Supporting Information

Nickel-Catalyzed Intramolecular [3 + 2 + 2] Cycloadditions of Alkylidenecyclopropanes. A Straightforward Entry to Fused 6,7,5- Tricyclic Systems

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General procedures

Dry solvents were freshly distilled under argon from an appropriate drying agent before use. Toluene was distilled from Na, THF from Na / benzophenone and CH_2Cl_2 and Et_3N were distilled from CaH_2. Pd_2dba_3 was generously provided by Johnson Matthey; $Ni(COD)_2$ was obtained from Alfa Aesar; triphenylphosphine, tris[(4-trifluoromethyl)phenyl] phosphine, tricyclohexyl phosphine, 1,2-bis(diphenylphosphino)ethane were purchased from Sigma Aldrich; 1,3-bis(diphenylphosphino)propane was purchased from TCI chemicals. N-heterocyclic carbenes IPr and IMes were purchased from Aldrich. Commercial reagents were purchased from Sigma Aldrich and were used without further purification.

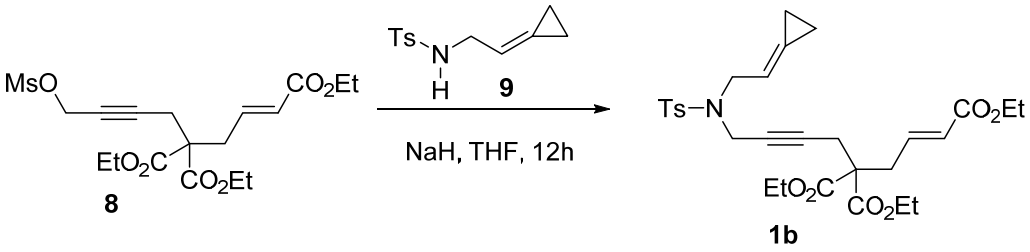
All reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. External bath temperatures were used to record all reaction temperatures. The abreviation "rt" refers to reactions carried out at 23°C. Reaction mixtures were stirred using Teflon-coated magnetic stir bars. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualized by observation under UV light, and / or by treating the plates with *p*-anisaldehyde or ninhidrine solutions, 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 Buchi rotary evaporator (10 mmHg aprox) followed by residual solvent removal under high vacuum.

NMR spectra were recorded in $CDCl_3$, at 300 MHz (Varian) for cycloaddition precursors, and 500 MHz (Bruker) for cycloadducts. Carbon types and structure assignments were determined from DEPT-NMR and 2D experiments (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestReNova© NMR data processing software (www.mestrelab.com). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; dd, double doublet; td, triple doublet; m, multiplet; br, broad. Mass spectra were acquired using chemical ionization (CI) or electronspray techniques (ESI) and were recorded at the CACTUS facility of the University of Santiago de Compostela. The reactions were monitored by GC-MS using the Agilent Technologies 6890N, Network GC System, equipped with the Agilent 190915-433 column and the Agilent 5973 Inert Mass Selective Detector in Electron Impact or Chemical Ionization Mode (with Methane).

(E)-Pentaethyl 11-cyclopropylideneundec-1-en-6-yne-1,4,4,9,9-pentacarboxylate (**1a**), (E)-Ethyl 4-((4-(2-cyclopropylideneethoxy)but-2-yn-1-yl)oxy)but-2-enoate (**1f**), Diethyl 2-(4-(but-2-yn-1-yloxy)but-2-yn-1-yl)-2-(2-cyclopropylideneethyl)malonate (**1i**) and diethyl 2-(2-cyclopropylideneethyl)-2-(4-(prop-2-yn-1-yloxy)but-2-yn-1-yl)malonate (**1k**) are known compounds and were synthesized according to previously reported procedures.[2]

Procedures for the synthesis of cycloaddition precursors.

(*E*)-Triethyl 8-(N-(2-cyclopropylideneethyl)-4-methylphenylsulfonamido)oct-1-en-6-yne-1,4,4-tricarboxylate (1b)



To a solution of NaH (58 mg, 1.40 mmol) in THF (10 mL) were added dropwise N-(2-cyclopropylideneethyl)-4-methylbenzenesulfonamide[3] (**9**) (345 mg, 1.40 mmol). After stirring a rt for 30 min, a solution of *(E)*- triethyl (E)-8-((methylsulfonyl)oxy)oct-1-en-6-yne-1,4,4-tricarboxylate **8**[4] (553 mg, 1.3 mmol) in THF (2 mL) was added an the reaction mixture was stirred 12 h a rt. Then, it was 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 (15 % Et_2O / hexanes) to yield **1b** as a colourless oil (496 mg, 68 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.33 – 7.27 (m, 2H), 6.66 (dt, ***J*** = 15.6, 7.8 Hz, 1H), 5.81 (dt, ***J*** = 15.5, 1.3 Hz, 1H), 5.74 – 5.65 (m, 1H), 4.23 – 4.11 (m, 6H), 4.03 (t, ***J*** = 2.1 Hz, 2H), 3.93 (d, ***J*** = 6.8 Hz, 2H), 2.71 (dd, ***J*** = 7.8, 1.3 Hz, 2H), 2.57 (t, ***J*** = 2.1 Hz, 2H), 2.42 (s, 3H), 1.34 – 1.16 (m, 9H), 1.08 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.5 (C), 143.7 (C), 142.1 (CH), 136.9 (C), 129.7

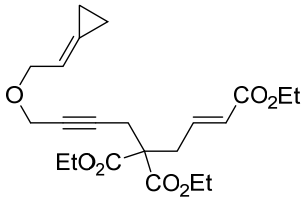
[2] G. Bhargava, B. Trillo, M. Araya, F. López, L. Castedo, J. M. Mascareñas, *Chem. Commun*. **2010**, *46*, 270.

[3] *N*-(2-Cyclopropylideneethyl)-4-methylbenzenesulfonamide was prepared as described in: A. Stolle, J. Olliver, P. P. Piras, J. Salaun, A. De Meijere *J. Am. Chem. Soc.* **1992**, *114*, 4051.

[4] Mesylate **8** is a known compound, see ref 2: G. Bhargava, B. Trillo, M. Araya, F. López, L. Castedo, J. M. Mascareñas, *Chem. Commun*. **2010**, *46*, 270.

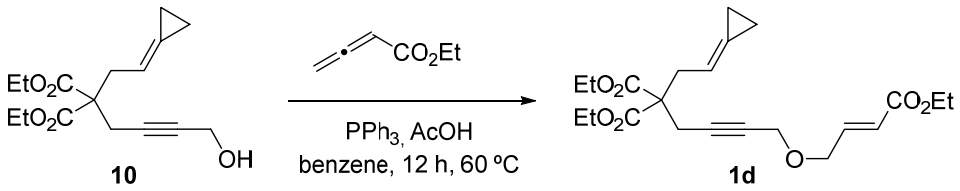
(CH), 128.7 (C), 127.9 (CH), 125.8 (CH), 112.3 (CH), 79.3 (C), 76.9 (C), 61.8 (CH_2), 60.3 (CH_2), 56.1 (C), 47.5 (CH_2), 35.7 (CH_2), 34.5 (CH_2), 22.8 (CH_2), 21.1 (CH_3), 13.8 (CH_3), 13.6 (CH_3), 2.1 (CH_2), 1.4 (CH_2); **LRMS** (EI): 582 ([M^+ + Na]); **HRMS** calculated for $C_{29}H_{37}NO_8S$ 559.2248, found 559.2240.

Triethyl (*E*)-8-(2-cyclopropylideneethoxy)oct-1-en-6-yne-1,4,4-tricarboxylate (1c).[5]



Colorless oil. 48% yield. **^{1}H RMN** (300 MHz, $CDCl_3$) δ 6.75 (dt, ***J*** = 15.5, 7.8 Hz, 1H), 5.95 – 5.83 (m, 2H), 4.26 – 3.99 (m, 10H), 2.91 (dd, ***J*** = 7.8, 1.3 Hz, 2H), 2.83 (t, ***J*** = 2.1 Hz, 2H), 1.29 – 1.14 (m, 9H), 1.08 (s, 4H); **^{13}C RMN** (75 MHz, $CDCl_3$) δ 169.7 (C), 166.2 (C), 142.2 (CH), 128.0 (C), 125.8 (CH), 114.2 (CH), 80.3 (C), 79.9 (C), 69.4 (CH_2), 60.2 (CH_2), 56.8 (CH_2), 56.3 (C), 34.6 (CH_2), 23.0 (CH_2), 13.7 (CH_3), 13.6 (CH_3), 1.8 (CH_2), 1.2 (CH_2); **EMBR** (ESI): 429 ([M^++Na]); **EMAR** calculated for $C_{22}H_{30}NaO_7$ 429.1884 found 429.1883.

(*E*)-Diethyl 2-(2-cyclopropylideneethyl)-2-(4-((4-ethoxy-4-oxobut-2-en-1-yl)oxy)but-2-yn-1-yl)malonate (**1d**)



To a solution of diethyl 2-(2-cyclopropylideneethyl)-2-(4-hydroxybut-2-yn-1-yl)malonate (**10**)[6] (480 mg, 1.60 mmol), ethyl 2,3-butadienoate (0.38 mL, 3.3 mmol) and PPh_3 (21 mg, 0.08 mmol) in benzene (8 mL) was added acetic acid (19 µL, 0.33 mmol). The reaction mixture was heated for 12 h at 60 °C.[7] After completion of the reaction, the mixture was cooled to rt, concentrated and the crude residue was purified by flash chromatography (5 % Et_2O / hexanes) to yield **1d** as a colourless oil (445 mg, 67 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.98 – 6.80 (m, 1H), 6.12 – 5.93 (m,

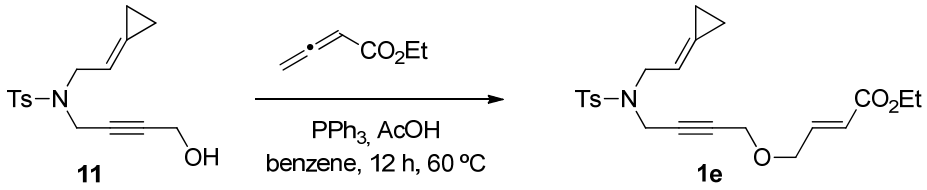
[5] Pepared from triethyl (E)-8-hydroxyoct-1-en-6-yne-1,4,4-tricarboxylate and 1-vinylcyclopropyl 4-methylbenzenesulfonate, according to the procedure described in G. Bhargava, B. Trillo, M. Araya, F. López, L. Castedo, J. M. Mascareñas, *Chem. Commun*. **2010**, *46*, 270.

[6] A. Delgado, J. R. Rodríguez, L. Castedo, J. L. Mascareñas, *J. Am. Chem. Soc.* **2003**, *125*, 9282-9283.

[7] C. Zhang, X. Lu, *Synlett*, **1995**, 645.

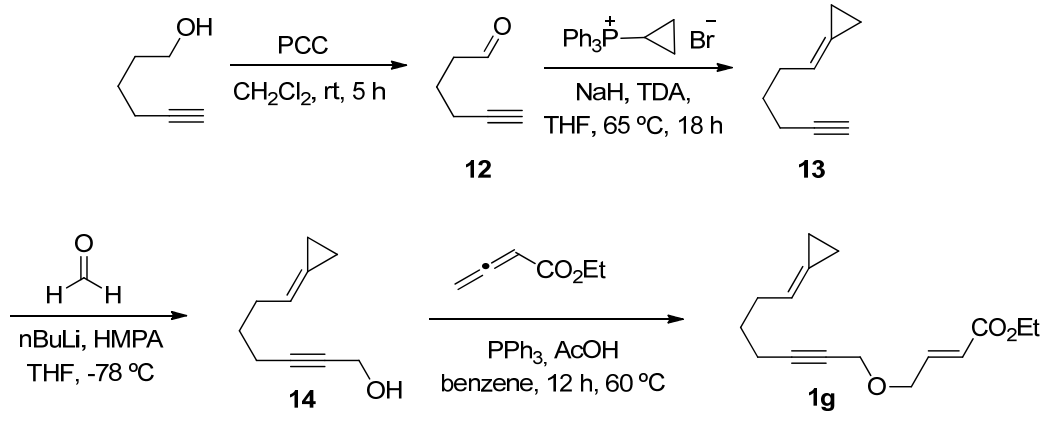
1H), 5.62 – 5.47 (m, 1H), 4.20 – 4.05 (m, 10H), 2.91 – 2.82 (m, 2H), 2.82 – 2.57 (m, 2H), 1.34 – 1.11 (m, 9H), 1.01 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.8 (C), 166.0 (C), 143.4 (CH), 127.1 (C), 121.6 (CH), 111.3 (CH), 82.2 (C), 78.1 (C), 67.5 (CH_2), 61.4 (CH_2), 60.2 (CH_2), 58.0 (CH_2), 56.9 (C), 34.6 (CH_2), 22.8 (CH_2), 14.1 (CH_3), 14.0 (CH_3), 13.9 (CH_3), 2.8 (CH_2), 1.8 (CH_2); **LRMS** (CI) 406 ([M^+ + 1], 3), 333 (55), 287 (78), 129 (100); **HRMS** calculated for $C_{22}H_{30}NaO_7$ 429.1879, found 429.1884.

(*E*)-Ethyl 4-((4-(N-(2-cyclopropylideneethyl)-4-methylphenyl-sulfonamido)but-2-yn-1-yl)oxy)but-2-enoate (**1e**)



Prepared according to the above-described procedure for the synthesis of **1d.** White solid. 69 % yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.71 (d, ***J*** = 8.3 Hz, 2H), 7.27 (d, ***J*** = 8.4 Hz, 2H), 6.84 (dt, ***J*** = 15.8, 5.0 Hz, 1H), 5.98 (dd, ***J*** = 15.8, 2.6 Hz, 1H), 5.74 – 5.60 (m, 1H), 4.18 (q, ***J*** = 7.1 Hz, 2H), 4.08 (s, 2H), 3.97 – 3.88 (m, 6H), 2.39 (s, 3H), 1.26 (dt, ***J*** = 6.6, 6.0 Hz, 3H), 1.05 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.5 (C), 143.7 (C), 143.5 (CH), 136.5 (C), 129.6 (CH), 128.9 (C), 127.9 (CH), 121.8 (CH), 112.0 (CH), 80.4 (C), 79.8 (C), 67.7 (CH_2), 60.2 (CH_2), 57.6 (CH_2), 47.7 (CH_2), 35.6 (CH_2), 21.0 (CH_3), 13.8 (CH_3), 2.1 (CH_2), 1.4 (CH_2); **LRMS** (ESI) 440 ([M^++Na]); **HRMS** calculated for $C_{22}H_{27}NNaO_5S$ 440.1502, found 440.1501.

(E)-Ethyl 4-((7-cyclopropylidenehept-2-yn-1-yl)oxy)but-2-enoate (1g)



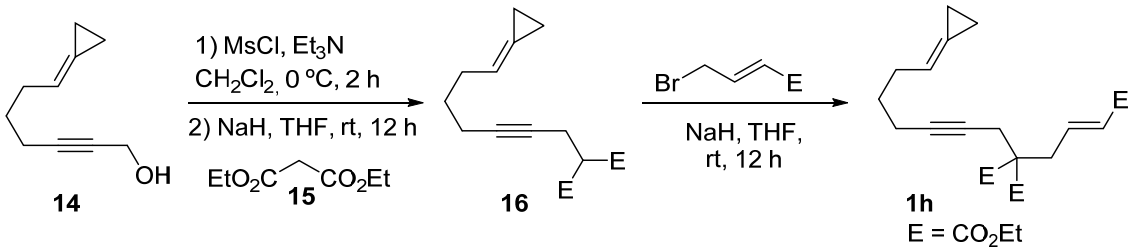
To a solution of 5-hexyn-1-ol (5 g, 50.9 mmol) in CH_2Cl_2 (100 mL) was added PCC (11.5 g, 53.5 mmol). The reaction mixture was stirred for 5 h at rt. After completion of the reaction, the mixture was filtered through celite. The filtrate was concentrated and purified by flash chromatography (30 % Et_2O / hexanes) to afford 2.4 g of **12**, as colourless oil (50 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.79 (s, ***J*** = 1.0 Hz, 1H), 2.60 (td, ***J*** = 7.2, 1.1 Hz, 2H), 2.26 (td, ***J*** = 6.9, 2.6 Hz, 2H), 1.97 (t, ***J*** = 2.6 Hz, 1H), 1.84 (p, ***J*** = 7.0 Hz, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 201.5 (CH), 83.0 (C), 69.2 (CH), 42.3 (CH_2), 20.7 (CH_2), 17.6 (CH_2); **HRMS** calculated for C_6H_9O 97.0648, found 97.0652.

To a solution of cyclopropyltriphenylphosphonium bromide (10.4 g, 27.0 mmol) and NaH (1.3 g, 31.2 mmol) in THF (105 mL) was added the compound **13** (2.0 g, 20.8 mmol) and tris[2-(2-methoxyethoxy)ethyl]amine (TDA) (3.4 mL, 10.4 mmol). The resulting mixture was heated for 6h at 65 °C. After completion of the reaction, the mixture was cooled to rt, pentane was added (40 mL) and the mixture was filtered through a pad of celite and concentrated in vacuo. The crude residue was purified by flash chromatography (hexanes) to afford 1.55 g of **13** as a colourless oil (62 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.78 – 5.68 (m, 1H), 2.33 – 2.23 (m, 2H), 2.19 (td, ***J*** = 7.2, 2.6 Hz, 2H), 1.94 (t, ***J*** = 2.6 Hz, 1H), 1.69 (p, ***J*** = 7.3 Hz, 2H), 1.03 (dd, ***J*** = 3.3, 1.6 Hz, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 122.1 (C), 117.0 (CH), 84.5 (C), 68.1 (CH), 30.8 (CH_2), 28.1 (CH_2), 17.9 (CH_2), 2.1 (CH_2), 1.9 (CH_2); **LRMS** (CI) 119 ([M^+ +1], 10), 105 (56), 91 (100), 79 (95).

^{n}BuLi (4.5 mL, 2.5 M) was added dropwise to a solution of **13** (1 g, 8.3 mmol) in THF (16 mL) at -78 °C. The resulting solution was stirred for 30 minutes at the same temperature before HMPA (1.61 mL, 9.1 mmol) and ***p***-formaldehyde (790 mg, 25.0 mmol) at 0°C. The reaction mixture was stirred for 2 h at rt and then, the reaction was poured into NH_4Cl sat 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 (20 % Et_2O / hexanes) to provide 812 mg of **14** as a colourless oil (65 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.78 – 5.64 (m, 1H), 4.25 (s, 2H), 2.31 – 2.15 (m, 4H), 1.74 – 1.62 (m, 2H), 1.27 – 1.17 (m, 2H), 1.05 – 1.00 (m, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 117.7 (C), 114.3 (CH), 82.1 (C), 79.9 (C), 51.6 (CH_2), 27.9 (CH_2), 27.5 (CH_2), 19.2 (CH_2), 3.9 (CH_2), 2.4 (CH_2); **LRMS**: 149 ([M^+ +1], 2), 117 (32), 91 (100), 79 (94).

(E)-Ethyl 4-((7-cyclopropylidenehept-2-yn-1-yl)oxy)but-2-enoate (**1g**) was prepared according to the previously described general procedure for the synthesis of compounds **1d-e** using alcohol **14** as starting material. Purification by flash chromatography (5 % Et_2O / hexanes) provided **1g** as a colourless oil (68 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.95 (dt, ***J*** = 15.8, 4.5 Hz, 1H), 6.12 – 6.03 (d, ***J*** = 15.7 Hz, 1H), 5.79 – 5.68 (m, 1H), 4.24 – 4.14 (m, 6H), 2.33 – 2.14 (m, 4H), 1.73 – 1.56 (m, 2H), 1.28 (t, ***J*** = 7.1 Hz, 3H), 1.02 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.7 (C), 144.0 (CH), 122.3 (C), 121.9 (CH), 117.3 (CH), 87.6 (C), 75.4 (C), 67.8 (CH_2), 60.3 (CH_2), 58.4 (CH_2), 30.6 (CH_2), 27.9 (CH_2), 17.9 (CH_2), 13.8 (CH_3), 1.7 (CH_2), 1.4 (CH_2); **LRMS** (EI) 262 ([M^+], 32), 131 (78), 117 (65), 105 (96), 91 (100); **HRMS** calculated for $C_{16}H_{22}NaO_3$ 285.1461, found 285.1459.

(E)-Triethyl 11-cyclopropylideneundec-1-en-6-yne-1,4,4-tricarboxylate (1h)



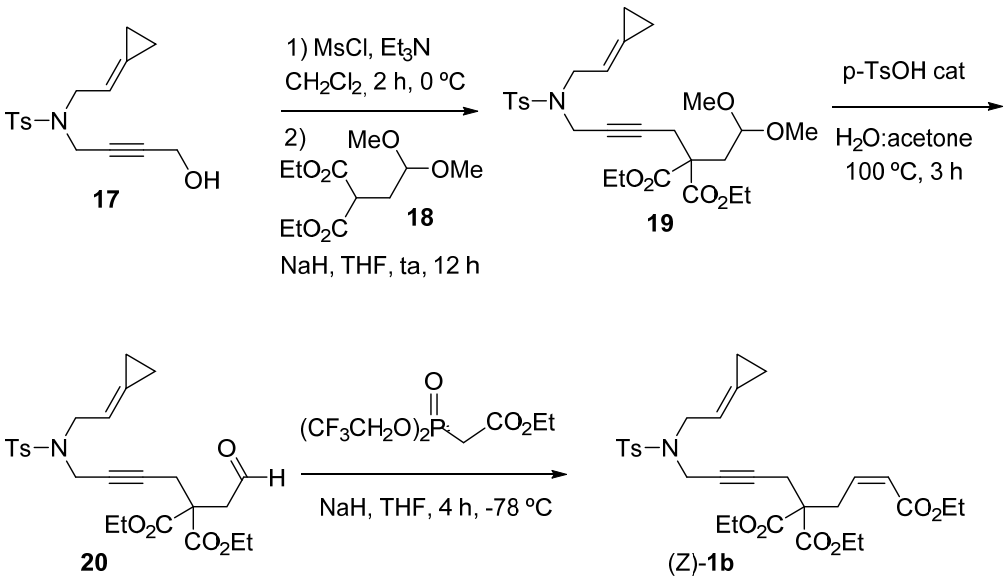
Diethyl malonate (1.7 mL, 11.6 mmol) was added dropwise to a suspension of NaH (464 mg, 11.6 mmol) in THF (12 mL) at rt. After stirring for 30 min, a solution of the mesylate of **14**[8] in THF (5 mL) was slowly added. The reaction mixture was stirred for 12 h at rt, poured into water and extracted with Et_2O (3 x 20 mL). The organic phases were dried, filtered and concentrated to give a crude oil residue which was purified by flash chromatography (2 % Et_2O / hexanes) to give 500 mg of the product **16** as colourless oil (74 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.77 – 5.65 (m, 1H), 4.28 – 4.13 (m, 4H), 3.51 (t, ***J*** = 7.8 Hz, 1H), 2.74 (dt, ***J*** = 7.7, 2.4 Hz, 2H), 2.23 (dd, ***J*** = 14.2, 7.2 Hz, 2H), 2.12 (dt, ***J*** = 7.0, 2.3 Hz, 2H), 1.68 – 1.50 (m, 2H), 1.33 – 1.20 (m, 6H), 1.01 (s, ***J*** = 1.5 Hz, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.7 (C), 117.4 (CH), 114.0 (C), 82.4 (C), 75.7 (C), 61.5 (CH_2), 51.7 (CH), 30.5 (CH_2), 28.1 (CH_2), 18.5 (CH_2), 17.8 (CH_2), 13.7 (CH_3), 1.7 (CH_2), 1.4 (CH_2); **LRMS** (ESI) 315

[8] The mesylate was prepared from the corresponding alcohol **15** with methanesulfonyl chloride and Et_3N in CH_2Cl_2 at 0 ° C after 2 h.

([M^++Na]); **HRMS** calculated for $C_{17}H_{24}NaO_4$ 315.1567, found 315.1568.

A solution of **16** in THF (9 mL) was added in small portions to. NaH (75 mg, 1.8 mmol). The resulting solution was stirred at rt for 30 minutes and the ethyl 4-bromocrotonate (429 mg, 2.2 mmol) was added. After stirring for 12 h, 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 415 mg of **1h** a colourless oil (60 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.78 (ddd, ***J*** = 15.6, 8.4, 7.2 Hz, 1H), 5.91 (dd, ***J*** = 15.5, 1.2 Hz, 1H), 5.80 – 5.61 (m, 1H), 4.31 – 4.05 (m, 6H), 2.92 (d, ***J*** = 7.8 Hz, 2H), 2.76 (s, 2H), 2.18 (dd, ***J*** = 13.8, 6.9 Hz, 4H), 1.72 – 1.50 (m, 2H), 1.36 – 1.17 (m, 9H), 1.01 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.5 (C), 165.8 (C), 142.3 (CH), 125.4 (CH), 121.9 (C), 117.2 (CH), 84.1 (C), 73.9 (C), 61.7 (CH_2), 60.3 (CH_2), 56.8 (C), 34.9 (CH_2), 30.9 (CH_2), 28.5 (CH_2), 23.4 (CH_2), 18.2 (CH_2), 14.2 (CH_3), 14.0 (CH_3), 2.1 (CH_2), 1.9 (CH_2); **LRMS** (ESI) 427 ([M^++Na]); **HRMS** calculated for $C_{23}H_{32}NaO_8$ 427.2091, found 427.2092.

(*Z*)-Triethyl 8-(N-(2-cyclopropylideneethyl)-4-methylphenylsulfonamido)oct-1-en-6-yne-1,4,4-tricarboxylate (Z)-1b



A solution of **18**[9] (790 mg, 3.2 mmol) in THF (9 mL) was added in small portions to NaH (128 mg, 3.2 mmol). The resulting solution was stirred at rt for 30 minutes and the mesylate of alcohol **17** (815 mg, 2.1 mmol) was added. After stirring for 12 h, the solvent was evaporated and the residue was poured into water and

[9] For the synthesis of **18,** see: N. Vignola, B. List, *J. Am. Chem. Soc*. **2004**, *136*, 450

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 (10 % Et_2O / hexanes) to yield 638 mg of **19** as colourless oil (56 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 (d, ***J*** = 8.3 Hz, 2H), 7.31 (d, ***J*** = 8.0 Hz, 2H), 5.73 – 5.61 (m, 1H), 4.35 – 4.27 (m, 1H), 4.20 – 4.09 (m, 4H), 4.02 (t, ***J*** = 2.0 Hz, 2H), 3.92 (d, ***J*** = 6.7 Hz, 2H), 3.26 (s, 6H), 2.65 (t, ***J*** = 2.1 Hz, 2H), 2.44 (s, 3H), 2.24 (d, ***J*** = 5.7 Hz, 2H), 1.35 – 1.16 (m, 9H), 1.08 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.2 (C), 143.6 (C), 136.8 (C), 129.7 (CH), 128.6 (C), 127.8 (CH), 112.2 (CH), 101.9 (CH), 79.9 (C), 76.4 (C), 61.4 (CH_2), 54.1 (C), 53.2 (CH_2), 47.4 (CH_2), 35.7 (CH_2), 34.8 (CH_2), 23.16 (CH_3), 21.11 (CH_3), 13.5 (CH_3), 2.1 (CH_2), 1.3 (CH_2); **LRMS** (ESI) 558 ([M^++Na]), 504; **LRMS** calculated for $C_{27}H_{37}NNaO_8S$ 558.2132, found 558.2117.

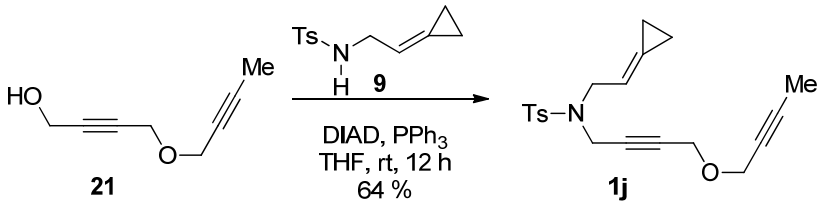
p-Toluensulfonic acid (38 mg, 0.2 mmol) was added to a solution of **19** (600 mg, 1.1 mmol) in a mixture H_2O:acetone (1:1, 5 mL). The resulting mixture was heated at reflux temperature for 1h. The mixture was cooled to rt, the solvent was removed and the residue was extracted with Et_2O (3 x 5 mL). The organic phases were dried and evaporated to give a crude residue which was purified by flash chromatography (10 % Et_2O / hexanes) to yield 488 mg of **20** as colourless oil (89 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.70 (d, ***J*** = 8.4 Hz, 2H), 7.29 (d, ***J*** = 8.4 Hz, 2H), 5.74 – 5.56 (m, 1H), 4.17 (q, ***J*** = 7.1 Hz, 4H), 4.00 (t, ***J*** = 2.0 Hz, 2H), 3.91 (d, ***J*** = 7.0 Hz, 2H), 2.98 (d, ***J*** = 0.9 Hz, 2H), 2.74 (t, ***J*** = 2.0 Hz, 2H), 2.43 (s, 3H), 1.22 (t, ***J*** = 7.1 Hz, 6H), 1.07 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.0 (CH), 169.2 (C), 143.8 (C), 136.8 (C), 129.7 (CH), 128.7 (C), 127.9 (CH), 112.2 (CH), 79.6 (C), 77.1 (C), 62.1 (CH_2), 53.6 (C), 47.5 (CH_2), 45.5 (CH_2), 35.7 (CH_2), 23.5 (CH_2), 21.1 (CH_3), 13.5 (CH_3), 2.1 (CH_2), 1.4 (CH_2); **LRMS** (ESI) 512 ([M^++Na]); **HRMS** calculated for $C_{25}H_{31}NNaO_7S$ 512.1713, found 512.1713.

