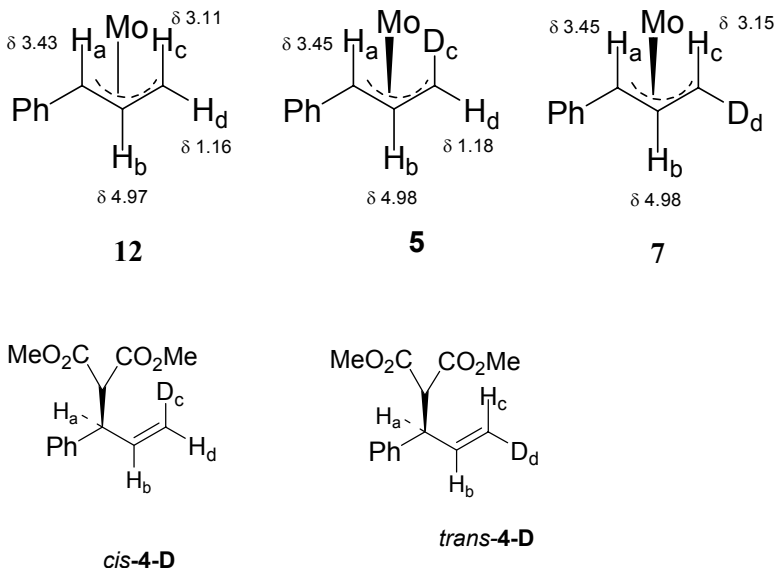


## Supporting Text

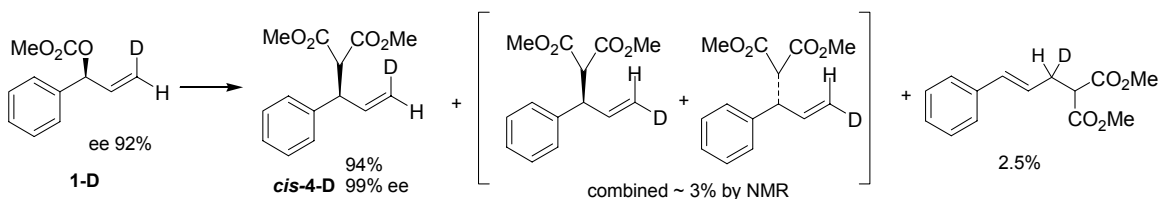


**Stoichiometric Reaction of Branched Carbonate 2-D.** The reaction was carried out similarly to that for 1-D with comparable reaction times. For  $\pi$ -allyl complex formation,  $^1\text{H}$  NMR analysis indicated 50% conversion to the complex in 5 h, and 90% conversion in 22 h. (The conversion is based on the ratio of complex 11 to  $\pi$ -allyl complex. Since the reaction stoichiometry (1) is 2 mol of complex 11 affording 1 mol each of  $\pi$ -allyl complex, free ligand, and molybdenum hexacarbonyl, the maximum yield of  $\pi$ -allyl complex is 50% based on complex 11.) Relative to the protio complex (12), the signal at 1.16 ppm was nearly absent ( $\sim$ 5%, corresponding to the level of the minor enantiomer in 2-D), confirming the location of the deuterium in the complex as that shown in complex 7.  $^1\text{H}$  NMR analysis of the product mixture after addition of sodium dimethyl malonate (5.5 h at 50°C) indicated complete conversion to 95% *trans*-4-D and  $\sim$ 5% *cis*-4-D, the ratio corresponding to the enantiomeric ratio of the initial carbonate 2-D. Relative to the protio product, the resonance at 4.99 ppm due to H<sub>d</sub> is absent in *trans*-4-D, and H<sub>c</sub> at 5.03 ppm is collapsed to doublet of doublets with a coupling constant of 16.8 Hz consistent with a *trans*-orientation relative to H<sub>b</sub>. [There is also a small ( $<1\text{Hz}$ ) coupling to H<sub>a</sub>.] A 0.1-ml sample of the reaction mixture was added to 2 ml of 10% *i*-PrOH/90% hexanes and 2 ml of 0.5 M HCl. The organic layer was filtered, and a chiral HPLC analysis (2) of this solution was carried out with a Whelko column. The enantiomeric excess (ee) of combined products *trans*-4-D and *cis*-4-D was 98%.

