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# Heck–Matsuda Reaction for Allylic Nitro Compounds: A Short Asymmetric Synthesis of an FTY720 Derivative

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**Keywords:** Synthetic methods / C–C coupling / Allylic compounds / Nitro compounds / Palladium

The Heck–Matsuda reaction for allylic nitro compounds effectively afforded cinnamyl nitro compounds in good yields. Aryldiazonium salts that have an electron-donating substituent underwent a smooth reaction in the presence of $Pd_2dba_3$. A palladium complex that coordinated with an electron-rich ligand was necessary for the reaction to progress with electron-deficient aryldiazonium salts. An optically active allylic nitro compound underwent reaction without the loss of optical purity at the stereogenic center. A short synthesis of an optically active FTY720 derivative was achieved by this method.

## Introduction

Allylic nitro compounds are valuable synthetic building blocks, because they are readily prepared and can be converted into various compounds in a short number of steps. The nitro group frequently serves as a precursor to a nitrogen-based functional group, such as an amine.[1] A typical reaction for allylic nitro compounds is the Tsuji–Trost-type substitution reaction,[2,3] in which the nitro group is substituted by various nucleophiles in the presence of palladium-complex catalysts.[4] In this case, the allylic carbon attached to the nitro group is $sp^3$ hybridized with a chiral configuration, but the chirality is lost during this $S_N2'$-type reaction. In contrast, if a Heck-type reaction is achieved for the allylic nitro compound,[5] the stereochemistry at the allylic asymmetric center is maintained as elaboration occurs with a carbon source at the terminal vinyl group. To the best of our knowledge, there is no report for employing the Heck reaction on allylic nitro compounds.

FTY720, 2-amino[2-(4-octylphenyl)ethyl]-1,3-propanediol is a potent immunosuppressive agent used therapeutically to treat autoimmune diseases such as multiple sclerosis.[6] Chiral analogues of FTY720 are of interest for probing biological activity that is dependent on the stereogenic center.[7] So far, several syntheses of these analogues have been reported, however, they use long preparation sequences.[8] In this paper, we report a three-step synthesis for a chiral FTY720 analogue employing the Heck–Matsuda reaction on a chiral allylic nitro compound.

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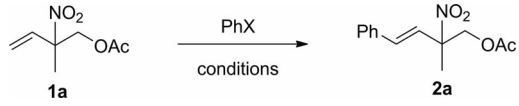
## Results and Discussion

Allylic nitro compounds **1** were prepared from nitroalkene and formaldehyde in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane).[9] The hydroxy group was protected by treatment with acetic anhydride. Exposing **1a** to various conditions for the Heck reaction resulted in the desired carbon bond elaboration (see Scheme 1), and these results are summarized in Table 1.




**1a** **2a**

Scheme 1.

Initially, we examined **1a** under classical conditions for the Heck reaction. However, the reaction did not progress, and the desired Heck adduct **2a** was not observed in the reaction mixture (Table 1, Entry 1). Changing the additive and the solvent did not give the desirable results (Table 1, Entries 2 and 3), and using iodobenzene also failed to give **2a** (Table 1, Entries 4 and 5). The benzenediazonium salt is a strong aryl donor and is often used for palladium chemistry and in coupling reactions.[5h,10] Therefore, we examined various conditions for the Heck–Matsuda reaction of **1a** with the benzenediazonium salt. The treatment of **1a** with $PhN_2BF_4$ in the presence of 5 mol-% $Pd(OAc)_2$ failed to form **2a** (Table 1, Entry 6). The use of Xphos as an additive gave limited amounts of **2a** in only 10% yield (Table 1, Entry 7). $PdCl_2(dppf)_2$ was also ineffective for providing a good yield of the adduct (Table 1, Entry 8). Recently, Correia reported that using $Pd_2dba_3$ (**3a**) as the catalyst and

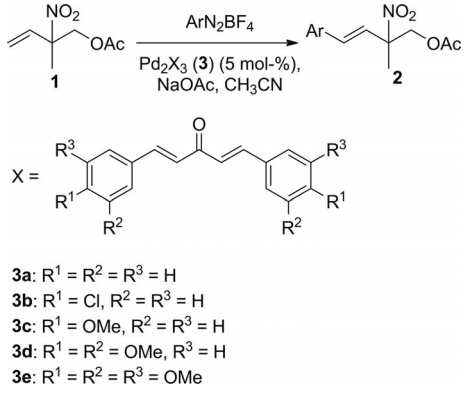
Table 1. Heck reaction of compound **1a**.

