Electronic Supplementary Information

Palladium-Catalyzed [3C+2C+2C] Cycloaddition of Enynilydenecyclopropanes. Efficient Construction of 5-7-5 fused Tricyclic Systems

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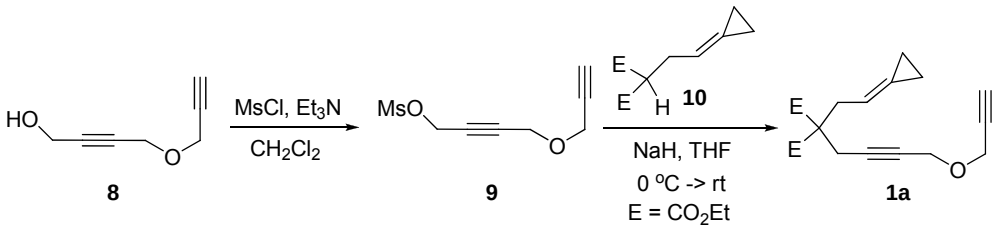
General experimental procedures

All dry solvents were freshly distilled under argon form an appropriate drying agent before use. Toluene and THF were distilled from sodium/benzophenone, CH_2Cl_2 and Et_3N were distilled form CaH_2, and dioxane was distilled from sodium. $Pd_2(dba)_3$ and other Pd sources were generously provided by Johnson Matthey. Tri-isopropyl phosphite, triphenylphosphite, triphenylphosphine and diethyl 2-allylmalonate were purchased from Aldrich. Tris(2,4-*t*-butylphenyl)phosphite was purchased from Strem. All reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. External bath temperatures were used to record all reaction temperatures. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, or by treating the plates with either *p*-anisaldehyde or cerium nitrate followed by heating. Flash chromatography was carried out on silica gel unless otherwise stated. Dryings were performed with anhydrous Na_2SO_4. Concentration refers to the removal of volatile solvents via distillation using a Büchi rotary evaporator with a Büchi V-700 vacuum pump, followed by residual solvent removal at high vacuum (aprox. 0.5 mmHg). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, at 250 MHz and 62.9 MHz, respectively and 300, 400 and 500 MHz (75.5, 100 and 125.7 for ^{13}C) for cycloadducts. Carbon types were determined from Dept experiments. NMR spectra were analyzed using MestReC© and MestreNova NMR data processing software (www.mestrec.com). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. The reactions were monitored by GC-MS using the Agilent Technologies 6890N, equipped with the Agilent 190915-433 column and the Agilent 5973 Inert Mass Selective Detector in Electron Impact or Chemical Ionization Mode (with methane).

General procedure for the preparation of 1a-b, 1d, and 1j-k from 10. Exemplified for 1a

Diethyl 2-(2-cyclopropylideneethyl)-2-(4-(prop-2-ynyloxy)but-2-ynyl)malonate (1a)

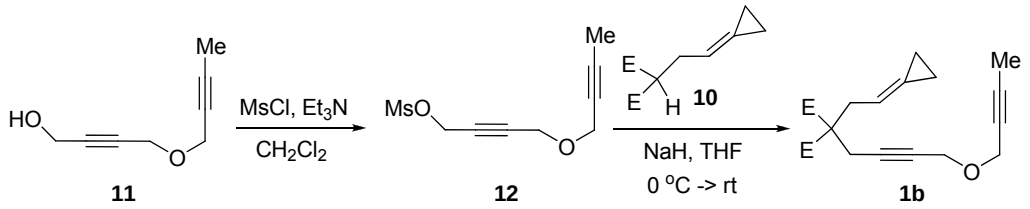


Et_3N (355.1 mg; 3.51 mmol; 489 μL) and methanesulphonyl chloride (340 mg; 2.97 mmol; 230 μL) were successively added to a solution of 4-(prop-2-ynyloxy)but-2-yn-1-ol (**8**)[1] (332 mg, 2.70 mmol) in CH_2Cl_2 (3 mL) at 0 ºC. After stirring at that temperature for 1h, the mixture was poured into water and extracted with CH_2Cl_2 (3 x 10 mL). The organic phases were dried, filtered concentrated and the crude

[1] For the synthesis of **8**, see: S. Bräse, H. Wertal, D. Frank, D. Vidovic and A. de Meijere, *Eur. J. Org. Chem.*, 2005, 4167.

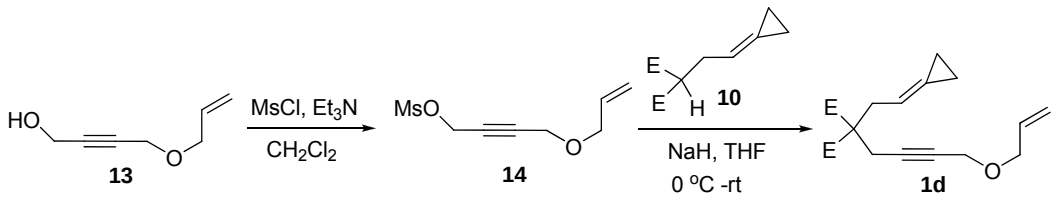
residue was used without further purification. Mesylate **9** was immediately used in the next step. A solution of diethyl 2-(2-cyclopropylideneethyl)malonate (**10**,[2] 542 mg, 2.397 mmol) in dry THF (10 mL) was added to a suspension of sodium hydride (60.3 mg, 2.52 mmol) in THF at 0 ºC. After stirring at rt for 30 min, a solution of mesylate **9** (489 mg, 2.42 mmol) was added and the reaction mixture was stirred overnight at rt, poured into water and extracted with Et_2O (3 x 20 mL). The organic phases were dried, filtered and concentrated to give a crude oily residue which was purified by flash chromatography (1:9 Et_2O:hexane) to yield **1a** as a colourless oil (650 mg, 82% yield). ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 5.64-5.53 (m, 1H), 4.29-4.12 (m, 8H), 2.96-2.90 (m, 2H), 2.86-2.80 (m, 2H), 2.49-2.40 (m, 1H), 1.35-1.16 (m, 6H), 1.11-1.01 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$), δ ppm 169.94 (CO), 127.19 (C), 111.28 (CH), 82.3(C), 77.7 (C), 77.51 (C), 74.73 (C), 61.50 (CH_2), 56.97 (CH_2), 56.69 (CH_2), 55.96 (C), 34.60 (CH_2), 22.87 (CH_2), 14.00 (CH_3), 2.91 (CH_2), 1.87 (CH_2). LRMS: 332 $(M)^+$, 332, 157, 129, 91.

Diethyl 2-(4-(but-2-ynyloxy)but-2-ynyl)-2-(2-cyclopropylideneethyl)malonate (1b)



Diethyl 2-(4-(but-2-ynyloxy)but-2-ynyl)-2-(2-cyclopropylideneethyl)malonate (**1b**) was prepared according to the previously described general procedure using 4-(but-2-ynyloxy)but-2-yn-1-ol (**11**),[3] as starting material. Purification by flash chromatography (1:9 Et_2O/hexane) provided **1b** as a colourless oil (74% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 5.55-5.46 (m, 1H), 4.17-4.06 (m, 8H), 2.85 (d, J = 7.45 Hz, 2H), 2.80-2.69 (m, 2H), 1.78 (t, J = 2.31 Hz, 3H), 1.22-1.10 (m, 6H), 1.04-0.91 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$), δ ppm, 169.77 (CO), 126.96 (C), 111.20 (CH), 82.61 (C), 81.75 (C), 78.01 (C), 74.22 (C), 61.32 (CH_2), 56.84 (CH_2), 56.48 (CH_2), 56.34 (C), 34.45 (CH_2), 22.73 (CH_2), 13.84 (CH_3), 3.35 (CH_3), 2.75 (CH_2), 1.71 (CH_2); LRMS: 346 $(M)^+$, 273, 199, 129.

Diethyl 2-(4-(allyloxy)but-2-ynyl)-2-(2-cyclopropylideneethyl)malonate (1d)

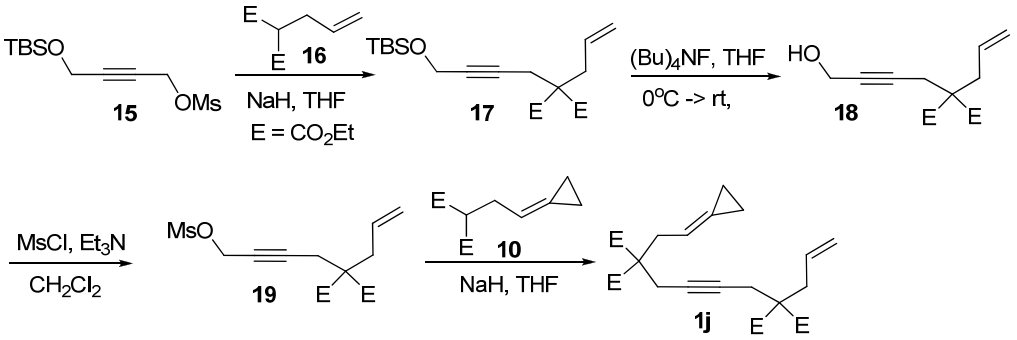


[2] J. Durán, M. Gulías, L. Castedo, and J. L. Mascareñas, *Org. Lett.*, 2005, **7**, 5693−5696.
[3] Alcohol **11** and its corresponding mesylate are known compounds, see: E. Negishi, L. S. Harring, Z. Owczarczyk, M. M. Mohamud and M. Ay, *Tetrahedron Lett.,* 1992, **33**, 3253-3256.

Diethyl 2-(4-(allyloxy)but-2-ynyl)-2-(2-cyclopropylideneethyl)malonate (**1d**) was prepared according to the previously described general procedure using 4-(allyloxy)but-2-yn-1-ol (**13**,[4] 800 mg, 6.35 mmol) as starting material. Purification by flash chromatography (1:9 Et_2O/hexane) provided **1d** (1.0 g, 3.0 mmol) as colourless oil (62% yield). **4-(Allyloxy)but-2-ynyl methanesulfonate** (**14**): ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 5.98-5.82 (m, 1H), 5.30 (ddd, *J* = 10.45, 9.20, 4.68 Hz, 2H), 4.91 (dd, *J* = 4.39, 2.62 Hz, 2H), 4.25-4.19 (m, 2H), 4.05 (td, *J* = 5.71, 1.24 Hz, 2H), 3.12 (s, 3H).

Diethyl 2-(4-(allyloxy)but-2-ynyl)-2-(2-cyclopropylideneethyl)malonate (**1d**): ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 5.91-5.75 (m, 1H), 5.52 (ddd, *J* = 7.31, 4.63, 1.87 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 2H), 4.10-4.02 (m, 6H), 3.97 (dd, *J* = 5.68, 1.20 Hz, 2H), 2.87 (d, *J* = 7.43 Hz, 2H), 2.77 (t, *J* = 1.85 Hz, 2H), 1.24-1.14 (m, 6H), 0.99 (bs, 4H); ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm 169.74 (CO), 133.94 (CH), 125.9 (C), 117.34 (CH_2), 111.24 (CH), 81.38 (C), 78.61 (C), 69.90 (CH_2), 61.25 (CH_2), 57.12 (CH_2), 56.87 (C), 34.47 (CH_2), 22.75 (CH_2), 13.83 (CH_3), 2.72 (CH_2), 1.71 (CH_2). LRMS: 335.2 (M+1), 231. HRMS calculated for $C_{19}H_{26}O_5$ 335.1858, found 335.1856.

Tetraethyl 1-cyclopropylideneundec-10-en-5-yne-3,3,8,8-tetracarboxylate (**1j**)



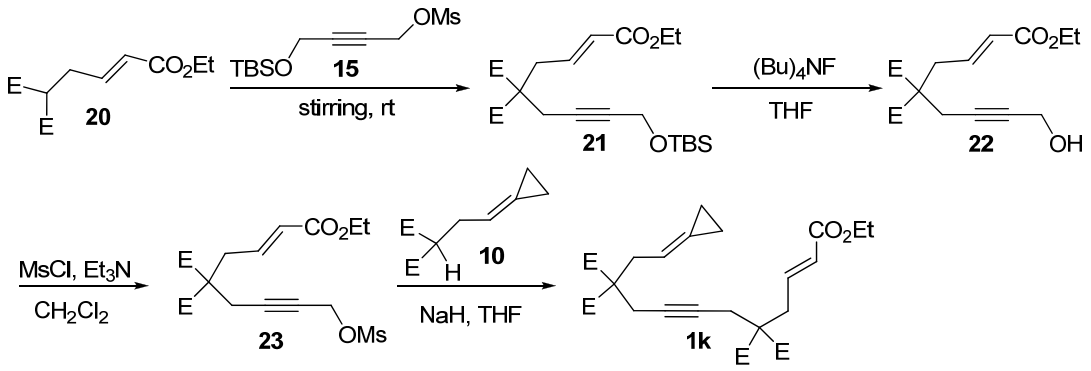
NaH (192 mg, 8.00 mmol) was added in small portions to a solution of **16** (800 mg, 4.00 mmol) in THF. The resulting solution was stirred at 0 ºC for 10 min and the mesylate **15**[5] (1.11g, 3.99 mmol), in THF (10 mL), was added. After stirring for 12h, the solvent was evaporated and the residue was poured into water and extracted with Et_2O (3 x 10 mL). The organic phases were dried and evaporated to give a crude residue which was purified by flash chromatography to yield 1.16 g of **17** as a colourless oil (76 % yield). **Diethyl 2-allyl-2-(4-(tert-butyldimethylsilyloxy)but-2-ynyl)malonate** (**17**): ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 5.65-5.48 (m, 1H), 5.07 (m, 2H), 4.22-4.06 (m, 6H), 2.73 (dd, *J* = 8.46, 4.92 Hz, 4H), 1.22-1.13 (m, 6H), 0.82 (d, *J* = 2.78 Hz, 9H), 0.03 (d, *J* = 2.78 Hz, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 169.56 (C=O), 131.73 (CH), 119.46 (CH_2), 81.66 (C), 79.28 (C), 61.34 (CH_2), 56.58 (C), 51.56 (CH_2), 36.25 (CH_2), 25.60 (CH_3), 22.68 (CH_2), 18.23 (C), 13.90 (CH_3), -5.37 (CH_3). A solution of **17** (1.6 g, 4.19 mmol) was subjected to standard *tetra*-butyl ammonium fluoride TBS-deprotection (1.09 g, 4.176 mmol) and the crude alcohol so obtained was purified by flash chromatography (4 : 6 Et_2O/hexane) to give 1.08 g

[4] Alcohol **13** is a known compound: W. J. Zuercher, M. Scholl, M.and R. H. Grubbs, *J. Org. Chem.,* 1998, **63**, 4291-4298.
[5] For the synthesis of **15**, see: A. Padwa, H. Lipka, S. H. Watterson, S. S. Murphree, *J. Org. Chem.* 2003, **68**, 6238-6250.

of **18** as a colourless oil (81% yield). **Diethyl 2-allyl-2-(4-hydroxybut-2-ynyl)malonate** (**18**): ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 5.62-5.42 (m, 1H), 5.03 (dd, *J* = 14.98, 13.59 Hz, 2H), 4.09 (m, 6H), 2.68 (dd, *J* = 7.74, 5.12 Hz, 4H), 1.14 (t, *J* = 7.11 Hz, 6H) ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 169.68 (CO), 131.45 (CH), 119.50 (CH_2), 81.61 (C), 79.59 (C), 61.42 (CH_2), 56.49 (C), 50.42 (CH_2), 36.13 (CH_2), 22.58 (CH_2), 13.75 (CH_3). The transformation of **18** (650 mg, 2.06 mmol) into **1j** was carried out according to the general procedure described above for the synthesis of **1a**. (91 % yield, colourless oil). **Diethyl 2-allyl-2-(4-(methylsulfonyloxy)but-2-ynyl)malonate** (**19**): ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 5.57-5.40 (m, 1H), 5.03 (dd, *J* = 13.35, 11.66 Hz, 2H), 4.70 (d, *J* = 2.03 Hz, 2H), 4.07 (dq, *J* = 7.05, 1.62 Hz, 4H), 2.97 (d, *J* = 1.72 Hz, 3H), 2.72 (d, *J* = 1.99 Hz, 2H), 2.63 (d, *J* = 7.35 Hz, 2H), 1.13 (dt, *J* = 7.09, 1.67 Hz, 6H). ^{13}C NMR (63 MHz, $CDCl_3$), δ ppm 169.04 (CO), 131.15 (CH), 119.62 (CH_2), 84.75 (C), 75.07 (C), 61.38 (CH_2), 57.68 (CH_2), 56.02 (C), 38.34 (CH_3), 36.21 (CH_2), 22.47 (CH_2), 13.61 (CH_3).

Tetraethyl 1-cyclopropylideneundec-10-en-5-yne-3,3,8,8-tetracarboxylate (**1j**): ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 5.61-5.44 (m, 2H), 5.18-4.97 (m, 2H), 4.20-4.02 (m, 8H), 2.82 (d, *J* = 7.40 Hz, 2H), 2.74-2.60 (m, 6H), 1.26-1.04 (m, 12H), 1.02-0.89 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 169.77 (CO), 169.53 (CO), 131.81 (CH), 126.71 (C), 119.37 (CH_2), 111.39 (CH), 77.91 (C), 77.21 (C), 61.24 (CH_2), 56.97 (C), 56.57 (C), 36.08 (CH_2), 34.25 (CH_2), 22.58 (CH_2), 22.52 (CH_2), 13.83 (CH_3), 2.70 (CH_2), 1.73 (CH_2); LRMS: $(CI)^+$ 499.2, 258.0. HRMS: calculated for $C_{26}H_{36}O_8$, 477.2410 (M+1), found 477.2486.

(*E*)-Pentaethyl 11-cyclopropylideneundec-1-en-6-yne-1,4,4,9,9-pentacarboxylate (1k)



NaH (38 mg, 1.583 mmol) was added to a solution of **20**[6] (235 mg, 0.860 mmol) in THF (5 mL). The resulting mixture was stirred for 15 min, 4-(tert-butyldimethylsilyloxy)but-2-ynyl methanesulfonate **15** (239 mg, 0.859 mmol) was added and the solution was stirred overnight. After completion of the reaction, the solution was evaporated, poured into water and extracted with Et_2O. The combined organic layers were dried and concentrated to give a crude residue which was purified by flash chromatography (2:8 Et_2O/Hexane) to yield 248 mg of 9-(*E*)-triethyl 8-(*tert*-butyldimethylsilyloxy)oct-1-en-6-yne-1,4,4-tricarboxylate (**21,** 63% yield). **21**: ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 6.73 (td, *J* = 15.54, 7.78 Hz, 1H),

[6] Prepared by alkylation of ethyl malonate with commercial available (*E*)-ethyl 4-bromobut-2-enoate.

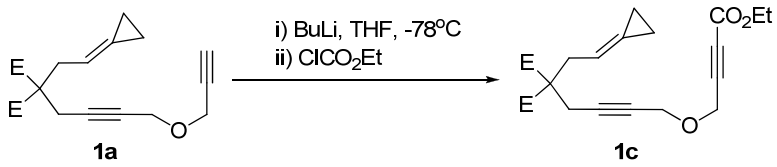
5.92 (d, *J* = 15.55 Hz ,1H), 4.25-4.09 (m, 8H), 2.88 (d, *J* = 7.78 Hz, 2H), 2.80 (s, 2H), 1.29-1.16 (m, 9H), 0.87 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 169.16 (CO), 166.2 (CO), 141.87 (CH), 125.46 (CH), 82.40 (C), 79.30 (C), 61.82 (CH_2), 60.30 (CH_2), 56.39 (C), 51.62 (CH_2), 34.83 (CH_2), 25.70 (CH_3), 23.26 (CH_2), 18.17 (C), 14.14 (CH_3), 13.95 (CH_3), -5.29 (CH_3). Compound **21** (205 mg, 0.450 mmol) was subjected to standard TBS-deprotection with *tetra*-butylammonium fluoride in THF and the crude alcohol was purified by flash chromatography (5:5 Et_2O:Hexane) to yield 137 mg of (*E*)-triethyl 8-hydroxyoct-1-en-6-yne-1,4,4-tricarboxylate **22** as a colourless oil (78 % yield). **22**: ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm, 6.77 (td, *J* = 15.51, 7.76 Hz, 1H), 5.88 (d, *J* = 15.51 Hz, 1H), 4.23-4.07 (m, 8H), 2.86 (dd, *J* = 7.76, 1.04 Hz, 2H), 2.78 (t, *J* = 1.87 Hz, 2H), 2.61 (s, 1H), 1.20 (m, 9H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 169.22 (C=O), 165.95 (C=O), 142.17 (CH), 125.15 (CH), 82.37 (C), 79.66 (C), 61.89 (CH_2), 60.39 (CH_2), 56.42 (C), 50.70 (CH_2), 35.08 (CH_2), 23.27 (CH_2), 14.06 (CH_3), 13.89 (CH_3). (*E*)-triethyl 8-hydroxyoct-1-en-6-yne-1,4,4-tricarboxylate **22** was then converted into **1k** following the general alkylation procedure previously described for related precursors (38 % yield).

(*E*)-Triethyl 8-(methylsulfonyloxy)oct-1-en-6-yne-1,4,4-tricarboxylate (23). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 6.64 (ddd, *J* = 10.54, 9.91, 4.90 Hz, 1H), 5.88-5.78 (m, 1H), 4.75-4.69 (m, 2H), 4.17-4.01 (m, 6H), 3.04 (s, 3H), 2.83-2.75 (m, 4H), 1.21-1.09 (m, 9H); ^{13}C NMR (63 MHz, $CDCl_3$), δ ppm, 168.70 (CO), 165.40 (CO), 141.22 (CH), 125.51 (CH), 84.35(C), 75.72 (C), 61.87 (CH_2), 60.19 (CH_2), 57.56 (CH_2), 55.94 (C), 38.53 (CH_3), 34.80 (CH_2), 23.11 (CH_2), 13.93 (CH_3), 13.73 (CH_3).

(*E*)-Pentaethyl 11-cyclopropylideneundec-1-en-6-yne-1,4,4,9,9-pentacarboxylate (1k) ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 6.68 (ddd, *J* = 15.46, 8.14, 7.26 Hz, 1H), 5.90 (dd, *J* = 15.50, 0.93 Hz, 1H), 5.51 (dd, *J* = 7.34, 6.37 Hz, 1H), 4.19-4.07 (m, 10H), 2.88-2.80 (m, 4H), 2.69 (s, 4H), 1.25-1.14 (m, 15H), 0.98 (br s, 4H);^{13}C NMR (63 MHz, $CDCl_3$), δ ppm 169.83 (CO), 169.07 (CO), 165.68 (CO), 141.95 (CH), 126.87 (CH), 125.3 (C), 111.32 (CH), 78.57 (C), 76.76 (C), 61.69 (CH_2), 61.31 (CH_2), 60.17 (CH_2), 56.95 (C), 56.38 (C), 34.58 (CH_2), 34.30 (CH_2), 23.09 (CH_2), 22.62 (CH_2), 14.06 (CH_3), 13.87 (CH_3), 2.79 (CH_2), 1.77 (CH_2). LRMS: 548 $(M)^+$; HRMS calculated for $C_{29}H_{40}O_{10}$ (M + 1) 549.2700, found 549.2694.

Experimental Procedures for the Preparation of Compounds 1c, 1e–i and 1l.

Diethyl 2-(2-cyclopropylideneethyl)-2-(4-(4-ethoxy-4-oxobut-2-ynyloxy)but-2-ynyl)malonate (1c)

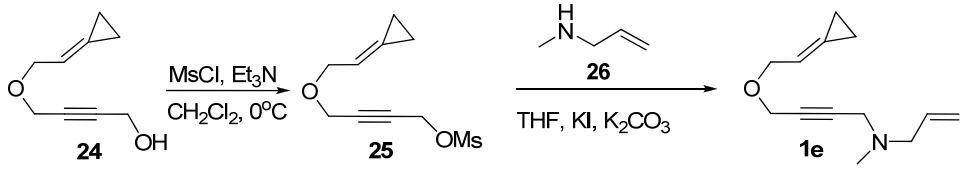


1a **1c**

n-Butyl Lithium (0.92 mL, 2.06 mmol) was added to a solution of **1a** (548 mg, 1.65mmol) in THF (30 mL) at -78^{o}C and the resulting solution was stirred for 30 min at that temperature before ethyl chloroformate (223.9 mg, 2.06 mmol) was added. The reaction mixture was stirred overnight, the solvent was evaporated and the residue diluted with Et_2O, poured into water and extracted with Et_2O (3 x 20 mL).

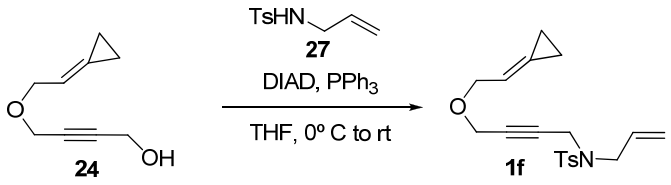
The organic phases were dried, filtered and concentrated to give a crude oily residue which was purified by flash chromatography (1:9 Et_2O: Hexane) to afford 140 mg of **1c** as pale yellow oil (38% yield). ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 5.54 (ddd, J = 7.41, 5.57, 2.07 Hz, 1H), 4.31 (d, J = 4.78 Hz, 2H), 4.24-4.08 (m, 8H), 2.88 (d, J = 7.45 Hz, 2H), 2.79 (s, 2H), 1.41-1.13 (m, 9H), 1.13-0.80 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$), δ ppm 169.85 (C), 127.23 (C), 111.19 (CH), 83.00 (C), 82.40 (C), 77.51 (C), 77.2 (C), 62.04 (CH_2), 61.48 (CH_2), 57.17 (CH_2), 56.89 (CH_2), 55.56 (CH_2), 34.59 (CH_2), 22.83 (CH_2), 13.91 (CH_3), 2.88 (CH_2), 1.82 (CH_2); LRMS: 346 $(M)^+$, 404, 331, 267.

N-Allyl-4-(2-cyclopropylideneethoxy)-N-methylbut-2-yn-1-amine (1e)



Methane sulphonyl chloride (340 mg, 2.98 mmol) and Et_3N (356 mg, 3.52 mmol) were added to a solution of 4-(2-cyclopropylideneethoxy)but-2-yn-1-ol (**24**,[7] 412 mg, 2.71 mmol) in CH_2Cl_2 at 0 ºC, and the solution was stirred for 30 min. The progress of the reaction was monitored by *tlc* and after completion the solvent was removed, the residue was poured into water and extracted with Et_2O. The organic phases were dried and evaporated to give a crude residue (**25**) which was immediately used as such for the next step. A solution of allyl-methyl-amine (**26**, 288 mg, 4.05 mmol) in THF (2 mL) was added dropwise to the solution of **25** (623 mg, 2.71 mmol) in THF (10 mL) at 0ºC. This is followed by the addition of activated potassium carbonate (5.42 mg, 1.12 mmol) and a pinch of potassium iodide. After completion of the reaction, the solvent was removed and the residue was poured into water and extracted with Et_2O. The organic phases were dried and evaporated to give a crude residue which was purified by flash chromatography (Et_2O/hexane in 5:5) to provide 378 mg of **1e** as a colourless oil (68% overall yield); ^{1}H NMR (250 MHz, $CDCl_3$)δ ppm 5.99-5.76 (m, 2H), 5.26-5.14 (m, 2H), 4.24-4.15 (m, 4H), 3.38 (d, J = 1.86 Hz, 2H), 3.06 (dd, J = 4.54, 1.89 Hz, 2H), 2.31 (d, J = 2.14 Hz, 3H), 1.11 (s, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 135.31, 118.0, 114.10, 69.6, 59.03, 57.15, 45.40, 41.60, 29.68, 2.36, 1.76; LRMS 206.1 $(M+1)^+$ 169.0, 154.0, 137.0; HRMS calculated for $C_{13}H_{19}NO$ (M+1) 206.1544, found 206.1542.

