

Practical Synthesis of Chiral Ligands for Catalytic Enantioselective Cyanosilylation of Ketones and Ketoimines

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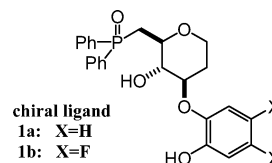
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Abstract: A practical synthesis of chiral ligands that are useful for catalytic enantioselective cyanosilylation of ketones and ketoimines is described. Compared with the previous synthetic route, the number of total steps is decreased and the total yield is greatly improved. Furthermore, both (+)- and (–)-ligands are readily available by this new synthetic route.

We recently developed a highly general and practical catalytic enantioselective cyanosilylation of ketones^{1,2} and ketoimines (Strecker reaction)^{3,4} using D-glucose-derived chiral ligands **1a** and **1b** (Scheme 1). In the cyanosilylation of ketones, both (R)- and (S)-cyanohydrins can be synthesized with generally high enantioselectivity by changing the center metals: the **1**–Ti (1:1) complex is

SCHEME 1



(R)-selective^{1a–c} and the **1**–Ln (Gd or Sm) (2:3) complex is (S)-selective.^{1d–g} The (S)-selective catalytic enantioselective Strecker reaction with **1b**–Gd is also general and practical.³ The combined use of a catalytic amount of TMSCN and a stoichiometric amount of HCN allows for the catalyst amount to be reduced to as low as 0.1 mol % while maintaining excellent enantioselectivity. In the catalytic enantioselective Strecker reaction, however, the (R)-amidonitriles were not obtained efficiently with use of the natural (thus inexpensive) D-glucose-derived ligand **1b**, even though the center metal of the catalyst was changed.⁵ Previously, these chiral ligands were synthesized from D-glucose.⁶ Therefore, the synthesis of ligands in the opposite enantiomeric series required expensive L-glucose, which made the synthetic cost of (R)-amidonitriles much higher than that of (S)-amidonitriles, using our catalytic enantioselective Strecker reaction. In addition, the previous ligand synthesis required 12 steps, and the total yield was not satisfactory (total yield: 21% yield). Herein, we report a new and highly practical synthetic route for chiral ligands in which both enantiomers of the ligands **1** can be synthesized in much higher chemical yields.

Recently, Trost and co-workers reported an efficient method to synthesize chiral dihydrofurans and dihydropyrans using π -allylpalladium chemistry and Ru-catalyzed ring-closing metathesis.⁷ We developed a new (versatile) route for chiral ligand synthesis based on these methods and the regioselective S_N2 reaction to the cyclic sulfate **10** with catechol derivatives that we previously reported.

The diene **5** (90% ee) was synthesized from the racemic allyl oxirane ($\pm$)-**2** and 3-buten-1-ol **3** following Trost's procedure.^{7,8} Both enantiomers of chiral phosphine ligand **4** are commercially available, therefore both (+)- and (–)-**5** can be easily synthesized. The synthesis of unnatural L-glucose-derived ligand (*ent*-**1**) with this new synthetic route is shown in Scheme 2. Tosylation of **5**, followed by Ru-catalyzed ring-closing metathesis⁹ gave

(5) With use of **1b**–Ti (1:1) complex at 0 °C, (R)-amidonitriles are obtained predominantly, despite with low enantioselectivity (up to 12% ee).

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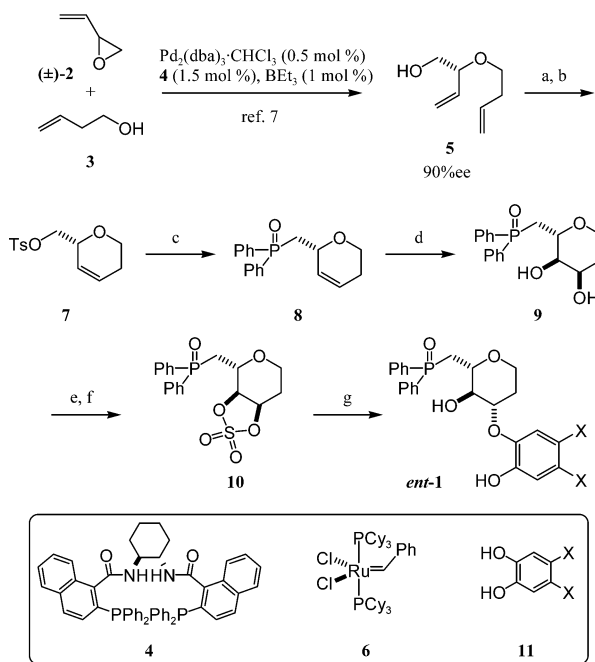
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SCHEME 2^a

