DOI: 10.1002/adsc.200600234

Highly Efficient Suzuki Coupling Reaction of α-Chloroalkylidene-β-lactones and β-Lactams with Organoboronic Acids

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Received: May 22, 2006; Accepted: August 7, 2006

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Abstract: The activation of C–Cl bond of (*Z*)-α-chloroalkylidene-β-lactones and (*E*)-α-chloroalkylidene-β-lactams *via* the Suzuki cross-coupling reaction is reported in this paper. Alkyl, heteroaromatic, substituted phenyl- and alkenylboronic acids can be coupled with a wide variety of α-chloroalkylidene-β-lactones and β-lactams in excellent yields within a short period of time. The cross-coupling reaction of optically active substrates leads to the optically active compounds without racemization of the corresponding chiral center.

Keywords: activation of C–Cl bonds; β-lactams; β-lactones; organoboronic acids; Suzuki coupling

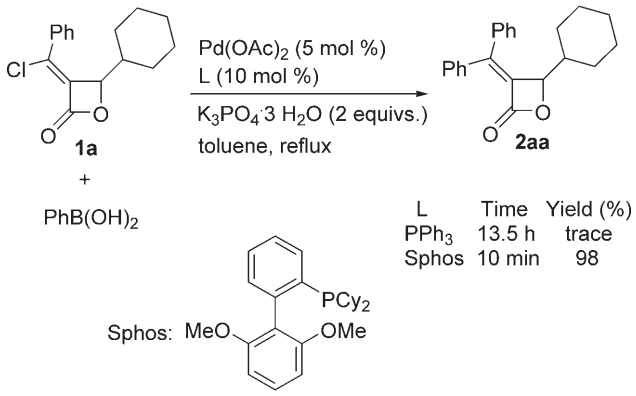
Introduction

β-Lactones[1] and β-lactams[2] are commonly observed structural units in biologically active natural products. Recently, we reported the efficient $PdCl_2$-catalyzed transformation of propargylic alcohols and amines to (*Z*)-α-haloalkylidene-β-lactones and (*E*)-α-chloroalkylidene-β-lactams.[3] Although the coupling reactions of (*Z*)-α-bromoalkylidene-β-lactones were quite smooth to afford the corresponding products in high yields,[3b] the reaction may be synthetically not so attractive due to the fact that the yields of the (*Z*)-α-bromoalkylidene-β-lactones were relatively low. Since the yields of chloro-β-lactones and β-lactams are much higher, in this paper we report our study on the derivatization of these β-lactones and β-lactams at the carbon-chlorine bond by Suzuki coupling with organoboronic acids.[4,5]

Results and Discussion

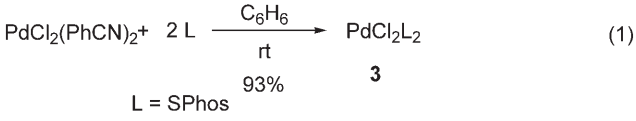
At first we employed the $Pd(OAc)_2/Ph_3P$ system to promote the Suzuki cross-coupling reaction.[6] However, most of the substrate **1a** was left unchanged after 13.5 h. After 3 days of refluxing, there was still 20% of substrate **1a** left (Scheme 1).

Recently, Buchwald et al. developed a very practical and efficient catalyst system based on the ligand Sphos.[5] When we employed Sphos instead of Ph_3P, it took just 10 min to afford the coupling product **2aa** in 98% yield (Scheme 1).



Scheme 1.

In order to use and store it more easily, the catalyst **3** was prepared in advance by stirring 2 equivs. of Sphos with $PdCl_2(PhCN)_2$ in benzene for 1 day at room temperature [Eq. (1)]. The *trans*-structure of **3** was determined by an X-ray diffraction study which indicated that two molecules of Sphos coordinate



(1)

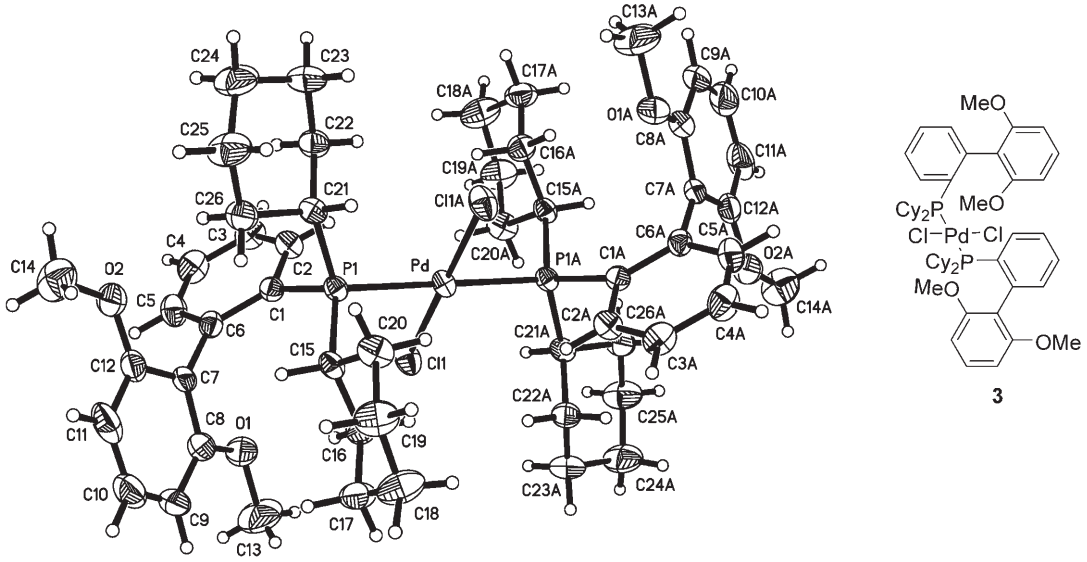
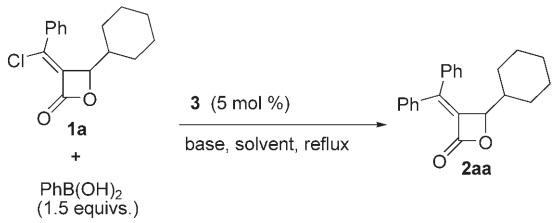


Figure 1. ORTEP representation of $PdCl_2L_2$ (**3**).

with one Pd atom (Figure 1).[5b,7] The cross-coupling reaction with 5 mol% of **3** afforded the product **2aa** in 99% yield after 10 min.

Thus, we tested the effects of base and solvent in this Suzuki reaction (Table 1). The reaction in toluene failed to yield the coupling product using Et_3N as the base (entry 2, Table 1); on using K_2CO_3 (entry 1, Table 1), Cs_2CO_3 (entry 3, Table 1), or KOH (entry 4, Table 1) as the base, the reaction afforded the product **2aa** in 82–88% yields. $K_3PO_4{\cdot}3H_2O$ was the best base, affording the product **2aa** in the excellent yield within a short reaction time (entry 5, Table 1). Compared with the results in dioxane (entry 6, Table 1), DMF (entry 7, Table 1), CH_3CN (entry 8, Table 1), and Cl_3CCH_3 (entry 9, Table 1), toluene proved to be the best solvent (entry 5, Table 1). After reducing the loading of catalyst **3** to 1 mol%, the reaction time had to be prolonged to 30 min to afford 95% of product **2aa** (entry 10, Table 1).

Table 1. Base and solvent effects in the Suzuki reaction of **1a** with $PhB(OH)_2$.



Entry	Base (2 equivs.)	Solvent	Time	Yield of **2aa**[a] [%]
1	K_2CO_3	Toluene	1 h	82
2	Et_3N	Toluene	11 h	trace
3	Cs_2CO_3	Toluene	2 h	87
4	KOH	Toluene	50 min	88
5	$K_3PO_4{\cdot}3H_2O$	Toluene	10 min	99
6	$K_3PO_4{\cdot}3H_2O$	Dioxane	5 h	93
7[b]	$K_3PO_4{\cdot}3H_2O$	DMF	5 h	42
8	$K_3PO_4{\cdot}3H_2O$	CH_3CN	1 h	95
9	$K_3PO_4{\cdot}3H_2O$	Cl_3CCH_3	9 h	trace
10[c]	$K_3PO_4{\cdot}3H_2O$	Toluene	30 min	95

[a] Isolated yields.
[b] The reaction was conducted at 110 °C.
[c] 1 mol% of catalyst **3** was used.

