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Simple Preparation of α-Diazo Esters

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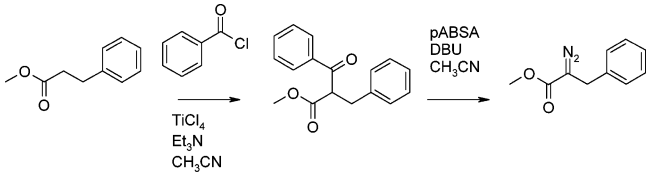
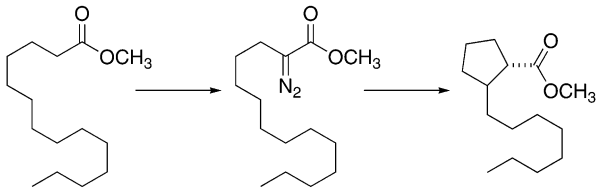


The $TiCl_4$-mediated reaction of an ester with benzoyl chloride results in high yields of the α-benzoylated ester. Diazo transfer of the benzoylated ester utilizing *p*-acetoamidobenzenesulfonyl azide affords the α-diazo ester in good yield. Using this simplified procedure, it is easy to prepare gram quantities of α-diazo esters.

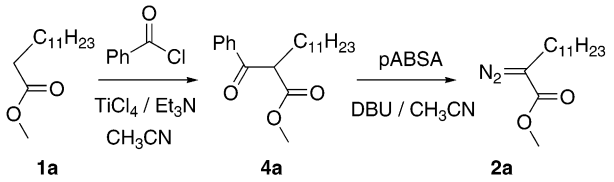
Several years ago, we reported a new method for the diastereoselective construction of cyclopentanes, diazo transfer followed by rhodium-mediated C−H insertion, e.g., **2a** to **3a**.[1] The key to this approach was the diazo transfer to the ester.



1a **2a** **3a**

We found[2] that benzoylation followed by diazo transfer was a general method for the preparation of α-diazo esters. The original procedure was to condense the methyl ester with sodium hydride and methyl benzoate. The yield of this reaction was limited by the continued reaction of the sodium methoxide with the benzoylated ester. Danheiser introduced 2,2,2-trifluoroethyl trifluoroacetate and lithium bis(trimethylsilyl) amide as a more efficient acylation method.[3] While effective, this method requires the use of an expensive strong base and cryogenic conditions.

Building on the results of Tanabe,[4] we have now found that the combination of benzoyl chloride, titanium(IV) chloride, triethylamine, and acetonitrile at room temperature converts an ester to the α-benzoylated ester (method A). While this procedure worked well with methyl esters (Table 1), yields were lower with branched esters. We found that the addition of triethylamine *before* the addition of the titanium(IV) chloride provided a buffer against hydrolysis, thereby resulting in higher yields of the α-benzoylated ester (method B). Utilizing either method, we could then effect diazo transfer directly on the crude benzoylated ester. The diazo ester so prepared is usually pure enough to carry directly into subsequent transformations.



1a **4a** **2a**

α-Diazo esters are versatile intermediates in organic synthesis.[10−12] Rhodium(II) octanoate (5 mol %, CH_2Cl_2, rt) efficiently catalyzes the hetero-H insertion of α-diazo esters (Scheme 1). β-Hydride elimination to form the (*Z*) alkene **7**[13] is always a competing side reaction. Nevertheless, N−H, O−H, and S−H insertions proceed smoothly.

We expect that the diazo transfer procedure described here will make α-diazo esters readily available as intermediates for organic synthesis.