^a Reagents and conditions: (a) TsCl, DMAP, pyridine, 50 °C, 98%; (b) **6** (1 mol %), CH₂Cl₂, reflux, 99%; (c) Ph₂PK, THF, 0 °C, H₂O₂; (d) OsO₄, NMO, acetone–H₂O, 92% (2 steps), 37:1 diastereoselectivity; recrystallization (Et₂O–CHCl₃), 85%, >99% ee; (e) SOCl₂, CH₂Cl₂; (f) RuCl₃·nH₂O, NaIO₄, CCl₄–CH₃CN–H₂O, 90% (2 steps); (g) **11**, Cs₂CO₃, CH₃CN, reflux; 20% H₂SO₄ aq, CHCl₃, Et₂O, reflux, 75% (X = H), 55% (X = F).

dihydropyran **7**. Dihydropyran **7** was treated with potassium diphenylphosphide, and then oxidation with hydrogen peroxide afforded the phosphine oxide **8**. Dihydroxylation of **8** proceeded predominantly from the less hindered face, and gave the desired diol **9** with 37:1 diastereoselectivity. Enantiomerically and diastereomerically pure **9** was obtained after recrystallization. The enantiomeric purity of **9** was determined by ¹H NMR analysis after conversion to (*R*)-MTPA diester. The key cyclic sulfate **10** was synthesized following the reported procedure.¹⁰ Finally, regioselective addition of catechol moieties with Cs₂CO₃ as a base,¹¹ followed by hydrolysis of the sulfuric ester gave the chiral ligand *ent*-**1** in good yield. Unprotected catechols were used under these conditions.¹² Although relatively expensive Trost ligand and Grubbs catalyst are required in this new synthetic route, their amounts are catalytic (Trost ligand, 1.5 mol %; Grubbs catalyst, 1 mol %). Moreover, the number of total steps is decreased and total yield is greatly improved compared with the previous route. Therefore, the new synthetic route is more efficient than the previous route also in terms of cost performance.

In conclusion, we have developed a practical synthesis of chiral ligands that are very useful for catalytic enantioselective cyanosilylation of ketones and ketoimines (total of 8 steps and 49% yield from the racemic allyl

oxirane (±)-**2**). Importantly, both enantiomers of the ligand are readily available, which allows for the synthesis of (*S*)- and (*R*)-ketone cyanohydrins and amidonitriles with the same efficiency.

Experimental Section

Toluene-4-sulfonic Acid 5,6-Dihydro-2H-pyran-2-ylmethyl Ester (7). TsCl (1.69 g, 8.86 mmol) was added to a solution of **5** (841 mg, 5.91 mmol) and DMAP (47.5 mg, 0.39 mmol) in pyridine (20 mL) at room temperature, and the mixture was stirred at 50 °C for 1 h. The solvent was removed, and the residue was dissolved in ethyl acetate. The solution was washed twice with 1 M HCl aq and then with brine, dried over Na₂SO₄, and concentrated in vacuo. The reaction mixture was purified by silica gel column chromatography (hexane/AcOEt 7:3) to afford the tosylate (**7**) (1.71 g, 98%) as a colorless oil: [α]_D²³ –13.9 (c 1.50, CHCl₃) (90% ee); IR (neat) ν 1363, 1177, 980 cm^{–1}; ¹H NMR (500 MHz, CDCl₃) δ 2.23 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 3.32 (dt, *J* = 9.2, 6.7 Hz, 1H), 3.48 (dt, *J* = 9.2, 6.7 Hz, 1H), 3.89 (m, 3H), 4.98 (dd, *J* = 10.1, 1.7 Hz, 1H), 5.03 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 5.29 (d, *J* = 17.4 Hz, 1H), 5.58 (ddd, *J* = 17.4, 10.4, 6.5 Hz, 1H), 5.73 (ddt, *J* = 17.1, 10.1, 6.7 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 21.6, 34.1, 68.6, 71.4, 78.3, 116.4, 119.6, 127.9, 129.7, 133.0, 133.7, 134.9, 144.7; ESI-MS *m/z* 319 (M + Na); FAB-HRMS calcd for C₁₅H₂₁O₄S (M + H) 297.1161, found 297.1159.

