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On the mechanism of the silicon-tethered reductive Pauson–Khand reaction

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Abstract—The reductive Pauson–Khand reaction (PKR) of tethered vinyl silanes likely proceeds as usual to the bicyclopentenones **2**, but rapid loss of the allylic silane initiates a fragmentation process culminating in propargylic carbon reduction. Damp nitrile solvents are crucial for efficient reaction, and under dry conditions additional products are obtained including dimerized cyclopentadienones and 5-(1-amino-alkylidine) cyclopentenes. Solvent incorporated enones likely arise from enolate attack on a cobalt coordinated nitrile. A unified reaction mechanism is proposed. The first example of a PKR with an allyloxy ethynylsilane is also reported.

The Pauson–Khand reaction (PKR) is regarded as an important reaction for cyclopentenone construction and has been extensively reviewed.[1] Recently, we reported the first PKR of 4-oxa-3-sila-hept-1-en-6-ynes (**1**) that provided cyclopentenones formally derived from an intermolecular reaction between an alkyne and ethylene.[2] The method offered distinct advantages over reactions with ethylene in that high pressures or special equipment were not required, and the traceless silicon tether[3] circumvents the regiochemical ambiguity observed in the carbonyl insertion when ethylene is used (e.g. **3** vs **4**).[4] As summarized in Table 1, the method succeeded with a variety of substituents at the alkyne terminus and at the propargylic position. While Lewis acid mediated cleavage of the silicon–carbon bond may be expected with enones of type **2**, reduction of the carbon–oxygen bond implicates a more complicated mechanism. In this paper, we disclose the details of the reductive PKR of silicon-tethered enynes and propose a unified mechanistic hypothesis consistent with deuterium labeling studies and products observed under dry conditions (Scheme 1).

Given the unusual reduction occurring with this PKR, experiments designed to provide insight into the reaction mechanism were undertaken. Simple deuterium labeling studies indicated that the two new enone hydrogens originated from water present in the nitrile solvent at the onset of the reaction (Table 1), and not from aqueous work-up or the nitrile. The carbons and hydrogens at C(4) and C(5) of the enones resonate at similar chemical shift, and their identity was established by selective deuterium labeling at the C(5)-carbon by deprotonation with *t*BuLi followed by a D_2O work-up (Scheme 2). Spiking the reaction of enyne **8** with 1 equiv. of enone **15** showed that significant intermolecular proton exchange was not occurring (Scheme 3). Additionally, no hydrogen (deuterium) exchange at the propargylic position was observed (Scheme 4).

While detailed experimental evidence supporting a particular mechanism of the PKR has not been forthcoming, most authors support the mechanism postulated by Magnus,[5] which was recently bolstered by theorists' calculations.[6] Given the high pressures necessary to effect the intermolecular PKR with ethylene,[4] tether loss likely occurred subsequent to the first carbon–carbon bond forming step in a Magnus-like mechanism. A mechanistic hypothesis that accounts for the reduction is shown in Scheme 5.

Although no bicyclic enones of type **25** were detected in the course of our investigations, invoking their formation and subsequent demise facilitates the formulation of a reasonable reaction mechanism. We speculate that the transient enones **25** terminate in a facile desilylation event (possibly aided by a nitrile–silicon ate complex) to give the resonance stabilized enolate **26**. Both ring strain and coordination by a cobalt carbonyl species might be expected to facilitate loss of the silicon, in what is essentially an activated allyl silane-like environment.[7] Fissure of the carbon–oxygen bond did not occur with the pivaldehyde-derived enynes **17** and **19**, and the silanol **20** was characterized by X-ray crystallography.[2] For the carbon–oxygen cleavage to occur in this case the already severe A(1,3) strain between the *t*Bu group and the *n*Pr C(2) side chain would be exacerbated as the allylic carbon becomes trigonal planar.[8] Hindered rotation about the enone C(3) and allylic carbon of **20** manifested in the ^1H NMR as duplicated and line broadened signals.

Keywords: carbonylations; enynes; reductions; silicon; tether.
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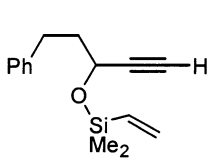
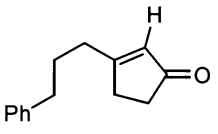
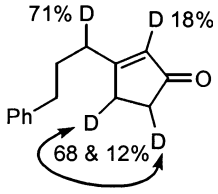
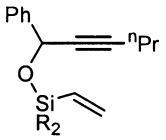
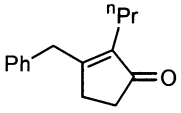
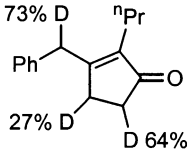
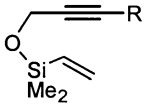
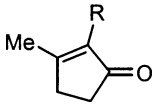
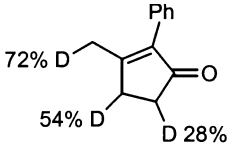
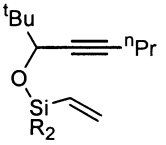
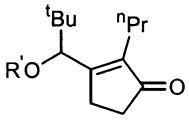
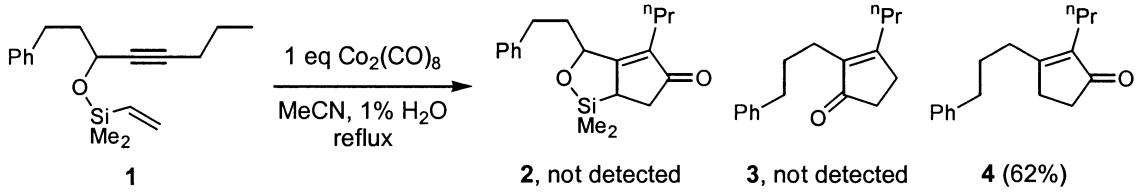
Table 1. PKR of vinylsilane-derived enynes

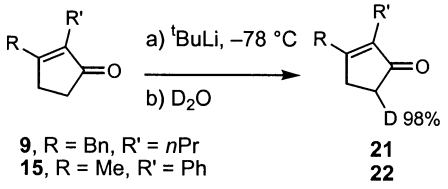
Entry	Substrate	Product(s) and additives	
		1% H_2O	1% D_2O[a]
1	 **5**	 **6**, 45%[b]	 **7a**, 8%[c]
2	 **8**, R=Me	 **9**, 65%	 **10**, 49%
3	**11**, R=Ph	**9**, 69%	–
4	 **12**, R=^{n}Pr	 **13**, R=^{n}Pr, 75%	–
5	**14**, R=Ph	**15**, R=Ph, 74%	 **16**, 56%
6	 **17**, R=Me	 **18**, R′=H, 65%	
7	**19**, R=Ph	**20**, R′=$SiPh_2(OH)$, 37%	

Reaction conditions: 1 equiv. $Co_2(CO)_8$, 1 equiv. enyne, 1% H_2O or D_2O, refluxing MeCN (0.25 M), 30 min.
[a] Mixture of stereoisomers, average %D incorporation.
[b] Reaction time: 24 h.
[c] Reaction time: 30 min.



