JOC The Journal of Organic Chemistry

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pubs.acs.org/joc

Enantioselective Synthesis of α-Tri- and α-Tetrasubstituted Allylsilanes by Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Silylboronates

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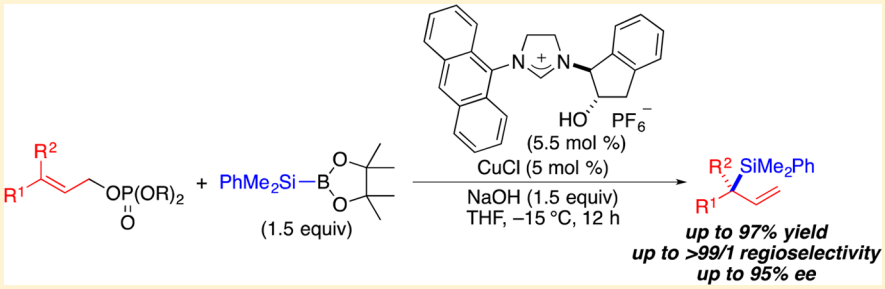
Supporting Information



ABSTRACT: A copper/*N*-heterocyclic carbene-catalyzed asymmetric allylic substitution of allyl phosphates with a silylboronate has been developed to give highly enantioenriched allylsilanes. High regioselectivity has been achieved by employing NaOH as the base, and this catalyst system is effective for both γ-mono- and disubstituted allyl phosphates.

INTRODUCTION

Copper-catalyzed asymmetric allylic substitution with organometallic reagents is one of the reliable and efficient ways of constructing γ-stereogenic enantioenriched alkenes.[1] Although traditional approaches typically employ highly reactive carbon nucleophiles such as Grignard reagents,[2] diorganozincs,[3] and triorganoaluminums,[4] significant progress has been recently made in the use of less reactive organoboron nucleophiles,[5] including the use of diboron reagents for the preparation of synthetically useful enantioenriched allylboron compounds.[6] In contrast, copper-catalyzed silylative allylic substitution has been much less explored and mostly limited to the use of disilylzinc reagents in the context of nonasymmetric reactions.[7,8] Despite the high utility of resulting enantioenriched allylsilanes in synthetic organic chemistry,[9] no catalytic enantioselective variants had been reported until a very recent publication by Oestreich and co-workers.[10,11] In this context, herein we describe the development of a copper/*N*-heterocyclic carbene complex-catalyzed asymmetric carbon−silicon bond-forming allylic substitution of simple allylic electrophiles with silylboronates to provide a straightforward access to chiral allylsilanes with high regio- and enantioselectivities.[12]

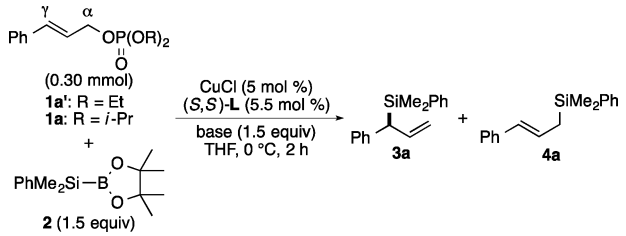
RESULTS AND DISCUSSION

In 2010, Oestreich and co-workers reported a copper-catalyzed allylic substitution of allyl chlorides with a silylboronate,[8a,13] and we recently described that a chiral *N*-heterocyclic carbene (NHC) ligand derived from (*S*,*S*)-**L** is particularly effective for a copper-catalyzed asymmetric allylic substitution of allyl phosphates with aryl- and alkenylboronates.[5a] On the basis of these reports, we initially conducted a reaction of (*E*)-cinnamyl diethyl phosphate (**1a**′) with dimethylphenylsilylboronate **2**[14] in the presence of CuCl (5 mol %) and chiral NHC salt (*S*,*S*)-**L**[15] (5.5 mol %) in THF at 0 °C and found that the reaction outcome was strongly influenced by the choice of metal alkoxide base. KO-*t*-Bu, which is often used for copper-catalyzed reactions of organoboronates,[16] turned out to be ineffective, giving a 43/57 mixture of γ-substituted allylsilane **3a** and α-substituted allylsilane **4a** in low combined yield with full consumption of the substrate, and **3a** thus obtained was only 16% ee (Table 1, entry 1). In contrast, the reaction proceeded cleanly by using NaO-*t*-Bu as the base to give allylsilanes **3a** and **4a** in 97% combined yield in the ratio of 67/33 with improved ee of 41% for **3a** (entry 2). Further improvement on both regio- and enantioselectivities was observed by changing the

Received: April 25, 2013
Published: April 28, 2013

   dx.doi.org/10.1021/jo400888b | *J. Org. Chem.* 2013, 78, 5007−5017

Table 1. Copper-Catalyzed Asymmetric Allylic Substitution of (*E*)-Cinnamyl Phosphates 1 with Silylboronate 2: Optimization



entry	substrate	base	yield (%)[a]	3a/4a[b]	ee of 3a (%)[c]
1	(*E*)-**1a**′	KO*t*-Bu	28[b]	43/57	16
2	(*E*)-**1a**′	NaO*t*-Bu	97[b]	67/33	41
3	(*E*)-**1a**′	NaOEt	85[b]	87/13	70
4	(*E*)-**1a**′	NaOMe	89	97/3	86
5	(*E*)-**1a**′	NaOH	92	>99/1	85
6[d]	(*E*)-**1a**′	NaOH	86	99/1	90
7[d]	(*E*)-**1a**	NaOH	91	98/2	92
8[d,e]	(*E*)-**1a**	NaOH	86	95/5	71

[a]Combined yield of **3a** and **4a**. [b]Determined by ^{1}H NMR. [c]Determined by chiral HPLC on a Chiralcel OD-H column with hexane/2-propanol = 95/5 after converting **3a** to alcohol **5a** by a hydroboration−oxidation sequence. [d]The reaction was conducted at −15 °C for 12 h. [e](*S,S*)-**L**′ was used instead of (*S,S*)-**L**.

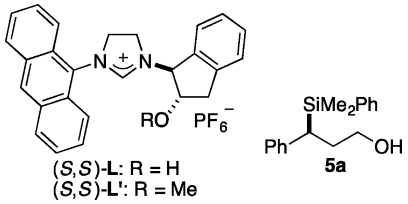
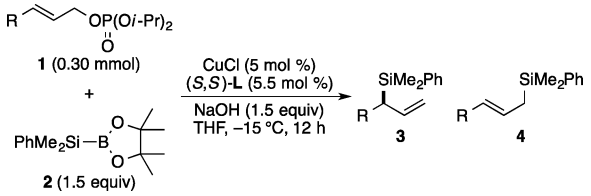
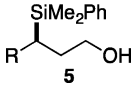


Table 2. Copper-Catalyzed Asymmetric Allylic Substitution of (*E*)-1 with Silylboronate 2: Scope



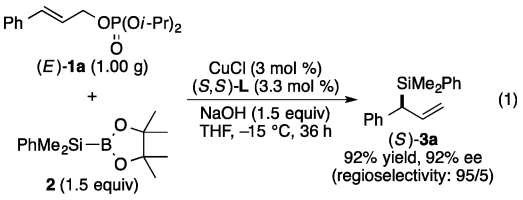
entry	1 (R)	product	yield[a] (%)	3/4[b]	ee of 3[c] (%)
1	(*E*)-**1a** (Ph)	(*S*)-**3a**	91	98/2	92
2	(*E*)-**1b** (4-MeC_6H_4)	(*S*)-**3b**	90	98/2	92
3	(*E*)-**1c** (4-ClC_6H_4)	(*S*)-**3c**	87	99/1	90
4	(*E*)-**1d** (3-MeC_6H_4)	(*S*)-**3d**	87	99/1	91
5	(*E*)-**1e** (3-MeO$CH_2OC_6H_4$)	(*S*)-**3e**	84	97/3	90
6	(*E*)-**1f** (2-MeC_6H_4)	(*S*)-**3f**	91	>99/1	95
7	(*E*)-**1g** (2-BrC_6H_4)	(*S*)-**3g**	83	99/1	94
8	(*E*)-**1h** (2-naphthyl)	(*S*)-**3h**	96	>99/1	90
9	(*E*)-**1i** (1-naphthyl)	(*S*)-**3i**	78	98/2	93
10	(*E*)-**1j** (3-thienyl)	(*S*)-**3j**	94	99/1	89
11	(*E*)-**1k** (Me)[d]	(*R*)-**3k**	90	95/5	86
12	(*E*)-**1l** ($PhCH_2CH_2$)	(*R*)-**3l**	93	99/1	91
13	(*E*)-**1m** ($PhCO_2CH_2$)	(*S*)-**3m**	89	>99/1	88
14	(*E*)-**1n** (Cy)	(*S*)-**3n**	97	98/2	91
15	(*E*)-**1o** (*t*-Bu)	(*S*)-**3o**	72	77/23	95

[a]Combined yield of **3** and **4**. [b]Determined by ^{1}H NMR. [c]Determined by chiral HPLC with hexane/2-propanol after converting **3** to alcohol **5** by a hydroboration−oxidation sequence. [d]*E*/*Z* = 97/3.



base to NaOEt (87/13, 70% ee; entry 3) and to NaOMe (97/3, 86% ee; entry 4), and even better selectivity toward **3a** was realized by using NaOH (>99/1, 85% ee; entry 5). Somewhat higher enantioselectivity was achieved by conducting the reaction at −15 °C (90% ee, entry 6), and the change of substrate from diethyl phosphate (**1a**′) to diisopropyl phosphate (**1a**) led to further enhancement of enantioselectivity (92% ee; entry 7). The absolute configuration of **3a** thus obtained was determined to be *S* by comparing the value of its optical rotation with the reported value in the literature.[3a] In comparison, the use of (*S,S*)-**L**′ having a methoxy group instead of a hydroxy group resulted in significantly lower enantioselectivity (71% ee; entry 8).[5a,16e]

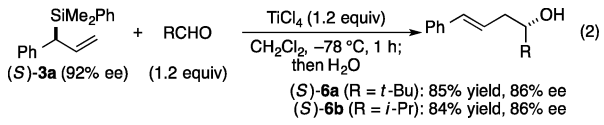
Under the conditions described in Table 1, entry 7, various substituted phenyl groups are tolerated at the γ-position of allyl diisopropyl phosphates **1** for the reaction with silylboronate **2** to give the corresponding allylsilanes **3** with high regio- and enantioselectivities (**3**/**4** ≥ 97/3, 90−95% ee; Table 2, entries 1−7). Substrates with naphthyl or thienyl groups can also be employed with similarly high efficiency (**3**/**4** ≥ 98/2, 89−93% ee: entries 8−10). The present catalysis is applicable to γ-alkyl-substituted allyl phosphates **1** as well. Thus, crotyl phosphate **1k** can be effectively converted to the corresponding allylsilane **3k** with reasonably high enantioselectivity (**3k**/**4k** = 95/5, 86% ee from **1k** with *E*/*Z* = 97/3; entry 11). In addition, both primary and secondary alkyl groups are also suitable γ-substituents in the present silylative allylic substitution reaction (**3**/**4** ≥ 98/2, 88−91% ee; entries 12−14), and even tertiary alkyl groups can be incorporated with high enantioselectivity, although somewhat lower reactivity and regioselectivity are observed (**3o**/**4o** = 77/23, 95% ee; entry 15). It is worth noting that functional groups such as halides, acetals, and esters are well tolerated under the present reaction conditions (entries 3, 5, 7, and 13), and the reaction can also be conducted on a gram scale with a reduced catalyst loading (3 mol %) as demonstrated in eq 1.



Of course, enantioenriched allylsilanes **3** obtained in the present catalysis can be used for the synthesis of enantioenriched homoallyl alcohols by reacting them with aldehydes.[17] For example, the reaction of (*S*)-**3a** (92% ee) with pivalaldehyde in the presence of $TiCl_4$ smoothly proceeded to give geometrically pure homoallyl alcohol (*S*)-**6a** in 85% yield with 93% chirality transfer (eq 2). Similarly, the use of isobutyraldehyde gave (*S*)-**6b** in 84% yield with 93% chirality transfer.

