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Supporting Information

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Platinum-Catalyzed Intramolecular [4C+3C] Cycloaddition between Dienes and Allenes

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General procedures

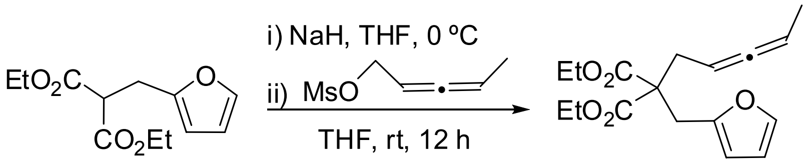
Dry solvents were freshly distilled under argon from an appropriate drying agent before use. Toluene was distilled from Na, THF from Na / benzophenone and CH_2Cl_2 and Et_3N were distilled from CaH_2. Pd_2dba_3 was obtained from Johnson Matthey; $PtCl_2$, $AuCl_3$, AuCl, $PtBr_2$ and $PtCl_4$ were purchased from Strem. $AgSbF_6$ and Ph_3PAuCl were purchased from Aldrich.

Reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. The abbreviation "rt" refers to reactions carried out at 23°C. Reaction mixtures were stirred using Teflon-coated magnetic stir bars. Reaction temperatures were maintained using Thermowatch-controlled silicone oil baths. 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 cerium nitrate solutions, followed by heating. 1,2,3-Trimetoxy-benzene was used as internal standard for the optimization of the reaction conditions (Table 1). 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 (18 mmHg aprox) followed by residual solvent removal under high vacuum.

NMR spectra were recorded in $CDCl_3$ or C_6D_6, at 250 MHz (Bruker) and 300 MHz (Varian) for cycloaddition precursors, and typically 400 MHz (Varian) or 500 MHz (Bruker) for cycloadducts. Carbon types and structure assignments were determined from DEPT-NMR and two-dimensional experiments (HMQC and HMBC, COSY and NOESY). NMR spectra were analyzed using MestReC© NMR data processing software (www.mestrec.com). The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; td, triple doublet; m, multiplet; br, broad. Mass spectra were acquired using chemical ionization (CI) or electron impact techniques (EI) 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).

General Procedure for the Synthesis of compounds 1a, 1b, 1d, 1e and 1f (exemplified for the preparation of 1a)

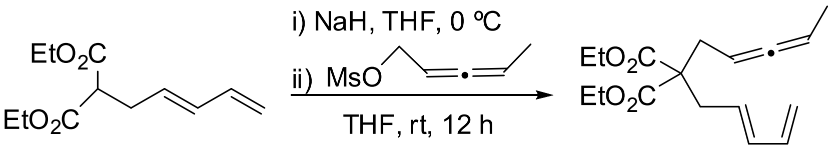
Diethyl 2-(furan-2-ylmethyl)-2-(penta-2,3-dienyl)malonate (1a).



1a

A solution of diethyl 2-(furan-2-ylmethyl)malonate[1] (650 mg, 2.72 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (109 mg, 2.72 mmol) in THF (10 mL) cooled to 0 °C. After stirring for 30 min penta-2,3-dienyl methanesulfonate[2] (972 mg, 6 mmol) was slowly added. The mixture was stirred overnight at rt, poured into water and extracted with Et_2O (3x20 mL). The organic phases were dried, filtered and concentrated to give a crude oil residue that was purified by flash chromatography (2% Et_2O/hexanes) to give 420 mg of the allene **1a** (51 %). Colourless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm), 7.27-7.26 (1H, m), 6.26-6.24 (1H, m), 6.05-6.04 (1H, m), 5.11-5.00 (1H, m), 4.98-4.90 (1H, m), 4.22-4.15 (4H, m), 3.31 (2H, s), 2.54-2.50 (2H, m), 1.65-1.61 (3H, m), 1.24 (6H, t, *J* = 7.1 Hz); **^{13}C-NMR** (75.5 MHz, $CDCl_3$): δ (ppm) 206.7 (C), 170.2 (CO), 170.2 (CO), 150.5 (C), 141.7 (CH), 110.1 (CH), 108.2 (CH), 85.4 (CH), 84.2 (CH), 61.3 (CH_2), 57.6 (C), 31.9 (CH_2), 30.5 (CH_2), 14.1 (CH_3), 13.9 (CH_3), 13.9 (CH_3); **MS** (*m/z, I*): 307 ([M$^+$ +1], 62), 261 (56), 233 (67), 215 (69); **HRMS** calculated for $C_{17}H_{23}O_5$ 307.1545, found 307.1539.

(*E*)-Diethyl 2-(penta-2,3-dienyl)-2-(penta-2,4-dienyl)malonate (1b)



1b

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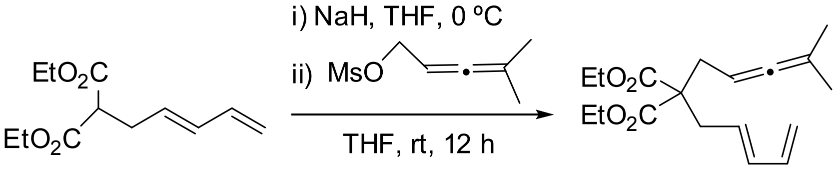
[1] Diethyl 2-(furan-2-ylmethyl)malonate was synthesized by alkylation of the sodium salt of diethylmalonate with 2-(bromomethyl)furan, previously prepared by treatment of furfuryl alcohol with PBr_3 under standard conditions.

[2] Penta-2,3-dienyl methanesulfonate was prepared from penta-2,3-dien-1-ol following the procedure described in: P. A., Wender, F. Glorius, C. O. Husfeld, E. Langkopf, J. A. Love. *J. Am. Chem. Soc.* **1999**, *121*, 5348-5349. Penta-2,3-dien-1-ol is a known compound and was prepared according to the general procedures described in: M. Murakami, S. Kadowaki, T. Matsuda, *Org. Lett.* **2005**, *7*, 3953-3956 and L. Brandsma, H. D. Verkruijsse, *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier Publishing, Co. New York, **1981**; pp 65, 171 and 188.

Prepared according to the above described general procedure using (*E*)-diethyl 2-(penta-2,4-dienyl)malonate[3] and penta-2,3-dienyl methanesulfonate.[2] Colourless oil (53 %). **^{1}H-NMR** (250 MHz, $CDCl_3$): δ (ppm) 6.31-6.18 (1H, m), 6.11-6.02 (1H, m), 5.55-5.45 (1H, m), 5.10-4.95 (3H, m), 4.88-4.82 (1H, m), 4.19-4.11 (4H, m), 2.68 (2H, d, *J* = 7.6 Hz), 2.56-2.53 (2H, m), 1.62-1.58 (3H, m), 1.24-1.19 (6H, m); **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 206.6 (C), 170.5 (CO), 136.6 (CH), 134.9 (CH), 127.9 (CH), 116.2 (CH_2), 85.4 (CH), 84.2 (CH), 61.2 (CH_2), 57.7 (C), 35.4 (CH_2), 32.4 (CH_2), 14.2 (CH_3), 14.0 (CH_3); **MS** (*m/z, I*): 293 ([M^+ +1], 44), 219 (100), 145 (71); **HRMS** calculated for $C_{17}H_{25}O_4$ 293.1753, found 293.1743.

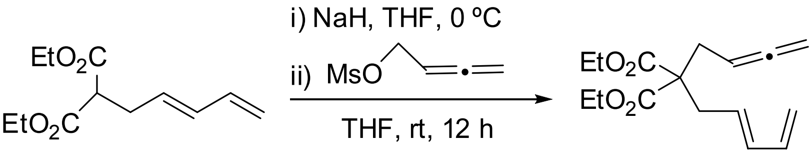
(*E*)-Diethyl 2-(4-methylpenta-2,3-dienyl)-2-(penta-2,4-dienyl) malonate (1d)



1d

Prepared according to the above described general procedure using (*E*)-diethyl 2-(penta-2,4-dienyl)malonate[3] and 4-methylpenta-2,3-dienyl methanesulfonate.[4] Colourless oil (70 %). **^{1}H-NMR** (250 MHz, $CDCl_3$): δ (ppm), 6.33-6.18 (1H, m), 6.12-6.02 (1H, m), 5.57-5.45 (1H, m), 5.12-4.96 (2H, m), 4.79-4.70 (1H, m), 4.21-4.10 (4H, m), 2.69 (2H, d, *J* = 7.6 Hz), 2.53 (2H, d, *J* = 7.6 Hz), 1.65 (3H, s), 1.63 (3H, s), 1.22 (6H, t, *J* = 7.1 Hz); **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 203.6 (C), 170.7 (CO), 136.6 (CH), 134.9 (CH), 128.1 (CH), 116.2 (CH_2), 95.0 (C), 82.6 (CH), 61.2 (CH_2), 57.8 (C), 35.3 (CH_2), 32.6 (CH_2), 20.4 (CH_3), 14.1 (CH_3); **MS** (*m/z, I*): 307 ([M^+ +1], 8), 233 (100), 159 (44); **HRMS** calculated for $C_{18}H_{27}O_4$ 307.1909, found 307.1900.

(*E*)-Diethyl 2-(buta-2,3-dienyl)-2-(penta-2,4-dienyl)malonate (1e)



1e

Prepared according to the above described general procedure using (*E*)-diethyl 2-(penta-2,4-dienyl)malonate[3] and buta-2,3-dienyl methanesulfonate.[5]

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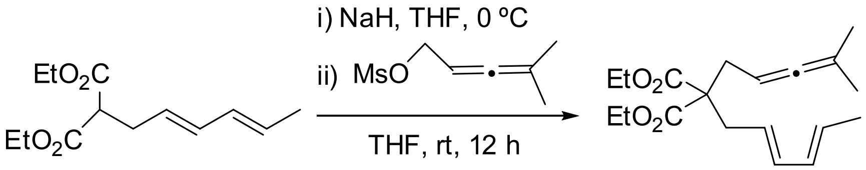
[3] (*E*)-Diethyl 2-(penta-2,4-dienyl)malonate was prepared as described in: M. Kimura, A. Ezoe, M. Mori, Y. Tamaru, *J. Am. Chem. Soc.* **2005**, *127*, 201-209.

[4] 4-Methylpenta-2,3-dienyl methanesulfonate and its corresponding alcohol precursor are known compounds and were prepared following the procedures reported in reference 2.

[5] Buta-2,3-dienyl methanesulfonate and its corresponding alcohol precursor are known compounds and were prepared following the procedures reported in reference 2.

Colourless oil. ^{1}**H-NMR** (250 MHz, $CDCl_3$): δ (ppm), 6.33-6.02 (2H, m), 5.56-5.44 (1H, m), 5.12-4.87 (3H, m), 4.66-4.62 (2H, m), 4.16 (4H, q, ***J*** = 7.1 Hz), 2.68 (2H, d, ***J*** = 7.6 Hz), 2.60-2.55 (2H, m), 1.22 (6H, t, ***J*** = 7.1 Hz); ^{13}**C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 210 (C), 170.5 (CO), 136.5 (CH), 135.1 (CH), 127.7 (CH), 116.3 (CH_2), 84.1 (CH), 74.5 (CH_2), 61.2 (CH_2),57.7 (C), 35.5 (CH_2), 31.9 (CH_2), 14.0 (CH_3); **MS** (*m/z, I*): 279 ([M^+ +1], 84), 205 (83), 187 (100); **HRMS** calculated for $C_{16}H_{23}O_4$ 279.1596, found 279.1597.

Diethyl 2-((*2E*,*4E*)-hexa-2,4-dienyl)-2-(4-methylpenta-2,3-dienyl) malonate (1f)

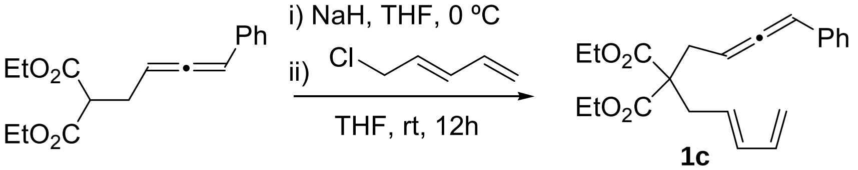


1f

Prepared according to the above described general procedure using diethyl 2-((2*E*,4*E*)-hexa-2,4-dienyl)malonate[6] and 4-methylpenta-2,3-dienyl methanesulfonate.[5] Colourless oil (56 %). ^{1}**H-NMR** (300 MHz, $CDCl_3$): δ (ppm) 6.07-5.93 (2H, m), 5.63-5.51 (1H, m), 5.39-5.29 (1H, m), 4.79-4.72 (1H, m), 4.21-4.11 (4H, m), 2.67 (2H, d, ***J*** = 7.6 Hz), 2.53 (2H, d, ***J*** = 7.6 Hz), 1.71 (3H, d, ***J*** = 6.9 Hz), 1.65 (3H, s), 1.64 (3H, s), 1.23 (6H, t, ***J*** = 7.1 Hz); ^{13}**C-NMR** (75.5 MHz, $CDCl_3$): δ (ppm) 203.7 (C), 170.8 (CO), 134.4 (CH), 131.2 (CH), 128.3 (CH), 124.6 (CH), 94.9 (C), 82.7 (CH), 61.1 (CH_2), 57.9 (C), 35.3 (CH_2), 32.5 (CH_2), 20.4 (CH_3), 17.9 (CH_3), 14.1 (CH_3); **MS** (*m/z, I*): 321 ([M^+ +1], 10), 247 (100), 191 (46); **HRMS** calculated for $C_{19}H_{29}O_4$ 321.2066, found 321.2063.

General Procedure for Synthesis of Compounds 1c, 1i and 1j (exemplified for substrate **1c**)

(*E*)-Diethyl 2-(penta-2,4-dienyl)-2-(4-phenylbuta-2,3-dienyl)malo nate (1c).



1c

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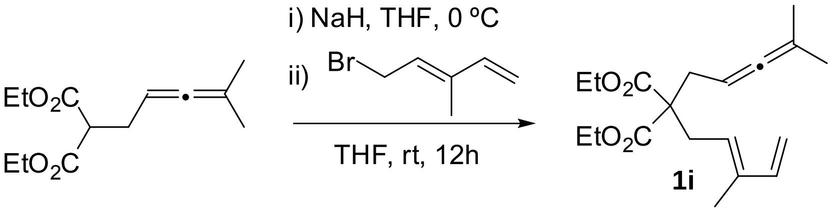
[6] Diethyl 2-(*2E,4E*)-hexa-2,4-dienyl)malonate was prepared by alkylation of the sodium salt of diethylmalonate with (*2E,4E*)-1-bromohexa-2,4-diene, which was synthesized as reported in: T. Kim, G. Mirafzal, J. Liu, N. Bauld, *J. Am. Chem. Soc.* **1993**, *115*, 7653-7664.

A solution of diethyl 2-(4-phenylbuta-2,3-dienyl)malonate[7] (400 mg, 1.39 mmol) in THF (2 mL) was added dropwise to a suspension of NaH (56 mg, 1.39 mmol) in THF (8 mL), cooled to 0 °C. After stirring for 30 minutes at rt (*E*)-5-chloropenta-1,3-diene[8] (285 mg, 2.78 mmol) was slowly added. The mixture was stirred overnight at rt, poured into water and extracted with Et_2O (3 x 15 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 400 mg of the allene **1c** (82 %). Colourless oil. **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) 7.32-7.15 (5H, m), 6.31-6.01 (3H, m), 5.57-5.35 (2H, m), 5.06-4.95 (2H, m), 4.22-4.12 (4H, m), 2.78-2.70 (4H, m), 1.26-1.17 (6H, m); **^{13}C-NMR** (75.5 MHz, $CDCl_3$): δ (ppm) 206.8 (C), 170.5 (CO), 136.5 (CH), 135.2 (CH), 134.0 (C), 128.5 (CH), 127.6 (CH), 126.9 (CH), 126.8 (CH), 116.5 (CH_2), 94.6 (CH), 89.0 (CH), 61.4 (CH_2), 57.6 (C), 35.6 (CH_2), 32.3 (CH_2), 14.1 (CH_3), 14.0 (CH_3); **MS** (*m/z, I*): 355 ([M^+ +1], 5), 325 (72), 281 (94). **HRMS** calculated for $C_{22}H_{27}O_4$ 355.1909, found 355.1904.

(*E*)-Diethyl 2-(4-methylpenta-2,3-dienyl)-2-(3-methylpenta-2,4-dienyl)malonate (1i)



Prepared according to the general procedure described above using diethyl 2-(4-methylpenta-2,3-dienyl)malonate[9] and (*E*)-5-bromo-3-methylpenta-1,3-diene.[10] Colourless oil (87 %). **^{1}H-NMR** (250 MHz, $CDCl_3$): δ (ppm), 6.30 (1H, dd, ***J*** = 17.4 and 10.8 Hz), 5.31 (1H, t, ***J*** = 7.5 Hz), 4.92 (1H, d, ***J*** = 10.8 Hz), 5.07 (1H, d, ***J*** = 17.4 Hz), 4.78-4.69 (1H, m), 4.14 (4H, q, ***J*** = 7.1 Hz), 2.77 (2H, d, ***J*** = 7.6 Hz), 2.53 (2H, d, ***J*** = 7.6 Hz), 1.72 (3H, s), 1.62 (3H, s), 1.60 (3H, s), 1.20 (6H, t, ***J*** = 7.2 Hz); **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 203.6 (C), 170.8 (CO), 141.2 (CH), 136.9 (C), 125.9 (CH), 111.5 (CH_2), 95.0 (C), 82.7 (CH), 61.1 (CH_2), 57.6 (C), 32.7 (CH_2), 30.7 (CH_2), 20.4 (CH_3), 14.0 (CH_3), 11.8 (CH_3); **MS** (*m/z, I*): 321 ([M^+ +1], 13), 247 (100), 173 (85); **HRMS** calculated for $C_{19}H_{29}O_4$ 321.2066, found 321.2056.

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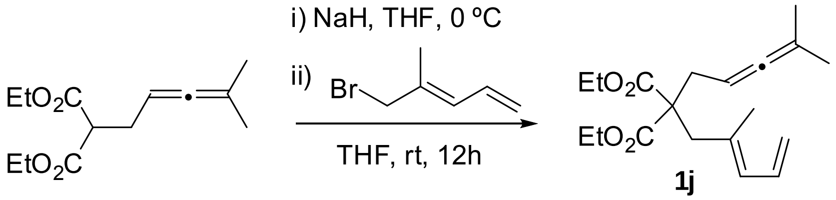
[7] 2-(4-Phenylbuta-2,3-dienyl)malonate was prepared from benzaldehyde following the procedure developed by T. Hayashi, and described in: M. Ogasawara, H. Ikeda, T. Hayashi, *Angew. Chem. Int. Ed.* **2000**, *39*, 1042-1044.

[8] Prepared following the procedure described in: M. Kimura, A. Ezoe, M. Mori, Y. Tamaru, *J. Am. Chem. Soc.* **2005**, *127*, 201-209.

[9] Diethyl 2-(4-methylpenta-2,3-dienyl)malonate was prepared from the corresponding allenyl alcohol following the procedure described in: J. Franzen, J. Löfstedt, J. Falk, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2003**, *125*, 14140-14148.

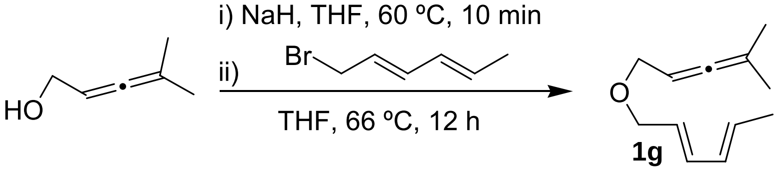
[10] (*E*)-5-Bromo-3-methylpenta-1,3-diene is a known compound and was synthesized following the procedure described in: T. Shing, X. Zhu, Y. Yeung, *Chem. Eur. J.* **2003**, *9*, 5489-5500.

(*E*)-Diethyl 2-(4-methylpenta-2,3-dienyl)-2-(2-methylpenta-2,4-dienyl)malonate (1j)



Prepared according to the above described general procedure using diethyl 2-(4-methylpenta-2,3-dienyl)malonate[9] and (*E*)-5-Bromo-4-methylpenta-1,3-diene.[11] Colourless oil (60 %). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ (ppm) 6.55-6.43 (1H, m), 5.87 (1H, d, ***J*** = 10.9 Hz), 5.09-4.98 (2H, m), 4.81-4.74 (1H, m), 4.14 (4H, q, ***J*** = 7.1 Hz), 2.74 (2H, s), 2.54 (2H, d, ***J*** = 7.5 Hz), 1.67 (3H, s), 1.64 (3H, s), 1.63 (3H, s), 1.23 (6H, t, ***J*** = 7.1 Hz); **^{13}C-NMR** (75.5 MHz, $CDCl_3$): δ (ppm) 203.7 (C), 171.0 (CO), 133.8 (C), 132.8 (CH), 130.5 (CH), 116.0 (CH_2), 95.0 (C), 83.1 (CH), 61.1 (CH_2), 57.7 (C), 41.7 (CH_2), 32.4 (CH_2), 20.4 (CH_3), 17.4 (CH_3), 14.0 (CH_3); **MS** (*m/z, I*): 321 ([M^+ +1], 13), 247 (100), 173 (56); **HRMS** calculated for $C_{19}H_{29}O_4$ 321.2066, found 321.2053.

Preparation of (*2E,4E*)-1-(4-methylpenta-2,3-dienyloxy)hexa-2,4-diene (1g)



4-Methylpenta-2,3-dien-1-ol[12] (522 mg, 5.33 mmol) was added dropwise to a suspension of NaH (245 mg, 6.13 mmol) in THF (20 mL). After stirring for 10 minutes at 60 °C, the reaction mixture was allowed to warm up to rt and (*2E,4E*)-1-bromohexa-2,4-diene[13] (1.24 g, 7.72 mmol) was slowly added. The mixture was stirred overnight at 60 °C, worked up with of saturated NH_4Cl (20 mL), and extracted with Et_2O (3 x 15mL). The organic phases were dried, filtered and concentrated to give a crude oil residue that was purified by flash chromatography (2% Et_2O/hexanes) to give 425 mg of the allene **1g** (45 %). Colourless oil. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ (ppm) 6.22-5.97 (2H, m), 5.73-5.52 (2H, m), 5.06-4.98 (1H, m), 3.97 (2H, d, ***J*** = 6.2 Hz), 3.91 (2H, d, ***J*** = 6.9 Hz), 2.14 (3H, s), 173-1.66 (6H, m); **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 202.8

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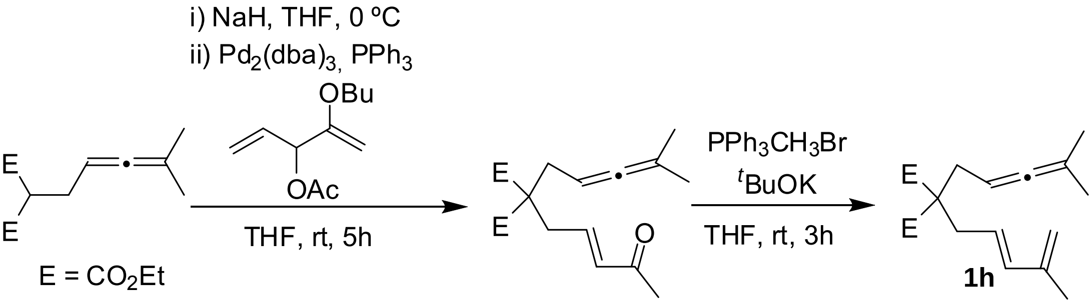
[11] (*E*)-5-Bromo-4-methylpenta-1,3-diene was prepared from acrylaldehyde as previously described in: E. Piers, G. L. Jung, E. H. Ruediger, *Can J. Chem.* **1987**, *65*, 670-82. See also: M. Gulías, J. Durán, F. López, L. Castedo, J. L. Mascareñas, *J. Am. Chem. Soc.* **2007**, *129*, 11026-11027.

[12] Prepared as described in: M. Murakami, S. Kadowaki, T. Matsuda, *Org. Lett.* **2005**, *7*, 3953-3956.

[13] Prepared as described in: T. Kim, G. Mirafzal, J. Liu, N. Auld, *J. Am. Chem. Soc.* **1993**, *115*, 7653-7664.

(C), 133.2 (CH), 130.8 (CH), 129.7 (CH), 126.6 (CH), 95.7 (C), 86.2 (CH), 69.7 (CH_2), 68.6 (CH_2), 30.80 (CH_3), 20.3 (CH_3), 18.0 (CH_3). **MS** (*m/z, I*): 179 ([M^+ +1], 11), 113 (50), 97 (100). **HRMS** calculated for $C_{12}H_{19}O$ 179.1436, found 179.1430.

Preparation of (*E*)-Diethyl 2-(4-methylpenta-2,3-dienyl)-2-(4-methylpenta-2,4-dienyl)malonate (1h)



Diethyl 2-(4-methylpenta-2,3-dienyl)malonate[9] (400 mg, 1.67 mmol) was added dropwise to a suspension of NaH (70 mg, 1.75 mmol) in THF (15 mL) cooled to 0 °C. After stirring for 10 min at this temperature, the reaction mixture was allowed to warm up to rt and stirred for further 5 min. Then, a solution containing $Pd_2(dba)_3$ (31 mg, 0.03 mmol), PPh_3 (35 mg, 0.13 mmol) and 2-butoxypenta-1,4-dien-3-yl acetate[14] (330 mg, 1.67 mmol) in THF (5 mL), previously stirred for 10 min, was added via cannula. The resulting mixture was stirred for 5h at rt, filtered through a short pad of silica gel (10% EtOAc/hexanes), poured into HCl(10% aq) (50 mL) and extracted with Et_2O (3 x 30 mL). The organic phases were dried, filtered and concentrated to give a crude oil residue that was purified by flash chromatography (10% Et_2O/hexanes) to give 360 mg of (E)-diethyl 2-(4-methylpenta-2,3-dienyl)-2-(4-oxopent-2-enyl)malonate (67 %). Colourless oil. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ (ppm), 6.69-6.57 (1H, m), 6.04 (1H, d, *J* = 15.9 Hz), 4.76-4.68 (1H, m), 4.15 (4H, q, *J* = 7.1 Hz), 2.79 (2H, d, *J* = 7.6 Hz), 2.52 (2H, d, *J* = 7.6 Hz), 2.18 (3H, s), 1.62 (3H, s), 1.61 (3H, s), 1.20 (6H, t, *J* = 7.1 Hz); **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 203.8 (C), 197.9 (CO), 170.1 (CO), 142.1 (CH), 134.3 (CH), 95.4 (C), 82.2 (CH), 62.4 (CH_2), 57.3 (C), 35.2 (CH_2), 33.1 (CH_2), 26.3 (CH_3), 20.3 (CH_3), 14.0 (CH_3).

