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Cobalt- and rhodium-catalyzed cross-coupling reaction of allylic ethers and halides with organometallic reagents

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Abstract—Reactions of 2-alkenyl methyl ether with phenyl, trimethylsilylmethyl, and allyl Grignard reagents in the presence of cobalt(II) complexes are discussed. The success of the reactions heavily depends on the combination of the substrate, ligand, and Grignard reagent. In the reaction of cinnamyl methyl ether, the formation of the linear coupling products predominates over that of the relevant branched products. In the cobalt-catalyzed allylation of allylic ethers, addition of a diphosphine ligand can change the regioselectivity, mainly providing the corresponding branched products. Rhodium complexes catalyze the reactions of allylic ethers and halides with allylmagnesium chloride and allylzinc bromide, respectively, in which the branched coupling product is the major product.

1. Introduction

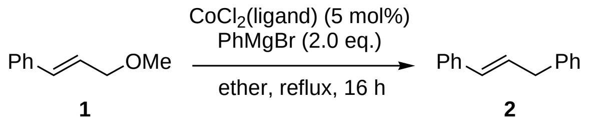
Palladium-, nickel-, and copper-catalyzed cross-coupling reactions of allylic substrates with organometallic reagents are recognized as one of the most useful reactions catalyzed by transition metals.[1] On the other hand, cobalt-catalyzed cross-coupling reactions of allylic substrates are quite rare.[2] We have been interested in cobalt-catalyzed cross-coupling reactions.[3] Here we report the reactions of allylic ethers with phenyl, trimethylsilylmethyl, and allyl Grignard reagents in the presence of cobalt complexes.[4] Rhodium-catalyzed coupling reactions are also disclosed herein.[5]

2. Results and discussions

2.1. Cobalt-catalyzed phenylation reaction of allylic ethers

The coupling reaction of cinnamyl methyl ether (**1**) with phenylmagnesium bromide was first performed (Table 1). A number of ligands were screened, and 1,5-bis(diphenylphosphino)pentane (DPPPEN) proved to be most effective for the phenylation reaction. 3,3-Diphenyl-1-propene was not detected at all. A small amount of β-methylstyrene was the only byproduct in each experiment, along with untouched **1**. The reaction of branched ether **3** with phenylmagnesium reagent under $CoCl_2$(dpppen) catalysis provided linear **2** selectively in good yield (Eq. 1). The regioselectivity of the phenylations suggests that the reactions proceed via a π-allylcobalt intermediate. The phenylation reaction of **1** at 25 °C decreased the yield of **2**. The choice of the solvent was essential to obtain **2** in satisfactory yield. A similar reaction in THF resulted in very low conversion of **1**.

Table 1. Cobalt-catalyzed reaction of cinnamyl methyl ether (**1**) with phenylmagnesium bromide



Entry	Ligand	Yield (%)
1	None	29
2	PPh_3 (10 mol%)	30
3	DPPM	24
4	DPPE	15
5	DPPP	27
6	DPPB	50
7	DPPPEN	72
8	DPPH	58

Ligands DPPM–DPPH represent $Ph_2P(CH_2)_nPPh_2$, $n=1$: DPPM; $n=2$: DPPE; $n=3$: DPPP; $n=4$: DPPB; $n=5$: DPPPEN; $n=6$: DPPH.

Keywords: Cross-coupling reaction; Cobalt; Grignard reagent; Rhodium; Allylzinc reagent.

