Stephens–Castro-Coupling[1] of Halogenated Vinylic and Allylic Silanes with (Homo-)Propargylic Compounds

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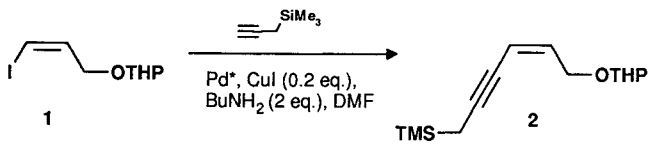
Vinyl halides containing vinylic and allylic silane terminators undergo a stereospecific palladium(0)-catalyzed cross-coupling with derivatives of terminal propargylic and homopropargylic alcohols to polyunsaturated silanes. Basic stable and unstable protecting groups were tolerated under slightly different reaction conditions.

Organosilanes containing stereodefined conjugated polyunsaturated moieties are interesting compounds for many synthetically useful transformations.[4] Synthetic methods for preparation of eneyne or enediyne compounds are of general interest especially with regard to syntheses of enediyne cytostatica/antibiotics[5] or similar molecular models. During investigations concerning the synthesis of calicheamicinone model systems[6–8] we developed a useful and versatile method for the coupling of (homo-) propargylic compounds with a terminal triple bond to vinyl bromides and vinyl iodides containing vinylic and allylic silane groups.[9]

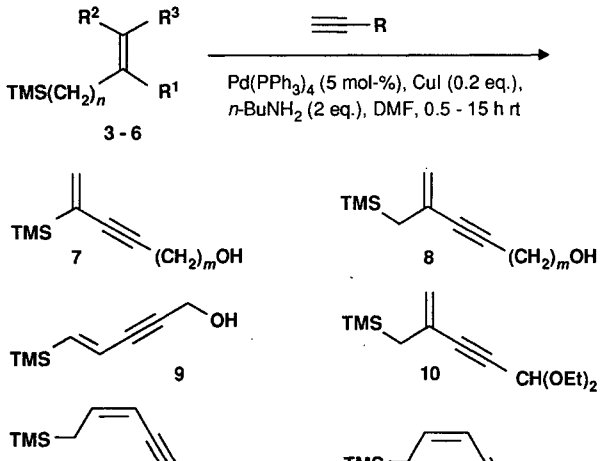
These coupling reactions were optimized in the coupling of vinyl iodide **1** with propargyltrimethylsilane.[10] Using $Pd(PPh_3)_4$ 71% of the desired product **2** was obtained during 2 hours. On the other hand, $PdCl_2(MeCN)_2$ resulted in a sluggish reaction and only 37% of **2** was isolated after 72 hours. $PdCl_2(PPh_3)_2$ also did not match the results obtained with $Pd(PPh_3)_4$, which turned out to be the catalyst of choice for this application (Scheme 1).



Scheme 1

Therefore, couplings with silicon containing vinyl halides were generally done in the presence of 5 mol% of $Pd(PPh_3)_4$ and 20 mol% of copper(I) iodide (0.2 equiv) as a co-catalyst in dimethylformamide at room temperature (Scheme 2). Results for the described coupling procedure are summarized in Table 1.

For example, treatment of commercially available bromovinylsilane **3a** with ethoxyethyl (EE)-protected propargyl alcohol[11] under these conditions yielded **7a** in 63% after subsequent deprotection. However, using unprotected propargyl alcohol the reaction rate significantly increased and 86% of **7a** was isolated (Table 1, entries 1/2; Scheme 3). Similar results concerning this effect were also obtained for other systems (entries 8/9). From these findings it was deduced that an unprotected hydroxy group of (homo-)propargylic alcohols favours the coupling with vinyl halides.

