Supporting Information for

Dicobalt Octacarbonyl-Caralyzed Carbonylated Cycloaddition of Triynes to Highly-Strained Tetra-cycles

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1. Characterization of new compounds

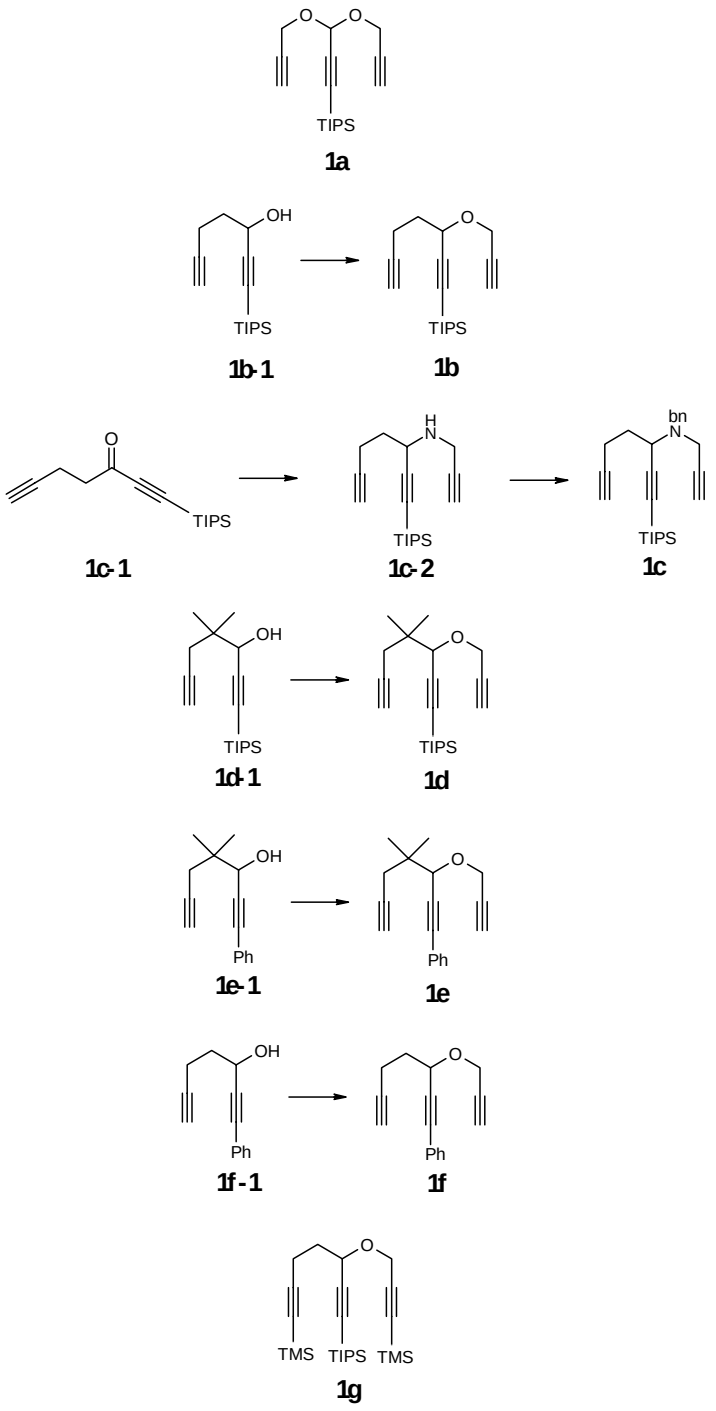


Chart 1

Chart 1 shows compounds, which are numbered in the Text and Supporting Information.

Characterization of cycloaddition products:

To a stainless steel reactor were addied **1b** (0.12g, 0.334mmol), $Co_2(CO)_8$ (2.8mg, 2.5mol%), and 15 mL of CH_2Cl_2. The solution was bubbled by CO for 5min, subjected by 30 atm of CO, and was heated at 130oC for 18h. After the reactor was cooled to room temperature and released to evacuate the excess CO, the solution was filtered, concentrated, and chromatographed on a silica gel column eluting with hexane and diethyl ether (v/v , 1:1). After the solvent removed, a product **2b** (0.084g) was obtained in 70.8 % yield.

2b ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.46 (s, 1 H), 5.06 (d, 4.8 Hz, 1 H), 4.29 (d, 8.0 Hz, 1 H), 3.93 (d, 8.0 Hz, 1 H), 3.26 (s, 1 H), 2.86 (dd, 6.8, 1.2 Hz, 2 H), 2.54 (m, 1 H), 1.97 (m, 1 H), 1.34 (m, 3 H), 1.03 (m, 18 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 202.7, 197.5, 188.8, 180.3, 125.2, 120.3, 72.2, 68.9, 65.3, 59.8, 35.5, 23.3, 18.5, 11.0 ppm; IR νC=O 1726, 1692 cm^{-1}; HRMS (M^+) calcd. 359.2042, obsd. 359.2044; Anal. Calcd. for $C_{21}H_{30}O_3Si$: C, 70.35; H, 8.43. Found: C, 70.25; H, 8.72.

