

**Silyl Tosylate Precursors to Cyclohexyne, 1,2-Cyclohexadiene, and 1,2-Cycloheptadiene**

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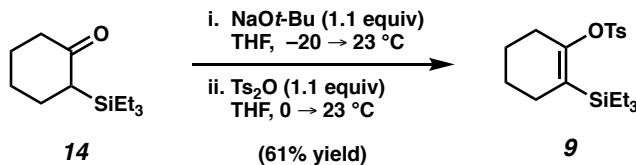
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**Materials and Methods.** Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (passed through activated alumina columns). All commercially obtained reagents were used as received unless otherwise specified. Imidazole (**20**), *p*-toluenesulfonic anhydride ( $\text{Ts}_2\text{O}$ ), *n*-butyllithium (*n*-BuLi), tetrabutylammonium fluoride (TBAF), and potassium *tert*-butoxide ( $\text{KO}t\text{-Bu}$ ) were obtained from Sigma-Aldrich. Sodium *tert*-butoxide ( $\text{Na}O\text{t-Bu}$ ), 1,3-diphenylisobenzofuran (**16**), *N*-*tert*-butyl- $\alpha$ -phenylnitron (18), and 1,3,5-trimethoxybenzene were obtained from Alfa Aesar. Styrene (**25**) was obtained from Fisher Scientific and filtered through basic alumina prior to use. Cesium fluoride (CsF) was obtained from Strem Chemicals. Diisopropylamine was obtained from Acros Organics and distilled over  $\text{CaH}_2$  prior to use. Reaction temperatures were controlled using an IKAmag temperature modulator, and reactions were performed at room temperature (approximately 23 °C) unless otherwise stated. Thin-layer chromatography (TLC) was conducted with EMD gel 60 F254 pre-coated plates (0.25 mm for analytical chromatography and 0.50 mm for preparative chromatography) and visualized using a combination of UV, anisaldehyde, and potassium permanganate staining techniques. Silicycle Siliaflash P60 (particle size 0.040–0.063 mm) was used for flash column chromatography.  $^1\text{H}$  NMR spectra were recorded on Bruker spectrometers (500 and 600 MHz) and are reported relative to residual solvent signals. Data for  $^1\text{H}$  NMR spectra are reported as follows: chemical shift ( $\delta$  ppm), multiplicity, coupling constant (Hz), integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift (at 125 MHz). IR spectra were recorded on a Perkin-Elmer UATR Two FT-IR spectrometer and are reported in terms of absorption frequency ( $\text{cm}^{-1}$ ). DART-MS spectra were collected on a Thermo Exactive Plus Orbitrap (Thermo Scientific) equipped with an ID-CUBE ion source and a Vapur Interface (IonSense Inc.). Both the source and MSD were controlled by Excalibur software v. 3.0. The analyte was spotted onto OpenSpot sampling cards (IonSense Inc.) using  $\text{CH}_2\text{Cl}_2$  as the solvent. Ionization was accomplished using UHP He plasma with no additional ionization agents. The mass calibration was carried out using Pierce LTQ Velos ESI (+) and (−) Ion calibration solutions (Thermo Fisher Scientific).

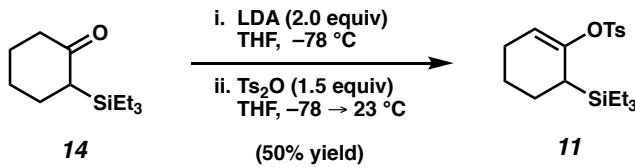
Note: Supporting information for the syntheses of silyl triflates **8a** and **10a**,<sup>1</sup> silyl ketone **14**,<sup>1</sup> and silyl enol ether **31**<sup>2</sup> have been published, and spectral data match those previously reported.

