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Improved Yields with Added Copper(I) Salts in Carbonylative Stille Couplings of Sterically Hindered Vinylstannanes

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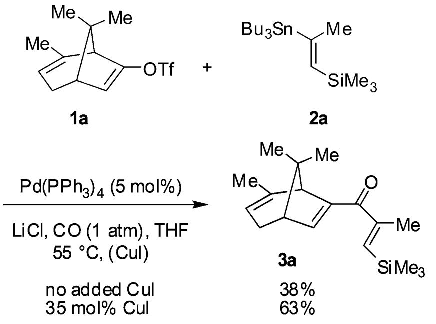
Abstract: Stille coupling under standard carbonylative conditions proceeds in poor yield when using hindered alkenylstannane and enol triflate partners. The inclusion of 35 mol % CuI or CuBr significantly improves the efficiency of the coupling, providing a variety of complex 1,4-dien-3-ones in good to excellent yield.

Cross-conjugated 1,4-dien-3-ones are useful synthetic building blocks, especially with regard to their use in the Nazarov reaction[1] and its variations.[2] Their two-step preparation from addition of alkenyl nucleophiles into unsaturated aldehydes is often straightforward, although generation of more elaborate alkenylmetal partners can present challenges. Moreover, intermediate dienols can be quite sensitive, and oxidation under the necessary mild conditions (e.g., $BaMnO_4$)[3] can be inefficient. Palladium-catalyzed cross-coupling of alkenylstannanes with alkenyl triflates (Stille reaction) under carbonylative conditions[4] presents an attractive alternative, as it convergently assembles the desired dienones in a single step from readily available and relatively stable precursors. The Stille coupling is well established as a useful method for formation of carbon−carbon bonds in organic synthesis.[5] Although quite general for unhindered substrates, it frequently fails with increasing steric bulk on the coupling partners. In particular, the use of 1-substituted vinylstannanes can result in low overall yields due to slow reaction rates and competing side reactions.[6] In regular cross-couplings, these limitations have been addressed by the addition of copper(I) salts which facilitate the transmetalation step in the catalytic cycle.[7] However, the use of cocatalytic Cu(I) in *carbonylative* couplings appears to be uncommon, and we are aware of only one report.[8] Our continuing interest in the Nazarov cyclization prompted an examination of the scope of the carbonylative Stille coupling as a synthetic route to a variety of sterically congested cyclization precursors. We report here that a substantial improvement in yields in a variety of examples of this process can be obtained through the inclusion of substoichiometric quantities of CuI or CuBr.

The bicyclic trienone **3a** was required for use in a study of diastereoselectivity in sterically biased Nazarov systems (eq 1).[9] Palladium-catalyzed carbonylative coupling of bicyclic enol triflate **1a** and vinylstannane **2a**[10] in the presence of LiCl (400 mol %)[11] gave the desired dienone **3a**, but only in a disappointing 38% yield. However, upon addition of 35 mol % purified[12] CuI the reaction proceeded cleanly and dienone **3a** was obtained in 63% isolated yield.



(1)

This result prompted a more general survey of several representative substrates and conditions. As summarized in Table 1, Cu(I) salts were consistently effective in

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(1) Reviews: (a) Habermas, K. L.; Denmark, S. E.; Jones, T. K. *Org. React. (N.Y.)* **1994**, *45*, 1. (b) Denmark, S. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, pp 751−784.

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(6) Examples: (a) Mitchell, T. N.; Reimann, W. *Organometallics* **1986**, *5*, 2801. (b) Pearson, W. H.; Postich, M. J. *J. Org. Chem.* **1994**, *59*, 5662. (c) Busaca, C. A.; Swestock, J.; Johnson, R. E.; Bailey, T. R.; Musza, L.; Roger, C. A. *J. Org. Chem.* **1994**, *59*, 7553.

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(10) Preparation of alkenylstannanes **2a**, **2b**, and **2e** has previously been described. **2a**: Nicolaou, K. C.; Piscopio, A. D.; Bertinato, P.; Chakraborty, T. K.; Minowa, N.; Koide, K. *Chem. Eur. J.* **1995**, *1*, 318. **2b**: Cunico, R. F.; Clayton, F. J. *J. Org. Chem.* **1976**, *41*, 1480. **2e**: Piers, E.; Chong, J. M. *Can. J. Chem.* **1988**, *66*, 1425. See the Supporting Information for preparation of **2c**,**d**.

