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Rhodium(II)-catalyzed enantioselective intramolecular CH insertion with alkyl diazo(trialkylsilyl) acetates

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Abstract—The decomposition of cyclohexyl diazo(triethylsilyl)acetate **2a** and the *t*-butyl derivatives **3a**,**b** with $[Rh_2\{(S)\text{-nttl}\}_4]$ and similar chiral Rh(II)-catalysts proceeds in toluene at room temperature to produce silylated lactones in up to 90% yield. The reaction is highly stereoselective. Enantioselectivities of up to 79% have been observed.

1. Introduction

The intra-[1] and intermolecular[2] carbon–hydrogen bond insertion of diazoacetate esters in the presence of chiral, non-racemic catalysts proceeds with very high enantioselectivities. Attractive applications based on this methodology have been described with alkyl diazoacetate, alkyl vinyl- or alkyl phenyldiazoacetate esters.[3]

Diazo compounds carrying silyl substituents have been known for some time. Thus, trimethylsilyldiazomethane[4] cyclopropanates olefins in the presence of $PdCl_2$[5] or CuCl.[6] Some time ago, we observed enantioselective olefin cyclopropanations with trimethylsilyldiazomethane in the presence of $[R_2\{(2S)\text{-mepy}\}_4]$ with ee's of up to 54%. However, owing to problems encountered in the attempted desilylation of the cyclopropanes, this research was not continued.[7] In the absence of catalysts trimethylsilyldiazomethane affords aziridines with imines.[8] Aziridines are also formed upon transition metal-catalyzed decomposition of trimethylsilyldiazomethane[9] and enantioselectivities of up to 72% ee have been reported.[10] The photolysis of ethyl diazo(trimethylsilyl)acetate in the presence of simple olefins has been reported by Schöllkopf et al. in 1969.[11] However, only a few isolated studies concerning the transition metal-catalyzed decomposition of silylated diazoacetates have been carried out. Maas et al. investigated the diastereoselectivity of the intermolecular olefin cyclopropanation of silylated diazoacetate esters in the presence of Ru(I)-catalysts, and a preference for the sterically less congested stereoisomer was observed.[12] Subsequently, the stereoselectivity of methyl diazoacetates having different trialkylsilyl groups was examined with [Cu(OTf)], $[Rh_2(OAc)_4]$ and $[Ru(CO)_4(\mu\text{-}OAc)_2]_n$ and the predominance of the less congested diastereomer was confirmed.[13]

Recent investigations of Marsden et al. revealed that silylated diazoacetate esters undergo intramolecular CH insertions in the presence of $[Rh_2(OAc)_4]$ to afford silylated lactones,[14] or oxasilacyclopentanes,[15] respectively, in a highly diastereoselective manner. The observations of Marsden et al. combined with our own results on enantioselective olefin cyclopropanation with trimethylsilyldiazomethane suggested the possibility of carrying out enantioselective intramolecular CH insertions with silylated diazoacetate esters (Scheme 1).

2. Results and discussion

2.1. Synthesis of cyclohexyl diazo(triorganylsilyl)-acetates

The diazo esters **2a**–**c** and **3a**,**b** were prepared by treatment of the appropriate cyclohexyl diazoacetates (**1a**–**c**)[1,16] with trialkylsilyl triflate and ethyl diisopropylamine in ether at −78°C.[17] They were isolated in yields varying from 83 to 94%. The dimethylphenylsilyl derivative **2d**, in turn, was synthesized by treatment of **1a** with (dimethylphenyl)silyl chloride in the presence of LDA. The compound was highly labile, and decomposed partially upon attempted purification (chromatography on SiO_2).

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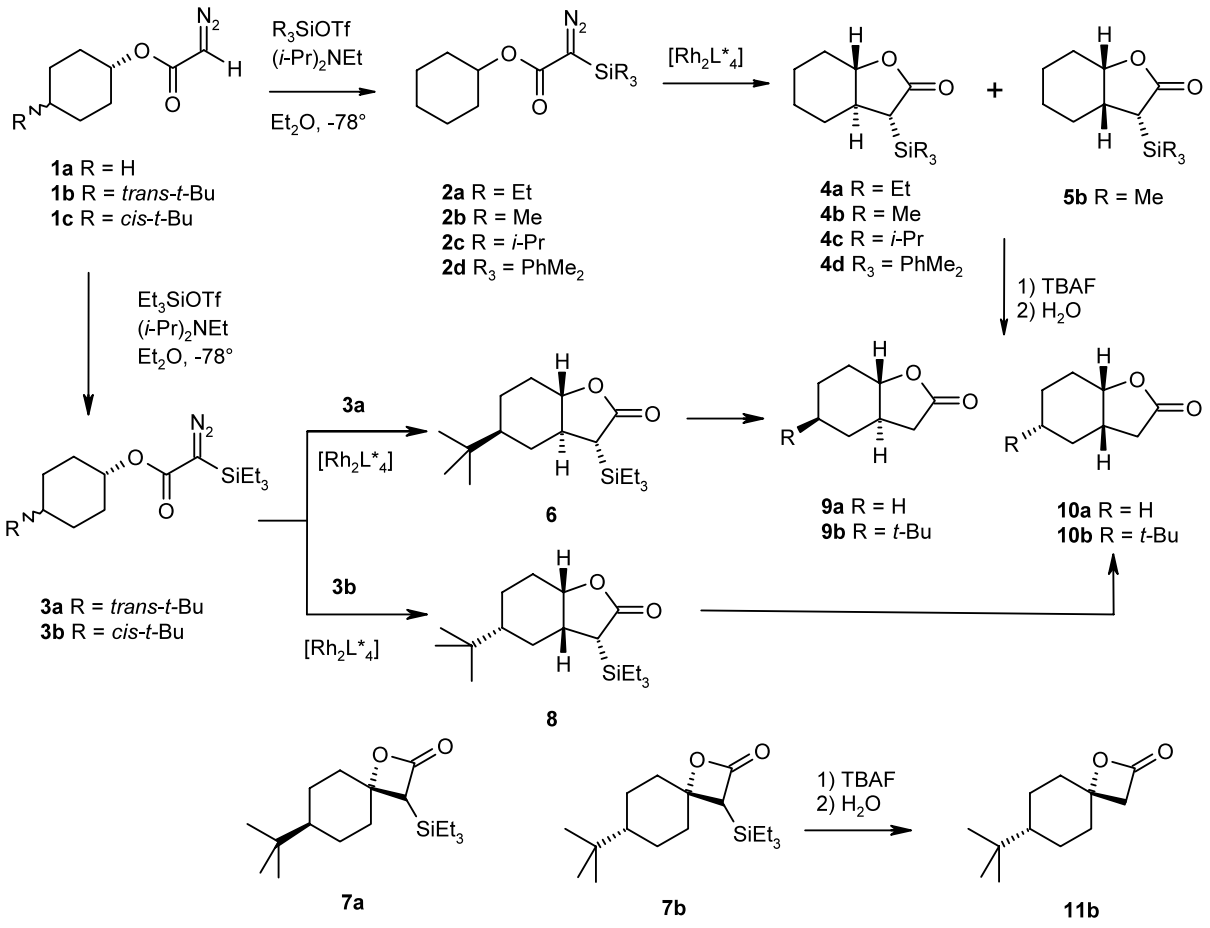


Scheme 1.