## Experimental Procedures

### A. Syntheses of Silyl Tosylates 9 and 11



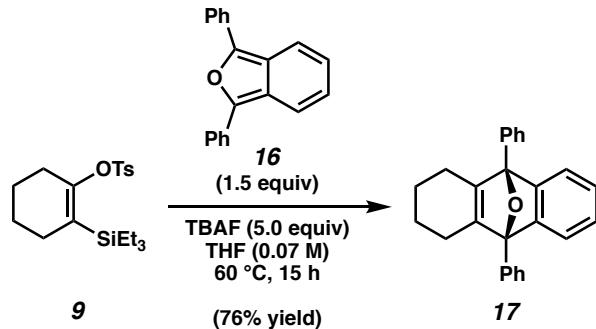
**Silyl Tosylate 9.** To a stirring suspension of sodium *tert*-butoxide (498 mg, 5.18 mmol, 1.1 equiv) in THF (5 mL) at  $-20^\circ\text{C}$  was added silyl ketone **14** (1.00 g, 4.71 mmol, 1.0 equiv) in THF (5 mL) via cannula addition over 5 min. The resulting dark orange-red solution was then warmed to  $0^\circ\text{C}$  and stirred for 1 h. Next, the ice bath was removed, and the solution was stirred at  $23^\circ\text{C}$  for 30 min, then recooled to  $0^\circ\text{C}$ . *p*-Toluenesulfonic anhydride (1.69 g, 5.18 mmol, 1.1 equiv) in THF (7.0 mL) was then added over 7 min. The cooling bath was removed, and the off-white, heterogeneous solution was stirred at  $23^\circ\text{C}$  for 5 h before being quenched with sat. aqueous  $\text{NaHCO}_3$  (20 mL). The layers were separated and the aqueous layer was extracted with diethyl ether ( $3 \times 20$  mL). The organic layers were combined, washed sequentially with deionized  $\text{H}_2\text{O}$  ( $1 \times 20$  mL) and brine ( $1 \times 20$  mL), dried with  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The crude reaction mixture was purified via column chromatography (3:97  $\text{Et}_2\text{O}$ :hexanes) to provide silyl tosylate **9** (1.06 g, 61% yield) as a white, crystalline solid. Silyl tosylate **9**:  $R_f$  0.55 (9:1 hexanes: $\text{EtOAc}$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.82–7.79 (m, 2H), 7.34–7.30 (m, 2H), 2.44 (s, 3H), 2.23–2.20 (m, 2H), 2.11–2.06 (m, 2H), 1.64–1.58 (m, 2H), 1.53–1.47 (m, 2H), 0.88 (t,  $J = 8.1$ , 9H), 0.61 (q,  $J = 7.5$ , 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.5, 144.4, 135.8, 129.6, 127.6, 121.9, 28.8, 28.2, 23.0, 22.1, 21.7, 7.5, 3.1; IR (film): 2950, 2875, 1642, 1368, 1191  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ ) [M + H] $^+$  calcd for  $\text{C}_{19}\text{H}_{31}\text{O}_3\text{SSi}^+$ , 367.1755; found 367.1754.



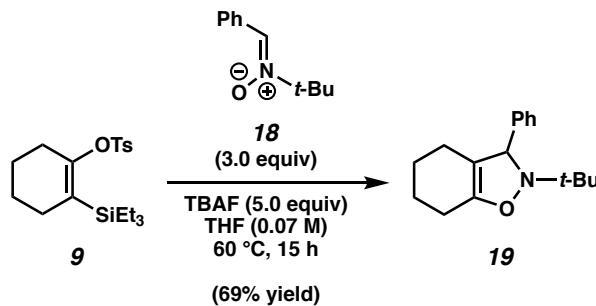
**Silyl Tosylate 11.** To a stirring solution of diisopropylamine (1.41 mL, 9.88 mmol, 2.1 equiv) in THF (14 mL) at  $-78\text{ }^\circ\text{C}$  was added *n*-butyllithium (2.50 M in hexanes, 3.78 mL, 9.44 mmol, 2.0 equiv) dropwise over 3 min. After stirring for 20 min, the reaction was warmed to  $23\text{ }^\circ\text{C}$  and stirred for 10 min, before recooling the reaction to  $-78\text{ }^\circ\text{C}$ . Next, silyl ketone **14** (1.00 g, 4.72 mmol, 1.0 equiv) in THF (14 mL) was added dropwise via cannula addition over 10 min. The resulting pale-yellow solution was stirred for 1 h. Then, a solution of *p*-toluenesulfonic anhydride (2.31 g, 7.08 mmol, 1.5 equiv) in THF (18 mL) was added dropwise via cannula addition over 6 min. The cooling bath was allowed to melt, gradually warming the reaction to  $23\text{ }^\circ\text{C}$  over 18 h, at which point it was quenched with sat. aqueous  $\text{NaHCO}_3$  (40 mL). The layers were separated and the aqueous layer was extracted with diethyl ether ( $3 \times 40$  mL). The combined organic layers were then dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure to provide a yellow oil. The crude oil was passed through a silica plug (3:97 Et<sub>2</sub>O:hexanes), and the eluate was concentrated to give a pale-yellow oil. This oil was dissolved in refluxing hexanes and cooled gradually to  $-78\text{ }^\circ\text{C}$  over 4 h to induce crystallization. The crystals were filtered off, washed with cold hexanes, and the mother liquor was concentrated to give a clear oil. This oil was subjected to the same crystallization procedure, and both crops of crystals were combined to afford silyl tosylate **11** (860 mg, 50% yield) as a white, crystalline solid. Silyl tosylate **11**:  $R_f$  0.57 (1:1 hexanes:benzene); <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (d,  $J = 8.1$ , 2H), 7.32 (d,  $J = 8.1$ , 2H), 5.19–5.16 (m, 1H), 2.45 (s, 3H), 2.01–1.90 (m, 2H), 1.82–1.74 (m, 2H), 1.62–1.56 (m, 1H), 1.53–1.45 (m, 1H), 1.36–1.27 (m, 1H), 0.92 (t,  $J = 7.9$ , 9H), 0.60 (q,  $J = 8.2$ , 6H); <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.4, 144.7, 133.5, 129.4, 128.5, 114.3, 25.5, 25.3, 24.1, 21.8, 21.7, 7.5, 3.0; IR (film): 2954, 2877, 1370, 1179, 1191  $\text{cm}^{-1}$ ; HRMS–APCI ( $m/z$ ) [ $\text{M} + \text{H}]^+$  calcd for  $\text{C}_{19}\text{H}_{31}\text{O}_3\text{SSi}^+$ , 367.1755; found 367.1758.

