A novel Suzuki-type cross-coupling reaction of cyclopropylboronic esters with benzyl bromides

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The Suzuki-type coupling reaction of cyclopropylboronic acids (esters) with benzyl bromides readily takes place by using Ag_2O with KOH as the base. The reaction rate and the cross-coupling product yields of cyclopropylboronate esters of ethylene glycol or propane-1,3-diol were higher and better than those of cyclopropylboronic acids. However, the coupling reaction of the cyclopropylboronate esters of glycol with larger substituents was sluggish. The highly optically active benzyl-substituted cyclopropanes could be obtained by the coupling reactions of corresponding optically active cyclopropylboronate esters with benzyl bromides. A novel, ideal method for preparing stereo-defined benzyl-substituted cyclopropanes, especially optically active benzyl-substituted cyclopropanes, is described here.

Introduction

The cross-coupling reactions of organometallic reagents with electrophiles in the presence of transition metals are versatile and powerful methods for the formation of carbon–carbon bonds.[1] Miyaura and Suzuki reported a number of palladium cross-coupling reactions of aryl-, alkenyl-, and alkyl-boron compounds with electrophiles and showed that the cross-coupling reactions of organoboron compounds had many advantages.[2] Recently the Suzuki-type coupling reaction of cyclopropylboronates attracted increasing interest from chemists[3] because it is easily obtained by the stereo-defined cyclopropanation of the corresponding alkenylboronic acids (esters),[4] which are readily prepared by the hydroboration of alkynes or other convenient routes.[5] Moreover, the cyclopropylboronic acids are very stable in air, may be purified by recrystallization from water, and are easy to handle.

Catalytic cross-coupling reactions using benzyl halides as electrophiles with various aryl metallic reagents have been reported.[6] Suzuki and co-workers also reported the coupling reaction of alkenylboranes with allylic bromides and benzyl bromides,[7] and more recently Chowdhury and Georghiou have reported the catalyzed cross-coupling between phenyl- or naphthylboronic acids and benzyl bromide.[8] However, to the best of our knowledge, there are few reports about the coupling reactions of cyclopropyl metallic compounds with benzyl bromide, although some reports of cross-coupling of cyclopropyl metallic compounds with aryl and cyclopropyl halides in the presence of palladium(0) have appeared in the literature.[3,9] Our group have previously studied the cross-coupling of cyclopropylboronic acids with aryl bromides and bromoacrylates, and are interested in expanding this study by examining the chemical transformation of cyclopropylboronic acids (esters) in cross-coupling reactions. The possibility of cross-coupling of cyclopropylboronic acids (esters) and benzyl bromides was also investigated and various reaction conditions were employed. Herein we wish to report the experimental results.

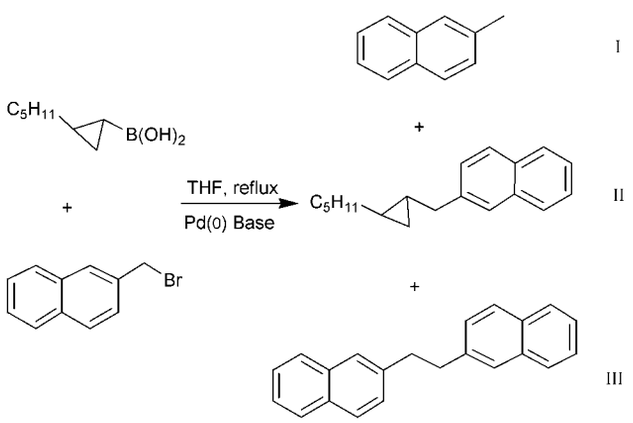
Results and discussion

Initially, because of the sp^2 character of the cyclopropyl group,[10] the possibility of reaction of *trans*-2-pentylcyclopropylboronic acids with 2-(bromomethyl)naphthalene was explored. Under the conditions used in the coupling of alkenylboranes with the benzyl bromides, no desired cross-coupling product (II) was detected, but reduction (I) and homocoupling (III) products of 2-(bromomethyl)naphthalene were obtained (Scheme 1). Next, various coupling conditions were explored and the results are shown in Table 1.

