Fused cyclohexadiene platform for diversified synthesis of 5,6,5-tricyclic lactone scaffolds

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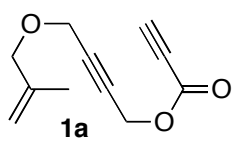
Supplementary Information

1. General Considerations

Column chromatography was performed on silica gel (Cica silica gel 60N) with solvents specified below. ^{1}H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$, CD_2Cl_2, or CD_3OD solutions at 25 ˚C. ^{1}H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at δ 7.26 ppm for chloroform or to the quinted at δ 3.30 ppm for methanol. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiplet. Coupling constants are reported in Hz. ^{13}C NMR spectra were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ 77.0 ppm for $CDCl_3$, the quintet at δ 53.8 ppm for CD_2Cl_2, or the septet at δ 49.0 ppm for CD_3OD. $[Cp^*RuCl_2]_2$ was prepared according to the report.[1] Cyclohexadienes **12a** and **12b** and their enediyne precursors were reported in the literatures.[2] Dry solvents were purchased and used as received.

2. Preparations of Enediyne Substrates



1a

General Procedure for Condensation of Alkynyl Alcohols with Propiolic Acid – Synthesis of 1a: To a solution of 4-(2-methylallyloxy)but-2-yn-1-ol[3] (3.516 g, 25.1 mmol) in dry CH_2Cl_2 (68 mL) was added DCC (6.79 g, 32.9 mmol) and DMAP (309.6 mg, 2.53 mmol) at 0 ˚C under an argon atmosphere. To this mixture was added a solution of propiolic acid (2.00 mL 32.6 mmol) in dry CH_2Cl_2 (2 mL) and the rmixture was stirred at 0 ˚C under an argon atmosphere for 2 h. Insolubule materials were filtered off through a pad of celite (eluted with ether), and the filtrate was comcentrated in vacuo. The obtained crude product was purified with column chromatography on silica gel (elution with hexane/AcOEt = 15:1) to give **1a** (3.11 g, 65% yield) as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.75 (s, 3 H), 2.94 (s, 1 H), 3.96 (s, 2 H), 4.17 (s, 2 H), 4.84 (s, 2 H), 4.93 (s, 1 H), 4.99 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 19.3, 53.6, 56.9, 73.6, 73.8, 75.8, 78.8, 83.9, 113.0, 141.1, 151.7; IR ($CHCl_3$) 3943 (C≡CH), 2121 (C≡C), 1724 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}O_3$•Na 215.0684, found 215.0679 $[M+Na]^+$.

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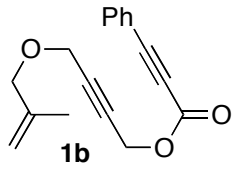
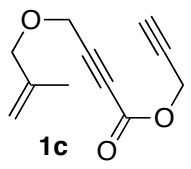
[1] (a) N. Oshima, H. Suzuki, Y. Moro-oka, *Chem. Lett.* **1984**, 1161. (b) Y. Yamamoto, K. Hattori, *Tetrahedron* **2008**, *64*, 847.

[2] (a) A. Geny, S. Gaudrel, F. Slowinski, M. Amatore, G. Chouraqui, M. Malacria, C. Aubert, V. Gandon, *Adv. Synth. Catal.* **2009**, *351*, 271. (b) Y. Yamamoto, S. Kuwabara, Y. Ando, H. Nagata, H. Nishiyama, K. Itoh, *J. Org. Chem.* **2004**, *69*, 6697.

[3] A. Padwa, H. Lipka, S. H. Watterson, S. S. Murphree, *J. Org. Chem.* **2003**, *68*, 6238.

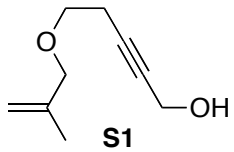


Analytical data for 1b: yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.75 (s, 3 H), 3.97 (s, 2 H), 4.19 (t, *J* = 2.0 Hz, 1 H), 4.88 (t, *J* = 2.0 Hz, 2 H), 4.94 (s, 1 H), 5.00 (s, 1 H), 7.38 (tt, *J* = 7.6, 1.2 Hz, 2 H), 7.47 (tt, *J* = 7.6, 1.2 Hz, 1 H), 7.60 (dt, *J* = 7.6, 1.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 19.5, 53.5, 57.0, 73.7, 79.2, 79.9, 83.8, 87.4, 113.0, 119.3, 128.6, 130.8, 133.0, 141.2, 153.1; IR ($CHCl_3$) 2222 (C≡C), 1715 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{16}O_3$•Na 291.0997, found 291.0979 $[M+Na]^+$.



Procedures for Synthesis of Enediyne 1c

A mixture of 4-(2-methylallyloxy)but-2-yn-1-ol [4] (154 mg, 1.1 mmol), 1-Me-AZADO$^+BF_4^-$ [5] (14 mg, 0.055 mmol), and $NaClO_2$ (597 mg, 6.6 mmol) in CH_3CN (3.7 mL) and sodium phosphate buffer (1 M, pH 6.8, 3.7 mL) was stirred at room temperature for 5.5 h. To this mixture was added 2-methyl-2-butene (1.5 mL and the mixture was then diluted with AcOEt (5 mL). The resultant mixture was treated with sodium phosphate buffer (pH 2, 15 mL) and extracted with AcOEt (5 mL × 2). The combined organic layer was dried with $MgSO_4$ and concentrated in vacuo. The obtained crude product was diluted with dry DMF (3.4 mL) and to this solution was added K_2CO_3 (304 mg, 2.2 mmol) and propargyl bromide (104 μL, 1.21 mmol). After stirring at room temperature for 15 h, insoluble materials were filtered off through a pad of celite (elution: AcOEt) and the filtrate was washed with H_2O (5 mL × 2) and brine (5 mL), and dried with $MgSO_4$. The solvent was evaporated and the obtained crude product was purified with column chromatography on silica gel (elution with hexane/AcOEt = 6:1) to give **1c** (64.8 g, 31% yield) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.75 (s, 3 H), 2.53 (t, *J* = 2.4 Hz, 1 H), 3.99 (s, 2 H), 4.27 (s, 2 H), 4.77 (d, *J* = 2.4 Hz, 2 H), 4.96 (s, 1 H), 5.00 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 19.3, 53.1, 56.5, 74.0, 75.8, 76.4, 84.9, 113.5, 113.6, 140.7, 152.1; IR ($CHCl_3$) 3295 (C≡CH), 2240 (C≡C), 1722 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}O_3$•Na 215.0684, found 215.0678 $[M+Na]^+$.



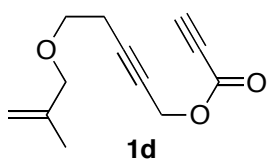
Procedures for Synthesis of Enediyne 1d

Synthesis of enyne S1: To a suspension of NaH (ca. 60 wt% in mineral oil, 1.32 g, 33 mmol) in dry THF (130 mL) was added 3-buyn-1-ol (2.27 mL, 30 mmol) at 0 ˚C under argon, and the mixture was stirred at 0 ˚C for 30 min. To this mixture was added methallyl bromide (3.4 mL, 33 mmol) and *n*Bu_4NI (1.11 g, 3.0 mmol) at 0 ˚C, and the mixture was stirred at 0 ˚C for 4.5 h. The reaction was quenched with sat. NH_4Cl (50 mL) and the organic layer was separated. The aqueous layer was extracted with Et_2O (30 mL × 3)

[4] A. Padwa, H. Lipka, S. H. Watterson, S. S. Murphree, *J. Org. Chem.* **2003**, *68*, 6238.
[5] M. Shibuya, T. Sato, M. Tomizawa, Y. Iwabuchi, *Chem. Commun.* **2009**, 1739.

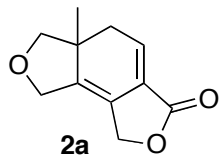
and the combined organic layer was dried with $MgSO_4$. The solvent was removed by distillation and the residue was roughly purified by bulb-to-bulb distillation (50 ˚C, 86 hPa) to give known 4-(2-methylallyloxy)but-1-yne[6] (1.193 g) as a colorless oil, which was directly used for the next step.

To a solution of the enyne prepoared above (1.193 g, 9.6 mmol) in dry THF (28 mL) was added dropwise a solution of *n*BuLi (1.6 M in hexane, 6.47 mL, 10 mmol) at –50 ˚C under argon and the solution was stirred at this temperature for 30 min. To this mixture was added paraformaldehyde (865 mg, 28.8 mmol) at –50 ˚C and the mixture was further stirred at room temperature for 5 h. The reaction was quenched with sat. NH_4Cl (15 mL) and the organic layer was separated. The aqueous layer was extracted with AcOEt (8 mL × 3) and the combined organic layer was dried with $MgSO_4$. After concentration in vacuo, the obtained residue was purified by column chromatography on silica gel (hexane/AcOEt = 4:1–3:1) to give **S1** (949 mg, 21% in two steps) as pale-yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.63 (br s, 1 H), 1.74 (s, 3 H), 2.49–2.54 (m, 2 H), 3.51 (t, *J* = 6.8 Hz, 2 H), 3.92 (s, 2 H), 4.25 (br s, 2 H), 4.90 (s, 1 H), 4.97 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 19.3, 20.0, 51.0, 67.8, 74.7, 79.5, 82.8, 122.5, 141.8; IR (neat) 3399 (OH), 2227 (C≡C) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_9H_{14}O_2$•Na 177.0891, found 177.0902 $[M+Na]^+$.


1d

Condensation of S1 with propioloic acid: The condensation of **S1** (949 mg, 6.15 mmol) with propiolic acid was carried out as described for the synthesis of **1a** to obtain **1d** (935 mg, 74% yield) as pale-yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.74 (s, 3 H), 2.50–2.55 (m, 2 H), 2.92 (s, 1 H), 3.52 (t, *J* = 7.0 Hz, 2 H), 3.91 (s, 2 H), 4.77(t, *J* = 2.2 Hz, 2 H), 4.91 (s, 1 H), 4.96 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 19.4, 20.2, 54.3, 67.5, 73.7, 74.1, 74.9, 75.5, 85.6, 122.5, 141.9, 151.9; IR (neat) 3269 (C≡CH), 2120 (C≡C), 1723 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{14}O_3$•Na 229.0841, found 229.0833 $[M+Na]^+$.

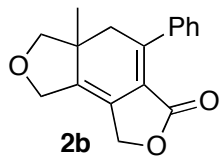
3. Ruthenium-Catalyzed Cyclization of Enediynes


2a

Synthesis of 2a: To a solution of $[Cp^*RuCl_2]_2$ (9.1 mg, 0.015 mmol) in dry degassed 1,2-dichloroethane (15 mL) was added dropwise in 20 min a solution of enediyne **1a** (192.1 mg, 1.00 mmol) in dry degassed 1,2-dichloroethane (5 mL) at room temperature under an argon atmosphere. The reaction mixture was stirred at room temperature under Ar for 1.5 h. After concentration in vacuo, the crude product was purified by column chromatography on silica gel (toluene/acetone = 9:1) to give **2a** (159.3 mg, 83%) as a colorless solid (mp 84.4–84.9 ˚C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.14 (s, 3 H),

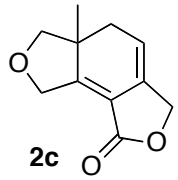
[6] O. Lavastre, P. H. Dixneuf, A. Pacreau, J.-P. Vairon, *Organometallics* **1994**, *13*, 2500.

2.42 (br d, J = 18.8 Hz, 1 H), 2.57 (dd, J = 18.8, 6.0 Hz, 1 H), 3.53 (d, J = 8.2 Hz, 1 H), 3.97 (d, J = 8.2 Hz, 1 H), 4.35 (br d, J = 15.6 Hz, 1 H), 4.58 (br d, J = 15.6 Hz, 1 H), 4.81 (dt, J = 14.0, 2.8 Hz, 1 H), 4.87 (dt, J = 14.0, 2.8 Hz, 1 H), 6.65 (dd, J = 4.4, 3.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 22.0, 34.3, 42.9, 66.6, 68.1, 80.5, 119.6, 125.8, 129.9, 137.4, 168.8; IR ($CHCl_3$) 1765 (C=O) cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{12}O_3$•Na 215.0684, found 215.0690 $[M+Na]^+$.



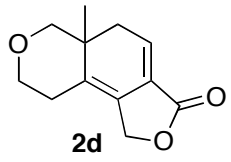
2b

Synthesis of 2b: To a solution of $[Cp^*RuCl_2]_2$ (9.3 mg, 0.0151 mmol) in dry degassed 1,2-dichloroethane (5 mL) was added dropwise in 10 min a solution of enediyne **1b** (78.1 mg, 0.291 mmol) in dry degassed 1,2-dichloroethane (10 mL) at 80 ˚C under an argon atmosphere. The reaction mixture was stirred at 80 ˚C under Ar for 10 min. After concentration in vacuo, the crude product was purified by column chromatography on silica gel (hexane/acetone = 7:3) to give **2b** (64.5 mg, 83%) as a yellow solid (mp 108.8–110.2 ˚C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.21 (s, 3 H), 2.70 (d, J = 17.4 Hz, 1 H), 2.91 (d, J = 17.4 Hz, 1 H), 3.61 (d, J = 7.8 Hz, 1 H), 4.02 (d, J = 7.8 Hz, 1 H), 4.40 (d, J = 15.4 Hz, 1 H), 4.64 (dq, J = 15.4, 2.0 Hz, 1 H), 4.80 (dt, J = 13.6, 2.4 Hz, 1 H), 4.86 (dt, J = 13.6, 1.2 Hz, 1 H), 7.36–7.44 (m, 3 H), 7.47–7.51 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 21.1, 42.3, 43.7, 66.8, 80.9, 118.5, 121.7, 127.9, 128.2, 129.3, 136.2, 136.8, 145.5, 167.8; IR ($CHCl_3$) 1759 (C=O) cm^{-1}; HRMS (ESI) m/z calcd for $C_{17}H_{16}O_3$•Na 291.0997, found 291.0987 $[M+Na]^+$.



2c

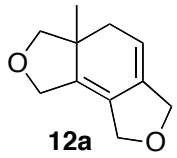
Synthesis of 2c: In the same manner for the synthesis of **2a**, the cyclization of **1c** (357 mg, 1.86 mmol) was carried out for 1 h. Purification by column chromatography (SiO_2, hexane/AcOEt = 1:1) gave **2c** (309 mg, 87%) as a colorless solid (mp 121.0–122.0 ˚C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 ˚C): δ 1.19 (s, 3 H), 2.31–2.44 (m, 2 H), 3.54 (d, J = 8.0 Hz, 1 H), 4.01 (d, J = 8.0 Hz, 1 H), 4.74 (d, J = 18.8 Hz, 1 H), 4.91–5.01 (m, 3 H), 5.51–5.55 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ˚C): δ 21.5, 32.8, 44.0, 68.0, 70.0, 79.9, 113.7, 114.3, 130.9, 155.9, 168.4; IR ($CHCl_3$) 1756 (C=O) cm^{-1}; HRMS (ESI) m/z calcd for $C_{11}H_{12}O_3$•Na 215.0684, found 215.0668 $[M+Na]^+$.



2d

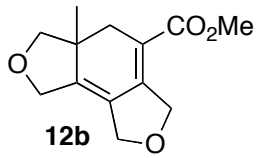
Synthesis of 2d: To a solution of $[Cp^*RuCl_2]_2$ (12.5 mg, 0.0203 mmol) in dry degassed 1,2-dichloroethane (5 mL) was added dropwise in 15 min a solution of enediyne **1d** (40.6 mg, 0.197 mmol) in dry degassed 1,2-dichloroethane (15 mL) at 60 ˚C under an argon atmosphere. The reaction mixture was stirred at 60 ˚C under Ar for 10 min. After concentration in vacuo, the crude product was purified by column chromatography on silica gel (toluene/acetone = 6:1) to give **2d** (36.4 mg, 90%) as a pale-yellow

oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.12 (s, 3 H), 2.02 (dd, *J* = 15.4, 1.8 Hz, 1 H), 2.18 (d, *J* = 16.0 Hz, 1 H), 2.23 (dd, *J* = 18.6, 5.0 Hz, 1 H), 2.49–2.62 (m, 1 H), 3.27 (d, *J* = 10.8 Hz, 1 H), 3.39 (ddd, *J* = 12.4, 10.8, 2.8 Hz, 1 H), 3.79 (d, *J* = 10.8 Hz, 1 H), 4.13 (ddd, *J* = 10.8, 6.4, 0.8 Hz, 1 H), 4.83 (dd, *J* = 13.2, 1.6 Hz, 1 H), 4.91 (dd, *J* = 13.2, 2.4 Hz, 1 H), 6.67 (t, *J* = 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 22.0, 25.7, 35.0, 35.2, 67.1, 68.2, 79.5, 123.9, 124.8, 128.7, 131.6, 169.0; IR ($CHCl_3$) 1768 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{14}O_3$•Na 229.0841, found 229.0848 $[M+Na]^+$.



12a

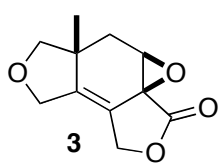
Synthesis of 12a:[2a] To a solution of $[Cp^*RuCl_2]_2$ (9.7 mg, 0.0158 mmol) in dry degassed 1,2-dichloroethane (10 mL) was added dropwise in 10 min a solution of 1-(2-methylallyloxy)-4-(prop-2-ynyloxy)but-2-yne (186 mg, 1.02 mmol) in dry degassed 1,2-dichloroethane (2 mL) at room temperature under an argon atmosphere. The reaction mixture was stirred at room temperature under Ar for 5 min. After concentration in vacuo, the crude product was purified by column chromatography on silica gel (hexane/AcOEt = 5:1) to give **12a** (173 mg, 93%) as a pale-yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.11 (s, 3 H), 2.02–2.27 (m, 2 H), 3.50 (d, *J* = 8.0 Hz, 1 H), 3.92 (d, *J* = 8.0 Hz, 1 H), 4.29 (d, *J* = 14.4 Hz, 1 H), 4.29–4.41 (m, 3 H), 4.44 (t, *J* = 2.4 Hz, 1 H), 4.51 (d, *J* = 14.4 Hz, 1 H), 5.40 (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 21.7, 33.7, 42.6, 67.2, 68.6, 70.1, 81.0, 110.6, 124.8, 133.5, 136.4.



12b

Synthesis of 12b:[2b] In the same manner for the synthesis of **12a**, the cyclization of methyl 4-(4-(2-methylallyloxy)but-2-ynyloxy)but-2-ynoate (83.1 mg, 0.35 mmol) was carried out for 1.5 h. Purification by column chromatography (SiO_2, AcOEt) gave **12b** (74.8 mg, 90%) as a colorless solid (mp 73.0–74.2 °C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.11 (s, 3 H), 2.36 (br d, *J* = 16.8 Hz, 1 H), 2.74 (dd, *J* = 16.8, 0.8 Hz, 1 H), 3.56 (d, *J* = 8.0 Hz, 1 H), 3.77 (s, 3 H), 3.98 (d, *J* = 8.0 Hz, 1 H), 4.33 (d, *J* = 14.8 Hz, 1 H), 4.34–4.42 (m, 2 H), 4.57 (d, *J* = 15.6 Hz, 1 H), 4.82 (d, *J* = 13.4 Hz, 1 H), 4.86 (d, *J* = 13.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 21.9, 33.2, 44.1, 51.6, 67.4, 68.3, 72.0, 80.8, 114.1, 125.6, 142.2, 148.9, 167.5.

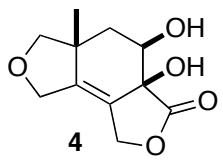
4. Epoxidation, Dihydroxylation and Conjugate Borylation/oxidation of 2a



3

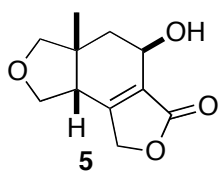
Epoxidation with DMDO: To a solution of **2a** (20 mg, 0.10 mmol) in CH_2Cl_2 (0.5 mL) was added a preformed solution of DMDO in acetone (0.08 M, 2.5 mL, 0.20 mmol) at –30 °C under an argon atmosphere and the solution was stirred for 11 h at this temperature. The solvent was removed in vacuo at –30 °C and

the crude product was purified by column chromatography on silica gel (elution: AcOEt) to give epoxide **3** (11 mg, 51% yield) as a colorless solid (mp 125.3–127.6 °C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.28 (s, 3 H), 1.44 (d, *J* = 15.0 Hz, 1 H), 2.39 (dd, *J* = 15.0, 1.6 Hz, 1 H), 3.32 (d, *J* = 8.4 Hz, 1 H), 3.86 (d, *J* = 8.4 Hz, 1 H), 4.11 (s, 1 H), 4.31 (br d, *J* = 15.2 Hz, 1 H), 4.51 (dt, *J* = 15.2, 2.4 Hz, 1 H), 4.94 (br d, *J* = 13.4 Hz, 1 H), 5.06 (dt, *J* = 13.4, 2.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 29.3, 30.6, 43.4, 53.7, 61.9, 67.3, 68.3, 80.8, 116.7, 143.1, 172.2; IR ($CHCl_3$) 1790 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{12}O_4$•Na 231.0633, found 231.0632 $[M+Na]^+$.



4

Dihydroxylation with OsO_4/NMO: To a solution of **2a** (57.5 mg, 0.30 mmol) and N-methylmorpholine N-oxide (69.3 mg, 0.60 mmol) in THF/H_2O (2 mL/0.4 mL) was added an aqueous solution of OsO_4 (0.164 M, 91.5 μL, 0.015 mmol) at room temperature under an argon atmosphere and the solution was stirred for 20 min at this temperature. To this solution was added AcOEt (2 mL), sat. $NaHCO_3$ (2 mL), and sat. Na_2SO_3 (2 mL), and organic layer was separated. The aqueous layer was extracted with AcOEt (3 mL × 3). The aqueous layer was acidified with 3% HCl (pH 5) and further extracted with AcOEt (3 mL × 3). The combined organic layer was dried with $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (elution: acetone/toluene 1:1) to give diol **4** (59.7 mg, 88% yield) as a colorless solid (mp 161.5–162.5 °C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.32 (s, 3 H), 1.73 (dd, *J* = 14.0, 11.0 Hz, 1 H), 1.95 (dd, *J* = 14.0, 6.8 Hz, 1 H), 3.25 (s, 1 H), 3.37 (d, *J* = 8.0 Hz, 1 H), 3.72 (ddd, *J* = 11.0, 6.8, 1.6 Hz, 1 H), 3.76 (s, 1 H), 3.77 (d, *J* = 8.0 Hz, 1 H), 4.28 (d, *J* = 14.2 Hz, 1 H), 4.43 (d, *J* = 14.2 Hz, 1 H), 4.72 (d, *J* = 12.4 Hz, 1 H), 4.91 (d, *J* = 12.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 27.7, 30.5, 43.5, 65.7, 68.5, 68.7, 69.4, 77.6, 120.6, 145.6, 177.7; IR ($CHCl_3$) 3410 (OH), 1770 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{11}H_{14}O_5$•Na 249.0739, found 249.0728 $[M+Na]^+$.

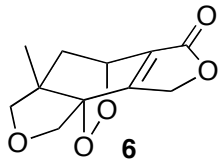


5

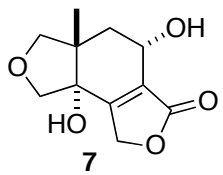
Conjugate borylation/oxidations: A solution of CuCl (3 mg, 0.03 mmol), DPEphos (16 mg, 0.03 mmol), and NaO^{t}Bu (9 mg, 0.09 mmol) in dry degassed THF (2 mL) was stirred at room temperature under an argon atmosphere for 30 min. To this catalyst solution was added a solution of $B_2(pin)_2$ (279 mg, 1.1 mmol) in dry degassed THF (2 mL) at room temperature and the solution was stirred for 10 min. To this solution was added a solution of **2a** (192 mg, 1.0 mmol) in dry degassed THF (1.5 mL) and then absolute MeOH (80 μL, 4.0 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was filered through a pad of celite and concentrated in vacuo. To the crude product was added THF (5 mL), H_2O (5 mL), and $NaBO_3$ (409 mg, 5.0 mmol) and the reaction mixture was stirred at room temperature for 3 h under

air. The mixture was extracted with AcOEt (5 mL × 3) and the combined organic layer was washed with brine (5 mL) and dried over $MgSO_4$. After concentrated in vacuo, the obtained crude product was purified by column chromatography on silica gel (elution: hexane/AcOEt 1:1) to give alcohol **5** (141 mg, 67% yield) as a colorless solid (mp 118.7–118.9 °C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.29 (s, 3 H), 1.75 (dd, *J* = 14.0, 7.2 Hz, 1 H), 2.15 (dd, *J* = 14.0, 5.8 Hz, 1 H), 2.71 (dd, *J* = 7.8, 4.6 Hz, 1 H), 3.07 (d, *J* = 2.0 Hz, 1 H), 3.54 (d, *J* = 8.8 Hz, 1 H), 3.64 (d, *J* = 8.8 Hz, 1 H), 3.66 (dd, *J* = 14.0, 4.8 Hz, 1 H), 4.16 (t, *J* = 8.6 Hz, 1 H), 4.65 (br s, 1 H), 4.70 (d, *J* = 17.2 Hz, 1 H), 4.76 (dd, *J* = 17.2, 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 25.8, 38.1, 42.4, 45.0, 60.3, 70.6, 70.9, 77.6, 127.6, 161.8, 172.6; IR ($CHCl_3$) 3439 (OH), 1747 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{28}O_8$•Na 443.1682, found 443.1677 $[2M+Na]^+$.

5. Synthesis of Diol 7 and Amino Alcohol 9 from 2a.

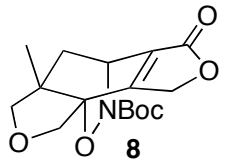

6

Diels–Alder reaction with singlet oxygen: Into a solution of **2a** (96 mg, 0.50 mmol) and rose Bengal (5 mg, 0.005 mmol) in degassed absolute ethanol (30 mL), O_2 was continuously babled at room temperature while irrading the reaction mixture with a 160W incandescent lamp for 2 h. The solvent was removed in vacuo and the crude product was purified by column chromatography on silica gel (elution: $CHCl_3$/MeOH = 9:1) to give endoperoxide **6** (74 mg, 65% yield) as a colorless solid (mp 135.6–136.6 °C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.93 (s, 3 H), 1.44 (dd, *J* = 13.6, 2.8 Hz, 1 H), 2.36 (dd, *J* = 13.6, 2.8 Hz, 1 H), 3.94 (d, *J* = 8.0 Hz, 1 H), 4.00 (d, *J* = 11.6 Hz, 1 H), 4.07 (d, *J* = 8.0 Hz, 1 H), 4.18 (d, *J* = 11.6 Hz, 1 H), 4.96 (d, *J* = 18.4 Hz, 1 H), 5.11 (d, *J* = 18.4 Hz, 1 H), 5.24 (t, *J* = 2.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 24.6, 32.1, 45.4, 66.0, 69.3, 69.7, 76.2, 89.0, 131.5, 163.3, 167.9; IR ($CHCl_3$) 1769 (C=O) cm^{-1}; HRMS (EI) *m/z* calcd for $C_{11}H_{12}O_5$ 224.0685, found 224.0686 $[M]^+$.


7

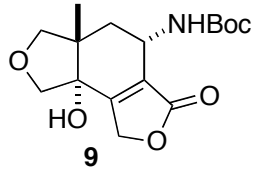
Conversion of endoperoxide 6 to diol 7: To a solution of crude **6** prepared as above from **2a** (96 mg, 0.50 mmol) in absolute methanol (3 mL) was added thiourea (42 mg, 0.55 mmol) at room temperature under an argon atmosphere. The reaction mixture was stirred for 2 h. Insoluble materials were filtered off through a pad of celite and the filtrate was concentrated in vacuo. The crude product was purified with column chromatography on silica gel (elution: AcOEt/MeOH = 9:1) to give **7** (95 mg, 83% yield) as a colorless solid (mp 135.7–138.6 °C): ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ 0.96 (s, 3 H), 2.08 (dd, *J* = 12.4, 7.4 Hz, 1 H), 2.12 (dd, *J* = 12.4, 8.8 Hz, 1 H), 3.59 (d, *J* = 6.4 Hz, 1 H), 3.86 (d, *J* = 8.4 Hz, 2 H), 3.92 (d, *J* = 8.8 Hz, 1 H), 4.59–4.66 (m, 1 H), 4.87 (dd, *J* = 18.2, 3.2 Hz, 1 H), 5.00 (dd, *J* = 18.2, 1.8 Hz, 1 H); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ 22.0, 35.1, 50.2, 63.3, 70.2, 71.9, 76.0, 77.3, 130.1, 162.7, 174.6; IR ($CHCl_3$) 3340 (OH), 1747 (C=O)

cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{11}H_{14}O_5$•Na 249.0739, found 249.0726 $[M+Na]^+$.



8

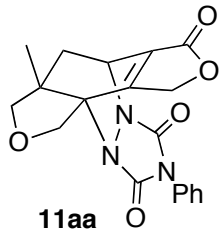
Diels–Alder reaction with *tert*-butyl nitrosoformate: To a solution of **2a** (96.2 mg, 0.50 mmol) and ^{n}Bu$_4$NIO$_4$ (261.0 mg, 0.60 mmol) in CH_2Cl_2 (5 mL) was added a solution of *N*-Boc hydroxylamine (100.2 mg, 0.75 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C under an argon atmosphere. The reaction mixture was stirred for 3 h at room temperature. The reaction was quenched with sat. $Na_2S_2O_3$ (4 mL) and was extracted with CH_2Cl_2 (4 mL × 3). The combined organic layer was washed with brine (4 mL), dried with $MgSO_4$ and concentrated in vacuo. The obtained crude product was purified with column chromatography on silica gel (elution: acetone/toluene 1:4) to give **8** (129.4 mg, 80% yield) as a yellow solid (mp 169.4–170.6 °C): ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ 0.86 (s, 3 H), 1.38 (dd, *J* = 13.6, 3.6 Hz, 1 H), 1.43 (s, 9 H), 2.17 (dd, *J* = 13.6, 2.4 Hz, 1 H), 3.88 (d, *J* = 7.6 Hz, 1 H), 4.03 (d, *J* = 7.6 Hz, 1 H), 4.16 (d, *J* = 11.0 Hz, 1 H), 4.29 (d, *J* = 11.0 Hz, 1 H), 4.92 (d, *J* = 17.8 Hz, 1 H), 5.07 (d, *J* = 17.8 Hz, 1 H), 5.19 (dd, *J* = 3.6, 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ 24.2, 27.7, 30.9, 47.2, 50.6, 66.8, 69.6, 76.2, 83.7, 90.0, 129.7, 157.2, 161.2, 167.9; IR ($CHCl_3$) 1770 (C=O) cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{16}H_{21}NO_6$•Na 346.1267, found 346.1252 $[M+Na]^+$.



9

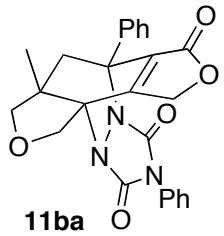
Conversion of 8 to anibo alcohol 9: A solution of **8** (32.4 mg, 0.10 mmol) and $Mo(CO)_6$ (79.7 mg, 0.30 mmol) in CH_3CN/H_2O (1.75 mL/0.25 mL) was refluxed under an argon atmosphere while irrading the reaction mixture with a 160W incandescent lamp for 5 h. Insoluble materials were filtered off through a pad of celite and the filtrate was concentrated in vacuo. The crude product was purified with column chromatography on silica gel (elution: acetone/toluene = 1:3) to give **9** (23.7 mg, 73% yield) as a colorless solid (mp 167.4–168.6 °C): ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ 0.98 (s, 3 H), 1.38 (s, 9 H), 2.04 (dd, *J* = 13.6, 8.6 Hz, 1 H), 2.45 (dd, *J* = 13.6, 8.8 Hz, 1 H), 3.64 (d, *J* = 7.0 Hz, 1 H), 3.86 (dd, *J* = 8.4, 2.6 Hz, 1 H), 3.94 (d, *J* = 7.0 Hz, 1 H), 4.00 (d, *J* = 8.8 Hz, 1 H), 4.02–4.08 (m, 1 H), 4.75 (dd, *J* = 18.0, 3.6 Hz, 1 H), 5.06 (dd, *J* = 18.0, 1.8 Hz, 1 H), 5.53 (br d, *J* = 7.6 Hz, 1 H), 5.56 (br d, *J* = 2.8 Hz, 1 H); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ 22.0, 28.2, 30.7, 42.2, 48.7, 68.8, 70.4, 75.0, 81.3, 126.5, 156.0, 161.3, 171.8; IR ($CHCl_3$) 3341 (OH), 1761 (C=O), 1680 (C=O) cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{16}H_{23}NO_6$•Na 348.1423, found 348.1407 $[M+Na]^+$.

6. Diels–Alder Reactions of 2a with Triazolinedione 10a and Maleimide 10b



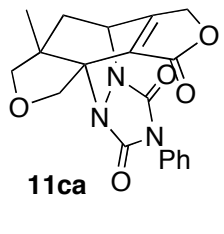
11aa

General procedures for Diels–Alder reaction with triazolinedione 10a – Synthesis of 11aa: A solution of cyclohexadiene **2a** (38 mg, 0.20 mmol) and triazolinedione **10a** (39 mg, 0.22 mmol) in degassed toluene (2 mL) was stirred at room temperature under an argon atmosphere for 30 min. The solvent was removed in vacuo and the obtained crude product was purified by column chromatography on silica gel (elution: toluene/acetone 1:1) to give cycloadduct **11aa** (70 mg, 95% yield) as a colorless solid (mp 227.5–227.8 °C): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.00 (s, 3 H), 1.54 (d, *J* = 13.6 Hz, 1 H), 2.39 (dd, *J* = 13.6, 2.4 Hz, 1 H), 3.98 (d, *J* = 8.0 Hz, 1 H), 4.08 (d, *J* = 8.0 Hz, 1 H), 4.15 (d, *J* = 10.4 Hz, 1 H), 4.97 (d, *J* = 18.8 Hz, 1 H), 5.05 (d, *J* = 18.8 Hz, 1 H), 5.47 (t, *J* = 2.8 Hz, 1 H), 5.77 (d, *J* = 10.8 Hz, 1 H), 7.34–7.39 (m, 3 H), 7.41–7.47 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 24.9, 32.8, 48.1, 48.4, 64.8, 70.0, 73.8, 75.3, 125.3, 127.3, 128.7, 129.2, 130.5, 154.5, 156.9, 162.5, 167.1; IR ($CHCl_3$) 1758 (C=O), 1717 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}N_3O_5$•Na 390.1066, found 390.1059 $[M+Na]^+$.



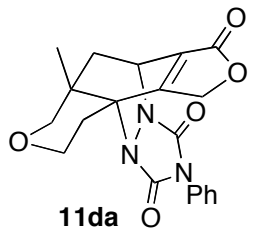
11ba

Analytical data for 11ba: colorless solid (mp 170.0–170.4 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.05 (s, 3 H), 1.61 (d, *J* = 14.0 Hz, 1 H), 2.55 (d, *J* = 14.0 Hz, 1 H), 4.00 (d, *J* = 7.2 Hz, 1 H), 4.17 (d, *J* = 7.2 Hz, 1 H), 4.20 (d, *J* = 4.0 Hz, 1 H), 4.97 (d, *J* = 18.6 Hz, 1 H), 5.02 (d, *J* = 18.6 Hz, 1 H), 6.01 (d, *J* = 10.4 Hz, 1 H), 7.29–7.46 (m, 8 H), 7.80–7.84 (m, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ 24.6, 46.7, 48.6, 64.7, 66.6, 69.1, 75.5, 76.3, 126.1, 127.9, 128.1, 128.4, 128.7, 128.9, 129.3, 131.1, 134.4, 154.0, 156.5, 162.6, 166.8; IR ($CHCl_3$) 1743 (C=O), 1719 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{21}N_3O_5$•Na 466.1379, found 466.1372 $[M+Na]^+$.



