Relay Catalytic Cascade Hydrosiloxylation and Asymmetric Hetero-Diels–Alder Reaction

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Abstract: The hybrid gold(I)/Brønsted acid binary catalyst system enables enynes to participate in an asymmetric relay catalytic cascade intramolecular hydrosiloxylation and asymmetric hetero-Diels–Alder reaction with fluorenyl glyoxylate.

Key words: Diels–Alder reaction, enantioselectivity, silicon, heterocycles, enynes

The hetero-Diels–Alder reaction (HDA) is one of the most important transformations for the synthesis of six-membered heterocycles, which are commonly found in natural products and unnatural biologically active molecules;[1] it has received a great deal of research interest over a long period.[2] The asymmetric oxo-hetero-Diels–Alder of 2-siloxy-1,3-dienes with aldehydes gives directly chiral dihydropyranone derivatives, which have been widely applied in the total synthesis of a diverse spectrum of natural products as key intermediates, stands out in particular for its importance and it has been intensely investigated.[3,4] The 2-siloxy-1,3-dienes exploited in the asymmetric hetero-Diels–Alder reaction were preformed from enolizable carbonyls, wherein a stoichiometric or more amount of strong base was required. In contrast, the use of in situ generated 2-siloxy-1,3-dienes for the asymmetric hetero-Diels–Alder reaction avoids additional workup and purification processes associated with the classical methods and, therefore, is unarguably more interesting. However, this protocol has been much less explored.

The robust capability of gold complexes in the activation of the carbon–carbon triple bond allowed the emergence of numerous nucleophilic addition reactions of heteroatoms to alkynes and enynes, leading to the generation of functionalized compounds that could participate in a diverse range of transformations.[5] More interestingly, the gold complexes are highly compatible with Brønsted acids allowing the design of relay catalytic asymmetric reactions.[6,7] In recent years, we have established a range of asymmetric relay catalytic cascade reactions by using hybrid gold/chiral phosphoric acid binary catalyst systems.[7c,8] Very recently, we demonstrated that the gold(I)/Brønsted acid binary catalyst enabled enynes and alkynes to act as latent 1,3-siloxydienes and silyl enol ethers to undergo a highly enantioselective Diels–Alder reaction with quinones[9] and Mukaiyama aldol reaction with glyoxylates,[10] respectively (Scheme 1, equations 1 and 2). As our interest continues in the asymmetric relay catalysis, we now report a cascade intermolecular hydrosiloxylation and oxo-hetero-Diels–Alder reaction of [2-(but-3-en-1-ynyl)phenyl]diphenylsilanol derivatives with glyoxylates (Scheme 1, equation 3).

Terada and co-workers have previously demonstrated that chiral phosphoric acids could effectively catalyze the oxo-hetero-Diels–Alder reaction of glyoxylates with dienes.[4d] We have found that the cationic gold(I) complexes were able to effect intramolecular hydrosiloxylation to generate dienes.[9] Therefore, we initially investigated the cascade reaction of enynyldiethylsilanol **1a** with fluorenyl glyoxylate **2**[10] in the presence of the gold complex **3** alone. Unfortunately, the desired cascade reaction was not observed and a diene generated from the gold-catalyzed intermolecular hydrosiloxylation was isolated (Table 1, entry 1).[11] The use of the combined gold complex **3**[12] and **4a** was also unable to promote the cascade reaction (entry 2). The addition of the phosphoric acid **4b** bearing two bulkier substituents as a chiral co-catalyst led to trace amount of product (entry 3). To our delight, the use of chiral *N*-triflyl phosphoramide **4c**,[13] in combination of gold complex **3**, was able to afford the cascade reaction although the desired adduct **5a** was isolated in 15% yield with moderate enantioselectivity (entry 4). Interestingly, the addition of either anhydrous magnesium or sodium sulfate as an additive enhanced the yield and maintained enantioselectivity (entries 5 and 6). The enynyldiphenylsilanol **1b** gave an even better result in terms of the yield and stereochemical outcome (entry 7). Then, we screened a variety of structurally diverse chiral *N*-triflyl phosphoramides **4d**–**h** derived from 3,3′-disubstituted 1,1′-bi-2-naphthols (BINOLs) for the reaction and found that chiral *N*-triflyl phosphoramide **4h** was the optimal catalyst giving the cyclic product **5b** in 70% yield and 86% ee (entries 8–12). In addition, various solvents were investigated for the reaction; nonpolar solvents were more suitable media and, in particular, toluene was the solvent of choice in terms of both the yield and enantioselectivity (entries 12–16). Significantly, the loading of gold complex **3** could be reduced to as little as 1 mol% without diminishing the reaction efficiency (entry 17).