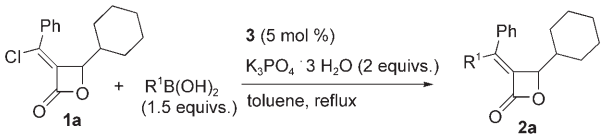
As shown in Table 2, different boronic acids could couple with (*Z*)-α-chloroalkylidene-β-lactones to give the products in excellent yields in a very short period of time (from 10 min to 3 h, Table 2). It is observed that the reactions of the aromatic boronic acids with electron-withdrawing groups on the phenyl ring were more efficient than those with a phenyl group bearing an electron-donating group.[8] 2-Thiophenyl, 2-benzofuranyl and 2-indolyl groups could be easily introduced *via* the coupling protocol (entries 6–8, Table 2). 1-Alkenylboronic acids behaved similarly to afford the products **2ai** and **2aj** in good yields, with the configuration of the C=C bond in the 1-alkenylboronic acid being retained (entries 9 and 10, Table 2), which was established by an X-ray diffraction study of **2ai**[9] (Figure 2). Furthermore, alkylboronic acids could also afford the desired products (entries 11 and 12, Table 2).

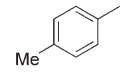
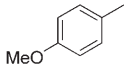
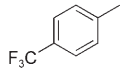
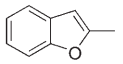
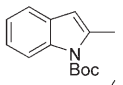
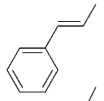
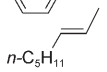
More examples of the cross-coupling reaction of differently substituted (*Z*)-α-chloroalkylidene-β-lactones with boronic acids are shown in Table 3.

The cross-coupling reaction of (*E*)-α-chloroalkylidene-β-lactams with different organoboronic acids was also smooth, affording the related coupling products **6** or **7** in moderate to high yields (Table 4).

We also studied the Suzuki coupling of optically active (*Z*)-α-chloroalkylidene-β-lactones and (*E*)-α-

Table 2. Coupling reaction of (*Z*)-α-(1-chlorobenzylidene)-β-cyclohexyl-β-lactone (**1a**) with different organoboronic acids.



Entry	R^1	Time [min]	Product **2a**	Yield of **2a**[a] [%]
1		10	**2aa**	99
2		10	**2ab**	93
3		80	**2ac**	68
4		60	**2ad**	94
5		180	**2ae**	81
6[b]		150	**2af**	87
7		60	**2ag**	86
8		180	**2ah**	63
9		180	**2ai**	97
10		90	**2aj**	91
11		120	**2ak**	88
12[b]	*n*-Bu-	120	**2al**	45[c]

[a] Isolated yields.
[b] 3 equivs. of boronic acid were used.
[c] 85% purity as determined by HPLC analysis.

chloroalkylidene-β-lactams with aromatic boronic acids. It can be concluded that no racemization of the corresponding chiral centers in (*R*)-**1c**, (*S*)-**1f**, (*S*)-**5b** or (*R*)-**5a** was observed (Scheme 2).

Conclusions

We have achieved activation of the C–Cl bond of (*Z*)-α-chloroalkylidene-β-lactones and (*E*)-α-chloroalkylidene-β-lactams *via* the Suzuki cross-coupling reaction. Alkyl, heteroaromatic, substituted phenyl, and alkenylboronic acids can be coupled with a wide variety of α-chloroalkylidene-β-lactones and β-lactams in excellent yields within a short period of time. We have also performed the cross-coupling reaction of optically active substrates leading to optically active compounds without racemization of the corresponding chiral center. Further studies in this area are in progress in our laboratory.

Experimental Section

Synthesis of Starting Materials

Compounds **1a–i**, **4a–d**, **5a–c**, (*R*)-**1c**, (*S*)-**1f**, (*S*)-**5b** and (*R*)-**5a** were prepared according to the method developed in this group.[3]

$PdCl_2L_2$ (3)

A solution of $PdCl_2(PhCN)_2$ (380 mg, 0.99 mmol) and Sphos (818 mg, 2 mmol) in 5 mL of dry benzene was stirred for 2 days as monitored by TLC (petroleum ether/ethyl acetate, 5:1). Rotary evaporation and recrystallization from ethyl ether afforded a yellow solid product **3**;[5b,7] yield: 912 mg (0.913 mmol, 93%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.33.

α-(1-Phenylbenzylidene)-β-cyclohexyl-β-lactone (2aa); Typical Procedure

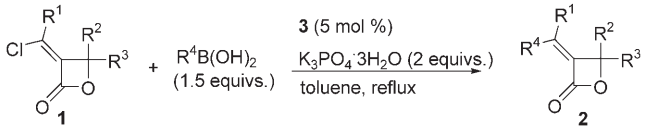
To a stirred solution of (*Z*)-α-(1-chlorobenzylidene)-β-cyclohexyl-β-lactone (**1a**) (50 mg, 0.18 mmol) and **3** (9 mg, 0.01 mmol) in 2 mL of dry toluene were added $K_3PO_4 \cdot 3H_2O$ (106 mg, 0.4 mmol) and phenylboronic acid (36 mg, 0.3 mmol). The reaction mixture was refluxed under argon for 10 min. After the reaction was complete as monitored by TLC (petroleum ether/ethyl acetate, 5:1), rotary evaporation and flash chromatography on silica gel (petroleum ether/ethyl ether, 10:1) afforded the solid product **2aa**; yield: 57 mg (0.18 mmol, 99%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.67; mp 101–102 °C (petroleum ether/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.35 (m, 8H), 7.30–7.20 (m, 2H), 5.17 (d, J = 3.6 Hz, 1H), 1.75–1.50 (m, 4H), 1.50–1.20 (m, 2H), 1.20–0.90 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 163.6, 147.1, 137.9, 135.9, 131.8, 130.1, 130.0, 129.5, 129.3, 128.6, 128.1, 82.5, 39.3, 28.3, 25.9, 25.8, 25.7, 25.6; MS (EI): *m/z* (%) = 318 (M^+, 25.13), 235 (100); IR (neat): ν = 3058, 2943, 2925, 2854, 1794, 1712, 1665, 1445, 1061 cm^{-1}; anal. calcd. for $C_{22}H_{22}O_2$: C 82.99, H 6.96; found: C 82.88, H 6.84.

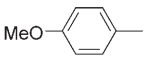
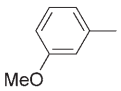
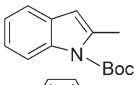
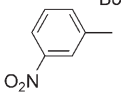
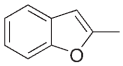
The following compounds were prepared similarly.

(*Z*)-α-(1-*p*-Tolylbenzylidene)-β-cyclohexyl-β-lactone (2ab)

The reaction of **1a** (54 mg, 0.20 mmol), 4-methylphenylboronic acid (41 mg, 0.30 mmol), **3** (11 mg, 0.011 mmol), and $K_3PO_4 \cdot 3H_2O$ (111 mg, 0.42 mmol) in toluene (2 mL) afforded the solid **2ab**; yield: 60 mg (0.18 mmol, 93%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.67; mp 129–130 °C (petro-

Table 3. Coupling reaction of (*Z*)-α-chloroalkylidene-β-lactones with organoboronic acids.



Entry	Substrate **1**	R^1	R^2	R^3	R^4	Time [min]	Product **2**	Yield of **2**[a] [%]
1	**1b**	Ph	*i*-Pr	H	Ph	180	**2ba**	92
2[b]	**1b**	Ph	*i*-Pr	H	*n*-Bu	120	**2bb**	50
3	**1c**	*n*-Bu	Me	H	Ph	120	**2ca**	76
4	**1d**	*n*-Bu	-$(CH_2)_5$-			120	**2da**	87
5[b]	**1d**	*n*-Bu	-$(CH_2)_5$-		*n*-Bu	180	**2db**	37
6	**1e**	*n*-Bu	Cyclohexyl	H		60	**2ea**	93
7	**1f**	*n*-Bu	Et	H		60	**2fa**	97
8[c]	**1g**	*n*-C_6H_{13}	Et	H		180	**2ga**	62
9	**1h**	$PhCH_2CH_2$	*i*-Pr	H		120	**2ha**	90
10	**1i**	Ph	-$(CH_2)_5$-			120	**2ia**	94

[a] Isolated yields.
[b] 3 equivs. of boronic acid were used.
[c] 1 equiv. of boronic acid was used.

