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Synthesis of Silyloxy Dienes by Silylene Transfer to Divinyl Ketones: Application to the Asymmetric Synthesis of Substituted Cyclohexanes

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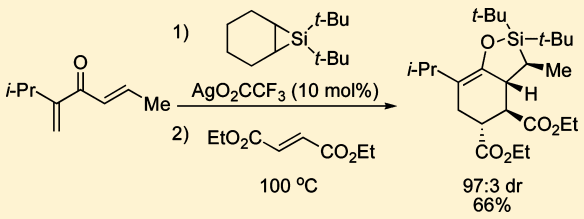
Supporting Information

ABSTRACT: Silver-catalyzed silylene transfer to divinyl ketones provided 2-silyloxy-1,3-dienes with control of stereochemistry and regioselectivity. The products participated in Diels–Alder reactions with electron-deficient alkenes and imines to form six-membered-ring products diastereoselectively. Cycloaddition reactions with alkenes bearing chiral auxiliaries provided access to chiral, nonracemic cyclohexenes. The methodology, therefore, represents a synthesis of diastereomerically and enantiomerically pure products in a single flask. The highly substituted cyclohexene products could be functionalized stereoselectively to provide cyclohexanols after oxidation of the carbon–silicon bond.



INTRODUCTION

Conjugated dienes are important precursors to complex organic products. In addition to the polymerization of 1,3-dienes, an important industrial transformation,[1] dienes have been used in stereoselective synthesis, such as the vinylogous aldol reaction.[2,3] Among the most important transformations of dienes is the Diels–Alder reaction because it enables the synthesis of cyclohexenes with a high degree of control. The importance of dienes has required the development of new routes for their synthesis.[4] In particular, the synthesis of highly substituted 2-silyloxy-1,3-dienes, which are important intermediates,[5] has been difficult to achieve with control of stereochemistry.[6−8]

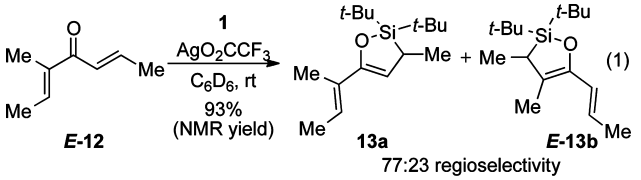
In this Article, we report the synthesis of 2-silyloxy-1,3-dienes from divinyl ketones by transfer of a silylene moiety (R_2Si). The resulting silyloxy dienes participated in stereoselective Diels–Alder cycloaddition reactions. Treatment of these dienes with chiral dienophiles allowed for kinetic resolution of the chiral diene to afford enantiopure cyclohexene products.

RESULTS AND DISCUSSION

Because silylene transfer to unsaturated carbonyl compounds forms cyclic silyl enol ethers,[9−11] initial experiments focused on reactions of divinyl ketones with silylene intermediates. The synthesis of silyloxy dienes was general for a range of substrates (Table 1). The reaction was regioselective: silylene transfer occurred to the side of the divinyl ketone bearing a β-substituent over the side bearing an α-substituent. This regioselectivity is consistent with the observed selectivity of nucleophilic additions to divinyl ketones.[12] Increasing the steric bulk of the α-substituent further increased this regioselectivity for transfer to the side bearing a β-substituent (Table 1, entry 5). The regioselectivity was further enhanced upon using THF as the solvent as well as cooling the reaction mixture to −78 °C (Table 1, entry 6).

The regioselectivity of this reaction can be understood by considering the structure of the divinyl ketone. It is likely that α-substitution blocks the lone pair of the carbonyl group's oxygen atom[13] from forming the silacarbonyl ylide[14−17] intermediate on that side of the divinyl ketone, whereas β-substitution does little to block the oxygen lone pair (Figure 1). It is also expected that α-substitution forces the alkene into the *s*-trans configuration, or possibly even out of plane,[18−22] thus preventing formation of the silacarbonyl ylide on this side of the carbonyl group.

The geometry of the alkene has a profound effect on the regioselectivity of silylene transfer. The regioselectivity of silylene transfer to ketone *E*-**12** (eq 1) closely matched the



regioselectivity found in silylene transfer to methyl-substituted divinyl ketone (Table 1, entry 1). This result indicates the significance of α-substitution for the observed selectivity. In contrast, addition across a *Z*-double bond was highly disfavored. Silylene transfer to ketone *Z*-**12** favored transfer across the C=C bond that contained an α-methyl substituent

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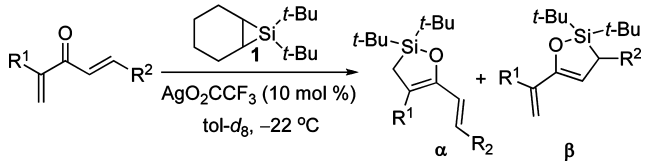
Table 1. Silylene Transfer to Divinyl Ketones[a]



entry	ketone	R^1	R^2	product	α:β ratio	NMR yield
1	**2**	Me	Me	**3a**:**3b**	25:75	100%
2	**4**	Ph	Me	**5a**:**5b**	27:73	100%
3	**6**	Me	Ph	**7a**:**7b**	26:74	97%
4	**8**	Me	*i*-Pr	**9a**:**9b**	37:63	88%
5	**10**	*i*-Pr	Me	**11a**:**11b**	15:85	100%
6[b]	**10**	*i*-Pr	Me	**11a**:**11b**	7:93	96%

[a]^{1}H NMR spectroscopic analysis was used to determine both regioisomeric ratios and yields relative to an internal standard ($PhSiMe_3$). [b]Transfer was run in THF at −78 °C instead of tol-d_8. Silyloxy dienes were carried onto cycloaddition reactions without further purification due to their instability to isolation conditions.

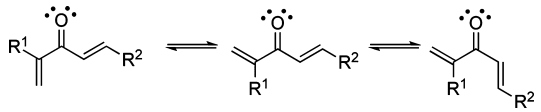
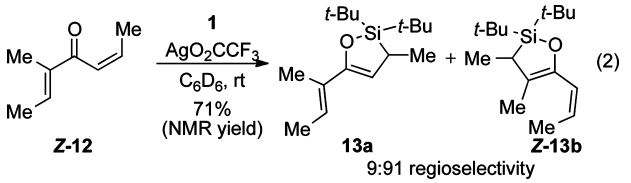


Figure 1. Possible conformations of divinyl ketones.

rather than the C═C bond that contained an α-hydrogen and *Z*-β-methyl substituent (eq 2). The high preference for the *Z*-



alkene to react at the α-substituted double bond may arise because only conformers *Z*-**12a** and *Z*-**12b** are populated because the conformers *Z*-**12c** and *Z*-**12d** are too sterically crowded (Figure 2). For the conformers *Z*-**12a** and *Z*-**12b**, in

