Creating Quaternary Centers with High Exo Stereoselectivity

Using Activated α -Alkynyl Dienophiles

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I. Full citation for reference 12.

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

II. Experimental details for Diels-Alder cycloadditions.

General. All non-aqueous reactions were carried out in oven-dried glassware under a slight positive pressure of argon unless otherwise noted. All reagents were commercially available and used without further purification from Sigma-Aldrich and TCI America, unless indicated otherwise. Solvents were reagent grade and purified by standard techniques: THF was distilled from Na-benzophenone or filtered through a dry-solvent system; CH₂Cl₂ was distilled from CaH₂ or filtered through a dry-solvent system; all other solvents were Aldrich “anhydrous” grade solvents, unless indicated otherwise. Reactions were magnetically stirred and monitored by thin layer chromatography on Merck silica gel 60-F254 coated 0.25 mm plates. Preparative thin layer chromatography was performed with Merck silica gel 60-F254 coated 0.50 mm plates. Flash chromatography was performed with Sorbent Technology silica gel 60 (particle size 32-63 μm), unless indicated otherwise. Yields reported are for isolated, spectroscopically pure compounds. Melting points are uncorrected. CDCl₃ was allowed to stand over K₂CO₃ and 4Å MS to neutralize and dry prior to NMR sample preparation. NMR spectra were recorded on Bruker DRX 300, DRX 400 or DMX 500MHz spectrometers. ¹H and ¹³C chemical shifts were referenced to residual solvent peaks. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer. High

resolution mass spectra were acquired in the Columbia University Mass Spectral Core facility on a JEOL HX110 spectrometer.

Representative procedure for DA reaction of diene 2 with acrylate (entry 1, Table 1). A mixture of diene **2**¹ (735 mg, 4.28 mmol, 91% purity) and ethyl (4-methoxy benzyloxy)methyl acrylate **5**² (559 mg, 2.23 mmol) in toluene (5 mL) including 2,6-di-*tert*-butyl-4-methylphenol (BHT, 6 mg, 0.03 mmol) was heated at 145 °C in sealed tube for 48 h. After the reaction mixture was cooled to 23 °C, the solvent was removed under reduced pressure. The resulting crude oil was diluted with tetrahydrofuran (10 mL) and tetrabutylammonium fluoride (3.21 mL, 1.0 M in THF) was slowly added. The mixture was stirred for 15 min and quenched with ammonium chloride (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (2.5:1 to 2:1 hexane/ethyl acetate) to give the *endo*-hydroxy ester (452 mg, 61%) and the *exo*-hydroxy ester (202 mg, 27%) as yellowish oils.

(±)-(1*S*,2*S*)-Ethyl 2-hydroxy-1-((4-methoxybenzyloxy)methyl)-4-methylcyclohex-3-ene carboxylate (entry 1, Table 1): R_f = 0.23 (2:1 hexane/ethyl acetate). ¹H NMR (CDCl₃, 400 MHz) δ : 7.20 (ddd, J = 8.7, 2.8, 2.0 Hz, 2H), 6.86 (ddd, J = 8.7, 2.8, 2.0 Hz, 2H), 5.49-5.28 (m, 1H), 4.45 (d, J = 11.9 Hz, 1H), 4.40 (d, J = 11.9 Hz, 1H), 4.23-4.15 (m, 3H), 3.80 (s, 3H), 3.58 (d, J = 8.9 Hz, 1H), 3.47 (d, J = 8.9 Hz, 1H), 2.81 (br s, 1H), 2.07-1.86 (m, 4H), 1.65 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃, 100

¹ Colvin, E. W.; Thom, I. G. *Tetrahedron* **1986**, 42, 3137-3146.

² Okamoto, Yoshio; Habagami, Shigeki; Nakano, Tamaki. Jpn. Kokai Tokkyo Koho (2004), 14 pp. JP 2004027207 A2 20040129. However, we prepared **12a** from ethyl α -(hydroxymethyl)acrylate (Byun, H.-S.; Reddy, K. C.; Bittman, R. *Tetrahedron Lett.* **1994**, 35, 1371-1374) by protection of PMB group (PMB trichloroacetimidate, CSA, CH₂Cl₂, 97%)

MHz) δ : 175.0, 159.1, 137.7, 130.3, 129.0, 122.8, 113.7, 73.0, 71.3, 67.6, 60.7, 55.2, 51.2, 27.3, 23.1, 22.9, 14.1. IR (neat): 3490, 2966, 2908, 2838, 1738, 1613, 1513, 1447, 1367, 1248, 1175, 1104, 1034 cm^{-1} . HRMS (FAB) m/z found for $(\text{M}+\text{Na})^+$ 357.1697, calcd for $\text{C}_{19}\text{H}_{26}\text{O}_5\text{Na}$ 357.1678. **Exo** : R_f = 0.28 (2:1 hexane/ethyl acetate). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.19 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 5.49 (m, 1H), 4.54 (m, 1H), 4.43 (d, J = 11.9 Hz, 1H), 4.39 (d, J = 11.9 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 3.72 (d, J = 9.1 Hz, 1H), 3.57 (d, J = 9.1 Hz, 1H), 2.51 (br s, 1H), 1.97-1.72 (m, 4H), 1.64 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 174.5, 159.0, 137.2, 130.1, 129.0, 122.6, 113.6, 72.8, 71.4, 66.8, 60.5, 55.1, 50.2, 27.1, 23.8, 23.0, 14.0. HRMS (FAB) m/z found for M^+ 334.1773, calcd for $\text{C}_{19}\text{H}_{26}\text{O}_5$ 334.1780.

(±)-(1R,2S)-Methyl 4-methyl-2-(trimethylsilyloxy)cyclohex-3-ene-1-carboxylate (entry 2, Table 1):

^1H NMR (CDCl_3 , 400 MHz) δ : 5.45 (m, 1H), 4.45 (dd, J = 4.1, 4.1 Hz, 1H), 3.67 (s, 3H), 2.47-2.42 (m, 1H), 2.05-1.78 (m, 4H), 1.69 (s, 3H), 0.07 (s, 9H). ^{13}C NMR (CDCl_3 , 75 MHz) δ : 173.7, 138.5, 122.8, 65.4, 51.3, 46.2, 29.9, 23.5, 18.6, 0.3. IR (neat): 2954, 2913, 1736, 1438, 1250 cm^{-1} . HRMS (EI) m/z found for M^+ 242.1333, calcd for $\text{C}_{12}\text{H}_{22}\text{O}_3\text{Si}$ 242.1338. **Exo**: ^1H NMR (CDCl_3 , 400 MHz) δ : 5.26 (m, 1H), 4.52-4.50 (m, 1H), 3.68 (s, 3H), 2.49-2.42 (m, 1H), 2.05-1.70 (m, 4H), 1.66 (s, 3H), 0.10 (s, 9H).

(±)-(1S,2S)-1-((4-Methoxybenzyloxy)methyl)-4-methyl-2-(trimethylsilyloxy)cyclohex-3-ene-1-carboxaldehyde (entry 3, Table 1): R_f = 0.43 (8:1 hexane/ethyl acetate). ^1H NMR (CDCl_3 , 500 MHz) δ : 9.74 (s, 1H), 7.20 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 5.38 (m, 1H), 4.42-4.37 (m, 3H), 3.80 (s, 3H), 3.51 (d, J = 9.3 Hz, 1H), 3.41 (d, J = 9.3 Hz, 1H), 2.00-1.82 (m, 4H), 1.67 (s, 3H), 0.10 (s, 9H).

^{13}C NMR (CDCl_3 , 100 MHz) δ : 205.7, 159.1, 137.4, 129.0, 123.4, 123.2, 113.6, 73.0, 69.2, 67.5, 55.1, 53.2, 26.8, 23.0, 22.7, 0.2. IR (neat): 2957, 2912, 2858, 1725, 1674, 1613, 1587, 1515, 1445, 1303, 1250, 1173, 1080, 1047 cm^{-1} . HRMS (FAB) m/z found for $(\text{M}-\text{H})^+$ 361.1821, calcd for $\text{C}_{20}\text{H}_{29}\text{O}_4\text{Si}$ 361.1835. **Exo**: partial ^1H NMR (CDCl_3 , 400 MHz) δ : 9.65 (s, 1H), 1.63 (s, 3H).

(±)-(1*S*,2*S*)-Methyl 4-methyl-1-((trimethylsilyl)ethynyl)-2-(trimethylsilyloxy)cyclohex-3-ene-1-carboxylate (entry 4, Table 1)³: R_f = 0.58 (8:1 hexane/ethyl acetate). mp 54-55 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 5.39-5.38 (m, 1H), 4.36 (d, J = 5.2 Hz, 1H), 3.73 (s, 3H), 2.28-2.11 (m, 2H), 2.00-1.95 (m, 1H), 1.90-1.86 (m, 1H), 1.70 (s, 3H), 0.11 (s, 9H), 0.07 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 171.4, 138.4, 120.7, 103.6, 87.5, 69.8, 52.2, 48.0, 27.8, 23.9, 23.3, 0.4, -0.1. IR (neat): 3018, 2959, 2903, 2168, 1748, 1674, 1435, 1250, 1167, 1064, 892, 842 cm^{-1} . HRMS (FAB) m/z found for $(\text{M}-\text{H})^+$ 337.1637, calcd for $\text{C}_{17}\text{H}_{29}\text{O}_3\text{Si}_2$ 337.1655. **Exo**: partial ^1H NMR (CDCl_3 , 400 MHz) δ : 5.31 (m, 1H), 4.57 (m, 1H), 3.74 (s, 3H), 1.66 (s, 3H).

Representative procedure for DA reaction of diene with the aldehyde 3 (entry 6, Table 1). To a solution of 2-methylene-4-(trimethylsilyl)but-3-yn-1-ol⁴ (21 mg, 0.14 mmol) in dichloromethane (1 mL) cooled to 0 °C was added Dess-Martin periodinane (64 mg, 0.15 mmol). The reaction mixture was stirred at 0 °C for 20 min and then sodium bicarbonate (25 mg, 0.30 mmol) and pentane (0.5 mL) were

³ Methyl α -(trimethylsilyl)ethynyl acrylate **8** was synthesized by the literature procedure (Spino, C.; Crawford, J.; Bishop, J. *J. Org. Chem.* **1995**, 60, 844.).

⁴ Thongsornkleeb, C.; Danheiser, R. L. *J. Org. Chem.* **2005**, 70, 2364-2367.

added. (The formation of the aldehyde **3** was confirmed by TLC.) The solution was quickly filtered through a pad of silica gel with the aid of the solution of 4% ethyl acetate in pentane. The filtrate was concentrated under reduced pressure at low temperature to give the aldehyde **3**. (The remaining solvent should be dried for a short period of time under vacuum at -78 °C to prevent dimerization.) To a solution of the aldehyde **3** in dichloromethane (0.5 mL) cooled to 0 °C was added a solution of the Danishefsky's diene **9** (59 μ L, 0.27 mmol, 90%) in dichloromethane (0.5 mL) and the resulting mixture was stirred at 0 °C for 30 min. The solvent was removed under reduced pressure. The product was dried thoroughly under vacuum pressure to give a 13:1 mixture (confirmed by NMR analysis) of *endo* and *exo* isomers (29 mg, 67%) as oils, which became white solids upon standing in the refrigerator.