2c. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.04 (m, 5 H), 5.42 (d, 1.6 Hz, 1 H), 3.96 (d, 3.6 Hz, 1 H), 3.92 (s, 2 H), 3.39 (d, 14.0 Hz, 1 H), 3.31 (d, 14.0 Hz, 1 H), 3.18 (s, 1 H), 2.80 (d, 9.3 Hz, 1 H), 2.36 (m, 1 H), 1.82 (m, 1 H), 1.31 (m, 3 H), 1.05-0.97 (m, 18 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.3, 198.3, 191.2, 182.2, 138.8, 128.4, 128.2, 127.4, 125.8, 120.4, 66.2, 61.2, 59.9, 59.0, 55.9, 35.4, 24.4, 18.7, 11.1 ppm; IR νC=O 1721, 1685 cm^{-1}; HRMS $(M+1)^+$ calcd. 448.2668, obsd. 448.2672.

2d. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.40 (s, 1 H), 4.76 (d, 15.3 Hz, 1 H), 4.66 (d, 15.3 Hz, 1 H), 4.36 (s, 1 H), 3.17 (s, 1 H), 2.01 (d, 13.4 Hz, 1 H), 1.89 (d, 13.4 Hz, 1 H), 1.44 (s, 3 H), 1.38 (m, 3 H), 1.05 (m, 18 H), 0.98 (s, 1 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.4, 197.6, 192.3, 179.8, 118.4, 81.9, 64.8, 62.8, 61.5, 43.5, 42.0, 30.4, 23.2, 18.7, 18.6, 11.4 ppm; IR νC=O 1725, 1692 cm^{-1}; HRMS $(M+1)^+$ calcd. 387.2355, obsd. 387.2352.

2e. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (m, 2 H), 7.34 (m, 3 H), 5.56 (s, 1 H), 4.79 (s, 1 H), 4.25 (d, 7.9 Hz, 1 H), 3.96 (d, 7.9 Hz, 1 H), 3.44 (s, 1 H), 2.72 (d, 15.0 Hz, 1 H), 2.50 (d, 15.0 Hz, 1 H), 1.33 (s, 3 H), 0.87 (s, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$):

δ 197.1, 196.9, 178.5, 172.2, 129.6, 128.8, 128.5, 127.9, 122.3, 79.9, 68.2, 61.0, 59.0, 45.3, 38.2, 26.9, 24.0 ppm; IR νC=O 1726, 1693 cm^{-1}; HRMS $(M+1)^+$ calcd. 307.1334, obsd. 307.1324.

Synthesis and Characterization of triynes:

Synthesis of **1a**. TIPS-C≡CCHO (0.12 g, 0.57 mmol), propargyl alcohol (132 μL, 2.28 mmol), TsOH (11 mg, 0.06 mmol), and benzene (2 mL) were placed in a 50 mL round-bottomed flask fitted with a Dean and Stark water separator and reflux condenser. The reaction mixture was heated at reflux overnight and then benzene was removed in vacuum. Chromatography on a silica gel eluting with hexane and ethyl acetate (v/v, 50:1) gave an oily compound **1a** in 84% yield (0.146 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.57 (s, 1 H), 4.34 (d, 2.4 Hz, 4 H), 2.46 (t, 2.4 Hz, 2 H), 1.09 (s, 21 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 126.3, 100.3, 90.2, 89.6, 79.3, 75.2, 53.3, 18.9, 11.4 ppm; FABMS $(M+1)^+$ obsd. 305.1945.

1b-1. Similar procedure of **1d-1.** Yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.49 (t, 6.4 Hz, 1 H), 2.36 (m, 2 H), 1.91 (m, 1 H), 1.86 (t, 6.5 Hz, 2 H), 0.99 (s, 21 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 107.7, 86.2, 83.4, 68.9, 61.7, 36.3, 18.5, 14.4, 11.0 ppm; HRMS $(M-1)^+$ calcd. 263.1831, obsd. 263.1830.

1b. Similar procedure of **1d** Yield: 67%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.45 (t, 6.5 Hz, 1 H), 4.36 (d, 16.0 Hz, 1 H), 4.26 (d, 16.0 Hz, 1 H), 2.42 (m, 2 H), 2.37 (m, 1 H), 2.02 (m, 2 H), 1.95 (m, 1 H), 1.07 (s, 21 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 104.5, 88.2, 83.4, 79.4, 74.4, 68.7, 67.4, 55.7, 34.5, 18.6, 14.5, 11.1 ppm; HRMS $(M+1)^+$ calcd. 303.2144, obsd. 303.2135.