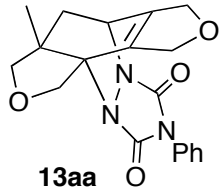
11ca

Analytical data for 11ca: colorless solid (mp 181.4–182.4 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.96 (s, 3 H), 1.58 (dd, *J* = 13.8, 3.6 Hz, 1 H), 2.42 (dd, *J* = 13.8, 2.8 Hz, 1 H), 3.95 (d, *J* = 7.6 Hz, 1 H), 4.05 (d, *J* = 7.6 Hz, 1 H), 4.50 (d, *J* = 11.2 Hz, 1 H), 5.04 (d, *J* = 18.8 Hz, 1 H), 5.11 (d, *J* = 18.8 Hz, 1 H), 5.37 (t, *J* = 3.0 Hz, 1 H), 5.82 (d, *J* = 11.2 Hz, 1 H), 7.33–7.36 (m, 3 H), 7.37–7.46 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 25.0, 32.2, 48.1, 49.5, 63.6, 70.0, 73.3, 75.1, 125.4, 128.6, 128.7, 129.1, 130.5, 154.8, 155.8, 161.0, 166.8; IR ($CHCl_3$) 1757 (C=O), 1717 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}N_3O_5$•Na 390.1066, found 390.1048 $[M+Na]^+$.



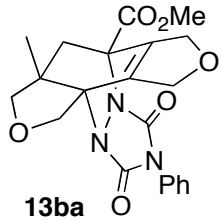
11da

Analytical data for 11da: colorless solid (mp 239.3–239.6 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.11 (s, 3 H), 1.48 (dd, *J* = 13.6, 2.8 Hz, 1 H), 1.89 (dd, *J* = 13.6, 2.8 Hz, 1 H), 2.38 (ddd, *J* = 14.0, 11.2, 6.0 Hz, 1 H), 3.20 (d, *J* = 14.0 Hz, 1 H), 3.63 (d, *J* = 12.0 Hz, 1 H), 3.98 (d, *J* = 12.0 Hz, 1 H), 4.05–4.16 (m, 2 H), 4.91 (d, *J* = 18.8 Hz, 1 H), 5.03 (d, *J* = 18.8 Hz, 1 H), 5.40 (t, *J* = 3.0 Hz, 1 H), 7.32–7.48 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 23.3, 23.6, 36.1, 38.0, 47.2, 63.4, 65.8, 69.3, 71.8, 125.4, 127.4, 128.5, 129.1, 130.7, 153.6, 154.3, 165.2, 167.3; IR ($CHCl_3$) 1758 (C=O), 1712 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}N_3O_5$•Na 404.1222, found 404.1206 $[M+Na]^+$.



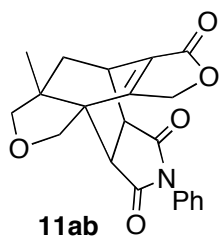
13aa

Analytical data for 13aa: colorless solid (mp 209.0–210.2 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.02 (s, 3 H), 1.48 (dd, *J* = 13.2, 3.4 Hz, 1 H), 2.28 (dd, *J* = 13.2, 2.6 Hz, 1 H), 3.93 (d, *J* = 7.2 Hz, 1 H), 4.00 (d, *J* = 7.2 Hz, 1 H), 4.02 (d, *J* = 10.6 Hz, 1 H), 4.69–4.89 (m, 4 H), 5.15 (t, *J* = 3.0 Hz, 1 H), 5.74 (d, *J* = 10.6 Hz, 1 H), 7.31–7.39 (m, 3 H), 7.40–7.46 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 25.0, 32.5, 47.8, 49.6, 65.5, 73.9, 74.2, 75.5, 125.4, 128.4, 129.0, 130.8, 135.2, 136.5, 155.8, 157.4; IR ($CHCl_3$) 1717 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{19}N_3O_4$•Na 376.1273, found 376.1271 $[M+Na]^+$.



13ba

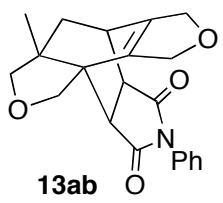
Analytical data for 13ba: colorless solid (mp 185.5–186.7 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.03 (s, 3 H), 1.54 (d, *J* = 13.2 Hz, 1 H), 2.61 (d, *J* = 13.2 Hz, 1 H), 3.92 (s, 3 H), 3.95 (d, *J* = 7.6 Hz, 1 H), 4.02 (d, *J* = 10.6 Hz, 1 H), 4.10 (d, *J* = 7.6 Hz, 1 H), 4.73–4.78 (m, 2 H), 4.99 (ddd, *J* = 14.0, 6.4, 5.0 Hz, 1 H), 5.17 (dt, *J* = 14.0, 6.0 Hz, 1 H), 5.78 (d, *J* = 10.6 Hz, 1 H), 7.32–7.40 (m, 3 H), 7.41–7.47 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 24.7, 37.5, 48.0, 53.4, 63.7, 65.3, 73.8, 75.2, 75.4, 75.5, 125.4, 128.7, 128.8, 129.0, 129.1, 130.4, 135.1, 135.9, 156.1, 157.4, 167.1; IR ($CHCl_3$) 1749 (C=O), 1723 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}N_3O_6$•Na 434.1328, found 434.1321 $[M+Na]^+$.



11ab

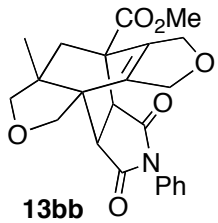
General procedures for Diels–Alder reaction with maleimide 10b – Synthesis of 11ab: A solution of cyclohexadiene **2a** (38 mg, 0.20 mmol) and maleimide **10b** (38 mg, 0.22 mmol) in degassed toluene (2 mL) was refluxed (bath temp. 140 °C) under an argon atmosphere for 6 h. The solvent was removed in vacuo and the obtained crude product was purified by column chromatography on silica gel (elution: toluene/acetone 2:1) to give cycloadduct **11ab** (61 mg, 83% yield) as a colorless solid (mp 199.2–200.3 °C): ^{1}H NMR (400

MHz, $CDCl_3$, 25 °C): δ 0.90 (s, 3 H), 1.47 (dd, *J* = 13.2, 1.6 Hz, 1 H), 1.83 (d, *J* = 13.2 Hz, 1 H), 3.25 (dd, *J* = 8.0, 3.2 Hz, 1 H), 3.37 (d, *J* = 8.0 Hz, 1 H), 3.76 (d, *J* = 8.4 Hz, 1 H), 3.90 (t, *J* = 1.2 Hz, 1 H), 3.96 (d, *J* = 8.4 Hz, 1 H), 4.09 (d, *J* = 8.4 Hz, 1 H), 4.76 (d, *J* = 18.2 Hz, 1 H), 4.88 (d, *J* = 18.2 Hz, 1 H), 5.02 (d, *J* = 9.2 Hz, 1 H), 6.97–7.02 (m, 2 H), 7.35–7.44 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 25.7, 31.5, 34.4, 42.5, 45.9, 48.1, 55.8, 65.8, 70.8, 76.1, 126.1, 129.0, 129.3, 130.9, 166.7, 169.2, 174.7, 176.1; IR ($CHCl_3$) 1754 (C=O), 1709 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{19}NO_5$•Na 388.1161, found 388.1147 $[M+Na]^+$.



13ab

Analytical data for 13ab: colorless solid (mp 162.0–162.8 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.92 (s, 3 H), 1.40 (dd, *J* = 13.2, 4.4 Hz, 1 H), 1.70 (d, *J* = 13.2 Hz, 1 H), 3.15–3.20 (m, 2 H), 3.53 (br s, 1 H), 3.67 (d, *J* = 8.4 Hz, 1 H), 3.91 (d, *J* = 7.6 Hz, 1 H), 3.96 (d, *J* = 8.8 Hz, 1 H), 4.57– 4.71 (m, 3 H), 4.75–4.82 (m, 1 H), 4.97 (d, *J* = 8.8 Hz, 1 H), 7.05–7.08 (m, 2 H), 7.36–7.48 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 25.7, 32.6, 34.3, 42.6, 46.5, 48.1, 53.9, 66.8, 75.07, 75.12, 76.3, 126.6, 128.9, 129.3, 131.5, 136.3, 137.4, 176.4, 177.0; IR ($CHCl_3$) 1707 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}NO_4$•Na 374.1368, found 374.1353 $[M+Na]^+$.



13bb

Analytical data for 13bb: colorless solid (mp 192.5–193.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 0.95 (s, 3 H), 1.46 (d, *J* = 13.4 Hz, 1 H), 2.08 (d, *J* = 13.4 Hz, 1 H), 3.28 (d, *J* = 8.2 Hz, 1 H), 3.69 (d, *J* = 8.2 Hz, 1 H), 3.75 (d, *J* = 8.0 Hz, 1 H), 3.85 (s, 3 H), 3.94 (t, *J* = 8.0 Hz, 2 H), 4.55–4.64 (m, 1 H), 4.65–4.73 (m, 1 H), 4.76–4.83 (m, 1 H), 5.00 (d, *J* = 9.2 Hz, 1 H), 5.08–5.15 (m, 1 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 7.35–7.46 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 25.5, 39.4, 42.5, 48.4, 49.2, 49.5, 52.7, 54.6, 66.4, 74.9, 76.1, 76.2, 126.5, 129.0, 129.4, 131.3, 134.9, 137.7, 171.8, 174.8, 176.1; IR ($CHCl_3$) 1737 (C=O), 1712 (C=O) cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{23}H_{23}NO_6$•Na 432.1423, found 432.1420 $[M+Na]^+$.

7. Sigle Crystal X-ray Diffraction Study

Single crystals of **3**–**5**, **6**, **8**, and **11aa** were mounted on a glass fiber, and diffraction data were collected in θ ranges specified in Tables S1 and S2 at 103 K on a Brucker SMART APEX CCD diffractometer (**3**, **5**, **6**, and **11aa**) and Brucker D8 QUEST diffractomter (**4** and **8**) with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The absorption correction was made using SADABS. The structure was solved by direct methods and refined by the full-matrix least-squares on F^2 by using SHELXTL 5.1 (**3**, **5**, **6**, and **11aa**) and SHELXL-2013 (**4** and **8**).[7] All non-hydrogen

[7] (a) Sheldrick, G. M. SHELXTL 5.1, Bruker AXS Inc., Madison, Wisconsin, **1997**. (b) Sheldrick, G. M. SHELXL-2013, Bruker AXS Inc., Madison, Wisconsin, **2013**.

atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. Final refinement details are compiled in Tables S1–S3. The supplementary crystallographic data for this paper (CCDC 1043689–1043693, and 1050808) can also be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table S1. Selected Crystallographic data and collection parameters for **3** and **5**.

compound	**3**	**5**
formula	$C_{11}H_{12}O_4$	$C_{11}H_{14}O_4$
fw	208.21	210.22
crystal system	orthorhombic	monoclinic
space group	Pna2(1)	P2(1)/n
a , Å	14.7139(15)	7.5247(12)
b , Å	6.7243(7)	15.808(3)
c , Å	19.1182(19)	8.9072(14)
β, deg		113.311(3)
volume, Å^3	1891.6(3)	973.0(3)
Z	8	4
D (calcd), Mg m^{-3}	1.462	1.435
μ, mm^{-1}	0.112	0.109
F(000)	880	448
crystal size, mm	0.6 x 0.3 x 0.1	0.2 x 0.2 x 0.2
θ range for data collection, deg	2.13 to 28.28	2.58 to 28.33
index ranges	-15≤h≤19, -8≤k≤8, -25≤l≤25	-9≤h≤10, -16≤k≤21, -11≤l≤11
reflections collected	12971	7151
independent reflections [*R*(int)]	4650 [R(int) = 0.0228]	2409 [R(int) = 0.0265]
completeness to theta = 28.29°	100.0%	99.5%
data / restraints / parameters	4650 / 1 / 273	2409 / 0 / 138
goodness-of-fit on F^2	1.022	1.038
R_1 [$I > 2s(I)$]	0.0390	0.0413
wR_2 [$I > 2s(I)$]	0.1014	0.1095
R_1 (all data)	0.0422	0.0460
wR_2 (all data)	0.1043	0.1133
absolute structure parameter	0.8(8)	
largest diff. peak and hole, e Å^{-3}	0.408 and -0.169	0.474 and -0.208

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[(w(F_o^2-F_c^2)^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2. Selected Crystallographic data and collection parameters for **6** and **11aa**.

compound	**6**	**11aa•CH_2Cl_2**
formula	$C_{11}H_{12}O_5$	$C_{20}H_{19}Cl_2N_3O_5$
fw	224.21	452.28
crystal system	monoclinic	monoclinic
space group	P2(1)/c	P2(1)/n
a , Å	12.939(3)	8.4382(17)
b , Å	6.3984(13)	27.021(5)
c , Å	11.757(3)	8.8106(16)
β, deg	94.899(5)	104.625(4)
volume, $Å^3$	969.8(3)	1943.8(6)
Z	4	4
D (calcd), Mg m^{-3}	1.152	1.545
μ, mm^{-1}	0.092	0.374
F(000)	354	936
crystal size, mm	0.6 x 0.4 x 0.05	0.3 x 0.3 x 0.1
θ range for data collection, deg	1.58 to 28.30	1.51 to 28.31
index ranges	-17≤h≤14, -8≤k≤6, -15≤l≤15	-11≤h≤9, -34≤k≤35, -11≤l≤10
reflections collected	6980	14696
independent reflections [*R*(int)]	2402 [R(int) = 0.0314]	4824 [R(int) = 0.0358]
completeness to theta = 28.29°	99.6%	99.7%
data / restraints / parameters	2402 / 0 / 146	4824 / 0 / 272
goodness-of-fit on F^2	1.022	1.093
R_1 [$I > 2s(I)$]	0.0476	0.0539
wR_2 [$I > 2s(I)$]	0.1205	0.1262
R_1 (all data)	0.0594	0.0645
wR_2 (all data)	0.1278	0.1311
largest diff. peak and hole, e $Å^{-3}$	0.423 and -0.218	0.723 and -0.472

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[(w(F_o^2-F_c^2)^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S3. Selected Crystallographic data and collection parameters for **4** and **8**.

compound	**4**	**8**
formula	$C_{11}H_{14}O_5$	$C_{16}H_{21}NO_6$
fw	226.22	323.34
crystal system	monoclinic	monoclinic
space group	P2(1)/c	P2(1)/n
a , Å	24.3516(13)	16.6489(7)
b , Å	7.9830(4)	9.9633(5)
c , Å	10.7485(5)	20.3053(9)
β, deg	101.3458(14)	109.2010(12)
volume, Å^3	2048.66(18)	3180.8(3)
Z	8	4
D (calcd), Mg m^{-3}	1.467	0.675
μ, mm^{-1}	0.116	0.104
F(000)	960	1376
crystal size, mm	0.4 x 0.4 x 0.2	0.3 x 0.3 x 0.1
θ range for data collection, deg	2.56 to 25.06	2.30 to 25.07
index ranges	-29≤h≤26, -9≤k≤9, -12≤l≤12	-19≤h≤18, -11≤k≤11, -24≤l≤23
reflections collected	14197	21783
independent reflections [*R*(int)]	3618 [R(int) = 0.0279]	5561 [R(int) = 0.0408]
coverage of independent reflections	99.6%	98.9%
data / restraints / parameters	3618 / 0 /296	5561 / 0 / 423
goodness-of-fit on F^2	1.024	1.020
R_1 [4730 data; $I > 2s(I)$]	0.0339	0.0356
wR_2 [4730 data; $I > 2s(I)$]	0.0862	0.0866
R_1 (all data)	0.0376	0.0449
wR_2 (all data)	0.0890	0.0921
largest diff. peak and hole, e Å^{-3}	0.294 and -0.205	0.277 and -0.210
R.M.S. deviation from mean, e Å^{-3}	0.044	0.043

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[(w(F_o^2-F_c^2)^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

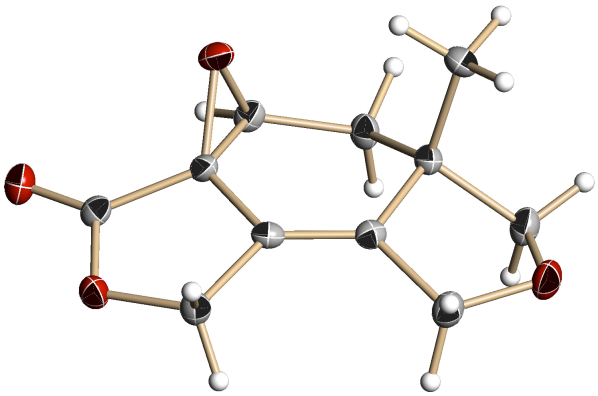


Figure S1. ORTEP drawing of **3**.

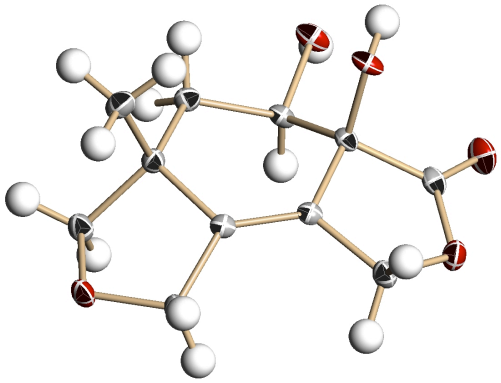


Figure S2. ORTEP drawing of **4**.

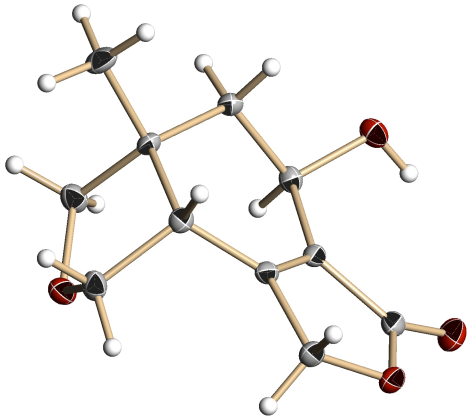


Figure S3. ORTEP drawing of **5**.

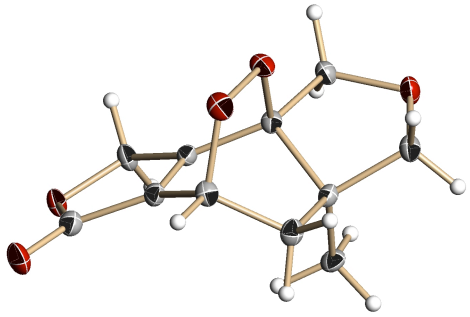


Figure S4. ORTEP drawing of **6**.

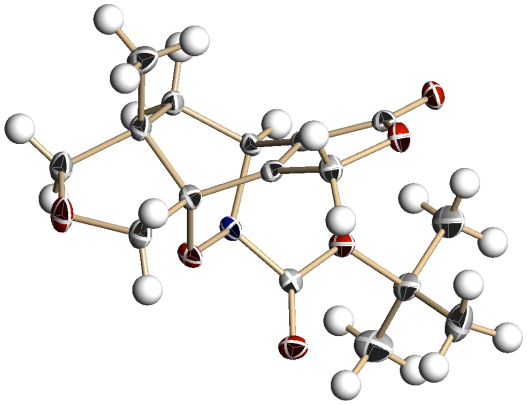


Figure S5. ORTEP drawing of **8**.

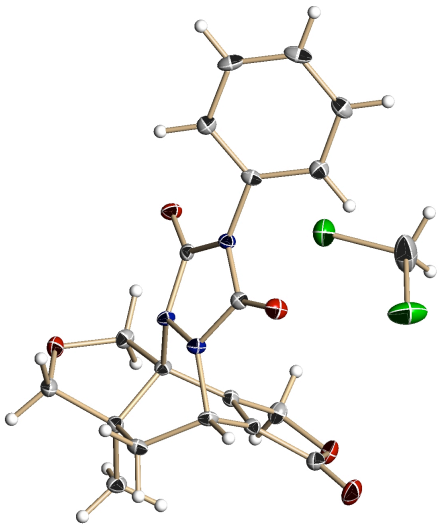


Figure S6. ORTEP drawing of **11aa**.

8. DFT Caluculations

The Gaussian 09 program package was used for all geometry optimizations.[8] The geometries of stationary points and transition states were fully optimized by means of the M06-2X[9] level of theory with the 6-31G(d) basis set.[10] The vibrational frequencies and thermal correction to Gibbs free energy (TCGFE), which includes zero-point energy, were calculated at the same level of theory. The obtained structures were characterized by the number of imaginary frequencies (one or zero for transition or ground states, respectively). The connectivity of each step was further confirmed by IRC calculation[11] from the transition states followed by optimization of the resulted geometries. Total energies in toluene were obtained by performing single-point energy calculations for gas-phase geometries obtained by the above method, using the polarizable continuum model (PCM)[12] method with the same functional and the 6-311++G(d,p) basis set.[13] The obtained results are summarized in Table S3. HOMO energies were also obtained by single-point energy calculations for optimized geometries at the HF/6-311+G(d,p) level. Activation, distortion, and

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[8] Gaussian 09, Revision C.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.

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[10] (a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257. (b) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213. (c) M. M. Fracl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654.

[11] (a) K. Fukui, *Acc. Chem. Res.,* **1981**, *14*, 363. (b) C. Gonzalez, H. B. Schlegel, *J. Chem. Phys.,* **1989**, *90*, 2154. (c) C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.,* **1990**, *94*, 5523.

[12] (a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117. (b) J. L. Pascual-Ahuir, E. Silla, J. Tomasi, R. Bonaccorsi, *J. Comput. Chem.* **1987**, *8*, 778. (c) F. Floris, J. Tomasi, *J. Comput. Chem.* **1989**, *10*, 616. (d) M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327. (e) E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *22*, 3032. (f) V. Barone, M. Cossi, J. Tomasi, *J. Chem. Phys.* **1997**, *22*, 3210.

[13] (a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.,* **1980**, *72*, 650. (b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639. (c) M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.,* **1984**, *80*, 3265. (d) T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, *J. Comp. Chem.,* **1983**, *4*, 29.

intaraction energies ($\Delta E^{\ddagger}_{act}$, $\Delta E^{\ddagger}_{dist}$, and $\Delta E^{\ddagger}_{int}$, respectively) were computed at the M06-2X/6-31G(d) level. These data were summarized in Tables S3 and S4.

Table S3. Summary of DFT calculations (293.15 K, 1 atm).

Compound	PCM energy/au	TCGFE/au	IF/cm^{-1}
2a[a]	–651.95628992	0.183174	
12a[a]	–577.90644593	0.202137	
10a[a]	–622.45851902	0.094397	
$TS_{\mathbf{2a\text{-}11aa}}$[a]	–1274.42248211	0.303757	330.1360i
11aa[a]	–1274.48713338	0.307593	
$TS_{\mathbf{12a\text{-}13aa}}$[a]	–1200.37327619	0.322863	324.3962i
13aa[a]	–1200.43577242	0.325539	
2a	–651.95628992	0.179129	
10c	–359.40188547	0.040135	
anti/*endo* $TS_{\mathbf{2a\text{-}11ac}}$	–1011.34523446	0.245967	402.1579i
anti/*endo* **11ac**	–1011.42490536	0.250305	
anti/*exo* $TS_{\mathbf{2a\text{-}11ac}}$	–1011.33381780	0.244807	442.9675i
anti/*exo* **11ac**	–1011.41803488	0.251449	
syn/*endo* $TS_{\mathbf{2a\text{-}11ac}}$	–1011.33647304	0.245314	393.4215i
syn/*endo* **11ac**	–1011.42759918	0.250059	
syn/*exo* $TS_{\mathbf{2a\text{-}11ac}}$	–1011.31812931	0.243706	419.1962i
syn/*exo* **11ac**	–1011.41950289	0.251467	
2b	–882.97390986	0.254582	
$TS_{\mathbf{2b\text{-}11bc}}$	–1242.35564026	0.321851	425.0291i
11bc	–1242.43253347	0.325864	
2c	–651.95766398	0.178889	
$TS_{\mathbf{2c\text{-}11cc}}$	–1011.34602749	0.245717	412.1465i
11cc	–1011.42443801	0.250314	
2d	–691.27009995	0.207747	
$TS_{\mathbf{2d\text{-}11dc}}$	–1050.65998096	0.274931	397.0319i
11dc	–1050.73998661	0.279179	
12a	–577.90644593	0.198189	
$TS_{\mathbf{12a\text{-}13ac}}$	–937.29627103	0.265088	427.3200i
13ac	–937.37166040	0.268860	
12b	–805.77688029	0.235477	

$TS_{12b\text{-}13bc}$	–1165.16232880	0.305159	444.4320i
13bc	–1165.23448582	0.307138	

[a]273.15 K, 1atm.

Table S4. Summary of DFT calculations for distortion/interaction analysis (au).

	E_{4e}	$E^{‡}_{TS}$	$E^{‡}_{4e\text{-fragment}}$	$E^{‡}_{2e\text{-fragment}}$
2a	–651.76652915	–1011.04279857	–651.73278494	–359.27377729
2b	–882.72893599	–1241.99792819	–882.68919295	–359.27030937
2c	–651.76852227	–1011.04378480	–651.73498143	–359.27314754
2d	–691.06976858	–1050.34671963	–691.03880507	–359.27281230
12a	–577.74175050	–937.01997446	–577.70466853	–359.27245501
12b	–805.54186676	–1164.81706771	–805.49964279	–359.27098772

E_{2e} = –359.28535209

Table S5. Calculated parameters for Diels-Alder reactions of **3b**–**f**, **5b**, and **5c** with **11c**.[a]

	HOMO	$\Delta G^{‡}$	ΔG_{rxn}	$\Delta E^{‡}_{act}$	$\Delta E^{‡}_{dist,4e}$	$\Delta E^{‡}_{dist,2e}$	$\Delta E^{‡}_{dist,all}$	$\Delta E^{‡}_{int}$
2a	–8.8	24.9	–22.4	5.7	21.2	7.3	28.5	–22.8
2b	–8.1	29.7	–16.1	10.3	24.9	9.4	34.3	–24.0
2c	–8.8	25.2	–21.1	6.3	21.0	7.7	28.7	–22.4
2d	–8.7	24.5	–23.0	5.3	19.4	7.9	27.3	–22.0
12a	–8.3	24.4	–20.6	4.5	23.3	8.1	31.4	–26.9
12b	–8.6	28.9	–15.2	6.4	26.5	9.0	35.5	–29.1

[a] $\Delta E^{‡}_{act} = E_{TS}{}^{‡} - (E_{4e} + E_{2e})$, $\Delta E^{‡}_{dist,4e} = E^{‡}_{4e\text{-fragment}} - E_{4e}$, $\Delta E^{‡}_{dist,2e} = E^{‡}_{2e\text{-fragment}} - E_{2e}$, $\Delta E^{‡}_{dist,all} = \Delta E^{‡}_{dist,4e} + \Delta E^{‡}_{dist,2e}$, $\Delta E^{‡}_{int} = \Delta E^{‡}_{act} - \Delta E^{‡}_{dist,all}$. Homo and other energies are given in eV and kcal/mol, respectively.

Standard Orientations

2a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.610101	1.451433	-0.712138
2	6	0	-1.311951	0.609322	0.521829

3	6	0	-0.102952	0.662207	1.076499
4	6	0	0.953242	1.439237	0.437665
5	6	0	0.871397	1.907005	-0.811200
6	6	0	-0.378495	1.608560	-1.609963
7	6	0	-2.762672	0.624604	-1.295748
8	8	0	-3.492989	0.176310	-0.163078
9	6	0	-2.559699	-0.168764	0.851391
10	6	0	0.506155	0.067584	2.323338
11	8	0	1.815300	0.645497	2.420450
12	6	0	2.122083	1.439642	1.353731
13	8	0	3.177918	1.994316	1.242924
14	6	0	-2.132775	2.821525	-0.250765
15	1	0	1.715385	2.413868	-1.271087
16	1	0	-0.557073	2.390191	-2.356841
17	1	0	-0.193139	0.677775	-2.171362
18	1	0	-2.373204	-0.230474	-1.872018
19	1	0	-3.448394	1.200029	-1.923234
20	1	0	-2.999065	0.089195	1.821561
21	1	0	-2.359540	-1.251669	0.843505
22	1	0	0.614487	-1.021192	2.268379
23	1	0	-0.046132	0.320548	3.233206
24	1	0	-2.407251	3.432817	-1.118261
25	1	0	-1.368066	3.355310	0.321503
26	1	0	-3.019938	2.696984	0.376886

12a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.643898	1.558975	-0.597299
2	6	0	-1.301600	0.772239	0.658230
3	6	0	-0.043301	0.710253	1.086427
4	6	0	1.037363	1.323738	0.299004
5	6	0	0.853250	1.713696	-0.963817

6	6	0	-0.502227	1.511189	-1.615820
7	6	0	-2.929418	0.825389	-0.998920
8	8	0	-3.576892	0.525697	0.229971
9	6	0	-2.578709	0.162286	1.175493
10	6	0	0.599239	0.111703	2.312357
11	8	0	1.999841	0.186982	2.077374
12	6	0	2.265393	1.251272	1.170810
13	6	0	-1.970756	3.005966	-0.197604
14	1	0	1.672492	2.096592	-1.567054
15	1	0	-0.669941	2.264816	-2.394034
16	1	0	-0.491446	0.533475	-2.124546
17	1	0	-2.690727	-0.099566	-1.548539
18	1	0	-3.618784	1.429986	-1.594749
19	1	0	-2.886438	0.542953	2.156067
20	1	0	-2.490260	-0.933276	1.247654
21	1	0	0.339534	-0.938864	2.479208
22	1	0	0.328090	0.681102	3.215321
23	1	0	-2.269406	3.585344	-1.079196
24	1	0	-1.097039	3.485940	0.253463
25	1	0	-2.794514	3.023887	0.522163
26	1	0	3.183092	1.011570	0.628189
27	1	0	2.416197	2.194797	1.719376

10a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.176881	-0.302478	-1.407665
2	6	0	-0.694802	-1.224589	-0.576565
3	8	0	2.299441	-0.016221	-1.683191
4	8	0	-1.498139	-1.896315	-0.009862
5	7	0	0.688328	-1.300183	-0.580028
6	7	0	-0.021926	0.421147	-1.935327
7	7	0	-1.048404	-0.082156	-1.476510

8	6	0	1.476094	-2.250489	0.137656
9	6	0	1.007098	-3.554052	0.284942
10	6	0	2.699250	-1.856573	0.675761
11	6	0	1.778450	-4.471433	0.990130
12	1	0	0.051091	-3.841313	-0.136646
13	6	0	3.463244	-2.790977	1.366645
14	1	0	3.050764	-0.839882	0.546159
15	6	0	3.006048	-4.095886	1.528615
16	1	0	1.415306	-5.486597	1.112357
17	1	0	4.419122	-2.490570	1.783265
18	1	0	3.604968	-4.818439	2.073338

$TS_{\mathbf{2a–11aa}}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.434168	1.669582	-0.750059
2	6	0	-1.129860	0.522500	0.194079
3	6	0	0.103106	0.455760	0.779996
4	6	0	1.186105	1.056682	0.110076
5	6	0	1.065959	1.495726	-1.203313
6	6	0	-0.267750	2.023070	-1.695020
7	6	0	-2.720266	1.131877	-1.392452
8	8	0	-3.396621	0.484369	-0.322374
9	6	0	-2.427875	-0.176371	0.479757
10	6	0	0.658791	-0.327005	1.943628
11	8	0	2.066572	-0.078120	1.907376
12	6	0	2.426605	0.684120	0.834942
13	8	0	3.567440	0.944509	0.575607
14	6	0	-1.778320	2.880625	0.141108
15	1	0	1.965048	1.784395	-1.742092
16	1	0	-0.188110	3.114878	-1.765223
17	1	0	-0.432541	1.645891	-2.708998
18	1	0	-2.481153	0.423088	-2.195405

19	1	0	-3.379064	1.918575	-1.769208
20	1	0	-2.728947	-0.094066	1.531157
21	1	0	-2.346346	-1.241190	0.221554
22	1	0	0.485879	-1.407250	1.854865
23	1	0	0.273463	0.016558	2.908170
24	1	0	-2.090398	3.718564	-0.492173
25	1	0	-0.906364	3.191638	0.724760
26	1	0	-2.598860	2.643216	0.824216
27	6	0	2.007954	-1.045377	-1.533707
28	6	0	0.116887	-1.963997	-0.718800
29	8	0	3.136600	-0.822009	-1.856977
30	8	0	-0.659669	-2.697852	-0.161463
31	7	0	1.508822	-2.019382	-0.678344
32	7	0	0.837054	-0.317089	-2.025431
33	7	0	-0.242911	-0.866596	-1.584367
34	6	0	2.294102	-2.970780	0.039047
35	6	0	1.826464	-4.275345	0.194400
36	6	0	3.519114	-2.572291	0.574207
37	6	0	2.599144	-5.188755	0.903141
38	1	0	0.870129	-4.562947	-0.225009
39	6	0	4.281433	-3.504013	1.270951
40	1	0	3.874484	-1.555729	0.443535
41	6	0	3.826289	-4.808692	1.439936
42	1	0	2.237891	-6.204380	1.029046
43	1	0	5.236163	-3.199043	1.686841
44	1	0	4.426148	-5.527749	1.988757

11aa

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.160534	2.149981	-0.816318
2	6	0	-1.739408	1.026123	0.194312
3	6	0	-0.721251	1.611805	1.118789

4	6	0	0.335809	2.111676	0.467798
5	6	0	0.327946	1.963452	-1.027866
6	6	0	-0.929486	2.623999	-1.621876
7	6	0	-3.261919	1.382359	-1.546215
8	8	0	-3.957010	0.692305	-0.512531
9	6	0	-3.101432	0.474160	0.605655
10	6	0	-0.506035	1.745293	2.594464
11	8	0	0.763729	2.384217	2.698159
12	6	0	1.314410	2.610964	1.460349
13	8	0	2.381419	3.128449	1.306186
14	6	0	-2.792964	3.328826	-0.064833
15	1	0	1.256178	2.260290	-1.516348
16	1	0	-0.836340	3.712328	-1.574053
17	1	0	-0.997650	2.329519	-2.673750
18	1	0	-2.842924	0.674105	-2.272589
19	1	0	-3.973810	2.042154	-2.051174
20	1	0	-3.475481	1.030951	1.475282
21	1	0	-3.067907	-0.586600	0.848604
22	1	0	-0.467182	0.773927	3.100588
23	1	0	-1.261280	2.369765	3.084793
24	1	0	-3.087886	4.091123	-0.793085
25	1	0	-2.085723	3.791773	0.630672
26	1	0	-3.691156	3.028113	0.480979
27	6	0	1.222943	-0.331587	-1.106995
28	6	0	-0.547238	-1.159785	0.095088
29	8	0	2.337466	-0.142882	-1.522259
30	8	0	-1.171541	-1.809303	0.899486
31	7	0	0.744834	-1.413142	-0.365527
32	7	0	0.128084	0.517574	-1.300075
33	7	0	-0.987285	-0.011683	-0.583218
34	6	0	1.510963	-2.561677	-0.005217
35	6	0	0.879630	-3.802684	0.060575
36	6	0	2.870764	-2.431093	0.270884
37	6	0	1.622893	-4.923682	0.411572
38	1	0	-0.181104	-3.881933	-0.147022
39	6	0	3.602644	-3.565719	0.606747

40	1	0	3.346145	-1.460262	0.207302
41	6	0	2.984479	-4.810375	0.680909
42	1	0	1.133189	-5.890466	0.469749
43	1	0	4.663189	-3.469286	0.815821
44	1	0	3.561302	-5.689673	0.949066

