(s, 3 H, OCH_3); IR ($CDCl_3$) 1726 (shoulder), 1705 cm^{-1}; EIHRMS calcd for $C_{15}H_{15}NO_4$ 273.1001, found 273.1006. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.12. Found: C, 65.99; H, 5.57; N, 5.06.

Dimethyl 9,9a-Dihydro-3*H*-pyrrolo[1,2-*a*]indole-9,9a-dicarboxylate (18a). The more polar, major isomer was obtained as a pale yellow solid. Recrystallization from ethanol gave pale yellow crystals, mp 79–80 °C: ^1H NMR (250 MHz, $CDCl_3$) δ 7.23–7.15 (m, 2 H, Ar), 6.90–6.84 (m, 2 H, Ar), 5.97 (ddd, 1 H, J = 5.7, 2.0, 1.5 Hz, olefinic), 5.88 (ddd, 1 H, J = 5.7, 2.6, 1.8 Hz, olefinic), 4.52 (s, 1 H, H-9), 4.35 (ddd, 1 H, J = 15.7, 2.6, 1.4 Hz, H-3), 4.02 (dt, 1 H, J = 15.7, 2.0 Hz, H-3′), 3.73 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 171.7 (C=O), 171.4 (C=O), 154.2 (s, Ar), 130.8 (C-1 or C-2), 130.7 (C-1 or C-2), 129.3 (d, Ar), 126.4 (s, Ar), 124.4 (d, Ar), 121.7 (d, Ar), 113.7 (d, Ar), 86.5 (C-9a), 61.7 (C-3), 55.0 (C-9), 52.4 (OCH_3), 52.3 (OCH_3); IR ($CDCl_3$) 1741 cm^{-1}; EIMS (20 eV) m/z 273 (13), 214 (77), 182 (7), 154 (100); EIHRMS calcd for $C_{15}H_{15}NO_4$ 273.1001, found 273.0997. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.12. Found: C, 65.84; H, 5.53; N, 5.08.

The chromatographic fraction containing the mixture of **18b** and **23** was dissolved in Et_2O and extracted with 6 M HCl following the procedure employed for the extraction of **13**. Evaporation of the CH_2Cl_2 solution containing the basic compounds yielded the minor isomer **18b** (0.0652 g, 16%) as an oil. Chromatographic purification (hexanes–ethyl acetate, 7:3) gave pure **18b** (0.051 g, 12%) as a pale yellow glass.

Dimethyl 9,9a-dihydro-3*H*-pyrrolo[1,2-*a*]indole-9,9a-dicarboxylate (18b) (less polar, minor isomer): ^1H NMR (250 MHz, $CDCl_3$) δ 7.26–7.18 (m, 2 H, Ar), 6.93 (td, 1 H, J = 7.5, 1.0 Hz, Ar), 6.84 (d, 1 H, J = 7.9 Hz), 6.06 (dt, 1 H, J = 5.9, 1.8 Hz, olefinic), 5.90 (dt, 1 H, J = 5.9, 2.3 Hz, olefinic), 4.77 (s, 1 H, H-9), 4.32 (ddd, 1 H, J = 15.3, 2.6, 1.6 Hz, H-3), 4.02 (dt, 1 H, J = 15.3, 2.1 Hz, H-3′), 3.80 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 173.0 (C=O), 170.6 (C=O), 153.6 (s, Ar), 131.2 (C-1 or C-2), 129.1 (d, Ar), 127.3 (C-1 or C-2), 126.5 (s, Ar), 125.7 (d, Ar), 121.6 (d, Ar), 113.1 (d, Ar), 85.7 (C-9a), 61.9 (C-3), 53.3 (C-9), 53.0 (OCH_3), 52.1 (OCH_3); IR ($CDCl_3$) 1739 cm^{-1}; EIMS (20 eV) m/z 273 (16), 214 (72), 182 (8), 154 (100); EIHRMS calcd for $C_{15}H_{15}NO_4$ 273.1001, found 273.0996. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.12. Found: C, 65.79; H, 5.56; N, 5.07.

The ethereal extract containing the neutral products was washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography (hexane–ethyl acetate, 7:3) of the residue gave **23** (0.0393 g, 12%) as a glass.

Radical Cyclization of 33. To a refluxing solution of the iodide **33** (0.075 g, 0.263 mmol), n-Bu_3SnH (0.0842 g, 0.289 mmol), and ACN (0.005 g, 0.02 mmol) in toluene (29 mL) was added a solution of AIBN (0.005 g, 0.03 mmol) in toluene (1 mL) over 2 h, via syringe pump. After the addition was finished, the reaction mixture was heated at reflux for an additional 1 h. Evaporation of the solvent under reduced pressure furnished a yellow oil. TLC (hexane–ethyl acetate, 4:1) analysis of the crude material showed the presence of three main spots. The residue was dissolved in Et_2O (30 mL) and extracted with 2 M HCl, following the procedure employed for the extraction of **13**. Evaporation of the CH_2Cl_2 solution containing the basic compounds yielded the tetrahydropyrroloindole **34** (0.021 g, 50%) as an oil. Chromatographic purification (hexanes–ethyl acetate, 9:1) afforded pure **34**[18a] (0.0189 g, 45%) as a colorless oil that darkened on standing.

2,3,9,9a-Tetrahydro-1*H*-pyrrolo[1,2-*a*]indole (34): ^1H NMR (250 MHz, $CDCl_3$) δ 7.15–7.06 (m, 2 H, Ar), 6.76 (td, 1 H, J = 7.4, 1.0 Hz, Ar), 6.61 (d, 1 H, J = 7.7 Hz), 3.94 (tdd, 1 H, J = 9.2, 6.1, 2.9 Hz, H-9a), 3.44 (ddd, 1 H, J = 10.7, 7.1, 5.2 Hz, H-3), 3.25–3.13 (m, 2 H, H-3′, and H-9), 2.96 (dd, 1 H, J = 16.0, 2.7 Hz, H-9′), 1.96–1.79 (m, 3 H, H-1, H-2, and H-2′), 1.41–1.27 (m, 1 H, H-1′); ^{13}C NMR ($CDCl_3$) δ 154.6 (s, Ar), 129.9 (s, Ar), 127.5 (d, Ar), 127.5 (d, Ar), 124.8 (d, Ar), 119.2 (d, Ar), 110.9 (d, Ar), 65.2 (C-9a), 52.2 (C-3), 33.9 (C-9), 31.3 (C-2), 25.8 (C-1); EIMS (20 eV) m/z 160 (M + H, 7), 159 (M, 29), 158 (100), 130 (43); CIHRMS calcd for $C_{11}H_{14}N$ (M + H) 160.1126, found 160.1114. Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.08; H, 8.13; N, 8.87.

The ethereal extract containing the neutral products was treated with KF solution and concentrated. Flash chromatography (hexane–ethyl acetate, 19:1) of the residue gave first 1-(1-propyl)-1*H*-indole (0.011 g, 26%)[19] and then the dihydropyrroloindole **35** (0.004 g, 10%).

2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indole (35) was obtained as an off-white solid. Recrystallization from ethanol gave colorless crystals: mp 78–79 °C [lit.[18a] mp 79–80 °C (ethanol)]; ^1H NMR (250 MHz, $CDCl_3$) δ 7.57 (dd, 1 H, J = 6.8, 1.4 Hz, Ar), 7.26 (m, 1 H, Ar), 7.17–7.05 (m, 2 H, Ar), 6.19 (d, 1 H, J = 1.0 Hz, H-9), 4.08 (t, 2 H, J = 7.0 Hz, H-3), 3.05 (t, 2 H, J = 7.3 Hz, H-1), 2.63 (pent, 2 H, J = 7.1 Hz, H-2); EIMS (20 eV) m/z 157 (97), 156 (97), 130 (100), 129 (37), 84 (21); EIHRMS calcd for $C_{11}H_{11}N$ 157.0891, found 157.0904. Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.95; H, 7.01; N, 8.87.

Acknowledgment. This work was supported by a grant from the National Cancer Institute, NIH (CA-39976). We are grateful to Dr. Zhong-li Zheng for preliminary studies in this area. We thank Mr. Dan Pentek of the Yale Chemical Instrumentation Center for recording the high resolution mass spectra.

The Use of $R_3SiSnR'_3$ in Organic Synthesis. A Novel Palladium-Catalyzed Tandem Transmetalation–Cyclization Reaction

Miwako Mori,* Naotake Kaneta, and Masakatsu Shibasaki*

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

Received July 10, 1990 (Revised Manuscript Received October 22, 1990)

The intramolecular coupling of vinyl triflates **12** with vinyl halides proceeded smoothly in the presence of $Bu_3SnSiMe_3$ (**1a**) and a palladium catalyst and gave cyclic products **13** via tandem intermolecular and intramolecular transmetalations.

Introduction

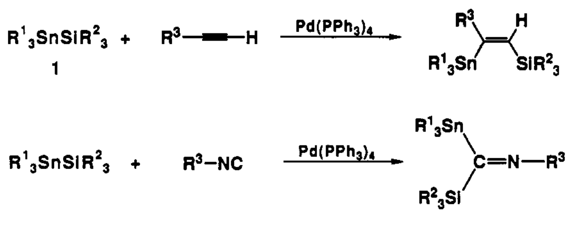
Organometallic reagents that possess a metal–metal bond are synthetically useful. Among such reagents, those species that possess a Si–Sn bond are especially interesting because of the increasing use of organosilicon and organostannane compounds in organic synthesis. Recent reports have described the utility of $R_3SnSiR'_3$ (**1**).[1] For example, Mitchell[2] and Chenard[3] independently reported

---

[1] Schumann, H.; Ronecker, S. *Z. Naturforsch, Teil B* **1967**, *22*, 452.