2.2. Decomposition of cyclohexyl diazo(triethylsilyl)-acetates 2a and 3a,b

Initially, the insertions were carried out with **2a** and the *cis*- and *trans*-*t*-butyl derivatives **3a**,**b** under the conditions reported by Marsden, i.e. with $[Rh_2(OAc)_4]$ in refluxing benzene (Table 1). The reactions proceeded sluggishly and only in moderate yields to afford the corresponding lactones **4a**, **6** and **8**, respectively. The stereochemistry at the ring junction was established via desilylation with TBAF which afforded the known lactones **9a**,**b** and **10b**.[1] In all cases, only insertion into the equatorial CH bond was observed, i.e. the *trans*-lactones **4a** and **6** were formed exclusively from **2a**, and **3a**, and the *cis*- lactone **8** from **3b**. This contrasts with the behavior of the unsilylated diazoester **1a** which, upon diazo decomposition with $[Rh_2(OAc)_4]$ yields a mixture of *trans*- and *cis*-lactones **9a** and **10a**.

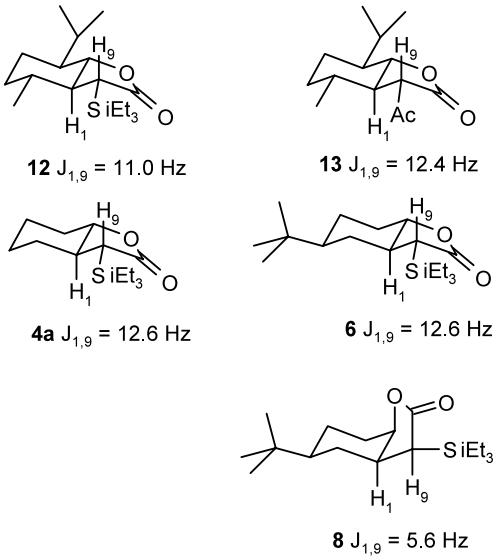
The formation of *trans*-lactone **4a** from **2a** necessarily involves that conformation of the cyclohexane ring where the diazoester occupies an equatorial position. The same conformation could in principle also lead to a *cis*-lactone via insertion into an axial CH bond, as is the case with **1a**,[1] but this pathway is not followed with the triethylsilyl substituent. An axial diazoacetate group, in turn, must result in a *cis*-lactone for steric reasons. As expected, with the conformationally blocked 4-*t*-butylcyclohexyl diazo acetates, the *trans* isomer **3a**, in which the substituent is equatorial, yields exclusively *trans*-lactone **6**, while in the case of the *cis*-*t*-butyl derivative **3b** the resulting lactone **8** has a *cis*-configuration at the ring junction. This is consistent with the previously observed preferential insertion into equatorial CH bonds of cyclohexyl diazoacetates upon decomposition with Rh(II)-catalysts (Scheme 2).

Table 1. $[Rh_2(OAc)_4]$-catalyzed intramolecular CH insertion of cyclohexyl diazo(triethylsilyl)acetates **2a** and **3a**,**b**[a]

Compound	Solvent, T (°C)	Time	Yield (%)
2a	C_6H_6, 80	15 h	42
2a	$PhCH_3$, 25	4 days	33
2a	CH_2Cl_2, 25	1 day	61
3a	C_6H_6, 80	15 h	34
3b	C_6H_6, 80	15 h	21

[a] With 2% of catalyst.

The orientation of the silyl substituent in the lactones was assigned on the grounds of the ^1H NMR spectra or by X-ray crystallography: Marsden has assigned the configuration of **12** via comparison of the vicinal H-C(1)/H-C(9) coupling constants of 11.0 Hz, consistent with a dihedral angle of ca. 140°, and in good agreement with that of **13** with 12.4 Hz. The analogous



Scheme 2.

coupling constants of 12.6 Hz in **4a** and **6**, respectively, suggests the same relative configuration. In contrast, in **8** where the oxygen of the lactone occupies an axial position on the cyclohexane ring, the dihedral angle of H-C(1) and H-C(9) is reduced to ca. 100°, which results in a coupling constant of 5.6 Hz. On these grounds, the relative configuration was tentatively assigned. Unfortunately, NOE experiments to confirm this assignment were not conclusive. However, since **8** is crystalline, the assignment was confirmed by X-ray structure analysis on the racemic compound (Fig. 1).

That $[Rh_2(OAc)_4]$ is only partially satisfactory for diazo decomposition of silylated diazoacetates has been reported by others. Despite this, we have screened a variety of chiral Rh(II)-catalysts for the insertion of **2a** (Table 2). The enantiomers of **4a** were separated by GC (see Section 4). The Rh(II) carboxamidate-catalysts of Doyle, such as $[Rh_2\{(4S)\text{-meox}\}_4]$ produced no decomposition even at 80°C. The reportedly more reactive $[Rh_2\{(4S)\text{-bnaz}\}_4]$ was tested in different solvents at elevated temperatures. Although the yields were disappointing, enantioselectivities of up to 71% were observed. Pirrung's binol phosphate catalyst $[Rh_2\{(R)$ or $(S)\text{-bnp}\}_4]$ provided low yields even at 80°C, and

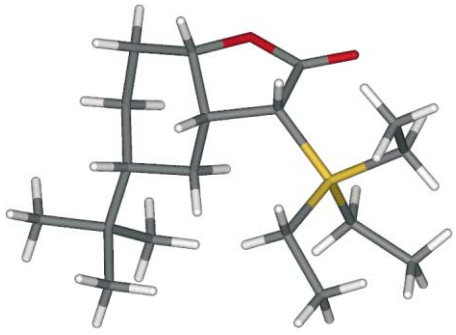


Figure 1. X-Ray crystal structure of *rac*-**8**.

