC*H$_3$*), 2.54-2.61 (m, 2H, C*H$_2$*C=CH), 2.63-2.72 (m, 2H, SC*H$_2$*), 2.95 (s, 3H, NC*H$_3$*), 3.06 (s, 3H, NC*H$_3$*), 3.83 (s, 2H, C*H$_2$*CONMe$_2$), 4.13 (q, *J* = 7.17 Hz, 2H, -OC*H$_2$*CH$_3$), 5.87 (s, 1H, =C*H*CO$_2$Et); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (*C*H$_3$CH$_2$O-), 15.6 (S*C*H$_3$), 31.9 (S*C*H$_2$), 35.6 (*C*H$_2$C=CH), 36.5 (N*C*H$_3$), 37.4 (N*C*H$_3$), 38.3 (*C*H$_2$C=CH), 59.9 (-O*C*H$_2$CH$_3$), 118.6 (=*C*HCO$_2$Et), 155.0 (*C*=CHCO$_2$Et), 166.2 (*C*=O), 169.6 (*C*=O).

Compound **4a´**: R_f = 0.14 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 260.134434; $[M + H]^+$ calculated for $C_{12}H_{22}NO_3S$ 260.13204; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.25 (t, *J* = 7.17 Hz, 3H, -OCH$_2$C*H$_3$*), 2.11 (s, 3H, SC*H$_3$*), 2.49 (m, 2H, C*H$_2$*C=CH), 2.62-2.70 (m, 2H, SC*H$_2$*), 2.96 (s, 3H, NC*H$_3$*), 3.03 (s, 3H, NC*H$_3$*), 3.49 (s, 2H, C=C*H$_2$*CO$_2$Et), 4.13 (q, *J* = 7.17 Hz, 2H, -OC*H$_2$*CH$_3$), 6.08 (s, 1H, =C*H*CONMe$_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.3 (*C*H$_3$CH$_2$O-), 15.4 (S*C*H$_3$), 31.8 (S*C*H$_2$), 32.5 (*C*H$_2$C=CH), 35.6 (N*C*H$_3$), 37.8 (N*C*H$_3$), 43.7 (*C*H$_2$C=CH), 59.9 (-O*C*H$_2$CH$_3$), 119.4 (=*C*HCONMe$_2$), 154.6 (*C*=CHCONMe$_2$), 165.7 (C=O), 169.1 (C=O).

Compounds 4b/4b´:



4b **4b´**

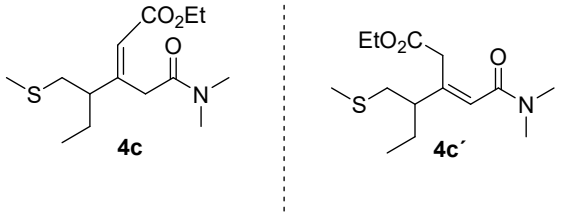
Following the general procedure with: Sulfonium salt **1a** (103 mg, 0.56 mmol, 1.0 eq.), allenoate **3b** (71 mg, 0.56 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.56 mL, 0.56 mmol, 1.0 eq.) in 10 mL of ^{t}BuOH, affording, after purification through flash column chromatography using a gradient of eluent (20% to 50% of AcOEt in hexanes), 47 mg of compound **4b** as a colorless oil and 55 mg of compound **4b´** as a colorless oil. Overall yield: **68%**.

Compound **4b**: R_f = 0.17 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 274.14714; $[M + H]^+$ calculated for $C_{13}H_{24}NO_3S$ 274.14769; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.15 (d, *J* = 6.81 Hz, 3H, C*H$_3$*CH), 1.19 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 2.03 (s, 3H, SC*H$_3$*), 2.41 (dd, J_1 = 12.80 Hz; J_2 = 8.17 Hz; 1H, SC*H$_2$*), 2.54 (tq, J_1 = 8.17 Hz; J_2 = 6.81 Hz, 1H, CH$_3$C*H*CH$_2$S), 2.67 (dd, J_1 = 12.80 Hz; J_2 = 5.62 Hz; 1H, SC*H$_2$*), 2.88 (s, 3H, NC*H$_3$*), 3.00 (s, 3H, NC*H$_3$*), 3.68 (d, *J* = 15.33 Hz, 1H, C=C*H$_2$*CO$_2$Et), 3.78 (d, *J* = 15.33 Hz, 1H, C=C*H$_2$*CONMe$_2$), 4.05 (q, *J* = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 5.80 (s, 1H, =C*H*CO$_2$Et);

^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (*C*H_3CH_2O-), 16.1 (S*C*H_3), 18.7 (*C*H_3CH), 35.5 (*C*H_2C=CH), 36.4 (*C*HCH_3), 37.4 (S*C*H_2), 40.2 (N*C*H_3), 41.3 (N*C*H_3), 59.8 (-O*C*H_2CH_3), 117.4 (=*C*HCO_2Et), 160.3 (*C*=$CHCO_2Et$), 166.5 (*C*=O), 169.7 (*C*=O).

Compound **4b´**: R_f = 0.11 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 274.14706; $[M + H]^+$ calculated for $C_{13}H_{24}NO_3S$ 274.14769; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.13 (d, *J* = 6.63 Hz, 3H, C*H*$_3$CH), 1.18 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H*$_3$), 2.03 (s, 3H, SC*H*$_3$), 2.40-2.49 (m, 2H, CH$_3$CHC*H*$_2$S), 2.62 (dd, J_1 = 11.68 Hz; J_2 = 4.91 Hz, 1H, CH$_3$C*H*CH$_2$S), 2.89 (s, 3H, NC*H*$_3$), 2.94 (d, *J* = 10.51 Hz, 1H), 2.99 (s, 3H, NC*H*$_3$), 3.41 (d, *J* = 2.15 Hz, 2H, C*H*$_2$CONMe$_2$), 4.06 (q, *J* = 7.15 Hz, 2H, -OC*H*$_2$CH$_3$), 6.01 (s, 1H, =C*H*CONMe$_2$); ^{13}C-NMR (125 MHz): 14.2 (*C*H_3CH_2O-), 16.3 (S*C*H_3), 18.6 (*C*H_3CH), 34.9 (*C*H_2C=CH), 36.0 (*C*HCH_3), 37.7 (S*C*H_2), 40.1 (N*C*H_3), 41.1 (N*C*H_3), 60.7 (-O*C*H_2CH_3), 121.1 (=*C*$HCONMe_2$), 147.9 (*C*=$CHCONMe_2$), 167.7 (*C*=O), 170.9 (*C*=O).

Compounds 4c/4c´:

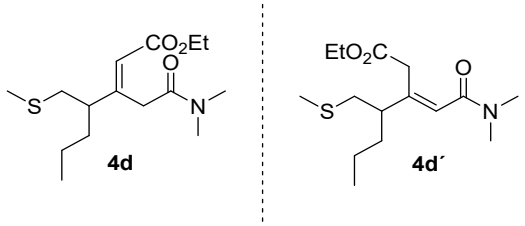


Following the general procedure with: Sulfonium salt **1a** (154 mg, 0.84 mmol, 1.0 eq), allenoate **3c** (118 mg, 0.84 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.84 mL, 0.84 mmol, 1.0 eq.) in 10 mL of ^{t}BuOH, affording, after purification through flash column chromatography, 76 mg of compound **4c** as a colorless oil and 80 mg of compound **4c´** as a colorless oil. Overall yield: **65%**.

Compound **4c**: R_f = 0.35 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 288.16272; $[M + H]^+$ calculated for $C_{14}H_{26}NO_3S$ 288.16334; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.84 (t, *J* = 7.39 Hz, 3H, C*H*$_3$CH$_2$), 1.20 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H*$_3$), 1.49 (sept, *J* = 7.34 Hz, 1H, CH$_3$C*H*$_2$CH), 1.64 (dq, J_1 = 7.40 Hz, J_2 = 1.82 Hz, 1H, CH$_3$C*H*$_2$CH), 2.03 (s, 3H, SC*H*$_3$), 2.36 (q, *J* = 6.89 Hz, 1H, CH$_3$CH$_2$C*H*), 2.49 (dd, J_1 = 13.04 Hz; J_2 = 7.42 Hz; 1H, SC*H*$_2$), 2.63 (dd, J_1 = 13.03 Hz; J_2 = 6.61 Hz; 1H, SC*H*$_2$), 2.88 (s, 3H, NC*H*$_3$), 3.00 (s, 3H, NC*H*$_3$), 3.66 (d, *J* = 15.20 Hz, 1H, C=C*H*$_2$CONMe$_2$), 3.73 (d, *J* = 15.20 Hz, 1H, C=C*H*$_2$CONMe$_2$), 4.06 (q, *J* = 7.14 Hz, 2H, -OC*H*$_2$CH$_3$), 5.77 (s, 1H, =C*H*CO_2Et); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 11.5 (*C*H_3CH_2), 14.2 (-OCH$_2$*C*H$_3$) , 16.1 (S*C*H_3), 25.6 (CH$_3$*C*H$_2$CH), 35.6 (N*C*H_3), 36.6 (*C*H_2C=CH), 37.4 (N*C*H_3), 38.3 (S*C*H_2), 48.4 (CH$_3$CH$_2$*C*H), 59.8 (-O*C*H_2CH_3), 118.4 (=*C*HCO_2Et), 158.5 (*C*=$CHCO_2Et$), 166.3 (C=O), 169.7 (C=O).

Compound **4c´**: R_f = 0.21 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 288.16132; $[M + H]^+$ calculated for $C_{14}H_{26}NO_3S$ 288.16334; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.83 (t, *J* = 7.39 Hz, 3H, C*H*$_3$CH$_2$), 1.18 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H*$_3$), 1.42 (dq, J_1 = 6.72 Hz, J_2 = 1.26 Hz, 1H, CH$_3$C*H*$_2$CH), 1.59 (dq, J_1 = 7.41 Hz, J_2 = 2.14 Hz, 1H, CH$_3$C*H*$_2$CH), 2.02 (s, 3H, SC*H*$_3$), 2.18-2.24 (m, 1H, CH$_3$CH$_2$C*H*), 2.48 (dd, J_1 = 13.01 Hz; J_2 = 6.86 Hz; 1H, SC*H*$_2$), 2.56 (dd, J_1 = 12.98 Hz; J_2 = 7.12 Hz; 1H, SC*H*$_2$), 2.89 (s, 3H, NC*H*$_3$), 3.00 (s, 3H, NC*H*$_3$), 3.38 (d, *J* = 2.68 Hz, 2H, C=C*H*$_2$CO$_2$Et), 4.04 (q, *J* = 7.14 Hz, 2H, -OC*H*$_2$CH$_3$), 6.00 (s, 1H, =C*H*CONMe$_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 11.7 (*C*H$_3$CH$_2$), 14.1 (-OCH$_2$*C*H$_3$), 16.2 (S*C*H$_3$), 25.2 (CH$_3$*C*H$_2$CH), 34.8 (N*C*H$_3$), 35.6 (*C*H$_2$C=CH), 37.6 (N*C*H$_3$), 38.1 (S*C*H$_2$), 49.0 (CH$_3$CH$_2$*C*H), 60.6 (-O*C*H$_2$CH$_3$), 122.4 (=*C*HCONMe$_2$), 146.0 (*C*=CHCONMe$_2$), 167.5 (C=O), 170.7 (C=O).

Compounds 4d/4d´:

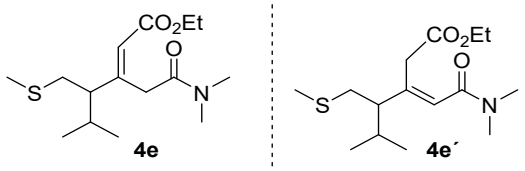


Following the general procedure with: Sulfonium salt **1a** (152 mg, 0.83 mmol, 1.0 eq), allenoate **3d** (128 mg, 0.83 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.91 mL, 0.91 mmol, 1.0 eq.) in 12 mL of ^{t}BuOH, affording after purification through flash column chromatography, 95 mg of compound **4d** as a colorless oil and 66 mg of compound **4d´** as a colorless oil. Overall yield: **67%**.

Compound **4d**: R_f = 0.45 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 302.17822; $[M + H]^+$ calculated for $C_{15}H_{28}NO_3S$ 302.17899; ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 0.86 (t, *J* = 7.30 Hz, 3H, C*H*$_3$CH$_2$CH$_2$), 1.22 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H*$_3$), 1.24-1.32 (m, 2H, CH$_3$C*H*$_2$CH$_2$), 1.40-1.48 (m, 1H, CH$_3$CH$_2$C*H*$_2$CH), 1.50-1.58 (m, 1H, CH$_3$CH$_2$C*H*$_2$CH), 2.05 (s, 3H, SC*H*$_3$), 2.38-2.52 (m, 1H, CH$_3$CH$_2$CH$_2$C*H*), 2.50 (dd, J_1 = 11.98 Hz; J_2 = 7.30 Hz; 1H, SC*H*$_2$), 2.67 (dd, J_1 = 11.68 Hz; J_2 = 5.40 Hz; 1H, SC*H*$_2$), 2.89 (s, 3H, NC*H*$_3$), 3.02 (s, 3H, NC*H*$_3$), 3.72 (s, 2H, C*H*$_2$CONMe$_2$), 4.08 (q, *J* = 7.14 Hz, 2H, -OC*H*$_2$CH$_3$), 5.81 (s, 1H, =C*H*CO$_2$Et); ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 14.1 (*C*H$_3$CH$_2$), 14.2 (-OCH$_2$*C*H$_3$), 16.1 (S*C*H$_3$), 20.3 (CH$_3$*C*H$_2$), 35.1 (*C*H$_2$CH), 35.6 (N*C*H$_3$), 36.5 (*C*H$_2$C=CH), 37.4 (N*C*H$_3$), 38.7 (S*C*H$_2$), 46.6 (CH$_3$CH$_2$CH$_2$*C*H), 59.8 (-O*C*H$_2$CH$_3$), 118.3 (=*C*HCO$_2$Et), 158.8 (*C*=CHCO$_2$Et), 166.3 (C=O), 169.6 (C=O).

Compound **4d´**: R_f = 0.36 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 302.17844; $[M + H]^+$ calculated for $C_{15}H_{28}NO_3S$ 302.17899; ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 0.86 (t, *J* = 7.27 Hz, 3H, C*H*$_3$CH$_2$CH$_2$), 1.21 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H*$_3$), 1.21-1.34 (m, 2H, CH$_3$C*H*$_2$CH$_2$), 1.40 (m, 1H, CH$_3$CH$_2$C*H*$_2$CH), 1.48-1.59 (m, 1H, CH$_3$CH$_2$C*H*$_2$CH), 2.05 (s, 3H, SC*H*$_3$), 2.22-2.45 (m, 1H, CH$_3$CH$_2$CH$_2$C*H*), 2.50 (dd, J_1 = 12.93 Hz; J_2 = 6.77 Hz; 1H, SC*H*$_2$), 2.60 (dd, J_1 = 12.92 Hz; J_2 = 7.21 Hz; 1H, SC*H*$_2$), 2.92 (s, 3H, NC*H*$_3$), 3.03 (s, 3H, NC*H*$_3$), 3.42 (s, 2H, C=C*H*$_2$CO$_2$Et), 4.07 (q, *J* = 7.14 Hz, 2H, -OC*H*$_2$CH$_3$), 6.03 (s, 1H, =C*H*CONMe$_2$); ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 14.0 (*C*H$_3$CH$_2$), 14.1 (-OCH$_2$*C*H$_3$), 16.3 (S*C*H$_3$), 20.4 (CH$_3$*C*H$_2$), 34.6 (*C*H$_2$CH), 34.8 (N*C*H$_3$), 35.5 (*C*H$_2$C=CH), 37.6 (N*C*H$_3$), 38.5 (S*C*H$_2$), 47.2 (CH$_3$CH$_2$CH$_2$*C*H), 60.7 (-O*C*H$_2$CH$_3$), 122.4 (=*C*HCONMe$_2$), 146.2 (*C*=CHCONMe$_2$), 167.6 (C=O), 170.7 (C=O).

Compounds 4e/4e´:

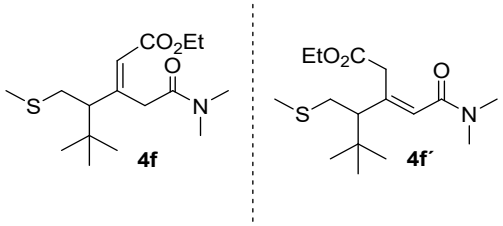


Following the general procedure with: Sulfonium salt **1a** (185 mg, 1.01 mmol, 1.0 eq), allenoate **3e** (171 mg, 1.11 mmol, 1.1 eq.) and 1M solution of ^{t}BuOK (1.11 mL, 1.11 mmol, 1.1 eq.) in 15 mL of ^{t}BuOH, affording, after purification through flash column chromatography, 89 mg of compound **4e** as a colorless oil and 73 mg of compound **4e´** as a colorless oil. Overall yield: **54%**.

Compound **4e**: R_f = 0.25 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 302.17844; $[M + H]^+$ calculated for $C_{15}H_{28}NO_3S$ 302.17899; ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm):): 0.88 (d, *J* = 2.12 Hz, 3H, (C*H*$_3$)$_2$CH), 0.90 (d, *J* = 2.08 Hz, 3H, (C*H*$_3$)$_2$CH), 1.22 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H*$_3$), 1.86 (sext, *J* = 6.81 Hz, 1H, (CH$_3$)$_2$C*H*), 2.03 (s, 3H, SC*H*$_3$), 2.30 (dd, J_1 = 13.63 Hz; J_2 = 7.53 Hz; 1H, SC*H*$_2$), 2.64 (d, *J* = 3.24 Hz; 1H, SC*H*$_2$), 2.66 (d, *J* = 1.33 Hz, 1H, C*H*C=CH), 2.88 (s, 3H, NC*H*$_3$), 3.01 (s, 3H, NC*H*$_3$), 3.50 (d, *J* = 15.05 Hz, 1H, C*H*$_2$CONMe$_2$), 3.89 (d, *J* = 15.05 Hz, 1H, C*H*$_2$CONMe$_2$), 4.08 (q, *J* = 7.14 Hz, 2H, -OC*H*$_2$CH$_3$), 5.78 (s, 1H, =C*H*CO$_2$Et); ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 14.2 (OCH$_2$*C*H$_3$), 16.2 (S*C*H$_3$), 19.9 ((*C*H$_3$)$_2$CH), 20.7 ((*C*H$_3$)$_2$CH), 30.3 ((CH$_3$)$_2$*C*H), 35.5 (N*C*H$_3$), 35.6 (*C*H$_2$C=CH), 37.5 (N*C*H$_3$), 37.6 (S*C*H$_2$), 52.9 ((CH$_3$)$_2$CH*C*H), 59.8 (-O*C*H$_2$CH$_3$), 118.9 (=*C*HCO$_2$Et), 157.5 (*C*=CHCO$_2$Et), 166.3 (C=O), 169.6 (C=O).

Compound **4e´**: R_f = 0.19 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 302.17831; $[M + H]^+$ calculated for $C_{15}H_{28}NO_3S$ 302.17899; ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 0.88 (d, *J* = 6.68 Hz, 3H, $(CH_3)_2CH$), 0.91 (d, *J* = 6.66 Hz, 3H, $(CH_3)_2CH$), 1.20 (t, *J* = 7.15 Hz, 3H, $-OCH_2CH_3$), 1.77 (sext, *J* = 6.93 Hz, 1H, $(CH_3)_2CH$), 2.04 (s, 3H, SCH_3), 2.00-2.15 (m, 1H, CHC=CH), 2.56 (dd, J_1 = 12.82 Hz; J_2 = 9.56 Hz; 1H, SCH_2), 2.68 (dd, J_1 = 12.82 Hz; J_2 = 4.57 Hz; 1H, SCH_2), 2.91 (s, 3H, NCH_3), 3.03 (s, 3H, NCH_3), 3.37 (d, *J* = 15.70 Hz, 1H, $C=CH_2CO_2Et$), 3.45 (d, *J* = 15.67 Hz, 1H, $C=CH_2CO_2Et$), 4.06 (q, *J* = 7.15 Hz, 2H, $-OCH_2CH_3$), 5.99 (s, 1H, $=CHCONMe_2$); ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 14.2 ($-OCH_2CH_3$), 16.8 (SCH_3), 20.1 ($(CH_3)_2CH$), 21.3 ($(CH_3)_2CH$), 30.0 ($(CH_3)_2CH$), 34.8 (NCH_3), 35.9 ($CH_2C=CH$), 36.8 (NCH_3), 38.4 (SCH_2), 54.6 ($(CH_3)_2CHCH$), 61.2 ($-OCH_2CH_3$), 123.6 ($=CHCONMe_2$), 144.9 ($C=CHCONMe_2$), 167.5 (C=O), 170.7 (C=O).

Compounds 4f/4f´:

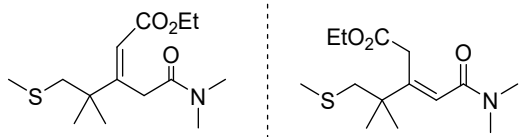


Following the general procedure with: Sulfonium salt **1a** (210 mg, 1.14 mmol, 1.0 eq), allenoate **3f** (192 mg, 1.14 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.14 mL, 1.14 mmol, 1.0 eq.) in 20 mL of ^{t}BuOH, affording, after purification through Isolera Biotage® chromatography, 80 mg of compound **4f** as white brilliant monocrystals and 116 mg of compound **4f´** as a colorless oil. Overall yield: **54%**.

Compound **4f**: R_f = 0.45 (AcOEt-Hex, 2:3). Elemental Analysis: 60.818 %C, 9.069 %H, 4.159 %N, 9.994 %S, 17.161 %O; HRMS (ESI) m/z: 316.19403; $[M + H]^+$ calculated for $C_{16}H_{30}NO_3S$ 316.19464; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.91 (s, 9H, $(CH_3)_3C$), 1.21 (t, *J* = 7.14 Hz, 3H, $-OCH_2CH_3$), 2.00 (s, 3H, SCH_3), 2.46-2.60 (m, 2H, SCH_2, CHC=), 2.60-2.70 (m, 1H, SCH_2), 2.85 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 3.11 (d, *J* = 14.65 Hz, 1H, CH_2CONMe_2), 4.07 (q, *J* = 7.14 Hz, 2H, $-OCH_2CH_3$), 4.45 (d, *J* = 14.00 Hz, 1H, CH_2CONMe_2), 5.77 (s, 1H, $=CHCO_2Et$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (OCH_2CH_3), 16.1 (SCH_3), 28.1 ($(CH_3)_3C$), 35.0 ($CH_2C=CH$), 35.7 (NCH_3), 37.6 (NCH_3), 39.3 (CHC=), 39.4 (SCH_2), 59.9 (OCH_2CH_3), 119.6 ($=CHCO_2Et$), 157.4 ($C=CHCO_2Et$), 166.2 (C=O), 169.3 (C=O).

Compound **4f´**: R_f = 0.28 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 316.19412; $[M + H]^+$ calculated for $C_{16}H_{30}NO_3S$ 316.19464; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.89 (s, 9H, $(CH_3)_3C$), 1.17 (t, *J* = 7.15 Hz, 3H, -OCH_2CH_3), 2.00 (s, 3H, SCH_3), 2.19 (d, *J* = 11.4 Hz, 1H, C*H*C=), 2.56 (t, *J* = 12.14 Hz, 1H, SCH_2), 2.68 (d, *J* = 12.65 Hz, 1H, SCH_2), 2.88 (s, 3H, NCH_3), 3.00 (s, 3H, NCH_3), 3.20 (d, *J* = 15.38 Hz, 1H, C=CH_2CO_2Et), 3.66 (d, *J* = 15.38 Hz, 1H, C=CH_2CO_2Et), 4.02 (q, *J* = 7.15 Hz, 2H, -OCH_2CH_3), 5.94 (s, 1H, =C*H*$CONMe_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1 (OCH_2CH_3), 16.2 (SCH_3), 28.3 ($(CH_3)_3C$), 34.6 (CH_2C=CH), 34.7 (NCH_3), 37.5 (NCH_3), 57.3 (*C*HC=), 60.5 (OCH_2CH_3), 124.7 (=*C*H$CONMe_2$), 144.3 (*C*=$CHCONMe_2$), 167.8 (C=O), 170.3 (C=O).

Compounds 4g/4g´:

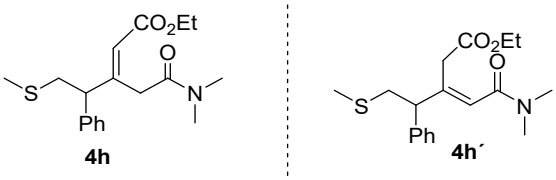


4g **4g´**

Following the general procedure with: Sulfonium salt **1a** (123 mg, 0.67 mmol, 1.0 eq), allenoate **3g** (104 mg, 0.74 mmol, 1.1 eq.) and 1M solution of ^{t}BuOK (0.74 mL, 0.74 mmol, 1.0 eq.) in 10 mL of ^{t}BuOH, affording, after flash column chromatography, 110 mg of compound **4g´** as a colorless oil. Overall yield: **57%**. (No traces of the other isomer **4g** were detected).

Compound **4g´**: R_f = 0.11 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 288.16257; $[M + H]^+$ calculated for $C_{14}H_{26}NO_3S$ 288.16334; ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 1.14 (s, 6H, 2 x CH_3C), 1.19 (t, *J* = 7.15 Hz, 3H, -OCH_2CH_3), 2.04 (s, 3H, SCH_3), 2.56 (s, 2H, SCH_2), 2.90 (s, 3H, NCH_3), 3.03 (s, 3H, NCH_3), 3.46 (s, 2H, C=CH_2CO_2Et), 4.05 (q, *J* = 7.15 Hz, 2H, -OCH_2CH_3), 6.09 (s, 1H, =C*H*$CONMe_2$); ^{13}C-NMR (100 MHz, $CDCl_3$, δ ppm): 14.1 (OCH_2CH_3), 17.8 (SCH_3), 26.01 ($(CH_3)_2C$), 33.9 (CH_2C=CH), 34.7 (NCH_3), 37.6 (NCH_3), 41.7 ($C(CH_3)_2$), 46.6 (CH_2CO_2Et), 60.6 (OCH_2CH_3), 121.7 (=*C*H$CONMe_2$), 148.6 (*C*=$CHCONMe_2$), 168.3 (C=O), 171.0 (C=O).

Compounds 4h/4h´:



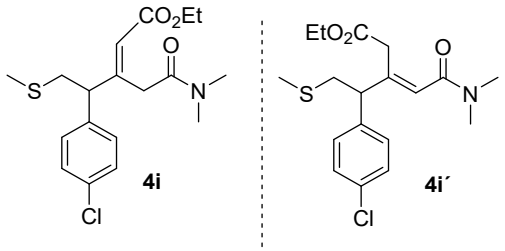
4h **4h´**

Following the general procedure with: Sulfonium salt **1a** (159 mg, 0.87 mmol, 1.0 eq), allenoate **3h** (164 mg, 0.87 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.87 mL, 0.87 mmol, 1.0 eq.) in 14 mL of ^{t}BuOH, affording, after flash column chromatography, 80 mg of compound **4h** as a colorless oil and 35 mg of compound **4h´** as a colorless oil. Overall yield: **40%**.

Compound **4h**: R_f = 0.27 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 336.16279; $[M + H]^+$ calculated for $C_{18}H_{26}NO_3S$ 336.16334; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.21 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H$_3$*), 1.94 (s, 3H, SC*H$_3$*), 2.81 (s, 3H, NC*H$_3$*), 2.83 (s, 3H, NC*H$_3$*), 2.94 (d, *J* = 7.37 Hz, 1H, C*H$_2$*S), 3.02 (d, *J* = 15.6 Hz, 1H, C*H$_2$*CONMe$_2$), 2.98-3.12 (m, 1H, SC*H$_2$*), 3.07 (d, *J* = 15.4 Hz, 1H, C*H$_2$*CONMe$_2$), 3.82 (dd, J_1 = 9.11 Hz, J_2 = 5.87 Hz, 1H, C*H*Ph), 4.07 (q, *J* = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 5.95 (s, 1H, =C*H*CO$_2$Et), 7.10-7.22 (m, 3H, Ph), 7.19-7.32 (m, 2H, Ph); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (OCH$_2$*C*H$_3$), 16.3 (S*C*H$_3$), 35.5 (*C*H$_2$C=CH), 36.3 (N*C*H$_3$), 37.3 (N*C*H$_3$), 38.5 (*C*HPh), 52.5 (*C*H$_2$CO$_2$Et), 60.1 (O*C*H$_2$CH$_3$), 117.9 (=*C*HCO$_2$Et), 127.4 (Ph), 128.6 (Ph), 140.1 (Ph), 157.8 (*C*=CHCO$_2$Et), 166.4 (C=O), 169.8 (C=O).

Compound **4h´**: R_f = 0.14 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 336.16254; $[M + H]^+$ calculated for $C_{18}H_{26}NO_3S$ 336.16334; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.12 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 1.98 (s, 3H, SC*H$_3$*), 2.83 (dd, J_1 = 12.92 Hz, J_2 = 7.88 Hz, 1H, SC*H$_2$*), 2.90 (s, 3H, NC*H$_3$*), 2.98 (dd, J_1 = 12.91 Hz, J_2 = 7.15 Hz, 1H, SC*H$_2$*), 3.00 (s, 3H, NC*H$_3$*), 3.06 (d, *J* = 16.07 Hz, 1H, C=C*H$_2$*CO$_2$Et), 3.47 (d, *J* = 16.07 Hz, 1H, C=C*H$_2$*CO$_2$Et), 3.66 (t, *J* = 7.48 Hz, 1H, C*H*Ph), 3.97 (q, *J* = 7.15 Hz, 2H, -OC*H$_2$*CH$_3$), 6.13 (s, 1H, =C*H*CONMe$_2$), 7.10-7.23 (m, 3H, Ph), 7.18-7.30 (m, 2H, Ph); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1 (OCH$_2$*C*H$_3$), 16.4 (S*C*H$_3$), 34.9 (*C*H$_2$C=CH), 36.7 (N*C*H$_3$), 37.8 (N*C*H$_3$), 38.3 (*C*HPh), 51.9 (*C*H$_2$CO$_2$Et), 60.7 (O*C*H$_2$CH$_3$), 122.4 (=*C*HCONMe$_2$), 127.3 (Ph), 128.4 (Ph), 128.6 (Ph), 140.3 (Ph), 145.0 (*C*=CHCONMe$_2$), 167.6 (C=O), 170.6 (C=O).

Compounds 4i/4i´:

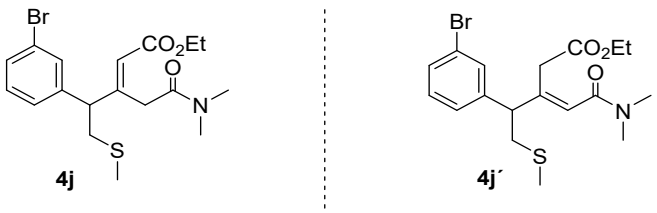


Following the general procedure with: Sulfonium salt **1a** (199 mg, 1.08 mmol, 1.0 eq), allenoate **3i** (240 mg, 0.87 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.08 mL, 1.08 mmol, 1.0 eq.) in 20 mL of ^{t}BuOH, affording, after purification through Isolera Biotage®, 80 mg of compound **4i** as a colorless oil and 170 mg of compound **4i´** as a colorless oil. Overall yield: **63%**.

Compound **4i**: R_f = 0.30 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 370.12382; $[M + H]^+$ calculated for $C_{18}H_{25}ClNO_3S$ 370.12437; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.21 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H$_3$*), 2.08 (s, 3H, SC*H$_3$*), 2.83 (s, 3H, NC*H$_3$*), 2.87 (s, 3H, NC*H$_3$*), 2.78-.2.99 (m, 2H, C*H$_2$*S), 3.02 (d, *J* = 15.6 Hz, 1H, C*H$_2$*CONMe$_2$), 3.08 (d, *J* = 15.6 Hz, 1H, C*H$_2$*CONMe$_2$), 3.81 (dd, J_1 = 9.11 Hz, J_2 = 5.87 Hz, 1H, C*H*PhCl), 4.06 (q, *J* = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 5.91 (s, 1H, =C*H*CO$_2$Et), 7.13 (d, *J* = 8.43 Hz, 2H, *p*-ClPh), 7.23 (d, *J* = 8.43 Hz, 2H, *p*-ClPh); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (OCH$_2$*C*H$_3$), 16.3 (S*C*H$_3$), 35.5 (*C*H$_2$C=CH), 36.2 (N*C*H$_3$), 37.3 (N*C*H$_3$), 38.4 (*C*HPh), 51.8 (*C*H$_2$CONMe$_2$), 60.1 (O*C*H$_2$CH$_3$), 118.2 (=*C*HCO$_2$Et), 128.7 (Ph), 130.0 (Ph), 133.2 (Ph), 138.6 (Ph), 157.4 (*C*=CHCO$_2$Et), 166.2 (C=O), 169.6 (C=O).

Compound **4i´**: R_f = 0.10 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 370.12314; $[M + H]^+$ calculated for; $C_{18}H_{25}ClNO_3S$ 370.12437; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.13 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 1.99 (s, 3H, SC*H$_3$*), 2.78 (dd, J_1 = 12.91 Hz, J_2 = 8.18 Hz, 1H, SC*H$_2$*), 2.90 (s, 3H, NC*H$_3$*), 2.96 (dd, J_1 = 12.90 Hz, J_2 = 6.81 Hz, 1H, SC*H$_2$*), 2.99 (s, 3H, NC*H$_3$*), 3.06 (d, *J* = 16.14 Hz, 1H, C=C*H$_2$*CO$_2$Et), 3.45 (d, *J* = 16.14 Hz, 1H, C=C*H$_2$*CO$_2$Et), 3.64 (t, *J* = 7.45 Hz, 1H, C*H*Ph), 3.98 (q, *J* = 7.15 Hz, 2H, -OC*H$_2$*CH$_3$), 6.10 (s, 1H, =C*H*CONMe$_2$), 7.11 (d, *J* = 8.37 Hz, 2H, PhCl), 7.22 (d, *J* = 8.43 Hz, 2H, PhCl); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1 (OCH$_2$*C*H$_3$), 16.4 (S*C*H$_3$), 34.9 (*C*H$_2$C=CH), 36.7 (N*C*H$_3$), 37.8 (N*C*H$_3$), 38.2 (*C*HPh), 51.2 (*C*H$_2$CO$_2$Et), 60.8 (O*C*H$_2$CH$_3$), 122.8 (=*C*HCONMe$_2$), 128.8 (Ph), 129.8 (Ph), 133.2 (Ph), 138.7 (Ph), 144.6 (*C*=CHCONMe$_2$), 167.4 (C=O), 170.6 (C=O).

Compounds 4j/4j´:

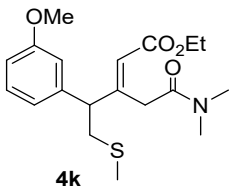


Following the general procedure with: Sulfonium salt **1a** (180 mg, 0.98 mmol, 1.0 eq), allenoate **3j** (261 mg, 0.98 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.00 mL, 1.00 mmol, 1.02 eq.) in 25 mL of ^{t}BuOH, affording, after purification through Isolera Biotage®, 102 mg of compound **4j** as a yellow oil and 56 mg of compound **4j´** as a yellow oil. Overall yield: **40%**.

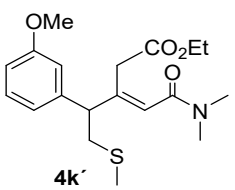
Compound **4j**: R_f = 0.30 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 414.07330; $[M + H]^+$ calculated for $C_{18}H_{25}BrNO_3S$ 414.07385; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.22 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H$_3$*), 1.97 (s, 3H, SC*H$_3$*), 2.80 (m, 1H), 2.83 (s, 3H, NC*H$_3$*), 2.87 (s, 3H, NC*H$_3$*), 2.92 (m, 2H, C*H$_2$*S), 3.01 (m, 1H, C*H$_2$*CONMe$_2$), 2.98-3.12 (m, 1H, C*H$_2$*CONMe$_2$), 3.81 (dd, J_1 = 9.11 Hz, J_2 = 5.87 Hz, 1H, C*H*PhBr), 4.09 (q, *J* = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 5.93 (s, 1H, =C*H*CO$_2$Et), 7.00-7.20 (m, 2H, *m*-BrPh), 7.21-7.40 (m, 3H, *m*-BrPh); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (OCH$_2$*C*H$_3$), 16.3 (S*C*H$_3$), 29.7 (*C*H$_2$C=CH), 35.5 (N*C*H$_3$), 36.2 (N*C*H$_3$), 37.3 (*C*HPhBr), 38.3, 52.1 (*C*H$_2$CO$_2$Et), 60.2 (O*C*H$_2$CH$_3$), 118.4 (=*C*HCONMe$_2$), 122.8 (BrPh), 130.1 (BrPh), 130.5 (BrPh), 131.4 (BrPh), 142.6 (BrPh), 157.0 (*C*=CHCONMe$_2$), 166.2 (C=O), 169.6 (C=O).

Compound **4j´**: R_f = 0.16 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 414.07315; $[M + H]^+$ calculated for; $C_{18}H_{25}BrNO_3S$ 414.07385; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.22 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H$_3$*), 2.00 (s, 3H, SC*H$_3$*), 2.48-2.65 (m, 1H), 2.73 (s, 3H, NC*H$_3$*), 2.87-2.98 (m, 2H, C*H$_2$*S), 3.00 (s, 3H, NC*H$_3$*), 3.12 (d, 1H, *J* = 16.4 Hz, 1H, C*H$_2$*CO$_2$Et), 3.48 (d, 1H, *J* = 16.4 Hz, C*H$_2$*CO$_2$Et), 3.57 (dd, J_1 = 9.11 Hz, J_2 = 5.87 Hz, 1H, C*H*PhBr), 3.99 (q, *J* = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 6.25 (s, 1H, =C*H*CO$_2$NMe$_2$), 7.05-7.26 (m, 2H, *m*-BrPh), 7.21-7.40 (m, 3H, *m*-BrPh); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (OCH$_2$*C*H$_3$), 16.4 (S*C*H$_3$), 34.9 (*C*H$_2$C=CH), 36.7 (N*C*H$_3$), 37.8 (N*C*H$_3$), 38.1 (*C*HPhBr), 51.5 (*C*H$_2$CO$_2$Et), 60.8 (O*C*H$_2$CH$_3$), 122.9 (=*C*HCONMe$_2$), 127.1 (BrPh), 130.2 (BrPh), 130.5 (BrPh), 131.4 (BrPh), 142.7 (BrPh), 144.4 (*C*=CHCONMe$_2$), 167.3 (C=O), 170.5 (C=O).

Compounds 4k/4k´:



4k



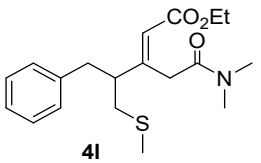
4k´

Following the general procedure with: Sulfonium salt **1a** (156 mg, 0.85 mmol, 1.0 eq), allenoate **3k** (185 mg, 0.85 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.85 mL, 0.85 mmol, 1.0 eq.) in 15 mL of ^{t}BuOH, affording, after purification through Isolera Biotage®, 56 mg of compound **4k** as a colorless oil and 115 mg of compound **4k´** as a colorless oil. Overall yield: **55%**

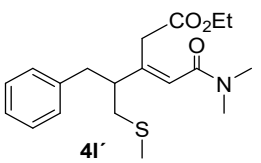
Compound **4k**: R_f = 0.20 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 366.17336; $[M + H]^+$ calculated for $C_{19}H_{28}NO_4S$ 366.17390; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.21 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 1.96 (s, 3H, SC*H$_3$*), 2.79-2.83 (m, 1H, SC*H$_2$*), 2.83 (s, 3H, NC*H$_3$*), 2.86 (s, 3H, NC*H$_3$*), 2.87-2.94 (m, 1H, SC*H$_2$*), 3.03 (d, *J* = 16.11 Hz, 1H, C=C*H$_2$*CONMe$_2$), 3.73 (s, 3H, O*Me*), 3.80 (dd, 1H), 4.04-4.12 (m, 2H, -OC*H$_2$*CH$_3$), 5.95 (s, 1H, =C*H*CO$_2$Et), 6.68-6.82 (m, 2H, *Ph*OMe), 6.81-6.90 (m, 1H), 7.13-7.19 (m, 1H, *Ph*OMe); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (OCH$_2$*C*H$_3$), 16.3 (S*C*H$_3$), 35.5 (*C*H$_2$C=CH), 36.1 (N*C*H$_3$), 37.2 (N*C*H$_3$), 38.4 (*C*HPhOMe), 52.5 (*C*H$_2$CONMe$_2$), 55.2 (O*C*H$_3$), 60.0 (O*C*H$_2$CH$_3$), 112.3 (MeO*Ph*), 114.7 (MeO*Ph*), 117.8, 121.0 (MeO*Ph*), 129.0 (MeO*Ph*), 141.8 (MeO*Ph*), 159.7 (MeO*C*=), 166.3 (C=O), 169.7 (C=O).

Compound **4k´**: R_f = 0.14 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 366.17303; $[M + H]^+$ calculated for; $C_{19}H_{28}NO_4S$ 366.17390; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.13 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 1.99 (s, 3H, SC*H$_3$*), 2.82 (dd, *J$_1$* = 12.83 Hz, *J$_2$* = 7.84 Hz, 1H, SC*H$_2$*), 2.90 (s, 3H, NC*H$_3$*), 2.97 (dd, *J$_1$* = 12.96 Hz, *J$_2$* = 7.10 Hz, 1H, SC*H$_2$*), 3.00 (s, 3H, NC*H$_3$*), 3.06 (d, *J* = 16.11 Hz, 1H, C=C*H$_2$*CO$_2$Et), 3.48 (d, *J* = 16.11 Hz, 1H, C=C*H$_2$*CO$_2$Et), 3.63 (t, *J* = 7.45 Hz, 1H, C*H*PhOMe), 3.72 (s, 3H, O*Me*), 3.98 (q, *J* = 7.15 Hz, 2H, -OC*H$_2$*CH$_3$), 6.13 (s, 1H, =C*H*CONMe$_2$), 6.71 (d, *J* = 9.79 Hz, 2H, *Ph*OMe), 6.75 (d, *J* = 7.57 Hz, 1H, *Ph*OMe), 7.16 (t, *J* = 8.43 Hz, 1H, *Ph*OMe); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1 (OCH$_2$*C*H$_3$), 16.4 (S*C*H$_3$), 34.9 (*C*H$_2$C=CH), 36.7 (N*C*H$_3$), 37.8 (N*C*H$_3$), 38.2 (*C*HPhOMe), 51.9 (*C*H$_2$CO$_2$Et), 55.2 (O*C*H$_3$), 60.7 (O*C*H$_2$CH$_3$), 112.4 (MeO*Ph*), 114.4 (MeO*Ph*), 120.7 (MeO*Ph*), 122.3 (=*C*HCONMe$_2$), 129.6 (MeO*Ph*), 141.9 (MeO*Ph*), 145.0 (*C*=CHCONMe$_2$), 159.8 (MeO*C*=), 167.6 (C=O), 170.7 (C=O).

