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Note

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Organosilicon Reducing Reagents for Stereoselective Formations of Silyl Enol Ethers from α–Halo Carbonyl Compounds

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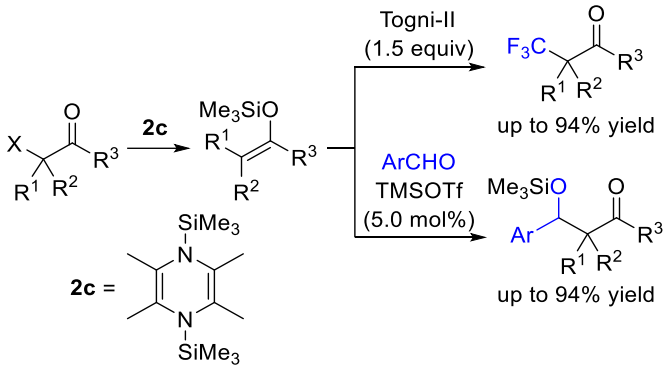
ABSTRACT



Salt-free stereoselective synthesis of silyl enol ethers was achieved by treating α-halo carbonyl compounds with 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-dihydropyrazine. In this reaction, easily removable trimethylsilyl halides and 2,3,5,6-tetramethylpyrazine were generated as the reaction byproducts. Due to the inertness of the reaction byproducts, we found a one-pot transformation of the *in situ*-generated silyl enol ethers into various α–functionalized carbonyls by the reaction with Togni-II reagent or aldehydes.

Silyl enol ethers are important intermediates in organic chemistry as the synthetic equivalent of enol ether anions that are often used with Lewis acid catalysts for a variety of C—C bond-forming reactions with electrophiles.[1–3] The versatility of silyl enol ethers thus led to the development of various synthetic methodologies as exemplified in Figure 1. Figure 1(a) shows the well-established synthetic route, in which chlorosilanes trap metal enolates *in situ*-generated by treating carbonyl compounds with strong base[4] or α-halo carbonyl compounds with metal powder,[5] though equimolar amounts of metal salt-waste are coproduced. Other examples include metal-catalyzed reactions with hydrosilanes such as 1,4-hydrosilylation of conjugated enones (Figure 1(b))[6] and α-C—H bond activation of ketones followed by silylation (Figure 1(c)).[7] Metal-catalyzed methods, however, are not widely applied to a variety of carbonyl compounds because hydrosilanes are highly reactive to various functional groups in the presence of metal catalysts, resulting in narrow functional group tolerance as well as contamination of silyl ethers *via* C=O reduction.[6c,7b,7e] Accordingly, the development of more convenient synthetic methods without contamination by salt-waste and side reactions is in high demand.

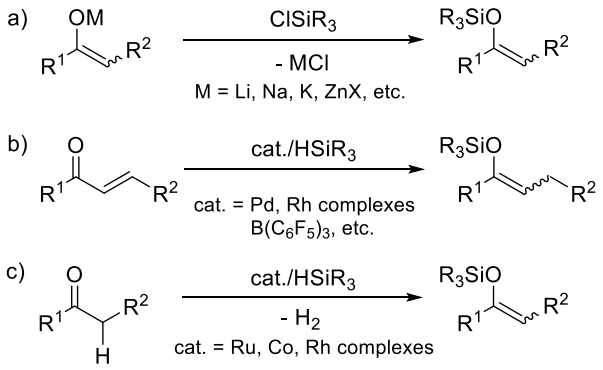


Figure 1. General strategies for silyl enol ethers formation: a) metal enolates with chlorosilanes, b) hydrosilylation of enones, c) dehydrogenative silylation of ketones.

We recently developed a series of organosilicon compounds **1-3** for their unique ability to reduce not only transition metal halides, but also organic halides without the formation of any salt waste (Figure 2).[8] These organosilicon reductants are synthesized by treating toluene or *N*-heterocyclic compounds with sodium or potassium metal and trimethylsilyl chloride, and are soluble in common organic solvents to keep the homogeneity during the reaction. Herein, we developed a new salt-free method for synthesizing silyl enol ethers by treating enolizable α-halo carbonyl compounds with **1-3** and demonstrated the regio- and stereoselective synthesis of trisubstituted silyl enol ethers under mild reaction conditions. Furthermore, due to the formation of silyl enol ethers was achieved in a salt-free manner and the inertness of the reaction byproducts to keep the reaction mixture in homogeneous, the one-pot protocol was exemplified by reactions with an electrophilic trifluoromethylation reagent (Togni-II reagent), aldehydes in the presence of Me_3SiOTf as the Lewis acid catalyst, and the Ni-catalyzed Kumada-Tamao cross-coupling reaction with Grignard reagents.

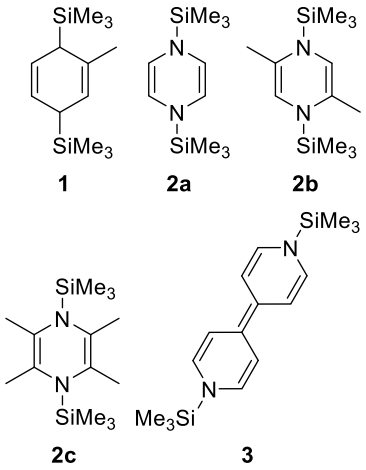
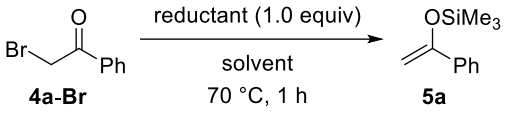


Figure 2. Organosilicon reductants **1-3**.

We first searched for the best organosilicon reductant among **1**-**3** for the salt-free formation of silyl enol ether **5a** by treating **4a**-**Br** in CD_3CN at 70 °C, and the results are shown in Table 1. Although no conversion was observed for **1** (entry 1), reductant **2c** afforded **5a** in 98% yield accompanied by trimethylsilylbromide and tetramethylpyrazine, both of which could be easily separated and removed from the products either by column chromatography or by evaporation as the volatile (entry 4). When **2a** and **2b** were used, **5a** was obtained in lower yields (entries 2 and 3). Moreover, **3** exhibited the same efficiency as **2c**, giving **5a** in 97% yield (entry 5). We selected **2c** as the best reductant, and the solvent effects were examined next: a high polar solvent, DMF, afforded **5a** in lower yield (26%) (entry 6), as well as the reaction in an ethereal solvent, THF, gave **5a** in poor yield (entry 7). Silyl enol ether formation was less effective in non-polar solvents such as benzene and toluene (entries 8 and 9). Acetonitrile was thus selected as the best solvent for silyl enol ether formation.

Table 1. Optimization of silyl enol ether synthesis from α–bromo carbonyl.[a]



4a-Br **5a**

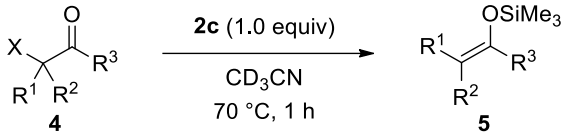
entry	reductant	solvent	yield (%)[b]
1	**1**	CD_3CN	0
2	**2a**	CD_3CN	67
3	**2b**	CD_3CN	34
4	**2c**	CD_3CN	98
5	**3**	CD_3CN	97
6	**2c**	DMF	26
7	**2c**	THF	4
8	**2c**	C_6D_6	12
9	**2c**	toluene-d_8	14

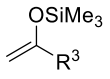
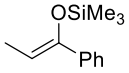
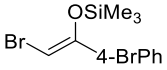
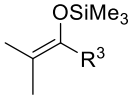
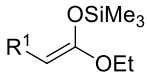
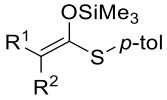
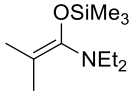
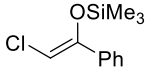
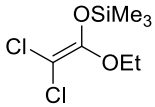
[a]Reaction conditions: **4a**-**Br** (1.0 equiv, 0.10 mmol), reductant (1.0 equiv, 0.10 mmol), in above mentioned solvent at 70 °C for 1 h. [b]Yields were measured by ^{1}H NMR spectroscopy in the presence of mesitylene as an internal standard.