0022-3263/91/1956-3486$02.50/0

Scheme I



Scheme II

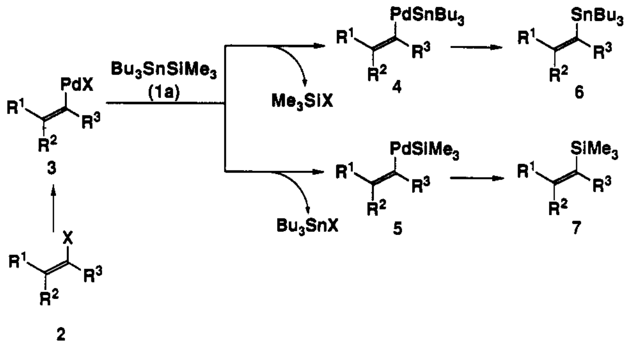


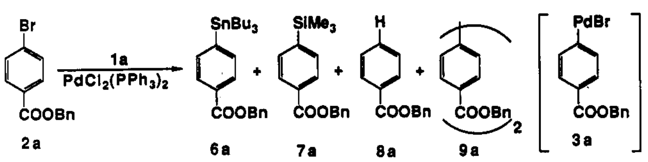
Table I. Reaction of 2a with 1a

run	solvent	reaction conditions T (°C)	reaction conditions time (h)	yield (%) 6a	yield (%) 7a	yield (%) 8a	yield (%) 9a
1	toluene	110	24		29	48	20
2	HMPA	80	5	36	20	28	8

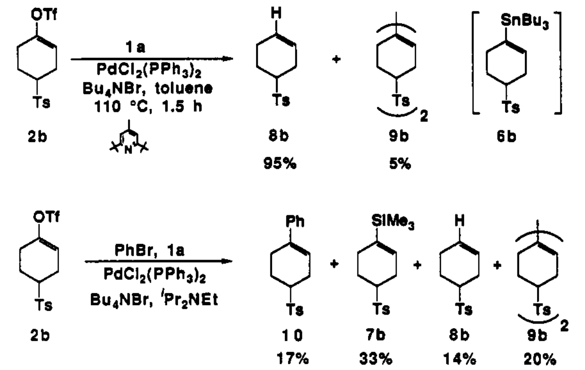
the addition of $R_3SnSiR'_3$ to the carbon–carbon triple bond of 1-alkynes to yield alkenes posessing vicinal silyl and stannyl substituents. Ito et al.[4] reported that isonitriles insert into Si–Sn bonds in the presence of $Pd(PPh_3)_4$ (Scheme I). In both cases, palladium catalysts played a key role. The active species was believed to be $R_3SnPdSiR'_3(PPh_3)_2$, which was generated by the oxidative addition of $R_3SnSiR'_3$ (1)[1] to $Pd(PPh_3)_4$. In contrast, the uncatalyzed bisfunctionalization of α,β-unsaturated ketones by $R_3SnSiR'_3$ has been reported by two groups.[3,5]

However, the transmetalation of $R_3SnSiR'_3$ by organopalladium complexes has not been studied in detail. Many palladium-catalyzed organometallic reactions involve a transmetalation that generates an organopalladium species.[6] We believed that if vinylpalladium complex 3 could be transmetalated by $R_3SnSiR'_3$ (1), vinylstannane 6 or vinylsilane 7 would be formed from vinylpalladium stannane 4 or vinylpalladium silane 5, respectively (Scheme II). Therefore, we undertook a study of the transmetalation of $R_3SnSiR'_3$ (1) by arylpalladium bromides. We now report a new palladium-catalyzed tandem transmetalation–cyclization reaction that involves $Bu_3SnSiMe_3$ (1a).

Scheme III



Scheme IV



Results and Discussion

Intermolecular Reaction of Aryl Halides or Vinyl Triflates with $Bu_3SnSiMe_3$. A first attempt of transmetalate $Bu_3SnSiMe_3$ (1a) by reaction with an arylpalladium bromide gave rather complicated results. Thus, when a toluene solution of benzyl *p*-bromobenzoate (2a), $Bu_3SnSiMe_3$ (1a), and $PdCl_2(PPh_3)_2$[7] was heated at 110 °C for 24 h, arylsilane 7a was produced in 29% yield (Table I, run 1). On the other hand, when hexamethylphosphoramide (HMPA) was the solvent, arylstannane 6a was produced in 36% yield, along with arylsilane 7a (20% yield). However, significant amounts of the dehalogenation product 8a and the dimer 9a were also formed in both cases. It appeared that the dehalogenation product 8a was derived from arylstannane 6a by protonolysis and that the dimer 9a arose from the reaction of arylstannane 6a and arylpalladium bromide 3 (Scheme III). Thus, in both cases, the major initial product appeared to have been arylstannane 6a, which was formed by transmetalation of arylpalladium complex 3a by 1a.[8]

In marked contrast to these results, when a toluene solution of vinyl triflate 2b, $Bu_3SnSiMe_3$ (1a; 2 equiv), $PdCl_2(PPh_3)_2$ (5 mol %), and 2,6-di-*tert*-butyl-4-methylpyridine (1 equiv) was heated at 110 °C in the presence of Bu_4NBr[6] (3 equiv) under argon for 1.5 h, 4-tosyl-1-cyclohexene (8b) was obtained in 95% yield, along with the dimer 9b (5% yield). Products 8b and 9b appeared to have arisen from vinylstannane 6b.[9] Attempts to isolate compound 6b were unsuccessful. Thus, in order to obtain

---

(2) (a) Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354. (b) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schnider, U. *J. Org. Chem.* **1987**, *52*, 4868.

(3) (a) Chenard, B. L.; Van Zyl, C. M.; Sanderson, D. R. *Tetrahedron Lett.* **1986**, *27*, 2801. Chenard, B. L.; Van Zyl, C. M. *J. Org. Chem.* **1986**, *51*, 3561. (b) Chenard, B. L.; Laganis, E. D.; Davidson, F.; RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3666.

(4) Ito, Y.; Bando, T.; Matsuura, T.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1986**, 980.

(5) Lipshutz, B. H.; Reuter, D. C.; Ellsworth, E. L. *J. Org. Chem.* **1989**, *54*, 4975.

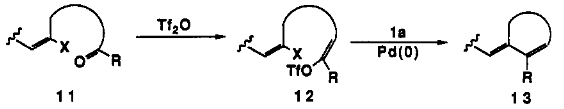
(6) (a) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (b) Scott, W. J.; Stille, J. K. Ibid. **1986**, *108*, 3033. (c) Wulff, W. D.; Peterson, G. A.; Bauta, W. E.; Chan, K.-S.; Faron, K. L.; Gilbertson, S. R.; Kaesler, R. W.; Yang, D. C.; Murray, C. K. *J. Org. Chem.* **1986**, *51*, 277.

(7) $PdCl_2(PPh_3)_2$ was reduced to the zero-valent palladium complex by $Me_3SiSnBu_3$.

(8) Pidocock reported that the reaction of *p*-bromotoluene with 1a in the presence of $Pd(PPh_3)_4$ afforded *p*-(trimethylsilyl)toluene in 40% yield. See: Azazian, H.; Eaborn, C.; Pidocock, A. *J. Organomet. Chem.* **1981**, *215*, 49.

(9) In order to establish the source of the hydrogen atom that replaced the triflate group, the reaction was performed in toluene-d_8. However, the mass spectrum of the product 8b did not indicate any incorporation of deuterium. If, however, a small amount of D_2O was added to the reaction mixture, the mass spectrum indicated that deuterium had, in fact, been incorporated into 8b. Therefore, compound 8b appeared to have been formed by hydrolysis of vinyl stannane 6b by traces of water that were present in the reaction mixture.

Scheme V



Scheme VI

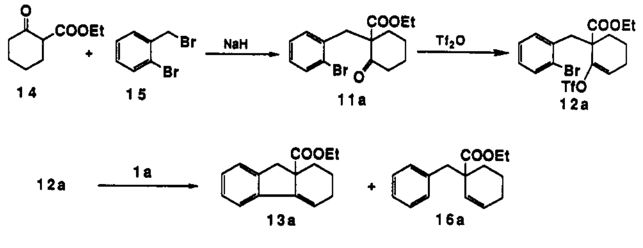


Table II. Reaction of 12a with 1a under Various Conditions

run	Bu$_3$Sn-SiMe$_3$ (1a; equiv)	base (1 equiv)	Bu$_4$NBr (equiv)	reaction time (h)	yield (%)		
					13a	16a	12a
1	1.1	*i*-Pr$_2$NEt	3	0.5	54	13	
2		*i*-Pr$_2$NEt	3	1.5			89
3	1.1	Li$_2$CO$_3$	3	1.5	70	25	
4	1.1		3	1.5	42	11	7
5	1.1	Li$_2$CO$_3$		1.5			86
6	*a*	Li$_2$CO$_3$	3	3	64	8	

[a] Bu$_3$SnSnBu$_3$ was used instead of Bu$_3$SnSiMe$_3$.

evidence for the intermediary of vinylstannane **6b**, the reaction was performed in the presence of bromobenzene (4 equiv). The coupling product **10** was isolated in 17% yield. These results indicated that transmetalation of **1a** by vinylpalladium bromide **3** afforded vinylpalladium stannane **4**. This was a reflection of the "softness" displayed by a stannyl group, compared to that of a silyl group, toward the "soft" divalent palladium complex (Scheme IV).

