Synthesis and Reactivity of an α-Stannyl β-Silyl Enamide

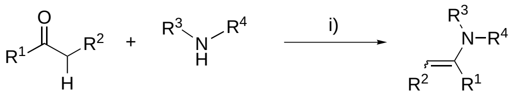
Laurianne Timbart and Jean-Christophe Cintrat*[a]

Abstract: We describe here an unprecedented approach to the synthesis of stereodefined 1,2-bis-substituted enamides. Starting from bis-metallated enamides, a palladium–copper coupling reaction allows the introduction of various groups at C1, whilst iododesilylation affords a new entry for the functionalization at C2.

Keywords: cross-coupling · enamides · palladium · Stille · tin

Introduction

Enamines are versatile tools in organic synthesis and have been widely used in numerous total syntheses.[1] The most popular synthesis of 1,2-disubstituted enamines concerns the condensation of primary or secondary amines with ketones or aldehydes, but in most cases such a strategy affords no real control of the configuration of the enamine double bond (Scheme 1).[2]

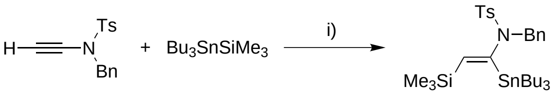


Scheme 1. Preparation of disubstituted enamines. i) H^+, $(-H_2O)$.

With this main drawback in mind, we tried to design a new approach with the purpose of preparing regio- and stereodefined disubstituted acyclic enamines. The idea was to first set up the stereodefined enamine moiety bearing two distinct carbon–metal bonds to serve as a single precursor, and, in a second step, to create the carbon–carbon bonds consecutively.

Results and Discussion

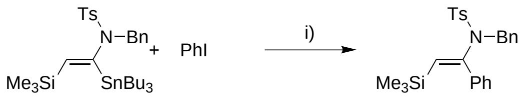
We have recently reported the Stille-like cross-coupling reaction of *N*-benzyl,*N*-(1-tributylstannylvinyl)-tosylamide[3] with various electrophiles to obtain the pure α-substituted enamine. We also previously showed that silastannation of *N*-benzyl,*N*-tosyl amino acetylene with trimethyl(tributylstannyl)silane in the presence of a palladium catalyst furnishes the α-stannylated, β-silylated *N*-tosyl enamides (Scheme 2).[4] The reaction proceeds smoothly with the standard protocol and gives compound **2** in a regioselective fashion (α-stannyl, β-silyl isomer exclusively).[5]



1 **2**

Scheme 2. Preparation of enamide **2**. i) $Pd(PPh_3)_4$, THF, 50 °C.

The reactivity of the C–Sn bond of compound **2** in palladium-catalyzed cross-coupling reactions was then checked. Using conditions identical to those used in our previous work[3] also allowed the introduction of a phenyl group at C1 in 68% yield according to Scheme 3.



2 **3**

Scheme 3. Cross-coupling of **2** with PhI. i) Pd_2dba_3 (8 mol%), $AsPh_3$ (14 mol%), CuCl (5 eq), THF, RT, 68%.

Here, the reactivity of the C–Sn bond allowed the introduction of a phenyl residue without affecting the C–Si bond.[6] This reactivity was further exemplified with other organic halides and the results are summarized in Table 1.

On the basis of these results, it appears that the modified Stille coupling procedure[7] outlined herein has broad applicability. Indeed, we have been able to transfer the β-silylated enamine moiety to a wide range of halides. Coupling with iodonaphthalene is efficient (entry 1) despite a low yield relative to iodobenzene. The coupling with heteroaromatics (entry 2) also takes place despite a modest yield. Coupling

