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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b02998 • Publication Date (Web): 28 Jan 2017

Just Accepted

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Copper-Catalyzed Carbenoid Insertion Reactions of α-Diazoesters and α-Diazoketones into Si–H and S–H Bonds

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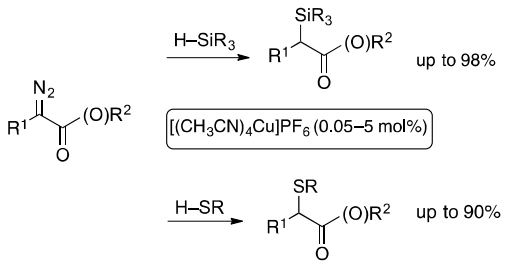


ABSTRACT: An efficient copper-catalyzed carbenoid insertion reaction of α-diazo carbonyl compounds into Si–H and S–H bonds was developed. A wide range of α-silylesters and α-thioesters was obtained in high yields (up to 98%) from α-diazoesters using 5 mol % of a simple copper(I) salt as catalyst. Using 0.05 mol % of the same catalyst, α-diazoketones led to α-silylketones in low to good yields (up to 70%).

INTRODUCTION

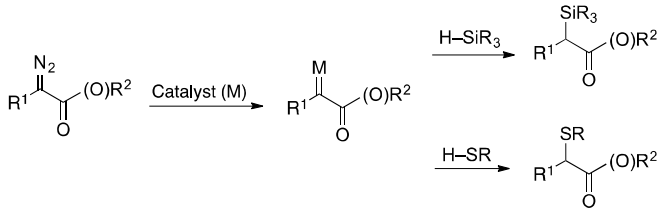
Metal-catalyzed reactions of diazo compounds have been commonly used in organic synthesis.[1] The resulting metal-carbenoid intermediates are capable of undergoing a broad range of reactions, sometimes ideal for initiating cascade sequences leading to the rapid generation of structural complexity.[2] Diazo compounds, which are commonly used as carbene precursors, have

been extensively employed as versatile cross-coupling partners in various transition metal-catalyzed reactions.[3] Diazo compounds can be converted into highly reactive free carbene intermediates under thermolytic or photolytic conditions.[4] Because of the limited synthetic applications of the latter due to their lack of selectivity for most chemical transformations, there has been a significant interest for the transition metal-catalyzed decomposition of diazo compounds.[4] Metal carbene species can undergo diverse transformations, such as X–H insertion reactions (X = C, Si, N, O, S, etc).[5] Formation of diazocarbonyl compounds *via* diazo transfer is applicable to a wide range of active methylene compounds, typically ketones and carboxylic acid derivatives, and their subsequent derivatization allows to reach a wide molecular variety. Watanabe was the first to develop the reaction of various silanes with methyl α-diazoacetate in the presence of copper powder as catalyst.[6] The efficient use of $Rh_2(OAc)_2$ in the formation of α-silyl carbonyl compounds was also demonstrated.[7] Various asymmetric insertion reactions of α-diazoesters into Si–H and S–H bonds involving chiral rhodium and iridium catalysts and only a few examples involving copper ones have been disclosed, but in the presence of expensive and complicated ligands. Doyle and Moody investigated chiral dirhodium(II) complexes as efficient catalysts for Si–H insertion.[8] High enantioselectivities in the Si–H bond insertion of α-vinyldiazoacetates and α-diazophenylacetates, catalyzed by rhodium(II) prolinate complexes, have been reported by Davies.[9] Hashimoto demonstrated the effective use of Rh_2(*S*-PTPA)$_4$ and Rh_2(*S*-PTPG)$_4$ as catalysts for the enantioselective Si–H insertion reaction.[10] Ball developed a strategy to use natural polypeptide ligands in the development of chiral dirhodium catalysts.[11] In 2013, Lacour used Rh(II) complexes derived from enantiopure binaphtyl ligand.[12] Katsuki developed a Si–H carbenoid insertion reaction using an iridium complex as catalyst.[13] Rhodium(I)-catalyzed asymmetric Si–H insertion reactions have been developed by Xu.[14] Che demonstrated that chiral iridium

porphyrin displays excellent reactivity and stereoselectivity towards carbene insertion.[15] Asymmetric copper-catalyzed Si–H insertion reaction was reported by Panek using $[Cu(OTf)]_2 \cdot PhH$ and $[(CH_3CN)_4Cu]PF_6$ in the presence of a chiral diimine ligand.[16] In 2008, Zhou also developed an asymmetric Si–H insertion reaction using $Cu(OTf)_2$ with *spiro* diimine ligands.[17] Pérez also reported a chiral silver complex as efficient catalyst for insertion reactions.[18] Moreover, Gouverneur reported X–H (X = Si, B, P, S, N) insertion reactions on other types of substrates than esters, such as 1-aryl 2,2,2-trifluoro-1-diazoalkanes, using $[(CH_3CN)_4Cu]PF_6$ as catalyst.[19] Regarding the S–H insertion reaction, in recent years, a number of methods have been proven useful, involving bis(NHC)ruthenium(II)-porphyrins,[20] Cu(I)-zeolites,[21] urea and phosphates,[22] biocatalysts,[23] and chiral Rh(II) and Cu(I) catalysts.[24] An enantioselective version of the S–H insertion reaction was also achieved using copper(I) *spiro* diimine complexes.[25]

Because most of the asymmetric versions of the insertion reactions of α-diazoesters into Si–H and S–H bonds involve expensive and complicated ligands, a general and practical method for Si–H and S–H bond insertion reactions of silanes and thiols with α-diazoesters and α-diazoketones would thus represent a valuable addition to the toolbox of synthetic chemistry. The challenge also resides in developing the reaction with α-diazoketones that have never been used for the insertion reaction into Si–H or S–H using a copper catalyst. In this article, we report Si–H and S–H insertion reactions of α-diazoesters and α-diazoketones and demonstrate the scope and applicability of the reaction using practical conditions (Scheme 1). α-Diazoesters and α-diazoketones were easily prepared from commercially available esters and ketones according to known procedures.[17,26] Given that most of the catalyzed X–H insertion reactions with α-diazoesters involve rhodium complexes, we focused here on an efficient and green metal catalytic system to probe the reactivity of α-diazoesters and α-diazoketones into Si–H and S–H bonds.

Scheme 1. General scheme for Si–H and S–H insertion reactions using α-diazoesters and α-diazoketones

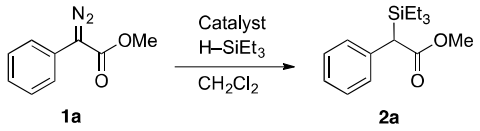


RESULTS AND DISCUSSION

The reaction of α-diazophenylacetate **1a** and triethylsilane in dichloromethane was first examined at room temperature with $[(CH_3CN)_4Cu]PF_6$ as catalyst. The reaction was complete within 0.1 h at 25 ºC and the Si–H insertion product was obtained in 68% yield (Table 1, entry 1). By using a slow addition protocol, the yield was improved to 85% within 0.5 h at 25 ºC (Table 1, entry 2). Using the same reaction conditions, different copper sources such as $Cu(OTf)_2$, $[Cu(OTf)]_2 \cdot PhMe$ and CuCl were tested but none of them afforded the same reactivity as $[(CH_3CN)_4Cu]PF_6$ (Table 1, entries 3–5). No conversion was obtained using $Cu(OAc)_2$ (Table 1, entry 6). We checked the solubility of all copper catalysts used in this study. All copper salts have shown high solubility in dichloromethane, except $Cu(OAc)_2$, which is scarcely used in diazo decomposition reactions anyway. $[Cu(OTf)]_2 \cdot PhH$ led to a decreased yield but because of increased dimerization pathway. Consequently, the observed reactivity is not thought to be influenced by any solubility issue. By decreasing the temperature to 0 ºC, –10 and –20 ºC, the yield was improved by using slow addition of α-diazophenylacetate, with the compromise of a longer reaction time (Table 1, entries 7–9). A catalyst loading of 5 mol % was effective, whereas the product was formed in lower yield when the catalytic loading was decreased to 2 mol % (Table

1, entries 10–13). Once the slow addition protocol had been established, $[(CH_3CN)_4Cu]PF_6$ (5 mol %) was selected for further studies, because it appeared superior to other copper catalysts.

Table 1. Screening of copper sources for Si–H insertion of methyl α-diazophenylacetate (1a)[a]



1a **2a**

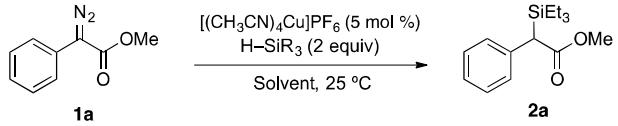
Entry	[Cu] (mol %)	T (ºC)	Time (h)	Yield (%)
1[b]	$[(CH_3CN)_4Cu]PF_6$ (5)	25	0.1	68
2	$[(CH_3CN)_4Cu]PF_6$ (5)	25	0.5	85
3	$Cu(OTf)_2$ (5)	25	0.5	70
4	$[Cu(OTf)]_2 \cdot PhMe$ (5)	25	0.5	65
5	CuCl (5)	25	3	60
6	$Cu(OAc)_2$ (5)	25	48	–
7	$[(CH_3CN)_4Cu]PF_6$ (5)	0	1	89
8	$[(CH_3CN)_4Cu]PF_6$ (5)	–10	18	98
9	$[(CH_3CN)_4Cu]PF_6$ (5)	–20	24	90
10	$[(CH_3CN)_4Cu]PF_6$ (2)	25	1.5	80
11	$[(CH_3CN)_4Cu]PF_6$ (2)	0	2	85
12	$[(CH_3CN)_4Cu]PF_6$ (2)	–10	24	88
13	$[(CH_3CN)_4Cu]PF_6$ (2)	–20	48	90
14	–	25	48	–

[a]Reaction conditions: copper salt (2–5 mol %), silane (1 mmol), methyl α-diazophenylacetate **1a** (0.5 mmol), CH_2Cl_2 (1 mL), slow addition (1 h) of methyl α-diazophenylacetate (**1a**). [b]Without slow addition of methyl α-diazophenylacetate (**1a)**

Next, the effects of various solvents were studied on the efficiency of the insertion reaction. Chloroform, 1,2-dichloroethane and toluene were all suitable solvents and moderate to very good yields were obtained (Table 2, entries 1–3). When the reaction was run in polar, coordinating

solvents, such as THF, the conversion was lower and the reaction time was extended, whereas acetonitrile led to a good yield (Table 2, entries 4 and 5). Diethyl ether and hexane afforded low yields (Table 2, entries 6 and 7); dimethylcarbonate led to more diazo dimerization into the tetrasubstituted olefin after subsequent irreversible extrusion of nitrogen and coupling (Table 2, entry 8). However, none of these solvents gave results superior to dichloromethane, which was consequently chosen in further studies.