Compounds 4l/4l´:



4l



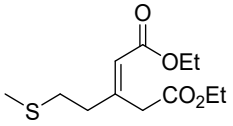
4l´

Following the general procedure with: Sulfonium salt **1a** (205 mg, 1.12 mmol, 1.0 eq), allenoate **3l** (226 mg, 1.12 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.12 mL, 1.12 mmol, 1.0 eq.) in 20 mL of ^{t}BuOH, affording, after purification through Isolera Biotage®, 67 mg of compound **4l** as a colorless oil and 212 mg of compound **4l´** as a colorless oil. Overall yield: **71%**

Compound **4l**: R_f = 0.21 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 350.17828; $[M + H]^+$ calculated for $C_{19}H_{28}NO_3S$ 350.17899; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.20 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 2.00 (s, 3H, SC*H$_3$*), 2.48-2.52 (m, 1H, SC*H$_2$*), 2.64 (dd, *J$_1$* = 13.22 Hz, *J$_2$* = 6.51 Hz, 1H, SC*H$_2$*), 2.75-2.78 (m, 1H, C*H$_2$*Ph), 2.79-2.81 (m, 1H), 2.82 (s, 3H, NC*H$_3$*), 2.83 (s, 3H, NC*H$_3$*), 2.88-2.91 (m, 1H, C*H$_2$*Ph), 3.58 (d, *J* = 15.20 Hz, 1H, C=C*H$_2$*CO$_2$Et), 3.74 (d, *J* = 15.21 Hz, 1H, C=C*H$_2$*CO$_2$Et), 4.06 (q, *J* = 7.15 Hz, 2H, -OC*H$_2$*CH$_3$), 5.81 (s, 1H, =C*H*CONMe$_2$), 7.08-7.14 (m, 3H, *Ph*), 7.20 (t, *J* = 7.61 Hz, 2H, *Ph*); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (OCH$_2$*C*H$_3$), 16.2 (S*C*H$_3$), 35.6 (*C*H$_2$C=CH), 37.3 (N*C*H$_3$), 37.6 (N*C*H$_3$), 38.2 (S*C*H$_2$), 39.6 (*C*HC=), 48.0 (*C*H$_2$Ph), 59.9 (O*C*H$_2$CH$_3$), 118.5 (=*C*HCO$_2$Et), 126.3 (*Ph*), 128.3 (*Ph*), 129.2 (*Ph*), 139.5 (*Ph*), 158.7 (*C*=CHCO$_2$Et), 166.4 (C=O), 169.6 (C=O).

Compound **4l´**: R_f = 0.17 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 350.17828; $[M + H]^+$ calculated for; $C_{19}H_{28}NO_3S$ 350.17899; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.16 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 1.98 (s, 3H, SC*H$_3$*), 2.50 (dd, *J$_1$* = 12.63 Hz, *J$_2$* = 6.51 Hz, 1H, SC*H$_2$*), 2.60 (dd, *J$_1$* = 12.68 Hz, *J$_2$* = 6.57 Hz, 1H, SC*H$_2$*), 2.64 (t, *J* = 6.73 Hz, 1H, C*H*C=), 2.73 (dd, *J$_1$* = 13.83 Hz, *J$_2$* = 7.15 Hz, 1H, C*H$_2$*Ph), 2.76 (s, 3H, NC*H$_3$*), 2.83 (s, 3H, NC*H$_3$*), 2.86 (dd, *J$_1$* = 13.76 Hz, *J$_2$* = 6.66 Hz, 1H, C*H$_2$*Ph), 3.30 (d, *J* = 15.89 Hz, 1H, C=C*H$_2$*CONMe$_2$), 3.43 (d, *J* = 15.90 Hz, 1H, C=C*H$_2$*CONMe$_2$), 4.04 (q, *J* = 7.15 Hz, 2H, -OC*H$_2$*CH$_3$), 5.85 (s, 1H, =C*H*CONMe$_2$), 6.95-7.15 (m, 3H, *Ph*), 7.19 (t, *J* = 7.61 Hz, 2H, *Ph*); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (OCH$_2$*C*H$_3$), 16.2 (S*C*H$_3$), 34.8 (*C*H$_2$C=CH), 36.3 (N*C*H$_3$), 37.4 (N*C*H$_3$), 37.4 (S*C*H$_2$), 38.7 (*C*HC=), 48.5 (*C*H$_2$Ph), 60.7 (O*C*H$_2$CH$_3$), 122.9 (=*C*HCONMe$_2$), 126.2 (*Ph*), 128.3 (*Ph*), 129.2 (*Ph*), 139.4 (*Ph*), 145.4 (*C*=CHCONMe$_2$), 167.3 (C=O), 170.7 (C=O).

Compound 4m:



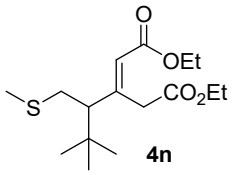
4m

Following the general procedure with: Sulfonium salt **1b** (234 mg, 1.022 mmol, 1.0 eq), allenoate **3a** (115 mg, 1.022 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.02 mL, 1.02

mmol, 1.0 eq.) in 25 mL of ^{t}BuOH, affording, after purification through Isolera Biotage®, 80 mg of compound **4m** as a yellow oil. Yield: **30%**

Compound **4m**: R_f = 0.81 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 261.11548; $[M + H]^+$ calculated for $C_{12}H_{21}O_4S$ 261.11605 ; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.26 (t, *J* = 7.17 Hz, 3H, -OCH$_2$C*H$_3$*), 1.27 (t, *J* = 7.17 Hz, 3H, -OCH$_2$C*H$_3$*), 2.12 (s, 3H, SC*H$_3$*), 2.48-2.59 (m, 2H, C*H$_2$*C=CH), 2.64 (m, 2H, SC*H$_2$*), 3.73 (s, 2H, C*H$_2$*CO$_2$OEt), 4.06-4.24 (m, 4H, 2 x -OC*H$_2$*CH$_3$), 5.87 (s, 1H, =C*H*CO$_2$Et); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1 (*C*H$_3$CH$_2$O-), 14.2 (*C*H$_3$CH$_2$O-), 15.6 (S*C*H$_3$), 31.7 (S*C*H$_2$), 37.3 (*C*H$_2$C=), 38.5 (*C*H$_2$CO$_2$Et), 60.0 (-O*C*H$_2$CH$_3$), 60.9 (-O*C*H$_2$CH$_3$), 119.7 (=*C*HCO$_2$Et), 152.1 (*C*=CHCO$_2$Et), 165.9 (C=O), 170.2 (C=O).

Compound 4n:

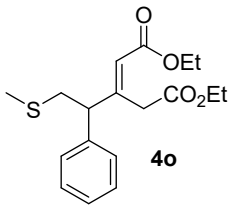


4n

Following the general procedure with: Sulfonium salt **1b** (151 mg, 0.66 mmol, 1.0 eq), allenoate **3f** (111 mg, 0.66 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.66 mL, 0.66 mmol, 1.0 eq.) in 18 mL of ^{t}BuOH, affording, after purification through Prime Isolera Biotage®, a quite major product (43 mg of a colorless oil) was isolated. Yield: **21%**

Compound **4n**: R_f = 0.42 (AcOEt-Hex, 1:9). HRMS (ESI) m/z: 317.17810; $[M + H]^+$ calculated for $C_{16}H_{29}O_4S$ 317.17866; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.90 (s, 9H, (C*H$_3$*)$_3$C), 1.19 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H$_3$*), 1.20 (t, *J* = 7.14 Hz, 3H, -OCH$_2$C*H$_3$*), 2.00 (s, 3H, SC*H$_3$*), 2.22 (dd, *J$_1$* = 11.15 Hz, *J$_2$* = 3.66 Hz, 1H, C*H*^{t}Bu), 2.55 (dd, *J$_1$* = 12.87 Hz, *J$_2$* = 11.21 Hz, 1H, SC*H$_2$*), 2.71 (dd, *J$_1$* = 12.94 Hz, *J$_2$* = 3.68 Hz, 1H, SC*H$_2$*), 3.24 (d, *J* = 16.23 Hz, 1H, C*H$_2$*CO$_2$Et), 3.85 (d, *J* = 16.04 Hz, 1H, C*H$_2$*CO$_2$Et), 4.07 (q, *J* = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 4.08 (q, *J* = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 5.80 (s, 1H, =C*H*CO$_2$Et); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1 (*C*H$_3$CH$_2$O-), 14.2 (*C*H$_3$CH$_2$O-), 16.2 (S*C*H$_3$), 28.3 (^{t}Bu) 34.8 (S*C*H$_2$), 38.3 (*C*H$_2$CO$_2$Et), 58.6 (*C*H^{t}Bu), 59.9 (-O*C*H$_2$CH$_3$), 60.7 (-O*C*H$_2$CH$_3$), 122.3 (=*C*HCO$_2$Et), 153.8 (*C*=CHCO$_2$Et), 165.9 (C=O), 169.8 (C=O).

Compound 4o:

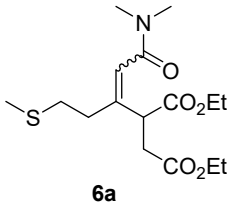


4o

Following the general procedure with: Sulfonium salt **1b** (350 mg, 1.53 mmol, 1.0 eq), allenoate **3h** (288 mg, 1.53 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.53 mL, 1.53 mmol, 1.0 eq.) in 35 mL of ^{t}BuOH, affording, after purification through flash column chromatography, 144 mg of compound **4o** as a colorless oil. Overall yield: **28%**

Compound **4o**: R_f = 0.78 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 337.14741; $[M + H]^+$ calculated for $C_{18}H_{25}O_4S$ 337.14735; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.13 (t, J = 7.14 Hz, 3H, -OCH$_2$C*H$_3$*), 1.21 (t, J = 7.14 Hz, 3H, -OCH$_2$C*H$_3$*), 1.95 (s, 3H, SC*H$_3$*), 2.84 (dd, J_1 = 12.89 Hz, J_2 = 8.80 Hz, 1H, SC*H$_2$*), 2.98 (dd, J_1 = 12.89 Hz, J_2 = 6.22 Hz, 1H, SC*H$_2$*), 3.16 (d, J = 16.27 Hz, 1H, C*H$_2$*CO$_2$Et), 3.65 (dd, J_1 = 8.24 Hz, J_2 = 6.71 Hz, 1H, C*H*^{t}Ph), 3.79 (d, J = 16.27 Hz, 1H, C*H$_2$*CO$_2$Et), 3.99 (q, J = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 4.09 (q, J = 7.14 Hz, 2H, -OC*H$_2$*CH$_3$), 5.97 (s, 1H, =C*H*CO$_2$Et), 7.00-7.26 (m, 3H, Ph), 7.18-7.32 (m, 2H, Ph); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1 (*C*H$_3$CH$_2$O-), 14.2 (*C*H$_3$CH$_2$O-), 16.4 (S*C*H$_3$), 37.0 (S*C*H$_2$), 38.0 (*C*H$_2$CO$_2$Et), 53.3 (*C*HPh), 60.2 (-O*C*H$_2$CH$_3$), 60.8 (-O*C*H$_2$CH$_3$), 119.2 (=*C*HCO$_2$Et), 127.6 (Ph), 128.5 (Ph), 128.7 (Ph), 139.4 (Ph), 154.4 (*C*=CHCO$_2$Et), 166.1 (C=O), 170.1 (C=O).

Compounds 6a:



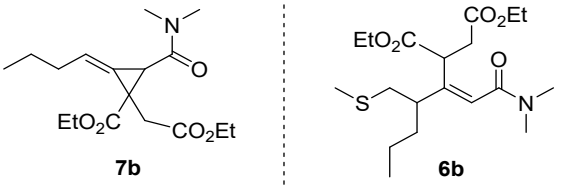
6a

Following the general procedure with: Sulfonium salt **1a** (153 mg, 0.83 mmol, 1.0 eq), allenoate **5a** (165 mg, 0.83 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.83 mL, 0.83 mmol, 1.0 eq.) in 20 mL of ^{t}BuOH, affording, after purification through flash column chromatography, 184 mg of compound **6a** as mixture of isomers. Yield: **64%**

Compound **6a**: R_f = 0.16 (AcOEt-Hex, 1:1). HRMS (ESI) m/z: 346.16797; $[M + H]^+$ calculated for $C_{16}H_{28}O_5S$ 346.16882; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.19 (t, J = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 1.22 (t, J = 7.15 Hz, 3H, -OCH$_2$C*H$_3$*), 1.96 (s, 3H, SC*H$_3$*), 2.05 (bs, 1H), 2.50-2.66 (m, 2H, SC*H$_2$*), 2.84-2.90 (m, 2H, C*H*CO$_2$Et), 2.91 (s, 3H, NC*H$_3$*), 2.94 (s, 3H, NC*H$_3$*), 2.94-3.00 (m, 2H, C*H$_2$*CO$_2$Et), 4.03-4.18 (m, 4H, -OC*H$_2$*CH$_3$), 5.98

(s, 1H, =C*H*CONMe$_2$); ^{13}C-NMR (125 MHz, CDCl$_3$, δ ppm): 14.0, 14.2, 17.4, 32.4, 33.3, 35.0, 37.0, 38.2, 54.4, 60.7, 61.5, 118.9, 149.6 168.1, 170.8, 172.3

Compounds 7b/6b:



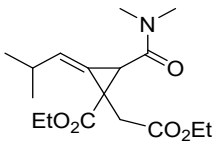
Following the general procedure with: Sulfonium salt **1a** (230 mg, 1.25 mmol, 1.0 eq), allenoate **5b** (300 mg, 1.25 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.25 mL, 1.25 mmol, 1.0 eq.) in 30 mL of ^{t}BuOH, affording, after purification through Isolera Prime Biotage®, 188 mg of compound **7b** as a yellow oil and 116 mg of compound **6b** *(mixture of diastereoisomers)* as a yellow oil. Overall yield: **63%**

Compound **7b**: R_f = 0.19 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 326.19681; $[M + H]^+$ calculated for $C_{17}H_{28}NO_5$ 326.19675; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.82 (t, *J* = 7.37 Hz, 3H, C*H*$_3$CH$_2$), 1.16 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H*$_3$), 1.17 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H*$_3$), 1.37 (sext, *J* = 7.32 Hz, 1H, (CH$_3$C*H*$_2$CH$_2$), 2.05-2.12 (m, 2H, C*H*$_2$CH=), 2.62 (d, *J* = 17.83 Hz, 1H, C*H*$_2$CO$_2$Et), 2.86 (s, 3H, NC*H*$_3$), 2.88 (dd, J_1 = 18.80 Hz, J_2 = 1.61 Hz, 1H, C*H*$_2$CONMe$_2$), 3.11 (d, *J* = 17.79 Hz, 1H, C*H*$_2$CO$_2$Et), 3.12 (s, 3H, NC*H*$_3$), 3.34 (d, *J* = 1.61 Hz, 1H, C*H*CONMe$_2$), 4.00-4.07 (m, 2H, -OC*H*$_2$CH$_3$), 4.12 (q, *J* = 7.15 Hz, 2H, -OC*H*$_2$CH$_3$), 5.90 (dt, J_1 = 7.09 Hz, J_2 = 1.88 Hz, 1H, CH$_2$=C*H*C); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 13.7, 14.1, 14.2, 22.0, 27.9, 30.6, 32.5, 33.2, 35.8, 37.8, 60.5, 61.4, 122.5, 124.7, 167.7, 170.8, 171.5

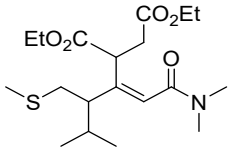
Compound **6b**: R_f = 0.14 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 388.21484; $[M + H]^+$ calculated for; $C_{19}H_{34}NO_5S$ 388.21577; 1H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.82 (t, *J* = 7.32 Hz, 3H, C*H*$_3$CH$_2$), 1.16 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H*$_3$), 1.18 (t, *J* = 7.15 Hz, 3H, -OCH$_2$CH$_3$), 1.21-1.33 (m, 2H, CH$_3$C*H*$_2$), 1.36-1.46 (m, 1H, CH$_3$CH$_2$C*H*$_2$), 1.49-1.57 (m, 1H, CH$_3$CH$_2$C*H*$_2$), 1.58-1.66 (m, 1H), 2.04 (s, 3H, SC*H*$_3$), 2.32 (sext, *J* = 6.86 Hz, 1H, CH$_2$C*H*CH$_2$), 2.41 (dd, J_1 = 13.06 Hz; J_2 = 7.76 Hz; 1H, SC*H*$_2$), 2.48 (dd, J_1 = 13.00 Hz; J_2 = 9.39 Hz; 1H, C*H*CO$_2$Et), 2.60 (dd, J_1 = 13.00 Hz; J_2 = 6.93 Hz; 1H, C*H*$_2$CO$_2$Et), 2.89 (s, 3H, NC*H*$_3$), 2.96 (s, 3H, NC*H*$_3$), 3.15 (dd, J_1 = 17.00 Hz, J_2 = 10.37 Hz, 1H, C*H*$_2$CO$_2$Et), 3.98-4.10 (m, 4H, -OC*H*$_2$CH$_3$), 5.96 (s, 1H, =C*H*CONMe$_2$); ^{13}C-NMR (125

MHz, $CDCl_3$, δ ppm): 14.0, 14.1, 14.2, 16.5, 20.4, 35.4, 35.9, 37.7, 39.5, 42.6, 44.5, 60.6, 60.9, 121.9, 149.3, 167.2, 171.8, 172.0, 172.1.

Compounds 7c/6c:



7c



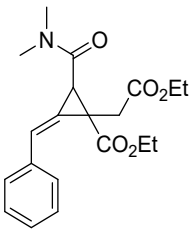
6c

Following the general procedure with: Sulfonium salt **1a** (120 mg, 0.65 mmol, 1.0 eq), allenoate **5c** (156 mg, 0.65 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.65 mL, 0.72 mmol, 1.0 eq.) in 20 mL of ^{t}BuOH, affording, after purification through flash column chromatography using as eluent 20% of AcOEt in hexanes, 76 mg of compound **7c** as a yellow oil and 64 mg of compound **6c** as a yellow oil. Overall yield: **61%**

Compound **7c**: R_f = 0.24 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 326.19747; $[M + H]^+$ calculated for $C_{17}H_{28}NO_5$ 326.19675; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.94 (d, *J* = 6.72 Hz, 3H, $(CH_3)_2CH$), 0.97 (d, *J* = 6.72 Hz, 3H, $(CH_3)_2CH$), 1.17 (t, *J* = 7.15 Hz, 3H, $-OCH_2CH_3$), 1.19 (t, *J* = 7.15 Hz, 3H, $-OCH_2CH_3$), 1.85 (sept, *J* = 7.00 Hz, 1H), 2.26-2.32 (m, 1H, CH_2CO_2Et), 2.34-2.44 (m, 1H), 2.87 (s, 3H, NCH_3), 3.12 (s, 3H, NCH_3), 3.29 (bs, 1H, $CHCONMe_2$), 4.01-4.15 (m, 4H, $-OCH_2CH_3$), 5.87 (dd, J_1 = 6.92 Hz, J_2 = 2.06 Hz, 1H, $(CH_3)_2CH=CHC$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1, 14.2, 21.9, 22.3, 27.0, 30.7, 30.9, 32.9, 60.4, 61.4, 122.5, 128.9, 167.7, 170.9, 171.4;

Compound **6c**: R_f = 0.16 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 388.21518; $[M + H]^+$ calculated for; $C_{19}H_{34}NO_5S$ 388.21577; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 0.86 (d, *J* = 6.72 Hz, 3H, $(CH_3)_2CH$), 0.89 (d, *J* = 6.63 Hz, 3H, $(CH_3)_2CH$), 1.17 (t, *J* = 7.15 Hz, 3H, $-OCH_2CH_3$), 1.19 (t, *J* = 7.15 Hz, 3H, $-OCH_2CH_3$), 1.75 (sept, *J* = 7.00 Hz, 1H, $(CH_3)_2CH$), 2.01 (s, 3H, SCH_3), 1.99-2.10 (m, 1H, CHC=CH), 2.14 (m, 1H), 2.54 (dd, J_1 = 12.85 Hz; J_2 = 9.56 Hz; 1H, SCH_2), 2.64 (dd, J_1 = 12.82 Hz; J_2 = 4.63 Hz; 1H, SCH_2), 2.89 (s, 3H, NCH_3), 3.00 (s, 3H, NCH_3), 3.35 (d, *J* = 15.66 Hz, 1H, $C=CH_2CO_2Et$), 3.43 (d, *J* = 15.66 Hz, 1H, $C=CH_2CO_2Et$), 4.02 (q, *J* = 7.15 Hz, 2H, $-OCH_2CH_3$), 4.05 (q, *J* = 7.15 Hz, 2H, $-OCH_2CH_3$), 5.96 (s, 1H, $=CHCONMe_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.1, 16.4, 20.2, 21.2, 29.9, 35.5, 36.1, 54.4, 60.7, 123.4, 145.0, 167.7, 170.7;

Compound 7d:

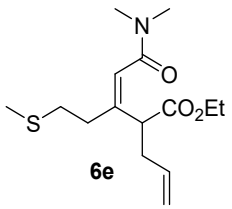


7d

Following the general procedure with: Sulfonium salt **1a** (148 mg, 0.81 mmol, 1.0 eq), allenoate **5d** (222 mg, 0.81 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.81 mL, 0.81 mmol, 1.0 eq.) in 20 mL of ^{t}BuOH, affording, after purification through flash column chromatography, 159 mg of compound **7d** as a yellow oil. Yield: **55%**

Compound **7d**: R_f = 0.35 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 360.18562; $[M + H]^+$ calculated for $C_{20}H_{26}NO_5$ 360.18110; ^{1}H-NMR (500 MHz): 1.22 (t, *J* = 7.09 Hz, 3H, OCH_2CH_3), 1.24 (t, *J* = 7.05 Hz, 3H, OCH_2CH_3), 2.66 (d, *J* = 17.91 Hz, 1H), 2.94 (s, 3H, NCH_3), 3.26 (s, 3H, NCH_3), 3.42 (d, *J* = 17.96 Hz, 1H), 3.59 (d, *J* = 2.05 Hz, 1H), 4.08-4.14 (m, 2H, OCH_2CH_3), 4.18-4.28 (m, 2H, OCH_2CH_3), 6.87 (d, *J* = 2.10 Hz, 1H, PhC*H*=C), 7.23-7.26 (m, 2H, Ph), 7.31-7.32 (m, 3H); ^{13}C-NMR (125 MHz): 14.2, 26.4, 31.6, 32.0, 35.8, 37.9, 60.6, 61.8, 121.9, 125.4, 127.4, 128.0, 128.7, 135.3, 167.4, 170.0, 171.3

Compounds 6e:



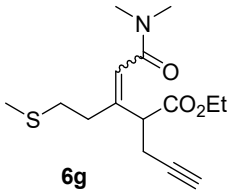
6e

Following the general procedure with: Sulfonium salt **1a** (190 mg, 1.03 mmol, 1.0 eq), allenoate **5e** (157 mg, 1.03 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (1.03 mL, 1.03 mmol, 1.0 eq.) in 18 mL of ^{t}BuOH, affording, after purification through flash column

chromatography, 49 mg of compound **6e** as a colorless oil and 104 mg of a non defined compound as a colorless oil. Overall yield: **50%**

Compound **6e**: R_f = 0.14 (AcOEt-Hex, 1:1). HRMS (ESI) m/z: 300.16348; $[M + H]^+$ calculated for $C_{15}H_{26}NO_3S$ 300.16334; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.17 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H*$_3$), 2.05 (s, 3H, SC*H*$_3$), 2.25-2.41 (m, 3H), 2.49-2.65 (m, 4H), 2.88 (d, *J* = 11.16 Hz, 1H), 2.91 (s, 3H, NC*H*$_3$), 2.97 (s, 3H, NC*H*$_3$), 4.03-4.09 (m, 2H, -OC*H*$_2$CH$_3$), 4.94 (dd, J_1 = 10.18 Hz, J_2 = 1.63 Hz, 1H, CH=C*H*$_2$), 5.02 (ddt, 1H, CH=C*H*$_2$), 5.64-5.76 (m, 1H, C*H*=CH$_2$), 5.95 (s, 1H, =C*H*CONMe$_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (*C*H$_3$CH$_2$O-), 15.6 (S*C*H$_3$), 32.0, 32.4, 34.1, 34.8, 37.8 (N*C*H$_3$), 47.2, 60.7 (-O*C*H$_2$CH$_3$), 116.7 (CH=*C*H$_2$), 122.3 (=*C*HCONMe$_2$), 135.3 (*C*H=CH$_2$), 145.6 (*C*=CHCONMe$_2$), 167.5 (C=O), 172.5 (C=O).

Compound 6g:



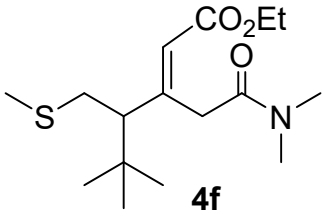
6g

Following the general procedure with: Sulfonium salt **1a** (120 mg, 0.65 mmol, 1.0 eq), allenoate **5g** (98 mg, 0.65 mmol, 1.0 eq.) and 1M solution of ^{t}BuOK (0.65 mL, 0.65 mmol, 1.0 eq.) in 15 mL of ^{t}BuOH, affording, after purification through Isolera Biotage®, 110 mg of compound **6g** as a colorless oil and inseparable mixture of Z/E isomers (ratio: 71/29)**.** Overall yield: **57%**

Compound **6g**: R_f = 0.32 (AcOEt-Hex, 2:3). HRMS (ESI) m/z: 298.14782; $[M + H]^+$ calculated for $C_{15}H_{24}NO_3S$ 298.14769; ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm): 1.18 (t, *J* = 7.15 Hz, 3H, -OCH$_2$C*H*$_3$), 1.89 (t, *J* = 2.65 Hz, 1H, C*H*CO$_2$Et), 1.93-1.96 (m, 1H), 2.06 (s, 3H, SC*H*$_3$), 2.39 (dd, J_1 = 4.63 Hz, J_2 = 2.65 Hz, 1H, C*H*$_2$C≡CH), 2.54-2.63 (m, 3H), 2.90 (d, *J* = 8.51 Hz, 1H), 2.91 (s, 3H, NC*H*$_3$), 2.94 (d, *J* = 8.51 Hz, 1H), 2.99 (s, 3H, NC*H*$_3$), 4.07-4.13 (m, 2H, -OC*H*$_2$CH$_3$), 6.04 (s, 1H, =C*H*CONMe$_2$); ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 14.2 (*C*H$_3$CH$_2$O-), 15.7 (S*C*H$_3$), 19.8 (*C*H$_2$C≡CH), 32.5 (*C*H$_2$C=), 33.1 (S*C*H$_2$), 34.9 (N*C*H$_3$), 37.9 (N*C*H$_3$), 46.6 (*C*HCH$_2$C≡CH), 61.2 (-O*C*H$_2$CH$_3$), 69.9 (C≡*C*H), 81.4 (*C*≡CH), 122.7 (=*C*HCONMe$_2$), 145.5 (*C*=CHCONMe$_2$), 167.1 (C=O), 171.5 (C=O).

X-RAY CRYSTAL STRUCTURE REPORT

Compound **4f**



4f

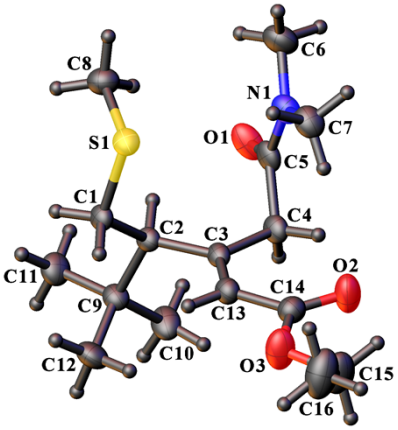


Figure Captions

1. *ORTEP*[1] representation of the molecule (50% probability ellipsoids; H-atoms given arbitrary displacement parameters for clarity)

Definition of Terms

Function minimized: $\Sigma w(F_o^2 - F_c^2)^2$

where $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$

$F_o^2 = S(C - RB)/Lp$

and $\sigma^2(F_o^2) = S^2(C + R^2B)/Lp^2$

S = Scan rate

C = Total integrated peak count

R = Ratio of scan time to background counting time

B = Total background count

Lp = Lorentz-polarization factor

R-factors: $R_{int} = \Sigma|<F_o^2> - F_o^2|/\Sigma F_o^2$ summed only over reflections for which more

than one symmetry equivalent was measured.

$R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ summed over all observed reflections.

$wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ summed over all reflections.

Standard deviation of an observation of unit weight (goodness of fit):

$[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$

where N_o = number of observations; N_v = number of variables

NOTES

The structure of $C_{16}H_{29}NO_3S$ (compound **4f′**) has been solved and refined successfully with no unusual features. Since the space group is centrosymmetric, the compound in the crystal is racemic. The crystal was cut from a large irregular lump, but was not of very high quality and consequently the overall quality of the data and results is slightly suboptimal.

EXPERIMENTAL

Crystal-Structure Determination. – A crystal of $C_{16}H_{29}NO_3S$, obtained from EtOAc / $CHCl_3$, was mounted on a cryo-loop and used for a low-temperature X-ray structure determination. All measurements were made on a *Rigaku Oxford Diffraction SuperNova* area-detector diffractometer[2] using Cu $K\alpha$ radiation (λ = 1.54184 Å) from a micro-focus X-ray source and an *Oxford Instruments Cryojet XL* cooler. The unit cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 8196 reflections in the range $6° < 2\theta < 146°$. A total of 2554 frames were collected using ω scans with κ offsets, 3.5-15.0 seconds exposure time and a rotation angle of 1.0° per frame, and a crystal-detector distance of 55.0 mm.

Data reduction was performed with *CrysAlisPro*[2]. The intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction[3] was applied. The space group was determined from packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure. Equivalent reflections were merged. The data collection and refinement parameters are given in *Table 1*. A view of the molecule is shown in the *Figure*.

The structure was solved by dual space methods using *SHELXT-2018*[4], which revealed the positions of all non-hydrogen atoms. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent atom ($1.5U_{eq}$ for the methyl groups). The refinement of the structure was carried out on F^2 by using full-

matrix least-squares procedures, which minimised the function $\Sigma w(F_o^2 - F_c^2)^2$. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\Sigma w(F_o^2 - F_c^2)^2$ versus $F_c/F_c(\max)$ and resolution showed no unusual trends. A correction for secondary extinction was not applied. Three reflections, whose intensities were considered to be extreme outliers, were omitted from the final refinement.

Neutral atom scattering factors for non-hydrogen atoms were taken from Maslen, Fox and O'Keefe[5a], and the scattering factors for H-atoms were taken from Stewart, Davidson and Simpson[6]. Anomalous dispersion effects were included in F_c[7]; the values for f' and f'' were those of Creagh and McAuley[5b]. The values of the mass attenuation coefficients are those of Creagh and Hubbel[5c]. The *SHELXL-2018* program[8] was used for all calculations.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) NV2222

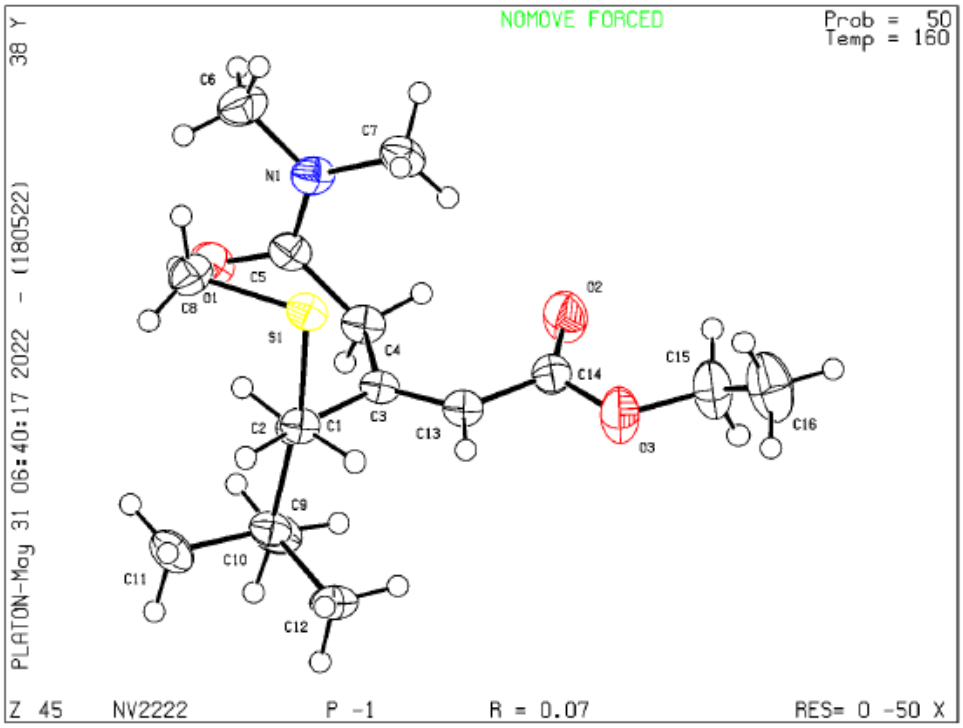
THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: NV2222

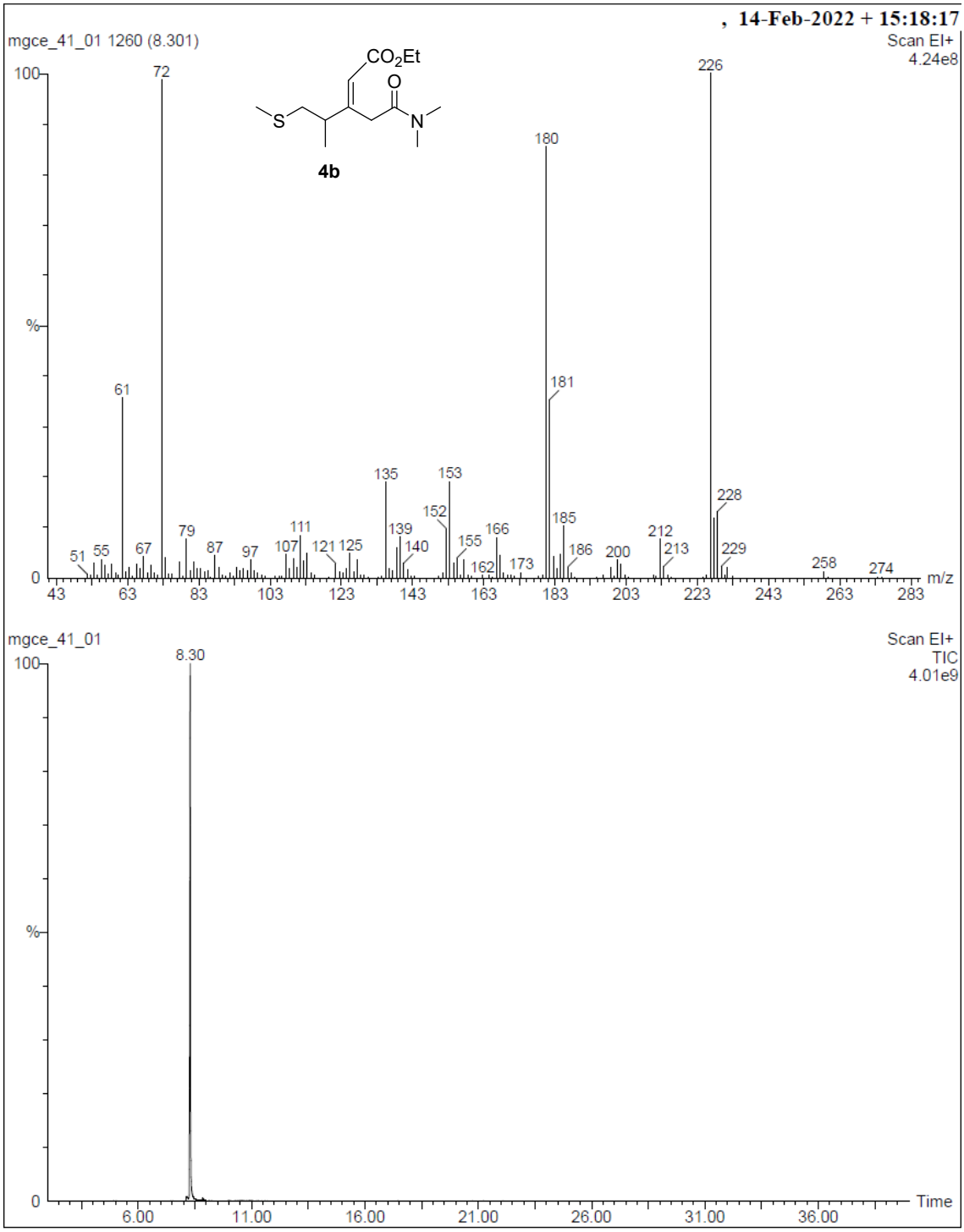
```
Bond precision:   C-C = 0.0031 A          Wavelength=1.54184

Cell:           a=7.4240(3)        b=8.9236(4)       c=14.0704(6)
                alpha=104.564(4)   beta=99.048(3)    gamma=94.974(4)
Temperature:    160 K

                 Calculated                Reported
Volume           883.16(7)                 883.16(7)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C16 H29 N O3 S            C16 H29 N O3 S
Sum formula      C16 H29 N O3 S            C16 H29 N O3 S
Mr               315.46                    315.46
Dx,g cm-3        1.186                     1.186
Z                2                         2
Mu (mm-1)        1.701                     1.701
F000             344.0                     344.0
F000'            345.56
h,k,lmax         9,11,17                   9,10,17
Nref             3533                      3448
Tmin,Tmax        0.767,0.934               0.637,1.000
Tmin'            0.724

Correction method= # Reported T Limits: Tmin=0.637 Tmax=1.000
AbsCorr = GAUSSIAN

Data completeness= 0.976          Theta(max)= 73.140

R(reflections)= 0.0653( 3058)                    wR2(reflections)=
                                                 0.1783( 3445)
S = 1.080                 Npar= 197
```

Datablock NV2222 - ellipsoid plot

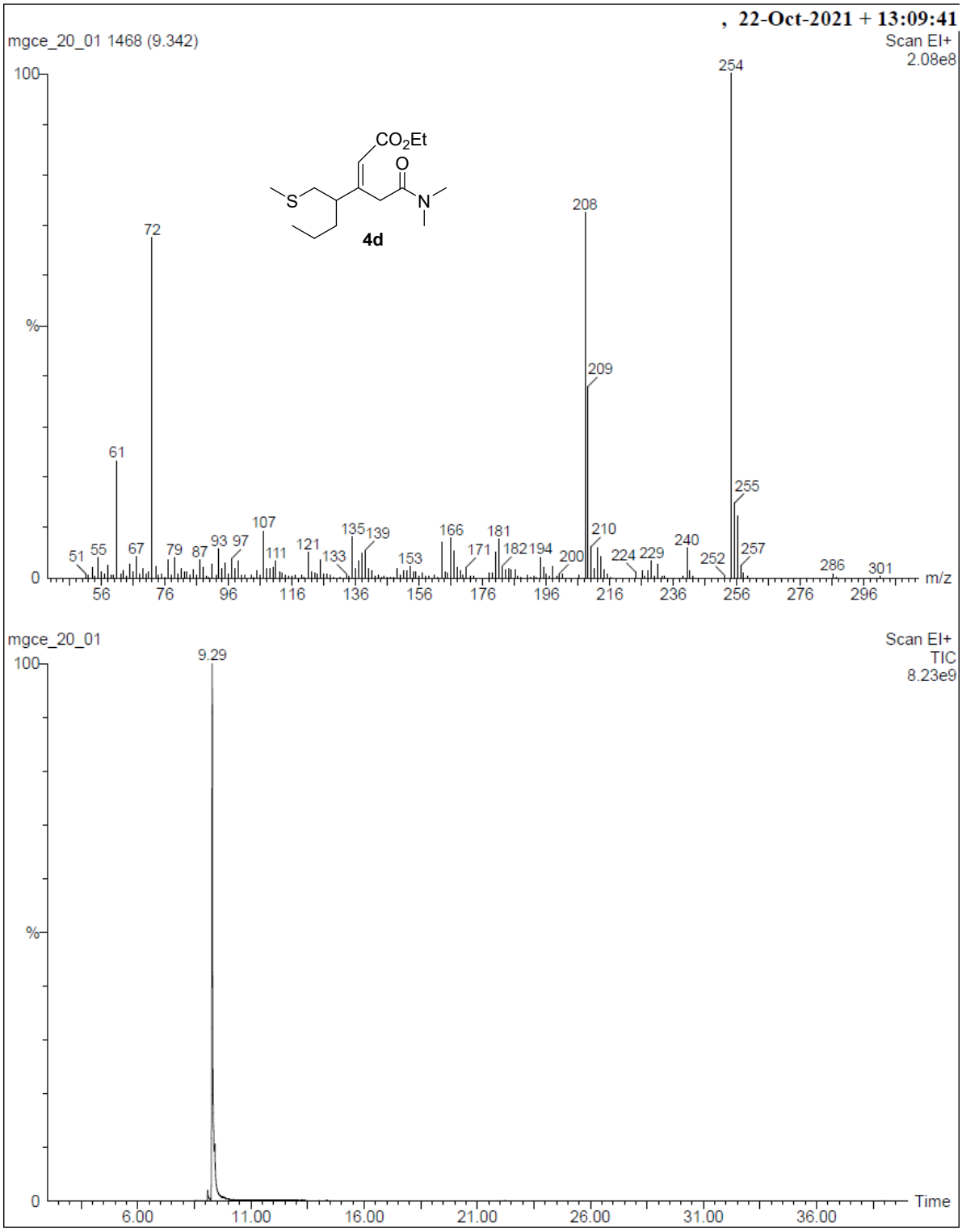


CIF Structure of compound 4f

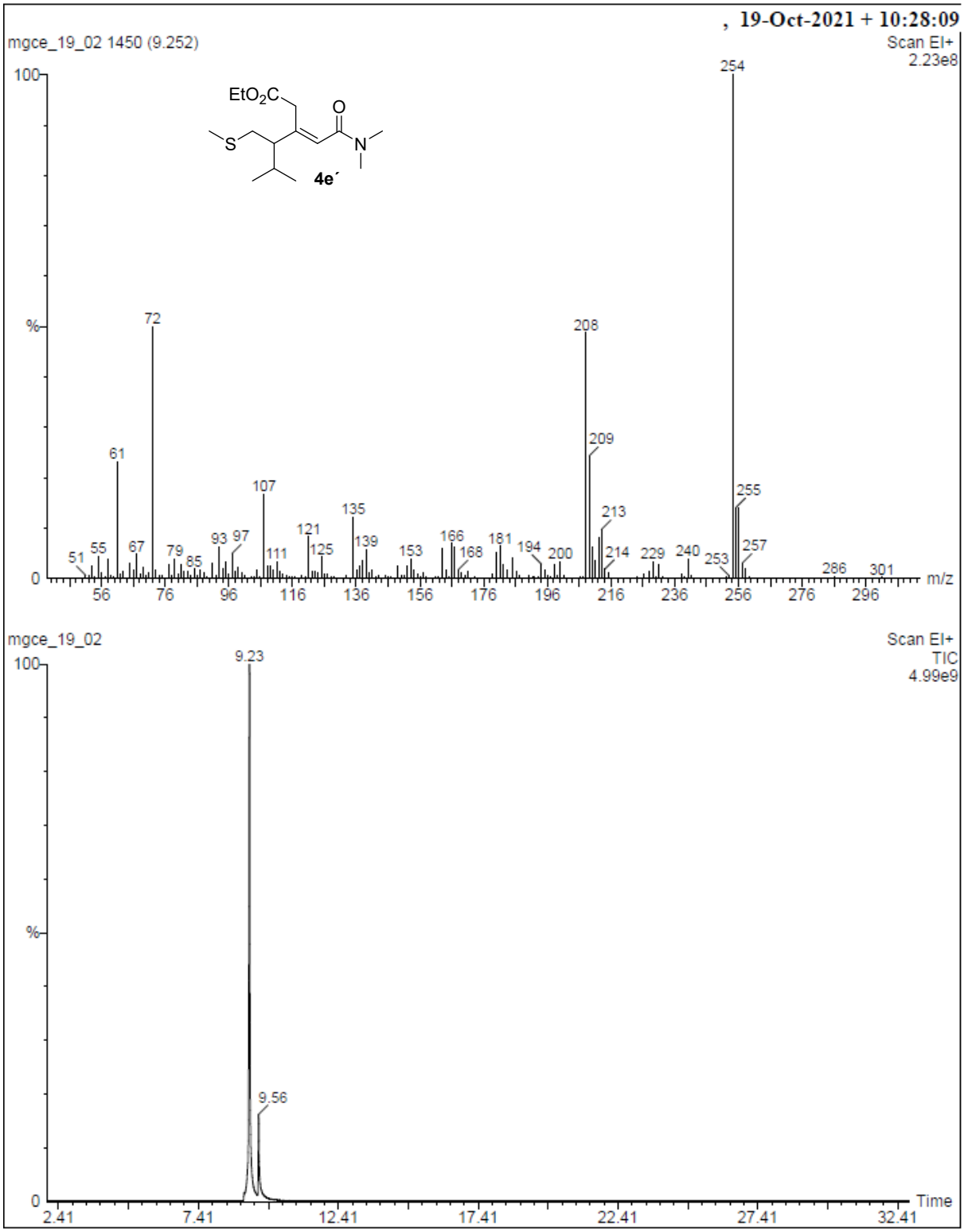
Selected GC-MS spectra



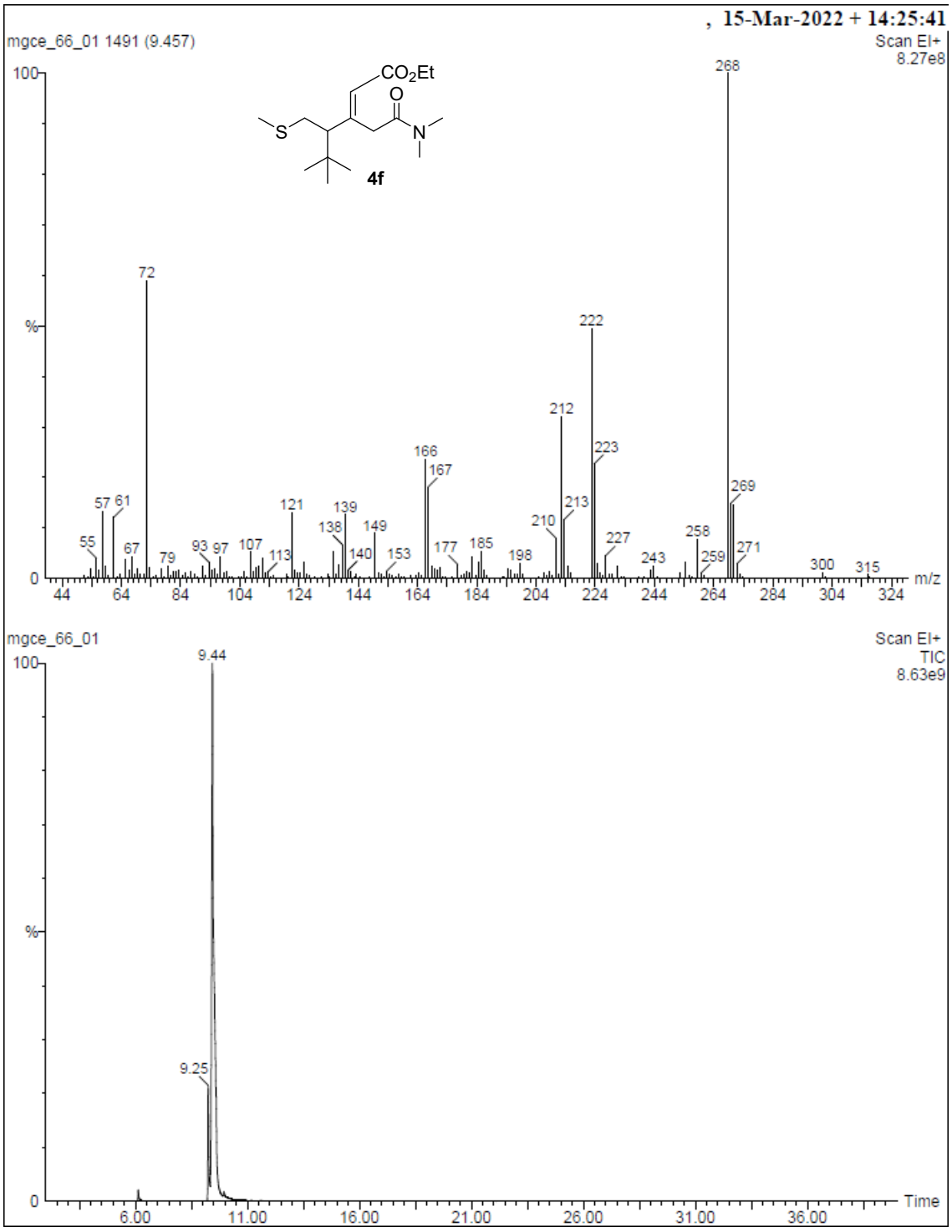
Gas Chromatography-Mass Spectrometry of compound **4b**



