Supporting Information

Rhodium-Catalyzed Cyclopropanation with Ene-yne-imino Ether Compounds as Precursors of (2-Pyrrolyl)carbenoid

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General Procedures. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates or silica gel FL 100DX Fuji Silysia Chemical NH plates. Column chromatographies were performed with Merck silica gel 60, Fuji Silysia Chemical silica gel FL 100DX, or Floridin Co. Florisil® (150-250 μm , 60-100 mesh). NMR spectra were measured for solutions in CDCl_3 with Me_4Si as an internal standard or CD_2Cl_2 (^1H and ^{13}C): the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded with an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. Solvents were dried by the usual methods and distilled before use.

Typical Procedure for Synthesis of Ene-yne-imino Ether 4.

To a solution of an amide **13** (5.0 mmol), which was prepared by our reported procedure,¹ in dichloromethane (50 mL) was added MeOTf (0.58 mL, 5.0 mmol) under N_2 , and the solution was stirred at room temperature for 96–144 h.² The reaction mixture was washed with 1 N NaOH solution (25 mL) and then the organic phase was dried over MgSO_4 . The organic solvent was removed under reduced

pressure, and the residue was subjected to column chromatography on SiO₂ with hexane/AcOEt (v/v = 20/1) to afford the corresponding imino ether as a pale yellow oil. To a solution of the imino ether (1.0 mmol) in MeOH (10 mL) was added K₂CO₃ (0.21 g, 1.5 mmol), and the solution was stirred at room temperature for 30 min. The reaction mixture was poured into water, and the aqueous phase was extracted with Et₂O (20 mL x 3). The combined organic phase was dried over MgSO₄. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO₂ with hexane/AcOEt (v/v = 20/1) as an eluent to afford the compound **4** as a pale yellow oil.

Ene-yne-carbonyl compound 13a.

A white solid (85% yield); mp. 73.8–75.5 °C; IR (KBr) 699, 761, 855, 888, 1043, 1249, 1551, 1605, 1641 (C=O), 2142 (C≡C), 2927, 3322 (N-H) cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 0.18 (s, 9H), 1.55–1.64 (m, 4H), 2.21–2.28 (m, 2H), 2.37–2.44 (m, 2H), 2.85 (d, *J* = 3.0 Hz, 3H), 7.00 (br s, 1H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ -0.2, 21.6, 21.7, 25.8, 26.2, 31.2, 101.2, 104.5, 120.6, 140.8, 168.5. Anal. Calcd for C₁₃H₂₁NOSi: C, 66.33; H, 8.99; N, 5.95. Found: C, 66.24; H, 8.82; N, 5.96.

Ene-yne-carbonyl compound 13b.

A pale yellow oil (92% yield); IR (neat) 698, 760, 845, 886, 1250, 1285, 1527, 1650 (C=O), 2140 (C≡C), 2936, 3307 (N-H) cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 0.18 (s, 9H), 1.59–1.63 (m, 4H), 2.26–2.30 (m, 2H), 2.40–2.44 (m, 2H), 3.97 (dd, *J* = 5.2, 5.7 Hz, 2H), 5.13 (dd, *J* = 1.5, 10.5 Hz, 1H), 5.25 (dd, *J* = 1.5, 16.5 Hz, 1H), 5.88 (ddd, *J* = 5.7, 10.5, 16.5 Hz, 1H), 7.23 (br s, 1H); ¹³C NMR (75 MHz,

CDCl₃, 25 °C) δ -0.2, 21.7, 21.8, 26.3, 31.6, 42.1, 102.1, 104.4, 116.5, 121.1, 134.2, 140.1, 167.4. Anal. Calcd for C₁₅H₂₃NOSi: C, 68.91; H, 8.87; N, 5.36. Found: C, 68.51; H, 8.82; N, 5.27.

Ene-yne-carbonyl compound 13c.

A pale yellow solid (91% yield); mp. 100.8–102.5 °C; IR (KBr) 696, 758, 845, 876, 910, 1248, 1321, 1442, 1548, 1599, 1649 (C=O), 2144 (C≡C), 2941, 3288 (N-H) cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 25 °C) δ 0.15 (s, 9H), 1.63–1.68 (m, 4H), 2.33–2.38 (m, 2H), 2.47–2.53 (m, 2H), 7.10 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.33 (dd, *J* = 7.5, 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 8.79 (s, 1H); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ -0.2, 21.6, 21.8, 26.2, 31.7, 103.4, 103.8, 119.7, 121.9, 124.1, 128.9, 137.9, 140.7, 165.7. Anal. Calcd for C₁₈H₂₃NOSi: C, 72.68; H, 7.79; N, 4.71. Found: C, 72.59; H, 7.64; N, 4.61.

Ene-yne-carbonyl compound 13d.

A pale yellow solid (82% yield); mp. 54.1–55.2 °C; IR (KBr) 618, 760, 846, 1249, 1401, 1597, 1641 (C=O), 2141 (C≡C), 2961, 3368 (N-H) cm⁻¹; ¹H NMR (270 MHz, CDCl₃, 25 °C) δ 0.24 (s, 9H), 1.86 (quint, *J* = 7.6 Hz, 2H), 2.65 (tt, *J* = 7.6, 2.2 Hz, 2H), 2.76 (tt, *J* = 7.6, 2.2 Hz, 2H), 2.88 (d, *J* = 5.1 Hz, 3H), 7.29 (br s, 1H); ¹³C NMR (67.8 MHz, CDCl₃, 25 °C) δ -0.2, 21.8, 25.9, 33.9, 38.9, 101.2, 105.7, 125.1, 145.0, 164.6. Anal. Calcd for C₁₂H₁₉NOSi: C, 65.11; H, 8.65; N, 6.33. Found: C, 64.85; H, 8.64; N, 6.20.

Ene-yne-carbonyl compound 13f.

A white solid (77% yield); mp. 46.2–47.8 °C; IR (KBr) 693, 757, 840, 890, 1129, 1248, 1290, 1520, 1638 (C=O), 2140 (C≡C), 2940, 3383 (N-H) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 0.18 (s, 9H), 1.57–1.61 (m, 4H), 2.23–2.28 (m, 2H), 2.29 (dt, J = 6.9, 6.9 Hz, 2H), 2.36–2.40 (m, 2H), 3.39 (dt, J = 6.0, 6.9 Hz, 2H), 5.05 (dd, J = 1.2, 10.2 Hz, 1H), 5.09 (dd, J = 1.2, 17.1 Hz, 1H), 5.79 (ddt, J = 10.2, 17.1, 6.9 Hz, 1H), 7.03 (br s, 1H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ -0.2, 21.6, 21.8, 26.2, 31.5, 33.7, 38.8, 101.4, 104.4, 116.9, 120.6, 135.3, 140.4, 167.8. Anal. Calcd for $\text{C}_{16}\text{H}_{25}\text{NOSi}$: C, 69.76; H, 9.15; N, 5.08. Found: C, 69.78; H, 8.96; N, 5.06.

Ene-yne-imino ether compound 4a.