Table 1 Effect of base and solvent on the cross-coupling reaction of *trans*-2-pentylcyclopropylboronic acids with 2-(bromomethyl)naphthalene[a]

Entry	Conditions	Yield of (II) (%)[b]
1	KOH, 3% $Pd(PPh_3)_4$	0
2	$K_3PO_4 \cdot 3H_2O$, 3% $(PPh_3)_4$	0
3	DME, Bu^tOK, 3% $Pd(PPh_3)_4$	Trace
4	TlOH, 3% $Pd(PPh_3)_4$	0
5	Ag_2O, 3% $Pd_2(dba)_3 \cdot CHCl_3$, 30% $AsPh_3$	33
6	Ag_2O, Cs_2CO_3, 3% $PdCl_2(dppf)$[c]	46
7	Ag_2O, KOH, 3% $PdCl_2(dppf)$	68

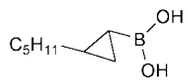
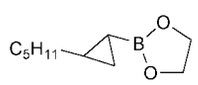
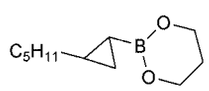
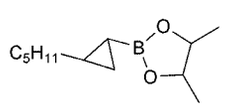
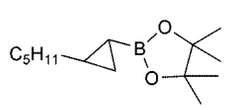
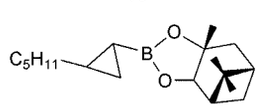
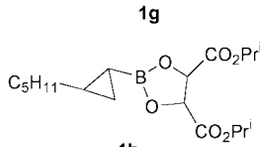
[a] All the reactions were carried out using a mixture of the *trans*-2-pentylcyclopropylboronic acid (1.1 mmol), 2-(bromomethyl)-naphthalene (1.0 mmol) and base (2 equiv.) in 4 mL solvent, refluxed for 16 h (except for entry 2, at 80 °C), under nitrogen atmosphere. [b] Isolated yields. [c] dppf is 1,1′-bis(diphenylphosphino)ferrocene.



Scheme 1

Table 1 demonstrates that the coupling reaction does not proceed smoothly in the presence of general bases such as KOH and $K_3PO_4 \cdot 3H_2O$, (entries 1 and 2). This is probably due to the

Table 2 The effect of the different *trans*-2-pentylcyclopropylboron compounds on the cross-coupling reaction with 2-(bromomethyl)naphthalene

Entry[a]	2-Pentylcyclopropylboron compounds	Yield of reduction product (I) (%)[b]	Yield of cross-coupling product (II) (%)[b]	Yield of homocoupling product (III) (%)[b]
1	 **1a**	7	71	22
2	 **1b**	6	82	12
3	 **1c**	6	84	10
4	 **1d**	8	70	22
5	 **1e**	7	21	65
6	 **1g**	7	Trace	73
7	 **1h**	7	23	69

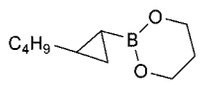
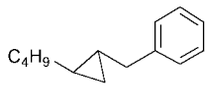
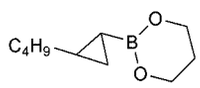
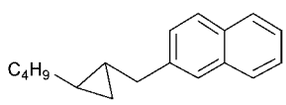
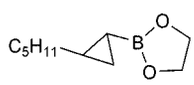
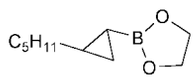
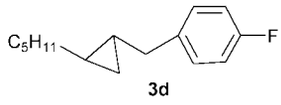
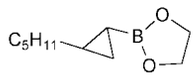
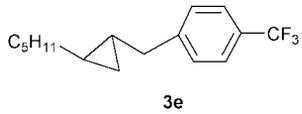
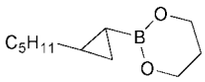
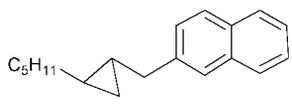
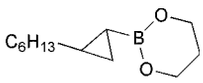
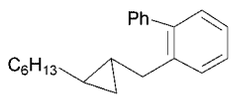
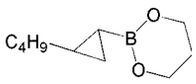
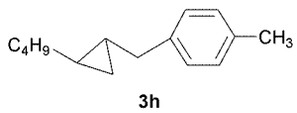
[a] All the reactions were carried out using a mixture of cyclopropylboronate (1.1 mmol) and 2-(bromomethyl)naphthalene (1.0 mmol), 2 equiv. Ag_2O, 2 equiv. KOH (based on 2-(bromomethyl)naphthalene) and 3% $PdCl_2$(dppf) in 4 mL THF, refluxed for 16 h under a nitrogen atmosphere. [b] Determined by GC-MS.