Table 2. Intramolecular insertion of cyclohexyl diazo (triethylsilyl)acetate **2a** in benzene[a]

Catalyst	T (°C)	Time	Yield[b] (%)	ee (%)
$[Rh_2\{(4S)\text{meox}\}_4]$	80	6 h	0	0
$[Rh_2\{(2S)\text{mepy}\}_4]$	80	2 days	16	0
$[Rh_2\{(4S)\text{-bnaz}\}_4]$	80	5 h	10	71
$[Rh_2\{(-)\text{campha}\}_4]$	80	15 h	62	02
$[Rh_2\{(-)\text{-mpmt}\}_4]$	40	2.5 h	34	07
$[Rh_2\{(-)\text{-tbsp}\}_4]$	80	1.5 h	45	13
$[Rh_2\{(-)\text{-dosp}\}_4]$	80	1.5 h	49	13
$[Rh_2\{(S)\text{-bnp}\}_4]$	80	2.5 h	30	40
$[Rh_2\{(R)\text{-bnp}\}_4]$	80	21 h	21	39
$[Rh_2\{(S)\text{-ptpa}\}_4]$	80	2 h	50	19
$[Rh_2\{(S)\text{-pttl}\}_4]$	60	1 h	67	60
$[Rh_2\{(S)\text{-nttl}\}_4]$	80	15 h	68	59

[a] 2% of catalyst.
[b] Isolated yield.

lower enantioselectivity (40%). The proline derived catalysts $[Rh_2\{(-)\text{-tbsp}\}_4]$ and $[Rh_2\{(-)\text{-dosp}\}_4]$ were equally unsatisfactory both with respect to yield and enantioselectivity.

The effect of temperature and solvent on the decomposition of **2a** was investigated with several catalysts (Table 3). With $[Rh_2\{(4S)\text{-bnaz}\}_4]$ an increase of temperature to 110°C and a solvent change to 1,2-dichloroethane (DCE) or trifluorotoluene had no significant effect on the yield, although in trifluorotoluene the ee went up to 79%. Surprisingly, however, we found that the Ikegami-type catalysts such as $[Rh_2\{(S)\text{-ptpa}\}_4]$ and, in particular our recently developed $[Rh_2\{(S)\text{-nttl}\}_4]$[18] were much more efficient than all the other catalysts tried, and in the end reactions could be carried out at room temperature and with short reaction times. Yields were in the range of 74–90%, and the enantioselectivity culminated at 66%, slightly below the 79% ee obtained with $[Rh_2\{(4S)\text{-bnaz}\}_4]$ (Scheme 3).

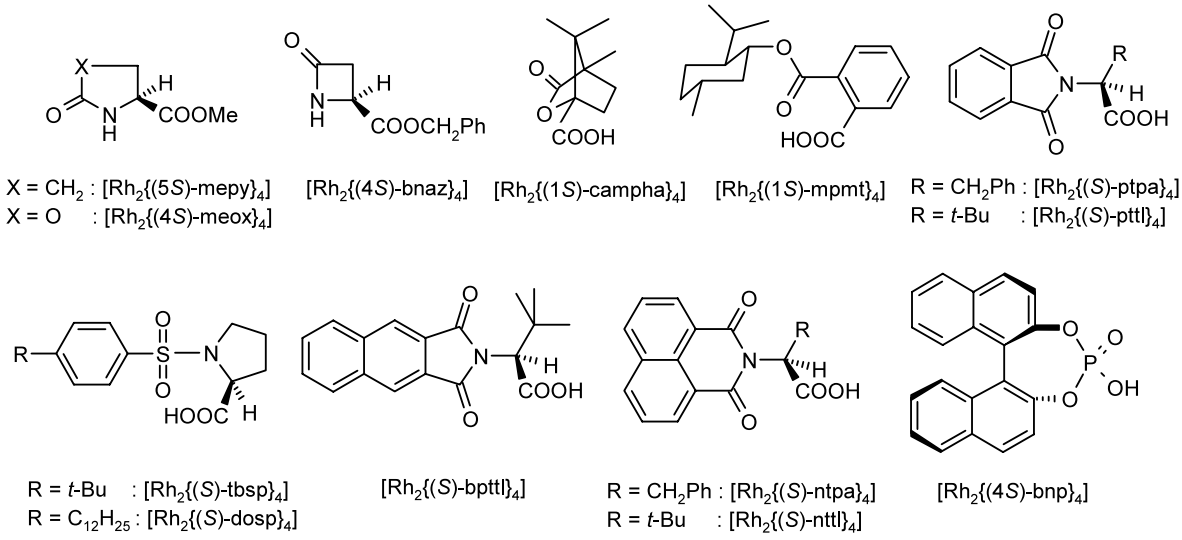
The abs. configuration of **4a** was determined by comparison of the specific rotation of the desilylated **9a** with data previously reported in the literature. The specific rotation of authentic (1*R*,6*S*)-**9a** is $[\alpha]_D^{25} = -75.0$ (*c* 0.2, MeOH).[19] The insertion product **4a** resulting from reaction of **2a** with $[Rh_2\{(S)\text{-nttl}\}_4]$ had $[\alpha]_D^{20} = -16.1$ for 66% ee and **9a** obtained via desilylation of **4a** had $[\alpha]_D^{20} = -42.4$ for 61% ee, which corresponds to (1*S*,6*S*,9*R*)-configuration of **4a**. Note that the Si-substituent at C(9) inverts the CIP priorities of the substituents at C(1) in going from **4a** to **9a**.

Some asymmetric insertions were also carried out with **3a**,**b**. The insertions were accompanied by formation of β-lactones **7a**,**b** in the range of 4–5% upon decomposition of **3a** and 21–27% from **3b**. Their structure was assigned on the grounds of the IR-stretching frequency of the carbonyl group at 1796 and 1798 cm^{-1}, respectively, and a singlet at 2.92 in the ^1H NMR attributed to H-C(9). The silylated β-lactone **7b** was desilylated to afford **11b**. The ee of the β-lactones **7a**,**b** was not determined. The results for the γ-lactones are summa-

Table 3. Effect of solvent and temperature on the intramolecular insertion of cyclohexyl diazo (triethylsilyl)acetate **2a**[a]

Catalyst	Solvent	T (°C)	Time (h)	Yield (%)	ee (%)
$[Rh_2\{(4S)\text{-bnaz}\}_4]$	DCE	83	20	11	74
$[Rh_2\{(4S)\text{-bnaz}\}_4]$	$PhCH_3$	110	4	4	79
$[Rh_2\{(4S)\text{-bnaz}\}_4]$	$PhCF_3$	103	3	7	62
$[Rh_2\{(S)\text{-ptpa}\}_4]$	$PhCF_3$	103	3	48	16
$[Rh_2\{(S)\text{-nttl}\}_4]$	C_6H_6	20	2.5	82	62
$[Rh_2\{(S)\text{-nttl}\}_4]$	CH_2Cl_2	40	1	87	56
$[Rh_2\{(S)\text{-nttl}\}_4]$	CH_2Cl_2	20	2	90	56
$[Rh_2\{(S)\text{-nttl}\}_4]$	$PhCH_3$	20	1.5	76	61
$[Rh_2\{(S)\text{-pttl}\}_4]$	$PhCH_3$	20	1.5	75	64
$[Rh_2\{(S)\text{-bpttl}\}_4]$	$PhCH_3$	20	1.0	74	66

[a] With 2% of catalyst.