A solution of the aldehyde **20** (100 mg, 0.2 mmol) in THF (2 mL) was added to NaH (16.3 mg, 0.4 mmol) at 0° C. The mixture was stirred for 1h. Then, a solution of ethyl 2-bis (2,2,2-trifluoroethoxy)phosphoryl)acetate[10] (102 mg, 0.3 mmol)in THF (1 mL) was added at -78 °C and the resulting mixture was stirred for 3h at the same temperature. The reaction was poured into $NH_4Cl_{(sat)}$ solution and extracted with Et_2O (3 x 5 mL). The organic phases were dried and evaporated to give a crude residue

[10] a) W. C. Still, C. Gennari, ***Tetrahedron Lett***. **1983**, ***24***, 4405. b) G. Reddipalli, H. M. Venkataia, N. W. Fadnauis, ***Tetrahedron: Asymmetry*** **2010**, ***21***, 320

which was purified by flash chromatography (10 % Et_2O / hexanes) to provide 75 mg of (*Z*)-**1b** as colourless oil (65 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.71 (d, ***J*** = 8.4 Hz, 2H), 7.29 (d, ***J*** = 8.4 Hz, 2H), 6.08 (dt, ***J*** = 11.6, 7.2 Hz, 1H), 5.83 (dt, ***J*** = 11.6, 1.7 Hz, 1H), 5.68 (dd, ***J*** = 8.8, 4.5 Hz, 1H), 4.21 – 4.09 (m, 6H), 4.01 (t, ***J*** = 2.0 Hz, 2H), 3.91 (d, ***J*** = 6.9 Hz, 2H), 3.25 (dd, ***J*** = 7.2, 1.7 Hz, 2H), 2.59 (t, ***J*** = 2.0 Hz, 2H), 2.42 (s, 3H), 1.31 – 1.17 (m, 9H), 1.08 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.0 (C), 165. 7 (C), 143.6 (C), 143.2 (CH), 136.9 (C), 129.7 (CH), 128.8 (C), 127.9 (CH), 122.7 (CH), 112.2 (CH), 79.6 (C), 77.4 (C), 61.6 (CH_2), 59.9 (CH_2), 56.2 (C), 47.5 (CH_2), 35.7 (CH_2), 31.5 (CH_2), 23.7 (CH_2), 21.2 (CH_3), 13.9 (CH_3), 13.6 (CH_3), 2.1 (CH_2), 1.4 (CH_2); **LRMS** (ESI) 582 ([M^++Na]), 514, 442, 355; **HRMS** calculated for $C_{29}H_{37}NNaO_8S$ 582.2132, found 582.2122.

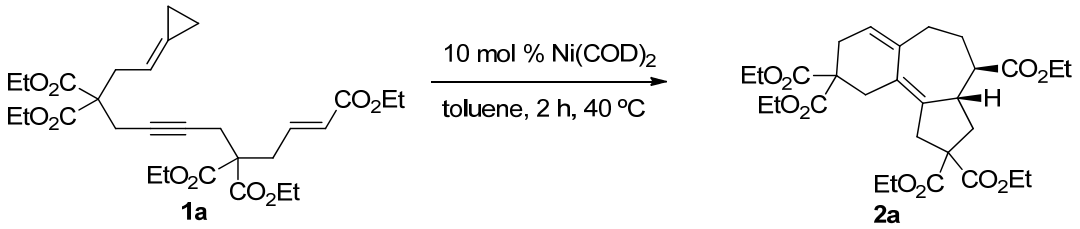
N-(4-(but-2-yn-1-yloxy)but-2-yn-1-yl)-N-(2-cyclopropylidene-ethyl)-4-methylbenzenesulfonamide (1j)



PPh_3 (384 mg, 1.46 mmol) and alcohol **21**[11] (150 mg, 1.09 mmol) were added to a solution of ***N***-(2-cyclopropylideneethyl)-4-methylbenzenesulfonamide (**9**, 296 mg, 1.26 mmol) in THF (11 mL). The mixture was cooled to 0 °C and diisopropyl azodicarboxylate (DIAD) (288 µL, 1.46 mmol) was added dropwise. The reaction was stirred for 12 h at rt, poured into water and extracted with Et_2O (3 x 10 mL). The organic phases were dried, filtered and concentrated to give a crude oil residue that was purified by flash chromatography (20% Et_2O/hexanes) to give 248 mg of the product **1j** as yellow oil (64 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.72 (d, ***J*** = 8.3 Hz, 2H), 7.29 (d, ***J*** = 8.0 Hz, 2H), 5.74 – 5.62 (m, 1H), 4.09 (t, ***J*** = 1.9 Hz, 2H), 3.98 – 3.89 (m, 6H), 2.41 (s, 3H), 1.84 (t, ***J*** = 2.3 Hz, 3H), 1.07 (s, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.7 (C), 136.4 (C), 129.6 (CH), 128.9 (C), 127.9 (CH), 112.1 (CH), 83.0 (C), 80.6 (C), 79.5 (C), 74.1 (C), 56.7 (CH_2), 56.0 (CH_2), 47.7 (CH_2), 35.7 (CH_2), 21.1 (CH_3), 3.1 (CH_3), 2.1 (CH_2), 1.4 (CH_2); **LRMS** (ESI) 380 ([M^++Na]); **HRMS** calculated for $C_{20}H_{23}NNaO_3S$ 380.1291, found 380.1292.

[11] For the synthesis of **21**, see: S. Brässe, H. Wertal, D. Frank, D. Vidovic, A. de Meijere, *Eur. J. Org. Chem.* **2005**, 4167.

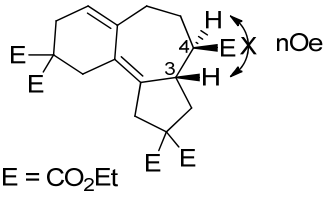
General Procedure for the Ni-catalyzed [3+2+2] Cycloaddition Reaction, exemplified for the cycloaddition of **1a** (Table 1, entry 2, main manuscript).



$Ni(COD)_2$ (5.0 mg, 0.018 mmol) was placed on a dry sealed tube under argon. Then, a solution of compound **1a** (100 mg, 0.18 mmol) in toluene (0.9 mL) was added. The reaction mixture was heated for 2 h at 40 °C,[12] allowed to cool down to *rt* and filtered through a short pad of a mixture of florisil and silica gel, eluting with Et_2O. The filtrate was concentrated and purified by flash chromatography on silica gel (10 % Et_2O / hexanes) to afford 83 mg of the product **2a** as colorless oil (83 % yield).

(3aS*,4R*)-Pentaethyl 3a,4,5,6-tetrahydrobenzo[e]azulene-2,2,4,9,9(1H,3H,8H,10H)-pentacarboxylate (2a)

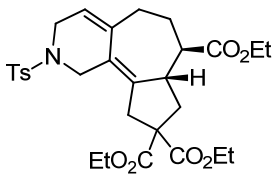
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (s, 1H), 4.31 – 3.99 (m, 10H), 3.18 – 3.08 (m, 2H), 3.05 – 2.92 (m, 1H), 2.89 (d, *J* = 14.0 Hz, 1H), 2.85 – 2.73 (m, 1H), 2.60 – 2.40 (m, 5H), 2.27 – 2.13 (m, 1H), 1.94 – 1.78 (m, 3H), 1.32 – 1.18 (m, 15H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.4 (C), 172.0 (C), 171.9 (C), 171.8 (C), 170.9 (C), 139.9 (C), 136.5 (C), 127.8 (C), 122.2 (CH), 61.4 (CH_2), 61.3 (CH_2), 61.3 (CH_2), 60.2 (CH_2), 57.8 (C), 53.7 (C), 49.5 (CH), 41.8 (CH), 39.5 (CH_2), 39.1 (CH_2), 33.5 (CH_2), 32.5 (CH_2), 31.2 (CH_2), 30.3 (CH_2), 13.8 (CH_3), 13.7 (CH_3), 13.6 (CH_3); **LRMS** (EI) 548 ([M^+], 12), 473 (14), 401 (32), 327 (45), 253 (76), 91 (100); **HRMS** calculated for $C_{29}H_{40}O_{10}$ 548.2621, found 548.2615.



The structure and stereochemical assignments of **2a** were determined on the basis of 2D-NMR experiments (COSY, NOESY, HMBC and HMQC or HSQC), in addition to standard ^{1}H, ^{13}C and DEPT and nOe experiments. ***Stereochemistry of* 2a:** The absence of nOe between H_3 and H_4 suggests that we have the isomer that retains the *trans* stereochemistry of the parent alkene. This was further demonstrated by X-ray analysis of an analog (vide infra).

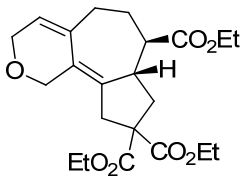
[12] The time and temperature required for any particular cycloaddition are indicated in the main manuscript.

(7R*,7aS*)-Triethyl 2-tosyl-2,3,6,7,7a,8-hexahydroazuleno[4,5-c]pyridine-7,9,9(1H,5H,10H)-tricarboxylate (2b)



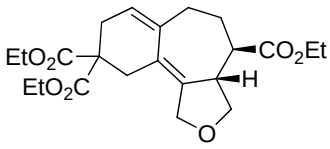
White solid. 67 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, ***J*** = 8.2 Hz, 2H), 7.27 (t, ***J*** = 6.0 Hz, 2H), 5.29 (s, 1H), 4.27 – 4.03 (m, 8H), 3.67 (d, ***J*** = 18.4 Hz, 1H), 3.46 (d, ***J*** = 14.1 Hz, 1H), 3.08 (d, ***J*** = 17.7 Hz, 1H), 3.00 (dd, ***J*** = 18.3, 9.6 Hz, 1H), 2.86 (d, ***J*** = 17.8 Hz, 1H), 2.49 – 2.39 (m, 4H), 2.23 – 2.14 (m, 1H), 2.14 – 2.06 (m, 1H), 1.85 – 1.73 (m, 2H), 1.73 – 1.55 (m, 2H), 1.31 – 1.21 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.8 (C), 172.2 (C), 172.1 (C), 144.5 (C), 140.5 (C), 136.6 (C), 136.0 (C), 130.4 (CH), 128.2 (CH), 125.7 (C), 120.0 (CH), 62.2 (CH_2), 62.1 (CH_2), 60.8 (CH_2), 58.4 (C), 49.1 (CH), 46.3 (CH_2), 45.7 (CH_2), 42.1 (CH), 39.4 (CH_2), 39.1 (CH_2), 33.0 (CH_2), 30.2 (CH_2), 21.6 (CH_3), 14.4 (CH_3), 14.1 (CH_3), 14.0 (CH_3); **LRMS** (CI) 560 ([M^+], 70), 514 (35), 404 (100), 330 (38), 256 (24), 125 (42); **HRMS** calculated for $C_{29}H_{38}NO_8S$ 560.2318, found 560.2327.

(7R,*7aS*)-Triethyl 6,7,7a,8-tetrahydro-1H-azuleno[4,5-c]pyran-7,9,9(3H,5H,10H)-tricarboxylate (2c)



Colourless oil. 54 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.48 (s, 1H), 4.30 – 4.01 (m, 10H), 3.27 – 3.14 (m, 1H), 2.99 – 2.83 (m, 2H), 2.72 – 2.57 (m, 2H), 2.54 (ddd, ***J*** = 12.7, 7.4, 1.8 Hz, 1H), 2.29 – 2.15 (m, 1H), 1.99 – 1.81 (m, 3H), 1.34 – 1.16 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.7 (C), 171.8 (C), 171.7 (C), 137.1 (C), 135.1 (C), 127.8 (C), 122.6 (CH), 66.4 (CH_2), 65.7 (CH_2), 61.5 (CH_2), 60.3 (CH_2), 58.3 (C), 49.4 (CH), 41.8 (CH), 38.8 (CH_2), 38.3 (CH_2), 32.4 (CH_2), 29.7 (CH_2), 13.8 (CH_3), 13.6 (CH_3); **LRMS** (ESI) 429 ([M^++Na]); **HRMS** calculated for $C_{22}H_{30}NaO_7$ 429.1884, found 429.1894.

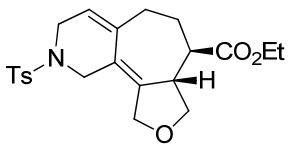
(3aS,4R)-Triethyl 3a,4,5,6-tetrahydro-1H-benzo[3,4]cyclohepta-[1,2-c]furan-4,9,9(3H,8H,10H)-tricarboxylate (2d)



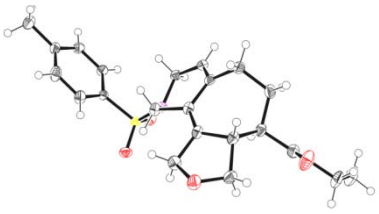
Colourless oil. 85 % yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.47 (t, J = 3.6 Hz, 1H), 4.49 (d, ***J*** = 14.1 Hz, 2H), 4.40 (d, ***J*** = 14.1 Hz, 2H), 4.22 – 4.03 (m, 7H), 3.35 – 3.21 (m, 2H), 2.72 (dd, ***J*** = 17.9, 4.1 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.55 – 2.46 (m, 3H), 2.22 (dt, ***J*** = 14.2, 4.1 Hz, 1H), 1.96 – 1.83 (m, 2H), 1.25 – 1.18 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.3 (C),

171.6 (C), 171.02 (C), 139.6 (C), 136.4 (C), 125.2 (C), 122.7 (CH), 73.5 (CH_2), 71.5 (CH_2), 61.4 (CH_2), 61.3 (CH_2), 60.3 (CH_2), 53.5 (C), 47.0 (CH), 42.6 (CH), 33.1 (CH_2), 32.4 (CH_2), 31.0 (CH_2), 30.0 (CH_2), 13.8 (CH_3), 13.6 (CH_3); **LRMS** (EI) 406 (3), 332 (12), 259 (32), 185 (50), 157 (65), 129 (90), 91 (100); **HRMS** calculated for $C_{22}H_{30}O_7$ 406.1992, found 406.1983.

(3aS*,4R*)-Ethyl 9-tosyl-3,3a,4,5,6,8,9,10-octahydro-1H-furo[3',4':6,7]cyclohepta[1,2-c]pyridine-4-carboxylate (2e)

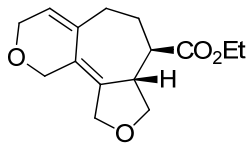


White solid. 74 % yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 (d, ***J*** = 8.3 Hz, 1H), 7.28 (d, ***J*** = 8.4 Hz, 1H), 5.37 (s, 1H), 4.50 – 4.33 (m, 2H), 4.18 – 3.99 (m, 4H), 3.91 (d, ***J*** = 14.3 Hz, 1H), 3.74 (d, ***J*** = 17.5 Hz, 1H), 3.47 (dd, ***J*** = 10.9, 3.4 Hz, 1H), 3.32 – 3.21 (m, 1H), 3.15 (dd, ***J*** = 17.5, 8.5 Hz, 1H), 2.55 – 2.43 (m, 1H), 2.41 (s, 3H), 2.25 (dt, ***J*** = 10.6, 8.5 Hz, 1H), 2.15 (dt, ***J*** = 14.3, 4.1 Hz, 1H), 1.88 – 1.65 (m, 2H), 1.25 (t, ***J*** = 7.1 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.1 (C), 144.1 (C), 139.7 (C), 135.9 (C), 135.5 (C), 129.8 (CH), 127.8 (CH), 122.8 (C), 120.1 (CH), 73.1 (CH_2), 70.8 (CH_2), 60.5 (CH_2), 46.2 (CH), 45.1 (CH_2), 42.7 (CH), 32.3 (CH_2), 29.6 (CH_2), 21.1 (CH_3), 13.8 (CH_3); **LRMS** (CI) 418 (36), 400 (33), 276 (19), 262 (100), 186 (18), 91 (21); **HRMS** calculated for $C_{22}H_{28}NO_5S$ 418.1688, found 418.1670.



The structure of this cycloadduct was confirmed by X-ray diffraction structure.[13]

(3aS*,4R*)-Ethyl 1,3,3a,4,5,6,8,10-octahydrofuro[3',4':6,7]cyclo-hepta[1,2-c]pyran-4-carboxylate (2f)

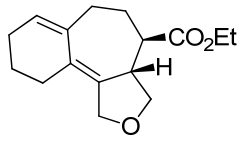


Colourless oil. 53 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.55 (s, 1H), 4.44 – 4.32 (m, 2H), 4.21 – 4.17 (m, 3H), 4.16 – 4.06 (m, 3H), 4.05 – 3.95 (m, 1H), 3.43 – 3.32 (m, 2H), 2.77 – 2.65 (m, 2H), 2.29 (dt, ***J*** = 13.9, 4.0 Hz, 1H), 2.05 – 1.93 (m, 2H), 1.25 (t, ***J*** = 7.1 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.4 (C), 136.9 (C), 134.9 (C), 125.4 (C), 123.2 (CH), 73.2 (CH_2), 70.3 (CH_2), 65.7 (CH_2), 65.6 (CH_2), 60.5 (CH_2), 46.9 (CH), 42.7 (CH), 32.2

[13] CCDC 986511 (**2e**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

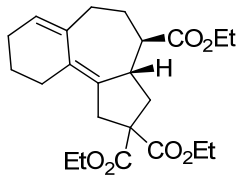
(CH_2), 29.5 (CH_2), 13.8 (CH_3); **LRMS** (EI) 264 ([M^+], 1), 246 (32), 191 (23), 173 (78), 91 (100); **HRMS** calculated for $C_{15}H_{20}O_4$ 264.1362, found 264.1368.

(3aS*,4R*)-Ethyl 3,3a,4,5,6,8,9,10-octahydro-1H-benzo[3,4]cyclohepta[1,2-c]furan-4-carboxylate (2g)



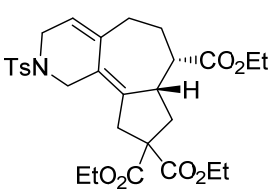
Colourless oil. 63% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.53 (t, ***J*** = 3.7 Hz, 1H), 4.42 (d, ***J*** = 13.8 Hz, 1H), 4.34 (d, ***J*** = 13.8 Hz, 1H), 4.16 (t, ***J*** = 7.9 Hz, 1H), 4.10 (q, ***J*** = 7.1 Hz, 2H), 3.38 (t, ***J*** = 8.7 Hz, 1H), 3.29 (dd, ***J*** = 17.6, 8.8 Hz, 1H), 2.70 – 2.58 (m, 2H), 2.20 (dt, ***J*** = 14.2, 4.1 Hz, 1H), 2.11 – 1.98 (m, 4H), 1.98 – 1.85 (m, 2H), 1.75 – 1.64 (m, 1H), 1.64 – 1.53 (m, 1H), 1.25 – 1.20 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.6 (C), 136.7 (C), 135.6 (C), 129.2 (C), 126.4 (CH), 73.5 (CH_2), 71.5 (CH_2), 60.2 (CH_2), 47.2 (CH), 42.4 (CH), 33.0 (CH_2), 30.2 (CH_2), 28.1 (CH_2), 25.3 (CH_2), 22.0 (CH_2), 13.8 (CH_3); **LRMS** (ESI) 285 ([M^++Na]); **HRMS** calculated for $C_{16}H_{22}NaO_3$ 285.1461, found 285.1459.

(3aS*,4R*)-Triethyl 3a,4,5,6,9,10-hexahydrobenzo[e]azulene-2,2,4(1H,3H,8H)-tricarboxylate (2h)



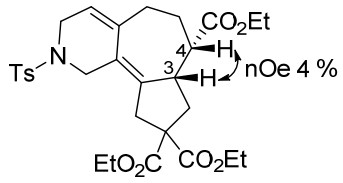
Colourless oil. 80 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.45 (t, ***J*** = 3.8 Hz, 1H), 4.20 – 4.13 (m, 4H), 4.13 – 4.07 (m, 2H), 3.17 – 3.07 (m, 1H), 3.07 – 2.98 (m, 1H), 2.85 (d, ***J*** = 17.6 Hz, 1H), 2.63 – 2.52 (m, 2H), 2.52 – 2.45 (m, 1H), 2.25 – 2.18 (m, 1H), 2.16 – 2.10 (m, 1H), 2.09 – 1.96 (m, 3H), 1.92 – 1.79 (m, 3H), 1.72 – 1.64 (m, 1H), 1.58 – 1.48 (m, 1H), 1.28 – 1.18 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.8 (C), 172.2 (C), 171.9 (C), 136.8 (C), 135.7 (C), 131.8 (C), 125.9 (CH), 61.3 (CH_2), 60.1 (CH_2), 57.9 (C), 49.6 (CH), 41.6 (CH), 39.5 (CH_2), 39.1 (CH_2), 33.2 (CH_2), 30.5 (CH_2), 28.6 (CH_2), 25.5 (CH_2), 22.2 (CH_2), 13.8 (CH_3), 13.6 (CH_3); **LRMS** (ESI) 427 ([M^++Na]); **HRMS** calculated for $C_{23}H_{32}NaO_6$ 427.2091, found 427.2093.

(3aS,4S)-Pentaethyl 3a,4,5,6-tetrahydrobenzo[e]azulene-2,2,4,9,9 (1H,3H,8H,10H)-pentacarboxylate (2b')

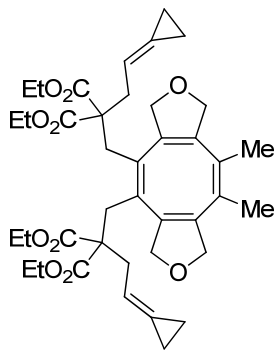


Colourless oil. 58 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, ***J*** = 8.2 Hz, 2H), 7.29 (d, ***J*** = 8.1 Hz, 2H), 5.31 – 5.25 (m, 1H), 4.26 – 4.00 (m, 6H), 3.77 – 3.57 (m, 3H), 3.53 – 3.42 (m, 1H), 3.30 – 3.21 (m, 1H), 3.17 – 2.96 (m, 2H), 2.85 (dt, ***J*** = 8.1, 3.1 Hz, 1H), 2.60 – 2.52 (m, 1H), 2.49 – 2.36 (m, 4H), 2.21 – 2.09 (m, 2H), 1.94 – 1.76 (m, 2H), 1.31 – 1.17 (m, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.5 (C), 172.2 (C), 171.5 (C), 143.7 (C), 139.9 (C), 136.9 (C), 133.8 (C), 129.8 (CH), 127.7 (CH), 124.4 (C), 119.4 (CH), 61.6 (CH_2), 61.5 (CH_2), 60.5 (CH_2), 58.9 (C), 46.4 (CH_2), 45.7 (CH), 44.9 (CH_2), 41.3 (CH), 39.5 (CH_2), 38.1 (CH_2), 32.5 (CH_2), 28.2 (CH_2), 21.1 (CH_3), 13.8 (CH_3), 13.7 (CH_3), 13.6 (CH_3); **LRMS** (ESI) 582 ([M^++Na]); **HRMS** calculated for $C_{29}H_{37}NNaO_8S$ 582.2132, found 582.2122.

The structure and stereochemical assignment of **2b'** was determined on the basis of 2D NMR experiments (COSY, NOESY, HMBC and HMQC or HSQC), in addition to standard ^{1}H, ^{13}C, DEPT and nOe experiments. The observation of 4% nOe between H_3 and H_4 is in accordance with the syn disposition of both hydrogens.

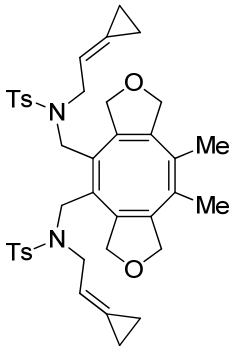


Tetraethyl 2,2'-(((4*Z*,9*Z*)-9,10-dimethyl-1,3,6,8-tetrahydrocyclo octa[1,2-c:5,6-c']difuran-4,5-diyl)bis(methylene))bis(2-(2-cyclopropylideneethyl)malonate) (4i)

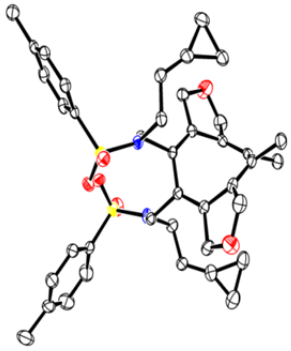


Colourless oil. 44 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.62 – 5.50 (m, 2H), 4.34 (dd, ***J*** = 23.9, 13.3 Hz, 2H), 4.26 – 4.14 (m, 6H), 4.14 – 3.99 (m, 6H), 3.93 – 3.79 (m, 2H), 3.09 – 3.00 (m, 2H), 2.87 (dd, ***J*** = 14.7, 6.2 Hz, 2H), 2.76 (dd, ***J*** = 14.6, 7.7 Hz, 2H), 2.61 – 2.52 (m, 2H), 1.71 (s, ***J*** = 10.5 Hz, 6H), 1.28 – 1.11 (m, 12H), 1.04 – 0.84 (m, 8H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.4 (C), 171.1 (C), 142.5 (C), 136.2 (C), 136.1 (C), 132.9 (C), 125.9 (C), 112.7 (CH), 68.7 (CH_2), 67.9 (CH_2), 61.1 (CH_2), 57.5 (C), 34.5 (CH_2), 34.1 (CH_2), 18.2 (CH_3), 13.6 (CH_3), 2.2 (CH_2), 1.4 (CH_2); **LRMS** (ESI) 715 ([M^++Na]); **HRMS** calculated for $C_{40}H_{52}NaO_{10}$ 715.3453, found 715.3458.

***N,N'*-(((4Z,9Z)-9,10-Dimethyl-1,3,6,8-tetrahydrocycloocta[1,2-c:5,6-c']difuran-4,5-diyl)bis(methylene))bis(N-(2-cyclopropylideneethyl)-4-methylbenzenesulfonamide) (4j)**

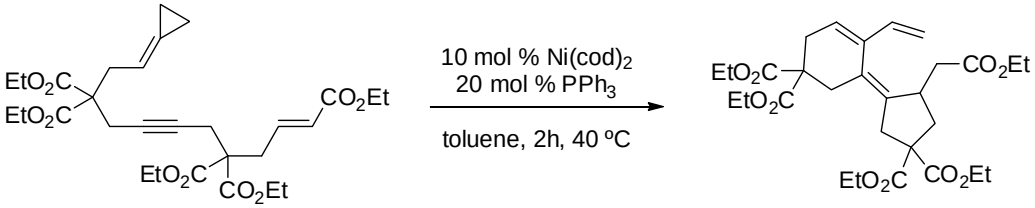


White solid. 34 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, ***J*** = 8.3 Hz, 2H), 7.31 (d, ***J*** = 8.2 Hz, 2H), 5.38 – 5.30 (m, 1H), 5.15 (d, ***J*** = 20.1 Hz, 1H), 5.03 – 4.94 (m, 2H), 4.66 (d, ***J*** = 14.1 Hz, 2H), 4.30 (t, ***J*** = 12.0 Hz, 4H), 4.21 – 4.08 (m, 2H), 3.98 – 3.89 (m, 2H), 3.74 – 3.66 (m, 2H), 3.19 (d, ***J*** = 14.1 Hz, 2H), 2.46 – 2.42 (m, 6H), 1.76 (s, ***J*** = 8.6 Hz, 6H), 1.03 – 0.80 (m, 8H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.6 (C), 142.3 (C), 137.6 (C), 136.6 (C), 135.8 (C), 132.5 (C), 132.4 (C), 132.2 (C), 130.8 (C), 130.1 (C), 130.0 (C), 129.8 (CH), 128.8 (C), 128.7 (C), 127.7 (CH), 127.3 (C), 112.4 (CH), 69.0 (CH_2), 68.0 (CH_2), 47.3 (CH_2), 46.3 (CH_2), 21.6 (CH_3), 21.2 (CH_3), 18.6 (CH_3), 1.9 (CH_2), 1.3 (CH_2); **LRMS** (ESI) 737 ([M^++Na]); **HRMS** calculated for $C_{40}H_{46}N_2NaO_6S_2$ 737.2689, found 737.2677.



The structure of this cycloadduct was confirmed by X-ray diffraction analysis.[14]

General Procedure for the Ni-catalyzed [3+2+2] Cycloaddition Reaction with an external ligand, exemplified for the cycloaddition of **1a** (Table 1, entry 4, main manuscript).



1a **3a**

$Ni(COD)_2$ (2.5 mg, 0.009 mmol) and PPh_3 (4.8 mg, 0.018 mmol) in toluene (0.3 mL) was placed on a dry sealed tube under argon

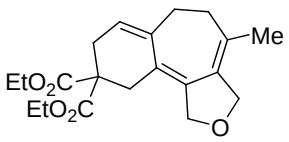
[14] Conpound **4j** could not be isolated from column chromatography in a completely pure form (impurity estimated in 6% yield). However, its identity was fully confirmed by X-ray analysis. CCDC 986513 (**4j**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

atmosphere. After stirring for 30 min at rt a solution of **1a** (50 mg, 0.018 mmol) in toluene (0.5 mL) was added. The reaction mixture was heated for 2 h at 40 °C,[15] allowed to cool down to *rt* and filtered through a short pad of a mixture of florisil and silica gel, eluting with Et_2O. The filtrate was concentrated and purified by flash chromatography on silica gel (10 % Et_2O / hexanes) to afford 43 mg of **3a** as a colorless oil (86 % yield).

(*Z*)-Diethyl 5-(2-(2-ethoxy-2-oxoethyl)-4,4-bis(ethoxycarbonyl)cyclopentylidene)-4-vinylcyclohex-3-ene-1,1-dicarboxylate (3a)

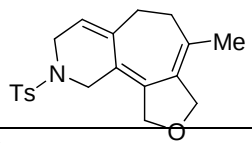
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.29 (dd, ***J*** = 17.3, 10.6 Hz, 1H), 5.73 (t, ***J*** = 5.0 Hz, 1H), 5.19 (dd, ***J*** = 17.2, 2.1 Hz, 1H), 5.03 (d, ***J*** = 10.8 Hz, 1H), 4.37 – 3.98 (m, 10H), 3.50 – 3.39 (m, 1H), 3.18 – 2.81 (m, 4H), 2.81 – 2.66 (m, 1H), 2.54 (d, ***J*** = 12.6 Hz, 1H), 2.49 – 2.38 (m, 2H), 1.96 – 1.80 (m, 2H), 1.31 – 1.17 (m, 15H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 172.6 (C), 172.3 (C), 172.1 (C), 141.4 (C), 137.7 (C), 136.4 (CH), 126.9 (CH), 124.3 (C), 114.6 (CH_2), 61.7 (CH_2), 61.4 (CH_2), 60.0 (CH_2), 58.5 (C), 54.6 (C), 39.8 (CH_2), 39.5 (CH_2), 39.1 (CH_2), 37.1 (CH), 34.9 (CH_2), 31.6 (CH_2), 13.8 (CH_3), 13.6 (CH_3); **HRMS** calculated for $C_{29}H_{40}O_{10}$ 548.2621, found 548.2618.

Diethyl 4-methyl-5,6,8,10-tetrahydro-1H-benzo[3,4]cyclohepta[1,2-c]furan-9,9(3H)-dicarboxylate (2i)



Colourless oil. 65 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.41 – 5.32 (m, 1H), 4.65 (s, 2H), 4.50 (d, ***J*** = 1.0 Hz, 2H), 4.23 – 4.05 (m, 4H), 2.72 – 2.62 (m, 4H), 2.41 (dd, ***J*** = 6.5, 3.6 Hz, 2H), 2.28 (t, ***J*** = 8.0 Hz, 2H), 1.70 (s, 3H), 1.30 – 1.12 (m, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.5 (C), 138.2 (C), 133.8 (C), 133.6 (C), 130.8 (C), 124.2 (C), 124.1 (C), 123.4 (CH), 73.8 (CH_2), 73.4 (CH_2), 61.4 (CH_2), 53.9 (C), 35.7 (CH_2), 34.1 (CH_2), 33.5 (CH_2), 31.1 (CH_2), 22.2 (CH_3), 13.6 (CH_3);**HRMS** calculated for $C_{20}H_{26}NaO_5$ 346.1892, found 346.1874.