Potassium *tert*-butoxide (91 mg, 0.81 mmol) was added to a solution of methyltriphenylphosphonium bromide (333 mg, 0.93 mmol) in THF (6 mL) cooled to 0 °C,. After stirring for 15 min at this temperature, a solution of (*E*)-diethyl 2-(4-methylpenta-2,3-dienyl)-2-(4-oxopent-2-enyl)malonate (200 mg,

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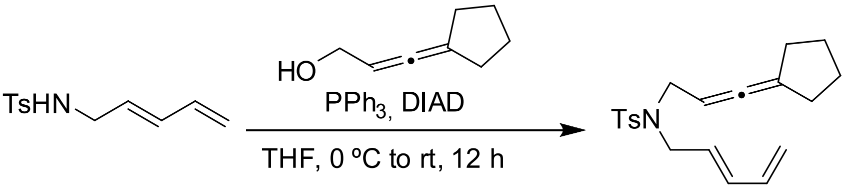
[14] P. A. Wender, A. J. Dyckman, C. O. Husfeld, D. Kadereit, J. A. Love, H. Rieck, *J. Am. Chem. Soc.* **1999**, *121*, 10442-10443.

0.62 mmol) in THF (4 mL) was added. The reaction mixture was allowed to warm up to rt, stirred for 3h, poured into water and extracted with Et_2O (3x10 mL). The organic phases were dried, filtered and concentrated to give a crude oil residue that was purified by flash chromatography (4% Et_2O/hexanes) to give 150 mg of the allene **1h** (75 %). Colourless oil. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ (ppm), 6.15 (1H, d, ***J*** = 15.5 Hz), 5.45 (1H, dt, ***J*** = 15.4 and 7.6 Hz), 4.86 (2H, d, ***J*** = 6.5 Hz), 4.80-4.70 (1H, m), 4.20-4.11 (4H, m), 2.71 (2H, d, ***J*** = 7.5 Hz), 2.53 (2H, d, ***J*** = 7.6 Hz), 1.77 (3H, s), 1.64 (3H, s), 1.63 (3H, s), 1.22 (6H, t, ***J*** = 7.1 Hz); **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 203.7 (C), 170.7 (CO), 141.6 (C), 136.8 (CH), 123.8 (CH), 115.5 (CH_2), 94.9 (C), 82.7 (CH), 61.1 (CH_2), 57.9 (C), 35.4 (CH_2), 32.7 (CH_2), 20.4 (CH_3), 18.5 (CH_3), 14.0 (CH_3); **MS** (*m/z, I*): 321 ([M^+ +1], 33), 247 (100), 173 (72); **HRMS** calculated for $C_{19}H_{29}O_4$ 321.2066, found 321.2053.

Preparation of (*E*)-*N*-(3-cyclopentylideneallyl)-4-methyl-n-(penta-2,4-dienyl)benzenesulfonamide (1k)



PPh_3 (354 mg, 1.35 mmol) and 3-cyclopentylideneprop-2-en-1-ol[15] (113 mg, 1.15 mmol) were added to a solution of (*E*)-4-methyl-N-(penta-2,4-dienyl) benzenesulfonamide[8] (237 mg, 1 mmol), in THF (5 mL). The mixture was cooled to 0 °C and diisopropyl azodicarboxylate (DIAD) (266 µL, 1.35 mmol) was added dropwise. The reaction was stirred overnight 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 275 mg of the allene **1k** (80 %).[16] Colourless oil. **^{1}H-NMR** (250 MHz, $CDCl_3$): δ (ppm) 7.62-7.58 (2H, m), 7.19 (2H, d, ***J*** = 8.2 Hz), 6.23-5.92 (2H, m), 5.46-5.32 (1H, m), 5.09-4.96 (2H, m), 4.75-4.66 (1H, m), 3.81-3.64 (4H, m), 2.31 (3H, s), 2.22-2.20 (4H, m), 1.57-1.51 (4H, m); **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 198.5 (C), 142.9 (C), 137.3 (C), 135.7 (CH), 134.4 (CH), 129.4 (CH), 129.4 (CH), 127.7 (CH), 126.9 (CH), 126.9 (CH), 117.5 (CH_2), 104.9 (C), 86.2 (CH), 47.7 (CH_2), 46.5 (CH_2), 32.5 (CH_2), 30.9 (CH_2), 26.7 (CH_2), 24.8 (CH_2), 21.2 (CH_3).; **MS** (*m/z, I*): 344 ([M^+ +1], 16), 250 (100), 190 (49); **HRMS** calculated for $C_{20}H_{26}NO_2S$ 344.1684 , found 344.1682.

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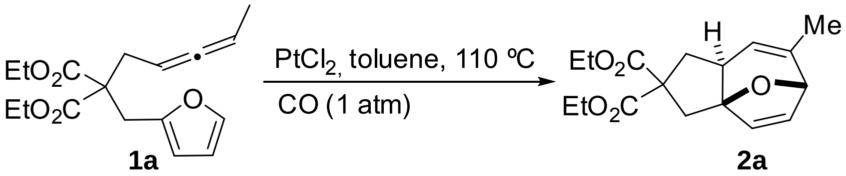
[15] 3-Cyclopentylideneprop-2-en-1-ol was prepared as reported in: B. M. Trost, A. Pinkerton, M. Seidel, *J. Am. Chem. Soc.* **2001**, *123*, 12466-12476.

[16] Compound **1k** could not be completely purified by flash chromatography and was used in this way in the cycloaddition.

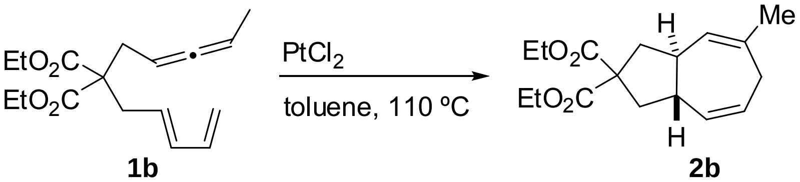
General Procedure for the Cycloaddition Reaction, exemplified for the cycloaddition of **1a** (see Table 1, entry 12), and **1b** (see Table 2, entry 1).

Standard Cycloaddition under CO (1 atm):



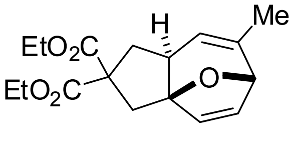
$PtCl_2$ (8.7 mg, 0.033 mmol) and a solution of compound **1a** (100 mg, 0.33 mmol) in toluene (1.6 mL) were added to a dried Schlenk tube under argon. Carbon monoxide was bubbled for 5-10 min and the mixture was heated at 110°C under a CO atmosphere (1 atm) for 1 h. The mixture was allowed to cooled down to rt and filtered through a short pad of florisil eluting with Et_2O. The filtrate was concentrated and purified by flash chromatography (4% Et_2O/hexanes) to afford 45 mg of the tricycle **2a**. (45% yield)

Standard Cycloaddition under argon:



$PtCl_2$ (9.1 mg, 0.034 mmol) and a solution of compound **1b** (100 mg, 0.34 mmol) in toluene (1.6 mL) were added to a dried Schlenk tube under argon. The mixture was refluxed for 5 h.[17] The mixture was allowed to cool down to rt and filtered through a short pad of florisil eluting with Et_2O. The filtrate was concentrated and purified by flash chromatography on silica gel (1-4% Et_2O/hexanes) to afford 62 mg of **2b** (62 %).

Cycloadduct 2a



Colourless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 6.48 (1H, dd, *J* = 5.8 and 1.8 Hz), 5.94 (1H, d, *J* = 5.8 Hz), 5.22 (1H, br s), 4.52 (1H, br s), 4.23-4.16 (4H, m), 2.82 (1H, d, *J* = 15.5 Hz), 2.58 (1H, d, *J* = 15.5 Hz), 2.54 (1H, dd, *J* = 13.5 and 7.9 Hz), 2.30 (1H, dd, *J* = 12.7 and 12.7 Hz), 2.03-1.95 (1H, m), 1.71 (3H, t, *J* = 1.8 Hz), 1.28-1.21 (6H, m); **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ (ppm) 172.6

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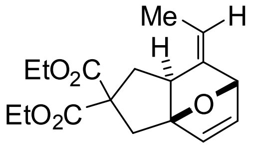
[17] See the time and temperature required for any particular cycloaddition in the Table 2 of the main manuscript.

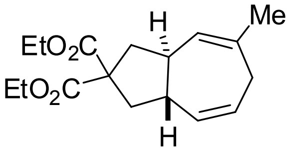
(CO), 171.2 (CO), 139.2 (C), 137.1 (CH), 130.9 (CH), 120.0 (CH), 91.2 (C), 80.9 (CH), 61.6 (CH_2), 61.4 (CH_2), 58.2 (C), 41.1 (CH_2), 41.0 (CH), 38.7 (CH_2), 19.6 (CH_3), 14.0 (CH_3). **MS:** 306, 215, 131 (100%).

Cycloadduct 4



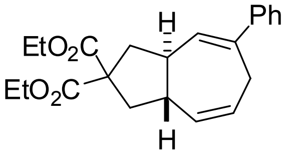
Colourless oil. Mixture of two diastereoisomers. Data of the major component (*exo* configuration)[18]: **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.38-6.37 (1H, m), 6.34-6.33 (1H, m), 5.49 (1H, dq, *J* = 6.7 and 1.8 Hz), 4.91 (1H, br s), 4.25-4.16 (4H, m), 2.87-2.83 (1H, m), 2.74-2.65 (2H, m), 2.47-2.42 (1H, m), 2.24-2.18 (1H, m), 1.62 (3H, d, *J* = 6.7 Hz), 1.29-1.22 (6H, m); **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ (ppm), 172.6 (CO), 171.1 (CO), 141.4 (C), 136.0 (CH), 135.6 (CH), 116.2 (CH), 98.2 (C), 83.8 (CH), 61.7 (CH_2), 61.5 (CH_2), 58.3 (C), 46.9 (CH), 37.5 (CH_2), 35.9 (CH_2), 15.5 (CH_3), 14.0 (CH_3). **MS:** 306, 203, 159 (100%).

(3aR*,4*Z*,7*Z*,8aS*)-Diethyl 5-methyl-1,3,3a,8a-tetrahydroazulene-2,2(6H)-dicarboxylate (2b)



Colourless oil (62% yield). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 5.63 (1H, dd, *J* = 11.2 and 2.1 Hz), 5.53-5.48 (1H, m), 5.43 (1H, br s), 4.21-4.15 (4H, m), 2.96 (1H, d, *J* = 20.0 Hz), 2.69-2.60 (3H, m), 2.60-2.53(1H, m), 2.51-2.43 (1H, m), 1.92 (1H, d, *J* = 12.0 Hz), 1.86 (1H, d, *J* = 12.6 Hz), 1.69 (3H, s), 1.25-1.22 (6H, m); **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ (ppm) 172.6 (CO), 135.3 (C), 131.8 (CH), 126.6 (CH), 126.0 (CH), 61.4 (CH_2), 57.6 (C), 43.9 (CH), 43.3 (CH), 41.1 (CH_2), 41.0 (CH_2), 34.4 (CH_2), 26.1 (CH_3), 14.0 (CH_3); **MS** (*m/z, I*): 293 ([M^+ +1], 7), 173 (69), 55 (100); **HRMS** calculated for $C_{17}H_{24}O_4$ 292.1675, found 292.1662.

(3aR*,4*E*,7*Z*,8aS*)-Diethyl 5-phenyl-1,3,3a,8a-tetrahydroazulene-2,2(6H)-dicarboxylate (2c)



Colourless oil (95% combined yield of a mixture of **2c** +**3c**).[19] **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.25-7.13 (5H, m), 5.87 (1H, dd, *J* = 4.5 and 2.2 Hz), 5.62 (1H, d, *J* = 11.4 Hz),5.60-5.54 (1H, m), 4.16-4.09 (4H, m), 3.41 (1H, ddd, *J* = 18.5, 3.1 and 1.9 Hz), 3.08 (1H, dd, *J* = 19.0 and 6.3 Hz), 2.88-2.76 (1H, m), 2.70 (1H, dd, *J* = 13.3 and 7.4 Hz), 2.62 (1H, dd, *J* = 13.3 and 7.2 Hz), 2.51-2.41 (1H, m), 1.98 (1H, dd, *J* = 13.1 and 12.3 Hz), 1.87 (1H, dd, *J* =

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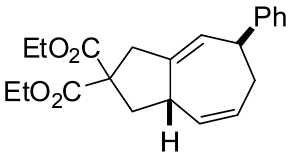
[18] Deduced, based on two-dimension NMR experiments, from the spectra of a 3.5:1 mixture of the *exo* and *endo* adducts.

[19] Cycloadducts **2c** and **3c** could not be completely separated by column chromatography: Typically, 85 to 90% of pure cycloadduct **2c** could be isolated from the crude reaction mixture. Accordingly, cycloadduct **3c** remained contaminated with 10-15% of **2c**.

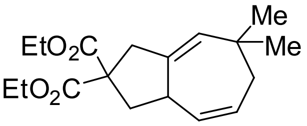
12.8 and 12.8 Hz), 1.23-1.15 (6H, m); **^{13}C-NMR** (125.8 MHz, CDCl$_3$): δ (ppm) 172.6 (CO), 143.9 (C), 140.6 (C), 131.8 (CH), 130.6 (CH), 128.2 (CH), 126.7 (CH), 125.9 (CH), 125.6 (CH), 61.4 (CH$_2$), 57.7 (C), 43.6 (CH), 43.6 (CH), 40.8 (CH$_2$), 40.8 (CH$_2$), 32.3 (CH$_2$), 14.0 (CH$_3$). **MS:** 354, 280, 207 (100%), 173.

(3aS*,4Z,7S*,8Z)-Diethyl 7-phenyl-3,3a,6,7-tetrahydroazulene-2,2(1H)-dicarboxylate (3c)



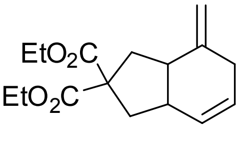
Colourless oil. **^{1}H-NMR** (500 MHz, CDCl$_3$): δ (ppm) 7.24-7.13 (5H, m), 5.86-5.81 (1H, m), 5.76 (1H, d, *J* = 9.8 Hz), 5.41 (1H, s), 4.17-4.10 (4H, m), 3.72 (1H, br s), 3.34-3.31 (1H, m), 2.99 (1H, d, *J* = 16.4 Hz), 2.86 (1H, dd, *J* = 16.4 and 2.3 Hz), 2.72-2.56 (2H, m), 2.10 (1H, dd, *J* = 12.6 and 10.1 Hz), 2.09 (1H, m), 1.23-1.17 (6H, m); **^{13}C-NMR** (125.8 MHz, CDCl$_3$): δ (ppm) 171.7 (CO), 171.5 (CO), 146.7 (C), 140.1 (C), 136.5 (CH), 129.3 (CH), 128.4 (CH), 127.5 (CH), 126.2 (CH), 125.2 (CH), 61.5 (CH$_2$), 58.4 (C), 43.0 (CH), 42.0 (CH$_2$), 40.8 (CH$_2$), 38.9 (CH), 34.4 (CH$_2$), 14.0 (CH$_3$); **MS** (*m/z, I*): 355 ([M$^+$ +1], 24), 308 (34), 281 (34), 133 (61); **HRMS** calculated for C$_{22}$H$_{27}$O$_4$ 355.1909, found 355.1907.

(4Z,8Z)-Diethyl 7,7-dimethyl-3,3a,6,7-tetrahydroazulene-2,2(1H)-dicarboxylate (3d)



Colourless oil (98%, entry 7). **^{1}H-NMR** (500 MHz, CDCl$_3$): δ (ppm), 5.75-5.66 (2H, m), 5.16 (1H, br s), 4.23-4-13 (4H, m), 3.55 (1H, t, *J* = 9.2 Hz), 2.94 (2H, dd, *J* = 16.4 and 1.1 Hz), 2.86 (1H, td, *J* = 16.4 and 2.2 Hz), 2.58 (1H, dd, *J* = 12.6 and 9.4 Hz), 2.48 (1H, dd, *J* = 13.9 and 4.7 Hz), 2.07 (1H, dd, *J* = 12.6 and 11.2 Hz), 1.89-1.82 (1H, m), 1.27-1.20 (6H, m), 0.99 (3H, s), 0.94 (3H, s); **^{13}C-NMR** (125.8 MHz, CDCl$_3$): δ (ppm) 171.8 (CO), 171.6 (CO), 136.8 (C), 135.2 (CH), 132.3 (CH), 128.8 (CH), 61.4 (CH$_2$), 58.3 (C), 41.8 (CH$_2$), 40.8 (CH$_2$), 39.0 (CH$_2$), 38.9 (CH), 34.3 (C), 31.5 (CH$_3$), 28.6 (CH$_3$), 14.0 (CH$_3$); **MS** (*m/z, I*): 307 ([M$^+$ +1], 24), 247 (38), 233 (100); **HRMS** calculated for C$_{18}$H$_{27}$O$_4$ 307.1909, found 307.1903.

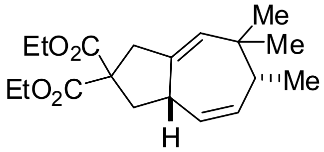
(3aS*,4Z, 6R*,8Z)-Diethyl 7-methylene-3,3a,7,7a-tetrahydro-1H-indene-2,2(6H)-dicarboxylate (6e)



Colourless oil. **^{1}H-NMR** (500 MHz, CDCl$_3$): δ (ppm), 5.80 (1H, dd, *J* = 9.7 and 1.1 Hz), 5.63-5.59 (1H, m), 4.76 (1H, s), 4.70 (1H, s), 4.21-4.16 (4H, m), 2.94 (1H, dd, *J* = 20.6 and 2.5 Hz), 2.82 (1H, dd, *J* = 20.6 and 2.3 Hz), 2.68 (1H, dd, *J* = 12.8 and 6.7 Hz), 2.57 (1H, dd, *J* = 12.9 and 5.6 Hz), 2.25-2.19 (1H, m), 2.17-2.12 (1H, m), 2.06 (1H, t, *J* = 12.3 Hz), 1.79 (1H, t, *J* = 12.7 Hz), 1.27-1.23 (6H, m); **^{13}C-NMR** (125.8 MHz, CDCl$_3$): δ (ppm) 172.7 (CO), 146.7 (C), 128.3 (CH), 127.2

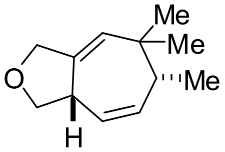
(CH), 104.4 (CH_2), 61.4 (CH_2), 58.4 (C), 48.4 (CH), 45.5 (CH), 39.0 (CH_2), 35.3 (CH_2), 34.7 (CH_2), 14.0 (CH_3). **MS:** 278, 204, 173, 131 (100%).

(3aS*,4*Z*,6R*,8*Z*)-diethyl 6,7,7-trimethyl-3,3a,6,7-tetrahydroazu lene-2,2(1H)-dicarboxylate (3f)



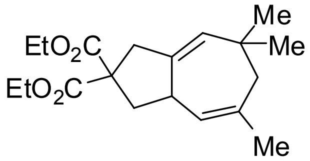
Colourless oil (81%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 5.63 (1H, ddd, ***J*** = 10.2, 2.9 and 1.7 Hz), 5.39-5.32 (1H, m), 5.14 (1H, dd, ***J*** = 4.6 and 2.1 Hz), 4.21-4.12 (4H, m), 3.53-3.46 (1H, m), 2.96 (1H, dd, ***J*** = 16.5 and 1.5 Hz), 2.87 (1H, td, ***J*** = 16.5 and 2.2 Hz), 2.64-2.53 (2H, m), 2.06 (1H, dd, ***J*** = 12.6 and 11.0 Hz), 1.23 (6H, q, ***J*** = 7.3 Hz), 0.99 (3H, s), 0.98 (3H, d, ***J*** = 7.9 Hz), 0.85 (3H, s); **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ (ppm) 171.8 (CO), 171.6 (CO), 137.1 (C), 136.6 (CH), 133.5 (CH), 132.7 (CH), 61.4 (CH_2), 58.3 (C), 41.9 (CH_2), 40.9 (CH_2), 40.0 (CH), 39.1 (CH), 36.7 (C), 28.9 (CH_3), 23.3 (CH_3), 16.1 (CH_3), 14.0 (CH_3); **MS** (*m/z, I*): 321 ($[M^+ +1]$, 58), 293 (67), 269 (55); **HRMS** calculated for $C_{19}H_{29}O_4$ 321.2066, found 321.2060.

(3aS*,4*Z*,6*R**,8*Z*)-Diethyl 6,7,7-trimethyl-3,3a,6,7-tetrahydroazu lene-2,2(1H)-dicarboxylate (3g).



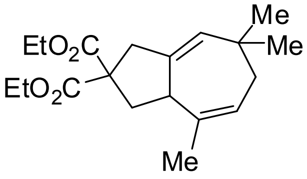
Colourless oil (62%). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ (ppm) 5.59 (1H, dd, ***J*** = 10.1 and 4.1 Hz), 5.47-5.42 (1H, m), 5.15-5.14 (1H, m), 4.34 (1H, d, ***J*** = 12.3 Hz), 4.24-4.29 (2H, m), 3.62-3.58 (1H, m), 3.50 (1H, dd, ***J*** = 10.0 and 7.9 Hz), 2.70-2.63 (1H, m), 1.04-1.02 (6H, m), 0.90 (3H, s); **^{13}C-NMR** (100.6 MHz, $CDCl_3$): δ (ppm) 137.8 (CH), 137.5 (C), 130.4 (CH), 128.7 (CH), 74.3 (CH_2), 72.9 (CH_2), 40.5 (CH), 40.3 (CH), 36.3 (C), 28.9 (CH_3), 23.1 (CH_3), 16.1 (CH_3); **MS** (*m/z, I*): 179 ($[M^+ +1]$, 85), 149 (87), 123 (90); **HRMS** calculated for $C_{12}H_{19}O$ 179.1436, found 179.1437.

(4*Z*,8*Z*)-Diethyl 5,7,7-trimethyl-3,3a,6,7-tetrahydroazulene-2,2(1H)-dicarboxylate (3h)



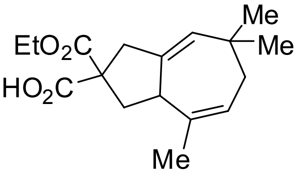
Colourless oil (72%). **^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm),5.39 (1H, s), 5.05 (1H, s), 4.17-4.10 (4H, m), 3.40 (1H, br s), 2.81 (1H, d, ***J*** = 16.5 Hz), 2.89 (1H, d, ***J*** = 16.4 Hz), 2.62 (1H, d, ***J*** = 13.7 Hz), 2.52 (1H, dd, ***J*** = 12.0 and 8.9 Hz), 2.01 (1H, dd, ***J*** = 11.9 and 12.0 Hz), 1.68 (3H, s), 1.58 (1H, d, ***J*** = 13.3 Hz), 1.21-1.17 (6H, m), 0.93 (3H, s), 0.90 (3H, s); **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ (ppm) 171.8 (CO), 171.6 (CO), 137.1 (C), 131.3 (CH), 128.7 (CH), 61.3 (CH_2), 61.3 (CH_2), 58.4 (C), 44.2 (CH_2), 41.7 (CH_2), 41.0 (CH_2), 38.6 (CH), 34.0 (C), 32.0 (CH_3), 28.3 (CH_3), 26.0 (CH_3), 14.0 (CH_3), 14.0 (CH_3). **MS:** 320, 246 (100%), 173.

(4*Z*,8*Z*)-diethyl-4,7,7-trimethyl-3,3a,6,7-tetrahydroazulene-2,2 (1H)-dicarboxylate (3i)[20]



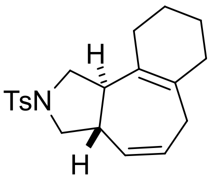
Colourless oil (73%). **^{1}H-NMR** (250 MHz, $CDCl_3$): δ (ppm) 5.55-5.50 (1H, m), 5.17 (1H, s), 4.25-4.14 (4H, m), 3.69-3.61 (1H, m), 2.89-2.86 (2H, m), 2.61-2.53 (1H, m), 2.46-2.38 (1H, m), 2.16 (1H, t, ***J*** = 12.6 Hz), 1.75 (3H, s), 1.64-1.59 (1H, m), 1.28-1.22 (6H, m), 0.96 (3H, s), 0.92 (3H, s); **^{13}C-NMR** (62.9 MHz, $CDCl_3$): δ (ppm) 171.7 (CO), 171.6 (CO), 140.0 (C), 136.2 (C), 129.0 (CH), 128.2 (CH), 61.4 (CH_2), 58.1 (C), 41.6 (CH_2), 41.6 (CH_2), 38.6 (CH), 37.8 (CH_2), 34.0 (C), 31.7 (CH_3), 28.3 (CH_3), 21.8 (CH_3), 14.0 (CH_3); **MS** (*m/z, I*): 321 ($[M^+$ +1], 100), 275 (87), 247 (90); **HRMS** calculated for $C_{19}H_{29}O_4$ 321.2066, found 321.2061.

(4*Z*,8*Z*)-2-(ethoxycarbonyl)–4,7,7–trimethyl–1,2,3,3a,6,7–hexahy droazulene–2-carboxylic acid (3i')[21]



^{1}H-NMR (500 MHz, CDCl3): δ (ppm) 5.55-5.52 (1H, m), 5.18 (1H, s), 4.26-4.22 (2H, m), 3.68-3.65 (1H, m), 2.97-2.87 (2H, m), 2.63-2.59 (1H, m), 2.44-2.40 (1H, m), 2.22 (1H, t, J = 12.6 Hz), 1.76 (3H, s), 1.65-1.63 (1H, m), 1.28 (3H, t, ***J*** = 7.1 Hz), 1.10 (1H, s), 0.97 (3H, s), 0.93 (3H, s); **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ (ppm) 176.4 (CO), 171.3 (CO), 139.9 (C), 135.9 (C), 132.8 (CH), 124.1 (CH), 61.8 (CH_2), 57.9 (C), 41.7 (CH_2), 41.7 (CH), 38.6 (CH_2), 38.1 (CH_2), 34.1 (C), 31.7 (CH_3), 28.2 (CH_3), 21.7 (CH_3), 14.0 (CH_3).

