An unexpected Ireland Claisen Rearrangement cascade during the synthesis of a tricyclic core of Curcusone C: Mechanistic elucidation by trial-and-error and automatic DFT computations

Chung Whan Lee,[†‖§] Buck L. H. Taylor,[‡▽§] Galina P. Petrova,[⊥] Ashay Patel,[‡#] Keiji Morokuma,[⊥] K. N. Houk,[‡*] Brian M. Stoltz[†*]

[†]*Warren and Katharine Schlinger Laboratory for Chemistry and Chemical Engineering, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States*

[‡]*Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, United States*

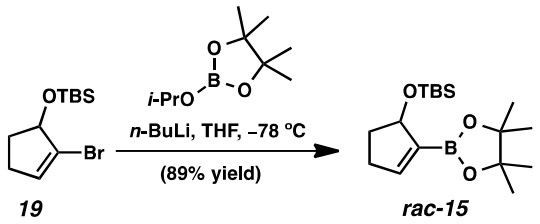
[§]*Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan*

Table of Contents

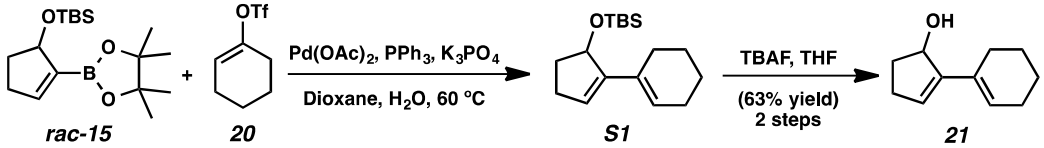
Materials and Methods

Unless stated otherwise, reactions were performed under an argon or nitrogen atmosphere using dry, deoxygenated solvents (distilled or passed over a column of activated alumina).[1] Et_3N, *i*-Pr_2NEt, *i*-Pr_2NH, pyridine, and *i*-PrOH were distilled from calcium hydride immediately prior to use. Commercially obtained reagents were used as received unless otherwise stated. *p*-ABSA,[2] $Cu(TBS)_2$,[3] and $MoCl_3(THF)_2$[4] were prepared by known methods. Reaction temperatures were controlled by an IKAmag temperature modulator. Microwave reactions were performed with a Biotage Initiator Eight 400 W apparatus at 2.45 GHz. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, or potassium permanganate, iodine, or anisaldehyde staining. Silia*Flash* P60 Academic Silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 600 (600 MHz and 151 MHz respectively), Varian Inova 500 (at 500 MHz and 126 MHz respectively), Bruker AV III HD spectrometer equipped with a Prodigy liquid nigrogen temperature cryoprobe (400 MHz and 101 MHz, respectively) and are reported relative to $CHCl_3$ (δ 7.26 & 77.16 respectively), C_6H_6 (δ 7.16 & 128.06 respectively), CH_2Cl_2 (δ 5.32 & 53.84 respectively), CH_3OH (δ 3.31 & 49.00 respectively) and $(CH_3)_2SO$ (δ 2.05 & 39.52 respectively). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). IR spectra were recorded on a Perkin Elmer Paragon 1000 Spectrometer and are reported in frequency of absorption (cm^{-1}). HRMS were acquired from the Caltech Mass Spectral Facility using a JEOL JMS-600H High Resolution Mass Spectrometer in fast atom bombardment (FAB+) or electron ionization (EI+) mode or using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) or mixed (MM) ionization mode. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path length cell at 589 nm.

Preparative Procedures



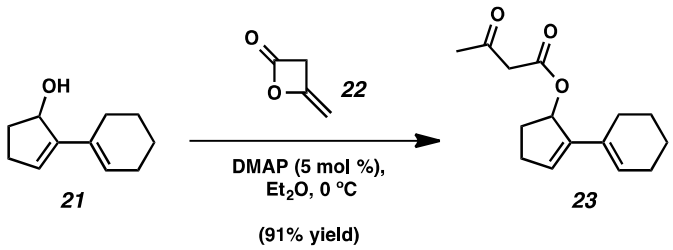
Vinylboronate *rac*-15: To a flame-dried round-bottom flask with a magnetic stir bar were added bromide **19** (440 mg, 1.59 mmol) and THF (6 mL). The flask was cooled to −78 ºC and stirred for 10 min. *n*-Butyllithium solution (2.1 M in hexanes, 0.95 mL, 2.00 mmol) was added dropwise. The reaction mixture was stirred at −78 ºC for 30 min then isopropyl pinacolyl borate (0.40 mL, 1.96 mmol) was added. The reaction mixture was stirred at −78 ºC for 30 min then quenched with HCl solution (2 N in Et_2O, 1.0 mL, 2.00 mmol). Following addition, the reaction mixture was diluted with Et_2O (10 mL) and warmed up to 23 ºC. The reaction mixture was filtered and was concentrated under reduced pressure. The residue was purified by flash column chromatography (20:1 hexanes, EtOAc) to afford vinylboronate *rac*-**15** as a colorless oil (460 mg, 1.42 mmol, 89% yield); R_f = 0.60; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (td, *J* = 2.4, 1.0 Hz, 1H), 5.00 (dddt, *J* = 6.1, 3.9, 2.1, 1.1 Hz, 1H), 2.56 (dddt, *J* = 17.8, 8.9, 4.6, 2.3 Hz, 1H), 2.34–2.20 (m, 1H), 2.20–2.08 (m, 1H), 1.75–1.65 (m, 1H), 1.25 (d, *J* = 1.6 Hz, 12H), 0.89 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 83.1, 80.0, 34.7, 33.0, 26.1, 25.1, 25.0, 18.5, 14.1, –4.6; IR (Neat Film, NaCl) 3040, 2978, 2929, 2856, 2708, 1622, 1472, 1409, 1372, 1318, 1249, 1214, 1146, 1060, 1005, 964, 952, 936, 875, 855 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{17}H_{32}SiO_3B$ $[M+H–H_2]^+$: 323.2214, found 323.2222.



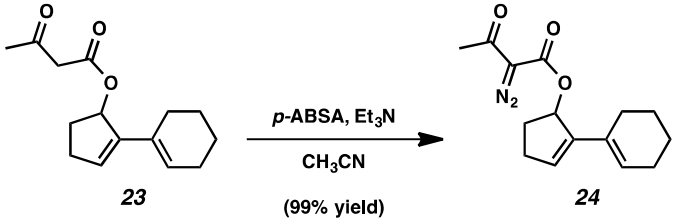
Diene 21: To a flame-dried round-bottom flask equipped with a magnetic stir bar were added boronate *rac*-**15** (2.25 g, 6.94 mmol), triflate **20** (1.71 g, 7.43 mmol), palladium acetate (70 mg, 0.311 mmol), triphenylphosphine (180 mg, 0.686 mmol), and potassium phosphate tribasic (4.43 g, 20.87 mmol). The mixture was evacuated and back filled with argon (3x). The mixture was dissolved in dioxane (35 mL) then added water (3.5 mL). The reaction was immersed in a 60 ºC oil bath. After 9 h of stirring, the reaction was cooled to ambient temperature, diluted with EtOAc (10 mL), and quenched with saturated NH_4Cl solution (10 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford a crude mixture of **S1**. The residue was used for the next reaction without further purification.

To a round-bottom flask with a magnetic stir bar were added the crude product from former step (1.72 g, 6.18 mmol) and THF (21 mL). To the mixture was added TBAF (1.0 M in THF, 5.0 mL, 5.0 mmol) and stirred for 24 h at 23 ºC. The reaction mixture was quenched by saturated aqueous NH_4Cl (20 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (4:1 hexanes:EtOAc) to afford diene allylic alcohol **21** (714 mg, 4.35 mmol, 63% yield over two steps) as a colorless oil; R_f = 0.67 (10:1, hexanes:EtOAc) ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05–5.95 (m, 1H), 5.83–5.75 (m, 1H), 5.01 (dt, *J* = 7.2, 1.9 Hz, 1H), 2.65–2.53 (m, 1H), 2.35–2.26 (m, 1H), 2.26–2.10 (m, 3H), 1.87 (ddt, *J* = 13.9, 8.0, 2.4 Hz, 1H), 1.73–1.53 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ146.39, 131.82, 127.36, 125.35, 77.16, 76.22, 33.82, 30.48, 26.39,

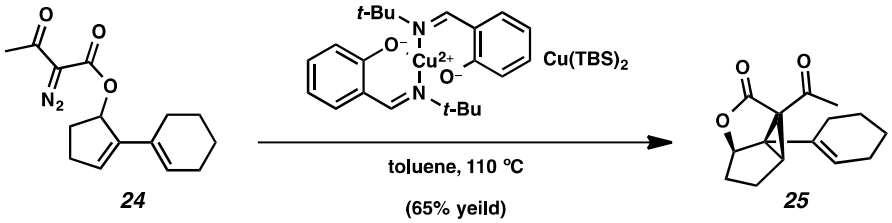
25.81, 22.81, 22.43; IR (Neat Film, NaCl) 3339, 3045, 2925, 2855, 1435, 1302, 1044, 986, 941, 823 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{11}H_{16}O$ $[M\bullet]^+$: 164.1201, found 164.1170.



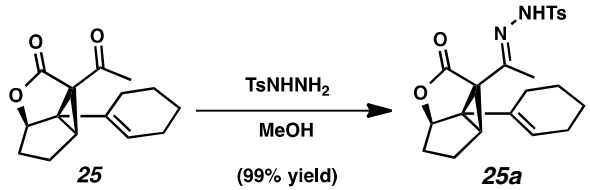
***ß*-ketoester 23**: To a flame-dried round-bottom flask equipped with a magnetic stir bar were added allylic alcohol **21** (60 mg, 0.365 mmol), 4-dimethylaminopyridine (0.2 mg, 0.0016 mmol) and Et_2O (1.5 mL). The flask was cooled to 0 ºC and stirred for 10 min. Diketene (0.03 mL, 0.389 mmol) was added dropwise. The reaction mixture was stirred for 15 min at 0 ºC was then quenched by cold water (0 ºC, 1.5 mL). The mixture was extracted with Et_2O (3 x 3 mL). The combined organic layers were washed by brine (3 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was purified by flash column chromatography (4:1 hexanes, EtOAc) to afford *ß*-ketoester **23** (82.7 mg, 0.333 mmol, 91% yield) as a colorless oil; R_f = 0.52 (4:1, hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (dt, *J* = 7.2, 1.8 Hz, 1H), 5.98–5.94 (m, 1H), 5.76–5.72 (m, 1H), 3.43 (s, 2H), 2.61–2.53 (m, 1H), 2.40–2.24 (m, 2H), 2.22 (s, 3H), 2.21–2.16 (m, 2H), 2.16–2.07 (m, 2H), 1.96–1.88 (m, 2H), 1.71–1.51 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.7, 167.3, 142.2, 131.1, 130.7, 125.9, 79.9, 50.7, 31.6, 30.8, 30.2, 26.6, 25.8, 22.7, 22.3; IR (Neat Film, NaCl) 2926, 2853, 1718, 1643, 1412, 1358, 1310, 1243, 1147, 1027, 977, 936, 896, 800 cm^{-1}; HRMS (MM) *m/z* calc'd for $C_{15}H_{19}O_3$ $[M-H]^-$: 247.1340, found 247.1362.



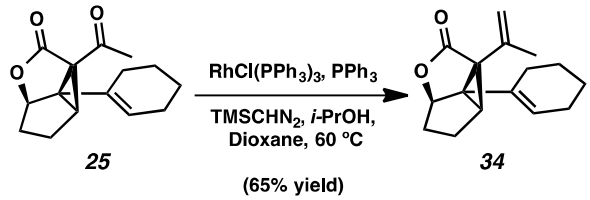
Diazo ester 24: To a round-bottom flask equipped with a magnetic stir bar were added *ß*-ketoester **23** (80 mg, 0.322 mmol), CH_3CN (3 mL), and *p*-ABSA (130 mg, 0.541 mmol). TEA (0.2 mL, 1.43 mmol) was added dropwise. The reaction mixture was stirred for 2 h at 23 ºC. The reaction mixture was filtered through a silica gel plug (pentanes:Et_2O 2:1) was then concentrated under reduced pressure to afford diazo ester **24** (88.2 mg, 0.322 mmol, 99% yield) as a yellowish oil; R_f = 0.44 (6:1, hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.08 (dt, J = 1.66 Hz, 1.66 Hz, 7.75 Hz, 1H), 5.95 (d, *J* = 2.62 Hz, 1H), 5.71 (s, 1H), 2.58–2.55 (m, 1H), 2.44 (s, 3H), 2.31–2.24 (m, 1H), 2.22 (s, 3H), 2.39-2.26 (m, 2H), 2.18–2.09 (m, 4H), 1.95–1.90 (m, 1H), 1.68–1.52 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 161.6, 142.1, 131.2, 130. 7, 125.5, 80.3, 31.7, 30.7, 28.4, 26.3, 25.8, 22.7, 22.3; IR (Neat Film, NaCl) 3298, 3050, 2929, 2856, 2390, 2297, 2208, 2138, 1712, 1661, 1652, 1447, 1435, 1365, 1312, 1247, 1149, 1061, 1024, 965, 926, 854, 836, 816, 800, 746 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{15}H_{19}O_3N_2$ $[M+H]^-$: 275.1396, found 275.1389.



Cyclopropane 25: To a flame-dried two neck round-bottom flask equipped with a magnetic stir bar was added copper catalyst (20 mg, 0.0459 mmol) in a nitrogen-filled glove box. The flask was sealed with rubber septums and removed from the glove box. One of the rubber septum was replaced with a reflux condenser connected to a nitrogen inlet. A solution of diazo ester **24** (254.8 mg, 0.929 mmol) in toluene (46 mL) was added. The reaction was heated to reflux in a 110 ºC oil bath. After 2 h of stirring, the reaction mixture was cooled to 23 ºC and stirred for 15 min. The mixture was concentrated and purified by flash column chromatography (15:1 hexanes, EtOAc) to afford cyclopropane **25** (148 mg, 0.601 mmol, 65% yield) as a yellowish oil; R_f = 0.36 (6:1 hexanes:EtOAc eluent); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72–5.70 (m, 1H), 4.81 (d, *J* = 1.30 Hz, 1H), 3.10 (d, J = 6.40 Hz, 1H), 2.45 (s, 3H), 2.31–2.24 (m, 1H), 2.15–2.12 (m, 1H), 2.04–1.98 (m, 3H), 1.91–1.85 (m, 1H), 1.80–1.78 (m, 1H), 1.71–1.49 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 172.9, 123.0, 128.3, 85.3, 66.7, 51.6, 39.4, 38.1, 30.1, 28.3, 25.3, 24.0, 22.6, 22.0; IR (Neat Film, NaCl) 2929, 1760, 1699, 1435, 1360, 1311, 1243, 1159, 1089, 1008, 979, 956, 925, 906, 855, 799, 756 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found 247.1327.

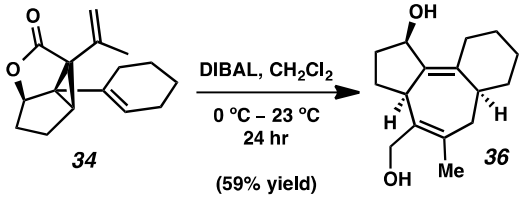


Hydrazone 25a: To a round-bottom flask equipped with a magnetic stir bar were added cyclopropane **25** (54 mg, 0.219 mmol), methanol (1 mL), and *p*-toluenesulfonyl hydrazide (61 mg, 0.328 mmol). The reaction was stirred for 12 h at 23 ºC. The reaction was concentrated and purified by flash column chromatography (4:1 hexanes, EtOAc) to afford hydrazone **25a** (90 mg, 0.217 mmol, 99% yield) as a white solid; R_f = 0.50 (2:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ7.82–7.79 (m, 2H), 7.65 (s, *2*H), 7.32–7.26 (m, 2H), 5.27 (t, *J* = 1.72 Hz, 1H), 4.91 (d, *J* = 0.95 Hz, 1H), 2.93 (d, J = 6.36 Hz, 1H), 2.43 (s, 3H), 2.28–2.22 (m, 1H), 2.04–1.96 (m, 1H), 1.88–1.79 (m, 5H), 1.76–1.67 (m, 3H), 1.52–1.38 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 147.6, 144.4, 135.4, 129.7, 128.5, 128.2, 127.5, 85.4, 62.2, 50.3, 38.3, 33.4, 28.1, 25.2, 23.7, 22.7, 22.0, 21.8, 16.0; IR (Neat Film, NaCl) 3214, 2926, 2360, 1748, 1339, 1168, 1094, 1057, 1002, 906, 814, 754 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{22}H_{27}O_4N_2S$ $[M+H]^+$: 415.1686, found 415.1698.

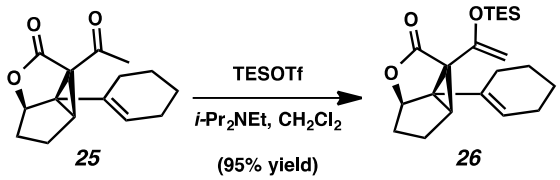


Vinyl lactone 34: To a flame-dried round-bottom flask equipped with a magnetic stir bar were added Wilkinson's catalyst (4.3 mg, 0.00465 mmol) and PPh_3 (54 mg, 0.206 mmol) in a nitrogen-filled glove box. The flask was sealed with a rubber septum, removed from the glove box and connected to a nitrogen inlet. Dioxane (2 mL) was added, and the reaction was immersed in a 60 ºC oil bath. Isopropanol (0.21 mL, 2.75 mmol) was added, followed by a solution of cyclopropane **25** (46 mg, 0.187 mmol) in dioxane

(0.5 mL) to give a reddish solution. A solution of trimethylsilyldiazomethane (2 M in Et_2O, 0.22 mL, 0.44 mmol) was added to the reaction mixture. The reaction was stirred for 5 h at 60 ºC. The reaction was allowed to cool to ambient temperature and concentrated under reduced pressure. The residue was purified by flash column chromatography (15:1, hexanes:EtOAc) to afford vinyl lactone **34** (30 mg, 0.123 mmol, 65% yield) as a colorless oil. R_f = 0.40 (6:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.30–5.23 (m, 1H), 4.96 (dd, *J* = 3.0, 1.5 Hz, 1H), 4.85 (dd, *J* = 1.5, 0.8 Hz, 1H), 4.53 (d, *J* = 1.0 Hz, 1H), 2.06 (dd, *J* = 4.1, 3.5 Hz, 1H), 1.83–1.77 (m, 5H), 1.75–1.60 (m, 4H), 1.58–1.45 (m, 1H), 1.46–1.25 (m, 5H); ^{13}C NMR (126 MHz, C_6D_6) δ 173.5, 138.4, 138.4, 125.5, 116.5, 83.9, 58.9, 50.2, 38.9, 33.3, 28.0, 25.5, 23.6, 23.0, 22.3, 22.0; IR (Neat Film, NaCl), 3498, 2918, 2850, 1960, 1645, 1539, 1436, 1373, 1335, 1302, 1289, 1262, 1212, 1161, 1137, 1093, 1077, 1044, 1012, 997, 906, 841, 802, 751 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{16}H_{21}O_2$ $[M+H]^+$: 245.1536, found 245.1555.

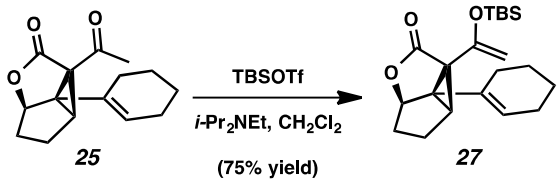


Diol 36: To a flame-dried round-bottom flask equipped with a magnetic stir bar were added vinyl lactone **34** (10 mg, 0.0403 mmol) and DCM (1 mL). The flask was cooled to 0 ºC and stirred for 10 min. A solution of DIBAL (1 M in DCM, 0.4 mL, 0.4 mmol) was added dropwise. The reaction mixture was slowly warmed up to 23 ºC and remained stirring for 24 h. The reaction was quenched by methanol (0.4 mL). Saturated aqueous potassium sodium tartarate solution (1 mL) was added to the mixture. The phases were separated and the aqueous phases were extracted with DCM (5 x 2 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (2:1, hexanes:EtOAc) to afford diol **36** as a white solid (6 mg, 0.024 mmol, 59% yield); R_f = 0.08 (2:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 4.61 (d, *J* = 4.2 Hz, 1H), 4.20 (d, *J* = 11.3 Hz, 1H), 3.96 (d, *J* = 11.3 Hz, 1H), 3.58–3.49 (m, 1H), 3.04 (dd, *J* = 13.6, 4.1 Hz, 1H), 2.75 (dd, *J* = 12.8, 3.5 Hz, 1H), 2.41 (qd, *J* = 12.4, 6.1 Hz, 1H), 1.95–1.83 (m, 2H), 1.76–1.67 (m, 5H), 1.64–1.57 (m, 1H), 1.52 (dd, *J* = 13.6, 3.6 Hz, 1H), 1.43–1.27 (m, 6H); ^{13}C NMR (126 MHz, C_6D_6) δ 138.9, 138.7, 138.3, 134.2, 73.2, 60.1, 41.6, 40.5, 38.5, 34.8, 34.6, 34.2, 30.2, 29.4, 27.6, 26.5, 21.9; IR (Neat Film, NaCl) 3338, 2927, 2853, 1740, 1447, 1373, 1242, 1177, 1043, 965, 913 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{16}H_{23}O_2$ [M+□–□□]$^+$: 247.1698, found 247.1692.

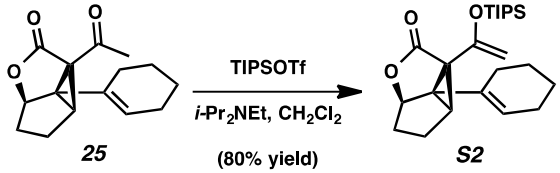


TES enol ether 26: To a flame-dried round-bottom flask equipped with a magnetic stir bar were added cyclopropane **25** (22.5 mg, 0.0913 mmol), DCM (2 mL), and *i*-Pr_2NEt (0.05 mL, 0.287 mmol). The flask was cooled to 0 ºC and stirred for 10 min. TESOTf (0.05 mL, 0.210 mmol) was added dropwise. The reaction mixture was stirred for 30 min at 0 ºC. The reaction mixture was filtered through a silica gel plug (henxanes:EtOAc 10:1) was then concentrated under reduced pressure to afford TES enol ether **26** (28 mg, 95% yield) as colorless oil. R_f = 0.60 (6:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.38 (t, *J* = 1.79 Hz, 1H), 4.53 (d, *J* = 1.68 Hz, 1H), 4.45 (dd, *J* = 0.78 Hz, 1.69, 1H), 4.37 (d, *J* = 1.68 Hz, 1H), 2.30–2.28 (m, 1H), 2.13–2.08 (m, 1H), 1.95–1.85 (m, 3H), 1.70–1.60 (m, 2H), 1.56–1.42 (m, 4H),

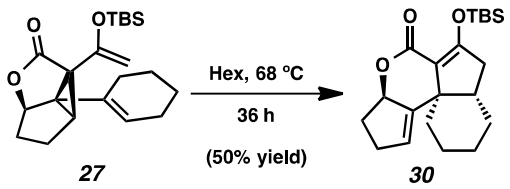
1.37–1.30 (m, 2H), 1.02 (t, J = 7.94 Hz, 9H), 0.71 (ddd, J = 1.34 Hz, 7.94 Hz, 9.90 Hz, 6H); ^{13}C NMR (126 MHz, C_6D_6) δ 172.8, 151.7, 131.3, 125.7, 93.7, 84.0, 58.9, 48.7, 38.9, 34.0, 27.7, 25.6, 23.6, 23.1, 22.5, 7.0, 5.2; IR (Neat Film, NaCl) 3518, 3119, 2934, 2876, 2836, 2734, 2365, 1769, 1629, 1458, 1437, 1413, 1334, 1290, 1258, 1196, 1161, 1137, 1075, 1042, 1003, 981, 933, 907, 821, 770, 747 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{21}H_{32}O_3Si$ $[M\bullet]^+$: 360.2121, found 360.2117.



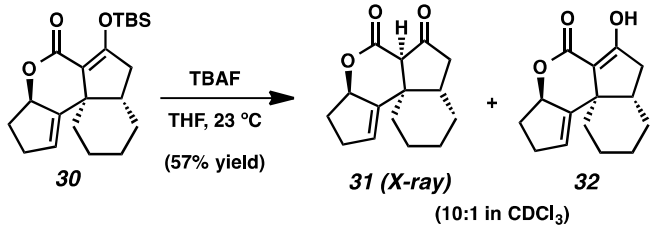
TBS enol ether 27: To a flame-dried round-bottom flask equipped with a magnetic stir bar were added cyclopropane **25** (41 mg, 0.167mmol), DCM (3.4 mL), and *i*-Pr_2NEt (0.06 mL, 0.344 mmol). The flask was cooled to 0 ºC and stirred for 10 min. TBSOTf (0.04 mL, 0.174 mmol) was added dropwise. The reaction mixture was stirred for 30 min at 0 ºC. The reaction mixture was filtered through a silica gel plug (henxanes:EtOAc 10:1) was then concentrated under reduced pressure to afford TBS enol ether **27** (45.3 mg, 75% yield) as colorless oil. R_f = 0.50 (6:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.39 (dt, J = 3.8, 2.0 Hz, 1H), 4.47 (dt, J = 2.9, 0.8 Hz, 1H), 4.44 (d, J = 1.6 Hz, 1H), 4.36 (d, J = 1.7 Hz, 1H), 2.26 (ddd, J = 6.7, 1.6, 0.7 Hz, 1H), 2.10 (dddt, J = 14.2, 6.1, 4.2, 2.0 Hz, 1H), 1.98–1.83 (m, 2H), 1.72–1.60 (m, 2H), 1.56–1.40 (m, 5H), 1.39–1.28 (m, 2H), 0.96 (s, 9H), 0.28 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 167.1, 161.2, 144.2, 124.9, 113.2, 83.5, 45.5, 40.5, 38.1, 33.2, 32.1, 30.3, 25.9, 25.42, 21.6, 21.5, 18.9, –3.6, –4.50; IR (Neat Film, NaCl) 3520, 2929, 2857, 1630, 1471, 1463, 1361, 1335, 1291, 1257, 1196, 1161, 1141, 1175, 1042, 1026, 1002, 938, 907, 892, 830, 782 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{33}SIO_3$ $[M+H]^+$: 361.2199, found 361.2182.



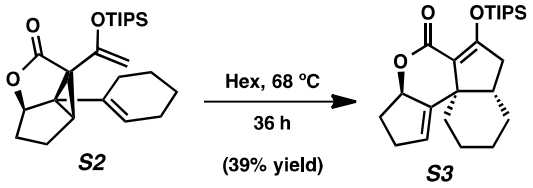
TIPS enol ether S2: To a flame-dried round-bottom flask equipped with a magnetic stir bar were added cyclopropane **25** (23 mg, 0.0934 mmol), DCM (2 mL), and *i*-Pr_2NEt (0.05 mL, 0.287 mmol). The flask was cooled to 0 ºC and stirred for 10 min. TBSOTf (0.04 mL, 0.148 mmol) was added dropwise. The reaction mixture was stirred for 30 min at 0 ºC. The reaction mixture was filtered through a silica gel plug (henxanes:EtOAc 10:1) was then concentrated under reduced pressure to afford TIPS enol ether **S2** (30 mg, 0.0745 mmol, 80% yield) as colorless oil. R_f = 0.50 (6:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.45–5.37 (m, 1H), 4.52–4.46 (m, 1H), 4.41 (d, J = 1.7 Hz, 1H), 4.37 (d, J = 1.7 Hz, 1H), 2.28 (dt, J = 6.5, 1.2 Hz, 1H), 2.17–2.08 (m, 1H), 2.01–1.84 (m, 3H), 1.74–1.61 (m, 2H), 1.61–1.43 (m, 4H), 1.40–1.10 (m, 21H); ^{13}C NMR (126 MHz, C_6D_6) δ 172.7, 151.7, 131.0, 125.8, 93.9, 84.1, 58.9, 49.3, 39.0, 33.6, 27.6, 25.5, 23.5, 23.0, 22.4, 18.5, 18.4, 13.0; IR (Neat Film, NaCl) 3521, 3121, 2929, 2866, 2717, 2233, 2077, 1770, 1626, 1463, 1383, 1362, 1335, 1302, 1290, 1258, 1197, 1161, 1138, 1075, 1043, 1003, 920, 907, 883, 821, 769, 740, 709 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{24}H_{39}SIO_3$ $[M+H]^+$: 403.2669, found 403.2688.



Tetracycle 30: To a flame-dried two neck round-bottom flask equipped with a magnetic stir bar and a reflux condenser was added TBS enol ether **27** (15.8 mg, 0.0438 mmol) and hexane (4.4 mL). The reaction was heated to reflux in a 68 ºC oil bath. After 36 h of stirring, the reaction mixture was cooled to 23 ºC and stirred for 15 min. The mixture was concentrated and purified by flash column chromatography (15:1 hexanes, EtOAc) to afford tetracycle **30** (8 mg, 0.0222 mmol, 50% yield) as a colorless oil; R_f = 0.45 (6:1 hexanes:EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 5.36–5.17 (m, 1H), 5.17–5.00 (m, 1H), 2.44 (dd, *J* = 16.2, 12.1 Hz, 1H), 2.25–2.16 (m, 1H), 2.11–1.99 (m, 2H), 1.96–1.85 (m, 2H), 1.75–1.61 (m, 2H), 1.45–1.34 (m, 3H), 1.27–1.20 (m, 1H), 1.20–1.11 (m, 1H), 1.04 (s, 9H), 1.01–0.79 (m, 2H), 0.42 (s, 3H), 0.31 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 167.11, 161.17, 144.16, 128.06, 124.93, 113.19, 83.49, 45.48, 40.49, 38.06, 33.22, 32.11, 30.30, 25.92, 25.42, 21.55, 21.45, 18.87, –3.64, –4.50; IR (Neat Film, NaCl) 3409, 3051, 2924, 2854, 1771, 1713, 1606, 1463, 1379, 1362, 1342, 1328, 1304, 1251, 1222, 1193, 1172, 1157, 1111, 1095, 1064, 1049, 1001, 968, 939, 926, 904, 865, 839, 790, 721 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{33}O_3Si$ $[M+H]^+$: 361.2199, found 361.2184.

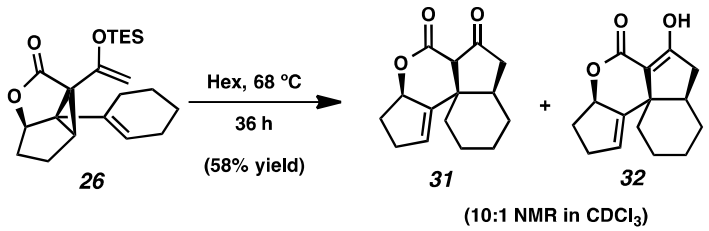


***β*-Ketolactone 31:** To a round-bottom flask with a magnetic stir bar were added tetracycle **30** (7.7 mg, 0.0214 mmol) and THF (1 mL). To the mixture was added TBAF (1.0 M in THF, 0.022 mL, 0.022 mmol) and stirred for 5 min at 23 ºC. The reaction mixture was quenched by saturated aqueous NH_4Cl (1 mL). The mixture was extracted with Et_2O (3 x 1 mL). Organic layers were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (2:1 hexanes:EtOAc) provided *β*-ketolactone **31** (3 mg, 0.0212 mmol, 57% yield) as a colorless oil; R_f = 0.10 (6:1, hexanes:EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ5.25–5.21 (m, 1H), 4.75–4.69 (m, 1H), 2.97 (s, 1H), 2.16 (dd, J = 18.9, 8.3 Hz, 1H), 2.04–1.93 (m, 1H), 1.90–1.69 (m, 4H), 1.67–1.58 (m, 1H), 1.40–0.71 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.3, 141.4, 129.1, 126.3, 85.0, 59.0, 47.7, 43.5, 42.5, 42.2, 37.0, 34.6, 33.8, 31.9, 30.9, 30.7, 30.4, 29.5, 27.7, 25.7, 22.6, 21.1; IR (Neat Film, NaCl) 3441, 2929, 2857, 1760, 1451, 1407, 1354, 1310, 1241, 1180, 1152, 1089, 1038, 949, 822, 803, 744 cm^{-1}; HRMS (MM+) *m/z* calc'd for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1329, found 247.1294.

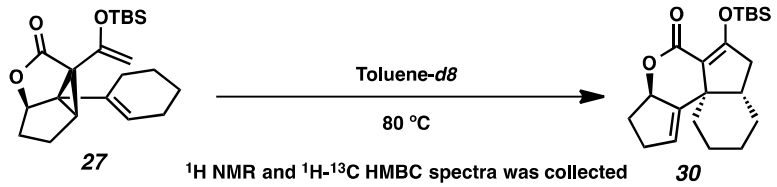


Tetracycle S3: To a flame-dried two neck round-bottom flask equipped with a magnetic stir bar and a reflux condenser was added TIPS enol ether **S2** (28 mg, 0.0695 mmol) and hexane (8 mL). The reaction was heated to reflux in a 68 ºC oil bath. After 36 h of stirring, the reaction mixture was cooled to 23 ºC

and stirred for 15 min. The mixture was concentrated and purified by flash column chromatography (15:1 hexanes, EtOAc) to afford tetracycle **S3** (10.9 mg, 0.0271 mmol, 39% yield) as a colorless oil; R_f = 0.45 (6:1 hexanes:EtOAc); ^{1}H NMR (400 MHz, C_6D_6) δ 5.25 (dt, *J* = 3.1, 1.8 Hz, 1H), 5.12–5.05 (m, 1H), 2.56 (dd, *J* = 16.1, 12.0 Hz, 1H), 2.28 (ddt, *J* = 11.9, 7.5, 3.6 Hz, 1H), 2.15–1.83 (m, 4H), 1.79–1.67 (m, 1H), 1.51–1.11 (m, 28H); ^{13}C NMR (101 MHz, C_6D_6) δ 166.8, 160.9, 144.4, 124.8, 112.8, 83.4, 45.3, 40.7, 38.1, 33.0, 32.2, 30.3, 25.5, 21.7, 21.5, 18.2, 13.6; IR (Neat Film, NaCl) 3416, 3051, 2928, 2864, 2719, 2243, 1768, 1712, 1605, 1463, 1450, 1430, 1382, 1363, 1342, 1328, 1304, 1279, 1240, 1223, 1193, 1172, 1155, 1132, 1112, 1096, 1063, 1048, 1000, 967, 926, 903, 882, 864, 835, 805, 781, 768 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{24}H_{38}O_3Si$ $[M\bullet]^+$: 402.2590, found 402.2602. TIPS enol ether **S2** (5.6 mg, 0.0139 mmol, 20% yield) was recovered.



***ß*-ketolactone 31**: To a flask equipped with reflux condenser were added TES enol ether **26** (70 mg, 0.194 mmol) and hexane (20 mL, 0.01 M). The reaction was then heated to 110 ºC and stirred for 36 h. The mixture was cooled down to ambient temperature, concentrated and purified by flash column chromatography (8:1 hexanes, EtOAc) to afford tetracycle **31** (28 mg, 0.114 mmol, 58% yield).



NMR Screening: To a NMR tube was added a solution of silyl enol ether **27** (39.1 mg, 0.108 mmol) in toluene-*d8* (0.5 mL). The NMR tube was inserted to Varian Inova 600 and the reaction temperature was set to 80 ºC. ^{1}H NMR and ^{1}H-^{13}C HMBC spectra was collected to monitor reaction.

Computational Details for DFT Studies

DFT calculations were performed with Gaussian 09.[5] Computed structures are illustrated using CYLView.[6]

Geometries were optimized with the B3LYP[7] functional with the 6-31G(d) basis set, in the gas phase. Thermal corrections were calculated from unscaled vibrational frequencies at the same level of theory using a standard state of 298.15 K and 1 atm. IRC calculations were performed to link each transition state to the relevant intermediates. Conformational analysis was performed by manually rotating bonds, mainly the cyclohexane and silyl groups; only lowest-energy conformers are reported.

Electronic energies were obtained from single-point energy calculations using B3LYP-D3BJ,[8] M11-L,[9] and M06-2X,[10] using the larger 6-311++G(2d,2p) basis set and the IEF-PCM solvation model for n-hexane. All of these functionals account for dispersion, either with empirical corrections or parameterization, and they represent a range of functional types, including hybrid with empirical dispersion correction (B3LYP-D3BJ), hybrid meta (M06-2X), and dual-range local meta (M11-L). Results with M06-2X are shown in the Supporting Information, because this functional has been shown to give accurate barriers for pericyclic reactions,[11] but unreliable (overestimated) energies for diradical processes.[12]

Table S1. Energies with all functionals

	B3LYP/6-31G(d)		*B3LYP-D3/ 6-311++G(2d,2p) PCM(hexane)*		*M06-2X/ 6-311++G(2d,2p) PCM(hexane)*		*M11L/ 6-311++G(2d,2p) PCM(hexane)*	
	ΔH	**ΔG**	**ΔH**	**ΔG**	**ΔH**	**ΔG**	**ΔH**	**ΔG**
Figure 8: Reaction of 37								
TS38	25.6	28.2	23.2	25.9	28.8	31.5	25.5	28.2
39	6.0	9.4	5.0	8.4	8.1	11.4	6.8	10.1
TS45	19.8	25.4	20.0	25.7	22.2	27.9	18.0	23.7
46	11.3	14.8	10.6	14.0	13.5	17.0	10.3	13.8
TS47	23.0	24.4	18.9	20.3	31.5	32.9	18.6	20.0
48-eq	–3.7	–2.4	–3.4	–2.0	–1.4	–0.1	–5.6	–4.3
48	–2.8	–2.1	–3.1	–2.3	–0.7	0.1	–4.8	–4.0
TS49	17.6	18.9	12.9	14.1	26.0	27.3	9.8	11.1
50	–15.8	–14.0	–16.2	–14.4	–13.3	–11.6	–16.9	–15.1
TS51	–5.9	–1.3	–3.6	0.9	–1.2	3.4	–6.8	–2.2
44	–20.2	–18.0	–19.6	–17.4	–17.1	–14.9	–20.3	–18.1
Figure 4: Reaction of 40								
TS41	19.3	20.6	17.2	18.5	25.2	26.5	19.1	20.4
36	–13.6	–13.8	–14.7	–14.8	–12.8	–12.9	–16.2	–16.3
Figure 9: Alkylidene cyclobutane derivatives								
48	–2.8	–2.1	–3.1	–2.3	–0.7	0.1	–4.8	–4.0
48b	–9.5	–9.5	–6.3	–6.3	–3.2	–3.2	–8.7	–8.7
48c	–15.5	–14.9	–17.3	–16.6	–14.0	–13.4	–18.6	–18.0
48d	–24.1	–23.7	–22.0	–21.6	–16.3	–16.0	–22.8	–22.5
Figure 10: Reaction of 37d								
TS38d	18.3	21.0	16.7	19.4	22.0	24.8	18.3	21.0
39d	–2.0	0.6	–1.5	1.1	1.4	4.0	–0.8	1.8
TS45d	12.4	17.5	14.3	19.4	16.1	21.2	11.2	16.3
46d	5.5	6.4	5.9	6.7	9.5	10.3	5.6	6.5
TS47d	17.9	19.1	16.1	17.3	30.4	31.6	13.6	14.9
48d	–24.1	–23.7	–22.0	–21.6	–16.3	–16.0	–22.8	–22.5
TS49d	20.0	20.8	18.4	19.2	33.5	34.3	15.7	16.5
50d	–20.2	–18.3	–17.9	–16.0	–14.8	–13.0	–19.6	–17.7
TS51d	–8.9	–4.7	–4.6	–0.4	–1.7	2.5	–8.0	–3.8
44d	–23.9	–22.1	–21.1	–19.2	–17.9	–16.0	–22.4	–20.5

	B3LYP/6-31G(d)		*B3LYP-D3/ 6-311++G(2d,2p) PCM(hexane)*		*M06-2X/ 6-311++G(2d,2p) PCM(hexane)*		*M11L/ 6-311++G(2d,2p) PCM(hexane)*	
	ΔH	**ΔG**	**ΔH**	**ΔG**	**ΔH**	**ΔG**	**ΔH**	**ΔG**
Figure S1: Diradical Claisen rearrangement of 46								
SI-TS1	20.3	22.9	12.0	14.6	28.0	30.6	16.0	18.6
SI-2	13.8	13.2	13.4	12.8	24.8	24.1	16.0	15.3
SI-TS3	21.5	22.3	19.1	19.9	31.5	32.3	19.9	20.7
SI-TS4	17.3	18.4	13.0	14.0	25.5	26.5	10.5	11.6
SI-5-ax	13.6	12.9	15.5	14.8	24.5	23.8	11.0	10.4
SI-5-eq	12.6	12.4	10.8	10.7	26.2	24.5	8.4	8.3
SI-TS6	15.6	16.9	10.6	11.8	23.8	25.0	7.9	9.1
Figure S2: Diradical Claisen rearrangement of 46d								
SI-TS1d	19.2	21.2	17.0	19.0	31.0	33.0	16.3	18.3
SI-2d	11.0	9.4	12.1	10.5	23.5	21.9	18.5	17.0
SI-TS3d	15.1	15.2	14.8	15.0	27.5	27.6	14.4	14.5
SI-TS4d	16.9	16.7	16.6	16.4	29.3	29.1	16.0	15.8
SI-5d	8.8	8.5	10.6	10.3	21.8	21.5	12.2	11.9
SI-TS6d	16.4	17.4	15.6	16.6	30.5	31.5	14.6	15.6

Comparison of Closed-Shell and Diradical Claisen Pathways

The Claisen/retro-Claisen Rearrangement pathway from silyl enol ether **46** was studied with both closed-shell (restricted) and open-shell (unrestricted) calculations. The closed-shell pathway was shown in the main manuscript (Figure 7) and is reproduced in green below in Figure S1. **TS47** and **TS49** are somewhat dissociative in nature, characterized by very long C–O bonds compared to typical Claisen rearrangements.

A stepwise diradical pathway for the Claisen/retro-Claisen sequence is shown in purple. Homolysis of the C–O bond via **SI-TS1** gives diradical **SI-2**. Formation of the new C–C bond in cyclobutane **48** is the rate-limiting step (**SI-TS3**). The sequence then reverses, breaking the other allylic C–C bond via **SI-TS4** to form diradical **SI-5** and re-forming the C–O bond via **SI-TS6**. Although the concerted and stepwise Claisen pathways have distinct transition states, the barriers for the two pathways are virtually identical.

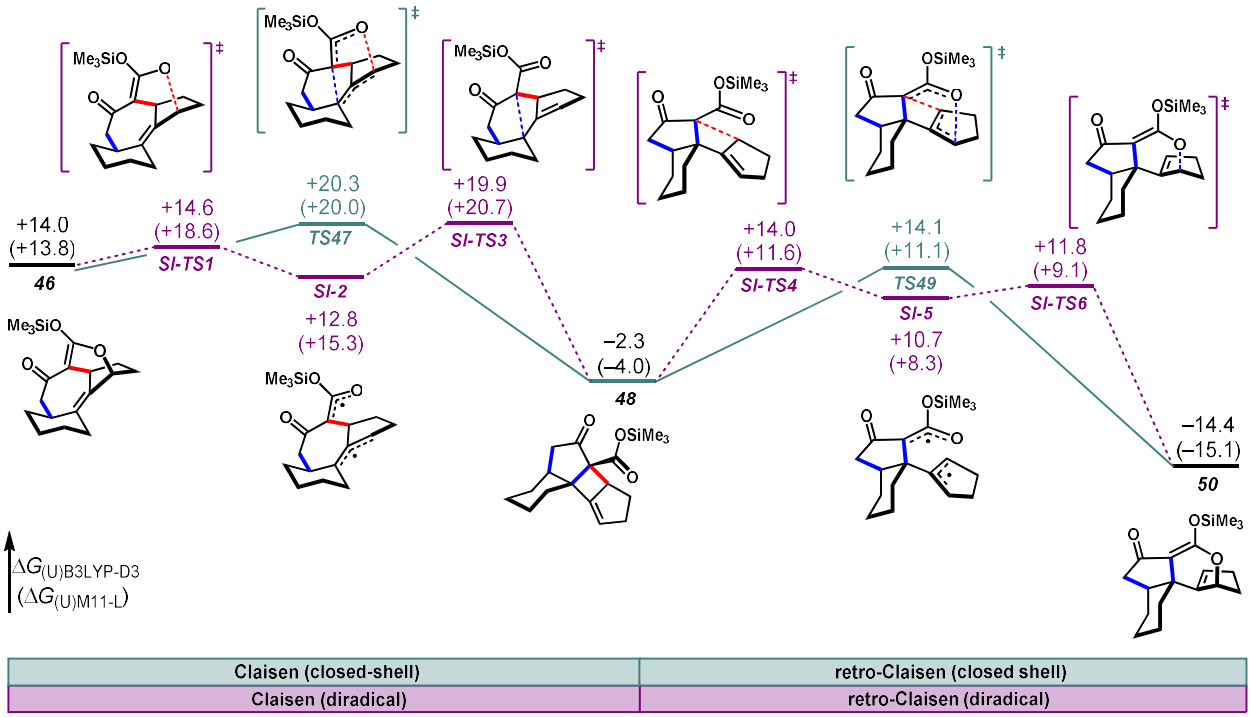


Figure S1. Comparison of closed-shell and diradical Claisen pathways for formation of silyl enol ether **50**

It is worth noting that B3LYP and B3LYP-D3 predict open-shell (diradical) electronic structures to the stepwise intermediates and transition states, as judged by a non-zero total spin operator, S^2. An exception is **SI-TS1**, which appears to be closed-shell (S^2 = 0.0). It is possible that **SI-TS1** starts to form a zwitterionic intermediate, but upon reaching this intermediate (**SI-2**), the diradical electronic structure is more stable. For open-shell structures, we ensured the most stable wavefunction was found using the keyword `stable=opt` (generally the most stable wavefunction was already found). Zwitterionic intermediates are not expected to be stable in hexane. However, M11L gives closed-shell solutions to most transition states (S^2 = 0.0), but open-shell diradical wavefunctions for intermediates **SI-2** and **SI-5**. Nevertheless, the barriers predicted by these methods are very similar and we view the Claisen and retro-Claisen steps as concerted but highly asynchronous.

Similar results were found for the Claisen/retro-Claisen rearrangement of simplified silyl enol ether **46d** (Figure S2). In this case, formation of the diradical **SI-2d** via **SI-TS1d** is rate-limiting, since cyclobutane **48d** is relatively unstrained. The closed-shell process via **TS47d** is predicted to be favored.

Formation of **48d** is the final product in this system, as retro-Claisen rearrangement has a prohibitively high barrier through either closed shell or diradical pathways.

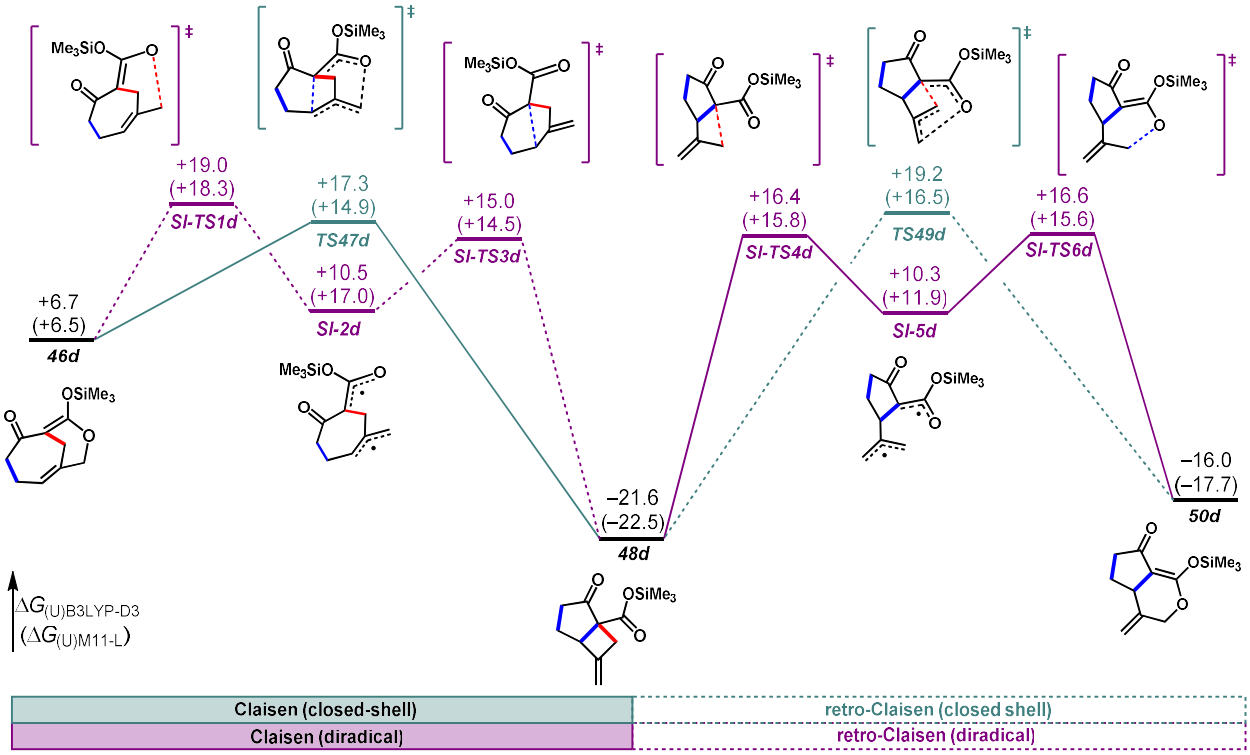


Figure S2. Comparison of closed-shell and diradical Claisen pathways for formation of alkylidene cyclobutane **48d**

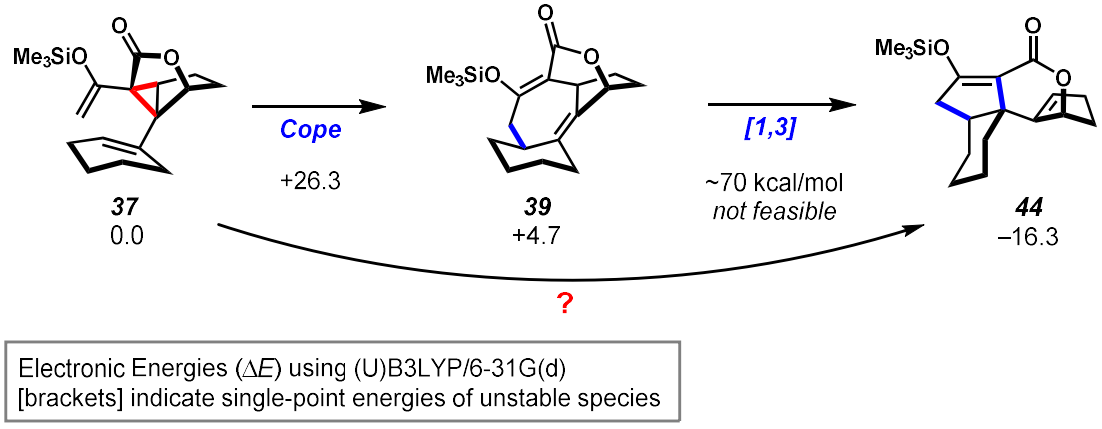
Other Disfavored Diradical Pathways

During this project a number of other pathways were explored using conventional computational chemistry techniques (bond scans to form or break desired bonds). Most pathways involved diradical intermediates and were found to be highly unfavorable. In all cases, unrestricted calculations were performed (UB3LYP) with broken symmetry (guess=mix,always) for singlet diradicals or carbenes.

Typically, diradicals were optimized as triplet species and the corresponding singlet state was unstable (collapsing to a closed-shell intermediate). In these cases, as single-point energy calculation was performed at the singlet state, which is indicated with brackets.

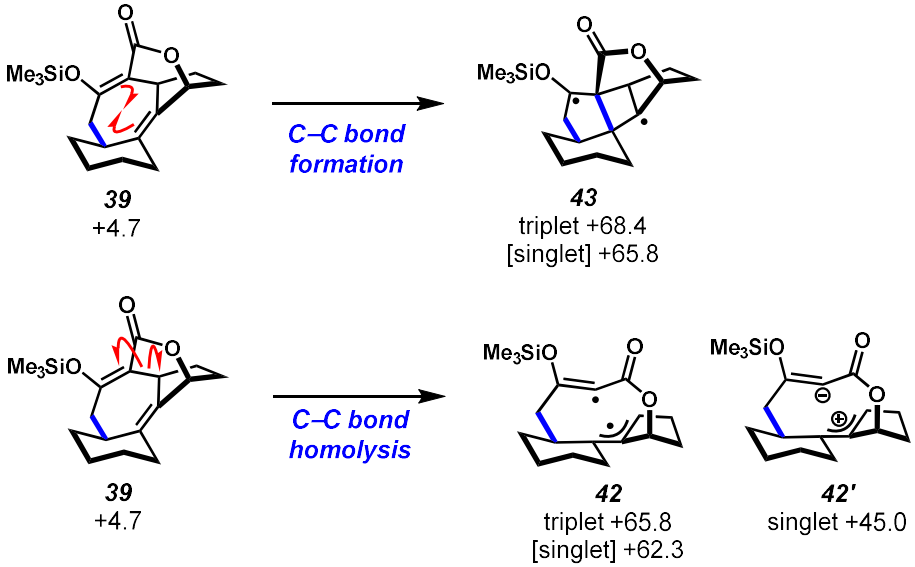
We explored pathways beginning with either starting material **37** or the product of the proposed Cope rearrangement, **39** (Scheme S1).

Scheme S1. Overview of Other Pathways Explored



Starting from Cope intermediate **39**, formation of the required C–C bond leads to cyclobutylcarbinyl diradical **43**, which is very high in energy (Scheme S2). This structure was also located on the potential energy surface in Figure 5 of the main paper. Similarly, breaking the allylic C–C bond (required for the formal 1,3-shift) was also located in Figure 5. This homolysis gives allylic/vinylic diradical **42**, which is very high in energy on both triplet and singlet surfaces. The singlet structure of **42** is unstable and optimizes to a structurally similar Zwitterion **42′** (a closed-shell structure, despite the unrestricted calculation). This allylic carbocation/enolate structure is more stable than the diradical, but still too high in energy to be a feasible intermediate.

Scheme S2. Diradical Pathways Beginning at Cope Intermediate **39**

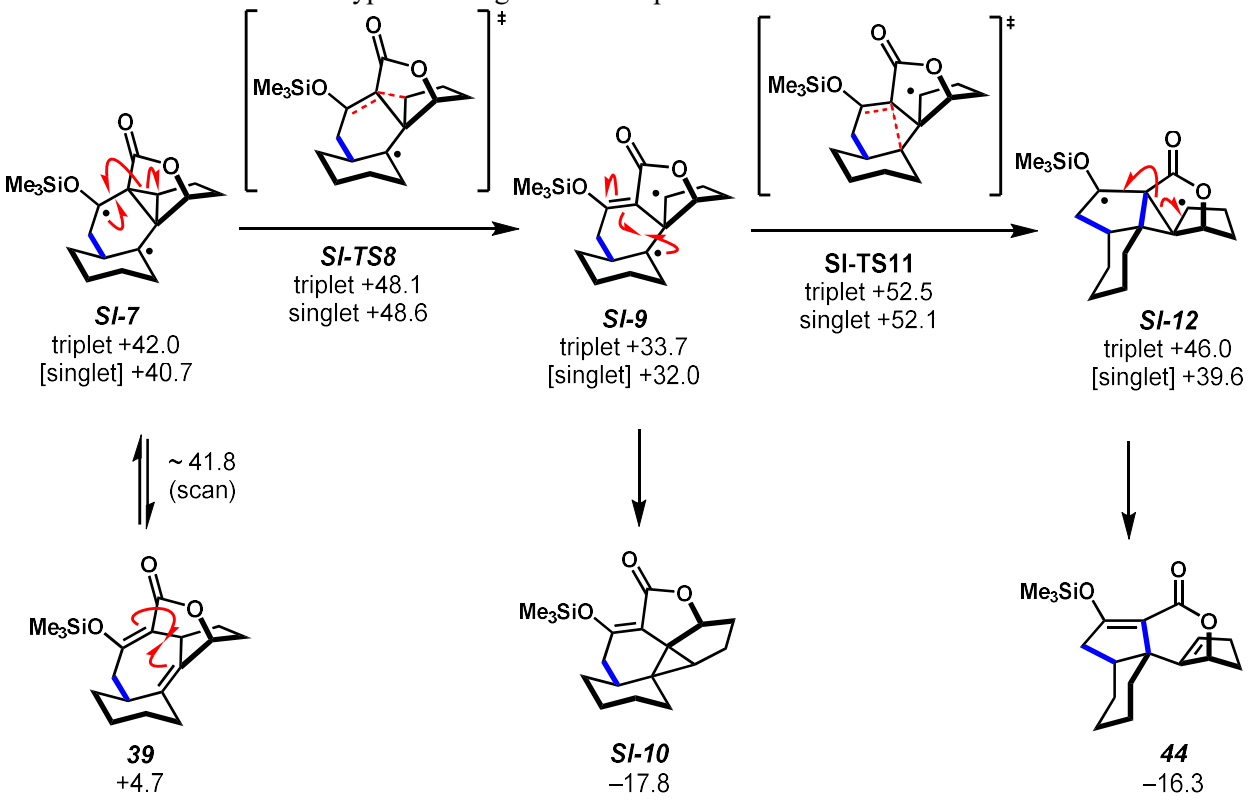


It was also envisioned that Cope intermediate **39** could undergo a di-pi-methane type rearrangement (though the reaction discussed here is not photochemical), as shown in Scheme S3. Bond-formation between the vicinal ends of the alkenes gives cyclopropylcarbinyl diradical **SI-1**. This structure is only stable as a triplet; when optimized on the singlet surface it reverts to **39**. Singlet and triplet structures are very close in energy, suggesting that that a spin-crossing might be possible. However, at about 42 kcal/mol, the compound is unlikely to form at room temperature. No transition state could be located between **39** and **SI-1**, and bond scans indicated a negligible barrier for collapsing from **SI-1** to **39**.

A diradical pathway was found connecting **SI-1** to the observed product 44, though the high energy of **SI-1** rules out this sequence. Cyclopropane **SI-1** can rearrange to homoallylic diradical **SI-3** via **SI-TS2**, which lies at about 48 kcal/mol on both the singlet and triplet surfaces. **SI-3** has essentially undergone a 1,2-shift of the enol ether moiety from **39** (half of the required 1,3-shift). **SI-3** is not stable as a singlet, collapsing to a surprisingly stable (and yet unobserved) vinylcyclopropane **SI-4**. The stability of **SI-3** relative to **39** highlight the amount of strain imparted by the anti-Bredt olefins in **39**.

Returning to **SI-3**, a second rearrangement to cyclopropylcarbinyl diradical **SI-6** can occur via **SI-TS5**. **SI-6** is again unstable on the singlet surface but collapses to the observed product **44**. This diradical sequence, while intriguing, is far too high in energy and requires singlet-triplet crossing near **SI-1** and returning to the singlet surface near **SI-6**. In fact, it seems more likely that this sequence would lead to **SI-4** than the observed product **44**, due to the relative stability of **SI-3** and **SI-4**, and we can confidently rule this out.

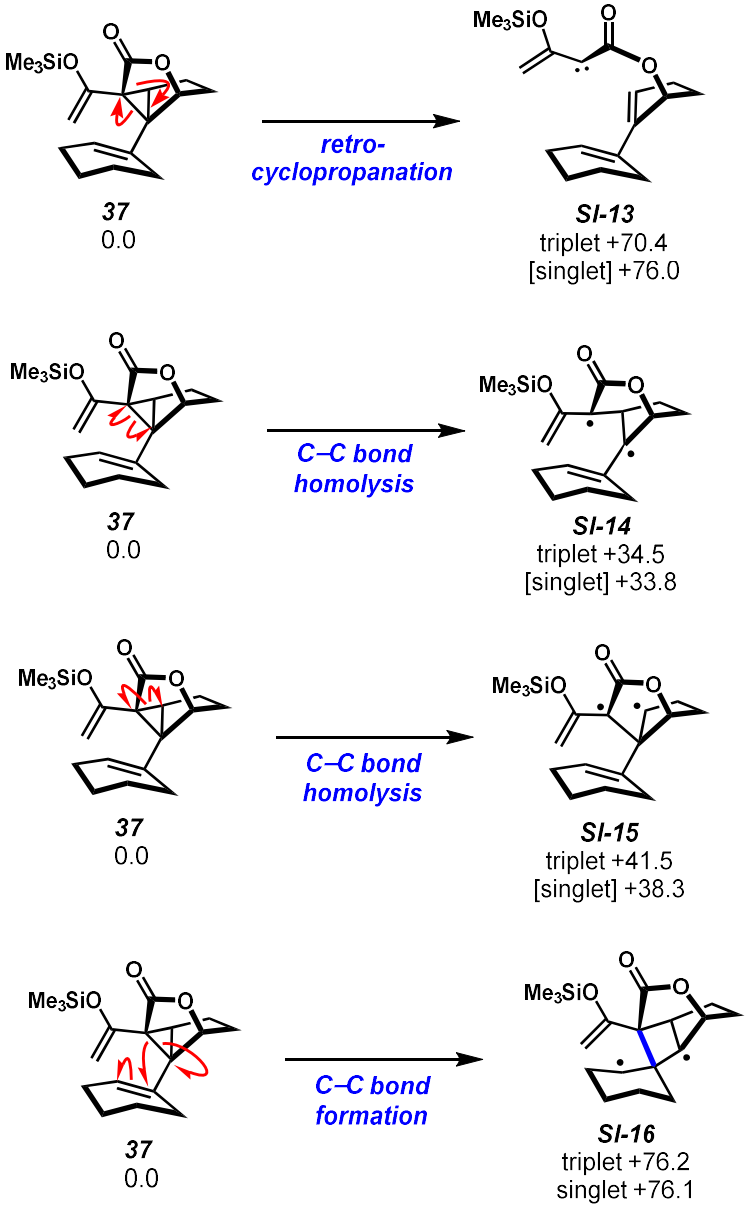
Scheme S3. Di-Pi-Methane Type Rearrangement of Cope Intermediate **39**



Several pathways were also explored beginning with reactant **37** (Scheme S4). From this structure, two of the cyclopropane bonds must be broken (a retro-cyclopropanation), which leads to very high energy carbene **SI-7**. We next considered breaking each of the cyclopropane C–C bonds individually, leading to diradical intermediates **SI-8** and **SI-9**. Both intermediates could only be located as triplet structures, with singlets reverting to reactant **37**. Furthermore, both diradicals are too high in energy to be experimentally feasible.

Lastly, formation of the required C–C bond from cyclopropane **37** leads cyclobutyl diradical **SI-10**. Although this compound can be located as a singlet diradical, it has a prohibitively high energy, similar to cyclobutylcarbinyl diradical **43**.

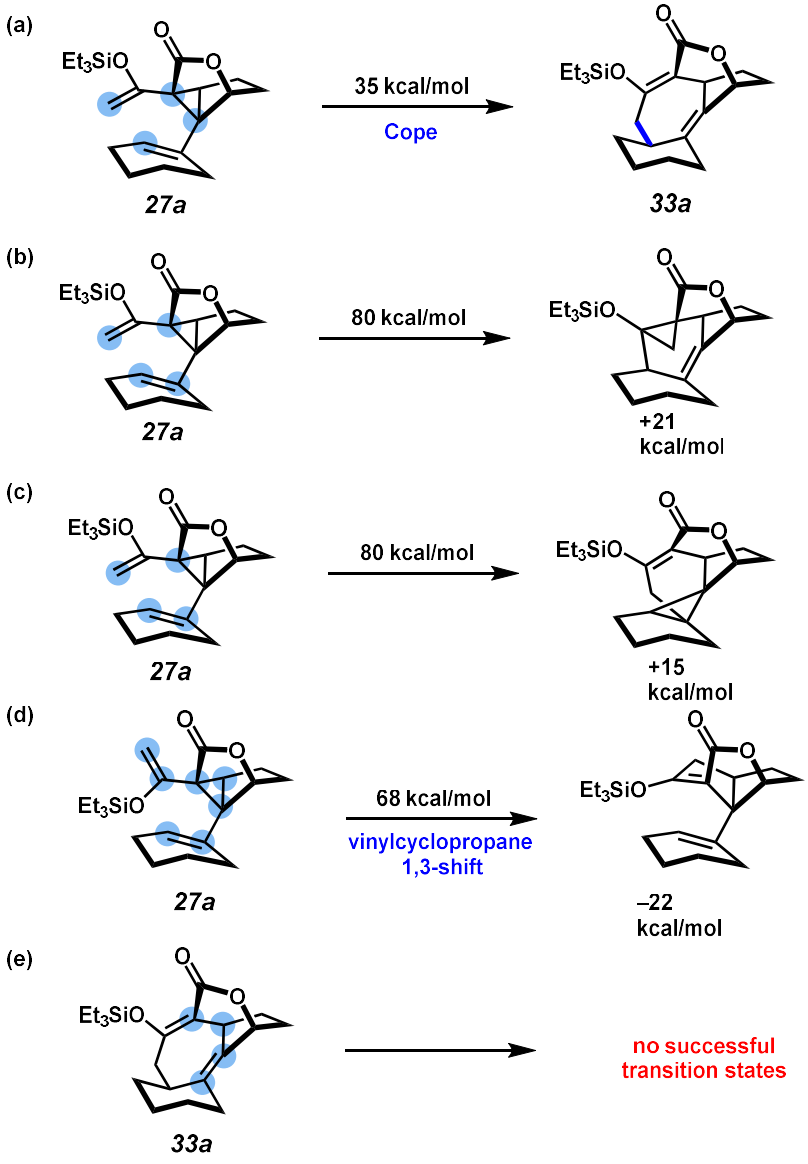
Scheme S4. Diradical Pathways Beginning at Reactant **37**



Summary of AFIR Simulations

A large number of AFIR simulations were run from TES model reactant **27a,** and representative results are shown in Scheme S5. Blue circles indicate which atoms were defined as reactive (between which the program applies artificial force to follow reaction pathways). The only process with a reasonable barrier is the Cope rearrangement to **33a**. Several other rearrangements of the vinylcyclopropane moiety were found, but the barriers were greater than 60 kcal/mol. No successful transition states were found when beginning with the Cope product **33a**.