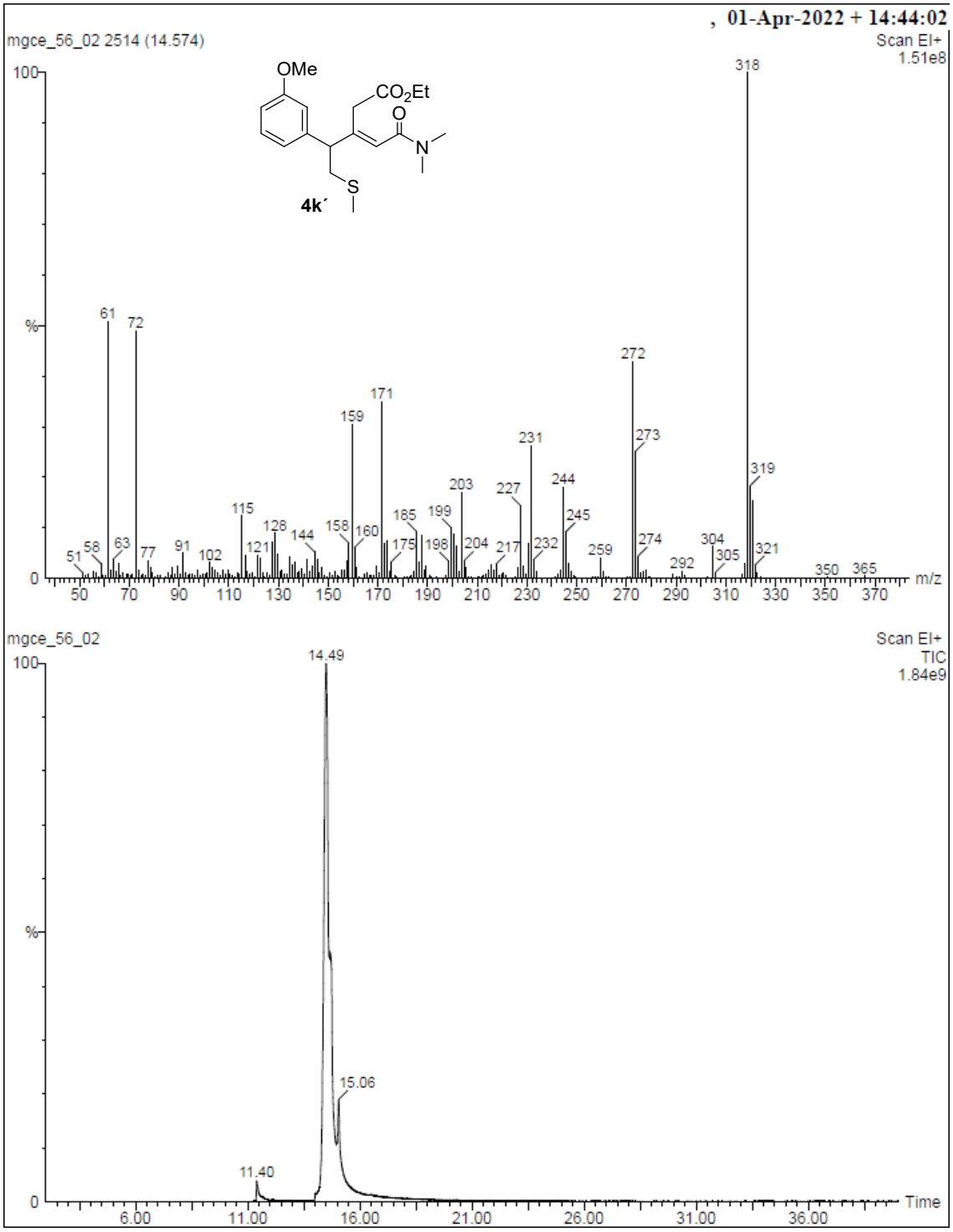
Gas Chromatography-Mass Spectrometry of compound **4d**



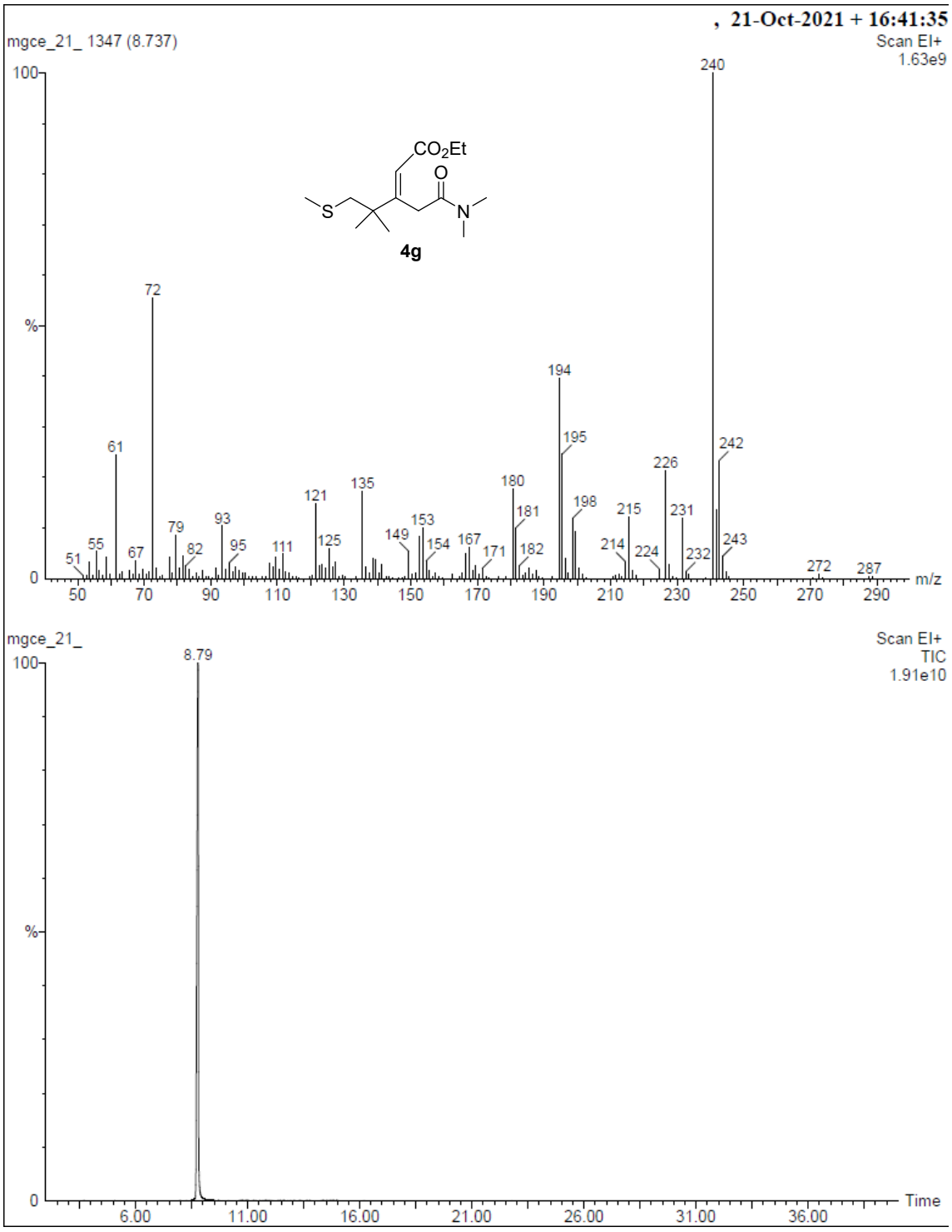
Gas Chromatography-Mass Spectrometry of compound **4e´**



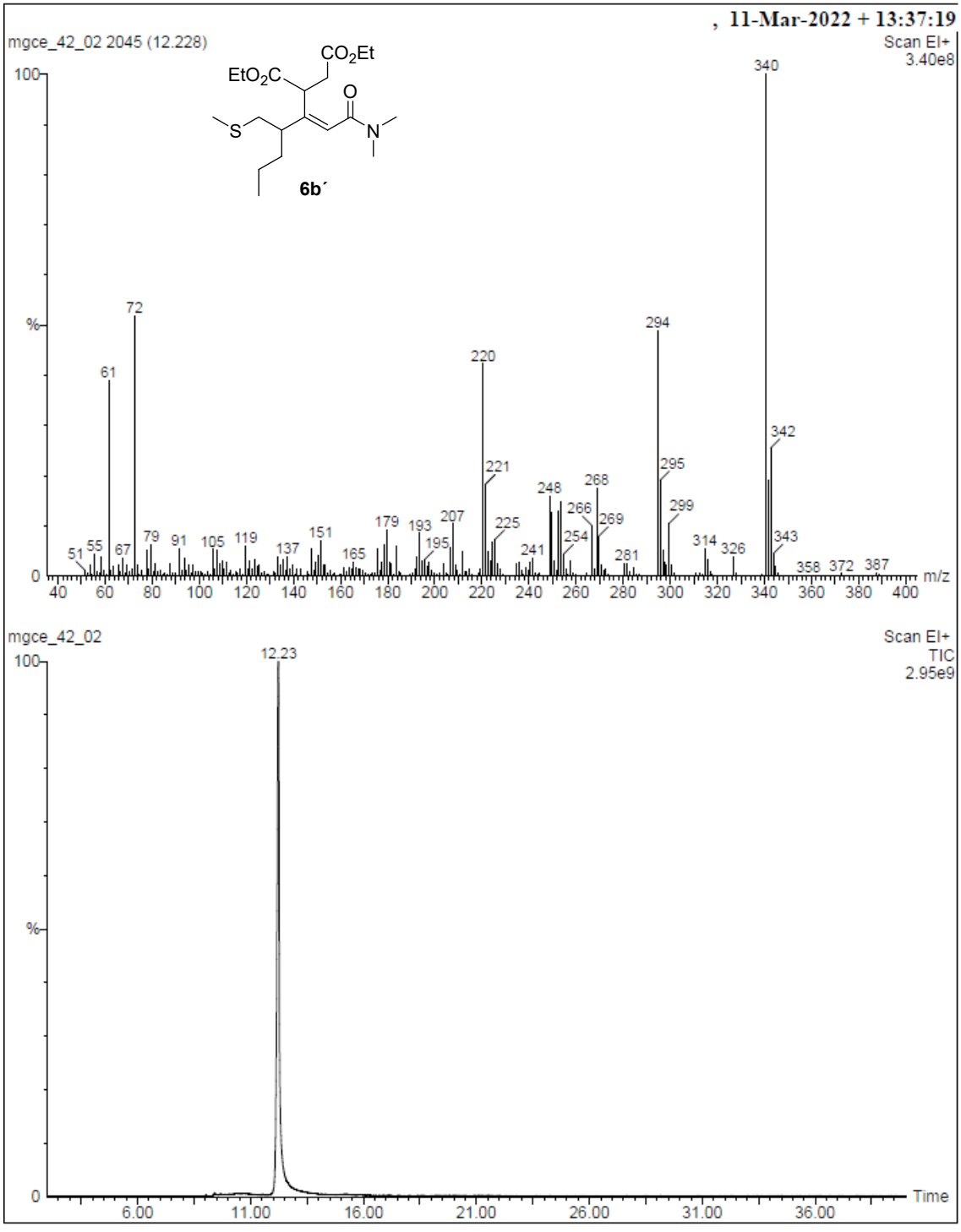
Gas Chromatography-Mass Spectrometry of compound **4f**



Gas Chromatography-Mass Spectrometry of compound **4k´**



Gas Chromatography-Mass Spectrometry of compound **4g**

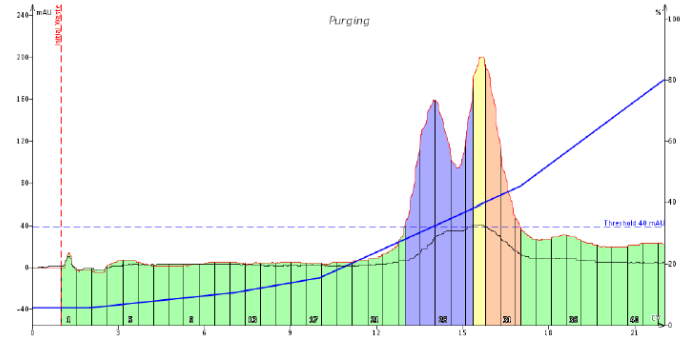


Gas Chromatography-Mass Spectrometry of compound **6b´**

Selected examples of Isolera Prime Biotage® Purifications

Biotage **Isolera™ Prime Archive Report - 2022-Feb-24 17.39** 1.

User	Chemist		
Sample Name	2022-Feb-24 17.39		
Date	2022-Feb-24 18.00		
Method	Miguel 4		
Cartridge	Sfar HC Duo 10g	**Detection Mode**	UV1+UV2
Flowrate	40 ml/min	**UV1 (Collection)**	254 nm (Red)
Solvent A	n-Hexane	**UV2 (Collection)**	280 nm (Black)
Solvent B	Ethyl acetate	**Collect All**	On
		Start Threshold	40 mAU
Rack Type	13x100 mm		
Max Fraction Volume	8 ml		
Dispense Order	Z		
Initial Waste	1 CV		



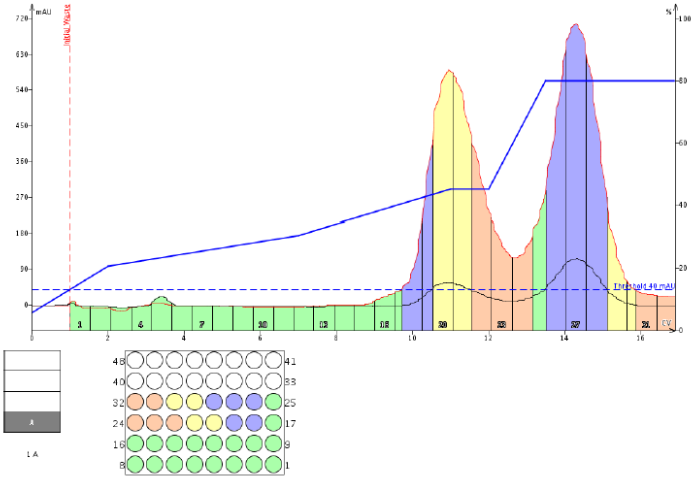
Gradient

	Solvents	Mix	Length (CV)	
Equil.	A/B	5%	2.0	flowrate 40 ml/min
1	A/B	5%	2.0	
2	A/B	5% - 10%	5.0	
3	A/B	10% - 15%	3.0	
4	A/B	15% - 45%	7.0	
5	A/B	45% - 80%	5.0	

Effective separation of compounds **4d/4d´**

Biotage **Isolera™ Prime Fractions Report 2022-Feb-23 13.21** 1.

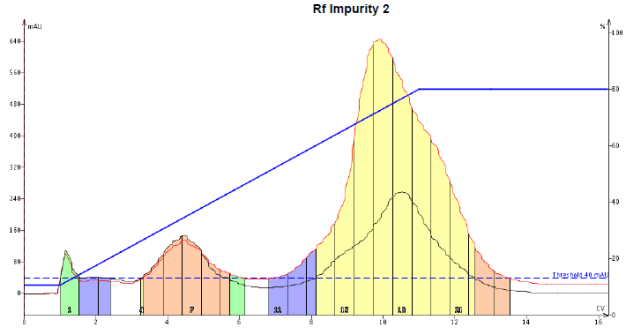
User	Chemist	**Cartridge**	Sfar HC Duo 10g
Sample Name	2022-Feb-23 13.21	**Rack Type**	13x100 mm
Date	2022-Feb-23 13.26	**Max Fraction Volume**	8 ml
Method	MGC_66	**Solvent A**	n-Hexane
Detection Mode	UV1+UV2	**Solvent B**	Ethyl acetate
UV1 (Collection)	254 nm (Red)		
UV2 (Collection)	280 nm (Black)		



Effective separation of compounds **4f/4f´**

Biotage **Isolera™ Prime Archive Report - MGC_49** 1.

User	Chemist		
Sample Name	MGC_49		
Date	2021-Dec-22 11.44		
Method			
Cartridge	Sfar HC Duo 10g	**Detection Mode**	UV1+UV2
Flowrate	40 ml/min	**UV1 (Collection)**	254 nm (Red)
Solvent A	n-Hexane	**UV2 (Collection)**	280 nm (Black)
Solvent B	Ethyl acetate	**Start Threshold**	40 mAU
Rack Type	13x100 mm	**Solvent Condition**	40%
Max Fraction Volume	8 ml	**Rf Product**	0.18
Dispense Order	Z	**Rf Impurity 1**	0.25
		Rf Impurity 2	



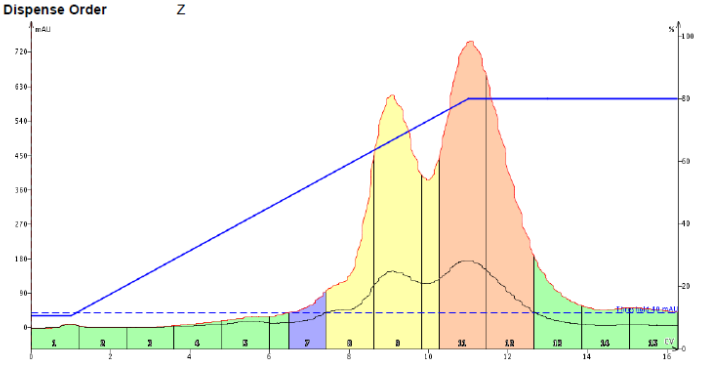
Gradient

	Solvents	Mix	Length (CV)	
Equil.	A/B	10%	2.0	flowrate 40 ml/min
1	A/B	10%	1.0	
2	A/B	10% - 80%	10.0	
3	A/B	80%	2.0	
4	A/B	80%	3.2	Auto Extend

Effective separation of compounds **4h/4h´**

Biotage **Isolera™ Prime Archive Report - MGC-54** 1.

User	Chemist		
Sample Name	MGC-54		
Date	2021-Dec-16 11.47		
Method	Miguel1		
Cartridge	Sfar Duo 10g	**Detection Mode**	UV1+UV2
Flowrate	40 ml/min	**UV1 (Collection)**	254 nm (Red)
Solvent A	n-Hexane	**UV2 (Collection)**	280 nm (Black)
Solvent B	Ethyl acetate	**Collect All**	On
		Start Threshold	40 mAU
Rack Type	16x150 mm		
Max Fraction Volume	18 ml		
Dispense Order	Z		

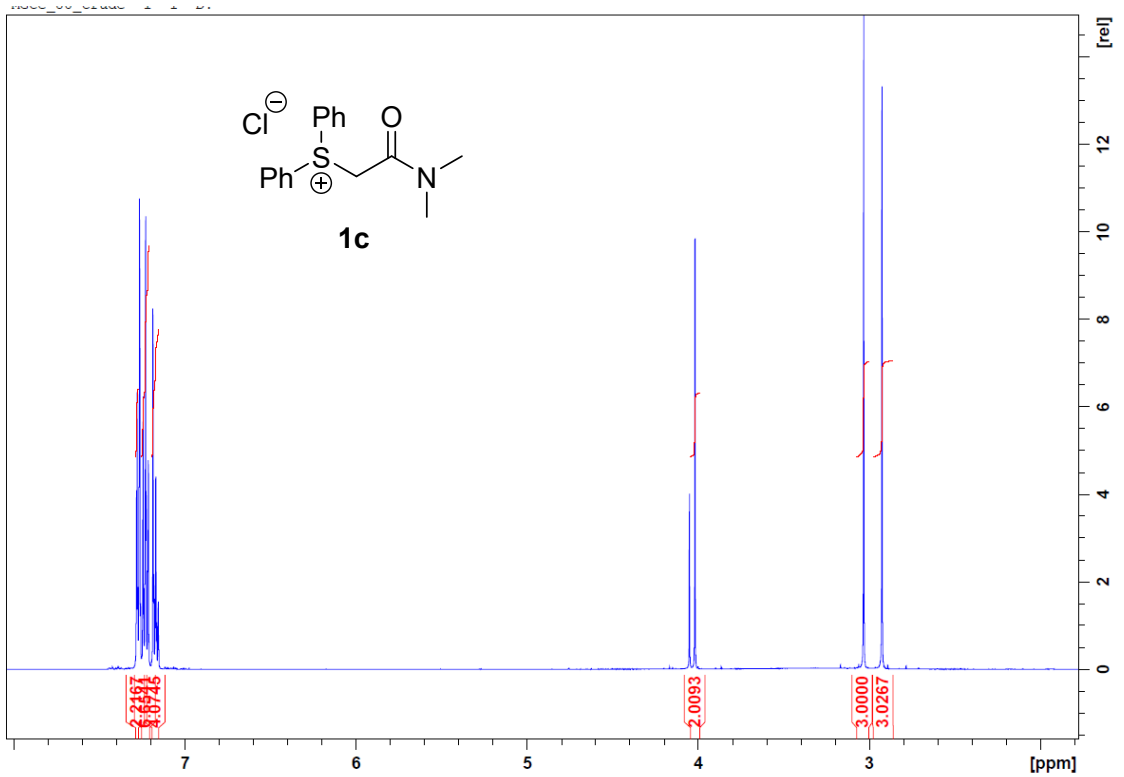


Gradient

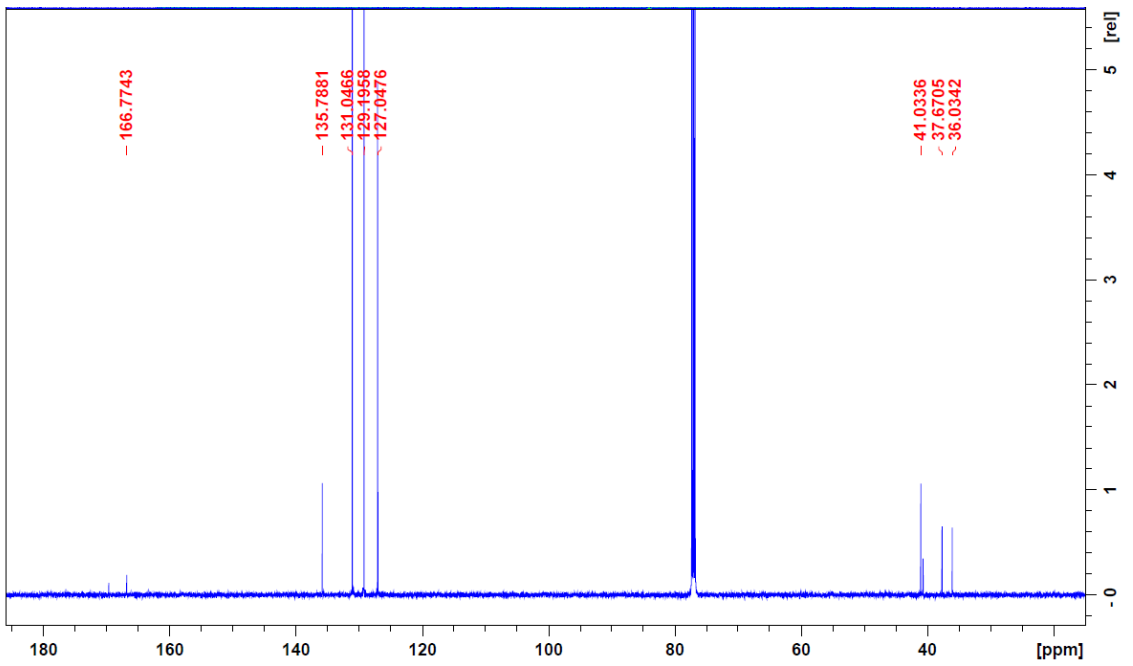
	Solvents	Mix	Length (CV)	
Equil.	A/B	10%	2.0	flowrate 40 ml/min
1	A/B	10%	1.0	
2	A/B	10% - 80%	10.0	
3	A/B	80%	2.0	
4	A/B	80%	3.2	Auto Extend

Effective separation of compounds **4i/4i´**

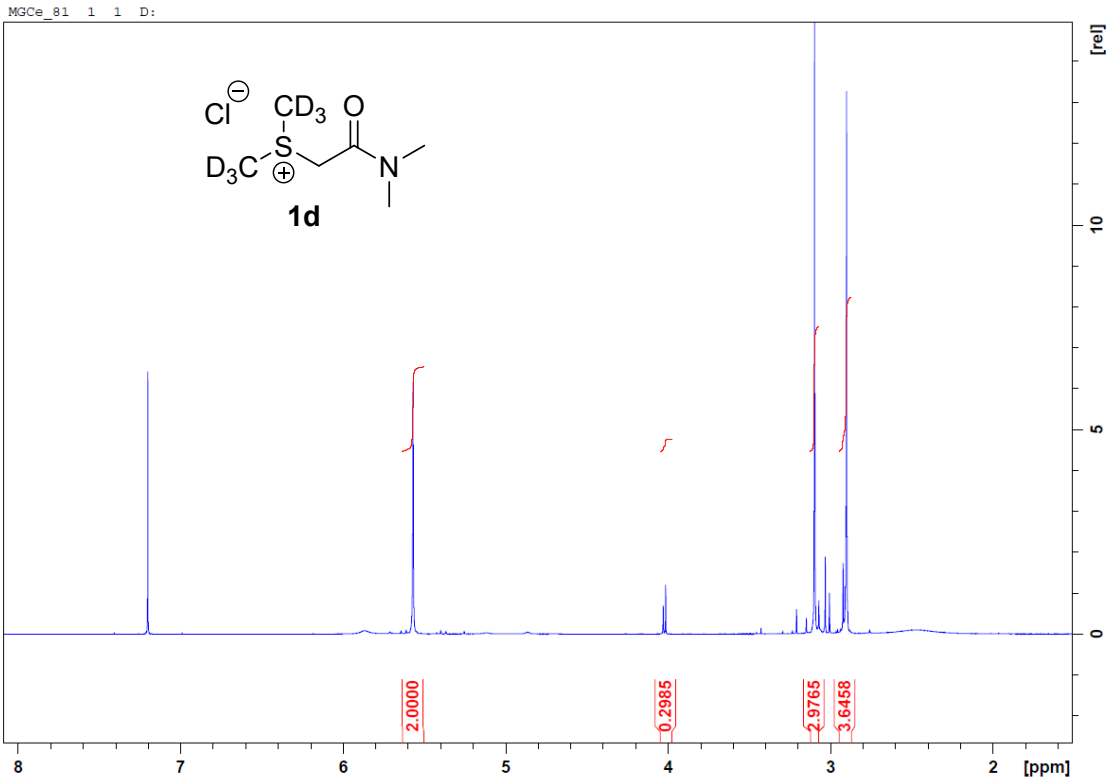
NMR Spectra



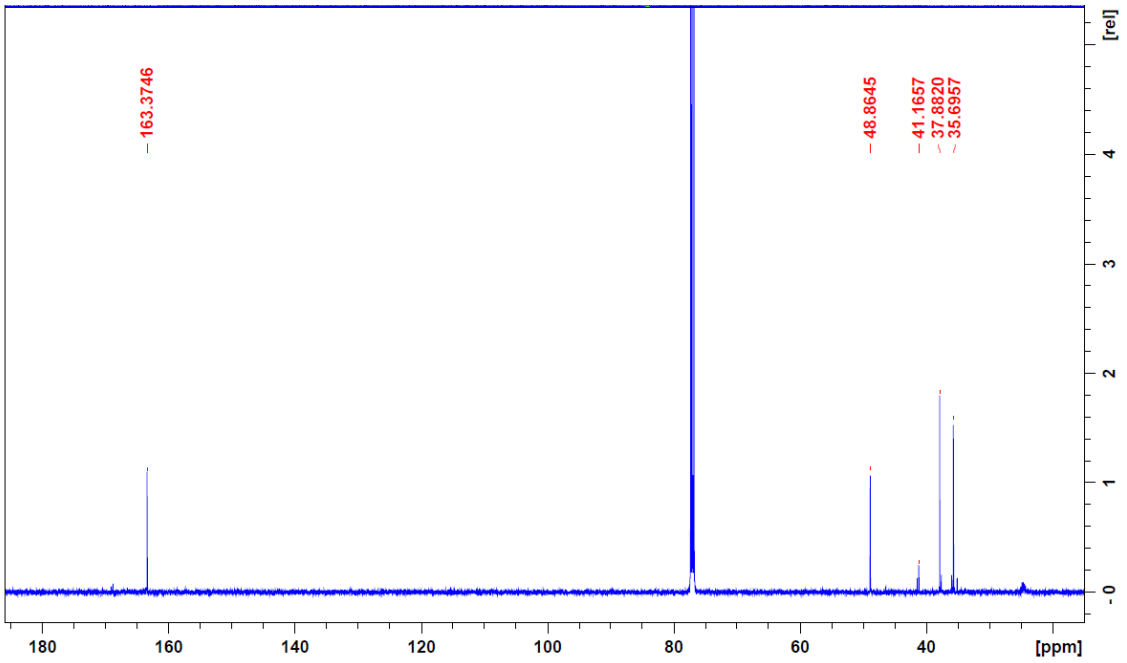
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **1c**



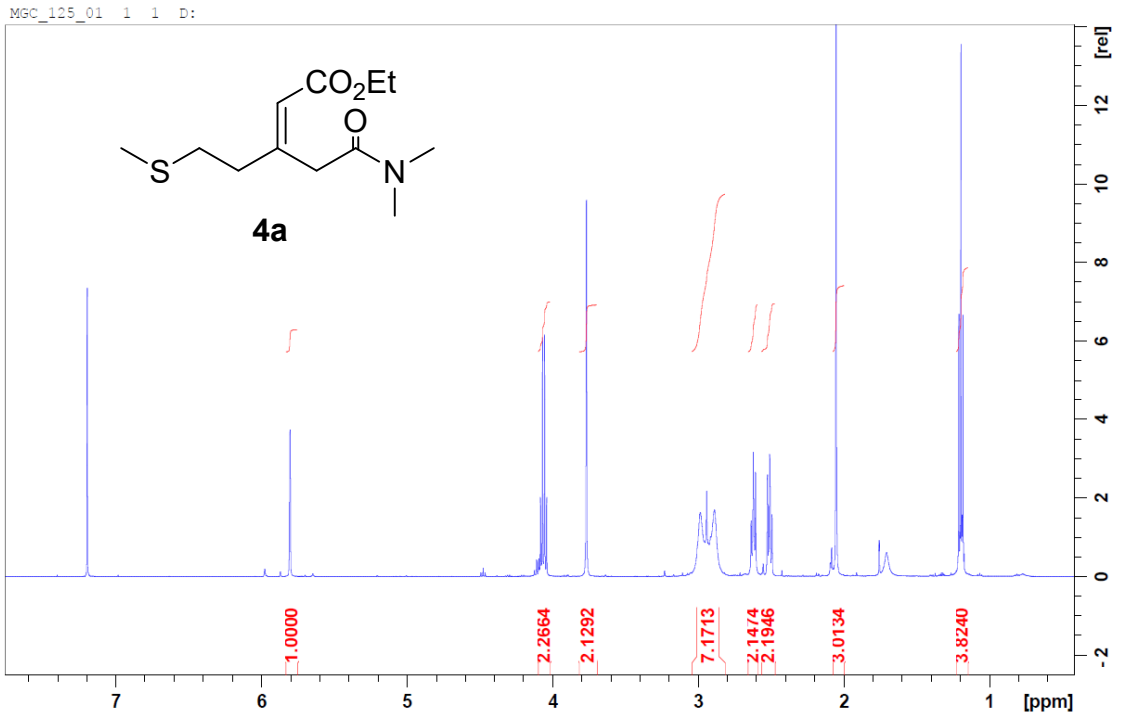
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **1c**



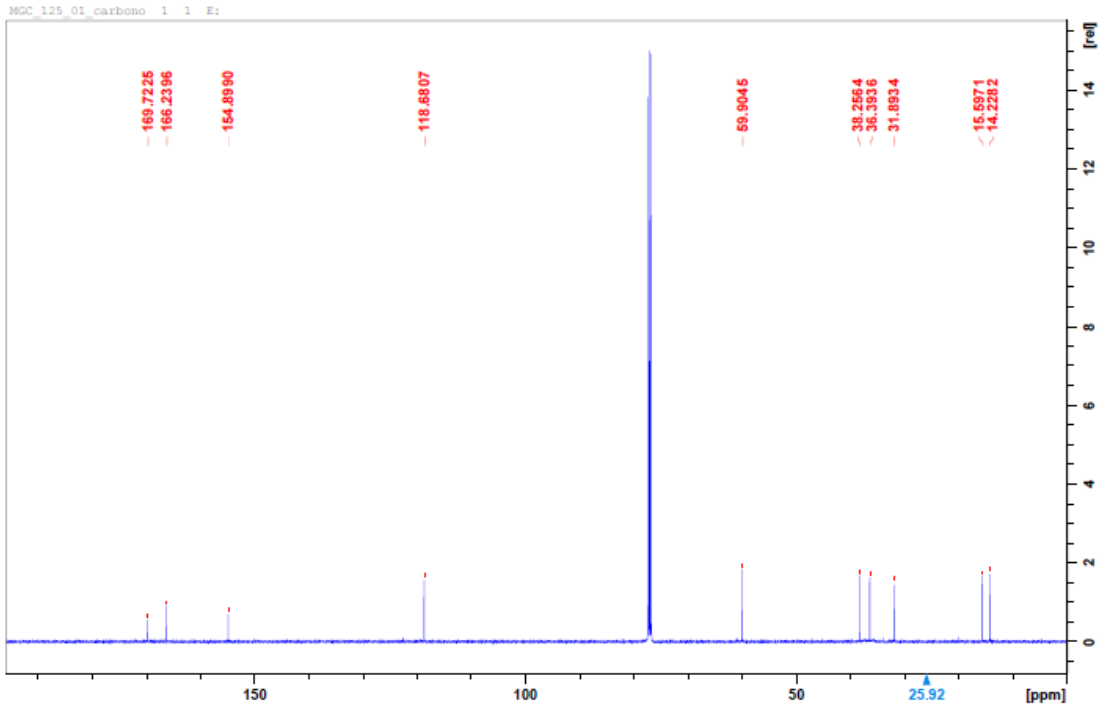
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **1d**



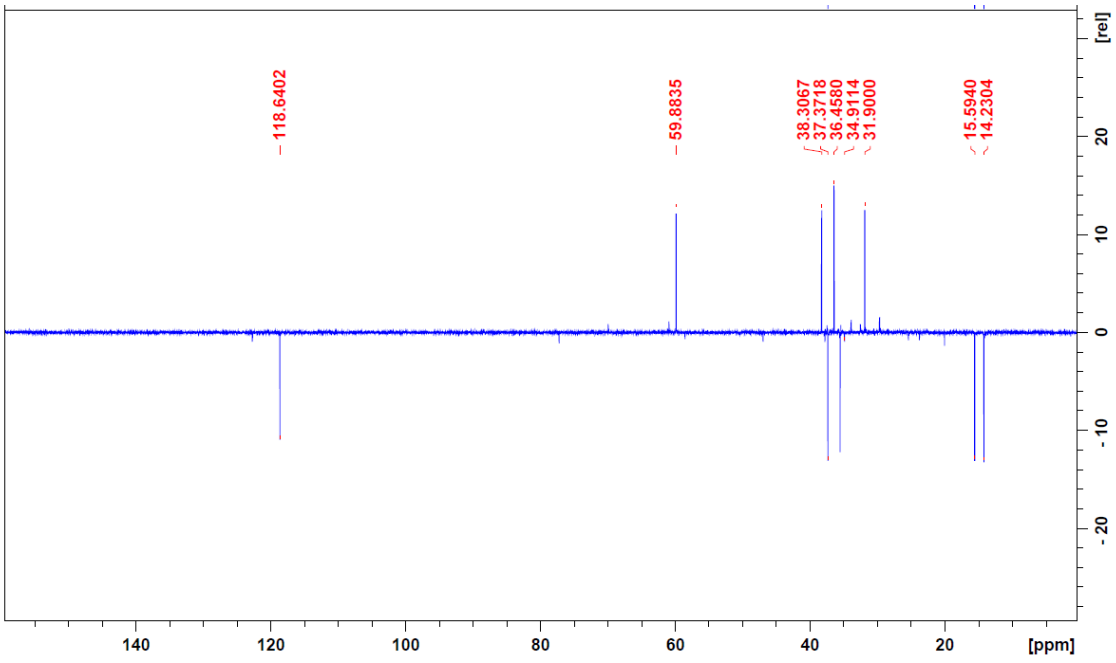
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **1d**



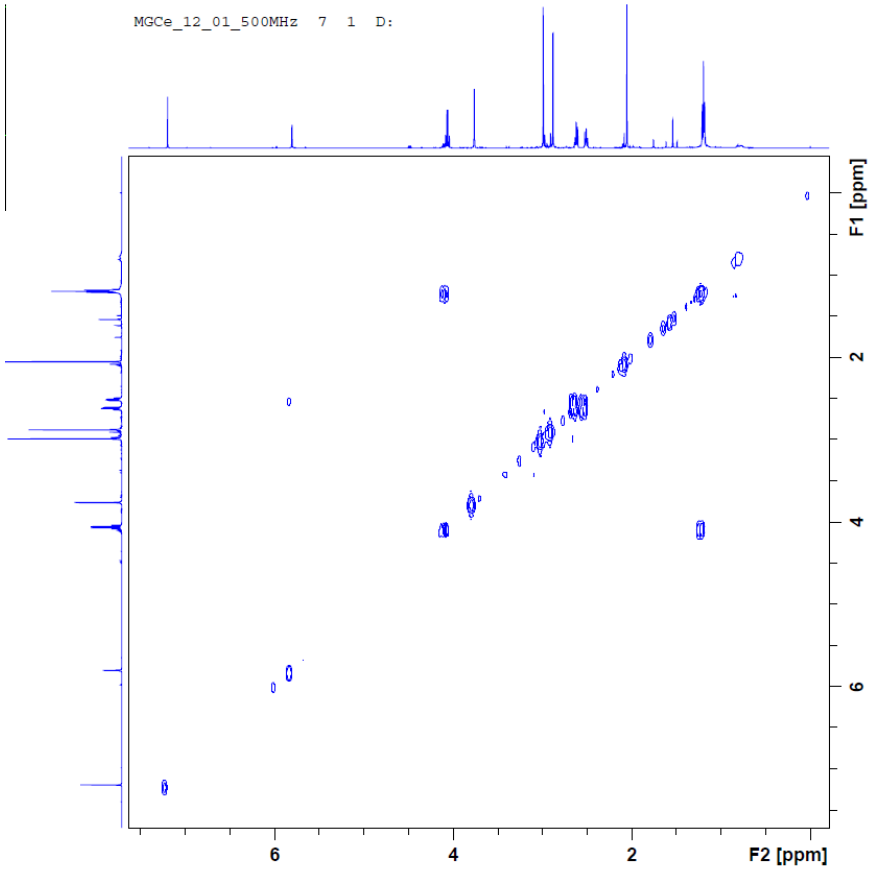
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4a**