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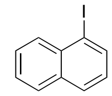
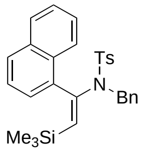
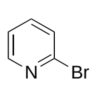
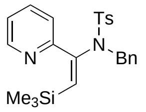
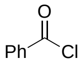
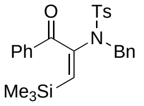
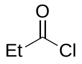
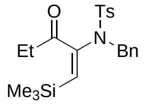
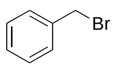
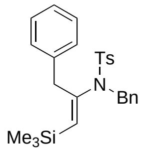
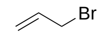
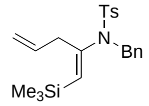
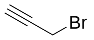
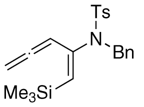
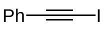
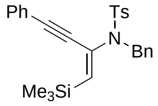
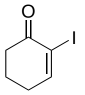
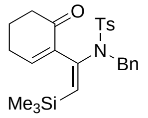
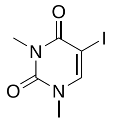
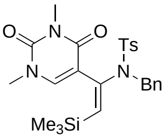
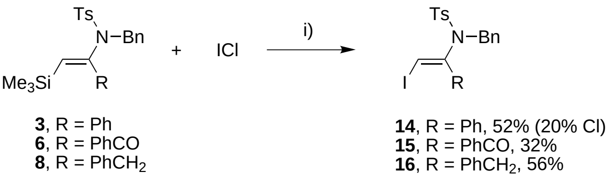
Table 1. Cross-coupling reaction of **2**.

Entry	EX	product		yield [%]
1			**4**	37
2			**5**	47
3			**6**	70
4			**7**	61
5			**8**	80
6			**9**	66
7			**10**	38
8			**11**	28
9			**12**	61
10			**13**	33

with both aromatic (entry 3) and aliphatic (entry 4) acyl chlorides affords α-amino α-enones, which may serve as highly functionalized Michael acceptors. Cross-coupling with benzyl or allyl bromide was also investigated, and the expected products were obtained in fair yields (entries 5 and 6). As expected, the coupling process with propargyl bromide occurred with complete transposition to give enamino-allene **10** as the sole isomer (entry 7). In addition, a functionalized enyne was obtained in a low yield starting from an iodoacetylenic derivative (entry 8). We also reacted 2-iodocyclohex-2-enone with compound **2**. The reaction gave an acceptable yield of silylated 1,3-diene, which might have synthetic potential in cycloaddition or in 1,4-conjugate addition reactions (entry 9). In a similar manner, reaction with 5-iodo-1,3-dimethyluracil affords a highly functionalized uracil derivative (entry 10).

The above-mentioned reaction proceeds smoothly at room temperature, whereas heating under reflux with tetrahydrofuran was necessary to obtain a complete conversion for the α-stannylated analogue (H instead of Me_3Si at the β position). This difference in reactivity may be attributed to a steric decongestion in the Sn/Si compound. This was confirmed by semi-empirical calculation that clearly shows an important modification of the Sn-C-N and Sn-C-C angles, 125° and 111°, respectively, for the unsilylated compound and 109.5° and 129.1° for compound **2**. The same holds true for the H-C-C and Si-C-C angles with values of 122.6° and 131°.[8] Strong electronic effects have also been noted; indeed HOMO density is located on the C=C double bond for the unsilylated compound, whereas most of the density in compound **2** is located on the carbon that bears the tin substituent; this gives a stronger nucleophilic character to the latter.

In order to extend the potential of our strategy towards the synthesis of stereodefined α,β-disubstituted enamines, we then focused on the reactivity of the C–Si bond. First, reaction of **8** with PhCOCl in the presence of $AlCl_3$[9] only resulted in complete degradation of the starting enamide. Attempts to react **8** with iodobenzene by using palladium catalysis according to previously described protocols,[10] either with or without fluoride ions,[11] only led to a protodesilylation compound. Since direct C–C bond formation was not successful, we attempted to synthesize iodovinyl derivatives. Therefore, compounds **3**, **6**, and **8** were subjected to iododesilylation with ICl (Scheme 4).[12] The three β-silyl enamides were cleanly converted into the corresponding vinyl iodides. Surprisingly, **14** was also accompanied by 20 % of the chloro derivative, which we could not separate from the iodo derivative.



Scheme 4. Iododesilylation of vinylsilanes. i) CCl_4, 0 °C.

Although this route requires one more step, that is, the synthesis of a vinyl iodide, this should allow the synthesis of regio- and stereodefined disubstituted enamides, compounds **14**–**16** acting as electrophiles in transition-metal-catalyzed cross-couplings.

