Stille Cross-Couplings of Unactivated Secondary Alkyl Halides using *Monoorganotin Reagents*

David A. Powell, Toshihide Maki, and Gregory C. Fu*

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge,
Massachusetts 02139*

Supporting Information

I. General

The following chemicals were purchased and used as received: NiCl₂ (Alfa-Aesar or Strem), 2,2'-bipyridine (Alfa-Aesar or Aldrich), anhydrous KO*t*-Bu (Alfa-Aesar), anhydrous *t*-BuOH (Alfa-Aesar or Aldrich), anhydrous *i*-BuOH (Aldrich), SnCl₄ (Alfa-Aesar), PhSnCl₃ (Alfa-Aesar or Aldrich), 4-bromotoluene (Alfa-Aesar), 2-bromotoluene (Aldrich), 4-bromoanisole (Aldrich), 4-fluorobromobenzene (Alfa-Aesar), phenylacetylene (Alfa-Aesar), Bu₃SnH (Aldrich), AIBN (Aldrich), Mg turnings (Fisher), 4-bromochlorobenzene (Aldrich), Bu₃SnCl (Aldrich), TBSCl (Alfa-Aesar), imidazole (Avocado), MeMgBr (Aldrich), PPh₃ (Alfa-Aesar), bromine (Alfa-Aesar), *N*-bromosuccinimide (Aldrich), 2,3-dihydrofuran (Alfa-Aesar), TBAF (1.0 M in THF, Aldrich), 10-undecenal (Aldrich), cholesteryl chloroformate (Aldrich), pyrrole (Aldrich), 2,3-dihydrofuran (Aldrich), 1-bromo-6-chlorohexane (Alfa-Aesar), sodium iodide (Alfa-Aesar), 3-phenyl-2-propyn-1-ol (Alfa-Aesar), PtO₂ (Aldrich), allyl alcohol (Aldrich), *exo*-2-bromonorbornane (Aldrich), and 2-bromoadamantane (Aldrich).

The following chemicals were purchased and purified (by distillation and/or flash chromatography) prior to use: cyclohexyl bromide (Alfa-Aesar), cyclopentene (Fluka), 2-bromononane (Lancaster), cyclooctyl bromide (Alfa-Aesar), 1-bromobenzocyclobutane (Aldrich), cyclopentyl bromide (Alfa-Aesar), and benzyl 4-bromobutyl ether (Aldrich).

All experiments were conducted under an argon or nitrogen atmosphere in oven-dried glassware with magnetic stirring, unless otherwise specified.

II. Preparation of Substrates

A. Preparation of Aryltrichlorotin Reagents

General procedure. Magnesium turnings (1.1 equiv) and dry THF (1 mL/mmol of substrate) were added to a two-neck, round-bottom flask equipped with a reflux condenser. The aryl bromide (1.0 equiv) was added, and the reaction mixture was heated to 60 °C for 3 h to ensure complete formation of the Grignard reagent. The solution was then cooled to room temperature, and SnCl₄ (0.25 equiv) was added dropwise over 30 min. The resulting suspension was refluxed for 16 h and then cooled to room temperature. The reaction was quenched with saturated aqueous NH₄Cl (added dropwise), and the reaction mixture was poured into a separatory funnel that contained aqueous 0.5 M HCl. It was then extracted with EtOAc, and the combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure to yield the tetraarylstannane.

The tetraarylstannane (1.0 equiv) was placed in a round-bottom flask equipped with a reflux condenser. SnCl₄ (3.1 equiv) was added dropwise, and the resulting mixture was heated slowly to 150-200 °C for 4 h. It was then cooled to room temperature, and the reflux condenser was exchanged for a short-path distillation head. The dark mixture was distilled under reduced pressure to afford the aryltrichlorotin reagent, which was stored under argon.

Trichloro-4-tolylstannane [51353-34-5]. This compound was prepared from 4-bromotoluene (4.92 mL, 40.0 mmol). Purification by short-path distillation yielded 6.83 g (54% yield for the two steps) of a colorless liquid (bp 83-85 °C at 0.5 torr).

¹H NMR (500 MHz, CDCl₃) δ 7.60-7.53 (2H, m), 7.47-7.37 (2H, m), 2.45 (3H, s).

¹³C NMR (125 MHz, CDCl₃) δ 144.0, 133.8, 131.1, 124.7, 21.7.

¹¹⁹Sn {¹H} NMR (186 MHz, CDCl₃) δ -55.9.

Trichloro-2-tolylstannane [51729-82-9]. This compound was prepared from 2-bromotoluene (5.0 mL, 41.6 mmol). Purification by short-path distillation yielded 8.00 g (61% yield for the two steps) of a colorless liquid (bp 95-98 °C at 0.3 torr).

¹H NMR (500 MHz, CDCl₃) δ 7.66-7.64 (1H, m), 7.57-7.54 (1H, m), 7.45-7.43 (2H, m), 2.68 (3H, s).

¹³C NMR (125 MHz, CDCl₃) δ 143.0, 136.8, 134.3, 133.3, 131.5, 127.1, 21.7.

¹¹⁹Sn {¹H} NMR (186 MHz, CDCl₃) δ -60.4.

Trichloro-(4-fluorophenyl)stannane [17236-60-1]. This compound was prepared from 4-fluorobromobenzene (7.5 mL, 68.3 mmol). Purification by short-path distillation yielded 11.1 g (51% yield for the two steps) of a light-yellow liquid (bp 105-108 °C at 0.7 torr).

¹H NMR (500 MHz, CDCl₃) δ 7.71-7.68 (2H, m), 7.36-7.32 (2H, m).

^{13}C NMR (125 MHz, CDCl_3) δ 165.4 (d, $J_{\text{C-F}} = 254$ Hz), 136.2 (d, $J_{\text{C-F}} = 8.0$ Hz), 131.0 (d, $J_{\text{C-F}} = 4.0$ Hz), 117.8 (d, $J_{\text{C-F}} = 21.0$ Hz).

^{19}F (282 MHz, CDCl_3) δ -103.4 (m).

^{119}Sn $\{^1\text{H}\}$ NMR (186 MHz, CDCl_3) δ -57.4.

Trichloro-(4-methoxyphenyl)stannane [51729-79-4]. This compound was prepared from 4-bromoanisole (7.5 mL, 60.0 mmol). Purification by short-path distillation yielded 10.9 g (55% yield for the two steps) of a light-yellow liquid (bp 115-118 °C at 0.4 torr).

^1H NMR (500 MHz, CDCl_3) δ 7.59-7.55 (2H, m), 7.13-7.11 (2H, m), 3.88 (3H, s).

^{13}C NMR (125 MHz, CDCl_3) δ 163.2, 135.4, 126.3, 115.9, 55.5.

^{119}Sn $\{^1\text{H}\}$ NMR (186 MHz, CDCl_3) δ -54.7.

B. Preparation of Aryl- and Alkenyltributyltin Reagents

Tributyl-(4-chlorophenyl)stannane [17151-48-3]. A suspension of Mg turnings (0.99 g, 41.3 mmol) in THF (60 mL) was treated with 4-bromochlorobenzene (7.50 g, 39.3 mmol). The reaction mixture was heated to 50 °C for 3 h, at which time no Mg could be seen. The reaction mixture was then cooled to room temperature, and Bu₃SnCl (12.8 mL, 47.2 mmol) was added. The reaction mixture was refluxed for 4 h, and then cooled to room temperature and stirred overnight. The reaction was quenched by the dropwise addition of saturated aqueous NH₄Cl. The resulting mixture was poured into a separatory funnel that contained H₂O (100 mL) and then extracted with EtOAc (3 x 25 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered, and concentrated. Purification by column chromatography (eluant: 100% heptanes) furnished 10.5 g (67%) of the desired product as a colorless oil.

R_f = 0.90 (100% hexanes).

¹H NMR (500 MHz, CDCl₃) δ 7.44-7.42 (2H, m), 7.35-7.33 (2H, m), 1.61-1.55 (6H, m), 1.41-1.34 (6H, m), 1.13-1.09 (6H, m), 0.94 (9H, t, *J* = 7.5 Hz).

¹³C NMR (125 MHz, CDCl₃) δ 140.0, 137.6, 134.3, 128.1, 29.0, 27.4, 13.7, 9.6.

(*E*)-1-Phenyl-(2-tributylstannyl)ethene [66680-88-4]. This compound was prepared from phenylacetylene (1.65 mL, 15.0 mmol), Bu₃SnH (4.00 mL, 15.0 mmol), and 2,2'-azobisisobutyronitrile (AIBN; 100 mg, 0.60 mmol) according to a literature procedure.¹ The product was purified by column chromatography through a short plug of silica gel (eluant: hexanes), which furnished 4.25 g (74%) of a light-yellow oil (>95% pure by ¹H NMR).

R_f = 0.90 (100% hexanes).

¹H NMR (300 MHz, CDCl₃) δ 7.53-7.31 (5H, m), 6.99 (2H, s), 1.71-1.65 (6H, m), 1.50-1.43 (6H, m), 1.12-0.99 (15H, m).

¹³C NMR (75 MHz, CDCl₃) δ 146.0, 138.8, 129.4, 128.4, 127.5, 126.0, 29.1, 27.3, 13.7, 9.6.

C. Preparation of Alkyl Halides

Dodec-11-en-2-ol [21951-49-5]. A solution of 10-undecenal (5.00 mL, 24.1 mmol) in dry Et₂O (25 mL) was cooled to 0 °C in an ice bath. To the cooled solution was added MeMgBr (3.0 M in Et₂O; 16.0 mL, 48.2 mmol) over a 30-min period. The resulting solution was stirred at 0 °C for 2 h, the ice bath was removed, and the mixture was stirred for 12 h. The reaction was quenched by the dropwise addition of saturated aqueous NH₄Cl (20 mL) (caution: exothermic reaction), and the resulting suspension was poured into a separatory funnel that contained 1 M aqueous HCl (50 mL). The mixture was extracted with Et₂O (3 x 30 mL), and the combined organic layers were washed with brine (50 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography (eluant: 90:10 hexanes:EtOAc), which furnished 2.63 g (59%) of product as a colorless oil.

R_f = 0.45 (80:20 hexanes:EtOAc).

¹H NMR (300 MHz, CDCl₃) δ 5.84-5.71 (1H, m), 4.98-4.87 (2H, m), 3.75-3.71 (1H, m), 2.00 (2H, apparent quartet, *J* = 7.0 Hz), 1.89 (1H, br s), 1.34-1.15 (14H, m), 1.13 (3H, d, *J* = 6.5 Hz).

¹³C NMR (75 MHz, CDCl₃) δ 139.1, 114.0, 67.9, 43.9, 33.7, 30.1, 29.6, 29.5, 29.4, 29.0, 29.1, 28.8.

11-Bromododec-1-ene. A solution of PPh₃ (3.75 g, 14.3 mmol) in CH₂Cl₂ (20 mL) was cooled to 0 °C and treated with bromine (730 μL). This mixture was stirred for 1 h, and then a solution of dodec-11-en-2-ol (2.50 g, 13.6 mmol) in CH₂Cl₂ (5 mL) was added dropwise over 30 min. The resulting solution was stirred at 0 °C for 1 h, and then it was concentrated under reduced pressure to an oil, which was diluted with Et₂O (50 mL) and stirred vigorously to induce precipitation. The precipitate was removed by filtration through filter paper and washed with Et₂O. The resulting filtrate was poured into a separatory funnel containing a 5% w/w aqueous solution of Na₂SO₃. The organic layer was separated and washed with brine (25 mL), dried over MgSO₄, filtered, and concentrated. The crude reaction product was purified by column chromatography (eluant: 100% heptanes), which furnished 1.46 g (49%) of a colorless oil.

R_f = 0.60 (100% hexanes).