Experimental Section

Representative Benzoylation Procedure by Method A. Titanium tetrachloride (2.87 g, 15 mmol) was added over 30 min to a solution of benzoyl chloride (4.26 g, 30 mmol) and methyl tetradecanoate **1a** (2.45 g, 10 mmol) in 10 mL of dry CH_3CN at 0 °C. After 15 min, triethylamine (6.13 g, 60 mmol) was added over 30 min. The mixture was warmed to reflux for 15 min. The mixture was cooled, then partitioned between water and EtOAc

(1) Taber, D. F.; Hennessey, M. J.; Louey, J. P. *J. Org. Chem.* **1992**, *57*, 436.
(2) Taber, D. F.; You, K.; Song, Y. *J. Org. Chem.* **1995**, *60*, 1093.
(3) Danheiser, R. L.; Miller, R. F.; Brisbois, R. G.; Park, S. Z. *J. Org. Chem.* **1990**, *55*, 1959.
(4) Yoshida, Y.; Matsumoto, R. H.; Tanabe, Y. *Tetrahedron Lett.* **2001**, *40*, 4227. Tanabe, Y.; Yoshida, Y.; Hayashi, R. *Tetrahedron Lett.* **1997**, *38*, 8727−8730. Tanabe, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1917.
(5) Taber, D. F.; Herr, R. J.; Pack, S. K. *J. Org. Chem.* **1996**, *61*, 2908.
(6) Sundar, N.; Bhat, V. *Synth. Commun.* **1998**, *28*, 2311.
(7) Aitken, R. A.; Armstrong, J. M.; Drysdale, M. J.; Ross, F. C.; Ryan, B. M. *J. Chem. Soc., Perkin Trans. 1* **1999**, *5*, 593.
(8) Queignec, R.; Kirschleger, B.; Lambert, F.; Aboutaj, M. *Synth. Commun.* **1988**, *18*, 1213.
(9) Calo, V.; Nacci, A.; Lopez, L.; Napola, A. *Tetrahedron Lett* **2001**, *42*, 4701.
(10) For examples of Rh-mediated O−H insertion, see: (a) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds. From Cyclopropanes to Ylides*; Wiley-Interscience: New York, 1998. (b) Miller, D. J.; Moody, D. J. *Tetrahedron* **1995**, *40*, 10811. (c) Aller, E.; Brown, D. S.; Cox, G. G.; Miller, D. J.; Moody, C. J. *J. Org. Chem.* **1995**, *60*, 4449. (d) Sengupta, S.; Das, D.; Sarma, D. S. *Tetrahedron Lett.* **1996**, *37*, 8815 (e) Moody, C. J.; Miller, D. J. *Tetrahedron* **1998**, *54*, 2257.
(11) For examples of Rh-mediated S−H insertion, see: McKervey, M. A. *Tetrahedron Let.* **1982**, *23*, 2509.
(12) For examples of Rh-mediated N−H insertion, see: (a) Aller, E.; Buck, R. T.; Drysdale, M. J.; Ferris, L.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Sanghera, J. B. *J. Chem. Soc., Perkins Trans.* **1996**, *24*, 2879. (b) Davis, F. A.; Fang, T.; Goswami, R. *Org Lett.* **2002**, *4*, 1599. (c) Buck, R. T.; Clarke, P. A.; Coe, Diane M., Drysdale, M. J.; Ferris, L.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Swann, E. *Chem. Eur. J.* **2000**, *6*, 2160. (d) Ferris, L.; Haigh, D.; Moody, C. J. *J. Chem. Soc., Perkin Trans.* **1996**, *24*, 2885.
(13) Nakamura, S.; Hayakawa, T.; Nishi, T.; Watanabe, Y.; Toru, T. *Tetrahedron* **2001**, *57*, 6703.