Scheme 3. Ligands and abbreviations of Rh(II)-catalysts.

rized in Table 4. Note that the enantioselectivity for formation of the *cis*-lactone **8** tends to be generally lower than that for **6**.

The abs. configuration of **8** ($[\alpha]_D^{20} = -18.5$ for 66% ee) obtained with $[Rh_2\{(S)\text{-nttl}\}_4]$ was determined by comparison of the specific rotation of the desilylated product **10b** ($[\alpha]_D^{20} = -11.5$) with the value available in the literature for (1*S*,3*R*,6*S*)-**10b** {($[\alpha]_D^{25} = -30.8$ (*c* 0.12, $CHCl_3$)},[12] which gives (1*R*,3*R*,6*S*,9*R*)-configuration for **8**. The abs. configuration of **6** could not be determined owing to the lack of data in the literature. However it may reasonably be assumed to be (1*S*,3*S*,6S,9*R*) in analogy to that of **4a**.

Table 4. Intramolecular insertion with *cis*- and *trans*-*t*-butylcyclohexyl diazo(triethylsilyl)acetate **3a**,**b**[a]

Compound	Catalyst	Solvent	T (°C)	Yield (%)	ee (%)
3a	$[Rh_2\{(4S)\text{-bnaz}\}_4]$	C_6H_6	80	**6**: 16	64
3a	$[Rh_2\{(R)\text{-bnp}\}_4]$	C_6H_6	80	**6**: 18	24
3a	$[Rh_2\{(4S)\text{-ptpa}\}_4]$	C_6H_6	80	**6**: 7	2
3a	$[Rh_2\{(S)\text{-pttl}\}_4]$	$PhCH_3$	20	**6**: 73	77
3a	$[Rh_2\{(S)\text{-nttl}\}_4]$	$PhCH_3$	20	**6**: 73	78
3a	$[Rh_2\{(S)\text{-bpttl}\}_4]$	$PhCH_3$	20	**6**: 63	69
3b	$[Rh_2\{(4S)\text{-bnaz}\}_4]$	C_6H_6	80	**8**: 5	43
3b	$[Rh_2\{(4S)\text{-ptpa}\}_4]$	C_6H_6	80	**8**: 23	13
3b	$[Rh_2\{(S)\text{-nttl}\}_4]$	$PhCH_3$	20	**8**: 50	43
3b	$[Rh_2\{(S)\text{-pttl}\}_4]$	$PhCH_3$	20	**8**: 28	66
3b	$[Rh_2\{(S)\text{-bpttl}\}_4]$	$PhCH_3$	20	**8**: 42	8

[a] With 2% of catalyst, 2 h.

2.3. Variation of the silyl substituents of cyclohexyl diazo(triorganylsilyl)acetates

The trimethylsilyl- and triisopropylsilyl derivatives **2b**,**c** of **1a** were prepared in analogy to **2a**. Decomposition of **2b** with $[Rh_2\{S\text{-pttl}\}_4]$ and $[Rh_2\{S\text{-nttl}\}_4]$ afforded a ca. 4:1 mixture of *trans* and *cis*-lactones **4b** and **5b** with modest enantioselectivities, from which **4b** could be separated (Table 5). This contrasts with the decomposition of **2a**, where only the *trans*-lactone is formed. The orientation of the silyl substituent in **4b** was assigned in analogy to that of **4a**. Desilylation of the mixture afforded **9a** and **10a**. No cyclization product could be obtained from the TIPS derivative **2c**, however. Elevated temperatures ($PhCH_3$, reflux) were required in order to achieve total decomposition of **2d**, but yields of insertion products were poor. In view of the substantial losses encountered during purification of **2d**, some reactions were effected without purification. The respective yields in Table 5 refer to both preparation and decomposition of **2d**. Only a little improvement could be achieved by this procedure, however. The configuration of the silyl substituent was assigned on the grounds of the vicinal coupling constant of 12.6 Hz, as before. Desilylation of **4d** with TBAF in THF afforded **9a**. The oxidative replacement of the silyl substituent was attempted under a large variety of conditions,[20] but so far failed, and the desired alcohol could not be isolated.

Table 5. Intramolecular insertion with cyclohexyl diazo(triorganylsilyl)acetates **2b**,**d**[a]

Compound	Catalyst	T (°C)/t	Yield (%)	ee (%)
2b	$[Rh_2\{4S\text{-pttl}\}_4]$	25/2.5 h	**4b**: 65	31
			5b: 17	27
2b	$[Rh_2\{(S)\text{-nttl}\}_4]$	25/1 h	**4b**: 66	33
			5b: 17	0
2d	$[Rh_2(OAc)_4]$[b]	110/2 h	**4d**: 29[c]	–
2d	$[Rh_2(OAc)_4]$	110/3 h	**4d**: 14[d]	–
2d	$[Rh_2\{(S)\text{-nttl}\}_4]$	25/2 days	**4d**: 34[d]	41
2d	$[Rh_2\{(S)\text{-pttl}\}_4]$	110/2 h	**4d**: 27[d]	42
2d	$[Rh_2\{(4S)\text{-bpttl}\}_4]$[e]	110/2.5 h	**4d**: 4[d]	43

[a] In $PhCH_3$, 2% of catalyst.
[b] In $PhCH_3$, 3% of catalyst.
[c] With purified **2d**.
[d] Overall yield, two steps.
[e] In $PhCH_3$, 1% of catalyst.

3. Conclusion

The present investigation shows that triorganylsilyl-substituted alkyl diazoacetates undergo intramolecular CH insertion in high yields and with encouraging enantioselectivities, with appropriate Rh(II)-catalysts. Current research is directed towards extension of this methodology, in particular towards stereoselective desilylation.