Under the optimized reaction conditions, the generality of this reaction for enynes was then explored (Scheme 2). To our delight, the asymmetric relay catalytic reaction toler-

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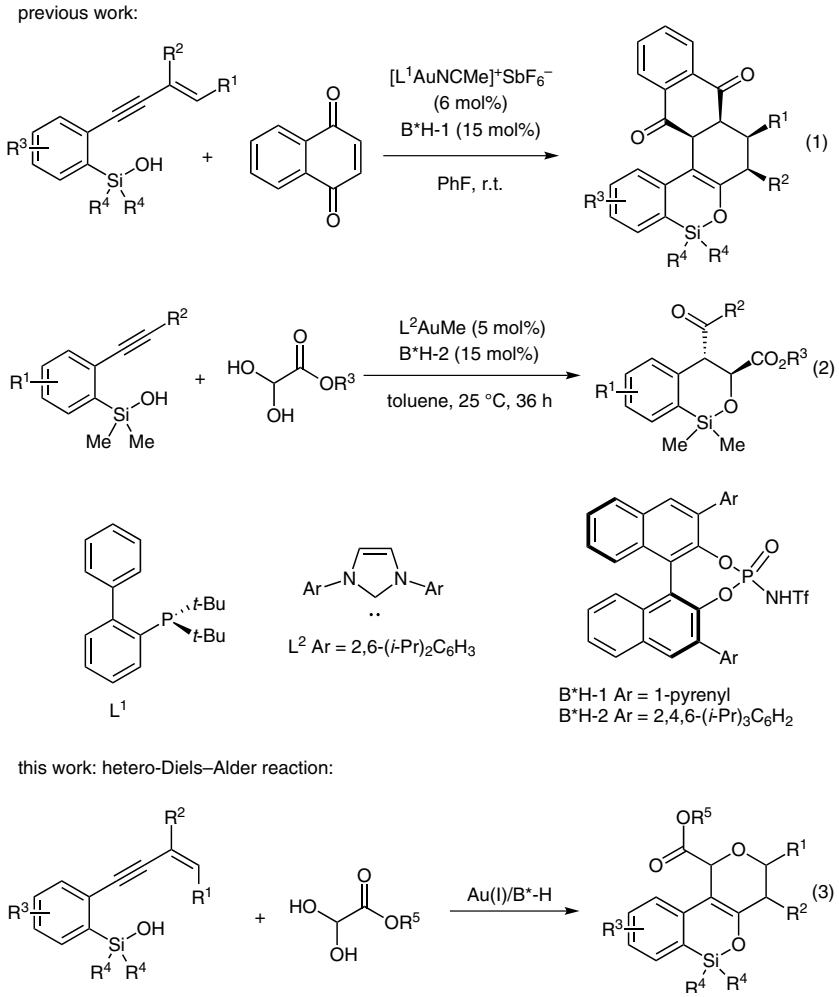

Scheme 1 Gold(I)-catalyzed hydrosiloxylation and related cascade reactions

ated a wide spectrum of enynyldiphenylsilanols bearing either an electron-donating or -withdrawing aryl substituent, giving the desired compounds **5c** and **5d** in moderate yields and enantioselectivities. The enynyldiphenylsilanols with an alkyl or phenyl substituent at C3 underwent the cascade reaction cleanly, furnishing the desired products **5e–i** in moderate yields (50–73%) and with high levels of diastereo- and enantioselectivities (up to >20:1 dr and 93% ee). Surprisingly, the enynyldiphenylsilanol **1j** with a methyl substituent at C4 provided the product **5j** in 63% yield, but with only 2:1 diastereomeric ratio and moderate enantioselectivities of 67% and 45% ee, respectively. However, if a phenyl substituent was introduced at C4 of the enyne, the desired hetero-Diels–Alder adduct was not observed. The configuration of **5g** was determined by X-ray crystallographic analysis (Figure 1).

In the presence of triethylamine, the cyclic compound **5b** obtained from the relay catalytic cascade reaction could be transformed into an *anti*-disubstituted cyclohexanone

