Dirhodium(II) Tetra(*N*-(dodecylbenzenesulfonyl)prolinate) Catalyzed Enantioselective Cyclopropenation of Alkynes

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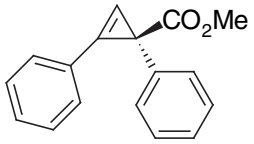
Supporting Information

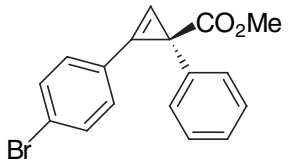
General Methods: ^{1}H NMR spectra were run at either 300, 400, or 500 MHz, and ^{13}C NMR at either 75 or 125 MHz in $CDCl_3$ unless otherwise noted. Mass spectral determinations were carried out at 70 eV. Melting points were uncorrected. IR spectra were obtained using a Nicolet Impact series 420 IR. Optical rotations were measured using a Jaso DIP-370 digital polarimeter. Glasswares were flame dried prior to use. Solvent hexanes were distilled over sodium with triglyme and benzophenone. Reactions were carried out under an atmosphere of argon. Elemental analysis performed by Atlantic Microlab, Inc.; Norcoss, Georgia. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). Commercially available reagents were used without additional purification unless noted. Rh_2(*S*-DOSP)$_4$ (**1**) was prepared by following the literature procedure.[1]

General procedure for Rhodium(II)-Catalyzed Decompositions of Methyl Phenyldiazoacetate in the Presence of Alkynes: A mixture of alkyne (2.5 — 10.0 equiv) and Rh(II) catalyst (0.01 equiv) in 10 mL of hexane was stirred at room temperature under an argon atmosphere. To this solution was added the methyl phenyldiazoacetate (1 equiv, 0.5 mmol) in 5 mL of hexane via syringe pump over 5 h, and the mixture was then

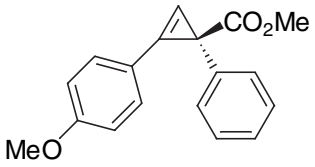
stirred for 8 h. The mixture was then concentrated *in vacuo*, and the residue was purified on silica using ether/pentane as the eluent in the ratio specified in parenthesis.



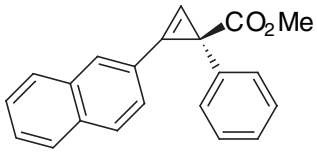
(1*R*)-1,2-Diphenyl-cycloprop-2-enecarboxylic acid methyl ester (2). 10.0 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 10:1) gave compound **2** in 62% yield (31 mg). 90% ee (determined by HPLC (*S*, *S*)-Whelk 10% i-PrOH in hexanes). $[\alpha]^{25}_D$ +41.980° (*c* 1.77, $CHCl_3$); IR (neat) 1721, 1449, 1215 cm^{-1}; ^{1}H-NMR (400 MHz) δ 7.61 (m, 2H), 7.41-7.36 (m, 5H), 7.26 (t, 2H, *J* = 7.2 Hz), 7.20 (m, 2H), 3.71 (s, 3H); ^{13}C-NMR (125 MHz) δ 175.0, 140.8, 129.9, 129.8, 128.8, 128.1, 128.0, 126.4, 125.3, 117.2, 100.2, 52.1, 33.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{14}O_2$, 250.0988, found 250.0991.



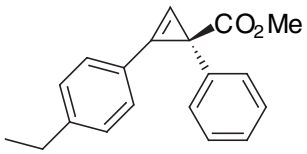
(1*R*)-2-(4-Bromo-phenyl)-1-phenyl-cycloprop-2-enecarboxylic acid methyl ester (3). 10.0 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 10:1) gave compound **3** in 63% yield (95.3 mg) as a white shiny solid. 92% ee (determined by HPLC: (S, S)-Whelk, 10% i-PrOH in hexanes). $[\alpha]^{25}_D$ +45.348° (*c* 0.86, $CHCl_3$); IR (neat) 1721, 1428, 1231 cm^{-1}; ^{1}H-NMR (500 MHz) δ 7.56 (d, 2H, *J* = 8.5 Hz), 7.47 (d, 2H, *J* = 8.5 Hz), 7.34 (d, 2H, *J* = 7.5 Hz), 7.3 — 7.2 (m, 4H), 3.72 (s, 3H); ^{13}C-NMR (125 MHz) δ 174.6, 140.4, 132.1, 131.2, 128.1, 128.0, 126.6, 124.3, 116.5, 101.2, 101.2, 52.2, 33.5. Anal. Calc for $C_{17}H_{13}BrO_2$: C, 62.03; H, 3.98. Found: C, 62.02; H, 4.01.