| Entry | Catalyst[a] | X | Conditions | % Yield **2a**[b] |
|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ (2) dppp (31) | Br | toluene/$Et_3N$ 110 °C/12 h | 0 |
| 2 | $Pd(OAc)_2$ (5) dppf (5) | Br | toluene/$Et_3N$ 110 °C/12 h | 0 |
| 3 | $Pd(OAc)_2$ (5) dppf (5) | Br | DMF/$Et_3N$ 110 °C/12 h | 0 |
| 4 | $Pd(OAc)_2$ (5) dppf (5) | I | toluene/$Et_3N$ 110 °C/12 h | 0 |
| 5 | $Pd(OAc)_2$ (5) $PPh_3$ (10) | I | DMF/$Et_3N$ 90 °C/14 h | 0 |
| 6 | $Pd(OAc)_2$ (5) | $N_2BF_4$ | $CH_3CN$/NaOAc r.t./6 d | trace |
| 7 | $Pd(OAc)_2$ (6) Xphos (10) | $N_2BF_4$ | $CH_3CN$/NaOAc r.t./7 d | 10 |
| 8 | $PdCl_2(dppf)_2$ (5) | $N_2BF_4$ | $CH_3CN$/NaOAc r.t./6 d | 0 |
| 9 | $Pd_2dba_3$ (**3a**, 5) | $N_2BF_4$ | MeOH/NaOAc r.t./30 h | 51 (37)[c] |
| 10 | $Pd_2dba_3$ (**3a**, 5) | $N_2BF_4$ | $CH_3CN$/$Et_3N$ r.t./30 h | 0 |
| 11 | $Pd_2dba_3$ (**3a**, 5) | $N_2BF_4$ | $CH_3CN$/NaOAc r.t./30 h | 90 |

[a] Equivalents are in parentheses. [b] Isolated yield. [c] Recovered starting material.

benzonitrile as the solvent offered the best results for the Heck–Matsuda reaction.[10a] Although they employed benzonitrile in the reaction, we used $CH_3CN$ instead, because it is readily removed by evaporation during the workup process. The reaction performed in MeOH afforded **2a** in 51% yield along with the recovery of **1a** in 37% (Table 1, Entry 9). The use of $Et_3N$ is not recommended, because of the immediate decomposition of $PhN_2BF_4$ (Table 1, Entry 10). Finally, we found that the reaction proceeded smoothly in the presence of $Pd_2dba_3$ (**3a**) in $CH_3CN$, and the desired **2a** was obtained in 90% yield (Table 1, Entry 11).

With the optimized reaction conditions, we examined the Heck–Matsuda reaction in which **1a** was treated with various aryldiazonium salts (Scheme 2). The results are summarized in Table 2.




**3a**: $R^1 = R^2 = R^3 = H$
**3b**: $R^1 = Cl$, $R^2 = R^3 = H$
**3c**: $R^1 = OMe$, $R^2 = R^3 = H$
**3d**: $R^1 = R^2 = OMe$, $R^3 = H$
**3e**: $R^1 = R^2 = R^3 = OMe$

Scheme 2.

For example, exposing the *p*-toluenediazonium salt to the optimized conditions resulted in the formation of **2b** in 89% yield (Table 2, Entry 1). The diazonium salts bearing electron-donating groups at the *para* position underwent smooth Heck–Matsuda reactions in the presence of the catalyst **3a** to give the corresponding adducts **2** in good yields (Table 2, Entries 2, 3, and 5), but the *p*-(dimethylamino) benzenediazonium salt was the exception and provided an unsatisfactory result (Table 2, Entry 4). In contrast, the reactions with *meta*-substituted aryldiazonium salts occurred at slow rates and afforded poor yields of **2** (Table 2, Entries 6 and 7). The presence of an electron-withdrawing group at the *para* position slowed the reaction rate and decreased the yields of **2**. For example, the treatment of the *p*-chlorobenzenediazonium salt in the presence of $Pd_2dba_3$ (**3a**) resulted in the formation of **2i** in 77% yield (Table 2, Entry 8), however, at room temperature, the rate for this reaction was considerably slow. The ligand in the palladium complex was important for improving the yield of **2**. Although reaction progress failed to occur with complex **3b**, palladium complex **3c** catalyzed the reaction smoothly at room temperature and give **2i** in 84% yield (Table 2, Entries 9 and 10, respectively).[11] Similar results were observed in the formation of **2j**. The reaction catalyzed by **3a** afforded **2j** in only 35% yield (Table 2, Entry 11), however, by using palladium complex **3c**, the yield of **2j** improved to 62%, but the reaction required 144 h for completion. Catalyst **3d**, with two methoxy groups on each aryl ring, offered the best results, and the yield of **2j** increased to 73% (Table 2, Entry 14). However, using complex **3e** as the catalyst did not improve the yield of **2j** (Table 2, Entry 15). Furthermore, the aryldiazonium salt substituted with a strong electron-deficient group failed to give **2k** (Table 2, Entry 16), but gave the allylic substituted products **4** in 25% (see Scheme 3).