Palladium-Catalyzed Tandem Transmetalation–Intramolecular Cyclization Involving the Use of Bu$_3$SnSiMe$_3$. With the results described previously in mind, the cyclization of compound **12**, which posesses two functional groups, each of which could add oxidatively to a low-valent metal complex, was attempted. It was believed that treatment of **12** with **1a** and a palladium catalyst would generate cyclic products **13** via tandem intermolecular and intramolecular transmetalations. The starting material **12a** was easily prepared by treating the condensation product of ethyl 2-oxocyclohexanecarboxylate (**14**) and *o*-bromobenzyl bromide (**15**) with Tf$_2$O in the presence of 2,6-di-*tert*-butyl-4-methylpyridine.[10] Thus, when a toluene solution of **12a**, Bu$_3$SnSiMe$_3$ (1.1 equiv), a catalytic amount of PdCl$_2$(PPh$_3$)$_2$ (3 mol %), Bu$_4$NBr (3 equiv), and *i*-Pr$_2$NEt (1 equiv) was heated at 110 °C for 1.5 h under argon, the cyclic product **13a** was obtained in 54% yield, along with compound **16a** (13% yield). LiAlH$_4$ reduction of compound **13a** afforded the corresponding alcohol, the structure of which was established by ^{1}H NMR spectroscopic analysis (Schemes V and VI).

The reaction was performed under various conditions. Cyclization did not occur in the absence of Bu$_3$SnSiMe$_3$ (Table II, run 2). It was found to be advantageous to add a base, and Li$_2$CO$_3$ gave good results (70% yield, run 3). Transmetalation did not occur in the absence of halide ion (run 5).[6] The reaction of **12a** with Bu$_3$SnSnBu$_3$ in place of Bu$_3$SnSiMe$_3$ afforded the desired cyclic product (64% yield). However, in this case, the reproducibility was invariably poor (run 6).[11]

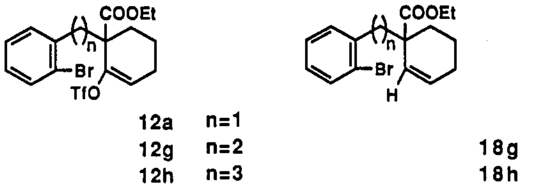
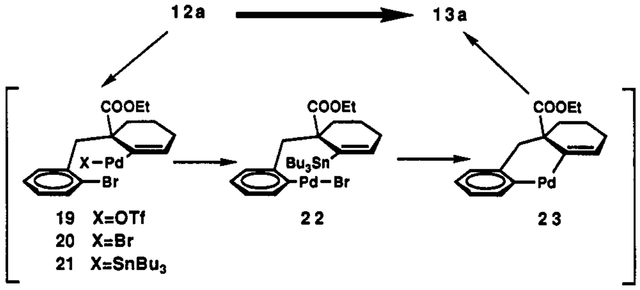


Figure 1.

Scheme VII. Possible Mechanism of the Reaction



The behavior of other compounds in this tandem transmetalation–cyclization reaction was examined. The vinyl triflate starting materials were prepared in good yield by treating the corresponding ketone **11** with Tf$_2$O in the presence of base. A toluene solution of vinyl triflate **12**, Bu$_3$SnSiMe$_3$, Bu$_4$NBr, Li$_2$CO$_3$, and a catalytic amount of PdCl$_2$(PPh$_3$)$_2$ (3 mol %) was heated at 110 °C for several hours. The results, which are summarized in Table III, showed that the intramolecular coupling of aromatic halides with internal vinyl triflates proceeded smoothly to provide cyclic products in good to moderate yield. Intramolecular coupling of vinyl bromides with internal vinyl triflates also gave cyclic products (run 5 and 6). However, the cyclization of **12g** gave a remarkably small yield of cyclic product (run 7).

A Possible Mechanism for the Cyclization (Scheme VII). The initial step appears to be the formation of vinylpalladium triflate **19**[12] by intermolecular oxidative addition of a vinyl triflate to the Pd(0) species. The product of this reaction is then converted to vinylpalladium bromide **20** by reaction with Bu$_4$NBr. Transmetalation of vinylpalladium bromide **20** by **1a** affords vinylpalladium stannane **21**. The reductive elimination of a vinylstannane from **21** is followed by intramolecular oxidative addition of an aryl bromide to form arylpalladium complex **22**. The intramolecular transmetalation of a vinyl group from the vinylstannane to the arylpalladium bromide affords palladametalacycle **23**,[13] which upon reductive elimination provides **13a**.

The most critical step seems to be the formation of arylpalladium bromide **22**. Yamamoto[14] and Kochi[15] re-

---

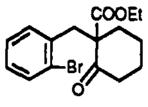
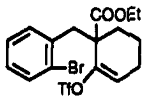
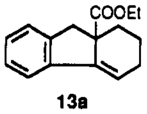
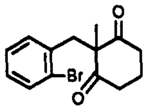
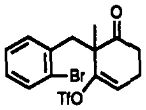
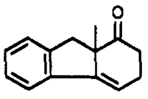
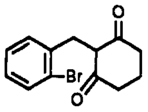
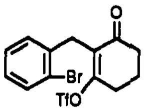
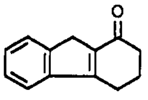
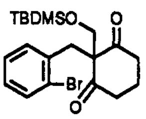
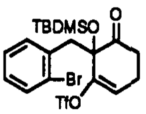
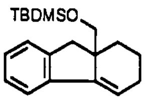
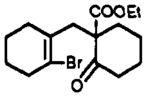
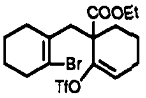
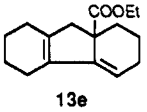
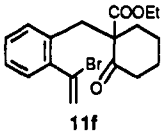
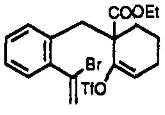
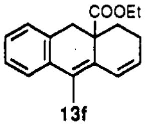
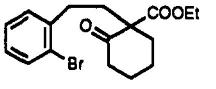
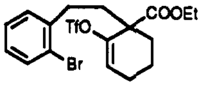
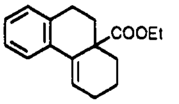
[10] Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

[11] The reaction of the vinyl triflate with Bu$_3$SnSnBu$_3$ in the presence of palladium catalyst afforded only a small amount of stannylated product.[6b,c] Furthermore, it was recently reported that the intramolecular cyclization of aryl bromides or triflates occurred in the presence of Me$_3$SnSnMe$_3$ and Pd(PPh$_3$)$_4$. See: Kelly, T. R.; Li, Q.; Bhushan, V. *Tetrahedron Lett.* **1990**, *31*, 161.

[12] When catalyzed by PdCl$_2$(PPh$_3$)$_2$, the oxidative addition of an aryl triflate to a low-valent palladium complex is faster than that of an aryl bromide.[6a]

[13] The intramolecular coupling of a vinyl triflate with a vinylstannane in the presence of Pd(PPh$_3$)$_4$ has been reported. See: (a) Piers, E.; Friesen, R. W.; Keay, B. A. *J. Chem. Soc., Chem. Commun.* **1985**, 809. (b) Piers, E.; Lu, Y.-F. *J. Org. Chem.* **1988**, *53*, 926.

Table III. Cyclization of 12 in the Presence of 1a

run	ketone	triflate	reaction time[a] (h)	cyclized product
1	 11a	 84% 12a	1.5	 13a 70%
2	 11b	 66% 12b	2	 13b 50%
3	 11c	 92% 12c	6[b]	 13c 38%[c]
4	 11d	 90% 12d	1.5	 13d 61%
5	 11e	 73% 12e	8[d]	 13e 41%[e]
6	 11f	 40% 12f	1	 13f 56%
7	 11g	 90% 12g	3.5[b]	 13g 10%[f]

[a] Typical reaction conditions; triflate (0.1 M, in toluene), $Bu_3SnSiMe_3$ (1.1 molar equiv), Bu_4NBr (3 molar equiv), Li_2CO_3 (1 molar equiv), $PdCl_2(PPh_3)_2$ (3 mol %), 110 °C. [b] Triflate (0.01 M, in toluene). [c] Detriflated product 18c was obtained in 43% yield. [d] 4A molecular sieve was added. [e] Detriflated product 18e was obtained in 13% yield and starting materials 12e was recovered in 13% yield. [f] Detriflated product 18g was obtained in 43% yield.

ported that the rate of reductive elimination of ArR from an arylalkylnickel complex accelerated in the presence of an aryl halide. They claimed that the carbon–halogen bond of an aryl bromide or chloride acted as an electron acceptor in an electron-transfer process.[15] Analogously, in the reactions described here, the reductive elimination of a vinylstannane from vinylpalladium stannane **21** to form **22** must have been accelerated by the carbon–bromine bond that was also present in **21**. Thus, cyclization of compound **12a** (n = 1) gave **13a** in good yield. However, **12g** (n = 2) afforded the desired compound **13g** in only 10% yield. No cyclic product was obtained from **12h** (n = 3). The carbon–bromine bond of aryl bromides **12g** and **12h** apparently could not act as an electron acceptor because of its distance from the carbon–metal bond. Hence, only the detriflated products **18g** and **18h** were formed (Figure 1).

In conclusion, the intramolecular coupling of a vinyl triflate with either an aryl or vinyl halide proceeded smoothly in the presence of $Bu_3SnSiMe_3$ and a catalytic amount of $PdCl_2(PPh_3)_2$. The most remarkable features of this reaction are that the oxidative addition, the double transmetalations, and the reductive elimination occur in tandem. The cyclization takes place chemoselectively between two functional groups, either of which can add oxidatively to a low-valent palladium complex.