$TS_{12a–13aa}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.466120	1.664128	-0.672962
2	6	0	-0.948748	0.695613	0.369926
3	6	0	0.386762	0.641153	0.637565
4	6	0	1.297108	1.062713	-0.359966
5	6	0	0.848226	1.263682	-1.662734
6	6	0	-0.566976	1.753100	-1.918778
7	6	0	-2.880044	1.097664	-0.865139
8	8	0	-3.273710	0.702904	0.443724
9	6	0	-2.141755	0.136020	1.089759
10	6	0	1.185411	0.019450	1.757826
11	8	0	2.509684	-0.079301	1.252707
12	6	0	2.685404	0.840640	0.181847
13	6	0	-1.558151	3.040281	0.015363
14	1	0	1.574178	1.429258	-2.454217
15	1	0	-0.505969	2.800214	-2.239395
16	1	0	-0.979345	1.182910	-2.757456
17	1	0	-2.859409	0.237881	-1.546908
18	1	0	-3.602682	1.839585	-1.215307
19	1	0	-2.168129	0.416056	2.149661
20	1	0	-2.145219	-0.961365	1.016127
21	1	0	0.841873	-0.985984	2.028757
22	1	0	1.157051	0.649850	2.659537
23	1	0	-2.007314	3.763387	-0.674825
24	1	0	-0.562170	3.397880	0.294962

25	1	0	-2.181755	2.988762	0.912577
26	6	0	1.654376	-1.338761	-1.633695
27	6	0	-0.132927	-2.028035	-0.452714
28	8	0	2.738608	-1.182424	-2.132385
29	8	0	-0.850416	-2.638198	0.299933
30	7	0	1.255600	-2.189950	-0.619843
31	7	0	0.452031	-0.638409	-2.070586
32	7	0	-0.568056	-1.045453	-1.392287
33	6	0	2.101662	-3.067586	0.121943
34	6	0	3.345236	-3.435820	-0.396683
35	6	0	1.684835	-3.554992	1.363545
36	6	0	4.169091	-4.279728	0.340281
37	1	0	3.667179	-3.060063	-1.357951
38	6	0	2.522639	-4.400764	2.082180
39	1	0	0.707496	-3.301827	1.750250
40	6	0	3.767319	-4.765030	1.580697
41	1	0	5.135082	-4.559754	-0.068306
42	1	0	2.189477	-4.777033	3.044267
43	1	0	4.416176	-5.423679	2.148956
44	1	0	3.383036	0.405764	-0.538654
45	1	0	3.103207	1.791445	0.550076

13aa

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.041874	2.235009	-0.783298
2	6	0	-1.489974	1.274247	0.323392
3	6	0	-0.273287	1.902135	0.926613
4	6	0	0.667753	2.187111	0.022552
5	6	0	0.342141	1.787212	-1.394244
6	6	0	-0.965549	2.445097	-1.869123
7	6	0	-3.306569	1.457079	-1.144477
8	8	0	-3.816568	1.009327	0.108176

9	6	0	-2.772119	0.939002	1.076759
10	6	0	0.241751	2.169732	2.309937
11	8	0	1.530010	2.735472	2.090426
12	6	0	1.913683	2.650935	0.719996
13	6	0	-2.451021	3.579798	-0.169245
14	1	0	1.160340	1.900214	-2.105757
15	1	0	-0.801334	3.511888	-2.044783
16	1	0	-1.251393	1.981066	-2.818665
17	1	0	-3.081352	0.603988	-1.797211
18	1	0	-4.068908	2.084184	-1.617286
19	1	0	-2.936807	1.689834	1.860939
20	1	0	-2.753280	-0.052018	1.527212
21	1	0	0.316243	1.245362	2.902802
22	1	0	-0.371671	2.884064	2.874502
23	1	0	-2.827082	4.230167	-0.965977
24	1	0	-1.601158	4.082520	0.301854
25	1	0	-3.251476	3.462230	0.566137
26	6	0	1.091154	-0.535591	-1.158782
27	6	0	-0.531501	-1.038145	0.381364
28	8	0	2.153393	-0.485789	-1.729539
29	8	0	-1.073605	-1.523684	1.345870
30	7	0	0.666022	-1.459156	-0.203991
31	7	0	0.021431	0.338169	-1.348664
32	7	0	-0.990542	0.040986	-0.387555
33	6	0	1.420274	-2.601581	0.194384
34	6	0	2.125362	-3.311840	-0.777004
35	6	0	1.450462	-2.995642	1.531265
36	6	0	2.868681	-4.424344	-0.400665
37	1	0	2.101055	-2.984223	-1.809572
38	6	0	2.187419	-4.120731	1.888047
39	1	0	0.893718	-2.437835	2.273015
40	6	0	2.899133	-4.835522	0.929361
41	1	0	3.421528	-4.973895	-1.155798
42	1	0	2.206209	-4.433578	2.927201
43	1	0	3.476112	-5.708669	1.216686
44	1	0	2.739470	1.935118	0.590518

45	1	0	2.264813	3.636094	0.389300

10c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.755151	-2.308698	-1.091684
2	6	0	0.018993	-1.767139	-2.029753
3	1	0	-1.764022	-2.691685	-1.168564
4	1	0	-0.189545	-1.588934	-3.076292
5	6	0	1.341974	-1.393577	-1.414736
6	6	0	0.000484	-2.331594	0.210678
7	8	0	2.292697	-0.882109	-1.946908
8	8	0	-0.369149	-2.743030	1.279647
9	7	0	1.241513	-1.766877	-0.076527
10	1	0	1.978150	-1.642301	0.603514

anti/*endo*-$TS_{\mathbf{2a–11ac}}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.496506	1.582956	-0.872019
2	6	0	-1.097541	0.665083	0.276187
3	6	0	0.107633	0.903945	0.888550
4	6	0	1.156240	1.372753	0.082694
5	6	0	1.018123	1.482468	-1.288580
6	6	0	-0.333379	1.880610	-1.852566
7	6	0	-2.704525	0.827205	-1.444451
8	8	0	-3.211858	-0.002041	-0.401142
9	6	0	-2.359229	0.004634	0.741601
10	6	0	0.690711	0.506690	2.219417
11	8	0	2.089533	0.777580	2.104231

12	6	0	2.415989	1.244960	0.861206
13	8	0	3.540202	1.486099	0.529615
14	6	0	-1.973824	2.905694	-0.239331
15	1	0	1.906076	1.668475	-1.890281
16	1	0	-0.305650	2.962177	-2.037360
17	1	0	-0.494798	1.414394	-2.829983
18	1	0	-2.417721	0.203017	-2.301753
19	1	0	-3.500163	1.506020	-1.771389
20	1	0	-2.832446	0.571318	1.557745
21	1	0	-2.190950	-1.022202	1.082819
22	1	0	0.542738	-0.555675	2.445076
23	1	0	0.292654	1.103850	3.046444
24	1	0	-2.338695	3.575492	-1.026107
25	1	0	-1.149676	3.400008	0.283468
26	1	0	-2.791483	2.740005	0.469685
27	6	0	-0.279902	-1.123547	-1.022588
28	6	0	0.762030	-0.647224	-1.797710
29	1	0	-1.305341	-1.312381	-1.313267
30	1	0	0.725515	-0.412779	-2.853757
31	6	0	2.050489	-1.097244	-1.184280
32	6	0	0.304484	-1.826749	0.155590
33	8	0	3.170724	-0.996204	-1.610470
34	8	0	-0.262829	-2.399355	1.061575
35	7	0	1.682112	-1.655043	0.047796
36	1	0	2.349060	-2.061722	0.691995

anti/*endo*-**11ac**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.655682	1.216893	-0.759266
2	6	0	-1.220535	0.029928	0.177268
3	6	0	-0.054450	0.529320	0.959415
4	6	0	0.960297	0.951781	0.196940

5	6	0	0.800597	0.840632	-1.290304
6	6	0	-0.495022	1.588907	-1.712643
7	6	0	-2.920969	0.591204	-1.348538
8	8	0	-3.490798	-0.189255	-0.298309
9	6	0	-2.559949	-0.380569	0.770276
10	6	0	0.309748	0.682949	2.402628
11	8	0	1.616463	1.250244	2.371220
12	6	0	2.049119	1.428012	1.078193
13	8	0	3.117497	1.895585	0.810239
14	6	0	-2.065531	2.445138	0.067711
15	1	0	1.679548	1.185225	-1.839218
16	1	0	-0.321219	2.668248	-1.683761
17	1	0	-0.728497	1.327636	-2.751934
18	1	0	-2.695134	-0.047796	-2.214742
19	1	0	-3.654163	1.341901	-1.661880
20	1	0	-2.832668	0.245256	1.630400
21	1	0	-2.580236	-1.428012	1.077411
22	1	0	0.342233	-0.278288	2.928904
23	1	0	-0.360769	1.358544	2.946594
24	1	0	-2.377989	3.243958	-0.612972
25	1	0	-1.231427	2.826283	0.665325
26	1	0	-2.909283	2.228820	0.729181
27	6	0	-0.645888	-1.130755	-0.699572
28	6	0	0.513084	-0.652957	-1.593738
29	1	0	-1.460163	-1.599058	-1.261336
30	1	0	0.307420	-0.769772	-2.662125
31	6	0	1.698605	-1.538171	-1.233047
32	6	0	-0.022331	-2.195696	0.205446
33	8	0	2.801168	-1.510489	-1.712289
34	8	0	-0.542385	-2.755077	1.141223
35	7	0	1.283127	-2.386512	-0.211002
36	1	0	1.910287	-3.038902	0.245359

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anti/*exo*-$TS_{\mathbf{2a–11ac}}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.161824	0.744484	-2.668251
2	6	0	-0.572678	0.918540	-1.210540
3	6	0	0.446914	1.165832	-0.324803
4	6	0	1.684210	0.555769	-0.576721
5	6	0	1.821615	-0.402461	-1.570959
6	6	0	1.007151	-0.247614	-2.843945
7	6	0	-1.515048	0.398743	-3.301462
8	8	0	-2.459760	1.159415	-2.561733
9	6	0	-2.043558	1.254499	-1.206101
10	6	0	0.485036	1.714193	1.076413
11	8	0	1.784398	1.385593	1.570478
12	6	0	2.489377	0.643674	0.663824
13	8	0	3.552664	0.149702	0.912506
14	6	0	0.268174	2.135656	-3.176500
15	1	0	2.738283	-0.986301	-1.624933
16	1	0	1.684731	0.153333	-3.609071
17	1	0	0.682373	-1.219471	-3.226476
18	1	0	-1.737661	-0.673954	-3.247208
19	1	0	-1.588419	0.717647	-4.345039
20	1	0	-2.239780	2.276530	-0.858844
21	1	0	-2.616678	0.555517	-0.582085
22	1	0	-0.266658	1.257085	1.731950
23	1	0	0.362463	2.801175	1.114073
24	1	0	0.484790	2.076679	-4.249362
25	1	0	1.168255	2.477625	-2.658192
26	1	0	-0.529564	2.869504	-3.026950
27	6	0	-0.605598	-1.338707	-0.303132
28	6	0	0.651771	-1.882829	-0.527180
29	6	0	-1.582833	-2.018070	-1.197035
30	6	0	0.509501	-2.925524	-1.602554
31	8	0	-2.779831	-1.866173	-1.258627
32	8	0	1.366161	-3.622332	-2.085478
33	7	0	-0.831196	-2.897864	-1.982687

34	1	0	-1.226744	-3.492495	-2.698593
35	1	0	-0.964301	-0.887475	0.612104
36	1	0	1.433612	-2.011006	0.211128

anti/*exo*-**11ac**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.267945	0.867026	-1.336061
2	6	0	-0.809401	0.644432	0.126642
3	6	0	0.285254	1.164228	1.005006
4	6	0	1.467010	0.571238	0.804190
5	6	0	1.511356	-0.546300	-0.196805
6	6	0	0.975369	-0.019894	-1.563938
7	6	0	-1.553265	0.599979	-2.120354
8	8	0	-2.589692	1.167335	-1.328605
9	6	0	-2.195232	1.281208	0.036460
10	6	0	0.452206	2.276372	1.994331
11	8	0	1.831809	2.224971	2.345633
12	6	0	2.479895	1.226408	1.657127
13	8	0	3.649473	1.005459	1.785877
14	6	0	0.098999	2.344091	-1.563395
15	1	0	2.497707	-1.001999	-0.300070
16	1	0	1.758083	0.556832	-2.064386
17	1	0	0.756168	-0.876851	-2.212423
18	1	0	-1.730167	-0.469807	-2.293604
19	1	0	-1.561091	1.102601	-3.092768
20	1	0	-2.168903	2.342624	0.317563
21	1	0	-2.932173	0.767244	0.660730
22	1	0	-0.151646	2.150156	2.899858
23	1	0	0.228869	3.259273	1.561613
24	1	0	0.384885	2.475447	-2.612330
25	1	0	0.948983	2.658649	-0.951582
26	1	0	-0.750014	3.006582	-1.367547

27	6	0	-0.885613	-0.876488	0.512591
28	6	0	0.478735	-1.570356	0.327920
29	6	0	-1.878770	-1.737715	-0.266221
30	6	0	0.220887	-2.708650	-0.651864
31	8	0	-3.076861	-1.625470	-0.303903
32	8	0	1.033084	-3.455755	-1.133937
33	7	0	-1.145050	-2.729344	-0.910198
34	1	0	-1.580564	-3.432307	-1.496524
35	1	0	-1.221819	-0.909335	1.554076
36	1	0	0.842595	-2.011764	1.260695

syn/*endo*-$TS_{\mathbf{2a–11ac}}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.662698	2.655522	2.620461
2	6	0	0.762180	2.476376	1.386876
3	6	0	1.261704	1.795077	0.299251
4	6	0	2.123717	0.711120	0.505829
5	6	0	2.572232	0.413404	1.764789
6	6	0	2.769229	1.577875	2.717239
7	6	0	2.110044	4.081880	2.241723
8	8	0	0.909271	4.739309	1.842096
9	6	0	0.020098	3.784724	1.252452
10	6	0	0.819661	1.754809	-1.142480
11	8	0	1.430593	0.577200	-1.680363
12	6	0	2.162518	-0.093905	-0.741767
13	8	0	2.713642	-1.133030	-0.961221
14	6	0	0.917288	2.769006	3.961396
15	1	0	3.103450	-0.518680	1.947124
16	1	0	2.848528	1.216600	3.746912
17	1	0	3.749545	2.012426	2.472519
18	1	0	2.839846	4.054388	1.419133
19	1	0	2.530901	4.644275	3.080565

20	1	0	-0.934618	3.800871	1.791399
21	1	0	-0.173342	4.041784	0.204958
22	1	0	1.171828	2.619153	-1.716361
23	1	0	-0.266564	1.670153	-1.251159
24	1	0	1.609573	3.168558	4.709852
25	1	0	0.568768	1.801083	4.329097
26	1	0	0.067623	3.455241	3.901836
27	6	0	0.434547	-0.214661	2.583587
28	1	0	0.853795	-0.394389	3.565516
29	6	0	-0.455553	0.774900	2.218049
30	1	0	-0.942565	1.498345	2.857566
31	6	0	0.346314	-1.316128	1.581357
32	6	0	-1.115925	0.369028	0.937281
33	8	0	0.875265	-2.396571	1.583010
34	8	0	-1.965759	0.962827	0.313039
35	7	0	-0.507005	-0.824156	0.574978
36	1	0	-0.754085	-1.358597	-0.248828

syn/*endo*-**11ac**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.680139	1.464055	1.464688
2	6	0	-0.431807	1.084010	0.421805
3	6	0	0.263450	0.580748	-0.808011
4	6	0	1.072256	-0.462686	-0.634042
5	6	0	1.228795	-0.919304	0.779806
6	6	0	1.729818	0.327063	1.561179
7	6	0	1.114649	2.786489	0.824674
8	8	0	-0.080177	3.386660	0.322327
9	6	0	-1.125111	2.419555	0.210429
10	6	0	0.222579	0.945125	-2.258838
11	8	0	1.112344	0.012899	-2.870666
12	6	0	1.646000	-0.847537	-1.942760

13	8	0	2.423373	-1.711702	-2.227724
14	6	0	0.089967	1.760111	2.850510
15	1	0	1.893589	-1.778442	0.892598
16	1	0	1.895015	0.060555	2.610809
17	1	0	2.695816	0.635952	1.148510
18	1	0	1.824601	2.612272	0.002895
19	1	0	1.571220	3.479302	1.538662
20	1	0	-1.897754	2.601531	0.968211
21	1	0	-1.593782	2.503622	-0.774733
22	1	0	0.575588	1.964520	-2.454252
23	1	0	-0.777540	0.827931	-2.692380
24	1	0	0.889990	2.115048	3.508258
25	1	0	-0.340747	0.868836	3.318008
26	1	0	-0.674216	2.541832	2.812136
27	6	0	-0.199087	-1.265000	1.310064
28	1	0	-0.140776	-1.476017	2.382414
29	6	0	-1.200904	-0.132551	0.966850
30	1	0	-1.818320	0.152170	1.825198
31	6	0	-0.752030	-2.496462	0.601180
32	6	0	-2.115722	-0.729377	-0.095191
33	8	0	-0.325446	-3.619446	0.653705
34	8	0	-2.913739	-0.129644	-0.774119
35	7	0	-1.841064	-2.083695	-0.165277
36	1	0	-2.322445	-2.708583	-0.801750

syn/*exo*-$TS_{\mathbf{2a–11ac}}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.441982	2.506850	3.056872
2	6	0	-0.207206	2.260333	1.686371
3	6	0	0.644121	2.043292	0.626583
4	6	0	1.823759	1.318984	0.816584
5	6	0	2.166673	0.868091	2.066247

6	6	0	1.756259	1.709315	3.255928
7	6	0	0.552016	4.033250	2.833748
8	8	0	-0.724889	4.404988	2.302570
9	6	0	-1.302222	3.290461	1.605000
10	6	0	0.424281	2.161250	-0.860433
11	8	0	1.483780	1.404611	-1.453384
12	6	0	2.287594	0.837910	-0.505649
13	8	0	3.176964	0.079405	-0.768338
14	6	0	-0.462832	2.353022	4.291517
15	1	0	2.987445	0.165356	2.194008
16	1	0	1.682525	1.071680	4.143886
17	1	0	2.592242	2.395281	3.457777
18	1	0	1.358025	4.277753	2.127600
19	1	0	0.698480	4.594170	3.761702
20	1	0	-2.225708	2.973928	2.103160
21	1	0	-1.534682	3.582544	0.574826
22	1	0	0.487928	3.193282	-1.221553
23	1	0	-0.531080	1.735364	-1.187185
24	1	0	0.039125	2.842956	5.133179
25	1	0	-0.618984	1.316718	4.577321
26	1	0	-1.433521	2.834168	4.159592
27	6	0	0.472799	-0.699656	1.978528
28	6	0	-0.719954	-0.044724	1.724785
29	6	0	0.435682	-1.199388	3.390434
30	6	0	-1.585785	-0.157052	2.941718
31	8	0	1.308759	-1.745282	4.018743
32	8	0	-2.695037	0.283529	3.115961
33	7	0	-0.838842	-0.887182	3.870135
34	1	0	-1.121507	-1.022446	4.832151
35	1	0	1.097380	-1.210003	1.257987
36	1	0	-1.197380	0.078726	0.762378

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syn/*exo*-**11ac**

Center	Atomic	Atomic	Coordinates (Angstroms)		

Number	Number	Type	X	Y	Z
1	6	0	0.060088	1.182535	1.037769
2	6	0	-0.775775	0.625361	-0.177606
3	6	0	0.180268	0.614500	-1.342589
4	6	0	1.287648	-0.107573	-1.191393
5	6	0	1.425811	-0.775759	0.139292
6	6	0	1.380244	0.376731	1.180579
7	6	0	0.157419	2.635325	0.547061
8	8	0	-1.091315	2.917863	-0.093954
9	6	0	-1.823315	1.714060	-0.334442
10	6	0	0.219982	1.318159	-2.663744
11	8	0	1.458449	0.902962	-3.236389
12	6	0	2.136459	0.058554	-2.390451
13	8	0	3.208632	-0.403287	-2.655839
14	6	0	-0.694208	1.210210	2.377819
15	1	0	2.330120	-1.377601	0.247528
16	1	0	1.457944	-0.042933	2.189674
17	1	0	2.256845	1.016617	1.032930
18	1	0	0.980607	2.766669	-0.169305
19	1	0	0.293844	3.348833	1.365571
20	1	0	-2.647335	1.600158	0.377835
21	1	0	-2.243366	1.758807	-1.345682
22	1	0	0.211536	2.409094	-2.553051
23	1	0	-0.595058	1.030205	-3.337519
24	1	0	-0.089676	1.780599	3.091025
25	1	0	-0.838653	0.220055	2.811834
26	1	0	-1.666523	1.703420	2.300260
27	6	0	0.159167	-1.664648	0.272946
28	6	0	-1.144808	-0.864012	0.010642
29	6	0	-0.031465	-2.275860	1.655029
30	6	0	-2.050503	-1.180319	1.195054
31	8	0	0.790068	-2.849560	2.322246
32	8	0	-3.163924	-0.764422	1.394335
33	7	0	-1.357268	-2.055456	2.024336
34	1	0	-1.733685	-2.373073	2.910749

35	1	0	0.250930	-2.500499	-0.428588
36	1	0	-1.667544	-1.215413	-0.885101

2b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.326157	0.825045	-0.264069
2	6	0	-2.066445	0.138127	1.062738
3	6	0	-0.821870	0.072965	1.528665
4	6	0	0.302130	0.614325	0.765375
5	6	0	0.199467	0.929257	-0.547053
6	6	0	-1.144682	0.629891	-1.209275
7	6	0	-3.621880	0.103183	-0.658023
8	8	0	-4.326661	-0.060421	0.564550
9	6	0	-3.381119	-0.390429	1.573415
10	6	0	-0.260640	-0.472385	2.815015
11	8	0	1.122339	-0.116717	2.802138
12	6	0	1.499207	0.514364	1.651734
13	8	0	2.633034	0.867160	1.484680
14	6	0	-2.610000	2.314605	-0.016288
15	1	0	-1.266788	1.256585	-2.098939
16	1	0	-1.116005	-0.417521	-1.552925
17	1	0	-3.398769	-0.875540	-1.113126
18	1	0	-4.262320	0.677526	-1.332588
19	1	0	-3.710290	0.069596	2.512114
20	1	0	-3.336538	-1.480663	1.724490
21	1	0	-0.338504	-1.563347	2.883906
22	1	0	-0.721368	-0.032003	3.704851
23	1	0	-2.832786	2.821135	-0.962375
24	1	0	-1.745328	2.803564	0.442699
25	1	0	-3.471858	2.428185	0.647788
26	6	0	1.284090	1.447652	-1.402582
27	6	0	2.200198	2.398269	-0.935472

28	6	0	1.377071	1.021166	-2.735724
29	6	0	3.191416	2.892588	-1.775109
30	1	0	2.130543	2.747843	0.087239
31	6	0	2.378391	1.504588	-3.568323
32	1	0	0.671553	0.289033	-3.118801
33	6	0	3.288039	2.445129	-3.090053
34	1	0	3.891616	3.631091	-1.397825
35	1	0	2.446306	1.149965	-4.592115
36	1	0	4.065697	2.830567	-3.742258

$TS_{\mathbf{2b–11bc}}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.431329	1.473082	-0.926807
2	6	0	-1.038941	0.578111	0.238500
3	6	0	0.142286	0.878044	0.883438
4	6	0	1.224358	1.335720	0.118716
5	6	0	1.128447	1.452910	-1.274852
6	6	0	-0.248500	1.776045	-1.865934
7	6	0	-2.612942	0.686343	-1.507576
8	8	0	-3.151060	-0.091151	-0.438089
9	6	0	-2.319197	-0.039764	0.720726
10	6	0	0.626817	0.540015	2.263637
11	8	0	2.029116	0.778172	2.220863
12	6	0	2.440419	1.191210	0.985831
13	8	0	3.599940	1.366457	0.743527
14	6	0	-1.952400	2.794802	-0.326050
15	1	0	-0.239410	2.851312	-2.086388
16	1	0	-0.355547	1.283584	-2.838067
17	1	0	-2.292064	0.021645	-2.321722
18	1	0	-3.400533	1.342160	-1.894411
19	1	0	-2.796524	0.576987	1.496830
20	1	0	-2.176214	-1.049863	1.116756

21	1	0	0.440326	-0.504041	2.539520
22	1	0	0.186167	1.191116	3.026991
23	1	0	-2.299409	3.448229	-1.134227
24	1	0	-1.155471	3.310234	0.218170
25	1	0	-2.792515	2.624723	0.354632
26	6	0	-0.236632	-1.176535	-0.866396
27	6	0	0.815645	-0.773965	-1.678445
28	1	0	-1.245561	-1.420148	-1.176720
29	1	0	0.757809	-0.613540	-2.744040
30	6	0	2.093463	-1.221047	-1.058482
31	6	0	0.347617	-1.864232	0.328121
32	8	0	3.213542	-1.187696	-1.495095
33	8	0	-0.229213	-2.405940	1.247460
34	7	0	1.721465	-1.713364	0.208472
35	1	0	2.386393	-2.113459	0.858903
36	6	0	2.265177	1.893643	-2.135552
37	6	0	3.166539	2.857526	-1.669140
38	6	0	2.380531	1.466769	-3.464580
39	6	0	4.170121	3.351367	-2.495119
40	1	0	3.082908	3.223946	-0.653617
41	6	0	3.388299	1.952910	-4.287247
42	1	0	1.687440	0.737615	-3.871140
43	6	0	4.290681	2.896495	-3.803784
44	1	0	4.860726	4.093836	-2.108191
45	1	0	3.468797	1.591102	-5.307350
46	1	0	5.079388	3.276455	-4.445622

11bc

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.267656	0.798134	-0.192498
2	6	0	-1.846128	-0.378888	0.748753
3	6	0	-0.671214	0.100492	1.523968

4	6	0	0.366672	0.504893	0.778985
5	6	0	0.225041	0.396598	-0.726273
6	6	0	-1.107409	1.117176	-1.150164
7	6	0	-3.552379	0.195486	-0.763255
8	8	0	-4.127321	-0.561645	0.300304
9	6	0	-3.187425	-0.764084	1.357944
10	6	0	-0.320607	0.173137	2.974319
11	8	0	1.014935	0.658703	2.981134
12	6	0	1.481704	0.853628	1.702461
13	8	0	2.594846	1.235399	1.488040
14	6	0	-2.636659	2.049751	0.618671
15	1	0	-0.921768	2.194485	-1.173265
16	1	0	-1.324699	0.813260	-2.181824
17	1	0	-3.350003	-0.456916	-1.625257
18	1	0	-4.271490	0.959514	-1.076734
19	1	0	-3.436824	-0.125566	2.216224
20	1	0	-3.225719	-1.807945	1.673482
21	1	0	-0.357648	-0.810332	3.458568
22	1	0	-0.958731	0.864866	3.536962
23	1	0	-2.942816	2.843072	-0.071159
24	1	0	-1.783164	2.421475	1.194477
25	1	0	-3.472841	1.864573	1.299313
26	6	0	-1.279251	-1.551083	-0.114631
27	6	0	-0.082610	-1.113405	-0.991116
28	1	0	-2.089439	-2.002191	-0.696494
29	1	0	-0.287378	-1.248355	-2.057621
30	6	0	1.057876	-2.054721	-0.597695
31	6	0	-0.713875	-2.624217	0.817943
32	8	0	2.157413	-2.139730	-1.077835
33	8	0	-1.278392	-3.166789	1.738701
34	7	0	0.596671	-2.846220	0.450110
35	1	0	1.187596	-3.526904	0.913393
36	6	0	1.357996	0.999930	-1.539672
37	6	0	1.795149	2.284622	-1.199939
38	6	0	1.893049	0.392706	-2.675468
39	6	0	2.750860	2.940983	-1.962958

40	1	0	1.391463	2.771576	-0.315636
41	6	0	2.850430	1.051443	-3.445097
42	1	0	1.600611	-0.612937	-2.953947
43	6	0	3.282482	2.324532	-3.093395
44	1	0	3.084455	3.931572	-1.670539
45	1	0	3.263561	0.557420	-4.319054
46	1	0	4.033224	2.832468	-3.690846

2c

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.686915	1.580115	-0.792631
2	6	0	-1.239048	0.737175	0.384222
3	6	0	0.050451	0.728166	0.720515
4	6	0	1.058489	1.419452	-0.073875
5	6	0	0.785925	1.878584	-1.297026
6	6	0	-0.603565	1.658065	-1.874930
7	6	0	-2.969251	0.814927	-1.155174
8	8	0	-3.514953	0.419329	0.094666
9	6	0	-2.437865	0.021190	0.935810
10	8	0	2.043750	0.441741	1.821754
11	6	0	2.335789	1.331072	0.730877
12	6	0	-2.046373	2.978777	-0.263720
13	1	0	1.548646	2.326222	-1.928811
14	1	0	-0.853347	2.456809	-2.582597
15	1	0	-0.582554	0.722629	-2.457224
16	1	0	-2.731630	-0.064865	-1.774827
17	1	0	-3.719556	1.424023	-1.666069
18	1	0	-2.672821	0.292813	1.969330
19	1	0	-2.283878	-1.067232	0.898820
20	1	0	-2.426683	3.599941	-1.082745
21	1	0	-1.166382	3.468076	0.164169
22	1	0	-2.821407	2.907011	0.504561

23	1	0	3.172852	0.912042	0.166430
24	1	0	2.638656	2.295312	1.152020
25	6	0	0.729641	0.080496	1.860330
26	8	0	0.271350	-0.636584	2.706626

$TS_{2c-11cc}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.501277	1.568235	-0.883866
2	6	0	-1.075244	0.643576	0.243543
3	6	0	0.138019	0.913331	0.830812
4	6	0	1.183267	1.404349	0.036954
5	6	0	1.013136	1.505246	-1.331997
6	6	0	-0.361708	1.844380	-1.892865
7	6	0	-2.747764	0.838569	-1.404477
8	8	0	-3.239460	0.046043	-0.328876
9	6	0	-2.318247	-0.007550	0.761912
10	8	0	2.029469	0.785713	2.124785
11	6	0	2.436006	1.357477	0.876542
12	6	0	-1.930384	2.896314	-0.225881
13	1	0	1.871471	1.710246	-1.969266
14	1	0	-0.369317	2.913586	-2.139818
15	1	0	-0.524151	1.317065	-2.839462
16	1	0	-2.508893	0.197254	-2.264424
17	1	0	-3.535478	1.534901	-1.712981
18	1	0	-2.718356	0.546322	1.622881
19	1	0	-2.155748	-1.045359	1.068684
20	1	0	-2.319924	3.571365	-0.996022
21	1	0	-1.079682	3.378988	0.263422
22	1	0	-2.718107	2.737169	0.517124
23	6	0	-0.287802	-1.122572	-1.068135
24	6	0	0.802949	-0.648599	-1.776927
25	1	0	-1.289952	-1.303617	-1.433711

26	1	0	0.837583	-0.415633	-2.833466
27	6	0	2.051450	-1.075996	-1.069173
28	6	0	0.222901	-1.885129	0.105249
29	8	0	3.202713	-0.887237	-1.389311
30	8	0	-0.382465	-2.537271	0.918980
31	7	0	1.613724	-1.685939	0.098996
32	1	0	2.232566	-2.104231	0.782550
33	1	0	3.219525	0.733249	0.432925
34	1	0	2.844461	2.353464	1.075303
35	6	0	0.701648	0.468922	2.125852
36	8	0	0.151512	-0.068980	3.044313

11cc

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.488987	1.279190	-0.891192
2	6	0	-1.022664	0.093611	0.030825
3	6	0	0.156415	0.602925	0.784683
4	6	0	1.149513	1.074368	0.023118
5	6	0	0.967015	0.937951	-1.460425
6	6	0	-0.365034	1.618975	-1.896667
7	6	0	-2.794942	0.675642	-1.414657
8	8	0	-3.316466	-0.102299	-0.342172
9	6	0	-2.336511	-0.305877	0.683753
10	8	0	1.765513	1.339952	2.231132
11	6	0	2.259311	1.549846	0.909166
12	6	0	-1.839232	2.523938	-0.061291
13	1	0	1.821018	1.289461	-2.043249
14	1	0	-0.228609	2.702485	-1.957821
15	1	0	-0.607401	1.267905	-2.907361
16	1	0	-2.631887	0.042375	-2.299574
17	1	0	-3.530495	1.442088	-1.681960
18	1	0	-2.552526	0.319635	1.557355

19	1	0	-2.358073	-1.354039	0.987174
20	1	0	-2.198737	3.308577	-0.735686
21	1	0	-0.970484	2.915243	0.475682
22	1	0	-2.633414	2.319546	0.661940
23	6	0	-0.483745	-1.054932	-0.891806
24	6	0	0.744588	-0.576285	-1.690385
25	1	0	-1.299370	-1.422630	-1.519873
26	1	0	0.651140	-0.776468	-2.763107
27	6	0	1.918731	-1.380027	-1.142513
28	6	0	0.029067	-2.230031	-0.061510
29	8	0	3.088101	-1.203998	-1.382686
30	8	0	-0.603003	-2.952764	0.665144
31	7	0	1.401571	-2.325367	-0.275474
32	1	0	1.981111	-2.990485	0.223324
33	1	0	3.180556	0.972053	0.769276
34	1	0	2.488869	2.613546	0.782069
35	6	0	0.511249	0.783324	2.207393
36	8	0	-0.110515	0.530213	3.199534

2d

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.492266	1.490900	-0.724546
2	6	0	-1.224214	0.611102	0.496960
3	6	0	0.039753	0.457956	0.904264
4	6	0	1.155070	1.075723	0.207116
5	6	0	1.043642	1.634526	-1.000018
6	6	0	-0.289703	1.525661	-1.690700
7	6	0	0.623319	-0.196006	2.135651
8	8	0	2.010928	0.166242	2.141378
9	6	0	2.365065	0.904632	1.050141
10	8	0	3.481682	1.299542	0.870369
11	6	0	-1.817939	2.907243	-0.221482

12	1	0	1.902220	2.075469	-1.499076
13	1	0	-0.429342	2.340666	-2.410296
14	1	0	-0.270942	0.594019	-2.281490
15	1	0	0.556283	-1.289181	2.113506
16	1	0	0.174256	0.163967	3.066579
17	1	0	-2.015281	3.573145	-1.069822
18	1	0	-0.979556	3.315634	0.351677
19	1	0	-2.709043	2.896609	0.411822
20	6	0	-2.425571	0.110129	1.253761
21	1	0	-2.151341	-0.713694	1.922699
22	1	0	-2.826993	0.918933	1.880155
23	6	0	-3.528656	-0.328851	0.288412
24	1	0	-4.460422	-0.532923	0.820970
25	6	0	-2.705185	0.930653	-1.486448
26	1	0	-3.038182	1.645749	-2.246147
27	8	0	-3.808349	0.695985	-0.641454
28	1	0	-3.223154	-1.243427	-0.244852
29	1	0	-2.419494	-0.007588	-1.992043

$TS_{\mathbf{2d–11dc}}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.592373	2.377947	-0.321512
2	6	0	-1.287278	1.418077	0.832164
3	6	0	-0.048251	1.564491	1.417033
4	6	0	1.044692	1.964679	0.641508
5	6	0	0.931192	2.087125	-0.730491
6	6	0	-0.393993	2.561616	-1.293679
7	6	0	0.476255	1.131742	2.761095
8	8	0	1.891554	1.315982	2.682664
9	6	0	2.275967	1.764906	1.449302
10	8	0	3.420267	1.942241	1.147374
11	6	0	-1.920656	3.739533	0.328645