A pale yellow oil (72% yield for two steps); IR (neat) 694, 823, 1028, 1080, 1254, 1281, 1435, 1629, 1678 (C=N), 2094 (C≡C), 2360, 2940, 3286 ($\equiv\text{C-H}$) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 1.65–1.70 (m, 4H), 2.14–2.20 (m, 2H), 2.22–2.28 (m, 2H), 2.96 (s, 1H), 3.03 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 21.4, 21.8, 27.2, 29.2, 36.0, 52.8, 79.2, 82.6, 119.5, 138.6, 163.0. HRMS (FAB): calcd for $\text{C}_{11}\text{H}_{16}\text{NO}$ ($\text{M}+\text{H}^+$), 178.1232; found, 178.1234.

Ene-yne-imino ether compound 4b.

A pale yellow oil (76% yield for two steps); IR (neat) 639, 915, 1032, 1075, 1197, 1254, 1280, 1358, 1434, 1627, 1674 (C=N), 2091 (C≡C), 2940, 3289 ($\equiv\text{C-H}$) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 1.62–1.68 (m, 4H), 2.12–2.18 (m, 2H),

2.20–2.28 (m, 2H), 2.96 (s, 1H), 3.74 (s, 3H), 3.90 (d, $J = 5.4$ Hz, 2H), 5.05 (dd, $J = 1.6, 10.5$ Hz, 1H), 5.20 (dd, $J = 1.6, 17.0$ Hz, 1H), 5.97 (ddd, $J = 5.4, 10.5, 17.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 21.1, 21.8, 27.5, 29.1, 51.6, 53.0, 79.6, 82.5, 114.2, 119.4, 137.2, 138.8, 162.5. HRMS (FAB): calcd for $\text{C}_{13}\text{H}_{18}\text{NO}$ ($\text{M}+\text{H}^+$), 204.1388; found, 204.1391.

Ene-yne-imino ether compound 4c.

A pale yellow oil (46% yield for two steps); IR (neat) 640, 697, 763, 891, 1047, 1072, 1180, 1258, 1289, 1359, 1434, 1600, 1624, 1661 ($\text{C}=\text{N}$), 2096 ($\text{C}\equiv\text{C}$), 2371, 2941, 3286 ($\equiv\text{C}-\text{H}$) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , 25 °C) δ 1.36–1.46 (m, 4H), 1.88–1.96 (m, 2H), 2.08–2.15 (m, 2H), 3.10 (s, 1H), 3.88 (s, 3H), 6.88 (d, $J = 7.2$ Hz, 2H), 7.01 (dd, $J = 7.2, 7.2$ Hz, 1H), 7.23 (dd, $J = 7.2, 7.2$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C) δ 21.1, 21.4, 27.4, 29.1, 53.8, 80.2, 83.1, 121.4, 123.0, 128.4, 128.8, 139.6, 147.6, 162.2. HRMS (FAB): calcd for $\text{C}_{16}\text{H}_{18}\text{NO}$ ($\text{M}+\text{H}^+$), 240.1388; found, 240.1378.

Ene-yne-imino ether compound 4d.

A pale yellow oil (40% yield for two steps); IR (neat) 668, 922, 1012, 1097, 1216, 1263, 1435, 1621, 1674 ($\text{C}=\text{N}$), 2096 ($\text{C}\equiv\text{C}$), 2359, 2945, 3289 ($\equiv\text{C}-\text{H}$) cm^{-1} ; ^1H NMR (270 MHz, CD_2Cl_2 , 25 °C) δ 1.96 (quint, $J = 7.6$ Hz, 2H), 2.59 (t, $J = 7.6$ Hz, 2H), 2.59 (t, $J = 7.6$ Hz, 2H), 3.04 (s, 3H), 3.23 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (67.8 MHz, CD_2Cl_2 , 25 °C) δ 23.1, 35.7, 36.7, 37.5, 52.7, 79.7, 83.2, 124.6, 142.0, 159.5. HRMS (FAB): calcd for $\text{C}_{10}\text{H}_{14}\text{NO}$ ($\text{M}+\text{H}^+$), 164.1075; found, 164.1073.

Ene-yne-imino ether compound 4f.

A pale yellow oil (50% yield for two steps); IR (neat) 642, 668, 913, 1038, 1083, 1197, 1252, 1280, 1434, 1640, 1674 (C=N), 2095 (C≡C), 2360, 2940, 3291 (≡C-H) cm^{-1} ; ^1H NMR (270 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 1.62–1.66 (m, 4H), 2.12–2.16 (m, 2H), 2.20–2.24 (m, 2H), 2.28 (dddt, J = 1.4, 1.4, 7.0, 7.3 Hz, 2H), 2.99 (s, 1H), 3.26 (t, J = 7.3 Hz, 2H), 3.63 (s, 3H), 4.97 (ddt, J = 0.5, 10.0, 1.4 Hz, 1H), 5.05 (ddt, J = 0.5, 17.3, 1.4 Hz, 1H), 5.86 (ddt, J = 10.0, 17.3, 7.0 Hz, 1H); ^{13}C NMR (67.8 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 21.7, 22.2, 28.0, 29.6, 36.6, 49.2, 52.9, 79.3, 83.2, 115.3, 119.3, 137.6, 139.5, 161.6. HRMS (FAB): calcd for $\text{C}_{14}\text{H}_{20}\text{NO}$ ($\text{M}+\text{H}^+$), 218.1545; found, 218.1543.

Synthesis of ene-yne-imino compound 4e.

To a solution of the compound **14**¹ (0.21 g, 1.0 mmol) in dichloromethane (10 mL) were added Na_2SO_4 (1.14 g, 8.0 mmol) and *tert*- BuNH_2 (0.32 mL, 3.0 mmol) under N_2 , and the solution was stirred at room temperature for 40 h. The reaction mixture was filtered, and the organic solvent was removed under reduced pressure to afford the corresponding imine as a yellow oil. To a solution of the obtained imine in MeOH (10 mL) was added K_2CO_3 (0.21 g, 1.5 mmol), and the solution was stirred at room temperature for 30 min. The reaction mixture was poured into water, and the aqueous phase was extracted with Et_2O (20 mL x 3). The combined organic phase was dried over MgSO_4 . The organic solvent was removed under reduced pressure to afford the compound **4e** (0.15 g, 0.78 mmol, 78% yield) as a pale yellow oil; IR (neat) 696, 735, 1077, 1210, 1365, 1435, 1629, 1677 (C=N), 2094 (C≡C), 2360, 2925, 3286 (≡C-H) cm^{-1} ; ^1H NMR (270 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 1.19 (s, 9H), 1.62–1.68 (m, 4H), 2.30–2.34 (m, 4H), 3.35 (s, 1H), 8.54 (s, 1H); ^{13}C NMR (67.8 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$)

δ 22.1, 22.7, 24.7, 29.9, 31.7, 57.5, 82.7, 83.4, 125.9, 144.4, 156.1. HRMS (FAB): calcd for $C_{13}H_{20}N$ ($M+H^+$), 190.1596; found, 190.1595.

Typical Procedure for Rhodium-Catalyzed Cyclopropanations of Alkenes.