## B. Cyclohexyne Trapping Experiments

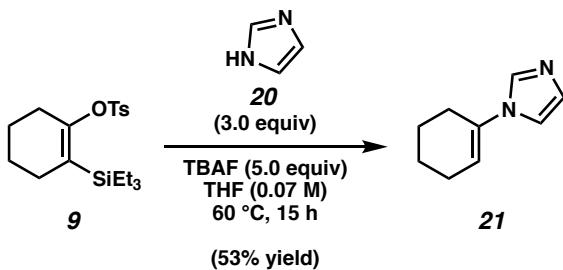
### Representative Procedure A (Table 1, entry 1 is used as an example)



**Cycloadduct 17.** To a stirred solution of silyl tosylate **9** (49.6 mg, 135  $\mu$ mol, 1.0 equiv), and 1,3-diphenylisobenzofuran (**16**) (54.9 mg, 203  $\mu$ mol, 1.5 equiv) in THF (1.35 mL, 0.07 M) was added TBAF (1.0 M in THF, 677  $\mu$ L, 677  $\mu$ mol, 5.0 equiv). The reaction vessel was purged with N<sub>2</sub>, sealed with a teflon cap, and placed in a preheated, 60 °C aluminum heating block. After stirring for 15 h, the reaction was cooled to 23 °C. The resultant yellow solution was filtered through a plug of silica gel (EtOAc eluent, 10 mL) and concentrated under reduced pressure to afford a crude yellow solid. Purification by preparative thin layer chromatography (3:2 benzene:hexanes) provided cycloadduct **17** (36.2 mg, 76% yield, average of two experiments) as a pale-yellow solid. Cycloadduct **17**: Spectral data match those previously reported.<sup>1</sup>



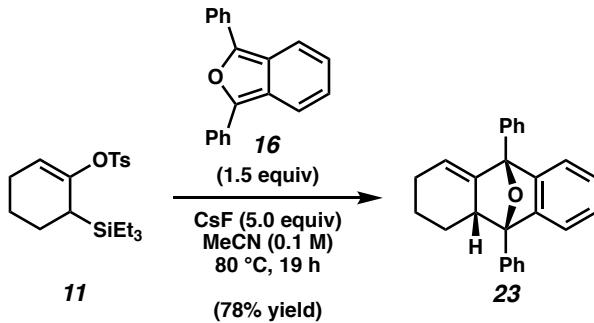
**Cycloadduct 19.** Followed Representative Procedure A. Purification by preparative thin layer chromatography (9:1 Hexanes:EtOAc) provided cycloadduct **19** (24.2 mg, 69% yield, average of two experiments) as a white solid. Cycloadduct **19**: Spectral data match those previously reported.<sup>3</sup>