¹H NMR (300 MHz, CDCl₃) δ 5.83 (1H, ddt, *J* = 17.0, 10.0, 6.5 Hz), 4.98 (1H, apparent dq, *J* = 17.0, 1.5 Hz), 4.93 (1H, ddt, *J* = 10.0, 2.0, 1.0 Hz), 4.14 (1H, dqd, *J* = 8.0, 7.0, 5.5 Hz), 2.08-2.01 (2H, m), 1.89-1.70 (2H, m), 1.71 (3H, d, *J* = 6.5 Hz), 1.50-1.26 (12H, m).

¹³C NMR (75 MHz, CDCl₃) δ 139.1, 114.1, 51.9, 41.1, 33.8, 29.4, 29.3, 29.1, 28.9, 28.8, 27.7, 26.4.

IR (neat) 2926, 2855, 1641, 1464, 1378, 1226, 993, 909 cm⁻¹.

HRMS (EI) *m/e* [M-C₃H₆]⁺ calcd for C₉H₁₇Br: 204.0508, found 204.0519.

***trans*-(2-Bromocyclohexyloxy)-*tert*-butyldimethylsilane.** A solution of *trans*-2-bromocyclohexanol² (2.20 g, 12.3 mmol), TBSCl (2.83 g, 14.7 mmol), and imidazole (1.00 g, 14.7 mmol) in dry DMF (8 mL) was stirred at room temperature for 1 h. The mixture

was then poured into H₂O (50 mL) and extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over MgSO₄, filtered, and concentrated. The reaction mixture was purified by column chromatography (eluant: 100% hexanes), which furnished 3.13 g (87% yield) of the title compound as a clear oil.

R_f = 0.35 (100% hexanes).

¹H NMR (500 MHz, CDCl₃) δ 3.90 (1H, ddd, J = 9.5, 7.5, 4.0 Hz), 3.69 (1H, apparent td, J = 7.5, 4.0 Hz), 2.34-2.28 (1H, m), 2.05-2.00 (1H, m), 1.83-1.64 (3H, m), 1.41-1.28 (3H, m), 0.91 (9H, s), 0.13 (3H, s), 0.08 (3H, s).

¹³C NMR (125 MHz, CDCl₃) δ 74.6, 58.1, 34.7, 34.0, 25.8, 25.0, 23.0, 18.1, -4.5, -4.6.

IR (neat) 2936, 1472, 1372, 1257, 1114, 837, 776, 669 cm⁻¹.

HRMS (EI) m/e [M-C₄H₉]⁺ calcd for C₈H₁₆BrOSi: 235.0154, found 235.0171.

Cholesteryl iodide [2930-80-5]. This compound was prepared on a 5.0-mmol scale from cholesteryl chloroformate according to a literature procedure³. Recrystallization from acetone gave 3.83 g (70%) of a white crystalline solid.

Mp 106-107 °C (lit. mp 107-108 °C).³

¹H NMR (300 MHz, CDCl₃) δ 5.35-5.33 (1H, m), 4.05 (1H, apparent tt, J = 12.0, 4.5 Hz), 2.98-2.88 (1H, m), 2.68 (1H, ddd, J = 14.0, 4.5, 2.0 Hz), 2.32-2.18 (2H, m), 2.05-1.70 (4H, m), 1.57-0.88 (20H, m), 1.05 (3H, s), 0.91 (3H, d, J = 6.5 Hz), 0.88 (3H, d, J = 6.5 Hz), 0.86 (3H, d, J = 6.5 Hz), 0.68 (3H, s).

¹³C NMR (75 MHz, CDCl₃) δ 142.7, 121.7, 56.6, 56.1, 50.3, 46.4, 42.3, 41.9, 39.6, 39.5, 36.6, 36.4, 36.1, 35.8, 31.7, 31.6, 30.5, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 20.8, 19.2, 18.7, 11.8.

$[\alpha]_D^{22}$ -13.4 (c = 0.053 g/mL, CHCl₃).

1-(6-Chlorohexyl)-1H-pyrrole [144366-93-0].⁴ A mixture of pyrrole (1.25 mL, 18.0 mmol) and finely crushed KOH (1.31 g, 23.4 mmol) in dry DMSO (40 mL) was sonicated for 20 min and then cooled to 0 °C. 1-Bromo-6-chlorohexane (8.00 mL, 54.0 mmol) was added over 15 min, and the resulting mixture was stirred at room temperature for 4 h. The suspension was poured into a separatory funnel that contained H₂O (150 mL) and then extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by column chromatography (eluant: 100% hexanes → 98:2 hexanes:EtOAc) furnished 2.69 g (81%) of the title compound as a colorless oil.

R_f = 0.35 (99:1 hexanes:EtOAc).

¹H NMR (300 MHz, CDCl₃) δ 6.76-6.73 (2H, m), 6.26-6.23 (2H, m), 3.99-3.94 (2H, m), 3.64-3.58 (2H, m), 1.92-1.80 (4H, m), 1.60-1.50 (2H, m), 1.45-1.35 (2H, m).

¹³C NMR (75 MHz, CDCl₃) δ 120.2, 107.7, 49.2, 44.7, 32.2, 31.2, 26.2, 25.8.

1-(6-Iodoethyl)-1H-pyrrole. A suspension of 1-(6-chlorohexyl)-1H-pyrrole (2.69 g, 14.5 mmol) and sodium iodide (6.50 g, 43.6 mmol) in MeCN (80 mL) was refluxed for 20 h. The cooled reaction mixture was poured into a separatory funnel that contained H₂O (100 mL) and then extracted with Et₂O (3 x 30 mL). The combined organic layers were washed with saturated aqueous Na₂SO₃ (50 mL), brine (50 mL), dried over MgSO₄,

filtered, and concentrated under reduced pressure. Purification by column chromatography (eluant: 98:2 hexanes:EtOAc) furnished 2.13 g (53%) of the desired product as a slightly yellow oil.

$R_f = 0.35$ (99:1 hexanes:EtOAc).

^1H NMR (300 MHz, CDCl_3) δ 6.74 (2H, apparent t, $J = 2.0$ Hz), 6.23 (2H, apparent t, $J = 2.0$ Hz), 3.96 (2H, t, $J = 7.0$ Hz), 3.25 (2H, t, $J = 7.0$ Hz), 1.94-1.81 (4H, m), 1.56-1.49 (2H, m), 1.46-1.34 (2H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 120.2, 107.6, 49.2, 33.0, 31.1, 29.8, 25.4, 6.9.

IR (neat) 2931, 2856, 1500, 1450, 1282, 1196, 1089, 722, 617 cm^{-1} .

***trans*-1-Allyloxy-2-bromocyclopentane** [174619-43-3]. Freshly distilled cyclopentene (5.00 mL, 56.6 mmol) was added dropwise over a 20-min period to a suspension of *N*-bromosuccinimide (10.1 g, 56.6 mmol) in dry CH_2Cl_2 (100 mL). The resulting yellow suspension was stirred at room temperature for 1 h, and then allyl alcohol (7.70 mL, 113.2 mmol) was added dropwise over 2 h. The reaction mixture was stirred at room temperature for 4 h, during which time it became colorless. The solvent was then removed, and the crude reaction mixture was poured into a separatory funnel that contained H_2O (100 mL). The mixture was extracted with Et_2O (3 x 50 mL), and the combined organic layers were washed with brine (50 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. Purification by column chromatography (eluant: 100% hexanes) furnished 0.82 g (7%) of the title compound as a clear oil.

$R_f = 0.25$ (100% hexanes).

^1H NMR (300 MHz, CDCl_3) δ 5.88 (1H, ddt, $J = 17.0, 10.5, 5.5$ Hz), 5.27 (1H, apparent dq, $J = 17.0, 1.5$ Hz), 5.17 (1H, apparent dq, $J = 10.5, 1.5$ Hz), 4.26-4.24 (1H, m), 4.12-4.10 (1H, m), 4.02 (1H, ddt, $J = 13.0, 5.5, 1.5$ Hz), 3.99 (1H, ddt, $J = 13.0, 5.5, 1.5$ Hz), 2.34-2.26 (1H, m), 2.18-2.11 (1H, m), 2.03-1.97 (1H, m), 1.89-1.77 (2H, m), 1.68-1.62 (1H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 134.5, 116.9, 87.3, 70.3, 54.2, 34.7, 39.9, 21.7.

***trans*-2-Allyloxy-3-bromotetrahydrofuran** [143037-46-1]. This compound was prepared on a 42.0 mmol scale according to a literature procedure.⁵

$R_f = 0.40$ (95:5 hexanes: Et_2O).

^1H NMR (300 MHz, CDCl_3) δ 5.85 (1H, dddd, $J = 17.0, 10.0, 6.0, 5.0$ Hz), 5.27 (1H, ddt, $J = 17.0, 5.0, 1.5$ Hz), 5.23 (1H, s), 5.19-5.14 (1H, ddt, $J = 10.0, 3.5, 1.5$ Hz), 4.23-3.91 (5H, m), 2.69-2.57 (1H, m), 2.23-2.15 (1H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 133.9, 117.2, 107.8, 67.9, 66.6, 49.9, 33.8.

III. Stille Cross-Coupling Reactions of Alkyl Halides

Preparation of a stock solution of 1.0 M KO*t*-Bu in *t*-BuOH:*i*-BuOH (7:3). To a 200-mL round-bottom flask equipped with a reflux condenser was added 11.2 g (0.10 mol) of anhydrous KO*t*-Bu. Anhydrous *i*-BuOH (30 mL) and anhydrous *t*-BuOH (50 mL) were added via cannula, and the resulting suspension was heated to 60 °C for 3 h to ensure complete dissolution of the solids. The cooled, slightly yellow solution was transferred via cannula into an oven-dried bottle sealed with a septum. Anhydrous *t*-BuOH was added until the total volume of the solution was 100 mL.

Use of commercially available anhydrous 1.0 M KO*t*-Bu in *t*-BuOH (Aldrich) and 1.0 M KO*i*-Bu in *i*-BuOH (Aldrich) in a 7:3 ratio leads to similar yields in the cross-coupling protocol.

Note: It is important that the KO*t*-Bu and the solvents are anhydrous and handled/stored under nitrogen or argon.

General procedure for Stille cross-couplings (Table 2, Table 3, and eq 4). Into a 20-mL sample vial was added NiCl₂ (13 mg, 0.10 mmol) and 2,2'-bipyridine (23 mg, 0.15 mmol); these compounds were weighed in air, and no special handling precautions were employed. The vial was sealed with a septum screw-cap and purged under a steady stream of argon (nitrogen may also be used) for 20 min. A 1.0 M stock solution of KO*t*-Bu in *t*-BuOH:*i*-BuOH (7:3) (7.0 mL, 7.0 mmol of KO*t*-Bu) was added, followed by the aryltrichlorotin reagent (1.2 mmol) and the alkyl halide (1.0 mmol). The reaction mixture was heated in an oil bath to 60 °C for 12 h, with vigorous stirring under an argon atmosphere (the reaction mixture typically turns deep purple within 1 h of heating). Then, the cooled reaction mixture was poured into a separatory funnel that contained an aqueous 1 M HCl solution (50 mL), and the mixture was extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with brine (40 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting crude reaction mixture was purified by column chromatography.

Note: The reaction is air- and moisture-sensitive. The KO*t*-Bu solution and the tin reagent should be handled/stored under nitrogen or argon.

(1-Methyloctyl)benzene (Table 2, entry 1) [51770-89-9]. Solvent used for chromatography: 100% heptanes. Colorless oil. First run: 147 mg (72%) of product. Second run: 146 mg (72%) of product.

R_f = 0.80 (100% hexanes).

