Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 768–775

Palladium-catalyzed cross-coupling reaction of alkenyl bromides with potassium alkyltrifluoroborates

Gary A. Molander,[a,*] Jungyeob Ham[a] and Dave G. Seapy[b]

[a]*Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Campus Box 215, Philadelphia, PA 19104-6323, United States*
[b]*Department of Chemistry, Eastern University, St. Davids, PA 19087-3696, United States*

Received 16 August 2006; revised 24 October 2006; accepted 27 October 2006
Available online 16 November 2006

Abstract—The Suzuki–Miyaura-type cross-coupling reaction of potassium alkyltrifluoroborates with various alkenyl bromides in the presence of 10 mol % of $PdCl_2(dppf)\cdot CH_2Cl_2$ and 3.0 equiv of Cs_2CO_3 in aqueous toluene at 80 °C provided the desired compounds in 63–95% yields. A variety of functional groups in the potassium alkyltrifluoroborates were tolerated under the basic conditions.

1. Introduction

The discovery of carbon–carbon bond-forming reactions using palladium catalysts is important to the development of synthetic organic chemistry.[1] Among the various methods, the Suzuki–Miyaura cross-coupling reaction has many advantages for the formation of new carbon–carbon bonds such as mild reaction conditions, high regio- and stereoselectivity, and tolerance of many functional groups. Additionally, this reaction is an environmentally sound reaction.[2] Moreover, organoboron compounds are commercially available and readily prepared from the corresponding alkene and/or alkyne via transmetalation or hydroboration reactions.

Most of the previous studies of palladium-catalyzed Suzuki–Miyaura cross-coupling reactions have been performed with halide- and triflate-substituted alkenes and arenes as the electrophiles, and boronic acids or boronate esters with sp- or sp^2-hybridized carbons as the nucleophiles. In contrast, carbon–carbon bond-forming reactions of sp^3-hybridized organoborons, which possess β-hydrogens, have been restricted and are rather uncommon due to β-hydride elimination from the generated alkylpalladium intermediate.[1–3]

In 1986 and 1989, Miyaura and co-workers reported the coupling of alkylboron compounds with various organic halides using a catalytic amount of $PdCl_2(dppf)\cdot CH_2Cl_2$ in the presence of base, such as K_3PO_4, K_2CO_3, and NaOH.[3] To date, these coupling reactions using alkyl moieties in Suzuki–Miyaura cross-coupling reactions have proven to be among the more useful methods for the synthesis of natural products and other biologically active compounds.[4] However, boronic acids and boronate esters used in carbon–carbon bond coupling reactions possess many limitations, such as difficulties in purification, uncertain stoichiometry, high costs, and in some cases, instability to air and moisture.

Recently, organotrifluoroborate reagents have attracted considerable interest as useful intermediates for Suzuki–Miyaura-type cross-coupling reactions because they are air- and moisture-stable crystalline solids.[5] Moreover, the potassium organotrifluoroborates show greater nucleophilicity than that of the corresponding organoboranes and boronic acid derivatives.[6] Our research group has previously investigated the cross-coupling of various organotrifluoroborate derivatives, including alkyltrifluoroborates.[5a] Additionally, we have explored novel syntheses of functionalized organotrifluoroborates to expand their chemistry through direct epoxidation,[7] cis-dihydroxylation,[8] nucleophilic substitution,[9] and 1,3-dipolar cycloaddition reactions.[10] In this paper, we report the results of palladium-catalyzed cross-coupling reactions with various alkenyl bromides and potassium alkyltrifluoroborates to forge (C)sp^2–(C)sp^3 bonds.

2. Results and discussion

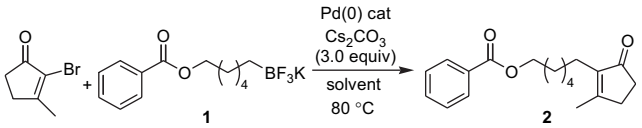
Initially we examined the Suzuki–Miyaura cross-coupling reaction of 2-bromo-3-methyl-2-cyclopenten-1-one with potassium 6-(benzoyloxy)hexyltrifluoroborate (**1**) to determine the optimal conditions in the presence of several different palladium(0) precatalysts and 3.0 equiv of base (Table 1).

A number of different palladium catalysts, such as $Pd(PPh_3)_4$, $Pd(OAc)_2/2PCy_3$, and $PdCl_2(dppf)\cdot CH_2Cl_2$, were screened

* Corresponding author. Tel.: +1 215 573 8604; fax: +1 215 573 7165; e-mail: gmolandr@sas.upenn.edu

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.10.088

Table 1. Optimization of reaction conditions for the formation of **2**[a]



Entry	Catalyst/ligand (10 mol %)	Solvent (v/v=3/1)	Time (h)	Yield[b] (%)
1	$Pd(PPh_3)_4$	Toluene/H_2O	24	13
2[c]	$Pd(OAc)_2$/2PCy_3	Toluene/H_2O	7	41
3	$PdCl_2(dppf)\cdot CH_2Cl_2$	Toluene/H_2O	7	74
4[d]	$PdCl_2(dppf)\cdot CH_2Cl_2$	Toluene/H_2O	24	68
5	$PdCl_2(dppf)\cdot CH_2Cl_2$	THF/H_2O	7	13
6	$PdCl_2(dppf)\cdot CH_2Cl_2$	Toluene/pH 9	7	62
7[e]	$PdCl_2(dppf)\cdot CH_2Cl_2$	Toluene/H_2O	7	39

[a] All reactions were carried out using 0.10 mmol of 2-bromo-3-methyl-2-cyclopenten-1-one and 0.11 mmol of alkyltrifluoroborate (**1**).
[b] Yields are given for isolated products.
[c] $Pd(OAc)_2$ (4 mol %) and PCy_3 (8 mol %) were used.
[d] Reaction was performed with 5 mol % of $PdCl_2(dppf)_2\cdot CH_2Cl_2$.
[e] K_2CO_3 (3 equiv) was used as a base.