**Imidazole adduct 21.** Followed Representative Procedure A. Purification by preparative thin layer chromatography (EtOAc) provided cycloadduct **21** (10.7 mg, 53% yield, average of two experiments) as an off-white solid. Imidazole adduct **21**: Spectral data match those previously reported.<sup>3</sup>

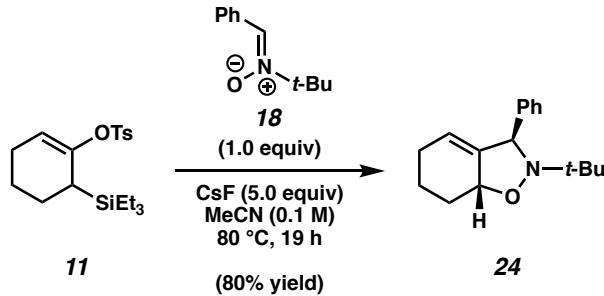
### C. 1,2-Cyclohexadiene Trapping Experiments

#### Representative Procedure B (Table 2, entry 1 is used as an example)

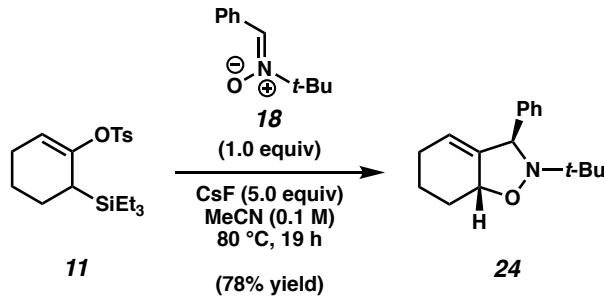


**Cycloadduct 23.** To a stirred solution of silyl tosylate **11** (49.7 mg, 136 µmol, 1.0 equiv) and 1,3-diphenylisobenzofuran (**16**) (55.5 mg, 205 µmol, 1.5 equiv) in MeCN (1.40 mL, 0.1 M) was added CsF (100 mg, 0.68 mmol, 5.0 equiv). The reaction vessel was purged with N<sub>2</sub>, sealed with a teflon cap and teflon tape, and placed in a preheated, 80 °C aluminum heating block. The reaction was allowed to stir at this temperature for 19 h. After cooling to 23 °C, the yellow, heterogenous solution was filtered through a plug of silica gel (EtOAc eluent, 10 mL) and concentrated under reduced pressure to afford a crude yellow solid. Purification by preparative thin layer chromatography (2:1 hexanes:CH<sub>2</sub>Cl<sub>2</sub> with 2% acetone) provided cycloadduct **23** as a pale-yellow solid (36.9 mg, 78% yield, 2.7:1 d.r. by <sup>1</sup>H NMR analysis of the crude material, average of two experiments). Cycloadduct **23**: Spectral data match those previously reported.<sup>1</sup>

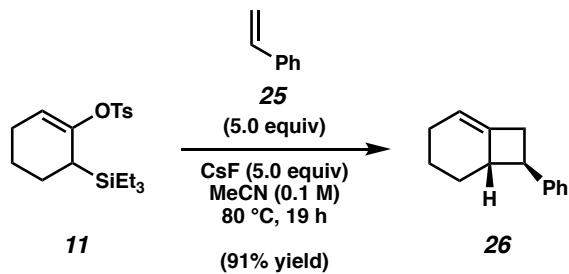
Any modification of the conditions shown in the representative procedure above are specified in the following scheme



**Cycloadduct 24.** Followed Representative Procedure B. Purification by preparative thin layer chromatography (1:1 hexanes:benzene) provided cycloadduct **24** as a white solid (30.2 mg, 80% yield, 9.3:1 d.r. by <sup>1</sup>H NMR analysis of the crude material, average of two experiments). Cycloadduct **24**: Spectral data match those previously reported.<sup>4</sup>