12	1	0	1.832372	2.236584	-1.322983
13	1	0	-0.295356	3.632699	-1.513098
14	1	0	-0.591729	2.078207	-2.258261
15	1	0	0.260268	0.079582	2.981728
16	1	0	0.093420	1.749446	3.580909
17	1	0	-2.180294	4.463037	-0.453130
18	1	0	-1.055750	4.121142	0.878684
19	1	0	-2.772158	3.659870	1.009346
20	6	0	-0.498096	-0.441293	-0.514852
21	6	0	0.596387	-0.007750	-1.241304
22	1	0	-1.506538	-0.582730	-0.874086
23	1	0	0.611392	0.225236	-2.298411
24	6	0	1.832483	-0.538086	-0.583979
25	6	0	-0.005413	-1.186751	0.673874
26	8	0	2.971865	-0.499132	-0.967467
27	8	0	-0.637613	-1.747048	1.544809
28	7	0	1.384307	-1.087294	0.624705
29	1	0	2.001232	-1.537618	1.289301
30	6	0	-2.469852	0.844966	1.571617
31	1	0	-2.175401	-0.069135	2.099831
32	1	0	-2.792107	1.575142	2.327628
33	6	0	-3.646987	0.557358	0.638916
34	1	0	-4.558216	0.381020	1.214252
35	6	0	-2.841231	1.911322	-1.084484
36	1	0	-3.172990	2.700363	-1.767497
37	8	0	-3.918297	1.650119	-0.216303
38	1	0	-3.448829	-0.345854	0.040991
39	1	0	-2.615543	1.018429	-1.690927

11dc

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.379479	1.320934	-0.752016

2	6	0	-1.047677	0.109800	0.211114
3	6	0	0.173687	0.529296	0.970427
4	6	0	1.229844	0.854726	0.221047
5	6	0	1.061160	0.756645	-1.263270
6	6	0	-0.156385	1.622935	-1.663104
7	6	0	0.538028	0.646015	2.417589
8	8	0	1.894412	1.083712	2.399806
9	6	0	2.352003	1.222594	1.110929
10	8	0	3.463599	1.583715	0.852792
11	6	0	-1.726244	2.576670	0.063545
12	1	0	1.964656	1.019429	-1.817762
13	1	0	0.107956	2.681830	-1.590210
14	1	0	-0.396796	1.424709	-2.716229
15	1	0	0.472219	-0.314010	2.943394
16	1	0	-0.068231	1.383438	2.956714
17	1	0	-1.906545	3.410860	-0.623201
18	1	0	-0.900829	2.865282	0.722152
19	1	0	-2.632303	2.441446	0.657323
20	6	0	-0.536529	-1.102200	-0.648235
21	6	0	0.633803	-0.701899	-1.570645
22	1	0	-1.360886	-1.547715	-1.212158
23	1	0	0.386568	-0.783479	-2.633695
24	6	0	1.755450	-1.682374	-1.260254
25	6	0	0.044032	-2.204322	0.243746
26	8	0	2.831859	-1.752122	-1.792423
27	8	0	-0.484696	-2.747310	1.185335
28	7	0	1.319921	-2.484063	-0.210915
29	1	0	1.907749	-3.187603	0.221104
30	6	0	-2.291761	-0.255944	1.028372
31	1	0	-2.115859	-1.175895	1.592761
32	1	0	-2.501400	0.543992	1.746898
33	6	0	-3.505735	-0.441084	0.115498
34	1	0	-4.415830	-0.550385	0.709782
35	6	0	-2.620215	0.938527	-1.569566
36	1	0	-2.916146	1.774723	-2.211525
37	8	0	-3.724526	0.667917	-0.735898

38	1	0	-3.395477	-1.355958	-0.489378
39	1	0	-2.408847	0.075055	-2.224692

$TS_{12a–13ac}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.501026	1.566241	-0.888286
2	6	0	-1.079466	0.642553	0.245738
3	6	0	0.123708	0.905295	0.862124
4	6	0	1.171376	1.382950	0.059102
5	6	0	1.004993	1.464186	-1.316721
6	6	0	-0.352468	1.850140	-1.882613
7	6	0	-2.728041	0.823327	-1.432805
8	8	0	-3.234739	0.025962	-0.366258
9	6	0	-2.338171	-0.002431	0.743441
10	6	0	0.690758	0.513242	2.201862
11	8	0	2.103704	0.584727	2.043139
12	6	0	2.434811	1.342203	0.882500
13	6	0	-1.956513	2.891413	-0.245651
14	1	0	1.872058	1.661388	-1.944947
15	1	0	-0.335326	2.926354	-2.097069
16	1	0	-0.518673	1.354492	-2.845295
17	1	0	-2.464242	0.181348	-2.284546
18	1	0	-3.517337	1.509817	-1.759697
19	1	0	-2.771847	0.562398	1.582661
20	1	0	-2.178626	-1.036385	1.066277
21	1	0	0.416810	-0.505348	2.501106
22	1	0	0.357402	1.207197	2.988805
23	1	0	-2.335312	3.563591	-1.024000
24	1	0	-1.118440	3.380425	0.259432
25	1	0	-2.758932	2.729272	0.481471
26	6	0	-0.291511	-1.129988	-1.050578
27	6	0	0.775351	-0.645759	-1.794319

28	1	0	-1.298680	-1.337961	-1.386417
29	1	0	0.774085	-0.433734	-2.855824
30	6	0	2.045347	-1.058255	-1.121770
31	6	0	0.260690	-1.838748	0.135181
32	8	0	3.187553	-0.867203	-1.470726
33	8	0	-0.320029	-2.423841	1.024443
34	7	0	1.643787	-1.669636	0.060711
35	1	0	2.283247	-1.953635	0.791890
36	1	0	3.268793	0.853169	0.367686
37	1	0	2.749468	2.357605	1.167737

13ac

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.501700	1.279261	-0.741236
2	6	0	-1.042487	0.107804	0.197651
3	6	0	0.129483	0.614561	0.975987
4	6	0	1.132741	1.054934	0.213821
5	6	0	0.951479	0.927867	-1.275890
6	6	0	-0.356136	1.642951	-1.712913
7	6	0	-2.774463	0.648859	-1.308387
8	8	0	-3.321277	-0.133459	-0.248156
9	6	0	-2.372881	-0.305395	0.810122
10	6	0	0.502120	0.706840	2.424856
11	8	0	1.798363	1.298537	2.413036
12	6	0	2.283244	1.469295	1.083297
13	6	0	-1.901530	2.514941	0.079405
14	1	0	1.814499	1.271559	-1.851286
15	1	0	-0.201299	2.725872	-1.719791
16	1	0	-0.591098	1.345353	-2.742628
17	1	0	-2.563241	0.010169	-2.178833
18	1	0	-3.516354	1.396521	-1.609600
19	1	0	-2.637533	0.329605	1.665924

20	1	0	-2.386909	-1.349406	1.128930
21	1	0	0.536347	-0.282364	2.906156
22	1	0	-0.180906	1.340126	3.008229
23	1	0	-2.220418	3.309088	-0.604328
24	1	0	-1.060679	2.893463	0.668209
25	1	0	-2.738952	2.303885	0.750622
26	6	0	-0.479251	-1.057768	-0.684438
27	6	0	0.702725	-0.577087	-1.546323
28	1	0	-1.289494	-1.506141	-1.267595
29	1	0	0.543725	-0.739762	-2.617353
30	6	0	1.899095	-1.405172	-1.098179
31	6	0	0.112737	-2.143839	0.213236
32	8	0	3.039211	-1.299337	-1.475421
33	8	0	-0.442236	-2.760435	1.090064
34	7	0	1.449280	-2.290367	-0.129716
35	1	0	2.067394	-2.925404	0.361648
36	1	0	3.172122	0.841822	0.916907
37	1	0	2.581290	2.516603	0.939458

12b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.018096	0.936374	-0.272220
2	6	0	-1.719342	0.243350	1.044912
3	6	0	-0.471224	0.175883	1.508134
4	6	0	0.636482	0.702447	0.708224
5	6	0	0.479154	1.034771	-0.585783
6	6	0	-0.860888	0.790148	-1.259737
7	6	0	-3.316000	0.205820	-0.639533
8	8	0	-3.993287	0.031638	0.598003
9	6	0	-3.022800	-0.280109	1.588118
10	6	0	0.115548	-0.313645	2.807754
11	8	0	1.521553	-0.258637	2.629240

12	6	0	1.853523	0.662059	1.594307
13	6	0	-2.319191	2.416665	0.014722
14	1	0	-0.992531	1.481024	-2.097777
15	1	0	-0.849517	-0.224478	-1.687392
16	1	0	-3.094809	-0.769008	-1.103212
17	1	0	-3.975507	0.777204	-1.298111
18	1	0	-3.329295	0.190700	2.529247
19	1	0	-2.966183	-1.367658	1.753045
20	1	0	-0.159654	-1.345617	3.051211
21	1	0	-0.197387	0.330606	3.644384
22	1	0	-2.592567	2.930989	-0.913720
23	1	0	-1.442514	2.913719	0.440960
24	1	0	-3.152774	2.507695	0.717254
25	1	0	2.750100	0.307134	1.084154
26	1	0	2.067932	1.661865	2.001647
27	6	0	1.651256	1.500366	-1.351991
28	8	0	2.731855	1.774422	-0.874179
29	8	0	1.394516	1.587883	-2.671262
30	6	0	2.494983	2.024605	-3.465623
31	1	0	3.326467	1.320983	-3.382695
32	1	0	2.125144	2.063844	-4.489137
33	1	0	2.834019	3.009836	-3.138090

$TS_{\mathbf{12b–13bc}}$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.515395	1.577295	-0.868145
2	6	0	-1.062042	0.607405	0.214733
3	6	0	0.114713	0.914161	0.879377
4	6	0	1.152159	1.462471	0.123446
5	6	0	0.994998	1.615873	-1.254720
6	6	0	-0.372243	1.972105	-1.827923
7	6	0	-2.702669	0.812300	-1.466987

8	8	0	-3.185615	-0.058652	-0.445434
9	6	0	-2.309938	-0.084479	0.680746
10	6	0	0.657579	0.509765	2.224090
11	8	0	2.065400	0.652309	2.110238
12	6	0	2.411178	1.416759	0.956254
13	6	0	-2.039211	2.840597	-0.155684
14	1	0	-0.401589	3.058623	-1.979931
15	1	0	-0.491815	1.528547	-2.820334
16	1	0	-2.400950	0.223291	-2.343777
17	1	0	-3.516440	1.479947	-1.770921
18	1	0	-2.769193	0.452610	1.524167
19	1	0	-2.129094	-1.119857	0.985585
20	1	0	0.419329	-0.527858	2.486805
21	1	0	0.264564	1.164879	3.017255
22	1	0	-2.435487	3.538779	-0.901311
23	1	0	-1.232981	3.336978	0.391940
24	1	0	-2.845694	2.600450	0.544272
25	6	0	-0.254837	-1.027851	-1.063019
26	6	0	0.778027	-0.510797	-1.839201
27	1	0	-1.252624	-1.287374	-1.393336
28	1	0	0.734915	-0.248028	-2.887878
29	6	0	2.077033	-0.925662	-1.235378
30	6	0	0.363800	-1.779051	0.069917
31	8	0	3.199458	-0.721665	-1.638037
32	8	0	-0.174169	-2.415109	0.949400
33	7	0	1.735956	-1.567649	-0.046323
34	1	0	2.411544	-1.892643	0.633729
35	1	0	3.246383	0.932445	0.442339
36	1	0	2.733629	2.428762	1.237887
37	6	0	2.206259	1.980042	-2.046366
38	8	0	3.249739	2.352197	-1.566288
39	8	0	2.009082	1.821158	-3.365111
40	6	0	3.188644	1.980879	-4.157621
41	1	0	3.933479	1.244033	-3.848954
42	1	0	2.877560	1.813904	-5.187612
43	1	0	3.597795	2.985190	-4.033199

13bc

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.991759	0.945854	-0.209354
2	6	0	-1.502335	-0.257365	0.672453
3	6	0	-0.349824	0.246621	1.480228
4	6	0	0.646026	0.759249	0.755103
5	6	0	0.478082	0.693783	-0.741140
6	6	0	-0.856254	1.394079	-1.155609
7	6	0	-3.241429	0.307232	-0.817830
8	8	0	-3.769780	-0.542767	0.198908
9	6	0	-2.823898	-0.736546	1.255948
10	6	0	-0.009974	0.308202	2.938961
11	8	0	1.274525	0.916115	2.970968
12	6	0	1.759566	1.207986	1.658715
13	6	0	-2.432197	2.125994	0.670015
14	1	0	-0.726225	2.479422	-1.100268
15	1	0	-1.063587	1.142939	-2.202239
16	1	0	-3.005567	-0.280444	-1.717231
17	1	0	-4.003487	1.046799	-1.086253
18	1	0	-3.111835	-0.149541	2.137778
19	1	0	-2.810624	-1.794116	1.526526
20	1	0	0.028826	-0.690585	3.399044
21	1	0	-0.724229	0.914028	3.516372
22	1	0	-2.767567	2.945965	0.025905
23	1	0	-1.607614	2.496281	1.286441
24	1	0	-3.269145	1.855888	1.319986
25	6	0	-0.906738	-1.359219	-0.262674
26	6	0	0.257781	-0.802710	-1.096944
27	1	0	-1.702118	-1.799603	-0.871834
28	1	0	0.106481	-0.897971	-2.175579
29	6	0	1.478779	-1.617758	-0.697464

30	6	0	-0.280898	-2.476984	0.572385
31	8	0	2.613236	-1.447426	-1.071419
32	8	0	-0.815666	-3.156379	1.413210
33	7	0	1.058259	-2.571809	0.214123
34	1	0	1.696139	-3.213031	0.671177
35	1	0	2.695582	0.665343	1.469948
36	1	0	1.974891	2.278680	1.570049
37	6	0	1.659469	1.269590	-1.496700
38	8	0	2.544915	1.916768	-0.997429
39	8	0	1.580041	0.995187	-2.805030
40	6	0	2.712954	1.409903	-3.571743
41	1	0	3.604193	0.888893	-3.215343
42	1	0	2.490242	1.135723	-4.601496
43	1	0	2.860735	2.487559	-3.479327

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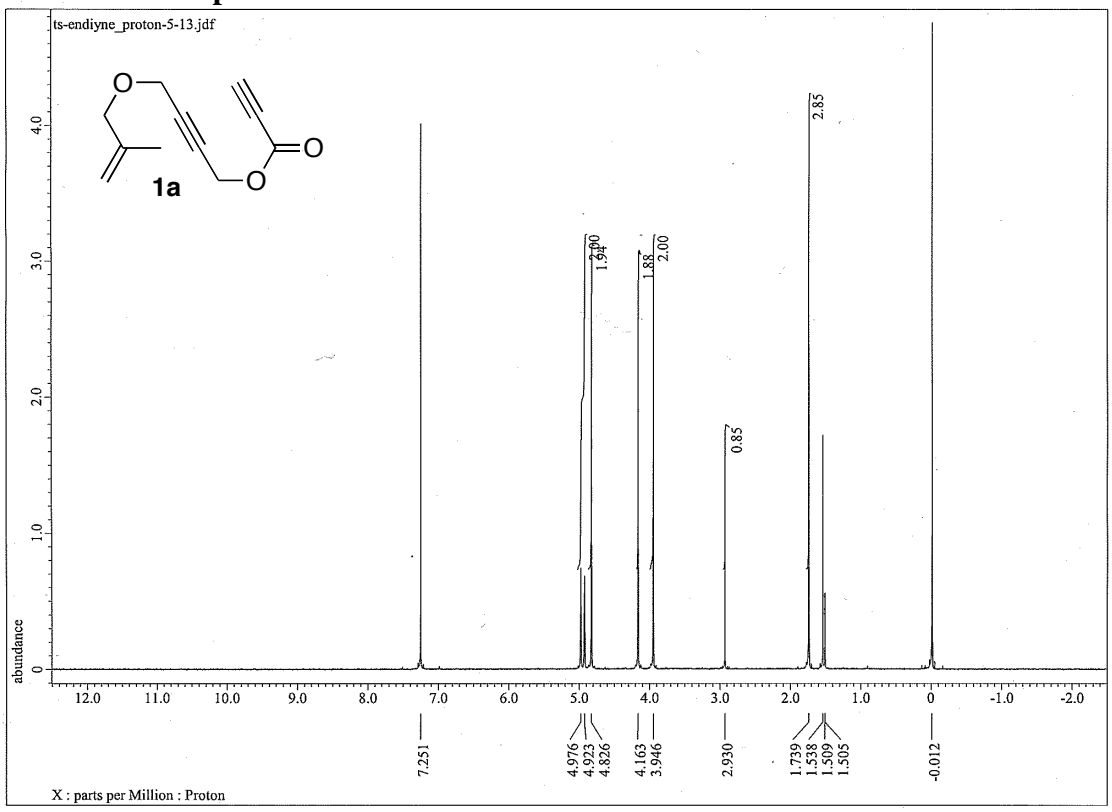
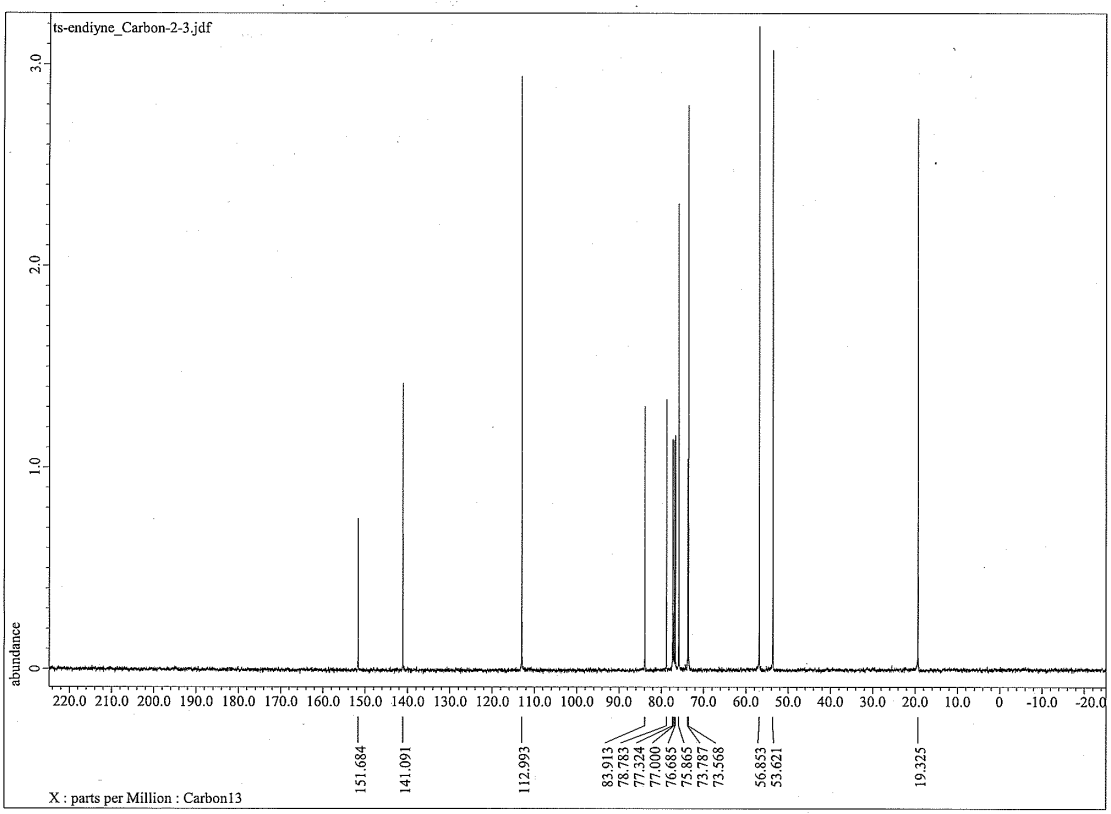
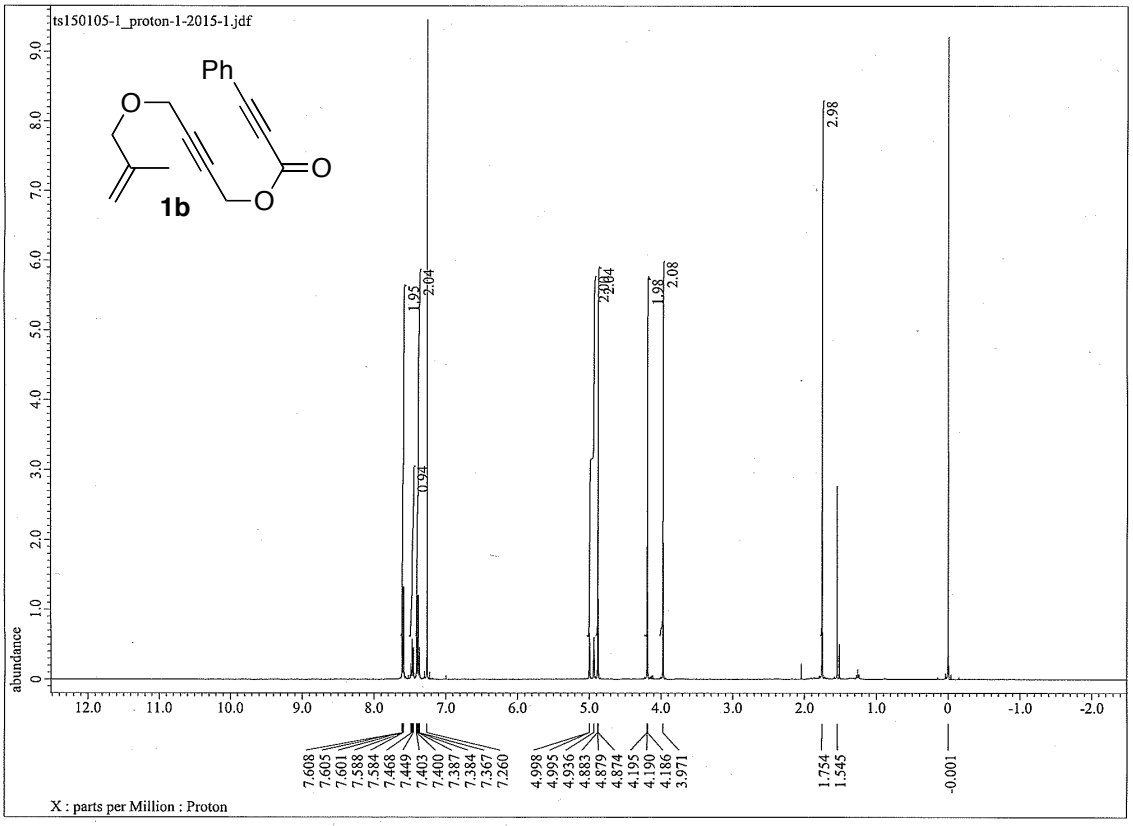
9. ^{1}H and ^{13}C NMR Spectra