4. Experimental

4.1. General

See Ref. 21

4.2. Synthesis of cyclohexyl diazo(triethylsilyl)acetates 2a–2c, 3a,b

4.2.1. General procedure. Ethyldiisopropylamine (290 μl, 1.68 mmol) followed by triethylsilyl triflate (380 μl, 1.68 mmol) in Et_2O (2.5 mL) were added at −78°C to the diazoester **1** (1.50 mmol) in Et_2O (5.0 mL). The mixture was allowed to warm up to rt, and was stirred for 24 h. It was neutralized with Na_2CO_3, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2, pentane/AcOEt, 97:3).

4.2.2. Cyclohexyl diazo(triethylsilyl)acetate 2a. Yield 94%, yellow oil. IR (NaCl): 2937m, 2088s, 1684s, 1078w. ^{1}H NMR (500 MHz, $CDCl_3$): 0.74 (q, $J=7.8$, 6H); 0.97 (t, $J=7.9$, 9H); 1.23–1.29 (m, 1H); 1.32–1.46 (m, 4H); 1.50–1.55 (m, 1H); 1.67–1.73 (m, 2H); 1.83–1.88 (m, 2H); 4.78–4.83 (m, 1H). ^{13}C NMR (125 MHz): 3.2 (t); 7.1 (q); 23.7 (t); 25.4 (t); 31.8 (t); 42.8 (s); 73.0 (d); 169.3 (s). MS: 282 (M^+, 2), 171 (48), 143 (13), 115 (100), 87 (61), 55 (30). HR MS: 282.1743 ($C_{14}H_{26}O_2N_2Si^+$; calcd 282.1764).

4.2.3. Cyclohexyl diazo(trimethylsilyl)acetate 2b. Yield 68%, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): 0.25 (s, 9H); 1.22–1.53 (m, 6H); 1.66–1.71 (m, 2H); 1.80–1.86 (m, 2H); 4.77–4.84 (m, 1H). ^{13}C NMR (125 MHz): −1.4 (q); 23.6 (t); 25.4 (t); 31.8 (t); 72.8 (d); 169.0 (s).

4.2.4. Cyclohexyl diazo(triisopropylsilyl)acetate 2c. Yield 91%, yellow oil. IR (NaCl): 2942s, 2866m, 2085s, 1684s, 1465m, 1254s, 1073w. ^{1}H NMR (500 MHz, $CDCl_3$): 1.13 (d, $J=11.9$, 18H); 1.24–1.49 (m, 8H); 1.52–1.63 (m, 1H); 1.63–1.80 (m, 2H); 1.87–1.97 (m, 2H); 4.79–4.86 (m, 1H). ^{13}C NMR (125 MHz): 11.5 (t); 18.3 (q); 23.9 (t); 25.4 (t); 31.9 (t); 73.3 (d); 169.7 (s). MS: 281 ($M-C_3H_7^+$, 12), 199 (100), 131 (69), 103 (21), 101 (10), 84 (15). HR MS: 281.1724 ($C_{14}H_{25}O_2N_2Si^+$; calcd 281.1685). Anal. calcd for $C_{17}H_{32}O_2N_2Si$ (324.54): C, 62.92; H, 9.94; N, 8.63. Found: C, 62.81; H, 10.00; N, 8.51.

4.2.5. Synthesis of cyclohexyl diazo(dimethylphenylsilyl)acetate 2d. Diisopropylamine (135 μL, 0.96 mmol) in Et_2O (1.0 mL) was treated with BuLi (600 μL, 0.96 mmol) at −78°C. After 15 min the precooled (at −78°C) diazo ester **1a** (136 mg, 0.81 mmol) in Et_2O (1.0 mL) was added dropwise. After 30 min of stirring, precooled dimethylphenylsilyl chloride (220 μL, 0.97 mmol) in Et_2O (1.0 mL) was added dropwise. After 1 h of stirring, the mixture was warmed to rt, washed with $NaHCO_3$ (30 mL) which was extracted with Et_2O (3×30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo, and the residue was purified by flash chromatography (SiO_2, pentane/AcOEt, 98:2) to afford **2d**, (370 mg, 16%). IR (neat): 2937m, 2092s, 1682s, 1257s, 1082w. ^{1}H NMR (400

MHz, $CDCl_3$): 0.56 (s, 6H); 1.29–1.42 (m, 5H); 1.48–1.53 (m, 1H); 1.63–1.65 (m, 2H); 1.79–1.81 (m, 2H); 4.77–4.83 (m, 1H); 7.39–7.41 (m, 3H); 7.58–7.60 (m, 2H). ^{13}C NMR (100 MHz): –2.0 (q); 22.3 (t); 25.3 (t); 31.7 (t); 42.8 (s); 73.0 (d); 127.9 (t); 133.8 (t). MS: 302 (M^+, 2), 192 (36), 177 (19), 135 (100), 83 (28), 55 (31). HR MS: 302.1470 ($C_{16}H_{22}O_2N_2Si^+$; calcd 302.1450).

4.2.6. *trans*-4-*tert*-Butylcyclohexyl diazo(triethylsilyl)-acetate 3a. Yield 88% according to Section 4.2.1; yellow solid. IR ($CHCl_3$): 3019m, 2094s, 1671m, 1272w, 1214s. ^{1}H NMR (500 MHz, $CDCl_3$): 0.76 (q, $J=7.9$, 6H); 0.85 (s, 9H); 0.99 (t, $J=7.9$, 9H); 1.11 (qd, $J=13.2$, 3.1, 2H); 1.30 (qd $J=13.2$, 3.2, 2H); 1.79–1.82 (m, 2H); 2.05 (td, $J=12.6$, 4.4, 2H); 4.65–4.72 (m, 1H). ^{13}C NMR (125 MHz): 3.2 (t); 7.0 (q); 25.3 (t); 27.5 (q); 32.3 (t); 42.9 (s); 47.0 (d); 74.0 (d); 169.4 (s). MS: 338 (M^+, 1), 309 (2), 115 (100), 103 (23), 87 (37), 57 (53). HR MS: 338.2368 ($C_{18}H_{34}O_2N_2Si^+$; calcd 338.2390).

