#### Electronic Supporting Information

#### Angle-Strained Sila-Cycloalkynes

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## 1. General Information

General Experimental Procedures: All experiments unless otherwise noted were performed under a nitrogen or argon atmosphere with the exclusion of air or moisture via standard Schlenk line technique or in a nitrogen glovebox. All glassware was dried prior to use in a 175 °C oven.

Instrumentation: <sup>1</sup>H NMR, <sup>29</sup>Si {<sup>1</sup>H} DEPT NMR, and <sup>13</sup>C {<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance III 400 MHz Spectrometer, a Bruker Avance 300 MHz Spectrometer, and a Bruker Avance 400 MHz Spectrometer. Chemical shifts are reported in parts per million (ppm). Spectra were recorded in chloroform-d or benzene- $d_6$  with the residual solvent peak as the internal standard (<sup>1</sup>H NMR: CHCl<sub>3</sub>,  $\delta$  = 7.26 ppm; C<sub>6</sub>D<sub>6</sub>,  $\delta$  = 7.16 ppm;  $CD_2Cl_2$ ,  $\delta = 5.32$  ppm. <sup>13</sup>C NMR: CHCl\_3,  $\delta = 77.16$  ppm;  $C_6D_6$ ,  $\delta = 128.06$  ppm;  $CD_2Cl_2$ ,  $\delta$  = 53.84 ppm). <sup>29</sup>Si {<sup>1</sup>H} DEPT NMR experiments evolution times are correlated to J coupling values reported as  ${}^{2}J_{Si-H} = 7$  Hz. Multiplicities are as indicated: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), h (heptet), m (multiplet), and br (broad). Coupling constants, J, are reported in Hertz (Hz) and integration is provided, along with assignments, as indicated. Attenuated total reflection infrared (ATR-IR) spectroscopy was performed on a Thermo NicoletNexus 670 FTIR spectrometer. Mass spectrometry and high-resolution mass spectrometry were performed in the Department of Chemistry at Johns Hopkins University using a VG Instruments VG70S/E magnetic sector mass spectrometer with electron ionization (EI) (70 eV). The UNIIab Plus Glove Box by MBRAUN was maintained under nitrogen atmosphere. All column chromatography was performed on a Teledyne ISCO Combiflash Rf+ using Redisep Rf silica columns.

Materials: Unless otherwise specified, all chemicals were used as purchased without further purification. Solvents used for column chromatography and polymer workup were reagent grade and used as received. Reaction solvent THF, toluene, diethyl ether (Et<sub>2</sub>O), dichloromethane (DCM) (Sigma Aldrich, HPLC grade) was dried on a J. C. Meyer Solvent Dispensing System (SDS) using stainless steel columns packed with neutral alumina and Q5 reactant, a copper (II) oxide oxygen scavenger, following the manufacturer's recommendations for solvent preparation and dispensation. 1,4-dichloro-2-butyne, 0.5 M benzyl azide solution in DCM, and benzene were purchased from Sigma-Aldrich. Benzyl azide (94%) was purchased from Alfa Aesar. **D1** and **D2** were synthesized based on previously reported procedures.<sup>1,2</sup>

# 2. Supplemental Figures

α = 13.0 28 1.12 Å 27 162.2° 166 Si Si	29 8° 30 Si	ω = 16.5 30 1.12 Å 29 173.5° 174 Si Si	31 ,7° 32 Si Si
Si-CHy		Si-CO	У
Bond Distances (Å)		Bond Distances (Å)	
C28–C29	1.196(3)	C30–C31	1.205(6) /
			1.195(6)
Bond Angles (deg)		Bond Angles (deg)	
∠C27-C28-C29	162.1(2)	∠C29-C30-C31	174.3(5) /
			173.4(5)
∠C28-C29-C30	166.8(2)	∠C30-C31-C32	173.2(4) /
			174.7(5)
Distortion from Linearity (deg)		Distortion from Linearity (deg)	
∠C27-C28-C29	17.9(2)	∠C29-C30-C31	5.7(5) / 6.6(5)
∠C28-C29-C30	13.2(2)	∠C30-C31-C32	6.8(4) / 5.3(5)
Torsion Angles (deg)		Torsion Angles (deg)	
∠C27-C28-C29-C30	-13.0(14)	∠C29-C30-C31-C32	-6(8) / 16(9)

**Table S1.** Selected bond distances, bond angles, and torsion angles from single crystal X-ray crystallography. The crystal structure of Si-COy contains an asymmetric unit with two crystallographically independent molecules. Bond distances, bond angles, and torsion angles are reported for both structures of Si-COy.