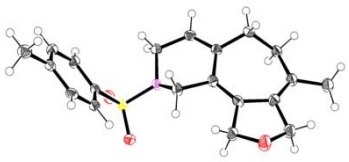
4-Methyl-9-tosyl-3,5,6,8,9,10-hexahydro-1H-furo[3',4':6,7]cyclohepta[1,2-c]pyridine (2j)



White solid. 60 % yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, ***J*** = 8.3 Hz, 2H), 7.22 (d, ***J*** = 8.1 Hz,

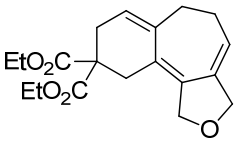
[15] The time and temperature required for any particular cycloaddition are indicated in the main manuscript.

2H), 5.26 – 5.16 (m, 1H), 4.59 (s, 2H), 4.48 (s, 2H), 3.87 (s, 2H), 3.78 (s, 2H), 2.38 (s, 3H), 2.27 (dd, ***J*** = 15.9, 11.8 Hz, 2H), 2.11 – 2.00 (m, 2H), 1.67 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.3 (C), 137.9 (C), 135.5 (C), 135.3 (C), 134.4 (C), 130.1 (CH), 128.5 (CH), 122.0 (C), 120.9 (CH), 73.6 (CH_2), 73.5 (CH_2), 46.9 (CH_2), 45.7 (CH_2), 35.8 (CH_2), 33.2 (CH_2), 22.8 (CH_3), 21.6 (CH_3).



The structure of this cycloadduct was confirmed by X-ray diffraction analysis.[16]

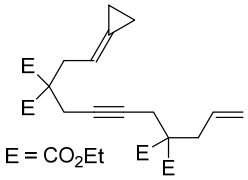
Diethyl 5,6,8,10-tetrahydro-1H-benzo[3,4]cyclohepta[1,2-c]furan-9,9(3H)-dicarboxylate (2k)



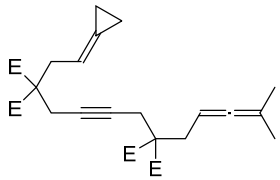
Colourless oil. 74 % yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.71 (t, ***J*** = 5.3 Hz, 1H), 5.43 (t, ***J*** = 4.1 Hz, 1H), 4.64 (s, 2H), 4.46 – 4.42 (m, 2H), 4.24 – 4.06 (m, 4H), 2.75 – 2.64 (m, 4H), 2.46 – 2.36 (m, 2H), 2.34 – 2.22 (m, 2H), 1.28 – 1.12 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.4 (C), 138.4 (C), 136.9 (C), 133.7 (C), 126.5 (C), 125.3 (CH), 123.5 (CH), 74.6 (CH_2), 73.6 (CH_2), 61.5 (CH_2), 53.9 (C), 34.2 (CH_2), 33.8 (CH_2), 31.3 (CH_2), 28.8 (CH_2), 13.7 (CH_3); **LRMS** (CI) 332 (10), 258 (100), 229 (21), 185 (36), 129 (85), 91 (15); **HRMS** calculated for $C_{19}H_{24}O_5$ 332.1624, found 332.1626.

[16] CCDC 986512 (**2j**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Experiments with cycloaddition precursors containing an electronically non-activated alkene and an allene (**1m** and **1n**)



1m



1n

The reactions of substrates **1m** and **1n** in the presence of $Ni(COD)_2$ (10%) or $Ni(COD)_2$ (10%)/PPh_3 (20%) led to the recovery of the starting materials, even after prolonged heating (24h at 40°C or 24h 90°C), confirming that, under these conditions, an activated alkene or an alkyne is required as third cycloaddition component.

Computational Details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[17] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[18] using the double-ζ quality plus polarization def2-SVP basis set[19] for all atoms. Reactants and products were characterized by frequency calculations,[20] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[21] Solvents effects were taken into account using the Polarizable Continuum Model (PCM).[22] Single

[17] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[18] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1998**, *37*, 785; c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.

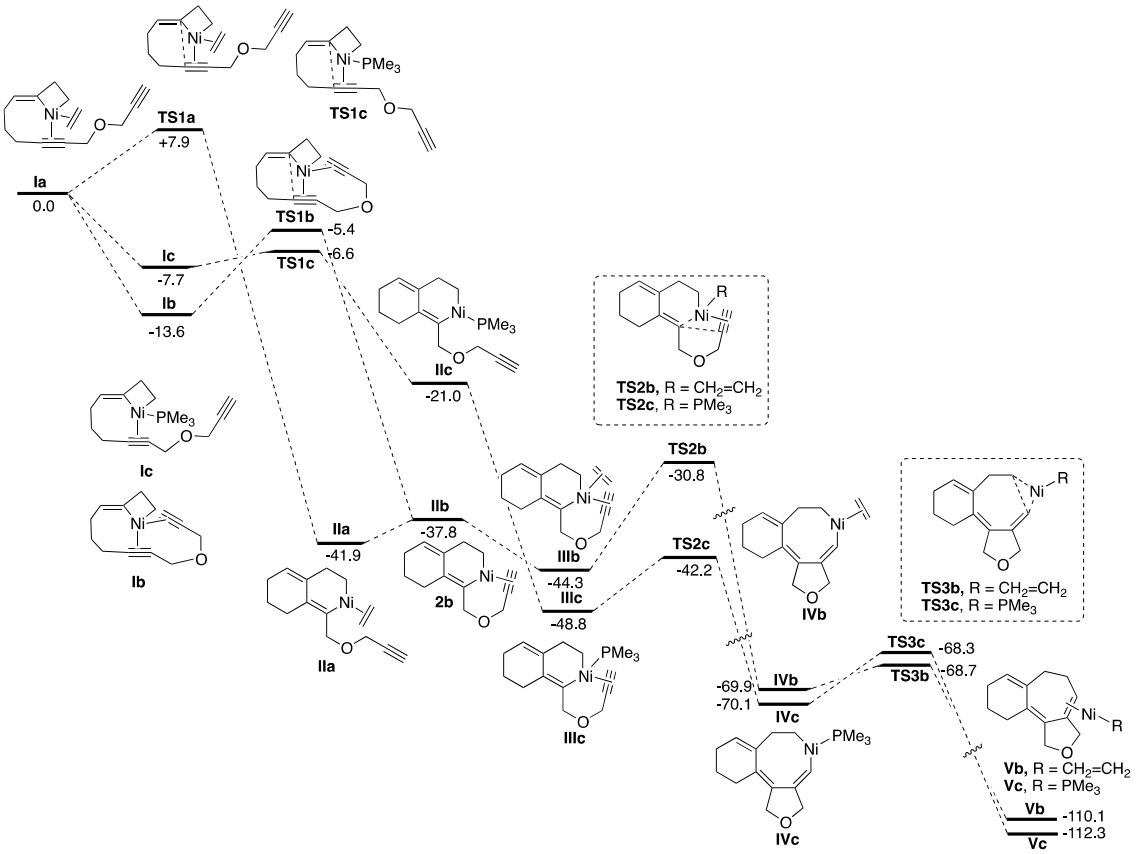
[19] F. Weigend, R. Alhrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[20] J. W. McIver, A. K. Komornicki, *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[21] C. González, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.

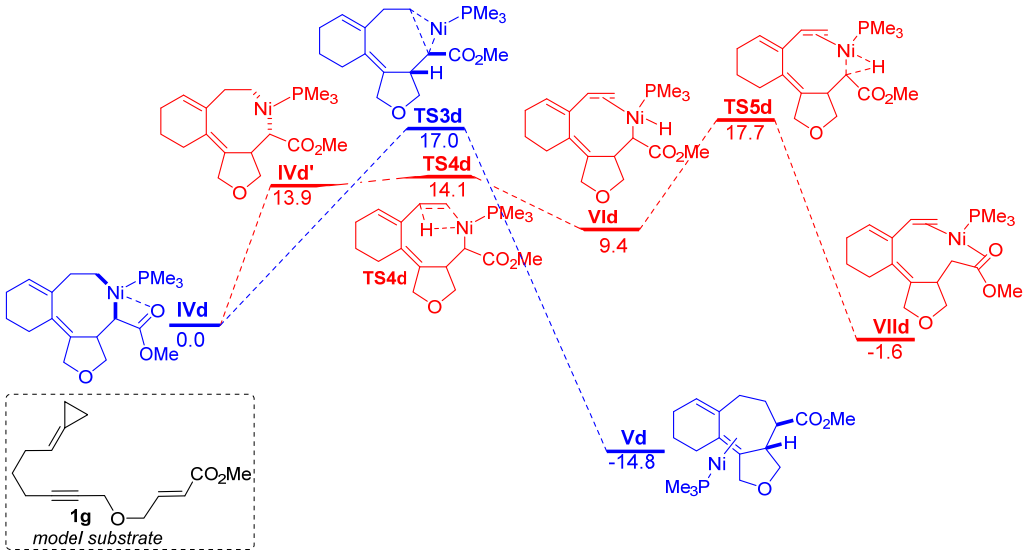
[22] a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117; b) J. L. Pascual-Ahuir, E. Silla, I. Tuñón, *J. Comp. Chem.* **1994**, *15*, 1127; c) V. Barone, M. Cossi, *J. Phys. Chem. A*, **1998**, *102*, 1995.

point calculations (PCM-M06/def2-SVP) on the gas-phase optimized geometries were performed to estimate the change in the Gibbs energies in the presence of toluene as solvent using the dispersion corrected M06[23] functional. This level is denoted PCM(toluene)-M06/def2-SVP//B3LYP/def2-SVP.



Scheme S1. Calculated profile (PCM(toluene)-M06/def2-SVP//B3LYP/def2-SVP level) for the reaction of **1l** and $[Ni(CH_2=CH_2)_2]$, with or without PMe_3. Free energies (ΔG_{298}) are given in kcal mol^{-1}.

[23] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.



Scheme S2. Calculated reductive and β-H elimination pathways for **IVd** (from **1g**).

Cartesian coordinates (in Å) and free energies (in a. u.) of all the stationary points discussed in the text (Schemes 1 and 2) and in the supplementary information (Scheme S1). All calculations have been performed at the PCM(toluene)M06/def2-SVP//B3LYP/def2-SVP level.

Ia: E= -2165.478443

C	-0.742839000	-0.384367000	0.123917000
C	-0.113010000	0.649445000	0.490293000
C	0.055376000	2.068632000	0.870069000
C	0.386301000	2.983670000	-0.335053000
C	1.408779000	2.385503000	-1.325926000
C	2.632112000	1.804216000	-0.656854000
C	2.688481000	0.599115000	-0.075168000
C	3.692290000	-0.007708000	0.839042000
C	-2.009525000	-1.084873000	-0.146932000
C	2.569695000	-0.792741000	1.510670000
H	0.866698000	2.144901000	1.611434000
H	-0.868963000	2.423425000	1.357399000
H	-0.542561000	3.210710000	-0.885488000
H	0.757444000	3.942523000	0.065789000
H	0.900949000	1.600449000	-1.910033000
H	1.696916000	3.167779000	-2.047432000
H	3.530447000	2.441689000	-0.608343000
H	4.283873000	0.679385000	1.474097000
H	4.391473000	-0.677843000	0.309585000
H	-2.017035000	-1.461384000	-1.192928000
H	-2.084555000	-1.985787000	0.499905000
H	2.726872000	-1.859490000	1.729058000
H	2.108502000	-0.267912000	2.357914000
Ni	1.243162000	-0.694924000	0.063840000
C	2.150912000	-2.287854000	-0.975775000
H	2.436343000	-1.870572000	-1.946484000
H	2.975065000	-2.661960000	-0.364817000
C	0.849417000	-2.673920000	-0.731671000
H	0.599424000	-3.315692000	0.118959000
H	0.086729000	-2.598755000	-1.509887000
O	-3.109238000	-0.224046000	0.073801000
C	-4.348726000	-0.854689000	-0.152837000
H	-4.468778000	-1.740559000	0.508473000
H	-4.414517000	-1.236277000	-1.195288000
C	-5.452414000	0.074591000	0.086821000
C	-6.382669000	0.824508000	0.279188000
H	-7.204037000	1.494441000	0.451471000

Ib: E= -2087.072334

C	-0.939979000	1.254645000	0.560920000
C	0.294855000	1.262787000	0.772061000
C	1.639892000	1.808773000	1.048303000
C	2.397847000	2.220964000	-0.237398000
C	2.294095000	1.197930000	-1.389189000
C	2.567611000	-0.223303000	-0.957061000
C	1.682399000	-1.020274000	-0.345719000
C	1.848170000	-2.319322000	0.359535000
C	-2.333046000	1.754135000	0.501479000
C	0.689072000	-1.956185000	1.282606000
H	2.231768000	1.050520000	1.584223000
H	1.550485000	2.682650000	1.717124000
H	2.013514000	3.192501000	-0.593031000

H	3.454188000	2.381887000	0.038510000
H	1.281793000	1.263834000	-1.820501000
H	2.989367000	1.500857000	-2.189404000
H	3.586446000	-0.612340000	-1.118882000
H	2.830130000	-2.523793000	0.829001000
H	1.589714000	-3.177742000	-0.285026000
H	-2.325365000	2.842469000	0.329359000
H	-2.819192000	1.574174000	1.483777000
H	-0.058782000	-2.725566000	1.517906000
H	0.994198000	-1.397951000	2.178239000
Ni	-0.152536000	-0.612517000	0.118134000
O	-3.111119000	1.211701000	-0.542508000
C	-3.312459000	-0.183652000	-0.455396000
H	-3.864964000	-0.440056000	0.473595000
H	-3.957234000	-0.444614000	-1.309913000
C	-2.067893000	-0.978997000	-0.501285000
C	-1.303252000	-1.945369000	-0.753774000
H	-1.079982000	-2.942737000	-1.113152000

Ic: E= -2547.759919

C	0.771316000	-0.130663000	-0.066692000
C	0.591803000	1.076772000	-0.404556000
C	1.136790000	2.432416000	-0.649075000
C	1.131458000	3.321845000	0.616299000
C	-0.160237000	3.174855000	1.452752000
C	-1.394090000	3.126468000	0.586240000
C	-1.746186000	2.079009000	-0.170093000
C	-2.897328000	1.937501000	-1.102047000
C	1.849134000	-1.101394000	0.216398000
C	-3.057643000	0.444240000	-0.824350000
H	0.562028000	2.925564000	-1.446503000
H	2.172341000	2.307835000	-1.009549000
H	2.001010000	3.069318000	1.247157000
H	1.266084000	4.369025000	0.295341000
H	-0.085502000	2.242966000	2.037533000
H	-0.216987000	3.998229000	2.183577000
H	-1.993696000	4.047631000	0.500227000
H	-2.579314000	2.108865000	-2.147044000
H	-3.772290000	2.595086000	-0.912715000
H	1.838746000	-1.374690000	1.294042000
H	1.697805000	-2.050773000	-0.342601000
H	-3.797640000	0.251381000	-0.034442000
H	-3.268693000	-0.193807000	-1.701667000
Ni	-1.193925000	0.200460000	-0.187998000
O	3.103089000	-0.540395000	-0.123526000
C	4.182359000	-1.405424000	0.140927000
H	4.072559000	-2.359779000	-0.419635000
H	4.214524000	-1.681916000	1.217701000
C	5.450263000	-0.777301000	-0.229417000
C	6.511308000	-0.277770000	-0.528427000
H	7.449297000	0.171559000	-0.795743000
P	-1.663704000	-1.953081000	0.200266000
C	-3.429477000	-2.414036000	0.492991000
H	-3.808626000	-1.874529000	1.373785000
H	-4.046060000	-2.130127000	-0.370576000
H	-3.526558000	-3.497417000	0.665837000
C	-1.223992000	-3.094915000	-1.185378000
H	-1.498699000	-4.137624000	-0.959196000
H	-1.756420000	-2.771684000	-2.092638000
H	-0.145183000	-3.038426000	-1.390342000

C	-0.887422000	-2.761032000	1.672492000
H	-1.133569000	-2.177054000	2.572522000
H	-1.257986000	-3.790252000	1.802309000
H	0.205224000	-2.786309000	1.572419000

TS1b: E= -2087.059186

C	-0.574771000	-1.132350000	-0.410461000
C	0.654909000	-0.913585000	-0.673541000
C	1.928694000	-1.606778000	-1.036580000
C	2.746716000	-2.008009000	0.216127000
C	2.611593000	-0.961968000	1.354212000
C	2.592657000	0.422929000	0.771476000
C	1.591604000	0.902246000	0.019548000
C	1.581711000	2.179897000	-0.753999000
C	-1.685386000	-2.112916000	-0.476344000
C	0.186131000	2.649743000	-0.345456000
H	2.533166000	-0.963285000	-1.691764000
H	1.665725000	-2.508125000	-1.616689000
H	2.410163000	-2.991831000	0.584062000
H	3.803065000	-2.122477000	-0.077627000
H	1.669673000	-1.155028000	1.892162000
H	3.427737000	-1.089030000	2.082030000
H	3.516081000	1.020568000	0.817408000
H	1.619231000	1.970378000	-1.838619000
H	2.433394000	2.855867000	-0.524579000
H	-1.329694000	-3.117116000	-0.195145000
H	-2.053042000	-2.168164000	-1.523619000
H	0.209430000	3.267303000	0.563446000
H	-0.417332000	3.140319000	-1.125019000
Ni	-0.399545000	0.779254000	-0.032331000
O	-2.754767000	-1.827230000	0.401492000
C	-3.320911000	-0.556682000	0.188236000
H	-3.771027000	-0.490938000	-0.825594000
H	-4.134918000	-0.455524000	0.923315000
C	-2.367992000	0.565175000	0.353750000
C	-1.983917000	1.718153000	0.665012000
H	-2.122488000	2.730668000	1.017705000

TS1c: E= -2547.758180

C	0.659407000	-0.282327000	-0.060107000
C	0.707813000	0.950715000	-0.421669000
C	1.670088000	2.055594000	-0.704601000
C	1.959672000	2.918975000	0.545937000
C	0.709119000	3.065931000	1.449398000
C	-0.534561000	3.216989000	0.616093000
C	-1.040559000	2.252815000	-0.165765000
C	-2.205767000	2.373263000	-1.094947000
C	1.624739000	-1.387063000	0.114771000
C	-2.914838000	1.079613000	-0.681917000
H	1.286682000	2.689071000	-1.518072000
H	2.600798000	1.579460000	-1.053189000
H	2.776476000	2.461452000	1.128533000
H	2.315931000	3.909343000	0.216590000
H	0.629067000	2.159381000	2.071321000
H	0.838500000	3.914395000	2.139673000
H	-0.989569000	4.216897000	0.538059000
H	-1.867989000	2.308454000	-2.145774000
H	-2.769470000	3.328009000	-0.997984000
H	1.541963000	-1.813050000	1.138061000

H	1.383128000	-2.220400000	-0.582044000
H	-3.589687000	1.250806000	0.172003000
H	-3.469659000	0.565602000	-1.487686000
Ni	-1.190454000	0.268207000	-0.139710000
O	2.951852000	-0.941154000	-0.113753000
C	3.912823000	-1.955824000	0.052209000
H	3.723470000	-2.800430000	-0.646296000
H	3.862303000	-2.385904000	1.076602000
C	5.259869000	-1.435381000	-0.181564000
C	6.382645000	-1.024965000	-0.371196000
H	7.376338000	-0.654827000	-0.540502000
P	-2.181048000	-1.642403000	0.189497000
C	-3.814904000	-1.565286000	1.043277000
H	-3.686129000	-1.095023000	2.029880000
H	-4.510014000	-0.945764000	0.460695000
H	-4.243336000	-2.571410000	1.175370000
C	-2.585621000	-2.544307000	-1.370234000
H	-3.125487000	-3.483113000	-1.166869000
H	-3.205406000	-1.900413000	-2.010887000
H	-1.655526000	-2.771442000	-1.912600000
C	-1.340940000	-2.956292000	1.183915000
H	-1.067765000	-2.550724000	2.169792000
H	-1.994977000	-3.831699000	1.325165000
H	-0.419935000	-3.277871000	0.678017000

IIb: E= -2087.110894

C	0.207325000	0.818234000	-0.412628000
C	-1.117005000	0.614464000	-0.147666000
C	-2.113440000	1.694532000	0.257435000
C	-3.563914000	1.317413000	-0.069137000
C	-3.938218000	-0.047879000	0.520104000
C	-2.913175000	-1.089337000	0.158595000
C	-1.639382000	-0.773997000	-0.156980000
C	-0.626106000	-1.811628000	-0.612479000
C	0.881960000	2.153478000	-0.489242000
C	0.244867000	-2.535739000	0.329869000
H	-1.863495000	2.656108000	-0.214918000
H	-2.025198000	1.859137000	1.348565000
H	-4.248614000	2.097303000	0.302827000
H	-3.691233000	1.277647000	-1.165261000
H	-4.032695000	0.027932000	1.621858000
H	-4.933845000	-0.362795000	0.162856000
H	-3.228025000	-2.138433000	0.133077000
H	0.070315000	-1.066405000	-1.336918000
H	-0.960406000	-2.432385000	-1.460418000
H	0.209775000	2.986228000	-0.228849000
H	1.229781000	2.324505000	-1.531736000
H	0.032087000	-2.452790000	1.400698000
H	0.595502000	-3.525446000	0.018090000
Ni	1.134965000	-0.880276000	-0.226286000
O	1.980976000	2.301102000	0.405466000
C	3.075728000	1.452242000	0.155895000
H	3.484424000	1.620099000	-0.863791000
H	3.857190000	1.738232000	0.879498000
C	2.747956000	0.015258000	0.302103000
C	2.841689000	-1.197862000	0.647089000
H	3.347898000	-2.025107000	1.128954000

IIc: E= -2547.781075

C	0.527743000	-0.170175000	-0.107822000
C	0.887038000	1.114420000	-0.351140000
C	2.284422000	1.705869000	-0.551230000
C	2.645093000	2.734430000	0.551169000
C	1.408773000	3.191653000	1.370392000
C	0.174844000	3.267703000	0.516797000
C	-0.154725000	2.240420000	-0.299373000
C	-1.406586000	2.352554000	-1.207371000
C	1.360993000	-1.399099000	-0.031931000
C	-2.626640000	1.553667000	-0.670599000
H	2.281119000	2.217155000	-1.530044000
H	3.025816000	0.902953000	-0.599055000
H	3.385089000	2.301214000	1.243462000
H	3.121880000	3.615716000	0.092009000
H	1.235904000	2.445847000	2.168104000
H	1.609403000	4.149222000	1.875652000
H	-0.438865000	4.176604000	0.531576000
H	-1.145421000	2.015375000	-2.225629000
H	-1.650885000	3.428633000	-1.286931000
H	1.136362000	-1.918566000	0.926235000
H	1.029567000	-2.102886000	-0.829773000
H	-3.109207000	2.094745000	0.162489000
H	-3.380216000	1.363252000	-1.453281000
Ni	-1.319673000	0.255529000	-0.164299000
O	2.768725000	-1.215764000	-0.130731000
C	3.484228000	-2.420430000	-0.036449000
H	3.185371000	-3.125030000	-0.844077000
H	3.260529000	-2.940997000	0.921224000
C	4.925687000	-2.181679000	-0.122122000
C	6.121456000	-2.005855000	-0.191273000
H	7.180835000	-1.842618000	-0.253485000
P	-2.594607000	-1.353506000	0.225100000
C	-3.913088000	-1.000678000	1.465034000
H	-3.447609000	-0.715349000	2.420381000
H	-4.518026000	-0.152979000	1.113370000
H	-4.560608000	-1.877737000	1.625611000
C	-3.547539000	-1.943781000	-1.239485000
H	-4.222781000	-2.772707000	-0.972439000
H	-4.135091000	-1.109199000	-1.647588000
H	-2.848184000	-2.284052000	-2.017791000
C	-1.865683000	-2.920716000	0.875668000
H	-1.346838000	-2.712435000	1.823190000
H	-2.638879000	-3.687480000	1.046104000
H	-1.125210000	-3.304597000	0.158827000

IIIb: E= -2165.548888

C	2.582012000	1.186421000	0.657197000
C	1.451256000	0.287691000	0.175716000
C	0.140086000	0.493405000	0.442699000
C	-0.404526000	-1.854825000	-0.667426000
C	-2.023227000	1.188524000	-1.098134000
H	-0.127676000	-2.576066000	0.115095000
H	-1.219751000	-2.275079000	-1.285637000
H	2.255963000	1.836426000	1.481576000
H	2.884648000	1.861577000	-0.166363000
C	-3.054282000	0.500475000	-0.981835000
H	-4.096354000	0.241407000	-1.092484000
C	3.796958000	0.357333000	1.094357000
H	3.499838000	-0.289971000	1.938245000
H	4.598294000	1.016815000	1.466922000

C	0.804099000	-1.491863000	-1.497145000
H	0.500494000	-0.820929000	-2.322633000
H	1.209800000	-2.404862000	-1.972486000
C	1.889989000	-0.827424000	-0.689389000
C	3.190965000	-1.173147000	-0.809134000
H	3.463354000	-1.970994000	-1.509950000
C	4.312812000	-0.514012000	-0.054588000
H	4.910774000	0.100874000	-0.757513000
H	5.014934000	-1.278682000	0.324027000
C	-0.374097000	1.774534000	1.051051000
H	-1.301381000	1.598243000	1.636885000
H	0.342151000	2.244657000	1.744075000
Ni	-1.504748000	-0.452201000	0.072814000
C	-3.089290000	-1.571797000	1.034718000
H	-3.911342000	-0.889627000	1.264424000
H	-3.346048000	-2.431880000	0.408861000
C	-1.924951000	-1.556136000	1.780685000
H	-1.259433000	-2.419869000	1.820785000
H	-1.800747000	-0.835964000	2.597000000
O	-0.645947000	2.774884000	0.056888000
C	-1.061247000	2.303635000	-1.212432000
H	-1.535447000	3.162213000	-1.717019000
H	-0.200890000	1.977373000	-1.825735000

IIIc: E= -2547.825307

C	2.585270000	-1.623157000	-0.644344000
C	1.441649000	-0.849280000	0.005305000
C	0.140882000	-1.052218000	-0.331915000
C	-0.245334000	1.384352000	1.961540000
C	-2.085375000	-1.538175000	1.004307000
H	0.020536000	2.390856000	1.598503000
H	-0.799668000	1.516959000	2.902545000
H	2.227309000	-2.260888000	-1.465191000
H	3.052342000	-2.297068000	0.099950000
C	-2.232545000	-0.787047000	2.018233000
H	-2.638941000	-0.614697000	3.009992000
C	3.649478000	-0.648747000	-1.169989000
H	3.183496000	0.007096000	-1.927080000
H	4.458258000	-1.193929000	-1.684972000
C	1.024684000	0.540645000	2.209977000
H	0.726384000	-0.398892000	2.710670000
H	1.673213000	1.066455000	2.938989000
C	1.905329000	0.149487000	1.019456000
C	3.184102000	0.593810000	0.985959000
H	3.523853000	1.261393000	1.787041000
C	4.222228000	0.200366000	-0.030202000
H	5.022304000	-0.363050000	0.490550000
H	4.726535000	1.099382000	-0.430660000
C	-0.324177000	-2.160360000	-1.247310000
H	-0.098552000	-1.941986000	-2.305811000
H	0.196335000	-3.110093000	-0.996580000
Ni	-1.050275000	0.068251000	0.709426000
O	-1.726274000	-2.392800000	-1.214032000
C	-2.204697000	-2.686521000	0.081645000
H	-3.266991000	-2.958963000	-0.033304000
H	-1.677337000	-3.569378000	0.503204000
P	-0.975706000	1.524795000	-0.853826000
C	-2.261150000	2.813998000	-0.551287000
H	-3.237377000	2.321613000	-0.427293000
H	-2.028617000	3.352049000	0.378435000

H	-2.320477000	3.528730000	-1.387975000
C	-1.461440000	0.871612000	-2.510836000
H	-2.278123000	0.146089000	-2.388522000
H	-1.770434000	1.683682000	-3.187941000
H	-0.606032000	0.341179000	-2.952855000
C	0.533287000	2.502287000	-1.239295000
H	0.344465000	3.169182000	-2.095186000
H	0.831437000	3.101926000	-0.368845000
H	1.356424000	1.815504000	-1.479400000

TS2b: E= -2165.527335

C	2.346070000	1.604031000	0.071904000
C	1.187945000	0.640153000	-0.183736000
C	-0.094117000	0.955563000	0.148213000
C	-0.445561000	-2.234518000	-0.687774000
C	-1.869030000	0.639267000	-1.086706000
H	-0.021329000	-2.843106000	0.124160000
H	-1.084431000	-2.873325000	-1.313022000
H	2.020504000	2.491036000	0.630032000
H	2.735149000	1.965356000	-0.900102000
C	-2.301356000	-0.537469000	-1.358354000
H	-2.921863000	-1.137384000	-2.018152000
C	3.482336000	0.906377000	0.829972000
H	3.095709000	0.547204000	1.799736000
H	4.291063000	1.621011000	1.055567000
C	0.659409000	-1.561464000	-1.504438000
H	0.211514000	-0.979783000	-2.326689000
H	1.257528000	-2.359369000	-1.985439000
C	1.626232000	-0.668563000	-0.741640000
C	2.922906000	-1.050026000	-0.651148000
H	3.215606000	-1.997487000	-1.118885000
C	4.020661000	-0.274598000	0.020186000
H	4.724693000	0.088157000	-0.755530000
H	4.621889000	-0.947764000	0.657839000
C	-0.530227000	2.314406000	0.627554000
H	-0.556941000	2.366120000	1.729942000
H	0.150951000	3.111448000	0.268666000
Ni	-1.256962000	-0.707453000	0.231288000
C	-1.758379000	-1.863542000	1.825002000
H	-2.835787000	-1.698244000	1.941607000
H	-1.464689000	-2.908279000	1.702990000
C	-0.852802000	-0.891628000	2.247449000
H	0.201880000	-1.138166000	2.401073000
H	-1.198422000	0.020474000	2.741749000
O	-1.849346000	2.621849000	0.183223000
C	-2.056564000	2.116301000	-1.111564000
H	-3.096148000	2.347165000	-1.392668000
H	-1.382309000	2.593097000	-1.854255000

TS2c: E= -2547.814766

C	-2.589851000	1.161430000	-1.070415000
C	-1.479125000	0.743064000	-0.103781000
C	-0.191623000	1.149238000	-0.330684000
C	0.151296000	-1.132837000	2.230546000
C	1.195423000	1.942598000	0.933497000
H	0.007935000	-2.185941000	1.933492000
H	0.632102000	-1.126824000	3.220592000
H	-2.191026000	1.695893000	-1.941718000
H	-3.258046000	1.874592000	-0.548799000