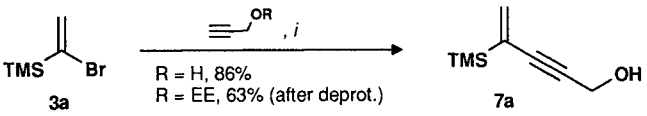


Scheme 2

Table 1. Cross-Coupling of Propargylic Compounds with Vinyl Halides

Entry	Starting silane					Acetylene		Product		Yield[a] (%)
	n	R^1	R^2	R^3		R[c]	*m*			
1	0	Br	H	H	**3a**	CH_2OEE	1	**7a**		63
2	0	Br	H	H	**3a**	CH_2OH	1	**7a**		86
3	0	Br	H	H	**3a**	CH_2OMs				–[b]
4	0	I	H	H	**3b**	CH_2OMs				–[b]
5	0	Br	H	H	**3a**	CH_2CH_2OTHP	2	**7b**		74
6	0	I	H	H	**3b**	CH_2CH_2OTHP	2	**7b**		94
7	0	H	H	Br	**4**	CH_2OH		**9**		82
8	1	Br	H	H	**5a**	CH_2OH	1	**8a**		90
9	1	I	H	H	**5b**	CH_2OEE	1	**8a**		64
10	1	Br	H	H	**5a**	CH_2CH_2OH	2	**8b**		89
11	1	I	H	H	**5b**	CH_2CH_2OH	2	**8b**		96
12	1	I	H	H	**5b**	$CH(OEt)_2$		**10**		42
13	1	H	I	H	**6**[d]	$CH(OEt)_2$		**11**		80
14	1	H	I	H	**6**[d]	CH_2CH_2OH		**12**		95

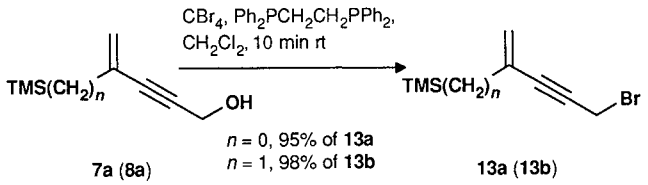
[a] Yields obtained for isolated acetals and alcohols after deprotection.
[b] Decomposition of starting material during the reaction.
[c] EE: 1-Ethoxyethyl, THP: Tetrahydropyranyl.
[d] For preparation of starting material see experimental section.



Conditions: i) $Pd(PPh_3)_4$ (5 mol-%), CuI (0.2 eq.), $BuNH_2$ (2 eq.), DMF

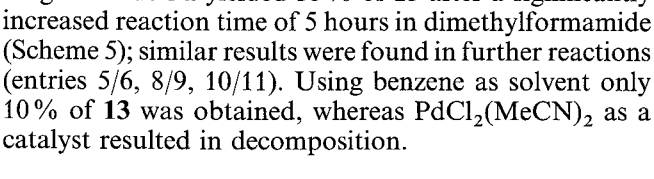
Scheme 3

The conjugated propargyl bromides **13a** and **13b** may be obtained in quantitative yields from the corresponding alcohols **7a** and **8a**, respectively, by a nucleophilic substitution,[12] while a direct coupling of halogenated vinylic silanes with propargyl bromide failed (Scheme 4).



Scheme 4

Vinyl bromides generally give good results for coupling with terminal acetylenic compounds. However, vinyl iodides showed a much higher reactivity as demonstrated by the reaction of endiyne **14**.[13] With 2-iodo-3-(trimethylsilyl)propene **(5b)**[14] silane **15** was obtained in 64% during 30 minutes in dimethylformamide. The corresponding bromide **5a** yielded 35% of **15** after a significantly increased reaction time of 5 hours in dimethylformamide (Scheme 5); similar results were found in further reactions (entries 5/6, 8/9, 10/11). Using benzene as solvent only 10% of **13** was obtained, whereas $PdCl_2(MeCN)_2$ as a catalyst resulted in decomposition.

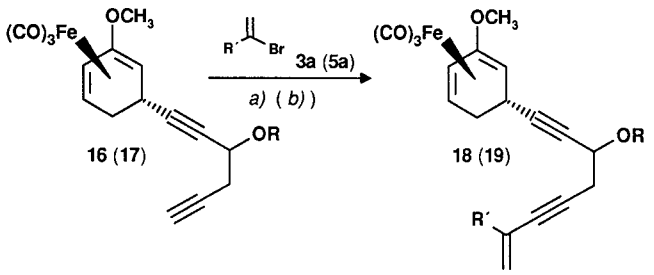


Conditions: *a)* **5a** (X = Br), $Pd(PPh_3)_4$ (5 mol-%), CuI (0.2 eq.), *n*-$BuNH_2$ (2 eq.), DMF, 5 h rt, 35%.
b) **5b** (X = I), $Pd(PPh_3)_4$ (5 mol-%), CuI (0.2 eq.), *n*-$BuNH_2$ (2 eq.), DMF, 30 min rt, 64%.