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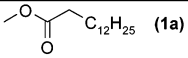
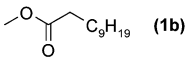
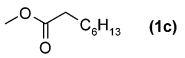
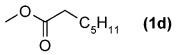
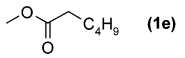
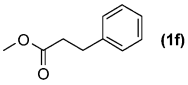
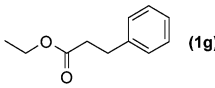
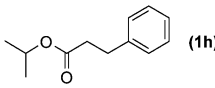
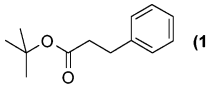
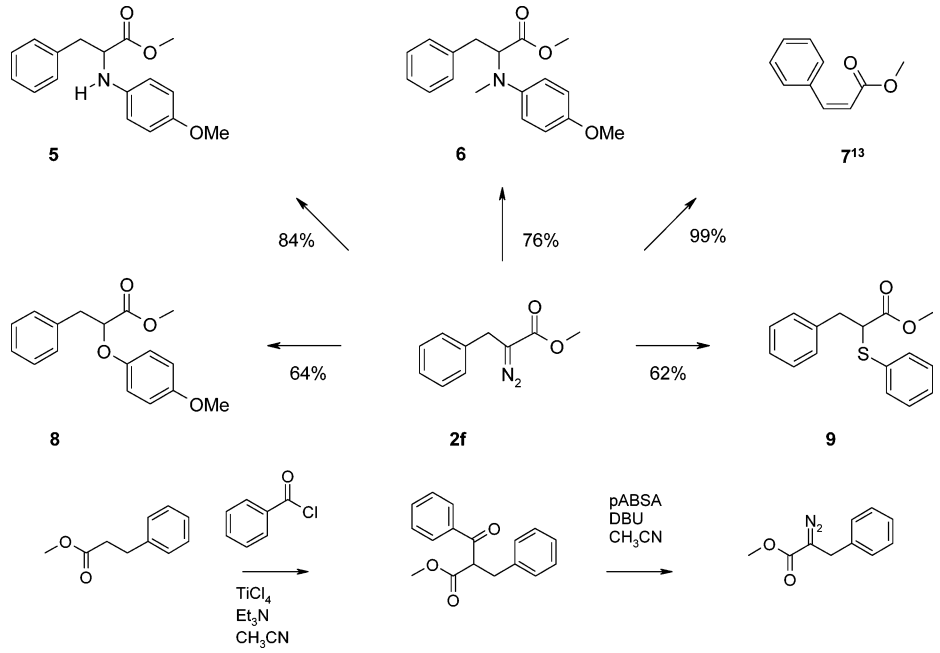
TABLE 1. Benzoylation and Diazo Transfer

entry	ester	method	benzoylation yield (%)[a]	diazo transfer yield (%)[a]	overall yield (%)[b]
1	 (1a)	A	78	85[1]	66
2	 (1b)	A	87	79[5]	68
3	 (1c)	A	84	82	66
4	 (1d)	A	93	84	77
5	 (1e)	A	90	84	74
6	 (1f)	A	85[6]	84[7]	69
7	 (1g)	B	76[8]	82[7]	61
8	 (1h)	B	68	83	53
9	 (1i)	B	67[9]	81	50

[a] Chromatographed yield. [b] Chromatographed yield without purification of the intermediate α-benzoylated ester.

SCHEME 1



(3 × 30 mL). The combined organic extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed to give methyl 2-benzoyltetradecanoate **4a** (2.70 g, 78% yield) as an oil: TLC $R_f = 0.31$ (95% H/EtOAc). ^{1}H NMR δ 7.97 (d, $J = 8.5$ Hz, 2H), 7.56 (t, $J = 8.5$ Hz, 1H), 7.48 (t, $J = 8.5$ Hz, 2H), 4.35 (t, $J = 6.9$ Hz, 1H), 3.68 (s, 3H), 2.03 (m, 2H), 1.25 (bs, 20H) 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR δ u: 193.5, 169.0, 131.9, 50.9, 30.3, 28.1, 28.0, 27.9, 27.8, 27.6, 26.1, 21.1 d: 131.9, 127.2, 127.0, 52.5, 12.6; IR 1744, 1689, 1597, 1581, 1448 cm^{-1}; HRMS calcd for $C_{22}H_{34}O_3$ 346.5102, obsd 346.5114. Anal. Calcd for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C, 76.30; H, 9.96.