4.2.7. *cis*-4-*tert*-Butylcyclohexyl diazo(triethylsilyl)-acetate 3b. Yield 91% according to Section 4.2.1; yellow oil. IR ($CHCl_3$): 3019m, 2093m, 1668m, 1266w, 1215s. ^{1}H NMR (500 MHz, $CDCl_3$): 0.77 (q, $J=8.0$, 6H); 0.87 (s, 9H); 0.99 (t, $J=8.0$, 9H); 1.28 (qd, $J=12.6$, 3.1 2H); 1.47 (tt, $J=14.1$, 2.8, 2H); 1.60 (dd, $J=12.6$, 1.8, 2H); 1.97 (td, $J=15.1$, 2.8, 2H); 5.09 (quint. $J=2.5$, 1H). ^{13}C NMR (125 MHz): 3.3 (t); 7.1 (q); 21.7 (t); 27.4 (q); 30.8 (t); 32.5 (s); 43.3 (s); 47.5 (d); 70.1 (d); 169.6 (s). MS: 338 (M^+, 1), 309 (1), 115 (100), 103 (21), 87 (38), 57 (59). HR MS: 338.2372 ($C_{18}H_{34}O_2N_2Si^+$; calcd 338.2390).

4.3. Diazo decomposition of cyclohexyl diazo-(triorganylsilyl)acetates 2a–2d, 3a,b

4.3.1. General procedure. To a suspension of catalyst ([Rh_2L_4], 2 mol%) under Ar was added the diazoester **2** or **3** (ca. 150 mg, 0.50 mmol) in the appropriate solvent (2.5 mL) in 10 min at rt. The mixture was stirred for the time and at the temperature indicated in Tables 1–5. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was evaporated and the residue purified by flash chromatography, (SiO_2, pentane/AcOEt, 97:3).

4.3.2. (1*S*,6*S*,9*R*)-9-(Triethylsilyl)-7-oxabicyclo[4.3.0]-nonan-8-one 4a. Colorless oil, $[\alpha]_D^{20}=-16.1$ (*c* 1.02, $CHCl_3$ for 66% ee). IR (NaCl): 2947s, 2875s, 1760s 1198w, 1135w, 1027m. ^{1}H NMR (500 MHz, $CDCl_3$): 0.68–0.76 (m, 6H); 0.99 (t, $J=7.9$, 9H); 1.23–1.45 (m, 3H); 1.52 (qd, $J=12.0$, 3.8, 1H); 1.77–1.81 (m, 2H); 1.83 (s, 1H); 1.90–1.96 (m, 2H); 2.20–2.23 (m, 1H); 3.63–3.68 (m, 1H). ^{13}C NMR (125 MHz): 2.7 (t); 7.3 (q); 24.1 (t); 29.2 (t); 30.2 (t); 33.4 (d); 47.0 (d); 85.6 (d); 178.8 (s). MS: 254 (M^+, 1), 225 (100), 181 (16), 153 (10), 103 (26), 75 (20), 59 (19). HR MS: 254.1687 ($C_{14}H_{26}O_2Si^+$; calcd 254.1702). Enantiomer separation by GC (β-Dex, 5 min at 120°C, 1°C/min to 180°C, 20 min; $\tau_1=52.2$, $\tau_2=52.9$ min).

4.3.3. *trans*-9-(Trimethylsilyl)-7-oxabicyclo[4.3.0]nonan-8-one 4b. Colorless oil, $[\alpha]_D^{20}=-5.0$ (*c* 1.00, EtOH for 33% ee). ^{1}H NMR (500 MHz, $CDCl_3$): 0.14 (s, 9H); 1.25–1.44 (m, 3H); 1.51 (qd, $J=11.9$, 3.6, 1H); 1.67–1.79 (m, 3H); 1.89–1.96 (m, 2H); 2.18–2.21 (m, 1H); 3.62–3.68 (m, 1H). ^{13}C NMR (125 MHz): –2.4 (q); 24.1 (t); 25.5 (t); 29.2 (t); 30.0 (t); 36.7 (d); 46.8 (d); 85.5 (d); 178.6 (s). MS: 212 (M^+, 3), 197 (16), 153 (13), 122 (26), 94 (23), 73 (100), 59 (24). HR MS: 212.1213 ($C_{11}H_{20}O_2Si^+$; calcd 212.1232). Enantiomer separation by GC (Lip-E, 2 min at 100°C, 1°C/min to 150°C, 10 min; $\tau_1=49.1$, $\tau_2=52.7$ min).

4.3.4. (1*S*,6*S*,9*R*)-9-(Dimethylphenylsilyl)-7-oxabicyclo [4.3.0]nonan-8-one 4d. The diazo decomposition was carried out according to the general procedure (Section 4.3.1). Colorless oil. $[\alpha]_D^{20}=-13.9$ (EtOH, *c* 1.07, for 43% ee). IR (NaCl): 2939s, 2861m, 1760s, 1200w, 1069w, 1025m. ^{1}H NMR (MHz, $CDCl_3$): 0.49 (s, 3H); 0.50 (s, 3H); 1.06 (qd, $J=12.3$, 3.5, 1H); 1.10–1.86 (m, 7H); 1.96 (d, $J=12.6$, 1H); 2.15–2.19 (m, 1H); 3.65 (td, $J=11.3$, 3.8, 1H); 7.36–7.42 (m, 3H); 7.57 (dd, $J=7.2$, 1.6, 2H). ^{13}C NMR (500 MHz): –4.9 (q); –3.2 (q); 24.0 (t); 28.9 (t); 30.0 (t); 36.6 (t); 46.9 (d); 85.6 (d); 127.9 (d); 129.5 (d); 133.9 (fd); 136.0 (s); 178.4 (s). MS: 274 (M^+, 17), 259 (29), 197 (27), 135 (100), 121 (24), 103 (26), 75 (17), 55 (14). HR MS: 274.1378 ($C_{16}H_{22}O_2Si^+$; calcd 274.1389).

4.3.5. *cis*-9-(Trimethylsilyl)-7-oxabicyclo[4.3.0]nonan-8-one 5b (data obtained from mixture with 4b). Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): 0.16 (s, 9H); 1.12–1.20 (m, 1H); 1.24–1.46 (m, 2H); 1.46–1.56 (m, 2H); 1.67–1.77 (m, 2H); 1.88–1.94 (m, 2H); 2.14 (d, $J=6.0$, 1H); 2.16–2.23 (m, 1H); 2.29–2.35 (m, 1H); 3.62–3.67 (m, 1H); 4.33–4.35 (m, 1H). ^{13}C NMR (125 MHz): –1.2 (q); 19.5 (t); 23.8 (t); 26.7 (t); 27.6 (t); 38.9 (d); 39.9 (d); 79.7 (d); 179.3 (s). Enantiomer separation by GC (β-Dex, 5 min at 120°C, 1°C/min to 180°C, 20 min; $\tau_1=45.0$, $\tau_2=46.5$ min).