C	1.349626000	1.368742000	2.080318000
H	1.643017000	1.545728000	3.112668000
C	-3.423429000	-0.035253000	-1.540527000
H	-2.765088000	-0.747650000	-2.067526000
H	-4.186216000	0.288259000	-2.268189000
C	-1.207315000	-0.397199000	2.296582000
H	-1.056053000	0.586968000	2.771781000
H	-1.903245000	-0.946150000	2.961239000
C	-1.955945000	-0.175879000	0.978814000
C	-3.143508000	-0.817137000	0.830509000
H	-3.476779000	-1.459345000	1.653938000
C	-4.075593000	-0.724257000	-0.343572000
H	-4.983107000	-0.165943000	-0.036708000
H	-4.440234000	-1.730970000	-0.617357000
C	0.196490000	2.025734000	-1.505267000
H	0.229433000	1.454215000	-2.449255000
H	-0.529458000	2.853851000	-1.642685000
Ni	0.920475000	-0.000947000	0.836995000
O	1.486631000	2.575790000	-1.319628000
C	1.573045000	3.049222000	0.004983000
H	2.614181000	3.357120000	0.185792000
H	0.917981000	3.935402000	0.151665000
P	1.401378000	-1.525754000	-0.668386000
C	1.972939000	-3.171707000	-0.060191000
H	2.760321000	-3.021874000	0.693372000
H	1.136340000	-3.694814000	0.426350000
H	2.363049000	-3.796727000	-0.879448000
C	2.857643000	-0.938732000	-1.644265000
H	3.728444000	-0.870809000	-0.974180000
H	3.099899000	-1.615239000	-2.479727000
H	2.651683000	0.073782000	-2.021844000
C	0.190162000	-2.001646000	-1.976961000
H	0.612759000	-2.749381000	-2.666900000
H	-0.713221000	-2.412344000	-1.501558000
H	-0.103108000	-1.107591000	-2.545563000

IVb: E= -2165.589601

C	2.559386000	1.529325000	-0.354862000
C	1.479482000	0.603709000	0.185702000
C	1.588157000	-0.743023000	-0.008128000
C	-1.795983000	0.158139000	1.517337000
C	0.667041000	-1.860324000	0.265645000
H	-2.448841000	1.039707000	1.372479000
H	-2.275922000	-0.520091000	2.243310000
H	3.241124000	1.000882000	-1.034559000
H	3.178398000	1.905547000	0.482784000
C	-0.683533000	-1.897546000	0.331475000
H	-1.131021000	-2.882971000	0.557155000
C	1.930076000	2.724472000	-1.083856000
H	1.322429000	2.346340000	-1.924568000
H	2.712518000	3.365597000	-1.521933000
C	-0.413503000	0.589899000	1.991597000
H	0.140853000	-0.277845000	2.373766000
H	-0.540353000	1.281957000	2.846040000
C	0.424909000	1.311815000	0.946567000
C	0.277509000	2.654025000	0.815423000
H	-0.438662000	3.161556000	1.473268000
C	1.047144000	3.532013000	-0.129800000
H	1.670961000	4.227655000	0.466888000
H	0.355729000	4.185500000	-0.693005000

C	2.849135000	-1.398139000	-0.575025000
H	3.076855000	-1.076283000	-1.607056000
H	3.734880000	-1.149014000	0.046770000
Ni	-1.919311000	-0.623402000	-0.204939000
C	-3.725055000	-0.043749000	-1.054359000
H	-4.079612000	-0.915913000	-1.616406000
H	-4.379909000	0.294934000	-0.245552000
C	-2.705659000	0.743986000	-1.541698000
H	-2.497639000	1.739903000	-1.139067000
H	-2.223874000	0.510803000	-2.498934000
O	2.623635000	-2.795240000	-0.589204000
C	1.558327000	-3.093247000	0.293792000
H	1.053206000	-4.007894000	-0.052841000
H	1.935911000	-3.281329000	1.324547000

IVc: E= -2547.860251

C	2.826889000	1.960289000	-0.570937000
C	2.048179000	0.832601000	0.091942000
C	2.390699000	-0.463415000	-0.170421000
C	-0.865729000	-0.205430000	1.910285000
C	1.767019000	-1.747726000	0.189436000
H	-1.651538000	0.575513000	1.936360000
H	-1.101287000	-0.947448000	2.694850000
H	3.486210000	1.584745000	-1.364802000
H	3.481214000	2.450637000	0.176142000
C	0.476880000	-2.053314000	0.474630000
H	0.301899000	-3.120537000	0.716873000
C	1.868478000	3.008259000	-1.152939000
H	1.220998000	2.517298000	-1.900810000
H	2.429659000	3.793409000	-1.686235000
C	0.494836000	0.438905000	2.166633000
H	1.237768000	-0.333842000	2.404132000
H	0.418321000	1.086314000	3.062065000
C	1.008111000	1.312098000	1.030215000
C	0.586246000	2.600980000	0.974398000
H	-0.097618000	2.953517000	1.756573000
C	1.008775000	3.620712000	-0.045227000
H	1.573214000	4.423980000	0.470135000
H	0.122887000	4.127547000	-0.471535000
C	3.654079000	-0.837845000	-0.948338000
H	3.646432000	-0.466087000	-1.989104000
H	4.557377000	-0.414819000	-0.459568000
Ni	-1.067288000	-1.068520000	0.236101000
O	3.720606000	-2.250629000	-0.985669000
C	2.877928000	-2.773406000	0.025832000
H	2.514252000	-3.763826000	-0.289586000
H	3.438670000	-2.905390000	0.979322000
P	-3.013278000	-0.165665000	-0.497537000
C	-4.461836000	-0.301884000	0.640503000
H	-4.678756000	-1.363997000	0.830218000
H	-4.211724000	0.169688000	1.603050000
H	-5.359064000	0.182956000	0.223231000
C	-3.675972000	-0.878752000	-2.069575000
H	-3.855670000	-1.956806000	-1.938120000
H	-4.616596000	-0.393590000	-2.376372000
H	-2.932077000	-0.753927000	-2.871425000
C	-2.968626000	1.641924000	-0.870044000
H	-3.950978000	2.020045000	-1.196041000
H	-2.646063000	2.188964000	0.028675000
H	-2.224876000	1.830243000	-1.658801000

TS3b: E= -2165.587717

C	3.073367000	-2.090452000	-0.409368000
C	3.750955000	-0.730820000	-0.606951000
C	2.714319000	0.353239000	-0.908310000
C	1.491297000	0.340655000	0.006399000
C	1.295254000	-0.843639000	0.865460000
C	2.021062000	-1.970755000	0.657691000
C	0.659095000	1.422971000	-0.020881000
C	1.001062000	2.726862000	-0.731035000
C	0.368887000	-0.760042000	2.067504000
C	-1.116648000	-0.969536000	1.778432000
Ni	-1.736793000	-0.905670000	-0.085092000
C	-0.680981000	1.630146000	0.535495000
C	-1.667119000	0.725152000	0.761462000
C	-3.197692000	-1.469737000	-1.326918000
C	-1.987873000	-1.435309000	-2.013264000
H	-2.620152000	1.089671000	1.170947000
H	-1.334438000	-2.052468000	1.601728000
H	-1.736062000	-0.670986000	2.636056000
O	-0.082400000	3.614573000	-0.517068000
H	1.946248000	3.156933000	-0.334988000
H	1.139877000	2.598662000	-1.820420000
H	2.367335000	0.233901000	-1.953333000
H	3.197037000	1.344592000	-0.873032000
H	4.494951000	-0.773276000	-1.419133000
H	4.299021000	-0.475345000	0.316589000
H	1.876115000	-2.819960000	1.334836000
H	0.505081000	0.222453000	2.545736000
H	0.695559000	-1.512811000	2.805981000
H	2.630717000	-2.431512000	-1.366824000
H	3.811749000	-2.860029000	-0.130217000
H	-3.612002000	-2.421541000	-0.971359000
H	-3.921985000	-0.651937000	-1.410596000
H	-1.715126000	-0.584830000	-2.646914000
H	-1.423529000	-2.358454000	-2.195069000
C	-0.870717000	3.135703000	0.560574000
H	-1.913868000	3.453452000	0.406007000
H	-0.522738000	3.569029000	1.525394000

Vb: E= -2165.653716

C	-3.983378000	-0.456017000	0.811128000
C	-3.748513000	1.046334000	0.660230000
C	-2.260623000	1.373807000	0.788339000
C	-1.359607000	0.549775000	-0.126438000
C	-1.882382000	-0.752472000	-0.570157000
C	-3.066783000	-1.221762000	-0.098726000
C	-0.114663000	1.049988000	-0.411502000
C	0.328733000	2.442496000	0.034495000
C	-1.142016000	-1.591346000	-1.592017000
C	0.330401000	-1.909949000	-1.269041000
Ni	1.540540000	-0.840304000	0.396061000
C	1.050916000	0.499375000	-1.114598000
C	1.296573000	-0.796642000	-1.554760000
C	2.028633000	-1.268821000	2.252742000
C	2.753737000	-0.166502000	1.746174000
H	2.157056000	-0.991034000	-2.202963000
H	0.382457000	-2.218943000	-0.166149000
H	0.649336000	-2.822045000	-1.795128000

O	1.679131000	2.599338000	-0.354948000
H	-0.310849000	3.218220000	-0.439091000
H	0.264472000	2.588742000	1.126081000
H	-1.945523000	1.206279000	1.837784000
H	-2.109364000	2.448393000	0.602354000
H	-4.325383000	1.613018000	1.408974000
H	-4.109837000	1.366775000	-0.332731000
H	-3.396690000	-2.214781000	-0.422846000
H	-1.164747000	-1.079518000	-2.570279000
H	-1.694628000	-2.534408000	-1.721043000
H	-3.818849000	-0.762663000	1.863912000
H	-5.033049000	-0.715581000	0.591029000
H	1.201736000	-1.117036000	2.958365000
H	2.508914000	-2.252851000	2.331124000
H	3.799538000	-0.289756000	1.433820000
H	2.498369000	0.860376000	2.036356000
C	1.956738000	1.681189000	-1.394061000
H	3.027433000	1.429762000	-1.372104000
H	1.724834000	2.124120000	-2.388436000

TS3c: E= -2547.857352

C	3.209411000	-2.439401000	-0.843208000
C	3.872888000	-1.189271000	-1.428966000
C	2.871122000	-0.036729000	-1.521430000
C	2.029073000	0.180852000	-0.264820000
C	2.043242000	-0.883113000	0.757699000
C	2.580502000	-2.097370000	0.478847000
C	1.318747000	1.343521000	-0.161085000
C	1.501865000	2.525255000	-1.108652000
C	1.576677000	-0.585011000	2.172302000
C	0.068984000	-0.623647000	2.404221000
Ni	-1.234730000	-0.660480000	0.990346000
C	0.278509000	1.764656000	0.777566000
C	-0.654613000	1.011020000	1.424880000
H	-1.343691000	1.561009000	2.088815000
H	-0.310513000	-1.690962000	2.339456000
H	-0.188982000	-0.269322000	3.414134000
O	0.562635000	3.512404000	-0.717048000
H	2.539210000	2.922074000	-1.047626000
H	1.316751000	2.269225000	-2.166842000
H	2.187957000	-0.227875000	-2.372825000
H	3.405556000	0.893065000	-1.780461000
H	4.299911000	-1.395740000	-2.424350000
H	4.713183000	-0.899427000	-0.774247000
H	2.603947000	-2.855064000	1.269936000
H	1.951032000	0.409698000	2.463562000
H	2.062771000	-1.306814000	2.852394000
H	2.453069000	-2.829487000	-1.554507000
H	3.945883000	-3.250365000	-0.716654000
C	0.221443000	3.275112000	0.643100000
H	-0.773323000	3.704518000	0.837726000
H	0.949708000	3.778951000	1.318412000
P	-2.630929000	-0.633568000	-0.658623000
C	-4.218377000	0.245814000	-0.297146000
H	-4.850139000	0.340778000	-1.195535000
H	-4.775128000	-0.301309000	0.478773000
H	-3.989655000	1.249347000	0.091724000
C	-3.240765000	-2.183893000	-1.469957000
H	-3.762389000	-2.806661000	-0.727019000
H	-3.928333000	-1.970019000	-2.304615000

H	-2.383005000	-2.758866000	-1.851318000
C	-1.977232000	0.322254000	-2.097513000
H	-1.120932000	-0.217128000	-2.529687000
H	-2.743073000	0.469725000	-2.876186000
H	-1.613389000	1.298079000	-1.742046000

Vc: E= -2547.927439

C	-1.180941000	3.363646000	-0.249168000
C	-2.191100000	2.783282000	-1.248732000
C	-1.915118000	1.300737000	-1.530999000
C	-1.486273000	0.491748000	-0.295384000
C	-1.383862000	1.207409000	0.995858000
C	-1.222824000	2.555610000	1.016512000
C	-1.533417000	-0.916083000	-0.356888000
C	-1.944429000	-1.707778000	-1.588738000
C	-1.564220000	0.439834000	2.295054000
C	-0.429603000	-0.518307000	2.692127000
Ni	0.416487000	-0.494250000	0.012607000
C	-0.940436000	-1.875726000	0.555646000
C	-0.137523000	-1.609791000	1.677916000
H	0.413169000	-2.469321000	2.081647000
H	0.485005000	0.060715000	2.911014000
H	-0.710944000	-0.995267000	3.652560000
O	-1.295321000	-2.963059000	-1.492464000
H	-3.050660000	-1.829079000	-1.609771000
H	-1.646140000	-1.236384000	-2.537988000
H	-1.133617000	1.217479000	-2.304205000
H	-2.822113000	0.853380000	-1.973992000
H	-2.182890000	3.347886000	-2.196018000
H	-3.200769000	2.898588000	-0.819095000
H	-1.169842000	3.074977000	1.978804000
H	-2.497459000	-0.145726000	2.224576000
H	-1.708871000	1.165756000	3.110483000
H	-0.167390000	3.342863000	-0.699183000
H	-1.401842000	4.423616000	-0.042754000
C	-1.020598000	-3.226062000	-0.128175000
H	-0.086116000	-3.806507000	-0.054226000
H	-1.832986000	-3.832586000	0.328969000
P	2.392375000	0.271995000	-0.252795000
C	3.663328000	-0.059737000	1.055899000
H	4.671373000	0.267509000	0.751696000
H	3.379645000	0.468365000	1.979412000
H	3.679448000	-1.137744000	1.275643000
C	2.717288000	2.066110000	-0.589483000
H	2.356009000	2.663117000	0.261752000
H	3.788857000	2.272238000	-0.747277000
H	2.153130000	2.375919000	-1.481941000
C	3.165107000	-0.529747000	-1.733508000
H	2.562042000	-0.302377000	-2.625287000
H	4.198775000	-0.183316000	-1.897351000
H	3.167234000	-1.621422000	-1.596443000

IVc': E= -2547.855129

C	-2.839374000	-0.184275000	1.476324000
C	-1.819665000	-0.057525000	0.340179000
C	-1.291216000	1.194272000	0.099509000
C	-0.030108000	-0.926216000	-2.260668000
C	-0.212916000	1.784026000	-0.729828000
H	-0.769746000	-0.200577000	-2.608146000

H	0.499905000	-1.408716000	-3.097617000
H	-2.965934000	0.752489000	2.028381000
H	-2.444033000	-0.909767000	2.213404000
C	0.910923000	1.226981000	-1.247330000
H	1.587432000	1.902756000	-1.796501000
C	-4.193709000	-0.694162000	0.973042000
H	-4.568172000	-0.006675000	0.195064000
H	-4.941748000	-0.697637000	1.783259000
C	-0.477312000	-1.840181000	-1.167074000
H	0.421709000	-2.033866000	-0.417332000
H	-0.629838000	-2.883369000	-1.491390000
C	-1.679006000	-1.375996000	-0.358880000
C	-2.696412000	-2.273957000	-0.290282000
H	-2.553885000	-3.239041000	-0.790041000
C	-4.018540000	-2.099132000	0.396830000
H	-4.089011000	-2.853680000	1.206016000
H	-4.838179000	-2.353665000	-0.299682000
C	-1.886629000	2.425294000	0.805755000
H	-2.974845000	2.371987000	0.951537000
H	-1.422467000	2.566543000	1.809781000
Ni	1.206855000	-0.548573000	-0.878695000
O	-1.637117000	3.531040000	-0.031356000
C	-0.466555000	3.289472000	-0.782738000
H	-0.630823000	3.651630000	-1.814051000
H	0.394036000	3.856893000	-0.368996000
P	2.776910000	-0.405607000	0.665736000
C	3.530743000	-1.953862000	1.345211000
H	2.750396000	-2.553836000	1.838267000
H	3.945854000	-2.551615000	0.519040000
H	4.332904000	-1.742197000	2.070869000
C	2.289248000	0.500162000	2.197608000
H	1.483847000	-0.050213000	2.706526000
H	3.138509000	0.625926000	2.888297000
H	1.895588000	1.487313000	1.913383000
C	4.268842000	0.532157000	0.114066000
H	5.018460000	0.621800000	0.916784000
H	4.723428000	0.024250000	-0.750018000
H	3.958061000	1.536758000	-0.208888000

TS4c: E= -2547.851827

C	3.419158000	-0.517923000	-0.580843000
C	2.027822000	-0.197024000	0.005994000
C	1.672582000	1.134025000	-0.062997000
C	0.100236000	-0.215590000	2.420879000
C	0.464519000	1.960595000	0.193173000
H	0.854225000	0.568993000	2.387952000
H	-0.408218000	-0.329417000	3.386060000
H	4.184447000	0.066421000	-0.042231000
H	3.452036000	-0.144502000	-1.620968000
C	-0.759273000	1.646263000	0.686018000
H	-1.445369000	2.501356000	0.808216000
C	3.845929000	-1.985931000	-0.594507000
H	4.189437000	-2.295751000	0.407182000
H	4.700918000	-2.113577000	-1.278960000
C	0.261573000	-1.383934000	1.608355000
H	-1.093407000	-1.678698000	0.987552000
H	0.155145000	-2.367081000	2.083445000
C	1.279056000	-1.392638000	0.496651000
C	1.564353000	-2.619587000	-0.016769000
H	1.005026000	-3.481809000	0.362843000

C	2.668002000	-2.875060000	-0.996564000
H	2.353701000	-2.636120000	-2.032141000
H	2.945677000	-3.941335000	-0.997139000
C	2.704191000	2.140442000	-0.587523000
H	3.699246000	2.028282000	-0.128864000
H	2.843182000	2.010473000	-1.686384000
Ni	-1.193798000	-0.159378000	0.940806000
O	2.234620000	3.431612000	-0.285423000
C	0.825930000	3.374006000	-0.256604000
H	0.448682000	4.149985000	0.429246000
H	0.407348000	3.587490000	-1.266745000
P	-2.786601000	-0.289889000	-0.554202000
C	-2.153891000	-0.517117000	-2.272014000
H	-1.473975000	0.314455000	-2.509950000
H	-1.577117000	-1.452493000	-2.324739000
H	-2.971111000	-0.547181000	-3.010566000
C	-3.880497000	1.185980000	-0.729103000
H	-3.261433000	2.064400000	-0.962462000
H	-4.632024000	1.046986000	-1.522639000
H	-4.393961000	1.377138000	0.225449000
C	-4.015305000	-1.658739000	-0.386014000
H	-4.779026000	-1.631095000	-1.180225000
H	-3.487715000	-2.623604000	-0.421406000
H	-4.513612000	-1.581903000	0.592531000

VIc: E= -2547.863460

C	-3.383191000	1.627530000	0.052758000
C	-2.174270000	0.682857000	0.149072000
C	-2.428356000	-0.651128000	-0.009454000
C	0.320554000	-0.316902000	1.899460000
C	-1.589209000	-1.842625000	-0.209597000
H	-0.554852000	-0.944012000	2.060678000
H	1.143317000	-0.431306000	2.611799000
H	-4.086105000	1.415031000	0.878010000
H	-3.940566000	1.387581000	-0.871034000
C	-0.246755000	-2.014760000	-0.265659000
H	0.042123000	-3.055402000	-0.481208000
C	-3.055276000	3.122627000	0.037663000
H	-2.876563000	3.488122000	1.063205000
H	-3.914757000	3.688499000	-0.357289000
C	0.280563000	0.792048000	1.084099000
H	1.695005000	-1.539164000	-1.154638000
H	1.095226000	1.514176000	1.181217000
C	-0.854523000	1.332282000	0.312615000
C	-0.676522000	2.590260000	-0.186256000
H	0.297800000	3.074431000	-0.060224000
C	-1.792269000	3.383424000	-0.793567000
H	-1.968874000	3.081587000	-1.844896000
H	-1.538410000	4.455102000	-0.817442000
C	-3.865857000	-1.150874000	-0.124036000
H	-4.535202000	-0.741113000	0.650202000
H	-4.298095000	-0.859499000	-1.109991000
Ni	1.172055000	-0.804907000	0.006900000
O	-3.824404000	-2.550740000	0.022131000
C	-2.568370000	-2.992249000	-0.453141000
H	-2.290405000	-3.914598000	0.082145000
H	-2.623115000	-3.235972000	-1.537471000
P	3.237024000	0.034167000	-0.156373000
C	4.510701000	-1.293018000	-0.000907000
H	4.443940000	-1.749162000	0.998751000

H	4.303772000	-2.076055000	-0.744214000
H	5.529417000	-0.900291000	-0.149631000
C	3.908683000	1.315677000	1.006505000
H	3.804383000	0.966100000	2.045531000
H	4.971779000	1.528461000	0.809858000
H	3.340926000	2.253456000	0.904653000
C	3.630839000	0.784412000	-1.795573000
H	4.682935000	1.105545000	-1.858244000
H	3.421391000	0.048124000	-2.584788000
H	2.976812000	1.653812000	-1.963530000

TS5c: E= -2547.860538

C	-3.009728000	1.853266000	-0.149906000
C	-1.934332000	0.780949000	0.110203000
C	-2.322993000	-0.514075000	-0.130940000
C	0.143959000	-0.535964000	2.179628000
C	-1.643931000	-1.812866000	-0.196622000
H	-0.811851000	-1.056987000	2.188146000
H	0.842641000	-0.787702000	2.983914000
H	-3.857766000	1.698566000	0.540584000
H	-3.425664000	1.690500000	-1.160573000
C	-0.329137000	-2.146946000	-0.098416000
H	-0.132855000	-3.228434000	-0.162214000
C	-2.548196000	3.309363000	-0.056242000
H	-2.521459000	3.638846000	0.996203000
H	-3.269532000	3.960772000	-0.576574000
C	0.336917000	0.631566000	1.465489000
H	0.903526000	-1.683746000	-0.950691000
H	1.177204000	1.269480000	1.754473000
C	-0.608486000	1.299522000	0.539990000
C	-0.236814000	2.550328000	0.134698000
H	0.727220000	2.944790000	0.473092000
C	-1.139542000	3.458002000	-0.642240000
H	-1.153917000	3.191196000	-1.717642000
H	-0.785658000	4.499632000	-0.585371000
C	-3.782327000	-0.825845000	-0.461077000
H	-4.503666000	-0.284780000	0.171258000
H	-4.008177000	-0.548922000	-1.517551000
Ni	1.028109000	-0.891378000	0.287696000
O	-3.964190000	-2.206330000	-0.242744000
C	-2.728747000	-2.851787000	-0.467487000
H	-2.660572000	-3.731726000	0.194984000
H	-2.663503000	-3.219964000	-1.515592000
P	3.008579000	-0.088852000	-0.309436000
C	4.263832000	-1.428426000	-0.539209000
H	4.420366000	-1.951377000	0.416783000
H	3.879535000	-2.160070000	-1.265104000
H	5.229763000	-1.032984000	-0.893861000
C	3.952201000	1.098751000	0.757896000
H	4.087093000	0.666066000	1.761300000
H	4.942358000	1.334063000	0.335109000
H	3.384860000	2.035859000	0.866436000
C	3.061021000	0.775485000	-1.942040000
H	4.079302000	1.105364000	-2.204648000
H	2.683366000	0.096065000	-2.720456000
H	2.392996000	1.649549000	-1.906347000

VIIc: E= -2547.915798

C	3.616249000	0.649321000	0.704941000

C	2.279697000	0.312467000	0.055375000
C	1.366917000	1.313477000	-0.106340000
C	-0.202315000	-2.339595000	0.068541000
C	0.003373000	1.328361000	-0.684487000
H	-0.010586000	-2.453157000	1.143458000
H	-0.804473000	-3.144564000	-0.370072000
H	3.517731000	0.540829000	1.803765000
H	3.880025000	1.702177000	0.527127000
C	-0.411145000	0.804346000	-1.910980000
H	-1.312682000	1.210260000	-2.383171000
C	4.756586000	-0.248813000	0.219807000
H	5.698394000	0.025113000	0.722842000
H	4.911226000	-0.082866000	-0.860882000
C	0.726797000	-1.634802000	-0.738586000
H	0.301667000	0.328513000	-2.588785000
H	0.750255000	-1.893713000	-1.808123000
C	2.041544000	-1.119886000	-0.218388000
C	3.017785000	-2.034395000	0.018339000
H	2.770073000	-3.090567000	-0.132038000
C	4.418328000	-1.718523000	0.459681000
H	5.133366000	-2.378157000	-0.063450000
H	4.531078000	-1.965306000	1.535095000
C	1.578527000	2.725628000	0.436372000
H	1.766183000	2.706993000	1.531243000
H	2.434665000	3.243613000	-0.030801000
Ni	-0.841523000	-0.510310000	-0.434973000
O	0.402884000	3.460813000	0.141860000
C	-0.656181000	2.536888000	-0.033785000
H	-1.106306000	2.274165000	0.948808000
H	-1.433878000	3.002730000	-0.657776000
P	-2.931539000	-0.381061000	0.335912000
C	-4.033275000	1.059401000	-0.060073000
H	-3.622936000	1.977826000	0.386007000
H	-4.070754000	1.200708000	-1.151454000
H	-5.059381000	0.910985000	0.314118000
C	-3.161682000	-0.509330000	2.169134000
H	-2.686666000	0.354089000	2.659994000
H	-4.226976000	-0.540142000	2.451051000
H	-2.663420000	-1.420449000	2.532975000
C	-3.980459000	-1.784148000	-0.264736000
H	-3.512883000	-2.735564000	0.028618000
H	-5.003883000	-1.739586000	0.142496000
H	-4.031668000	-1.758236000	-1.364236000

IVd: E= -2776.626482

C	4.751798000	1.514332000	-0.763942000
C	4.907647000	0.730202000	0.536213000
C	3.538583000	0.483820000	1.172202000
C	2.557885000	-0.240468000	0.251717000
C	2.680954000	0.096777000	-1.190499000
C	3.669477000	0.920878000	-1.619778000
C	1.652170000	-1.077126000	0.820477000
C	1.631451000	-1.385485000	2.318350000
C	1.717056000	-0.445334000	-2.230117000
C	0.312368000	0.141215000	-2.192217000
Ni	-0.674597000	0.671641000	-0.705076000
C	0.496610000	-1.879593000	0.233384000
C	-0.793714000	-1.056002000	0.130182000
C	-1.858493000	-1.732997000	-0.650481000
O	-1.711356000	-2.590395000	-1.494811000

H	-1.157884000	-0.820445000	1.141032000
H	0.351806000	1.245266000	-2.442803000
H	-0.332002000	-0.354092000	-2.940340000
H	2.599376000	-1.824983000	2.642526000
H	1.454132000	-0.496245000	2.949372000
H	3.099263000	1.461417000	1.456038000
H	3.669437000	-0.070116000	2.112573000
H	5.566784000	1.262496000	1.241805000
H	5.386770000	-0.240907000	0.319949000
H	3.701442000	1.164292000	-2.687944000
H	0.719009000	-2.331204000	-0.737772000
H	1.650626000	-1.541190000	-2.149913000
H	2.165224000	-0.267743000	-3.225380000
H	4.518142000	2.575577000	-0.541464000
H	5.702036000	1.538739000	-1.325925000
O	0.574978000	-2.300847000	2.535377000
C	0.350943000	-2.975183000	1.308219000
H	-0.646895000	-3.436638000	1.340355000
H	1.102042000	-3.778061000	1.152814000
O	-3.111538000	-1.271248000	-0.325104000
C	-4.186913000	-1.845572000	-1.060212000
H	-4.086997000	-1.641219000	-2.138045000
H	-4.223567000	-2.937568000	-0.924680000
H	-5.107612000	-1.388360000	-0.673273000
P	-2.066399000	1.951187000	0.600111000
C	-1.418811000	3.564660000	1.233169000
H	-0.562355000	3.377391000	1.898847000
H	-1.063432000	4.176852000	0.389794000
H	-2.186338000	4.129645000	1.786682000
C	-2.763303000	1.171351000	2.117158000
H	-3.265719000	0.238386000	1.822877000
H	-1.949790000	0.920476000	2.814516000
H	-3.479242000	1.839229000	2.621825000
C	-3.589811000	2.469978000	-0.308303000
H	-3.311264000	3.051367000	-1.200671000
H	-4.119339000	1.564845000	-0.640281000
H	-4.260996000	3.076248000	0.321137000

TS3d: E= -2776.608876

C	4.383424000	-1.737558000	-0.844030000
C	4.357549000	-0.709863000	0.292562000
C	3.167429000	0.247021000	0.123737000
C	1.862254000	-0.532129000	0.156947000
C	1.848266000	-1.713654000	-0.740983000
C	3.008851000	-2.224340000	-1.213485000
C	0.895091000	-0.241020000	1.101760000
C	1.054337000	0.754101000	2.244491000
C	0.518266000	-2.270446000	-1.220377000
C	-0.480415000	-1.154636000	-1.474663000
Ni	-0.153462000	0.521090000	-0.584938000
C	-0.348756000	-1.074538000	1.451129000
C	-1.410632000	-0.796539000	0.390428000
C	-2.401626000	-1.873704000	0.187917000
O	-2.284346000	-3.023373000	0.565171000
H	-1.942632000	0.158288000	0.539549000
H	-0.034097000	-0.338708000	-2.152378000
H	-1.395730000	-1.487879000	-1.977028000
H	1.828394000	0.398542000	2.961771000
H	1.328453000	1.771417000	1.935156000
H	3.266565000	0.767951000	-0.846793000

H	3.193527000	1.025132000	0.899744000
H	5.306527000	-0.149250000	0.326018000
H	4.261031000	-1.229646000	1.261796000
H	2.959467000	-3.052127000	-1.930565000
H	-0.149129000	-2.153288000	1.502756000
H	0.086898000	-2.997789000	-0.510932000
H	0.686302000	-2.843177000	-2.149892000
H	4.857633000	-1.294311000	-1.742541000
H	5.027869000	-2.594907000	-0.576925000
O	-0.210130000	0.803140000	2.881251000
C	-0.709422000	-0.525087000	2.849850000
H	-1.789871000	-0.498603000	3.051617000
H	-0.221174000	-1.136807000	3.635875000
O	-3.493876000	-1.446058000	-0.495558000
C	-4.491342000	-2.427857000	-0.758192000
H	-4.081518000	-3.262728000	-1.347780000
H	-4.899401000	-2.839109000	0.178276000
H	-5.283023000	-1.919129000	-1.323297000
P	-0.539180000	2.678162000	-0.578497000
C	0.834671000	3.901426000	-0.308326000
H	1.293405000	3.735240000	0.678355000
H	1.613335000	3.750885000	-1.071852000
H	0.477044000	4.943127000	-0.360137000
C	-1.757072000	3.226834000	0.705760000
H	-2.740271000	2.786773000	0.476308000
H	-1.434588000	2.836596000	1.683318000
H	-1.859081000	4.323505000	0.750991000
C	-1.288138000	3.377256000	-2.125846000
H	-0.589275000	3.237100000	-2.964965000
H	-2.211840000	2.827598000	-2.361394000
H	-1.519803000	4.451086000	-2.028307000