Synthesis of **1c-1**. To a solution of HC≡C-TIPS (0.8 mL, 3.6 mmol) in 3 mL of THF at –78 °C was added n-BuLi (3.6 mmol, 2.5 M in hexane). After the solution was stirred for 5 min, the solution was transferred via cannular to a solution of HC≡C-$(CH_2)_2C(O)N(CH_3)(OCH_3)$ (0.410 g, 2.88 mmol) in 3 mL of THF at –78 °C. After the reaction mixture was stirred for 1 h, sat. NH_4Cl solution was added to the solution. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4, evaporated to dryness,

and chromatographed on a silica gel column eluting with hexane to yield **1c-1** (0.57 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.84 (t, 7.8 Hz, 2 H), 2.55 (td, 7.7, 2.7 Hz, 2 H), 1.98 (t, 2.7 Hz, 1 H), 1.11 (m, 21 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.8, 103.5, 96.8, 82.2, 69.2, 44.1, 18.4, 13.2, 10.9 ppm; HRMS $(M)^+$ obsd. 263.1836.

Synthesis of **1c-2**. To a solution of **1c-1** (0.23 g, 0.86 mmol), propargyl amine (71μL, 1.0 mmol), and acetic acid (59μL, 1.0 mmol) in 2 mL of MeOH was added $NaBH_3CN$ (81 mg, 1.3 mmol). After the reaction mixture was stirred overnight, 5 mL of sat. $NaHCO_3$ was added. The reaction mixture was washed with ethyl acetate (3 x 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4, evaporated to dryness, and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 9:1) to yield **1c-2** in 90% yield (0.23 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (t, 7.4 Hz, 1 H), 3.64 (dd, 16.0, 2.5 Hz, 2 H), 3.52 (dd, 16.0, 2.5 Hz, 2 H), 2.42 (m, 2 H), 2.21 (t, 2.5 Hz, 1 H), 1.96 (t, 2.6 Hz, 1 H), 1.87 (m, 2 H), 1.07 (s, 21 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 107.2, 85.3, 83.4, 81.6, 71.4, 68.8, 49.0, 36.0, 34.5, 18.5, 15.3, 11.1 ppm; FABMS $(M)^+$ obsd. 302.2300.

Synthesis of **1c**. To a solution of **1c-2** (0.17 g, 0.56 mmol), benzaldehyde (114 μL, 1.1 mmol), and acetic acid (64 μL, 1.1mmol) in 2 mL of dichloroethane was added $NaBH(OAc)_3$ (0.35 g, 1.7 mmol). After the solution was stirred overnight, 5 mL of sat. $NaHCO_3$ was added. The reaction mixture was washed with ethyl acetate (3 x 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4, evaporated to dryness, and chromatographed on a silica gel column eluting with hexane and ethyl acetate (v/v, 50:1) to yield **1c** in 62% yield (0.14 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.22 (m, 5 H), 4.01 (d, 14.0 Hz, 1 H), 3.80 (t, 7.5 Hz, 1 H), 3.47 (d, 14.0 Hz, 1 H), 3.35 (d, 17.0 Hz, 1 H), 3.22 (d, 17.0 Hz, 1 H), 2.36 (t, 7.3 Hz, 2 H), 2.19 (t, 2.4 Hz, 1 H), 1.92 (m, 2 H), 1.89 (t, 2.5 Hz, 1 H), 1.08 (s, 21 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.1, 129.4, 128.7, 127.5, 126.3, 104.9, 86.9, 84.1, 81.2, 72.5, 69.0, 55.4, 53.2, 40.6, 33.3, 19.1, 15.9, 11.6 ppm; FABMS $(M+1)^+$ obsd. 392.2776.

Synthesis of **1d-1**. HC≡C-TIPS (0.6 mL, 2.6 mmol) was dissolved in THF (15 mL) and was cooled to –78 °C. To the solution at –78 °C was added n-BuLi (3 mmol, 2.5 M in hexane). After the solution was stirred for 2 h, $HC{\equiv}CCH_2C(Me)_2CHO$ (0.27 g,

2.46 mmol) was added to the solution. The reaction mixture was allowed to warm to room temperature (rt), stirred overnight, washed with sat. NH_4Cl solution (mL), and extracted with diethyl ether (3 x 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated to dryness. The oily residue was purified by chromatography on a silica gel eluting with hexane. Removal of the solvent gave pale yellow liquid **1d-1** in 97% yield (0.70 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.28 (br s, 1 H), 2.37 (dd, 17.0, 2.7 Hz, 1 H), 2.23 (dd, 17.0, 2.7 Hz, 1 H), 2.01 (t, 2.7 Hz, 1 H), 1.07 (s, 3 H), 1.06 (s, 21 H), 1.05 (s, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 106.6, 81.9, 70.4, 69.8, 38.6, 28.0, 22.9, 22.2, 18.5, 11.2 ppm; HRMS $(M)^+$ calcd. 292.2222, obsd. 292.2227.