$[Rh(OAc)_2]_2$ (2.2 mg, 0.005 mmol) was placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated CH_2Cl_2 (1.0 mL). To the solution were added an alkene (0.40 mmol) and a solution of **4** (0.20 mmol) in CH_2Cl_2 (1.0 mL) at room temperature under N_2 . After the reaction was complete, the organic solvent and an excess alkene were removed under reduced pressure, and the residue was filtered with short Florisil[®] column or subjected to column chromatography on Fuji Silysia Chemical silica gel FL 100DX with hexane /AcOEt (v/v = 50/1) as an eluent to afford the cyclopropanes.

Cyclopropane 6a.

A yellow oil (82% yield, *cis/trans* = 4/96); IR (neat) 698, 750, 944, 1040, 1218, 1385, 1446, 1544, 1602, 1705, 2359, 2852, 2928, 3400 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$, 25 $^{\circ}C$): *cis* isomer, δ 1.26 (ddd, J = 5.6, 6.4, 6.4 Hz, 1H), 1.49 (ddd, J = 5.6, 8.8, 8.8 Hz, 1H), 1.56–1.62 (m, 4H), 1.80 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.17 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.52–2.58 (m, 4H), 2.88 (s, 3H), 3.60 (s, 3H), 6.76 (d, J = 7.6 Hz, 2H), 7.03–7.31 (m, 3H); *trans* isomer, δ 1.29 (ddd, J = 5.2, 6.0, 8.8 Hz, 1H), 1.36 (ddd, J = 5.2, 6.0, 8.8 Hz, 1H), 1.65–1.73 (m, 4H), 1.84 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 2.07 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 2.54–2.60 (m, 4H), 3.36 (s, 3H), 3.82 (s, 3H), 7.14–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 $^{\circ}C$): *cis* isomer, δ 13.7, 16.7, 20.9, 22.2, 23.0, 24.1, 24.3, 28.0, 61.0, 99.4, 116.4, 125.1, 125.6, 126.3, 127.5, 128.3, 140.1; *trans* isomer, δ 15.8, 18.7, 21.0, 22.5, 23.8, 23.9, 24.1, 28.6, 60.9, 99.2, 114.3, 118.1, 125.5, 125.6, 128.3, 140.6, 142.5. HRMS (FAB): calcd for $C_{19}H_{23}NO$ (a mixture of *cis* and *trans* isomers) (M^+), 281.1780; found, 281.1778.

Cyclopropane 7a.

A yellow oil (88% yield, d.r. = 88/12, as a mixture of *cis* and *trans* isomers); IR (neat) 700, 763, 1029, 1070, 1244, 1264, 1382, 1397, 1445, 1600, 1705, 2360, 2932, 3392 cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 1.19 (s, 3H), 1.22–1.27 (m, 1H), 1.24–1.26 (m, 1H), 1.47–1.53 (m, 1H), 1.47–1.53 (m, 1H), 1.60 (s, 3H), 1.65–1.70 (m, 4H), 1.70–1.78 (m, 4H), 1.91–1.96 (m, 1H), 1.91–1.96 (m, 1H), 2.36–2.42 (m, 4H), 2.50–2.62 (m, 4H), 2.95 (s, 3H), 3.28 (s, 3H), 3.57 (s, 3H), 3.78 (s, 3H), 6.98–7.13 (m, 6H), 7.27–7.34 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ 20.2, 20.7, 20.9, 21.2, 21.4, 23.3, 23.4, 24.4, 24.7, 24.8, 24.8, 24.9, 25.0, 25.0, 25.5, 25.7, 28.4, 28.8, 61.1, 61.2, 99.4, 99.6, 115.3, 115.5, 115.5, 116.4, 125.2, 125.6, 126.0, 126.6, 127.5, 128.6, 140.8, 143.0, 147.3, 151.5. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{25}\text{NO}$ (a mixture of *cis* and *trans* isomers) (M^+), 295.1936; found, 295.1943.

Cyclopropane 8a.

A yellow oil (90% yield, *cis/trans* = 10/90); IR (neat) 1032, 1192, 1241, 1363, 1434, 1599, 1682, 1712, 2390, 2858, 2932, 3400 cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): *cis* isomer, δ 0.76–0.80 (m, 1H), 0.98 (ddd, J = 4.0, 5.2, 8.4 Hz, 1H), 1.28 (s, 9H), 1.48–1.54 (m, 1H), 1.60–1.72 (m, 4H), 2.48–2.55 (m, 4H), 3.36 (s, 3H), 3.37–3.41 (m, 1H), 3.76 (s, 3H); *trans* isomer, δ 0.79 (ddd, J = 4.0, 5.6, 7.2 Hz, 1H), 1.03 (ddd, J = 5.6, 6.0, 9.6 Hz, 1H), 1.24 (s, 9H), 1.51 (ddd, J = 4.0, 4.0, 9.6 Hz, 1H), 1.60–1.72 (m, 4H), 2.48–2.55 (m, 4H), 3.37 (s, 3H), 3.38 (ddd, J = 4.0, 6.0, 7.2 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): *cis* isomer, δ 14.0, 15.8, 21.3, 22.9, 24.3, 24.6, 28.4, 28.5, 52.2, 61.2, 74.9, 99.5, 114.0, 117.0, 140.7; *trans* isomer, δ 11.2, 13.4, 21.4, 22.9, 24.5, 24.7, 28.2, 28.6, 50.0, 61.3, 74.9, 99.7, 115.3,

115.8, 140.6. HRMS (FAB): calcd for C₁₇H₂₇NO₂ (a mixture of *cis* and *trans* isomers) (M⁺), 277.2042; found, 277.2040.

Cyclopropane 9a.

A yellow oil (100% yield); IR (neat) 694, 754, 955, 989, 1052, 1379, 1435, 1542, 1598, 1705, 2360, 2859, 2929, 3445 cm⁻¹; ¹H NMR (270 MHz, CD₂Cl₂, 25 °C) δ 1.14 (t, *J* = 7.3 Hz, 3H), 1.19 (dd, *J* = 5.1, 7.0 Hz, 1H), 1.21 (t, *J* = 7.3 Hz, 3H), 1.31 (dd, *J* = 5.1, 10.3 Hz, 1H), 1.56–1.67 (m, 4H), 1.98 (dd, *J* = 7.0, 10.3 Hz, 1H), 2.48–2.53 (m, 4H), 3.37 (s, 3H), 3.46–3.58 (m, 2H), 3.63–3.73 (m, 2H), 3.76 (s, 3H); ¹³C NMR (67.8 MHz, CD₂Cl₂, 25 °C) δ 15.6, 15.6, 18.7, 21.3, 21.6, 23.0, 24.3, 24.6, 28.7, 61.3, 61.5, 62.4, 91.4, 99.9, 114.3, 115.7, 140.7. HRMS (FAB): calcd for C₁₇H₂₇NO₃ (M⁺), 293.1991; found, 293.1992.

Cyclopropane 10a.