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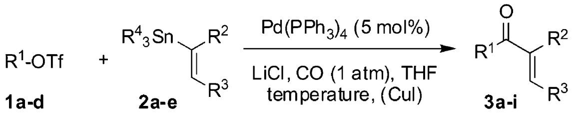
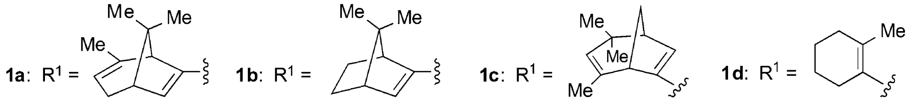
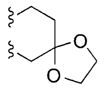
TABLE 1. CuX-Promoted Carbonylative Stille Couplings[a]





entry	enol triflate	vinylstannane	R^2	R^3	R^4	CuX (mol%)	temp (°C)	dienone	yield (%)[b]
1	**1a**	**2a**	Me	$SiMe_3$	Bu	-	55	**3a**	38
2	**1a**	**2a**	Me	$SiMe_3$	Bu	CuI (15)	55	**3a**	54
3	**1a**	**2a**	Me	$SiMe_3$	Bu	CuI (35)	55	**3a**	63
4	**1a**	**2a**	Me	$SiMe_3$	Bu	CuI (35)	65	**3a**	76
5	**1a**	**2a**	Me	$SiMe_3$	Bu	CuCN (35)	65	**3a**	64
6	**1a**	**2a**	Me	$SiMe_3$	Bu	CuBr (35)	65	**3a**	90
7	**1a**	**2c**			Me	-	55	**3b**	33
8	**1a**	**2c**	as above		Me	CuI (35)	55	**3b**	63
9	**1a**	**2c**	as above		Me	CuI (35)	65	**3b**	82
10	**1a**	**2c**	as above		Me	CuI (5)	65	**3b**	39
11	**1a**	**2d**	$(CH_2)_3OH$	$SiMe_3$	Bu	CuI (5)	65	**3c**	--[c]
12	**1a**	**2d**	$(CH_2)_3OH$	$SiMe_3$	Bu	CuI (35)	65	**3c**	60
13	**1a**	**2d**	$(CH_2)_3OH$	$SiMe_3$	Bu	CuBr (35)	65	**3c**	56
14	**1a**	**2e**	$(CH_2)_3OH$	H	Me	CuI (35)	65	**3d**	76
15	**1b**	**2a**	Me	$SiMe_3$	Bu	CuI (35)	65	**3e**	81
16	**1b**	**2b**	H	$SiMe_3$	Bu	CuI (35)	65	**3f**	72
17	**1c**	**2a**	Me	$SiMe_3$	Bu	CuI (35)	65	**3g**	64
18	**1c**	**2b**	H	$SiMe_3$	Bu	CuI (35)	65	**3h**	62
19	**1d**	**2a**	Me	$SiMe_3$	Bu	--	65	**3i**	60
20	**1d**	**2a**	Me	$SiMe_3$	Bu	CuI (35)	65	**3i**	98
21	**1d**	**2a**	Me	$SiMe_3$	Bu	CuBr (35)	65	**3i**	98

[a] See the Experimental Section for reaction conditions. [b] Isolated yields after chromatography. [c] No dienone products were isolated.

promoting carbonylative Stille couplings of sterically hindered substrates: coupling of bicyclic enol triflates **1a**–**c** or tetrasubstituted enol triflate **1d** with vinylstannanes **2a**–**e** provided the corresponding dienones **3a**–**i** in moderate to excellent yields. These couplings were performed under atmospheric pressure of CO, avoiding the use of special glassware or high-pressure equipment. A preliminary screening of the reaction conditions showed that the product distribution was highly dependent upon the amount of CuI and the reaction temperature.[13] As discussed earlier, in the absence of CuI the carbonylative coupling of **1a** and **2a** in THF at 55 °C furnished the desired dienone **3a** in only 38% yield (entry 1). Higher CO pressures under these conditions produced only marginal yield increases, consistent with the absence of any apparent direct coupling products. However, upon addition of CuI a dramatic increase in yield was observed and 35 mol % was found to give optimum results (entries 2 and 3). In initial experiments, the coupling was carried out at 55 °C, but it became apparent that improved yields of the desired dienones could be obtained at higher

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(11) For background on the role of LiCl, see: (a) Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 3033. (b) Chen, Q.-Y.; He, Y.-B. *Chin. J. Chem.* **1990**, 451.

(12) Teter, J. *Inorg. Synth.* **1967**, 9.