¹H NMR (300 MHz, CDCl₃) δ 7.36-7.31 (2H, m), 7.26-7.20 (3H, m), 2.72 (1H, apparent sextet, *J* = 7.0 Hz), 1.64-1.59 (2H, m), 1.30-1.23 (13H, m), 0.93 (3H, t, *J* = 6.5 Hz).

¹³C NMR (75 MHz, CDCl₃) δ 148.0, 128.2, 127.0, 125.7, 40.0, 38.5, 31.9, 29.7, 29.3, 27.7, 22.7, 22.3, 14.1.

2-Phenyladamantane (Table 2, entry 2) [19066-24-1]. Solvent used for chromatography: 100% heptanes. Colorless oil. First run: 160 mg (75%) of product. Second run: 152 mg (72%) of product.

R_f = 0.75 (100% hexanes).

^1H NMR (300 MHz, CDCl_3) δ 7.46-7.36 (4H, m), 7.27-7.22 (1H, m), 3.09 (1H, br s), 2.55 (2H, br s), 2.11-1.85 (10H, m), 1.66-1.61 (2H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 144.3, 128.1, 126.8, 125.1, 46.7, 39.1, 37.9, 31.9, 31.0, 28.0, 27.8.

7-*p*-Tolylbicyclo[4.2.0]octa-1,3,5-triene (Table 2, entry 3) [661476-70-6]. Solvent used for chromatography: 100% heptanes. Colorless oil. First run: 159 mg (82%) of product. Second run: 163 mg (84%) of product.

R_f = 0.35 (100% hexanes).

^1H NMR (300 MHz, CDCl_3) δ 7.42-7.24 (8H, m), 4.90 (1H, dd, J = 5.5, 2.5 Hz), 3.84 (1H, dd, J = 14.0, 5.5 Hz), 3.21 (1H, dd, J = 14.0, 2.5 Hz), 2.47 (3H, s).

^{13}C NMR (75 MHz, CDCl_3) δ 147.9, 144.1, 139.8, 135.9, 129.1, 127.5, 127.0, 126.8, 123.2, 122.6, 47.1, 40.0, 21.0.

1-Cyclohexyl-2-methylbenzene (Table 2, entry 4) [4501-35-3]. Solvent used for chromatography: 100% heptanes. Colorless oil. First run: 84 mg (48%) of product. Second run: 77 mg (45%) of product.

R_f = 0.60 (100% hexanes).

^1H NMR (300 MHz, CDCl_3) δ 7.28-7.09 (4H, m), 2.80-2.70 (1H, m), 2.38 (3H, s), 1.91-1.79 (5H, m), 1.54-1.38 (5H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 145.9, 135.1, 130.2, 126.1, 125.4, 125.3, 40.1, 33.6, 27.2, 26.3, 19.3.

(4-Fluorophenyl)cyclooctane (Table 2, entry 5). Solvent used for chromatography: 100% heptanes. Colorless oil. First run: 136 mg (66%) of product. Second run: 140 mg (68%) of product.

R_f = 0.20 (100% hexanes).

^1H NMR (300 MHz, CDCl_3) δ 7.19-7.14 (2H, m), 7.00-6.95 (2H, m), 2.82-2.75 (1H, m), 1.90-1.56 (14H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 161.3 (d, $J_{\text{C-F}}$ = 243 Hz), 145.9 (d, $J_{\text{C-F}}$ = 3.5 Hz), 128.1 (d, $J_{\text{C-F}}$ = 7.5 Hz), 114.8 (d, $J_{\text{C-F}}$ = 21.0 Hz), 43.9, 34.7, 26.9, 26.2, 25.9.

^{19}F NMR (282 MHz, CDCl_3) δ -118.7 (m).

IR (neat) 2921, 1604, 1509, 1468, 1446, 1229, 1158, 838, 803 cm^{-1} .

HRMS (EI) m/e (M^+) calcd for $\text{C}_{14}\text{H}_{19}\text{F}$: 206.1471, found 206.1466.

1-Methoxy-4-(1-methylundec-10-enyl)benzene (Table 2, entry 6). Solvent used for chromatography: 100% hexanes. Light-yellow oil. First run: 192 mg (70%) of product. Second run: 178 mg (65%) of product.

R_f = 0.20 (100% hexanes).

^1H NMR (300 MHz, CDCl_3) δ 7.27-7.12 (2H, m), 6.90-6.85 (2H, m), 5.86 (1H, ddt, J = 17.0, 10.0, 6.5 Hz), 5.07-4.95 (2H, m), 3.83 (3H, s), 2.73-2.61 (1H, apparent sextet, J = 7.0 Hz), 2.11-2.03 (2H, m), 1.60-1.53 (2H, m), 1.43-1.27 (12H, m), 1.24 (3H, d, J = 7.0 Hz).

^{13}C NMR (75 MHz, CDCl_3) δ 157.6, 140.0, 139.2, 127.7, 114.1, 113.6, 55.1, 39.0, 38.6, 33.8, 29.7, 29.5, 29.4, 29.1, 28.9, 27.7, 22.5.

IR (neat) 2926, 1612, 1513, 1247, 1178, 1040, 909, 828 cm^{-1} .

HRMS (ESI) m/e ($\text{M}+\text{H}^+$) calcd for $\text{C}_{19}\text{H}_{31}\text{O}$: 275.2375, found 275.2373.

***trans-tert*-Butyl-[2-(4-fluorophenyl)cyclohexyloxy]dimethylsilane (Table 2, entry 7).** GC-MS of the crude reaction mixture revealed a 96:4 mixture of stereoisomers, tentatively assigned as the *trans* and *cis* diastereomers. Solvent used for chromatography: 99:1 hexanes:EtOAc. Column chromatography was performed twice in order to remove impurities. A single diastereomer was isolated after column chromatography, and it was assigned as the *trans* isomer based on the magnitude of the $J_{\text{H1-H2}}$ coupling constant (10 Hz) in the ^1H NMR spectrum. First run: 151 mg (49%) of product. Second run: 142 mg (46%) of product. This compound was also characterized as the secondary alcohol.

R_f = 0.25 (100% hexanes).

^1H NMR (300 MHz, CDCl_3) δ 7.17-7.12 (2H, m), 6.98-6.93 (2H, m), 3.47 (1H, apparent td, J = 10.0, 4.5 Hz), 2.44 (1H, ddd, J = 12.5, 10.0, 3.3 Hz), 2.00-1.97 (1H, m), 1.86-1.72 (3H, m), 1.60-1.46 (1H, m), 1.42-1.26 (3H, m), 0.68 (9H, s), -0.17 (3H, s), -0.50 (3H, s).

^{13}C NMR (75 MHz, CDCl_3) δ 162.9 (d, $J_{\text{C-F}}$ = 243 Hz), 140.7 (d, $J_{\text{C-F}}$ = 3.0 Hz), 129.5 (d, $J_{\text{C-F}}$ = 7.5 Hz), 114.5 (d, $J_{\text{C-F}}$ = 21.0 Hz), 76.0, 52.2, 36.6, 32.8, 26.0, 25.6, 25.2, 17.8, -4.6, -5.6.

^{19}F NMR (282 MHz, CDCl_3) δ -118.3 (m).

IR (neat) 2931, 2857, 1606, 1583, 1511, 1250, 1228, 1098, 836, 775 cm^{-1} .

***trans*-2-(4-Fluorophenyl)cyclohexanol.** A solution of *trans-tert*-butyl-[2-(4-fluorophenyl)cyclohexyloxy]dimethylsilane (150 mg, 0.49 mmol) in dry THF (3 mL) was treated with TBAF (1.0 M in THF; 1.46 mL, 1.46 mmol). The reaction was stirred at room temperature for 4 h and then concentrated. Purification by column chromatography (eluant: 90:10 hexanes:EtOAc) furnished 83 mg (87%) of the secondary alcohol as a white solid.

Mp 70-71 $^{\circ}\text{C}$ (hexanes:EtOAc).

R_f = 0.20 (90:10 hexanes:EtOAc).

^1H NMR (300 MHz, CDCl_3) δ 7.23-7.18 (2H, m), 7.04-6.99 (2H, m), 3.58 (1H, apparent td, J = 10.0, 4.1 Hz), 2.40 (1H, ddd, J = 13.0, 10.0, 3.3 Hz), 2.11-2.07 (1H, m), 1.86-1.73 (3H, m), 1.50-1.34 (4H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 161.6 (d, $J_{\text{C-F}}$ = 243 Hz), 139.0 (d, $J_{\text{C-F}}$ = 3.0 Hz), 129.1 ($J_{\text{C-F}}$ = 7.5 Hz), 115.3 ($J_{\text{C-F}}$ = 21.0 Hz), 74.3, 52.3, 34.5, 33.4, 25.9, 24.9.

^{19}F NMR (282 MHz, CDCl_3) δ -116.8 (m).

IR (KBr) 3333, 2936, 2855, 1605, 1510, 1228, 1060, 825 cm^{-1} .

HRMS (ESI) m/e (M^+) calcd for $\text{C}_{12}\text{H}_{15}\text{FO}$: 194.1107, found 194.1099.

3*S*-(4-Methoxyphenyl)cholesterol (Table 3, entry 1) [78406-16-3]. Solvent used for chromatography: 99:1 hexanes:EtOAc. White crystalline solid. Diastereomeric purity: >97:3. First run: 265 mg (56%) of product. Second run: 254 mg (53%) of product. The stereochemistry of the product was determined to be 3*S* based on an X-ray crystal structure (X-ray quality crystals were obtained from hot acetone).

Mp 120-121 °C (hexanes:EtOAc).

R_f = 0.20 (99:1 hexanes:EtOAc).

^1H NMR (500 MHz, CDCl_3) δ 7.27-7.16 (2H, m), 6.87-6.85 (2H, m), 5.35 (1H, dd, J = 3.0, 2.0 Hz), 3.80 (3H, s), 2.48 (1H, apparent tt, J = 12.0, 4.0 Hz), 2.43-2.38 (1H, m), 2.19-2.16 (1H, m), 2.06-1.95 (3H, m), 1.87-1.83 (1H, m), 1.76-1.71 (2H, m), 1.64-1.46 (6H, m), 1.42-0.99 (14H, m), 1.09 (3H, s), 0.94 (3H, d, J = 6.5 Hz), 0.89 (3H, d, J = 6.5 Hz), 0.87 (3H, d, J = 6.5 Hz), 0.71 (3H, s).

^{13}C NMR (75 MHz, CDCl_3) δ 157.7, 143.0, 139.3, 127.5, 120.0, 113.7, 56.8, 56.2, 55.2, 50.5, 44.9, 42.3, 40.9, 39.9, 39.8, 39.5, 36.9, 36.2, 35.8, 31.9, 31.8, 30.2, 28.3, 28.0, 24.3, 23.8, 22.8, 22.6, 20.9, 19.6, 18.7, 11.9.

IR (KBr) 2931, 1612, 1511, 1461, 1365, 1240, 1040, 825, 801 cm^{-1} .

HRMS (EI) m/e (M^+) calcd for $\text{C}_{34}\text{H}_{52}\text{O}$: 476.4018, found 476.4023.

$[\alpha]_D^{22} = -0.42$ (c = 0.034 g/mL, CHCl_3)

(4-Benzyloxybutyl)benzene (Table 3, entry 2) [101747-16-4]. Solvent used for chromatography: 97:3 hexanes:EtOAc. Colorless oil. First run: 144 mg (60%) of product. Second run: 146 mg (61%) of product.

R_f = 0.45 (95:5 hexanes:EtOAc).

^1H NMR (300 MHz, CDCl_3) δ 7.41-7.31 (7H, m), 7.26-7.22 (3H, m), 4.55 (2H, s), 3.54 (2H, t, J = 6.0 Hz), 2.69 (2H, t, J = 7.5 Hz), 1.81-1.72 (4H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 142.4, 138.5, 128.4, 128.3, 128.2, 127.6, 127.4, 125.6, 72.8, 70.1, 35.7, 29.4, 28.0.