Table 2. Screening of solvents for Si–H insertion reaction of methyl α-diazophenylacetate (1a)[a]



1a 2a

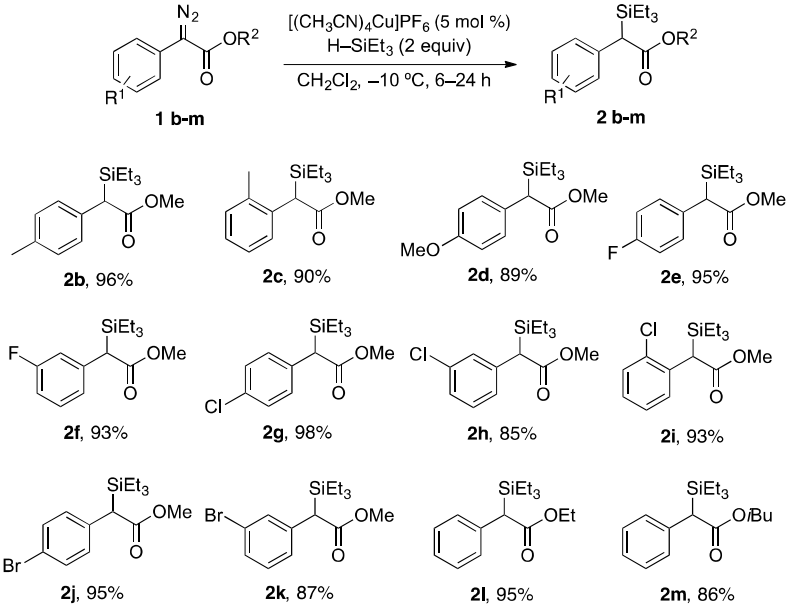
Entry	Solvent	Silane	T (h)	Yield (%)
1	$CHCl_3$	Et_3SiH	0.5	87
2	DCE	Et_3SiH	0.5	81
3	Toluene	Et_3SiH	5	58
4	CH_3CN	Et_3SiH	48	85
5	THF	Et_3SiH	48	34
6	Et_2O	Et_3SiH	12	10
7	Hexane	Et_3SiH	12	18
8	DMC	Et_3SiH	24	35
9	CH_2Cl_2	$PhMe_2SiH$	1	95
10	CH_2Cl_2	Ph_3SiH	1	75
11	CH_2Cl_2	Ph_2MeSiH	1	85

[a]Reaction conditions: $[(CH_3CN)_4Cu]PF_6$ (5 mol %), silane (1 mmol), methyl α-diazophenylacetate (**1a**) (0.5 mmol), solvent (1 mL), 25 °C.

Other silanes, such as phenyldimethylsilane, triphenylsilane and diphenylmethylsilane were also successfully used in this transformation, affording the desired α-silylesters in moderate to high yields (Table 2, entries 9–11).

A variety of α-diazoesters were examined to expand the scope of the substrates used for the Si–H insertion reaction with triethylsilane, run under the optimal reaction conditions. All substrates reacted to produce the corresponding α-silylesters in very good to excellent yields (Scheme 2, **2b–m**; 85–98%), regardless of the nature and position of the substituents on the phenyl ring of the α-diazoesters (Scheme 2, **2b–m**). However, the reactivity of the substrate was influenced by the electronic properties of substituents on the phenyl ring of the α-diazoarylacetates. α-Diazoarylacetates containing electron-donating groups such as methyl and methoxy (Scheme 2, **2b–d**) required shorter reaction time to reach complete conversion and high yields. However, α-diazoarylacetates containing electron-withdrawing groups, such as Br, F, Cl (Scheme 2, **2e–k**), required an increased reaction time to reach complete conversion.

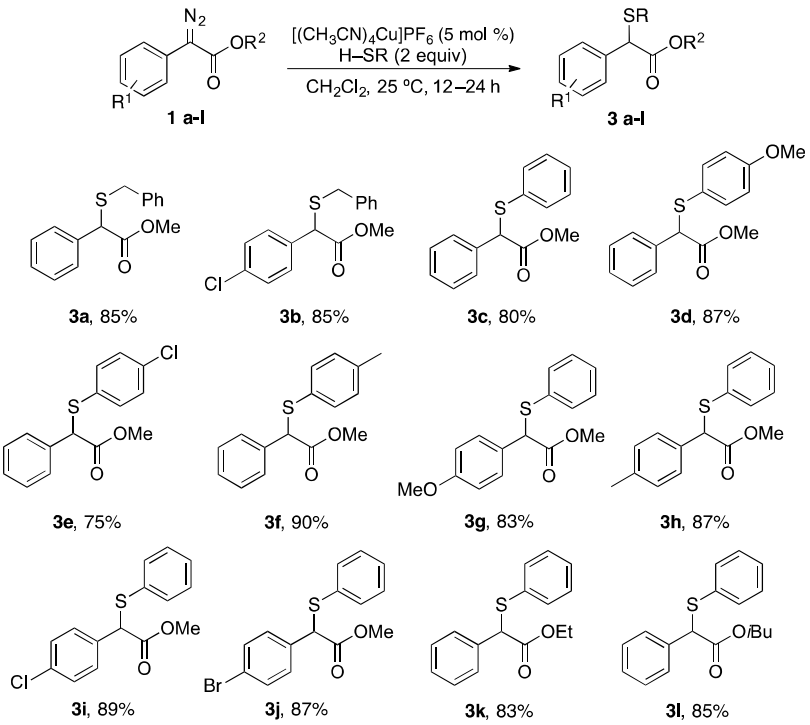
Scheme 2. Copper-catalyzed Si–H insertion reaction of methyl α-diazoarylacetate[a]



[a]Reaction conditions: $[(CH_3CN)_4Cu]PF_6$ (5 mol %), Et_3SiH (1 mmol), α-diazoarylacetate (0.5 mmol), CH_2Cl_2 (1 mL), –10 °C.

$[(CH_3CN)_4Cu]PF_6$ proved to be an efficient catalyst for α-diazoester insertion reactions into the S–H bond as well. The substrate and scope of α-diazoester were next investigated for this reaction. The S–H bond insertion reactions of benzyl mercaptan and various substituted thiophenols with different α-diazoesters were run under the optimal reaction conditions using 5 mol % of $[(CH_3CN)_4Cu]PF_6$ in dichloromethane at room temperature (Scheme 3). High yields were obtained using substituted thiophenols containing electron-donating groups, such as methyl and methoxy, and electron-withdrawing groups in the *para*-position such as Cl (Scheme 3, **3d-3f**). Good yields were also obtained using substituted α-diazoester substrates containing electron-donating groups and electron-withdrawing groups in S–H bond reaction (Scheme 3, **3g-3j**).

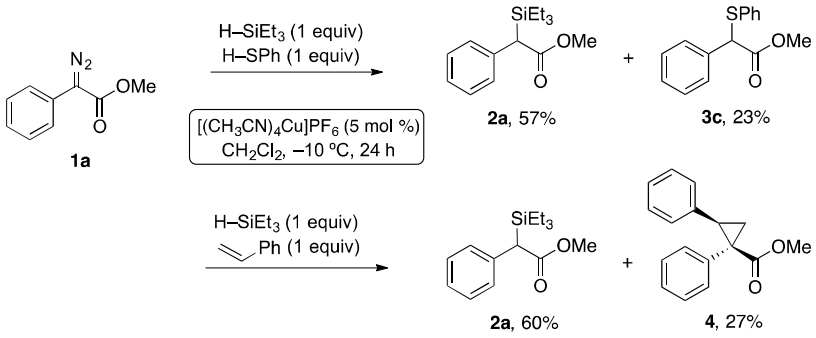
Scheme 3. Copper-catalyzed S–H bond insertion reaction of α-diazoesters with various thiols[a]



[a]Reaction conditions: $[(CH_3CN)_4Cu]PF_6$ (5 mol %), thiol (1 mmol), α-diazoarylacetate (0.5 mmol), CH_2Cl_2 (1 mL), 25 °C.

The reaction of methyl α-diazophenylacetate (**1a)** with triethylsilane, thiophenol and styrene under Cu(I) catalysis afforded products of Si–H, S−H insertion and cyclopropanation (Scheme 4). This competition experiment showed that the product of Si–H insertion was formed in a better yield *vs.* S–H insertion and cyclopropanation using Cu(I) as a catalyst at –10 ºC. The selectivity of the reaction was only moderate, and running the reaction at lower temperature (at –20 °C) did not improve it.