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Ph
O
O
O
1b
abundance
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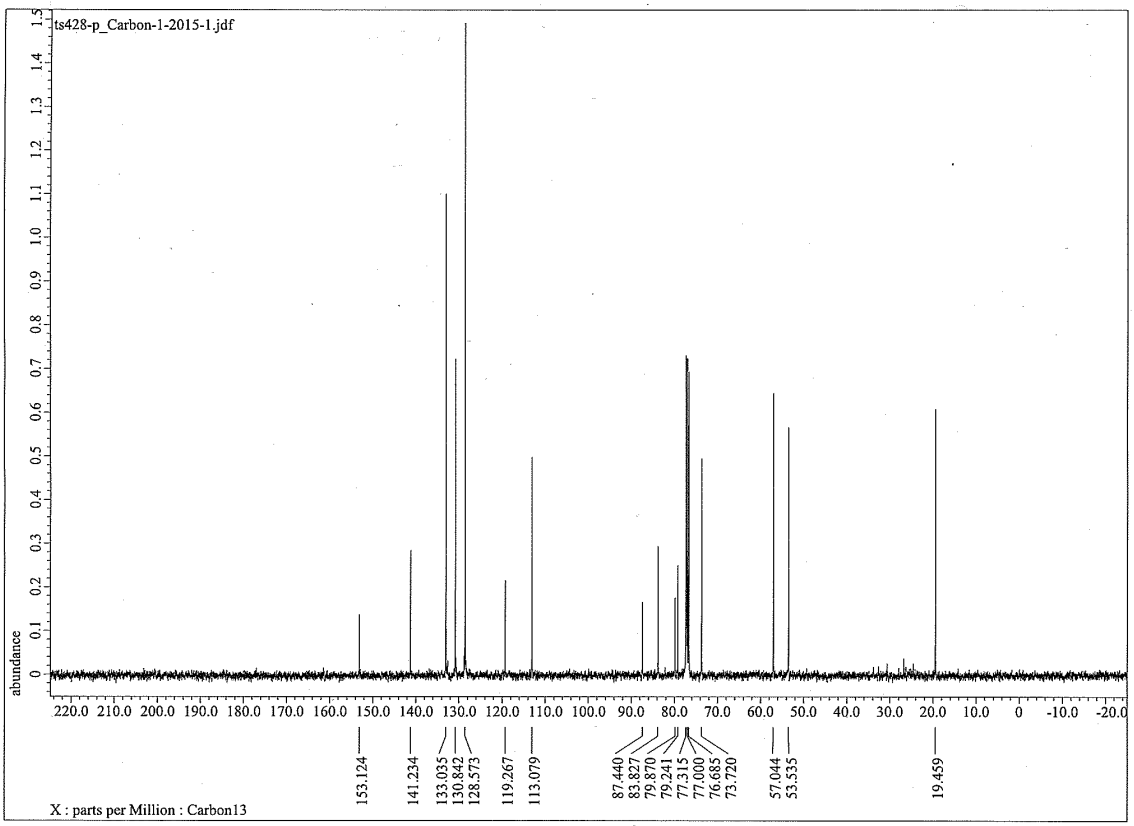
7.608
7.605
7.601
7.588
7.584
7.468
7.449
7.403
7.400
7.387
7.384
7.367
7.260
4.998
4.995
4.936
4.883
4.879
4.874
4.195
4.190
4.186
3.971
1.754
1.545
-0.001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abundance
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130.842
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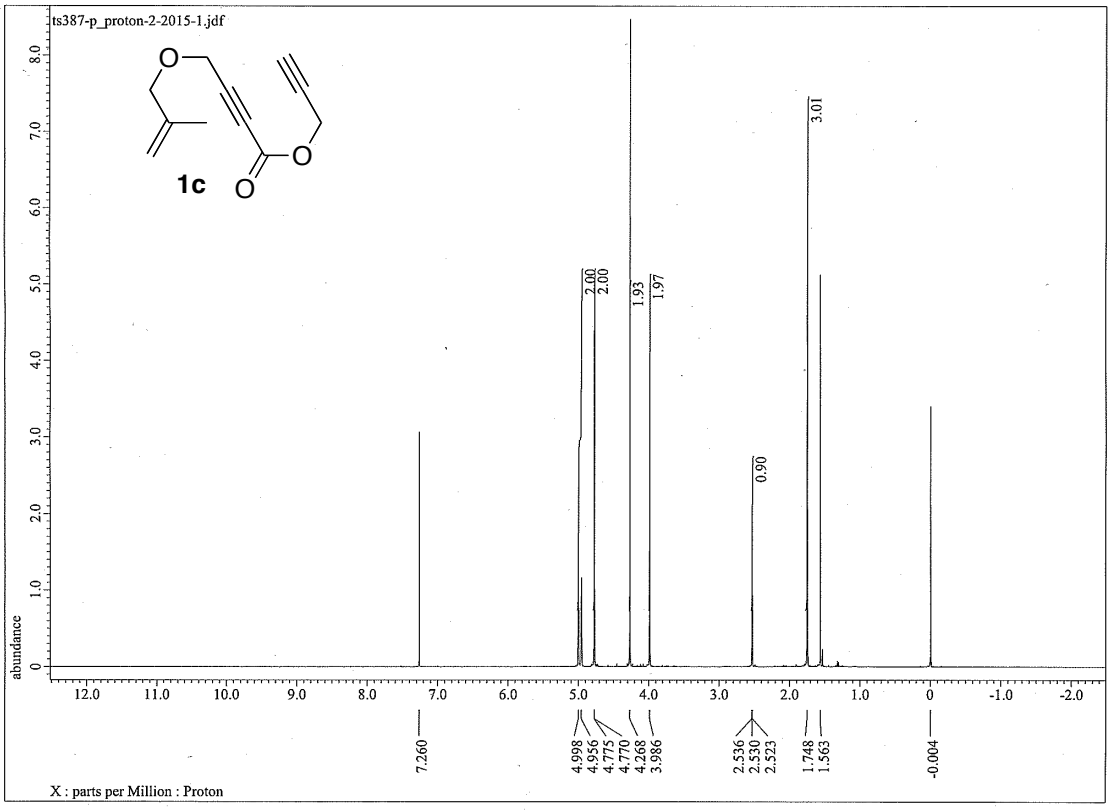
119.267
113.079
87.440
83.827
79.870
79.241
77.315
77.000
76.685
73.720
57.044
53.535
19.459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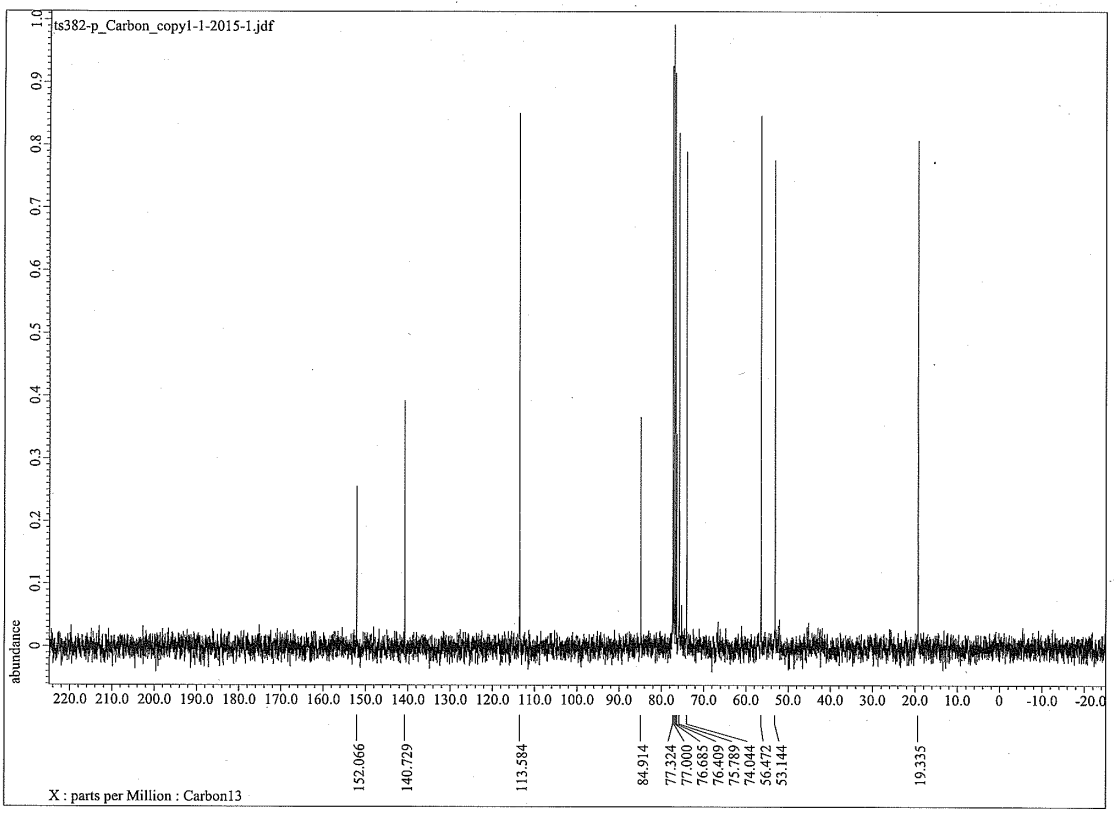
1c
abundance
2.00
2.00
1.93
1.97
0.90
3.01
7.260
4.998
4.956
4.775
4.770
4.268
3.986
2.536
2.530
2.523
1.748
1.563
-0.004
X : parts per Million : Proton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abundance
152.066
140.729
113.584
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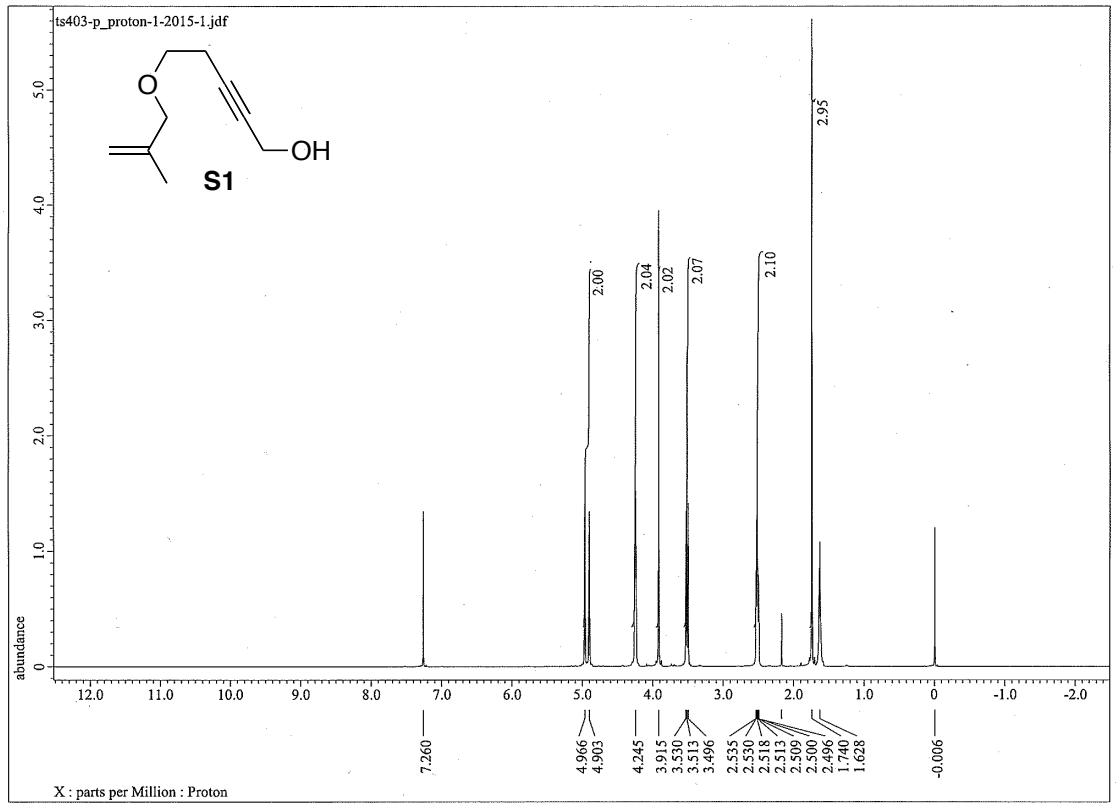
77.324
77.000
76.683
76.409
75.789
74.044
56.472
53.144
19.335
X : parts per Million : Carbon13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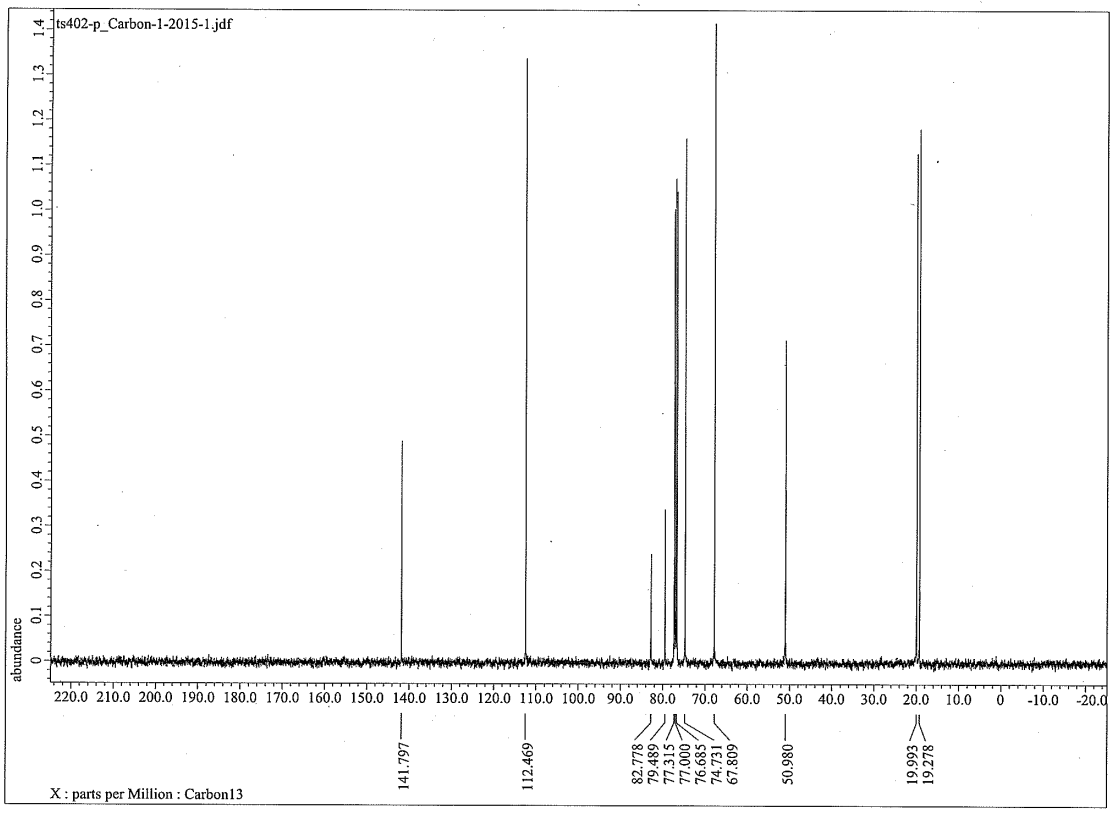
O
OH
S1
abundance
2.00
2.04
2.02
2.07
2.10
2.95
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.260
4.966
4.903
4.245
3.915
3.530
3.513
3.496
2.535
2.530
2.518
2.513
2.509
2.500
2.496
1.740
1.628
-0.006
X : parts per Million : Proton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abundance
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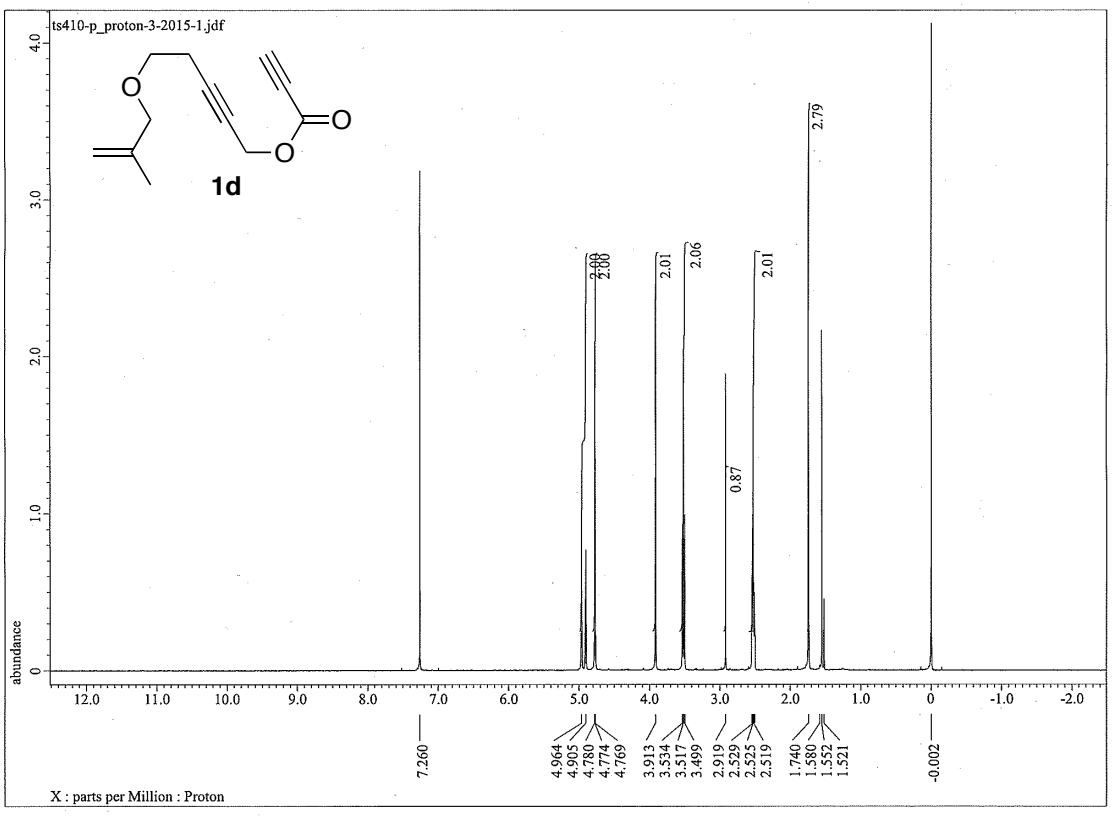
141.797
112.469
82.778
79.489
77.315
77.000
76.685
74.731
67.809
50.980
19.993
19.278
X : parts per Million : Carbon13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1d
abundance
X : parts per Million : Proton
7.260
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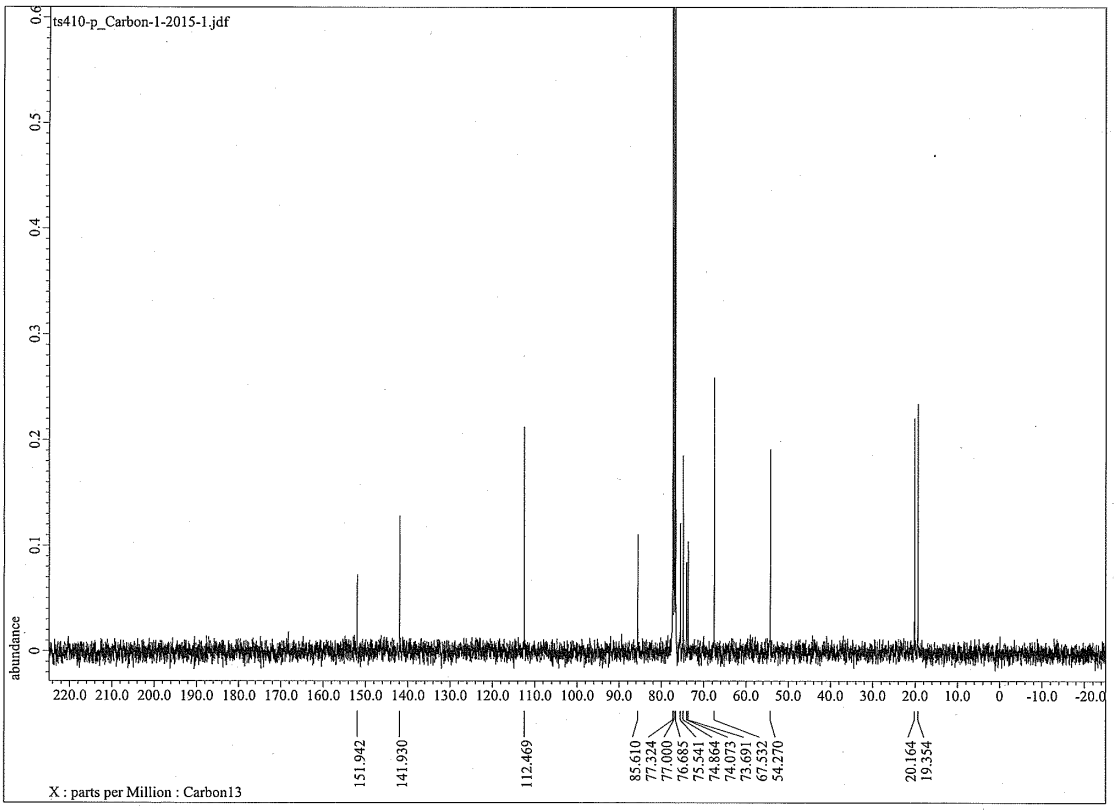
4.780
4.774
4.769
3.913
3.534
3.517
3.499
2.919
2.529
2.525
2.519
1.740
1.580
1.552
1.521
-0.002
2.00
2.00
2.01
2.06
0.87
2.01
2.79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abundance
X : parts per Million : Carbon13
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112.469
85.610
77.324
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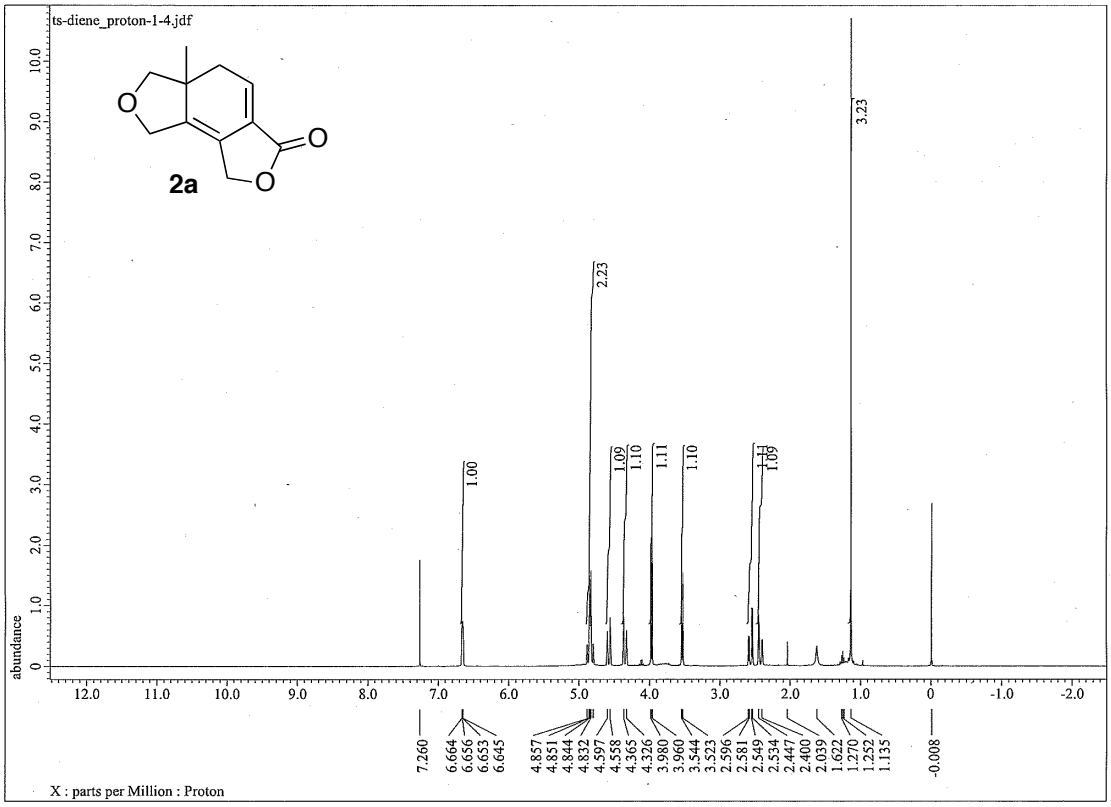
74.073
73.691
67.532
54.270
20.164
19.354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2a
abundance
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6.656
6.653
6.645
4.857
4.851
4.844
4.832
4.597
4.558
4.365
4.326
3.980
3.960
3.544
3.523
2.596
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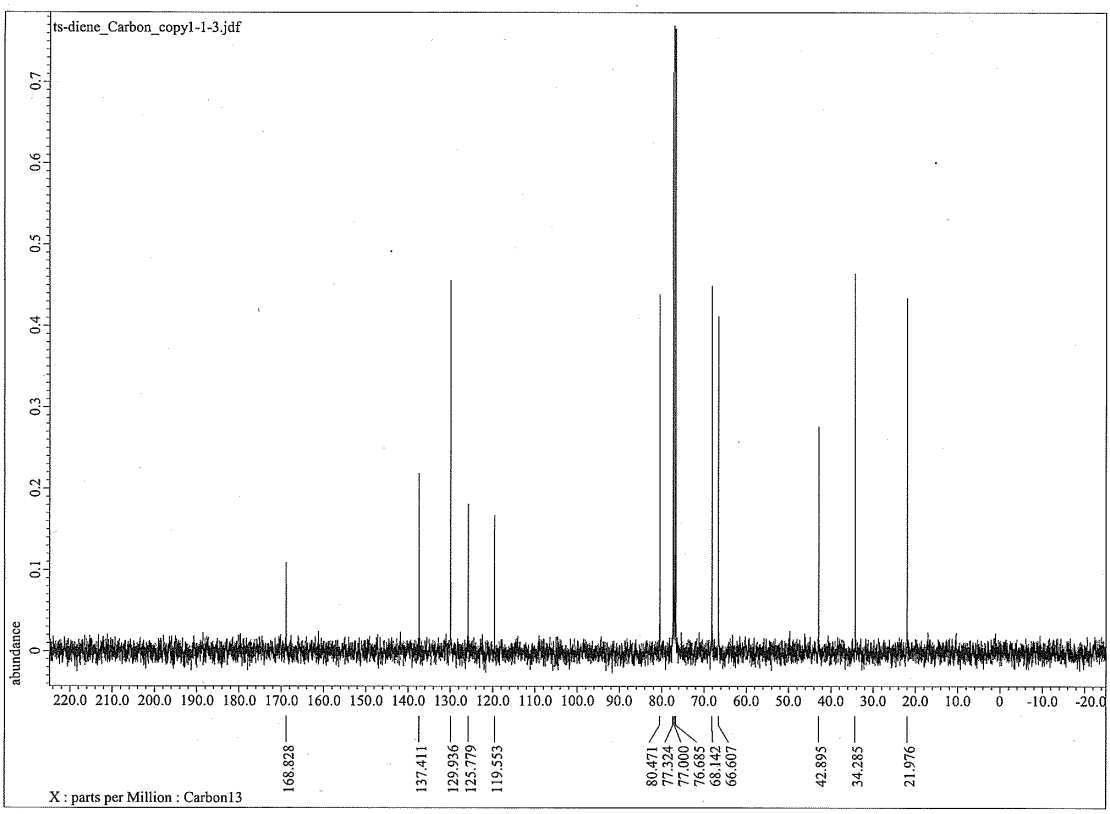
2.447
2.400
2.039
1.622
1.270
1.252
1.135
-0.008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80.471
77.324
77.000
76.685
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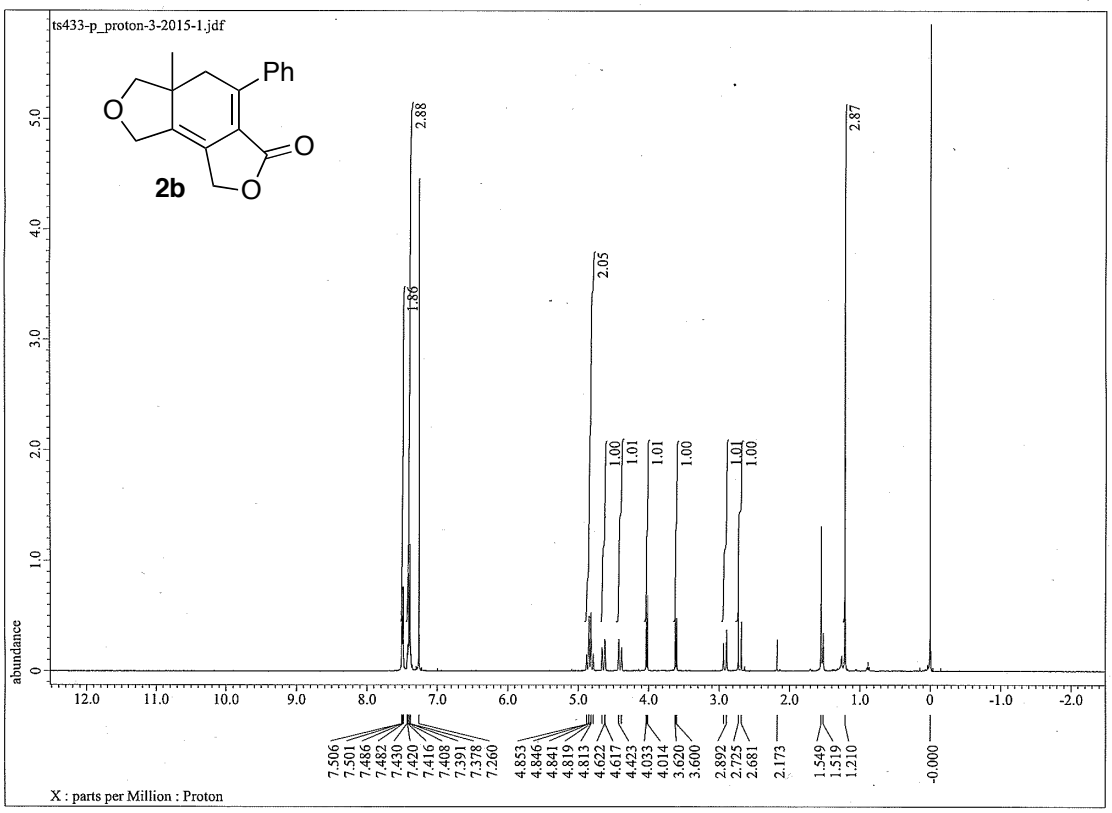
66.607
42.895
34.285
21.976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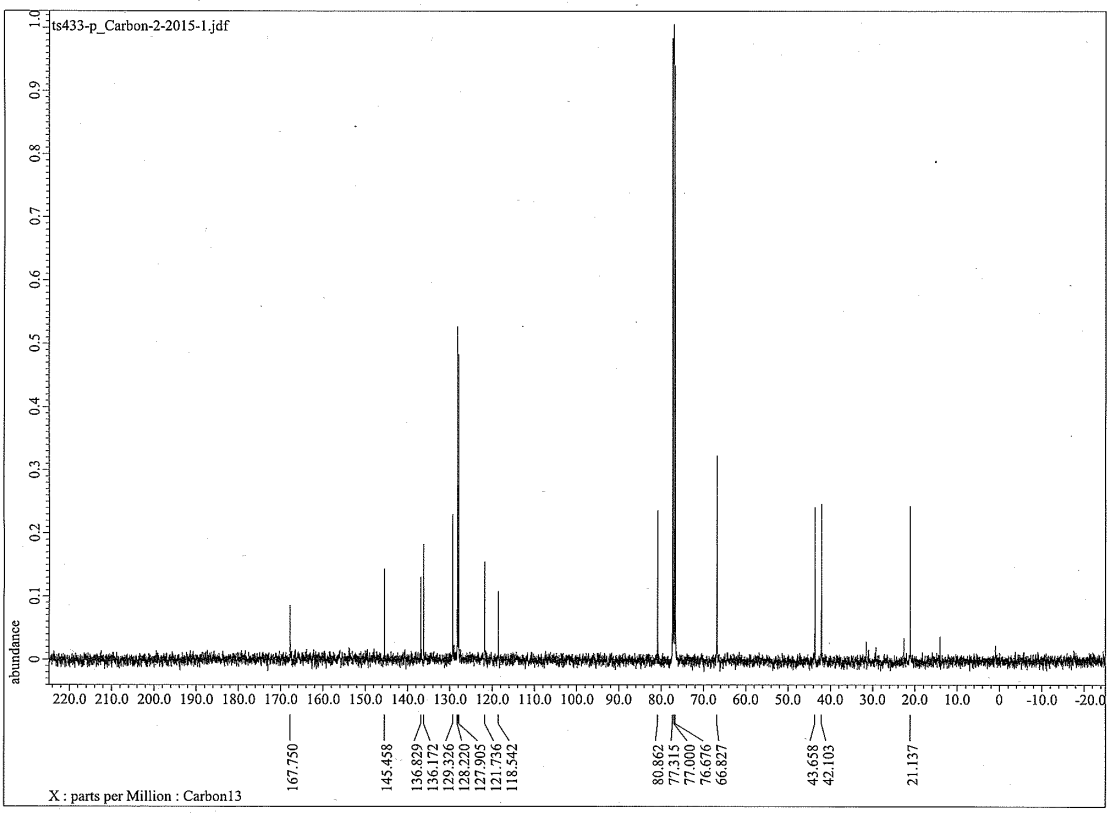
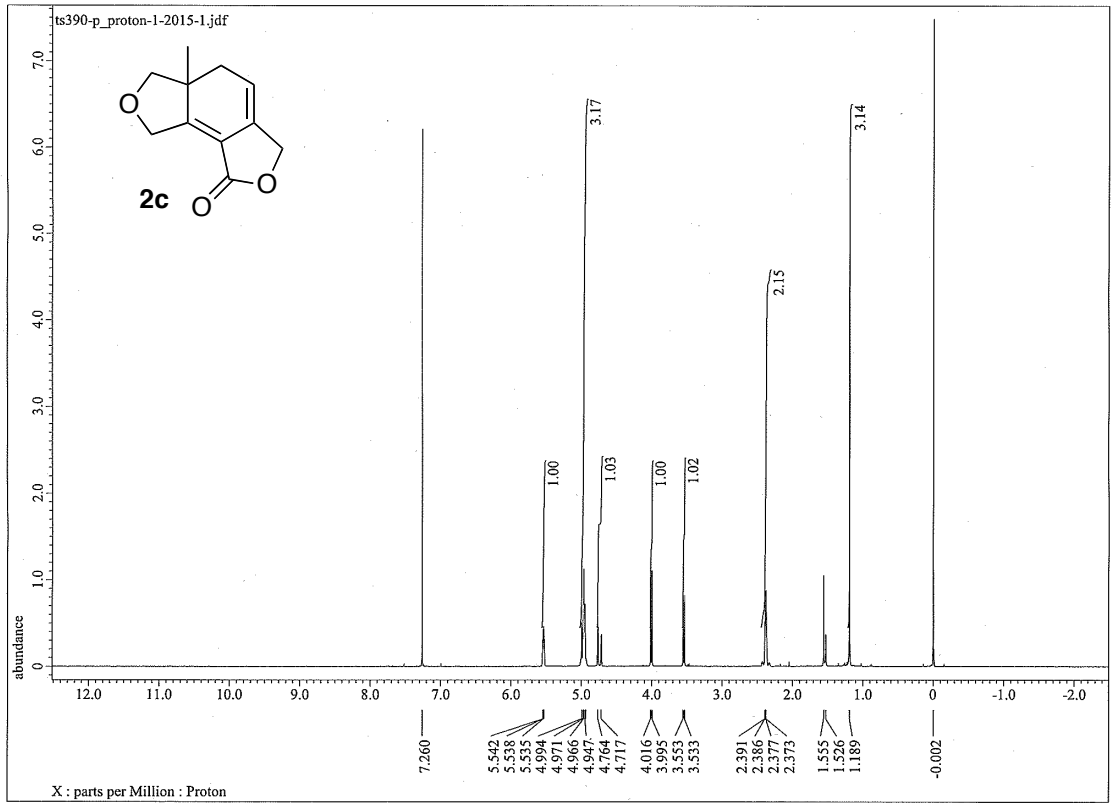
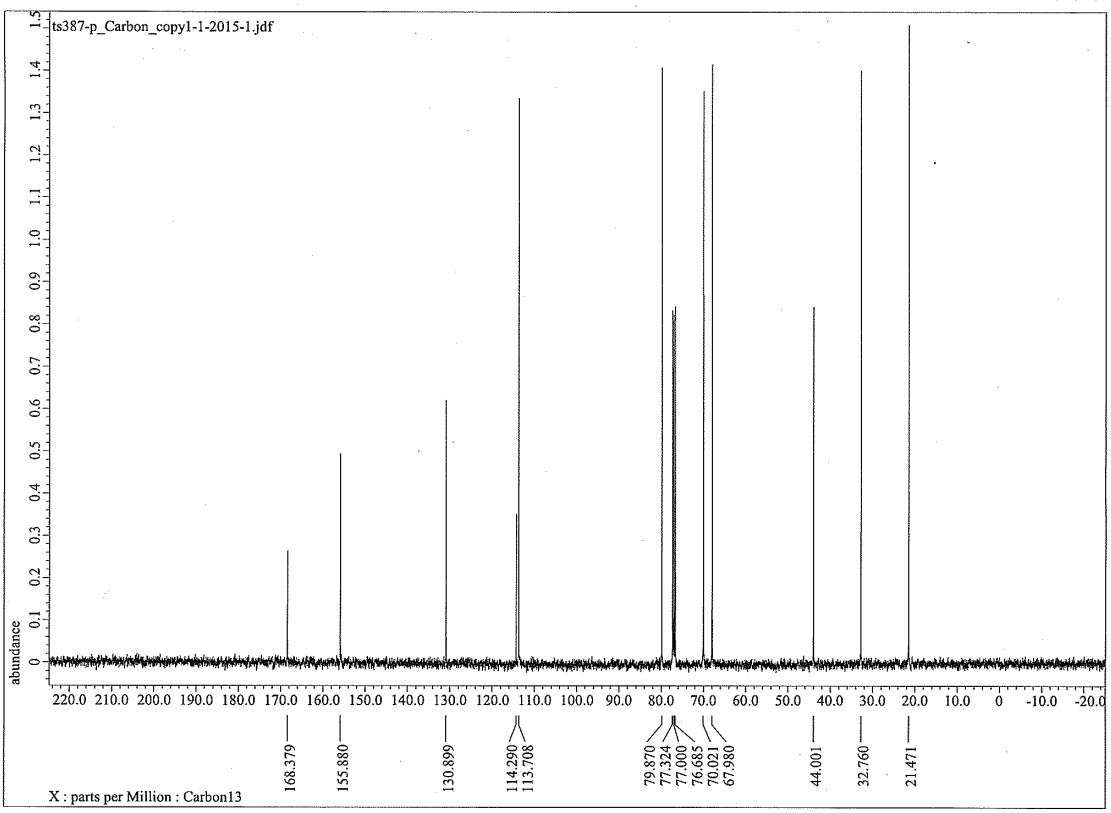
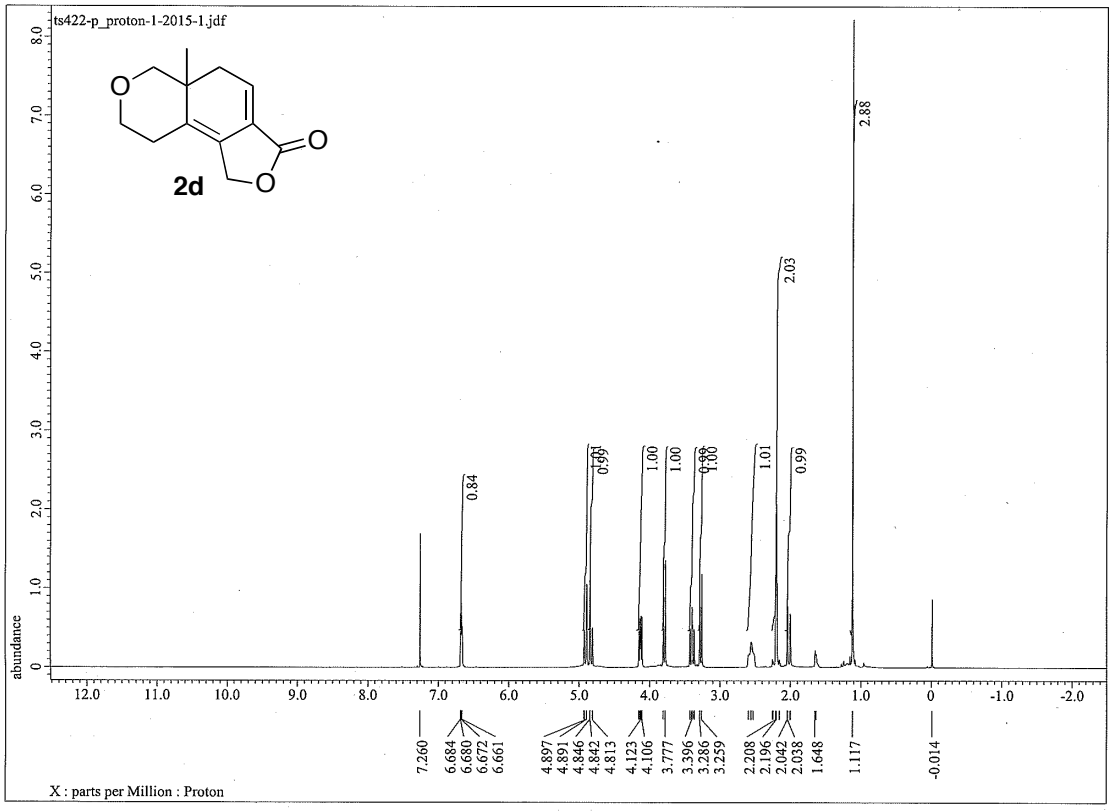
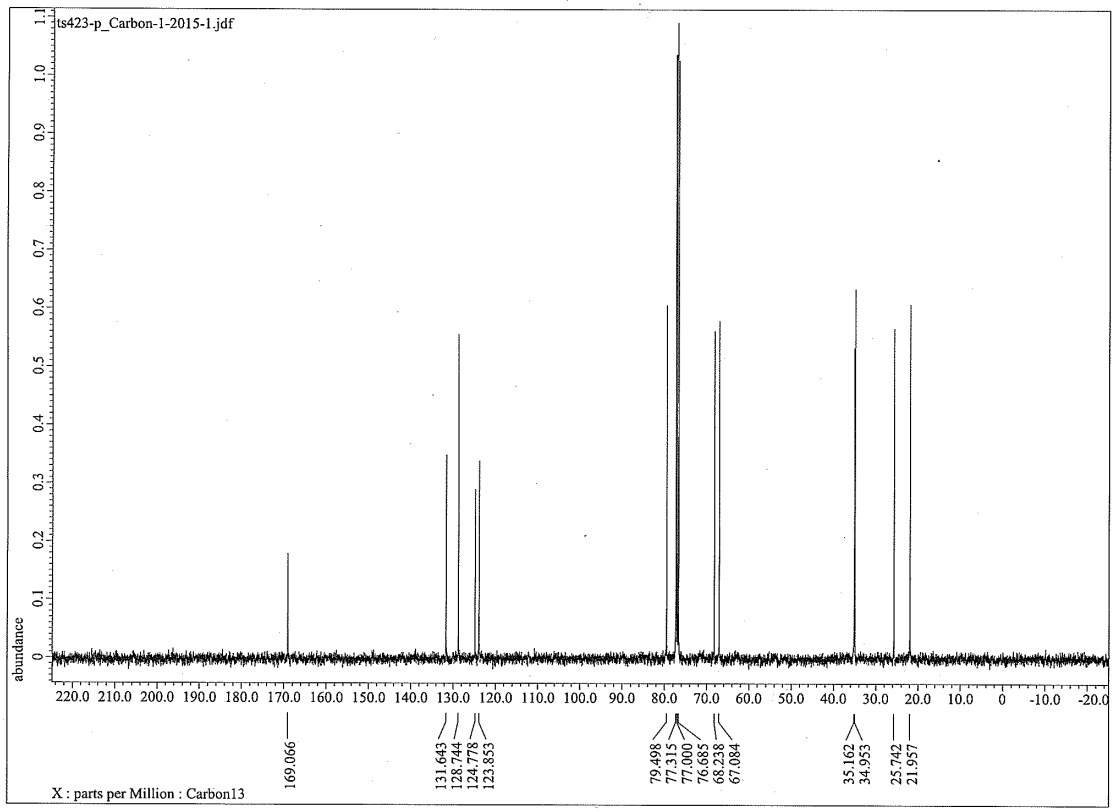
Ph
O
O
O
2b
2.88
2.87
2.05
1.86
1.00
1.01
1.01
1.00
1.01
1.00
abundance
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.506 7.501 7.486 7.482 7.430 7.420 7.416 7.408 7.391 7.378 7.260
4.853 4.846 4.841 4.819 4.813 4.622 4.617 4.423 4.033 4.014 3.620 3.600
2.892 2.725 2.681 2.173 1.549 1.519 1.210 -0.000
X : parts per Million : Proton

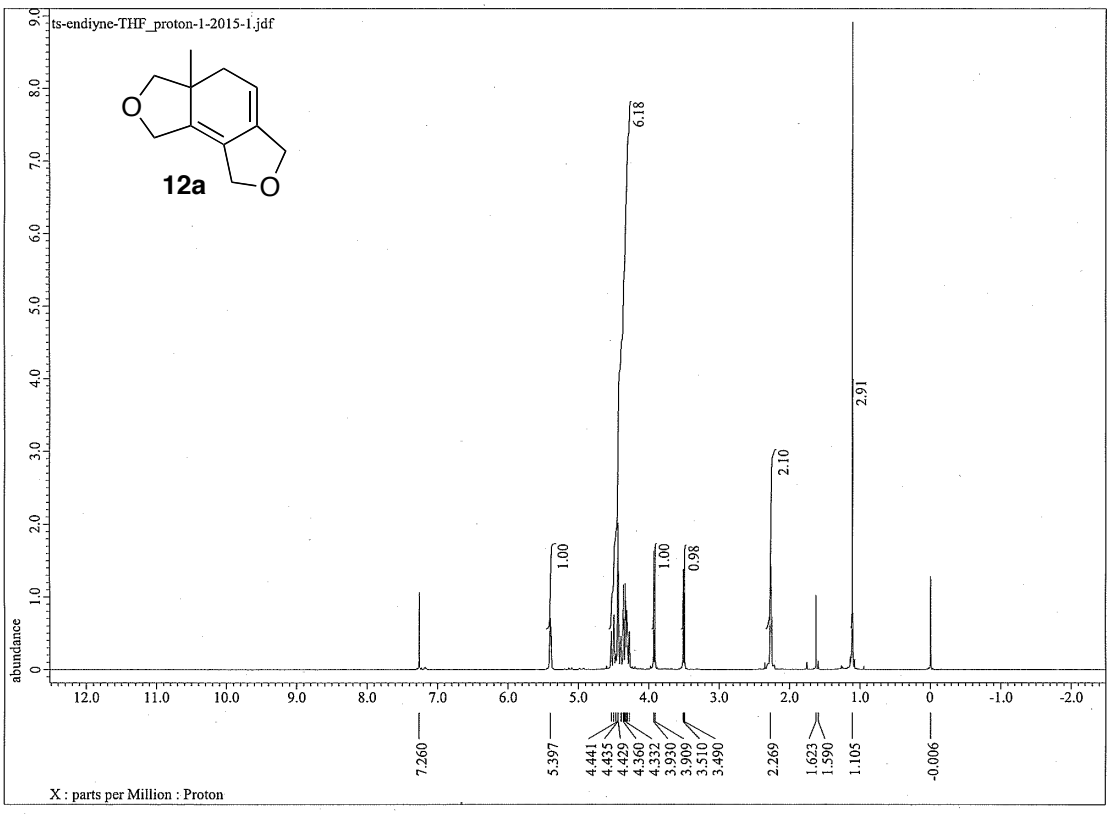

ts433-p_Carbon-2-2015-1.jdf
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.750
145.458
136.829 136.172 129.326 128.220 127.905 121.736 118.542
80.862 77.315 77.000 76.676 66.827
43.658 42.103
21.137
X : parts per Million : Carbon13