Scheme S5. Representative results from AFIR simulations



Details of the AFIR simulations

We performed a systematic TS search by using the artificial force induced reaction (AFIR)[13-15] and single-component AFIR for intramolecular paths starting from local minima (SC-AFIR).[16,17] The computational procedure included AFIR search of reaction pathways, followed by optimization of the reaction pathways by applying locally updated planes (LUP) method.[18,19] Once a TS structure was located and optimized an intrinsic reaction coordinate simulation (IRC)[20] was performed to locate the corresponding local minima conformations of the initial and final states. AFIR and IRC simulations and the following full optimization of the structures were performed at the relatively low HF/3-21G level (denoted as level H) in gas phase by applying GRRM program[21] and Gaussian09.

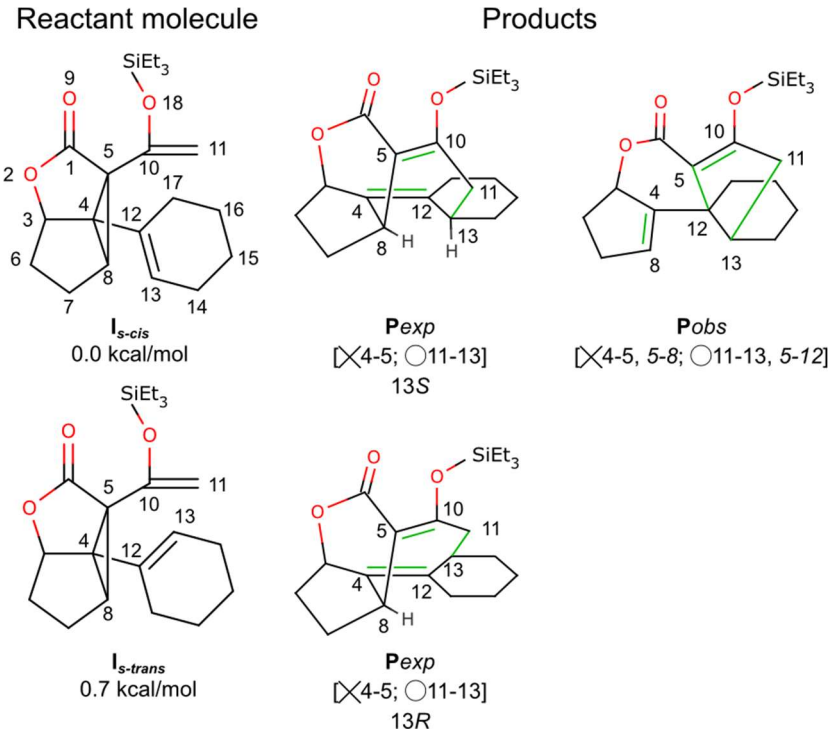


Figure S3. Reactant and expected **P***exp*/observed **P***obs* products and numbering of the atoms as used for the discussion of the AFIR results (may differ from the main text). Broken/formed bonds in the two products with respect to the initial structure are denoted with x/o.

Initially, we started from a single input molecule (*s*-cis or *s*-trans conformer of the reactant molecule; Fig. S3) and used different combinations of target atoms. First the group of the target atoms included carbon atoms 5, 12, 11 and 13 at collision energy γ = 400 kJ/mol, i.e. a bond formation between any two of 5, 12, 11 and 13 should be tried out by the program and 5-12 bond formation was essential for obtaining the observed product. The formation of the expected reaction product was observed in both cases: reaction pathways C1_1 and T1_1 (Table S2). The TS and product of the *s*-cis conformation, C1_1_TSII and C1_1_III with 13*S* configuration, were found much more stable with relative energies 36.2 and 4.3 kcal/mol (Grel@H), respectively, vs. 64.4 and 53.8 kcal/mol for T1_1_TSII and T1_1_III from the *s*-trans reactant. Several additional pathways were found only in the case of the *s*-trans reactant (paths T1_*n*, *n* = 2-6) but none of them featured the formation of 5-12 bond. The SC-AFIR simulations were repeated with defining a target group inlcuding all atoms expected to be somehow involved in the rearrangement, 4, 5, 8, 10-13 at γ = 800 kJ/mol. For both *s*-cis and *s*-trans reactant the lowest path showed formation of the expected product, pathways C2_1 and T2_1 identical to C1_1 and T1_1 (Table S2). Other pathways were

too high in energy with relative energy of the TS structures (with respect to the most stable conformer of the reactant molecule) above 80 kcal/mol. Only one path showed formation of 5-12 bond, T2_4 with relative energy of the TS structure 95.2 kcal/mol (Grel@H). Thus, the formation of 5-12 bond did not seem probable in the reactant molecule.

For this reason, we concentrated on rearrangement of the expected product to the observed one. T1_1_III and C1_1_III with *R*- and *S*-configuration of C13 as obtained from the *s*-trans and *s*-cis reactant, respectively, were used as starting points. Applying force between 5 and 12 in these structures (at $\gamma = 400$ kJ/mol) even if 5-8 was cleaved parallel by applying negative force between the atoms also did not result in the required TS structure.

Table S2. Relative energy, Erel, and relative Gibbs energy, Grel (both in kcal/mol), of the TS structures and the intermediates they connect to. Interatomic distances (in Å) and angles (in degrees) are provided only for the TS structures. Broken/formed bonds in the obtained intermediates with respect to the initial structure are denoted with x/o.

Structure		I	TSII	III	Information	Bonds	Distances
T1_1	Erel@H	0.5	63.0	50.5	**P***exp*	x4-5	1.94
	Grel@H	1.0	64.4	53.8		o11-13	2.01
T1_2	Erel@H	0.5	83.4	-4.1		o10-13	2.32
	Grel@H	1.0	82.5	-1.1	Hydrogen transfer	x17-H	1.36
						oH-11	1.49
						[17H11]	157.4
T1_3	Erel@H	0.5	83.8	3.1	**P***exp*	x4-5	1.60
	Grel@H	1.0	84.3	7.2		o11-13	1.59
T1_4	Erel@H	3.2	93.3	-8.1		o10-17	3.25
	Grel@H	2.7	91.3	-4.1	Hydrogen transfer	x17-H	1.09
						o11-H	2.38
						[17H11]	138.0
T1_5	Erel@H	3.2	100.8	16.5		x4-5	2.15
	Grel@H	2.7	104.4	15.4		x10-18	1.72
						o13-18	1.59
T1_6	Erel@H	0.5	120.3	79.5		x4-5	2.07
	Grel@H	1.0	118.8	73.5		x10-18	1.53
					Hydrogen transfer	x13-H	2.78
						oH-18	0.98
						[13H18]	173.9
T2_1	Erel@H	0.7	***63.0***	49.7	**P***exp*	x4-5	1.94
	Grel@H	1.0	***63.9***	53.3		o11-13	2.02
T2_2	Erel@H	3.6	69.0	-24.0		x5-8	2.22
	Grel@H	2.8	68.1	-22.3		o8-11	2.53
T2_3	Erel@H	0.5	83.4	-4.1		o10-13	2.32
	Grel@H	1.0	82.5	-1.1	Hydrogen transfer	x17-H	1.36
						oH-11	1.49

						[17H11]	157.4
T2_4	Erel@H	3.5	95.6	72.1		x4-5	1.99
	Grel@H	2.7	95.2	70.7		x4-12	1.74
						o5-12	1.79
T2_5	Erel@H	0.8	100.6	68.9		x4-12	1.83
	Grel@H	0.9	98.8	66.6		o4-13	1.86
T2_6	Erel@H	2.9	102.0	76.3		x5-10	1.77
	Grel@H	2.7	98.6	73.9		x5-8	2.00
						o8-10	1.76
T2_7	Erel@H	4.3	102.4	68.3		x4-8	1.94
	Grel@H	4.1	100.9	66.9		x4-12	1.79
						o8-12	1.80
T2_8	Erel@H	0.8	110.9	72.9		x5-10	1.86
	Grel@H	0.9	109.1	71.4		x4-5	1.95
						o4-10	1.82
T2_9	Erel@H	0.7	115.6	71.1		x4-5	1.95
	Grel@H	1.0	115.5	75.3		o11-12	1.67
						o4-13	2.19
T2_10	Erel@H	4.3	148.3	27.4		x4-8	2.06
	Grel@H	4.1	145.3	28.3		x3-6	1.91
						o8-12	1.69
						o6-13	2.35
C1_1	Erel@H	0.3	35.1	0.5	**P***exp*	x4-5	1.92
	Grel@H	0.0	36.2	4.3		o11-13	2.24
C2_1	Erel@H	0.3	35.1	0.5	**P***exp*	x4-5	1.92
	Grel@H	0.0	36.2	4.3		o11-13	2.24
C2_2	Erel@H	-0.3	83.0	14.6		x4-5	1.94
	Grel@H	0.0	83.2	19.0		o11-12	2.06
						o4-13	2.09
C2_3	Erel@H	0.4	88.3	20.8		x4-5	1.90
	Grel@H	0.1	89.6	25.8		o5-11	2.15
						o10-13	1.98

Then, taking into account our recent experience with AFIR successful application in modeling ACDC Hosomi-Sakurai reaction involving $SiMe_3$ group migration / transfer, we turned our attention to the TES substituent. The rearrangement mechanism involving migration of the TES group from O18 to O9 was found via a series of AFIR simulations (See Table S3 and Figs. S4). TES migration to C5 was also checked out but it was found successful only for T1_1_III; however, both TS structures for migration of TES to O9 or C5 in T1_1_III were found high in energy with Grel@H = 88.8 and 74.5 kcal/mol, respectively. Futher rearrangements with these structures were not simulated.

Table S3. Relative energy, Erel, and relative Gibbs energy, Grel (both in kcal/mol), of the TS structures and the intermediates they connect to. Interatomic distances (in Å) are provided only for the TS structures. Broken/formed bonds in the obtained intermediates with respect to the initial structure are denoted with x/o.

Initial structure	AFIR information		Initial	TS	Final	Bonds	Distances
T1_1_III	Si<->9	Erel@H	49.7	85.2	40.1	xSi-9	1.90
	Si<->5	Grel@H	52.7	88.8	44.4	oSi-5	2.48
	γ = 300 kJ/mol						
	Si<->9	Erel@H	49.7	70.0	52.8	xSi-18	1.90
	5<->12	Grel@H	52.7	74.9	53.7	oSi-9	1.93
	γ = 300 kJ/mol						
C1_1_III	Si<->9	Erel@H	-	-	-	-	-
	Si<->5	Grel@H					
	γ = 300 kJ/mol						
C1_1_III = III	Si<->9	Erel@H	0.8	16.8	6.9	xSi-18	1.91
(in Fig. S3)	5<->12	Grel@H	4.8	22.1	10.1	oSi-9	1.92
	γ = 300 kJ/mol						
V	5<->12	Erel@H	6.9	47.2	-7.7	x2-3	2.24
	5<->8 (negative)	Grel@H	10.1	48.1	-6.1	o5-12	2.40
	γ = 300 kJ/mol						
		Erel@H	-4.6	35.5	-29.6	x5-8	2.46
		Grel@H	-3.8	34.8	-26.6	o2-3	2.56

The energy diagram in case of $\mathbf{I}_{s\text{-}cis}$ reactant and the optimized structures of all intermediates and TSs are presented on Fig. S4 (Erel@H). In intermediate **III** (corresponding to C1_1_III from the previous simulations) the migration of the TES group from 18 to 9 proceeds relatively easy through **TSIV** with low relative energy, 16.8 kcal/mol. In the formed intermediate **V** 5-12 could be formed at expense of breaking the lactone ring (2-3 cleavage). The stage is exothermic process, while the transition state **TSVI**, 47.2 kcal/mol, is high in energy but still possible under the n-hexane reflux conditions of the experiment. The back formation of the lactone ring in intermediate **VII** results in simultaneous cleavage of bond 5-8 and formation of stable intermediate **IX** with relative energy -29.6 kcal/mol. Intermediate **IX** resembles the observed product **P***obs* with TES still connected to 9. Interestingly, TSVI and TSVIII were found within a single AFIR run (see Table S3 and Fig. S5). On Figure S5 the AFIR path (electron energy is relative with respect to the initial structure for this step, **V**) is shown with the two maxima corresponding to the two TS structures.

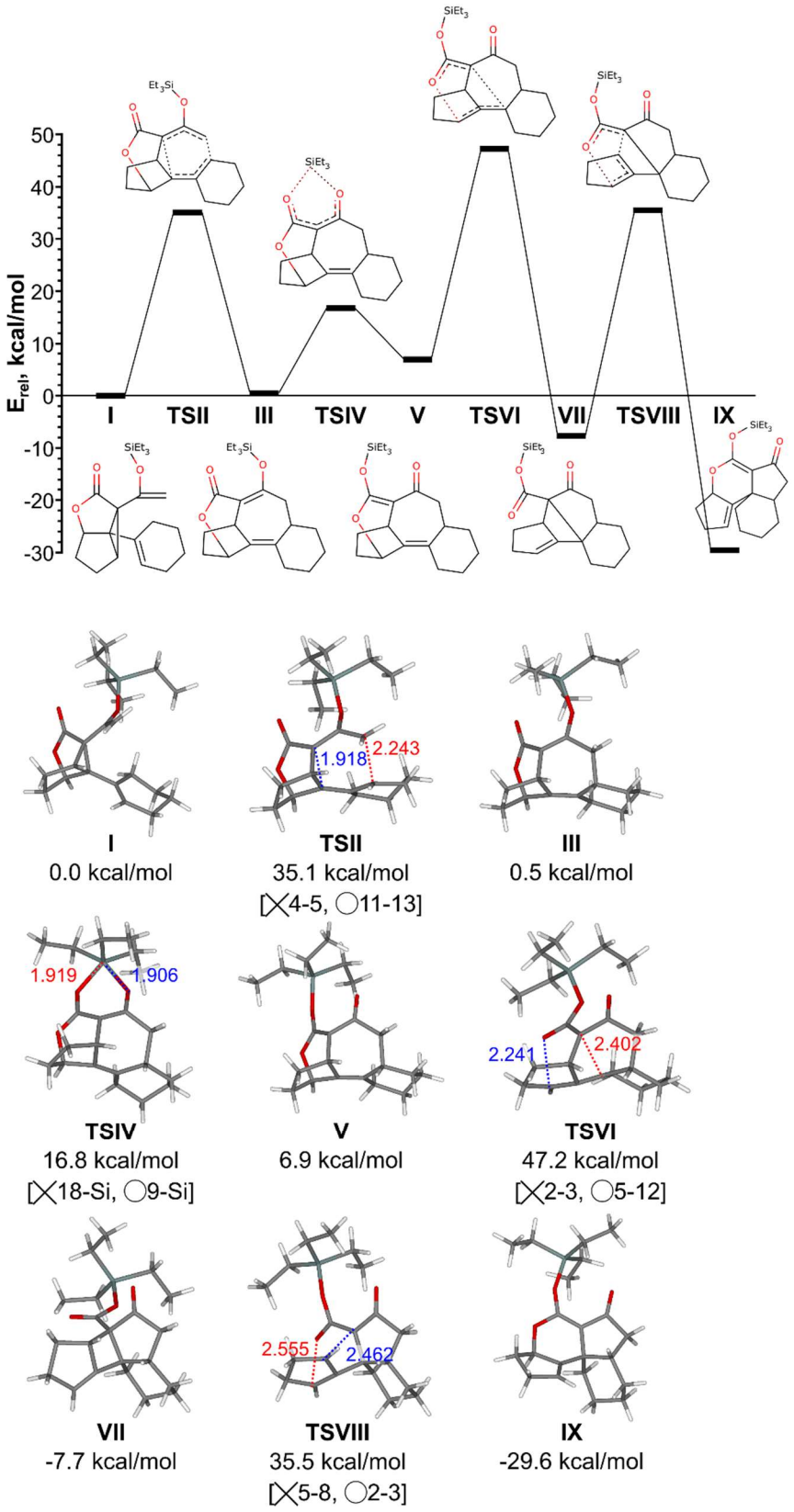


Figure S4. Reaction mechanism (@ level H) based on AFIR simulations.

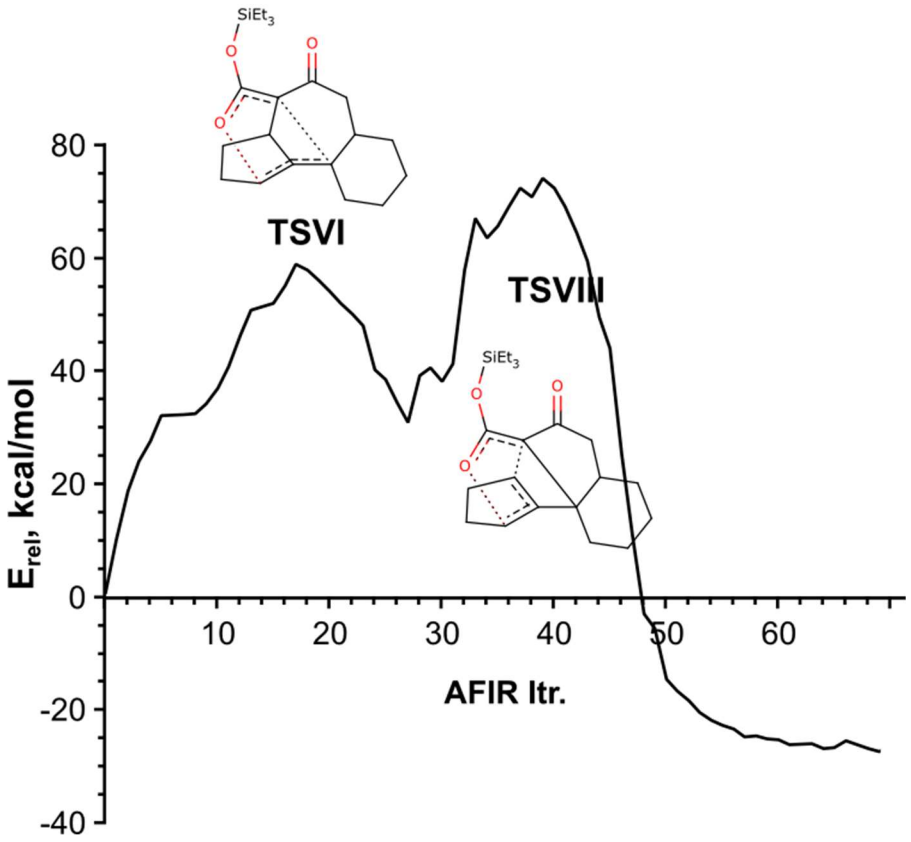
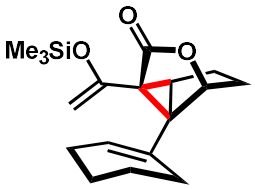


Figure S5. AFIR path (@ level H) obtained via applying positive force between atoms 5 & 12 (bond formation) and negative force between atoms 5 & 8 (bond cleavage).

Cartesian coordinates (Å), energies (hartree) and thermal corrections for optimized structures

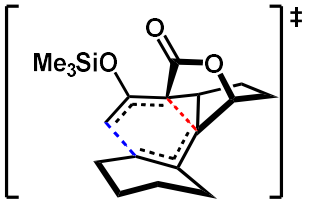
Figures 3, 6, 7, & 8: *Formation of* ***44*** *by a [1,5]-silyl shift/Claisen/retro-Claisen rearrangement cascade*



37

SCF Energy (B3LYP-D3BJ, hexane): -1217.199094
SCF Energy (M11-L, hexane): -1216.860955
SCF Energy (M06-2X, hexane): -1216.672457
SCF Energy (B3LYP, gas-phase): -1216.774297
Enthalpy Correction: 0.431624
Free-Energy Correction: 0.353238

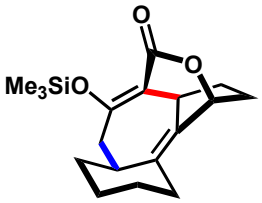
C	1.87809800	-1.72280400	-1.09747800
C	1.52796100	-0.70120000	0.01661400
C	1.38418500	-1.57796300	1.22816800
C	2.02887100	-2.94776000	0.97997700
C	2.73137300	-2.77963200	-0.39194700
H	2.32552500	-1.28696800	-1.99224400
H	1.46209700	-1.13423400	2.21536200
H	1.28667000	-3.75363900	0.95432600
H	2.73954000	-3.19237300	1.77539700
H	2.80609300	-3.70484300	-0.97144100
H	3.74247100	-2.37783000	-0.25083100
C	0.13078200	-1.15273300	0.45373400
O	0.63629400	-2.35133400	-1.50468200
C	-0.36809400	-2.08053500	-0.62560600
O	-1.47980500	-2.52773700	-0.76994300
C	2.01055200	0.70679300	-0.03409700
C	3.33727600	2.62002700	0.93304200
C	1.77298200	3.04333800	-1.00114500
C	3.16575900	3.32019000	-0.42317200
C	1.55573800	1.53878200	-1.22084600
C	2.80398800	1.20954100	0.92376600
H	2.82298400	3.19352400	1.72098200
H	1.01101600	3.41676700	-0.30318200
H	3.92713900	2.94794900	-1.12298700
H	2.09535900	1.21496300	-2.12539300
H	4.39635200	2.60921600	1.22621700
H	1.62972100	3.58356800	-1.94477500
H	3.33616500	4.39822200	-0.31559700
H	0.49566300	1.33377200	-1.41187600
H	3.08938300	0.57450900	1.76159900
C	-0.88259300	-0.24046700	1.06280200
C	-1.10951400	-0.13312000	2.37700100
H	-1.82830500	0.57682800	2.77171600
H	-0.58513100	-0.75945400	3.08786800
O	-1.53340600	0.49523500	0.11284600
Si	-3.20951900	0.73114900	-0.09145700
C	-4.16285800	-0.72966500	0.60874800
H	-5.21721300	-0.67291200	0.31019500
H	-4.12614500	-0.76888200	1.70245500
H	-3.74287300	-1.66483700	0.22384800
C	-3.42120100	0.86998500	-1.95366100
H	-4.46347400	1.08063700	-2.22292200
H	-3.12790400	-0.06582400	-2.44219900
H	-2.80118400	1.67462500	-2.36591900
C	-3.70038400	2.34771600	0.75055400
H	-4.75708400	2.57876900	0.56477100
H	-3.10562600	3.18803400	0.37354800
H	-3.56018700	2.30206000	1.83698200



TS38

SCF Energy (B3LYP-D3BJ, hexane):	-1217.160973
SCF Energy (M11-L, hexane):	-1216.819139
SCF Energy (M06-2X, hexane):	-1216.625412
SCF Energy (B3LYP, gas-phase):	-1216.732461
Enthalpy Correction:	0.430506
Free-Energy Correction:	0.356381

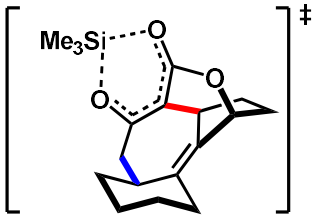
C	-2.10974100	-1.83299400	0.87066900
C	-1.94539600	-0.70030600	-0.12925000
C	-1.37357400	-1.40185700	-1.32468400
C	-1.88941800	-2.86107100	-1.29948700
C	-2.70492400	-2.95982100	0.01790500
H	-2.67709900	-1.58260700	1.76767200
H	-1.45627600	-0.92562000	-2.29893000
H	-1.06109200	-3.57648100	-1.31881000
H	-2.51169200	-3.06554700	-2.17565100
H	-2.62330200	-3.93076000	0.51428600
H	-3.76640000	-2.75542600	-0.16698300
C	-0.05210800	-1.11851300	-0.62168800
O	-0.80890600	-2.30074300	1.33427000
C	0.27101300	-1.95708200	0.56769200
O	1.37480400	-2.32989500	0.90014300
C	-2.13769100	0.66704000	0.04469000
C	-2.01595700	3.03485200	-0.94586600
C	-1.96745900	2.71458500	1.55295200
C	-2.59517900	3.50163000	0.39902100
C	-2.33625100	1.22839100	1.44943300
C	-1.90972100	1.51807700	-1.05842700
H	-1.02627800	3.49045400	-1.07880400
H	-0.87475900	2.82403200	1.52060100
H	-3.68380800	3.34839700	0.40923000
H	-3.39207900	1.10801100	1.73898900
H	-2.62901600	3.41586500	-1.77317700
H	-2.29873000	3.10943000	2.52098200
H	-2.42724500	4.57866700	0.52093500
H	-1.75169200	0.65028800	2.17468100
H	-2.19361600	1.11894100	-2.02573900
C	0.64734600	0.07684500	-0.84752900
C	0.17794400	1.02487500	-1.76376600
H	0.67339600	1.99100200	-1.78009200
H	-0.21557800	0.69253500	-2.71622700
O	1.52890100	0.49631800	0.11428800
Si	3.22521700	0.41671300	0.08638600
C	3.79408100	-0.92827500	-1.09983700
H	4.88857600	-1.00484400	-1.10155200
H	3.47382300	-0.72973600	-2.12943200
H	3.37970800	-1.89323700	-0.79175800
C	3.73076000	0.06231500	1.85924800
H	4.82180500	0.01817900	1.96460700
H	3.31177200	-0.89760000	2.17786100
H	3.36037400	0.83764800	2.54026600
C	3.87208100	2.10452700	-0.46401400
H	4.96888000	2.13390500	-0.43875500
H	3.50402600	2.90209300	0.19236500
H	3.56003300	2.34368100	-1.48794400



39

SCF Energy (B3LYP-D3BJ, hexane):	-1217.193247
SCF Energy (M11-L, hexane):	-1216.852326
SCF Energy (M06-2X, hexane):	-1216.661721
SCF Energy (B3LYP, gas-phase):	-1216.766836
Enthalpy Correction:	0.433782
Free-Energy Correction:	0.360700

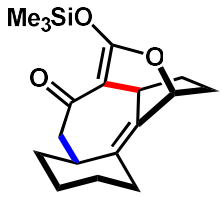
C	-2.30708100	-1.76151500	0.72105300
C	-2.11381500	-0.71083500	-0.34745600
C	-1.16840500	-1.44838100	-1.27735100
C	-1.57442300	-2.95008000	-1.21743300
C	-2.58765800	-3.04858300	-0.04680000
H	-2.99172500	-1.53463700	1.53774900
H	-1.18089000	-1.09507700	-2.30533200
H	-0.69884000	-3.58454400	-1.04688700
H	-2.02055500	-3.26872400	-2.16422400
H	-2.44995300	-3.93502600	0.57838900
H	-3.62268300	-3.04097900	-0.41035700
C	0.12501700	-1.09463700	-0.56772600
O	-0.99519700	-1.96307300	1.38911400
C	0.21462800	-1.65440300	0.80276300
O	1.21711900	-1.79031100	1.47405800
C	-2.28699200	0.62303400	-0.30394500
C	-1.07853600	2.86083200	-0.35631400
C	-2.81520900	2.47511400	1.40807000
C	-2.22319700	3.49521700	0.43519400
C	-3.30888200	1.24821200	0.62975200
C	-1.46052600	1.59340100	-1.17592400
H	-0.27507500	2.58733000	0.34080000
H	-2.04955700	2.17181100	2.13517200
H	-3.00792700	3.84753300	-0.25123800
H	-4.16457700	1.57044900	0.01223300
H	-0.64669400	3.59261200	-1.05075700
H	-3.64563400	2.90934500	1.97878700
H	-1.85520400	4.37929500	0.97103300
H	-3.70693700	0.49031000	1.31233900
H	-2.08028400	1.92553000	-2.02329000
C	0.65651200	0.12488700	-0.86209900
C	-0.10823500	1.04237000	-1.80131800
H	-0.31031100	0.54292400	-2.75229400
H	0.52134700	1.90645500	-2.03208000
O	1.66668700	0.72184700	-0.20150700
Si	3.29306600	0.29719600	0.12598700
C	3.55850500	0.40185500	1.97986200
H	2.95204100	-0.34822200	2.49411200
H	4.61365800	0.23095400	2.22886700
H	3.28452400	1.39252900	2.36177900
C	3.71455200	-1.38258000	-0.60367200
H	3.17105900	-2.17741800	-0.08703000
H	3.47487900	-1.43248900	-1.67232100
H	4.79073000	-1.57063800	-0.49750300
C	4.29225800	1.64430300	-0.74147100
H	4.15175000	1.61414700	-1.82864700
H	3.99886400	2.64217200	-0.39489900
H	5.36511700	1.52664700	-0.54264900



TS45

SCF Energy (B3LYP-D3BJ, hexane):	-1217.168462
SCF Energy (M11-L, hexane):	-1216.833486
SCF Energy (M06-2X, hexane):	-1216.638284
SCF Energy (B3LYP, gas-phase):	-1216.744015
Enthalpy Correction:	0.432863
Free-Energy Correction:	0.363508

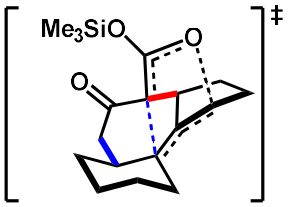
C	-1.69053400	2.01086600	-0.96690600
C	-1.94298700	1.05072200	0.16867100
C	-1.04708900	1.65574300	1.23626200
C	-1.10351400	3.19702400	1.03092300
C	-1.77941900	3.39946500	-0.35264900
H	-2.23058000	1.85907300	-1.89971500
H	-1.32150000	1.39574500	2.25644900
H	-0.09726500	3.62576200	1.05708700
H	-1.67958500	3.67502300	1.82889200
H	-1.28903400	4.15271000	-0.97540600
H	-2.83476900	3.67915100	-0.24695600
C	0.25781300	1.00767200	0.82234400
O	-0.24471600	1.82877200	-1.37409400
C	0.60304000	1.19034900	-0.54434300
O	1.61002800	0.65636200	-1.09750100
C	-2.36836600	-0.22814500	0.13215800
C	-1.69895300	-2.66117800	0.48508900
C	-2.96528100	-2.05573400	-1.58889500
C	-2.79262500	-3.10186300	-0.48815800
C	-3.31317500	-0.70044500	-0.95918800
C	-1.93460700	-1.28469600	1.17505400
H	-0.74202500	-2.61388400	-0.05215200
H	-2.03514700	-1.97110600	-2.16728000
H	-3.74502000	-3.23374400	0.04712300
H	-4.31349900	-0.79384000	-0.50353200
H	-1.56904900	-3.41169900	1.27462300
H	-3.75469400	-2.34799500	-2.29238500
H	-2.53369500	-4.07931000	-0.91378600
H	-3.41328100	0.07177000	-1.72893800
H	-2.74898700	-1.41771000	1.90396400
C	0.47295600	-0.31529600	1.21624900
C	-0.62286200	-0.99404200	2.02071100
H	-0.86340600	-0.39477000	2.90278000
H	-0.24203600	-1.95332400	2.38137500
O	1.42893900	-1.04978100	0.75997300
Si	3.00017100	-0.43539700	-0.21639800
C	3.92947900	-0.10515000	-1.86208100
H	3.92232200	0.95217500	-2.14623000
H	4.97167200	-0.43762700	-1.77419100
H	3.48060700	-0.66558700	-2.69261400
C	3.71174700	0.73825300	1.08563200
H	3.46753100	1.78566700	0.87874200
H	3.37302500	0.50328100	2.09992200
H	4.80518500	0.64706300	1.06805300
C	3.59717200	-2.23437200	0.06925000
H	3.45774500	-2.56787100	1.10240400
H	3.04455100	-2.93370800	-0.57263800
H	4.65776000	-2.32754700	-0.19377900



46

SCF Energy (B3LYP-D3BJ, hexane):	-1217.184439
SCF Energy (M11-L, hexane):	-1216.846735
SCF Energy (M06-2X, hexane):	-1216.653098
SCF Energy (B3LYP, gas-phase):	-1216.758402
Enthalpy Correction:	0.433790
Free-Energy Correction:	0.360957

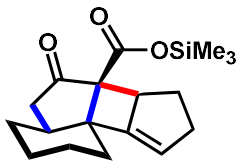
C	-1.08351000	2.16302600	-0.98193900
C	-1.71450300	1.31894100	0.09140200
C	-0.79722400	1.65007800	1.25420200
C	-0.39457300	3.14505600	1.07573600
C	-0.87788700	3.53012300	-0.34844200
H	-1.51957600	2.14338900	-1.97941900
H	-1.23818600	1.50298900	2.23556000
H	0.68785800	3.26597700	1.17978600
H	-0.86575500	3.76948300	1.84098400
H	-0.16024000	4.13798600	-0.90667100
H	-1.83437400	4.06654000	-0.32020300
C	0.30815400	0.63807900	0.98112100
O	0.31488900	1.62595400	-1.19105900
C	0.82540400	0.75062900	-0.29808900
C	-2.48655200	0.22157700	-0.01970100
C	-2.47814500	-2.29098700	0.32556500
C	-3.27172100	-1.37854600	-1.87234600
C	-3.48988200	-2.45512200	-0.80951900
C	-3.37999800	0.01112200	-1.22898900
C	-2.50040800	-0.90392300	1.03601800
H	-1.46589700	-2.46061100	-0.06618400
H	-2.27708200	-1.50094200	-2.32266700
H	-4.51415100	-2.37746000	-0.41444100
H	-4.42343700	0.14568500	-0.89712800
H	-2.64093200	-3.06029400	1.09054500
H	-4.00494500	-1.46973000	-2.68367500
H	-3.39705900	-3.45819000	-1.24475400
H	-3.20257500	0.79720000	-1.97037100
H	-3.44468600	-0.84740900	1.60134600
C	0.08078000	-0.70516800	1.51438800
C	-1.33461400	-0.93662800	2.09586000
H	-1.53765700	-0.24075500	2.91471100
H	-1.31925400	-1.93812600	2.53538400
O	0.85861500	-1.65640000	1.41056500
O	1.73915400	-0.01292300	-0.86123800
Si	3.27091700	-0.62516400	-0.36305600
C	3.70310100	-0.10934800	1.38996000
H	3.55983600	0.96625000	1.54242100
H	4.75970200	-0.33449200	1.58500200
H	3.09013900	-0.64602800	2.11756700
C	4.45927000	0.18819700	-1.58140500
H	4.47525900	1.27789300	-1.46107600
H	4.17321200	-0.02703900	-2.61729500
H	5.48336300	-0.17779700	-1.43445800
C	3.23659200	-2.47955700	-0.63118700
H	2.95959600	-2.72087600	-1.66412300
H	2.51147600	-2.94372000	0.04169700
H	4.22556900	-2.91596200	-0.44169900



TS47

SCF Energy (B3LYP-D3BJ, hexane):	-1217.167683
SCF Energy (M11-L, hexane):	-1216.830033
SCF Energy (M06-2X, hexane):	-1216.620958
SCF Energy (B3LYP, gas-phase):	-1216.736275
Enthalpy Correction:	0.430301
Free-Energy Correction:	0.354130

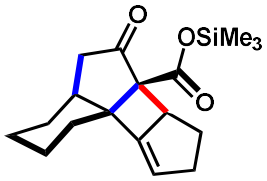
C	-1.98754700	2.13997500	-1.42412500
C	-2.05797500	1.22662400	-0.42008300
C	-1.48690700	1.78069000	0.85950700
C	-1.13448800	3.26369100	0.54915600
C	-1.55151600	3.49297900	-0.93493900
H	-2.10101700	1.92508100	-2.48199700
H	-2.18198300	1.76112600	1.70048000
H	-0.07164600	3.45966600	0.68581300
H	-1.68913400	3.92549900	1.22192000
H	-0.71549800	3.85735100	-1.54508400
H	-2.34902600	4.24656600	-1.02362200
C	-0.40530000	0.72352900	1.08514100
O	1.07238000	1.69991900	-0.48401200
C	0.83815200	0.80658100	0.33385100
C	-2.07911000	-0.21102800	-0.49625000
C	-1.95041100	-2.60020900	0.42250900
C	-1.47789000	-2.21658200	-2.00013500
C	-2.11764400	-3.16365600	-0.98805100
C	-2.08872800	-0.81127100	-1.88604900
C	-2.52033300	-1.16781100	0.61339400
H	-0.88453900	-2.58735500	0.68387500
H	-1.60886100	-2.57899800	-3.02649900
H	-3.18530100	-3.29079800	-1.22206000
H	-3.14774400	-0.86886200	-2.19653700
H	-2.44150300	-3.25048500	1.15592600
H	-1.66173200	-4.15949200	-1.04667100
H	-1.59777900	-0.13199700	-2.58655100
H	-3.61836100	-1.24115200	0.49262000
C	-0.70597900	-0.31658100	2.07924000
C	-2.19373200	-0.72466000	2.05408900
H	-2.85002000	0.08350200	2.38817400
H	-2.32928200	-1.55975200	2.74644100
O	0.09830800	-0.91556300	2.77970000
O	1.69733100	-0.22030700	0.53381200
Si	3.23102300	-0.31360000	-0.22910100
C	4.27483000	1.18501900	0.22260700
H	3.81647500	2.10447500	-0.15297300
H	5.28293300	1.10224600	-0.20285800
H	4.37910400	1.27508100	1.31027500
C	3.01388200	-0.49036900	-2.09247100
H	2.52892600	0.39713200	-2.50981400
H	2.39676200	-1.36403200	-2.33613700
H	3.98268900	-0.62178300	-2.59077300
C	3.95509200	-1.88454700	0.50995900
H	3.33680500	-2.75807600	0.27341400
H	4.01654600	-1.80990700	1.60140000
H	4.96518900	-2.07507400	0.12654000
H	-0.39685200	-2.15619100	-1.81800400



48-eq

SCF Energy (B3LYP-D3BJ, hexane):	-1217.204741
SCF Energy (M11-L, hexane):	-1216.870213
SCF Energy (M06-2X, hexane):	-1216.674955
SCF Energy (B3LYP, gas-phase):	-1216.780457
Enthalpy Correction:	0.431923
Free-Energy Correction:	0.355632

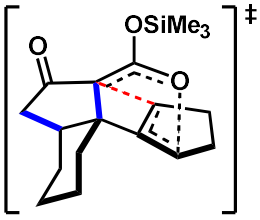
H	-0.71124500	4.45117300	-1.23695500
C	-0.98856200	3.84529100	-0.36612900
C	-2.10249000	2.85062400	-0.69277200
C	-1.88116300	1.72004000	-0.01641700
C	-0.59404400	1.75006900	0.75800000
C	0.17730400	2.91083300	0.09852800
H	-1.27467900	4.55148400	0.42858300
H	-2.85977400	3.03134200	-1.44997400
H	-0.68755200	1.92680300	1.83776200
H	0.72659200	2.55847300	-0.78103600
H	0.89333700	3.40018700	0.76661800
C	-0.47458300	0.18933500	0.44786900
C	0.72874900	-0.30472700	-0.31196500
O	0.69105500	-1.14462300	-1.19259300
C	-0.62829100	-0.54771000	1.79363400
O	0.25807800	-1.08944200	2.41486300
C	-1.95556600	0.20632700	-0.18410600
C	-3.02496300	-2.05965900	0.46644100
C	-3.46899300	-2.27488400	-0.98144800
C	-2.84820400	-0.57319400	0.84228000
C	-2.23304700	-0.17777000	-1.65068200
H	-3.73763500	-2.51059200	1.16971300
H	-2.07006000	-2.58562400	0.61932000
H	-3.59648600	-3.34679400	-1.17776800
H	-1.43670500	0.22792600	-2.28252700
O	1.86423500	0.24559500	0.14061900
Si	3.43166900	-0.41116300	-0.20070700
C	3.45045500	-2.22331600	0.29143100
H	3.03367400	-2.34759900	1.29736700
H	4.47494000	-2.61579300	0.29658100
H	2.85347500	-2.82863600	-0.39711500
C	3.84735100	-0.13782300	-2.01424000
H	3.81123900	0.92643100	-2.27518500
H	3.14210400	-0.67117400	-2.65905700
H	4.85843300	-0.50016500	-2.23928500
C	4.53572800	0.61792000	0.91914100
H	4.46539100	1.68507100	0.67928900
H	5.58687900	0.32160400	0.81672500
H	4.25221000	0.49112500	1.96994400
H	-3.83569800	-0.09818900	0.89031300
C	-2.10375000	-0.48050700	2.18680800
H	-2.28942000	0.47758800	2.69031200
H	-2.35010400	-1.27922600	2.89178300
H	-4.45091200	-1.80552800	-1.14596000
H	-3.15343500	0.35615500	-1.93310900
C	-2.43200700	-1.67111800	-1.93241100
H	-1.47504500	-2.19103300	-1.81618400
H	-2.74338400	-1.79934100	-2.97714900



48

SCF Energy (B3LYP-D3BJ, hexane):	-1217.204291
SCF Energy (M11-L, hexane):	-1216.868836
SCF Energy (M06-2X, hexane):	-1216.673737
SCF Energy (B3LYP, gas-phase):	-1216.779028
Enthalpy Correction:	0.431825
Free-Energy Correction:	0.354690

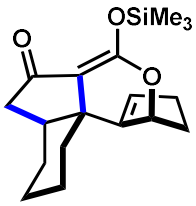
H	-2.17361900	4.00268300	-1.61537800
C	-2.48381000	3.33344200	-0.80350100
C	-2.68628600	1.90245600	-1.29749600
C	-2.22190300	1.05331800	-0.38146400
C	-1.52799700	1.73371100	0.76686800
C	-1.37109300	3.19610800	0.29282400
H	-3.41056700	3.75906400	-0.38862600
H	-3.07602400	1.66224600	-2.28271000
H	-2.06108300	1.68013000	1.72538700
H	-0.39101900	3.34479700	-0.16128000
H	-1.48907900	3.91931000	1.10625100
C	-0.47474700	0.53634900	0.71365200
C	0.86225700	0.77962000	0.04714200
O	1.16992900	1.76173300	-0.59967900
C	-0.32222200	-0.25800100	2.02638300
O	0.27090200	0.12965100	3.00732500
C	-1.54304600	-0.28416400	-0.16906000
C	-2.04265900	-2.08369700	-1.93040500
C	-3.09237000	-2.33464300	0.34165400
C	-2.44142700	-3.07607800	-0.83204600
C	-2.24392700	-1.18321000	0.91427700
C	-1.02918500	-1.06971400	-1.38404500
H	-2.93876200	-1.56456300	-2.30006900
H	-4.04370500	-1.91131300	-0.00956900
H	-1.54907400	-3.62333700	-0.49438700
H	-0.12450200	-1.61864200	-1.08983000
H	-1.60771000	-2.60981500	-2.78921000
H	-3.34729800	-3.03171200	1.15047900
H	-3.13817900	-3.82883100	-1.22126100
H	-0.72528400	-0.35892500	-2.16137400
C	-1.11229700	-1.55718700	1.88833700
H	-1.44901600	-1.92587600	2.86167500
H	-0.44203200	-2.31257100	1.45251100
H	-2.93107000	-0.53756500	1.47624200
O	1.69356100	-0.26980900	0.21944000
Si	3.34323600	-0.26122500	-0.32240700
C	3.38755900	-0.14759100	-2.19825800
H	2.82177000	-0.96548100	-2.65972700
H	4.41948900	-0.20965300	-2.56592000
H	2.95794700	0.79889400	-2.53954300
C	4.25593000	1.15043100	0.51425400
H	4.17760900	1.07694800	1.60500900
H	3.84532700	2.11717600	0.20824000
H	5.32148500	1.13221400	0.25337500
C	3.95600400	-1.93374300	0.27819100
H	3.86847300	-2.01798600	1.36724800
H	5.01023300	-2.08317200	0.01465100
H	3.38258100	-2.75390500	-0.16902000



TS49

SCF Energy (B3LYP-D3BJ, hexane):	-1217.175903
SCF Energy (M11-L, hexane):	-1216.842642
SCF Energy (M06-2X, hexane):	-1216.628317
SCF Energy (B3LYP, gas-phase):	-1216.743505
Enthalpy Correction:	0.428936
Free-Energy Correction:	0.352538

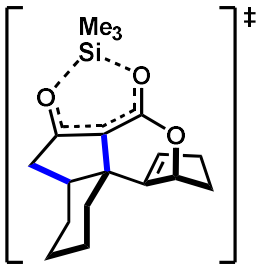
H	-0.31900200	3.98934600	0.23576200
C	0.54160200	3.60828400	-0.32698900
C	1.28267200	2.55491900	0.44483700
C	1.45944100	1.41044400	-0.28669300
C	0.83504900	1.56386200	-1.54291600
C	0.13561400	2.87826600	-1.63578300
H	1.17858600	4.47880300	-0.54420400
H	1.59095000	2.68946900	1.47536000
H	0.95554300	0.89802100	-2.38705600
H	-0.95163600	2.71126700	-1.67374000
H	0.39054300	3.42365600	-2.55375700
C	0.35092800	-0.60476600	-0.34736400
C	-0.88548400	-0.14360600	0.25471600
O	-0.92850800	0.66042300	1.19338800
C	0.54888200	-1.84641700	-1.10348300
O	-0.28740300	-2.56570500	-1.63388000
C	1.69773200	-0.03011100	0.10568600
C	3.49438600	-0.11374500	1.96240200
C	4.17471700	-0.74667000	-0.37620000
C	4.35781800	-1.05539900	1.11482800
C	2.70947900	-0.76838800	-0.84834900
C	2.01243500	-0.27315700	1.60067300
H	3.81812700	0.92519700	1.79603000
H	4.58543700	0.25526100	-0.56962800
H	4.07408300	-2.09623900	1.32674700
H	1.70700800	-1.30062800	1.84355600
H	3.63600800	-0.31774000	3.03129700
H	4.76072300	-1.44185500	-0.99160500
H	5.41750700	-0.96110000	1.38340000
H	1.37018600	0.37455300	2.20375600
C	2.06217400	-2.14084200	-1.08839600
H	2.37900900	-2.62110100	-2.01960500
H	2.27136700	-2.84594400	-0.27122400
H	2.68733300	-0.25051900	-1.81635700
O	-2.01038300	-0.63465800	-0.31617900
Si	-3.57798700	-0.36561700	0.32092500
C	-3.67916200	-1.02154100	2.08222700
H	-3.44502200	-2.09210600	2.11388900
H	-4.68798200	-0.88901700	2.49315500
H	-2.97165600	-0.49866100	2.73273200
C	-4.01861700	1.46520700	0.22701300
H	-3.93321300	1.83876000	-0.80106100
H	-3.35338600	2.05573300	0.86411000
H	-5.05203300	1.63714200	0.55374500
C	-4.66735500	-1.36743700	-0.83864500
H	-4.59024000	-1.00180300	-1.86895300
H	-5.72191100	-1.31439500	-0.54077500
H	-4.36802100	-2.42134800	-0.84052400



50

SCF Energy (B3LYP-D3BJ, hexane): -1217.226265
SCF Energy (M11-L, hexane): -1216.889245
SCF Energy (M06-2X, hexane): -1216.695092
SCF Energy (B3LYP, gas-phase): -1216.800859
Enthalpy Correction: 0.433017
Free-Energy Correction: 0.357445

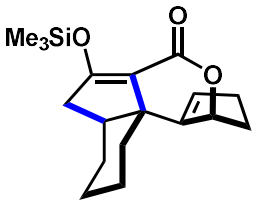
H	0.34804300	3.42260300	0.68372300
C	-0.56230600	3.45423900	0.07626800
C	-0.64637500	2.13004600	-0.70337900
C	-1.55406400	1.25420900	0.13568800
C	-2.19410600	1.99233200	1.05005300
C	-1.81380300	3.45430100	0.99213400
H	-0.49850400	4.32991400	-0.57566400
H	-1.04952300	2.27108100	-1.71542300
H	-2.93052000	1.61240500	1.75213500
H	-1.61004600	3.88114900	1.98209000
H	-2.62749000	4.05543800	0.56040200
C	-0.08308200	-0.61775200	-0.33899000
C	0.89336900	0.26245400	-0.70580900
O	0.68665900	1.58206000	-0.90664700
C	0.12587000	-1.98115400	0.14017200
O	1.16155100	-2.63952000	0.17374600
C	-1.54600600	-0.21463100	-0.18236200
C	-3.85457800	-0.52196300	-1.30747900
C	-3.55642500	-1.35358600	1.05967400
C	-4.24613000	-1.60090400	-0.28997700
C	-2.03072500	-1.17566800	0.95344200
C	-2.33401600	-0.49682000	-1.50438600
H	-4.20129900	0.46038800	-0.95587200
H	-3.99080300	-0.44900000	1.50755800
H	-3.96484800	-2.58759600	-0.68453000
H	-2.00689700	-1.46805100	-1.89859600
H	-4.34932600	-0.70431600	-2.26990300
H	-3.77622700	-2.17271200	1.75733900
H	-5.33405400	-1.62417800	-0.14901500
H	-2.05009400	0.24214400	-2.26386000
C	-1.22262500	-2.46670100	0.69873500
H	-1.06852500	-3.07370100	1.59614900
H	-1.70454600	-3.11408800	-0.04745200
H	-1.66796700	-0.75325700	1.90021600
O	2.15336400	-0.06542400	-0.93022300
Si	3.53657500	-0.17781500	0.07227800
C	2.99752100	-0.29336900	1.86979700
H	2.35317500	0.54487500	2.16046700
H	3.87357700	-0.27886700	2.53025300
H	2.45115900	-1.22525900	2.04348000
C	4.44330300	-1.70634900	-0.51717900
H	4.73134200	-1.61553000	-1.57083400
H	3.78633500	-2.57529400	-0.41421500
H	5.35539400	-1.88105800	0.06663900
C	4.54166000	1.38664600	-0.22961600
H	5.47786800	1.37077400	0.34274500
H	3.98367200	2.28315300	0.06428500
H	4.80056100	1.48947200	-1.28972500



TS51

SCF Energy (B3LYP-D3BJ, hexane):	-1217.205678
SCF Energy (M11-L, hexane):	-1216.87251
SCF Energy (M06-2X, hexane):	-1216.675172
SCF Energy (B3LYP, gas-phase):	-1216.784487
Enthalpy Correction:	0.432393
Free-Energy Correction:	0.361304

H	1.38896200	3.71140900	-0.87291100
C	2.09437800	3.36762300	-0.10997700
C	1.46123000	2.15244800	0.59046100
C	2.08881800	0.94957200	-0.09533500
C	3.13942100	1.33186300	-0.83007700
C	3.38276900	2.82202200	-0.77851600
H	2.27885800	4.20142900	0.57273800
H	1.65629600	2.14434000	1.67111000
H	3.78183400	0.65953600	-1.39201200
H	3.55867000	3.25823600	-1.76955900
H	4.27571300	3.05105800	-0.17892300
C	-0.04738600	-0.13092200	0.11799500
C	-0.68691000	1.10644400	0.25587400
O	0.00415900	2.23349200	0.47466900
C	-0.74472900	-1.16424600	-0.48833900
C	1.44423500	-0.38830400	0.15678500
C	3.23745400	-1.68299000	1.49381700
C	2.85108100	-2.34447500	-0.91281200
C	3.19073700	-2.84842300	0.49742500
C	1.58721100	-1.46903700	-0.97721000
C	1.88211600	-0.96865700	1.54032100
H	4.02423800	-0.97389800	1.19851700
H	3.70390700	-1.75734000	-1.28124200
H	2.44034300	-3.57872800	0.83320100
H	1.11480800	-1.68231300	1.86984200
H	3.49971000	-2.04468700	2.49588400
H	2.74334900	-3.18818600	-1.60739800
H	4.15030700	-3.37978800	0.47588100
H	1.88705300	-0.16650000	2.28914400
C	0.23256800	-2.23288800	-0.94234600
H	-0.05248700	-2.65131900	-1.91304800
H	0.23741000	-3.06417300	-0.22274300
H	1.60215900	-0.91665700	-1.92556500
O	-1.93946000	1.25546300	0.10603600
O	-2.00265200	-1.20954800	-0.70992800
Si	-3.42246700	-0.05709200	0.00773500
C	-4.17891500	1.08131300	1.35709900
C	-4.15913700	0.41262600	-1.66025300
C	-4.12329200	-1.71818100	0.66703900
H	-4.10081700	2.14386500	1.10785800
H	-5.23780100	0.82897800	1.49998200
H	-3.68259200	0.93717700	2.32639900
H	-3.80037400	1.39614600	-1.98273000
H	-3.90426500	-0.31784000	-2.43484100
H	-5.25236000	0.46447200	-1.58523000
H	-4.08897500	-2.51800100	-0.07877300
H	-3.55472700	-2.06436300	1.54144600
H	-5.16093300	-1.58355400	0.99677500

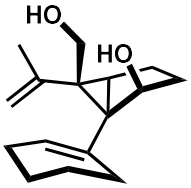


44

SCF Energy (B3LYP-D3BJ, hexane):	-1217.232002
SCF Energy (M11-L, hexane):	-1216.894911
SCF Energy (M06-2X, hexane):	-1216.701355
SCF Energy (B3LYP, gas-phase):	-1216.808120
Enthalpy Correction:	0.433281
Free-Energy Correction:	0.358375

H	-2.31264800	-3.44805500	-0.91316500
C	-2.98181000	-2.94429600	-0.20810200
C	-2.13954100	-1.92011200	0.57602700
C	-2.33157300	-0.62686700	-0.18670100
C	-3.37161600	-0.72650200	-1.02233500
C	-4.02241300	-2.09077900	-0.97681600
H	-3.42980900	-3.70859200	0.43309200
H	-2.49091200	-1.82229200	1.61310600
H	-3.74132700	0.07345400	-1.65770500
H	-4.24150800	-2.49074100	-1.97460200
H	-4.98388200	-2.05057400	-0.44356100
C	0.04447300	-0.17339900	0.03931600
C	0.30253200	-1.55691300	0.42448600
O	-0.76613600	-2.36680700	0.68188600
C	0.94222200	0.70047700	-0.49758100
C	-1.34464200	0.46934600	0.09281500
C	-2.73422100	2.12269000	1.51344300
C	-2.24481000	2.73408500	-0.88741800
C	-2.42703700	3.26786000	0.54091800
C	-1.23185200	1.58156200	-0.99770900
C	-1.59443100	1.09619200	1.50444900
H	-3.67823700	1.63667100	1.22843300
H	-3.22055200	2.38033300	-1.24783300
H	-1.51578000	3.78620000	0.87287400
H	-0.66880500	1.59132700	1.82730500
H	-2.87395600	2.51002000	2.53055400
H	-1.94707500	3.54492700	-1.56583600
H	-3.23004800	4.01530100	0.55482200
H	-1.77943200	0.30028200	2.23629100
C	0.25979900	1.97795800	-0.94197300
H	0.65303200	2.31800600	-1.90658900
H	0.46031600	2.78298600	-0.21873300
H	-1.38232100	1.08321700	-1.96411600
O	1.41316000	-2.05864900	0.50186000
O	2.24513300	0.61014900	-0.72433400
Si	3.68373700	-0.04399000	-0.05135600
C	3.56206200	-0.18034800	1.81941300
H	3.16905600	0.74367200	2.26090800
H	4.56089800	-0.34438300	2.24412100
H	2.91700000	-1.01117900	2.11300400
C	4.93215600	1.29825500	-0.50132400
H	4.68342700	2.25616400	-0.02970800
H	4.96868500	1.46043100	-1.58493100
H	5.94160800	1.01858000	-0.17409800
C	4.15518700	-1.63308100	-0.93144700
H	4.15442400	-1.48726400	-2.01841300
H	3.46169200	-2.43986600	-0.68607200
H	5.16968100	-1.93707500	-0.64222600

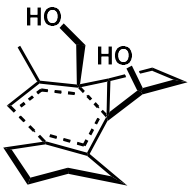
Figure 4: *Computed structures for Cope rearrangement of reduced divinylcyclopropane* ***40***



40

SCF Energy (B3LYP-D3BJ, hexane):	-774.8669329
SCF Energy (M11-L, hexane):	-774.6086577
SCF Energy (M06-2X, hexane):	-774.4527005
SCF Energy (B3LYP, gas-phase):	-774.5227161
Enthalpy Correction:	0.393272
Free-Energy Correction:	0.330881

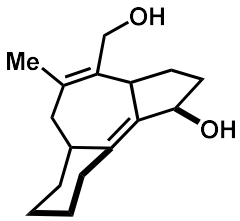
C	1.13263600	-0.38575500	0.25375200
C	1.92299400	0.02521800	1.25593700
C	3.42852900	0.10172600	1.19250200
C	4.00895200	-0.65715200	-0.00923900
C	3.18282500	-0.37836900	-1.26922000
C	1.72776000	-0.83002400	-1.07716300
C	-1.17424000	0.09068300	1.51894900
H	1.68793000	-1.93149400	-1.14698300
H	1.10859600	-0.44752000	-1.90054400
H	3.85423600	-0.28709300	2.12802100
H	3.73385800	1.15975300	1.15206600
C	-2.23645300	-0.92754200	1.93297300
C	-0.36382100	-0.46668900	0.36498000
H	-1.92707700	-1.37993200	2.88272200
C	-2.27737400	-1.99562400	0.81615400
H	-3.22002000	-0.47451200	2.10773300
C	-1.25208100	0.79814700	0.18161600
C	-0.96561600	-1.84513900	0.02057400
H	-3.11753300	-1.84646900	0.13240900
H	-2.38139000	-3.00872100	1.21693200
C	-0.54439000	2.13369800	0.06455600
C	-0.51818000	3.01137700	1.07391600
C	0.03446500	2.47782100	-1.28778100
H	-0.94901900	2.79442700	2.04730900
H	-0.06638300	3.99326700	0.95496700
H	1.46878900	0.34282500	2.19205800
H	0.91670600	1.86103300	-1.50029900
H	0.34039400	3.52797600	-1.33315800
H	-0.68659400	2.27675000	-2.08702500
H	-0.24028700	-2.60098300	0.35290500
H	-0.67565300	0.62274500	2.32336600
C	-2.53105500	0.78183500	-0.67896900
H	-2.94324900	1.79589400	-0.68587400
H	-3.29754500	0.14215100	-0.22302700
O	-1.24862300	-2.08529300	-1.37401400
H	-0.39923600	-2.14842100	-1.83825400
O	-2.31706900	0.43432500	-2.03617900
H	-2.00316600	-0.49289500	-2.02618800
H	3.61884500	-0.87987200	-2.14187900
H	3.20054900	0.69950700	-1.48221800
H	3.99445800	-1.73632500	0.19898400
H	5.05861700	-0.37961100	-0.16369500



TS41

SCF Energy (B3LYP-D3BJ, hexane):	-774.8379028
SCF Energy (M11-L, hexane):	-774.5764938
SCF Energy (M06-2X, hexane):	-774.4109307
SCF Energy (B3LYP, gas-phase):	-774.4902984
Enthalpy Correction:	0.391613
Free-Energy Correction:	0.331293

C	-1.20689600	-1.87692700	-0.01729500
C	-0.32331400	-0.76544100	0.53096700
C	-1.12622700	0.10200400	1.46915300
C	-2.35664700	-0.73641700	1.85623700
C	-2.55633600	-1.77085200	0.72469900
H	-0.71748900	-2.83782800	0.20080500
H	-0.60987600	0.48484000	2.35340400
H	-3.25166500	-0.13106400	2.03729800
H	-2.12672800	-1.25106400	2.79653300
H	-3.31662300	-1.45284300	0.00579900
H	-2.87844800	-2.74281200	1.11059000
C	-1.25192700	1.10912400	0.34416800
O	-1.48373800	-1.85692700	-1.43942700
C	-2.50535400	1.18160900	-0.52414900
C	1.06802900	-0.69998300	0.32363600
C	3.36593800	0.23939800	0.93119300
C	3.18645200	-1.40859500	-0.94410500
C	3.79024600	-0.07028900	-0.50801000
C	1.65190700	-1.33897500	-0.93401200
C	1.87768100	0.07897500	1.14510600
H	3.68218700	1.24896500	1.22199200
H	1.25028700	-2.35720400	-1.05257300
H	3.89737100	-0.44315800	1.61609100
H	1.31844100	-0.76767200	-1.81587900
H	1.54710700	0.22605600	2.16591400
C	-0.23016700	2.06512900	0.11597800
C	0.82474100	2.23749200	0.99747100
H	1.61742800	2.93931200	0.74903000
H	0.70437500	2.04555800	2.05482700
C	-0.21692100	2.84574900	-1.18847500
H	-0.63442000	-1.91891300	-1.90471100
H	-2.79733700	2.23667700	-0.58726200
H	-0.50814700	2.22707900	-2.03995300
H	0.77390000	3.27546400	-1.36921100
H	-0.92602400	3.68518400	-1.14853400
O	-2.37914700	0.75154000	-1.87254200
H	-3.33984300	0.66953900	-0.02765300
H	3.43784700	0.72629800	-1.17812600
H	4.88405200	-0.09233500	-0.58415500
H	3.53626600	-1.69247000	-1.94404100
H	3.52396200	-2.19564200	-0.25501600
H	-2.11077500	-0.19087300	-1.84478500

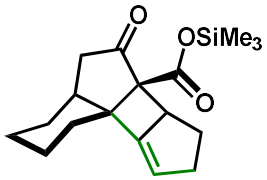


36

SCF Energy (B3LYP-D3BJ, hexane):	-774.8916823
SCF Energy (M11-L, hexane):	-774.6357987
SCF Energy (M06-2X, hexane):	-774.4744398
SCF Energy (B3LYP, gas-phase):	-774.5457696
Enthalpy Correction:	0.394595
Free-Energy Correction:	0.331994

C	0.10536000	1.09931700	-0.17457400
C	1.27876500	0.44882400	-0.17921900
C	1.28121500	-1.01860900	-0.58232300
C	0.64594600	-1.84516400	0.55223500
C	-0.87291300	-1.77331700	0.65569800
C	-1.67672000	-0.82958600	0.11195100
C	-1.24413100	0.48463500	-0.56673100
C	-0.09149500	2.56020600	0.19307700
C	-3.18064400	-1.04613500	0.01614300
C	-2.24805100	1.65173100	-0.30850200
H	-1.24426600	0.31119600	-1.65577700
C	2.55844500	1.05068500	0.38141500
C	2.66027900	-1.54858700	-1.04129100
H	-2.59344700	1.62037900	0.73036100
H	-3.11987500	1.59535800	-0.96423900
C	-1.40918000	2.91956000	-0.49454700
H	-1.86287700	3.81376800	-0.05597600
H	-1.22258800	3.11494700	-1.55888100
H	0.74165800	3.19372900	-0.14218000
O	-0.29142900	2.74145200	1.60838200
H	2.64101400	-2.64621200	-1.04675800
C	3.84536600	-1.02811900	-0.22121200
H	2.81678900	-1.23959800	-2.08464300
H	1.10432000	-1.59129100	1.52081500
H	0.89062400	-2.90768800	0.39342400
C	3.84951500	0.50323000	-0.24505800
H	4.71581300	0.90325200	0.29611200
H	3.93736000	0.84890900	-1.28499100
H	2.60287000	0.82259900	1.46049300
H	2.53353900	2.14373200	0.31011200
H	4.78339000	-1.42529500	-0.62898800
H	3.78157800	-1.38043500	0.81902500
H	-3.74144500	-0.24155900	0.49801100
H	-3.49264300	-1.98396600	0.48415000
O	-3.61783900	-1.02027100	-1.35168300
H	0.33782300	2.15975500	2.06132300
H	-3.12520600	-1.71720100	-1.81388300
C	-1.38982900	-2.97958700	1.42555500
H	-2.40948900	-2.87993000	1.79893900
H	-1.33557700	-3.89619700	0.82018500
H	-0.74667700	-3.15250200	2.29842900
H	0.60988400	-1.12969500	-1.44435700

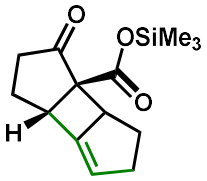
Figure 9: *Stability of alkylidene cyclobutane* ***48*** *and derivatives*



48

SCF Energy (B3LYP-D3BJ, hexane):	-1217.204291
SCF Energy (M11-L, hexane):	-1216.868836
SCF Energy (M06-2X, hexane):	-1216.673737
SCF Energy (B3LYP, gas-phase):	-1216.779028
Enthalpy Correction:	0.431825
Free-Energy Correction:	0.354690