We applied the optimized conditions in Table 1 for the transformation of α-halo carbonyl compounds **4** into the corresponding silyl enol ethers **5** using **2c**, and the results were shown in Table 2. In the initial attempt, we checked the formation of disubstituted silyl enol ethers from α-bromoketones **4b**—**e**. Reactions of **2c** with 4'-methoxyphenacyl bromide (**4b**) and 4'-methylphenacyl bromide (**4c**), in which electron-donating *para*-substituents attached to the phenyl ring, gave the corresponding silyl enol ethers **5b** in 99% yield and **5c** in 97% yield (entries 1 and 2). Treatment of **2c** with 4'-chlorophenacyl bromide (**4d**) afforded **5d**, quantitatively (entry 3). The reaction with bulky *tert*-butyl substituted aliphatic substrate **4e** was slow, and a longer reaction time (24 h) was required to give **5e** in quantitative yield (entry 4). We next evaluated the synthesis of tri-substituted silyl enol ethers by controlling the *E*/*Z* stereochemistry, and achieved highly *Z*-selective formation of the silyl enol ethers, which is advantageous compared to literature mentioned procedures; in fact, low temperature reaction and selection of the appropriate bases and solvents are crucial to accomplish the formation of Z-selective silyl enol ethers.[3a,4e,f] 2-Bromopropiophenone (**4f**) afforded trisubstituted silyl enol ether **5f** in 96% yield with 98% *Z*-selectivity (entry 5). Similarly, geminal dibromo compound **4g** was transformed in a perfect *Z*-selective manner to **5g**, in which one synthetically useful C(sp^2)—Br bond remained (entry 6). 2-Bromo-2-methylpropiophenone (**4h**) and 3-bromo-3-methyl-2-butanone (**4i**), both of which contained a *tert*-carbon—bromide bond, were converted to the corresponding tetrasubstituted silyl enol ethers **5h** in 99% yield and **5i** in 97% yield, respectively (entries 7 and 8). Reduction of ethyl α-bromophenylacetate (**4j**) and diethyl bromomalonate (**4k**) proceeded in excellent yields to give the corresponding ethoxy silyl enol ethers **5j** with a *Z*-selectivity of 86% and **5k** with a *Z*-selectivity of 99%, respectively (entries 9

and 10). In fact, the applicability of α-bromothioester **4l**—**n** and α-bromoamide **4o** for the generation of silyl enol ethers was examined by the treatment with reductant **3** due to its high reactivity, which resulted in the formation of **5l**—**o** in excellent yield (94—97% yield, entries 11—14). In contrast, primary and secondary α-bromoamides produced the corresponding α-silylated amides under similar conditions, as silyl group migration proceeded from the silyl enol ether to the α-position of the amides.[9,10]

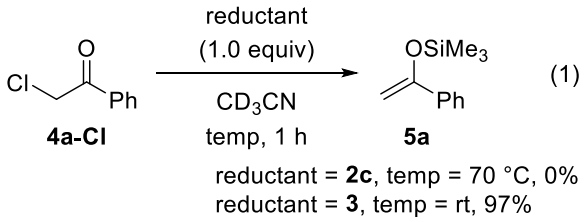
Table 2. Substrate scope for silyl enol ethers synthesis from α–halo carbonyls.[a]



entry	product	yield [%][b]
1		99 (**5b**, X = Br, R^3 = 4-$MeOC_6H_4$)
2		97 (**5c**, X = Br, R^3 = 4-MeC_6H_4)
3		99 (**5d**, X = Br, R^3 = 4-ClC_6H_4)
4		95 (**5e**, X = Br, R^3 = ^{t}Bu)[c]
5		96 (**5f**, X = Br), *E*/*Z* = 2/98
6		97 (**5g**, X = Br), *E*/*Z* = <1/>99
7		99 (**5h**, X = Br, R^3 = Ph)
8		97 (**5i**, X = Br, R^3 = Me)
9		98 (**5j**, X = Br, R^1 = Ph), *E*/*Z* = 14/86
10		96 (**5k**, X = Br, R^1 = CO_2Et), *E*/*Z* = 1/99
11		96 (**5l**, X = Br, R^1 = R^2 = H)[d]
12		94 (**5m**, X = Br, R^1 = Me, R^2 = H), *E*/*Z* = >99/<1[d]
13		99 (**5n**, X = Br, R^1 = R^2 = Me)[d]
14		97 (**5o**, X = Br)[d]
15		93 (**5p**, X = Cl), *E*/*Z* = 2/98
16		95 (**5q**, X = Cl)

[a]Reaction conditions: **4** (1.0 equiv, 0.40 mmol), **2c** (1.0 equiv, 0.40 mmol), in CD_3CN at 70 °C for 1 h. [b]Yields and *E*/*Z* ratio (for entries 5—8 and 11) were measured by ^{1}H NMR spectroscopy in the presence of mesitylene as an internal standard. [c]Reaction was 24 h. [d]The reaction was performed at rt for 1 h in the presence of **3** (1 equiv).

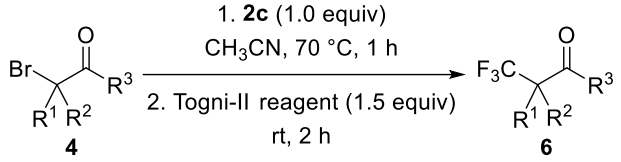
Noteworthy was that one of two C—Cl bonds in 2,2-dichloroacetophenone (**4p**) selectively reacted to give trisubstituted silyl enol ether **5p** with a high *Z*-selectivity of 98% (entry 13), and one of three C—Cl bonds of ethyl 2,2,2-trichloroacetate (**4q**) was reduced by **2c** to produce tetrasubstituted silyl enol ether **5q** (entry 16). Although the activated C—Cl bonds of **4p** and **4q** were reducible by **2c**, reduction of the C—Cl bond of phenacyl chloride (**4a-Cl**), giving **5a**, required the use of **3**, which has a more negative redox potential, as no reduction was observed with **2c** (eq. 1).

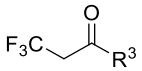
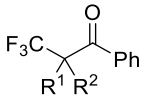
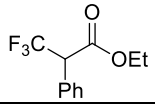


Because the reactions of **2c** with α-bromo carbonyls smoothly generated the corresponding silyl enol ethers in excellent yields without any metal-derived wastes that sometimes suppress further transformation in the reaction mixture, a one-pot reaction was conducted with electrophiles. In fact, successive addition of an electrophilic trifluoromethylation reagent, Togni-II reagent, to the reaction mixture afforded α-trifluoromethylated compounds **6**, although silyl enol ether trapping by Togni-II reagent was previously reported,[11] and the results were summarized in Table 3. After mixing **2c** and **4a-Br** in CH_3CN at 70 °C for 1 h, Togni-II reagent (1.5 equiv) was added at room temperature for 2 h to afford trifluoromethylated product **6a** in 91% yield (entry 1). Silyl enol ethers **5b**—**d** generated *in situ* from phenacyl bromides with

electron–donating and –withdrawing substituents at the *para*-position of the aromatic ring readily reacted with Togni–II reagent to give the corresponding trifluoromethylated products **6b**—**d** in excellent yields in all cases (entries 2—4). Formation of silyl enol ether **5e** required a longer reaction time (*vide supra*), but the one-pot trifluoromethylation proceeded to form **6e** in 84% yield (entry 5). In contrast, *in situ*-generated trisubstituted silyl enol ethers **5f** and **5j** as well as tetrasubstituted silyl enol ether **5h** resulted relatively in lower yields of trifluoromethylated products **6f**, **6j**, and **6h** (81%, 67%, and 56%), respectively (entries 6—8).

Table 3. Substrate scope for one–pot reaction of silyl enol ether formation followed by trifluoromethylation of α–bromo carbonyls.[a]



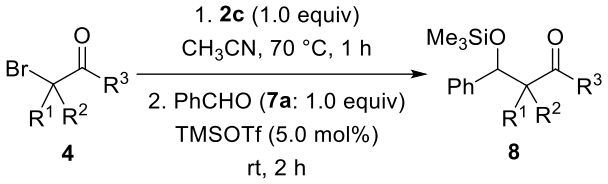
entry	product	yield [%]
1		91 (**6a**, R^3 = Ph)
2		93 (**6b**, R^3 = 4-$MeOC_6H_4$)
3		91 (**6c**, R^3 = 4-MeC_6H_4)
4		92 (**6d**, R^3 = 4-ClC_6H_4)
5		84 (**6e**, R^3 = ^{t}Bu)[b,c]
6		81 (**6f**, R^1 = Me, R^2 = H)
7		56 (**6h**, R^1 = R^2 = Me)[d]
8		67 (**6j**)

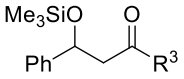
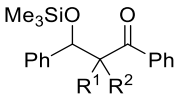
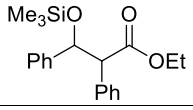
[a]Reaction conditions: **4** (1.0 equiv, 0.40 mmol), **2c** (1.0 equiv, 0.40 mmol), in CH_3CN at 70 °C for 1 h, then Togni-II reagent (1.5 equiv, 0.60 mmol) was added at rt and stirred for 2 h. [b]Silyl enol ether formation reaction was performed for 24 h. [c]Yield was measured by ^{1}H NMR spectroscopy. [d]Second step was performed for 18 h at rt.

