Supporting Information

Transition Metal-Catalyzed Aldehydic C–H Activation by Azodicarboxylates

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Experimental Section

Typical experimental procedure

General. All reactions were monitored by thin-layer chromatography (TLC) using precoated Silica Gel plates. Yields refer to chromatographically and spectroscopically pure compounds, except as noted. Proton and carbon-13 NMR spectra were recorded on 250 and 300 MHz spectrometers. Proton and carbon-13 chemical shifts are reported in δ values relative to the internal standard, tetramethylsilane (TMS). High resolution mass spectra were obtained using Leu5-enkephalin or erythromycin as a lock mass on a LCT ESI-TOF spectrometer.

Typical Procedure for the Synthesis of 7a-o. A solution of **6a** (150 mg, 2.6 mmol), **1a** (522 mg, 2.6 mmol), and $[\text{Rh}(\text{OAc})_2]_2$ (23 mg, 0.5 mmol) in ethyl acetate (2.6 mL) was stirred at room temperature. Once complete, the solution was evaporated and the residue purified by column chromatography on silica gel using hexane:ethyl acetate (6:1) as the eluent to yield **7a** (652 mg, 97%).

Hydroacylation Product 2 (84%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 6.60 (bs, 1 H), δ 5.10-4.91 (m, 2 H), δ 2.89 (t, $J = 6.9$ Hz, 2 H), δ 1.64-

1.62 (m, 2 H), δ 1.35-1.27 (m, 16 H), δ .90 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 174.1, 155.3, 152.8, 72.3, 70.6, 37.2, 31.5, 24.5, 22.6, 22.1, 21.9, 14.1; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 325.1739, found: 325.1734.

THF-adduct 3: ^1H NMR (CDCl_3 , 300 MHz) δ 6.53 (s, 1 H), δ 6.01 (bs, 1 H), δ 4.96 (sept, J = 6 Hz, 2 H), δ 3.99 (q, J = 6.9 Hz, 1 H), δ 3.76 (q, J = 6.9 Hz, 1 H), δ 2.06-1.81 (m, 4 H), δ 1.27-1.25 (m, 12 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 156.5, 155.1, 87.5, 70.6, 69.8, 68.7, 28.4, 25.4, 22.1, 22.0; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 297.1426, found: 297.1412.

Ether-adduct 4: ^1H NMR (CDCl_3 , 300 MHz) δ 6.48 (s, 1 H), δ 5.61-5.45 (m, 1 H), δ 4.96 (sept, J = 6 Hz, 2 H), δ 3.47 (bs, 2 H), δ 1.34 (d, J = 5.7 Hz, 2 H), δ 1.27 (d, J = 5.7 Hz, 12 H), δ 1.18 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 156.3, 155.5, 82.4, 70.3, 69.6, 69.4, 22.1, 18.7, 18.1, 15.1; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{24}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 299.1583, found: 299.1597.

1,4-Dioxane-adduct 5: ^1H NMR (CDCl_3 , 300 MHz) δ 6.74-6.62 (bm, 1 H), δ 5.50 (bs, 1 H), δ 5.02-4.93 (m, 2 H), δ 3.94-3.83 (m, 3 H), δ 3.68-3.50 (m, 3 H), δ 1.27 (d, J = 6 Hz, 12 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ

156.4, 154.7, 80.9, 71.2, 70.1, 67.5, 66.8, 65.7, 22.1, 22.0, 21.9; HRMS (ESI) calcd for $C_{12}H_{22}N_2O_6(M+Na)^+$ 313.1376, found: 313.1386.

Hydroacylation Product 7a (97%, oil): 1H NMR ($CDCl_3$, 300 MHz) δ 6.92 (s, 1 H), δ 5.10-4.91 (m, 2 H), δ 2.91 (bq, $J = 6.6$ Hz, 2 H), δ 1.32 (d, $J = 6.3$ Hz, 6 H), δ 1.27 (bs, 6 H), δ 1.17 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 174.8, 155.3, 152.8, 72.1, 70.4, 30.6, 22.0, 21.8, 15.1, 8.9; HRMS (ESI) calcd for $C_{11}H_{20}N_2O_5(M+Na)^+$ 283.1270, found: 283.1281.