#### 3. Experimental Procedures and Tabulated Characterization

#### 3.1 Synthesis of **Si-CHy**.



In a nitrogen filled glovebox, an oven dried 100 mL Schlenk flask equipped with a stir bar was charged with D1 (250.0 mg, 0.242 mmol, 1.00 equiv.) and sealed with a rubber septum and stopcock. In the glovebox, an oven dried 10 mL round bottom flask was charged 1.4-dichloro-2-butyne (0.10 mL). The Schlenk flask containing **D1** and flask containing dichlorobutyne were removed from the glove box and transported to the hood, where they were placed under an argon atmosphere. D1 was dissolved in benzene (24 mL) to 0.01 M. The 1,4-dichloro-2-butyne was diluted with benzene (3 mL) to create a stock solution (0.34 M). The butyne stock solution (0.857 mL, 0.290 mmol, 1.20 equiv.) was added to the solution of **D1** via syringe. The reaction color was observed to change from deep burgundy to a clear light orange solution then become eventually colorless. The reaction was allowed to stir at room temperature for 30 minutes. After 30 minutes, the reaction was opened to air and then guenched with 20 mL of deionized H<sub>2</sub>O (added slowly with a pipette first, then completed with an addition funnel) and 20 mL of a saturated aqueous solution of NH<sub>4</sub>Cl (added slowly with a pipette first, then completed with an addition funnel). The biphasic mixture was transferred to a 125 mL separatory funnel and the aqueous layer was separated from the organic layer. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> before being concentrated by rotatory evaporation. The unpurified reaction mixture is a pale-yellow solid yielding Si-CHy (111.2 mg, 97%). No further purification was performed and was carried forward. Crystals can be grown by the vapor deposition of MeOH into a saturated solution of **Si-CHy** in DCM. <sup>1</sup>H (400 MHz, C<sub>6</sub>D<sub>6</sub>) 7.51 -6.99 (m, 20H), 2.06 (s, 4H), 0.50 (s, 6H) ppm .<sup>13</sup>C (101 MHz, C<sub>6</sub>D<sub>6</sub>) 135.9, 134.9, 129.0, 128.0, 86.5, 4.2, -4.9 ppm. <sup>29</sup>Si (79 MHz, C<sub>6</sub>D<sub>6</sub>) -21.79, -42.45 ppm. ATR IR (cm<sup>-1</sup>) 3066, 2133, 1896, 1483, 1426, 1097, 1026, 997, 838, 802, 694. HRMS (EI) m/z [M]+ Calc 474.1655 for C<sub>30</sub>H<sub>30</sub>Si<sub>3</sub>; Found 474.1663.

#### 3.2 Synthesis of **Si-COy**.



In a nitrogen filled glovebox, an oven dried 100 mL Schlenk flask equipped with a stir bar was charged with **D2** (285.5 mg, 0.262 mmol, 1.00 equiv.) and sealed with a rubber septum and stopcock. In the glovebox, an oven dried 10 mL round bottom flask was