(3aS*,10bR*,*Z*)-2-Tosyl-2,3,3a,6,7,8,9,10,10b-hexahydro-1H-benzo [7]annulene[5,6-c]pyrrole (2k)



Colourless oil (75%).**^{1}H-NMR** (500 MHz, $CDCl_3$): δ (ppm) 7.71 (2H, d, ***J*** = 8.2 Hz), 7.32 (2H, d, ***J*** = 8.0 Hz), 5.66-5.62 (1H, m), 5.47 (1H, d, ***J*** = 10.8 Hz), 3.61-3.58 (2H, m), 3.20 (1H, dd, ***J*** = 11.3 and 9.7 Hz), 2.94 (1H, dd, ***J*** = 11.1 and 9.6 Hz), 2.88 (1H, d, ***J*** = 18.4 Hz), 2.80-2.74 (1H, m), 2.58-2.51 (1H, m), 2.47 (1H, dd, ***J*** = 18.4 and 6.7 Hz), 2.43 (3H, s), 1.93-1.89 (3H, m), 1.76-1.73 (1H, m), 1.54-1.47 (4H, m); **^{13}C-NMR** (125.8 MHz, $CDCl_3$): δ (ppm) 143.3 (C), 134.3 (C), 132.6 (C), 129.7 (CH), 129.2 (C), 128.6 (CH), 128.5 (CH), 127.4 (CH), 52.8 (CH_2), 50.7 (CH_2), 45.1 (CH), 41.6 (CH), 33.8 (CH_2), 32.6 (CH_2), 27.1 (CH_2),

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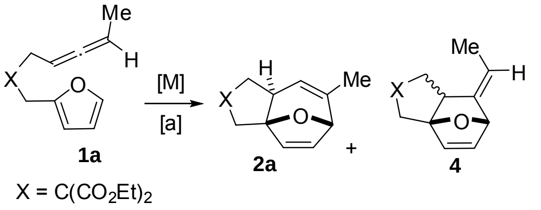
[20] Cycloadduct **3i** was better characterized after hydrolysis to the corresponding monoester **3i'** in order to remove a small impurity impossible to separate by column chromatography on silica gel. The yield of Table 2 (73%) refers to the global yield of the cycloaddition and subsequent hydrolysis.

[21] **3i'** was obtained by treating a solution of **3i** in THF/H_2O (1:1) with LiOH (3 equiv). After stirring for 5h at rt, the mixture was acidified (HCl, 10% aq.) and extracted with Et_2O. The combined organic phases were dried, filtered and concentrated to give a crude which was chromatographed (25-50% Et_2O/Hexanes) to give **3i´** (73% global yield from **1i**)

22.8 (CH_2), 22.6 (CH_2), 21.5 (CH_3); **MS** (*m/z, I*): 345 ([M^+ +1], 23), 344 (100), 123 (33); **HRMS** calculated for $C_{20}H_{26}NO_2S$ 344.1684, found 344.1681.

Further details on the study of the cycloaddition of 1a.

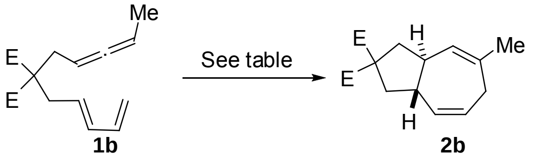
Table I (extended Table 1 of the main manuscript).[22]



Entry[a]	[M]	Products (ratio)[b]	T (ºC)	Time (h)	Yield (%)[c]
1	$Ph_3PAuCl/AgSbF_6$	**2a**	24	24	30[d]
2	$Ph_3PAuCl/AgSbF_6$	**2a**	40	24	25[e]
3	$Ph_3PAuCl/AgSbF_6$	**2a**	75	6	10[f]
4	$Ph_3PAuCl/AgSbF_6$	**4** : **2a** (6.2 : 1)	110	6	25
5	$AuCl_3$	**2a**	40	24	26[g]
6	AuCl	**2a**	40	24	5[h]
7	$AuCl_3$	**4** : **2a** (6.1 : 1)	110	8	57
8	AuCl	**4** : **2a** (19 : 1)	110	8	89[i]
9	$PtBr_2$	**4** :**2a** (45 : 1)	110	8	78
10	$[PtCl_2(H_2C{=}CH_2)]_2$ /(*p*-$CF_3C_6H_4)_3P$	**4**	110	8	82
11	$PtCl_4$	**4** :**2a** (4.4 : 1)	110	8	57
12	$PtCl_2$	**4** : **2a** (3.4 : 1)	110	8	73
13	$PtCl_2$ / CO (1 atm)	**2a**	110	1	45[i]

[a] Conditions: **1a** (0.1-0.2 M), 10 mol% [M]. Reactions at 23 ºC or 40 ºC were carried out in CH_2Cl_2. Otherwise toluene was employed. Conversions > 99% unless otherwise noted. [b] Ratio of products determined by ^{1}H-NMR in the crude reaction mixtures. [c] Determined by ^{1}H-NMR spectroscopy against an internal standard (1,2,3-trimetoxybenzene), unless otherwise noted.[d] 65% conversion. [e] 55% conversion; [f] 77% conversion; [g] 66% conversion; [h] 10% conversion. [i] Isolated yield.

Cycloaddition of 1b



Entry	Catalyst (10 mol%)	Solvent	T (ºC)	Time (h)	Conv.(%)[a]	**2b** (%)[b]
1	$PtCl_2$	Toluene	110	5	88	80[c]
2	$PtCl_2$ / CO	Toluene	110	3	88	79
3	$PtCl_2$	Toluene	80	24	80	65
4	$PtCl_2$	$ClCH_2CH_2Cl$	80	24	80	63
5	$PtCl_2$	$ClCH_2CH_2Cl$	23	4	0	0
6	$PtCl_4$	Toluene	110	5	83	64
7	$PtBr_2$	Toluene	110	5	70	53
8	AuCl	Toluene	110	24	7	0
9	$AuCl_3$	$ClCH_2CH_2Cl$	80	15	15	6
10	$Ph_3PAuCl/AgSbF_6$	CH_2Cl_2	23	48	46	17

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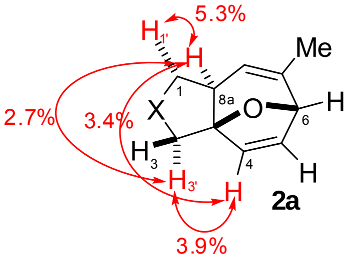
[22] The catalyst [M] (0.011 mmol) and a solution of **1a** (33 mg, 0.11 mmol) in toluene (0.5 mL) were added to a dried Schlenk tube under argon. A solution of 1,2,3-trimetoxybenzene in toluene (0.055 ml, 1.0 M) was added as an internal standard, and the mixture was stirred at the appropriate temperature. The mixture was allowed to cooled down to rt and filtered through a short pad of florisil eluting with Et_2O. The filtrate was concentrated and analyzed by ^{1}H-NMR.

[a] Conversion determined by GC analysis; [b] determined by GC; [c] Results included in Table 2 of the main manuscript, entry 1; 62 % isolated yield.

Stereochemical Analysis of the Products

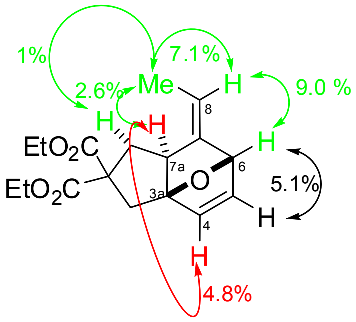
The stereochemical assignments of the cycloadducts was determined on the basis of two dimensional NMR experiments (COSY, NOESY, HMBC and HMQC or HSQC), in addition to standard ^{1}H, ^{13}C and DEPT and nOe experiments.

Stereochemistry of **2a**: The observation of nOe between H4 and H8a is only compatible with the stereochemistry corresponding to the exo-cycloadduct. Furthermore, nOes between H4-H3′, H3′-H8a and H3-H6 also warrants that stereochemistry.

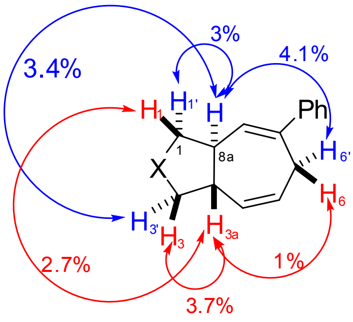


2a

Stereochemistry of **4a**: The observation of nOe between H4 and H7a is only compatible with the stereochemistry corresponding to the exo-cycloadduct. On the other hand, the strong nOe's between H8 and H6 and the nOes of the methyl group unambiguously determine the alkene regiochemistry.

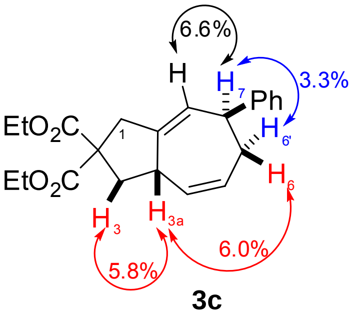


Stereochemistry of **2c**: Due to an overlap between key signals in the $CDCl_3$-^{1}H-NMR spectrum (500 MHz), the determination of the stereochemistry was carried out using C_6D_6 as solvent. The observation of nOe's between H3a, H3, H6 and H1 as well as those between H8a, H1′,H3′ and H6′ is only compatible with a trans fusion of the bicyclic system. Accordingly there is not nOe between H8a and H3a. **^{1}H-NMR** (500 MHz, C_6D_6): δ (ppm) 7.19-7.07 (5H, m), 5.87-5.85 (1H, m), 5.61 (1H, d, ***J*** = 11.2 Hz), 5.51-5.43 (1H, m), 4.02-3.93 (4H, m), 3.24 (1H, d, ***J*** = 18.7 Hz), 3.03-2.88 (4H, m), 2.69-2.58 (1H, m), 2.19 (1H, dd, ***J*** = 14.8 and 15.4 Hz), 2.12 (1H, dd, ***J*** = 12.8 and 12.8 Hz), 0.95-0.89 (6H, m); **^{13}C-NMR** (125.8 MHz, C_6D_6): δ (ppm) 172.4 (CO), 144.4 (C), 141.1 (C), 132.0 (CH), 131.0 (CH), 128.4 (CH), 126.9 (CH), 126.4 (CH), 125.9 (CH), 61.3 (CH_2), 58.1 (C), 44.2 (CH),44.1 (CH),41.5 (CH_2) 41.3 (CH_2), 32.5 (CH_2), 14.3 (CH_3).



2c

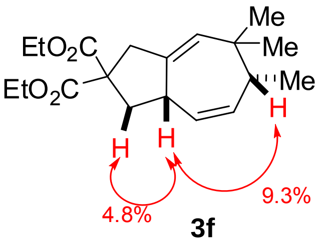
***Stereochemistry of* 3c**: The observation of important nOes between H3-H3a and H3a-H6 confirms that the three atoms are cis. nOe between H7 and H6' together with the absence of nOe between H7 and H6, H3a or H3 determines the stereochemistry at the C7 position.



3c

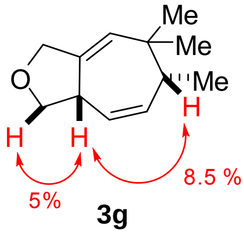
***Stereochemistry of* 2b**: Stereochemistry of **2b** was determined by nOe experiments similar to those reported for **2c**.

Stereochemistry of* 3f**: Due to an overlap between key signals in the $CDCl_3$-^1H-NMR spectrum (500 MHz), the determination of the stereochemistry was more conveniently carried out in C_6D_6. **^{1}H-NMR** (500 MHz, C_6D_6): δ (ppm) 5.66 (1H, d, ***J = 10.2 Hz), 5.37-5.32 (1H, m), 5.16 (1H, br s), 3.98-3.92 (4H, m), 3.70 (1H, t, ***J*** = 9.1 Hz), 3.26 (1H, d, ***J*** = 16.5 Hz), 3.15 (1H, d, ***J*** = 16.4 Hz), 2.77 (1H, dd, ***J*** = 12.6 and 8.5 Hz), 2.60-2.52 (1H, m), 2.22 (1H, dd, ***J*** = 12.5 and 11.0 Hz), 0.96-0.87 (15H, m); **^{13}C-NMR** (125.8 MHz, C_6D_6): δ (ppm) 171.6 (CO), 171.3 (CO), 138.0 (C), 136.6 (CH), 133.7 (CH), 133.2 (CH), 61.3 (CH_2), 61.2 (CH_2), 58.7 (C), 42.5 (CH_2), 41.5 (CH_2), 40.5 (CH), 39.7 (CH), 37.0 (C), 29.0 (CH_3), 23.6 (CH_3), 16.4 (CH_3), 14.0 (CH_3), 14.0 (CH_3).



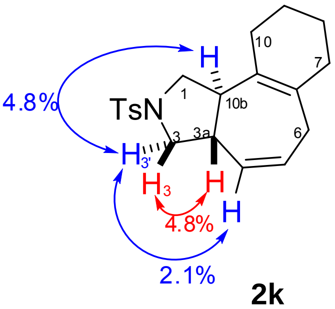
3f

***Stereochemistry of* 3g**: Stereochemistry of **3g** was determined by nOe experiments similar to those reported for **3f**.



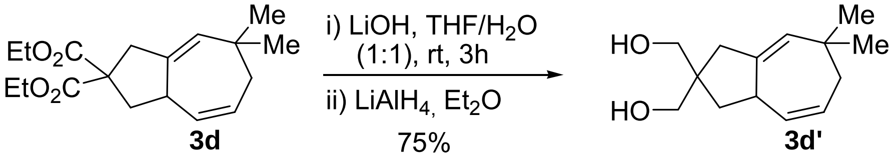
3g

***Stereochemistry of* 2k:** The observation of nOes between H3a and H3 as well as those between H10b, H3' and H4 is only compatible with a trans fusion of the bicyclic system.

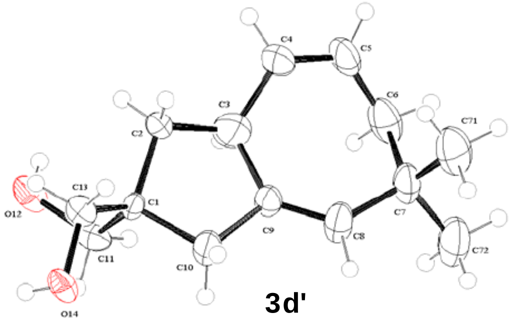


2k

Derivatization of 3d and X-Ray structure of 3d'



LiOH (5.9 mg, 0.245 mmol) was added to a solution of cycloadduct **3d** (30 mg, 0.098 mmol) in THF / water (1:1, 3 mL) at rt. After stirring for 5h at rt, the mixture was acidified with HCl (10% aq.) and extracted with Et_2O (3x3 mL). The combined organic phases were dried, filtered and concentrated to afford a crude oil that was dissolved in THF (2 mL) and added dropwise to a suspension of $LiAlH_4$ (15 mg, 0.39 mmol) in THF (2 mL) cooled at 0 °C. After stirring for 30 minutes, MeOH (1 mL) was added dropwise, and the mixture poured into water (25 mL) and extracted with Et_2O (3x3 mL). The organic phases were dried, filtered and concentrated to give a crude oil that was purified by silica gel chromatography (30-50 % Et_2O/hexanes) to give 19 mg of product **3d'** (88 % yield). ^{1}**H-NMR** (250 MHz, $CDCl_3$): δ (ppm) 5.71 (2H, s), 5.15 (1H, s), 3.70-3.53 (5H, br s), 2.53-2.46 (1H, m), 2.19 (2H, s), 2.09-2.00 (1H, m), 1.92-1.84 (1H, m), 1.61 (2H, br s), 1.49-1.40 (1H, m), 1.01 (3H, s), 0.96 (3H, s). Suitable crystals for X-Ray were grown up from a solution of **3d** in CH_2Cl_2, Et_2O and hexane. Diffraction experiments were carried out in a Brucker SMART 1000 difractometer.



3d'

Table 1. Crystal data and structure refinement for **3d′**.

Identification code	**3d′** (lm02fo2n)	
Empirical formula	C14 H22 O2	
Formula weight	222.32	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 37.882(9) Å	α= 90°.
	b = 6.1133(15) Å	β= 91.471(5)°.
	c = 11.153(3) Å	γ = 90°.
Volume	2582.0(11) Å^3	
Z	8	
Density (calculated)	1.144 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	976	
Crystal size	0.22 x 0.12 x 0.03 mm^3	
Theta range for data collection	1.08 to 21.71°.	
Index ranges	-38<=h<=38, 0<=k<=6, 0<=l<=11	
Reflections collected	7648	
Independent reflections	1522 [R(int) = 0.059]	
Completeness to theta = 21.71°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9978 and 0.9838	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1522 / 0 / 170	
Goodness-of-fit on F^2	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1345	
R indices (all data)	R1 = 0.0843, wR2 = 0.1705	
Largest diff. peak and hole	0.226 and -0.263 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **3d′**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6878(1)	4284(5)	4024(3)	22(1)
C(2)	6831(1)	2709(5)	5082(3)	25(1)
C(3)	6474(1)	1671(7)	4893(4)	30(1)
C(4)	6327(1)	694(7)	6028(4)	50(1)
C(5)	6013(1)	-188(7)	6037(5)	53(1)
C(6)	5750(1)	-104(6)	5013(4)	53(1)
C(7)	5619(1)	2209(6)	4693(4)	43(1)
C(71)	5462(1)	3301(7)	5797(4)	61(1)
C(72)	5326(1)	2014(7)	3723(4)	65(1)

C(8)	5907(1)	3630(6)	4208(4)	43(1)
C(9)	6253(1)	3513(5)	4324(3)	32(1)
C(10)	6502(1)	5155(5)	3792(4)	40(1)
C(11)	6999(1)	3037(5)	2926(3)	33(1)
O(12)	7323(1)	1902(4)	3144(2)	41(1)
C(13)	7140(1)	6070(5)	4346(3)	31(1)
O(14)	7165(1)	7673(4)	3421(2)	33(1)
C(3B)	6438(5)	2970(30)	5478(19)	30(1)

Table 3. Bond lengths [Å] and angles [°] for **3d′**.

C(1)-C(13)	1.513(4)
C(1)-C(11)	1.522(4)
C(1)-C(10)	1.536(4)
C(1)-C(2)	1.537(4)
C(2)-C(3)	1.503(5)
C(2)-C(3B)	1.57(2)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.518(6)
C(3)-C(9)	1.532(5)
C(3)-H(3)	0.9800
C(4)-C(5)	1.307(6)
C(4)-C(3B)	1.582(18)
C(4)-H(4)	1.02(4)
C(5)-C(6)	1.497(6)
C(5)-H(5)	0.99(5)
C(6)-C(7)	1.538(5)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-C(8)	1.505(5)
C(7)-C(71)	1.534(5)
C(7)-C(72)	1.535(6)
C(71)-H(71A)	0.9600
C(71)-H(71B)	0.9600
C(71)-H(71C)	0.9600
C(72)-H(72A)	0.9600
C(72)-H(72B)	0.9600
C(72)-H(72C)	0.9600
C(8)-C(9)	1.316(5)
C(8)-H(8)	0.97(4)
C(9)-C(3B)	1.488(19)
C(9)-C(10)	1.511(5)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-O(12)	1.424(4)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
O(12)-H(12)	0.89(5)
C(13)-O(14)	1.427(4)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
O(14)-H(14)	0.76(4)
C(3B)-H(3B)	0.9800
C(13)-C(1)-C(11)	110.0(3)
C(13)-C(1)-C(10)	112.9(3)
C(11)-C(1)-C(10)	109.6(3)
C(13)-C(1)-C(2)	111.0(3)
C(11)-C(1)-C(2)	110.3(2)
C(10)-C(1)-C(2)	102.7(2)
C(3)-C(2)-C(1)	106.2(3)
C(3)-C(2)-C(3B)	39.5(8)

C(1)-C(2)-C(3B)	106.4(7)
C(3)-C(2)-H(2A)	110.5
C(1)-C(2)-H(2A)	110.5
C(3B)-C(2)-H(2A)	138.7
C(3)-C(2)-H(2B)	110.5
C(1)-C(2)-H(2B)	110.5
C(3B)-C(2)-H(2B)	74.0
H(2A)-C(2)-H(2B)	108.7
C(2)-C(3)-C(4)	113.3(3)
C(2)-C(3)-C(9)	103.2(3)
C(4)-C(3)-C(9)	115.3(3)
C(2)-C(3)-H(3)	108.2
C(4)-C(3)-H(3)	108.2
C(9)-C(3)-H(3)	108.2
C(5)-C(4)-C(3)	121.4(4)
C(5)-C(4)-C(3B)	128.0(8)
C(3)-C(4)-C(3B)	39.2(8)
C(5)-C(4)-H(4)	125(2)
C(3)-C(4)-H(4)	114(2)
C(3B)-C(4)-H(4)	98(2)
C(4)-C(5)-C(6)	124.7(4)
C(4)-C(5)-H(5)	117(2)
C(6)-C(5)-H(5)	118(2)
C(5)-C(6)-C(7)	114.4(3)
C(5)-C(6)-H(6A)	108.7
C(7)-C(6)-H(6A)	108.7
C(5)-C(6)-H(6B)	108.7
C(7)-C(6)-H(6B)	108.7
H(6A)-C(6)-H(6B)	107.6
C(8)-C(7)-C(71)	109.7(3)
C(8)-C(7)-C(72)	108.0(3)
C(71)-C(7)-C(72)	108.2(3)
C(8)-C(7)-C(6)	112.4(3)
C(71)-C(7)-C(6)	110.1(3)
C(72)-C(7)-C(6)	108.4(3)
C(7)-C(71)-H(71A)	109.5
C(7)-C(71)-H(71B)	109.5
H(71A)-C(71)-H(71B)	109.5
C(7)-C(71)-H(71C)	109.5
H(71A)-C(71)-H(71C)	109.5
H(71B)-C(71)-H(71C)	109.5
C(7)-C(72)-H(72A)	109.5
C(7)-C(72)-H(72B)	109.5
H(72A)-C(72)-H(72B)	109.5
C(7)-C(72)-H(72C)	109.5
H(72A)-C(72)-H(72C)	109.5
H(72B)-C(72)-H(72C)	109.5
C(9)-C(8)-C(7)	131.5(4)
C(9)-C(8)-H(8)	115(2)
C(7)-C(8)-H(8)	113(2)
C(8)-C(9)-C(3B)	122.9(8)
C(8)-C(9)-C(10)	123.9(3)
C(3B)-C(9)-C(10)	101.6(7)
C(8)-C(9)-C(3)	127.8(3)
C(3B)-C(9)-C(3)	40.3(8)
C(10)-C(9)-C(3)	108.0(3)
C(9)-C(10)-C(1)	106.9(3)
C(9)-C(10)-H(10A)	110.3
C(1)-C(10)-H(10A)	110.3
C(9)-C(10)-H(10B)	110.3
C(1)-C(10)-H(10B)	110.3
H(10A)-C(10)-H(10B)	108.6
O(12)-C(11)-C(1)	112.5(3)

O(12)-C(11)-H(11A)	109.1
C(1)-C(11)-H(11A)	109.1
O(12)-C(11)-H(11B)	109.1
C(1)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.8
C(11)-O(12)-H(12)	112(3)
O(14)-C(13)-C(1)	112.3(3)
O(14)-C(13)-H(13A)	109.1
C(1)-C(13)-H(13A)	109.1
O(14)-C(13)-H(13B)	109.1
C(1)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.9
C(13)-O(14)-H(14)	108(3)
C(9)-C(3B)-C(2)	102.0(12)
C(9)-C(3B)-C(4)	114.1(13)
C(2)-C(3B)-C(4)	106.3(12)
C(9)-C(3B)-H(3B)	111.3
C(2)-C(3B)-H(3B)	111.3
C(4)-C(3B)-H(3B)	111.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3) for **3d'**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ..+ 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	16(2)	20(2)	29(2)	2(2)	0(1)	1(1)
C(2)	27(2)	24(2)	24(2)	2(2)	3(2)	1(2)
C(3)	31(2)	21(2)	36(3)	3(2)	1(2)	-1(2)
C(4)	40(3)	54(3)	57(3)	24(2)	9(2)	2(2)
C(5)	46(3)	43(2)	71(3)	21(2)	20(3)	2(2)
C(6)	45(3)	35(2)	80(3)	-1(2)	21(2)	-12(2)
C(7)	26(2)	43(2)	59(3)	1(2)	7(2)	-3(2)
C(71)	52(3)	58(3)	73(3)	-3(2)	20(2)	5(2)
C(72)	35(3)	77(3)	81(3)	1(3)	4(2)	-10(2)
C(8)	28(3)	31(2)	69(3)	6(2)	3(2)	1(2)
C(9)	28(2)	27(2)	40(2)	4(2)	3(2)	-3(2)
C(10)	30(2)	29(2)	61(3)	14(2)	5(2)	0(2)
C(11)	45(2)	27(2)	26(2)	4(2)	-1(2)	-10(2)
O(12)	47(2)	24(1)	53(2)	3(1)	24(1)	5(1)
C(13)	34(2)	28(2)	31(2)	0(2)	3(2)	-5(2)
O(14)	35(2)	24(1)	41(2)	2(1)	16(1)	-3(1)
C(3B)	31(2)	21(2)	36(3)	3(2)	1(2)	-1(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3d'**.

