1-Methyl-1-vinyl- and 1-Methyl-1-(prop-2-enyl)silacyclobutane: Reagents for Palladium-Catalyzed Cross-Coupling Reactions of Aryl Halides

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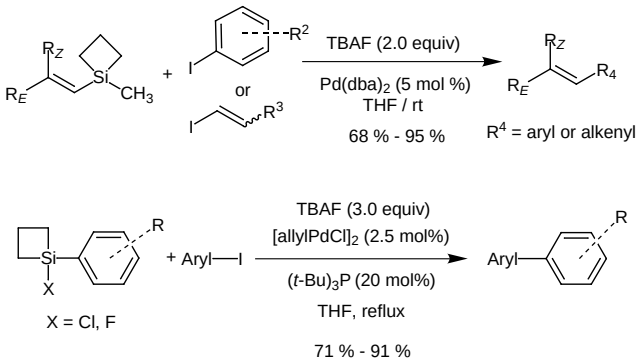
Abstract: 1-Methyl-1-vinylsilacyclobutane (**1**) and 1-methyl-1-(prop-2-enyl)silacyclobutane (**2**) undergo rapid and high yielding cross-coupling with aromatic halides. Many different substituents and patterns on the aromatic moiety are tolerated. All reactions can be run at room temperature and require the presence of tetrabutylammonium fluoride and $Pd(dba)_2$. Both silacyclobutanes can be made in one step from commercially available precursors.

Key words: cross-coupling, organosilicon, palladium catalysis, styrenes, alkenes

Recent disclosures from these laboratories have described the use of alkenyl-[1a] and arylsilacyclobutanes[1b] as viable partners in palladium-catalyzed cross-coupling reactions with aryl and alkenyl halides (Scheme 1). For alkenylsilacyclobutanes, the reactions are effectively promoted by 2−3 equivalents of tetrabutylammonium fluoride in the presence of $Pd(dba)_2$ (5 mol%) at room temperature. Within 10 minutes to 3 hours the reactions are complete and afford excellent yields of coupling products. Good functional group compatibility is observed and the alkenyl-alkenyl cross-couplings are highly stereospecific. For arylsilacyclobutanes, the reactions required a heteroatom activating group on the silicon moiety. The aryl-aryl cross couplings were slightly slower requiring 1−5 hours in refluxing THF. For these reactions, the superior catalyst is $(allylPdCl)_2$ in combination with t-Bu_3P to suppress homocoupling.



Scheme 1

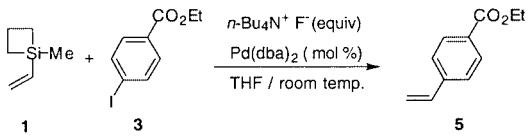
In continuation of these studies we are interested in establishing the scope of the cross coupling with respect to the substitution on the alkenylsilane component. The foregoing investigations were limited to the use of *E* and *Z*-2-substituted alkenylsilanes and showed good generality. In this disclosure we report the preparation and use of two new reagents, 1-methyl-1-vinylsilacyclobutane (**1**) and 1-methyl-1-(prop-2-enyl)silacyclobutane (**2**) which represent two new classes of alkene donors (Figure).

Figure Structures of 1-methyl-1-vinylsilacyclobutane **(1)** and 1-methyl-1-(prop-2-enyl)silacylobutane **(2)**

Although the vinyl derivative **1** is a known compound[2] we found the literature procedure to be unnecessarily cumbersome. By adaptation of the method of Utimoto[3] we prepared **1** from simple combination of vinylmagnesium bromide and 1-chloro-1-methylsilacyclobutane[4] in 58% yield on a 15g scale. The previously unknown propenyl analog **2** was prepared by a similar procedure in 65% yield. Both compounds are stable, colorless but volatile fluids (**1**, bp 108−110 °C; **2**, bp 124−126 °C).