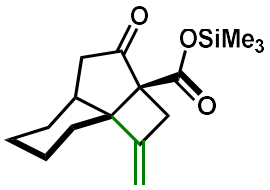
H	-2.17361900	4.00268300	-1.61537800
C	-2.48381000	3.33344200	-0.80350100
C	-2.68628600	1.90245600	-1.29749600
C	-2.22190300	1.05331800	-0.38146400
C	-1.52799700	1.73371100	0.76686800
C	-1.37109300	3.19610800	0.29282400
H	-3.41056700	3.75906400	-0.38862600
H	-3.07602400	1.66224600	-2.28271000
H	-2.06108300	1.68013000	1.72538700
H	-0.39101900	3.34479700	-0.16128000
H	-1.48907900	3.91931000	1.10625100
C	-0.47474700	0.53634900	0.71365200
C	0.86225700	0.77962000	0.04714200
O	1.16992900	1.76173300	-0.59967900
C	-0.32222200	-0.25800100	2.02638300
O	0.27090200	0.12965100	3.00732500
C	-1.54304600	-0.28416400	-0.16906000
C	-2.04265900	-2.08369700	-1.93040500
C	-3.09237000	-2.33464300	0.34165400
C	-2.44142700	-3.07607800	-0.83204600
C	-2.24392700	-1.18321000	0.91427700
C	-1.02918500	-1.06971400	-1.38404500
H	-2.93876200	-1.56456300	-2.30006900
H	-4.04370500	-1.91131300	-0.00956900
H	-1.54907400	-3.62333700	-0.49438700
H	-0.12450200	-1.61864200	-1.08983000
H	-1.60771000	-2.60981500	-2.78921000
H	-3.34729800	-3.03171200	1.15047900
H	-3.13817900	-3.82883100	-1.22126100
H	-0.72528400	-0.35892500	-2.16137400
C	-1.11229700	-1.55718700	1.88833700
H	-1.44901600	-1.92587600	2.86167500
H	-0.44203200	-2.31257100	1.45251100
H	-2.93107000	-0.53756500	1.47624200
O	1.69356100	-0.26980900	0.21944000
Si	3.34323600	-0.26122500	-0.32240700
C	3.38755900	-0.14759100	-2.19825800
H	2.82177000	-0.96548100	-2.65972700
H	4.41948900	-0.20965300	-2.56592000
H	2.95794700	0.79889400	-2.53954300
C	4.25593000	1.15043100	0.51425400
H	4.17760900	1.07694800	1.60500900
H	3.84532700	2.11717600	0.20824000
H	5.32148500	1.13221400	0.25337500
C	3.95600400	-1.93374300	0.27819100
H	3.86847300	-2.01798600	1.36724800
H	5.01023300	-2.08317200	0.01465100
H	3.38258100	-2.75390500	-0.16902000



48b

SCF Energy (B3LYP-D3BJ, hexane): -1061.083058
SCF Energy (M11-L, hexane): -1060.798467
SCF Energy (M06-2X, hexane): -1060.642431
SCF Energy (B3LYP, gas-phase): -1060.72925
Enthalpy Correction: 0.334587
Free-Energy Correction: 0.264607

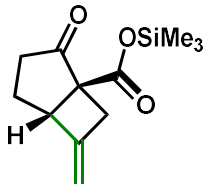
H	3.47866200	-3.26517300	-0.15885200
C	3.61562200	-2.18636200	-0.01527000
C	3.19853800	-1.39353200	-1.25264500
C	2.58362400	-0.27615300	-0.86706400
C	2.36352700	-0.19846700	0.62059500
C	2.68343000	-1.62666800	1.11408900
H	4.67917400	-2.03924000	0.22807200
H	3.32428500	-1.75942500	-2.26776100
H	2.97501900	0.55409900	1.13734700
H	1.76931800	-2.22007900	1.16925000
H	3.15741800	-1.64144900	2.10080100
C	0.95112800	0.45010400	0.26605200
C	-0.30272400	-0.38604900	0.37682300
O	-0.40233500	-1.46336800	0.92733700
C	0.72347900	1.84966700	0.87892100
O	0.43742200	2.06391400	2.03409300
C	1.48364400	0.70277900	-1.20722200
C	1.85805400	2.21484000	-1.24791800
C	0.95015800	2.89539300	-0.21207100
H	1.33593800	3.82847000	0.20809200
H	-0.03769500	3.10907900	-0.64564600
H	2.91009400	2.34701100	-0.97163800
O	-1.34123700	0.23518300	-0.22388300
Si	-2.95554100	-0.40238500	-0.20461100
C	-2.98880300	-2.02191100	-1.15846100
H	-2.62502900	-1.88661500	-2.18380800
H	-4.01117200	-2.41560700	-1.21882800
H	-2.36160200	-2.77427600	-0.67065200
C	-3.53673300	-0.59006300	1.57061400
H	-3.46240300	0.35934800	2.11334600
H	-2.93494300	-1.33238300	2.10287300
H	-4.58565600	-0.91077600	1.60114800
C	-3.91311000	0.94293700	-1.10382600
H	-3.84347500	1.89994800	-0.57422300
H	-4.97577900	0.68228600	-1.18099300
H	-3.53319000	1.09350000	-2.12082700
H	1.73639800	2.62919200	-2.25267100
H	0.81240600	0.43056300	-2.02654900



48c

SCF Energy (B3LYP-D3BJ, hexane):	-1139.773999
SCF Energy (M11-L, hexane):	-1139.457939
SCF Energy (M06-2X, hexane):	-1139.281903
SCF Energy (B3LYP, gas-phase):	-1139.377403
Enthalpy Correction:	0.39448
Free-Energy Correction:	0.32016

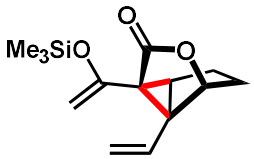
C	2.97675400	-1.57500400	-2.12635900
C	2.15383900	-1.41800700	-1.09443800
C	1.22207000	-2.36215100	-0.34726700
H	3.50285000	-0.73545300	-2.57395500
H	1.70164800	-2.98277400	0.41821400
C	0.48242700	-1.11449300	0.23856500
C	-0.89594100	-0.89817900	-0.35585900
O	-1.37301400	-1.56420800	-1.25300400
C	0.47795300	-0.93799000	1.76839400
O	-0.18398800	-1.59073000	2.54321600
C	1.66113600	-0.20380100	-0.31281800
C	2.44288000	2.08419200	-1.20846200
C	3.55417500	1.18082500	0.85829900
C	3.01817100	2.44029500	0.16683000
C	2.52422100	0.04424100	0.98368100
C	1.28625300	1.08487500	-1.06216200
H	3.23843000	1.66209900	-1.83888200
H	4.40411400	0.80525700	0.27149700
H	2.23539700	2.91187100	0.77889800
H	0.47564200	1.58343700	-0.51434600
H	2.08225700	2.98398500	-1.72226000
H	3.95095800	1.42011300	1.85350400
H	3.82440800	3.17812700	0.07167200
H	0.87812000	0.81661000	-2.04405900
C	1.48799300	0.15209000	2.11560300
H	1.89319600	0.01716200	3.12254200
H	0.96165700	1.11785100	2.08784400
H	3.09198300	-0.87651500	1.17370700
O	-1.53498500	0.13953300	0.21893000
Si	-3.18816100	0.53922200	-0.13114900
C	-3.33128100	1.10209400	-1.91892600
H	-2.67333800	1.95512400	-2.12242800
H	-4.35858000	1.41491500	-2.14421800
H	-3.06224900	0.29277000	-2.60438700
C	-4.27208000	-0.94438100	0.25482400
H	-4.13486400	-1.27082300	1.29208600
H	-4.03060200	-1.78591800	-0.40111800
H	-5.33229500	-0.69634500	0.11960500
C	-3.50371700	1.95617700	1.06303800
H	-3.35815400	1.63708900	2.10125200
H	-4.53173500	2.32690300	0.96864200
H	-2.82832100	2.79827400	0.87289600
H	3.14885600	-2.55167100	-2.57259300
H	0.58164200	-2.99265400	-0.96883100



48d

SCF Energy (B3LYP-D3BJ, hexane):	-983.6561337
SCF Energy (M11-L, hexane):	-983.3887882
SCF Energy (M06-2X, hexane):	-983.2506403
SCF Energy (B3LYP, gas-phase):	-983.3310841
Enthalpy Correction:	0.297045
Free-Energy Correction:	0.229665

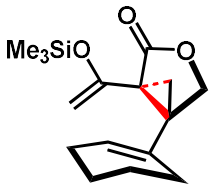
C	4.28668900	-1.38389100	-0.65560000
C	3.05966000	-1.03022000	-0.28772200
C	2.27177000	-1.13546100	1.00886100
H	4.66244900	-1.18224200	-1.65636500
H	2.75835000	-0.78945800	1.92772700
C	1.19692500	-0.18916500	0.38820000
C	-0.23863600	-0.65054100	0.46536300
O	-0.61361200	-1.63509200	1.06967400
C	1.36842500	1.27907700	0.83326700
O	0.84253000	1.77249400	1.80448700
C	1.93915100	-0.26888900	-0.99631700
C	2.23759400	1.17932400	-1.44189100
C	2.31976800	1.98566000	-0.13654800
H	3.32922000	1.93178500	0.29571400
H	2.05968600	3.04355800	-0.22692900
H	3.15051000	1.24210800	-2.04280200
O	-1.05431500	0.15192000	-0.24363200
Si	-2.77878200	-0.03794800	-0.25974400
C	-3.21211300	-1.67901800	-1.06809500
H	-2.80093800	-1.74285200	-2.08247700
H	-4.30001600	-1.80008400	-1.14356100
H	-2.81447700	-2.51548200	-0.48552000
C	-3.43316200	0.10805100	1.49375000
H	-3.12427700	1.05541400	1.95025200
H	-3.06038700	-0.70722300	2.12083400
H	-4.52982400	0.07411700	1.50151100
C	-3.32117300	1.41373000	-1.32355400
H	-3.01294800	2.36692300	-0.87932200
H	-4.41248800	1.43357700	-1.43228900
H	-2.88803000	1.35617900	-2.32875200
H	1.40659800	1.54518400	-2.05647200
H	1.42759200	-0.84882000	-1.77182100
H	1.84209300	-2.12553600	1.19724400
H	4.96361700	-1.89238200	0.02691900



37b

SCF Energy (B3LYP-D3BJ, hexane):	-1061.072173
SCF Energy (M11-L, hexane):	-1060.783673
SCF Energy (M06-2X, hexane):	-1060.636406
SCF Energy (B3LYP, gas-phase):	-1060.713173
Enthalpy Correction:	0.333709
Free-Energy Correction:	0.263696

C	2.65108600	-0.52598000	-1.09159500
C	1.88313700	0.63806100	-0.41922600
C	2.17385900	0.42948100	1.04210800
C	3.37971000	-0.50423700	1.21309300
C	3.90637900	-0.69915800	-0.23257300
H	2.83220600	-0.39392900	-2.16010600
H	2.04927900	1.25636300	1.73403300
H	3.09723500	-1.45955200	1.66959200
H	4.13296300	-0.04918900	1.86343200
H	4.39387000	-1.66385400	-0.40259300
H	4.61777500	0.09701300	-0.48465000
C	0.86034200	-0.09272800	0.45435600
O	1.83748200	-1.71654700	-0.93814000
C	0.83043000	-1.51743500	-0.04244700
O	0.04560000	-2.38771500	0.24247700
C	1.64744400	1.91960200	-1.12048400
C	1.92446000	3.12780600	-0.62613700
H	2.37670200	3.25860700	0.35367500
C	-0.45409500	0.50157600	0.83686400
C	-0.71440200	1.03799700	2.03471500
H	-1.67279600	1.49273300	2.26048700
H	0.02917400	1.02435200	2.82209500
O	-1.33937100	0.44941800	-0.19922500
Si	-2.97144600	-0.03527800	-0.19942800
C	-3.25939800	-1.33321400	1.12952500
H	-4.24766000	-1.79361900	1.00602900
H	-3.20935000	-0.91284300	2.13943000
H	-2.49944300	-2.11864900	1.05657100
C	-3.23238600	-0.73513400	-1.92397500
H	-4.27877600	-1.02388400	-2.08165500
H	-2.60974500	-1.62308900	-2.07995400
H	-2.96934900	-0.00024500	-2.69362400
C	-4.06293700	1.48218300	0.06239300
H	-5.12462300	1.21827200	-0.02546200
H	-3.85007600	2.25555900	-0.68495600
H	-3.91628100	1.92821300	1.05298800
H	1.19742500	1.83517500	-2.10989200
H	1.70025400	4.03228100	-1.18404300

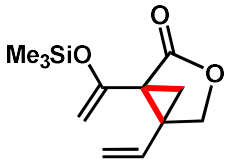


37c

SCF Energy (B3LYP-D3BJ, hexane): -1139.746768
SCF Energy (M11-L, hexane): -1139.428545
SCF Energy (M06-2X, hexane): -1139.259890
SCF Energy (B3LYP, gas-phase): -1139.352951
Enthalpy Correction: 0.394753
Free-Energy Correction: 0.319438

C	-1.39685400	2.30751100	-1.12264400
C	-1.45238100	1.34492200	0.06436200
C	-1.10403400	1.98210400	1.37243500
H	-1.53361800	1.78575400	-2.07524800
H	-1.42412200	1.46410200	2.27034000
C	0.00029200	1.29943800	0.58398500
O	-0.08939000	2.90999100	-1.12915600
C	0.76913000	2.24876100	-0.29704700
O	1.95675600	2.45877900	-0.31358600
C	-2.34212200	0.14634700	-0.03780400
C	-4.31413600	-1.20248400	0.77201500
C	-2.74319700	-2.19291900	-0.93622200
C	-4.21064400	-1.99756900	-0.53826700
C	-2.04978400	-0.84027300	-1.15678400
C	-3.35975700	-0.03632900	0.81711100
H	-4.11178900	-1.86264900	1.63072700
H	-2.22013800	-2.73928100	-0.13939800
H	-4.73022400	-1.45039000	-1.33734000
H	-2.37672000	-0.41730400	-2.12001900
H	-5.34117300	-0.84075000	0.92000900
H	-2.66489500	-2.80396700	-1.84348200
H	-4.71935800	-2.96357100	-0.43505900
H	-0.96509500	-0.97879500	-1.23981000
H	-3.52377100	0.69394100	1.60849600
C	0.70815000	0.07692500	1.05789600
C	0.74474900	-0.33186800	2.33122300
H	1.23030400	-1.26054300	2.61140800
H	0.29538600	0.25607000	3.12177700
O	1.28358800	-0.60767500	0.02333300
Si	2.90691900	-1.09799300	-0.16138100
C	4.02419700	-0.09691400	0.97102400
H	5.07712400	-0.30019600	0.73863200
H	3.86394900	-0.32659100	2.02956100
H	3.83871600	0.97218700	0.82379900
C	3.29102600	-0.77058000	-1.97178900
H	4.30751800	-1.09193200	-2.23010900
H	3.20900500	0.30092600	-2.18516100
H	2.59522500	-1.30164800	-2.63181800
C	3.00563600	-2.94266400	0.22157500
H	4.01583300	-3.32826700	0.03424000
H	2.31026200	-3.51575500	-0.40291500
H	2.76157000	-3.15227700	1.26987700
H	-2.13656300	3.11109800	-1.04829800
H	-1.08354200	3.06652200	1.45797700

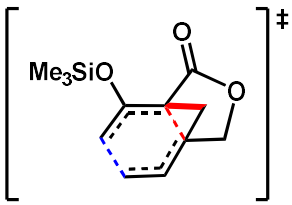
Figure 10: *Formation of alkylidene cyclobutane* ***48d****, which is unable to undergo further rearrangement*



37d

SCF Energy (B3LYP-D3BJ, hexane):	-983.6208480
SCF Energy (M11-L, hexane):	-983.3521128
SCF Energy (M06-2X, hexane):	-983.2243539
SCF Energy (B3LYP, gas-phase):	-983.2924610
Enthalpy Correction:	0.296752
Free-Energy Correction:	0.228866

C	2.79939500	-1.06962400	-1.00452100
C	2.40253600	0.20540700	-0.26452300
C	2.52227900	0.12507500	1.22523800
H	2.56298600	-0.99711600	-2.07272300
H	2.55731400	1.06343000	1.76891000
C	1.18622000	-0.21011100	0.58905100
O	2.03163100	-2.14937600	-0.44395800
C	0.99915100	-1.68157700	0.32076500
O	0.11055500	-2.40181000	0.69993400
C	2.47216500	1.48377900	-1.01481600
C	3.06889000	2.59950900	-0.59202100
H	3.58029000	2.65348600	0.36554100
C	-0.03852300	0.61683600	0.76905600
C	-0.25779000	1.41963700	1.81639100
H	-1.14479400	2.04067000	1.87928200
H	0.44503400	1.46682400	2.63905100
O	-0.88803200	0.47889100	-0.29057900
Si	-2.55828900	0.14398300	-0.28651900
C	-3.02860400	-0.78610000	1.27778000
H	-4.05081700	-1.17596800	1.19435200
H	-2.98319400	-0.15361800	2.17046400
H	-2.34826500	-1.63106300	1.42943300
C	-2.81274600	-0.91052100	-1.82153200
H	-3.87301800	-1.14823900	-1.97167100
H	-2.26421600	-1.85492400	-1.73315500
H	-2.45562700	-0.39585200	-2.72116000
C	-3.50214100	1.77076900	-0.43994400
H	-4.58016600	1.58827500	-0.53456600
H	-3.18135300	2.33188700	-1.32543300
H	-3.35314100	2.41548600	0.43434100
H	3.10035600	-0.67980500	1.67377600
H	3.85944700	-1.31766000	-0.89186700
H	1.98256600	1.47416800	-1.98908900
H	3.06441800	3.50414300	-1.19292300

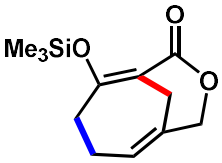


TS38d

SCF Energy (B3LYP-D3BJ, hexane):	-983.5932557
SCF Energy (M11-L, hexane):	-983.3219425
SCF Energy (M06-2X, hexane):	-983.1881650
SCF Energy (B3LYP, gas-phase):	-983.2622830
Enthalpy Correction:	0.295697
Free-Energy Correction:	0.232185

C	2.99388200	-1.17078500	-0.79830300
C	2.73870200	0.18828600	-0.19799800
C	2.41038300	0.13369000	1.25326200
H	2.90204200	-1.14805300	-1.88996300

H	2.46502500	1.06871700	1.80482600
C	1.04353300	-0.22314300	0.71181300
O	2.05974200	-2.14338000	-0.28551000
C	0.91504400	-1.63918900	0.28028600
O	-0.04588300	-2.35892700	0.43024000
C	2.62163900	1.34916400	-0.96865600
C	2.24680800	2.56934400	-0.42085800
H	2.59293200	2.86112500	0.56287400
C	0.06087400	0.74262400	0.42360000
C	0.26019800	2.09193900	0.70421600
H	-0.45295400	2.80821600	0.30912600
H	0.76428400	2.38255600	1.61630500
O	-0.91174200	0.38631300	-0.47032800
Si	-2.54537600	0.04019100	-0.14934900
C	-2.74265100	-0.54349900	1.62798600
H	-3.78477700	-0.82045100	1.83044700
H	-2.45980800	0.23271800	2.34869900
H	-2.11130900	-1.42030700	1.80365400
C	-3.00141700	-1.29423900	-1.38791000
H	-4.05460000	-1.58630100	-1.29434600
H	-2.38171100	-2.18188400	-1.22214500
H	-2.83866300	-0.95393000	-2.41724300
C	-3.54645800	1.61209500	-0.45281700
H	-4.62022500	1.42674800	-0.32217100
H	-3.39595800	1.98752200	-1.47191300
H	-3.26366200	2.41124500	0.24309000
H	2.89355500	-0.66727000	1.81587200
H	3.98988100	-1.55127300	-0.54030500
H	2.56214300	1.21924800	-2.04873400
H	2.00890300	3.39893500	-1.08013800

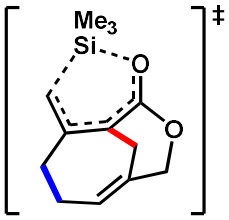


39d

SCF Energy (B3LYP-D3BJ, hexane): -983.6258231
SCF Energy (M11-L, hexane): -983.3560085
SCF Energy (M06-2X, hexane): -983.2247949
SCF Energy (B3LYP, gas-phase): -983.2983590
Enthalpy Correction: 0.299399
Free-Energy Correction: 0.235661

C	3.12461500	-1.31849900	-0.55257100
C	2.93719800	0.09193400	-0.07785800
C	2.25820700	0.08511700	1.26597900
H	3.27503300	-1.38107900	-1.63487200
H	2.32131000	1.03111300	1.80523800
C	0.86132600	-0.22245300	0.75785700
O	1.94682500	-2.12844800	-0.23277300
C	0.75150800	-1.58554500	0.19318800
O	-0.25338900	-2.25286400	0.06490900
C	2.84753800	1.18139100	-0.85512300
C	2.15475100	2.43134500	-0.36051000
H	2.77224700	2.94145000	0.38908100
C	0.12790600	0.81905700	0.27702500
C	0.70079100	2.22615900	0.29107800
H	0.74502100	2.58609900	1.32550700
H	-0.01325900	2.86478800	-0.23342700
O	-1.01644700	0.70106700	-0.41954200
Si	-2.56559600	0.04865700	-0.09203800
C	-2.63990600	-0.64945700	1.65073600
H	-2.36286700	0.09966800	2.40193200
H	-3.66279100	-0.97835000	1.87458100
H	-1.97107900	-1.50813000	1.75005700

C	-3.72437600	1.53029500	-0.24950700
H	-3.50939200	2.29365800	0.50782000
H	-3.63479800	2.00288400	-1.23467900
H	-4.77046700	1.22372500	-0.12308300
C	-2.95463700	-1.21139000	-1.42558200
H	-2.26653300	-2.05842700	-1.36196800
H	-3.98079100	-1.58537500	-1.31780400
H	-2.86746200	-0.76647100	-2.42395100
H	2.63203500	-0.70438900	1.92578000
H	3.95538500	-1.82720200	-0.04975000
H	3.11863300	1.12580800	-1.90803600
H	2.05267900	3.13325300	-1.19292500

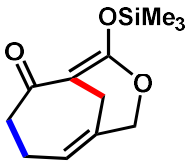


TS45d

SCF Energy (B3LYP-D3BJ, hexane): -983.5998486
SCF Energy (M11-L, hexane): -983.3359495
SCF Energy (M06-2X, hexane): -983.2003917
SCF Energy (B3LYP, gas-phase): -983.2744348
Enthalpy Correction: 0.298474
Free-Energy Correction: 0.238734

C	-1.69053400	2.01086600	-0.96690600
C	-1.94298700	1.05072200	0.16867100
C	-1.04708900	1.65574300	1.23626200
C	-1.10351400	3.19702400	1.03092300
C	-1.77941900	3.39946500	-0.35264900
H	-2.23058000	1.85907300	-1.89971500
H	-1.32150000	1.39574500	2.25644900
H	-0.09726500	3.62576200	1.05708700
H	-1.67958500	3.67502300	1.82889200
H	-1.28903400	4.15271000	-0.97540600
H	-2.83476900	3.67915100	-0.24695600
C	0.25781300	1.00767200	0.82234400
O	-0.24471600	1.82877200	-1.37409400
C	0.60304000	1.19034900	-0.54434300
O	1.61002800	0.65636200	-1.09750100
C	-2.36836600	-0.22814500	0.13215800
C	-1.69895300	-2.66117800	0.48508900
C	-2.96528100	-2.05573400	-1.58889500
C	-2.79262500	-3.10186300	-0.48815800
C	-3.31317500	-0.70044500	-0.95918800
C	-1.93460700	-1.28469600	1.17505400
H	-0.74202500	-2.61388400	-0.05215200
H	-2.03514700	-1.97110600	-2.16728000
H	-3.74502000	-3.23374400	0.04712300
H	-4.31349900	-0.79384000	-0.50353200
H	-1.56904900	-3.41169900	1.27462300
H	-3.75469400	-2.34799500	-2.29238500
H	-2.53369500	-4.07931000	-0.91378600
H	-3.41328100	0.07177000	-1.72893800
H	-2.74898700	-1.41771000	1.90396400
C	0.47295600	-0.31529600	1.21624900
C	-0.62286200	-0.99404200	2.02071100
H	-0.86340600	-0.39477000	2.90278000
H	-0.24203600	-1.95332400	2.38137500
O	1.42893900	-1.04978100	0.75997300
Si	3.00017100	-0.43539700	-0.21639800
C	3.92947900	-0.10515000	-1.86208100
H	3.92232200	0.95217500	-2.14623000
H	4.97167200	-0.43762700	-1.77419100

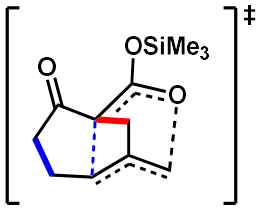
H	3.48060700	-0.66558700	-2.69261400
C	3.71174700	0.73825300	1.08563200
H	3.46753100	1.78566700	0.87874200
H	3.37302500	0.50328100	2.09992200
H	4.80518500	0.64706300	1.06805300
C	3.59717200	-2.23437200	0.06925000
H	3.45774500	-2.56787100	1.10240400
H	3.04455100	-2.93370800	-0.57263800
H	4.65776000	-2.32754700	-0.19377900



46d

SCF Energy (B3LYP-D3BJ, hexane): -983.6138206
SCF Energy (M11-L, hexane): -983.3454756
SCF Energy (M06-2X, hexane): -983.2116061
SCF Energy (B3LYP, gas-phase): -983.2859989
Enthalpy Correction: 0.299079
Free-Energy Correction: 0.232592

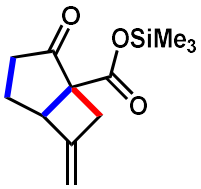
C	0.98799900	2.33724900	0.23111000
C	2.12498400	1.36461300	0.21320300
C	2.27987800	0.81797100	-1.18160200
H	0.58608500	2.51457900	1.23234500
H	3.23627100	0.32837400	-1.36334400
C	1.11034800	-0.14967100	-1.17133600
O	-0.13140400	1.80113100	-0.59047800
C	-0.08674200	0.48104800	-0.92796400
C	2.56900600	0.64922900	1.25641200
C	3.34196000	-0.64388300	1.06696300
H	4.37966700	-0.42872500	0.77789300
C	1.33614400	-1.47063500	-0.56069200
C	2.75562000	-1.69126800	0.02376300
H	3.45301300	-1.77445000	-0.81972600
H	2.71557500	-2.67613300	0.49499600
O	0.47996100	-2.33469900	-0.39828600
O	-1.26063600	-0.11483000	-0.95484800
Si	-2.51294500	-0.15434100	0.22103200
C	-3.44120400	-1.72374300	-0.20877900
H	-3.87038400	-1.66583400	-1.21551000
H	-4.25990800	-1.91492600	0.49551300
H	-2.75533200	-2.57718700	-0.18582200
C	-3.58587700	1.37801400	0.02362600
H	-4.00780600	1.43385900	-0.98650000
H	-3.00753100	2.29208000	0.19494200
H	-4.42216100	1.36484700	0.73389900
C	-1.71790600	-0.24689300	1.92432500
H	-1.01965500	-1.09012400	1.96736400
H	-2.47803000	-0.39479600	2.70140200
H	-1.16684000	0.66765800	2.17208500
H	2.15196400	1.59083200	-1.94716400
H	1.22604600	3.29614600	-0.23998700
H	2.26468200	0.91134000	2.26873900
H	3.40694400	-1.14177100	2.03914800



TS47d

SCF Energy (B3LYP-D3BJ, hexane): -983.5936381
SCF Energy (M11-L, hexane): -983.3288440
SCF Energy (M06-2X, hexane): -983.1744082
SCF Energy (B3LYP, gas-phase): -983.2624387
Enthalpy Correction: 0.295208
Free-Energy Correction: 0.229305

C	2.29783200	2.76848800	0.32854400
C	2.50821500	1.44525300	0.07325500
C	2.15721300	0.77696000	-1.24043800
H	2.26154100	3.14945000	1.34551200
H	3.01361200	0.30518200	-1.72773300
C	1.12930800	-0.22271800	-0.75700400
C	-0.20600100	0.33393200	-0.57663100
O	-0.45170200	1.51254900	-0.84893000
C	1.50621500	-1.60764500	-0.48539600
O	0.74928300	-2.57100600	-0.45794600
C	2.71597400	0.52853600	1.13103600
C	3.23221500	-0.87861200	1.14409600
C	2.98347000	-1.76493400	-0.08282600
H	3.65326200	-1.50074800	-0.90800200
H	3.16149600	-2.81431500	0.16347400
H	4.30968500	-0.81906600	1.38707200
O	-1.12480200	-0.49243300	-0.04061200
Si	-2.76275900	-0.03761800	0.21044700
C	-2.85400100	1.34825300	1.48191300
H	-2.39256000	1.04557200	2.42948800
H	-3.89633800	1.61906200	1.69239200
H	-2.33339800	2.23886200	1.11740600
C	-3.55067100	0.45074400	-1.42702500
H	-3.48482900	-0.36738600	-2.15390800
H	-3.05032200	1.32558900	-1.85256200
H	-4.61272100	0.69203500	-1.29283400
C	-3.52317600	-1.62028800	0.88193400
H	-3.40779000	-2.44287200	0.16747300
H	-4.59449300	-1.49198500	1.08041500
H	-3.04255900	-1.92609500	1.81820000
H	2.11147100	3.47472500	-0.47257100
H	1.71246800	1.48810800	-1.93737300
H	2.78338200	-1.36762000	2.02038500
H	2.72492100	0.97746400	2.12806500

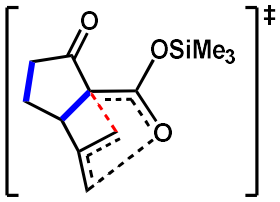


48d

SCF Energy (B3LYP-D3BJ, hexane): -983.6561337
SCF Energy (M11-L, hexane): -983.3887882
SCF Energy (M06-2X, hexane): -983.2506403
SCF Energy (B3LYP, gas-phase): -983.3310841
Enthalpy Correction: 0.297045
Free-Energy Correction: 0.229665

C	4.28668900	-1.38389100	-0.65560000
C	3.05966000	-1.03022000	-0.28772200
C	2.27177000	-1.13546100	1.00886100
H	4.66244900	-1.18224200	-1.65636500
H	2.75835000	-0.78945800	1.92772700
C	1.19692500	-0.18916500	0.38820000
C	-0.23863600	-0.65054100	0.46536300

O	-0.61361200	-1.63509200	1.06967400
C	1.36842500	1.27907700	0.83326700
O	0.84253000	1.77249400	1.80448700
C	1.93915100	-0.26888900	-0.99631700
C	2.23759400	1.17932400	-1.44189100
C	2.31976800	1.98566000	-0.13654800
H	3.32922000	1.93178500	0.29571400
H	2.05968600	3.04355800	-0.22692900
H	3.15051000	1.24210800	-2.04280200
O	-1.05431500	0.15192000	-0.24363200
Si	-2.77878200	-0.03794800	-0.25974400
C	-3.21211300	-1.67901800	-1.06809500
H	-2.80093800	-1.74285200	-2.08247700
H	-4.30001600	-1.80008400	-1.14356100
H	-2.81447700	-2.51548200	-0.48552000
C	-3.43316200	0.10805100	1.49375000
H	-3.12427700	1.05541400	1.95025200
H	-3.06038700	-0.70722300	2.12083400
H	-4.52982400	0.07411700	1.50151100
C	-3.32117300	1.41373000	-1.32355400
H	-3.01294800	2.36692300	-0.87932200
H	-4.41248800	1.43357700	-1.43228900
H	-2.88803000	1.35617900	-2.32875200
H	1.40659800	1.54518400	-2.05647200
H	1.42759200	-0.84882000	-1.77182100
H	1.84209300	-2.12553600	1.19724400
H	4.96361700	-1.89238200	0.02691900

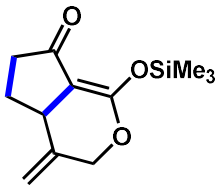


TS49d

SCF Energy (B3LYP-D3BJ, hexane): -983.5893741
SCF Energy (M11-L, hexane): -983.3249592
SCF Energy (M06-2X, hexane): -983.1688014
SCF Energy (B3LYP, gas-phase): -983.2584437
Enthalpy Correction: 0.294568
Free-Energy Correction: 0.227956

C	1.94471400	2.84457300	-0.12956600
C	2.31716400	1.54685300	-0.36300400
C	2.30323200	0.99919800	-1.64448900
H	1.93283600	3.25969400	0.87139600
H	2.64111300	-0.00843000	-1.84582000
C	1.18518900	-0.36346300	0.29511800
C	-0.14270500	0.20752100	0.40120100
O	-0.31535400	1.32691700	0.89821500
C	1.58971800	-1.71714000	-0.08067500
O	0.88492800	-2.64258800	-0.46038800
C	2.35646900	0.48045900	0.72635600
C	3.57967600	-0.49008300	0.73332000
C	3.12292700	-1.80269400	0.06120500
H	3.55898500	-1.94718800	-0.93681500
H	3.38544800	-2.69650600	0.63620600
H	4.44823900	-0.04298300	0.23918500
O	-1.14709400	-0.53451000	-0.09953000
Si	-2.79885100	-0.06066800	-0.03730300
C	-3.33126200	0.16875200	1.75268900
H	-3.17296300	-0.74911500	2.33099600
H	-4.39795000	0.41929700	1.81216800
H	-2.76272000	0.97354900	2.22828700
C	-3.04885900	1.50357800	-1.05485000
H	-2.72944400	1.35431300	-2.09310500
H	-2.47127400	2.33272200	-0.63511500

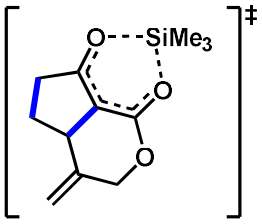
H	-4.10674200	1.79449900	-1.07203300
C	-3.66867900	-1.52806100	-0.82509500
H	-3.32711700	-1.68262900	-1.85477100
H	-4.75542400	-1.38013400	-0.84905400
H	-3.46517600	-2.44951200	-0.26834500
H	3.87049700	-0.67777500	1.77134800
H	2.21222000	0.95178500	1.70298800
H	1.61169200	3.48699800	-0.93950800
H	2.08635100	1.61526100	-2.51540100



50d

SCF Energy (B3LYP-D3BJ, hexane): -983.6513755
SCF Energy (M11-L, hexane): -983.3853379
SCF Energy (M06-2X, hexane): -983.2499679
SCF Energy (B3LYP, gas-phase): -983.3265928
Enthalpy Correction: 0.298752
Free-Energy Correction: 0.233827

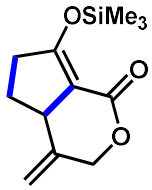
C	-1.87124900	-2.23784100	0.34569800
C	-2.85188800	-1.13990500	0.02563400
C	-3.99773500	-1.38148200	-0.61273100
H	-1.79967200	-2.38441200	1.43277100
H	-4.72181100	-0.59617700	-0.81079200
C	-0.89964100	0.37022500	0.15846900
C	-0.10293400	-0.68859500	-0.16918300
O	-0.52837000	-1.96938400	-0.13083200
C	-0.59224700	1.78241100	-0.02701800
O	0.49167600	2.31370500	-0.25160500
C	-2.36834500	0.19821400	0.51969300
C	-3.01410900	1.48229800	-0.05005900
C	-1.91875800	2.55144500	0.11696800
H	-1.96964500	3.37166500	-0.60472300
H	-1.94745700	3.00054900	1.12046300
H	-3.22762900	1.33380200	-1.11535100
O	1.12435500	-0.62290600	-0.64705400
Si	2.65218300	-0.17826300	-0.00249800
C	2.44464800	0.51312600	1.73220600
H	1.93209100	1.47825000	1.70222600
H	3.42854400	0.65647200	2.19663600
H	1.87402300	-0.16604700	2.37670600
C	3.63191400	-1.78727300	0.04102400
H	3.68849700	-2.24209300	-0.95460700
H	3.17317600	-2.51972900	0.71538900
H	4.65855300	-1.61127500	0.38642500
C	3.41150100	1.03266700	-1.21209300
H	4.42139400	1.32261400	-0.89588400
H	2.79044400	1.93020800	-1.27458000
H	3.48894000	0.59217000	-2.21293400
H	-3.95373300	1.74000600	0.44940700
H	-2.48565300	0.21388200	1.61894800
H	-2.14923100	-3.18782700	-0.11478100
H	-4.25962700	-2.37944700	-0.95607900



TS51d

SCF Energy (B3LYP-D3BJ, hexane):	-983.6294607
SCF Energy (M11-L, hexane):	-983.3662383
SCF Energy (M06-2X, hexane):	-983.2283318
SCF Energy (B3LYP, gas-phase):	-983.3079718
Enthalpy Correction:	0.298086
Free-Energy Correction:	0.236905

C	2.60684900	-1.89233700	-0.38756600
C	3.15715800	-0.53385200	-0.01468500
C	4.25111200	-0.40589800	0.73730200
H	2.67916100	-2.05211400	-1.47188000
H	4.67564900	0.56620700	0.97284600
C	0.88020800	0.23474000	-0.39516200
O	1.20734000	-2.09628800	-0.02881600
C	0.38643800	-1.03705200	-0.08835000
O	-0.82222700	-1.25671500	0.22451800
C	2.33282300	0.59054100	-0.59982600
C	2.41113500	2.00901700	0.03298000
H	2.67616800	1.91167100	1.09190500
C	0.10391000	1.33668500	-0.07837300
C	0.97245900	2.58336400	-0.07909600
H	0.70159800	3.26068600	0.73652100
H	0.82183400	3.13310300	-1.01911100
O	-1.13584000	1.33297600	0.22930300
Si	-2.45615600	-0.11496700	0.07999700
C	-3.16624700	-1.70379300	-0.72952300
H	-2.93257500	-2.60993100	-0.16274600
H	-4.25696500	-1.61231500	-0.81563700
H	-2.77613800	-1.84503700	-1.74641700
C	-2.99061400	-0.06830300	1.88419100
H	-2.79380800	0.90763200	2.33935400
H	-4.06600900	-0.27124700	1.95934000
H	-2.46635300	-0.83261800	2.46824400
C	-3.39974000	1.16007600	-0.99916600
H	-3.40946600	2.16212900	-0.56003600
H	-2.94142500	1.24559900	-1.99425300
H	-4.43415400	0.82931100	-1.15412800
H	4.77115300	-1.27121100	1.14100700
H	3.13935200	-2.69916200	0.11829700
H	3.16107900	2.64775400	-0.44321000
H	2.56995200	0.66017400	-1.67644300



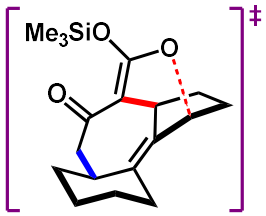
44d

SCF Energy (B3LYP-D3BJ, hexane):	-983.6567928
SCF Energy (M11-L, hexane):	-983.3900598
SCF Energy (M06-2X, hexane):	-983.2551710
SCF Energy (B3LYP, gas-phase):	-983.3329019
Enthalpy Correction:	0.299067
Free-Energy Correction:	0.234160

C	-3.19191900	-1.48702100	0.36179600
C	-3.32433700	-0.04168800	-0.03908400
C	-4.34257000	0.39914200	-0.77901900
H	-3.34933900	-1.59514500	1.44513500
H	-4.46109700	1.44922100	-1.03096300
C	-0.86884600	0.10349900	0.20314200
O	-1.90544300	-2.07259600	0.05623100

C	-0.75415800	-1.33847300	0.03170600
O	0.28707700	-1.93931800	-0.17869100
C	-2.19635800	0.78673700	0.51766600
C	-1.98646300	2.22402600	-0.00409800
H	-2.27358400	2.26906800	-1.06092700
C	0.10204000	1.03974900	0.00694300
C	-0.46523300	2.44217100	0.11949400
H	-0.04535300	3.09806600	-0.65043100
H	-0.18587400	2.87478300	1.09208800
O	1.39227500	0.94574300	-0.27216100
Si	2.76295800	-0.06861000	-0.04878500
C	2.68691700	-0.95924700	1.60428600
H	1.94791800	-1.76325800	1.58713700
H	3.66921800	-1.39141200	1.83518600
H	2.43730400	-0.26695900	2.41766600
C	3.00143700	-1.18423000	-1.53815700
H	2.21792000	-1.94294900	-1.58738200
H	2.98629900	-0.60093000	-2.46660400
H	3.97652700	-1.68526400	-1.48058700
C	4.14470500	1.21547200	-0.00484500
H	4.16565500	1.81118300	-0.92479200
H	4.02426100	1.90664500	0.83747900
H	5.12420100	0.73182300	0.09937500
H	-3.92218200	-2.11770000	-0.15069900
H	-5.10651700	-0.27736000	-1.15436300
H	-2.57732700	2.96801100	0.53870800
H	-2.33199900	0.82126300	1.61496700

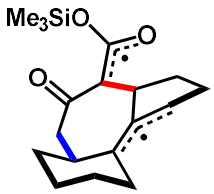
Figure S1: *Diradical Claisen rearrangement of* ***46***



SI-TS1

SCF Energy (B3LYP-D3BJ, hexane):	-1217.179123
SCF Energy (M11-L, hexane):	-1216.834577
SCF Energy (M06-2X, hexane):	-1216.627047
SCF Energy (B3LYP, gas-phase):	-1216.741133
Enthalpy Correction:	0.43079
Free-Energy Correction:	0.35654

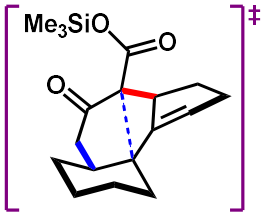
C	-0.82236400	1.95851600	-1.41473900
C	-1.59383000	1.32826000	-0.41063900
C	-1.09749000	1.95031500	0.90424700
C	-0.52477800	3.34643900	0.50406600
C	-0.48154100	3.36618500	-1.04771700
H	-0.64796700	1.55043500	-2.40393800
H	-1.90049300	2.08956200	1.62523700
H	0.47176200	3.48977200	0.92660500
H	-1.16651200	4.14351400	0.89356500
H	0.48607400	3.66971100	-1.45444700
H	-1.24323900	4.04268400	-1.46839200
C	-0.11632100	0.91014700	1.38816700
O	1.06445200	1.37184400	-0.58418000
C	0.95837800	0.70132100	0.50473900
C	-2.30356100	0.16125800	-0.48573700
C	-2.29584200	-2.18309200	0.40972200
C	-2.37918100	-1.81884600	-2.08181800
C	-2.82655800	-2.71284000	-0.92448400
C	-2.78973700	-0.35597000	-1.82057500
C	-2.70698900	-0.70643500	0.70595000
H	-1.20122600	-2.25441600	0.43463600
H	-1.28767400	-1.87204400	-2.19160800
H	-3.92572300	-2.75186900	-0.89670200
H	-3.89045200	-0.30167800	-1.81924100
H	-2.66172500	-2.80203400	1.23694100
H	-2.81298000	-2.15317600	-3.03199300
H	-2.48064400	-3.74229500	-1.07950300
H	-2.45573300	0.29639300	-2.63240600
H	-3.81019400	-0.69452800	0.73535600
C	-0.65419200	-0.18922400	2.18912600
C	-2.19708200	-0.32649200	2.12663400
H	-2.70732100	0.57047500	2.48975600
H	-2.46659500	-1.13948400	2.80708400
O	0.00023300	-1.05484400	2.76262700
O	1.83504100	-0.29575900	0.73576300
Si	3.13373000	-0.72033900	-0.28987000
C	3.96898200	-2.10897700	0.66236800
H	4.32053900	-1.75739800	1.63880900
H	4.83307400	-2.50516500	0.11464000
H	3.27358200	-2.93632700	0.84254300
C	4.30154900	0.74007100	-0.51275100
H	4.66559600	1.10056000	0.45656200
H	3.79744100	1.57104000	-1.01525000
H	5.17607800	0.45377400	-1.11066700
C	2.48129900	-1.34675400	-1.94495900
H	1.79937600	-2.19401900	-1.80261000
H	3.30175300	-1.68697500	-2.58934100
H	1.93873600	-0.55498400	-2.47073500



SI-2

SCF Energy (B3LYP-D3BJ, hexane): -1217.176488
SCF Energy (M11-L, hexane): -1216.834241
SCF Energy (M06-2X, hexane): -1216.631704
SCF Energy (B3LYP, gas-phase): -1216.75101
Enthalpy Correction: 0.430331
Free-Energy Correction: 0.350964

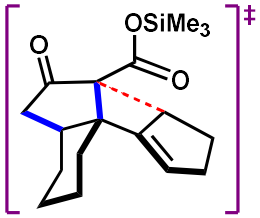
C	-1.71964900	2.22460000	-1.30203600
C	-1.90313200	1.37426600	-0.21777700
C	-0.92759200	1.80956500	0.91387800
C	-0.40157000	3.19324700	0.44729100
C	-0.65623900	3.25679600	-1.07435000
H	-2.19461900	2.09324600	-2.26841700
H	-1.49063700	1.94120500	1.84371800
H	0.64229300	3.35140300	0.71808600
H	-0.99890000	3.96391100	0.94606800
H	0.25268700	3.00933800	-1.64715900
H	-0.95303800	4.26136000	-1.40537400
C	0.06086600	0.69671200	1.13631100
O	2.21827500	1.65694700	0.81707100
C	1.45004200	0.73117000	0.60360300
C	-2.74785200	0.26166700	-0.13791300
C	-2.41849900	-2.18451400	0.27366200
C	-3.44239200	-1.39626600	-1.90915200
C	-3.38691500	-2.51986700	-0.86749100
C	-3.74481200	-0.04000900	-1.23397500
C	-2.74144300	-0.81340900	0.93692100
H	-1.38850200	-2.16199100	-0.10596200
H	-2.47841100	-1.32702400	-2.43124900
H	-4.39393700	-2.67703500	-0.45309800
H	-4.75255000	-0.09556000	-0.79020900
H	-2.45388700	-2.96737300	1.04196100
H	-4.20421100	-1.61115000	-2.66937900
H	-3.09374600	-3.46561300	-1.34046100
H	-3.78079200	0.75850000	-1.97899000
H	-3.77776900	-0.89379000	1.30927400
C	-0.36605600	-0.48406900	1.87373300
C	-1.85451100	-0.60463700	2.18755800
H	-2.20232500	0.26979300	2.75014500
H	-1.96649300	-1.47422100	2.84188800
O	0.42915300	-1.36309600	2.22452900
O	1.76596900	-0.34461100	-0.12552500
Si	3.38183700	-0.74652400	-0.59993700
C	3.14728300	-2.42933800	-1.40141200
H	2.72186500	-3.14513000	-0.68930600
H	4.10295600	-2.83413900	-1.75632900
H	2.47049900	-2.36941300	-2.26150900
C	4.45651500	-0.84976600	0.93614400
H	4.00549300	-1.52037900	1.67629000
H	4.57486900	0.13432700	1.39949700
H	5.45351100	-1.23676400	0.69119800
C	4.00378900	0.52326600	-1.84037400
H	3.35489200	0.56795300	-2.72305300
H	5.01429300	0.26910900	-2.18428900
H	4.03657900	1.52038100	-1.39054900



SI-TS3

SCF Energy (B3LYP-D3BJ, hexane):	-1217.166645
SCF Energy (M11-L, hexane):	-1216.827256
SCF Energy (M06-2X, hexane):	-1216.620245
SCF Energy (B3LYP, gas-phase):	-1216.737962
Enthalpy Correction:	0.429576
Free-Energy Correction:	0.352496

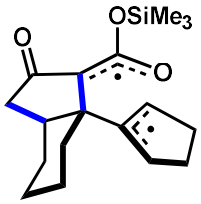
H	-0.35845200	4.15178500	-1.29613100
C	-1.07261600	3.80308100	-0.54042200
C	-1.80061700	2.56447500	-0.98628200
C	-1.73817500	1.56834200	-0.05257900
C	-0.97420500	2.01731100	1.06268600
C	-0.38821200	3.36515000	0.78428800
H	-1.76574900	4.63833600	-0.36045400
H	-2.25190400	2.47563300	-1.96757900
H	-0.99912700	1.61158900	2.06258500
H	0.69981300	3.26964400	0.64863700
H	-0.53295700	4.06327000	1.61798300
C	-0.47669500	-0.26921600	0.45413200
C	0.78895100	-0.11701200	-0.25560000
O	0.88229600	0.38990500	-1.37507100
C	-0.67517000	-0.79825600	1.81197500
O	0.16188000	-1.18632600	2.61525300
C	-1.83443900	0.05496100	-0.20187900
C	-3.17464400	-2.11696000	0.32281600
C	-3.45440600	-2.31516700	-1.16673000
C	-2.86943500	-0.66022500	0.74824300
C	-2.05504600	-0.29985900	-1.69096000
H	-4.01380400	-2.47679800	0.93273000
H	-2.31323800	-2.74553500	0.59251000
H	-3.63198800	-3.37820600	-1.37308200
H	-1.21238900	0.09036200	-2.26504300
O	1.86940400	-0.54768100	0.42772900
Si	3.46807600	-0.47583500	-0.19585000
C	3.59615600	-1.50586300	-1.76565500
H	3.29745100	-2.54401400	-1.57814800
H	4.62717000	-1.52011400	-2.14115800
H	2.94924100	-1.10178400	-2.54986300
C	3.96546100	1.31826400	-0.48437000
H	3.88097700	1.90334700	0.43951600
H	3.32729000	1.77948100	-1.24412100
H	5.00702400	1.38533700	-0.82313000
C	4.47829500	-1.23540100	1.19532400
H	4.35963000	-0.66649200	2.12424400
H	5.54648400	-1.25759800	0.94610700
H	4.15721300	-2.26351600	1.39650400
H	-3.80525600	-0.08818800	0.76337500
C	-2.18311200	-0.70812900	2.12298100
H	-2.37293400	0.19366600	2.72216300
H	-2.49602300	-1.55799800	2.73726100
H	-4.36985500	-1.77927400	-1.45947400
H	-2.95704400	0.23790300	-2.02044700
C	-2.27047100	-1.78634100	-1.97896300
H	-1.36492900	-2.35599800	-1.72604500
H	-2.43805800	-1.92526400	-3.05437400



SI-TS4

SCF Energy (B3LYP-D3BJ, hexane):	-1217.175448
SCF Energy (M11-L, hexane):	-1216.841281
SCF Energy (M06-2X, hexane):	-1216.628927
SCF Energy (B3LYP, gas-phase):	-1216.743793
Enthalpy Correction:	0.428707
Free-Energy Correction:	0.35198

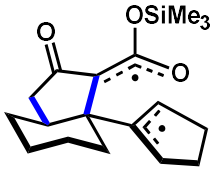
H	-0.25809300	4.03520100	0.24258200
C	0.55318300	3.61297200	-0.36185800
C	1.34113500	2.58659400	0.40619800
C	1.47563900	1.42379300	-0.29459800
C	0.77767700	1.52671900	-1.52727000
C	0.03842700	2.82374800	-1.60070400
H	1.18064400	4.46031200	-0.67632600
H	1.69588300	2.75343400	1.41715600
H	0.92319200	0.88380300	-2.38507800
H	-1.04281400	2.63580500	-1.51673200
H	0.18742000	3.33985000	-2.55727600
C	0.35777200	-0.56965200	-0.35678300
C	-0.88246400	-0.13407800	0.27182000
O	-0.92540600	0.63902000	1.23174400
C	0.54831700	-1.81097900	-1.12536000
O	-0.29388100	-2.51110000	-1.66924400
C	1.71321500	-0.01384800	0.10458300
C	3.50468500	-0.12403800	1.96290300
C	4.18229200	-0.76027200	-0.37452500
C	4.35550400	-1.07731500	1.11583500
C	2.71862200	-0.75897600	-0.85169700
C	2.02092900	-0.26072700	1.59938200
H	3.84369100	0.91002500	1.79809400
H	4.60770400	0.23631700	-0.56264100
H	4.05438200	-2.11417900	1.32367900
H	1.69880100	-1.28273300	1.84494800
H	3.64103700	-0.33103200	3.03186500
H	4.76012900	-1.46135200	-0.99098200
H	5.41569400	-1.00098900	1.38798200
H	1.38927100	0.39995600	2.19931800
C	2.05644100	-2.12232200	-1.10299100
H	2.37262500	-2.60329400	-2.03399800
H	2.25166800	-2.83272800	-0.28685700
H	2.70621800	-0.23328600	-1.81559200
O	-2.00212100	-0.61985500	-0.30950400
Si	-3.57497300	-0.37456400	0.33003800
C	-3.67495300	-1.07027700	2.07566600
H	-3.43490200	-2.13995500	2.08451200
H	-4.68567000	-0.95260300	2.48636700
H	-2.97255100	-0.55766900	2.73972600
C	-4.02137200	1.45599000	0.27477800
H	-3.93537700	1.85189100	-0.74481800
H	-3.36009600	2.03562100	0.92589000
H	-5.05609000	1.61702900	0.60288800
C	-4.65338900	-1.35683600	-0.85562600
H	-4.57249200	-0.96939100	-1.87761600
H	-5.70966300	-1.31435800	-0.56226800
H	-4.34968900	-2.40926100	-0.87783000



SI-5-ax

SCF Energy (B3LYP-D3BJ, hexane):	-1217.171737
SCF Energy (M11-L, hexane):	-1216.840683
SCF Energy (M06-2X, hexane):	-1216.630700
SCF Energy (B3LYP, gas-phase):	-1216.749958
Enthalpy Correction:	0.428921
Free-Energy Correction:	0.349483

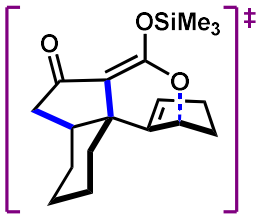
H	0.72686000	4.25908400	0.40225400
C	1.53596800	3.67709900	-0.06097800
C	1.73607400	2.36153700	0.63580400
C	1.56238100	1.29020000	-0.23488800
C	1.25153200	1.77694400	-1.50448200
C	1.20460800	3.27562000	-1.52558000
H	2.43333200	4.30984100	-0.00056300
H	1.96126600	2.28294900	1.69211600
H	1.05402700	1.16504800	-2.37767900
H	0.21450400	3.63648700	-1.83927900
H	1.91742400	3.69756800	-2.24898600
C	0.18134400	-0.75118000	-0.23624800
C	-1.03871300	-0.13201200	0.28629700
O	-1.02634800	0.65689900	1.22928600
C	0.28098700	-2.05603200	-0.88742700
O	-0.63474200	-2.79960700	-1.22712700
C	1.55549500	-0.19750700	0.08207900
C	3.42880600	-0.43284400	1.86265700
C	3.96065300	-1.02513400	-0.52974400
C	4.22221800	-1.36914700	0.94265400
C	2.47082900	-1.01655400	-0.90838800
C	1.92494500	-0.51645500	1.56480700
H	3.78564300	0.59765500	1.72627200
H	4.37473700	-0.02696700	-0.73199300
H	3.93378200	-2.41026600	1.14637900
H	1.58693900	-1.53713300	1.78916700
H	3.60373900	-0.69050000	2.91515000
H	4.49614500	-1.72027600	-1.18969600
H	5.29649700	-1.29890400	1.15401700
H	1.33914300	0.13865300	2.21558700
C	1.77447000	-2.38151100	-1.02993000
H	1.97391300	-2.89547000	-1.97547500
H	2.06006700	-3.07084300	-0.22284400
H	2.38767000	-0.53831500	-1.89208500
O	-2.16479000	-0.50058600	-0.34710800
Si	-3.74481600	-0.07006500	0.18619400
C	-4.01632200	-0.74136500	1.92203500
H	-3.88191400	-1.82905700	1.94515600
H	-5.03342700	-0.52381700	2.27153200
H	-3.30946800	-0.29503100	2.62821400
C	-3.96609600	1.79727400	0.10121900
H	-3.79219300	2.17045300	-0.91509700
H	-3.26607400	2.30099000	0.77443900
H	-4.98633400	2.08166700	0.38826900
C	-4.84135600	-0.94193800	-1.06558800
H	-4.64890300	-0.57828100	-2.08136300
H	-5.90372600	-0.77850100	-0.84623400
H	-4.65613200	-2.02173500	-1.06018000



SI-5-eq

SCF Energy (B3LYP-D3BJ, hexane):	-1217.179348
SCF Energy (M11-L, hexane):	-1216.845036
SCF Energy (M06-2X, hexane):	-1216.631726
SCF Energy (B3LYP, gas-phase):	-1216.751780
Enthalpy Correction:	0.429110
Free-Energy Correction:	0.350493

H	-2.08620300	4.08946400	0.31061900
C	-2.46840000	3.37015200	-0.42733000
C	-1.57871200	2.16850800	-0.52395900
C	-2.28535000	0.99096600	-0.27902900
C	-3.61711700	1.30065400	-0.01020100
C	-3.85169300	2.78546400	-0.03076900
H	-2.50545400	3.91719600	-1.38089300
H	-0.53630900	2.21023100	-0.81180200
H	-4.40652500	0.58475100	0.18825000
H	-4.19670700	3.16236500	0.94317800
H	-4.63724500	3.05614300	-0.75047900
C	-0.26188700	-0.19180500	0.41582100
C	0.98354100	0.13822200	-0.27196200
O	1.02195100	0.61824100	-1.40804200
C	-0.41505000	-0.36473100	1.86503300
O	0.41389700	-0.15311100	2.74250500
C	-1.60935700	-0.38751700	-0.26726800
C	-1.15539600	-2.40736800	-1.81150000
C	-1.89636500	-2.82240800	0.55650500
C	-1.99655300	-3.30274200	-0.89491100
C	-2.32232200	-1.35225900	0.74823100
C	-1.60494000	-0.94534500	-1.71453300
H	-1.23163600	-2.74050300	-2.85418500
H	-0.97861700	-0.30399300	-2.33934300
H	-0.09493800	-2.49187700	-1.53464800
H	-2.50832900	-3.44992200	1.21777000
H	-1.66884900	-4.34748400	-0.96667200
H	-2.63291600	-0.86774000	-2.09640800
C	-1.85661100	-0.83132100	2.11692900
H	-1.88946900	-1.57668700	2.91786600
H	-3.40967200	-1.28980800	0.62664300
O	2.09285500	-0.12695200	0.43479400
Si	3.68696700	0.27874200	-0.07749700
C	4.10840400	-0.65230100	-1.65765400
H	4.00031000	-1.73435300	-1.51728600
H	5.14626300	-0.45955900	-1.95751600
H	3.45120600	-0.34834200	-2.47790100
C	3.81444900	2.14313800	-0.29323600
H	3.54205900	2.66427200	0.63194300
H	3.14911100	2.48923100	-1.09008900
H	4.83965000	2.43665400	-0.55150100
C	4.73221100	-0.31920100	1.36396600
H	4.42128500	0.16182000	2.29783800
H	5.79445500	-0.09694100	1.20406700
H	4.63298000	-1.40198700	1.50095200
H	-0.85732500	-2.94437700	0.89501200
H	-3.04629900	-3.27960700	-1.22467600
H	-2.45110900	0.03260300	2.44538400

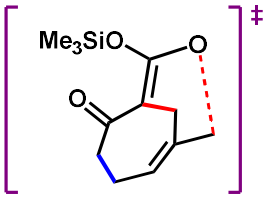


SI-TS6

SCF Energy (B3LYP-D3BJ, hexane):	-1217.179123
SCF Energy (M11-L, hexane):	-1216.845247
SCF Energy (M06-2X, hexane):	-1216.631407
SCF Energy (B3LYP, gas-phase):	-1216.746287
Enthalpy Correction:	0.428533
Free-Energy Correction:	0.352087

H	-0.46662000	3.80807600	0.00788000
C	0.59891100	3.56549000	-0.10024100
C	0.93216800	2.30261300	0.62299500
C	1.44985900	1.32004700	-0.24334200
C	1.45668500	1.84336800	-1.51721000
C	0.98808900	3.26307000	-1.56675100
H	1.14771000	4.42041500	0.31969100
H	0.88950300	2.22228300	1.69927000
H	1.74042800	1.30119200	-2.41240500
H	0.14344300	3.36477400	-2.26207500
H	1.76837400	3.93990600	-1.94365800
C	0.26983900	-0.78821600	-0.23388100
C	-0.94495700	-0.17484300	0.18615800
O	-0.97929100	0.81588400	0.95982600
C	0.45714400	-2.07487200	-0.88582300
O	-0.38775500	-2.86739700	-1.29071700
C	1.61064100	-0.15212500	0.10458600
C	3.48020000	-0.12819200	1.89307100
C	4.07825900	-0.80849800	-0.46437500
C	4.36624200	-1.03271100	1.02675700
C	2.59234100	-0.92217400	-0.84708100
C	1.99920000	-0.39290200	1.59269000
H	3.72539200	0.92692800	1.69659000
H	4.42514900	0.20108000	-0.73089400
H	4.17857300	-2.08188500	1.29572100
H	1.78252600	-1.44387800	1.82221700
H	3.68001300	-0.30259100	2.95808600
H	4.66484900	-1.50478900	-1.07802300
H	5.42853800	-0.84639000	1.22901200
H	1.33996700	0.18804900	2.24417700
C	1.97876900	-2.32850200	-0.94334200
H	2.25271100	-2.86469600	-1.85720000
H	2.26191100	-2.96824200	-0.09529700
H	2.48629800	-0.49370000	-1.85096900
O	-2.08820800	-0.69309400	-0.31188100
Si	-3.65571600	-0.24376600	0.20426100
C	-3.83353700	-0.54228500	2.05501500
H	-3.63081300	-1.59134400	2.30061100
H	-4.85171000	-0.31189500	2.39330500
H	-3.13480900	0.08044000	2.62206300
C	-4.01781900	1.54969800	-0.25084100
H	-3.87470000	1.71965500	-1.32475700
H	-3.35574300	2.22910700	0.29446400
H	-5.05574100	1.81194200	-0.00956200
C	-4.75685700	-1.40982000	-0.77611100
H	-5.81664200	-1.25233100	-0.54011200
H	-4.51136900	-2.45442300	-0.55502600
H	-4.62623900	-1.26298600	-1.85423500

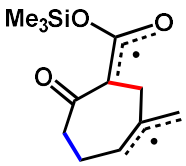
Figure S2: *Diradical Claisen rearrangement of* ***46d***



SI-TS1d

SCF Energy (B3LYP-D3BJ, hexane):	-983.5925465
SCF Energy (M11-L, hexane):	-983.3249026
SCF Energy (M06-2X, hexane):	-983.1737876
SCF Energy (B3LYP, gas-phase):	-983.2607172
Enthalpy Correction:	0.295588
Free-Energy Correction:	0.230847

C	-1.36240500	-2.60670600	0.25418400
C	-2.21326700	-1.50629000	0.09218600
C	-2.14875100	-0.81995500	-1.27514300
H	-0.98810500	-2.88919900	1.23373100
H	-3.11807000	-0.44960800	-1.60764000
C	-1.15149200	0.27316700	-1.00227600
O	0.34270300	-1.49307500	-0.69677800
C	0.13454100	-0.23719700	-0.70193800
C	-2.69225400	-0.79254400	1.15819900
C	-3.30048500	0.58200700	1.18822900
H	-4.37467800	0.47786400	1.41658500
C	-1.63199400	1.55829700	-0.49614000
C	-3.10022800	1.54506900	-0.00687700
H	-3.78719800	1.29978200	-0.82349800
H	-3.33931600	2.56065000	0.31920900
O	-0.95361800	2.56766500	-0.34028100
O	1.10769400	0.60685400	-0.31405400
Si	2.67070200	0.13467700	0.19882100
C	3.50648400	1.78707400	0.52074700
H	3.54431800	2.39066900	-0.39297900
H	4.53463700	1.65131600	0.87858700
H	2.95926800	2.36479100	1.27393100
C	3.55288800	-0.81319200	-1.16744100
H	3.59469400	-0.22220700	-2.08994400
H	3.03683300	-1.75204700	-1.38995200
H	4.58471600	-1.04708100	-0.87588400
C	2.55332900	-0.87599700	1.78563600
H	2.02509000	-0.31869100	2.56847600
H	3.55253600	-1.11854700	2.16885100
H	2.01765500	-1.81462600	1.61195600
H	-1.77825000	-1.52281400	-2.02461600
H	-1.16990500	-3.29478300	-0.55781800
H	-2.65505500	-1.27750200	2.13522900
H	-2.88142300	1.06261200	2.08498900

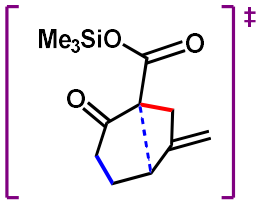


SI-2d

SCF Energy (B3LYP-D3BJ, hexane):	-983.5988204
SCF Energy (M11-L, hexane):	-983.3198328
SCF Energy (M06-2X, hexane):	-983.1841691
SCF Energy (B3LYP, gas-phase):	-983.2721827
Enthalpy Correction:	0.293968
Free-Energy Correction:	0.223613

C	2.88033300	1.07733400	-1.66533500
C	2.61470300	1.43833800	-0.35031000
C	2.55530500	2.76621900	0.04418100
H	2.88371400	0.04499500	-1.99650200

H	2.68599900	3.56771600	-0.67729200
C	1.09048100	-0.42196500	0.32305100
C	-0.22626000	0.22483800	0.42575500
O	-0.35573000	1.31580100	0.97199200
C	1.39130300	-1.80173700	-0.06795800
O	0.59533000	-2.66728900	-0.41356700
C	2.33326200	0.33572100	0.68429900
C	3.43835100	-0.76541900	0.78964100
C	2.91213000	-1.99272300	0.02142100
H	3.31412800	-2.05144500	-0.99890300
H	3.14270200	-2.94907700	0.50072300
H	4.39867200	-0.40520500	0.41138700
O	-1.23847500	-0.46575300	-0.11162700
Si	-2.88246500	0.06912100	-0.08902500
C	-3.45330900	0.26262200	1.69189000
H	-3.34167800	-0.67607500	2.24706100
H	-4.51246700	0.54683000	1.72971600
H	-2.87313900	1.03480300	2.20590700
C	-3.02391800	1.67003900	-1.06543300
H	-2.66765900	1.53773300	-2.09373400
H	-2.43307300	2.46439400	-0.59938500
H	-4.06804400	2.00347800	-1.11608300
C	-3.76922700	-1.34519200	-0.94850700
H	-3.39959500	-1.47968300	-1.97120200
H	-4.84937300	-1.16161400	-1.00209500
H	-3.61317900	-2.28861300	-0.41370400
H	3.57970900	-1.02119500	1.84519500
H	2.19159100	0.83630300	1.64846900
H	2.33807100	3.04695800	1.06854000
H	3.11021700	1.83147800	-2.41229500