Synthesis of **1d**. To the solution of sodium hydride (0.10 g, 61 wt% oil mixture) in 10 mL of THF at –10 °C was added **1d-1** (0.70 g, 2.4 mmol) in 10 mL of THF. After the solution was stirred for 1 h, propargyl bromide (0.3 mL, 80 wt% toluene) was added to the solution. The reaction mixture was allowed to warm to rt, stirred overnight, washed with sat. NH_4Cl solution, and extracted with diethyl ether (3 x 10 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and evaporated to dryness. The oily residue was purified by chromatography on a silica gel eluting with hexane. Removal of the solvent gave pale yellow liquid **1d** in 73.4% yield (0.58 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.36 (d, 16.0 Hz, 1 H), 4.26 (d, 16.0 Hz, 1 H), 4.19 (s, 1 H), 2.40 (t, 2.4 Hz, 1 H), 2.31 (m, 2 H), 1.98 (t, 2.5 Hz, 1 H), 1.09 (s, 3 H), 1.06 (s, 21 H), 1.05 (s, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 103.6, 88.8, 81.9, 75.4, 74.2, 70.1, 56.0, 38.0, 28.2, 23.3, 22.4, 18.6, 17.7, 11.2 ppm; HRMS $(M+1)^+$ calcd. 331.2379, obsd. 331.2446.

1e-1. Similar procedure of **1d-1**Yield: 82% ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (m, 2 H), 7.32 (m, 3 H), 4.49 (s, 1 H), 2.43 (d, 16.0 Hz, 1 H), 2.28 (d, 16.0 Hz, 1 H), 2.04 (t, 2.7 Hz, 1 H), 1.14 (s, 3 H), 1.12 (s, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.7, 128.5, 128.3, 122.5, 86.3, 81.8, 70.6, 69.8, 38.9, 28.1, 25.8, 22.9, 22.4 ppm; HRMS $(M)^+$ calcd. 212.1201, obsd. 212.1193.

1e. Similar procedure of **1d**. Yield: 64%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (m, 2 H), 7.24 (m, 3 H), 4.32 (d, 16.0 Hz, 1 H), 4.30 (s, 1 H), 4.23 (d, 16.0 Hz, 1 H), 2.35 (t,

2.4 Hz, 1 H), 2.28 (m, 2 H), 1.92 (t, 2.6 Hz, 1 H), 1.07 (s, 6 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.7, 128.4, 128.3, 122.5, 87.5, 81.8, 79.5, 75.4, 74.5, 70.3, 56.3, 38.4, 28.3, 23.3, 22.5 ppm; HRMS $(M+1)^+$ calcd. 251.1436, obsd. 251.1430.

1f -1. Similar procedure of **1d-1**. Yield : 64%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (m, 2 H), 7.30 (m, 3 H), 4.77 (t, 6.4 Hz, 1 H), 2.46 (m, 2 H), 2.00 (m, 2 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.6, 128.5, 128.3, 122.3, 89.1, 83.4, 69.1, 61.6, 36.2, 31.4, 14.5 ppm; HRMS $(M)^+$ calcd. 185.0966, obsd. 185.0967.

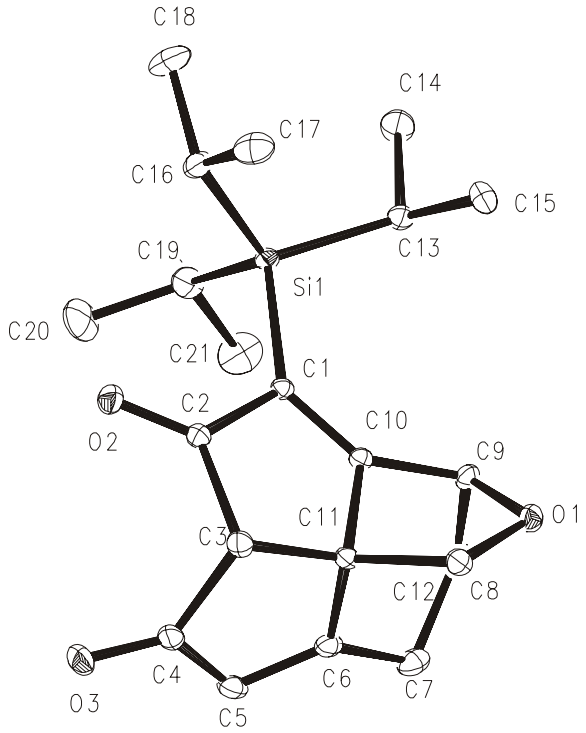
1f. Similar procedure of **1d**. Yield : 98%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (m, 2H), 7.31 (m, 3H), 4.65 (t, 6.2 Hz, 1H), 4.40 (d, 16 Hz, 1H), 4.31 (d, 16Hz, 1H), 2.46 (t, 2.7 Hz, 1H), 2.44 (m, 2H). 2.04 (m, 2H), 1.98 (t, 2.7 Hz, 1H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.7, 128.5, 128.2, 122.2, 86.7, 86.2, 83.3, 79.4, 74.6, 68.8, 67.4, 55.9, 34.4, 14.5 ppm; obsd. HRMS $(M+1)^+$ calcd. 223.1123, obsd. 223.1124..