The palladium catalyzed vinylation of iodoarenes was investigated first. To establish the optimal conditions for coupling, two electronically complementary arenes were chosen, ethyl 4-iodobenzoate (**3**) and 4-iodoanisole (**4**). As starting point, the reaction conditions developed previously in these laboratories for substituted alkenylsilanes were tested. The results from coupling of **1** with ester **3** are

Table 1 Optimization of the Coupling of **1** with **3**



Entry	**1** (Equiv)	TBAF (Equiv)	$Pd(dba)_2$ (mol %)	Time (min)	Conversion (%)
1	1.1	3.0	5.0	10	100
2	1.1	2.0	5.0	10	100
3	1.1	1.0	5.0	10	68
4	1.2	2.0	5.0	10	100
5	1.2	2.0	3.0	10	100
6	1.2	2.0	1.0	60	100

compiled in Table 1. Under these conditions (Entry 1) 100% conversion of **3** was achieved in only 10 minutes. Clearly **1** was extremely reactive and we were able to reduce the amount of promoter and catalyst significantly. Thus with just two equivalents of TBAF and 1 mol% of $Pd(dba)_2$ complete consumption of **3** was accomplished in 60 minutes. The amount of silane **1** was slightly adjusted to 1.2 equivalents based on **3** to suppress the formation of a minor byproduct (symmetrical stilbene) which arose from a Heck arylation subsequent to the coupling.

The optimization of the coupling with anisole **4** was not as straightforward. Unlike the reaction with the electron-deficient arene **3**, these couplings were much more sluggish and precipitation of the palladium catalyst became a problem. The results presented in Table 2 show that no combination of silane, TBAF and catalyst could drive the reaction to completion at room temperature in a reasonable period of time. Consequently, we examined the effect of additives to facilitate the cross-coupling. A number of structurally diverse phosphine ligands were tested without success (Entries 6–8). However, the addition of 10 mol% of triphenylarsine[5] dramatically accelerated the reaction (Entries 9, 10). In this case as well, a small amount of the Heck reaction byproduct was observed which could be removed by increasing the amount of silane to 1.5 equivalent.

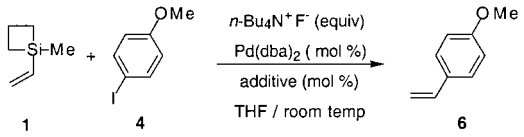
With two optimized procedures in hand, we were now in a position to survey the generality of the vinylation with respect to aryl electrophiles. The results of cross coupling with 2-, 3-, and 4-substituted aryl halides are compiled in Table 3. As expected the coupling with electron-deficient 4-substituted iodobenzenes (ester, ketone, cyano, nitro) is rapid and high yielding with as little as 1 mol% catalyst. Even 4-bromoacetophenone could be employed, but required the use of $(allylPdCl)_2$ as the catalyst and 40 °C reaction temperature. The electron rich 4-substituted cases were slightly slower and required the addition of Ph_3As as discussed above.

Similar trends were noted in the 2- and 3-substituted cases wherein electron-withdrawing substituents gave rise to rapid reaction with a minimal amount of catalyst, while the donor substituents led to significantly slower couplings. The 2-substituted cases also provided insights into the steric effect on the rate and yield of reactions. Whereas 2-nitroiodobenzene showed little steric influence compared to the 3- and 4-nitro isomers (compare **10**, **16**, and **22**) the 2-carboxy substituent had a dramatic decelerating effect (compare **3**, **18**, and **24**). In this case the steric effect overrides the electronic activation as seen in the similar rates of **24** and 2-iodotoluene (**26**) and 2-iodoanisole (**28**). The decelerating effect of an ortho substituent was also manifest in the coupling of 1-iodonaphthalene (**30**). The functional group compatibility of this process as illustrated in these examples is noteworthy.

We briefly examined the coupling of silane **1** with alkenyl electrophiles, (*E*)- and (*Z*)-6-iodohex-5-enol (Scheme 2). For this purpose we found that $(allylPdCl)_2$ was the catalyst of choice. The reactions proceeded rapidly albeit in modest yield compared to the previously reported couplings of these substrates. In both cases, however the stereospecificity was excellent as determined by GC analysis.

To evaluate the utility of the propenylsilacyclobutane analog **2** we selected a subset of the coupling partners used with reagent **1**. From the extensive optimization of reac-

Table 2 Optimization of the Coupling of **1** with **4**



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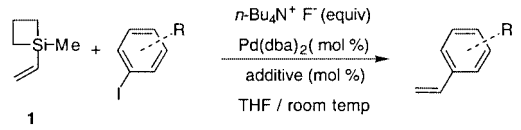
Entry	**1** (Equiv)	TBAF (Equiv)	$Pd(dba)_2$ (mol %)	Additive (mol %)	Conv. (4 h), %	Conv. (24 h), %
1	1.2	3.0	5	–	43	68
2	2.4	6.0	5	–	57	72
3	4.8	12.0	5	–	56	82
4	1.2	3.0	8	–	52	62
5[a]	1.2	2.0	5	–	79	79
6	1.2	3.0	5	Ph_3P, 10	11	29
7	1.2	3.0	5	dppp, 10	18	47
8	1.2	3.0	5	$furyl_3P$, 10	25	71
9	1.2	3.0	5	Ph_3As, 10	100[b]	–
10	1.5	4.5	5	Ph_3As, 10	100	–

[a] Reaction run at 40 °C.
[b] 3% of the Heck coupling byproduct was formed.