Methyl 2-benzoylundecanoate **4b** (2.65 g, 87% yield) as an oil: TLC $R_f = 0.29$ (95% H/EtOAc); ^{1}H NMR δ 7.98 (d, $J = 7.2$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 2H), 4.33 (t, $J = 7.2$ Hz, 1H), 3.67 (s, 3H), 2.00 (m, 2H), 1.24 (s, 14H), 0.87 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR δ u: 193.6, 169.0, 134.7, 50.8, 30.3, 27.9, 27.8, 27.7, 27.6, 26.1, 21.1 d: 131.9, 127.2, 127.1, 127.0, 126.5, 52.4, 12.5; HRMS calcd for $C_{19}H_{28}O_3$ 304.4295, obsd 304.4297. Anal. Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.99; H, 9.29.

Methyl 2-benzoyloctanoate **4c** (2.20 g, 84% yield) as an oil: TLC $R_f = 0.27$ (95% H/EtOAc); ^{1}H NMR δ 7.98 (d, $J = 7.2$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 7.2$ Hz, 2H), 4.33 (t, $J = 7.2$ Hz, 1H), 3.68 (s, 3H), 2.00 (m, 2H), 1.29 (s, 8H) 0.86 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR δ u: 193.7, 169.0, 134.7, 50.8, 29.9, 27.6, 27.5, 26.0, 20.9 d: 132.0, 127.2, 127.1, 127.0, 52.5, 12.5; HRMS calcd for $C_{16}H_{22}O_3$ 262.3489, obsd 262.3490. Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.28; H, 8.46.

Methyl 2-benzoylheptanoate **4d** (2.31 g, 93% yield) as an oil: TLC $R_f = 0.25$ (95% H/EtOAc); ^{1}H NMR δ 7.99 (d, $J = 7.2$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 7.2$ Hz, 2H), 4.32 (t, $J = 7.2$ Hz, 1H), 3.68 (s, 3H), 2.03 (m, 2H), 1.31 (s, 6H) 0.87 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR δ u: 193.7, 169.0, 134.6, 50.9, 30.0, 27.5, 25.8, 20.8 d: 131.9, 127.2, 127.0, 52.5, 12.4; HRMS calcd for $C_{15}H_{20}O_3$ 248.3220, obsd 248.3221. Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found C, 72.56; H, 8.14.

Methyl 2-benzoylhexanoate **4e** (2.11 g, 90% yield) as an oil: TLC $R_f = 0.23$ (95% H/EtOAc); ^{1}H NMR δ 7.98 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 2H), 4.34 (t, $J = 7.2$ Hz, 1H), 3.67 (s, 3H), 2.02 (m, 2H), 1.34 (s, 4H), 0.90 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR δ u: 193.7, 168.9,134.6, 50.8, 28.2, 27.3, 21.0 d: 131.9, 127.2, 127.0, 52.4, 12.2; HRMS calcd for $C_{14}H_{18}O_3$ 234.2951, obsd 234.2996. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found C, 71.79; H, 7.79.

Methyl 2-benzoylhydrocinnamate **4f** (2.28 g, 85% yield) as an oil:[6] TLC $R_f = 0.17$ (95% H/EtOAc); ^{1}H NMR δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 8.4$ Hz, 2H), 7.21−7.25 (m, 5H), 4.65 (t, $J = 7.5$ Hz, 1H), 3.64 (s, 3H), 3.32 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR δ u: 192.9, 168.2, 136.8, 134.6, 33.3 d: 132.1, 127.4, 127.2, 127.0, 125.2, 54.4, 51.0; IR 1739, 1686, 1596, 1495, 1448 cm^{-1}; HRMS calcd for $C_{17}H_{16}O_3$ 268.3122, obsd 268.3123. Anal. Calcd for $C_{17}H_{16}O_3$: C, 73.25; H, 8.45. Found: C, 73.28; H, 8.46.