The one-pot silyl enol ether formation was applied to the Mukaiyama-Aldol reaction in the presence of a Lewis acid catalyst, and results are provided in Table 4. The one-pot mixture of

phenacyl bromide (**4a**-**Br**) and its derivatives having methoxy, methyl, and chloro substituents at the *para*-position (**4b**—**d**) and **2c** at 70 °C for 1 h was quenched by adding benzaldehyde (**7a**) in the presence of trimethylsilyl triflate (Me_3SiOTf, 5 mol%) at room temperature for 2 h to give the aldol products **8aa**—**da** in excellent yields (entries 1—4). *In situ*-generated silyl enol ether **5e** bearing a bulky ^{t}Bu group on the carbonyl carbon also reacted with **7a** to selectively afford **8ea** in 93% yield (entry 5). Sterically hindered tri- and tetrasubstituted silyl enol ethers from **4f**, **4h**, and **4j** produced the corresponding β-silyloxycarbonyl products **8fa**, **8ha**, and **8ja** in 92%, 89%, and 91% yields, respectively (entries 6—8), in which **8fa** and **8ja** was obtained as diastereomeric mixtures in 60:40 and 67:33 ratios.[27] For the transformation of **4j**, *in situ*-generated Me_3SiBr promoted the reaction. A variety of aryl aldehydes were also applied for the one-pot reaction with **4j** as the α-bromoester without TMSOTf (Table 5). Both of electron-rich and –defficient aldehydes **7c** and **7e** as well as sterically bulky aldehyde **7f** afforded **8jc**, **8je** , and **8jf** in excellent yield as a mixture of two diastereomers in approximately 7:3 to 8:2 ratio (entries 1-3). When heteroaryl substituted aldehydes **7g**, **7h**, and **7i** were used, the corresponding products **8jg**—**ji** were formed in good to excellent yields (entries 4-6).

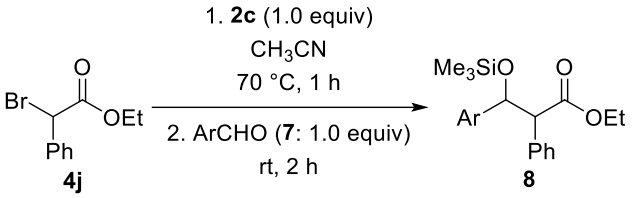
Table 4. Substrate scope for one–pot reaction of silyl enol ether formation and followed by Mukaiyama-Aldol reaction of α–bromo carbonyls.[a]

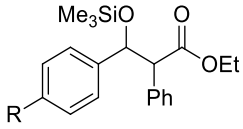
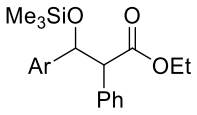


entry	product	yield (%) [d.r.][b]
1		90 (**8aa**, R^3 = Ph)
2		94 (**8ba**, R^3 = 4-$MeOC_6H_4$)
3		91 (**8ca**, R^3 = 4-MeC_6H_4)
4		92 (**8da**, R^3 = 4-ClC_6H_4)
5		93 (**8ea**, R^3 = ^{t}Bu)[c]
6		92 (**8fa**, R^1 = Me, R^2 = H) [60:40]
7		89 (**8ha**, R^1 = R^2 = Me)
8		91 (**8ja**) [67:33][d]

[a]Reaction conditions: **4** (1.0 equiv, 0.40 mmol), **2c** (0.40 mmol), in CH_3CN at 70 °C for 1 h, then **7a** (1.0 equiv, 0.40 mmol) and Me_3SiOTf (0.05 equiv, 0.02 mmol) added at rt and stirred for 2 h. [b]Diastereomeric ratios were measured by ^1H NMR spectroscopy. [c]Silyl enol ether formation reaction was performed for 24 h. [d]No Me_3SiOTf was added.

Table 5. Substrate scope of aldehydes for one–pot silyl enol ether formation and Mukaiyama–Aldol reaction.[a]

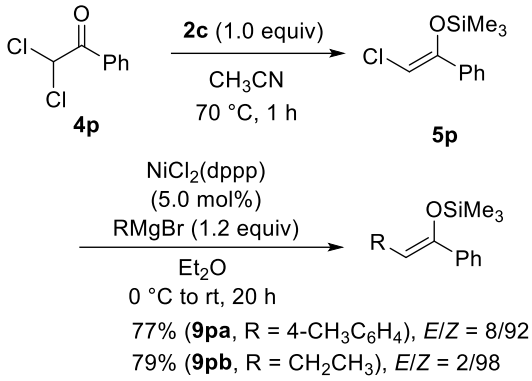


entry	product	yield (%) [d.r.][b]
1		84 (**8jc**, R = NMe_2) [68:32]
2		93 (**8je**, R = CF_3) [61:39]
3		93 (**8jf**, Ar = 2,4,6-Me_3Ph) [81:19]
4		71 (**8jg**, Ar = 2-Mepy) [53:47]
5		89 (**8jh**, Ar = thienyl) [65:35]
6		94 (**8ji**, Ar = furyl) [62:38]

[a]Reaction conditions: **4j** (1.0 equiv, 0.40 mmol), **2c** (1.0 equiv, 0.40 mmol), in CH_3CN at 70 °C for 1 h, and then **7** (1.0 equiv, 0.40 mmol) was added at room temperature and stirred for 2 h. [b]Diastereomeric ratios were measured by ^{1}H NMR spectroscopy in the presence of mesitylene as an internal standard.

We performed the derivatization of C(sp^2)—X bond containing silyl enol ether **5p**, obtained from vicinal dichloro compound **4p**, by a Kumada-Tamao coupling reaction (Scheme 1).[12] The reaction between *in situ*-generated silyl enol ether **5p** and Grignard reagents (*p*-tolylmagnesium bromide and ethylmagnesium bromide) in the presence of the Ni catalyst produced the corresponding C—C coupled products **9pa** and **9pb** in high yield and maintained the high *Z*-selectivity.

Scheme 1. One-pot silyl enol ether formation and Kumada-Tamao coupling reaction of 2,2-dichloroacetophenone.



In conclusion, we demonstrated the formation of silyl enol ethers by a simple treatment of α–halo carbonyl compounds with **2c**, from which Me_3SiX and tetramethylpyrazine were easily removed. Additionally, a one-pot mixture of halo carbonyls and **2c** was successfully applied to trifluoromethylation and Mukaiyama-Aldol reactions. Application of **1—3** as versatile transition metal-free reducing reagents are ongoing.

EXPERIMENTAL SECTION

General information. All reactions and manipulations involving air- and moisture-sensitive organometallic compounds were operated using the standard Schlenk or glovebox techniques under argon atmosphere. Organosilicon reductants **1**, **2a**—**c**, and **3** were prepared according to the modified procedure of the literature by replacing potassium metal by sodium metal except for the synthesis of **2c** that needed the use of potassium.[13] Anhydrous solvents were purchased from Kanto Chemical, and further purified by pass through activated alumina under positive argon pressure as described by Grubbs *et al*.[14] Deuterated solvents (CD_3CN, toluene-d_8, THF-d_8, C_6D_6) and DMF were distilled over CaH_2, degassed, and stored under Ar-filled glovebox. 1-Trifluoromethyl-1,2-benziodoxol-3(1*H*)-one (Togni-II Reagent) was purchased from Tokyo Chemical Industry CO. LTD. (TCI) and used without further purification (the substance contains 60% diatomaceous earth). Other chemicals were purchased and used without further purification. α-Halocarbonyl compounds of thioesters **4l,m,n** and *N*,*N*-diethylamides **4o,r,s** were synthesized according to the literature procedures as described below.[15,16] ^{1}H NMR (400 MHz), $^{13}C\{^1H\}$ NMR (100 MHz), and $^{19}F\{^1H\}$ NMR (376 MHz) spectra were measured on Bruker Avance III-400 spectrometers. All ^{1}H NMR chemical shifts were recorded in ppm (δ) referenced to the chemical shifts of residual solvent resonances ($CHCl_3$ was used as internal standard, δ 7.26 or CH_3CN was used as internal standard, δ 1.97). All $^{13}C\{^1H\}$ NMR chemical shifts were recorded in ppm (δ) relative to carbon resonances in $CDCl_3$ at δ 77.16 and or CD_3CN at δ 118.26. Mass spectra were obtained on Bruker Daltonics MicroTOF II-HB and JEOL JMS 700. Flash column chromatography was performed by using silica gel 60 (0.040–0.0663 nm, 230–400 mesh ASTM).