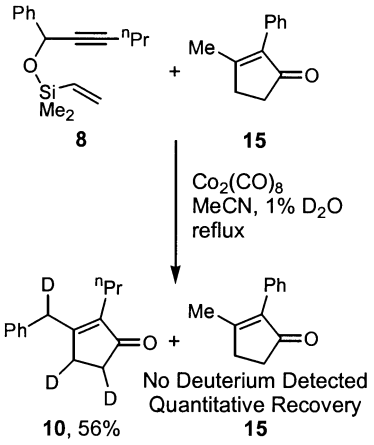
Scheme 1.

Carbon–oxygen bond cleavage and departure of the neutral tether remnants as polysiloxane can be envisaged to occur in a stepwise manner giving the trimethylene methane-like intermediate **27**,[9] followed by reduction to the cobalt(II) enolate **28**.[10] Alternatively, donation of an electron from cobalt into the enone pi system of **26**, likely generating an anion radical, subsequent loss of siloxane and transfer of a second electron leads to the same intermediate **28**.[24] Invocation of the dianionic intermediate **28** can be circumvented simply by enolate protonation prior to siloxane loss. In either case, the formation of a blue/green precipitate during the course of the reaction is consistent with cobalt serving as the reducing agent.

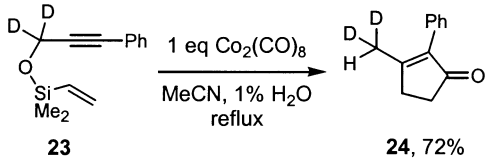


Scheme 2.

At the temperature of refluxing acetonitrile, dienolate tautomerization by [1,5]-H sigmatropic rearrangements is a viable alternative to intermolecular proton transfer, a



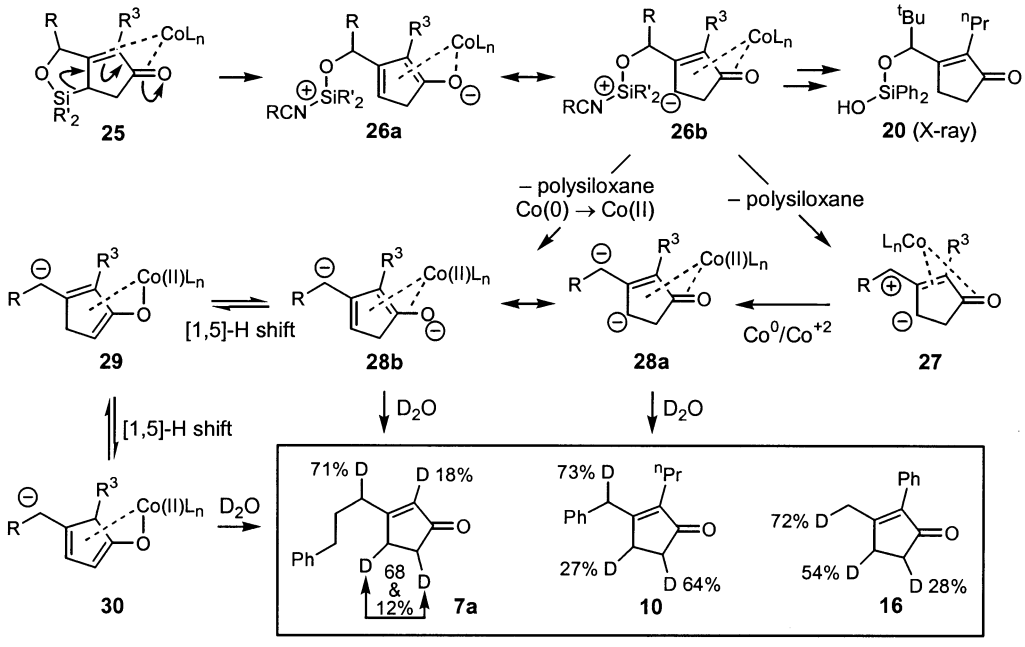
Scheme 3.



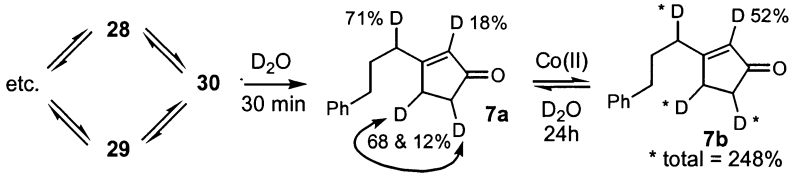
Scheme 4.

pathway which is disfavored in light of the crossover experiment shown in Scheme 3. The [1,5]-H sigmatropic rearrangement can account for deuterium incorporation at C(2) of enone **7**, and C(5) of all the deuterium-labeled enones (Table 1). In all cases examined deuterium incorporation was less complete at the allylic carbon, which suggests that an intramolecular proton transfer to make a Cp anion may be favored. The reaction with the terminal alkyne **5** was sluggish, and extended reaction times (24 h) were required compared to the other enynes (30 min). After a 30 min reaction time the percent deuterium incorporation in enone **7a** was consistent with the other examples, although the yield was low (12%, 84% based on recovered starting material). However, after the extended reaction time necessary for complete consumption of starting material (24 h) extensive deuterium incorporation occurred (Scheme 6), which suggests that subsequent to the initial protonolysis the cobalt(II) facilitates further enolization. The enol tautomers may also be subject to [1,5]-H sigmatropic rearrangement.

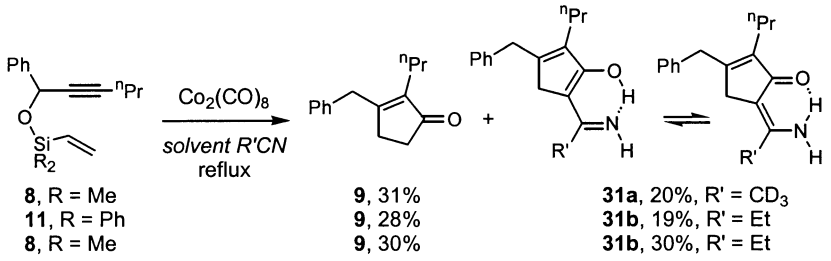
At the onset of these investigations, several established procedures for effecting the PKR were explored, including catalytic,[11–13] promoted[14] and other transition metal mediated variants,[15] but enones were only observed from the reaction with stoichiometric $Co_2(CO)_8$ in refluxing acetonitrile or similar solvents.[16] Nitriles are excellent



Scheme 5. Nitrile solvent with 1% D_2O.



Scheme 6.



Scheme 7.