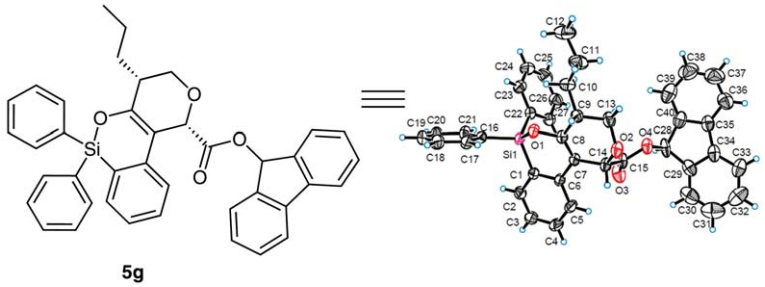

Figure 1 X-ray crystal structure of **5g**

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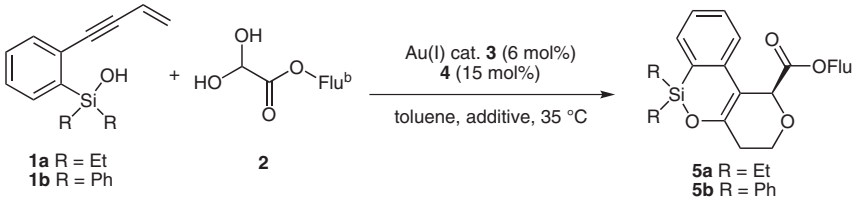
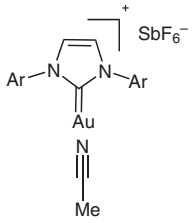
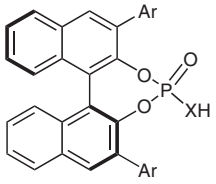
Table 1 Catalyst Screening and Optimization of the Reaction Conditions[a]





3 Ar = 2,6- (*i*-Pr)$_2$C$_6$H$_3$



4a X = O, Ar = Ph
4b X = O, Ar = 9-anthracenyl
4c X = NTf, Ar = 9-anthracenyl
4d X = NTf, Ar = 1-pyrenyl
4e X = NTf, Ar = 4-$O_2NC_6H_4$
4f X = NTf, Ar = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$
4g X = NTf, Ar = 2,6-(*i*-Pr)$_2$, 4-(*t*-Bu)C$_6$H$_2$
4h X = NTf, Ar = 2,4,6-(Cy)$_3$C$_6$H$_2$

Entry	R	**4**	Additive	Yield[c] (%)	ee[d] (%)
1	Et	–	–	–[e]	–
2	Et	**4a**	–	–[e]	–
3	Et	**4b**	–	trace	–
4	Et	**4c**	–	15	60
5	Et	**4c**	$MgSO_4$	23	60
6	Et	**4c**	Na_2SO_4	30	60
7	Ph	**4c**	Na_2SO_4	48	62
8	Ph	**4d**	Na_2SO_4	–[e]	–
9	Ph	**4e**	Na_2SO_4	–[e]	–
10	Ph	**4f**	Na_2SO_4	45	77
11	Ph	**4g**	Na_2SO_4	64	74
12	Ph	**4h**	Na_2SO_4	70	86
13	Ph	**4h**	Na_2SO_4	58	80[f]
14	Ph	**4h**	Na_2SO_4	70	83[g]
15	Ph	**4h**	Na_2SO_4	60	86[h]
16	Ph	**4h**	Na_2SO_4	62	84[i]
17	Ph	**4h**	Na_2SO_4	70	86[j]

[a] Unless indicated otherwise, reaction conditions: **1** (0.1 mmol), **2** (0.2 mmol), gold catalyst **3** (6 mol%), Brønsted acid **4** (15 mol%), additive (50 mg), toluene (2 mL), 35 °C.
[b] Flu = 9*H*-fluoren-9-yl.
[c] Isolated yield.
[d] The ee was determined by HPLC.
[e] The desired product was not obtained.
[f] In CH_2Cl_2.
[g] In $CHCl_3$.
[h] In PhF.
[i] In DCE.
[j] 1 mol% of **3** was used.