1-(6-Phenylhexyl)-1*H*-pyrrole (Table 3, entry 3). Solvent used for chromatography: 99:1 hexanes:Et₂O. Colorless oil. First run: 143 mg (63%) of product. Second run: 136 mg (60%) of product

R_f = 0.45 (99:1 hexanes:Et₂O).

^1H NMR (300 MHz, CDCl_3) δ 7.32-7.16 (5H, m), 6.66-6.65 (2H, m), 6.17-6.15 (2H, m), 3.87 (2H, t, J = 7.0 Hz), 2.61 (2H, t, J = 7.5 Hz), 1.82-1.73 (2H, m), 1.68-1.54 (2H, m), 1.39-1.28 (4H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 142.5, 128.3, 128.2, 125.6, 120.4, 107.7, 49.5, 35.8, 31.5, 31.3, 28.8, 26.6.

IR (neat) 2931, 2856, 1499, 1453, 1281, 1089, 1062, 722, 618 cm^{-1} .

HRMS (EI) m/e (M^+) calcd for $\text{C}_{16}\text{H}_{21}\text{N}$: 227.1674, found: 227.1674.

General procedure for eq 2 and eq 3. In a glovebox, the tin reagent (0.60 mmol) and SnCl_4 (70 μL , 0.60 mmol) were added to a 20-mL sample vial, and the resulting solution was stirred for 1 h (vinylstannane) or 6 h (arylstannane). To the neat reaction

mixture was added NiCl₂ (7.0 mg, 0.050 mmol), 2,2'-bipyridine (12 mg, 0.075 mmol), and a stock solution of KO*t*-Bu in *t*-BuOH:*i*-BuOH (7:3) (1.0 M; 3.5 mL, 3.5 mmol of KO*t*-Bu). The suspension was stirred at room temperature for 10 min, and then the alkyl halide (0.5 mmol) was added. The vial was sealed with a teflon-coated screw cap, taped, and heated to 60 °C for 20 h. Then, the cooled reaction mixture was diluted with a saturated aqueous solution of KF (15 mL) and filtered through a pad of celite on a sintered glass funnel, washing with Et₂O. The filtrate was poured into a separatory funnel that contained an aqueous 1 M HCl solution (50 mL), and the mixture was extracted with Et₂O (3 x 20 mL). The combined organic layers were washed with brine (40 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. The resulting crude reaction mixture was purified by column chromatography.

1-Chloro-4-cyclopentylbenzene [91335-74-9]. Solvent used for chromatography: 100% heptanes. Colorless oil. First run: 60 mg (66%) of product. Second run: 59 mg (66%) of product.

R_f = 0.75 (100% hexanes).

¹H NMR (300 MHz, CDCl₃) δ 7.28-7.25 (2H, m), 7.21-7.17 (2H, m), 2.98 (1H, tt, *J* = 9.5, 7.5 Hz), 2.13-2.03 (2H, m), 1.88-1.65 (4H, m), 1.63-1.50 (2H, m).

¹³C NMR (75 MHz, CDCl₃) δ 144.9, 131.2, 128.4, 128.2, 45.3, 34.6, 25.4.

HRMS (EI) *m/e* (*M*⁺) calcd for C₁₁H₁₃Cl: 180.0706, found 180.0707.

***exo*-(*E*)-2-Styrylbicyclo[2.2.1]heptane** [76217-04-4]. Solvent used for chromatography: 100% heptanes. Colorless oil. First run: 60 mg (61%) of product. Second run: 61 mg (62%) of product. ¹H NMR analysis revealed that the (*E*)-alkene was formed in a 98:2 ratio. The stereochemistry at the 2 position was deduced through conversion to the known bicyclo[2.2.1]heptane-2-carboxylic acid⁶ through oxidative cleavage of the alkene with KMnO₄ fused on silica gel.⁷ A sample of commercially available bicyclo[2.2.1]heptane-2-carboxylic acid (*endo:exo* = 67:33, as determined by ¹H NMR analysis) did not isomerize when subjected to the oxidative conditions described above.

R_f = 0.65 (100% hexanes).

¹H NMR (300 MHz, CDCl₃) δ 7.45-7.34 (4H, m), 7.30-7.24 (1H, m), 6.40 (1H, d, *J* = 16.0 Hz), 6.22 (1H, dd, *J* = 16.0, 8.0 Hz), 2.40-2.33 (2H, m), 2.25-2.22 (1H, m), 1.70-1.24 (8H, m).

¹³C NMR (75 MHz, CDCl₃) δ 137.9, 136.3, 128.4, 127.2, 126.6, 125.9, 45.4, 42.7, 37.9, 36.6, 35.8, 29.7, 29.0.

IR (neat) 3025, 2959, 2869, 1598, 1497, 1449, 1310, 963, 743, 692 cm⁻¹.

HRMS (EI) *m/e* (*M*⁺) calcd for C₁₅H₁₈: 198.1409, found: 198.1403.

3-Benzylhexahydrocyclopenta[*b*]furan (3; eq 4). GC analysis of the crude reaction mixture revealed a 68:32 mixture of diastereomers. These diastereomers were difficult to separate by column chromatography and were isolated as a mixture. Solvent used for chromatography: 95:5 hexanes:Et₂O. Clear oil. First run: 131 mg (65%) of product.

Second run: 137 mg (68%) of product. The diastereomers were separated by preparative HPLC (Alltech Econosphere 10 μ silica gel column, 250 mm x 22 mm, eluted with 95:5 hexanes:Et₂O at a flow rate of 10 mL/min, observing at 210 nm).

(3*R, 3*aS**, 6*aR**)-3-Benzylhexahydrocyclopenta[*b*]furan (major diastereomer).**

R_f = 0.15 (95:5 hexanes:Et₂O).

¹H NMR (500 MHz, CDCl₃) δ 7.31-7.27 (2H, m), 7.22-7.19 (3H, m), 4.52 (1H, apparent td, J = 6.0, 2.0 Hz), 3.82 (1H, dd, J = 8.5, 7.0 Hz), 3.46 (1H, dd, J = 10.0, 8.5 Hz), 2.77-2.72 (1H, m), 2.68-2.62 (2H, m), 2.54-2.49 (1H, m), 1.83-1.51 (6H, m).

¹³C NMR (75 MHz, CDCl₃) δ 141.0, 128.5, 128.4, 125.9, 86.1, 71.9, 46.4, 44.9, 34.6, 34.1, 26.0, 25.4.

IR (neat) 3027, 2954, 1603, 1496, 1453, 1150, 1041, 752, 700 cm⁻¹.

HRMS (EI) m/e (M^+) calcd for C₁₄H₁₈O: 202.1358, found: 202.1348.

(3*R, 3*aR**, 6*aR**)-3-Benzylhexahydrocyclopenta[*b*]furan (minor diastereomer).**

R_f = 0.15 (95:5 hexanes:Et₂O).

¹H NMR (500 MHz, CDCl₃) δ 7.31-7.27 (2H, m), 7.22-7.17 (3H, m), 4.49-4.47 (1H, m), 3.85 (1H, dd, J = 8.5, 6.5 Hz), 3.33 (1H, apparent t, J = 8.5 Hz), 2.75 (1H, dd, J = 13.5, 7.0 Hz), 2.67 (1H, dd, J = 13.5, 8.0 Hz), 2.34-2.30 (1H, m), 2.10-2.03 (1H, m), 1.81-1.69 (1H, m), 1.59-1.48 (4H, m), 1.35-1.33 (1H, m).

¹³C NMR (75 MHz, CDCl₃) δ 140.7, 128.6, 128.4, 126.0, 85.1, 73.1, 49.4, 49.1, 39.0, 34.1, 32.2, 23.9.

IR (neat) 3026, 2932, 1604, 1496, 1453, 1205, 1049, 745, 700 cm⁻¹.

HRMS (EI) m/e (M^+) calcd for C₁₄H₁₈O: 202.1358, found: 202.1352.

Determination of the relative stereochemistry via independent synthesis.

[3-(2-Bromocyclopentyloxy)prop-1-ynyl]benzene. *N*-Bromosuccinimide was added to a 250-mL round-bottom flask (10.1 g, 56.8 mmol) that contained a solution of freshly distilled cyclopentene (5.02 mL, 56.8 mmol) in CH₂Cl₂ (100 mL). 3-Phenyl-2-propyn-1-ol (4.64 mL, 37.9 mmol) was added dropwise via syringe pump to this suspension over a 4-h period. The reaction mixture was stirred at room temperature for an additional 12 h, and then the opaque yellow suspension was concentrated under reduced pressure.

The residue was taken up in Et₂O (50 mL) and poured into a 250-mL separatory funnel that contained H₂O (100 mL). The aqueous layer was extracted with Et₂O (3 x 30 mL), and the combined organic layers were washed with brine (50 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure. Purification by column chromatography (eluant: 99:1 hexanes:Et₂O) furnished 1.96 g (19%) of the product as a light-yellow oil.

R_f = 0.15 (hexanes).

¹H NMR (300 MHz, CDCl₃) δ 7.50-7.47 (2H, m), 7.36-7.32 (3H, m), 4.43 (2H, s), 4.40-4.34 (2H, m), 2.41-2.20 (2H, m), 2.10-2.00 (1H, m), 1.92-1.71 (3H, m).

¹³C NMR (75 MHz, CDCl₃) δ 131.7, 128.5, 128.2, 122.4, 87.4, 86.2, 84.9, 57.6, 54.0, 34.7, 29.9, 21.7.

IR (neat) 2970, 2190, 1662, 1490, 1351, 1078, 757, 691 cm⁻¹.

HRMS (ESI) m/e (M+Na⁺) calcd for C₁₄H₁₅BrONa: 301.0204, found: 301.0208.

3-Benzylhexahydrocyclopenta[*b*]furan (3). A solution of [3-(2-bromocyclopentyloxy)prop-1-ynyl]benzene (1.00 g, 3.58 mmol), 2,2'-azobisisobutyronitrile (AIBN; 20 mg, 0.18 mmol), and Bu₃SnH (1.05 mL, 3.94 mmol) in benzene (36 mL) was heated to reflux for 12 h. The cooled reaction mixture was concentrated under reduced pressure and purified by column chromatography (eluant: 99:1 hexanes:Et₂O), which furnished 582 mg (81%) of a clear oil that was used directly in the next step.

A suspension of the above compound (100 mg, 0.50 mmol) and PtO₂ (11 mg, 0.050 mmol) in EtOH (4 mL) was stirred at room temperature in a high-pressure hydrogenation apparatus under a pressure of 1000 psi of hydrogen for 4 days. The reaction mixture was then filtered through a pad of celite on a sintered glass funnel (Et₂O washings), and the filtrate was concentrated under reduced pressure. GC analysis revealed an 82:18 ratio of diastereomers. The reaction mixture was purified by column chromatography (eluant: 90:10 hexanes:Et₂O), which furnished 90 mg (90%) of a clear oil. The major diastereomer is identical (GC and ¹H NMR) with the major diastereomer **3** from the cyclization/cross-coupling reaction illustrated in eq 4. Based on related hydrogenations of methylenhexahydrofuro[2,3-*b*]furan⁸ and the expected delivery of hydrogen from the less hindered convex face, we have assigned the major diastereomer as the 3*R**,3*aS**,6*aR** (*endo*) isomer.

(3*R, 3*aS**,6*aR**)-3-Benzylhexahydrofuro[2,3-*b*]furan (4; eq 4).** GC analysis of the crude reaction mixture revealed a 96:4 mixture of diastereomers. Solvent used for chromatography: 90:10 hexanes:Et₂O. Slightly yellow oil. First run: 116 mg (57%) of product. Second run: 117 mg (57%) of product.