Experimental Section

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. All the reaction solvents were degassed by a freeze–pump–thaw cycle procedure. Solvents were distilled under an argon atmosphere from either sodium benzophenone ketyl (THF, Et_2O, dioxane), CaH_2 (HMPA, DMF, Et_3N, t-BuOH), Na (toluene), or P_2O_5 (CH_2Cl_2, $ClCH_2CH_2Cl$). All other reagents and solvents were purified when necessary by standard procedures. NMR spectra were recorded at 100 MHz. Melting points are uncorrected. $Me_3SiSnBu_3$ was prepared by the literature method.[1,3a]

4-(p-Toluenesulfonyl)cyclohexanone. A solution of p-tolyl vinyl sulfone[16] (1.23 g, 6.72 mmol), 2-(trimethylsiloxy)-1,3-butadiene (1.94 g, 13.6 mmol), and toluene (5 mL) was refluxed for 106.5 h. The mixture was cooled, and the solvent was evaporated. The residue was dissolved in 65% aqueous AcOH (3 mL), and the solution was stirred for 2 h. To the solution was then added aqueous $NaHCO_3$. The two liquid layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried (Na_2SO_4), and the solvent

---

[14] Uchino, M.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1970**, *24*, C64.

[15] (a) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262. (b) Smith, G.; Kochi, J. K. *J. Organomet. Chem.* **1980**, *198*, 199.

[16] Vennstra, G. E.; Zwanenburg, B. *Synthesis* **1975**, 519.

was evaporated to give colorless crystals (991 mg, 3.93 mmol, 58%): mp 104–106 °C (CH_2Cl_2/Et_2O); IR (Nujol) 1705, 1600, 1465 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.76–2.80 (m, 8 H), 2.47 (s, 3 H), 3.32 (m, 1 H), 7.39 (d, J = 8 Hz, 2 H), 7.77 (d, J = 8 Hz, 2 H); MS m/z 252 (M^+), 234 ($M^+ - H_2O$), 157, 140, 139, 127, 96, 92, 91, 69, 65, 55, 41, 39. Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39; S, 12.71. Found: C, 61.92; H, 6.47; S, 12.49.

Ethyl 1-(2-Bromobenzyl)-2-oxocyclohexane-1-carboxylate (11a). To a suspension of NaH (60%, 140 mg, 3.5 mmol) in THF (10 mL) was added ethyl 2-oxocyclohexane-1-carboxylate (14, 532 mg, 3.13 mmol) at 0 °C. The solution was stirred for 30 min at room temperature. A solution of 2-bromobenzyl bromide (15, 959 mg, 3.84 mmol) in THF (2 mL) was then added, and the mixture was refluxed for 84 h. Water was added. The two liquid layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc (10:1)) to give **11a** (1.04 g, 3.07 mmol, 98%) as a colorless prisms: mp 56.0–57.0 °C (hexane–Et_2O); IR (Nujol) 1740, 1715, 1440, 1190 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.21 (t, J = 7.3 Hz, 3 H), 1.36–1.86 (m, 4 H), 1.86–2.18 (m, 1 H), 2.20–2.64 (m, 3 H), 3.49 and 3.27 (ABq, J = 14.1 Hz, 2 H), 4.16 and 4.17 (each peak, q, J = 7.3 Hz, 2 H), 6.96–7.24 (m, 3 H), 7.51–7.60 (m, 1 H); MS m/z 341, 339 (M^+ + 1), 259, 185. Anal. Calcd for $C_{16}H_{19}BrO_3$: C, 56.65; H, 5.65; Br, 23.55. Found: C, 56.65; H, 5.58; Br, 23.48.

2-(2-Bromobenzyl)-2-methylcyclohexane-1,3-dione (11b). To a solution of 2-methylcyclohexane-1,3-dione (501 mg, 3.97 mmol) and aqueous Bu_4NOH (40%, 2.7 mL) was added a solution of 2-bromobenzyl bromide (1.50 g, 6.03 mmol) in dioxane (4 mL). The solution was stirred for 36 h. The solution was neutralized with 10% aqueous HCl. The two liquid layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc (3:1)) to give **11b** (703 mg, 2.38 mmol, 60%): IR (Nujol) 1700, 1595, 1035 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.29 (s 3 H), 1.70–2.04 (m, 2 H), 2.66 (t, J = 6.8 Hz, 4 H), 3.31 (s, 2 H), 6.94–7.32 (m, 3 H), 7.49–7.60 (m, 1 H); MS m/z 296, 294 (M^+), 281, 279 (M^+ – Me), 253, 251, 227, 225, 215 (M^+ – Br), 187, 171, 169, 159, 145, 55; HR-MS calcd for $C_{14}H_{15}BrO_2$ 290.0255, found 290.0274.

2-(2-Bromobenzyl)-1,3-cyclohexanedione (11c). To a solution of 1,3-cyclohexanedione (1.01 g, 8.97 mmol) was added a THF solution of Bu_4NF (1 M, 9 mL).[17] The solvent was evaporated. To the residue was added a solution of 2-bromobenzyl bromide (2.23 g, 8.93 mmol) and Bu_4NI (3.31 g, 8.97 mmol) in $CHCl_3$ (10 mL). The solution was stirred at room temperature for 60 h. The solvent was then evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc (1:1 then 1:5)) to give **11c** (585 mg, 2.08 mmol, 23%): IR (Nujol) 1640, 1560, 1280 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.80–2.20 (m, 2 H), 2.36–2.76 (m, 4 H), 3.28 (d, J = 5.9 Hz, $^1/_2$ H, benzylic proton of keto form (keto/enol = 1/3)), 3.78 (s, $^3/_2$ H, benzylic protone of enol form), 3.94 (t, J = 5.9 Hz, $^1/_4$ H, keto form), 6.92–7.30 (m, 3 H), 7.36–7.54 (m, 1 H); MS m/z 283, 281 (M^+ + 1), 282, 280 (M^+), 201 (M^+ – Br); HR-MS calcd for $C_{13}H_{13}BrO_2$ 280.0099, found 280.0096.

2-(2-Bromobenzyl)-2-[[(*tert*-butyldimethylsilyl)oxy]-methyl]cyclohexanone (11d). To a solution of LDA (prepared from the reaction of i-Pr_2NH (361 mg, 3.57 mmol) and BuLi (1.75 mL, 1.62 N hexane solution, 2.84 mmol) in THF (6 mL) at 0 °C for 30 min) was added a solution of ethyl 1,4-dioxaspiro[4.5]decanecarboxylate[18] (473 mg, 2.21 mmol) in THF (2 mL). The solution was stirred at 0 °C for 30 min. A solution of 2-bromobenzyl bromide (829 mg, 3.32 mmol) in THF (2 mL) was then added, and the mixture was stirred at 0 °C for 16 h. Saturated aqueous NH_4Cl was added. The two liquid layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc (10:1)) to give the alkylation product (397 mg, 1.04 mmol, 47%): ^1H NMR δ ($CDCl_3$) 1.12 (t, J = 7.3 Hz, 3 H), 1.20–2.12 (m, 8 H), 3.19 and 3.49 (ABq, J = 14.4 Hz, 2 H), 3.94–4.10 (m, 2 H), 4.09 and 4.07 (each peak, q, J = 7.3 Hz, 2 H), 6.94–7.20 (m, 3 H), 7.45–7.57 (m, 1 H). To a solution of the product (387 mg, 1.01 mmol) in Et_2O (7 mL) was added $LiBH_4$ (22.1 mg, 1.01 mmol) at 0 °C. The solution was stirred for 6 h at 0 °C. MeOH was then added at 0 °C. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc (5:1)) to give alcohol (237 mg, 0.695 mmol, 69%): IR (neat) 3350, 1660, 1505, 1480, 1175 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.06–1.97 (m, 9 H), 3.05 and 3.19 (ABq, J = 12.4 Hz, 2 H), 3.38 and 3.95 (ABq, J = 12.1 Hz, 2 H), 4.02 (m, 4 H), 6.88–7.32 (m, 2 H), 7.40–7.60 (m, 2 H). To a solution of the alcohol (227 mg, 0.697 mmol), NEt_3 (145 mg, 1.43 mmol), a catalytic amount (4 mg, 5 mol %) of DMAP, and CH_2Cl_2 (3 mL) was added t-$BuMe_2SiCl$ (323 mg, 2.15 mmol). The solution was stirred for 16 h. Water was then added. The two liquid layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc (5:1)) to give **11d**[19] (236 mg, 0.574 mmol, 82%): IR (neat) 1715, 1250, 1100 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.05 (s, 6 H), 0.90 (s, 9 H), 1.55–2.02 (m, 6 H), 2.26–2.62 (m, 2 H), 3.21 (s, 2 H), 3.64 and 3.81 (ABq, J = 10.0 Hz, 2 H), 6.94–7.33 (m, 3 H), 7.47–7.56 (m, 1 H); MS m/z 397, 395 (M^+ – Me), 355, 353 (M^+ – t-Bu), 325, 323 (M^+ – t-$BuMe_2$), 215, 213, 183, 171, 169, 75; HR-MS calcd for $C_{19}H_{28}BrO_2Si$ (M^+ – Me) 395.1042, found 395.1051.