($\pm$)-(1*S*,2*S*)-2-methoxy-1-((trimethylsilyl)ethynyl)-4-(trimethylsilyloxy)cyclohex-3-ene-1-

carboxaldehyde (entry 6, Table 1): R_f = 0.50 (8:1 hexane/ethyl acetate). ^1H NMR (CDCl_3 , 400 MHz) δ : 9.47 (s, 1H), 5.12-5.10 (m, 1H), 4.14 (d, J = 5.4 Hz, 1H), 3.29 (s, 3H), 2.34-2.25 (m, 1H), 2.13-2.01 (m, 2H), 1.90-1.80 (m, 1H), 0.22 (s, 9H), 0.13 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 195.1, 156.5, 100.9, 100.4, 91.4, 77.0, 55.9, 50.9, 27.3, 22.1, 0.2, -0.1. IR (neat): 2959, 2168, 1723, 1664, 1252 cm^{-1} . HRMS (FAB) m/z found for $(\text{M-CHO})^+$ 295.1550, calcd for 295.1550 $\text{C}_{15}\text{H}_{27}\text{O}_2\text{Si}_2$. **Exo**: partial ^1H NMR (CDCl_3 , 400 MHz) δ : 9.59 (s, 1H).

($\pm$)-(1*S*,2*S*)-4-Methyl-1-((trimethylsilyl)ethynyl)-2-(trimethylsilyloxy)cyclohex-3-ene-1-

carboxaldehyde (entry 5, Table 1): ^1H NMR (CDCl_3 , 400 MHz) δ : 9.51 (s, 1H), 5.39 (dq, J = 4.0, 1.2 Hz, 1H), 4.45 (d, J = 4.0 Hz, 1H), 2.15-2.00 (m, 3H), 1.82-1.76 (m, 1H), 1.70 (s, 3H), 0.12 (s, 9H), 0.13 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 196.8, 138.8, 121.6, 102.4, 91.1, 69.9, 51.5, 27.2, 23.4, 23.3, 0.4, 0.0. IR (neat): 3016, 2961, 2903, 2714, 2168, 1738, 1672, 1447, 1380, 1252, 1169, 1055, 842, 760 cm^{-1} . HRMS (FAB) m/z found for $(\text{M-CHO})^+$ 279.1614, calcd for $\text{C}_{15}\text{H}_{27}\text{OSi}_2$ 279.1600. **Exo**:

partial ^1H NMR (CDCl_3 , 400 MHz) δ : 9.54 (s, 1H).

(±)-(1*R*,2*S*)-2-Methyl-1-((trimethylsilyl)ethynyl)cyclohex-3-ene-1-carbaldehyde (entry 7, Table 1):

^1H NMR (CDCl_3 , 400 MHz) δ : 9.54 (s, 1H), 5.70-5.65 (m, 1H), 5.60-5.57 (m, 1H), 2.68-2.65 (m, 1H), 2.25-2.19 (m, 1H), 2.14-2.06 (m, 1H), 1.95 (ddd, $J = 13.5, 7.6, 5.9$ Hz, 1H), 1.79 (ddd, $J = 13.5, 6.1, 6.1$ Hz, 1H), 1.05 (d, $J = 7.3$ Hz, 3H), 0.15 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 197.8, 129.5, 126.3, 104.9, 90.2, 50.1, 36.7, 25.0, 22.4, 16.8, 0.0. IR (neat): 2958, 2924, 2143, 1732, 1625, 1250 cm^{-1} . HRMS (EI) m/z found for M^+ 220.1296, calcd for $\text{C}_{13}\text{H}_{20}\text{OSi}$ 220.1283. **Exo**: partial ^1H NMR (CDCl_3 , 400 MHz) δ : 9.52 (s, 1H), 1.08 (d, $J = 7.2$ Hz, 3H).

regioselectivity = 4:1

Mixture of (±)-(R)-4-Methyl-1-((trimethylsilyl)ethynyl)cyclohex-3-ene-1-carboxaldehyde and (±)-

(R)-3-methyl-1-((trimethylsilyl)ethynyl)cyclohex-3-ene-1-carboxaldehyde (entry 8, Table 1): ^1H

NMR (CDCl_3 , 400 MHz) δ : 9.45 (s, 1.14), 5.40-5.38 (m, 0.22H), 5.35-5.33 (m, 1.00H), 2.46-2.37 (m, 1.30H), 2.46-2.37 (m, 2.68H), 2.06-1.90 (m, 1.52H), 1.90-1.71 (m, 2.62H), 1.69 (d, $J = 1.0$ Hz, 0.72H), 1.65 (s, 3.19H), 0.14 (s, 11.37H). ^{13}C NMR (major compound, CDCl_3 , 100 MHz) δ : 197.6, 133.8, 117.2, 104.7, 89.8, 31.1, 28.2, 26.8, 23.3, 22.0, 0.0. IR (neat): 2961, 2928, 2166, 1731, 1679, 1250 cm^{-1} . HRMS (FAB) m/z found for $(\text{M}+\text{H})^+$ 221.1358, calcd for $\text{C}_{13}\text{H}_{21}\text{OSi}$ 221.1362.

(±)-(1*S*,2*S*,5*S*)-2-((Trimethylsilyl)ethynyl)bicyclo[2.2.2]oct-5-ene-2-carboxaldehyde (entry 9, Table 1): ^1H NMR (CDCl_3 , 400 MHz) δ : 9.25 (s, 1H), 6.28 (dd, $J = 7.6, 7.6$ Hz, 1H), 6.04 (ddd, $J = 7.6, 7.6, 1.0$ Hz, 1H), 2.85-2.83 (m, 1H), 2.29-2.24 (m, 1H), 2.19 (ddd, $J = 13.0, 2.8, 2.8$ Hz, 1H), 1.70-1.64 (m, 1H), 1.62 (dd, $J = 9.6, 2.4$ Hz, 1H), 1.28-1.22 (m, 2H), 0.17 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 195.7, 136.3, 130.5, 105.6, 90.2, 51.6, 36.2, 34.4, 30.0, 24.8, 20.9, 0.0. IR (neat): 2953, 2869, 2158, 1736, 1628, 1250, 1173 cm^{-1} . HRMS (FAB) m/z found for $(\text{M}-\text{H})^+$ 231.1193, calcd for $\text{C}_{14}\text{H}_{20}\text{OSi}$ 231.1205. **Exo**: partial ^1H NMR (CDCl_3 , 400 MHz) δ : 9.48 (s, 1H), 6.43-6.31 (m, 2H), 2.92 (m, 1H).

(±)-(4*aR*,8*S*,8*aS*)-6-Methyl-8*a*-((trimethylsilyl)ethynyl)-8-(trimethylsilyloxy)-3,4,4*a*,5,8,8*a*-

hexahydronaphthalen-1(2*H*)-one (**14**): A mixture of α -trimethylsilyl ethynyl cyclohexenone **13**⁵ (18 mg, 0.081 mmol) and diene **2** (40 mg, 0.20 mmol, 80%) in benzene- d_6 (0.6 mL) was heated at 85-90 °C in NMR tube for 40 h. After the reaction mixture was cooled to 23 °C, the solvent was removed under reduced pressure. The crude oil was purified by flash column chromatography on silica gel (30:1 hexane/ethyl acetate) to give the ketone **14** (27 mg, 96%, endo/exo >20:1). ^1H NMR (CDCl_3 , 400 MHz) δ : 5.40 (q, $J = 1.6$ Hz, 1H), 4.29 (m, 1H), 2.79 (ddd, $J = 15.4, 6.2, 6.0$ Hz, 1H), 2.46-2.28 (m, 3H), 2.03-1.76 (m, 5H), 1.71 (s, 3H), 0.16 (s, 9H), 0.14 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 207.1, 133.5, 122.0, 107.0, 88.7, 71.6, 54.5, 41.0, 40.3, 32.8, 26.3, 23.7, 23.5, 0.2, 0.0. IR (neat): 2957, 2898, 2167, 1714, 1250, 1048 cm^{-1} . HRMS (FAB) m/z found for $(\text{M}-\text{H})^+$ 347.1861, calcd for $\text{C}_{19}\text{H}_{31}\text{O}_2\text{Si}_2$ 347.1863. **Exo**: partial ^1H NMR (CDCl_3 , 400 MHz) δ : 5.49 (m, 1H), 4.48 (d, $J = 4.8$ Hz, 1H), 3.11-3.20 (m, 1H), 1.66 (s, 3H), 0.19 (s, 9H), 0.16 (s, 9H).

⁵ Miller, M. W.; Johnson, C. R. *J. Org. Chem.* **1997**, 62, 1582.
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(±)-(4aR,8S,8aS)-8-Methoxy-8a-((trimethylsilyl)ethynyl)-6-(trimethylsilyloxy)-3,4,4a,5,8,8a-hexahydronaphthalen-1(2H)-one (15): Following the same procedure as above, the DA reaction of Danishefsky's diene (28 mg, 0.14 mmol) with **13** (16 mg, 0.070 mmol) gave the ketone **15** (25 mg, 95%). ^1H NMR (CDCl_3 , 400 MHz) δ : 5.08 (m, 1H), 3.94 (d, $J = 4.5$ Hz, 1H), 3.25 (s, 3H), 2.57-2.47 (m, 3H), 2.35-2.30 (m, 1H), 2.09-2.05 (m, 1H), 1.96-1.90 (m, 2H), 1.75-1.63 (m, 2H), 0.21 (s, 9H), 0.12 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 207.4, 151.6, 105.8, 101.2, 87.8, 81.0, 57.5, 53.2, 40.5, 40.2, 33.5, 26.4, 23.3, 0.3, 0.0. IR (neat): 2957, 2900, 2165, 1714, 1672, 1250 cm^{-1} . HRMS (FAB) m/z found for $(\text{M}+\text{H})^+$ 365.1953, calcd for $\text{C}_{19}\text{H}_{33}\text{O}_3\text{Si}_2$ 365.1968. *Exo*: parital ^1H NMR (CDCl_3 , 400 MHz) δ : 3.42 (s, 3H).