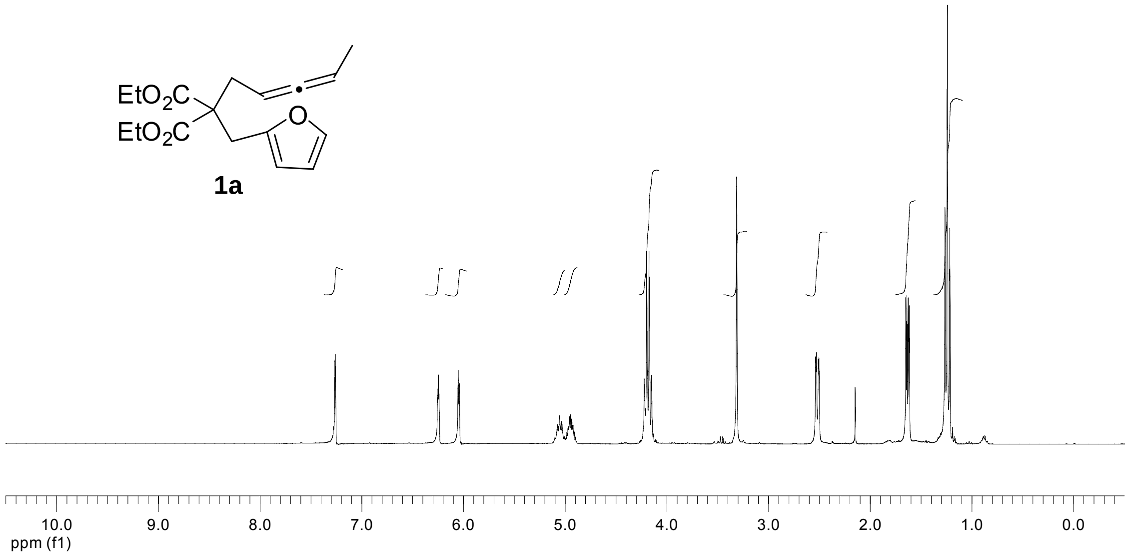
	x	y	z	U(eq)
H(2A)				
H(2B)	6841	3501	5836	30
H(3)	6496	498	4301	36
H(6A)	5548	-999	5212	63
H(6B)	5856	-741	4312	63
H(71A)	5642	3453	6413	91
H(71B)	5273	2414	6089	91
H(71C)	5372	4719	5581	91

H(72A)	5236	3444	3529	97
H(72B)	5138	1122	4015	97
H(72C)	5420	1357	3018	97
H(8)	5818(9)	4920(60)	3790(30)	51
H(10A)	6475	6573	4169	48
H(10B)	6455	5311	2938	48
H(11A)	6818	1995	2684	39
H(11B)	7029	4058	2271	39
H(13A)	7070	6777	5080	37
H(13B)	7371	5420	4493	37
H(3B)	6415	4156	6063	36
H(12)	7287(12)	490(80)	3310(40)	87(17)
H(14)	7312(9)	7330(50)	3010(30)	26(12)
H(4)	6503(11)	680(60)	6730(40)	64(13)
H(5)	5953(11)	-1080(70)	6750(40)	72(13)

Table 6. Torsion angles [°] for **3d'**.

C(13)-C(1)-C(2)-C(3)	156.2(3)
C(11)-C(1)-C(2)-C(3)	-81.5(3)
C(10)-C(1)-C(2)-C(3)	35.3(3)
C(13)-C(1)-C(2)-C(3B)	115.1(9)
C(11)-C(1)-C(2)-C(3B)	-122.7(9)
C(10)-C(1)-C(2)-C(3B)	-5.9(9)
C(1)-C(2)-C(3)-C(4)	-160.1(3)
C(3B)-C(2)-C(3)-C(4)	-63.8(11)
C(1)-C(2)-C(3)-C(9)	-34.7(4)
C(3B)-C(2)-C(3)-C(9)	61.6(10)
C(2)-C(3)-C(4)-C(5)	176.9(4)
C(9)-C(3)-C(4)-C(5)	58.3(5)
C(2)-C(3)-C(4)-C(3B)	63.8(11)
C(9)-C(3)-C(4)-C(3B)	-54.8(11)
C(3)-C(4)-C(5)-C(6)	-7.7(6)
C(3B)-C(4)-C(5)-C(6)	39.8(13)
C(4)-C(5)-C(6)-C(7)	-64.1(6)
C(5)-C(6)-C(7)-C(8)	66.3(5)
C(5)-C(6)-C(7)-C(71)	-56.3(4)
C(5)-C(6)-C(7)-C(72)	-174.4(3)
C(71)-C(7)-C(8)-C(9)	100.4(5)
C(72)-C(7)-C(8)-C(9)	-141.9(4)
C(6)-C(7)-C(8)-C(9)	-22.4(6)
C(7)-C(8)-C(9)-C(3B)	-41.7(11)
C(7)-C(8)-C(9)-C(10)	-178.1(4)
C(7)-C(8)-C(9)-C(3)	7.9(7)
C(2)-C(3)-C(9)-C(8)	-164.5(4)
C(4)-C(3)-C(9)-C(8)	-40.4(6)
C(2)-C(3)-C(9)-C(3B)	-66.1(11)
C(4)-C(3)-C(9)-C(3B)	58.0(11)
C(2)-C(3)-C(9)-C(10)	20.7(4)
C(4)-C(3)-C(9)-C(10)	144.8(4)
C(8)-C(9)-C(10)-C(1)	-174.2(3)
C(3B)-C(9)-C(10)-C(1)	42.1(9)
C(3)-C(9)-C(10)-C(1)	0.9(4)
C(13)-C(1)-C(10)-C(9)	-141.2(3)
C(11)-C(1)-C(10)-C(9)	95.7(3)
C(2)-C(1)-C(10)-C(9)	-21.6(3)
C(13)-C(1)-C(11)-O(12)	64.3(3)
C(10)-C(1)-C(11)-O(12)	-171.0(3)
C(2)-C(1)-C(11)-O(12)	-58.6(3)
C(11)-C(1)-C(13)-O(14)	63.1(3)
C(10)-C(1)-C(13)-O(14)	-59.7(4)
C(2)-C(1)-C(13)-O(14)	-174.5(3)

C(8)-C(9)-C(3B)-C(2)	172.0(5)
C(10)-C(9)-C(3B)-C(2)	-43.8(11)
C(3)-C(9)-C(3B)-C(2)	60.4(11)
C(8)-C(9)-C(3B)-C(4)	57.8(17)
C(10)-C(9)-C(3B)-C(4)	-158.0(11)
C(3)-C(9)-C(3B)-C(4)	-53.7(11)
C(3)-C(2)-C(3B)-C(9)	-64.4(11)
C(1)-C(2)-C(3B)-C(9)	31.4(12)
C(3)-C(2)-C(3B)-C(4)	55.4(9)
C(1)-C(2)-C(3B)-C(4)	151.2(9)
C(5)-C(4)-C(3B)-C(9)	-38.7(19)
C(3)-C(4)-C(3B)-C(9)	56.4(12)
C(5)-C(4)-C(3B)-C(2)	-150.3(7)
C(3)-C(4)-C(3B)-C(2)	-55.2(10)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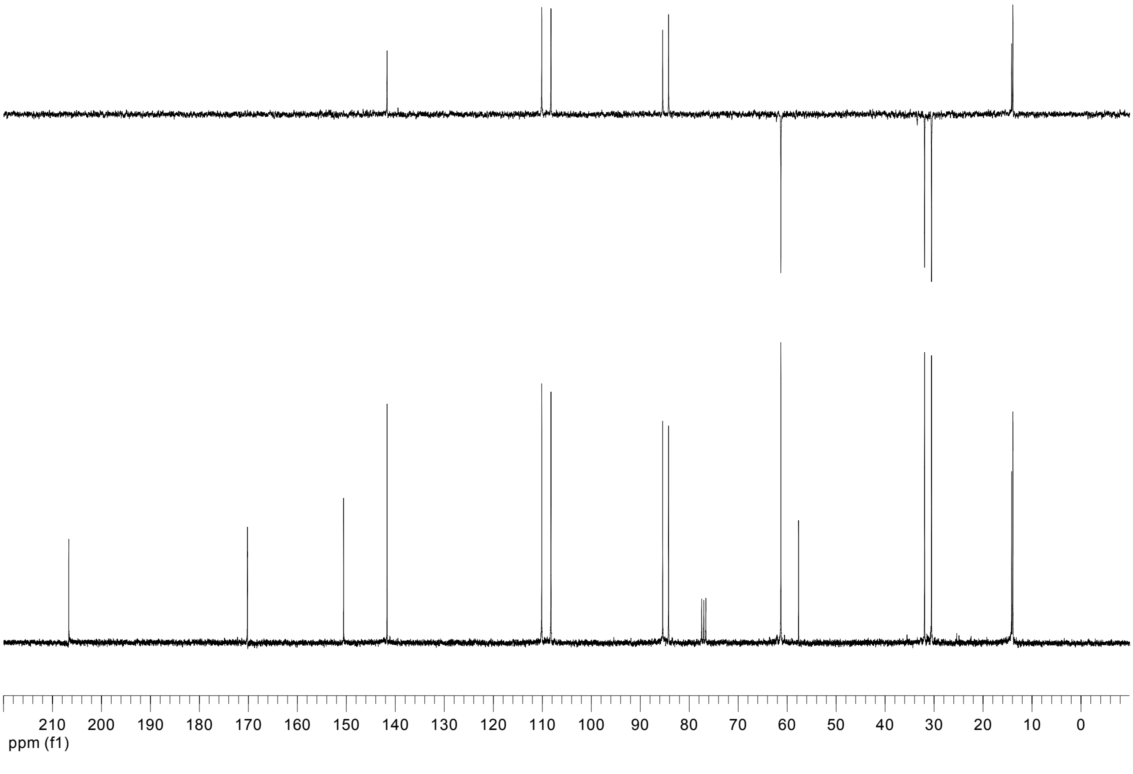
1a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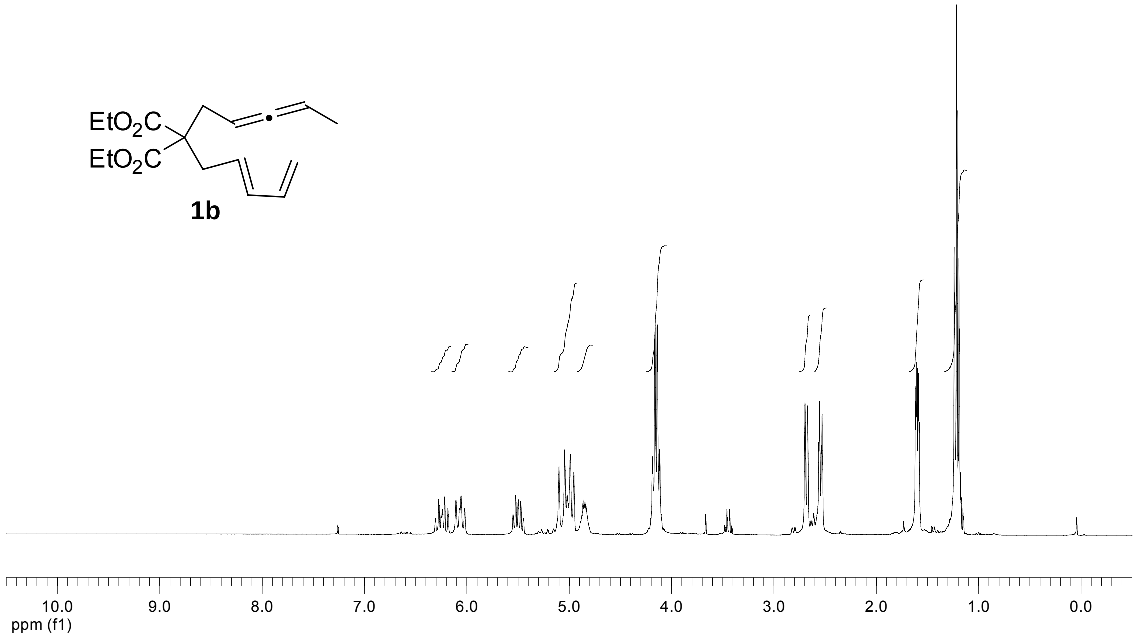
ppm (f1)



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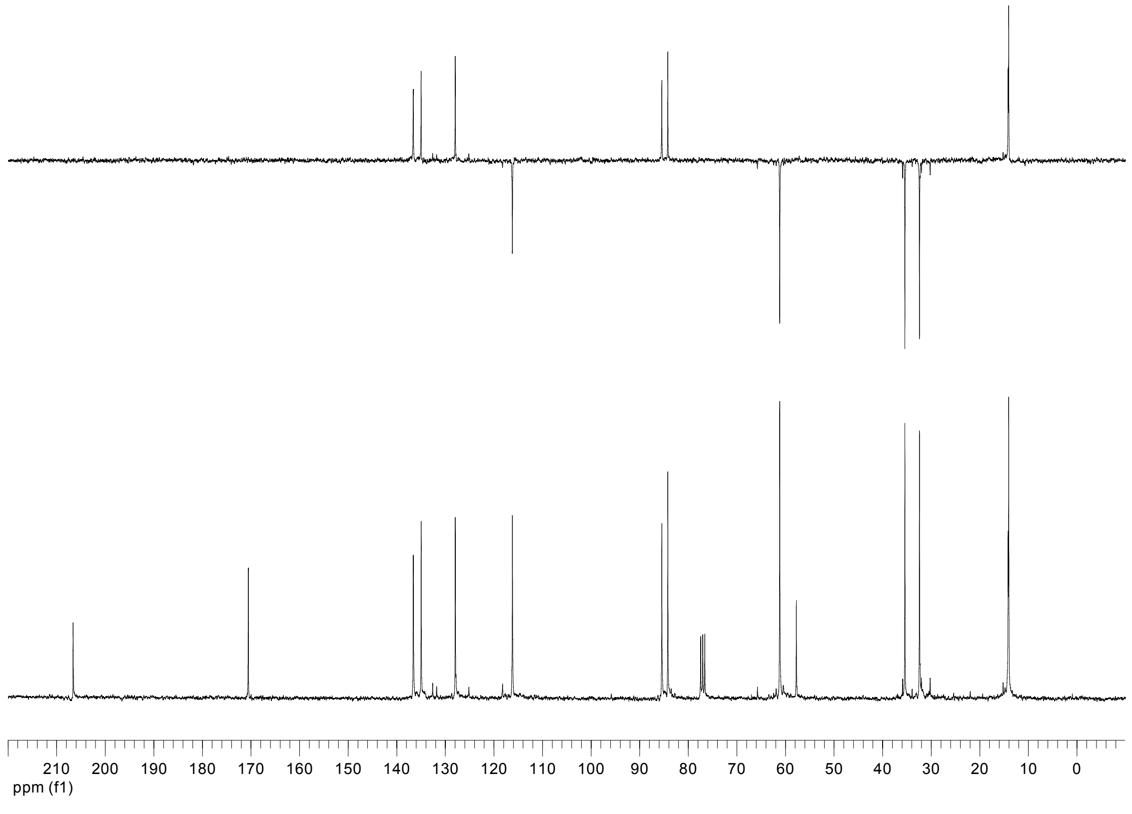
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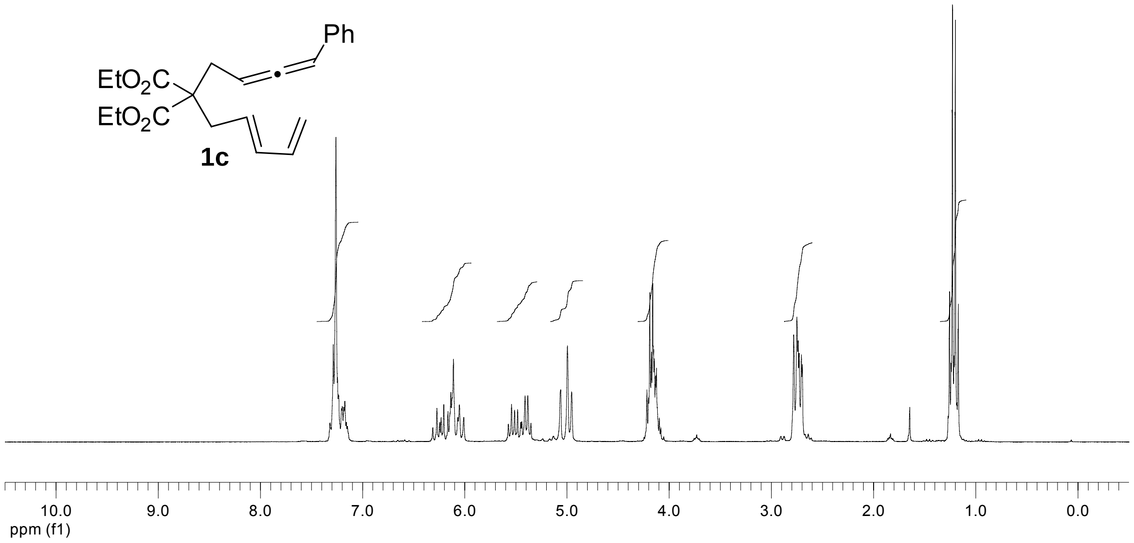
ppm (f1)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EtO2C
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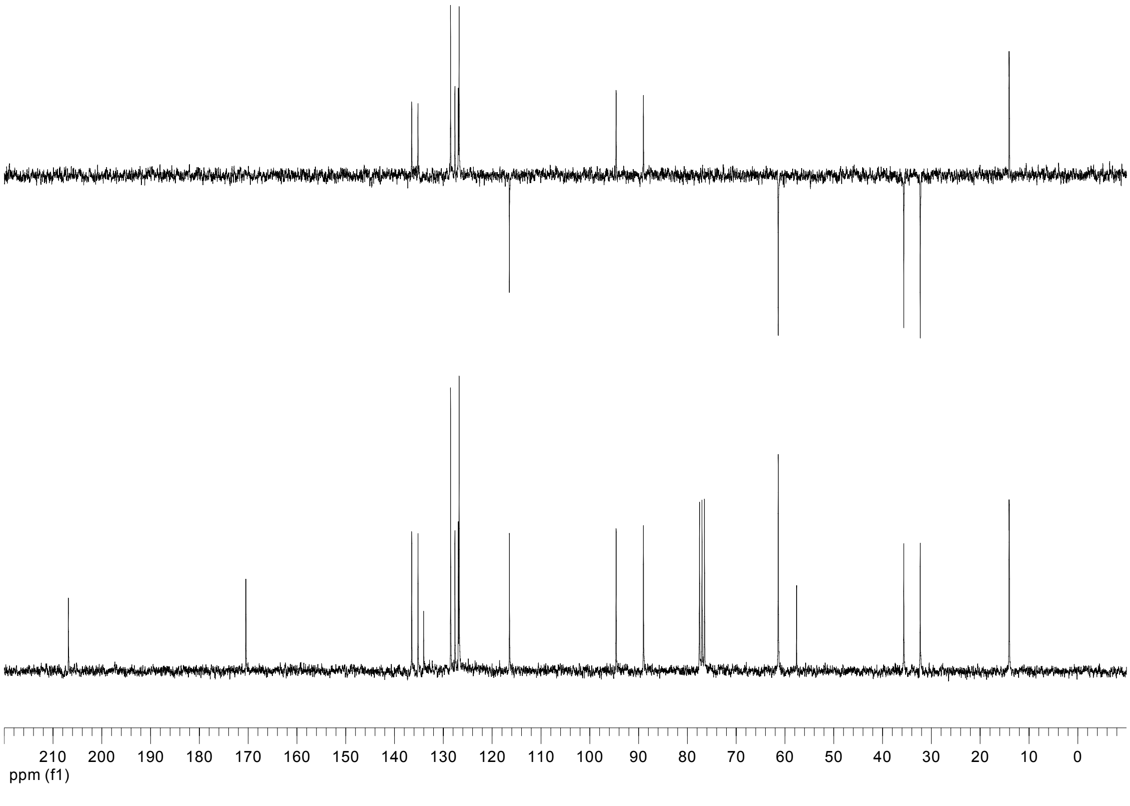
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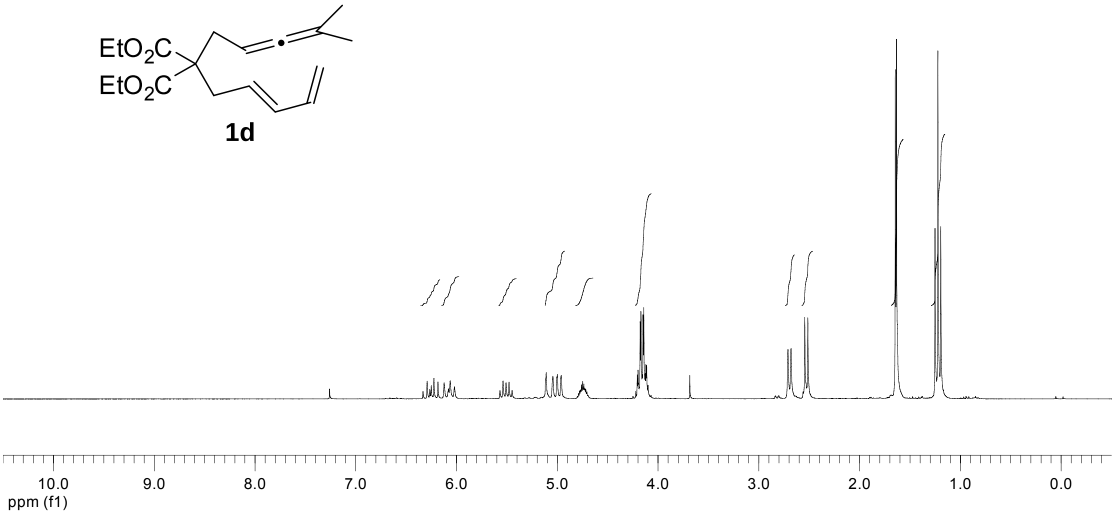
ppm (f1)



1d

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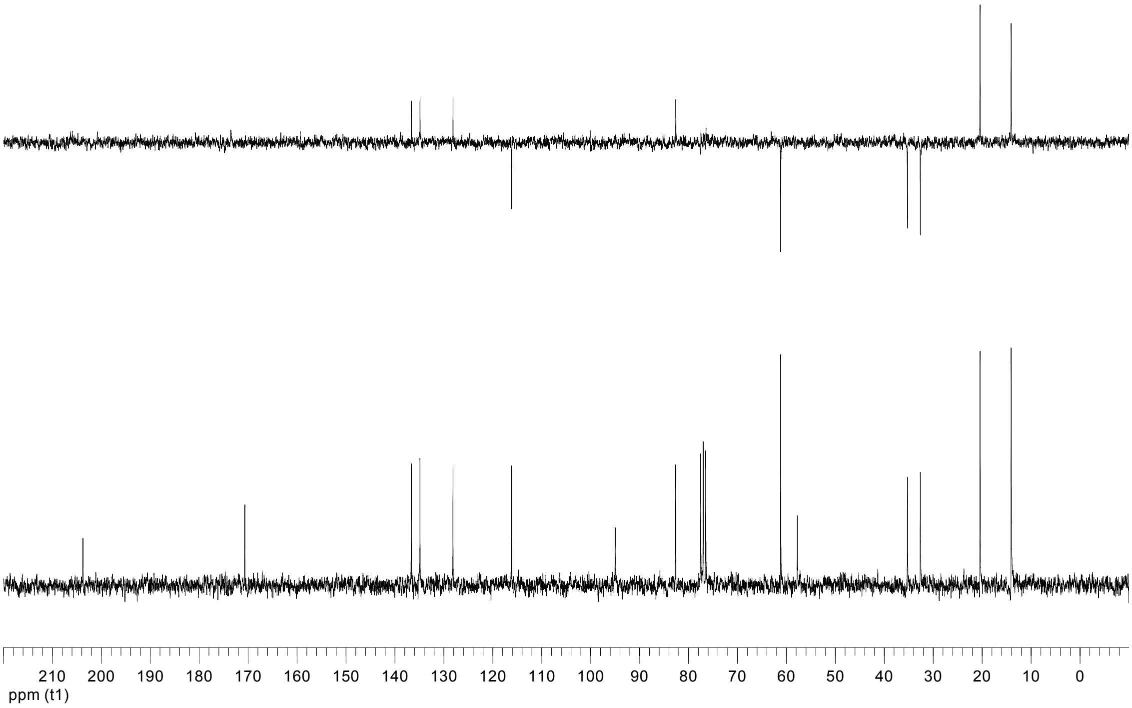
ppm (f1)