Abstract in French: *Le couplage de type Stille de l'énamide bis-métallé **2** est décrit et permet l'accès à de nombreuses énamines N-tosylées α-substituées et β-silylées facilement convertibles en dérivés iodés vinyliques correspondants.*

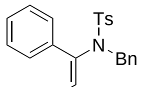
Conclusion

In summary, we describe here an original route to α-substituted β-iodo (or β-silyl) enamides based on palladium/copper cross-coupling reactions of organic halides with bismetalated enamides. This reaction cleanly leads to geometrically defined disubstituted *N*-tosyl enamines. In addition, the well-documented reactivity of vinyl iodides in cross-coupling reactions makes the C–C bond formation at C2 possible.

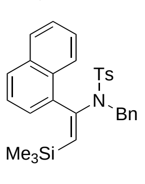
Experimental Section

General considerations: All reactions were performed in flame-dried Schlenk tubes or flasks under an atmosphere of nitrogen. Organic halides were from Aldrich or Acros and used without further purification. Tris(dibenzylideneacetone)dipalladium(0), triphenyl arsine, and copper chloride were from Aldrich. 2-Iodocyclohex-2-enone and iodoethynyl benzene were prepared according to literature procedures.[13, 14] THF was distilled under nitrogen from sodium benzophenone ketyl. Yields in Table 1 refer to isolated compounds (column chromatography and crystallization) of greater than 95 % purity as determined by ^{1}H NMR spectroscopy. All new compounds were fully characterized by spectroscopic methods (^{1}H NMR, ^{13}C NMR, MS, IR), HRMS, and, in the case of crystalline compounds, by melting point.

Representative procedure for *N*-benzyl,*N*-[(*E*)-(1-phenyl)trimethylsilylvinyl] toluenesulfonamide (3): A flame-dried Schlenk tube was charged with CuCl (162 mg, 1.6 mmol) and AsPh$_3$ (15 mg, 0.05 mmol), and the mixture was degassed (3 ×) under vacuum with a dry nitrogen purge. Anhydrous THF (20 mL) was introduced with concomitant stirring, and the resulting mixture was again degassed (2 ×) by the freeze–thaw process. Pd$_2$dba$_3$ (23 mg, 0.25 mmol) was then introduced and the mixture was degassed (1 ×). After the mixture had warmed to room temperature (30 min), PhI (46 µL, 0.4 mmol) was added, and the mixture turned brownish. The resulting suspension was stirred for 30 minutes before **2** was added (220 mg, 0.32 mmol). This mixture was stirred at room temperature, and completion of reaction was monitored by TLC. The reaction mixture was cooled, filtered over a plug of Celite (1 cm), and rinsed with ether (5 × 10 mL). The solution was concentrated to a residue that was purified by flash chromatography over silica gel and recrystallized from pentane/diethyl ether (90:10) to give 95 mg (68 % yield) of **3** as a colorless oil.

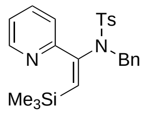


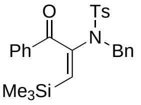
***N*-Benzyl,*N*-[(*E*)-(1-phenyl)trimethylsilylvinyl] toluenesulfonamide (3)**: ^{1}H NMR: –0.25 (s, 9H; Me$_3$Si), 2.45 (s, 3H; PhCH$_3$), 4.53 (s, 2H; PhCH$_2$), 5.62 (s, 1H; HC=), 6.92 (dt, $J=1.2$, 7.3 Hz, 2H; Ar), 7.15–7.32 (m, 10H; Ar), 7.75 (d, $^3J=8.6$, 2H; Ar); ^{13}C NMR: –0.12, 21.69, 52.45, 127.63, 127.83, 128.15, 128.38, 128.70, 128.93, 129.32, 129.45, 136.85, 137.02, 138.99, 143.61, 149.5; MS (CI): *m*/*z* (%): 436 [M^++1]; HR-MS (EI): *m*/*z*: calcd for $C_{25}H_{28}NO_2SSi$ [M^+ – H]: 434.161, found: 434.1679; calcd for $C_{24}H_{26}NO_2SSi$ [M^+ – Me]: 420.14535, found: 420.1457; calcd for $C_{25}H_{28}NSi$ [M^+ – H – SO$_2$]: 370.1991, found: 370.1959; IRTF (NaCl): 1589, 1573, 1495, 1444, 1347, 1161.