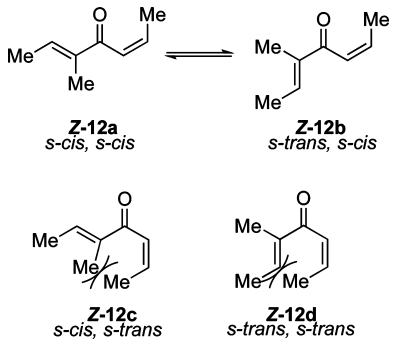
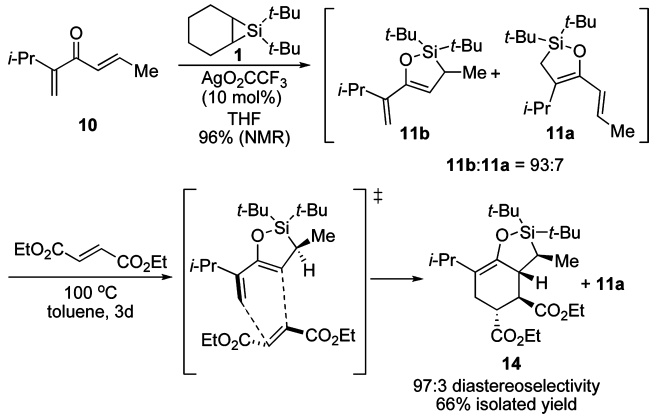


Figure 2. Rationale for regioselective transfer to *Z*-**12**.

neither case can a silylene moiety approach the carbonyl group from the side of the β-substituted double bond.

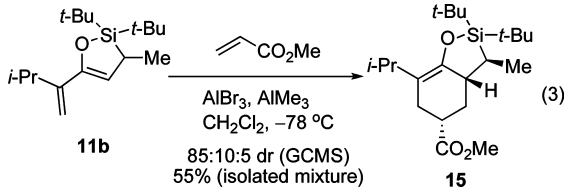
The silyloxy diene obtained by silylene transfer to a divinyl ketone participated in a thermal Diels–Alder cycloaddition with high diastereoselectivity and chemoselectivity (Scheme 1). Silylene transfer to **10**, for example, produced diene **11b** along with small amounts (7%) of its regioisomer **11a**. Heating this mixture with diethyl fumarate produced cycloadduct **14**, which is the result of cycloaddition with regioisomer **11b**. The

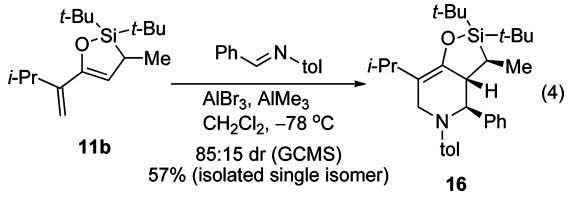
Scheme 1. Synthesis of Cycloadduct



cycloadduct showed both high endo-selectivity and a high π-facial preference in which the dienophile approached the diene from the face opposite to the methyl substituent of the silyloxy diene **11b**. No cycloadducts were observed from regioisomer **11a**, presumably due to the high energy of the *s*-cis conformation that is necessary for cycloaddition.[23]

The highly substituted silyloxy diene also engaged in Diels–Alder cycloadditions with other π-systems. Although other Lewis acids decomposed the diene, the use of $AlBr_3$ with $AlMe_3$ acting as a proton scavenger and desiccant[24] promoted Diels–Alder cycloadditions with a variety of dienophiles (eqs 3 and 4).





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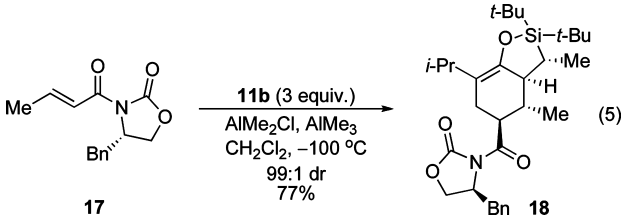
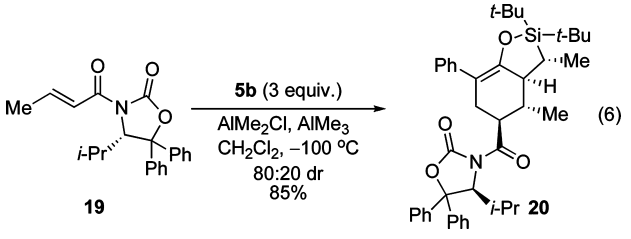
The cyclic silyloxy dienes also could be used for the synthesis of enantiomerically enriched cyclohexenes. We considered that the high π-facial selectivity of the silyloxy diene could be combined with the high facial selectivity of a chiral *N*-acyloxazolidinone[25] to enable a Diels–Alder/kinetic resolution reaction.[26,27] Upon treatment with an excess of a chiral, nonracemic dienophile, the enantiomer of the silyloxy diene with a stereochemical preference matched to the dienophile should react to form a nonracemic cycloadduct with high diastereoselectivity, leaving behind the opposite enantiomer of the diene. Treating chiral dienophile **17** with an excess (3 equiv) of silyloxy diene **11b** allowed for selective cycloaddition to one enantiomer of the racemic diene, affording cycloadduct **18** with 99:1 diastereoselectivity (eq 5). Because of the high



sensitivity of the silyloxy diene **11b** to even mild acids, such as silica gel, the selectivity with respect to this component could not be determined. ^{1}H NOE spectroscopic correlation revealed that cycloadduct **18** was the endo-product, but the relative configuration of the auxiliary to the cyclohexene ring could not be determined. The chiral, nonracemic dienophile[28] **19** kinetically resolved the phenyl-substituted silyloxy diene **5b** (albeit with lower selectivity). The cycloadduct **20**, however, was crystalline, so its configuration was determined by X-ray crystallography (eq 6). The relative configuration of this



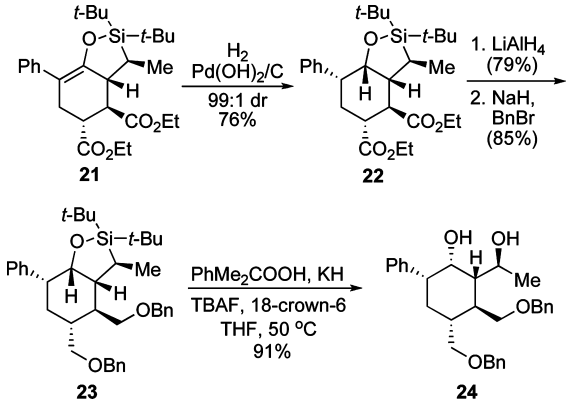
product was used to assign the three-dimensional structure of cycloadduct **18**. This kinetic resolution is an example of double stereoinduction[29,30] for which there are few examples using the Diels–Alder cycloaddition.[26,29]

Further functionalization of the Diels–Alder adducts demonstrates the utility of these silyloxy dienes (Scheme 2). Hydrogenation of cycloadduct **21**, formed in 62% from divinyl ketone **4** in a one-flask synthesis as a single diastereomer after purification, established two new stereocenters diastereoselectively. Oxidation[31,32] of intermediate **23** produced diol **24** containing six contiguous stereocenters. The synthesis of highly substituted cyclohexanes[33] is important for the preparation of natural products.[34–37]

CONCLUSION

Silylene transfer to divinyl ketones afforded silyloxy dienes regioselectively. Subsequent Diels–Alder cycloadditions of these silyloxy dienes afforded cyclohexene products chemo- and diastereoselectively. In addition, treatment with chiral dienophiles afforded enantioenriched cyclohexenes. Further

Scheme 2. Functionalization of Cycloadducts



functionalization of these cycloadducts led to cyclohexanes containing multiple contiguous stereocenters.