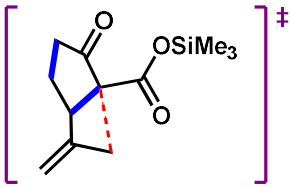


SI-TS3d

SCF Energy (B3LYP-D3BJ, hexane):	-983.5950559
SCF Energy (M11-L, hexane):	-983.3270406
SCF Energy (M06-2X, hexane):	-983.1784813
SCF Energy (B3LYP, gas-phase):	-983.2662236
Enthalpy Correction:	0.294624
Free-Energy Correction:	0.226909

C	2.87567800	2.67365500	0.36542700
C	2.69643200	1.35499600	0.11919800
C	2.21293100	0.77310500	-1.18990400
H	3.01130800	3.04576000	1.37787300
H	2.98598700	0.24110200	-1.75354700
C	1.12421200	-0.15897500	-0.67917900
C	-0.23062400	0.41267000	-0.58064100
O	-0.51708100	1.50188200	-1.06621700
C	1.40528800	-1.59769500	-0.52691500
O	0.58527300	-2.49190500	-0.67944900
C	2.60261000	0.37837700	1.17696500
C	3.08652200	-1.04996300	1.19878100
C	2.83823100	-1.88121000	-0.06781600
H	3.55409000	-1.62334500	-0.85698600
H	2.93785100	-2.95084000	0.13168900
H	4.15960200	-1.04025500	1.45941100
O	-1.10149500	-0.33609700	0.11557000
Si	-2.78086600	0.03131000	0.24082200
C	-3.01209000	1.65319600	1.16575600
H	-2.55096400	1.61212000	2.15969200
H	-4.07796700	1.87464100	1.30347900
H	-2.55710500	2.48076000	0.61337000

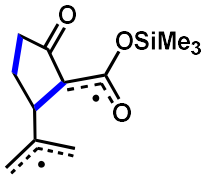
C	-3.53692700	0.07515100	-1.47987300
H	-3.37253800	-0.87381400	-2.00332400
H	-3.09599600	0.87663100	-2.08041700
H	-4.61986000	0.24351900	-1.42583000
C	-3.43155900	-1.42170600	1.23939900
H	-3.23083100	-2.36914900	0.72706900
H	-4.51482700	-1.34326800	1.39358600
H	-2.95632600	-1.46978800	2.22588700
H	2.58900500	-1.54635800	2.04185200
H	2.50010800	0.79672200	2.18152700
H	1.78437600	1.53913500	-1.83884300
H	2.86841100	3.40743500	-0.43441800



SI-TS4d

SCF Energy (B3LYP-D3BJ, hexane): -983.5915025
SCF Energy (M11-L, hexane): -983.3237068
SCF Energy (M06-2X, hexane): -983.1746973
SCF Energy (B3LYP, gas-phase): -983.2626304
Enthalpy Correction: 0.293843
Free-Energy Correction: 0.225659

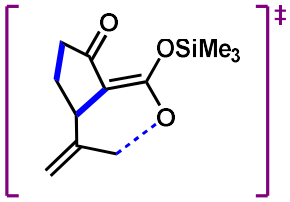
C	2.35409000	2.87736500	-0.07172500
C	2.40329800	1.55333000	-0.36482000
C	2.09381800	1.01152500	-1.64490800
H	2.51954900	3.24191100	0.93667800
H	2.47289900	0.04643400	-1.95695400
C	1.19206300	-0.33354900	0.16973400
C	-0.14162700	0.24323000	0.39474400
O	-0.30502200	1.23638100	1.09484800
C	1.49840900	-1.74737000	-0.11150300
O	0.74698600	-2.60537400	-0.54901900
C	2.42563200	0.41821900	0.63896600
C	3.60203000	-0.60287600	0.48951300
C	2.96233600	-1.99177800	0.29002400
H	3.46410000	-2.61299300	-0.45896100
H	2.95123900	-2.57355100	1.22129800
H	4.22250300	-0.33888200	-0.37330400
O	-1.13984400	-0.40492900	-0.22564600
Si	-2.80550300	-0.00412800	-0.03171100
C	-3.28010600	-0.16888000	1.78012100
H	-3.08729300	-1.18352000	2.14782700
H	-4.34769200	0.03971100	1.92392700
H	-2.70825700	0.53212900	2.39562000
C	-3.11790900	1.72888000	-0.69495400
H	-2.82176400	1.80793600	-1.74767500
H	-2.55073600	2.47026400	-0.12400100
H	-4.18277700	1.98574400	-0.63025400
C	-3.65527600	-1.30430200	-1.08815900
H	-3.35208800	-1.22139800	-2.13799900
H	-4.74642500	-1.19991000	-1.04438000
H	-3.39799000	-2.31365700	-0.74851500
H	1.68339800	1.63441300	-2.43772300
H	2.12734300	3.61540900	-0.83623600
H	4.25689800	-0.56855000	1.36436100
H	2.33660000	0.78490900	1.66659500



SI-5d

SCF Energy (B3LYP-D3BJ, hexane): -983.6022015
SCF Energy (M11-L, hexane): -983.3309589
SCF Energy (M06-2X, hexane): -983.1879524
SCF Energy (B3LYP, gas-phase): -983.2767338
Enthalpy Correction: 0.295057
Free-Energy Correction: 0.226661

C	3.11911700	2.60851100	0.46228700
C	2.93051400	1.26134500	0.19146600
C	2.08171400	0.88698200	-1.03218700
H	3.68114100	2.93073900	1.33434800
H	2.73182000	0.47435700	-1.81495300
C	0.99658800	-0.09050400	-0.68710200
C	-0.38725000	0.43914100	-0.60601600
O	-0.71398500	1.46165900	-1.19744900
C	1.31423000	-1.50743800	-0.49835000
O	0.45637200	-2.39054200	-0.49811900
C	3.48347000	0.28388400	1.02170400
C	3.41427200	-1.21433800	0.94072300
C	2.78910000	-1.85501100	-0.31407200
H	3.36029100	-1.56056600	-1.20386900
H	2.84715600	-2.94373300	-0.23308400
H	4.43636600	-1.60812200	1.05170500
O	-1.21534000	-0.26553300	0.16899800
Si	-2.91286900	0.03982200	0.29479100
C	-3.19099100	1.73373500	1.06254400
H	-2.70849000	1.80620700	2.04436100
H	-4.26213100	1.92468700	1.20443500
H	-2.78329800	2.52295600	0.42378400
C	-3.68812100	-0.11796700	-1.40981700
H	-3.48839500	-1.10614200	-1.83995900
H	-3.29109600	0.63869100	-2.09341500
H	-4.77660600	0.00844300	-1.35467100
C	-3.47530900	-1.33577600	1.44276400
H	-3.23155800	-2.31823100	1.02368400
H	-4.55926900	-1.29635300	1.60618900
H	-2.98684000	-1.26044300	2.42096100
H	2.87720700	-1.59154700	1.82709800
H	4.07135500	0.65410000	1.86175000
H	1.61754300	1.78571100	-1.44104800
H	2.70457400	3.38167800	-0.17548200



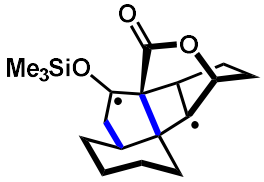
SI-TS6d

SCF Energy (B3LYP-D3BJ, hexane): -983.5931658
SCF Energy (M11-L, hexane): -983.3260512
SCF Energy (M06-2X, hexane): -983.1729106
SCF Energy (B3LYP, gas-phase): -983.2634795
Enthalpy Correction: 0.293921
Free-Energy Correction: 0.227658

C	-1.47600400	-2.68170500	0.10039500
C	-2.26656100	-1.57681300	-0.27811000
C	-2.72823300	-1.43075900	-1.54833600
H	-1.38239200	-2.98231300	1.13500100
H	-3.25584200	-0.53850400	-1.86965500
C	-1.16939700	0.45170500	0.44337800
C	0.12399700	-0.14023500	0.43760400

O	0.28607300	-1.34681200	0.76632100
C	-1.57078600	1.76403100	-0.04700300
O	-0.85622300	2.69649500	-0.39426600
C	-2.35387000	-0.42396800	0.73801500
C	-3.58373000	0.52679300	0.64262800
C	-3.11115500	1.79490100	-0.09454500
H	-3.41703600	1.81297300	-1.14907400
H	-3.48361100	2.72312800	0.35015700
H	-4.43742500	0.03963700	0.16077100
O	1.15736300	0.60711500	0.02058700
Si	2.78580800	0.07016000	-0.07658900
C	3.38658300	-0.46469200	1.62461700
H	3.27677400	0.34768600	2.35259700
H	4.44824500	-0.74041000	1.59290500
H	2.81956900	-1.32650900	1.98958900
C	2.92345000	-1.31695100	-1.34247300
H	2.55632000	-0.99134900	-2.32292500
H	2.33891100	-2.18791300	-1.03045200
H	3.96751600	-1.63095900	-1.46632700
C	3.68225800	1.61317600	-0.66271400
H	4.75662500	1.42759000	-0.78419900
H	3.55993300	2.43361200	0.05309300
H	3.28715600	1.95486100	-1.62581900
H	-3.89957600	0.78250300	1.65918100
H	-2.29130400	-0.88137300	1.73445400
H	-1.05288300	-3.34536700	-0.64741100
H	-2.62931600	-2.22682600	-2.28150400

Scheme S2: *Diradical Pathways Beginning at Cope Intermediate* ***39***



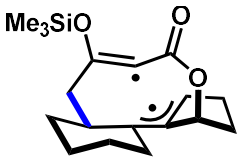
43

SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.665293
singlet, single-point:	-1216.669407

C	2.44608100	2.04345500	0.29680400
C	2.26821000	0.94447900	-0.74524000
C	0.95731700	1.38906900	-1.36113100
C	0.84169200	2.92079100	-1.25144300
C	2.11834300	3.32534000	-0.46836300
H	3.38619700	2.04302500	0.84992100
H	0.69088000	0.99292500	-2.34024100
H	-0.06804000	3.22577800	-0.72190800
H	0.80172200	3.38439000	-2.24184400
H	1.97690200	4.17617000	0.20365400
H	2.94086300	3.55872800	-1.15532000
C	0.38358200	0.41513200	-0.20080800
O	1.39412400	1.94026900	1.35025000
C	0.28946000	1.18950300	1.08953400
O	-0.61998200	1.15007100	1.88787000
C	1.78169700	-0.39667500	-0.21429900
C	1.66426300	-3.00050100	-0.71654300
C	2.46977000	-2.28191900	1.50337300
C	2.76672100	-3.19988900	0.31917100
C	2.54778600	-0.81786400	1.06449000
C	1.49352900	-1.55666000	-1.25937300

H	0.72082000	-3.30533900	-0.24227200
H	1.47257900	-2.51499200	1.90248800
H	3.75548500	-2.96400200	-0.10147500
H	3.60615700	-0.60153300	0.85366700
H	1.79977700	-3.66696100	-1.57816200
H	3.18154900	-2.44069900	2.32314300
H	2.79650700	-4.25152600	0.63070300
H	2.27734700	-0.16594600	1.89994800
H	2.18058700	-1.42612600	-2.10331900
C	-0.65087800	-0.54756000	-0.68145500
C	0.01358800	-1.40701800	-1.72709000
H	-0.06495600	-0.92730700	-2.71768500
H	-0.47881300	-2.38100800	-1.83547300
O	-1.94101500	-0.17798800	-0.88500000
Si	-3.31317800	-0.23045500	0.12194700
C	-2.98474800	-1.35592700	1.59242000
H	-2.18173300	-0.94442000	2.21151800
H	-3.88306200	-1.45035900	2.21534900
H	-2.69464300	-2.36358200	1.27193200
C	-3.74795100	1.51933600	0.65391200
H	-2.95346600	1.93733300	1.27934100
H	-3.88986800	2.17533400	-0.21336200
H	-4.68042100	1.52963600	1.23267400
C	-4.67341300	-0.92825800	-0.98054000
H	-4.80508900	-0.31810200	-1.88184000
H	-4.44314500	-1.95080000	-1.30167900
H	-5.63494100	-0.95205100	-0.45248600



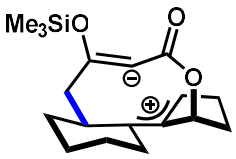
42

SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.669393
singlet, single-point:	-1216.674956

C	1.90678900	1.99066700	0.65266900
C	1.99815800	1.10134100	-0.59041900
C	1.75539000	1.86851700	-1.69422400
C	1.44261300	3.30362200	-1.36231200
C	1.17648100	3.25774400	0.15965600
H	2.90168300	2.23792500	1.03947200
H	1.84870000	1.51617200	-2.71722600
H	0.58897800	3.69623700	-1.93021500
H	2.29500300	3.95805900	-1.60338000
H	0.10582100	3.12688600	0.34490100
H	1.50019900	4.15856200	0.68881200
C	-0.40092200	0.30217300	0.40822700
O	1.27714900	1.37566500	1.79595000
C	0.19709500	0.54679200	1.67639300
O	-0.25043200	0.04883300	2.70299700
C	2.29255900	-0.29955400	-0.50689100
C	1.42725700	-2.68936600	-0.71938200
C	3.11486700	-2.16546100	1.05544300
C	2.70618700	-3.16583900	-0.02784100
C	3.36692900	-0.77985500	0.43966800
C	1.55255700	-1.29373300	-1.38695400
H	0.62339400	-2.64645100	0.02866900
H	2.31565500	-2.09367200	1.80541000
H	3.51816100	-3.27185200	-0.76348400
H	4.31799800	-0.82972700	-0.12422600

H	1.10704300	-3.40993400	-1.48283100
H	4.01723700	-2.50110600	1.58108100
H	2.54408300	-4.16056000	0.40591300
H	3.53357200	-0.04113400	1.23114900
H	2.12093500	-1.44146200	-2.32452800
C	-0.78584700	-0.33717300	-0.69050000
C	0.13614500	-0.82086900	-1.80433600
H	0.18982300	-0.01699000	-2.54805100
H	-0.38065600	-1.65356100	-2.29486200
O	-2.09200700	-0.54831900	-1.01841200
Si	-3.46575900	-0.26357500	-0.02240900
C	-3.31986300	-1.28050100	1.54918700
H	-2.43842100	-0.99362100	2.13359600
H	-4.20646500	-1.13874400	2.18051600
H	-3.24502200	-2.35002100	1.31889400
C	-3.63098600	1.57847700	0.33667400
H	-2.82732400	1.94363700	0.98377300
H	-3.61805100	2.16660000	-0.58844400
H	-4.58338000	1.77878100	0.84399300
C	-4.87803400	-0.85356500	-1.11417700
H	-4.92946200	-0.27967100	-2.04645400
H	-4.75976300	-1.91064200	-1.37770900
H	-5.84105700	-0.74358800	-0.60061100



42′

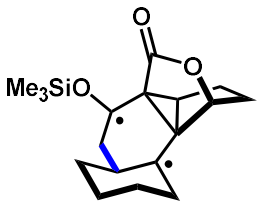
SCF Energy (B3LYP, gas-phase)
singlet, optimized: -1216.702591

[unrestricted calculation led to
closed-shell structure]

C	1.40160400	2.17435800	0.75301900
C	1.72427600	1.33806100	-0.48353100
C	1.73686700	2.14271800	-1.55835700
C	1.13029200	3.49610200	-1.24867300
C	0.52568000	3.29307200	0.16581000
H	2.31253600	2.60687800	1.18606000
H	2.06853800	1.85533600	-2.55156100
H	0.36816200	3.78889300	-1.98215100
H	1.88200400	4.30098600	-1.25261300
H	-0.51170900	2.94879100	0.10889500
H	0.55512300	4.20025700	0.77673400
C	-0.18490300	-0.23335800	0.44300800
O	0.88662400	1.41512800	1.85598700
C	0.29611300	0.18302700	1.71950300
O	0.15707500	-0.46706300	2.75037600
C	1.89147000	-0.10539800	-0.32673500
C	1.75653200	-2.55878200	-1.06341400
C	3.03032600	-2.02353500	1.01031600
C	3.01309500	-2.87327200	-0.25618500
C	2.97928300	-0.52997900	0.64816800
C	1.62534000	-1.06394700	-1.45993800
H	0.87175800	-2.84037300	-0.48173900
H	2.17628100	-2.27326100	1.64723100
H	3.90876200	-2.65545200	-0.85828900
H	3.92969500	-0.27206300	0.14513400
H	1.73257100	-3.15393300	-1.98469100
H	3.93623500	-2.21709300	1.59651200
H	3.05113900	-3.94196900	-0.01245700
H	2.95325900	0.09039800	1.54282200

H	2.34720700	-0.88122000	-2.27666400
C	-0.63214200	-0.62050400	-0.74385100
C	0.23986800	-0.77201400	-1.96189100
H	0.20208400	0.20502200	-2.46163700
H	-0.13858700	-1.51391700	-2.67446800
O	-1.95602600	-0.58501800	-1.10832800
Si	-3.27250400	-0.39127800	-0.03392300
C	-3.20151500	-1.73647300	1.27690800
H	-2.28208300	-1.67052700	1.87087700
H	-4.05329100	-1.65090400	1.96362500
H	-3.24285500	-2.73200200	0.81928700
C	-3.23709400	1.32947000	0.73426000
H	-2.38905600	1.45852800	1.41471700
H	-3.17720100	2.10549500	-0.03788300
H	-4.15321700	1.50668000	1.31225800
C	-4.76242100	-0.57869100	-1.16649300
H	-4.76771200	0.19044800	-1.94712500
H	-4.76231100	-1.55688900	-1.66052600
H	-5.69967800	-0.48972500	-0.60327000

Scheme S3: *Di-Pi-Methane Type Rearrangement of Cope Intermediate* ***39***



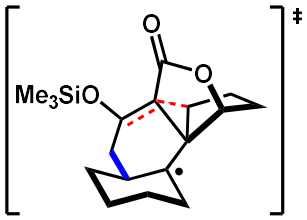
SI-7

SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.707442
singlet, single-point:	-1216.709377

C	-2.19058000	-1.62864900	0.75289700
C	-1.68897200	-0.62741300	-0.30801500
C	-1.15328100	-1.55856900	-1.40032900
C	-1.69674900	-2.97533700	-1.18808200
C	-2.72836200	-2.82041000	-0.04008300
H	-2.87470000	-1.21558800	1.49533600
H	-1.05637100	-1.18940200	-2.41610700
H	-0.90489800	-3.68387400	-0.91795800
H	-2.16094100	-3.34897600	-2.10578500
H	-2.83807900	-3.71531800	0.57979900
H	-3.71278000	-2.55982100	-0.44894700
C	-0.18345300	-0.93332700	-0.39038400
O	-1.01136700	-2.08577900	1.47568800
C	0.14049900	-1.77321100	0.81406300
O	1.21716800	-2.14724100	1.21156100
C	-2.17738800	0.73948100	-0.51669800
C	-0.94645100	2.81001700	0.12393500
C	-3.19637400	2.25775900	1.19697300
C	-2.24848000	3.36939100	0.72089500
C	-3.46925000	1.23926100	0.06051200
C	-1.23888900	1.80982000	-1.02797900
H	-0.36114900	2.30196800	0.90111900
H	-2.74352100	1.73123200	2.04858900
H	-2.76166800	3.97528000	-0.04120000
H	-4.05260300	1.75347000	-0.72238500
H	-0.32296800	3.63117900	-0.25597400
H	-4.14235600	2.68709200	1.55225800
H	-2.01777900	4.04746900	1.55245500
H	-4.10027600	0.42039400	0.42624300

H	-1.76467400	2.38703000	-1.80998100
C	0.71526200	0.16844400	-0.82662600
C	0.06276600	1.23759500	-1.66561700
H	-0.18761900	0.83651700	-2.65715400
H	0.77884700	2.05009600	-1.82762700
O	1.63917400	0.59678200	0.08958400
Si	3.31655100	0.31588900	0.09929900
C	3.78287500	0.15419600	1.91081800
H	3.27990400	-0.71413400	2.34849400
H	4.86535500	0.02745000	2.03588500
H	3.48339600	1.04308900	2.47844400
C	3.73311800	-1.22977100	-0.88924500
H	3.22267600	-2.09711200	-0.45992200
H	3.42728200	-1.13449900	-1.93776100
H	4.81363100	-1.41985700	-0.87336900
C	4.14568200	1.82926900	-0.66967100
H	3.85102400	1.96026500	-1.71806800
H	3.87799600	2.74606800	-0.13117600
H	5.23892100	1.73616900	-0.64425800



SI-TS8

SCF Energy (B3LYP, gas-phase)

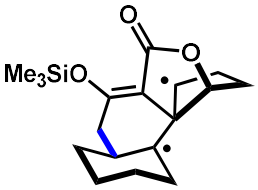
triplet, optimized: -1216.697618

singlet, optimized: -1216.696901

(triplet structure given)

C	1.77280400	1.91353200	0.54551500
C	1.36666900	0.73401100	-0.39366200
C	0.56053600	1.45341300	-1.44672300
C	0.67877200	2.95650000	-1.33216200
C	1.86633000	3.14364300	-0.35798100
H	2.65727800	1.72529100	1.15734400
H	0.24531000	0.94701800	-2.35122000
H	-0.22949100	3.43029300	-0.93346700
H	0.86182900	3.41526000	-2.31197500
H	1.83091600	4.07480500	0.21516700
H	2.81628000	3.11073300	-0.90685200
C	-0.03918900	0.41576100	0.02718800
O	0.65927200	2.11096600	1.45284500
C	-0.40736400	1.31364000	1.14447700
O	-1.43958500	1.37821100	1.77312700
C	2.28547000	-0.39397200	-0.68679800
C	2.13679400	-2.56435800	0.52260200
C	4.20797700	-1.09069800	0.76179500
C	3.65824500	-2.52544900	0.73596400
C	3.77194500	-0.30412900	-0.50277300
C	1.72638800	-1.79447200	-0.76544300
H	1.62269400	-2.11789000	1.38497700
H	3.83050800	-0.57274200	1.65459600
H	4.14772800	-3.08227000	-0.07732600
H	4.28318900	-0.74996300	-1.37218000
H	1.79297500	-3.60525800	0.45140900
H	5.30300900	-1.10131200	0.83911700
H	3.91964700	-3.04375100	1.66724200
H	4.11681200	0.73537900	-0.44198000
H	2.22080400	-2.31800900	-1.60130200
C	-0.59508700	-0.84848600	-0.23547400
C	0.20411500	-1.84809900	-1.02660700
H	0.01828200	-1.69519900	-2.10523100

H	-0.17962700	-2.85049200	-0.80177400
O	-1.86981800	-1.21084200	0.01680900
Si	-3.43756300	-0.54992700	-0.02710800
C	-3.46611600	1.15035600	-0.83520800
H	-2.94420600	1.15119500	-1.79926700
H	-4.50566600	1.44822900	-1.02384600
H	-3.00777500	1.90506400	-0.19094500
C	-4.40687400	-1.77064800	-1.09187900
H	-4.03534900	-1.79151400	-2.12331500
H	-4.33403900	-2.78850900	-0.69140900
H	-5.47067200	-1.50314300	-1.12701900
C	-4.12533700	-0.54367300	1.71914100
H	-4.09941300	-1.55004600	2.15343700
H	-3.54079100	0.12423400	2.35707400
H	-5.16977200	-0.20634200	1.72416900



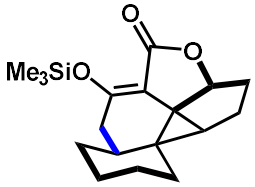
SI-9

SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.720603
singlet, single-point:	-1216.723352

C	1.84049200	1.75973500	0.70636100
C	1.39491200	0.73899000	-0.40532700
C	1.41187100	1.62375300	-1.65220100
C	1.75348800	3.04710800	-1.34671400
C	2.50031900	2.94364600	0.00042300
H	2.46192100	1.31153200	1.48750600
H	1.00105600	1.28512100	-2.59884700
H	0.85127300	3.67388200	-1.23451900
H	2.35580000	3.52043400	-2.13358500
H	2.44814400	3.85070100	0.60962900
H	3.55819500	2.71155700	-0.17295900
C	-0.04042700	0.44223000	0.02718300
O	0.62151800	2.21626600	1.34137500
C	-0.46206100	1.45391700	0.99679800
O	-1.55049600	1.66370600	1.49331700
C	2.19799600	-0.53570000	-0.52153700
C	1.70744300	-2.81272800	0.37342400
C	3.87639400	-1.61977400	0.99335200
C	3.19553000	-2.97043900	0.72256900
C	3.65588800	-0.63599600	-0.18418000
C	1.51457900	-1.84291800	-0.82517000
H	1.15735200	-2.42283900	1.24116200
H	3.45998200	-1.17921000	1.91007000
H	3.70771600	-3.46889700	-0.11440700
H	4.21681300	-1.01954800	-1.05505800
H	1.27126000	-3.79121000	0.12991600
H	4.95074200	-1.76275400	1.16807300
H	3.30919200	-3.62984600	1.59230400
H	4.09169500	0.34137700	0.05253100
H	2.03038700	-2.31422600	-1.68092900
C	-0.70035000	-0.67429200	-0.36085200
C	0.03077600	-1.67904900	-1.22056300
H	-0.03473200	-1.35415700	-2.26962600
H	-0.49392900	-2.63777600	-1.15706300
O	-1.94516000	-1.03470000	-0.02630500
Si	-3.52598000	-0.37753100	-0.02571600
C	-3.58088000	1.23759900	-0.98672400

H	-3.10455800	1.13788600	-1.96958500
H	-4.62451800	1.53121600	-1.15756000
H	-3.08249000	2.03884600	-0.43592500
C	-4.52394800	-1.69554300	-0.93588100
H	-4.19387400	-1.80683500	-1.97551900
H	-4.42711000	-2.67299600	-0.44904200
H	-5.59047500	-1.43748500	-0.95170200
C	-4.13366800	-0.23808800	1.74290100
H	-4.05766300	-1.20224200	2.25955600
H	-3.54705000	0.50091400	2.29338500
H	-5.18843600	0.06509500	1.76194700

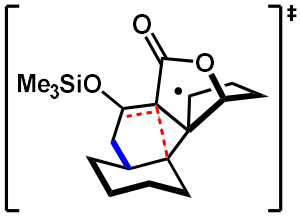


SI-10

SCF Energy (B3LYP, gas-phase)
singlet, optimized: -1216.802683

C	1.74580300	1.91428000	0.64296600
C	1.32526900	0.68205000	-0.14845500
C	1.96911000	0.72372100	-1.52678000
C	2.87181100	1.96477500	-1.56291900
C	2.39741000	2.86430800	-0.38351300
H	2.40204800	1.70294100	1.49522200
H	1.37010400	0.51842200	-2.41044200
H	2.76410000	2.48637100	-2.51905800
H	3.93420800	1.71207500	-1.46894200
H	1.61511800	3.54851100	-0.73112200
H	3.19986800	3.47368600	0.04568200
C	-0.10763800	0.46996600	0.13644400
O	0.51251200	2.43650000	1.19524000
C	-0.55941400	1.60764900	0.94761100
O	-1.66128700	1.88320100	1.37585000
C	2.26254700	-0.42261300	-0.56678400
C	1.59539200	-2.63087700	0.49355800
C	3.67730400	-1.45898800	1.28929000
C	3.02278600	-2.81706500	1.01727300
C	3.65882400	-0.58221500	0.02916000
C	1.52143400	-1.75983800	-0.78246600
H	0.98313700	-2.16353300	1.27764500
H	3.13395800	-0.94997400	2.09829400
H	3.62014300	-3.36758700	0.27489800
H	4.30816200	-1.03898900	-0.73386200
H	1.13908400	-3.60652700	0.28153600
H	4.71053400	-1.58795700	1.63556300
H	3.01243100	-3.42981800	1.92734700
H	4.10098600	0.39375100	0.25718800
H	2.02770400	-2.30618400	-1.59260600
C	-0.75847500	-0.61470900	-0.34990000
C	0.03602400	-1.59014500	-1.20076300
H	-0.03161400	-1.26430200	-2.24810900
H	-0.46540100	-2.56302200	-1.15777900
O	-2.03844700	-0.96426200	-0.18976500
Si	-3.61572400	-0.30719800	-0.08625200
C	-3.72656300	1.30076000	-1.05335500
H	-3.32964700	1.18629500	-2.06931900
H	-4.77688100	1.60613600	-1.14505400
H	-3.17968400	2.10101300	-0.54877900
C	-4.64784300	-1.64027600	-0.93080900

H	-4.36761500	-1.76128000	-1.98368400
H	-4.52199500	-2.61138800	-0.43808000
H	-5.71511700	-1.38743000	-0.89714500
C	-4.13078900	-0.15430100	1.71137000
H	-4.03234700	-1.11469700	2.23124300
H	-3.51854500	0.58989400	2.22575300
H	-5.18277000	0.15195600	1.77897500



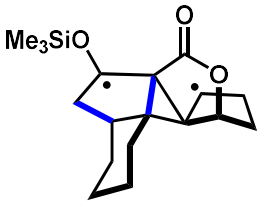
SI-TS11

SCF Energy (B3LYP, gas-phase)
triplet, optimized: -1216.690559
singlet, optimized: -1216.691213

(triplet structure given)

C	-2.05320000	-1.86979400	0.64569600
C	-1.63874900	-0.85430000	-0.44930400
C	-1.91636900	-1.55858500	-1.73107800
C	-2.30790800	-2.98818800	-1.49711800
C	-1.90982200	-3.24509400	-0.02630200
H	-3.07169300	-1.70770200	1.01000200
H	-2.00819400	-1.06396900	-2.69083800
H	-1.82191000	-3.68845400	-2.19026900
H	-3.39334400	-3.13260100	-1.64086700
H	-0.85882300	-3.54951000	0.03264500
H	-2.50931500	-4.01768200	0.46353800
C	-0.26175500	-0.41249400	0.04865700
O	-1.17068400	-1.69414100	1.76521400
C	-0.05997500	-0.96649800	1.40126300
O	0.88692200	-0.86020500	2.14775800
C	-1.89242900	0.59347800	-0.18174800
C	-1.17624800	2.98223200	-0.64540700
C	-2.52316800	2.48115000	1.41574900
C	-2.32515300	3.45534500	0.25016600
C	-2.81917000	1.05823300	0.91276700
C	-1.41111600	1.57644700	-1.23952700
H	-0.24985000	2.95870300	-0.05455200
H	-1.61160300	2.46344300	2.02819400
H	-3.25385900	3.52713600	-0.33643100
H	-3.85456500	1.03146400	0.52263600
H	-1.00744300	3.68955500	-1.46753700
H	-3.33932700	2.81279900	2.06942100
H	-2.11552600	4.46380900	0.62833800
H	-2.80261600	0.36028800	1.75746200
H	-2.17633000	1.65781800	-2.02899400
C	0.63809500	0.29398100	-0.77543600
C	-0.07972900	1.03459000	-1.87295000
H	-0.30106000	0.37655700	-2.72129200
H	0.53909400	1.85415700	-2.25019600
O	1.82547100	0.79242600	-0.34746400
Si	3.33127500	0.06576000	-0.03668200
C	3.20578500	-1.81116600	-0.11167500
H	2.74296400	-2.14781700	-1.04704000
H	4.20718800	-2.25676500	-0.05953600
H	2.61688700	-2.19794200	0.72491800
C	4.48223200	0.68683000	-1.39779300
H	4.15606800	0.34227200	-2.38655300
H	4.51312800	1.78247000	-1.42102600
H	5.50789700	0.32852300	-1.24292200
C	3.89666800	0.68541700	1.64134500

H	3.95527600	1.78001400	1.66050800
H	3.18801500	0.36531300	2.41082100
H	4.88949400	0.29334300	1.89523000



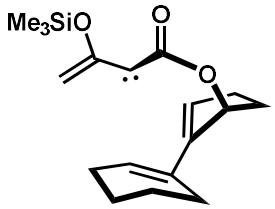
SI-12

SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.700972
singlet, single-point:	-1216.711130

C	1.57050400	2.23641500	0.44391500
C	1.39417200	1.02478800	-0.47374200
C	1.36384100	1.51495300	-1.85095100
C	1.41656700	3.01594100	-1.86934600
C	1.08487300	3.42226400	-0.41044600
H	2.60088200	2.37768400	0.78847900
H	1.37383800	0.88979600	-2.73497300
H	0.72008300	3.46250700	-2.59134400
H	2.41917100	3.37891200	-2.15690500
H	0.00017700	3.50712200	-0.28357500
H	1.53323300	4.37330800	-0.10921400
C	0.28639800	0.17707800	0.25435300
O	0.76817000	2.02529500	1.62492700
C	-0.04889100	0.93224000	1.49230100
O	-0.91584400	0.69141000	2.30149700
C	1.70488400	-0.34742600	0.06152900
C	2.14387900	-2.80524500	-0.33557600
C	2.68486200	-0.57252300	1.21195700
C	1.61668300	-1.50888900	-0.96986800
H	1.50534500	-3.05725200	0.52205000
H	2.03758900	-3.63275600	-1.04744400
H	2.95009700	0.37121200	1.69843700
H	2.25260500	-1.27082700	-1.83356900
C	-0.64035100	-0.69372400	-0.49935700
C	0.13047400	-1.60654700	-1.41638700
O	-1.89381700	-0.30376800	-0.85017400
Si	-3.38445400	-0.47682800	-0.04815700
C	-3.89521800	1.18750700	0.66398200
H	-3.91006200	1.96405400	-0.11022500
H	-4.90265400	1.13200700	1.09611500
H	-3.20442400	1.49978900	1.45359100
C	-4.58882900	-0.99819100	-1.40079400
H	-4.60837800	-0.26474700	-2.21544200
H	-4.31124200	-1.96706900	-1.83199200
H	-5.60981000	-1.08615300	-1.00880100
C	-3.23121800	-1.78696600	1.29169700
H	-2.93382600	-2.75833600	0.87928300
H	-2.48212200	-1.47828000	2.02811300
H	-4.18663600	-1.92385000	1.81329600
H	2.20654100	-1.18903500	1.98506000
H	-0.00496000	-1.29539900	-2.46408000
H	-0.23150300	-2.64515900	-1.36748900
C	3.61469200	-2.68362500	0.11714600
H	4.28087300	-2.89574700	-0.72835900
C	3.94470100	-1.28215900	0.69144200
H	4.68917500	-1.36266100	1.49166500
H	4.39905100	-0.65609200	-0.08782100
H	3.81912000	-3.45626700	0.86822200

Scheme S4: *Diradical Pathways Beginning at Reactant **37***

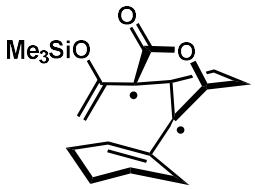


SI-13

SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.662099
singlet, single-point:	-1216.653242

C	-1.65933800	1.63347100	-1.21477500
C	-2.25765700	1.09740700	0.08174800
C	-2.07144500	1.98313000	1.07786700
C	-1.32934600	3.22576800	0.66811700
C	-1.12592000	3.04693400	-0.85861400
H	-2.42757200	1.68217900	-1.99217400
H	-2.42068300	1.82442000	2.09516500
H	-0.37993800	3.32113800	1.21166800
H	-1.90752000	4.13135400	0.89609800
H	-0.07884500	3.14670800	-1.15644000
H	-1.68711700	3.80231800	-1.41724100
C	0.67290100	0.67008100	0.11842000
O	-0.67975200	0.77760600	-1.87224500
C	0.47097800	0.38492700	-1.27602100
O	1.28948100	-0.23689000	-1.94563300
C	-3.03458200	-0.15948900	0.15563300
C	-5.11838100	-1.38750000	0.89137700
C	-3.20486500	-2.68766800	-0.09969300
C	-4.72384600	-2.48856900	-0.10293900
C	-2.47003700	-1.40340400	-0.51325400
C	-4.22491700	-0.17788500	0.78481600
H	-5.08000100	-1.78031500	1.92073700
H	-2.88487100	-2.97879300	0.91080700
H	-5.05023500	-2.20048900	-1.11187500
H	-2.50371200	-1.27914400	-1.60539000
H	-6.16295600	-1.08523700	0.73412900
H	-2.91736100	-3.50790900	-0.76825700
H	-5.24015800	-3.42448800	0.14239000
H	-1.40477600	-1.49786300	-0.26779000
H	-4.59387100	0.74390600	1.23258400
C	1.73402700	0.64103100	1.02507800
C	1.50277300	0.76098600	2.38082900
H	2.32881900	0.76494500	3.08326700
H	0.49065400	0.85566700	2.75619400
O	3.02028400	0.59126400	0.56868900
Si	3.98894000	-0.73465500	0.10754100
C	5.38191100	-0.80754900	1.37862800
H	6.10083200	-1.59821000	1.12891900
H	4.99933700	-1.01339300	2.38550800
H	5.93147300	0.14021000	1.41818800
C	4.67778800	-0.34935400	-1.59453600
H	5.37002800	-1.13295700	-1.92739300
H	5.22664900	0.59977600	-1.59051700
H	3.86439900	-0.27260900	-2.32206200
C	2.98116000	-2.32284900	0.14481000
H	3.62188600	-3.18376700	-0.08362200
H	2.18038100	-2.28680800	-0.59984100
H	2.53268000	-2.49810800	1.12993800

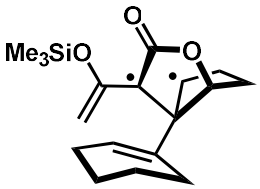


SI-14

SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.719313
singlet, single-point:	-1216.720462

C	-1.57964700	2.03372200	-0.23126300
C	-1.92727600	0.69773300	0.34401800
C	-0.75727300	0.44924300	1.27273700
C	-0.63282000	1.82102800	2.01584300
C	-1.14965400	2.87076600	0.98826600
H	-2.33669700	2.51482200	-0.84958700
H	-0.91837600	-0.37342700	1.96756300
H	0.39356100	2.01257900	2.34242300
H	-1.26704300	1.80622900	2.90895900
H	-0.39281000	3.60592400	0.69873100
H	-2.01070700	3.42051400	1.38379200
C	0.46327800	0.19504900	0.39846200
O	-0.43658600	1.87171800	-1.13513000
C	0.58342100	1.00610800	-0.83543900
O	1.52758700	0.98939600	-1.60557100
C	-3.01210600	-0.12937400	0.04113500
C	-4.32718900	-2.30533800	0.38142700
C	-4.96799300	-0.75207100	-1.48703900
C	-5.49572500	-1.62426000	-0.34445400
C	-4.06631900	0.36800200	-0.94859600
C	-3.17147000	-1.37918000	0.63106600
H	-3.97527200	-3.16511500	-0.21503900
H	-4.39827200	-1.37786100	-2.18822300
H	-6.05268200	-0.99471400	0.36364900
H	-4.69180400	1.12797000	-0.45687900
H	-4.66427800	-2.74031400	1.33379300
H	-5.79534100	-0.31317700	-2.05757200
H	-6.19811500	-2.37872400	-0.71815500
H	-3.57490200	0.87392600	-1.78721800
H	-2.39992100	-1.74307800	1.30515600
C	1.45458900	-0.75721500	0.76919500
C	1.46792600	-1.38546300	2.00215200
H	2.23210700	-2.12451900	2.21262600
H	0.75075800	-1.16795100	2.78191000
O	2.40464600	-1.12817300	-0.12868800
Si	3.99633000	-0.57940400	-0.34331800
C	4.19739500	1.18333400	0.29102400
H	5.25394400	1.47846800	0.26629900
H	3.85656900	1.27892800	1.32926800
H	3.62779000	1.88596100	-0.32389400
C	4.35047900	-0.74624100	-2.17678100
H	5.38354900	-0.46035700	-2.41054100
H	3.67113600	-0.10572600	-2.74643000
H	4.20607200	-1.78021100	-2.51144900
C	5.12094400	-1.73121700	0.64901600
H	6.17791000	-1.48281700	0.48838000
H	4.97782600	-2.77722500	0.35292800
H	4.92785000	-1.65972900	1.72644800

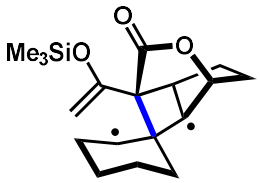


SI-15

SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.708221
singlet, single-point:	-1216.713258

C	-1.52916500	1.93302900	-0.73656400
C	-1.23996100	0.71269300	0.21674900
C	-1.21696400	1.37459000	1.58495400
C	-1.42071300	2.85389000	1.51267300
C	-2.09559700	3.05067800	0.13959600
H	-2.18469800	1.67526500	-1.57340600
H	-0.87865800	0.84641200	2.47058500
H	-0.45662600	3.39178900	1.54693300
H	-2.01897900	3.25101000	2.34350400
H	-1.92181900	4.03394200	-0.30686400
H	-3.17815100	2.90454800	0.23083900
C	0.16317100	0.31201500	-0.22985200
O	-0.26125500	2.32781000	-1.29081100
C	0.70928200	1.37956800	-1.08087200
O	1.82495500	1.53080900	-1.53441600
C	-2.31786100	-0.37440700	0.05638000
C	-4.40574500	-1.54536800	0.86776400
C	-3.21073900	-2.41909500	-1.16747100
C	-4.57603900	-2.08093100	-0.56068000
C	-2.31364700	-1.17432300	-1.23575500
C	-3.26593000	-0.56312700	0.98758400
H	-4.23521600	-2.38161600	1.56486000
H	-2.71911100	-3.18372800	-0.54981100
H	-5.06691000	-1.31747900	-1.18041400
H	-2.64384800	-0.53000600	-2.06598100
H	-5.33432500	-1.06805200	1.21065000
H	-3.32427300	-2.84852000	-2.17008500
H	-5.23326300	-2.95885100	-0.56119400
H	-1.28925000	-1.47125900	-1.48703800
H	-3.22956100	0.02604700	1.90285100
C	0.89646700	-0.81364900	0.19982800
C	0.40467500	-1.71946300	1.12680800
H	1.00083200	-2.58131900	1.40426300
H	-0.58364900	-1.61180400	1.55412500
O	2.10918100	-1.06088900	-0.36135300
Si	3.67787800	-0.66036600	0.15238100
C	3.65951200	0.90767000	1.19445600
H	4.65951400	1.10584500	1.60030500
H	2.97248700	0.82366200	2.04529400
H	3.35589800	1.76823600	0.59116500
C	4.67566200	-0.47504700	-1.42395500
H	5.72777600	-0.25082000	-1.20934400
H	4.26111300	0.33724800	-2.02858400
H	4.64390100	-1.39436600	-2.02020500
C	4.32069200	-2.10496400	1.18714600
H	5.36346700	-1.93952300	1.48673700
H	4.28296600	-3.04448100	0.62325000
H	3.73444600	-2.24144400	2.10415600



SI-16

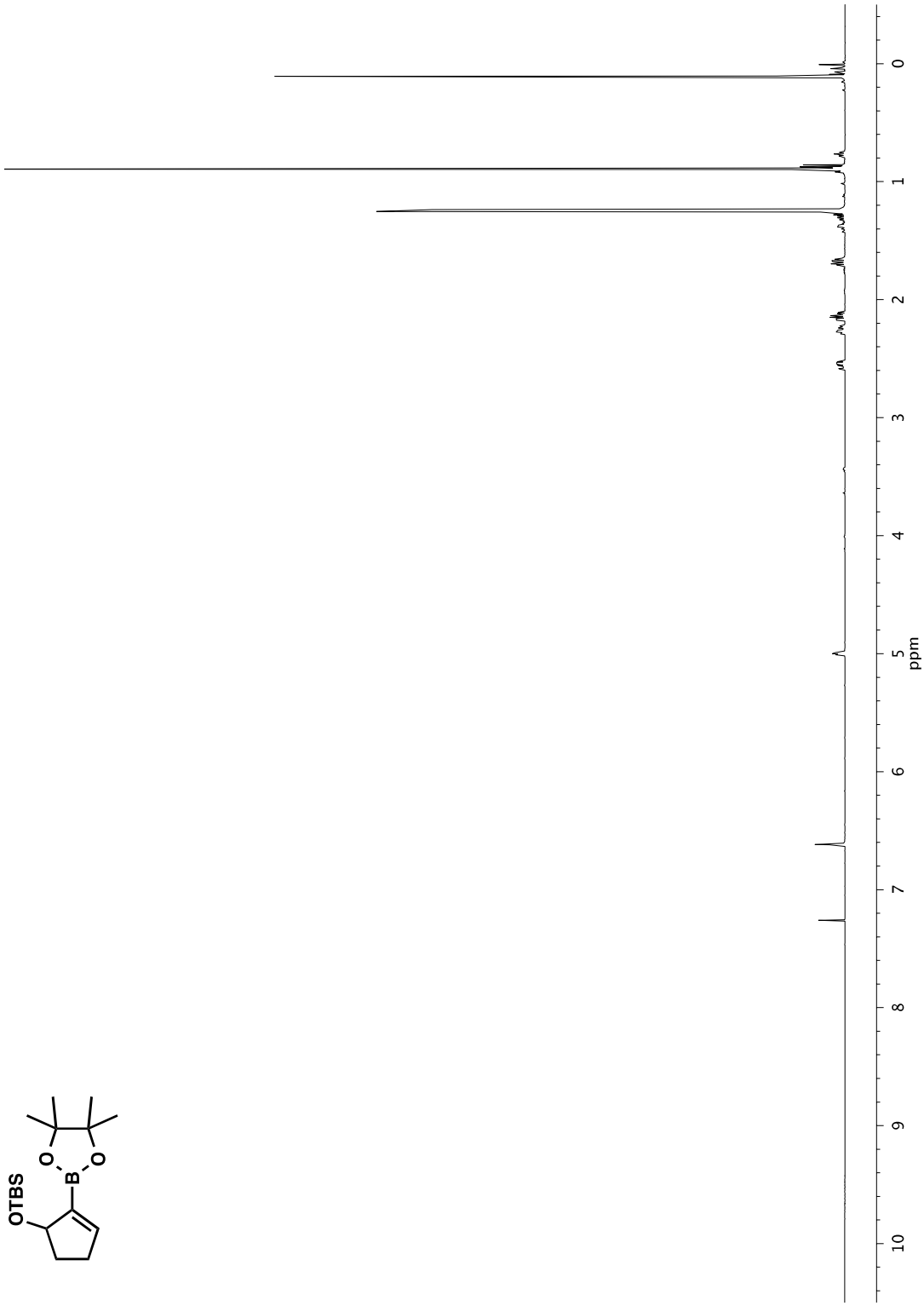
SCF Energy (B3LYP, gas-phase)

triplet, optimized:	-1216.652828
singlet, optimized:	-1216.653013

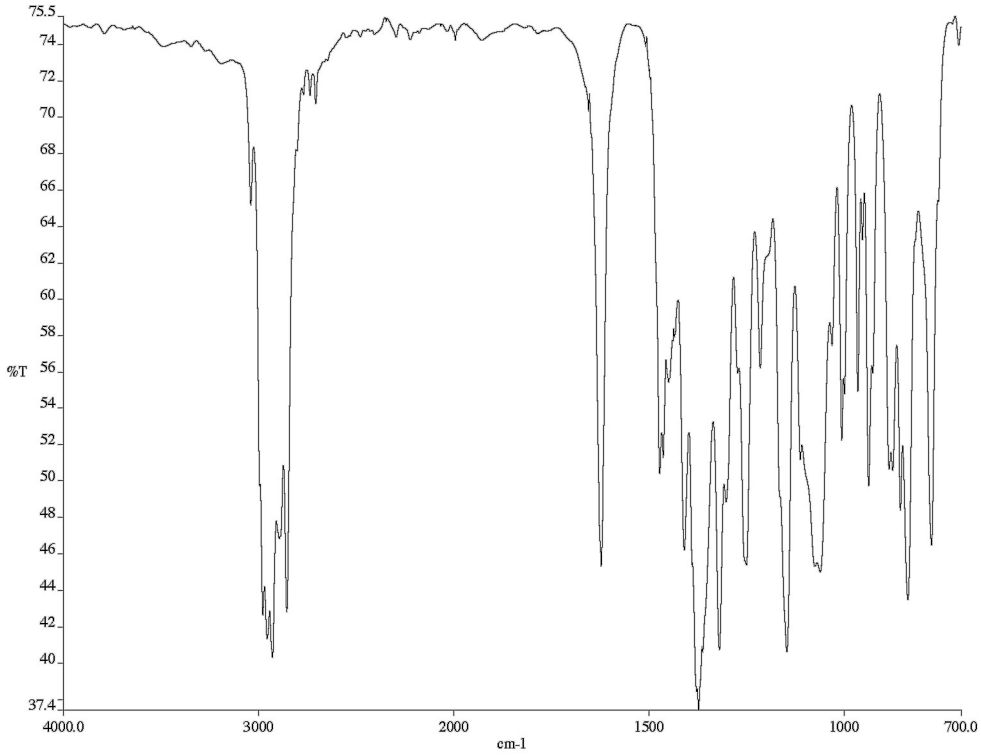
(triplet structure given)

C	3.25186200	-0.45255600	-0.81608500
C	2.71302200	0.37327900	0.32585100
C	2.12400300	-0.70079400	1.22152300
C	2.91866500	-2.00573100	1.00193300
C	3.92787500	-1.63892700	-0.12237700
H	3.85741400	0.07129600	-1.55758200
H	1.96202300	-0.43511000	2.26727000
H	2.26495700	-2.83182200	0.70079200
H	3.42840600	-2.32103500	1.91724500
H	4.12794600	-2.45620600	-0.82080700
H	4.88270100	-1.31014900	0.30562200
C	0.81257900	-0.41075000	0.38749000
O	2.11870400	-1.01561600	-1.58585000
C	0.91021800	-1.10816400	-0.96806000
O	0.00473600	-1.68885800	-1.52268400
C	1.42150500	1.14866000	0.14254300
C	-0.02479500	3.01733300	1.25814600
C	-0.09657500	2.70940600	-1.24547600
C	-0.13776900	3.72881300	-0.10281200
C	1.18745900	1.86946400	-1.19953900
C	1.10072200	2.03156000	1.29877800
H	-0.97734800	2.49226200	1.45331800
H	-0.96539600	2.04478400	-1.17778100
H	0.69611900	4.43641900	-0.21386500
H	2.05151300	2.53555300	-1.34495000
H	0.08967100	3.74747000	2.06947500
H	-0.15565900	3.22001400	-2.21510300
H	-1.06255100	4.31773800	-0.14128600
H	1.20326300	1.16329000	-2.03391900
H	1.58123300	1.83012500	2.25177400
C	-0.53139800	-0.56775600	1.04691300
C	-0.70614200	-1.15265200	2.23921200
H	-1.68699000	-1.21167600	2.69891600
H	0.12112400	-1.59608900	2.77870400
O	-1.54343200	0.00068200	0.33246400
Si	-3.03267400	-0.67292500	-0.15225500
C	-2.99765700	-2.55061200	-0.05687600
H	-3.92136900	-2.96027700	-0.48511400
H	-2.91189000	-2.92303300	0.96909600
H	-2.15101300	-2.93762300	-0.63211900
C	-3.28256300	-0.08550900	-1.92001600
H	-4.24524700	-0.42771200	-2.31971800
H	-2.48682200	-0.47734800	-2.56253800
H	-3.26481400	1.00857300	-1.98688000
C	-4.36819600	0.04286200	0.97428800
H	-5.36618200	-0.28717300	0.65891100
H	-4.35893500	1.13907400	0.95101200
H	-4.23167200	-0.26762700	2.01704500

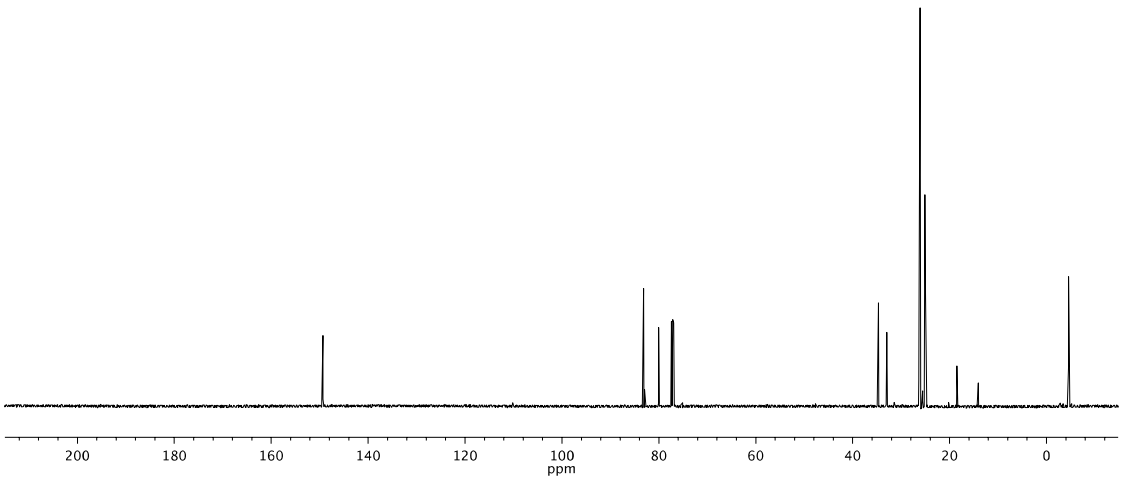
Spectra



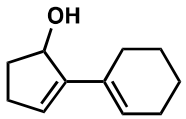
^{1}H NMR (500 MHz, $CDCl_3$) of compound *rac*-**15**

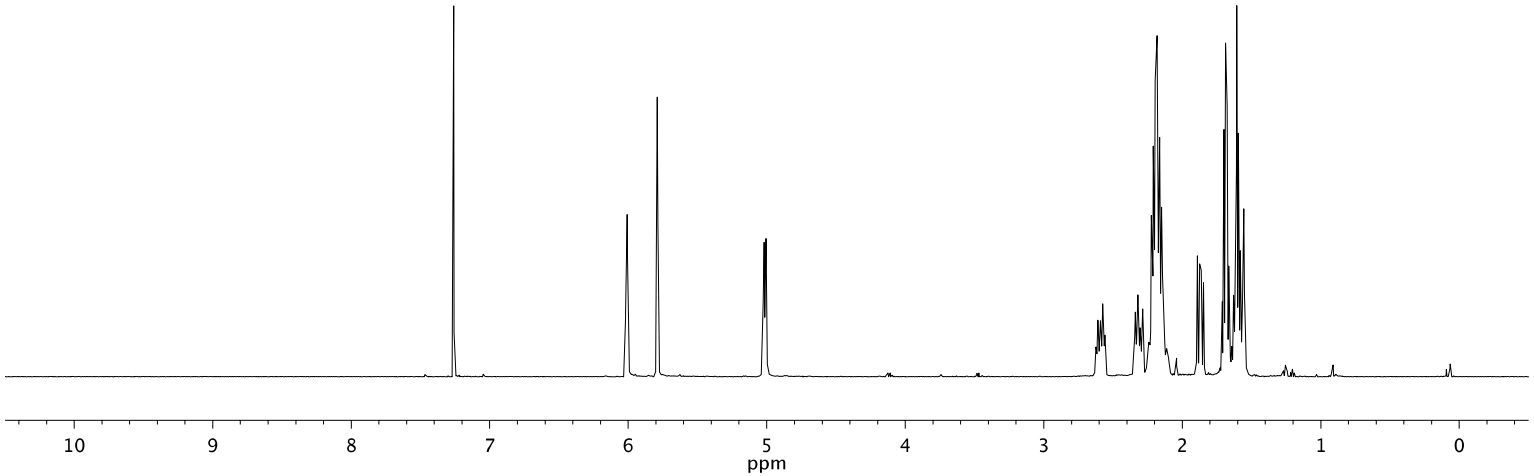


Infrared spectrum (thin film/NaCl) of compound *rac*-**15**

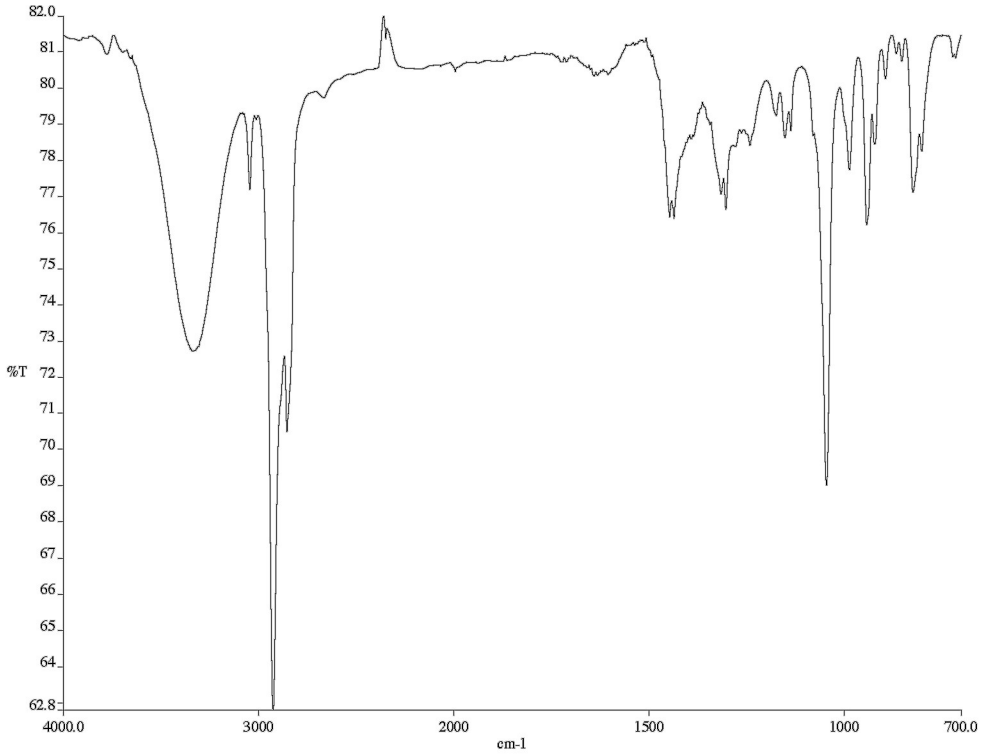


^{13}C NMR (126 MHz, $CDCl_3$) of compound *rac*-**15**

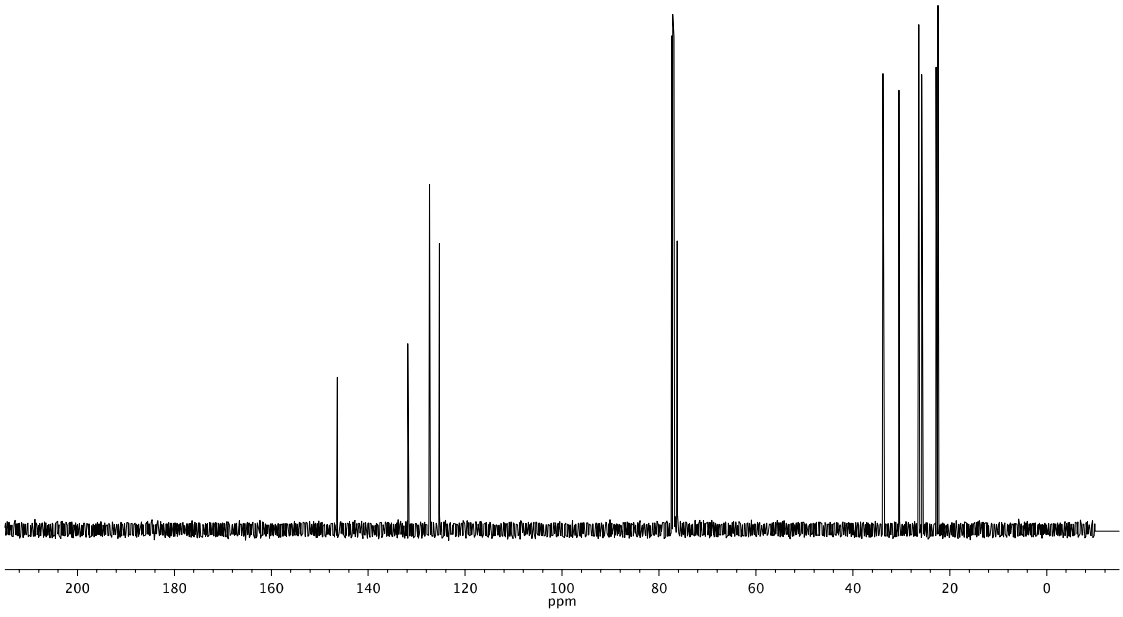




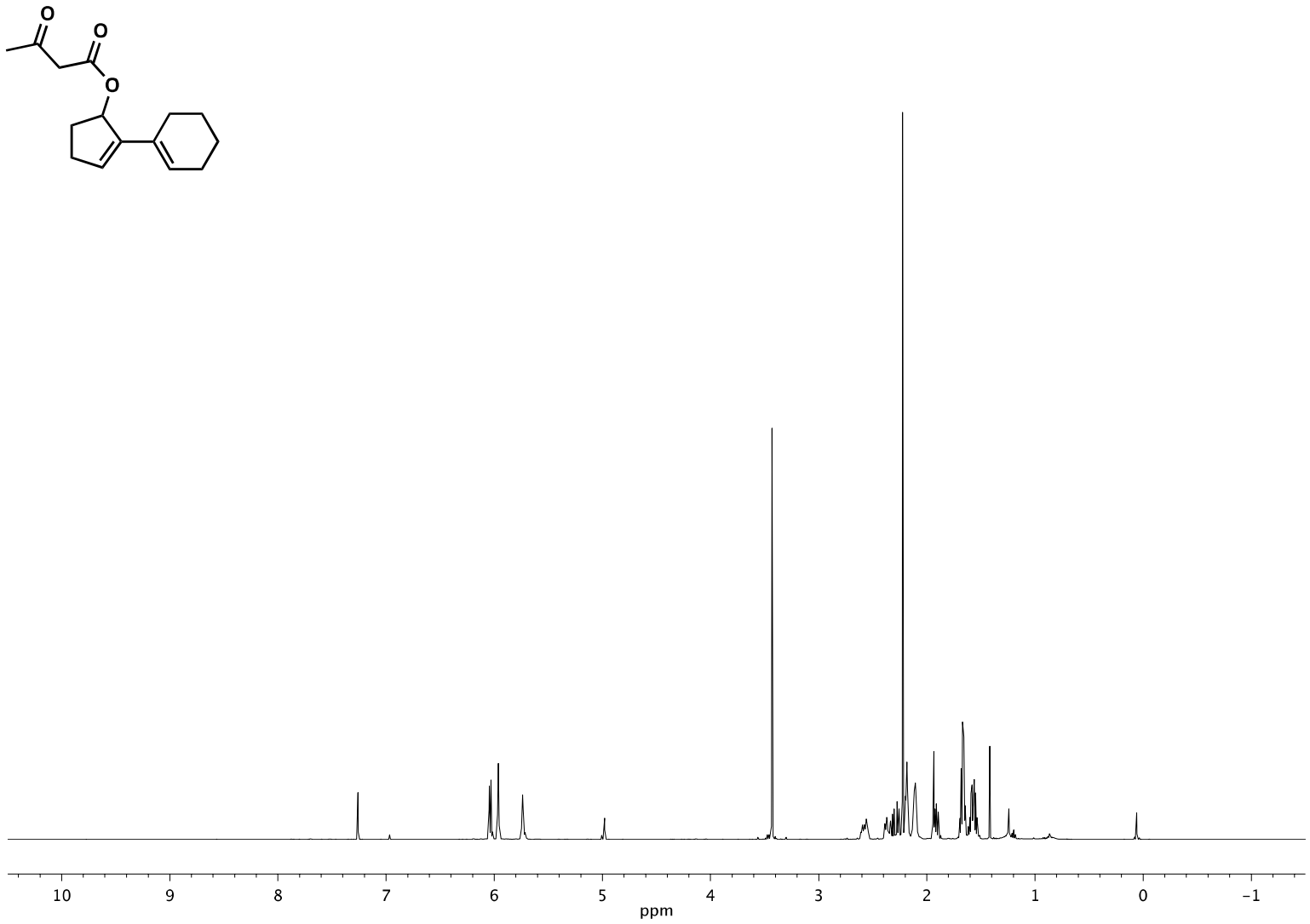
^{1}H NMR (500 MHz, $CDCl_3$) of compound **21**