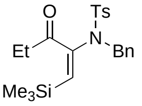
***N*-Benzyl,*N*-[(*E*)-(1-naphthalen-1-yl)trimethylsilylvinyl] toluenesulfonamide (4)**: White crystals; m.p. 133–133.2 °C; ^{1}H NMR: 0.26 (s, 9H; Me$_3$Si), 2.44 (s, 3H; PhCH$_3$), 4.56 (s, 2H; PhCH$_2$), 5.73 (s, 1H; HC=), 6.21 (dd, $J=1.2$, 8 Hz, 1H; Ar), 6.93 (t, $J=7.3$ Hz, 1H; Ar), 7.1–7.45 (m, 9H; Ar), 7.65 (d, $^4J=7.9$, 3H; Ar), 7.75 (d, $^3J=7.9$, 1H; Ar), 7.9 (d, $^3J=8.5$, 1H; Ar); ^{13}C NMR: –0.02, 21.69, 53.52, 124.17, 124.59, 125.73, 126.08, 126.21, 127.92, 128.09, 128.25, 128.38, 128.44, 129.64, 130.12, 132.81, 134.46, 136.34, 136.95, 137.69, 138.37, 143.45, 143.71; *MS* (CI) *m*/*z* (%): 486 [M^++1]; *HR-MS* (EI) *m*/*z*: calcd for $C_{29}H_{31}NO_2SSi$ [M^+]: 485.18448, found: 485.1878; IRFT (KBr): 1603, 1497, 1441, 1349, 1160.

***N*-Benzyl,*N*-[(*E*)-(1-pyridin-2-yl)trimethylsilylvinyl] toluenesulfonamide (5)**: Yellow amorphous solid; ^{1}H NMR: –0.25 (s, 9H; Me$_3$Si), 2.45 (s, 3H; PhCH$_3$), 4.51 (s, 2H; PhCH$_2$), 5.57 (s, 1H; HC=), 7.1–7.34 (m, 9H; Ar), 7.67 (d, $J=8.5$ Hz, 2H; Ar), 8.07 (d, $J=1.2$ Hz, 1H; Ar), 8.46 (dd, $J=4.9$, 1.2 Hz, 1H; Ar); ^{13}C NMR: –0.15, 21.75, 53.23, 122.78, 128.12, 128.6, 129.32, 129.67, 131, 135.49, 135.98, 136.21, 136.27, 144, 146.56, 149.6, 150.12; MS (CI): *m*/*z* (%): 437 [M^++1]; HR-MS (EI): *m*/*z*: calcd for $C_{23}H_{25}N_2O_2SSi$ [M^+ – Me]: 421.14060, found: 421.1392; IRFT (NaCl): 1598, 1581, 1495, 1455, 1349, 1164.

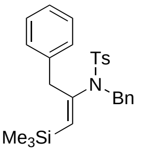




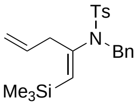
***N*-Benzyl,*N*-[(*E*)-(1-phenylmethanoyl)trimethylsilylvinyl] toluenesulfonamide (6)**: White crystals; m.p. 124.5–124.7 °C; ^{1}H NMR: –0.11 (s, 9H; Me$_3$Si), 2.44 (s, 3H; PhCH$_3$), 4.49 (s, 2H; PhCH$_2$), 5.52 (s, 1H; HC=), 7.2–7.45 (m, 12H; Ar), 7.75 (d, $^3J=7.9$ Hz, 2H; Ar); ^{13}C NMR: –0.41, 21.78, 50.8, 127.99, 128.15, 128.22, 128.31, 128.51, 129.67, 129.96, 132.55, 134.2, 134.56, 137.6, 144.29, 146.17, 193.89; MS (CI): *m*/*z* (%): 481 [M^++18]; HR-MS (EI): *m*/*z*: calcd for $C_{26}H_{29}NO_3SSi$ [M^+]: 463.16374, found: 463.1656; IRFT (KBr): 1669, 1598, 1352, 1166.