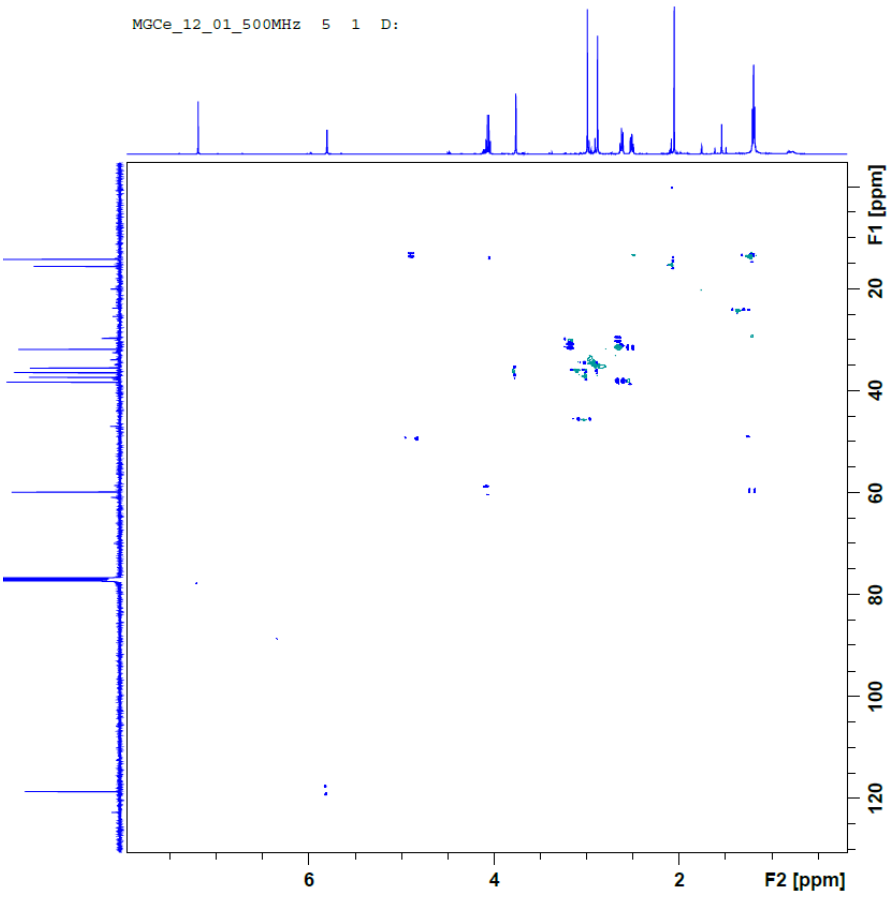
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4a**



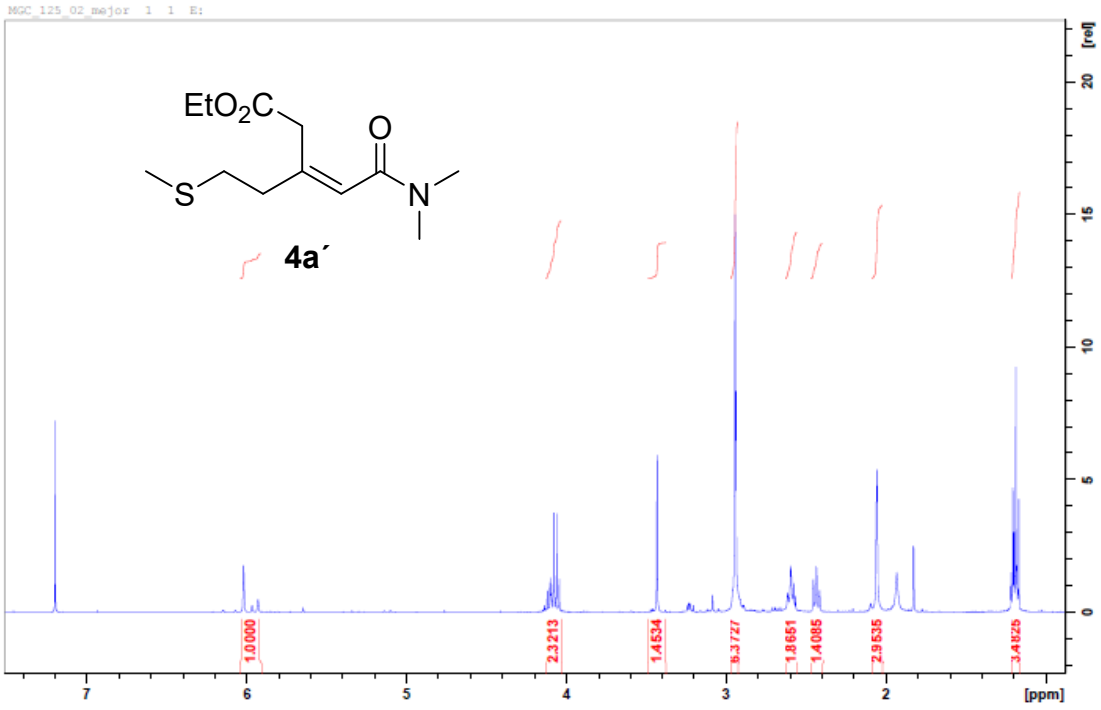
DEPT-135-NMR ($CDCl_3$) of compound **4a**



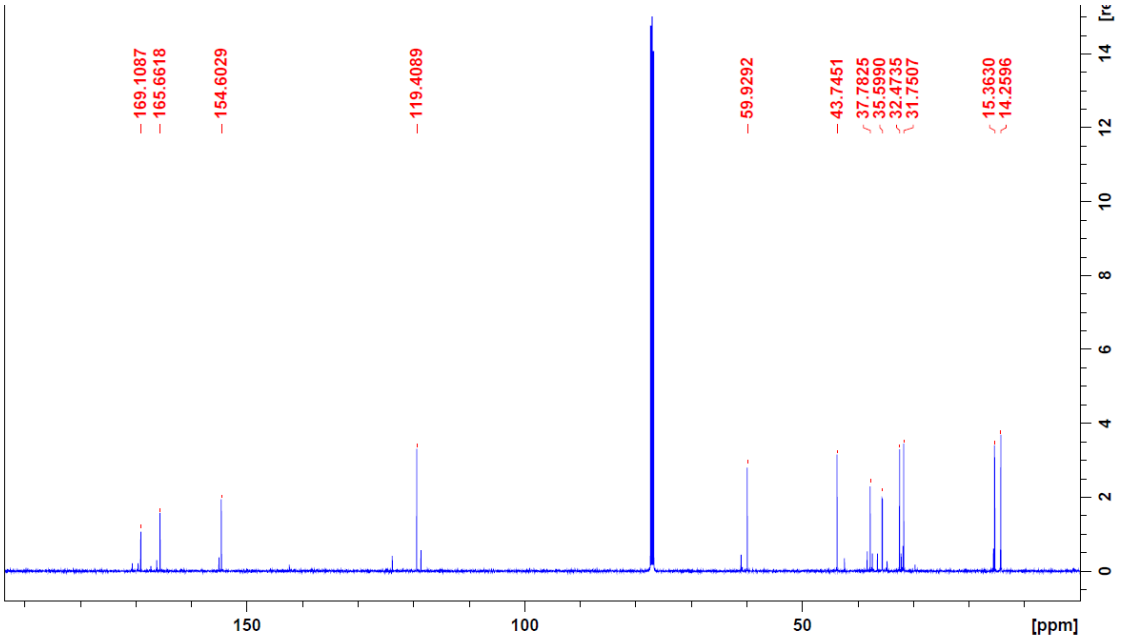
Bidimensional COSY-experiment of compound **4a**



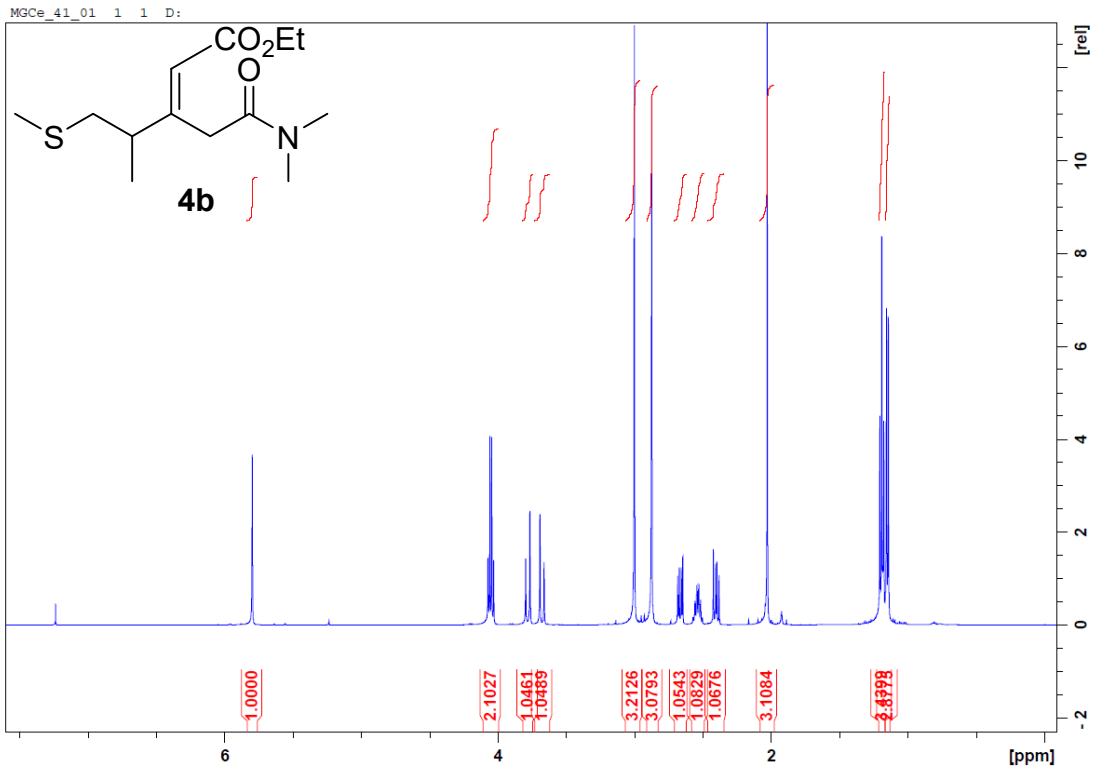
Bidimensional HSQC-experiment of compound **4a**



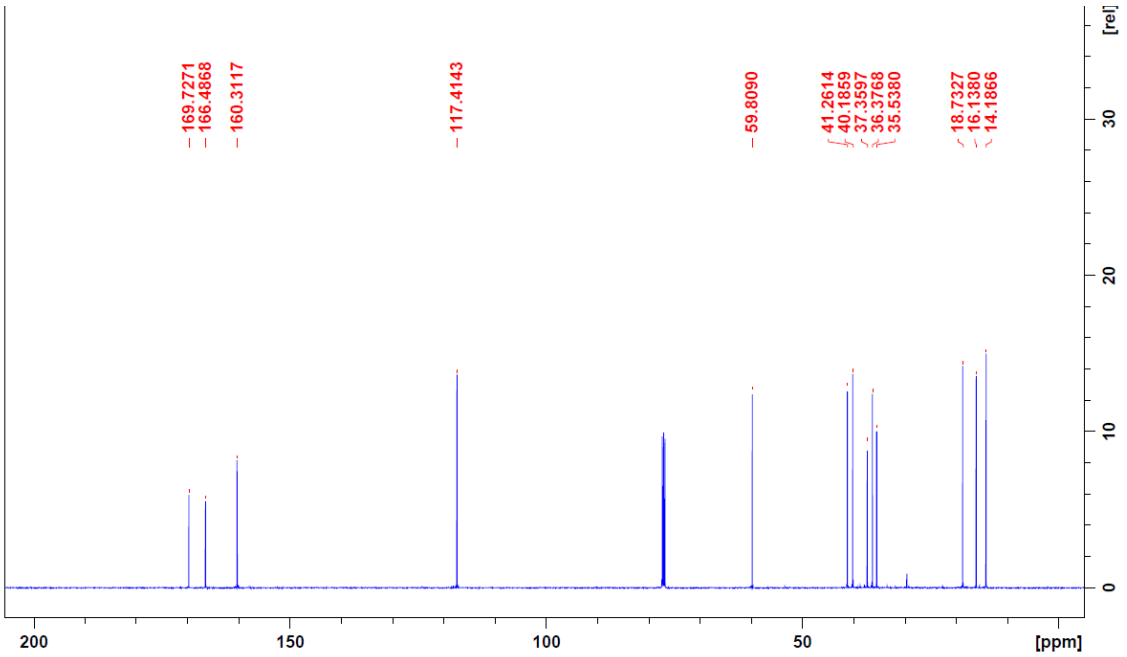
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4a´**



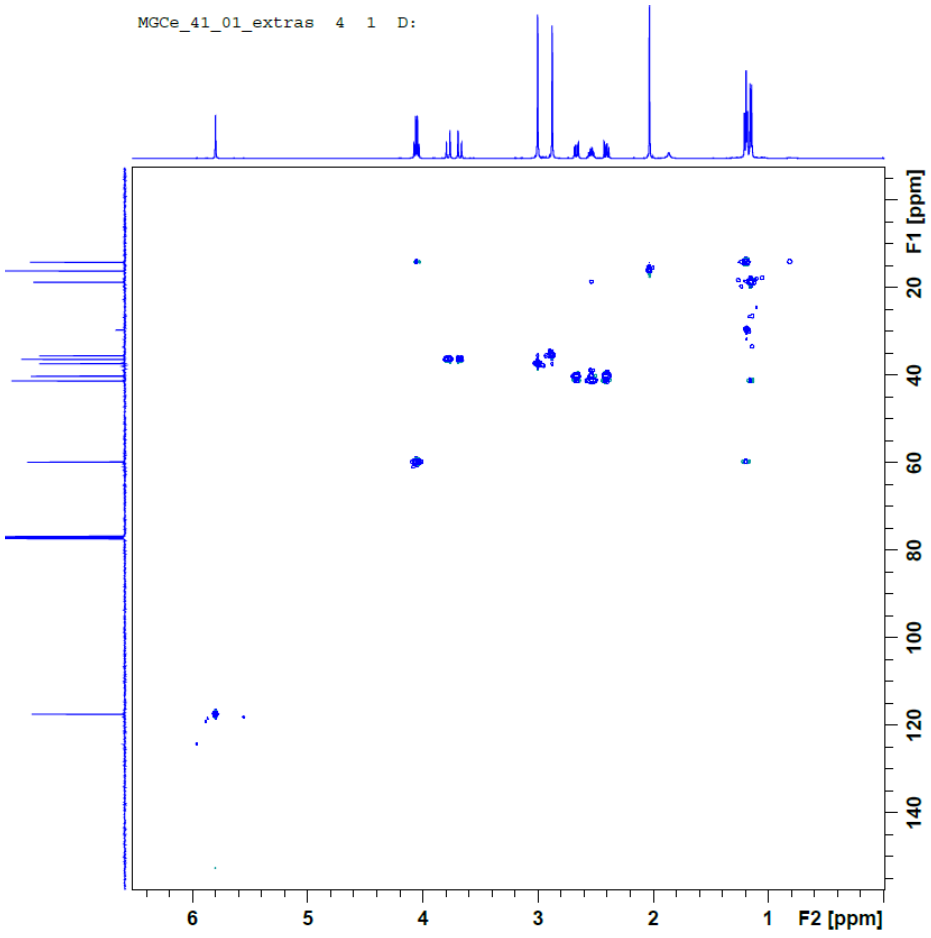
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4a´**



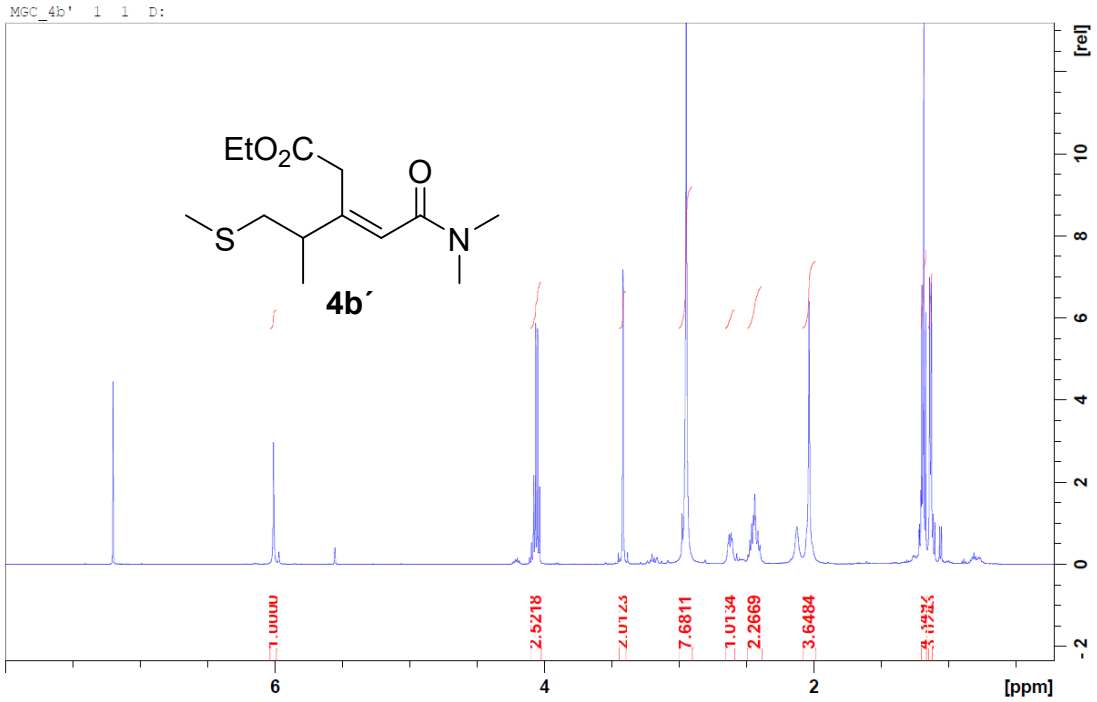
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4b**



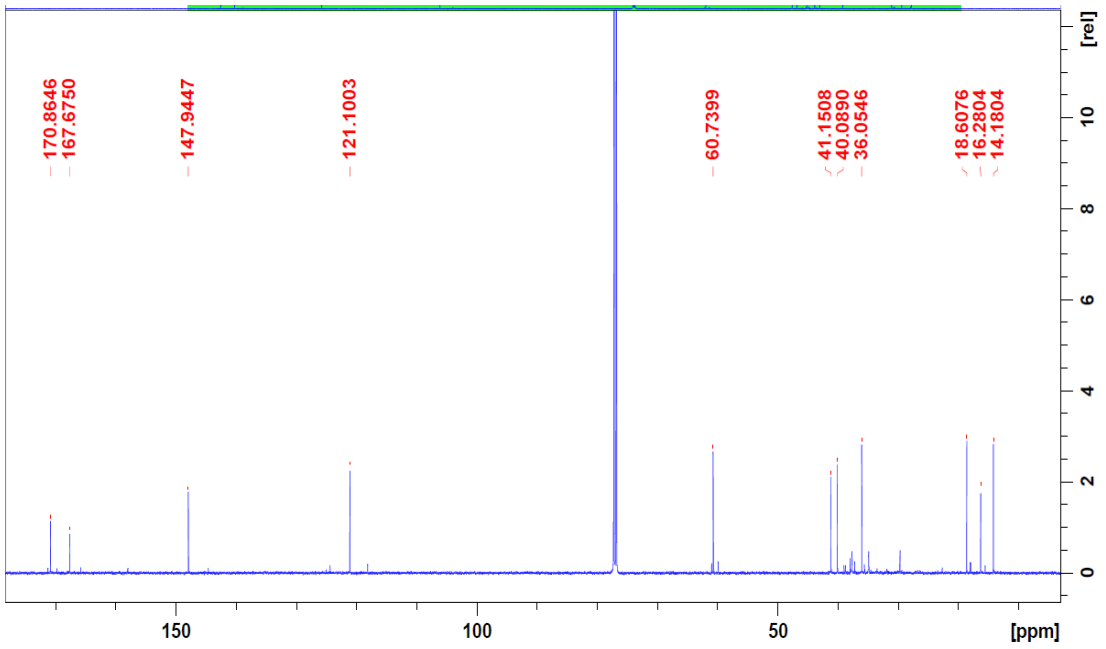
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4b**



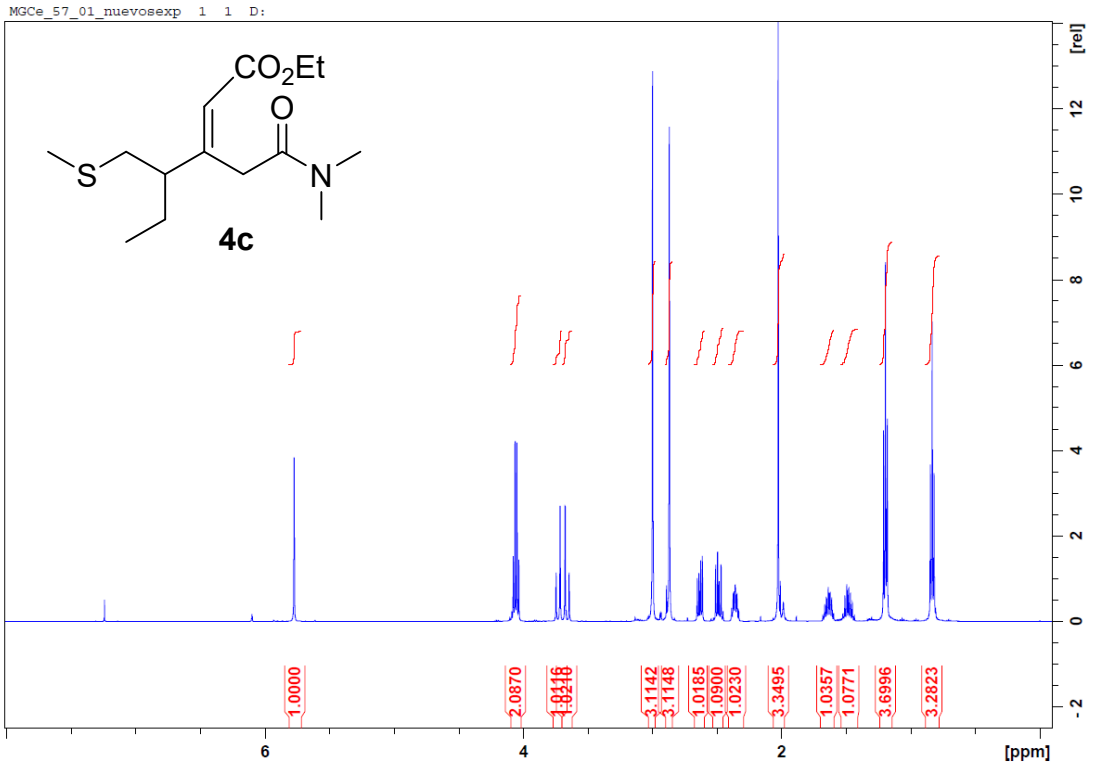
Bidimensional HSQC-experiment of compound **4b**



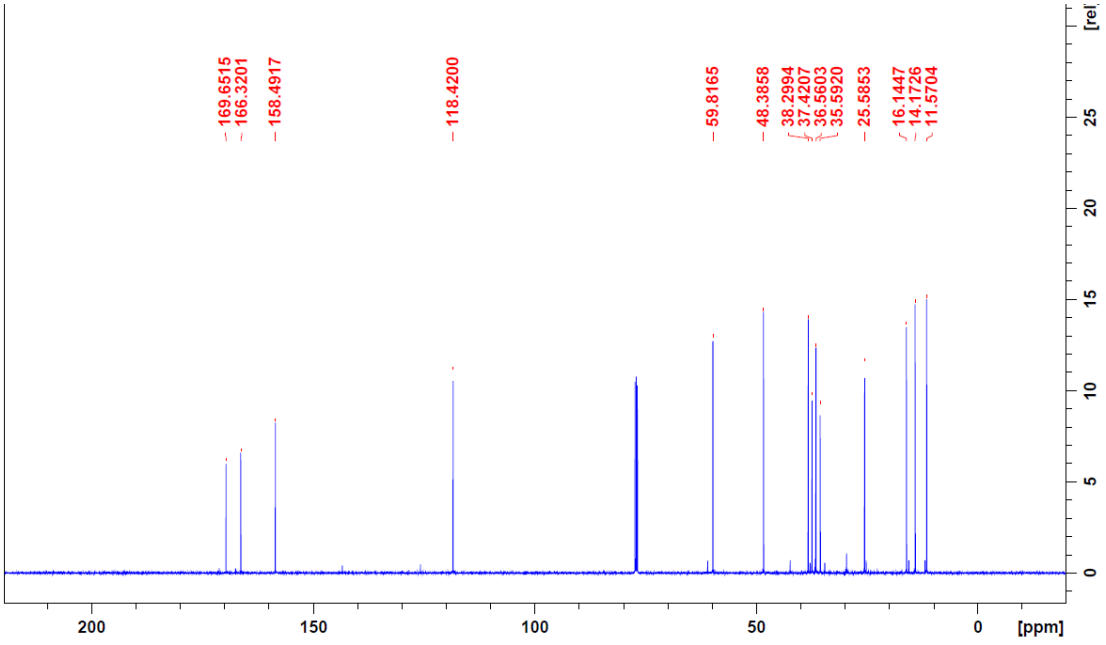
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4b´**



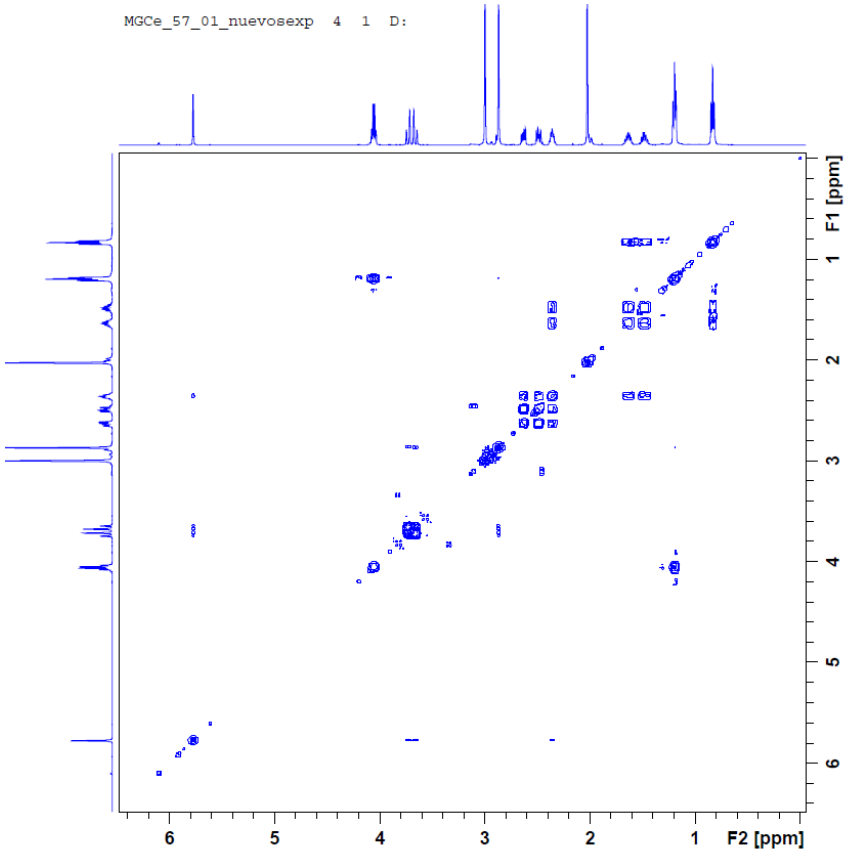
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4b´**



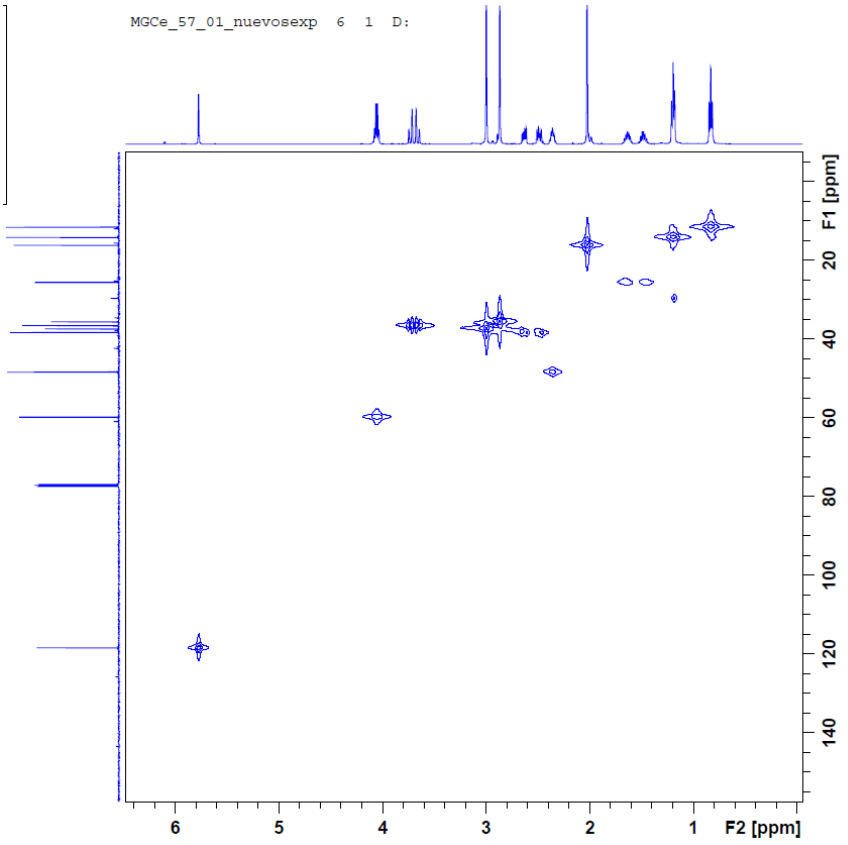
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4c**



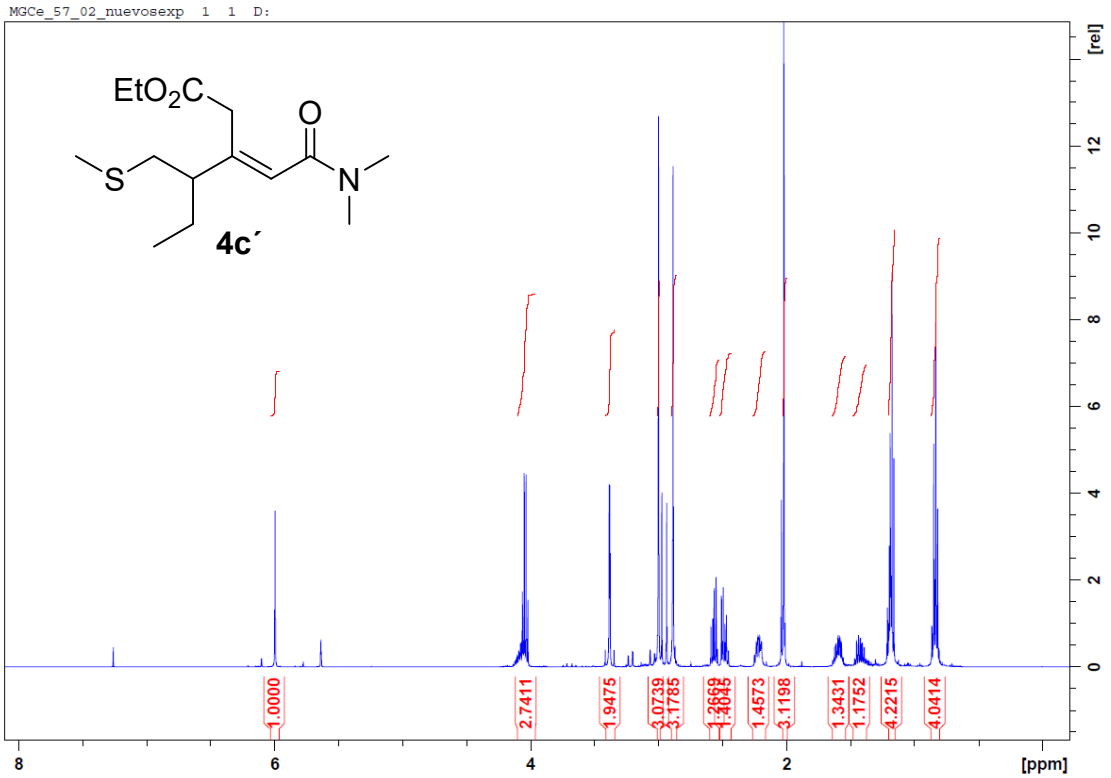
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4c**



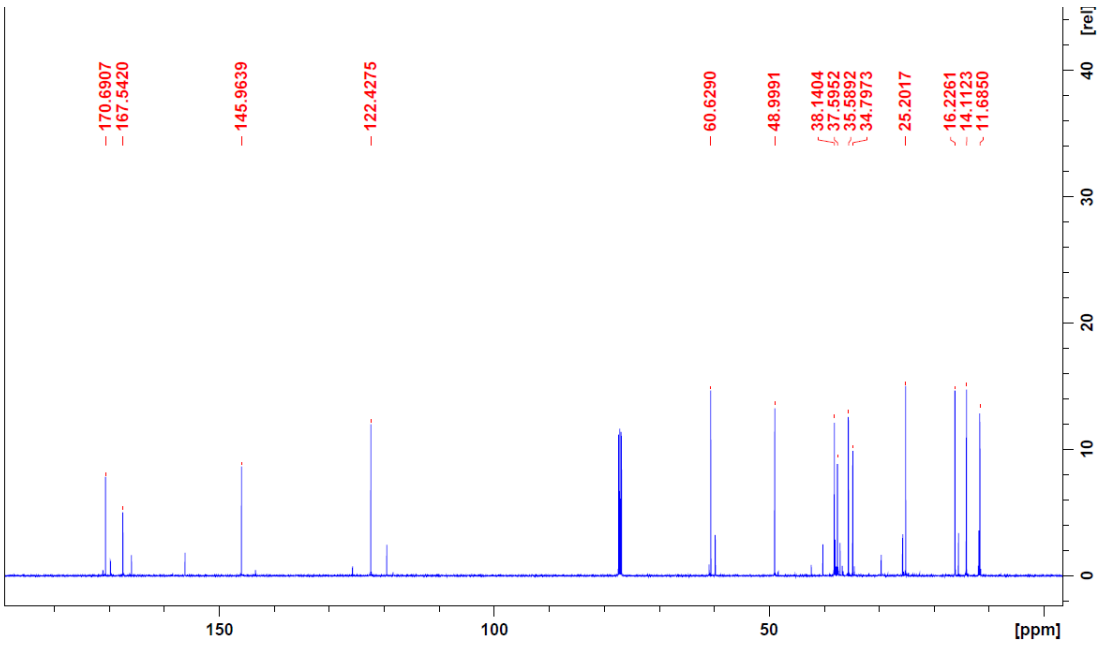
Bidimensional COSY-experiment of compound **4c**



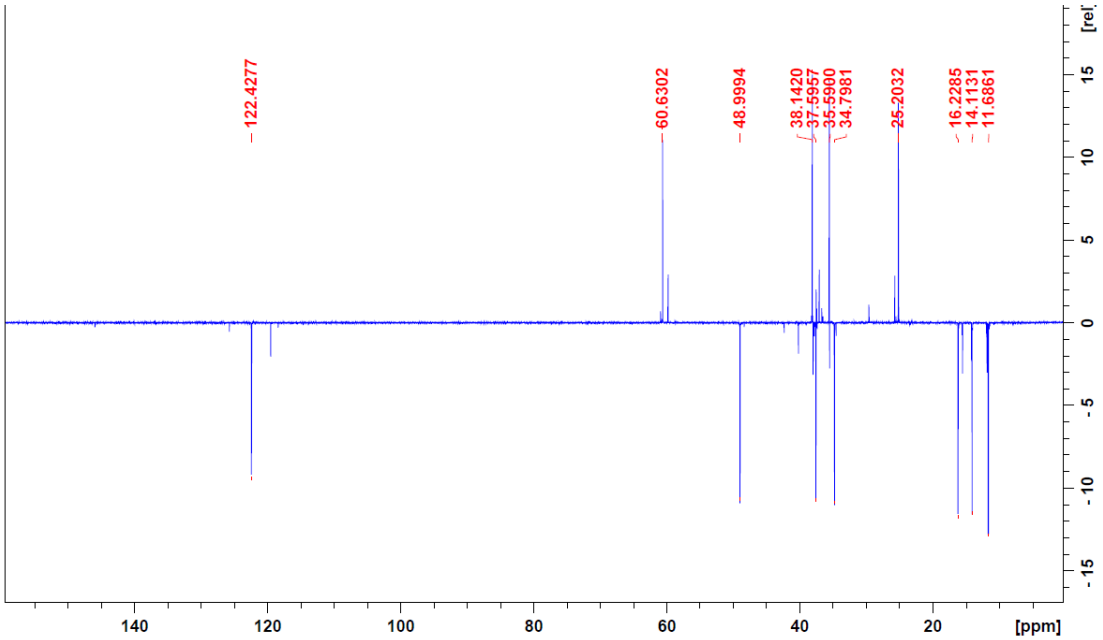
Bidimensional HMQC-experiment of compound **4c**



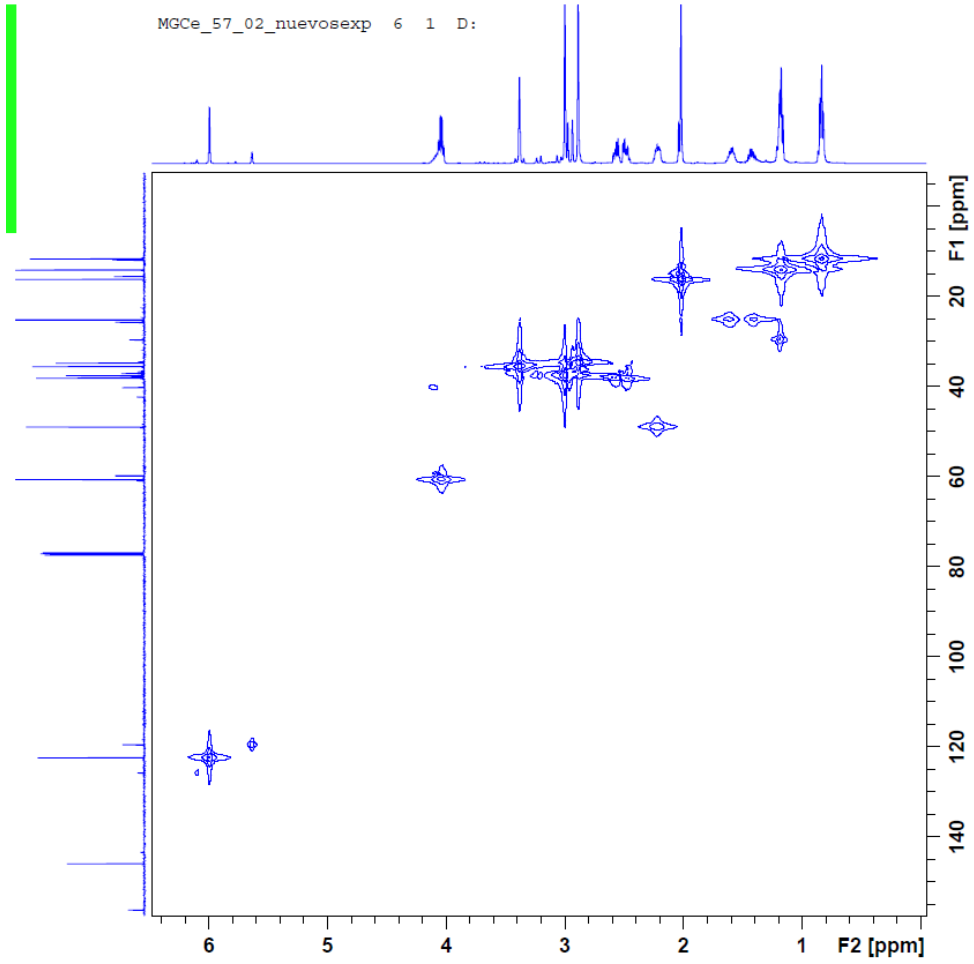
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4c´**



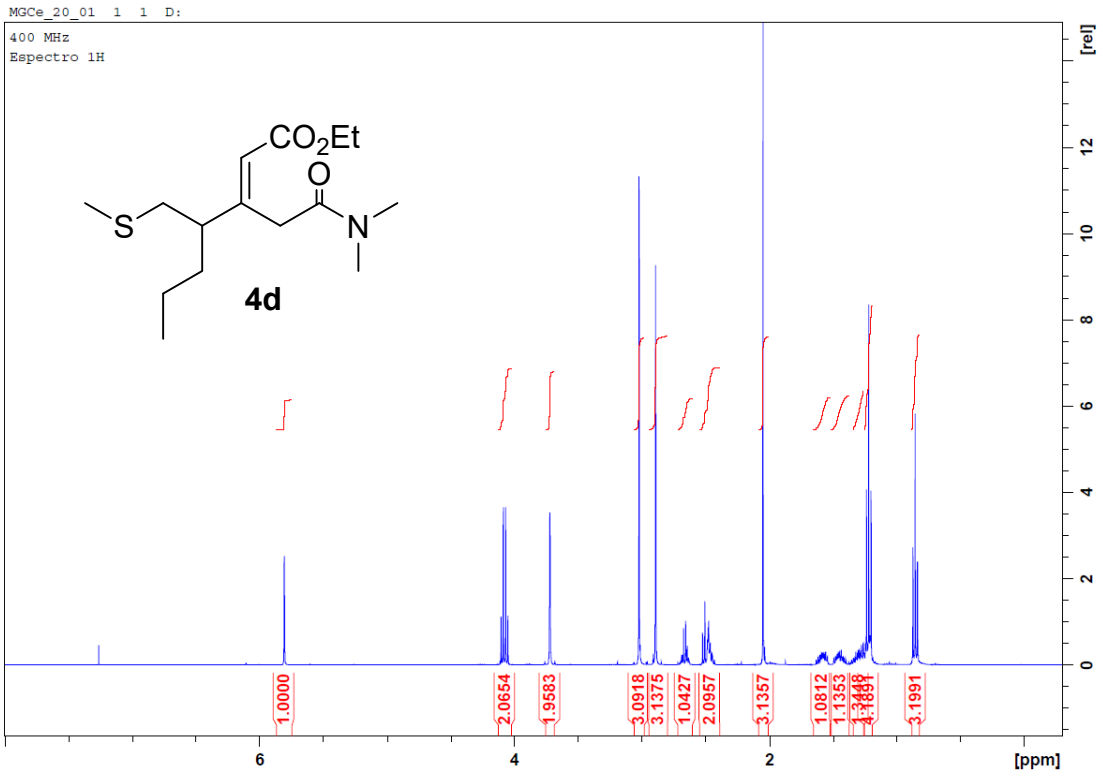
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4c´**



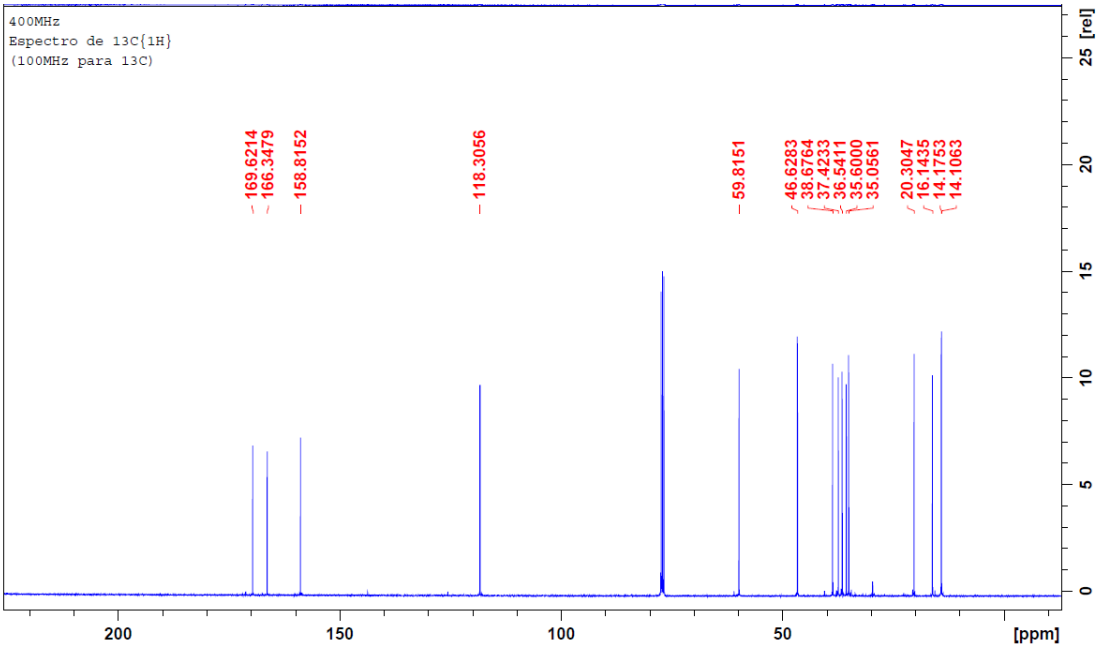
DEPT-135-NMR ($CDCl_3$) of compound **4c´**