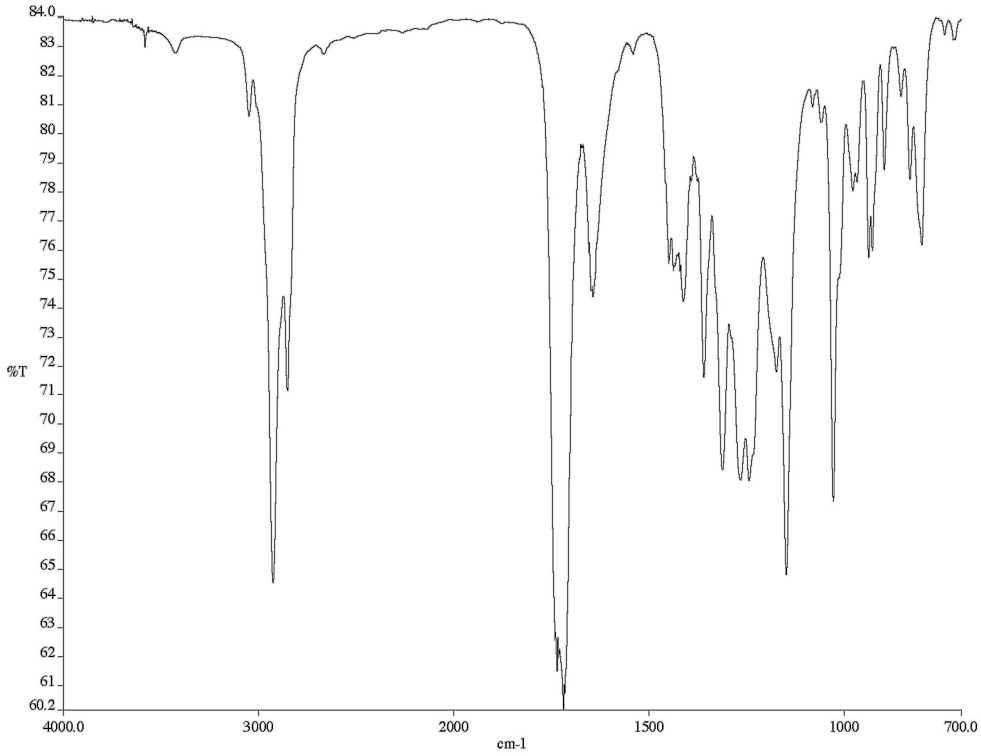
Infrared spectrum (thin film/NaCl) of compound **21**



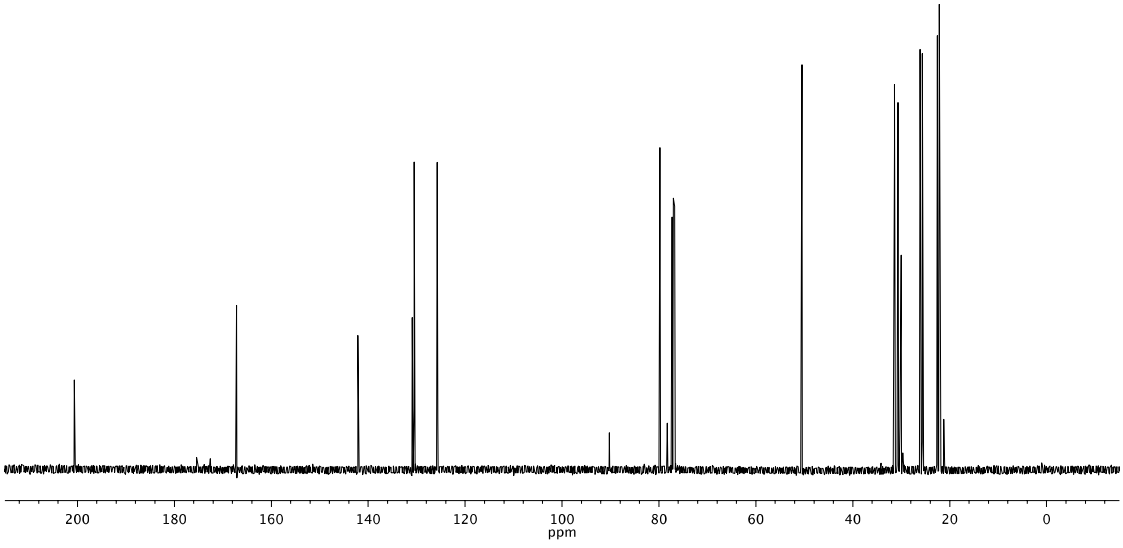
^{13}C NMR (126 MHz, $CDCl_3$) of compound **21**



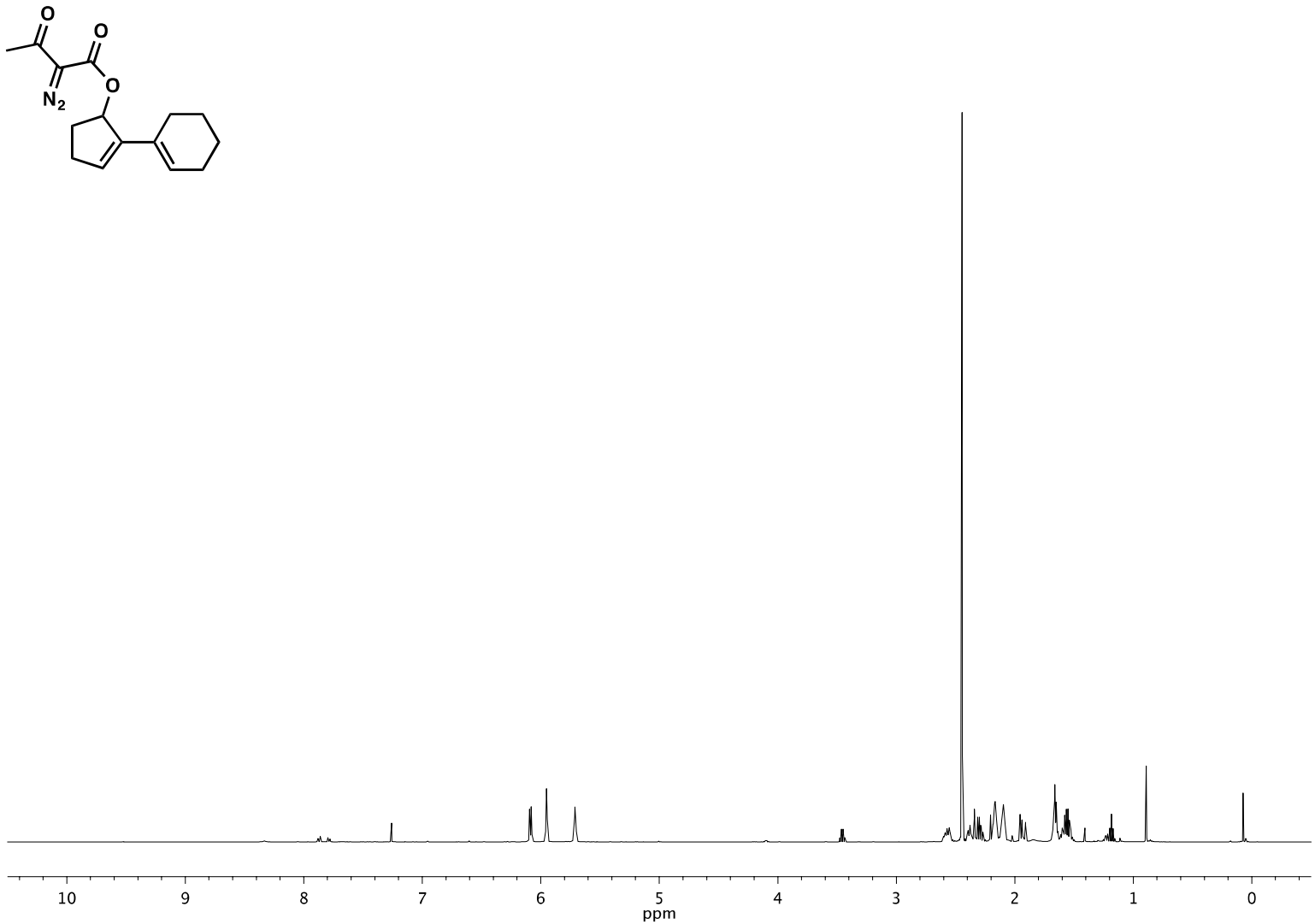
^{1}H NMR (500 MHz, $CDCl_3$) of compound **23**



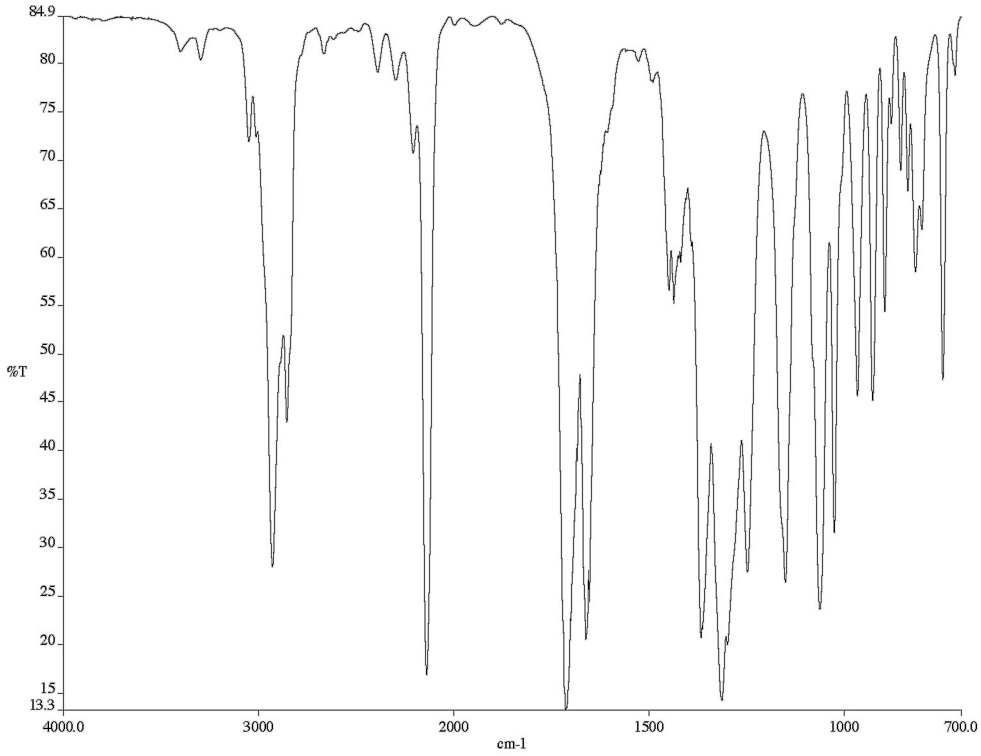
Infrared spectrum (thin film/NaCl) of compound **23**



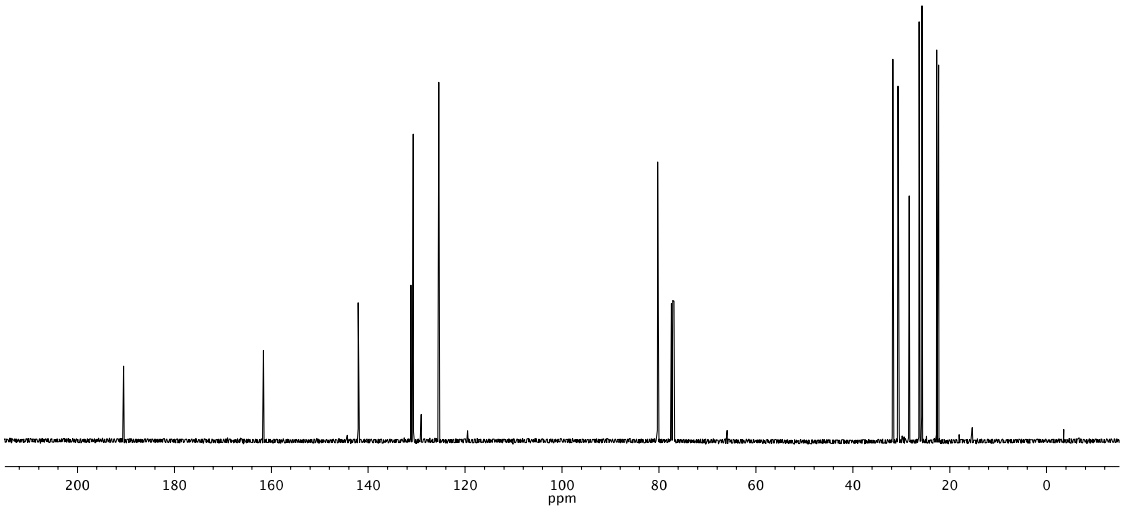
^{13}C NMR (126 MHz, $CDCl_3$) of compound **23**



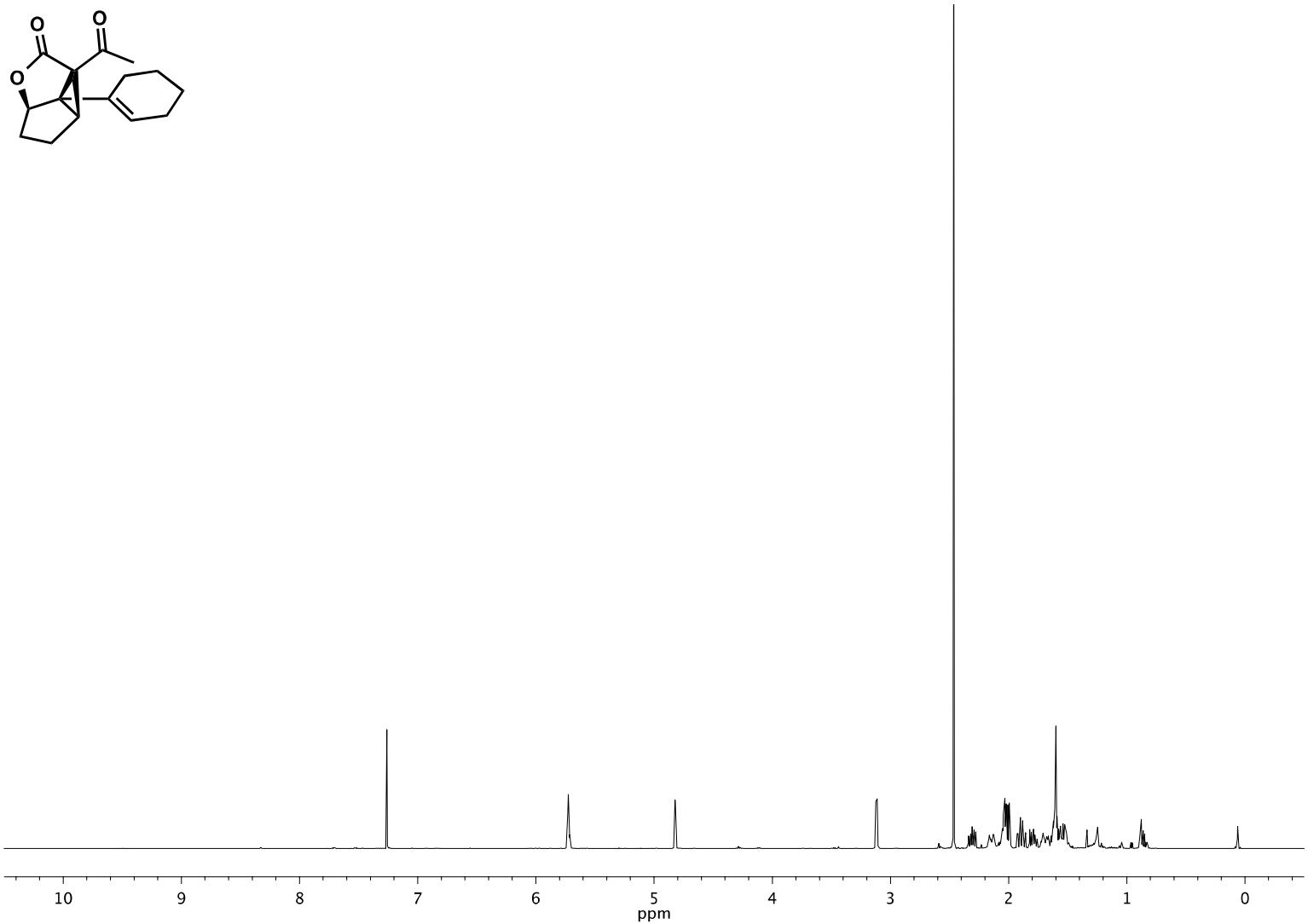
^{1}H NMR (500 MHz, $CDCl_3$) of compound **24**



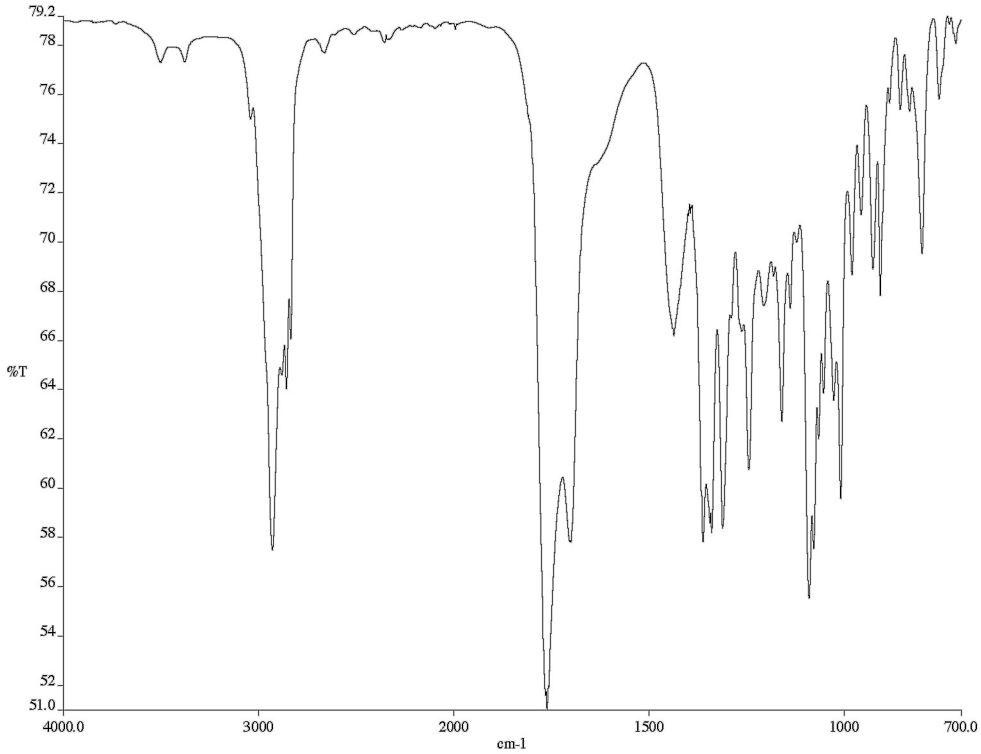
Infrared spectrum (thin film/NaCl) of compound **24**



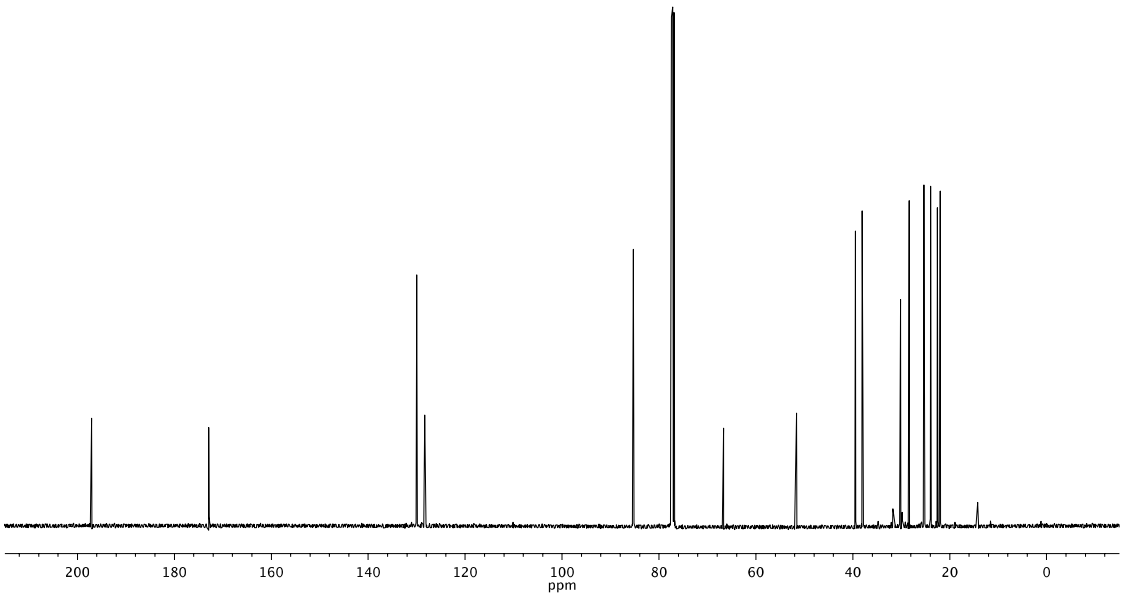
^{13}C NMR (126 MHz, $CDCl_3$) of compound **24**



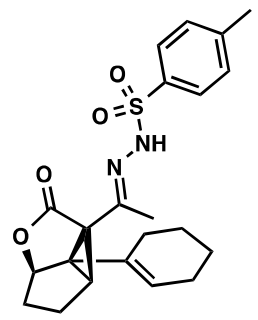
^{1}H NMR (500 MHz, $CDCl_3$) of compound **25**

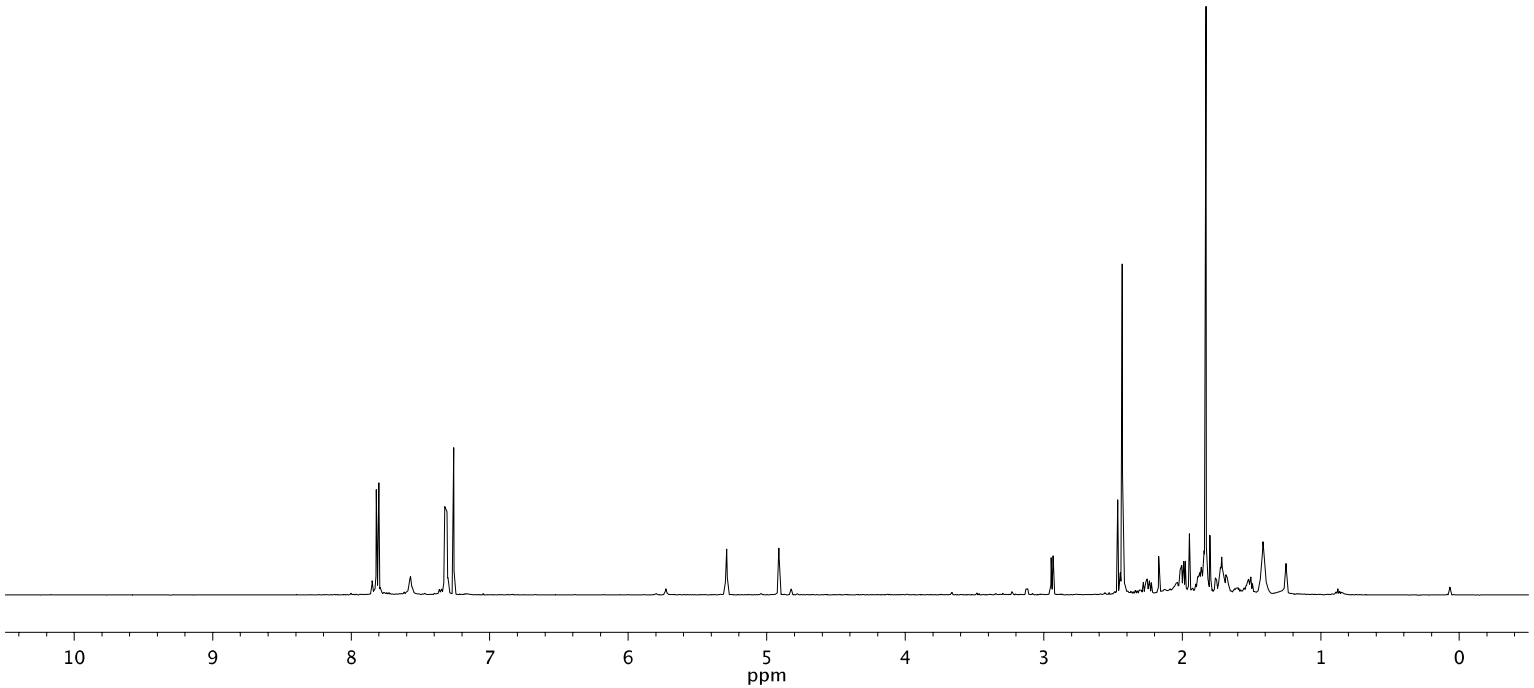


Infrared spectrum (thin film/NaCl) of compound **25**

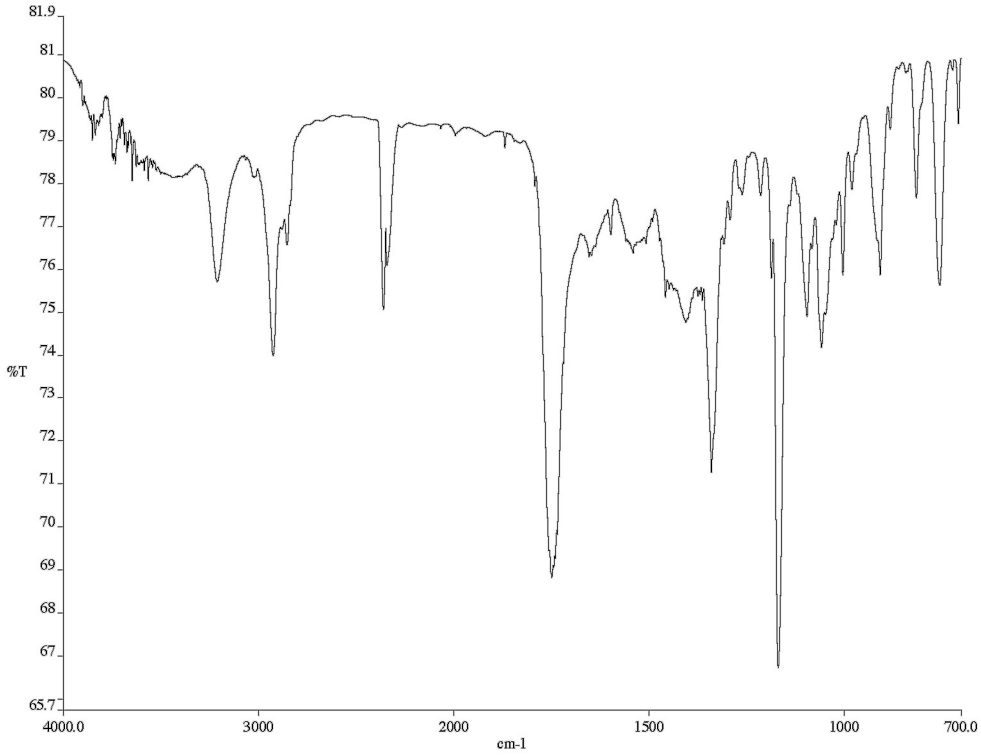


^{13}C NMR (126 MHz, $CDCl_3$) of compound **25**

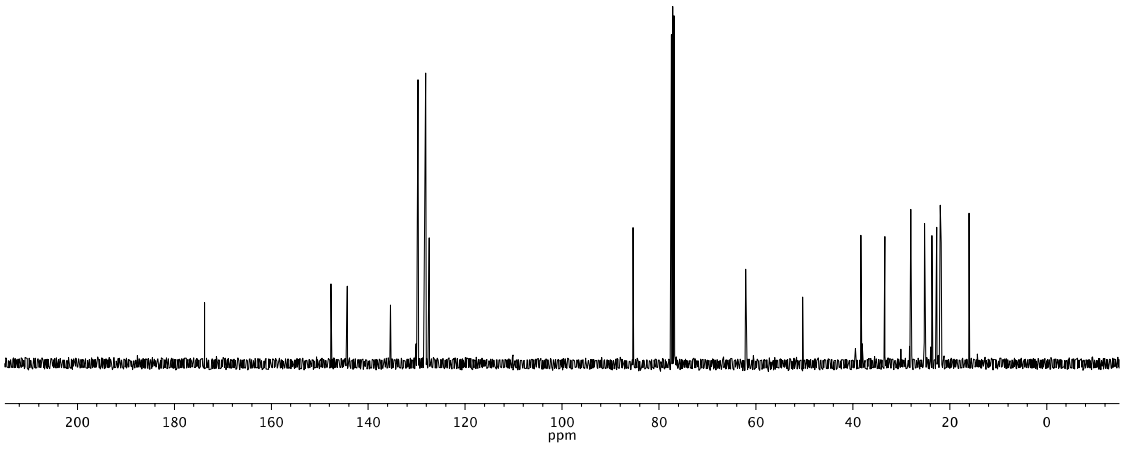




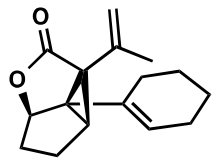
^{1}H NMR (500 MHz, $CDCl_3$) of compound **25a**

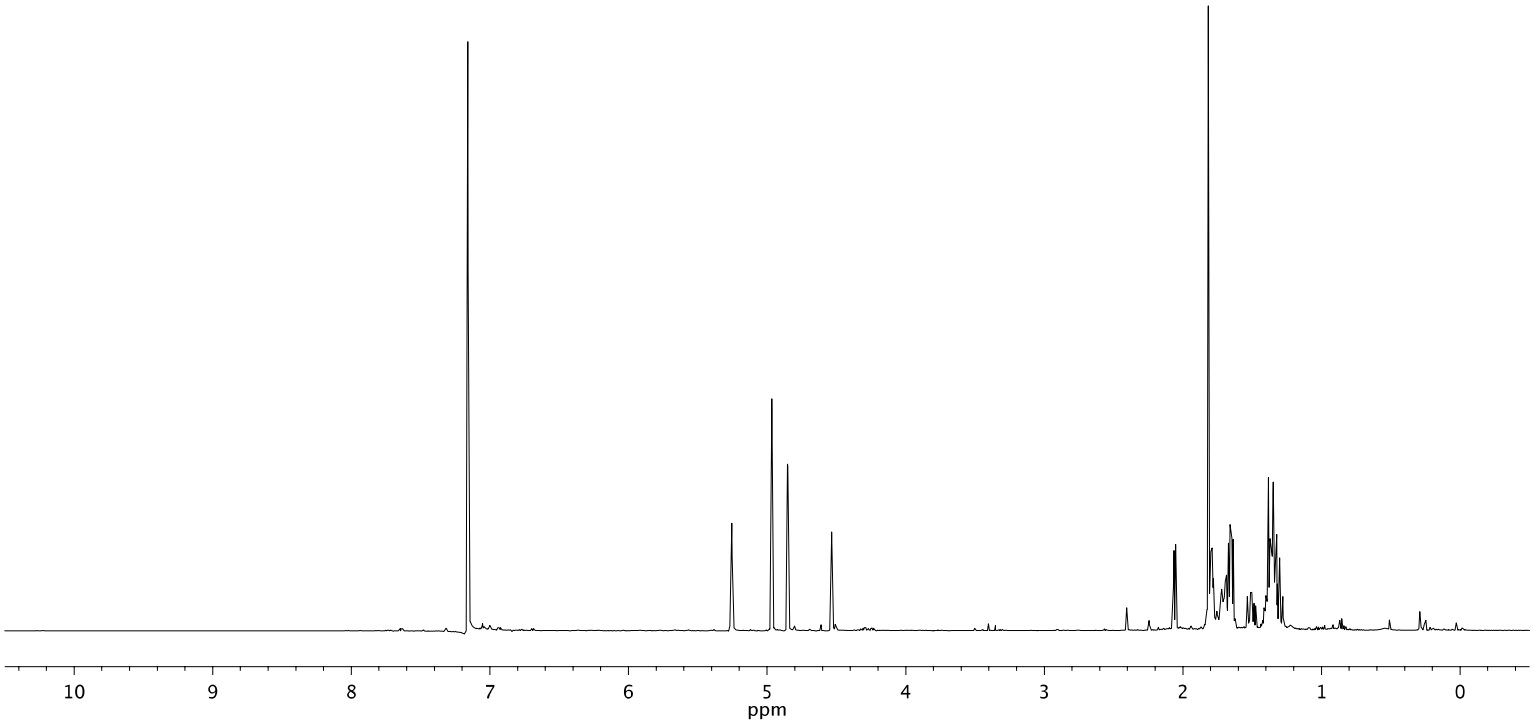


Infrared spectrum (thin film/NaCl) of compound **25a**

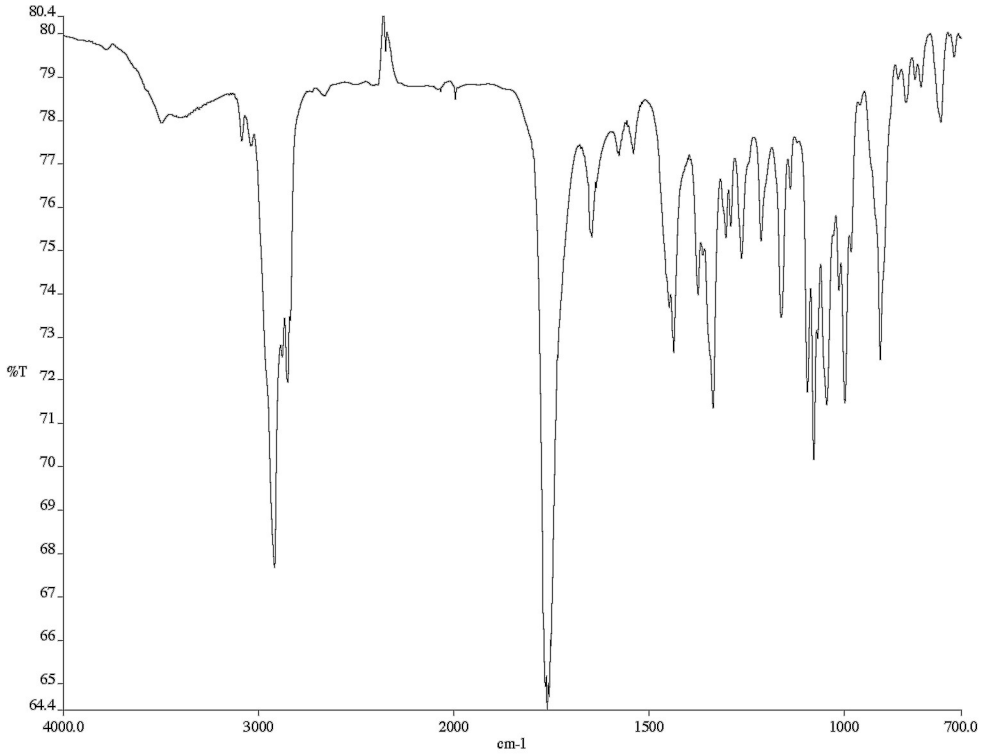


^{13}C NMR (126 MHz, $CDCl_3$) of compound **25a**

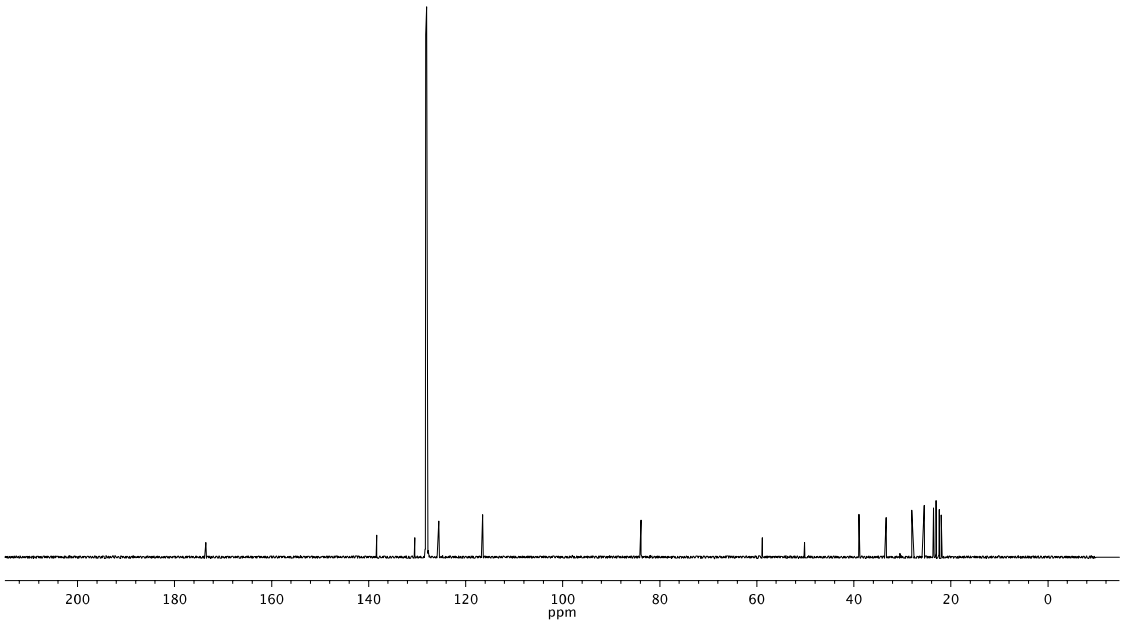




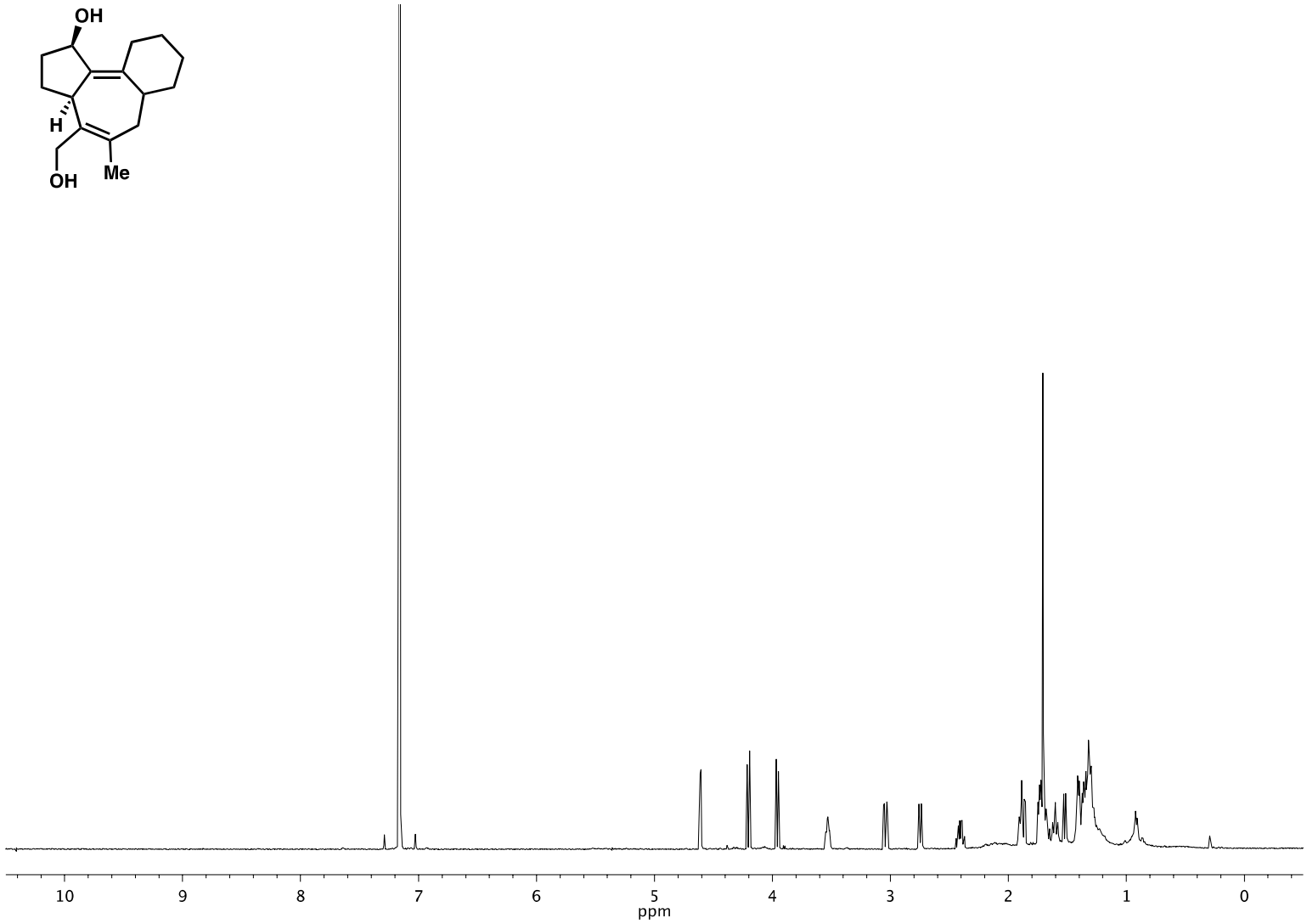
^{1}H NMR (500 MHz, C_6D_6) of compound **34**



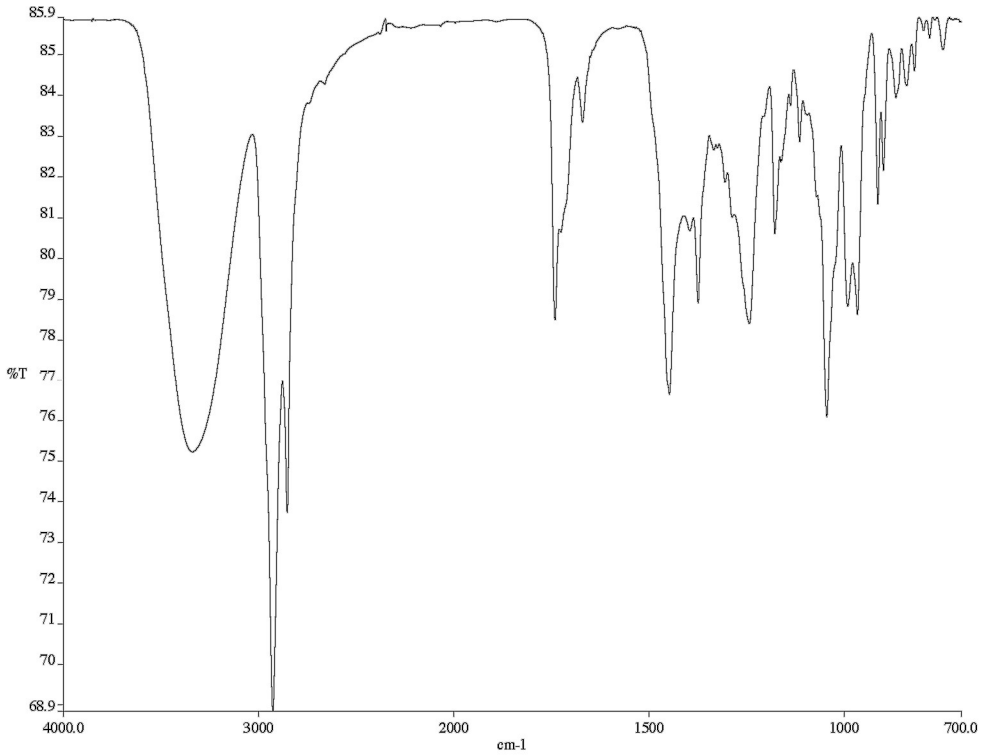
Infrared spectrum (thin film/NaCl) of compound **34**



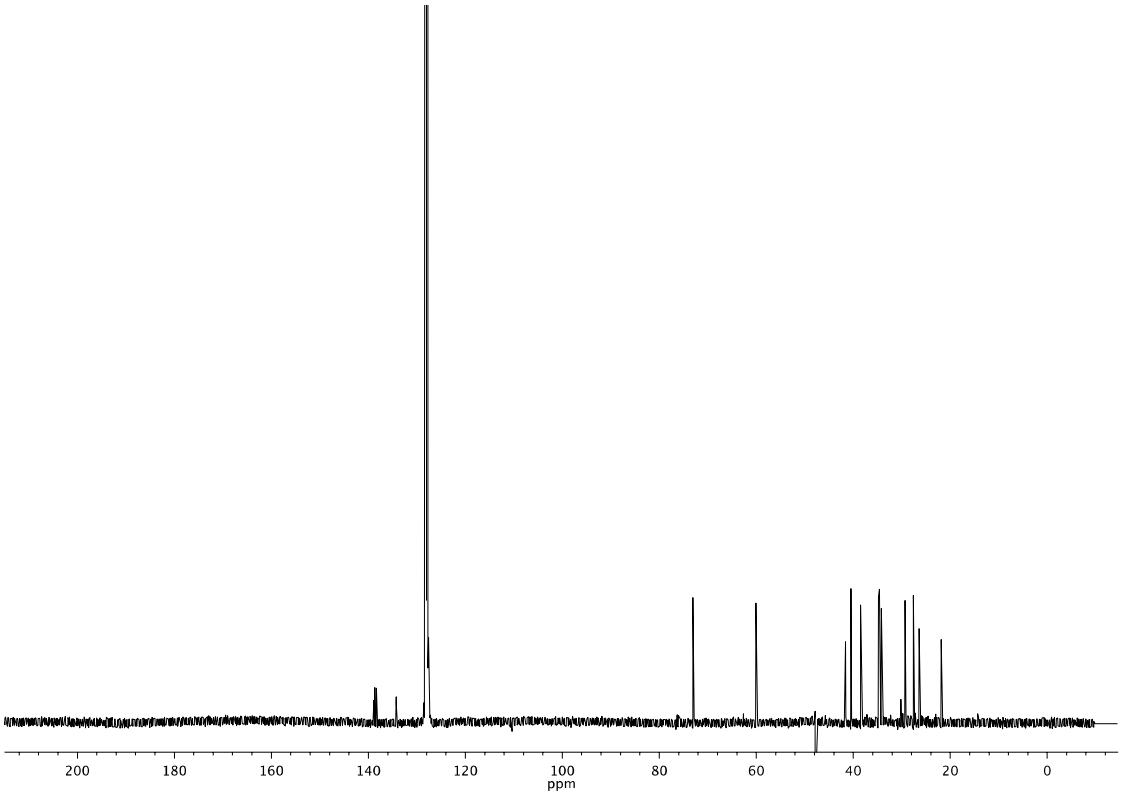
^{13}C NMR (126 MHz, C_6D_6) of compound **34**



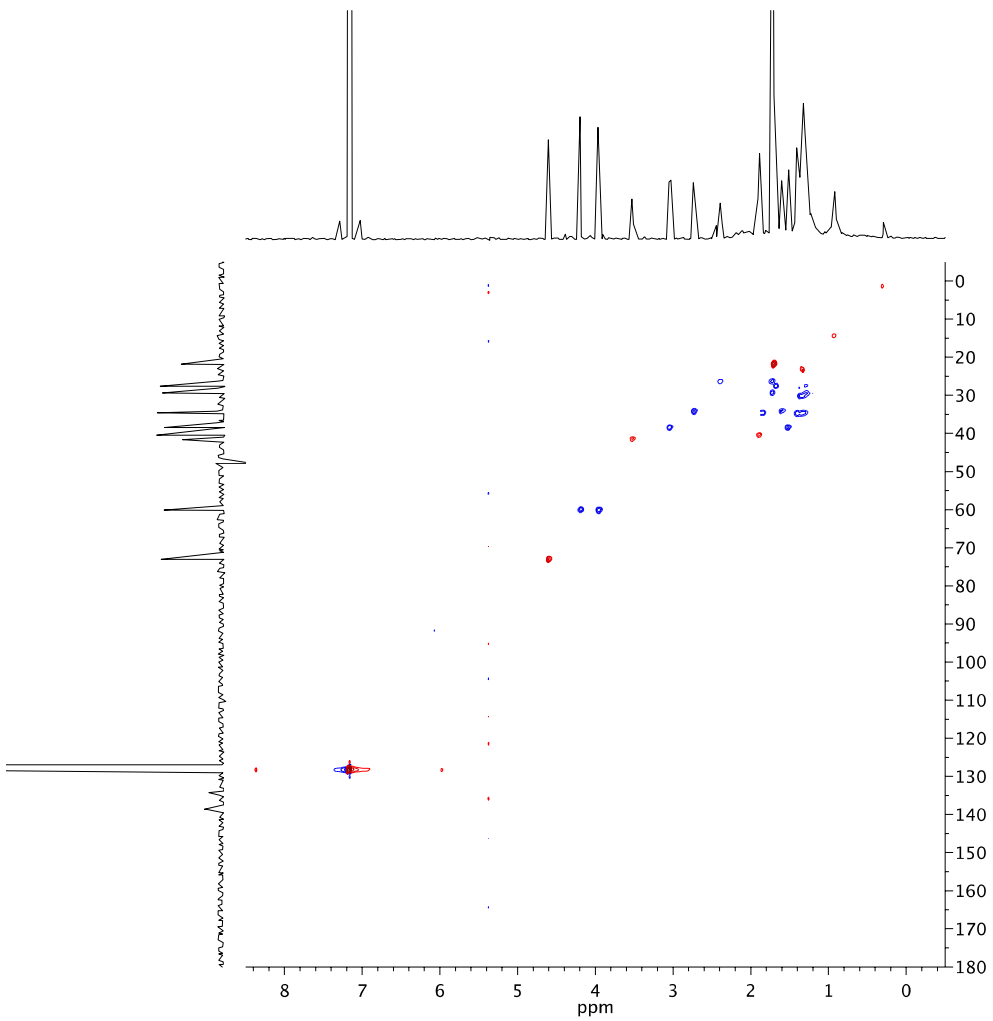
^{1}H NMR (500 MHz, C_6D_6) of compound **36**



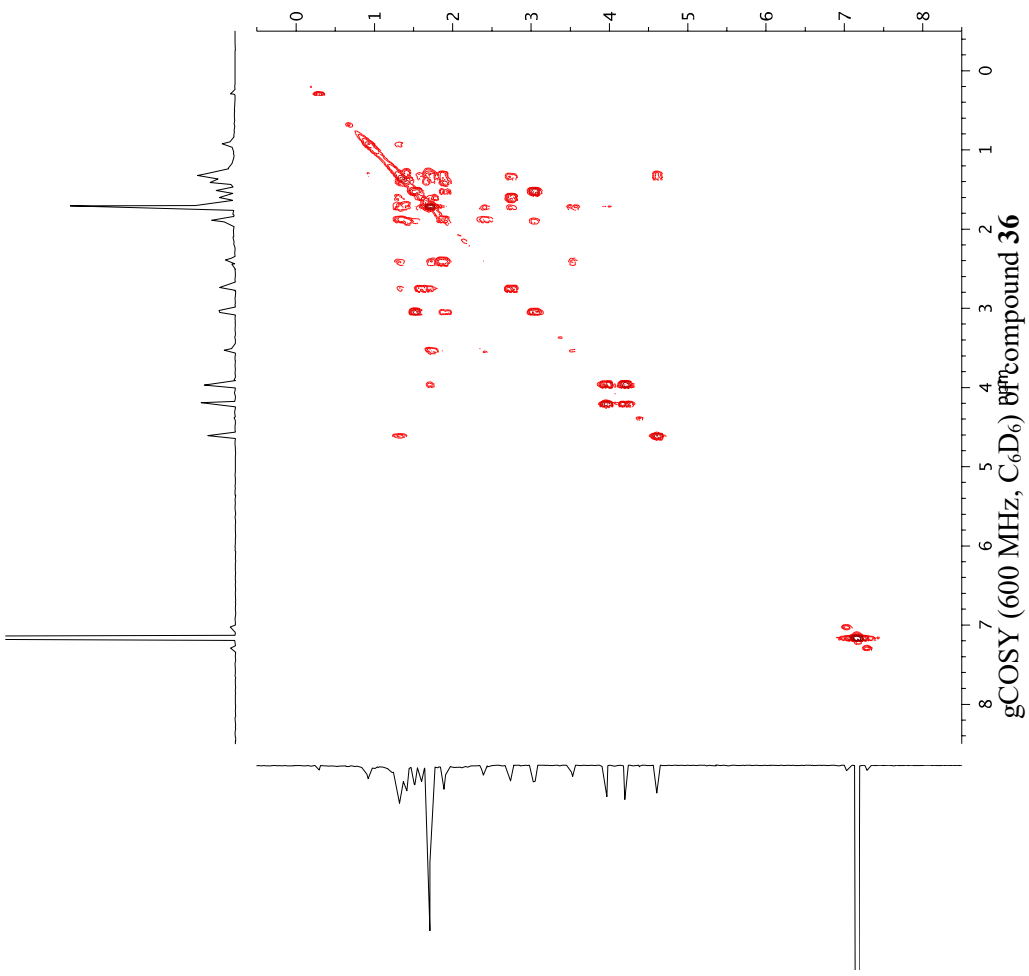
Infrared spectrum (thin film/NaCl) of compound **36**



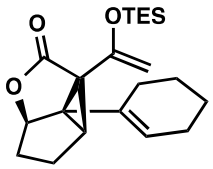
^{13}C NMR (126 MHz, C_6D_6) of compound **36**

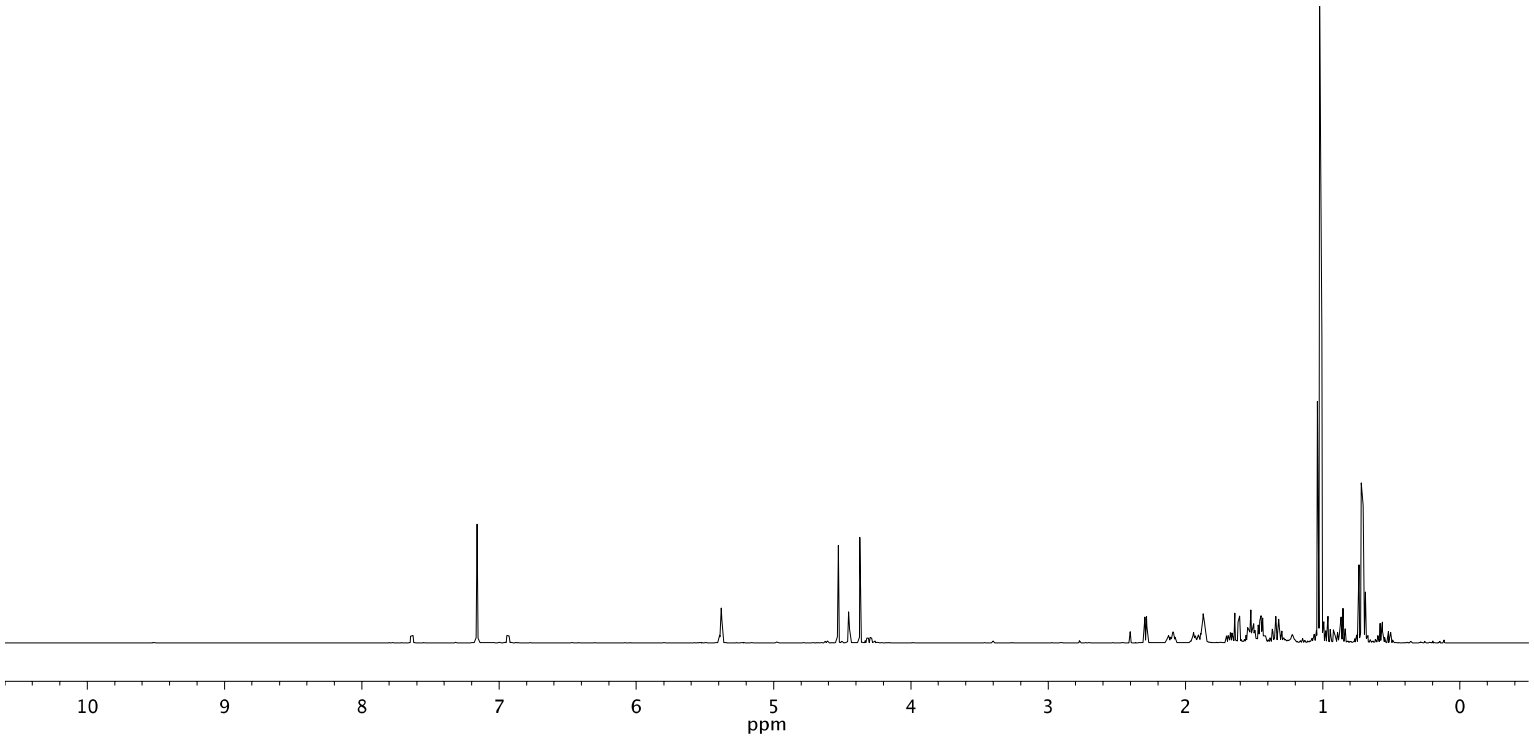


^{1}H-^{13}C HSQC (600 MHz, C_6D_6) of compound **36**

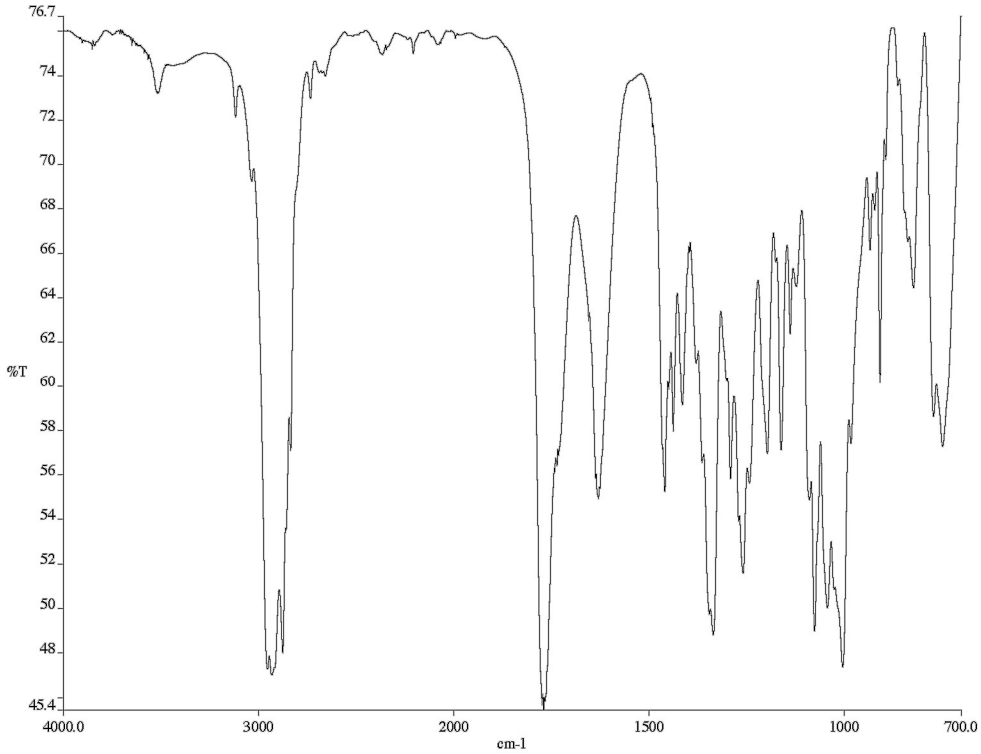


gCOSY (600 MHz, C_6D_6) of compound **36**





^{1}H NMR (500 MHz, C_6D_6) of compound **26**



Infrared spectrum (thin film/NaCl) of compound **26**

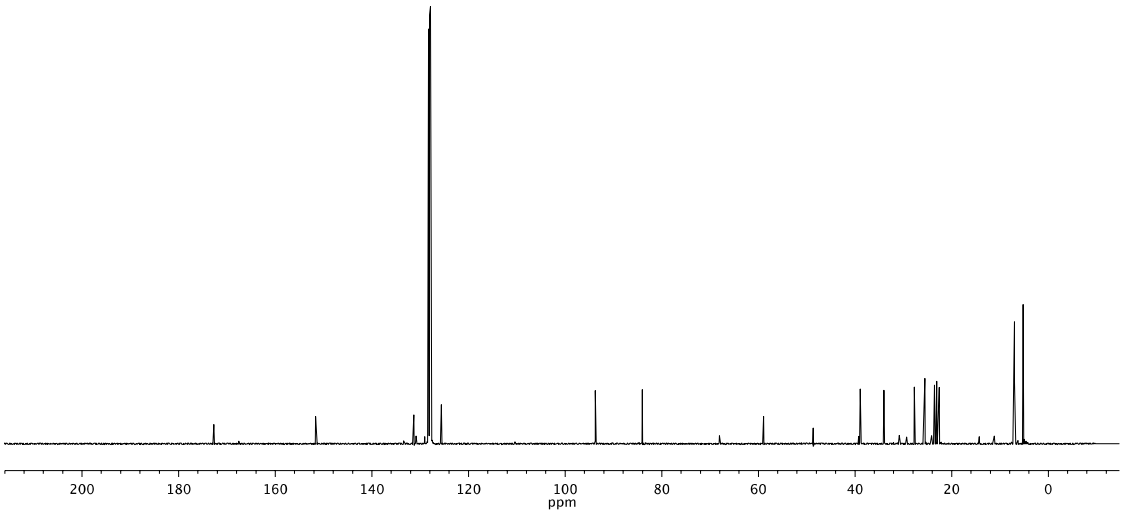
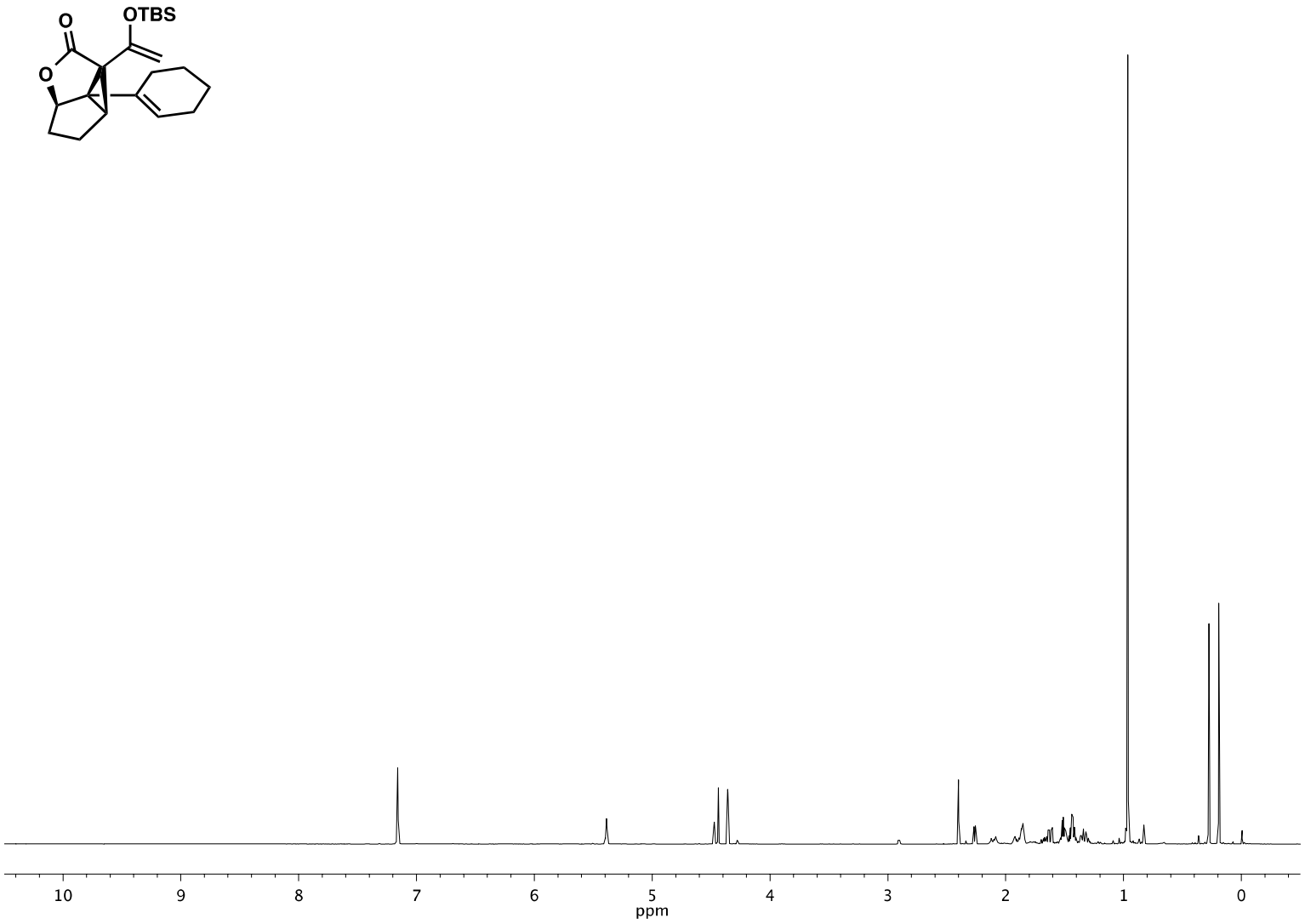
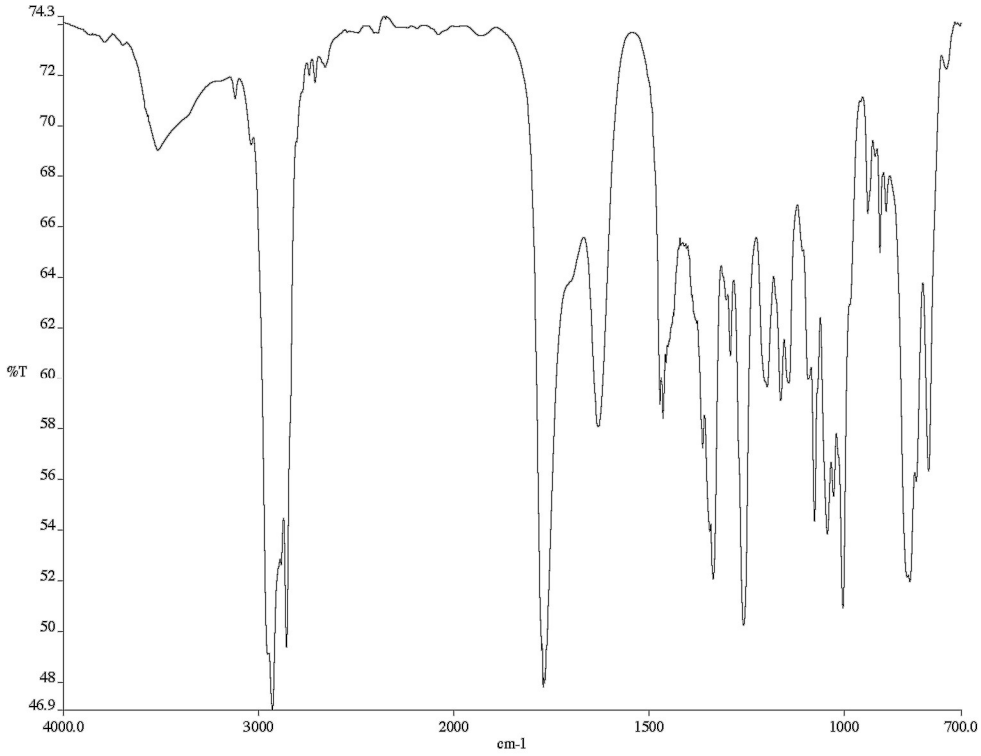