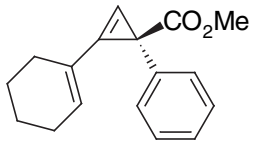
(1*R*)-2-(4-Methoxy-phenyl)-1-phenyl-cycloprop-2-enecarboxylic acid methyl ester (4). 10.0 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 7:1) gave compound **4** in 67% yield (93.7 mg). 86% ee (determined by HPLC (S, S)-Whelk, 10% I-PrOH in hexanes). $[\alpha]^{25}_D$ +47.096° (*c* 4.65, $CHCl_3$); IR (neat) 1726, 1433, 1252 cm^{-1}; ^{1}H-NMR (500 MHz) δ 7.55 (d, 2H, *J* = 8.5 Hz), 7.36 (d, 2H, *J* = 7.0 Hz), 7.26 (t, 2H, *J* = 7.5 Hz), 7.19 (t, 1H, *J* = 7.5 Hz), 7.05 (s, 1H), 6.94 (d, 2H, *J* = 9.0 Hz), 3.83 (s, 3H), 3.71 (s, 3H); ^{13}C-NMR (125 MHz) δ 175.2, 160.9, 141.0, 131.5, 128.1, 127.9, 126.3, 117.9, 116.5, 114.3, 97.4, 55.3, 52.1, 33.3. HRMS (ESI) *m/z* calcd for $C_{18}H_{16}O_3$, 280.1094, found 280.1095.



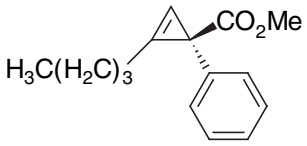
(1*R*)-2-Naphthalen-2-yl-1-phenyl-cycloprop-2-enecarboxylic acid methyl ester (5). 10.0 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 10:1) gave compound **5** in 60% yield (90 mg) as a white solid. 96% ee (determined by HPLC: (S, S)-Whelk, 10% i-PrOH in hexanes). $[\alpha]^{25}_D$ —30.399 (*c* 0.25, $CHCl_3$); IR (neat) 1715, 1438, 1215 cm^{-1}; ^{1}H-NMR (300 MHz) δ 8.42 (d, 1H, *J* = 8.1 Hz), 7.90 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 1H, *J* = 6.9 Hz), 7.66-7.45 (m, 6H), 3.73 (s, 3H); ^{13}C-NMR (75 MHz) δ 174.8, 140.7, 133.5, 132.2, 130.7, 129.7, 128.5, 128.1, 128.0, 127.3, 126.4, 126.3, 125.4, 124.4, 121.6, 115.2, 102.7, 52.1, 31.9. Anal. Calc for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.68; H, 5.40.



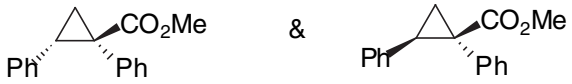
(1*R*)-2-(4-Ethyl-phenyl)-1-phenyl-cycloprop-2-enecarboxylic acid methyl ester (6). 10.0 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 10:1) gave compound **6** in 48% yield (67 mg) as oil. 87% ee (determined by HPLC: (S, S)-Whelk, 10% i-PrOH in hexanes). $[\alpha]^{25}_D$ +41.445° (*c* 0.83, $CHCl_3$); IR (neat) 1721, 1438, 1215 cm^{-1}; ^{1}H-NMR (300 MHz) δ 7.55 (d, 2H, *J* = 7.8 Hz), 7.38 (d, 2H, *J* = 7.2 Hz), 7.30-7.19 (m, 5H), 7.13 (s, 1H), 3.70 (s, 3H) 2.65 (q, 2H, *J* = 7.5 Hz), 1.23 (t, 3H, *J* = 7.5 Hz); ^{13}C-NMR (75 MHz) δ 175.1, 146.6, 130.0, 129.9, 128.4, 128.1, 128.0, 126.4, 122.8, 117.1, 99.1, 52.1, 33.4, 28.9, 15.3. HRMS (ESI) *m/z* calcd for $C_{19}H_{18}O_2$, 278.1301, found 278.13049.



