Supporting Information

Ruthenium-Catalyzed [2+2] Cycloadditions of 2-Substituted Norbornenes

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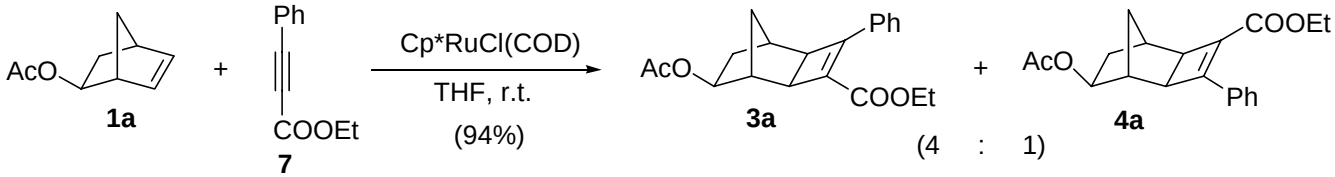
General Information: All reactions were carried out in an atmosphere of dry nitrogen at ambient temperature unless otherewise stated. Standard column chromatography was performed on 230-400 mesh silica gel (obtained from Silicycle) using flash column chromatography techniques.[12] Analytical thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} plates. All glassware was flame dried under an inert atmosphere of dry nitrogen. Infrared spectra were taken on a Bomem MB-100 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0 ppm). High resolution mass spectra were done by Mass Spectrometry Laboratory Services Division at the University of Guelph. Elemental analyses were performed by Canadian Microanalytical Service Ltd., British Columbia or by Quantitative Technologies Inc., New Jersey.

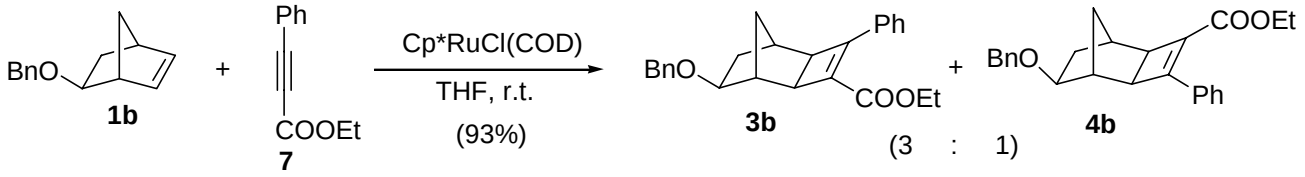
Reagents: Unless stated otherwise, commercial reagents were used without purification. Solvents were purified by distillation under dry nitrogen: from CaH_2 (1,2-dichloroethane, hexanes, chloroform, DMF, Et_3N, pyridine); from sodium (toluene); and from potassium/benzophenone (THF). Cp*RuCl(COD) and alkyne **7** were prepared according to literatre procedures.[13,14]

[12] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
[13] Fagan, P. J.; Mahoney , W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics.* **1990**, *9*, 1843.
[14] Yamamoto, H.; Maruoka, K. *J. Am. Chem. Soc.* **1981**, *103*, 6133.