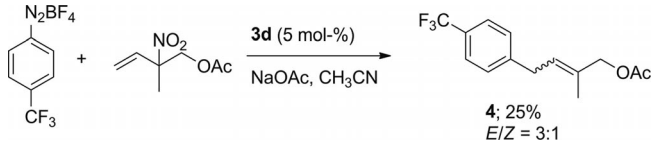
Table 2. Heck–Matsuda reactions of **1a** with various aryldiazonium salts.

| Entry | Ar | | Time [h] | Temp. [°C] | % Yield **2**[a] |
|---|---|---|---|---|---|
| 1 | *p*-$MeC_6H_4$ | **3a** | 24 | r.t. | **2b**, 89 |
| 2 | *p*-$tBuC_6H_4$ | **3a** | 48 | r.t. | **2c**, 100 |
| 3 | *p*-$MeOC_6H_4$ | **3a** | 40 | r.t. | **2d**, 95 |
| 4 | *p*-$Me_2NC_6H_4$ | **3a** | 240 | r.t. | **2e**, 0 |
| 5 | 3,4-$MeO_2C_6H_3$ | **3a** | 32 | r.t. | **2f**, 71 |
| 6 | *m*-$MeOC_6H_4$ | **3a** | 96 | r.t. | **2g**, 0 |
| 7 | *m*-$MeC_6H_4$ | **3a** | 124 | r.t. | **2h**, 40 |
| 8 | *p*-$ClC_6H_4$ | **3a** | 60 | 70 | **2i**, 77 |
| 9 | *p*-$ClC_6H_4$ | **3b** | 72 | r.t.–50 | **2i**, 0 |
| 10 | *p*-$ClC_6H_4$ | **3c** | 144 | r.t. | **2i**, 84 |
| 11 | *p*-$IC_6H_4$ | **3a** | 48 | r.t. | **2j**, 35 |
| 12 | *p*-$IC_6H_4$ | **3a** | 46 | 60 | **2j**, 10 |
| 13 | *p*-$IC_6H_4$ | **3c** | 144 | r.t. | **2j**, 62 |
| 14 | *p*-$IC_6H_4$ | **3d** | 60 | r.t. | **2j**, 73 |
| 15 | *p*-$IC_6H_4$ | **3e** | 96 | r.t. | **2j**, 20 |
| 16 | *p*-$CF_3C_6H_4$ | **3d** | 73 | r.t. | **2k**, 0 |

[a] Isolated yield.

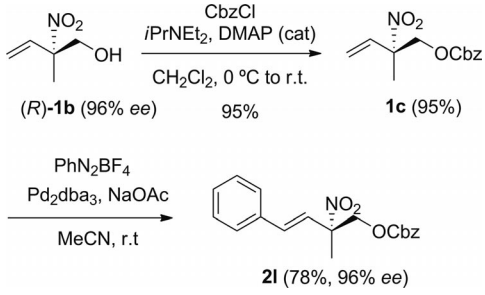
Next, we examined the use of chiral allylic nitro compounds in the transformation (see Scheme 4). Optically active nitro alcohol (*R*)-**1b** was obtained by using lipase for the optical resolution of racemic **1a**.[12] Thus, Cbz (carbobenzyloxy) protection of (*R*)-**1b** (96%*ee*) was performed under standard conditions to give (*R*)-**1c** in 95% yield.



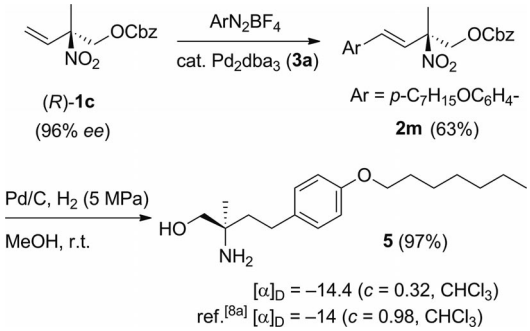

Scheme 3.

Treatment of (*R*)-**1c** with benzenediazonium tetrafluoroborate under optimized conditions resulted in the formation of (*R*)-**2l** in 78% yield. The optical purity of (*R*)-**2l** was determined by chiral HPLC analysis to be 96%*ee*. Thus, the Heck–Matsuda reaction occurred with the complete retention of configuration at the tertiary nitro C atom (see Scheme 4).




Scheme 4.

The Heck–Matsuda reaction was used for the synthesis of the FTY720 derivative **5** (see Scheme 5). Compound **1c** (96%*ee*) was treated with *p*-heptyloxyphenyldiazonium salt in the presence of 5 mol-% of complex **3a** to give the desired product, that is, optically active **2m** in 63% yield. The nitro group of **2m** was readily reduced under hydrogenation conditions catalyzed by Pd-C, resulting in the removal of the Cbz group in a one-pot process, and the desired **5** was obtained in 97% yield. The optical rotation of the synthetic sample of **5** was –14.4°, which is in good agreement with the reported data for (*R*)-**5**.[8a,8f] Thus, the absolute configurations of **1b**, **1c**, **2l**, **2m**, and **5** were unambiguously determined to be *R*, which is reasonable in comparison to the previous data regarding lipase optical resolutions.[13]




Scheme 5.

This method for the preparation of the FTY720 derivative provided a short and economical process in which only two steps were necessary for the total synthesis. The allylic nitro compound starting materials were easily produced on a large scale in three steps by using nitromethane, acetaldehyde, and formalin. Because the optical resolution of **1** is already established,[12] the Heck–Matsuda reaction for chiral **1** provides a new and useful methodology for the preparation of compounds with a nitrogen-substituted chiral tertiary alkyl functional group. Further application of the present method for heterocyclic synthesis is currently in progress.