Vd: E= -2776.659582

C	-2.396244000	3.868130000	-0.821367000
C	-2.677175000	3.394892000	0.605928000
C	-2.423218000	1.887622000	0.718283000
C	-0.992182000	1.505428000	0.325191000
C	-0.384135000	2.324286000	-0.748674000
C	-1.071519000	3.351807000	-1.314064000
C	-0.276742000	0.538712000	1.086031000
C	-0.745616000	-0.016562000	2.426477000
C	1.023407000	2.037833000	-1.266511000
C	1.403727000	0.556430000	-1.407589000
Ni	-1.140954000	-0.331061000	-0.435890000
C	1.255766000	0.428440000	1.161898000
C	1.946265000	-0.094193000	-0.108575000
C	3.450607000	0.115869000	-0.007591000
O	4.012922000	0.877699000	0.743399000
H	1.789058000	-1.181360000	-0.199324000
H	0.510433000	-0.024173000	-1.723789000
H	2.148714000	0.427310000	-2.208595000
H	-0.750910000	0.778317000	3.209256000
H	-1.741841000	-0.479308000	2.413997000
H	-3.150749000	1.369554000	0.059566000
H	-2.648078000	1.543047000	1.738373000
H	-3.712705000	3.633228000	0.900888000
H	-2.010763000	3.928751000	1.306174000
H	-0.616375000	3.881114000	-2.158704000
H	1.683369000	1.419567000	1.377494000
H	1.762902000	2.543005000	-0.619577000

H	1.118295000	2.525938000	-2.248876000
H	-3.214902000	3.539857000	-1.493473000
H	-2.406069000	4.971675000	-0.873447000
O	0.205614000	-1.013781000	2.753688000
C	1.473434000	-0.477780000	2.404420000
H	2.159263000	-1.319660000	2.220083000
H	1.882248000	0.113166000	3.246340000
O	4.115205000	-0.657561000	-0.891592000
C	5.534462000	-0.510876000	-0.920025000
H	5.818255000	0.520768000	-1.178836000
H	5.973787000	-0.753764000	0.059503000
H	5.900225000	-1.208118000	-1.684193000
P	-1.662058000	-2.407692000	-0.589967000
C	-3.270092000	-2.806249000	0.243093000
H	-3.228019000	-2.473677000	1.291145000
H	-4.087403000	-2.261181000	-0.253232000
H	-3.491174000	-3.886199000	0.218742000
C	-0.487668000	-3.513306000	0.314893000
H	0.465805000	-3.554537000	-0.234134000
H	-0.291448000	-3.075517000	1.305848000
H	-0.884760000	-4.536365000	0.420726000
C	-1.870077000	-3.303990000	-2.201403000
H	-2.662408000	-2.820061000	-2.793330000
H	-0.933527000	-3.241057000	-2.776336000
H	-2.131564000	-4.365036000	-2.054312000

IVd': E= -2776.613908

C	-4.026468000	0.132249000	0.288292000
C	-2.535510000	0.178028000	-0.121120000
C	-1.890733000	1.326909000	0.252217000
C	-0.193140000	0.085727000	-2.135766000
C	-0.464192000	1.907307000	0.177430000
H	-0.766667000	1.010340000	-2.092514000
H	0.454270000	0.035651000	-3.024476000
H	-4.551883000	0.988300000	-0.167855000
H	-4.087036000	0.304235000	1.377929000
C	0.764820000	1.027335000	0.379530000
C	-4.800096000	-1.147210000	-0.026199000
H	-5.080925000	-1.176972000	-1.092765000
H	-5.738792000	-1.159188000	0.552286000
C	-0.912885000	-1.157674000	-1.804609000
H	-0.095283000	-1.918892000	-1.354587000
H	-1.191832000	-1.803935000	-2.658210000
C	-2.052765000	-1.073885000	-0.792083000
C	-2.691095000	-2.246138000	-0.549661000
H	-2.325478000	-3.147552000	-1.055410000
C	-3.932989000	-2.368932000	0.280302000
H	-3.698889000	-2.400567000	1.362897000
H	-4.459837000	-3.308972000	0.050880000
C	-2.699992000	2.436978000	0.934954000
H	-3.576981000	2.761530000	0.349646000
H	-3.089097000	2.079062000	1.914712000
Ni	0.727095000	-0.641804000	-0.618273000
O	-1.855566000	3.549682000	1.113315000
C	-0.545687000	3.041103000	1.218285000
H	0.169677000	3.852132000	1.018368000
H	-0.350267000	2.644206000	2.238762000
P	2.100313000	-1.944740000	0.612420000
C	1.747983000	-3.756808000	0.741338000
H	0.783224000	-3.909104000	1.249330000

H	1.672412000	-4.189919000	-0.268019000
H	2.534785000	-4.289435000	1.299884000
C	2.417659000	-1.468412000	2.363009000
H	1.479245000	-1.493264000	2.937686000
H	3.149870000	-2.142590000	2.835407000
H	2.808583000	-0.440369000	2.354225000
C	3.794988000	-1.906627000	-0.113833000
H	4.497651000	-2.527676000	0.464903000
H	3.766616000	-2.265856000	-1.153859000
H	4.129213000	-0.858510000	-0.104786000
H	-0.375043000	2.412106000	-0.797319000
H	0.805184000	0.662204000	1.418030000
C	2.077583000	1.614314000	0.054173000
O	3.150283000	1.279076000	0.541228000
O	2.024630000	2.579000000	-0.903918000
C	3.269086000	3.109556000	-1.338574000
H	3.844042000	3.524055000	-0.496298000
H	3.884511000	2.334310000	-1.823294000
H	3.031198000	3.901299000	-2.061320000

TS4d: E= -2776.613574

C	-3.988329000	0.172565000	0.310117000
C	-2.501165000	0.221211000	-0.107734000
C	-1.842928000	1.351145000	0.295855000
C	-0.178880000	0.120120000	-2.176120000
C	-0.410838000	1.918631000	0.221735000
H	-0.642414000	1.089068000	-2.018240000
H	0.480583000	0.064329000	-3.050506000
H	-4.500780000	1.069411000	-0.075876000
H	-4.038082000	0.263857000	1.410516000
C	0.812963000	1.023846000	0.393027000
C	-4.790411000	-1.062071000	-0.097557000
H	-5.060996000	-1.009049000	-1.165948000
H	-5.734894000	-1.089781000	0.470608000
C	-0.883636000	-1.063560000	-1.803687000
H	0.175068000	-1.959813000	-1.221873000
H	-1.006245000	-1.862590000	-2.547160000
C	-2.030546000	-1.007606000	-0.828994000
C	-2.698835000	-2.179770000	-0.663840000
H	-2.329254000	-3.061117000	-1.199687000
C	-3.960418000	-2.325273000	0.129443000
H	-3.747376000	-2.446439000	1.210309000
H	-4.506409000	-3.231259000	-0.179052000
C	-2.634648000	2.447039000	1.020188000
H	-3.518769000	2.791744000	0.457894000
H	-3.010069000	2.064494000	1.996138000
Ni	0.683686000	-0.688551000	-0.585559000
O	-1.780957000	3.550025000	1.212617000
C	-0.472964000	3.031240000	1.286568000
H	0.245251000	3.841959000	1.095084000
H	-0.265629000	2.610556000	2.294917000
P	2.021323000	-1.949465000	0.663504000
C	1.555691000	-3.716362000	0.935720000
H	0.602876000	-3.762412000	1.485167000
H	1.410412000	-4.210368000	-0.036775000
H	2.325972000	-4.259636000	1.506732000
C	2.475570000	-1.388286000	2.358121000
H	1.576061000	-1.325905000	2.989531000
H	3.197283000	-2.077653000	2.824663000
H	2.920367000	-0.387069000	2.262502000

C	3.662608000	-2.067365000	-0.166187000
H	4.356330000	-2.706979000	0.402966000
H	3.539051000	-2.476694000	-1.180012000
H	4.069942000	-1.047694000	-0.236328000
H	-0.327094000	2.445974000	-0.741933000
H	0.891216000	0.691878000	1.439316000
C	2.116449000	1.577653000	-0.005259000
O	3.208440000	1.219908000	0.420255000
O	2.035489000	2.537050000	-0.970009000
C	3.267695000	3.035596000	-1.471683000
H	3.891602000	3.448039000	-0.663864000
H	3.843607000	2.242232000	-1.975203000
H	3.011289000	3.823956000	-2.191964000

VId: E= -2776.621012

C	-3.997393000	-1.300435000	-0.093711000
C	-2.580740000	-0.714355000	-0.216783000
C	-2.485894000	0.634274000	-0.312152000
C	0.184726000	-0.659131000	-1.831171000
C	-1.311637000	1.602725000	-0.268193000
H	-0.477758000	0.144288000	-2.147355000
H	1.021154000	-0.882994000	-2.497900000
H	-4.577790000	-1.056135000	-1.000946000
H	-4.514741000	-0.777386000	0.730730000
C	-0.119101000	1.267270000	0.636078000
H	-0.474389000	1.003177000	1.644108000
C	-4.070621000	-2.805878000	0.171378000
H	-3.935344000	-3.369398000	-0.767433000
H	-5.068791000	-3.067026000	0.558951000
C	-0.190989000	-1.575285000	-0.874688000
H	1.877172000	0.291010000	1.202781000
H	0.406422000	-2.489758000	-0.796390000
C	-1.464967000	-1.692195000	-0.144436000
C	-1.649822000	-2.850483000	0.548802000
H	-0.828408000	-3.573025000	0.595873000
C	-2.968148000	-3.228551000	1.151672000
H	-3.121062000	-2.722210000	2.125220000
H	-3.004503000	-4.310122000	1.356820000
C	-3.736878000	1.503954000	-0.380383000
H	-4.389311000	1.263186000	-1.237949000
H	-4.351913000	1.366337000	0.537362000
Ni	1.107702000	-0.187511000	0.049104000
O	-3.303781000	2.839312000	-0.499777000
C	-2.045139000	2.904693000	0.139560000
H	-1.526141000	3.812464000	-0.197226000
H	-2.158115000	2.950346000	1.243620000
P	3.019418000	-1.322172000	-0.049009000
C	4.477580000	-0.196702000	-0.131766000
H	4.408765000	0.423734000	-1.038367000
H	4.461104000	0.474071000	0.739083000
H	5.424850000	-0.758997000	-0.150177000
C	3.394449000	-2.511840000	-1.422786000
H	3.364647000	-1.984069000	-2.388552000
H	4.389097000	-2.970580000	-1.303232000
H	2.639784000	-3.313215000	-1.449382000
C	3.377029000	-2.347744000	1.442290000
H	4.372826000	-2.815493000	1.384351000
H	3.319841000	-1.710517000	2.336465000
H	2.614906000	-3.136228000	1.538888000
H	-0.959114000	1.785457000	-1.298104000

C	0.795059000	2.434024000	0.805136000
O	1.238560000	2.885719000	1.837845000
O	1.127296000	2.996297000	-0.405267000
C	1.995326000	4.118509000	-0.349911000
H	1.557920000	4.935841000	0.245398000
H	2.963691000	3.853850000	0.104685000
H	2.144647000	4.448545000	-1.387115000

TS5d: E= -2776.607742

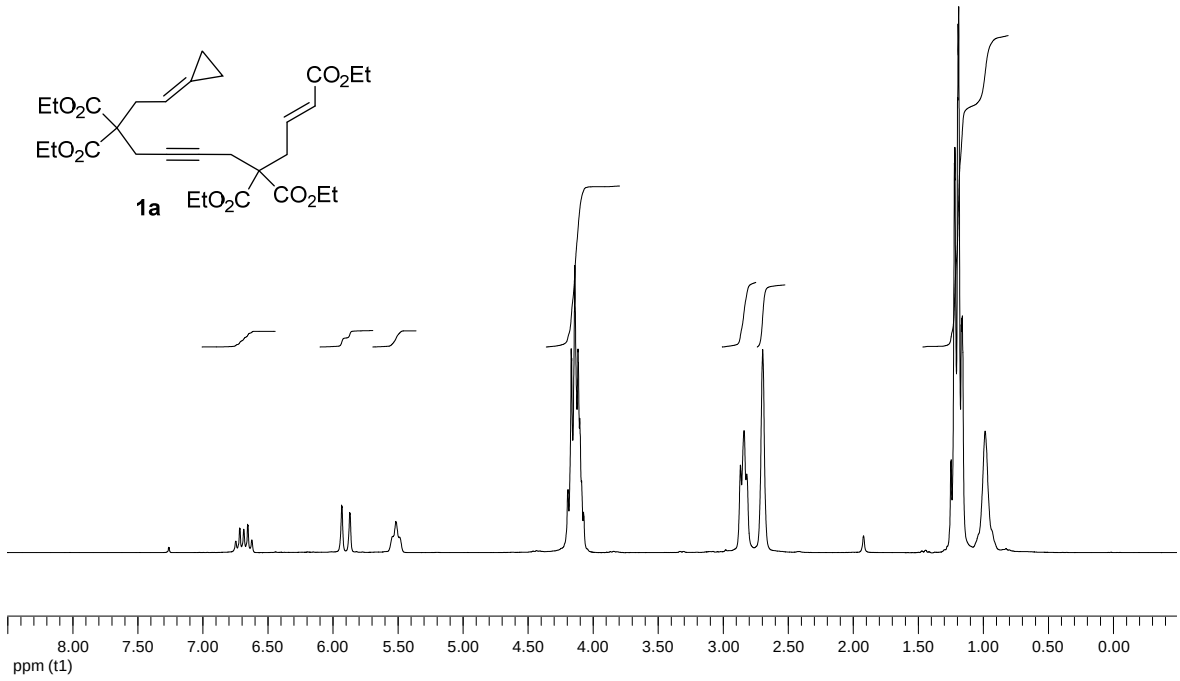
C	3.790327000	-1.177840000	0.047540000
C	2.392683000	-0.544654000	0.217810000
C	2.311681000	0.770597000	-0.120872000
C	-0.112862000	0.079702000	2.096045000
C	1.190336000	1.815186000	-0.190472000
H	0.600450000	0.900210000	2.080910000
H	-0.893658000	0.148916000	2.859785000
H	4.492865000	-0.701738000	0.754418000
H	4.165655000	-0.914699000	-0.956788000
C	-0.191982000	1.491638000	-0.775640000
H	-0.132650000	1.604935000	-1.872659000
C	3.870592000	-2.698608000	0.196004000
H	3.920397000	-2.982168000	1.260679000
H	4.795948000	-3.066886000	-0.277048000
C	0.181496000	-1.161556000	1.551504000
H	-0.918791000	0.260531000	-1.212138000
H	-0.346549000	-2.041074000	1.935080000
C	1.324257000	-1.493486000	0.670283000
C	1.438039000	-2.804494000	0.308667000
H	0.673918000	-3.507594000	0.655911000
C	2.627323000	-3.351359000	-0.419485000
H	2.585452000	-3.121857000	-1.502710000
H	2.663656000	-4.448922000	-0.335298000
C	3.576978000	1.535609000	-0.512882000
H	4.398156000	1.425944000	0.214289000
H	3.963080000	1.167403000	-1.490643000
Ni	-0.881381000	-0.228320000	0.154180000
O	3.238433000	2.902319000	-0.590852000
C	1.883931000	2.954975000	-0.969363000
H	1.481633000	3.948401000	-0.721826000
H	1.768166000	2.793601000	-2.063939000
P	-2.528715000	-1.576597000	-0.352213000
C	-4.105301000	-0.611720000	-0.290795000
H	-4.290556000	-0.290600000	0.745760000
H	-3.986518000	0.294983000	-0.902553000
H	-4.966918000	-1.202042000	-0.643249000
C	-2.936945000	-3.041955000	0.710124000
H	-3.034400000	-2.721513000	1.759015000
H	-3.874487000	-3.530270000	0.397564000
H	-2.120516000	-3.779077000	0.655998000
C	-2.610037000	-2.335771000	-2.037103000
H	-3.536300000	-2.914472000	-2.187392000
H	-2.555656000	-1.536390000	-2.791315000
H	-1.743373000	-2.998626000	-2.183160000
H	1.037157000	2.199256000	0.827366000
C	-1.321028000	2.383427000	-0.353932000
O	-2.398776000	2.441357000	-0.913065000
O	-1.044456000	3.144183000	0.735741000
C	-2.105991000	3.961775000	1.216085000
H	-2.461436000	4.650223000	0.434395000
H	-2.958664000	3.347075000	1.545198000

H	-1.699251000	4.526700000	2.064792000

VIId: E= -2776.638573

C	3.333056000	2.157743000	-0.358129000
C	2.260390000	1.047864000	-0.284654000
C	2.724351000	-0.196824000	-0.001875000
C	-0.066959000	-0.368108000	-1.991641000
C	2.077159000	-1.548755000	0.307442000
H	0.831177000	-0.980046000	-1.913611000
H	-0.678898000	-0.571912000	-2.878421000
H	3.898623000	2.055923000	-1.302189000
H	4.067274000	1.979463000	0.444104000
C	0.803439000	-1.615984000	1.167765000
H	0.943547000	-2.390394000	1.947684000
C	2.820380000	3.596972000	-0.209791000
H	2.548518000	4.019020000	-1.191351000
H	3.622303000	4.233962000	0.199354000
C	-0.148062000	0.902453000	-1.402252000
H	0.623210000	-0.672988000	1.702585000
H	-0.816689000	1.636748000	-1.864719000
C	0.861405000	1.539609000	-0.510691000
C	0.549742000	2.757370000	0.009366000
H	-0.441162000	3.178652000	-0.190717000
C	1.571758000	3.621636000	0.685838000
H	1.833407000	3.244787000	1.693646000
H	1.194749000	4.647339000	0.821089000
C	4.230517000	-0.456003000	0.104282000
H	4.789916000	-0.155073000	-0.797213000
H	4.664493000	0.111169000	0.957666000
Ni	-1.266723000	-0.375920000	-0.387068000
O	4.403449000	-1.843584000	0.294291000
C	3.253756000	-2.292205000	0.968836000
H	3.180254000	-3.385399000	0.866983000
H	3.301465000	-2.046159000	2.052976000
P	-3.104279000	0.795203000	0.258058000
C	-4.604921000	-0.278978000	0.182148000
H	-4.844319000	-0.505579000	-0.868363000
H	-4.368937000	-1.225436000	0.690511000
H	-5.481121000	0.191614000	0.657425000
C	-3.709261000	2.364530000	-0.513374000
H	-3.892625000	2.200379000	-1.586665000
H	-4.639307000	2.723206000	-0.043104000
H	-2.940132000	3.146241000	-0.418165000
C	-3.036932000	1.232304000	2.050620000
H	-3.991712000	1.637204000	2.423950000
H	-2.775492000	0.320619000	2.608449000
H	-2.238452000	1.972090000	2.214675000
H	1.884639000	-2.077701000	-0.639507000
C	-0.461238000	-1.993780000	0.418123000
O	-1.619440000	-1.760745000	0.917006000
O	-0.249718000	-3.126115000	-0.340053000
C	-1.377816000	-3.688765000	-0.976671000
H	-2.170498000	-3.936946000	-0.252709000
H	-1.797342000	-2.994222000	-1.727676000
H	-1.033377000	-4.601760000	-1.481647000

NMR Spectra


EtO2C
EtO2C
CO2Et
EtO2C
CO2Et
1a
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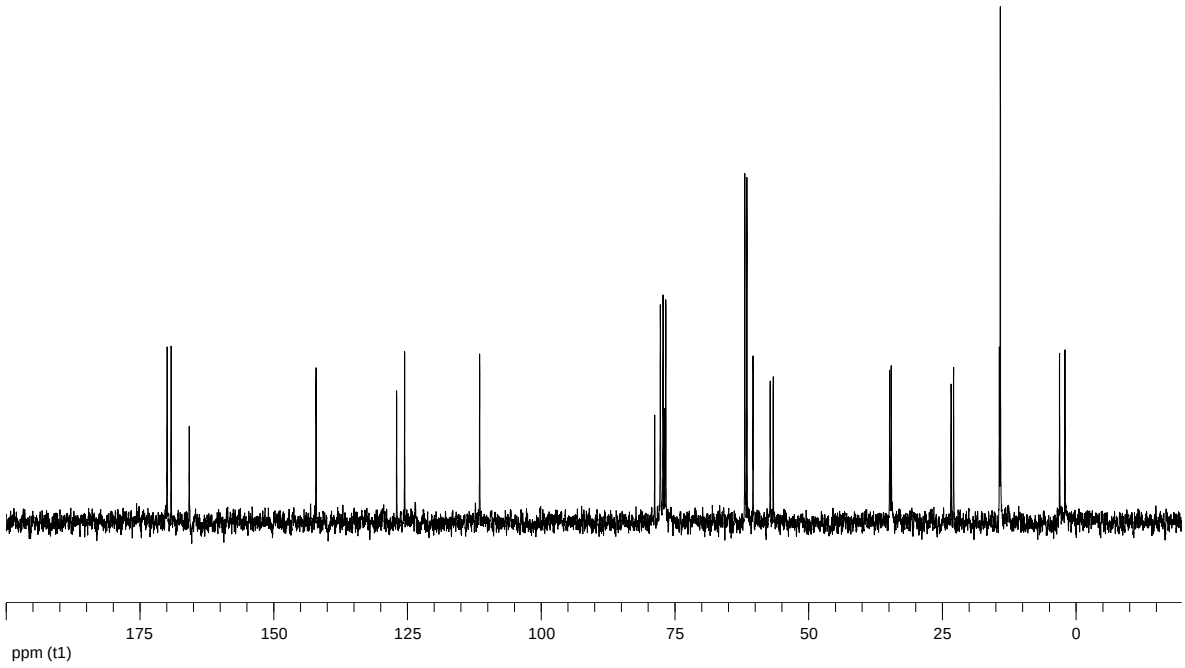
ppm (t1)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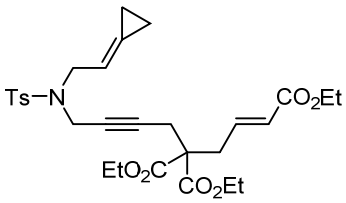
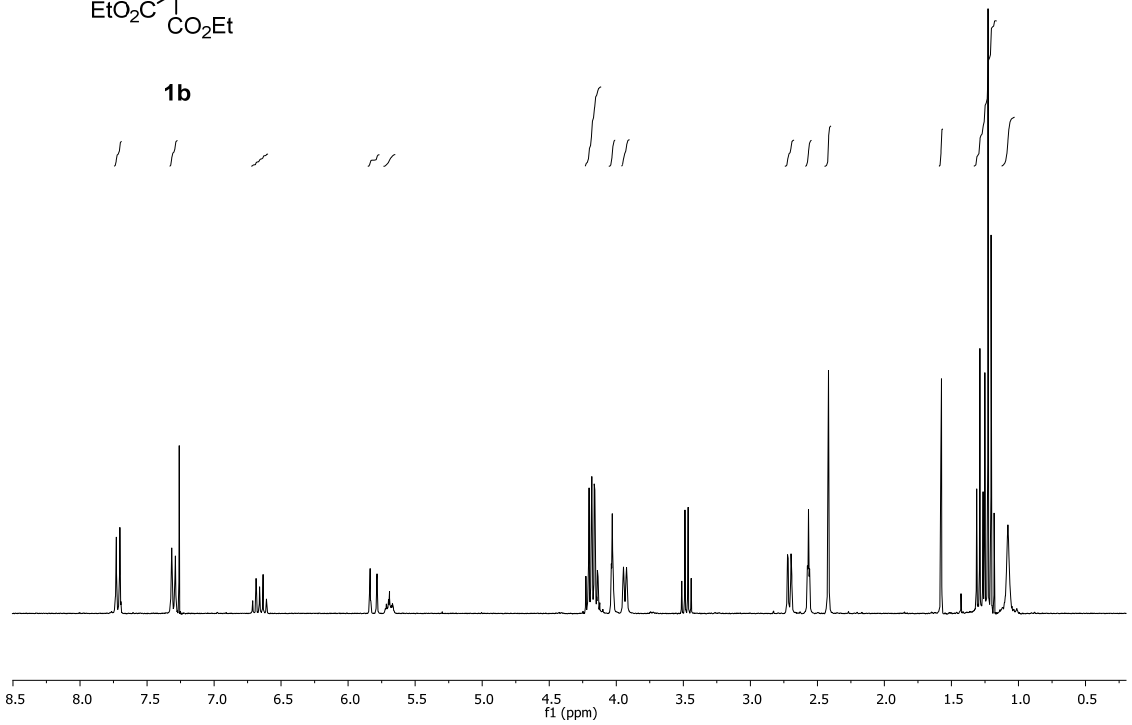

Ts—N
CO2Et
EtO2C
CO2Et

1b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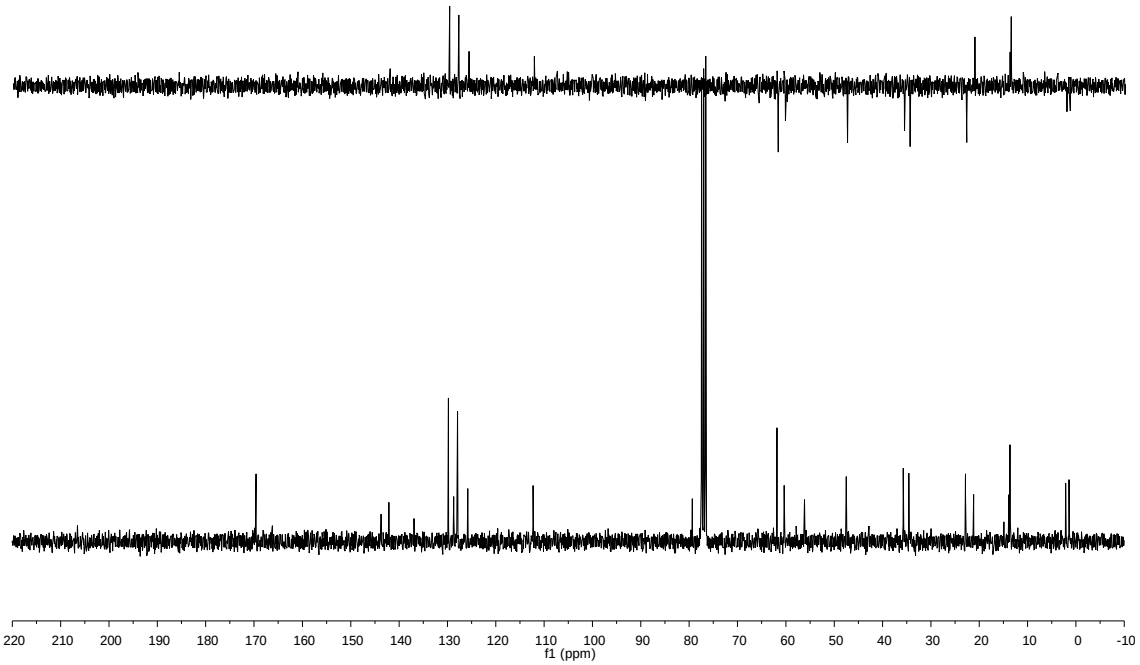
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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180
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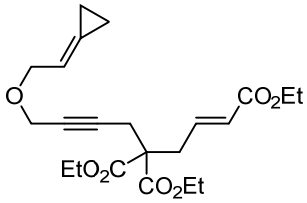
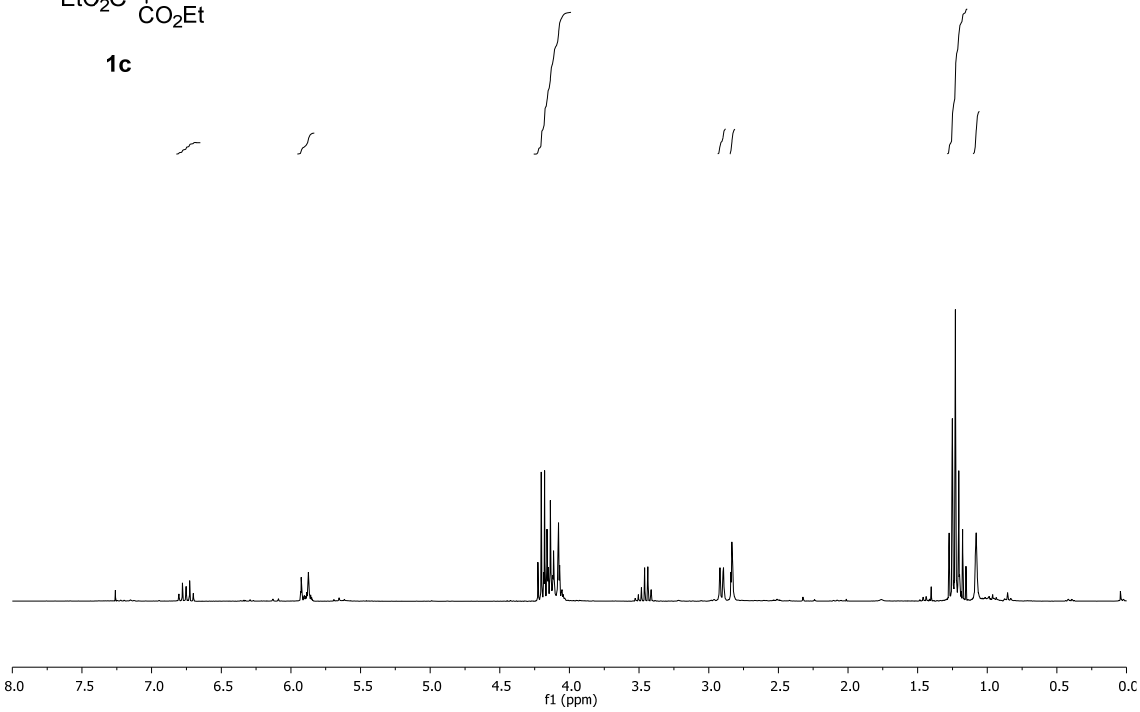
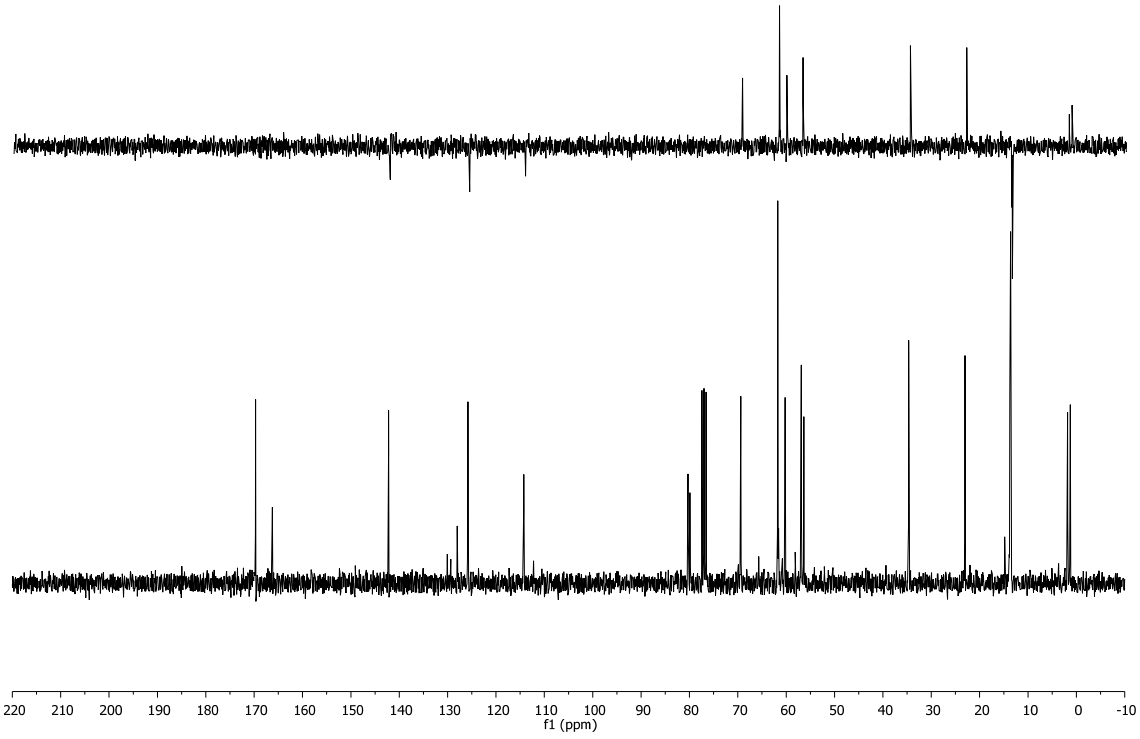
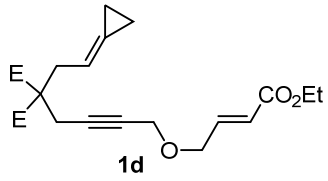
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
CO2Et
EtO2C
CO2Et