(±)-Methyl 2-((4S,4aR,8aR)-4-methoxy-2,5-dioxodecahydronaphthalen-4a-yl)acetate (16). To a stirred solution of cyclohexene (64 μL , 0.63 mmol) in tetrahydrofuran (0.8 mL) cooled to 0 $^\circ\text{C}$ was added $\text{BH}_3\cdot\text{DMS}$ (30 μL , 0.30 mmol). The mixture was warmed to 23 $^\circ\text{C}$ and stirred for 1 h and then recooled to 0 $^\circ\text{C}$. A solution of ketone **15** (23 mg, 0.023 mmol) in tetrahydrofuran (0.7 mL) was added dropwise, and the reaction was again allowed to 23 $^\circ\text{C}$ and stirred for 1.5 h. The reaction mixture was quenched with saturated sodium bicarbonate (0.5 mL) followed by hydrogen peroxide (30%, 0.2 mL). The reaction was stirred for 3 h and recooled to 0 $^\circ\text{C}$ and acetic acid (0.1 mL) was added. The reaction

was stirred overnight at 23 °C, diluted with water (5 mL) and extracted with dichloromethane (3 x 5 mL). The extract was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (1:2 hexane/acetate, 1% methanol) to give the diketo acid (7 mg, 44%). This acid was dissolved in benzene (0.3 mL) and methanol (0.3 mL), and (trimethylsilyl)diazomethane (0.05 mL, 2.0 M in hexane) was added at 23 °C. The reaction mixture was stirred for 5 min and the solvent was removed under reduced pressure. The crude oil was purified by column chromatography on silica gel (1:1 hexane/ethyl acetate) to afford the ester **16** (6 mg, 81%) as white solid. ¹H NMR (CDCl₃, 400 MHz) δ : 3.67 (s, 3H), 3.64 (ddd, J = 3.3, 3.3, 1.2 Hz, 1H), 3.19 (s, 3H), 3.11 (d, J = 16.8 Hz, 1H), 2.71 (ddd, J = 15.1, 3.1, 2.3 Hz, 1H), 2.68 (d, J = 16.8 Hz, 1H), 2.66-2.59 (m, 3H), 2.45 (ddd, J = 15.1, 3.5, 0.6 Hz, 1H), 2.40 (dd, J = 11.9, 7.9 Hz, 1H), 2.38-2.32 (m, 1H), 2.09-1.99 (m, 1H), 1.96-1.85 (m, 2H), 1.69-1.64 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ : 213.3, 207.9, 171.5, 87.9, 57.2, 51.9, 43.9, 40.9 (2C), 40.6, 39.5, 29.2, 22.2 (one quaternary carbon not shown). ¹³C NMR (C₆D₆, 100 MHz) δ : 212.1, 206.1, 172.0, 88.9, 57.2, 52.5, 51.9, 44.3, 41.5, 41.4, 41.1, 40.1, 30.2, 23.1. IR (neat): 2951, 2871, 1734, 1719, 1701, 1437, 1356, 1201, 1093 cm⁻¹. HRMS (FAB) m/z found for M⁺ 268.1302, calcd for C₁₄H₂₀O₅ 268.1311.

III. Spectra and X-ray structure of the compound 16

^1H NMR of the compound **16** (CDCl_3 , 400MHz)

^{13}C NMR of the compound **16** (C_6D_6 , 100MHz)

NOESY of the compound **16** (CDCl₃, 500MHz)

Current Data Parameters
 NAME sm-III-22
 EXPNO 4
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070307
 Time 20.44
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG noesyphz
 TD 1024
 SOLVENT CDCl3
 NS 64
 DS 16
 SWH 2500.000 Hz
 FIDRES 2.441406 Hz
 AQ 0.2048500 sec
 RG 128
 DW 200.000 usec
 DE 4.50 usec
 TE 300.0 K
 D0 0.00019139 sec
 D1 2.00000000 sec
 D8 0.50000000 sec
 D16 0.00020000 sec
 INO 0.00039997 sec
 MCOREST 0.00000000 sec
 MCMRK 2.00000000 sec
 TAU 0.47471601 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 5.75 usec
 P3 20000.00 usec
 PL 2.00 dB
 SFO1 500.1312633 MHz

===== GRADIENT CHANNEL =====
 GPNAM1 sine.100
 GPX0 0.00 %
 GPX1 0.00 %
 GPY0 0.00 %
 GPY1 0.00 %
 GPZ0 20.00 %
 GPZ1 40.00 %
 P31 5000.00 usec

F1 - Acquisition parameters
 MD0 1
 TP 256
 SFO1 500.1313 MHz
 FIDRES 9.766235 Hz
 SW 4.999 ppm
 FMODE TPPI

F2 - Processing parameters
 SI 1024
 SF 500.1300130 MHz

X-ray structure of the compound **16**

Table 1. Crystal data and structure refinement for t3twin5.

Identification code	t3twin5
Empirical formula	C ₁₄ H ₂₀ O ₅
Formula weight	268.30
Temperature	125(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P $\bar{1}$
Unit cell dimensions	a = 11.1692(3) Å alpha = 88.696(3) [°] b = 11.2436(3) Å beta = 75.996(2) [°] c = 11.3820(3) Å gamma = 75.586(2) [°]
Volume, Z	1342.17(6) Å ³ , 4
Density (calculated)	1.328 Mg/m ³
Absorption coefficient	0.100 mm ⁻¹
F(000)	576
Crystal size	0.21 x 0.14 x 0.08 mm
Θ range for data collection	1.85 to 32.44 [°]
Limiting indices	-15 ≤ h ≤ 16, -16 ≤ k ≤ 16, 0 ≤ l ≤ 17
Reflections collected	13391
Independent reflections	13391 (R _{int} = 0.0511)
Completeness to Θ = 32.44 [°]	93.4 %
Absorption correction	EMPIRICAL
Max. and min. transmission	0.9920 and 0.9793
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	13391 / 0 / 344
Goodness-of-fit on F ²	1.030
Final R indices [I > 2σ(I)]	R1 = 0.0530, wR2 = 0.1081
R indices (all data)	R1 = 0.1003, wR2 = 0.1347
Largest diff. peak and hole	0.447 and -0.278 eÅ ⁻³

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for t3twin5. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(6)	1323(2)	-844(2)	2246(2)	35(1)
O(7)	4877(1)	1618(1)	4275(1)	24(1)
O(8)	2072(1)	1232(1)	4119(1)	22(1)
O(9)	6675(1)	735(1)	1761(1)	24(1)
O(10)	7610(1)	-1245(1)	1981(1)	25(1)
C(21)	4208(2)	444(2)	2949(2)	14(1)
C(22)	3106(2)	156(2)	3945(2)	16(1)
C(23)	2664(2)	-946(2)	3612(2)	20(1)
C(24)	2346(2)	-785(2)	2398(2)	22(1)
C(25)	3408(2)	-560(2)	1389(2)	22(1)
C(26)	3919(2)	531(2)	1676(2)	18(1)
C(27)	3057(2)	1767(2)	1470(2)	24(1)
C(28)	3652(2)	2807(2)	1661(2)	27(1)
C(29)	3791(2)	2868(2)	2958(2)	24(1)
C(30)	4372(2)	1656(2)	3435(2)	18(1)
C(31)	5429(2)	-567(2)	2923(2)	17(1)
C(32)	6610(2)	-257(2)	2156(2)	18(1)
C(33)	8827(2)	-1043(2)	1308(2)	30(1)
C(34)	1224(2)	1362(3)	5286(2)	41(1)
C(1)	8403(2)	4583(2)	2073(2)	14(1)
O(1)	4536(1)	6148(2)	2852(2)	41(1)
O(2)	10319(1)	3390(1)	780(1)	24(1)
C(2)	7618(2)	4883(2)	1096(2)	16(1)
O(3)	7117(1)	3857(1)	979(1)	21(1)
C(3)	6524(2)	6045(2)	1437(2)	22(1)
O(4)	10415(1)	4320(1)	3292(1)	26(1)
C(4)	5688(2)	5951(2)	2671(2)	24(1)
O(5)	10648(1)	6209(1)	2808(1)	20(1)
C(5)	6376(2)	5639(2)	3658(2)	25(1)
C(6)	7546(2)	4518(2)	3356(2)	18(1)
C(7)	7167(2)	3295(2)	3583(2)	23(1)
C(8)	8353(2)	2228(2)	3357(2)	26(1)
C(9)	9136(2)	2161(2)	2051(2)	23(1)
C(10)	9391(2)	3360(2)	1591(2)	17(1)
C(11)	9127(2)	5580(2)	2067(2)	16(1)
C(12)	10121(2)	5266(2)	2792(2)	17(1)
C(13)	11609(2)	6042(2)	3491(2)	26(1)
C(14)	6933(2)	3680(2)	-188(2)	35(1)

Table 3. Bond lengths [Å] and angles [°] for t3twin5.