A yellow oil (88% yield, d.r. = 76/24, as a mixture of *cis* and *trans* isomers); IR (neat) 754, 845, 1035, 1050, 1253, 1379, 1435, 1597, 1707, 2360, 2859, 2935, 3400 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ -0.04 (s, 9H), 0.15 (s, 9H), 0.86 (dd, *J* = 5.2, 6.8 Hz, 1H), 0.93 (dd, *J* = 5.2, 9.6 Hz, 1H), 1.12 (dd, *J* = 5.2, 6.4 Hz, 1H), 1.23 (dd, *J* = 5.2, 9.6 Hz, 1H), 1.37–1.41 (m, 1H), 1.37–1.41 (m, 1H), 1.47 (s, 3H), 1.53 (s, 3H), 1.54–1.58 (m, 4H), 1.65–1.70 (m, 4H), 2.42–2.53 (m, 4H), 2.42–2.53 (m, 4H), 3.32 (s, 3H), 3.35 (s, 3H), 3.73 (s, 3H), 3.76 (s, 3H); ¹³C NMR (100 MHz, CD₂Cl₂, 25 °C) δ 1.07, 1.51, 19.4, 19.7, 20.4, 21.3, 21.4, 21.8, 22.1, 23.0, 23.2, 24.4, 24.6, 24.7, 24.8, 26.7, 28.6, 28.8, 56.8, 58.0, 61.1, 61.3, 99.5, 99.6, 115.3, 116.0, 121.7, 122.5, 140.5, 146.6. HRMS (FAB): calcd for C₁₇H₂₉NO₂Si (a mixture of *cis* and *trans* isomers) (M⁺), 307.1968; found, 307.1967.

Cyclopropane 6b.

A yellow oil (88% yield, *cis/trans* = 3/97); IR (neat) 639, 915, 1032, 1075, 1197, 1254, 1280, 1434, 1627, 1673, 2860, 2940, 3289 cm^{-1} ; ^1H NMR (400 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): *cis* isomer, δ 1.30 (ddd, J = 4.8, 6.4, 6.4 Hz, 1H), 1.47 (ddd, J = 4.8, 8.8, 8.8 Hz, 1H), 1.74–1.85 (m, 4H), 2.10 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.18 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.45–2.57 (m, 4H), 3.59 (s, 3H), 3.83–3.99 (m, 2H), 4.85 (dd, J = 1.6, 17.2 Hz, 1H), 5.00 (dd, J = 1.6, 10.4 Hz, 1H), 5.68 (ddt, J = 10.4, 17.2, 5.6 Hz, 1H), 6.81 (d, J = 6.8 Hz, 2H), 7.06–7.13 (m, 3H); *trans* isomer, δ 1.27 (ddd, J = 4.8, 5.6, 8.4 Hz, 1H), 1.36 (ddd, J = 4.8, 5.6, 8.4 Hz, 1H), 1.63–1.75 (m, 4H), 1.82 (ddd, J = 4.8, 4.8, 8.4 Hz, 1H), 2.05 (ddd, J = 4.8, 4.8, 8.4 Hz, 1H), 2.52–2.65 (m, 4H), 3.79 (s, 3H), 4.37–4.39 (m, 2H), 4.77 (ddd, J = 1.6, 3.6, 16.8 Hz, 1H), 5.05 (ddd, J = 1.6, 3.6, 10.4 Hz, 1H), 5.87 (ddt, J = 10.4, 16.8, 5.2 Hz, 1H), 7.14–7.21 (m, 3H), 7.28–7.32 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^\circ\text{C}$): *cis* isomer, δ 13.7, 17.2, 21.3, 22.5, 23.5, 24.4, 24.7, 44.1, 61.4, 99.8, 113.8, 115.0, 117.0, 125.4, 126.9, 127.7, 136.0, 140.5, 140.6; *trans* isomer, δ 16.1, 19.3, 21.4, 23.1, 24.0, 24.3, 24.6, 44.5, 61.4, 99.7, 114.9, 115.4, 117.8, 125.8, 128.6, 128.8, 136.0, 140.7, 143.1. HRMS (FAB): calcd for $\text{C}_{21}\text{H}_{25}\text{NO}$ (a mixture of *cis* and *trans* isomers) (M^+), 307.1936; found, 307.1931.

Cyclopropane 6c.

A white solid (81% yield, *cis/trans* = 27/73); mp. 102.8–104.2 $^\circ\text{C}$; IR (KBr) 698, 754, 988, 1029, 1071, 1244, 1379, 1454, 1501, 1547, 1599, 1705, 2855, 2931, 3391 cm^{-1} ; ^1H NMR (300 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$): *cis* isomer, δ 1.21–1.24 (m, 1H), 1.33 (ddd, J = 5.2, 8.8, 8.8 Hz, 1H), 1.68–1.77 (m, 4H), 1.73–1.82 (m, 1H), 2.17–2.23 (m, 1H), 2.52–2.67 (m, 4H), 3.46 (s, 3H), 6.42–6.44 (m, 2H), 6.69–6.73 (m, 2H),

6.96–7.02 (m, 3H), 7.18–7.23 (m, 3H); *trans* isomer, δ 1.05–1.09 (m, 2H), 1.68–1.77 (m, 4H), 1.73–1.82 (m, 2H), 2.52–2.67 (m, 4H), 3.59 (s, 3H), 6.74–6.76 (m, 2H), 7.05–7.15 (m, 3H), 7.20–7.33 (m, 5H); ^{13}C NMR (75 MHz, CD_2Cl_2 , 25 °C): *cis* isomer, δ 14.4, 18.0, 21.2, 22.9, 23.4, 24.3, 24.6, 61.2, 101.0, 115.4, 118.6, 125.1, 126.1, 126.7, 127.5, 127.7, 128.2, 137.6, 140.4, 142.7; *trans* isomer, δ 16.3, 20.0, 21.3, 23.0, 24.3, 24.6, 25.0, 61.3, 101.0, 116.2, 119.5, 125.5, 125.8, 126.7, 127.9, 128.1, 128.8, 137.9, 140.9, 142.6. HRMS (FAB): calcd for $\text{C}_{24}\text{H}_{25}\text{NO}$ (a mixture of *cis* and *trans* isomers) (M^+), 343.1936; found, 343.1932.

Cyclopropane 6d.