(1*R*)-2-Cyclohex-1-enyl-1-phenyl-cyclopro-2-enecarboxylic acid methyl ester (7). 10.0 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 15:1) gave compound **7** in 74% yield (93.6 mg). 92% ee (determined by HPLC: (S, S)-Whelk, 10% i-PrOH in hexanes). $[\alpha]^{25}_D$ +12.860° (*c* 2.11, $CHCl_3$); IR (neat) 1721, 1433, 1220 cm^{-1}; ^{1}H-NMR (500 MHz) δ 7.33-7.25 (m, 4H), 7.20 (t, 1H, *J* = 7.0 Hz), 6.85 (s, 1H), 6.23 (s, 1H), 3.69 (s, 3H) 2.37 (dd, 1H, *J* = 2.5, 2.0 Hz), 2.25 (dt, 1H, *J* = 1.5, 8.5 Hz), 2.18 (d, 2H, *J* = 2.5 Hz), 1.70 (tt, 2H, *J* = 6.0, 3.0 Hz), 1.63 (tt, 2H, *J* = 6.0, 3.0 Hz); ^{13}C-NMR (75 MHz) δ 175.2, 141.2, 135.9, 128.2, 127.8, 126.1, 124.2, 118.7, 97.7, 51.9, 33.3, 26.7, 25.6, 22.0, 21.6. HRMS (ESI) *m/z* calcd for $C_{17}H_{18}O_2$, 254.1301, found 254.1307.

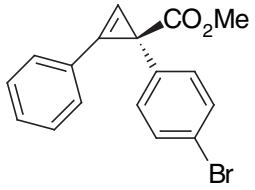


(1R)-2-Butyl-1-phenyl-cycloporp-2-enecarboxylic acid methyl ester (8). 10.0 equivalent of alkyne was used. Purification by silica gel column chromatography (dichloromethane) gave compound **8** in 51% yield (234.5 mg). 84% ee (determined by HPLC: chiracel OJ, 1% i-PrOH in hexanes). $[\alpha]^{25}_{D}$ –10.378° (*c* 4.35, $CHCl_3$); ^{1}H-NMR (500 MHz) δ 7.28-7.27 (m, 4H), 7.20-7.17 (m, 1H), 6.66 (s, 1H), 3.67 (s, 3H), 2.55 (t, 2H, *J* = 7.5 Hz), 1.57 (t, 2H, *J* = 7.5 Hz), 1.39-1.33 (m, 2H), 0.87 (t, 3H, *J* = 7.5 Hz). ^{1}H NMR data consistent with published data.[2]

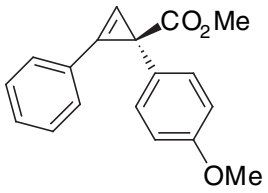


1,2-Diphenyl-cyclopropanecarboxylic acid methyl ester (9a & 9b). To dipotassium azodicarboxylate,[3] prepared from azodicarbonamide (52 mg, 0.26 mmol) in dry THF, was added 0.13 mmol of **1** in THF. Acetic acid was added in portions of 2.5 mL over a period of 15 min, and the resulting mixture was stirred overnight at 25 °C. After dilution with water, the mixture was washed three times with 100 mL portions of CH_2Cl_2. The combined dichloromethane solution was washed with water until the aqueous extract was neutral, dried over anhydrous $MgSO_4$, and concentrated. Two diastereomers were purified by silica gel column chromatography (pentane/Et_2O, 8:1) gave compound **9a** in 12% yield (4 mg). $[\alpha]^{25}_{D}$ —20.0°(*c* 0.15, $CHCl_3$); lit[3] $[\alpha]^{25}_{D}$ —28.5°(*c* 1.1, $CHCl_3$) for 89% ee. ^{1}H-NMR (500 MHz) δ 7.16-6.99 (m, 8H), 6.73 (m, 2H), 3.65 (s, 3H), 3.11 (dd, 1H, *J* = 9.4, 7.3 Hz), 2.15 (dd, 1H, *J* = 9.4, 4.9 Hz), 1.87 (dd, 1H, *J* = 7.3, 4.9 Hz). ^{1}H NMR data are consistent with published data.[4] Compound 9b was formed in 13% yield