difficulty involved in transmetallation between the cyclopropyl group on boron and the RPdX species because of the very low nucleophilicity of the organic group on boron. Even using strong bases, such as KOBu^t, only a trace of the cross-coupling product was obtained (entry 3), although Hildebrand and Marsden reported that KOBu^t in DMF was a good combination for the coupling reactions of cyclopropylboronate esters with aryl halides.[3a] Kishi and co-workers have reported in their work on palytoxin synthesis,[11a] that Ag_2O and TlOH in particular dramatically enhance the rate of some couplings of vinylboronic acids, however using TlOH as the base in our cross-coupling reaction proved unsuccessful (entry 4). Fortunately, the use of Ag_2O greatly accelerated the reaction (entries 5 and 6) and the optimum yield obtained in the reaction was achieved using the combination of the bases Ag_2O and KOH (entry 7).

Charette and De Freitas-Gil investigated the effect of cyclopropylboronic acid and its boronate ester derivatives on the cross-coupling reaction of cyclopropylboronate compounds with iodocyclopropanes and found that the nature of the ester group of the boronate ester affected the rate and yield of the cross-coupling reaction.[3b] Thus the effect of different *trans*-2-pentylcyclopropylboron compounds on the cross-coupling reactions of 2-(bromomethyl)naphthalene was studied. The results are summarized in Table 2.

The results shown in Table 2 suggest that although in the case of the cyclopropylboronic acid, the cross-coupling product was detected in 71% yield as the main product (entry 1), the cyclopropylboronate esters derived from propane-1,3-diol (entry 3) or ethylene glycol (entry 2) more readily undergo cross-coupling with 2-(bromomethyl)naphthalene to give higher yields of cross-coupling products (II) and less of the by-products (I and III). This observation is consistent with the findings of Charette and De Freitas-Gil in the cross-coupling reaction between iodocyclopropanes and cyclopropylboronate esters.[3b] However, by increasing the number of substituted groups, increasing the steric hindrance, on the cyclopropylboronate esters derived from ethylene glycol, the yield of the cross-coupling product (II) was clearly decreased (entries 4–7). These facts may be rationalized by the assumption that the steric hindrance of larger groups on the cyclopropylboronate esters of ethylene glycol does not favor the transmetallation, which is essential in the catalytic cross-coupling process between cyclopropylboron compounds and 2-(bromomethyl)naphthalene. Pietruszka and co-workers also found that the *trans*-cyclopropylboronate esters with bulky groups on the glycol esters underwent Suzuki-type cross-coupling reactions with aryl bromides only with some difficulty.[12b,d] It is quite obvious that the nature of the ester group of the boronate ester derivative plays a very important role in the coupling process.