General procedure for the synthesis of α-bromo thioesters.[15] In an argon filled Schlenk tube equipped with a magnetic stir bar, 2-bromoacetyl bromide or its mono- and dimethylated

derivatives (1.0 equiv, 14.86 mmol) was dissolved in CH_2Cl_2 (10 mL). *p*-Tolylthiophenol (0.80 equiv, 11.89 mmol) was added at 0°C. NEt_3 (1.5 equiv, 22.29 mmol) was added further dropwise to the reaction mixture in a period of 15 minutes at 0°C. The resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with 1M HCl, and extracted with CH_2Cl_2 (50 mL). The combined organic layer was washed with saturated $NaHCO_3$ and brine solution, and then dried over anhydrous Na_2SO_4. The organic layer was evaporated and crude product was purified by flash column chromatography on silica gel by using hexane as eluent to give corresponding α-bromo thioesters, *S*-(*p*-tolyl) 2-bromoethanethioate (**4l**), *S*-(*p*-tolyl) 2-bromopropanethioate (**4m**), and *S*-(*p*-tolyl) 2-bromo-2-methylpropanethioate (**4n**).

General procedure for the synthesis of α-bromo amides.[16] In an argon filled Schlenk tube equipped with a magnetic stir bar, diethylamine (2.0 equiv, 29.72 mmol) and anhydrous diethyl ether (15 mL) were added and the Schlenk tube was placed in an ice bath at 0°C. 2-bromoacetyl bromide or its mono- and dimethylated derivatives (1.0 equiv, 14.86 mmol) was added dropwise to the reaction mixture in a period of 15 minutes, and the mixture was allowed to warm up to room temperature and stirred for 4 h. The resulting suspension was filtered off and the yellowish filtrate was washed with saturated ammonium chloride (20 mL), saturated sodium bicarbonate (20 mL), and a saturated brine solution (20 mL). After drying with magnesium sulfate ($MgSO_4$), the organic layer was evaporated and crude product was purified by flash column chromatography on silica gel by using hexane and ethyl acetate as eluent to afford corresponding α-bromo amides, 2-bromo-*N*,*N*-diethylacetamide (**4r**), 2-bromo-*N*,*N*-diethylpropanamide (**4s**), 2-bromo-*N*,*N*-diethyl-2-methylpropanamide (**4o**).

General procedure for the formation of silyl enol ethers from α-halo carbonyls. To a solution of reductant **2c** or **3** (1.0 equiv, 0.40 mmol) in acetonitrile (1.2 mL), α-halo carbonyl

compound **4** (1.0 equiv, 0.40 mmol) was added under argon atmosphere. The reaction was heated at 70 °C for 1 h. The clean formation of silyl enol ether was observed, and the yield was determined by ^{1}H NMR spectroscopy by using mesitylene as an internal standard. Stable silyl enol ethers were isolated either by column chromatography or by evaporation of the volatile for long time.

α-Silylation of α-bromo amides by organosilicon reductant 3. To a solution of reductant **3** (1.0 equiv, 0.40 mmol) in acetonitrile (1.2 mL), α-bromo amides **4r** or **4s** (1.0 equiv, 0.40 mmol) were added under argon atmosphere. The mixture was stirred at room temperature for 1 h. The clean formations of α-silylated amides, *N*,*N*-diethyl-2-(trimethylsilyl)acetamide (**10r**) and *N*,*N*-diethyl-2-(trimethylsilyl)propanamide (**10s**), were observed from ^{1}H NMR spectroscopy, and we did not find any *O*-silylated products. The reaction mixture was evaporated and was directly purified by flash column chromatography on silica gel using ethyl acetate and hexane as eluent. The products contain small amount of 4,4'-bipyridine, even after column chromatography.

General procedure for the trifluoromethylation of α-halo carbonyls. To a solution of reductant **2c** (1.0 equiv, 0.40 mmol) in acetonitrile (1.2 mL), α-bromo carbonyl compounds **4** (1.0 equiv, 0.40 mmol) was added under argon atmosphere. The mixture was heated at 70 °C for 1 h followed by addition of Togni-II reagent (474.0 mg, the substance contains 60% diatomaceous earth, 1.5 equiv, 0.60 mmol), and the reaction was stirred at room temperature for 2 h. The reaction mixture was filtered through a plug of silica to remove insoluble materials and eluted with ethyl acetate. The solvent was evaporated, and the mixture was purified by flash column chromatography on silica gel by using dichloromethane, ethyl acetate and hexane as eluent.

General procedure for the Mukaiyama-Aldol reaction of α-halo carbonyls. To a solution of reductant **2c** (1.0 equiv, 0.40 mmol) in acetonitrile (1.2 mL), α-bromo carbonyl compounds **4** (1.0 equiv, 0.40 mmol) was added under argon atmosphere. The mixture was stirred at 70 °C for 1 h followed by addition of aldehydes (1.0 equiv, 0.40 mmol) and TMSOTf (4.5 mg, 0.05 equiv, 0.02 mmol) if mentioned in Table 4. The resultant reaction mixture was stirred at room temperature for 2 h. The mixture was directly purified by flash column chromatography on silica gel using ethyl acetate and hexane as eluent.

Application for one-pot Kumada-Tamao Coupling. To a solution of reductant **2c** (1.0 equiv, 0.40 mmol) in acetonitrile (1.2 mL), **4n** (1.0 equiv, 0.40 mmol) was added under argon atmosphere. The mixture was stirred at 70 °C for 1 h, and then, the solvent was evaporated under vacuum. Under inert atmosphere $NiCl_2$(dppp) (0.05 equiv, 0.02 mmol) and diethyl ether (2.0 mL) were added. The reaction mixture was kept in an ice bath with slow addition of the corresponding Grignard reagent (1.2 equiv, 0.48 mmol) over 15 minutes. The reaction mixture was turned to brown. After competition of the addition, the mixture was stirred at 0°C for 30 minutes and then warned to room temperature for 20 h. After that, dichloromethane (20 mL) was added into the reaction mixture and the organic part was evaporated. The crude mixture was purified by flash column chromatography on silica gel by using hexane as eluent.

Spectral Data for Organic Compounds.

For thioesters: *S*-(*p*-Tolyl) 2-bromoethanethioate[15] (**4l**). Purified by flash column chromatography (silica gel, hexane); Yellow oil; IR (neat KBr, ν/cm^{-1}) 2919, 2851, 1790, 1701, 1655, 1637, 1618, 662; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.13 (s, 2H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 191.4, 140.4, 134.5, 130.3, 123.4, 33.2, 21.4; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_9H_{10}OBrS$:

244.9630, found 244.9636. *S*-(*p*-Tolyl) 2-bromopropanethioate (**4m**). Purified by flash column chromatography (silica gel, hexane); Yellow oil; IR (neat KBr, ν/cm^{-1}) 2960, 2921, 2847, 1702, 1685, 1655, 723, 518; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.64 (q, *J* = 6.8 Hz, 1H), 2.41 (s, 3H), 1.92 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 195.2, 140.3, 134.6, 130.3, 123.5, 47.7, 22.2, 21.5; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_{10}H_{12}OBrS$: 258.9787, found 258.9793. *S*-(*p*-Tolyl) 2-bromo-2-methylpropanethioate (**4n**). Purified by flash column chromatography (silica gel, hexane); Red oil; IR (neat KBr, ν/cm^{-1}) 2987, 2924, 2858, 1815, 1693, 1598, 711, 647, 549; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.05 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 198.7, 140.0, 134.9, 130.2, 124.4, 64.2, 31.6, 21.4; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_{11}H_{14}OBrS$: 272.9943, found 272.9940.

For *N*,*N*-diethylamides:

2-Bromo-*N*,*N*-diethyl-2-methylpropanamide[16] (**4o**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/10); Yellowish oil; IR (neat KBr, ν/cm^{-1}) 2974, 2925, 2851, 1637, 1277, 1126, 1107, 793; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 3.67–3.34 (br, 4H), 1.92 (s, 6H), 1.15 (br, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 169.6, 57.4, 32.9; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_8H_{17}ONBr$: 222.0488, found 222.0484.

2-Bromo-*N*,*N*-diethylacetamide[17] (**4r**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/10); Yellowish oil; IR (neat KBr, ν/cm^{-1}) 2977, 2935, 2875, 1646, 1285, 1216, 1097, 705, 610; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 3.81 (s, 2H), 3.35 (q, *J* = 6.8 Hz, 4H), 1.22 (t, *J* = 6.8 Hz, 3H), 1.10 (t, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 166.0, 43.0, 40.6, 26.5, 14.4, 12.6; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_6H_{13}ONBr$: 194.0175, found 194.0183.