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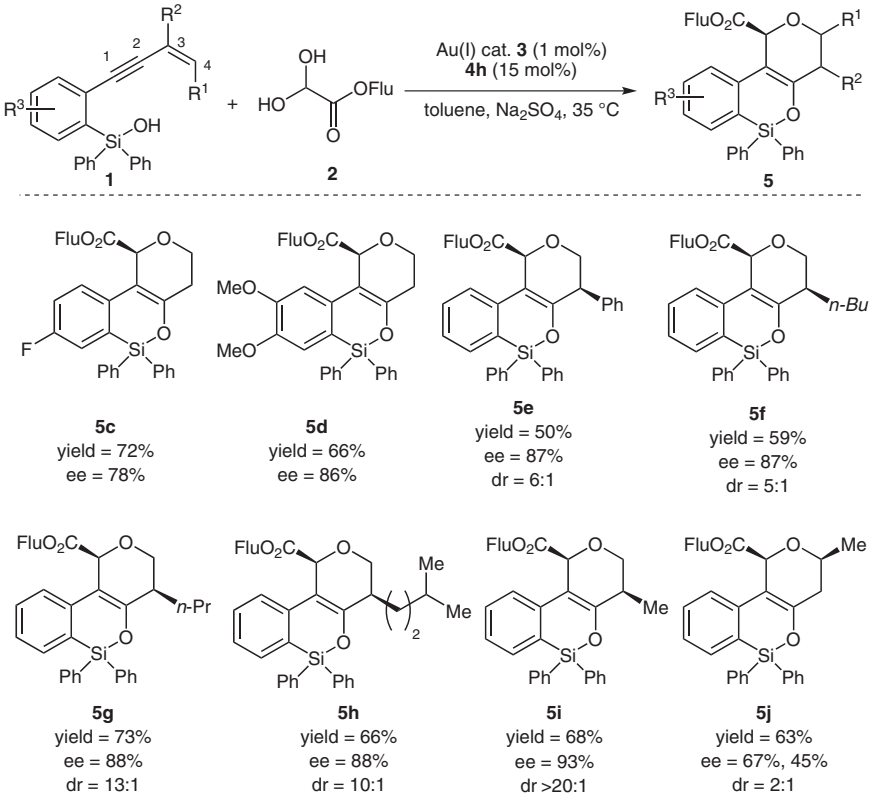
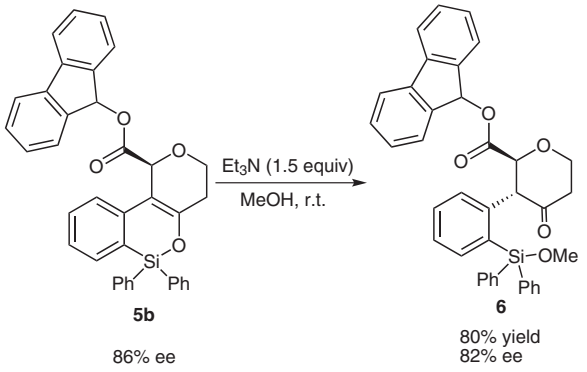


Scheme 2 Generality of the reaction. *Reagents and conditions*: **1** (0.1 mmol), **2** (0.2 mmol), gold catalyst **3** (1 mol%), Brønsted acid **4h** (15 mol%), anhyd Na_2SO_4 (50 mg), toluene (2 mL), 35 °C; dr was determined from the ^1H NMR spectra of the crude reaction mixture.

derivative **6** in methanol in 80% yield and almost maintaining the enantiomeric excess (Scheme 3).



Scheme 3

In summary, we have established an unprecedented relay catalytic cascade intramolecular hydrosiloxylation and asymmetric hetero-Diels–Alder reaction between enynyldiphenylsilanols and fluorenyl glyoxylate. The 3,3′-bis(2,4,6-tricyclohexylphenyl)-BINOL-based phosphoramide showed the highest stereochemical control. A wide range of enynyldiphenylsilanols were able to participate in the relay catalytic cascade reaction, leading to generation of 3,6-dihydropyran derivatives in fairly good yields and with high levels of enantioselectivity.

NMR spectra were recorded on a Bruker 400 MHz spectrometer. FT-ICRMS spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. IR spectra were recorded on a Nicolet MX-1E FT-IR spectrophotometer. HPLC analysis was performed on Waters-Breeze (2487 dual absorbance detector and 1525 binary HPLC pump, UV detection: 254nm) and Agilent 1200. Chiralpak AD, IC, and IA columns were purchased from Daicel Chemical Industries, Ltd. The absolute configuration of **5g** was assigned by X-ray analysis. Analytical grade solvents for the column chromatography and commercially available reagents were used as received. DCE, MeCN, and CH_2Cl_2 were dried over CaH_2 and distilled prior to use. Toluene, THF, and Et_2O were dried over Na and distilled prior to use. The gold complex[14] and Brønsted acid catalysts[15] were prepared following the literature report. The substrates[9] and fluorenyl glyoxylate[10] were synthesized according to the literature.

[2-(But-3-en-1-ynyl)-5-fluorophenyl]diphenylsilanol (1c)
Isolated as a light yellow oil; yield: 492 mg (1.43 mmol, 77%).

IR (KBr): 3383, 3081, 2971, 2861, 1733, 1587, 1468, 1267, 1207, 1168, 854, 634, 506 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.32 (m, 11 H), 7.16–6.99 (m, 2 H), 5.70 (dd, *J* = 17.4, 11.3 Hz, 1 H), 5.37 (dd, *J* = 11.3, 2.0 Hz, 1 H), 5.26 (dd, *J* = 17.4, 1.9 Hz, 1 H), 3.05 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1 (d, *J* = 162 Hz, 1 C), 136.4, 136.0, 134.4, 134.2, 134.1, 130.3, 129.8, 127.9, 127.9, 127.5, 116.3, 91.5, 90.4.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{22}H_{17}FNaOSi$: 367.09249; found: 367.09206.