A yellow oil (93% yield, *cis/trans* = 45/55); IR (neat) 698, 799, 1042, 1074, 1261, 1354, 1403, 1461, 1573, 1619, 1715, 2850, 2946, 3400 cm^{-1} ; ^1H NMR (270 MHz, CD_2Cl_2 , 25 °C): *cis* isomer, δ 1.27 (ddd, J = 5.1, 5.9, 5.9 Hz, 1H), 1.39 (ddd, J = 5.1, 8.6, 8.6 Hz, 1H), 2.09–2.28 (m, 4H), 2.49–2.56 (m, 2H), 2.63 (t, J = 7.3 Hz, 2H), 2.69 (s, 3H), 3.70 (s, 3H), 6.87 (dd, J = 1.6, 7.6 Hz, 2H), 7.04–7.12 (m, 3H); *trans* isomer, δ 1.22–1.36 (m, 2H), 1.84 (ddd, J = 5.4, 8.9, 8.9 Hz, 1H), 1.99 (ddd, J = 5.4, 8.9, 8.9 Hz, 1H), 2.09–2.28 (m, 2H), 2.44–2.56 (m, 2H), 2.63 (t, J = 7.3 Hz, 2H), 3.29 (s, 3H), 3.84 (s, 3H), 7.06–7.19 (m, 3H), 7.25–7.31 (m, 2H); ^{13}C NMR (67.8 MHz, CDCl_3 , 25 °C): *cis* isomer, δ 11.7, 17.9, 23.4, 25.6, 25.8, 28.7, 32.1, 58.6, 103.7, 111.3, 125.4, 127.2, 127.3, 127.7, 138.3, 140.0; *trans* isomer, δ 15.6, 20.1, 24.8, 25.4, 25.5, 29.1, 32.0, 58.7, 104.0, 115.6, 124.4, 125.7, 125.8, 128.5, 138.5, 143.0. HRMS (FAB): calcd for $\text{C}_{18}\text{H}_{21}\text{NO}$ (a mixture of *cis* and *trans* isomers) (M^+), 267.1623; found, 267.1620.

Cyclopropane 6e.

A yellow oil (18% yield, as a mixture of *cis* and *trans* isomers); IR (neat) 696, 735, 772, 1077, 1187, 1224, 1300, 1365, 1459, 1497, 1677, 2851, 2926, 2977, 3245, 3299 cm^{-1} ; ^1H NMR (270 MHz, d_8 -THF, 25 °C) δ 1.32 (s, 9H), 1.55 (s, 9H), 1.52–1.62 (m, 8H), 1.62–1.70 (m, 4H), 1.77–1.96 (m, 2H), 2.13 (ddd, J = 5.9, 8.6, 8.6 Hz, 1H), 2.23 (ddd, J = 5.9, 5.9, 8.6 Hz, 1H), 2.40–2.61 (m, 8H), 6.44 (s, 1H), 6.51 (s, 1H), 6.82–6.85 (m, 3H), 7.00–7.19 (m, 5H), 7.26–7.31 (m, 2H); ^{13}C NMR (67.8 MHz, CD_2Cl_2 , 25 °C) δ 17.0, 19.2, 22.1, 22.6, 22.7, 23.1, 24.5, 24.5, 24.7, 25.1, 25.2, 25.2, 25.4, 26.2, 31.5, 31.6, 56.2, 56.3, 114.3, 115.2, 117.2, 120.9, 121.9, 122.2, 125.3, 125.3, 125.7, 125.8, 127.1, 127.8, 128.6, 129.8, 141.3, 143.1. HRMS (FAB): calcd for $\text{C}_{21}\text{H}_{27}\text{N}$ (a mixture of *cis* and *trans* isomers) (M^+), 293.2144; found, 293.2144.

Synthesis of Pyrrolin-2-one Derivatives 11.

$[\text{Rh}(\text{OAc})_2]_2$ (2.2 mg, 0.005 mmol) was placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated CH_2Cl_2 (1.0 mL). To this solution were added an alkene (0.40 mmol) and a solution of **4** (0.20 mmol) in CH_2Cl_2 (1.0 mL) at room temperature under N_2 . After the reaction was complete, the organic solvent and excess alkene were removed under reduced pressure to afford the compound **6** as a yellow oil. To a solution of the crude compound **6** in EtOH/ H_2O was added 1 N HCl solution (3 drops), and the solution was stirred at 60 °C for 3 h. The reaction mixture was poured into water and the aqueous phase was extracted with EtOAc (20 mL x 3). The combined organic phase was dried over MgSO_4 . The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with $\text{CH}_2\text{Cl}_2/\text{AcOEt}$ (v/v = 10/1) as an eluent to afford the compound **11** as a pale yellow oil.

Pyrrolin-2-one derivative 11a.

A pale yellow oil (81% yield, as a mixture of two diastereoisomers); IR (neat) 698, 751, 1036, 1256, 1399, 1428, 1680 ($\text{C}=\text{O}$), 2930, 3364 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ 0.81–0.89 (m, 2H), 1.02 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 1.06–1.13 (m, 2H), 1.18 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 1.59–1.77 (m, 8H), 1.87 (ddd, J =

5.2, 5.2, 8.8 Hz, 1H), 1.95 (ddd, $J = 5.2, 5.2, 8.8$ Hz, 1H), 2.15–2.34 (m, 8H), 3.01 (s, 3H), 3.04–3.07 (m, 2H), 3.07 (s, 3H), 7.04–7.06 (m, 4H), 7.15–7.20 (m, 2H), 7.24–7.30 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C) δ 11.5, 14.5, 18.8, 20.2, 20.3, 21.7, 21.8, 21.9, 22.2, 22.3, 23.5, 23.6, 23.7, 23.9, 27.4, 27.4, 68.9, 68.9, 125.5, 125.5, 125.8, 125.9, 128.4, 128.4, 131.3, 131.4, 141.1, 141.2, 152.8, 152.9, 171.0, 171.0. HRMS (FAB): calcd for $\text{C}_{18}\text{H}_{22}\text{NO}$ (a mixture of *cis* and *trans* isomers) ($\text{M}+\text{H}^+$), 268.1701; found, 268.1696.

Pyrrolin-2-one derivative 11b.

A pale yellow oil (87% yield, as a mixture of two diastereoisomers); IR (neat) 698, 752, 1409, 1434, 1682 ($\text{C}=\text{O}$), 2928, 3417 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3 , 25 °C) δ 0.81–0.90 (m, 2H), 0.98–1.07 (m, 2H), 1.07–1.16 (m, 2H), 1.58–1.80 (m, 8H), 1.86 (ddd, $J = 5.2, 5.2, 8.8$ Hz, 1H), 1.92 (ddd, $J = 5.2, 5.2, 8.8$ Hz, 1H), 2.15–2.30 (m, 8H), 3.20 (d, $J = 9.2$ Hz, 1H), 3.22 (d, $J = 9.2$ Hz, 1H), 3.65 (dd, $J = 8.0, 16.0$ Hz, 1H), 3.88 (dd, $J = 8.0, 16.0$ Hz, 1H), 4.49–4.62 (m, 2H), 5.12–5.18 (m, 4H), 5.68–5.83 (m, 2H), 7.02–7.05 (m, 4H), 7.14–7.20 (m, 2H), 7.25–7.29 (m, 4H); ^{13}C NMR (67.8 MHz, CDCl_3 , 25 °C) δ 12.1, 14.7, 19.3, 20.3, 20.3, 21.5, 21.8, 22.0, 22.3, 22.3, 23.7, 23.8, 23.8, 23.8, 42.3, 42.6, 66.2, 66.4, 116.5, 116.6, 125.4, 125.5, 125.9, 125.9, 128.4, 128.4, 131.0, 131.2, 134.4, 134.4, 141.3, 141.3, 153.5, 153.6, 170.7, 170.7. HRMS (FAB): calcd for $\text{C}_{20}\text{H}_{24}\text{NO}$ (a mixture of *cis* and *trans* isomers) ($\text{M}+\text{H}^+$), 294.1858; found, 294.1854.