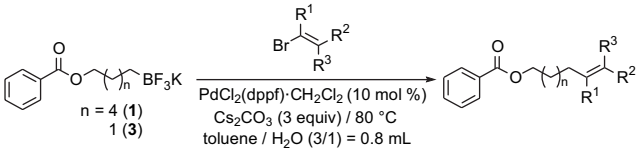
for their effectiveness in accomplishing the cross-coupling reaction (Table 1, entries 1–3), and it was found that $PdCl_2(dppf)\cdot CH_2Cl_2$ provided the fastest reaction time and the highest isolated yield (Table 1, entry 3). It was observed that a decrease in the catalyst loading from 10 to 5 mol % under the same conditions resulted in a dramatic increase in reaction times and a slightly decreased product yield (Table 1, entries 3 and 4). In the study of various reaction medium, a mixed solvent system composed of toluene/H_2O (v/v=3/1) was confirmed to be the optimal solvent, whereas toluene/pH 9.0 buffer solution and especially THF/H_2O showed lower reaction rates and isolated yields during the same reaction times (Table 1, entries 3, 5, and 6). Interestingly, the reaction rate, yield, and purity of compound **2** were improved with higher concentration (0.1 mmol/0.8 mL, data not shown). Also, when K_2CO_3 was used as a base instead of Cs_2CO_3, the product yield declined (Table 1, entry 7).

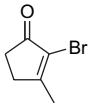
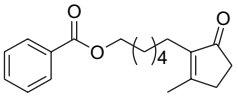
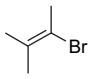
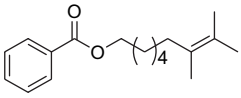
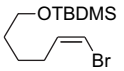
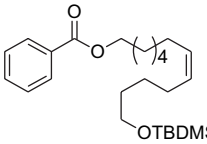
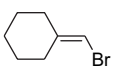
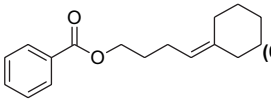
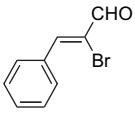
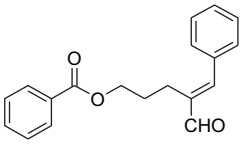
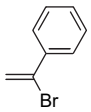
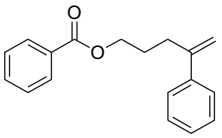
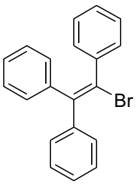
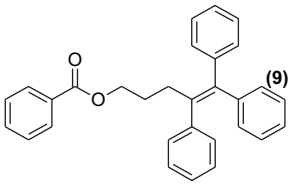
Using our optimized conditions, we were able to perform the Suzuki–Miyaura-type cross-coupling reaction of various alkenyl bromides with potassium 6-(benzoyloxy)hexyltrifluoroborate (**1**) and 3-(benzoyloxy)propyltrifluoroborate (**3**) in the presence of 10 mol % $PdCl_2(dppf)\cdot CH_2Cl_2$ and 3.0 equiv of Cs_2CO_3 in aqueous toluene at 80 °C. The results are summarized in Table 2.

The cross-coupling reactions of enones and enals containing an alkenyl bromide (Table 2, entries 1 and 5) required longer reaction times. From previous studies of cross-coupling reactions with potassium organotrifluoroborates, the silylated alcohol group was known to be stable under the reaction conditions in the presence of a fluoride counterion (Table 2, entry 3).[11a] When α-bromostyrene was used, although the reaction proceeded quickly, the product **8** was obtained only in 54% yield (Table 2, entry 6). Interestingly, 2-bromo-3-methyl-2-butene and triphenylethenyl bromide, though sterically hindered, reacted quickly with accompanying high yields (Table 2, entries 2 and 7).

Next, we proceeded to examine the Suzuki–Miyaura-type cross-coupling reactions of various potassium alkyltrifluoroborates (**1**) with alkenyl bromides under the same reaction conditions, the results of which are summarized in Table 3.

Table 2. Cross-coupling of various alkenyl bromides with potassium 6-(benzoyloxy)hexyltrifluoroborate (**1**) and 3-(benzoyloxy)propyltrifluoroborate (**3**)[a]

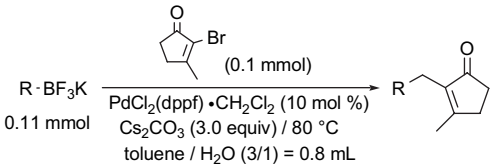


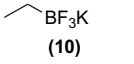
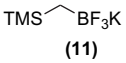
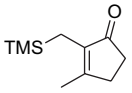
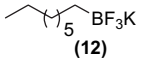
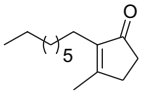
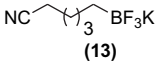
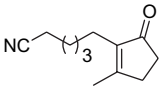
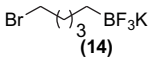
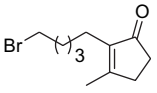
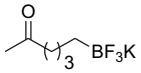
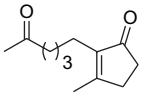
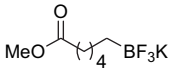
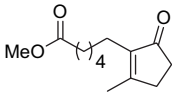
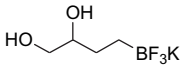
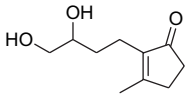
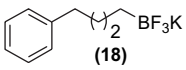
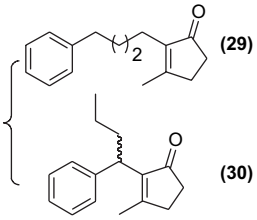
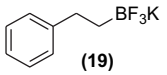
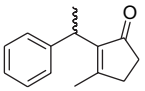
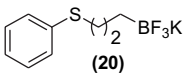
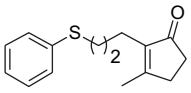
Entry	Alkenyl bromide	Reaction time	Product	Isolated yield (%)
1		7		**(2)** 74 (78)[b]
2		3		**(4)** 93
3		2		**(5)** 78
4		5		**(6)** 82
5		12		**(7)** 69[c]
6[d]		3		**(8)** 54
7		3		**(9)** 91

[a] All reactions were carried out with 0.1 mmol of alkenyl bromide and 0.12 mmol of potassium alkyltrifluoroborate.
[b] This reaction was performed on 1.0 mmol scale.
[c] 2-Bromo-3-methyl-2-cyclopenten-1-one (5.9 mg, 28%) as the starting material was recovered.
[d] Purity of commercial α-bromostyrene was 90%.