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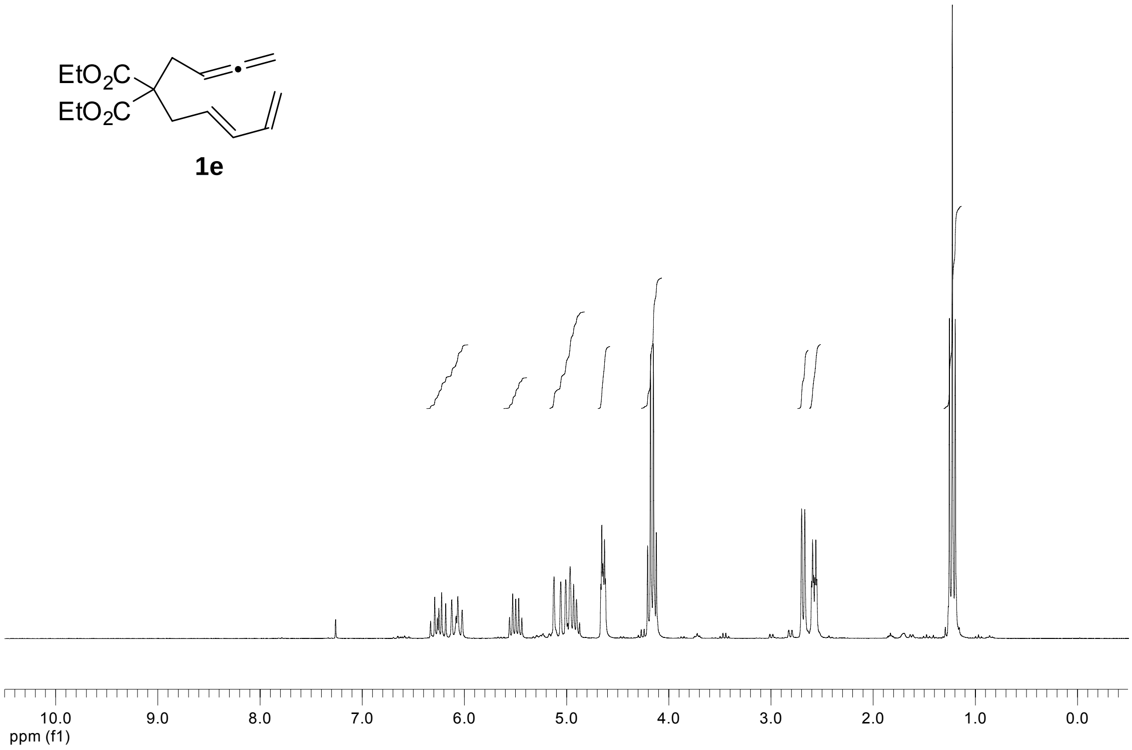
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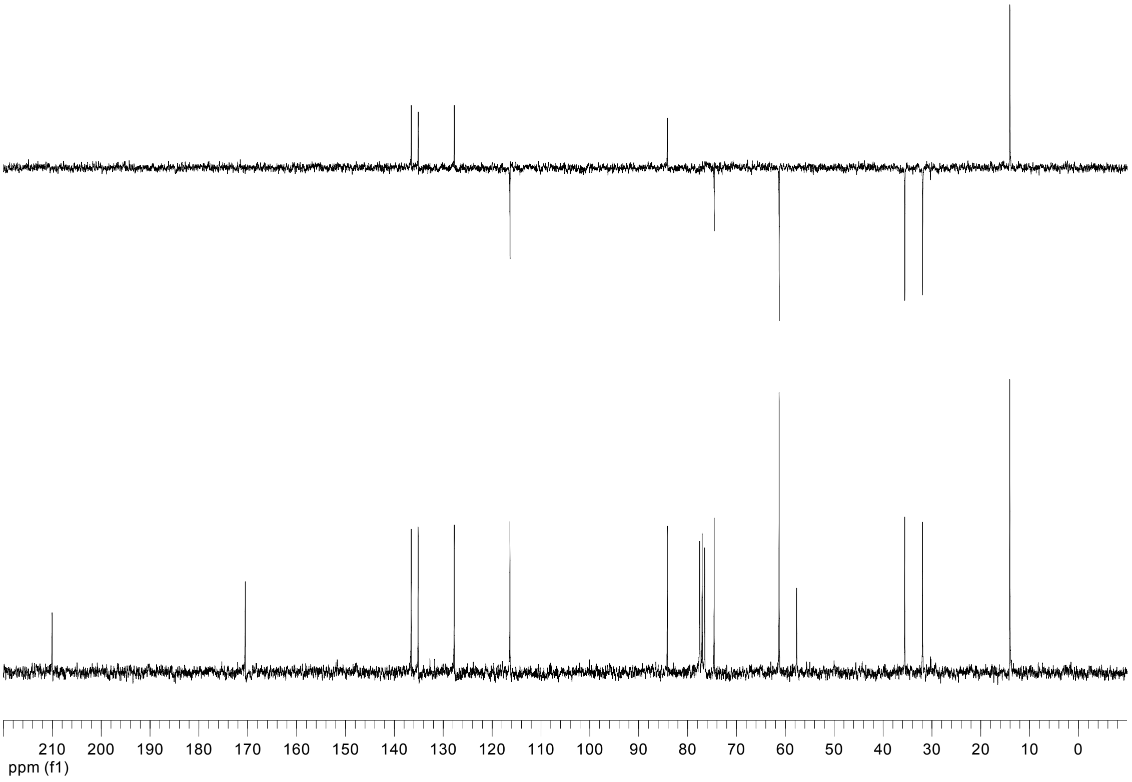
1e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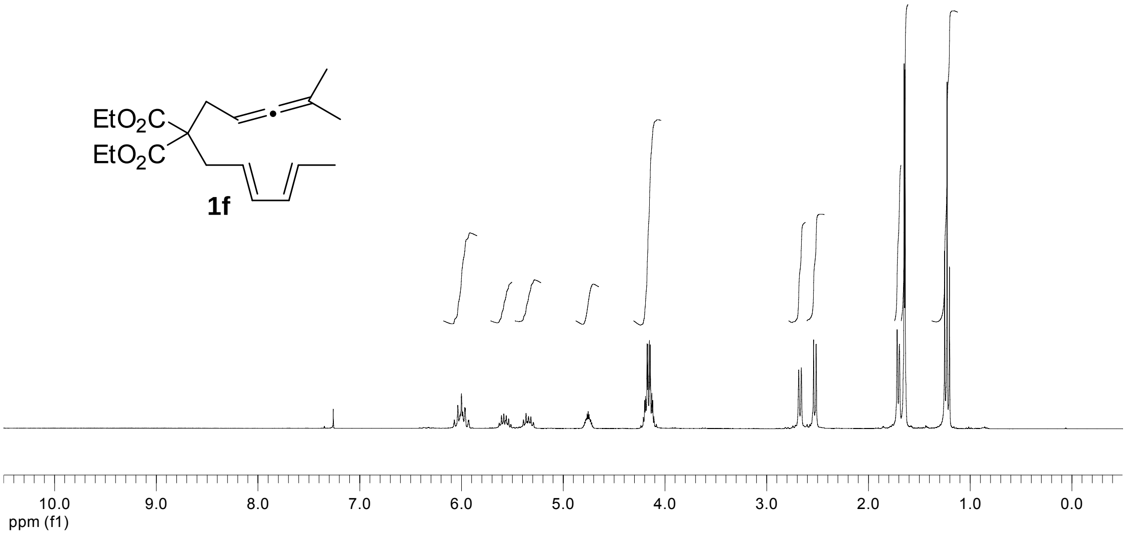
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EtO$_2$C
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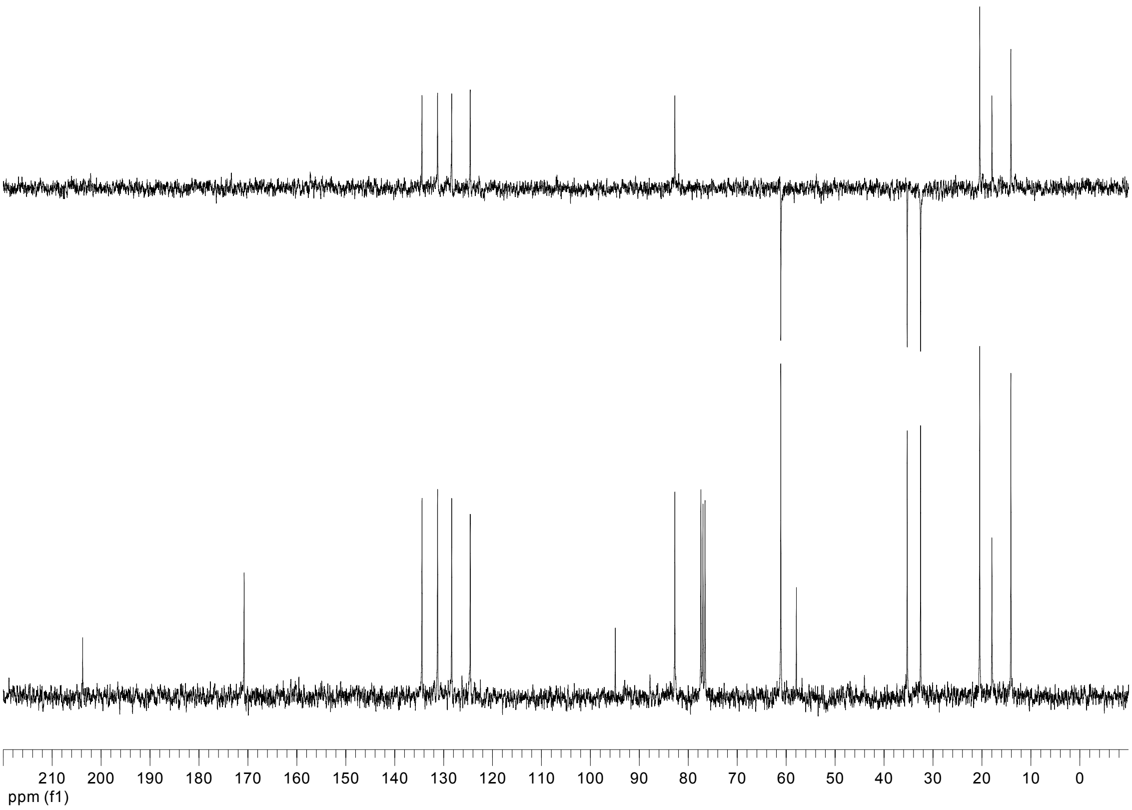
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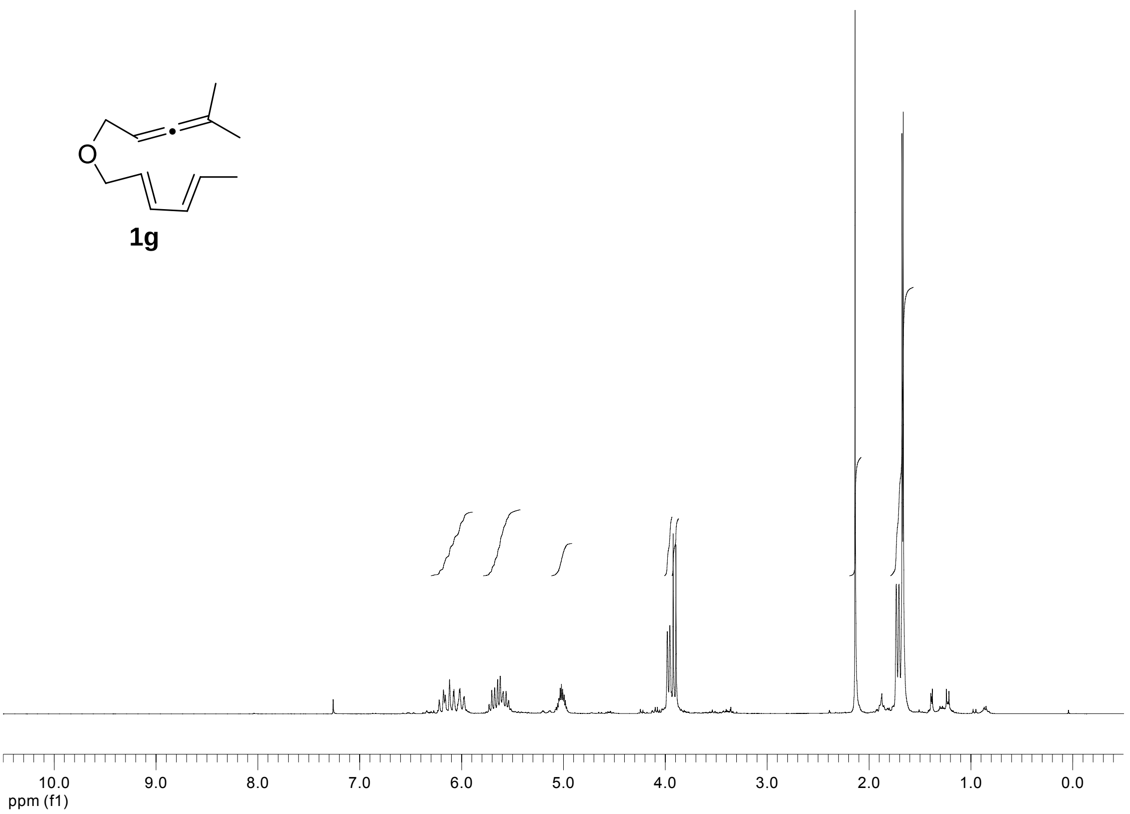
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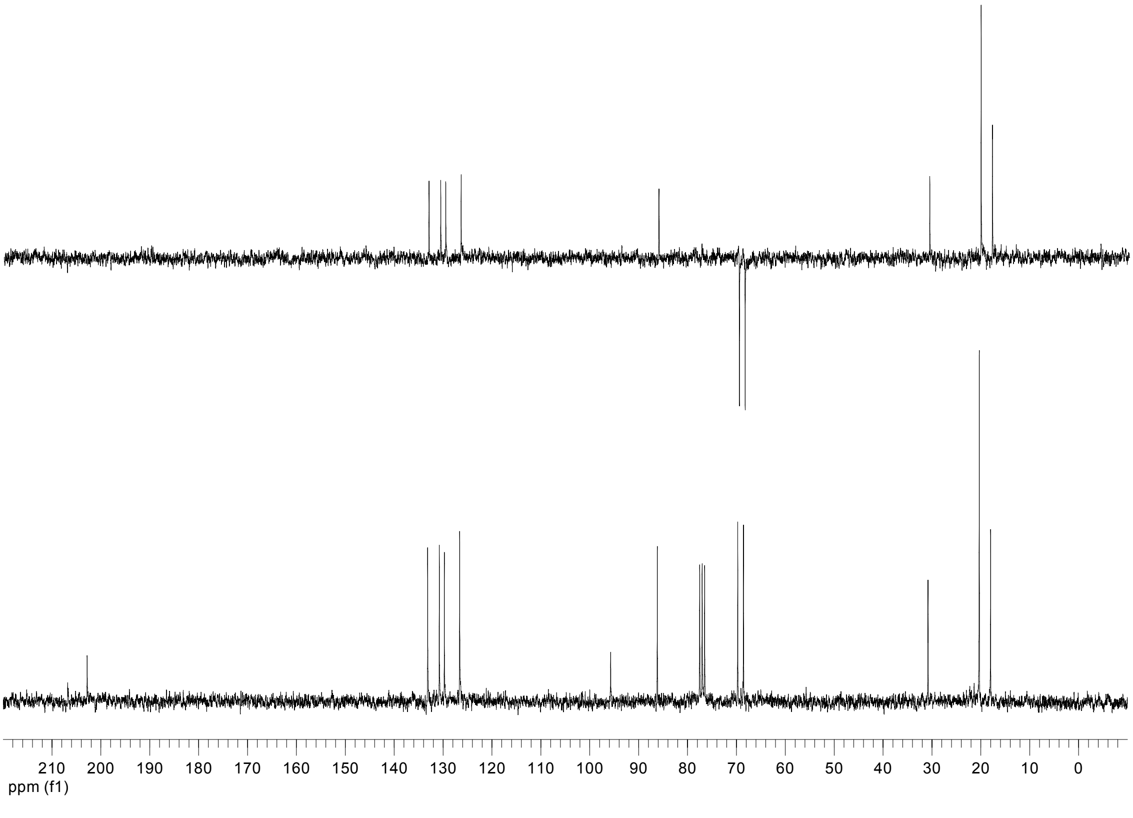
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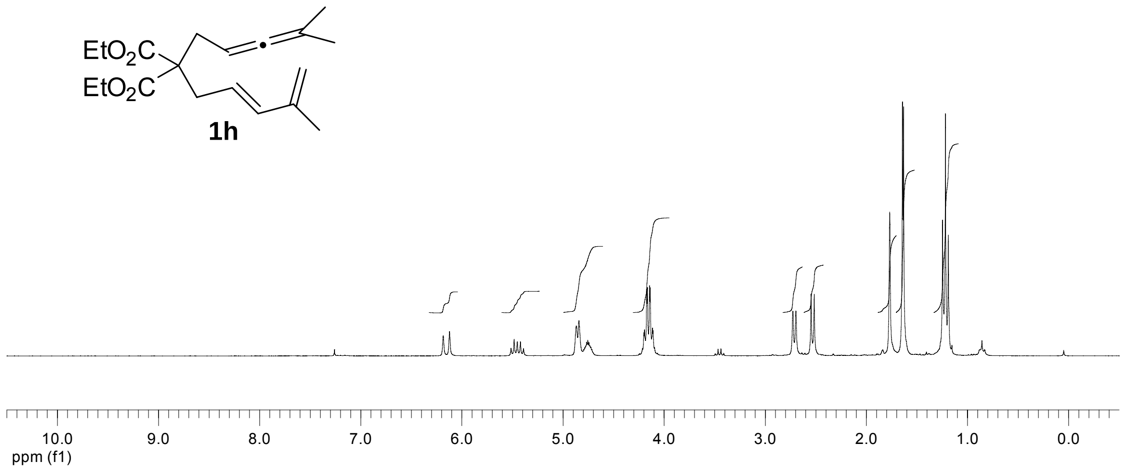

1h

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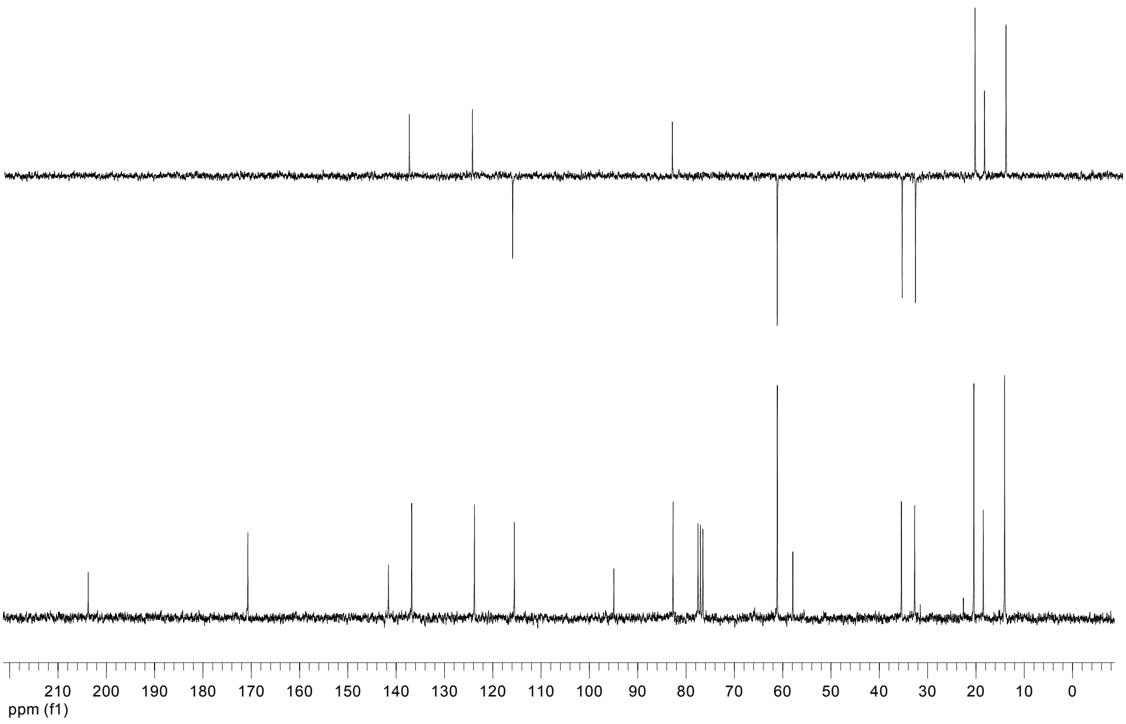
ppm (f1)



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10
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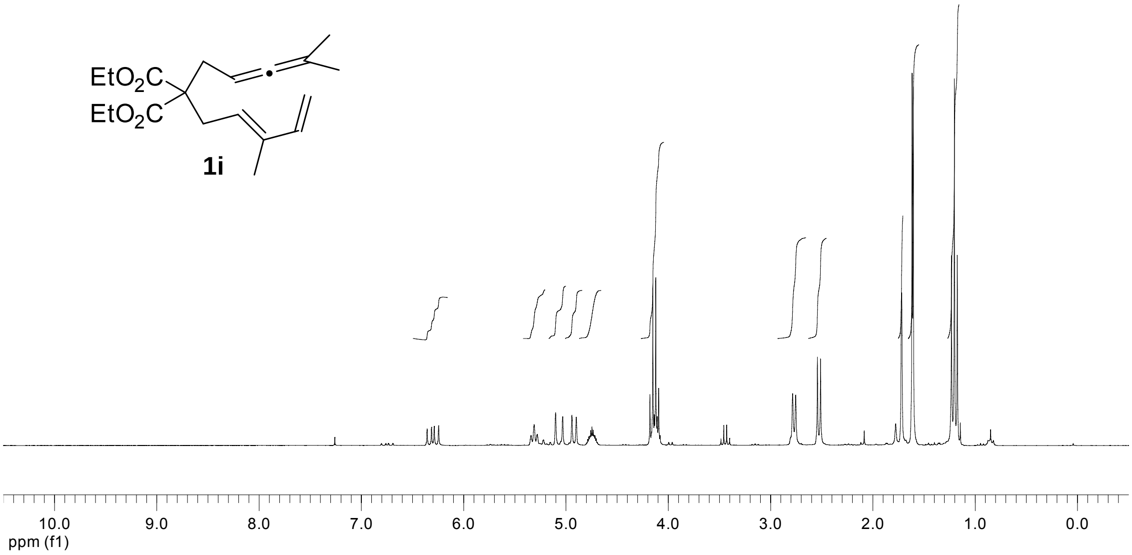
ppm (f1)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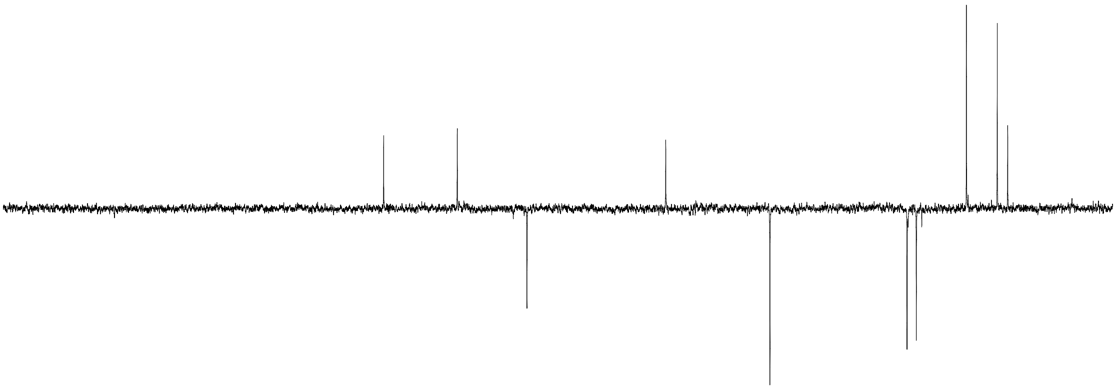
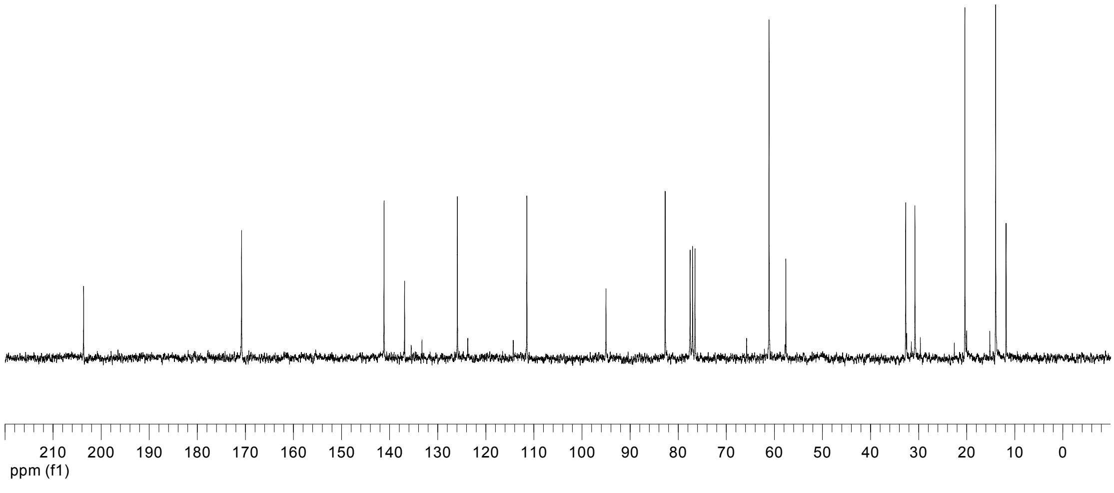
0.0
ppm (f1)

1i

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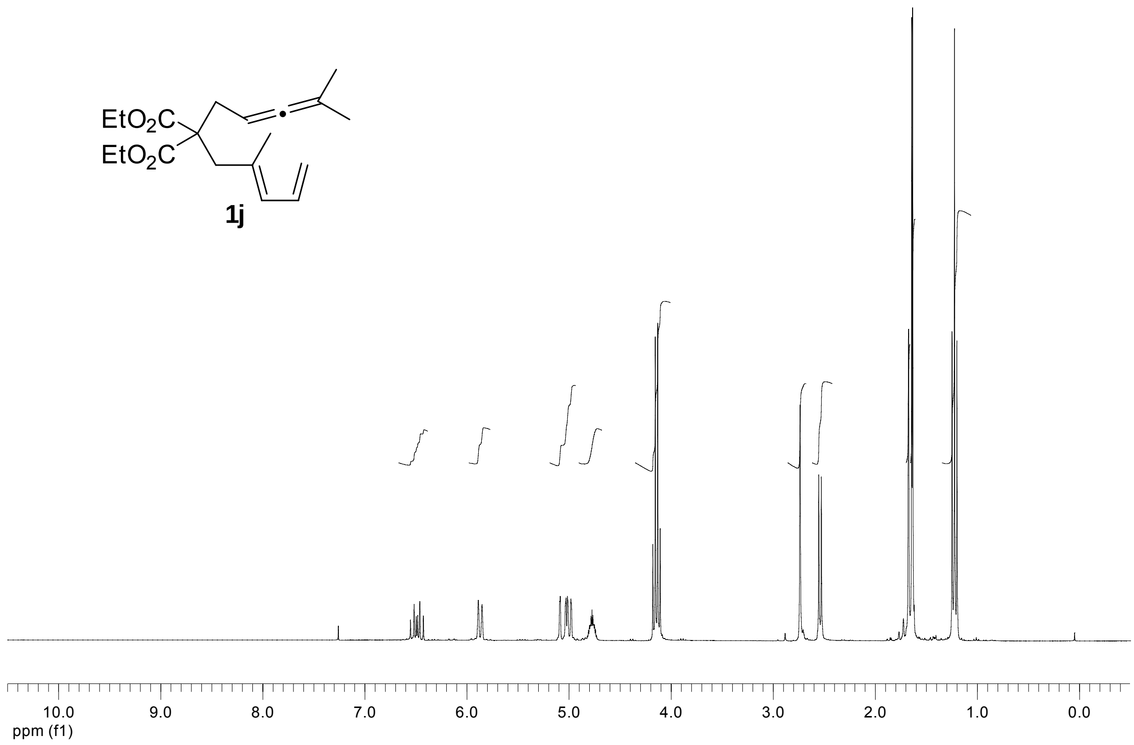
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EtO2C
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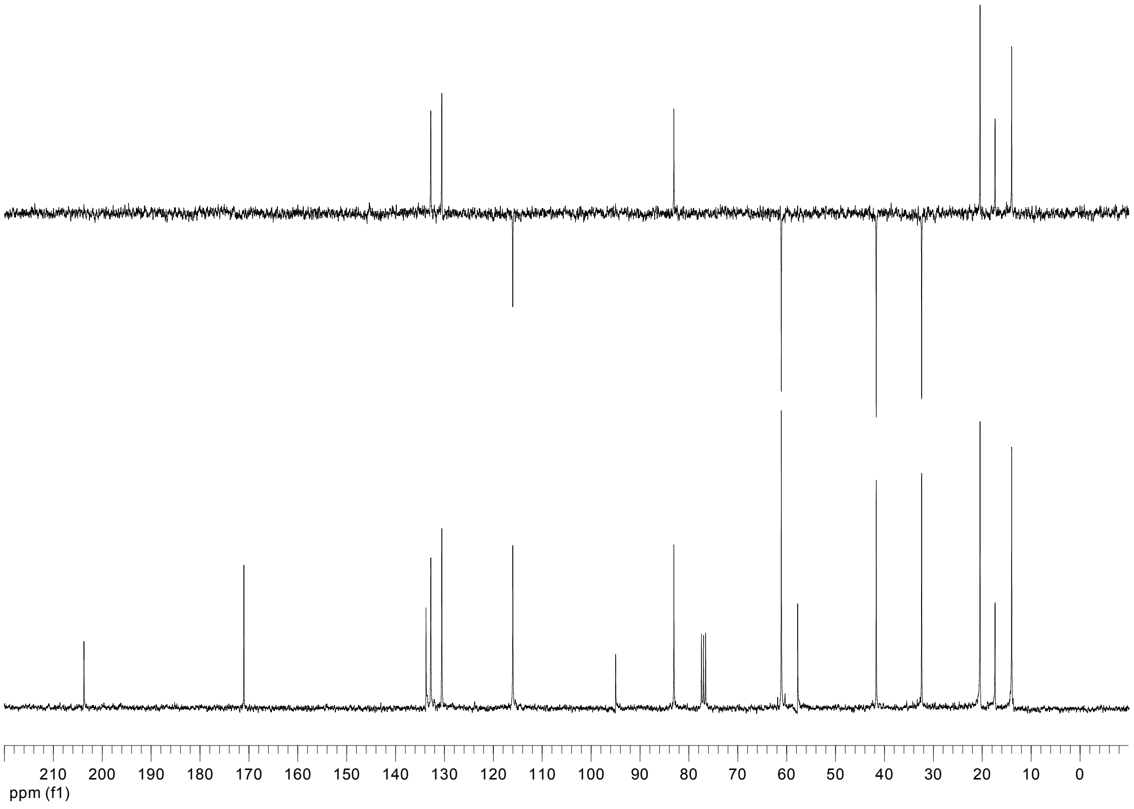
0.0
ppm (f1)