EXPERIMENTAL SECTION

(*E*)-2-Methylhexa-1,4-dien-3-one (2). Representative Procedure for the Synthesis of Divinyl Ketones. To a solution of isopropenyl magnesium bromide (100 mL, 0.5 M, 50 mmol) in THF cooled to 0 °C was added crotonaldehyde (4.54 mL, 55.0 mmol) dropwise. The mixture was allowed to warm to rt and stir overnight. To the mixture was added a saturated aqueous solution of NH_4Cl (50.0 mL), and the layers were allowed to separate. The aqueous layer was extracted with 3 × 15 mL of ether. The organic layers were combined, washed with brine (15 mL), and dried over $MgSO_4$. The mixture was filtered and concentrated in vacuo. The resulting residue was diluted with CH_2Cl_2 (250 mL), and activated MnO_2 (43.4 g, 500 mmol) was added. The slurry was allowed to stir at rt for 7 days. The slurry was filtered over a layer of Celite on top of a layer of SiO_2, and the filtrate was concentrated in vacuo to afford a yellow oil. The oil was purified by flash chromatography (10:90 ether/pentane) to afford (*E*)-2-methylhexa-1,4-dien-3-one (3.024 g, 55%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (dq, J = 15.3, 6.9 Hz, 1H), 6.67 (d, J = 15.3 Hz, 1H), 5.91 (s, 1H), 5.76 (s, 1H), 1.93 (dd, J = 1.6, 0.8 Hz, 3H), 1.91 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 145.3, 143.6, 126.8, 124.4, 18.6, 18.2; IR (thin film) 2971, 1668, 1622, 1446, 1348, 966 cm^{-1}; HRMS (ESI) m/z calcd for $C_7H_{11}O$ (M + H)$^+$ 111.0810, found 111.0813.

(*E*)-2-Phenylhexa-1,4-dien-3-one (4). The representative procedure for the synthesis of divinyl ketones was followed using a Grignard prepared from α-bromostyrene (91.0 mL, 0.3 M, 30 mmol), crotonaldehyde (2.47 mL, 30.0 mmol), and MnO_2 (23.7 g, 273 mmol) to afford (*E*)-2-phenylhexa-1,4-dien-3-one (2.34 g, 50%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 5H), 7.03 (dq, J = 15.4, 6.9 Hz, 1H), 6.52 (dq, J = 15.4, 1.6 Hz, 1H), 5.93 (q, J = 0.7 Hz, 2H), 1.95 (dd, J = 6.9, 1.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 149.3, 145.7, 137.2, 129.9, 128.5, 128.3, 127.8, 122.0, 18.5; IR (thin film) 3057, 1884, 1670, 1621, 1443, 937 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{13}O$ (M + H)$^+$ 173.0966, found 173.0966.

(*E*)-4-Methyl-1-phenylpenta-1,4-dien-3-one (6). The representative procedure for the synthesis of divinyl ketones was followed using isopropenyl magnesium bromide (100 mL, 0.5 M, 50 mmol), cinnamaldehyde (6.29 mL, 50 mmol), and MnO_2 (43.4 g, 500 mmol) to afford (*E*)-4-methyl-1-phenylpenta-1,4-dien-3-one (8.13 g, 95%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 15.7 Hz, 1H), 7.58 (dt, J = 5.4, 3.4 Hz, 2H), 7.42–7.36 (m, 3H), 7.30 (d, J = 15.6 Hz, 1H), 6.04 (s, 1H), 5.84 (d, J = 0.9 Hz, 1H), 2.02–1.98 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 145.8, 143.8, 135.2, 130.5, 129.1, 128.5, 124.5, 121.6, 18.4. ^{1}H NMR and ^{13}C NMR spectroscopic data match those previously reported.[38]

(*E*)-2,6-Dimethylhepta-1,4-dien-3-one (8). The representative procedure for the synthesis of divinyl ketone was followed using isopropenyl magnesium bromide (25.0 mL, 0.5 M, 13 mmol), (*E*)-4-

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methylpent-2-enal (1.45 mL, 12.5 mmol), and MnO_2 (10.9 g, 125 mmol) to afford (*E*)-2,6-dimethylhepta-1,4-dien-3-one (0.88 g, 51%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (dd, J = 15.5, 6.8 Hz, 1H), 6.58 (dd, J = 15.5, 1.2 Hz, 1H), 5.91 (d, J = 0.5 Hz, 1H), 5.78−5.74 (m, 1H), 2.54−2.43 (m, 1H), 1.93 (s, 3H), 1.09 (dd, J = 6.8, 2.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 154.6, 145.5, 124.3, 122.3, 31.5, 21.6, 18.3; IR (thin film) 2962, 1668, 1622, 1359, 1083, 984 cm^{-1}; HRMS (ESI) m/z calcd for $C_9H_{14}NaO$ $(M + Na)^+$ 161.0942, found 161.0940. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.98; H, 10.50.

(*E*)-6-Methyl-5-methylenehept-2-en-4-one (10). The representative procedure for the synthesis of divinyl ketone was followed using propenyl magnesium bromide (100.0 mL, 0.5 M, 50 mmol), 3-methyl-2-methylenebutanal (7.01 g, 50.0 mmol) prepared using the method described by Breit,[39] and MnO_2 (43.5 g, 500 mmol) to afford 6-methyl-5-methylenehept-2-en-4-one (3.17 g, 46%) as a 2:1 *E*/*Z* mixture of isomers that were separated by flash chromatography. Spectroscopic data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (dq, J = 15.3, 6.9 Hz, 1H), 6.57 (dq, J = 15.3, 1.5 Hz, 1H), 5.80 (s, 1H), 5.63 (d, J = 1.2 Hz, 1H), 3.00−2.87 (m, 1H), 1.94−1.89 (m, 3H), 1.05 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 156.7, 141.7, 126.2, 121.1, 27.9, 21.9, 15.9; IR (thin film) 2964, 1668, 1622, 1444, 1292, 939 cm^{-1}; HRMS (ESI) m/z calcd for $C_9H_{14}NaO$ $(M + Na)^+$ 161.0942, found 161.0937. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.24; H, 10.26.