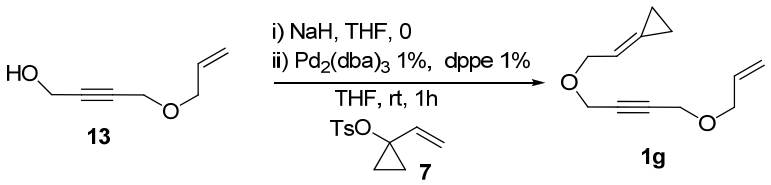
N-Allyl-N-(4-(2-cyclopropylideneethoxy)but-2-ynyl)-4-methylbenzenesulfonamide (1f).



[7] For the synthesis of **24**, see: (a) A. Delgado, J. R. Rodríguez, L. Castedo, J. L. Mascareñas, *J. Am. Chem. Soc.,* 2003, **125**, 9282-9283. (b) F. López, A. Delgado, J. R. Rodríguez, L. Castedo, J. L. Mascareñas, *J. Am. Chem. Soc.* 2004, **126**, 10262-10263.

Triphenylphosphine (1.37 g, 5.22 mmol) and **27** (633 mg, 3.00 mmol)[8] were added to a solution of 4-(2-cyclopropylideneethoxy)but-2-yn-1-ol (**24**, [7] 397 mg, 2.61 mmol) in THF (10 mL) at 0 ºC, then DIAD (1.03 mL, 5.22 mmol) was slowly added dropwise and the solution was stirred overnight. After completion of the reaction, the residue was poured into water and extracted with Et_2O. The organic phases were dried and evaporated to give a crude residue which was purified by flash chromatography (5 % Et_2O/hexane) to provide 468 mg of **1f** as a white solid (52% overall yield); ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 7.74 (d, *J* = 8.27 Hz, 2H), 7.29 (d, *J* = 8.42 Hz, 2H), 5.88-5.66 (m, 2H), 5.32-5.21 (m, 2H), 4.13 (s, 2H), 4.00 (d, *J* = 6.77 Hz, 2H), 3.88 (t, *J* = 1.79 Hz, 2H), 3.82 (d, *J* = 6.39 Hz, 2H), 2.41 (s, 3H), 1.16-1.04 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 143.2 (C), 135.7 (C), 131.7 (CH), 129.2 (CH), 128.9 (C), 127.5 (CH), 119.5 (CH_2), 113.7 (CH), 81.6 (C), 78.3 (C), 69.3 (CH_2), 56.4 (CH_2), 48.8 (CH_2), 35.9 (CH_2), 21.2 (CH_3), 2.1 (CH_2), 1.5 (CH_2). LRMS 346 (M^++1), 262, 192, 157, 125, 93.

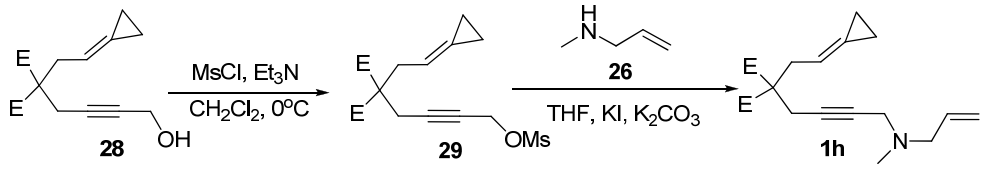
(2-(4-(Allyloxy)but-2-ynyloxy)ethylidene)cyclopropane (1g)



4-(allyloxy)but-2-yn-1-ol **13**[4] (300 mg, 2.38 mmol) was added slowly to a suspension of NaH (96 mg, 4.00 mmol) in THF (15 mL), cooled at 0ºC. After stirring for 15 min, a solution of allylcylopropyltosilate **7**[9] (566 mg, 2.38 mmol), $Pd_2(dba)_3$ (22 mg, 0.024 mmol) and dppe (19 mg, 0.048 mmol) in THF (5 mL), (previously stirred for 20 min), was added "*via* cannula". The reaction mixture was stirred overnight at *rt*, poured into water and extracted with Et_2O (3 x 20 mL). The organic phases were dried, filtered and concentrated to give a crude oily residue that was purified by flash chromatography (10 % Et_2O/hexanes) to yield 232 mg of **1g** as pale yellow oil (51 % yield). ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 6.01-5.68 (m, 2H), 5.21 (d, *J* = 17.1 Hz, 1H), 5.12(d, *J* = 10.4 Hz, 2H), 4.22-4.04 (m, 6H), 4.03-3.89 (m, 2H), 1.02 (s, 4H); ^{13}C NMR (63 MHz, $CDCl_3$), δ ppm 133.64 (CH), 127.35 (C), 117.19 (CH_2), 113.71 (CH), 82.16 (C), 81.65 (C), 70.05 (CH_2), 69.26 (CH_2), 56.95 (CH_2), 56.58 (CH_2), 1.93 (CH_2), 1.36 (CH_2). LRMS: 192 (M^+), 133, 105, 91, 79, 57, 55.

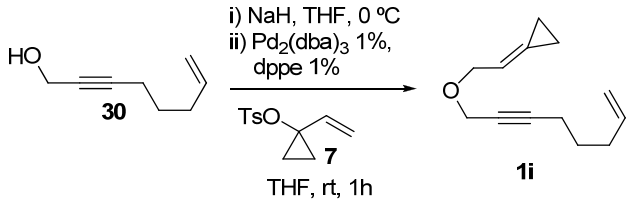
[8] M. Poornachandran and R. Raghavachary Raghunathan, *Tetrahedron,* 2008, **64**, 6461–6474.
[9] (a) S. Racouchot, I. Silvestre, J. Ollivier, Y. Kozyrkov, A. Pukin, O. Kulinkovich and J. Salaün *Eur. J. Org. Chem.* 2002, 2160; (b) I. Silvestre, J. Olliver and J. Salaün, *Tetrahedron. Lett.,* 2001, **42**, 1991.

Diethyl 2-(4-(allyl(methyl)amino)but-2-ynyl)-2-(2-cyclopropylideneethyl)malonate (1h)



Methane sulphonyl chloride (212 mg, 1.86 mmol) and Et_3N (222 mg, 2.19 mmol) were added to a solution of 2-(2-cyclopropylidene-ethyl)-2-(4-hydroxy-but-2-ynyl)-malonic acid diethyl ester (**28**,[7b] 500 mg, 1.695 mmol) in CH_2Cl_2 at 0 ºC, and the solution was stirred for 30 min. The progress of the reaction was monitored by *tlc* and after completion the solvent was removed, the residue was poured into water and extracted with Et_2O. The organic phases were dried and evaporated to give a crude residue (**29**) which was immediately used as such for the next step. A solution of allyl-methyl-amine (**26**, 148 mg, 2.085 mmol) in THF (2 mL) was added dropwise to the solution of **29** (500 mg, 1.40 mmol) in THF (10 mL) at 0ºC. This is followed by the addition of activated potassium carbonate (153 mg, 1.12 mmol) and a pinch of potassium iodide. After completion of the reaction the solvent was removed and the residue was poured into water and extracted with Et_2O. The organic phases were dried and evaporated to give a crude residue which was purified by flash chromatography (Et_2O/hexane in 5:5) to provide 305 mg of **1h** as a colourless oil (62% overall yield).^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 5.88-5.71 (m, 1H), 5.61-5.55 (m, 1H), 5.24-5.10 (m, 2H), 4.17 (q, *J* = 7.15 Hz, 4H), 3.27-3.24 (m, 2H), 3.01-2.98 (m, 2H), 2.93 (d, *J* = 7.42 Hz, 2H), 2.81-2.76 (m, 2H), 2.25 (d, *J* = 1.45 Hz, 3H), 1.27-1.18 (m, 6H), 1.06-0.99 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 169.63 (CO), 135.65 (CH), 126.71 (C), 117.47 (CH_2), 111.23 (CH), 79.72 (C), 77.0 (C), 61.00 (CH_2), 58.31 (CH_2), 56.84 (C), 44.82 (CH_2), 41.11 (CH_3), 34.23 (CH_2), 22.52 (CH_2), 13.70 (CH_3), 2.55 (CH_2), 1.60 (CH_2); LRMS: 348.2 $(M+1)^+$; HRMS calculated for $C_{20}H_{29}NO_4$ 348.2175, found 348.2174.

(2-(Oct-7-en-2-ynyloxy)ethylidene)cyclopropane (1i)

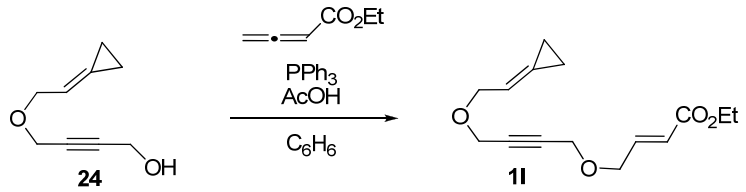


Alcohol **30**[10] (280 mg, 2.26 mmol) was added dropwise to a suspension of NaH (108 mg, 4.50 mmol) in THF (5 mL) cooled at 0ºC. After stirring for 15 min, a solution containing allylcyclopropyltosylate **7** (537 mg, 2.256 mmol), $Pd_2(dba)_3$ (82 mg 0.090 mmol) and dppe (72 mg, 0.181 mmol) in THF (15 mL), that had been previously stirred for 20 min, was added "*via cannula*". The reaction mixture was stirred for 1h at *rt* poured into water and extracted with Et_2O (3 x 20 mL). The organic phases were dried, filtered and concentrated to give a crude oily residue that was purified by flash chromatography (10 % Et_2O/hexanes) to

[10] V. Bagutski, N. Moszner, F. Zeuner, U. K. Fischer and A.de Meijere, *Adv. Synth. Catal.* 2006, **348**, 2133-2147.

yield 280 mg of **1i** as pale yellow oil (66 % yield). ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 5.81 (tdd, J = 10.49, 8.40, 4.18 Hz, 1H), 5.66-5.46 (m, 1H), 4.97-4.65 (m, 2H), 4.06 (dd, J = 6.75, 0.90 Hz, 2H), 3.95-3.83 (m, 2H), 2.16-1.83 (m, 4H), 1.49 (p, J = 7.28 Hz, 2H), 0.98-0.80 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$), δ ppm 137.64 (CH), 127.44 (C), 115.02 (CH_2), 114.12 (CH), 86.21 (C), 76.20 (C), 69.39 (CH_2), 57.24 (CH_2), 32.64 (CH_2), 27.64 (CH_2), 18.02 (CH_2), 2.20 (CH_2), 1.61 (CH_2). LRMS 191 (M^+), 131, 117, 105, 91, 79, 67, 53. HRMS: calculated for $C_{13}H_{18}O$ $(M+1)^+$ 191.1435, found 191.1434.

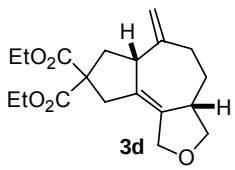
(*E*)-Ethyl 4-(4-(2-cyclopropylideneethoxy)but-2-ynyloxy)but-2-enoate (1l)



(E)-ethyl 4-(4-(2-cyclopropylideneethoxy)but-2-ynyloxy)but-2-enoate (**1l**) was prepared according to the previously described standard procedure[11] using 4-(2-cyclopropylideneethoxy)but-2-yn-1-ol (**24**)[7] as starting material. Purification by flash chromatography (5 % Et_2O/hexane) provided **1l** as colourless oil (67% yield); ^{1}H NMR (250 MHz, $CDCl_3$)δ ppm 6.85 (dt, J = 15.77, 4.40 Hz, 1H), 6.03-5.95 (m, 1H), 5.87-5.77 (m, 1H), 4.18-4.07 (m, 10H), 1.19 (t, J = 7.13 Hz, 3H), 1.02 (s, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 165.8 (C), 143.2 (CH), 127.6 (C), 121.5 (CH), 113.8 (CH), 82.9 (C), 81.2 (C), 69.5 (CH_2), 67.8 (CH_2), 60.1 (CH_2), 57.9 (CH_2), 56.7 (CH_2), 13.9 (CH_3), 2.1 (CH_2), 1.5(CH_2). LRMS 265 (M^+ +1), 177, 152, 107, 84; HRMS calculated for $C_{15}H_{21}O_4$ (M+1) 265.1440, found 265.1440.

General Procedure for the [3C + 2C + 2C] cycloadditions (exemplified for the cycloaddition of 1d).

Freshly distilled dioxane (1 mL) was added to a Schlenk tube, previously charged with $Pd_2(dba)_3$ (13.6 mg, 0.015 mmol, 10 mol%) and **L1** (25.2 mg, 0.039 mmol, 26 mol %), under argon. After stirring for 5 minutes at room temperature, a solution of **1d** (50 mg, 0.150 mmol) in dioxane (1 mL) was added and the reaction mixture was heated at 90 ºC temperature for 1 to 2 hours. The progress of reaction was monitored by *tlc*. After completion of the reaction, the mixture was cooled to room temperature, diluted with Et_2O (8 mL) and filtered through a short pad of silica eluting with Et_2O. The filtrate was concentrated and purified by flash chromatography (60-90 % Et_2O/hexanes) to afford 34 mg of **3d**, as a colourless oil (68 % yield).

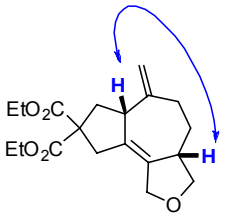


(*3aS*,6aR)-Diethyl 6-methylene-3,3a,4,5,6,6a,7,9-octahydroazuleno[4,5-c]furan-8,8(1H)-dicarboxylate (3d).** Colourless oil (68 % yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm 4.77 (s, 1H), 4.75 (s, 1H), 4.34 (d, J = 13.17 Hz, 1H), 4.22-4.13 (m, 5H), 4.15-4.11 (m, 1H), 3.37 (t, J = 8.64 Hz, 1H), 3.32-3.22 (m, 1H),

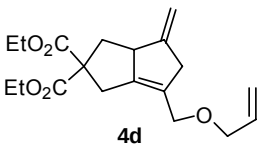
[11] C. Zhang, X. Lu. *Synlett*, 1995, 645-646.

2.91-2.70 (m, 3H), 2.63 (ddd, *J* = 13.18, 6.16, 2.83 Hz, 1H), 2.50 (ddd, *J* = 12.72, 6.98, 1.57 Hz, 1H), 2.31 (t, *J* = 12.37 Hz, 1H), 2.17-2.03 (m, 1H), 1.86 (ddd, *J* = 12.93, 6.35, 3.22 Hz, 1H), 1.28-1.22 (m, 6H) 1.25-1.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δppm 171.39 (CO), 148.05(C), 135.08 (C), 129.93 (C), 108.15 (CH_2), 75.39 (CH_2), 71.68 (CH_2), 61.57 (CH_2), 61.51 (CH_2), 58.70 (C), 47.99 (CH), 44.05 (CH), 39.05 (CH_2), 38.61 (CH_2), 37.89 (CH_2), 30.84 (CH_2), 14.02 (CH_3).

^{1}H NMR (500 MHz, C_6D_6), δppm 4.76 (s, 1H), 4.67 (s, 1H), 4.32 (d, *J* = 13.19 Hz, 1H), 4.04 (ddd, J = 13.19, 3.68, 2.12 Hz, 1H), 3.99-3.93 (m, 4H), 3.91 (t, *J* = 8.00 Hz, 1H), 3.45-3.41 (m, 1H), 3.19 (t, *J* = 8.57 Hz, 1H), 2.95 (d, *J* = 16.48 Hz, 1H), 2.85-2.77 (m, 2H), 2.55 (t, *J* = 12.29 Hz, 1H), 2.46-2.40 (m, 1H), 2.37 (ddd, *J* = 13.13, 6.26, 2.90 Hz, 1H), 1.85-1.79 (m, 1H), 1.40-1.34 (m, 1H), 0.99 (ddd, *J* = 24.38, 11.76, 2.88 Hz, 1H), 0.92-0.88 (m, 6H). ^{13}C NMR (126 MHz, C_6D_6), δppm 171.4 (CO), 171.3 (CO), 148.4 (C), 136.0 (C), 129.9 (C), 108.3 (CH_2), 75.4 (CH_2), 71.7 (CH_2), 61.4 (CH_2), 61.3 (CH_2), 59.2 (C), 48.5 (CH), 44.3 (CH), 39.5 (CH_2), 38.8 (CH_2), 38.7 (CH_2), 31.0 (CH_2), 14.0 (CH_3). LRMS: (ESI-TOF): 335, 333, 317, 305. HRMS calculated for $C_{19}H_{26}O_5$ (M+1) 335.1858, found 335.1848.

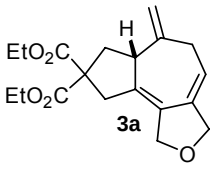


The stereochemical assignment of **3d** was determined on the basis of standard ^{1}H, ^{13}C, DEPT, nOe experiments, and 2D-NMR analyses (COSY, NOESY, HMBC and HMQC) carried out in $CDCl_3$ and C_6D_6 solvents. The observation of nOe between H3a-H6a, confirms the *cis* stereochemistry in the fusion of the rings.



4d

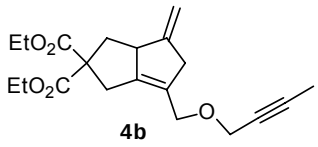
Diethyl 6-(allyloxymethyl)-4-methylene-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (4d). Colourless oil (27 % yield). ^{1}H NMR (500 MHz, $CDCl_3$), δppm 5.87-5.81 (m, 1H), 5.21 (dd, *J* = 17.23, 1.62 Hz, 1H), 5.11 (dd, *J* = 10.53, 1.58 Hz, 1H), 4.82 (s, 1H), 4.76 (s, 1H), 4.16-4.08 (m, 4H), 3.94 (s, 2H), 3.87-3.85 (m, 2H), 3.56 (t, *J* = 8.23 Hz, 1H), 3.36 (d, *J* = 20.39 Hz, 1H), 3.05 (d, *J* = 19.36 Hz, 1H), 2.92 (d, *J* = 17.30 Hz, 1H), 2.73 (d, *J* = 16.86 Hz, 1H), 2.56 (dd, J = 12.59, 7.87 Hz, 1H), 1.73 (dd, *J* = 12.52, 11.24 Hz, 1H), 1.26-1.15 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δppm 172.2 (CO), 171.5 (CO), 151.6 (C), 144.5 (C), 134.8 (CH), 128.3 (C), 116.9 (CH_2), 106.8 (CH_2), 71.0 (CH_2), 66.7 (CH_2), 61.6 (CH_2), 61.5 (CH_2), 54.3 (CH), 37.4 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 14.0 (CH_3). LRMS: 335 (M+1), 277, 235. HRMS calculated for C_{19} $H_{27}O_5$ (M+1) 335.1780, found 335.1853.



3a

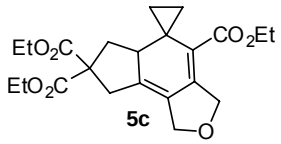
Diethyl 6-methylene-3,5,6,6a,7,9-hexahydroazuleno[4,5-c]furan-8,8(1H)-dicarboxylate (3a). Yellow oil (52 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δppm 5.49 (s, 1H), 4.92 (s, 1H), 4.86 (s, 1H), 4.52-4.29 (m, 4H), 4.21 (dq, *J* = 7.12, 2.59 Hz, 4H), 3.48-3.45 (m, 1H), 3.08 (s, 2H), 2.95 (d, *J* = 18.21 Hz, 1H), 2.82 (d, *J* = 18.11 Hz, 1H), 2.57 (ddd, *J* = 12.59, 6.64, 2.03 Hz, 1H), 2.38 (t, *J* = 12.62 Hz, 1H), 1.28-1.24 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δppm 171.4 (CO), 171.(CO), 142.2 (C), 135.0 (C), 132.9 (C), 127.7 (C), 116.8 (CH), 108.8 (CH_2), 74.0 (CH_2), 72.6 (CH_2), 61.7 (CH_2), 61.7 (CH_2), 58.7 (C), 49.1 (CH), 40.2 (CH_2), 38.8 (CH_2),

37.7 (CH_2), 14.0 (CH_3), 14.0 (CH_3). LRMS: 333 (M+1), 263. HRMS calculated for C_{17} $H_{25}O_5$ (M+1) 333.1624, found 333.1697.



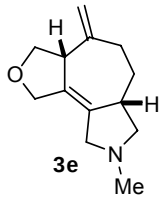
4b

Diethyl 6-((but-2-ynyloxy)methyl)-4-methylene-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (4b). Colourless oil (27 % yield). ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm 4.88 (s, 1H), 4.82 (s, 1H), 4.25-4.12 (m, 4H), 4.06-3.97 (m, 4H), 3.63 (t, *J* = 9.40 Hz, 1H), 3.42 (d, *J* = 18.22 Hz, 1H), 3.11 (d, *J* = 19.57 Hz, 1H), 3.01 (d, *J* = 17.04 Hz, 1H), 2.81 (d, *J* = 17.53 Hz, 1H), 2.62 (dd, *J* = 12.67, 7.87 Hz, 1H), 1.85 (t, *J* = 2.34 Hz, 3H), 1.67-1.61 (m, 1H), 1.28-1.20 (m, 6H).



5c

Triethyl 5a',6'-dihydrospiro[cyclopropane-1,5'-indeno[4,5-c]furan]-4',7',7'(1'H,3'H,8'H)-tricarboxylate (5c). Colourless oil (53 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.74 (q, *J* = 15.81 Hz, 2H), 4.47 (dddd, *J* = 14.00, 12.64, 6.47, 2.87 Hz, 2H), 4.27-4.09 (m, 6H), 3.26-3.08 (m, 1H), 2.94-2.83 (m, 1H), 2.27 (ddd, *J* = 12.28, 6.94, 1.33 Hz, 1H), 1.89 (ddd, *J* = 10.03, 5.71, 4.51 Hz, 1H), 1.74 (t, *J* = 12.59 Hz, 1H), 1.37-1.18 (m, 9H), 0.98-0.80 (m, 2H), 0.69 (ddd, *J* = 9.82, 6.99, 4.87 Hz, 1H), 0.47-0.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.06 (CO), 165.99 (CO), 149.89 (C), 135.70 (C), 128.59 (C), 120.82 (C), 115.91 (C), 72.83 (CH_2), 68.68 (CH_2), 61.84 (CH_2), 60.13 (CH_2), 58.98 (C), 45.12 (CH), 37.06 (CH_2), 34.82 (CH_2), 14.26 (CH_3), 14.00 (CH_3), 10.80 (CH_2), 9.26 (CH_2).

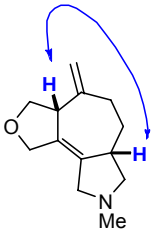


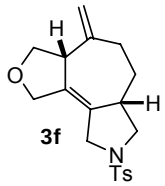
3e

(*3aR*,6aS)-8-Methyl-4-methylene-1,3,3a,4,5,6,6a,7,8,9-decahydro-2-oxa-8-aza-cyclopenta[e]a zulene** (**3e**). Yellow oil (84 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.76 (s, 1H), 4.67 (s, 1H), 4.26 (d, *J* = 12.7 Hz, 1H), 4.19 (d, *J* = 12.8 Hz, 1H), 4.11-4.01 (m, 1H), 3.92 (t, *J* = 8.54 Hz, 1H), 3.38-3.34 (m, 1H), 3.24 (d, *J* = 13.24 Hz, 1H), 3.01 (dd, *J* = 8.4 and 7.6 Hz, 1H), 2.90-2.76 (m, 2H), 2.59 (ddd, *J* = 13.2, 6.0 and 3.0 Hz, 1H), 2.34 (s, 3H), 2.18 (d, *J* = 10.89 Hz, 1H), 2.09 (t, *J* = 8.56 Hz, 1H), 1.93-1.86 (m, 1H), 1.38-1.23 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm 146.63 (C), 133.01 (C), 131.37 (C), 107.85 (CH_2), 72.01 (CH_2), 70.71 (CH_2), 63.60 (CH_2), 60.16 (CH_2), 48.97 (CH), 44.11 (CH), 42.28 (CH_3), 39.10 (CH_2), 32.61 (CH_2).

^{1}H NMR (500 MHz, C_6D_6), δ ppm 4.66 (s, 1H), 4.64 (t, *J* = 1.38 Hz, 1H), 4.17-4.08 (m, 2H), 3.96-3.88 (m, 2H), 3.11 (s, 1H), 2.92 (d, *J* = 13.01, 1H), 2.74 (dd, *J* = 8.43, 7.23 Hz, 1H), 2.66-2.63 (m, 1H), 2.52 (dtd, *J* = 13.00, 3.87, 1.86 Hz, 1H), 2.37 (ddd, *J* = 13.07, 6.05, 3.09 Hz, 1H), 2.13 (s, 3H), 1.93-1.86 (m, 2H), 1.59-1.53 (m, 1H), 1.25 (dtd, *J* = 12.88, 11.60, 3.12 Hz, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 147.1 (C), 133.6 (C), 131.6 (C), 107.8 (CH_2), 72.2 (CH_2), 70.8 (CH_2), 63.9 (CH_2), 60.3 (CH_2), 49.5 (CH), 44.4 (CH), 42.3 (CH_3), 39.4 (CH_2), 33.0 (CH_2). LRMS 206.1 $(M+1)^+$; HRMS calculated for $C_{13}H_{19}NO$ $(M+1)^+$ 206.1544, found 206.1541.

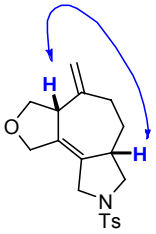
The stereochemical assignment of **3e** was determined on the basis of standard ^{1}H, ^{13}C, DEPT, nOe experiments, and 2D-NMR analyses (COSY, NOESY, HMBC and HMQC) carried out in $CDCl_3$ and C_6D_6 solvents. The observation of nOe between the hydrogens of the fusion confirms the *cis* stereochemistry in the fusion of the rings.