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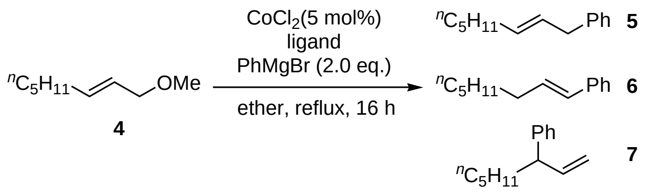
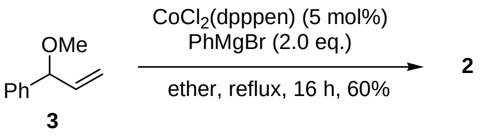
Table 2. Cobalt-catalyzed phenylation reaction of *trans*-2-octenyl methyl ether (**4**)



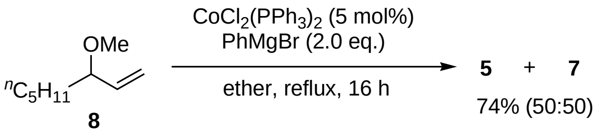
Entry	Ligand (amount)	Combined yield (%)	**5/6/7**
1	DPPPEN (5 mol%)	12	Not determined
2	None	47	58:10:32
3	DPPE (5 mol%)	32	10:53:37
4	PPh_3 (10 mol%)	78	36:7:57
5	$P(2\text{-}MeC_6H_4)_3$ (10 mol%)	39	66:<1:33
6	$P(4\text{-}MeC_6H_4)_3$ (10 mol%)	49	42:6:52
7	$P[3,5\text{-}(CF_3)_2C_6H_3]_3$ (10 mol%)	Trace	Not determined
8	$P(4\text{-}MeOC_6H_4)_3$ (10 mol%)	41	31:16:53

It is worth noting that treatment of cinnamyl bromide under similar conditions furnished a mixture of dimeric compounds such as 1,6-diphenyl-1,5-hexadiene and 3,4-diphenyl-1,5-hexadiene, in addition to a trace of **2**. The formation of the dimeric products implies that single electron transfer from a cobalt complex would yield cinnamyl radical that is destined to dimerize.[2a,c,d]



(1)

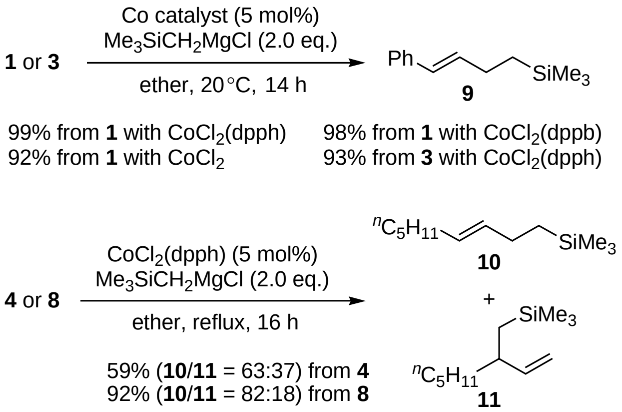
The cobalt-catalyzed phenylation reaction of *trans*-2-octenyl methyl ether (**4**) required triphenylphosphine as a ligand (Table 2, entry 4). A mixture of the corresponding coupling products **5**, **6**, and **7** was obtained. Under the reaction conditions, a part of **5** was transformed into **6**. In contrast to the reaction of **1**, the use of $CoCl_2$(dpppen) led to very poor conversion (entry 1). Without any phosphine ligand, coupling products were obtained in moderate combined yield (entry 2). Other monodentate phosphine ligands were inferior to triphenylphosphine (entries 5–8). Under $CoCl_2(PPh_3)_2$ catalysis, branched ether **8** was also converted into **5** and **7** (Eq. 2), in which no isomerization from **5** to **6** was observed.



(2)