Scheme 5

Another application on enediyne chemistry for this reaction is the cross-coupling of η^4-tricarbonyliron complexes **16** and **17**[15] (Scheme 6). For protecting groups stable to basic conditions as benzyl (Bn), good yields of the coupling product with bromide **3a** were obtained (47% of **18**). On the other hand, using the sensitive acetate group, coupling failed due to decomposition under the reaction conditions. However, in a wide range of possible amines[7] we found "proton sponge", 1,8-bis(dimethylamino)-naphthalene, to be the only useful reagent in this case. The coupling product **19** was obtained in 89% yield.

In summary, the described reaction is a powerful and simple procedure for the cross-coupling of terminal acetylenic compounds with halogenated vinylic and allylic silanes. Unprotected (homo-)propargyl alcohol as well as protected derivatives were coupled in high yields. For protecting groups sensitive to basic conditions slightly different reaction conditions using 1,8-bis(dimethylamino)naphthalene as a base were established.



Conditions: *a)* **3a** (R'= TMS), **16** (R = Bn), $Pd(PPh_3)_4$ (5 mol-%), CuI (0.2 eq.), *n*-$BuNH_2$ (2 eq.), DMF, 12 h rt, 47% of **18**.
b) **5a** (R = CH_2TMS), **17** (R = Ac), $Pd(PPh_3)_4$ (5 mol-%), CuI (0.2 eq.), *"proton sponge"* (2 eq.), DMF, 12 h rt, 89% of **19**.

Scheme 6

All experiments were performed under N_2 in flame dried glassware. DMF was dried over CaH_2 and stored over molecular sieves. Flash chromatography was usually done using pentane/Et_2O (7:3) as eluent on Baker silica gel (230–400 mesh). FT-IR: Nicolet 320 as capillary film (neat). MS (70 eV): Finnigan MAT 8430. NMR (^1H: 400 MHz; ^{13}C: 100 MHz): Bruker AM 400, $CDCl_3$ as solvent. Microanalyses were performed at the Institut für Pharmazeutische Chemie der TU Braunschweig. Satisfactory microanalyses were obtained for **1** and 1-iodo-3-(trimethylsilyl)prop-1-yne: C ± 0.12, H ± 0.06.

4-Methylene-5-trimethylsilylpent-2-yn-1-ol (8a); Typical Procedure: A mixture of $Pd(PPh_3)_4$ (592 mg, 0.52 mmol), CuI (446 mg, 2.07 mmol) and a 0.5 M solution of the vinyl bromide **5a**[16] (2.0 g, 10.4 mmol) in DMF (20 mL) was treated with $BuNH_2$[16] (2.2 mL, 20.7 mmol). After 10 min propargyl alcohol (0.62 mL, 10.87 mmol) was added and stirring was continued for 15 h (TLC control). The mixture was poured into pentane (25 mL) and filtered through a short column of silica (eluent: pentane/Et_2O, 7:3).[17] The filtrate was washed with brine (3 mL) and dried ($MgSO_4$). After the solvent was removed under reduced pressure 1.57 g (90%) of **8a** was isolated by subsequent chromatographic separation (Table 2).