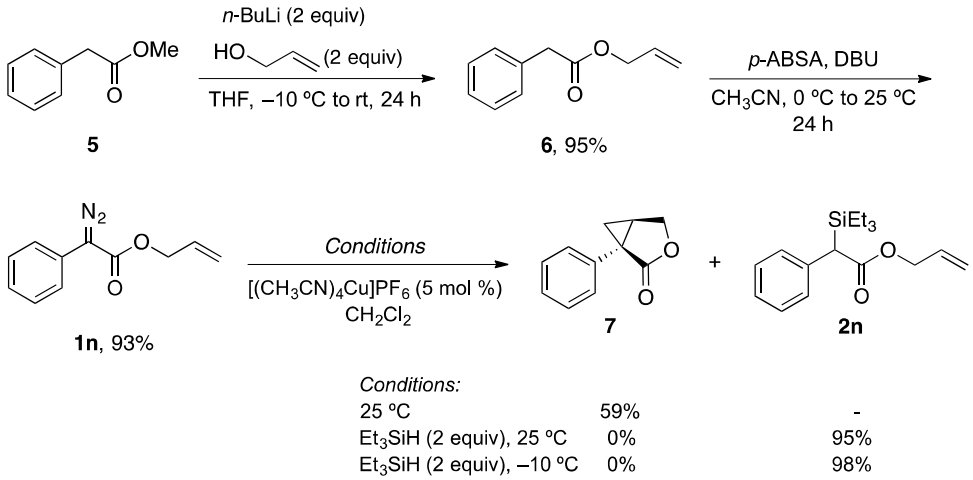
Scheme 4. Competition experiments–Copper-catalyzed Si−H insertion *versus* S–H insertion with 1a and copper-catalyzed Si–H insertion *vs.* cyclopropanation with 1a



The intramolecular cyclopropanation reaction of α-phenyldiazoacetate (**1n)** using $[(CH_3CN)_4Cu]PF_6$ as catalyst was also examined.[27] Cyclopropane **7** was formed in a 59% yield when the reaction was performed at 25 °C without a silane. The reaction of **1n** with triethylsilane under Cu(I) catalysis at –10 ºC and 25 ºC afforded only the product of Si–H insertion (**2n**) in almost quantitative yields (Scheme 5). These competition experiments led to the product of Si–H insertion as the only product *vs.* intramolecular cyclopropanation. This demonstrates the com-

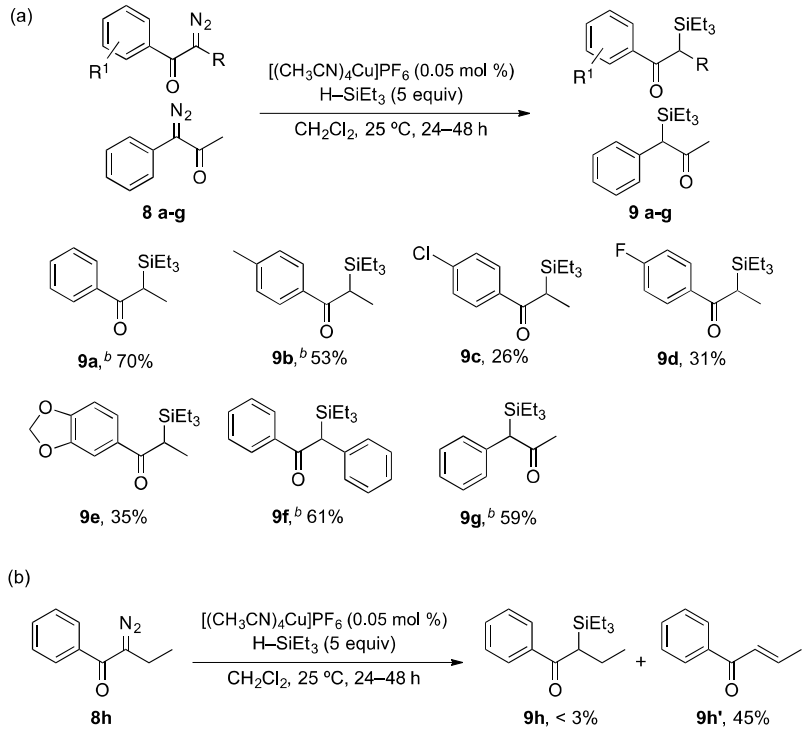
plete selectivity for the *intermolecular* Si–H insertion reaction *vs. intramolecular* cyclopropanation.

Scheme 5. Competition experiments–Copper-catalyzed Si–H insertion *versus* cyclopropanation with 1n



A variety of α-diazoketones (Scheme 6, eq. a, **8a-g)** were studied as substrates for the Si–H insertion reaction with triethylsilane. After screening, the optimal conditions found for the synthesis of the α-silylketones involved a very low catalyst loading (0.05 mol %) of $[(CH_3CN)_4Cu]PF_6$ using 5 equiv of triethylsilane in dichloromethane at room temperature. Using a higher amount of the catalyst or less than 5 equiv of triethylsilane increased the formation of the undesired dimerization alkene product. All substrates afforded the corresponding α-silylketones **9a-g** in poor to good yields (Scheme 6, eq. a, 26–70%). α-Diazophenylketone **8a** was the most reactive, giving 70% of insertion product (*C*-silylated product). α-Diazophenylketone **8f** gave 61% of insertion product (*C*-silylated product) and 12% yield of the corresponding silyl enol ether (*O*-silylated product). Between 1–5% of the *O*-silylated products were isolated using the other α-diazoketones.

Scheme 6. Copper-catalyzed Si–H bond insertion of α-diazoketones



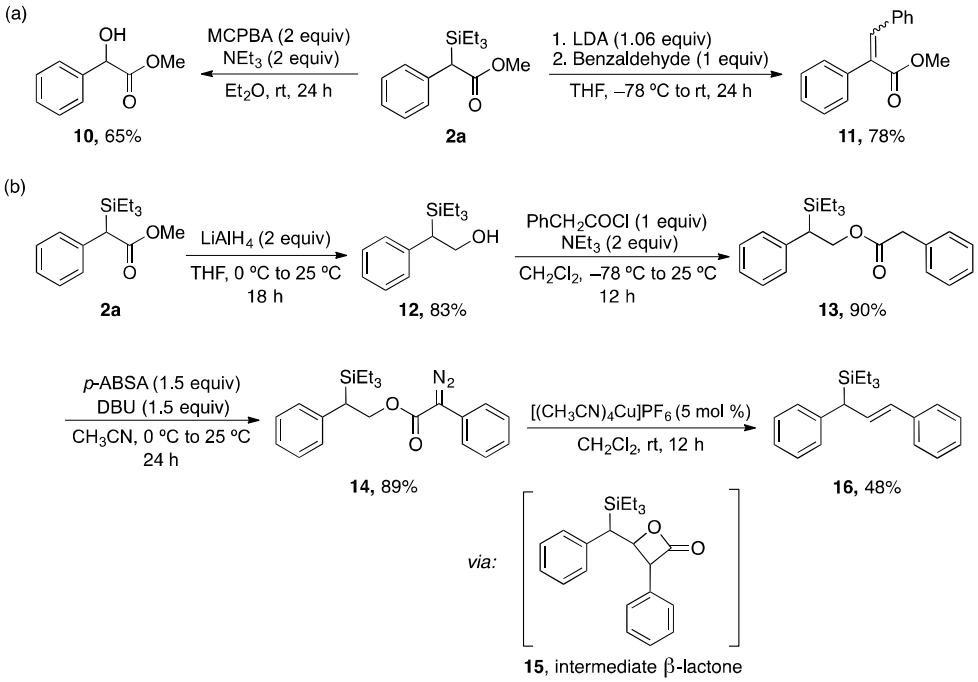
[a]Reaction conditions: $[(CH_3CN)_4Cu]PF_6$ (0.05 mol %), silane (3 mmol), α-diazoketone (0.6 mmol), CH_2Cl_2 (1.2 mL), 25 °C. [b]Reaction was performed using 4Å molecular sieves (50 mg).

However, the reactivity of the substrate was influenced by the electronic properties of substituents on the phenyl ring of the α-diazoketones. α-Diazoketones containing electron-donating groups such as methyl and dioxolane group led to the silylated product in higher yields (Scheme 6, **9b** and **9e**) than α-diazoketones containing electron-withdrawing groups such as F and Cl (Scheme 6, eq. a, **9c** and **9d**). Only traces of α-silylketone were obtained using 2-diazo-1-phenylbutan-1-one (**8h)** as substrate and gave 1-phenyl-2-buten-1-one (**9h**') (*E*/*Z* = 1:0.03) as undesired product (Scheme 6, eq. b, 45% yield). The preparation of unsaturated carbonyl compounds through β-hydride elimination of α-diazo carbonyl derivatives has already been disclosed

in the literature.[28] Moreover, in an attempt of running a competition experiment using an α-diazoketone *vs.* an α-diazoester (Scheme 4), the reaction of α-diazoketone (**8a)** with triethylsilane and styrene under Cu(I) catalysis only afforded the product of Si–H insertion without any traces of cyclopropanation.

The obtained α-silylesters **2** can readily be used and transformed into other useful products. α-Silylester **2a** was converted into α-hydroxylester **10**, using MCPBA as an oxidant (Scheme 7, eq. a).[29] A Peterson elimination of **2a** allowed the conversion in two steps into the corresponding α-alkylated-α,β-unsaturated ester **11** via the silylation condensation-elimination sequence shown in Scheme 7, eq. a.[30] Synthesis of allylsilane **16** was also performed starting from α-hydroxy silane **2a**. Davies' procedure to synthesize various allylsilanes originally took advantage of a $Rh_2(OAc)_4$-catalyzed C–H insertion on **14**, through β-lactone intermediate **15**.[31] We advantageously replaced this Rh(II) catalyst in the last key step, using the same copper catalyst employed for the Si–H insertion. Reduction of the ester using $LiAlH_4$ afforded **12** in 83% yield.[32] Subsequent esterification of **12** with phenacetyl chloride and diazo synthesis produced **14** in good overall yield. Allylsilane **16** was formed using 5 mol % of $[(CH_3CN)_4Cu]PF_6$ as catalyst (Scheme 7, eq. b). (*E*)-Stereochemistry of the allylsilane was confirmed by NOE.[43]

Scheme 7. Derivatization of 2a



CONCLUSION

To sum up, we have successfully developed an efficient copper-catalyzed protocol for the carbenoid insertion reaction of α-diazoesters and α-diazoketones into Si–H and S–H bonds. By using $[(CH_3CN)_4Cu]PF_6$, a wide range of α-silylesters were synthesized in good to excellent yields using this catalyst. For the first time, the insertion of α-diazoketones into Si–H bonds using the same catalyst, though in much lower loading, has been reported. The desired products were obtained in excellent yields using low catalytic loadings, *i.e.* 5 mol % for α-silylesters and 0.05 mol % for α-silylketones, and short reaction times. This catalyst has been shown to be efficient for carbenoid insertion into S–H bond in high yields as well. Further developments will be reported in due course.

EXPERIMENTAL SECTION

General procedures. All reactions were performed in flame-dried flasks and tubes under an atmosphere of argon. Solvents (CH_2Cl_2, THF, MeOH, Et_2O, $CHCl_3$, …) were distilled prior to use. $[(CH_3CN)_4Cu]PF_6$ was purchased from Sigma-Aldrich. Thin-layer chromatography (TLC) was carried out on 250 μm commercial silica gel plates and compounds were visualized using UV absorbance and/or aqueous $KMnO_4$. Flash column chromatography was performed on silica gel (230–400 mesh). ^1H and $^{13}C\{H\}$ NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$. For ^1H NMR (400 MHz), chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) used as internal standard ($\delta = 0$ ppm), and coupling constant and integration (in Hz). High-resolution mass spectra (HRMS) were recorded on ESI TOF (time of flight) mass spectrometer. IR spectra were recorded on a FT–IR spectrometer with ZnSe ATR accessory and are reported in reciprocal centimeter (cm^{-1}). Melting points (mp) are uncorrected and were recorded on a melting point apparatus.