Pyrrolin-2-one derivative 11c.

A pale yellow oil (96% yield, as a mixture of two diastereoisomers); IR (neat) 698, 753, 1090, 1409, 1434, 1682 ($\text{C}=\text{O}$), 2929, 3399 cm^{-1} ; ^1H NMR (270 MHz,

CDCl₃, 25 °C) δ 0.72–0.92 (m, 3H), 0.951.18 (m, 3H), 1.53–1.89 (m, 9H), 1.92–2.04 (m, 1H), 2.13–2.37 (m, 8H), 3.88–3.96 (m, 2H), 6.65–6.73 (m, 4H), 7.06–7.20 (m, 8H), 7.22–7.47 (m, 8H); ¹³C NMR (67.8 MHz, CDCl₃, 25 °C) δ 6.8, 8.4, 19.0, 20.0, 20.4, 20.5, 21.8, 21.9, 22.3, 22.5, 22.8, 23.2, 23.8, 24.6, 61.6, 63.2, 125.6, 125.7, 125.9, 126.0, 126.0, 126.2, 127.7, 127.9, 128.0, 128.2, 128.6, 128.8, 130.6, 131.4, 137.0, 137.1, 137.9, 137.9, 154.7, 154.7, 170.2, 170.2. HRMS (FAB): calcd for C₂₃H₂₄NO (a mixture of *cis* and *trans* isomers) (M+H⁺), 330.1858; found, 330.1855.

Rhodium-Catalyzed Intramolecular Cyclopropanation.

Tetracyclic Compound **12**.

[Rh(OAc)₂]₂ (2.2 mg, 0.005 mmol) was placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated ClCH₂CH₂Cl (15 mL) at room temperature under N₂. To this solution was added a solution of **4f** (44 mg, 0.20 mmol) in ClCH₂CH₂Cl (5.0 mL) at 60 °C for 1 h. After the reaction was complete, the organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on Fuji Silysia Chemical silica gel FL 100DX with hexane /AcOEt (v/v = 50/1) as an eluent to afford the compound **12** (18 mg, 0.08 mmol, 40%) as a yellow oil; IR (neat) 740, 829, 917, 995, 1057, 1227, 1335, 1386, 1445, 1585, 1710, 2853, 2927, 3400 cm⁻¹; ¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ 0.61 (ddd, *J* = 4.8, 4.8, 5.2 Hz, 1H), 0.80 (ddd, *J* = 5.2, 8.4, 8.4 Hz, 1H), 1.38–1.45 (m, 1H), 1.60–1.70 (m, 4H), 1.84 (ddd, *J* = 4.8, 8.4, 8.4 Hz, 1H), 1.92–2.07 (m, 2H), 2.21–2.41 (m, 1H), 2.45–2.55 (m, 4H), 3.17 (ddd, *J* = 4.8, 12.4, 12.4 Hz, 1H), 3.72 (s, 3H), 3.80–3.85 (m, 1H); ¹³C NMR (100 MHz, CD₂Cl₂, 25 °C) δ 8.3, 8.5, 11.1, 21.2, 21.6, 22.6, 24.6, 24.6, 35.8, 61.5, 99.7, 111.5, 115.9, 139.1. HRMS (FAB): calcd for C₁₄H₂₁NO (M+H⁺), 218.1545; found, 218.1543.

References

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Washizuka, K.-i.; Minakata, S.; Ryu, I.; Komatsu, M. *Tetrahedron* **1999**, *55*, 12969.

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 RGAIN

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OBNUC 1H
EXMOD NON

OBERQ 399.65 MHz
OBSF 124.00 KHz
OBSF 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 2.952 sec
PWI 8.5 us
IRNUC 1H
CTEMP 25.8 c
CDCL3
SLVNT
EXREF 0.00 ppm
BF 0.15 Hz
RGAIN 16

C:\WINNR98\COMMON\DEFAULT.ALS
FN-C-414-florisil-13C

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT FN-C-414-florisil-13C
DATIM Sat Jul 13 13:07:39 2002
OBNUC 13C
EXMOD ECM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 382
ACQTM 1.206 sec
PD 1.794 sec
FID 5.0 us
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.15 Hz
RGAIN 33

In pages S29 and S30, the diastereomeric ratio (*cis:trans*) of **6b** before and after Florisil column chromatography was shown. It is clear that it changed from 68:32 to 3:97.

C:\WINNR98\COMMON_DEFAULT.ALS
FN-C-407-florisil

DFILE C:\WINNR98\COMMON_DEFAULT.ALS
COMNT FN-C-407-florisil
DATIM Fri Jul 05 13:05:08 2002

EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OFFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 2.952 sec
PUL 8.5 us
PRG 1H
TNUC 1H
TEMP 26.3 C
SOLNT CDCl3
EXREF 0.00 ppm
BF 0.10 Hz
RGAIN 21

After Florisil column chromatography

6b (*cis:trans* = 3:97)

C:\WINNR98\COMMON\DEFAULT.ALS
FN-C-385-13CinCDCL3

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT FN-C-385-13CinCDCL3
DATIM Sat May 18 16:33:41 2002
ORNUC 13C
EXMOD BCM
OBFREQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQ 27173.9 Hz
SCANS 548
ACQTM 1.206 sec
PD 1.794 sec
PWL 5.0 us
IRNUC 1H
CTEMP 26.9 c
SIVNT CDCL3
EXREF 77.00 ppm
BF 1.00 Hz
RGAIN 33

C:\WINNR98\COMMON\DEFAULT.ALS
 FN-C-513-fri in CD2CL2

MENUC NON
 OBNUC 1H
 OFR 300.40 MHz
 OBSET 130.00 KHz
 OFIN 1150.0 Hz
 PW1 5.6 us
 DEADT 97.2 us
 PREDL 0.2000 ms
 TWT 1.0 sec
 POINT 32768
 SFO 32768
 TIMES 16
 SCANS 16
 DUMIT 1
 FREQU 6013.2 Hz
 FLT 3000 Hz
 DELAY 66.7 us
 ACQTM 5.449 sec
 PD 1.551 sec
 ADBIT 16.00
 RGAIN 17
 BF 0.10 Hz
 T1 0.00
 T2 0.00
 T3 90.00
 T4 100.00
 EXMOD NON
 EXPCM NON:Single, coupled:PW1_ACQTM_PD:1H
 INUC 1H
 IFR 300.40 MHz
 IRSET 130.00 KHz
 IRFIN 1150.0 Hz
 IRREW 45 us
 IRATN 511
 C:\WINNR98\COMMON\DEFAULT.ALS
 THS
 SF 25.50 KHz
 LKSET 63.0 Hz
 LKFIN 180
 LKLEV 16
 LKAIN 83
 LKPHS 503
 LKSIG 10 Hz
 CSFED
 FILDG
 FILDG