O(6)-C(24)	1.214(2)	O(7)-C(30)	1.217(2)
O(8)-C(34)	1.419(2)	O(8)-C(22)	1.428(2)
O(9)-C(32)	1.206(2)	O(10)-C(32)	1.344(2)
O(10)-C(33)	1.459(2)	C(21)-C(31)	1.537(2)
C(21)-C(30)	1.550(2)	C(21)-C(22)	1.553(2)
C(21)-C(26)	1.555(2)	C(22)-C(23)	1.530(2)
C(23)-C(24)	1.504(3)	C(24)-C(25)	1.505(3)
C(25)-C(26)	1.547(3)	C(26)-C(27)	1.530(3)
C(27)-C(28)	1.525(3)	C(28)-C(29)	1.526(3)
C(29)-C(30)	1.507(3)	C(31)-C(32)	1.510(2)
C(1)-C(11)	1.536(2)	C(1)-C(10)	1.548(2)
C(1)-C(6)	1.552(2)	C(1)-C(2)	1.558(2)
O(1)-C(4)	1.216(3)	O(2)-C(10)	1.217(2)
C(2)-O(3)	1.423(2)	C(2)-C(3)	1.532(2)
O(3)-C(14)	1.418(2)	C(3)-C(4)	1.505(3)
O(4)-C(12)	1.205(2)	C(4)-C(5)	1.498(3)
O(5)-C(12)	1.338(2)	O(5)-C(13)	1.445(2)
C(5)-C(6)	1.548(3)	C(6)-C(7)	1.536(2)
C(7)-C(8)	1.523(3)	C(8)-C(9)	1.524(3)
C(9)-C(10)	1.503(2)	C(11)-C(12)	1.508(2)
C(34)-O(8)-C(22)	114.07(15)	C(32)-O(10)-C(33)	115.75(15)
C(31)-C(21)-C(30)	108.08(14)	C(31)-C(21)-C(22)	108.35(13)
C(30)-C(21)-C(22)	103.34(13)	C(31)-C(21)-C(26)	110.10(14)
C(30)-C(21)-C(26)	114.10(14)	C(22)-C(21)-C(26)	112.50(14)
O(8)-C(22)-C(23)	109.54(14)	O(8)-C(22)-C(21)	106.49(13)
C(23)-C(22)-C(21)	113.48(14)	C(24)-C(23)-C(22)	110.29(15)
O(6)-C(24)-C(23)	122.62(19)	O(6)-C(24)-C(25)	123.07(19)
C(23)-C(24)-C(25)	114.30(16)	C(24)-C(25)-C(26)	113.14(15)
C(27)-C(26)-C(25)	111.77(15)	C(27)-C(26)-C(21)	113.80(15)
C(25)-C(26)-C(21)	111.65(14)	C(28)-C(27)-C(26)	109.94(16)
C(27)-C(28)-C(29)	111.36(16)	C(30)-C(29)-C(28)	115.07(16)
O(7)-C(30)-C(29)	120.80(16)	O(7)-C(30)-C(21)	118.85(16)
C(29)-C(30)-C(21)	120.04(15)	C(32)-C(31)-C(21)	112.78(14)
O(9)-C(32)-O(10)	123.62(17)	O(9)-C(32)-C(31)	125.78(16)
O(10)-C(32)-C(31)	110.59(15)	C(11)-C(1)-C(10)	108.07(14)
C(11)-C(1)-C(6)	110.20(14)	C(10)-C(1)-C(6)	113.98(14)
C(11)-C(1)-C(2)	108.12(13)	C(10)-C(1)-C(2)	103.91(13)
C(6)-C(1)-C(2)	112.21(14)	O(3)-C(2)-C(3)	109.70(14)
O(3)-C(2)-C(1)	107.31(13)	C(3)-C(2)-C(1)	112.38(14)
C(14)-O(3)-C(2)	114.24(15)	C(4)-C(3)-C(2)	110.69(15)
O(1)-C(4)-C(5)	122.9(2)	O(1)-C(4)-C(3)	122.1(2)
C(5)-C(4)-C(3)	114.98(17)	C(12)-O(5)-C(13)	115.68(15)
C(4)-C(5)-C(6)	114.67(16)	C(7)-C(6)-C(5)	112.17(15)
C(7)-C(6)-C(1)	113.82(14)	C(5)-C(6)-C(1)	111.58(15)
C(8)-C(7)-C(6)	110.16(15)	C(7)-C(8)-C(9)	111.62(15)
C(10)-C(9)-C(8)	114.66(15)	O(2)-C(10)-C(9)	121.34(16)
O(2)-C(10)-C(1)	118.59(15)	C(9)-C(10)-C(1)	119.85(15)
C(12)-C(11)-C(1)	113.27(14)	O(4)-C(12)-O(5)	123.84(17)
O(4)-C(12)-C(11)	126.52(16)	O(5)-C(12)-C(11)	109.64(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for t3twin5.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [(ha^*)^2 U_{11} + \dots + 2hka^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
O(6)	26(1)	46(1)	41(1)	3(1)	-14(1)	-17(1)
O(7)	30(1)	24(1)	23(1)	0(1)	-11(1)	-10(1)
O(8)	16(1)	21(1)	23(1)	-1(1)	0(1)	0(1)
O(9)	19(1)	24(1)	30(1)	7(1)	-4(1)	-7(1)
O(10)	14(1)	20(1)	37(1)	-4(1)	-1(1)	-3(1)
C(21)	14(1)	15(1)	14(1)	2(1)	-4(1)	-3(1)
C(22)	15(1)	17(1)	16(1)	2(1)	-3(1)	-3(1)
C(23)	18(1)	19(1)	22(1)	3(1)	-4(1)	-7(1)
C(24)	23(1)	20(1)	26(1)	1(1)	-9(1)	-9(1)
C(25)	24(1)	27(1)	18(1)	-1(1)	-8(1)	-9(1)
C(26)	16(1)	22(1)	15(1)	3(1)	-4(1)	-6(1)
C(27)	24(1)	26(1)	23(1)	9(1)	-11(1)	-5(1)
C(28)	28(1)	22(1)	31(1)	11(1)	-10(1)	-5(1)
C(29)	24(1)	17(1)	32(1)	2(1)	-8(1)	-5(1)
C(30)	16(1)	18(1)	19(1)	1(1)	-2(1)	-5(1)
C(31)	14(1)	17(1)	19(1)	2(1)	-4(1)	-3(1)
C(32)	16(1)	20(1)	18(1)	-2(1)	-6(1)	-3(1)
C(33)	14(1)	28(1)	42(1)	-8(1)	2(1)	-6(1)
C(34)	26(1)	57(2)	26(1)	-6(1)	4(1)	6(1)
C(1)	14(1)	15(1)	16(1)	2(1)	-4(1)	-4(1)
O(1)	16(1)	44(1)	58(1)	-9(1)	-5(1)	-4(1)
O(2)	20(1)	24(1)	23(1)	0(1)	0(1)	-3(1)
C(2)	16(1)	16(1)	18(1)	2(1)	-6(1)	-7(1)
O(3)	26(1)	20(1)	21(1)	1(1)	-10(1)	-10(1)
C(3)	21(1)	18(1)	29(1)	2(1)	-11(1)	-3(1)
O(4)	26(1)	22(1)	34(1)	9(1)	-15(1)	-8(1)
C(4)	16(1)	18(1)	37(1)	-4(1)	-5(1)	-2(1)
O(5)	18(1)	19(1)	27(1)	2(1)	-9(1)	-8(1)
C(5)	20(1)	26(1)	24(1)	-3(1)	2(1)	-4(1)
C(6)	18(1)	22(1)	15(1)	1(1)	-2(1)	-7(1)
C(7)	24(1)	26(1)	21(1)	7(1)	-2(1)	-12(1)
C(8)	32(1)	22(1)	27(1)	10(1)	-11(1)	-11(1)
C(9)	25(1)	15(1)	29(1)	3(1)	-7(1)	-5(1)
C(10)	18(1)	16(1)	17(1)	1(1)	-7(1)	-3(1)
C(11)	15(1)	15(1)	19(1)	2(1)	-5(1)	-6(1)
C(12)	14(1)	18(1)	19(1)	-1(1)	-2(1)	-6(1)
C(13)	23(1)	24(1)	36(1)	-2(1)	-16(1)	-7(1)
C(14)	44(1)	46(1)	25(1)	-3(1)	-10(1)	-27(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for t3twin5.

	x	y	z	U(eq)
H(22A)	3388	-3	4716	20
H(23A)	3346	-1707	3585	23
H(23B)	1902	-1026	4237	23
H(25A)	3096	-397	643	27
H(25B)	4117	-1313	1229	27
H(26A)	4755	454	1075	21
H(27A)	2939	1773	635	28
H(27B)	2209	1888	2042	28
H(28A)	3111	3598	1484	32
H(28B)	4501	2678	1091	32
H(29A)	4324	3442	3000	29
H(29B)	2938	3214	3497	29
H(31A)	5526	-699	3761	20
H(31B)	5344	-1345	2600	20
H(33A)	9496	-1807	1252	44
H(33B)	9036	-400	1728	44
H(33C)	8767	-787	491	44
H(34A)	538	2111	5335	61
H(34B)	1689	1415	5903	61
H(34C)	859	648	5425	61
H(2A)	8197	4995	305	19
H(3A)	6878	6770	1435	26
H(3B)	6009	6160	828	26
H(5A)	5769	5473	4397	30
H(5B)	6662	6363	3846	30
H(6A)	8070	4578	3941	22
H(7A)	6666	3296	4430	28
H(7B)	6627	3196	3037	28
H(8A)	8097	1448	3537	31
H(8B)	8885	2326	3911	31
H(9A)	9962	1552	1984	27
H(9B)	8682	1857	1522	27
H(11A)	9546	5709	1219	19
H(11B)	8508	6362	2400	19
H(13A)	11924	6784	3461	39
H(13B)	12318	5339	3140	39
H(13C)	11238	5889	4336	39
H(14A)	6594	2958	-199	53
H(14B)	7750	3554	-791	53
H(14C)	6329	4407	-381	53

VI. X-ray structure of the DA adduct (entry 5, table 1)

Table 1. Crystal data and structure refinement for SMCCS10.

Identification code	smccs10
Empirical formula	C ₁₆ H ₂₈ O ₂ Si ₂
Formula weight	308.56
Temperature	243(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.4464(9) Å alpha = 110.742(2) deg. b = 13.2552(18) Å beta = 103.158(3) deg. c = 13.564(2) Å gamma = 103.447(3) deg.
Volume	991.1(2) Å ³
Z, Calculated density	2, 1.034 Mg/m ³
Absorption coefficient	0.179 mm ⁻¹
F(000)	336
Crystal size	0.30 x 0.15 x 0.02 mm
Theta range for data collection	1.71 to 26.37 deg.
Limiting indices	-8<=h<=3, -14<=k<=16, -16<=l<=16
Reflections collected / unique	6365 / 4007 [R(int) = 0.0281] S20

Completeness to theta = 26.37 99.0 %
 Absorption correction EMPIRICAL
 Max. and min. transmission 0.9964 and 0.9483
 Refinement method Full-matrix least-squares on F²
 Data / restraints / parameters 4007 / 0 / 186
 Goodness-of-fit on F² 1.031
 Final R indices [I>2sigma(I)] R1 = 0.0541, wR2 = 0.1212
 R indices (all data) R1 = 0.1106, wR2 = 0.1442
 Extinction coefficient 0.011(4)
 Largest diff. peak and hole 0.255 and -0.214 e.A⁻³

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (A² x 10³) for SMCCS10.
 U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si(1)	5130(2)	9704(1)	8001(1)	61(1)
C(1)	4444(5)	6287(2)	9699(2)	50(1)
O(1)	7361(4)	5517(2)	6488(2)	84(1)
Si(2)	792(1)	3174(1)	6193(1)	50(1)
C(2)	2788(5)	5705(2)	8723(2)	48(1)
O(2)	3052(3)	4302(1)	7081(2)	47(1)
C(3)	3068(4)	5460(2)	7608(2)	42(1)
C(4)	5368(4)	6254(2)	7718(2)	41(1)
C(5)	7257(4)	6312(2)	8681(2)	49(1)
C(6)	6841(5)	6785(3)	9781(2)	62(1)
C(7)	5270(4)	7398(2)	7884(2)	45(1)
C(8)	5213(5)	8319(2)	7955(2)	54(1)
C(9)	5743(5)	5762(2)	6607(2)	56(1)
C(10)	4037(7)	6497(3)	10794(3)	81(1)
C(11)	-1323(7)	2918(3)	6883(3)	105(1)
C(12)	-550(6)	3415(3)	4991(3)	79(1)
C(13)	1859(7)	1981(3)	5790(4)	121(2)
C(14)	7280(7)	10854(3)	9326(3)	100(1)
C(15)	5770(7)	9827(3)	6770(3)	101(1)
C(16)	2249(6)	9747(3)	7908(3)	95(1)

Table 3. Bond lengths [Å] and angles [deg] for SMCCS10.