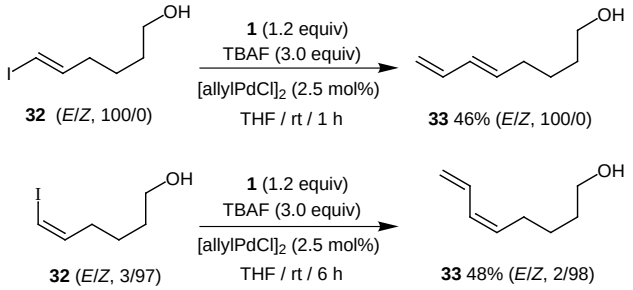
Table 3 Survey of Cross-Coupling of **1** with Aryl Halides[a]



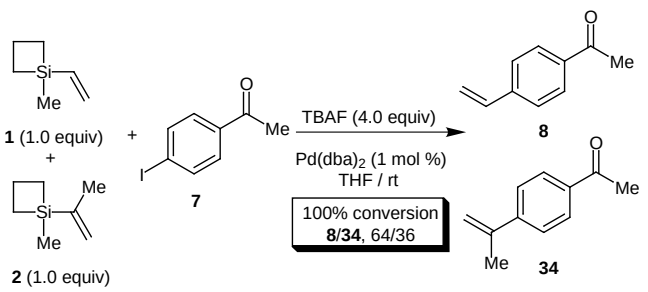
1

Aryl, R (Comp. No.)	**1** (Equiv)	TBAF (Equiv)	$Pd(dba)_2$ (mol %)	Time (h)	Product	Yield (%)
4-CO_2Et (**3**)	1.2	2.0	1	1	**5**	93
4-COMe (**7**)	1.2	2.0	1	1	**8**	85
4-COMe (**9**)[b]	1.2	3.0	2.5[c]	0.5[d]	**8**	75
4-NO_2 (**10**)	1.2	2.0	1	1	**11**	90
4-CN (**12**)	1.2	2.0	1	1	**13**	87
4-OMe (**4**)	1.5	4.5	5[e]	4	**6**	74
4-*t*-Bu (**14**)	1.2	3.0	5[e]	6	**15**	80
3-NO_2 (**16**)	1.2	2.0	1	1	**17**	92
3-CO_2Et (**18**)	1.2	2.0	3	1	**19**	90
3-CH_2OH (**20**)	1.2	3.0	5[e]	7.5	**21**	79
2-NO_2 (**22**)	1.2	2.0	1	1.5	**23**	86
2-CO_2Me (**24**)	1.2	3.0	5[e]	14	**25**	85
2-Me (**26**)	1.2	3.0	5[e]	16	**27**	70
2-OMe (**28**)	1.5	4.5	5[e]	10	**29**	75
1-napthyl-I (**30**)	1.2	3.0	5	4	**31**	86

[a] All reactions run on 2.0 mmol scale or larger.
[b] 4-Bromoacetophenone.
[c] 2.5 5 mol % of $(allylPdCl)_2$ used as catalyst.
[d] 40 °C.
[e] 10 mol % of Ph_3As added.



Scheme 2

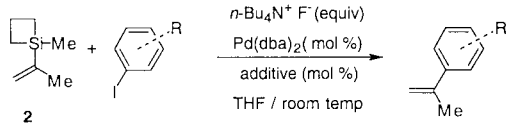


Scheme 3

tion parameters developed for the vinylations above, we had an excellent starting point for the survey of various aromatic substrates. Indeed, as shown in the results in Table 4, the only optimization that was necessary was the evaluation of the slower acting partners **22** and **24** with regard to the need for Ph_3As as an additive. Surprisingly, these reactions proceeded more readily than with the vinyl silane **1**. In fact, two of the more difficult substrates encountered in the vinylation reaction, **4** and **28**, reacted much more rapidly and without the need for Ph_3As additive. Only **24** bearing a 2-methoxycarbonyl group required the additive for complete reaction.

