Note

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Enantioselective C–C Bond Formation during the Oxidation of 5-Phenylpent-2-enyl Carboxylates with Hypervalent Iodine(III)

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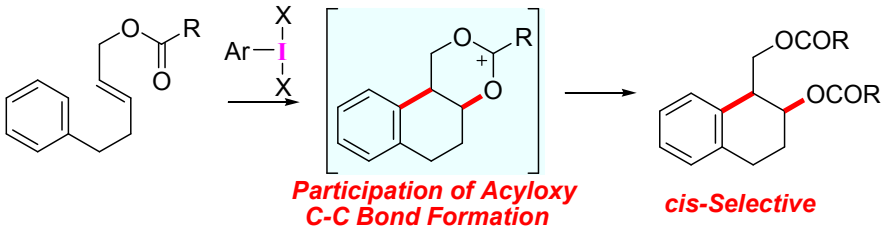


Abstract: The oxidation of (5-acyloxypent-3-enyl)benzene with hypervalent iodine(III) afforded 2-oxy-1-(oxymethyl)tetrahydronaphthalene under metal-free conditions. The acyloxy group may nucleophilically participate in the oxidative cyclization. A lactate-based chiral hypervalent iodine afforded an enantioselective variant of oxyarylation with up to 89% ee.

Oxidative 1,2-difunctionalization of alkenes with hypervalent iodine reagents offers a powerful strategy for constructing useful molecular complexity, because a wide range of functional groups, such as halogen, oxygen, nitrogen, and sulfur nucleophiles, is incorporated into the C=C of alkene substrates.[1–4] In particular, highly enantioselective oxidation was achieved in several types of vicinal difunctionalization reactions using lactate-based chiral hypervalent iodine reagents.[4,5] There are few examples of the addition of a carbon nucleophile compared to many examples of the addition of a heteroatom nucleophile. Transition-metal catalysts facilitate carbon-carbon bond formation during the oxidation of alkenes with hypervalent iodine.[6,7] However, metal-free reactions are limited to achiral or racemic transformation using electron-rich aryl-substituted substrates.[8] Under these circumstances, we recently found that enantioselective C–C bond formation was achieved by using 6-aryl-1-silyloxyhex-3-ene substrates and lactate-based chiral hypervalent iodine reagents.[9]

In this study, we employed neighboring group participation of an acyloxy group for oxidative arylation. Reactions involving neighboring group participation are advantageous in terms of powerful stereocontrol and unique stereoselectivity.[10] This

participation usually accelerates the formation of the product. Herein, we demonstrate oxidative C–C formation promoted by neighboring group participation of an acyloxy group. This reaction stereoselectively provides the tetrahydro-2-hydroxy-1-(hydroxymethyl)naphthalene structure, which is found in serrulatane diterpenes (Figure 1).[11]

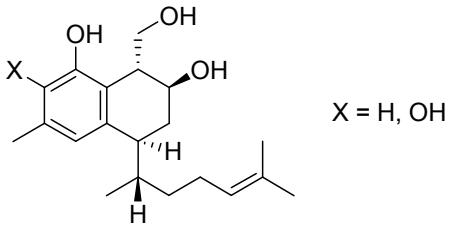
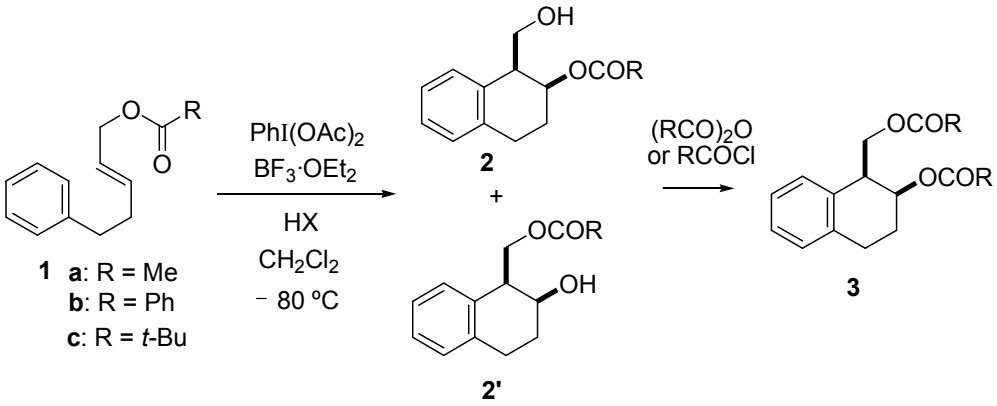