The majority of potassium alkyltrifluoroborates was easily prepared according to the previous literature protocols.[8–15] However, the methyl ester **16** was obtained from potassium *trans*-1-hex-5-enoic acid trifluoroborate methyl ester in excellent yield via hydrogenation with hydrogen gas in the presence of Pd/C catalyst.

Table 3. Cross-coupling reaction of 2-bromo-3-methyl-2-cyclopenten-1-one with various potassium alkyltrifluoroborates



Entry	R–BF_3K	Reaction time (h)	Product	Isolated yield (%)
1	 **(10)**	4	 **(21)**	83
2	 **(11)**	8	 **(22)**	95
3	 **(12)**	8	 **(23)**	53
4	 **(13)**	7	 **(24)**	86[a]
5	 **(14)**	22	 **(25)**	69
6	 **(15)**	11	 **(26)**	87
7	 **(16)**	18	 **(27)**	63
8	 **(17)**	16	 **(28)**	94
9	 **(18)**	18	 **(29)** **(30)**	63 36
10	 **(19)**	9	 **(31)**	92
11	 **(20)**	12	 **(32)**	41 (90)[b]

[a] 2-Bromo-3-methyl-2-cyclopenten-1-one (9%, 1.6 mg) as the starting material was recovered.
[b] The reaction was carried out with 10 mol % of $Pd(PPh_3)_4$ instead of $PdCl_2(dppf)\cdot CH_2Cl_2$.

As shown in Table 3, all alkyltrifluoroborates gave rise to the corresponding products in moderate yields. The coupling reaction of potassium ethyltrifluoroborate (**10**) led to the corresponding target compound **21** in 83% yield. Also, a high yield (95%) was obtained for the coupling reaction of trimethylsilylmethyltrifluoroborate with the alkenyl bromide (Table 2, entry 2). Interestingly, increasing the carbon chain length of alkyltrifluoroborates extended the reaction time and resulted in a lower yield (Table 3, entry 3).

As expected, the coupling reactions can tolerate a variety of functional groups such as silyl, nitrile, halide, and carbonyl

groups present in the alkyltrifluoroborate despite the use of aqueous basic conditions (Table 3, entries 2 and 4–6). However, when alkyltrifluoroborate **16** containing an ester functionality was used following the same conditions for 18 h, a moderate yield (63%) was obtained (Table 3, entry 7). Presumably, this is due to the fact that the prolonged reaction time under basic conditions induced the saponification of the ester group. The reaction yield of the coupling with the dihydroxy alkyltrifluoroborate **17** was not significantly influenced by the unprotected alcohols (Table 3, entry 8).

Interestingly, when potassium 4-phenylbutyltrifluoroborate (**18**) was used as the coupling partner, the desired product **29** and by-product **30** were obtained in 63% and 36% yields, respectively (Table 3, entry 9). Although the reaction mechanism for generating by-product **30** has not been confirmed, the product appears to form as a result of a series of β-hydride elimination/reinsertion processes. The coupling of a secondary alkyl carbon center was surprising, because concerted efforts to achieve this previously had uniformly failed.[12] A similar process transpired with potassium 2-phenylethyltrifluoroborate (**19**), wherein the secondary carbon coupling product **31** was isolated in 92% yield (Table 3, entry 10). We are unaware of other instances where such β-hydride elimination/reinsertion processes have been reported in this context.

Although in the cross-coupling reaction of the thioalkyltrifluoroborate **20** the desired compound **32** was obtained in only 41% yield, we could successfully obtain a 90% yield by changing the catalyst from 10 mol % $PdCl_2(dppf)\cdot CH_2Cl_2$ to 10 mol % $Pd(PPh_3)_4$ (Table 3, entry 11).

3. Conclusion

In summary, we have developed the Suzuki–Miyaura-type cross-coupling reactions between sp^2-hybridized alkenyl bromides and sp^3-hybridized alkyltrifluoroborates in good yields. Potassium alkyltrifluoroborates were easily prepared by transmetalation or hydroboration reactions, as well as by hydrogenation of the corresponding alkenyltrifluoroborates. Also, we confirmed that these coupling reactions can tolerate a variety of functional groups under the optimized conditions. On the other hand, we observed that under the same conditions, the coupling reactions with 2-phenylethyl- and 4-phenylbutyltrifluoroborates generated the secondary coupling compounds **30** and **31**.

4. Experimental

4.1. General considerations

^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 500.39, 125.82, and 470.79 MHz, respectively. ^{19}F NMR chemical shifts were referenced to external $CFCl_3$ (0.0 ppm). ^{11}B NMR spectra at 128.4 MHz were obtained on a spectrometer equipped with the appropriate decoupling accessories. All ^{11}B-chemical shifts were referenced to external $BF_3\cdot OEt_2$ (0.0 ppm) with a negative sign indicating an upfield shift. Mass spectra of potassium organotrifluoroborates were performed using negative ion electrospray at the mass spectrometry facilities at the University of Pennsylvania. Toluene and H_2O were distilled and degassed under argon. Commercially available reagents were used without further purification.