2-Bromo-*N*,*N*-diethylpropanamide[18] (**4s**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/10); Yellowish oil; IR (neat KBr, ν/cm^{-1}) 2976, 2933, 2872, 1649, 1263, 1221, 1135, 1086, 793, 604; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 4.50 (qd, *J* = 6.4 Hz, *J* = 0.6 Hz, 1H), 3.52–3.45 (m, 2H), 3.26–3.18 (m, 2H), 1.78 (dd, *J* = 6.4 Hz, *J* = 1.0 Hz, 3H), 1.21 (td, *J* = 7.2 Hz, *J* = 1.0 Hz, 3H), 1.10 (td, *J* = 7.2 Hz, *J* = 1.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 168.5, 42.3, 40.9, 38.6, 21.9, 14.7, 12.5; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_7H_{15}ONBr$: 208.0332, found 208.0337.

For isolated silyl enol ethers:

Trimethyl((1-(*p*-tolyl)vinyl)oxy)silane[19,20] (**5c**). The crude reaction mixture was kept into high vacuum at 30 °C for 2 h to remove the reaction solvent acetonitrile and the byproducts trimethylsilyl bromide and Me_4-pyrazine. Yellow oil (75 mg, 91% yield); IR (neat KBr, ν/cm^{-1}) 2960, 2922, 2958, 1685, 1617, 1183, 1111, 1012; ^{1}H NMR (400 MHz, CD_3CN, 30 °C) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 4.95 (d, *J* = 1.2 Hz, 1H), 4.43 (d, *J* = 1.2 Hz, 1H), 2.35 (s, 3H), 0.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 30 °C) δ 156.7, 139.3, 135.7, 129.8, 126.1, 91.2, 21.2, 0.1; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_{12}H_{19}OSi$: 207.1200, found 207.1205.

((1-(4-Chlorophenyl)vinyl)oxy)trimethylsilane[20] (**5d**). The crude reaction mixture was kept into high vacuum at 30 °C for 2 h to remove the reaction solvent acetonitrile and the byproducts trimethylsilyl bromide and Me_4-pyrazine. Yellow oil (82 mg, 90% yield); IR (neat KBr, ν/cm^{-1}) 2960, 2918, 2847, 1685, 1655, 1637, 1618, 1105, 1012, 753, 553; ^{1}H NMR (400 MHz, CD_3CN, 30 °C) δ 7.61 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 1H), 5.00 (d, *J* = 1.8 Hz, 1H), 4.51 (d, *J* = 1.8 Hz, 1H), 0.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 30 °C) δ 155.5, 137.3, 134.6,

129.2, 127.8, 92.5, 0.1; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_{11}H_{16}ClOSi$: 227.0653, found 227.0667.

(Trimethyl((2-methyl-1-phenylprop-1-en-1-yl)oxy)silane[22] (**5h**). Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/5); Colorless oil (81 mg, 92% yield); IR (neat KBr, ν/cm^{-1}) 2918, 2847, 1699, 1685, 1655, 1637, 1094, 1023; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.36–7.24 (m, 5H), 1.82 (s, 3H), 1.71 (s, 3H), 0.01 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 143.7, 139.2, 129.3, 127.8, 127.2, 113.0, 19.9, 18.4, 0.5; HRMS (FAB$^+$, *m/z*): $[M]^+$ calculated for $C_{13}H_{20}OSi$: 220.1278, found 220.1282.

(*Z*)-((1-Ethoxy-2-phenylvinyl)oxy)trimethylsilane[21] (**5j**). The crude reaction mixture was kept into high vacuum at 30 °C for 2 h to remove the reaction solvent acetonitrile and the byproducts trimethylsilyl bromide and Me_4-pyrazine. Colorless oil (83 mg, 88% yield); IR (neat KBr, ν/cm^{-1}) 3028, 2979, 2900, 1699, 1685, 1648, 1599, 1158, 1059; NMR spectroscopic data for the *Z*-isomer (major) are as follows: ^{1}H NMR (400 MHz, CD_3CN, 30 °C) δ 7.43 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 4.75 (s, 1H), 4.07 (q, *J* = 7.0 Hz, 2H), 1.32 (t, *J* = 7.0 Hz, 3H), 0.33 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 155.5, 138.2, 129.12, 129.09, 127.6, 124.7, 87.2, 63.6, 15.5, -0.05. NMR spectroscopic data for the *E*-isomer (minor) are as follows: Selected peak for ^{1}H NMR (400 MHz, CD_3CN, 30 °C) δ 4.67 (s, 1H), 3.92 (q, *J* = 7.0 Hz, 2H), 1.34 (t, *J* = 7.0 Hz, 3H), 0.31 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 157.9, 138.7, 130.4, 129.5, 128.0, 127.4, 124.4, 80.2, 64.9, 14.9, 0.7; HRMS (FAB$^+$, *m/z*): $[M]^+$ calculated for $C_{13}H_{20}O_2Si$: 236.1233, found 236.1232.

For trifluoromethylated products:

3,3,3-Trifluoro-1-phenylpropan-1-one[23,24] (**6a**). Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/5). White solid (69 mg, 91% yield); mp = 33—36°C; IR (neat KBr,

ν/cm^{-1}) 1684, 1419, 1373, 1262, 1227, 1098, 854, 758, 624, 592 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 3.80 (q, *J* = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 189.8 (q, *J* = 2.3 Hz), 136.0, 134.3, 129.1, 128.5, 124.2 (q, *J* = 277 Hz), 42.2 (q, *J* = 28.3 Hz); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C) δ –62.04; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_9H_7F_3O$: 188.0449, found 188.0448.

3,3,3-Trifluoro-1-(4-methoxyphenyl)propan-1-one[23,24] (**6b**). Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/4). Yellow solid (81 mg, 93% yield); mp = 41—42°C; IR (neat KBr, ν/cm^{-1}) 2974, 2945, 1683, 1600, 1513, 1458, 1370, 1279, 1236, 1114, 996, 918, 835, 781, 591, 532 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.91 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.73 (q, *J* = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 188.2 (q, *J* = 2.4 Hz), 164.5, 130.9, 129.1, 124.3 (q, *J* = 277 Hz), 114.2, 55.7, 41.9 (q, *J* = 28 Hz); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30°C) δ –61.97; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{10}H_9F_3NaO_2$: 241.0452, found 241.0457.

3,3,3-Trifluoro-1-(p-tolyl)propan-1-one[23,24] (**6c**). Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/4). White solid (74 mg, 91% yield); mp = 54—55°C; IR (neat KBr, ν/cm^{-1}) 1686, 1605, 1416, 1370, 1266, 1131, 1100, 809, 657, 590, 529 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.78 (q, *J* = 10.0 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 189.4 (q, *J* = 2.5 Hz), 145.4, 133.6, 129.7, 128.6, 124.2 (q, *J* = 277 Hz), 42.1 (q, *J* = 28 Hz), 21.7; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C) δ –62.04; HRMS (ESI, *m/z*): $[M + Na]^+$ calculated for $C_{10}H_9F_3NaO$: 225.0503, found 225.0516.

1-(4-Chlorophenyl)-3,3,3-trifluoropropan-1-one[24] (**6d**). Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/4). White solid (82 mg, 92% yield); mp = 55—56°C; IR (neat KBr, ν/cm^{-1}) 1695, 1590, 1402, 1371, 1274, 1226, 1135, 1100, 999, 856, 821, 729, 639 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 3.77 (q, *J* = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 188.7 (q, *J* = 2.5 Hz), 141.0, 134.3, 129.9, 129.5, 124.0 (q, *J* = 277.1 Hz), 42.3 (q, *J* = 28.5 Hz); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C) δ –62.01; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_9H_6ClF_3O$: 222.0059, found 222.0053.

1,1,1-Trifluoro-4,4-dimethylpentan-3-one[24] (**6e**). Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/10). (note: due to low boiling point difficult to purify from reaction solvent); Colorless liquid; IR (neat KBr, ν/cm^{-1}) 2959, 2924, 2854, 1727, 1463, 1367, 1258, 1058, 833, 797, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 3.33 (q, *J* = 10.0 Hz, 2H), 1.19 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 205.1 (q, *J* = 1.7 Hz), 124.2 (q, *J* = 277 Hz), 44.9, 40.0 (q, *J* = 27.9 Hz), 25.9; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C) δ –61.07.