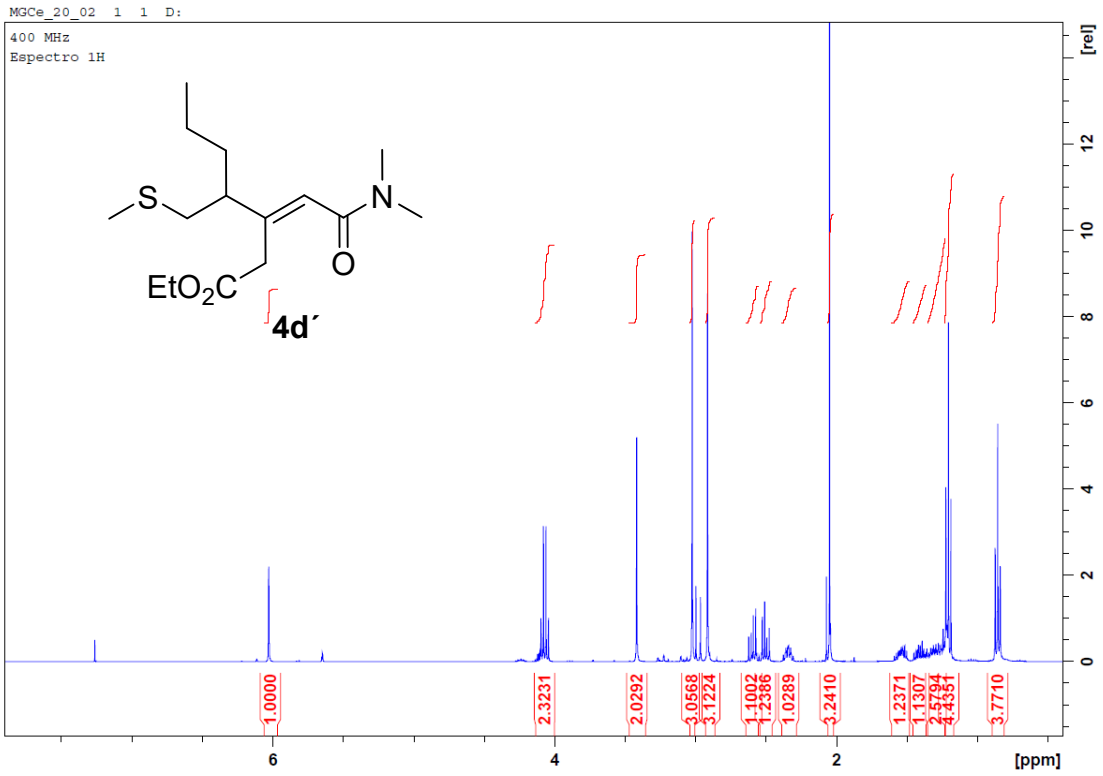
Bidimensional HMQC-experiment of compound **4c´**



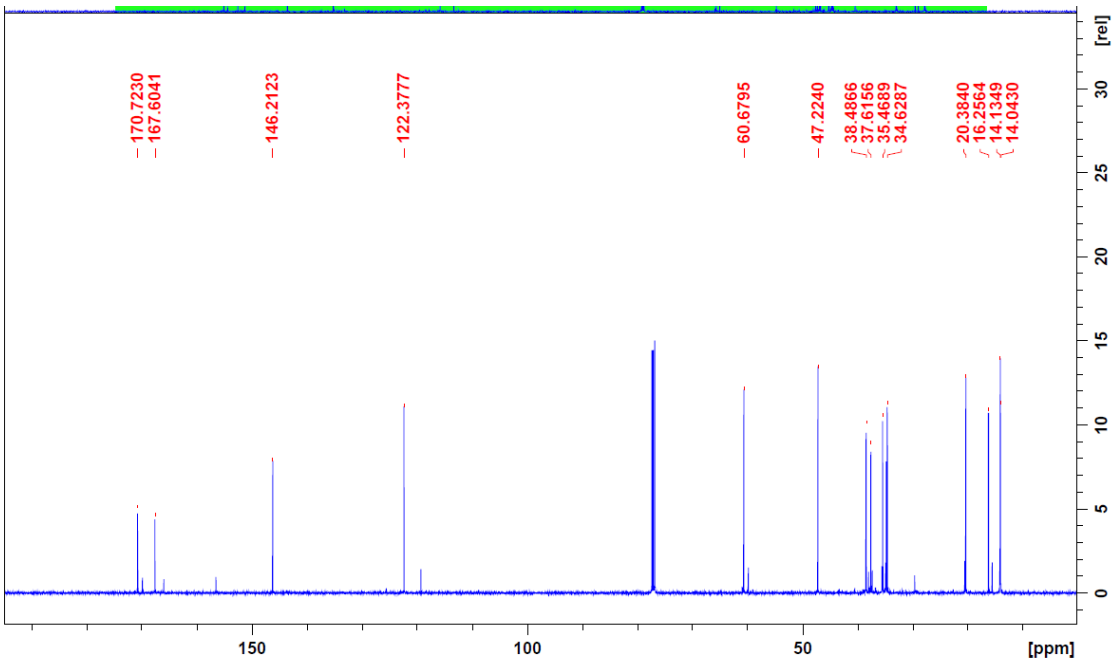
^{1}H-NMR ($CDCl_3$, 400 MHz) of compound **4d**



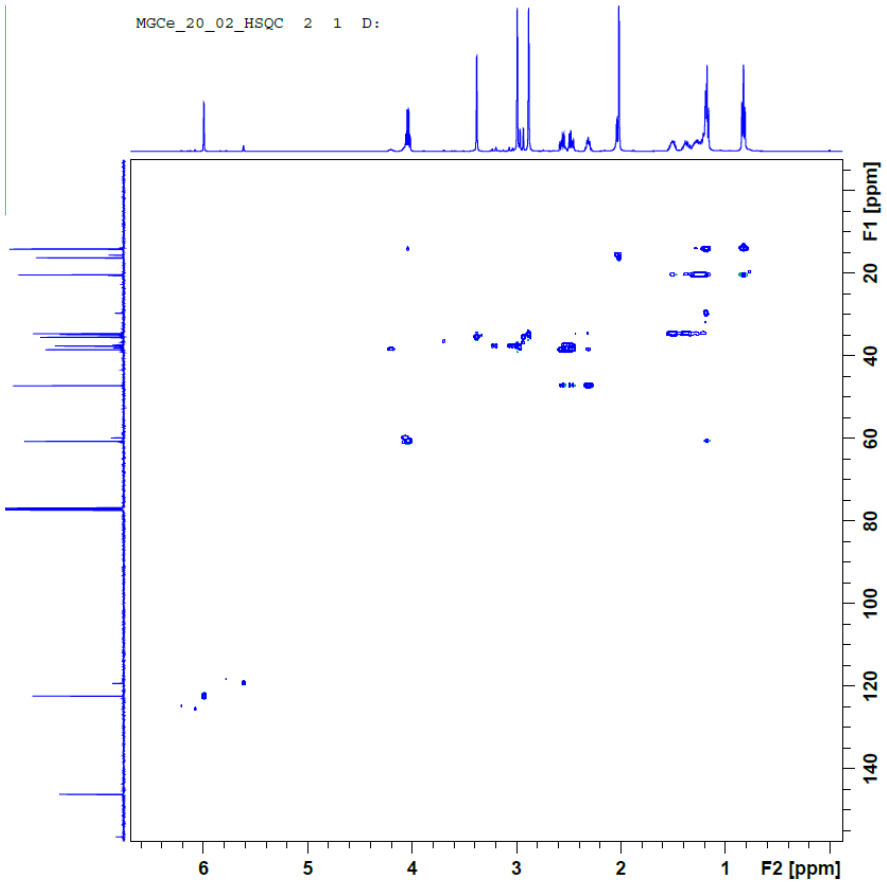
^{13}C-NMR ($CDCl_3$, 100 MHz) of compound **4d**



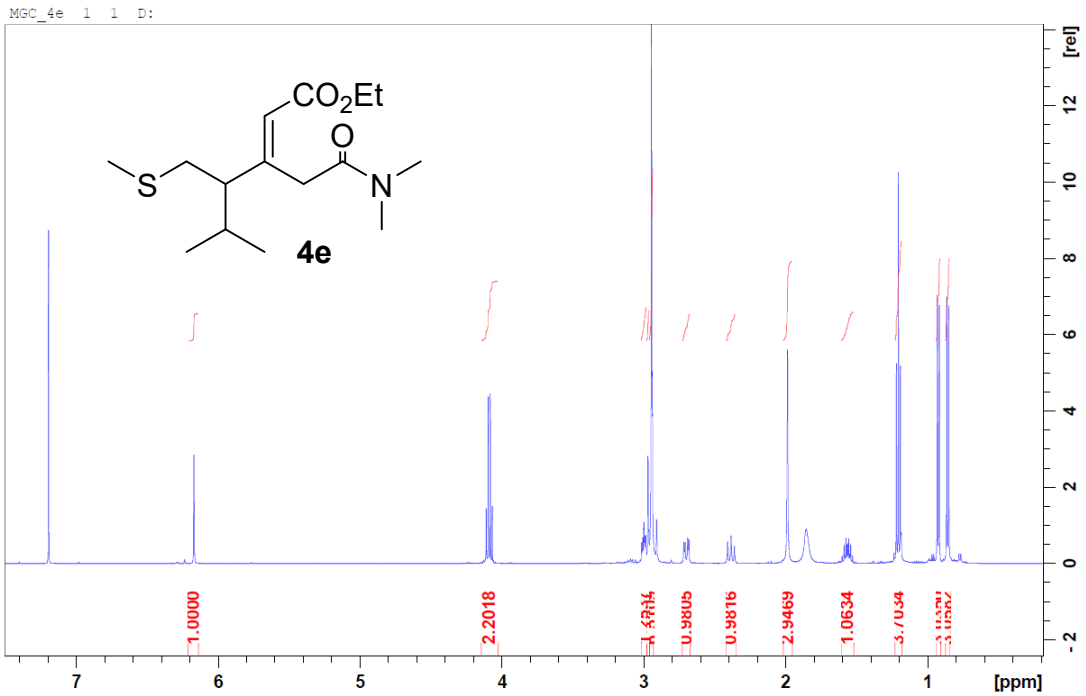
^{1}H-NMR ($CDCl_3$, 400 MHz) of compound **4d´**



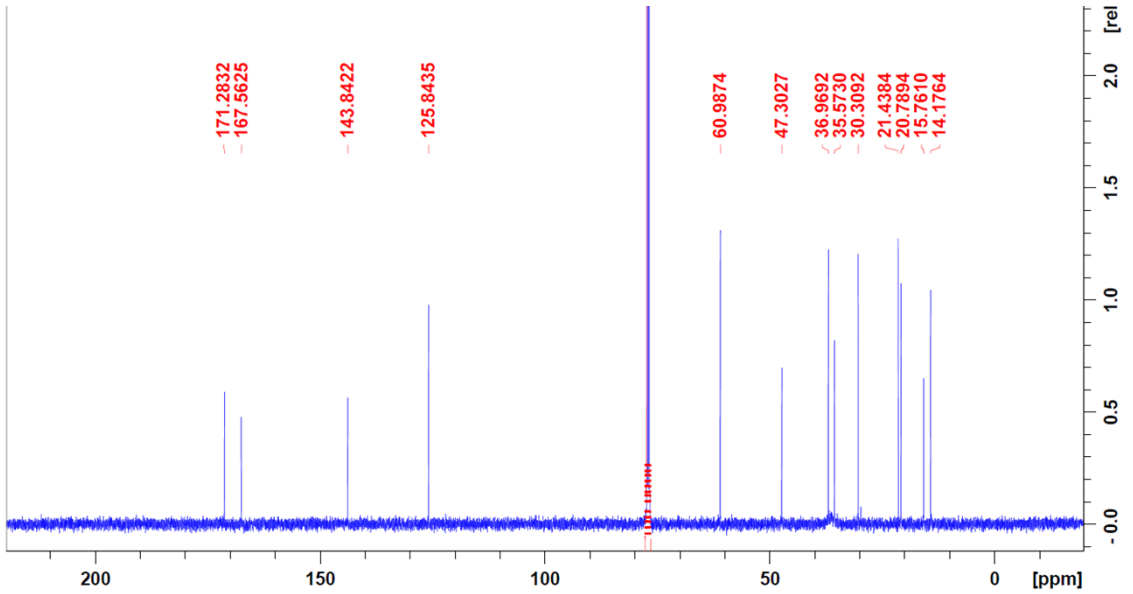
^{13}C-NMR ($CDCl_3$, 100 MHz) of compound **4d´**



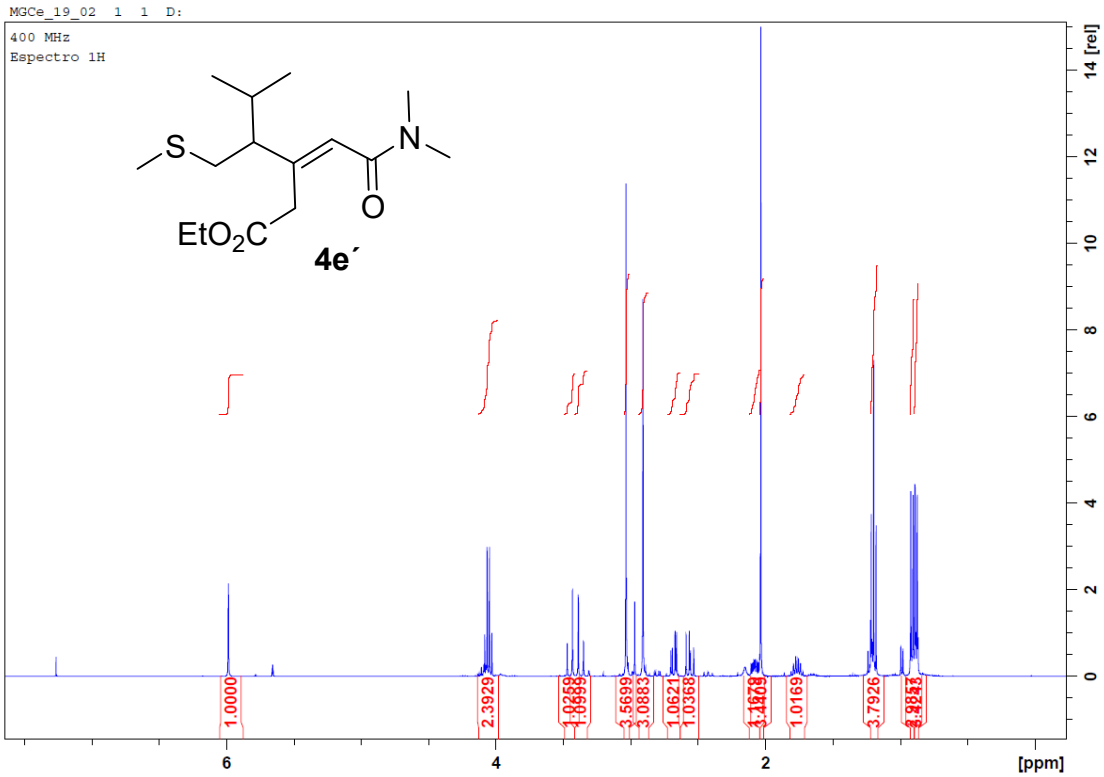
Bidimensional HSQC-experiment of compound **4d´**



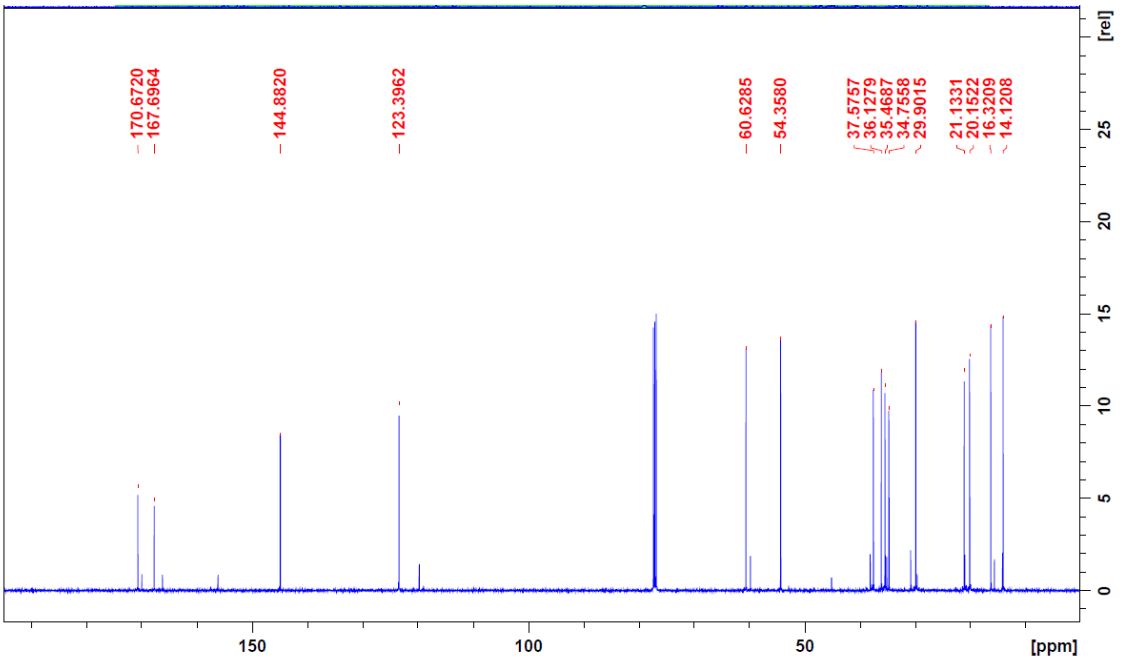
^{1}H-NMR ($CDCl_3$, 400 MHz) of compound **4e**



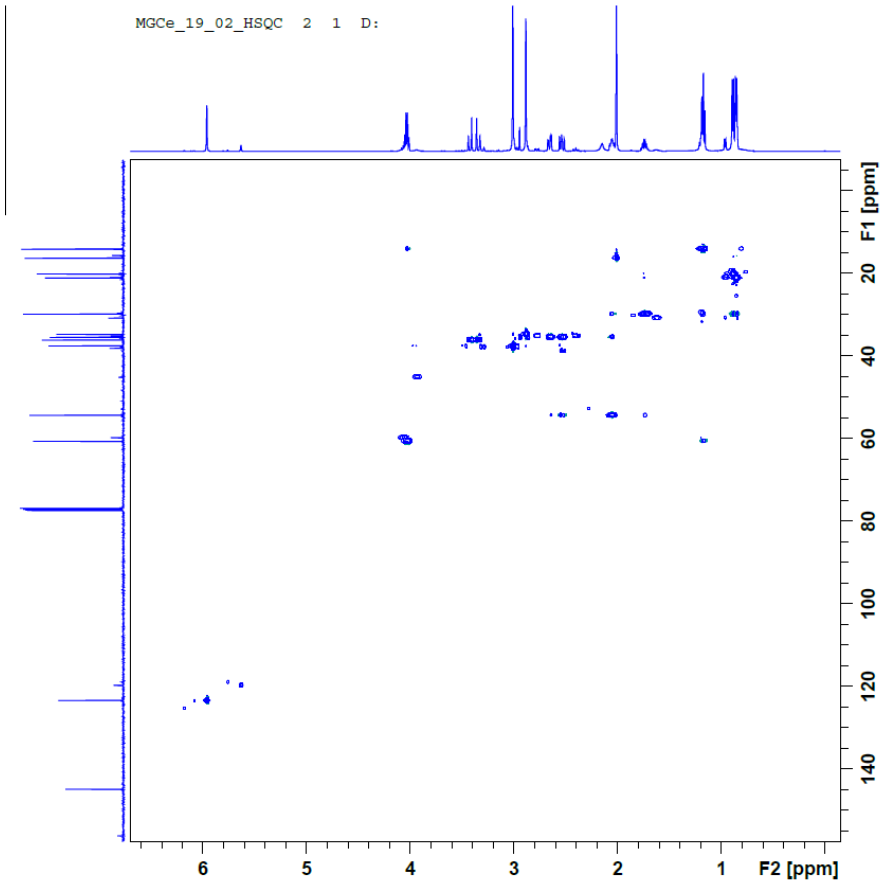
^{13}C-NMR ($CDCl_3$, 100 MHz) of compound **4e**



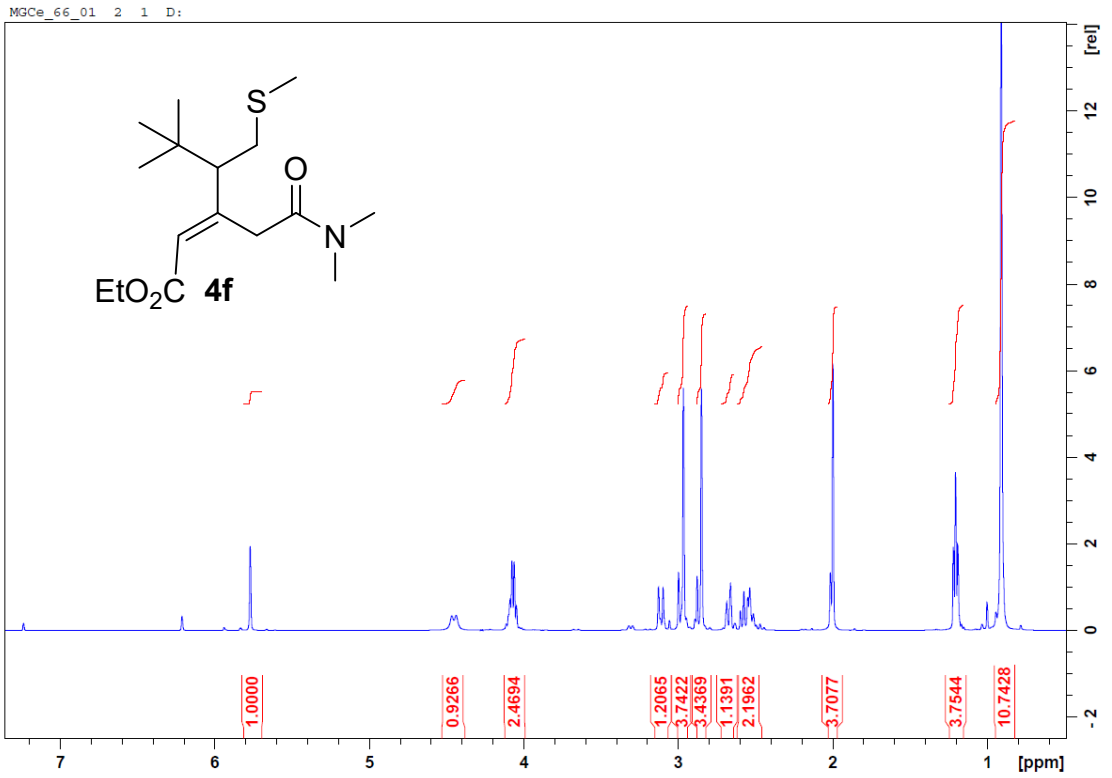
^{1}H-NMR ($CDCl_3$, 400 MHz) of compound **4e´**



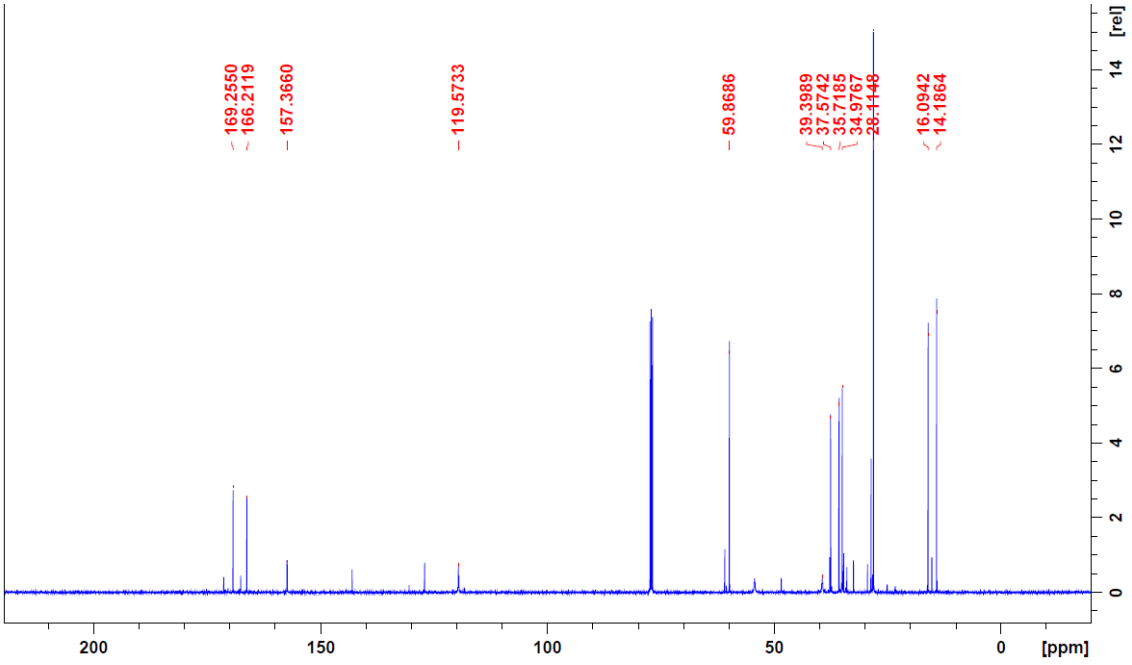
^{13}C-NMR ($CDCl_3$, 100 MHz) of compound **4e´**



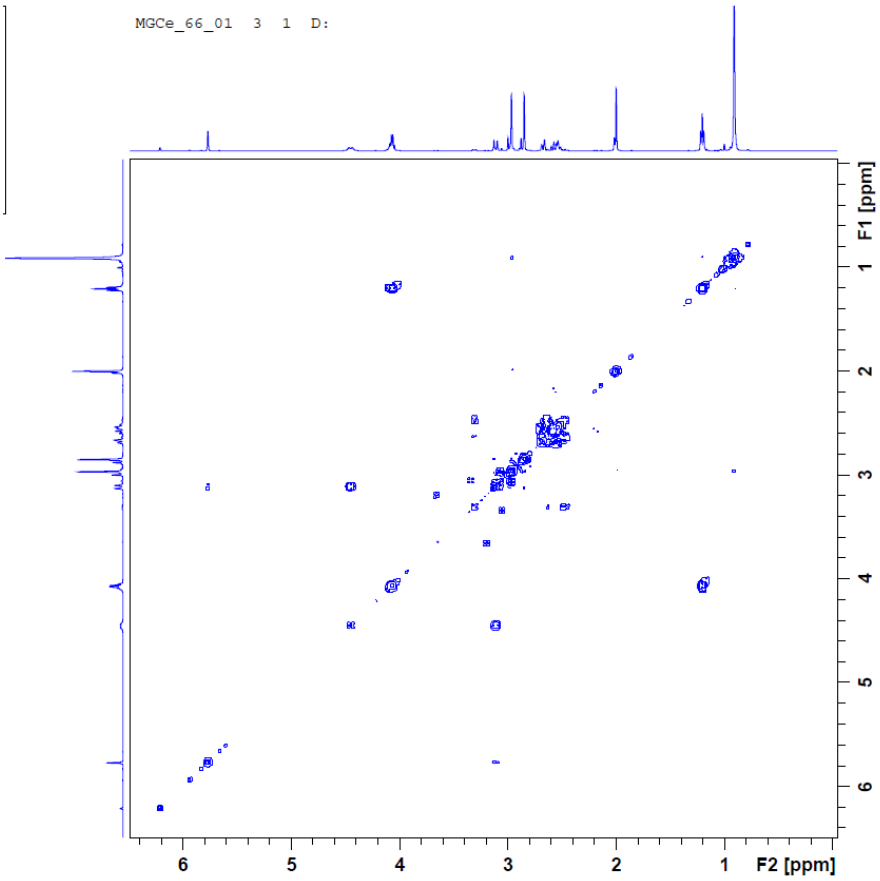
Bidimensional HSQC-experiment of compound **4e´**



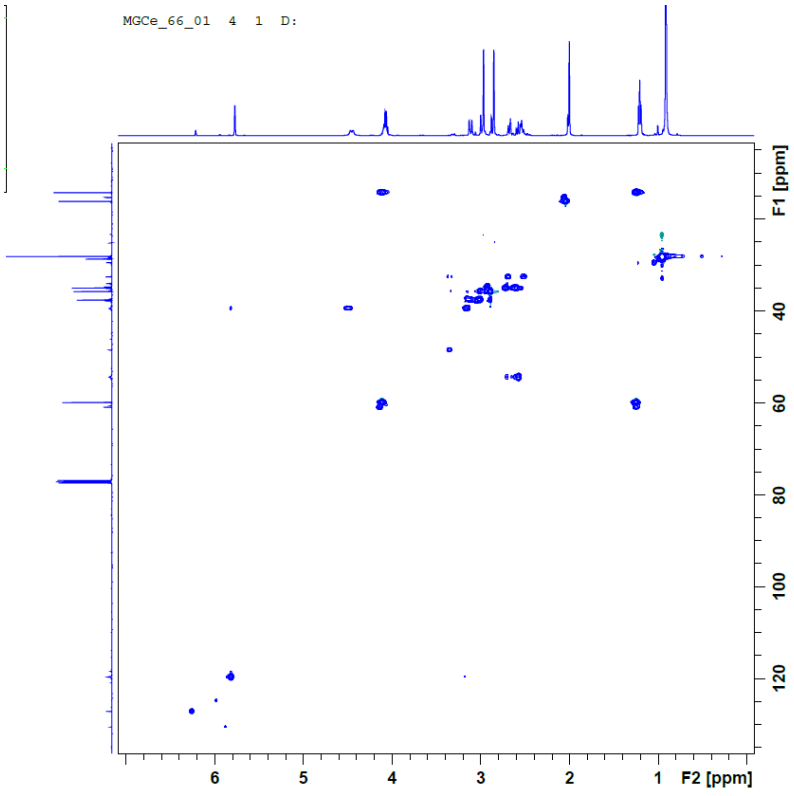
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4f** (It contains 12% of isomer **4f´**)



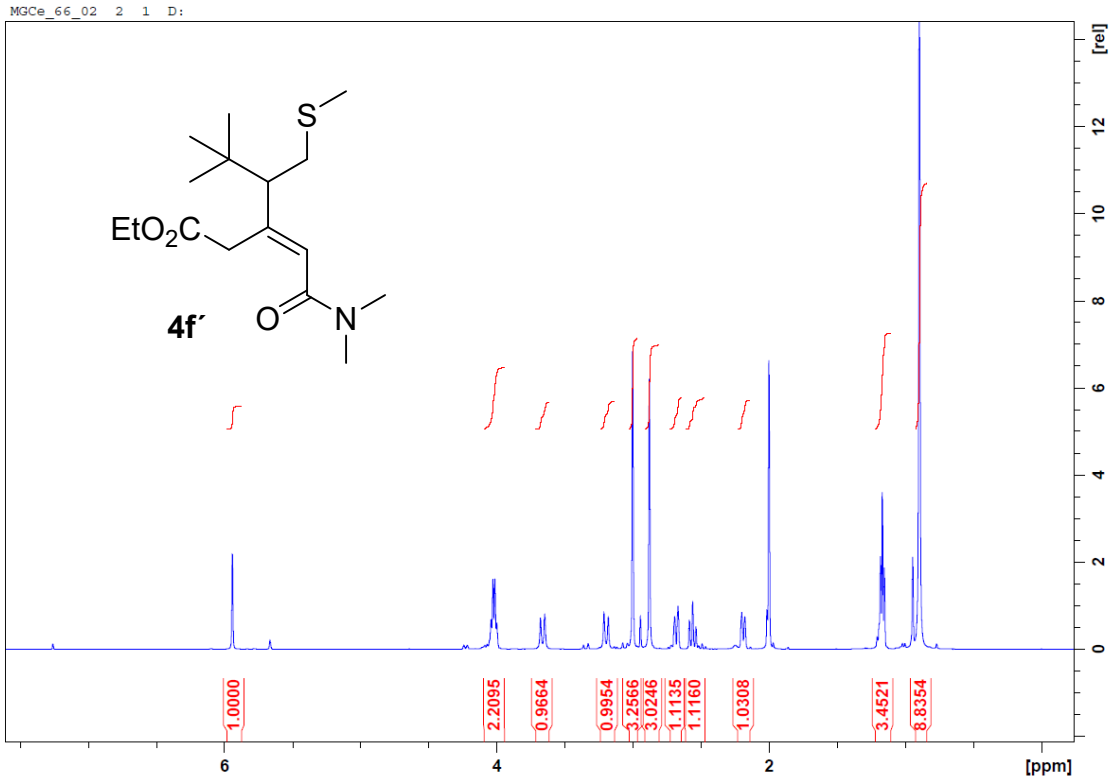
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4f**



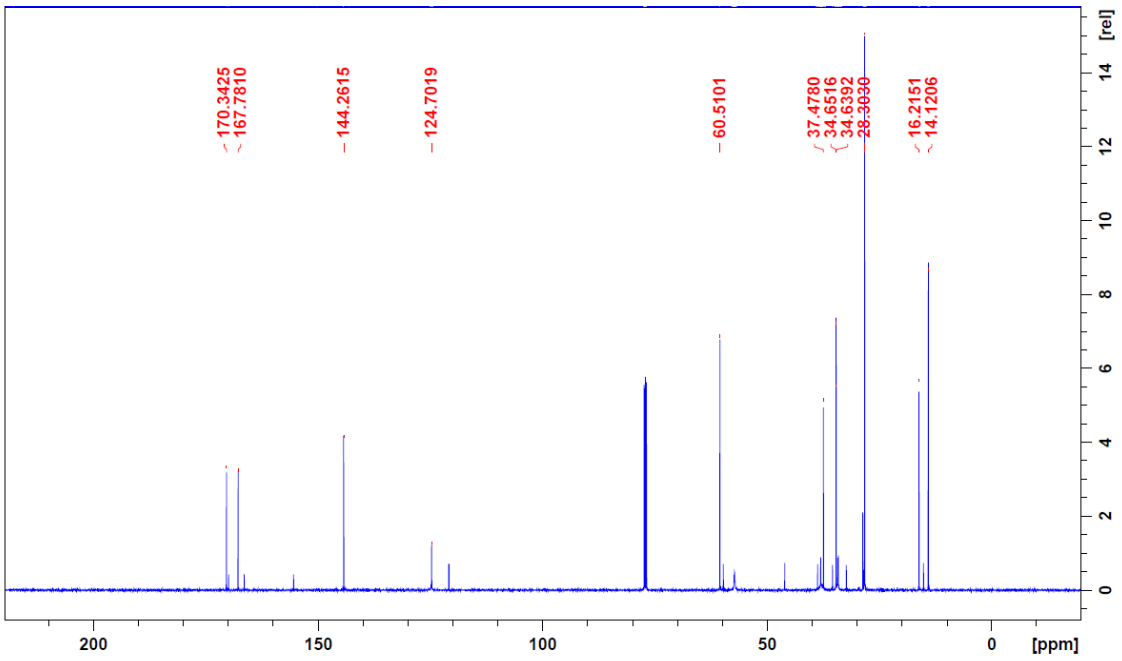
Bidimensional COSY-experiment of compound **4f**



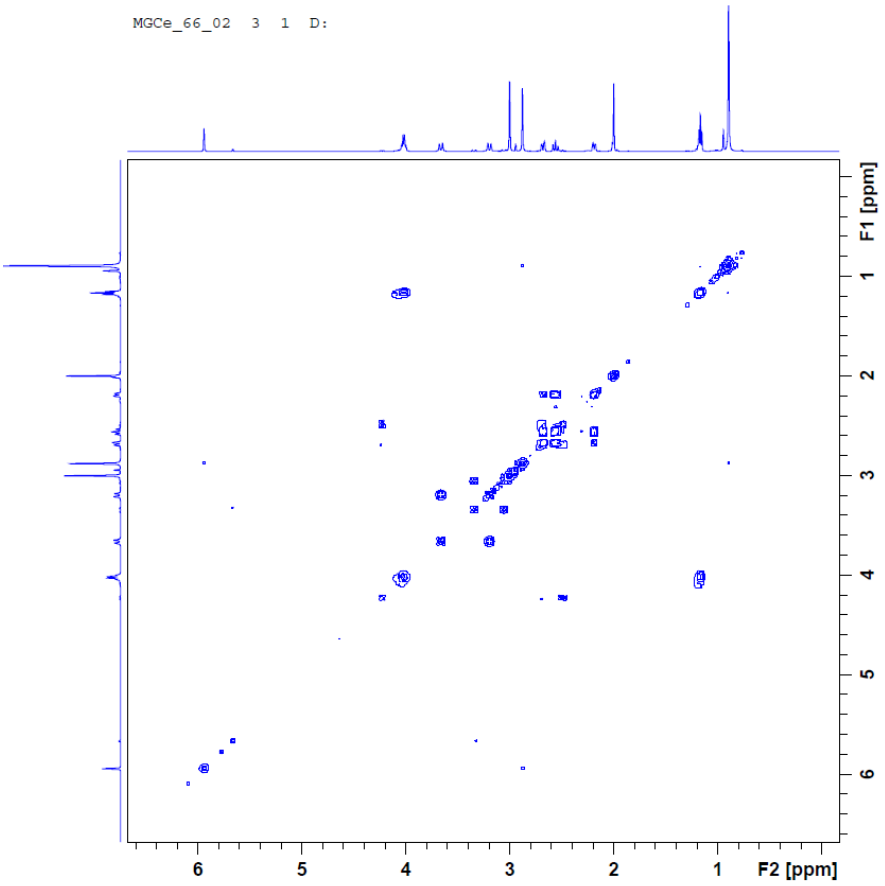
Bidimensional HSQC-experiment of compound **4f**



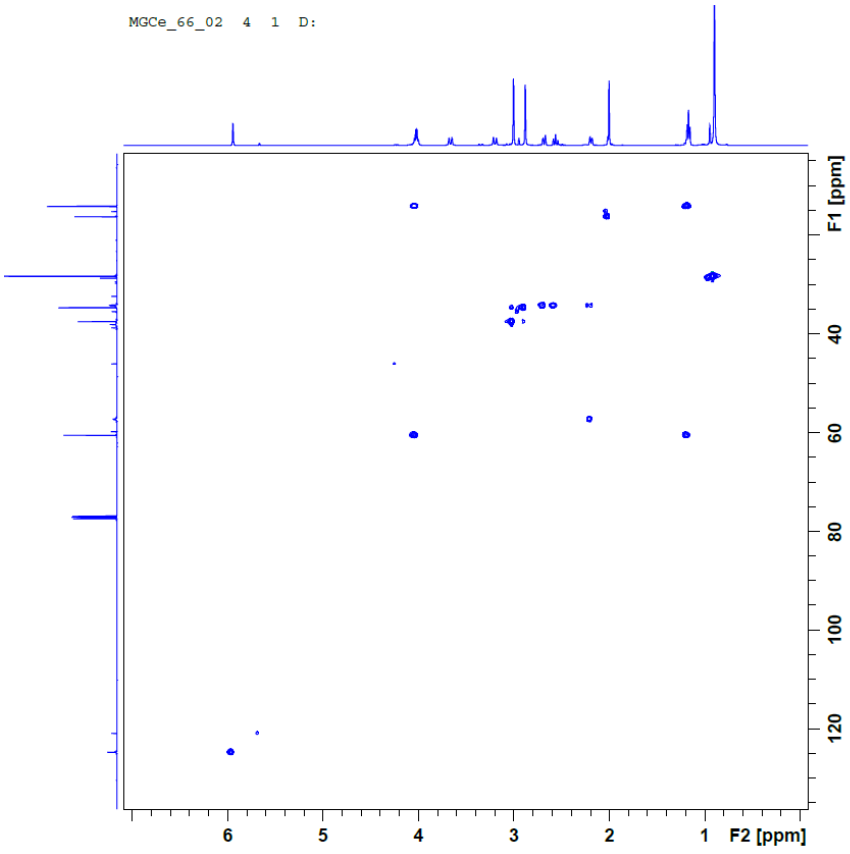
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4f´**



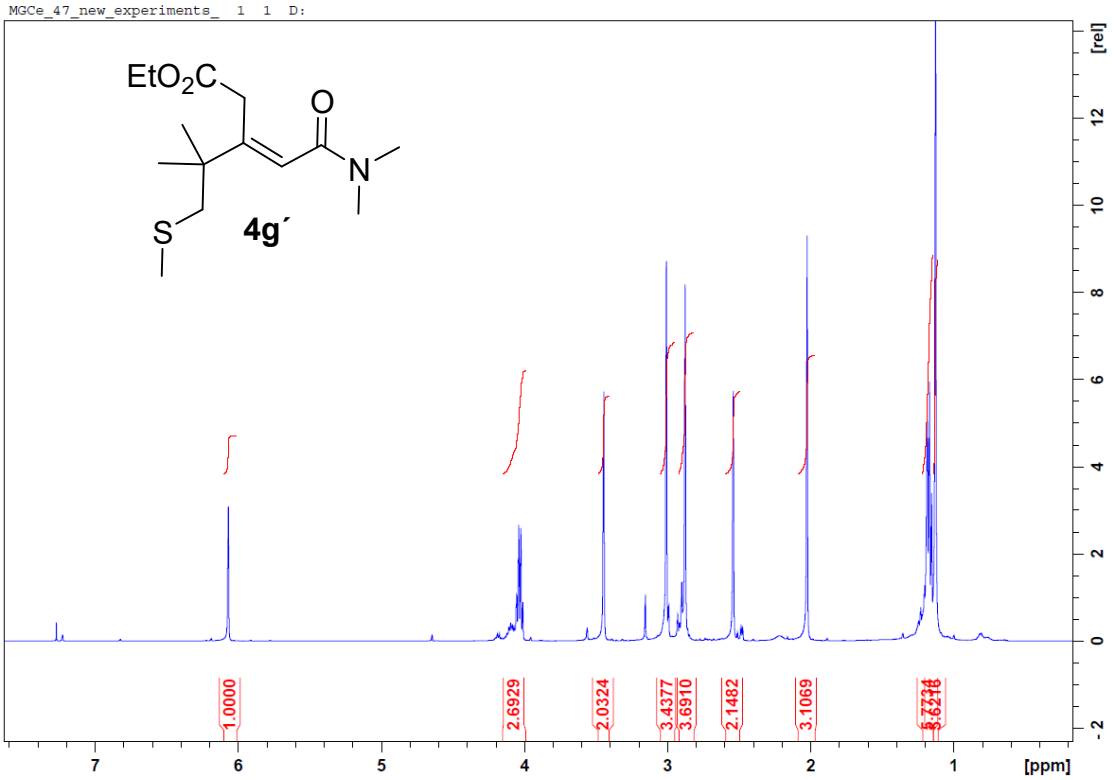
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4f´**