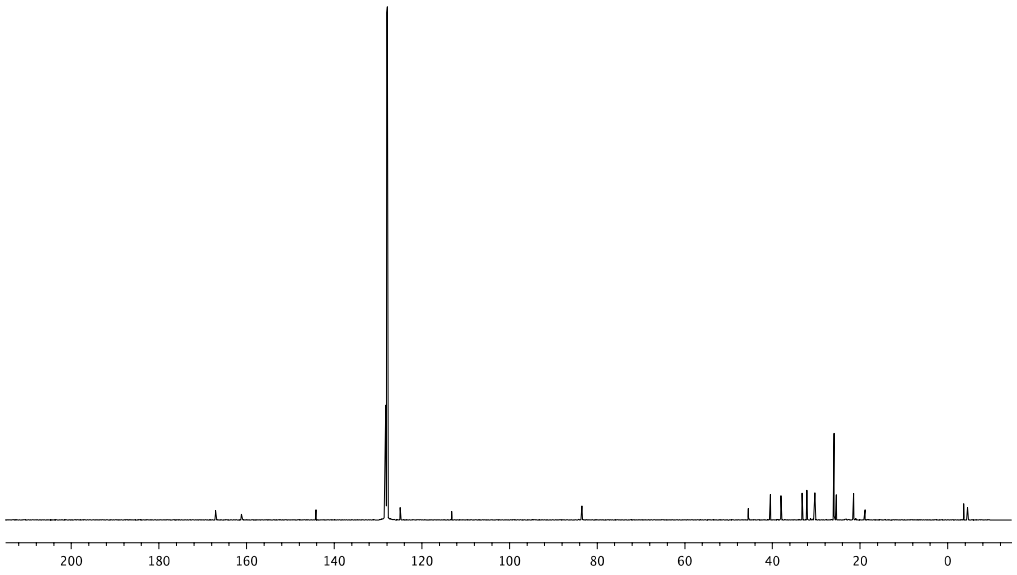
Figure A3.27 ^{13}C NMR (126 MHz, C_6D_6) of compound **26**



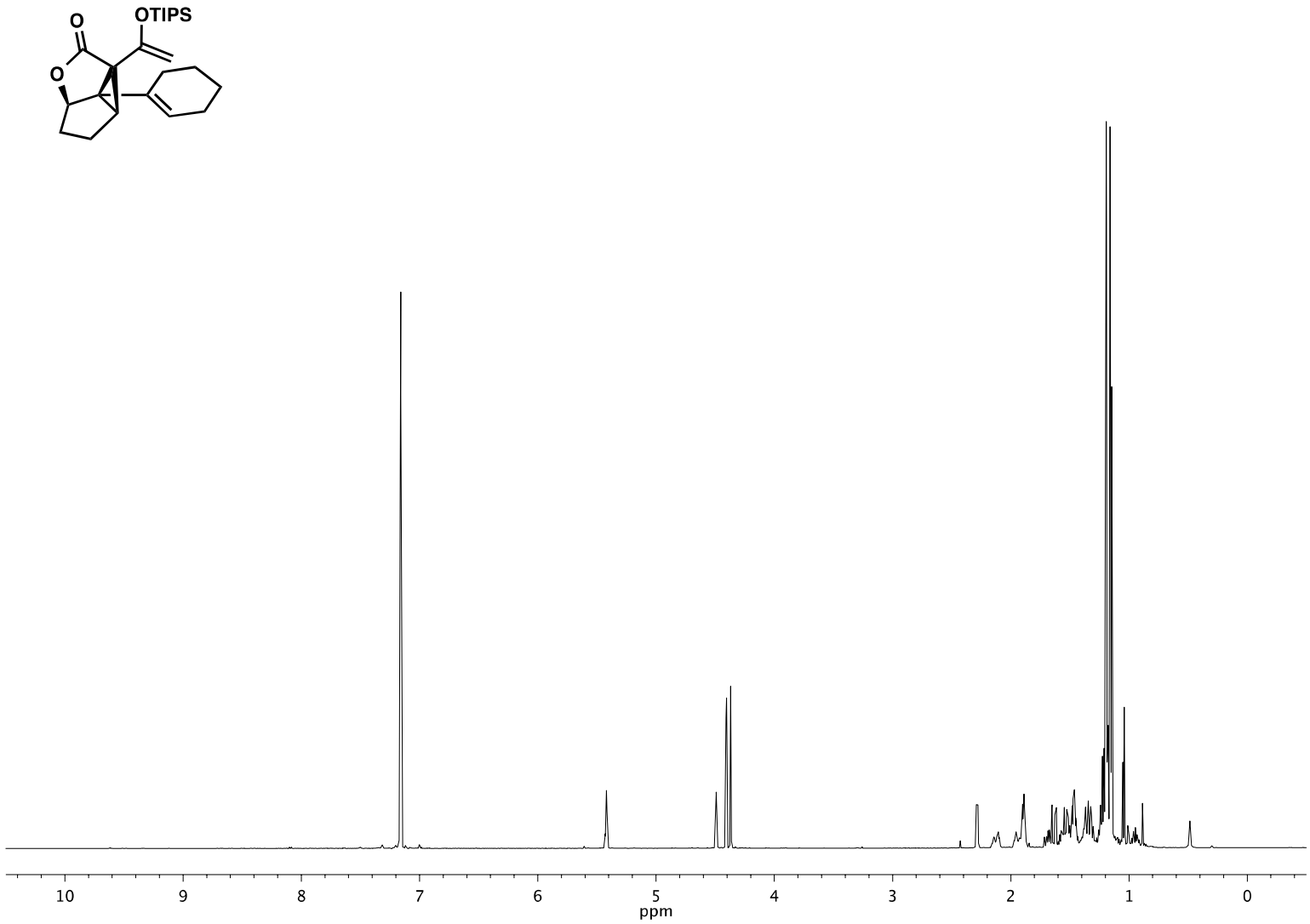
^{1}H NMR (500 MHz, C_6D_6) of compound **27**



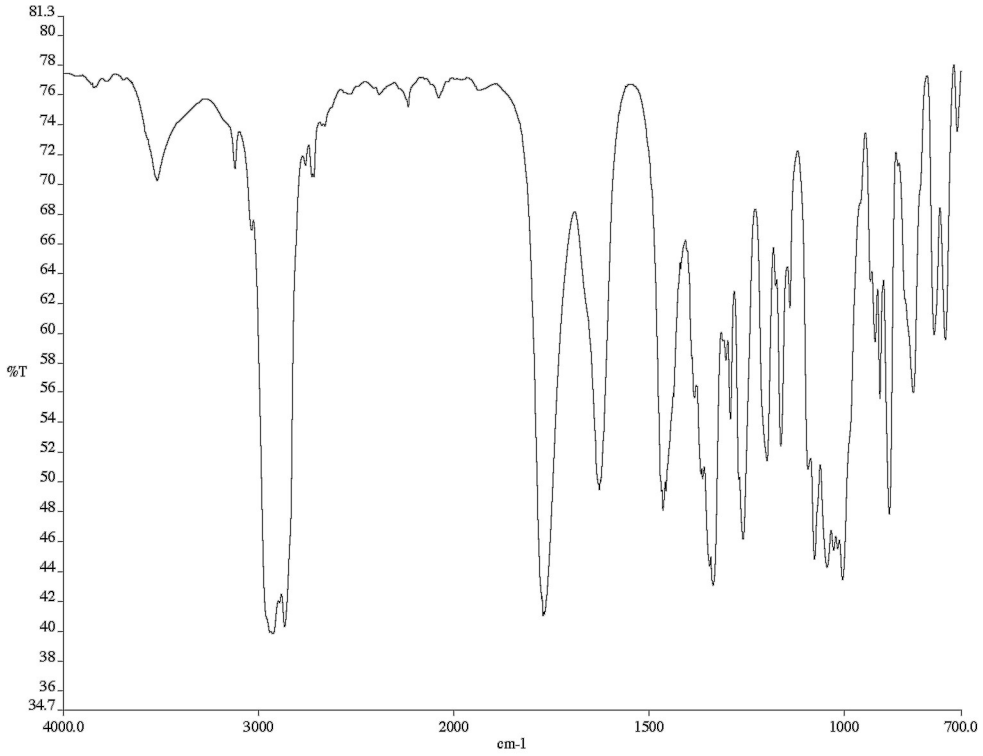
Infrared spectrum (thin film/NaCl) of compound **27**



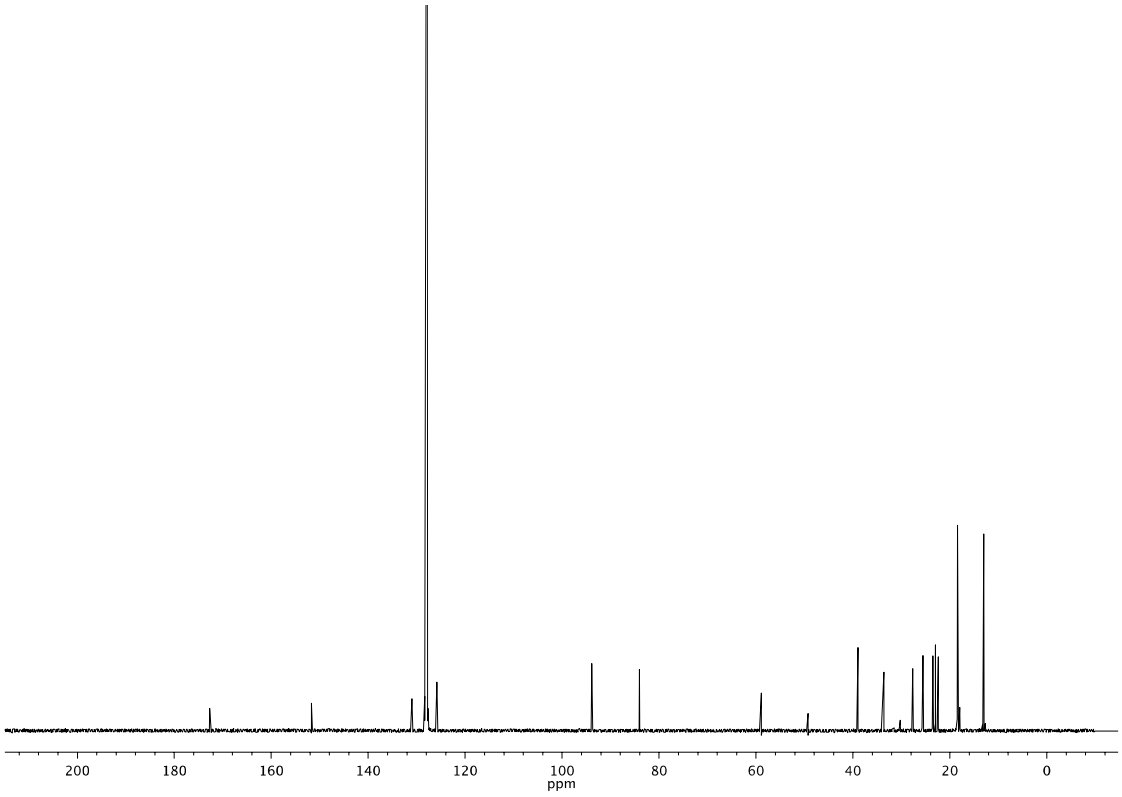
^{13}C NMR (126 MHz, C_6D_6) of compound **27**



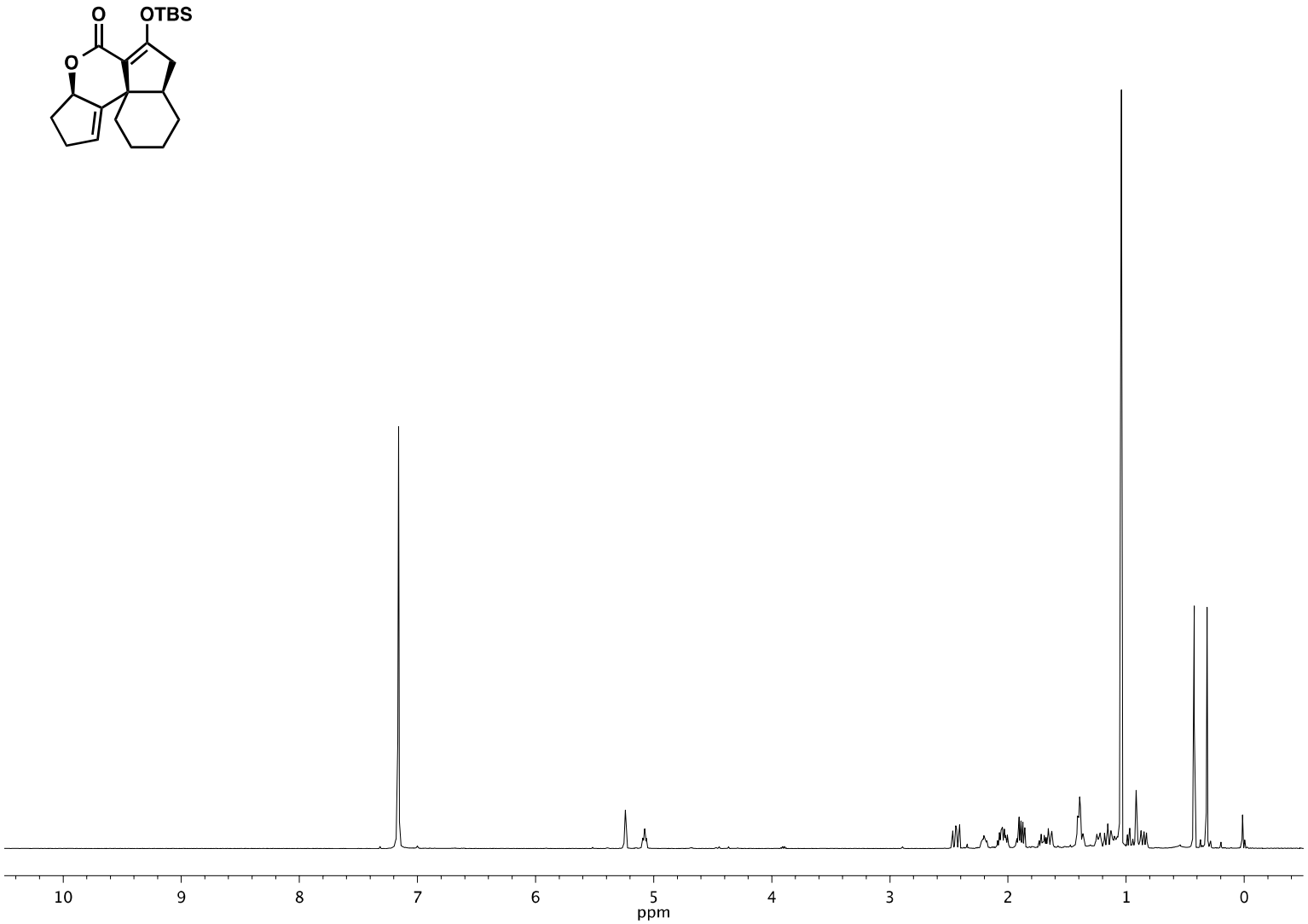
^{1}H NMR (500 MHz, C_6D_6) of compound **S2**



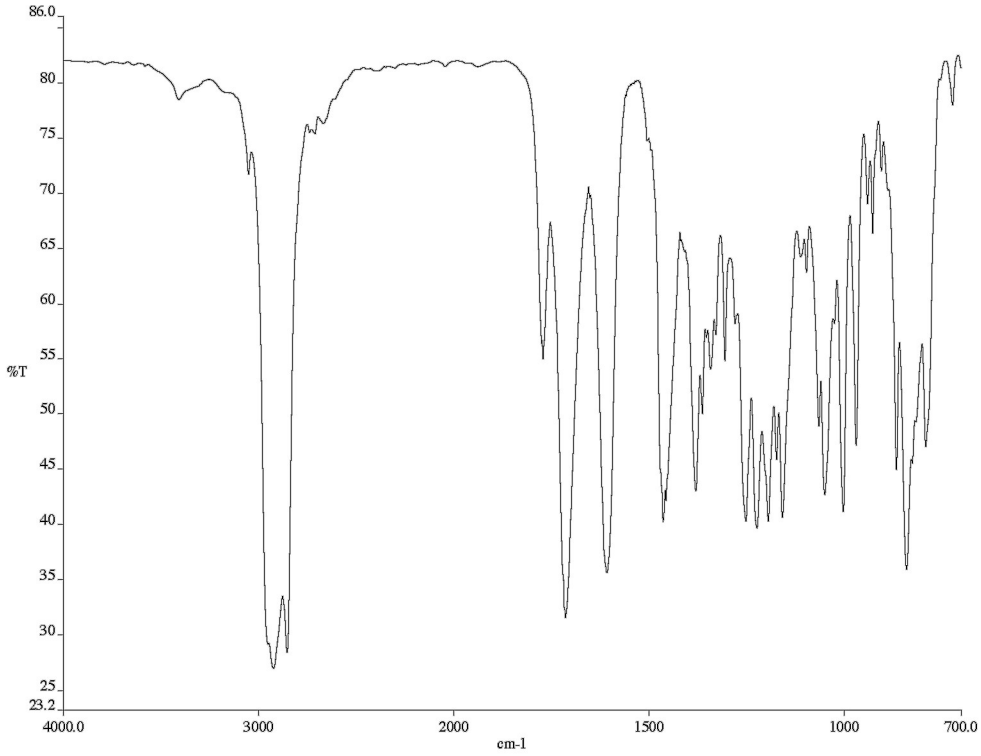
Infrared spectrum (thin film/NaCl) of compound **S2**



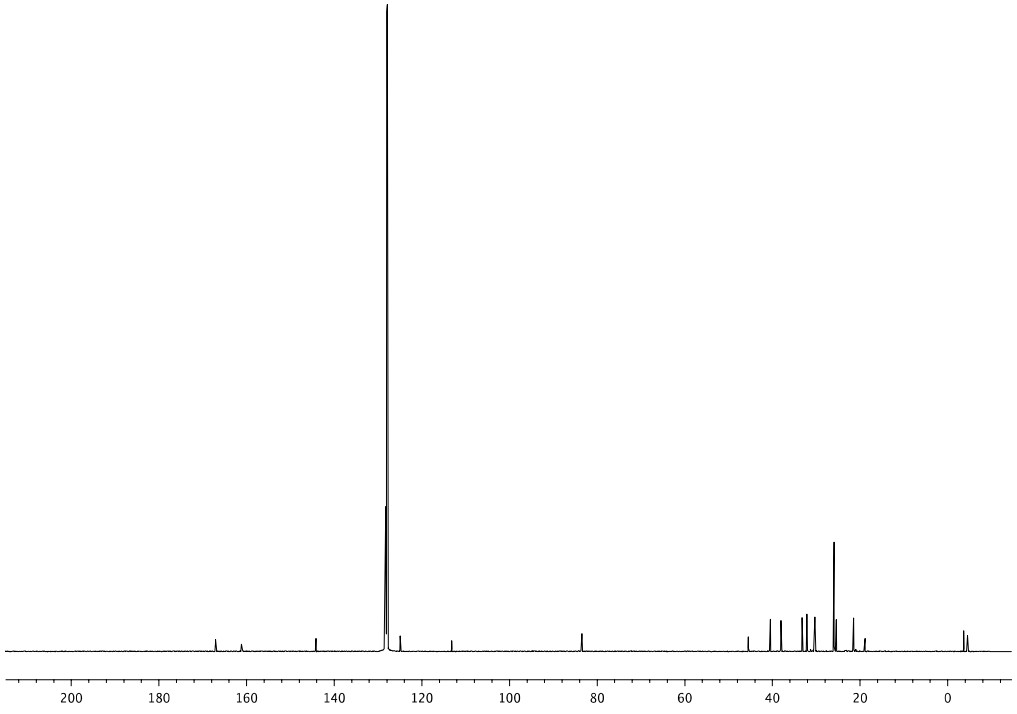
^{13}C NMR (126 MHz, C_6D_6) of compound **S2**



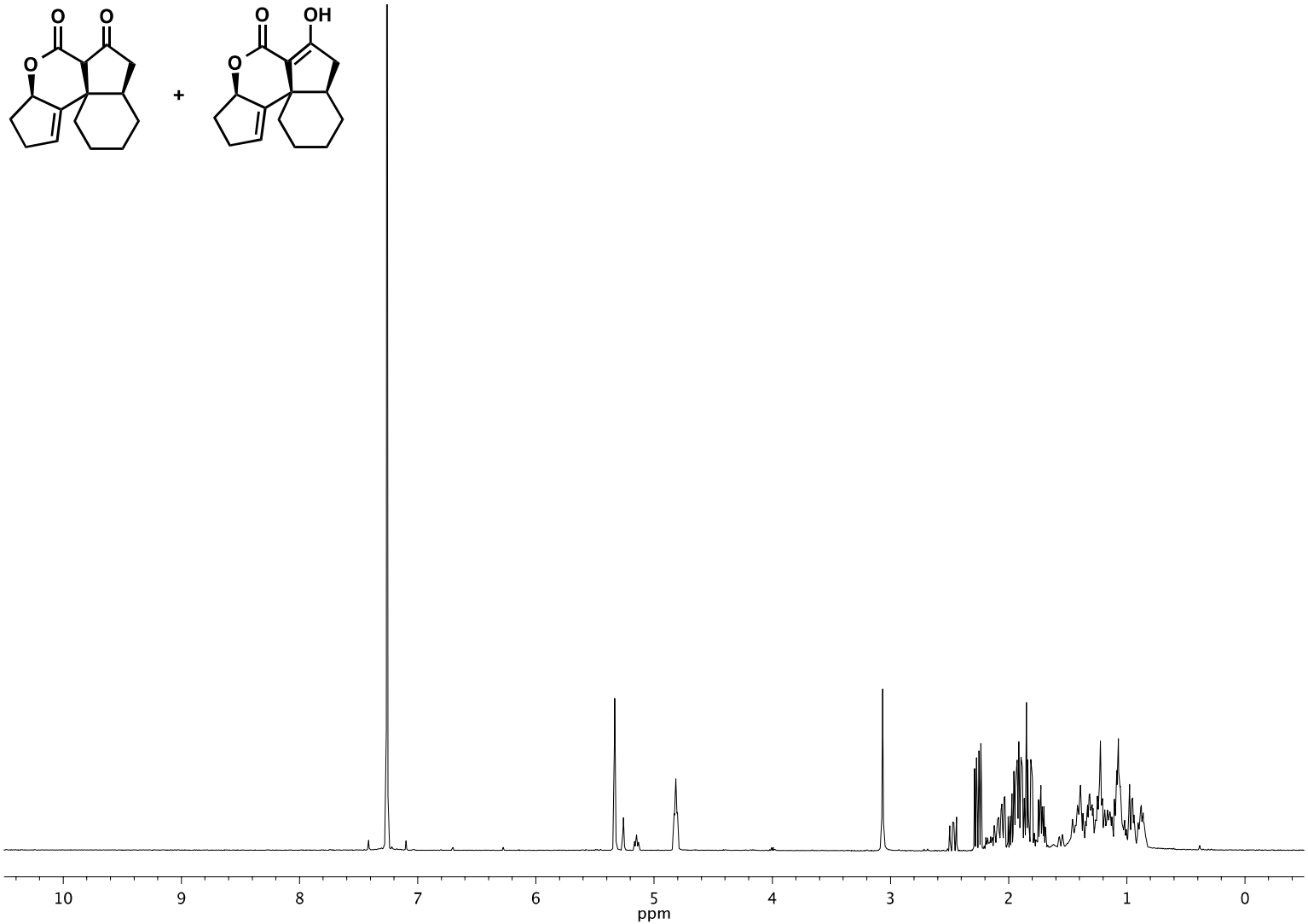
^{1}H NMR (500 MHz, C_6D_6) of compound **30**



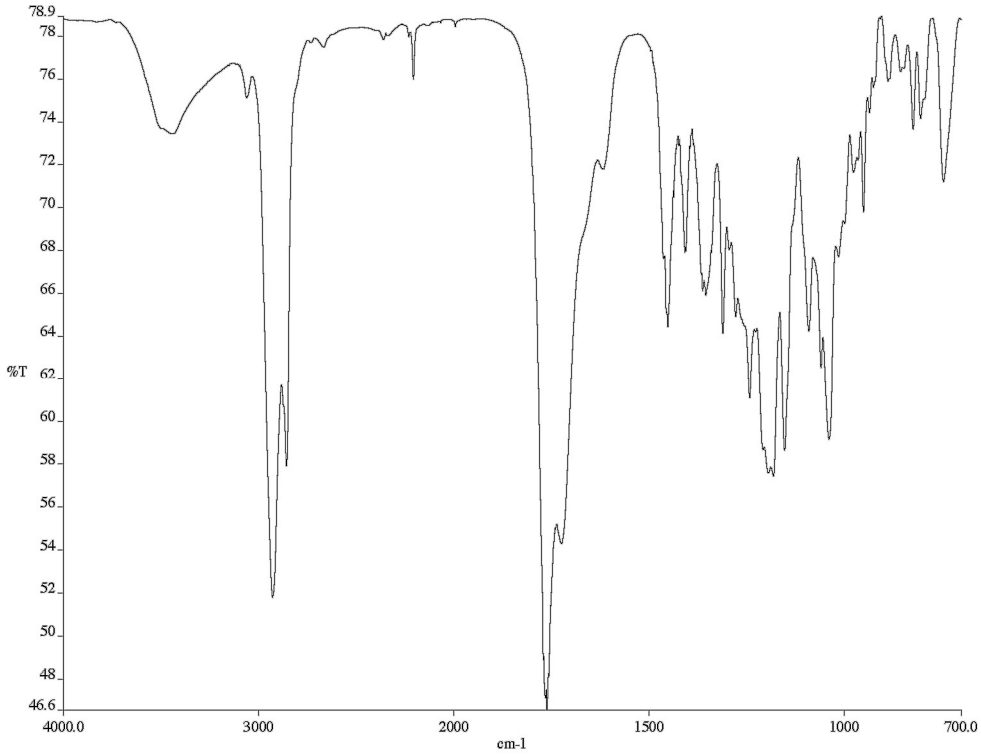
Infrared spectrum (thin film/NaCl) of compound **30**



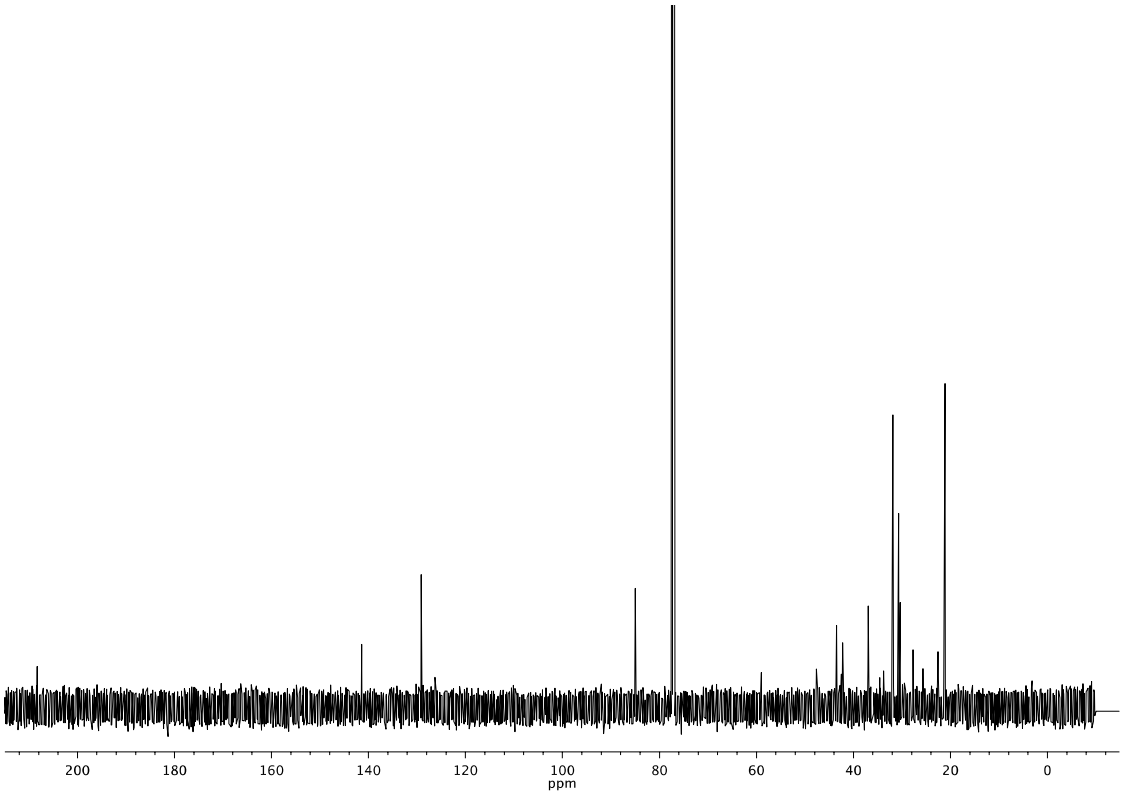
^{13}C NMR (126 MHz, C_6D_6) of compound **30**



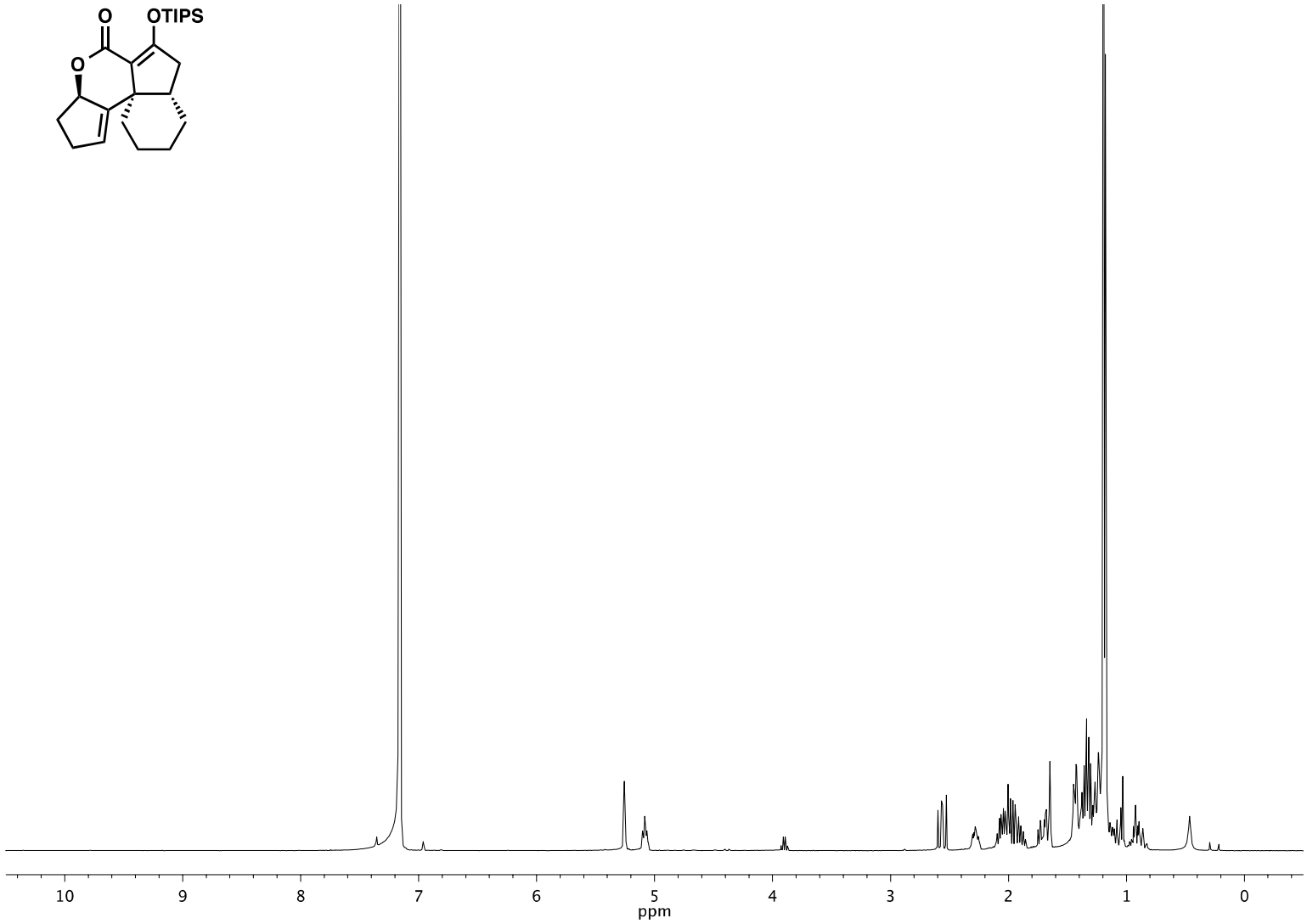
^{1}H NMR (500 MHz, $CDCl_3$) of compound **31**



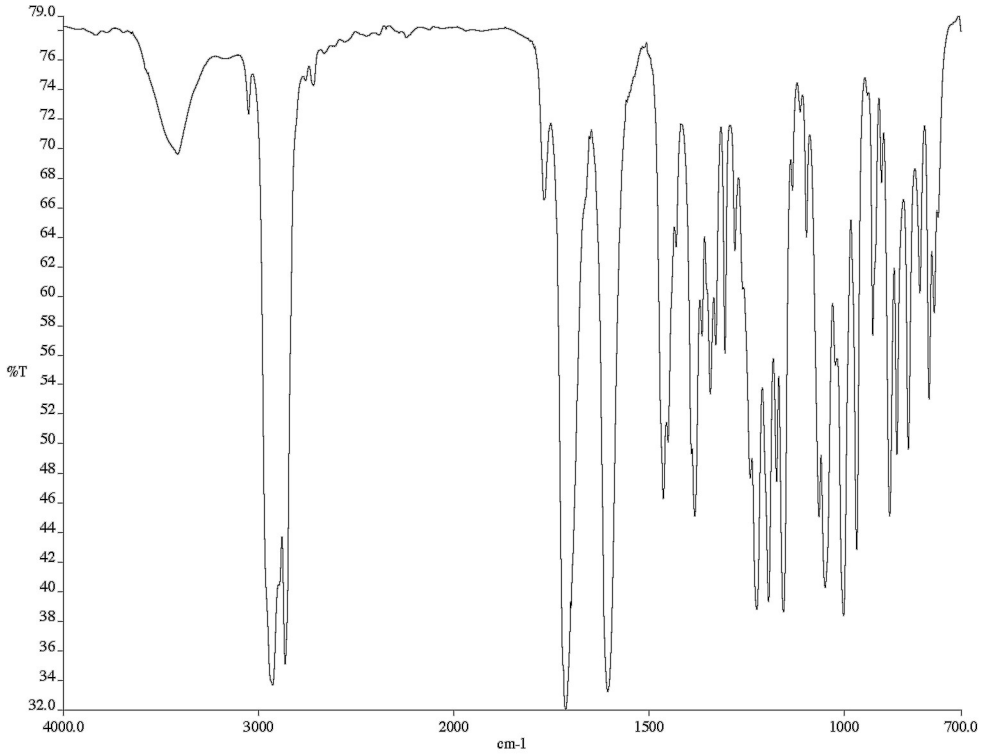
Infrared spectrum (thin film/NaCl) of compound **31**



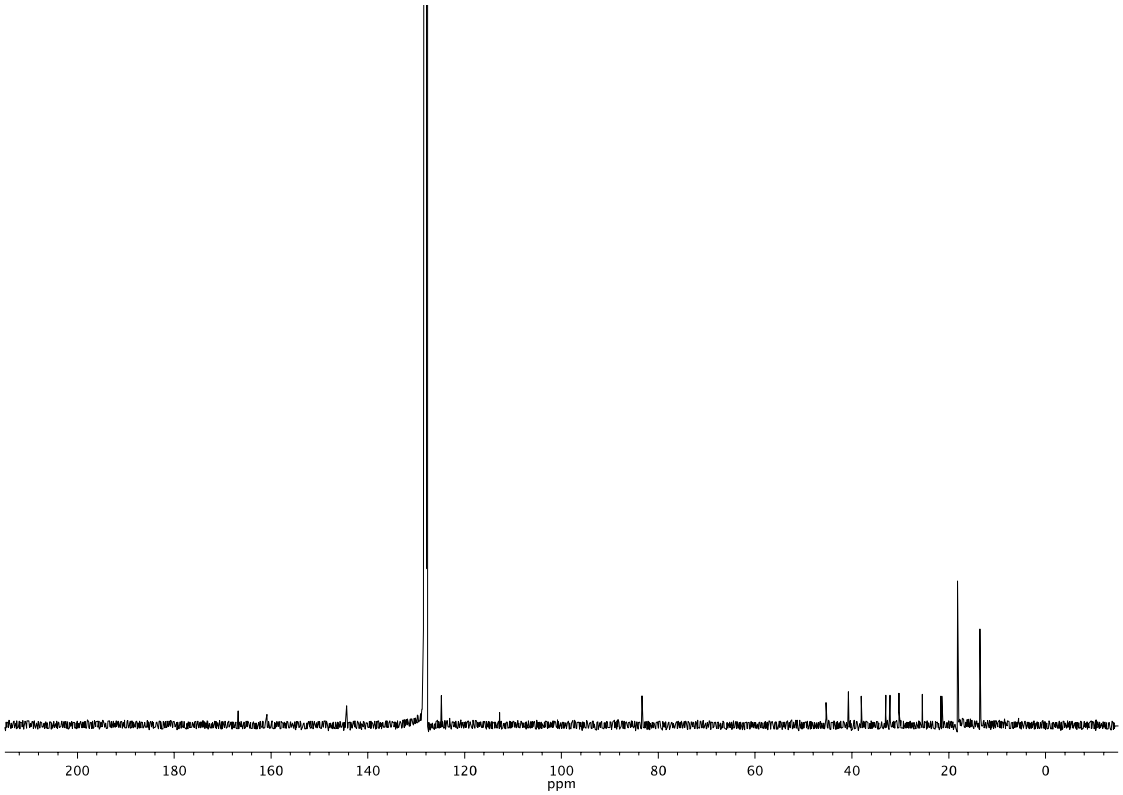
^{13}C NMR (126 MHz, $CDCl_3$) of compound **31**



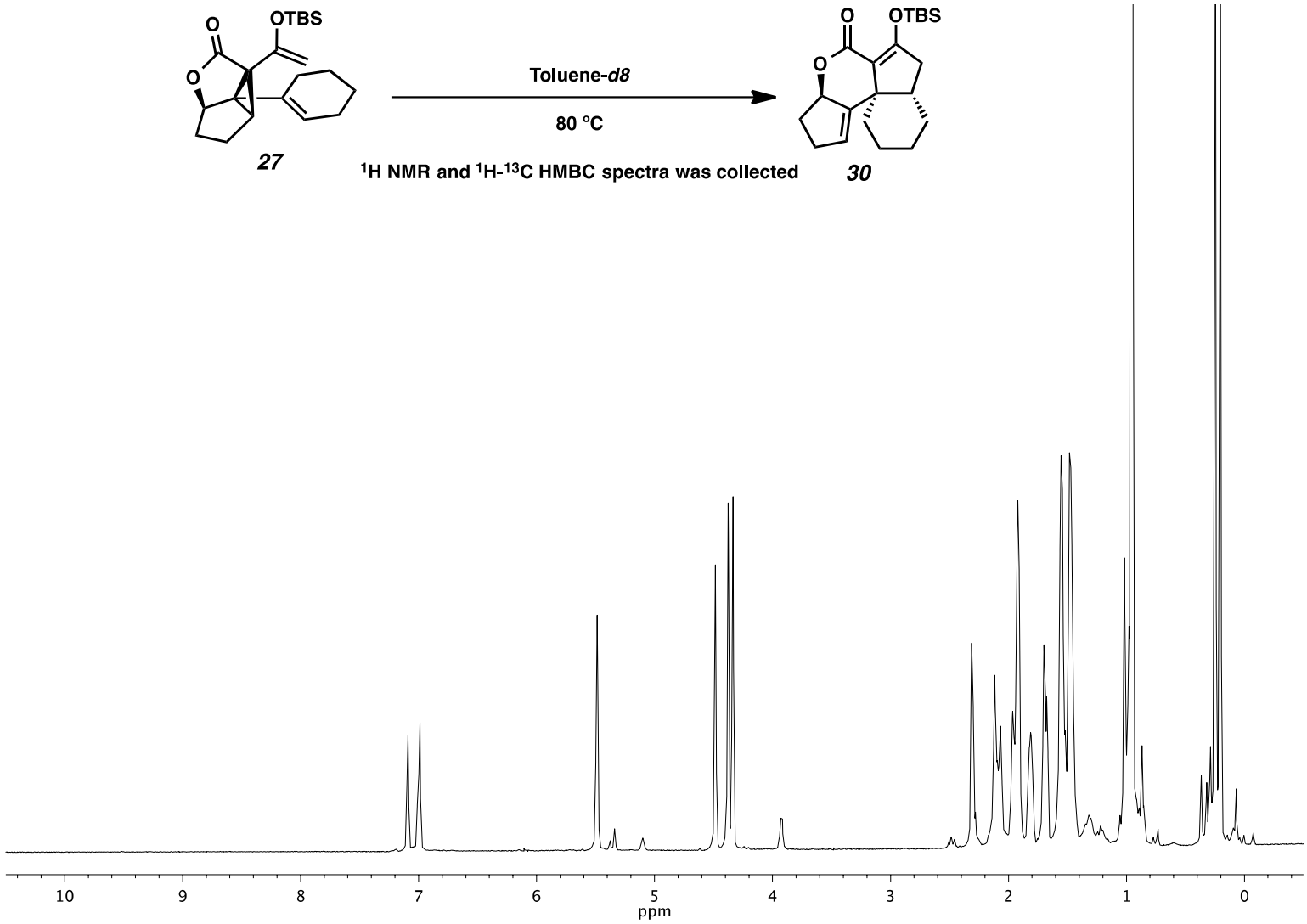
^{1}H NMR (400 MHz, C_6D_6) of compound **S3**



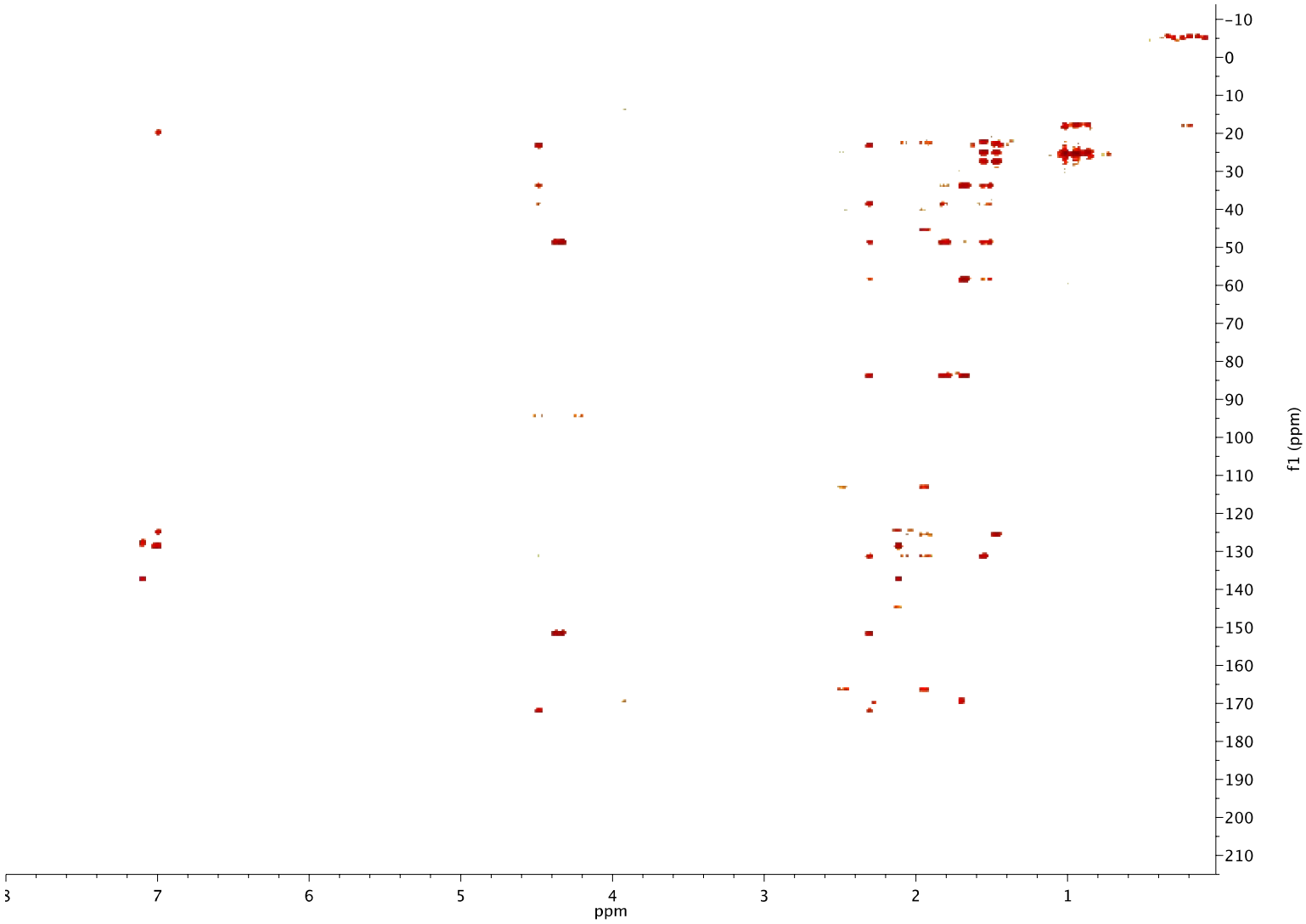
Infrared spectrum (thin film/NaCl) of compound **S3**



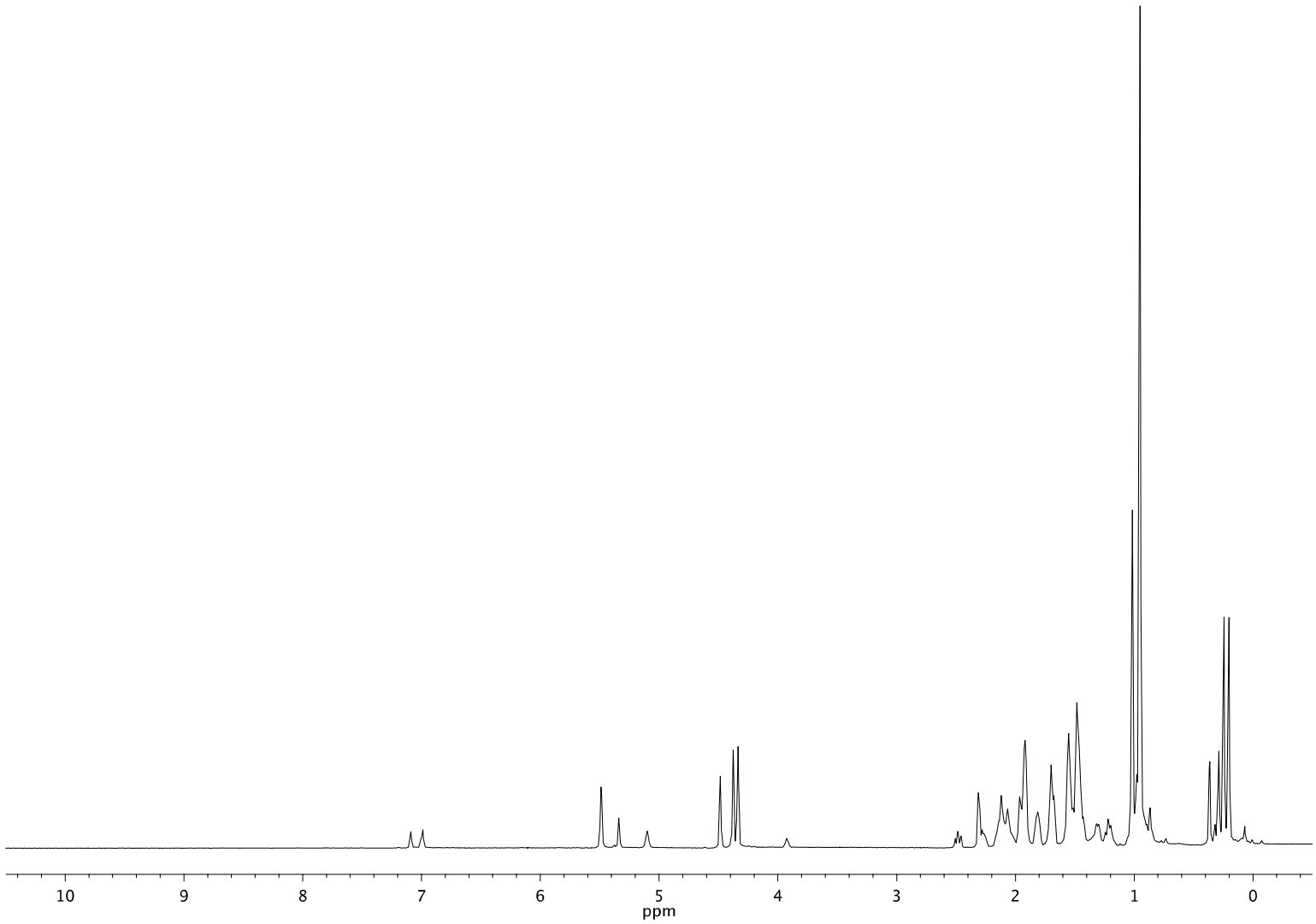
^{13}C NMR (101 MHz, C_6D_6) of compound **S3**



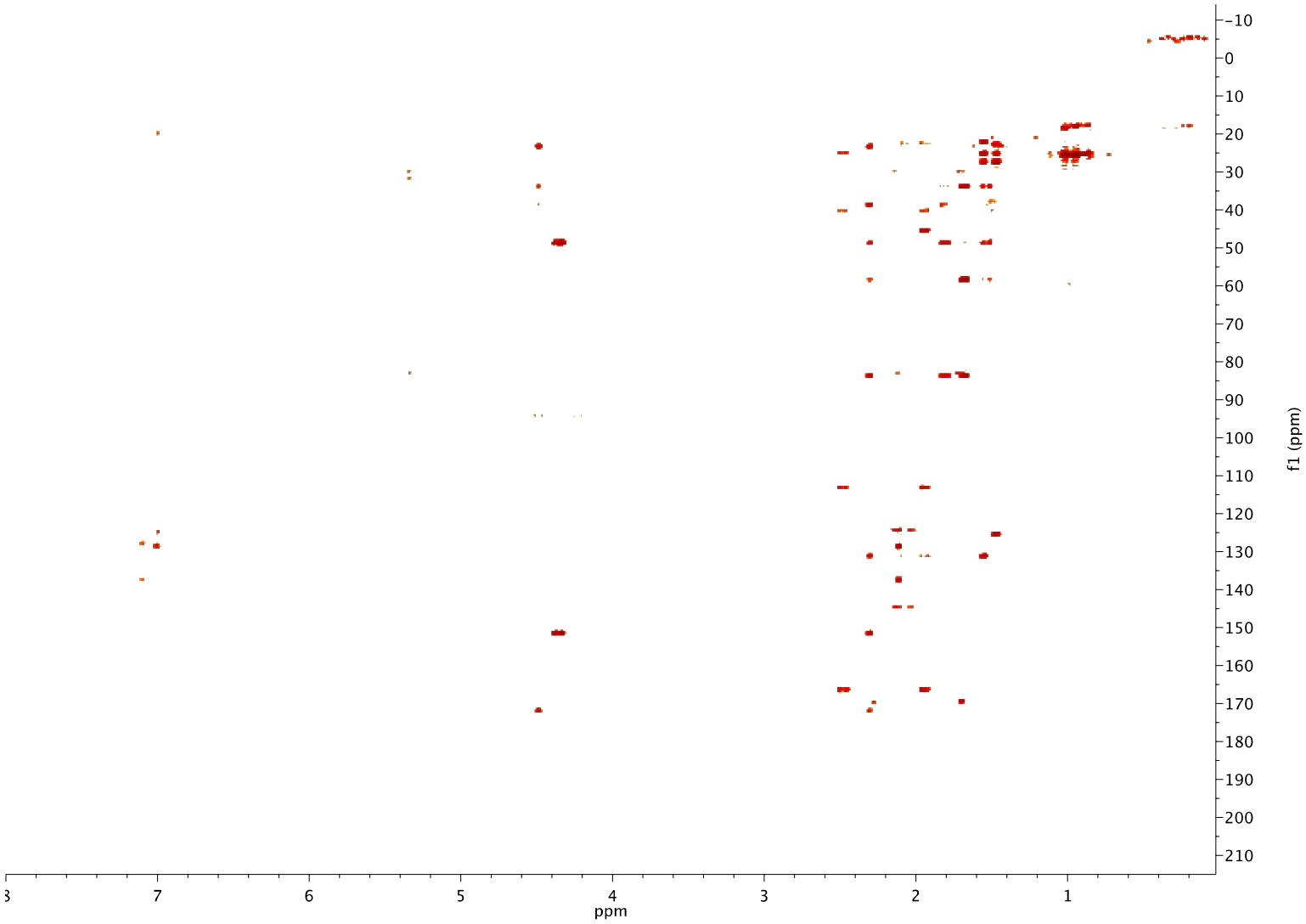
^{1}H NMR (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 5 min) of compound **27** to **30**



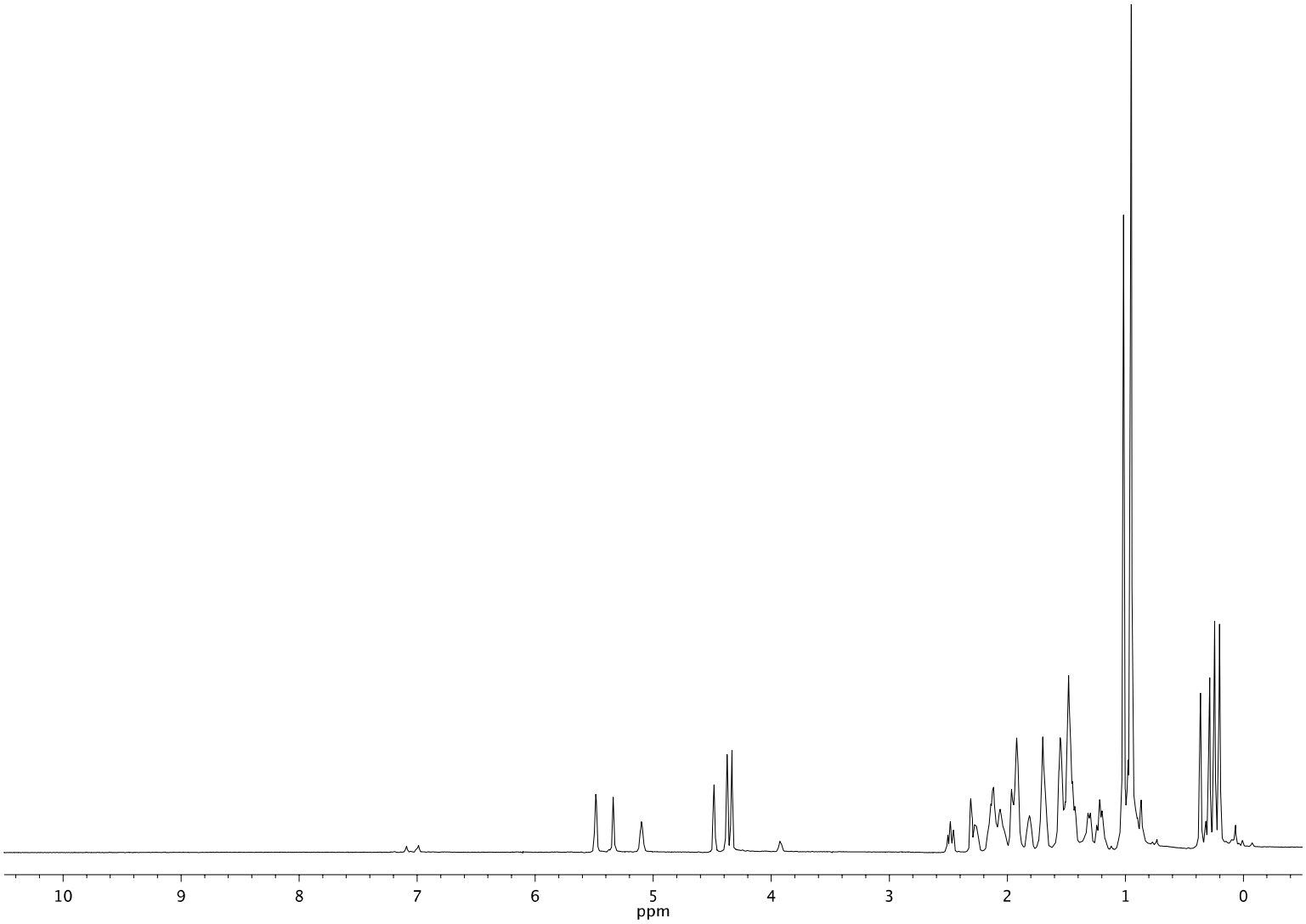
^{1}H-^{13}C HMBC (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 10 min – 44 min) of compound **27** to **30**



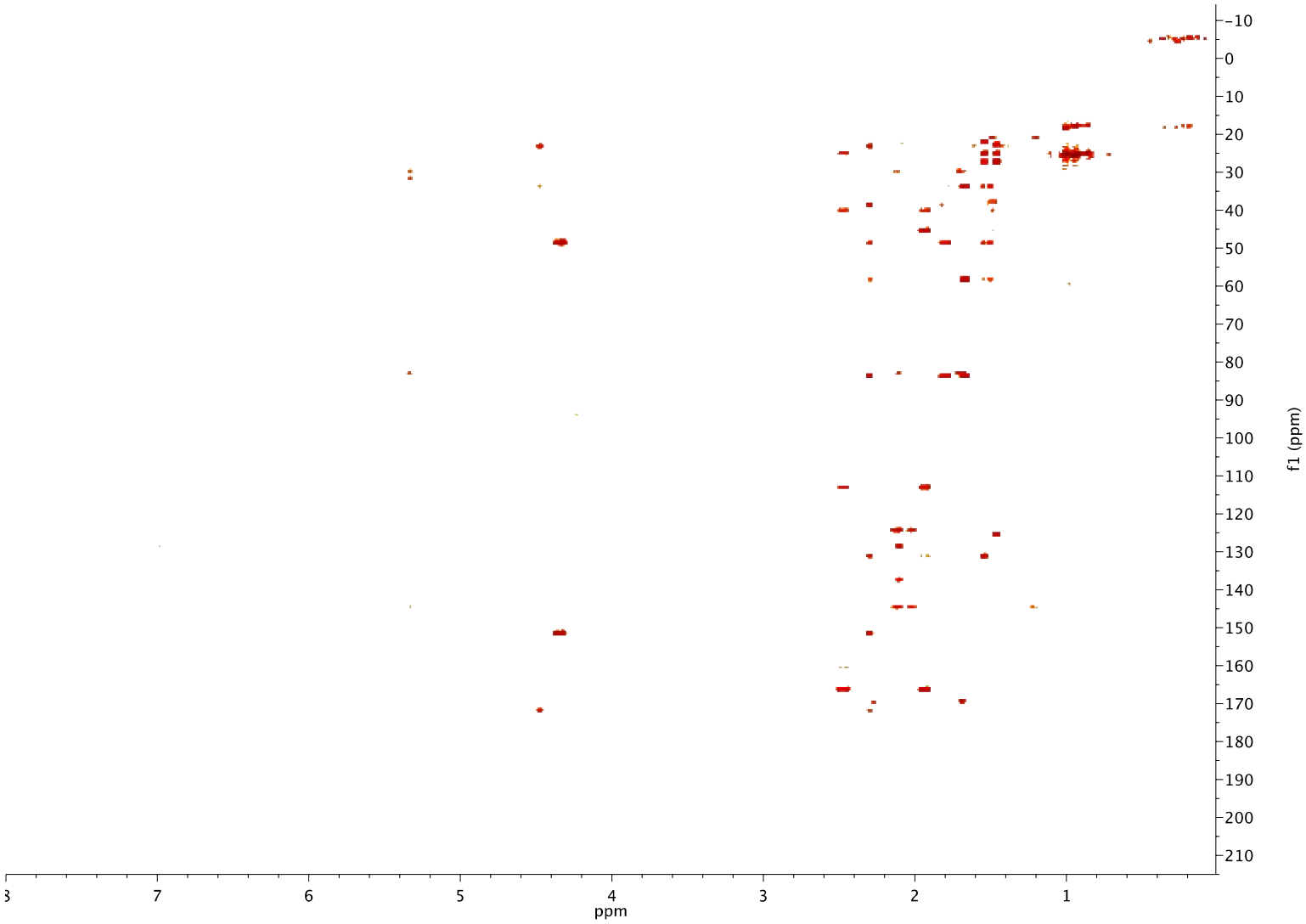
^{1}H NMR (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 44 min) of compound **27** to **30**



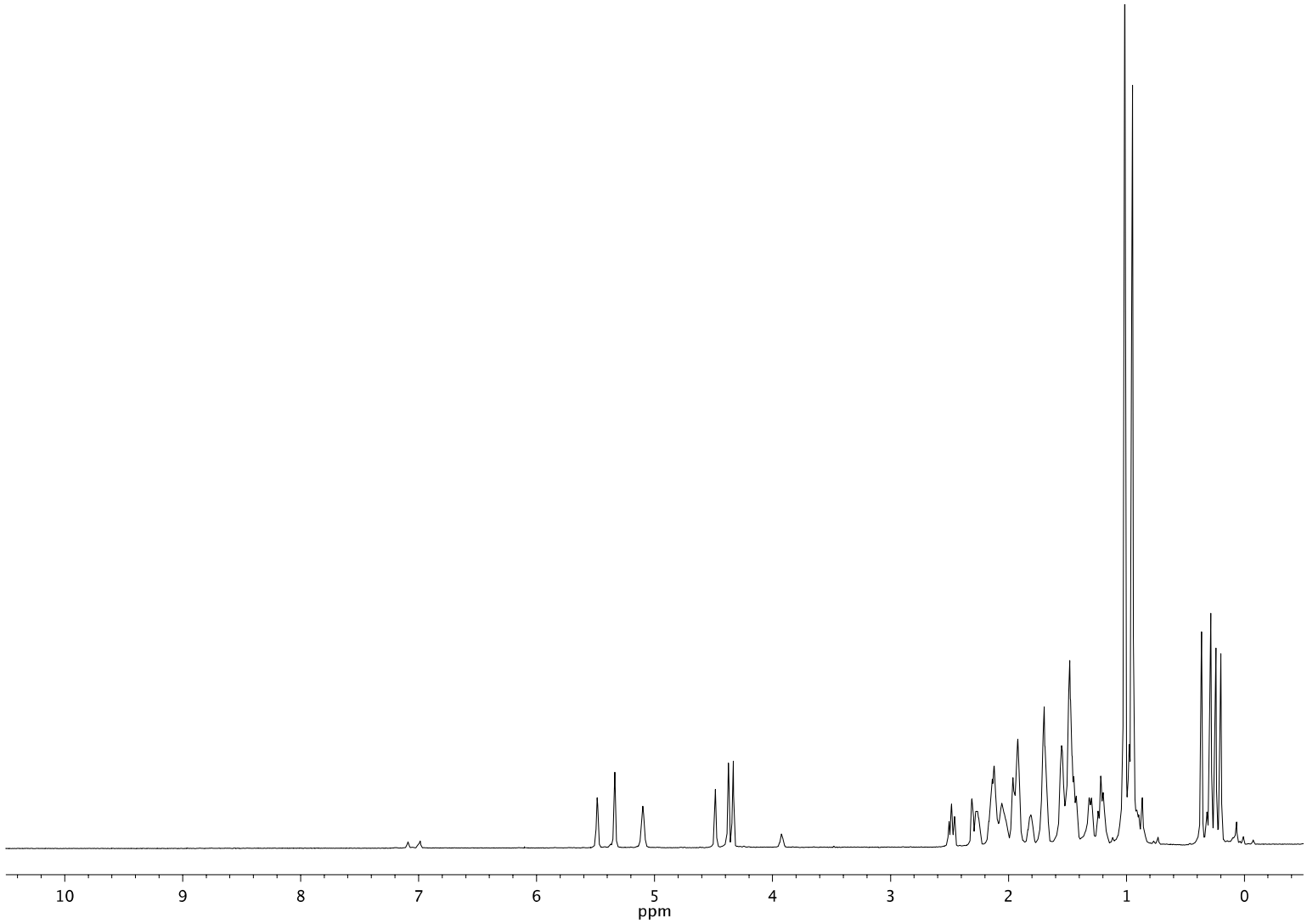
^{1}H-^{13}C HMBC (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 44 min–78 min) of compound **27** to **30**