2.2. Cobalt-catalyzed trimethylsilylmethylation reaction of allylic ethers

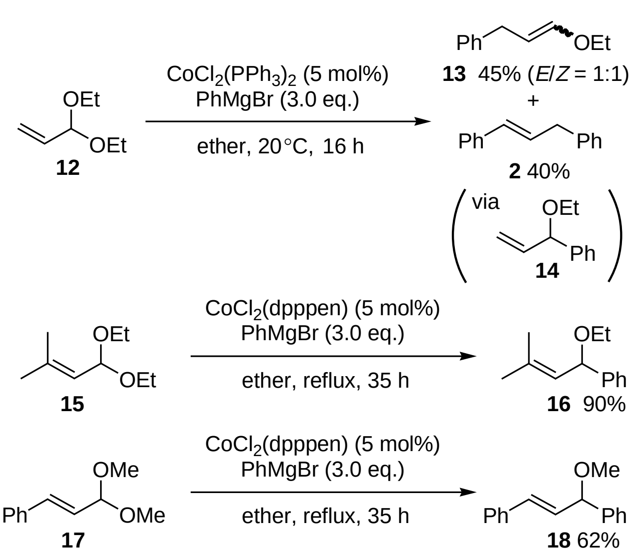
Cross-coupling reaction with Me_3SiCH_2MgCl proceeded much more smoothly than that with PhMgBr (Scheme 1). Treatment of **1** with Me_3SiCH_2MgCl in the presence of $CoCl_2$(dpph) for 14 h at 20 °C afforded the corresponding linear product **9** in 99% yield. Whereas the choice of the ligand was crucial to establish the phenylation, ligandless $CoCl_2$ and $CoCl_2$(dppb) also effected the allylation to afford **9** in 92 and 98% yields, respectively. Reactions of branched **3** with Me_3SiCH_2MgCl afforded **9** in excellent yield. On the other hand, alkyl-substituted allylic ethers **4** and **8** were converted into mixtures of regioisomers **10** and **11**. The reaction required a higher temperature to complete the reaction within a satisfactory reaction time. Trimethylsilylmethylation of branched ether **8** afforded a higher yield of **10** and **11** than that of **4**.



Scheme 1.

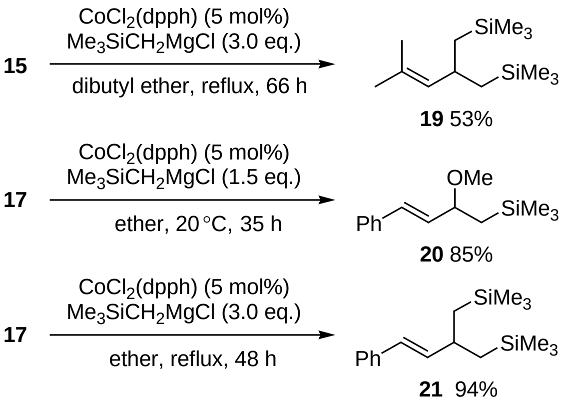
2.3. Cobalt-catalyzed reaction of α,β-unsaturated aldehyde dialkyl acetal

Treatment of acrolein diethyl acetal (**12**) with phenylmagnesium bromide in the presence of $CoCl_2(PPh_3)_2$ afforded a mixture of **2** and vinyl ether **13** (Scheme 2) Formation of doubly phenylated **2** would indicate a reaction path via the intermediate **14**. Monophenylation of acetals **15** and **17** having substituents at the terminal olefinic positions was successful under $CoCl_2$(dpppen) catalysis. The dimethyl and phenyl groups of **16** and **18** would interfere with further phenylation.



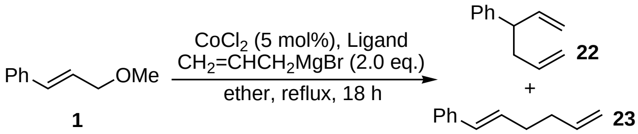
Scheme 2.

In contrast to the reaction with phenylmagnesium bromide, bis(trimethylsilylmethylation) occurred in the reaction of **15** with 3 equimolar amounts of Me_3SiCH_2MgCl in refluxing dibutyl ether (Scheme 3). Intriguingly, in the reaction of **17**, we could completely control the distribution of the product by changing the amount of the Grignard reagent and reaction time. The reaction with 1.5 equimolar amounts of Me_3SiCH_2MgCl at ambient temperature for 35 h afforded monosubstituted product **20** exclusively in 85% yield. On the other hand, treatment of **17** with 3 equimolar amounts of the Grignard reagent in refluxing ether for 48 h furnished doubly substituted product **21** in 94% yield.



Scheme 3.