3,3,3-Trifluoro-2-methyl-1-phenylpropan-1-one[23] (**6f**). Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/4). Colorless liquid (66 mg, 81% yield); IR (neat KBr, ν/cm^{-1}) 1693, 1597, 1462, 1382, 1223, 1170, 1133, 1001, 970, 687, 633 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 4.29–4.21 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 194.5 (q, *J* = 1.9 Hz), 135.9, 134.1, 129.0, 128.7, 125.5 (q, *J* = 280 Hz), 44.5 (q, *J* = 26.5 Hz), 11.8 (q, *J* = 2.8 Hz); ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 30 °C) δ –68.28; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{10}H_9F_3O$: 202.0605, found 202.0606.

1-(4-Methoxyphenyl)-2-(trifluoromethyl)pentan-1-one[25] (**6h**). Purified by flash column chromatography (silica gel, CH_2Cl_2/hexane = 1/5); Colorless liquid (48 mg, 56 % yield); IR (neat KBr, ν/cm^{-1}) 2993, 2953, 1687, 1597, 1474, 1446, 1400, 1312, 1264, 1197, 1128, 961, 705, 641 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 1.56 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 200.9, 138.3, 131.6, 129.2 (q, *J* = 276 Hz), 128.4, 127.8, 53.5 (q, *J* = 24.6 Hz), 20.9 (q, *J* = 2.5 Hz); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 30 °C) δ –72.63; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{11}H_{11}F_3O$: 216.0762, found 216.0760.

Ethyl 3,3,3-trifluoro-2-phenylpropanoate[25] (**6j**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25) (note: $PhCH_2CO_2Et$ present with the target compound as an impurity due to the product and $PhCH_2CO_2Et$ both has same R_f value); Colorless oil (62 mg, 67% yield); IR (neat KBr, ν/cm^{-1}) 2964, 2917, 2851, 1735, 1685, 1655, 1637, 1260, 1165, 1111, 1027; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.48–7.28 (m, 5H), 4.35–4.15 (m, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 171.7, 129.6, 129.4, 129.3, 129.0, 128.7, 125.2 (q, *J* = 278 Hz), 62.2, 55.7 (q, *J* = 28.6 Hz), 14.0; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 30 °C) δ –67.66.

For Mukaiyama-Aldol products:

1,3-Diphenyl-3-((trimethylsilyl)oxy)propan-1-one[26] (**8aa**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil (108 mg, 90% yield); IR (neat KBr, ν/cm^{-1}) 3023, 2957, 2917, 2854, 1686, 1595, 1449, 1251, 1096, 951, 843, 751, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.00–7.97 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49–7.43 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.30–7.28 (m, 1H), 5.41 (dd, *J* = 8.8 Hz, *J* = 4.0 Hz, 1H), 3.59 (dd, *J* = 15.5 Hz, *J* = 8.8 Hz, 1H), 3.06 (dd, *J* = 15.5 Hz, *J* = 4.0 Hz, 1H), 0.01 (s, 9H); $^{13}C\{^1H\}$ NMR

(100 MHz, $CDCl_3$, 30 °C) δ 198.6, 144.9, 137.8, 133.1, 128.6, 128.54, 128.47, 127.5, 125.9, 71.8, 49.8, 0.06; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{18}H_{22}O_2Si$: 298.1389, found 298.1388.

1-(4-Methoxyphenyl)-3-phenyl-3-((trimethylsilyl)oxy)propan-1-one (**8ba**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil (124 mg, 94% yield); IR (neat KBr, ν/cm^{-1}) 3027, 2957, 2900, 2840, 1676, 1601, 1509, 1260, 1169, 1094, 1028, 840, 700, 571 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.45–7.25 (m, 5H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.39 (dd, *J* = 8.8 Hz, *J* = 4.0 Hz, 1H), 3.89 (s, 3H), 3.53 (dd, *J* = 15.3 Hz, *J* = 8.8 Hz, 1H), 3.00 (dd, *J* = 15.3 Hz, *J* = 4.0 Hz, 1H), 0.01 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 197.1, 163.6, 145.0, 131.0, 130.9, 128.4, 127.4, 125.9, 113.7, 71.9, 55.6, 49.5, 0.07; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{19}H_{24}O_3Si$: 328.1495, found 328.1488.

3-Phenyl-1-(*p*-tolyl)-3-((trimethylsilyl)oxy)propan-1-one (**8ca**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil (113 mg, 91% yield); IR (neat KBr, ν/cm^{-1}) 3030, 2957, 2900, 1683, 1607, 1250, 1095, 942, 842, 750, 700, 570 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.38–7.34 (m, 2H), 7.30–7.24 (m, 3H), 5.41 (dd, *J* = 8.8 Hz, *J* = 4.0 Hz, 1H), 3.56 (dd, *J* = 15.5 Hz, *J* = 8.8 Hz, 1H), 3.03 (dd, *J* = 15.5 Hz, *J* = 4.0 Hz, 1H), 2.43 (s, 3H), 0.00 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 198.2, 145.0, 143.8, 135.3, 129.3, 128.7, 128.4, 127.4, 125.9, 71.8, 49.7, 21.7, 0.07; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{19}H_{24}O_2Si$: 312.1546, found 312.1543.

1-(4-Chlorophenyl)-3-phenyl-3-((trimethylsilyl)oxy)propan-1-one (**8da**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil (122 mg, 92% yield); IR (neat KBr, ν/cm^{-1}) 3031, 2957, 2900, 1687, 1590, 1399, 1251, 1092, 842, 757, 700, 557 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.45–7.42 (m, 4H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 5.37 (dd, *J* = 8.8 Hz, *J* = 3.8 Hz, 1H), 3.55 (dd, *J* = 15.4 Hz,

J = 8.8 Hz, 1H), 2.99 (dd, *J* = 15.4 Hz, *J* = 3.8 Hz, 1H), 0.02 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 197.5, 144.6, 139.6, 136.1, 130.0, 128.9, 128.5, 127.6, 125.8, 71.9, 49.7, 0.04; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{18}H_{21}ClO_2Si$: 332.0999, found 332.0990.

4,4-Dimethyl-1-phenyl-1-((trimethylsilyl)oxy)pentan-3-one (**8ea**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/50); Colorless oil (105 mg, 93% yield); IR (neat KBr, ν/cm^{-1}) 2964, 2914, 2868, 1707, 1610, 1543, 1477, 1365, 1251, 1070, 843, 751, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.38–7.31 (m, 5H), 5.30 (dd, *J* = 8.8 Hz, *J* = 4.0 Hz, 1H), 3.11 (dd, *J* = 16.2 Hz, *J* = 8.8 Hz, 1H), 2.53 (dd, *J* = 16.2 Hz, *J* = 4.0 Hz, 1H), 1.09 (s, 9H), 0.03 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 213.4, 145.0, 129.0, 128.4, 128.3, 127.3, 125.9, 71.3, 48.0, 44.3, 25.9, 0.15; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{16}H_{26}O_2Si$: 278.1702, found 278.1700.

2-Methyl-1,3-diphenyl-3-((trimethylsilyl)oxy)propan-1-one[27] (**8fa**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25), *syn*/*anti* mixture was obtained in a ratio of 60/40, which was determined by the integration of 5.03 and 4.90 ppm C*H*OSiMe_3 signals according to the literature; Colorless oil (115 mg, 92% yield); IR (neat KBr, ν/cm^{-1}) 3060, 3032, 2959, 2875, 1774, 1736, 1718, 1685, 1655, 1066; ^{1}H NMR spectroscopic data for the major diastereomer are as follows: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.09–7.12 (overlap with minor isomer) (m, 10H), 5.03 (d, *J* = 7.6 Hz, 1H), 3.88–3.79 (overlap with minor isomer) (m, 1H), 1.33 (d, *J* = 6.8 Hz, 3H), 0.02 (s, 9H); NMR spectroscopic data for the minor diastereomer are as follows: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.09–7.12 (overlap with major isomer) (m, 10H), 4.90 (d, *J* = 9.2 Hz, 1H), 3.88-3.79 (overlap with major isomer) (m, 1H), 0.89 (d, *J* = 6.8 Hz, 3H), –0.15 (s, 9H); Combined $^{13}C\{^{1}H\}$ NMR spectroscopic data for both diastereomers are as follows: $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 204.5, 203.0, 143.6, 143.1, 142.2, 138.5,

137.2, 132.7, 131.7, 129.8, 129.6, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.4, 127.2, 126.7, 78.5, 76.5, 50.2, 49.4, 14.7, 14.4, 0.02, -0.15; HRMS (FAB^+, *m/z*): $[M+H]^+$ calculated for $C_{19}H_{25}O_2Si$: 313.1618, found 313.1623.