Si(1)-C(8)	1.828(3)
Si(1)-C(16)	1.848(4)
Si(1)-C(14)	1.849(4)
Si(1)-C(15)	1.860(4)
C(1)-C(2)	1.319(4)
C(1)-C(6)	1.493(4)
C(1)-C(10)	1.507(4)
O(1)-C(9)	1.190(3)
Si(2)-O(2)	1.6491(18)
Si(2)-C(13)	1.828(3)
Si(2)-C(12)	1.834(3)
Si(2)-C(11)	1.855(4)
C(2)-C(3)	1.492(4)
O(2)-C(3)	1.443(3)
C(3)-C(4)	1.546(4)
C(4)-C(7)	1.471(3)
C(4)-C(9)	1.515(4)
C(4)-C(5)	1.535(3)
C(5)-C(6)	1.513(4)
C(7)-C(8)	1.200(3)
C(8)-Si(1)-C(16)	108.90(16)
C(8)-Si(1)-C(14)	108.33(15)
C(16)-Si(1)-C(14)	111.33(19)
C(8)-Si(1)-C(15)	108.01(16)
C(16)-Si(1)-C(15)	109.3(2)
C(14)-Si(1)-C(15)	110.9(2)
C(2)-C(1)-C(6)	121.6(3)
C(2)-C(1)-C(10)	122.3(3)
C(6)-C(1)-C(10)	116.1(3)
O(2)-Si(2)-C(13)	104.75(14)
O(2)-Si(2)-C(12)	110.32(13)
C(13)-Si(2)-C(12)	112.48(19)
O(2)-Si(2)-C(11)	110.36(14)
C(13)-Si(2)-C(11)	111.0(2)
C(12)-Si(2)-C(11)	107.92(19)
C(1)-C(2)-C(3)	125.2(3)
C(3)-O(2)-Si(2)	125.28(15)
O(2)-C(3)-C(2)	110.8(2)
O(2)-C(3)-C(4)	106.03(19)
C(2)-C(3)-C(4)	111.7(2)
C(7)-C(4)-C(9)	105.9(2)
C(7)-C(4)-C(5)	112.0(2)
C(9)-C(4)-C(5)	111.6(2)
C(7)-C(4)-C(3)	110.3(2)
C(9)-C(4)-C(3)	107.6(2)
C(5)-C(4)-C(3)	109.3(2)
C(6)-C(5)-C(4)	111.0(2)
C(1)-C(6)-C(5)	113.8(2)
C(8)-C(7)-C(4)	175.8(3)
C(7)-C(8)-Si(1)	177.5(3)
O(1)-C(9)-C(4)	125.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for SMCCS10.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
<hr/>						
Si(1)	65(1)	40(1)	77(1)	27(1)	14(1)	21(1)
C(1)	70(2)	45(2)	50(2)	26(1)	23(2)	32(2)

O(1)	85(2)	98(2)	93(2)	39(2)	55(2)	52(2)
Si(2)	51(1)	38(1)	52(1)	18(1)	7(1)	10(1)
C(2)	48(2)	42(2)	64(2)	25(2)	27(2)	23(1)
O(2)	44(1)	35(1)	55(1)	16(1)	9(1)	16(1)
C(3)	38(1)	35(1)	49(2)	15(1)	8(1)	17(1)
C(4)	39(1)	38(1)	45(2)	18(1)	12(1)	16(1)
C(5)	37(2)	46(2)	60(2)	23(1)	7(1)	15(1)
C(6)	64(2)	61(2)	49(2)	21(2)	0(2)	22(2)
C(7)	46(2)	42(2)	45(2)	18(1)	12(1)	15(1)
C(8)	57(2)	43(2)	60(2)	23(2)	14(2)	19(1)
C(9)	67(2)	52(2)	57(2)	26(2)	27(2)	25(2)
C(10)	135(3)	76(2)	67(2)	42(2)	54(2)	61(2)
C(11)	93(3)	93(3)	95(3)	37(2)	28(2)	-18(2)
C(12)	89(2)	66(2)	53(2)	24(2)	-5(2)	9(2)
C(13)	105(3)	55(2)	132(4)	-9(2)	-17(3)	39(2)
C(14)	95(3)	52(2)	112(3)	20(2)	-6(2)	18(2)
C(15)	124(3)	85(3)	118(3)	70(3)	43(3)	35(3)
C(16)	87(3)	83(3)	120(3)	43(2)	25(2)	47(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for SMCCS10.

	x	y	z	U(eq)
H(1)	1280(50)	5420(20)	8710(20)	59(8)
H(3A)	1817	5564	7120	51
H(5A)	7324	5540	8517	59
H(5B)	8721	6803	8743	59
H(6A)	7839	6635	10332	74
H(6B)	7249	7620	10056	74
H(9A)	4606	5640	5961	67
H(10A)	2440	6131	10647	121
H(10B)	4483	7316	11243	121
H(10C)	4927	6177	11196	121
H(11A)	-650	2790	7524	157
H(11B)	-2632	2247	6355	157
H(11C)	-1792	3582	7131	157
H(12A)	523	3548	4613	118
H(12B)	-1013	4080	5250	118
H(12C)	-1869	2744	4473	118
H(13A)	2962	2135	5433	182
H(13B)	608	1278	5270	182
H(13C)	2573	1895	6452	182
H(14A)	8774	10819	9345	151
H(14B)	6958	10750	9956	151
H(14C)	7235	11596	9374	151
H(15A)	7278	9799	6814	151
H(15B)	5703	10549	6768	151
H(15C)	4664	9195	6086	151
H(16A)	1161	9141	7202	143
H(16B)	2198	10486	7949	143
H(16C)	1874	9636	8525	143

V. B3LYP Cartesian coordinates for reactants and transition structures.

3-Methyl-1-siloxybutadiene (5)

C	-0.291759963	-0.8388093301	-0.0002606993
C	0.5059964811	0.2426228683	-0.0000529445
C	1.9692616598	0.2007558899	-0.0002209293
C	2.6796563643	1.3428727428	-0.0000653707
O	-1.6551005205	-0.8413212785	-0.0001262405
H	0.0965483248	-1.8527646016	-0.0005855486
H	0.0581965088	1.2360556492	0.0002393688
H	3.765679981	1.338360888	-0.0001840005
H	2.1962292485	2.3166117251	0.0001799657
C	2.6596173616	-1.1438797192	-0.0006195779
H	2.3833376083	-1.7352768696	0.881904474
H	2.3820200494	-1.7354240292	-0.882633911
H	3.7467170989	-1.0262482796	-0.0014395151
Si	-2.6809175775	0.4859450054	0.0006011887
H	-4.0446222529	-0.0881523032	0.000628715
H	-2.4733011407	1.3259104419	1.2104154392
H	-2.4737865992	1.3268928225	-1.2086145753

Sum of electronic and zero-point Energies=	-561.121106
Sum of electronic and thermal Energies=	-561.111953
Sum of electronic and thermal Enthalpies=	-561.111009
Sum of electronic and thermal Free Energies=	-561.155587

Ethylene

C	0.00000	0.00000	0.66547
C	0.00000	0.00000	-0.66547
H	0.00000	0.92359	1.23959
H	0.00000	-0.92359	-1.23959
H	0.00000	-0.92359	1.23959
H	0.00000	0.92359	-1.23959

Sum of electronic and zero-point Energies=	-639.617355
Sum of electronic and thermal Energies=	-639.605658
Sum of electronic and thermal Enthalpies=	-639.604713
Sum of electronic and thermal Free Energies=	-639.655629

Butadiene

C	-0.32608	0.65176	0.0
C	0.32608	1.82294	0.0
C	0.32608	-0.65176	0.0
C	-0.32608	-1.82294	0.0
H	-0.20119	2.77204	0.0
H	0.20119	-2.77204	0.0
H	1.41308	1.86819	0.0
H	-1.41308	-1.86819	0.0
H	-1.41661	0.64473	0.0
H	1.41661	-0.64473	0.0

Sum of electronic and zero-point Energies=	-155.906652
Sum of electronic and thermal Energies=	-155.902007
Sum of electronic and thermal Enthalpies=	-155.901063
Sum of electronic and thermal Free Energies=	-155.932442

Butenyne

C	1.6633	-0.37325	-0.00007
C	0.63749	0.49078	0.00004
H	1.50518	-1.44742	0.00007
C	-0.73559	0.11054	0.00034
C	-1.91323	-0.17034	-0.00034
H	2.68947	-0.01897	-0.00005
H	0.83772	1.56204	-0.00034
H	-2.9442	-0.44202	0.00051

Sum of electronic and zero-point Energies=	-154.672623
Sum of electronic and thermal Energies=	-154.668125
Sum of electronic and thermal Enthalpies=	-154.667181
Sum of electronic and thermal Free Energies=	-154.698657

1-Silylbutenyne

C	0.0182920674	-2.1053846442	1.4776745602
C	0.4680444592	-0.8412520612	1.5085270751
H	0.5489624844	-2.887722997	0.943748859
C	1.6555068764	-0.3972702214	0.8643410869
C	2.6685393409	0.0201964119	0.3262513492
H	-0.8973269054	-2.3826757494	1.9906419196
H	-0.0929967399	-0.0838842747	2.0557761932
Si	4.1827582966	0.6147250309	-0.4912269546
H	4.1463071141	0.2878151591	-1.94088164
H	4.3035851356	2.087754242	-0.3354410651
H	5.3797487706	-0.0291004961	0.1110715664

Sum of electronic and zero-point Energies=	-445.370974
Sum of electronic and thermal Energies=	-445.364012
Sum of electronic and thermal Enthalpies=	-445.363068
Sum of electronic and thermal Free Energies=	-445.403278

Methylacrylate

C	2.33945	0.85757	0.0000
C	1.45993	-0.1462	0.00000
H	1.99625	1.88835	0.00000
H	1.7655	-1.18826	0.000000
H	3.41051	0.67937	0.00000
C	0.0	0.12535	0.000000
O	-0.52044	1.2227	0.00000
O	-0.69985	-1.03467	0.00000
C	-2.12727	-0.88642	0.00000
H	-2.45756	-0.3424	0.88923
H	-2.45756	-0.3424	-0.88923
H	-2.52755	-1.90075	0.0000

Acrolein

C	-0.1382770676	-0.6022797762	-1.6584805857
C	0.2077593946	-0.5833377144	-0.3661329975
H	0.1183937424	-1.4266569803	-2.3170604912
H	-0.6972787309	0.2197048442	-2.1023695013
C	-0.15446409	0.5520311276	0.5031390472
O	0.1310624181	0.6299466575	1.6819067441
H	-0.7254525396	1.3615498726	-0.0062358297
H	0.7657287611	-1.3926528186	0.0992590855

Sum of electronic and zero-point Energies=	-191.850322
Sum of electronic and thermal Energies=	-191.845967
Sum of electronic and thermal Enthalpies=	-191.845023
Sum of electronic and thermal Free Energies=	-191.876602

1-Formyl-1-silylbutenyne

C	1.8984403402	1.5992182885	0.00000000
C	1.2735443935	0.4051871171	0.0000000000
H	1.3518571628	2.5359739715	0.0000000000
C	-0.1429731672	0.2470916329	0.0000000000
C	-1.3459078341	0.043208717	0.0000000000
H	2.983713507	1.6275478814	0.0000000000
C	2.1009823156	-0.8538464089	0.0000000000
O	3.3128301548	-0.8607182281	0.0000000000
H	1.514633094	-1.7947962679	0.0000000000
Si	-3.1506440742	-0.22948437	0.0000000000
H	-3.7554137167	0.3856409404	-1.2094182431
H	-3.4375168188	-1.6866365393	0.0000000000
H	-3.7554137167	0.3856409404	1.2094182431

Sum of electronic and zero-point Energies=	-558.680863
Sum of electronic and thermal Energies=	-558.672129
Sum of electronic and thermal Enthalpies=	-558.671185
Sum of electronic and thermal Free Energies=	-558.716011

Propene

C	1.282696	0.220558	0.000002
C	0.133765	-0.456000	-0.000003
H	2.245057	-0.284307	0.000001
H	0.164848	-1.546762	-0.000007
H	1.304667	1.308821	0.000007
C	-1.235034	0.162267	-0.000002
H	-1.813180	-0.149220	-0.879190
H	-1.812454	-0.147615	0.880228
H	-1.177496	1.258139	-0.001022