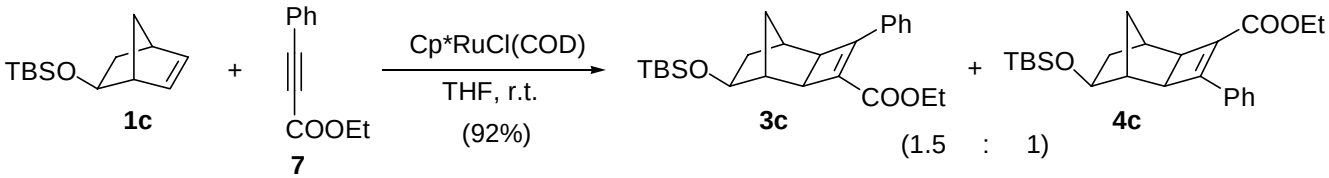


Cycloadducts 3a and 4a. A mixture of norbornene **1a** (189 mg, 1.25 mmol), acetylene **7** (43.0 mg, 0.247 mmol) and THF (0.25 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 6.8 mg, 0.018 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19, 1:9) to give an inseparable mixture of cycloadducts **3a** and **4a** (75.6 mg, 0.232 mmol, 94%, **3a**:**4a** = 4:1 measured by GC and ^{1}H NMR) as white crystals. R_f 0.39 (EtOAc:hexanes=1:9); GC (HP-1 column): retention time for major isomer **3a**=30.571 min. and retention time for minor isomer **4a**=30.695 min.; IR (CH_2Cl_2) 3066 (w), 2937 (m), 2969 (m), 1734 (s), 1704 (s), 1617 (s), 1492 (m), 1448 (m), 1374 (m), 1297 (m), 1244 (s), 1217 (s), 1204 (s), 1136 (m), 1109 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (m, 2H), 7.36 (m, 3H), 4.65 (dm, 1H, *J* = 4.6 Hz), 4.23 (q, 2H, *J* = 7.1 Hz), 2.81 (d, 0.8H, *J* = 3.3 Hz), 2.75 (d, 0.2H, *J* = 3.3 Hz), 2.69 (d, 0.2H, *J* = 3.3 Hz), 2.66 (d, 0.8H, *J* = 3.3 Hz), 2.40 (br. s, 0.2H), 2.34-2.36 (m, 1.8H), 2.02 (s, 3H), 1.75 (dd, 1H, *J* = 13.3, 7.3 Hz), 1.60 (ddd, 1H, 13.3, 3.9, 2.7 Hz), 1.39 (br. s, 2H), 1.33 (t, 3H, *J* = 7.1Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3a**: δ 170.7, 162.7, 154.0, 132.1, 130.1, 128.8, 128.3, 76.2, 60.0, 44.6, 41.3, 40.1, 38.2, 33.7, 27.7, 21.2, 14.3; visible peaks for minor isomer **4a**: δ 170.6, 155.6, 132.2, 127.0, 72.3, 45.0, 41.3, 40.8, 39.7, 38.6, 34.0, 27.8.

Fractional recrystallization of the above mixture in EtOAc:hexanes (1:9) afforded a pure sample of **3a** as white crystals. The regiochemistry of **3a** was determined by NMR experiments (^{1}H NMR, APT, HMBC, HCOSY, HSQC and NOESY). R_f 0.39 (EtOAc:hexanes=1:9); mp 71 ºC; GC (HP-1 column): retention time for major isomer **3a**=30.571 min.; IR (CH_2Cl_2) 3066 (w), 2969 (m), 2937 (m), 1734 (s), 1704 (s), 1617 (s), 1492 (m), 1448 (m), 1374 (m), 1297 (m), 1244 (s), 1217 (s), 1204 (s), 1136 (m), 1109 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (m, 2H), 7.31 (m, 3H), 4.63 (dm, 1H, *J* = 5.3 Hz), 4.22 (q, 2H, *J* = 7.1 Hz), 2.79 (d, 1H, *J* = 3.3 Hz), 2.64 (d, 1H, *J* = 3.3 Hz), 2.35 (br. s, 1H), 2.33 (d, 1H, *J* = 4.0 Hz), 2.00 (s, 3H), 1.73 (dd, 1H, *J* = 13.3, 7.3 Hz), 1.58 (ddd, 1H, *J* = 13.3, 3.9, 2.7 Hz), 1.37 (br. s, 2H), 1.31 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5, 162.5, 153.9, 132.0, 130.0, 128.7, 128.6, 128.2, 76.1, 59.9, 44.5, 41.2, 40.0, 38.1, 33.6, 27.6, 21.1, 14.2. Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found C, 73.56; H, 6.77.