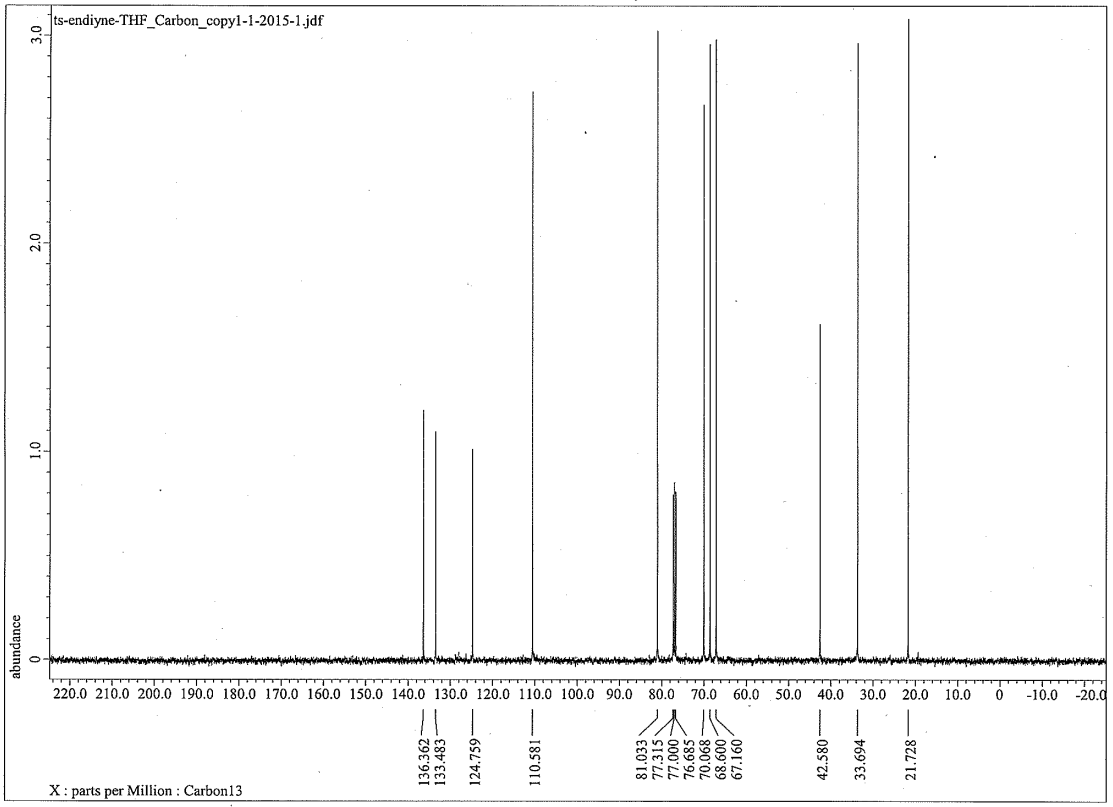

ts390-p_proton-1-2015-1.jdf
2c
abundance
X : parts per Million : Proton
7.260
5.542
5.538
5.535
4.994
4.971
4.966
4.947
4.764
4.717
4.016
3.995
3.553
3.533
2.391
2.386
2.377
2.373
1.555
1.526
1.189
-0.002
1.00
1.03
1.00
1.02
2.15
3.17
3.14

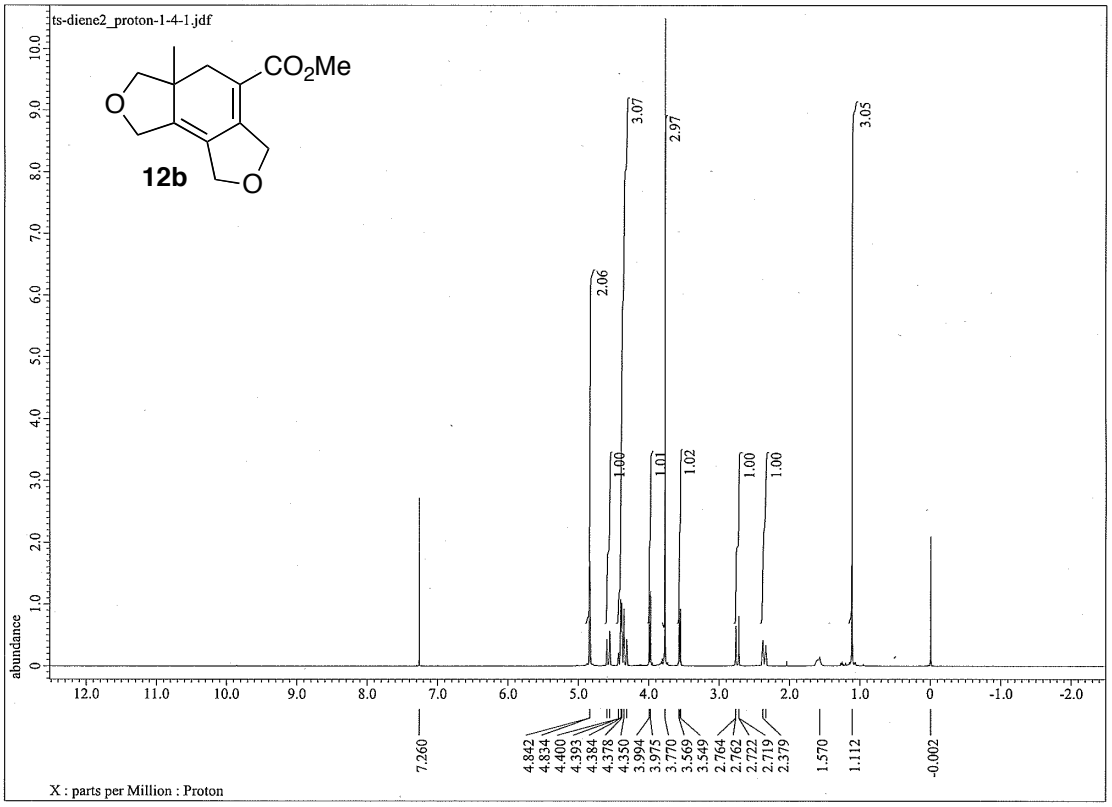

ts387-p_Carbon_copy1-1-2015-1.jdf
abundance
X : parts per Million : Carbon13
168.379
155.880
130.899
114.290
113.708
79.870
77.324
77.000
76.685
70.021
67.980
44.001
32.760
21.471

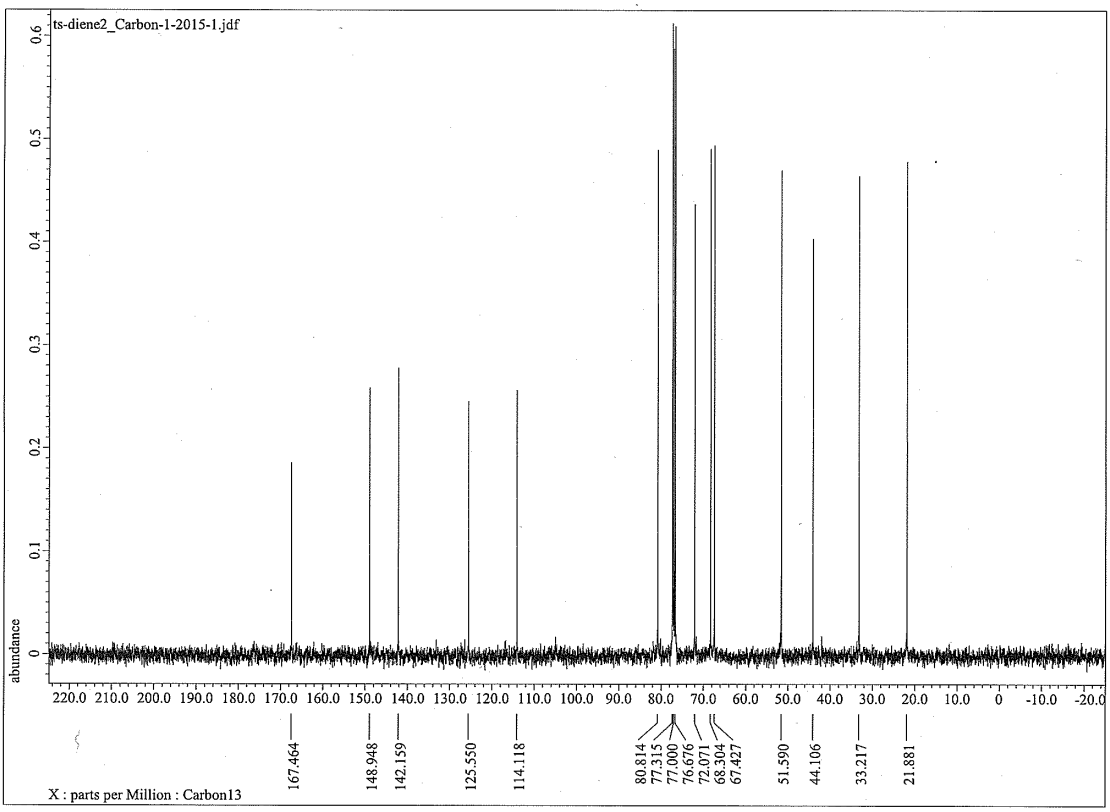

ts422-p_proton-1-2015-1.jdf
2d
abundance
X : parts per Million : Proton
7.260
6.684
6.680
6.672
6.661
4.897
4.891
4.846
4.842
4.813
4.123
4.106
3.777
3.396
3.286
3.259
2.208
2.196
2.042
2.038
1.648
1.117
-0.014
0.84
0.99
1.00
1.00
1.00
1.01
2.03
0.99
2.88

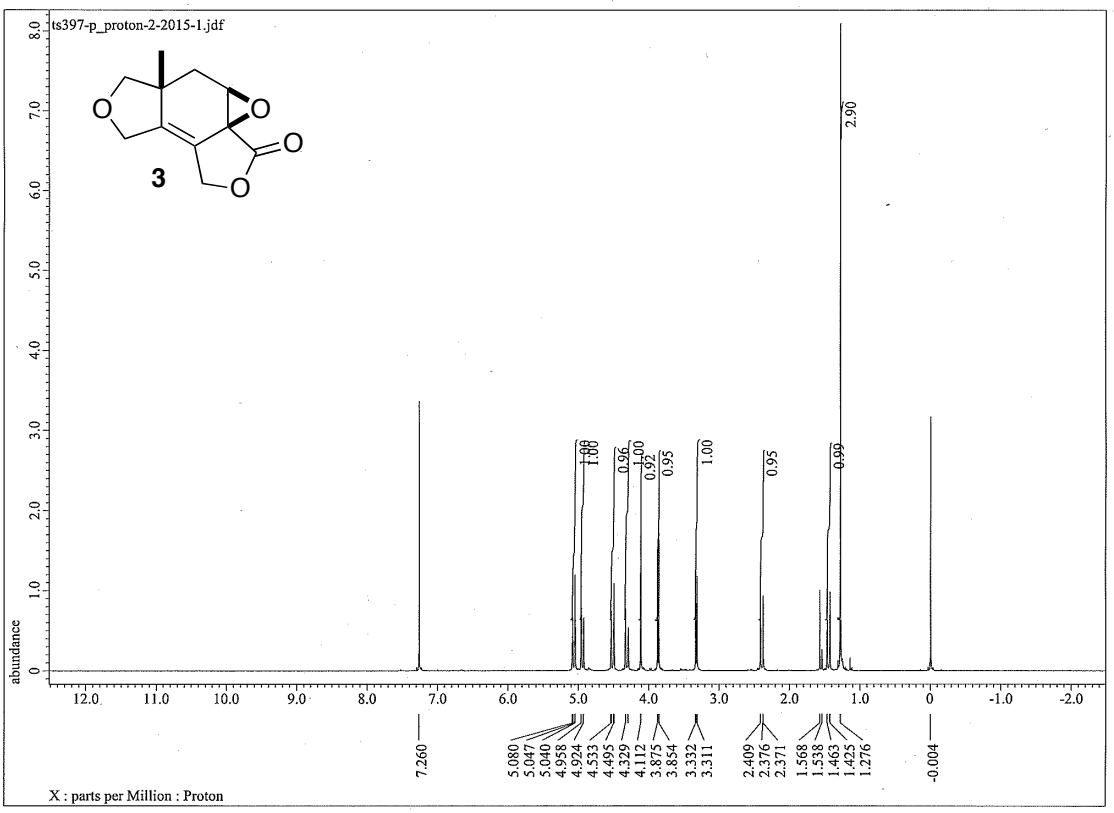

ts423-p_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13
169.066
131.643
128.744
124.778
123.853
79.498
77.315
77.000
76.685
68.238
67.084
35.162
34.953
25.742
21.957

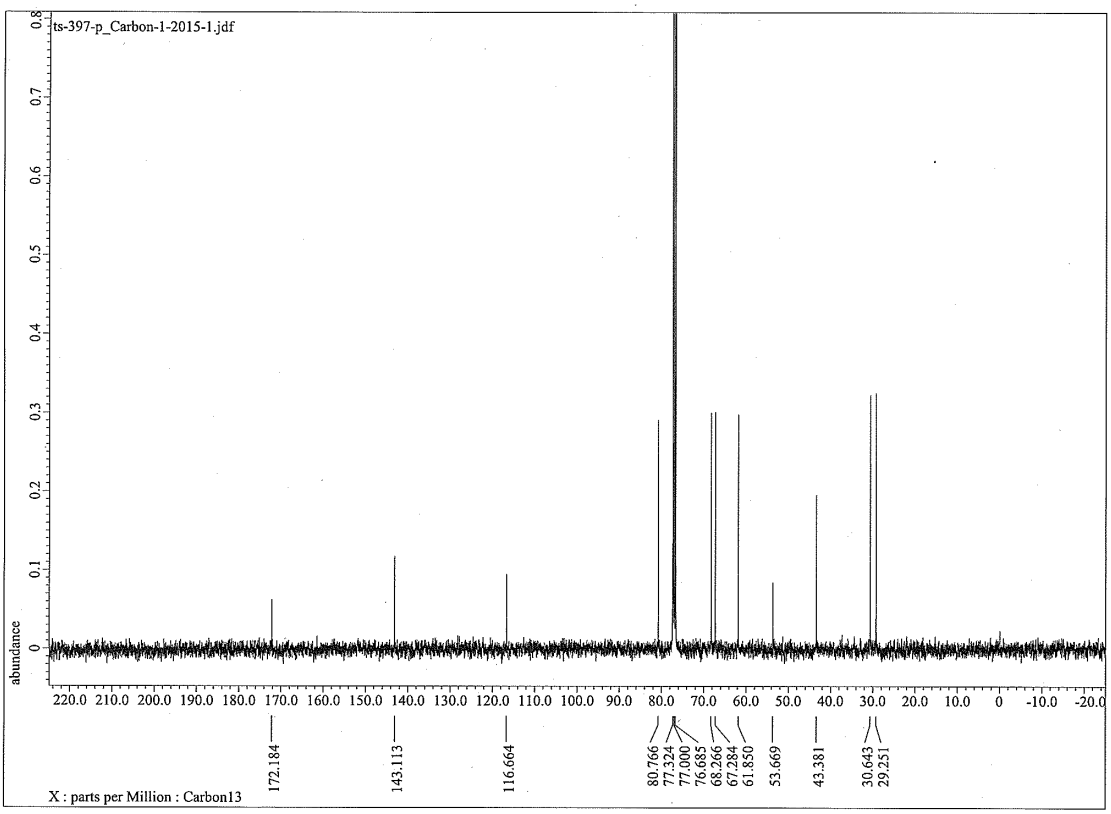

ts-endiyne-THF_proton-1-2015-1.jdf
12a
6.18
2.91
2.10
1.00
1.00
0.98
abundance
X : parts per Million : Proton
7.260
5.397
4.441
4.435
4.429
4.360
4.332
3.930
3.909
3.510
3.490
2.269
1.623
1.590
1.105
-0.006

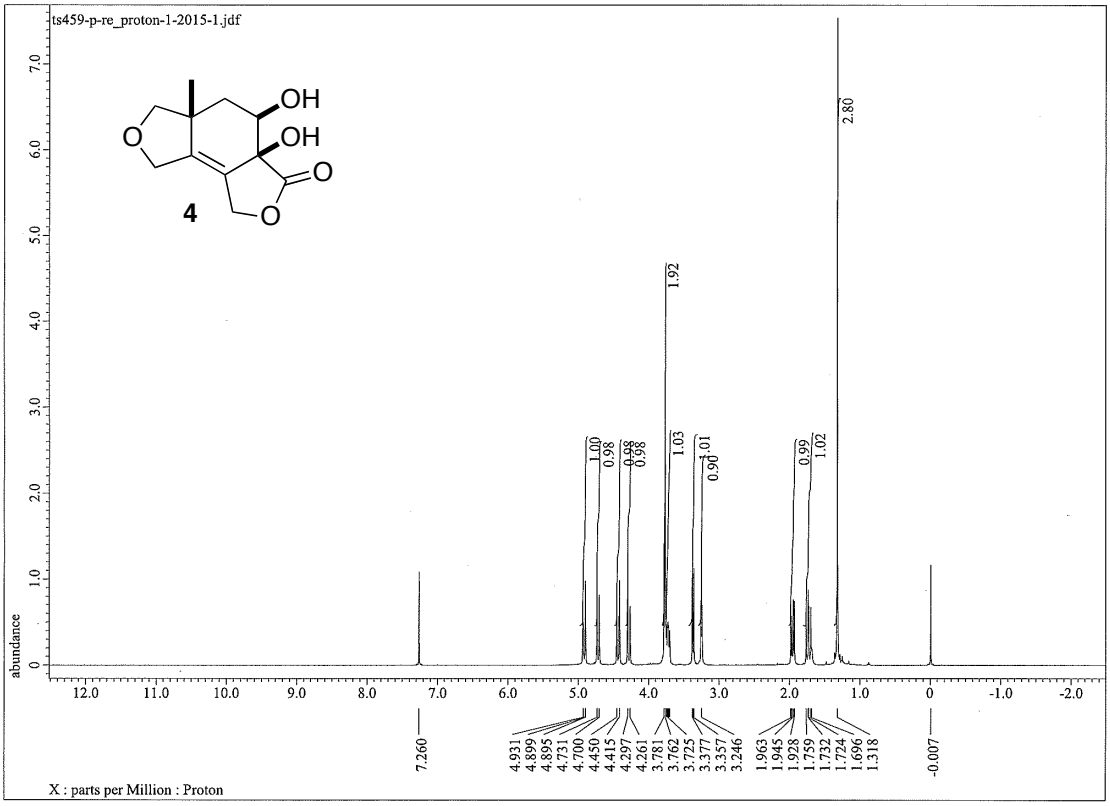

ts-endiyne-THF_Carbon_copy1-1-2015-1.jdf
abundance
X : parts per Million : Carbon13
136.362
133.483
124.759
110.581
81.033
77.315
77.000
76.685
70.068
68.600
67.160
42.580
33.694
21.728

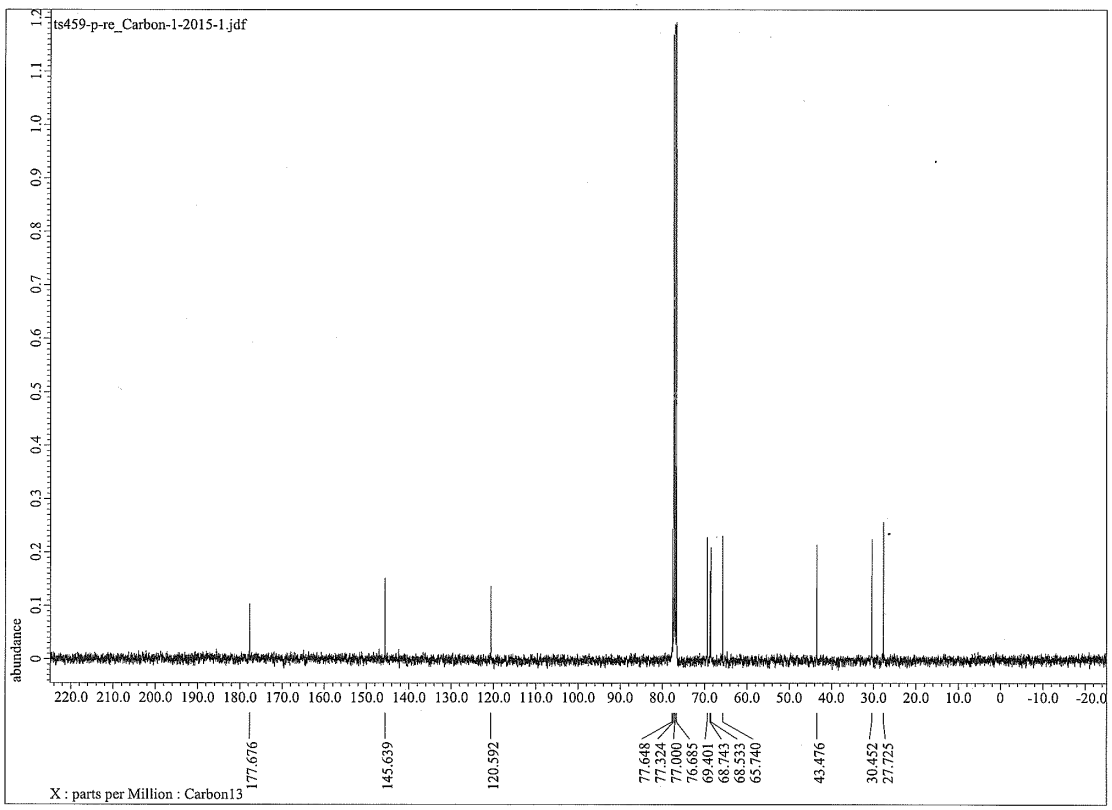

ts-diene2_proton-1-4-1.jdf
CO2Me
O
O
12b
abundance
X : parts per Million : Proton
7.260
4.842
4.834
4.400
4.393
4.384
4.378
4.350
3.994
3.975
3.770
3.569
3.549
2.764
2.762
2.722
2.719
2.379
1.570
1.112
-0.002

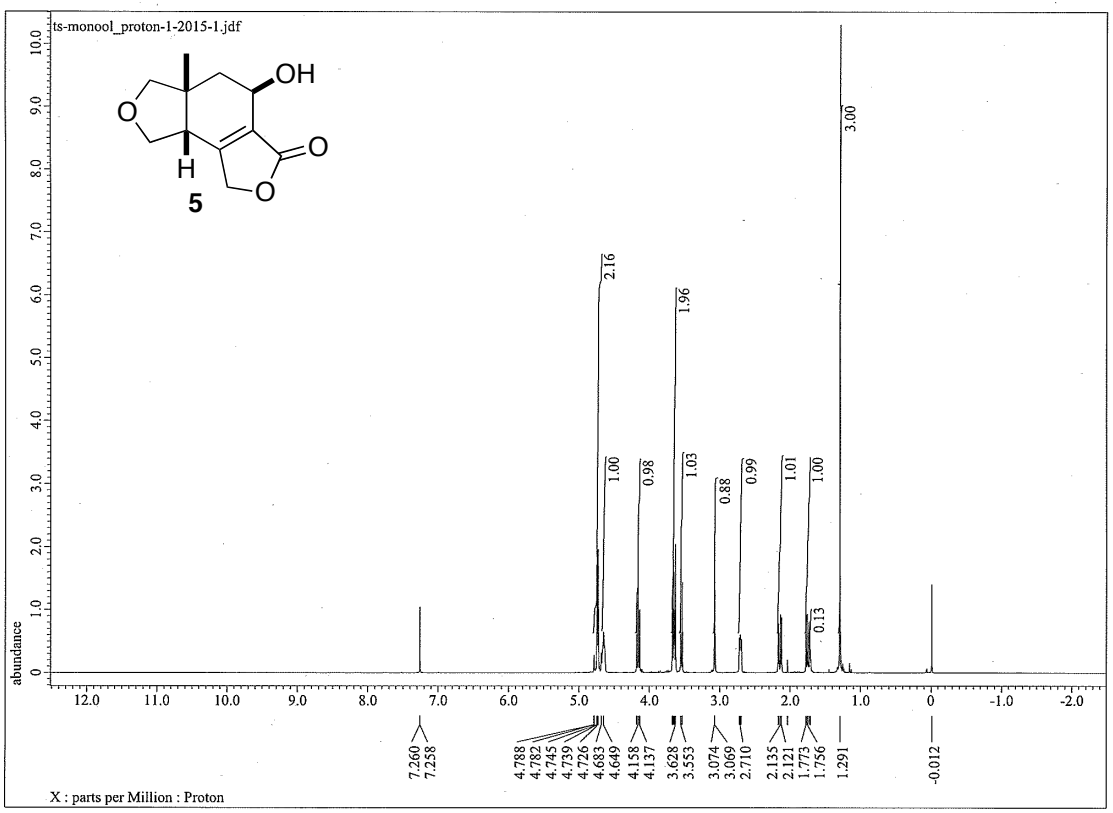

ts-diene2_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13
167.464
148.948
142.159
125.550
114.118
80.814
77.315
77.000
76.676
72.071
68.304
67.427
51.590
44.106
33.217
21.881

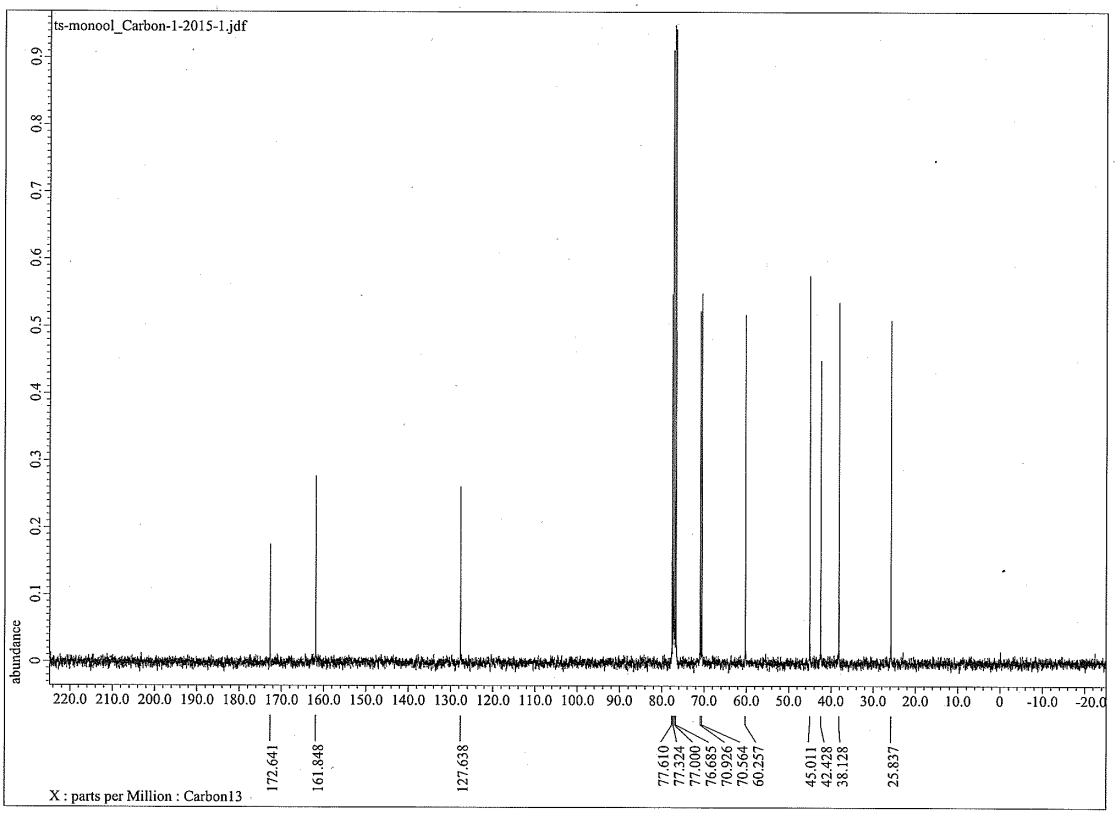

ts397-p_proton-2-2015-1.jdf
3
abundance
X : parts per Million : Proton
7.260
5.080
5.047
5.040
4.958
4.924
4.533
4.495
4.329
4.112
3.875
3.854
3.332
3.311
2.409
2.376
2.371
1.568
1.538
1.463
1.425
1.276
-0.004
2.90
0.95
0.99

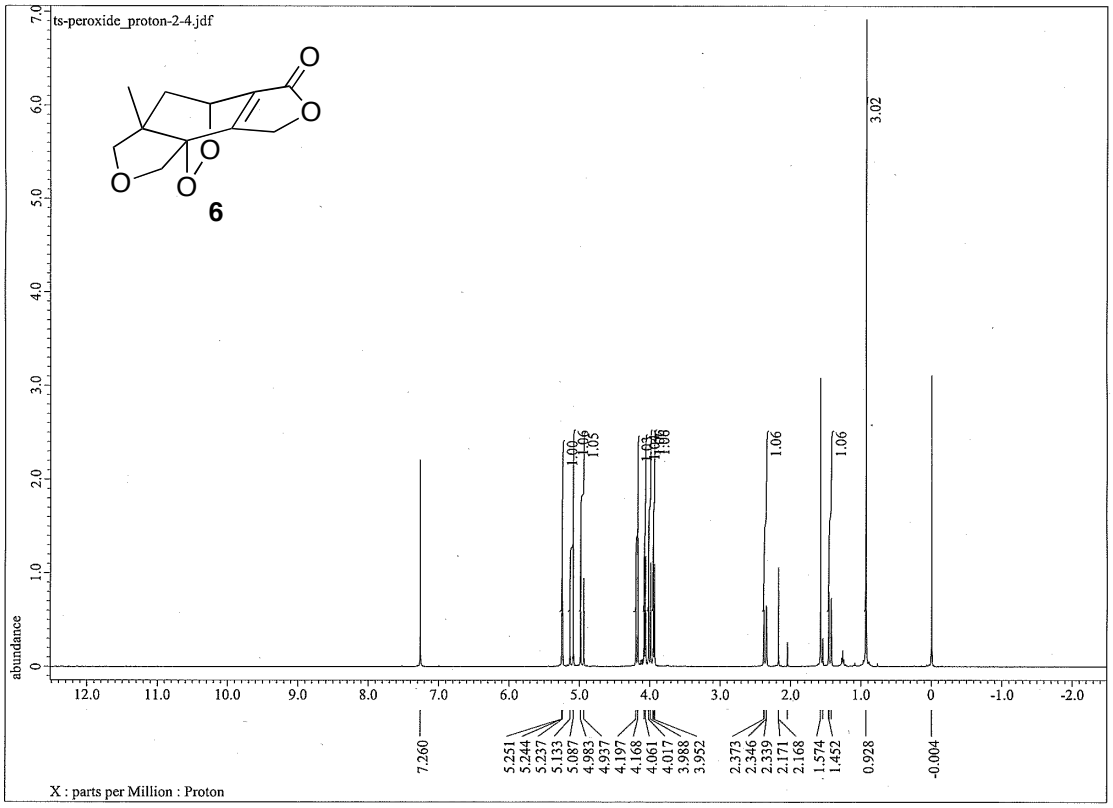

ts-397-p_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13
172.184
143.113
116.664
80.766
77.324
77.000
76.685
68.266
67.284
61.850
53.669
43.381
30.643
29.251

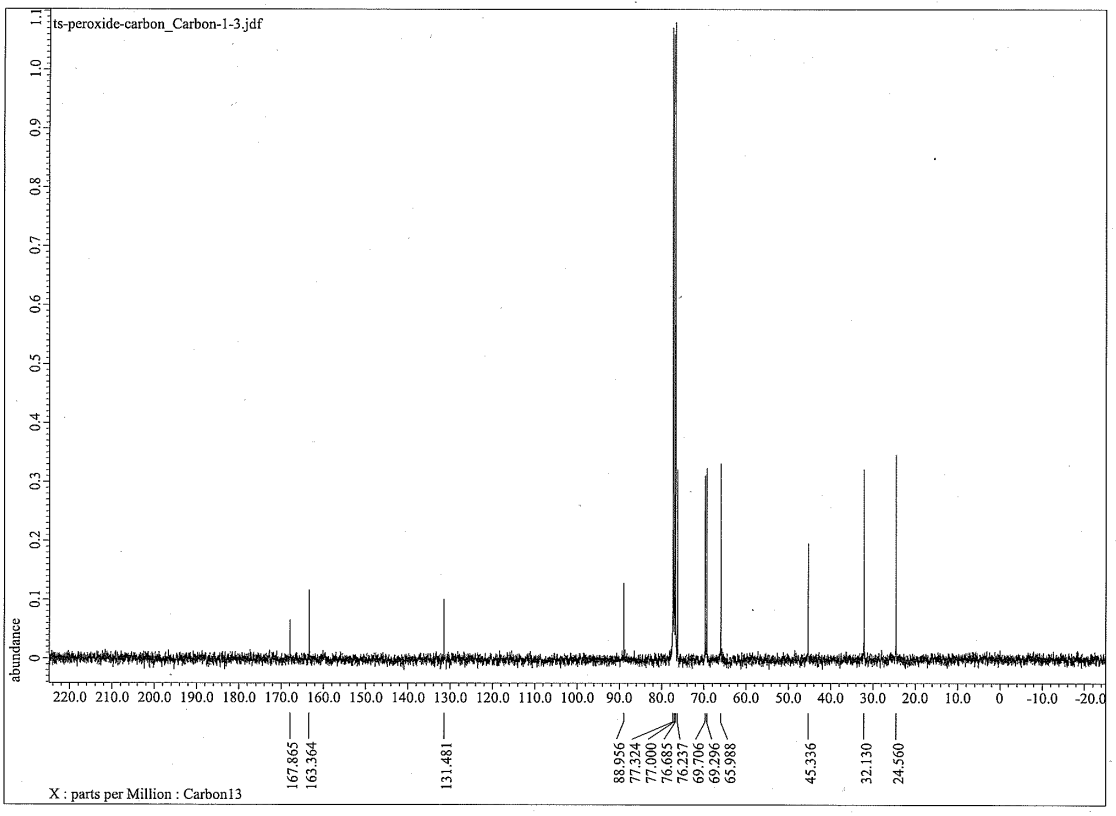

ts459-p-re_proton-1-2015-1.jdf
OH
OH
O
O
O
4
abundance
X : parts per Million : Proton
7.260
4.931
4.899
4.895
4.731
4.700
4.450
4.415
4.297
4.261
3.781
3.762
3.725
3.377
3.357
3.246
1.963
1.945
1.928
1.759
1.732
1.724
1.696
1.318
-0.007
1.00
0.98
0.98
0.98
1.92
1.03
1.01
0.90
0.99
1.02
2.80

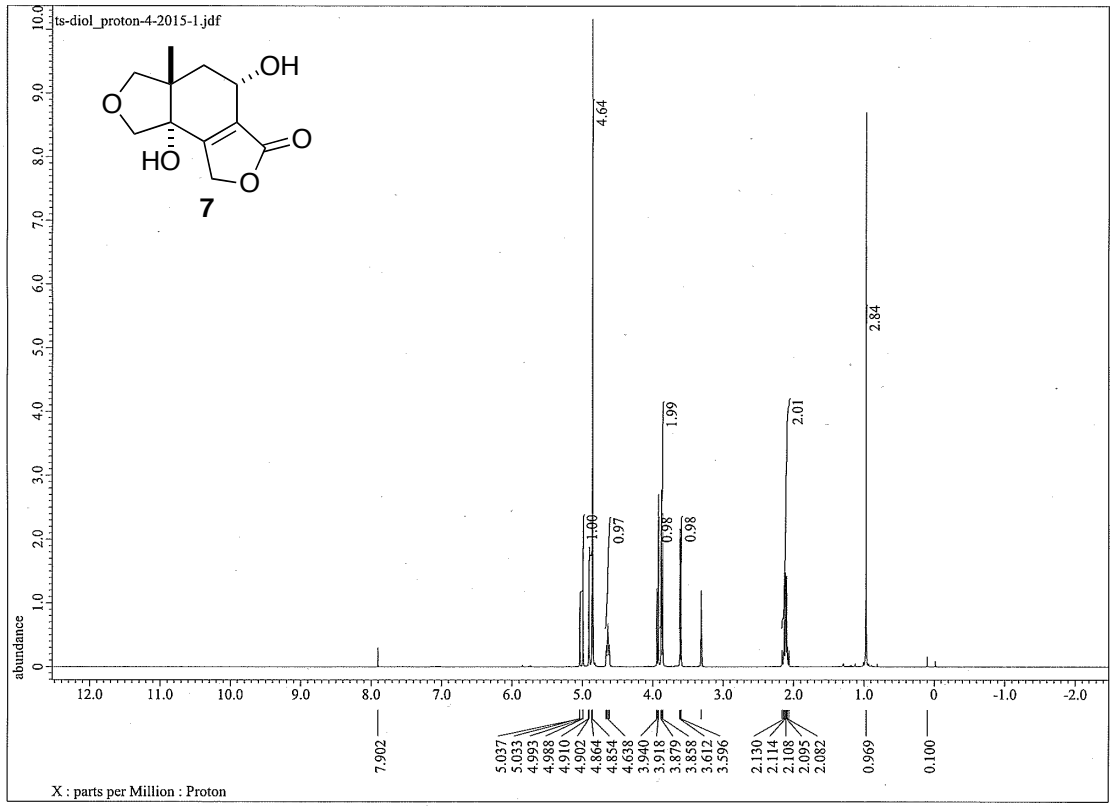

ts459-p-re_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13
177.676
145.639
120.592
77.648
77.324
77.000
76.685
69.401
68.743
68.533
65.740
43.476
30.452
27.725