3-Iodo-1-(tetrahydropyranyloxy)prop-2-ene (1):

3-Iodo-1-(tetrahydropyranyloxy)prop-2-yne:

To a solution of 1.6 M BuLi in hexane (23.5 mL, 37.6 mmol) and THF (30 mL) at −78 °C was added a solution of 1-(tetrahydropyranyloxy)-prop-2-yne (4.8 g, 34.2 mmol) in THF (5 mL) over a period of 1 h. Stirring was continued for 15 min and the mixture was allowed to warm up to 0 °C over a period of 30 min. I_2 (8.7 g, 34.2 mmol) in THF (30 mL) was added and stirring continued for 15 min at r.t. The mixture was poured into a sat. ice-cooled aq solution of Na_2SO_3 (15 mL), extracted with Et_2O (3 × 30 mL), washed with brine (20 mL) and finally dried ($MgSO_4$). After careful removal of the solvent under reduced pressure the residue was distilled in a Kugelrohr (50–75 °C/0.001 mbar) to yield the 3-iodo-1-(tetrahydropyranyloxy)prop-2-yne (6.43 g, 71%) as a pale yellow, light-sensitive liquid, which crystallised on cooling to −18 °C.

^1H NMR ($CDCl_3$): δ = 4.77 (t, J = 3.3 Hz, 1 H), 4.40 (d, J = 22.9 Hz, 1 H), 4.36 (d, J = 22.9 Hz, 1 H), 3.79 (ddd, J = 11.1, 9.3, 3.1 Hz, 1 H), 3.51 (ddt, J = 11.1, 4.2, 1.2 Hz, 1 H), 1.85–1.48 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 96.8 (C4), 90.4 (C2), 62.0 (C8), 55.6 (C1), 30.1 (C5), 25.3 (C7), 18.9 (C6), 2.3 (C3).

IR (film): ν = 2943, 2187, 1121, 1060, 1027 cm^{-1}.

MS: m/z = 266 (1, M^+), 165 (87), 85 (100).

HRMS ($C_8H_{10}IO_2$): calc. 264.972556; found 264.9725.

3-Iodo-1-(tetrahydropyranyloxy)prop-2-ene **(1)**:

This was obtained from the above iodopropyne using the similar procedure as described for **6**. 1.34 g of **1** (54%) was isolated by Kugelrohr distillation (50–75 °C/0.001 mbar) as a colourless, light-sensitive liquid.

Table 2. Spectroscopic Data of Products **2, 7–15, 18, 19**[18,19]