charged 1,4-dichloro-2-butyne (0.10 mL). The Schlenk flask containing **D2** and flask containing dichlorobutyne were removed from the glove box and transported to the hood, where they were placed under an argon atmosphere. D2 was dissolved in benzene (26.2 mL, 0.01 M). The 1,4-dichloro-2-butyne was diluted with benzene (3 mL) to create a stock solution (0.34 M). The butyne stock solution (1.12 mL, 0.315 mmol, 1.20 equiv.) was added to the solution of **D2** via syringe. The reaction color was observed to change from deep burgundy to a clear light orange solution then eventually colorless. The reaction was allowed to stir at room temperature for 30 minutes. After 30 minutes, the reaction was opened to air and then guenched with 20 mL of deionized H<sub>2</sub>O (added slowly with a pipette first then completed with a funnel) and 20 mL of a saturated aqueous solution of NH<sub>4</sub>Cl (added slowly with a pipette first then completed with a funnel). The biphasic mixture was transferred to a 125 mL separatory funnel and the aqueous layer was separated from the organic layer. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> before being concentrated by rotatory evaporation. The unpurified reaction mixture is a pale-yellow solid yielding Si-COy (135.4 mg, 97%). No further purification was performed and was carried forward. Crystals can be grown by the vapor deposition of MeOH into a saturated solution of **Si-COy** in DCM. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) 7.50 (dd, J = 7.7, 1.8 Hz, 8H), 7.39 -7.29 (m, 12H), 2.08 (s, 4H), 0.04 (s, 12H) ppm. <sup>13</sup>C (101 MHz, CDCl<sub>3</sub>) 136.0, 135.1, 129.2, 128.1, 79.3, 3.9, -5.3 ppm. <sup>29</sup>Si (79 MHz, CDCl<sub>3</sub>) -14.78, -42.78 ppm. ATR-IR Spectroscopy (cm<sup>-1</sup>) 422, 445, 464, 515, 693, 730, 795, 834, 908, 997, 1098, 1167, 1188, 1240, 1427, 1484, 1587, 1769, 1822, 1883, 1956, 2125, 2995, 3066. HRMS (EI)m/z [M]+ Calc 532.1894 for C<sub>32</sub>H<sub>36</sub>Si<sub>4</sub>; Found 532.18807.

3.3 Azide-Alkyne Cycloaddition.



\*Warning\* – Benzyl azide is a flammable liquid that poses an explosion risk. The benzyl azide should be handled with explosion proof equipment and non-sparking tools.

In a fume hood, 86.7 mg (0.183 mmol, 1.00 equiv.) of **Si-CHy** was added to an oven dried 10 mL round bottom flask with a stir bar. **Si-CHy** was diluted with 1.00 mL of toluene. 0.500 mL (0.183 mmol, 1.00 equiv.) of benzyl azide was added to the solution of **Si-CHy**, from a 0.36 M stock solution of benzyl azide in toluene. A reflux condenser was attached, and the apparatus was submerged into a sand bath and began to stir. The sand bath was heated to 110 °C and water was circulated through the reflux condenser. The reaction was allowed to stir at reflux for 16 h. After 16 h, the reaction was cooled to room temperature and then concentrated under reduced pressure. The crude was purified via automated column chromatography with 100% hexanes then with a gradient to 50% EtOAc/50% hexanes yielding **4** as a white sticky solid (13.8 mg, 12%). Crystals can be grown by the vapor deposition of MeOH into a saturated solution of **4** in DCM. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub> 7.94 – 6.56 (m, 25H), 4.56 (s, 2H), 2.96 (s, 2H), 2.51 (s, 2H), 0.11 (s, 6H)

ppm. <sup>13</sup>C (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 141.0, 135.5, 135.4, 135.4, 135.2, 134.1, 130.0, 129.7, 129.2, 128.7, 128.3, 128.2, 127.93, 127.87, 127.0, 50.9, 11.8, 9.7, -5.6 ppm. <sup>29</sup>Si (79 MHz, CD<sub>2</sub>Cl<sub>2</sub>)-19.19, -21.20, -49.51 ppm. ATR-IR Spectroscopy (cm<sup>-1</sup>) 3048, 2927, 1952, 1586, 1547, 1497, 1486, 1452, 1425, 1356, 1344, 1304, 1256, 1224, 1187, 1162, 1101, 1023, 997, 970, 920, 843, 810, 779, 768, 724. HRMS (EI) m/z [M]+ Calc 607.22953 for C<sub>37</sub>H<sub>37</sub>N<sub>3</sub>Si<sub>3</sub>; Found 607.22958.

