**Rhodium Carboxylate Catalyzed Decomposition of Vinyldiazoacetates
in the Presence of Heterodienes: Enantioselective Synthesis of the 6-
Azabicyclo[3.2.2]nonane and 6-Azabicyclo[3.2.2]nonanone Ring
Systems**

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Supporting Information:

Spectral data for **9a-c**, **13e-i** and **14e**, and proton NMR spectra for **6**, **9a**, **13i**, **19** and **21**

2-Ethoxy-2-oxoethyl (6-methyl-6-azabicyclo[3.2.2]nona-3,8-diene-7-one)-4-carboxylate [9a] ($\text{Rh}_2(\text{OOct})_4$, EtOAc, 36%). ^1H NMR (500 MHz, CDCl_3) δ 6.83 (dd, $J = 4.0, 3.7$ Hz, 1 H), 6.52 (ddd, $J = 7.2, 7.2, 1.2$ Hz, 1 H), 6.14 (dd, $J = 7.3, 7.3$ Hz, 1 H), 4.70 (d, $J = 15.9$ Hz, 1 H), 4.64 (d, $J = 15.9$ Hz, 1 H), 4.61 (d, $J = 6.4$ Hz, 1 H), 4.21 (q, $J = 7.3$ Hz, 2 H), 3.18 (m, 1 H), 2.95 (s, 3H), 2.76 (ddd, $J = 21.0, 3.7, 3.7$ Hz, 1 H), 2.35 (d, $J = 21.0, 3.7, 3.7$ Hz, 1 H), 1.26 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.9, 167.6, 165.1, 142.9, 133.9, 132.8, 128.1, 61.5, 61.2, 53.6, 42.1, 33.0, 28.0, 14.1; IR (neat): 1759, 1716, 1668 cm^{-1} . HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_5$: 279.1107; found 279.1091.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (6-methyl-6-azabicyclo[3.2.2]nona-3,8-diene-7-one)-4-carboxylate [9b] ($\text{Rh}_2(\text{OOct})_4$, EtOAc, 33%). ^1H NMR (Major diastereomer (39% de, determined from the ^1H NMR of the crude reaction mixture), 500 MHz, CDCl_3) δ 6.85 (br s, 1 H), 6.55 (ddd, $J = 8.2, 6.4, 1.5$ Hz, 1 H), 6.17 (dd, $J = 7.6, 6.7$ Hz, 1 H), 5.14 (q, $J = 7.0$ Hz, 1 H), 4.63 (dd, $J = 6.4$ Hz, 1 H), 4.22 (q, $J = 7.0$ Hz, 2 H), 3.20 (m, 1 H), 2.98 (s, 3 H), 2.77 (d, $J = 20.8, 4.0, 4.0$ Hz, 1 H), 2.39 (d, $J = 20.8, 3.7, 3.7$ Hz, 1 H), 1.54 (d, $J = 7.2$ Hz), 1.28 (t, $J = 7.2$ Hz, 3 H); IR (neat): 1753, 1710, 1670 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_5$: C, 61.42; H, 6.53; N, 4.78. Found: C, 61.33; H, 6.58; N, 4.70.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (2 α ,6-dimethyl-6-azabicyclo[3.2.2]-nona-3,8-diene-7-one)-4-carboxylate [9c] (**4a**, 2:1 EtOAc/hexanes, 78%). ^1H NMR (Major diastereomer (51% de, determined from the ^1H NMR of the crude reaction mixture), 500

MHz, CDCl₃) δ 6.64 (br s, 1 H), 6.60 (dd, J = 7.6, 7.3 Hz, 1 H), 6.06 (dd, J = 7.3, 7.0 Hz, 1 H), 5.13 (q, J = 7.0 Hz, 1 H), 4.57 (d, J = 6.1 Hz, 1 H), 4.23 (q, J = 7.0 Hz, 2 H), 3.22 (m, 1 H), 2.96 (s, 3 H), 2.85 (m, 1 H), 1.55 (d, J = 7.0 Hz, 3 H), 1.29 (t, J = 7.0 Hz, 3 H), 1.14 (d, J = 7.3 Hz, 3 H); IR (neat): 1751, 1711, 1670, 1634 cm⁻¹; MS m/z (rel. intensity): 307 (M⁺, 39), 189 (100). Anal. Calcd for C₁₆H₂₁NO₅: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.60; H, 6.91; N, 4.51.