Table 3. Cobalt-catalyzed coupling reaction of **1** with allylmagnesium bromide



Entry	Ligand	Yield (%)	**22/23**
1	None	78	<1:99
2	NBu_3	79	<1:99
3	TMEDA	75	<1:99
4	DPPE	57	51:49
5	DPPP	70	70:30
6	DPPB	54	19:81
7	DPPF	32	54:46

TMEDA and DPPF denote *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and 1,1′-bis(diphenylphosphino)ferrocene, respectively.

2.4. Cobalt-catalyzed cross-coupling reaction of cinnamyl methyl ether with allyl Grignard reagent

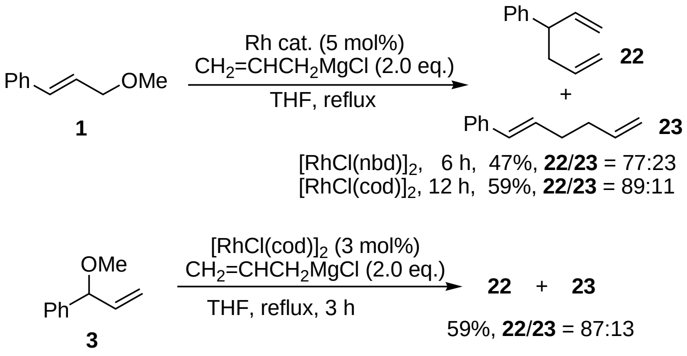
To extend the scope of the cobalt-catalyzed cross-coupling reactions, the allylation reaction of cinnamyl methyl ether was examined. The regioselectivity of the title reaction heavily depended on the ligand used (Table 3). Cobalt(II) chloride by itself catalyzed the cross-coupling to yield linear **23** exclusively (entry 1). Addition of amines as a ligand did not influence the regioselectivity (entries 2 and 3). Phosphine ligands allowed us to obtain significant amounts of branched **22**. Among them, DPPP exhibited the highest **22/23** selectivity, 70:30.

Judging from the results of Table 1, Scheme 1, and Table 3, trimethylsilylmethylmagnesium reagent proved to be the most reactive, and phenyl- and allylmagnesium reagents have similar reactivity. The low reactivity of allylmagnesium reagent may be due to the formation of π-allylcobalt that has less vacant coordination sites than phenyl- or trimethylsilylmethylcobalt has and that hence interacts weakly with the substrates at the initial oxidative addition stage.

The reactions of **1** and **3** with other Grignard reagents including vinylmagnesium bromide, methylmagnesium iodide, and alkynylmagnesium bromide failed to yield satisfactory amounts of the cross-coupling products.

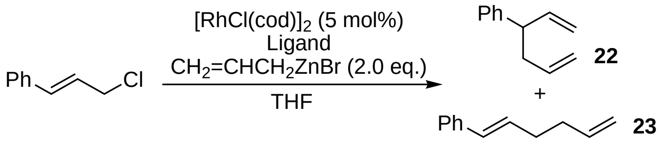
2.5. Rhodium-catalyzed cross-coupling reaction of allylic ethers with allylmagnesium reagents

Although the catalytic activity of rhodium is lower than that of cobalt, rhodium complexes also catalyzed allylation of **1** (Scheme 4). Treatment of **1** with allylmagnesium chloride in the presence of $[RhCl(nbd)]_2$ (NBD = norbornadiene) in refluxing THF yielded the corresponding dienes in 47% combined yield. The branched form **22** was mainly obtained, and the selectivity is opposite to that of cobalt-catalyzed allylation. The use of $[RhCl(cod)]_2$ (COD = 1,5-cyclooctadiene) instead of $[RhCl(nbd)]_2$ slightly improved the efficiency and selectivity of the reaction. Other rhodium complexes such as Wilkinson's catalyst and rhodium(III) acetylacetonate as well as an iridium complex $[IrCl(cod)]_2$ exhibited no catalytic activity. Branched ether **3** yielded **22** and **23** in good yield in a similar ratio under the $[RhCl(cod)]_2$ catalysis.