Figure 1. Serrulatane diterpenes.

Reactions of 5-phenylpent-2-enyl carboxylate **1** with (diacetoxyiodo)benzene are summarized in Table 1. Boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) has been widely used as an activator for oxidation with hypervalent iodine reagents.[12] Thus, the reaction of 5-phenylpent-2-enyl acetate (**1a**) with (diacetoxyiodo)benzene was examined in the presence of $BF_3 \cdot OEt_2$ at −80 °C for 10 h. However, the reaction did not proceed and substrate **1a** was recovered. In addition to $BF_3 \cdot OEt_2$, triflic acid or acetic acid was employed, and the reaction temperature was elevated from −80 °C to 0 °C (entries 1 and 2). Pleasingly, the substrate was consumed under the reaction conditions and a regioisomeric mixture of the acetoxyhydroxy products **2a** and **2a'** was obtained. The structures of **2a** and **2a'** were confirmed by the fact that acetylation of the mixture led to single diacetoxy compound **3a**. The oxidation led to carbon-carbon bond formation as a result of oxidative arylation of the alkene. When HF·pyridine was used as a coactivator together with $BF_3 \cdot OEt_2$, the oxidative arylation of **1a** proceeded even at −80 °C within 1 h (entries 3 and 4). The lower yield of isolated **2a** + **2a'** (entry 3) compared to that of **3a** (entry 4) might be due to some loss of the hydroxy products, **2a** and **2a'**, during purification through column chromatography. The oxidation of benzoate substrate **1b** at −80 °C for 1 h followed by benzoylation also yielded oxidative arylation product **3b** in 61% yield (entry 5). In the absence of HF·pyridine, the reaction of **1b** required warming to −40 °C and a longer reaction time (11 h), which resulted in a low 26% yield (entry 6). The oxidative arylation of pivalate substrate **1c** yielded a mixture of **2c** and **2c'** with a 9:1 ratio (entry 7). Another run of the oxidation of **1c** followed by pivalation yielded **3c** in 59% yield.

Table 1. Oxidative Arylation of **1** with (Diacetoxyiodo)benzene[a]



entry	**1** (R)	HX	**2** / **2'**	yield (%)
1	**1a** (Me)	TfOH[b,c]	7:3	36 (**3a**)[d]
2	**1a** (Me)	AcOH[c,e]	6:4	70 (**3a**)[d]
3	**1a** (Me)	HF·py[f]	7:3	56 (**2a**+**2a'**)
4	**1a** (Me)	HF·py[f]	nd	67 (**3a**)[d]
5	**1b** (Ph)	HF·py[f]	6:4	61 (**3b**)[d]
6	**1b** (Ph)	- [g]	5:5	26 (**3b**)[d]
7	**1c** (*t*-Bu)	HF·py[f]	9:1	78 (**2c**+**2c'**)