1j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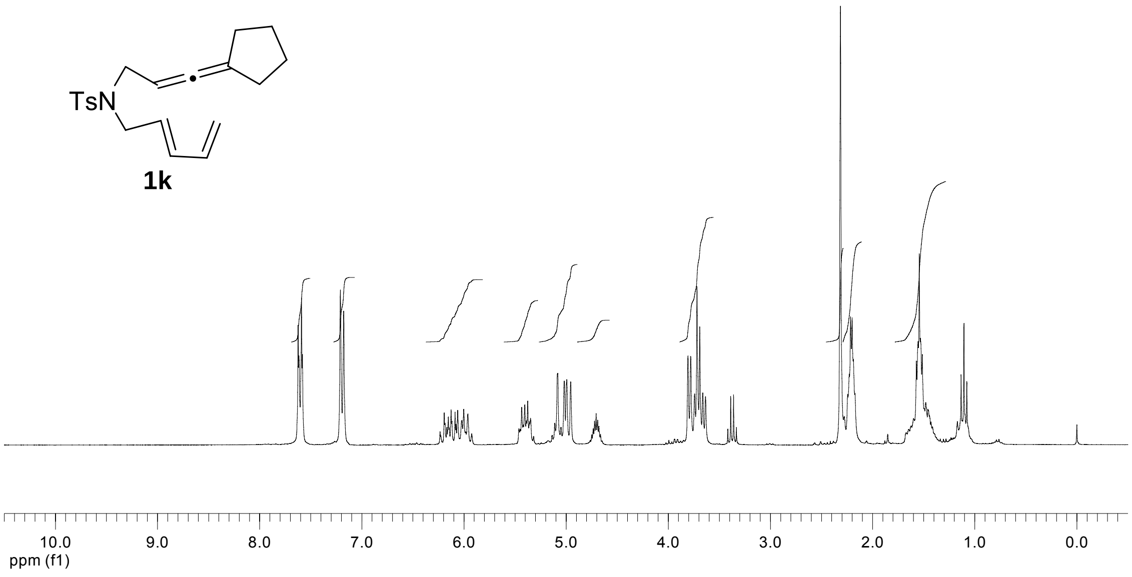
ppm (f1)



1k

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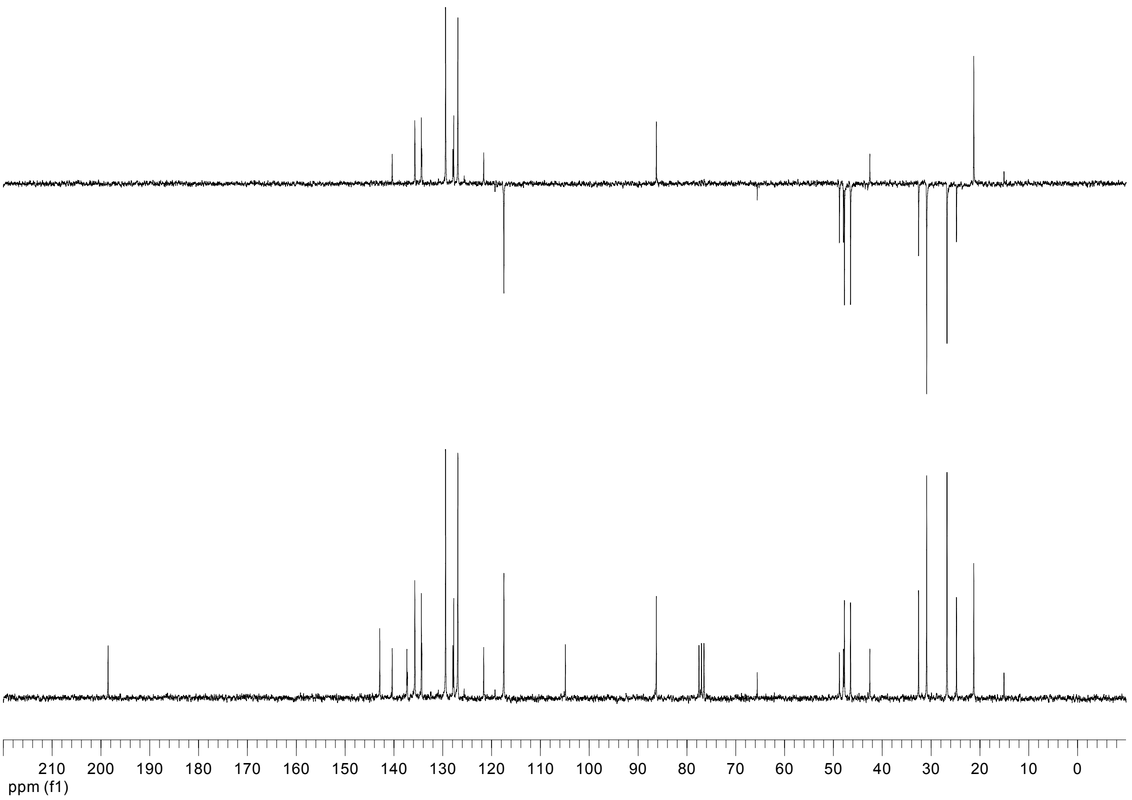
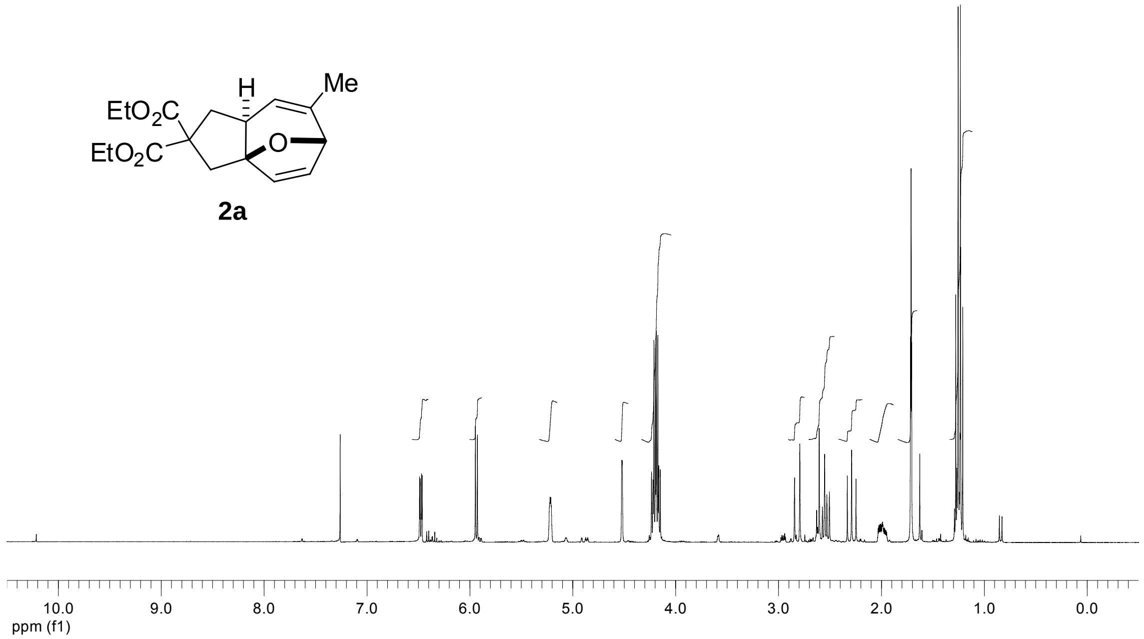
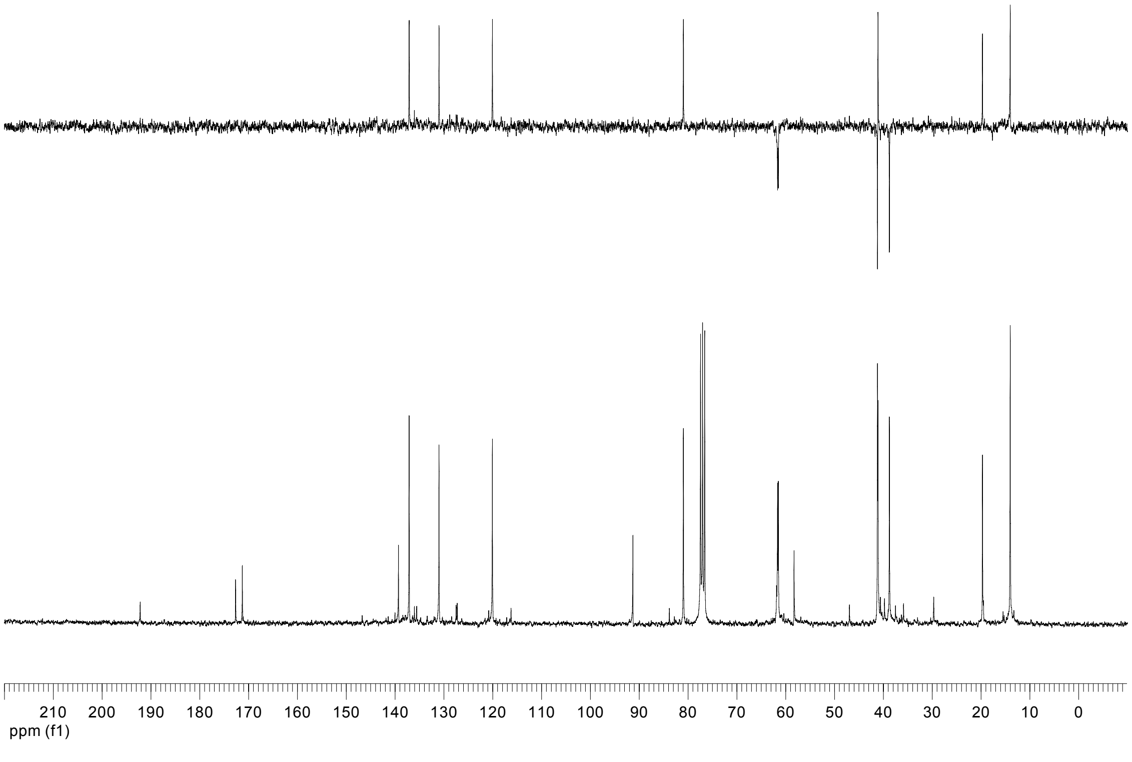
0.0
ppm (f1)



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


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

2a


210
200
190
180
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160
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140
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120
110
100
90
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50
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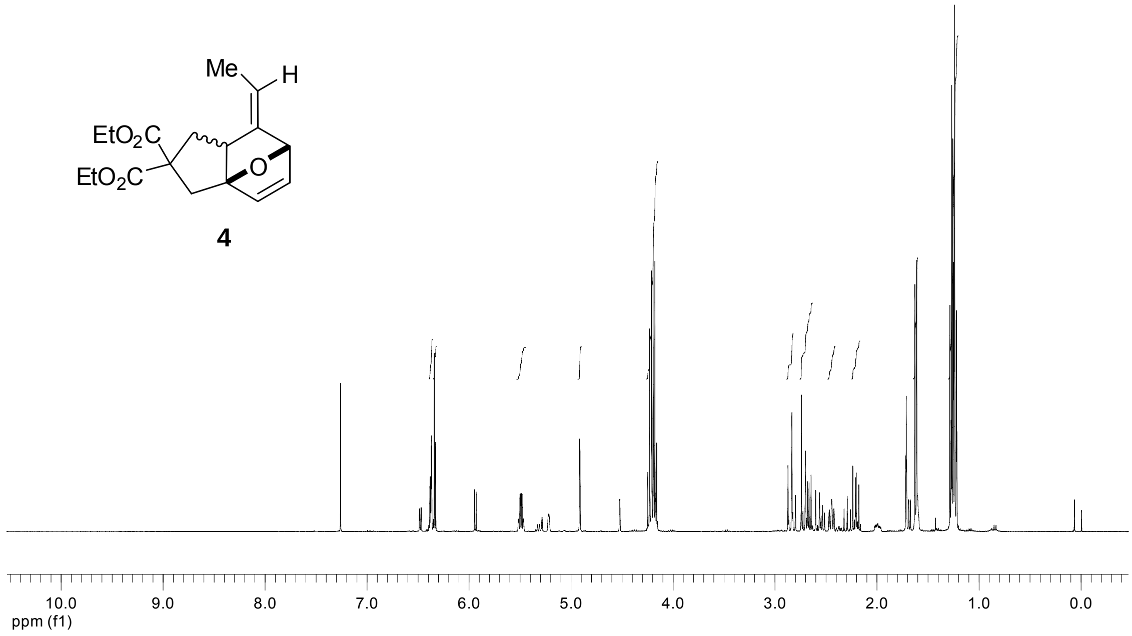
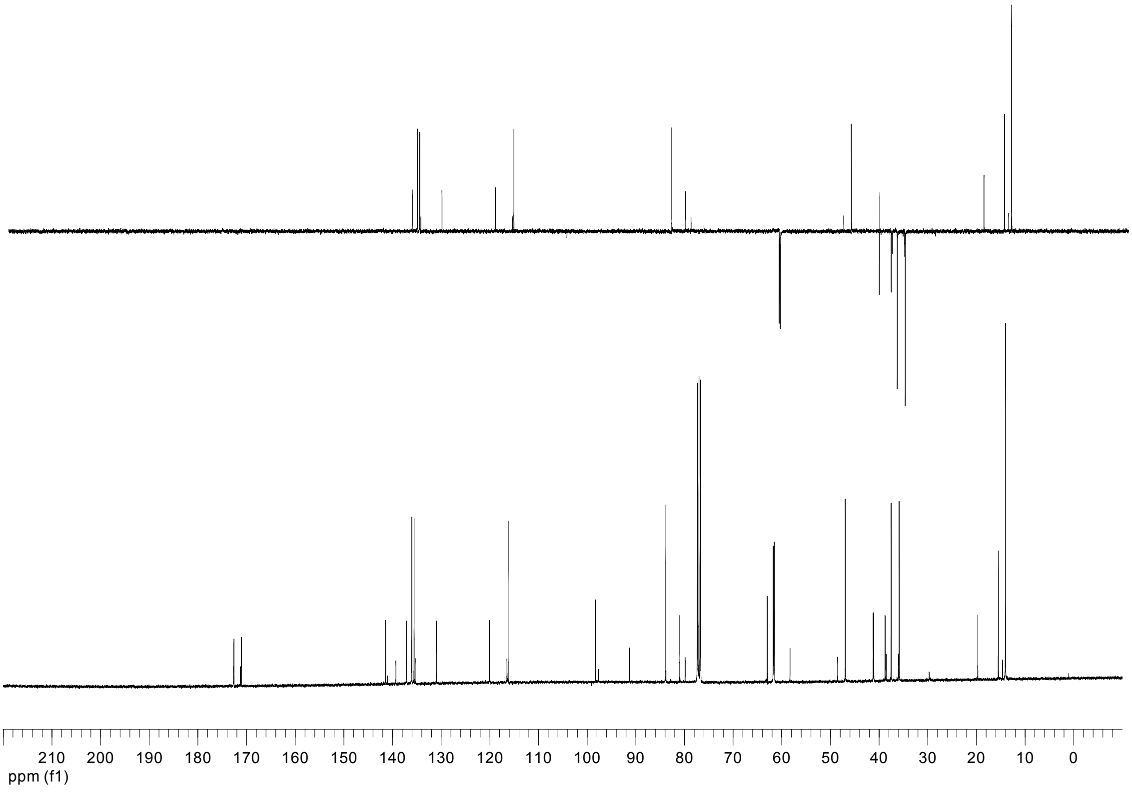
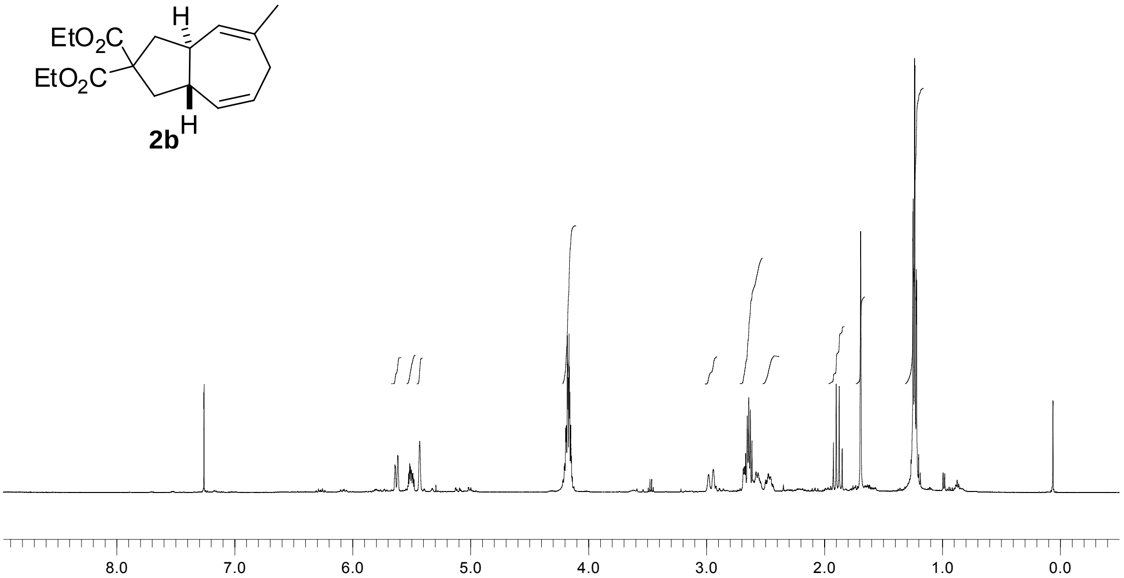
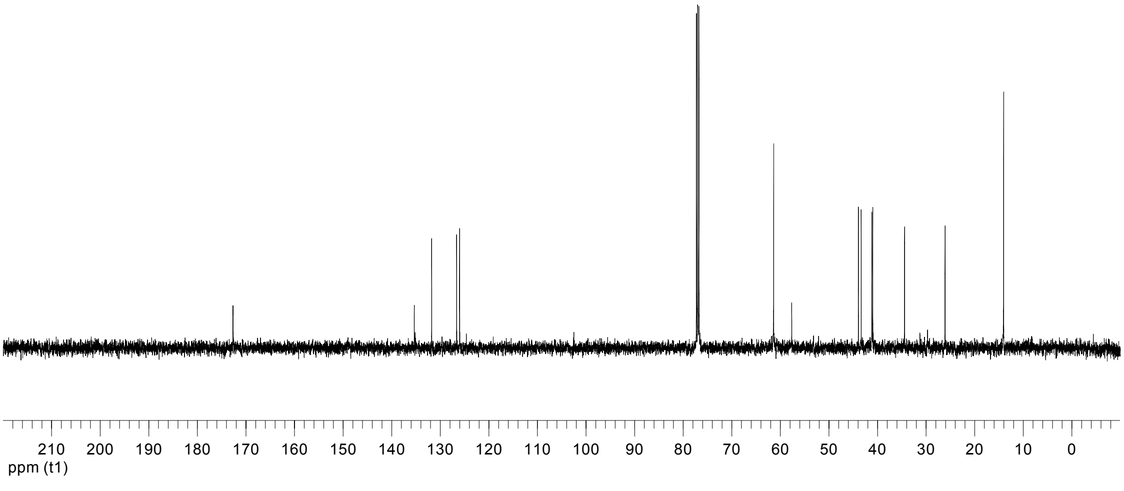
20
10
0
ppm (f1)