[2-(But-3-en-1-ynyl)-4,5-dimethoxyphenyl]diphenylsilanol (1d)
Isolated as a yellow oil; yield: 539 mg (1.48 mmol, 81%).

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IR (KBr): 3512, 3081, 3017, 2952, 2192, 1585, 1493, 1322, 1257, 1110, 1056, 845, 698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.88–7.41 (m, 10 H), 7.14 (s, 1 H), 7.10 (s, 1 H), 5.79 (dd, *J* = 17.2, 11.4 Hz, 1 H), 5.43 (d, *J* = 11.0 Hz, 1 H), 5.33 (d, *J* = 17.5 Hz, 1 H), 3.99 (s, 3 H), 3.84 (s, 3 H), 3.39 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 148.8, 135.2, 135.0, 130.6, 129.9, 127.8, 126.7, 121.4, 118.2, 116.6, 115.3, 91.5, 90.6, 55.8, 55.7.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{23}FO_3Si$: 387.14110; found: 387.14081.

[2-(6-Methyl-3-methylenehept-1-ynyl)phenyl]diphenylsilanol (1h)
Isolated as a yellow oil; yield: 576 mg (1.54 mmol, 86%).

IR (KBr): 3512, 3429, 3090, 3035, 2952, 1477, 1449, 1120, 1056, 836, 772, 698, 506 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.12 (m, 14 H), 5.04 (d, *J* = 1.6 Hz, 1 H), 4.90 (d, *J* = 2.0 Hz, 1 H), 3.14 (s, 1 H), 1.94–1.79 (m, 2 H), 1.43–1.33 (m, 1 H), 1.19–1.12 (m, 2 H), 0.74 (d, *J* = 3.2 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 136.1, 135.2, 134.9, 132.5, 131.4, 130.0, 129.9, 128.5, 127.9, 127.8, 127.6, 121.6, 93.9, 90.3, 37.2, 34.6, 27.4, 22.5.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{27}H_{29}OSi$: 397.19822; found: 397.19753.

[(*Z*)-2-(Pent-3-en-1-ynyl)phenyl]diphenylsilanol (1j)
Isolated as a yellow oil; yield: 477 mg (1.50 mmol, 85%).

IR (KBr): 3357, 3050, 2962, 2921, 1431, 1110, 836, 744, 698, 506 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.22 (m, 14 H), 5.92 (dq, *J* = 10.8, 6.9 Hz, 1 H), 5.44 (dd, *J* = 10.7, 1.7 Hz, 1 H), 3.21 (s, 1 H), 1.63 (dd, *J* = 6.9, 1.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 139.4, 136.0, 135.1, 134.2, 132.5, 132.1, 130.0, 129.8, 127.9, 127.8, 127.3, 95.2, 92.3, 18.8.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{23}H_{21}OSi$: 341.13562; found: 341.13540.

9*H*-Fluoren-9-yl (*S*)-6,6-Diphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylates 5b–j; General Procedure
To a solution of gold complex **3** (1 mol%), *N*-triflyl phosphoramide **4h** (15 mol%), fluorenyl glyoxylate **2** (0.2 mmol), and Na_2SO_4 (50 mg) in toluene (1 mL) was added a solution of enynylsilanol **1** (0.1 mmol) in toluene (1 mL) in one portion under argon. The resulting mixture was stirred at 35 °C for 6 d, and then the mixture was directly subjected to flash column chromatography (silica gel, EtOAc–petroleum ether) to afford product **5**.

9*H*-Fluoren-9-yl (*S*)-6,6-Diphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5b)
Isolated as a yellow oil; yield: 39.5 mg (0.07 mmol, 70%); $[\alpha]_D^{20}$ –15.1 (*c* 0.44, $CHCl_3$); 86% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 90:10, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 6.24 (minor), 7.34 min (major)]; the absolute configuration was tentatively assigned by analogy.

IR (KBr): 3474, 3070, 2923, 1731, 1631, 1429, 1107, 898, 743, 697, 514 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78–7.10 (m, 22 H), 6.81 (s, 1 H), 5.42 (s, 1 H), 4.31–4.20 (m, 1 H), 4.02–3.91 (m, 1 H), 2.77–2.61 (m, 1 H), 2.45–2.32 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.7, 149.5, 141.7, 141.5, 141.1, 141.0, 139.7, 135.2, 135.1, 134.2, 134.1, 133.0, 132.8, 130.8, 130.7, 130.7, 130.1, 129.8, 129.5, 129.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 126.0, 125.9, 125.7, 121.4, 120.0, 119.9, 107.3, 75.7, 74.3, 62.0, 30.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{37}H_{28}O_4NaSi$: 587.16491; found: 587.16415.