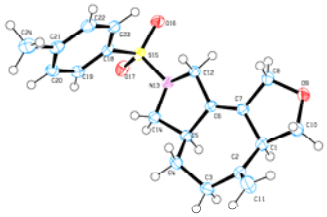
3f. White solid (58 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.68 (d, *J* = 8.14 Hz, 2H), 7.32 (d, *J* = 8.03 Hz, 2H), 4.73 (s, 1H); 4.61 (s, 1H), 4.21 (d, *J* = 13.04 Hz, 1H), 4.13 (d, *J* = 13.63 Hz, 1H), 4.07-4.04 (m, 1H), 3.82 (t, *J* = 8.79 Hz, 1H), 3.74 (d, *J* = 13.67 Hz, 1H), 3.61-3.58 (m, 1H), 3.49-3.42 (m, 1H), 3.31 (s, 1H), 2.91-2.89 (m, 1H), 2.63 (t, *J* = 8.88 Hz, 1H), 2.52 (ddd, *J* = 13.28, 6.31, 3.02 Hz, 1H), 2.42 (s, 3H), 2.16-2.11 (m, 1H), 1.86 (tdd, *J* = 13.15, 6.57, 3.40 Hz, 1H), 1.24-1.18 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 145.4 (C), 143.8 (C), 133.7 (C), 131.7 (C), 129.6 (CH), 128.4 (C), 128.0 (CH), 108.8 (CH_2), 71.9 (CH_2), 70.6 (CH_2), 54.5 (CH_2), 51.4 (CH_2), 49.3 (CH), 42.8 (CH), 37.9 (CH_2), 32.1 (CH_2), 21.5 (CH_3). LRMS: 346 (M+1), 277. HRMS calculated for $C_{19}H_{24}NO_3S$ (M+1) 346.1432, found 346.1471.

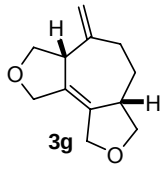
The stereochemical assignment of **3f** was determined on the basis of standard ^{1}H, ^{13}C, DEPT, nOe experiments, and 2D-NMR analyses (COSY, NOESY, HMBC and HMQC). The observation of nOe between the hydrogens of the fusion, confirms the stereochemistry in the fusion of the rings.



Further confirmation of the structure of **3f** was obtained by X-ray crystallography.

Crystal structure obtained from a sample of **3f**:

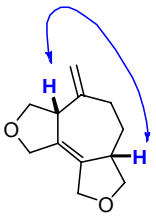




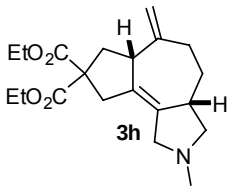
(*3aR*,6aS)-4-Methylene-1,3a,4,5,6,6a,7,9-octahydro-3H-2,8-dioxa-cyclopenta[e]azulene (3g).** Colourless oil (51 % yield). ^{1}H NMR (250 MHz, $CDCl_3$), δ ppm 4.79 (s, 1H), 4.67 (s, 1H), 4.25-4.06 (m, 6H), 3.93 (t, *J* = 8.65 Hz, 1H), 3.39 (t, *J* = 8.52 Hz, 2H), 2.89-2-86 (m, 1H), 2.62 (ddd, *J* = 13.15, 6.04, 2.79 Hz, 1H), 2.26-2.14 (m, 1H), 1.96-1.86 (m, 1H), 1.45-1.30 (m, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 146.14 (C), 132.29 (C), 130.58 (C), 108.34 (CH_2), 74.96 (CH_2), 71.78 (CH_2), 70.64 (CH_2), 70.42 (CH_2), 49.32 (CH), 44.19 (CH), 38.51 (CH_2), 31.42 (CH_2).

^{1}H NMR (500 MHz, C_6D_6) δ ppm 4.64 (s, 1H), 4.59 (s, 1H), 3.99-3.86 (m, 6H), 3.82 (t, *J* = 8.51 Hz, 1H), 3.17 (t, *J* = 8.37 Hz, 1H), 3.05 (s, 1H), 2.46-2.41 (m, 1H), 2.31 (ddd, *J* = 13.14, 6.12, 2.95 Hz, 1H), 1.85-

1.79 (m, 1H), 1.43-1.38 (m, 1H), 1.04 (ddd, *J* = 24.60, 11.70, 2.91 Hz, 1H); ^{13}C NMR (126 MHz, C_6D_6) δ ppm 146.6 (C), 132.7 (C), 131.0 (C), 108.1 (CH_2), 75.0 (CH_2), 71.8 (CH_2), 70.6 (CH_2), 70.4 (CH_2), 49.8 (CH), 44.5 (CH), 38.9 (CH_2), 31.4 (CH_2). LRMS: 193.1 $(M+1)^+$, 177.1, 163.1, 147.1, 135.1, 121.1; HRMS calculated for $C_{12}H_{16}O_2$ $(M+1)^+$ 193.1225, found 193.1227.

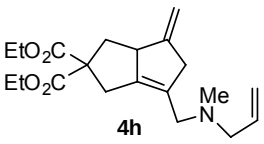


The stereochemical assignment of **3g** was determined on the basis of standard ^{1}H, ^{13}C, DEPT, nOe experiments, and 2D-NMR analyses (COSY, NOESY, HMBC and HMQC). The observation of nOe between the hydrogens of the fusion, confirms the stereochemistry in the fusion of the rings.

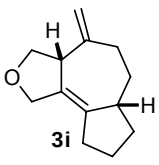


(3aS*,6aR*)-Diethyl 2-methyl-6-methylene-2,3,3a,4,5,6,6a,7-octahydro-1H-azuleno[4,5-c]pyrrole-8,8(9H)-dicarboxylate (**3h**). Yellow oil (49 % yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 4.72 (s, 1H), 4.69 (s, 1H), 4.27-4.04 (m, 4H), 3.39 (d, *J* = 13.4 Hz, 1H), 3.26-3.22 (m, 1H), 3.07-2.96 (m, 1H), 2.89-2.66 (m, 4H), 2.57 (ddd, *J* = 13.14, 6.07, 2.93 Hz, 1H), 2.48 (ddd, *J* = 12.70, 7.06, 1.51 Hz, 1H), 2.33 (s, 3H), 2.23 (t, *J* = 12.25 Hz, 1H), 2.17-2.03 (m, 2H), 1.89-1.82 (m, 1H), 1.27-1.18 (m, 6H), 1.20-1.16 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.55 (CO), 171.35 (CO), 148.40 (C), 135.36 (C), 131.23 (C), 107.75 (CH_2), 63.90 (CH_2), 61.51 (CH_2), 61.45 (CH_2), 60.94 (CH_2), 58.66 (C), 47.69 (CH), 43.84 (CH), 42.20 (CH_3), 39.33 (CH_2), 39.08 (CH_2), 38.03 (CH_2), 32.38 (CH_2), 14.03 (CH_3), 14.01 (CH_3). LRMS 348.2$(M+1)^+$; HRMS calculated for $C_{20}H_{29}NO_4$ $(M+1)^+$ 348.2174, found 348.2174.

The stereochemical assignment of **3h** was determined by comparison of its NMR data with that of related analogs **3d**, **3e**, **3g**, **3i**, **3j** and **3k**.



Diethyl 6-((allyl(methyl)amino)methyl)-4-methylene-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (4h). Yellow oil (23 % yield) ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 5.89-5.81 (m, 1H), 5.18-5.12 (m, 2H), 4.87 (s, 1H), 4.82 (s, 1H), 4.18 (qd, *J* = 25.21, 7.12 Hz, 4H), 3.60 (t, *J* = 8.46 Hz, 1H), 3.41 (d, *J* = 19.32 Hz, 1H), 3.13 (d, *J* = 19.53 Hz, 1H), 2.95-2.94 (m, 4H), 2.74 (d, *J* = 16.60 Hz, 1H), 2.62 (dd, *J* = 12.68, 7.89 Hz, 1H), 2.15 (s, 3H), 1.78 (dd, *J* = 12.67, 10.98 Hz, 1H), 1.33-1.21 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 172.3 (CO), 171.7 (CO), 152.1 (C), 135.7 (CH), 117.6 (CH_2), 106.6 (CH_2), 103.8 (C), 62.8 (C), 61.6 (CH_2), 61.5 (CH_2), 60.5 (CH_2), 55.5 (CH_2), 54.1 (CH), 45.3 (CH_2), 42.3 (CH_3), 37.6 (CH_2), 31.9 (CH_2), 14.0 (CH_3). LRMS: 348 (M+1), 301, 277. HRMS calculated for $C_{20}H_{30}NO_4$ (M+1) 348.2131, found 348.2169.

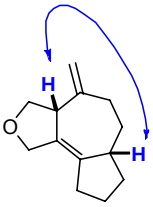


(3aR*,6aS*)-4-methylene-1,3,3a,4,5,6,6a,7,8,9-decahydroazuleno[5,4-c]furan (3i). Colourless oil (16 % yield) ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm 4.73 (s, 1H), 4.65 (s, 1H), 4.26 (q, *J* = 12.75 Hz, 2H), 4.08-4.04 (m, 1H), 3.94 (t, *J* = 8.46 Hz, 1H), 3.35-3.31 (m, 1H), 2.58-2.53 (m, 2H), 2.28-2.02 (m, 3H), 1.98-1.89 (m, 2H), 1.78-1.70 (m, 1H),

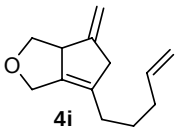
1.56-1.43 (m, 1H), 1.38-1.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 147.49 (C), 136.57 (C), 131.23 (C), 107.06 (CH_2), 72.26 (CH_2), 71.32 (CH_2), 49.06 (CH), 44.55 (CH), 39.55 (CH_2), 35.25 (CH_2), 34.84 (CH_2), 32.46 (CH_2), 25.27 (CH_2).

^{1}H NMR (500 MHz, C_6D_6), δ ppm 4.70 (1H, s), 4.68 (t, *J* = 1.42 Hz, 1H), 4.29-4.19 (m, 2H), 4.03-3.94 (m, 2H), 3.25 (q, *J* = 6.99 Hz, 1H), 3.16 (s, 1H), 2.41 (ddd, *J* = 13.02, 6.04, 3.11 Hz, 1H), 2.33-2.26 (m, 1H), 1.99-1.94 (m, 1H), 1.86-1.82 (m, 2H), 1.74-1.64 (m, 2H), 1.56-1.48 (m, 1H), 1.34-1.04 (m, 2H).

LRMS: 190 (M^+), 160, 145, 131, 117, 105, 91, 79, 65, 53. HRMS calculated for $C_{13}H_{18}O$ $(M+1)^+$ 191.1435, found 191.1434.

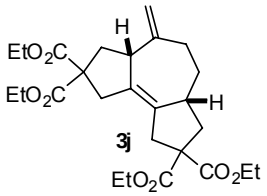


The stereochemical assignment of **3i** was initially determined on the basis of standard ^{1}H, ^{13}C, DEPT, nOe experiments, and 2D-NMR analyses (COSY, NOESY, HMBC and HMQC). The observation of nOe between the hydrogens of the fusion, confirms the stereochemistry in the fusion of the rings.



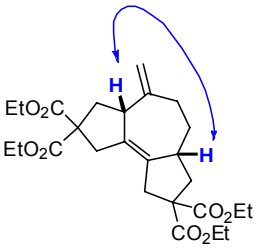
4i

4-Methylene-6-(pent-4-enyl)-3,3a,4,5-tetrahydro-1H-cyclopenta[c]furan (4i). Colourless oil (44 % yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 5.91-5.70 (m, 1H), 5.02-4.98 (m, 3H), 4.78 (s, 1H), 4.32-4.29 (m, 1H), 4.19-4.08 (m, 2H), 3.91-3.82 (m, 1H), 3.57 (dd, *J* = 19.49, 1.14 Hz, 1H), 3.27 (dd, *J* = 9.69, 7.27 Hz, 1H), 3.13 (d, *J* = 19.49 Hz, 1H), 2.14-2.03 (m, 4H), 1.60-1.45 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ ppm 149.23 (C), 140.68 (C), 138.60 (CH), 133.45 (C), 114.81 (CH_2), 107.52 (CH_2), 69.74 (CH_2), 63.61 (CH_2), 55.23 (CH), 47.21 (CH_2), 33.39 (CH_2), 29.06 (CH_2), 26.86 (CH_2).

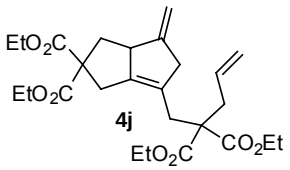


3j

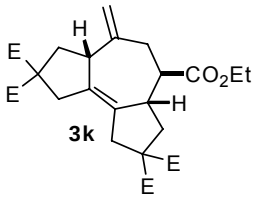
4-Methylene-1,3a,4,5,6,6a,7,9-octahydro-3H-cyclopenta[e]azulene-2,2,8,8-tetracarboxylic acid tetraethyl ester (3j). Colourless oil (48 %). ^{1}H NMR (500 MHz, $CDCl_3$), *δ* ppm 4.72 (s, 1H), 4.70 (s, 1H), 4.23-4.14 (m, 8H), 3.18 (m, 1H), 2.94-2.90 (m, 2H), 2.81-2.77 (m, 2H), 2.67 (m, 1H), 2.62-2.53 (m, 2H), 2.52-2.38 (m, 1H), 2.33-2.28 (m, 1H), 2.08 (dt, *J* = 12.69, 2.57 Hz, 1H), 1.95-1.86 (m, 1H), 1.80 (dd, *J* = 12.68, 10.77 Hz, 1H), 1.38-1.14 (m, 12H), 1.13 (d, *J* = 9.89 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$), *δ* ppm 171.5 (CO), 148.6 (C), 135.01 (C), 132.7 (C), 107.3 (CH_2), 61.4 (CH_2), 61.39 (CH_2), 61.36 (CH_2), 61.33 (CH_2), 58.8 (C), 58.4 (C), 47.5 (CH), 43.1 (CH), 42.0 (CH_2), 40.5 (CH_2), 39.8 (CH_2), 39.6 (CH_2), 37.9 (CH_2), 34.27 (CH_2), 13.99 (CH_3). LRMS: 477 (M+1), 309, 231, 154, 137. HRMS calculated for C_{26} $H_{37}O_8$ (M+1) 477.2488, found 477.2489.



The stereochemical assignment of **3j** was determined on the basis of standard ^{1}H, ^{13}C, DEPT, nOe experiments, and 2D-NMR analyses (COSY, NOESY, HMBC and HMQC). The observation of nOe between the hydrogens of the fusion, confirms the stereochemistry in the fusion of the rings.

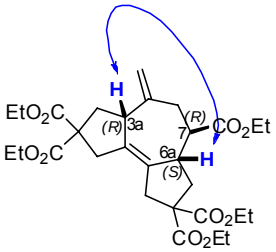


Diethyl 6-(2,2-bis(ethoxycarbonyl)pent-4-enyl)-4-methylene-3,3a,4,5-tetrahydro pentalene-2,2(1H)-dicarboxylate (4j). Colourless oil (36 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 5.72-5.64 (m, 1H), 5.12-5.06 (m, 2H), 4.81 (s, 1H), 4.78 (s, 1H), 4.22-4.12 (m, 8H), 3.54 (s, 1H), 3.35 (dd, *J* = 19.18, 2.09 Hz, 1H), 2.92-2.84 (m, 2H), 2.77 (d, *J* = 14.10 Hz, 1H), 2.74-2.67 (m, 1H), 2.65 (dd, *J* = 14.24, 7.49 Hz, 2H), 2.61-2.53 (m, 2H), 1.79 (dd, *J* = 12.72, 10.90 Hz, 1H), 1.30-1.19 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 172.18 (CO), 171.55 (CO), 170.87 (CO), 152.25 (C), 146.13 (C), 132.54 (CH), 126.77 (C), 119.04 (CH_2), 106.38 (CH_2), 62.80 (C), 61.56 (CH_2), 61.29 (CH_2), 57.33 (C), 53.59 (CH), 46.80 (CH_2), 37.45 (CH_2), 37.43 (CH_2), 32.87 (CH_2), 32.20 (CH_2), 14.02 (CH_3).

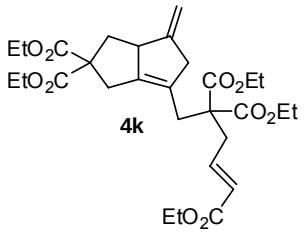


3k. Colourless oil (75 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 4.80 (s, 1H), 4.79 (s, 1H), 4.17 (m, 10H), 3.26-3.22 (m, 1H), 3.00-2.89 (m, 3H), 2.79 (t, *J* = 13.71 Hz, 2H), 2.64 (d, *J* = 13.02 Hz, 1H), 2.57-2.47 (m, 2H), 2.43-2.20 (m, 3H), 1.93-1.87 (m, 1H), 1.24 (m, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.46 (C), 171.43 (C), 171.39 (C), 171.28 (C), 171.13 (C), 145.23 (C), 133.97 (C), 132.54 (C), 109.91 (CH_2), 61.56 (CH_2), 61.53 (CH_2), 61.47 (CH_2), 61.44 (CH_2), 60.46 (CH_2), 58.52 (C), 58.40 (C), 50.48 (CH), 47.49 (CH), 43.68 (CH), 41.79 (CH_2), 40.31 (CH_2), 39.96 (CH_2), 39.89 (CH_2), 38.33 (CH_2), 14.23 (CH_3), 14.02 (CH_3), 13.98 (CH_3).

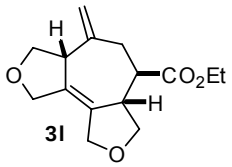
^{1}H NMR (500 MHz, C_6D_6) δ ppm 4.74 (s, 1H), 4.69 (s, 1H), 4.07-3.87 (m, 10H), 3.42-3.38 (m, 1H), 3.28-3.26 (m, 1H), 3.17 (dt, *J* = 17.15, 1.63 Hz, 2H), 2.98 (ddd, *J* = 12.80, 7.46, 1.72 Hz, 1H), 2.94-2.81 (m, 2H), 2.75 (ddd, *J* = 12.67, 7.12, 2.02 Hz, 1H), 2.67 (d, *J* = 10.18 Hz, 1H), 2.51 (dd, *J* = 12.56, 11.80 Hz, 1H), 2.42-2.34 (m, 2H), 2.23 (dd, *J* = 12.84, 10.05 Hz, 1H), 0.97-0.87 (m, 15H). ^{13}C NMR (126 MHz, C_6D_6) δ 174.1 (CO), 171.3 (CO), 171.2 (CO), 171.1 (CO), 145.7 (C), 134.4 (C), 133.2 (C), 109.9 (CH_2), 61.3 (CH_2), 60.3 (CH_2), 59.1 (C), 58.9 (C), 51.0 (CH), 47.9 (CH), 44.3 (CH), 42.3 (CH_2), 40.9 (CH_2), 40.8 (CH_2), 40.4 (CH_2), 38.9 (CH_2), 14.2 (CH_3), 14.0 (CH_3), 14.0 (CH_3). LRMS 548, 502, 474, 401, 327. HRMS calculated for $C_{29}H_{41}O_{10}$ $(M+1)^{+}$ 549.26997, found 549.26999.



The stereochemical assignment of **3k** was determined on the basis of standard ^{1}H, ^{13}C, DEPT, nOe experiments, and 2D-NMR analyses (COSY, NOESY, HMBC and HMQC). The observation of nOe between the hydrogens of the fusion H3a-H6, confirms the stereochemistry in the fusion of the rings. The lack of nOe between H7 and H6a or H7 and H3a strongly suggest the proposed stereochemistry at C7. Further confirmation is being pursued by obtaining suitable crystals of an immediate derivative for X-ray crystallography.

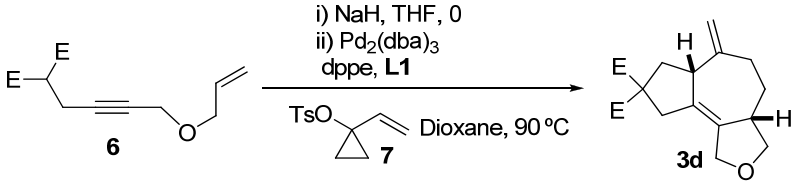


(E)-Triethyl 5-(5,5-bis(ethoxycarbonyl)-3-methylene-2,3,3a,4,5,6-hexahydropentalen-1-yl)pent-1-ene-1,4,4-tricarboxylate (4k). ^{1}H NMR (250 MHz, $CDCl_3$) δ ppm 6.88-6.75 (m, 1H), 5.84 (d, *J* = 15.54 Hz, 1H), 4.80 (s, 2H), 4.24-4.11 (m, 10H), 3.59-3.50 (m, 1H), 3.39-3.21 (m, 2H), 3.03-2.47 (m, 4H), 2.39-2.17 (m, 2H), 1.91 (dd, *J* = 12.84, 9.95 Hz, 1H), 1.78 (dd, *J* = 12.59, 11.06 Hz, 1H), 1.30-1.20 (m, 15H).



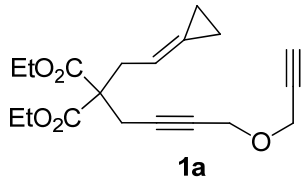
3l. Colourless oil (60 % yield). ^{1}H NMR (500 MHz, C_6D_6) δ ppm 4.71 (s, 1H), 4.61 (s, 1H), 4.15 (dd, *J* = 8.82, 7.28 Hz, 1H), 3.95-3.82 (m, 7H), 3.64 (t, *J* = 8.61 Hz, 1H), 3.54 (dd, *J* = 8.82, 7.03 Hz, 1H), 3.06 (s, 2H), 2.56 (dd, *J* = 12.17, 2.64 Hz, 1H), 2.40-2.32 (m, 2H), 0.90 (t, *J* = 7.12 Hz, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 173.7 (C), 143.5 (C), 131.9 (C), 130.3 (C), 110.9 (CH_2), 74.0 (CH_2), 72.0 (CH_2), 70.4 (CH_2), 70.3 (CH_2), 60.5 (CH_2), 49.6 (CH), 48.4 (CH), 45.2 (CH), 40.6 (CH_2), 14.2 (CH_3). The stereochemical assignment of **3k** was determined on the basis of standard ^{1}H, ^{13}C, DEPT, nOe experiments, and 2D-NMR analyses (COSY, NOESY, HMBC and HMQC), as well as by analogy with **3k**. LRMS 265 (M^+ +1), 247, 219, 173. HRMS calculated for $C_{15}H_{21}O_4$ (M+1) 265.1440, found 265.1437.

Experimental procedure for the tandem reaction



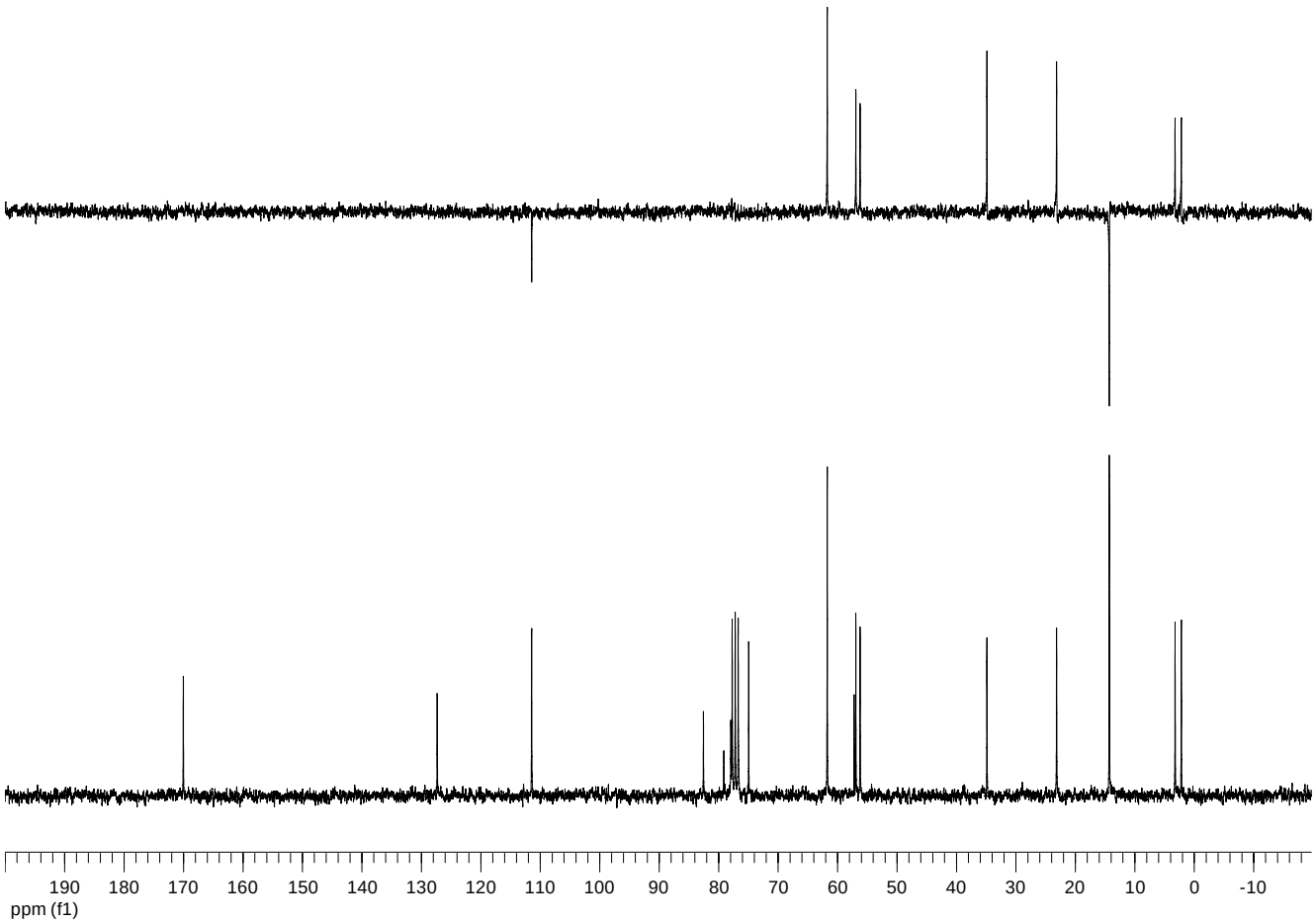
Diethyl 2-(4-(allyloxy)but-2-ynyl)malonate (**6**)[12] (85 mg, 0.318 mmol) was added dropwise to a suspension of NaH (9 mg, 0.382 mmol) in dioxane (2 mL), cooled at 0ºC. After stirring for 15 min, a solution containing allylcyclopropyltosylate **7** (75 mg, 0.318 mmol), $Pd_2(dba)_3$ (29 mg, 0.032 mmol), dppe (2.4 mg, 0.006 mmol) and **L1** (45 mg, 0.070 mmol) in dioxane (3 mL), that had been previously stirred for 20 min, was added "*via* cannula". The reaction mixture was stirred for 1h at 90 ºC, filtered through florisil and the crude residue was purified by flash chromatography (10 % Et_2O/hexanes) to yield 63 mg of **3d** as a pale yellow oil (62 % yield).

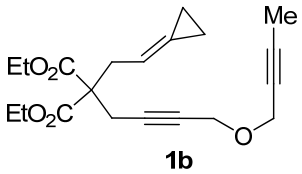
[12] For the synthesis of **6**, see : B. L. Ashfeld and S. F. Martin, *Org. Lett.* 2005, **7**, 4535-4537.