The unexpected increase in reaction rate for **2** compared to **1** was quantified in a competition experiment with an electron-deficient aryl coupling partner (Scheme 3). Combination of equimolar amounts of **1**, **2** and **7** in the presence of 4 equiv of TBAF and 1 mol% $Pd(dba)_2$ afforded the coupling products **8** and **34** in a 64/36 ratio (100% conversion). Thus, the difference in rate between vinyl- and prop-2-enylsilanes is somewhat substrate dependent; **1** reacts faster with electron-poor compared to electron-rich aryl halides while **2** shows the opposite trend.

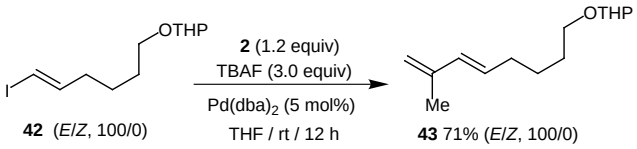
Table 4 Survey of Cross-Coupling of **2** with Aryl Halides[a]



Aryl, R (Comp. No.)	**1** (Equiv)	TBAF (Equiv)	$Pd(dba)_2$, (mol %)	Time (min)	Product	Yield (%)
4-COMe (**7**)	1.2	2.0	1	60	**34**	89
4-OMe (**4**)	1.2	3.0	5	10	**35**	85
3-NO_2 (**16**)	1.2	2.0	1	60	**36**	84
3-CH_2OH (**20**)	1.2	3.0	5	10	**37**	87
2-NO_2 (**22**)	1.2	3.0	5[b]	240	**38**	79
2-CO_2Me (**24**)	1.2	3.0	5[b]	20 h	**39**	78
2-OMe (**28**)	1.2	3.0	5	60	**40**	73
1-napthyl-I (**30**)	1.2	3.0	5	10	**41**	84

[a] All reactions run on 2.0 mmol scale or larger.
[b] 10 mol % of Ph_3As added.

In a preliminary examination, we have shown that **2** also undergoes rapid and highly stereospecific cross-coupling with alkenyl iodide *(E)*-**42**, Scheme 4. Interestingly, this transformation is higher yielding than the related coupling with **1** and could be performed with $Pd(dba)_2$ as the catalyst.



Scheme 4

In conclusion, we have demonstrated the synthetic utility of vinyl and 2-propenylsilacyclobutane reagents **1** and **2**. These compounds are easily synthesized on a large scale, and represent low molecular weight, non-toxic alternatives to tin-based reagents for vinylation of aromatic and olefinic halides. The generality of the reaction was shown to be high with regard to aryl halide functionality and substitution pattern. Further studies on the scope of silicon-based cross coupling reactions and origin of the rate and stereoselectivity are in progress.

1-Methyl-1-ethenylsilacyclobutane (1)

To a solution of 1-methyl-1-chlorosilacyclobutane (28.9 g, 0.24 mol) in THF (50 mL) was added dropwise vinylmagnesium bromide (290 mL, 1 M, 0.29 mol) at 0−5 °C in 60 min. The mixture was stirred at 0−5 °C for 2 h. Then 1 M aq HCl (100 mL) was added cautiously (the temperature of reaction mixture should never exceed 10 °C). The layers were separated, and the aqueous layer was extracted by Et_2O (3 × 100 mL). The combined organic layer was washed with H_2O (50 mL) aq sat. of $NaHCO_3$ (2 × 50 mL) and brine, and dried (Na_2SO_4). The solvents were removed by distillation, and fraction distillation of the residue afforded the product; yield: 15.4 g (58%); bp 108−110 °C/760 Torr.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.34 (dd, *J* = 20.3, 14.4, 1 H), 6.06 (dd, *J* = 14.4, 3.7, 1 H), 5.84 (dd, *J* = 20.3, 3.9, 1 H), 2.10 (m, 2 H), 1.06 (m, 4 H), 0.36 (s, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 138.4, 132.8, 18.3, 14.2, −1.9.

IR ($CHCl_3$): ν = 3051 (m), 2966 (s), 2942 (s), 2930 (s), 2873 (m), 1590 (w), 1403 (s), 1251 (s), 1201 (s), 868 (s).