Table 3 Silver oxide assisted palladium-catalyzed cross-coupling reaction of cyclopropylboronate esters with various benzyl bromides[a]

Entry	Cyclopropylboronate esters	Benzyl bromides[c]	Products	Yields[b] (%)
1		Benzyl bromide	 **3a**	75
2		2-(Bromomethyl)naphthalene	 **3b**	76
3		3-Methoxybenzyl bromide	 **3c**	66
4		4-Fluorobenzyl bromide	 **3d**	71
5		4-(Trifluoromethyl)benzyl bromide	 **3e**	70
6		2-(Bromomethyl)naphthalene	 **3f**	72
7		2-(Bromomethyl)biphenyl	 **3g**	76
8		4-Methylbenzyl bromide	 **3h**	69

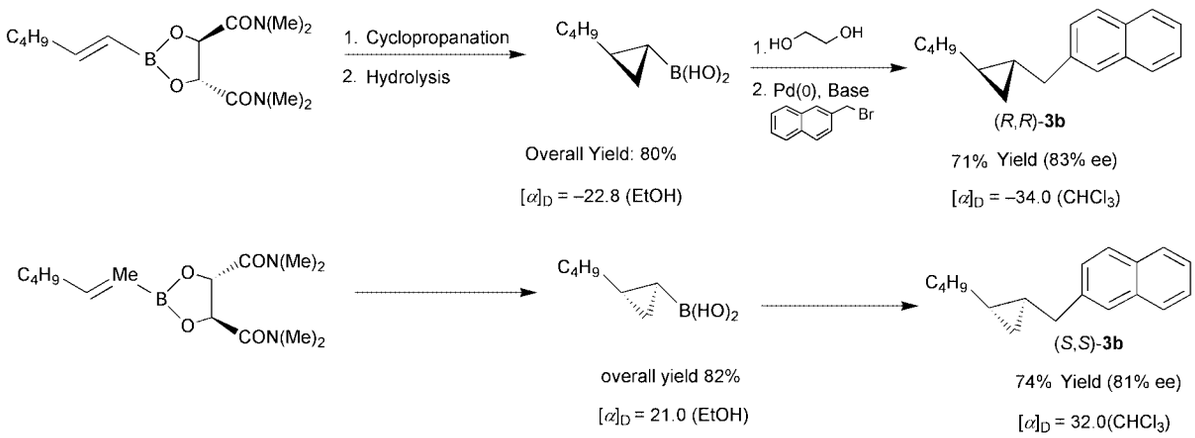
[a] All the reactions were carried out using a mixture of cyclopropylboronate esters (1.4 mol) and various benzyl bromides (1.0 mol), 2 equiv. Ag_2O, 2 equiv. KOH (based on benzyl bromides) and 3% $PdCl_2$(dppf) in 4 mL THF, refluxed for 16–24 h, under a nitrogen atmosphere. [b] Yields of isolated product based on the benzyl bromide. [c] All the products were identified by ^{1}H NMR, IR and mass spectral and elemental analysis or HRMS.

Thus, the coupling reaction of various benzyl bromides with appropriate cyclopropylboronate esters was accomplished under optimized conditions and the results are shown in Table 3.

It is shown in Table 3 that the cross-coupling reaction of cyclopropylboron compounds with all benzyl bromides proceeds readily. Thus the reaction was general, the conditions were also mild and the yield of the desired product was satisfactory. The ^{1}H NMR spectrum of the products and 2D ^{1}H NMR of some of the products showed that the configurations of the cyclopropyl groups of the organoboron moiety were retained.

According to our previous procedure,[12c] the asymmetric cyclopropanation of (*E*)-hexenylboronic ester with the optically pure (+)-*N*,*N*,*N*′,*N*′-tetramethyltartaric acid diamide (+)-TMTA as the chiral auxiliary, followed by hydrolysis, afforded the corresponding (1*R*,2*R*)-butylcyclopropylboronic acids (the (1*S*,2*S*)-isomer was obtained by using (−)-TMTA as the auxiliary). The cross-coupling reaction of 2-(bromomethyl)-naphthalene with optically active cyclopropylboronate esters of ethylene glycol, which were generated from the previously mentioned optically active cyclopropylboronic acids, was also accomplished to give the corresponding chiral 2-naphthylmethyl-substituted cyclopropanes with an enantiomeric excess of approximately 83% (Scheme 2).