9*H*-Fluoren-9-yl (*S*)-8-Fluoro-6,6-diphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5c)
Isolated as a colorless oil; yield: 41.9 mg (0.072 mmol, 72%); $[\alpha]_D^{20}$ –5.1 (*c* 0.312, $CHCl_3$); 78% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 90:10, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 8.06 (minor), 9.12 min (major)]; the absolute configuration was tentatively assigned by analogy.

IR (KBr): 3439, 2932, 1733, 1429, 1192, 1120, 999, 743, 698, 504 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79–6.92 (m, 21 H), 6.80 (s, 1 H), 5.38 (s, 1 H), 4.39–4.19 (m, 1 H), 4.05–3.88 (m, 1 H), 2.81–2.58 (m, 1 H), 2.47–2.29 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 160.7 (d, *J* = 249.4 Hz, 1 C), 159.5, 148.9, 141.6, 141.4, 141.1, 141.0, 136.48, 135.7, 135.7, 135.2, 135.0, 134.2, 132.3, 131.8, 131.0, 130.9, 129.8, 129.6, 129.5, 129.0, 128.9, 128.2, 128.1, 128.0, 127.9, 127.8, 125.9, 125.6, 123.7, 123.6, 120.2, 120.0, 120.0, 117.7, 117.5, 106.9, 75.8, 74.2, 62.0, 29.8.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{37}H_{27}O_4FNaSi$: 605.15549; found: 605.15527.

9*H*-Fluoren-9-yl (*S*)-8,9-Dimethoxy-6,6-diphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5d)
Isolated as a yellow oil; yield: 41.2 mg (0.066 mmol, 66%); $[\alpha]_D^{20}$–5.5 (*c* 0.35, $CHCl_3$); 86% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 70:30, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 6.63 (minor), 7.20 min (major)]; the absolute configuration was tentatively assigned by analogy.

IR (KBr): 3071, 2932, 2852, 2247, 1731, 1630, 1503, 1447, 1365, 1256, 907, 714, 494 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.09 (m, 18 H), 6.90 (s, 1 H), 6.79 (s, 1 H), 6.66 (s, 1 H), 5.40 (s, 1 H), 4.36–4.29 (m, 1 H), 4.00–3.94 (m, 1 H), 3.78 (s, 3 H), 3.41 (s, 3 H), 2.78–2.54 (m, 1 H), 2.48–2.29 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9, 151.0, 148.3, 147.3, 141.6, 141.4, 141.0, 141.0, 135.2, 135.1, 133.9, 133.4, 133.0, 130.7, 130.7, 129.6, 129.5, 128.1, 128.0, 127.9, 127.9, 126.1, 125.7, 120.0, 120.0, 117.1, 115.7, 106.8, 105.8, 75.9, 74.2, 62.0, 56.0, 55.3, 29.8.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{39}H_{32}O_6NaSi$: 647.18604; found: 647.18604.

9*H*-Fluoren-9-yl (1*S*,4*R*)-4,6,6-Triphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5e)
Isolated as a yellow oil; yield: 32.1 mg (0.05 mmol, 50%); $[\alpha]_D^{20}$ –21.1 (*c* 0.32, $CHCl_3$); 87% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 90:10, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 6.08 (minor), 6.58 min (major)]; the absolute configuration was tentatively assigned by analogy.

IR (KBr): 3053, 2923, 1732, 1632, 1429, 1361, 1193, 1135, 912, 697, 513 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74–6.86 (m, 27 H), 6.85 (s, 1 H), 5.61 (d, *J* = 1.3 Hz, 1 H), 4.19–4.08 (m, 2 H), 3.73 (t, *J* = 5.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 149.2, 140.5, 140.4, 140.0, 139.9, 138.5, 138.3, 134.4, 133.7, 133.1, 131.5, 131.2, 129.7, 129.6, 129.1, 128.4, 128.3, 127.9, 127.0, 126.8, 126.7, 126.7, 126.5, 125.4, 125.3, 125.2, 125.0, 124.6, 120.6, 118.9, 118.8, 108.0, 74.7, 68.5, 45.2, 28.6.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{43}H_{32}O_4NaSi$: 663.19621; found: 663.19589.