## Conclusions

We have successfully achieved the Heck–Matsuda reaction with allylic nitro compounds, which were readily available by the condensation reaction of a nitroalkene and formalin. Benzenediazonium salts served as good aryl donors for the reaction. The stereogenic center at the allylic nitro group was well maintained during the reaction, and chiral adducts were isolated in good yields. The reaction was effectively applied to the short synthesis of a FTY720 derivative.

## Experimental Section

**General Comments:** All $^1$H and $^{13}$C NMR spectroscopic data were recorded with a JEOL delta-500 or lamda-500 (500 MHz for $^1$H and 126 MHz for $^{13}$C) spectrometer. High resolution mass spectra (HRMS) were recorded at the Integrated Center for Sciences, Ehime University, Matsuyama, Japan. All of the reactions were performed under a nitrogen atmosphere unless otherwise mentioned. The aryldiazonium salts were prepared by the reported method.[14] The palladium complexes were prepared by the literature method.[15] $CH_3CN$ was dried with $CaH_2$. Palladium complexes **3** were prepared by the reported method.[11c] Compounds **1a** and **1b** were prepared by the method reported in the literature.[9] The optical resolution of **1b** was performed by the reported method.[12]

**2-Methyl-2-nitrobut-3-en-1-yl Acetate (1a):** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 6.13 (dd, $J$ = 17.4, 10.9 Hz, 1 H), 5.46 (d, $J$ = 10.9 Hz, 2 H), 5.46 (d, $J$ = 17.3 Hz, 1 H), 4.57 (d, $J$ = 11.9 Hz, 1 H), 4.40 (d, $J$ = 12.0 Hz, 1 H), 2.07 (s, 3 H), 1.74 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.1, 133.8, 119.6, 89.3, 67.5, 20.6, 19.7 ppm. HRMS (ESI): calcd. for $C_7H_{12}NO_4$ $[M + H]^+$ 174.0766; found 174.0766.

**(*R*)-2-Methyl-2-nitrobut-3-en-1-ol (1b):** The enantiomeric purity was determined by HPLC analysis. HPLC [CHIRALPAK AD (0.46 cm × 25 cm) from Daicel Chemical Ind., Ltd.; hexane/*i*PrOH, 95:5; 0.5 mL/min]: $t_R$ (retention time) = 25.5 min [(*S*)-**1b**] and 30.0 min [(*R*)-**1b**] as 96%*ee*. $[\alpha]_D^{26}$ = –80.8 ($c$ = 0.14, $CDCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 6.14 (dd, $J$ = 17.5, 10.9 Hz, 1 H), 5.44 (d, $J$ = 10.9 Hz, 1 H), 5.43 (d, $J$ = 17.5 Hz, 2 H), 4.11 (dd, $J$ = 12.4, 6.5 Hz, 1 H), 3.82 (dd, $J$ = 12.4, 6.9 Hz, 1 H), 2.17 (s, 1 H), 1.72 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 134.4, 119.0, 92.2, 67.6, 19.2 ppm. HRMS (ESI): calcd. for $C_5H_{10}NO_3$ $[M + H]^+$ 132.0661; found 132.0688.

**(*E*)-2-Methyl-2-nitro-4-phenylbut-3-en-1-yl Acetate (2a):** A solution of **1a** (186.0 mg, 1.074 mmol) in dry $CH_3CN$ (5 mL) was purged with nitrogen, and NaOAc (266.0 mg, 3.243 mmol), $Pd_2dba_3$ (49.0 mg, 0.054 mmol), and $PhN_2BF_4$ (309.0 mg, 1.609 mmol) were added. The resulting mixture was stirred at room temperature for 24 h. $PhN_2BF_4$ (102 mg) was added, and the mixture was stirred

for an additional 6 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **2a** (242.0 mg, 90%) as a pale, reddish oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.44–7.29 (m, 5 H), 6.75 (d, $J$ = 16.3 Hz, 1 H), 6.42 (d, $J$ = 16.2 Hz, 1 H), 4.68 (d, $J$ = 11.9 Hz, 1 H), 4.49 (s, 1 H), 4.46 (s, 1 H), 2.09 (s, 3 H), 1.86 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.1, 135.0, 134.20, 129.0, 128.8, 126.98, 126.97, 124.3, 89.3, 67.6, 20.5, 19.9 ppm. $C_{13}H_{15}NO_4$ (249.27): calcd. C 62.64, H 6.07, N 5.62; found C 62.28, H 6.09, N 5.58.