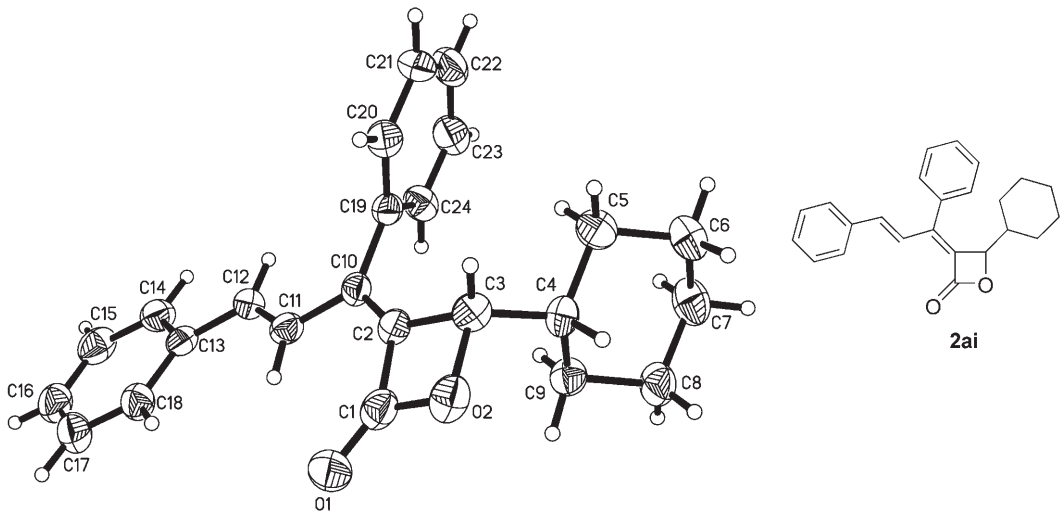
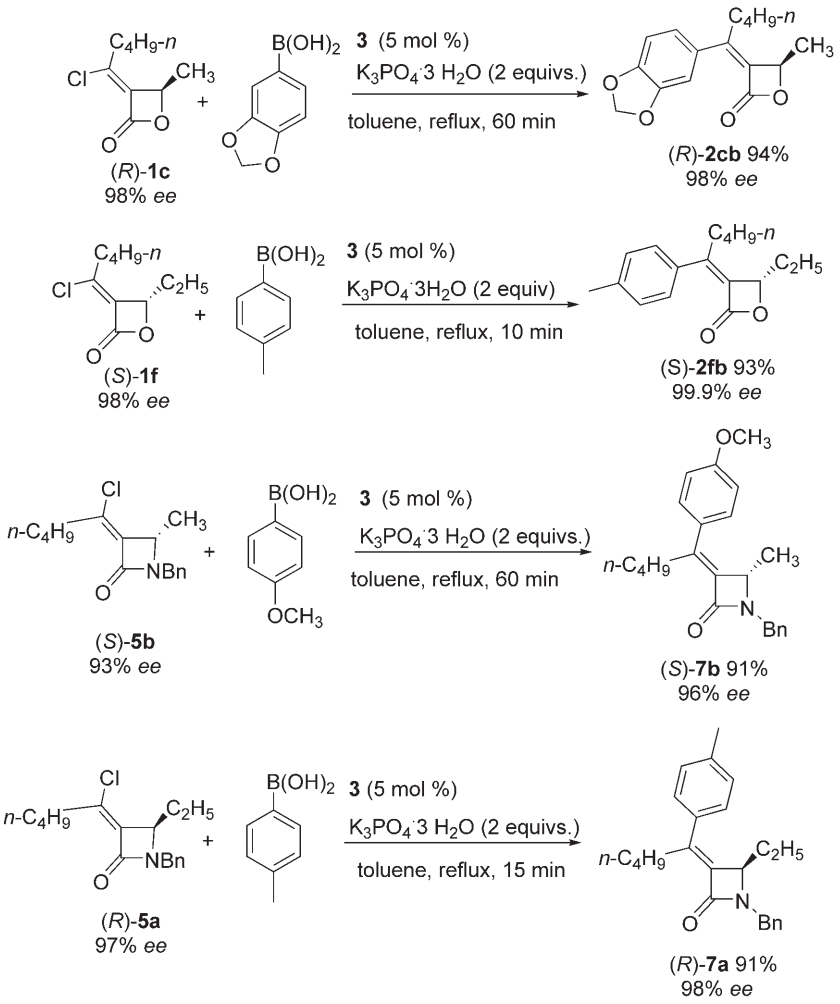


Figure 2. ORTEP representation of **2ai**.



Scheme 2.

leum ether/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.30 (m, 5H), 7.28–7.12 (m, 4H), 5.13 (d, J = 3.9 Hz, 1H), 2.37 (s, 3H), 1.72–1.50 (m, 4H), 1.49–1.20 (m, 2H), 1.16–0.92 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 163.8, 147.2, 140.3, 138.1, 133.1, 131.0, 130.0, 129.3, 129.2, 128.8, 128.5, 82.4, 39.4, 28.3, 25.9, 25.8, 25.7, 25.6, 21.4; MS (EI) m/z (%) 332 (M^+, 11.20), 249 (100); IR (neat): ν = 2927, 2854, 1798, 1658, 1609, 1446, 1065 cm^{-1}; anal. calcd. for $C_{23}H_{24}O_2$: C 83.10, H 7.28; found: C 82.99, H 7.23.

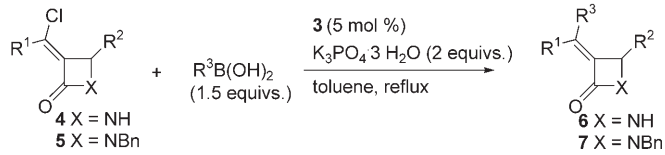
(*Z*)-α-[1-(4′-Methoxyphenyl)-benzylidene]-β-cyclohexyl-β-lactone (2ac)

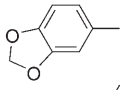
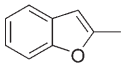
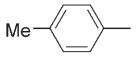
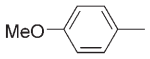
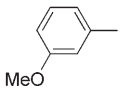
The reaction of **1a** (56 mg, 0.2 mmol), 4-methoxyphenylboronic acid (46 mg, 0.3 mmol), **3** (9 mg, 0.01 mmol), and $K_3PO_4{\cdot}3H_2O$ (107 mg, 0.4 mmol) in toluene (2 mL) afforded the solid **2ac**; yield: 46 mg (0.132 mmol, 68%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.60; mp 122–123 °C (petroleum ether/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (d, J = 9.6 Hz, 2H), 7.38–7.25 (m, 3H), 7.22–7.12 (m, 2H), 6.81 (d, J = 9.6 Hz, 2H), 5.02 (d, J = 3.9 Hz, 1H), 3.76 (s, 3H), 1.60–1.40 (m, 4H), 1.40–1.25 (m, 1H) , 1.25–1.10 (m, 1H) , 1.10–0.80 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 164.0, 161.1, 146.9, 138.2, 131.9, 129.9, 129.3, 129.2, 128.6, 128.4, 113.5, 82.4, 55.3, 39.4, 28.3, 25.89, 25.85, 25.7, 25.6; MS (EI): m/z (%) = 348 (M^+, 54.89), 265 (100); IR (neat): ν = 2933, 2856, 1789, 1655, 1604, 1513, 1257 cm^{-1}; anal. calcd. for $C_{23}H_{24}O_3$: C 79.28, H 6.94; found: C 78.95, H 6.80.

(*Z*)-α-[1-(4′-Trifluoromethylphenyl)benzylidene]-β-cyclohexyl-β-lactone (2ad)

The reaction of **1a** (55 mg, 0.20 mmol), 4-(trifluoromethyl)-phenylboronic acid (57 mg, 0.30 mmol), **3** (11 mg, 0.011 mmol), and $K_3PO_4{\cdot}3H_2O$ (111 mg, 0.42 mmol) in toluene (2 mL) afforded the solid **2ad**; yield: 72 mg (0.186 mmol, 94%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.60; mp 176–177 °C (petroleum ether/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.47–7.39 (m, 3H), 7.26–7.20 (m, 2H), 5.22 (d, J = 3.6 Hz, 1H), 1.75–1.52 (m, 4H), 1.51–1.36 (m, 2H), 1.18–0.95 (m, 5H); ^{19}F NMR (282 MHz, $CDCl_3$, CF_3COOH): δ = −77.0), −63.20; MS (EI): m/z (%) = 386 (M^+, 2.76), 233 (100); IR (neat): ν = 2928, 2855, 1796, 1671, 1324 cm^{-1}; anal. calcd. for $C_{23}H_{21}F_3O_2$: C 71.49, H 5.48; found: C 71.57, H 5.53.

Table 4. Coupling reaction of (*E*)-α-chloroalkylidene-β-lactams **4** or **5** with organoboronic acids.



Entry	Substrate **4** or **5**	X	R^1	R^2	R^3	Time [min]	Product **6** or **7**	Yield of **6** or **7**[a] [%]
1	**4a**	NH	*n*-Bu	*n*-Pentyl	Ph	30	**6a**	79
2	**4b**	NH	*n*-Bu	Et		60	**6b**	82
3	**4c**	NH	$PhCH_2CH_2$	*i*-Pr		60	**6c**	48
4	**4d**	NH	*n*-Pentyl	*n*-Bu		20	**6d**	70
5	**5a**	NBn	*n*-Bu	Et		10	**7a**	91
6	**5b**	NBn	*n*-Bu	Me		60	**7b**	91
7	**5c**	NBn	*n*-Bu	*i*-Pr		60	**7c**	86

[a] Isolated yields.