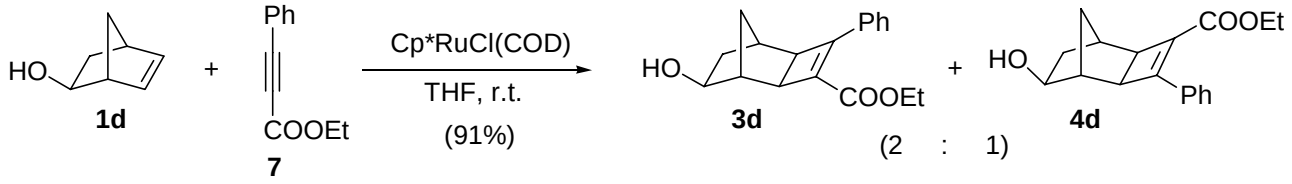


Cycloadducts 3b and 4b. A mixture of norbornene **1b** (234 mg, 1.17 mmol), acetylene **7** (40.6 mg, 0.233 mmol) and THF (0.23 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 6.5 mg, 0.017 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19) to give an inseparable mixture of cycloadducts **3b** and **4b** (81.2 mg, 0.217 mmol, 93%, **3b**:**4b** = 3:1 measured by ^{1}H NMR) as a colourless oil. R_f 0.29 (EtOAc:hexanes=1:19); IR (neat) 3065 (m), 3030 (m), 2959 (s), 2934 (s), 2875 (m), 1704 (s), 1695 (s), 1616 (s), 1572 (m), 1492 (s), 1448 (m), 1391 (w), 1367 (m), 1351 (m), 1331 (m), 1296 (m), 1274 (m), 1217 (s), 1204 (s), 1185 (m), 1135 (s), 1111 (m), 1074 (s), 1027 (m), 911 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (m, 2H), 7.34-7.44 (m, 7H), 7.30 (m, 1H), 4.57 (d_{AB}, 0.25H, J = 11.8 Hz), 4.56 (d_{AB}, 0.75H, J = 11.8 Hz), 4.52 (d_{AB}, 0.75H, J = 11.8 Hz), 4.51 (d_{AB}, 0.25H, J = 11.8 Hz), 4.26 (q, 2H, J = 7.1 Hz), 3.55-3.56 (m, 1H), 2.73 (d, 0.25H, J = 3.6 Hz), 2.68 (d, 0.75H, J = 3.6 Hz), 2.64 (d, 0.75H, J = 3.6 Hz), 2.59 (d, 0.25H, J = 3.6 Hz), 2.53 (s, 0.25H), 2.44 (s, 0.75H), 2.35 (d, 0.75H, J = 3.3 Hz), 2.33 (d, 0.25H, J = 3.3 Hz), 1.63-1.68 (m, 2H), 1.52 (d, 1H, J = 10.7 Hz), 1.372 (t, 0.75H, J = 7.1 Hz), 1.370 (m, 1H), 1.35 (t, 2.25H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3b** δ 162.85, 154.3, 138.65, 132.4, 130.0, 128.9, 128.8, 128.30, 127.6, 127.54, 127.50, 81.15, 70.7, 60.00, 45.2, 42.0, 39.2, 38.5, 33.6, 27.5, 14.3; visible peaks for minor isomer **4b**: δ 162.90, 155.6, 138.74, 128.31, 127.4, 127.3, 81.12, 70.6, 60.03, 45.6, 41.4, 38.8, 33.9, 27.51, 14.34.

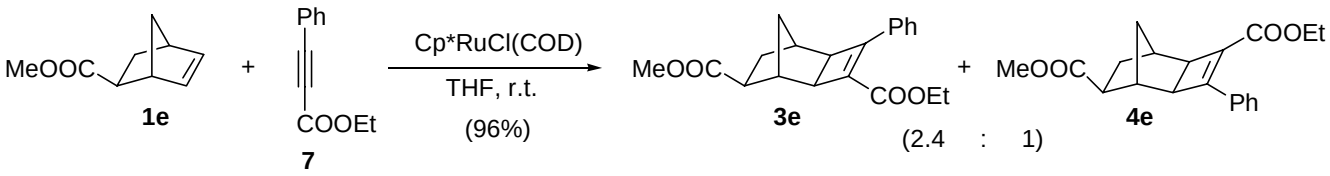


Cycloadducts 3c and 4c. A mixture of norbornene **1c** (247 mg, 1.10 mmol), acetylene **7** (38.2 mg, 0.220 mmol) and THF (0.22 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 5.9 mg, 0.016 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes= 0:1, 1:19) to give an inseparable mixture of cycloadducts **3c** and **4c** (80.8 mg, 0.203 mmol, 92%, **3c**:**4c** = 1.5:1 measured by ^{1}H NMR) as white crystals. R_f 0.54