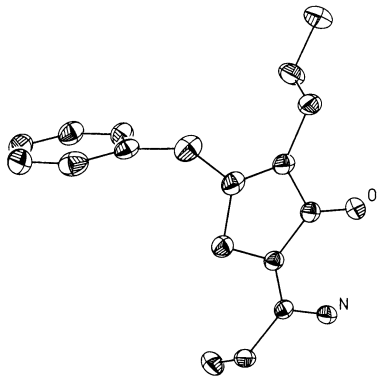


Figure 1. ORTEP representation of **31b.**

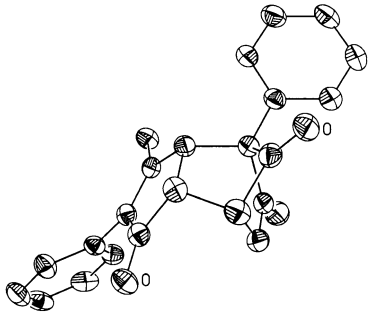


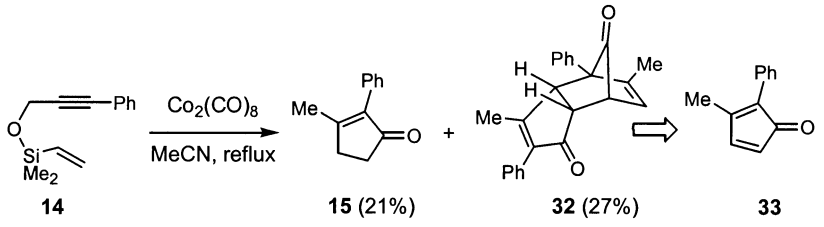
Figure 2. ORTEP representation of **32**.

ligands for many transition metals, and are known to displace carbon monoxide in metal carbonyl clusters.[17] Electronic modification of cobalt by replacing CO for a nitrile likely facilitates olefin insertion into the alkyne–cobalt complex. However, the use of dry acetonitrile in these experiments had a markedly deleterious effect on reaction efficiency. In addition to lowering the yields reported in Table 1 by 30–65%, interesting new products were obtained under anhydrous conditions. For example, in dry acetonitrile or propionitrile the benzaldehyde-derived enynes **8** and **11** provided the curious solvent incorporated enones **31a**, **b** (Scheme 7). Solvent inclusion occurred with either dimethyl or diphenyl substitution at silicon, but at the current stage of development navigating the reaction exclusively through the solvent alkylation pathway remains elusive. The structure of **31b** (mp 90–91°C, Et_2O) was unambiguously established by X-ray crystallography (Fig. 1).[18]

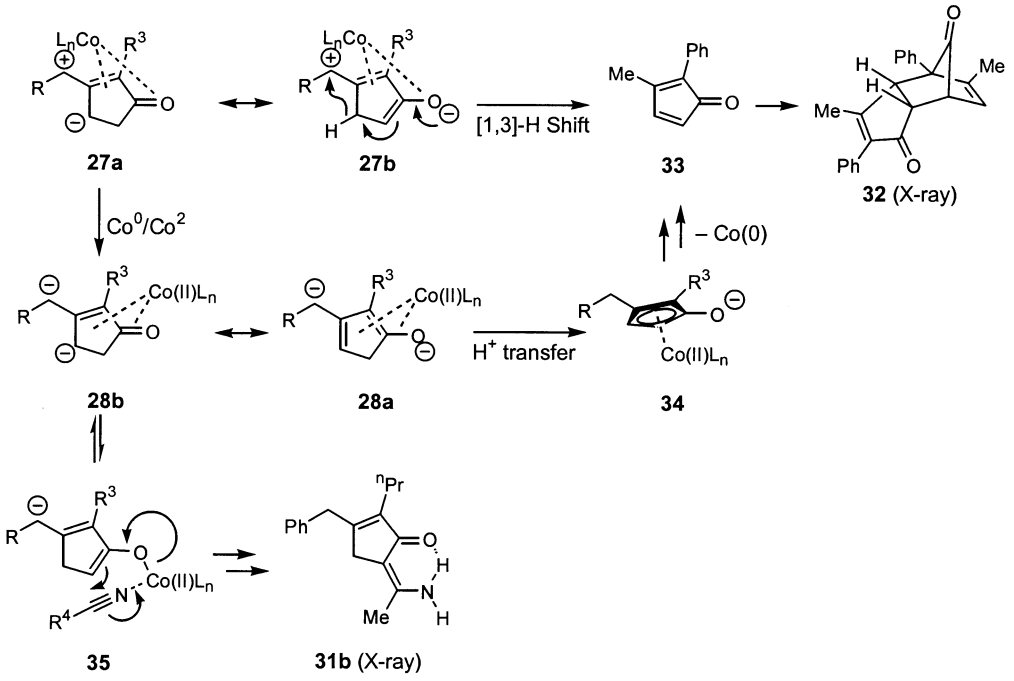
The reaction of enyne **14**, which has no propargylic substitution, provided the expected enone **15** (21%) and the new tricyclic enone **32** (27%, Scheme 8), the structure of **32** was confirmed by X-ray analysis (Fig. 2).[18] Enone **32** appears to have originated from an intermolecular Diels–Alder reaction of dieneone **33**.[19] While minor amounts of Diels–Alder products were generated from several enynes, no others provided sufficient material for adequate characterization.

Further elaboration of the mechanistic pathway invoked above can help rationalize the products generated under anhydrous conditions (Scheme 9). Nitriles are excellent ligands for a variety of transition metals, and cobalt complexes are particularly effective at activating nitriles to nucleophilic attack.[20] In this regard, nitriles are generally insufficiently electrophilic to react with ketone enolates, but enhanced nitrile electrophilicity resulting from cobalt coordination might be expected to make an enolate alkylation pathway accessible.[21] With nitrile coordination to cobalt, an intramolecular alkylation proceeding through a six-membered transition state becomes feasible (**35**). The one enyne that provided appreciable amounts of the nitrile alkylation product reassuringly showed the highest deuterium incorporation at C(5) in labeling experiments (Table 1, entry 2). While additional information is necessary to define parameters for achieving efficient or generalized nitrile alkylation, the extensive conjugation afforded by the propargylic phenyl group is a plausible alkylation asset.

Formation of the Diels–Alder adduct **32** required cyclopentenone oxidation to the dienone. A [1,3]-hydride shift



Scheme 8.

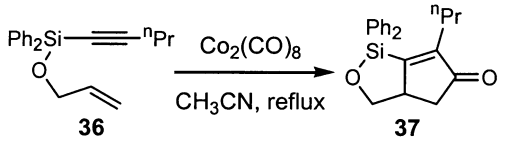


Scheme 9. Dry nitrile solvent.

to the exocyclic cation in the zwiterionic intermediate **27b** can account for the regional redox adjustments without involving cobalt. Interestingly, the only enyne which generated appreciable amounts of Diels–Alder product would involve formation of a comparatively unstable primary carbocation (**27**, R=H). Alternatively, a proton transfer from **28a** to form an η^5-CpCo complex such as **34** leads to the requisite dienone oxidation state. The latter mechanistic route helps explain the potent peroxidase activity displayed only by crude reaction mixtures of enyne **14**.