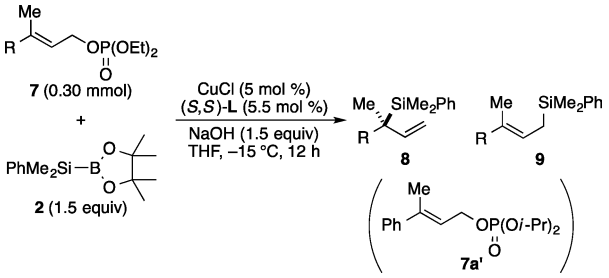
In addition to the scope illustrated in Table 2, the present catalysis turned out to be effective for the synthesis of allylsilanes having a tetrasubstituted carbon stereocenter by employing γ,γ-disubstituted allyl phosphates.[3a,4d] Although the

dx.doi.org/10.1021/jo400888b | J. Org. Chem. 2013, 78, 5007−5017



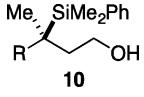
reaction of diisopropyl (*E*)-3-phenyl-2-butenyl phosphate (**7a**′) with silylboronate **2** gave an 80/20 mixture of γ-substitution product **8a** and α-substitution product **9a**, **8a** was obtained with as high as 95% ee (Table 3, entry 1). We subsequently found

Table 3. Copper-Catalyzed Asymmetric Allylic Substitution of 7 with Silylboronate 2: Examples



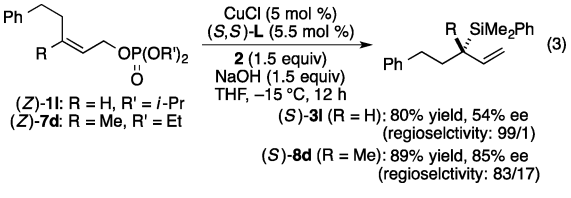
entry	7 (R)	product	yield[a] (%)	8/9[b]	ee of 8[c] (%)
1	(*E*)-**7a**′	(*S*)-**8a**	86	80/20	95
2	(*E*)-**7a** (Ph)	(*S*)-**8a**	84[d]	92/8	95
3[e]	(*E*)-**7a**	(*S*)-**8a**	86	42/58	91
4	(*E*)-**7b** (4-ClC_6H_4)	(*S*)-**8b**	88	92/8	95
5	(*E*)-**7c** (2-naphthyl)	(*S*)-**8c**	94	93/7	94
6	(*E*)-**7d** ($PhCH_2CH_2$)	(*R*)-**8d**	75	97/3	89

[a]Combined yield of **8** and **9** unless otherwise noted. [b]Determined by ^{1}H NMR. [c]Determined by chiral HPLC with hexane/2-propanol after converting **8** to alcohol **10** by a hydroboration−oxidation sequence. [d]Isolated yield of **8**. [e]NaOMe was used instead of NaOH.

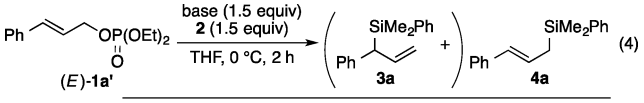


that the change of substrate to the corresponding diethyl phosphate (**7a**) could improve the γ-selectivity in high yield with the same level of enantioselectivity (**8a**/**9a** = 92/8, 95% ee; entry 2). It is important to note that the choice of base shows much more profound effect on the regioselectivity for this type of substrate. Thus, NaOMe, which gives reasonably high γ-selectivity for the reaction of γ-monosubstituted substrate **1a**′ (**3a**/**4a** = 97/3; Table 1, entry 4), is significantly inferior to NaOH for substrate **7a**, giving **8a**/**9a** in the ratio of 42/58 (entry 3). Several other allyl phosphates **7** can also be efficiently employed under the same conditions as those in entry 2 to give allylsilanes **8** in good yield with high regio- and enantioselectivities (entries 4−6).

In contrast to the (*E*)-substrates employed so far, the use of (*Z*)-**1l** leads to the formation of **3l** with 54% ee with an absolute configuration opposite to that in Table 2, entry 12 (eq 3). Similarly, γ,γ-disubstituted (*Z*)-**7d** also gives α-tetrasubstituted allylsilane **8d** with 85% ee with an absolute configuration opposite to that in Table 3, entry 6. These results indicate that the position of phosphate, rather than the position of γ-substituent, primarily controls the facial selectivity of the allylic substrate.[18]

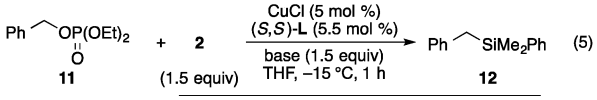


To gain some insight into the origin of the regioselectivity depending on the base as demonstrated in Table 1, we conducted the following two sets of control experiments. First, the effect of base was examined for the reaction of (*E*)-cinnamyl phosphate **1a**′ with silylboronate **2** in the absence of CuCl and (*S*,*S*)-**L**, and we found that the consumption of **1a**′ became slower in the order of KO-*t*-Bu, NaO-*t*-Bu, NaOMe, and NaOH, and the yield of α-substitution product **4a** became lower in the same order (eq 4). It is worth noting that no



base	conv. of **1a**′ (%)[a]	yield of **3a** (%)[a]	yield of **4a** (%)[a]
KO*t*-Bu	>99	0	18
NaO*t*-Bu	76	0	17
NaOMe	20	0	11
NaOH	<1	0	0

[a] Determined by ^{1}H NMR.



base	conv. of **11** (%)[a,b]	yield of **12** (%)[a,b]
KO*t*-Bu	63 (57)	63 (42)
NaO*t*-Bu	69 (26)	66 (25)
NaOMe	49 (<1)	47 (0)
NaOH	3 (<1)	0 (0)

[a] Determined by ^{1}H NMR. [b] The values in parentheses are obtained in the absence of CuCl and (*S*,*S*)-**L**.

formation of γ-substitution product **3a** was observed regardless of the base, indicating that **3a** could only be produced in the presence of CuCl/(*S*,*S*)-**L**. In addition, we employed model substrate **11** to compare the effect of base for the S_N2-type reaction catalyzed by CuCl/(*S*,*S*)-**L** under the similar conditions as those in Table 1 (eq 5). In these reactions, both the consumption of **11** and the yield of substitution product **12** were relatively high with KO-*t*-Bu and NaO-*t*-Bu and somewhat lower with NaOMe. In contrast, almost no **11** was consumed with NaOH, and compound **12** was not produced at all. On the basis of these experiments, the observed high γ-selectivity by using NaOH as the base in the present asymmetric allylic substitution reaction could be attributed to the effective suppression of both the base-promoted uncatalyzed reaction and the copper-catalyzed S_N2-type reaction toward the formation of the α-substitution product.

■ CONCLUSION

We have developed a copper/*N*-heterocyclic carbene-catalyzed asymmetric allylic substitution of allyl phosphates with a silylboronate to give highly enantioenriched allylsilanes. We have found that the use of NaOH as the base is particularly beneficial for achieving high regioselectivity, and the present catalyst system is effective for both γ-mono- and disubstituted allyl phosphates. Future studies will be directed toward the mechanistic investigation to understand the catalytic cycle[19] as well as the origin of the stereoselectivity in the present catalysis.

dx.doi.org/10.1021/jo400888b | J. Org. Chem. 2013, 78, 5007−5017

EXPERIMENTAL SECTION

General Methods. All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glovebox under argon. Et_2O, CH_2Cl_2, THF, and toluene were purified by passing through neutral alumina columns under nitrogen. Et_3N was distilled over KOH under nitrogen. 2-Propanol was distilled over CaH_2 under nitrogen. CuCl was washed with HCl(aq) and dried under vacuum prior to use. NaOH was ground into powder and dried under vacuum prior to use. (*E*)-**1a**′,[20] (*E*)-**7a**,[5a] (*E*)-**7b**,[4e] (*E*)-**7c**,[4d] (*S*,*S*)-**L**,[16f] (*S*,*S*)-**L**′,[16f] (*E*)-3-(4-methylphenyl)-2-propenol,[21] (*E*)-3-(4-chlorophenyl)-2-propenol,[22] (*E*)-3-(3-methylphenyl)-2-propenol,[5a] 3-methoxymethoxybenzaldehyde,[23] (*E*)-3-(2-methylphenyl)-2-propenol,[24] (*E*)-3-(2-bromophenyl)-2-propenol,[25] (*E*)-3-(2-naphthyl)-2-propenol,[22] (*E*)-3-(1-naphthyl)-2-propenol,[22] (*E*)-3-(3-thienyl)-2-propenol,[26] (*E*)-crotyl alcohol,[27] (*E*)-5-phenyl-2-pentenol,[28] (*E*)-2-butene-1,4-diol,[29] (*E*)-3-cyclohexyl-2-propenol,[30] (*E*)-4,4-dimethyl-2-pentenol,[31] (*Z*)-5-phenyl-2-pentenol,[32] (*E*)-3-phenyl-2-butenol,[33] (*E*)-3-methyl-5-phenyl-2-pentenol,[34] and *tert*-butyl (*Z*)-3-methyl-5-phenyl-2-pentenoate[35] were synthesized following the literature procedures. All other commercial chemicals and solvents were used as received.

Diisopropyl Chlorophosphate (CAS 2574-25-6). 2-Propanol (19.2 mL, 250 mmol) in Et_2O (120 mL) was added dropwise to a solution of phosphoryl chloride (9.32 mL, 100 mmol) and Et_3N (34.8 mL, 250 mmol) in Et_2O (80 mL) at −78 °C, and the mixture was stirred for 20 h while the temperature was gradually raised from −78 °C to room temperature. The precipitate that formed was filtered off with Et_2O, and the resulting solution was washed with saturated NaCl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residual oil was passed through a pad of alumina and silica gel with EtOAc, and the solvent was removed. The residue was then purified by distillation under vacuum to afford diisopropyl chlorophosphate as a colorless oil (12.0 g, 59.8 mmol; 60% yield). ^{1}H NMR ($CDCl_3$): δ 4.83 (d of sept, $^3J_{HP}$ = 9.0 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 1.41 (d, $^3J_{HH}$ = 5.7 Hz, 6H), 1.40 (d, $^3J_{HH}$ = 5.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 75.6 (d, $^2J_{CP}$ = 6.7 Hz), 23.6 (d, $^3J_{CP}$ = 5.7 Hz), 23.3 (d, $^3J_{CP}$ = 5.7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 2.9 (s).

Diisopropyl (*E*)-3-Phenyl-2-propenyl phosphate ((*E*)-1a) (CAS 101494-38-6). 4-(Dimethylamino)pyridine (122 mg, 1.00 mmol) and Et_3N (1.67 mL, 12.0 mmol) were added to a solution of (*E*)-cinnamyl alcohol (1.34 g, 10.0 mmol) in CH_2Cl_2 (10 mL), and the resulting solution was cooled to 0 °C. Diisopropyl chlorophosphate (2.40 g, 12.0 mmol) in CH_2Cl_2 (20 mL) was added dropwise, and the mixture was stirred for 12 h at room temperature. The reaction was quenched with saturated NH_4Cl(aq) and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 1/1 and further purified by GPC with $CHCl_3$ to afford compound **1a** as a colorless oil (1.14 g, 3.82 mmol; 76% yield). ^{1}H NMR ($CDCl_3$): δ 7.39 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 7.33 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 7.26 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 6.67 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 6.30 (dt, $^3J_{HH}$ = 15.9 and 6.1 Hz, 1H), 4.71−4.61 (m, 4H), 1.35 (d, $^3J_{HH}$ = 6.1 Hz, 6H), 1.34 (d, $^3J_{HH}$ = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 136.2, 133.5, 128.7, 128.1, 126.7, 124.0 (d, $^3J_{CP}$ = 6.7 Hz), 72.5 (d, $^2J_{CP}$ = 6.2 Hz), 67.6 (d, $^2J_{CP}$ = 5.7 Hz), 23.72 (d, $^3J_{CP}$ = 5.2 Hz), 23.71 (d, $^3J_{CP}$ = 5.2 Hz).

Diisopropyl (*E*)-3-(4-Methylphenyl)-2-propenyl Phosphate ((*E*)-1b). This was synthesized from (*E*)-3-(4-methylphenyl)-2-propenol following the procedure for compound **1a**. Colorless oil, 71% yield (1.11 g). ^{1}H NMR ($CDCl_3$): δ 7.28 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.13 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 6.63 (d, $^3J_{HH}$ = 15.6 Hz, 1H), 6.25 (dt, $^3J_{HH}$ = 15.7 and 6.2 Hz, 1H), 4.71−4.60 (m, 4H), 2.34 (s, 3H), 1.342 (d, $^3J_{HH}$ = 6.1 Hz, 6H), 1.336 (d, $^3J_{HH}$ = 6.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 138.1, 133.6, 133.5, 129.4, 126.7, 123.0 (d, $^3J_{CP}$ = 6.7 Hz), 72.5 (d, $^2J_{CP}$ = 6.2 Hz), 67.9 (d, $^2J_{CP}$ = 5.7 Hz), 23.8 (d, $^3J_{CP}$ = 5.2 Hz), 21.3. HRMS (ESI-TOF): calcd for $C_{16}H_{25}O_4PNa$ (M + Na^+) 335.1383, found 335.1381.

Diisopropyl (*E*)-3-(4-Chlorophenyl)-2-propenyl Phosphate ((*E*)-1c). This was synthesized from (*E*)-3-(4-chlorophenyl)-2-propenol following the procedure for compound **1a**. Colorless oil, 69% yield (1.15 g). ^{1}H NMR ($CDCl_3$): δ 7.33−7.27 (m, 4H), 6.62 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 6.27 (dt, $^3J_{HH}$ = 15.7 and 6.0 Hz, 1H), 4.72−4.60 (m, 4H), 1.344 (d, $^3J_{HH}$ = 6.1 Hz, 6H), 1.337 (d, $^3J_{HH}$ = 6.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 134.7, 133.8, 132.1, 128.8, 127.9, 124.7 (d, $^3J_{CP}$ = 7.2 Hz), 72.5 (d, $^2J_{CP}$ = 5.7 Hz), 67.4 (d, $^2J_{CP}$ = 5.7 Hz), 23.71 (d, $^3J_{CP}$ = 4.7 Hz), 23.69 (d, $^3J_{CP}$ = 4.7 Hz). HRMS (ESI-TOF): calcd for $C_{15}H_{22}ClO_4PNa$ (M + Na^+) 355.0836, found 355.0831.