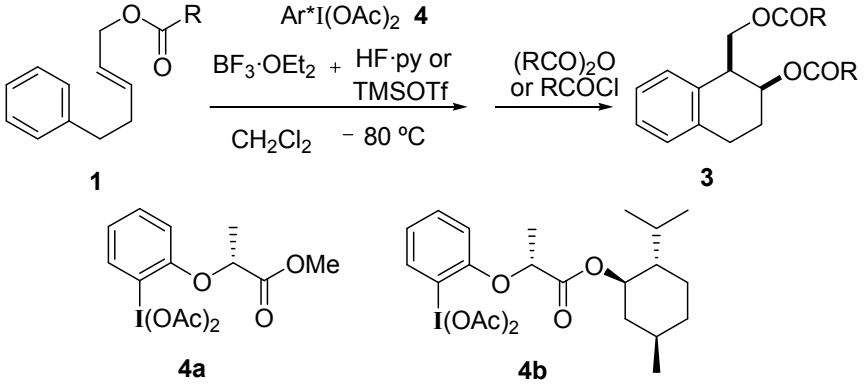
[a] **1** (0.20 mmol), $PhI(OAc)_2$ (0.24 mmol), and $BF_3{\cdot}OEt_2$ (0.80 mmol) in CH_2Cl_2 (8 mL) at −80 °C, unless otherwise noted. [b] TfOH (0.57 mmol) was added. [c] Reaction temperature was elevated from −80 °C to 0 °C. [d] The crude reaction mixture was acylated. [e] AcOH (1.75 mmol) was added. [f] HF·py (50 μL) was added. [g] Reaction temperature was elevated from −80 °C to −40 °C.

To determine the *cis/trans* configuration of **3**, we initially focused on the coupling constant between the 1-H and 2-H ($J_{1,2}$) in the ^{1}H NMR spectrum. A relatively small coupling constant ($J_{1,2}$ = 4.8 Hz) was observed for acetate **3a**. In the cases of benzoate **3b** and pivalate **3c**, the coupling constant $J_{1,2}$ was 5.5 Hz. Such moderate coupling constant is compatible with *cis*- and *trans*-configurations. Even in the *trans*-isomer, the 2-substituent located in a pseudoaxial position would reduce the coupling constant. In fact, 6 Hz for $J_{1,2}$ was reported for a *trans* derivative,[11a] which was isolated as a serrulatane diterpene.[11] The *trans* configuration of the natural product was confirmed by single crystal X-ray crystallography.[11b] Accordingly, we undertook stereochemical

determination of **3** by X-ray crystallographic analysis. Fortunately, a single crystal of **3b** was obtained and successfully subjected to X-ray crystallographic analysis,[13] which disclosed the *cis*-configuration of **3b**.

On the basis of the reaction conditions summarized in Table 1, an enantioselective variant of the oxidative arylation of **1** was examined using lactate-based chiral hypervalent iodine reagents **4a** and **4b** (Table 2). Immediate progress at a low reaction temperature (−80 °C) is one of the attractive aspects of this reaction, and thus HF·pyridine was used as a coactivator together with the $BF_3{\cdot}OEt_2$ activator (entries 1 and 2). Bulky mentyl reagent **4b** led to a slight increase in enantioselectivity (74% ee; entry 2) in comparison with simple reagent **4a** (69% ee; entry 1). Aiming at a further increase in the enantioselectivity, we found that trimethylsilyl triflate functioned as a suitable coactivator leading to high enantioselectivity (85% ee; entry 3). The enantioselectivity further increased in the oxidative arylation of pivalate substrate **1c** (89% ee; entry 4).

Table 2. Enantioselectivity in Oxyarylation of **1**[a]