#### 4. Computational Details

All density functional theory (DFT) calculations were all carried out using ORCA v. 5.01.<sup>3</sup> Initial geometries of possible conformers of reaction reactants and products were generated using Conformer-Rotamer Ensemble Sampling Tool (CREST v.2.11<sup>4</sup>), using the semiempirical GFN2-xTB<sup>5</sup> level of theory. All conformers within 8 kcal/mol of the lowest energy conformer at the GFN2-xTB level of theory were further optimized and studied using DFT. All geometry optimizations and frequency calculations were performed using the B3LYP<sup>6-8</sup> functional with the DFT-D4<sup>9</sup> dispersion correction and a def2-SVP basis set. Geometry optimizations were carried out using the BFGS<sup>10</sup> algorithm in redundant internal coordinates implemented to the default tolerances of  $3 \times 10^{-4}$ hartree/bohr for the maximum gradient and  $5 \times 10^{-6}$  hartree for the change in energy between steps. To optimize transition state structures, we initially carried out constrained optimization where two newly forming C-N bond distances in the TS were constrained to 2.20 Å. The converged constrained structure was then used to carry out a Hessian mode following algorithm<sup>11</sup> to locate transition state structures. Transition state identities were verified by performing frequency calculations to ensure that a single imaginary frequency was obtained. Single-point calculations were carried out using def2-TZVPP basis set, range-separated meta-GGA hybrid, ωB97M-V<sup>12</sup> which utilizes VV10 non-local correlation<sup>13</sup> that can accurately describe dispersion interactions, and an implicit solvent (Toluene,  $\varepsilon = 2.4$ ) using the C-PCM continuum solvation model.<sup>14</sup>

## 5. Single Crystal X-Ray Crystallography

**Si-CHy**: All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Mo  $K\alpha$  radiation ( $\lambda$  = 0.71073 Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.42.49, Rigaku OD, 2022). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2018/3<sup>15</sup> and was refined on  $F^2$  with SHELXL-2018/3.<sup>15</sup>Numerical absorption correction based on gaussian integration over a multifaceted crystal model was performed using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instruction AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5  $U_{eq}$  of the attached C atoms. The structure of **Si-CHy** is ordered.

Si-COy: All reflection intensities were measured at 110(2) K using a SuperNova diffractometer (equipped with Atlas detector) with Cu  $K\alpha$  radiation ( $\lambda = 1.54178$  Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.42.49, Rigaku OD, 2022). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2018/3<sup>15</sup> and was refined on F<sup>2</sup> with SHELXL-2018/3.<sup>15</sup> Analytical numeric absorption correction using a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5  $U_{eq}$  of the attached C atoms. The asymmetric unit contains two crystallographically independent molecules. The structure was treated as ordered, but there are some relatively large residual electron density peaks ranging from 1.33 to 1.55 e<sup>-</sup> Å<sup>-3</sup>, that are not chemically meaningful. The reciprocal lattice slices 1 kl and *h*11 show the existence of diffuse scattering which might indicate some structural disorder. Check for twinning was performed using TwinRotMat in Platon<sup>16</sup>, but fail to identify any potential twin relationships. It is likely disorder occurs in the structure even though the displacement ellipsoids do not show any signs of elongation of abnormal electron distribution. Although data quality was not of the highest quality (both Rint and R<sub>sigma</sub> are relatively large), the structure of **4** remains correct.

**4**: All reflection intensities were measured at 110.00(10) K using a Rigaku XtaLAB Synergy R (equipped with a rotating-anode X-ray source and HyPix-6000HE detector) with Cu *K*α radiation ( $\lambda$  = 1.54178 Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.42.49, Rigaku OD, 2022). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXT-2018/2<sup>15</sup> and was refined on *F*<sup>2</sup> with SHELXL-2019/3.<sup>15</sup> Analytical numeric absorption correction using a multifaceted crystal was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryostream 1000 from Oxford Cryosystems. The H atoms were placed at calculated positions using the instructions AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 *U*<sub>eq</sub> of the attached C atoms. The structure is partly disordered. One phenyl ground is found to be disordered over two orientations, and the occupancy factor of the major component of the disorder refines to 0.676(7). The asymmetric unit also contains one site that contains possibly a mixture of lattice solvent molecules, and that contribution was removed from the final refinement using the SQUEEZE procedure in Platon.<sup>17</sup>