Diisopropyl (*E*)-3-(3-Methylphenyl)-2-propenyl Phosphate ((*E*)-1d). This was synthesized from (*E*)-3-(3-methylphenyl)-2-propenol following the procedure for compound **1a**. Colorless oil, 75% yield (1.18 g). ^{1}H NMR ($CDCl_3$): δ 7.24−7.16 (m, 3H), 7.10−7.06 (m, 1H), 6.64 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 6.29 (dt, $^3J_{HH}$ = 15.9 and 6.2 Hz, 1H), 4.71−4.61 (m, 4H), 2.35 (s, 3H), 1.344 (d, $^3J_{HH}$ = 6.2 Hz, 6H), 1.339 (d, $^3J_{HH}$ = 6.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 138.2, 136.2, 133.6, 128.9, 128.6, 127.4, 123.8, 123.7 (d, $^3J_{CP}$ = 7.2 Hz), 72.5 (d, $^2J_{CP}$ = 5.7 Hz), 67.7 (d, $^2J_{CP}$ = 5.7 Hz), 23.73 (d, $^3J_{CP}$ = 5.2 Hz), 23.72 (d, $^3J_{CP}$ = 5.2 Hz), 21.4. HRMS (ESI-TOF): calcd for $C_{16}H_{25}O_4PNa$ (M + Na^+) 335.1383, found 335.1378.

(*E*)-3-(3-Methoxymethoxyphenyl)-2-propenol (CAS 474009-18-2). Triethyl phosphonoacetate (2.10 mL, 10.6 mmol) was added to a suspension of NaH (393 mg, 9.82 mmol; 60 wt %) in THF (25 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. 3-(Methoxymethoxy)benzaldehyde (1.36 g, 8.18 mmol) in THF (5 mL) was added, and the resulting mixture was stirred for 5 h at room temperature. The reaction was quenched with H_2O at 0 °C, and this was extracted with EtOAc. The organic layer was washed with saturated NaCl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 to afford ethyl (*E*)-3-(3-methoxymethoxyphenyl)-2-propenoate as a colorless oil (808 mg, 3.42 mmol; 42% yield). ^{1}H NMR ($CDCl_3$): δ 7.65 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 7.30 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 7.21 (t, $^4J_{HH}$ = 2.0 Hz, 1H), 7.17 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.06 (ddd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 2.4 and 0.7 Hz, 1H), 6.42 (d, $^3J_{HH}$ = 16.0 Hz, 1H), 5.19 (s, 2H), 4.27 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 3.49 (s, 3H), 1.34 (t, $^3J_{HH}$ = 7.1 Hz, 3H).

Diisobutylaluminum hydride (7.52 mL, 7.52 mmol; 1.0 M solution in hexane) was added dropwise over 5 min to a solution of ethyl (*E*)-3-(3-methoxymethoxyphenyl)-2-propenoate (808 mg, 3.42 mmol) in toluene (10 mL) at −78 °C. The mixture was stirred for 12 h while the temperature was gradually raised to room temperature. The reaction was quenched with H_2O, and the precipitate that formed was filtered off through Celite with EtOAc. The organic layer was washed with saturated NaCl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 3/1 to afford (*E*)-3-(3-methoxymethoxyphenyl)-2-propenol as a colorless oil (453 mg, 2.33 mmol: 68% yield). ^{1}H NMR ($CDCl_3$): δ 7.24 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 7.08 (dd, $^4J_{HH}$ = 2.2 and 1.8 Hz, 1H), 7.04 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 6.93 (ddd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 2.4 and 0.8 Hz, 1H), 6.59 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 6.37 (dt, $^3J_{HH}$ = 15.9 and 5.7 Hz, 1H), 5.18 (s, 2H), 4.37−4.27 (m, 2H), 3.49 (s, 3H), 1.44 (bs, 1H).

Diisopropyl (*E*)-3-[3-(Methoxymethoxy)phenyl]-2-propenyl Phosphate ((*E*)-1e). This was synthesized from (*E*)-3-[3-(methoxylmethoxy)phenyl]-2-propenol following the procedure for compound **1a**. Colorless oil, 87% yield (727 mg). ^{1}H NMR ($CDCl_3$): δ 7.24 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 7.07 (t, $^4J_{HH}$ = 2.0 Hz, 1H), 7.03 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 6.95 (ddd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 2.4 and 0.8 Hz, 1H), 6.63 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 6.29 (dt, $^3J_{HH}$ = 15.8 and 6.0 Hz, 1H), 5.18 (s, 2H), 4.71−4.61 (m, 4H), 3.48 (s, 3H), 1.35 (d, $^3J_{HH}$ = 6.2 Hz, 6H), 1.34 (d, $^3J_{HH}$ = 6.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 157.7, 137.8, 133.2, 129.8, 124.5 (d, $^3J_{CP}$ = 7.2 Hz), 120.6, 116.1, 114.5, 94.6, 72.6 (d, $^2J_{CP}$ = 5.7 Hz), 67.6 (d, $^2J_{CP}$ = 5.2 Hz), 56.1, 23.81 (d, $^3J_{CP}$ = 5.2 Hz), 23.80 (d, $^3J_{CP}$ = 5.2 Hz). HRMS (ESI-TOF): calcd for $C_{17}H_{27}O_6PNa$ (M + Na^+) 381.1437, found 381.1432.

Diisopropyl (*E*)-3-(2-Methylphenyl)-2-propenyl Phosphate ((*E*)-1f). This was synthesized from (*E*)-3-(2-methylphenyl)-2-propenol following the procedure for compound **1a**. Colorless oil, 64% yield (709 mg). ^{1}H NMR ($CDCl_3$): δ 7.46−7.41 (m, 1H), 7.20−7.12 (m, 3H), 6.89 (dt, $^3J_{HH}$ = 15.8 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 6.19 (dt, $^3J_{HH}$ = 15.7 and 6.1 Hz, 1H), 4.72−4.62 (m, 4H), 2.35 (s, 3H), 1.351 (d, $^3J_{HH}$ = 6.2 Hz, 6H), 1.347 (d, $^3J_{HH}$ = 6.2 Hz, 6H). ^{13}C NMR

dx.doi.org/10.1021/jo400888b | J. Org. Chem. 2013, 78, 5007−5017

($CDCl_3$): δ 135.8, 135.4, 131.4, 130.5, 128.1, 126.3, 126.0, 125.4 (d, $^3J_{CP}$ = 7.2 Hz), 72.6 (d, $^2J_{CP}$ = 6.2 Hz), 67.9 (d, $^2J_{CP}$ = 5.7 Hz), 23.81 (d, $^3J_{CP}$ = 4.7 Hz), 23.80 (d, $^3J_{CP}$ = 4.7 Hz), 19.8. HRMS (ESI-TOF): calcd for $C_{16}H_{25}O_4PNa$ (M + Na^+) 335.1383, found 335.1391.

Diisopropyl (*E*)-3-(2-Bromophenyl)-2-propenyl Phosphate ((*E*)-1g). This was synthesized from (*E*)-3-(2-bromophenyl)-2-propenol following the procedure for compound **1a**. Colorless oil, 73% yield (469 mg). ^{1}H NMR ($CDCl_3$): δ 7.55 (dd, $^3J_{HH}$ = 7.9 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 7.51 (dd, $^3J_{HH}$ = 7.7 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.27 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.12 (td, $^3J_{HH}$ = 7.7 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.01 (d, $^3J_{HH}$ = 15.7 Hz, 1H), 6.25 (dt, $^3J_{HH}$ = 15.8 and 5.9 Hz, 1H), 4.73−4.63 (m, 4H), 1.35 (d, $^3J_{HH}$ = 6.1 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 136.2, 133.1, 131.8, 129.4, 127.6, 127.3, 127.0 (d, $^3J_{CP}$ = 7.2 Hz), 123.8, 72.6 (d, $^2J_{CP}$ = 6.2 Hz), 67.2 (d, $^2J_{CP}$ = 5.2 Hz), 23.78 (d, $^3J_{CP}$ = 4.7 Hz), 23.76 (d, $^3J_{CP}$ = 5.2 Hz). HRMS (ESI-TOF): calcd for $C_{15}H_{22}BrO_4PNa$ (M + Na^+) 399.0331, found 399.0335.

Diisopropyl (*E*)-3-(2-Naphthyl)-2-propenyl Phosphate ((*E*)-1h). This was synthesized from (*E*)-3-(2-naphthyl)-2-propenol following the procedure for compound **1a**. Colorless oil, 81% yield (1.42 g). ^{1}H NMR ($CDCl_3$): δ 7.84−7.76 (m, 3H), 7.75 (s, 1H), 7.60 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 7.50−7.42 (m, 2H), 6.83 (d, $^3J_{HH}$ = 15.8 Hz, 1H), 6.43 (dt, $^3J_{HH}$ = 15.8 and 6.2 Hz, 1H), 4.76−4.63 (m, 4H), 1.36 (d, $^3J_{HH}$ = 6.2 Hz, 6H), 1.35 (d, $^3J_{HH}$ = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 133.7, 133.64, 133.61, 133.3, 128.4, 128.1, 127.8, 127.0, 126.5, 126.2, 124.4 (d, $^3J_{CP}$ = 7.2 Hz), 123.6, 72.6 (d, $^2J_{CP}$ = 5.7 Hz), 67.8 (d, $^2J_{CP}$ = 5.7 Hz), 23.80 (d, $^3J_{CP}$ = 4.7 Hz), 23.79 (d, $^3J_{CP}$ = 4.6 Hz). HRMS (ESI-TOF): calcd for $C_{19}H_{25}O_4PNa$ (M + Na^+) 371.1383, found 371.1387.

Diisopropyl (*E*)-3-(1-Naphthyl)-2-propenyl Phosphate ((*E*)-1i). This was synthesized from (*E*)-3-(1-naphthyl)-2-propenol following the procedure for compound **1a**. Colorless oil, 66% yield (758 mg). ^{1}H NMR ($CDCl_3$): δ 8.10 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.86 (dd, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.80 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.60 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.55−7.47 (m, 2H), 7.47−7.41 (m, 2H), 6.34 (dt, $^3J_{HH}$ = 15.6 and 6.0 Hz, 1H), 4.79 (ddd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 6.0 Hz, and $^4J_{HH}$ = 1.5 Hz, 2H), 4.70 (d of sept, $^3J_{HP}$ = 6.9 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 1.37 (d, $^3J_{HH}$ = 6.1 Hz, 6H), 1.36 (d, $^3J_{HH}$ = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 134.0, 133.7, 131.2, 130.6, 128.6, 128.5, 127.2 (d, $^3J_{CP}$ = 6.7 Hz), 126.3, 126.0, 125.7, 124.2, 123.8, 72.6 (d, $^2J_{CP}$ = 6.2 Hz), 67.8 (d, $^2J_{CP}$ = 5.7 Hz), 23.81 (d, $^3J_{CP}$ = 5.2 Hz), 23.79 (d, $^3J_{CP}$ = 5.2 Hz). HRMS (ESI-TOF): calcd for $C_{19}H_{25}O_4PNa$ (M + Na^+) 371.1383, found 371.1377.

Diisopropyl (*E*)-3-(3-Thienyl)-2-propenyl Phosphate ((*E*)-1j). This was synthesized from (*E*)-3-(3-thienyl)-2-propenol following the procedure for compound **1a**. Colorless oil, 70% yield (1.07 g). ^{1}H NMR ($CDCl_3$): δ 7.28 (ddd, $^3J_{HH}$ = 5.1 Hz and $^4J_{HH}$ = 2.9 and 0.6 Hz, 1H), 7.21 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.19 (dd, $^4J_{HH}$ = 2.8 and 1.1 Hz, 1H), 6.67 (d, $^3J_{HH}$ = 15.7 Hz, 1H), 6.15 (dt, $^3J_{HH}$ = 15.7 and 6.2 Hz, 1H), 4.70−4.60 (m, 4H), 1.34 (d, $^3J_{HH}$ = 6.2 Hz, 6H), 1.33 (d, $^3J_{HH}$ = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 138.9, 127.8, 126.3, 125.1, 123.8 (d, $^3J_{CP}$ = 7.2 Hz), 123.2, 72.5 (d, $^2J_{CP}$ = 5.7 Hz), 67.7 (d, $^2J_{CP}$ = 5.7 Hz), 23.77 (d, $^3J_{CP}$ = 4.7 Hz), 23.76 (d, $^3J_{CP}$ = 4.6 Hz). HRMS (ESI-TOF): calcd for $C_{13}H_{21}O_4PSNa$ (M + Na^+) 327.0790, found 327.0788.

Diisopropyl (*E*)-2-Butenyl Phosphate ((*E*)-1k). This was synthesized from (*E*)-crotyl alcohol following the procedure for compound **1a**. Colorless oil, 31% yield (740 mg, *E*/*Z* = 97/3). ^{1}H NMR ($CDCl_3$): δ 5.83−5.74 (m, 1H), 5.66−5.57 (m, 1H), 4.62 (d of sept, $^3J_{HP}$ = 7.1 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 4.46−4.41 (m, 2H), 1.74−1.70 (m, 3H), 1.324 (d, $^3J_{HH}$ = 6.2 Hz, 6H), 1.320 (d, $^3J_{HH}$ = 6.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 130.8, 126.0 (d, $^3J_{CP}$ = 6.7 Hz), 72.2 (d, $^2J_{CP}$ = 5.7 Hz), 67.8 (d, $^2J_{CP}$ = 5.7 Hz), 23.7 (d, $^3J_{CP}$ = 5.2 Hz), 17.7. HRMS (ESI-TOF): calcd for $C_{10}H_{21}O_4PNa$ (M + Na^+) 259.1070, found 259.1069.