R_f = 0.07 (90:10 hexanes:Et₂O).

¹H NMR (500 MHz, C₆D₆) δ 7.13-7.10 (2H, m), 7.06-7.03 (1H, m), 6.87-6.85 (2H, m), 5.70 (1H, d, J = 5.0 Hz), 3.68-3.64 (2H, m), 3.57-3.53 (1H, m), 3.33-3.27 (1H, m), 2.22-2.12 (2H, m), 2.19 (2H, d, J = 2.5 Hz), 1.42 (1H, ddt, J = 12.5, 7.0, 5.0 Hz), 1.24 (1H, ddt, J = 12.5, 10.0, 7.5 Hz).

^{13}C NMR (75 MHz, CDCl_3) δ 139.9, 128.5, 128.2, 126.2, 109.7, 72.1, 69.0, 45.4, 43.7, 33.7, 25.0.

IR (neat) 3510, 3027, 2948, 1603, 1496, 1454, 1110, 1014, 942, 701 cm^{-1} .

HRMS (EI) m/e (M^+) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: 204.1150, found: 204.1152.

Determination of the relative stereochemistry via independent synthesis.

3-Bromo-2-(3-phenylprop-2-ynyloxy)tetrahydrofuran. Into an oven-dried round-bottom flask was added *N*-bromosuccinimide (3.60 g, 20.4 mmol) and dry CH_2Cl_2 (100 mL). The resulting suspension was cooled to -20 to $-25\text{ }^\circ\text{C}$, and 2,3-dihydrofuran (1.54 mL, 20.4 mmol) was added dropwise over a 20-min period. This mixture was stirred for 20 min, and then 3-phenyl-2-propyn-1-ol (4.50 mL, 36.8 mmol) was added dropwise over a 30-min period. The reaction mixture was warmed to room temperature over a 6-h period, and then the reaction mixture was concentrated under reduced pressure. The resulting oil was taken up in Et_2O (30 mL) and poured into a separatory funnel that contained H_2O (150 mL). The aqueous layer was extracted with Et_2O (3 x 30 mL), and the combined organic layers were washed with brine (50 mL), dried over MgSO_4 , filtered, and concentrated under reduced pressure. Purification by column chromatography (eluant: 90:10 hexanes: Et_2O) furnished 2.83 g (49%) of the desired product as a clear oil.

R_f = 0.50 (80:20 hexanes: Et_2O).

^1H NMR (300 MHz, CDCl_3) δ 7.49-7.46 (2H, m), 7.34-7.31 (3H, m), 5.49 (1H, s), 4.45 (2H, d, J = 4.0 Hz), 4.32 (1H, d, J = 6.0 Hz), 4.21 (1H, td, J = 8.5, 7.5 Hz), 4.10 (1H, td, J = 8.5, 3.0 Hz), 2.74-2.61 (1H, m), 2.27-2.19 (1H, m).

^{13}C NMR (75 MHz, CDCl_3) δ 131.7, 128.4, 128.2, 122.2, 106.8, 86.2, 84.2, 66.9, 54.6, 49.8, 33.6.

IR (neat) 2899, 2240, 1599, 1490, 1442, 1335, 1198, 1027, 757, 691 cm^{-1} .

HRMS (EI) m/e (M^+) calcd for $\text{C}_{13}\text{H}_{13}\text{BrO}_2$: 280.0099, found: 280.0093.

3-Benzylhexahydrofuro[2,3-*b*]furan. A solution of 3-bromo-2-(3-phenylprop-2-ynyloxy)tetrahydrofuran (1.27 g, 4.50 mmol), 2,2'-azobisisobutyronitrile (AIBN; 37 mg, 0.23 mmol), and Bu_3SnH (1.33 mL, 5.00 mmol) in benzene (50 mL) was heated to $80\text{ }^\circ\text{C}$

for 8 h. The cooled reaction mixture was concentrated under reduced pressure and purified by column chromatography (eluant: 80:20 hexanes:Et₂O), which furnished 563 mg (62%) of a clear oil that was used directly in the next step.

A suspension of the above compound (200 mg, 1.00 mmol) and PtO₂ (25 mg, 0.10 mmol) in EtOH (5 mL) was stirred at room temperature under a hydrogen atmosphere (balloon) for 16 h. The reaction mixture was filtered through a pad of celite on a sintered glass funnel (Et₂O washings), and then the filtrate was concentrated under reduced pressure. GC analysis revealed a 73:27 ratio of diastereomers. The reaction mixture was purified by column chromatography (eluant: 80:20 hexanes:Et₂O), which furnished 184 mg (90%) of a clear oil. The major diastereomer is identical (GC and ¹H NMR) with the major diastereomer **4** from the cyclization/cross-coupling reaction illustrated in eq 4. Based on related hydrogenations of methylenhexahydrofuro[2,3-*b*]furan⁸ and the expected delivery of hydrogen from the less hindered convex face, we have assigned the major diastereomer as the 3*R**,3*aS**,6*aR** (*endo*) compound.

Ligand effect on the nickel-catalyzed reaction of alkyl bromide 1 (eq 4; determined by GC analysis):

<u>Entry</u>	<u>Ligand</u>	<u>Yield (%)</u>	<u>d.r.</u>
1	2,2'-bipyridine	60	67:33
2	bathophenanthroline	52	67:33
3	4,4'-di- <i>t</i> -butyl-2,2'-bipyridine	61	67:33
4	4,4'-diphenyl-2,2'-bipyridine	53	67:33
5	4,4'-dimethoxy-2,2'-bipyridine	57	67:33

Ligand effect on the nickel-catalyzed reaction of alkyl bromide 2 (eq 4; determined by GC analysis):

<u>Entry</u>	<u>Ligand</u>	<u>Yield (%)</u>	<u>d.r.</u>
1	2,2'-bipyridine	53	96:4
2	bathophenanthroline	21	96:4
3	4,4'-di- <i>t</i> -butyl-2,2'-bipyridine	40	96:4
4	4,4'-diphenyl-2,2'-bipyridine	21	96:4
5	4,4'-dimethoxy-2,2'-bipyridine	43	96:4

IV. Crystal Structure of the Product of Table 3, Entry 1.

Table 1. Crystal data and structure refinement for 04134dpm.

Identification code	04134dpm	
Empirical formula	C ₃₄ H ₅₂ O	
Formula weight	476.76	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 16.275(3) Å	$\alpha = 90^\circ$.
	b = 9.4620(19) Å	$\beta = 95.45(3)^\circ$.
	c = 18.925(4) Å	$\gamma = 90^\circ$.
Volume	2901.2(10) Å ³	
Z	4	
Density (calculated)	1.092 Mg/m ³	
Absorption coefficient	0.063 mm ⁻¹	
F(000)	1056	
Crystal size	0.31 x 0.38 x 0.1 mm ³	
Theta range for data collection	1.08 to 28.29°.	
Index ranges	-21 ≤ h ≤ 19, -12 ≤ k ≤ 12, -25 ≤ l ≤ 16	
Reflections collected	21748	
Independent reflections	13996 [R(int) = 0.0908]	
Completeness to theta = 28.29°	99.8 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	13996 / 134 / 659	
Goodness-of-fit on F ²	0.802	
Final R indices [I > 2σ(I)]	R1 = 0.0625, wR2 = 0.1298	
R indices (all data)	R1 = 0.1128, wR2 = 0.1508	
Absolute structure parameter	-0.2(18)	
Largest diff. peak and hole	0.200 and -0.212 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 04134dpm. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	6156(1)	5158(2)	2812(1)	57(1)
C(100)	6592(2)	3884(4)	2955(2)	63(1)
C(101)	5357(2)	5054(3)	2510(1)	43(1)
C(102)	4974(2)	3799(3)	2307(2)	50(1)
C(103)	4930(2)	6297(3)	2405(2)	57(1)
C(104)	4118(2)	6292(3)	2112(2)	58(1)
C(105)	4156(2)	3818(3)	2011(2)	52(1)
C(106)	3709(2)	5063(3)	1908(1)	44(1)
C(107)	2806(2)	5025(3)	1640(1)	45(1)
C(108)	2244(2)	5112(3)	2251(1)	48(1)
C(109)	2541(2)	6185(3)	1101(2)	52(1)
C(110)	1639(2)	6076(3)	832(1)	43(1)
C(111)	1019(2)	5994(3)	1388(1)	39(1)
C(112)	1338(2)	4930(3)	1973(1)	45(1)
C(113)	1411(2)	6048(3)	136(2)	50(1)
C(114)	548(2)	5952(3)	-199(1)	48(1)
C(115)	-97(2)	6215(3)	326(1)	39(1)
C(116)	170(2)	5475(3)	1039(1)	37(1)
C(117)	-528(2)	5546(3)	1540(1)	46(1)
C(118)	-1364(2)	5020(3)	1202(1)	46(1)
C(119)	-1636(2)	5832(3)	513(1)	41(1)
C(120)	-934(2)	5660(3)	28(1)	40(1)
C(121)	-1303(2)	6205(3)	-690(1)	52(1)
C(122)	-2207(2)	5695(4)	-735(2)	56(1)
C(123)	-2362(2)	5175(3)	26(1)	47(1)
C(124)	953(2)	7474(3)	1724(2)	52(1)
C(125)	-1810(2)	7389(3)	668(2)	56(1)
C(126)	-3264(2)	5443(4)	179(2)	57(1)
C(127)	-3439(2)	5011(5)	931(2)	81(1)
C(128)	-3855(2)	4666(4)	-378(2)	67(1)

C(129)	-4745(2)	5077(6)	-427(2)	98(1)
C(130)	-5251(2)	4474(4)	-1081(2)	75(1)
C(131)	-6173(4)	4544(8)	-1136(4)	65(2)
C(132)	-6563(10)	3980(20)	-1838(7)	85(4)
C(133)	-6427(6)	6086(9)	-1028(6)	93(3)
C(31B)	-6042(6)	5261(16)	-1315(6)	84(3)
C(32B)	-6500(12)	4460(30)	-1921(10)	98(8)
C(33B)	-6570(8)	5350(20)	-679(8)	145(7)
O(2)	-1565(1)	5801(3)	3658(1)	64(1)
C(200)	-1842(2)	6792(4)	3118(2)	61(1)
C(201)	-739(2)	5855(4)	3906(2)	49(1)
C(202)	-185(2)	6836(3)	3699(2)	54(1)
C(203)	-472(2)	4843(4)	4395(2)	63(1)
C(204)	634(2)	6793(3)	3989(2)	52(1)
C(205)	348(2)	4800(4)	4675(2)	58(1)
C(206)	920(2)	5784(3)	4476(1)	43(1)
C(207)	1824(2)	5770(3)	4766(1)	40(1)
C(208)	2322(2)	4593(3)	4444(1)	41(1)
C(209)	1969(1)	5641(3)	5577(1)	43(1)
C(210)	3231(2)	4688(3)	4680(1)	37(1)
C(211)	3469(2)	4758(3)	5485(1)	35(1)
C(212)	2885(1)	5802(3)	5826(1)	39(1)
C(213)	3786(2)	4720(3)	4208(1)	40(1)
C(214)	4697(2)	4818(3)	4373(1)	41(1)
C(215)	4977(2)	4585(3)	5160(1)	35(1)
C(216)	4376(1)	5301(3)	5629(1)	35(1)
C(217)	4712(1)	5239(3)	6418(1)	40(1)
C(218)	5604(1)	5764(3)	6573(1)	39(1)
C(219)	6196(1)	4986(3)	6126(1)	36(1)
C(220)	5844(1)	5159(3)	5343(1)	36(1)
C(221)	6538(2)	4647(3)	4918(1)	43(1)
C(222)	7334(1)	5091(3)	5368(1)	41(1)
C(223)	7071(1)	5643(3)	6088(1)	36(1)
C(224)	3370(2)	3279(3)	5802(2)	45(1)
C(225)	6285(2)	3422(3)	6343(2)	49(1)
C(226)	7740(2)	5402(3)	6704(1)	41(1)

C(227)	7457(2)	5858(4)	7418(2)	63(1)
C(228)	8544(2)	6171(3)	6573(2)	45(1)
C(229)	9266(2)	5896(3)	7124(2)	51(1)
C(230)	10069(2)	6595(3)	6967(2)	50(1)
C(231)	10732(2)	6622(3)	7591(2)	50(1)
C(232)	10954(2)	5178(4)	7882(2)	70(1)
C(233)	11494(2)	7419(4)	7403(2)	61(1)

Table 3. Bond lengths [Å] and angles [°] for 04134dpm.