Representative Benzoylation Procedure by Method B. Titanium tetrachloride (2.87 g, 15 mmol) was added over 30 min to a solution of benzoyl chloride (4.26 g, 30 mmol), **1g** (1.78 g, 10 mmol), and triethylamine (6.13 g, 60 mmol) in 10 mL of dry CH_3CN at 0 °C. The mixture was warmed to reflux for 15 min. The mixture was cooled and then partitioned between water and EtOAc (3 × 30 mL). The combined organic extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed to give ethyl 2-benzoylhydrocinnamate **4g** (2.14 g, 78% yield) as an oil:[8] TLC: $R_f = 0.22$ (95% H/EtOAc); ^{1}H NMR δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 8.4$ Hz, 2H), 7.21−7.25 (m, 5H), 4.63 (t, $J = 7.3$ Hz, 1H), 4.08 (q, $J = 7.1$ Hz, 2H), 3.32 (d, $J = 7.3$ Hz, 2H), 1.10 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR δ u: 192.9, 167.7, 136.9, 134.6, 59.9, 33.2 d: 132.0, 127.4, 127.1, 126.9, 125.1, 54.6, 12.4; IR 1736, 1687, 1597, 1495 cm^{-1}; HRMS calcd for $C_{18}H_{18}O_3$ 282.3391, obsd 283.3398. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.61; H, 6.54.

Isopropyl 2-benzoylhydrocinnamate **4h** (2.01 g, 68% yield) as an oil: TLC $R_f = 0.26$ (95% H/EtOAc). ^{1}H NMR δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 8.4$ Hz, 2H), 7.21−7.25 (m, 5H), 4.94 (m, $J = 7.5$ Hz, 1 H) 4.63 (t, $J = 7.5$ Hz, 1H), 3.32 (d, $J = 7.5$ Hz, 2H), 1.12 (d, $J = 6.4$ Hz, 3H), 1.02 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR δ u: 192.9, 167.3, 136.9, 134.7, 33.1 d: 131.9, 127.4, 127.1, 126.9, 125.0, 67.5, 55.0, 19.9, 19.8; IR 1730, 1679, 1597, 1495 cm^{-1}; HRMS calcd for $C_{17}H_{16}O_3$ 296.3660, obsd 296.3663. Anal. Calcd for $C_{17}H_{16}O_3$: C, 77.00; H, 6.80. Found: C, 77.07; H, 6.89.

tert-Butyl 2-benzoylhydrocinnamate **4i** (2.10 g, 67% yield) as an oil:[9] TLC $R_f = 0.30$ (95% H/EtOAc); ^{1}H NMR δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 7.3$ Hz, 1H), 7.43 (t, $J = 8.4$ Hz, 2H), 7.17−7.26 (m, 5H), 4.51 (t, $J = 7.2$ Hz, 1H), 3.29 (d, $J = 7.2$ Hz, 2H), 1.28 (s, 9H); ^{13}C NMR δ u: 193.3, 166.9, 137.1, 134.9, 80.5, 33.0 d: 131.8, 127.5, 127.1, 127.0, 125.0, 55.7, 26.2; IR 1728, 1686, 1597, 1495 cm^{-1}; HRMS calcd for $C_{20}H_{22}O_3$ 310.3929, obsd 310.3930. Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.45; H, 7.19.

Diazo Transfer. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 0.153 mL, 1.0 mmol) was added over 30 min to a solution of the benzoylated ester (**4a**, 346 mg, 1 mmol) and 4-acetoamidobenzenesulfonyl azide (248 mg, 1.0 mmol) in 10 mL of dry CH_3CN at 0 °C. After the initial exotherm had subsided, additional 4-acetoamidobenzenesulfonyl azide (124 mg, 0.5 mmol) and DBU (0.076 mL, 0.5 mmol) were added over 30 min. After an additional 30 min, the mixture was partitioned between water and EtOAc (3 × 30 mL). The combined organic extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed to give methyl 2-diazotetradecanoate **2a** (228 mg, 85% yield) as a yellow oil:[1] TLC $R_f = 0.37$ (95% H/EtOAc); ^{1}H NMR δ *3.76* (s, 3H), 2.30 (t, 2H, $J = 7.4$ Hz), 1.53−1.44 (m, 2H), 1.25 (s, 20 H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR δ u: 168.0, 31.9, 29.6, 29.5, 29.3, 29.2, 29.0, 28.7, 27.5, 23.0, 22.6 d: 51.7, 14.0; IR 1702, 1698, 1438 cm^{-1}; HRMS calcd for $C_{15}H_{28}O_2N_2$ 268.3995 (240.3861 loss N_2), obsd 240.3862. Anal. Calcd for $C_{15}H_{28}O_2N_2$: C, 67.13; H, 10.52. Found: C, 67.15; H, 10.55.