Compound	IR (film) ν (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS-EI m/z (%)
2[b] (0.50)	3048, 2953, 2203, 1455, 1250, 1030, 852	5.89 (dt, J = 10.7, 6.5, 1H), 5.58 (dtt, J = 10.7, 2.5, 1.5, 1H), 4.63 (t, J = 3.6, 1H), 4.41 (ddd, J = 12.9, 5.9, 1.5, 1H), 4.27 (ddd, J = 12.9, 6.9, 1.5, 1H), 3.86 (ddd, J = 11.1, 9.2, 3.1, 1H), 3.53 (dt, J = 11.1, 4.2, 1H), 1.83–1.47 (m, 6H), 1.61 (d, J = 2.5, 2H), 0.09 [s, 9H, $Si(CH_3)_3$]	136.8 (C2), 112.3 (C3), 98.4 (C7), 94.6 (C4), 75.4 (C5), 65.3 (C1), 62.2 (C11), 30.7 (C8), 25.5 (C10), 19.5 (C9), 8.3 (C6), −2.0 [$Si(CH_3)_3$]	252 (0.6, M^+), 167 (5), 85 (100), 73 (58)
7a[a] (0.24)	3332 (br.), 2959, 2202, 1571, 1250, 1069, 855, 843	6.08 (d, J = 3.3, 1H), 5.69 (d, J = 3.3, 1H), 4.42 (d, J = 5.4, 2H), 1.72 (t, J = 5.8, OH), 0.14 [s, 9H, $Si(CH_3)_3$]	134.6 (C5), 134.0 (C4), 91.3 (C3), 87.0 (C2), 51.8 (C1), −2.2 [$Si(CH_3)_3$]	154 (5, M^+), 139 (6), 75 (54), 73 (100)
7b[a] (0.42)	3412 (br.), 2959, 2213, 1741, 1250, 1047, 844	6.03 (d, J = 3.4, 1H), 5.64 (d, J = 3.4, 1H), 3.72 (t, J = 6.3, 2H), 2.62 (t, J = 6.3, 2H), 1.81 (br s, OH), 0.14 [s, 9H, $Si(CH_3)_3$]	134.7 (C5), 133.7 (C6), 90.2 (C4), 83.8 (C3), 61.4 (C1), 24.1 (C2), −2.1 [$Si(CH_3)_3$]	168 (6, M^+), 103 (43), 75 (48), 73 (100)
8a[c] (0.40)	3332 (br), 3096, 2956, 2226, 1250, 1059, 880, 855	5.18 (d, J = 1.8, 1H), 5.02 (dt, J = 1.0, 1.8, 1H), 4.36 (d, J = 5.3, 2H), 1.66 (d, J = 1.0, 2H), 1.51 (t, J = 5.7, OH), 0.06 [s, 9H, $Si(CH_3)_3$]	128.3 (C4), 119.4 (C5), 87.9 (C3), 86.2 (C2), 51.6 (C1), 28.2 (C6), −1.6 [$Si(CH_3)_3$]	168 (4, M^+), 167 (4), 78 (100), 75 (60), 73 (99)
8b	–	5.14 (d, J = 2.0, 1H), 4.98 (m, 1H), 3.73 (t, J = 6.3, 2H), 2.57 (t, J = 6.3, 2H), 1.84 (br s, OH), 1.66 (d, J = 2.0, 2H), 0.07 [s, 9H, $Si(CH_3)_3$]	128.8 (C5), 118.4 (C6), 85.2 (C4), 84.8 (C3), 61.2 (C1), 28.5 (C7), 23.7 (C2), −1.6 [$Si(CH_3)_3$]	182 (5, M^+), 167 (12), 91 (66), 75 (50), 73 (100)
9a[a] (0.24)	3332 (br.), 2957, 1573, 1250, 1015, 868, 843	6.44 (d, J = 19.3, 1H), 5.94 (dt, J = 19.3, 1.8, 1H), 4.38 (dd, J = 6.1, 1.8, 2H), 1.71 (t, J = 6.1, OH), 0.07 [s, 9H, $Si(CH_3)_3$]	146.4 (C4), 122.6 (C5), 87.6 (C3), 86.0 (C2), 51.6 (C1), −1.7 [$Si(CH_3)_3$]	154 (2, M^+), 139 (26), 75 (100), 73 (90)
10[b] (0.57)	2977, 2930, 1251, 1120, 1056, 858, 847	5.35 (s, 1H), 5.26 (d, J = 1.9, 1H), 5.06 (dt, J = 1.9, 0.7, 1H), 3.73 (dq, J = 9.4, 7.2, 2H), 3.58 (dq, J = 9.4, 7.2, 2H), 1.67 (d, J = 0.7, 2H), 1.23 (t, J = 7.1, 6H), 0.06 [s, 9H, $Si(CH_3)_3$]	127.7 (C2), 120.5 (C1), 91.8 (C5), 87.2 (C3), 83.4 (C4), 60.9 (C7), 27.9 (C6), 15.1 (C8), −1.7 [$Si(CH_3)_3$]	–
11[b] (0.57)	3027, 2979, 2211, 1251, 1055, 861, 843	6.02 (dt, J = 10.7, 8.8, 1H), 5.40 (d, J = 1.1, 1H), 5.36 (dd, J = 10.7, 1.1, 1H), 3.75 (dq, J = 9.4, 7.1, 2H), 3.60 (dq, J = 9.4, 7.1, 2H), 1.84 (d, J = 8.8, 2H), 1.23 (t, J = 7.1, 6H), 0.03 [s, 9H, $Si(CH_3)_3$]	142.9 (C3), 105.1 (C2), 92.0 (C6), 88.3 (C4), 83.0 (C5), 60.8 (C7), 23.2 (C1), 15.2 (C8), −1.6 [$Si(CH_3)_3$]	240 (1, M^+), 195 (23), 115 (25), 103 (100), 94 (22), 75 (67), 73 (91)
12	–	5.92 (dt, J = 10.8, 8.7, 1H), 5.31 (dm, J = 10.8, 1H), 3.72 (t, J = 6.3, 2H), 2.61 (dt, J = 6.3, 2.2, 2H), 1.86 (br s, OH), 1.79 (dd, J = 8.7, 1.0, 2H), 0.03 [s, 9H, $Si(CH_3)_3$]	140.6 (C5), 106.0 (C6), 89.9 (C4), 80.0 (C3), 61.4 (C1), 24.0 (C7), 22.6 (C2), −1.6 [$Si(CH_3)_3$]	182 (6, M^+), 167 (12), 91 (59), 75 (22), 73 (100)