O(1)-C(101)	1.374(3)
O(1)-C(100)	1.412(4)
C(101)-C(103)	1.371(4)
C(101)-C(102)	1.378(4)
C(102)-C(105)	1.395(4)
C(103)-C(104)	1.383(4)
C(104)-C(106)	1.377(4)
C(105)-C(106)	1.388(4)
C(106)-C(107)	1.509(4)
C(107)-C(109)	1.531(4)
C(107)-C(108)	1.542(4)
C(108)-C(112)	1.528(3)
C(109)-C(110)	1.511(4)
C(110)-C(113)	1.332(4)
C(110)-C(111)	1.527(4)
C(111)-C(124)	1.547(4)
C(111)-C(116)	1.554(3)
C(111)-C(112)	1.549(4)
C(113)-C(114)	1.489(4)
C(114)-C(115)	1.534(4)
C(115)-C(120)	1.517(3)
C(115)-C(116)	1.545(3)
C(116)-C(117)	1.549(3)
C(117)-C(118)	1.530(4)
C(118)-C(119)	1.542(4)
C(119)-C(125)	1.534(4)
C(119)-C(120)	1.541(3)
C(119)-C(123)	1.557(4)
C(120)-C(121)	1.522(3)
C(121)-C(122)	1.543(4)
C(122)-C(123)	1.566(4)
C(123)-C(126)	1.543(4)
C(126)-C(127)	1.533(4)
C(126)-C(128)	1.545(4)

C(128)-C(129)	1.495(4)
C(129)-C(130)	1.530(5)
C(130)-C(131)	1.497(7)
C(130)-C(31B)	1.517(10)
C(131)-C(132)	1.516(9)
C(131)-C(133)	1.535(9)
C(31B)-C(32B)	1.510(12)
C(31B)-C(33B)	1.546(13)
O(2)-C(201)	1.381(3)
O(2)-C(200)	1.428(4)
C(201)-C(203)	1.372(4)
C(201)-C(202)	1.377(4)
C(202)-C(204)	1.394(4)
C(203)-C(205)	1.389(4)
C(204)-C(206)	1.377(4)
C(205)-C(206)	1.393(4)
C(206)-C(207)	1.521(3)
C(207)-C(209)	1.535(4)
C(207)-C(208)	1.536(4)
C(208)-C(210)	1.508(3)
C(209)-C(212)	1.528(3)
C(210)-C(213)	1.329(3)
C(210)-C(211)	1.537(3)
C(211)-C(224)	1.538(4)
C(211)-C(212)	1.554(3)
C(211)-C(216)	1.562(3)
C(213)-C(214)	1.489(3)
C(214)-C(215)	1.532(3)
C(215)-C(220)	1.521(3)
C(215)-C(216)	1.539(3)
C(216)-C(217)	1.541(3)
C(217)-C(218)	1.535(3)
C(218)-C(219)	1.529(4)
C(219)-C(225)	1.539(4)
C(219)-C(220)	1.546(3)
C(219)-C(223)	1.561(3)

C(220)-C(221)	1.526(3)
C(221)-C(222)	1.540(3)
C(222)-C(223)	1.557(4)
C(223)-C(226)	1.535(3)
C(226)-C(227)	1.530(4)
C(226)-C(228)	1.538(3)
C(228)-C(229)	1.518(3)
C(229)-C(230)	1.518(3)
C(230)-C(231)	1.523(4)
C(231)-C(232)	1.504(4)
C(231)-C(233)	1.523(4)

C(101)-O(1)-C(100)	117.2(2)
O(1)-C(101)-C(103)	116.5(3)
O(1)-C(101)-C(102)	124.2(3)
C(103)-C(101)-C(102)	119.3(2)
C(101)-C(102)-C(105)	119.3(3)
C(101)-C(103)-C(104)	120.4(3)
C(106)-C(104)-C(103)	122.2(3)
C(106)-C(105)-C(102)	122.3(3)
C(104)-C(106)-C(105)	116.4(2)
C(104)-C(106)-C(107)	122.9(3)
C(105)-C(106)-C(107)	120.5(3)
C(106)-C(107)-C(109)	114.3(2)
C(106)-C(107)-C(108)	112.0(2)
C(109)-C(107)-C(108)	108.2(2)
C(112)-C(108)-C(107)	110.9(2)
C(110)-C(109)-C(107)	112.3(2)
C(113)-C(110)-C(109)	120.3(2)
C(113)-C(110)-C(111)	122.7(2)
C(109)-C(110)-C(111)	117.0(2)
C(110)-C(111)-C(124)	108.3(2)
C(110)-C(111)-C(116)	110.0(2)
C(124)-C(111)-C(116)	111.5(2)
C(110)-C(111)-C(112)	109.2(2)
C(124)-C(111)-C(112)	109.0(2)

C(116)-C(111)-C(112)108.8(2)
C(108)-C(112)-C(111)114.8(2)
C(110)-C(113)-C(114)125.8(3)
C(113)-C(114)-C(115)112.9(2)
C(120)-C(115)-C(114)110.4(2)
C(120)-C(115)-C(116)109.6(2)
C(114)-C(115)-C(116)109.8(2)
C(117)-C(116)-C(115)110.7(2)
C(117)-C(116)-C(111)113.6(2)
C(115)-C(116)-C(111)113.2(2)
C(118)-C(117)-C(116)113.9(2)
C(117)-C(118)-C(119)111.4(2)
C(125)-C(119)-C(120)112.1(2)
C(125)-C(119)-C(118)111.1(2)
C(120)-C(119)-C(118)106.3(2)
C(125)-C(119)-C(123)110.7(2)
C(120)-C(119)-C(123)99.8(2)
C(118)-C(119)-C(123)116.2(2)
C(121)-C(120)-C(115)118.6(2)
C(121)-C(120)-C(119)104.1(2)
C(115)-C(120)-C(119)115.6(2)
C(120)-C(121)-C(122)103.7(2)
C(121)-C(122)-C(123)106.4(2)
C(126)-C(123)-C(122)111.1(2)
C(126)-C(123)-C(119)120.4(2)
C(122)-C(123)-C(119)103.8(2)
C(127)-C(126)-C(123)113.2(2)
C(127)-C(126)-C(128)110.4(3)
C(123)-C(126)-C(128)109.6(3)
C(129)-C(128)-C(126)117.1(3)
C(128)-C(129)-C(130)113.3(3)
C(131)-C(130)-C(31B)30.6(4)
C(131)-C(130)-C(129)119.9(4)
C(31B)-C(130)-C(129)115.5(6)
C(130)-C(131)-C(132)112.2(9)
C(130)-C(131)-C(133)108.3(7)

C(132)-C(131)-C(133)111.0(9)
 C(32B)-C(31B)-C(130)108.7(11)
 C(32B)-C(31B)-C(33B)110.3(12)
 C(130)-C(31B)-C(33B)108.5(11)
 C(201)-O(2)-C(200) 116.8(2)
 C(203)-C(201)-C(202)119.2(3)
 C(203)-C(201)-O(2) 116.0(3)
 C(202)-C(201)-O(2) 124.7(3)
 C(201)-C(202)-C(204)119.7(3)
 C(201)-C(203)-C(205)120.6(3)
 C(206)-C(204)-C(202)122.3(3)
 C(206)-C(205)-C(203)121.3(3)
 C(204)-C(206)-C(205)116.8(3)
 C(204)-C(206)-C(207)120.1(2)
 C(205)-C(206)-C(207)123.1(3)
 C(206)-C(207)-C(209)114.3(2)
 C(206)-C(207)-C(208)113.0(2)
 C(209)-C(207)-C(208)107.6(2)
 C(210)-C(208)-C(207)112.3(2)
 C(212)-C(209)-C(207)110.7(2)
 C(213)-C(210)-C(208)120.9(2)
 C(213)-C(210)-C(211)122.8(2)
 C(208)-C(210)-C(211)116.3(2)
 C(210)-C(211)-C(224)108.8(2)
 C(210)-C(211)-C(212)109.4(2)
 C(224)-C(211)-C(212)108.9(2)
 C(210)-C(211)-C(216)109.45(19)
 C(224)-C(211)-C(216)111.3(2)
 C(212)-C(211)-C(216)108.9(2)
 C(209)-C(212)-C(211)115.3(2)
 C(210)-C(213)-C(214)126.0(2)
 C(213)-C(214)-C(215)113.1(2)
 C(220)-C(215)-C(214)110.7(2)
 C(220)-C(215)-C(216)109.7(2)
 C(214)-C(215)-C(216)110.6(2)
 C(215)-C(216)-C(217)110.9(2)

C(215)-C(216)-C(211)113.3(2)
C(217)-C(216)-C(211)113.57(19)
C(218)-C(217)-C(216)114.5(2)
C(217)-C(218)-C(219)111.9(2)
C(218)-C(219)-C(225)111.3(2)
C(218)-C(219)-C(220)106.44(19)
C(225)-C(219)-C(220)111.9(2)
C(218)-C(219)-C(223)117.4(2)
C(225)-C(219)-C(223)109.4(2)
C(220)-C(219)-C(223)99.82(19)
C(215)-C(220)-C(221)118.9(2)
C(215)-C(220)-C(219)115.6(2)
C(221)-C(220)-C(219)104.2(2)
C(220)-C(221)-C(222)104.4(2)
C(221)-C(222)-C(223)106.74(19)
C(226)-C(223)-C(222)112.4(2)
C(226)-C(223)-C(219)119.4(2)
C(222)-C(223)-C(219)103.6(2)
C(227)-C(226)-C(223)112.2(2)
C(227)-C(226)-C(228)110.0(2)
C(223)-C(226)-C(228)111.1(2)
C(229)-C(228)-C(226)115.0(2)
C(230)-C(229)-C(228)114.5(2)
C(229)-C(230)-C(231)114.5(2)
C(232)-C(231)-C(230)113.3(2)
C(232)-C(231)-C(233)111.3(3)
C(230)-C(231)-C(233)111.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 04134dpm. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	40(1)	73(1)	57(1)	1(1)	4(1)	4(1)
C(100)	47(2)	77(2)	64(2)	-1(2)	-3(2)	15(2)
C(101)	36(2)	60(2)	35(1)	2(1)	8(1)	4(1)
C(102)	42(2)	50(2)	58(2)	7(2)	9(2)	6(1)
C(103)	53(2)	57(2)	60(2)	-15(2)	-3(2)	-1(2)
C(104)	52(2)	60(2)	59(2)	-14(2)	-1(2)	15(2)
C(105)	47(2)	53(2)	57(2)	6(2)	7(2)	-1(1)
C(106)	46(2)	51(2)	35(1)	-2(1)	5(1)	3(1)
C(107)	42(2)	53(2)	40(2)	-6(1)	4(1)	5(1)
C(108)	44(2)	63(2)	36(1)	1(2)	1(1)	6(1)
C(109)	44(2)	67(2)	45(2)	4(2)	8(1)	0(1)
C(110)	39(2)	47(2)	45(2)	6(1)	8(1)	4(1)
C(111)	38(1)	42(2)	38(1)	-2(1)	6(1)	5(1)
C(112)	44(2)	57(2)	34(1)	0(1)	4(1)	1(1)
C(113)	45(2)	65(2)	42(2)	8(2)	16(1)	4(1)
C(114)	46(2)	62(2)	36(1)	4(1)	7(1)	5(1)
C(115)	41(2)	42(2)	35(1)	3(1)	6(1)	3(1)
C(116)	41(2)	38(2)	34(1)	-2(1)	5(1)	4(1)
C(117)	44(2)	64(2)	30(1)	3(1)	6(1)	3(1)
C(118)	44(2)	60(2)	36(1)	4(1)	6(1)	1(1)
C(119)	40(1)	47(2)	36(1)	1(1)	4(1)	3(1)
C(120)	44(2)	42(2)	33(1)	7(1)	2(1)	3(1)
C(121)	53(2)	66(2)	35(2)	10(1)	2(1)	5(2)
C(122)	53(2)	74(2)	41(2)	5(2)	-1(1)	0(2)
C(123)	46(2)	55(2)	39(2)	4(1)	1(1)	3(1)
C(124)	47(2)	49(2)	59(2)	-11(2)	2(2)	0(1)
C(125)	48(2)	58(2)	61(2)	-2(2)	6(2)	6(1)
C(126)	40(2)	75(2)	57(2)	1(2)	5(1)	2(1)
C(127)	53(2)	134(3)	59(2)	-2(2)	16(2)	-14(2)
C(128)	54(2)	86(3)	61(2)	-2(2)	2(2)	0(2)