Synthesis of **1g**. To a solution of **1b** (0.25 g, 0.83 mmol) in 25 mL of THF at 0 °C was added *n*-BuLi (0.73 mL, 1.83 mmol, 2.5 M in hexane). After the solution was stirred for 1 h, TMSCl (0.32 mL, 2.5 mmol) was added. After the resulting solution was stirred for 2 h at rt, the solution was quenched with sat. NH_4Cl and extracted with diethyl ether (20 mL x 3). The ether solution was dried over anhydrous $MgSO_4$ and chromatographed on a silica gel column eluting with hexane. Removal of the solvent gave oily product **1g** in 74% (0.27 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.39 (t, 6.6 Hz, 1 H), 4.34 (d, 16.0 Hz, 1 H), 4.22 (d, 16.0 Hz, 1 H), 2.42 (t, 7.4 Hz, 2 H), 1.95 (m, 2 H), 1.07 (s, 21 H), 0.17 (s, 9 H), 0.14 (s, 9 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 06.3, 104.7, 101.3, 91.3, 88.1, 84.7, 67.7, 56.4, 34.6, 18.6, 16.0, 11.1, 0.13, -0.18 ppm; HRMS $(M+1)^+$ calcd. 447.2935, obsd. 447.2934.

2. X-ray data for 2b

S1. Crystal data and structure refinement for **2b**.

Empirical formula	C_{21} H_{30} O_3 Si
Formula weight	358.54
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	TRICLINIC P-1
Unit cell dimensions	a = 7.8074(3) Å α = 104.428(2) deg.
	b = 14.7100(6) Å β = 94.084(3) deg.
	c = 18.4775(8) Å γ = 92.151(3) deg.
Volume	2046.58(14) $Å^3$
Z, Calculated density	2, 0.582 Mg/m^3
Absorption coefficient	0.065 mm^-1
F(000)	388
Theta range for data collection	2.37 to 27.54 deg.
Limiting indices	-9<=h<=10, -19<=k<=19, -23<=l<=24
Reflections collected / unique	14968 / 9139 [R(int) = 0.0727]
Completeness to theta = 27.54	96.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9139 / 0 / 463
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0716, wR2 = 0.1759
R indices (all data)	R1 = 0.1158, wR2 = 0.2080
Largest diff. peak and hole	0.478 and -0.335 $e.A^{-3}$



S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2b**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Si(1)	682(1)	8340(1)	3180(1)	40(1)
O(1)	-2097(3)	7883(1)	659(1)	50(1)
O(2)	3001(3)	6629(2)	2290(1)	59(1)
O(3)	1881(4)	4659(2)	1040(2)	96(1)
C(1)	460(3)	7512(2)	2211(1)	35(1)
C(2)	1756(3)	6800(2)	1934(2)	41(1)
C(3)	1252(4)	6288(2)	1100(2)	48(1)
C(4)	822(5)	5236(2)	1012(2)	62(1)
C(5)	-1045(5)	5096(2)	913(2)	66(1)
C(6)	-1790(4)	5883(2)	866(2)	50(1)
C(7)	-3613(4)	6129(3)	819(2)	65(1)
C(8)	-3874(4)	7087(3)	1372(2)	62(1)
C(9)	-2391(3)	7800(2)	1412(1)	44(1)
C(10)	-750(3)	7411(2)	1643(1)	35(1)
C(11)	-453(3)	6679(2)	936(1)	38(1)
C(12)	-780(4)	7260(2)	364(2)	47(1)
C(13)	-777(4)	9332(2)	3153(2)	51(1)
C(14)	-342(5)	9914(2)	2603(2)	70(1)
C(15)	-982(6)	9983(3)	3935(2)	87(1)
C(16)	3038(4)	8708(2)	3415(2)	61(1)
C(17)	3837(4)	9135(3)	2841(2)	78(1)
C(18)	3480(6)	9297(4)	4208(3)	101(2)
C(19)	-132(5)	7680(3)	3851(2)	72(1)
C(20)	-2047(7)	7375(4)	3668(3)	121(2)
C(21)	919(8)	6838(4)	3893(3)	117(2)
Si(2)	5730(1)	3296(1)	3222(1)	38(1)
O(4)	7426(2)	2862(1)	731(1)	47(1)
O(5)	2756(3)	1566(2)	2342(1)	61(1)
O(6)	3200(4)	-421(2)	1047(1)	81(1)
C(22)	5454(3)	2411(2)	2280(1)	34(1)
C(23)	3939(3)	1716(2)	1994(2)	41(1)
C(24)	4070(3)	1221(2)	1155(2)	44(1)
C(25)	4312(5)	169(2)	1029(2)	55(1)
C(26)	6132(5)	24(2)	900(2)	54(1)
C(27)	6961(4)	829(2)	875(1)	44(1)
C(28)	8797(4)	1085(2)	821(2)	56(1)
C(29)	9400(4)	2027(2)	1379(2)	55(1)
C(30)	8020(3)	2740(2)	1464(1)	43(1)
C(31)	6438(3)	2327(2)	1696(1)	35(1)
C(32)	5757(3)	1625(2)	984(1)	36(1)
C(33)	5925(4)	2232(2)	429(2)	44(1)
C(34)	4440(4)	2865(2)	3908(2)	53(1)
C(35)	4959(7)	1938(3)	4063(3)	88(1)
C(36)	4305(7)	3608(3)	4644(2)	99(2)
C(37)	8111(4)	3510(2)	3501(2)	51(1)
C(38)	8996(5)	2642(3)	3621(3)	78(1)
C(39)	8576(5)	4353(3)	4166(2)	82(1)
C(40)	4795(4)	4402(2)	3056(2)	57(1)
C(41)	5752(5)	4796(3)	2486(2)	76(1)
C(42)	2863(5)	4258(3)	2806(3)	86(1)

S3. Bond lengths [Å] and angles [deg] for **2b**.