Methyl (4 α -methyl-6-phenoxy-carbonyl-6-azabicyclo[3.2.2]nona-2,8-diene)-2-carboxylate [14e] and Methyl (2 α -methyl-6-phenoxy-carbonyl-6-azabicyclo[3.2.2]nona-3,8-diene)-4-carboxylate [13e] (Rh₂(OPiv)₄, 4:1 to 2:1 petroleum ether/Et₂O) to give both **14e** (3%) and **13e** (58%). When the reaction was carried out with [Rh₂(S-TBSP)₄] in toluene **13e** was formed in 48% yield and 65% ee (determined by HPLC: Chiralcel OD, 2% *i*-PrOH in hexane, 1.0 mL/min, λ = 254 nm, t_R = 35.3 min, major; t_R = 38.5 min, minor).

¹H NMR (**14e**, 2:1 ratio of rotamers, 400 MHz, CDCl₃) δ 7.36 (m, 2 H), 7.20 (m, 1 H), 7.12 (d, J = 8.2 Hz, 2 H), 6.68 (m, 1 H), 6.58 (m, 1 H), 6.13 (m, 1 H), 4.75, 4.71 (dd, J = 5.5, 5.1 Hz, 1 H total), 3.91, 3.81 (d, J = 11.4 Hz, 1 H total), 3.78, 3.77 (s, 3 H total), 3.71 (m, 1 H), 3.51, 3.39 (dd, J = 11.0, 3.3 Hz, 1 H total), 3.00 (m, 1 H), 1.08, 1.06 (d, J = 7.3 Hz, 3 H total); IR (neat) 1716, 1638, cm⁻¹; MS m/e (rel int) 313 (M⁺, 76), 281 77 (100). Anal. Calcd for C₁₈H₁₉NO₄: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.87; H, 6.17; N, 4.31.

¹H NMR (**13e**, 1:1 ratio of rotamers, 400 MHz, CDCl₃) δ 7.33 (t, J = 7.9 Hz, 2 H), 7.17 (t, J = 7.5 Hz, 1 H), 7.11 (t, J = 7.3 Hz, 2 H), 6.64 (m, 2 H), 6.11 (m 1 H), 5.65, 5.60 (d, J = 7.3 Hz, 1 H total), 3.84, 3.74 (d, J = 11.4 Hz, 1 H total), 3.77, 3.76 (s, 3 H total), 3.72,

3.57 (dd, $J = 12.1, 4.8$ Hz, 1 H total), 2.73 (m, 2 H), 1.14 (d, $J = 6.6$ Hz, 3 H); IR (neat) 1716, 1641 cm^{-1} ; MS m/e (rel int) 313 (M^+ , 94), 220 (29), 188 (83), 163 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.93; H, 6.16; N, 4.47.

1-Methyl-4-propionyl-(6-phenoxy-carbonyl-6-azabicyclo[3.2.2]nona-3,8-diene) [**13f**] ($\text{Rh}_2(\text{OPiv})_4$, 4:1 petroleum ether/ Et_2O to 2:1 petroleum ether/ Et_2O) to give **13f** (32%). ^1H NMR (**13f**, 3:2 ratio of rotamers, 500 MHz, CDCl_3) δ 7.30 (m, 2 H), 7.14 (m, 2 H), 7.06 (d, 1 H), 6.62 (m, 1 H), 6.46 (m, 1 H), 5.89, 5.87 (d, $J = 9.5$ Hz, 1 H total), 5.81, 5.70 (d, $J = 7.0$ Hz, 1 H total), 3.74, 3.64 (d, $J = 11.3$ Hz, 1 H total), 3.37, 3.22 (dd, $J = 11.3, 2.7$ Hz, 1 H total), 2.79-2.37 (m, 4 H), 1.23 (s, 3 H total), 1.12-1.03 (m, 3 H); IR (neat) 1716, 1666 cm^{-1} ; MS m/e (rel int) 311 (M^+ , 19), 231 (18), 181 (47), 169 (37), 131 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.04; H, 6.92; N, 4.37.