(13) No apparent advantage over THF was seen with other polar aprotic solvents such as DME (comparable yields) or DMF (poor conversion to **3**)

temperatures, and carbonylative coupling of **1a** with **2a** in the presence of 35 mol % CuI at 65 °C in THF gave dienone **3a** in 76% yield (entry 4). The suitability of other copper(I) salts was also examined in the coupling of **1a** with **2a**. Cuprous cyanide (entry 5) also had a beneficial effect under the standard conditions (35 mol % CuX; 65 °C), though not as pronounced as CuI. On the other hand, coupling in the presence of CuBr furnished **3a** in excellent yield (entry 6).

Coupling of **1a** with stannane **2c** followed a similar trend to what was seen with **2a**: carbonylative coupling of **1a** with **2c** at 55 °C in the absence of CuI gave the desired product **3b** in low yield (entry 7).[14] Addition of 35 mol % CuI and maintaining the temperature at 55 °C led to an improved yield of 63% (entry 8) which could be further optimized by raising the reaction temperature to 65 °C, affording **3b** in 82% yield (entry 9). Use of smaller amounts (5 mol %) of CuI gave unsatisfactory yields of the coupling product (entries 10 and 11). Even highly unreactive stannanes could be successfully employed in CuI-promoted carbonylative couplings as illustrated by the coupling of **1a** with **2d** furnishing the expected dienone **3c** in 60% yield (entry 12).[15] Comparable results were seen using CuBr (entry 13).

Since yields in this case were modest even with added CuX, we examined the similar trimethylstannyl derivative **2e**, which was expected to exhibit increased reactivity compared to the tributylstannane **2d**.[16] Under otherwise identical conditions, an improved yield of 76% could be obtained (entry 14). Although alkenyl trimethylstannanes are more prone to protodestannylation, which can complicate their purification, they should be considered as alternative substrates if the coupling of the corresponding alkenyl tributylstannanes is sluggish and low yielding.

Other enol triflates and 1-unsubstituted vinylstannanes were also examined in the CuX-promoted carbonylative Stille coupling. Carbonylative coupling of **1b** with **2a** in the presence of 35% mol of CuI yielded dienone **3e** in 81% yield at 65 °C in THF (entry 15). Under identical conditions, the unsubstituted stannane **2b**[9] afforded the desired product **3f** in comparable yield (entry 16) but the reaction was completed in 16 h compared to the 48 h reaction time in the case of **2a**. A similar trend was observed with enol triflate **1c**. CuI promoted carbonylative coupling of **1c** with **2a** gave the expected product **3g** in 64% yield after a reaction time of 48 h while coupling of **1c** with **2b** was completed after 14 h and afforded dienone **3h** in 62% yield (entries 17 and 18). These results are in agreement with earlier observations suggesting that 1-substituted vinystannanes exhibit a reduced reactivity compared to the unsubstituted stannanes.[4] However, in CuI-promoted couplings, the 1-substituted stannanes gave similar or better yields of the desired products if compared to the unsubstituted cases (entries 15–18). The presence of CuI in couplings of this type may suppress side reactions (e.g., cine substitution[7,17] or homocoupling[7c]) which could otherwise lead to diminished overall yields and/or complex product mixtures. Finally, carbonylative coupling of the known tetrasubstituted enol triflate **1d**[4b] with **2a** was examined. In the absence of CuX, dienone product **3i** was obtained in 60% yield. In the presence of either CuI or CuBr, near-quantitative yields of **3i** were obtained.

In summary, copper(I) salts (especially CuI or CuBr) are effective cocatalysts for the carbonylative Stille coupling of vinylstannanes with enol triflates. The optimized conditions (1 atm CO, 5 mol % $Pd(PPh_3)_4$, 35 mol % CuX, 400 mol % LiCl, THF, 65 °C) allow for efficient coupling of 1-substituted vinylstannanes in yields comparable to or better than the corresponding unsubstituted stannanes. No special glassware or high-pressure equipment is needed since the couplings proceed readily under 1 atm of CO.

Experimental Section

Representative Procedure for Carbonylative Coupling. A mixture of LiCl (0.255 g, 6.02 mmol) and $Pd(PPh_3)_4$ (0.114 g, 0.099 mmol) in THF (8 mL) was stirred under nitrogen for 15 min. CuI (0.136 g, 0.71 mmol) was added in one solid portion, and the dark brown solution was saturated with CO (1 atm) for 20 min. A solution of the stannane (2.55 mmol) and enol triflate (1.98 mmol) in THF (8 mL) was added via cannula, and the resulting mixture was saturated with CO (1 atm) for an additional 20 min. The reaction mixture was heated to 65 °C and kept under a static pressure of CO until no more enol triflate could be detected by TLC (24–72 h). The reaction mixture was cooled, and the reaction was quenched by the addition of H_2O (16 mL). The layers were separated, and the organic layer was washed with 1 N NaOH (2 × 16 mL) and H_2O (16 mL). Drying ($MgSO_4$), filtration, and concentration under reduced pressure yielded a brown oil which was purified by flash chromatography on silica gel.