Diisopropyl (*E*)-5-Phenyl-2-pentenyl Phosphate ((*E*)-1l). This was synthesized from (*E*)-5-phenyl-2-pentenol following the procedure for compound **1a**. Colorless oil, 72% yield (1.05 g). ^{1}H NMR ($CDCl_3$): δ 7.28 t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.21−7.15 (m, 3H), 5.82 (dtt, $^3J_{HH}$ = 15.2 and 6.7 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 5.63 (dtt, $^3J_{HH}$ = 15.4 and 6.2 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 4.62 (d of sept, $^3J_{HP}$ = 7.0 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 4.47−4.42 (m, 2H), 2.71 (t, $^3J_{HH}$ = 7.9 Hz, 2H), 2.42−2.35 (m, 2H), 1.33 (d, $^3J_{HH}$ = 6.1 Hz, 6H), 1.32 (d, $^3J_{HH}$ = 6.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 141.5, 134.7, 128.43, 128.39, 126.0, 125.4 (d, $^3J_{CP}$ = 7.2 Hz), 72.3 (d, $^2J_{CP}$ = 6.2 Hz), 67.7 (d, $^2J_{CP}$ = 5.7 Hz), 35.3, 33.9, 23.7 (d, $^3J_{CP}$ = 4.8 Hz). HRMS (ESI-TOF): calcd for $C_{17}H_{27}O_4PNa$ (M + Na^+) 349.1539, found 349.1535.

(*E*)-4-(Benzoyloxy)-2-butenol (CAS 118017-15-5). NaH (263 mg, 6.58 mmol; 60 wt %) was added to a solution of (*E*)-2-butene-1,4-diol (565 mg, 6.41 mmol) in THF (10 mL) at 0 °C, and the mixture was stirred for 30 min at 0 °C. Benzoyl chloride (745 μL, 6.41 mmol) in THF (10 mL) was then added, and this was stirred for 3 h at 0 °C. The reaction was quenched with H_2O and extracted with Et_2O. The organic layer was washed with saturated NaCl(aq), dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 3/1 to afford (*E*)-4-(benzoyloxy)-2-butenol as a colorless oil (957 mg, 4.98 mmol; 78% yield). ^{1}H NMR ($CDCl_3$): δ 8.08−8.04 (m, 2H), 7.56 (tt, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 7.44 (t, $^3J_{HH}$ = 7.9 Hz, 2H), 6.03 (dtt, $^3J_{HH}$ = 15.6 and 5.0 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 5.95 (dtt, $^3J_{HH}$ = 15.5 and 5.6 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 4.86−4.82 (m, 2H), 4.22 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 1.2 Hz, 2H), 1.46 (bs, 1H).

Diisopropyl (*E*)-4-(Benzoyloxy)-2-butenyl Phosphate ((*E*)-1m). This was synthesized from (*E*)-4-(benzoyloxy)-2-butenol, following the procedure for compound **1a**. Colorless oil, 42% yield (753 mg). ^{1}H NMR ($CDCl_3$): δ 8.07−8.02 (m, 2H), 7.56 (t, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 7.44 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 6.02 (dt, $^3J_{HH}$ = 15.5 and 5.1 Hz, 1H), 5.96 (dt, $^3J_{HH}$ = 15.6 and 4.6 Hz, 1H) 4.84 (d, $^3J_{HH}$ = 4.6 Hz, 2H), 4.64 (d of sept, $^3J_{HP}$ = 6.8 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 4.57−4.52 (m, 2H), 1.33 (d, $^3J_{HH}$ = 6.2 Hz, 6H), 1.32 (d, $^3J_{HH}$ = 6.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 166.1, 133.1, 130.0, 129.6, 128.7 (d, $^3J_{CP}$ = 7.7 Hz), 128.4, 127.6, 72.5 (d, $^2J_{CP}$ = 6.2 Hz), 66.5 (d, $^2J_{CP}$ = 5.7 Hz), 64.2, 23.66 (d, $^3J_{CP}$ = 5.2 Hz), 23.65 (d, $^3J_{CP}$ = 5.2 Hz). HRMS (ESI-TOF): calcd for $C_{17}H_{25}O_6PNa$ (M + Na^+) 379.1281, found 379.1284.

Diisopropyl (*E*)-3-Cyclohexyl-2-propenyl Phosphate ((*E*)-1n). This was synthesized from (*E*)-3-cyclohexyl-2-propenol following the procedure for compound **1a**. Colorless oil, 79% yield (1.01 g). ^{1}H NMR ($CDCl_3$): δ 5.71 (dd, $^3J_{HH}$ = 15.5 and 6.6 Hz, 1H), 5.53 (dtd, $^3J_{HH}$ = 15.5 and 6.3 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 4.62 (d of sept, $^3J_{HP}$ = 6.9 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 4.47−4.41 (m, 2H), 2.02−1.92 (m, 1H), 1.75−1.60 (m, 5H), 1.323 (d, $^3J_{HH}$ = 6.1 Hz, 6H), 1.320 (d, $^3J_{HH}$ = 6.2 Hz, 6H), 1.32−1.01 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 141.4, 122.2 (d, $^3J_{CP}$ = 7.2 Hz), 72.1 (d, $^2J_{CP}$ = 5.7 Hz), 68.1 (d, $^2J_{CP}$ = 5.7 Hz), 40.2, 32.5, 26.1, 25.9, 23.6 (d, $^3J_{CP}$ = 4.7 Hz). HRMS (ESI-TOF): calcd for $C_{15}H_{29}O_4PNa$ (M + Na^+) 327.1696, found 327.1694.

Diisopropyl (*E*)-4,4-Dimethyl-2-pentenyl Phosphate ((*E*)-1o). This was synthesized from (*E*)-4,4-dimethyl-2-pentenol following the procedure for compound **1a**. Colorless oil. 45% yield (699 mg). ^{1}H NMR ($CDCl_3$): δ 5.78 (dt, $^3J_{HH}$ = 15.6 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 5.50 (dt, $^3J_{HH}$ = 15.6 and 6.3 Hz, 1H), 4.63 (d of sept, $^3J_{HP}$ = 6.8 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 4.46 (ddd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 6.3 Hz, and $^4J_{HH}$ = 1.2 Hz, 2H), 1.33 (d, $^3J_{HH}$ = 6.2 Hz, 12H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 146.4, 119.7 (d, $^3J_{CP}$ = 6.7 Hz), 72.2 (d, $^2J_{CP}$ = 6.2 Hz), 68.2 (d, $^2J_{CP}$ = 5.7 Hz), 33.0, 29.3, 23.68 (d, $^3J_{CP}$ = 5.2 Hz), 23.67 (d, $^3J_{CP}$ = 5.2 Hz). HRMS (ESI-TOF): calcd for $C_{13}H_{27}O_4PNa$ (M + Na^+) 301.1539, found 301.1535.

Diisopropyl (*Z*)-5-Phenyl-2-pentenyl Phosphate ((*Z*)-1l). This was synthesized from (*Z*)-5-phenyl-2-pentenol following the procedure for compound **1a**. Colorless oil, 69% yield (539 mg). ^{1}H NMR ($CDCl_3$): δ 7.28 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.21−7.14 (m, 3H), 5.69−5.56 (m, 2H), 4.61 (d of sept, $^3J_{HP}$ = 6.9 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 4.49−4.43 (m, 2H), 2.69 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 2.45−2.38 (m, 2H), 1.32 (d, $^3J_{HH}$ = 6.1 Hz, 6H), 1.31 (d, $^3J_{HH}$ = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 141.4, 133.5, 128.54, 128.45, 126.1, 125.3 (d, $^3J_{CP}$ = 7.2 Hz), 72.4 (d, $^2J_{CP}$ = 6.2 Hz), 62.8 (d, $^2J_{CP}$ = 5.7 Hz), 35.6, 29.4, 23.7 (d, $^3J_{CP}$ = 5.2 Hz). HRMS (ESI-TOF): calcd for $C_{17}H_{27}O_4PNa$ (M + Na^+) 349.1539, found 349.1540.

dx.doi.org/10.1021/jo400888b | J. Org. Chem. 2013, 78, 5007−5017

Diisopropyl (*E*)-3-Phenyl-2-butenyl Phosphate ((*E*)-7a′). This was synthesized from (*E*)-3-phenyl-2-butenol following the procedure for compound **1a**. Colorless oil, 71% yield (764 mg). ^{1}H NMR ($CDCl_3$): δ 7.42−7.38 (m, 2H), 7.36−7.30 (m, 2H), 7.30−7.25 (m, 1H), 5.94 (tq, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 4.76−4.71 (m, 2H), 4.66 (d of sept, $^3J_{HP}$ = 6.8 Hz and $^3J_{HH}$ = 6.2 Hz, 2H), 2.12−2.09 (m, 3H), 1.343 (d, $^3J_{HH}$ = 6.1 Hz, 6H), 1.339 (d, $^3J_{HH}$ = 6.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 142.6, 139.9 (d, $^4J_{CP}$ = 1.0 Hz), 128.4, 127.6, 125.9, 122.3 (d, $^3J_{CP}$ = 7.2 Hz), 72.4 (d, $^2J_{CP}$ = 5.7 Hz), 64.2 (d, $^2J_{CP}$ = 5.7 Hz), 23.8 (d, $^3J_{CP}$ = 4.7 Hz), 16.3. HRMS (ESI-TOF): calcd for $C_{16}H_{25}O_4PNa$ (M + Na^+) 335.1383, found 335.1382.

Diethyl (*E*)-3-Methyl-5-phenyl-2-pentenyl Phosphate ((*E*)-7d). This was synthesized from (*E*)-3-methyl-5-phenyl-2-pentenol following the procedure for compound **1a**. Colorless oil, 92% yield (809 mg). ^{1}H NMR ($CDCl_3$): δ 7.27 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.21−7.14 (m, 3H), 5.46−5.39 (m, 1H), 4.56 (t, ^3J = 7.6 Hz, 2H), 4.10 (quint, ^3J = 7.3 Hz, 4H), 2.73 (t, $^3J_{HH}$ = 8.1 Hz, 2H), 2.34 (t, $^3J_{HH}$ = 8.1 Hz, 2H), 1.75 (s, 3H), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 142.0, 141.8, 128.44, 128.39, 126.0, 119.6 (d, $^3J_{CP}$ = 6.7 Hz), 64.1 (d, $^2J_{CP}$ = 5.2 Hz), 63.7 (d, $^2J_{CP}$ = 6.2 Hz), 41.4, 34.3, 16.7, 16.2 (d, $^3J_{CP}$ = 6.7 Hz). HRMS (ESI-TOF): calcd for $C_{16}H_{25}O_4PNa$ (M + Na^+) 335.1383, found 335.1377.

Diethyl (*Z*)-3-Methyl-5-phenyl-2-pentenyl Phosphate ((*Z*)-7d). This was synthesized from *tert*-butyl (*Z*)-3-methyl-5-phenyl-2-pentenoate following the procedure for compound **1e**. Colorless oil, 73% yield (238 mg). ^{1}H NMR ($CDCl_3$): δ 7.30−7.25 (m, 2H), 7.21−7.14 (m, 3H), 5.44−5.38 (m, 1H), 4.38−4.31 (m, 2H), 4.12−4.03 (m, 4H), 2.70 (t, $^3J_{HH}$ = 7.9 Hz, 2H), 2.39 (t, $^3J_{HH}$ = 7.9 Hz, 2H), 1.82−1.78 (m, 3H), 1.31 (td, $^3J_{HH}$ = 7.1 Hz and $^4J_{HP}$ = 0.9 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 141.5, 141.3, 128.3, 128.2, 125.9, 120.5 (d, $^3J_{CP}$ = 6.7 Hz), 63.44 (d, $^2J_{CP}$ = 5.7 Hz), 63.37 (d, $^2J_{CP}$ = 5.7 Hz), 34.3, 34.0, 23.4, 16.0 (d, $^3J_{CP}$ = 6.7 Hz). HRMS (ESI-TOF): calcd for $C_{16}H_{25}O_4PNa$ (M + Na^+) 335.1383, found 335.1383.

General Procedure for Tables 2 and 3 and eq 3. A solution of CuCl (1.5 mg, 15 μmol), (*S*,*S*)-**L** (8.7 mg, 17 μmol), and NaOH (18.0 mg, 0.450 mmol) in THF (0.40 mL) was stirred for 5 min at room temperature and diluted with THF (0.30 mL). Allyl phosphate **1** (0.300 mmol) with THF (0.30 mL) and a solution of silylboronate **2** (118 mg, 0.450 mmol) in THF (0.50 mL) were successively added, and the mixture was stirred for 12 h at −15 °C. After dilution with Et_2O, the reaction mixture was passed through a pad of silica gel with EtOAc, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with hexane/CH_2Cl_2 = 10/1 to afford compounds **3** and **4**. Further purification by GPC with $CHCl_3$ was carried out when necessary.