4.2. Preparation of potassium alkyltrifluoroborates

4.2.1. Potassium (6-benzoyloxy)hexyltrifluoroborate (1). This organotrifluoroborate **1** was prepared according to the literature procedure.[12]

4.2.2. Potassium (3-benzoyloxy)propyltrifluoroborate (3). This organotrifluoroborate **3** was prepared according to the literature procedure.[13]

4.2.3. Potassium ethyltrifluoroborate (10). This organotrifluoroborate **10** was prepared according to the literature procedure.[11d]

4.2.4. Potassium (trimethylsilyl)methyltrifluoroborate (11). This organotrifluoroborate **11** was prepared according to the literature procedure.[13]

4.2.5. Potassium octyltrifluoroborate (12). This organotrifluoroborate **12** was prepared according to the literature procedure.[12]

4.2.6. Potassium 5-cyanopentyltrifluoroborate (13). This organotrifluoroborate **13** was prepared according to the literature procedure.[9]

4.2.7. Potassium 5-bromopentyltrifluoroborate (14). This organotrifluoroborate **14** was prepared according to the literature procedure.[9]

4.2.8. Potassium (5-oxo)hexyltrifluoroborate (15). This organotrifluoroborate **15** was prepared according to the literature procedure.[12]

4.2.9. Potassium methyl 6-(trifluoroborato)hexanoate (16). To a solution of potassium *trans*-1-hex-5-enoic acid trifluoroborate methyl ester[14] (234 mg, 1 mmol) in MeOH (10 mL) was added 10% Pd/C (23 mg, 10 wt % of substrate). The reaction mixture was vigorously stirred at room temperature under ordinary hydrogen pressure (balloon). After 10 h, the reaction mixture was filtered off using Celite and then the solvent was removed under high vacuum. The crude solid was purified by dissolving in a minimal amount of dry acetone (1 mL) and precipitating with ether (15 mL) to obtain the desired pure compound **16** as a white solid (234 mg, 99% yield). Mp=183–185 °C. ^1H NMR (500 MHz, acetone-d_6) δ 3.59 (s, 3H), 2.23 (t, 2H, J= 7.5 Hz), 1.54 (m, 2H), 1.25 (m, 4H), 0.12 (br s, 2H, CH_2–BF_3K). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 173.5, 50.4, 33.7, 32.8, 25.2, missing B-CH_2. ^{19}F NMR (470.8 MHz, acetone-d_6) δ −141.4. ^{11}B NMR (128.4 MHz, acetone-d_6) δ 5.80. FTIR (neat) ν 2921, 1737, 1438, 1264, 1068, 960, 883 cm^{-1}. HRMS (ESI): m/z calcd for $C_7H_{13}BF_3O_2$ $[M-K^+]^-$ 197.0961, found 197.0952.

4.2.10. Potassium 3,4-dihydroxybutyltrifluoroborate (17). This organotrifluoroborate **17** was prepared according to the literature procedure.[8]

4.2.11. Potassium 4-phenylbutyltrifluoroborate (18). To a solution of 4-phenyl-1-butene (660 mg, 5 mmol) in CH_2Cl_2 (20 mL) was added a solution of $HBBr_2 \cdot SMe_2$ (1 M in CH_2Cl_2, 5 mL, 5 mmol) at room temperature. The resulting suspension was stirred at 40 °C for 15 h and then allowed to cool to room temperature. The mixture was cooled further to 0 °C, and H_2O (5 mL) and ether (10 mL) were slowly added. After the suspension was stirred for 30 min, the solvent was evaporated. The residual solids were dissolved in ether (20 mL), and KHF_2 (1.2 g, 15 mmol) was added followed by the addition of H_2O (1 mL) over 1 h. After 30 min, all the solvent was removed under high vacuum. The resulting white solid was purified by dissolving in a minimal amount of dry acetone (5 mL) and precipitating with ether (25 mL) to obtain the desired pure compound **18** as a white solid (504 mg, 42% yield). Mp>250 °C. ^{1}H NMR (500 MHz, acetone-d_6) δ 7.23–7.09 (m, 5H), 2.55 (t, 2H, J=7.8 Hz), 1.56 (m, 2H), 1.33 (m, 2H), 0.20 (m, 2H, –CH_2–BF_3K). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 143.7, 128.3, 128.0, 125.1, 36.2, 35.7, 25.4, missing B-CH_2. ^{19}F NMR (470.8 MHz, acetone-d_6) δ −141.3. ^{11}B NMR (128.4 MHz, acetone-d_6) δ 5.80. FTIR (neat) ν 2917, 2849, 1453, 1344, 1291, 1212, 1095, 1038, 936, 846, 742, 696 cm^{-1}. HRMS (ESI): m/z calcd for $C_{10}H_{13}BF_3$ $[M-K^+]^-$ 201.1062, found 201.1060.

4.2.12. Potassium 2-phenylethyltrifluoroborate (19). This organotrifluoroborate **19** was prepared according to the literature procedure.[12,15]

4.2.13. Potassium 3-phenylsulfenylpropyltrifluoroborate (20). This organotrifluoroborate **20** was prepared according to the literature procedure.[13]

4.3. Cross-coupling reactions

4.3.1. General procedure. To a 10×75 mm test tube were added the potassium alkyltrifluoroborate (0.11 mmol), Cs_2CO_3 (97.8 mg, 0.3 mmol), $PdCl_2(dppf) \cdot CH_2Cl_2$ (8.2 mg, 0.01 mmol), and alkenyl bromide (0.1 mmol) with a stirring bar. The reaction mixture was purged with N_2. Degassed toluene (0.6 mL) and H_2O (0.2 mL) were added and the mixture was heated in an oil bath at 80 °C. The reaction was monitored by TLC. After the alkenyl bromide was totally consumed, the reaction mixture was cooled to room temperature and was diluted with ethyl acetate (2 mL). The organic layer was filtered through a small amount of silica gel and evaporated under reduced pressure to give the crude product. The pure product was isolated by preparation TLC (500 μm).