[Cl₂(PCy₃)₂RuCHPh] (4.5 mg, 5.47 μmol) was added to a degassed solution of the above tosylate (162 mg, 545 μmol) in CH₂Cl₂ (10 mL) at room temperature and the mixture was heated to reflux. The mixture was stirred for 2 h at the same temperature and cooled to room temperature. The mixture was then filtrated through a silica gel pad and washed with CH₂Cl₂. The solvent was removed in vacuo. The reaction mixture was purified by silica gel column chromatography (hexane/AcOEt 8:2) to afford **7** (145 mg, 99%) as an orange oil: [α]_D²⁴ +18.9 (c 0.98, CHCl₃) (90% ee); IR (neat) ν 1360, 1176, 979 cm^{–1}; ¹H NMR (500 MHz, CDCl₃) δ 1.94 (br d, *J* = 17.4 Hz, 1H), 2.17 (dtd, *J* = 17.4, 8.9, 3.4 Hz, 1H), 2.42 (s, 3H), 3.60 (ddd, *J* = 11.3, 8.9, 4.3 Hz, 1H), 3.84 (ddd, *J* = 11.3, 5.4, 3.4 Hz, 1H), 4.00 (d, *J* = 5.5 Hz, 2H), 4.29 (td, *J* = 5.5, 2.2 Hz, 1H), 5.52 (dd, *J* = 10.1, 2.2 Hz, 1H), 5.94 (ddd, *J* = 10.1, 8.9, 2.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 21.6, 24.9, 62.7, 71.0, 71.4, 124.5, 128.0, 128.2, 129.8, 133.0, 144.8; ESI-MS *m/z* 291 (M + Na); FAB-HRMS calcd for C₁₃H₁₇O₄S (M + H) 269.0848, found 269.0841.

6-(Diphenylphosphinoylmethyl)-3,6-dihydro-2H-pyran (8). Ph₂PK (0.5 M, 1.5 mL, 750 μmol) was added to a solution of **7** (136 mg, 507 μmol) in THF (1.5 mL) at 0 °C, and the mixture was stirred at 0 °C. After the solution was stirred for 30 min at the same temperature, sat. NH₄Cl aq was added, followed by the addition of 30% H₂O₂ aq (120 μL) under vigorous stirring. The mixture was then poured slowly into sat. Na₂S₂O₃ aq at 0 °C. Evaporation of THF, extraction of the aqueous layer with CHCl₃, and concentration gave a crude oil **8** (217 mg, mixture).

2-(Diphenylphosphinoylmethyl)tetrahydropyran-3,4-diol (9). OsO₄ (0.2 M in *t*-BuOH, 125 μL, 25.0 μmol) was added to a solution of **8** (217 mg, mixture) and NMO (179 mg, 1.53 mmol) in acetone (1.6 mL)/H₂O (200 μL) at room temperature, and the mixture was stirred for 14 h. The reaction was quenched with sat. Na₂SO₃ aq. After evaporation of acetone, the aqueous layer was extracted with CHCl₃. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography (MeOH/CHCl₃ 1:20) to afford **9** (155 mg, 92% in 2 steps) as an amorphous solid. Recrystallization of **9** from CHCl₃ (200 μL)/Et₂O (2 mL) gave **9** (132 mg, 85%) as a needle crystal: mp. 174–176 °C; [α]_D²⁶ +21.4 (c 0.79, CHCl₃); IR (film) ν 3340, 1099, 748 cm^{–1}; ¹H NMR (500 MHz, CDCl₃) δ 1.73–1.82 (m, 2H), 2.62–2.71 (m, 2H), 3.34–3.43 (m, 2H), 3.50 (dt, *J* = 10.8, 3.5 Hz, 1H), 3.67 (td, *J* = 10.8, 4.6 Hz, 1H), 3.84 (ddd, *J* = 16.2, 7.3, 5.5 Hz, 1H), 4.12 (d, *J* = 2.8 Hz, 1H), 6.34 (br s,

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(12) In the previous synthetic route,⁶ monomethylated catechol derivatives were used for the introduction of a catechol moiety.