For ee analysis, compound **3** was converted to the corresponding alcohol **5** through a hydroboration−oxidation sequence: BH_3·SMe_2 (0.15 mL, 0.30 mmol; 2.0 M solution in THF) was added to a solution of compound **3** in THF (1.0 mL) at 0 °C, and the mixture was stirred for 1 h at 0 °C. NaOH(aq) (1 M, 0.45 mL) and 30% H_2O_2(aq) (61 μL, 0.600 mmol) were then added, and the resulting mixture was stirred for 1 h at 0 °C. The reaction was quenched with saturated NaCl(aq) and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with hexane/EtOAc = 4/1 to afford compound **5**.

Table 2, Entry 1 ((*S*)-3a) (CAS 945684-74-2 for (*R*)). Colorless oil, 91% yield (69.0 mg, **3a**/**4a** = 98/2). $[\alpha]^{25}_D$ = +9.5 (*c* 1.09, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[3a] ^{1}H NMR ($CDCl_3$): δ 7.38−7.33 (m, 3H), 7.33−7.27 (m, 2H), 7.19 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.08 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 6.95−6.89 (m, 2H), 6.11 (ddd, $^3J_{HH}$ = 17.0, 10.1, and 9.6 Hz, 1H), 4.95 (ddd, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 1.7 Hz, and $^4J_{HH}$ = 0.8 Hz, 1H), 4.91 (ddd, $^3J_{HH}$ = 17.0 Hz, $^2J_{HH}$ = 1.7 Hz, and $^4J_{HH}$ = 1.1 Hz, 1H), 3.15 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 0.27 (s, 3H), 0.25 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 141.8, 137.9, 136.9, 134.5, 129.3, 128.3, 127.64, 127.62, 124.9, 113.2, 44.4, −4.1, −4.7.

(*S*)-5a (CAS 1279814-79-7 for (*S*)). Colorless oil, 73% yield (47.6 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 10.0 min [minor enantiomer], 12.1 min [major enantiomer]. 92% ee. $[\alpha]^{30}_D$ = −18.4 (*c* 0.90, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.42−7.29 (m, 5H), 7.20 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.09 (tt, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 6.97−6.92 (m, 2H), 3.53−3.48 (m, 1H), 3.46−3.35 (m, 1H), 2.38 (dd, $^3J_{HH}$ = 11.8 and 4.0 Hz, 1H), 2.07−1.91 (m, 2H), 1.12 (bs, 1H), 0.26 (s, 3H), 0.19 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.3, 137.4, 134.2, 129.2, 128.3, 128.0, 127.8, 124.9, 62.2, 32.7, 32.4, −3.9, −5.3.

Table 2, Entry 2 ((*S*)-3b). Colorless oil, 90% yield (72.2 mg, **3b**/**4b** = 98/2). $[\alpha]^{30}_D$ = +30.0 (*c* 0.92, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. 85% yield. ^{1}H NMR ($CDCl_3$): δ 7.39−7.33 (m, 3H), 7.33−7.28 (m, 2H), 7.00 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 6.08 (ddd, $^3J_{HH}$ = 17.0, 10.1, and 9.6 Hz, 1H), 4.93 (ddd, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 1.8 Hz, and $^4J_{HH}$ = 0.8 Hz, 1H), 4.88 (ddd, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 1.7 Hz, and $^4J_{HH}$ = 1.1 Hz, 1H), 3.11 (d, $^3J_{HH}$ = 9.7 Hz, 1H), 2.28 (s, 3H), 0.26 (s, 3H), 0.24 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.6, 138.2, 137.1, 134.5, 134.2, 129.2, 129.0, 127.61, 127.56, 113.0, 43.8, 21.1, −4.0, −4.7. HRMS (ESI-TOF): calcd for $C_{18}H_{22}SiNa$ (M + Na^+) 289.1383, found 289.1388.

(*S*)-5b. Colorless oil, 46% yield (35.6 mg). The ee was determined on a Daicel Chiralpak AS-H column with hexane/2-propanol = 95/5, flow = 0.9 mL/min. Retention times: 7.9 min [major enantiomer], 15.6 min [minor enantiomer]. 92% ee. $[\alpha]^{25}_D$ = −14.3 (*c* 1.30, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.44−7.39 (m, 2H), 7.39−7.30 (m, 3H), 7.01 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 6.84 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 3.57−3.47 (m, 1H), 3.46−3.36 (m, 1H), 2.34 (dd, $^3J_{HH}$ = 11.6 and 4.3 Hz, 1H), 2.29 (s, 3H), 2.03−1.89 (m, 2H), 1.08 (bs, 1H), 0.25 (s, 3H), 0.17 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.0, 137.6, 134.28, 134.26, 129.2, 129.0, 127.9, 127.8, 62.3, 32.5, 32.2, 21.1, −3.8, −5.3. HRMS (ESI-TOF): calcd for $C_{18}H_{24}OSiNa$ (M + Na^+) 307.1489, found 307.1490.

Table 2, Entry 3 ((*S*)-3c). Colorless oil, 87% yield (75.3 mg, **3c**/**4c** = 99/1). $[\alpha]^{25}_D$ = +27.7 (*c* 0.93, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. ^{1}H NMR ($CDCl_3$): δ 7.39−7.28 (m, 5H), 7.14 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.82 (d, $^3J_{HH}$ = 8.3 Hz 2H), 6.04 (ddd, $^3J_{HH}$ = 16.8, 10.1, and 9.6 Hz, 1H), 4.97 (ddd, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 1.6 Hz, and $^4J_{HH}$ = 0.8 Hz, 1H), 4.91 (ddd, $^3J_{HH}$ = 16.8 Hz, $^2J_{HH}$ = 1.5 Hz, and $^4J_{HH}$ = 1.1 Hz, 1H), 3.12 (d, $^3J_{HH}$ = 9.5 Hz, 1H), 0.262 (s, 3H), 0.255 (s, 3H). ^{13}C NMR ($CDCl_3$): 140.4, 137.4, 136.4, 134.5, 130.5, 129.5, 128.8, 128.4, 127.7, 113.6, 43.9, −4.3, −4.7. HRMS (ESI-TOF): calcd for $C_{17}H_{19}ClSiNa$ (M + Na^+) 309.0837, found 309.0843.

(*S*)-5c. Colorless oil, 61% yield (46.1 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 9.6 min [major enantiomer], 10.9 min [minor enantiomer]. 90% ee. $[\alpha]^{25}_D$ = −4.4 (*c* 0.71, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.40−7.35 (m, 3H), 7.35−7.30 (m, 2H), 7.16 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.85 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 3.58−3.46 (m, 1H), 3.44−3.32 (m, 1H), 2.38 (dd, $^3J_{HH}$ = 10.7 and 5.0 Hz, 1H), 2.02−1.90 (m, 2H), 1.10 (bs, 1H), 0.25 (s, 3H), 0.20 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.9, 136.8, 134.2, 130.4, 129.4, 129.2, 128.4, 127.9, 61.9, 32.3, 32.2, −4.0, −5.3. HRMS (ESI-TOF): calcd for $C_{17}H_{21}ClOSiNa$ (M + Na^+) 327.0942, found 327.0939.

Table 2, Entry 4 ((*S*)-3d). Colorless oil, 87% yield (66.9 mg, **3d**/**4d** = 99/1). $[\alpha]^{25}_D$ = +14.4 (*c* 1.04, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. ^{1}H NMR ($CDCl_3$): δ 7.39−7.34 (m, 3H), 7.34−7.28 (m, 2H), 7.08 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.90 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 6.74 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 6.69 (s, 1H), 6.10 (ddd, $^3J_{HH}$ = 16.9, 10.1, and 9.7 Hz, 1H), 4.97−4.93 (m, 1H), 4.93−4.87 (m, 1H), 3.11 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 2.24 (s, 3H), 0.27 (s, 3H), 0.25 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 141.6, 138.0, 137.7, 137.0, 134.5, 129.2, 128.5, 128.1, 127.6, 125.6, 124.6, 113.1, 44.3, 21.6, −4.1, −4.7. HRMS (ESI-TOF): calcd for $C_{18}H_{22}SiNa$ (M + Na^+) 289.1383, found 289.1388.

(*S*)-5d. Colorless oil, 69% yield (51.0 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 10.5 min [minor enantiomer], 11.6 min [major enantiomer]. 91% ee. $[\alpha]^{25}_D$ = −14.8 (*c* 1.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.42−7.30 (m, 5H), 7.09 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.90 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 6.75 (d, $^3J_{HH}$ = 7.8 Hz, 1H),

dx.doi.org/10.1021/jo400888b | J. Org. Chem. 2013, 78, 5007−5017

6.72 (s, 1H), 3.57−3.49 (m, 1H), 3.46−3.37 (m, 1H), 2.33 (dd, $^3J_{HH}$ = 11.9 and 3.9 Hz, 1H), 2.25 (s, 3H), 2.04−1.90 (m, 2H), 1.09 (t, $^3J_{HH}$ = 5.2 Hz, 1H), 0.25 (s, 3H), 0.18 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.1, 137.7, 137.5, 134.3, 129.2, 128.9, 128.1, 127.7, 125.7, 125.0, 62.3, 32.6, 32.3, 21.6, −3.9, −5.3. HRMS (ESI-TOF): calcd for $C_{18}H_{24}OSiNa$ (M + Na^+) 307.1489, found 307.1485.

Table 2, Entry 5 ((*S*)-3e). Colorless oil, 84% yield (90.3 mg, **3e**/**4e** = 97/3). $[\alpha]^{20}_D$ = +11.0 (*c* 1.32, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. ^{1}H NMR ($CDCl_3$): δ 7.39−7.33 (m, 3H), 7.33−7.27 (m, 2H), 7.10 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.78−6.73 (m, 1H), 6.62−6.56 (m, 2H), 6.09 (dt, $^3J_{HH}$ = 16.9 and 9.9 Hz, 1H), 5.05 (s, 2H), 4.96 (dd, $^3J_{HH}$ = 10.1 Hz and $^2J_{HH}$ = 1.4 Hz, 1H), 4.91 (dt, $^3J_{HH}$ = 16.9 Hz and J_{HH} = 1.2 Hz, 1H), 3.44 (s, 3H), 3.13 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 0.28 (s, 3H), 0.26 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.3, 143.5, 137.6, 136.8, 134.5, 129.3, 129.2, 127.6, 121.2, 115.6, 113.3, 112.8, 94.5, 56.0, 44.5, −4.3, −4.7. HRMS (ESI-TOF): calcd for $C_{19}H_{24}O_2SiNa$ (M + Na^+) 335.1438, found 335.1430.

(*S*)-5e. Colorless oil, 72% yield (59.8 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 14.4 min [major enantiomer], 19.2 min [minor enantiomer]. 90% ee. $[\alpha]^{25}_D$ = −10.2 (*c* 0.88, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.42−7.29 (m, 5H), 7.11 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.79−6.74 (m, 1H), 6.64−6.56 (m, 2H), 5.07 (s, 2H), 3.60−3.50 (m, 1H), 3.49−3.39 (m, 1H), 3.45 (s, 3H), 2.36 (dd, $^3J_{HH}$ = 11.7 and 4.1 Hz, 1H), 2.05−1.89 (m, 2H), 1.12 (t, $^3J_{HH}$ = 5.4 Hz, 1H), 0.27 (s, 3H), 0.20 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 157.3, 144.1, 137.3, 134.2, 129.23, 129.17, 127.8, 121.7, 116.1, 112.7, 94.6, 62.2, 56.0, 32.8, 32.3, −4.0, −5.3. HRMS (ESI-TOF): calcd for $C_{19}H_{26}O_3SiNa$ (M + Na^+) 353.1543, found 353.1536.

Table 2, Entry 6 ((*S*)-3f). Colorless oil, 91% yield (73.1 mg, **3f**/**4f** > 99/1). $[\alpha]^{25}_D$ = +12.5 (*c* 1.13, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. ^{1}H NMR ($CDCl_3$): δ 7.40−7.33 (m, 3H), 7.32−7.27 (m, 2H), 7.11−7.04 (m, 2H), 7.03−6.96 (m, 2H), 6.09 (ddd, $^3J_{HH}$ = 17.0, 10.1, and 9.1 Hz, 1H), 4.93 (ddd, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 1.7 Hz, and $^4J_{HH}$ = 0.9 Hz, 1H), 4.88 (ddd, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 1.7 Hz, and $^4J_{HH}$ = 1.1 Hz, 1H), 3.40 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 2.10 (s, 3H), 0.32 (s, 3H), 0.26 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.1, 138.6, 137.3, 135.0, 134.4, 130.6, 129.3, 127.6, 127.2, 125.9, 124.7, 113.1, 39.1, 20.3, −3.9, −4.8. HRMS (ESI-TOF): calcd for $C_{18}H_{22}SiNa$ (M + Na^+) 289.1383, found 289.1387.