**(*E*)-2-Methyl-2-nitro-4-(*p*-tolyl)but-3-en-1-yl Acetate (2b):** A solution of **1a** (226.0 mg, 1.305 mmol) in dry $CH_3CN$ (6 mL) was purged with nitrogen, and NaOAc (323.0 mg, 3.938 mmol), $Pd_2dba_3$ (61.0 mg, 0.067 mmol), and *p*-Tol$N_2BF_4$ (539.0 mg, 2.616 mmol) were added. The resulting mixture was stirred at room temperature for 24 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **2b** (305.0 mg, 89%) as a white solid; m.p. 42–43 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.30 (d, $J$ = 8.0 Hz, 2 H), 7.15 (d, $J$ = 8.0 Hz, 2 H), 6.73 (d, $J$ = 16.3 Hz, 1 H), 6.37 (d, $J$ = 16.2 Hz, 1 H), 4.69 (d, $J$ = 11.9 Hz, 1 H), 4.46 (d, $J$ = 12.0 Hz, 1 H), 2.34 (s, 3 H), 2.07 (s, 3 H), 1.84 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.0, 139.0, 134.1, 132.1, 129.4, 126.9, 123.2, 89.3, 67.6, 21.1, 20.4, 19.8 ppm. $C_{14}H_{17}NO_4$ (263.29): calcd. C 63.87, H 6.51, N 5.32; found C 64.08, H 6.42, N 5.18.

**(*E*)-4-[4-(*tert*-Butyl)phenyl]-2-methyl-2-nitrobut-3-en-1-yl Acetate (2c):** A solution of **1a** (92.0 mg, 0.531 mmol) in dry $CH_3CN$ (3 mL) was purged with nitrogen, and NaOAc (132.0 mg, 1.609 mmol), $Pd_2dba_3$ (24.0 mg, 0.026 mmol), and *p*-*t*Bu$C_6H_4N_2BF_4$ (264.0 mg, 1.064 mmol) were added. The resulting mixture was stirred at room temperature for 48 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **2c** (163.0 mg, 100%) as a white solid; m.p. 103–103.5 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.38 (d, $J$ = 8.0 Hz, 2 H), 7.34 (d, $J$ = 8.4 Hz, 2 H), 6.73 (d, $J$ = 16.5 Hz, 1 H), 6.37 (d, $J$ = 15.9 Hz, 1 H), 4.68 (d, $J$ = 11.6 Hz, 1 H), 4.46 (d, $J$ = 12.1 Hz, 1 H), 2.09 (s, 3 H), 1.85 (s, 3 H), 1.31 (s, 9 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.1, 152.4, 134.0, 132.2, 126.8, 125.8, 123.6, 89.3, 67.7, 34.6, 31.1, 20.5, 20.0 ppm. $C_{17}H_{23}NO_4$ (305.37): calcd. C 66.86, H 7.59, N 4.59; found C 67.03, H 7.53, N 4.45.

**(*E*)-4-(4-Methoxyphenyl)-2-methyl-2-nitrobut-3-en-1-yl Acetate (2d):** A solution of **1a** (91.0 mg, 0.525 mmol) in dry $CH_3CN$ (2 mL) was purged with nitrogen, and NaOAc (129.0 mg, 1.573 mmol), $Pd_2dba_3$ (25.0 mg, 0.027 mmol) and *p*-Me$OC_6H_4N_2BF_4$ (236.0 mg, 1.063 mmol) were added. The resulting mixture was stirred at room temperature for 40 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **2d** (139.0 mg, 95%) as a brown oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.34 (d, $J$ = 9.1 Hz, 2 H), 6.88 (d, $J$ = 9.1 Hz, 2 H), 6.70 (d, $J$ = 16.1 Hz, 1 H), 6.26 (d, $J$ = 16.7 Hz, 1 H), 4.69 (d, $J$ = 12.1 Hz, 1 H), 4.44 (d, $J$ = 12.0 Hz, 1 H), 3.82 (s, 3 H), 2.09 (s, 3 H), 1.84 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.0, 160.3, 133.7, 128.3, 127.6, 121.9, 114.1, 89.3, 67.7, 55.1, 20.4, 19.8 ppm. HRMS (ESI): calcd. for $C_{14}H_{18}NO_5$ [M + H]$^+$ 280.1185; found 280.1181.

**(*E*)-4-(3,4-Dimethoxyphenyl)-2-methyl-2-nitrobut-3-en-1-yl Acetate (2f):** A solution of **1a** (98.0 mg, 0.566 mmol) in dry $CH_3CN$ (3 mL) was purged with nitrogen, and NaOAc (140.0 mg, 1.707 mmol), $Pd_2dba_3$ (26.0 mg, 0.028 mmol), and 3,4-$(MeO)_2C_6H_3N_2BF_4$ (570.0 mg, 2.261 mmol) were added. The resulting mixture was stirred at room temperature for 12 h. 3,4-$(MeO)_2C_6H_3N_2BF_4$ (285 mg) was added, and the mixture was stirred for an additional 20 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **2f** (125.0 mg, 71%) as a brown oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 6.97–6.90 (m, 2 H), 6.84 (d, $J$ = 8.3 Hz, 1 H), 6.69 (d, $J$ = 16.1 Hz, 1 H), 6.26 (d, $J$ = 16.3 Hz, 1 H), 4.71 (d, $J$ = 11.9 Hz, 1 H), 4.44 (d, $J$ = 11.8 Hz, 1 H), 3.91 (s, 3 H), 3.89 (s, 3 H), 2.09 (s, 3 H), 1.85 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.2, 150.0, 149.2, 134.1, 127.9, 122.2, 120.7, 111.1, 109.1, 89.4, 67.7, 55.9, 20.5, 19.9 ppm. HRMS (ESI): calcd. for $C_{15}H_{20}NO_6$ [M + H]$^+$ 310.1291; found 310.1310.