4.3.6. (1*S*,3*S*,6*S*,9*R*)-3-*tert*-Butyl-9-(triethylsilyl)-7-oxabi cyclo[4.3.0]nonan-8-one 6. Colorless oil. $[\alpha]_D^{20}=-0.6$ (*c* 1.00, EtOH for 77% ee). IR (neat): 2951s, 2873m, 1757s, 1457m, 1181m, 1072m. ^{1}H NMR: (500 MHz, $CDCl_3$): 0.67–0.75 (m, 6H); 0.88 (s, 9H); 0.99 (t, $J=8.2$, 9H); 0.99–1.08 (m, 1H); 1.12–1.27 (m, 2H); 1.49–1.56 (m, 1H); 1.77–1.86 (m, 2H); 1.94–2.01 (m, 2H); 2.21–2.25 (m, 1H); 3.57–3.62 (m, 1H). ^{13}C NMR (125 MHz): 2.7 (t); 7.3 (q); 25.0 (t); 27.6 (q); 29.8 (t); 32.4 (s); 33.7 (d); 46.9 (d); 47.9 (d); 85.8 (d); 179.1 (s). MS: 281 ($M-C_2H_5^+$, 100), 237 (13), 157 (25), 103 (38), 87 (31), 75 (31), 57 (51). HR MS: 281.1922 ($C_{16}H_{29}O_2Si^+$; calcd 281.1937). Enantiomer separation by GC (β-Dex, 5 min at 140°C, 1°C/min to 180°C, 20 min; $\tau_1=53.2$, $\tau_2=53.7$ min).

4.3.7. *rel*-(4*S*,7*S*)-7-*tert*-Butyl-3-(triethylsilyl)-1-oxaspiro[3,5] nonan-2-one 7a. Yield 4–5%. Colorless oil. IR (neat): 2951s, 2868m, 1798s, 1168m, 1080w. ^{1}H NMR: (300 MHz, $CDCl_3$): 0.67–0.76 (m, 6H); 0.85 (s, 9H); 1.00 (t, $J=8.1$, 9H); 0.99–1.06 (m, 1H); 1.29–1.45 (m, 2H); 1.62–1.77 (m, 4H); 1.92–1.98 (m, 1H); 2.06–2.13

(m, 1H); 2.92 (s, 1H). ^{13}C NMR (75 MHz): 3.9 (t); 7.3 (q); 23.3 (t); 23.7 (t); 27.4 (q); 32.3 (s); 34.9 (t); 38.6 (t); 46.5 (d); 48.7 (d); 80.0 (d); 171.5 (s). MS: 310 (M^+, 1), 281 (52), 237 (100), 209 (35), 157 (10), 87 (35), 103 (49), 57 (56). HR MS: 310.2310 ($C_{18}H_{34}O_2Si^+$; calcd 310.2328).

4.3.8. (1*R*,3*R*,6*S*,9*R*)-3-*tert*-Butyl-9-(triethylsilyl)-7-oxabicyclo[4.3.0]nonan-8-one 8. White solid. Mp 68°C. $[\alpha]_D^{20}=-18.5$ (*c* 1.01, EtOH for 66% ee). IR (neat): 2951s, 2868m, 1744s, 1160s, 1010m. ^{1}H NMR (500 MHz, $CDCl_3$): 0.66–0.78 (m, 6H); 0.83 (s, 9H); 0.84–0.97 (m, 2H); 0.97–1.00 (t, $J=8.2$, 9H); 1.10–1.16 (m, 1H); 1.53–1.60 (m, 2H); 1.73–1.77 (m, 1H); 2.27–2.32 (m, 3H); 4.32–4.33 (m, 1H).^{13}C NMR (125 MHz): 4.0 (t); 7.6 (q); 20.7 (t); 27.3 (q); 28.3 (t); 28.7 (t); 32.3 (s); 36.9 (d); 40.0 (d); 45.9 (d); 79.5 (d); 179.4 (s). MS: 310 (M^+, 3), 281 (100), 237 (14), 211 (15), 137 (46), 115 (25), 103 (51), 57 (94). HR MS: 310.2315 ($C_{18}H_{34}O_2Si^+$; calcd 310.2328). Enantiomer separation by GC (β-Dex, 5 min at 140°C, 1°C/min to 180°C, 20 min; $\tau_1=53.2$, $\tau_2=53.7$ min).

4.3.9. *rel*-(4*S*,7*R*)-7-*tert*-Butyl-3-(triethylsilyl)-1-oxaspiro[3,5] nonan-2-one 7b. Yield 27% with [Rh_2{*S*}-pttl}$_4$]; 21% with Rh_2{*S*}-nttl}$_4$]; 26% with Rh_2{*S*}-bpttl}$_4$]. Colorless oil. IR (neat): 2951s, 2868m, 1798s, 1168m, 1080w. ^{1}H NMR: (300 MHz, $CDCl_3$): 0.67–0.76 (m, 6H); 0.85 (s, 9H); 1.00 (t, $J=8.1$, 9H); 0.99–1.06 (m, 1H); 1.29–1.45 (m, 2H); 1.62–1.77 (m, 4H); 1.92–1.98 (m, 1H); 2.06–2.13 (m, 1H); 2.92 (s, 1H). ^{13}C NMR (75 MHz): 3.9 (t); 7.3 (q); 23.3 (t); 23.7 (t); 27.4 (q); 32.3 (s); 34.9 (t); 38.6 (t); 46.5 (d); 48.7 (d); 80.0 (d); 171.5 (s). MS: 310 (M^+, 1), 281 (52), 237 (100), 209 (35), 157 (10), 87 (35), 103 (49), 57 (56). HR MS: 310.2310 ($C_{18}H_{34}O_2Si^+$; calcd 310.2328).

4.4. Desilylation of 7-oxabicyclo[4.3.0]nonan-8-ones (4a–4d, 6, 8) and spiro-lactone 7b

4.4.1. General procedure. Tetrabutylammonium fluoride (TBAF, 1 M in THF, 1.0 mL) was added dropwise to the respective silane (ca. 0.5 mmol) in THF (1 mL) at rt. After stirring for 2–4 h, H_2O (2.0 mL) was added, and the mixture was extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by flash chromatography (SiO_2, pentane/AcOEt, 97:3, then 95:5).