(2*E*,5*E*)-3-Methylhepta-2,5-dien-4-one (*E*-12) and (2*E*,5*Z*)-3-Methylhepta-2,5-dien-4-one (*Z*-12). The representative procedure for the synthesis of divinyl ketone was followed using propenyl magnesium bromide (50.0 mL, 0.5 M, 25 mmol), tiglic aldehyde (2.42 mL, 25 mmol), and MnO_2 (21.7 g, 250 mmol) to afford 3-methylhepta-2,5-dien-4-one (1.92 g, 62%) as a 1:1 *E*/*Z* mixture of isomers that were separated by flash chromatography. Spectroscopic data for *E* isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (dq, J = 15.2, 6.8 Hz, 1H), 6.74−6.69 (m, 1H), 6.67 (dq, J = 15.2, 1.6 Hz, 1H), 1.91 (dd, J = 6.8, 1.6 Hz, 3H), 1.87 (dq, J = 6.9, 1.1 Hz, 3H), 1.84 (qn, J = 1.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 142.3, 139.0, 137.4, 127.0, 18.6, 15.0, 11.7; IR (thin film) 2918, 1666, 1444, 1296, 1080, 966 cm^{-1}; HRMS (ES) m/z calcd for $C_8H_{12}NaO$ $(M + Na)^+$ 147.0786; found, 147.0782. Spectroscopic data for *Z* isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (qq, J = 6.9, 1.4 Hz, 1H), 6.47 (dq, J = 11.7, 1.8 Hz, 1H), 6.16 (dq, J = 11.7, 7.2 Hz, 1H), 1.97 (dd, J = 7.2, 1.8 Hz, 3H), 1.87−1.85 (m, 3H), 1.83−1.82 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.9, 140.0, 139.8, 138.5, 126.1, 16.0, 15.0, 11.1; IR (thin film) 2927, 1664, 1444, 1296, 1080, 966 cm^{-1}; HRMS (ESI) m/z calcd for $C_8H_{12}NaO$ $(M + Na)^+$ 147.0786, found 147.0779.

Silyloxy Dienes 3a and 3b. Representative Procedure for Silylene Transfer to Divinyl Ketones for the Synthesis of Silyloxy Dienes. To an NMR tube was added a solution of (*E*)-2-methylhexa-1,4-dien-3-one (**2**) (0.011 g, 0.10 mmol) and AgO_2CCF_3 (0.002 g, 0.01 mmol) in tol-d_8 (0.25 mL). The solution was cooled to −22 °C, and a solution containing cyclohexene silacyclopropane **1** (0.028 g, 0.12 mmol)[40] and $PhSiMe_3$ (internal standard, 0.008 g, 0.05 mmol) in tol-d_8 (0.25 mL), also cooled to −22 °C, was added to the NMR tube. The mixture was allowed to warm to rt. The α/β regioisomeric ratio was found to be 25:75 by ^{1}H NMR spectroscopy, and the yield was determined by ^{1}H NMR spectroscopy to be 100% relative to the internal standard. Representative peaks for the α-regioisomer (**3a**): ^{1}H NMR (400 MHz, tol-d_8) δ 6.33−6.25 (m, 1H), 6.22 (d, J = 12.0 Hz, 1H), 1.74 (s, 3H), 1.70 (d, J = 6.5 Hz, 3H), 1.05 (s, 18H). Representative peaks for the β-regioisomer (**3b**): ^{1}H NMR (400 MHz, tol-d_8) δ 5.81 (d, J = 1.9 Hz, 1H), 5.08 (d, J = 3.2 Hz, 1H), 5.01 (s, 1H), 2.13 (qd, J = 7.7, 3.3 Hz, 1H), 1.82 (s, 3H), 1.11 (s, 9H), 1.04 (s, 9H).

Silyloxy Dienes 5a and 5b. The representative procedure for the silylene transfer to divinyl ketones was followed using (*E*)-2-phenylhexa-1,4-dien-3-one (**4**) (0.017 g, 0.10 mmol). The α/β regioisomeric ratio was found to be 27:73 by ^{1}H NMR spectroscopy, and the yield was determined by ^{1}H NMR spectroscopy to be 100% relative to the internal standard. Representative peaks for the α-regioisomer (**5a**): ^{1}H NMR (500 MHz, tol-d_8) δ 6.43−6.30 (m, 1H), 6.23 (dq, J = 15.5, 1.5 Hz, 1H), 1.06 (s, 18H). Representative peaks for the β-regioisomer (**5b**): ^{1}H NMR (500 MHz, tol-d_8) δ 5.94−5.89 (m, 1H), 5.16 (ddd, J = 2.4, 1.1, 0.7 Hz, 1H), 4.99 (d, J = 3.3 Hz, 1H), 1.12 (s, 9H), 1.05 (s, 9H).

Silyloxy Dienes 7a and 7b. The representative procedure for the silylene transfer to divinyl ketones was followed using (*E*)-4-methyl-1-phenylpenta-1,4-dien-3-one (**6**) (0.017 g, 0.10 mmol). The α/β regioisomeric ratio was found to be 26:74 by ^{1}H NMR spectroscopy, and the yield was determined by ^{1}H NMR spectroscopy to be 97% relative to the internal standard. Representative peaks for the α-regioisomer (**7a**): ^{1}H NMR (500 MHz, tol-d_8) δ 2.09 (qn, J = 2.2 Hz, 1H), 1.05 (s, 18H). Representative peaks for the β-regioisomer (**7b**): ^{1}H NMR (500 MHz, tol-d_8) δ 5.79 (t, J = 1.5 Hz, 1H), 5.28 (d, J = 3.2 Hz, 1H), 5.01 (s, 1H), 3.59 (d, J = 3.0 Hz, 1H), 1.88 (s, 3H), 1.11 (s, 9H), 0.82 (s, 9H).

Silyloxy Dienes 9a and 9b. The representative procedure for the silylene transfer to divinyl ketones was followed using (*E*)-2,6-dimethylhepta-1,4-dien-3-one (**8**) (0.014 g, 0.10 mmol). The α/β regioisomeric ratio was found to be 37:63 by ^{1}H NMR spectroscopy, and the yield was determined by ^{1}H NMR spectroscopy to be 88% relative to the internal standard. Representative peaks for the α-regioisomer (**9a**): ^{1}H NMR (400 MHz, tol-d_8) δ 6.37 (dd, J = 15.2, 6.7 Hz, 1H), 6.24 (d, J = 15.2 Hz, 1H), 1.77 (s, 3H), 1.08 (s, 18H). Representative peaks for the β-regioisomer (**9b**): ^{1}H NMR (400 MHz, tol-d_8) δ 5.81 (dd, J = 1.8, 0.8 Hz, 1H), 5.33 (d, J = 2.9 Hz, 1H), 5.01 (d, J = 0.7 Hz, 1H), 2.33 (dq, J = 13.6, 6.8 Hz, 1H), 1.83 (s, 3H), 1.14 (s, 9H), 1.04 (s, 9H).

Silyloxy Dienes 11a and 11b. The representative procedure for the silylene transfer to divinyl ketones was followed using 6-methyl-5-methylenehept-2-en-4-one (**10**) (0.014 g, 0.10 mmol). The α/β regioisomeric ratio was found to be 15:85 by ^{1}H NMR spectroscopy, and the yield was determined by ^{1}H NMR spectroscopy to be 100% relative to the internal standard. Representative peaks for the α-regioisomer (**11a**): ^{1}H NMR (500 MHz, tol-d_8) δ 6.39−6.25 (m, 1H), 6.23 (d, J = 15.3 Hz, 1H), 2.81 (sept, J = 6.8 Hz, 1H), 1.70 (d, J = 6.2 Hz, 3H), 1.04 (s, 18H). Representative peaks for the β-regioisomer (**11b**): ^{1}H NMR (500 MHz, tol-d_8) δ 5.76 (s, 1H), 5.11 (d, J = 3.2 Hz, 1H), 5.02 (s, 1H), 2.60−2.50 (m, 1H), 1.09 (s, 9H), 1.02 (s, 9H).