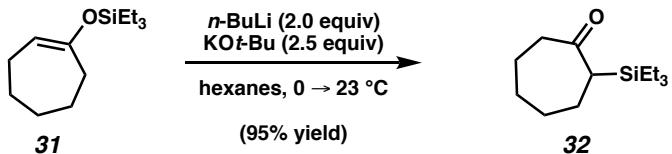


**Cycloadduct 24 (mmol scale).** To a stirred solution of silyl tosylate **11** (367 mg, 1.00 mmol, 1.0 equiv) and *N*-*tert*-butyl- $\alpha$ -phenylnitronate (**18**) (181 mg, 1.02 mmol, 1.0 equiv) in MeCN (10.0 mL, 0.1 M) was added CsF (761 mg, 5.01 mmol, 5.0 equiv). The reaction vessel was purged with N<sub>2</sub>, sealed with a teflon cap and teflon tape, and placed in a preheated, 80 °C aluminum heating block. The reaction was allowed to stir at this temperature for 19 h. After cooling to 23 °C, the white, heterogenous solution was filtered through a plug of silica gel (EtOAc eluent, 30 mL) and concentrated under reduced pressure to afford a crude off-white solid. Purification by flash chromatography (4:1 to 1:1 hexanes:benzene) provided cycloadduct **24** as a white solid (200.2 mg, 78% yield, 9.0:1 d.r.). Cycloadduct **24**: Spectral data match those previously reported.<sup>4</sup>



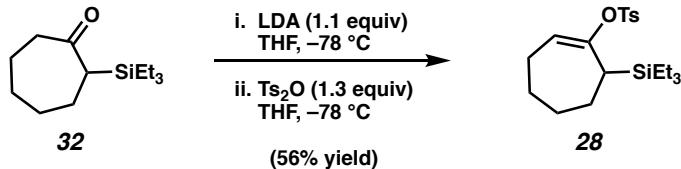
**Cycloadduct 26.** Followed a modified Representative Procedure B by adding 1,3,5-trimethoxybenzene as an external standard to the crude residue obtained by filtration of the reaction mixture.  $^1\text{H}$  NMR analysis of this crude mixture showed cycloadduct **26** (91% yield, 2.0:1 d.r., average of two experiments). The volatility of **26** hampered isolation attempts. Cycloadduct **26**: Spectral data match those previously reported.<sup>5</sup>

#### D. Synthesis of Silyl Tosylate 28



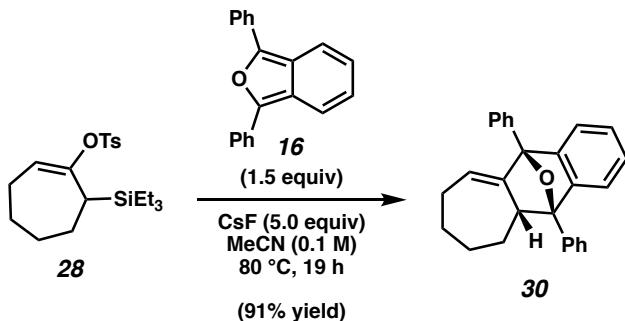
**Silyl ketone 32.** To a heterogeneous solution of potassium *tert*-butoxide (186 mg, 1.66 mmol, 2.5 equiv) in hexanes (1.3 mL) at 0 °C was added *n*-butyllithium (2.36 M in hexanes, 0.561 mL, 1.32 mmol, 2.0 equiv) dropwise over 2 min. The solution was removed from the ice bath and stirred at 23 °C for an additional 20 min. A solution of silyl enol ether **31** (150 mg, 0.662 mmol, 1.0 equiv) in hexanes (1.3 mL) was then added dropwise over 5 min and stirred at 23 °C. After stirring for 2 h, deionized H<sub>2</sub>O (5.0 mL) was added to the reaction, and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by flash chromatography (1.5:98.5 EtOAc:hexanes) to afford silyl ketone **32** (142 mg, 95% yield) as a clear, colorless oil. Silyl ketone **32**: R<sub>f</sub> 0.36 (99:1 benzene:Et<sub>2</sub>O);  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>): δ 2.63–2.56 (m, 1H), 2.37 (dd, *J* = 11.9, 4.9, 1H), 2.33–2.27 (m, 1H), 2.03–1.95 (m, 1H), 1.93–1.82 (m, 3H), 1.72–1.61 (m, 1H), 1.46–1.29 (m, 2H), 1.18–1.07 (m, 1H), 0.94 (t, *J* = 8.0, 9H), 0.60 (q, *J* = 7.5, 6H);  $^{13}\text{C}$

NMR (125 MHz, CDCl<sub>3</sub>): δ 215.9, 47.6, 43.6, 31.1, 30.5, 25.9, 25.7, 7.3, 2.4; IR (film): 2880, 1670, 1417, 1208, 879 cm<sup>-1</sup>; HRMS-APCI (*m/z*) [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>27</sub>OSi<sup>+</sup>, 227.1826; found 227.1826.