4.4.2. (1*S*,6*S*)-7-Oxabicyclo[4.3.0]nonan-8-one 9a. Yield 57%, colorless oil, $[\alpha]_D^{20}=-42.4$ (*c* 0.93, for 61% ee). IR ($CHCl_3$): 2944m, 1777s, 1448w, 1191m, 1030s. ^{1}H NMR (500 MHz, $CDCl_3$): 1.25–1.46 (m, 3H); 1.51–1.58 (qd, $J=12.0$, 3.8, 1H); 1.78–1.81 (m, 1H); 1.91–1.98 (m, 3H); 2.19–2.25 (m, 2H); 2.51 (dd, $J=16.4$, 6.6, 1H); 3.79 (td, $J=10.4$, 3.8, 1H). ^{13}C NMR (125 MHz): 24.0 (t); 25.3 (t); 28.3 (t); 30.2 (t); 35.8 (t); 44.8 (d); 85.1 (d); 176.5 (s). MS: 141 (2), 140 (M^+, 2), 139 (4), 111 (3), 96 (16), 83 (23), 68 (56), 67 (100), 55 (49). HR MS: 140.0839 ($C_8H_{12}O_2^+$; calcd 140.0837). Enantiomer separation by GC (Lip-E, 2 min at 120°C, 1°C/min to 150°C, 20 min; $\tau_1=34.9$, $\tau_2=35.7$ min).

4.4.3. (1*R*,3*S*,6*S*)-3-*tert*-Butyl-7-oxabicyclo[4.3.0]nonan-8-one 9b.[16] Yield 68%, white solid, $[\alpha]_D^{20}=-42.6$ (*c* 0.98, EtOH for 89% ee). ^{1}H NMR (300 MHz, $CDCl_3$): 0.87 (s, 9H); 0.93–1.27 (m, 3H); 1.48–1.60 (m, 1H); 1.87–2.04 (m, 3H); 2.17–2.26 (m, 2H); 2.50 (dd, $J=16.1$, 6, 1H); 3.72 (td, $J=10.9$, 3.9, 1H). ^{13}C NMR (75 MHz): 25.0 (t); 27.7 (q); 29.0 (t); 29.9 (t); 32.5 (s); 36.1 (t); 44.7 (d); 47.5 (d); 85.3 (d); 176.9 (s). Enantiomer separation by GC (Lip-E, 2 min at 120°C, 1°C/min to 150°C, 20 min; $\tau_1=41.8$, $\tau_2=43.1$ min).

4.4.4. *cis*-7-Oxabicyclo[4.3.0]nonan-8-one 10a.[16] (Data from mixture with **9a**.) Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): 0.16 (s, 9H); 1.12–1.20 (m, 1H); 1.24–1.46 (m, 2H); 1.46–1.56 (m, 2H); 1.67–1.77 (m, 2H); 1.88–1.94 (m, 2H); 2.14 (d, $J=6.0$, 1H); 2.16–2.23 (m, 1H); 2.29–2.35 (m, 1H); 3.62–3.67 (m, 1H); 4.33–4.35 (m, 1H). ^{13}C NMR (125 MHz): 19.8 (t); 22.7 (t); 27.1 (t); 27.7 (t); 34.8 (t); 37.4 (d); 79.1 (d); 177.5 (s). Enantiomer separation by GC (β-Dex, 5 min at 120°C, 1°C/min to 180°C, 20 min; $\tau_1=45.0$, $\tau_2=46.5$ min).

4.4.5. (1*S*,3*R*,6*S*)-3-*tert*-Butyl-7-oxabicyclo[4.3.0]nonan-8-one 10b.[16] Yield 52%, yellow oil. $[\alpha]_D^{20}=-11.5$ (*c* 1.00, EtOH for 64% ee). ^{1}H NMR (300 MHz, $CDCl_3$): 0.84 (s, 9H); 0.89–1.18 (m, 2H); 1.52–1.65 (m, 2H); 1.75–1.82 (m, 1H); 2.20 (d, $J=16.7$, 1H); 2.29–2.35 (m, 2H); 2.70 (dd, $J=16.7$, 6.6, 1H); 4.46–4.49 (m, 1H). ^{13}C NMR (75 MHz): 20.6 (t); 27.3 (q); 28.3 (t); 29.0 (t); 32.3 (s); 36.2 (d); 38.9 (t); 45.6 (d); 78.9 (d); 177.6 (s). Enantiomer separation by GC (Lip-E, 2 min at 120°C, 1°C/min to 150°C, 20 min; $\tau_1=27.4$, $\tau_2=29.4$ min).

4.4.6. *rel*-(4*R*,7*R*)-7-*tert*-Butyl-1-oxaspiro[3,5]nonan-2-one 11b. Yield 69%, white solid. Mp = 93°C. IR (neat): 2929s, 2863m, 1802s, 1202m, 1089w. ^{1}H NMR (500 MHz, $CDCl_3$): 0.87 (m, 9H); 1.04 (tt, $J=12.2$, 3.0, 1H); 1.35 (qd, $J=12.9$, 3.5, 2H); 1.67–1.78 (m, 4H); 2.02 (dd, $J=14.8$, 4.6, 2H); 3.07 (s, 2H). ^{13}C NMR (125 MHz): 23.2 (t); 27.4 (q); 32.4 (s); 35.9 (t); 46.5 (d); 47.3 (t); 78.4 (s); 168.6 (s). MS: 152 ($M-CO_2^+$, 3), 140 (6), 122 (13), 96 (20), 95 (13), 80 (45), 67 (12), 57 (100). HR MS: 152.1569 ($C_{11}H_{20}^+$; calcd 152.1565). Anal. calcd for $C_{12}H_{20}O_2$: C, 73.48; H, 10.27; found C, 73.48; H, 10.34.

4.5. X-Ray structure of *rac*-8

$C_{18}H_{34}O_2Si$, $M_r=310.6$; $\mu=0.13$ mm^{-1}, $d_x=1.078$ g cm^{-3}, triclinic, $P\bar{1}$, $Z=2$, $a=6.7793(10)$, $b=11.165(2)$, $c=13.662(3)$ Å, $\alpha=111.94$ (2), $\beta=93.73(2)$, $\gamma=90.28(2)°$, $V=956.7(5)$ Å^3; cell dimensions and intensities were measured at 200 K on a Stoe IPDS diffractometer. Full-matrix least-squares refinement based on *F* using weight of $1/(\sigma^2(F_o)+0.0001(F_o^2))$ gave final values $R=0.041$, $\omega R=0.038$ and $S=1.01(2)$ for 190 variables and 1090 contributing reflections.

Crystallographic data (excluding structure factors) for **8** have been deposited to the Cambridge Crystallographic Data Base as supplementary publication number CCDC 202750. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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