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9*H*-Fluoren-9-yl (1*S*,4*R*)-4-Butyl-6,6-diphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5f)
Isolated as a yellow oil; yield: 36.6 mg (0.059 mmol, 59%); $[\alpha]_D^{20}$ –33.3 (*c* 0.04, $CHCl_3$); 87% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 95:5, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 7.20 (minor), 8.55 min (major)]; the absolute configuration was tentatively assigned by analogy.

IR (KBr): 3070, 2917, 2858, 1728, 1621, 1467, 1159, 1118, 741, 696, 510 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.00 (m, 22 H), 6.82 (s, 1 H), 5.47 (s, 1 H), 3.99–3.93 (m, 2 H), 2.53 (s, 1 H), 1.12–0.98 (m, 4 H), 0.94–0.82 (m, 2 H), 0.62 (t, *J* = 6.9 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.7, 152.4, 141.7, 141.0, 140.9, 139.9, 135.3, 135.1, 134.0, 133.0, 132.6, 130.7, 130.7, 130.5, 129.4, 129.4, 128.0, 127.8, 127.7, 127.7, 126.0, 125.8, 125.6, 121.6, 119.9, 119.9, 107.6, 75.3, 74.2, 66.9, 38.6, 29.7, 29.1, 22.8, 13.7.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{41}H_{36}O_4NaSi$: 643.22751; found: 643.22690.

9*H*-Fluoren-9-yl (1*S*,4*R*)-6,6-Diphenyl-4-propyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5g)
Isolated as a yellow solid; yield: 44.2 mg (0.073 mmol, 73%); $[\alpha]_D^{20}$ –40.8 (*c* 0.16, $CHCl_3$); 88% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 95:5, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 7.39 (minor), 8.53 min (major)]; the absolute configuration was determined by X-ray crystallography analysis.

IR (KBr): 3066, 2959, 2926, 1730, 1629, 1159, 1123, 906, 743, 504 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.05–6.95 (m, 22 H), 6.82 (s, 1 H), 5.46 (s, 1 H), 3.96 (dd, *J* = 5.9, 2.3 Hz, 2 H), 2.62–2.44 (m, 1 H), 1.46–1.34 (m, 2 H), 1.20–1.12 (m, 2 H), 0.67 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 152.4, 141.7, 141.5, 141.0, 140.9, 135.2, 135.0, 134.0, 130.7, 130.7, 130.5, 129.4, 129.4, 128.0, 127.8, 127.8, 127.7, 126.0, 125.8, 125.7, 121.6, 119.9, 119.9, 107.6, 75.7, 75.3, 66.9, 38.5, 31.6, 19.8, 14.1.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{40}H_{34}O_4NaSi$: 629.21186; found: 629.21220.

9*H*-Fluoren-9-yl (1*S*,4*R*)-4-Isopentyl-6,6-diphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5h)
Isolated as a yellow oil; yield: 41.8 mg (0.066 mmol, 66%); $[\alpha]_D^{20}$ –15.0 (*c* 0.12, $CHCl_3$); 88% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 95:5, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 7.34 (minor), 8.37 min (major)]; the absolute configuration was tentatively assigned by analogy.

IR (KBr): 2956, 2920, 1732, 1622, 1451, 1265, 1119, 1016, 198, 735, 510 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.85–6.98 (m, 22 H), 6.82 (s, 1 H), 5.48 (s, 1 H), 3.95 (d, *J* = 5.5 Hz, 2 H), 2.65–2.22 (m, 1 H), 0.97–0.82 (m, 5 H), 0.63 (d, *J* = 6.6 Hz, 3 H), 0.56 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 151.3, 140.7, 140.5, 140.0, 139.9, 138.8, 134.2, 134.1, 133.0, 131.9, 131.6, 129.7, 129.6, 129.5, 128.4, 128.3, 127.0, 126.8, 126.7, 124.9, 124.8, 124.6, 120.5, 118.9, 118.8, 106.5, 74.5, 74.3, 65.0, 37.8, 34.3, 27.2, 26.3, 21.3, 21.1.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{42}H_{38}O_4NaSi$: 657.24316; found: 657.24276.

9*H*-Fluoren-9-yl (1*S*,4*R*)-4-Methyl-6,6-diphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5i)
Isolated as a yellow oil; yield: 39.3 mg (0.068 mmol, 68%); $[\alpha]_D^{20}$ –20.5 (*c* 0.35 $CHCl_3$); 93% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 90:10, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 5.54 (minor), 6.21 min (major)]; the absolute configuration was tentatively assigned by analogy.