(*Z*)-α-[1-(3-Nitrophenyl)benzylidene]-β-cyclohexyl-β-lactone (2ae)

The reaction of **1a** (52 mg, 0.19 mmol), 3-nitrophenylboronic acid (53 mg, 0.32 mmol), **3** (11 mg, 0.01 mmol), and $K_3PO_4{\cdot}3H_2O$ (114 mg, 0.43 mmol) in toluene (2 mL) afforded **2ae** (eluent for preparative TLC: petroleum ether/ethyl ether, 15:1) as a liquid; yield: 55 mg (0.157 mmol, 81%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.55; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (dm, J = 8.4 Hz, 1H), 8.20 (s, 1H), 7.88 (d, J = 6 Hz, 1H), 7.60 (t, J = 8.4 Hz, 1H), 7.55–7.40 (m, 3H), 7.28–7.18 (m, 2H), 5.23 (d, J = 3.6 Hz, 1H), 1.75–1.55 (m, 4H), 1.55–1.40 (m, 2H), 1.20–0.90 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 163.1, 148.1, 144.1, 137.4, 136.6, 136.0, 134.2, 130.2, 129.3, 129.14, 129.11, 124.8, 124.5, 82.9, 39.5, 28.3, 26.0, 25.82, 25.77, 25.5; MS (EI): *m/z* (%) = 363 (M^+, 29.28), 280 (100); IR (neat): ν = 2933, 2856, 1783, 1658, 1526, 1350 cm^{-1}; HRMS (EI): *m/z* = 363.1459, calcd. for $C_{22}H_{21}NO_4$: 363.1471.

(*Z*)-α-[1-(2′-Thiophenyl)benzylidene]-β-cyclohexyl-β-lactone (2af)

The reaction of **1a** (55 mg, 0.20 mmol), 2-thiopheneboronic acid (77 mg, 0.6 mmol), **3** (10 mg, 0.01 mmol), and $K_3PO_4{\cdot}3H_2O$ (109 mg, 0.41 mmol) in toluene (2 mL) afforded the solid **2af**; yield: 56 mg (0.173 mmol, 87%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.55; mp 139–140 °C (*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (dd, J = 1.1 and 3.8 Hz, 1H), 7.49–7.40 (m, 4H), 7.38–7.32 (m, 2H), 7.11 (dd, J = 3.9 and 5.1 Hz, 1H), 4.93 (d, J = 2.1 Hz,1H), 1.64–1.45 (m, 4H), 1.44–1.30 (m, 1H), 1.08–0.84 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 163.4, 139.5, 139.1, 137.5, 132.1, 130.3, 129.5, 128.9, 128.7, 128.6, 128.0, 82.1, 39.2, 28.3, 25.9, 25.8, 25.6, 25.3; MS (EI) *m/z* (%) = 324 (M^+, 21.72), 241 (100); IR (neat): ν = 2928, 2853, 1789, 1648, 1445, 1416, 1367, 1071, 1055 cm^{-1}; HR-MS (EI): *m/z* = 324.1181, calcd. for $C_{20}H_{20}O_2S$: 324.1184.

(*Z*)-α-[1-(2′-Benzofuranyl)benzylidene]-β-cyclohexyl-β-lactone (2ag)

The reaction of **1a** (82 mg, 0.3 mmol), 2-benzofuranylboronic acid (67 mg, 0.42 mmol), **3** (15 mg, 0.015 mmol), and $K_3PO_4{\cdot}3H_2O$ (173 mg, 0.65 mmol) in toluene (3 mL) afforded the solid **2ag**; yield: 91 mg (0.254 mmol, 86%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.67; mp 91–92 °C (petroleum ether/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, J = 7.5 Hz, 1H), 7.55–7.25 (m, 8H), 7.24 (t, J = 6.9 Hz, 1H), 5.03 (d, J = 3 Hz, 1H), 1.75–1.45 (m, 4H), 1.52–1.35 (m, 1H), 1.35–0.80 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 162.3, 155.5, 151.2, 134.6, 134.5, 132.2, 129.6, 128.9, 128.7, 128.0, 126.4, 123.3, 122.0, 112.4, 111.8, 82.0, 39.3, 28.4, 25.9, 25.8, 25.6, 25.5; MS (EI): *m/z* (%) = 358 (M^+, 38.83), 275 (100); IR (neat); ν = 2933, 2854, 1803, 1654, 1128, 1096, 1069 cm^{-1}; anal. calcd. for $C_{24}H_{22}O_3$: C 80.42, H 6.19; found: C 80.05, H 6.30.

(*Z*)-α-{1-[2′-(1′-*tert*-Butoxycarbonyl)indolyl]-benzylidene}-β-cyclohexyl-β-lactone (2ah)

The reaction of **1a** (56 mg, 0.2 mmol), 1-(*tert*-butoxycarbonyl)-2-indoleboronic acid (81 mg, 0.3 mmol), **3** (10 mg, 0.01 mmol), and $K_3PO_4 \cdot 3H_2O$ (107 mg, 0.4 mmol) in toluene (2 mL) afforded the solid **2ah**; yield: 58 mg (0.127 mmol, 63%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.33; mp 119–120 °C (petroleum ether/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.40–7.30 (m, 4H), 7.30–7.20 (m, 1H), 7.20–7.15 (m, 2H), 6.96 (s, 1H), 5.41 (d, J = 3.3 Hz, 1H), 1.75–1.55 (m, 6H), 1.37 (s, 9H), 1.30–1.00 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 163.6, 149.0, 138.1, 137.2, 136.3, 132.7, 132.0, 129.7, 128.52, 128.49, 128.45, 125.4, 123.0, 121.4, 115.2, 114.9, 84.1, 83.2, 39.2, 28.7, 27.6, 26.0, 25.8, 25.64, 25.59; MS (ESI): *m/z* (%) = 458 ($M+H^+$, 100), 475 ($M+NH_4^+$, 45), 480 ($M+Na^+$, 20); IR (neat): ν = 2929, 1802, 1736, 1329 cm^{-1}; anal. calcd. for $C_{29}H_{31}O_4N$: C 76.12, H 6.83, N 3.06; found: C 76.15, H 7.01, N, 2.87.

(*E*)-α-[1-(*E*-2′-Phenylethenyl)benzylidene]-β-cyclohexyl-β-lactone (2ai)

The reaction of **1a** (55 mg, 0.2 mmol), *E*-2-phenylvinylboronic acid (43 mg, 0.3 mmol), **3** (11 mg, 0.01 mmol), and $K_3PO_4 \cdot 3H_2O$ (109 mg, 0.4 mmol) in toluene (2 mL) afforded the solid **2ai**; yield: 67 mg (0.195 mmol, 97%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.67; mp 89–90 °C (petroleum ether/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, J = 16.2 Hz, 1H), 7.55–7.40 (m, 5H), 7.35–7.20 (m, 5H), 6.61 (d, J = 16.2 Hz, 1H), 4.95 (d, J = 3.6 Hz, 1H), 1.75–1.45 (m, 4H), 1.40–1.20 (m, 2H), 1.17–0.80 (m, 5H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 164.1, 144.8, 138.5, 135.7, 134.6, 132.3, 129.1, 129.0, 128.69, 128.66, 128.5, 127.4, 124.5, 83.0, 39.7, 28.2, 25.8, 25.6; MS (EI): *m/z* (%) = 345 (M^+, 3.08), 41 (100); IR (neat): ν = 2928, 2853, 1794, 1655, 1448, 1092, 1070 cm^{-1}; anal. calcd. for $C_{24}H_{24}O_2$: C 83.69, H 7.02; found: C 83.49, H 7.02.

(*E*)-α-[1-(Hept-1′(*E*)-enyl)benzylidene]-β-cyclohexyl-β-lactone (2aj)

The reaction of **1a** (54 mg, 0.2 mmol), hept-1(*E*)-enylboronic acid (40 mg, 0.28 mmol), **3** (10 mg, 0.01 mmol), and $K_3PO_4 \cdot 3H_2O$ (112 mg, 0.4 mmol) in toluene (2 mL) afforded **2aj** as a liquid; yield: 60 mg (0.177 mmol, 91%); R_f (petroleum ether/ethyl ether, 5:1) = 0.67; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 3H), 7.20–7.10 (m, 2H), 7.06 (d, J = 15.5 Hz, 1H), 5.77 (dt, J = 15.5, 7.2 Hz, 1H), 4.81 (d, J = 3.6 Hz, 1H), 2.09 (q, J = 7.2 Hz, 2H), 1.60–1.40 (m, 4H), 1.40–1.00 (m, 9H), 1.00–0.85 (m, 4H), 0.80 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 164.3, 145.1, 143.2, 135.1, 130.3, 128.8, 128.5, 126.6, 82.8, 39.6, 33.1, 31.4, 28.4, 28.2, 25.84, 25.82, 25.7, 25.6, 22.4, 13.9; MS (EI): *m/z* (%) = 338 (M^+, 20.75), 84 (100); IR (neat): ν = 2958, 2931, 2857, 1795, 1664, 1450 cm^{-1}; HR-MS (EI): *m/z* = 338.2244, calcd. for $C_{23}H_{30}O_2$: 338.2246.