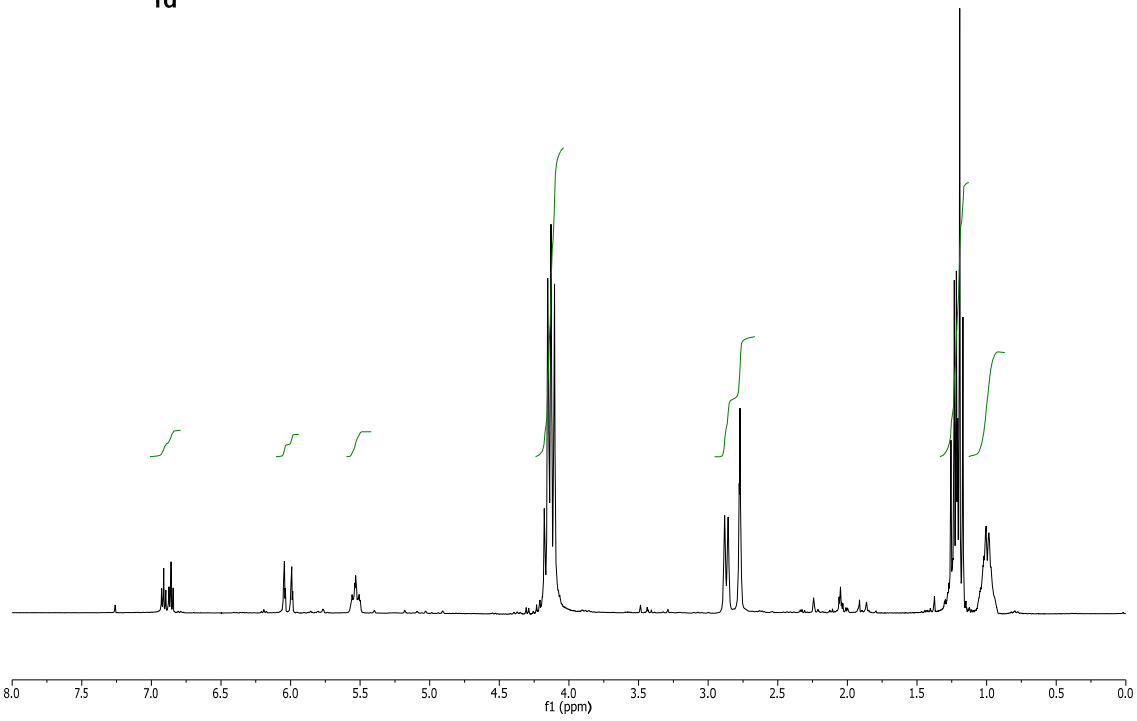
1c

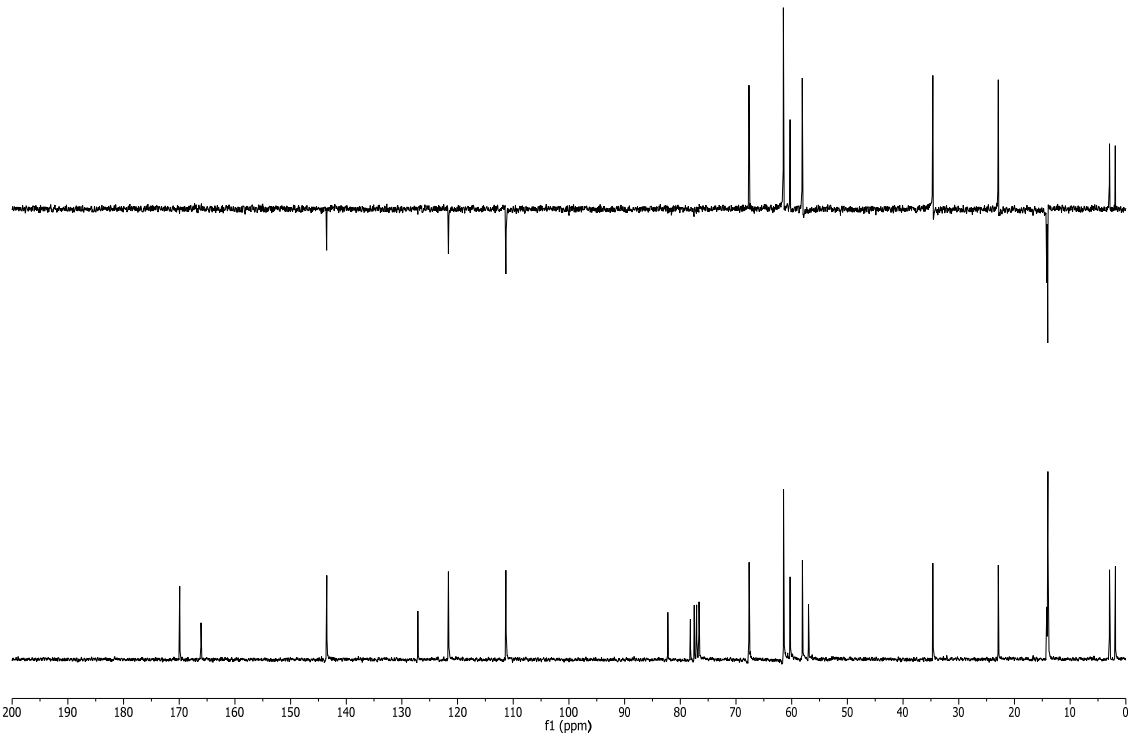

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

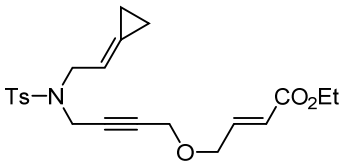

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


E
E
CO2Et
O

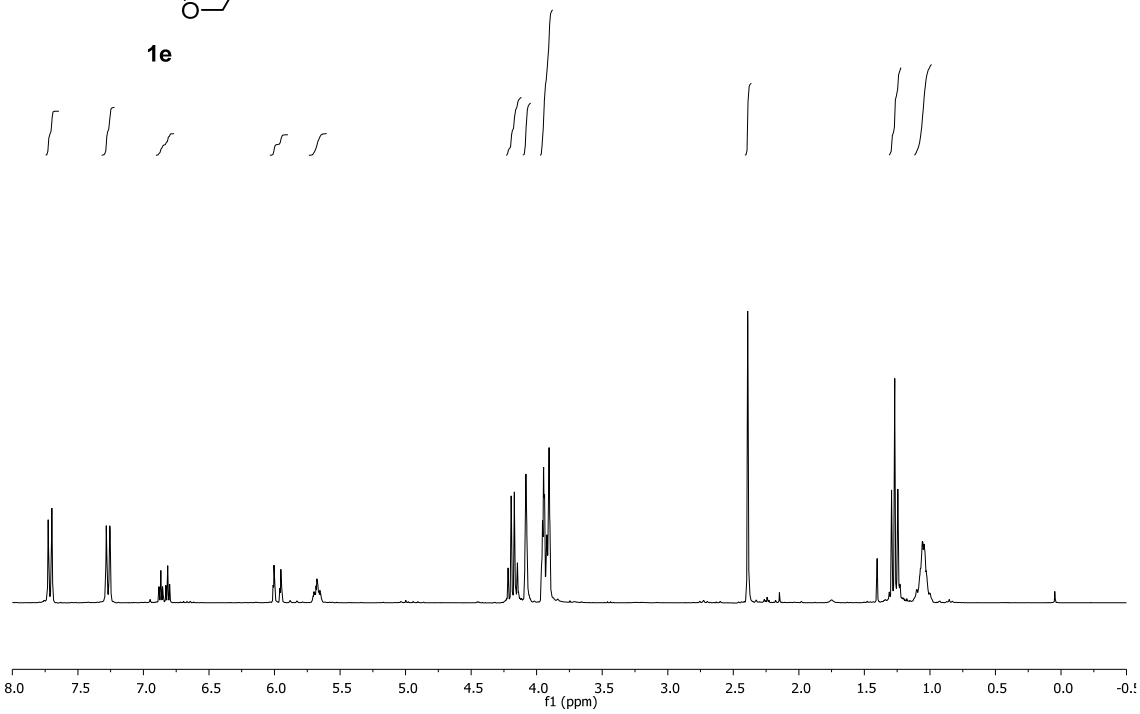
1d

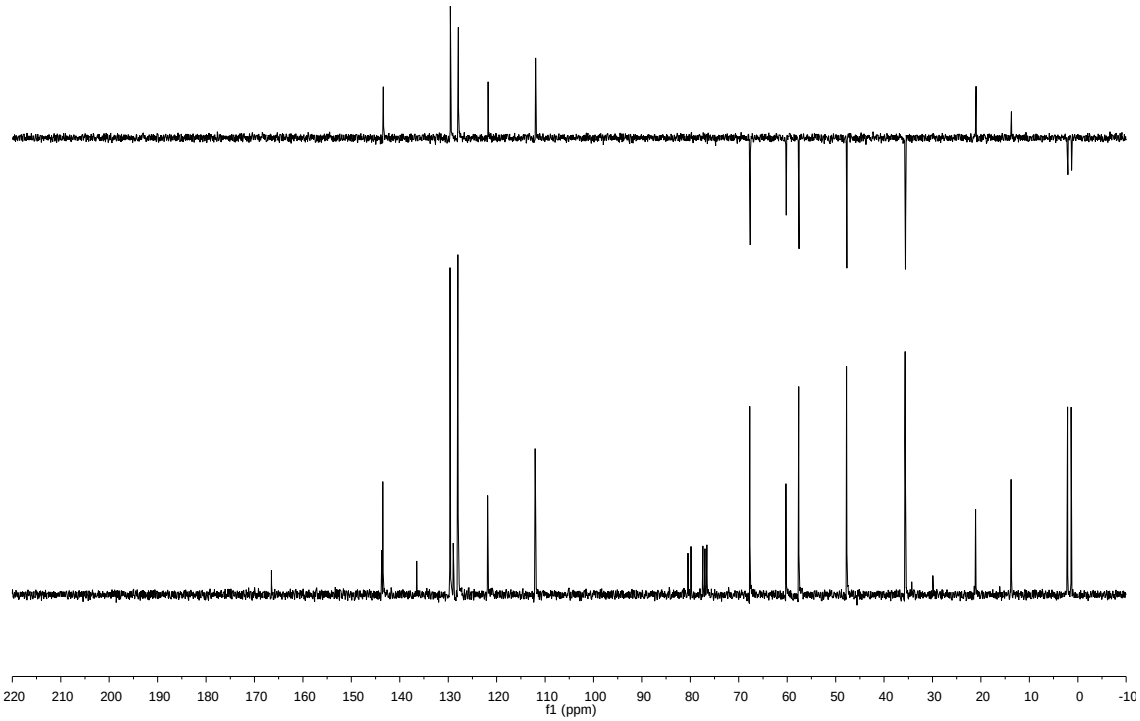

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

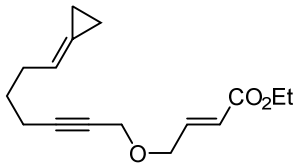

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts–N
CO2Et
O

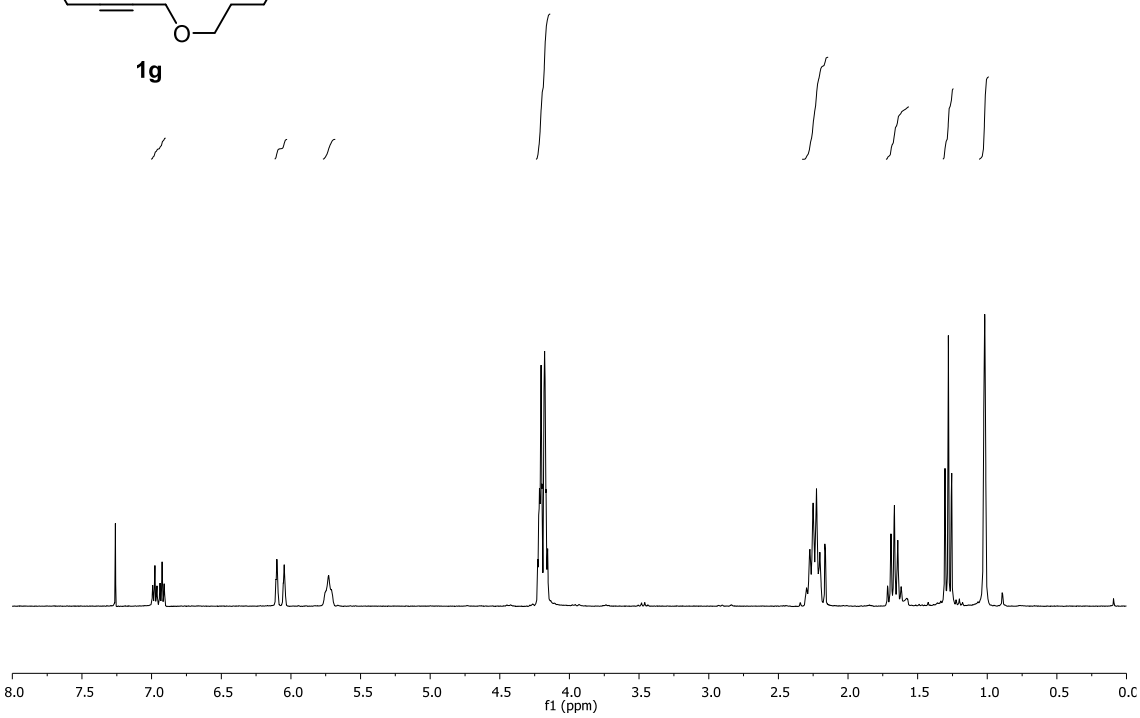
1e

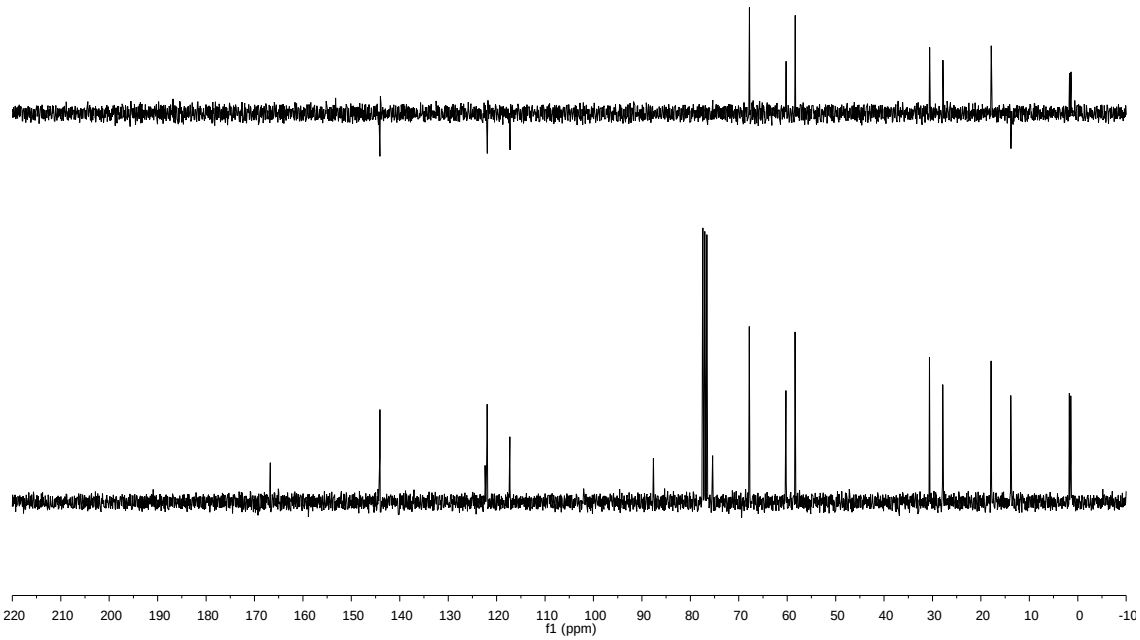

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

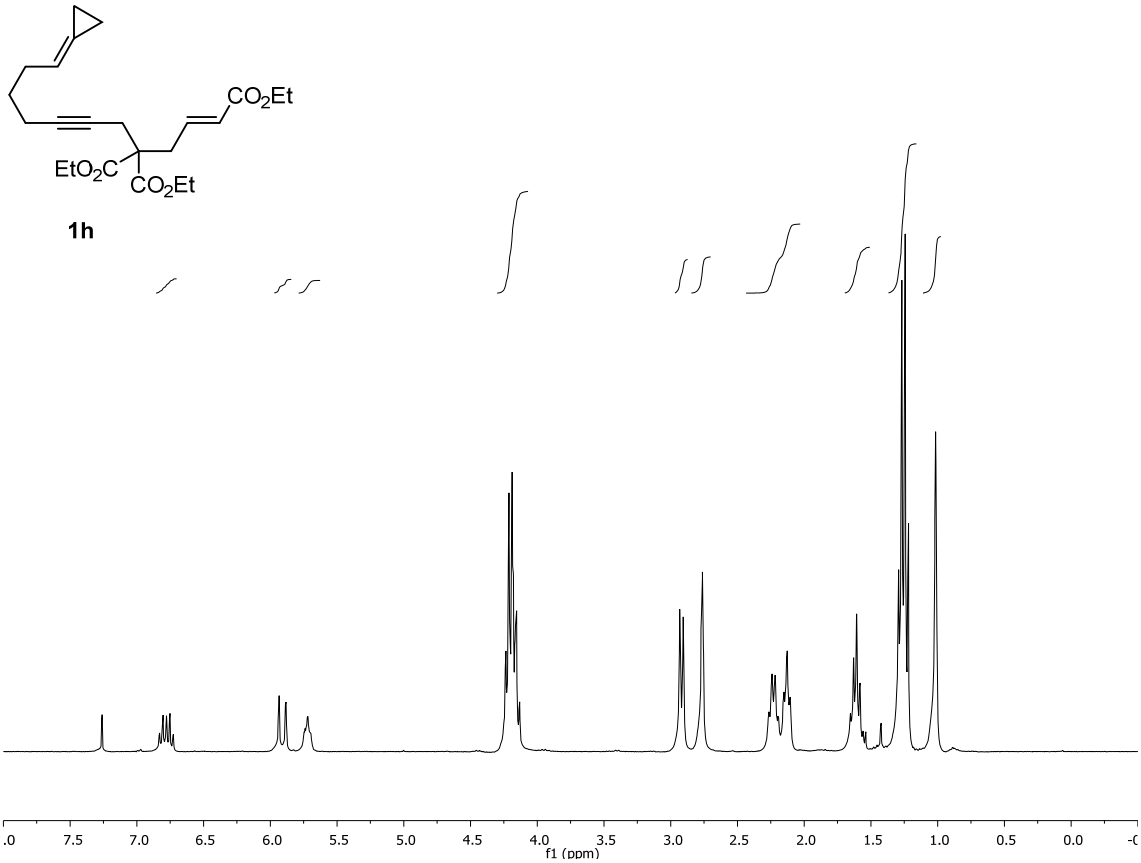

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

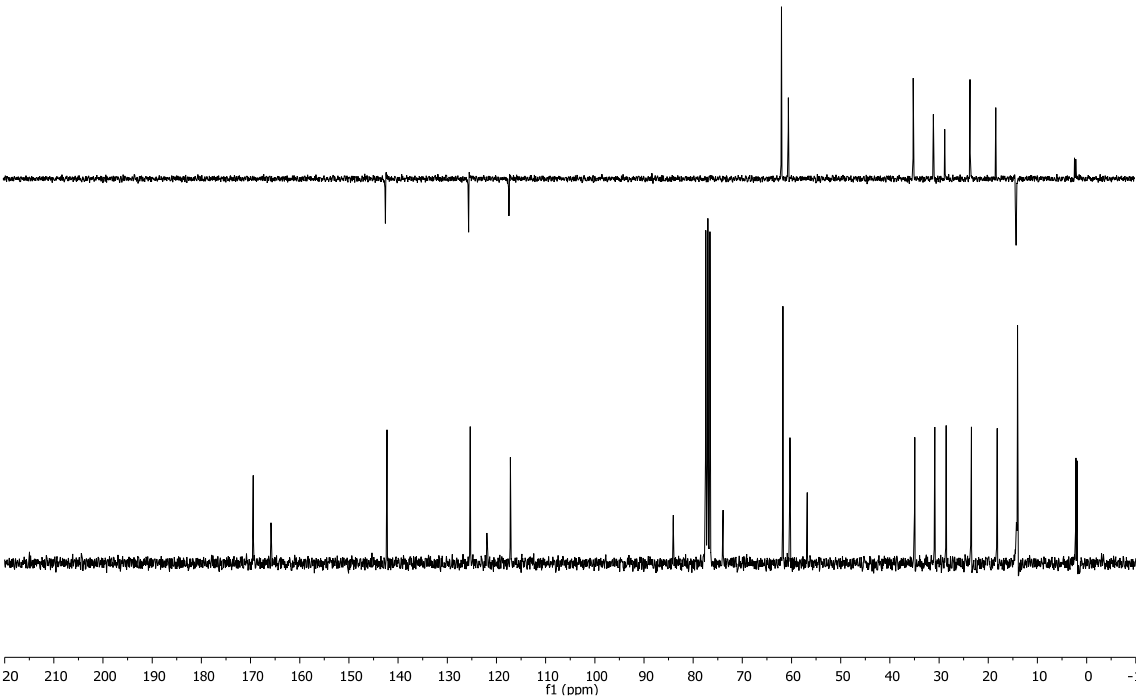

CO2Et
O

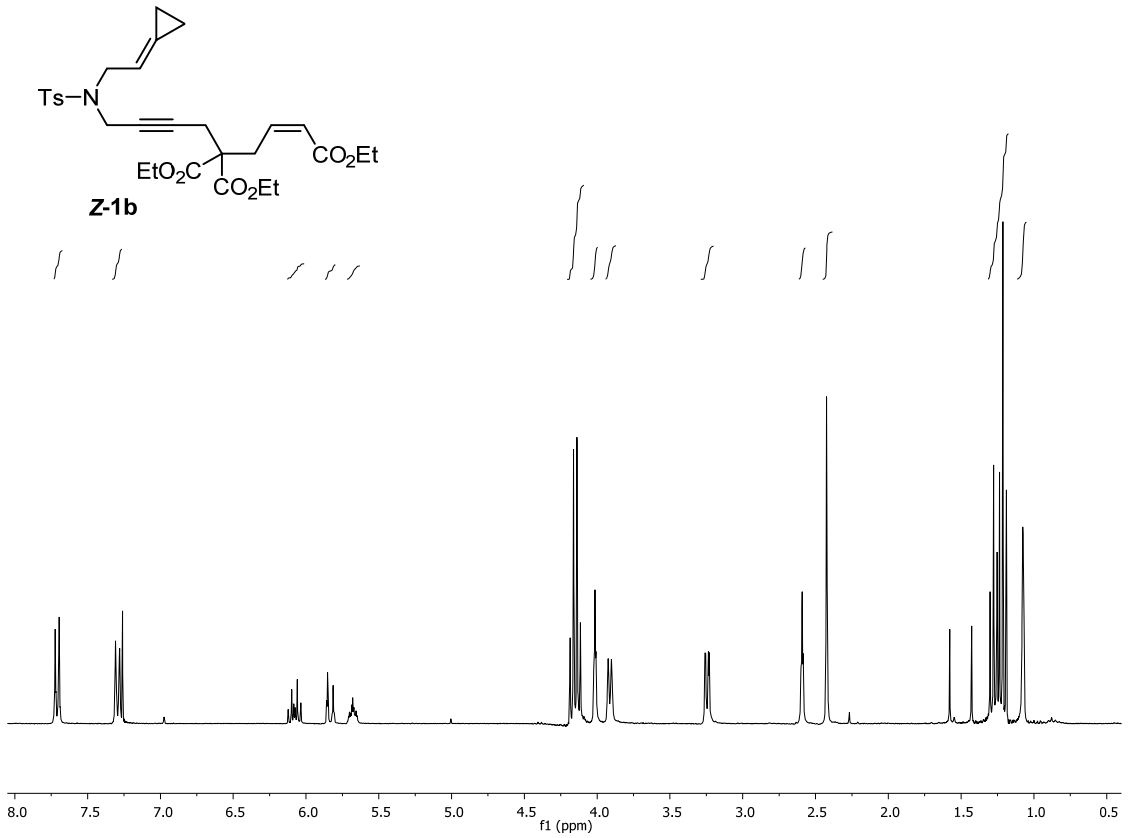
1g

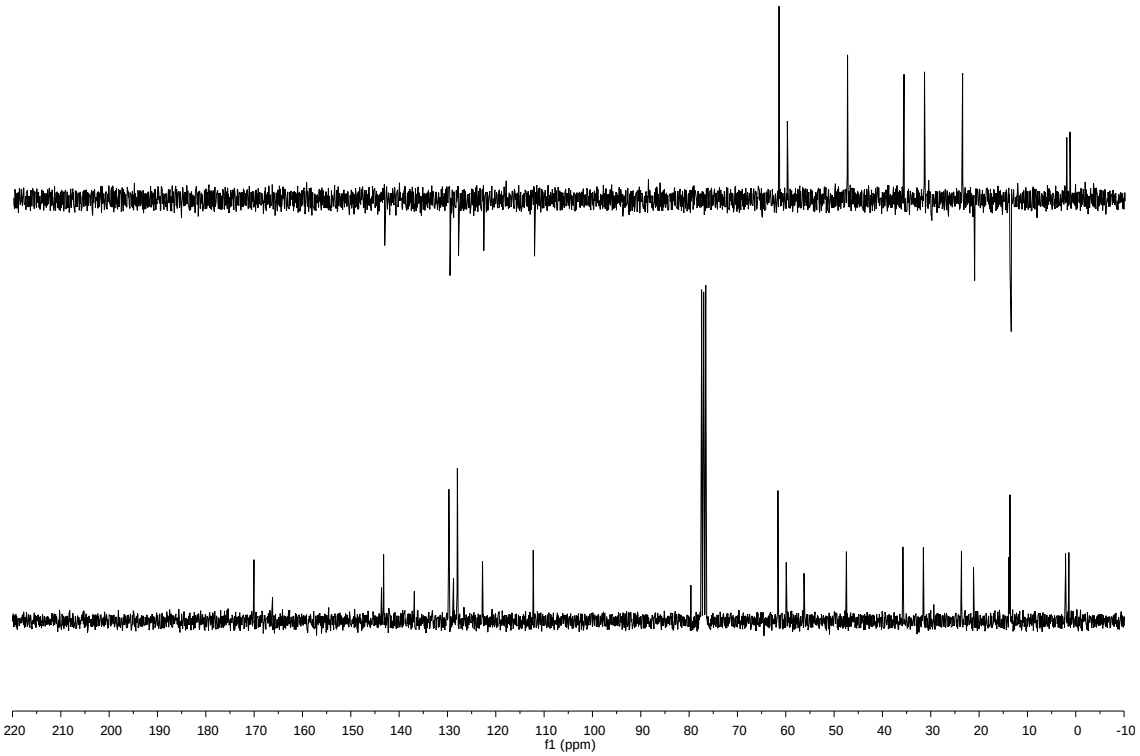

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

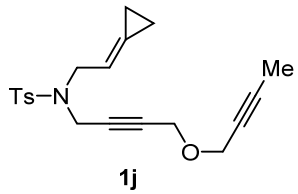

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


CO2Et
EtO2C
CO2Et
1h
f1 (ppm)

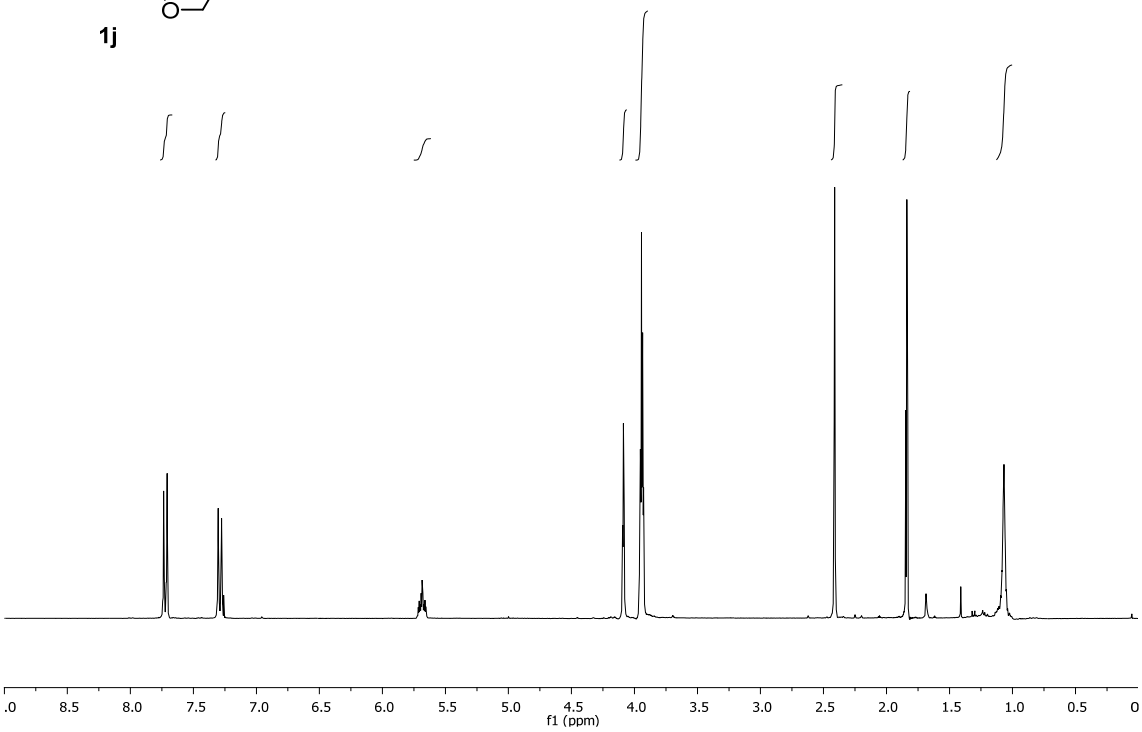

f1 (ppm)