Silyloxy Dienes 11a and 11b. To a solution of 6-methyl-5-methylenehept-2-en-4-one (**10**) (0.014 g, 0.10 mmol) and AgO_2CCF_3 (0.002 g, 0.01 mmol) in THF (0.25 mL) cooled to −78 °C was added a solution containing cyclohexene silacyclopropane **1** (0.028 g, 0.12 mmol) and $PhSiMe_3$ (internal standard, 0.008 g, 0.05 mmol) in THF (0.25 mL). The mixture was allowed to warm slowly to rt over 5 h. The THF was removed in vacuo, and the resulting residue was dissolved in C_6D_6 for ^{1}H NMR spectroscopic analysis. The α/β regioisomeric ratio was found to be 7:93 by ^{1}H NMR spectroscopy, and the yield was determined by ^{1}H NMR spectroscopy to be 96% relative to the internal standard. Representative peaks matched those above.

Silyloxy Dienes 13a and *E*-13b. The representative procedure for silylene transfer to divinyl ketones was followed using (2*E*,5*E*)-3-methylhepta-2,5-dien-4-one (*E*-**12**) (0.012 g, 0.10 mmol) at rt. The **13a**/*E*-**13b** regioisomeric ratio was found to be 77:23 by ^{1}H NMR spectroscopy, and the yield was determined by ^{1}H NMR spectroscopy to be 93% relative to the internal standard. Representative peaks for oxasilacyclopentene **13a**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.35 (q, J = 7.0 Hz, 1H), 4.98 (d, J = 3.2 Hz, 1H), 1.27 (d, J = 7.7 Hz, 3H), 1.10 (s, 9H), 1.03 (s, 9H). Representative peaks for oxasilacyclopentene *E*-**13b**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.38−6.29 (m, 1H), 6.23 (dd, J = 15.0, 1.4 Hz, 1H), 2.20−2.12 (m, 1H), 1.71 (d, J = 6.6 Hz, 3H), 1.13 (s, 9H), 1.05 (s, 9H).

Oxasilacyclopentenes 13a and *Z*-13b. The representative procedure for silylene transfer to divinyl ketones was followed using (2*E*,5*Z*)-3-methylhepta-2,5-dien-4-one (*Z*-**12**) (0.012 g, 0.10 mmol) at rt. The **13a**/*Z*-**13b** regioisomeric ratio was found to be 9:91 by ^{1}H NMR spectroscopy, and the yield was determined by ^{1}H NMR spectroscopy to be 71% relative to the internal standard. Representative peaks for oxasilacyclopentene **13a** are the same as above. Representative peaks for oxasilacyclopentene *Z*-**13b**: ^{1}H NMR

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(400 MHz, C_6D_6) δ 6.01−5.97 (m, 1H), 5.47 (dqq, J = 11.7, 7.2, 0.5 Hz, 1H), 1.61−1.60 (m, 3H), 1.08 (s, 9H), 1.00 (s, 9H).

Cycloadduct 14. To AgO_2CCF_3 (0.079 g, 0.36 mmol) was added a solution of (*E*)-6-methyl-5-methylenehept-2-en-4-one (**10**) (0.500 g, 3.62 mmol) in THF (9.0 mL), and the mixture was cooled to −78 °C. A solution of cyclohexene silacyclopropane **1** (0.898 g, 4.00 mmol) in THF (9.0 mL) was added, and the mixture was allowed to warm to room temperature. The solvent was removed in vacuo, and the residue was diluted with toluene (18.0 mL). Diethyl fumarate (2.16 mL, 10.8 mmol) was added, and the mixture was heated to 100 °C for 3 days. The mixture was cooled to rt and concentrated in vacuo to afford a brown oil. GCMS analysis of the unpurified reaction mixture revealed that two diastereomers were formed (97:3 dr). The oil was purified by flash chromatography (20:80 EtOAc/hexanes) to afford a yellow oil (1.076 g, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23−4.05 (m, 4H), 3.08 (sept, J = 7.1 Hz, 1H), 2.86 (td, J = 11.4, 5.8 Hz, 1H), 2.51 (dd, J = 16.8, 5.9 Hz, 1H), 2.47−2.40 (m, 1H), 2.34 (ddd, J = 16.3, 5.8, 1.8 Hz, 1H), 2.15−2.05 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.28−1.22 (m, 4H), 1.16 (d, J = 7.1 Hz, 3H), 1.08 (s, 9H), 1.00 (s, 9H), 0.97 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 174.7, 147.1, 112.0, 60.9, 60.7, 50.6, 47.6, 44.3, 28.0, 27.9, 26.5, 25.8, 22.6, 21.5, 21.2, 21.1, 20.4, 14.4, 14.3, 13.7; IR (thin film) 2964, 2862, 1728, 1647, 1471, 1300 cm^{-1}; HRMS (ESI) m/z calcd for $C_{25}H_{44}NaO_5Si$ (M + Na)$^+$ 475.2856, found 475.2850. Anal. Calcd for $C_{25}H_{44}O_5Si$: C, 66.33; H, 9.80. Found: C, 66.44; H, 9.89.

Cycloadduct 15. To silyloxy diene **11b** (0.028 g, 0.10 mmol) and methyl acrylate (0.027 mL, 0.30 mmol), diluted with CH_2Cl_2 (1.0 mL) and cooled to −78 °C, was added $AlMe_3$ (0.015 mL, 2.0 M, 0.030 mmol). The mixture was allowed to stir for 5 min. $AlBr_3$ (0.15 mL, 1.0 M, 0.15 mmol) was added, and the mixture was allowed to warm to −45 °C and stir for 2 h. Pyridine (1.0 mL) was added, and the mixture was allowed to warm to rt. The resulting slurry was filtered through a pad of SiO_2. GCMS analysis of the filtrate showed a mixture of diastereomers (85:10:5 dr). The filtrate was concentrated in vacuo, and the resulting residue was purified by flash chromatography (10:90 EtOAc/hexanes) to afford a colorless oil (0.020 g, 55%) as an inseparable mixture of diastereomers. Representative peaks for the major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.09 (sept, J = 7.0 Hz, 1H), 2.53 (tdd, J = 12.0, 5.6, 2.6 Hz, 1H), 2.46−2.35 (m, 1H), 2.27−2.08 (m, 3H), 1.26−1.22 (m, 1H), 1.24 (d, J = 7.4 Hz, 3H), 1.08 (s, 9H), 1.00 (s, 9H), 0.97 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 148.7, 111.9, 51.9, 45.0, 40.4, 33.1, 28.0, 26.4, 25.5, 24.1, 23.9, 21.6, 21.1, 20.6, 13.3; IR (thin film) 2957, 2860, 1739, 1471, 1165, 824 cm^{-1}; HRMS (ESI) m/z calcd for $C_{21}H_{38}NaO_3Si$ (M + Na)$^+$ 389.2488, found 389.2488. Anal. Calcd for $C_{21}H_{38}O_3Si$: C, 68.80; H, 10.45. Found: C, 69.01; H, 10.55.