(*E*)-α-[1-(Cyclopropyl)benzylidene]-β-cyclohexyl-β-lactone (2ak)

The reaction of **1a** (56 mg, 0.2 mmol), cyclopropylboronic acid (28 mg, 0.3 mmol), **3** (10 mg, 0.01 mmol), and $K_3PO_4 \cdot 3H_2O$ (108 mg, 0.4 mmol) in toluene (2 mL) afforded **2ak** as a liquid; yield: 50 mg (0.177 mmol, 88%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.80; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 3H), 7.10–7.00 (m, 2H), 4.71 (d, J = 3.3 Hz, 1H), 2.70–2.55 (m, 1H), 1.70–1.45 (m, 4H), 1.40–1.25 (m, 1H), 1.20–0.80 (m, 8H), 0.80–0.70 (m, 1H) , 0.50–0.30 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.0, 151.6, 133.9, 130.7, 128.5, 128.3, 127.8, 82.9, 39.5, 28.3, 25.9, 25.8, 25.7, 25.5, 14.9, 6.8, 6.1; MS (EI): *m/z* (%) = 282 (M^+, 20.92), 153 (100); IR (neat): ν = 2928, 2854, 1794, 1686, 1443, 1069, 1055 cm^{-1}; HR-MS (EI): *m/z* = 282.1622, calcd. for $C_{19}H_{22}O_2$: 282.1620.

(*E*)-α-(1-Butylbenzylidene)-β-cyclohexyl-β-lactone (2al)

The reaction of **1a** (56 mg, 0.2 mmol), *n*-butylboronic acid (68 mg, 0.67 mmol), **3** (11 mg, 0.011 mmol), and $K_3PO_4 \cdot 3H_2O$ (115 mg, 0.43 mmol) in toluene (2 mL) afforded **2al** as a liquid; yield: 27 mg [0.090 mmol, 45%, 85% purity as determined by HPLC analysis (Waters Spherisorb® Silica, *n*-hexane:*i*-PrOH = 9:1, 230 nm, 0.7 mL min^{-1}), t_r 5.5 (major)]; R_f (petroleum ether/ethyl acetate, 10:1) = 0.80; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.37 (m, 3H), 7.30–7.24 (m, 2H), 5.07 (d, J = 2.7 Hz, 1H), 3.23–3.13 (m, 1H), 2.74–2.64 (m, 1H), 1.66–1.19 (m, 10H), 1.12–0.92 (m, 5H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 164.9, 149.5, 136.9, 131.3, 129.3, 128.7, 127.2, 83.4, 39.3, 31.9, 30.5, 28.5, 25.9, 25.8, 25.7, 25.5, 22.2, 13.7; MS (EI): *m/z* (%) = 298 (M^+, 8.88), 145 (100); IR (neat): ν = 2929, 2855, 1800, 1687, 1447, 1064 cm^{-1}; HR-MS (MALDI/DHB): *m/z* = 299.2012, calcd. for $C_{20}H_{27}O_2$ ($M+H^+$): 299.2006.

α-(1-Phenylbenzylidene)-β-(isopropyl)-β-lactone (2ba)

The reaction of **1b** (116 mg, 0.5 mmol), phenylboronic acid (93 mg, 0.75 mmol), **3** (23 mg, 0.025 mmol), and $K_3PO_4 \cdot 3H_2O$ (267 mg, 1 mmol) in toluene (4 mL) afforded the solid **2ba**; yield: 126 mg (0.453 mmol, 92%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.67; mp 104–105 °C (petroleum ether/ethyl ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.45 (m, 2H), 7.45–7.30 (m, 6H), 7.25–7.20 (m, 2H), 5.21 (d, J = 3.6 Hz, 1H), 1.80–1.60 (m, 1H), 0.89 (d, J = 6.6 Hz, 3H), 0.82 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 163.5, 147.1, 137.8, 135.8, 132.0, 130.00, 129.96, 129.5, 129.2, 128.6, 128.1, 82.9, 29.5, 18.0, 15.2; MS (EI): *m/z* (%) = 278 (M^+, 26.45), 235 (100); IR (neat): ν = 3087, 2974, 1793, 1663, 1445 cm^{-1}; anal. calcd. for $C_{19}H_{18}O_2$: C 81.99, H 6.52; found: C 81.99, H 6.61.

(*E*)-α-(1-Butylbenzylidene)-β-(isopropyl)-β-lactone (2bb)

The reaction of **1b** (48 mg, 0.20 mmol), *n*-butylboronic acid (65 mg, 0.64 mmol), **3** (10 mg, 0.01 mmol), and $K_3PO_4 \cdot 3H_2O$ (116 mg, 0.44 mmol) in toluene (2 mL) afforded **2bb** as a liquid; yield: 26 mg (0.101 mmol, 50%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.67; ^{1}H NMR (300 MHz,

$CDCl_3$): $\delta = 7.39–7.33$ (m, 3H), 7.27–7.23 (m, 2H), 5.08 (d, $J = 3.6$ Hz, 1H), 3.20–3.09 (m, 1H), 2.74–2.62 (m, 1H), 1.79–1.64 (m, 1H), 1.40–1.25 (m, 4H), 0.83 (t, $J = 7.2$ Hz, 3H), 0.81 (d, $J = 7.2$ Hz, 3H), 0.67 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 164.9$, 149.5, 136.9, 131.6, 129.3, 128.8, 127.2, 83.8, 31.9, 30.5, 29.5, 22.2, 18.2, 15.3, 13.7; MS (EI): *m/z* (%) = 258 (M^+, 3.83), 145 (100); IR (neat): ν = 2962, 2930, 1798, 1688, 1466, 1059 cm^{-1}; HR-MS (EI): *m/z* = 258.1613, calcd. for $C_{17}H_{22}O_2$: 258.1620.

(*Z*)-α-(1-Butylbenzylidene)-β-methyl-β-lactone (2ca)

The reaction of **1c** (118 mg, 0.63 mmol), phenylboronic acid (117 mg, 0.945 mmol), **3** (30 mg, 0.03 mmol), and $K_3PO_4 \cdot 3H_2O$ (340 mg, 1.26 mmol) in toluene (5 mL) afforded **2ca** as a liquid; 109 mg (0.473 mmol, 76%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.60–7.50$ (m, 2H), 7.48–7.35 (m, 3H), 5.12 (q, $J = 6.3$ Hz, 1H), 2.60–2.35 (m, 2H), 1.66 (d, $J = 6.6$ Hz, 3H), 1.42–1.20 (m, 4H), 0.86 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 163.0$, 148.2, 134.6, 133.6, 129.4, 128.2, 127.9, 74.2, 32.5, 30.0, 22.4, 19.3, 13.6; MS (EI): *m/z* (%) = 230 (M^+, 20.16), 129 (100); IR (neat): ν = 2960, 2933, 1801, 1685, 1260 cm^{-1}; HR-MS (EI): m/z = 230.1321, calcd. for $C_{15}H_{18}O_2$: 230.1307.

(*Z*)-3-[1-(*p*-Methoxyphenyl)pentylidene]-1-oxaspiro[3.5]nonan-2-one (2da)

The reaction of **1d** (49 mg, 0.20 mmol), 4-methoxyphenylboronic acid (46 mg, 0.30 mmol), **3** (10 mg, 0.01 mmol), and $K_3PO_4 \cdot 3H_2O$ (110 mg, 0.41 mmol) in toluene (2 mL) afforded **2da** as a liquid; yield: 55 mg (0.175 mmol, 87%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.40; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.49$ (d, $J = 8.7$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 2H), 3.82 (s, 3H), 2.47 (t, $J = 7.2$ Hz, 2H), 2.03–1.58 (m, 9H), 1.36–1.21 (m, 5H), 0.85 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 164.0$, 160.4, 147.4, 134.7, 129.6, 127.2, 113.5, 85.5, 55.2, 34.3, 32.2, 30.6, 24.8, 22.6, 22.1, 13.8; MS (EI): *m/z* (%) = 314 (M^+, 53.35), 213 (100); IR (neat): ν = 2934, 2860, 1788, 1674, 1605, 1513, 1168 cm^{-1}; HR-MS (EI): *m/z* = 314.1876, calcd. for $C_{20}H_{26}O_3$: 314.1882.