Sum of electronic and zero-point Energies=	-117.827470
Sum of electronic and thermal Energies=	-117.823392
Sum of electronic and thermal Enthalpies=	-117.822448
Sum of electronic and thermal Free Energies=	-117.852478

Methylvinylether

C	-0.8138465341	-1.267095021	-0.4051827641
C	-0.3651084365	-0.5682542579	0.6423518452
H	-0.6341546016	-0.98787958	-1.4368229223
H	-1.3918031282	-2.1665751546	-0.227569059
H	-0.5620288307	-0.8744011885	1.6663962915
O	0.3687997699	0.5740205635	0.6439621429
C	0.7136152777	1.1110133344	-0.6241358292
H	1.2940174971	2.0141072022	-0.4271429531
H	1.3196560703	0.4011164013	-1.2025251507
H	-0.1840470088	1.3674834789	-1.2022328608

Sum of electronic and zero-point Energies=	-193.028268
Sum of electronic and thermal Energies=	-193.023538
Sum of electronic and thermal Enthalpies=	-193.022594
Sum of electronic and thermal Free Energies=	-193.054964

TS: 5 + Ethylene

C	0.4655317581	-0.4231756651	-0.2782494477
C	0.0409122549	0.5777874582	-1.1328964934
C	-0.0457547223	1.9282398261	-0.7490949291
C	0.3303730152	2.3152028482	0.5338527548
H	0.2025818409	3.3526950337	0.8362442727
C	-1.0730414864	1.2393578341	1.8020910132
C	-1.0395941671	-0.1155172405	1.5021280938
O	0.3934308757	-1.7251416387	-0.7101581996
H	-1.9188634226	1.8375818014	1.4774961365
H	1.1455247591	1.8088097544	1.0397356555
H	1.2017501733	-0.2357878575	0.4977887522
H	-0.5886790176	1.5986360137	2.7064217378
H	-0.422326541	0.2596176498	-2.065399416
C	-0.8225263071	2.8818960517	-1.6337601226
H	-0.6879205486	2.6361702213	-2.6929076504
H	-1.9021942276	2.833956778	-1.4281483732
H	-0.5078745372	3.920199828	-1.4864431655
Si	0.8849794631	-3.0622317321	0.1625796891
H	-0.1482324795	-3.4968202227	1.1398121162
H	1.1131802078	-4.139166621	-0.8275316634
H	2.142035198	-2.7566191977	0.9020405981
H	-1.818129542	-0.5720235202	0.9012242296
H	-0.483413424	-0.7976189782	2.1403915054

Sum of electronic and zero-point Energies=	-639.617355
Sum of electronic and thermal Energies=	-639.605658
Sum of electronic and thermal Enthalpies=	-639.604713
Sum of electronic and thermal Free Energies=	-639.655629

Exo TS: 5 + Butadiene

C	0.3457171704	-0.8230679776	0.0037672827
C	-0.8239550338	-1.4147157782	0.4131785308

C	-2.0715532897	-1.1831556526	-0.2070496376
C	-2.1795056494	-0.2581885414	-1.256406254
H	-3.1592924923	-0.123158541	-1.7129815362
C	-1.8360224873	1.5594991623	-0.4494726456
C	-0.5863039425	1.672061942	0.18061196
O	1.4756546334	-0.931326301	0.7440856693
H	-1.9718035883	2.1057337473	-1.3828034871
C	0.5687689152	2.2641763785	-0.4478337896
C	1.7333238658	2.5718073401	0.1644708355
H	-1.3695518578	-0.1788568369	-1.9760435013
H	0.4718183373	-0.3901912026	-0.9822739558
H	-2.7209396547	1.5661305345	0.1818279704
H	-0.7916459987	-1.9816572507	1.3418323396
Si	3.0571991671	-0.8081489533	0.1894674117
H	3.8153918862	0.0600833726	1.1175816293
H	3.6649798675	-2.1669622912	0.1998346991
H	3.0791658944	-0.2804514886	-1.1981040443
C	-3.3234615752	-1.6883914339	0.4724716689
H	-3.1103202821	-2.5460517432	1.1189578358
H	-3.7745772075	-0.9096957953	1.1078234112
H	-4.0873393451	-1.9913635716	-0.2522723639
H	2.5519032751	3.0409393901	-0.3726866174
H	1.8780004039	2.4015601943	1.2288169405
H	0.4705239756	2.4905502754	-1.5126393813
H	-0.5143864607	1.4679343266	1.2454732353

Sum of electronic and zero-point Energies= -716.990166
Sum of electronic and thermal Energies= -716.976306
Sum of electronic and thermal Enthalpies= -716.975362
Sum of electronic and thermal Free Energies= -717.031118

Endo TS: 5 + Butadiene

C	0.4095499407	-0.8072629499	-0.4746207136
C	-0.7357329933	-1.3922865283	0.0061566948
C	-2.0399878935	-1.0469523009	-0.4056514251
C	-2.2468876841	0.0132458548	-1.3031972614
H	-3.2741182786	0.2262016797	-1.597700829
C	-1.7328421119	1.7028582016	-0.3570979873
C	-0.3716986896	1.7841097917	-0.0215270554
O	1.5944998379	-1.0531220413	0.1304904271
H	-2.0758426069	2.3233055833	-1.1828298113
C	0.1476561867	1.646734759	1.3137763321
C	1.4014651966	1.9574272502	1.7120110356
H	-1.5441594796	0.1581525502	-2.1193705249
H	0.44517137	-0.2412481761	-1.3994413125
H	-2.446000041	1.6557361102	0.4639005494
H	-0.6130483793	-2.0720153133	0.847296141
Si	3.1043767039	-0.5474856998	-0.3969154928
H	3.0006649116	0.7599872971	-1.0965187891
H	3.9762279272	-0.4650684972	0.7938532385
H	3.6633920461	-1.5432858759	-1.3530512802

C	-3.2215586323	-1.6662485581	0.304975238
H	-3.6345604277	-2.5104014916	-0.265779604
H	-2.9528455594	-2.0476639668	1.2964559822
H	-4.0356817991	-0.941753172	0.4290832998
H	1.7143881244	1.8434121866	2.7449013641
H	2.1308953277	2.3781100173	1.0230943525
H	-0.5534571103	1.2677647432	2.0595042083
H	0.321921502	2.1487893316	-0.7794526484

Sum of electronic and zero-point Energies= -716.989006
Sum of electronic and thermal Energies= -716.975078
Sum of electronic and thermal Enthalpies= -716.974134
Sum of electronic and thermal Free Energies= -717.030182

Exo TS: 5 + Butenyne

C	0.620938738	1.2682556064	-0.4757215722
C	1.9900197635	1.1687497018	-0.4447184977
C	2.718874608	0.0696638041	-0.9501448501
C	2.0619307331	-1.0590857632	-1.4639558454
H	2.6834357727	-1.8600287864	-1.8628249165
C	1.1636488435	-1.9510604941	0.0855004184
C	0.1284759461	-1.1696839389	0.6263024271
O	0.0119503147	2.2988101845	0.1622065878
H	0.8734625147	-2.8175556177	-0.5049226216
C	-1.1865903293	-1.2148886506	0.1145130661
C	-2.3048446593	-1.2217728747	-0.3672114712
H	1.1361707702	-0.9296434137	-2.0187292685
H	-0.0081852726	0.6746309424	-1.1287997183
H	2.034587322	-2.1226181155	0.7122232184
H	2.5207698111	1.9373663296	0.1143710577
Si	-1.6429452653	2.5843426522	0.2741571811
H	-2.2386959215	1.8510640972	1.4168336831
H	-1.7604985562	4.0434295759	0.5074424576
H	-2.316056708	2.2034840926	-0.9940581141
C	4.2139412825	0.0289737669	-0.731647108
H	4.518134482	0.603337393	0.1507552664
H	4.5711728886	-1.000101147	-0.6097955503
H	4.7511742055	0.4519429052	-1.592553231
H	0.2990462462	-0.5956591308	1.5315576727
H	-3.2993122002	-1.3028680492	-0.7416089612

Sum of electronic and zero-point Energies= -715.761100
Sum of electronic and thermal Energies= -715.747321
Sum of electronic and thermal Enthalpies= -715.746377
Sum of electronic and thermal Free Energies= -715.801908

Endo TS: 5 + Butenyne

C	-1.4639167503	0.3892296342	-0.754443804
C	-1.1672100587	-0.6588709273	-1.5890353967
C	-1.3164157003	-2.0171256119	-1.2378917956
C	-1.7569808184	-2.3715697312	0.044583254

H	-1.8814832672	-3.4306556703	0.2650808066
C	-0.2877355423	-1.8649807038	1.3209964724
C	0.0737644539	-0.5073452556	1.2794340509
O	-1.1506287626	1.6549352417	-1.1337934617
H	0.4539224431	-2.5854236627	0.9857194614
C	1.251701274	-0.0330264833	0.658768835
C	2.2716591973	0.3920336954	0.151669011
H	-2.5064432878	-1.7521205144	0.5295755406
H	-2.1177625903	0.2936845818	0.1064586116
H	-0.8551151977	-2.1930245759	2.1894635938
H	-0.6534186209	-0.4083490611	-2.5148328496
C	-0.7033121024	-3.0638201758	-2.1391210666
H	-0.757087129	-2.7636255221	-3.1911819347
H	0.3611881958	-3.2162306298	-1.9044401938
H	-1.2024730936	-4.0329093258	-2.0356999566
Si	-1.2220690853	3.0059288455	-0.1406310312
H	-0.1935310051	2.9606390908	0.9271184406
H	-0.9983090943	4.1615544816	-1.0365124914
H	-2.5682734885	3.0918197349	0.4928302642
H	3.171876714	0.7478123927	-0.2934461152
H	-0.4467835634	0.1888811323	1.9349105252

Sum of electronic and zero-point Energies= -715.757045
Sum of electronic and thermal Energies= -715.743035
Sum of electronic and thermal Enthalpies= -715.742091
Sum of electronic and thermal Free Energies= -715.798694

Exo TS: 5 + 1-Silylbutenyne

C	0.6091099588	1.329374494	-0.2479889407
C	1.9752088887	1.2171269415	-0.2832799731
C	2.6727806568	0.1985010753	-0.9739345498
C	1.9873563482	-0.8290532179	-1.6399283908
H	2.586475539	-1.5468005609	-2.19797818
C	1.1731202547	-1.9795863399	-0.2368729881
C	0.1676503278	-1.3216153142	0.4957350124
O	0.0312154549	2.2618770437	0.5433073323
H	0.8474666689	-2.7323339813	-0.9518523452
C	-1.1678096159	-1.2831375908	0.0631655824
C	-2.3266454778	-1.2233795591	-0.342434371
H	1.0412410227	-0.6042139772	-2.1255100445
H	-0.0494290773	0.8103501379	-0.935340227
H	2.0756887803	-2.2547285159	0.30293734
H	2.5369970413	1.8972171137	0.3547328355
Si	-1.6215397325	2.5151551226	0.7660118506
H	-2.1540263711	1.6274617626	1.8269110392
H	-1.7328724736	3.9291367665	1.1936061116
H	-2.3422856964	2.2922899506	-0.5125487313
C	4.1608360883	0.080417047	-0.7396848449
H	4.6407335901	1.0657419849	-0.7376751791
H	4.3774945459	-0.3785334514	0.237263233
H	4.6455030696	-0.5325240474	-1.5056504229