Limited spectroscopic information suggests that solvent inclusion and Diels–Alder products formed in trace amounts in nearly all the reactions reported in this study. The compounds identified herein were limited to those that were readily visualized by TLC and isolated by flash chromatography.

While this Paper was concerned with the PKR of tethered vinyl silanes, there are in principle three distinct structural classes of silicon tethered 1,6- and 1,7-enynes based on the location of the silicon atom: the silicon can be bound directly to the alkyne, the olefin or it can be positioned somewhere in between. Enyne **36**, where the silicon atom is attached directly to the alkyne, was prepared to determine if silacycles like **37** would be stable in the absence of a low energy decomposition pathway (Scheme 10). The standard PKR conditions gave the stable bicyclopentenone **37** in 45% unoptimized yield (based on recovered starting material).



Scheme 10.

In conclusion, the reductive PKR of tethered vinyl silanes likely proceeds as usual to the bicyclopentenones **2**, but rapid loss of the allylic silane initiates a fragmentation process culminating in reduction of the propargylic carbon. In the absence of protic solvent, the reactive intermediates can attack the nitrile solvent to afford 5-(1-amino-alkylidines) **31**, or undergo Diels–Alder dimerization. Additionally, the conversion of enyne **36** to **37** constitutes the first reported 'normal' PKR with a silicon-tethered enyne.

1. Experimental

1.1. General

PKRs were run under an atmosphere of nitrogen. Flasks were oven or flamed-dried and allowed to cool in a desiccator prior to use. Solvents and reagents were purified by standard methods.[22] Nitrile solvents were distilled from CaH_2 and purged with CO or N_2 before use. Thin layer chromatography (TLC) was performed on EM 250 Kieselgel 60 F254 silica gel plates. The plates were visualized by staining with I_2 on silica, CAM,[23] ninhydrin, or potassium permanganate.

The ^1H and ^{13}C NMR data was obtained on a General Electric QE-300 spectrometer, a Varian Unity Plus 300 spectrometer, or a Varian INOVA 500. For ^1H NMR, chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and are, in all cases, referenced to the residual proton resonance peaks: δ 7.24 for $CHCl_3$, δ 7.15 for benzene-d_6, 2.49 for DMSO-d_6. The ^{13}C NMR chemical shifts were reported in ppm relative to the center peak of the solvent multiplet: δ 77.0 (t) for $CDCl_3$, 128.0 (t) for benzene-d_6. ^{13}C NMR spectra were routinely run with broadband ^1H decoupling. HRMS (CI) was made with a VG analytical ZAB2-E instrument. The

percent deuterium incorporation was determined by ^{1}H NMR integration.

1.1.1. 3,3-Dimethyl-5-phenylethyl-4-oxa-3-sila-1-decen-6-yne (1). To a 0°C, stirred solution of 1-phenyl-4-octyn-3-ol (6.48 g, 32.0 mmol) and triethylamine (8.90 mL, 64.0 mmol) in CH_2Cl_2 (100 mL) was added chlorodimethylvinylsilane (4.14 mL, 30.0 mmol), and the solution was allowed to warm to rt. After 1 h, the reaction mixture was poured into ice cold half-saturated aqueous NH_4Cl (100 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2×25 mL). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried ($MgSO_4$). After filtration through a small pad of celite (2 cm thick pad on a 2 cm diameter frit) the solvent was removed under reduced pressure. Purification of the residue by flash chromatography on silica gel using 3% EtOAc/hexanes for elution afforded the title compound **8** as a colorless oil (8.1 g, 94%). R_f 0.34 (20% EtOAc/hexanes); IR (thin film) ν 3027 (m), 2961 (s), 2231 (w), 1594 (m), 1455 (m), 1340 (m), 1251 (s), 1088 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.18 (m, 5H), 6.21 (dd, J=14.9, 19.0 Hz, 1H), 6.04 (dd, J=4.1, 14.9 Hz, 1H), 5.83 (dd, J=4.1, 21.3 Hz, 1H), 4.40 (m, 1H), 2.78 (t, J=6.9 Hz, 2H), 2.22 (dt, J=2.1, 7.2 Hz, 2H), 2.01–1.97 (m, 2H), 1.63–1.51 (m, 2H), 1.02 (t, J=7.4 Hz, 3H), 0.28 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 138.0, 133.3, 128.7, 128.6, 126.0, 85.5, 81.6, 62.8, 40.6, 31.8, 22.3, 21.0, 13.8, −1.1, −1.3; HRMS m/z calcd for $C_{18}H_{27}OSi$ $[M+H]^+$ 287.1831, found 287.1833.

1.1.2. 3,3-Dimethyl-5-phenylethyl-4-oxa-3-sila-1-hepten-6-yne (5). The title compound was prepared according to the general procedure as described above for the preparation of **1** to afford **5** as a colorless oil (4.20 g, 86%). R_f 0.62 (20% EtOAc/hexanes); IR (thin film) ν 3305 (s), 2955 (s), 2113 (w), 1943 (w), 1591 (w), 1496 (m), 1253 (s), 1093 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5H), 6.22 (dd, J=14.9, 20.0 Hz, 1H), 6.07 (dd, J=4.4, 14.9 Hz, 1H), 5.86 (dd, J=4.4, 20.0 Hz, 1H), 4.41 (dt, J=1.8, 6.4 Hz, 1H), 2.84–2.78 (m, 2H), 2.48 (t, J=2.05 Hz, 1H), 2.09–2.02 (m, 2H), 0.31 (s, 3H), 0.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7, 137.5, 133.8, 128.7, 128.6, 126.2, 85.2, 73.0, 62.3, 40.1, 31.5, −1.3, −1.4; HRMS m/z calcd for $C_{15}H_{21}OSi$ $[M+H]^+$ 245.1361, found 245.1354.

1.1.3. 3,3-Dimethyl-4-oxa-5-phenyl-3-sila-1-decen-6-yne (8). The title compound was prepared according to the general procedure as described above for the preparation of **1** to afford **8** as a colorless oil (2.10 g, 91%). R_f 0.77 (10% EtOAc/hexanes); IR (thin film) ν 3050 (w), 2963 (s), 2260 (w), 2230 (w), 1594 (m), 1252 (s), 1059 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54–7.28 (m, 5H), 6.23 (dd, J=14.9, 20.0 Hz, 1H), 6.06 (dd, J=4.4, 14.9 Hz, 1H), 5.85 (dd, J=4.1, 20.0 Hz, 1H), 5.52 (t, J=2.0 Hz, 1H), 2.25 (dt, J=2.0, 7.2 Hz, 2H), 1.61–1.54 (m, 2H), 1.01 (t, J=7.4 Hz, 3H), 0.32 (s, 3H), 0.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 137.7, 133.6, 128.5, 127.9, 126.7, 87.0, 81.1, 65.3, 22.2, 21.1, 13.8, −1.1, −1.2; HRMS m/z calcd for $C_{16}H_{23}OSi$ $[M+H]^+$ 259.1518, found 259.1510.