C:\WINNR98\COMMON\DEFAULT.ALS
 FN-C-513-fx1-13C in CD2CL2

```

MENUF          BCM
OBNUC          13C
OFR            75.45 MHz
OBSET          124.00 KHz
OBFIN          1840.0 Hz
PW1            4.5 us
DEADT          27.2 us
PREDL          0.2000 ms
IWT            1.0 sec
POINT          32768
SFO            32768
TIMES          3600
SCANS          830
DUMMY          1
FREQU          20408.1 Hz
FLT            10200 Hz
DELAY          19.6 us
ACQTM          1.606 sec
PD             1.394 sec
ADBIT          16.00
RGAIN          24
BF             0.10 Hz
T1             0.00
T2             0.00
T3             90.00
T4             100.00
EXMOD          BCM
EXPCM          Bilevel.complete.decoupling: Set_IR
IRNUC          1H
IFR            300.40 MHz
TESET          130.00 KHz
IRFIN          1150.0 Hz
IRREW          45 us
IRATN          511
DEFILE         C:\WINNR98\COMMON\DEFAULT.ALS
SF             THS
LKSET          25.50 KHz
LRFIN          63.0 Hz
LKLEV          180
LGAIN          16
LRPHS          83
LKSIG          475
CSPED          11 Hz
FILDG          FILDF
  
```

C:\WINNR98\COMMON\DEFAULT.ALS
FN-C-519-florisil in CD2Cl2

C:\WINNR98\COMMON\DEFAULT.ALS
COMNT FN-C-519-florisil in CD2Cl2
DATIM Fri Jan 24 20:05:31 2003

OBNUC 1H
EXMOD NON
270.05 MHz
112.00 KHz
5800.0 Hz
16384
POINT
5402.4 Hz
FREQU 16
SCANS 3.033 sec
ACQTM 2.000 sec
PD 5.6 us
PWL 25.4 c
IRNUC 1H
CTEMP CD2Cl
SLVNT 5.32 ppm
EXREF 1.00 Hz
BF 18
RGAIN

C:\WINMR98\COMMON\DEFAULT.ALS
FN-C-519-florisil-13C in CD2CL2

DFILE C:\WINMR98\COMMON\DEFAULT.ALS
COMNT FN-C-519-florisil-13C in CD2CL2
DATIM Fri Jan 24 20:54:30 2003
CENUC 13C
EXMOD ECM

OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 846
ACQTM 1.789 sec
PD 1.211 sec
PWL 4.2 us
IRNUC 1H
CTEMP 25.7 c
SLVNT CD2CL
EXREF 53.80 ppm
BF 1.00 Hz
RGAIN 28

C:\WINNMR98\COMMON_DEFAULT.ALS
FN-C-403-fr1

DFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMNT FN-C-403-fr1
DATIM Mon Jul 01 21:28:17 2002

OBNUC 1H
EXMOD NON
OBPRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6002.4 Hz
SCANS 16
ACQTM 5.459 sec
PD 1.551 sec
PWI 5.7 us
IRNUC 1H
CTEMP 24.8 c
SIVNT C4D8O2
EXREF 3.58 ppm
BF 2.00 Hz
RGAIN 17

C:\WINMR98\COMMON\DEFAULT.ALS
FN-C-520-fri-13C in CD2CL2

DFILE C:\WINMR98\COMMON\DEFAULT.ALS
COMNT FN-C-520-fri-13C in CD2CL2
DATIM Sat Jan 25 11:04:12 2003
ORNUC 13C
EXMOD BCM

OBFRQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 13391
ACQTM 1.789 sec
PD 1.211 sec
PW1 4.2 us
IRNUC 1H
CTEMP 25.3 C
CD2CL
SLVNT 53.80 ppm
EXREF 1.00 Hz
BF 28
RGAIN

DDFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SSLVT
EXREF
BF
RGAIN

```
C:\WINNMR98\COMMON\_DEFAULT.ALS
FN-C-471-crude
Mon Oct 07 21:59:52 2002
1H
NON
```

	399.65 MHz
	124.00 KHz
	10500.0 Hz
	16384
	8000.0 Hz
	16
	2.048 sec
	2.952 sec
	8.5 us
1H	
CD ₂ Cl ₂	27.0 °C
	5.32 ppm
	0.25 Hz
	14

C:\WINNMR98\COMMON_DEFAULT.ALS
FN-C-471-crude-13C

DEFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMNT FN-C-471-crude-13C
DATIM Mon Oct 07 22:28:40 2002

OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQ 27173.9 Hz
SCANS 409
ACQTM 1.206 sec
PD 1.794 sec
PWI 5.0 us
IRNUC 1H
CTEMP 27.0 c
SIVNT CD2CL
EXREF 53.80 ppm
BF 0.25 Hz
RGAIN 33

D:\1H NMR-1\tBu-vinyl ether in CD2Cl2 (400) 02-21.als
tBu-vinyl ether

DFILE D:\1H NMR-1\tBu-vinyl ether in CD2
COMNT tBu-vinyl ether
DATIM Fri Feb 21 22:00:39 2003
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 2.952 sec
PWL 5.4 us
IRNUC 1H
CTEMP 24.5 C
SLVNT CD2CL
EXREF BF
RGAIN 12

C:\WINNR98\COMMON\DEFAULT.ALS
tBu-vinyl ether-Florisil-13C

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
CONNT tBu-vinyl ether-Florisil-13C
DATIM Fri Feb 21 23:47:16 2003

OBNUC 13C
EXMOD BCM
OBSFQ 100.40 MHz
OBSET 125.00 KHz
OBSFQ 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 790
ACQTM 1.206 sec
PD 1.794 sec
PWL 5.0 us
IRNUC 1H
CTEMP 25.3 c
SLVNT CD2CL
EXREF 53.80 ppm
BF 0.25 Hz
RGAIN 33

8a

C:\WINMR98\COMMON\DEFAULT.ALS
 FN-C-474-crude in CD2CL2

DFILE C:\WINMR98\COMMON\DEFAULT.ALS
 COUNT FN-C-474-crude in CD2CL2
 DATIM Thu Oct 10 23:44:06 2002
 OBNUC 1H
 EXMOD NON

OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OBFIN 5800.0 Hz
 POINT 16384
 FREQU 5402.4 Hz
 SCANS 16
 ACQTM 3.033 sec
 PD 2.000 sec
 FW1 5.6 us
 IRNUC 1H
 CTEMP 24.5 c
 SLVNT CD2CL
 EXREF 5.32 ppm
 BF 0.12 Hz
 RGAIN 18

C:\WINNMR98\COMMON\DEFAULT.ALS
 FN-C-474-crude-13C in CD2CL2

DFILE C:\WINNMR98\COMMON\DEFAULT.ALS
 COMNT FN-C-474-crude-13C in CD2CL2
 DATIM Fri Oct 11 00:13:53 2002

OBNUC 13C
 EXMOD BCM
 OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.0 Hz
 POINT 32768
 FREQU 18315.0 Hz
 SCANS 426
 ACQTM 1.789 sec
 PD 1.211 sec
 PW1 4.2 us
 IRNUC 1H
 CTEMP 24.2 C
 SLVNT CD2CL
 EXREF 53.80 ppm
 BF 0.12 Hz
 RGAIN 28