Hydroacylation Product 7b (R = *i*-Pr) (77%, oil): 1H NMR ($CDCl_3$, 300 MHz) δ 7.00 (s, 1 H), δ 5.86-5.73 (m, 1 H), δ 5.10-4.90 (m, 4 H), δ 2.90 (t, $J = 6.3$ Hz, 2 H), δ 2.12 (q, $J = 7.2$ Hz, 2 H), δ 1.77 (p, $J = 7.5$ Hz, 2 H), δ 1.32 (d, $J = 6.3$ Hz), δ 1.27 (bs, 6 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 173.8, 155.2, 152.7, 137.9, 115.3, 72.1, 70.3, 36.3, 33.0, 23.8, 21.9, 21.7; HRMS (ESI) calcd for $C_{14}H_{24}N_2O_5(M+Na)^+$ 301.1763, found: 301.1758.

Hydroacylation Product 7b (R = Bn) (68%, solid): 1H NMR ($CDCl_3$, 300 MHz) δ 7.32 (bs, 10 H), δ 6.96 (bs, 1 H), δ 5.82-5.69 (m, 1 H), δ 5.21 (s, 2 H), δ 5.14 (s, 2 H), δ 5.00 (d, $J = 15.9$ Hz), δ 4.96 (d, $J = 9.3$ Hz, 1 H), δ 2.89 (bs, 2 H), δ 2.07 (bd, $J = 6.3$ Hz, 2 H), δ 1.74 (bt, $J = 6.6$ Hz, 2

H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 173.6, 155.6, 153.2, 137.9, 135.5, 134.9, 128.8, 128.8, 128.7, 128.6, 128.3, 127.7, 127.1, 115.5, 69.3, 68.2, 65.4, 35.4, 33.0, 23.8; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 419.1583, found: 419.1590.

Hydroacylation Product 7c (R = *i*-Pr) (74%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 7.04 (s, 1H), δ 5.04 (sept, J = 6.3 Hz, 1 H), δ 4.97 (sept, J = 6.3 Hz, 1 H), δ 3.05-3.01 (m, 2 H), δ 2.28 (td, J = 6.9, 2.7 Hz, 2 H), δ 1.99 (t, J = 2.7 Hz, 1 H), δ 1.89 (p, J = 6.9 Hz, 2 H), δ 1.32 (d, J = 6.3 Hz, 6 H), δ 1.28 (d, J = 6.0 Hz, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 173.3, 155.2, 152.6, 83.5, 72.2, 70.3, 69.2, 35.8, 23.4, 21.9, 21.7, 17.7; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 321.1426, found: 321.1412.

Hydroacylation Product 7c (R = Bn) (76%, solid): ^1H NMR (CDCl_3 , 300 MHz) δ 7.31-7.26 (m, 11 H), δ 5.18 (s, 2 H), δ 5.10 (s, 2 H), δ 2.98 (bs, 2 H), δ 2.19 (bs, 2 H), δ 1.94 (bt, J = 2.4 Hz, 1 H), δ 1.82 (bt, J = 6.6 Hz, 2 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 173.1, 155.5, 153.0, 135.4, 134.7, 128.7, 128.6, 128.5, 128.4, 128.1, 127.5, 127.0, 83.5, 69.3, 69.2, 68.0, 35.7, 23.3, 17.7; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 417.1426, found: 417.1423.

Hydroacylation Product 7d (81%, crystal): ^1H NMR (CDCl_3 , 300 MHz) δ 7.29-7.15 (m, 5 H), δ 6.91 (bs, 1 H), δ 5.08-4.90 (m, 2 H), δ 3.22 (t, $J = 7.5$ Hz, 2 H), δ 2.98 (t, $J = 7.5$ Hz, 2 H), δ 1.30 (d, $J = 6.3$ Hz, 6 H), δ 1.27 (bs, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 172.8, 154.9, 152.4, 140.5, 128.3, 128.2, 125.9, 71.9, 70.1, 38.5, 30.4, 21.7, 21.5, 14.8; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 359.1583, found: 359.1584.

Hydroacylation Product 7e (74%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 6.53 (bs, 1 H), δ 5.09-4.83 (m, 3 H), δ 2.95-2.82 (m, 2 H), δ 2.18-2.12 (m, 1 H), δ 1.49 (s, 3 H), δ 1.40 (s, 3 H), δ 1.33-1.19 (m, 14 H), δ .96 (d, $J = 6.6$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 173.4, 155.3, 152.8, 131.5, 124.6, 72.2, 70.4, 44.2, 37.0, 29.7, 25.8, 25.6, 22.0, 21.8, 19.7, 17.8; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 379.2209, found: 379.2203.