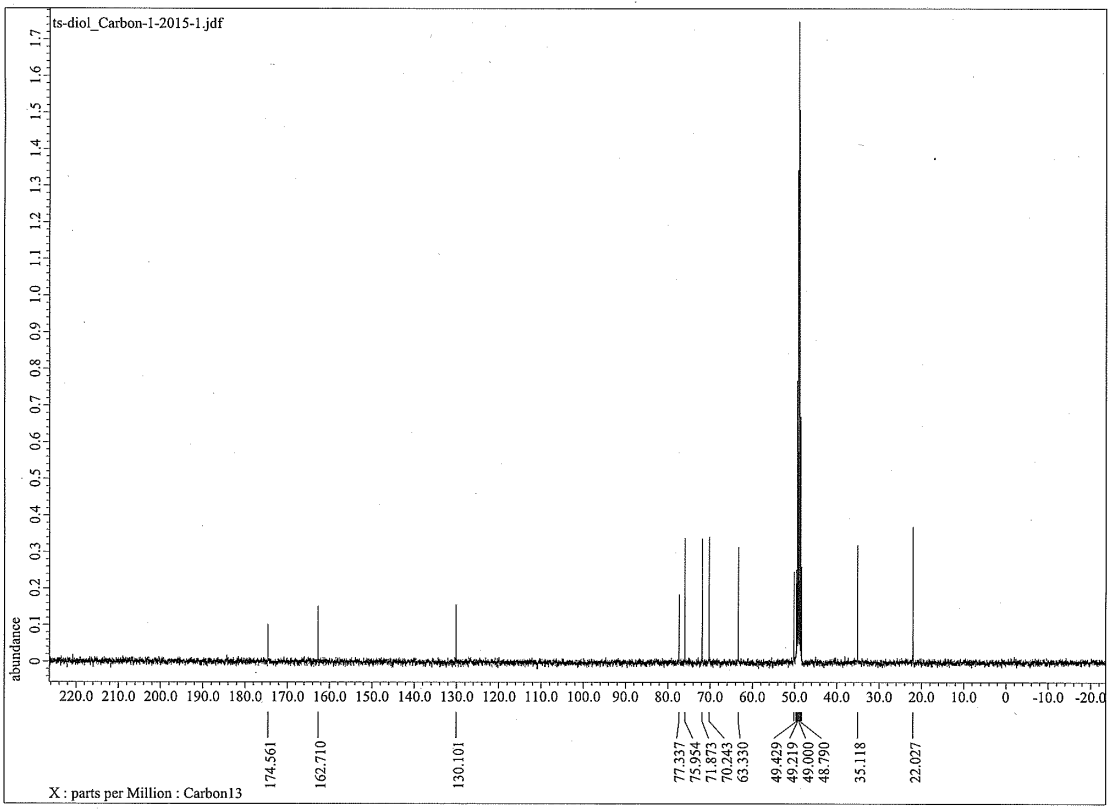

ts-monool_proton-1-2015-1.jdf
OH
O
O
H
O
5
abundance
2.16
1.96
3.00
1.00
0.98
1.03
0.88
0.99
1.01
1.00
0.13
7.260
7.258
4.788
4.782
4.745
4.739
4.726
4.683
4.649
4.158
4.137
3.628
3.553
3.074
3.069
2.710
2.135
2.121
1.773
1.756
1.291
-0.012
X : parts per Million : Proton

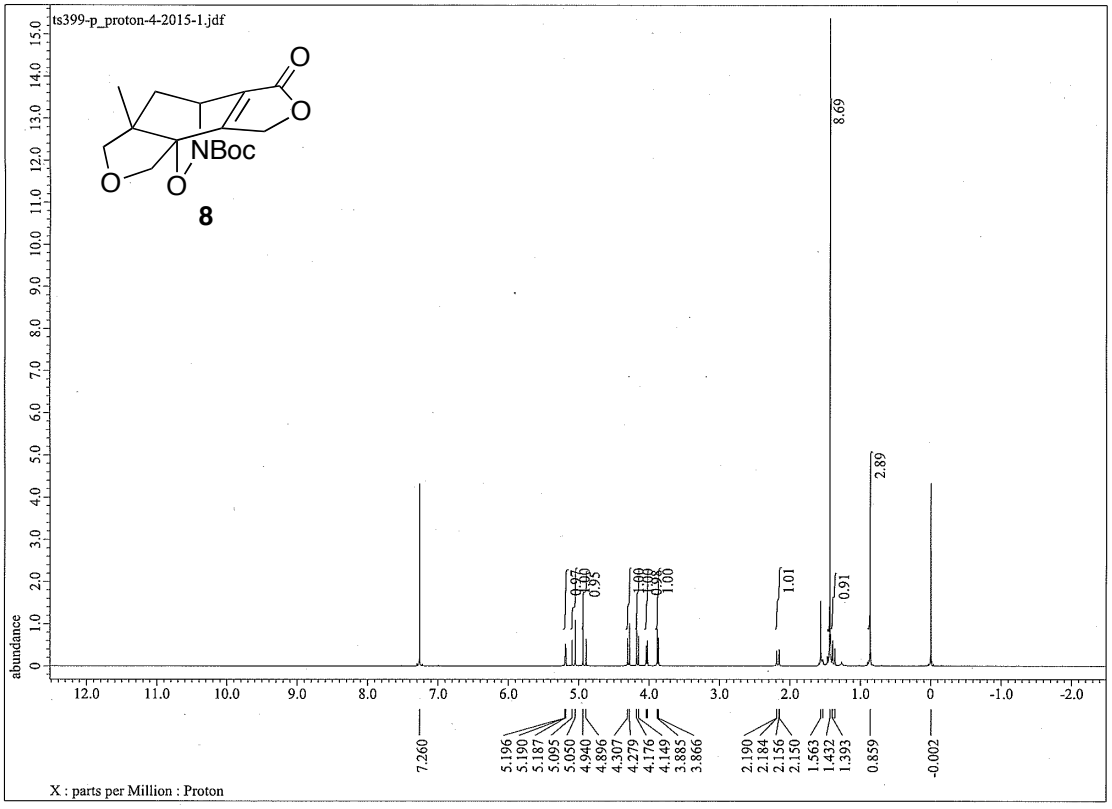

ts-monool_Carbon-1-2015-1.jdf
abundance
172.641
161.848
127.638
77.610
77.324
77.000
76.685
70.926
70.564
60.257
45.011
42.428
38.128
25.837
X : parts per Million : Carbon13

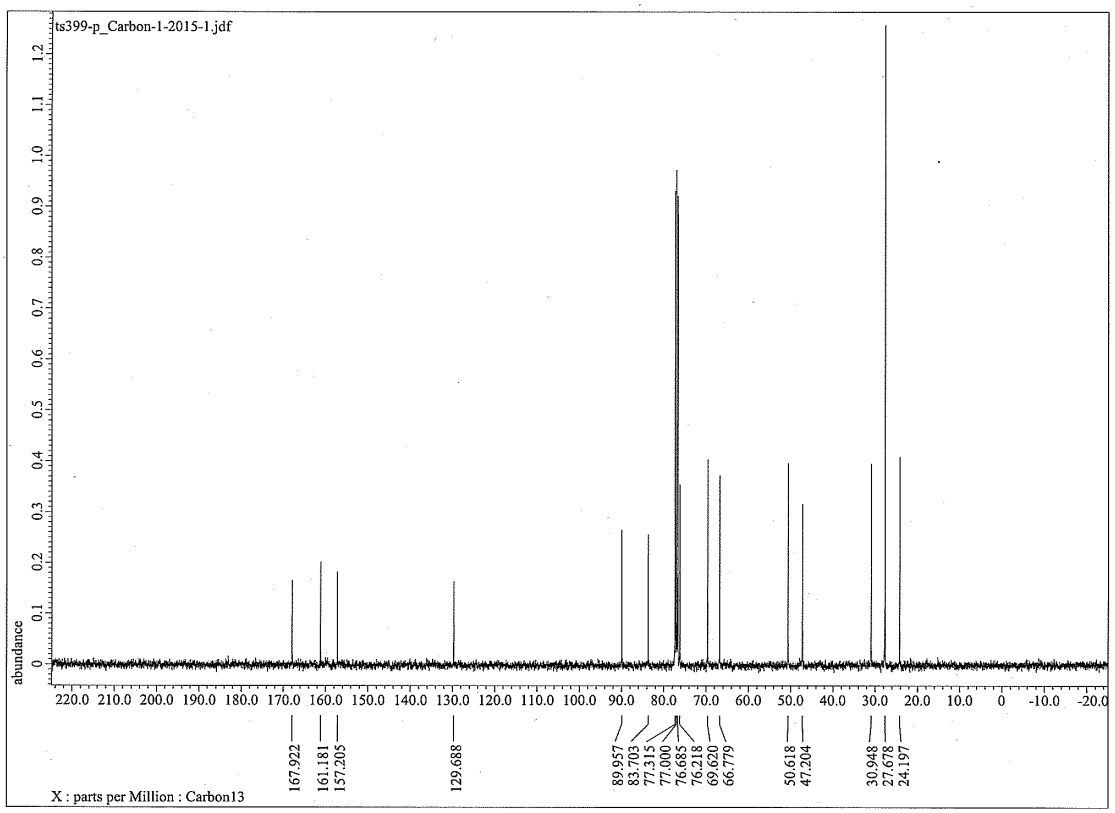

ts-peroxide_proton-2-4.jdf
6
abundance
X : parts per Million : Proton
7.260
5.251
5.244
5.237
5.133
5.087
4.983
4.937
4.197
4.168
4.061
4.017
3.988
3.952
2.373
2.346
2.339
2.171
2.168
1.574
1.452
0.928
-0.004
3.02
1.06
1.06

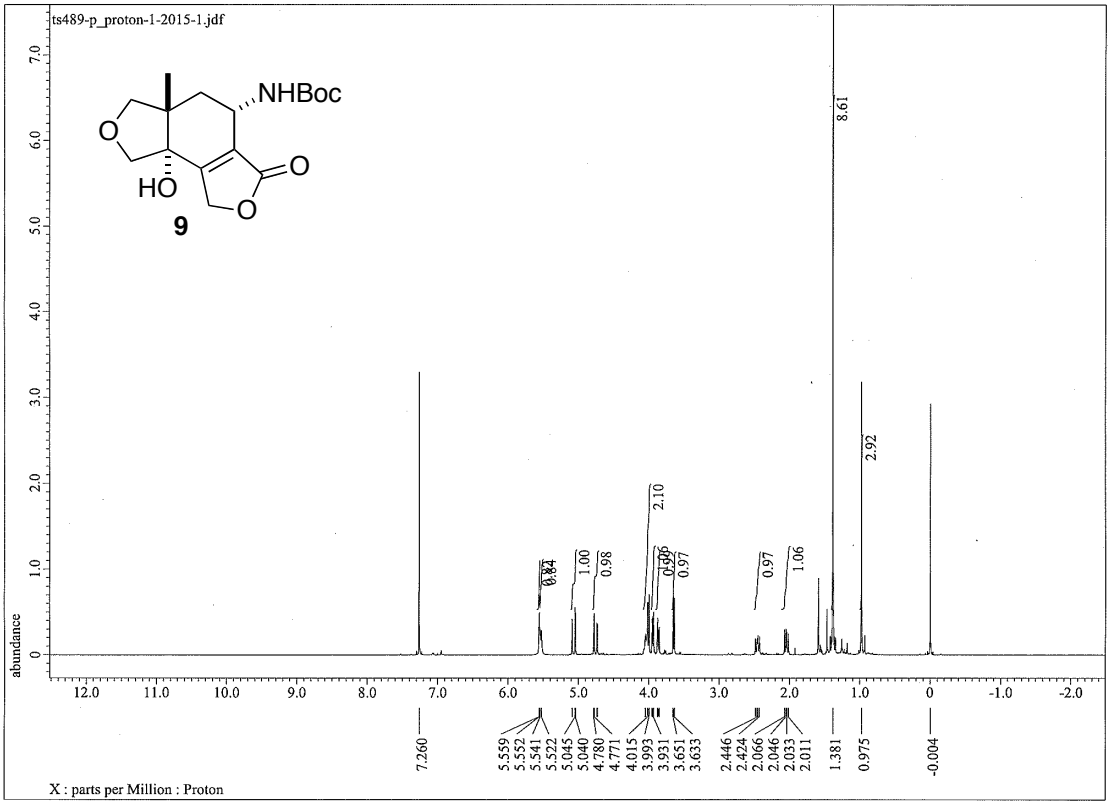

ts-peroxide-carbon_Carbon-1-3.jdf
abundance
X : parts per Million : Carbon13
167.865
163.364
131.481
88.956
77.324
77.000
76.685
76.237
69.706
69.296
65.988
45.336
32.130
24.560

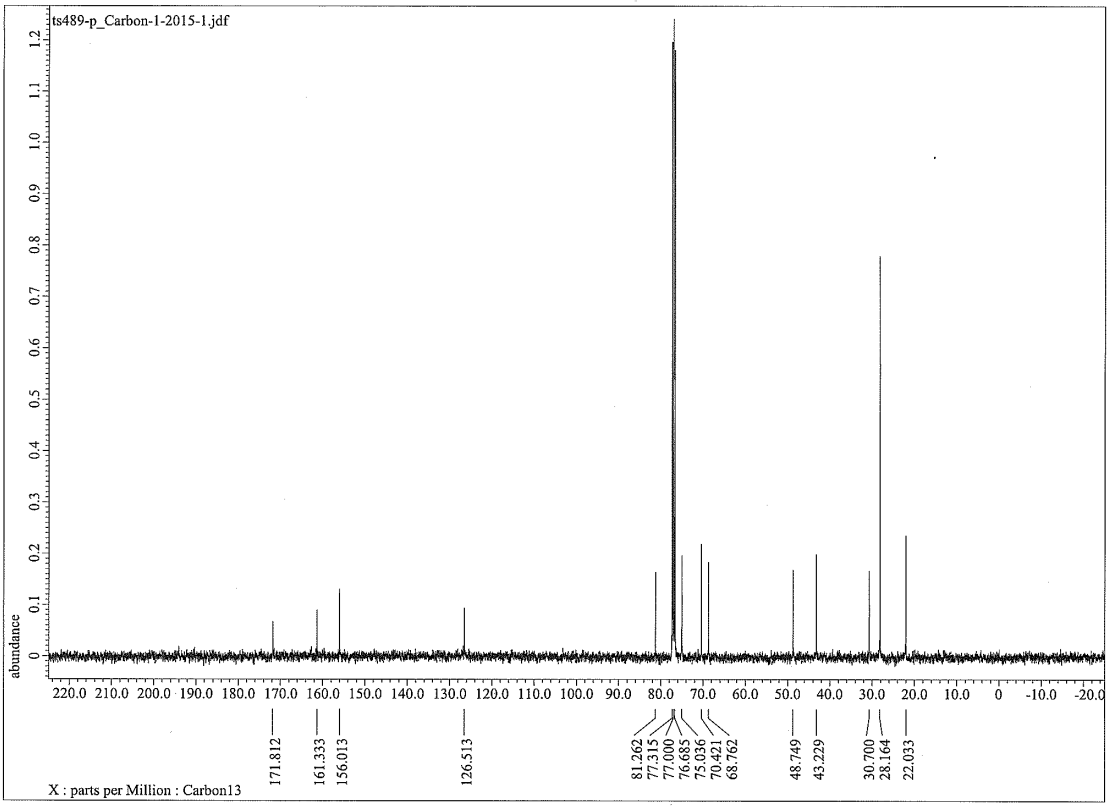

ts-diol_proton-4-2015-1.jdf
OH
O
HO
O
O
7
4.64
2.84
2.01
1.99
1.00
0.97
0.98
0.98
abundance
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.902
5.037 5.033 4.993 4.988 4.910 4.902 4.864 4.854 4.638 3.940 3.918 3.879 3.858 3.612 3.596
2.130 2.114 2.108 2.095 2.082
0.969
0.100
X : parts per Million : Proton

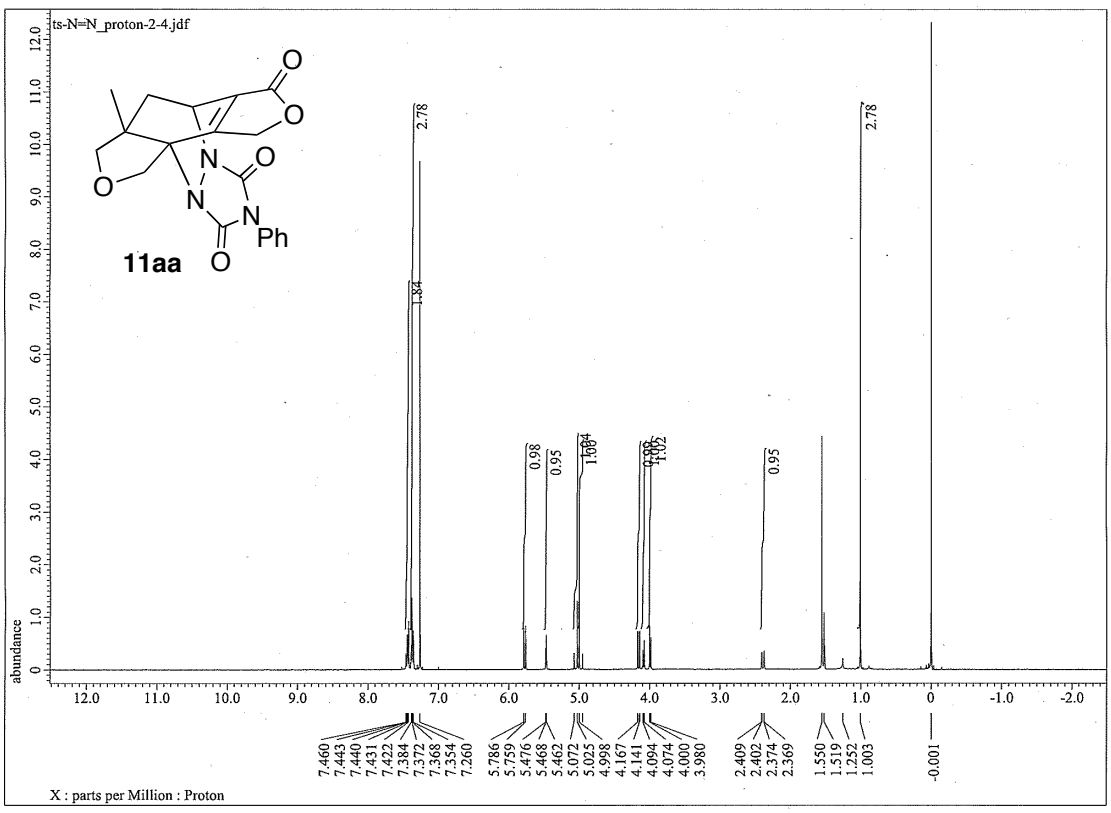

ts-diol_Carbon-1-2015-1.jdf
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
174.561
162.710
130.101
77.337 75.954 71.873 70.243 63.330
49.429 49.219 49.000 48.790
35.118
22.027
X : parts per Million : Carbon13

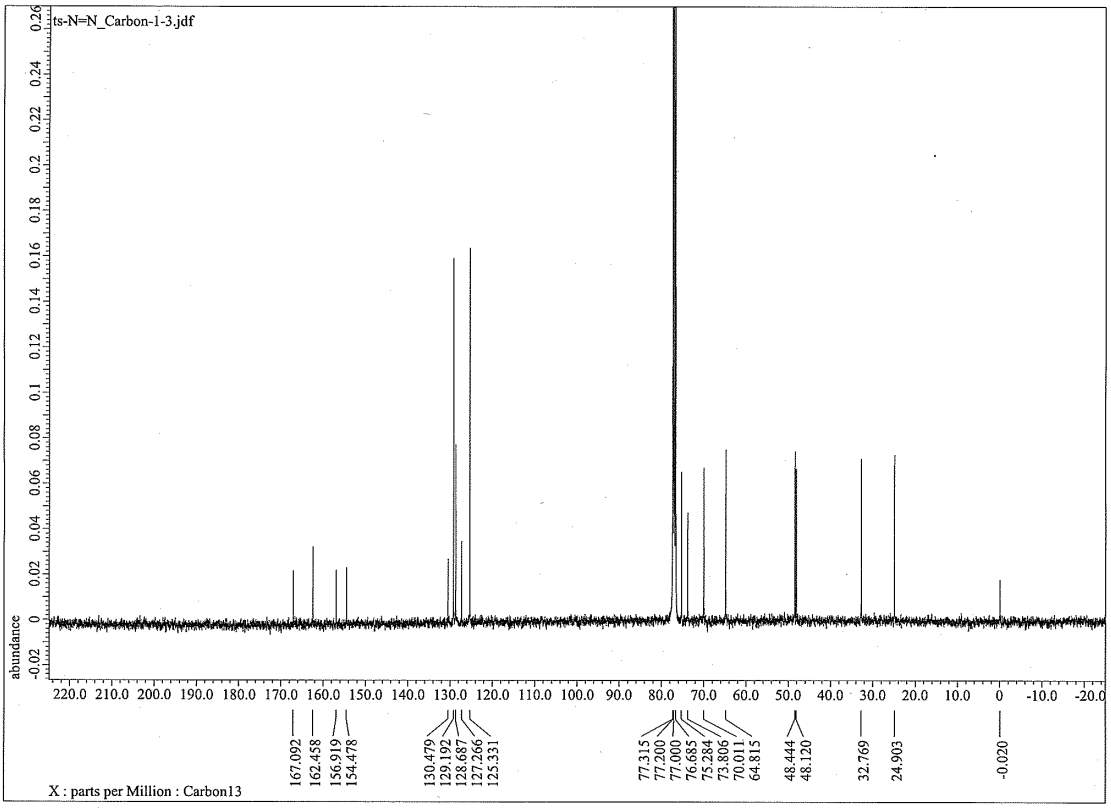

ts399-p_proton-4-2015-1.jdf
O
O
NBoc
O
O
8
abundance
X : parts per Million : Proton
7.260
5.196
5.190
5.187
5.095
5.050
4.940
4.896
4.307
4.279
4.176
4.149
3.885
3.866
2.190
2.184
2.156
2.150
1.563
1.432
1.393
0.859
-0.002
8.69
2.89
1.01
0.91

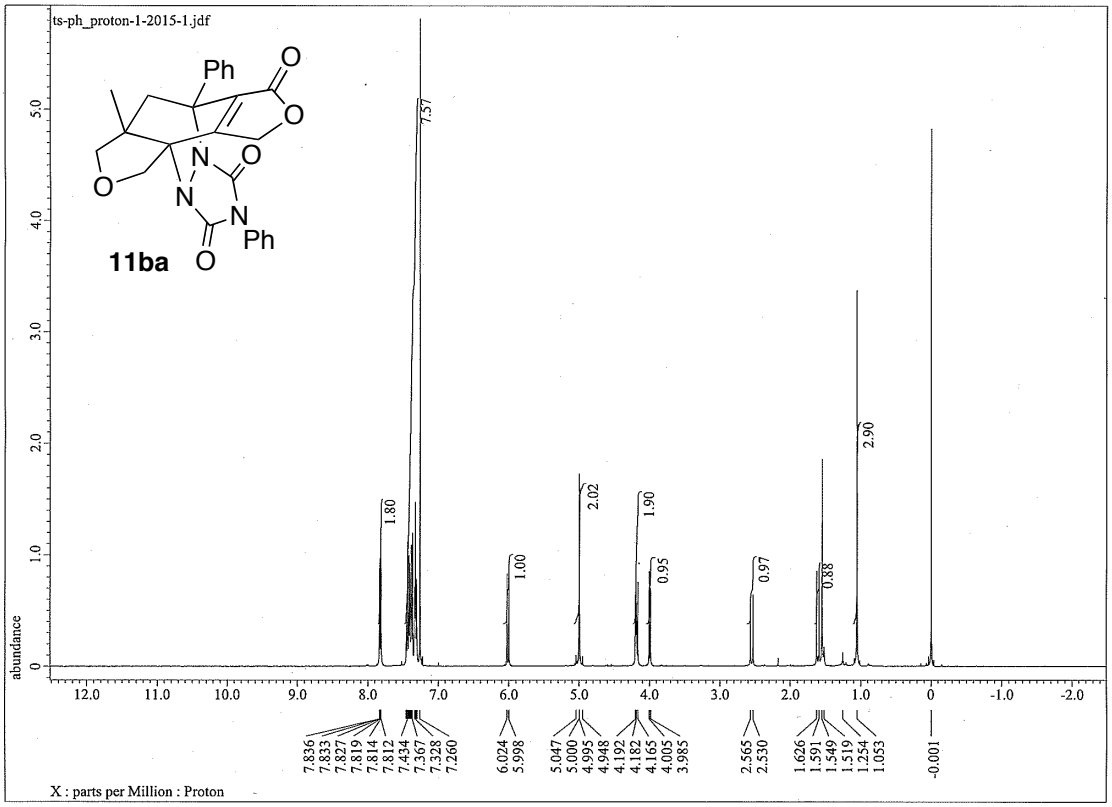

ts399-p_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13
167.922
161.181
157.205
129.688
89.957
83.703
77.315
77.000
76.685
76.218
69.620
66.779
50.618
47.204
30.948
27.678
24.197

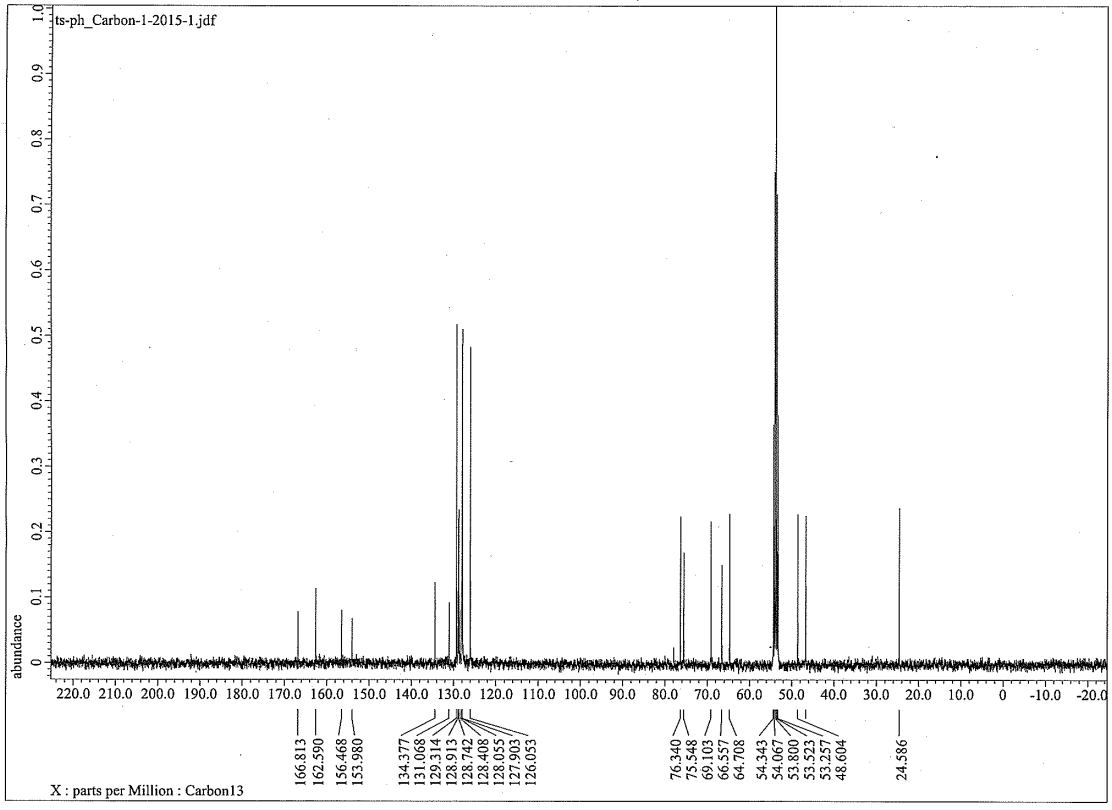

ts489-p_proton-1-2015-1.jdf
NHBoc
O
HO
O
O
9
abundance
8.61
2.92
2.10
1.00
0.98
0.97
0.97
1.06
7.260
5.559
5.552
5.541
5.522
5.045
5.040
4.780
4.771
4.015
3.993
3.931
3.651
3.633
2.446
2.424
2.066
2.046
2.033
2.011
1.381
0.975
-0.004
X : parts per Million : Proton

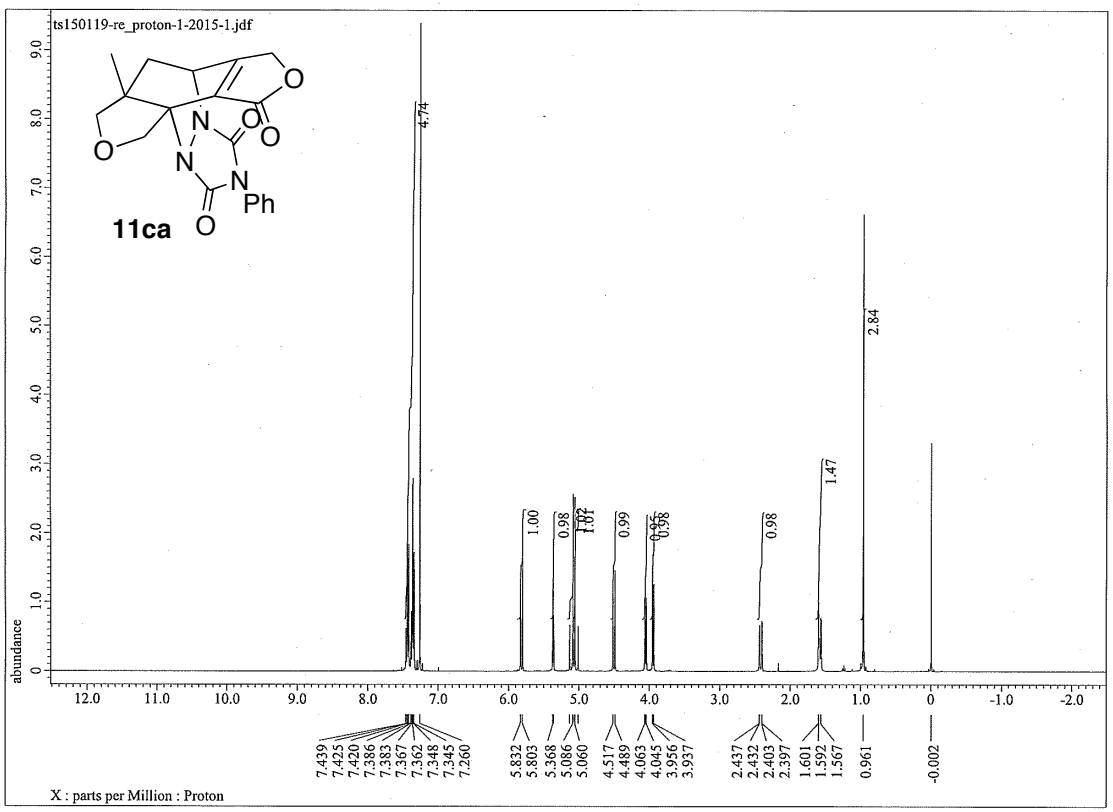

ts489-p_Carbon-1-2015-1.jdf
abundance
171.812
161.333
156.013
126.513
81.262
77.315
77.000
76.685
75.036
70.421
68.762
48.749
43.229
30.700
28.164
22.033
X : parts per Million : Carbon13