(*S*)-5f. Colorless oil, 66% yield (51.3 mg). The ee was determined on two Daicel Chiralcel OD-H columns with hexane/2-propanol = 90/10, flow = 0.8 mL/min. Retention times: 25.5 min [major enantiomer], 27.3 min [minor enantiomer]. 95% ee. $[\alpha]^{25}_D$ = −5.9 (*c* 1.20, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.40−7.34 (m, 3H), 7.33−7.29 (m, 2H), 7.12−7.04 (m, 2H), 6.99 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 6.95 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 3.49 (dt, $^2J_{HH}$ = 10.4 Hz and $^3J_{HH}$ = 5.9 Hz, 1H), 3.36 (dt, $^2J_{HH}$ = 10.4 Hz and $^3J_{HH}$ = 7.3 Hz, 1H), 2.71−2.63 (m, 1H), 2.13 (s, 3H), 2.06−1.97 (m, 2H), 1.33 (bs, 1H), 0.31 (s, 3H), 0.17 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.9, 137.7, 135.9, 134.2, 130.3, 129.2, 127.8, 126.5, 125.9, 124.5, 62.2, 33.4, 26.8, 20.6, −3.9, −5.2. HRMS (ESI-TOF): calcd for $C_{18}H_{24}OSiNa$ (M + Na^+) 307.1489, found 307.1494.

Table 2, Entry 7 ((*S*)-3g). Colorless oil, 83% yield (82.9 mg, **3g**/**4g** = 99/1). $[\alpha]^{25}_D$ = +32.8 (*c* 1.24, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. ^{1}H NMR ($CDCl_3$): δ 7.51 (dd, $^3J_{HH}$ = 7.9 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 7.44−7.40 (m, 2H), 7.38 (tt, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 7.32 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 7.16 (td, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 6.98−6.92 (m, 2H), 5.99 (ddd, $^3J_{HH}$ = 16.9, 10.1, and 9.0 Hz, 1H), 4.96 (ddd, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 1.5 Hz, and $^4J_{HH}$ = 0.9 Hz, 1H), 4.90 (ddd, $^3J_{HH}$ = 17.0 Hz, $^2J_{HH}$ = 1.5 Hz, and $^4J_{HH}$ = 1.2 Hz, 1H), 3.87 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 0.30 (s, 3H), 0.28 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 141.4, 137.4, 136.6, 134.6, 133.1, 129.4, 128.6, 127.7, 127.2, 126.3, 124.4, 113.9, 42.3, −3.7, −5.1. HRMS (ESI-TOF): calcd for $C_{17}H_{19}BrSiNa$ (M + Na^+) 353.0332, found 353.0330.

(*S*)-5g. Colorless oil, 72% yield (62.5 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 10.4 min [major enantiomer], 11.7 min [minor enantiomer]. 94% ee. $[\alpha]^{25}_D$ = +19.8 (*c* 0.96, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.52 (dd, $^3J_{HH}$ = 7.9 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.49−7.44 (m, 2H), 7.41−7.37 (m, 1H), 7.37−7.32 (m, 2H), 7.18 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 6.99−6.92 (m, 2H), 3.46 (ddd, $^2J_{HH}$ = 10.6 Hz and $^3J_{HH}$ = 7.4 and 4.3 Hz, 1H), 3.36 (ddd, $^2J_{HH}$ = 10.5 Hz and $^3J_{HH}$ = 7.8 and 6.8 Hz, 1H), 3.11 (dd, $^3J_{HH}$ = 12.3 and 3.4 Hz, 1H), 2.06−1.98 (m, 1H), 1.98−1.88 (m, 1H), 1.22 (bs, 1H), 0.29 (s, 3H), 0.23 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.3, 137.0, 134.3, 133.0, 129.4, 128.0, 127.9, 127.5, 126.3, 125.6, 61.9, 33.3, 30.6, −3.6, −5.5. HRMS (ESI-TOF): calcd for $C_{17}H_{21}BrOSiNa$ (M + Na^+) 371.0437, found 371.0431.

Table 2, Entry 8 ((*S*)-3h). Colorless oil, 96% yield (86.9 mg, **3h**/**4h** > 99/1). $[\alpha]^{25}_D$ = +44.7 (*c* 1.10, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. ^{1}H NMR ($CDCl_3$): δ 7.76 (dd, $^3J_{HH}$ = 7.9 Hz and $^4J_{HH}$ = 0.8 Hz, 1H), 7.66 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.44−7.33 (m, 6H), 7.33−7.28 (m, 2H), 7.07 (dd, $^3J_{HH}$ = 8.4 Hz and $^4J_{HH}$ = 1.7 Hz, 1H), 6.21 (ddd, $^3J_{HH}$ = 16.8, 10.1, and 9.5 Hz, 1H), 5.00 (ddd, $^3J_{HH}$ = 10.2 Hz, $^2J_{HH}$ = 1.7 Hz, and $^4J_{HH}$ = 0.8 Hz, 1H), 4.96 (ddd, $^3J_{HH}$ = 16.8 Hz, $^2J_{HH}$ = 1.7 Hz, and $^4J_{HH}$ = 1.1 Hz, 1H), 3.32 (d, $^3J_{HH}$ = 9.6 Hz, 1H), 0.29 (s, 3H), 0.28 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.5, 137.8, 136.8, 134.5, 133.8, 131.6, 129.4, 127.67, 127.66, 127.4, 127.2, 125.9, 125.3, 124.9, 113.4, 44.6, −4.1, −4.6. HRMS (ESI-TOF): calcd for $C_{21}H_{22}SiNa$ (M + Na^+) 325.1383, found 325.1387.

(*S*)-5h. Colorless oil, 71% yield (65.2 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 85/15, flow = 1.0 mL/min. Retention times: 11.1 min [major enantiomer], 16.3 min [minor enantiomer]. 90% ee. $[\alpha]^{25}_D$ = −3.7 (*c* 0.94, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.78 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.70−7.66 (m, 2H), 7.45−7.35 (m, 6H), 7.35−7.30 (m, 2H), 7.10 (dd, $^3J_{HH}$ = 8.4 Hz and $^4J_{HH}$= 1.8 Hz, 1H), 3.55 (ddd, $^2J_{HH}$ = 10.5 Hz and $^3J_{HH}$= 7.6 and 4.5 Hz, 1H), 3.44 (ddd, $^2J_{HH}$ = 10.5 Hz and $^3J_{HH}$= 7.8 and 6.9 Hz, 1H), 2.57 (dd, $^3J_{HH}$ = 12.4 and 3.5 Hz, 1H), 2.18−2.08 (m, 1H), 2.04 (dtd, $^2J_{HH}$ = 14.0 Hz and $^3J_{HH}$ = 7.8 and 3.5 Hz, 1H), 1.35 (bs, 1H), 0.28 (s, 3H), 0.22 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.0, 137.2, 134.3, 133.8, 131.7, 129.3, 127.8, 127.71, 127.67, 127.3, 126.0, 125.7, 124.8, 62.2, 32.9, 32.3, −3.8, −5.2. HRMS (ESI-TOF): calcd for $C_{21}H_{24}OSiNa$ (M + Na^+) 343.1489, found 343.1495.

Table 2, Entry 9 ((*S*)-3i). Colorless oil, 78% yield (78.2 mg, **3i**/**4i** = 98/2). $[\alpha]^{20}_D$ = +42.2 (*c* 1.30, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. ^{1}H NMR ($CDCl_3$): δ 8.01−7.94 (m, 1H), 7.84−7.77 (m, 1H), 7.63 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.46−7.38 (m, 4H), 7.38−7.32 (m, 2H), 7.29 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 7.15 (dd, $^3J_{HH}$ = 7.2 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 6.23 (ddd, $^3J_{HH}$ = 16.9, 10.1, and 9.2 Hz, 1H), 4.99 (ddd, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 1.6 Hz, and $^4J_{HH}$ = 0.8 Hz, 1H), 4.95 (ddd, $^3J_{HH}$ = 16.8 Hz, $^2J_{HH}$ = 1.6 Hz, and $^4J_{HH}$ = 1.1 Hz, 1H), 4.07 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 0.26 (s, 3H), 0.24 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.5, 138.3, 137.1, 134.5, 134.2, 131.6, 129.3, 129.0, 127.7, 125.5, 125.44, 125.39, 125.37, 124.5, 123.7, 113.6, 38.0, −3.5, −4.5. HRMS (ESI-TOF): calcd for $C_{21}H_{22}SiNa$ (M + Na^+) 325.1383, found 325.1386.

(*S*)-5i. Colorless oil, 58% yield (43.0 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 1.0 mL/min. Retention times: 9.7 min [minor enantiomer], 14.5 min [major enantiomer]. 93% ee. $[\alpha]^{25}_D$ = +26.6 (*c* 1.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.10−8.03 (m, 1H), 7.86−7.79 (m, 1H), 7.63 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.48−7.40 (m, 4H), 7.40−7.29 (m, 4H), 7.12 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 3.54−3.45 (m, 1H), 3.43−3.33 (m, 2H), 2.22−2.11 (m, 2H), 1.07 (t, $^3J_{HH}$ = 5.2 Hz, 1H), 0.23 (s, 3H), 0.10 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.1, 137.5, 134.3, 134.1, 132.6, 129.3, 129.0, 127.8, 125.5, 125.44, 125.39, 125.3, 123.64, 123.59, 62.0, 33.4, 25.3, −3.4, −5.2. HRMS (ESI-TOF): calcd for $C_{21}H_{24}OSiNa$ (M + Na^+) 343.1489, found 343.1484.

Table 2, Entry 10 ((*S*)-3j). Colorless oil, 94% yield (73.1 mg, **3j**/**4j** = 99/1). $[\alpha]^{25}_D$ = +31.5 (*c* 1.40, $CHCl_3$). The absolute configuration was assigned by analogy with entry 1. ^{1}H NMR ($CDCl_3$): δ 7.39−7.34 (m, 3H), 7.32 (t, $^3J_{HH}$ = 7.0 Hz, 2H), 7.17 (dd, $^3J_{HH}$ = 4.9 Hz and $^4J_{HH}$ = 3.0 Hz, 1H), 6.69 (d, $^3J_{HH}$ = 5.0 Hz, 1H), 6.66−6.63 (m, 1H), 6.07−5.98 (m, 1H), 4.98−4.93 (m, 1H), 4.91 (d, $^3J_{HH}$ = 17.0 Hz, 1H), 3.32

dx.doi.org/10.1021/jo400888b | J. Org. Chem. 2013, 78, 5007−5017

(d, $^3J_{HH}$ = 9.5 Hz, 1H), 0.29 (s, 3H), 0.26 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 141.4, 137.7, 137.0, 134.4, 129.3, 127.9, 127.7, 124.8, 118.2, 113.0, 39.6, −4.3, −4.5. HRMS (ESI-TOF): calcd for $C_{15}H_{18}SSiNa$ ($M + Na^+$) 281.0791, found 281.0792.

(*S*)-5j. Colorless oil, 43% yield (34.0 mg). The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 9.2 min [major enantiomer], 10.6 min [minor enantiomer]. 89% ee. $[\alpha]^{20}_D$ = −3.3 (*c* 0.82, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.42−7.30 (m, 5H), 7.19 (dd, $^3J_{HH}$ = 4.9 Hz and $^4J_{HH}$ = 2.9 Hz, 1H), 6.70 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 6.67−6.64 (m, 1H), 3.56 (ddd, $^2J_{HH}$ = 10.2 Hz and $^3J_{HH}$ = 6.8 and 4.9 Hz, 1H), 3.45 (dt, $^2J_{HH}$ = 10.2 Hz and $^3J_{HH}$ = 7.3 Hz, 1H), 2.55 (dd, $^3J_{HH}$ = 11.6 and 4.0 Hz, 1H), 1.99−1.86 (m, 2H), 1.16 (bs, 1H), 0.27 (s, 3H), 0.21 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.5, 137.4, 134.2, 129.3, 128.0, 127.8, 125.0, 118.4, 62.3, 33.0, 28.0, −4.0, −5.1. HRMS (ESI-TOF): calcd for $C_{15}H_{20}OSSiNa$ ($M + Na^+$) 299.0896, found 299.0893.

Table 2, Entry 11 ((*R*)-3k) (CAS 158342-33-7 for (*R*)). The reaction was conducted using **1k** with *E*/*Z* = 97/3. Colorless oil, 90% yield (51.5 mg, **3k**/**4k** = 95/5). $[\alpha]^{20}_D$ = +34.1 (*c* 1.05, C_6H_6). The absolute configuration was determined by comparison of the optical rotation with the literature value.[36] ^{1}H NMR ($CDCl_3$): δ 7.53−7.47 (m, 2H), 7.39−7.32 (m, 3H), 5.86 (ddd, $^3J_{HH}$ = 17.2, 10.3, and 7.3 Hz, 1H), 4.89−4.85 (m, 1H), 4.83−4.78 (m, 1H), 1.89−1.82 (m, 1H), 1.06 (d, $^3J_{HH}$ = 7.1 Hz, 3H), 0.27 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 141.3, 137.9, 134.2, 129.1, 127.8, 110.7, 27.3, 13.2, −4.8, −5.3.

(*R*)-5k (CAS 158342-33-7 for (*R*)). Colorless oil, 54% yield (28.8 mg). The ee was determined on two Daicel Chiralpak AD-H columns with hexane/2-propanol = 98/2, flow =0.7 mL/min. Retention times: 30.7 min [major enantiomer], 32.3 min [minor enantiomer]. 86% ee. $[\alpha]^{20}_D$ = −19.8 (*c* 1.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.53−7.46 (m, 2H), 7.38−7.31 (m, 3H), 3.73−3.65 (m, 1H), 3.63−3.54 (m, 1H), 1.75 (dtd, $^2J_{HH}$ = 13.8 Hz and $^3J_{HH}$ = 7.8 and 3.5 Hz, 1H), 1.36 (dddd, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 10.4, 7.1, and 4.7 Hz, 1H), 1.11 (bs, 1H), 1.06−0.97 (m, 1H), 0.96 (d, $^3J_{HH}$ = 6.2 Hz, 3H), 0.274 (s, 3H), 0.270 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.3, 134.0, 129.0, 127.9, 61.9, 34.7, 15.4, 14.0, −4.7, −5.1.