1-Methyl-1-(1'-methylethenyl)silacyclobutane (2)

To a solution of 1-methyl-1-chlorosilacyclobutane (12.0 g, 0.1 mol) in THF (15 mL) was added dropwise *i*-propenylmagnesium bromide (120 mL, 1 M, 0.12 mol) at 0−5 °C in 60 min. The reaction mixture was stirred at 0−5 °C for 2.5 h. Then the 1 M aq HCl solution (40 mL) was added cautiously (the temperature of the mixture should not exceed 10 °C). The layers were separated, and the aqueous layer was extracted with Et_2O (2 × 60 mL). The combined organic layers were washed with H_2O (50 mL), aq sat. of $NaHCO_3$ (2 × 50 mL) and brine (2 × 50 mL) and dried (Na_2SO_4). The solvents were removed by distillation, and fraction distillation afforded the product 8.2 g (65%); bp 124−126 °C/760 Torr; R_f 0.77 (hexane); GC: t_R 5.10 min (HP-5, 100 °C, 15 psi).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.67 (m, = C$H_a$$H_b$, 1 H), 5.40 (m, =C$H_a$$H_b$, 1 H), 2.09 (m, CCH_2C, 2 H), 1.93 (m, CCH_3, 3 H), 1.13 (m, $SiCH_2$, 2 H), 1.01 (m, $SiCH_2$, 2 H), 0.36 (s, $SiCH_3$, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 146.8 (C=*C*H_2), 126.1 (Si*C*=), 22.3 (*C*CH_2C), 18.4 (*C*CH_3), 13.6 ($SiCH_2$), −2.2 ($SiCH_3$).

IR (film): ν = 3047 (w), 2963 (s), 2934 (m), 1442 (w), 1249 (m), 1119 (m), 923 (s), 867 (m), 771 (s).

MS: (EI, 70 eV): *m*/*z* (%) = 127 (M^+ + 1, 2), 126 (M^+, 5), 111 (21), 98 (100), 85 (21), 72 (23), 58 (31).

Anal. calcd for $C_7H_{14}Si$ (126.3): C, 66.58; H, 11.18. Found: C, 66.34; H, 11.11.

Palladium-Catalyzed Cross Coupling Reaction of 1-Methyl-1-vinylsilacyclobutane (1) or 1-Methyl-1-(prop-2-enyl)silacyclobutane (2) with Aryl or Alkenyl Halides; General Procedure

A solution of TBAF in THF (2.4−9.0 mmol, 1 M) was added to a solution of **1** or **2** (1.2−3.6 mmol) in THF (1:1 vol%) cooled by ice-water (the temperature of the reaction mixture should not exceed 10 °C). The ice-bath was removed after completing the addition of TBAF. The reaction mixture was allowed to warm to r.t. and stirred for 10 min. Then aryl halide or alkenyl iodides, palladium catalyst (1−5 mol%) and ligand (0−10%) were sequentially added to the mixture. The mixture was stirred at r.t. for indicated time, Et_2O (10 mL) was added and stirred for another 5 min. The mixture was filtered through a short column of silica gel and washed with Et_2O (60−100 mL). The solvents were removed by rotary evaporator and/or in vacuo, the crude product was purified by column chromatography (silica gel) followed by Kugelrohr distillation to afford the corresponding product.

4-Ethenylbenzoic Acid Ethyl Ester (5)

Following the General Procedure, **1** (2.4 mmol, 1.2 equiv), a solution of TBAF in THF (4 mL, 1 M, 2 equiv), 4-iodobenzoic acid ethyl ester (552.1 mg, 2.0 mmol, 1 equiv) and $Pd(dba)_2$ (11.5 mg, 0.01 equiv) were stirred at r.t. for 60 min. Et_2O (10 mL) was added and the mixture was stirred for another 5 min, then filtered through silica gel. Purification by silica gel column chromatography (hexane/EtOAc, 50:1) and Kugelrohr distillation afforded 328.4 mg (93%) of **5** as colorless oil; bp 145−150 °C/0.1 Torr; R_f 0.14 (hexane/EtOAc, 50:1). GC: t_R 7.74 min (HP-5, 180 °C, 15 psi).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (m, 2 H), 7.45 (m, 2 H), 6.74 (dd, *J* = 17.6, 10.7, 1 H), 5.86 (dd, *J* = 17.6, 0.7, 1 H), 5.37 (dd, *J* = 10.7, 0.5, 1 H), 4.37 (q, *J* = 7.1, 2 H), 1.39 (t, *J* = 7.1, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.6, 142.0, 136.2, 129.8, 126.2, 116.6, 61.1, 14.5.