Preparation of *p*-tosyl azide.[33] To a flask of 100 mL, a solution of sodium azide (2.86 g, 44 mmol) in water (12 mL) and acetone (20 mL) was rapidly added a solution of *p*-toluenesulfonylchloride (7.62 g, 40 mmol) in acetone (20 mL). The mixture warmed slightly and two phases were formed. After stirring at room temperature for 4 h, acetone was evaporated under reduced pressure (bath temperature 35 ºC), the residue was extracted with CH_2Cl_2 (3 x 25 mL), washed with water (2 x 25 mL), dried over $MgSO_4$ and concentrated under reduced pressure (bath temperature 35 ºC) to give the compound as a colorless oil (7.78 g, 39.45 mmol, 98% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.86 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 2.48 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 146.3, 135.2, 130.2, 127.2, 21.3 ppm.

Preparation of *N*-acetylsulfanilyl azide.[33] A solution of sodium azide (6.14 g, 94 mmol) in acetone (300 mL) in a flask of 500 mL was cooled at 0 °C and *N*-acetylsulfanilyl chloride (20 g, 85.8 mmol) was added in small portions. After stirring at room temperature for 24 h, acetone was evaporated under reduced pressure (bath temperature 35 ºC), the residue was extracted with CH_2Cl_2 (3 x 75 mL), washed with water (2 x 30 mL), dried over $MgSO_4$ and concentrated under reduced pressure (bath temperature 35 ºC) to give compound as a white solid (19.2 g, 80.0 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.07 (s, 1H), 7.87 (d, J = 8.9 Hz, 2H), 7.78 (d, J = 8.9 Hz, 2H), 2.23 (s, 3H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 168.7, 143.8, 132.7, 129.0, 119.5, 24.8 ppm.

Preparation of methanesulfonyl azide.[33] To a flask of 500 mL, a solution of sodium azide (17 g, 0.26 mol) in water (100 mL) and acetone (160 mL) at 0 °C was added dropwise methanesulfonyl chloride (6.8 mL, 0.17 mol). After stirring at room temperature for 15 h, acetone was evaporated under reduced pressure (bath temperature 35 ºC), the residue was extracted with CH_2Cl_2 (3 x 75 mL), washed with water (2 x 35 mL), dried over $MgSO_4$ and concentrated under reduced pressure (bath temperature 35 ºC) to give compound as a colorless oil (7.78 g, 0.064 mol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.25 (s, 3H) ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 42.8 ppm.

General procedure for preparation of α-diazoesters.[17] To a mixture of ester (10 mmol) and tosyl azide (2.96 g, 15 mmol) in anhydrous CH_3CN (15 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.24 mL, 2.28 g, 15 mmol) was added. The reaction mixture was stirred at room temperature for overnight. Upon complete consumption of the starting materials, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (5 mL), extracted with CH_2Cl_2 (3 x 30

mL), washed with brine (3 x 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give the product. The residue was purified by flash chromatography (Hexane/EtOAc) to afford the α-diazoester.

*Methyl α-diazophenylacetate (**1a**).*[17] The product was obtained as a red oil (1.67 g, 9.48 mmol, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.18 (t, J = 8.0 Hz, 1H), 3.81 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 165.3, 128.8, 125.6, 125.4, 123.7, 63.3, 51.8 ppm; IR (ZnSe): 2951, 2078, 1693, 1243, 1048, 1023, 750, 688 cm^{-1}.

*Methyl α-diazo-4-methylphenylacetate (**1b**).*[17] The product was obtained as an orange solid (1.43 g, 7.52 mmol, 75% yield). mp: 40–42 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 3.85 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 165.8, 135.7, 129.6, 124.1, 122.0, 62.9, 51.9, 21.0 ppm; IR (ZnSe): 2956, 2078, 1689, 1469, 1245, 1151, 1044, 798 cm^{-1}.

*Methyl α-diazo-2-methylphenylacetate (**1c**).*[17] The product was obtained as a yellow oil (1.69 g, 8.89 mmol, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42–7.40 (m, 1H), 7.26–7.23 (m, 3H), 3.80 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 166.1, 137.6, 130.8, 130.7, 128.8, 126.3, 124.2, 60.5, 51.9, 19.8 ppm; IR (ZnSe): 2951, 2082, 1693, 1433, 1251, 1222, 1030 cm^{-1}.

*Methyl α-diazo-4-methoxylphenylacetate (**1d**).*[17] The product was obtained as a red solid (2.00 g, 9.70 mmol, 97% yield). mp: 48–50 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C

166.1, 158.0, 125.9, 116.8, 114.5, 62.3, 55.3, 51.9 ppm; IR (ZnSe): 2956, 2082, 1693, 1455, 1244, 1026, 831, 738 cm^{-1}.

*Methyl α-diazo-4-fluorophenylacetate (**1e**).*[17] The product was obtained as an orange oil (1.90 g, 9.79 mmol, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.46–7.42 (m, 2H), 7.11 (t, J = 8.0 Hz, 2H), 3.86 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 165.6, 161.01 (d, J = 246.3 Hz), 125.86 (d, J = 7.9 Hz), 121.19 (d, J = 3.2 Hz), 116.01 (d, J = 21.9 Hz), 62.5, 52.0 ppm; IR (ZnSe): 3020, 2954, 2080, 1692, 1507, 1434, 1153, 1039, 828 cm^{-1}

*Methyl α-diazo-3-fluorophenylacetate (**1f**).*[17] The product was obtained as an orange oil (1.73 g, 8.91 mmol, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.35–7.31 (m, 2H), 7.17 (d, J = 7.6 Hz, 1H), 6.88 (t, J = 9.3 Hz, 1H), 3.87 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 165.0, 163.18 (d, J = 245.5 Hz), 130.31 (d, J = 8.8 Hz), 128.03 (d, J = 9.5 Hz), 118.78 (d, J = 2.8 Hz), 112.44 (d, J = 21.4 Hz), 111.01 (d, J = 25.5 Hz), 63.4, 52.1 ppm; IR (ZnSe): 3021, 2955, 2082, 1696, 1243, 1187, 1048, 771 cm^{-1}.

*Methyl α-diazo-4-chlorophenylacetate (**1g**).*[17] The product was obtained as an orange solid (2.00 g, 9.50 mmol, 95% yield). mp: 64–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 9.0 Hz, 2H), 3.87 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 165.2, 131.4, 129.0, 125.0, 124.0, 63.3, 52.1 ppm; IR (ZnSe): 2953, 2090, 1686, 1434, 1246, 1068, 856 cm^{-1}.

*Methyl α-diazo-3-chlorophenylacetate (**1h**).*[17] The product was obtained as an orange solid (1.90 g, 9.02 mmol, 90% yield). mp: 50–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.54 (t, J = 8.0 Hz, 1H), 7.32 (m, 2H), 7.15 (d, J = 8.0 Hz, 1H), 3.87 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$):

δ_C 165.0, 135.0, 130.0, 127.6, 125.7, 123.6, 121.5, 63.2, 52.1 ppm; IR (ZnSe): 2955, 2089, 1694, 1480, 1356, 1275, 1044, 736 cm^{-1}.

*Methyl α-diazo-2-chlorophenylacetate (**1i**).*[17] The product was obtained as a yellow oil (1.79 g, 8.50 mmol, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.50 (d, J = 6.8 Hz, 1H), 7.33 (d, J = 7.3 Hz, 1H), 7.22–7.15 (m, 2H), 3.74 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 165.5, 133.4, 132.1, 129.9, 129.5, 127.0, 123.8, 61.7, 52.0 ppm; IR (ZnSe): 2951, 2093, 1694, 1432, 1239, 1025 cm^{-1}.

*Methyl α-diazo-4-bromophenylacetate (**1j**).*[17] The product was obtained as an orange solid (2.42 g, 9.49 mmol, 95% yield). mp: 40–42 °C; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.50 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 3.86 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 165.1, 132.0, 125.2, 124.6, 119.3, 62.9, 52.1 ppm; IR (ZnSe): 2952, 2088, 1692, 1434, 1310, 1154, 1039 cm^{-1}.

*Methyl α-diazo-3-bromophenylacetate (**1k**).*[17] The product was obtained as an orange solid (2.35 g, 9.21 mmol, 92% yield). mp: 68–70 °C; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.36 (d, J = 8.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.26–7.21 (m, 2H), 3.87 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 164.9, 130.2, 128.6, 127.9, 126.4, 123.1, 122.0, 63.0, 52.1 ppm; IR (ZnSe): 2953, 2087, 1690, 1589, 1274, 1041, 718 cm^{-1}.

*Ethyl α-diazophenylacetate (**1l**).*[17] The product was obtained as a red oil (1.75 g, 9.20 mmol, 92% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.51–7.49 (m, 2H), 7.39–7.35 (m, 2H), 7.19–7.15 (m, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz,

$CDCl_3$): δ_C 165.0, 128.8, 125.7, 125.6, 123.8, 63.2, 60.9, 14.4 ppm; IR (ZnSe): 2980, 2077, 1697, 1497, 1369, 1240, 1147, 751 cm^{-1}.

*Isobutyl α-diazophenylacetate (**1m**).*[26a] The product was obtained as a red oil (1.85 g, 8.48 mmol, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.52–7.49 (m, 2H), 7.39–7.37 (m, 2H), 7.21–7.17 (m, 1H), 4.09 (d, J = 7.1 Hz, 2H), 2.06–1.99 (m, 1H), 1.01 (d, J = 7.1 Hz, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 165.1, 128.9, 125.7, 125.6, 123.8, 70.8, 63.3, 27.9, 19.0 ppm; IR (ZnSe): 2961, 2094, 1686, 1392, 1238, 1163, 1015, 782 cm^{-1}.

*Allyl α-diazophenylacetate (**1n**).*[26b] The product was obtained as a red oil (1.88 g, 9.30 mmol, 95% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.51 (d, J = 8.6 Hz, 2H), 7.41–7.37 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 6.03–5.96 (m, 1H), 5.40 (dd, J = 17.1, 1.5 Hz, 1H), 5.36 (dd, J = 10.4, 1.3 Hz, 1H), 4.79 (dt, J = 5.6, 1.4 Hz, 2H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 164.8, 132.1, 128.9, 125.8, 125.4, 123.9, 118.3, 65.4, 51.9 ppm; IR (ZnSe): 2952, 2078, 1697, 1497, 1239, 1144, 1013, 752 cm^{-1}.