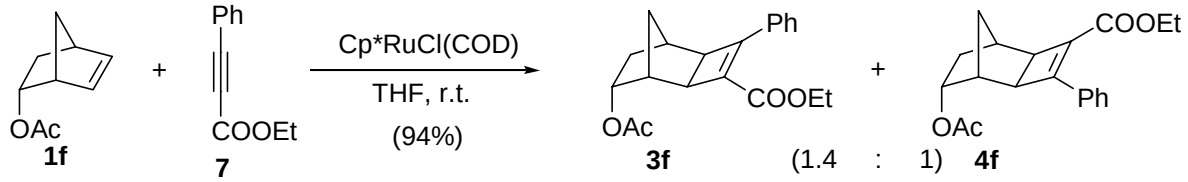
(EtOAc:hexanes=1:19); IR (CH_2Cl_2) 2956 (s), 2930 (s), 2886 (m), 2856 (m), 1705 (s), 1620 (m), 1573 (w), 1492 (m), 1472 (m), 1463 (m), 1448 (m), 1367 (m), 1273 (m), 1255 (m), 1216 (s), 1202 (s), 1182 (m), 1135 (m), 1079 (s), 1017 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (m, 2H), 7.39 (m, 3H), 4.25 (q, 2H, *J* = 7.1 Hz), 3.74 (d, 1H, *J* = 6.1 Hz), 2.67 (d, 0.4H, *J* = 3.8 Hz), 2.66 (d, 0.6H. *J* = 3.8 Hz), 2.59 (d, 0.6H, *J* = 3.4 Hz), 2.55 (d, 0.4H, *J* = 3.4 Hz), 2.28 (d, 0.6H, *J* = 4.8 Hz), 2.26 (d, 0.4H, *J* = 4.8 Hz), 2.19 (s, 0.4H), 2.12 (s, 0.6H), 1.49-1.66 (m, 3H), 1.35 (t, 1.2H, *J* = 7.1 Hz), 1.34 (t, 1.8H, *J* = 7.1 Hz), 1.27 (m, 1H), 0.904 (s, 3.6H), 0.899 (s, 5.4H), 0.087 (s, 3.6H), 0.079 (s, 2.4H); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3c**: δ 162.9, 154.5, 132.49, 129.9, 129.0, 128.7, 128.31, 74.2, 60.0, 45.0, 43.2, 42.0, 41.9, 33.7, 27.097, 25.85, 18.0, 14.32, -4.62, -4.64; visible peaks for minor isomer **4c**: 155.6, 132.51, 128.29, 127.5, 74.3, 45.5, 42.8, 41.3, 34.1, 27.066, 25.88, 18.1, 14.28, -4.7. Anal. Calcd. for $C_{24}H_{34}SiO_3$: C, 72.32; H, 8.60. Found C, 72.29; H, 8.61.



Cycloadducts 3d and 4d. A mixture of norbornene **1d** (129 mg, 1.17 mmol), acetylene **7** (40.4 mg, 0.232 mmol) and THF (0.23 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 7.1 mg, 0.019 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=1:9, 1:4, 2:3) to give an inseparable mixture of cycloadducts **3d** and **4d** (59.8 mg, 0.211 mmol, 91%, **3d**:**4d** = 2:1 measured by ^1H NMR) as a thick white paste. R_f 0.45 (EtOAc:hexanes=2:3); IR (CH_2Cl_2) 3399 (br. s), 2959 (m), 2935 (m), 1699 (s), 1620 (s), 1573 (w), 1492 (m), 1448 (w), 1216 (s), 1203 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (m, 2H), 7.39 (m, 3H), 4.24 (q, 2H, *J*=7.1 Hz), 3.84 (br. d, 1H, *J* = 6.2 Hz), 2.70 (d, 1H, *J* = 3.4 Hz), 2.605 (dd, 0.67H, *J* = 3.5 Hz), 2.600 (dd, 0.33H, *J* = 3.5 Hz), 2.33 (dd, 0.67H, *J* = 4.2 Hz), 2.32 (dd, 0.33H, *J*= 4.2 Hz), 2.27 (br. s., 0.33H), 2.22 (br. s., 0.67H), 1.77 (m, 1H), 1.70 (ddd, 0.67H, *J* = 13.1, 7.1, 2.4 Hz), 1.69 (ddd, 0.33H, *J* = 13.1, 7.1, 2.4 Hz), 1.45-1.50 (m, 2H), 1.35 (br. s., 1H), 1.34 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3d**: δ 162.9, 154.4, 132.3, 130.0, 128.9, 128.8, 128.3, 73.87, 60.1, 44.7, 43.0, 41.8, 41.17, 33.9, 27.09, 14.3; visible peaks for minor isomer **4d**: δ 155.7, 127.2, 73.90, 45.2, 42.7, 41.24, 41.0, 34.2, 27.05. Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found C, 76.05; H, 7.07.