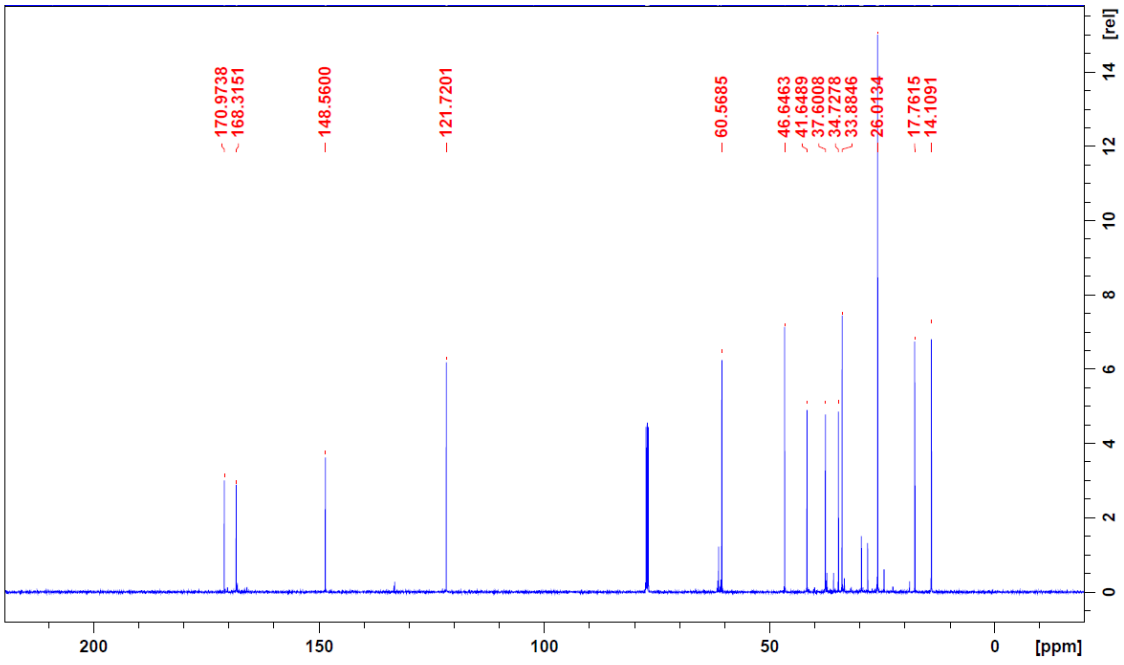
Bidimensional COSY-experiment of compound **4f´**



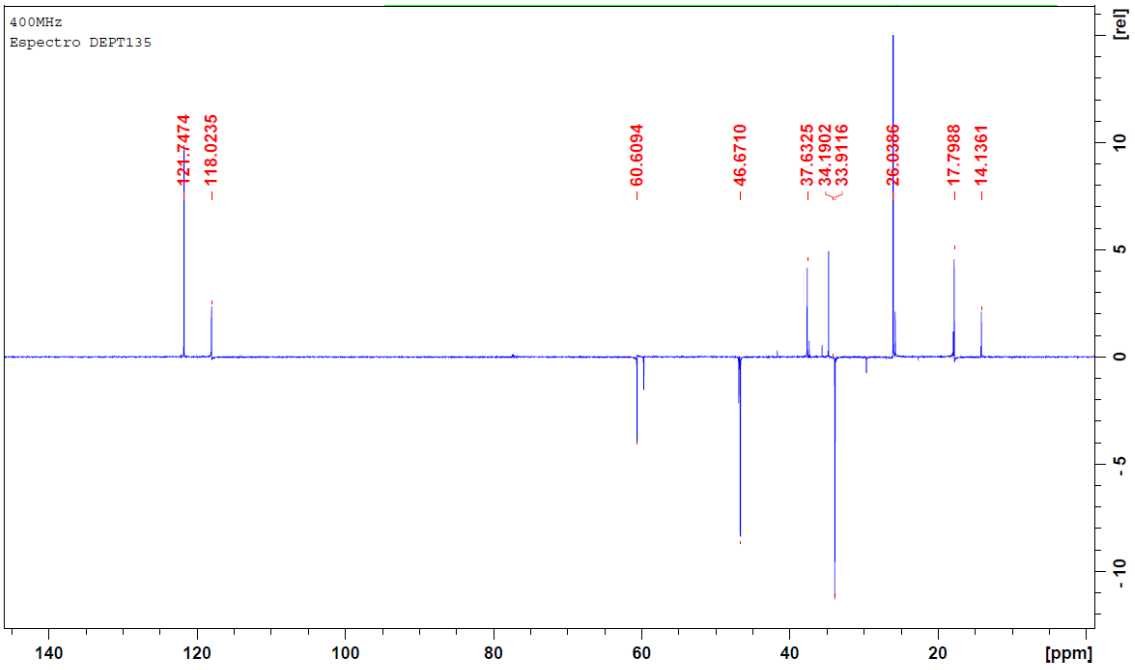
Bidimensional HSQC-experiment of compound **4f´**



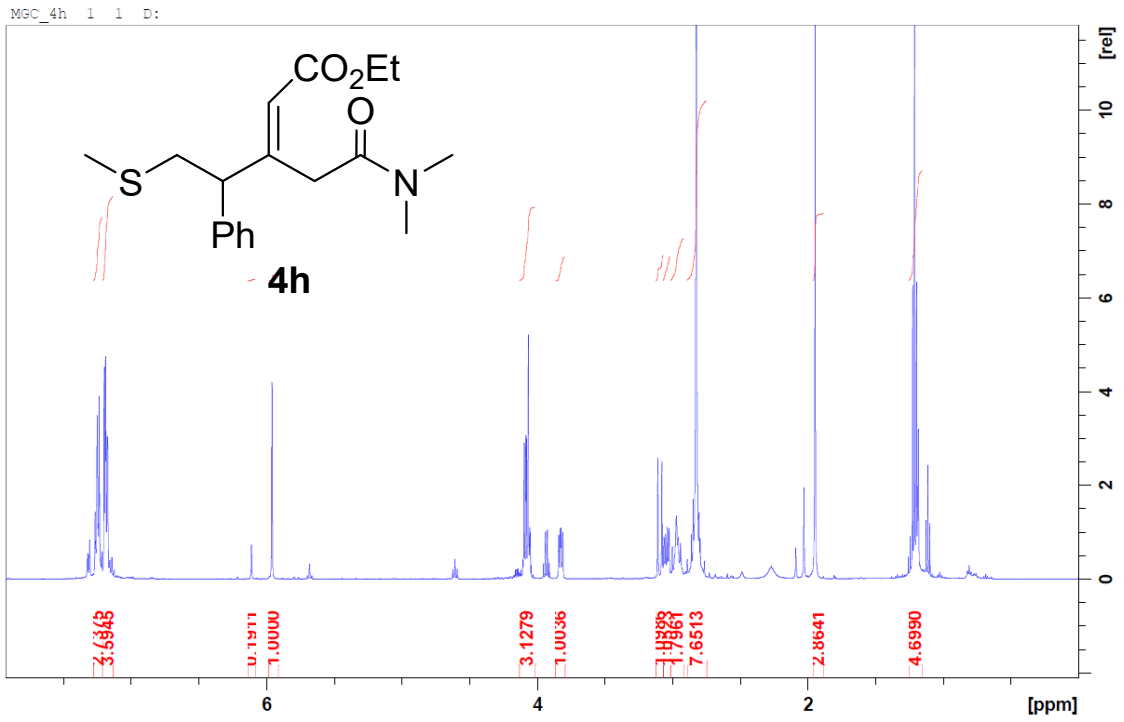
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4g´**



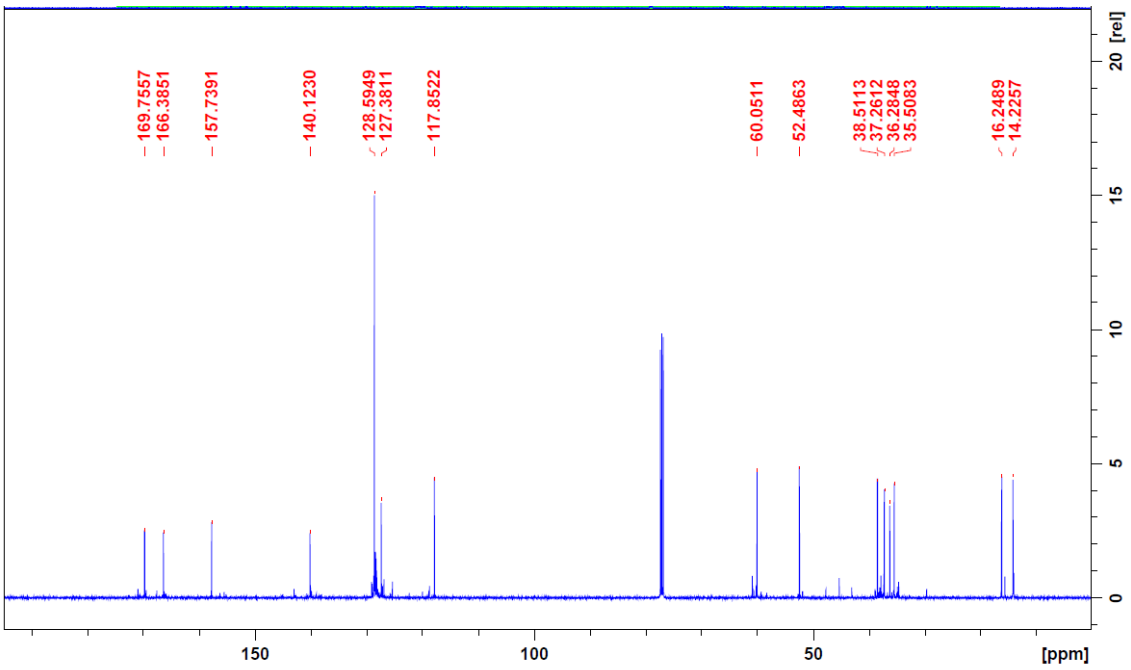
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4g´**



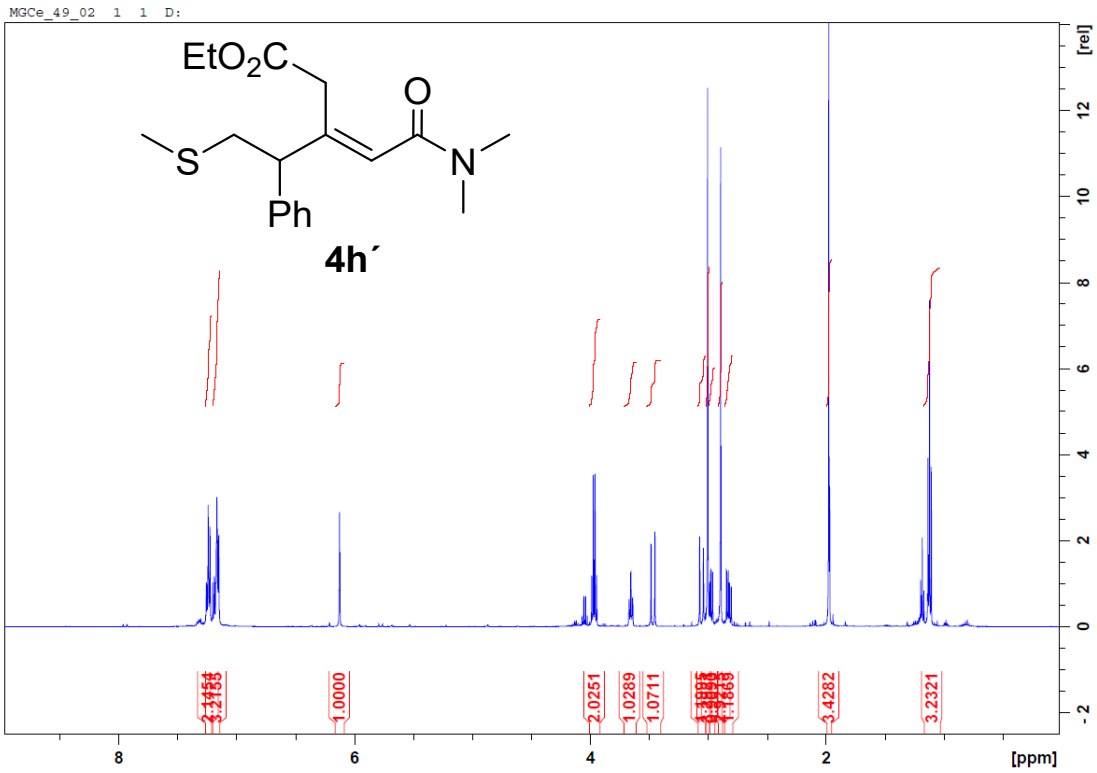
DEPT-135-NMR ($CDCl_3$) of compound **4g´**



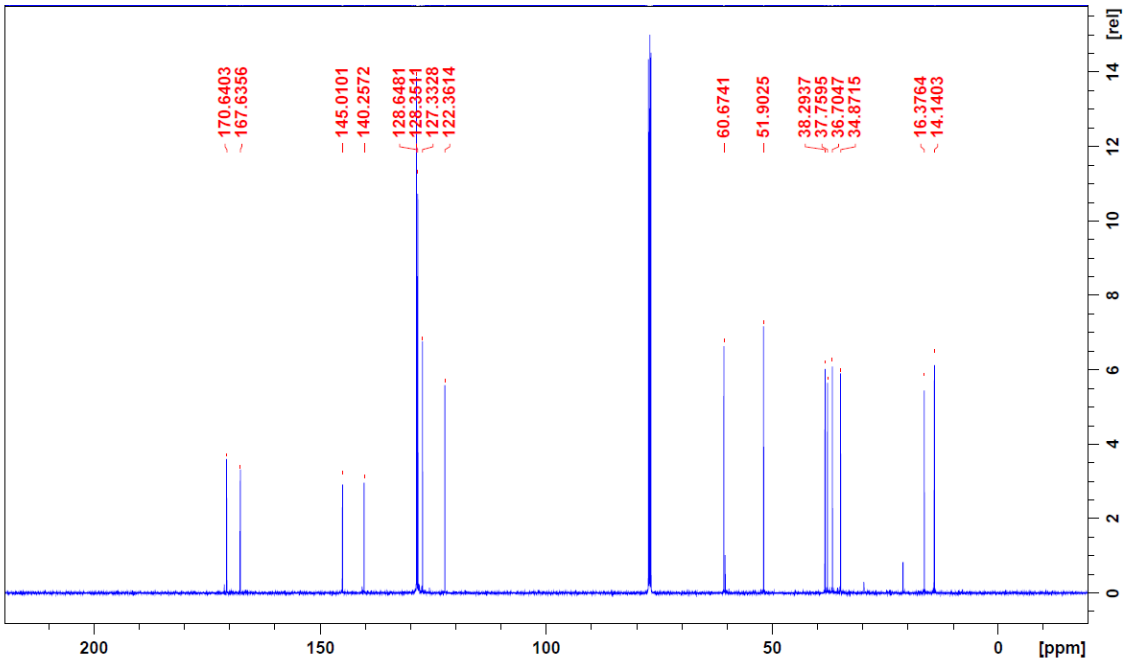
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4h** (It contains 16% of isomer **4h´**)



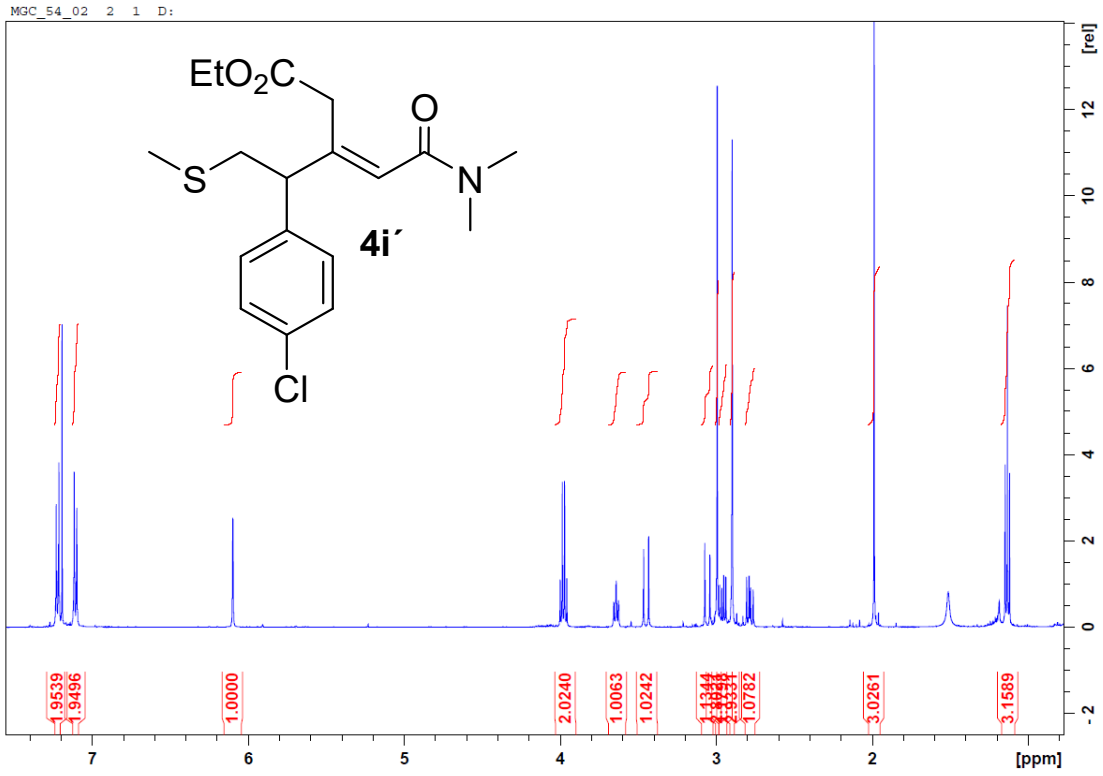
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4h**



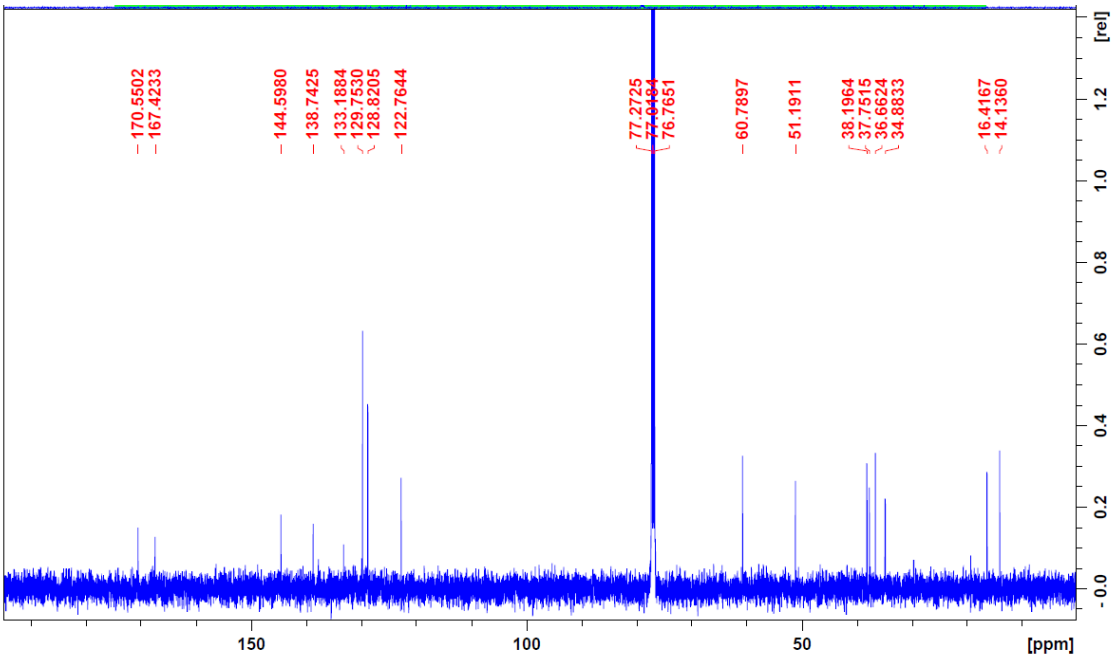
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4h´**



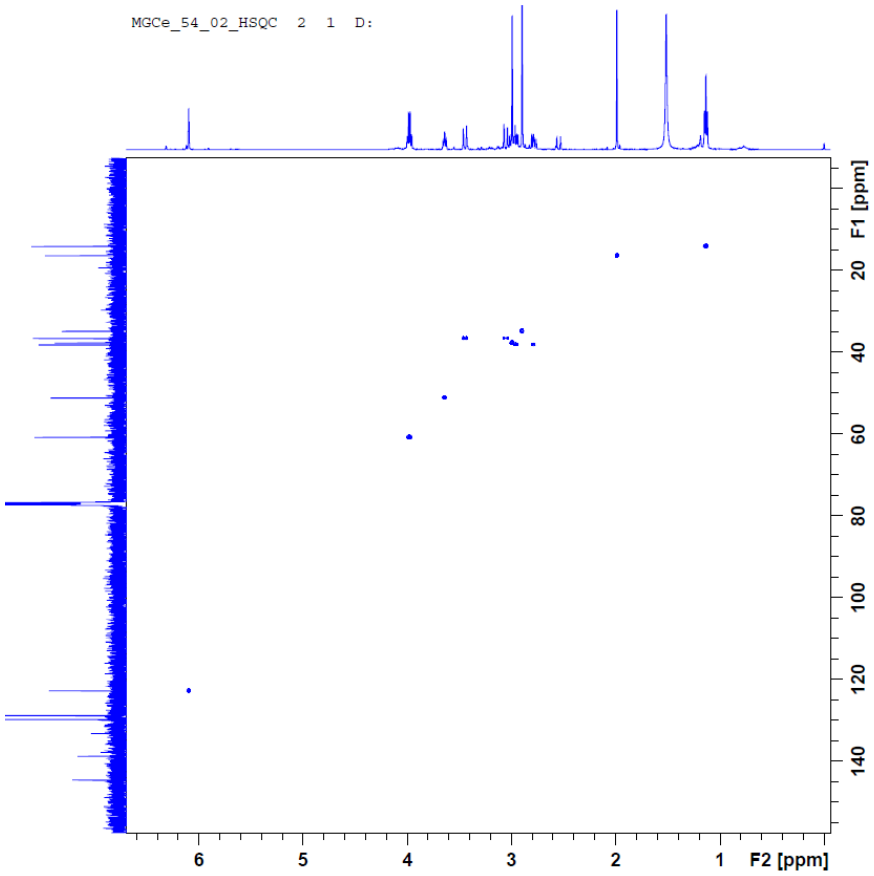
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4h´**



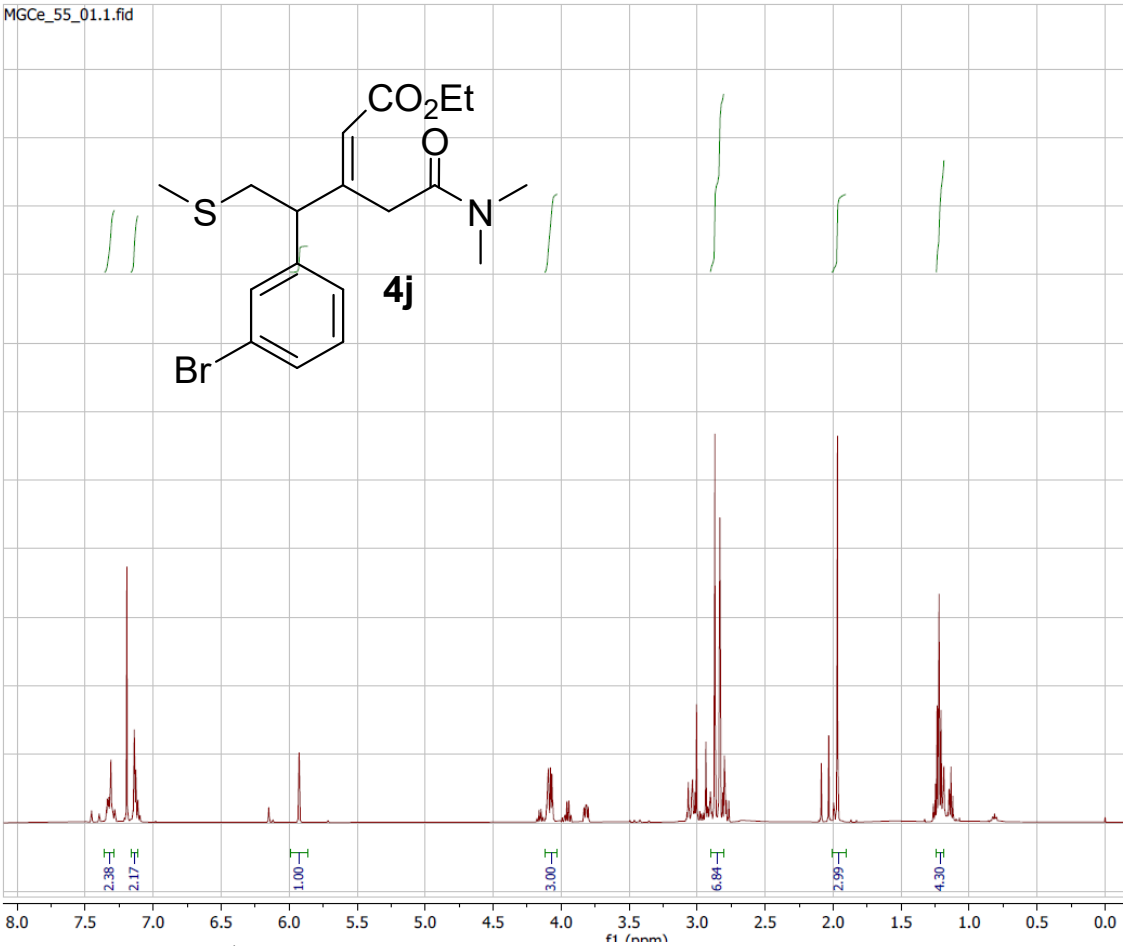
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4i´**



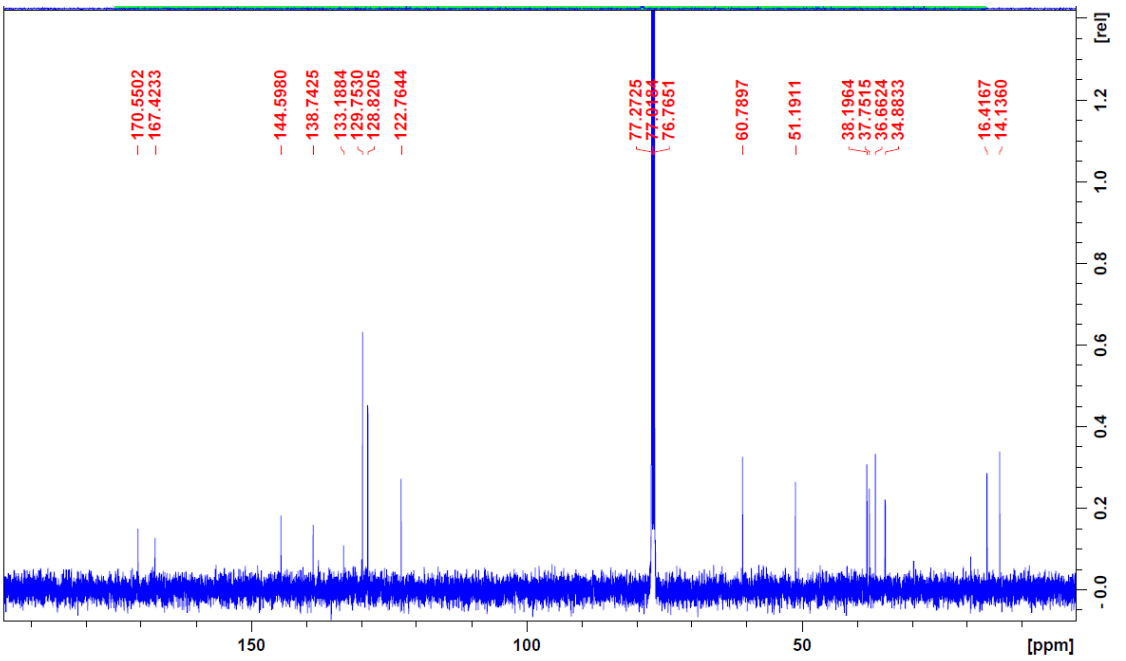
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4i´**



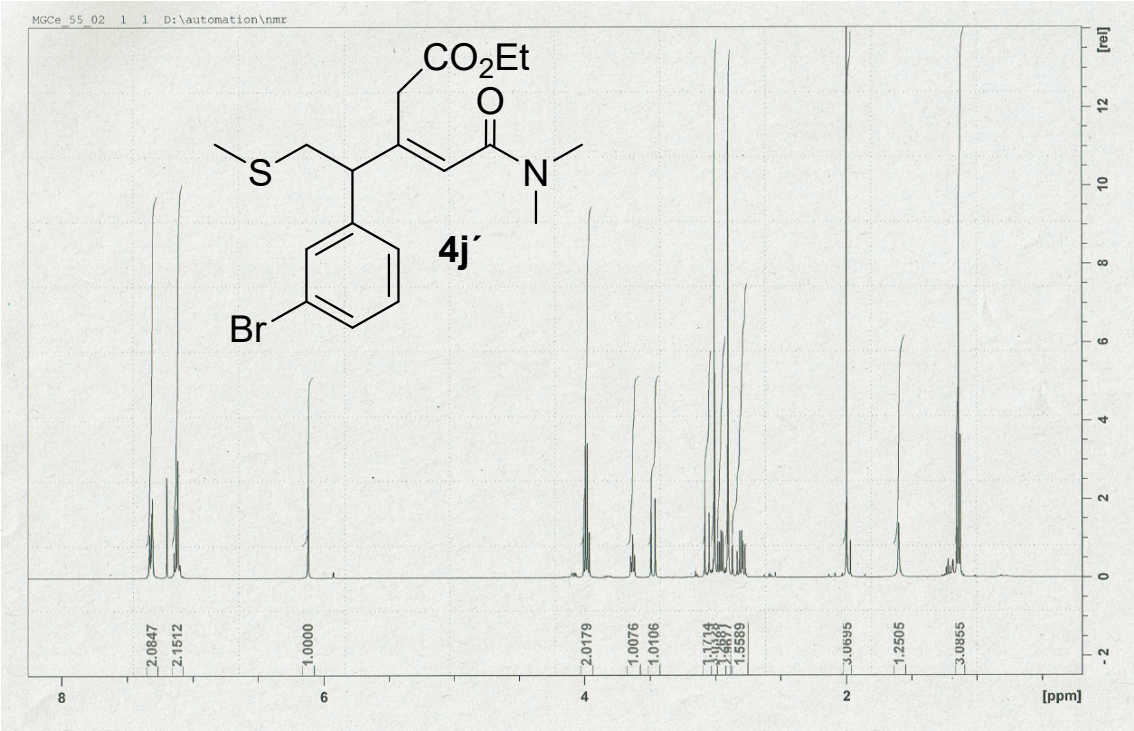
Bidimensional HSQC-experiment of compound **4i´**



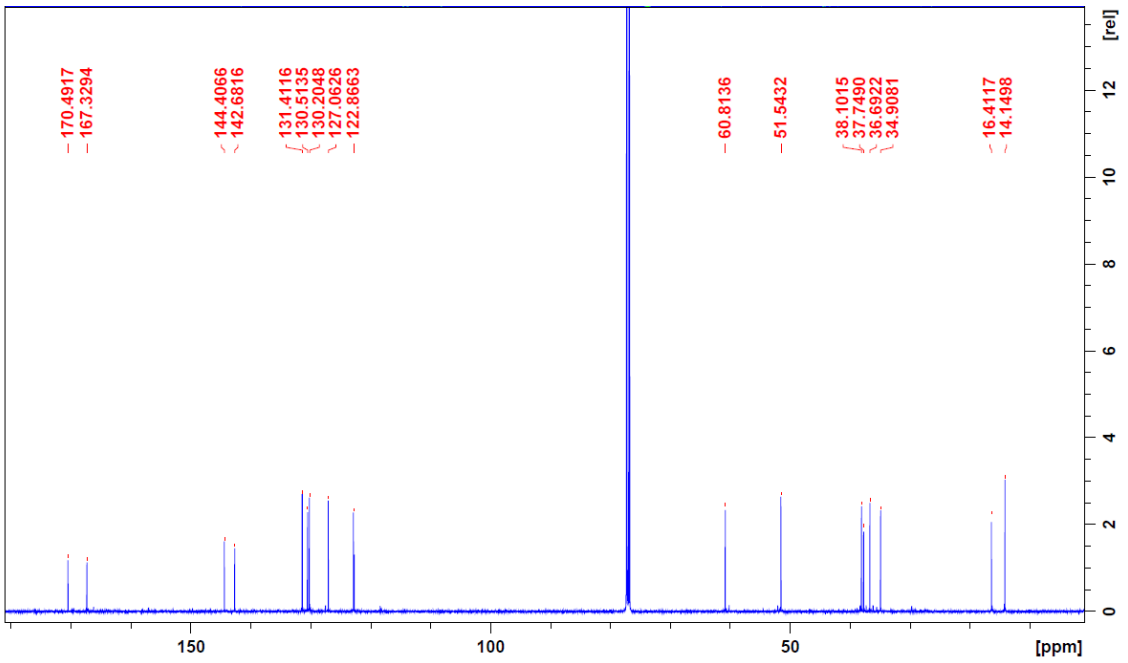
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4j** (91% purity)



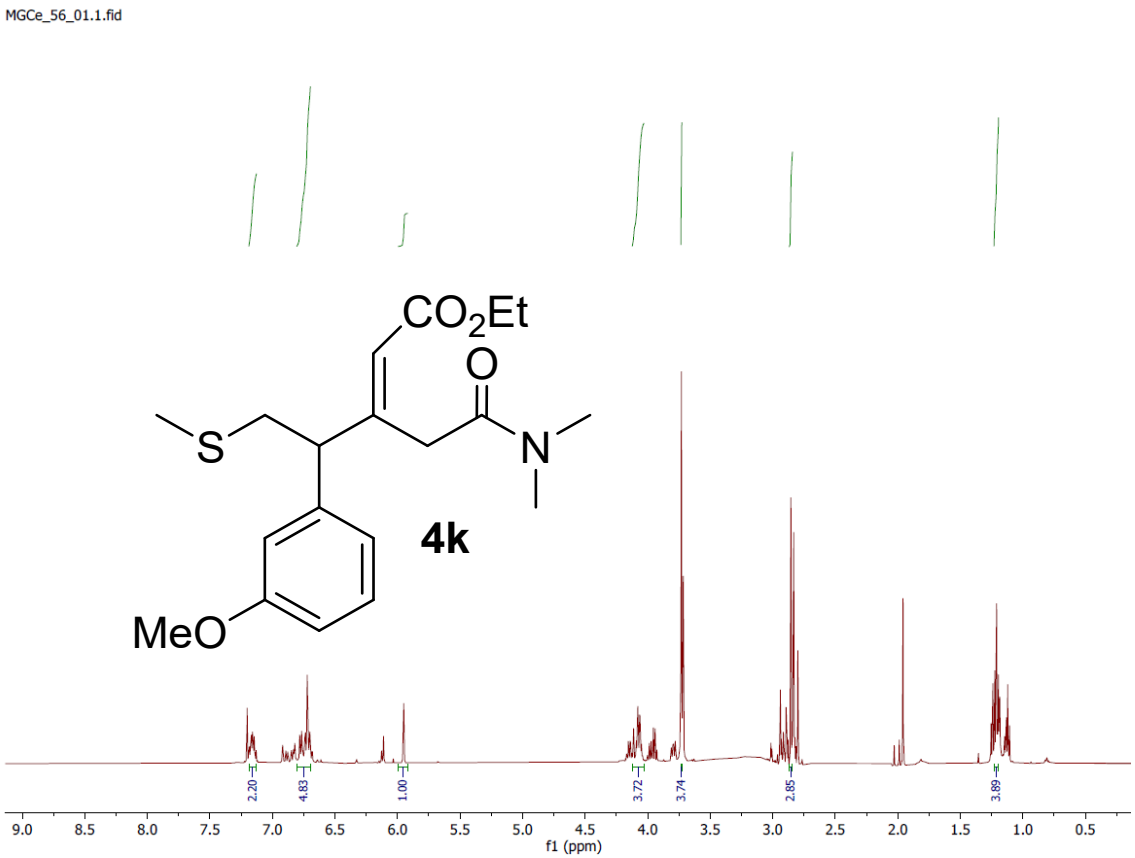
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4j**



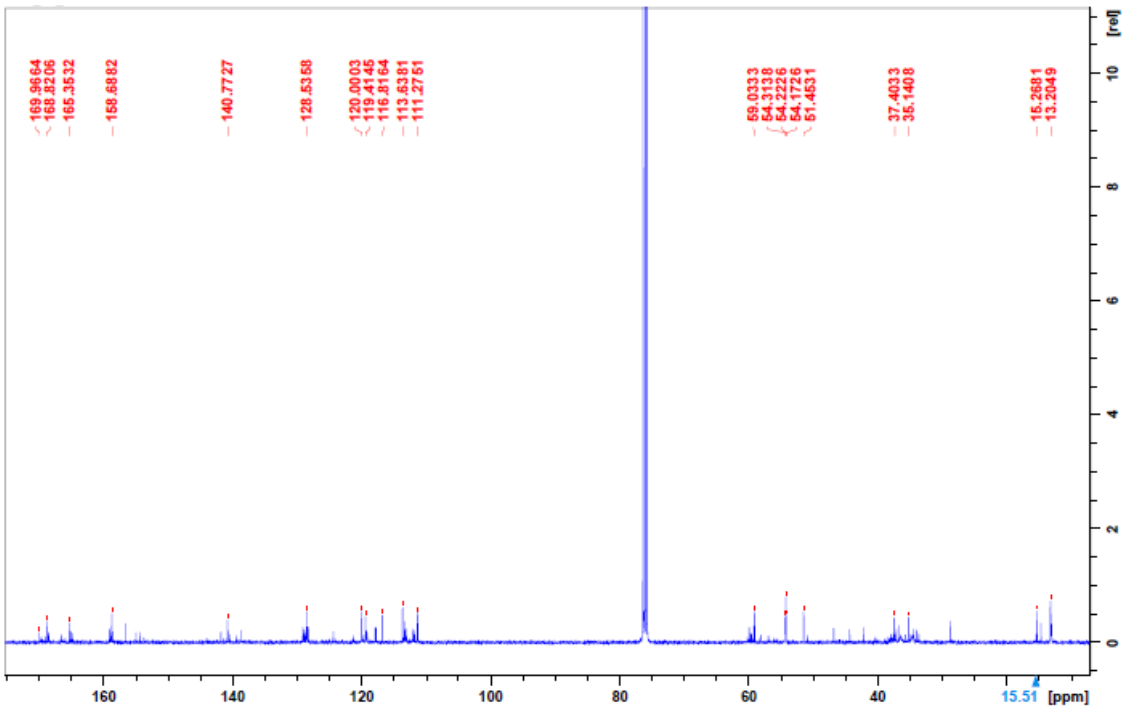
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4j´**



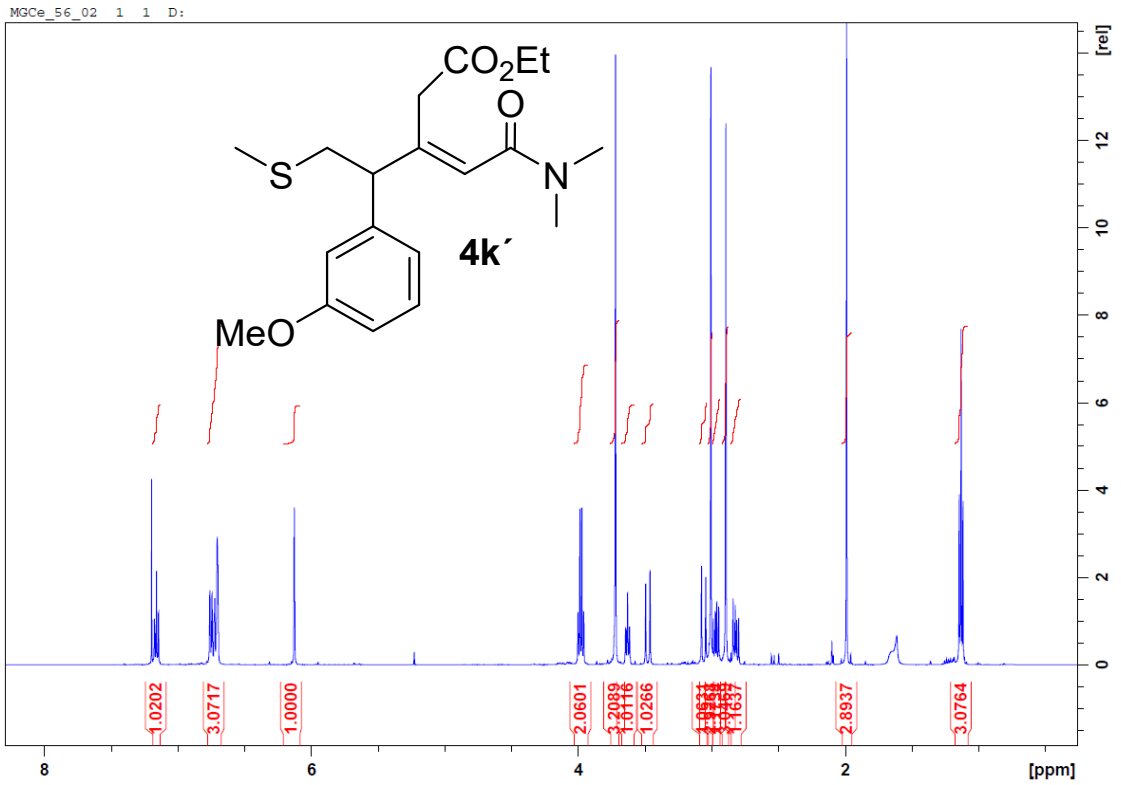
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4j´**



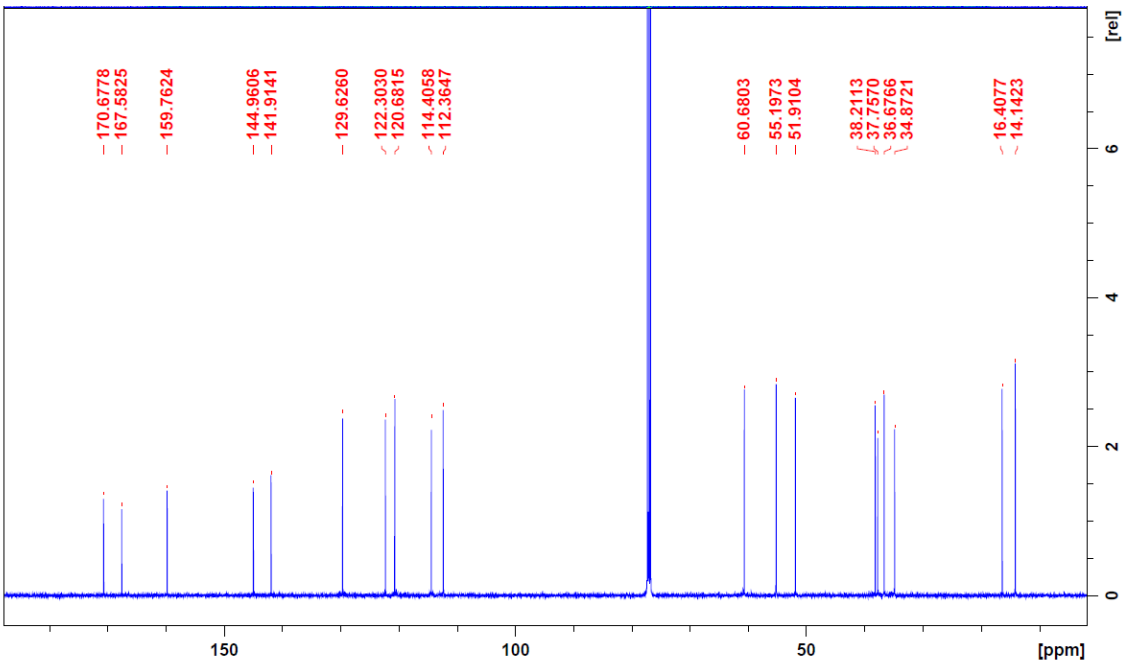
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4k** (It is a 70-30% mixture of inseparable isomers)