Table 2, Entry 12 ((*R*)-3l). (CAS 1270304-77-2 for (*S*)) Colorless oil, 93% yield (83.1 mg, **3l**/**4l** = 99/1). $[\alpha]^{25}_D$ −12.7 (*c* 0.85, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[37] ^{1}H NMR ($CDCl_3$): δ 7.48−7.42 (m, 2H), 7.38−7.30 (m, 3H), 7.25 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.16 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.09 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 5.66 (dt, $^3J_{HH}$ = 17.0 and 9.8 Hz, 1H), 4.98 (dd, $^3J_{HH}$ = 10.2 Hz and $^2J_{HH}$ = 1.8 Hz, 1H), 4.91−4.84 (m, 1H), 2.73 (ddd, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 9.4 and 4.5 Hz, 1H), 2.42 (ddd, $^2J_{HH}$ = 13.8 Hz and $^3J_{HH}$ = 9.3 and 7.2 Hz, 1H), 1.82−1.72 (m, 2H), 1.70−1.60 (m, 1H), 0.26 (s, 3H), 0.25 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.7, 139.5, 137.7, 134.2, 129.1, 128.7, 128.4, 127.8, 125.7, 113.3, 35.5, 34.0, 30.6, −4.3, −5.1. HRMS (ESI-TOF): calcd for $C_{19}H_{24}SiNa$ ($M + Na^+$) 303.1539, found 303.1537.

(*R*)-5l (CAS 1270304-97-6 for (*S*)). Colorless oil, 50% yield (38.7 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 11.2 min [major enantiomer], 12.5 min [minor enantiomer]. 91% ee. $[\alpha]^{25}_D$ = −2.2 (*c* 1.23, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.54−7.47 (m, 2H), 7.39−7.32 (m, 3H), 7.26 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 7.17 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.10−7.05 (m, 2H), 3.66−3.58 (m, 1H), 3.58−3.49 (m, 1H), 2.61 (ddd, $^2J_{HH}$ = 13.4 Hz and $^3J_{HH}$ = 10.5 and 5.6 Hz, 1H), 2.50 (ddd, $^2J_{HH}$ = 13.5 Hz and $^3J_{HH}$ = 10.5 and 6.0 Hz, 1H), 1.85−1.73 (m, 2H), 1.66−1.54 (m, 2H), 1.09 (bs, 1H) 1.00−0.93 (m, 1H), 0.32 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 142.7, 138.7, 134.0, 129.1, 128.5, 128.4, 128.0, 125.9, 62.4, 35.8, 33.1, 32.2, 21.1, −3.85, −3.94. HRMS (ESI-TOF): calcd for $C_{19}H_{26}OSiNa$ ($M + Na^+$) 321.1645, found 321.1644.

Table 2, Entry 13 ((*S*)-3m). Colorless oil, 89% yield (83.2 mg, **3m**/**4m** > 99/1). $[\alpha]^{20}_D$ = +1.3 (*c* 1.04, $CHCl_3$). The absolute configuration was assigned by analogy with entry 11. ^{1}H NMR ($CDCl_3$): δ 7.96−7.90 (m, 2H), 7.57−7.49 (m, 3H), 7.43−7.33 (m, 5H), 5.77 (ddd, $^3J_{HH}$ = 17.1, 10.4, and 9.1 Hz, 1H), 5.02−4.98 (m, 1H), 4.96 (dt, $^3J_{HH}$ = 17.2 Hz and J_{HH} = 1.3 Hz, 1H), 4.45 (dd, $^2J_{HH}$ = 11.2 Hz and $^3J_{HH}$ = 4.7 Hz, 1H), 4.41 (dd, $^2J_{HH}$ = 11.1 Hz and $^3J_{HH}$ = 10.0 Hz, 1H), 2.42 (ddd, $^3J_{HH}$ = 9.8, 9.2, and 4.6 Hz, 1H), 0.38 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 166.9, 136.5, 136.4, 134.1, 132.8, 130.6, 129.6, 129.5, 128.4, 128.0, 114.3, 65.5, 35.5, −4.0, −4.7. HRMS (ESI-TOF): calcd for $C_{19}H_{22}O_2SiNa$ ($M + Na^+$) 333.1281, found 333.1282.

(*S*)-5m. Colorless oil, 61% yield (50.8 mg). The ee was determined on three Daicel Chiralpak AD-H columns with hexane/2-propanol = 90/10, flow = 0.50 mL/min. Retention times: 60.7 min [major enantiomer], 63.1 min [minor enantiomer]. 88% ee. $[\alpha]^{25}_D$ = −10.6 (*c* 0.80, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.96−7.92 (m, 2H), 7.57−7.51 (m, 3H), 7.42 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.39−7.33 (m, 3H), 4.56 (dd, $^2J_{HH}$ = 11.2 Hz and $^3J_{HH}$ = 3.9 Hz, 1H), 4.31 (dd, $^2J_{HH}$ = 11.2 Hz and $^3J_{HH}$ = 7.8 Hz, 1H), 3.74 (ddd, $^2J_{HH}$ = 10.5 Hz and $^3J_{HH}$ = 7.5 and 5.5 Hz, 1H), 3.67 (dt, $^2J_{HH}$ = 10.5 Hz and $^3J_{HH}$ = 7.2 Hz, 1H), 1.86 (dtd, $^2J_{HH}$ = 13.9 Hz and $^3J_{HH}$ = 7.4 and 4.1 Hz, 1H), 1.77−1.68 (m, 1H), 1.58−1.51 (m, 1H), 1.49 (bs, 1H), 0.40 (s, 3H), 0.39 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 166.9, 137.3, 133.9, 133.0, 130.4, 129.6, 129.4, 128.5, 128.1, 66.9, 62.4, 31.2, 23.2, −3.8, −4.1. HRMS (ESI-TOF): calcd for $C_{19}H_{24}O_3SiNa$ ($M + Na^+$) 351.1387, found 351.1387.

Table 2, Entry 14 ((*S*)-3n) (CAS 857286-82-9 for Racemate). Colorless oil. 97% yield (75.2 mg, **3n**/**4n** = 98/2). $[\alpha]^{25}_D$ −2.2 (*c* 1.07, $CHCl_3$). The absolute configuration was assigned by analogy with entry 11. ^{1}H NMR ($CDCl_3$): δ 7.53−7.47 (m, 2H), 7.37−7.31 (m, 3H), 5.71 (ddd, $^3J_{HH}$ = 17.0, 10.7, and 10.3 Hz, 1H), 4.90 (dd, $^3J_{HH}$ = 10.1 Hz and $^2J_{HH}$ = 2.3 Hz, 1H), 4.78 (ddd, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 2.3 Hz, and $^4J_{HH}$ = 0.7 Hz, 1H), 1.74−1.52 (m, 5H), 1.51−1.41 (m, 2H), 1.21−0.92 (m, 5H), 0.30 (s, 3H), 0.28 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.1, 137.9, 134.1, 128.8, 127.7, 113.8, 42.4, 38.6, 34.3, 31.6, 26.91, 26.90, 26.4, −2.6, −3.3. HRMS (ESI-TOF): calcd for $C_{17}H_{26}SiNa$ ($M + Na^+$) 281.1696, found 281.1698.

(*S*)-5n. Colorless oil, 50% yield (21.2 mg). The ee was determined on two Daicel Chiralpak AS-H columns with hexane/2-propanol = 95/5, flow = 0.5 mL/min. Retention times: 31.5 min [major enantiomer], 34.3 min [minor enantiomer]. 91% ee. $[\alpha]^{25}_D$ = +4.8 (*c* 0.92, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.55−7.47 (m, 2H), 7.37−7.28 (m, 3H), 3.57−3.48 (m, 1H), 3.48−3.39 (m, 1H), 1.74−1.46 (m, 8H), 1.23−0.97 (m, 6H), 0.89−0.82 (m, 1H), 0.33 (s, 3H), 0.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.0, 133.9, 128.9, 127.9, 63.6, 39.7, 33.6, 31.9, 30.4, 28.8, 27.3, 27.2, 26.6, −1.8, −2.8. HRMS (ESI-TOF): calcd for $C_{17}H_{28}OSiNa$ ($M + Na^+$) 299.1802, found 299.1807.

Table 2, Entry 15 ((S)-3o). Colorless oil, 72% yield (50.0 mg, **3o**/**4o** = 77/23). $[\alpha]^{25}_D$ = −27.6 (*c* 0.98, $CHCl_3$). The absolute configuration was assigned by analogy with entry 11. ^{1}H NMR ($CDCl_3$): δ 7.55−7.47 (m, 2H), 7.37−7.29 (m, 3H), 5.75 (ddd, $^3J_{HH}$ = 16.8, 11.3, and 10.0 Hz, 1H), 4.92 (dd, $^3J_{HH}$ = 10.0 Hz and $^2J_{HH}$ = 2.3 Hz, 1H), 4.73 (ddd, $^3J_{HH}$ = 16.7 Hz, $^2J_{HH}$ = 2.3 Hz, and $^4J_{HH}$ = 0.7 Hz, 1H), 1.69 (d, $^3J_{HH}$ = 11.4 Hz, 1H), 0.86 (s, 9H), 0.35 (s, 3H), 0.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.0, 138.1, 134.4, 128.8, 127.7, 114.5, 48.8, 33.5, 30.7, −1.29, −1.32. HRMS (ESI-TOF): calcd for $C_{15}H_{24}SiNa$ ($M + Na^+$) 255.1539, found 255.1539.

(*S*)-5o. Colorless oil, 82% yield (6.6 mg). The ee was determined on two Daicel Chiralpak AD-H columns with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 15.1 min [major enantiomer], 16.1 min [minor enantiomer]. 95% ee. $[\alpha]^{25}_D$ = +33.2 (*c* 0.66, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.56−7.50 (m, 2H), 7.37−7.31 (m, 3H), 3.45−3.35 (m, 1H), 3.22−3.13 (m, 1H), 1.74−1.58 (m, 2H), 0.92 (s, 9H), 0.93−0.89 (m, 1H), 0.63 (t, $^3J_{HH}$ = 4.6 Hz, 1H), 0.40 (s, 3H), 0.36 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.8, 134.0, 128.9, 127.9, 64.8, 34.6, 34.3, 30.9, 30.7, 0.1, −1.9. HRMS (ESI-TOF): calcd for $C_{15}H_{26}OSiNa$ ($M + Na^+$) 273.1645, found 273.1648.

Table 3, Entry 2 ((*S*)-8a) (CAS 945684-77-5 for (*R*)). Colorless oil, 84% yield of **8a** (66.9 mg, **8a**/**9a** = 92/8). $[\alpha]^{20}_D$ = +20.2 (*c* 1.38, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[3a] ^{1}H NMR ($CDCl_3$): δ 7.37−7.33 (m, 1H), 7.30−7.24 (m, 4H), 7.23−7.18 (m, 2H), 7.13−7.06 (m, 3H), 6.47 (dd, $^3J_{HH}$ = 17.2 and 10.7 Hz, 1H), 5.09 (dd, $^3J_{HH}$ = 10.7 Hz and $^2J_{HH}$ = 1.2 Hz, 1H), 4.95 (dd, $^3J_{HH}$ = 17.2 Hz and $^2J_{HH}$ = 1.2 Hz, 1H), 1.47 (s, 3H), 0.25 (s, 3H), 0.24 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.6, 143.1, 136.6, 135.0, 129.2, 127.9, 127.4, 126.7, 124.8, 111.4, 37.7, 19.1, −5.07, −5.13.

dx.doi.org/10.1021/jo400888b | J. Org. Chem. 2013, 78, 5007−5017

(*S*)-10a. Colorless oil, 42% yield (30.2 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 9.5 min [major enantiomer], 12.2 min [minor enantiomer]. 95% ee. $[\alpha]^{20}_{D}$ = −37.6 (*c* 1.31, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.37−7.33 (m, 1H), 7.30−7.24 (m, 4H), 7.21 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.10 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.01 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 3.59 (td, J_{HH} = 10.1 Hz and $^3J_{HH}$ = 5.5 Hz, 1H), 3.48 (td, J_{HH} = 10.0 Hz and $^3J_{HH}$ = 5.2 Hz, 1H), 2.46 (ddd, $^2J_{HH}$ = 13.8 Hz and $^3J_{HH}$ = 9.9 and 5.4 Hz, 1H), 1.89 (ddd, $^2J_{HH}$ = 13.9 Hz and $^3J_{HH}$ = 9.9 and 5.6 Hz, 1H), 1.38 (s, 3H), 1.06 (bs, 1H), 0.21 (s, 3H), 0.20 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.0, 136.3, 135.0, 129.2, 127.9, 127.5, 126.8, 124.5, 59.2, 38.2, 30.0, 20.3, −5.7, −6.0. HRMS (ESI-TOF): calcd for $C_{18}H_{24}OSiNa$ (M + Na^+) 307.1489, found 307.1485.