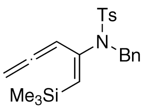
***N*-Benzyl,*N*-[(*E*)-2-oxo-1-(trimethylsilylmethylene)butyl] toluenesulfonamide (7)**: White needles; m.p. 122.6–123 °C. ^{1}H NMR: –0.03 (s, 9H; Me$_3$Si), 0.87 (t, $^3J=7.3$ Hz, 3H; CH$_3$CH$_2$), 2.46 (s, 3H; PhCH$_3$), 2.46 (q, $^3J=7.3$ Hz, 2H; CH$_3$CH$_2$), 4.36 (s, 2H; PhCH$_2$), 5.18 (s, 1H; HC=), 7.2–7.36 (m, 7H; Ar), 7.61 (d, $^3J=8.5$ Hz, 2H; Ar); ^{13}C NMR: –0.5, 7.91, 21.78, 32.3, 53.29, 128.38, 128.44, 128.64, 129.61, 129.9, 133.2, 134.78, 136.98, 144.39, 147.69, 201.94; MS (CI): *m*/*z* (%): 433 [M^++18]; HR-MS (EI): *m*/*z*: calcd for $C_{21}H_{26}NO_3SSi$ [M^+ – Me]: 400.14027, found: 400.1384; IRFT (KBr): 1697, 1579, 1494, 1455, 1347, 1164.



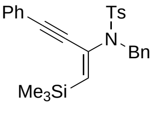
***N*-Benzyl,*N*-[(*E*)-(1-benzyl)trimethylsilylvinyl] toluenesulfonamide (8)**: White solid; m.p. 88.8–90 °C; ^{1}H NMR: 0.09 (s, 9H; Me$_3$Si), 2.44 (s, 3H; PhCH$_3$), 3.72 (s, 2H; PhCH$_2$), 4.19 (s, 2H; PhCH$_2$), 4.99 (s, 1H; HC=), 6.86 (m, 2H; Ar), 6.96–7.3 (m, 10H; Ar), 7.61 (d, $^3J=7.9$ Hz, 2H; Ar); ^{13}C NMR: 0.05, 21.72, 42.65, 53.88, 126.24, 127.28, 128.09, 128.25, 128.41, 128.51, 129.19, 129.25, 129.57, 134.52, 135.59, 137.27, 143.58, 150.34; MS (CI): *m*/*z* (%): 450 [M^++1]; HR-MS (EI): *m*/*z*: calcd for $C_{25}H_{28}NO_2SSi$ [M^+ – Me]: 434.161, found: 434.1594; IRFT (KBr): 1600, 1493, 1451, 1345, 1161.



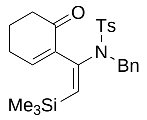
***N*-Benzyl,*N*-[(*E*)-1-(trimethylsilyl)methylene but-3-enyl] toluenesulfonamide (9)**: Amorphous white solid; ^{1}H NMR: 0.01 (s, 9H; Me$_3$Si), 2.44 (s, 3H; PhCH$_3$), 3.02 (d, $^3J=6.7$ Hz, 2H; CH$_2$CH=), 4.37 (s, 2H; PhCH$_2$), 4.70 (br d, $^3J=9.7$ Hz, 1H; CH$_2$C=), 4.81 (br d, $^3J=17.1$ Hz, 1H; CH$_2$C=), 4.98 (s, 1H; HC=), 5.1 (ddt, $J=6.7$, 9.7, 17.1 Hz, 1H; CHC=), 7.15–7.3 (m, 7H; Ar), 7.68 (d, $^3J=8.5$ Hz, 2H; Ar); ^{13}C NMR: –0.18, 21.69, 41.36, 53.88, 116.76, 127.8, 127.96, 128.18, 128.41, 129.28, 129.48, 129.99, 134.62, 134.98, 135.92, 143.58, 150.47; MS (CI): *m*/*z* (%): 400 [M^++1]; HR-MS (EI): *m*/*z*: calcd for $C_{21}H_{26}NO_2SSi$ [M^+ – Me]: 384.14535, found: 384.1446; IRFT (KBr): 1639, 1600, 1494, 1452, 1344, 1163.