In summary, we have found that the Suzuki-type coupling reaction of cyclopropylboronate esters with various benzyl bromides can be accomplished by the use of Ag_2O plus KOH as the base, and the reaction rate and the cross-coupling product yield of the cyclopropylboronate esters derived from ethylene glycol or propane-1,3-diol seem to be higher than that of cyclopropylboronic acid. The cyclopropylboronate esters derived from glycol with both more and bulkier substituent proved more difficult to react. Highly optically active cyclopropylboronate also undergoes the Suzuki-type cross-coupling reaction with benzyl bromide to give the corresponding optically active benzyl-substituted cyclopropanes. Additionally, the reaction conditions were mild and the yield of the products was satisfactory, the reaction procedure may be a novel, ideal method for preparing stereo-defined benzyl-substituted cyclopropanes, especially optically active benzyl-substituted cyclopropanes.



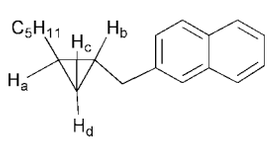
Scheme 2

Experimental

^{1}H NMR spectra were recorded on VXL-300 instruments using TMS as internal standard in $CDCl_3$ solution. ^{13}C NMR spectra were recorded on a Bruker AMX-300 instrument (75.4 MHz) using $CDCl_3$ as internal standard. ^{19}F NMR spectra were recorded on VXL-300 instruments using TFA as external standard in $CDCl_3$ solution. Infrared spectra were recorded on a Perkin-Elmer 983 FI-IR spectrometer as liquid films on potassium bromide plates. Mass spectral and GC-MS measurements were performed on a Finnigan GC-MS-4021 spectrometer. Elemental analyses were carried out on a MOD-1606 elemental analyzer. High-resolution mass spectra were recorded on an HP5989A mass spectrometer. The ee values of products were determined by HPLC with a Chiralcel OJ column; optical rotations were measured using a Perkin-Elmer 241 MC polarimeter with a thermally jacketed 10 cm cell at 20 °C (concentration given as g per 100 mL). $[\alpha]_D^{20}$ has units of 10^{-1} deg cm^2 g^{-1}. All the reactions were performed under a nitrogen atmosphere. All the benzyl bromides were commercially available and used without further purification. The racemic cyclopropylboronates[4] and optically active cyclopropylboronic acids[12c] were prepared according to the literature procedures.

General procedure for the cross-coupling reaction

The preparation of *trans*-2-[(2-pentylcyclopropyl)methyl]naphthalene (**3f**) is representative of the method used. To a solution of 2-(bromomethyl)naphthalene (1.0 mmol, 221 mg) in THF (4 mL), *trans*-2-pentylcyclopropylboronic acid ester (1.4 mmol, 274 mg), Ag_2O (2 mmol, 463 mg), KOH (2 mmol, 112 mg) and $PdCl_2$(dppf) (0.03 mmol, 22 mg) were added under a nitrogen atmosphere. The reaction mixture was refluxed for 16 h, then cooled to room temperature and diluted with petroleum ether, washed with saturated brine and dried over magnesium sulfate. The solvents were removed *in vacuo* and the residue purified by column chromatography, eluting with petroleum ether (60–90 °C) to yield *trans*-2-[(2-pentylcyclopropyl)methyl]naphthalene (**3f**) as a colorless oil (179 mg, 71%); ^{1}H NMR (CCl_3D–TMS) δ 7.72–7.81 (m, 3H), 7.67 (s, 1H), 7.24–7.46 (m, 3H), 2.70 (d, J = 6.9 Hz, 2H), 1.32–1.34 (q, J = 6.2 Hz, 2H), 1.21–1.26 (m, 6H), 0.82 (t, J = 6.8 Hz, 3H), 0.80–0.88 (m, 1H$_b$, overlapped with CH_3), 0.68–0.73 (m, 1H$_a$), 0.39–0.41 (dt, J = 4.6, 9.0 Hz, 1H$_d$), 0.29–0.35 (dt, J = 4.6, 9.2 Hz, 1H$_c$); ^{13}C NMR δ 12.147, 14.132, 19.150, 19.632, 22.782, 29.333, 31.783, 34.225, 40.323, 125.083, 125.856, 127.555, 127.681, 127.722, 132.148, 133.757; MS m/z 252 (M$^+$, 29.40), 141 (100), 154 (48.89%); IR (neat) 3058, 2924, 1602, 1509, 812, 744 cm^{-1}. Calcd for $C_{19}H_{24}$: C, 90.41; H, 9.59. Found: C, 90.38; H, 9.30%. In the 2D ^{1}H NMR, the proton H$_a$ showed strong NOE interaction with proton H$_d$ but very weak NOE interaction with H$_c$ and H$_b$.