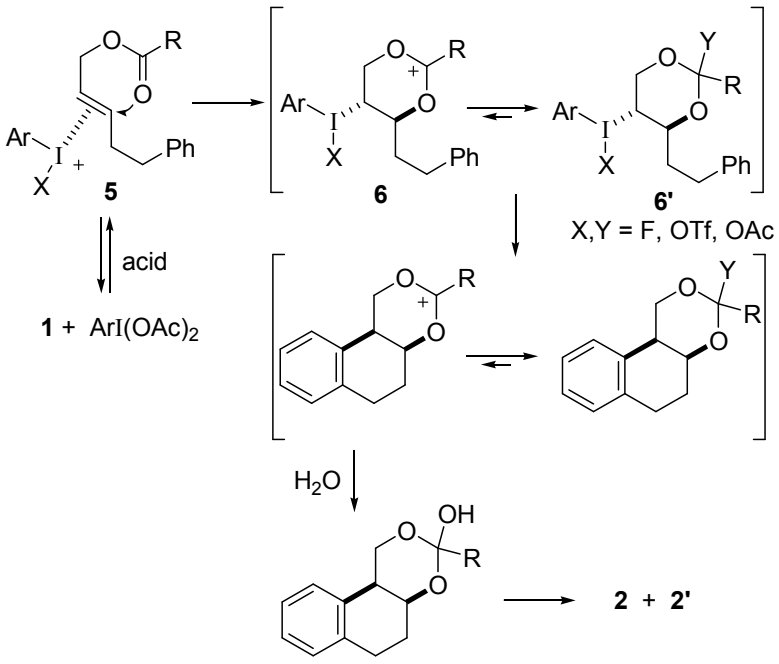


			3	
entry	**1** (R)	**4**	yield (%)	ee (%)
1	**1a** (Me)	**4a**	59	69
2	**1a** (Me)	**4b**	55	74
3[b]	**1a** (Me)	**4b**	59	85
4[b]	**1c** (*t*-Bu)	**4b**	37	89

[a] **1** (0.20 mmol), **4** (0.40 mol), HF·py (50 μL), and $BF_3{\cdot}OEt_2$ (0.80 mmol) in CH_2Cl_2 (8 mL) at −80 °C for 3–6 h, then acylation. [b] TMSOTf (0.80 mmol) was used instead of HF·py.

To obtain an insight into the mechanistic role of the acyloxy group of **1**, reactions of acyloxy-deficient substrates were examined. At first, (*E*)-5-phenylpent-2-en-1-ol and (*E*)-5-phenylpent-2-enyl methyl ether were subjected to the oxidation under the same conditions using (diacetoxyiodo)benzene in the presence of HF·pyridine and $BF_3{\cdot}OEt_2$ at −80 °C. In these reactions, most of the substrate was recovered and the formation of complex mixtures was observed. Therefore, the presence of carboxylate may be important for the oxidative arylation. We then examined the use of a trifluoroacetate substrate. The electron-deficient acyloxy group resulted in recovery of the substrate. These results indicate the importance of nucleophilic participation of the acyloxy group with respect to the promotion of oxidative arylation.

Scheme 1. Plausible Reaction Mechanism



A plausible reaction mechanism based on the above mentioned results is illustrated in Scheme 1. The oxidative arylation may be initiated by electrophilic attack of the activated hypervalent iodine reagent to the olefin substrate **1** to generate reactive species **5**. The lactate-based chiral hypervalent iodine reagent differentiates between the enantiotopic faces of the olefin. The enantioselectivity in the oxidative arylation of **1** is similar to that in the usual 1,2-difunctionalization of alkenes reported previously.[4] This is consistent with a reaction mechanism initiated by electrophilic attack of the iodine reagent to the olefin. Nucleophilic participation of the acyloxy group may trap reactive

species **5** to yield 1,3-dioxan-2-yl cation intermediate **6**, which may be reversibly trapped at the 2-position by a nucleophile, such as fluoride, triflate, or acetate, depending on the reaction conditions. The iodonio group of **6**/**6'** may be nucleophilically substituted by the phenyl group. The *cis*-configuration of oxidative arylation product **3** is rationalized by syn addition of the acyloxy group and the aryl group to the olefin as shown in the mechanism. Quenching the reaction with water results in the formation of the hemiorthoester, which is finally converted to a mixture of **2** and **2'**.

In summary, we have developed the enantioselective oxidative arylation of alkenes promoted by participation of the acyloxy group under metal-free conditions. This reaction stereoselectively provides the tetrahydro-2-hydroxy-1-(hydroxymethyl)naphthalene structure, which is found in serrulatane diterpenes.