EtO2C
EtO2C
O

1a

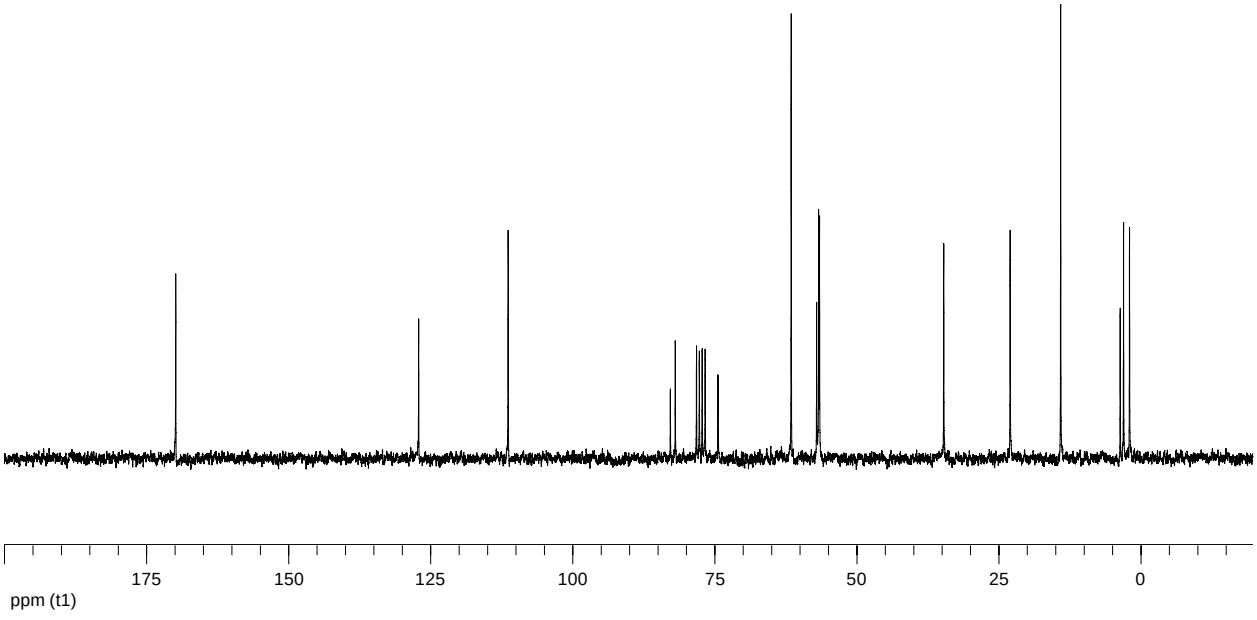
8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)

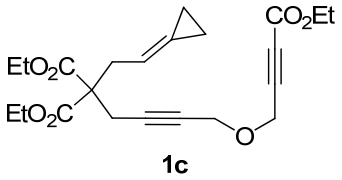

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (f1)


Me
EtO2C
EtO2C
O

1b

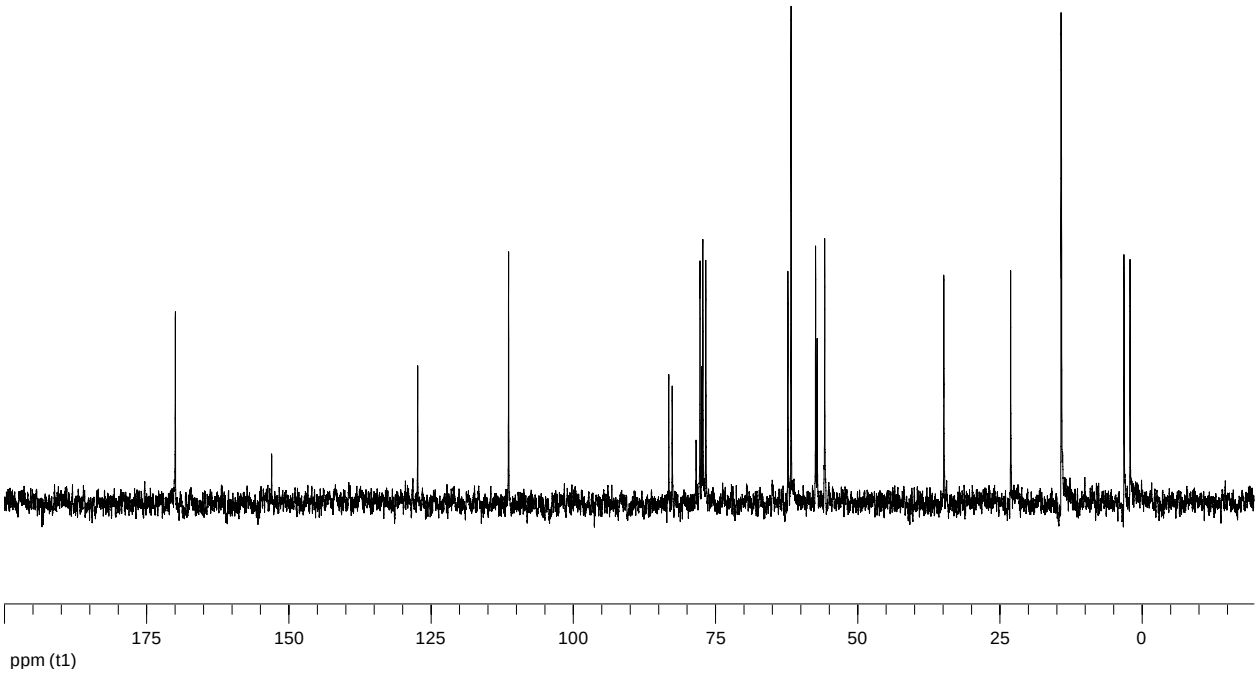
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (t1)

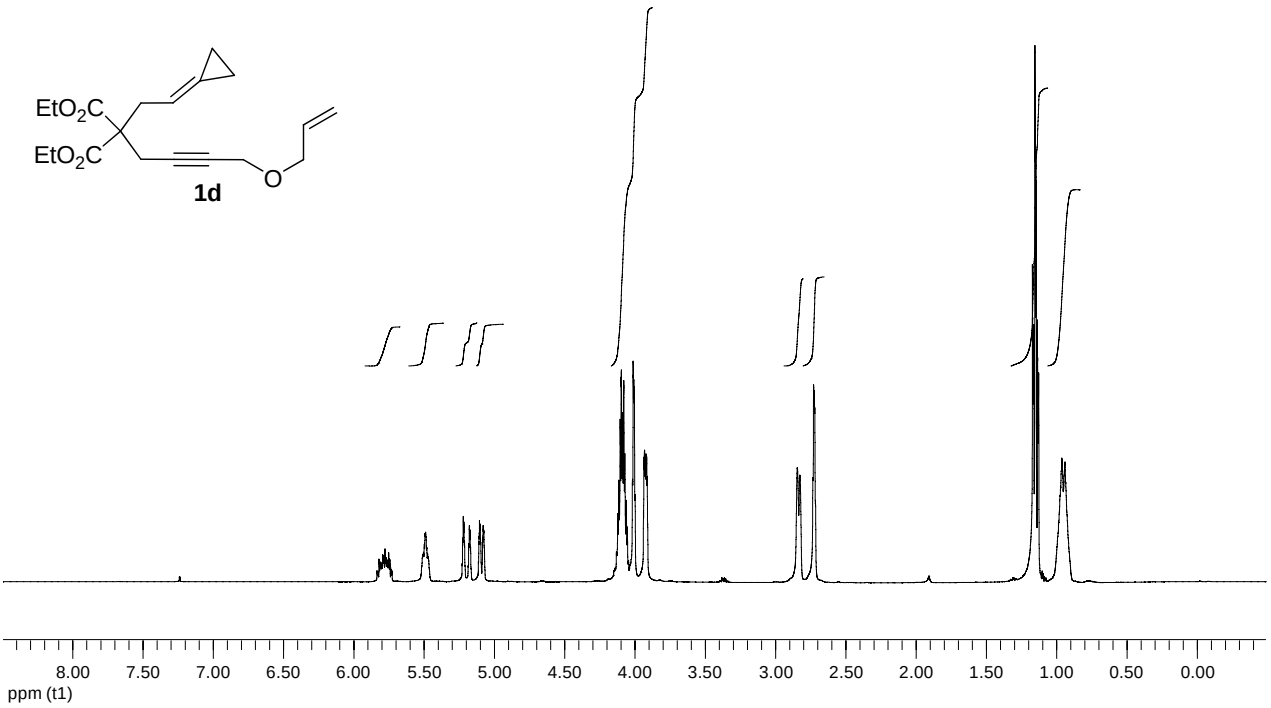

175
150
125
100
75
50
25
0
ppm (t1)

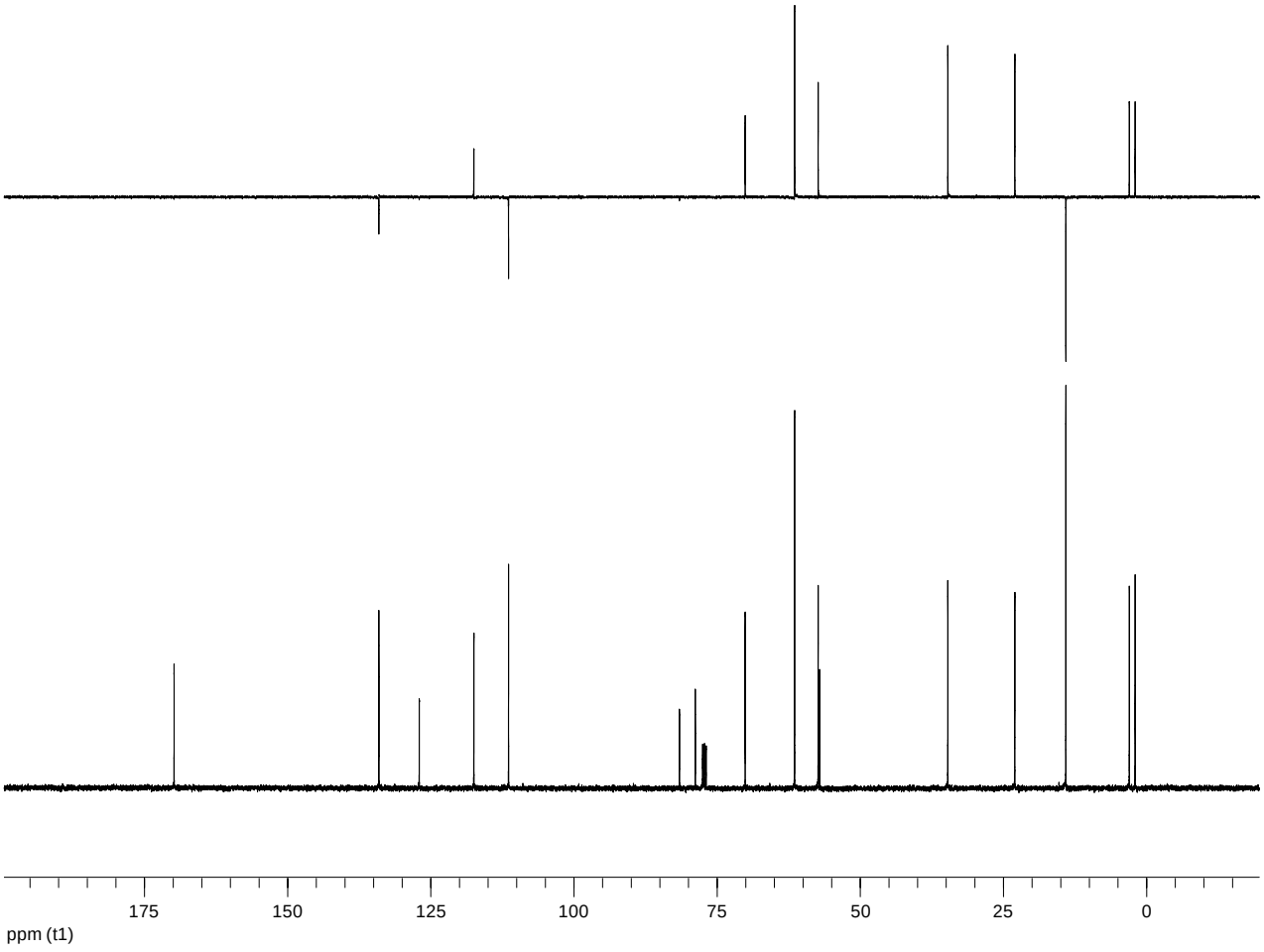

CO2Et
EtO2C
EtO2C
O

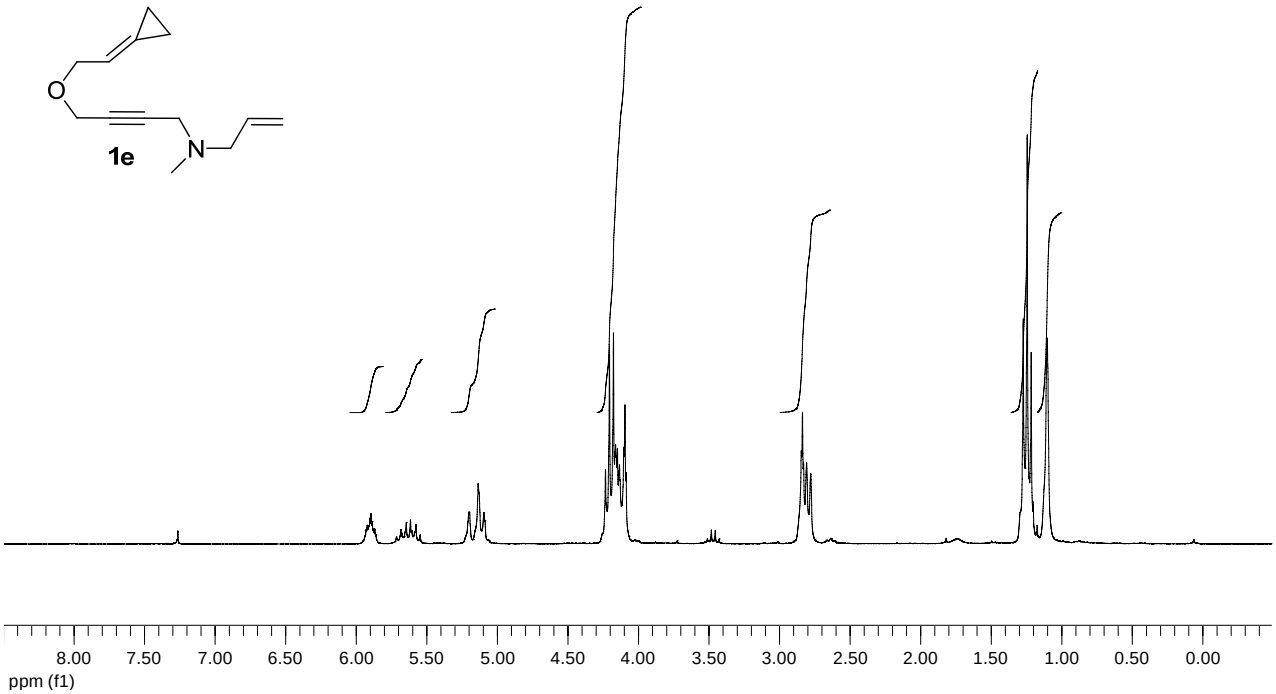
1c

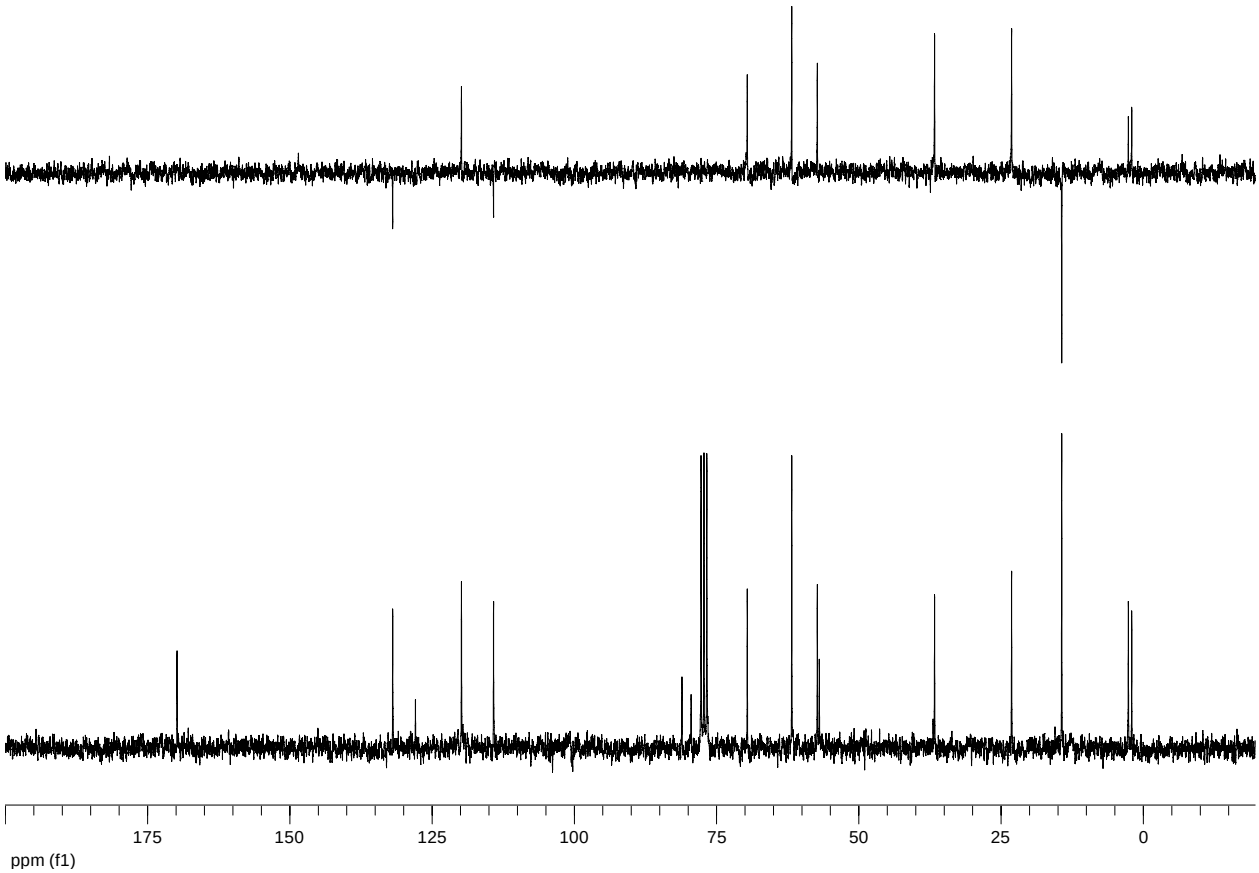
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (t1)

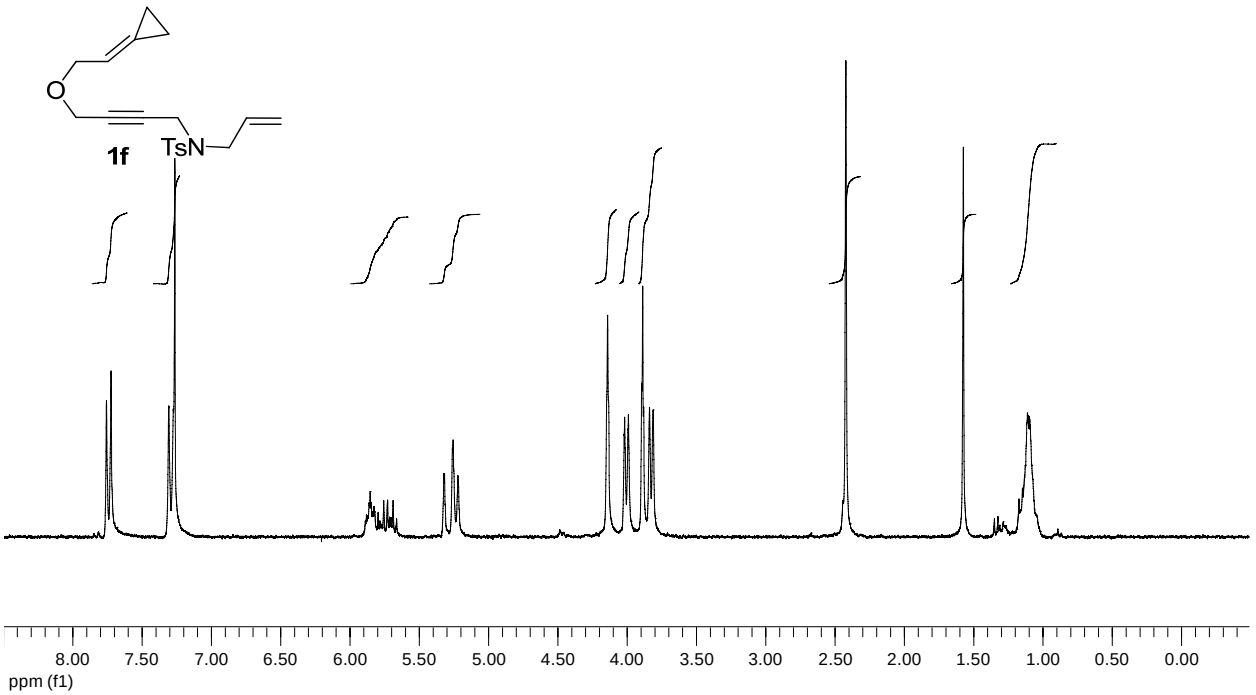

175
150
125
100
75
50
25
0
ppm (t1)

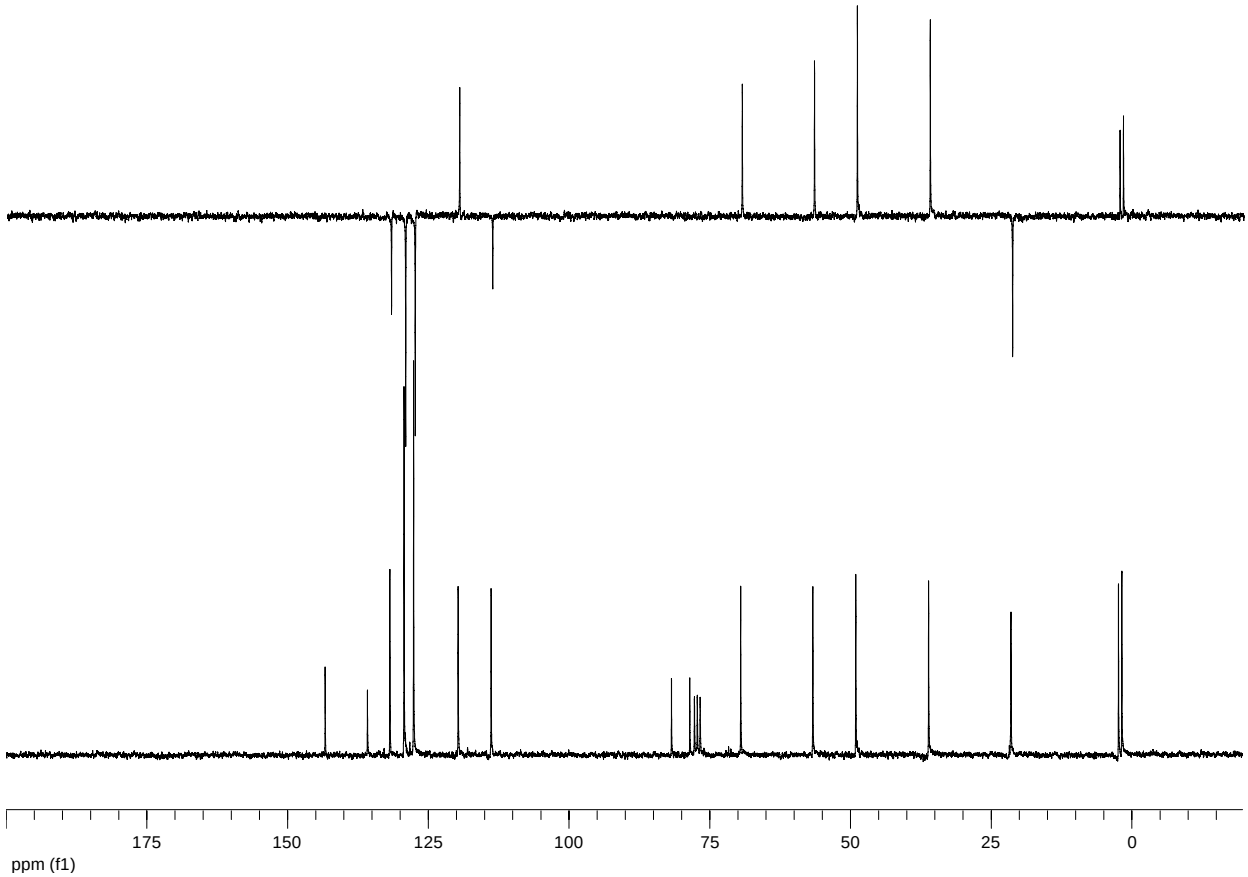

EtO2C
EtO2C
O
1d
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (t1)

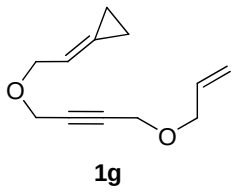

175
150
125
100
75
50
25
0
ppm (t1)


O
N
1e
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


175
150
125
100
75
50
25
0
ppm (f1)