General procedure for Si–H insertion into α-diazoacetate. In a flame-dried glass tube, under argon atmosphere, $[(CH_3CN)_4Cu]PF_6$ (9.32 mg, 0.025 mmol, 5 mol %) was diluted in CH_2Cl_2 (0.5 mL) at room temperature. The silane (1 mmol) was then introduced into the mixture, which was subsequently cool down to –10 ºC. Methyl α-diazoacetate (0.5 mmol), diluted in CH_2Cl_2 (0.5 mL), was added dropwise over 1 h using a syringe pump. The mixture was stirred for the specified time and subsequently filtered through celite and evaporated under reduced pressure (rotary evaporator). The residue was purified by flash chromatography (Hexane/EtOAc) to afford the product.

*Methyl α-phenyl-α-triethylsilylacetate (**2a**).*[12] The product was obtained as a colorless oil (130 mg, 0.49 mmol, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.41 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 3.69 (s, 3H), 3.57 (s, 1H), 0.90 (t, *J* = 7.6 Hz, 9H), 0.71–0.56 (m, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 173.5, 136.5, 128.4, 128.1, 51.3, 42.7, 42.6, 7.0, 2.7 ppm; IR (ZnSe): 2950, 2876, 1720, 1299, 1142, 1004, 785, 697 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{24}O_2Si$ ($[M + H]^+$) = 265.1618, Found 265.1599.

*Methyl α-(4-methylphenyl)-α-triethylsilylacetate (**2b**).* The product was obtained as a colorless oil (134 mg, 0.48 mmol, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.26 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.68 (s, 3H), 3.51 (s, 1H), 2.32 (s, 3H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.68–0.55 (m, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 173.8, 135.0, 133.3, 128.8, 128.3, 51.2, 42.2, 20.9, 7.0, 2.7 ppm; IR (ZnSe): 2950, 2875, 1719, 1511, 1303, 1141, 1005, 818 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{26}O_2Si$ ($[M + H]^+$) = 279.1775, Found 279.1770.

*Methyl α-(2-methylphenyl)-α-triethylsilylacetate (**2c**).* The product was obtained as a colorless oil (125 mg, 0.45 mmol, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.63 (d, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13–7.05 (m, 2H), 3.82 (s, 1H), 3.67 (s, 3H), 2.29 (s, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.68–0.55 (m, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 173.6, 134.9, 134.6, 130.1, 129.5, 125.7, 125.5, 51.3, 37.3, 20.5, 7.0, 3.1 ppm. IR (ZnSe): 2950, 2876, 1724, 1431, 1189, 1147, 1002 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{26}O_2Si$ ($[M + H]^+$) = 279.1775, Found 279.1770.

*Methyl α-(4-methoylphenyl)-α-triethylsilylacetate (**2d**).*[12] The product was obtained as a colorless oil (131 mg, 0.45 mmol, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.27 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 3.77 (s, 3H), 3.66 (s, 3H), 3.47 (s, 1H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.62–

0.57 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 173.9, 157.6, 129.4, 128.5, 113.5, 55.1, 51.2, 41.5, 7.0, 2.7 ppm; IR (ZnSe): 2050, 2876, 1718, 1508, 1243, 1141, 1004, 828 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{26}O_3Si$ ($[M + H]^+$) = 295.1724, Found 295.1723.

*Methyl α-(4-fluorophenyl)-α-triethylsilylacetate (**2e**).* The product was obtained as a colorless oil (134 mg, 0.48 mmol, 95% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.33 (t, J = 8.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 2H), 3.67 (s, 3H), 3.52 (s, 1H), 0.92 (t, J = 7.9 Hz, 9H), 0.61–0.56 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 173.6, 161.10 (d, J = 243.8 Hz), 132.23 (d, J = 3.4 Hz), 129.76 (d, J = 7.6 Hz), 114.87 (d, J = 21.2 Hz), 51.3, 41.7, 6.9, 2.6 ppm; IR (ZnSe): 2951, 2877, 1719, 1505, 1221, 1143, 1004, 705 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}FO_2Si$ ($[M + H]^+$) = 283.1524, Found 283.1516.

*Methyl α-(3-fluorophenyl)-α-triethylsilylacetate (**2f**).* The product was obtained as a colorless oil (131 mg, 0.47 mmol, 93% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.24–7.15 (m, 2H), 7.09 (d, J = 8.0 Hz, 1H), 6.88 (t, J = 8.0 Hz, 1H), 3.68 (s, 3H), 3.54 (s, 1H), 0.93 (t, J = 7.9 Hz, 9H), 0.61–0.56 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 173.1, 162.68 (d, J = 244.3 Hz), 139.11 (d, J = 8.1 Hz), 129.31 (d, J = 8.6 Hz), 124.06 (d, J = 2.7 Hz), 115.27 (d, J = 22.5 Hz), 112.38 (d, J = 21.1 Hz), 51.4, 42.6, 6.9, 2.5 ppm; IR (ZnSe): 2951, 1733, 1589, 1434, 1235, 1139, 1011, 756 cm^{-1}. HRMS (ESI): calcd for $C_{15}H_{23}FO_2Si$ ($[M + H]^+$) = 283.1524, Found 283.1514.

*Methyl α-(4-chlorophenyl)-α-triethylsilylacetate (**2g**).*[13] The product was obtained as a colorless oil (146 mg, 0.49 mmol, 98% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.40 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.67 (s, 3H), 3.49 (s, 1H), 0.92 (t, J = 7.9 Hz, 9H), 0.61–0.56 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 173.2, 135.6, 131.1, 130.0, 119.3, 51.4, 42.2, 7.0, 2.6

ppm; IR (ZnSe): 2951, 2876, 1717, 1489, 1144, 1089, 1011, 708 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}ClO_2Si$ ($[M + H]^+$) = 299.1228, Found 299.1226.

*Methyl α-(3-chlorophenyl)-α-triethylsilylacetate (**2h**).*[13] The product was obtained as a colorless oil (127 mg, 0.43 mmol, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.39 (t, *J* = 8.0 Hz, 1H), 7.24–7.21 (m, 2H), 7.19–7.13 (m, 1H), 3.68 (s, 3H), 3.51 (s, 1H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.62–0.58 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 173.0, 138.6, 133.9, 129.2, 128.3, 126.5, 125.7, 51.4, 42.5, 6.9, 2.6 ppm; IR (ZnSe): 2951, 2876, 1720, 1329, 1196, 1145, 1005, 690 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}ClO_2Si$ ($[M + H]^+$) = 299.1228, Found 299.1224.

*Methyl α-(2-chlorophenyl)-α-triethylsilylacetate (**2i**).*[13] The product was obtained as a colorless oil (139 mg, 0.47 mmol, 93% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.79 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 4.32 (s, 1H), 3.69 (s, 3H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.66–0.61 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 173.1, 134.5, 132.7, 130.8, 129.1, 126.7, 126.4, 51.4, 37.6, 6.9, 2.9 ppm; IR (ZnSe): 2951, 2876, 1720, 1329, 1196, 1145, 1005, 690 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}ClO_2Si$ ($[M + H]^+$) = 299.1228, Found 299.1221.

*Methyl α-(4-bromophenyl)-α-triethylsilylacetate (**2j**).*[15] The product was obtained as a colorless oil (163 mg, 0.48 mmol, 95% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.67 (s, 3H), 3.51 (s, 1H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.61–0.54 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 173.3, 135.1, 131.3, 129.6, 128.1, 51.4, 42.1, 7.0, 2.6 ppm; IR (ZnSe): 2951, 2876, 1719, 1489, 1265, 1145, 1012, 702 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}BrO_2Si$ ($[M + H]^+$) = 343.0723, Found 343.0720.

*Methyl α-(3-bromophenyl)-α-triethylsilylacetate (**2k**).* The product was obtained as a colorless oil (149 mg, 0.43 mmol, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.54 (d, J = 8.0 Hz, 1H), 7.31–7.27 (m, 2H), 7.5 (t, J = 8.0 Hz, 1H), 3.67 (s, 3H), 3.49 (s, 1H), 0.93 (t, J = 7.9 Hz, 9H), 0.62–0.57 (m, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 173.04, 138.9, 131.2, 129.5, 128.6, 127.0, 122.2, 51.4, 42.4, 7.0, 2.6 ppm; IR (ZnSe): 2951, 2876, 1720, 1475, 1263, 1132, 1009, 708 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}BrO_2Si$ ([M + H]$^+$) = 343.0723, Found 343.0709.

*Ethyl α-phenyl-α-triethylsilylacetate (**2l**).*[18] The product was obtained as a colorless oil (132 mg, 0.48 mmol, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 (t, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 4.18–4.10 (m, 2H), 3.52 (s, 1H), 1.30 (t, J = 7.6 Hz, 3H), 0.93 (t, J = 7.9 Hz, 9H), 0.63–0.56 (m, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 173.1, 136.6, 128.4, 128.0, 125.4, 60.2, 42.8, 14.3, 7.0, 2.7 ppm; IR (ZnSe): 2949, 1731, 1452, 1432, 1276, 1142, 1001, 692 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{26}O_2Si$ ([M + H]$^+$) = 279.1774, Found 279.1776.

*Isobutyl α-phenyl-α-triethylsilylacetate (**2m**).* The product was obtained as a colorless oil (131 mg, 0.43 mmol, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 3.92–3.80 (m, 2H), 3.54 (s, 1H), 1.97–1.90 (m, 1H), 0.97 (t, J = 7.9 Hz, 6H), 0.63–0.58 (m, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 173.3, 136.7, 128.5, 128.0, 125.4, 70.7, 42.8, 27.7, 19.3, 7.1, 2.7 ppm; IR (ZnSe): 2949, 1729, 1493, 1280, 1211, 1140, 1027, 762 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{30}O_2Si$ ([M + H]$^+$) = 307.2088, Found 307.2086.

*Allyl α-phenyl-α-triethylsilylacetate (**2n**).* The product was obtained as a colorless oil (142 mg, 0.49 mmol, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.6

Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 5.98–5.89 (m, 1H), 5.35–5.22 (m, 2H), 4.59 (dt, *J* = 5.9, 1.3 Hz, 2H), 3.55 (s, 1H), 0.92 (t, *J* = 7.8 Hz, 9H), 0.63–0.58 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 172.8, 136.4, 132.4, 128.4, 128.1, 125.5, 118.3, 65.1, 42.7, 7.0, 2.7 ppm; IR (ZnSe): 2949, 1731, 1452, 1432, 1276, 1142, 1001, 692 cm^{-1}; HRMS (ESI): calcd for $C_{17}H_{26}O_2Si$ ($[M + H]^+$) = 291.1775, Found 291.1781.