Scheme 4.

Table 4. Rhodium-catalyzed coupling reaction of cinnamyl chloride with allylzinc chloride



Entry	Ligand	Temperature (°C)	Time (h)	Yield (%)	**22/23**
1	None	−80	2	No reaction	—
2	None	−40	0.5	75	77:23
3	DPPB (10 mol%)	−40	2	Trace	—
4	PBu_3 (20 mol%)	−40	3	57	86:14
5	NEt_3 (20 mol%)	−40	2	70	83:17
6	NBu_3 (20 mol%)	−40	3.5	54	81:19
7	TMEDA (10 mol%)	−40	6.5	53	85:15
8	TMEDA (10 mol%)	−20	1.5	87	83:17
9	TMEDA (2.0 equiv to substrate)	−20	1.5	No reaction	—
10	$Me_2NCH_2NMe_2$ (10 mol%)	−20	1.5	73	87:13
11	$Me_2N(CH_2)_3NMe_2$ (10 mol%)	−20	1	62	84:16
12	2,2′-Bipyridyl (10 mol%)	−20	1	68	84:16
13	None, $CoCl_2$	−20	3	66	<1:99

2.6. Rhodium-catalyzed cross-coupling reaction of cinnamyl chloride with allylzinc reagents

Rhodium complexes also mediated the reaction of cinnamyl chloride with allylzinc bromide (Table 4). The reaction at −40 °C in the presence of $[RhCl(cod)]_2$ for 30 min furnished **22** and **23** in 75% yield in a ratio of 77:33 (entry 2). We screened many ligands to find that TMEDA is the best ligand with respect to the regioselectivity as well as the efficiency (entry 8). It is worth noting that a catalytic amount of diphosphine ligands such as DPPB (entry 3) and a stoichiometric amount of TMEDA (entry 9) completely inhibited the reaction. Interestingly, ligandless $CoCl_2$ effected the allylation to yield linear **23** exclusively (entry 13). An iridium complex $[IrCl(cod)]_2$ exhibited no catalytic activity.

3. Conclusion

The cobalt-catalyzed cross-coupling reaction with phenyl Grignard reagent proved to be a function of a substrate as well as of solvent and ligand. To attain high yields in the phenylation reaction, intensive tunings of variants are needed. In contrast, introduction of trimethylsilylmethyl group was facile and clean under cobalt catalysis. The reactions of cinnamyl methyl ether with both phenyl and trimethylsilylmethyl Grignard reagents yielded the corresponding linear products, irrespective of reaction conditions. The cross-coupling reactions of allylic ethers with allyl Grignard reagent with the aid of ligandless cobalt(II) chloride afforded the corresponding linear dienes. Interestingly, addition of DPPP could reverse the regioselectivity, leading to predominant formation of the branched dienes. Rhodium complexes catalyzed the reactions of allylic ethers and halides with allylmagnesium chloride and allylzinc bromide, respectively. Under rhodium catalysis, the branched coupling product was primarily formed. In both cobalt- and rhodium-catalyzed systems, π-allylmetal intermediates would be the key intermediates. The regioselectivity would depend on the ways how the carbon–carbon bonds are formed, that is, via the outer-sphere mechanism or the inner-sphere mechanism. The exact mechanism is not clear at this stage.

4. Experimental

4.1. Instrumental

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on Varian UNITY INOVA 500 spectrometers unless otherwise noted. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

4.2. Material

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF and ether were purchased from Kanto Chemical Co., stored under nitrogen, and used as they are. The starting materials **1**, **3**, **4**, and **8** are prepared by the conventional Williamson ether synthesis.