**Stoichiometric Reaction of Linear Carbonate 3.** Complex 11 was formed as follows: the ligand (11.7 mg, 0.036 mmol) and 0.7 ml tetrahydrofuran (THF)-*d*<sub>8</sub> were placed in an NMR tube with a Teflon valve, and the solution was degassed by passing a stream of argon through the solution for 2 min. Molybdenum tetracarbonyl norbornadiene (10.8 mg, 0.036 mmol) was added, and the resulting red solution was held at ambient

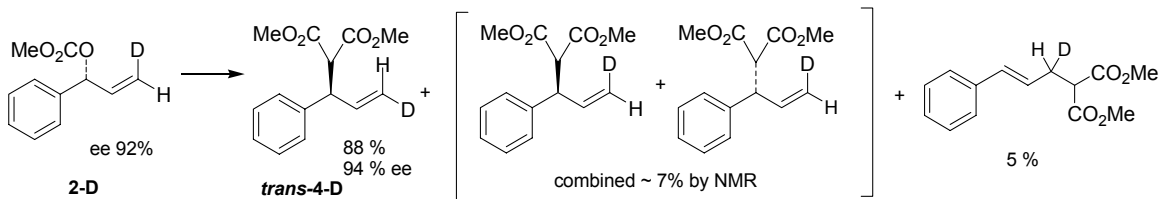
temperature for 50 min.  $^1\text{H}$  NMR analysis confirmed 90% conversion to complex **11**. Linear carbonate **3** (6.0 mg, 0.031 mmol, 92% ee) was added, and the solution was held at room temperature for 22 h.  $^1\text{H}$  NMR analysis showed only 12% conversion to the  $\pi$ -allyl complex. The reaction was placed in an oil bath at 55°C; it gave 35% conversion to the complex in 2.7 h and 75% conversion in 9.5h. (The conversion is based on the ratio of complex **11** to  $\pi$ -allyl complex. Because the reaction stoichiometry (1) is 2 mol of complex **11**, affording 1 mol each of  $\pi$ -allyl complex, free ligand, and molybdenum hexacarbonyl, the maximum yield of  $\pi$ -allyl complex is 50% based on complex **11**.)  $^1\text{H}$  NMR analysis indicated a 96:4 ratio of complexes **7/5**. Solid sodium dimethyl malonate (12 mg, 0.078 mmol) was added, and the reaction was heated in an oil bath at 50°C for 14 h to give complete reaction. The product ratio was 95% *trans*-**4-D**/5% *cis*-**4-D**.

### Catalytic Reaction of Branched Carbonate 1-D.



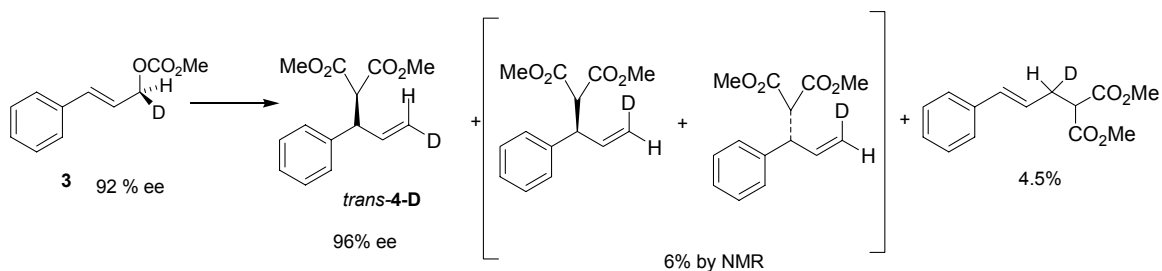
See main text for details.

### Catalytic Reaction of Branched Carbonate 2-D.



Complex **11** was formed in THF- $d_8$  (0.8 ml) from ligand (3.1 mg, 0.0095 mmol) and molybdenum tetracarbonyl norbornadiene (2.9 mg, 0.0097), and held at ambient temperature for 1.5 h to provide 85% complex **11** and 15% unreacted ligand. Carbonate **2-D** (12.0 mg, 0.063 mmol) and solid sodium dimethyl malonate (12 mg, 0.078 mmol) were added and the reaction was heated in an oil bath at 50°C.  $^1\text{H}$  NMR analysis showed 75% conversion in 6.3 h and 95% conversion in 23 h. The major product (88%) was *trans*-**4-D**. HPLC analysis indicated 94% ee.