IR ($CHCl_3$): ν = 3092 (w), 2984 (s), 2940 (m), 2258 (m), 1709 (s), 1608 (s), 1368 (s), 1279 (s), 1179 (s), 1108 (s), 860 (s).

MS (EI, 70 eV): *m*/*z* (%) = 177 (M^+ + 1, 5), 176 (M^+, 35), 148 (31), 131 (100), 103 (37), 77 (35).

Anal. calcd for $C_{11}H_{12}O_2$ (176.2): C, 74.98; H, 6.86%. Found: C, 74.97; H, 6.91%.

3-Ethenylbenzoic Acid Ethyl Ester (19)

Following the General Procedure, **1** (2.4 mmol, 1.2 equiv), a solution of TBAF in THF (4 mL, 1 M, 2 equiv), 3-iodobenzoic acid ethyl ester (552.1 mg, 2.0 mmol, 1 equiv) and $Pd(dba)_2$ (34.5 mg, 0.03 equiv) were stirred at r.t. for 60 min. Et_2O (10 mL) was added and the mixture was stirred for another 5 min and filtered through silica gel. Purification by silica gel column chromatography (hexane/EtOAc, 50:1) and Kugelrohr distillation afforded 316.6 mg (90%) of **19** as colorless oil; bp 160 °C/1.1 Torr; R_f 0.12 (hexane/EtOAc, 50:1); GC: t_R 7.43 min (HP-5, 180 °C, 15 psi).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (t, *J* = 1.9, 1 H), 7.93 (dt, *J* = 7.8, 1.5, 1 H), 7.58 (dt, *J* = 7.8, 1.2, 1 H), 7.39 (t, *J* = 7.8, 1 H), 6.75 (dd, *J* = 17.6, 11.0, 1 H), 5.83 (dd, *J* = 17.6, 0.7, 1 H), 5.32 (dd *J* = 11.0, 0.5, 1 H), 4.39 (q, *J* = 7.1, 2 H), 1.40 (t, *J* = 7.1, 3 H).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 166.8, 138.0, 136.2, 131.0, 130.6, 129.0, 128.7, 127.5, 115.3, 61.2, 14.5.

IR (film). ν = 3010 (w), 2982 (w), 1720 (s), 1602 (w), 1442 (w), 1283 (m), 1265 (m), 1195 (m), 911 (w), 762 (m).

MS (EI, 70 eV): *m*/*z* (%) = 177 (M^+ + 1, 6), 176 (M^+, 43), 148 (30), 131 (100), 103 (50), 77 (37).

Anal. calcd for $C_{11}H_{12}O_2$ (176.2): C, 74.98; H, 6.86. Found: C, 74.99; H, 6.91.

3-Ethenylbenzenemethanol (21)

Following the General Procedure, **1** (2.4 mmol, 1.2 equiv), a solution of TBAF in THF (6 mL, 1 M, 3 equiv), 3-iodobenzyl alcohol (492.1 mg, 2.0 mmol, 1 equiv), $Pd(dba)_2$ (57.5 mg, 0.05 equiv) and Ph_3As (61.2 mg, 0.10 equiv) were stirred at r.t. for 7.5 h. Et_2O (10 mL) was added and the mixture was stirred for another 5 min, then was filtered through silica gel. Purification by silica gel column chromatography (pentane/EtOAc, 8:1) and Kugelrohr distillation afforded 211.4 mg (79%) of **21** as colorless oil; bp 130−135 °C/0.18 Torr; R_f 0.23 (hexane/EtOAc, 8:1); GC: t_R 7.55 min (HP-5, 180 °C, 15 psi).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (m, 4 H), 6.72 (dd, *J* = 17.6, 10.7, 1 H), 5.77 (dd, *J* = 17.6, 0.7, 1 H), 5.26 (dd, *J* = 10.7, 0.7 1 H), 4.67 (d, *J* = 5.6, 2 H), 1.88 (t, *J* = 5.9, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 141.3, 138.0, 136.8, 128.9, 126.6, 125.7, 124.9, 114.4, 65.4.

IR (NaCl): ν = 3350 (m, br), 3168 (m), 2958 (m), 1631 (w), 1456 (w), 990 (m), 906 (m), 886 (w), 796 (m), 713 (s).