Ethyl 1-[(2′-Bromocyclohexenyl)methyl]-2-oxocyclohexane-1-carboxylate (11e). Compound **11e** was prepared in a manner similar to that used to prepare **11a**. The crude product, obtained by heating a mixture of **14** (192 mg, 1.13 mmol) and (2-bromocyclohex-1-enyl)methyl bromide[20] (308 mg, 1.38 mmol) for 17 h, was purified by column chromatography on silica gel (hexane/EtOAc (10:1)) to give **11e** (349 mg, 1.02 mmol, 90%): IR (Nujol) 1740, 1715, 1650, 1440, 1230, 1205 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.27 (t, J = 7.3 Hz, 3 H), 1.40–2.20 (m, 12 H), 2.20–2.70 (m, 4 H), 2.73–2.95 (m, 2 H), 4.19 and 4.18 (each peak, q, J = 7.3 Hz, 2 H); MS m/z 344, 342 (M^+), 343, 341 (M^+ – 1), 263 (M^+ – Br), 189; HR-MS calcd for $C_{16}H_{23}BrO_3$ 342.0830, found 342.0813.

Ethyl 1-[2-(1-Bromoethenyl)benzyl]-2-oxocyclohexane-1-carboxylate (11f). Compound **11f** was prepared in a manner similar to that used to prepare **11a**. The crude product, obtained by heating a mixture of **14** (213 mg, 1.25 mmol) and 1-[2-(bromomethyl)phenyl]vinyl bromide (500 mg, 1.81 mmol) for 24 h, was purified by column chromatography on silica gel (hexane/EtOAc (10:1)) to give **11f** (432 mg, 1.18 mmol, 95%): IR (Nujol) 1740, 1710, 1630, 1595 cm^{-1}; ^1H-NMR δ ($CDCl_3$) 1.18 (t, J = 7.1 Hz, 3 H), 1.00–2.16 (m, 5 H), 2.20–2.60 (m, 3 H), 3.33 and 3.47 (q, J = 16.0 Hz, 2 H), 4.12 and 4.13 (each peak; q, J = 7.1 Hz, 2 H), 5.75 (d, J = 1.7 Hz, 1 H), 5.89 (d, J = 1.7 Hz, 1 H), 6.96–7.34 (m, 4 H); MS m/z 366, 364 (M^+), 285 (M^+ – Br), 211, 183, 115; HR-MS calcd for $C_{18}H_{21}BrO_3$ 364.0674, found 364.0696.

Ethyl 1-[2-(2-Bromophenyl)ethyl]-2-oxocyclohexane-1-carboxylate (11g). To a solution of the potassium salt of **14** (532 mg, 3.13 mmol; prepared by treating **14** with t-BuOK (422 mg, 3.76 mmol) in t-BuOH (3 mL)) was added a solution of 2-(2-bromophenyl)ethyl iodide[21] (1.57 g, 5.05 mmol) in t-BuOH (1 mL). The solution was refluxed for 12 h. After the mixture cooled, water was added. The two liquid layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc (10:1)) to give **11g** (656 mg, 1.86 mmol, 59%): IR (neat) 1735, 1710, 1565, 1240, 1180 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.31 (t, J = 7.3 Hz, 3 H), 1.42–2.16 (m, 7 H), 2.34–2.82 (m, 5 H), 4.25 (q, J = 7.3 Hz, 2 H), 6.94–7.24 (m, 3 H), 7.47–7.54 (m, 1 H); MS m/z 355, 353 (M^+), 309, 307, 170, 141, 124; HR-MS

---

(17) Clark, J. H.; Miller, J. M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1743.

(18) Mursakulov, I. G.; Guseinov, M. M.; Kasumov, N. K.; Zefirov, N. S.; Samoshin, V. V.; Chalenko, E. G. *Tetrahedron* **1982**, *38*, 2213.

(19) Under the reaction conditions employed, the dioxalane protecting group was removed quantitatively.

(20) (a) Rajamannar, T.; Balasubramanian, K. K. *Tetrahedron Lett.* **1988**, *29*, 5789. (b) Arnold, Z.; Holy, A. *Collect. Czech. Chem. Commun.* **1961**, *26*, 3059.

(21) Wender, P. A.; White, A. W. *J. Am. Chem. Soc.* **1988**, *110*, 2218.

calcd for $C_{17}H_{21}BrO_3$ 352.0674, found 352.0670.

Ethyl 1-[3-(2-Bromophenyl)propyl]-2-oxocyclohexane-1-carboxylate (11h). Compound **11h** was prepared in a manner similar to that used to prepare **11a**. The crude product obtained by heating a mixture of **14** (266 mg, 1.56 mmol), KI (320 mg, 1.93 mmol), and 3-(2-bromophenyl)propyl 1-bromide[22] (529 mg, 1.90 mmol) in 1:1 THF/DMF (12 mL) at 80 °C for 32.5 h was purified by column chromatography on silica gel, eluting with hexane/EtOAc (10:1) to give **11f** (375 mg, 1.02 mmol, 65%): IR (neat) 1735, 1710, 1570, 1470, 1210, 1020 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.24 (t, J = 7.1 Hz, 3 H), 1.30–2.20 (m, 10 H), 2.24–2.84 (m, 4 H), 4.19 (q, J = 7.1 Hz, 2 H), 6.90–7.28 (m, 3 H), 7.47–7.54 (m, 1 H); MS m/z 368, 366 (M^+), 350, 348, 323, 321, 170, 124; HR-MS calcd for $C_{18}H_{23}BrO_3$ 366.0831, found 366.0853.

General Procedure for the Synthesis of Vinyl Triflates.[10] To a CH_2Cl_2 solution of the ketone (1 equiv) and the base (2.2 equiv) was slowly added a CH_2Cl_2 solution of Tf_2O (2 equiv) at 0 °C. The solution was warmed for several hours. The mixture was cooled, Et_2O was added, and the white precipitate that formed was collected by filtration. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel.

4-(*p*-Toluenesulfonyl)cyclohex-1-en-1-yl Triflate (2b). The crude product obtained by refluxing a mixture of 4-(*p*-toluenesulfonyl)cyclohexanone (1.10 g, 4.36 mmol), 2,6-di-*tert*-butylpyridine (2.08 g, 10.1 mmol), Tf_2O (2.52 g, 8.92 mmol), and CH_2Cl_2 (10 mL) for 16 h was purified by column chromatography on silica gel (hexane/Et_2O (2:3)) to give **2b** (1.50 g, 3.91 mmol, 90%) as colorless needles: mp 108.5–109.5 °C (Et_2O/hexane); IR ($CHCl_3$) 1695, 1600, 1420, 1320, 1145 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.74–1.98 (m, 1 H), 2.20–2.60 (m, 5 H), 2.47 (s, 3 H), 2.98–3.24 (m, 1 H), 5.64–5.84 (m, 1 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 2 H); MS m/z 385 (M^+ + 1), 251 ($M^+ - CF_3SO_2$), 228 (M^+ − TsH), 157, 139, 95. Anal. Calcd for $C_{14}H_{15}F_3O_5S_2$: C, 43.75; H, 3.93. Found: C, 43.65; H, 3.95.

6-(2-Bromobenzyl)-6-(ethoxycarbonyl)cyclohex-1-en-1-yl Triflate (12a). The crude product obtained by heating a mixture of ketone **11a** (215 mg, 0.634 mmol), 2,6-di-*tert*-butylpyridine (281 mg, 1.47 mmol), Tf_2O (369 mg, 1.31 mmol), and $ClCH_2CH_2Cl$ (1 mL) at 60 °C for 18 h was purified by column chromatography on silica gel (hexane/EtOAc (20:1)) to give **12a** (250 mg, 0.531 mmol, 84%) as a colorless oil: IR (neat) 1735, 1675, 1595, 1475, 1415, 1250, 1210 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.32 (t, J = 7.3 Hz, 3 H), 1.64–1.88 (m, 3 H), 1.96–2.40 (m, 3 H), 3.24 and 3.63 (ABq, J = 14.2 Hz, 2 H), 4.26 (q, J = 7.3 Hz, 2 H), 5.92 (dd, J = 3.7 Hz, 4.4 Hz, 1 H), 7.00–7.32 (m, 3 H), 7.52–7.65 (m, 1 H); MS m/z 473, 471 (M^+ + 1), 472, 470 (M^+), 391, 185, 171, 169; HR-MS calcd for $C_{17}H_{18}BrF_3O_5S$ 470.0011, found 470.0023.

6-(2-Bromobenzyl)-6-methyl-5-oxocyclohex-1-en-1-yl Triflate (12b). The crude product obtained by heating a mixture of ketone **11b** (505 mg, 1.71 mmol), 2,6-di-*tert*-butylpyridine (392 mg, 2.05 mmol), Tf_2O (520 mg, 1.84 mmol), and $ClCH_2CH_2Cl$ (8 mL) at 80 °C for 20 h was purified by column chromatography on silica gel (hexane/EtOAc (5:1)) to give **12b** (483 mg, 1.13 mmol, 66%) as a colorless oil: IR (neat) 1720, 1670, 1410, 1210, 1140 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.41 (s, 3 H), 1.84–2.58 (m, 4 H), 3.13 and 3.37 (ABq, J = 13.9 Hz, 2 H), 7.07 (m, 1 H), 6.94–7.32 (m, 3 H), 7.40–7.58 (m, 1 H); MS m/z 428, 426 (M^+), 347 (M^+ − Br), 197, 171, 169, 55; HR-MS calcd for $C_{15}H_{14}BrF_3O_4S$ 425.9748, found 425.9739.