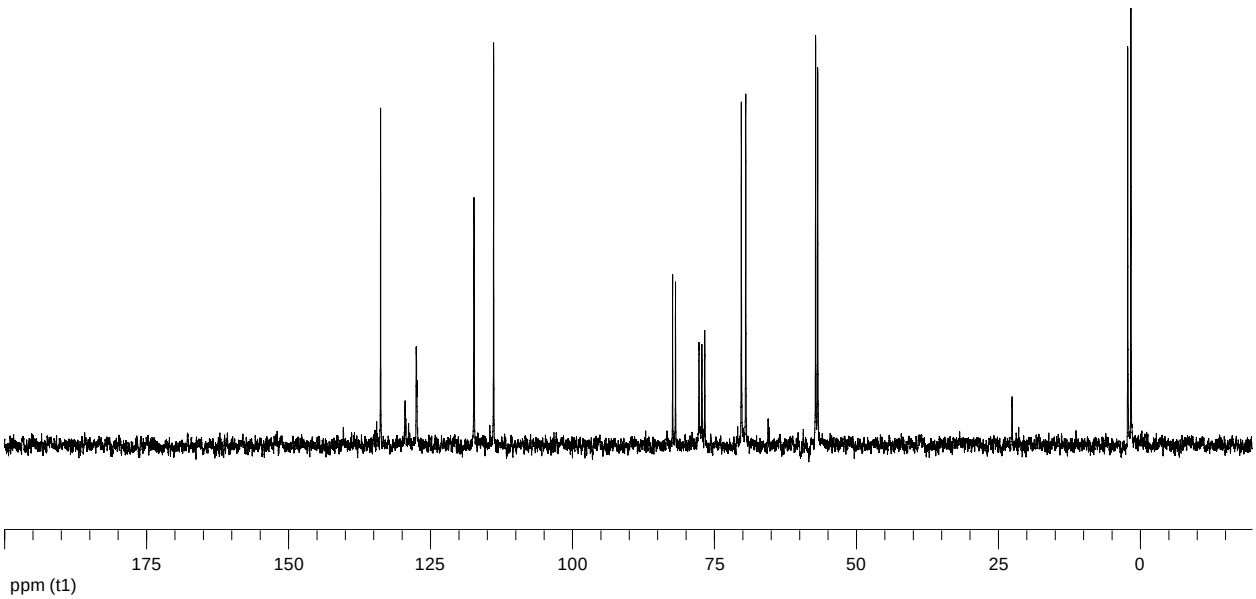

O
TsN
1f
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

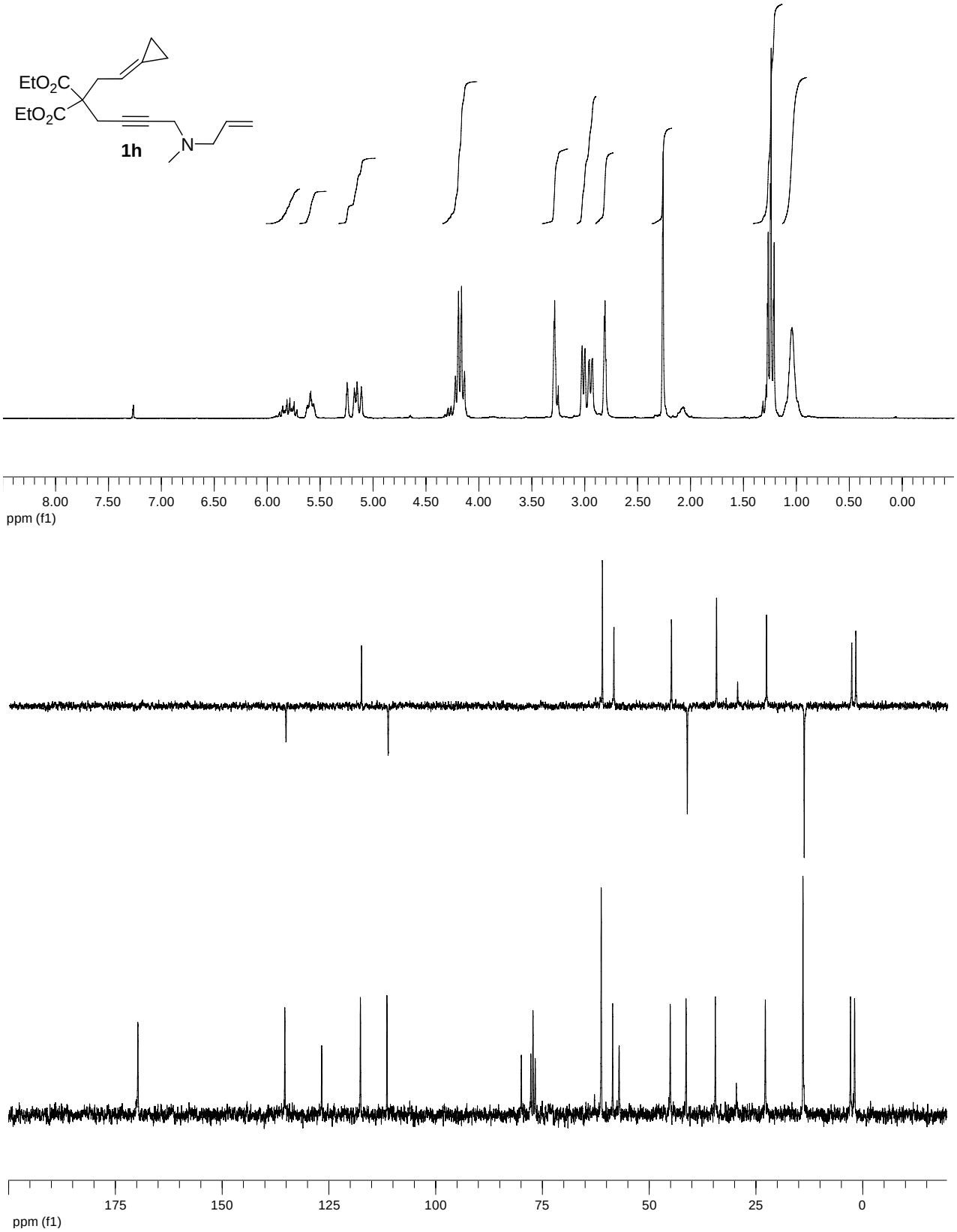

175
150
125
100
75
50
25
0
ppm (f1)

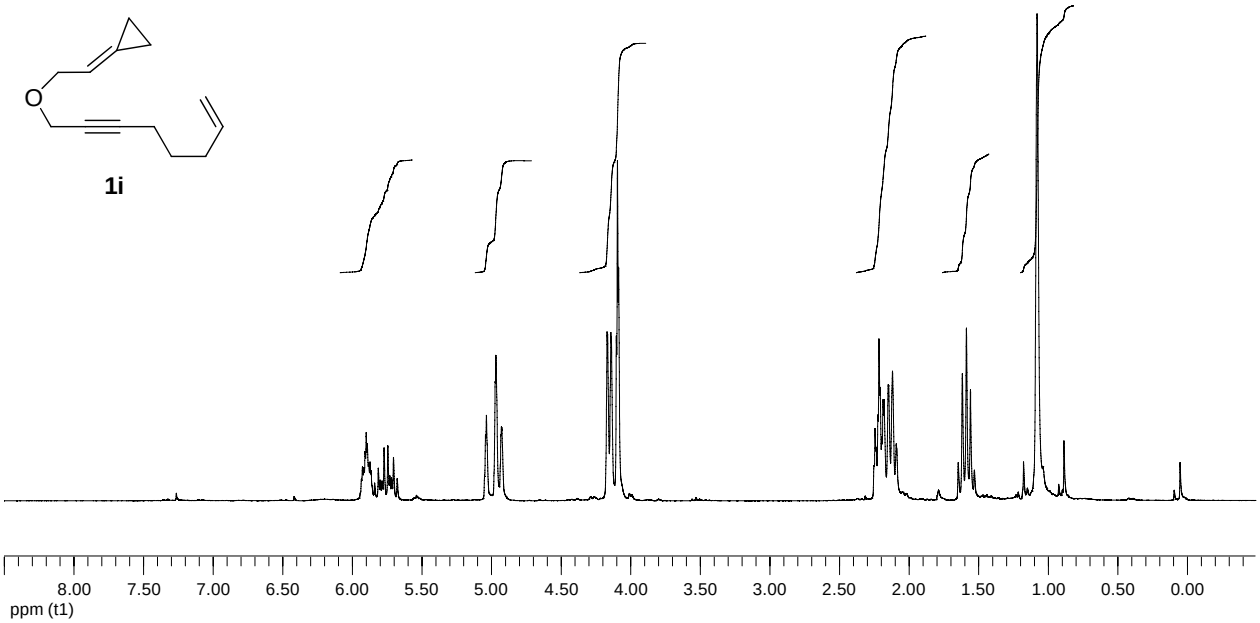

O
O

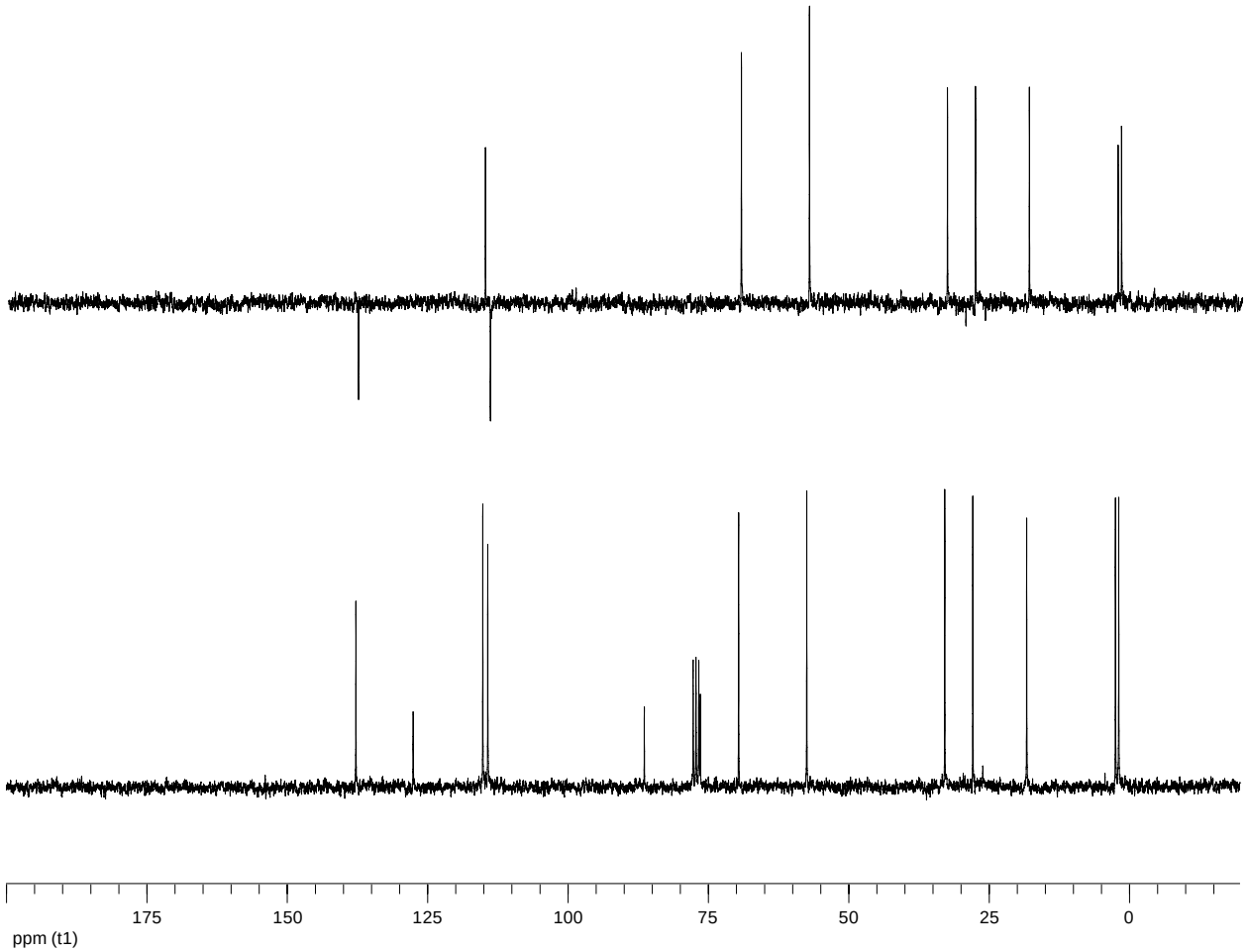
1g

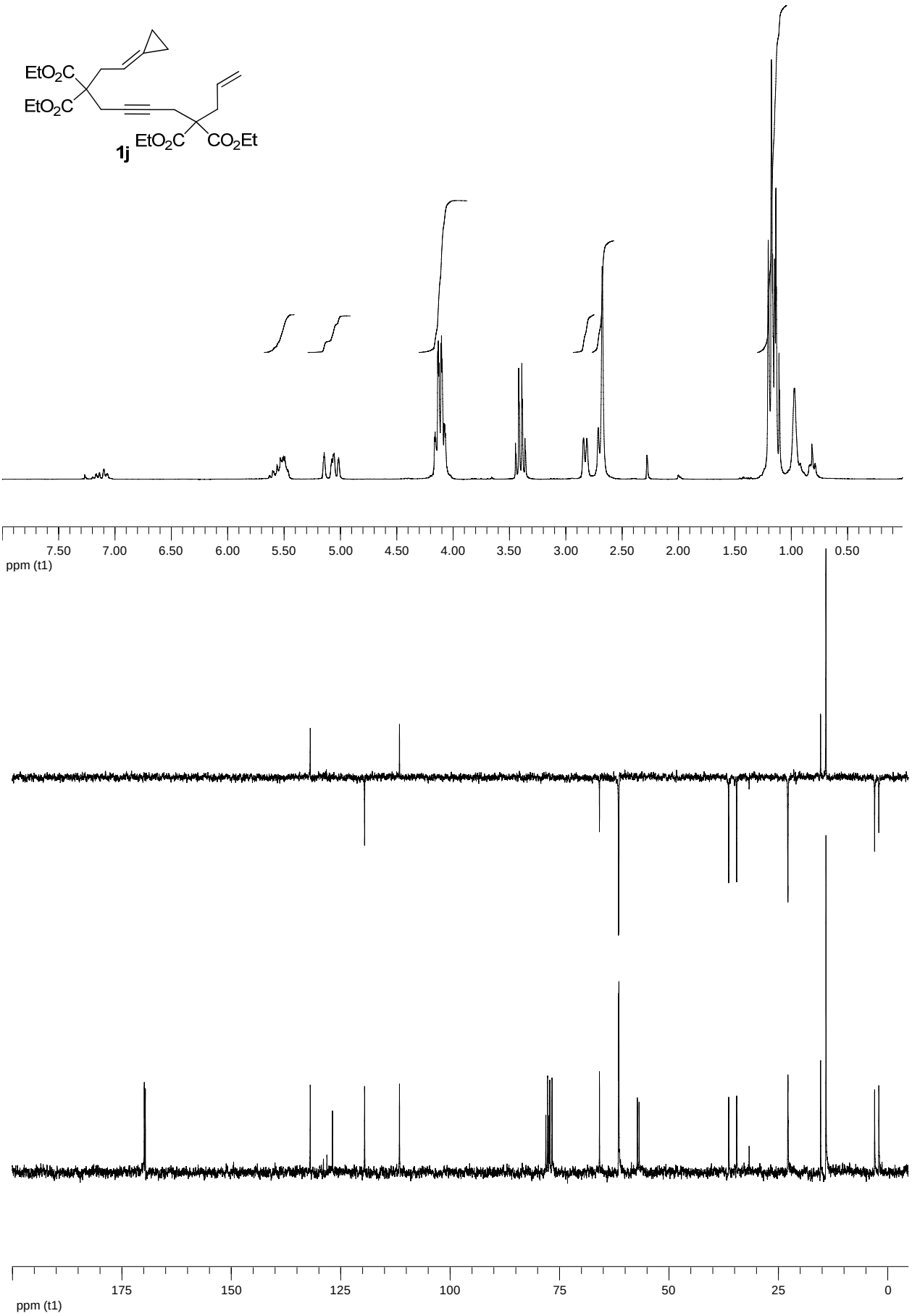
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (t1)

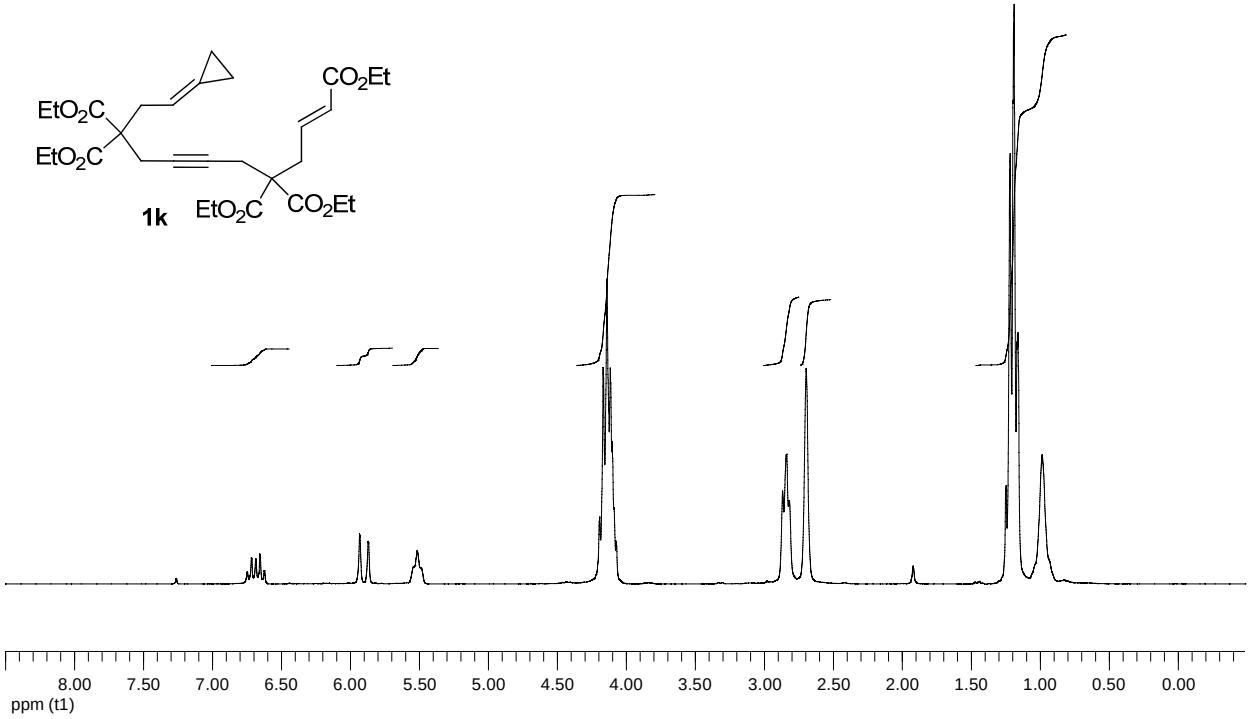

175
150
125
100
75
50
25
0
ppm (t1)

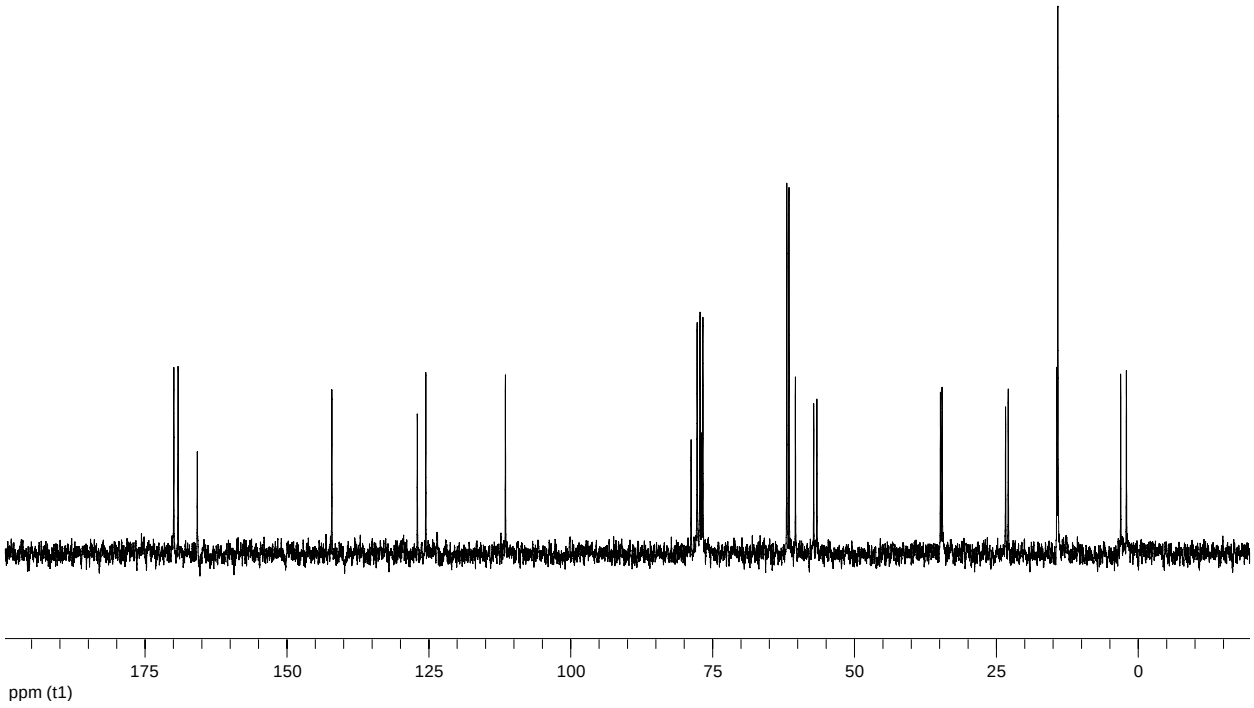

EtO2C
EtO2C
N
1h
8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)
175 150 125 100 75 50 25 0
ppm (f1)

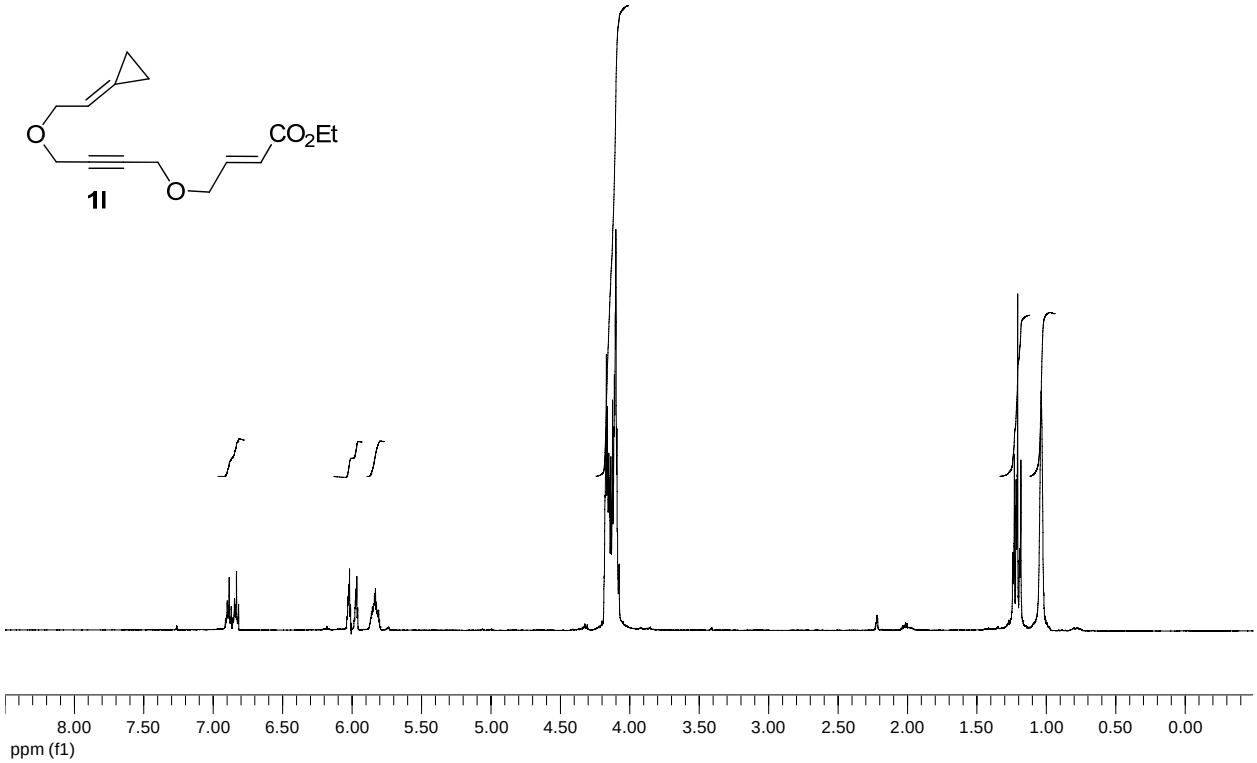

O
1i
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (t1)

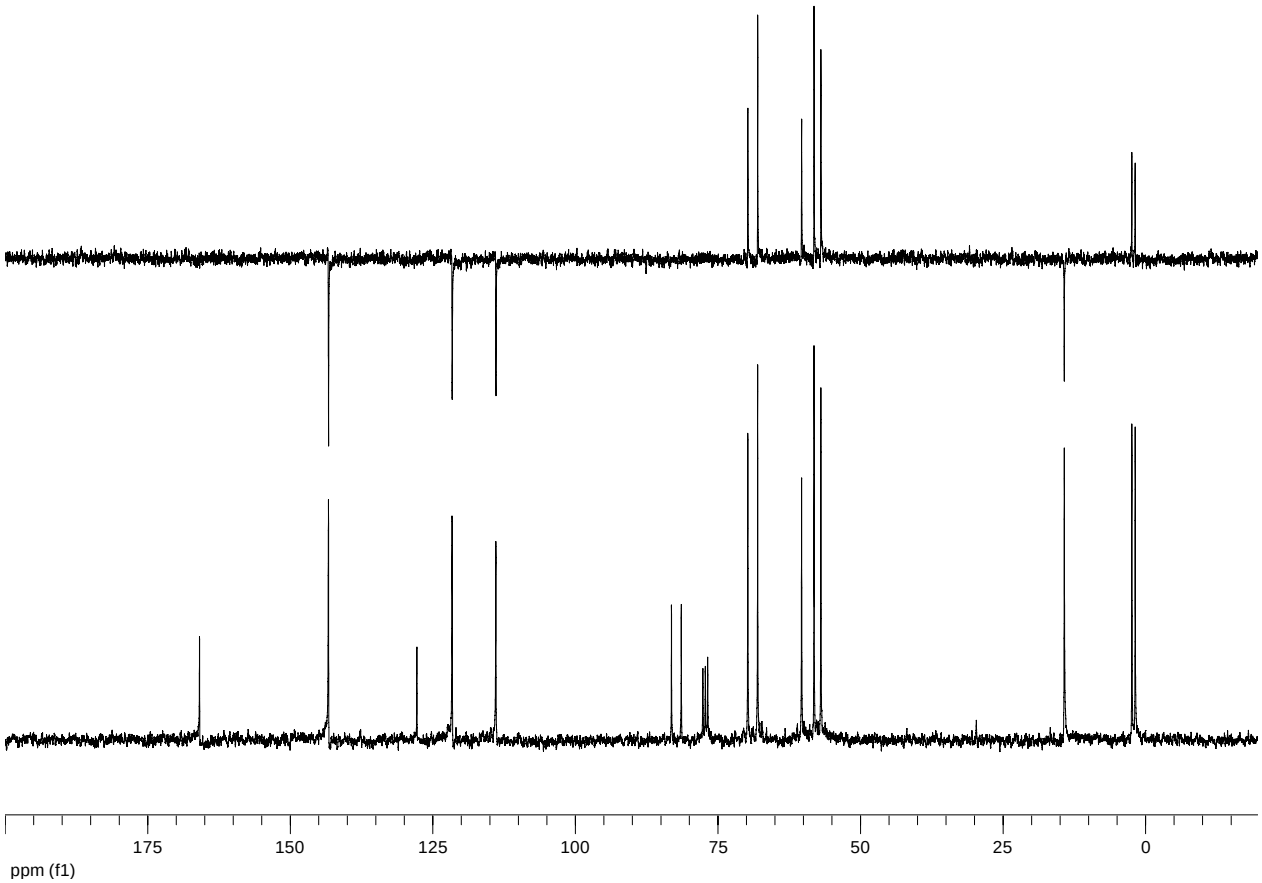

175
150
125
100
75
50
25
0
ppm (t1)