Experimental Section

General. Proton and $^{13}C\{^1H\}$NMR spectra were measured on a JEOL ECA-600 spectrometer as solutions in $CDCl_3$. Proton NMR spectra were recorded using the residual $CHCl_3$ as an internal reference (7.24 ppm) and $^{13}C\{^1H\}$NMR using $CDCl_3$ as an internal reference (77.00 ppm). For mass spectra measurements was used JEOL JMS-T100LC and ThermoFisher Exactive. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Gas chromatography was performed on Shimadzu GC-17A. Reaction temperature was controlled using EYELA, PSL-1800 and PSL-1810 low temperature baths with magnetic stirrer.

Material. Unless otherwise noted, the reagents were commercially available and were used without further purification. Dichloromethane was purified by distillation over calcium hydride. Boron trifluoride diethyl etherate was purified by distillation over $Ca(OH)_2$. Column chromatography was performed on silica gel 60 (0.063-0.200 mm) from Merck. Hypervalent iodine reagents, **4a**[4a] and **4b**[9] were prepared as reported previously.

(*E*)-5-Phenylpent-2-enyl acetate (1a).[15] The substrates **1a-c** were prepared from 3-phenylpropionaldehyde. The aldehyde (4 mL, 30 mmol) was reacted with triethyl phosphonoacetate in the presence of *n*-butyl lithium to yield ethyl 5-phenylpent-2-enoate (4.7 g, 23 mmol, 77% yield). Reduction of the 5-phenyl-2-enoate (4.7 g, 23 mmol) with DIBAL-H at 0 °C gave (*E*)-phenylpent-2-en-1-ol (3.51 g, 21.6 mmol, 94% yield). Acetylation of the alcohol (500 mg, 3.1 mmol) with acetic anhydride

gave **1a** (561 mg, 2.75 mmol, 89% yield); oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 5.80 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.58 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.49 (d, *J* = 6.9 Hz, 2H), 2.69 (t, *J* = 6.9 Hz, 2H), 2.36 (q, *J* = 6.9 Hz, 2H), 2.04 (s, 3H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 170.9, 141.5, 135.4, 128.4, 128.3, 125.9, 124.4, 65.1, 35.3, 34.0, 21.0; IR (neat) 2934, 1740, 1230 cm^{-1}.

(*E*)-5-Phenylpent-2-enyl benzoate (**1b**). (*E*)-Phenylpent-2-en-1-ol was prepared by reduction of (*E*)-ethyl-5-phenylpent-2-enoate in the same way as **1a**. Benzoylation of the alcohol (500 mg, 3.1 mmol) with benzoyl chloride gave **1b** (810 mg, 3.04 mmol, 98% yield); oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 5.88 (dt, *J* = 15.8, 6.9 Hz, 1H), 5.70 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.74 (d, *J* = 6.9 Hz, 2H), 2.71 (t, *J* = 6.9 Hz, 2H), 2.39 (q, *J* = 6.9 Hz, 2H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 166.4, 141.5, 135.3, 132.8, 130.3, 129.6, 128.4, 128.3, 125.9, 124.5, 65.5, 35.3, 34.1; HRMS (ESI-TOF) *m/z* calcd for $C_{18}H_{18}NaO_2$ $(M + Na)^+$ 289.1204, found 289.1200; IR (neat) 2932, 1717, 1269 cm^{-1}.

(*E*)-5-Phenylpent-2-enyl pivalate (**1c**). (*E*)-Phenylpent-2-en-1-ol was prepared by reduction of (*E*)-ethyl-5-phenylpent-2-enoate in the same way as **1a**. Pivaloylation of the alcohol (320 mg, 2 mmol) with pivaloyl chloride gave **1c** (551 mg, 1.13 mmol, 57% yield); oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.6 Hz, 2H), 7.18–7.14 (m, 3H), 5.76 (dt, *J* = 15.1, 6.9 Hz, 1H), 5.56 (dt, *J* = 15.1, 6.2 Hz, 1H), 4.47 (d, *J* = 6.2 Hz, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.36 (q, *J* = 7.6 Hz, 2H), 1.17 (s, 9H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 178.3, 141.5, 134.4, 128.4, 128.3, 125.8, 124.7, 64.8, 38.7, 35.3, 34.0, 27.2; HRMS (ESI-Orbitrap) *m/z* calcd for $C_{16}H_{26}NO_2$ $(M + NH_4)^+$ 264.1958, found 264.1957; IR (neat) 2973, 1730, 1152 cm^{-1}.