Hydroacylation Product 7f (70%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 6.78 (s, 1 H), δ 5.46-5.31 (m, 2 H), δ 5.10-4.91 (m, 2 H), δ 2.94 (bt, $J = 6.3$ Hz, 2 H), δ 2.40 (q, $J = 7.2$ Hz, 2 H), δ 2.04 (q, $J = 6.9$ Hz, 2 H), δ 1.37-1.29 (m, 18 H), δ .88 (t, $J = 6.3$ Hz, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 173.5, 155.3, 152.8, 131.6, 127.6, 72.3, 70.5, 37.2, 31.6, 29.4, 29.3, 27.3, 22.7, 22.6, 22.0, 21.8, 14.2; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 379.2209, found: 379.2209.

Hydroacylation Product 7g (81%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 6.79 (bs, 1 H), δ 5.11-4.90 (m, 2 H), δ 3.37 (tt, $J = 11.1$, 3 Hz, 1 H), δ 1.93 (bd, $J = 11.7$ Hz, 2 H), δ 1.79 (bd, $J = 11.7$ Hz, 2 H), δ 1.69 (bd, $J = 9.9$ Hz, 1 H), δ 1.46 (bd, $J = 10.8$ Hz, 2 H), δ 1.32 (d, $J = 6.3$ Hz, 6 H), δ 1.27 (bs, 6 H); ^{13}C NMR (CDCl_3 , 62.5 MHz) δ 180.9, 155.4, 152.8, 72.2, 70.4, 44.2, 42.9, 29.6, 29.0, 26.0, 25.9, 25.8, 25.5, 22.0, 21.9; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{26}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 337.1739, found: 379.1726.

Hydroacylation Product 7h (68%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 6.93 (bs, 1 H), δ 5.83-5.69 (m, 1 H), δ 5.09-4.95 (m, 4 H), δ 2.45 (d, $J = 7.8$ Hz, 2 H), δ 1.33-1.29 (m, 18 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 178.7, 155.8, 153.3, 134.4, 118.1, 72.3, 70.6, 45.5, 44.8, 25.3, 24.8, 22.0, 21.8; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{26}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 337.1739, found: 379.1727.

Hydroacylation Product 7i (84%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 7.14-7.02 (M, 2 H), δ 6.89 (bd, $J = 14.7$ Hz, 1 H), δ 6.87 (bs, 1 H), δ 5.10-4.91 (m, 2 H), δ 1.93 (dd, $J = 6.6$, 1.2 Hz, 3 H), δ 1.32 (d, $J = 6.3$ Hz, 6 H), δ 1.27 (bs, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 166.3, 155.3, 152.9, 145.9, 123.5, 72.1, 70.2, 21.9, 21.7, 18.5; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 295.1270, found: 295.1270.

Hydroacylation Product 7j (53%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 6.99 (bs, 1 H), δ 6.52 (bs, 1 H), δ 5.10-4.91 (m, 2 H), δ 2.56-2.47 (m, 2 H), δ 2.46-2.41 (m, 2 H), δ 2.12 (bs, 1 H), δ 1.32 (s, 3 H), δ 1.30 (d, J = 6.3 Hz, 6 H), δ 1.27 (d, J = 5.1 Hz, 6 H), δ .85 (s, 3 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 169.9, 155.3, 153.3, 143.7, 135.0, 72.1, 70.3, 43.3, 40.5, 40.3, 38.0, 32.3, 31.6, 26.0, 22.0, 21.8, 21.0; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_5$ ($\text{M}+\text{Na}$) $^+$ 375.1896, found: 375.1892.

Hydroacylation Product 7k (46%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 7.72 (d, J = 6.9 Hz, 2 H), δ 7.00 (bs, 1 H), δ 6.91 (dt, J = 9, 2.4 Hz, 2 H), δ 5.07-4.86 (m, 2 H), δ 3.86 (s, 3 H), δ 1.29 (d, J = 6.6 Hz, 6 H), δ 1.14 (d, J = 6 Hz, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz) δ 170.7, 163.2, 155.5, 153.4, 131.2, 127.1, 113.6, 72.4, 70.7, 55.6, 22.1, 21.9, 21.6; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_6$ ($\text{M}+\text{Na}$) $^+$ 361.1376, found: 361.1379.