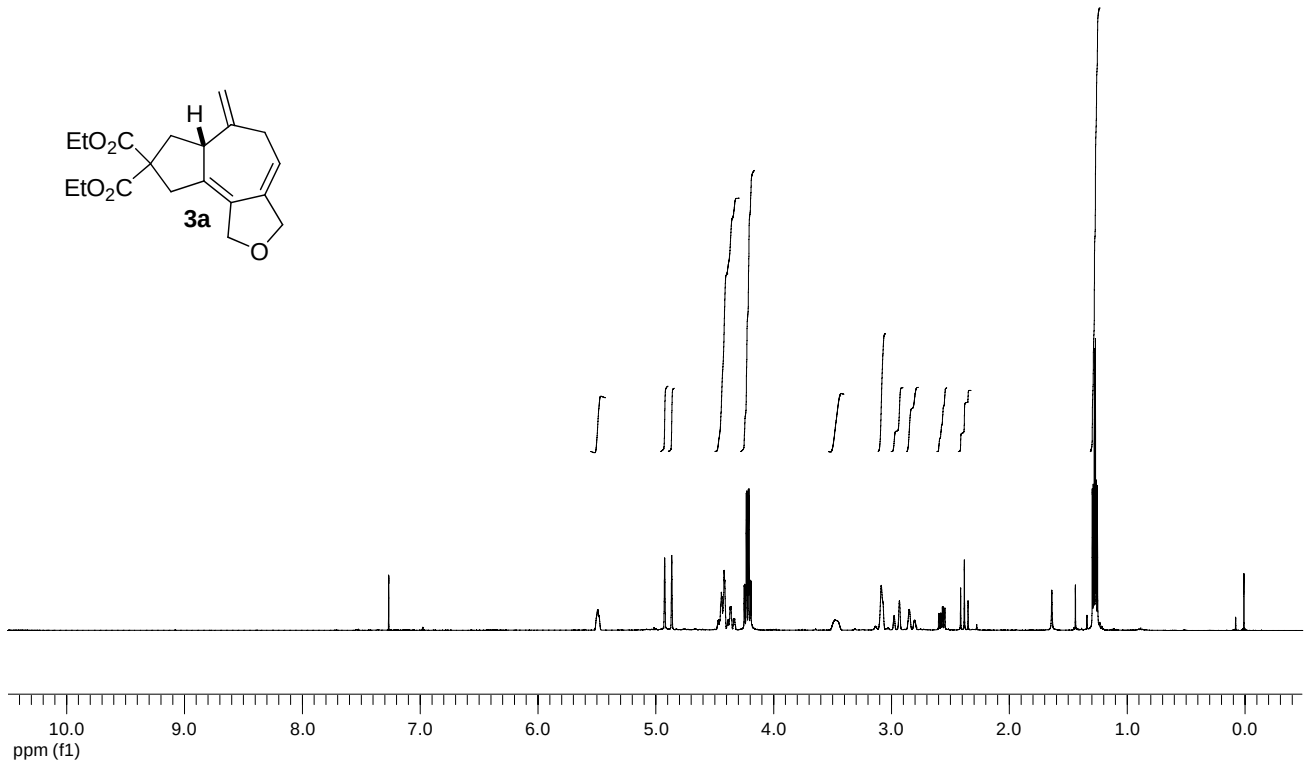

EtO2C
EtO2C
EtO2C
CO2Et
1j
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)
175
150
125
100
75
50
25
0
ppm (t1)

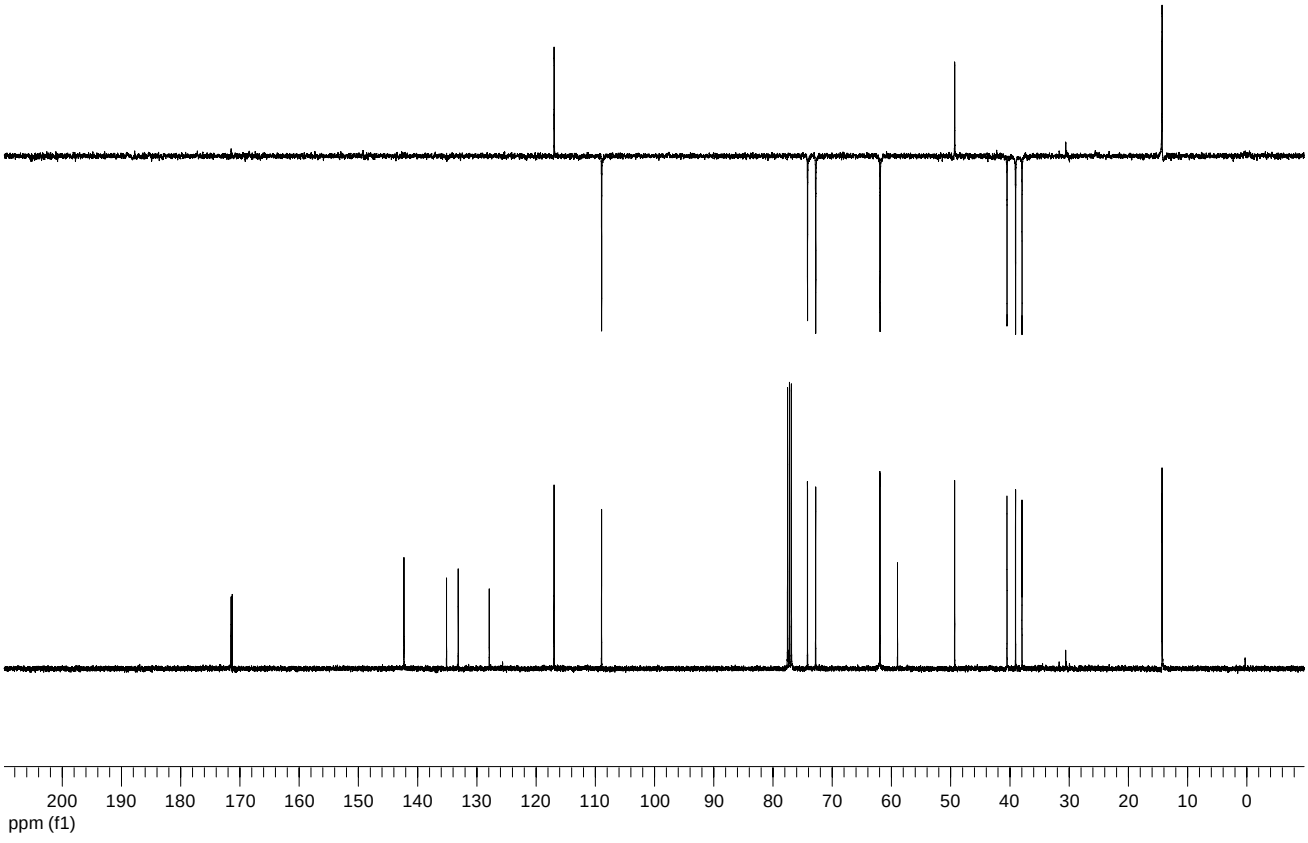

EtO2C
EtO2C
CO2Et
EtO2C
CO2Et
1k
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (t1)

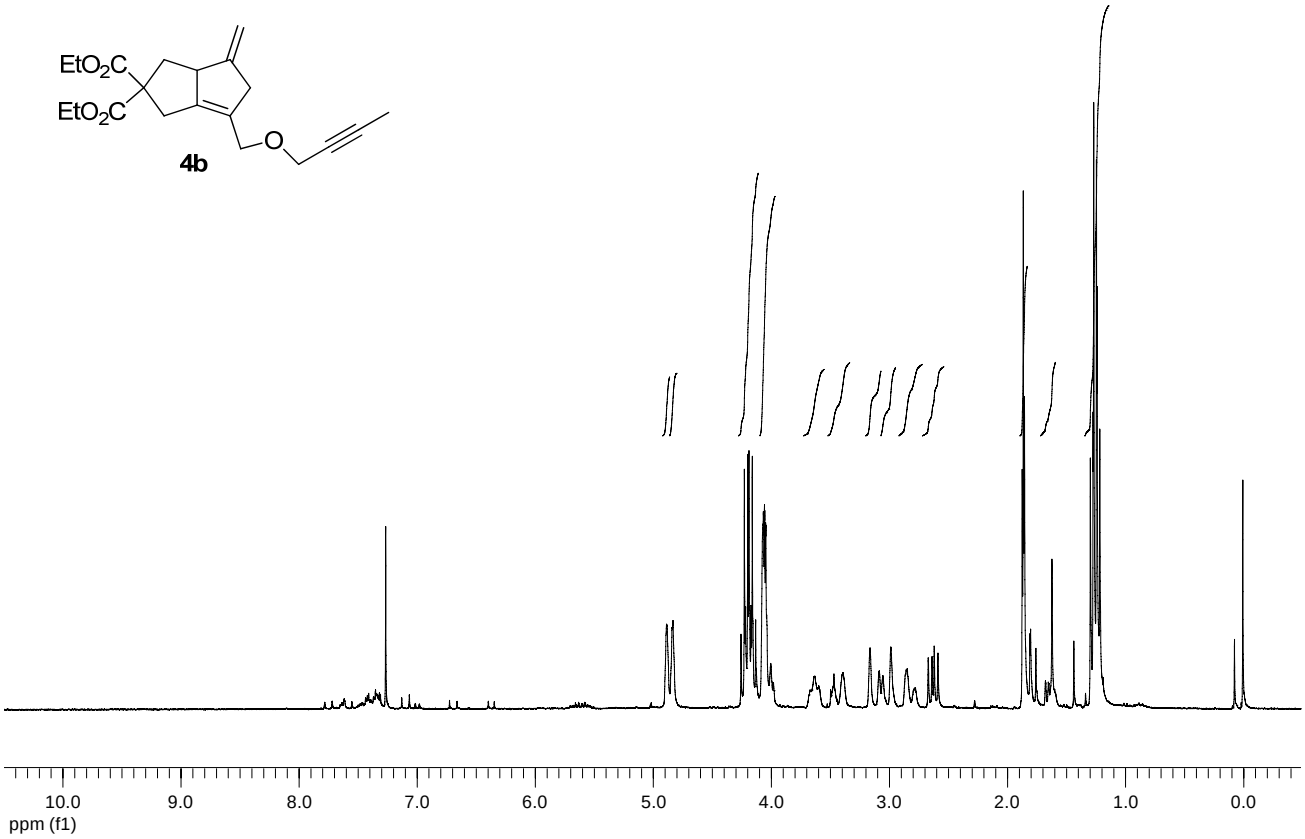

175
150
125
100
75
50
25
0
ppm (t1)

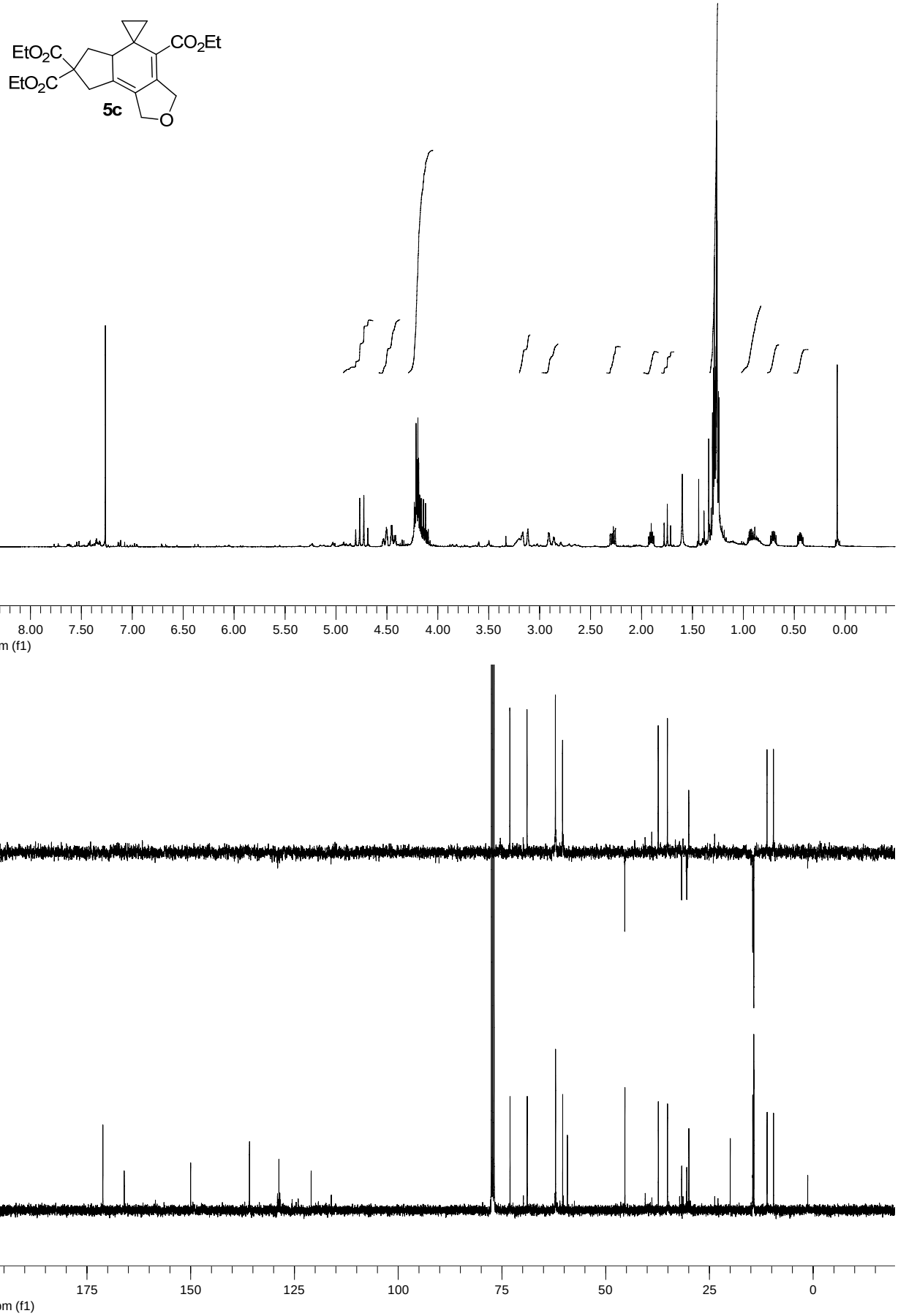

O
CO2Et
O
1l
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

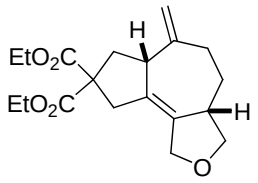

175
150
125
100
75
50
25
0
ppm (f1)


H
EtO2C
EtO2C
3a
O
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)

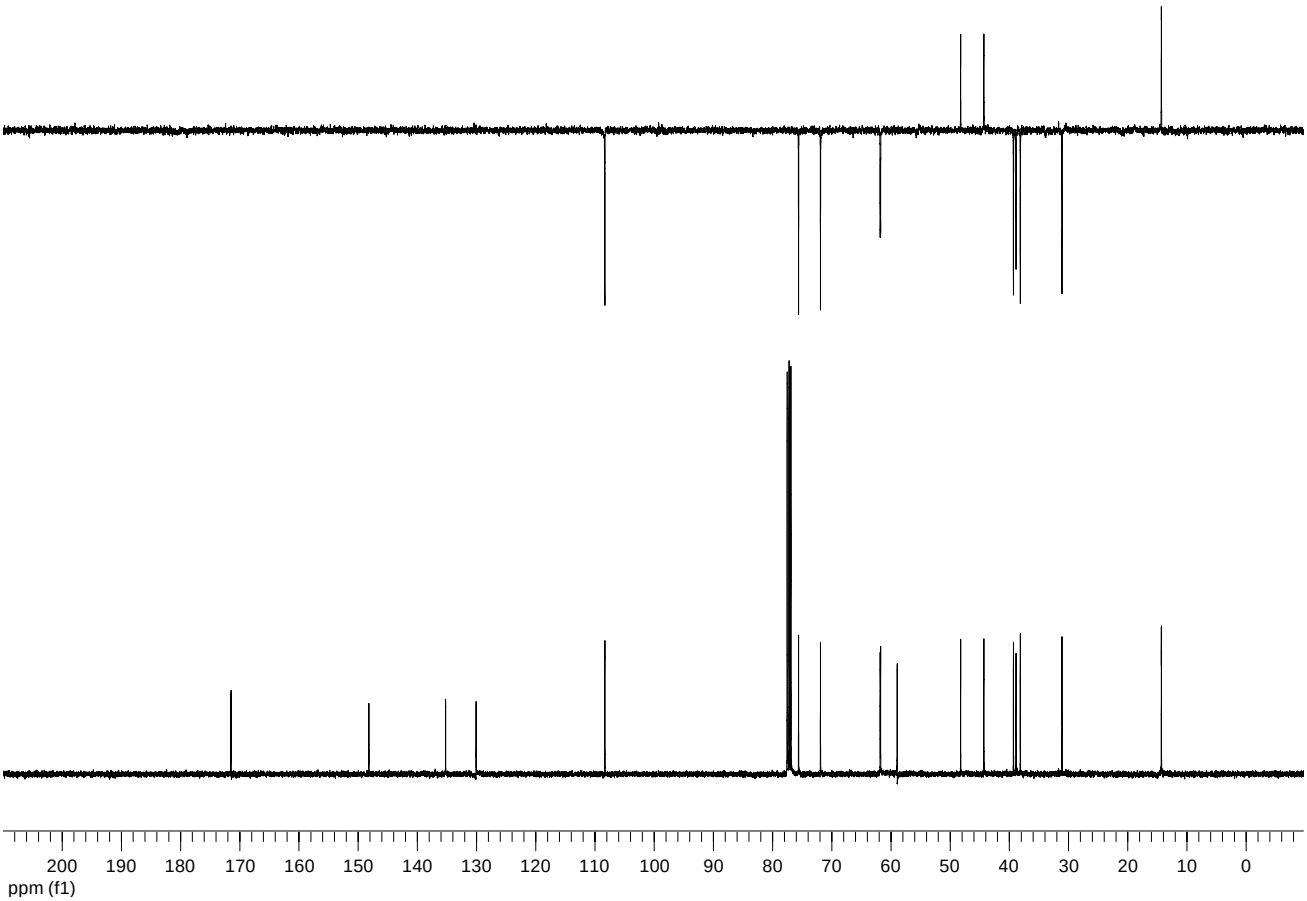

EtO2C
EtO2C
O
4b
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

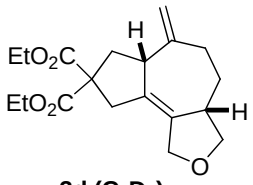

EtO2C
EtO2C
CO2Et
5c
O
8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)
175 150 125 100 75 50 25 0
ppm (f1)


H
EtO2C
EtO2C
H
O

3d ($CDCl_3$)

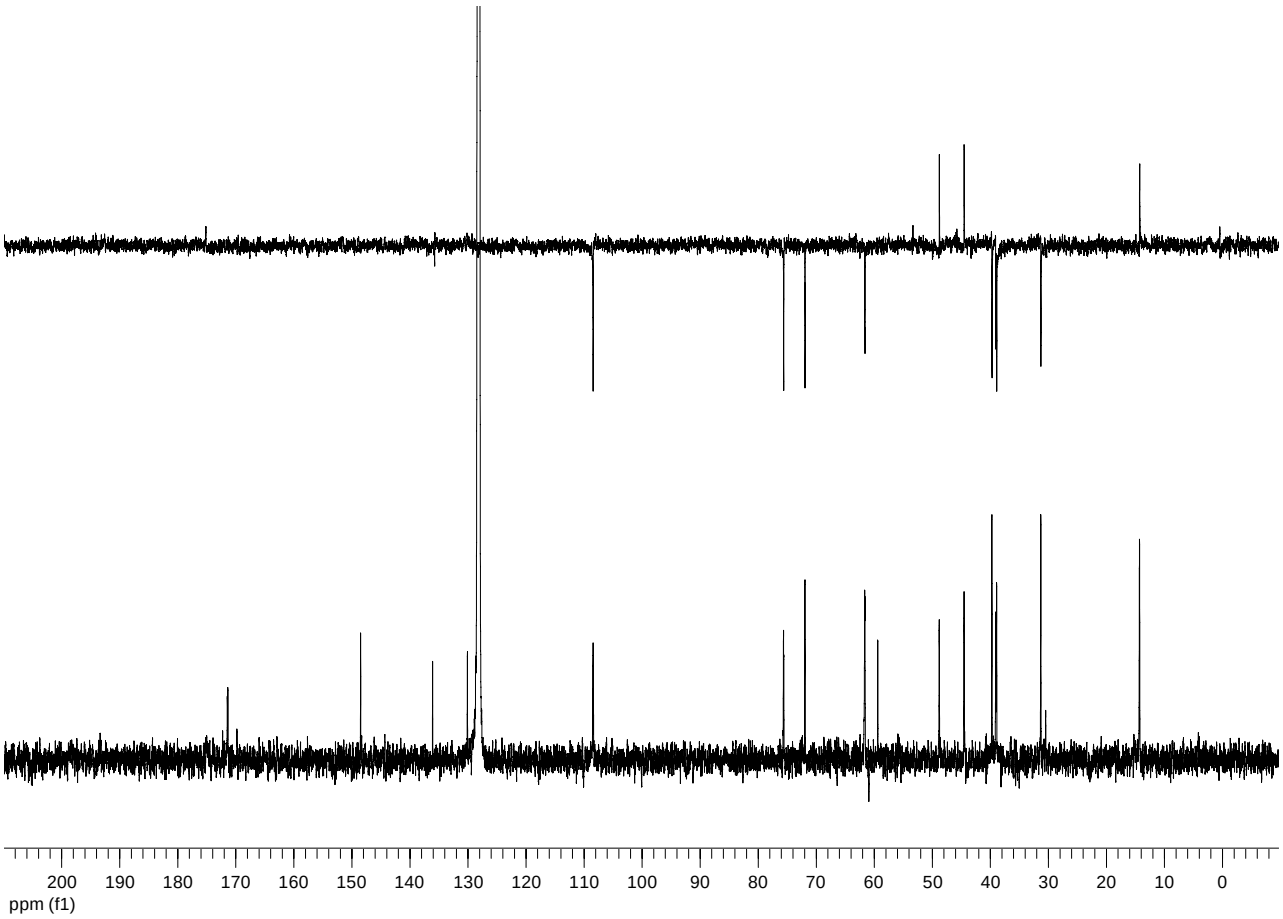
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

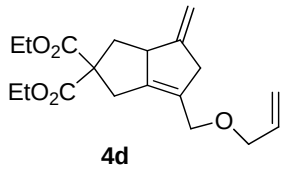

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)


H
EtO2C
EtO2C
H
O

3d (C_6D_6)

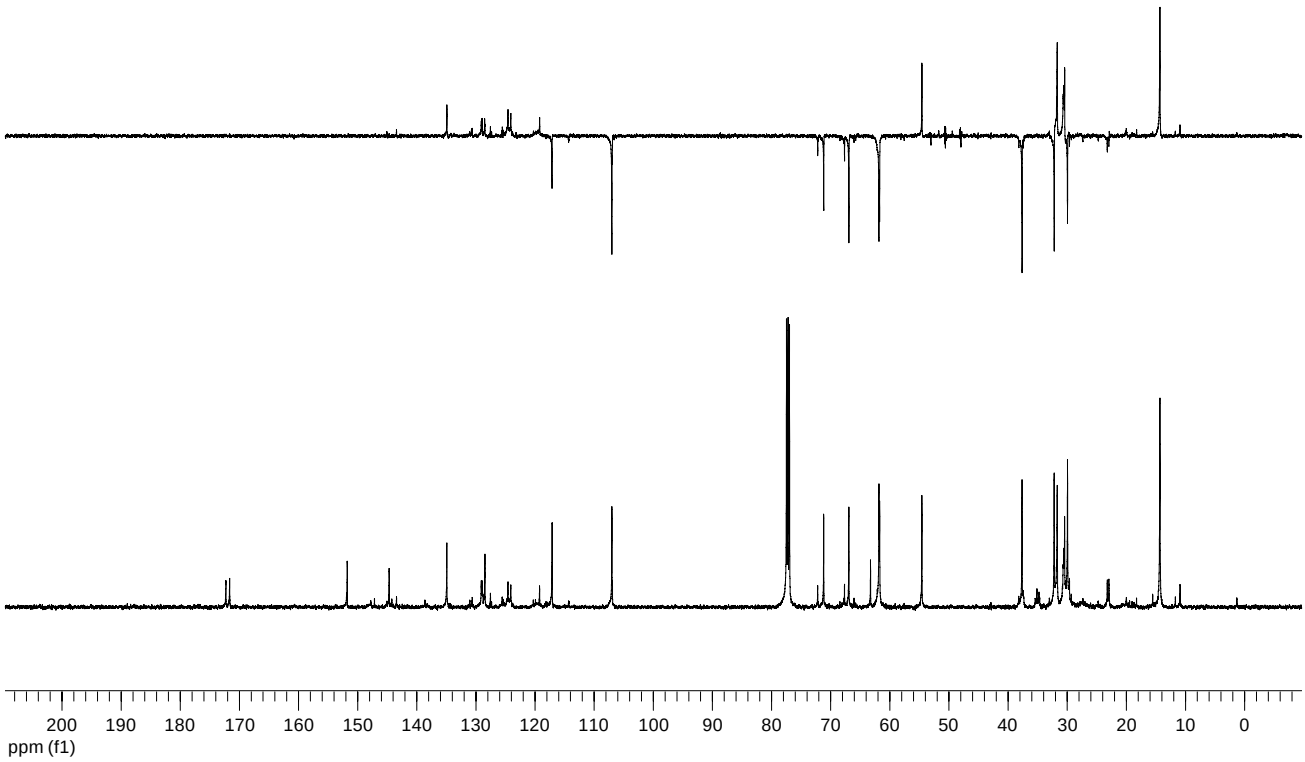
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

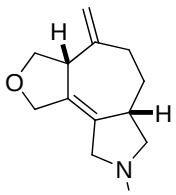

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)


EtO2C
EtO2C
O

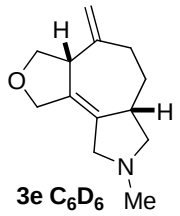
4d

7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f1)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)