MS (EI, 70 eV): *m*/*z* (%) = 135 (M^+ + 1, 14), 134 (M^+, 98), 133 (M^+ − 1, 46), 115 (28), 105 (100), 91 (37) 77 (50), 63 (14).

Anal. calcd for $C_9H_{10}O$ (134.2): C, 80.56; H, 7.51. Found: C, 80.40; H, 7.47.

(*Z*)-5,7-Octadien-1-ol [(*Z*)-33)]

Following the General Procedure, **1** (1.8 mmol, 1.2 equiv), a solution of TBAF in THF (4.5 mL, 1 M, 3 equiv), (*Z*)-6-iodohexen-1-ol (339.0 mg, 1.5 mmol, 1 equiv) and $(allylPdCl)_2$ (13.7 mg, 0.025 equiv) was stirred at r.t. for 6 h. Et_2O (10 mL) was added and the mixture was stirred for another 5 min, then filtered through silica gel. Purification by silica gel column chromatography (pentane/Et_2O, 4:1) and Kugelrohr distillation afforded 91.1 mg (48%) of (*Z*)-**33** as colorless oil; bp 90−95 °C/5 Torr; R_f 0.22 (pentane/Et_2O, 4:1); GC (*Z*)-**33**, t_R 26.76 min (98%); (*E*)-**33**, 26.14 min (2%) (HP-225, 70 °C 15 psi).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62 (ddt, *J* = 16.8, 10.3, 1.0, 1 H), 6.00 (t, *J* = 11.0, 1 H), 5.44 (m, 1 H), 5.18 (dd, *J* = 16.8, 2.0, 1 H), 5.08 (d, *J* = 10.3, 1 H), 3.64 (t, *J* = 5.9, 2 H), 2.22 (m, 2 H), 1.55 (m, 2 H), 1.45 (m, 3 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 132.6, 132.4, 129.7, 117.2, 62.9, 32.4, 27.6, 25.9.

IR (film): ν = 3343 (m, br), 3085 (m), 3025 (m), 3009 (m), 2935 (m), 1643 (w), 1063 (m), 997 (m), 902 cm^{-1} (m).

MS (EI, 70 eV): *m*/*z* (%) = 127 (M^+ + 1, 0.8), 126 (M^+, 4.9), 108 (23), 98 (22), 79 (100), 67 (80).

Anal. calcd for $C_8H_{14}O$ (126.2): C, 76.14; H, 11.18. Found: C, 76.19; H, 11.14.

3-(1-Methylethenyl)benzenemethanol (37)
Following the General Procedure, **2** (2.4 mmol, 1.2 equiv), a solution of TBAF in THF (6.0 mL, 1 M, 3 equiv), 3-iodobenzyl alcohol (468.0 mg, 2.0 mmol, 1 equiv) and $Pd(dba)_2$ (57.5 mg, 0.05 equiv) were stirred at r.t. for 10 min. Et_2O (10 mL) was added and the mixture was stirred for another 5 min, then was filtered through silica gel. Purification by silica gel column chromatography (pentane/Et_2O, 4:1) and Kugelrohr distillation afforded 258.6 mg (87%) of **37** as a colorless oil; bp 135−140 °C/0.5 Torr; R_f 0.11 (pentane/Et_2O, 5:1); GC: t_R 6.77 min (HP-5, 180 °C, 15 psi).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 1 H), 7.39 (m, 1 H), 7.32 (t, *J* = 7.6, 1 H), 7.26 (d, *J* = 7.8, 1 H), 5.38 (s, 1 H), 5.09 (qn, *J* = 1.5, 1 H), 4.68 (s, 2 H), 2.16 (s, 3 H), 1.83 (br s, 1 H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 143.1, 141.6, 140.8, 128.5, 126.0, 124.9, 124.2, 112.7, 65.4, 21.8.

IR (film): ν = 3334 (m, br), 2972 (w), 2875 (w), 1629 (w), 1451 (m), 1019 (m), 891 (m), 796 (m), 718 cm^{-1} (m).

MS (EI, 70 eV): *m*/*z* (%) = 149 (M^+ + 1, 14), 148 (M^+, 100), 133 (33), 119 (30), 107 (44), 91 (59), 77 (33), 65 (13).

Anal. calcd for $C_{10}H_{12}O$ (148.2): C, 81.04; H, 8.16. Found: C, 80.92; H, 8.31.

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