3-(1-Butylpentylidene)-1-oxaspiro[3.5]nonan-2-one (2db)

The reaction of **1d** (49 mg, 0.20 mmol), *n*-butylboronic acid (69 mg, 0.64 mmol), **3** (11 mg, 0.011 mmol), and $K_3PO_4 \cdot 3H_2O$ (115 mg, 0.41 mmol) in toluene (2 mL) afforded **2db** as a liquid; yield: 20 mg (0.076 mmol, 37%); R_f (petroleum ether/ethyl acetate, 25:1) = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.39$ (t, $J = 7.5$ Hz, 2H), 1.97 (t, $J = 7.5$ Hz, 2H), 1.84–1.44 (m, 10H), 1.38–1.08 (m, 8H), 0.84 (t, $J = 7.2$ Hz, 3H), 0.81 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 165.1$, 150.7, 135.6, 86.1, 34.3, 30.9, 30.2, 29.9, 29.8, 24.8, 22.9, 22.3, 22.1, 13.94, 13.87; MS (EI): *m/z* (%) = 264 (M^+, 13.03), 41 (100); IR (neat): ν = 2933, 2861, 1797, 1707, 1449, 1174, 1093 cm^{-1}; HR-MS (EI): *m/z* = 264.2088, calcd. for $C_{17}H_{28}O_2$:

(*Z*)-α-(1-(3′-Methoxyphenyl)pentylidene)-β-cyclohexyl-β-lactone (2ea)

The reaction of **1e** (84 mg, 0.33 mmol), 3-methoxyphenylboronic acid (76 mg, 0.50 mmol), **3** (16 mg, 0.016 mmol), and $K_3PO_4 \cdot 3H_2O$ (180 mg, 0.68 mmol) in toluene (3 mL) afforded **2ea** as a liquid; yield: 100 mg (0.304 mmol, 93%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$ (t, $J = 8.0$ Hz, 1H), 7.12 (s, 1H), 7.06 (d, $J = 7.7$ Hz, 1H), 6.93 (dd, $J = 2.7$ and 8.4 Hz, 1H), 4.92 (d, $J = 3.0$ Hz, 1H), 3.84 (s, 3H), 2.57–2.35 (m, 2H), 1.93–1.69 (m, 6H), 1.47–1.15 (m, 9H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 163.2$, 159.2, 148.2, 136.2, 131.1, 129.1, 120.1, 115.1, 113.6, 81.9, 55.2, 40.3, 33.2, 29.9, 29.1, 26.1, 25.9, 25.7, 25.3, 22.5, 13.7; MS (EI): *m/z* (%) = 328 (M^+, 43.20), 41 (100); IR (neat): ν = 2929, 2856, 1801, 1681, 1599, 1579, 1465, 1451, 1227, 1049 cm^{-1}; HR-MS (EI): *m/z* = 328.2049, calcd. for $C_{21}H_{28}O_3$: 328.2038.

(*Z*)-α-[1-(*E*-2′-Phenylvinyl)pentylidene]-β-ethyl-β-lactone (2fa)

The reaction of **1f** (89 mg, 0.44 mmol), *E*-phenylvinylboronic acid (100 mg, 0.68 mmol), **3** (22 mg, 0.022 mmol), and $K_3PO_4 \cdot 3H_2O$ (230 mg, 0.86 mmol) in toluene (4 mL) afforded **2fa** as a liquid; yield: 115 mg (0.425 mmol, 97%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.67; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.61$ (d, $J = 16.5$ Hz, 1H), 7.53 (d, $J = 7.5$ Hz, 2H), 7.39–7.26 (m, 3H), 6.90 (d, $J = 16.5$ Hz, 1H), 4.99 (dd, $J = 3.2$ and 7.8 Hz, 1H), 2.34 (t, $J = 7.7$ Hz, 2H), 2.14–1.99 (m, 1H), 1.89–1.70 (m, 1H), 1.68–1.31 (m, 4H), 1.07 (t, $J = 7.4$ Hz, 3H), 0.96 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 164.0$, 144.8, 135.8, 134.3, 133.0, 128.8, 128.6, 127.2, 123.3, 79.5, 31.3, 28.4, 26.2, 22.8, 13.7, 8.6; MS (EI): *m/z* (%) = 270 (M^+, 13.35), 91 (100); IR (neat): ν = 2933, 2873, 1795, 1667, 1449, 1235, 1147, 1054 cm^{-1}; HR-MS (EI): *m/z* = 270.1625, calcd. for $C_{18}H_{22}O_2$: 270.1620.

(*Z*)-α-{1-[2-(1-*tert*-butoxycarbonyl)indolyl]-heptylidene}-β-ethyl-β-lactone (2ga)

The reaction of **1g** (106 mg, 0.46 mmol), 1-(*tert*-butoxycarbonyl)indole-2-boronic acid (117 mg, 0.45 mmol), **3** (24 mg, 0.024 mmol), and $K_3PO_4 \cdot 3H_2O$ (250 mg, 0.94 mmol) in toluene (4 mL) afforded **2ga** as a liquid; yield: 118 mg (0.362 mmol, 62%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.40; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.09$ (d, $J = 8.4$ Hz, 1H), 7.56 (d, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.24 (t, $J = 7.4$ Hz, 1H), 6.70 (s, 1H), 5.08 (dd, $J = 3.2$ and 7.7 Hz, 1H), 2.52–2.35 (m, 2H), 2.21–2.07 (m, 1H), 2.00–1.83 (m, 1H), 1.66 (s, 9H), 1.43–1.23 (m, 8H), 1.15 (t, $J = 7.2$ Hz, 3H), 0.85 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 163.1$, 149.6, 141.0, 137.1, 133.5, 133.2, 128.7, 125.0, 122.9, 121.1, 115.5, 112.4, 84.3, 79.5, 34.0, 31.3, 29.1, 28.0, 27.9, 26.2, 22.4, 13.9, 8.6; MS (MALDI): *m/z* (%) = 412 ($M+H^+$, 60), 434 ($M+Na^+$, 100); IR (neat): ν = 2930, 2858, 1807, 1737, 1699, 1451, 1370, 1327 cm^{-1}; HR-MS (MALDI/DHB): *m/z* = 434.2309, calcd. for $C_{25}H_{33}NO_4Na$ ($M+Na^+$): 434.2302.

(*Z*)-α-[1-(3′-Nitrophenyl)-3-phenylpropylidene]-β-(isopropyl)-β-lactone (2ha)

The reaction of **1h** (87 mg, 0.33 mmol), 3-nitrophenylboronic acid (90 mg, 0.54 mmol), **3** (17 mg, 0.017 mmol), and $K_3PO_4 \cdot 3H_2O$ (186 mg, 0.70 mmol) in toluene (3 mL) afforded **2ha** as a liquid; yield: 104 mg (0.296 mmol, 90%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.25; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 8.26 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.5 Hz, 1H), 7.62 (t, J = 8.1 Hz, 1H), 7.31–7.19 (m, 3H), 7.04 (d, J = 6.0 Hz, 2H), 4.63 (d, J = 2.1 Hz, 1H), 2.96–2.78 (m, 2H), 2.78–2.59 (m, 2H), 2.19–2.08 (m, 1H), 1.09 (d, J = 7.2 Hz, 3H), 0.88 (d, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 162.6, 148.1, 143.8, 139.4, 136.3, 134.8, 134.7, 129.5, 128.7, 128.2, 126.7, 124.2, 122.6, 82.7, 35.2, 33.4, 30.4, 18.7, 14.8; MS (EI): *m/z* (%) = 351 (M^+, 0.25), 91 (100); IR (neat): ν = 3086, 3027, 2966, 2929, 1805, 1690, 1533, 1454, 1350, 1246, 1108 cm^{-1}; HR-MS (EI): *m/z* = 351.1469, calcd. for $C_{21}H_{21}NO_4$: 351.1471.

(*Z*)-3-(Benzofuran-2′-yl-phenylmethylene)-1-oxaspiro[3.5]nonan-2-one (2ia)

The reaction of **1i** (57 mg, 0.22 mmol), 2-benzofuranyl boronic acid (54 mg, 0.33 mmol), **3** (12 mg, 0.011 mmol), and $K_3PO_4 \cdot 3H_2O$ (130 mg, 0.44 mmol) in toluene (2 mL) the solid **2ia**; yield: afforded 70 mg (0.203 mmol, 94%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.80; mp 159–160 °C (petroleum ether/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, J = 7.5 Hz, 1H), 7.45–7.30 (m, 4H), 7.30–7.20 (m, 4H), 7.20–7.05 (m, 1H), 1.90–1.82 (m, 1H), 1.82–1.75 (m, 1H), 1.65–1.40 (m, 5H), 1.35–1.05 (m, 2H), 0.95–0.75 (m, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 162.5, 155.5, 152.0, 137.1, 133.9, 133.7, 129.1, 129.0, 128.3, 128.1, 126.4, 123.3, 121.9, 112.2, 111.8, 86.2, 34.5, 24.4, 21.8; MS (EI): *m/z* (%) = 344 (M^+, 23.62), 44 (100); IR (neat): ν = 2936, 2861, 1801, 1656, 1446, 1091 cm^{-1}; anal. calcd. for $C_{23}H_{20}O_3$: C 80.21, H 5.85; found: C 79.98, H 5.98.