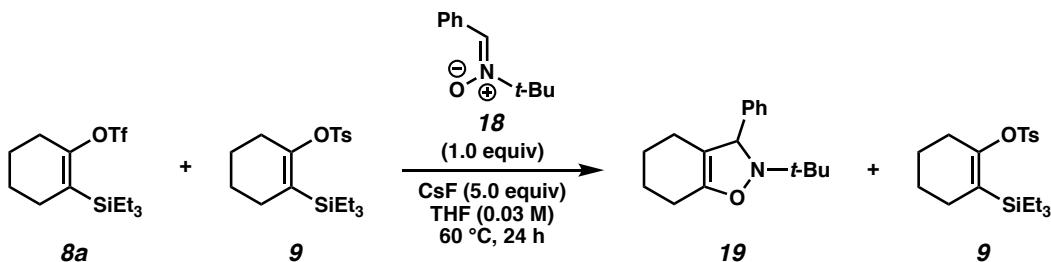
**Silyl tosylate 28.** To a solution of diisopropylamine (0.110 mL, 0.762 mmol, 1.15 equiv) in THF (0.5 mL) at -78 °C was added *n*-butyllithium (2.36 M in hexanes, 0.309 mL, 0.729 mmol, 1.1 equiv) dropwise over 2 min. The solution was stirred for 30 min at -78 °C, then warmed to 23 °C over 15 min before being cooled to -78 °C. Silyl ketone **32** (150 mg, 0.662 mmol, 1.0 equiv) in THF (0.5 mL) was added dropwise over 5 min and stirred for 1 h at -78 °C. Next, *p*-toluenesulfonic anhydride (281 mg, 0.861 mmol, 1.3 equiv) in THF (2.0 mL) was added dropwise over 5 min and allowed to stir at -78 °C. After stirring for 1 h, sat. aqueous NaHCO<sub>3</sub> (3.0 mL) was added to the reaction, and the stirring solution was warmed to 23 °C. The aqueous layer was then extracted with diethyl ether (3 x 3 mL), and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude solid was dissolved and passed through a plug of silica gel (2:1 hexanes:benzene eluent, 100 mL). The eluate was concentrated and divided into three equal portions. Each portion was purified by preparative thin layer chromatography (7:3 benzene:hexanes), and the individual portions were recombined to afford silyl tosylate **28** (141 mg, 56% yield) as a white solid. Silyl tosylate **28**: M.p. 39.9–40.8 °C; R<sub>f</sub> 0.79 (99:1 benzene:Et<sub>2</sub>O); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.82–7.79 (m, 2H), 7.35–7.31 (m, 2H), 5.22 (dd, *J* = 9.2, 4.4, 1H), 2.45 (s, 3H), 2.10 (t, *J* = 5.7, 1H), 2.07–2.00 (m, 1H), 1.94–1.87 (m, 1H), 1.83–1.76 (m, 1H), 1.75–1.65 (m, 2H), 1.55–1.49 (m, 1H), 1.49–1.41 (m, 1H), 1.37–1.28 (m, 1H), 0.94 (t, *J* = 8.1, 9H), 0.63 (q, *J* = 7.7, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 154.3, 144.6, 133.6, 129.5, 128.5, 118.4, 33.0, 28.2, 27.6, 26.0, 23.9, 21.7, 7.5, 3.6; IR (film): 2929, 2876, 1368, 1177, 994 cm<sup>-1</sup>; HRMS-APCI (*m/z*) [M + H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>33</sub>O<sub>3</sub>SSi<sup>+</sup>, 381.1914; found 381.1907.