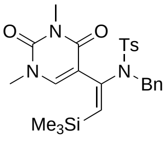
***N*-Benzyl,*N*-[(*E*)-1-(trimethylsilyl)methylene buta-2,3-dienyl] toluenesulfonamide (10)**: Slightly yellow oil. ^{1}H NMR: 0.02 (s, 9H; Me$_3$Si), 2.43 (s, 3H; PhCH$_3$), 4.46 (s, 2H; PhCH$_2$), 4.79 (dd, $J=1.8$, 6.7 Hz, 2H; CH$_2$C=), 5.10 (t, $J=1.8$ Hz, 1H; CHC=), 5.72 (t, $J=6.7$, 1H; CHC=), 7.2–7.4 (m, 7H; Ar), 7.7 (d, $^3J=8.5$, 2H; Ar); ^{13}C NMR: 0.95, 21.69, 53.91, 94.25, 127.05, 127.15, 127.57, 127.79, 128.15, 128.28, 128.73, 128.83, 129.32, 129.57, 130.03, 133.16, 136.34, 136.53, 143.32, 143.94, 211.91; MS (CI): *m*/*z* (%): 415 [M^++18]; HR-MS (EI): *m*/*z*: calcd for $C_{22}H_{27}NO_2SSi$ [M^+]: 397.15318, found: 397.1521; IRFT (NaCl): 1939, 1349, 1162, 857.



***N*-Benzyl,*N*-[(*E*)-3-phenyl-1-(trimethylsilyl)methylene prop-2-ynyl] toluenesulfonamide (11)**: Yellow oil; ^{1}H NMR: 0.1 (s, 9H; Me$_3$Si), 2.34 (s, 3H; PhCH$_3$), 4.58 (s, 2H; PhCH$_2$), 6.2 (s, 1H; HC=), 7.07 (m, 2 H; Ar), 7.2–7.4 (m, 10 H; Ar), 7.77 (d, $^3J = 7.9$, 2 H; Ar); ^{13}C NMR: −1.22, 21.59, 52.16, 85.29, 92.63, 122.23, 127.70, 128.18, 128.47, 128.96, 129.25, 129.54, 129.77, 130.58, 130.67, 131.42, 135.67, 135.95, 136.24, 143.19, 143.49, 143.68; MS (CI): *m*/*z* (%): 460 [M^++1]; HR-MS (EI): *m*/*z*: calcd for $C_{26}H_{26}NO_2SSi$ [M^+ − Me]: 444.14535, found: 444.1446; IRFT (NaCl): 2203, 1350, 1165.

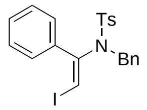


***N*-Benzyl,*N*-[(*E*)-(6-oxocyclohex-1-enyl)-trimethylsilylvinyl] toluenesulfonamide (12)**: White solid; m.p. 120.2–120.5 °C; ^{1}H NMR: −0.16 (s, 9 H; Me_3Si), 1.85–1.9 (m, 2 H; CH_2), 2.17–2.3 (m, 4 H; CH_2), 2.4 (s, 3 H; $PhCH_3$), 4.61 (s, 2 H; $PhCH_2$), 5.1 (s, 1 H; HC=), 6.6 (t, $^3J = 4.3$ Hz, 1 H; Ar), 7.2–7.4 (m, 7 H; Ar), 7.68 (d, $^3J =$ 8.5 Hz, 2 H; Ar); ^{13}C NMR: −0.25, 21.66, 21.24, 38.38, 53.81, 127.6, 128.18, 128.35, 128.77, 129.28, 129.38, 136.56, 137.37, 139.6, 144.07, 150.73, 197.19; MS (CI): *m*/*z* (%): 454 [M^++1]; HR-MS (EI): *m*/*z*: calcd for $C_{25}H_{31}NO_3SSi$ [M^+]: 453.17939, found: 453.1783; IRFT (NaCl): 1676, 1594, 1455, 1334, 1157.

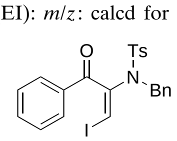


***N*-Benzyl,*N*-[(*E*)-(1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)trimethylsilylvinyl] toluenesulfonamide (13)**: Slightly brownish solid; m.p. 152.6–155.7 °C; ^{1}H NMR: −0.17 (s, 9 H; Me_3Si), 2.4 (s, 3 H; $PhCH_3$), 3.1 (s, 3 H; CO-NCH_3-CO), 3.3 (s, 3 H; NCH_3), 4.74 (s, 2 H; $PhCH_2$), 5.17 (s, 1 H; HC=), 6.84 (s, 1 H; Ar), 7.18–7.43 (m, 7 H; Ar), 7.61 (d, $^3J =$ 7.9 Hz, 2 H; Ar); ^{13}C NMR: −0.37, 21.66, 27.93, 37.22, 55.17, 113.14, 127.02, 127.92, 128.54, 129.25, 129.57, 132.62, 136.95, 137.73, 141.06, 143.45, 143.84, 151.35, 161.83; MS (ESI): *m*/*z* (%): 520 [M^++23]; HR-MS (EI): *m*/*z*: calcd for $C_{24}H_{28}N_3O_4SSi$ [M^+ − Me]: 482.15698, found: 482.1587; IRFT (NaCl): 1707, 1659, 1597, 1451, 1340, 1161.