2,2-Dimethyl-1,3-diphenyl-3-((trimethylsilyl)oxy)propan-1-one[28] (**8ha**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/20); Colorless oil (116 mg, 89% yield); IR (neat KBr, ν/cm^{-1}) 2918, 2851, 1774, 1736, 1718, 1701, 1685, 1655, 1637, 1161, 1077; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.45–7.28 (m, 8H), 5.23 (s, 1H), 1.22 (s, 3H), 1.11 (s, 3H), –0.08 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 211.4, 141.1, 140.7, 130.3, 128.3, 127.9, 127.6, 127.3, 80.1, 53.8, 24.2, 20.9, 0.07; HRMS (FAB^+, *m/z*): $[M+H]^+$ calculated for $C_{20}H_{27}O_2Si$: 327.1775, found 327.1782.

Ethyl 2,3-diphenyl-3-((trimethylsilyl)oxy)propanoate (**8ja**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/20); Colorless oil (125 mg 91% yield); IR (neat KBr, ν/cm^{-1}) 3031, 2958, 2901, 1733, 1496, 1455, 1370, 1251, 1157, 1088, 901, 842, 698, 557 cm^{-1}; NMR spectroscopic data for the major diastereomer are as follows: ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.49-7.03 (overlap with minor isomer) (m, 10H), 5.18 (d, *J* = 10.0 Hz, 1H), 4.34–4.26 (m, 1H), 4.19–4.11 (m, 1H), 3.83 (overlap with minor isomer) (d, 1H, *J* = 10.0 Hz), 1.31 (t, *J* = 6.8 Hz, 3H), 0.04 (s, 9H); NMR spectroscopic data for the minor diastereomer are as follows: ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.49-7.03 (overlap with major isomer) (m, 10H), 5.14 (d, *J* = 9.0 Hz, 1H), 3.97-3.87 (m, 2H), 3.84 (overlap with major isomer) (d, *J* = 9.0 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 3H), –0.23 (s, 9H); Combined $^{13}C\{^1H\}$ NMR spectroscopic data for both diastereomers are as follows: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 172.8, 171.8, 142.9, 141.8, 136.9, 135.2, 129.4, 129.0, 128.3, 128.2, 128.1, 127.8, 127.5, 127.4, 127.1, 127.0, 78.2,

77.2, 62.1, 61.5, 60.9, 60.5, 14.4, 14.0, 0.14, –0.27; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{20}H_{26}O_3Si$: 342.1651, found 342.1647.

Ethyl 3-(4-(dimethylamino)phenyl)-2-phenyl-3-((trimethylsilyl)oxy)propanoate[10] (**8jc**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil; IR (neat KBr, ν/cm^{-1}) 3031, 2956, 2917, 2850, 2801, 1732, 1615, 1523, 1446, 1350, 1249, 1158, 1071, 842, 698, 562 cm^{-1}; ^1H NMR spectroscopic data for the major diastereomer are as follows: ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.50–7.16 (overlap with minor isomer) (m, 5H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 5.10 (d, *J* = 10.2 Hz, 1H), 4.30-4.25 (overlap with minor isomer) (m, 1H), 4.16–4.12 (m, 1H), 3.84 (overlap with minor isomer) (d, *J* = 10.2 Hz, 1H), 2.88 (s, 6H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.02 (s, 9H); ^1H NMR spectroscopic data for the minor diastereomer are as follows: ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.50-7.16 (overlap with major isomer) (m, 5H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 5.05 (d, *J* = 9.2 Hz, 1H), 4.30–4.25 (overlap with minor isomer) (m, 1H), 3.96-3.88 (m, 1H), 3.84 (overlap with major isomer) (d, *J* = 9.2 Hz, 1H), 2.95 (s, 6H), 1.01 (t, *J* = 7.2 Hz, 3H), –0.24 (s, 9H); Combined $^{13}C\{^1H\}$ NMR spectroscopic data for both diastereomers are as follows: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 173.1, 172.0, 150.3, 149.9, 132.6, 129.1, 128.7, 128.2, 128.1, 127.8, 127.4, 127.2, 112.2, 111.9, 111.4, 77.9, 76.9, 62.1, 61.6, 60.7, 60.4, 40.6, 40.1, 14.4, 14.0, 0.21, –0.18; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{22}H_{31}NO_3Si$: 385.2073, found 385.2076.

Ethyl 2-phenyl-3-(4-(trifluoromethyl)phenyl)-3-((trimethylsilyl)oxy)propanoate[10] (**8je**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil; IR (neat KBr, ν/cm^{-1}) 3033, 2960, 2903, 1733, 1618, 1371, 1325, 1252, 1164, 1068, 1018 cm^{-1}; ^1H NMR spectroscopic data for the major diastereomer are as follows: ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.60-7.10 (overlap with minor isomer) (m, 9H), 5.23 (d, *J* = 10.0 Hz, 1H), 4.34–4.26 (m, 1H),

4.21–4.11 (m, 1H), 3.77 (overlap with minor isomer) (d, *J* = 10.0 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.05 (s, 9H); ^{1}H NMR spectroscopic data for the minor diastereomer are as follows: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.60-7.10 (overlap with major isomer) (m, 9H), 5.20 (d, *J* = 8.8 Hz, 1H), 3.99–3.89 (m, 2H), 3.79 (overlap with major isomer) (d, *J* = 8.8 Hz, 1H), 1.00 (t, *J* = 7.2 Hz, 3H), –0.22 (s, 9H); Combined ^{13}C{^{1}H} NMR spectroscopic data for both diastereomers are as follows: ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 172.4, 171.6, 147.1, 146.1, 136.3, 134.7, 129.9, 129.6, 129.43, 129.38, 128.9, 128.7, 128.5, 128.3, 127.8, 127.6, 127.4, 127.2, 125.1, 124.8, 77.5, 76.5, 62.0, 61.3, 61.0, 60.8, 14.4, 13.9, –0.10, –0.32; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{21}H_{25}F_3O_3Si$: 410.1525, found 410.1521.

Ethyl 3-mesityl-2-phenyl-3-((trimethylsilyl)oxy)propanoate[10] (**8jf**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless; IR (neat KBr, ν/cm^{-1}) 3031, 2958, 2917, 2868, 1734, 1611, 1455, 1370, 1250, 1158, 1074, 842 cm^{-1}; ^{1}H NMR spectroscopic data for the major diastereomer are as follows: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.40–7.10 (overlap with minor isomer) (m, 5H), 6.81 (s, 1H), 6.46 (s, 1H), 5.59 (d, *J* = 10.6 Hz, 1H), 4.37–4.16 (overlap with minor isomer) (m, 3H), 2.68 (s, 3H), 2.19 (s, 3H), 1.75 (s, 3H), 1.34 (t, 3H, *J* = 7.2 Hz), 0.01 (s, 9H); ^{1}H NMR spectroscopic data for the minor diastereomer are as follows: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.40–7.10 (overlap with major isomer) (m, 3H), 6.84 (s, 1H), 6.78 (s, 1H), 5.50 (d, *J* = 9.6 Hz, 1H), 4.37–4.16 (overlap with major isomer) (m, 1H), 2.64 (s, 3H), 2.52 (s, 3H), 2.26 (s, 3H), 0.88 (t, *J* = 7.2 Hz, 3H), –0.28 (s, 9H); Combined ^{13}C{^{1}H} NMR spectroscopic data for both diastereomers are as follows: ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 172.9, 171.8, 138.0, 137.4, 136.7, 136.4, 135.8, 135.0, 134.8, 133.7, 131.1, 130.7, 129.4, 129.3, 129.0, 128.8, 128.7, 128.5, 128.2, 128.0, 127.35, 127.33, 127.2,

74.2, 73.9, 60.7, 60.3, 58.1, 58.0, 21.0, 20.95, 20.91, 20.86, 20.6, 20.5, 14.4, 13.7, 0.04, –0.43; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{23}H_{32}O_3Si$: 384.2121, found 384.2128.