**(*E*)-2-Methyl-2-nitro-4-(*m*-tolyl)but-3-en-1-yl Acetate (2h):** A solution of **1a** (105.0 mg, 0.606 mmol) in dry $CH_3CN$ (3 mL) was purged with nitrogen, and NaOAc (151.0 mg, 1.841 mmol), $Pd_2dba_3$ (29.0 mg, 0.032 mmol), and *m*-Tol$N_2BF_4$ (500.0 mg, 2.425 mmol) were added. The resulting mixture was stirred at room temperature for 70 h. *m*-Tol$C_6H_4N_2BF_4$ (125 mg) was added, and the mixture was stirred for an additional 24 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **2h** (63.0 mg, 40%) as a pale, reddish oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.22 (m, 3 H), 7.13 (d, $J$ = 7.3 Hz, 1 H), 6.72 (d, $J$ = 16.3 Hz, 1 H), 6.40 (d, $J$ = 16.2 Hz, 1 H), 4.68 (d, $J$ = 11.9 Hz, 1 H), 4.47 (d, $J$ = 11.9 Hz, 1 H), 2.35 (s, 3 H), 2.08 (s, 3 H), 1.85 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.2, 138.6, 135.0, 134.4, 130.0, 128.8, 127.7, 124.3, 124.2, 89.4, 67.8, 21.4, 20.7, 20.2 ppm. HRMS (ESI): calcd. for $C_{14}H_{18}NO_4$ [M + H]$^+$ 264.1236; found 264.1243.

**(*E*)-4-(4-Chlorophenyl)-2-methyl-2-nitrobut-3-en-1-yl Acetate (2i):** A solution of **1a** (107.0 mg, 0.618 mmol) in dry $CH_3CN$ (3 mL) was purged with nitrogen, and NaOAc (152.0 mg, 1.853 mmol), $Pd_2$(*p*-MeOdba)$_3$ (34.0 mg, 0.031 mmol), and *p*-Cl$C_6H_4N_2BF_4$ (419.0 mg, 1.854 mmol) were added. The resulting mixture was stirred at room temperature for 96 h. *p*-Cl$C_6H_4N_2BF_4$ (140 mg) was added, and the mixture was stirred for an additional 36 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **2i** (147.0 mg, 84%) as a pale, orange oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.34 (s, 4 H), 6.70 (d, $J$ = 16.2 Hz, 1 H), 6.41 (d, $J$ = 16.2 Hz, 1 H), 4.66 (d, $J$ = 11.9 Hz, 1 H), 4.48 (d, $J$ = 11.8 Hz, 1 H), 2.09 (s, 3 H), 1.85 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.2, 134.9, 133.5, 133.1, 129.1, 128.3, 125.0, 89.2, 67.6, 20.6, 20.1 ppm. $C_{13}H_{14}ClNO_4$ (283.71): calcd. C 55.04, H 4.97, N 4.94; found C 55.45, H 5.04, N 4.70.

**(*E*)-4-(4-Iodophenyl)-2-methyl-2-nitrobut-3-en-1-yl Acetate (2j):** A solution of **1a** (151.0 mg, 0.872 mmol) in dry $CH_3CN$ (3 mL) was purged with nitrogen, and NaOAc (216.0 mg, 2.633 mmol), $Pd_2$[3,4-$(MeO)_2$dba]$_3$ (56.0 mg, 0.044 mmol), and *p*-I$C_6H_4N_2BF_4$ (556.0 mg, 1.749 mmol) were added. The resulting mixture was stirred at room temperature for 60 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **2j** (240.0 mg, 73%) as a pale, orange oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.69 (d, $J$ = 8.3 Hz, 2 H), 7.14 (d, $J$ = 8.1 Hz, 2 H), 6.66 (d, $J$ = 16.1 Hz, 1 H), 6.43 (d, $J$ = 16.8 Hz, 1 H), 4.65 (d, $J$ = 12.0 Hz, 1 H), 4.48 (d, $J$ = 12.0 Hz, 1 H), 2.09 (s, 3 H), 1.85 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 170.3, 138.1, 134.6, 133.4, 128.8, 125.3, 94.9, 89.3, 67.7, 20.7, 20.2 ppm. $C_{13}H_{14}INO_4$ (375.16): calcd. C 41.62, H 3.76, N 3.73; found C 42.01, H 3.81, N 3.70.