General procedure for S–H insertion into α-diazoesters. In a flame-dried glass tube, under argon atmosphere, $[(CH_3CN)_4Cu]PF_6$ (9.32 mg, 0.025 mmol, 5 mol %) was diluted in CH_2Cl_2 (0.5 mL) at room temperature. The thiol (1 mmol) was then introduced dropwise into the mixture. Methyl α-diazoacetate (0.5 mmol), diluted in CH_2Cl_2 (0.5 mL), was added dropwise over 1 h using a syringe pump. The mixture was stirred for the specified time and subsequently filtered through celite and evaporated under reduced pressure (rotary evaporator). The residue was purified by flash chromatography (Hexane/EtOAc) to afford the product.

*Methyl 2-(benzylthio)-2-phenylacetate (**3a**).*[35] The product was obtained as a colorless oil (116 mg, 0.42 mmol, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.43–7.40 (m, 2H), 7.35–7.28 (m, 8H), 4.44 (s, 1H), 3.79 (d, *J* = 13.5 Hz, 1H), 3.69 (s, 3H), 3.62 (d, *J* = 13.5 Hz, 1H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 171.1, 137.1, 135.7, 129.0, 128.7, 128.6, 128.5, 128.2, 127.2, 52.7, 51.4, 36.2 ppm; IR (ZnSe): 2953, 2872, 1703, 1471, 1255, 1141, 1083, 1013, 708 cm^{-1}.

*Methyl 2-(benzylthio)-2-(4-chlorophenyl)-acetate (**3b**).*[35] The product was obtained as a colorless oil (130 mg, 0.43 mmol, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.35–7.25 (m, 9H), 4.38 (s, 1H), 3.79 (d, *J* = 13.5 Hz, 1H), 3.69 (s, 3H), 3.62 (d, *J* = 13.5 Hz, 1H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 170.7, 136.8, 134.3, 134.1, 129.9, 129.0, 128.8, 128.5, 127.3, 52.8, 50.6, 36.2 ppm; IR (ZnSe): 2950, 2873, 1711, 1478, 1262, 1139, 1080, 1001, 711 cm^{-1}.

*Methyl 2-phenyl-2-(phenylthio)acetate (**3c**).*[36] The product was obtained as a white solid (103 mg, 0.40 mmol, 80% yield). mp: 46–48 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.48–7.27 (m, 10H), 4.95 (s, 1H), 3.68 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.9, 135.6, 133.6, 132.6, 129.0, 128.7, 128.5, 128.3, 128.0, 56.3, 52.7 ppm; IR (ZnSe): 2951, 2876, 1717, 1489, 1265, 1145, 1089, 1011, 705 cm^{-1}.

*Methyl 2-((4-methoxyphenyl)thio)-2-phenylacetate (**3d**).*[35] The product was obtained as a colorless oil (125 mg, 0.44 mmol, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (d, J = 8.0 Hz, 2H), 7.34–7.30 (m, 5H), 6.80 (d, J = 8.7 Hz, 2H), 4.87 (s, 1H), 3.77 (s, 3H), 3.66 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.0, 160.2, 136.2, 135.7, 128.6, 128.5, 128.2, 123.5, 114.4, 57.3, 55.2, 52.6 ppm; IR (ZnSe): 3005, 2961, 2938, 2837, 1573, 1510, 1495, 1285, 1259, 1030, 829, 775 cm^{-1}.

*Methyl 2-((4-chlorophenyl)thio)-2-phenylacetate (**3e**).* The product was obtained as a white solid (110 mg, 0.37 mmol, 75% yield). mp: 58–60 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42–7.40 (m, 2H), 7.35–7.26 (m, 5H), 7.24–7.23 (m, 2H), 4.87 (s, 1H), 3.69 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.6, 135.2, 134.4, 134.2, 131.9, 129.1, 128.7, 128.5, 128.4, 56.4, 52.8 ppm; IR (ZnSe): 2951, 1713, 1495, 1432, 1281, 1235, 1093, 1009, 823 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{13}ClO_2S$ ($[M + H]^+$) = 293.0397, Found 293.0395.

*Methyl 2-phenyl-2-(p-tolylthio)acetate (**3f**).*[37] The product was obtained as a white solid (122 mg, 0.45 mmol, 90% yield). mp: 60–62 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (d, J = 9.3 Hz, 2H), 7.35–7.25 (m, 5H), 7.24 (d, J = 8.4 Hz, 2H), 4.85 (s, 1H), 3.68 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.9, 138.4, 135.7, 133.3, 129.8, 129.7, 128.6, 128.5, 128.2, 56.7, 52.7, 21.1 ppm; IR (ZnSe): 2951, 1717, 1433, 1268, 1229, 1006, 811, 762, 695 cm^{-1}.

*Methyl 2-(4-methoxyphenyl)-2-(phenylthio)acetate (**3g**).*[22] The product was obtained as a white solid (120 mg, 0.42 mmol, 83% yield). mp: 78–80 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38–7.36 (m, 4H), 7.27–7.26 (m, 3H), 6.87 (d, J = 8.8 Hz, 2H), 4.89 (s, 1H), 3.79 (s, 3H), 3.67 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.0, 159.5, 133.8, 132.5, 129.6, 128.9, 127.9, 127.4, 114.0, 55.6, 55.2, 52.6 ppm; IR (ZnSe): 3002, 2954, 2835, 1718, 1508, 1438, 1252, 1173, 1028, 1003, 830 cm^{-1}.

*Methyl 2-(phenylthio)-2-(p-tolyl)acetate (**3h**).*[22] The product was obtained as white a solid (118 mg, 0.44 mmol, 87% yield). mp: 67–70 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42–7.36 (m, 4H), 7.29–7.27 (m, 3H), 7.16 (d, J = 7.9 Hz, 2H), 4.94 (s, 1H), 3.68 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.0, 138.2, 133.9, 132.5, 132.4, 129.4, 128.9, 128.3, 127.9, 56.0, 52.7, 21.1 ppm; IR (ZnSe): 3049, 2941, 1740, 1578, 1510, 1434, 1329, 1142, 1078, 792 cm^{-1}.

*Methyl 2-(4-chlorophenyl)-2-(phenylthio)acetate (**3i**).*[24] The product was obtained as a white solid (130 mg, 0.45 mmol, 89% yield). mp: 48–50 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39–7.34 (m, 4H), 7.27 (m, 5H), 4.88 (s, 1H), 3.68 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.4, 134.2, 134.2, 133.1, 133.0, 129.9, 129.0, 128.8, 128.3, 55.6, 52.8 ppm; IR (ZnSe): 3050, 2951, 1716, 1488, 1470, 1293, 1235, 849, 767 cm^{-1}.

*Methyl 2-(4-bromophenyl)-2-(phenylthio)acetate (**3j**).*[24] The product was obtained as a white solid (147 mg, 0.44 mmol, 87% yield). mp: 48–50 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45–7.43 (m, 2H), 7.37–7.26 (m, 7H), 4.85 (s, 1H), 3.68 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.4, 134.7, 133.0, 131.8, 131.7, 130.2, 129.0, 128.3, 122.4, 55.7, 52.8 ppm; IR (ZnSe): 3051, 2949, 1713, 1483, 1469, 1290, 1231, 838, 767 cm^{-1}.

*Ethyl 2-phenyl-2-(phenylthio)acetate (**3k**).* The product was obtained as a colorless oil (113 mg, 0.42 mmol, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.47 (d, J = 9.5 Hz, 2H), 7.42–7.38 (m, 2H), 7.36–7.30 (m, 3H), 7.29–7.25 (m, 3H), 4.93 (s, 1H), 4.19–4.07 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.4, 135.6, 133.8, 132.6, 128.9, 128.6, 128.5, 128.2, 127.9, 61.7, 56.3, 14.0 ppm; IR (ZnSe): 2948, 2881, 1719, 1469, 1257, 1139, 1010, 759 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{16}O_2S$ ([M + H]$^+$) = 273.0944, Found 273.0949.

*Isobutyl 2-phenyl-2-(phenylthio)acetate (**3l**).* The product was obtained as a colorless oil (128 mg, 0.43 mmol, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.51 (d, J = 9.6 Hz, 2H), 7.42–7.38 (m, 2H), 7.36–7.30 (m, 3H), 7.29–7.24 (m, 3H), 4.96 (s, 1H), 3.88 (d, J = 6.6 Hz, 2H), 1.90–1.83 (m, 1H), 0.84 (d, J = 6.7 Hz, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.4, 135.7, 133.9, 132.4, 128.9, 128.6, 128.5, 128.2, 127.8, 71.7, 56.5, 27.6, 18.9 ppm; IR (ZnSe): 3049, 2950, 2881, 1719, 1469, 1257, 1139, 1010 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{20}O_2S$ ([M + H]$^+$) = 301.1257, Found 301.1255.

*Methyl 1,2-diphenylcyclopropane-1-carboxylate (**4**).*[38] The product was obtained as a white soild (34 mg, 0.13 mmol, 27% yield). mp: 57–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.15–7.13 (m, 3H), 7.07–7.03 (m, 5H), 6.79–6.76 (m, 2H), 3.67 (s, 3H), 3.15 (dd, J = 9.2, 7.5 Hz, 1H), 2.17 (dd, J = 9.3, 4.9 Hz, 1H), 1.91 (dd, J = 7.2, 4.9 Hz, 1H); ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 174.3, 136.3, 134.7, 131.9, 128.0, 127.7, 127.6, 127.0, 126.2, 52.6, 37.3, 33.1, 20.4 ppm; IR (ZnSe): 3073, 1751, 1248, 1114, 1011, 979, 849, 676 cm^{-1}.

*Allyl 2-phenylacetate (**6**).*[39] The product was obtained as a colorless oil (1.67 g, 9.48 mmol, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.34–7.25 (m, 5H), 5.93–5.85 (m, 1H), 5.29–5.19 (m, 2H), 4.60 (s, 2H), 3.65 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.1, 133.9, 132.0,

129.2, 128.5, 127.1, 118.1, 65.4, 41.3 ppm; IR (ZnSe): 3075, 1751, 1253, 1115, 1003, 985, 853, 682 cm^{-1}.