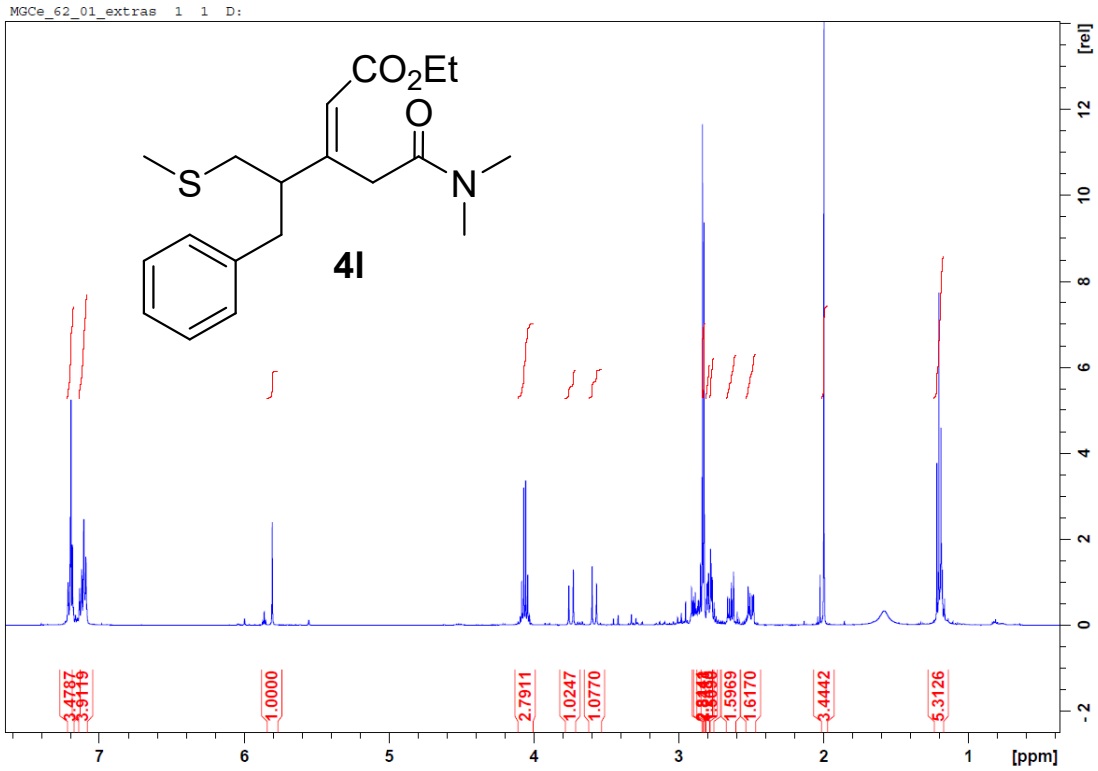
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4k** (It is a 70-30% mixture of inseparable isomers)



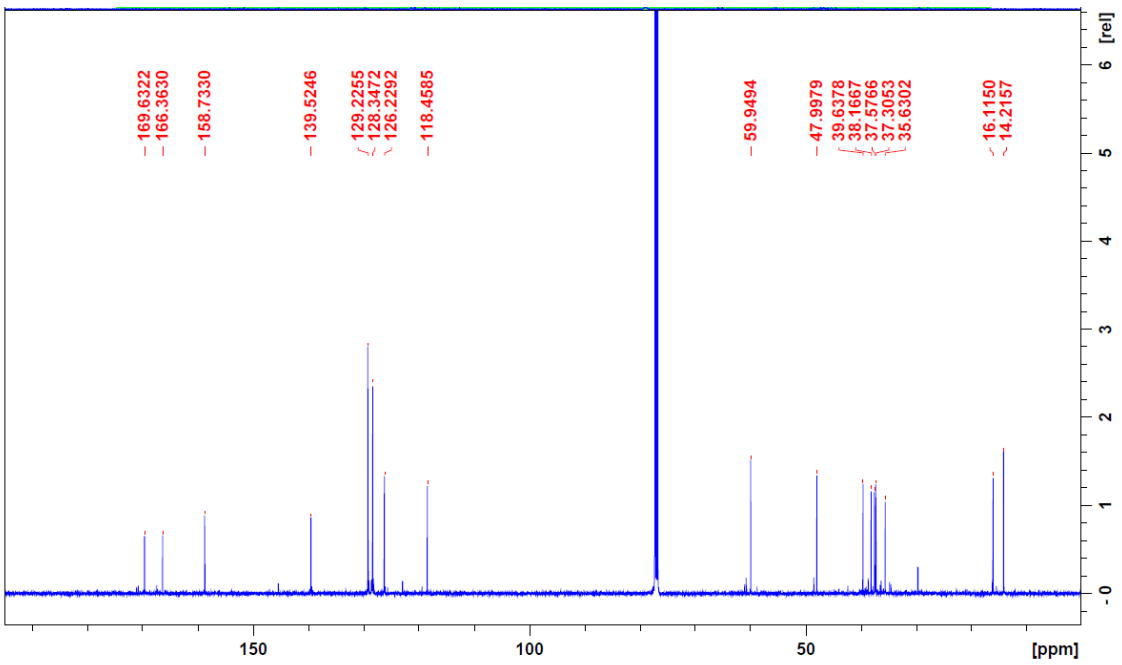
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4k´**



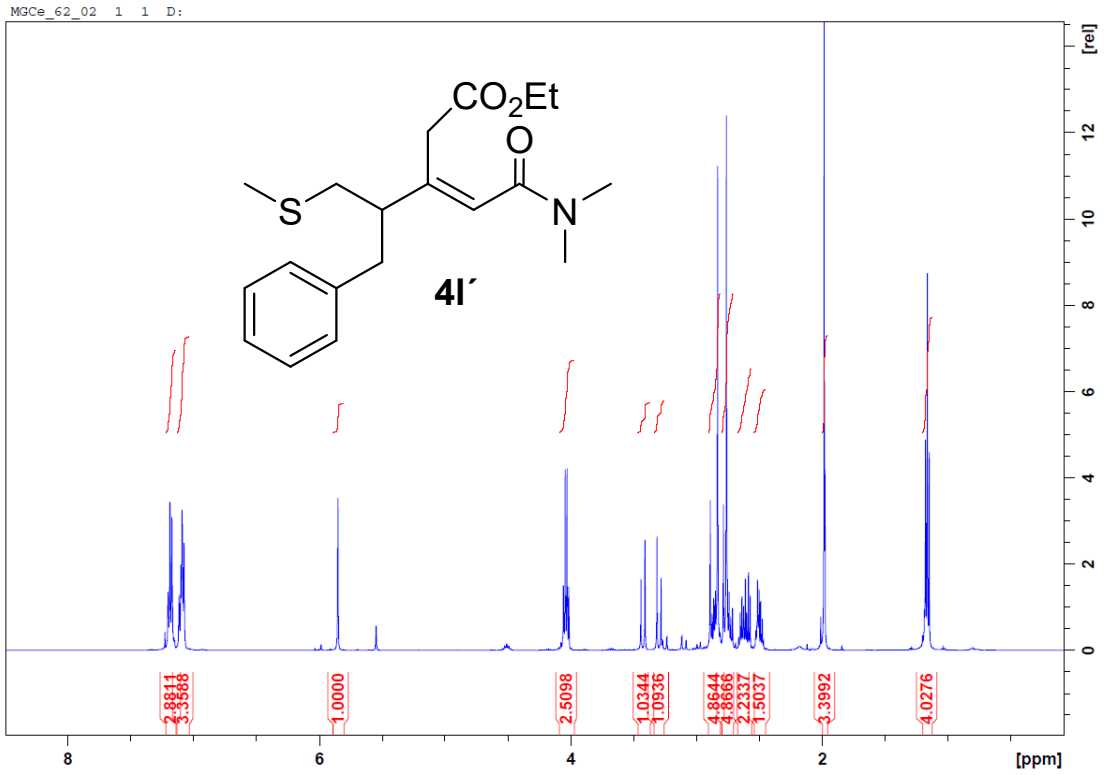
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4k´**



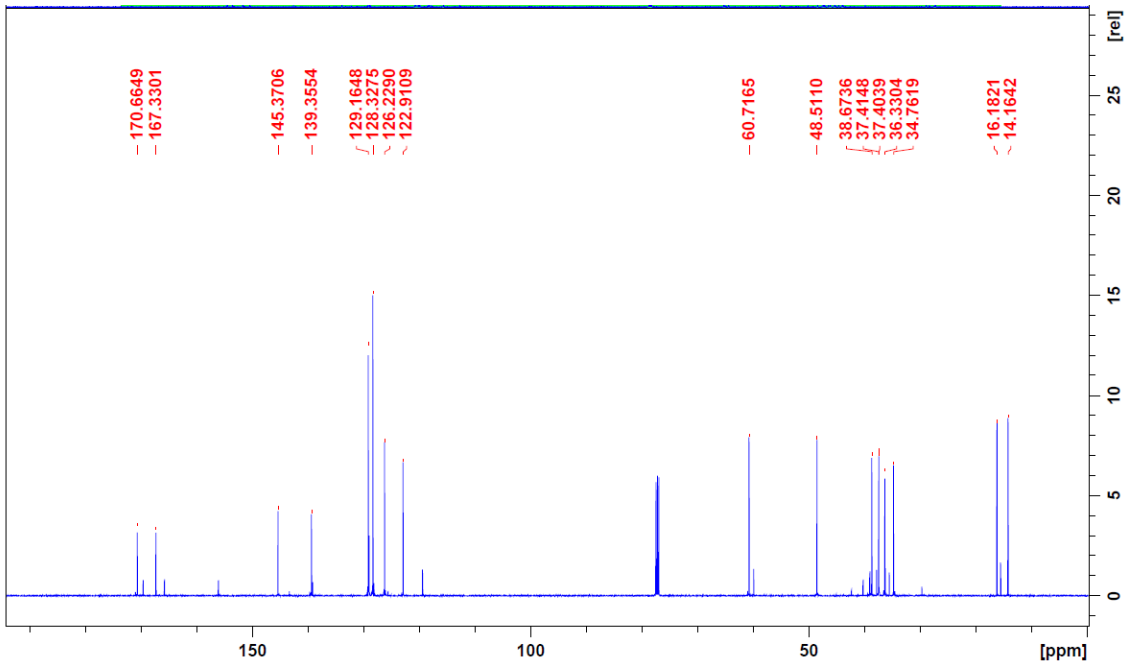
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4l**



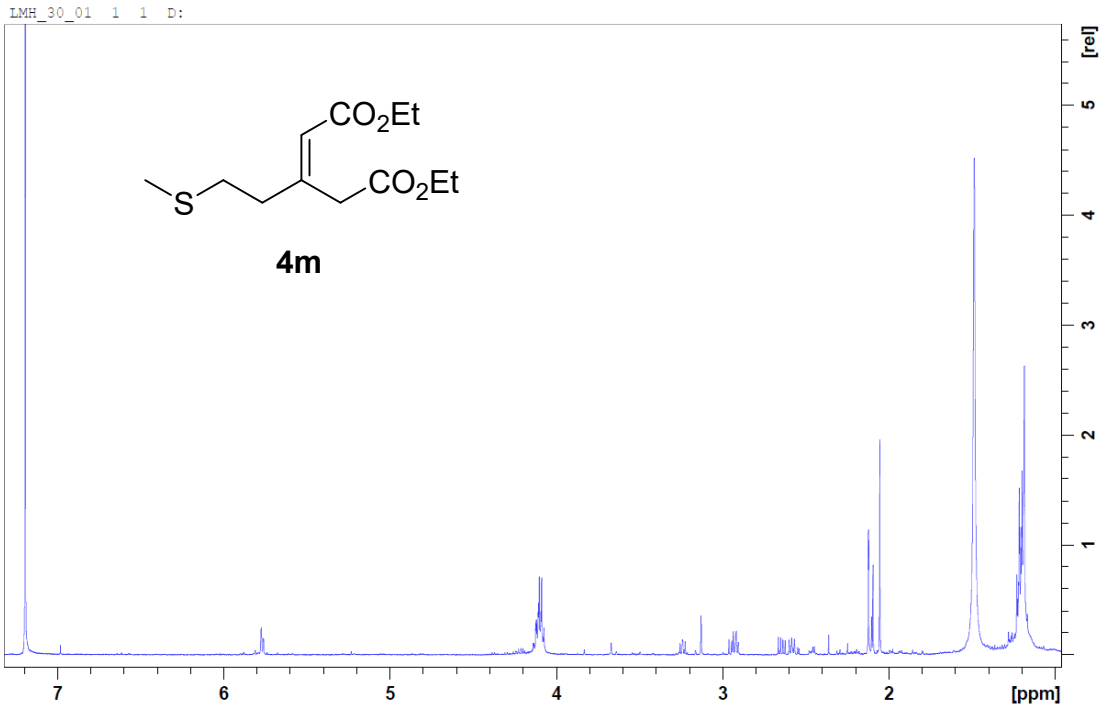
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4l**



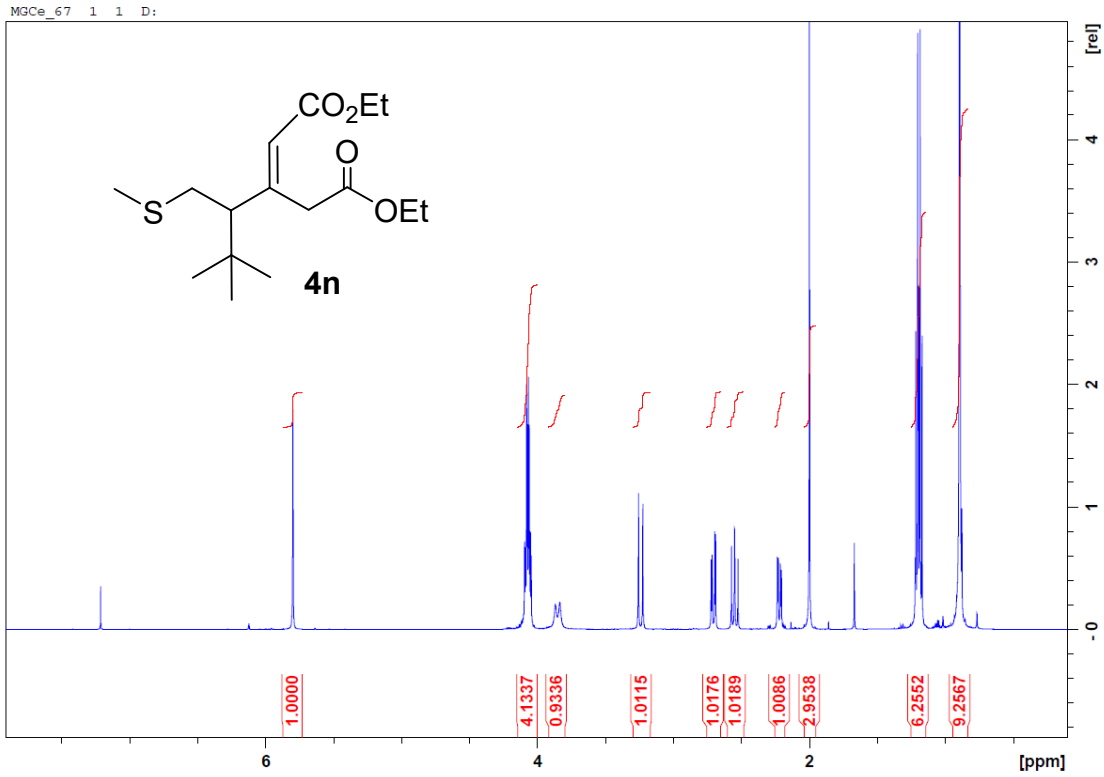
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4l´**



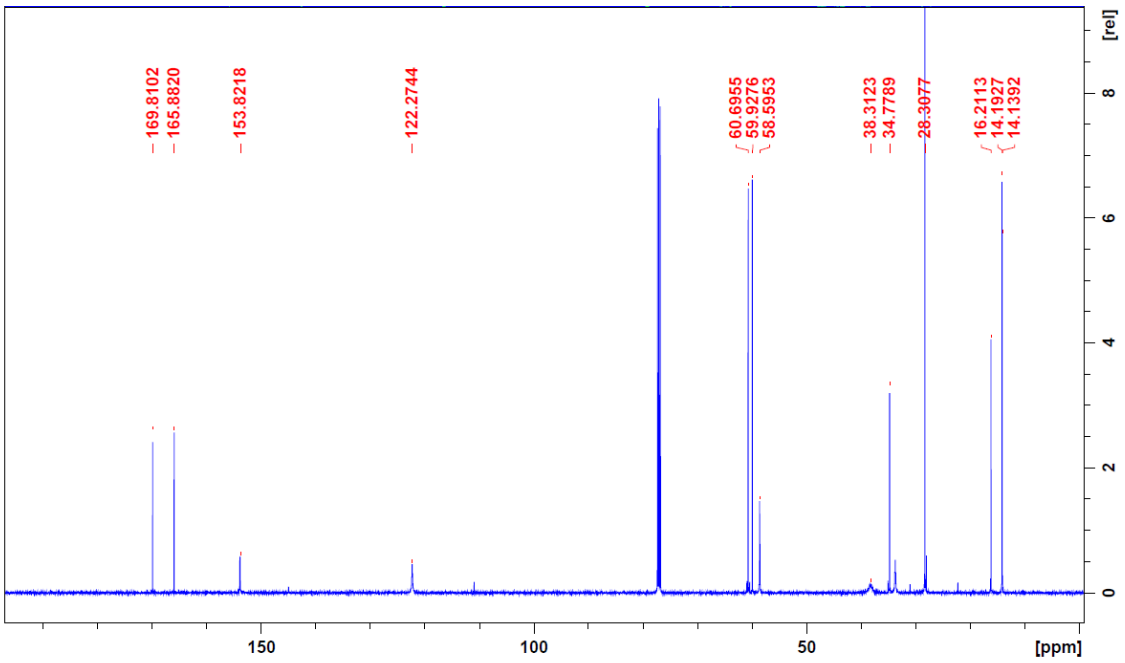
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4l´**



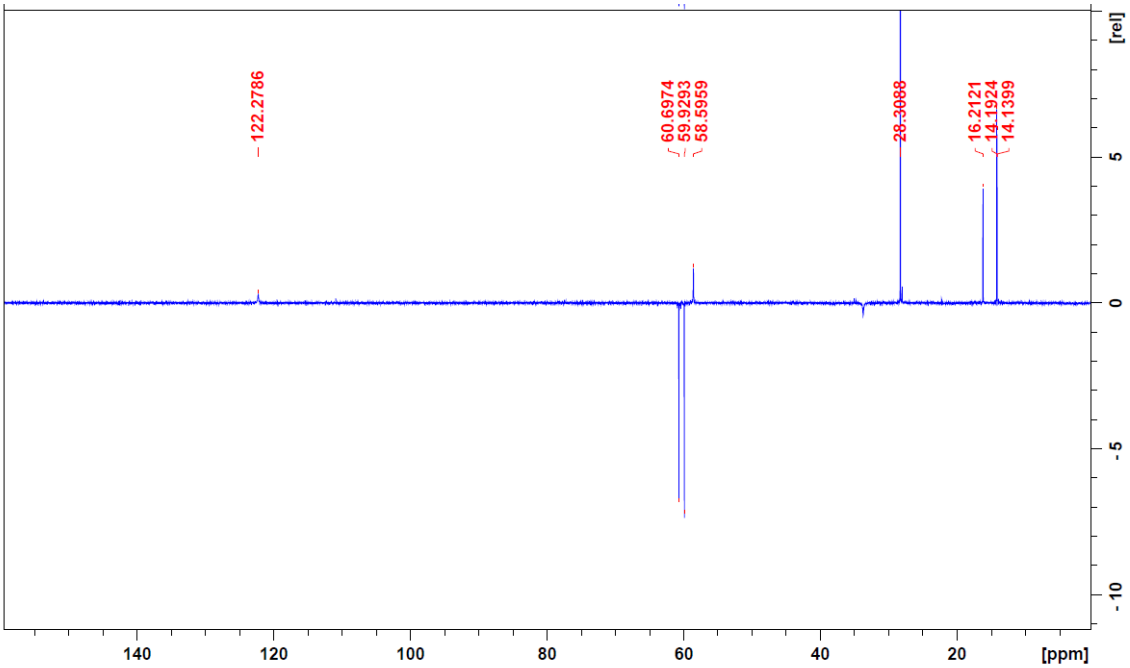
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4m** (90% purity)



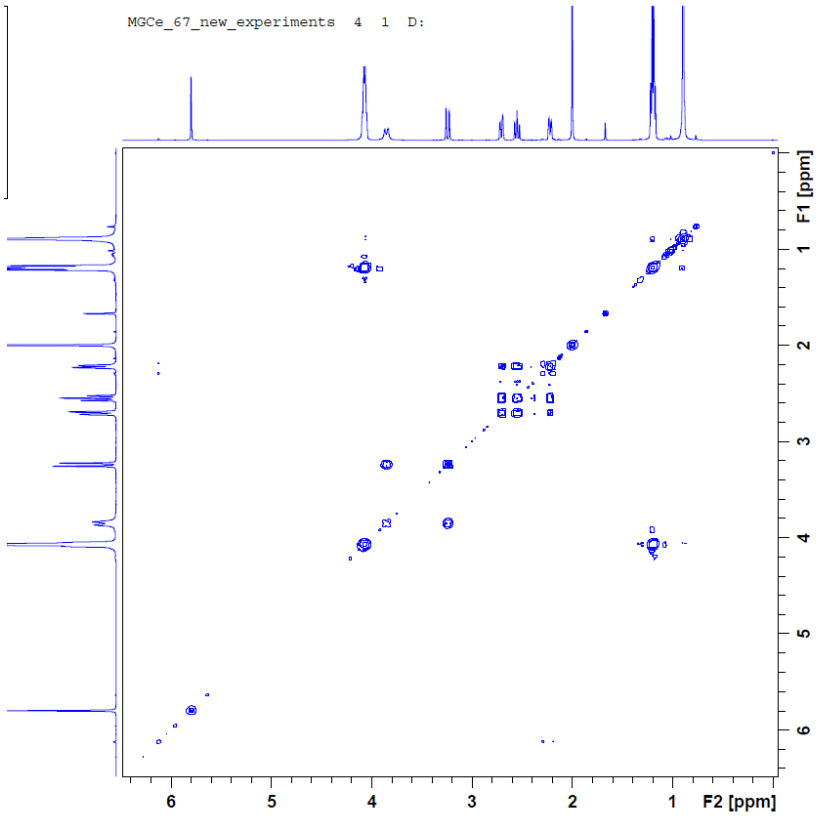
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4n**



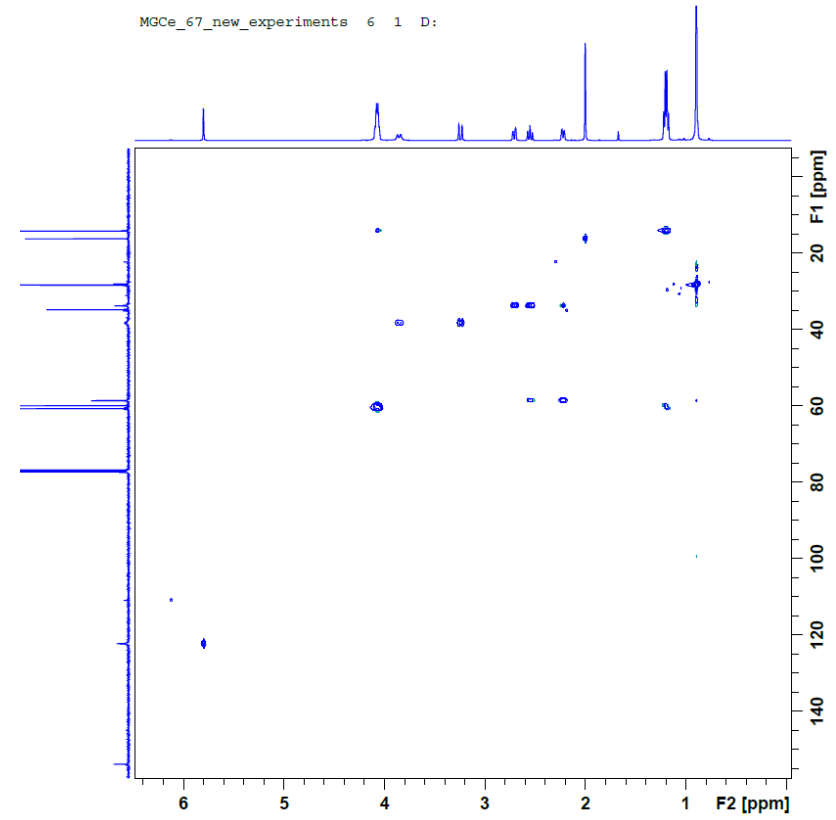
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4n**



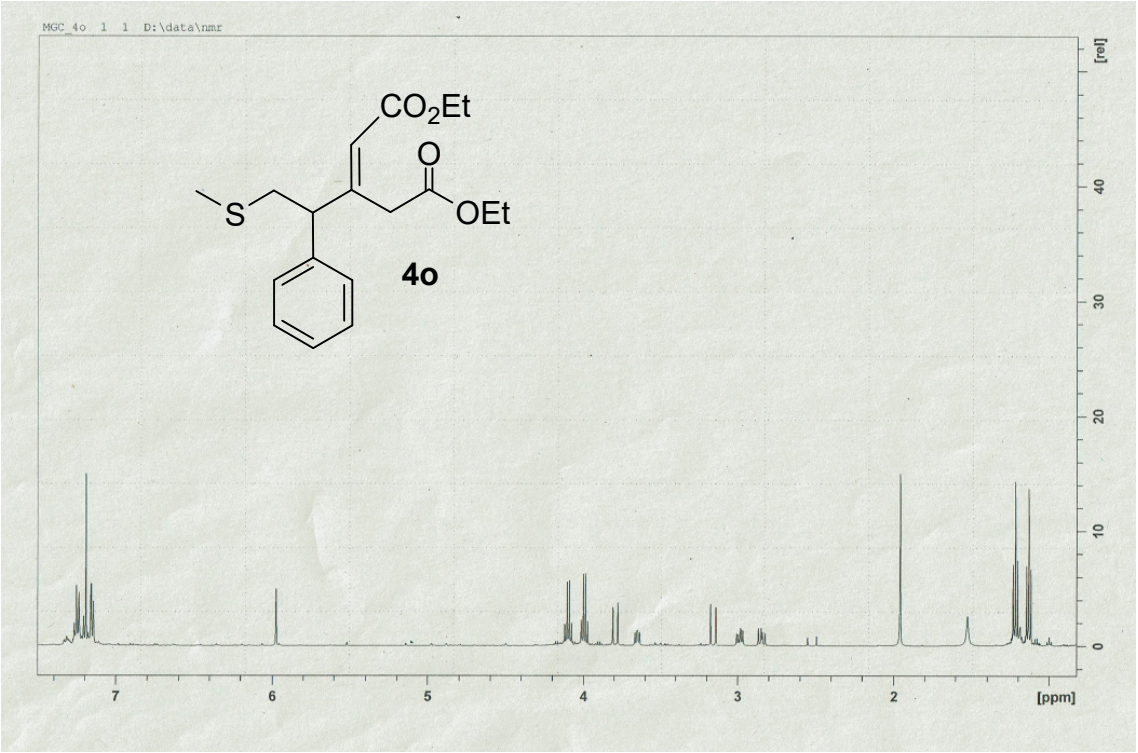
DEPT-135-NMR ($CDCl_3$) of compound **4n**



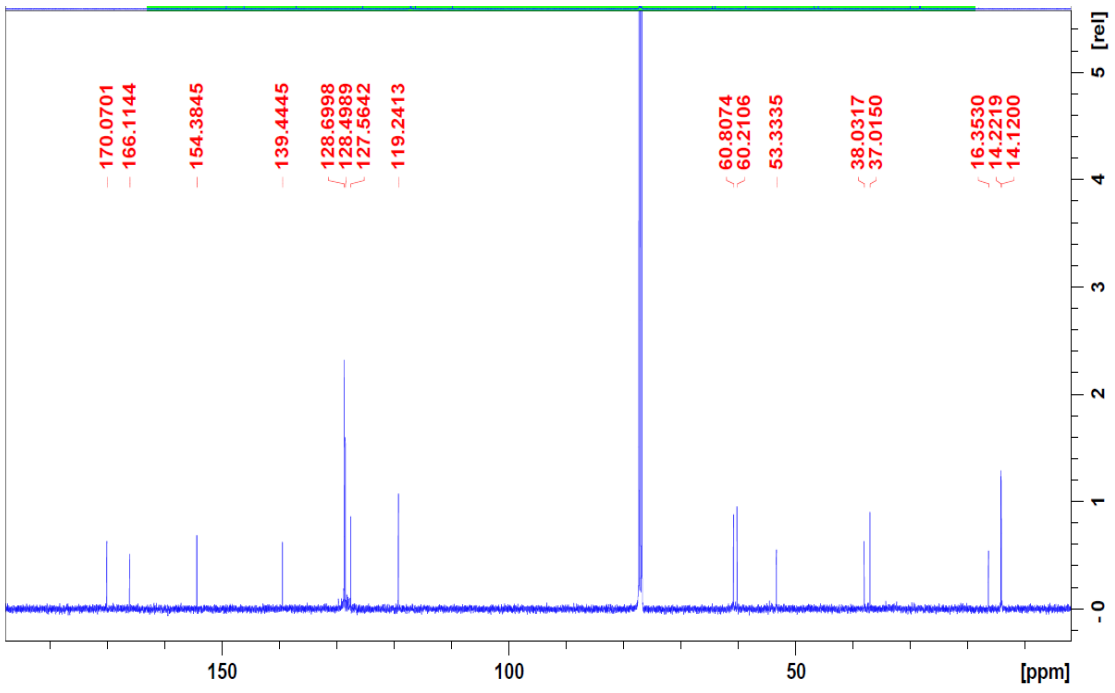
Bidimensional COSY-experiment of compound **4n**



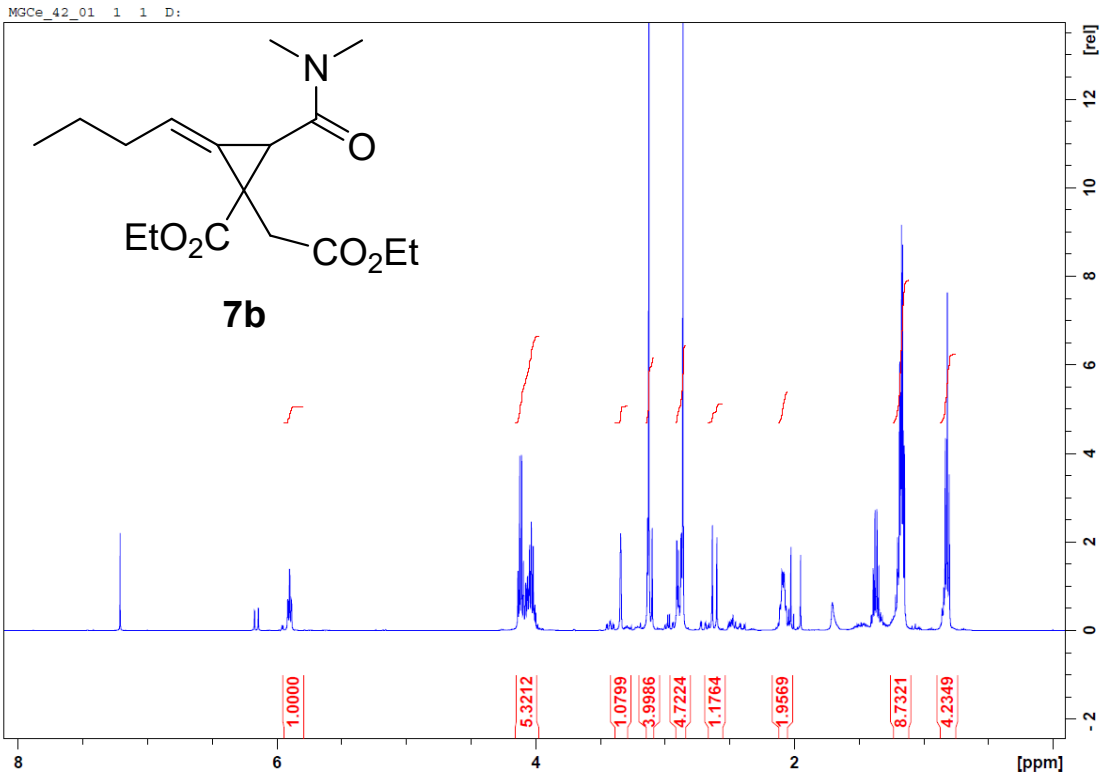
Bidimensional HSQC-experiment of compound **4n**



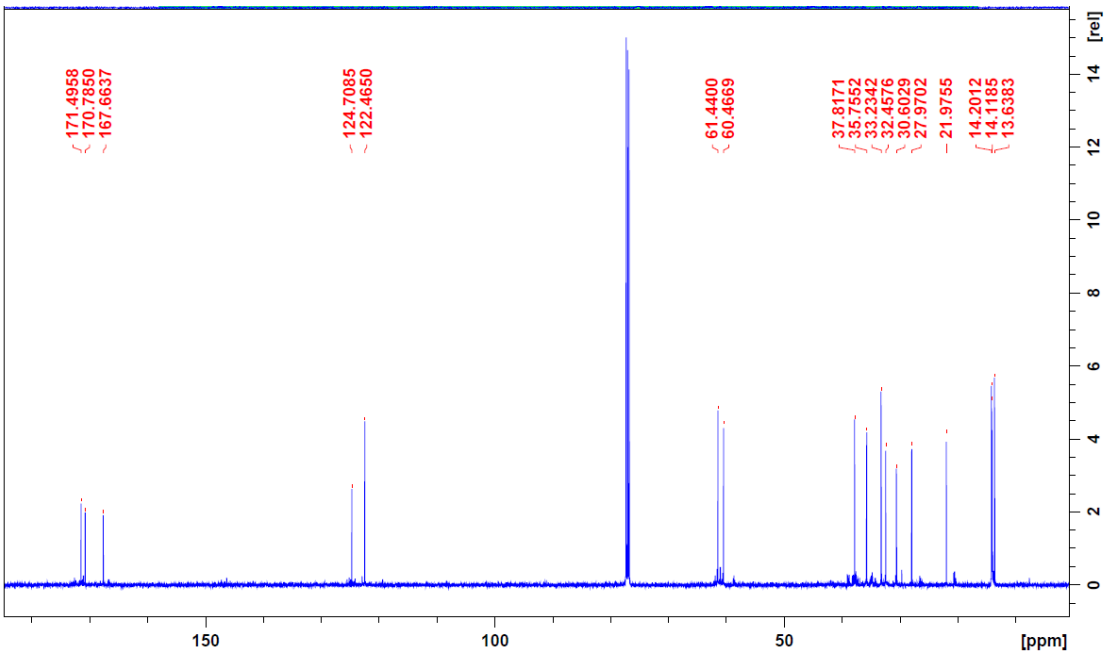
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **4o**



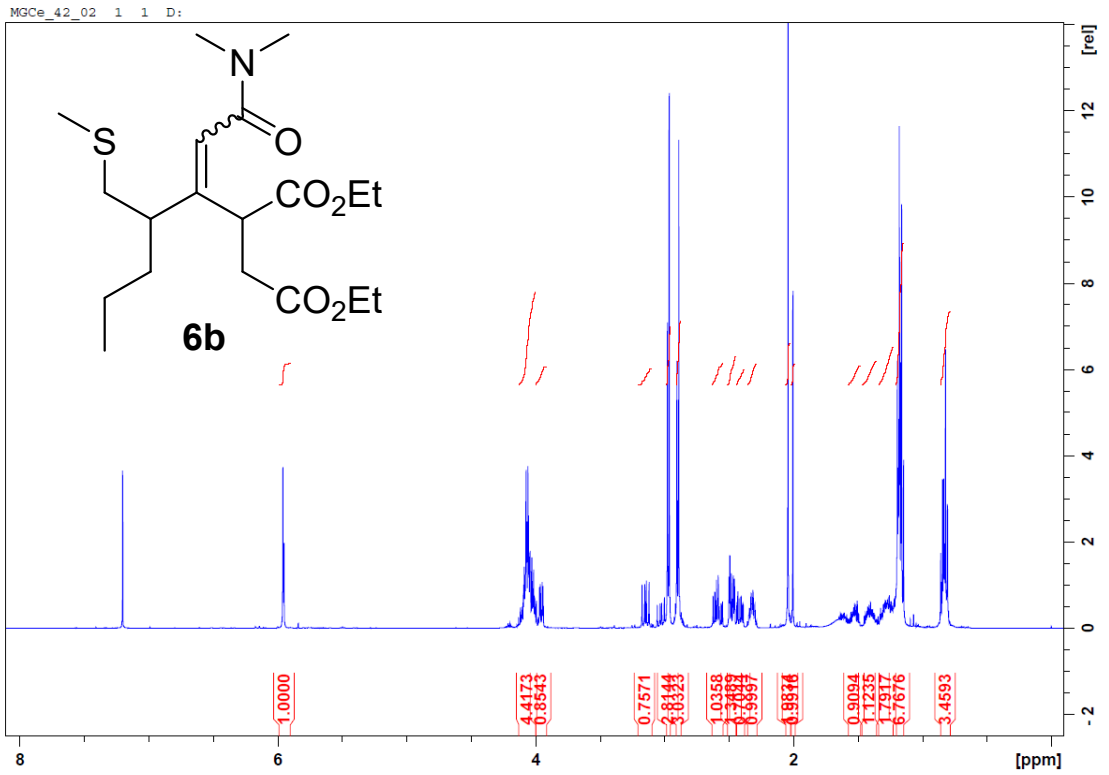
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **4o**



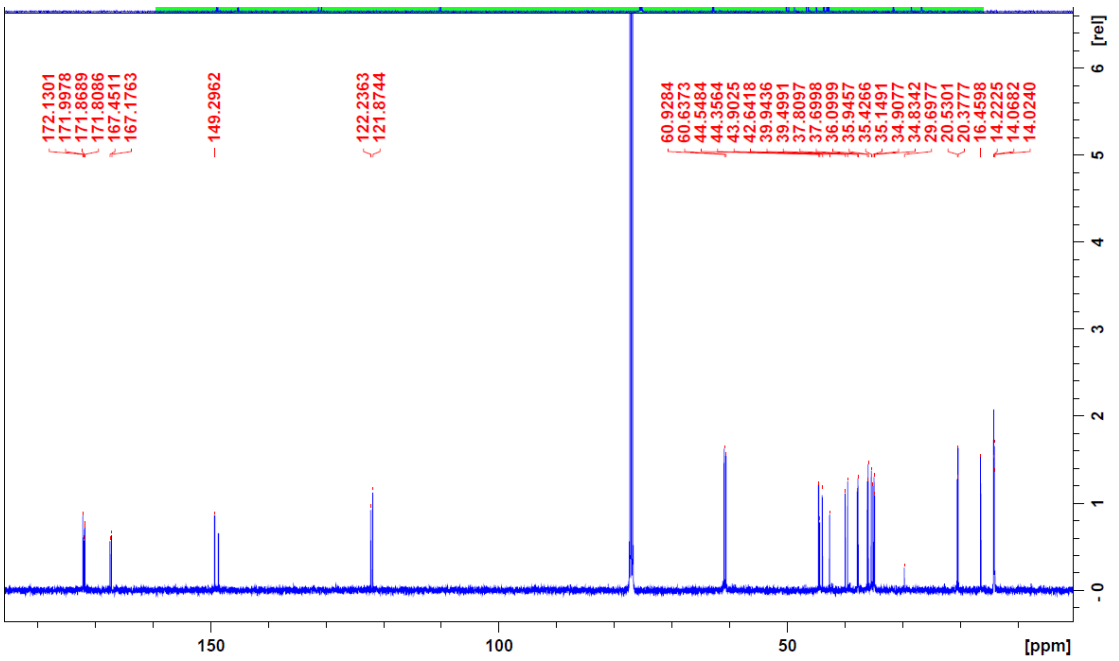
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **7b**



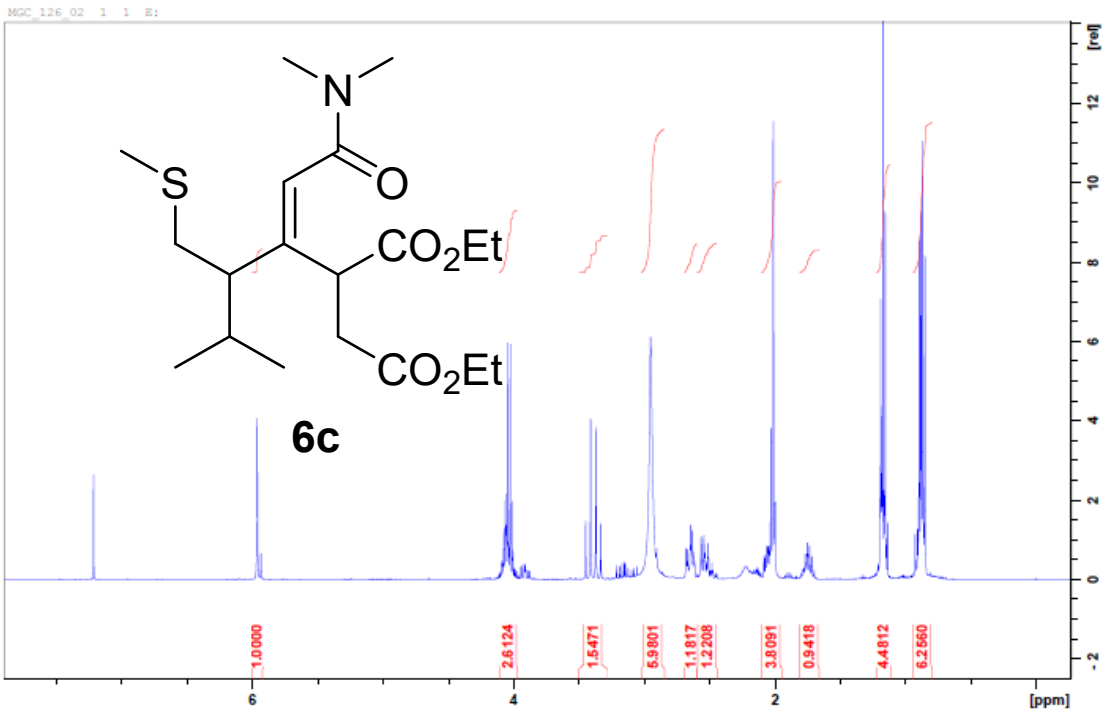
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **7b**



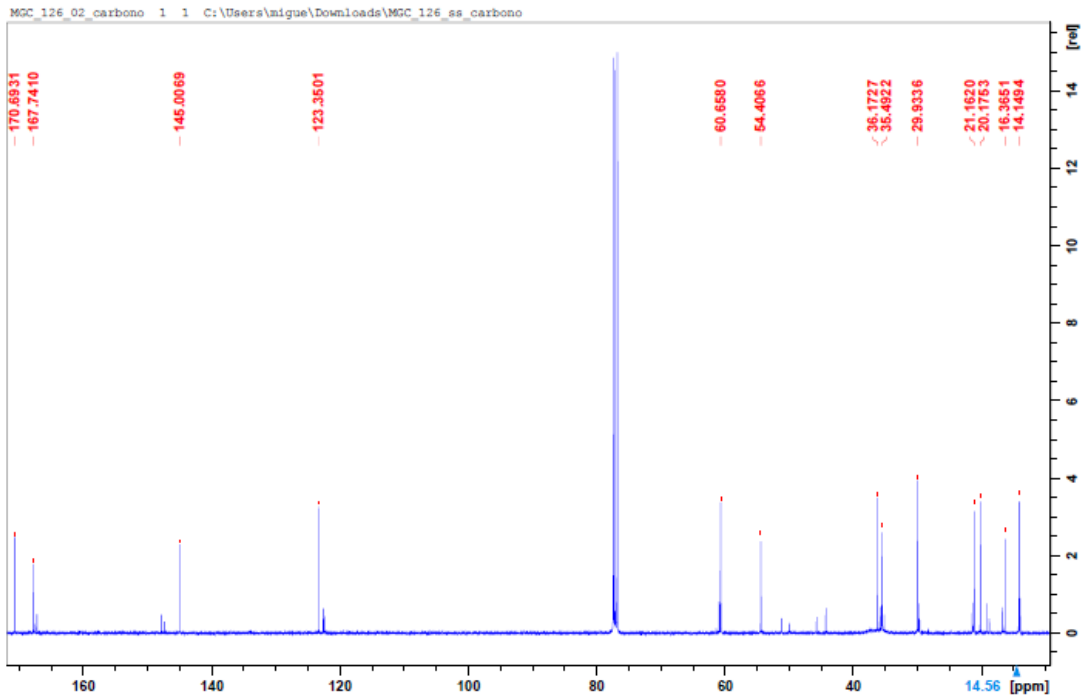
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **6b**