Hydroacylation Product 7l (26%, oil): ^1H NMR (CDCl_3 , 300 MHz) δ 7.75 (d, J = 9 Hz, 1 H), δ 7.70 (d, J = 8.1 Hz, 1 H), δ 6.90 (d, J = 8.7 Hz, 1 H), δ 6.62 (d, J = 9 Hz, 2 H), δ 5.05-4.87 (m, 2 H), δ 3.04 (s, 6 H), δ 1.28 (d, J = 6 Hz, 6 H), δ 1.16 (d, J = 6 Hz, 6 H); ^{13}C NMR (CDCl_3 , 75.4 MHz)

δ 155.6, 153.9, 153.6, 112.3, 110.6, 71.9, 70.5, 40.2, 22.1, 21.8; HRMS (ESI) calcd for $C_{17}H_{25}N_3O_5$ (M+Na)⁺ 374.1692, found: 374.1709.

Hydroacylation Product 7m (48%, oil): ¹H NMR (CDCl₃, 300 MHz) δ 7.70 (bd, J = 6 Hz, 2 H), δ 7.5 (tt, J = 7.5, 1.2 Hz, 1 H), δ 7.41 (bt, J = 6.6 Hz, 2 H), δ 7.1 (bs, 1 H), δ 5.00 (sept, J = 6 Hz, 1 H), δ 4.90 (sept, J = 6.3 Hz, 1 H), δ 1.29 (d, J = 6.3 Hz, 6 H), δ 1.07 (d, J = 6 Hz, 6 H); ¹³C NMR (CDCl₃, 75.4 MHz) δ 171.1, 155.1, 152.7, 135.0, 131.7, 127.9, 72.2, 72.2, 70.4, 21.7, 21.1; HRMS (ESI) calcd for $C_{15}H_{20}N_2O_5$ (M+Na)⁺ 331.1270, found: 331.1284.

Hydroacylation Product 7n (45%, solid): ¹H NMR (CDCl₃, 300 MHz) δ 7.63 (D, J = 7.2 Hz, 2 H), δ 7.39 (d, J = 8.4 Hz, 2 H), δ 7.25 (bs, 1 H), δ 5.00 (sept, J = 6 Hz, 1 H), δ 4.91 (sept, J = 6 Hz, 1 H), δ 1.28 (d, J = 6 Hz, 6 H), δ 1.12 (d, J = 6 Hz, 6 H); ¹³C NMR (CDCl₃, 75.4 MHz) δ 170.3, 155.4, 152.9, 138.3, 133.7, 129.8, 128.6, 72.8, 70.9, 22.0, 21.5; HRMS (ESI) calcd for $C_{15}H_{19}ClN_2O_5$ (M+Na)⁺ 365.0880, found: 365.0865.

Hydroacylation Product 7o (78%, oil): ¹H NMR (CDCl₃, 300 MHz) δ 7.30 (bs, 3 H), δ 7.15 (bs, 1 H), δ 5.05 (sept, J = 6.3 Hz, 1 H), δ 4.92 (sept, J = 6 Hz, 1 H), δ 1.30 (bs, 6 H), δ 1.08 (bs, 6 H); ¹³C NMR (CDCl₃, 75.4 MHz) δ 164.2, 154.8, 151.2, 136.3, 131.2, 130.6, 127.6, 72.9, 70.7, 21.9

21.3; HRMS (ESI) calcd for $C_{15}H_{18}Cl_2N_2O_5$ (M+Na)⁺ 399.0490, found: 399.0499.

Product 8: ¹H NMR (CDCl₃, 300 MHz) δ 9.73 (s, 1 H), 7.71 (d, *J* = 8.7 Hz, 2 H), δ 6.89 (d, *J* = 8.7 Hz, 2 H), δ 6.67 (bs, 1 H), δ 5.18 (bs, 2 H), δ 4.98-4.88 (m, 2 H), δ 3.15 (s, 3 H), δ 1.26-1.15 (bm, 12 H); ¹³C NMR (CDCl₃, 75.4 MHz) δ 190.7, 155.7, 153.0, 132.0, 126.8, 112.2, 70.8, 70.2, 65.7, 22.1, 22.0, 21.7; HRMS (ESI) calcd for $C_{17}H_{25}N_3O_5$ (M+Na)⁺ 374.1612, found: 374.1709.