### E. 1,2-Cycloheptadiene Trapping Experiment



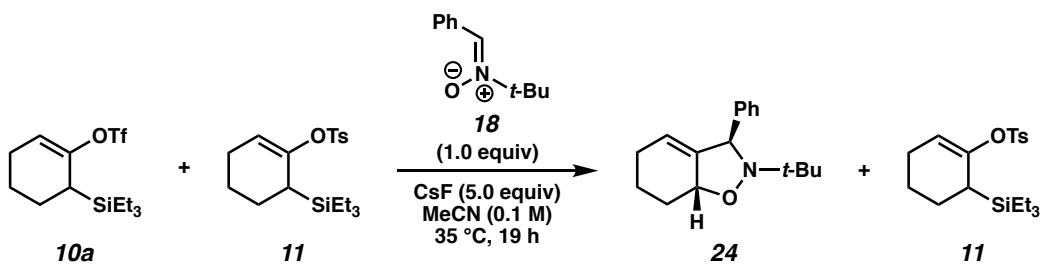
**Cycloadduct 30.** To a stirred solution of silyl tosylate **28** (19.8 mg, 52.0  $\mu\text{mol}$ , 1.0 equiv) and 1,3-diphenylisobenzofuran (**16**) (21.1 mg, 78.0  $\mu\text{mol}$ , 1.5 equiv) in MeCN (0.52 mL, 0.1 M) was added CsF (39.5 mg, 260  $\mu\text{mol}$ , 5.0 equiv). The reaction vessel was purged with  $\text{N}_2$ , sealed with a teflon cap and teflon tape, and placed in a preheated, 80  $^\circ\text{C}$  aluminum heating block. The reaction was allowed to stir at this temperature for 14 h. After cooling to 23  $^\circ\text{C}$ , the yellow, heterogeneous solution was filtered through a plug of silica gel (EtOAc eluent, 10 mL) and concentrated under reduced pressure to afford a crude yellow solid. Purification by preparative thin layer chromatography (2:1 hexanes:CH<sub>2</sub>Cl<sub>2</sub> with 2% acetone) provided cycloadduct **30** (17.3 mg, 91% yield, 6.3:1 d.r. by <sup>1</sup>H NMR analysis of the crude material). Cycloadduct **30**: Spectral data match those previously reported.<sup>6</sup>

### F. Silyl Tosylate and Silyl Triflate Competition Experiments



**Alkyne precursor competition experiment.** To a stirred solution of silyl triflate **8a** (25.0 mg, 72.6  $\mu\text{mol}$ , 1.0 equiv), silyl tosylate **9** (26.6 mg, 72.6  $\mu\text{mol}$ , 1.0 equiv), and *N*-*tert*-butyl- $\alpha$ -phenylnitronite (**18**) (12.9 mg, 72.6  $\mu\text{mol}$ , 1.0 equiv) in THF (2.4 mL, 0.03 M) was added CsF (55.1 mg, 363  $\mu\text{mol}$ , 5.0 equiv). The reaction vessel was purged with  $\text{N}_2$ , sealed with a teflon cap, and

placed in a preheated, 60 °C aluminum heating block. The reaction was allowed to stir at this temperature for 24 h. After cooling to 23 °C, the solution was filtered through a plug of silica gel (EtOAc eluent, 10 mL) and concentrated under reduced pressure to afford the crude reaction mixture. 1,3,5-trimethoxybenzene was added as an external standard. <sup>1</sup>H NMR analysis of the crude reaction mixture showed cycloadduct **19** (42% yield) and silyl tosylate **9** (100% remaining).



**Allene precursor competition experiment.** To a stirred solution of silyl triflate **10a** (25.0 mg, 72.6 μmol, 1.0 equiv), silyl tosylate **11** (26.6 mg, 72.6 μmol, 1.0 equiv), and *N*-*tert*-butyl- $\alpha$ -phenylnitrone (**18**) (12.9 mg, 72.6 μmol, 1.0 equiv) in MeCN (0.73 mL, 0.1 M) was added CsF (55.1 mg, 363 μmol, 5.0 equiv). The reaction vessel was purged with N<sub>2</sub>, sealed with a teflon cap, and placed in a preheated, 35 °C aluminum heating block. The reaction was allowed to stir at this temperature for 19 h. After cooling to 23 °C, the solution was filtered through a plug of silica gel (EtOAc eluent, 10 mL) and concentrated under reduced pressure to afford the crude reaction mixture. 1,3,5-trimethoxybenzene was added as an external standard. <sup>1</sup>H NMR analysis of the crude reaction mixture showed cycloadduct **24** (94% yield, 12.2:1 d.r.) and silyl tosylate **11** (94% remaining).

## References

- <sup>1</sup> Inoue, K.; Nakura, R.; Okano, K.; Mori, A. One-pot synthesis of silylated enol triflates from silyl enol ethers for cyclohexynes and 1,2-cyclohexadienes. *Eur. J. Org. Chem.* **2018**, 3343–3347.
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# NMR Spectra