cis-2-Acetoxy-1-(acetoxymethyl)-1,2,3,4-tetrahydronaphthalene (**3a**). To dichloromethane solution (8 mL) containing **1a** (41 mg, 0.2 mmol), (diacetoxyiodo)benzene (77 mg, 0.24 mmol), $BF_3{\cdot}OEt_2$ (0.1 mL) and HF·pyridine (50 μL) was added at –80 °C. After stirring at –80 °C for 1 h, the mixture was quenched by water and extracted with dichloromethane. The organic phase was dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was treated with acetic anhydride and pyridine, then purified by column chromatography (SiO_2, eluent 20% ethyl acetate in hexane) to give racemic **3a** (34.9 mg, 0.13 mmol, 67% yield). The reaction of **1a** (41 mg,

0.2 mmol) with **4b** (219 mg, 0.4 mmol) in the presence of $BF_3 \cdot OEt_2$ (0.1 mL) and TMSOTf (0.14 mL) at –80 °C for 2.5 h. gave a mixture of **2a** and **2a'**. The crude mixture was treated with acetic anhydride and pyridine, then purified by column chromatography to give optically active **3a** (30.1 mg, 0.11 mmol, 57% yield) with 85% ee. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24−7.21 (m, 1H), 7.18−7.13 (m, 2H), 7.12−7.08 (m, 1H), 5.31 (ddd, *J* = 8.2, 4.8, 3.4 Hz, 1H), 4.41 (dd, *J* = 11.0, 4.8 Hz, 1H), 4.36 (dd, *J* = 11.0, 6.9 Hz, 1H), 3.41 (dt, *J* = 6.9, 4.8 Hz, 1H), 2.94 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.83 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.12 (ddt, *J* = 13.7, 8.2, 6.9 Hz, 1H), 2.05 (s, 3H), 2.04 (s, 3H), 1.94 (dtd, *J* = 13.7, 6.9, 3.4 Hz, 1H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 170.9, 170.5, 135.8, 134.2, 128.8, 128.7, 126.8, 126.1, 70.1, 64.9, 40.5, 26.4, 25.0, 21.2, 21.0; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{18}NaO_4$ $(M + Na)^+$ 285.1103, found 285.1097; IR (neat) 1739, 1245 cm^{-1}; $[\alpha]_D^{20}$ = –34.1 (c = 0.60, $CHCl_3$) for 85% ee; Enantiomeric ratio of **3a** was determined by gas chromatography equipped with a chiral column (Chirasil-DEX-CB, 25 m × 0.25 mm × 0.25 μm film thickness). Retention times of (+)-**3a** and (−)-**3a** were 18.1 and 18.6 min, respectively, when the column temperature was maintained at 170 °C.

Proton NMR of **2a** and **2a'.** Selected data for **2a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23−7.11 (m, 4H), 5.43 (ddd, *J* = 8.9, 4.8, 3.4 Hz, 1H), 3.99 (dd, *J* = 11.0, 4.8 Hz, 1H), 3.87 (dd, *J* = 11.0, 7.6 Hz, 1H), 3.29−2.74 (m, 3H), 2.20−1.92 (m, 2H), 2.08 (s, 3H); Selected data for **2a'**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23−7.11 (m, 4H), 4.53 (dd, *J* = 11.0, 7.6 Hz, 1H), 4.48 (dd, *J* = 11.0, 5.5 Hz, 1H), 4.25 (dt, *J* = 8.9, 4.1 Hz, 1H), 3.29−2.74 (m, 3H), 2.20−1.92 (m, 2H), 2.08 (s, 3H).