(4.4 mg). ^{1}H-NMR (500 MHz) δ 7.51 (d, 2H, *J* = 8.5 Hz), 7.38-7.22 (m, 8H), 3.30 (s, 3H), 2.87 (t, 1H, *J* = 10.0 Hz), 2.33 (dd, 1H, *J* = 4.5, 2.5 Hz), 1.62 (dd, 1H, *J* = 5.5, 4.0 Hz). ^{1}H NMR data are consistent with published data.[5]

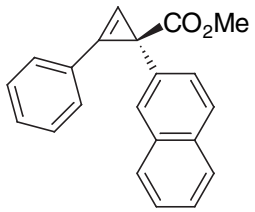


(1*R*)-1-(4-Bromo-phenyl)-2-phenyl-cycloprop-2-enecarboxylic acid methyl ester (10). 2.5 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 10:1) gave compound **10** in 62% yield (243.2 mg) as a white shiny solid. 88% ee (determined by HPLC: (S, S)-Whelk, 10% i-PrOH in hexanes). $[\alpha]^{25}_D$ +51.276° (*c* 1.88, $CHCl_3$); IR (neat) 1721, 1486, 1209 cm^{-1}; ^{1}H-NMR (400 MHz) δ 7.58 (dd, 2H, *J* = 2.0, 8.0 Hz), 7.43-7.37 (m, 5H), 7.25 (d, 2H, *J* = 8.0 Hz), 7.16 (s, 1H), 3.70 (s, 3H); ^{13}C-NMR (75 MHz) δ 174.5, 139.9, 131.1, 130.2, 129.9, 129.8, 128.9, 125.0, 120.3, 116.9, 99.7, 52.2, 32.9. Anal. Calc for $C_{17}H_{13}BrO_2$: C, 62.03; H, 3.98. Found: C, 61.79; H, 4.04.

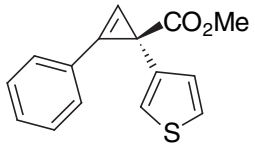


(1*R*)-1-(4-Methoxy-phenyl)-2-phenyl-cycloprop-2-enecarboxylic acid methyl ester (11). 2.5 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 7:1 to DCM/hexane, 2:1) gave compound **11** in 12% yield (17.2 mg). 73% ee (determined by HPLC (S, S)-Whelk, 15% I-PrOH in hexanes). $[\alpha]^{25}_D$ +25.123° (*c* 0.60, $CHCl_3$); IR (neat) 1721, 1444, 1257 cm^{-1}; ^{1}H-NMR (500 MHz) δ 7.61 (d, 2H, *J* = 6.5 Hz), 7.43-7.37 (m, 3H), 7.30 (d, 2H, *J* = 8.5 Hz), 7.20 (s, 1H), 6.82 (d, 2H, *J* = 8.5 Hz), 3.77 (s, 3H), 3.70 (s, 3H); ^{13}C-NMR (125 MHz) δ 175.3, 158.2,

133.0, 129.9, 129.8, 129.3, 128.8, 125.4, 117.5, 113.5, 100.5, 55.2, 52.2, 32.8. HRMS (ESI) *m/z* calcd for $C_{18}H_{16}O_3$, 280.1094, found 280.1100.