C(129)56(2)	148(4)	90(3)	-34(3)	0(2)	6(2)
C(130)55(2)	93(3)	75(2)	-11(2)	0(2)	-2(2)
C(131)53(3)	80(5)	64(4)	18(4)	11(3)	-10(3)
C(132)58(5)	136(10)	62(5)	-6(6)	14(4)	-23(6)
C(133)62(5)	113(6)	103(7)	3(5)	1(5)	26(5)
C(31B)73(6)	95(10)	87(7)	11(6)	17(4)	-11(6)
C(32B)35(6)	170(20)	89(9)	1(10)	4(6)	7(9)
C(33B)94(8)	187(18)	164(13)	-87(13)	60(9)	-28(10)
O(2) 33(1)	90(2)	69(1)	4(1)	0(1)	-2(1)
C(200)39(2)	90(2)	54(2)	-9(2)	1(2)	10(2)
C(201)32(2)	68(2)	47(2)	-6(2)	3(1)	-3(1)
C(202)40(2)	72(2)	49(2)	9(2)	2(1)	2(2)
C(203)42(2)	77(2)	68(2)	13(2)	7(2)	-15(2)
C(204)39(2)	63(2)	52(2)	9(2)	5(1)	-9(1)
C(205)44(2)	69(2)	62(2)	14(2)	0(2)	-6(2)
C(206)35(1)	54(2)	40(2)	-6(1)	6(1)	-2(1)
C(207)36(1)	45(2)	40(1)	-2(1)	5(1)	-8(1)
C(208)39(2)	51(2)	35(1)	-7(1)	4(1)	-7(1)
C(209)34(1)	53(2)	43(2)	-7(1)	9(1)	1(1)
C(210)39(1)	38(2)	35(1)	-6(1)	5(1)	-5(1)
C(211)34(1)	40(2)	32(1)	-4(1)	6(1)	-2(1)
C(212)37(1)	48(2)	33(1)	-3(1)	4(1)	-1(1)
C(213)40(1)	48(2)	31(1)	-4(1)	3(1)	-4(1)
C(214)41(2)	52(2)	32(1)	-7(1)	8(1)	-2(1)
C(215)36(1)	37(1)	33(1)	-1(1)	6(1)	0(1)
C(216)38(1)	37(2)	30(1)	0(1)	8(1)	1(1)
C(217)34(1)	55(2)	31(1)	0(1)	5(1)	2(1)
C(218)36(1)	52(2)	30(1)	-1(1)	3(1)	1(1)
C(219)32(1)	41(1)	35(1)	5(1)	3(1)	3(1)
C(220)37(1)	38(1)	32(1)	-2(1)	6(1)	2(1)
C(221)39(2)	49(2)	43(2)	-6(1)	11(1)	2(1)
C(222)38(1)	44(2)	42(2)	1(1)	10(1)	1(1)
C(223)33(1)	36(1)	39(1)	5(1)	3(1)	4(1)
C(224)41(2)	47(2)	47(2)	1(1)	9(1)	-4(1)
C(225)43(2)	49(2)	55(2)	9(1)	7(1)	-3(1)
C(226)34(1)	50(2)	39(1)	8(1)	3(1)	3(1)

C(227)40(2)	109(3)	40(2)	4(2)	-2(1)	-8(2)
C(228)35(1)	56(2)	45(2)	5(1)	1(1)	-1(1)
C(229)40(2)	62(2)	51(2)	12(2)	-1(1)	-8(1)
C(230)40(2)	67(2)	44(2)	4(2)	5(1)	-8(1)
C(231)37(2)	63(2)	48(2)	-2(2)	4(1)	-6(1)
C(232)45(2)	79(2)	84(3)	13(2)	-10(2)	-3(2)
C(233)45(2)	88(2)	51(2)	-6(2)	9(2)	-17(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 04134dpm.

	x	y	z	U(eq)
H(10A)	7150	4097	3169	94
H(10B)	6625	3362	2511	94
H(10C)	6303	3310	3284	94
H(102)	5264	2930	2368	60
H(103)	5193	7168	2534	69
H(104)	3834	7166	2048	69
H(105)	3896	2949	1874	63
H(107)	2697	4095	1398	54
H(10D)	2403	4364	2604	57
H(10E)	2321	6038	2491	57
H(10F)	2645	7120	1326	62
H(10G)	2879	6116	695	62
H(11A)	997	5025	2377	54
H(11B)	1258	3960	1783	54
H(113)	1838	6093	-172	60
H(11C)	458	5002	-411	57
H(11D)	470	6654	-588	57
H(115)	-141	7255	410	47
H(116)	241	4453	926	45
H(11E)	-365	4973	1968	55
H(11F)	-589	6537	1695	55
H(11G)	-1784	5143	1542	55
H(11H)	-1325	4000	1095	55
H(120)	-862	4619	-32	48
H(12A)	-1012	5802	-1080	62
H(12B)	-1274	7249	-711	62
H(12C)	-2296	4913	-1082	68
H(12D)	-2587	6477	-886	68
H(123)	-2278	4128	34	56
H(12C)	556	7444	2081	78

H(12D)	767	8158	1354	78
H(12E)	1495	7759	1949	78
H(12F)	-1988	7878	223	83
H(12G)	-1306	7834	890	83
H(12H)	-2246	7450	990	83
H(126)	-3373	6479	127	69
H(12I)	-3068	5526	1279	122
H(12J)	-3350	3993	992	122
H(12K)	-4013	5240	1002	122
H(12I)	-3653	4816	-850	80
H(12J)	-3816	3641	-276	80
H(12L)	-4787	6120	-438	118
H(12M)	-4986	4743	4	118
H(13A)	-5069	4963	-1502	90
H(13B)	-5096	3468	-1120	90
H(13A)	-4900	4468	-1481	90
H(13B)	-5391	3481	-981	90
H(131)	-6371	3962	-745	78
H(13C)	-7164	4079	-1860	127
H(13D)	-6422	2973	-1880	127
H(13E)	-6354	4505	-2229	127
H(13F)	-7030	6151	-1057	139
H(13G)	-6221	6678	-1398	139
H(13H)	-6193	6413	-561	139
H(31B)	-5910	6235	-1474	101
H(32A)	-6163	4430	-2323	147
H(32B)	-7023	4941	-2065	147
H(32C)	-6612	3497	-1768	147
H(33A)	-6278	5906	-298	218
H(33B)	-6666	4391	-504	218
H(33C)	-7100	5794	-830	218
H(20A)	-2433	6652	2983	92
H(20B)	-1536	6650	2702	92
H(20C)	-1748	7755	3299	92
H(202)	-361	7539	3359	64
H(203)	-852	4166	4542	75

H(204)	1008	7484	3846	62
H(205)	522	4086	5009	70
H(207)	2068	6691	4632	48
H(20D)	2111	3663	4586	50
H(20E)	2240	4655	3920	50
H(20F)	1649	6381	5800	51
H(20G)	1771	4709	5726	51
H(21A)	2957	5674	6347	47
H(21B)	3056	6779	5723	47
H(213)	3583	4677	3721	47
H(21C)	4884	5762	4229	50
H(21D)	4965	4103	4088	50
H(215)	4981	3547	5258	42
H(216)	4364	6324	5496	42
H(21E)	4351	5816	6696	48
H(21F)	4682	4250	6585	48
H(21G)	5784	5623	7082	47
H(21H)	5625	6789	6472	47
H(220)	5803	6201	5259	43
H(22A)	6502	5099	4445	52
H(22B)	6515	3608	4857	52
H(22C)	7621	5844	5124	49
H(22D)	7712	4274	5447	49
H(223)	6994	6688	6038	43
H(22C)	3738	2614	5591	67
H(22D)	2797	2965	5702	67
H(22E)	3512	3315	6317	67
H(22F)	6671	2955	6052	73
H(22G)	5745	2958	6269	73
H(22H)	6494	3357	6844	73
H(226)	7861	4366	6731	49
H(22I)	7901	5686	7795	95
H(22J)	6968	5313	7514	95
H(22K)	7321	6867	7402	95
H(22I)	8705	5883	6102	55
H(22J)	8435	7200	6554	55

H(22K)	9119	6236	7590	61
H(22L)	9357	4863	7162	61
H(23A)	9949	7579	6811	60
H(23B)	10289	6090	6567	60
H(231)	10500	7164	7980	59
H(23A)	11372	5266	8287	106
H(23B)	11174	4604	7512	106
H(23C)	10460	4722	8035	106
H(23D)	11332	8357	7220	92
H(23E)	11758	6893	7039	92
H(23F)	11884	7519	7827	92

Table 6. Torsion angles [°] for 04134dpm.