(*E*)-α-(1-Butylbenzylidene)-β-(*n*-pentyl)-β-lactam (6a)

The reaction of **4a** (65 mg, 0.27 mmol), phenylboronic acid (50 mg, 0.41 mmol), **3** (13 mg, 0.014 mmol), and $K_3PO_4 \cdot 3H_2O$ (147 mg, 0.54 mmol) in toluene (2.5 mL) afforded **6a** as a liquid; yield: 60 mg (0.210 mmol, 79%); R_f (petroleum ether/ethyl acetate, 3:1) = 0.50; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.20 (m, 5H), 6.88–6.77 (br, 1H), 4.34 (dd, J = 6.9 and 2.7 Hz, 1H), 3.30–3.18 (m, 1H), 2.70–2.55 (m, 1H), 1.40–1.25 (m, 5H), 1.23–1.00 (m, 7H), 0.84 (t, J = 7.2 Hz, 3H), 0.78 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.6, 143.0, 137.8, 128.3, 128.1, 127.4, 56.9, 31.8, 31.4, 31.1, 30.4, 24.8, 22.3, 22.2, 13.83, 13.79; MS (EI): *m/z* (%) = 285 (M^+, 6.51), 43 (100); IR (neat): ν = 3226, 2956, 2928, 2858, 1735, 1466, 1444, 1170 cm^{-1}; HR-MS (EI): m/z = 285.2094, calcd. for $C_{19}H_{27}NO$: 285.2093.

(*E*)-α-[1-(Benzo[1,3]dioxol-5-yl)pentylidene]-β-ethyl-β-lactam (6b)

The reaction of **4b** (36 mg, 0.18 mmol), 5-benzo-[1,3]dioxolylboronic acid (45 mg, 0.27 mmol), **3** (9 mg, 0.009 mmol), and $K_3PO_4 \cdot 3H_2O$ (100 mg, 0.38 mmol) in toluene (2 mL) afforded **6b** as a liquid; yield: 42 mg (0.146 mmol, 82%); R_f (petroleum ether/ethyl acetate, 3:1) = 0.50; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.89–6.69 (m, 4H), 5.98 (s, 2H), 4.32 (dd, J = 3.2 and 7.4 Hz, 1H), 3.29–3.16 (m, 1H), 2.59–2.48 (m, 1H), 1.55–1.39 (m, 1H), 1.38–1.16 (m, 5H), 0.84 (t, J = 7.1 Hz, 3H), 0.74 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.4, 147.7, 147.6, 142.9, 136.6, 131.6, 121.4, 108.3, 107.7, 101.2, 57.9, 31.2, 30.6, 24.6, 22.2, 13.9, 9.1; MS (EI): *m/z* (%) = 287 (M^+, 6.36), 84 (100); IR (neat): ν = 3245, 2959, 2925, 1732, 1489 cm^{-1}; HR-MS (MALDI/DHB): *m/z* = 288.1598, calcd. for $C_{17}H_{22}NO_3$ ($M+H^+$). 288.1594.

(*E*)-α-[1-(*E*-2′-Phenylvinyl)-3-phenylpropylidene]-β-(isopropyl)-β-lactam (6c)

The reaction of **4c** (45 mg, 0.17 mmol), *trans*-2-phenylvinylboronic acid (40 mg, 0.27 mmol), **3** (10 mg, 0.01 mmol), and $K_3PO_4 \cdot 3H_2O$ (101 mg, 0.38 mmol) in toluene (2 mL) afforded **6c** as a liquid; yield: 27 mg (0.081 mmol, 48%); R_f (petroleum ether/ethyl acetate, 3:1) = 0.40; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.15 (m, 10H), 6.88 (d, J = 16.4 Hz, 1H), 6.65 (d, J = 16.4 Hz, 1H), 6.34 (bs, 1H), 4.24 (d, J = 3.9 Hz, 1H), 3.24–3.01 (m, 2H), 2.94–2.86 (m, 2H), 2.18–2.07 (m, 1H), 1.03 (d, J = 7.2 Hz, 3H), 0.86 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.3, 141.3, 139.0, 138.3, 136.4, 133.7, 128.8, 128.58, 128.55, 128.3, 126.8, 126.0, 124.3, 61.7, 36.1, 30.4, 29.2, 19.9, 15.6; MS (EI): *m/z* (%) = 331 (M^+, 2.84), 288 ($M^+-C_3H_7$, 12.27), 84 (100); IR (neat): ν = 3239, 2961, 2926, 1731 1669, 1496, 1449 cm^{-1}; HR-MS (MALDI/DHB): *m/z* = 332.2019, calcd. for $C_{23}H_{26}NO$ ($M+H^+$): 332.2009.

(*E*)-α-[1-(2-Benzofuranyl)hexylidene]-β-(*n*-butyl)-β-lactam (6d)

The reaction of **4d** (79 mg, 0.33 mmol), phenylboronic acid (80 mg, 0.49 mmol), **3** (16 mg, 0.0165 mmol), and $K_3PO_4 \cdot 3H_2O$ (180 mg, 0.66 mmol) in toluene (3 mL) afforded **6d** as a liquid; yield: 74 mg (0.227 mmol, 70%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.50; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.5 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.26 (t, J = 6.9 Hz, 1H), 7.17 (t, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.84 (s, 1H), 4.50 (dd, J = 2.7, 8.7 Hz, 1H), 2.95–2.78 (m, 2H), 2.15–2.00 (m, 1H), 1.70–1.48 (m, 3H), 1.48–1.15 (m, 8H), 0.95–0.72 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 165.4, 155.0, 154.0, 138.6, 129.4, 128.1, 125.4, 123.1, 121.4, 110.9, 107.4, 58.3, 33.0, 32.3, 31.5, 28.3, 25.0, 22.42, 22.40, 13.9; MS (EI): *m/z* (%) = 325 (M^+, 82.05), 240 (100); IR (neat): ν = 3192, 2952, 1729, 1707, 1676, 1469, 1451 cm^{-1}; HR-MS (ESI): *m/z* = 326.2126, calcd. for $C_{21}H_{28}NO_2$ ($M+H^+$): 326.2115.

(*E*)-α-(1-*p*-Tolylpentylidene)-β-ethyl-*N*-benzyl-β-lactam (7a)

The reaction of **5a** (59 mg, 0.20 mmol), 4-methylphenylboronic acid (42 mg, 0.31 mmol), **3** (11 mg, 0.011 mmol), and $K_3PO_4 \cdot 3H_2O$ (109 mg, 0.41 mmol) in toluene (2 mL) afforded **7a** as a liquid; yield: 64 mg (0.184 mmol, 91%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.67; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 5H), 7.13 (s, 4H), 4.83

(d, $J=15.0$ Hz, 1H), 4.27 (t, $J=6.9$ Hz, 1H), 4.14 (d, $J=15.0$ Hz, 1H), 3.32–3.23 (m, 1H), 2.72–2.64 (m, 1H), 2.33 (s, 3H), 1.44–1.32 (m, 5H), 1.27–1.16 (m, 1H), 0.87 (t, $J=7.2$ Hz, 3H), 0.56 (t, $J=7.4$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=164.8$, 141.8, 137.9, 136.3, 134.9, 134.8, 129.0, 128.6, 128.2, 127.4, 127.2, 60.2, 44.4, 31.3, 30.7, 22.3, 21.4, 21.1, 13.8, 7.6; MS (EI): *m/z* (%) = 347 (M^+, 10.89), 91 (100); IR (neat): $\nu=2960$, 2927, 1737, 1695, 1455, 1386 cm^{-1}; HR-MS (EI): *m/z* = 347.2242, calcd. for $C_{24}H_{29}NO$: 347.2249.

(*E*)-α-[1-(4′-Methoxyphenyl)pentylidene]-β-methyl-*N*-benzyl-β-lactam (7b)

The reaction of **5b** (35 mg, 0.13 mmol), 4-methoxyphenylboronic acid (30 mg, 0.20 mmol), **3** (8 mg, 0.008 mmol), and $K_3PO_4\cdot 3H_2O$ (71 mg, 0.27 mmol) in toluene (2 mL) afforded **7b** as a liquid; yield: 40 mg (0.114 mmol, 91%); R_f (petroleum ether/ethyl acetate, 5:1) = 0.50; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.32$–7.19 (m, 5H), 7.13 (d, $J=8.7$ Hz, 2H), 6.79 (d, $J=8.7$ Hz, 2H), 4.69 (d, $J=15.3$ Hz, 1H), 4.17 (q, $J=6.0$ Hz, 1H), 4.14 (d, $J=15.3$ Hz, 1H), 3.74 (s, 3H), 3.23–3.15 (m, 1H), 2.61–2.52 (m, 1H), 1.38–1.21 (m, 4H), 0.84 (d, $J=6.3$ Hz, 3H), 0.80 (t, $J=7.5$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=164.3$, 159.4, 140.7, 137.2, 136.4, 129.6, 128.8, 128.7, 128.2, 127.5, 113.7, 55.6, 55.2, 43.8, 31.1, 30.8, 22.3, 15.7, 13.9; MS (EI): *m/z* (%) = 349 (M^+, 17.09), 91 (100); IR (neat): $\nu=2957$, 2925, 1732, 1606, 1512 cm^{-1}; HR-MS (EI): *m/z* = 349.2039, calcd. for $C_{23}H_{27}NO_2$: 349.2042.