	Si-CHy		
Crystal data	Crystal data		
Chemical formula	C <sub>30</sub> H <sub>30</sub> Si <sub>3</sub>		
M <sub>r</sub>	474.81		
Crystal system, space group	Monoclinic, $P2_1/c$		
Temperature (K)	110		
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.9325 (4), 18.2411 (6), 15.0008 (6)		
β (°)	102.356 (4)		
$V(Å^3)$	2654.89 (18)		
Ζ	4		
Radiation type	Μο Κα		
μ (mm <sup>-1</sup> )	0.20		
Crystal size (mm)	$0.49 \times 0.16 \times 0.10$		
	·		
Data collection			
Diffractometer	SuperNova, Dual, Cu at zero, Atlas		
Absorption correction	Gaussian <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.		
$T_{\min}, T_{\max}$	0.587, 1.000		
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	28222, 6096, 4805		
R <sub>int</sub>	0.050		
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.650		
Refinement			
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.042, 0.097, 1.04		
No. of reflections	6096		
No. of parameters	300		
H-atom treatment	H-atom parameters constrained		
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.41, -0.26		

# Table S2. Crystallographic data for Si-CHy

# Table S3. Crystallographic data for Si-COy

	Si-COy	
Crystal data		
Chemical formula	$C_{32}H_{36}Si_4$	
M <sub>r</sub>	532.97	
Crystal system, space group	Monoclinic, $P2_1/c$	
Temperature (K)	110	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	24.3501 (13), 11.0409 (4), 25.4353 (11)	
β (°)	115.708 (6)	
$V(Å^3)$	6161.3 (6)	
Ζ	8	
Radiation type	Cu <i>K</i> α	
μ (mm <sup>-1</sup> )	1.92	
Crystal size (mm)	$0.43 \times 0.04 \times 0.03$	
	·	
Data collection		
Diffractometer	SuperNova, Dual, Cu at zero, Atlas	
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.49 (Rigaku Oxford Diffraction, 2022) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	
$T_{\min}, T_{\max}$	0.681, 0.943	
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	44958, 11030, 6468	
R <sub>int</sub>	0.097	
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.598	
	·	
Refinement		
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.067, 0.189, 1.00	
No. of reflections	11030	
No. of parameters	657	
H-atom treatment	H-atom parameters constrained	
$\Delta \rho_{max}, \Delta \rho_{min} (e \text{ Å}^{-3})$	1.55, -0.30	

 Table S4. Crystallographic data for 4

	4
Crystal data	
Chemical formula	C <sub>37</sub> H <sub>37</sub> N <sub>3</sub> Si <sub>3</sub>
M <sub>r</sub>	607.96
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	110
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.98096 (8), 26.6317 (2), 10.50266 (7)
β (°)	91.5598 (6)
$V(Å^3)$	3629.48 (4)
Ζ	4
Radiation type	Cu Kα
μ (mm <sup>-1</sup> )	1.41
Crystal size (mm)	$0.30 \times 0.21 \times 0.05$
Data collection	
Diffractometer	XtaLAB Synergy R, HyPix
Absorption correction	Analytical <i>CrysAlis PRO</i> 1.171.42.80a (Rigaku Oxford Diffraction, 2023) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{\min}, T_{\max}$	0.754, 0.949
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	42916, 7099, 6727
R <sub>int</sub>	0.020
$(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)],$ $wR(F^2), S$	0.030, 0.082, 1.05
No. of reflections	7099
No. of parameters	439
No. of restraints	205
H-atom treatment	H-atom parameters constrained
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.31, -0.24

## 6. NMR Spectra

## 6.1 NMR Spectra Si-CHy

6.1.1 <sup>1</sup>H NMR Spectrum (400 MHz, Benzene-*d*<sub>6</sub>)





6.1.3 <sup>29</sup>Si {<sup>1</sup>H} NMR Spectrum (79 MHz, Benzene-d<sub>6</sub>)



## 6.3 NMR Spectra of Compound 4



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 <sup>13</sup>C / ppm



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