C:\WINNMR98\COMMON_DEFAULT.ALS
FN-C-472-Crude

DEFILE C:\WINNMR98\COMMON_DEFAULT.ALS
COMMIT FN-C-472-crude
DATE Mon Oct 07 22:38:47 2002
OENUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.0 Hz
POINT 16384
FREQ 8000.0 Hz
SCANS 8
2.048 sec
2.352 sec
8.5 us
PD
PWL 1H
IRNUC 26.2 c
CTEMP
SIVNT CD2CL
EXREF 5.32 ppm
BF 0.25 Hz
RGAIN 15

C:\WINNR98\COMMON_DEFAULT.ALS
FN-C-472-crude-13C

DFILE
COMNT
DATIM
OENUC
EXMOD
OBFRQ
OBSET
OBFIN
POINT
FREQU
SCANS
AQTM
PD
PWI
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\WINNR98\COMMON_DEFAULT.ALS
FN-C-472-crude-13C
Mon Oct 07 23:08:57 2002
13C

ECM
100.40 MHz
125.00 KHz
10500.0 Hz
32768
27173.9 Hz
400
1.206 sec
1.794 sec
5.0 us
1H
27.3 c
CD2CL
53.80 ppm
0.25 Hz
33

10a

D:\1H NMR-1\FN-C-518-fr1 in CDCL3 (400) 01-25.als
 FN-C-518-fr1 in CDCL3

DFILE D:\1H NMR-1\FN-C-518-fr1 in CDCL3
 COMNT FN-C-518-fr1 in CDCL3
 DATIM Sat Jan 25 21:51:19 2003
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBFIN 10500.0 Hz
 POINT 16384
 FREQU 6002.4 Hz
 SCANS 16
 ACQTM 2.730 sec
 PD 2.952 sec
 FWL 8.5 us
 IRNUC 1H
 CTEMP 23.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 14

C:\WINMR98\COMMON_DEFAULT.ALS
 FN-C-518-fri-13C in CDCL3

DFILE
 COMNT FN-C-518-fri-13C in CDCL3
 DATIM Sat Jan 25 22:07:35 2003
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.0 Hz
 POINT 32768
 FREQU 27173.9 Hz
 SCANS 181
 ACQTH 1.206 sec
 PD 1.794 sec
 FWH 5.0 us
 1H
 CDCL3 24.0 c
 IRNUC
 CTMP
 SLVNT
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 33

C:\WINNMR98\COMMON\FN\FN-C-514-fr1(2nd) in CDCL3 (270) 01-21.als
 FN-C-514-fr1(2nd)

DEFILE C:\WINNMR98\COMMON\FN\FN-C-514-1
 COMNT FN-C-514-fr1(2nd)
 DATIM Tue Jan 21 23:24:46 2003
 QENUC 1H
 EXMOD NON

OBFRQ 270.05 MHz
 OBSET 112.00 KHz
 OFIN 5800.0 Hz
 POINT 16384
 FREQU 5402.4 Hz
 SCANS 16
 ACQTM 3.033 sec
 PD 2.000 sec
 PW1 5.6 us

IRNUC 1H
 CTEMP 24.6 c
 SIVNT CDCL3
 EXREF 0.00 ppm
 BF 1.20 Hz
 RGAIN 17

C:\WINNR98\COMMON\DEFAULT.ALS
FN-C-514-fr1(2nd)-13C

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT FN-C-514-fr1(2nd)-13C
DATIM Tue Jan 21 23:47:12 2003

OBNUC 13C
EXMOD BCM
OBFREQ 67.80 MHz
OBSET 135.00 KHz
OBFIN 5200.0 Hz
POINT 32768
FREQU 18315.0 Hz
SCANS 334
ACQTM 1.789 sec
PD 1.211 sec
FID 4.2 us
IRNUC 1H
CTEMP 25.9 C
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.10 Hz
RGAIN 28

1H NMR spectrum of 1,3,5-trimethyl-2,4,6-trinitrobenzene (TNT) in CDCl₃. The spectrum shows peaks from 0 to 10 ppm. Aromatic protons appear as a multiplet between 7.4 and 7.8 ppm. Methyl protons appear as a singlet at approximately 2.3 ppm. Integration values are provided for several peaks: 1.4514, 1.7625, 4.1175, 1.716, 0.5584, 4.0355, 0.6693, 1.5585, 0.7616, 0.1382, 1.5680, and 0.4603.

EXPOR		270.05 MHz			
QFREQ	OBSE	112.00 KHz			
QFREQ	OBSF	580.0 Hz			
QFREQ	POINT	16384			
QFREQ	FREQU	5402.4 Hz			
SCANS		16			
ACQTM		3.033 sec			
PD		2.000 sec			
PW1		5.6 us			
IRNUC	1H			26.1 C	
CTEMP					
SIVNT	CDCL3				
XREF				0.00 ppm	
BF				1.00 Hz	
RGAIN				19

C:\WINNR98\COMMON\DEFAULT.ALS
 FN-C-534-Fri-13C in CDCL3

C:\WINNR98\COMMON\DEFAULT.ALS
 COMNT FN-C-534-Fri-13C in CDCL3
 DATIM Sat Feb 08 23:58:18 2003
 OBNUC 13C
 EXMOD BCM

OBFRQ 67.80 MHz
 OBSET 135.00 KHz
 OBFIN 5200.0 Hz
 POINT 32768
 FREQU 18315.0 Hz
 SCANS 1312
 ACQTM 1.789 sec
 PD 1.211 sec
 PW1 4.2 us
 IRNUC 1H
 CTMP 25.8 c
 CDCL3 77.00 ppm
 EXREF 1.00 Hz
 BF 28
 RGAIN

C:\WINNR98\COMMON\DEFAULT.ALS
FN-C-487-florisil

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT FN-C-487-florisil
DATIM Fri Oct 25 22:44:24 2002
OBNUC 1H
EXMOD NON

OBFRQ 399.65 MHz
OBSET 133.60 KHz
OBFIN 21.6 Hz
POINT 16384
FREQU 8000.0 Hz
SCANS 16
ACQTM 2.048 sec
PD 2.952 sec
PW1 8.5 us
IRNUC 1H
CTEMP 26.7 C
SLVNT CD2CL
EXREF 5.32 ppm
BF 0.20 Hz
RGAIN 17

12a

C:\WINNR98\COMMON\DEFAULT.ALS
FN-C-487-florisil-13C

DFILE C:\WINNR98\COMMON\DEFAULT.ALS
COMNT FN-C-487-florisil-13C
DATIM Fri Oct 25 23:44:24 2002
OBNUC 13C
EXMOD BCM
OBFREQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.0 Hz
POINT 32768
FREQU 27173.9 Hz
SCANS 1013
AQTM 1.206 sec
PD 1.794 sec
FW 5.0 us
IRNUC 1H
CTEMP 26.8 c
SLVNT CD2CL
EXREF 53.80 ppm
BF 0.20 Hz
RGAIN 32

12a