4.3.1.1. 6-(2-Methyl-5-oxo-cyclopent-1-enyl)hexyl benzoate (2). The title compound was obtained as a colorless oil (22.1 mg, 74% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium (6-benzoyloxy)hexyltrifluoroborate (**1**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, 2H, J=8.4 Hz), 7.55 (t, 1H, J=7.4 Hz), 7.44 (t, 2H, J=7.4 Hz), 4.30 (t, 2H, J=6.7 Hz), 2.48 (m, 2H), 2.35 (m, 2H), 2.18 (t, 2H, J=6.9 Hz), 2.04 (s, 3H), 1.76 (m, 2H), 1.48–1.32 (m, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.6, 170.0, 166.6, 140.5, 132.8, 130.5, 129.5, 128.3, 65.0, 34.3, 31.5, 29.2, 28.6, 28.2, 25.9, 22.9, 17.2. FTIR (neat) ν 2933, 2857, 1717, 1697, 1646, 1451, 1385, 1274, 1113, 712 cm^{-1}. HRMS (ESI): m/z calcd for $C_{19}H_{25}O_3$ $[M+H]^+$ 301.1804, found 301.1804.

4.3.1.2. 7,8-Dimethylnon-7-enyl benzoate (4). The title compound was obtained as a colorless oil (25.5 mg, 93% yield) using 2-bromo-3-methyl-2-butene and potassium (6-benzoyloxy)hexyltrifluoroborate (**1**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, 2H, J=8.4 Hz), 7.54 (t, 1H, J=7.4 Hz), 7.43 (t, 2H, J=7.6 Hz), 4.31 (t, 2H, J=6.7 Hz), 2.02 (t, 2H, J=6.8 Hz), 1.77 (m, 2H), 1.63 (s, 6H), 1.62 (s, 3H), 1.45 (m, 2H), 1.38–1.34 (m, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 167.0, 133.1, 130.9, 129.9, 128.7, 128.2, 124.2, 65.5, 34.7, 29.6, 29.1, 28.5, 26.4, 20.9, 20.5, 18.7. FTIR (neat) ν 2927, 2857, 1721, 1602, 1451, 1385, 1372, 1274, 1114, 1070, 1026, 710 cm^{-1}. HRMS (CI): m/z calcd for $C_{18}H_{26}O_2$ $[M]^+$ 274.1933, found 274.1933.

4.3.1.3. (*Z*)-12-(*tert*-Butyldimethylsilyloxy)dodec-7-enyl benzoate (5). The title compound was obtained as a colorless oil (32.7 mg, 78% yield) using ((*Z*)-6-bromohex-5-enyloxy)-(*tert*-butyl)dimethylsilane and potassium (6-benzoyloxy)-hexyltrifluoroborate (**1**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, 2H, J=8.4 Hz), 7.54 (t, 1H, J=7.4 Hz), 7.44 (t, 2H, J=7.6 Hz), 5.35 (m, 2H), 4.31 (t, 2H, J=6.7 Hz), 3.60 (t, 2H, J=6.6 Hz), 2.03 (m, 4H), 1.76 (m, 2H), 1.52 (m, 2H), 1.45 (m, 2H), 1.37 (m, 6H), 0.88 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.7, 132.8, 130.5, 129.8, 129.5, 128.3, 65.1, 63.1, 33.3, 32.5, 29.6, 28.9, 28.7, 28.2, 27.1, 27.0, 26.0, 25.3, 18.3, −5.2. FTIR (neat) ν 2930, 2857, 1722, 1452, 1387, 1273, 1255, 1109, 836, 775, 710 cm^{-1}. HRMS (CI): m/z calcd for $C_{25}H_{43}O_3Si$ $[M+H]^+$ 419.2981, found 419.2991.

4.3.1.4. 4-Cyclohexylidenebutyl benzoate (6). The title compound was obtained as a pale yellow oil (21.2 mg, 82% yield) using bromomethylenecyclohexane and potassium (3-benzoyloxy)propyltrifluoroborate (**3**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, 2H, J=8.4 Hz), 7.55 (t, 1H, J=7.4 Hz), 7.43 (t, 2H, J=7.6 Hz), 5.10 (t, 1H, J=7.1 Hz), 4.31 (t, 2H, J=6.6 Hz), 2.15 (q, 2H, J=7.2 Hz), 2.11 (m, 2H), 2.07 (m, 2H), 1.80 (p, 2H, J=6.9 Hz), 1.52–1.46 (m, 6H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.7, 140.9, 132.8, 130.5, 129.5, 128.3, 119.7, 64.5, 37.2, 29.0, 28.6, 27.8, 26.9, 23.4. FTIR (neat) ν 2927, 2852, 1720, 1450, 1273, 1115, 1069, 1026, 710 cm^{-1}. HRMS (CI): m/z calcd for $C_{17}H_{23}O_2$ $[M+H]^+$ 259.1698, found 259.1706.

4.3.1.5. (*E*)-4-Formyl-5-phenylpent-4-enyl benzoate (7). The title compound was obtained as a pale yellow oil (20.2 mg, 69% yield) using α-bromocinnamaldehyde and potassium (3-benzoyloxy)propyltrifluoroborate (**3**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.04 (d, 2H, J=8.4 Hz), 7.57 (t, 1H, J=7.4 Hz), 7.50 (m, 2H), 7.44 (t, 2H, J=7.9 Hz), 7.34 (m, 3H), 7.29 (s, 1H), 4.37 (t, 2H, J=6.1 Hz), 2.75 (t, 2H, J=7.9 Hz), 1.99 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 195.4, 166.5, 150.5, 141.9, 134.6, 132.9, 130.3, 129.7, 129.6, 128.8, 128.3, 64.6, 27.3, 21.6, missing 1C. FTIR (neat) ν 3061, 2956, 1718, 1680, 1624, 1451, 1377, 1274, 1156, 1115, 1070, 1026, 754, 712, 698 cm^{-1}. HRMS (CI): m/z calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1334, found 295.1337.