Product 9: ¹H NMR (CDCl₃, 300 MHz) δ 7.67 (d, *J* = 6.9 Hz, 2 H), δ 7.00 (bs, 1 H), δ 6.50 (bs, 1 H), δ 5.17 (bs, 2 H), δ 5.05-4.89 (m, 2 H), δ 3.11 (s, 3 H), δ 1.27 (d, *J* = 6 Hz, 6 H), δ 1.17 (d, *J* = 6.3 Hz, 6 H); ¹³C NMR (CDCl₃, 75.4 MHz) δ 170.8, 155.6, 153.7, 151.6, 131.5, 122.8, 111.5, 72.0, 70.5, 70.3, 66.0, 22.1, 21.7; HRMS (ESI) calcd for $C_{25}H_{39}N_5O_9$ (M+Na)⁺ 576.2645, found: 576.2625.

3

4

7d

7g

7h

7j

Inhibition Experiments

Uncatalyzed Reactions (Neat): To five separate reaction vessels containing propionaldehyde (50 mg, 0.86 mmol) and 0, 1.0, 2.5, 5.0, and 10.0 mol% of radical scavenger, 4,4'-dithiobis(2,6-di-*tert*-butylphenol), was added DIAD (174 mg, 0.86 mmol). The reactions were stirred at room temperature for 24 hours and analyzed by ^1H NMR

Uncatalyzed Reactions in Ethyl Acetate: To five separate reaction vessels containing a solution of propionaldehyde (50 mg, 0.86 mmol) in ethyl acetate (0.2 M) and 0, 1.0, 2.5, 5.0, and 10.0 mol% radical scavenger, 4,4'-dithiobis(2,6-di-*tert*-butylphenol), was added DIAD (174 mg, 0.86 mmol). The reactions were stirred at room temperature for 24 hours and analyzed by ^1H NMR.

Catalyzed Reactions (Neat): To five separate reaction vessels containing propionaldehyde (50 mg, 0.86 mmol), rhodium acetate dimer (40 mg, 10 mol %), and 0, 1.0, 2.5, 5.0, and 10.0 mol% of radical scavenger, 4,4'-dithiobis(2,6-di-*tert*-butylphenol), was added DIAD (174 mg, 0.86 mmol). The reactions were stirred at room temperature for 24 hours and analyzed by ^1H NMR

Catalyzed Reactions in Ethyl Acetate: To five separate reaction vessels containing a solution of propionaldehyde (50 mg, 0.86 mmol) in ethyl acetate (0.2 M), rhodium acetate dimer (40 mg, 10 mol %), and 0, 1.0, 2.5, 5.0, and 10.0 mol% radical scavenger, 4,4'-dithiobis(2,6-di-*tert*-butylphenol), was added DIAD (174 mg, 0.86 mmol). The reactions were stirred at room temperature for 24 hours and analyzed by ^1H NMR.

Catalyzed and Uncatalyzed Reactions with Radical Scavengers in Neat

The reaction did not proceed without catalyst in the presence of radical inhibitor after 24 hours. With catalyst, a 25% conversion was achieved with 1 mol% radical inhibitor present after 24 hours. A linear decrease in product formation occurred as the amount of radical inhibitor increased. At 10 mol% radical inhibitor, no reaction was seen after 24 hours.

Catalyzed and Uncatalyzed Reactions in EtOAc

The reaction did not proceed without catalyst in the presence of radical inhibitor after 24 hours in ethyl acetate (0.2 M). With catalyst, a 10% conversion was achieved with 1 mol% radical inhibitor present after 24 hours. A linear decrease in product formation occurred as the amount of radical increased. At 10 mol% radical inhibitor, no reaction was seen after 24 hours.

Trapping Experiments of an Acyl Radical with **6b**

Uncatalyzed Trapping Experiments: To two separate reaction vessels containing a solution of **6b** (50 mg, 0.51 mmol) in EtOAc (1.0, 0.1 M) was added DIAD (103 mg, 0.51 mmol). The reactions were stirred at room temperature, and after 24 hours, only the normal coupled product, **7b** (or **7b'**), was observed by ^1H NMR, without any evidence of the radical cyclization product.

Catalyzed Trapping Experiments: To two separate reaction vessels containing a solution of **6b** (50 mg, 0.51 mmol) in EtOAc (1.0, 0.1 M), and rhodium acetate dimer (11mg, 5.0 mol%), was added DIAD (103 mg, 0.51 mmol). The reactions were stirred at room temperature, and after 24 hours, only the normal coupled product, **7b** (or **7b'**), was observed by ^1H NMR, without any evidence of the radical cyclization product.