1.1.4. 3,3-Diphenyl-4-oxa-5-phenyl-3-sila-1-decen-6-yne (11). The title compound was prepared according to the general procedure as described above for the preparation of **1** to afford **11** as a colorless oil (2.20 g, 70%). R_f 0.60 (20% EtOAc/hexanes); IR (thin film) ν 3059 (m), 2962 (m), 2227 (w), 1890 (w), 1698 (m), 1117 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.25 (m, 15H), 6.65 (dd, J=14.9, 20.1 Hz, 1H), 6.50 (dd, J=4.3, 14.8 Hz, 1H), 5.95 (dd, J=4.2, 20.0 Hz, 1H), 5.60 (t, J=2.0 Hz, 1H), 1.50 (dt, J=2.0, 7.3 Hz, 2H), 1.55–1.40 (m, 2H), 0.95 (t, J=7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 137.4, 135.7, 134.7, 134.6, 134.3, 130.3, 128.6, 128.1, 126.9, 87.9, 81.3, 66.4, 22.3, 21.2, 13.9; HRMS m/z calcd for $C_{26}H_{27}OSi$ $[M+H]^+$ 383.1831, found 383.1819.

1.1.5. 3,3-Dimethyl-4-oxa-3-sila-1-decen-6-yne (12). The title compound was prepared according to the general procedure as described above for the preparation of **1** to afford **12** as a colorless oil (4.90 g, 89%). R_f 0.75 (20% EtOAc/hexanes); IR (thin film) ν 2963 (s), 2871 (s), 2230 (w), 1629 (m), 1255 (s), 1146 (s), 1077 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.15 (dd, J=14.9, 19.7 Hz, 1H), 6.01 (dd, J=4.6, 14.9 Hz, 1H), 5.79 (dd, J=4.6, 19.7 Hz, 1H), 4.25 (t, J=2.0 Hz, 2H), 2.15 (dt, J=2.0, 7.2 Hz, 2H), 1.54–1.47 (m, 2H), 0.95 (t, J=7.2 Hz, 3H), 0.22 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 133.8, 86.0, 78.6, 51.8, 22.2, 21.0, 13.8, −1.8; HRMS m/z calcd for $C_{10}H_{19}OSi$ $[M+H]^+$ 183.1205, found 183.1206.

1.1.6. 3,3-Dimethyl-4-oxa-7-phenyl-3-sila-1-hepten-6-yne (14). The title compound was prepared according to the general procedure as described above for the preparation of **1** to afford **14** as a colorless oil (4.51 g, 88%). R_f 0.95 (10% EtOAc/hexanes); IR (thin film) ν 3052 (s), 2957 (s), 2242 (w), 1256 (s), 1080 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44–7.28 (m, 5H), 6.20 (dd, J=14.9, 19.7 Hz, 1H), 6.06 (dd, J=4.4, 14.9 Hz, 1H), 5.85 (dd, J=4.4, 19.7 Hz, 1H), 4.51 (s, 2H), 0.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1, 134.1, 131.9, 128.6, 128.5, 123.1, 87.7, 85.4, 52.1, −1.7; HRMS m/z calcd for $C_{13}H_{17}OSi$ $[M+H]^+$ 217.1049, found 217.1051.

1.1.7. 3,3-Dimethyl-5-(1,1-dimethylethyl)-4-oxa-3-sila-1-decen-6-yne (17). The title compound was prepared according to the general procedure as described above for the preparation of **1** to afford **17** as a colorless oil (1.87 g, 85%). R_f 0.65 (20% EtOAc/hexanes); IR (thin film) ν 3051 (w), 2958 (s), 2228 (w), 1250 (m), 1073 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (dd, J=14.9, 19.8 Hz, 1H), 6.02 (dd, J=4.4, 14.4 Hz, 1H), 5.81 (dd, J=4.1, 20.2 Hz, 1H), 3.98 (t, J=2.1 Hz, 1H), 2.20 (dt, J=2.1, 6.9 Hz, 2H), 1.58–1.51 (m, 2H), 1.00 (t, J=7.4 Hz, 3H), 0.95 (s, 9H), 0.25 (s, 3H), 0.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 133.0, 85.5, 80.6, 72.0, 36.4, 25.7, 22.4, 21.0, 13.8, −1.2, −1.5; HRMS m/z calcd for $C_{14}H_{27}OSi$ $[M+H]^+$ 239.1831, found 239.1814.

1.1.8. 3,3-Diphenyl-5-(1,1-dimethylethyl)-4-oxa-3-sila-1-decen-6-yne (19). The title compound was prepared according to the general procedure as described above for the preparation of **1** to afford **19** as a colorless oil (4.80 g, 85%). R_f 0.65 (20% EtOAc/hexanes); IR (thin film) ν 3051 (w), 2958 (s), 2361 (w), 1428 (m), 1063 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68–7.39 (m, 10H), 6.52 (dd, J=14.9, 20.2 Hz, 1H), 6.29 (dd, J=3.8, 14.9 Hz, 1H),

5.98 (dd, J=3.6, 20.2 Hz, 1H), 4.04 (t, J=2.0 Hz, 1H), 2.24 (dt, J=1.8, 6.9 Hz, 2H), 1.62–1.54 (m, 2H), 1.04 (t, J=7.4 Hz, 3H), 1.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 135.7, 135.0, 134.9, 130.3, 128.1, 86.4, 80.3, 71.9, 36.1, 25.6, 22.5, 21.0, 13.8; HRMS m/z calcd for $C_{24}H_{31}OSi$ $[M+H]^+$ 363.2144, found 363.2123.

1.1.9. 2-Propyl-3-phenylpropyl-2-cylcopenten-1-one (4). To a solution of $Co_2(CO)_8$ (342 mg, 1.00 mmol) and H_2O (36 μL, 2 mmol) in MeCN (4 mL) under an atmosphere of N^2 was added enyne **1** (287 mg, 1.00 mmol) in MeCN (1 mL). After stirring for 1 h at rt, the reaction flask was placed into a preheated oil bath (135°C) to bring the reaction mixture quickly to reflux. After 30 min the reaction flask was removed from the oil bath and allowed to cool to rt. The volatile components were removed in vacuo, and the residue was purified by flash chromatography on silica gel using 40% EtOAc/hexanes for elution to afford the title compound **4** as a pale yellow oil (149 mg, 62%). R_f 0.65 (40% EtOAc/hexanes); IR (thin film) ν 3447 (br, m), 2930 (m), 1706 (s), 1614 (s) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.19 (m, 5H), 2.69 (t, J=7.8 Hz, 2H), 2.50–2.45 (m, 4H), 2.39–2.36 (m, 2H), 2.13 (t, J=7.5 Hz, 2H), 1.91–1.85 (m, 2H), 1.43–1.36 (m, 2H), 0.88 (t, J=7.5, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.3 (C), 173.7 (C), 141.7 (C), 140.8 (C), 128.7 (CH), 128.6 (CH), 126.3 (CH), 36.1 (CH_2), 34.5 (CH_2), 31.0 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 25.4 (CH_2), 22.1 (CH_2), 14.4 (CH_3); HRMS m/z calcd for $C_{17}H_{23}O$ $[M+H]^+$ 243.1749, found 243.1741.