4.3.1.6. 4-Phenylpent-4-enyl benzoate (8). The title compound was obtained as a colorless oil (14.4 mg, 54% yield) using α-bromostyrene and potassium (3-benzoyloxy)-propyltrifluoroborate (**3**). ^{1}H NMR (500 MHz, $CDCl_3$)

δ 8.04 (d, 2H, J=7.3 Hz), 7.54 (t, 1H, J=7.5 Hz), 7.43 (m, 4H), 7.33 (t, 2H, J=8 Hz), 7.25 (t, 1H, J=8.6 Hz), 5.32 (s, 1H), 5.11 (s, 1H), 4.34 (t, 2H, J=6.5 Hz), 2.68 (t, 2H, J=7.5 Hz), 1.94 (p, 2H, J=6.7 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.6, 147.2, 140.8, 132.8, 130.4, 129.5, 128.4, 128.3, 127.5, 126.1, 113.0, 64.3, 31.7, 27.2. FTIR (neat) ν 3059, 2955, 1718, 1601, 1493, 1451, 1314, 1274, 1115, 1070, 1026, 900, 778, 710 cm^{-1}. HRMS (CI): m/z calcd for $C_{18}H_{19}O_2$ $[M+H]^+$ 267.1385, found 267.1372.

4.3.1.7. 4,5,5-Triphenylpent-4-enyl benzoate (9). The title compound was obtained as a white solid (38.1 mg, 91% yield) using bromotriphenylethylene and potassium (3-benzoyloxy)propyltrifluoroborate (**3**). Mp=89–91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, 2H, J=7.4 Hz), 7.54 (t, 1H, J=7.4 Hz), 7.40 (t, 2H, J=7.6 Hz), 7.29–7.20 (m, 5H), 7.18–7.11 (m, 5H), 7.00 (m, 3H), 6.88 (m, 2H), 4.19 (t, 2H, J=6.3 Hz), 2.63 (m, 2H), 1.80 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 166.5, 143.2, 142.6, 141.8, 140.2, 139.4, 132.8, 130.6, 130.3, 129.6 (2C), 129.3, 128.3, 128.2, 128.0, 127.4, 126.6, 126.4, 125.9, 64.7, 32.5, 28.0. FTIR (neat) ν 3055, 3020, 2957, 1718, 1599, 1491, 1451, 1443, 1314, 1274, 1117, 1070, 1027, 910, 763, 700 cm^{-1}. HRMS (CI): m/z calcd for $C_{30}H_{26}O_2$ $[M]^+$ 418.1933, found 418.1932.

4.3.1.8. 2-Ethyl-3-methylcyclopent-2-enone (21). The title compound was obtained as a colorless oil (10.3 mg, 83% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium ethyltrifluoroborate (**10**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (m, 2H), 2.36 (m, 2H), 2.19 (q, 2H, J=7.6 Hz), 2.05 (s, 3H), 0.97 (t, 3H, J=7.6 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.6, 169.6, 142.0, 34.4, 31.5, 17.0, 16.2, 12.9. FTIR (neat) ν 2966, 2928, 1697, 1646, 1443, 1385, 1348, 1178, 1056, 935 cm^{-1}. HRMS (CI): m/z calcd for $C_8H_{12}O$ $[M]^+$ 124.0888, found 124.0895.

4.3.1.9. 3-Methyl-2-[(trimethylsilyl)methyl]cyclopent-2-enone (22). The title compound was obtained as a colorless oil (17.3 mg, 95% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium (trimethylsilyl)methyltrifluoroborate (**11**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (m, 2H), 2.34 (m, 2H), 1.97 (s, 3H), 1.60 (s, 2H), −0.03 (s, 9H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.2, 165.6, 138.6, 34.1, 31.4, 17.7, 13.3, −1.0. FTIR (neat) ν 2954, 2913, 1697, 1441, 1409, 1383, 1329, 1248, 1181, 1161, 1068, 841, 694 cm^{-1}. HRMS (CI): m/z calcd for $C_{10}H_{18}OSi$ $[M]^+$ 182.1127, found 182.1132.

4.3.1.10. 3-Methyl-2-octylcyclopent-2-enone (23). The title compound was obtained as a pale yellow oil (11.1 mg, 53% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium octyltrifluoroborate (**12**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (m, 2H), 2.35 (m, 2H), 2.16 (t, 2H, J=7.4 Hz), 2.04 (s, 3H), 1.35 (m, 2H), 1.26 (m, 10H), 0.87 (t, 3H, J=6.7 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.7, 170.2, 140.8, 34.3, 31.8, 31.5, 29.6, 29.4, 29.2, 28.4, 23.0, 22.6, 17.2, 14.1. FTIR (neat) ν 2925, 2855, 1701, 1648, 1442, 1385, 1339, 1177, 1073 cm^{-1}. HRMS (CI): m/z calcd for $C_{14}H_{25}O$ $[M+H]^+$ 209.1905, found 209.1903.

4.3.1.11. 6-(2-Methyl-5-oxocyclopent-1-enyl)hexanenitrile (24). The title compound was obtained as a pale yellow oil (16.5 mg, 86% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium 5-cyanopentyltrifluoroborate (**13**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.50 (m, 2H), 2.36 (m, 2H), 2.33 (t, 2H, J=7.1 Hz), 2.19 (m, 2H), 2.05 (s, 3H), 1.66 (m, 2H), 1.43 (m, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.9, 170.7, 140.4, 120.0, 34.6, 31.9, 28.8, 27.7, 25.5, 23.0, 17.6, 17.4. FTIR (neat) ν 2935, 2860, 2244, 1694, 1644, 1442, 1386, 1340, 1178, 1076 cm^{-1}. HRMS (CI): m/z calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1388, found 192.1387.

4.3.1.12. 2-(5-Bromopentyl)-3-methylcyclopent-2-enone (25). The title compound was obtained as a colorless oil (17 mg, 69% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium 5-bromopentyltrifluoroborate (**14**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.39 (t, 2H, J=6.7 Hz), 2.49 (m, 2H), 2.36 (m, 2H), 2.18 (m, 2H), 2.05 (s, 3H), 1.87 (m, 2H), 1.41 (m, 4H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.7, 170.3, 140.3, 34.3, 33.8, 32.5, 31.5, 28.0, 27.4, 22.8, 17.2. FTIR (neat) ν 2934, 2858, 1697, 1645, 1439, 1385, 1299, 1177, 1073, 938 cm^{-1}. HRMS (CI): m/z calcd for $C_{11}H_{18}OBr$ $[M+H]^+$ 245.0541, found 245.0529.