***trans*-1-[(2-Butylcyclopropyl)methyl]-4-methylbenzene (3h).** Colorless liquid, yield 69%; ^{1}H NMR (CCl_3D–TMS) δ 7.08–7.14 (m, 5H), 2.47–2.55 (dq, J = 6.8, J_{AB} = 14.6 Hz, 2H), 2.32 (s, 3H), 1.20–1.34 (m, 6H), 0.87 (t, J = 7 Hz, 3H), 0.68 (m, 1H$_b$), 0.59 (m, 1H$_a$), 0.33 (dt, J = 4.6, 9.2 Hz, 1H$_c$), 0.27 (dt, J = 4.6, 9.5 Hz, 1H$_d$); MS m/z 202 (M$^+$), 105 (100), 118 (40.74%); IR (neat) 3071, 2960, 1600 cm^{-1}. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.10; H, 11.06%.

***trans*-1-[(2-Hexylcyclopropyl)methyl]-2-phenylbenzene (3g).** Colorless liquid, yield 76%; ^{1}H NMR (CCl_3D–TMS) δ 7.21–7.44 (m, 9H), 2.44–2.52 (dq, J = 6.6, J_{AB} = 15.0 Hz, 2H), 1.16–1.26 (m, 10H), 0.85 (t, J = 6.8 Hz, 3H), 0.55 (m, 1H$_b$), 0.41 (m, 1H$_a$), 0.18 (t, J = 6.5 Hz, 1H$_c$ + 1H$_d$); MS m/z 292 (M$^+$), 179 (100), 180 (55.49%); IR (neat) 3061, 2924, 1479 cm^{-1}. Calcd for $C_{20}H_{24}$: C, 90.35; H, 9.65. Found: C, 90.01; H, 9.92%. In the 2D ^{1}H NMR, the proton H$_a$ showed strong NOE interaction with proton H$_d$ but very weak NOE interaction with H$_b$.

***trans*-1-[(2-Pentylcyclopropyl)methyl]-4-trifluoromethylbenzene (3e).** Colorless liquid, yield 70%; ^{1}H NMR (CCl_3D–TMS) δ 7.53 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 2.56–2.64 (dq, J = 7.0, J_{AB} = 15.0 Hz, 2H), 1.15–1.36 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H), 0.67 (m, 1H$_b$), 0.58 (m, 1H$_a$), 0.28–0.38 (m, 1H$_c$ + 1H$_d$); ^{19}F NMR (CCl_3D) δ 15 (s); MS m/z 270 (M$^+$), 172 (100), 186 (41.59%); IR (neat) 3065, 2926, 1327 cm^{-1}. HRMS for $C_{16}H_{21}F_3$, calcd: 270.1595. Found: 270.1612.