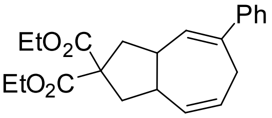

Me
H
EtO2C
EtO2C
O
4
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


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

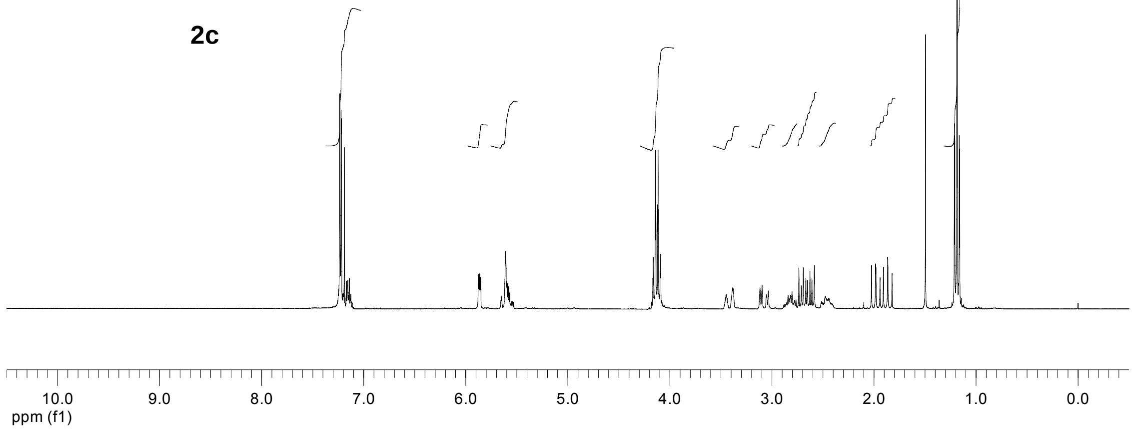

2b
EtO2C
EtO2C
H
H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

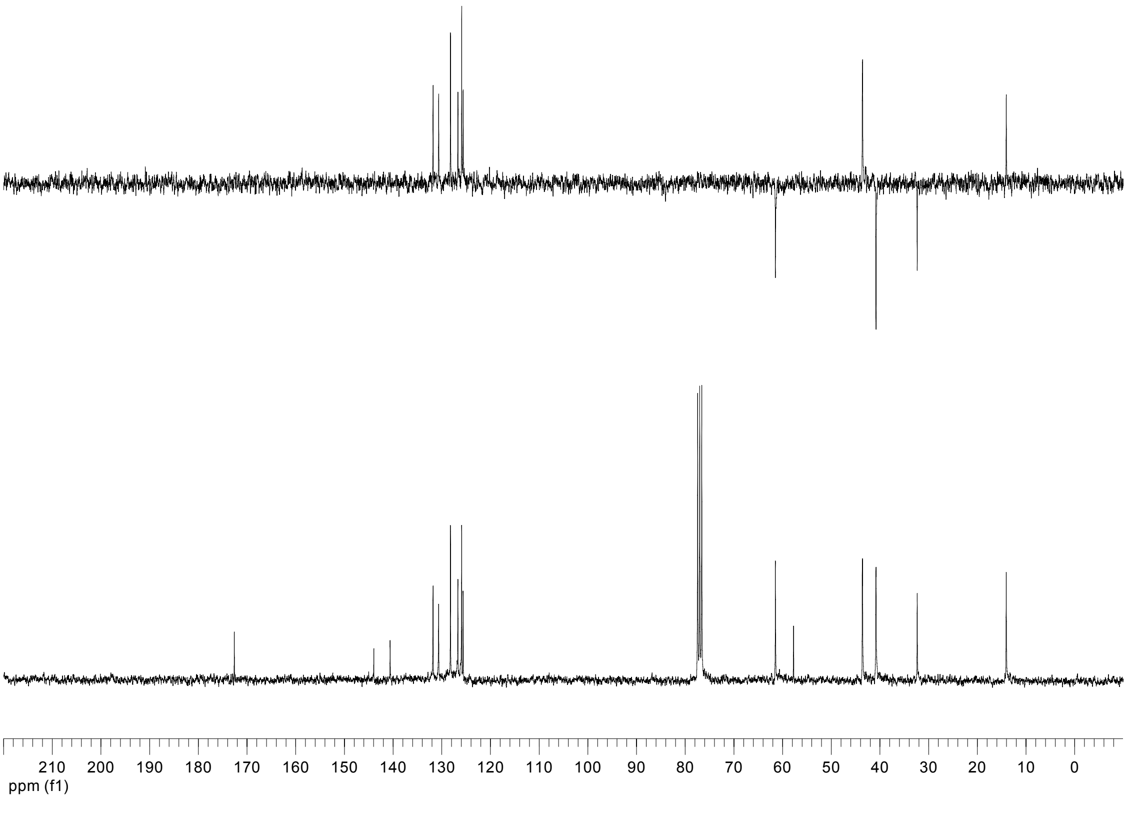

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

Cl_3CD

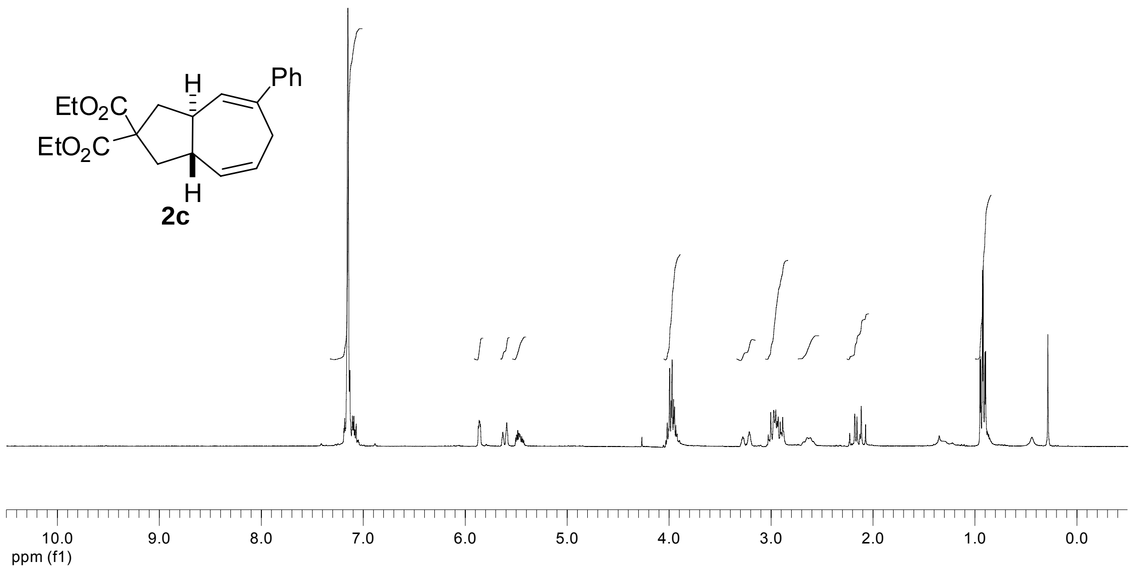


2c

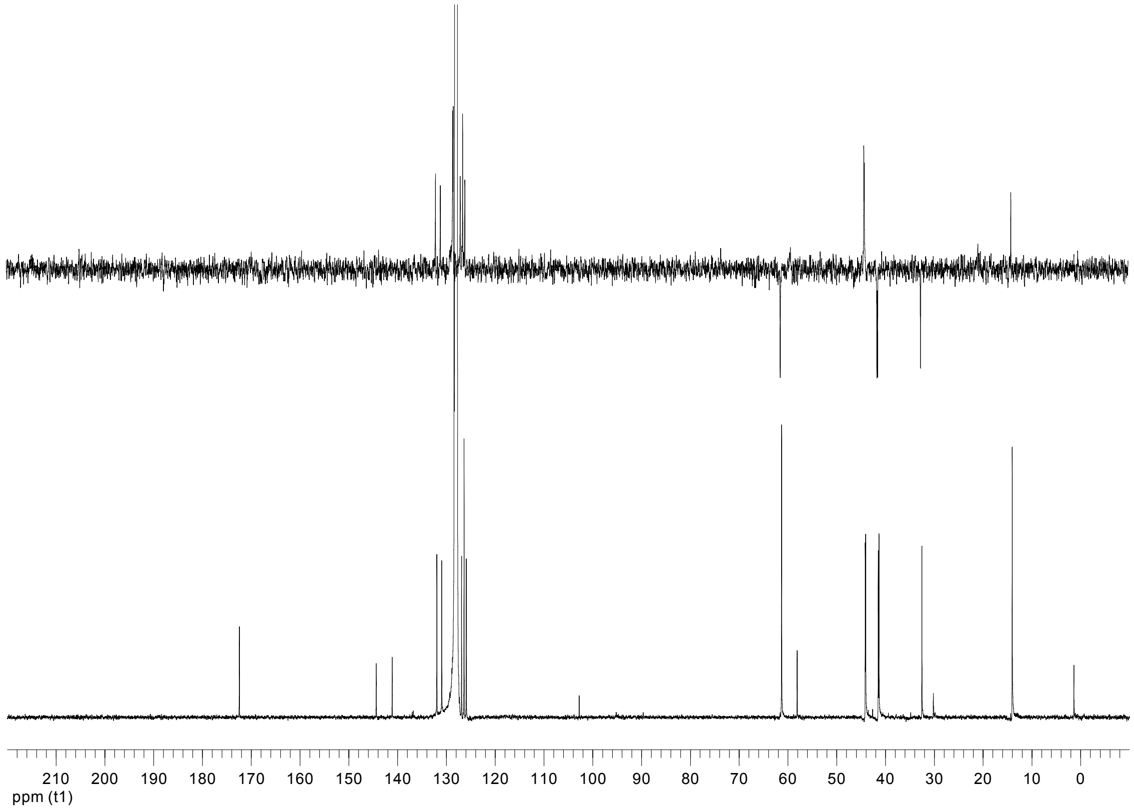

10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


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

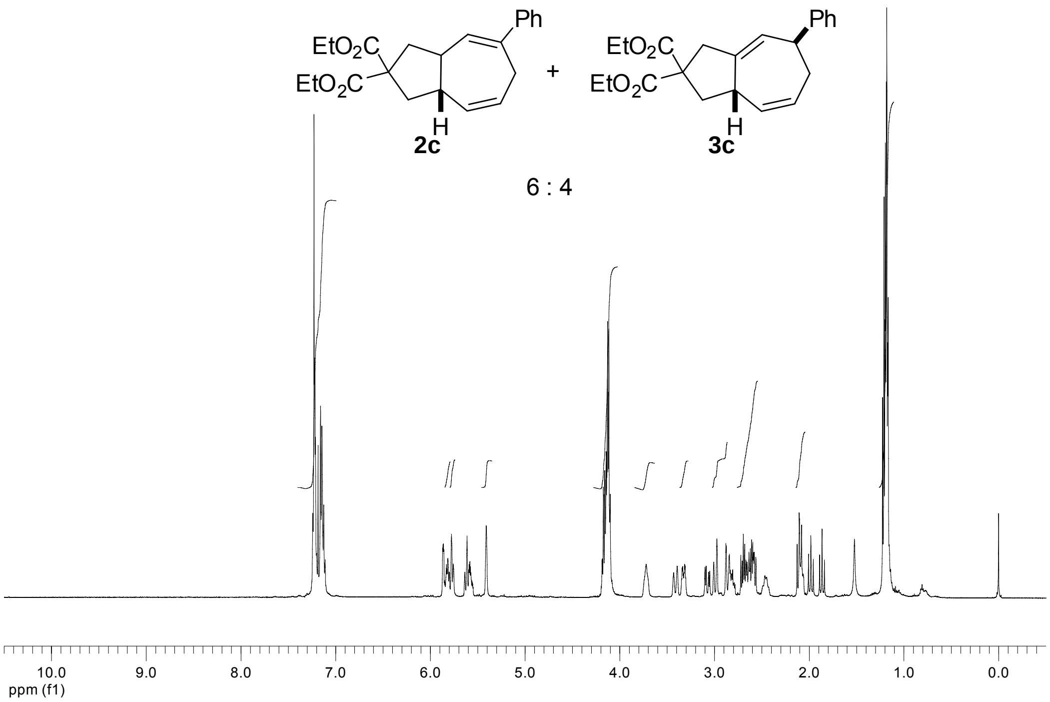
C_6D_6

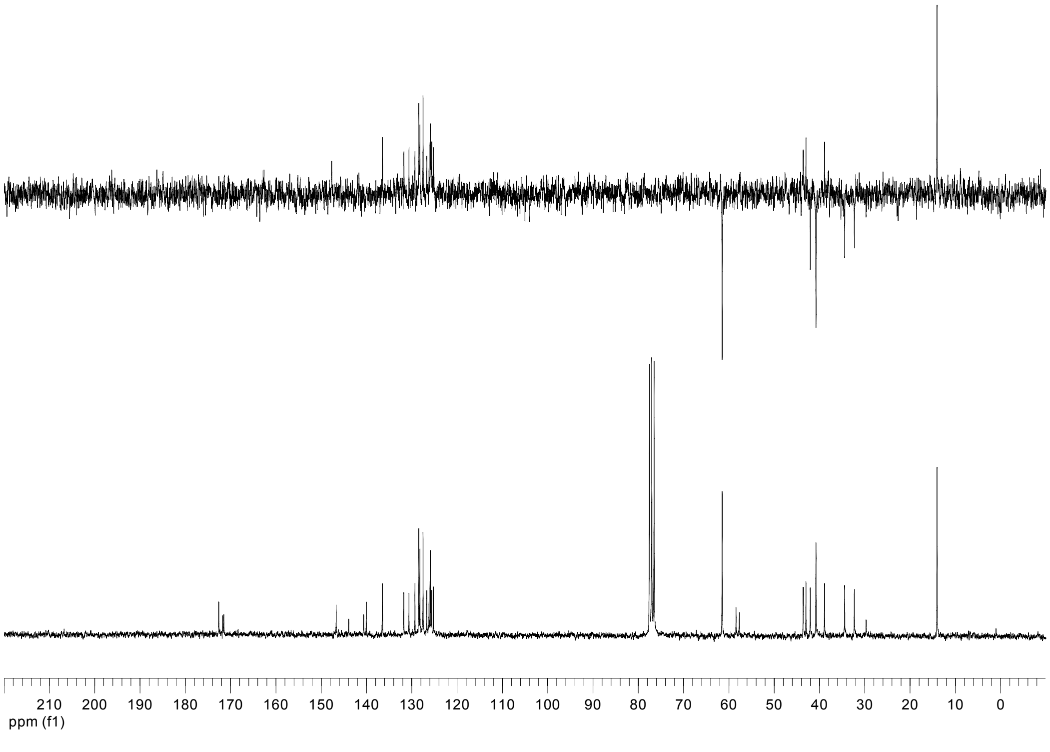


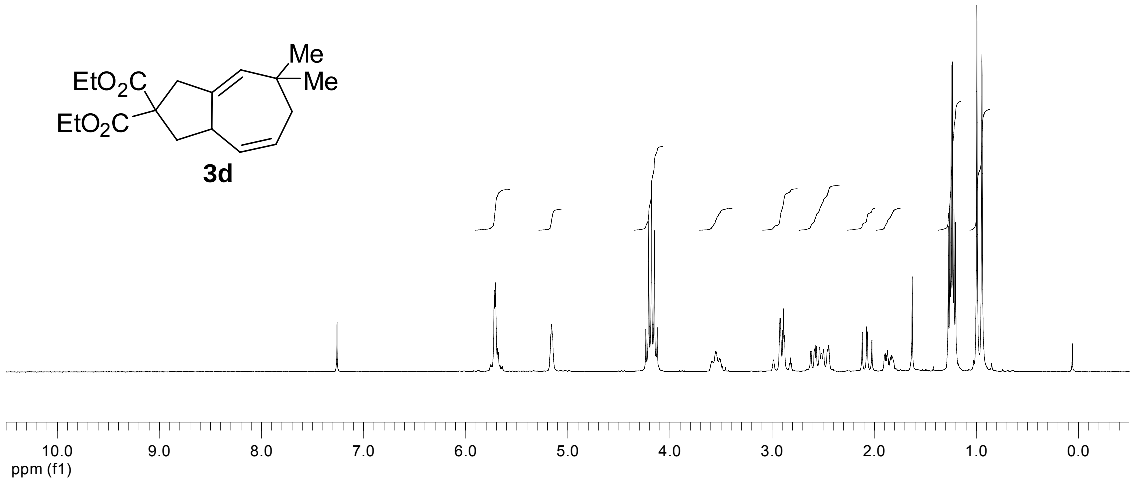
EtO2C
EtO2C
H
H
Ph
2c
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

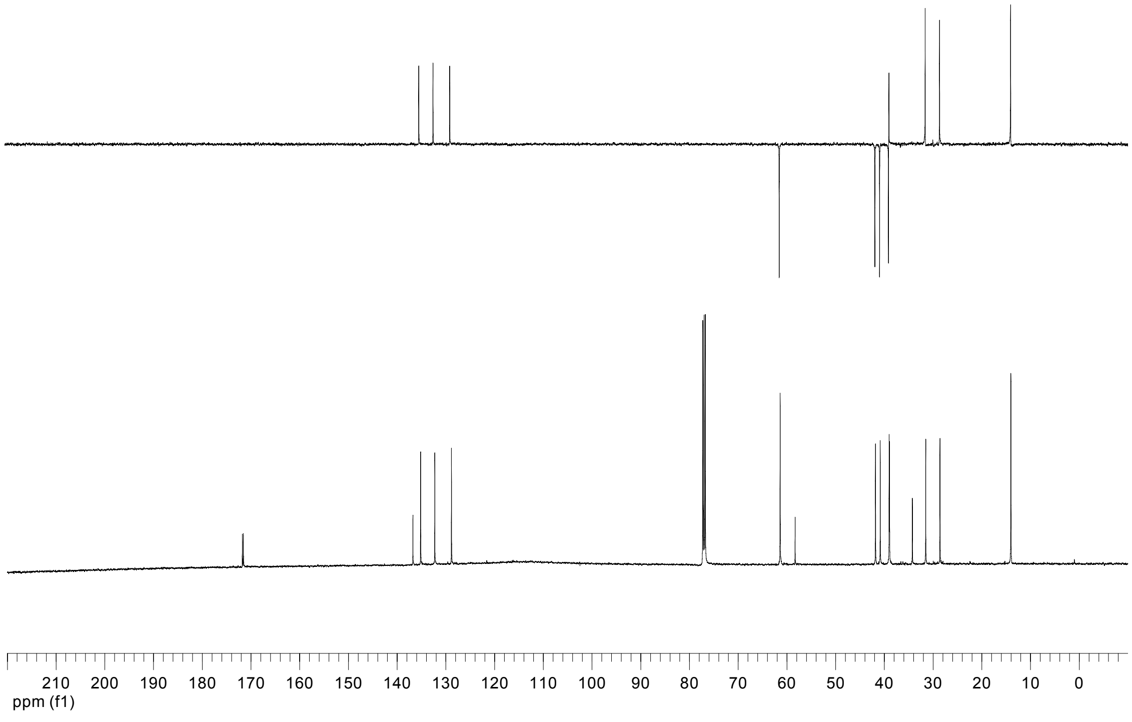


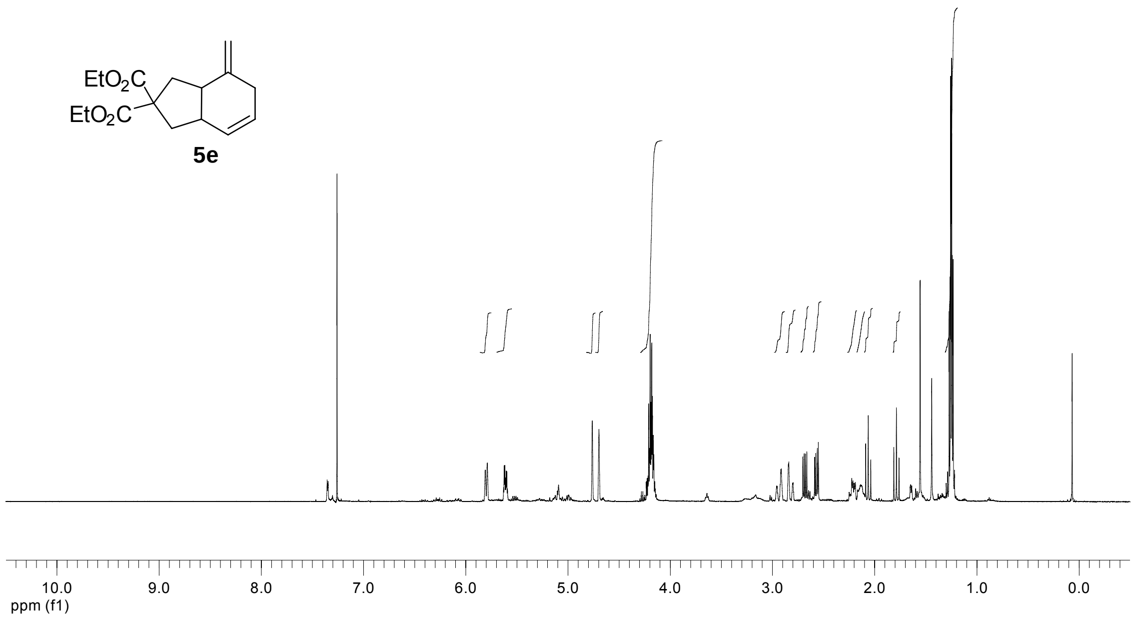
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

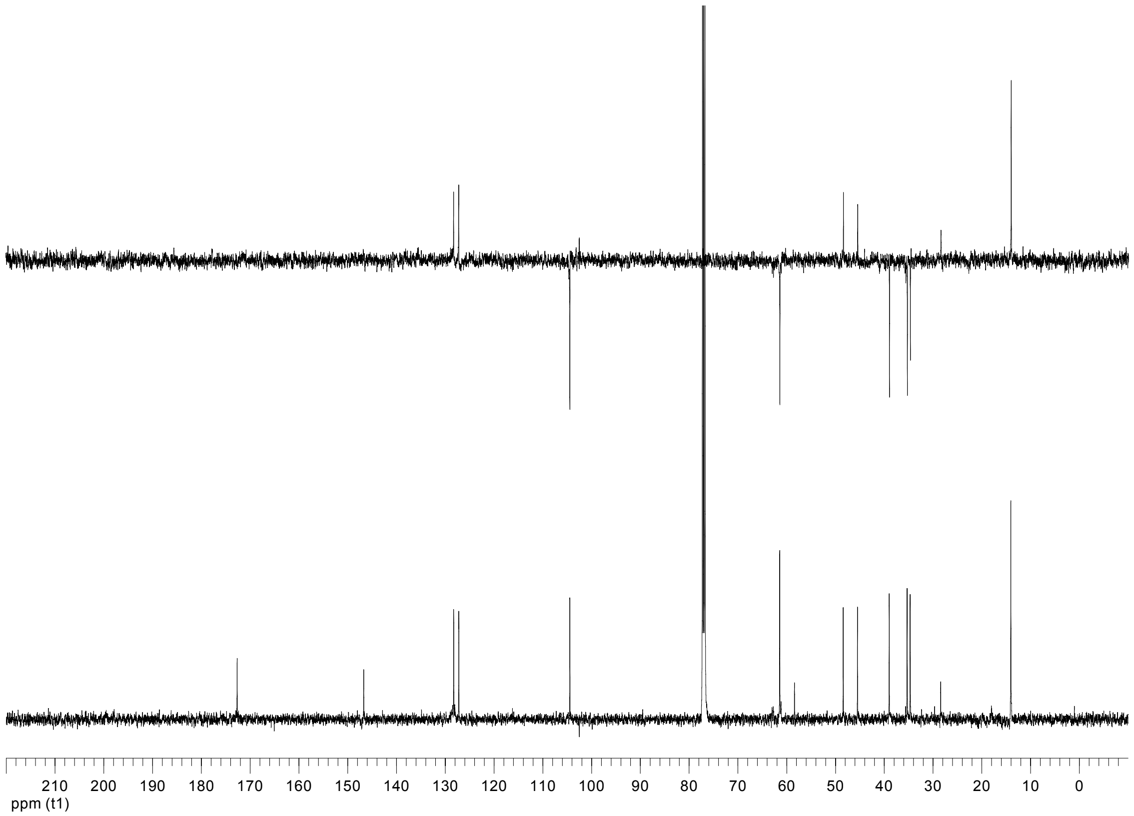

EtO2C
EtO2C
Ph
+
EtO2C
EtO2C
Ph
H
2c
H
3c
6 : 4
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


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

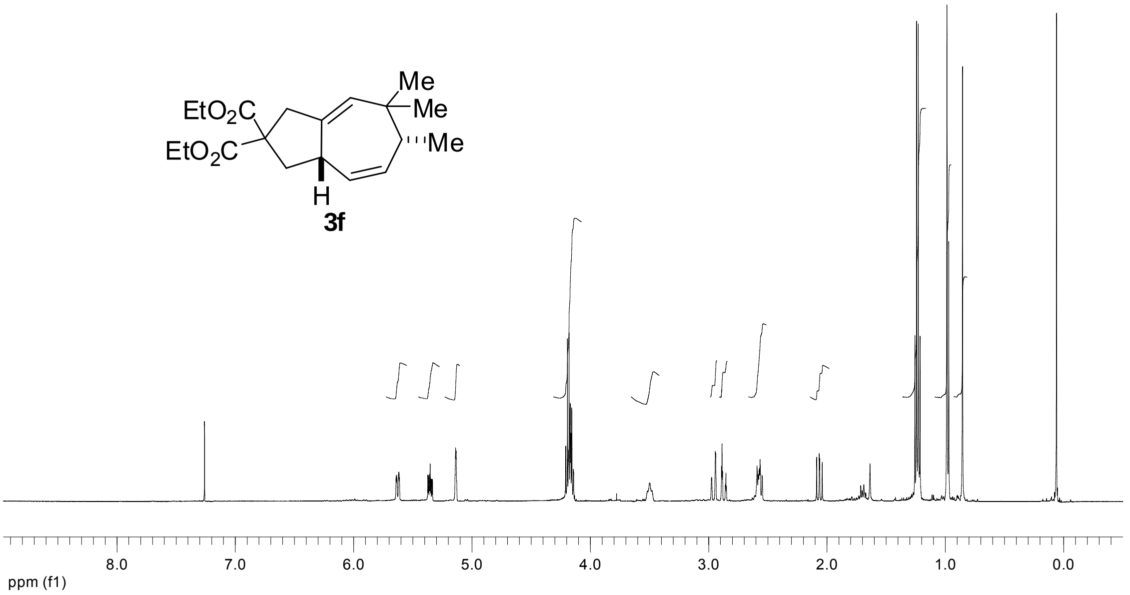

Me
EtO$_2$C
Me
EtO$_2$C
3d
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

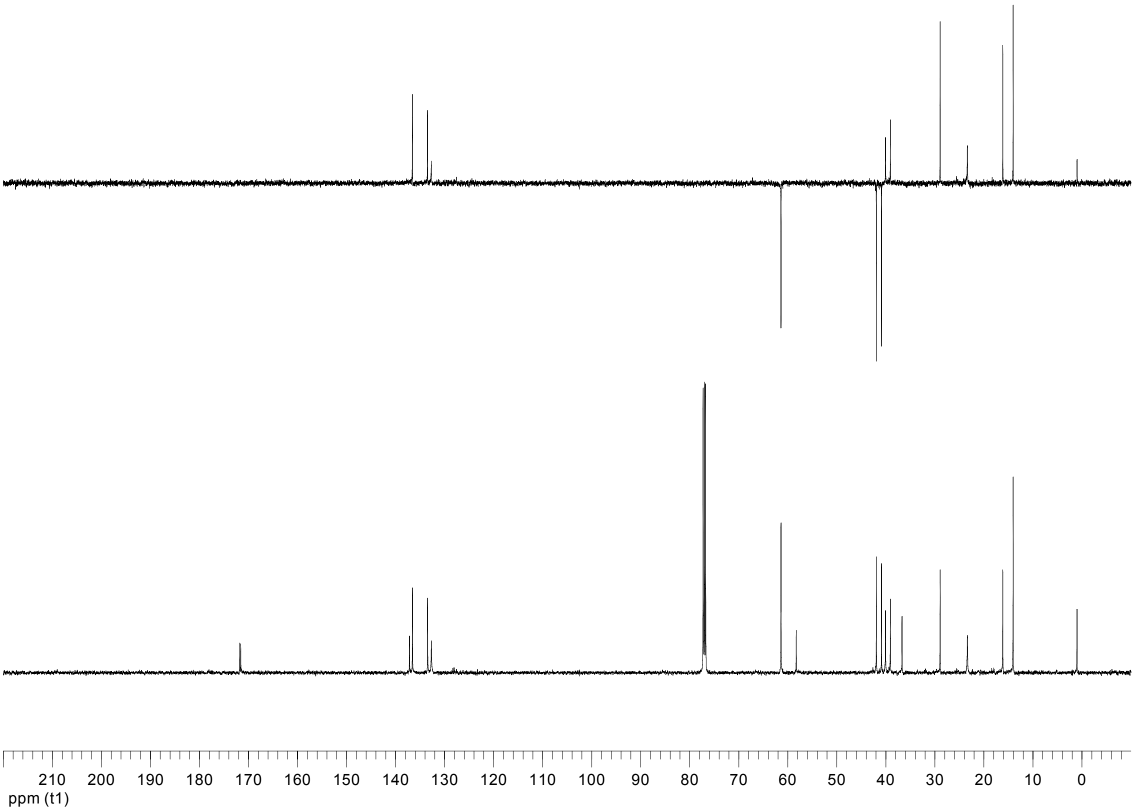

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)