4.3.1.13. 3-Methyl-2-(5-oxohexyl)cyclopent-2-enone (26). The title compound was obtained as a yellow oil (16.8 mg, 87% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium (5-oxo)hexyltrifluoroborate (**15**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49 (m, 2H), 2.43 (t, 2H, J=7.4 Hz), 2.36 (m, 2H), 2.18 (t, 2H, J=7.6 Hz), 2.12 (s, 3H), 2.05 (s, 3H), 1.54 (p, 2H, J=7.6 Hz), 1.38 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.7, 209.0, 170.5, 140.1, 43.4, 34.3, 31.5, 29.9, 27.7, 23.6, 22.7, 17.2. FTIR (neat) ν 2932, 2860, 1711, 1696, 1644, 1441, 1385, 1359, 1178, 1072 cm^{-1}. HRMS (CI): m/z calcd for $C_{12}H_{18}O_2$ $[M]^+$ 194.1307, found 194.1306.

4.3.1.14. Methyl 6-(2-methyl-5-oxocyclopent-1-enyl)-hexanoate (27). The title compound was obtained as a pale yellow oil (14.1 mg, 63% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium methyl 6-(trifluoroborato)hexanoate (**16**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.49 (m, 2H), 2.35 (m, 2H), 2.29 (t, 2H, J=7.5 Hz), 2.16 (t, 2H, J=7.3 Hz), 2.04 (s, 3H), 1.62 (p, 2H, J=7.6 Hz), 1.38 (m, 2H), 1.30 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.7, 174.2, 170.2, 140.4, 51.4, 34.3, 34.0, 31.7, 29.1, 28.0, 24.7, 22.8, 17.2. FTIR (neat) ν 2931, 2858, 1736, 1697, 1644, 1437, 1385, 1175 cm^{-1}. HRMS (CI): m/z calcd for $C_{13}H_{20}O_3$ $[M]^+$ 224.1412, found 224.1405.

4.3.1.15. 2-(3,4-Dihydroxybutyl)-3-methylcyclopent-2-enone (28). The title compound was obtained as a brown oil (17.3 mg, 94% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium 3,4-dihydroxybutyltrifluoroborate (**17**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.78 (br s, 1H, –OH), 3.55 (m, 1H), 3.45 (m, 2H), 2.54 (m, 2H), 2.41 (m, 2H), 2.38–2.30 (m, 2H), 2.09 (s, 3H), 1.53 (m, 1H), 1.40 (m, 1H), missing –OH. ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 211.5, 172.7, 139.9, 70.4, 66.6, 34.2, 31.8, 31.7, 18.3, 17.2. FTIR (neat) ν 3400, 2922, 1680, 1637, 1439, 1388, 1348, 1179, 1047, 865 cm^{-1}. HRMS (CI): m/z calcd for $C_{10}H_{17}O_3$ $[M+H]^+$ 185.1178, found 185.1171.

4.3.1.16. 3-Methyl-2-(4-phenylbutyl)cyclopent-2-enone (29). The title compound was obtained as a colorless oil (14.4 mg, 63% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium 4-phenylbutyltrifluoroborate (**18**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (m, 2H), 7.15 (m, 3H), 2.60 (t, 2H, J=7.7 Hz), 2.46 (m, 2H), 2.35 (m, 2H), 2.20 (t, 2H, J=7.6 Hz), 2.02 (s, 3H), 1.58 (m, 2H), 1.42 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.7, 170.2, 142.6, 140.5, 128.4, 128.2, 125.6, 35.7, 34.3, 31.5, 31.4, 28.0, 22.8, 17.2. FTIR (neat) ν 2956, 2928, 2870, 1694, 1631, 1493, 1451, 1381, 1332, 1175, 748, 700 cm^{-1}. HRMS (CI): m/z calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1592, found 229.1603.

4.3.1.17. 3-Methyl-2-(1-phenylbutyl)cyclopent-2-enone (30). The title compound was obtained as a colorless oil (8.4 mg, 36% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium 4-phenylbutyltrifluoroborate (**18**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.25 (m, 2H), 7.17 (m, 1H), 3.80 (t, 1H, J=7.4 Hz), 2.46 (m, 2H), 2.33 (m, 2H), 2.13–2.01 (s and m, 5H), 1.23 (m, 2H), 0.90 (t, 3H, J=7.3 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.1, 170.9, 143.7, 142.2, 128.2, 128.0, 126.0, 41.5, 34.4, 34.0, 31.9, 21.4, 17.6, 14.0. FTIR (neat) ν 3025, 2930, 2856, 1697, 1644, 1495, 1441, 1385, 1348, 1177, 1073, 748, 699 cm^{-1}. HRMS (CI): m/z calcd for $C_{16}H_{20}O$ $[M]^+$ 228.1514, found 228.1518.

4.3.1.18. 3-Methyl-2-(1-phenylethyl)cyclopent-2-enone (31). The title compound was obtained as a colorless oil (18.5 mg, 92% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium 2-phenylethyltrifluoroborate (**19**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 4H), 7.17 (m, 1H), 4.05 (q, 1H, J=7.3 Hz), 2.46 (m, 2H), 2.35 (m, 2H), 1.94 (s, 3H), 1.54 (d, 3H, J=7.3 Hz). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 208.9, 170.5, 144.2, 143.6, 128.2, 127.3, 125.9, 34.5, 34.3, 31.9, 17.7, missing 1C. FTIR (neat) ν 3026, 2966, 2916, 1694, 1634, 1494, 1450, 1382, 1332, 1297, 1259, 1174, 1093, 1024, 942, 767, 700 cm^{-1}. HRMS (CI): m/z calcd for $C_{14}H_{16}O$ $[M]^+$ 200.1201, found 200.1194.