13a[d] (0.46)	2959, 2205, 1251, 1202, 844	6.09 (d, J = 3.5, 1H), 5.72 (d, J = 3.5, 1H), 4.11 (s, 2H), 0.16 [s, 9H, $Si(CH_3)_3$]	135.2 (C5), 133.9 (C4), 88.4 (C2), 88.3 (C3), 15.9 (C1), −2.1 [$Si(CH_3)_3$]	218 (11, M^+), 139 (24), 73 (100)
13b[d] (0.46)	3022, 2955, 2223, 1598, 1250, 1160, 887, 855	5.21 (d, J = 1.8, 1H), 5.05 (dd, J = 1.8, 1.0, 1H), 4.03 (s, 2H), 1.65 (d, J = 1.0, 2H), 0.06 [s, 9H, $Si(CH_3)_3$]	128.1 (C4), 120.3 (C5), 88.9 (C3), 83.1 (C2), 28.1 (C6), 15.4 (C1), −1.7 [$Si(CH_3)_3$]	232 (2, M^+), 139 (10), 78 (100), 73 (70)
14[c] (0.46)	3289, 3049, 2944, 2207, 2096, 1202, 1055, 1038, 1025	5.93 (ddt, J = 11.0, 1.9, 0.8, 1H), 5.80 (dd, J = 11.0, 2.3, 1H), 4.89 (t, J = 3.4, 1H), 4.46 (d, J = 1.9, 2H), 3.84 (ddd, J = 11.1, 9.2, 3.1, 1H), 3.53 (ddt, J = 11.1, 4.2, 1.2, 1H), 3.32 (dd, J = 2.3, 0.8, 1H), 1.86–1.49 (m, 6H)	121.2 (C4), 118.8 (C5), 96.7 (C8), 93.5 (C3), 84.7 (C6), 82.8 (C2), 80.6 (C7), 62.1 (C12), 54.7 (C1), 30.3 (C9), 25.4 (C11), 19.1 (C10)	190 (1, M^+), 129 (5), 115 (7), 101 (12), 90 (15), 89 (100), 85 (62)
15[b] (0.44)	3027, 2947, 2187, 2040, 1597, 1250, 1202, 1056, 1024, 855	5.91 (d, J = 10.9, 1H), 5.80 (dt, J = 10.9, 1.9, 1H), 5.26 (d, J = 1.9, 1H), 5.08 (dt, J = 1.9, 1.0, 1H), 4.86 (t, J = 3.4, 1H), 4.47 (dd, J = 16.2, 1.9, 1H), 4.41 (dd, J = 16.2, 1.9, 1H), 3.84 (ddd, J = 11.1, 9.2, 3.1, 1H), 3.53 (ddt, J = 11.1, 4.2, 1.2, 1H), 1.86–1.49 (m, 6H), 1.71 (d, J = 1.0, 2H), 0.07 [s, 9H, $Si(CH_3)_3$]	128.7 (C8), 119.6 (C9), 119.6 (C4), 118.2 (C5), 99.0 (C6), 96.4 (C11), 92.9 (C3), 85.8 (C7), 83.1 (C2), 61.5 (C15), 54.4 (C1), 30.1 (C12), 27.7 (C10), 25.3 (C14), 18.8 (C13), −1.8 [$Si(CH_3)_3$]	302 (3, M^+), 202 (28), 187 (95), 173 (21), 128 (60), 85 (100), 73 (73)
18[a] (0.57)	3307, 3010, 2959, 2204, 2047, 1971, 1769, 1487, 1249, 1218, 862, 841	*Only characteristic signals of the diastereomeric mixture are given due to paramagnetic pollutions:* 7.41–7.39 (m, ΣH, Ar), 7.37–7.35 (m, ΣH, Ar), 3.64 + 3.63 (s, Σ3 H, OMe), 3.09–2.99 (m, Σ1 H), 0.14 + 0.13 [s, Σ9 H, $Si(CH_3)_3$]	210.7 (CO), 139.1 (C2), 138.3 (C16), 130.5 (C3), 128.8 (C17/C21), 128.5 (C18/20), 128.4 (C19), 77.3 (C12), 68.6 (C3),68.5 (C9), 55.9 (OMe), 54.6 (C1), 48.1/48.0 (C4), 32.1/31.9 (C5), 29.9 (C6), 29.8 (C15), −0.8/−1.0 [$Si(CH_3)_3$]	531 (4, M^+), 513 (24), 179 (100)
19[c] (0.37)	3009, 2956, 2234, 2047, 1968, 1747, 1487, 1249, 1228, 855	5.40 (tt, J = 6.4, 2.0, 1H), 5.20 (dd, J = 6.6, 1.5, 1H), 5.12 (dt, J = 1.8, 1.0, 1H), 4.96 (d, J = 1.0, 1H), 3.63 (s, 3H), 3.40 (dd, J = 3.3, 2.0, 1H), 2.93 (ddt, J = 11.0, 3.7, 2.0, 1H), 2.70 (ddd, J = 6.4, 3.3, 1.3, 2H), 2.64 (ddd, J = 6.6, 3.7, 2.2, 1H), 2.06 (s, 3H), 1.98 (dddd, J = 14.7, 11.0, 3.7, 1.5, 1H), 1.63 (s, 2H), 1.58–1.53 (dm, J = 14.7, 1H), 0.05 [s, 9H, $Si(CH_3)_3$]	210.6 (CO), 169.7 (C16), 139.2 (C2), 128.8 (C13), 118.5 (C14), 89.9/89.8 (C8), 84.9 (C11), 83.2 (C12), 76.4 (C7), 68.8 (C3), 62.6 (C9), 55.9 (C1), 54.8 (OMe), 47.9 (C4), 31.7 (C5), 29.0 (C6), 28.3 (C15), 26.6 (C10), 21.0 (C17), −1.6 [$Si(CH_3)_3$]	496 (1, M^+), 412 (74), 352 (11), 214 (15), 149 (35), 115 (20), 109 (90), 73 (100)