2-(2-Bromobenzyl)-2-oxocyclohex-1-en-1-yl Triflate (12c). The crude product obtained by stirring a mixture of ketone **11c** (102 mg, 0.364 mmol), 2,6-di-*tert*-butylpyridine (124 mg, 0.646 mmol), Tf_2O (159 mg, 0.565 mmol), and CH_2Cl_2 (4 mL) at 0 °C for 8 h was purified by column chromatography on silica gel (hexane/EtOAc (10:1 then 1:1)) to give **12c** (138 mg, 0.334 mmol, 92%) as a colorless oil: IR (neat) 1690, 1660, 1595, 1470, 1420, 1345, 1215 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 2.02–2.30 (m, 2 H), 2.48 (m, 2 H), 2.86 (t, J = 5.8 Hz, 2 H), 3.80 (s, 2 H), 6.88–7.28 (m, 3 H), 7.42–7.56 (m, 1 H); MS m/z 414, 412 (M^+), 333 (M^+ − Br), 281, 220, 200 (M^+ − BrOTf), 59, 41; HR-MS calcd for $C_{14}H_{12}BrF_3O_4S$ 411.9592, found 411.9609.

6-(2-Bromobenzyl)-6-[[(*tert*-butyldimethylsilyl)oxy]methyl]cyclohex-1-en-1-yl Triflate (12d). The crude product obtained by heating a mixture of ketone **11d** (234 mg, 0.570 mmol), 2,6-di-*tert*-butylpyridine (256 mg, 1.34 mmol), Tf_2O (335 mg, 1.19 mmol), and $ClCH_2CH_2Cl$ (2 mL) at 80 °C for 15 h was purified by column chromatography on silica gel (hexane) to give **12d** (278 mg, 0.512 mmol, 90%) as a colorless oil: IR (neat) 1680, 1480, 1415, 1250, 1215 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.07 (s, 6 H), 0.91 (s, 9 H), 1.40–2.20 (m, 6 H), 2.87 and 3.27 (ABq, J = 13.7 Hz, 2 H), 3.47 and 3.78 (ABq, J = 9.8 Hz, 2 H), 5.90 (t, J = 4.1 Hz, 1 H), 6.96–7.28 (m, 3 H), 7.51–7.59 (m, 1 H); MS m/z 529, 527 (M^+ − Me), 487, 485 (M^+ − *t*-Bu), 263, 261, 182, 167, 169, 89, 73; HR-MS calcd for $C_{20}H_{27}BrF_3O_4SSi$ (M^+ − Me) 527.0536, found 527.0553.

6-[(2-Bromocyclohexyl)methyl]-6-(ethoxycarbonyl)cyclohexyl-1-en-1-yl Triflate (12e). The crude product obtained by heating a mixture of ketone **11e** (356 mg, 1.04 mmol), 2,6-di-*tert*-butylpyridine (315 mg, 1.65 mmol), Tf_2O (419 mg, 1.49 mmol), and $ClCH_2CH_2Cl$ (3 mL) at 80 °C for 51 h was purified by column chromatography on silica gel (hexane/EtOAc (10:1)) to give **12e** (359 mg, 0.756 mmol, 73%) as a colorless oil: IR (neat) 2930, 1730, 1645, 1200 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.31 (t, J = 7.1 Hz, 3 H), 1.44–2.40 (m, 14 H), 2.40–2.64 (m, 2 H), 2.68 and 3.16 (ABq, J = 13.7 Hz, 2 H), 4.23 (q, J = 7.1 Hz, 2 H), 5.86 (t, J = 3.9 Hz, 1 H); MS m/z 476, 474 (M^+), 475, 473 (M^+ − 1), 395, 368, 302, 93; HR-MS calcd for $C_{17}H_{22}BrF_3O_5S$ 474.0325, found 474.0357.

6-[2-(1-Bromoethenyl)benzyl]-6-(ethoxycarbonyl)cyclohex-1-en-1-yl Triflate (12f). The crude product obtained by heating a mixture of ketone **11f** (408 mg, 1.12 mmol), 2,6-di-*tert*-butylpyridine (469 mg, 2.45 mmol), Tf_2O (637 mg, 2.26 mmol), and $ClCH_2CH_2Cl$ (10 mL) at 80 °C for 60 h was purified by column chromatography on silica gel (hexane/EtOAc (20:1)) to give **12f** (223 mg, 0.449 mmol, 40%) as a colorless oil: IR (neat) 1730, 1675, 1630, 1595, 1415, 1210 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.33 (t, J = 7.1 Hz, 3 H), 1.20–2.60 (m, 6 H), 3.28 and 3.57 (ABq, J = 14.4 Hz, 2 H), 4.26 (q, J = 7.1 Hz, 2 H), 5.74 (d, J = 1.7 Hz, 1 H), 5.91 (d, J = 1.7 Hz, 1 H), 5.91 (t, J = 4.0 Hz, 1 H), 6.80–7.48 (m, 4 H); MS m/z 498, 496 (M^+), 453, 451 (M^+ − OEt), 417 (M^+ − Br), 348, 346 (M^+ − OTf), 267, 197, 195, 116; HR-MS calcd for $C_{19}H_{20}BrF_3O_5S$ 496.0168, found 496.0177.

6-[2-(2-Bromophenyl)ethyl]-6-(ethoxycarbonyl)cyclohex-1-en-1-yl Triflate (12g). The crude product obtained by heating a mixture of ketone **11g** (640 g, 1.81 mmol), 2,6-di-*tert*-butyl-4-methylpyridine (767 mg, 4.01 mmol), Tf_2O (1.01 g, 3.57 mmol), and $ClCH_2CH_2Cl$ (10 mL) at 80 °C for 33 h was purified by column chromatography on silica gel (hexane/EtOAc (10:1)) to give **12g** (788 mg, 1.62 mmol, 90%) as a colorless oil: IR (neat) 1730, 1675, 1415, 1210, 1140, 1020 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.31 (t, J = 7.1 Hz, 3 H), 1.60–2.58 (m, 8 H), 2.66–2.86 (m, 2 H), 4.23 (q, J = 7.1 Hz, 2 H), 5.94 (t, J = 4.2 Hz, 1 H), 6.94–7.20 (m, 3 H), 7.48–7.56 (m, 1 H); MS m/z 486, 484 (M^+), 405 (M^+ − Br), 353, 351 (M^+ − Tf), 302; HR-MS calcd for $C_{18}H_{20}BrF_3O_5S$ 484.0166, found 484.0175.

6-[3-(2-Bromophenyl)propyl]-6-(ethoxycarbonyl)cyclohex-1-en-1-yl Triflate (12h). The crude product obtained by heating a mixture of ketone **11h** (146 mg, 0.398 mmol), 2,6-di-*tert*-butylpyridine (170 mg, 0.891 mmol), Tf_2O (226 mg, 0.802 mmol), and $ClCH_2CH_2Cl$ (4 mL) at 80 °C for 23 h was purified by column chromatography (hexane/EtOAc (10:1)) to give **12h** (134 mg, 0.269 mmol, 67%) as a colorless oil: IR (neat) 1730, 1670, 1410, 1210, 1140 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.27 (t, J = 7.3 Hz, 3 H), 1.38–2.00 (m, 8 H), 2.04–2.40 (m, 2 H), 2.65–2.81 (m, 2 H), 4.20 (q, J = 7.3 Hz, 2 H), 5.87 (t, J = 4.0 Hz, 1 H), 6.95–7.26 (m, 3 H), 7.47–7.56 (m, 1 H); MS m/z 501, 499 (M^+ + 1), 500, 498 (M^+), 415, 367, 365, 321, 319, 302, 277, 275, 196; HR-MS calcd for $C_{19}H_{22}BrF_3O_5S$ 498.0325, found 498.0317.

Reaction of Benzyl 4-Bromobenzoate (2a) with $Me_3SiSnBu_3$ (1a). To a solution of benzyl 4-bromobenzoate (41.5 mg, 0.143 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 0.005 mmol), and HMPA (1 mL) was added $Me_3SiSnBu_3$ (58 mg, 0.159 mmol). The solution was warmed at 80 °C for 5 h. Aqueous NH_3 (10%) was then added. The mixture was stirred for 30 min. The two liquid layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane/EtOAc (10:1)) to give **6a** (26.0 mg, 0.052 mmol, 36%),

---

(22) Parham, W. E.; Jones, L. D.; Sayed, Y. A. *J. Org. Chem.* **1976**, *41*, 1184.

(23) Nagasawa, H. T.; Gutmann, H. R. *J. Med. Chem.* **1966**, *9*, 719.

7a (8.0 mg, 0.028 mmol, 20%), **8a** (8.6 mg, 0.040 mmol, 28%), and **9a** (2.7 mg, 0.006 mmol, 8%). **6a**: IR (neat) 1720, 1590, 1270 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.76–1.72 (m, 27 H), 5.38 (s, 2 H), 7.30–7.60 (m, 7 H), 7.97–8.05 (m, 2 H); MS m/z 501 (M$^+$ – 1), 444, 388, 91; HR-MS calcd for $C_{26}H_{37}O_2Sn$ (M$^+$ – 1) 501.1815, found 501.1794. **7a**: IR (neat) 1720, 1600, 1275, 1095 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.29 (s, 9 H), 5.38 (s, 2 H), 7.26–7.63 (m, 7 H), 8.00–8.08 (m, 2 H); MS m/z 284 (M$^+$), 269 (M$^+$ – Me), 194, 177, 91, 73; HR-MS calcd for $C_{17}H_{20}O_2Si$ 284.1232, found 284.1258. **9a**: IR (neat) 1760, 1730, 1475, 1440, 1230, 1030 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 5.39 (s, 4 H), 7.30–7.45 (m, 10 H), 7.63–7.72 (m, 4 H), 8.12–8.21 (m, 4 H); MS m/z 422 (M$^+$), 315 (M$^+$ – OBn), 269, 239, 209, 91; HR-MS calcd for $C_{28}H_{22}O_4$ 422.1518, found 422.1526.