Methyl (1,2 α -dimethyl-6-phenoxy-carbonyl-6-azabicyclo[3.2.2]nona-3,8-diene)-4-carboxylate [**13g**] ($\text{Rh}_2(\text{OPiv})_4$, 4:1 to 2:1 petroleum ether/ Et_2O) to give **13g** (50%). ^1H NMR (1:1 ratio of rotamers, 400 MHz, CDCl_3) δ 7.33 (t, $J = 7.5$, 2 H), 7.17 (t, $J = 7.2$ Hz, 1 H), 7.10 (t, $J = 7.2$ Hz, 2 H), 6.65 (br s, 1 H), 6.53 (m, 1 H), 5.79, 5.76 (d, $J = 9.5$ Hz, 1 H total), 5.63, 5.59 (d, $J = 7.2$ Hz, 1 H total), 3.77, 3.76 (s, 3 H total), 3.71, 3.59 (d, $J = 11.7$ Hz, 1 H total), 3.45, 3.32 (d, $J = 11.7$ Hz, 1 H total), 2.41 (m, 1 H), 1.28, 1.27 (s, 3 H total), 1.07, 1.06 (d, $J = 7.3$ Hz, 3 H total); IR (neat) 1715, 1643 cm^{-1} ; MS m/e (rel int) 327 (M^+ , 92), 234 (27), 77 (100). Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_4$: C, 69.71; H, 6.47; N, 4.28. Found: C, 69.56; H, 6.52; N, 4.26.

Methyl (1-methyl-2 α -phenyl-6-phenoxy-carbonyl-6-azabicyclo[3.2.2]nona-3,8-diene)-4-carboxylate [**13h**] ($\text{Rh}_2(\text{OPiv})_4$, 4:1 to 2:1 petroleum ether/ Et_2O) to give **13h**

(71%). ^1H NMR (1:1 ratio of rotamers, 400 MHz, CDCl_3) δ 7.33 (m, 5 H), 7.14 (m, 5 H), 6.80 (br s, 1 H), 6.63, 6.61 (dd, $J = 8.4, 7.7$ Hz, 1 H total), 5.77, 5.72 (d, $J = 7.3$ Hz, 1 H total), 5.67, 5.65 (d, $J = 9.2$ Hz, 1 H total), 3.85, 3.73 (d, $J = 12.1$ Hz, 1 H total), 3.76 (s, 3 H), 3.51, 3.38 (d, $J = 12.1$ Hz, 1 H total), 3.49, 3.47 (d, $J = 3.3$ Hz, 1 H total), 1.07, 1.06 (s, 3 H total); IR (neat) 1715, 1641 cm^{-1} ; MS m/e (rel int) 389 (M^+ , 76), 296 (17). Anal. Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4$: C, 74.02; H, 5.95; N, 3.60. Found: C, 74.10; H, 6.02; N, 3.55.

Methyl (1-methyl-6-phenoxyacetyl-6-azabicyclo[3.2.2]nona-3,8-diene)-4-carboxylate [13i] ($\text{Rh}_2(\text{S-TBSP})_4$ in toluene, 4:1 to 2:1 petroleum ether/ Et_2O to give **13i** in 30% yield and 58% ee (determined by HPLC: Chiralcel OD, 2.5% *i*-PrOH in hexane, 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{R}} = 28.7$ min, major; $t_{\text{R}} = 32.0$ min, minor). ^1H NMR (1:1 ratio of rotamers, 500 MHz, CDCl_3) δ 7.33 (t, $J = 7.6$ Hz, 2 H), 7.17 (t, $J = 7.3$ Hz, 1 H), 7.11 (d, $J = 7.9$ Hz, 2 H), 6.78 (m, 1 H), 6.51 (m, 1 H), 5.91, 5.88 (d, $J = 9.0$ Hz, 1 H total), 5.66, 5.63 (d, $J = 7.0$ Hz, 1 H total), 3.75 (s, 3 H), 3.74, 3.63 (d, $J = 11.9$ Hz, 1 H total), 3.38, 3.23 (dd, $J = 11.3, 2.8$ Hz, 1 H total), 2.54, 2.49 (dd, $J = 10.7, 3.7$ Hz, 1 H total), 2.45, 2.43 (ddd, $J = 9.8, 4.3, 3.1$ Hz, 1 H total), 1.23, 1.22 (br s, 3 H total); IR (neat) 1718, 1646 cm^{-1} . HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_4$: 313.1325; found: 313.1314.