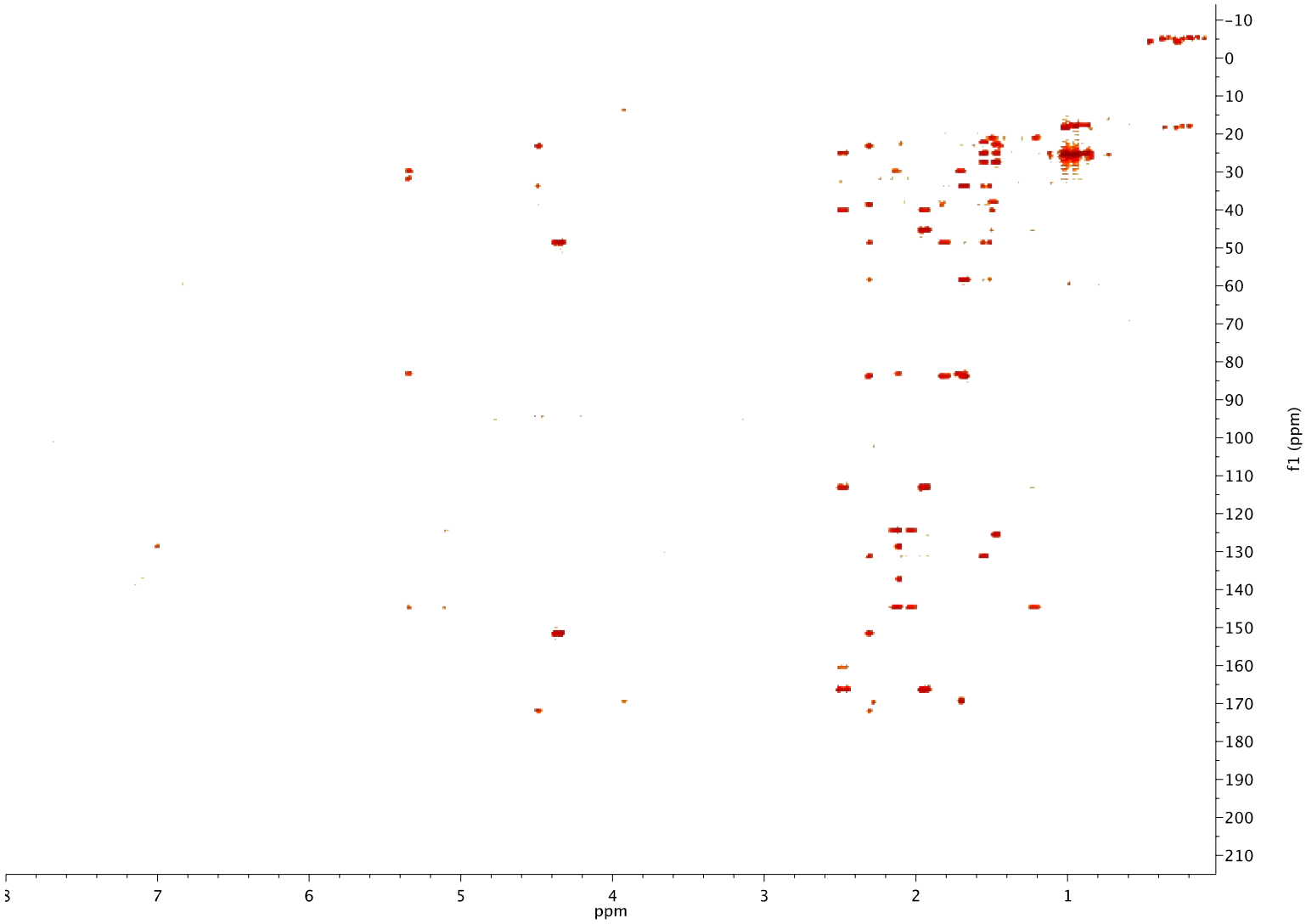
^{1}H NMR (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 78 min) of compound **27** to **30**



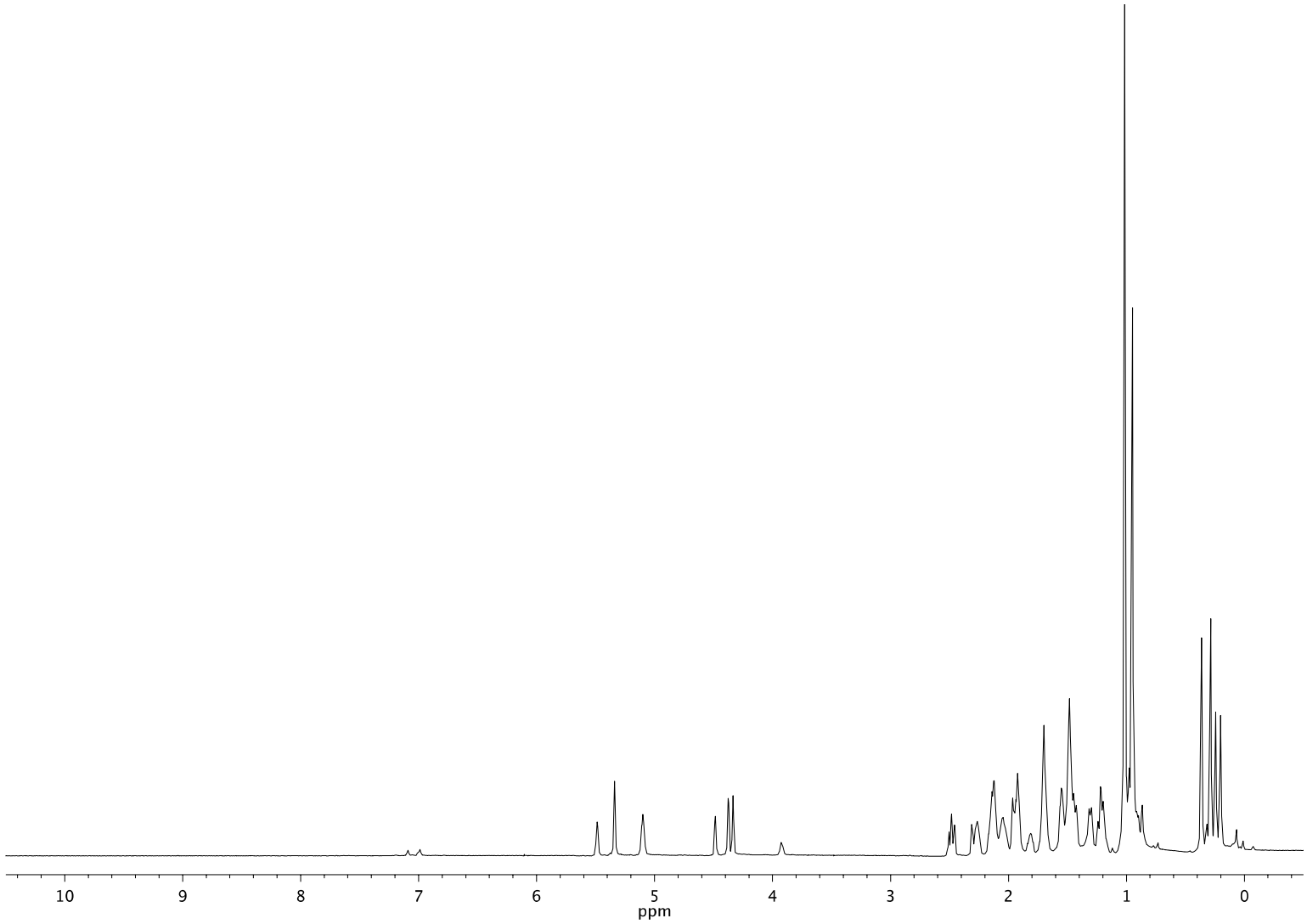
^{1}H-^{13}C HMBC (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 78 min–112 min) of compound **27** to **30**



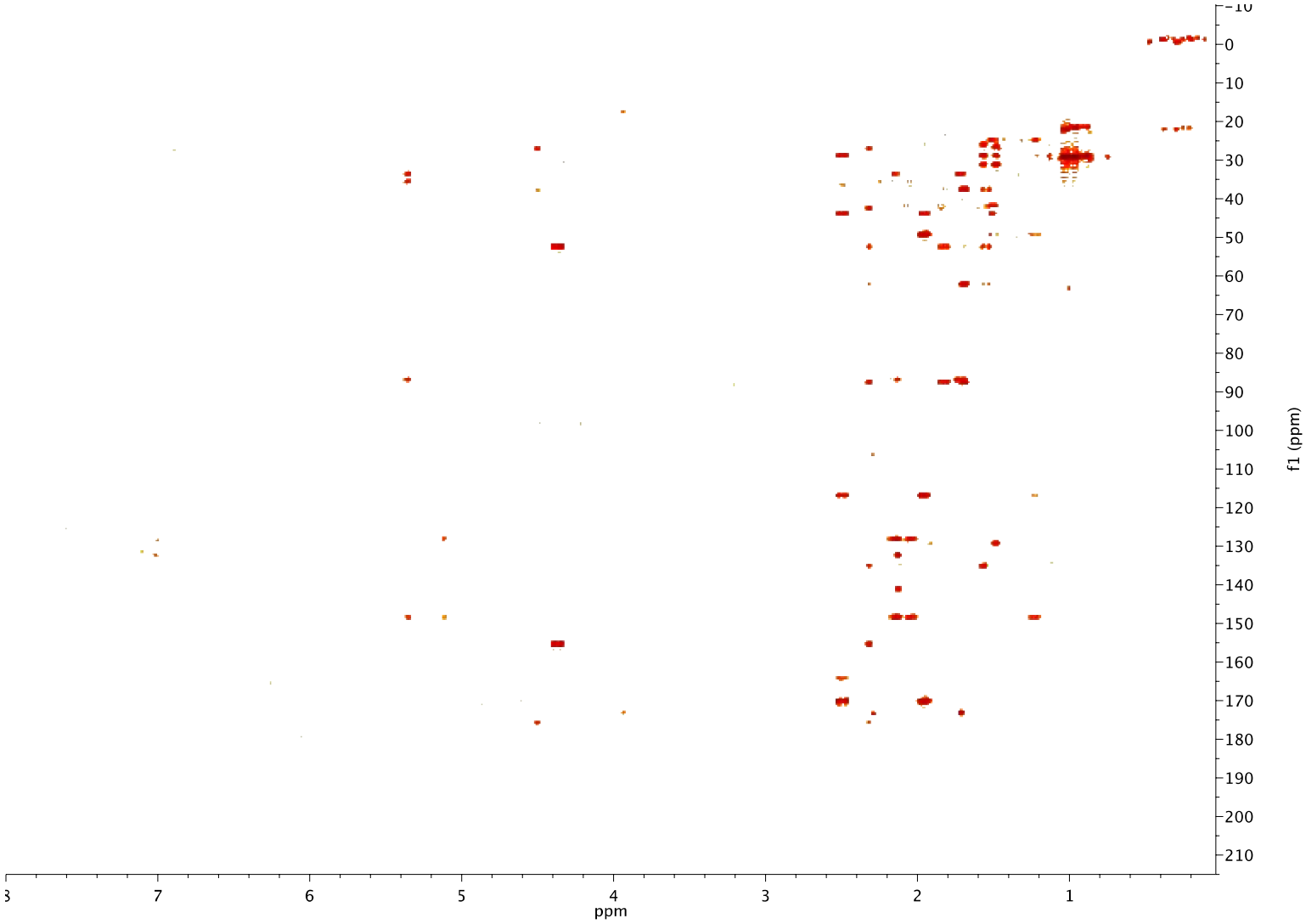
^{1}H NMR (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 112 min) of compound **27** to **30**



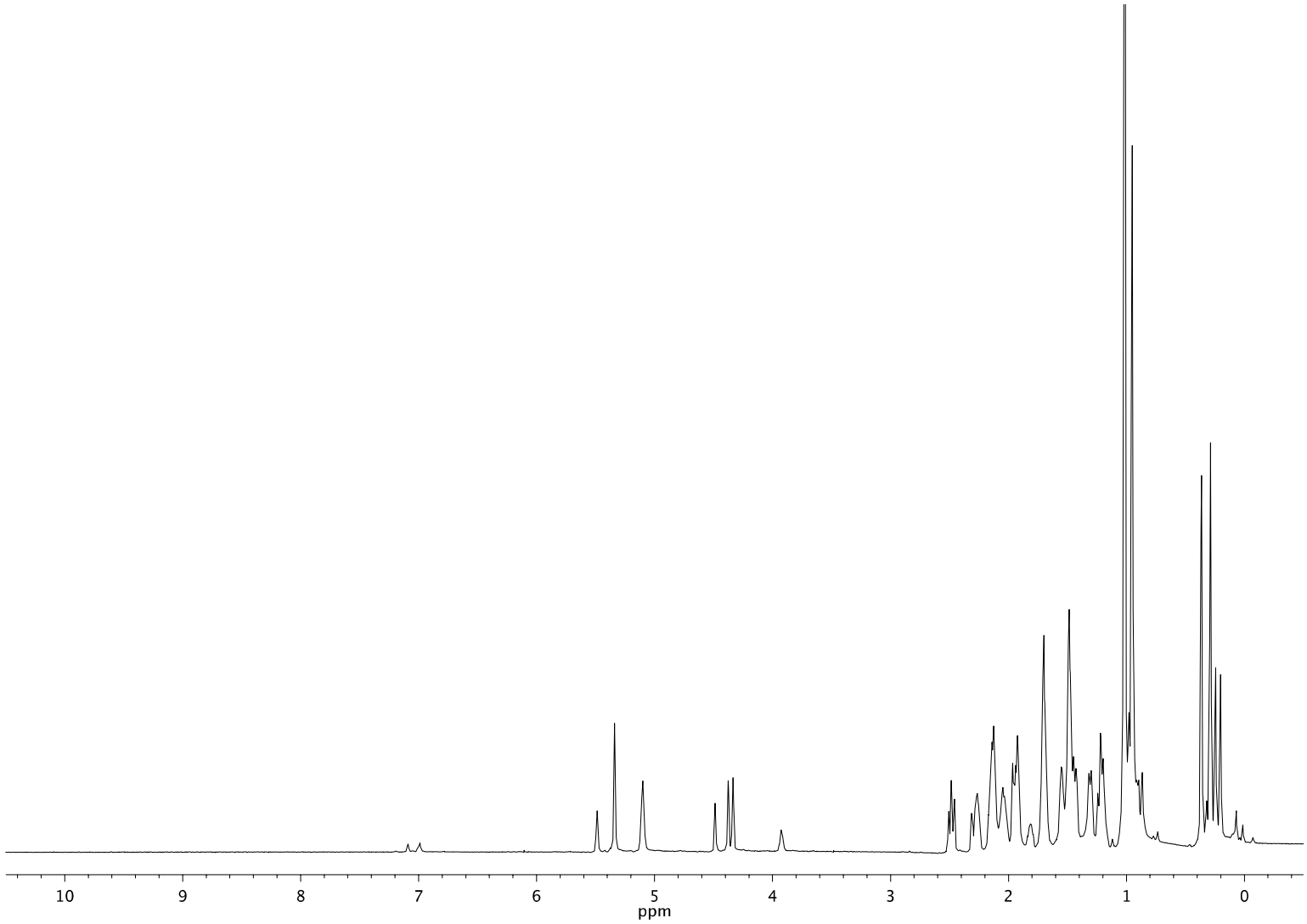
^{1}H-^{13}C HMBC (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 112 min–146 min) of compound **27** to **30**



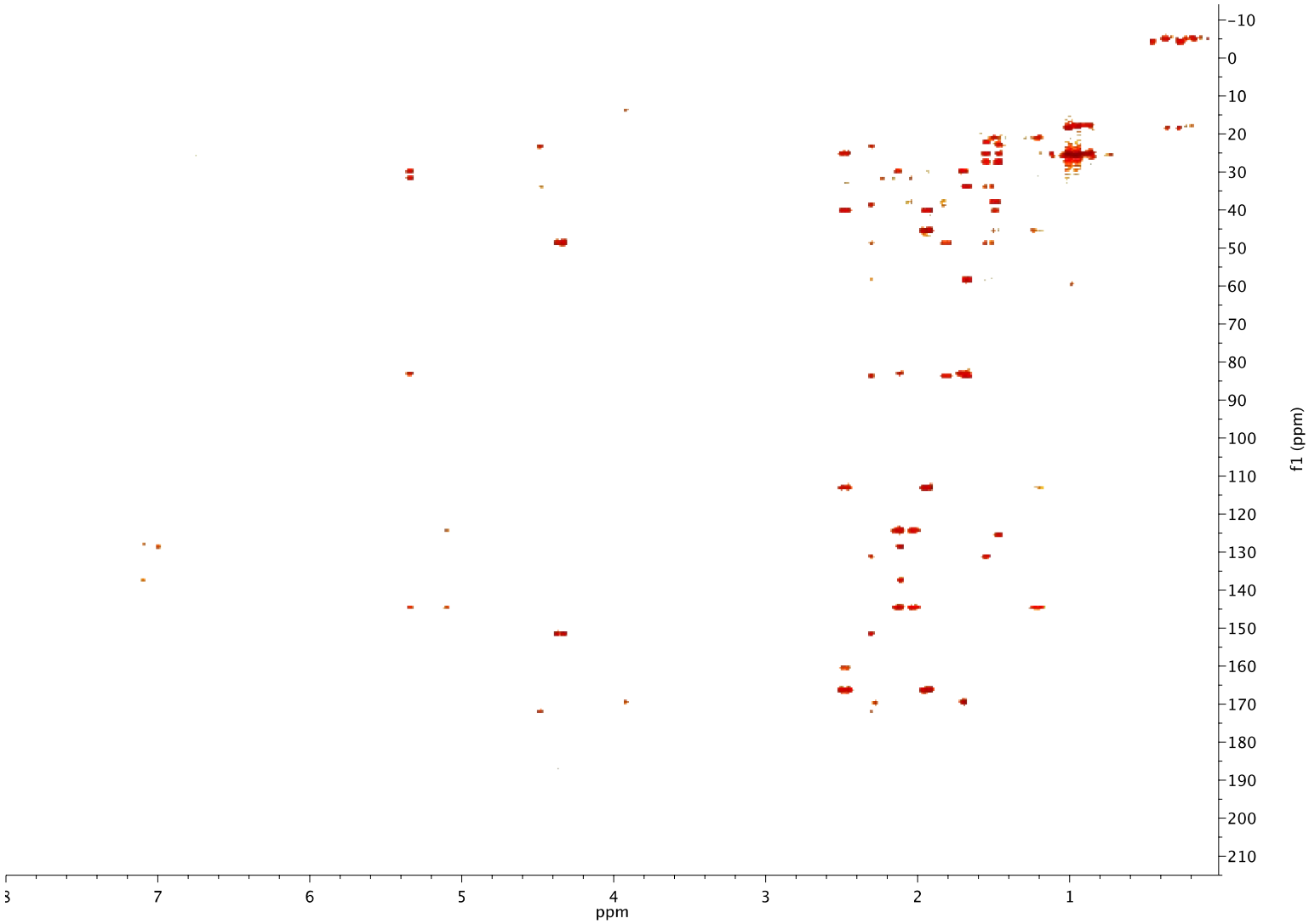
^{1}H NMR (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 146 min) of compound **27** to **30**



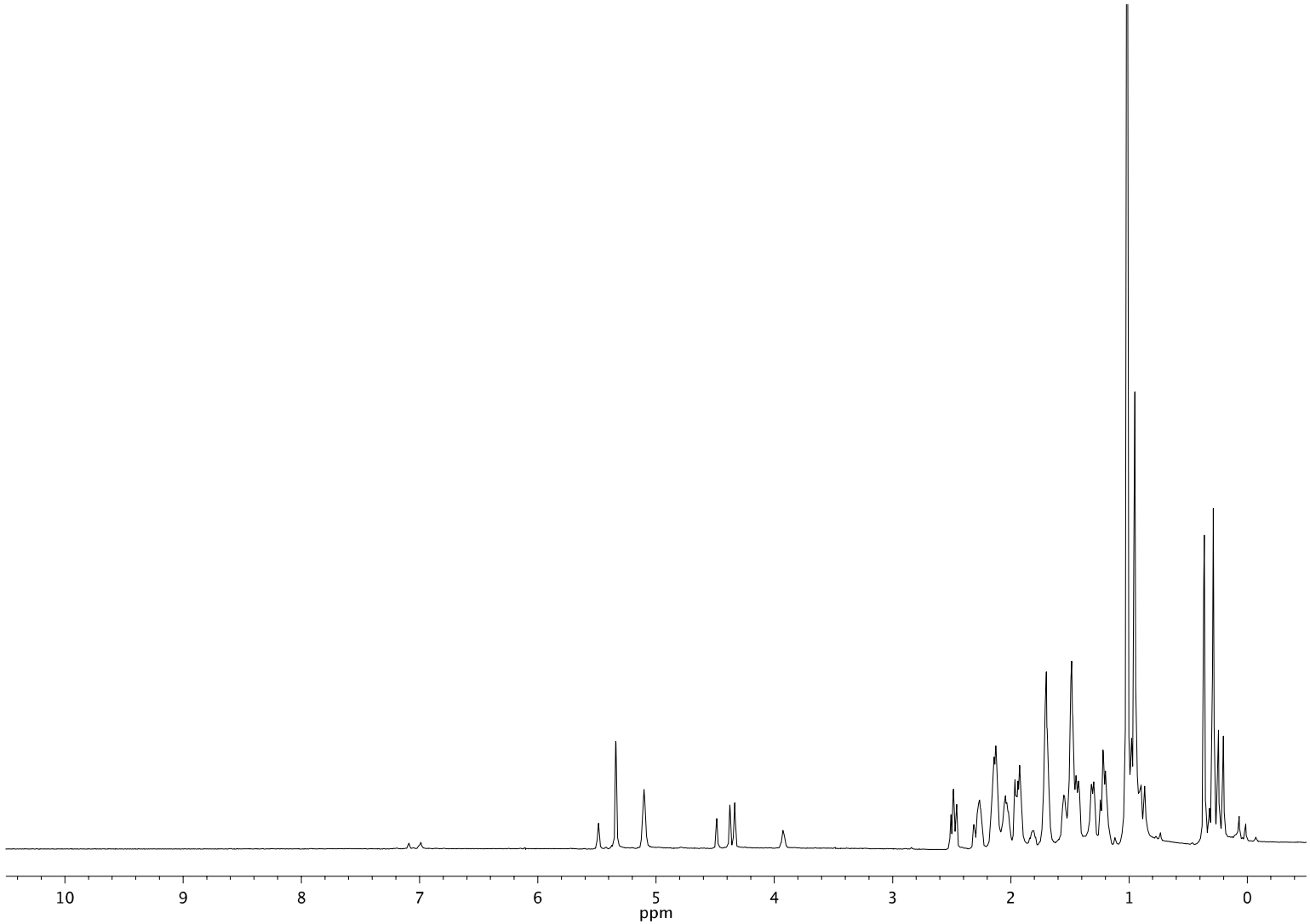
^{1}H-^{13}C HMBC (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 146 min – 180 min) of compound **27** to **30**



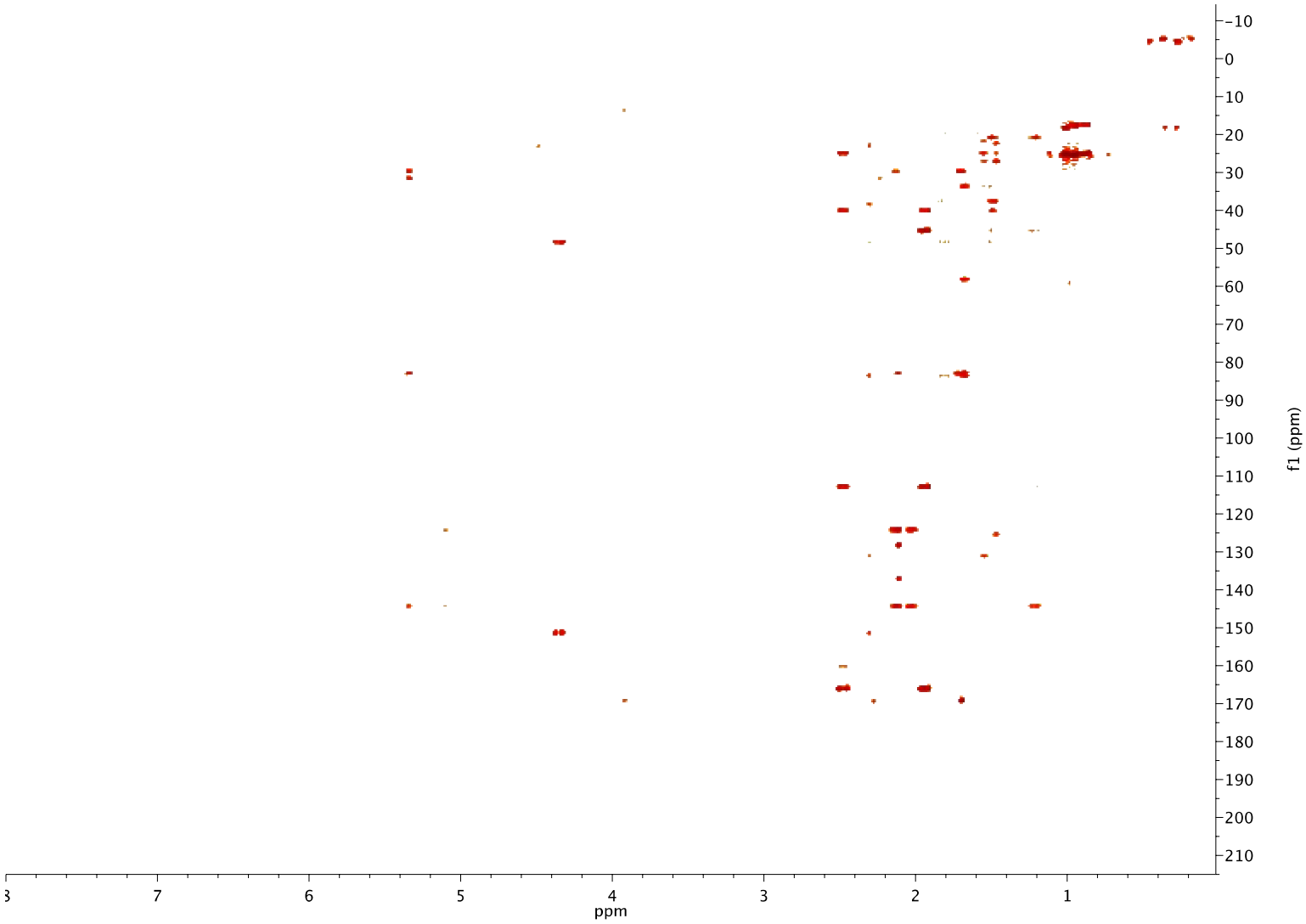
^{1}H NMR (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 180 min) of compound **27** to **30**



^{1}H-^{13}C HMBC (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 180 min – 214 min) of compound **27** to **30**



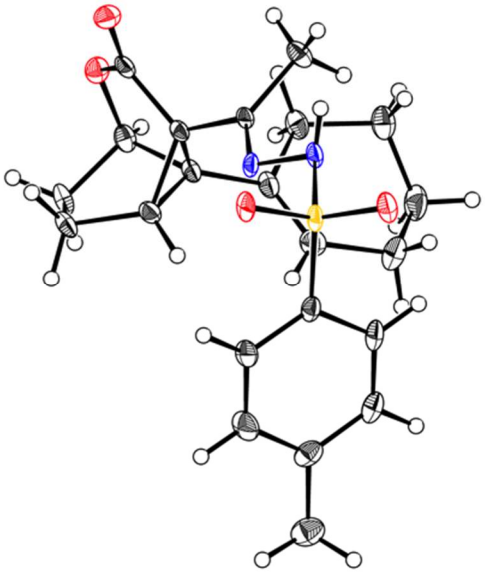
^{1}H NMR (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 214 min) of compound **27** to **30**



^{1}H-^{13}C HMBC (600 MHz, Toluene-*d8* at 80 ºC, reaction time: 214 min – 244 min) of compound **27** to **30**

X-ray Crystallography Reports

CRYSTAL STRUCTURE ANALYSIS OF 25a



25a

Crystal data and structure refinement for 25a.

Empirical formula	$C_{22}H_{26}N_2O_4S$	
Formula weight	414.51	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 19.3346(10) Å	α= 90.199(3)°
	b = 21.5305(11) Å	β= 93.729(3)°
	c = 9.9784(5) Å	γ = 90.810(3)°

Volume	4144.6(4) $Å^3$
Z	8
Density (calculated)	1.329 Mg/m^3
Absorption coefficient	0.187 mm^{-1}
F(000)	1760
Crystal size	0.35 x 0.33 x 0.10 mm^3
Theta range for data collection	2.045 to 32.962°.
Index ranges	-28<=h<=29, -32<=k<=32, -15<=l<=15
Reflections collected	272986
Independent reflections	29250 [R(int) = 0.0867]
Completeness to theta = 25.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8821
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	29250 / 0 / 1054
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0907, wR2 = 0.2272
R indices (all data)	R1 = 0.1406, wR2 = 0.2638
Extinction coefficient	n/a
Largest diff. peak and hole	3.274 and -1.435 $e.Å^{-3}$

Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters ($Å^2$x 10^4) for 25a.U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	13320(4)	13122(4)	9576(7)	150(2)
O(1)	49133(12)	21574(12)	19580(20)	194(5)
O(2)	44907(13)	12484(11)	11420(30)	211(5)
O(3)	15151(13)	11293(12)	-3620(20)	190(5)
O(4)	8084(12)	9653(12)	15920(20)	212(5)
N(1)	25759(13)	16229(13)	15610(20)	141(5)
N(2)	20329(13)	12431(13)	19710(20)	154(5)
C(1)	37110(16)	20221(14)	18900(30)	131(5)
C(2)	35319(17)	26494(15)	12570(30)	162(6)
C(3)	40319(18)	29526(16)	3160(30)	201(6)
C(4)	46367(19)	31992(17)	12740(30)	220(7)
C(5)	46470(17)	27472(16)	24340(30)	182(6)
C(6)	38727(16)	26291(14)	26600(30)	149(5)
C(7)	43909(16)	17536(15)	16040(30)	150(5)
C(8)	31453(16)	15936(14)	22810(30)	131(5)
C(9)	32779(18)	11975(16)	34940(30)	204(6)
C(10)	11225(16)	21054(16)	9060(30)	162(6)
C(11)	8810(18)	23791(18)	20540(30)	225(7)
C(12)	7000(19)	29940(18)	20140(40)	240(7)
C(13)	7617(17)	33456(17)	8660(40)	217(7)
C(14)	10150(20)	30670(18)	-2540(30)	270(8)
C(15)	11900(20)	24434(17)	-2480(30)	229(7)
C(16)	5700(20)	40190(19)	8610(40)	289(8)
C(17)	35745(18)	27620(15)	39590(30)	181(6)
C(18)	29230(20)	29568(17)	40370(40)	245(7)
C(19)	25920(20)	30390(20)	53470(40)	324(9)
C(20)	30980(20)	30028(19)	65620(40)	299(8)
C(21)	36180(20)	24935(19)	64100(40)	268(7)
C(22)	40298(19)	26011(17)	51900(30)	209(6)

S(1B)	13258(4)	12852(4)	59543(7)	158(2)
O(1B)	48049(13)	2551(12)	71500(30)	235(5)
O(2B)	45243(13)	11942(12)	63860(30)	240(5)
O(3B)	8386(13)	16497(12)	66270(20)	224(5)
O(4B)	15006(13)	14527(13)	46240(20)	214(5)
N(1B)	25455(14)	9277(12)	65110(20)	142(5)
N(2B)	20429(13)	13340(13)	69390(20)	140(5)
C(1B)	36234(16)	4545(14)	69050(30)	135(5)
C(2B)	34054(17)	-1502(15)	61640(30)	172(6)
C(3B)	39125(19)	-4647(16)	52690(40)	224(7)
C(4B)	44500(20)	-7532(17)	62690(40)	258(7)
C(5B)	44493(18)	-3253(16)	74870(40)	217(7)
C(6B)	36840(17)	-1734(14)	76100(30)	161(6)
C(7B)	43437(16)	6938(15)	67610(30)	174(6)
C(8B)	30958(16)	9018(14)	72880(30)	135(5)
C(9B)	32315(18)	12629(16)	85720(30)	184(6)
C(10B)	10660(16)	5029(16)	59400(30)	170(6)
C(11B)	10420(20)	1525(19)	47510(30)	251(7)
C(12B)	8420(20)	-4650(19)	47970(30)	261(7)
C(13B)	6617(17)	-7465(18)	59790(30)	225(7)
C(14B)	6810(20)	-3817(19)	71390(30)	262(7)
C(15B)	8802(19)	2314(18)	71350(30)	235(7)
C(16B)	4430(20)	-14150(20)	60160(40)	292(8)
C(17B)	32930(20)	-3298(15)	88040(30)	215(7)
C(18B)	26310(20)	-5250(20)	86790(40)	306(8)
C(19B)	22050(30)	-6570(30)	98570(50)	441(11)
C(20B)	26640(40)	-6770(30)	111880(50)	574(17)
C(21B)	32030(30)	-1710(20)	112750(50)	507(14)
C(22B)	36780(20)	-2140(20)	101310(40)	319(9)
S(1C)	12001(4)	59892(4)	58426(7)	159(2)
O(1C)	47966(11)	53435(11)	70150(20)	166(4)
O(2C)	43592(13)	62294(11)	62170(20)	189(5)
O(3C)	13902(13)	61910(12)	45460(20)	206(5)
O(4C)	6620(13)	63038(13)	64810(20)	235(5)
N(1C)	24509(13)	57423(14)	64920(20)	157(5)
N(2C)	18921(14)	60905(14)	68850(20)	163(5)

C(1C)	35919(15)	54088(14)	68830(30)	119(5)
C(2C)	34398(16)	47727(14)	62260(30)	139(5)
C(3C)	39586(17)	44999(16)	52950(30)	173(6)
C(4C)	45639(17)	42921(16)	62630(30)	188(6)
C(5C)	45393(16)	47354(14)	74430(30)	151(5)
C(6C)	37624(15)	48043(14)	76390(30)	125(5)
C(7C)	42663(15)	57166(14)	66440(30)	132(5)
C(8C)	30100(15)	58024(15)	72500(30)	133(5)
C(9C)	31215(18)	62083(17)	84720(30)	211(6)
C(10C)	10190(16)	51853(16)	57500(30)	171(6)
C(11C)	6450(20)	49013(19)	67320(40)	253(7)
C(12C)	5370(20)	42627(19)	66860(40)	280(8)
C(13C)	7957(17)	39030(17)	56930(30)	209(6)
C(14C)	11720(20)	41909(18)	47140(30)	251(7)
C(15C)	12810(20)	48307(18)	47320(30)	239(7)
C(16C)	6650(20)	32119(18)	56590(40)	271(7)
C(17C)	34480(17)	46447(15)	89070(30)	169(6)
C(18C)	28090(20)	43981(18)	89350(40)	273(8)
C(19C)	24650(30)	42670(20)	102160(50)	404(11)
C(20C)	29590(30)	43440(20)	114700(40)	408(11)
C(21C)	34510(20)	48930(20)	113750(40)	326(9)
C(22C)	38780(20)	48217(18)	101720(30)	249(7)
S(1D)	12549(4)	60151(4)	8655(7)	163(2)
O(1D)	47108(12)	72046(12)	21250(30)	221(5)
O(2D)	44078(13)	62556(11)	13520(30)	213(5)
O(3D)	7684(13)	56290(12)	15030(20)	217(5)
O(4D)	14494(13)	58580(13)	-4550(20)	225(5)
N(1D)	24626(13)	64383(13)	14950(20)	150(5)
N(2D)	19606(13)	60038(13)	18830(20)	150(5)
C(1D)	35252(16)	69711(14)	19390(30)	141(5)
C(2D)	33047(17)	75661(16)	12120(30)	178(6)
C(3D)	37996(19)	78934(17)	3020(30)	225(7)
C(4D)	43560(20)	82021(17)	12880(40)	249(7)
C(5D)	43667(19)	77748(16)	25010(30)	214(6)
C(6D)	35989(18)	76021(15)	26490(30)	174(6)
C(7D)	42440(17)	67559(15)	17510(30)	171(6)

C(8D)	30004(16)	64977(15)	23020(30)	136(5)
C(9D)	31320(18)	61505(17)	35780(30)	203(6)
C(10D)	9991(16)	67894(15)	8530(30)	152(5)
C(11D)	10280(20)	71519(19)	-2880(30)	272(8)
C(12D)	8490(20)	77700(20)	-2210(40)	292(8)
C(13D)	6363(17)	80359(18)	9490(30)	216(6)
C(14D)	5960(20)	76578(19)	20710(40)	255(7)
C(15D)	7735(19)	70414(18)	20390(30)	232(7)
C(16D)	4490(20)	87097(19)	10090(40)	282(8)
C(17D)	32200(20)	77514(16)	38530(30)	229(7)
C(18D)	25620(20)	79330(20)	37590(40)	348(9)
C(19D)	21470(30)	80520(30)	49430(50)	526(14)
C(20D)	25560(60)	79880(60)	62300(70)	1440(60)
C(21D)	31590(40)	76930(60)	63360(50)	1140(40)
C(22D)	36090(30)	76440(20)	51850(40)	356(10)

Bond lengths [Å] and angles [°] for 25a.

S(1)-O(3)	1.440(2)
S(1)-O(4)	1.431(2)
S(1)-N(2)	1.646(3)
S(1)-C(10)	1.761(3)
O(1)-C(5)	1.466(4)
O(1)-C(7)	1.352(4)
O(2)-C(7)	1.203(4)
N(1)-N(2)	1.404(4)
N(1)-C(8)	1.277(4)
N(2)-H(2)	0.8603
C(1)-C(2)	1.528(4)
C(1)-C(6)	1.532(4)
C(1)-C(7)	1.488(4)
C(1)-C(8)	1.493(4)
C(2)-H(2A)	1.0000
C(2)-C(3)	1.532(4)
C(2)-C(6)	1.509(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(4)	1.548(5)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.513(4)
C(5)-H(5)	1.0000
C(5)-C(6)	1.546(4)
C(6)-C(17)	1.481(4)
C(8)-C(9)	1.494(4)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-C(11)	1.396(4)
C(10)-C(15)	1.376(4)

C(11)-H(11)	0.9500
C(11)-C(12)	1.374(5)
C(12)-H(12)	0.9500
C(12)-C(13)	1.385(5)
C(13)-C(14)	1.386(5)
C(13)-C(16)	1.501(5)
C(14)-H(14)	0.9500
C(14)-C(15)	1.389(5)
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.340(5)
C(17)-C(22)	1.509(5)
C(18)-H(18)	0.9500
C(18)-C(19)	1.504(5)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(19)-C(20)	1.511(6)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(20)-C(21)	1.512(6)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(21)-C(22)	1.513(5)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
S(1B)-O(3B)	1.433(2)
S(1B)-O(4B)	1.437(2)
S(1B)-N(2B)	1.648(3)
S(1B)-C(10B)	1.751(4)
O(1B)-C(5B)	1.468(5)
O(1B)-C(7B)	1.349(4)
O(2B)-C(7B)	1.197(4)
N(1B)-N(2B)	1.403(3)
N(1B)-C(8B)	1.277(4)

N(2B)-H(2B)	0.8596
C(1B)-C(2B)	1.535(4)
C(1B)-C(6B)	1.529(4)
C(1B)-C(7B)	1.494(4)
C(1B)-C(8B)	1.480(4)
C(2B)-H(2BA)	1.0000
C(2B)-C(3B)	1.531(5)
C(2B)-C(6B)	1.508(4)
C(3B)-H(3BA)	0.9900
C(3B)-H(3BB)	0.9900
C(3B)-C(4B)	1.532(5)
C(4B)-H(4BA)	0.9900
C(4B)-H(4BB)	0.9900
C(4B)-C(5B)	1.522(5)
C(5B)-H(5B)	1.0000
C(5B)-C(6B)	1.532(5)
C(6B)-C(17B)	1.488(5)
C(8B)-C(9B)	1.502(4)
C(9B)-H(9BA)	0.9800
C(9B)-H(9BB)	0.9800
C(9B)-H(9BC)	0.9800
C(10B)-C(11B)	1.402(5)
C(10B)-C(15B)	1.396(4)
C(11B)-H(11B)	0.9500
C(11B)-C(12B)	1.381(6)
C(12B)-H(12B)	0.9500
C(12B)-C(13B)	1.390(5)
C(13B)-C(14B)	1.394(5)
C(13B)-C(16B)	1.495(6)
C(14B)-H(14B)	0.9500
C(14B)-C(15B)	1.370(6)
C(15B)-H(15B)	0.9500
C(16B)-H(16D)	0.9800
C(16B)-H(16E)	0.9800
C(16B)-H(16F)	0.9800
C(17B)-C(18B)	1.340(6)

C(17B)-C(22B)	1.496(5)
C(18B)-H(18B)	0.9500
C(18B)-C(19B)	1.504(6)
C(19B)-H(19C)	0.9900
C(19B)-H(19D)	0.9900
C(19B)-C(20B)	1.550(8)
C(20B)-H(20C)	0.9900
C(20B)-H(20D)	0.9900
C(20B)-C(21B)	1.496(9)
C(21B)-H(21C)	0.9900
C(21B)-H(21D)	0.9900
C(21B)-C(22B)	1.514(6)
C(22B)-H(22C)	0.9900
C(22B)-H(22D)	0.9900
S(1C)-O(3C)	1.435(2)
S(1C)-O(4C)	1.432(2)
S(1C)-N(2C)	1.652(3)
S(1C)-C(10C)	1.762(4)
O(1C)-C(5C)	1.468(4)
O(1C)-C(7C)	1.345(4)
O(2C)-C(7C)	1.200(4)
N(1C)-N(2C)	1.400(4)
N(1C)-C(8C)	1.283(4)
N(2C)-H(2C)	0.8602
C(1C)-C(2C)	1.533(4)
C(1C)-C(6C)	1.536(4)
C(1C)-C(7C)	1.488(4)
C(1C)-C(8C)	1.482(4)
C(2C)-H(2CA)	1.0000
C(2C)-C(3C)	1.532(4)
C(2C)-C(6C)	1.505(4)
C(3C)-H(3CA)	0.9900
C(3C)-H(3CB)	0.9900
C(3C)-C(4C)	1.541(5)
C(4C)-H(4CA)	0.9900
C(4C)-H(4CB)	0.9900

C(4C)-C(5C)	1.516(4)
C(5C)-H(5C)	1.0000
C(5C)-C(6C)	1.537(4)
C(6C)-C(17C)	1.478(4)
C(8C)-C(9C)	1.500(4)
C(9C)-H(9CA)	0.9800
C(9C)-H(9CB)	0.9800
C(9C)-H(9CC)	0.9800
C(10C)-C(11C)	1.393(4)
C(10C)-C(15C)	1.394(4)
C(11C)-H(11C)	0.9500
C(11C)-C(12C)	1.388(6)
C(12C)-H(12C)	0.9500
C(12C)-C(13C)	1.379(5)
C(13C)-C(14C)	1.397(5)
C(13C)-C(16C)	1.505(5)
C(14C)-H(14C)	0.9500
C(14C)-C(15C)	1.390(5)
C(15C)-H(15C)	0.9500
C(16C)-H(16G)	0.9800
C(16C)-H(16H)	0.9800
C(16C)-H(16I)	0.9800
C(17C)-C(18C)	1.340(5)
C(17C)-C(22C)	1.511(5)
C(18C)-H(18C)	0.9500
C(18C)-C(19C)	1.505(5)
C(19C)-H(19E)	0.9900
C(19C)-H(19F)	0.9900
C(19C)-C(20C)	1.531(7)
C(20C)-H(20E)	0.9900
C(20C)-H(20F)	0.9900
C(20C)-C(21C)	1.515(7)
C(21C)-H(21E)	0.9900
C(21C)-H(21F)	0.9900
C(21C)-C(22C)	1.508(5)
C(22C)-H(22E)	0.9900

C(22C)-H(22F)	0.9900
S(1D)-O(3D)	1.428(2)
S(1D)-O(4D)	1.434(2)
S(1D)-N(2D)	1.647(3)
S(1D)-C(10D)	1.746(3)
O(1D)-C(5D)	1.464(4)
O(1D)-C(7D)	1.348(4)
O(2D)-C(7D)	1.201(4)
N(1D)-N(2D)	1.411(4)
N(1D)-C(8D)	1.277(4)
N(2D)-H(2D)	0.8599
C(1D)-C(2D)	1.527(4)
C(1D)-C(6D)	1.531(4)
C(1D)-C(7D)	1.494(4)
C(1D)-C(8D)	1.490(4)
C(2D)-H(2DA)	1.0000
C(2D)-C(3D)	1.528(5)
C(2D)-C(6D)	1.509(4)
C(3D)-H(3DA)	0.9900
C(3D)-H(3DB)	0.9900
C(3D)-C(4D)	1.551(5)
C(4D)-H(4DA)	0.9900
C(4D)-H(4DB)	0.9900
C(4D)-C(5D)	1.521(5)
C(5D)-H(5D)	1.0000
C(5D)-C(6D)	1.542(5)
C(6D)-C(17D)	1.484(5)
C(8D)-C(9D)	1.488(4)
C(9D)-H(9DA)	0.9800
C(9D)-H(9DB)	0.9800
C(9D)-H(9DC)	0.9800
C(10D)-C(11D)	1.387(4)
C(10D)-C(15D)	1.397(4)
C(11D)-H(11D)	0.9500
C(11D)-C(12D)	1.383(6)
C(12D)-H(12D)	0.9500

C(12D)-C(13D)	1.387(5)
C(13D)-C(14D)	1.392(5)
C(13D)-C(16D)	1.502(5)
C(14D)-H(14D)	0.9500
C(14D)-C(15D)	1.376(5)
C(15D)-H(15D)	0.9500
C(16D)-H(16J)	0.9800
C(16D)-H(16K)	0.9800
C(16D)-H(16L)	0.9800
C(17D)-C(18D)	1.333(6)
C(17D)-C(22D)	1.504(5)
C(18D)-H(18D)	0.9500
C(18D)-C(19D)	1.495(6)
C(19D)-H(19G)	0.9900
C(19D)-H(19H)	0.9900
C(19D)-C(20D)	1.472(10)
C(20D)-H(20G)	0.9900
C(20D)-H(20H)	0.9900
C(20D)-C(21D)	1.334(12)
C(21D)-H(21G)	0.9900
C(21D)-H(21H)	0.9900
C(21D)-C(22D)	1.490(8)
C(22D)-H(22G)	0.9900
C(22D)-H(22H)	0.9900

O(3)-S(1)-N(2)	106.95(14)
O(3)-S(1)-C(10)	108.01(15)
O(4)-S(1)-O(3)	119.12(15)
O(4)-S(1)-N(2)	104.63(14)
O(4)-S(1)-C(10)	110.16(15)
N(2)-S(1)-C(10)	107.33(15)
C(7)-O(1)-C(5)	111.2(2)
C(8)-N(1)-N(2)	115.7(2)
S(1)-N(2)-H(2)	113.2
N(1)-N(2)-S(1)	111.25(19)
N(1)-N(2)-H(2)	113.3

C(2)-C(1)-C(6)	59.1(2)
C(7)-C(1)-C(2)	117.1(3)
C(7)-C(1)-C(6)	106.4(3)
C(7)-C(1)-C(8)	118.5(3)
C(8)-C(1)-C(2)	119.9(3)
C(8)-C(1)-C(6)	120.9(2)
C(1)-C(2)-H(2A)	117.9
C(1)-C(2)-C(3)	119.4(3)
C(3)-C(2)-H(2A)	117.9
C(6)-C(2)-C(1)	60.6(2)
C(6)-C(2)-H(2A)	117.9
C(6)-C(2)-C(3)	109.3(3)
C(2)-C(3)-H(3A)	111.0
C(2)-C(3)-H(3B)	111.0
C(2)-C(3)-C(4)	103.9(2)
H(3A)-C(3)-H(3B)	109.0
C(4)-C(3)-H(3A)	111.0
C(4)-C(3)-H(3B)	111.0
C(3)-C(4)-H(4A)	111.1
C(3)-C(4)-H(4B)	111.1
H(4A)-C(4)-H(4B)	109.1
C(5)-C(4)-C(3)	103.4(3)
C(5)-C(4)-H(4A)	111.1
C(5)-C(4)-H(4B)	111.1
O(1)-C(5)-C(4)	107.6(3)
O(1)-C(5)-H(5)	112.8
O(1)-C(5)-C(6)	106.2(3)
C(4)-C(5)-H(5)	112.8
C(4)-C(5)-C(6)	104.2(3)
C(6)-C(5)-H(5)	112.8
C(1)-C(6)-C(5)	102.9(2)
C(2)-C(6)-C(1)	60.3(2)
C(2)-C(6)-C(5)	103.1(2)
C(17)-C(6)-C(1)	121.8(3)
C(17)-C(6)-C(2)	129.3(3)
C(17)-C(6)-C(5)	122.3(3)

O(1)-C(7)-C(1)	110.6(3)
O(2)-C(7)-O(1)	122.4(3)
O(2)-C(7)-C(1)	127.0(3)
N(1)-C(8)-C(1)	115.7(3)
N(1)-C(8)-C(9)	126.0(3)
C(1)-C(8)-C(9)	118.2(3)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-S(1)	118.5(3)
C(15)-C(10)-S(1)	120.4(2)
C(15)-C(10)-C(11)	121.1(3)
C(10)-C(11)-H(11)	120.5
C(12)-C(11)-C(10)	119.0(3)
C(12)-C(11)-H(11)	120.5
C(11)-C(12)-H(12)	119.4
C(11)-C(12)-C(13)	121.2(3)
C(13)-C(12)-H(12)	119.4
C(12)-C(13)-C(14)	118.8(3)
C(12)-C(13)-C(16)	120.0(3)
C(14)-C(13)-C(16)	121.2(3)
C(13)-C(14)-H(14)	119.4
C(13)-C(14)-C(15)	121.1(3)
C(15)-C(14)-H(14)	119.4
C(10)-C(15)-C(14)	118.8(3)
C(10)-C(15)-H(15)	120.6
C(14)-C(15)-H(15)	120.6
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

C(6)-C(17)-C(22)	115.2(3)
C(18)-C(17)-C(6)	122.4(3)
C(18)-C(17)-C(22)	122.1(3)
C(17)-C(18)-H(18)	118.5
C(17)-C(18)-C(19)	123.0(3)
C(19)-C(18)-H(18)	118.5
C(18)-C(19)-H(19A)	108.9
C(18)-C(19)-H(19B)	108.9
C(18)-C(19)-C(20)	113.6(3)
H(19A)-C(19)-H(19B)	107.7
C(20)-C(19)-H(19A)	108.9
C(20)-C(19)-H(19B)	108.9
C(19)-C(20)-H(20A)	109.3
C(19)-C(20)-H(20B)	109.3
C(19)-C(20)-C(21)	111.5(3)
H(20A)-C(20)-H(20B)	108.0
C(21)-C(20)-H(20A)	109.3
C(21)-C(20)-H(20B)	109.3
C(20)-C(21)-H(21A)	109.4
C(20)-C(21)-H(21B)	109.4
C(20)-C(21)-C(22)	111.1(3)
H(21A)-C(21)-H(21B)	108.0
C(22)-C(21)-H(21A)	109.4
C(22)-C(21)-H(21B)	109.4
C(17)-C(22)-C(21)	112.4(3)
C(17)-C(22)-H(22A)	109.1
C(17)-C(22)-H(22B)	109.1
C(21)-C(22)-H(22A)	109.1
C(21)-C(22)-H(22B)	109.1
H(22A)-C(22)-H(22B)	107.9
O(3B)-S(1B)-O(4B)	119.67(15)
O(3B)-S(1B)-N(2B)	104.24(14)
O(3B)-S(1B)-C(10B)	109.80(16)
O(4B)-S(1B)-N(2B)	107.40(14)
O(4B)-S(1B)-C(10B)	108.51(15)
N(2B)-S(1B)-C(10B)	106.40(15)

C(7B)-O(1B)-C(5B)	110.8(3)
C(8B)-N(1B)-N(2B)	114.7(3)
S(1B)-N(2B)-H(2B)	113.6
N(1B)-N(2B)-S(1B)	111.1(2)
N(1B)-N(2B)-H(2B)	113.7
C(6B)-C(1B)-C(2B)	59.0(2)
C(7B)-C(1B)-C(2B)	117.5(3)
C(7B)-C(1B)-C(6B)	107.1(3)
C(8B)-C(1B)-C(2B)	120.5(3)
C(8B)-C(1B)-C(6B)	120.0(3)
C(8B)-C(1B)-C(7B)	117.9(3)
C(1B)-C(2B)-H(2BA)	117.9
C(3B)-C(2B)-C(1B)	119.6(3)
C(3B)-C(2B)-H(2BA)	117.9
C(6B)-C(2B)-C(1B)	60.3(2)
C(6B)-C(2B)-H(2BA)	117.9
C(6B)-C(2B)-C(3B)	109.7(3)
C(2B)-C(3B)-H(3BA)	111.0
C(2B)-C(3B)-H(3BB)	111.0
C(2B)-C(3B)-C(4B)	103.9(3)
H(3BA)-C(3B)-H(3BB)	109.0
C(4B)-C(3B)-H(3BA)	111.0
C(4B)-C(3B)-H(3BB)	111.0
C(3B)-C(4B)-H(4BA)	111.1
C(3B)-C(4B)-H(4BB)	111.1
H(4BA)-C(4B)-H(4BB)	109.0
C(5B)-C(4B)-C(3B)	103.5(3)
C(5B)-C(4B)-H(4BA)	111.1
C(5B)-C(4B)-H(4BB)	111.1
O(1B)-C(5B)-C(4B)	107.6(3)
O(1B)-C(5B)-H(5B)	112.3
O(1B)-C(5B)-C(6B)	107.2(3)
C(4B)-C(5B)-H(5B)	112.3
C(4B)-C(5B)-C(6B)	104.6(3)
C(6B)-C(5B)-H(5B)	112.3
C(1B)-C(6B)-C(5B)	102.1(3)

C(2B)-C(6B)-C(1B)	60.7(2)
C(2B)-C(6B)-C(5B)	102.6(3)
C(17B)-C(6B)-C(1B)	122.5(3)
C(17B)-C(6B)-C(2B)	127.3(3)
C(17B)-C(6B)-C(5B)	123.9(3)
O(1B)-C(7B)-C(1B)	109.8(3)
O(2B)-C(7B)-O(1B)	121.8(3)
O(2B)-C(7B)-C(1B)	128.4(3)
N(1B)-C(8B)-C(1B)	116.2(3)
N(1B)-C(8B)-C(9B)	125.5(3)
C(1B)-C(8B)-C(9B)	118.2(3)
C(8B)-C(9B)-H(9BA)	109.5
C(8B)-C(9B)-H(9BB)	109.5
C(8B)-C(9B)-H(9BC)	109.5
H(9BA)-C(9B)-H(9BB)	109.5
H(9BA)-C(9B)-H(9BC)	109.5
H(9BB)-C(9B)-H(9BC)	109.5
C(11B)-C(10B)-S(1B)	120.8(3)
C(15B)-C(10B)-S(1B)	118.9(3)
C(15B)-C(10B)-C(11B)	120.2(3)
C(10B)-C(11B)-H(11B)	120.7
C(12B)-C(11B)-C(10B)	118.6(3)
C(12B)-C(11B)-H(11B)	120.7
C(11B)-C(12B)-H(12B)	118.9
C(11B)-C(12B)-C(13B)	122.1(3)
C(13B)-C(12B)-H(12B)	118.9
C(12B)-C(13B)-C(14B)	117.8(4)
C(12B)-C(13B)-C(16B)	121.7(3)
C(14B)-C(13B)-C(16B)	120.6(3)
C(13B)-C(14B)-H(14B)	119.1
C(15B)-C(14B)-C(13B)	121.8(3)
C(15B)-C(14B)-H(14B)	119.1
C(10B)-C(15B)-H(15B)	120.3
C(14B)-C(15B)-C(10B)	119.4(3)
C(14B)-C(15B)-H(15B)	120.3
C(13B)-C(16B)-H(16D)	109.5

C(13B)-C(16B)-H(16E)	109.5
C(13B)-C(16B)-H(16F)	109.5
H(16D)-C(16B)-H(16E)	109.5
H(16D)-C(16B)-H(16F)	109.5
H(16E)-C(16B)-H(16F)	109.5
C(6B)-C(17B)-C(22B)	115.1(3)
C(18B)-C(17B)-C(6B)	121.6(3)
C(18B)-C(17B)-C(22B)	123.2(3)
C(17B)-C(18B)-H(18B)	118.3
C(17B)-C(18B)-C(19B)	123.4(4)
C(19B)-C(18B)-H(18B)	118.3
C(18B)-C(19B)-H(19C)	109.4
C(18B)-C(19B)-H(19D)	109.4
C(18B)-C(19B)-C(20B)	111.4(4)
H(19C)-C(19B)-H(19D)	108.0
C(20B)-C(19B)-H(19C)	109.4
C(20B)-C(19B)-H(19D)	109.4
C(19B)-C(20B)-H(20C)	109.1
C(19B)-C(20B)-H(20D)	109.1
H(20C)-C(20B)-H(20D)	107.9
C(21B)-C(20B)-C(19B)	112.3(4)
C(21B)-C(20B)-H(20C)	109.1
C(21B)-C(20B)-H(20D)	109.1
C(20B)-C(21B)-H(21C)	109.4
C(20B)-C(21B)-H(21D)	109.4
C(20B)-C(21B)-C(22B)	111.2(4)
H(21C)-C(21B)-H(21D)	108.0
C(22B)-C(21B)-H(21C)	109.4
C(22B)-C(21B)-H(21D)	109.4
C(17B)-C(22B)-C(21B)	112.8(4)
C(17B)-C(22B)-H(22C)	109.0
C(17B)-C(22B)-H(22D)	109.0
C(21B)-C(22B)-H(22C)	109.0
C(21B)-C(22B)-H(22D)	109.0
H(22C)-C(22B)-H(22D)	107.8
O(3C)-S(1C)-N(2C)	106.71(14)

O(3C)-S(1C)-C(10C)	108.08(15)
O(4C)-S(1C)-O(3C)	119.43(15)
O(4C)-S(1C)-N(2C)	104.18(14)
O(4C)-S(1C)-C(10C)	110.35(16)
N(2C)-S(1C)-C(10C)	107.40(15)
C(7C)-O(1C)-C(5C)	110.7(2)
C(8C)-N(1C)-N(2C)	115.1(3)
S(1C)-N(2C)-H(2C)	113.3
N(1C)-N(2C)-S(1C)	111.5(2)
N(1C)-N(2C)-H(2C)	113.5
C(2C)-C(1C)-C(6C)	58.74(19)
C(7C)-C(1C)-C(2C)	117.6(2)
C(7C)-C(1C)-C(6C)	106.6(2)
C(8C)-C(1C)-C(2C)	119.7(3)
C(8C)-C(1C)-C(6C)	121.1(2)
C(8C)-C(1C)-C(7C)	118.3(3)
C(1C)-C(2C)-H(2CA)	117.9
C(3C)-C(2C)-C(1C)	119.4(3)
C(3C)-C(2C)-H(2CA)	117.9
C(6C)-C(2C)-C(1C)	60.72(19)
C(6C)-C(2C)-H(2CA)	117.9
C(6C)-C(2C)-C(3C)	109.5(2)
C(2C)-C(3C)-H(3CA)	111.0
C(2C)-C(3C)-H(3CB)	111.0
C(2C)-C(3C)-C(4C)	103.8(2)
H(3CA)-C(3C)-H(3CB)	109.0
C(4C)-C(3C)-H(3CA)	111.0
C(4C)-C(3C)-H(3CB)	111.0
C(3C)-C(4C)-H(4CA)	111.0
C(3C)-C(4C)-H(4CB)	111.0
H(4CA)-C(4C)-H(4CB)	109.0
C(5C)-C(4C)-C(3C)	103.6(2)
C(5C)-C(4C)-H(4CA)	111.0
C(5C)-C(4C)-H(4CB)	111.0
O(1C)-C(5C)-C(4C)	107.6(2)
O(1C)-C(5C)-H(5C)	112.4

O(1C)-C(5C)-C(6C)	107.0(2)
C(4C)-C(5C)-H(5C)	112.4
C(4C)-C(5C)-C(6C)	104.4(3)
C(6C)-C(5C)-H(5C)	112.4
C(1C)-C(6C)-C(5C)	102.2(2)
C(2C)-C(6C)-C(1C)	60.54(19)
C(2C)-C(6C)-C(5C)	103.0(2)
C(17C)-C(6C)-C(1C)	121.9(2)
C(17C)-C(6C)-C(2C)	128.7(3)
C(17C)-C(6C)-C(5C)	122.9(3)
O(1C)-C(7C)-C(1C)	110.6(3)
O(2C)-C(7C)-O(1C)	121.9(3)
O(2C)-C(7C)-C(1C)	127.5(3)
N(1C)-C(8C)-C(1C)	115.4(3)
N(1C)-C(8C)-C(9C)	126.9(3)
C(1C)-C(8C)-C(9C)	117.7(3)
C(8C)-C(9C)-H(9CA)	109.5
C(8C)-C(9C)-H(9CB)	109.5
C(8C)-C(9C)-H(9CC)	109.5
H(9CA)-C(9C)-H(9CB)	109.5
H(9CA)-C(9C)-H(9CC)	109.5
H(9CB)-C(9C)-H(9CC)	109.5
C(11C)-C(10C)-S(1C)	119.9(3)
C(11C)-C(10C)-C(15C)	120.2(3)
C(15C)-C(10C)-S(1C)	119.8(3)
C(10C)-C(11C)-H(11C)	120.4
C(12C)-C(11C)-C(10C)	119.3(3)
C(12C)-C(11C)-H(11C)	120.4
C(11C)-C(12C)-H(12C)	119.3
C(13C)-C(12C)-C(11C)	121.4(3)
C(13C)-C(12C)-H(12C)	119.3
C(12C)-C(13C)-C(14C)	119.0(3)
C(12C)-C(13C)-C(16C)	120.3(3)
C(14C)-C(13C)-C(16C)	120.7(3)
C(13C)-C(14C)-H(14C)	119.7
C(15C)-C(14C)-C(13C)	120.7(3)

C(15C)-C(14C)-H(14C)	119.7
C(10C)-C(15C)-H(15C)	120.3
C(14C)-C(15C)-C(10C)	119.4(3)
C(14C)-C(15C)-H(15C)	120.3
C(13C)-C(16C)-H(16G)	109.5
C(13C)-C(16C)-H(16H)	109.5
C(13C)-C(16C)-H(16I)	109.5
H(16G)-C(16C)-H(16H)	109.5
H(16G)-C(16C)-H(16I)	109.5
H(16H)-C(16C)-H(16I)	109.5
C(6C)-C(17C)-C(22C)	115.2(3)
C(18C)-C(17C)-C(6C)	122.5(3)
C(18C)-C(17C)-C(22C)	122.2(3)
C(17C)-C(18C)-H(18C)	118.4
C(17C)-C(18C)-C(19C)	123.2(4)
C(19C)-C(18C)-H(18C)	118.4
C(18C)-C(19C)-H(19E)	109.0
C(18C)-C(19C)-H(19F)	109.0
C(18C)-C(19C)-C(20C)	112.9(4)
H(19E)-C(19C)-H(19F)	107.8
C(20C)-C(19C)-H(19E)	109.0
C(20C)-C(19C)-H(19F)	109.0
C(19C)-C(20C)-H(20E)	109.1
C(19C)-C(20C)-H(20F)	109.1
H(20E)-C(20C)-H(20F)	107.8
C(21C)-C(20C)-C(19C)	112.6(4)
C(21C)-C(20C)-H(20E)	109.1
C(21C)-C(20C)-H(20F)	109.1
C(20C)-C(21C)-H(21E)	109.6
C(20C)-C(21C)-H(21F)	109.6
H(21E)-C(21C)-H(21F)	108.1
C(22C)-C(21C)-C(20C)	110.2(3)
C(22C)-C(21C)-H(21E)	109.6
C(22C)-C(21C)-H(21F)	109.6
C(17C)-C(22C)-H(22E)	109.0
C(17C)-C(22C)-H(22F)	109.0

C(21C)-C(22C)-C(17C)	113.1(3)
C(21C)-C(22C)-H(22E)	109.0
C(21C)-C(22C)-H(22F)	109.0
H(22E)-C(22C)-H(22F)	107.8
O(3D)-S(1D)-O(4D)	119.56(16)
O(3D)-S(1D)-N(2D)	104.59(14)
O(3D)-S(1D)-C(10D)	111.06(15)
O(4D)-S(1D)-N(2D)	107.65(14)
O(4D)-S(1D)-C(10D)	108.15(15)
N(2D)-S(1D)-C(10D)	104.75(15)
C(7D)-O(1D)-C(5D)	111.1(3)
C(8D)-N(1D)-N(2D)	115.5(2)
S(1D)-N(2D)-H(2D)	113.3
N(1D)-N(2D)-S(1D)	111.66(19)
N(1D)-N(2D)-H(2D)	113.2
C(2D)-C(1D)-C(6D)	59.1(2)
C(7D)-C(1D)-C(2D)	116.5(3)
C(7D)-C(1D)-C(6D)	106.5(3)
C(8D)-C(1D)-C(2D)	120.8(3)
C(8D)-C(1D)-C(6D)	121.9(3)
C(8D)-C(1D)-C(7D)	117.8(3)
C(1D)-C(2D)-H(2DA)	117.7
C(1D)-C(2D)-C(3D)	120.0(3)
C(3D)-C(2D)-H(2DA)	117.7
C(6D)-C(2D)-C(1D)	60.6(2)
C(6D)-C(2D)-H(2DA)	117.7
C(6D)-C(2D)-C(3D)	109.5(3)
C(2D)-C(3D)-H(3DA)	110.9
C(2D)-C(3D)-H(3DB)	110.9
C(2D)-C(3D)-C(4D)	104.3(3)
H(3DA)-C(3D)-H(3DB)	108.9
C(4D)-C(3D)-H(3DA)	110.9
C(4D)-C(3D)-H(3DB)	110.9
C(3D)-C(4D)-H(4DA)	111.2
C(3D)-C(4D)-H(4DB)	111.2
H(4DA)-C(4D)-H(4DB)	109.1