Reaction of Triflate 2b with $Me_3SiSnBu_3$ (1a) in the Presence of Bromobenzene. A solution of triflate **2b** (112 mg, 0.291 mmol), $Bu_3SnSiMe_3$ (210 mg, 0.579 mmol), Bu_4NBr (382 mg, 1.18 mmol), $PdCl_2(PPh_3)_2$ (10.7 mg, 3 mol %), *i*-Pr_2NH_2 (37 mg, 0.29 mmol), bromobenzene (179 mg, 1.14 mmol), and toluene (1 mL) was heated at 110 °C for 17 h. The mixture was cooled, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (hexane/EtOAc (9:1)) to give **8b** (9.6 mg, 0.041 mmol, 14%), **9b** (14 mg, 0.030 mmol, 20%), **7b** (30 mg, 0.097 mmol, 33%), and **10** (15 mg, 0.048 mmol, 17%). **8b**: colorless prisms, mp 70.0–71.0 °C (Et_2O/hexane); IR (Nujol) 1650, 1595, 1150 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.64–1.90 (m, 1 H), 1.94–2.41 (m, 5 H), 2.44 (s, 3 H), 2.31–2.92 (m, 1 H), 5.64 (m, 2 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.75 (d, J = 8.4 Hz, 2 H); MS m/z 236 (M$^+$), 157, 139, 81, 79; Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82. Found: C, 65.89; H, 6.86. **7e**: IR ($CHCl_3$) 1720, 1620, 1600, 1210, 1200, 1140 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.64–2.42 (m, 6 H), 2.44 (s, 3 H), 2.84–3.28 (m, 1 H), 5.76–5.92 (m, 1 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.75 (d, J = 8.4 Hz, 2 H); MS m/z 308 (M$^+$), 293 (M$^+$ – Me), 157, 152, 136, 73; HR-MS calcd for $C_{16}H_{24}O_2SSi$ 308.1266, found 308.1265. **9b**: IR ($CHCl_3$) 1720, 1600, 1300, 1140 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.64–2.44 (m, 12 H), 2.44 (s, 3 H), 1.86–2.28 (m, 2 H), 5.54–5.80 (m, 2 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.76 (d, J = 8.4 Hz, 2 H); MS m/z 470 (M$^+$), 314 (M$^+$ – TsH), 158 (M$^+$ – 2TsH); HR-MS calcd for $C_{26}H_{30}O_4S_2$ 470.1586, found 470.1595. **10**: IR ($CHCl_3$) 1600, 1300, 1145, 1090 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.64–2.68 (m, 12 H), 2.44 (s, 3 H), 3.00–3.32 (m, 1 H), 5.88–6.04 (m, 1 H), 7.16–7.38 (m, 5 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.78 (d, J = 8.4 Hz, 2 H); MS m/z 312 (M$^+$), 156 (M$^+$ – TsH), 91, 77; HR-MS calcd for $C_{19}H_{20}O_2S$ 312.1184, found 312.1201.

General Procedure for the Cyclization of Triflate 12. To a solution of triflate **12** (1 equiv), Bu_4NBr (3 equiv), $PdCl_2(PPh_3)_2$ (3 mol %), Li_2CO_3 (1.1 equiv), and toluene was added $Bu_3SnSiMe_3$ (1.1 equiv). The solution was heated at 110 °C under Ar for several hours. After the mixture was cooled, 10% aqueous ammonia was added. The mixture was then stirred for 30 min. The two liquid layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated. The residue was purified by chromatography on silica gel to afford the cyclic product **13**.

Cyclization of Triflate 12a. The crude product obtained by heating a mixture of triflate **12a** (62.3 mg, 0.132 mmol), Bu_4NBr (127 mg, 0.395 mmol), $PdCl_2(PPh_3)_2$ (2.8 mg, 3 mol %), Li_2CO_3 (10.5 mg, 0.142 mmol), $Bu_3SnSiMe_3$ (53 mg, 0.145 mmol), and toluene (1.5 mL) at 110 °C for 1.5 h was purified by column chromatography (hexane/EtOAc (10:1)) to give a mixture of **13a** (22.5 mg, 0.093 mmol, 70%) and **16a** (8 mg, 0.035 mmol, 25%). The product ratio was determined by ^{1}H NMR. **13a**: IR (neat) 1725, 1665, 1605 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.12 (t, J = 7.3 Hz, 3 H), 1.40–2.40 (m, 6 H), 2.87 and 3.36 (ABq, J = 15.2 Hz, 2 H), 4.05 (q, J = 7.3 Hz, 2 H), 7.08 (t, J = 3.9 Hz, 1 H), 6.99–7.30 (m, 3 H), 7.35–7.51 (m, 1 H); MS m/z 242 (M$^+$), 213, 169, 168, 91; HR-MS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1292.

Cyclization of Triflate 12b. The crude product obtained by heating a mixture of triflate **12b** (66.6 mg, 0.156 mmol), Bu_4NBr (150 mg, 0.465 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 3 mol %), Li_2CO_3 (11.3 mg, 0.153 mmol), $Bu_3SnSiMe_3$ (63 mg, 0.17 mmol), and toluene (1.5 mL) at 110 °C for 2 h was purified by preparative thin-layer chromatography (hexane/EtOAc (3:1)) to give **13b** (15.4 mg, 0.078 mmol, 50%) as a colorless oil: IR (neat) 1710, 1465, 1345, 1250 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.32 (s, 3 H), 2.12–2.84 (m, 4 H), 2.77 and 3.40 (ABq, J = 16.6 Hz, 2 H), 7.18–7.36 (m, 1 H), 7.10–7.28 (m, 3 H), 7.32–7.54 (m, 1 H); MS m/z 198 (M$^+$), 183 (M$^+$ – Me), 156, 146, 129, 115, 91; HR-MS calcd for $C_{14}H_{14}O$ 198.1045, found 198.1070.

Cyclization of Triflate 12c. The crude product obtained by heating a mixture of triflate **12c** (43.3 mg, 0.105 mmol), Bu_4NBr (104 mg, 0.322 mmol), $PdCl_2(PPh_3)_2$ (2.1 mg, 3 mol %), Li_2CO_3 (7.8 mg, 0.11 mmol), $Bu_3SnSiMe_3$ (42 mg, 0.12 mmol) and toluene (10 mL) at 110 °C for 6 h was purified by preparative thin layer chromatography (hexane/EtOAc (4:1)) to give a colorless oil, a mixture of **13c**[22] (7.4 mg, 0.040 mmol, 38%), **18c** (12 mg, 0.045 mmol, 43%), and **12c** (2.7 mg, 0.007 mmol, 6%). **13c**: IR (neat) 1680, 1625, 1510, 1480, 1440, 1260 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 2.08–2.36 (m, 2 H), 2.48–2.64 (m, 2 H), 2.68–2.92 (m, 2 H), 3.61 (ABq, J = 2.7, 2.9 Hz, 2 H), 7.34–7.56 (m, 4 H); MS m/z 184 (M$^+$), 154, 149, 123, 119, 111, 105, 72, 59, 41; HR-MS calcd for $C_{13}H_{12}O$ 184.0888, found 184.0880.

Cyclization of Triflate 12d. The crude product obtained by heating a mixture of triflate **12d** (62.3 mg, 0.115 mmol), Bu_4NBr (111 mg, 0.345 mmol), $PdCl_2(PPh_3)_2$ (2.5 mg, 3 mol %), Li_2CO_3 (8.6 mg, 0.12 mmol), $Bu_3SnSiMe_3$ (47 mg, 0.13 mmol), and toluene (1 mL) at 110 °C for 1.5 h was purified by preparative thin-layer chromatography (hexane) to give a colorless oil, a mixture of **13d** (22 mg, 0.069 mmol, 61%) and **18d** (3 mg, 0.009 mmol, 7%). **13d**: IR (neat) 1665, 1605, 1475, 1465, 1250 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.03 (s, 6 H), 0.90 (s, 9 H), 1.24–1.96 (m, 4 H), 2.12–2.41 (m, 2 H), 2.51 and 3.21 (ABq, J = 15.2 Hz, 2 H), 3.18 and 3.58 (ABq, J = 10.7 Hz, 2 H), 5.97 (t, J = 3.9 Hz, 1 H), 7.04–7.36 (m, 4 H); MS m/z 314 (M$^+$), 299 (M$^+$ – Me), 257 (M$^+$ – *t*-Bu), 239, 227, 182 (M$^+$ – $OSiMe_2$ – *t*-Bu), 167, 154, 141, 128, 115, 89, 73; HR-MS calcd for $C_{20}H_{30}OSi$ 314.2066, found 314.2062.

Cyclization of Triflate 12e. The crude product obtained by heating a mixture of triflate **12e** (44.0 mg, 0.093 mmol), Bu_4NBr (90.2 mg, 0.279 mmol), $PdCl_2(PPh_3)_2$ (1.9 mg, 3 mol %), Li_2CO_3 (6.8 mg, 0.092 mmol), $Bu_3SnSiMe_3$ (37 mg, 0.10 mmol), 4A molecular sieves (92.6 mg), and toluene (1 mL) at 110 °C for 8 h was purified by preparative thin-layer chromatography (hexane/EtOAc (10:1)) to give a mixture of **13e**, **18e**, and **12e** (19 mg; 41%, 13%, and 13%; the product ratio was determined by ^{1}H NMR). **13e**: IR (neat) 1720, 1450, 1275 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.20 (t, J = 7.3 Hz, 3 H), 1.38–1.62 (m, 14 H), 4.06 (q, J = 7.3 Hz, 2 H), 5.31 (t, J = 5.1 Hz, 1 H); MS m/z 246 (M$^+$), 217 (M$^+$ – Et), 173 (M$^+$ – COOEt).; HR-MS calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1602.