4.3. General procedure for the cross-coupling reactions with Grignard reagents

The reaction of **1a** with trimethylsilylmethyl Grignard reagent is representative. Anhydrous $CoCl_2$ (7 mg, 0.05 mmol) was placed in a 50-mL two-necked flask and heated with a hair dryer in vacuo for 3 min. DPPH (27 mg, 0.06 mmol) and ether (1 mL) were sequentially added under argon. After the mixture was stirred for 30 min to obtain blue suspension, cinnamyl methyl ether (**1a**, 0.15 g, 1.0 mmol) and Me_3SiCH_2MgCl (1.0 M in ether, 2.0 mL, 2.0 mmol) were successively added to the reaction mixture at 0 °C. After being stirred for 14 h at 20 °C, the reaction mixture was poured into saturated NH_4Cl solution. The products were extracted with ethyl acetate (20 mL × 3) and the combined organic layer was dried over sodium sulfate and concentrated. Silica gel column purification of the crude product provided **9** (0.20 g, 0.99 mmol) in 99% yield as colorless oil.

4.4. Rhodium-catalyzed cross-coupling reactions of cinnamyl chloride with allylzinc bromide

Zinc powder (2.94 g, 45 mmol) was placed in a 50-mL reaction flask under argon. THF (3.4 mL) was added. Chlorotrimethylsilane (0.1 mL, 0.8 mmol) and dibromoethane (0.1 mL, 2 mmol) were sequentially added at ambient temperature to activate zinc. After the mixture was stirred for 5 min, allyl bromide (2.6 mL, 30 mmol) in THF (24 mL) was added dropwise to the suspension with vigorous stirring over 15 min at 0 °C. The mixture was stirred for an additional 1 h at 25 °C. The gray supernatant liquid obtained was transferred to another flask filled with argon. The concentration of allylzinc bromide was determined by quantitative allylation reaction of an excess of benzaldehyde with allylzinc bromide prepared. The concentration was 0.87 M. $[RhCl(cod)]_2$ (25 mg, 0.05 mmol) was placed in another 50-mL two-necked flask under argon. THF (5 mL) and TMEDA (15 μL, 0.10 mmol) were successively added. The resulting solution was stirred for 5 min. Cinnamyl chloride (153 mg, 1.0 mmol, dissolved in 5 mL of THF) was added. The solution was cooled at −20 °C, and allylzinc bromide (0.87 M in THF, 2.3 mL, 2.0 mmol) was added. After being stirred for 1.5 h at −20 °C, the reaction mixture was poured into 1 M hydrochloric acid. The product was extracted with ethyl acetate (2 × 20 mL). The combined organic phase was dried over sodium sulfate. Evaporation followed by silica gel column purification afforded a mixture of **22** and **23** (137 mg, 0.87 mmol, 87% combined yield) in a ratio of 83:17.

4.5. Characterization data

The spectral data of the products **5**,[6] **6**,[6] **7**,[7] **13**,[8] **18**,[9] **22**,[10] and **23**[10] are found in the literature.

4.5.1. (*E*)-4-Trimethylsilyl-1-phenyl-1-butene (9). IR (neat) 3061, 2953, 2903, 1497, 1248, 962, 862, 837, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27–7.35 (m, 4H), 7.17–7.20 (m, 1H), 6.37 (d, J = 16.0 Hz, 1H), 6.27 (dt, J = 16.0, 6.5 Hz, 1H), 2.23 (ddt, J = 10.0, 1.0, 6.5 Hz, 2H), 0.68–0.71 (m, 2H), −0.10 to 0.16 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 137.98, 133.83, 128.45, 128.26, 126.66, 125.87, 27.39, 16.27, −1.59. Found: C, 76.27; H, 9.73%. Calcd for $C_{13}H_{20}Si$: C, 76.40; H, 9.86%.