***trans*-1-[(2-Pentylcyclopropyl)methyl]-4-fluorobenzene (3d).** Colorless liquid, yield 71%; ^{1}H NMR (CCl_3D–TMS) δ 7.15–7.20 (m, 2H), 6.92–7.01 (m, 2H), 2.51–2.60 (dq, J = 7.0, J_{AB} = 14.8 Hz, 2H), 1.20–1.46 (m, 8H), 0.98 (t, J = 6.8 Hz, 3H), 0.72 (m, 1H$_b$), 0.61 (m, 1H$_a$), 0.28–0.36 (m, 1H$_c$ + 1H$_d$); ^{19}F NMR (CCl_3D) δ −41 (s); MS m/z 220 (M$^+$), 109 (100), 122 (41.59%); IR (neat) 3045, 2926, 1512 cm^{-1}. HRMS for $C_{15}H_{21}F$, calcd: 220.1627. Found: 220.1647.

***trans*-1-[(2-Pentylcyclopropyl)methyl]-3-methoxybenzene (3c).** Colorless liquid, yield 66%; ^{1}H NMR (CCl_3D–TMS) δ 7.17–7.21 (m, 1H), 6.82–6.88 (m, 2H), 6.67–6.71 (m, 1H), 3.80 (s, 3H), 2.56 (d, J = 6.8 Hz, 2H), 1.21–1.49 (m, 8H), 0.96 (t, J = 6.8 Hz, 3H), 0.74 (m, 1H$_b$), 0.62 (m, 1H$_a$), 0.30–0.43 (m, 1H$_c$ + 1H$_d$); MS m/z 232 (M$^+$), 121 (100), 57 (19.63%); IR (neat) 3004, 2926, 1268 cm^{-1}. HRMS for $C_{16}H_{24}O$, calcd: 232.1827. Found: 232.1816.

***trans*-2-[(2-Butylcyclopropyl)methyl]naphthalene (3b).** Colorless liquid, yield 76%; ^{1}H NMR (CCl_3D–TMS) δ 7.71–7.78 (m, 3H), 7.62 (s, 1H), 7.33–7.45 (m, 3H), 2.71 (d, J = 6.8 Hz, 2H), 1.22–1.39 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H), 0.84–0.90 (m, $1H_b$, overlapped with CH_3), 0.61–0.65 (m, $1H_a$), 0.38–0.44 (dt, J = 4.6, 9.1 Hz, $1H_c$), 0.29–0.35 (dt, J = 4.6, 9.2 Hz, $1H_d$); MS m/z 238 (M^+, 29.40), 141 (100), 154 (46.20%); IR (neat) 3060, 2957, 1602, 814 cm^{-1}. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.48; H, 9.36%.

The optically active coupling products (*R*,*R*)-**3b** and (*S*,*S*)-**3b** were prepared similarly by the general procedure for the cross-coupling reaction using the corresponding optically active cyclopropylboronate. (*R*,*R*)-**3b**: $[a]_D^{20}$ = 32.0, (c = 0.230, $CHCl_3$); (*S*,*S*)-**3b**: $[a]_D^{20}$ = −34, (c = 0.555, $CHCl_3$). The value of ee determined by Chiralcel OJ; mobile phase C_6H_{14}–IPA = 100 : 1; detector UV 254 nm; flow rate 0.7 ml min^{-1}; t_R/min = 12.343 (*R*,*R*) and 13.203 (*S*,*S*).

***trans*-1-[(2-Butylcyclopropyl)methylbenzene (3a).** Colorless liquid, yield 75%; ^{1}H NMR (CCl_3D–TMS) δ 7.15–7.30 (m, 5H), 2.56 (d, J = 6.8 Hz, 2H), 1.20–1.36 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H), 0.78–0.84 (m, $1H_b$, overlapped with CH_3), 0.64–0.68 (m, $1H_a$), 0.38–0.46 (m, $1H_c$ + $1H_d$); MS m/z 188 (M^+), 104 (100), 91 (97.57%); IR (neat) 3063, 2922, 1496, 697 cm^{-1}. Calcd for $C_{14}H_{20}$: C, 89.30; H, 10.70. Found: C, 89.58; H, 10.54%.