1H), 7.42–7.54 (m, 6H), 7.66–7.76 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 31.3, 36.0 (d, J = 70 Hz), 61.8, 66.5, 71.2, 73.1 (d, J = 4.1 Hz), 128.8 (d, J = 12.3 Hz), 130.4, 130.4, 130.5, 131.0, 131.1, 131.2, 132.0, 132.2, 132.8, 133.0, 133.2 (130.4–133.2, multiple peaks); ^{31}P NMR (202 MHz, CDCl_3) δ 34.6; ESI-MS m/z 355 (M + Na); FAB-HRMS calcd for $\text{C}_{18}\text{H}_{22}\text{O}_4\text{P}$ (M + H) 333.1256, found 333.1254.

The enantiomeric purity of **9** was determined as follows: (*R*)-MTPACl (8.3 μL , 44.4 μmol) was added to a solution of chromatographically purified **9** (7.2 mg, 21.7 μmol), Et_3N (30 μL , 215 μmol), and DMAP (4.0 mg, 32.7 μmol) in CH_2Cl_2 (500 μL), and the mixture was stirred at room temperature for 20 min. The mixture was filtrated through a silica gel pad and washed with $\text{MeOH}/\text{CHCl}_3$ 1:9. The solvent was removed in vacuo. The enantiomeric purity of **9** was determined by ^1H NMR analysis of the crude mixture.

Major product: colorless oil; $[\alpha]_D^{24}$ –11.6 (c 0.80, CHCl_3); IR (neat) ν 1754, 1172 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.65 (br d, J = 15.0 Hz, 1H), 1.84–1.98 (m, 1H), 2.37–2.47 (m, 2H), 3.06 (t, J = 11.8 Hz, 1H), 3.23 (s, 3H), 3.36 (s, 3H), 3.45 (dd, J = 11.8, 4.6 Hz, 1H), 4.06 (m, 1H), 5.05 (br d, J = 9.9 Hz, 1H), 5.58 (br s, 1H), 7.28–7.50 (m, 16H), 7.60–7.67 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 30.0, 32.5 (d, J = 72 Hz), 55.3, 55.3, 61.5, 69.3, 69.5 (d, J = 4.8 Hz), 73.9 (d, J = 13.2 Hz), 84.2, 84.4, 84.6, 84.8, 85.1 (84.2–85.1, multiple peaks), 123.0 (q, J = 290 Hz), 126.9, 127.3, 128.2, 128.3, 128.3, 128.4, 128.5, 128.6 (128.2–128.6, multiple peaks), 129.6, 129.8, 130.6, 130.7, 130.8, 131.1, 131.5, 131.7, 131.7 (130.6–131.7, multiple peaks), 132.8 (d, J = 101 Hz), 133.2 (d, J = 102 Hz), 165.3, 166.0; ^{31}P NMR (202 MHz, CDCl_3) δ 30.0; ^{19}F NMR (470 MHz, CDCl_3) δ –72.7, –71.8; ESI-MS m/z 787 (M + Na); FAB-HRMS calcd for $\text{C}_{38}\text{H}_{36}\text{F}_6\text{O}_8\text{P}$ (M + H) 765.2052, found 765.2050.

Minor product: colorless oil; $[\alpha]_D^{24}$ +42.3 (c 0.52, CHCl_3); IR (neat) ν 1754, 1172 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.81 (br d, J = 13.4 Hz, 1H), 1.97–2.10 (m, 2H), 2.26 (dt, J = 13.4, 10.6 Hz, 1H), 3.29–3.27 (m, 4H), 3.35 (s, 3H), 3.61 (dd, J = 11.6, 4.9 Hz, 1H), 3.93 (q, J = 10.6 Hz, 1H), 5.00 (dd, J = 10.6, 2.3 Hz, 1H), 5.64 (br s, 1H), 7.16–7.22 (m, 2H), 7.29–7.52 (m, 18 H); ^{13}C NMR (125 MHz, CDCl_3) δ 30.3, 32.1 (d, J = 72 Hz), 54.9, 55.6, 69.7 (d, J = 4.8 Hz), 70.1, 73.7 (d, J = 13.2 Hz), 84.0, 84.2, 84.5, 84.7, 84.9 (84.0–84.9, multiple peaks), 123.0 (q, J = 290 Hz), 123.0 (q, J = 290 Hz), 126.8, 127.5, 128.3 (d, J = 12.0 Hz), 128.5, 128.5, 128.6 (128.5–128.6, multiple peaks), 129.8, 129.8, 130.6, 130.7, 131.0, 131.0, 131.1, 131.5, 131.5, 131.6, 131.6, 131.7, 131.7, 132.3 (129.8–132.3, multiple peaks), 133.6 (d, J = 102 Hz), 165.6, 166.1; ^{31}P NMR (202 MHz, CDCl_3) δ 30.3; ^{19}F NMR (470 MHz, CDCl_3) δ –72.6, –71.9; ESI-MS m/z 787 (M + Na); FAB-HRMS calcd for $\text{C}_{38}\text{H}_{36}\text{F}_6\text{O}_8\text{P}$ (M + H) 765.2052, found 765.2059.