4.5.2. (*E*)-1-(Trimethylsilyl)-3-nonene/3-(trimethylsilylmethyl)-1-octene (10/11 = 82:18). IR (neat) 2955, 2926, 1460, 1248, 968, 862, 835, 756, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.52–5.59 (m, 0.18 × 1H), 5.35–5.46 (m, 0.82 × 2H), 4.91 (ddd, J = 17.0, 2.0, 0.5 Hz, 0.18 × 1H), 4.87 (ddd, J = 10.0, 2.0, 0.5 Hz, 0.18 × 1H), 2.05–2.13 (m, 0.18 × 1H), 1.95–2.02 (m, 0.82 × 4H), 1.23–1.37 (m, 0.82 × 6H + 0.18 × 8H), 0.88 (t, J = 7.0 Hz, 3H), 0.55–0.59 (m, 2H), −0.01 (s, 9H); ^{13}C NMR ($CDCl_3$). For major isomer, δ 113.03, 128.87, 32.48, 31.44, 29.35, 26.85, 22.57, 16.58, 14.08, −1.58. For minor isomer, δ 145.53, 112.56, 40.38, 38.55, 31.93, 23.26, 22.69, 14.12, −0.58. One of the sp^3-hybridized carbons of **11** could not been observed, probably due to overlapping. Found: C, 72.34; H, 12.94%. Calcd for $C_{12}H_{26}Si$: C, 72.69; H, 13.21%.

4.5.3. 1-Ethoxy-3-methyl-1-phenyl-2-butene (16). IR (neat) 2974, 2930, 1425, 1086, 756, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31–7.35 (m, 4H), 7.26–7.23 (m, 1H), 5.35 (d, J = 9.0 Hz, 1H), 5.01 (d, J = 9.0 Hz, 1H), 3.45–3.51 (m, 1H), 3.35–3.42 (m, 1H), 1.79 (s, 3H), 1.74 (s, 3H), 1.22 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 142.81, 134.99, 128.40, 127.19, 126.59, 126.43, 78.13, 63.39, 25.91, 18.40, 15.36. Found: C, 81.84; H, 9.54%. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54%.

4.5.4. 2-Methyl-5-trimethylsilyl-4-(trimethylsilylmethyl)-2-pentene (19). IR (neat) 2953, 2909, 1248, 837, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.86 (d, J = 10.0 Hz, 1H), 2.51–2.58 (m, 1H), 1.62 (s, 3H), 1.59 (s, 3H), 0.67 (dd, J = 14.7, 5.3 Hz, 2H), 0.57 (dd, J = 14.7, 8.5 Hz, 2H), −0.17 to 0.07 (m, 18H); ^{13}C NMR ($CDCl_3$) δ 134.73, 126.19, 30.41, 28.54, 25.63, 18.19, −0.72. Found: C, 64.59; H, 12.24%. Calcd for $C_{13}H_{30}Si_2$: C, 64.38; H, 12.47%.

4.5.5. (*E*)-3-Methoxy-4-trimethylsilyl-1-phenyl-1-butene (20). ^1H NMR (300 MHz, $CDCl_3$) δ 7.30–7.41 (m, 4H), 7.22–7.25 (m, 1H), 6.48 (d, J = 15.9 Hz, 1H), 6.01 (dd, J = 15.9, 8.4 Hz, 1H), 3.81 (q, J = 7.8 Hz, 1H), 3.27 (s, 3H), 1.14 (dd, J = 14.3, 6.8 Hz, 1H), 0.94 (dd, J = 14.3, 7.7 Hz, 1H), 0.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.04, 131.15, 128.49, 127.51, 126.34, 106.68, 80.60, 55.72, 25.05, −0.62. Found: C, 71.79; H, 9.45%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

4.5.6. (*E*)-1-Phenyl-4-trimethylsilyl-3-(trimethylsilylmethyl)-1-butene (21). ^1H NMR (300 MHz, $CDCl_3$) δ 7.28–7.33 (m, 4H), 7.15–7.21 (m, 1H), 6.27 (d, J = 15.6 Hz, 1H), 5.98 (dd, J = 15.6, 9.0 Hz, 1H), 2.47–2.59 (m, 1H), 0.70–0.84 (m, 4H), −0.02 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.22, 128.37, 126.61, 126.54, 125.82, 106.68, 36.42, 28.13, −0.41. Found: C, 70.21; H, 10.28%. Calcd for $C_{17}H_{30}Si_2$: C, 70.26; H, 10.41%.

Acknowledgements

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References and notes

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