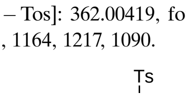
Representative procedure for iododesilylation: A solution of vinylsilane (1 eq) in CCl_4 (3 mL) was cooled to 0 °C for 1 h. ICl (1.2 eq) diluted in CCl_4 (2 mL) was then added dropwise at 0 °C, and the resulting slightly brown solution was stirred for 2 h at 0 °C. A solution of $Na_2S_2O_3$ (50 % in water, 15 mL) was added, and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were dried over Na_2SO_4 and evaporated, and the residue was purified by column chromatography with pentane/AcOEt (80:20) as eluent.



***N*-Benzyl,*N*-[(*E*)-2-iodo-1-phenylvinyl] toluenesulfonamide (14)**: White solid; ^{1}H NMR: 2.46 (s, 3 H; $PhCH_3$), 4.44 (s, 2 H; $PhCH_2$), 6.66 (s, 1 H; HC=), 6.9–7.4 (m, 12 H; Ar), 7.7 (d, $^3J = 7.9$ Hz, 2 H; Ar); ^{13}C NMR: 21.75, 52.77, 79.98, 127.53, 127.92, 128.28, 128.44, 128.63, 128.76, 128.92, 129.15, 129.25, 129.57, 129.8, 129.93, 135.98, 136.17, 137.24, 143.77, 144.16; MS (CI): *m*/*z* (%): 507 [M^++18]; HR-MS (EI): *m*/*z*: calcd for $C_{22}H_{20}INO_2S$ [M^+]: 489.02595, found: 489.0257.



***N*-Benzyl,*N*-[(*E*)-1-phenylmethanoyl-2-iodovinyl] toluenesulfonamide (15)**: Slightly yellow oil; ^{1}H NMR: 2.42 (s, 3 H; $PhCH_3$), 4.54 (s, 2 H; $PhCH_2$), 6.74 (s, 1 H; HC=), 7.1–7.7 (m, 14 H; Ar); ^{13}C NMR: 21.81, 52.48, 80.56, 128.18, 128.34, 128.66, 128.83, 128.96, 129.83, 130.19, 133.71, 135.14, 135.33, 135.52, 140.08, 144.42, 192.72; MS (CI): *m*/*z* (%): 518 [M^++1]; HR-MS (EI): *m*/*z*: calcd for $C_{16}H_{13}INO$ [M^+ − Tos]: 362.00419, found: 362.0034; IRFT (NaCl): 1673, 1596, 1451, 1353, 1164, 1217, 1090.



***N*-Benzyl,*N*-[(*E*)-1-benzyl-2-iodovinyl] toluenesulfonamide (16)**: White solid; m.p. 93.5–93.7 °C; ^{1}H NMR: 2.44 (s, 3 H; $PhCH_3$), 3.78 (s, 2 H; $PhCH_2$), 4.19 (s, 2 H; $PhCH_2$), 6.09 (s, 1 H; HC=), 6.80–7.30 (m, 12 H; Ar), 7.55 (d, $^3J = 7.9$ Hz, 2 H; Ar); ^{13}C NMR: 21.72, 41.65, 53.87, 84.25, 126.82, 127.83, 128.05, 128.41, 128.64, 128.93, 129.32, 129.70, 135.63, 135.79, 136.40, 143.94, 144.75; MS (CI): *m*/*z* (%): 521 [M^++18]; HR-MS (EI): *m*/*z*: calcd for $C_{23}H_{22}NO_2S$ [M^+ − I]: 376.13713, found: 376.1389; IRFT (NaCl): 1594, 1493, 1453, 1342, 1159.

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