(*E*)-α-[1-(3-Methoxyphenyl)pentylidene]-β-(isopropyl)-*N*-benzyl-β-lactam (7c)

The reaction of **5c** (49 mg, 0.16 mmol), 3-methoxyphenylboronic acid (40 mg, 0.26 mmol), **3** (9 mg, 0.009 mmol), and $K_3PO_4\cdot 3_2O$ (91 mg, 0.34 mmol) in toluene (2 mL) afforded **7c** as a liquid; yield: 52 mg (0.138 mmol, 86%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.33; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.26$–7.12 (m, 5H), 7.09 (d, $J=8.1$ Hz, 1H), 6.71–6.66 (m, 2H), 6.62 (s, 1H), 4.77 (d, $J=15.5$ Hz, 1H), 4.05 (d, $J=1.5$ Hz, 1H), 4.01 (d, $J=15.5$ Hz, 1H), 3.66 (s, 3H), 3.21–3.11 (m, 1H), 2.55–2.45 (m, 1H), 1.47–1.36 (m, 1H), 1.31–1.17 (m, 4H), 0.75 (t, $J=6.5$ Hz, 3H), 0.62 (d, $J=7.2$ Hz, 3H), 0.38 (d, $J=6.6$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=165.4$, 159.4, 142.1, 139.9, 136.4, 135.3, 129.3, 128.6, 128.2, 127.5, 120.0, 113.5, 112.9, 64.9, 55.2, 45.5, 32.1, 30.6, 27.8, 22.3, 19.3, 16.0, 13.8; MS (EI): *m/z* (%) = 377 (M^+, 7.61), 91 (100); IR (neat): $\nu=2959$, 2927, 1738, 1384 cm^{-1}; HR-MS (MALDI/DHB): *m/z* = 378.2433, calcd. for $C_{25}H_{32}NO_2$ ($M+H^+$): 378.2428.

(*Z*)-α-{1-(Benzo[1,3]dioxol-5-yl)pentylidene}-β-methyl-β-lactone (*Z*-2cb)

The reaction of **1c** (50 mg, 0.27 mmol), 5-benzo-[1,3]dioxolylboronic acid (56 mg, 0.34 mmol), **3** (13 mg, 0.013 mmol), and $K_3PO_4\cdot 3H_2O$ (149 mg, 0.56 mmol) in toluene (3 mL) afforded (*Z*)-**2cb** as a liquid; yield: 67 mg (0.244 mmol, 92%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.25; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.02$–6.97 (m, 2H), 6.73 (d, $J=8.7$ Hz, 1H), 5.89 (s, 2H), 5.00 (q, $J=6.2$ Hz, 1H), 2.42–2.20 (m, 2H), 1.55 (d, $J=6.3$ Hz, 3H), 1.35–1.15 (m, 4H), 0.77 (t, $J=6.8$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$); $\delta=163.2$, 148.7, 147.8, 147.6, 132.6, 128.5, 122.5, 108.3, 108.0, 101.3, 74.2, 32.6, 30.2, 22.5, 19.4, 13.7; MS (EI): *m/z* (%) = 274 (M^+, 100.00); IR (neat): $\nu=$ 2957, 2927, 1793, 1678, 1606, 1505, 1490, 1441, 1237 cm^{-1}; HR-MS (EI): *m/z* = 274.1205, calcd. for $C_{16}H_{18}O_4$: 274.1205.

(*R*)-(*Z*)-α-{1-(benzo[1,3]dioxol-5-yl)pentylidene}-β-methyl-β-lactone [(*R*)-(*Z*)-2cb]

The reaction of (*R*)-(+)-**1c** (51 mg, 0.27 mmol, 98% *ee*), 5-benzo[1,3]dioxolylboronic acid (68 mg, 0.41 mmol), **3** (14 mg, 0.014 mmol), and $K_3PO_4\cdot 3H_2O$ (148 mg, 0.56 mmol) in toluene (3 mL) afforded (*R*)-(*Z*)-**2cb**; yield: 70 mg (94%, 0.255 mmol); 98% *ee* as determined by HPLC analysis (Chiralcel OD-H, *n*-hexane:*i*-PrOH, 90:10, 230 nm): t_r 10.8 (minor), 11.8 (major); $[\alpha]_D^{20}$: −21.5 (*c* 1.0, $CHCl_3$).

(*Z*)-α-(1-*p*-Tolylpentylidene)-β-ethyl-β-lactone [(*Z*)-2fb]

The reaction of (*Z*)-**1f** (46 mg, 0.23 mmol), 4-methylphenylboronic acid (47 mg, 0.35 mmol), **3** (12 mg, 0.012 mmol), and $K_3PO_4\cdot 3H_2O$ (124 mg, 0.47 mmol) in toluene (3 mL) afforded the product (*Z*)-**2fb** as a liquid; yield: 54 mg (0.209 mmol, 92%); R_f (petroleum ether/ethyl acetate, 10:1) = 0.60; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.37$ (d, $J=8.1$ Hz, 2H), 7.13 (d, $J=8.4$ Hz, 2H), 4.93 (dd, $J=3.2$ and 7.7 Hz, 1H), 2.50–2.27 (m, 2H), 2.28 (s, 3H), 2.10–1.95 (m, 1H), 1.85–1.69 (m, 1H), 1.34–1.17 (m, 4H), 1.02 (t, $J=7.4$ Hz, 3H), 0.78 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=163.4$, 148.6, 139.7, 131.9, 131.2, 128.9, 127.9, 78.9, 32.8, 30.1, 26.2, 22.5, 21.2, 13.7, 8.5; MS (EI): *m/z* (%) = 258 (M^+, 14.12), 159 (100); IR (neat): $\nu=2958$, 2931, 1801, 1680, 1610, 1513, 1460, 1157, 1095, 1048 cm^{-1}; HR-MS (EI): *m/z* = 258.1619, calcd. for $C_{17}H_{22}O_2$: 258.1620.

(*S*)-(*Z*)-α-(1-*p*-Tolylpentylidene)-β-ethyl-β-lactone [(*S*)-(*Z*)-2fb]

The reaction of (*S*)-(*Z*)-**1f** (77 mg, 0.38 mmol, 98% *ee*), 4-methylphenylboronic acid (79 mg, 0.58 mmol), **3** (20 mg, 0.02 mmol), and $K_3PO_4\cdot 3H_2O$ (212 mg, 0.80 mmol) in toluene (4 mL) afforded the product (*S*)-(*Z*)-**2fb**; yield: 91 mg (0.352 mmol, 93%); 99.9% *ee* as determined by HPLC analysis (Chiralcel OJ-H, *n*-hexane:*i*-PrOH, 100:2, 230 nm): t_r 9.4 (major), 12.0 (minor); $[\alpha]_D^{20}$: −10.1 (*c* 1.0, $CHCl_3$).

(*S*)-(*E*)-α-[1-(4-Methoxyphenyl)pentylidene]-β-methyl-*N*-benzyl-β-lactam [(*S*)-(*E*)-7b]

The reaction of (*S*)-(*E*)-**5b** (42 mg, 0.15 mmol, 93% *ee*), 4-methoxylphenylboronic acid (35 mg, 0.23 mmol), **3** (8 mg, 0.008 mmol), and $K_3PO_4\cdot 3H_2O$ (81 mg, 0.30 mmol) in toluene (2 mL) afforded the product (*S*)-(*E*)-**7fb**; yield: 48 mg (0.137 mmol, 91%); 96% *ee* as determined by HPLC analysis (Chiralcel AD-H, *n*-hexane:*i*-PrOH, 90:10, 230 nm): t_r 12.1 (minor), 14.4 (major); $[\alpha]_D^{20}$: +121.6 (*c* 1.85, $CHCl_3$).

(*R*)-(*E*)-α-(1-*p*-Tolylpentylidene)-β-ethyl-*N*-benzyl-β-lactam [(*R*)-(*E*)-7a]

The reaction of (*R*)-(+)-**5a** (49 mg, 0.17 mmol, 97% *ee*), 4-methylphenylboronic acid (35 mg, 0.26 mmol), **3** (9 mg,

0.009 mmol), and $K_3PO_4 \cdot 3H_2O$ (91 mg, 0.34 mmol) in toluene (2 mL) afforded the product (*R*)-(*E*)-**7a** ; yield: 53 mg (0.153 mmol, 91%); 98% *ee* as determined by HPLC analysis (Chiralcel OD, *n*-hexane:*i*-PrOH, 95:5, 230 nm); t_r 8.2 (minor), 9.0 (major); $[\alpha]_D^{20}$: −89.1 (*c* 1.25, $CHCl_3$).

Acknowledgements

Financial support from National Natural Science Foundation of China (20121202 and 20332060) and Shanghai Municipal Committee of Science and Technology is greatly appreciated.

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