[a–d] Solvent mixture for R_f (in parenthesis): a. Petroleum ether/Et_2O, 7 : 3; b. Petroleum ether/EtOAc, 9 : 1; c. Petroleum ether/EtOAc, 4 : 1; d. Pentane.

^{1}H NMR ($CDCl_3$): δ = 6.47 (ddd, J = 7.7, 5.9, 5.3 Hz, 1 H), 6.37 (dt, J = 7.7, 1.7 Hz, 1 H), 4.64 (t, J = 3.5 Hz, 1 H), 4.28 (ddd, J = 13.4, 5.3, 1.7 Hz, 1 H), 4.09 (ddd, J = 13.4, 5.9, 1.7 Hz, 1 H), 3.87 (ddd, J = 11.1, 9.2, 3.1 Hz, 1 H), 3.53 (dt, J = 11.1, 4.2 Hz, 1 H), 1.85–1.50 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 138.3, (C2), 98.6 (C4), 82.8 (C3), 70.1 (C1), 62.3 (C8), 30.6 (C5), 25.4 (C7), 19.4 (C6).

IR (Film): ν = 3074, 2942, 1614, 1281, 1133, 1120, 1079, 1067, 1028 cm^{-1}.

MS: m/z = 267 (0.5, $M^+ - 1$), 167 (39), 85 (100).