Cycloadduct 16. To silyloxy diene **11b** (0.028 g, 0.10 mmol) was added (*E*)-*N*-benzylidene-4-methylaniline (0.060 g, 0.30 mmol). The mixture was diluted with CH_2Cl_2 (1.0 mL) and cooled to −78 °C. $AlMe_3$ (0.015 mL, 2.0 M, 0.030 mmol) was added, and the mixture was allowed to stir for 5 min. $AlBr_3$ (0.15 mL, 1.0 M, 0.15 mmol) was added, and the mixture was allowed to warm to rt over 16 h. Pyridine (1.0 mL) was added, and the resulting slurry was filtered through a pad of SiO_2. GCMS analysis of the filtrate showed a mixture of diastereomers (85:15 dr). The filtrate was concentrated in vacuo, and the resulting residue was purified by flash chromatography (10:90 EtOAc/hexanes) to afford a colorless solid (0.027 g, 57%) as a single diastereomer. The minor diastereomer is presumed unstable to chromatography conditions. Characteristic data for major diastereomer: mp 163−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.21 (m, 2H), 7.12 (dd, J = 10.1, 4.6 Hz, 2H), 7.05 (ddd, J = 7.4, 3.7, 1.3 Hz, 1H), 6.93−6.84 (m, 4H), 3.91 (d, J = 8.0 Hz, 1H), 3.69 (dd, J = 15.2, 2.2 Hz, 1H), 3.46 (dd, J = 15.2, 3.2 Hz, 1H), 3.07 (sept, J = 6.9 Hz, 1H), 2.69 (ddt, J = 10.9, 8.0, 2.6 Hz, 1H), 2.15 (s, 3H), 1.30−1.18 (m, 1H), 1.07 (s, 9H), 1.06 (d, J = 8.0 Hz, 3H), 1.04 (s, 9H), 0.99 (d, J = 7.1 Hz, 3H), 0.43 (d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 148.1, 142.3, 132.6, 129.3, 129.2, 128.1, 127.0, 125.3, 112.2, 70.6, 54.8, 52.5, 28.1, 26.3, 21.6, 21.3, 21.2, 21.0, 20.5, 13.9; IR (thin film) 2958, 2933, 2859, 1511, 1472, 1153 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{46}NOSi$ (M + H)$^+$ 476.3349, found 476.3350.

Cycloadduct 18. To AgO_2CCF_3 (0.066 g, 0.30 mmol) was added a solution of (*E*)-6-methyl-5-methylenehept-2-en-4-one (**10**) (0.415 g, 3.00 mmol) in CH_2Cl_2 (10.0 mL). The mixture was cooled to −78 °C, and a solution of cyclohexene silacyclopropane **1** (0.842, 3.75 mmol) in CH_2Cl_2 (5.0 mL) was added dropwise. The mixture was allowed to warm to rt and transferred to a flask containing (*S*,*E*)-4-benzyl-3-but-2-enoyloxazolidin-2-one (0.245 g, 1.00 mmol). The mixture was cooled to −100 °C, and $AlMe_3$ (0.50 mL, 2.0 M, 1.0 mmol) was added. The mixture was allowed to stir for 5 min, and $AlMe_2Cl$ (1.50 mL, 1.0 M, 1.5 mmol) was added. The mixture was allowed to warm slowly to rt over 18 h, then was treated with a saturated aqueous solution of sodium potassium tartrate (20.0 mL). The mixture was extracted with 3 × 10 mL of CH_2Cl_2. The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to afford a yellow oil. GCMS analysis of the oil showed a mixture of diastereomers (99:1 dr). The oil was purified by flash chromatography (20:80 EtOAc/hexanes) to afford a colorless solid (0.405 g, 77%): mp 60−62 °C; $[\alpha]_D^{25}$ + 114° (c 1.00, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.19 (m, 5H), 4.78 (td, J = 7.1, 3.7 Hz, 1H), 4.30−4.13 (m, 2H), 3.84 (td, J = 10.6, 5.7 Hz, 1H), 3.29 (dd, J = 13.3, 2.8 Hz, 1H), 3.15 (dt, J = 13.8, 6.9 Hz, 1H), 2.88 (dd, J = 13.3, 9.3 Hz, 1H), 2.36 (dd, J = 15.1, 5.0 Hz, 1H), 2.20−2.13 (m, 1H), 2.08 (d, J = 8.3 Hz, 1H), 1.99 (dt, J = 16.0, 8.2 Hz, 1H), 1.44 (d, J = 7.4 Hz, 3H), 1.37−1.20 (m, 1H), 1.15 (s, 12H), 1.06 (s, 9H), 1.03 (d, J = 6.8 Hz, 3H), 0.98 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 153.2, 148.0, 135.4, 129.6, 129.4, 129.0, 127.4, 111.6, 66.1, 55.3, 51.0, 45.8, 40.2, 38.1, 28.1, 27.9, 27.2, 26.7, 26.4, 23.0, 21.4, 20.9, 19.2, 16.3; IR (thin film) 2937, 2860, 1782, 1697, 1471, 1389 cm^{-1}; HRMS (ESI) m/z calcd for $C_{31}H_{47}NNaO_4Si$ (M + Na)$^+$ 548.3172, found 548.3165. Anal. Calcd for $C_{31}H_{47}NO_4Si$: C, 70.81; H, 9.01. Found: C, 70.58; H, 9.11.