Dienone 3a: R_f 0.55 (2.5% EtOAc/hexanes); IR (neat) 2954, 1634, 1249; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.26 (d, $J = 2.3$ Hz, 1H), 6.16 (s, 1H), 4.99–4.92 (m, 1H), 2.52 (s, 1H), 2.32–2.27 (m, 2H), 1.99 (s, 3H), 1.81–1.77 (m, 4H), 1.09 (s, 3H), 1.08 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.5, 152.3, 151.8, 143.7, 141.2, 137.9, 116.2, 54.0, 48.9, 44.4, 27.5, 26.2, 23.9, 20.7, 18.0, −0.20. Anal. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78. Found: C, 74.83; H, 9.81.

Dienone 3b: R_f 0.36 (hexanes/Et_2O 1:1); IR (thin film) 1626 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.50–6.45 (m, 1H), 6.26 (d, $J = 2.9$ Hz, 1H), 4.98–4.92 (m, 1H), 4.00 (s, 4H), 2.71–2.58 (m, 1H), 2.52–2.40 (m, 4H), 2.34–2.10 (m, 2H), 1.84–1.76 (m, 6H), 1.08 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.6, 152.2, 142.2, 141.0, 138.4, 135.4, 115.9, 107.4, 64.5, 64.4, 54.1, 48.5, 44.0, 36.2, 30.6, 27.2, 25.9, 23.6, 23.3, 20.4; HRMS for $C_{20}H_{26}O_3$ (M^+) calcd 314.1882, found 314.1890.

Dienone 3c: R_f 0.20 (hexanes/EtOAc 20%); IR (thin film) 3547, 1635 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.26 (d, $J = 2.9$ Hz, 1H), 6.08 (s, 1H), 4.93 (br s, 1H), 3.55 (td, $J = 6.3$, 1.0 Hz, 2H), 2.51 (s, 1H), 2.49 (dddt, $J = 26.7$, 13.6, 5.9, 7.6 Hz, 2H), 2.33–2.23 (m, 2H), 2.15 (br s, 1H), 1.80–1.73 (m, 4H), 1.60 (tt, $J = 7.6$, 6.3 Hz, 2H), 1.06 (s, 3H), 1.04 (s, 3H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 155.8, 153.0, 144.7, 141.0, 138.1, 116.1, 62.1, 53.7, 48.8, 44.4, 32.8, 28.4, 27.4, 26.1, 23.8, 20.7, 0.1; HRMS for $C_{20}H_{32}O_2Si$ (M^+) calcd 332.2172, found 332.2160.

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[14] Amann, C. M. Ph.D. Dissertation, University of Utah, 1998.

[15] No dienone products were isolated from the attempted carbonylative coupling of **1a** with **2d** with 5 mol % of CuI (entry 11, Table 1) or without CuX.

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[17] (a) Stork, G.; Isaacs, R. C. A. *J. Am. Chem. Soc.* **1990**, *112*, 7399. (b) Busacca, C. A.; Swestock, J.; Johnson, R. E.; Bailey, T. R.; Musza, L.; Rodger, C. A. *J. Org. Chem.* **1994**, *59*, 7553. (c) Farina, V.; Hossain, M. A. *Tetrahedron Lett.* **1996**, *37*, 6997. (d) Flohr, A. *Tetrahedron Lett.* **1998**, *39*, 5177. (e) Kang, S.-K.; Ryu, H.-C.; Lee, S.-W. *J. Organomet. Chem.* **2000**, *610*, 38.

Dienone 3d: R_f 0.13 (hexanes/EtOAc 20%); IR (thin film) 1635 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.32 (d, J = 3.2 Hz, 1H), 5.59 (s, 1H), 5.58−5.57 (m, 1H), 4.90 (br s, 1H), 3.55 (t, J = 6.3 Hz, 2H), 2.73 (br s, 1H), 2.48 (s, 1H), 2.37 (t, J = 7.5 Hz, 2H), 2.29−2.21 (m, 2H), 1.77−1.73 (m, 4H), 1.68−1.61 (m, 2H), 1.04 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 195.9, 152.9, 148.2, 144.7, 140.9, 123.1, 116.1, 61.6, 53.7, 48.7, 44.2, 31.8, 28.2, 27.3, 26.0, 23.7, 20.5; HRMS for $C_{17}H_{24}O_2$ (M$^+$) calcd 260.1776, found 260.1767.