C(100)-O(1)-C(101)-C(103)	177.0(3)
C(100)-O(1)-C(101)-C(102)	-3.5(4)
O(1)-C(101)-C(102)-C(105)	179.4(3)
C(103)-C(101)-C(102)-C(105)	-1.1(4)
O(1)-C(101)-C(103)-C(104)	-179.2(3)
C(102)-C(101)-C(103)-C(104)	1.2(4)
C(101)-C(103)-C(104)-C(106)	-0.6(5)
C(101)-C(102)-C(105)-C(106)	0.3(5)
C(103)-C(104)-C(106)-C(105)	-0.3(4)
C(103)-C(104)-C(106)-C(107)	175.2(3)
C(102)-C(105)-C(106)-C(104)	0.4(4)
C(102)-C(105)-C(106)-C(107)	-175.1(3)
C(104)-C(106)-C(107)-C(109)	44.6(4)
C(105)-C(106)-C(107)-C(109)	-140.1(3)
C(104)-C(106)-C(107)-C(108)	-78.8(4)
C(105)-C(106)-C(107)-C(108)	96.5(3)
C(106)-C(107)-C(108)-C(112)	-174.6(2)
C(109)-C(107)-C(108)-C(112)	58.7(3)
C(106)-C(107)-C(109)-C(110)	178.2(2)
C(108)-C(107)-C(109)-C(110)	-56.4(3)
C(107)-C(109)-C(110)-C(113)	-127.4(3)
C(107)-C(109)-C(110)-C(111)	52.2(3)
C(113)-C(110)-C(111)-C(124)	-106.8(3)
C(109)-C(110)-C(111)-C(124)	73.6(3)
C(113)-C(110)-C(111)-C(116)	15.3(4)
C(109)-C(110)-C(111)-C(116)	-164.3(2)
C(113)-C(110)-C(111)-C(112)	134.6(3)
C(109)-C(110)-C(111)-C(112)	-45.0(3)
C(107)-C(108)-C(112)-C(111)	-56.4(3)
C(110)-C(111)-C(112)-C(108)	47.0(3)
C(124)-C(111)-C(112)-C(108)	-71.1(3)
C(116)-C(111)-C(112)-C(108)	167.0(2)
C(109)-C(110)-C(113)-C(114)	-179.6(3)
C(111)-C(110)-C(113)-C(114)	0.8(5)

C(110)-C(113)-C(114)-C(115)	12.8(4)
C(113)-C(114)-C(115)-C(120)	-162.0(2)
C(113)-C(114)-C(115)-C(116)	-41.1(3)
C(120)-C(115)-C(116)-C(117)	-50.5(3)
C(114)-C(115)-C(116)-C(117)	-172.0(2)
C(120)-C(115)-C(116)-C(111)	-179.4(2)
C(114)-C(115)-C(116)-C(111)	59.2(3)
C(110)-C(111)-C(116)-C(117)	-172.4(2)
C(124)-C(111)-C(116)-C(117)	-52.3(3)
C(112)-C(111)-C(116)-C(117)	68.1(3)
C(110)-C(111)-C(116)-C(115)	-45.1(3)
C(124)-C(111)-C(116)-C(115)	75.0(3)
C(112)-C(111)-C(116)-C(115)	-164.6(2)
C(115)-C(116)-C(117)-C(118)	52.1(3)
C(111)-C(116)-C(117)-C(118)	-179.3(2)
C(116)-C(117)-C(118)-C(119)	-56.1(3)
C(117)-C(118)-C(119)-C(125)	-66.2(3)
C(117)-C(118)-C(119)-C(120)	56.0(3)
C(117)-C(118)-C(119)-C(123)	166.1(2)
C(114)-C(115)-C(120)-C(121)	-56.5(3)
C(116)-C(115)-C(120)-C(121)	-177.6(2)
C(114)-C(115)-C(120)-C(119)	178.8(2)
C(116)-C(115)-C(120)-C(119)	57.7(3)
C(125)-C(119)-C(120)-C(121)	-69.8(3)
C(118)-C(119)-C(120)-C(121)	168.6(2)
C(123)-C(119)-C(120)-C(121)	47.4(3)
C(125)-C(119)-C(120)-C(115)	62.1(3)
C(118)-C(119)-C(120)-C(115)	-59.5(3)
C(123)-C(119)-C(120)-C(115)	179.3(2)
C(115)-C(120)-C(121)-C(122)	-167.5(2)
C(119)-C(120)-C(121)-C(122)	-37.4(3)
C(120)-C(121)-C(122)-C(123)	12.3(3)
C(121)-C(122)-C(123)-C(126)	147.5(3)
C(121)-C(122)-C(123)-C(119)	16.7(3)
C(125)-C(119)-C(123)-C(126)	-45.2(3)
C(120)-C(119)-C(123)-C(126)	-163.5(3)

C(118)-C(119)-C(123)-C(126)	82.7(3)
C(125)-C(119)-C(123)-C(122)	79.8(3)
C(120)-C(119)-C(123)-C(122)	-38.5(3)
C(118)-C(119)-C(123)-C(122)	-152.3(2)
C(122)-C(123)-C(126)-C(127)	-177.5(3)
C(119)-C(123)-C(126)-C(127)	-56.0(4)
C(122)-C(123)-C(126)-C(128)	58.8(3)
C(119)-C(123)-C(126)-C(128)	-179.7(3)
C(127)-C(126)-C(128)-C(129)	69.1(4)
C(123)-C(126)-C(128)-C(129)	-165.5(3)
C(126)-C(128)-C(129)-C(130)	168.7(3)
C(128)-C(129)-C(130)-C(131)	168.0(5)
C(128)-C(129)-C(130)-C(31B)	-157.7(6)
C(31B)-C(130)-C(131)-C(132)	86.5(15)
C(129)-C(130)-C(131)-C(132)	176.6(9)
C(31B)-C(130)-C(131)-C(133)	-36.4(10)
C(129)-C(130)-C(131)-C(133)	53.7(9)
C(131)-C(130)-C(31B)-C(32B)	-68.8(15)
C(129)-C(130)-C(31B)-C(32B)	-175.0(11)
C(131)-C(130)-C(31B)-C(33B)	51.2(11)
C(129)-C(130)-C(31B)-C(33B)	-55.0(14)
C(200)-O(2)-C(201)-C(203)	-176.4(3)
C(200)-O(2)-C(201)-C(202)	3.7(4)
C(203)-C(201)-C(202)-C(204)	-0.3(5)
O(2)-C(201)-C(202)-C(204)	179.6(3)
C(202)-C(201)-C(203)-C(205)	-0.4(5)
O(2)-C(201)-C(203)-C(205)	179.7(3)
C(201)-C(202)-C(204)-C(206)	0.8(5)
C(201)-C(203)-C(205)-C(206)	0.6(5)
C(202)-C(204)-C(206)-C(205)	-0.6(4)
C(202)-C(204)-C(206)-C(207)	178.9(3)
C(203)-C(205)-C(206)-C(204)	-0.2(5)
C(203)-C(205)-C(206)-C(207)	-179.6(3)
C(204)-C(206)-C(207)-C(209)	132.0(3)
C(205)-C(206)-C(207)-C(209)	-48.6(4)
C(204)-C(206)-C(207)-C(208)	-104.4(3)

C(205)-C(206)-C(207)-C(208)	75.0(3)
C(206)-C(207)-C(208)-C(210)	174.1(2)
C(209)-C(207)-C(208)-C(210)	-58.7(3)
C(206)-C(207)-C(209)-C(212)	-173.7(2)
C(208)-C(207)-C(209)-C(212)	59.9(3)
C(207)-C(208)-C(210)-C(213)	-126.5(3)
C(207)-C(208)-C(210)-C(211)	52.9(3)
C(213)-C(210)-C(211)-C(224)	-105.5(3)
C(208)-C(210)-C(211)-C(224)	75.1(3)
C(213)-C(210)-C(211)-C(212)	135.6(3)
C(208)-C(210)-C(211)-C(212)	-43.8(3)
C(213)-C(210)-C(211)-C(216)	16.3(3)
C(208)-C(210)-C(211)-C(216)	-163.1(2)
C(207)-C(209)-C(212)-C(211)	-55.9(3)
C(210)-C(211)-C(212)-C(209)	45.4(3)
C(224)-C(211)-C(212)-C(209)	-73.4(3)
C(216)-C(211)-C(212)-C(209)	165.0(2)
C(208)-C(210)-C(213)-C(214)	179.8(2)
C(211)-C(210)-C(213)-C(214)	0.4(4)
C(210)-C(213)-C(214)-C(215)	11.5(4)
C(213)-C(214)-C(215)-C(220)	-161.3(2)
C(213)-C(214)-C(215)-C(216)	-39.4(3)
C(220)-C(215)-C(216)-C(217)	-50.1(3)
C(214)-C(215)-C(216)-C(217)	-172.6(2)
C(220)-C(215)-C(216)-C(211)	-179.2(2)
C(214)-C(215)-C(216)-C(211)	58.4(3)
C(210)-C(211)-C(216)-C(215)	-45.3(3)
C(224)-C(211)-C(216)-C(215)	74.9(3)
C(212)-C(211)-C(216)-C(215)	-164.9(2)
C(210)-C(211)-C(216)-C(217)	-173.0(2)
C(224)-C(211)-C(216)-C(217)	-52.7(3)
C(212)-C(211)-C(216)-C(217)	67.4(3)
C(215)-C(216)-C(217)-C(218)	50.9(3)
C(211)-C(216)-C(217)-C(218)	179.8(2)
C(216)-C(217)-C(218)-C(219)	-54.8(3)
C(217)-C(218)-C(219)-C(225)	-67.3(3)

C(217)-C(218)-C(219)-C(220)	54.9(3)
C(217)-C(218)-C(219)-C(223)	165.5(2)
C(214)-C(215)-C(220)-C(221)	-54.8(3)
C(216)-C(215)-C(220)-C(221)	-177.2(2)
C(214)-C(215)-C(220)-C(219)	180.0(2)
C(216)-C(215)-C(220)-C(219)	57.6(3)
C(218)-C(219)-C(220)-C(215)	-59.1(3)
C(225)-C(219)-C(220)-C(215)	62.8(3)
C(223)-C(219)-C(220)-C(215)	178.4(2)
C(218)-C(219)-C(220)-C(221)	168.5(2)
C(225)-C(219)-C(220)-C(221)	-69.7(3)
C(223)-C(219)-C(220)-C(221)	46.0(2)
C(215)-C(220)-C(221)-C(222)	-164.6(2)
C(219)-C(220)-C(221)-C(222)	-34.0(3)
C(220)-C(221)-C(222)-C(223)	8.3(3)
C(221)-C(222)-C(223)-C(226)	150.3(2)
C(221)-C(222)-C(223)-C(219)	20.1(3)
C(218)-C(219)-C(223)-C(226)	80.0(3)
C(225)-C(219)-C(223)-C(226)	-48.1(3)
C(220)-C(219)-C(223)-C(226)	-165.6(2)
C(218)-C(219)-C(223)-C(222)	-154.2(2)
C(225)-C(219)-C(223)-C(222)	77.8(2)
C(220)-C(219)-C(223)-C(222)	-39.8(2)
C(222)-C(223)-C(226)-C(227)	-176.3(2)
C(219)-C(223)-C(226)-C(227)	-54.7(3)
C(222)-C(223)-C(226)-C(228)	60.1(3)
C(219)-C(223)-C(226)-C(228)	-178.3(2)
C(227)-C(226)-C(228)-C(229)	60.1(3)
C(223)-C(226)-C(228)-C(229)	-175.1(2)
C(226)-C(228)-C(229)-C(230)	176.8(3)
C(228)-C(229)-C(230)-C(231)	166.1(3)
C(229)-C(230)-C(231)-C(232)	57.4(4)
C(229)-C(230)-C(231)-C(233)	-176.5(3)

Symmetry transformations used to generate equivalent atoms:

References

- (1) Labadie, J. W.; Tueting, D.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4634-4642.
- (2) This substrate was prepared according to a literature procedure. See: Bajwa, J. S.; Anderson, R. C. *Tetrahedron Lett.* **1991**, *32*, 3021-3024.
- (3) Kevill, D. N.; Weitz, F. L. *J. Org. Chem.* **1967**, *32*, 2633-2634.
- (4) For a related procedure, see: Artis, D. R.; Cho, I.-S.; Jaime-Figueroa, S.; Muchowski, J. M. *J. Org. Chem.* **1994**, *59*, 2456-2466.
- (5) Hackmann, C.; Schäfer, H. J. *Tetrahedron* **1993**, *49*, 4559-4574.
- (6) (a) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107-7120. (b) Eda, M.; Takemoto, T.; Ono, S.-i.; Okada, T.; Kosaka, K.; Gohda, M.; Matzno, S.; Nakamura, N.; Fukaya, C. *J. Med. Chem.* **1994**, *37*, 1983-1990.
- (7) Ferreira, J. T. B.; Cruz, W. O.; Vieira, P. C.; Yonashiro, M. *J. Org. Chem.* **1987**, *52*, 3698-3699.
- (8) Pezechk, M.; Brunetiere, A. P.; Lallemand, J. Y. *Tetrahedron Lett.* **1986**, *27*, 3715-3718.