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References

1 (*a*) J. P. Collon and L. S. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1980; (*b*) F. R. Hartley, *The Chemistry of the Metal–Carbon Bond*, ed. S. Patai, Wiley, New York, 1985; (*c*) *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Vol. 3; (*d*) J. Tusiji, *Palladium Reagents and Catalysts. Innovations in Organic Synthesis*, John Wiley, Chichester, 1995.

2 (*a*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (*b*) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147.

3 (*a*) J. P. Hildebrand and S. P. Marsden, *Synlett*, 1996, 893; (*b*) A. B. Charette and R. P. De Freitas-Gil, *Tetrahedron Lett.*, 1997, **38**, 2809; (*c*) X.-Z. Wang and M.-Z. Deng, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 2663; (*d*) S.-M. Zhou, Y.-L. Yan and M.-Z. Deng, *Synlett*, 1998, 198; (*e*) H.-R. Ma, X.-H. Wang and M.-Z. Deng, *Synth. Commun.*, 1999, **29**, 2477.

4 P. Fontani, B. Carboni, M. Vaultier and G. Mass, *Synthesis*, 1991, 605.

5 (*a*) H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, 1972, **94**, 4370; (*b*) H. C. Brown, N. G. Bhat and V. Somayayi, *Organometallics*, 1983, **2**, 1311; (*c*) C. E. Tucker, J. Davidson and J. Knochel, *J. Org. Chem.*, 1992, **57**, 3483; (*d*) H. C. Brown and T. Imai, *Organometallics*, 1984, **3**, 1392; (*e*) A. Kamabuchi, T. Moria, N. Miyaura and A. Suzuki, *Synth. Commun.*, 1993, **23**, 2635; (*f*) M. Serbnik, N. G. Bhat and H. C. Brown, *Tetrahedron Lett.*, 1988, **29**, 2635.

6 (*a*) S. Kamlage, M. Sefkow and M. G. Peter, *J. Org. Chem.*, 1999, **64**, 2938, and references cited therein; (*b*) R.-J. de Lang, M. J. C. M. van Hooijdonk and L. Brandsma, *Tetrahedron*, 1998, **54**, 2953.

7 N. Miyaura, T. Yano and A. Suzuki, *Tetrahedron Lett.*, 1980, **21**, 2865.

8 S. Chowdhury and P. E. Georghiou, *Tetrahedron Lett.*, 1999, **40**, 7599.

9 (*a*) E. Piers, M. Jean and P. S. Marrs, *Tetrahedron Lett.*, 1987, **28**, 5075; (*b*) T. Harada, T. Katsuhira, K. Hattori and A. Oku, *J. Org. Chem.*, 1993, **58**, 2958.

10 K. B. Wiberg, *Acc. Chem. Res.*, 1996, **29**, 229.

11 (*a*) J. Uenishi, J.-M. Beau, R. W. Armstrong and Y. Kishi, *J. Am. Chem. Soc.*, 1987, **109**, 4756; for recent use of Ag_2O in coupling reactions: (*b*) A. R. de Lera, A. Torrado, B. Iglesias and S. López, *Tetrahedron Lett.*, 1992, **33**, 6205; (*c*) T. Gillmann and T. Weeber, *Synlett*, 1994, 649; (*d*) J. C. Anderson, H. Namli and C. A. Roberts, *Tetrahedron*, 1997, **53**, 15123; (*e*) K. Hirabayashi, J. Kawashima, Y. Nishihara, A. Mori and T. Hiyama, *Org. Lett.*, 1999, **1**, 299.

12 (*a*) T. Imai, H. Mineta and S. Nishida, *J. Org. Chem.*, 1990, **55**, 4986; (*b*) J. Pietruszka and M. Widenmeyer, *Synlett*, 1997, 977; (*c*) S.-M. Zhou, M.-Z. Deng, L.-J. Xia and M.-H. Tang, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 2845; (*d*) J. E. A. Luithle and J. Pietruszka, *J. Org. Chem.*, 1999, **64**, 8287.