Si(1)-C(19)	1.884(3)
Si(1)-C(16)	1.887(3)
Si(1)-C(1)	1.890(2)
Si(1)-C(13)	1.891(3)
O(1)-C(12)	1.447(3)
O(1)-C(9)	1.460(3)
O(2)-C(2)	1.205(3)
O(3)-C(4)	1.214(4)
C(1)-C(10)	1.337(3)
C(1)-C(2)	1.506(4)
C(2)-C(3)	1.553(4)
C(3)-C(11)	1.510(4)
C(3)-C(4)	1.538(4)
C(4)-C(5)	1.456(5)
C(5)-C(6)	1.335(4)
C(6)-C(7)	1.484(5)
C(6)-C(11)	1.513(4)
C(7)-C(8)	1.551(5)
C(8)-C(9)	1.518(4)
C(9)-C(10)	1.501(4)
C(10)-C(11)	1.510(3)
C(11)-C(12)	1.531(3)
C(13)-C(14)	1.531(4)
C(13)-C(15)	1.545(4)
C(16)-C(18)	1.513(5)
C(16)-C(17)	1.519(5)
C(19)-C(21)	1.526(6)
C(19)-C(20)	1.534(6)
Si(2)-C(34)	1.886(3)
Si(2)-C(37)	1.887(3)
Si(2)-C(22)	1.890(2)
Si(2)-C(40)	1.892(3)
O(4)-C(33)	1.453(3)
O(4)-C(30)	1.456(3)
O(5)-C(23)	1.206(3)
O(6)-C(25)	1.213(4)
C(22)-C(31)	1.351(3)
C(22)-C(23)	1.508(3)
C(23)-C(24)	1.553(4)
C(24)-C(32)	1.511(3)
C(24)-C(25)	1.527(4)
C(25)-C(26)	1.472(5)
C(26)-C(27)	1.341(4)
C(27)-C(28)	1.485(4)
C(27)-C(32)	1.512(4)
C(28)-C(29)	1.542(5)
C(29)-C(30)	1.520(4)
C(30)-C(31)	1.492(3)
C(31)-C(32)	1.505(3)
C(32)-C(33)	1.527(3)
C(34)-C(35)	1.524(5)
C(34)-C(36)	1.531(5)
C(37)-C(39)	1.524(4)
C(37)-C(38)	1.530(5)
C(40)-C(42)	1.536(5)
C(40)-C(41)	1.545(5)

C(19)-Si(1)-C(16)	111.06(17)
C(19)-Si(1)-C(1)	107.72(14)
C(16)-Si(1)-C(1)	107.21(13)
C(19)-Si(1)-C(13)	108.40(16)
C(16)-Si(1)-C(13)	115.13(15)
C(1)-Si(1)-C(13)	107.01(12)
C(12)-O(1)-C(9)	109.22(19)
C(10)-C(1)-C(2)	105.7(2)
C(10)-C(1)-Si(1)	131.12(19)
C(2)-C(1)-Si(1)	123.17(19)
O(2)-C(2)-C(1)	126.8(3)
O(2)-C(2)-C(3)	123.4(2)
C(1)-C(2)-C(3)	109.8(2)
C(11)-C(3)-C(4)	104.5(3)
C(11)-C(3)-C(2)	103.3(2)
C(4)-C(3)-C(2)	110.8(2)
O(3)-C(4)-C(5)	128.5(3)
O(3)-C(4)-C(3)	124.6(4)
C(5)-C(4)-C(3)	106.9(3)
C(6)-C(5)-C(4)	111.6(3)
C(5)-C(6)-C(7)	132.8(3)
C(5)-C(6)-C(11)	110.8(3)
C(7)-C(6)-C(11)	116.2(3)
C(6)-C(7)-C(8)	111.1(3)
C(9)-C(8)-C(7)	112.1(2)
O(1)-C(9)-C(10)	102.2(2)
O(1)-C(9)-C(8)	109.9(2)
C(10)-C(9)-C(8)	109.1(2)
C(1)-C(10)-C(9)	142.7(2)
C(1)-C(10)-C(11)	115.7(2)
C(9)-C(10)-C(11)	101.6(2)
C(3)-C(11)-C(10)	105.4(2)
C(3)-C(11)-C(6)	105.6(2)
C(10)-C(11)-C(6)	106.4(2)
C(3)-C(11)-C(12)	124.5(2)
C(10)-C(11)-C(12)	99.2(2)
C(6)-C(11)-C(12)	113.9(2)
O(1)-C(12)-C(11)	104.9(2)
C(14)-C(13)-C(15)	110.3(3)
C(14)-C(13)-Si(1)	115.1(2)
C(15)-C(13)-Si(1)	113.4(2)
C(18)-C(16)-C(17)	112.0(3)
C(18)-C(16)-Si(1)	114.4(3)
C(17)-C(16)-Si(1)	113.9(2)
C(21)-C(19)-C(20)	110.6(4)
C(21)-C(19)-Si(1)	112.7(3)
C(20)-C(19)-Si(1)	111.8(3)
C(34)-Si(2)-C(37)	115.13(14)
C(34)-Si(2)-C(22)	109.44(12)
C(37)-Si(2)-C(22)	107.47(12)
C(34)-Si(2)-C(40)	109.01(14)
C(37)-Si(2)-C(40)	110.12(15)
C(22)-Si(2)-C(40)	105.21(13)
C(33)-O(4)-C(30)	109.53(18)
C(31)-C(22)-C(23)	105.5(2)
C(31)-C(22)-Si(2)	128.33(19)
C(23)-C(22)-Si(2)	125.83(17)
O(5)-C(23)-C(22)	126.8(2)
O(5)-C(23)-C(24)	123.4(2)