### Catalytic Reaction of Linear Carbonate 3.



Complex **11** was formed in THF-*d*<sub>8</sub> (1.6 ml) from ligand (7.5 mg, 0.023 mmol) and molybdenum tetracarbonyl norbornadiene (7.0 mg, 0.023) and held at ambient temperature for 1 h to provide 90% complex **11** and 10% unreacted ligand. Carbonate **3** (23.0 mg, 0.12 mmol) and solid sodium dimethyl malonate (22.5 mg, 0.146 mmol) were added. The mixture was sonicated for a few minutes to dissolve the sodium dimethyl malonate. The mixture was heated in an oil bath at 60–65°C. <sup>1</sup>H NMR analysis showed 60% conversion in 8.5 h, 90% conversion in 21 h, and 96% conversion in 33 h. The major product (89%) was *trans*-**4-D**.

## Procedures for Competition Experiments

**Competition Experiment 1.** Complex **11** was formed in acetonitrile (0.9 ml) from ligand (3.2 mg, 0.01 mmol) and molybdenum tetracarbonyl norbornadiene (1.6 mg, 0.0053 mmol) and held at ambient temperature for 1.5 h. Separately, A slurry of the sodium salt of dimethyl methylmalonate was prepared from sodium hydride (113 mg of 60% NaH, 2.82 mmol) and dimethyl methylmalonate (527 mg, 3.60 mmol) in acetonitrile (6 ml); three vacuum/Ar purge cycles at ambient temperature were followed by heating at 60°C for 0.5 h to complete conversion to the sodium salt. To the solution of complex **11** was added (*R*)-3-fluorophenyl carbonate **2b** (11.6 mg, 0.055 mmol) and 0.4 ml of the slurry of the sodium salt of dimethyl methylmalonate (0.19 mmol). The resulting heterogeneous mixture was warmed in a bath held at 62°C for 20 min. HPLC assay at this point indicated 15% conversion to product. At the 20-min time point, 4.8 mg of the  $\pi$ -allyl complex (**12**) was added and the reaction was held for 15 h in the 62°C bath. HPLC assay of the crude reaction mixture indicated >95% conversion to product with a 76% ee for the 3-F product and a 96% ee for the phenyl product, with a ratio of 3-F to Ph product of 4:1. The mixture was chromatographed by using 15 g of silica and an eluent of 8% EtOAc in hexanes to provide a mixture of the two products (14 mg) with an ee the same as the crude reaction mixture.

*HPLC Assay Conditions.* ChiralPak AD column, 4.6 × 25 mm; 1.0 ml/min flow; 220 nm detection; 30°C column temperature; gradient from 0.7% *i*-PrOH/hexanes to 1.0% *i*-PrOH/hexanes over 20 min; retention times: (*R*)-phenyl product (major), 6.9 min; (*S*)-phenyl product (minor), 15 min; (*R*)-3-fluorophenyl product (major), 7.1 min; (*S*)-3-fluorophenyl product (minor), 18 min.

**Competition Experiment 2.** Complex **11** was formed in acetonitrile (0.8 ml) from ligand (2.7 mg, 0.008 mmol) and molybdenum tetracarbonyl norbornadiene (1.7 mg, 0.0056 mmol) and held at ambient temperature for 1.5 h. To the solution of complex **11** was added (*R*)-3-fluorophenyl carbonate **2b** (11.0 mg, 0.052 mmol) and 0.3 ml of the slurry of the sodium salt of dimethyl methylmalonate (0.14 mmol) prepared as described in the preceding paragraph. The resulting heterogeneous mixture was warmed in a bath held at 62°C for 100 min. HPLC assay at this point indicated 46% conversion to product with an ee of 80%. At the 100-min time point, 9.0 mg of the  $\pi$ -allyl complex (**12**) was added and the reaction was held for 16 h in the 62°C bath. HPLC assay of the crude reaction mixture indicated >99% conversion to product with a 79% ee for the 3-F product and a 96% ee for the phenyl product, with a ratio of 3-F to Ph product of 3:1. The mixture was chromatographed by using 20 g of silica and an eluent of 8% EtOAc in hexanes to provide a mixture of the two products (13 mg) having an ee the same as the crude reaction mixture.

1. Krska, S. W., Hughes, D. L., Reamer, R. A., Mathre, D. J., Sun, Y. & Trost, B. M. (2002) *J. Am. Chem. Soc.* **124**, 12656–12657.
2. Hughes, D. L., Palucki, M., Yasuda, N., Reamer, R. A. & Reider, P. J. (2002) *J. Org. Chem.* **67**, 2762–2768.