IR (KBr): 3070, 3046, 2965, 2932, 1730, 1629, 1454, 1428, 1151, 1120, 875, 727, 509 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.05 (m, 22 H), 6.81 (s, 1 H), 5.46 (s, 1 H), 3.97 (dd, *J* = 11.2, 5.5 Hz, 1 H), 3.86 (dd, *J* = 11.2, 7.5 Hz, 1 H), 2.74–2.61 (m, 1 H), 1.05 (d, *J* = 6.9 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.7, 153.0, 141.7, 141.5, 141.1, 140.9, 139.8, 135.3, 135.0, 134.0, 133.0, 132.7, 130.8, 130.7, 130.6, 129.4, 129.4, 128.0, 127.9, 127.8, 127.7, 126.0, 126.0, 125.9, 125.7, 121.7, 120.0, 119.9, 107.1, 75.7, 75.1, 68.6, 33.7, 14.2.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{30}O_4NaSi$: 601.18056; found: 601.18014.

9*H*-Fluoren-9-yl (1*S*)-3-Methyl-6,6-diphenyl-1,3,4,6-tetrahydrobenzo[*c*]pyrano[3,4-*e*][1,2]oxasiline-1-carboxylate (5j)
Isolated as a yellow oil; yield: 36.4 mg (0.063 mmol, 63%); 67% ee (major), 45% ee (minor) [HPLC (Chiracel-IA-H, hexane–*i*-PrOH, 90:10, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 5.71 (major), 6.62 min (minor); t_R = 7.68 (major), 10.28 min (minor)]; the relative configuration of **5j** was determined by NOESY analysis of this compound, the absolute configuration was tentatively assigned by analogy.

IR (KBr): 3072, 3053, 2972, 1739, 1631, 1452, 1429, 1197, 1117, 908, 745, 713, 510 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.75–6.99 (m, 22 H, major), 7.75–6.99 (m, 22 H, minor), 6.84 (s, 1 H, minor), 6.74 (s, 1 H, major), 5.55 (s, 1 H, major), 5.43 (s, 1 H, minor), 4.17–4.05 (m, 1 H, minor), 3.96–3.85 (m, 1 H, major), 2.54–2.34 (m, 2 H, major), 2.32–2.24 (m, 2 H, minor), 1.33–1.30 (m, 3 H, major), 1.27–1.23 (m, 3 H, minor).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6, 149.9, 141.7, 141.5, 141.0, 140.8, 135.49, 135.2, 135.1, 134.9, 134.0, 130.8, 130.8, 130.7, 130.5, 129.5, 129.4, 129.3, 129.3, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 126.2, 125.8, 125.6, 125.6, 121.5, 120.0, 120.0, 119.8, 119.8, 107.1, 75.6, 74.5, 67.1, 37.7, 21.0.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{30}O_4NaSi$: 601.18056; found: 601.18134.

9*H*-Fluoren-9-yl (2*S*,3*R*)-3-[2-(Methoxydiphenylsilyl)phenyl]-4-oxotetrahydro-2*H*-pyran-2-carboxylate (6)
Compound **5a** (18 mg, 0.03 mmol) and Et_3N (5 mg, 0.045 mmol) were dissolved in MeOH (1 mL). The mixture was stirred at r.t. overnight, and then diluted with EtOAc and washed with H_2O and brine, dried (anhyd Na_2SO_4), and concentrated. The residue was purified by flash column chromatography to afford **6** (14.3 mg, 0.024 mmol, 80%) as a colorless oil; $[\alpha]_D^{20}$ +62.8 (*c* 0.23, $CHCl_3$); 82% ee [HPLC (Chiracel-IC-H, hexane–*i*-PrOH, 90:10, flow rate 1.0 mL/min, *T* = 30 °C, 254 nm): t_R = 9.30 (major), 11.11 min (minor)]; the absolute configuration was tentatively assigned by analogy.

IR (KBr): 3071, 2923, 1745, 1593, 1426, 1149, 1119, 998, 945, 736, 706, 504 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.02 (m, 21 H), 6.65 (d, *J* = 7.6 Hz, 1 H), 6.40 (s, 1 H), 4.20–4.03 (m, 2 H), 3.80 (t, *J* = 10.9 Hz, 1 H), 3.43 (d, *J* = 10.8 Hz, 1 H), 3.09 (s, 3 H), 2.14 (d, *J* = 12.7 Hz, 1 H), 2.05–1.93 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.6, 170.7, 141.8, 141.5, 141.0, 141.0, 140.8, 135.8, 134.8, 134.6, 134.3, 133.6, 130.8, 130.3, 130.2, 130.0, 129.5, 129.3, 127.9, 127.7, 127.7, 127.4, 126.9, 125.9, 119.7, 119.7, 99.5, 80.5, 77.3, 65.6, 53.2, 48.6, 35.6.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{32}O_5NaSi$: 619.19112; found: 619.19025.

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