Cycloadduct 20. To AgO_2CCF_3 (0.066 g, 0.30 mmol) was added a solution of (*E*)-2-phenylhexa-1,4-dien-3-one (**4**) (0.517 g, 3.00 mmol) in CH_2Cl_2 (10.0 mL). The mixture was cooled to −78 °C, and a solution of cyclohexene silacyclopropane **1** (0.842, 3.75 mmol) in CH_2Cl_2 (5.0 mL) was added dropwise. The mixture was allowed to warm to rt and transferred to a flask containing (*S*,*E*)-3-but-2-enoyl-4-isopropyl-5,5-diphenyloxazolidin-2-one[28] (0.349 g, 1.00 mmol). The mixture was cooled to −100 °C, and $AlMe_3$ (0.50 mL, 2.0 M, 1.0 mmol) was added. The mixture was allowed to stir for 5 min, and $AlMe_2Cl$ (1.50 mL, 1.0 M, 1.5 mmol) was added. The mixture was allowed to warm slowly to rt over 18 h, and then, it was treated with a saturated aqueous solution of sodium potassium tartrate (20.0 mL). The mixture was extracted with 3 × 10 mL of CH_2Cl_2. The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to afford a yellow oil. GCMS analysis of the oil showed two diastereomers (80:20 dr). The oil was purified by flash chromatography (20:80 EtOAc/hexanes) to afford a colorless solid (0.564 g, 77%) as a mixture of diastereomers. A small amount (0.060 g) of the major diastereomer was isolated by flash chromatography for the purpose of X-ray crystallographic analysis. Characteristic data for the major diastereomer: $[\alpha]_D^{25}$ − 18.8° (c 1.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67−6.98 (m, 15H), 5.47 (d, J = 3.6 Hz, 1H), 3.89 (td, J = 10.5, 5.8 Hz, 1H), 2.83−2.74 (m, 1H), 2.70 (dd, J = 15.3, 5.5 Hz, 1H), 2.16 (t, J = 10.0 Hz, 1H), 2.09−1.91 (m, 2H), 1.33 (d, J = 7.4 Hz, 3H), 1.29−1.21 (m, 1H), 1.10 (s, 9H), 0.90 (s, 9H), 0.86 (d, J = 7.0 Hz, 3H), 0.75 (d, J = 6.9 Hz, 3H), 0.59 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 152.9, 152.8, 142.6, 139.9, 138.0, 129.0, 128.9, 128.6, 128.5, 128.1, 127.5, 127.3, 127.2, 125.9, 125.7, 125.1, 106.1, 89.3, 64.9, 52.3, 45.7, 40.0, 32.4, 29.9, 28.6, 28.1, 28.0, 27.7, 27.6, 22.2, 21.8, 21.4, 21.0, 18.2, 16.5. Characteristic data for the mixture of diastereomers: mp 123−125 °C; IR (thin film) 2962, 2933, 1786, 1701, 1209, 1173 cm^{-1}; HRMS (ESI) m/z calcd for $C_{42}H_{53}NNaO_4Si$ (M + Na)$^+$ 686.3641, found 686.3657. Anal. Calcd for $C_{42}H_{53}NO_4Si$: C, 75.98; H, 8.05. Found: C, 76.08; H, 8.10.

Cycloadduct 21. To AgO_2CCF_3 (0.027 g, 0.12 mmol) was added a solution of (*E*)-2-phenylhexa-1,4-dien-3-one (**4**) (0.211 g, 1.22 mmol) in toluene (2.4 mL). The mixture was cooled to −22 °C, and a solution of cyclohexene silacyclopropane **1** (0.322 g, 1.44 mmol) in

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toluene (2.4 mL) was added. The mixture was allowed to warm to room temperature. Diethyl fumarate (0.59 mL, 3.6 mmol) was added, and the mixture was heated to 100 °C for 3 days. The mixture was concentrated in vacuo to afford a brown oil. GCMS analysis of the oil showed a mixture of diastereomers (90:10 dr). The oil was purified by flash chromatography (20:80 EtOAc/hexanes) to afford a colorless solid (0.368 g, 62%) as a single diastereomer: mp 90−92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67−7.62 (m, 2H), 7.29 (t, J = 7.8 Hz, 2H), 7.15 (dd, J = 10.6, 4.1 Hz, 1H), 4.28−4.09 (m, 4H), 3.06 (ddd, J = 11.1, 9.8, 7.5 Hz, 1H), 2.83−2.76 (m, 1H), 2.75−2.71 (m, 2H), 2.65 (t, J = 10.7 Hz, 1H), 1.40−1.33 (m, 1H), 1.32 (dd, J = 7.6, 6.8 Hz, 3H), 1.26 (dd, J = 7.6, 6.7 Hz, 3H), 1.22 (d, J = 7.4 Hz, 3H), 1.14 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 174.1, 151.7, 139.2, 127.8, 127.5, 125.6, 105.9, 61.0, 60.9, 50.4, 48.9, 44.5, 31.1, 28.0, 27.7, 21.9, 21.6, 21.1, 14.4, 14.3, 13.6; IR (thin film) 2935, 2860, 1738, 1659, 1471, 1171 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{42}NaO_5Si$ (M + Na)$^+$ 509.2699, found 509.2691. Anal. Calcd for $C_{28}H_{42}O_5Si$: C, 69.10; H, 8.70. Found: C, 68.94; H, 8.70.

Cyclohexane 22. Cycloadduct **21** (0.100 g, 0.21 mmol) was diluted with EtOH (9.5 mL). $Pd(OH)_2/C$ (0.029 g, 0.040 mmol) was added, and the suspension was sparged with H_2 for 15 min. The suspension was allowed to stir for 18 h under 1 atm of H_2. The reaction mixture was filtered through a pad of SiO_2, and the filtrate was concentrated in vacuo to afford a yellow oil. GCMS analysis of the oil showed a mixture of diastereomers (99:1 dr). The oil was purified by flash chromatography (20:80 EtOAc/hexanes) to afford a colorless solid (0.078 g, 76%): mp 93−95 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.30−7.17 (m, 3H), 4.35 (t, J = 3.2 Hz, 1H), 4.27−4.21 (m, 1H), 4.19−4.03 (m, 3H), 2.92 (t, J = 11.6 Hz, 1H), 2.81 (dt, J = 13.1, 3.1 Hz, 1H), 2.76 (td, J = 11.9, 3.2 Hz, 1H), 2.07 (q, J = 12.8 Hz, 1H), 1.93 (dt, J = 8.1, 3.8 Hz, 2H), 1.59 (q, J = 8.0 Hz, 1H), 1.29 (td, J = 7.1, 0.7 Hz, 3H), 1.26 (d, J = 8.1 Hz, 3H), 1.22 (td, J = 7.1, 0.8 Hz, 3H), 1.13 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 174.2, 143.3, 128.5, 128.0, 126.4, 76.7, 60.8, 60.7, 51.9, 46.9, 46.1, 45.6, 29.4, 29.3, 28.0, 23.4, 23.2, 20.4, 17.7, 14.5, 14.3; IR (thin film) 2937, 2860, 1736, 1475, 1250, 1180 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{44}NaO_5Si$ (M + Na)$^+$ 511.2856, found 511.2864. Anal. Calcd for $C_{28}H_{44}O_5Si$: C, 68.81; H, 9.07. Found: C, 69.02; H, 9.17.

Cyclohexane 23. To a slurry of $LiAlH_4$ (0.075 g, 2.0 mmol) in THF (5.0 mL) cooled to 0 °C was added a solution of cyclohexane **22** (0.485 g, 0.990 mmol) in THF (5.0 mL). The mixture was allowed to stir at 0 °C for 2 h. To the mixture was added a saturated aqueous solution of sodium potassium tartrate (10.0 mL), and the mixture was allowed to warm to rt. The layers were separated, and the aqueous layer was extracted with 3 × 5 mL of ether. The organic layers were combined, washed with brine (5 mL), dried over $MgSO_4$, and concentrated in vacuo to afford an oil. The oil was purified by flash chromatography (40:60 EtOAc/hexanes) to afford the diol as a colorless solid (0.316 g, 79%): mp 125−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.18 (m, 5H), 4.46 (br s, 2H), 4.32 (t, J = 3.4 Hz, 1H), 3.91 (d, J = 10.9 Hz, 1H), 3.69 (dd, J = 10.9, 2.0 Hz, 1H), 3.59 (qn, J = 5.4 Hz, 2H), 2.78−2.74 (m, 1H), 1.83 (q, J = 12.2 Hz, 1H), 1.62−1.61 (m, 2H), 1.51 (d, J = 12.4 Hz, 1H), 1.45 (dd, J = 10.8, 4.3 Hz, 1H), 1.37 (s, 3H), 1.32−1.25 (m, 1H), 1.11 (s, 9H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 128.4, 127.8, 126.0, 77.6, 68.0, 64.4, 51.1, 47.5, 45.5, 44.7, 29.4, 29.3, 28.9, 24.7, 23.3, 20.3, 18.7; IR (thin film) 3317, 2860, 1471, 1363, 1055, 821 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{40}NaO_3Si$ (M + Na)$^+$ 427.2644, found 427.2649. Anal. Calcd for $C_{24}H_{40}O_3Si$: C, 71.23; H, 9.96. Found: C, 71.10; H, 10.14.