**2-Methyl-4-[4-(trifluoromethyl)phenyl]but-2-en-1-yl Acetate (4):** A solution of **1a** (98.0 mg, 0.566 mmol) in dry $CH_3CN$ (3 mL) was

purged with nitrogen, and NaOAc (139.0 mg, 1.695 mmol), $Pd_2[3,4\text{-}(MeO)_2dba]_3$ (36.0 mg, 0.028 mmol), and *p*-$CF_3C_6H_4N_2BF_4$ (294.0 mg, 1.131 mmol) were added. The reaction mixture was stirred for 24 h at room temperature. NaOAc (92 mg) was added, and the reaction mixture was stirred at room temperature for an additional 48 h. The resulting mixture was poured into water, and the aqueous layer was extracted with EtOAc (3 × 25 mL). The combined organic layers were washed with brine (1 × 15 mL) and HCl (1 M solution, 1 × 3 mL). After drying with $Na_2SO_4$, the organic phase was concentrated in vacuo, and the residue was purified by flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give **4** (39.0 mg, 25%). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.54 (d, $J$ = 8.1 Hz, 2 H), 7.28 (d, $J$ = 8.0 Hz, 2 H), 5.63 (t, $J$ = 7.4 Hz, 0.75 H), 5.54 (t, $J$ = 7.8 Hz, 0.25 H), 4.67 (s, 0.5 H), 4.51 (s, 1.5 H), 3.49 (d, $J$ = 7.5 Hz, 0.5 H), 3.46 (d, $J$ = 7.4 Hz, 1.5 H), 2.08 (s, 3 H), 1.81 (s, 0.75 H), 1.76 (s, 2.25 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$, major isomer): $\delta$ = 171.1, 144.7, 132.2, 128.7, 126.8, 126.4, 125.5 (q, $J$ = 3.7 Hz), 69.7, 33.8, 21.0, 14.2 ppm. $^{13}$C NMR (126 MHz, $CDCl_3$, minor isomer): $\delta$ = 171.2, 144.8, 131.9, 128.8, 128.0, 126.8, 125.5 (q, $J$ = 3.7 Hz), 63.0, 33.9, 21.6, 21.0 ppm. IR (neat): $\tilde{\nu}$ = 1736, 1321, 1107, 1064, 827 cm$^{-1}$. HRMS (ESI): calcd. for $C_{14}H_{16}F_3O_2$ $[M + H]^+$ 273.1102; found 273.1112.

**(*R*)-Benzyl (2-Methyl-2-nitrobut-3-en-1-yl) Carbonate [(*R*)-1c]:** To a solution of (*R*)-**1b** (2.62 g, 19.98 mmol, 96% *ee*) in $CH_2Cl_2$ (30 mL) were added DMAP (4-dimethylaminopyridine, 2.45 g, 20.06 mmol) and *i*$Pr_2$NEt (5.1 mL, 30.0 mmol). A solution of CbzCl (3.5 mL, 24.5 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to the solution. The mixture was stirred at room temperature for 48 h and then was poured into HCl (1 M solution, 20 mL). The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 30 mL). The combined organic phases were dried with $Na_2SO_4$. After filtration, the filtrate was concentrated, and the residue was purified by flash chromatography (hexane/EtOAc, 3:1) to give (*R*)-**1c** (5.05 g, 95%) as an oil. The enantiomeric purity was determined by HPLC analysis. HPLC [CHIRALPAK IC (0.46 cm × 25 cm) from Daicel Chemical Ind., Ltd.; hexane/*i*PrOH, 98:2; 1.0 mL/min]: $t_R$ = 10.7 min [(*S*)-**1c**] and 11.6 min [(*R*)-**1c**] as 95% *ee*. $[\alpha]_D^{20}$ = +24.78 ($c$ = 1.67, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.39–7.34 (m, 5 H), 6.11 (dd, $J$ = 17.4, 10.9 Hz, 1 H), 5.46 (d, $J$ = 10.9 Hz, 1 H), 5.46 (d, $J$ = 17.4 Hz, 1 H), 5.16 (s, 2 H), 4.69 (d, $J$ = 11.7 Hz, 1 H), 4.42 (d, $J$ = 11.7 Hz, 1 H), 1.75 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 154.4, 134.8, 133.5, 128.9, 128.8, 128.6, 120.0, 89.2, 70.5, 70.4, 19.6 ppm. $C_{13}H_{15}NO_5$ (265.27): calcd. C 58.86, H 5.70, N 5.28; found C 58.75, H 5.77, N 5.26.