H	0.3975108475	-0.8961432671	1.4680929052
Si	-4.0470957692	-1.2389085739	-0.9045192445
H	-4.8169714851	-0.1432421412	-0.2531757735
H	-4.1193353742	-1.0421715614	-2.3787265716
H	-4.7260009203	-2.525506801	-0.5843073842

Sum of electronic and zero-point Energies=	-1006.461615
Sum of electronic and thermal Energies=	-1006.445329
Sum of electronic and thermal Enthalpies=	-1006.444385
Sum of electronic and thermal Free Energies=	-1006.507706

Endo TS: **5** + 1-Silylbutenyne

C	-1.3821362838	0.407716887	-0.7813554754
C	-1.1062171339	-0.6581987057	-1.5972668291
C	-1.3034851427	-2.0098257386	-1.2359946275
C	-1.7712319697	-2.3480027025	0.0417393071
H	-1.9479092308	-3.4015360217	0.2518262665
C	-0.2988467398	-1.9346333174	1.3313794218
C	0.112281041	-0.5891297303	1.3328828706
O	-1.0269655991	1.6566810831	-1.1646944178
H	0.4215648867	-2.6711804694	0.9850781858
C	1.2951675512	-0.138691564	0.7210204128
C	2.3376237941	0.2654495465	0.2137559726
H	-2.4989478214	-1.6986285425	0.5208272429
H	-2.0204342555	0.3349673726	0.0935397951
H	-0.8824692046	-2.2650071827	2.1882805297
H	-0.5811653397	-0.4341164378	-2.5234936692
C	-0.722795467	-3.0769970646	-2.1337669788
H	-0.8592365709	-2.8222380823	-3.1906712375
H	0.3598927076	-3.1872626064	-1.9710145614
H	-1.1842244864	-4.0533704089	-1.9559354405
Si	-1.0748027448	3.0213731445	-0.1827707728
H	-0.0263728227	2.9745539131	0.8646946916
H	-0.8620863021	4.1657296282	-1.0946035334
H	-2.4101658619	3.1123176178	0.4714354056
Si	3.8838439405	0.8322685078	-0.5315627948
H	3.953459477	0.4585201716	-1.9722521606
H	3.9978007174	2.3137765337	-0.4336728615
H	5.0750322439	0.2397920852	0.1399760806
H	-0.4019454827	0.1133254838	1.9871831275

Sum of electronic and zero-point Energies=	-1006.457982
Sum of electronic and thermal Energies=	-1006.441413
Sum of electronic and thermal Enthalpies=	-1006.440468
Sum of electronic and thermal Free Energies=	-1006.505869

Exo TS: **5** + Acrolein

C	0.47607	-0.82665	-0.23163
C	-0.68731	-1.50213	0.05168
C	-1.97542	-1.05867	-0.32369
C	-2.1743	0.17548	-0.95824

H	-3.18815	0.42996	-1.26175
C	-1.77047	1.57761	0.45471
C	-0.46315	1.45793	0.94527
O	1.63269	-1.19659	0.32562
H	-2.59851	1.33917	1.11659
H	-1.41989	0.54783	-1.64422
H	0.53658	-0.06877	-1.00676
H	-1.97726	2.41439	-0.21247
H	-0.60276	-2.35805	0.71853
C	-3.16189	-1.81102	0.2339
H	-3.01508	-2.89404	0.15366
H	-3.30566	-1.58918	1.30191
H	-4.08879	-1.55258	-0.28636
Si	3.19238	-0.5855	0.03698
H	3.73808	0.01585	1.26821
H	4.00143	-1.78502	-0.30968
H	3.15828	0.33423	-1.12275
C	0.63292	2.17214	0.34813
O	1.8229	2.07274	0.65875
H	0.33924	2.86152	-0.48055
H	-0.24483	0.86132	1.82513

Sum of electronic and zero-point Energies= -752.945617
Sum of electronic and thermal Energies= -752.932234
Sum of electronic and thermal Enthalpies= -752.931290
Sum of electronic and thermal Free Energies= -752.986175

Endo TS: 5 + Acrolein

C	-0.7288333715	-0.7750812955	0.0783340792
C	0.4216454716	-1.2565171643	-0.5038026552
C	1.6860760029	-1.272759967	0.1240434802
C	1.8888382981	-0.7231768353	1.3977822251
H	2.8844766012	-0.8085098514	1.8287639901
C	1.6916885004	1.2898150344	1.1619651806
C	0.3623676625	1.6361818897	0.8983160172
O	-1.836613493	-0.6074450737	-0.6422489582
H	2.0861309278	1.4833798918	2.1568699513
H	1.0986195105	-0.7863135191	2.1397074753
H	-0.8147693608	-0.6111106121	1.1486204374
H	2.4214785258	1.4422296102	0.3689128136
H	0.3567137304	-1.5189506982	-1.5577598869
C	-0.1286157326	1.941592922	-0.4180509042
O	-1.2995380039	2.2131805705	-0.7069088479
H	0.6466509589	1.9289573828	-1.217926205
Si	-3.2693353635	0.1709800318	-0.1572549809
H	-3.7382472277	1.0745565532	-1.2214113073
H	-4.2654995574	-0.9270726211	0.0004082522
H	-3.07729685	0.8076309647	1.1665895119
C	2.8764521467	-1.6762721448	-0.7167078436
H	2.8010785735	-2.7303316149	-1.0140808
H	2.9359749257	-1.0905380581	-1.6436207599

H	3.8172340727	-1.551176874	-0.1728412182
H	-0.3493202084	1.7254652885	1.7171073932

Sum of electronic and zero-point Energies=	-752.947601
Sum of electronic and thermal Energies=	-752.934425
Sum of electronic and thermal Enthalpies=	-752.933481
Sum of electronic and thermal Free Energies=	-752.987507

Exo TS: 5 + 1-Formyl-1-silylbutenyne

C	1.0558406963	1.3347067399	-0.7772912058
C	2.3436995243	1.0626694257	-0.4334409086
C	2.9160109809	-0.2463192279	-0.3803503652
C	2.2118482648	-1.3896523933	-0.737990122
H	2.7516049353	-2.3312343708	-0.7946256571
C	1.0284264265	-1.8593935374	0.9329669178
C	0.1685039847	-0.8101956727	1.2787374036
O	0.5896412464	2.5985264908	-0.748526683
H	0.6173519085	-2.7353795887	0.4407555706
C	-1.1336627613	-0.6894586596	0.7370632565
C	-2.258828535	-0.5733064247	0.2640068003
H	1.3644541716	-1.3196962538	-1.4127255824
H	0.3625860277	0.5793202843	-1.1379128763
H	1.8651949271	-2.0313322578	1.6012883905
H	2.9481954976	1.8997896515	-0.0925466896
C	0.6550255355	0.1842943076	2.2404204148
O	1.787959953	0.1817437912	2.7099232698
H	-0.0821920793	0.9589886745	2.5367993687
Si	-3.9576410743	-0.4777759508	-0.3648551639
H	-4.0701138257	-1.222401446	-1.647995812
H	-4.9308324682	-1.0570127537	0.6000487333
H	-4.3437567361	0.9385894163	-0.6126541622
Si	-1.0078576241	3.0887001441	-1.0006270114
H	-1.7589038494	3.0911153643	0.2763876424
H	-0.9091897306	4.4643824351	-1.5377152765
H	-1.6482022617	2.1781292901	-1.9829193816
C	4.2839450319	-0.3679264025	0.2454951478
H	4.9783161973	0.3645949853	-0.1835927938
H	4.220132511	-0.167497917	1.321984547
H	4.7083587152	-1.3660686839	0.1046682085

Sum of electronic and zero-point Energies=	-1119.785799
Sum of electronic and thermal Energies=	-1119.767282
Sum of electronic and thermal Enthalpies=	-1119.766338
Sum of electronic and thermal Free Energies=	-1119.835774

Endo TS: 5 + 1-Formyl-1-silylbutenyne

C	0.8329016678	1.4283964884	-0.5823410306
C	1.2764187965	1.3575717317	0.7031069744
C	2.2256493326	0.4055992698	1.1864084494
C	2.7742636285	-0.584516496	0.3795362342
H	3.5810002938	-1.1877010227	0.7883090108

C	1.3601962291	-2.0941483499	0.207469943
C	0.1394467185	-1.6555438001	-0.3278475003
O	-0.0933716567	2.3410005157	-0.9339511242
H	1.375415762	-2.4481057122	1.2330364851
C	-0.9970194469	-1.4256001409	0.4856138302
C	-1.9941035089	-1.2440642359	1.1730703058
H	2.8125318616	-0.4551089996	-0.6976312696
H	1.2373655878	0.8134070522	-1.3822370022
H	2.0279485624	-2.6051860502	-0.4795551513
H	0.827880335	2.0464115516	1.4157480842
C	2.5088949133	0.4191796953	2.6685086395
H	2.9124516123	1.3924037893	2.9770345237
H	1.5899924157	0.261413053	3.2485115554
H	3.2308361681	-0.3516305694	2.9518639018
Si	-0.8193152178	2.4617609037	-2.4568472648
H	-1.7922674307	1.3599699329	-2.6543571773
H	-1.5038502267	3.7719943249	-2.4453343432
H	0.2251091125	2.410246439	-3.5109302057
C	0.0347151333	-1.4533259285	-1.7699134171
O	0.9945628542	-1.4536569518	-2.54077711
H	-0.9938840571	-1.2767084597	-2.1476829023
Si	-3.4675803425	-0.9686057691	2.1922376615
H	-4.6294553255	-0.6198052582	1.3314287804
H	-3.8149363576	-2.183368226	2.9791031762
H	-3.2473108317	0.1475583557	3.1533782822

Sum of electronic and zero-point Energies= -1119.787623
Sum of electronic and thermal Energies= -1119.769278
Sum of electronic and thermal Enthalpies= -1119.768333
Sum of electronic and thermal Free Energies= -1119.836039

Exo TS: **5** + Methylacrylate

C	0.1371712492	-1.2741801128	-0.2120969363
C	-1.0431183566	-1.9283817722	0.0334348171
C	-2.3169725096	-1.4622147505	-0.3648237703
C	-2.4809135912	-0.2076096579	-0.9650437697
H	-3.4865307833	0.0685585838	-1.2781682749
C	-2.0919282904	1.1320783407	0.4685802195
C	-0.7467184148	1.1142243003	0.8535363268
O	1.2798010526	-1.7387772061	0.3403783737
H	-2.8347676176	0.8432947744	1.2068569406
H	-1.7077810077	0.1953651392	-1.6136261835
H	0.2458268389	-0.5006407397	-0.965723996
H	-2.3980532412	1.9482464252	-0.1814966707
H	-0.9846137058	-2.8070385245	0.67321467
C	-3.529126595	-2.2581167167	0.0609949714
H	-3.6761733146	-3.1251932713	-0.598074949
H	-3.4272509732	-2.6486272704	1.0809471073
H	-4.4416132378	-1.6555831728	0.0121456669
Si	2.852785474	-1.1917524636	0.1001238062
H	3.3542848543	-0.5282132482	1.3250004218