Cyclization of Triflate 12f. The crude product obtained by heating a mixture of triflate **12f** (26.0 mg, 0.052 mmol), Bu_4NBr (50.7 mg, 0.157 mmol), $PdCl_2(PPh_3)_2$ (1.2 mg, 3 mol %), Li_2CO_3 (3.9 mg, 0.052 mmol), $Bu_3SnSiMe_3$ (21 mg, 0.057 mmol), and toluene (0.5 mL) at 110 °C for 1 h was purified by preparative thin-layer chromatography (hexane/EtOAc (10:1)) to give **13f** (7.9 mg, 0.030 mmol, 56%) as a colorless oil: IR ($CHCl_3$) 1720, 1690, 1600, 1450, 1185 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.96 (t, J = 7.0 Hz, 3 H), 2.19 (s, 3 H), 2.16–2.36 (m, 4 H), 2.79 and 3.16 (ABq, J = 15.0 Hz, 2 H), 3.93 (q, J = 7.0 Hz, 2 H), 5.92–5.98 (m, 1 H), 6.69–6.73 (ddt, J = 1.6, 2.2, 10.3 Hz), 7.08–7.33 (m, 4 H); MS m/z 268 (M$^+$), 195 (M$^+$ – COOEt), 179, 165; HR-MS calcd for $C_{18}H_{20}O_2$ 268.1463, found 268.1464.

Cyclization of Triflate 12g. The crude product obtained by heating a mixture of triflate **12g** (41.6 mg, 0.086 mmol), Bu_4NBr (82.6 mg, 0.256 mmol), $PdCl_2(PPh_3)_2$ (1.9 mg, 3 mol %), Li_2CO_3 (6.4 mg, 0.087 mmol), $Bu_3SnSiMe_3$ (37 mg, 0.10 mmol), 4A molecular sieves (92.6 mg), and toluene (9 mL) at 110 °C for 3.5 h was purified by preparative thin-layer chromatography (hexane/EtOAc (10:1)) to give **13g** (2.2 mg, 0.009 mmol, 10%) and **18g** (12 mg, 0.036 mmol, 43%). **13g**: IR ($CHCl_3$) 1720, 1190 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.26 (t, J = 7.3 Hz, 3 H), 1.40–2.00 (m, 6 H), 2.04–2.52 (m, 2 H), 2.60–2.88 (m, 2 H), 4.07 (q, J = 7.3 Hz, 2 H), 6.40 (t, J = 4.0 Hz, 1 H), 6.96–7.22 (m, 3 H), 7.48–7.64 (m, 1 H); MS m/z 256 (M$^+$), 199, 141, 128, 105, 91; HR-MS calcd for $C_{17}H_{20}O_2$: 256.1464, found 256.1475. **18g**: IR (neat) 2920, 1730, 1600, 1470, 1180 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.29 (t, J = 7.3 Hz, 3 H), 1.40–2.40 (m, 8 H), 2.40–2.84 (m, 2 H), 4.18 (q, J = 7.3 Hz, 2 H), 5.76–5.83 (m, 2 H), 6.88–7.30 (m, 3 H), 7.47–7.54 (m, 1 H); MS m/z 338, 336 (M$^+$), 263, 261, 168; HR-MS calcd for $C_{17}H_{21}BrO_2$ 336.0725, found 336.0698.

$LiAlH_4$ Reduction of the Mixture of 13a and 16a. To a solution of a mixture of crude **13a** and **16a** (21.2 mg) in Et_2O (5 mL) was added $LiAlH_4$ (9.6 mg) at 0 °C. After 15 min, Na_2S-

$O_4 \cdot 10H_2O$ was added and the solution was stirred for several hours. The organic layer was decanted, the solvent was evaporated, and the residue was purified by preparative thin-layer chromatography on silica gel (hexane/EtOAc (5:1)) to give **17a** (11.3 mg): IR ($CHCl_3$) 3600, 2920, 1460, 1020 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.21–2.04 (m, 4 H), 2.06–2.36 (m, 3 H), 2.56 and 3.11 (ABq, $J = 15.6$ Hz, 2 H), 3.32 and 3.62 (ABq, $J = 11.0$ Hz, 2 H), 6.06 (t, $J = 3.7$ Hz, 1 H), 7.09–7.36 (m, 4 H); MS m/z 200 (M^+), 182 ($M^+ - H_2O$), 169 ($M^+ - CH_2OH$), 141, 128, 115, 91; HR-MS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1184.

Palladium Cross-Coupling Reactions of Aryl Fluorosulfonates: An Alternative to Triflate Chemistry

Gregory P. Roth*[1] and Carl E. Fuller

Chemical Process Research, Bristol-Myers Squibb Pharmaceutical Research Institute, P.O. Box 4755, Syracuse, New York 13221

Received December 14, 1990

A new and efficient electrophilic partner for palladium(0)-catalyzed cross coupling is reported. Aryl fluorosulfonates are readily prepared in high yield by treatment of the appropriate phenol with fluorosulfonate anhydride. The palladium-catalyzed coupling reactions of these fluorosulfonates with vinyl- and aryltin reagents, as well as organozinc chlorides, takes place under mild conditions in a regio- and stereoselective manner.

A variety of preparative methods have evolved that utilize substituted aryl compounds as organic electrophiles for carbon–carbon bond formation via cross coupling promoted by group 10 transition metals. The literature provides a wealth of examples demonstrating palladium-catalyzed coupling between organometallic species with popular substrates such as aryl halides,[2] aryl triflates,[3] aryl fluoroalkanesulfonates,[4] and aryl diazonium salts.[5]

The effectiveness of these previous substrates in the cross-coupling reaction prompted us to evaluate related reactions of the little used aryl fluorosulfonate esters **1a–g**. Historically, the fluorosulfonate moiety was utilized as a "super sulfate" leaving group in order to study the formation of the elusive aryl cation species.[6] However, from an experimental point of view, fluorosulfonates never gained popularity due to undesirable methods of preparation and the instability of fluorosulfonic acid, a problem that does not exist with triflic acid.

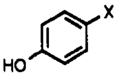
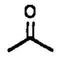
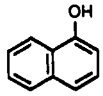
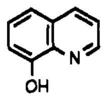
Aryl fluorosulfonates were first reported in 1930 and were prepared by pyrolysis of arenediazonium fluorosulfonate salts[7] (eq 1). More recenty, such compounds have been prepared by reaction of phenols with fluorosulfuryl chloride in the presence of pyridine.[8] Both methods require forcing conditions using difficult to handle reagents and furnish the desired products in low to modest yield.

(1)

$Z = N_2^+OSO_2F^-$ (heat, 10% yield), OH ($ClSO_2F$, 15% yield)

Table I. Preparation of Aryl Fluorosulfonates

$$ArOH + (FSO_2)_2O \xrightarrow[-78\ ^\circ C,\ 2\ h]{i\text{-}Pr_2NEt,\ CH_2Cl_2} ArOSO_2F$$

ArOH	X	yield[a] (%)	compd
		95	**1a**
	H	95	**1b**
	OCH_3	80	**1c**
	Br	75	**1d**
	NO_2	82	**1e**
		94	**1f**
		67	**1g**

[a] Isolated yield of pure product.

Results and Discussion

Since its initial preparation in 1951,[9,10] relatively few reactions involving fluorosulfonic anhydride ($(FSO_2)_2O$) with organic substrates have been reported. Typical uses of this reagent include the bulk polymerization of tetrahydrofuran to give poly(tetramethylene) ether glycol and the self-condensation of a variety of ketones, as well as an isolated example of its reaction with phenol to furnish **1b**

---

[1] Present address: Bristol-Myers Squibb Pharmaceutical Research Institute, 5 Research Parkway, Wallingford, CT 06492-7660.

[2] For some examples, see: McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422. Bailey, T. R. *Tetrahedron Lett.* **1986**, *27*, 4407. Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.

[3] Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. Martorell, G.; Garcia-Raso, A.; Saa, J. M. *Tetrahedron Lett.* **1990**, *31*, 2357. Ohe, T.; Miyaura, N.; Suzuki, A. *Synlett* **1990**, 221. Fu, J. M.; Snieckus, V. *Tetrahedron Lett.* **1990**, *31*, 1665.

[4] Chen, Q. Y.; Yang, Z. Y. *Tetrahedron Lett.* **1986**, *27*, 1171.

[5] Kikukawa, K.; Kono, K.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1983**, *48*, 1333.

[6] For a review of sulfonate leaving groups and related chemistry, see: Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

[7] Lange, W.; Mueller, E. *Ber. Dtsch. Chem. Ges. B* **1930**, *63*, 2653.

[8] Cramer, R.; Coffman, D. D. *J. Org. Chem.* **1961**, *26*, 4164.

[9] Hayek, E.; Koller, W. *Monatsh. Chem.* **1951**, *26*, 942. Boudakian, M. M.; Hyde, G. A.; Kongpricha, S. *J. Org. Chem.* **1971**, *36*, 940.

[10] Most preparations of perfluoroalkanesulfonic anhydrides call for the condensation of 2 equiv of the appropriate acid in the presence of phosphorus pentoxide; however, this procedure does not work in the preparation of $(FSO_2)_2O$. We have routinely prepared kilogram batches of the above reagent utilizing the method described by Kongpricha and co-workers involving dehydration in the presence of cyanuric chloride. The desired anhydride is formed in nearly quantitative yield and is a stable, slow to hydrolyze, low-boiling liquid (50 °C) that can be used in a manner similar to that of triflic anhydride: Kongpricha, S.; Preusse, W. C.; Schwarer, R. *Inorg. Synth.* **1968**, *11*, 151.