*1-Phenyl-3-oxabicyclo[3.1.0]hexan-2-one (**7**).*[40] The product was obtained as a colorless oil (26 mg, 0.15 mmol, 59% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.44–7.41 (m, 2H), 7.38–7.34 (m, 2H), 7.32–7.26 (m, 1H), 4.47 (dd, *J* = 9.2, 4.6 Hz, 1H), 4.31 (d, *J* = 9.3 Hz, 1H), 2.58–2.54 (m, 1H), 1.67 (dd, *J* = 7.8, 4.8 Hz, 1H), 1.38 (t, *J* = 4.8 Hz, 1H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 176.0, 134.0, 128.6, 128.3, 127.6, 68.0, 31.7, 25.0, 20.1 ppm; IR (ZnSe): 3060, 2973, 2907, 1758, 1602, 975, 850, 675 cm^{-1}.

General procedure for preparation of 2-diazopropiophenones. To a 25 mL flame-dried flask under argon was added a 60% dispersion of sodium hydride in mineral oil (0.71 g, 17.79 mmol), one drop of anhydrous ethyl alcohol and anhydrous diethyl ether (2 mL). The mixture was cooled with an ice-bath, then a solution of corresponding propiophenone derivatives (5.93 mmol) and ethyl formate (1.32 g, 17.79 mmol) in anhydrous diethyl ether (2 mL) was added dropwise. The mixture was stirred for 3 h at 0 °C, then 12 h at room temperature. Then, a solution of methanesulfonyl azide (2.15 g, 17.79 mmol) in anhydrous diethyl ether (5 mL) was added dropwise and the mixture was stirred another 2h. The mixture was quenched with water (2 mL), then the organic phases were washed with a solution of 10% NaOH in water. The organic phases were extracted with diethyl ether (2 x 25 mL) and the organic phases were combined, dried over $MgSO_4$ and evaporated under reduced pressure (temperature 30 °C). The crude product was purified on flash chromatography (Hexane/EtOAc).

*2-Diazo-1-phenylpropan-1-one (**8a**).*[26c] The product was obtained as a yellow liquid (0.702 g, 4.39 mmol, 74% yield). ^1H RMN (400 MHz, $CDCl_3$) δ_H 7.59–7.55 (m, 2H), 7.51–7.46 (m, 1H),

7.45–7.40 (m, 2H), 2.15 (s, 3H) ppm. $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 190.1, 137.6, 131.3, 128.5, 127.1, 62.8, 9.5 ppm; IR (ZnSe): 2062, 1600, 1571, 1445, 1277, 1000, 890, 781 cm^{-1}.

*2-Diazo-1-(p-tolyl)propan-1-one (**8b**).*[26c] The product was obtained as a yellow solid (0.494 g, 2.84 mmol, 48% yield). mp: 42–44 °C; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.48 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 2.38 (s, 3H), 2.14 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 189.9, 141.8, 134.9, 129.1, 127.6, 62.5, 21.5, 9.6 ppm; IR (ZnSe): 2072, 1592, 1340, 1277, 1022, 836, 736, 690 cm^{-1}.

*2-Diazo-1-(p-chlorophenyl)propan-1-one (**8c**).*[26d] The product was obtained as a yellow solid (0.433 g, 2.23 mmol, 38% yield). mp: 46–47 °C; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.52 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 2.14 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 188.6, 137.4, 135.8, 128.8, 128.6, 62.9, 9.6 ppm; IR (ZnSe): 2074, 1561, 1342, 1273, 1112, 997, 840, 681 cm^{-1}.

*2-Diazo-1-(p-fluorophenyl)propan-1-one (**8d**).*[26c] The product was obtained as a yellow solid (0.549 g, 3.08 mmol, 52% yield). mp: 57–59 °C; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.59 (dd, J = 8.8, 5.3 Hz, 2H), 7.10 (t, J = 8.6 Hz, 2H), 2.13 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 188.6, 164.3 (d, J = 252.2 Hz), 133.7 (d, J = 3.2 Hz), 129.6 (d, J = 8.8 Hz), 115.6 (d, J = 21.9 Hz), 62.8, 9.5 ppm; IR (ZnSe): 2058, 1620, 1341, 1219, 1178, 1004, 780, 740 cm^{-1}.

*1-(Benzo[d][1,3]dioxol-5-yl)-2-diazopropan-1-one (**8e**).*[26e] The product was obtained as a yellow solid (0.605 g, 2.96 mmol, 50% yield). mp: 66–68 °C; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.12 (dd, J = 8.0, 1.7 Hz, 1H), 7.05 (d, J = 1.7 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.00 (s, 2H), 2.11 (s, 3H)

ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 188.6, 150.2, 147.8, 131.7, 122.2, 107.92, 107.8, 101.6, 62.2, 9.7 ppm; IR (ZnSe): 2070, 1625, 1495, 1367, 1234, 1007, 751, 690 cm^{-1}.

General procedure for preparation of 2-diazo-1,2-diphenylethan-1-one and 1-diazo-1-phenylpropan-2-one. To a 25 mL flame-dried flask under argon was added the corresponding ketone (12 mmol), *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (3.60 g, 15 mmol) and anhydrous acetonitrile (15 mL). The mixture was cooled with an ice-bath and a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.35 mL, 2.40 g, 16 mmol) in anhydrous acetonitrile (5 mL) was added dropwise over 0.5 h. The mixture was stirred 1 h at 0 °C, then at room temperature until the reaction was completed. The reaction was then quenched with a solution of 10% NaOH in water. The organic phases were extracted with diethyl ether (2 x 25 mL), combined, dried over $MgSO_4$ and evaporated under reduced pressure (temperature 30 °C).

*2-Diazo-1,2-diphenylethan-1-one (**8f**).*[26c] The crude product was rapidly passed on 4 cm on silica gel with the solvent being hexanes: diethyl ether: triethylamine (70: 28: 2). The product was obtained as an orange solid (2.00 g, 9.01 mmol, 75% yield). mp: 70–73 °C; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.64–7.60 (m, 2H), 7.53–7.46 (m, 3H), 7.45–7.38 (m, 4H), 7.29–7.24 (m, 1H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 188.4, 137.9, 131.7, 129.0, 128.7, 128.5, 127.7, 127.0, 126.0, 57.8 ppm; IR (ZnSe): 2061, 1611, 1594, 1349, 1238, 1179, 848, 690 cm^{-1}.

*1-Diazo-1-phenylpropan-2-one (**8g**).*[26f] The crude was purified by flash chromatography. The product was obtained as a yellow solid (0.845 g, 5.28 mmol, 44% yield). mp: 44–47 °C; ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.49 (d, J = 7.3 Hz, 2H), 7.41 (t, J = 7.9 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 2.36 (s, 3H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 189.9, 129.0, 126.9, 125.8, 125.5, 109.9, 26.9 ppm; IR (ZnSe): 2070, 1625, 1495, 1367, 1234, 1006, 751, 690 cm^{-1}.

2-Diazo-1-phenylbutan-1-one (**8h**). The product was obtained as a yellow liquid (2.2 g, 12.64 mmol, 74% yield). ^{1}H RMN (400 MHz, $CDCl_3$) δ_H 7.61–7.54 (m, 2H), 7.52–7.43 (m, 1H), 7.46–7.37 (m, 2H), 2.57 (q, *J* = 7.5 Hz, 2H), 1.20 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C{H} NMR ($CDCl_3$, 100 MHz) δ_C 189.5, 137.8, 131.3, 128.5, 127.1, 68.4, 17.1, 11.4 ppm; IR (ZnSe): 2950, 2061, 1605, 1573, 1338, 1053, 872, 781cm^{-1}.

General procedure for Si–H insertion of α-diazoketones. In a flame-dried glass tube, under argon atmosphere, $[(CH_3CN)_4Cu]PF_6$ (0.11 mg, 0.0003 mmol, 0.05 mol %) was diluted in CH_2Cl_2 (0.5 mL) at room temperature. The triethylsilane (504 μL, 363.3 mg, 3 mmol) was then introduced into the mixture. Methyl α-diazoketone (0.6 mmol), diluted in CH_2Cl_2 (0.6 mL), and was added dropwise over 1.5 h using a syringe pump. The mixture was stirred for the specified time and subsequently filtered through celite and evaporated under reduce pressure (rotary evaporator). The residue was purified by flash chromatography to afford the product. 4Å Molecular sieves (50 mg) was used to form *C*-silylated product **9a**, **9b**, **9f** and **9g**.

*1-Phenyl-2-(triethylsilyl)propan-1-one (**9a**).*[7a] The product was obtained as a colorless oil (109 mg, 0.44 mmol, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.87–7.83 (m, 2H), 7.55–7.49 (m, 1H), 7.45–7.40 (m, 2H), 3.45 (q, *J* = 6.8 Hz, 1H), 1.36 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.49 (dtd, *J* = 8.3, 7.5, 2.2 Hz, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 204.0, 139.2, 132.2, 128.3, 127.8, 33.0, 12.0, 7.2, 2.4 ppm; IR (ZnSe): 2953, 2909, 2875, 1659, 1446, 1238, 1003, 687 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{24}OSi$ ($[M + H]^+$) = 249.1669, found 249.1672.

*1-(p-Tolyl)-2-(triethylsilyl)propan-1-one (**9b**).* The product was obtained as a colorless oil (87 mg, 0.33 mmol, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.76 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 2H), 3.41 (q, *J* = 6.8 Hz, 1H), 2.40 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 7.9 Hz,

9H), 0.50 (dtd, *J* = 8.3, 7.6, 3.1 Hz, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 203.5, 142.8, 136.6, 129.0, 128.0, 32.6, 21.5, 12.0, 7.2, 2.4 ppm; IR (ZnSe): 2952, 2910, 2874, 1655, 1224, 1207, 975, 705 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{26}OSi$ ($[M + H]^+$) = 263.1826, found 263.1819.

*1-(4-Chlorophenyl)-2-(triethylsilyl)propan-1-one (**9c**).* The product was obtained as a colorless oil (46 mg, 0.16 mmol, 26% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.80 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.7 Hz, 2H), 3.38 (q, *J* = 6.7 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.49 (dtd, *J* = 8.3, 7.5, 3.0 Hz, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 202.6, 138.6, 137.4, 129.3, 128.6, 33.0, 11.9, 7.2, 2.4 ppm; IR (ZnSe): 2954, 2910, 2875, 1658, 1460, 1214, 1119, 769, 696 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}ClOSi$ ($[M + H]^+$) = 283.1279, found 283.1274.