EtO$_2$C
EtO$_2$C
5e
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

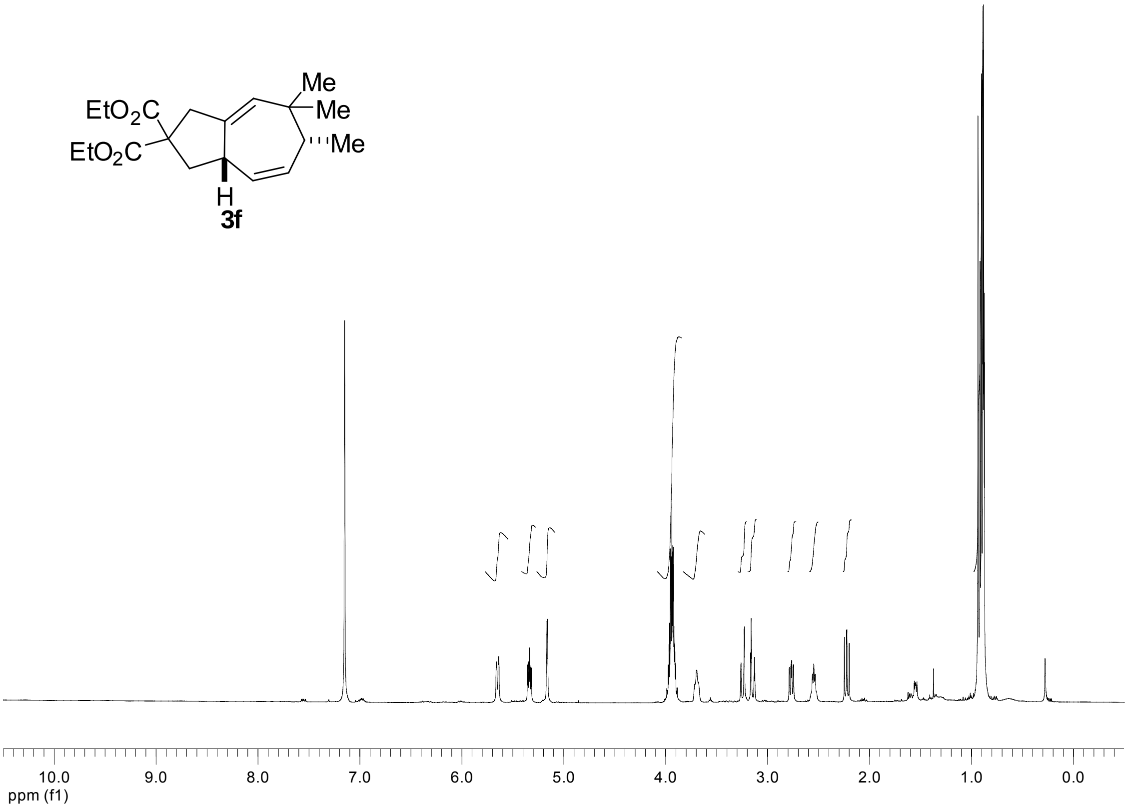

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

$CDCl_3$

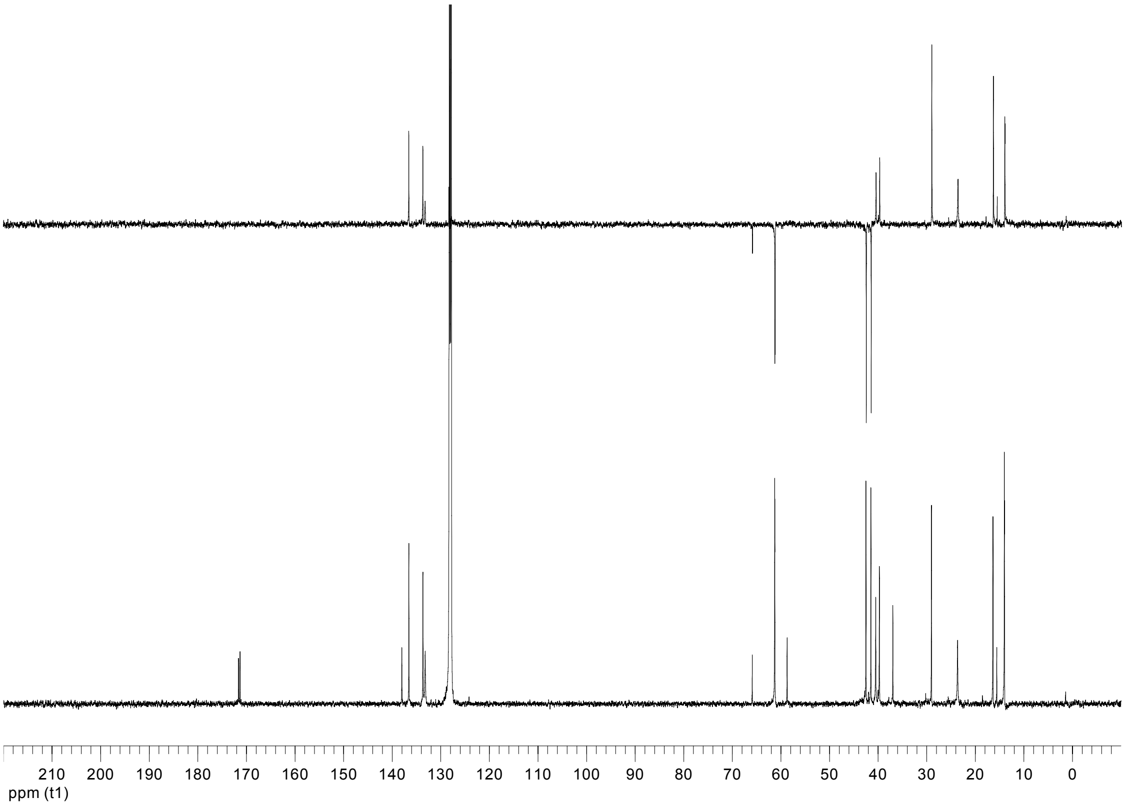

EtO2C
EtO2C
Me
Me
Me
H
3f
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

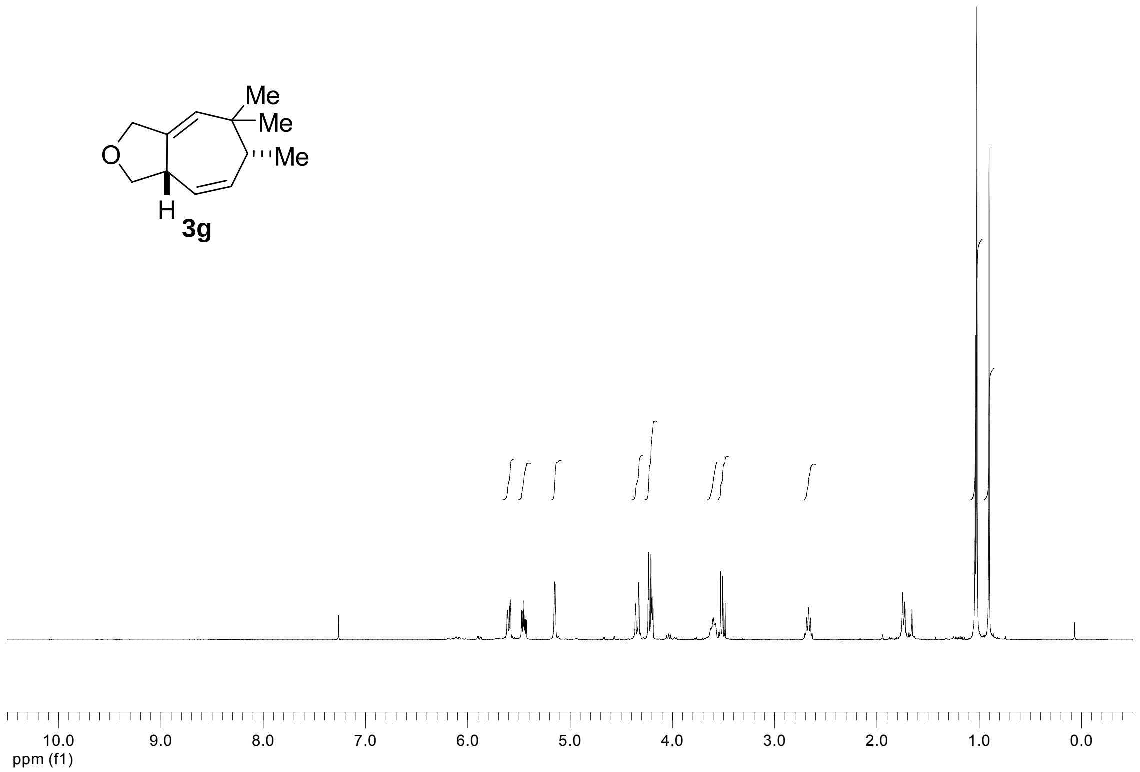

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

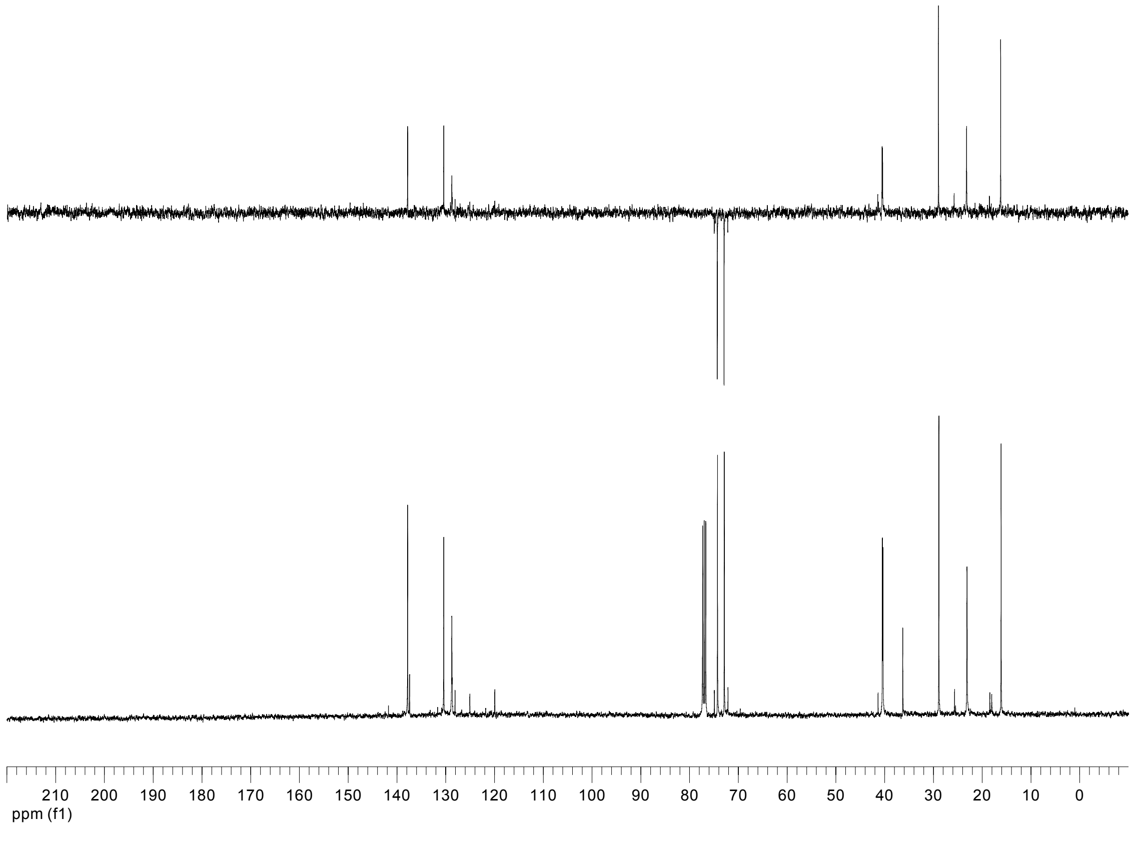
C_6D_6

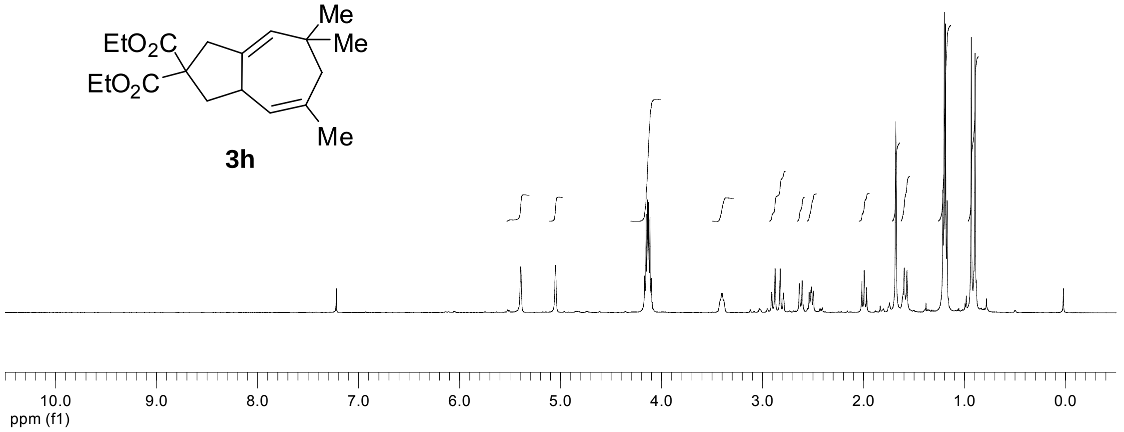

EtO2C
EtO2C
Me
Me
Me
H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

3f


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

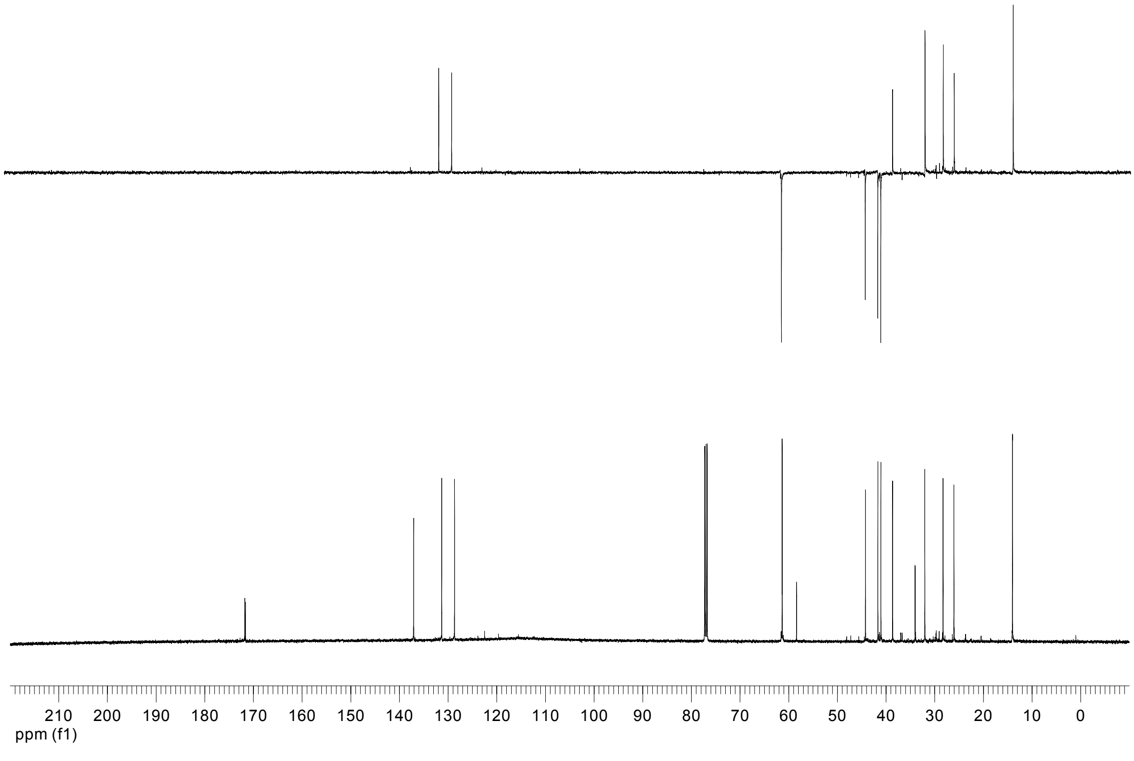

Me
Me
Me
O
H
3g
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


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

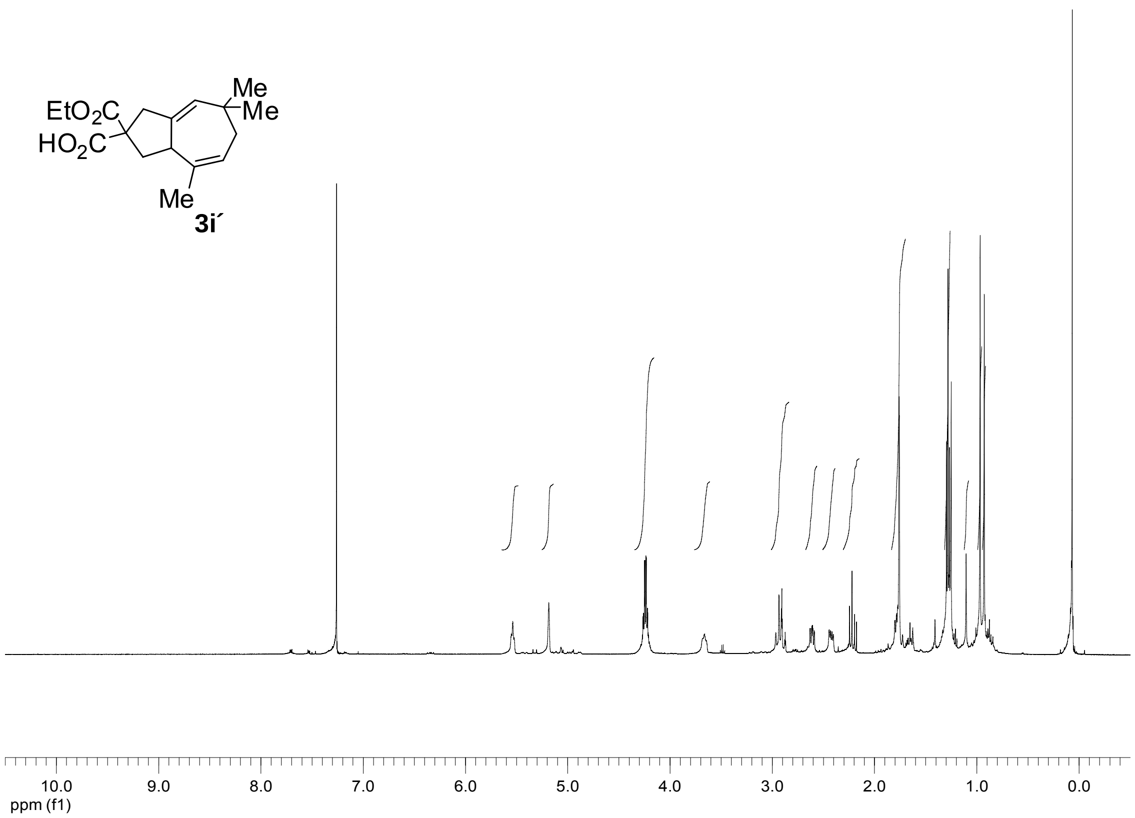


3h

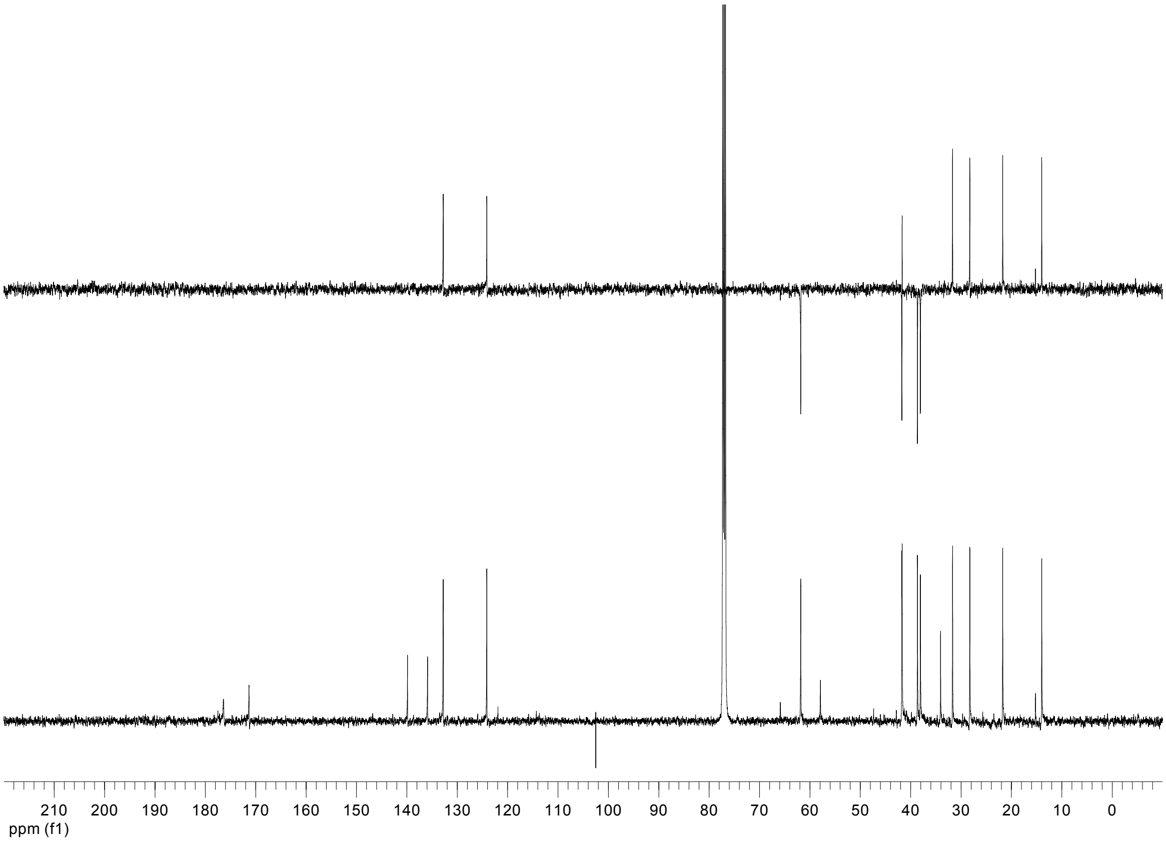
EtO2C
EtO2C
Me
Me
Me
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

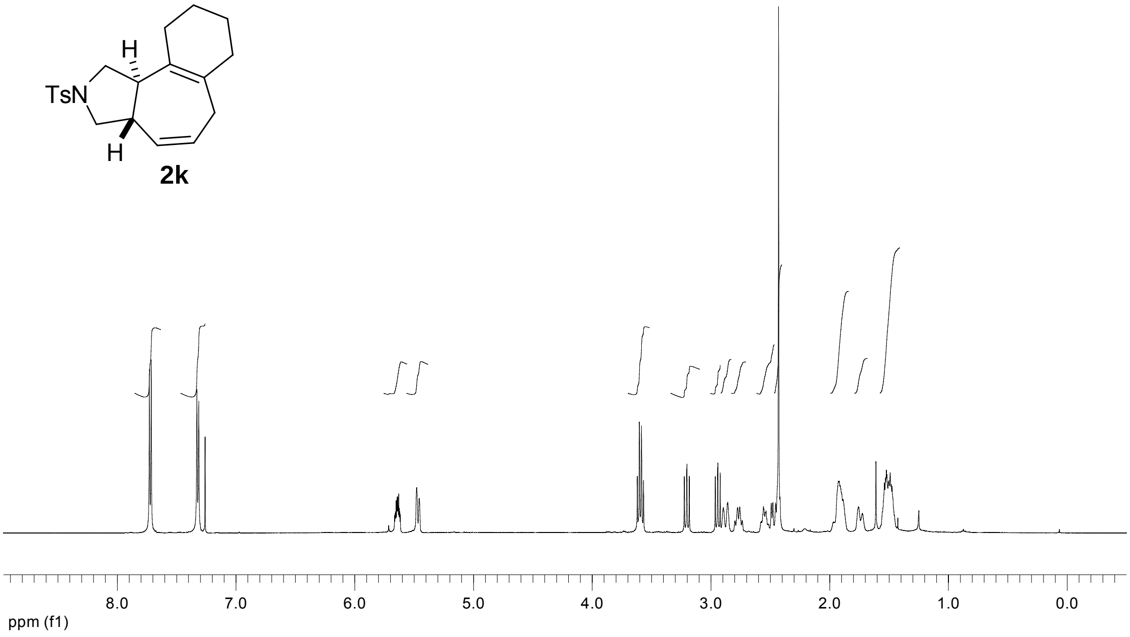


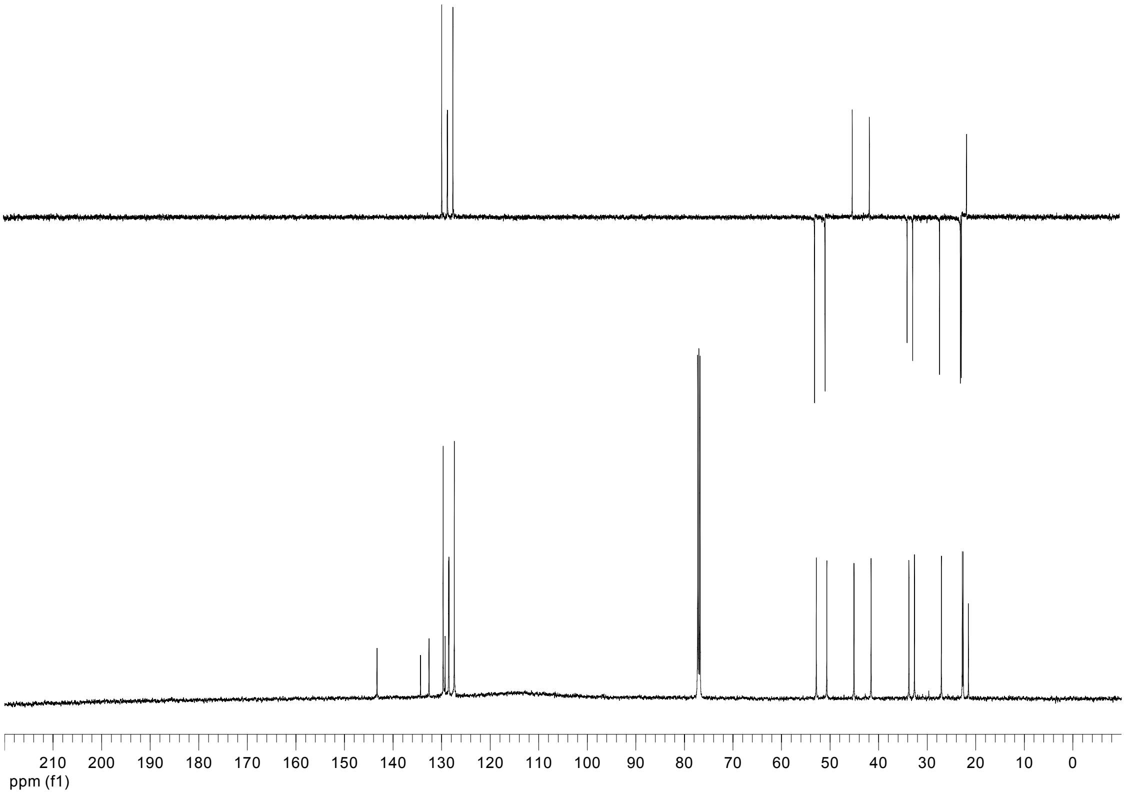
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)


EtO2C
HO2C
Me
Me
Me
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

3i´


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


TsN
H
H
2k
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


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