C(5D)-C(4D)-C(3D)	103.0(3)
C(5D)-C(4D)-H(4DA)	111.2
C(5D)-C(4D)-H(4DB)	111.2
O(1D)-C(5D)-C(4D)	107.0(3)
O(1D)-C(5D)-H(5D)	112.6
O(1D)-C(5D)-C(6D)	106.8(3)
C(4D)-C(5D)-H(5D)	112.6
C(4D)-C(5D)-C(6D)	104.6(3)
C(6D)-C(5D)-H(5D)	112.6
C(1D)-C(6D)-C(5D)	102.6(3)
C(2D)-C(6D)-C(1D)	60.3(2)
C(2D)-C(6D)-C(5D)	103.0(3)
C(17D)-C(6D)-C(1D)	122.3(3)
C(17D)-C(6D)-C(2D)	127.1(3)
C(17D)-C(6D)-C(5D)	123.8(3)
O(1D)-C(7D)-C(1D)	110.4(3)
O(2D)-C(7D)-O(1D)	122.8(3)
O(2D)-C(7D)-C(1D)	126.8(3)
N(1D)-C(8D)-C(1D)	116.4(3)
N(1D)-C(8D)-C(9D)	125.6(3)
C(9D)-C(8D)-C(1D)	118.0(3)
C(8D)-C(9D)-H(9DA)	109.5
C(8D)-C(9D)-H(9DB)	109.5
C(8D)-C(9D)-H(9DC)	109.5
H(9DA)-C(9D)-H(9DB)	109.5
H(9DA)-C(9D)-H(9DC)	109.5
H(9DB)-C(9D)-H(9DC)	109.5
C(11D)-C(10D)-S(1D)	121.4(3)
C(11D)-C(10D)-C(15D)	120.4(3)
C(15D)-C(10D)-S(1D)	118.2(2)
C(10D)-C(11D)-H(11D)	120.6
C(12D)-C(11D)-C(10D)	118.8(3)
C(12D)-C(11D)-H(11D)	120.6
C(11D)-C(12D)-H(12D)	119.0
C(11D)-C(12D)-C(13D)	121.9(3)
C(13D)-C(12D)-H(12D)	119.0

C(12D)-C(13D)-C(14D)	118.0(4)
C(12D)-C(13D)-C(16D)	121.3(3)
C(14D)-C(13D)-C(16D)	120.7(3)
C(13D)-C(14D)-H(14D)	119.3
C(15D)-C(14D)-C(13D)	121.4(3)
C(15D)-C(14D)-H(14D)	119.3
C(10D)-C(15D)-H(15D)	120.4
C(14D)-C(15D)-C(10D)	119.3(3)
C(14D)-C(15D)-H(15D)	120.4
C(13D)-C(16D)-H(16J)	109.5
C(13D)-C(16D)-H(16K)	109.5
C(13D)-C(16D)-H(16L)	109.5
H(16J)-C(16D)-H(16K)	109.5
H(16J)-C(16D)-H(16L)	109.5
H(16K)-C(16D)-H(16L)	109.5
C(6D)-C(17D)-C(22D)	115.7(3)
C(18D)-C(17D)-C(6D)	122.0(3)
C(18D)-C(17D)-C(22D)	122.2(4)
C(17D)-C(18D)-H(18D)	118.0
C(17D)-C(18D)-C(19D)	123.9(4)
C(19D)-C(18D)-H(18D)	118.0
C(18D)-C(19D)-H(19G)	109.1
C(18D)-C(19D)-H(19H)	109.1
H(19G)-C(19D)-H(19H)	107.8
C(20D)-C(19D)-C(18D)	112.7(5)
C(20D)-C(19D)-H(19G)	109.1
C(20D)-C(19D)-H(19H)	109.1
C(19D)-C(20D)-H(20G)	106.7
C(19D)-C(20D)-H(20H)	106.7
H(20G)-C(20D)-H(20H)	106.6
C(21D)-C(20D)-C(19D)	122.5(6)
C(21D)-C(20D)-H(20G)	106.7
C(21D)-C(20D)-H(20H)	106.7
C(20D)-C(21D)-H(21G)	106.9
C(20D)-C(21D)-H(21H)	106.9
C(20D)-C(21D)-C(22D)	121.8(6)

H(21G)-C(21D)-H(21H)	106.7
C(22D)-C(21D)-H(21G)	106.9
C(22D)-C(21D)-H(21H)	106.9
C(17D)-C(22D)-H(22G)	109.1
C(17D)-C(22D)-H(22H)	109.1
C(21D)-C(22D)-C(17D)	112.7(5)
C(21D)-C(22D)-H(22G)	109.1
C(21D)-C(22D)-H(22H)	109.1
H(22G)-C(22D)-H(22H)	107.8

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å²x 10⁴) for 25a. The anisotropic displacement factor exponent takes the form: -2p²[h² a*²U¹¹ + ... + 2 h k a* b* U¹²]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	133(3)	254(4)	66(3)	3(3)	22(2)	-17(3)
O(1)	151(10)	238(12)	190(11)	9(9)	3(8)	-10(9)
O(2)	222(12)	188(11)	224(12)	-5(9)	21(9)	41(9)
O(3)	224(11)	294(12)	55(9)	-20(8)	28(8)	-9(9)
O(4)	185(11)	310(13)	141(10)	45(9)	23(8)	-45(10)
N(1)	136(11)	208(12)	84(10)	3(9)	40(9)	8(9)
N(2)	140(11)	239(13)	86(10)	37(9)	19(9)	-9(10)
C(1)	176(13)	137(13)	78(11)	13(9)	4(10)	1(10)
C(2)	192(14)	168(14)	124(13)	29(10)	1(10)	13(11)
C(3)	272(16)	211(15)	122(13)	61(11)	19(12)	-11(13)
C(4)	280(17)	236(16)	147(14)	57(12)	49(12)	-71(13)
C(5)	203(15)	211(15)	132(13)	7(11)	8(11)	-42(12)
C(6)	188(14)	152(13)	107(12)	21(10)	20(10)	-9(11)
C(7)	167(13)	179(14)	104(12)	55(10)	-9(10)	-5(11)
C(8)	172(13)	148(13)	76(11)	10(10)	23(10)	14(10)
C(9)	220(15)	229(16)	158(14)	64(12)	-35(12)	-28(12)
C(10)	135(13)	242(15)	110(12)	-11(11)	18(10)	9(11)
C(11)	231(16)	301(18)	153(14)	-9(13)	99(12)	0(13)
C(12)	219(16)	311(18)	199(15)	-51(13)	86(13)	11(14)
C(13)	143(14)	293(17)	209(15)	-45(13)	-36(12)	42(12)
C(14)	400(20)	291(18)	116(14)	14(13)	19(13)	46(16)
C(15)	335(19)	276(17)	82(13)	7(12)	46(12)	74(14)
C(16)	253(17)	330(20)	279(18)	-45(15)	-47(14)	56(15)
C(17)	266(16)	146(13)	136(13)	-2(11)	54(11)	-26(12)
C(18)	317(18)	211(16)	212(16)	10(13)	50(14)	32(14)
C(19)	290(19)	390(20)	310(20)	-10(17)	151(16)	44(16)
C(20)	400(20)	299(19)	213(17)	-54(14)	147(15)	-23(16)
C(21)	307(19)	342(19)	157(15)	-6(14)	48(13)	-26(15)

C(22)	275(17)	242(16)	108(13)	-7(11)	14(12)	-20(13)
S(1B)	152(3)	264(4)	64(3)	30(3)	25(2)	61(3)
O(1B)	150(11)	249(12)	303(13)	-28(10)	-14(9)	44(9)
O(2B)	212(12)	212(12)	299(13)	-30(10)	54(10)	-37(9)
O(3B)	216(12)	326(13)	139(10)	10(9)	49(9)	112(10)
O(4B)	230(12)	362(14)	55(9)	64(9)	37(8)	61(10)
N(1B)	157(11)	174(12)	101(10)	15(9)	37(9)	45(9)
N(2B)	141(11)	200(12)	82(10)	8(9)	16(8)	46(9)
C(1B)	151(13)	144(13)	110(12)	7(10)	2(10)	18(10)
C(2B)	203(14)	154(13)	158(13)	-29(11)	23(11)	-6(11)
C(3B)	284(17)	194(15)	200(15)	-36(12)	49(13)	23(13)
C(4B)	294(18)	209(16)	278(18)	-44(13)	44(14)	98(14)
C(5B)	205(15)	218(16)	226(16)	-14(12)	-23(12)	81(12)
C(6B)	203(14)	144(13)	136(13)	2(10)	-3(11)	33(11)
C(7B)	150(13)	203(15)	168(14)	-52(11)	10(11)	-3(11)
C(8B)	155(13)	145(13)	110(12)	3(10)	27(10)	19(10)
C(9B)	216(15)	221(15)	112(13)	-33(11)	-15(11)	26(12)
C(10B)	144(13)	277(16)	91(12)	18(11)	18(10)	29(12)
C(11B)	328(19)	342(19)	90(13)	-4(13)	63(12)	25(15)
C(12B)	304(19)	350(20)	131(14)	-48(13)	19(13)	12(15)
C(13B)	137(14)	348(19)	188(15)	-16(13)	9(11)	-17(13)
C(14B)	269(18)	390(20)	133(14)	12(14)	64(13)	-59(15)
C(15B)	273(17)	340(19)	95(13)	-12(12)	51(12)	-22(14)
C(16B)	273(18)	350(20)	256(18)	-52(15)	74(14)	-79(15)
C(17B)	357(19)	154(14)	139(14)	10(11)	53(13)	38(13)
C(18B)	390(20)	330(20)	219(17)	-4(15)	153(15)	-23(17)
C(19B)	480(30)	520(30)	350(20)	40(20)	230(20)	0(20)
C(20B)	980(50)	440(30)	350(20)	160(20)	370(30)	220(30)
C(21B)	890(40)	430(30)	210(20)	9(18)	100(20)	190(30)
C(22B)	520(30)	284(19)	156(15)	41(14)	-10(16)	79(18)
S(1C)	139(3)	267(4)	73(3)	28(3)	19(2)	57(3)
O(1C)	99(9)	207(11)	193(11)	-16(9)	21(8)	-7(8)
O(2C)	210(11)	191(11)	169(11)	16(8)	36(9)	-34(9)
O(3C)	224(11)	314(13)	83(9)	45(9)	25(8)	51(10)
O(4C)	181(11)	369(14)	162(11)	11(10)	26(9)	118(10)
N(1C)	124(11)	270(14)	83(10)	12(10)	26(8)	46(10)

N(2C)	161(12)	249(13)	82(10)	9(9)	19(9)	57(10)
C(1C)	117(12)	152(13)	87(11)	13(10)	2(9)	-13(10)
C(2C)	131(12)	179(13)	105(12)	-4(10)	4(10)	-24(10)
C(3C)	191(14)	212(15)	119(13)	-34(11)	33(11)	9(12)
C(4C)	195(15)	191(15)	181(14)	-21(11)	36(11)	41(12)
C(5C)	135(13)	163(13)	154(13)	5(11)	3(10)	21(10)
C(6C)	137(12)	136(13)	104(12)	-17(10)	21(10)	7(10)
C(7C)	117(12)	168(13)	111(12)	-30(10)	4(9)	-16(10)
C(8C)	136(12)	194(14)	72(11)	27(10)	16(9)	15(10)
C(9C)	220(15)	276(17)	137(13)	-68(12)	13(11)	42(13)
C(10C)	128(13)	283(16)	106(12)	33(11)	21(10)	49(11)
C(11C)	263(17)	338(19)	174(15)	40(13)	119(13)	77(14)
C(12C)	251(17)	370(20)	238(17)	106(15)	132(14)	30(15)
C(13C)	151(14)	300(17)	172(14)	73(13)	-10(11)	-24(12)
C(14C)	294(18)	317(19)	147(14)	-6(13)	52(13)	12(14)
C(15C)	294(18)	318(18)	116(13)	15(12)	89(12)	7(14)
C(16C)	243(17)	306(19)	266(18)	81(15)	25(14)	-13(14)
C(17C)	231(15)	155(13)	128(13)	4(10)	55(11)	21(11)
C(18C)	311(19)	276(18)	242(17)	5(14)	119(14)	-65(15)
C(19C)	410(20)	420(20)	410(20)	36(19)	260(20)	-50(19)
C(20C)	590(30)	390(20)	270(20)	68(17)	240(20)	60(20)
C(21C)	450(20)	370(20)	174(16)	16(15)	73(16)	67(18)
C(22C)	349(19)	272(17)	127(14)	25(12)	7(13)	82(15)
S(1D)	142(3)	273(4)	75(3)	-2(3)	25(2)	-10(3)
O(1D)	155(11)	219(12)	284(13)	34(10)	-19(9)	-33(9)
O(2D)	211(11)	179(11)	254(12)	44(9)	45(9)	25(9)
O(3D)	174(11)	306(13)	172(11)	15(9)	39(9)	-39(10)
O(4D)	232(12)	362(14)	84(9)	-36(9)	53(8)	-12(10)
N(1D)	130(11)	235(13)	88(10)	28(9)	38(9)	5(10)
N(2D)	147(11)	226(13)	78(10)	16(9)	23(8)	-9(10)
C(1D)	169(13)	152(13)	101(12)	27(10)	3(10)	17(11)
C(2D)	203(15)	227(15)	106(12)	61(11)	7(11)	47(12)
C(3D)	286(17)	241(16)	154(14)	73(12)	49(12)	34(13)
C(4D)	327(19)	214(16)	205(16)	54(13)	11(14)	-26(14)
C(5D)	241(16)	201(15)	196(15)	34(12)	-11(12)	-37(12)
C(6D)	236(15)	167(14)	118(13)	32(11)	-2(11)	12(12)

C(7D)	171(14)	182(14)	156(13)	73(11)	-10(11)	-9(11)
C(8D)	146(13)	189(14)	77(11)	6(10)	24(10)	9(11)
C(9D)	208(15)	271(16)	125(13)	53(12)	-28(11)	-12(13)
C(10D)	138(13)	247(15)	70(11)	22(10)	-7(10)	26(11)
C(11D)	380(20)	360(20)	88(13)	32(13)	60(13)	9(16)
C(12D)	390(20)	360(20)	130(15)	68(14)	58(14)	16(17)
C(13D)	154(14)	320(18)	173(14)	25(13)	6(11)	12(13)
C(14D)	264(17)	350(20)	160(15)	36(13)	84(13)	68(15)
C(15D)	268(17)	337(19)	99(13)	49(12)	58(12)	61(14)
C(16D)	265(18)	360(20)	227(17)	82(15)	67(14)	64(15)
C(17D)	370(19)	170(15)	150(14)	20(11)	46(13)	-1(13)
C(18D)	450(20)	400(20)	211(17)	42(16)	135(16)	141(19)
C(19D)	680(40)	590(30)	350(20)	0(20)	280(20)	140(30)
C(20D)	1780(100)	2350(130)	280(30)	100(50)	410(50)	1470(100)
C(21D)	790(50)	2530(130)	110(20)	270(40)	50(30)	-420(70)
C(22D)	570(30)	320(20)	159(16)	-24(14)	-60(17)	-61(19)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 25a.

	x	y	z	U(eq)
H(2)	2151	864	2106	19
H(2A)	3032	2765	1151	19
H(3A)	3806	3296	-195	24
H(3B)	4198	2645	-325	24
H(4A)	5080	3196	832	26
H(4B)	4548	3627	1581	26
H(5)	4915	2910	3254	22
H(9A)	3044	794	3349	31
H(9B)	3099	1403	4276	31
H(9C)	3778	1136	3654	31
H(11)	843	2144	2850	27
H(12)	529	3181	2787	29
H(14)	1069	3307	-1038	32
H(15)	1353	2254	-1026	28
H(16A)	906	4254	1448	43
H(16B)	106	4062	1187	43
H(16C)	574	4180	-56	43
H(18)	2658	3047	3227	29
H(19A)	2229	2714	5419	39
H(19B)	2363	3447	5347	39
H(20A)	2841	2923	7371	36
H(20B)	3347	3406	6689	36
H(21A)	3371	2088	6320	32
H(21B)	3938	2480	7224	32
H(22A)	4369	2943	5385	25
H(22B)	4292	2222	5007	25
H(2B)	2194	1708	7071	17
H(2BA)	2899	-233	5965	21
H(3BA)	4133	-157	4690	27

H(3BB)	3674	-788	4694	27
H(4BA)	4312	-1182	6502	31
H(4BB)	4913	-760	5901	31
H(5B)	4663	-522	8318	26
H(9BA)	3020	1044	9305	28
H(9BB)	3031	1677	8469	28
H(9BC)	3733	1304	8779	28
H(11B)	1162	336	3931	30
H(12B)	826	-705	3994	31
H(14B)	553	-563	7954	31
H(15B)	892	470	7940	28
H(16D)	831	-1663	6385	44
H(16E)	304	-1558	5104	44
H(16F)	51	-1461	6585	44
H(18B)	2420	-584	7800	37
H(19C)	1959	-1060	9716	53
H(19D)	1853	-331	9919	53
H(20C)	2366	-638	11953	69
H(20D)	2895	-1084	11261	69
H(21C)	3481	-201	12141	61
H(21D)	2974	238	11248	61
H(22C)	3949	178	10086	38
H(22D)	4009	-554	10317	38
H(2C)	1995	6475	7039	20
H(2CA)	2945	4632	6096	17
H(3CA)	4115	4817	4661	21
H(3CB)	3752	4143	4778	21
H(4CA)	4497	3857	6549	23
H(4CB)	5011	4330	5839	23
H(5C)	4802	4580	8267	18
H(9CA)	2869	6596	8327	32
H(9CB)	3617	6301	8637	32
H(9CC)	2951	5992	9250	32
H(11C)	466	5142	7426	30
H(12C)	280	4069	7352	34
H(14C)	1354	3947	4028	30

H(15C)	1532	5024	4056	29
H(16G)	675	3053	6579	41
H(16H)	1026	3010	5173	41
H(16I)	210	3123	5203	41
H(18C)	2561	4301	8105	33
H(19E)	2276	3837	10184	48
H(19F)	2071	4552	10284	48
H(20E)	2684	4398	12264	49
H(20F)	3232	3961	11602	49
H(21E)	3184	5282	11293	39
H(21F)	3762	4922	12202	39
H(22E)	4229	4499	10366	30
H(22F)	4126	5218	10021	30
H(2D)	2123	5637	2009	18
H(2DA)	2797	7637	1036	21
H(3DA)	3554	8210	-259	27
H(3DB)	4013	7591	-292	27
H(4DA)	4814	8218	898	30
H(4DB)	4223	8628	1531	30
H(5D)	4591	7973	3329	26
H(9DA)	2900	6357	4297	30
H(9DB)	3632	6141	3812	30
H(9DC)	2951	5725	3464	30
H(11D)	1168	6978	-1103	33
H(12D)	872	8021	-999	35
H(14D)	442	7829	2877	31
H(15D)	743	6790	2814	28
H(16J)	854	8955	1347	42
H(16K)	73	8761	1612	42
H(16L)	296	8852	108	42
H(18D)	2345	7990	2887	42
H(19G)	1960	8478	4879	63
H(19H)	1749	7757	4920	63
H(20G)	2647	8414	6583	173
H(20H)	2250	7781	6855	173
H(21G)	3058	7264	6626	137

H(21H)	3442	7894	7082	137
H(22G)	3815	7226	5183	43
H(22H)	3992	7952	5305	43

Torsion angles [°] for 25a.

S(1)-C(10)-C(11)-C(12)	-178.4(3)
S(1)-C(10)-C(15)-C(14)	179.5(3)
O(1)-C(5)-C(6)-C(1)	-16.3(3)
O(1)-C(5)-C(6)-C(2)	-78.3(3)
O(1)-C(5)-C(6)-C(17)	125.3(3)
O(3)-S(1)-N(2)-N(1)	59.8(2)
O(3)-S(1)-C(10)-C(11)	175.7(3)
O(3)-S(1)-C(10)-C(15)	-3.7(3)
O(4)-S(1)-N(2)-N(1)	-172.9(2)
O(4)-S(1)-C(10)-C(11)	44.0(3)
O(4)-S(1)-C(10)-C(15)	-135.3(3)
N(2)-S(1)-C(10)-C(11)	-69.3(3)
N(2)-S(1)-C(10)-C(15)	111.3(3)
N(2)-N(1)-C(8)-C(1)	-176.8(2)
N(2)-N(1)-C(8)-C(9)	0.0(4)
C(1)-C(2)-C(3)-C(4)	-74.8(4)
C(1)-C(2)-C(6)-C(5)	97.5(3)
C(1)-C(2)-C(6)-C(17)	-108.5(4)
C(1)-C(6)-C(17)-C(18)	-78.9(4)
C(1)-C(6)-C(17)-C(22)	95.2(4)
C(2)-C(1)-C(6)-C(5)	-97.9(3)
C(2)-C(1)-C(6)-C(17)	120.2(3)
C(2)-C(1)-C(7)-O(1)	55.8(3)
C(2)-C(1)-C(7)-O(2)	-125.2(3)
C(2)-C(1)-C(8)-N(1)	31.1(4)
C(2)-C(1)-C(8)-C(9)	-146.0(3)
C(2)-C(3)-C(4)-C(5)	30.1(3)
C(2)-C(6)-C(17)-C(18)	-3.2(5)
C(2)-C(6)-C(17)-C(22)	170.9(3)
C(3)-C(2)-C(6)-C(1)	-113.6(3)
C(3)-C(2)-C(6)-C(5)	-16.1(3)
C(3)-C(2)-C(6)-C(17)	138.0(3)

C(3)-C(4)-C(5)-O(1)	71.8(3)
C(3)-C(4)-C(5)-C(6)	-40.7(3)
C(4)-C(5)-C(6)-C(1)	97.2(3)
C(4)-C(5)-C(6)-C(2)	35.1(3)
C(4)-C(5)-C(6)-C(17)	-121.2(3)
C(5)-O(1)-C(7)-O(2)	177.4(3)
C(5)-O(1)-C(7)-C(1)	-3.6(3)
C(5)-C(6)-C(17)-C(18)	146.5(3)
C(5)-C(6)-C(17)-C(22)	-39.4(4)
C(6)-C(1)-C(2)-C(3)	96.7(3)
C(6)-C(1)-C(7)-O(1)	-7.4(3)
C(6)-C(1)-C(7)-O(2)	171.6(3)
C(6)-C(1)-C(8)-N(1)	100.8(3)
C(6)-C(1)-C(8)-C(9)	-76.3(4)
C(6)-C(2)-C(3)-C(4)	-8.4(3)
C(6)-C(17)-C(18)-C(19)	174.4(3)
C(6)-C(17)-C(22)-C(21)	-156.5(3)
C(7)-O(1)-C(5)-C(4)	-98.2(3)
C(7)-O(1)-C(5)-C(6)	12.9(3)
C(7)-C(1)-C(2)-C(3)	3.1(4)
C(7)-C(1)-C(2)-C(6)	-93.6(3)
C(7)-C(1)-C(6)-C(2)	112.2(3)
C(7)-C(1)-C(6)-C(5)	14.3(3)
C(7)-C(1)-C(6)-C(17)	-127.6(3)
C(7)-C(1)-C(8)-N(1)	-124.7(3)
C(7)-C(1)-C(8)-C(9)	58.2(4)
C(8)-N(1)-N(2)-S(1)	-179.1(2)
C(8)-C(1)-C(2)-C(3)	-153.0(3)
C(8)-C(1)-C(2)-C(6)	110.3(3)
C(8)-C(1)-C(6)-C(2)	-108.6(3)
C(8)-C(1)-C(6)-C(5)	153.5(3)
C(8)-C(1)-C(6)-C(17)	11.7(4)
C(8)-C(1)-C(7)-O(1)	-147.8(3)
C(8)-C(1)-C(7)-O(2)	31.2(4)
C(10)-S(1)-N(2)-N(1)	-55.9(2)
C(10)-C(11)-C(12)-C(13)	-0.9(6)

C(11)-C(10)-C(15)-C(14)	0.2(5)
C(11)-C(12)-C(13)-C(14)	-0.3(6)
C(11)-C(12)-C(13)-C(16)	-179.0(3)
C(12)-C(13)-C(14)-C(15)	1.5(6)
C(13)-C(14)-C(15)-C(10)	-1.4(6)
C(15)-C(10)-C(11)-C(12)	0.9(5)
C(16)-C(13)-C(14)-C(15)	-179.8(4)
C(17)-C(18)-C(19)-C(20)	11.2(6)
C(18)-C(17)-C(22)-C(21)	17.6(5)
C(18)-C(19)-C(20)-C(21)	-40.8(5)
C(19)-C(20)-C(21)-C(22)	59.6(4)
C(20)-C(21)-C(22)-C(17)	-47.0(4)
C(22)-C(17)-C(18)-C(19)	0.7(6)
S(1B)-C(10B)-C(11B)-C(12B)	179.2(3)
S(1B)-C(10B)-C(15B)-C(14B)	-179.5(3)
O(1B)-C(5B)-C(6B)-C(1B)	16.8(3)
O(1B)-C(5B)-C(6B)-C(2B)	79.2(3)
O(1B)-C(5B)-C(6B)-C(17B)	-126.8(3)
O(3B)-S(1B)-N(2B)-N(1B)	171.6(2)
O(3B)-S(1B)-C(10B)-C(11B)	131.4(3)
O(3B)-S(1B)-C(10B)-C(15B)	-48.5(3)
O(4B)-S(1B)-N(2B)-N(1B)	-60.4(2)
O(4B)-S(1B)-C(10B)-C(11B)	-1.1(3)
O(4B)-S(1B)-C(10B)-C(15B)	179.0(3)
N(2B)-S(1B)-C(10B)-C(11B)	-116.4(3)
N(2B)-S(1B)-C(10B)-C(15B)	63.7(3)
N(2B)-N(1B)-C(8B)-C(1B)	177.0(2)
N(2B)-N(1B)-C(8B)-C(9B)	0.0(4)
C(1B)-C(2B)-C(3B)-C(4B)	73.9(4)
C(1B)-C(2B)-C(6B)-C(5B)	-96.9(3)
C(1B)-C(2B)-C(6B)-C(17B)	110.3(4)
C(1B)-C(6B)-C(17B)-C(18B)	81.9(4)
C(1B)-C(6B)-C(17B)-C(22B)	-94.4(4)
C(2B)-C(1B)-C(6B)-C(5B)	97.8(3)
C(2B)-C(1B)-C(6B)-C(17B)	-117.9(4)
C(2B)-C(1B)-C(7B)-O(1B)	-56.5(4)

C(2B)-C(1B)-C(7B)-O(2B)	124.7(4)
C(2B)-C(1B)-C(8B)-N(1B)	-31.3(4)
C(2B)-C(1B)-C(8B)-C(9B)	146.0(3)
C(2B)-C(3B)-C(4B)-C(5B)	-29.0(4)
C(2B)-C(6B)-C(17B)-C(18B)	5.9(5)
C(2B)-C(6B)-C(17B)-C(22B)	-170.4(3)
C(3B)-C(2B)-C(6B)-C(1B)	113.5(3)
C(3B)-C(2B)-C(6B)-C(5B)	16.6(3)
C(3B)-C(2B)-C(6B)-C(17B)	-136.2(3)
C(3B)-C(4B)-C(5B)-O(1B)	-73.4(3)
C(3B)-C(4B)-C(5B)-C(6B)	40.3(4)
C(4B)-C(5B)-C(6B)-C(1B)	-97.2(3)
C(4B)-C(5B)-C(6B)-C(2B)	-34.9(3)
C(4B)-C(5B)-C(6B)-C(17B)	119.2(3)
C(5B)-O(1B)-C(7B)-O(2B)	-176.7(3)
C(5B)-O(1B)-C(7B)-C(1B)	4.3(4)
C(5B)-C(6B)-C(17B)-C(18B)	-141.5(4)
C(5B)-C(6B)-C(17B)-C(22B)	42.2(4)
C(6B)-C(1B)-C(2B)-C(3B)	-97.0(3)
C(6B)-C(1B)-C(7B)-O(1B)	6.9(3)
C(6B)-C(1B)-C(7B)-O(2B)	-171.9(3)
C(6B)-C(1B)-C(8B)-N(1B)	-100.8(3)
C(6B)-C(1B)-C(8B)-C(9B)	76.5(4)
C(6B)-C(2B)-C(3B)-C(4B)	7.6(4)
C(6B)-C(17B)-C(18B)-C(19B)	-176.7(4)
C(6B)-C(17B)-C(22B)-C(21B)	160.8(3)
C(7B)-O(1B)-C(5B)-C(4B)	98.1(3)
C(7B)-O(1B)-C(5B)-C(6B)	-13.9(4)
C(7B)-C(1B)-C(2B)-C(3B)	-2.7(4)
C(7B)-C(1B)-C(2B)-C(6B)	94.3(3)
C(7B)-C(1B)-C(6B)-C(2B)	-112.2(3)
C(7B)-C(1B)-C(6B)-C(5B)	-14.4(3)
C(7B)-C(1B)-C(6B)-C(17B)	129.9(3)
C(7B)-C(1B)-C(8B)-N(1B)	125.5(3)
C(7B)-C(1B)-C(8B)-C(9B)	-57.2(4)
C(8B)-N(1B)-N(2B)-S(1B)	-174.5(2)

C(8B)-C(1B)-C(2B)-C(3B)	154.2(3)
C(8B)-C(1B)-C(2B)-C(6B)	-108.8(3)
C(8B)-C(1B)-C(6B)-C(2B)	109.7(3)
C(8B)-C(1B)-C(6B)-C(5B)	-152.4(3)
C(8B)-C(1B)-C(6B)-C(17B)	-8.1(5)
C(8B)-C(1B)-C(7B)-O(1B)	146.0(3)
C(8B)-C(1B)-C(7B)-O(2B)	-32.8(5)
C(10B)-S(1B)-N(2B)-N(1B)	55.6(2)
C(10B)-C(11B)-C(12B)-C(13B)	0.2(6)
C(11B)-C(10B)-C(15B)-C(14B)	0.6(5)
C(11B)-C(12B)-C(13B)-C(14B)	0.7(6)
C(11B)-C(12B)-C(13B)-C(16B)	179.8(4)
C(12B)-C(13B)-C(14B)-C(15B)	-1.0(6)
C(13B)-C(14B)-C(15B)-C(10B)	0.4(6)
C(15B)-C(10B)-C(11B)-C(12B)	-0.9(5)
C(16B)-C(13B)-C(14B)-C(15B)	179.9(4)
C(17B)-C(18B)-C(19B)-C(20B)	-12.3(7)
C(18B)-C(17B)-C(22B)-C(21B)	-15.5(6)
C(18B)-C(19B)-C(20B)-C(21B)	42.1(6)
C(19B)-C(20B)-C(21B)-C(22B)	-59.4(6)
C(20B)-C(21B)-C(22B)-C(17B)	44.9(5)
C(22B)-C(17B)-C(18B)-C(19B)	-0.7(6)
S(1C)-C(10C)-C(11C)-C(12C)	-176.7(3)
S(1C)-C(10C)-C(15C)-C(14C)	176.1(3)
O(1C)-C(5C)-C(6C)-C(1C)	16.8(3)
O(1C)-C(5C)-C(6C)-C(2C)	79.0(3)
O(1C)-C(5C)-C(6C)-C(17C)	-124.9(3)
O(3C)-S(1C)-N(2C)-N(1C)	-60.3(2)
O(3C)-S(1C)-C(10C)-C(11C)	-162.5(3)
O(3C)-S(1C)-C(10C)-C(15C)	20.8(3)
O(4C)-S(1C)-N(2C)-N(1C)	172.4(2)
O(4C)-S(1C)-C(10C)-C(11C)	-30.2(3)
O(4C)-S(1C)-C(10C)-C(15C)	153.0(3)
N(2C)-S(1C)-C(10C)-C(11C)	82.7(3)
N(2C)-S(1C)-C(10C)-C(15C)	-94.0(3)
N(2C)-N(1C)-C(8C)-C(1C)	176.7(2)

N(2C)-N(1C)-C(8C)-C(9C)	-1.1(5)
C(1C)-C(2C)-C(3C)-C(4C)	74.0(3)
C(1C)-C(2C)-C(6C)-C(5C)	-96.8(2)
C(1C)-C(2C)-C(6C)-C(17C)	109.0(3)
C(1C)-C(6C)-C(17C)-C(18C)	80.7(4)
C(1C)-C(6C)-C(17C)-C(22C)	-95.1(4)
C(2C)-C(1C)-C(6C)-C(5C)	98.2(2)
C(2C)-C(1C)-C(6C)-C(17C)	-119.6(3)
C(2C)-C(1C)-C(7C)-O(1C)	-55.9(3)
C(2C)-C(1C)-C(7C)-O(2C)	125.9(3)
C(2C)-C(1C)-C(8C)-N(1C)	-31.1(4)
C(2C)-C(1C)-C(8C)-C(9C)	146.9(3)
C(2C)-C(3C)-C(4C)-C(5C)	-28.9(3)
C(2C)-C(6C)-C(17C)-C(18C)	4.8(5)
C(2C)-C(6C)-C(17C)-C(22C)	-171.0(3)
C(3C)-C(2C)-C(6C)-C(1C)	113.5(3)
C(3C)-C(2C)-C(6C)-C(5C)	16.7(3)
C(3C)-C(2C)-C(6C)-C(17C)	-137.5(3)
C(3C)-C(4C)-C(5C)-O(1C)	-73.4(3)
C(3C)-C(4C)-C(5C)-C(6C)	40.1(3)
C(4C)-C(5C)-C(6C)-C(1C)	-97.1(3)
C(4C)-C(5C)-C(6C)-C(2C)	-34.9(3)
C(4C)-C(5C)-C(6C)-C(17C)	121.1(3)
C(5C)-O(1C)-C(7C)-O(2C)	-177.5(3)
C(5C)-O(1C)-C(7C)-C(1C)	4.3(3)
C(5C)-C(6C)-C(17C)-C(18C)	-144.8(3)
C(5C)-C(6C)-C(17C)-C(22C)	39.4(4)
C(6C)-C(1C)-C(2C)-C(3C)	-97.1(3)
C(6C)-C(1C)-C(7C)-O(1C)	7.0(3)
C(6C)-C(1C)-C(7C)-O(2C)	-171.1(3)
C(6C)-C(1C)-C(8C)-N(1C)	-100.4(3)
C(6C)-C(1C)-C(8C)-C(9C)	77.6(4)
C(6C)-C(2C)-C(3C)-C(4C)	7.4(3)
C(6C)-C(17C)-C(18C)-C(19C)	-176.3(4)
C(6C)-C(17C)-C(22C)-C(21C)	156.9(3)
C(7C)-O(1C)-C(5C)-C(4C)	97.9(3)

C(7C)-O(1C)-C(5C)-C(6C)	-13.8(3)
C(7C)-C(1C)-C(2C)-C(3C)	-3.6(4)
C(7C)-C(1C)-C(2C)-C(6C)	93.5(3)
C(7C)-C(1C)-C(6C)-C(2C)	-112.5(3)
C(7C)-C(1C)-C(6C)-C(5C)	-14.3(3)
C(7C)-C(1C)-C(6C)-C(17C)	127.9(3)
C(7C)-C(1C)-C(8C)-N(1C)	124.7(3)
C(7C)-C(1C)-C(8C)-C(9C)	-57.2(4)
C(8C)-N(1C)-N(2C)-S(1C)	179.4(2)
C(8C)-C(1C)-C(2C)-C(3C)	152.4(3)
C(8C)-C(1C)-C(2C)-C(6C)	-110.5(3)
C(8C)-C(1C)-C(6C)-C(2C)	108.1(3)
C(8C)-C(1C)-C(6C)-C(5C)	-153.7(3)
C(8C)-C(1C)-C(6C)-C(17C)	-11.5(4)
C(8C)-C(1C)-C(7C)-O(1C)	147.7(3)
C(8C)-C(1C)-C(7C)-O(2C)	-30.4(4)
C(10C)-S(1C)-N(2C)-N(1C)	55.4(2)
C(10C)-C(11C)-C(12C)-C(13C)	0.4(6)
C(11C)-C(10C)-C(15C)-C(14C)	-0.7(5)
C(11C)-C(12C)-C(13C)-C(14C)	-0.2(6)
C(11C)-C(12C)-C(13C)-C(16C)	-179.4(4)
C(12C)-C(13C)-C(14C)-C(15C)	-0.4(6)
C(13C)-C(14C)-C(15C)-C(10C)	0.8(6)
C(15C)-C(10C)-C(11C)-C(12C)	0.1(5)
C(16C)-C(13C)-C(14C)-C(15C)	178.8(3)
C(17C)-C(18C)-C(19C)-C(20C)	-9.4(6)
C(18C)-C(17C)-C(22C)-C(21C)	-18.9(5)
C(18C)-C(19C)-C(20C)-C(21C)	39.2(5)
C(19C)-C(20C)-C(21C)-C(22C)	-58.8(5)
C(20C)-C(21C)-C(22C)-C(17C)	47.5(5)
C(22C)-C(17C)-C(18C)-C(19C)	-0.8(6)
S(1D)-C(10D)-C(11D)-C(12D)	-177.0(3)
S(1D)-C(10D)-C(15D)-C(14D)	177.4(3)
O(1D)-C(5D)-C(6D)-C(1D)	-16.0(3)
O(1D)-C(5D)-C(6D)-C(2D)	-78.0(3)
O(1D)-C(5D)-C(6D)-C(17D)	128.0(3)

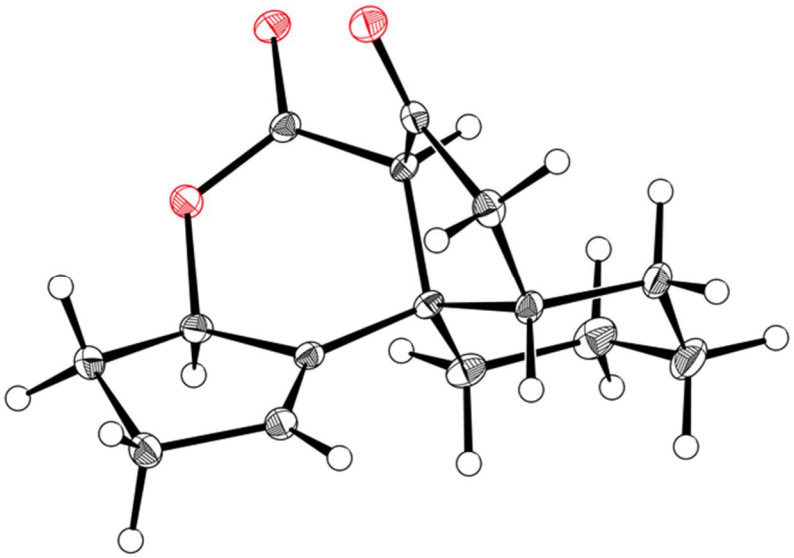
O(3D)-S(1D)-N(2D)-N(1D)	-171.3(2)
O(3D)-S(1D)-C(10D)-C(11D)	-135.3(3)
O(3D)-S(1D)-C(10D)-C(15D)	45.8(3)
O(4D)-S(1D)-N(2D)-N(1D)	60.6(2)
O(4D)-S(1D)-C(10D)-C(11D)	-2.3(3)
O(4D)-S(1D)-C(10D)-C(15D)	178.8(3)
N(2D)-S(1D)-C(10D)-C(11D)	112.3(3)
N(2D)-S(1D)-C(10D)-C(15D)	-66.6(3)
N(2D)-N(1D)-C(8D)-C(1D)	-177.8(3)
N(2D)-N(1D)-C(8D)-C(9D)	0.2(5)
C(1D)-C(2D)-C(3D)-C(4D)	-73.8(4)
C(1D)-C(2D)-C(6D)-C(5D)	97.3(3)
C(1D)-C(2D)-C(6D)-C(17D)	-109.8(4)
C(1D)-C(6D)-C(17D)-C(18D)	-81.7(5)
C(1D)-C(6D)-C(17D)-C(22D)	94.4(4)
C(2D)-C(1D)-C(6D)-C(5D)	-97.9(3)
C(2D)-C(1D)-C(6D)-C(17D)	117.4(4)
C(2D)-C(1D)-C(7D)-O(1D)	56.8(4)
C(2D)-C(1D)-C(7D)-O(2D)	-124.6(4)
C(2D)-C(1D)-C(8D)-N(1D)	33.1(4)
C(2D)-C(1D)-C(8D)-C(9D)	-145.1(3)
C(2D)-C(3D)-C(4D)-C(5D)	28.8(4)
C(2D)-C(6D)-C(17D)-C(18D)	-6.6(6)
C(2D)-C(6D)-C(17D)-C(22D)	169.5(3)
C(3D)-C(2D)-C(6D)-C(1D)	-114.1(3)
C(3D)-C(2D)-C(6D)-C(5D)	-16.9(3)
C(3D)-C(2D)-C(6D)-C(17D)	136.0(3)
C(3D)-C(4D)-C(5D)-O(1D)	73.0(3)
C(3D)-C(4D)-C(5D)-C(6D)	-40.0(3)
C(4D)-C(5D)-C(6D)-C(1D)	97.2(3)
C(4D)-C(5D)-C(6D)-C(2D)	35.2(3)
C(4D)-C(5D)-C(6D)-C(17D)	-118.8(3)
C(5D)-O(1D)-C(7D)-O(2D)	177.0(3)
C(5D)-O(1D)-C(7D)-C(1D)	-4.2(3)
C(5D)-C(6D)-C(17D)-C(18D)	141.0(4)
C(5D)-C(6D)-C(17D)-C(22D)	-42.8(5)

C(6D)-C(1D)-C(2D)-C(3D)	96.7(3)
C(6D)-C(1D)-C(7D)-O(1D)	-6.5(3)
C(6D)-C(1D)-C(7D)-O(2D)	172.2(3)
C(6D)-C(1D)-C(8D)-N(1D)	103.7(3)
C(6D)-C(1D)-C(8D)-C(9D)	-74.5(4)
C(6D)-C(2D)-C(3D)-C(4D)	-7.3(4)
C(6D)-C(17D)-C(18D)-C(19D)	176.3(4)
C(6D)-C(17D)-C(22D)-C(21D)	-169.7(6)
C(7D)-O(1D)-C(5D)-C(4D)	-98.4(3)
C(7D)-O(1D)-C(5D)-C(6D)	13.2(3)
C(7D)-C(1D)-C(2D)-C(3D)	2.6(4)
C(7D)-C(1D)-C(2D)-C(6D)	-94.1(3)
C(7D)-C(1D)-C(6D)-C(2D)	111.4(3)
C(7D)-C(1D)-C(6D)-C(5D)	13.5(3)
C(7D)-C(1D)-C(6D)-C(17D)	-131.1(3)
C(7D)-C(1D)-C(8D)-N(1D)	-121.3(3)
C(7D)-C(1D)-C(8D)-C(9D)	60.5(4)
C(8D)-N(1D)-N(2D)-S(1D)	174.0(2)
C(8D)-C(1D)-C(2D)-C(3D)	-152.1(3)
C(8D)-C(1D)-C(2D)-C(6D)	111.2(3)
C(8D)-C(1D)-C(6D)-C(2D)	-109.3(3)
C(8D)-C(1D)-C(6D)-C(5D)	152.8(3)
C(8D)-C(1D)-C(6D)-C(17D)	8.1(5)
C(8D)-C(1D)-C(7D)-O(1D)	-147.8(3)
C(8D)-C(1D)-C(7D)-O(2D)	30.9(5)
C(10D)-S(1D)-N(2D)-N(1D)	-54.4(2)
C(10D)-C(11D)-C(12D)-C(13D)	-0.6(6)
C(11D)-C(10D)-C(15D)-C(14D)	-1.5(5)
C(11D)-C(12D)-C(13D)-C(14D)	-1.0(6)
C(11D)-C(12D)-C(13D)-C(16D)	179.5(4)
C(12D)-C(13D)-C(14D)-C(15D)	1.3(6)
C(13D)-C(14D)-C(15D)-C(10D)	-0.1(6)
C(15D)-C(10D)-C(11D)-C(12D)	1.8(6)
C(16D)-C(13D)-C(14D)-C(15D)	-179.2(4)
C(17D)-C(18D)-C(19D)-C(20D)	3.8(10)
C(18D)-C(17D)-C(22D)-C(21D)	6.4(8)

C(18D)-C(19D)-C(20D)-C(21D)	-17.4(16)
C(19D)-C(20D)-C(21D)-C(22D)	27(2)
C(20D)-C(21D)-C(22D)-C(17D)	-19.8(14)
C(22D)-C(17D)-C(18D)-C(19D)	0.4(7)

Symmetry transformations used to generate equivalent atoms:

CRYSTAL STRUCTURE ANALYSIS OF 31



31

Crystal data and structure refinement for 31.

Empirical formula	$C_{15}H_{18}O_3$
Formula weight	246.29
Crystallization solvent	Dichloromethane/hexane
Crystal shape	slab
Crystal color	colorless
Crystal size	0.12 x 0.37 x 0.44 mm

Data Collection

Preliminary photograph(s)	rotation
Type of diffractometer	Bruker APEX-II CCD
Wavelength	0.71073 Å MoK
Data collection temperature	100 K
Theta range for 9118 reflections used in lattice determination	2.42 to 41.03°
Unit cell dimensions	a = 8.0015(4) Å α= 90° b = 10.2072(6) Å β= 90.669(3)° c = 14.8838(8) Å γ = 90°
Volume	1215.52(11) Å3
Z	4
Crystal system	monoclinic
Space group	P 1 21/c 1 (# 14)
Density (calculated)	1.346 g/cm3
F(000)	528
Theta range for data collection	2.4 to 41.6°
Completeness to theta = 25.000°	100.0%
Index ranges	-14 £ h £ 14, -18 £ k £ 18, -27 £ l £ 27
Data collection scan type	and scans
Reflections collected	83376
Independent reflections	8050 [Rint= 0.0411]
Reflections > 2s(I)	6562
Average s(I)/(net I)	0.0218
Absorption coefficient	0.09 mm-1

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9532

Structure Solution and Refinement

Primary solution method	dual
Secondary solution method	?
Hydrogen placement	difmap
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	8050 / 0 / 235
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.76
Final R indices [I>2s(I), 6562 reflections]	R1 = 0.0379, wR2 = 0.1076
R indices (all data)	R1 = 0.0511, wR2 = 0.1117
Type of weighting scheme used	calc
Weighting scheme used	
Max shift/error	0.001
Average shift/error	0.000
Extinction coefficient	n/a
Largest diff. peak and hole	0.73 and -0.25 e·Å-3

Programs Used

Cell refinement	SAINT V8.27B (Bruker-AXS, 2007)
Data collection	APEX2 2012.4-3 (Bruker-AXS, 2007)
Data reduction	SAINT V8.27B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2012/7 (Sheldrick, 2012)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 31. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
C(1)	2582(1)	2999(1)	3879(1)	10(1)

C(2)	2552(1)	1559(1)	4084(1)	11(1)
C(3)	2217(1)	517(1)	3570(1)	13(1)
C(4)	2307(1)	-752(1)	4089(1)	16(1)
C(5)	2394(1)	-289(1)	5078(1)	15(1)
C(6)	2960(1)	1140(1)	5028(1)	13(1)
C(7)	1538(1)	3132(1)	5540(1)	12(1)
C(8)	1423(1)	3615(1)	4585(1)	10(1)
C(9)	-338(1)	3348(1)	4189(1)	11(1)
C(10)	-176(1)	3116(1)	3187(1)	14(1)
C(11)	1677(1)	3328(1)	2979(1)	12(1)
C(12)	1995(1)	4738(1)	2671(1)	17(1)
C(13)	3846(1)	5080(1)	2663(1)	23(1)
C(14)	4600(1)	4910(1)	3603(1)	21(1)
C(15)	4396(1)	3498(1)	3924(1)	16(1)
O(1)	2128(1)	1920(1)	5713(1)	17(1)
O(2)	1036(1)	3773(1)	6164(1)	17(1)
O(3)	-1608(1)	3301(1)	4617(1)	17(1)

Bond lengths [Å] and angles [°] for 31

C(1)-C(2)	1.5015(7)
C(1)-C(8)	1.5433(6)
C(1)-C(11)	1.5520(6)
C(1)-C(15)	1.5386(6)
C(2)-C(3)	1.3351(6)
C(2)-C(6)	1.5009(6)
C(3)-H(3)	0.986(9)
C(3)-C(4)	1.5094(7)
C(4)-H(4A)	1.025(10)
C(4)-H(4B)	1.012(8)
C(4)-C(5)	1.5463(7)
C(5)-H(5A)	0.984(9)
C(5)-H(5B)	1.011(10)
C(5)-C(6)	1.5301(7)
C(6)-H(6)	0.983(8)
C(6)-O(1)	1.4605(6)
C(7)-C(8)	1.5062(6)
C(7)-O(1)	1.3487(6)
C(7)-O(2)	1.2096(6)
C(8)-H(8)	0.972(8)
C(8)-C(9)	1.5450(6)
C(9)-C(10)	1.5172(7)
C(9)-O(3)	1.2065(6)
C(10)-H(10A)	0.999(10)
C(10)-H(10B)	0.983(9)
C(10)-C(11)	1.5338(7)
C(11)-H(11)	0.994(9)
C(11)-C(12)	1.5322(7)
C(12)-H(12A)	0.996(11)
C(12)-H(12B)	1.003(9)
C(12)-C(13)	1.5221(9)
C(13)-H(13A)	1.038(10)
C(13)-H(13B)	0.998(10)
C(13)-C(14)	1.5271(9)
C(14)-H(14A)	1.028(10)
C(14)-H(14B)	0.982(10)
C(14)-C(15)	1.5271(8)
C(15)-H(15A)	0.998(8)
C(15)-H(15B)	1.032(9)

C(2)-C(1)-C(8)	104.44(4)
C(2)-C(1)-C(11)	112.23(4)
C(2)-C(1)-C(15)	109.42(4)
C(8)-C(1)-C(11)	102.78(4)
C(15)-C(1)-C(8)	114.19(4)
C(15)-C(1)-C(11)	113.36(4)
C(3)-C(2)-C(1)	131.88(4)
C(3)-C(2)-C(6)	110.41(4)
C(6)-C(2)-C(1)	117.72(4)

C(2)-C(3)-H(3)	125.9(5)
C(2)-C(3)-C(4)	112.54(4)
C(4)-C(3)-H(3)	121.5(5)
C(3)-C(4)-H(4A)	109.0(5)
C(3)-C(4)-H(4B)	112.7(5)
C(3)-C(4)-C(5)	103.04(4)
H(4A)-C(4)-H(4B)	108.8(7)
C(5)-C(4)-H(4A)	112.1(5)
C(5)-C(4)-H(4B)	111.2(5)
C(4)-C(5)-H(5A)	110.5(5)
C(4)-C(5)-H(5B)	114.0(5)
H(5A)-C(5)-H(5B)	107.3(7)
C(6)-C(5)-C(4)	104.79(4)
C(6)-C(5)-H(5A)	107.5(5)
C(6)-C(5)-H(5B)	112.6(5)
C(2)-C(6)-C(5)	104.83(4)
C(2)-C(6)-H(6)	112.5(5)
C(5)-C(6)-H(6)	111.2(5)
O(1)-C(6)-C(2)	113.77(4)
O(1)-C(6)-C(5)	110.34(4)
O(1)-C(6)-H(6)	104.4(5)
O(1)-C(7)-C(8)	119.93(4)
O(2)-C(7)-C(8)	122.09(4)
O(2)-C(7)-O(1)	117.88(4)
C(1)-C(8)-H(8)	112.0(5)
C(1)-C(8)-C(9)	102.82(3)
C(7)-C(8)-C(1)	118.57(4)
C(7)-C(8)-H(8)	106.2(5)
C(7)-C(8)-C(9)	110.30(4)
C(9)-C(8)-H(8)	106.4(5)
C(10)-C(9)-C(8)	108.29(4)
O(3)-C(9)-C(8)	125.18(4)
O(3)-C(9)-C(10)	126.50(4)
C(9)-C(10)-H(10A)	107.2(6)
C(9)-C(10)-H(10B)	108.3(5)
C(9)-C(10)-C(11)	105.70(4)
H(10A)-C(10)-H(10B)	107.2(8)
C(11)-C(10)-H(10A)	115.1(6)
C(11)-C(10)-H(10B)	113.0(5)
C(1)-C(11)-H(11)	109.4(5)
C(10)-C(11)-C(1)	103.75(4)
C(10)-C(11)-H(11)	112.0(5)
C(12)-C(11)-C(1)	112.54(4)
C(12)-C(11)-C(10)	110.90(4)
C(12)-C(11)-H(11)	108.2(5)
C(11)-C(12)-H(12A)	107.2(6)
C(11)-C(12)-H(12B)	108.4(5)
H(12A)-C(12)-H(12B)	106.6(8)
C(13)-C(12)-C(11)	112.52(5)
C(13)-C(12)-H(12A)	111.7(6)
C(13)-C(12)-H(12B)	110.2(5)
C(12)-C(13)-H(13A)	109.8(5)
C(12)-C(13)-H(13B)	108.7(5)
C(12)-C(13)-C(14)	109.89(4)

H(13A)-C(13)-H(13B)	109.2(8)
C(14)-C(13)-H(13A)	110.4(5)
C(14)-C(13)-H(13B)	108.9(6)
C(13)-C(14)-H(14A)	109.3(6)
C(13)-C(14)-H(14B)	112.7(6)
H(14A)-C(14)-H(14B)	106.0(8)
C(15)-C(14)-C(13)	110.59(5)
C(15)-C(14)-H(14A)	110.5(6)
C(15)-C(14)-H(14B)	107.8(6)
C(1)-C(15)-H(15A)	105.7(5)
C(1)-C(15)-H(15B)	108.2(5)
C(14)-C(15)-C(1)	113.75(4)
C(14)-C(15)-H(15A)	113.1(5)
C(14)-C(15)-H(15B)	105.2(5)
H(15A)-C(15)-H(15B)	110.9(7)
C(7)-O(1)-C(6)	121.80(4)

Symmetry transformations used to generate equivalent atoms:

Anisotropic displacement parameters (Å2x 104) for 31. The anisotropic displacement factor exponent takes the form: -2p2 [h2 a*2U 11 + ... + 2 h k a* b* U12]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	111(2)	121(2)	78(2)	-12(1)	10(1)	-10(1)
C(2)	100(2)	129(2)	87(2)	-3(1)	4(1)	9(1)
C(3)	150(2)	131(2)	109(2)	-10(1)	0(1)	3(1)
C(4)	193(2)	127(2)	148(2)	0(2)	5(2)	15(2)
C(5)	181(2)	147(2)	126(2)	23(2)	8(1)	39(2)
C(6)	134(2)	157(2)	94(2)	-3(1)	-7(1)	37(1)
C(7)	132(2)	141(2)	82(2)	-3(1)	6(1)	5(1)
C(8)	111(2)	118(2)	73(2)	-2(1)	5(1)	-3(1)
C(9)	116(2)	104(2)	122(2)	15(1)	-10(1)	2(1)
C(10)	159(2)	146(2)	113(2)	3(1)	-42(1)	2(2)
C(11)	175(2)	123(2)	71(2)	-1(1)	4(1)	-2(1)
C(12)	253(2)	138(2)	113(2)	18(2)	44(2)	-6(2)
C(13)	275(3)	202(2)	206(2)	24(2)	108(2)	-53(2)
C(14)	207(2)	200(2)	236(2)	-28(2)	57(2)	-88(2)
C(15)	119(2)	193(2)	163(2)	-27(2)	26(1)	-37(2)
O(1)	266(2)	168(2)	78(1)	4(1)	11(1)	79(1)
O(2)	242(2)	183(2)	90(1)	-18(1)	31(1)	43(1)
O(3)	122(1)	192(2)	201(2)	20(1)	28(1)	-7(1)

Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for 31.

	x	y	z	U_{iso}
H(3)	199(1)	53(1)	292(1)	24(2)
H(4A)	336(1)	-125(1)	391(1)	26(2)
H(4B)	130(1)	-133(1)	398(1)	24(2)
H(5A)	128(1)	-30(1)	535(1)	23(2)
H(5B)	315(1)	-84(1)	548(1)	31(2)
H(6)	416(1)	123(1)	517(1)	18(2)
H(8)	154(1)	456(1)	461(1)	15(2)
H(10A)	-96(1)	373(1)	288(1)	35(3)
H(10B)	-56(1)	222(1)	305(1)	27(2)
H(11)	207(1)	273(1)	250(1)	22(2)
H(12A)	147(1)	484(1)	207(1)	33(2)
H(12B)	138(1)	535(1)	308(1)	22(2)
H(13A)	400(1)	604(1)	244(1)	37(3)
H(13B)	442(1)	447(1)	224(1)	32(2)
H(14A)	403(1)	555(1)	404(1)	33(2)
H(14B)	580(1)	512(1)	363(1)	35(3)
H(15A)	477(1)	337(1)	456(1)	20(2)
H(15B)	510(1)	294(1)	349(1)	24(2)

Torsion angles [°] for 31.

C(1)-C(2)-C(3)-C(4)	-178.62(5)
C(1)-C(2)-C(6)-C(5)	165.91(4)
C(1)-C(2)-C(6)-O(1)	45.28(6)
C(1)-C(8)-C(9)-C(10)	-21.53(5)
C(1)-C(8)-C(9)-O(3)	156.69(5)
C(1)-C(11)-C(12)-C(13)	51.22(6)
C(2)-C(1)-C(8)-C(7)	42.15(5)
C(2)-C(1)-C(8)-C(9)	-79.79(4)
C(2)-C(1)-C(11)-C(10)	71.42(5)
C(2)-C(1)-C(11)-C(12)	-168.64(4)
C(2)-C(1)-C(15)-C(14)	172.17(4)
C(2)-C(3)-C(4)-C(5)	11.74(6)
C(2)-C(6)-O(1)-C(7)	-21.18(6)
C(3)-C(2)-C(6)-C(5)	-14.01(5)
C(3)-C(2)-C(6)-O(1)	-134.65(4)
C(3)-C(4)-C(5)-C(6)	-19.35(5)
C(4)-C(5)-C(6)-C(2)	20.41(5)
C(4)-C(5)-C(6)-O(1)	143.29(4)
C(5)-C(6)-O(1)-C(7)	-138.67(5)
C(6)-C(2)-C(3)-C(4)	1.30(6)
C(7)-C(8)-C(9)-C(10)	-148.91(4)
C(7)-C(8)-C(9)-O(3)	29.31(6)
C(8)-C(1)-C(2)-C(3)	126.52(5)
C(8)-C(1)-C(2)-C(6)	-53.39(5)
C(8)-C(1)-C(11)-C(10)	-40.24(4)
C(8)-C(1)-C(11)-C(12)	79.71(5)
C(8)-C(1)-C(15)-C(14)	-71.20(5)
C(8)-C(7)-O(1)-C(6)	11.90(7)
C(8)-C(9)-C(10)-C(11)	-3.29(5)
C(9)-C(10)-C(11)-C(1)	26.79(5)
C(9)-C(10)-C(11)-C(12)	-94.27(4)
C(10)-C(11)-C(12)-C(13)	166.94(4)
C(11)-C(1)-C(2)-C(3)	15.90(7)
C(11)-C(1)-C(2)-C(6)	-164.01(4)
C(11)-C(1)-C(8)-C(7)	159.47(4)
C(11)-C(1)-C(8)-C(9)	37.53(4)
C(11)-C(1)-C(15)-C(14)	46.07(6)
C(11)-C(12)-C(13)-C(14)	-59.11(6)
C(12)-C(13)-C(14)-C(15)	59.53(6)
C(13)-C(14)-C(15)-C(1)	-53.81(6)
C(15)-C(1)-C(2)-C(3)	-110.84(6)
C(15)-C(1)-C(2)-C(6)	69.25(5)
C(15)-C(1)-C(8)-C(7)	-77.33(5)
C(15)-C(1)-C(8)-C(9)	160.73(4)
C(15)-C(1)-C(11)-C(10)	-163.99(4)
C(15)-C(1)-C(11)-C(12)	-44.05(5)
O(1)-C(7)-C(8)-C(1)	-24.29(6)
O(1)-C(7)-C(8)-C(9)	93.79(5)
O(2)-C(7)-C(8)-C(1)	159.53(4)
O(2)-C(7)-C(8)-C(9)	-82.38(6)

O(2)-C(7)-O(1)-C(6)	-171.76(4)
O(3)-C(9)-C(10)-C(11)	178.52(5)

Symmetry transformations used to generate equivalent atoms:

References

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. "Safe and convenient procedure for solvent purification." *Organometallics* **1996**, *15*, 1518–1520.

(2) Davies, M. L. H.; Cantrell, R. W.; Jr.; Romines, R. K.; and Baum, S. J. "Synthesis of furans via rhodium(II) acetate-catalyzed reaction of acetylenes with α-diazocarbonyls: Ethyl 2-methyl-5-phenyl-3-furancarboxylate." *Org. Synth.* **1992**, 70, 93-100; *Coll. Vol. IX* **1998**, 422-426.

(3) Charles, R. G. "Copper (II) and Nickel (II) N-(n-alkyl)salicylaldimine Chelates." *J. Org. Chem.* **1957**, *22*, 677–679.

(4) McUliffe, C. A.; Hosseiny, A.; McCullough, F. P. "The chemistry of molybdenum and tungsten. Part XIV Oxomolybdenum(V) complexes of quinolones." *Inorg. Chim. Acta* **1979,** *33*, 5–10.

(5) Gaussian 09, Revision D.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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2010**.

(6) Legault, C. Y. CYLView, 1.0b; Université de Sherbrooke, Canada, **2009**; http://www.cylview.org.

(7) (a) Becke, A. D. "Density-functional thermochemistry. III. The role of exact exchange." *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density." *Phys. Rev. B* **1988**, *37*, 785.

(8) Grimme, S.; Ehrlich, S.; Goerigk, L. "Effect of the damping function in dispersion corrected density functional theory." *J. Comp. Chem.* **2011**, *32*, 1456.

(9) Peverati, R.; Truhlar, D. G. "M11-L: A Local Density Functional That Provides Improved Accuracy for Electronic Structure Calculations in Chemistry and Physics." *J. Phys. Chem. Lett.* **2012**, *3*, 117.

(10) Zhao, Y.; Truhlar, D. G. "The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals." *Theor. Chem. Acc.* **2008**, *120*, 215.

(11) Pieniazek, S. N.; Clemente, F. R.; Houk, K. N. "Sources of error in DFT computations of C-C bond formation thermochemistries: pi→sigma transformations and error cancellation by DFT methods." *Angew. Chem. Int. Ed.* **2008**, *47*, 7746.

(12) James, N. C.; Um, J. M.; Padias, A. B.; Hall Jr., H. K.; Houk, K. N. "Computational investigation of the competition between the concerted Diels-Alder reaction and formation of diradicals in reactions of acrylonitrile with nonpolar dienes." *J. Org. Chem.* **2013**, *78*, 6582.

(13) Maeda, S., Morokuma, K. "Communications: A systematic method for locating transition structures of A+B→X type reactions." *J. Chem. Phys.* **2010**, *132*, 241102/1−4.

(14) Maeda, S., Morokuma, K. "Finding Reaction Pathways of Type A + B → X: Toward Systematic Prediction of Reaction Mechanisms." *J. Chem. Theo. Comp.* **2011**, *7*, 2335−2345.

(15) Maeda, S., Ohno, K., Morokuma, K. "Systematic exploration of the mechanism of chemical reactions: the global reaction route mapping (GRRM) strategy using the ADDF and AFIR methods." *Phys. Chem. Chem. Phys.* **2013**, *15*, 3683−3701.

(16) Maeda, S., Taketsugu, T., Morokuma, K. “Exploring transition state structures for intramolecular pathways by the artificial force induced reaction method.” *J. Comp. Chem.* **2014**, *35*, 166−173.
(17) Isegawa, M., Maeda, S., Tantillo, D. J., Morokuma, K. “Predicting pathways for terpene formation from first principles – routes to known and new sesquiterpenes.” *Chem. Sci.* **2014**, *5*, 1555−1560.
(18) Ulitsky, A., Elber, R. A “A new technique to calculate steepest descent paths in flexible polyatomic systems.” *J. Chem. Phys.* **1990**, *92*, 1510−1511.
(19) Choi, C., Elber, R. “Reaction path study of helix formation in tetrapeptides: Effect of side chains.” *J. Chem. Phys.* **1991**, *94*, 751−760.
(20) Fukui, K. “The path of chemical reactions - the IRC approach.” *Acc. Chem. Res.* **1981**, *14*, 363−368.
(21) Maeda, S.; Osada, Y.; Morokuma, K.; Ohno, K. GRRM, a developmental version at Kyoto University.