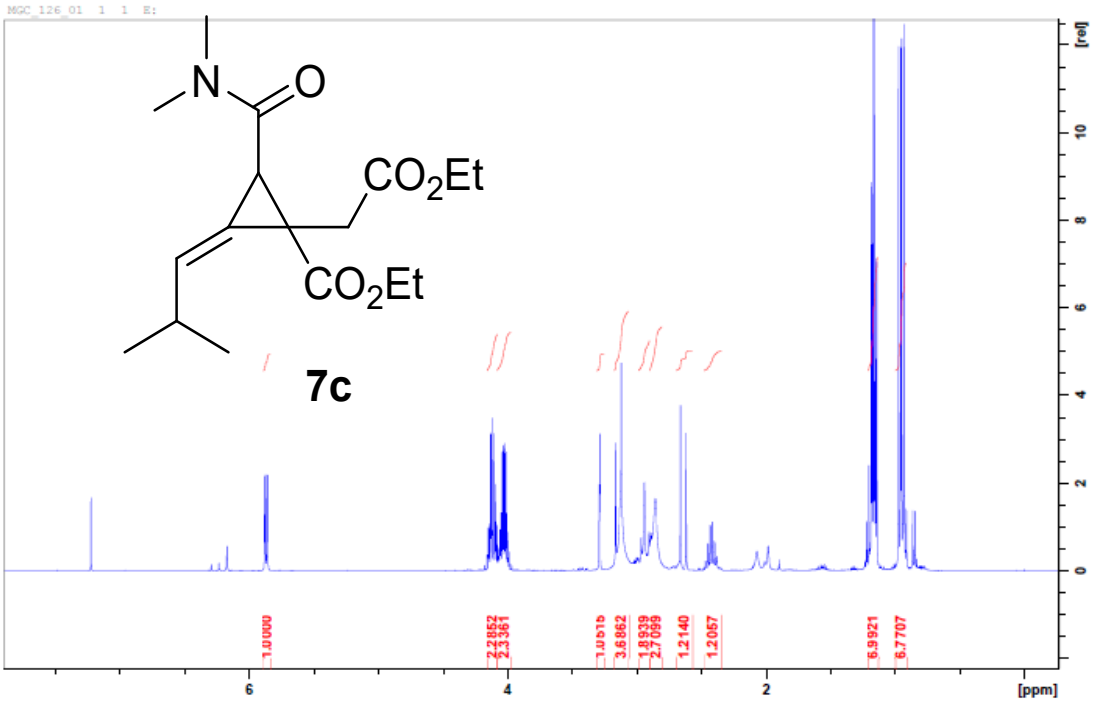
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **6b**



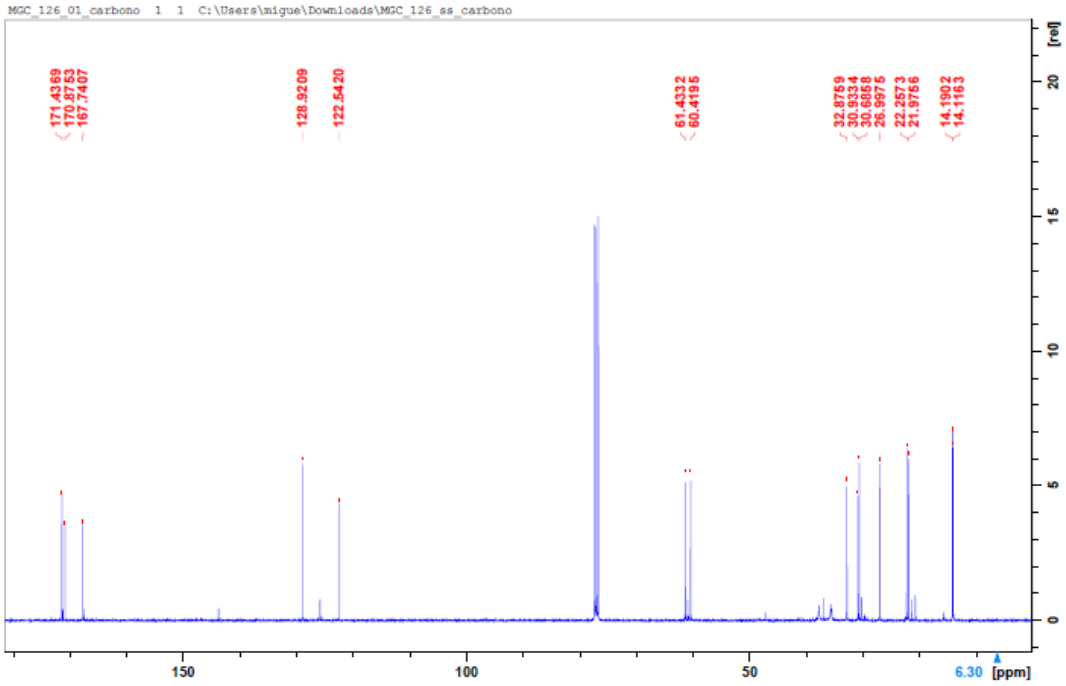
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **6c**



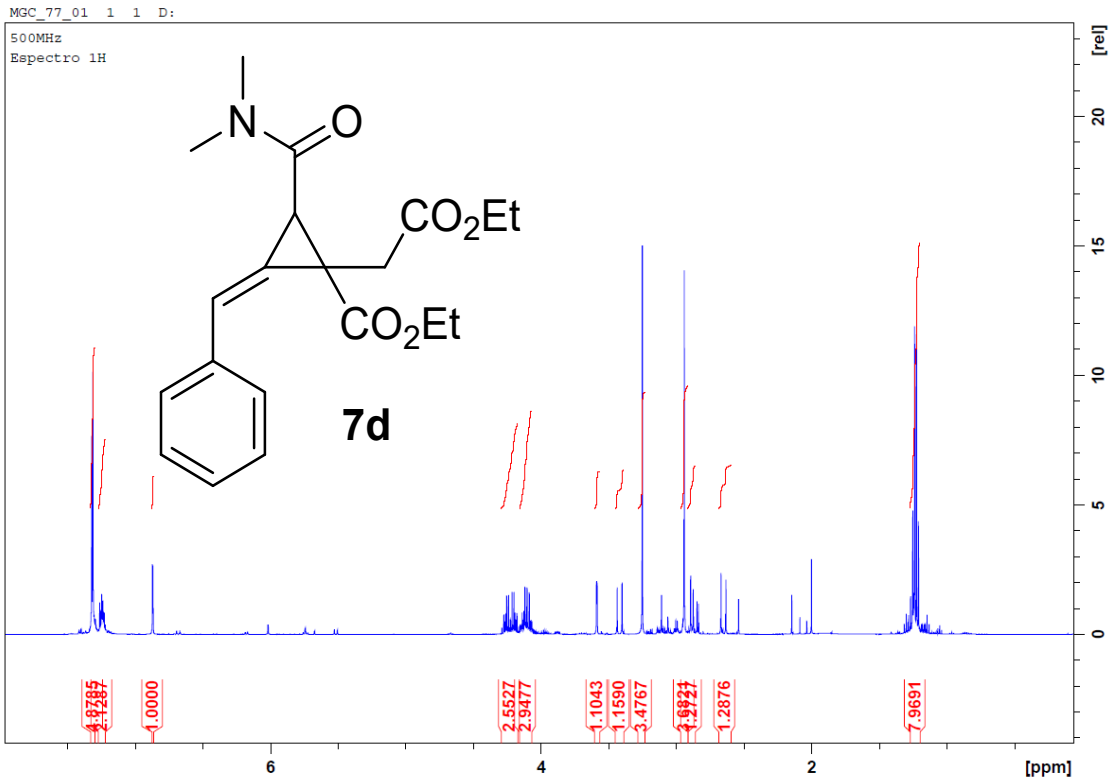
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **6c**



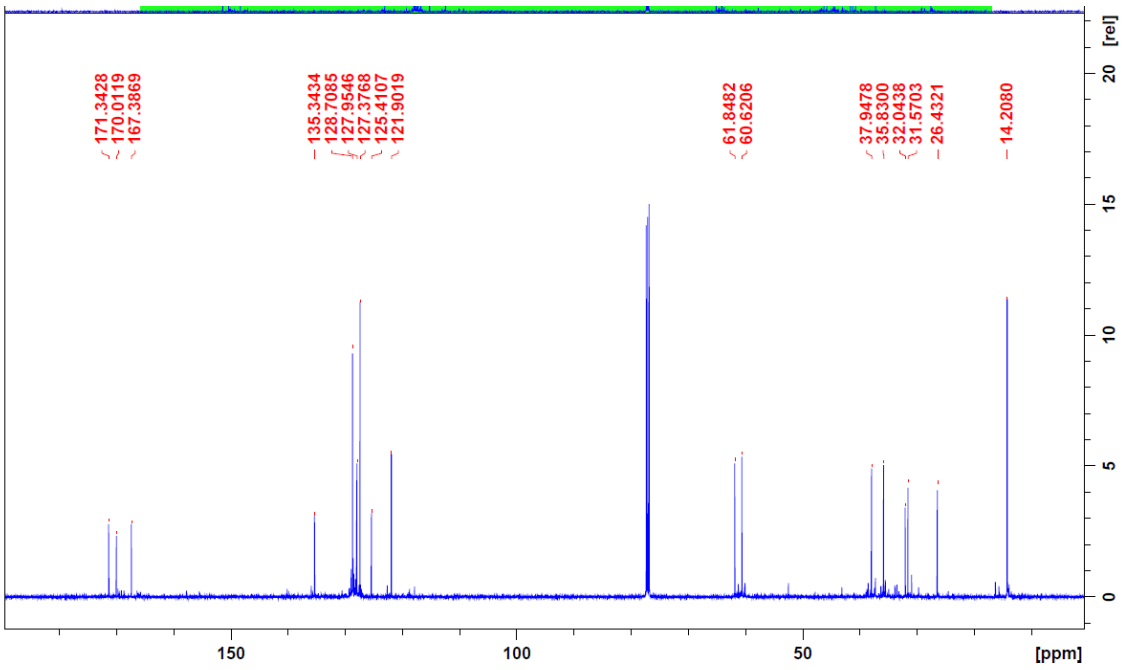
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **7c**



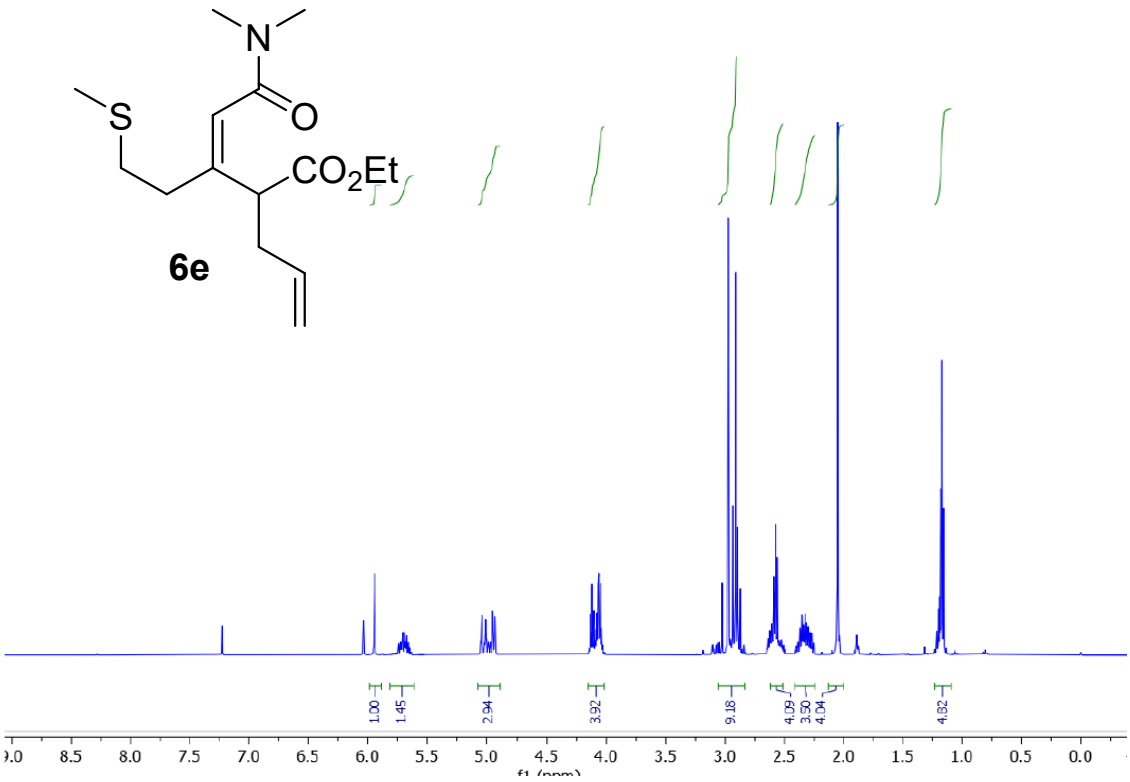
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **7c**



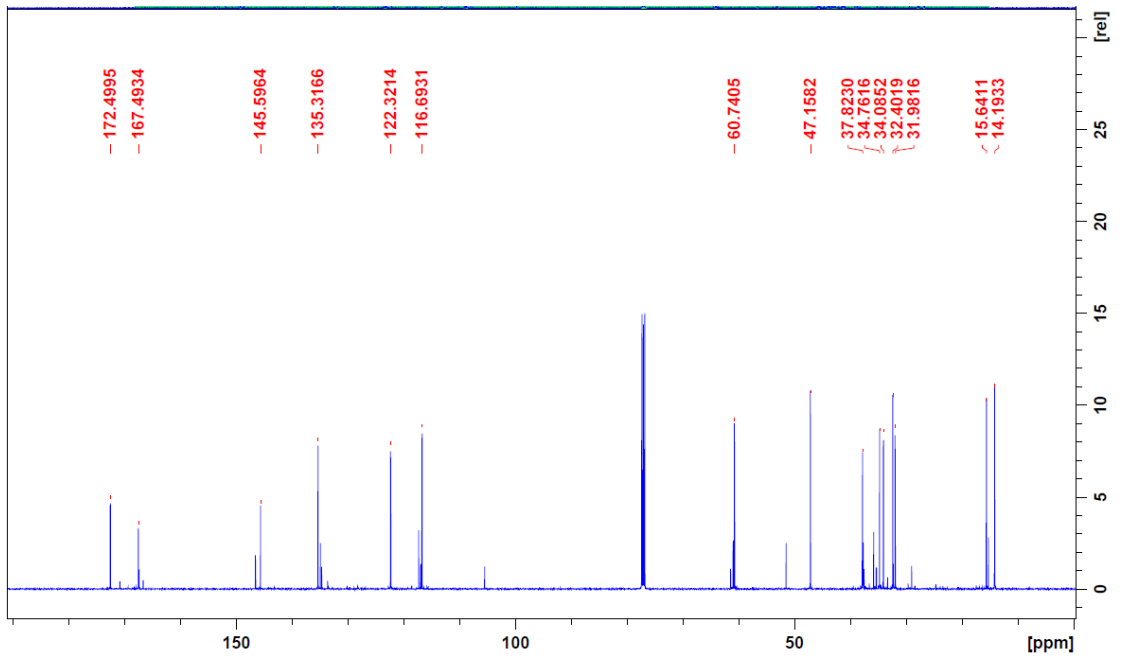
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **7d**



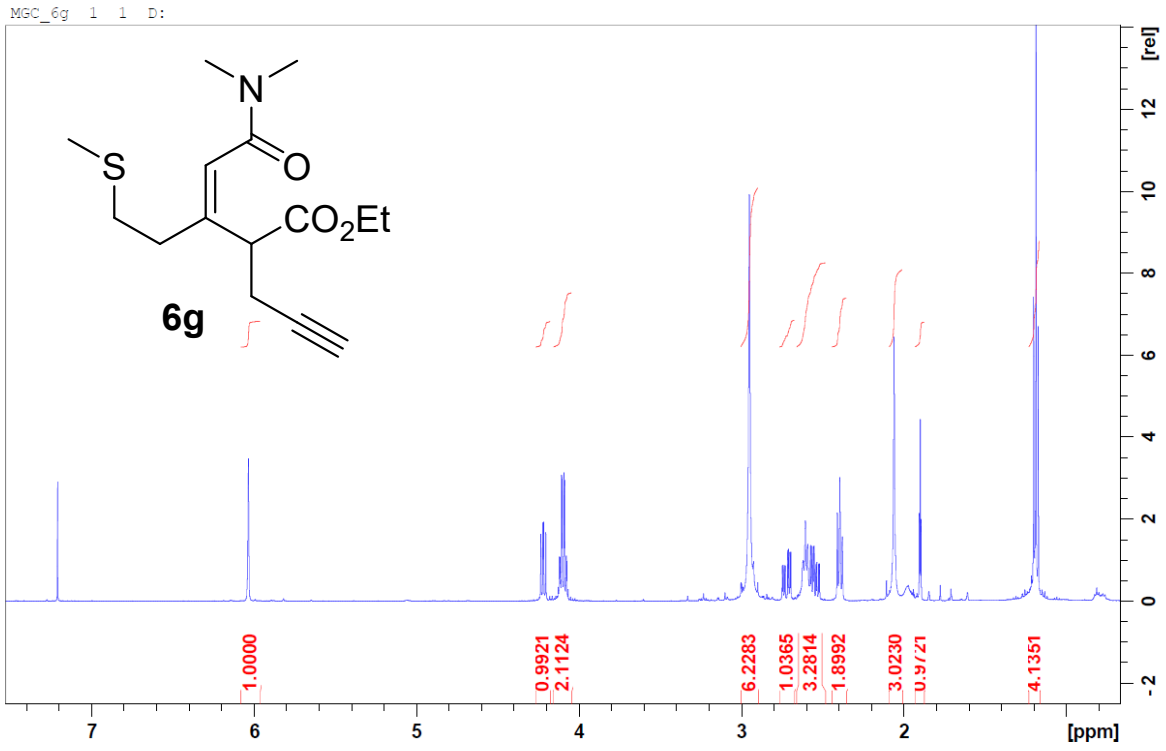
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **7d**



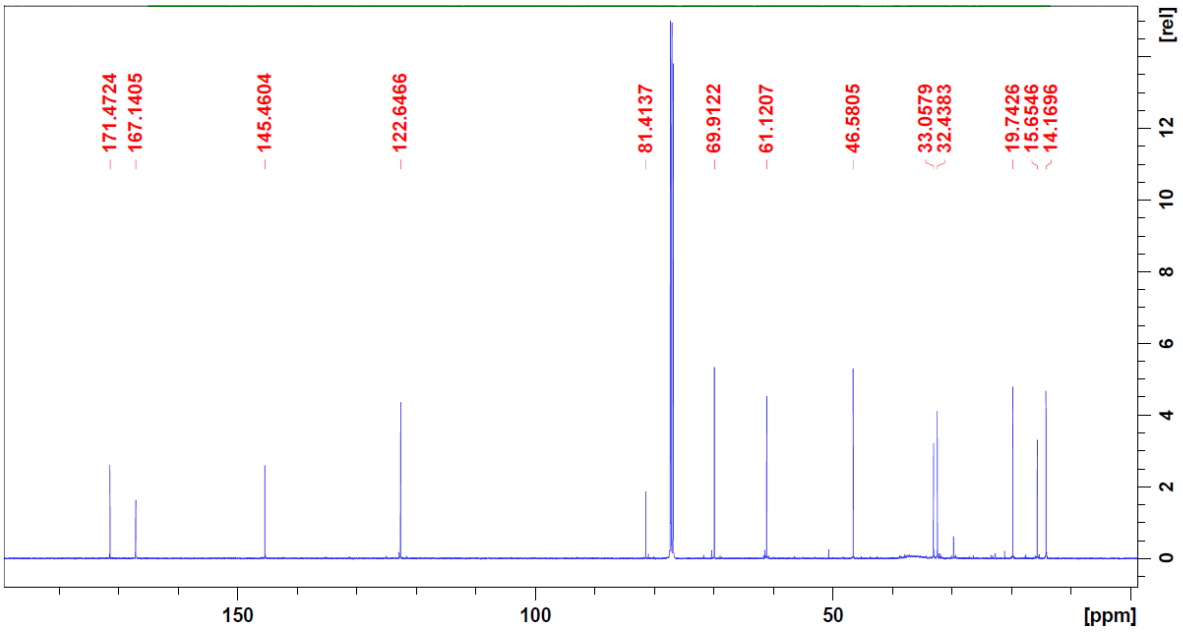
^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **6e**



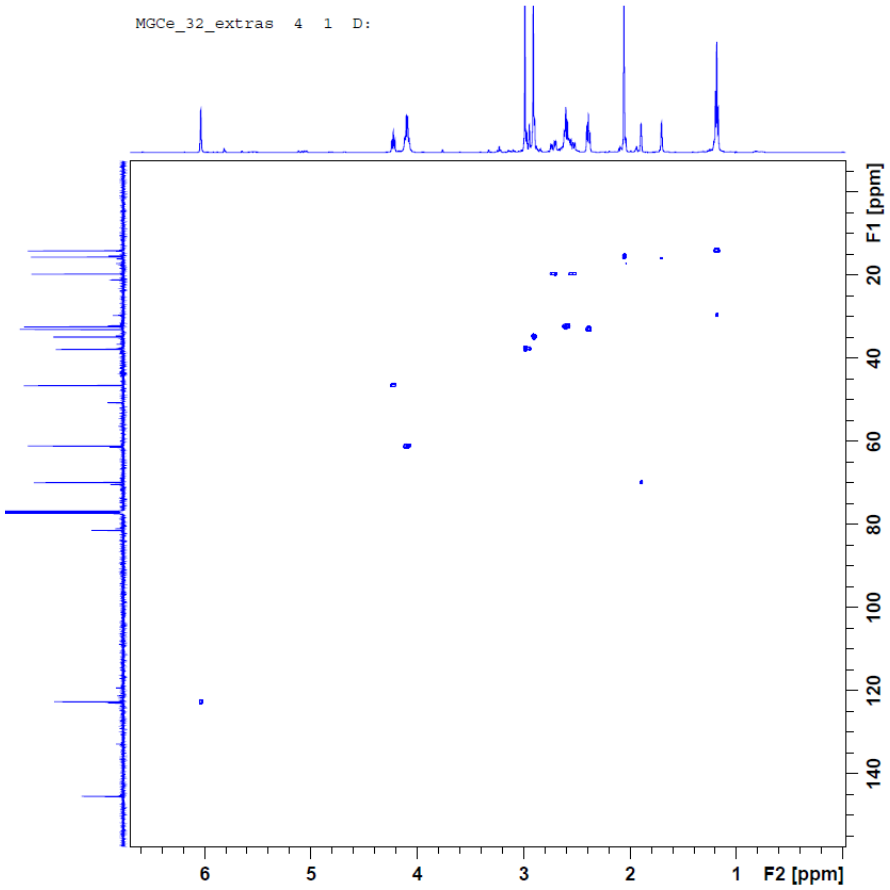
^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **6e**



^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **6g**



^{13}C-NMR ($CDCl_3$, 125 MHz) of compound **6g**



Bidimensional HSQC-experiment of compound **6g**

Reference 13: Non reproducible experiments employing another bases

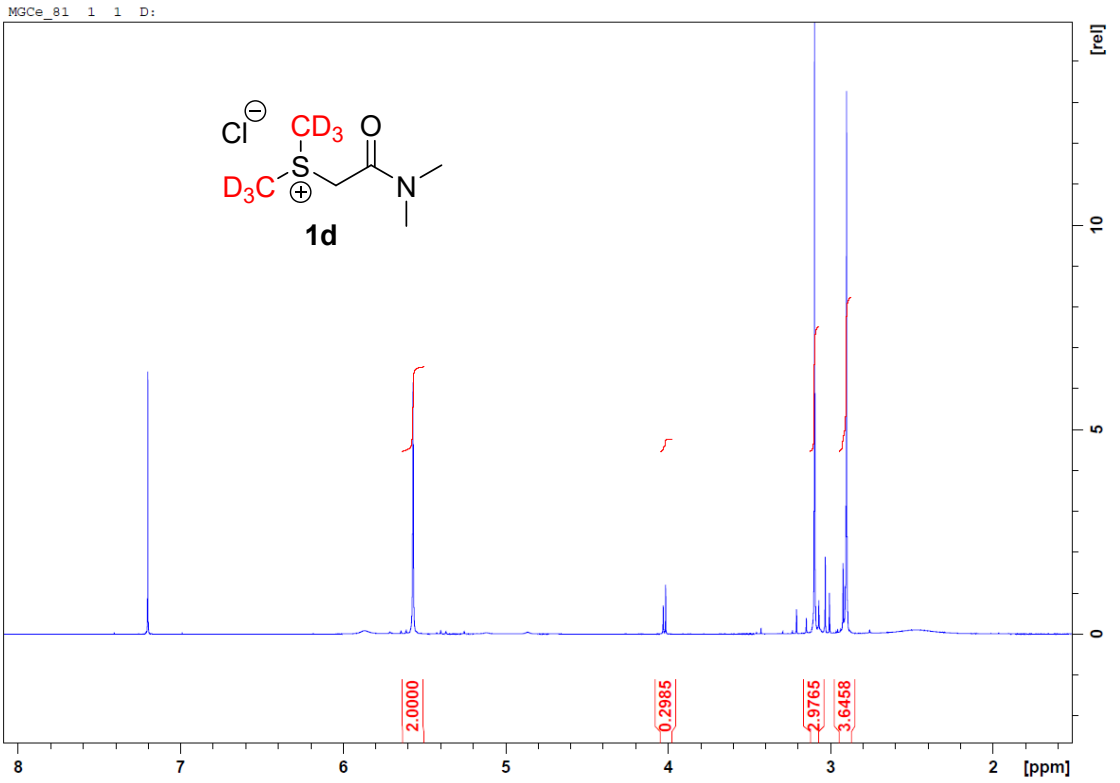
When sodium hydride was used as base to generate the sulfur ylide, using acetronitrile or DMF as solvent, reaction products were detected, and we could determine the reaction between 2 molecules of allenoate and 1 molecule of sulfur ylide. However, the experiments were non reproducible at all.

Mechanistic studies. Isotopic labelling

We synthesized sulfonium salt **1d** and we got confirmation by NMR analysis because of absence of signals assigned to methyl groups attached to sulfur atom. Then, we designed

an original and genuine protocol in order to isolate the deuterated compound **4e´**, what it would confirm our proposed mechanism.

Thus, our efforts were addressed to isolate the sulfur ylide **2d** itself. With this objective, we modified an earlier protocol used in our labs (F. Sarabia, **2008**) consisting in reaction between sulfonium salt **1d** (239 mg, 1.25 mmol, 1.0 equiv.) with NaH (60% mineral oil, 60 mg, 1.50 mmol, 1.2 equiv.) in acetonitrile at room temperature and stirred for 3 hours, with the presence of two drops of D_2O. Then, reaction mixture was filtered and concentrated in rotavapor, affording the freshly prepared sulfur ylide **2d**. This freshly prepared compound **2d** was redissolved in freshly distilled dichloromethane and allenoate **3e** (193 mg, 1.25 mmol, 1.0 equiv.) was then added (dissolved in 1mL of DCM) to reaction. Reaction was stirred at room temperature for 3 hours. Then, reaction mixture was directly concentrated in rotavapor and dried at high vacuum. Crude of reaction was then purified by flash column chromatography to separate both deuterated compounds **4e** and **4e´**. Then, we realized ^{1}H-NMR analysis of compounds using $CDCl_3$, and we could observe a good ratio of proton-deuterium exchange between acidic protons in α-position of sulfur atom and protons of solvent (*see first spectra serie,* **Figure S1***, page SI-83*). In order to avoid that easy exchange of protons, we realized another identical experiment but using benzene-d_6 to do the ^{1}H-NMR analysis, obtaining an excellent concordance with the expected spectra, where the absence of signals confirm our proposed mechanism. (*see second spectra serie,* **Figure S3***, page SI-85*).

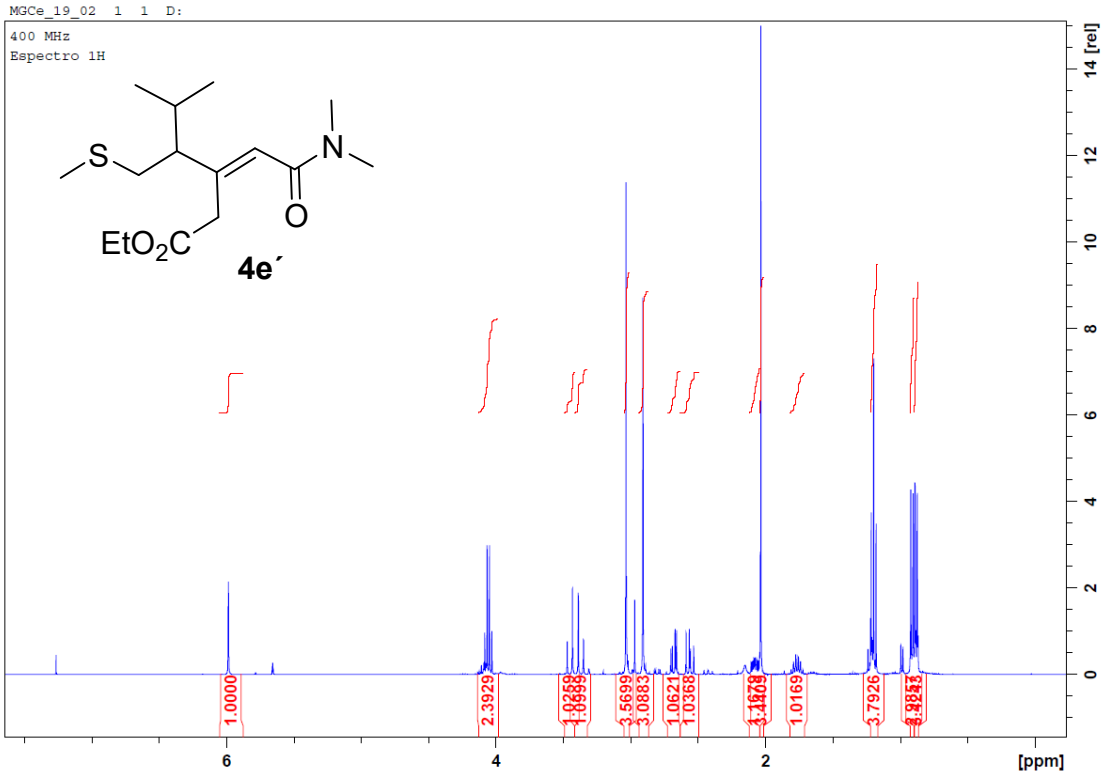


^{1}H-NMR ($CDCl_3$, 500 MHz) of compound **1d**

The proportion of deuterium on deuterated compound **4e´** based on NMR spectra was clearly observed in the methyl group attached to sulfur atom, where we observed a signal at 2.04 ppm, which integration is 0.7H (It is 3H in non-deuterated compound **4e´**). Moreover, we also observed the decreased integration at 2.33 ppm and 2.64 ppm corresponding to CD_2 attached to sulfur atom. That fact that integration is 0.74 H and 0.77 H instead of 0 H each one is due to the easy interconversion between hydrogen atoms and deuterium atoms with the solvent ($CHCl_3$ contained in $CDCl_3$) because of acidity of them . **(Figure S1)**

As we have already explained, in order to reduce the high ratio of interconversion between hydrogen atoms and deuterium atoms we programmed the second experiment, using benzene-d_6 as solvent for ^{1}H-NMR analysis.

First spectra serie registered in $CDCl_3$



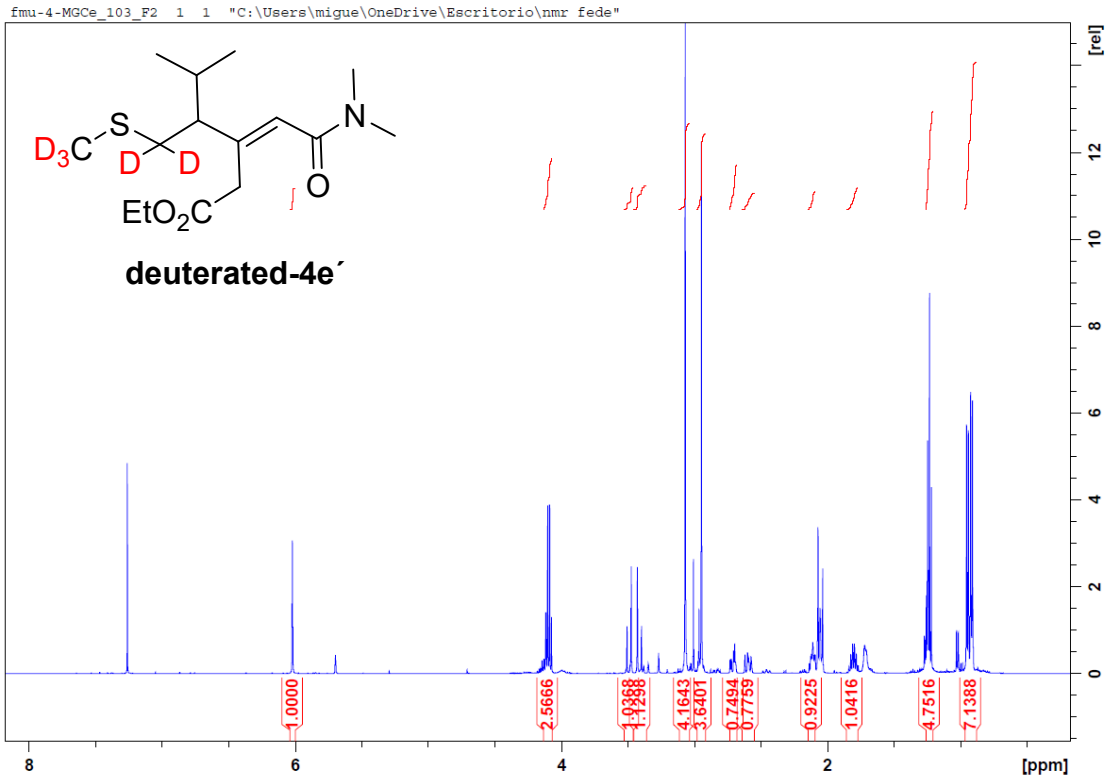
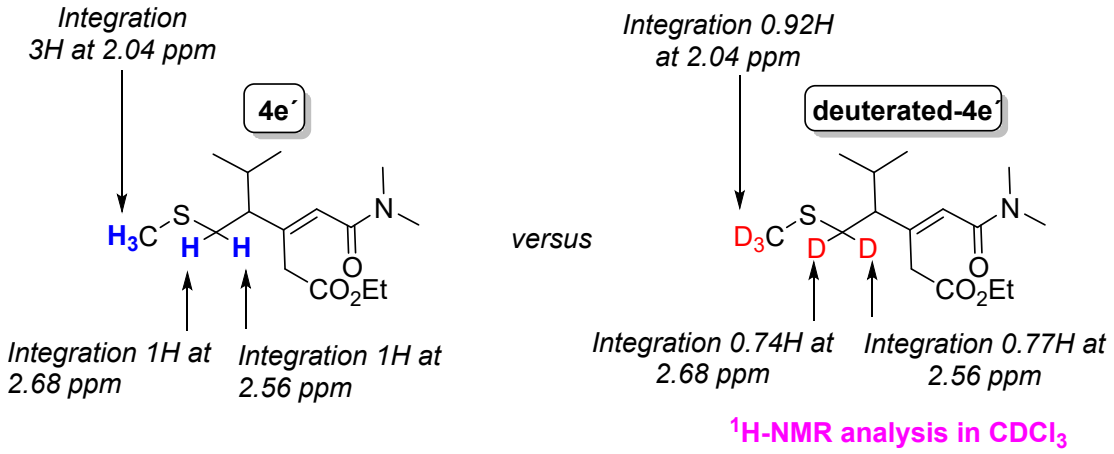


Figure S1. Up-spectra: ^{1}H-NMR (500 MHz) of compound **4e´** vs Down-spectra: ^{1}H-NMR (500 MHz) of deuterated compound **4e´**.

The proportion of deuterium on deuterated compound **4e´** based on NMR spectra was clearly observed in the methyl group attached to sulfur atom, where we did not observe a signal at 2.04 ppm, corresponding to methyl group attached to sulfur atom. Moreover, we also observed the decreased integration at 2.56 ppm and 2.68 ppm corresponding to CD_2 attached to sulfur atom. Now, these integrations are reduced up to 0.56 H and 0.43 H *versus* 1H each one in compound **4e´. (Figure S2 and S3)**



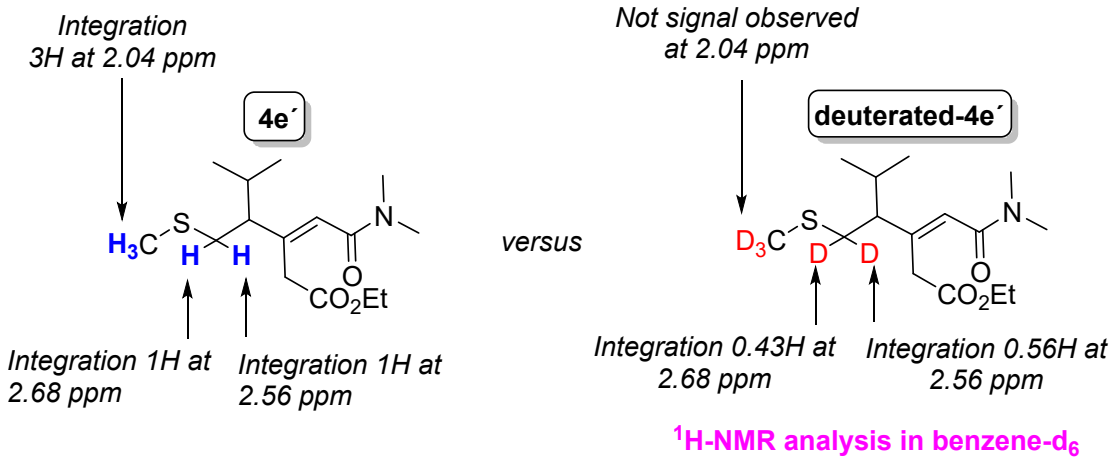
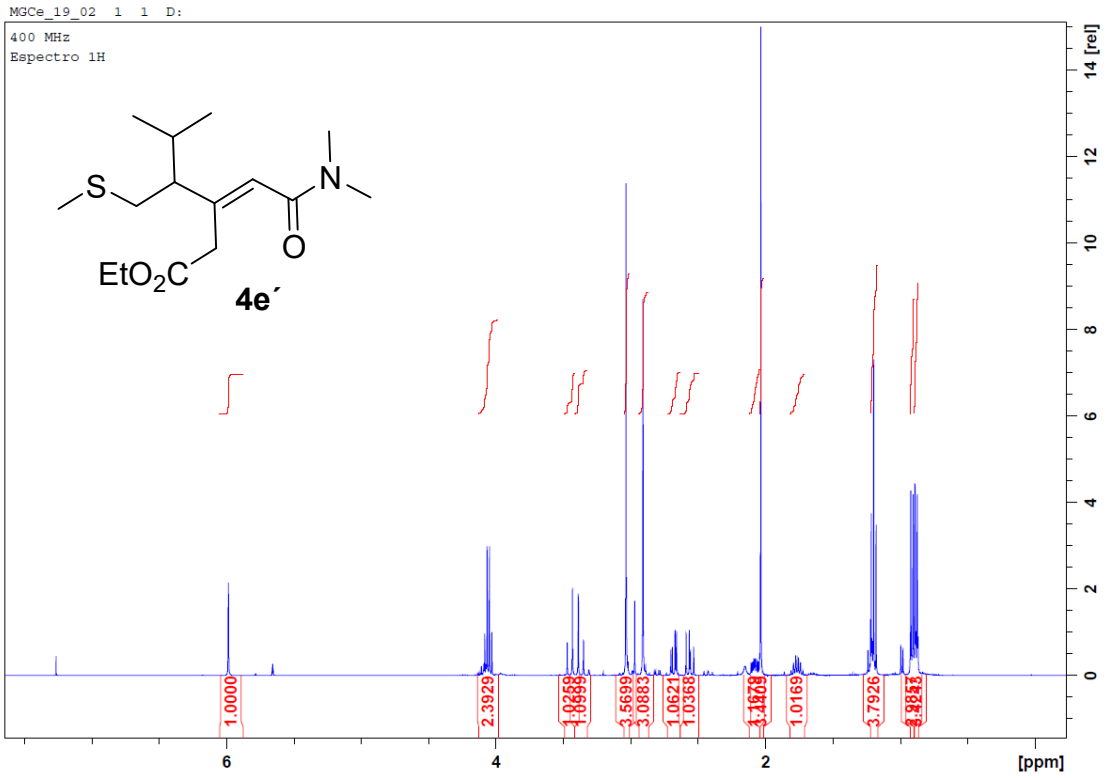


Figure S2. ^{1}H-NMR analyses of compounds **4e´**. Differences between proton-deuterium exchange in $CDCl_3$ and benzene-d_6

Second spectra serie registered in Benzene-d_6



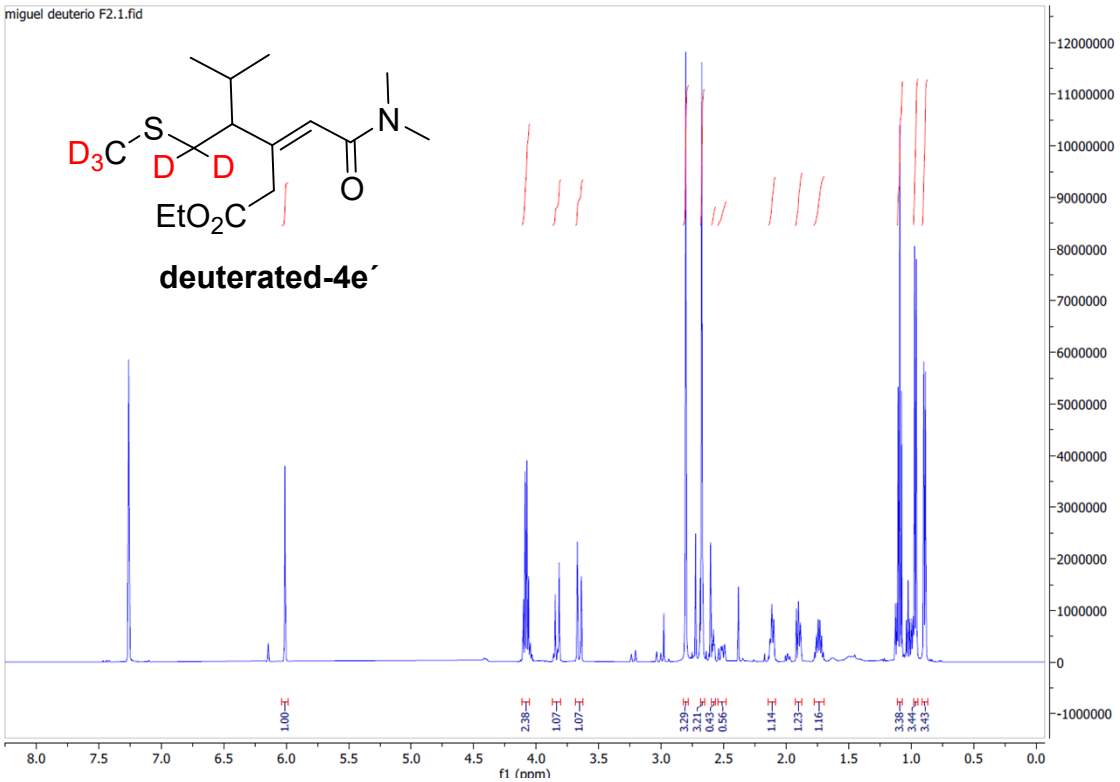


Figure S3. Up-spectra: ^{1}H-NMR (500 MHz) of compound **4e´** vs Down-spectra: ^{1}H-NMR (500 MHz) of deuterated compound **4e´**