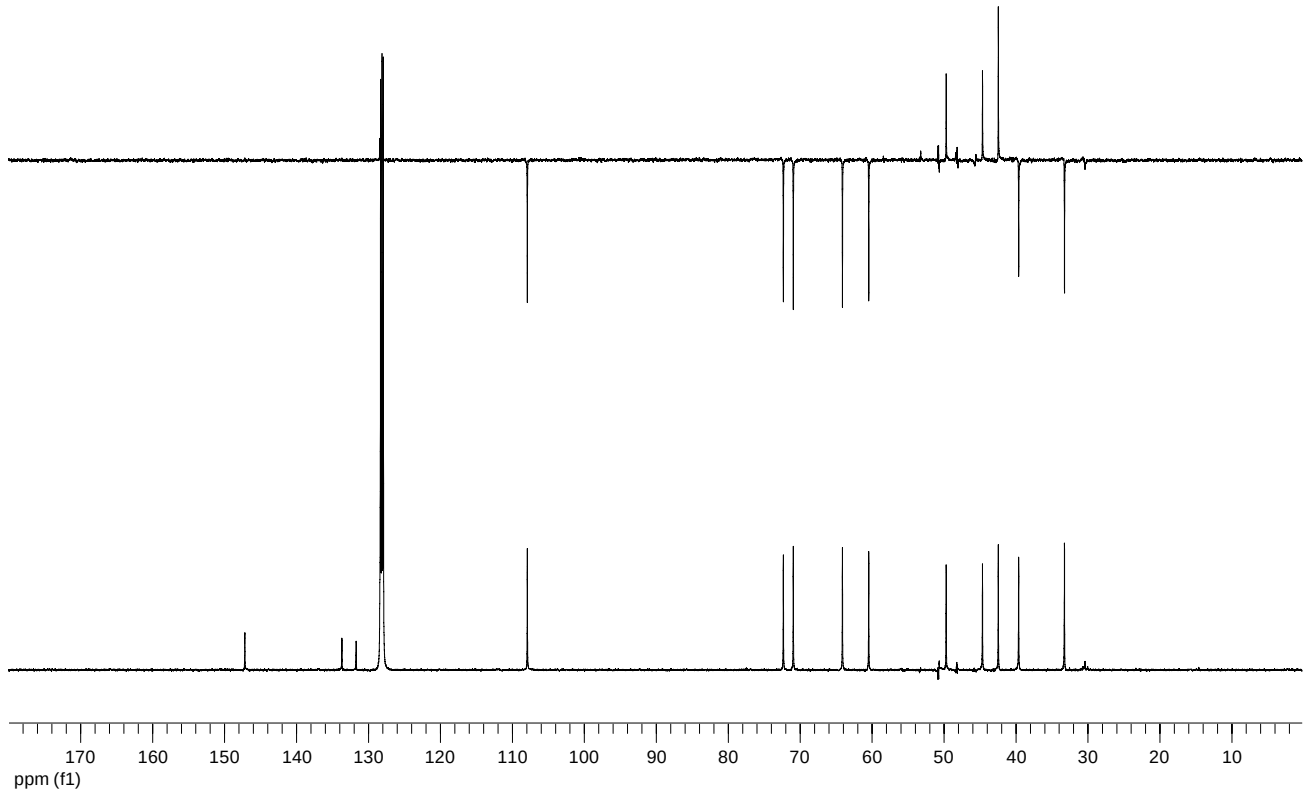


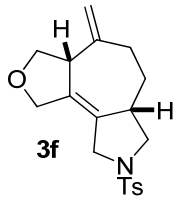
3e $CDCl_3$


H
O
H
N
Me

3e C_6D_6

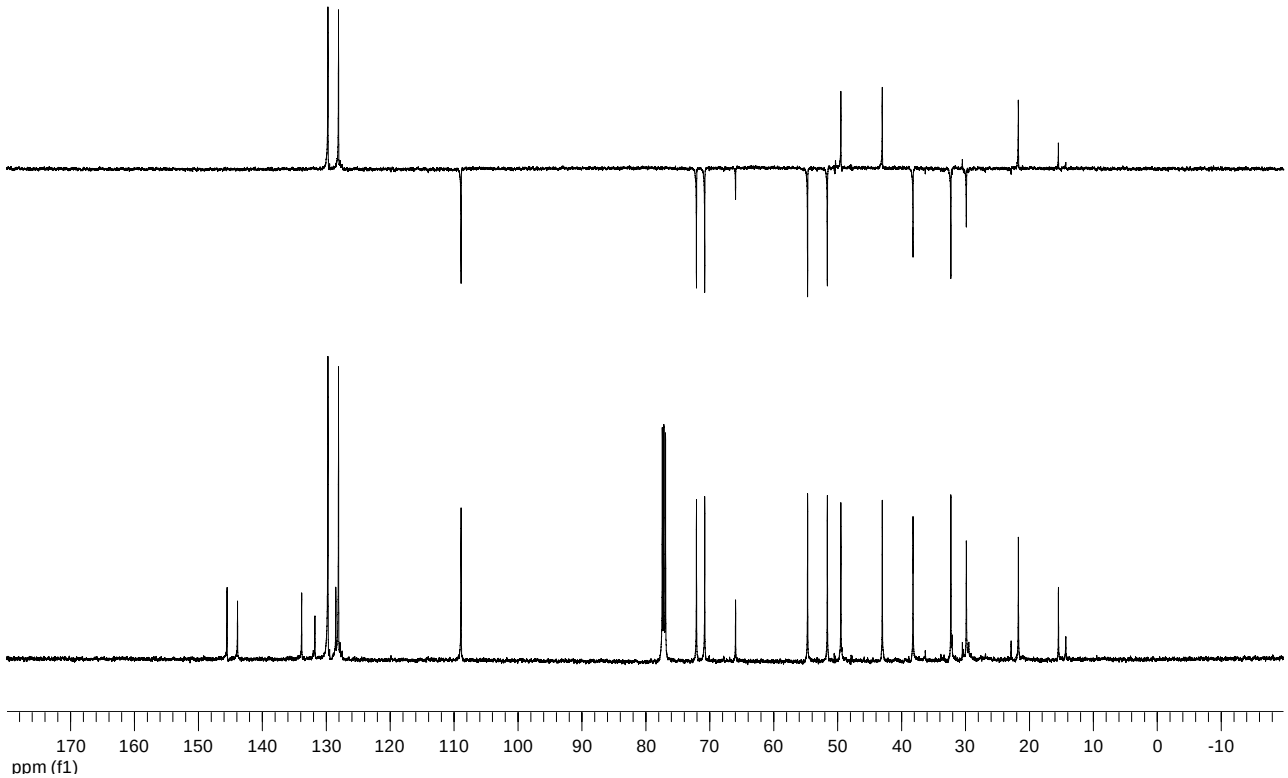
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

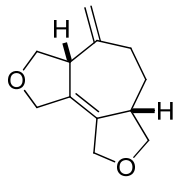

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)


H
O
H
N
Ts

3f

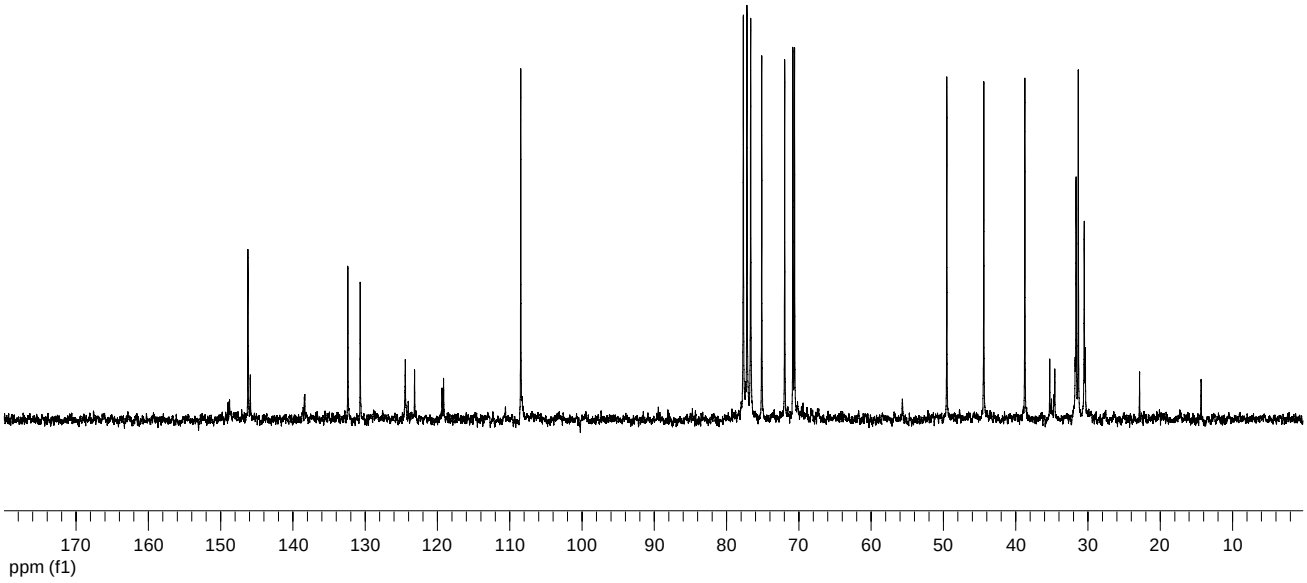
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
ppm (f1)

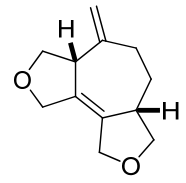

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (f1)


H
O
H
O

3g $CDCl_3$

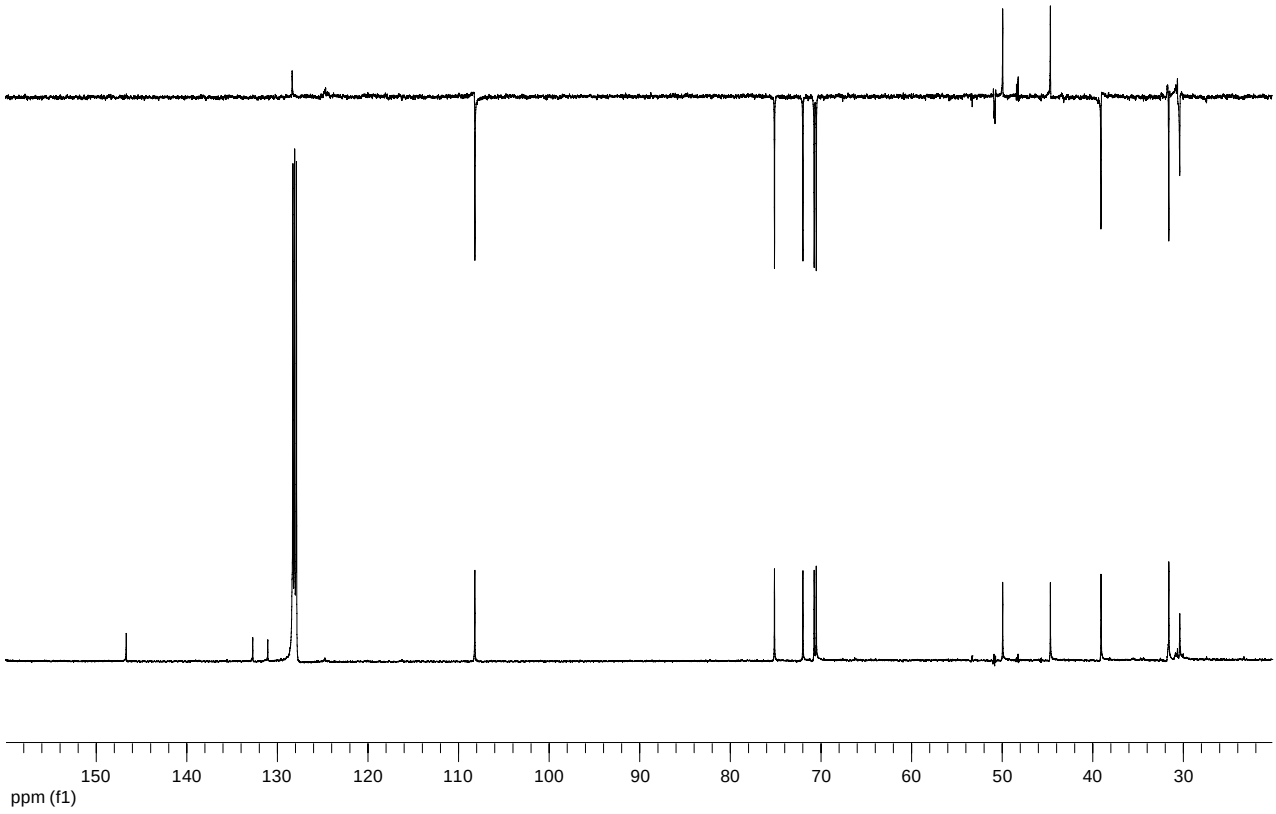
8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)

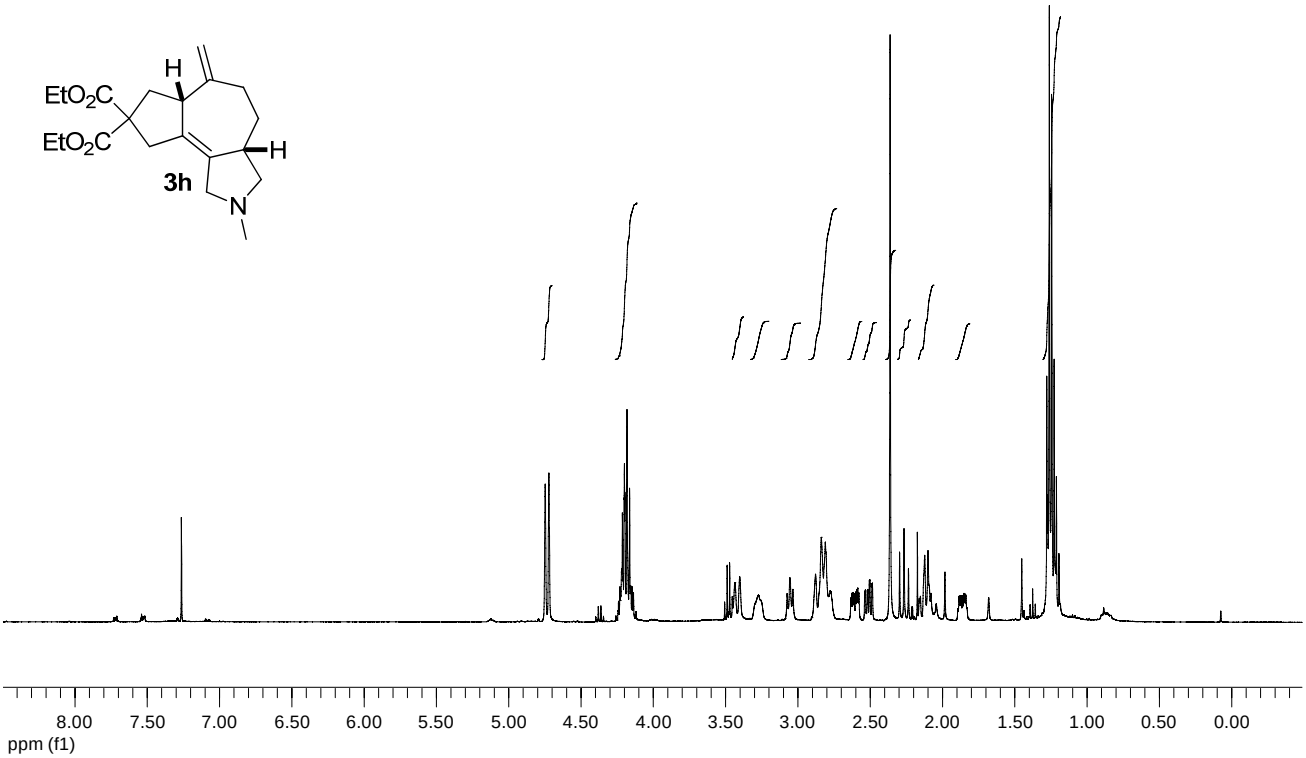

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (f1)

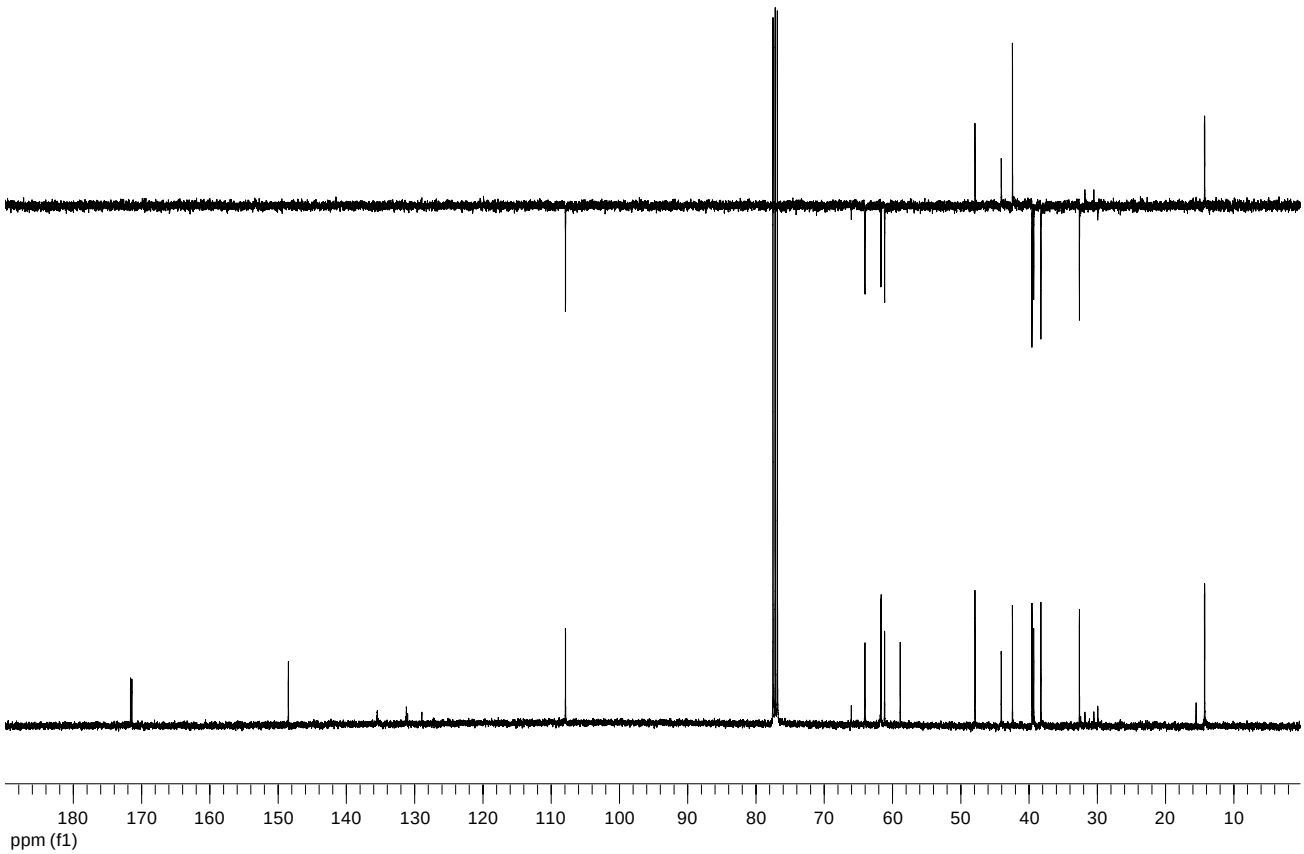

H
O
H
O

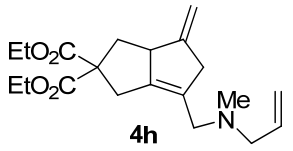
3g C_6D_6

8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


150
140
130
120
110
100
90
80
70
60
50
40
30
ppm (f1)

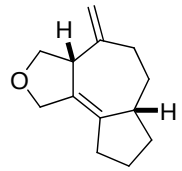

H
EtO2C
EtO2C
H
3h
N
8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm (f1)

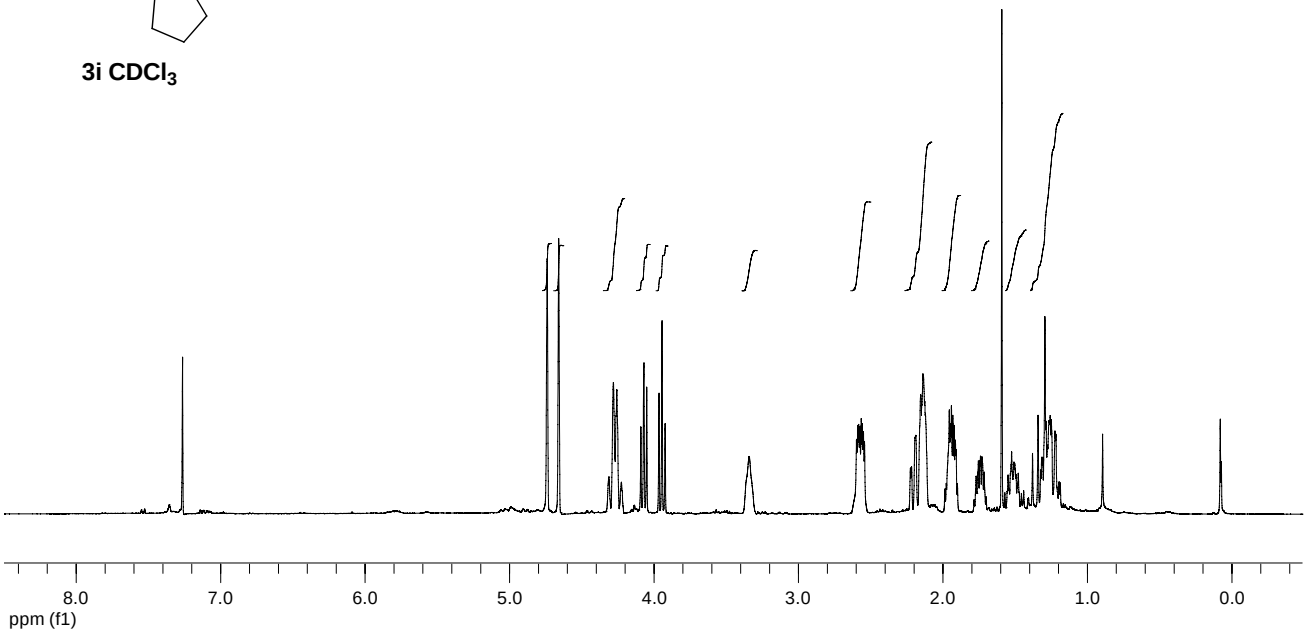

EtO2C
EtO2C
Me
N

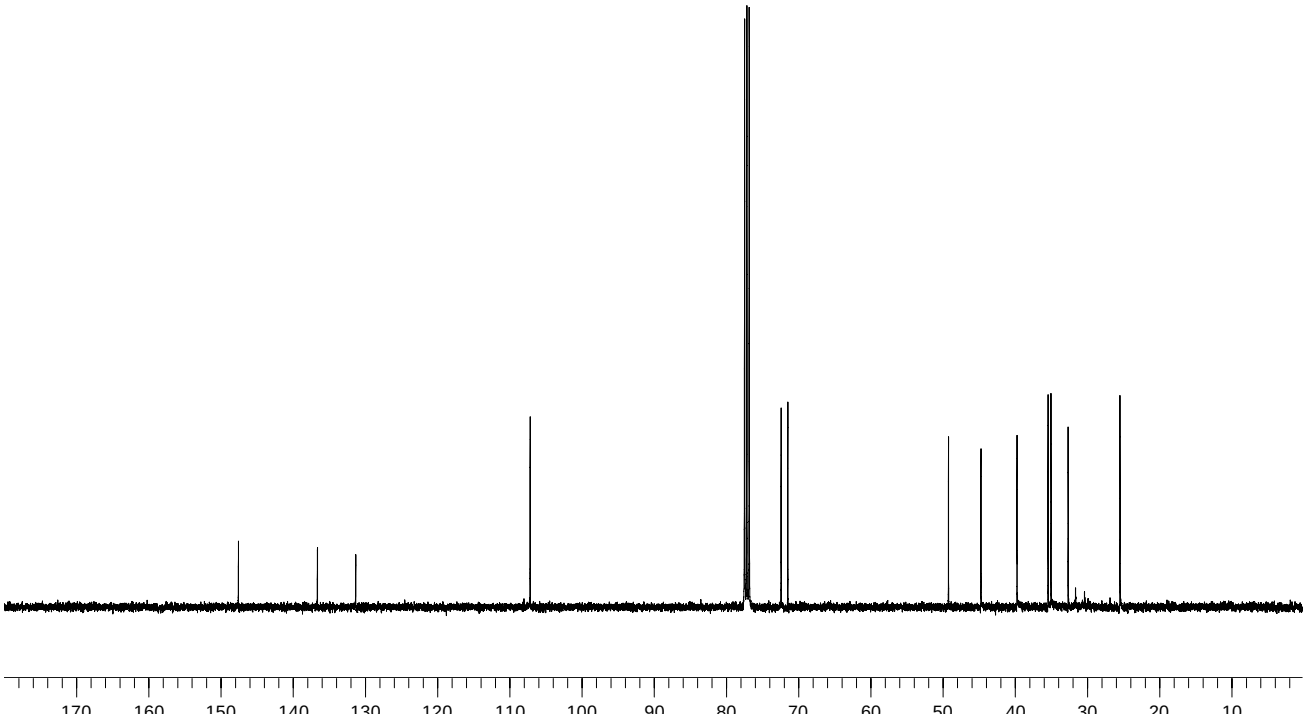
4h

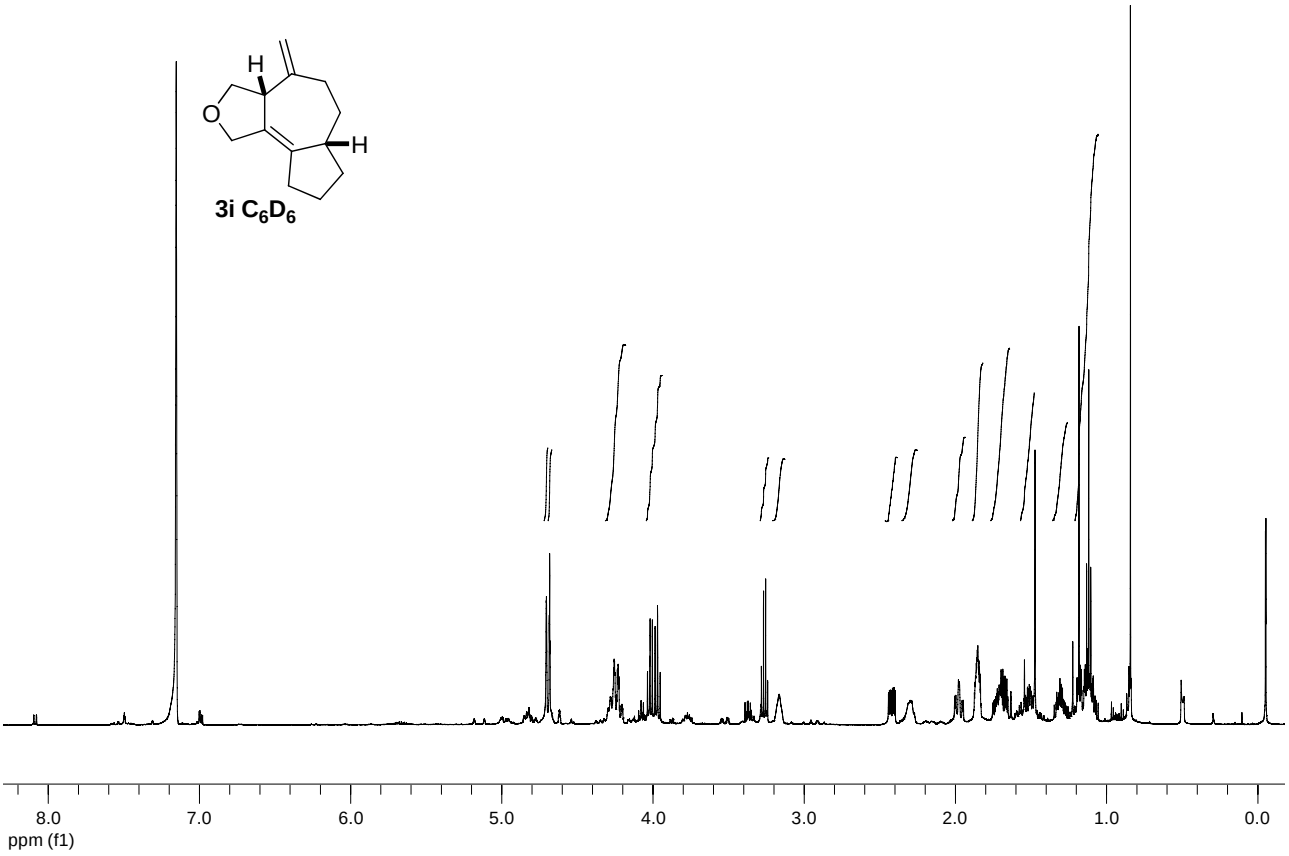
8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