C(22)-C(23)-C(24)	109.9(2)
C(32)-C(24)-C(25)	104.7(2)
C(32)-C(24)-C(23)	103.45(19)
C(25)-C(24)-C(23)	112.4(2)
O(6)-C(25)-C(26)	127.5(3)
O(6)-C(25)-C(24)	125.4(3)
C(26)-C(25)-C(24)	107.1(2)
C(27)-C(26)-C(25)	110.9(3)
C(26)-C(27)-C(28)	132.6(3)
C(26)-C(27)-C(32)	111.0(3)
C(28)-C(27)-C(32)	116.2(2)
C(27)-C(28)-C(29)	111.7(2)
C(30)-C(29)-C(28)	112.5(2)
O(4)-C(30)-C(31)	101.9(2)
O(4)-C(30)-C(29)	109.8(2)
C(31)-C(30)-C(29)	109.2(2)
C(22)-C(31)-C(30)	142.2(2)
C(22)-C(31)-C(32)	115.6(2)
C(30)-C(31)-C(32)	102.1(2)
C(31)-C(32)-C(24)	105.6(2)
C(31)-C(32)-C(27)	106.2(2)
C(24)-C(32)-C(27)	105.7(2)
C(31)-C(32)-C(33)	99.63(19)
C(24)-C(32)-C(33)	124.4(2)
C(27)-C(32)-C(33)	113.6(2)
O(4)-C(33)-C(32)	104.51(19)
C(35)-C(34)-C(36)	110.5(3)
C(35)-C(34)-Si(2)	115.5(2)
C(36)-C(34)-Si(2)	113.5(2)
C(39)-C(37)-C(38)	110.5(3)
C(39)-C(37)-Si(2)	114.1(2)
C(38)-C(37)-Si(2)	113.9(2)
C(42)-C(40)-C(41)	109.8(3)
C(42)-C(40)-Si(2)	112.2(2)
C(41)-C(40)-Si(2)	112.6(2)