*1-(4-Fluorophenyl)-2-(triethylsilyl)propan-1-one (**9d**).* The product was obtained as a colorless oil (52 mg, 0.19 mmol, 31% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.88 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 3.38 (q, *J* = 6.7 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.50 (qd, *J* = 7.9, 2.7 Hz, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 202.3, 165.2 (d, *J* = 253.1 Hz), 135.5 (d, *J* = 3.1 Hz), 130.3 (d, *J* = 9.2 Hz), 115.3 (d, *J* = 21.6 Hz), 32.9, 12.0, 7.2, 2.4 ppm; IR (ZnSe): 2954, 2910, 2876, 1658, 1596, 1216, 821, 704 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{23}FOSi$ ($[M + H]^+$) = 267.1575, found 267.1572.

*1-(Benzo[d][1,3]dioxol-5-yl)-2-(triethylsilyl)propan-1-one (**9e**).* The product was obtained as a colorless oil (64 mg, 0.22 mmol, 35% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.36 (d, *J* = 1.7 Hz, 1H), 6.80 (dd, *J* = 8.1, 0.4 Hz, 1H), 6.02 (q, *J* = 1.4 Hz, 2H), 3.31 (q, *J* = 6.8 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.50 (qd, *J* = 7.9, 3.3

Hz, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): 201.9, 151.0, 147.9, 133.9, 123.6, 107.9, 107.5, 101.6, 32.4, 12.1, 7.2, 2.4 ppm; IR (ZnSe): 2952, 2875, 1651, 1462, 1239, 1036, 933, 704 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{24}O_3Si$ ($[M + H]^+$) = 293.1567, found 293.1566.

*1,2-Diphenyl-2-(triethylsilyl)ethan-1-one (**9f**).* The product was obtained as a colorless oil (118 mg, 0.38 mmol, 61% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.37 (m, 1H), 7.98–7.94 (m, 2H), 7.57–7.46 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 4.75 (s, 1H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.55 (qd, *J* = 8.4, 7.9, 4.7 Hz, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 199.9, 139.2, 137.3, 132.4, 128.4, 128.2, 128.2, 128.1, 125.5, 47.5, 7.2, 2.8 ppm; IR (ZnSe): 2951, 2875, 1663, 1300, 1201, 1034, 998, 758 cm^{-1}; HRMS (ESI): calcd for $C_{20}H_{26}OSi$ ($[M + H]^+$) = 311.1826, found 311.1830.

*1-Phenyl-1-(triethylsilyl)propan-2-one (**9g**).* The product was obtained as a colorless oil (91 mg, 0.37 mmol, 59% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.32 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.29–7.26 (m, 2H), 7.19–7.14 (m, 1H), 3.89 (s, 1H), 2.21 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.61 (qd, *J* = 8.4, 7.9, 3.7 Hz, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 206.7, 136.9, 128.3, 128.1, 125.5, 53.5, 32.2, 7.2, 2.8 ppm; IR (ZnSe): 2063, 1571, 1445, 1278, 1001, 929, 890, 781 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{24}OSi$ ($[M + H]^+$) = 249.1669, found 249.1671.

1-Phenyl-2-(triethylsilyl)butan-1-one (**9h**). The product was obtained as a colorless liquid (13 mg, 0.05 mmol, 3% yield). ^1H RMN (400 MHz, $CDCl_3$) δ_H 7.92–7.84 (m, 2H), 7.57–7.48 (m, 1H), 7.48–7.39 (m, 2H), 3.32 (dd, *J* = 11.5, 2.6 Hz, 1H), 2.37–2.12 (m, 1H), 1.63–1.58 (m, 1H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.50 (q, *J* = 8.0 Hz, 6H) ppm; $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ_C 203.4, 140.1, 132.2, 128.3, 127.8, 42.4, 21.1, 15.5, 7.2, 2.6 ppm; IR

(ZnSe): 2898, 1600, 1366, 1089, 991, 820, 778, 710 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{27}OS$ ([M + H]$^+$) = 263.1831, found 263.1839.

(E)-1-Phenylbut-2-en-1-one (**9h'**).[41] The product was obtained as a colorless liquid (40 mg, 0.27 mmol, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.95–7.88 (m, 2H), 7.58–7.50 (m, 1H), 7.50–7.41 (m, 2H), 7.14–7.00 (m, 1H), 6.90 (dq, *J* = 15.3, 1.6 Hz, 1H), 1.99 (dd, *J* = 6.8, 1.6 Hz, 3H).

*Methyl 2-hydroxy-2-phenylacetate (**10**).*[42] The product was obtained as a white solid (108 mg, 0.65 mmol, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.43–7.30 (m, 5H), 5.15 (s, 1H), 3.76 (s, 3H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 174.1, 138.2, 128.6, 128.5, 126.6, 72.9, 53.0 ppm; IR (ZnSe): 3511, 3019, 2956, 1736, 1455, 1438, 1254, 1216, 1067, 753 cm^{-1}.

*Methyl-2,3-diphenylacrylate (**11**).*[30] The product was obtained as a yellow oil (93 mg, 0.39 mmol, 78% yield, 65:35 *E*/*Z* mixture, determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89 (s, 1H), 7.50–7.15 (m, 19H), 7.08–7.05 (m, 2H), 3.81 (s, 6H) ppm; ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.1 (*Z*), 168.3 (*E*), 140.5 (*E*), 136.8 (*Z*), 135.8 (*E*), 135.6 (*Z*), 134.8 (*Z*), 134.5 (*E*), 132.4 (*E*), 131.5 (*Z*), 130.6 (*E*), 129.7 (*E*), 129.0 (*E*), 128.7 (*Z*), 128.6 (*E*), 128.5 (*Z*), 128.3 (*Z*), 128.2 (*E*), 128.1 (*Z*), 127.8 (*E*), 126.4 (2C) (*Z*), 52.4 (*Z*), 52.2 (*E*) ppm; IR (ZnSe): 3014, 2953, 1708, 1624, 1493, 1448, 1435, 1257, 1193, 1168 cm^{-1}.

*2-Phenyl-2-(triethylsilyl)ethan-1-ol (**12**).* (The preparation of **12**, **13**, **14** and **16** was made according to the procedure reported on different substrate).[31] The product was obtained as a colorless oil (0.520 g, 2.20 mmol, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29–7.25 (m, 2H), 7.15–7.11 (m, 3H), 4.17 (t, *J* = 11.6 Hz, 1H), 3.94 (dd, *J* = 11.3, 4.1 Hz, 1H), 2.60 (dd, *J* = 11.8,

4.2 Hz, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.60–0.49 (m, 6H) ppm; $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 140.6, 128.5, 128.0, 125.2, 63.1, 39.3, 7.3, 6.5, 5.7, 2.4 ppm; IR (ZnSe): 3350, 2951, 2874, 1450, 1237, 1041, 1006, 804, 697 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{24}OSi$ ($[M + Na]^+$) = 259.1489, found 259.1494.

*2-Phenyl-2-(triethylsilyl)ethyl 2-phenylacetate (**13**).* The product was obtained as a pale yellow oil (0.297 g, 0.84 mmol, 90% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.26–7.03 (m, 10H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.50 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.47 (s, 2H), 2.70 (dd, *J* = 11.7, 4.3 Hz, 1H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.55–0.49 (m, 6H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 171.8, 140.6, 133.9, 129.1, 128.4, 128.2, 127.6, 126.8, 124.9, 65.9, 41.4, 34.7, 7.3, 2.4 ppm; IR (ZnSe): 2952, 2875, 1731, 1495, 1453, 1238, 1134, 1004, 971, 696 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{30}O_2Si$ ($[M + Na]^+$) = 377.1907, found 377.1915.

*2-Phenyl-2-(triethylsilyl)ethyl 2-diazo-2-phenylacetate (**14**).* The product was obtained as an orange oil (0.288 g, 0.76 mmol, 89% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.30–7.26 (m, 6H), 7.17–7.09 (m, 4H), 4.78–4.71 (m, 2H), 2.79 (dd, *J* = 10.8, 5.8 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.62–0.56 (m, 6H); $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 165.5, 140.5, 128.7, 128.3, 127.7, 125.6, 125.5, 125.1, 123.9, 66.2, 35.0, 7.3, 2.5 ($C=N_2$: not observed) ppm; IR (ZnSe): 3024, 2952, 2874, 2081, 1695, 1497, 1238, 1148, 1006, 752, 697 cm^{-1}; HRMS (ESI): calcd for $C_{22}H_{28}N_2O_2Si$ ($[M + Na]^+$) = 403.1812, found 403.1807.

*(E)-(1,3-Diphenylallyl)triethylsilane (**16**).* The product was obtained as a colorless oil (19 mg, 0.06 mmol, 48% yield). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.53–7.49 (m, 2H), 7.31–7.26 (m, 4H), 7.16 (dd, *J* = 8.2, 1.3 Hz, 4H), 5.23 (dd, *J* = 12.7, 11.3 Hz, 1H), 4.63 (dd, *J* = 11.4, 4.0 Hz, 1H), 2.90 (dd, *J* = 12.7, 4.0 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.62–0.56 (m, 6H); $^{13}C\{H\}$ NMR (100

MHz, $CDCl_3$): δ_C 186.8, 164.3, 139.8, 134.5, 132.1, 129.8, 128.6, 128.5, 127.8, 125.3, 67.2, 35.3, 7.3, 2.4 ppm; IR (ZnSe): 3061, 2953, 1683, 1595, 1449, 1197, 1174, 970 cm^{-1}; HRMS (ESI): calcd for $C_{21}H_{28}Si$ ($[M + Na]^+$) = 331.1852, found 331.1849.

ASSOCIATED CONTENT

Supporting Information Available.

^1H and ^{13}C NMR spectra.

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ACKNOWLEDGMENT

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), the Centre in Green Chemistry and Catalysis (CGCC) and Université Laval for financial support of our program. H. K. thanks CGCC for a scholarship.

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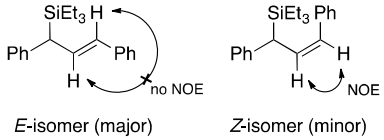
(43) *Note: The alkene geometry of* ***16*** *was determined by NOE correlations:*



E-isomer (major) *Z*-isomer (minor)