4-(Diphenylphosphinoylmethyl)tetrahydro[1,3,2]-dioxathiol[4,5-c]pyran-2,2-dioxide (10). SOCl_2 (600 μL , 8.22 mmol) was added to a solution of diol **9** (2.17 g, 6.53 mmol) in CH_2Cl_2 (25 mL), and the mixture was stirred for 30 min at room temperature. The reaction mixture was concentrated, followed by coevaporation with toluene two times. The resulting crude cyclic sulfite was dissolved in CCl_4 (10 mL)/ CH_3CN (10 mL)/ H_2O (20 mL), and NaIO_4 (2.12 g, 9.91 mmol) and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (16.1 mg, 77.6 μmol) were added in an ice bath. After the solution was stirred vigorously for 1 h, H_2O was added, and the aqueous layer was extracted with ethyl acetate. The solvent was removed, and the residue was dissolved in ethyl acetate. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography ($\text{MeOH}/\text{CHCl}_3$ 1:20) to afford **10** (2.33 g, 90%) as a white powder; $[\alpha]_D^{24}$ –41.4 (c 1.32, CHCl_3); IR (film) ν 1389, 1210 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 2.07–2.18 (m, 2H), 2.56 (ddd, J = 15.6, 12.2, 8.0 Hz, 1H), 2.74 (ddd, J = 15.6, 10.1, 3.4 Hz, 1H), 3.43 (td, J = 11.9, 3.1 Hz, 1H), 3.71

(dd, J = 11.9, 4.6 Hz, 1H), 4.08 (dddd, J = 11.3, 9.5, 8.0, 3.4 Hz, 1H), 5.00 (dd, J = 9.5, 4.6 Hz, 1H), 5.22 (br s, 1H), 7.41–7.53 (m, 4H), 7.65–7.76 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 26.9, 32.5 (d, J = 71 Hz), 62.0, 71.9 (d, J = 5.1 Hz), 79.1, 80.7 (d, J = 10.4 Hz), 128.5 (d, J = 12.4 Hz), 128.6 (d, J = 12.3 Hz), 130.6 (d, J = 9.3 Hz), 131.0 (d, J = 9.3 Hz), 131.8–132.7 (multiple peaks), 133.5 (d, J = 101 Hz); ^{31}P NMR (202 MHz, CDCl_3) δ 29.7; ESI-MS m/z 417 (M + Na); FAB-HRMS calcd for $\text{C}_{18}\text{H}_{20}\text{O}_6\text{P}$ (M + H) 395.0718.

General Procedure for the $\text{S}_\text{N}2$ Reaction by Catechols. Cs_2CO_3 (48.3 mg, 148 μmol) was added to a solution of cyclic sulfate **10** (55.4 mg, 140 μmol) and catechol **11** ($\text{X} = \text{H}$, 23.1 mg, 210 μmol) in CH_3CN (1.5 mL) at room temperature and the mixture was heated to reflux. The mixture was stirred for 1 h at the same temperature and cooled to room temperature. H_2SO_4 aq (20%; 4 mL) and Et_2O (2 mL)– CHCl_3 (2 mL) were added and the mixture was heated to reflux. The mixture was vigorously stirred for 6 h at the same temperature and cooled to room temperature. The aqueous layer was extracted with CHCl_3 and the combined organic layer was washed with brine. Drying over Na_2SO_4 , followed by concentration, gave a crude oil that was purified by silica gel column chromatography ($\text{MeOH}/\text{CHCl}_3$ 1:20). The chiral ligand **1a** was obtained as a white plate crystal (44.7 mg, 75%).