S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2b**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Si(1)	50(1)	40(1)	28(1)	6(1)	2(1)	2(1)
O(1)	64(1)	50(1)	38(1)	15(1)	1(1)	13(1)
O(2)	56(1)	61(1)	57(1)	9(1)	-6(1)	18(1)
O(3)	156(3)	55(1)	65(2)	-6(1)	-24(2)	51(2)
C(1)	41(1)	34(1)	30(1)	6(1)	5(1)	2(1)
C(2)	43(1)	38(1)	41(1)	8(1)	4(1)	5(1)
C(3)	59(2)	47(2)	37(1)	6(1)	10(1)	14(1)
C(4)	104(3)	44(2)	33(1)	1(1)	-7(2)	19(2)
C(5)	115(3)	36(2)	45(2)	10(1)	-8(2)	-10(2)
C(6)	71(2)	45(2)	32(1)	10(1)	-4(1)	-9(1)
C(7)	64(2)	72(2)	56(2)	19(2)	-7(2)	-23(2)
C(8)	43(2)	91(2)	54(2)	22(2)	2(1)	-1(2)
C(9)	49(1)	53(2)	30(1)	8(1)	0(1)	9(1)
C(10)	42(1)	34(1)	30(1)	7(1)	7(1)	1(1)
C(11)	55(2)	34(1)	25(1)	7(1)	7(1)	3(1)
C(12)	65(2)	43(1)	34(1)	12(1)	8(1)	4(1)
C(13)	58(2)	49(2)	41(2)	0(1)	3(1)	11(1)
C(14)	84(2)	49(2)	80(3)	23(2)	2(2)	13(2)
C(15)	113(3)	80(3)	57(2)	-11(2)	10(2)	40(2)
C(16)	55(2)	65(2)	54(2)	3(2)	-11(1)	2(2)
C(17)	53(2)	88(3)	84(3)	5(2)	10(2)	-14(2)
C(18)	92(3)	120(4)	68(3)	-7(3)	-25(2)	-16(3)
C(19)	111(3)	69(2)	40(2)	23(2)	15(2)	0(2)
C(20)	123(4)	153(5)	104(4)	67(4)	26(3)	-43(4)
C(21)	190(6)	89(3)	94(4)	60(3)	19(3)	18(3)
Si(2)	46(1)	34(1)	30(1)	4(1)	5(1)	3(1)
O(4)	59(1)	47(1)	37(1)	15(1)	5(1)	-6(1)
O(5)	46(1)	79(2)	53(1)	8(1)	11(1)	-15(1)
O(6)	121(2)	59(1)	54(1)	1(1)	21(1)	-38(1)
C(22)	38(1)	34(1)	30(1)	5(1)	1(1)	4(1)
C(23)	41(1)	44(1)	37(1)	8(1)	1(1)	-1(1)
C(24)	46(1)	46(2)	35(1)	8(1)	-4(1)	-7(1)
C(25)	90(2)	44(2)	27(1)	3(1)	4(1)	-14(2)
C(26)	92(2)	35(1)	36(1)	7(1)	7(1)	11(1)
C(27)	61(2)	43(2)	29(1)	9(1)	6(1)	12(1)
C(28)	59(2)	63(2)	52(2)	20(2)	16(1)	23(2)
C(29)	38(1)	79(2)	47(2)	17(2)	5(1)	2(1)
C(30)	44(1)	49(2)	33(1)	8(1)	3(1)	-5(1)
C(31)	38(1)	35(1)	32(1)	7(1)	-1(1)	2(1)
C(32)	43(1)	35(1)	30(1)	7(1)	-1(1)	0(1)
C(33)	57(2)	40(1)	33(1)	10(1)	-3(1)	1(1)
C(34)	64(2)	53(2)	41(2)	8(1)	15(1)	-1(1)
C(35)	126(4)	70(2)	82(3)	40(2)	20(2)	-2(2)
C(36)	155(4)	89(3)	49(2)	0(2)	47(2)	-4(3)
C(37)	53(2)	53(2)	39(1)	3(1)	-2(1)	-6(1)
C(38)	58(2)	85(3)	88(3)	19(2)	-9(2)	14(2)
C(39)	84(3)	82(3)	58(2)	-16(2)	-12(2)	-15(2)
C(40)	75(2)	43(2)	54(2)	10(1)	11(2)	16(1)
C(41)	100(3)	55(2)	86(3)	37(2)	18(2)	19(2)
C(42)	72(2)	93(3)	110(3)	51(3)	20(2)	37(2)

S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **2b**.

	x	y	z	U(eq)
H(3)	2116	6400	767	57
H(5)	-1643	4528	887	79
H(7A)	-4337	5642	934	78
H(7B)	-3959	6161	311	78
H(8A)	-4934	7333	1216	75
H(8B)	-3984	6991	1868	75
H(9)	-2583	8411	1748	53
H(12A)	259	7617	317	56
H(12B)	-1175	6857	-125	56
H(13)	-1920	9030	2972	61
H(14A)	-1319	10255	2504	84
H(14B)	-51	9503	2143	84
H(14C)	617	10349	2817	84
H(15A)	94	10323	4132	105
H(15B)	-1323	9612	4266	105
H(15C)	-1844	10420	3893	105
H(16)	3613	8121	3390	73
H(17A)	3323	9717	2836	94
H(17B)	3640	8708	2354	94
H(17C)	5051	9252	2971	94
H(18A)	4707	9390	4304	121
H(18B)	3031	8980	4555	121
H(18C)	2983	9896	4267	121
H(19)	-13	8115	4351	86
H(20A)	-2238	7021	3154	145
H(20B)	-2713	7921	3745	145
H(20C)	-2389	6991	3989	145
H(21A)	596	6597	4304	140
H(21B)	2121	7031	3968	140
H(21C)	703	6357	3433	140
H(24)	3099	1346	835	52
H(26)	6638	-549	843	65
H(28A)	8955	1130	315	67
H(28B)	9499	593	921	67
H(29A)	9723	1915	1865	66
H(29B)	10411	2286	1209	66
H(30)	8421	3339	1815	51
H(33A)	6093	1847	-67	52
H(33B)	4908	2583	397	52
H(34)	3265	2740	3669	64
H(35A)	6003	2043	4387	106
H(35B)	5137	1498	3599	106
H(35C)	4062	1690	4301	106
H(36A)	3440	3399	4919	119
H(36B)	3999	4189	4536	119
H(36C)	5393	3700	4937	119
H(37)	8620	3664	3073	61
H(38A)	10220	2750	3637	93
H(38B)	8624	2107	3216	93
H(38C)	8698	2524	4086	93
H(39A)	8096	4243	4603	99

H(39B)	8120	4906	4057	99
H(39C)	9805	4440	4256	99
H(40)	4929	4880	3535	68
H(41A)	5612	4353	2004	91
H(41B)	6954	4901	2651	91
H(41C)	5287	5379	2448	91
H(42A)	2435	4838	2742	103
H(42B)	2262	4060	3182	103
H(42C)	2684	3785	2341	103