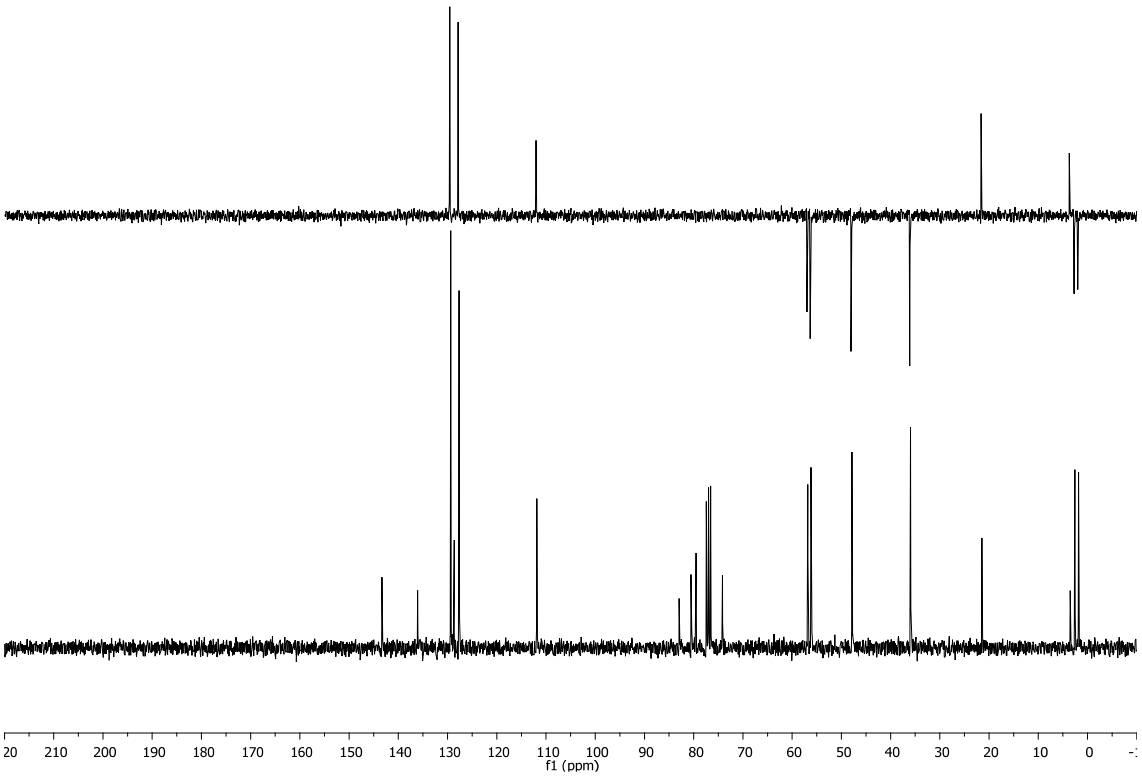

Ts–N
EtO2C
CO2Et
CO2Et
Z-1b
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

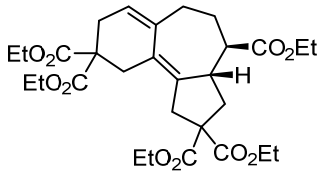

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Ts–N
O

1j

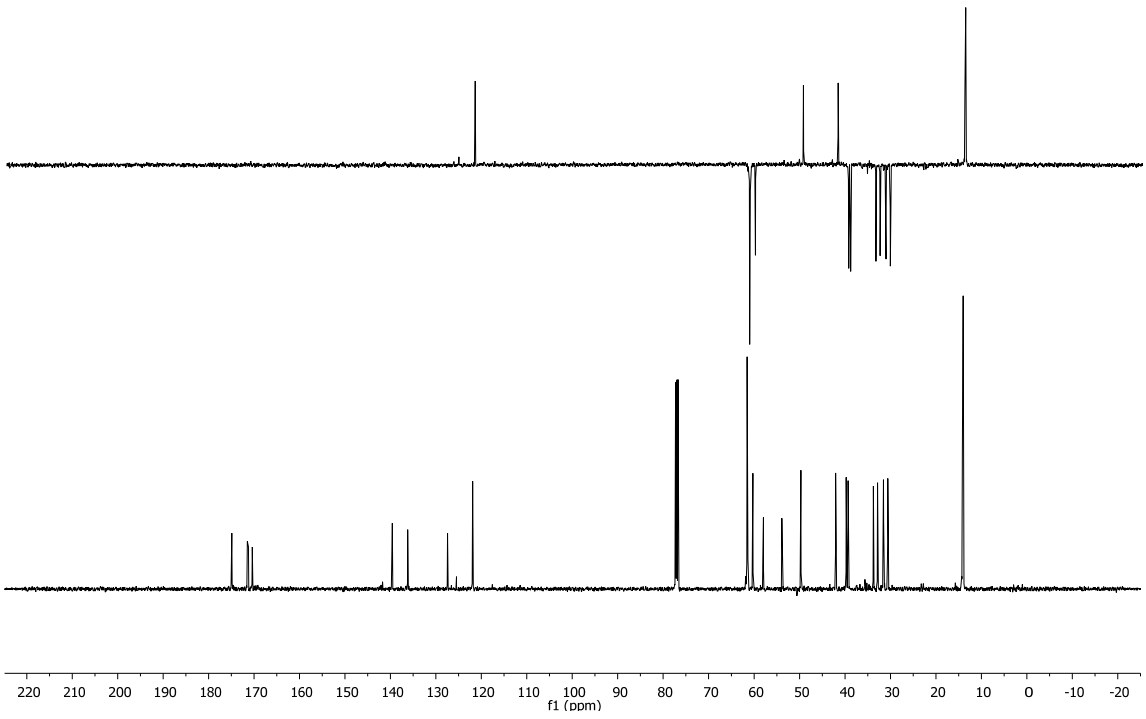

.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

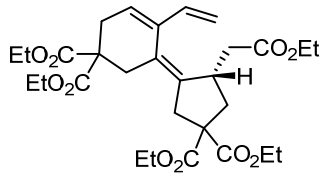

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


EtO2C
EtO2C
CO2Et
H
EtO2C
CO2Et

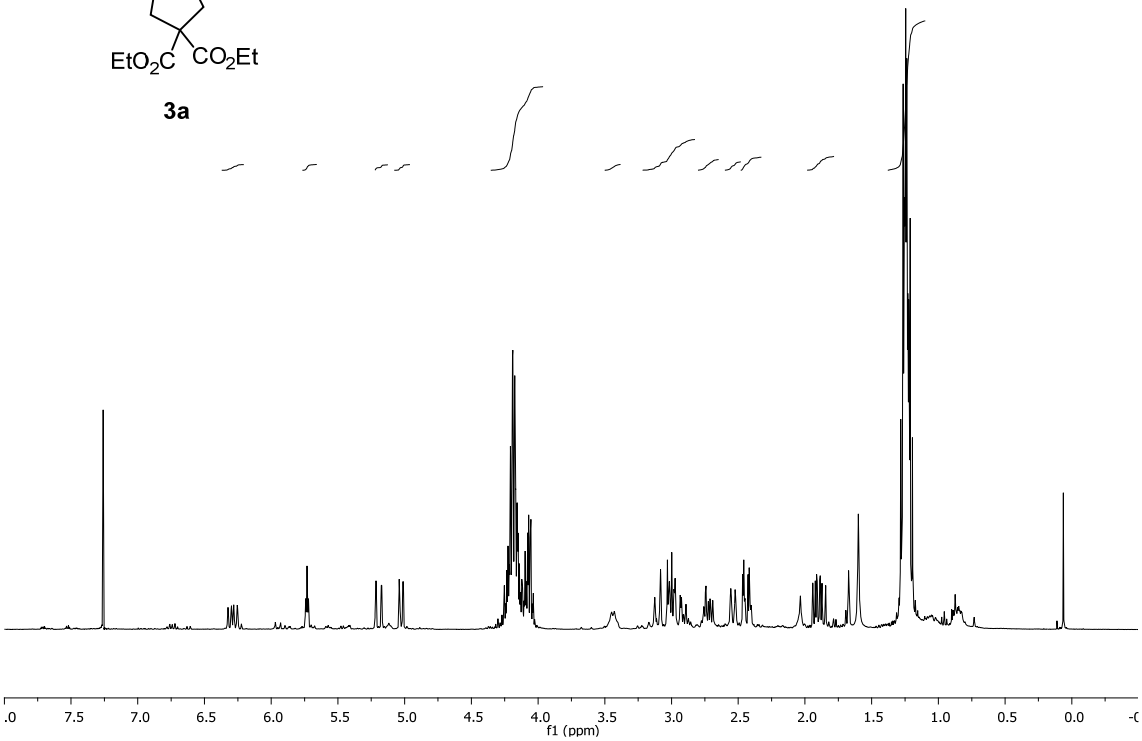
2a

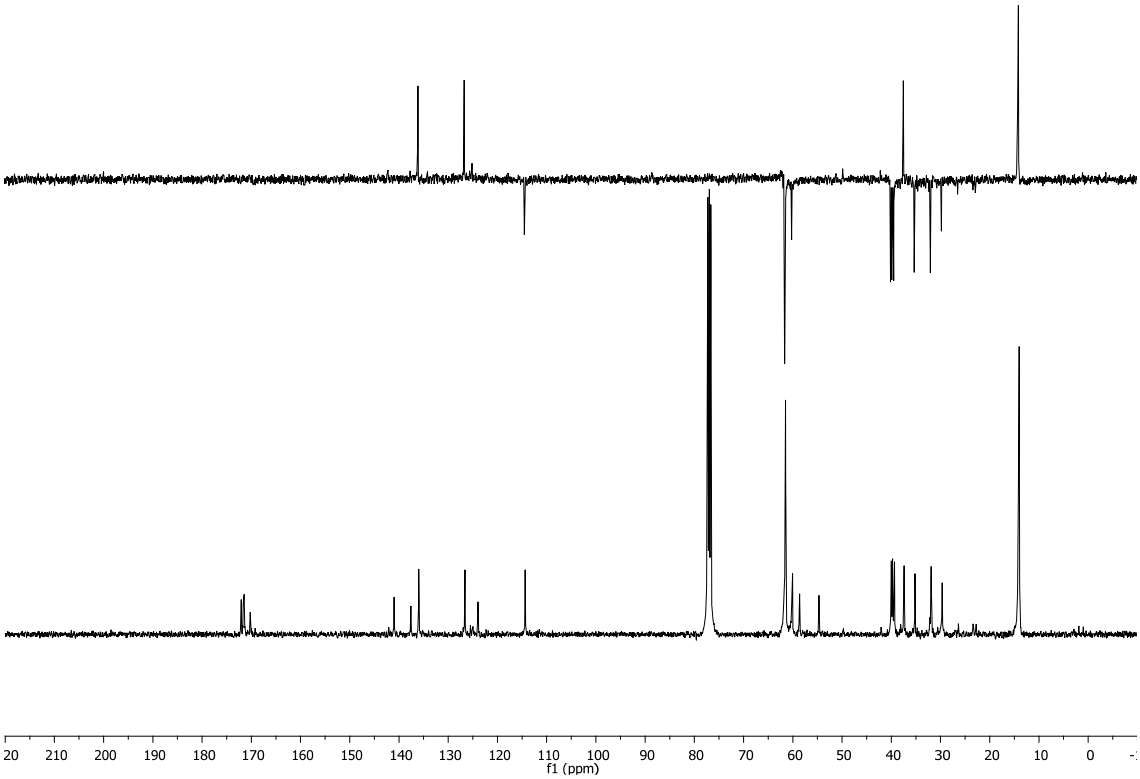
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

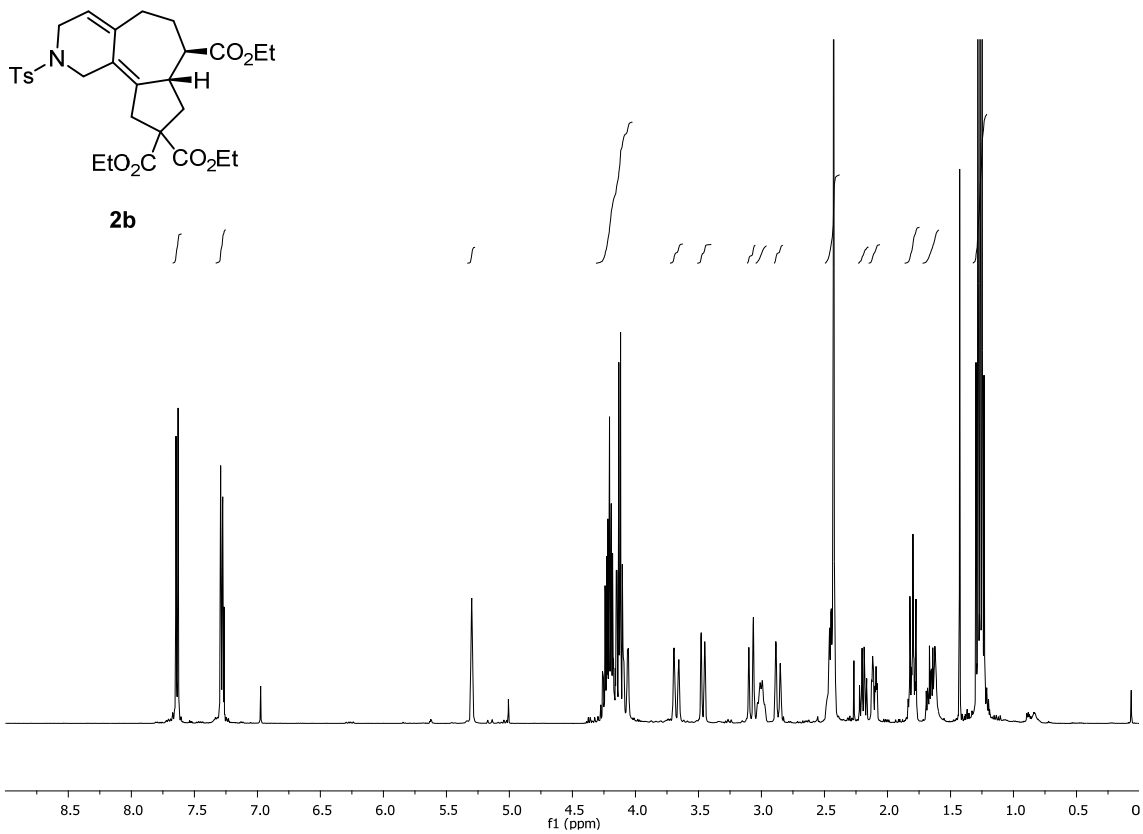

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


EtO2C
EtO2C
CO2Et
H
EtO2C
CO2Et

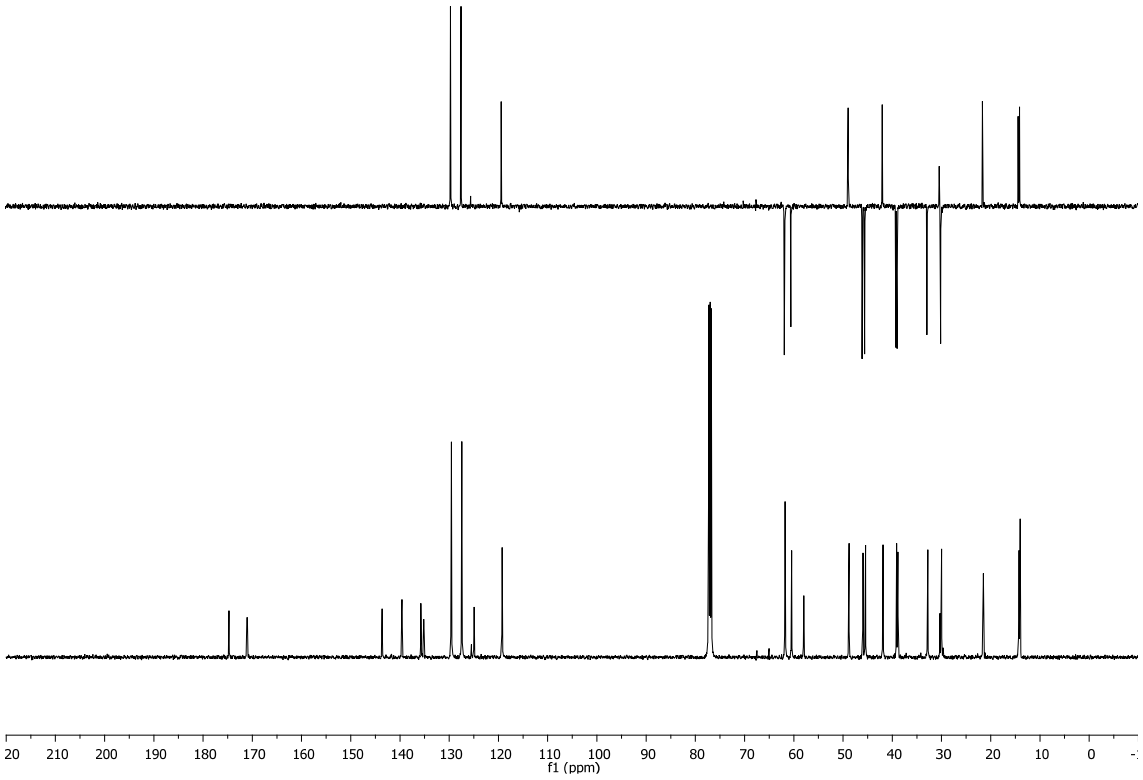
3a

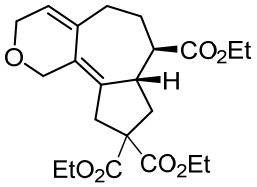

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
CO2Et
H
EtO2C
CO2Et
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

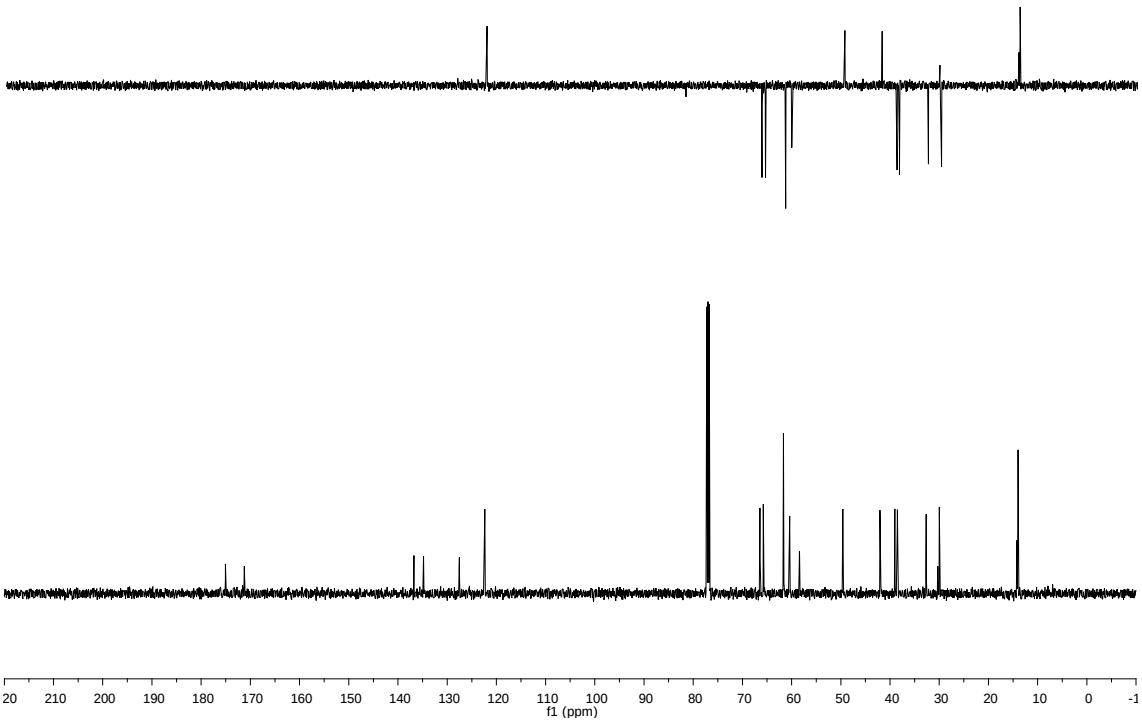
2b

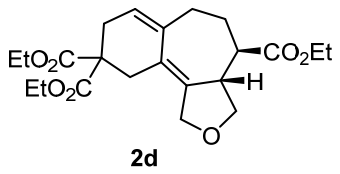

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
CO2Et
H
EtO2C
CO2Et

2c

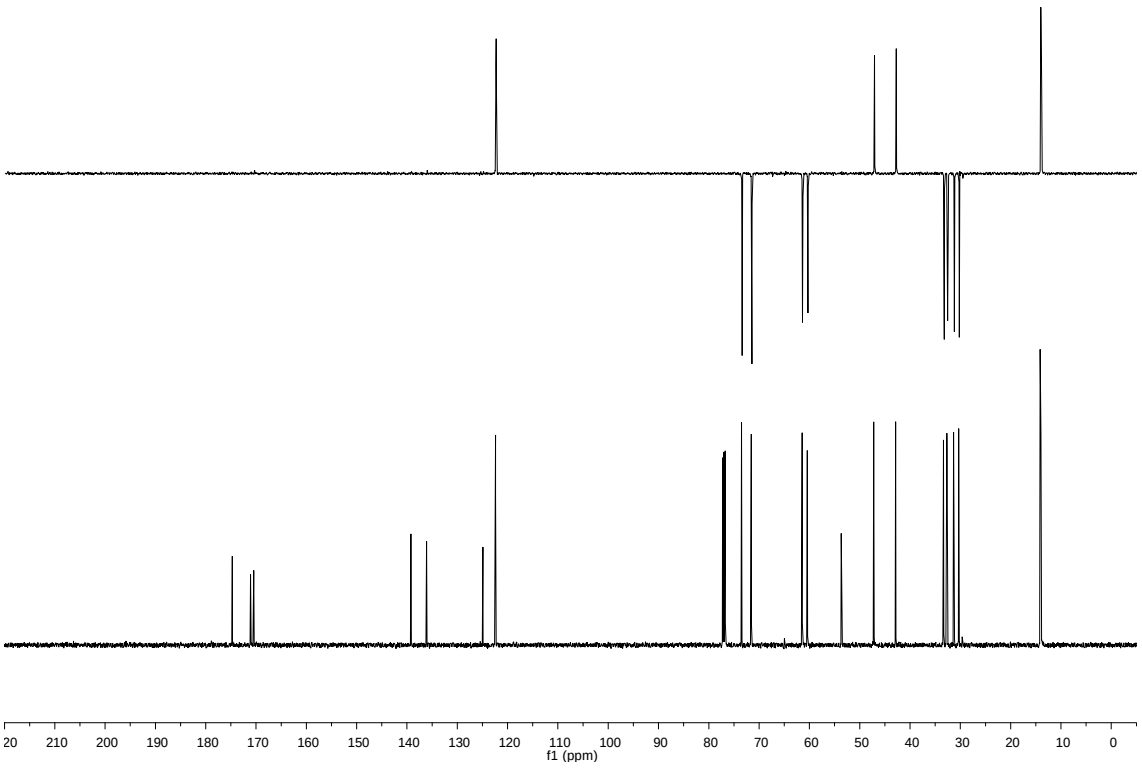
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

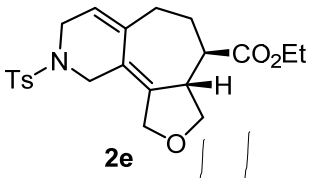

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


EtO2C
EtO2C
CO2Et
H
O

2d

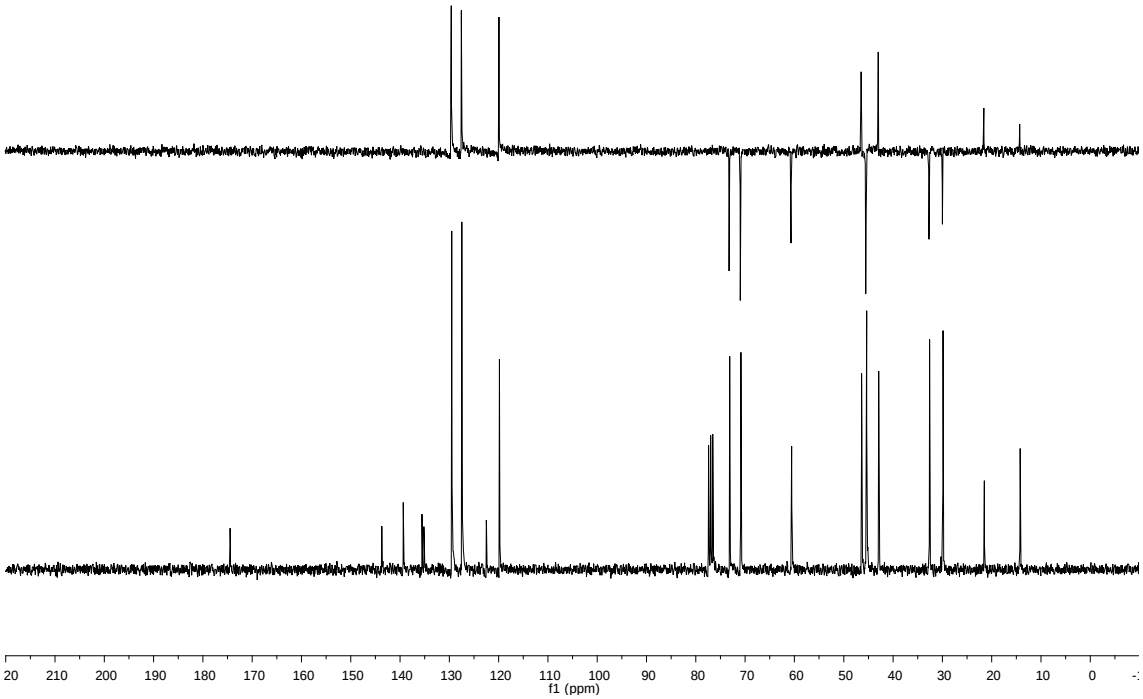
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

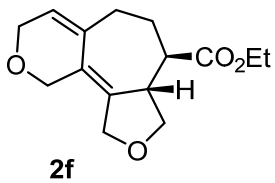

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ts
N
CO2Et
H
O

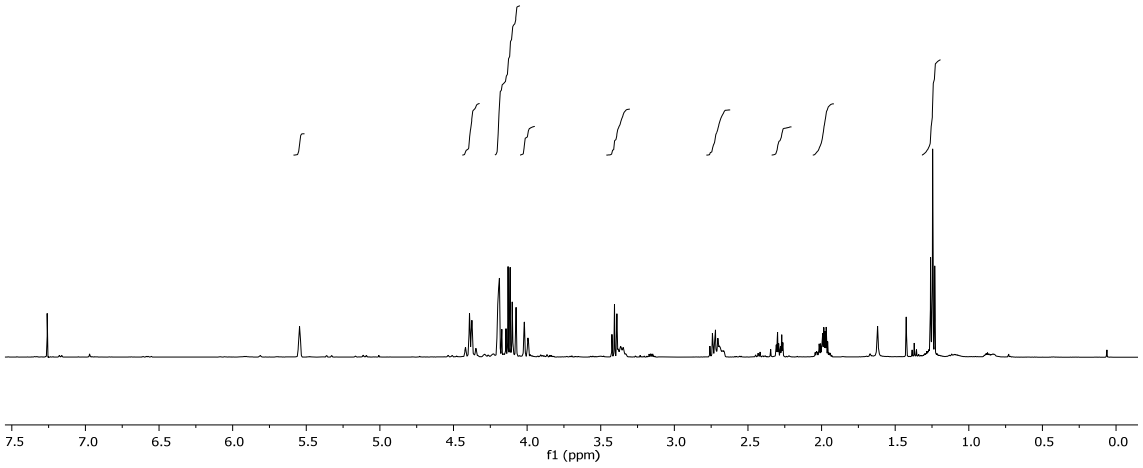
2e

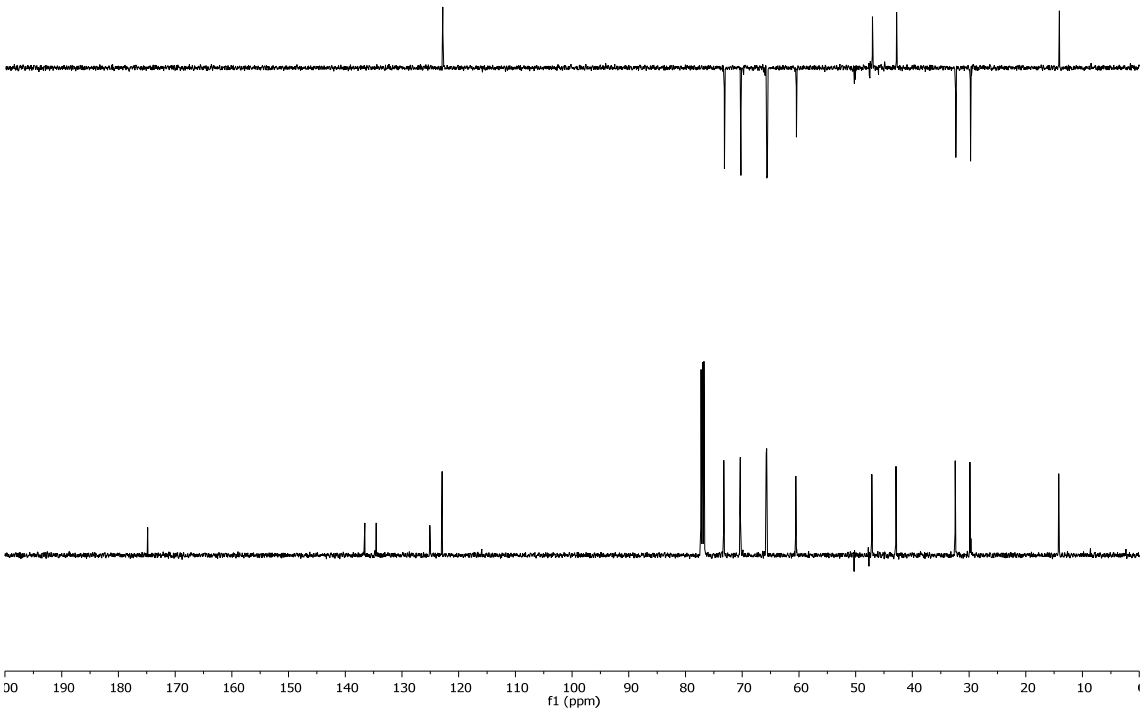
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