Dienone 3e: R_f 0.45 (5% EtOAc/hexanes); IR (neat) 2959, 1633, 1240 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.55 (d, J = 3.3 Hz, 1H), 6.24 (d, J = 1.0 Hz, 1H), 2.76−2.75 (m, 1H), 2.49 (ddd, J = 3.5, 3.5, 1.6 Hz, 1H), 2.01−1.92 (m, 2H), 1.97 (d, J = 1.0 Hz, 3H), 1.04−0.99 (m, 2H), 0.98 (s, 3H), 0.94 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 196.1, 151.7, 148.2, 147.7, 138.1, 55.2, 53.1, 50.6, 24.8, 24.0, 21.7, 21.6, 17.9, 0.3; HRMS for $C_{16}H_{26}OSi$ (M$^+$) calcd 262.1753, found 262.1748.

Dienone 3f: R_f 0.36 (5% EtOAc/hexanes); IR (neat) 2960, 1632, 1249 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.14 (d, J = 18.6 Hz, 1H), 6.97 (d, J = 18.6 Hz, 1H), 6.96 (d, J = 3.8 Hz, 1H), 2.86 (d, J = 2.2 Hz, 1H), 2.53 (app brs, 1H), 2.03−1.93 (m, 2H), 1.06−0.97 (m, 2H), 0.95 (s, 3H), 0.94 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 186.6, 150.1, 148.0, 145.9, 137.8, 55.5, 53.1, 49.6, 24.6, 23.9, 21.6 (2C), −1.5; HRMS for $C_{15}H_{24}OSi$ (M$^+$) calcd 248.1596, found 248.1592.

Dienone 3g: R_f 0.50 (5% EtOAc/hexanes); IR (neat) 2957, 1634, 1250 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.37 (d, J = 3.4 Hz, 1H), 6.12 (d, J = 1.0 Hz, 1H), 4.69−4.68 (m, 1H), 2.87 (d, J = 4.5 Hz, 1H), 2.58−2.61 (m, 1H), 2.06−2.03 (m, 1H), 1.99 (d, J = 9.0 Hz, 1H), 1.98 (d, J = 1.0 Hz, 3H), 1.80 (d, J = 1.5 Hz, 3H), 1.33 (s, 3H), 0.87 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 196.2, 152.4, 151.7, 145.9, 139.5, 138.5, 128.2, 51.5, 43.9, 39.8, 35.2, 30.7, 25.4, 23.2, 17.8, 0.23; HRMS for $C_{18}H_{28}OSi$ (M$^+$) calcd 288.1909, found 288.1897.

Dienone 3h: R_f 0.46 (5% EtOAc/hexanes); IR (neat) 2955, 1649, 1249 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.15 (d, J = 18.6 Hz, 1H), 6.98 (d, J = 18.6 Hz, 1H), 6.78 (d, J = 3.4 Hz, 1H), 4.66−4.65 (m, 1H), 2.96−2.95 (m, 1H), 2.65−2.63 (m, 1H), 2.01−1.99 (m, 2H), 1.74 (d, J = 1.9 Hz, 3H), 1.14 (s, 3H), 0.88 (s, 3H), 0.15 (s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 186.4, 155.3, 146.2, 145.7, 139.4, 137.7, 128.2, 51.7, 43.0, 39.7, 35.4, 30.7, 25.4, 23.2, 1.5; HRMS for $C_{17}H_{26}OSi$ (M$^+$) calcd 274.1753, found 274.1740.

Dienone 3i: R_f 0.51 (10% EtOAc/hexanes); IR (thin film) 2931, 1652, 1250 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.59 (s, 1H), 2.13−2.08 (m, 2H), 2.05−1.99 (m, 2H), 1.96 (s, 3H), 1.70−1.60 (m, 4H), 1.52 (s, 3H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 204.1, 150.9, 143.1, 133.4, 132.3, 31.0, 27.7, 22.6, 22.2, 21.1, 15.8, −0.7; HRMS for $C_{14}H_{24}OSi$ (M$^+$) calcd 236.1596, found 236.1591.

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Supporting Information Available: Experimental procedures and spectral data for enol triflates **1a**−**c** and vinylstannanes **2c**−**e** and NMR spectra for enol triflate **1c**, vinylstannane **2d**, and dienones **3b**−**i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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