Table 3, Entry 4 ((*S*)-8b). Colorless oil, 88% yield (80.0 mg, **8b**/**9b** = 92/8). $[\alpha]^{25}_{D}$ = +23.2 (*c* 0.99, $CHCl_3$). The absolute configuration was assigned by analogy with entry 2. ^{1}H NMR ($CDCl_3$): δ 7.36 (tt, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 7.32−7.22 (m, 4H), 7.16 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.97 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.39 (dd, $^3J_{HH}$ = 17.2 and 10.9 Hz, 1H), 5.10 (d, $^3J_{HH}$ = 10.7 Hz and $^2J_{HH}$ =1.1 Hz, 1H), 4.95 (d, $^3J_{HH}$ = 17.2 Hz and $^2J_{HH}$ =1.1 Hz, 1H), 1.44 (s, 3H), 0.24 (s, 3H), 0.23 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 144.2, 142.6, 136.1, 135.0, 133.7, 129.4, 128.0, 127.9, 127.5, 111.9, 37.4, 19.1, −5.2, −5.3. HRMS (ESI-TOF): calcd for $C_{18}H_{21}ClSiNa$ (M + Na^+) 323.0993, found 323.0995.

(*S*)-10b. Colorless oil, 38% yield (29.4 mg). The ee was determined on two Daicel Chiralpak AD-H columns with hexane/2-propanol = 98/2, flow = 0.7 mL/min. Retention times: 49.0 min [major enantiomer], 52.4 min [minor enantiomer]. 95% ee. $[\alpha]^{25}_{D}$ = −28.3 (*c* 1.23, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.36 (tt, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 7.29 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.26−7.23 (m, 2H), 7.17 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.91 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.63−3.53 (m, 1H), 3.47−3.38 (m, 1H), 2.38 (ddd, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 10.0 and 5.0 Hz, 1H), 1.90 (ddd, $^2J_{HH}$ = 13.8 Hz and $^3J_{HH}$ = 9.9 and 5.5 Hz, 1H), 1.36 (s, 3H), 1.03 (bs, 1H), 0.22 (s, 3H) 0.20 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.8, 135.8, 135.0, 130.3, 129.4, 128.1, 128.0, 127.6, 59.0, 38.2, 29.9, 20.4, −5.8, −6.2. HRMS (ESI-TOF): calcd for $C_{18}H_{23}ClOSiNa$ (M + Na^+) 341.1099, found 341.1094.

Table 3, Entry 5 ((*S*)-8c). Colorless oil, 94% yield (89.0 mg, **8c**/**9c** = 93/7). $[\alpha]^{25}_{D}$ = +61.2 (*c* 1.57, $CHCl_3$). The absolute configuration was assigned by analogy with entry 2. ^{1}H NMR ($CDCl_3$): δ 7.79−7.75 (m, 1H), 7.70−7.64 (m, 2H), 7.46 (s, 1H), 7.44−7.34 (m, 3H), 7.30−7.23 (m, 5H), 6.58 (dd, $^3J_{HH}$ = 17.2 and 10.7 Hz, 1H), 5.15 (dd, $^3J_{HH}$ = 10.8 Hz and $^2J_{HH}$ = 1.2 Hz, 1H), 5.00 (dd, $^3J_{HH}$ = 17.2 Hz and $^2J_{HH}$ = 1.2 Hz, 1H), 1.58 (s, 3H), 0.27 (s, 3H), 0.26 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.3, 143.1, 136.6, 135.1, 133.6, 131.3, 129.3, 127.9, 127.44, 127.41, 127.1, 126.1, 125.8, 125.1, 124.7, 111.7, 38.1, 19.4, −5.00, −5.01. HRMS (ESI-TOF): calcd for $C_{22}H_{24}SiNa$ (M + Na^+) 339.1539, found 339.1543.

(*S*)-10c. Colorless oil, 57% yield (53.2 mg). The ee was determined on two Daicel Chiralpak AD-H columns with hexane/2-propanol = 95/5, flow = 0.7 mL/min. Retention times: 68.8 min [major enantiomer], 77.2 min [minor enantiomer]. 94% ee. $[\alpha]^{25}_{D}$ = +6.2 (*c* 1.21, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.78 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.71−7.65 (m, 2H), 7.46−7.33 (m, 4H), 7.30−7.25 (m, 4H), 7.21 (dd, $^3J_{HH}$ = 8.7 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 3.66−3.55 (m, 1H), 3.52−3.42 (m, 1H), 2.58 (ddd, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 9.9 and 5.5 Hz, 1H), 1.97 (ddd, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ = 9.7 and 5.6 Hz, 1H), 1.50 (s, 3H), 1.06 (bs, 1H), 0.24 (s, 3H), 0.22 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.9, 136.2, 135.1, 133.5, 131.2, 129.3, 127.7, 127.5, 127.4, 127.1, 125.93, 125.87, 125.1, 124.9, 59.3, 38.3, 30.4, 20.5, −5.6, −6.0. HRMS (ESI-TOF): calcd for $C_{22}H_{26}OSiNa$ (M + Na^+) 357.1645, found 357.1642.

Table 3, Entry 6 ((*R*)-8d). Colorless oil, 75% yield (66.6 mg, **8d**/**9d** = 97/3). $[\alpha]^{20}_{D}$ = +30.7 (*c* 0.94, $CHCl_3$). The absolute configuration was assigned by analogy with entry 2. ^{1}H NMR ($CDCl_3$): δ 7.51−7.44 (m, 2H), 7.39−7.29 (m, 3H), 7.25 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.16 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.11 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 5.83 (dd, $^3J_{HH}$ = 17.5 and 10.7 Hz, 1H), 5.05 (dd, $^3J_{HH}$ = 10.7 Hz and $^2J_{HH}$ = 1.4 Hz, 1H), 4.77 (dd, $^3J_{HH}$ = 17.3 Hz and $^2J_{HH}$ = 1.5 Hz, 1H), 2.49 (ddd, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 12.4 and 5.4 Hz, 1H), 2.40 (ddd, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 12.6 and 4.6 Hz, 1H), 1.79 (ddd, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 12.4 and 4.5 Hz, 1H) 1.67 (ddd, $^2J_{HH}$ = 13.3 Hz and $^3J_{HH}$ = 12.3 and 5.5 Hz, 1H), 1.11 (s, 3H), 0.281 (s, 3H), 0.278 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 144.4, 143.6, 136.9, 134.9, 129.1, 128.5, 128.4, 127.6, 125.7, 111.6, 38.0, 31.2, 30.2, 17.3, −5.93, −5.94. HRMS (ESI-TOF): calcd for $C_{20}H_{26}SiNa$ (M + Na^+) 317.1696, found 317.1699.

(*R*)-10d. Colorless oil, 52% yield (36.1 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 12.8 min [minor enantiomer], 16.6 min [major enantiomer]. 89% ee. $[\alpha]^{20}_{D}$ = +4.1 (*c* 1.10, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.58−7.51 (m, 2H), 7.40−7.32 (m, 3H), 7.26 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.17 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.10 (d, $^3J_{HH}$ = 7.1 Hz, 2H), 3.75−3.64 (m, 2H), 2.61−2.50 (m, 2H), 1.82−1.56 (m, 4H), 1.08 (t, $^3J_{HH}$ = 5.1 Hz, 1H), 1.04 (s, 3H), 0.37 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 143.3, 138.0, 134.7, 129.1, 128.5, 128.4, 127.8, 125.8, 59.9, 39.8, 39.4, 31.1, 23.3, 22.3, −4.21, −4.22. HRMS (ESI-TOF): calcd for $C_{20}H_{28}OSiNa$ (M + Na^+) 335.1802, found 335.1802.

Equation 3 ((*S*)-3l: R = H, R′ = *i*-Pr) (CAS 1270304-77-2 for (*S*)). Colorless oil, 80% yield (67.6 mg, **3l**/**4l** = 99/1). $[\alpha]^{20}_{D}$ +7.2 (*c* 1.45, $CHCl_3$). The absolute configuration was determined by comparison of the optical rotation with the literature value.[37]

(*S*)-5l. Colorless oil, 68% yield (48.9 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 11.5 min [minor enantiomer], 12.8 min [major enantiomer]. 54% ee. $[\alpha]^{20}_{D}$ = +1.5 (*c* 0.99, $CHCl_3$).

Equation 3 ((*S*)-8d: R = Me, R′ = Et). Colorless oil, 89% yield (79.0 mg, **8d**/**9d** = 83/17). $[\alpha]^{20}_{D}$ = −30.4 (*c* 1.04, $CHCl_3$). The absolute configuration was assigned by analogy with Table 3, entry 2.

(*S*)-10d. Colorless oil, 85% yield (36.1 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 1.0 mL/min. Retention times: 13.1 min [major enantiomer], 17.1 min [minor enantiomer]. 85% ee. $[\alpha]^{20}_{D}$ = −3.9 (*c* 0.99, $CHCl_3$).

Procedure for Equation 2 ((*S*)-6a: R = *t*-Bu). $TiCl_4$ (0.260 mL, 0.260 mmol; 1.0 M solution in CH_2Cl_2) was added to a solution of (*S*)-**3a** (54.7 mg, 0.217 mmol; 92% ee) and pivalaldehyde (29.0 μL, 0.260 mmol) in CH_2Cl_2 (1.0 mL) at −78 °C, and the mixture was stirred for 1 h at −78 °C. The reaction was quenched with H_2O and passed through a pad of silica gel with EtOAc. After removal of the solvent under vacuum, the residue was purified by silica gel preparative TLC with hexane/EtOAc = 5/1 to afford compound (*S*)-**6a** (CAS 158342−35−9 for (*S*)) as a colorless oil (37.8 mg, 0.185 mmol; 85% yield). The ee was determined on a Daicel Chiralpak AD-H column with hexane/2-propanol = 95/5, flow = 0.8 mL/min. Retention times: 11.0 min [minor enantiomer], 12.7 min [major enantiomer]. 86% ee. $[\alpha]^{25}_{D}$ −47.5 (*c* 0.83, CCl_4). The absolute configuration was determined by comparison of the optical rotation with the literature value.[17a] ^{1}H NMR ($CDCl_3$): δ 7.36 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 7.30 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.21 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.50 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 6.28 (ddd, $^3J_{HH}$ = 15.9, 8.2, and 6.2 Hz, 1H), 3.35 (dd, $^3J_{HH}$ = 10.5 and 2.1 Hz, 1H), 2.51 (dd, $^2J_{HH}$ = 13.9 Hz and $^3J_{HH}$ = 6.1 Hz, 1H), 2.17 (ddd, $^2J_{HH}$ = 13.8 Hz and $^3J_{HH}$ = 9.6 and 9.1 Hz, 1H), 1.58 (bs, 1H), 0.96 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 137.5, 132.9, 128.7, 128.3, 127.3, 126.2, 78.8, 35.9, 34.9, 25.9.

Procedure for Equation 2 ((*S*)-6b: R = *i*-Pr). $TiCl_4$ (0.266 mL, 0.266 mmol; 1.0 M solution in CH_2Cl_2) was added to a solution of (*S*)-**3a** (56.1 mg, 0.222 mmol; 92% ee) and isobutyraldehyde (24.2 μL, 0.266 mmol) in CH_2Cl_2 (1.0 mL) at −78 °C, and the mixture was stirred for 1 h at −78 °C. The reaction was quenched with H_2O and TBAF (0.50 mL, 0.50 mmol; 1.0 M solution in THF) was added. The mixture was stirred for 15 min at room temperature and washed with saturated NaCl(aq). The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with hexane/EtOAc = 5/1 and then by GPC with $CHCl_3$ to afford compound (*S*)-**6b** (CAS 84170−99−0 for (*R*)) as a colorless oil (35.3 mg, 0.186 mmol; 84% yield). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol =95/5, flow =1.0 mL/min. Retention times: 11.0 min [major enantiomer], 14.3 min [minor enantiomer]. 86% ee. $[\alpha]^{25}_{D}$ = −27.5 (*c*

dx.doi.org/10.1021/jo400888b | J. Org. Chem. 2013, 78, 5007−5017

1.10, CCl_4). The absolute configuration was determined by comparison of the optical rotation with the literature value.[17a] ^{1}H NMR ($CDCl_3$): δ 7.38−7.34 (m, 2H), 7.30 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.21 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.50 (d, $^3J_{HH}$ = 15.9 Hz, 1H), 6.25 (ddd, $^3J_{HH}$ = 15.8, 7.9, and 6.6 Hz, 1H), 3.52−3.46 (m, 1H), 2.46 (dddd, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 6.7 and 5.1 Hz, and $^4J_{HH}$ = 1.8 Hz, 1H), 2.30 (dtd, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 8.3 Hz, and $^4J_{HH}$ = 1.1 Hz, 1H), 1.80−1.69 (m, 1H), 1.57 (d, $^3J_{HH}$ = 4.3 Hz, 1H), 0.98 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.97 (d, $^3J_{HH}$ = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 137.5, 133.1, 128.7, 127.4, 127.1, 126.2, 76.0, 38.2, 33.3, 18.9, 17.6.

■ ASSOCIATED CONTENT

Supporting Information

HPLC data for asymmetric reactions and ^{1}H and ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Support has been provided in part by a Grant-in-Aid for Young Scientists (B), the Ministry of Education, Culture, Sports, Science and Technology, Japan, and in part by the Asahi Glass Foundation. M.T. thanks JSPS for a fellowship.

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