Ethyl 3-(6-methylpyridin-2-yl)-2-phenyl-3-((trimethylsilyl)oxy)propanoate[10] (**8jg**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil; IR (neat KBr, ν/cm^{-1}) 3031, 2958, 2921, 2851, 1734, 1593, 1456, 1251, 1156, 1089, 843, 751, 699, 638 cm^{-1}; ^1H NMR spectroscopic data for the major diastereomer are as follows: ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.39 (t, *J* = 7.6 Hz, 1H), 7.33-7.12 (overlap with minor isomer) (m, 6H), 6.89 (d, *J* = 7.6 Hz, 1H), 5.28 (d, *J* = 9.6 Hz, 1H), 4.30–4.22 (m, 1H), 4.14–4.05 (overlap with minor isomer) (m, 2H) 4.12 (overlap with minor isomer) (d, *J* = 9.6 Hz, 1H), 2.40 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.02 (s, 9H); ^1H NMR spectroscopic data for the minor diastereomer are as follows: ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.44 (t, *J* = 7.6 Hz, 1H), 7.33–7.12 (m, 4H), 6.99–6.97 (m, 3H), 5.39 (d, *J* = 6.8 Hz, 1H), 4.14–4.05 (overlap with minor isomer) (m, 3H), 2.56 (s, 3H), 1.14 (t, *J* = 6.8 Hz, 3H), –0.08 (s, 9H); Combined $^{13}C\{^1H\}$ NMR spectroscopic data for both diastereomers are as follows: $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 30 °C) δ 172.5, 172.0, 161.3, 160.0, 157.5, 157.3, 136.4, 136.3, 136.0, 135.2, 130.1, 129.1, 128.2, 127.8, 127.3, 127.2, 121.9, 121.8, 118.9, 118.5, 78.7, 77.3, 60.8, 60.7, 60.1, 58.8, 24.5, 24.3, 14.3, 14.2, 0.14, 0.00; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{20}H_{27}NO_3Si$: 357.1760, found 357.1758.

Ethyl 2-phenyl-3-(thiophen-2-yl)-3-((trimethylsilyl)oxy)propanoate[10] (**8jh**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil; IR (neat KBr, ν/cm^{-1}) 3032, 2959, 2896, 2847, 1732, 1455, 1370, 1251, 1157, 1077, 844, 698, 542 cm^{-1}; ^1H NMR spectroscopic data for the major diastereomer are as follows: ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.24–7.10 (m, 5H), 7.11 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 6.70 (dd, *J* = 5.0 Hz, *J* = 3.2 Hz, 1H), 6.44 (d, *J* = 3.2 Hz, 1H), 5.48 (d, *J* = 10.2 Hz, 1H), 4.32–4.24 (m, 1H), 4.19–4.11 (m, 1H), 3.89

(overlap with minor isomer) (d, *J* = 10.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.10 (s, 9H); ^{1}H NMR spectroscopic data for the minor diastereomer are as follows: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.48 (dt, *J* = 6.8 Hz, *J* = 1.6 Hz, 1H), 7.38–7.28 (m, 5H), 7.01 (d, *J* = 3.2 Hz, 1H), 6.94 (dd, *J* = 3.2 Hz, *J* = 1.6 Hz, 1H), 5.44 (d, *J* = 9.2 Hz, 1H), 4.08–3.95 (m, 2H), 3.87 (overlap with major isomer) (d, *J* = 9.2 Hz, 1H), 1.08 (t, *J* = 6.8 Hz, 3H), 0.20 (s, 9H); Combined ^{13}C{^{1}H} NMR spectroscopic data for both diastereomers are as follows: ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 172.4, 171.7, 147.4, 145.9, 136.6, 135.2, 129.3, 128.8, 128.4, 128.3, 127.64, 127.59, 126.3, 126.0, 124.73, 124.70, 124.66, 124.5, 74.0, 73.0, 62.5, 62.1, 60.9, 60.7, 14.3, 14.0, 0.03, –0.39; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{18}H_{24}O_3SSi$: 348.1215, found 348.1216.

Ethyl 3-(furan-2-yl)-2-phenyl-3-((trimethylsilyl)oxy)propanoate[10] (**8ji**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/25); Colorless oil; IR (neat KBr, ν/cm^{-1}) 3032, 2959, 2903, 1734, 1603, 1497, 1455, 1371, 1251, 1154, 1076, 844, 698, 598, 537 cm^{-1}; ^{1}H NMR spectroscopic data for the major diastereomer are as follows: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.47–7.18 (overlap with minor isomer) (m, 6H), 6.12 (dd, *J* = 3.2 Hz, *J* = 1.8 Hz, 1H), 5.95 (dd, *J* = 3.2 Hz, *J* = 0.4 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 4.32–3.97 (overlap with minor isomer) (m, 3H) 4.18 (overlap with minor isomer) (d, *J* = 10.4 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.07 (s, 9H); ^{1}H NMR spectroscopic data for the minor diastereomer are as follows: ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.47–7.18 (overlap with minor isomer) (m, 6H), 6.33 (dd, *J* = 3.2 Hz, *J* = 1.8 Hz, 1H), 6.28 (d, *J* = 3.2 Hz, 1H), 5.20 (d, *J* = 9.6 Hz, 1H), 4.32–3.97 (overlap with major isomer) (m, 3H) 4.09 (overlap with minor isomer) (d, *J* = 9.6 Hz, 1H), 1.12 (t, *J* = 7.2 Hz, 3H), -0.18 (s, 9H); Combined ^{13}C{^{1}H} NMR spectroscopic data for both diastereomers are as follows: ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 172.3, 171.5, 155.2, 153.5, 141.9, 136.4, 135.0, 129.2, 128.5, 128.4, 128.3, 127.6, 110.2, 110.0, 108.2, 106.9, 71.0, 70.1, 60.9, 60.8, 58.7,

57.9, 14.3, 14.0, –0.19, –0.43; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{18}H_{24}O_4Si$: 332.1444, found 332.1449.

For Kumada-Tamao coupling products:

(*Z*)-Trimethyl((1-phenyl-2-(p-tolyl)vinyl)oxy)silane[29] (**9pa**). Purified by flash column chromatography (silica gel, hexane); Yellow oil (87 mg, 77% yield); IR (neat KBr, ν/cm^{-1}) 2960, 2918, 2851, 1685, 1655, 1637, 1092; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.63–7.52 (m, 4H), 7.37–7.29 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.12 (s, 1H), 2.35 (s, 3H), 0.07 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 150.3, 139.9, 135.9, 133.9, 128.9, 128.7, 128.2, 128.0, 126.3, 110.7, 21.4, 0.9; HRMS (EI, *m/z*): $[M]^+$ calculated for $C_{18}H_{22}OSi$: 282.1440, found 282.1444.

(*Z*)-Trimethyl((1-phenylbut-1-en-1-yl)oxy)silane[30] (**9pb**). Purified by flash column chromatography (silica gel, hexane); Colorless oil (70 mg, 79% yield); IR (neat KBr, ν/cm^{-1}) 2960, 2921, 2851, 1685, 1655, 1637, 1097, 1023; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.33–7.23 (m, 3H), 5.26 (t, *J* = 7.0 Hz, 2H), 2.25 (quint, *J* = 7.3 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H), 0.16 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 148.6, 139.4, 128.1, 127.4, 125.5, 113.4, 31.7, 19.7, 0.6.

For α-silylation of α-bromo amides[10]:

N,*N*-Diethyl-2-(trimethylsilyl)acetamide (**10r**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/10); Yellowish oil; IR (neat KBr, ν/cm^{-1}) 2964, 2919, 2851, 1844, 1718, 1655, 1261, 1092; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 3.37 (q, *J* = 7.1 Hz, 2H), 3.26 (q, *J* = 7.1 Hz, 2H), 1.94 (s, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.12 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 171.8, 43.0, 39.9, 29.8, 25.3, 13.4, –0.8; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_9H_{22}NOSi$: 188.1465, found 188.1469.

N,*N*-Diethyl-2-(trimethylsilyl)propanamide (**10s**). Purified by flash column chromatography (silica gel, EtOAc/hexane = 1/10); Yellowish oil; IR (neat KBr, ν/cm^{-1}) 2960, 2923, 2951, 1718, 1685, 1655, 1253, 1084; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 3.69 (dq, *J* = 14.0 Hz, *J* = 7.0 Hz, 1H), 3.41 (dq, *J* = 14.0 Hz, *J* = 7.0 Hz, 1H), 3.17–3.01 (m, 2H), 2.18 (q, *J* = 7.0 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.12 (dt, *J* = 20.7 Hz, *J* = 7.0 Hz, 6H), 0.06 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 30 °C) δ 175.7, 42.5, 40.3, 26.7, 14.8, 13.5, 12.8, –2.6; HRMS (FAB$^+$, *m/z*): $[M+H]^+$ calculated for $C_{10}H_{24}NOSi$: 202.1622, found 202.1626.

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ASSOCIATED CONTENT

SUPPORTING INFORMATION.

^{1}H and $^{13}C\{^{1}H\}$ NMR of starting materials and products are provided in supporting information.

These materials are available free of charge *via* the internet at http://pubs.acs.org.

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