cis-2-Benzoyloxy-1-(benzoyloxymethyl)-1,2,3,4-tetrahydronaphthalene (**3b**). To dichloromethane solution (8 mL) containing **1b** (53 mg, 0.2 mmol), (diacetoxyiodo)benzene (77 mg, 0.24 mmol), $BF_3 \cdot OEt_2$ (0.1 mL) and HF·pyridine (50 μL) was added at –80 °C. After stirring at –80 °C for 1 h, the mixture was quenched by water and extracted with dichloromethane. The organic phase was dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was treated with benzoyl chloride and triethylamine, then purified by column chromatography (SiO_2, eluent 10% ethyl acetate in hexane) to give racemic **3b** (47.3 mg, 0.12 mmol, 61% yield); colorless needle; mp = 96.5−97.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.54−7.45 (m, 2H), 7.41−7.37 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23−7.12 (m, 3H), 5.67 (ddd, *J* = 9.6, 5.5, 2.7 Hz, 1H), 4.79 (dd, *J* = 11.0, 5.5 Hz, 1H), 4.69 (dd, *J* = 11.0, 7.6 Hz, 1H), 3.74 (dt, *J* = 7.6, 5.5 Hz, 1H), 3.07 (dt, *J* =

17.2, 5.5 Hz, 1H), 2.95 (dt, *J* = 17.2, 6.8 Hz, 1H), 2.34 (dtd, *J* = 13.7, 9.6, 6.8 Hz, 1H), 2.14 (dtd, *J* = 13.7, 5.5, 2.7 Hz, 1H); $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) δ 166.4, 165.9, 135.9, 134.3, 132.9, 132.8, 130.1, 129.9, 129.6, 129.5, 129.0, 128.9, 128.3, 128.2, 126.9, 126.3, 71.0, 65.7, 41.0, 26.7, 25.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{25}H_{22}NaO_4$ $(M + Na)^+$ 409.1416, found 409.1410; IR (KBr) 1713, 1289 cm^{-1}; The structure of **3b** was confirmed by X-ray crystallography.[13]

Proton NMR of **2b** and **2b'.** Selected data for **2b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.23−7.12 (m, 4H), 5.72 (ddd, *J* = 8.2, 4.8, 2.7 Hz, 1H), 4.11 (dd, *J* = 11.0, 4.8 Hz, 1H), 3.91 (dd, *J* = 11.0, 8.2 Hz, 1H), 3.37 (dt, *J* = 8.2, 4.8 Hz, 1H), 3.11 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.93 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.31 (dq, *J* = 13.7, 6.9 Hz, 1H), 2.10 (dtd, *J* = 13.7, 6.9, 2.7 Hz, 1H); Selected data for **2b'**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.23−7.12 (m, 4H), 4.80 (dd, *J* = 11.0, 8.2 Hz, 1H), 4.73 (dd, *J* = 11.0, 4.8 Hz, 1H), 4.32 (ddd, *J* = 8.2, 4.8, 2.7 Hz, 1H), 3.37 (dt, *J* = 8.2, 4.8 Hz, 1H), 3.05 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.84 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.06 (dq, *J* = 13.7, 6.9 Hz, 1H), 1.98 (dtd, *J* = 13.7, 6.9, 2.7 Hz, 1H).