(1*R*)-1-Naphthalen-2-yl-2-phenyl-cycloprop-2-enecarboxylic acid methyl ester (12). 2.5 equivalent of alkyne was used. Purification by silica gel column chromatography (pentane/Et_2O, 10:1) gave compound **12** in 55% yield (165.4 mg) as a white shiny solid. 86% ee (determined by HPLC: (S, S)-Whelk, 10% i-PrOH in hexanes). $[\alpha]^{25}_D$ +51.999° (*c* 0.05, $CHCl_3$); IR (neat) 1721, 1433, 1247 cm^{-1}; ^{1}H-NMR (400 MHz) δ 7.79-7.73 (m, 4H), 7.64 (dd, 2H, *J* = 2.0, 8.0 Hz), 7.53 (dd, 1H, *J* = 1.6, 8.4 Hz), 7.44 — 7.38 (m, 5H), 7.28 (s, 1H), 3.73 (s, 3H); ^{13}C-NMR (125 MHz) δ 174.9, 138.4, 133.2, 132.1, 129.9, 129.8, 128.8, 127.6, 127.4, 127.4, 126.6, 126.5, 125.8, 125.4, 125.2, 117.4, 100.0, 52.1, 33.6. HRMS (ESI) *m/z* calcd for $C_{21}H_{16}O_2$, 300.1145, found 300.1139.



(1R)-2-Phenyl-1-thiophen-3-yl-cycloprop-2-enecarboxylic acid methyl ester (13). 2.5 equivalent of alkyne was used. Purification by silica gel chromatography (pentane/Et_2O, 10:1) gave compound **13** in 57% yield (72.6 mg). 88% ee (determined by HPLC: (R, R)-Whelk, 5% i-PrOH in hexanes). $[\alpha]^{25}_D$ +61.599° (*c* 0.75, $CHCl_3$); IR (neat) 1719, 1446, 1275, 1219, 1173 cm^{-1}; ^{1}H-NMR (500 MHz) δ 7.58 (dd, 2H, *J* = 1.5, 7.5 Hz),

7.41-7.39 (m, 3H), 7.34 (dd, 1H, J = 1.5, 3.0 Hz), 7.19 (dd, 1H, J = 3.0, 5.0 Hz), 7.10 (s, 1H), 7.04 (dd, 1H, J = 1.5, 4.5 Hz), 3.72 (s, 3H); ^{13}C-NMR (125 MHz) δ 174.6, 142.3, 130.0, 129.9, 128.8, 127.9, 124.9, 124.5, 121.8, 115.6, 99.8, 52.1, 33.1. HRMS (ESI) *m/z* calcd for $[C_{15}H_{12}SO_2Na]^+$, (M^+ + Na), 279.0450, found 279.0446.

General procedures for competition studies: An equimolar (10.0 equiv.: 10.0 equiv.) solution of phenylacetylene and alkyne in solvent was stirred with Rh(II) catalyst (0.01 equiv.) at room temperature under an argon atmosphere. To this solution was added diazo (1.0 equiv.) in solvent over 5 h and the reaction mixture was then stirred for a further 8 h. The solvent was removed by reduced pressure. The ratio of products was determined from ^{1}H-NMR (500 MHz) of the crude reaction residue.

References:

1. (a) Davies, H. M. L.; Bruzinski, P.; Hutchenson, D. K.; Kong, N.; Fall, M. J. J. Am. Chem. Soc. 1996, 118, 6897. (b) Bruzinski, P. R., Ph. D., Thesis, 1997, University at Buffalo, SUNY Buffalo, NY 14260.
2. Mueller, P.; Graenicher, C. *Helv. Chim. Acta*. **1993**, *76*, 521.
3. Pasto, J.; Taylor, R. T. *Org. React*. (*N. Y.*) **1991**, *40*, 91.
4. (a) Davies, H. M. L.; Bruzinski, P. R.; Fall, M. J. *Tetrahedron Lett*. **1996**, *37*, 4133. Optical rotation of **9a** was reported in Dr. Bruzinski s Ph. D. thesis (Ref. 1b).
5. Starmans, W. A. J.; Thijs, L.; Zwanenburg, B. *Tetrahedron* **1998**, *54*, 629.