1.1.10. 3-Phenylpropyl-2-cyclopenten-1-one (6). The title compound **6** was prepared from **5** according to the general procedure described for the preparation of **4** except that reaction time was 24 h (91 mg, 45%). R_f 0.25 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.19 (m, 5H), 5.99 (s, 1H), 2.71 (t, J=7.7 Hz, 2H), 2.60–2.58 (m, 2H), 2.46–2.41 (m, 4H), 2.00–1.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.3, 182.8, 141.6, 129.9, 128.7, 128.6, 126.4, 35.7, 35.5, 33.2, 31.8, 28.9.

1.1.11. 3-Phenyl(propyl-1-d1)-4,5-d2-2-cyclopenten-1-one (7a). The title compound **7a** was prepared from **5** according to the general procedure described for the preparation of **4** except that 1% of D_2O was used (16 mg, 8%). R_f 0.25 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.19 (m, 5H), 5.99 (s, 0.78H), 2.71 (t, J=7.7 Hz, 2H), 2.60–2.58 (m, 1.29H), 2.46–2.41 (m, 3H), 2.00–1.90 (m, 2H); HRMS m/z calcd for $C_{14}H_{15}D_2O$ $[M+H]^+$ 203.1405, found 203.1407.

1.1.12. 3-Phenyl(propyl-1-d1)-4,5-d2-2-cyclopenten-1-one (7b). The title compound **7b** was prepared from **5** according to the general procedure described for the preparation of **4** except that reaction time was 24 h (86 mg, 46%). R_f 0.25 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.19 (m, 5H), 5.99 (s, 0.46H), 2.71 (t, J=7.7 Hz, 2H), 2.60–2.58 (m, 1.38H), 2.46–2.41 (m, 2.12H), 2.00–1.90 (m, 2H); HRMS m/z calcd for $C_{14}H_{14}D_3O$ $[M+H]^+$ 203.145, found 204.146.

1.1.13. 3-Benzyl-2-propyl-2-cyclopenten-1-one (9). The title compound was prepared from **8** according to the general procedure described for the preparation of **4** (139 mg, 65%). R_f 0.70 (40% EtOAc/hexanes); IR (thin film) ν 3386 (w, br), 2959 (m), 1698 (s), 1640 (s), 1494 (w), 1360 (w) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.17 (m, 5H), 3.77 (s, 2H), 2.39–2.28 (m, 6H), 1.54–1.46 (m, 2H), 0.96 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.3, 171.4, 141.2, 137.7, 129.1, 128.7, 127.0, 37.7, 34.5, 29.2, 25.6, 22.2, 14.5; HRMS m/z calcd for $C_{15}H_{19}O$ $[M+H]^+$ 215.1436, found 215.1432.

1.1.14. 3-Phenyl(methyl-d1)-4,5-d2-2-propyl-2-cyclopenten-1-one (10). The title compound was prepared from **16** according to the general procedure described for the preparation of **4** in the presence of D_2O instead of H_2O (105 mg, 49%). R_f 0.70 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.17 (m, 5H), 3.78–3.75 (m, 1.27H), 2.41–2.39 (m, 1.73H), 2.39–2.28 (m, 3.36H), 1.53–1.46 (m, 2H), 0.96 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 171.2, 140.9, 137.4, 128.8, 128.4, 126.7, 37.4, 37.1 (J_{cd}=19.3 Hz, CDH), 34.2, 34.0 (J_{cd}=16.5 Hz, CDH), 28.9, 25.3, 21.9, 14.2; HRMS m/z calcd for $C_{15}H_{17}D_2O$ $[M+H]^+$ 216.1483, found 216.1476.

1.1.15. 3-Methyl-2-propyl-2-cyclopenten-1-one (13). The title compound **13** was prepared from **12** according to the general procedure described for the preparation of **4** (103 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.51–2.48 (m, 2H), 2.39–2.35 (m, 2H), 2.16 (t, J=7.7 Hz, 2H), 2.06 (s, 3H), 1.47–1.35 (m, 2H), 0.89 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 170.3, 140.9, 34.7, 31.9, 25.3, 21.9, 17.6, 14.4

1.1.16. 3-Methyl-2-phenyl-2-cyclopenten-1-one (15). The title compound was prepared from **14** according to the general procedure described for the preparation of **4** (187 mg, 74%). R_f 0.56 (40% EtOAc/hexanes); IR (thin film) ν 2922 (m), 1695 (s), 1653 (m), 1495 (m), 1132 (m) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.26 (m, 5H), 2.62–2.59 (m, 2H), 2.52–2.49 (m, 2H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9 (C), 172.0 (C), 140.6 (C), 132.1 (C), 129.4 (CH), 128.5 (CH), 127.9 (CH), 35.1 (CH_2), 32.1 (CH_2), 18.6 (CH_3); HRMS m/z calcd for $C_{12}H_{12}O$ $[M+H]^+$ 173.0966, found 173.0962.

1.1.17. 3-(Methyl-d1)-2-phenyl-4,5-d2-cyclopenten-1-one (16). The title compound was prepared from according to the general procedure described for the preparation of **4** except that 3 equiv. of D_2O was added (97 mg, 0.56 mmol, 56%). R_f 0.56 (40% EtOAc/hexanes); ^{1}H NMR (300 MHz, C_6D_6) δ 7.40–7.37 (m, 2H), 7.27–7.22 (m, 2H), 7.14–7.12 (m, 1H), 2.07–2.04 (m, 1.72H), 1.81–1.78 (m, 1.46H), 1.60–1.58 (m, 2.28H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.5 (C), 171.7 (C), 140.2 (C), 131.6 (C), 128.9 (CH), 128.0 (CH), 127.3 (CH), 34.6 (CH_2), 31.2 (J_{cd}=19.9 Hz, CDH), 17.9 (J_{cd}=19.3 Hz, CDH_2); ^{13}C NMR (75 MHz, C_6D_6) δ 205.5 (C), 169–8 (C), 140.1 (C), 132.7 (CH), 129.6 (CH), 77.9 (CH_2), 77.4 (J_{cd}=18.4 Hz, CDH), 31.3 (CH_2), 31.0 (J_{cd}=20.3 Hz, CDH), 17.8 (CH_3), 17.5 (J_{cd}=19.8 Hz, CD_2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.5 (C), 171.7 (C), 140.2 (C), 131.6 (C), 128.9 (CH), 128.2 (CH), 127.3 (CH), 34.6 (CH_2), 31.6 (CH_2), 31.2 (J_{cd}=19.9 Hz, CDH), 18.1 (CH_3), 31.2 (J_{cd}=19.3 Hz, CDH_2); HRMS m/z calcd for $C_{12}H_{10}D_2O$ $[M+H]^+$ 175.1092, found 175.1089.