**(*R*,*E*)-Benzyl (2-Methyl-2-nitro-4-phenylbut-3-en-1-yl) Carbonate [(*R*)-2l]:** A solution of (*R*)-**1c** (55.0 mg, 0.206 mmol) in dry $CH_3CN$ (1 mL) was purged with nitrogen, and NaOAc (52.0 mg, 0.634 mmol), $Pd_2dba_3$ (10.0 mg, 0.011 mmol), and $PhN_2BF_4$ (80.0 mg, 0.417 mmol) were added. The resulting mixture was stirred at room temperature for 168 h. $PhN_2BF_4$ (40 mg) was added, and the mixture was stirred for an additional 24 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give (*R*)-**2l** (55.0 mg, 78%). The enantiomeric purity was determined by HPLC analysis. HPLC [CHIRALPAK OD-H (0.46 cm × 25 cm) from Daicel Chemical Ind., Ltd.; hexane/*i*PrOH, 95:5; 1.0 mL/min]: $t_R$ = 26.1 min [(*R*)-**2l**] and 39.2 min [(*S*)-**2l**] as 96% *ee*. $[\alpha]_D^{20}$ = +18.04 ($c$ = 2.3, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.46–7.29 (m, 10 H), 6.77 (d, $J$ = 16.3 Hz, 1 H), 6.42 (d, $J$ = 16.3 Hz, 1 H), 5.18 (s, 2 H), 4.80 (d, $J$ = 11.6 Hz, 1 H), 4.54 (d, $J$ = 11.6 Hz, 1 H), 1.88 (s, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 154.5, 135.0, 134.8, 134.6, 129.2, 128.9, 128.9, 128.8, 128.6, 127.1, 124.1, 89.3, 70.8, 70.4, 20.1 ppm. HRMS (ESI): calcd. for $C_{19}H_{20}NO_5$ $[M + H]^+$ 342.1341; found 342.1353.

**(*R*,*E*)-Benzyl {4-[4-(Heptyloxy)phenyl]-2-methyl-2-nitrobut-3-en-1-yl} Carbonate [(*R*)-2m]:** A solution of (*R*)-**1c** (200.0 mg, 0.754 mmol) in dry $CH_3CN$ (4 mL) was purged with nitrogen, and NaOAc (188.0 mg, 2.292 mmol), $Pd_2dba_3$ (35.0 mg, 0.038 mmol), and *p*-$C_7H_{15}OC_6H_4N_2BF_4$ (464.0 mg, 1.516 mmol) were added. The resulting mixture was stirred at room temperature for 48 h. The reaction mixture was concentrated, and the residue was subjected to flash chromatography (silica gel; hexane/EtOAc, 12:1 then 10:1 then 6:1) to give (*R*)-**2m** (216.0 mg, 63%). $[\alpha]_D^{20}$ = +80.21 ($c$ = 0.46, $CHCl_3$). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.41–7.35 (m, 5 H), 7.32 (d, $J$ = 8.3 Hz, 2 H), 6.86 (d, $J$ = 8.2 Hz, 2 H), 6.70 (d, $J$ = 16.0 Hz, 1 H), 6.24 (d, $J$ = 16.8 Hz, 1 H), 5.17 (s, 2 H), 4.80 (d, $J$ = 11.3 Hz, 1 H), 4.48 (d, $J$ = 11.0 Hz, 1 H), 3.96 (t, $J$ = 6.6 Hz, 2 H), 1.85 (s, 3 H), 1.82–1.75 (m, 2 H), 1.51–1.25 (m, 8 H), 0.90 (t, $J$ = 6.8 Hz, 3 H) ppm. $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ = 160.1, 154.5, 134.3, 128.9, 128.8, 128.6, 128.5, 121.5, 114.8, 89.3, 70.9, 70.3, 68.2, 31.8, 29.2, 29.1, 26.0, 22.6, 19.9, 14.1 ppm. HRMS (ESI): calcd. for $C_{26}H_{34}NO_6$ $[M + H]^+$ 456.2386; found 456.2404.

**(*R*)-2-Amino-4-[4-(heptyloxy)phenyl]-2-methylbutan-1-ol [(*R*)-5]:** (*R*)-**2m** (199 mg, 0.0437 mmol) was dissolved in MeOH (3 mL), and Pd-C (10%, 20 mg) was added. The mixture was placed in an autoclave and stirred at room temperature under a hydrogen atmosphere at 5 MPa for 50 h. After filtration, the filtrate was concentrated to give (*R*)-**5** (130 mg, 97%) as a colorless oil. $[\alpha]_D^{20}$ = –14.4 ($c$ = 0.32, MeOH). $^1$H NMR (500 MHz, $CD_3OD$): $\delta$ = 7.10 (d, $J$ = 8.5 Hz, 2 H), 6.80 (d, $J$ = 8.6 Hz, 2 H), 3.92 (t, $J$ = 6.4 Hz, 2 H), 3.39 (d, $J$ = 10.6 Hz, 1 H), 3.36 (d, $J$ = 10.9 Hz, 1 H), 2.57 (ddd, $J$ = 2.4, 7.9, 10.2 Hz, 2 H), 1.81–1.69 (m, 2 H), 1.69–1.58 (m, 2 H), 1.52–1.42 (m, 2 H), 1.42–1.27 (m, 6 H), 1.09 (s, 3 H), 0.91 (t, $J$ = 6.4 Hz, 3 H) ppm. $^{13}$C NMR (126 MHz, $CD_3OD$): $\delta$ = 157.4, 134.6, 128.9, 114.1, 69.5, 67.7, 52.4, 41.2, 31.7, 29.2, 29.0, 28.9, 25.9, 22.8, 22.4, 13.2 ppm. HRMS (FAB): calcd. for $C_{18}H_{32}NO_2$ $[M + H]^+$ 294.2433; found 294.2428.

**Supporting Information** (see footnote on the first page of this article): Spectroscopic charts for compounds **1**, **2**, **4**, and **5**.

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