cis-1-(Hydroxymethyl)-2-pivaloyloxy-1,2,3,4-tetrahydronaphthalene (**2c**). To dichloromethane solution (8 mL) containing **1c** (49 mg, 0.2 mmol), (diacetoxyiodo)benzene (87 mg, 0.27 mmol), $BF_3{\cdot}OEt_2$ (0.1 mL) and HF·pyridine (50 μL) was added at –80 °C. After stirring at –80 °C for 5 h, the mixture was quenched by water and extracted with dichloromethane. The organic phase was dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by column chromatography (SiO_2, eluent 20% ethyl acetate in hexane) to give racemic **2c** (40.7 mg, 0.16 mmol, 78% yield); oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21−7.18 (m, 1H), 7.16−7.14 (m, 2H), 7.13−7.10 (m, 1H), 5.43 (ddd, *J* = 9.6, 4.8, 3.4 Hz, 1H), 4.01 (dd, *J* = 11.0, 4.8 Hz, 1H), 3.80 (dd, *J* = 11.0, 8.2 Hz, 1H), 3.24 (dt, *J* = 8.2, 4.8 Hz, 1H), 2.99 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.85 (dt, *J* = 17.2, 6.9 Hz, 1H), 2.19−2.08 (m, 1H), 2.01−1.88 (m, 1H), 1.18 (s, 9H); HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{22}NaO_3$ $(M + Na)^+$ 285.1467, found 285.1466.

cis-2-Pivaloyloxy-1-(pivaloyloxymethyl)-1,2,3,4-tetrahydronaphthalene (**3c**). To dichloromethane solution (8 mL) containing **1c** (48 mg, 0.2 mmol), (diacetoxyiodo)benzene (77 mg, 0.24 mmol), $BF_3{\cdot}OEt_2$ (0.1 mL) and HF·pyridine (50 μL) was added at –80 °C. After stirring at –80 °C for 1 h, the mixture was quenched by

water and extracted with dichloromethane. The organic phase was dried with Na_2SO_4, and concentrated in vacuo. The crude mixture was pivaloylated, then purified by column chromatography (SiO_2, eluent 6% ethyl acetate in hexane) to give racemic **3c** (39.5 mg, 0.11 mmol, 59% yield). The reaction of **1c** (49 mg, 0.20 mmol) with **4b** (219 mg, 0.4 mmol) in the presence of $BF_3{\cdot}OEt_2$ (0.10 mL) and TMSOTf (0.14 mL) at –80 °C for 17 h gave a mixture of **2c** and **2c'**. The crude mixture was treated with pivaloyl chloride and triethylamine, then purified by column chromatography to give optically active **3c** (25.5 mg, 0.07mmol, 37% yield) with 89% ee. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23−7.08 (m, 4H), 5.34 (ddd, *J* = 7.6, 5.5, 3.4 Hz, 1H), 4.48 (dd, *J* = 11.0, 5.5 Hz, 1H), 4.29 (dd, *J* = 11.0, 7.6 Hz, 1H), 3.38 (dt, *J* = 7.6, 5.5 Hz, 1H), 2.92 (ddd, *J* = 17.2, 7.6, 6.2 Hz, 1H), 2.79 (dt, *J* = 17.2, 6.2 Hz, 1H), 2.17 (ddt, *J* = 13.7, 7.6, 6.2 Hz, 1H), 1.88 (dtd, *J* = 13.7, 6.2, 3.4 Hz, 1H), 1.16 (s, 9H), 1.15 (s, 9H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$) δ 178.4, 177.7, 136.0, 134.2, 128.9, 128.1, 126.6, 126.0, 69.0, 64.4, 40.5, 39.0, 38.7, 27.1, 27.0, 25.7, 25.4; HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{30}NaO_4$ $(M + Na)^+$ 369.2042, found 369.2035; IR (neat) 2972, 1728, 1154 cm^{-1}; $[\alpha]_D^{20}$ = –14.6 (c = 0.24, $CHCl_3$) for 89% ee. Enantiomeric ratio of **3c** was determined by gas chromatography equipped with a chiral column (Chirasil-DEX-CB, 25 m × 0.25 mm × 0.25 μm film thickness). Retention times of (+)-**3c** and (−)-**3c** were 69.3 and 70.1 min, respectively, when the column temperature was maintained at 160 °C.

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Supporting Information

The X-ray crystallographic cif data of **3b**, the copies of ^{1}H NMR and ^{13}C{^{1}H}NMR spectra for all new compounds, and the copies of GLC chart for determination of the enantiomeric ratio of products. The Supporting Information is available free of charge on the ACS Publications website.

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