1.1.18. 3-(1-Hydroxy-2,2-dimethylpropyl)-2-propyl-2-cyclopenten-1-one (18). The title compound was prepared from **17** according to the general procedure described for the preparation of **4** (136 mg, 65%). R_f 0.35 (40% EtOAc/hexanes); IR (thin film) ν 3432 (s, br), 2962 (s), 2227 (w), 1730 (s), 1460 (s), 1367 (s), 1245 (s), 1048 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.48 (s, 1H), 2.86–2.80 (m, 1H), 2.62–2.55 (m, 1H), 2.40–2.38 (m, 2H), 2.28–2.13 (m, 2H), 1.87 (s, 1H), 1.50–1.40 (m, 2H), 1.03 (s, 9H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.7, 171.9, 142.7, 76.9, 36.9, 34.4, 27.0, 26.9, 26.6, 21.6, 14.6; HRMS m/z calcd for $C_{13}H_{23}O_2$ $[M+H]^+$ 211.1698, found 211.1692.

1.1.19. 3-[1-(Hydroxy-diphenyl-silanyloxy)-2,2-dimethyl-propyl]-2-propyl-2-cyclpenten-1-one (20). The title compound **20** was prepared from **19** according to the general procedure described for the preparation of **4** (143 mg, 37%). Mp 95–98°C (hexanes), R_f 0.10 (20% EtOAc/hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.67–7.28 (m, 10H), 4.70 (s, 1H), 3.60 (s, 1H), 2.82–2.70 (m, 1H), 2.58–2.44 (m, 1H), 2.22–2.17 (m, 1H), 2.05–1.99 (m, 1H), 1.98–1.78 (m, 2H), 1.22–1.17 (m, 2H), 0.98 (s, 9H), 0.78 (t, J=7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.4, 170.9, 142.2, 134.7, 134.4, 133.4, 133.3, 130.5, 127.9, 127.8, 37.0, 34.1, 26.9, 26.6, 26.5, 20.9, 14.5; HRMS m/z calcd for $C_{25}H_{33}O_3Si$ $[M+H]^+$ 408.2120, found 408.2118.

1.1.20. 3-Benzyl-2-propyl-5-d-2-cyclopenten-1-one (21). To a −78°C solution of enone **9** (99 mg, 0.46 mmol) in THF (2.0 mL) was added dropwise *t*BuLi (1.28 M in pentane 0.5 mL, 0.64 mmol). After 5 min, D_2O (0.25 mL, 12.5 mmol) was added in one portion. The solution was allowed to warm to rt, and after 1 h the solution was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography (silica gel, 20% EtOAc/hexanes) gave **21** as a pale yellow oil (49 mg, 0.23 mmol) in 49% yield. R_f 0.70 (40% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.17 (m, 5H), 3.77 (s, 2H), 2.40–2.28 (m, 5.H), 1.54–1.46 (m, 2H), 0.96 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.3, 171.4, 141.2, 137.7, 129.1, 128.7, 127.0, 37.7, 33.9 (J_{cd}= 20.3 Hz, CDH), 29.2, 25.6, 22.2, 14.5; HRMS m/z calcd for $C_{15}H_{18}DO$ $[M+H]^+$ 216.1499, found 216.1495.

1.1.21. 3-Methyl-2-phenyl-5-d-2-cyclopenten-1-one (22). To a −78°C solution of enone **15** (120 mg, 0.70 mmol) in THF (2.0 mL) was added dropwise *t*BuLi (1.28 M in pentane 1.0 mL, 1.28 mmol). After 5 min, D_2O (0.50 mL, 25 mmol) was added in one portion. The solution was allowed to warm to rt, and after 1 h the solution was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography (silica gel, 20% EtOAc/hexanes) gave **22** as a pale yellow oil (54 mg, 0.31 mmol) in 45% yield. R_f 0.56 (40% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.45–7.29 (m, 5H), 2.68–2.66 (m, 2H), 2.58–2.54 (m, 1H), 2.20 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6 (C), 171.8 (C), 140.2 (C), 131.7 (C), 129.0 (CH), 128.1 (CH), 127.5 (CH), 34.7 (J_{cd}=20.3 Hz, CDH), 31.7 (CH_2), 18.2 (CH_3); HRMS m/z calcd for $C_{12}H_{11}DO$ $[M+H]^+$ 174.1029, found 174.1032.

1.1.22. 1,1-d2-3-Phenyl-2-propyn-1-ol. To a −78°C, stirred solution of phenylacetylene (1.40 mL, 15.0 mmol) in THF (20 mL) was added dropwise *n*BuLi (2.7 M in hexane 5.0 mL, 13.5 mmol). After 5 min, paraformaldehyde-d2 (480 mg, 15.0 mmol) was added in one portion. The solution was allowed to warm to rt. After 1 h, the solution was treated with saturated aqueous NH_4Cl (20 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2×10 mL). The combined organic layers were washed with water (20 mL), brine (20 mL) and dried ($MgSO_4$). Flash chromatography (silica gel, 20% EtOAc/hexanes) gave the title compound as a pale yellow oil (1.42 g, 10.5 mmol) in 71% yield. R_f 0.42 (20% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.70–7.36 (m, 5H), 2.41 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.1 (C), 128.8 (CH), 128.7 (CH), 123.0 (CH), 86.6 (C), 86.0 (C), 51.4 (C, J not determined).

1.1.23. 5,5-d2-3,3-Dimethyl-4-oxa-3-sila-7-phenyl-hept-1-en-6-yne (23). The title compound was prepared from 1,1-d2-3-phenyl-2-propyn-1-ol according to the general procedure described for the preparation of **1**. Flash chromatography (silica gel, 10% EtOAc/hexanes) gave **23** as a pale yellow oil (1.43 g, 8.5 mmol) in 85% yield. R_f 0.85 (10% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.46–7.28 (m, 5H), 6.22 (dd, J=19.8, 14.9 Hz, 1H), 6.08 (dd, J=14.9, 4.3 Hz, 1H), 5.87 (dd, J=19.9, 4.3 Hz, 1H), 0.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3 (CH), 133.8 (C), 131.6 (CH), 128.2 (CH), 122.8 (CH_2), 87.3 (C), 85.0 (C), 51.2 (J_{cd}=22.6 Hz, CD_2), −2.0 (CH_3).

1.1.24. 3-(1,1-d2-Methyl)-2-phenyl-2-cyclopenten-1-one (24). The title compound was prepared from **23** according to the general procedure described for the preparation of **4** (34 mg, 0.20 mmol) in 22% yield. R_f 0.55 (40% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.26 (m, 5H), 2.65–2.64 (m, 2H), 2.55–2.53 (m, 2H), 2.13 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.6 (C), 171.7 (C), 140.4 (C), 131.8 (C), 129.1 (CH), 128.3 (CH), 127.6 (CH), 34.81 (CH_2), 31.8 (CH_2), 17.8 (J_{cd}=19.8 Hz, CHD_2); HRMS m/z calcd for $C_{12}H_{11}DO$ $[M+H]^+$ 175.1092, found 175.1089.