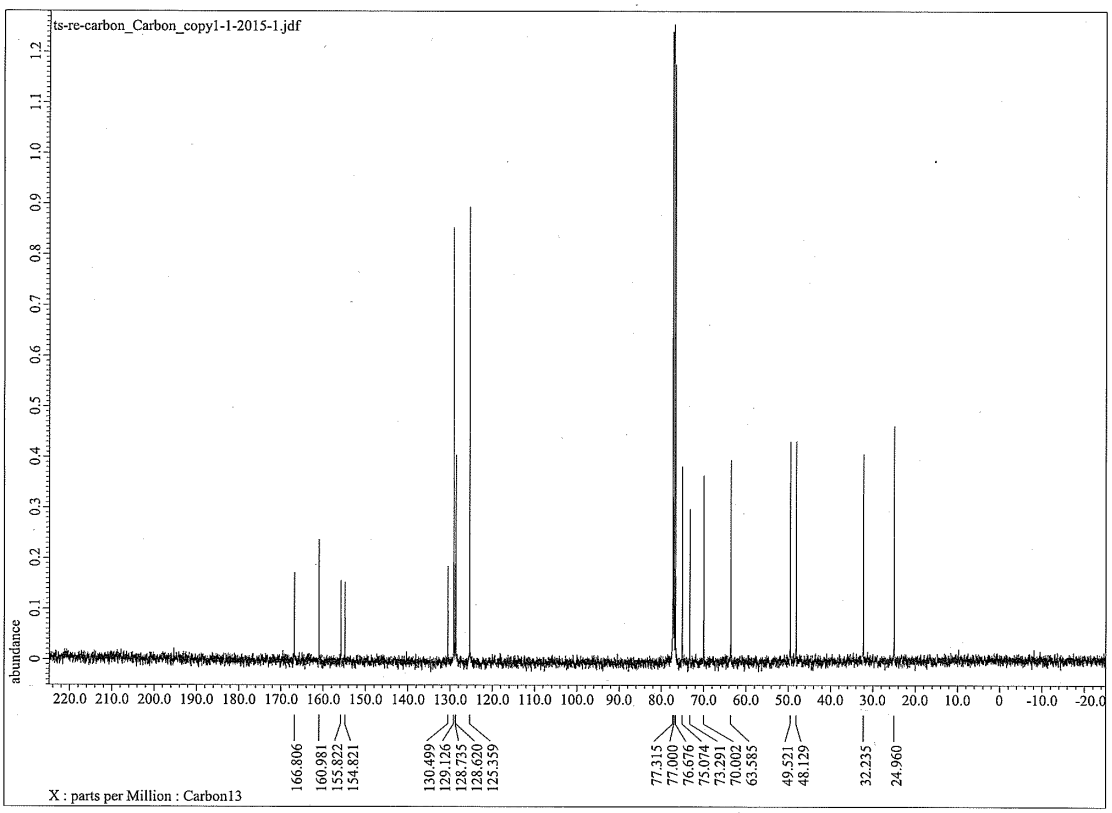

ts-N=N_proton-2-4.jdf
11aa
abundance
X : parts per Million : Proton

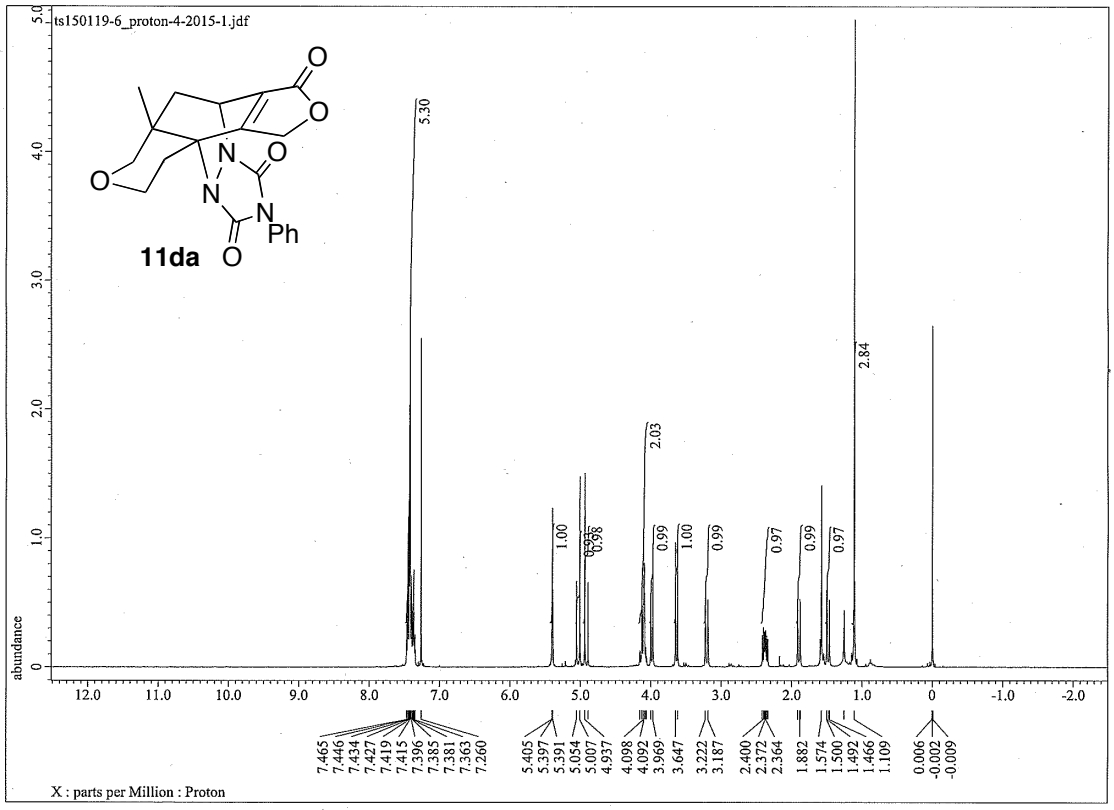

ts-N=N_Carbon-1-3.jdf
abundance
X : parts per Million : Carbon13

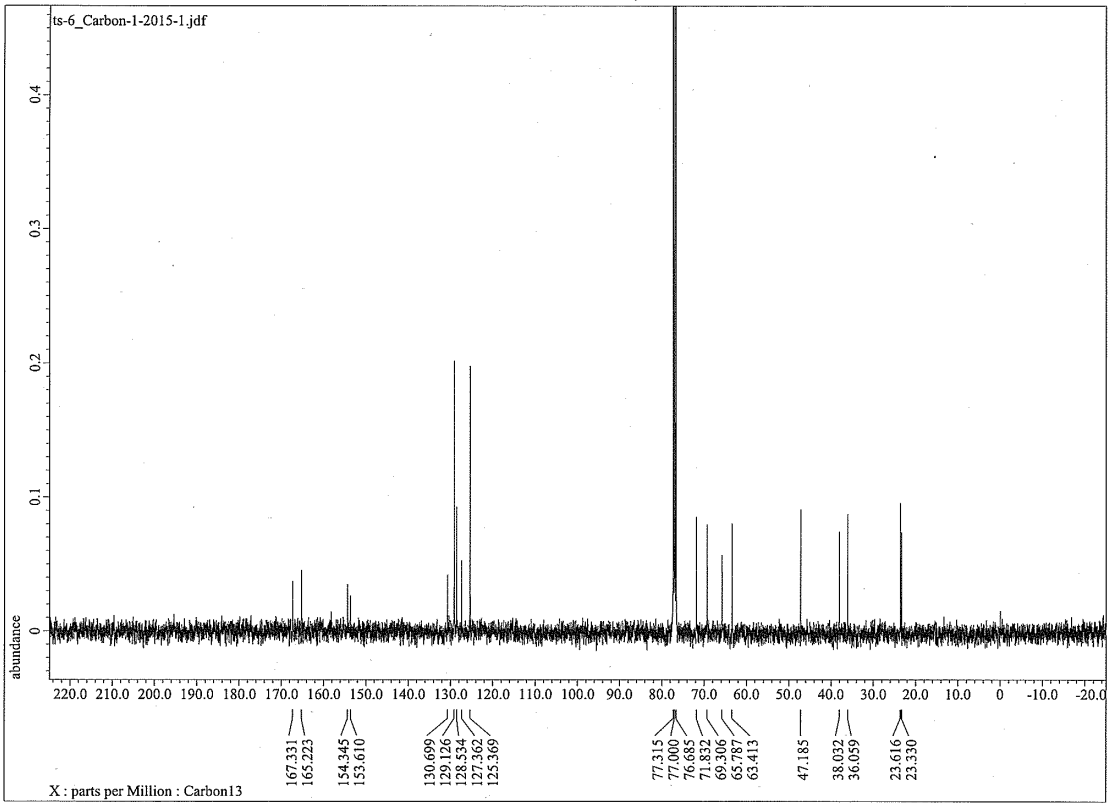

ts-ph_proton-1-2015-1.jdf
11ba
abundance
X : parts per Million : Proton

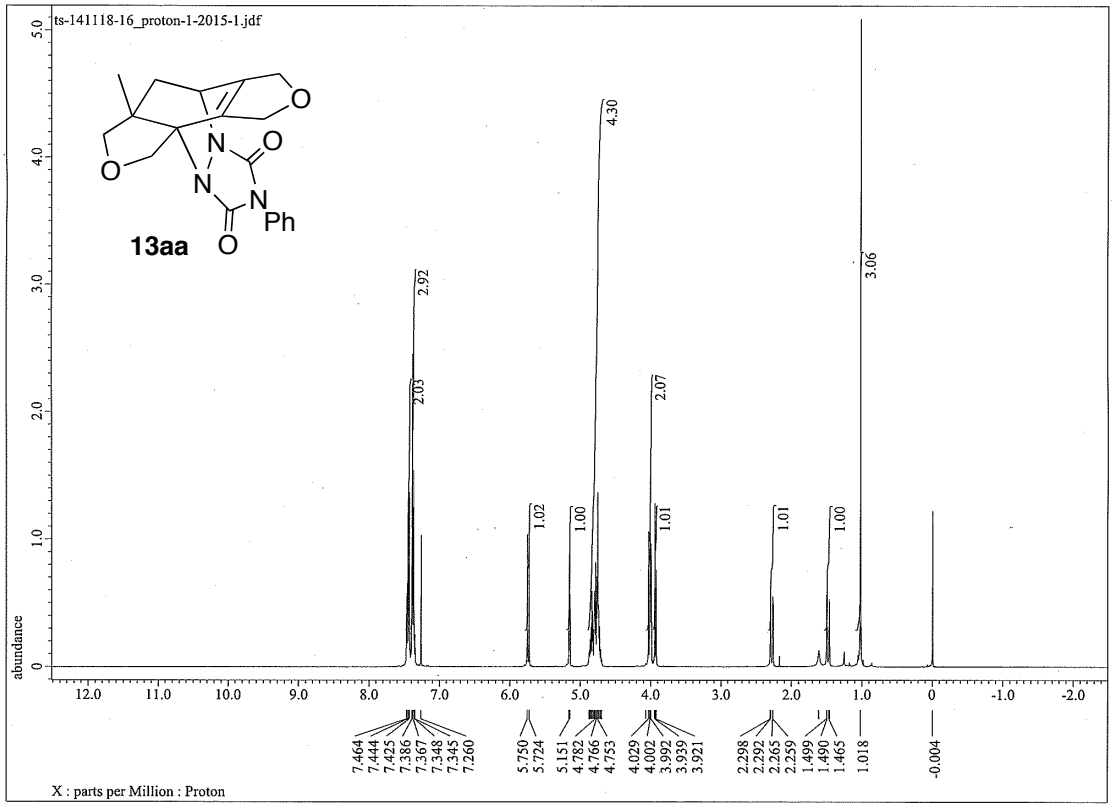

ts-ph_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13

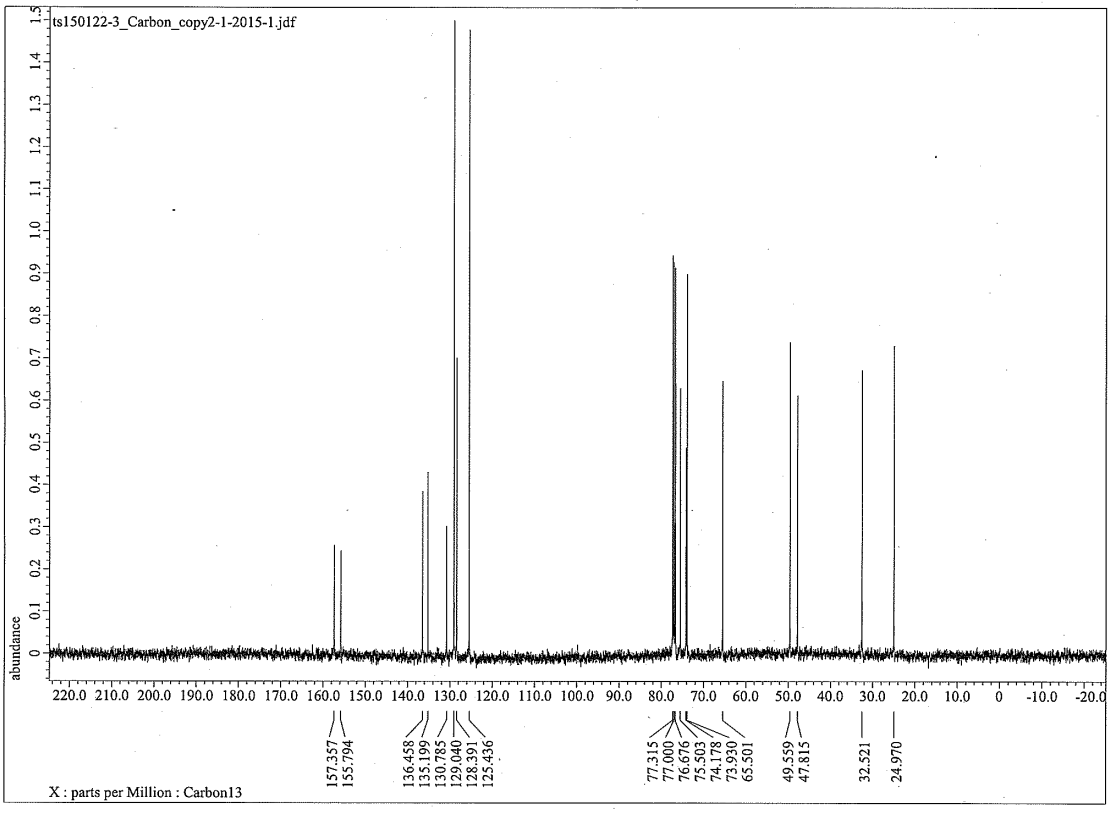

ts150119-re_proton-1-2015-1.jdf
11ca
abundance
X : parts per Million : Proton

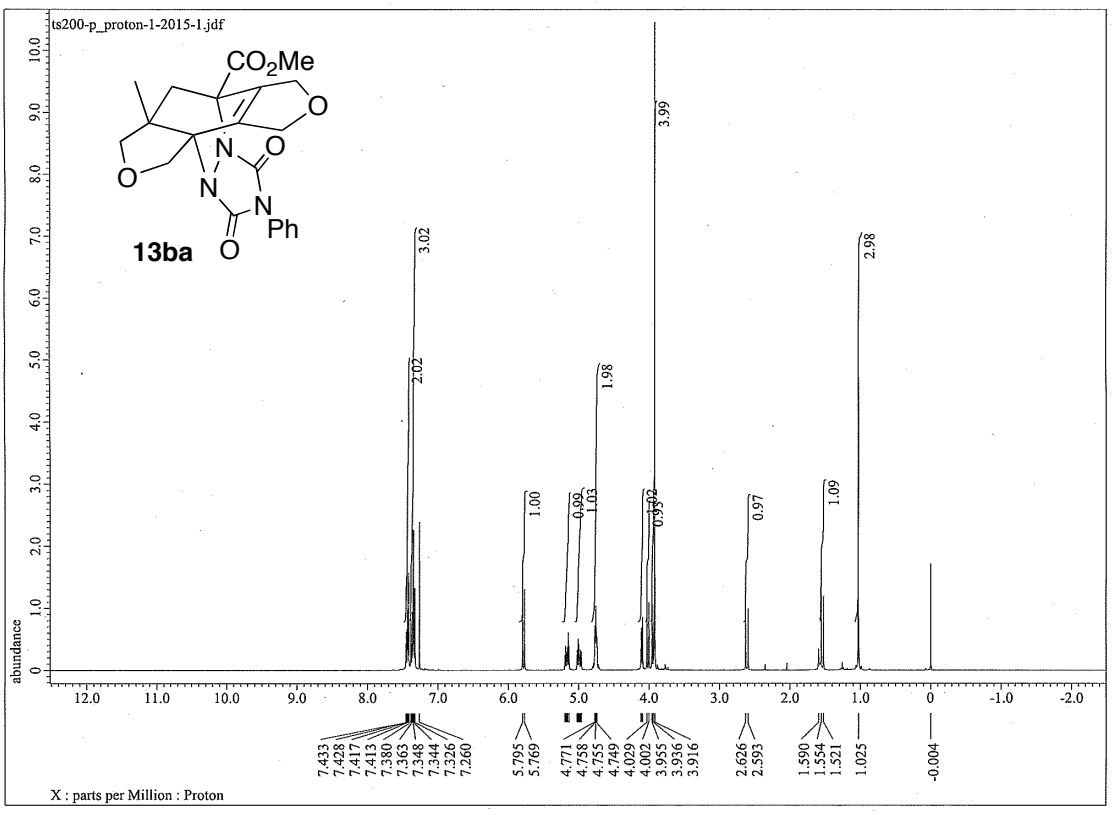

ts-re-carbon_Carbon_copy1-1-2015-1.jdf
abundance
X : parts per Million : Carbon13

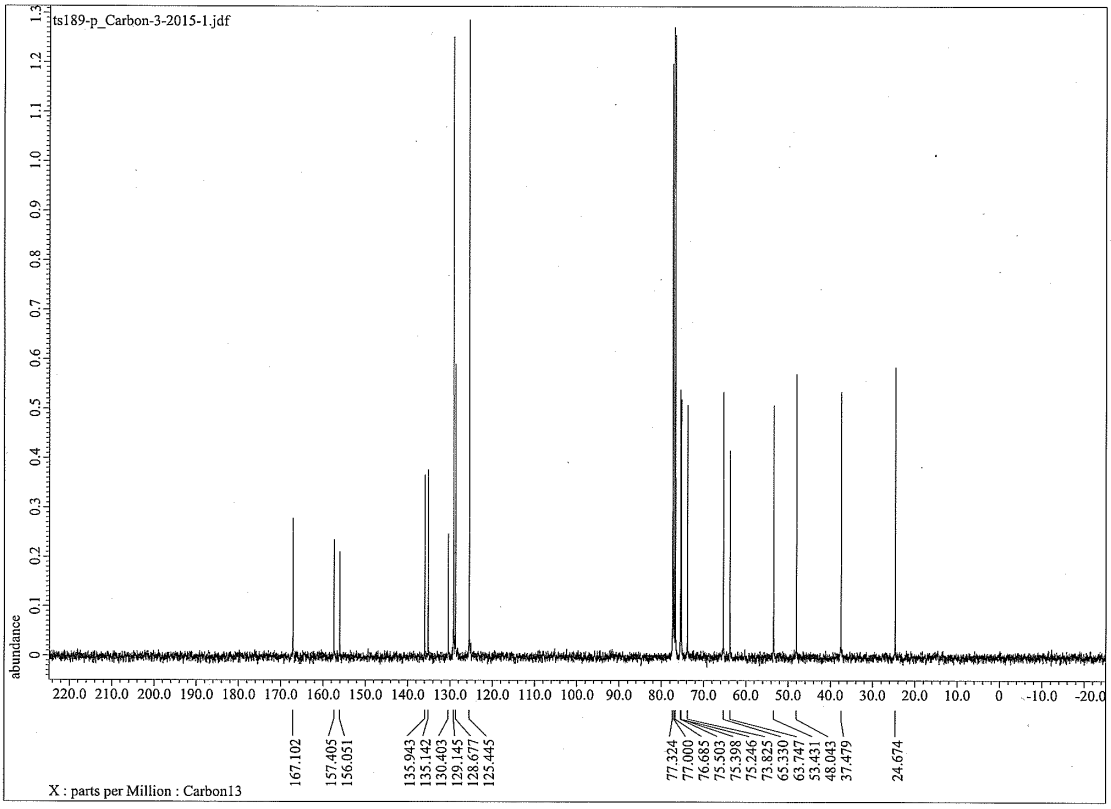

ts150119-6_proton-4-2015-1.jdf
11da
abundance
X : parts per Million : Proton


ts-6_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13

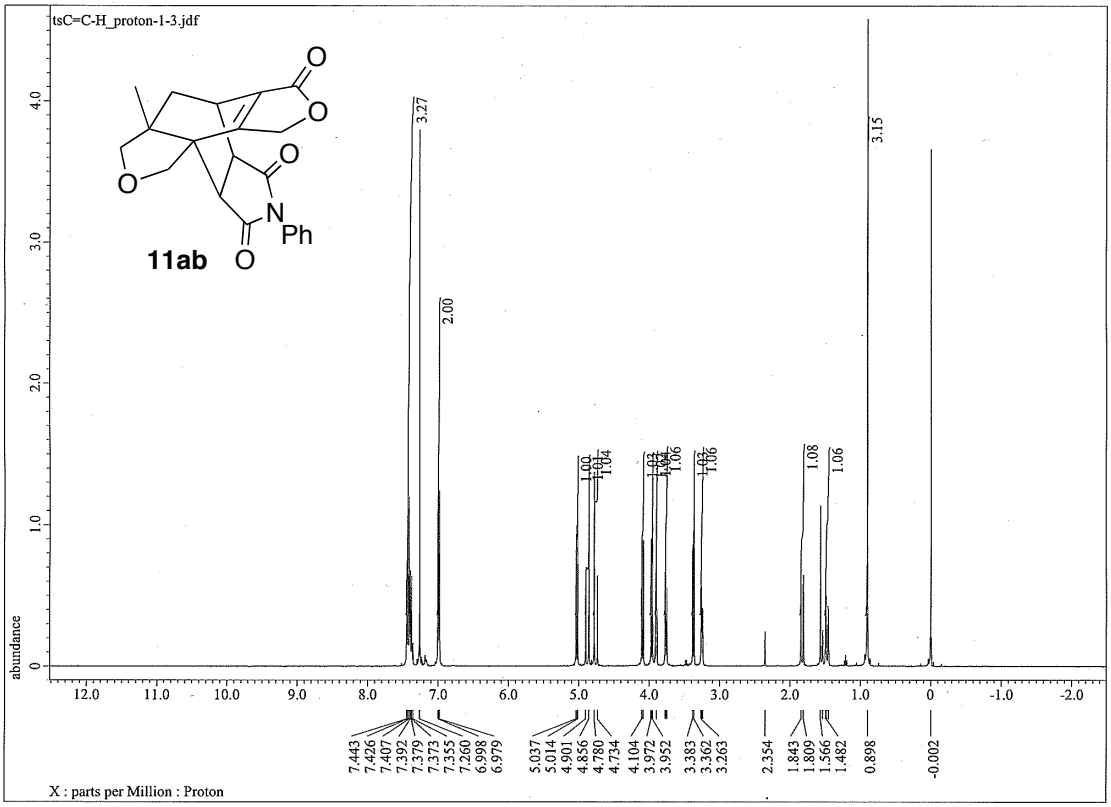

ts-141118-16_proton-1-2015-1.jdf
13aa
abundance
X : parts per Million : Proton

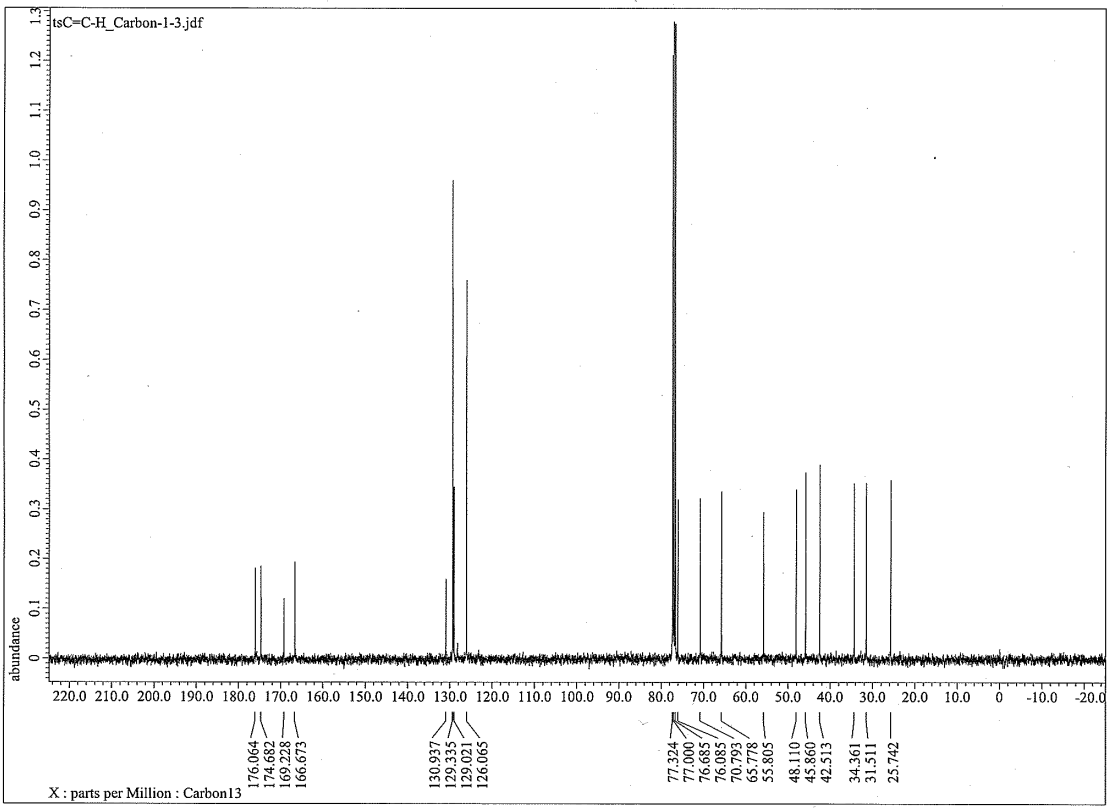

ts150122-3_Carbon_copy2-1-2015-1.jdf
abundance
X : parts per Million : Carbon13

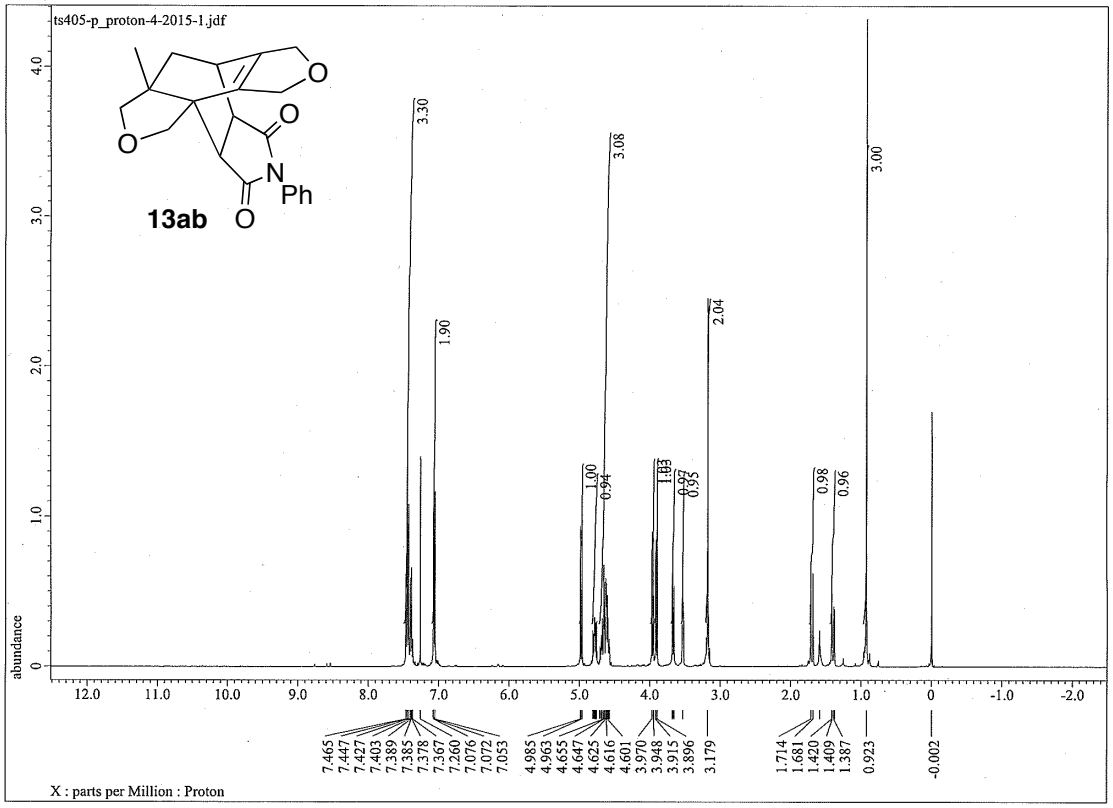

ts200-p_proton-1-2015-1.jdf
CO2Me
O
N
O
N
N
Ph
O
O
13ba
3.99
3.02
2.98
2.02
1.98
1.00
1.09
0.97
1.03
0.99
0.92
abundance
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.433 7.428 7.417 7.413 7.380 7.363 7.348 7.344 7.326 7.260
5.795 5.769
4.771 4.758 4.755 4.749
4.029 4.002 3.955 3.936 3.916
2.626 2.593
1.590 1.554 1.521
1.025
-0.004
X : parts per Million : Proton

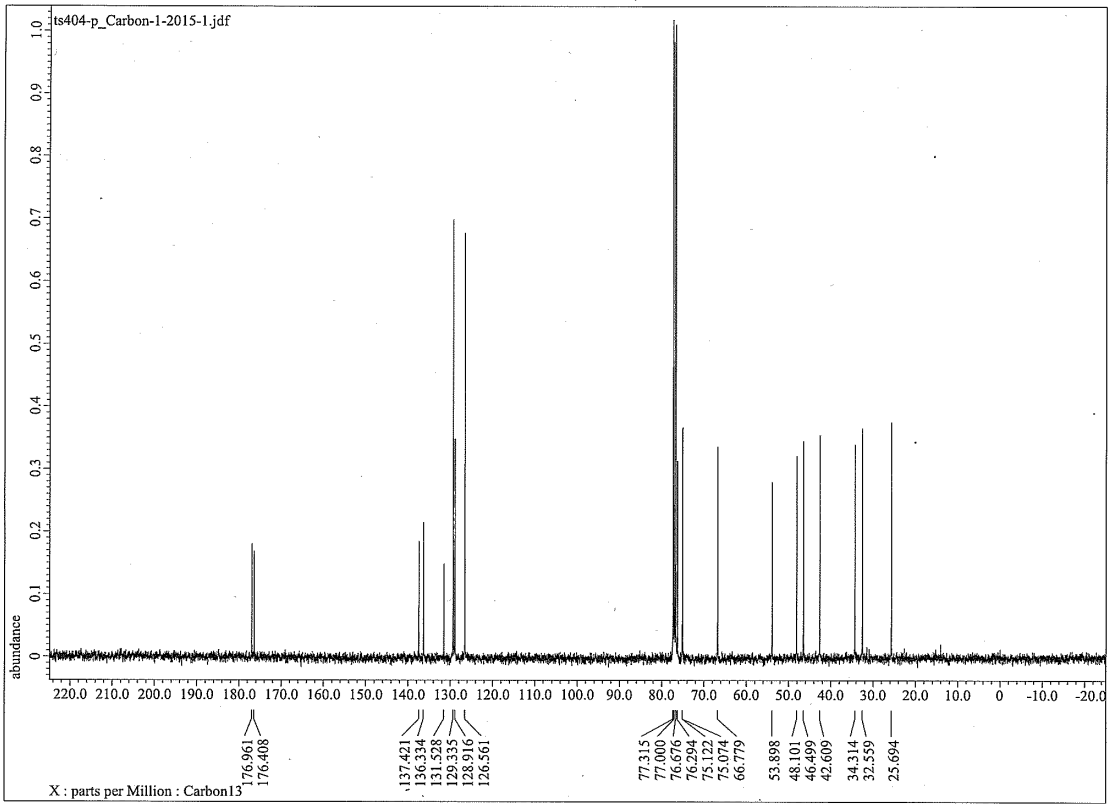

ts189-p_Carbon-3-2015-1.jdf
abundance
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.102
157.405
156.051
135.943
135.142
130.403
129.145
128.677
125.445
77.324
77.000
76.685
75.503
75.398
75.246
73.825
65.330
63.747
53.431
48.043
37.479
24.674
X : parts per Million : Carbon13

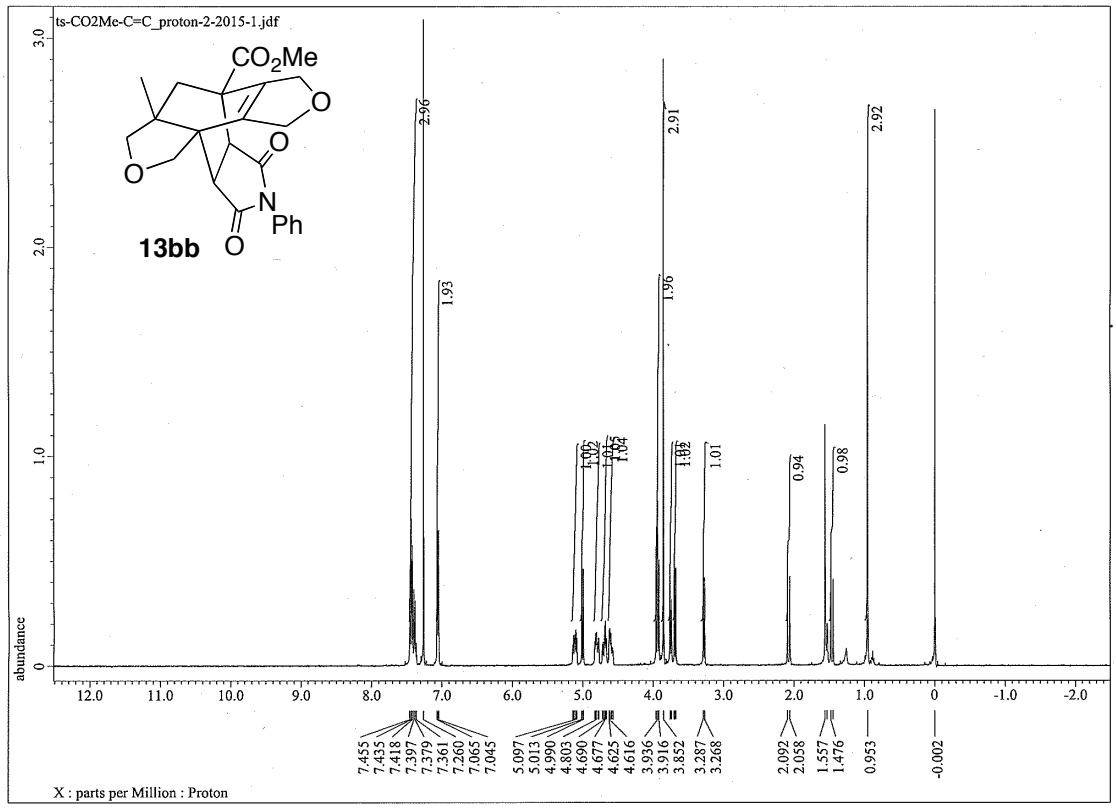
S

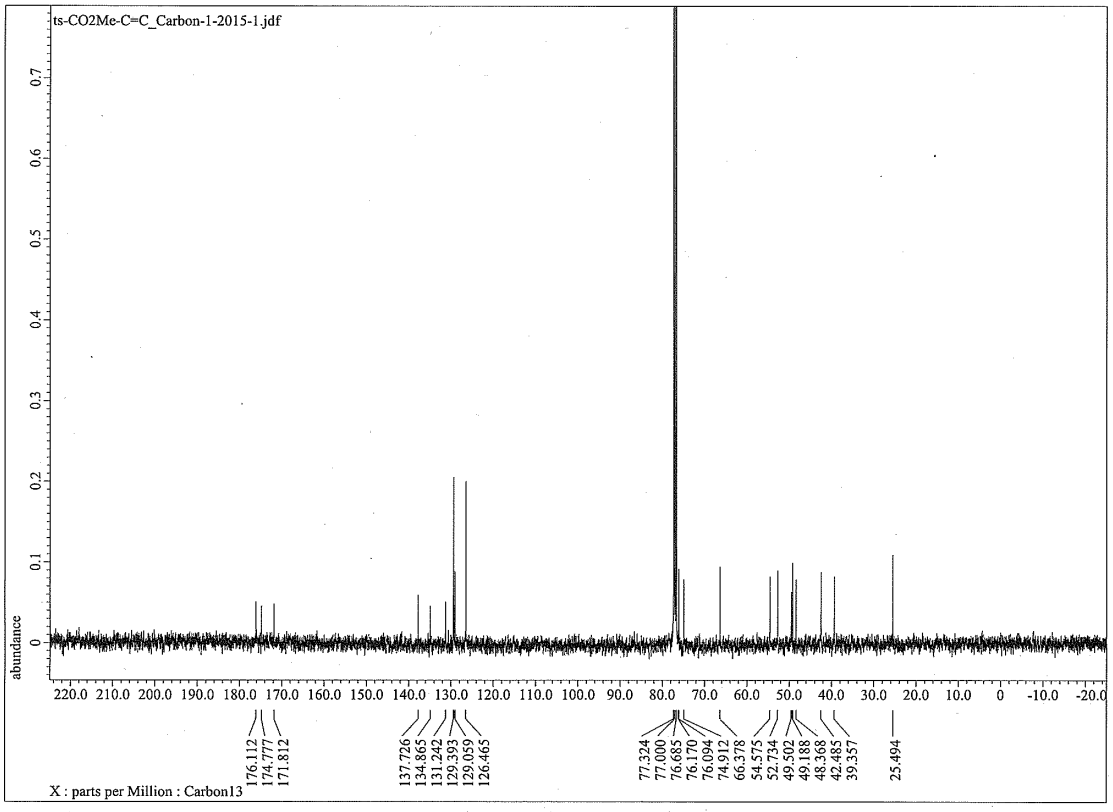

tsC=C-H_proton-1-3.jdf
11ab
abundance
X : parts per Million : Proton


tsC=C-H_Carbon-1-3.jdf
abundance
X : parts per Million : Carbon13


ts405-p_proton-4-2015-1.jdf
13ab
abundance
X : parts per Million : Proton


ts404-p_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13


ts-CO2Me-C=C_proton-2-2015-1.jdf
CO2Me
O
O
O
N
Ph
O
13bb
2.96
1.93
2.91
1.96
1.01
0.94
0.98
2.92
abundance
X : parts per Million : Proton


ts-CO2Me-C=C_Carbon-1-2015-1.jdf
abundance
X : parts per Million : Carbon13