4.3.1.19. 3-Methyl-2-[3-(phenylthio)propyl]cyclopent-2-enone (32). The title compound was obtained as a yellow oil (22.2 mg, 90% yield) using 2-bromo-3-methyl-2-cyclopenten-1-one and potassium 3-phenylsulfenylpropyltrifluoroborate (**20**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.17 (m, 4H), 7.15 (m, 1H), 2.87 (t, 2H, J=7.2 Hz), 2.48 (m, 2H), 2.35 (m, 2H), 2.32 (t, 2H, J=7.6 Hz), 2.03 (s, 3H), 1.73 (m, 2H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 209.4, 170.9, 139.5, 136.5, 129.1, 128.8, 125.8, 34.3, 33.3, 31.6, 27.5, 22.0, 17.2. FTIR (neat) ν 2916, 1694, 1645, 1480, 1438, 1384, 1302, 1261, 1178, 1075, 740, 691 cm^{-1}. HRMS (CI): m/z calcd for $C_{15}H_{18}OS$ $[M]^+$ 246.1078, found 246.1083.

4.3.2. Reaction on 1.0 mmol scale for the preparation of 6-(2-methyl-5-oxo-cyclopent-1-enyl)hexyl benzoate (2). To a 10 mL round-bottom flask were added the potassium (6-benzoyloxy)hexyltrifluoroborate (**1**) (343 mg, 1.1 mmol), Cs_2CO_3 (978 mg, 3.0 mmol), $PdCl_2(dppf)\cdot CH_2Cl_2$ (82 mg, 0.1 mmol), and 2-bromo-3-methyl-2-cyclopenten-1-one (175 mg, 1.0 mmol) with a stirring bar. The reaction mixture was purged with N_2. Degassed toluene (4 mL) and H_2O (1.4 mL) were added and the mixture was heated in an oil bath at 80 °C. The reaction was monitored by TLC. After 7 h, when the reaction was complete, the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3×5 mL). The combined organic extracts were dried, filtered, and then the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (eluting with hexane/EtOAc=5/2) to obtain the desired compound **2** (233 mg, 78% yield).

Acknowledgements

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-214-C00170). We thank the National Institutes of Health (GM35249), Merck Research Laboratories, Johnson Matthey and Amgen for their generous support.

References and notes

1. (a) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, UK, 1995; (b) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley-Interscience: New York, NY, 2002; (c) *Cross-Coupling Reactions: A Practical Guide*; Miyaura, N., Ed.; Springer: Berlin, 2002; (d) *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: New York, NY, 2004.
2. (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483; (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147–168; (c) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633–9695; (d) Suzuki, A.; Brown, H. C. *Organic Syntheses via Boranes*; Aldrich Chemical Company: Milwaukee, 2003; Vol. 3; (e) Suzuki, A. *Proc. Jpn. Acad., Ser. B Phys. Biol. Sci.* **2004**, *80*, 359–371; (f) Suzuki, A. *Chem. Commun.* **2005**, 4759–4763; (g) Netherton, M. R.; Dai, C.; Neuschütz, K.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 10099–10100; (h) Kirchhoff, J. H.; Dai, C.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 1945–1947; (i) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176–4211.
3. (a) Miyaura, N.; Ishiyama, T.; Ishikawa, M.; Suzuki, A. *Tetrahedron Lett.* **1986**, *27*, 6369–6372; (b) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314–321.
4. (a) Chemler, S. R.; Trauner, D.; Danishefsky, S. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4544–4568 and references therein; (b) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442–4489.
5. (a) Molander, G. A.; Figueroa, R. *Aldrichimica Acta* **2005**, *38*, 49–56; (b) Darses, S.; Genêt, J.-P. *Eur. J. Org. Chem.* **2003**, 4313–4327; (c) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020–3027; (d) Vedejs, E.; Fields, S. C.; Hayashi, R.; Hitchcock, S. R.; Powell, D. R.; Schrimpf, M. R. *J. Am. Chem. Soc.* **1999**, *121*, 2460–2470.
6. (a) Batey, R. A.; MacKay, D. B.; Santhakumar, V. *J. Am. Chem. Soc.* **1999**, *121*, 5075–5076; (b) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Tetrahedron Lett.* **1999**, *40*, 4289–4292; (c) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683–1686; (d) Batey, R. A.; Thadani, A. N.; Smil, D. V.; Lough, A. J. *Synthesis* **2000**, 990–998.

7. Molander, G. A.; Ribagorda, M. *J. Am. Chem. Soc.* **2003**, *125*, 11148–11149.
8. Molander, G. A.; Figueroa, R. *Org. Lett.* **2006**, *8*, 75–78.
9. Molander, G. A.; Ham, J. *Org. Lett.* **2006**, *8*, 2031–2034.
10. Molander, G. A.; Ham, J. *Org. Lett.* **2006**, *8*, 2767–2770.
11. For recent papers, see the following: (a) Molander, G. A.; Felix, L. A. *J. Org. Chem.* **2005**, *70*, 3950–3956; (b) See Ref. 8; (c) Molander, G. A.; Sommers, E. M.; Baker, S. R. *J. Org. Chem.* **2006**, *71*, 1563–1568; (d) Molander, G. A.; Yokoyama, Y. *J. Org. Chem.* **2006**, *71*, 2493–2498; (e) Molander, G. A.; Fumagalli, T. *J. Org. Chem.* **2006**, *71*, 5743–5747.
12. Molander, G. A.; Ito, T. *Org. Lett.* **2001**, *3*, 393–396.
13. Molander, G. A.; Yun, C.-S.; Ribagorda, M.; Biolatto, B. *J. Org. Chem.* **2003**, *68*, 5534–5539.
14. Molander, G. A.; Bernardi, C. R. *J. Org. Chem.* **2002**, *67*, 8424–8429.
15. Akiba, K.; Iseki, Y.; Wada, M. *Tetrahedron Lett.* **1982**, *23*, 429–432.