1.1.25. (*Z*)-5-(1-Aminoethylidene-d3)-3-benzyl-2-propyl-2-cyclopenten-1-one (31a). The title compound **31a** was prepared from **8** according to the general procedure described for the preparation of **4**, except that dry CD_3CN was used as solvent (19 mg, 20%). R_f 0.40 (40% EtOAc/hexanes); IR (thin film) ν 3369 (m, br), 2958 (m), 1636 (s), 1540 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30–7.12 (m, 5H), 3.73 (s, 2H), 2.79 (s, 2H), 2.33 (t, J=7.0 Hz, 2H), 2.62–1.51 (m, 2H), 0.94 (t, J=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 156.7, 151.7, 143.2, 139.3, 129.0, 128.8, 126.6, 104.0, 36.6, 34.2, 26.0, 22.5, 14.6; HRMS m/z calcd for $C_{17}H_{19}D_3NO$ $[M+H]^+$ 259.1890, found 259.1900

1.1.26. (*Z*)-5-(1-Aminopropylidene)-3-benzyl-2-propyl-2-cyclopenten-1-one (31b). The title compound **31b** was isolated from **11** according to the general procedure described for the preparation of **4**, except that dry EtCN

was used as solvent (85 mg, 21%). Mp 90–91°C (Et_2O), R_f 0.45 (40% EtOAc/hexanes); IR (thin film) ν 3377 (w, br), 2959 (m), 1636 (s), 1539 (s), 1453 (w), 1360 (w) cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 7.14–7.00 (m, 5H), 3.48 (s, 2H), 2.62 (s, 2H), 2.50 (t, J=7.4 Hz, 2H), 1.76–1.69 (m, 2H), 1.50 (q, J=7.7 Hz, 2H), 0.96 (t, J=7.4 Hz, 3H), 0.60 (t, J=7.7 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 195.6 (C), 155.7 (C), 155.1 (C), 143.8 (C), 139.6 (C), 129.0 (CH), 128.8 (CH), 126.5 (CH), 102.6 (C), 36.5 (CH_2), 33.6 (CH_2), 26.6 (CH_2), 26.3 (CH_2), 22.7 (CH_2), 14.5 (CH_3), 11.4 (CH_3); HRMS m/z calcd for $C_{18}H_{24}NO$ $[M+H]^+$ 270.1858, found 270.1863.

1.1.27. Dimer 32. ^1H NMR (300 MHz, $CDCl_3$) δ 7.48–7.32 (m, 8H), 7.17–7.14 (m, 2H), 6.22 (br s, 1H), 4.06 (d, J= 6.7 Hz, 1H), 3.59–3.36 (m, 1H), 3.18 (br s, 1H), 2.15 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.4, 199.9, 168.8, 148.5, 141, 8, 132.9, 131.2, 129.8, 129.3, 128.9, 128.7, 128.5, 128.0, 124.5, 66.2, 50.2, 46.1, 43.4, 31.2, 19.3, 16.7; HRMS m/z calcd for $C_{24}H_{21}O_2$ $[M+H]^+$ 341.1542, found 341.1540.

1.1.28. 5,5-Diphenyl-4-oxa-5-sila-1-decen-6-yne (36). To a cooled (0°C) solution of 1-pentyne (4.9 mL, 50 mmol) in THF (50 mL) was slowly added 0.825 M BuMgBr in Et_2O (50 mL, 41.3 mmol). The reaction mixture was stirred at rt for 1 h followed by addition of dichlorodiphenylsilane (8.4 mL, 40 mmol). The resulting slurry was brought to reflux and stirred for 1 h, allowed to cool, and concentrated in vacuo. The residue was triturated with Et_2O, and the Et_2O solution was concentration in vacuo. Vacuum distillation (115–120°C, 0.4 mm Hg) gave chlorosilane (5.02 g, 17.7 mmol, 43%) as a colorless viscous oil. To a cooled (0°C) solution of allyl alcohol (3.6 mL, 53.0 mmol) and Et_3N (7.5 mL, 53.9 mmol) in DCM (15 mL) was slowly added chlorosilane (5.02 g, 17.7 mmol). The reaction mixture was stirred at rt for 45 min, diluted with hexane (50 mL), filtered through celite, and concentrated in vacuo. Vacuum distillation (120–125°C, 0.4 mm Hg) gave 5,5-diphenyl-4-oxa-5-sila-1-decen-6-yne (1.02 g, 3.33 mmol) as a colorless oil in 19% yield. R_f 0.58 (10% EtOAc/hexanes); IR (thin film) ν 3069 (s), 2963 (s), 2726 (w), 2359 (w), 2176 (s), 1590 (m), 1116 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80–7.28 (m, 10H), 6.09–5.96 (m, 1H), 5.43–5.36 (m, 1H), 5.19–5.15 (m, 1H), 4.39–4.37 (m, 2H), 2.37 (t, J= 7.2 Hz, 2H), 1.70–1.63 (m, 2H), 1.07 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.8, 135.2, 135.0, 134.4, 132.8, 130.7, 130.1, 128.1, 115.0, 111.8, 79.0, 64.3, 22.4, 22.1, 13.8.

1.1.29. 1,1-Diphenyl-6-propyl-3a,4-dihydro-1*H*,3*H*-cyclopenta[*c*][1,2]oxasilol-5-one (37). To a solution of $Co_2(CO)_8$ (1.25 g, 3.33 mmol) in Et_2O (20 mL) was added **36** (1.02 g, 3.33 mmol). After stirring for 30 min at rt the reaction mixture and concentrated in vacuo at rt. Flash chromatography (SiO_2, hexane) gave the $Co_2(CO)_6$ complex of enyne **36** (1.84 g, 3.1 mmol) as a dark red brown viscous oil in 93% yield. R_f 0.27 (hexanes). A solution of enyne complex (155 mg, 0.26 mmol) in acetonitrile (4.0 mL) was heated at reflux for 16 h under an atmosphere of CO. The reaction was allowed to cool, volatiles were removed in vacuo, and the residue was dissolved in CH_2Cl_2 and filtrated through neutral Al_2O_3. Purification by flash chromatography (SiO_2, EtOAc/hexane 1:9–1:3 gradient for elution) gave recovered **36** (62 mg, 0.20 mmol, 77%) and bicyclic enone **37** (9 mg, 26.9 μmol) as a colorless oil in 10% yield. R_f 0.58 (25% EtOAc/hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.71–7.32 (m, 10H, ArH), 4.25 (dd, J=11.4, 3.9 Hz, 1H), 3.78–3.71 (m, 1H), 3.42 (br s, 1H), 2.56 (dd, J=19.2, 6.9 Hz, 1H), 1.97–1.85 (m, 3H), 1.04–0.88 (m, 2H), 0.45 (t, J=7.4 Hz, 3H); HRMS (CI) calcd for $C_{21}H_{22}O_2Si$ $[M+H]^+$ 335.1467, found 335.1472.

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