1-Iodo-3-(trimethylsilyl)prop-1-ene (6):

1-Iodo-3-(trimethylsilyl)prop-1-yne:

To $BrCH_2CH_2Br$-activated Mg turnings (1.58 g, 65 mmol) in THF (20 mL) was added a solution of EtBr (4.9 mL, 59 mmol) in THF (5 mL) at r.t. at such a rate to maintain a gentle reflux. After an additional 0.5 h propargyltrimethylsilane (18 mL, 59 mmol) in THF (20 mL) was added over a period of 20 min. Stirring was continued for 1.5 h, a solution of I_2 (15 g, 59 mmol) in THF (30 mL) was added at 0 °C and the mixture was allowed to warm up to r.t. for 15 min. The mixture was poured into a sat. ice-cooled solution of Na_2SO_3 in H_2O (15 mL), extracted with Et_2O (3 × 30 mL), washed with brine (20 mL) and finally dried ($MgSO_4$). After carefully removing the solvent under reduced pressure the residue was distilled in a Kugelrohr (20 °C/0.8 mbar) to yield 1-iodo-3-(trimethylsilyl)prop-1-yne (11.8 g, 84%) as a colourless, volatile and light sensitive liquid.

^{1}H NMR ($CDCl_3$): δ = 1.66 (s, 2 H), 0.09 (s, 9 H).

^{13}C NMR ($CDCl_3$): δ = 92.2 (C2), 9.7 (C3), −2.0 [$Si(CH_3)_3$], −2.3 (C1).

IR (Film): ν = 2957, 2189, 1251, 850 cm^{-1}.

MS: m/z = 238 (35, M^+), 223 (25), 195 (40), 111 (100), 83 (34), 73 (99).

1-Iodo-3-(trimethylsilyl)prop-1-ene **(6)**:

1-Iodo-3-(trimethylsilyl)prop-1-yne (13.3 g, 55.8 mmol) was added to a yellow solution of dipotassium azodicarboxylate (43.5 g, 223 mmol) in MeOH (180 mL). Then AcOH (22.4 mL, 391 mmol) in MeOH (90 mL) was added slowly in a rate of 3.5 mL/min. The mixture was diluted with petroleum ether/Et_2O (1:1, 300 mL) and the white precipitate formed was filtered off. After evaporation of solvent under reduced pressure the solution was treated with $BuNH_2$ (200 mL), allowed to stand at r.t. for 2 h and then extracted with petroleum ether. The organic phases were washed with 10 mL portions of 2 N H_2SO_4/brine (1:1) until neutral and dried ($MgSO_4$). After careful removal of the solvent under reduced pressure the residue was purified by Kugelrohr distillation (20 °C/4 to 1 mbar) to yield **6** (10.8 g, 80%) as a colourless, volatile and light sensitive liquid.

^{1}H NMR ($CDCl_3$): δ = 6.14 (dt, J = 8.2, 7.2 Hz, 1 H), 6.01 (dt, J = 7.2, 1.0 Hz, 1 H), 1.66 (dd, J = 8.2, 1.0 Hz, 2 H), 0.05 [s, 9 H, $Si(CH_3)_3$].

^{13}C NMR ($CDCl_3$): δ = 138.4 (C2), 79.5 (C1), 26.4 (C3), −1.4 [$Si(CH_3)_3$].

IR (Film): ν = 3072, 2955, 1604, 1249, 855 cm^{-1}.

MS: m/z = 240 (14, M^+), 185 (10), 73 (100).

HRMS ($C_6H_{13}ISi$): calc. 239.983130; found 239.9831.

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(14) Compound **5b** was prepared from 2-bromoallylsilane **(5a)** by halogen–metal exchange with *t*-BuLi and subsequent iodination in 88% yield; in an identical procedure 1-iodovinyl-1-trimethylsilane **(3b)** was obtained in 84% yield from **3a**.
(15) For synthesis of compounds **16** and **17**, see Refs. 6, 7.
(16) For tricarbonyliron complex **17** 2 equivalents of 1,8-bis(dimethylamino)naphthalene were used instead of $BuNH_2$.
(17) Classical aqueous workup with saturated solutions of NH_4Cl and NaCl may also be used.
(18) Satisfactory microanalyses were obtained for compounds **14**, **15**, and **19**: C ± 0.09, H ± 0.15.
(19) Corresponding HRMS were obtained for compounds **2**, **7a**, **8a**, **8b**, **11**, **12** and **13a**.