Methyl 2-diazoundecanoate **2b** (179 mg, 79% yield) as a yellow oil:[5] TLC $R_f = 0.35$ (95% H/EtOAc); ^{1}H NMR δ 3.76 (s, 3H), 2.30 (t, 2H, $J = 7.4$ Hz), 1.53−1.44 (m, 2H), 1.25 (s, 12H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR δ u: 166.5, 30.3, 27.9, 27.7, 27.2, 26.0, 21.4, 21.1 d: 50.2, 12.5; HRMS calcd for $C_{12}H_{22}O_2N_2$ 226.3189 (198.3055 loss N_2), obsd 198.3056. Anal. Calcd for $C_{12}H_{22}O_2N_2$: C, 63.69; H, 9.80. Found: C, 63.72; H, 9.88.

Methyl 2-diazooctanoate **2c** (151 mg, 82% yield) as a yellow oil. TLC: $R_f = 0.32$ (95% H/EtOAc); ^{1}H NMR δ 3.76 (s, 3H), 2.30 (t, 2H, $J = 7.4$ Hz), 1.49 (m, 2H), 1.32 (m, 6H), 0.89 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR δ u: 29.9, 26.8, 26.0, 21.5, 21.0 d: 50.3, 12.5; HRMS calcd for $C_9H_{16}O_2N_2$ 184.2382 (156.2248 loss N_2), obsd 156.2252. Anal. Calcd for $C_9H_{16}O_2N_2$: C, 58.67;, H, 8.75. Found: C, 58.68; H, 8.77.

Methyl 2-diazoheptanoate **2d** (143 mg, 84% yield) as a yellow oil: TLC $R_f = 0.30$ (95% H/EtOAc); ^{1}H NMR δ 3.75 (s, 3H), 2.30 (t, 2H, $J = 7.4$ Hz), 1.53−1.42 (m, 2H), 1.25 (s, 4H), 0.86 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR δ u: 168.1, 31.9, 29.1, 22.0, 21.5, d: 52.3, 14.3; HRMS calcd for $C_8H_{14}O_2N_2$ 170.2114 (142.1980 loss N_2), obsd 142.1981. Anal. Calcd for $C_8H_{14}O_2N_2$: C, 56.45; H, 8.29. Found: C, 56.49; H, 8.37.

Methyl 2-diazohexanoate **2e** (151 mg, 84% yield) as a yellow oil: TLC $R_f = 0.28$ (95% H/EtOAc); ^{1}H NMR δ 3.76 (s, 3H), 2.31 (t, 2H, $J = 7.4$ Hz), 1.58−1.31 (m, 4H), 0.93 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR δ u: 28.1, 21.2, 20.3, d: 50.3, 12.1; HRMS Calcd for $C_7H_{12}O_2N_2$ 156.1845 (128.1711 loss N_2), obsd 128.1716. Anal. Calcd for $C_7H_{12}O_2N_2$: C, 53.83; H, 7.74. Found: C, 53.88; H, 7.81.

Methyl 2-diazohydrocinnamate **2f** (160 mg, 84% yield) as a yellow oil:[7] TLC $R_f = 0.31$ (95% H/EtOAc); ^{1}H NMR δ 7.22−7.35 (m, 5H), 3.78 (s, 3H), 3.63 (s, 2H); ^{13}C NMR δ u: 164.2, 135.6, 27.8 d: 127.3, 126.8, 126.4, 125.6, 50.5; IR 1730, 1598, 1495, 1453 cm^{-1}; HRMS calcd for $C_{10}H_{10}O_2N_2$ 190.2016 (162.1882 loss N_2), obsd 162.1884. Anal. Calcd for $C_{10}H_{10}O_2N_2$: C, 63.15; H, 5.30. Found: C, 63.17; H, 5.37.