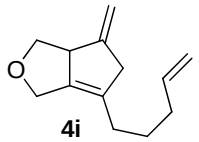

H
O
H

3i $CDCl_3$


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

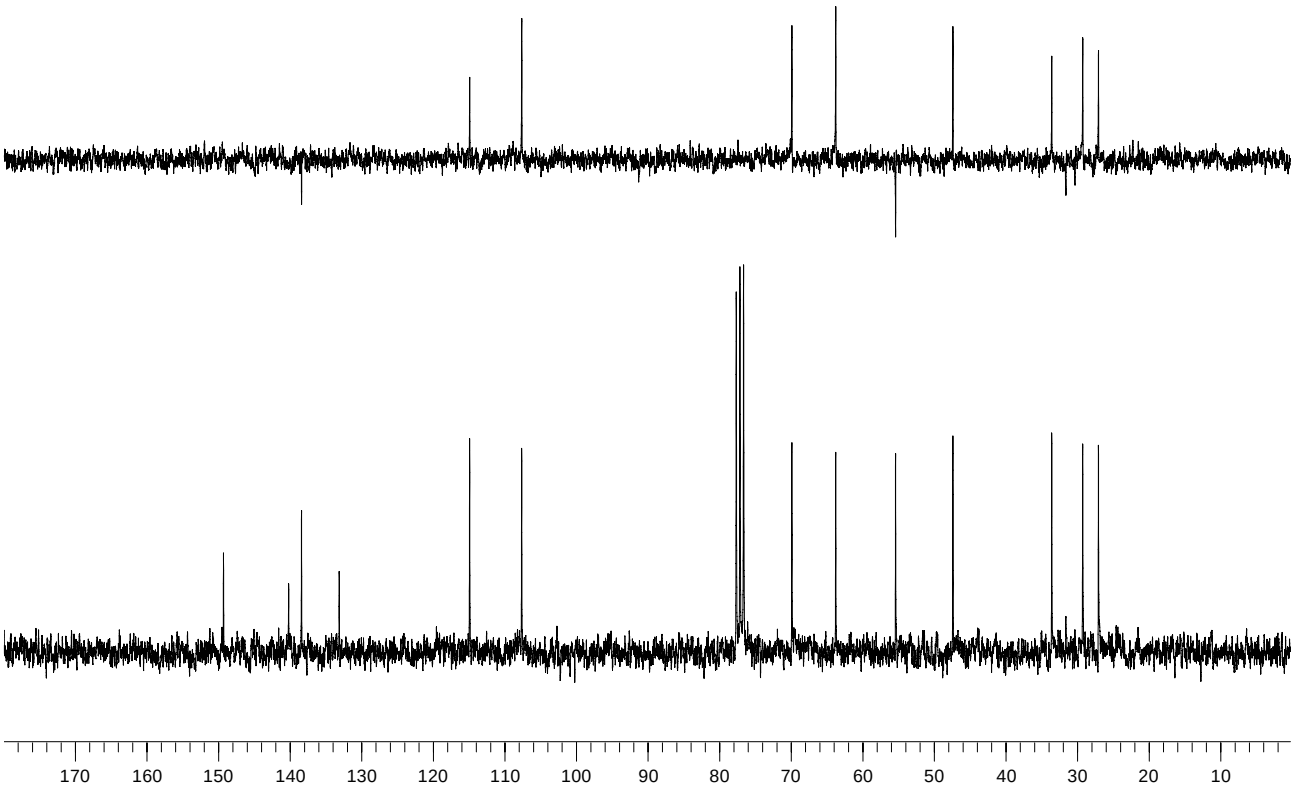

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

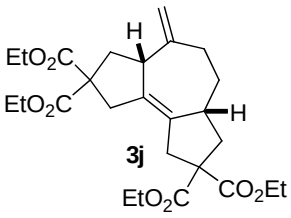

H
O
H
3i C_6D_6
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


O

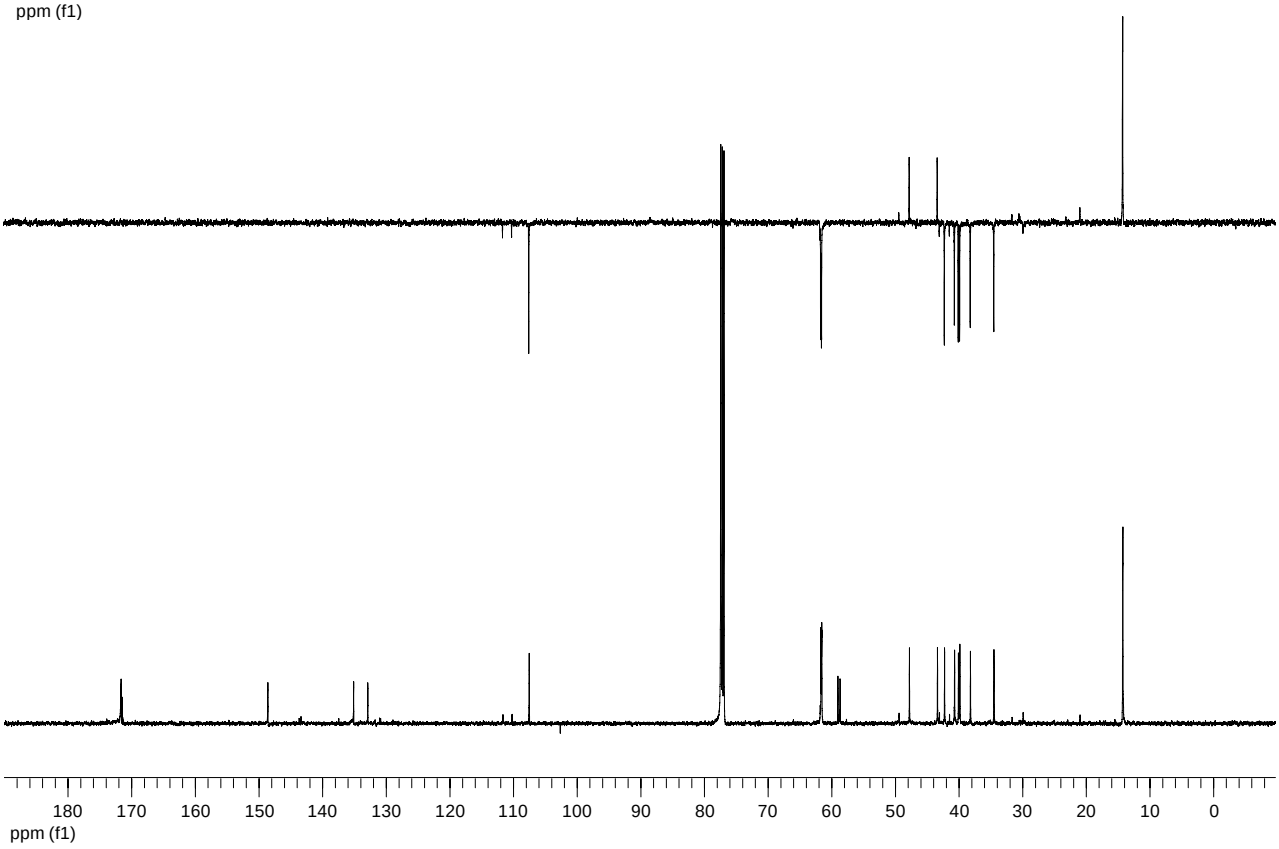
4i

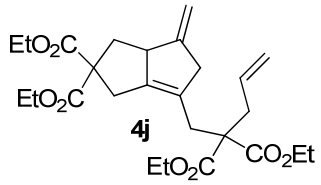
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


H
EtO2C
EtO2C
H
3j
EtO2C
CO2Et

8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)

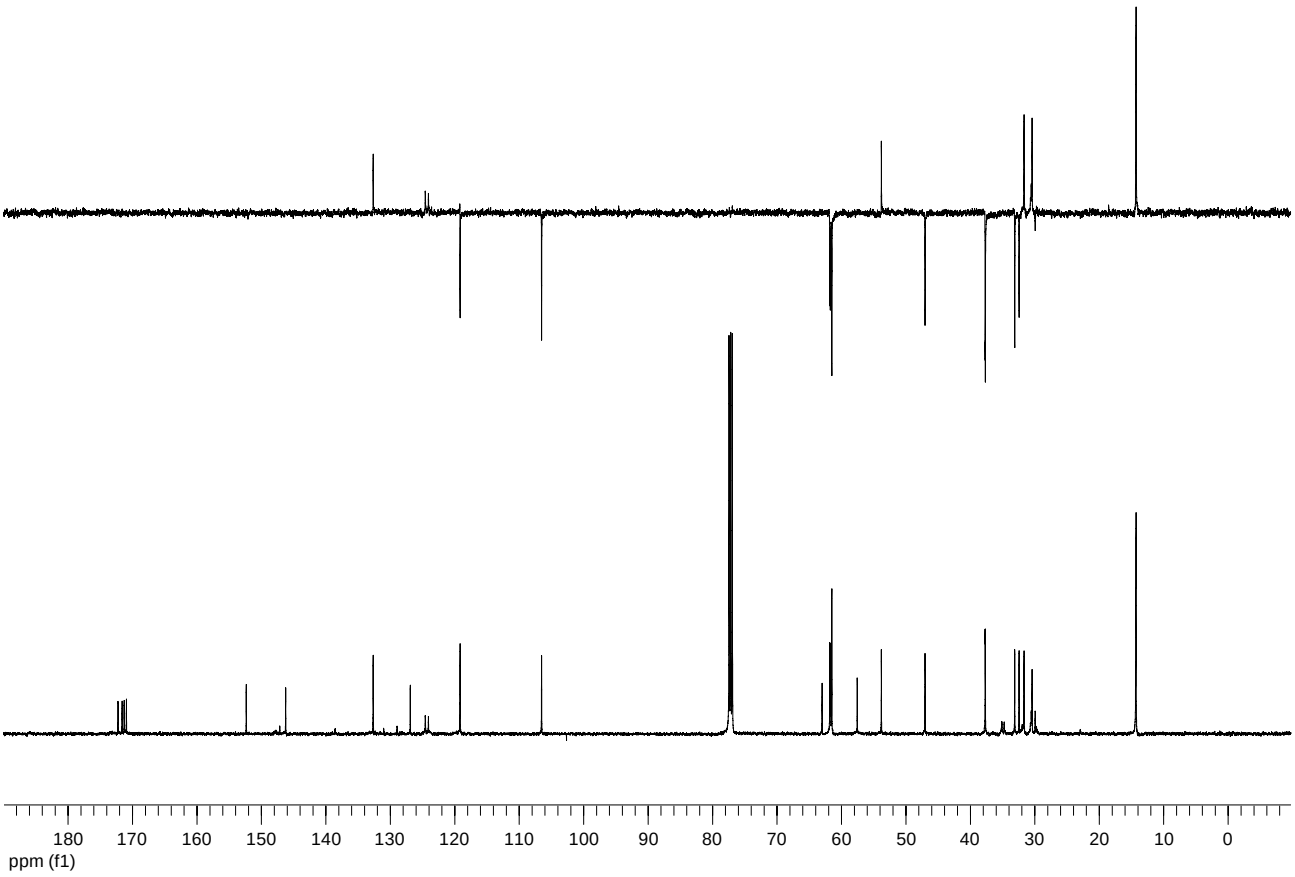

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

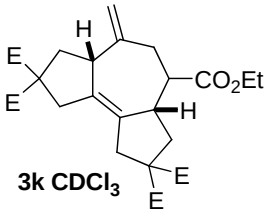

EtO2C
EtO2C

4j

EtO2C
CO2Et

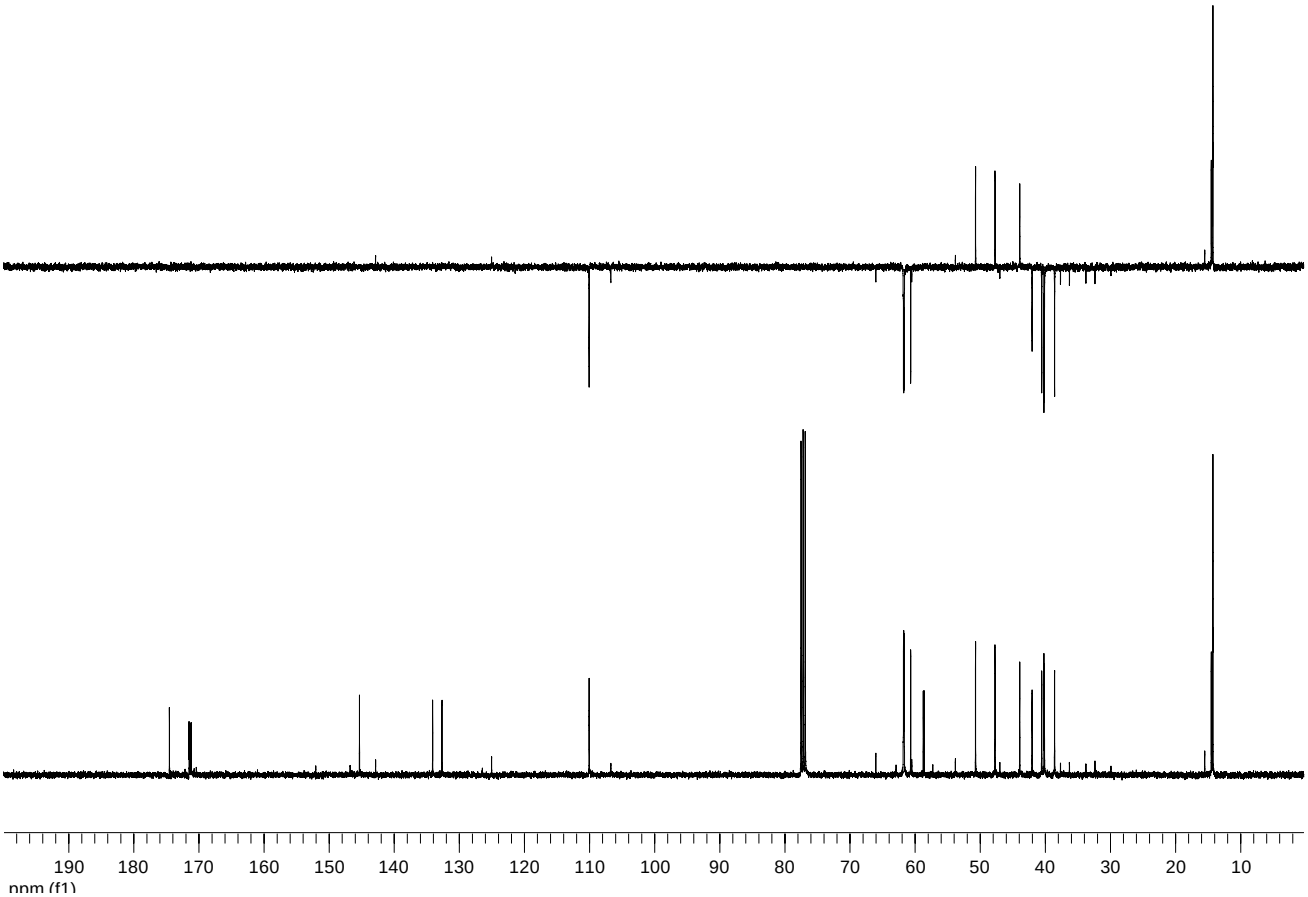
8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)

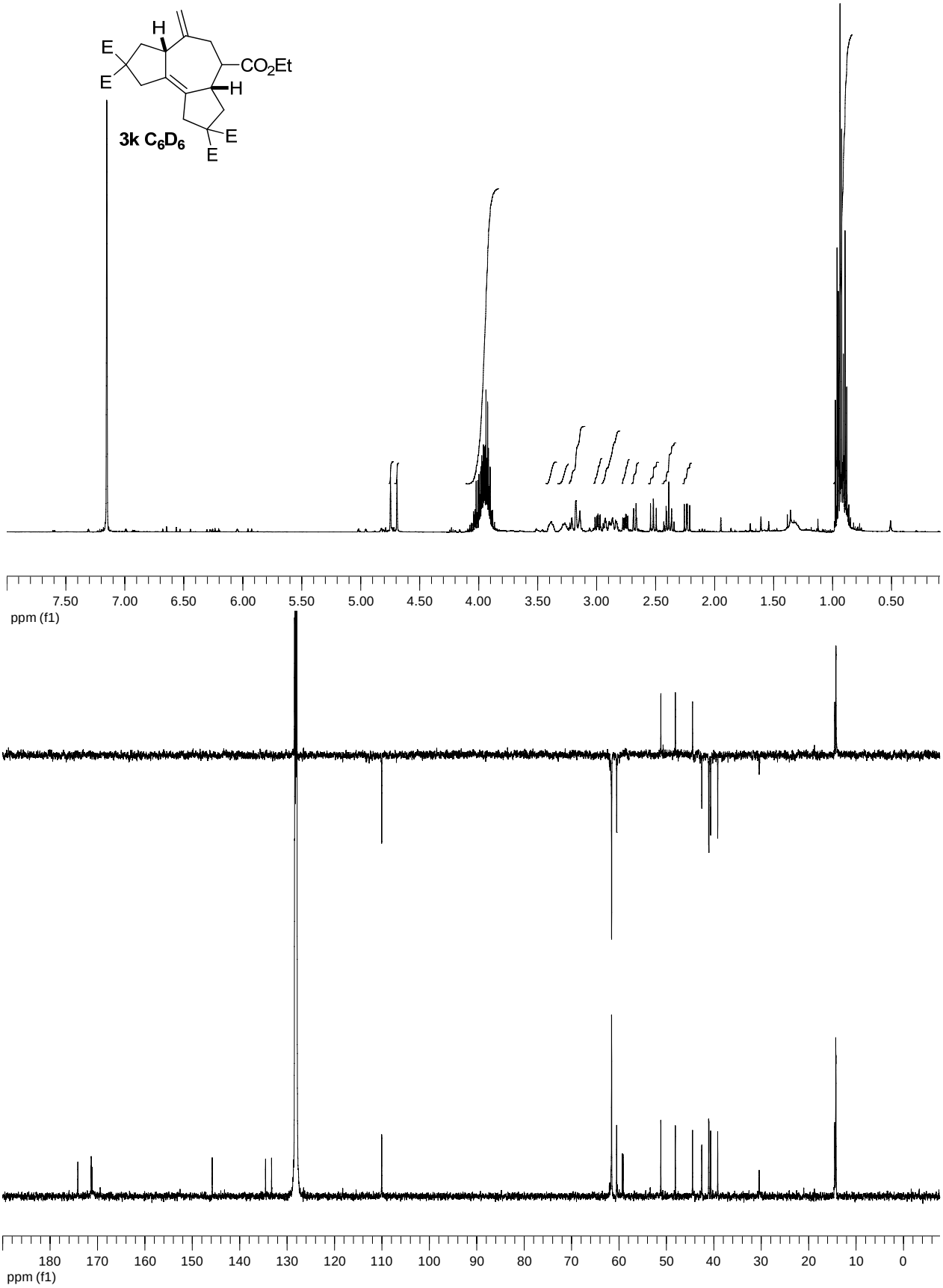

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

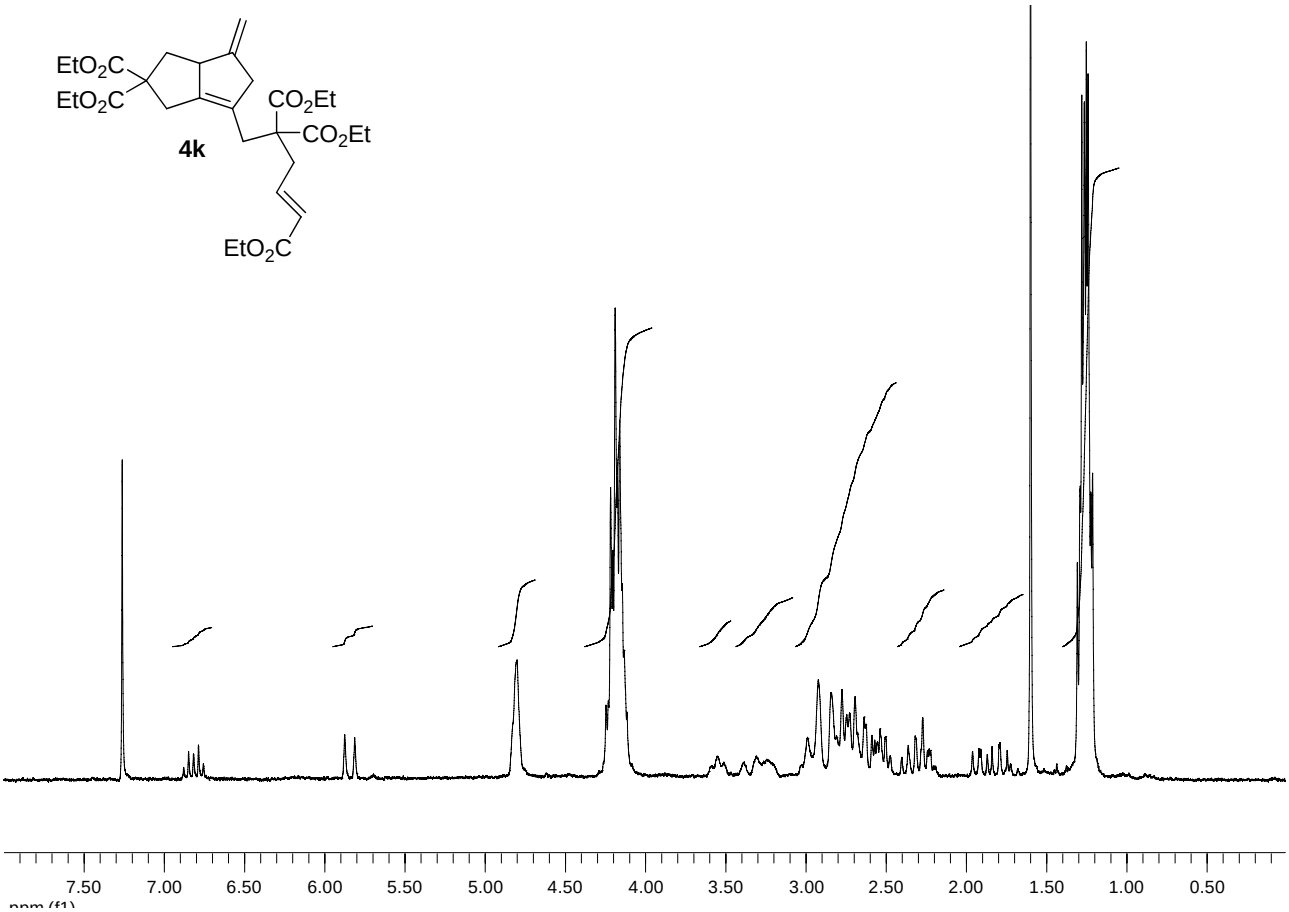

H
E
E
CO2Et
H
E
E

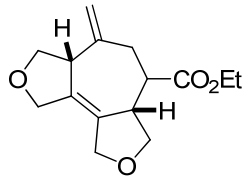
3k $CDCl_3$

7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f1)


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (f1)

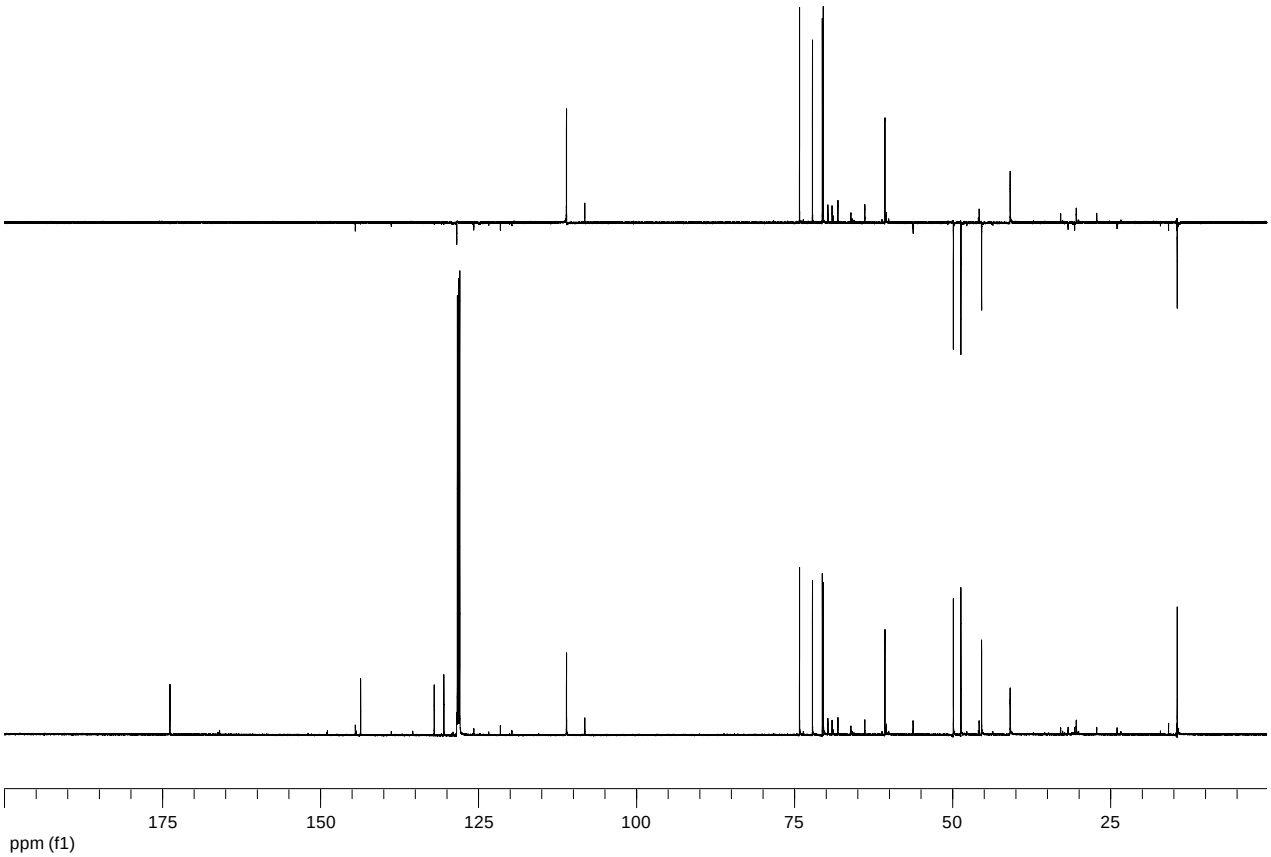

H
E
E
CO2Et
H
E
E
3k C6D6
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f1)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)


EtO2C
EtO2C
CO2Et
CO2Et
EtO2C
4k
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (f1)


H
O
CO2Et
H
O

3l (C_6D_6)

8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


175
150
125
100
75
50
25
ppm (f1)