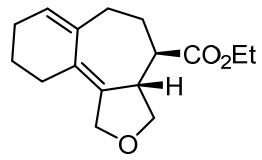

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
CO2Et
H
O

2f

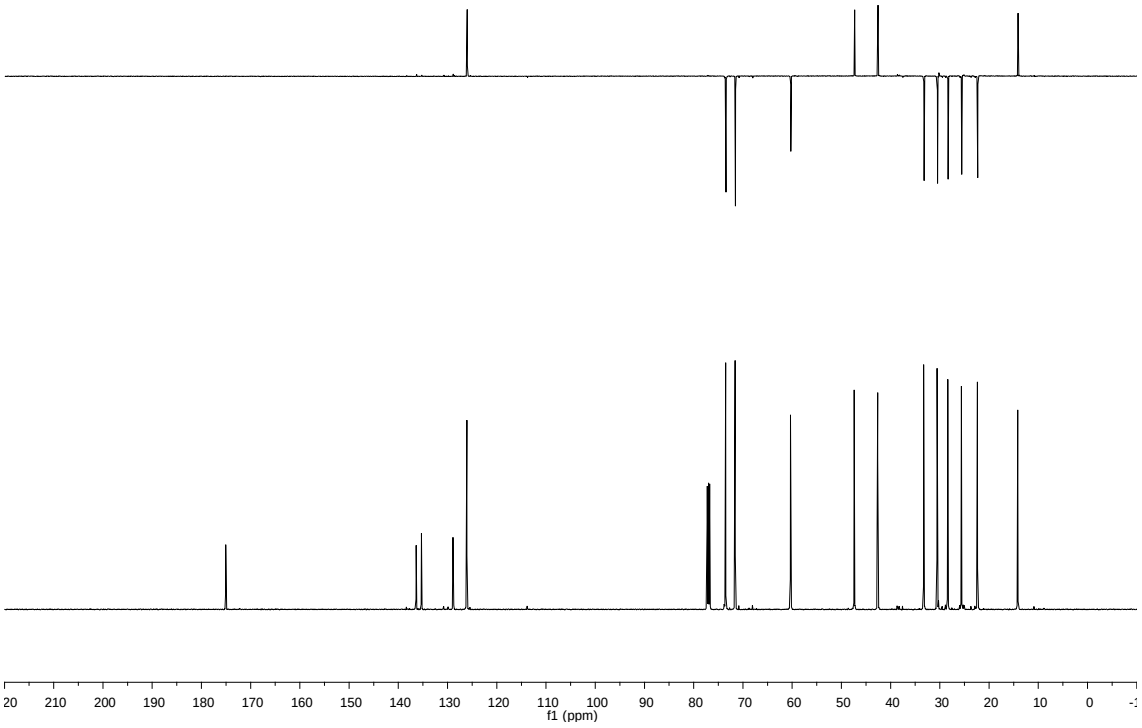

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

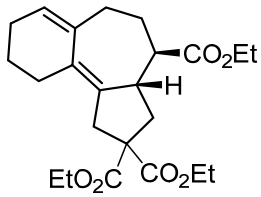

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


CO2Et
H
O

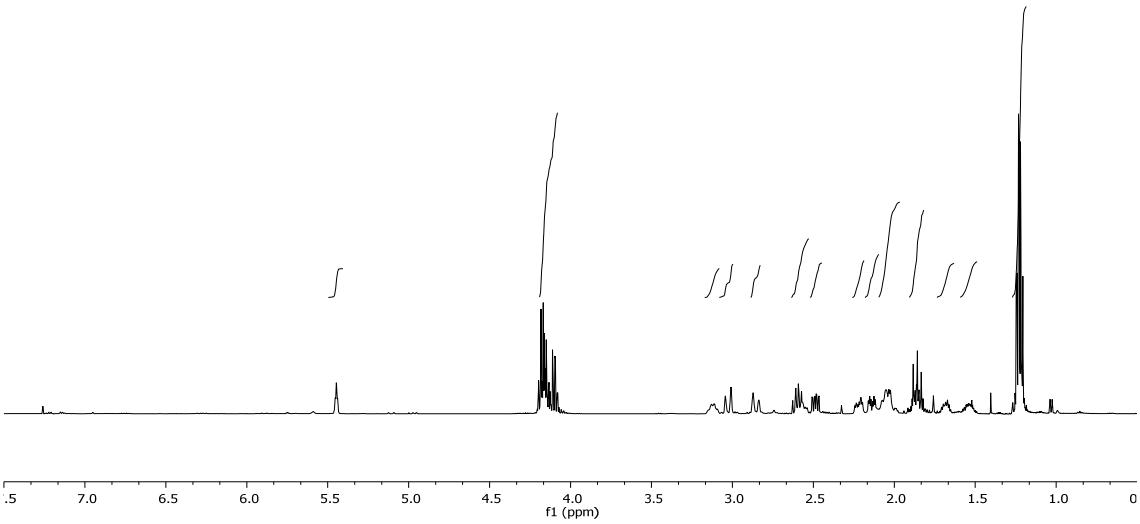
2g

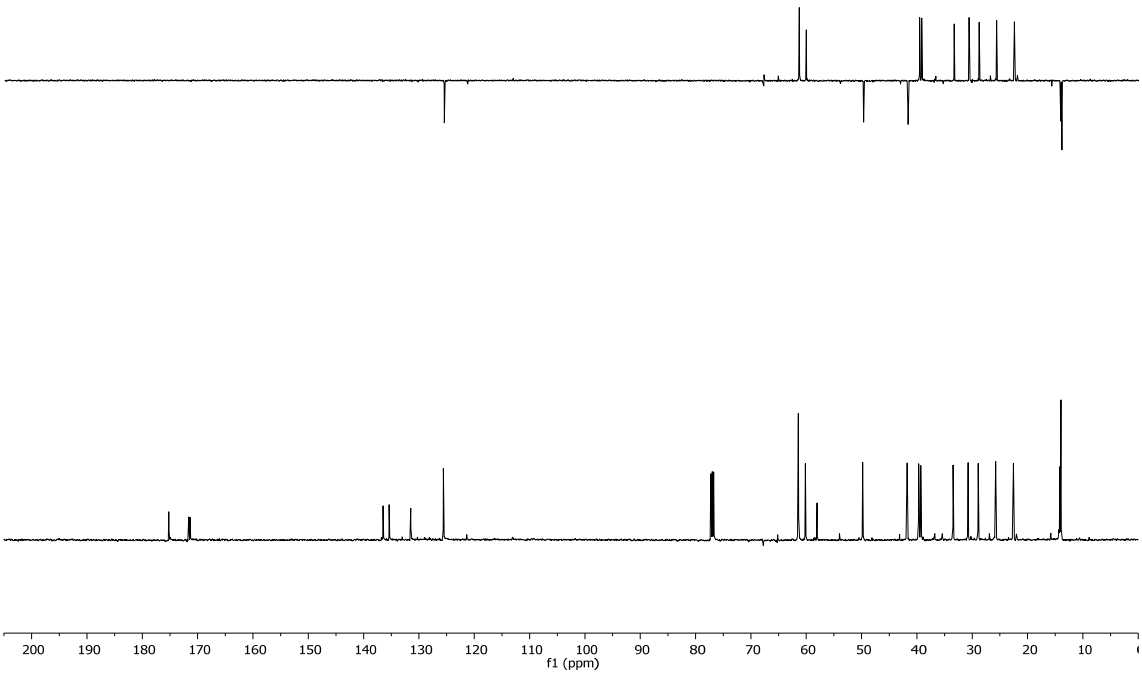
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

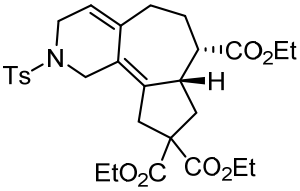

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CO2Et
H
EtO2C
CO2Et

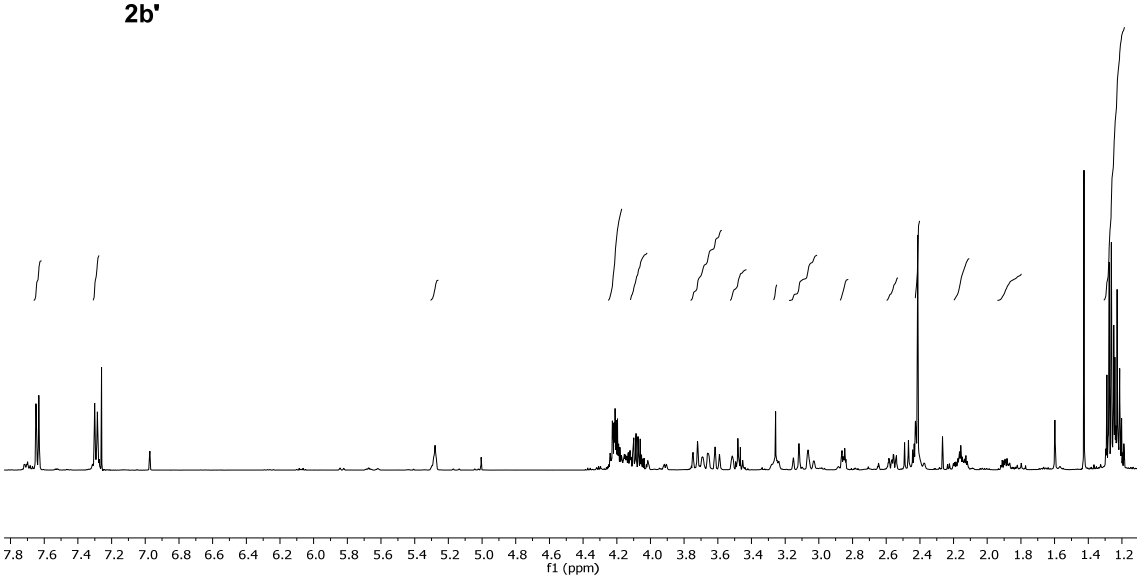
2h

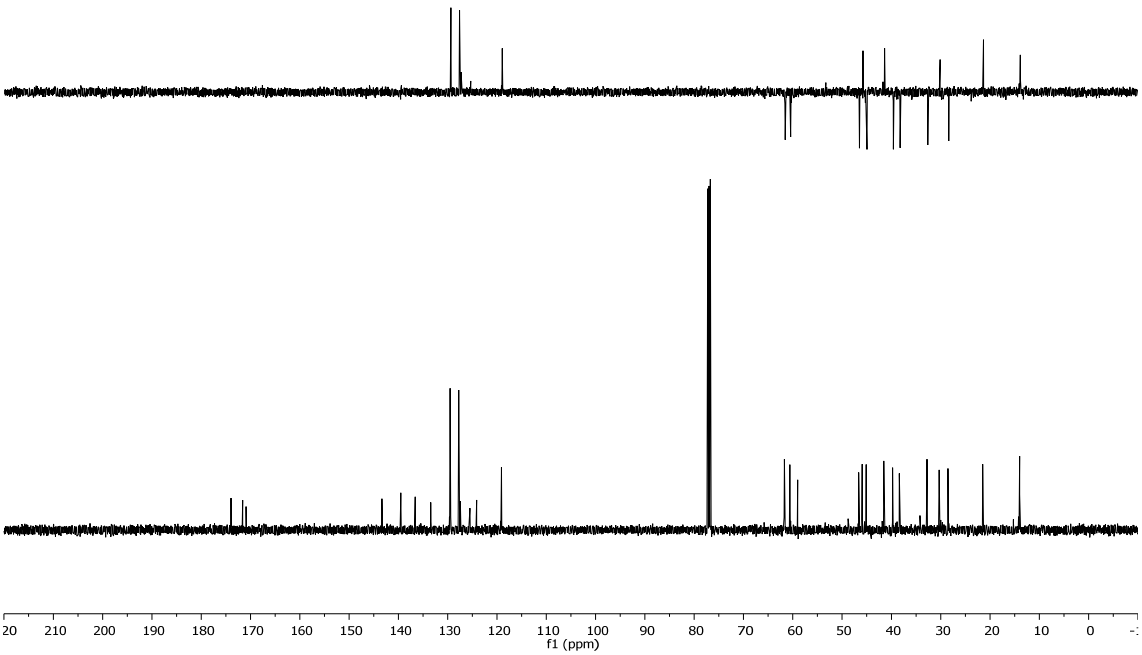

.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0
f1 (ppm)

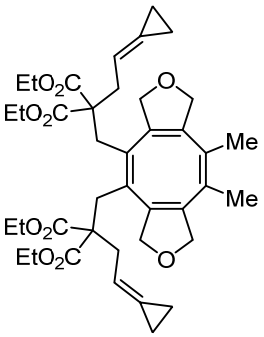

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ts
N
CO2Et
H
EtO2C
CO2Et

2b'

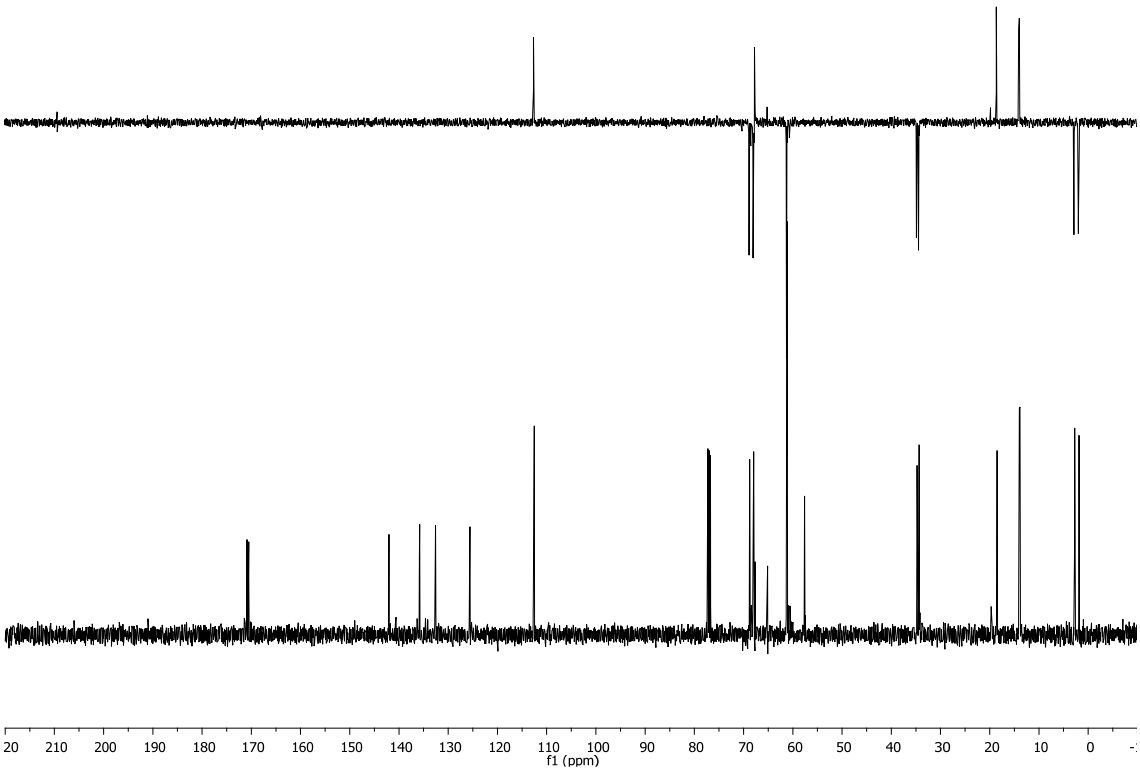

7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)

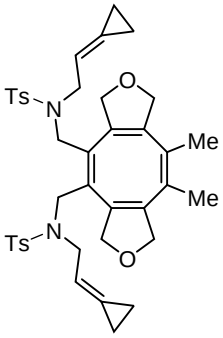

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


EtO2C
EtO2C
O
Me
Me
EtO2C
EtO2C
O

4i

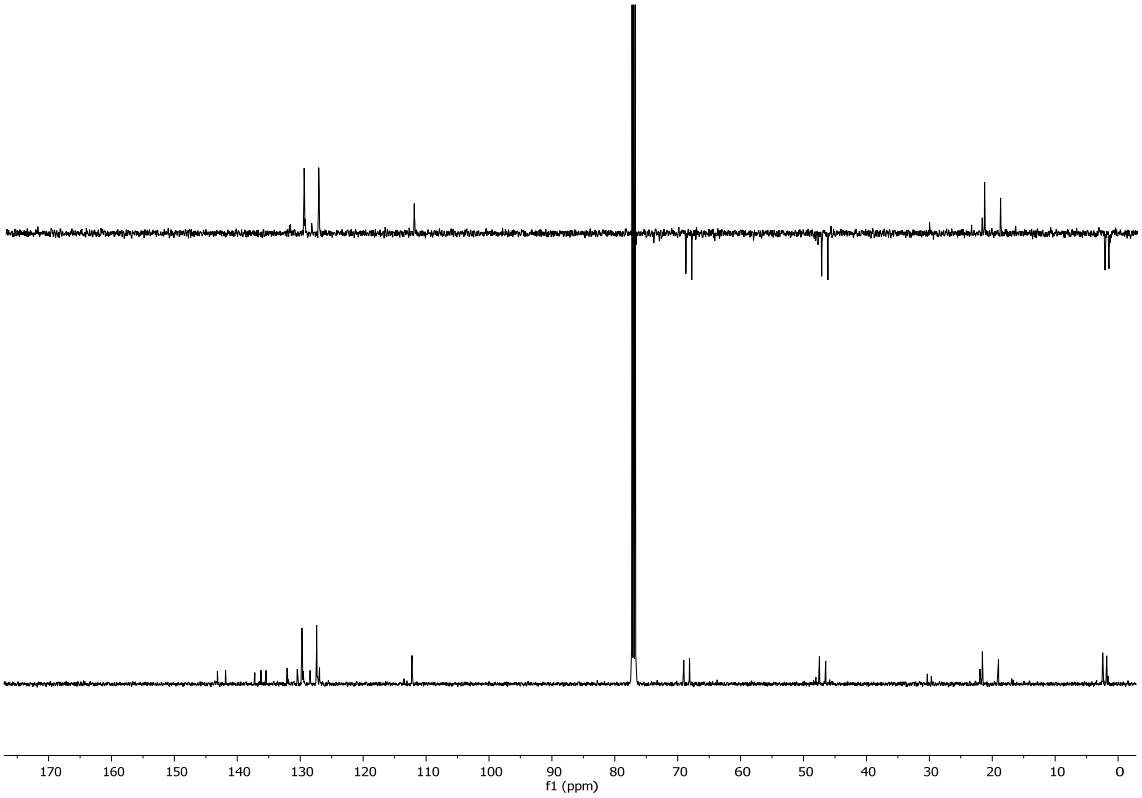
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

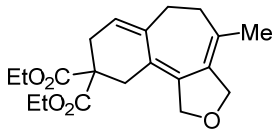

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ts
N
O
Me
Me
Ts
N
O

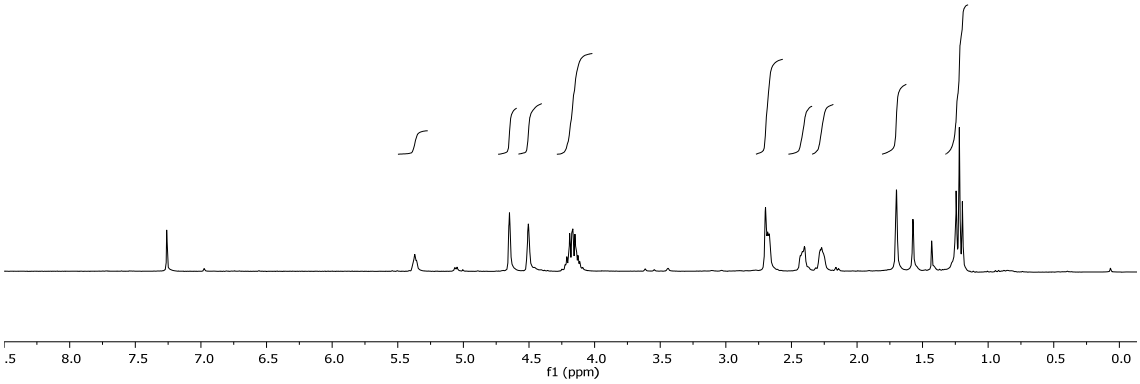
4j

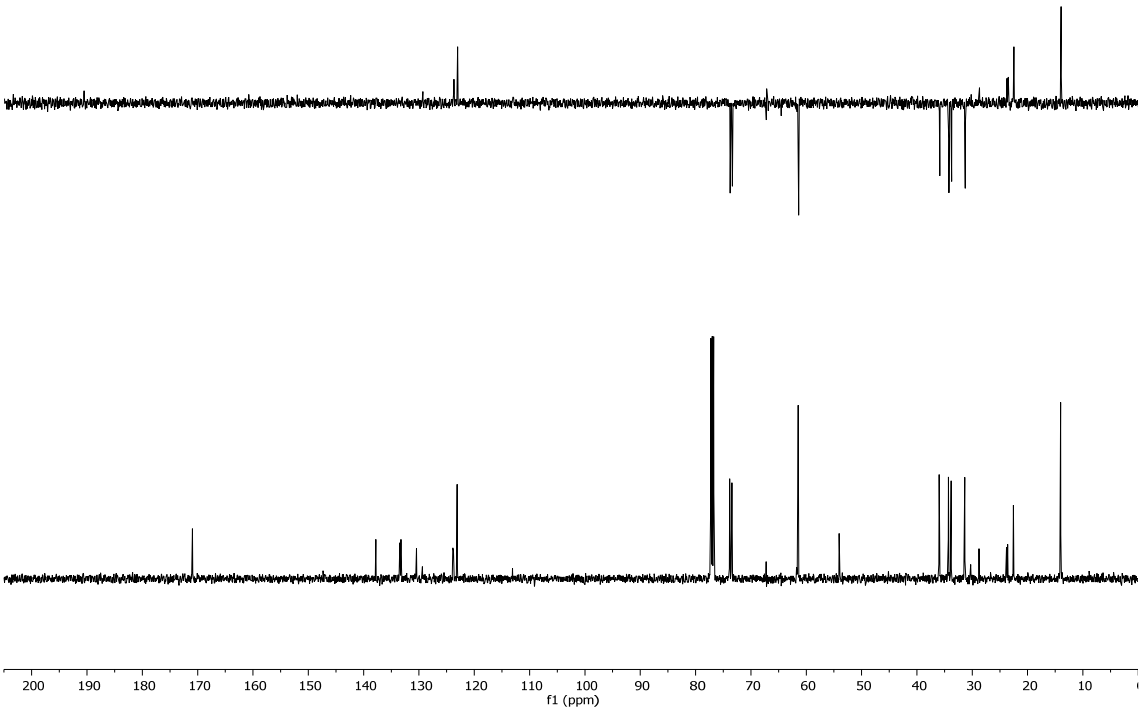
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

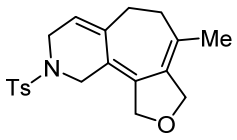

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
EtO2C
EtO2C
O

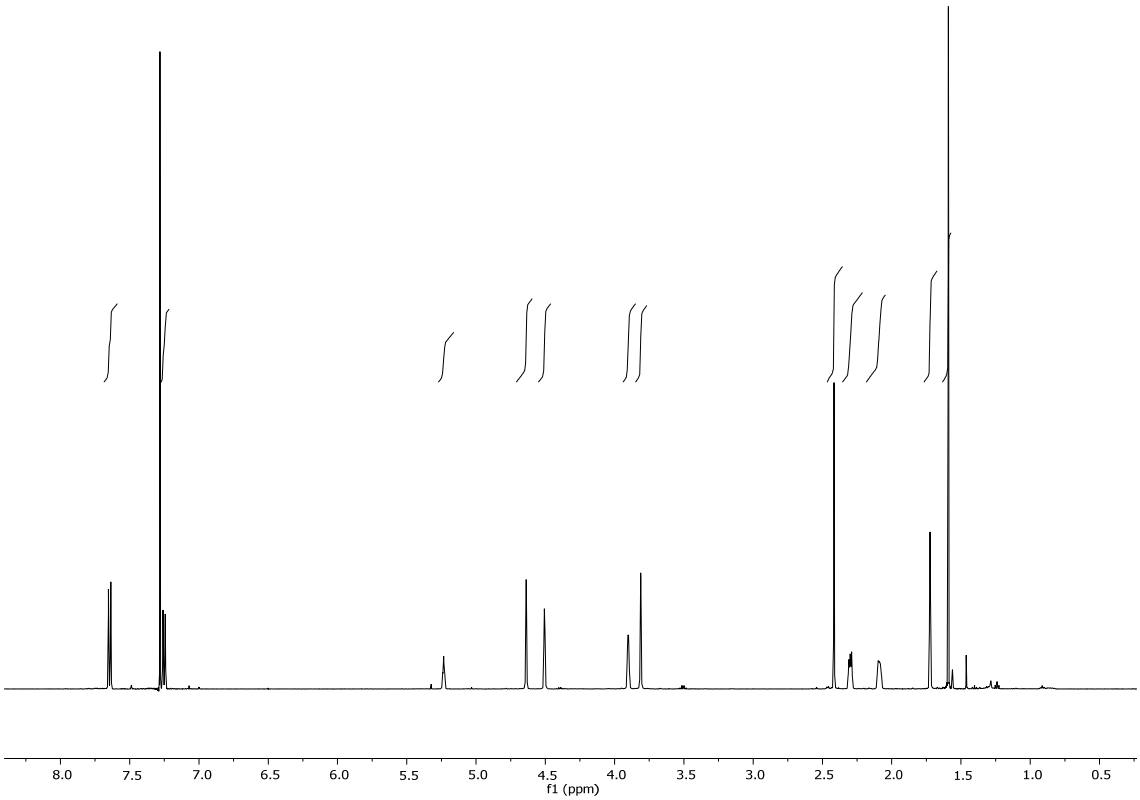
2i

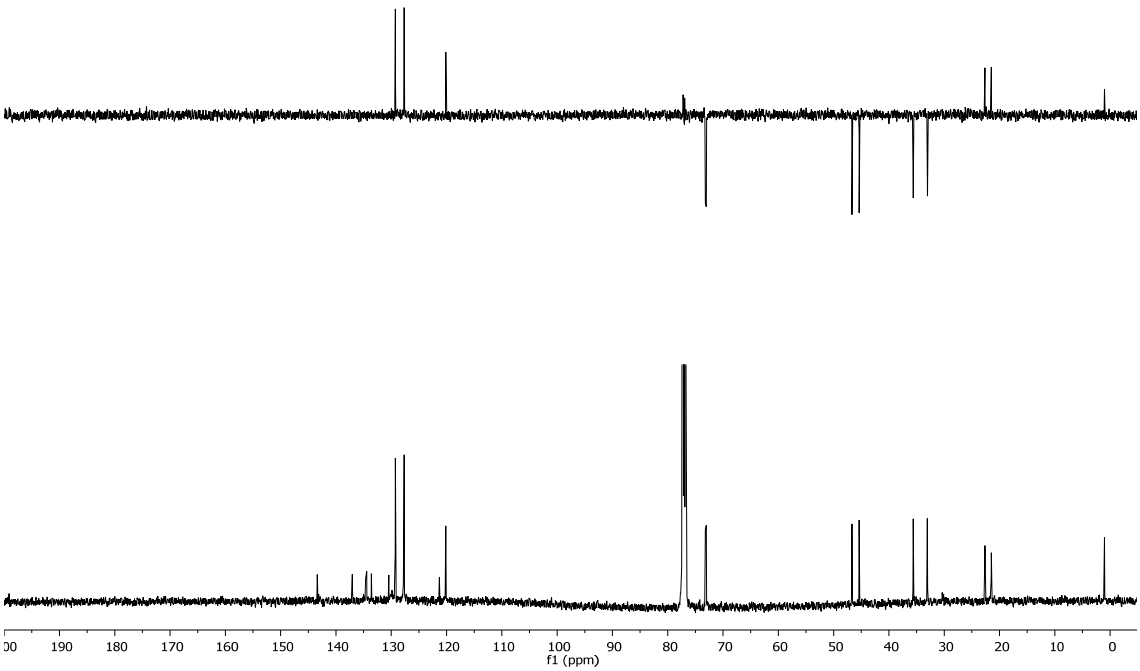

.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

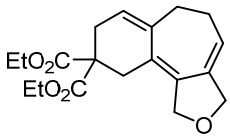

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me
N
Ts
O

2j

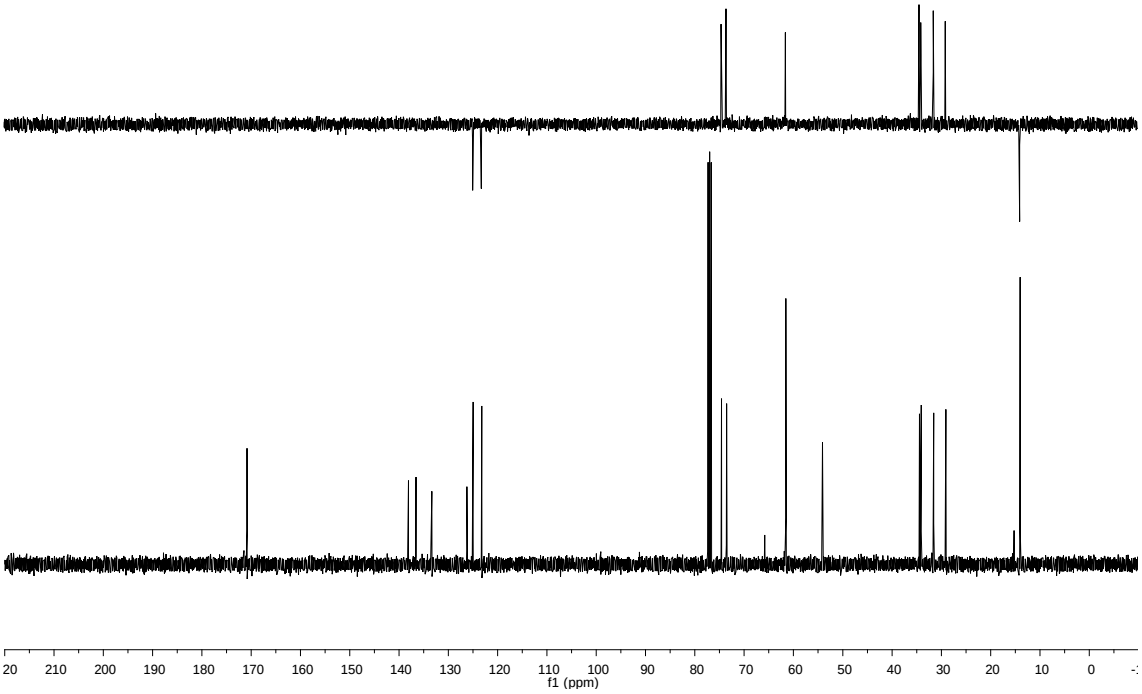

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


EtO2C
EtO2C
O

2k

7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


20
210
200
190
180
170
160
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140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)