Ethyl 2-diazohydrocinnamate **2g** (165 mg, 81% yield) as a yellow oil:[7] TLC $R_f = 0.33$ (95% H/EtOAc); ^{1}H NMR δ 7.22−7.35 (m, 5H), 4.24 (q, $J = 7.2$ Hz, 2 H) 3.63 (s, 2H), 1.28 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR δ u: 163.3, 135.7, 59.4, 27.8 d: 127.2, 126.8, 126.4, 125.6, 13.0; HRMS calcd for $C_{11}H_{12}O_2N_2$ 204.2285

(176.2151 loss N_2), obsd 176.2158. Anal. Calcd for $C_{11}H_{12}O_2N_2$: C, 64.69; H, 5.92. Found: C, 64.77; H, 6.00.

Isopropyl 2-diazohydrocinnamate **2h** (181 mg, 83% yield) as a yellow oil: TLC $R_f = 0.36$ (95% H/EtOAc); ^{1}H NMR δ 7.22−7.35 (m, 5H), 5.11 (m, $J = 6.2$ Hz, 1 H) 3.62 (s, 2H), 1.25 (d, $J = 6.2$ Hz, 6H); ^{13}C NMR δ u: 161.1, 135.8, 27.8 d: 127.2, 126.8, 126.4, 125.5, 66.9, 20.5; HRMS calcd for $C_{12}H_{14}O_2N_2$ 218.2554 (190.2420 loss N_2), obsd 190.2421. Anal. Calcd for $C_{12}H_{14}O_2N_2$: C, 66.04; H, 6.47. Found: C, 66.10; H, 6.53.

tert-Butyl 2-diazohydrocinnamate **2i (**188 mg, 81% yield) as a yellow oil: TLC $R_f = 0.40$ (95% H/EtOAc); ^{1}H NMR δ 7.22−7.35 (m, 5H), 3.58 (s, 2H), 1.48 (s, 9H); ^{13}C NMR δ u: 167.4, 136.3, 79.8, 27.8 d: 127.2, 126.8, 126.4, 125.5, 26.8; HRMS calcd for $C_{13}H_{16}O_2N_2$ 232.2822 (204.2688 loss N_2), obsd 204.2688. Anal. Calcd for $C_{13}H_{16}O_2N_2$: C, 67.22; H, 6.94. Found C, 67.29; H, 7.03.

Amine 5. Methyl 2-diazohydrocinnamate (190 mg, 1.0 mmol) in 10 mL of dry dichloromethane was added over 1 h to a solution of rhodium(II) octanoate dimer (0.4 mg, 5 mol %) and *p*-anisidine (123 mg, 1.0 mmol) in 10 mL of dry dichloromethane at 25 °C. The mixture was concentrated and chromatographed to give the amino ester **5** (239 mg, 84% yield) as an oil: TLC $R_f = 0.12$ (95% H/EtOAc); ^{1}H NMR δ 7.22−7.35 (m, 5H), 6.75 (d, $J = 9.0$ Hz, 2H), 6.57 (d, $J = 9.0$ Hz, 2H), 4.27 (t, $J = 6.3$ Hz, 1H), 3.73 (s, 3H), 3.64 (s, 3H), 4.27 (dd, $J = 3.2$, 6.3 Hz, 2H); ^{13}C NMR δ u: 172.4, 151.3, 138.9, 134.9, 37.4 d: 127.7, 126.9, 125.4, 113.7, 113.4, 57.4, 54.1, 50.4; IR 1738, 1619, 1513, 1453 cm^{-1}; HRMS calcd for $C_{17}H_{19}O_3N$ 285.3428, obsd 285.3429. Anal. Calcd for $C_{17}H_{19}O_3N$: C, 71.56; H, 6.71. Found: C, 71.64; H, 6.76.