H	3.677401311	-2.3936221126	-0.1764873839
H	2.8891267117	-0.2718234334	-1.0644194863
C	0.2185730497	1.8409802187	0.0555728158
O	0.0129022314	2.3266819624	-1.051947896
H	-0.420015521	0.6751684092	1.7878532174
O	1.4496799766	1.9184869332	0.6608308707
C	2.411327928	2.7210199277	-0.0329871539
H	3.3213937691	2.6754625202	0.5677449276
H	2.5974630498	2.3360421531	-1.0395051494
H	2.0634733311	3.7552060769	-0.115090055

Sum of electronic and zero-point Energies= -867.465089
Sum of electronic and thermal Energies= -867.449058
Sum of electronic and thermal Enthalpies= -867.448114
Sum of electronic and thermal Free Energies= -867.509824

Endo TS: 5 + Methylacrylate

C	-0.637455908	-1.1509092005	0.471628025
C	0.4914416541	-1.6868266335	-0.0923251009
C	1.761577405	-1.6823451967	0.5259590642
C	1.9426233638	-1.1274133855	1.7993554283
H	2.9317218639	-1.198018632	2.2477638269
C	1.7633014641	0.8648386411	1.5607124848
C	0.5454608947	1.2423601534	0.9880704928
O	-1.77344263	-1.0522001071	-0.2563125174
H	1.9120163505	1.0766216186	2.617201514
H	1.1402306052	-1.2082543963	2.527284404
H	-0.7254645459	-0.9317622359	1.5301625115
H	2.6470312758	0.9981778209	0.9432697007
H	0.4195872965	-1.986249429	-1.1353702346
C	0.4639654714	1.4641605336	-0.4427248205
O	1.3578091323	1.2694860586	-1.2563257946
Si	-3.2027577745	-0.303921113	0.218814613
H	-3.6970005077	0.5048912004	-0.9165441805
H	-4.2050613363	-1.3522219711	0.5445517972
H	-2.9580278722	0.5290144217	1.423885088
C	2.9618049055	-2.0143077299	-0.3288039691
H	2.7482467381	-2.849848082	-1.0048210301
H	3.2270675209	-1.1512202049	-0.9545647969
H	3.8346004297	-2.2774867602	0.2767389075
H	-0.3129223637	1.5057553883	1.5962853256
O	-0.7711617768	1.9370488121	-0.8169399226
C	-0.915524022	2.1889448794	-2.2185662103
H	-0.7746771507	1.2711738077	-2.7969355023
H	-1.9308876226	2.5676795974	-2.3480537834
H	-0.1866610139	2.930952959	-2.557464618

Sum of electronic and zero-point Energies= -867.465254
Sum of electronic and thermal Energies= -867.449296
Sum of electronic and thermal Enthalpies= -867.448352
Sum of electronic and thermal Free Energies= -867.509214

Exo TS: 5 + Propene

C	0.4242701626	-0.4043039741	-0.1167817291
C	-0.7444763513	-1.1100079922	0.0913367554
C	-1.9994354597	-0.6687466593	-0.3691149077
C	-2.0967075789	0.5385544929	-1.0605433524
H	-3.0814039744	0.9010107146	-1.3512899435
C	-1.4412298035	1.9973374898	0.368255083
C	-0.141258574	1.7319716264	0.7893078108
O	1.5773409819	-0.7796429265	0.5398731902
H	-1.6079766736	2.8181388791	-0.3272939425
H	-1.3042094337	0.8496362567	-1.7335157768
H	0.5834711014	0.2116429972	-0.997284398
H	-2.2690322282	1.8105039953	1.0445032427
H	-0.7016232477	-1.9308666816	0.80530589
Si	2.9677819594	-1.2834417915	-0.2382309629
H	4.0301151451	-1.3068763479	0.7935670871
H	2.8024597344	-2.6402243775	-0.8273009889
H	3.3271649513	-0.337224406	-1.3315269734
C	-3.2535726364	-1.3814895688	0.0901809707
H	-3.0854677547	-1.9591709668	1.005999546
H	-4.0662936694	-0.6707424937	0.2832455995
H	-3.6196911389	-2.0820422975	-0.6731738179
H	0.0029150616	1.2548900903	1.7543224721
C	1.0435825754	2.4923574913	0.2477744719
H	1.9655169901	1.9003298096	0.2867896598
H	0.8802184664	2.8068833104	-0.7911729036
H	1.2291273792	3.4054025747	0.8325825901

Sum of electronic and zero-point Energies= -678.904202
Sum of electronic and thermal Energies= -678.891058
Sum of electronic and thermal Enthalpies= -678.890113
Sum of electronic and thermal Free Energies= -678.944411

Endo TS: 5 + Propene

C	0.4589292175	-0.6818901364	-0.0743624113
C	-0.6470770778	-0.988546055	0.6965687736
C	-1.9665654898	-0.8392073676	0.2329171608
C	-2.1942061959	-0.3969536765	-1.0694283302
H	-3.2164551676	-0.2174857612	-1.3977709092
C	-1.3077625012	1.5778668159	-1.1472028916
C	-0.0375985175	1.5914036309	-0.5779030183
O	1.7010675932	-0.7378909223	0.5130902239
H	-2.1311786201	2.0297216535	-0.6005108067
H	-1.5282759181	-0.7044390278	-1.8690554815
H	0.4529131582	-0.7833696518	-1.155039364
H	-1.408111985	1.6248626323	-2.2283219797
H	-0.4705982318	-1.1679034542	1.7552989015
C	-3.1184973645	-0.9494268748	1.2095672192
H	-2.7938407621	-0.8073653211	2.2462569405
H	-3.8938872549	-0.2046358126	0.9931121775

H	-3.6004668887	-1.9351496288	1.1513164744
Si	3.1553916569	-0.5571878147	-0.289781441
H	3.4646074805	0.8717339896	-0.5655846327
H	4.1904764645	-1.1250381085	0.6034218921
H	3.1199507363	-1.2905501584	-1.5860800637
H	0.8170602347	1.57947938	-1.2530836101
C	0.2121007879	2.1641783139	0.7945573355
H	1.0887571782	1.7187720086	1.2785842511
H	0.3818103509	3.2503842319	0.74403739
H	-0.6527218697	2.0001919094	1.4473541768

Sum of electronic and zero-point Energies=	-678.904545
Sum of electronic and thermal Energies=	-678.891429
Sum of electronic and thermal Enthalpies=	-678.890485
Sum of electronic and thermal Free Energies=	-678.944573

Exo TS: 5 + Methylvinylether

C,0,0.2471770327,-0.922623866,-0.2050256846
C,0,-0.9615066012,-1.5405683285,0.0576450481
C,0,-2.1992055387,-0.9603708159,-0.2661950861
C,0,-2.2322342985,0.3041324239,-0.8700794768
H,0,-3.2019819608,0.7685869192,-1.0467299731
C,0,-1.3376033795,1.5800113279,0.5244803064
C,0,-0.0164814085,1.2234348869,0.7993099263
O,0,1.4013488334,-1.4825344861,0.2775644423
H,0,-1.5431531669,2.4843919198,-0.0402554314
H,0,-1.4988078304,0.5539786158,-1.6311905324
H,0,0.3819264964,-0.2505464164,-1.0468999299
H,0,-2.0518860393,1.3883614662,1.3172911169
H,0,-0.9366962897,-2.4193694453,0.6997845829
Si,0,2.9588835297,-0.914404749,0.0453683665
H,0,3.3874711957,0.0215206009,1.1147719751
H,0,3.8265543775,-2.117818772,0.0953757278
H,0,3.0823709646,-0.2591387454,-1.2854648744
C,0,-3.4759717195,-1.5679818294,0.2735965776
H,0,-3.2739037696,-2.3487845156,1.0148207283
H,0,-4.1086347125,-0.8080534541,0.7518785183
H,0,-4.0794214544,-2.0221409274,-0.5242997426
H,0,0.2602738863,0.7242951034,1.7181932325
O,0,1.1044339121,1.7809780632,0.2118422928
C,0,0.9141835506,2.7988767037,-0.7559641742
H,0,0.4177154206,3.6767449995,-0.3195823304
H,0,1.9115518657,3.0815636895,-1.0989948632
H,0,0.3258438124,2.4510638157,-1.6157138347

Sum of electronic and zero-point Energies=	-754.102477
Sum of electronic and thermal Energies=	-754.088448
Sum of electronic and thermal Enthalpies=	-754.087504
Sum of electronic and thermal Free Energies=	-754.143982

Endo TS: 5 + Methylvinylether

C,0,0.5573138636,-0.9467453231,-0.1936163535
 C,0,-0.5556250247,-1.2532169847,0.5696543068
 C,0,-1.87378032,-1.1464651083,0.0961178497
 C,0,-2.0834895369,-0.6960901803,-1.2121543003
 H,0,-3.1054330855,-0.5444547196,-1.5572644724
 C,0,-1.275884425,1.2257994215,-1.3089880009
 C,0,0.0065338632,1.3268935968,-0.7575976632
 O,0,1.7859244209,-0.9663437948,0.4220267791
 H,0,-2.1034206827,1.7217602188,-0.8127762908
 H,0,-1.4194568169,-1.0407049821,-1.9998600935
 H,0,0.5732493128,-1.0845613159,-1.2716282319
 H,0,-1.3258542641,1.2697283842,-2.3928833145
 H,0,-0.3821265986,-1.4117203718,1.6332201742
 C,0,-3.0127365669,-1.1703514322,1.0906105416
 H,0,-2.8217347455,-1.8894787297,1.8950958736
 H,0,-3.1593322327,-0.1884832329,1.5712851037
 H,0,-3.9620005672,-1.4421470623,0.6168785798
 Si,0,3.2404290695,-0.5594619104,-0.2848608816
 H,0,3.3684050545,0.902548994,-0.5235191589
 H,0,4.2886540583,-1.0070480701,0.6600320878
 H,0,3.3920449011,-1.2587375072,-1.5936535739
 H,0,0.8780331882,1.3188387764,-1.40288976
 O,0,0.3373849778,1.9214319439,0.4338574845
 C,0,-0.7079992505,2.2775028924,1.3193011863
 H,0,-1.3031424202,1.4066730495,1.6217142149
 H,0,-0.2231157229,2.7028819967,2.2008025027
 H,0,-1.3732471589,3.032704831,0.8764591927

Sum of electronic and zero-point Energies=	-754.098590
Sum of electronic and thermal Energies=	-754.084488
Sum of electronic and thermal Enthalpies=	-754.083544
Sum of electronic and thermal Free Energies=	-754.140269