Chiral ligand 1a: white plate crystal; mp. 219–221 $^\circ\text{C}$; $[\alpha]_D^{23}$ +11.0 (c 1.15, MeOH); IR (film) ν 3188, 1495, 736 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.87 (qd, J = 12.5, 4.6 Hz, 1H), 2.08 (dd, J = 12.5, 4.6 Hz, 1H), 2.70–2.85 (m, 2H), 3.15 (t, J = 12.5 Hz, 1H), 3.40 (dt, J = 13.7, 8.9 Hz, 1H), 3.58 (ddd, J = 12.5, 8.9, 4.6 Hz, 1H), 3.67 (t, J = 8.9 Hz, 1H), 3.79 (dd, J = 12.5, 4.6 Hz, 1H), 6.69 (td, J = 7.5, 1.9 Hz, 1H), 6.87–6.97 (m, 3H), 7.30 (br s, 1H), 7.41–7.53 (m, 6H), 7.66–7.75 (m, 4H), 8.93 (br s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 31.6, 35.6 (d, J = 69.0 Hz), 65.3, 74.7 (d, J = 5.1 Hz), 75.8, 84.5, 117.0, 119.1, 121.8, 125.0, 128.7 (d, J = 12.3 Hz), 130.5 (d, J = 9.3 Hz), 130.6 (d, J = 97.8 Hz), 131.0 (d, J = 10.4 Hz), 131.9 (d, J = 104 Hz), 132.2 (d, J = 4.1 Hz), 132.4 (d, J = 4.1 Hz), 145.8, 149.7; ^{31}P NMR (202 MHz, CDCl_3) δ 34.3; ESI-MS m/z 447 (M + Na); FAB-HRMS calcd for $\text{C}_{24}\text{H}_{26}\text{O}_5\text{P}$ (M + H) 425.1518, found 425.1517.

Chiral ligand 1b: white amorphous; $[\alpha]_D^{29}$ +99.0 (c 1.53, CHCl_3); IR (film) ν 3162, 1513, 1159 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.91 (qd, J = 12.2, 4.6 Hz, 1H), 2.07 (dd, J = 12.2, 4.6 Hz, 1H), 2.67 (td, J = 15.3, 10.1 Hz, 1H), 2.82 (br t, J = 15.3 Hz, 1H), 3.24 (t, J = 12.2 Hz, 1H), 3.32 (br dd, J = 10.1, 8.9 Hz, 1H), 3.49 (ddd, J = 12.2, 8.9, 4.6 Hz, 1H), 3.67 (t, J = 8.9 Hz, 1H), 3.88 (dd, J = 12.2, 4.6 Hz, 1H), 6.70–6.78 (m, 2H), 7.43–7.61 (m, 6H), 7.68–7.77 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 31.4, 36.9 (d, J = 68.0 Hz), 65.3, 74.7, 75.9, 85.6, 105.5 (d, J = 20.3 Hz), 111.1 (d, J = 20.4 Hz), 129.0 (d, J = 12.0 Hz), 129.1 (d, J = 12.0 Hz), 130.0 (d, J = 101 Hz), 130.5 (d, J = 9.6 Hz), 131.0 (d, J = 9.6 Hz), 131.6 (d, J = 107 Hz), 132.5, 132.5, 141.0 (dd, J = 8.4, 3.6 Hz), 142.5 (dd, J = 241, 13.2 Hz), 146.6 (dd, J = 9.6, 2.4 Hz), 147.4 (dd, J = 244, 13.2 Hz); ^{31}P NMR (202 MHz, CDCl_3) δ 34.1; ^{19}F NMR (470 MHz, CDCl_3) δ –149.8 (dt, J = 23.0, 11.3 Hz), –142.1 (dt, J = 20.2, 11.8 Hz); ESI-MS m/z 483 (M + Na); FAB-HRMS calcd for $\text{C}_{24}\text{H}_{24}\text{F}_2\text{O}_5\text{P}$ (M + H) 461.1329, found 461.1322.

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Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of **1a**, **1b**, **7**, **9**, and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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