Amine 6 (228 mg, 76% yield) as an oil: TLC $R_f = 0.19$ (95% H/EtOAc); ^{1}H NMR δ 7.15−7.28 (m, 5H), 6.77 (d, $J = 9.2$ Hz, 2H), 6.69 (d, $J = 9.2$ Hz, 2H), 4.45 (t, $J = 7.5$ Hz, 1H), 3.72 (s, 3H), 3.62 (s, 3H), 3.25 (dd, $J = 7.0$, 14.8 Hz, 1H), 3.04 (dd, $J = 8.0$, 14.0 Hz, 1H), 2.85 (s, 3H); ^{13}C NMR δ u: 170.9, 151.2, 142.8, 136.5, 34.0 d: 127.5, 127.3, 126.9, 125.0, 114.8, 112.9, 64.1, 54.1, 50.2, 32.5; IR 1735, 1604, 1512, 1454 cm^{-1}; HRMS calcd for $C_{18}H_{21}O_3N$ 299.3696, obsd 299.3700. Anal. Calcd for $C_{18}H_{21}O_3N$: C, 72.22. H, 7.07. Found: C, 72.23; H, 7.09.

Alkene 7 (160 mg, 99% yield) as an oil: TLC $R_f = 0.32$ (95% H/EtOAc); ^{1}H NMR δ 7.58 (d, $J = 7.4$ Hz, 2H), 7.22−7.39 (m, 3H), 6.95 (d, $J = 12.7$ Hz, 1H), 5.95 (d, $J = 12.7$ Hz, 1H), 3.71 (s, 3H); ^{13}C NMR δ u: 165.1, 133.2, d: 141.8, 128.2, 127.6, 126.5, 117.8, 49.9; IR 1710, 1630, 1430 cm^{-1}; HRMS calcd for $C_{10}H_{10}O_2$ 162.1882, obsd 162.1885. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.11; H, 6.35.

Ether 8 (183 mg, 64% yield) as an oil: TLC $R_f = 0.31$ (95% H/EtOAc); ^{1}H NMR δ 7.20−7.36 (m, 5H), 6.77 (d, $J = 2.4$ Hz, 4H), 4.47 (dd, $J = 4.5$, 6.8 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.13 (dd, $J = 4.5$, 13.9 Hz, 1H), 2.96 (dd, $J = 6.8$, 13.9 Hz, 1H); ^{13}C NMR δ u: 173.1, 152.2, 148.0, 134.7, 39.1 d: 127.9, 127.8, 127.1, 126.9, 125.4, 114.5, 113.3, 69.7, 54.2, 51.0; IR 1736, 1604, 1510, 1440 cm^{-1}; HRMS calcd for $C_{17}H_{18}O_4$ 286.3275, obsd 286.3277. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.33; H, 6.38.

Sulfide 9 (169 mg, 62% yield) as an oil: TLC $R_f = 0.32$ (95% H/EtOAc); ^{1}H NMR δ 7.16−7.44 (m, 10H), 3.90 (t, $J = 6.4$ Hz, 1H), 3.57 (s, 3H), 3.17 (dd, $J = 9.6$, 14.2 Hz, 1H), 3.07 (dd, $J = 6.4$, 14.2 Hz, 1H); ^{13}C NMR δ u: 170.5, 136.1, 36.5 d: 131.7, 131.6, 131.5, 127.9, 127.8, 127.7, 127.6, 127.5, 127.0, 126.9, 126.8, 126.6, 125.5, 125.4, 50.6; IR 1951, 1694, 1583, 1478, 1440 cm^{-1}; HRMS calcd for $C_{16}H_{16}O_2S$ 272.3678, obsd 272.3682. Anal. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92. Found: C, 70.61; H, 6.29.

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Supporting Information Available: General experimental procedure and spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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