NaH (0.054 g, 2.2 mmol) in THF (1.0 mL) cooled to 0 °C was added a solution of the diol prepared above (0.301 g, 0.74 mmol) in THF (0.5 mL) dropwise. The mixture was allowed to stir at 0 °C for 10 min, then benzyl bromide (0.27 mL, 2.2 mmol) was added. The mixture was allowed to warm to rt and stir for 3 days. The mixture was poured into a separatory funnel containing water (10 mL), which was extracted with 3 × 5 mL of ether. The organic layers were combined, washed with brine (5 mL), dried over $MgSO_4$, and concentrated in vacuo to afford a cloudy oil. The oil was purified by flash chromatography (10:90 EtOAc/hexanes) to afford a colorless oil (0.368 g, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.18 (m, 15H), 4.55−4.44 (m, 4H), 4.38−4.34 (m, 1H), 3.62 (ddd, J = 9.2, 4.6, 3.0 Hz, 2H), 3.54 (dd, J = 9.6, 3.0 Hz, 1H), 3.48 (dd, J = 9.3, 5.7 Hz, 1H), 2.81 (dd, J = 12.4, 2.9 Hz, 1H), 2.01 (dt, J = 19.5, 9.8 Hz, 2H), 1.90 (dd, J = 11.2, 4.7 Hz, 1H), 1.78 (dd, J = 13.2, 10.3 Hz, 2H), 1.30 (s, 4H), 1.09 (s, 9H), 0.99 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 139.1, 139.0, 138.0, 129.2, 129.0, 128.6, 128.0, 127.8, 127.4, 125.8, 122.2, 78.0, 73.7, 73.4, 72.3, 69.5, 50.7, 47.4, 40.0, 39.7, 33.7, 29.5, 29.3, 24.3, 23.3, 20.4, 18.3; IR (thin film) 3029, 2933, 2860, 1454, 1363, 1097 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{52}NaO_3Si$ (M + Na)$^+$ 607.3583, found 607.3592. Anal. Calcd for $C_{38}H_{52}O_3Si$: C, 78.03; H, 8.96. Found: C, 77.73; H, 8.88.

Diol 24. To KH (0.135 g, 3.36 mmol) in THF (6.0 mL) was added 18-crown-6 (0.888 g, 3.36 mmol), and the slurry was cooled to 0 °C. $PhMe_2COOH$ (0.49 mL, 88%, 3.36 mmol) was added slowly, and the mixture was allowed to warm to rt. Cyclohexane **23** (0.328 g, 0.560 mmol) in THF (6.0 mL) was added, followed by a solution of TBAF (3.36 mL, 1.0 M, 3.4 mmol). The mixture was heated to 50 °C for 24 h. The mixture was allowed to cool to rt and was diluted with saturated aqueous $Na_2S_2O_3$ solution (20 mL). The mixture was extracted with 3 × 10 mL of MTBE. The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo to afford an oil. The oil was purified by flash chromatography (40:60 EtOAc/hexanes) to afford a colorless oil (0.235 g, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.26 (m, 15H), 4.54−4.44 (m, 4H), 4.37 (s, 1H), 3.79 (dd, J = 9.9, 1.5 Hz, 1H), 3.59−3.54 (m, 2H), 3.49 (dd, J = 9.3, 5.6 Hz, 1H), 2.75 (d, J = 12.7 Hz, 1H), 2.19 (dtd, J = 18.3, 6.6, 5.2 Hz, 2H), 2.02−1.95 (m, 1H), 1.85 (d, J = 12.6 Hz, 1H), 1.74 (d, J = 11.6 Hz, 1H), 1.31 (d, J = 5.7 Hz, 4H), 1.06 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 138.8, 138.6, 128.7, 128.51, 128.46, 128.1, 127.9, 127.81, 127.79, 127.6, 126.8, 73.43, 73.39, 73.3, 71.3, 67.6, 67.2, 48.1, 47.1, 38.4, 35.2, 28.8, 27.4; IR (thin film) 3408, 3030, 2864, 1495, 1095, 737 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{36}NaO_4$ (M + Na)$^+$ 483.2511, found 483.2515.

Confirmation of the Structure of Diol 24: Preparation of Its *p*-Nitrobenzaldehyde Acetal. To diol **24** (0.088 g, 0.19 mmol) in benzene (10.0 mL) were added *p*-nitrobenzaldehyde (0.033 g, 0.22 mmol) and *p*-toluenesulfonic acid (0.0008 g, 0.004 mmol). The solution was heated at reflux for 1 h. The mixture was allowed to cool to rt and was treated with a saturated solution of $NaHCO_3$ (10.0 mL). The mixture was extracted with 3 × 5 mL of ether. The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, and concentrated in vacuo to afford an oil. The oil was purified by flash chromatography (20:80 EtOAc/hexanes) to afford the acetal as a pale yellow oil (0.087 g, 77%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 2H), 7.54 (d, J = 8.9 Hz, 2H), 7.37−7.20 (m, 16H), 4.51−4.37 (m, 6H), 3.65−3.57 (m, 2H), 3.55 (dd, J = 9.5, 3.4 Hz, 1H), 3.46 (dd, J = 9.3, 5.7 Hz, 1H), 2.78 (dt, J = 12.7, 2.6 Hz, 1H), 2.23 (t, J = 9.6 Hz, 1H), 2.18 (t, J = 10.9 Hz, 1H), 2.13−2.05 (m, 1H), 1.87 (dt, J = 12.3, 3.1 Hz, 1H), 1.71 (dd, J = 11.3, 1.8 Hz, 1H), 1.46 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 146.3, 143.6, 138.8, 138.7, 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 127.7, 127.4, 127.3, 126.7, 123.5, 92.8, 74.2, 73.4, 73.3, 70.3, 67.1, 47.6, 40.2, 38.2, 36.1, 30.1, 17.1; IR (thin film) 2922, 2868, 1524, 1348, 1097, 700 cm^{-1}; HRMS (ESI) m/z calcd for $C_{37}H_{39}NNaO_6$ (M + Na)$^+$ 616.2675, found 616.2659.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic and crystallographic data for the products (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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