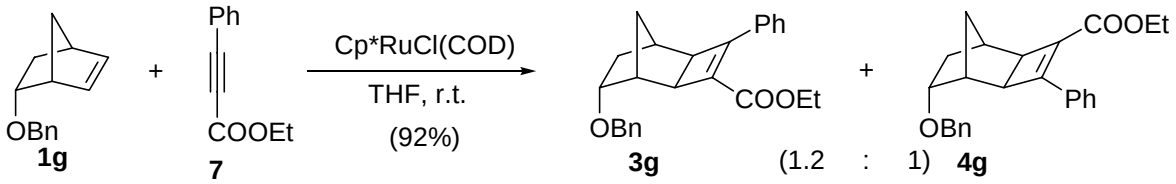
Cycloadducts 3e and 4e. A mixture of norbornene **1e** (134 mg, 0.878 mmol), acetylene **7** (29.9 mg, 0.172 mmol) and THF (0.18 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 4.4 mg, 0.012 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19, 1:9) to give an inseparable mixture of cycloadducts **3e** and **4e** (53.9 mg, 0.165 mmol, 96%, **3e**:**4e** = 2.4:1 measured by ^{1}H NMR) as a thick colourless oil. R_f 0.39 (EtOAc:hexanes=1:9); IR (neat) 3067 (w), 2953 (s), 2886 (w), 2844 (w), 1738 (s), 1729 (s), 1704 (s), 1699 (s), 1620 (s), 1573 (m), 1492 (s), 1464 (m), 1366 (m), 1318 (m), 1295 (m), 1205 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (m, 2H), 7.34-7.41 (m, 3H), 4.24 (q, 2H, *J* = 7.1 Hz), 3.69 (s, 0.87H), 3.68 (s, 2.13H), 2.86 (d, 0.71H, *J* = 3.6 Hz); 2.85 (d, 0.29H, *J* = 3.6 Hz), 2.76 (d, 0.29H, *J* = 3.7 Hz), 2.75 (d, 0.71H, *J* = 3.7 Hz), 2.58 (s, 0.29H), 2.55 (s, 0.71H), 2.32-2.35 (m, 2H), 2.03 (dt, 1H, *J* = 12.4, 4.7 Hz), 1.52 (ddd, 0.71H, *J* = 11.7, 9.3, 2.2 Hz), 1.50 (ddd, 0.29H, *J* = 11.7, 9.3, 2.2 Hz), 1.40 (d, 1H, *J* = 11.1 Hz), 1.34 (t, 3H, *J* = 7.1 Hz), 1.30 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3e**: δ 175.9, 162.8, 154.6, 132.2, 130.0, 129.0, 128.80, 128.3, 60.1, 51.8, 45.9, 45.4, 45.3, 39.2, 34.2, 32.7, 28.7, 14.3; visible peaks for minor isomer **4e**: δ 176.1, 155.9, 132.24, 130.1, 128.85, 127.8, 38.9, 34.5, 32.6, 28.6.



Cycloadducts 3f and 4f. A mixture of norbornene **1f** (185 mg, 1.22 mmol), acetylene **7** (42.0 mg, 0.241 mmol) and THF (0.24 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 7.6 mg, 0.020 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19, 1:9) to give a mixture of cycloadducts **3f** and **4f** (74.0 mg, 0.227 mmol, 94%, **3f**:**4f** = 1.4:1 measured by ^{1}H NMR) as white crystals. R_f for major isomer **3f**=0.40 and R_f for minor isomer **4f**=0.35 (EtOAc:hexanes=1:9); IR (CH_2Cl_2) 2969 (s), 1737 (s), 1733 (s), 1704 (s), 1699 (s), 1615 (m), 1558 (w), 1492 (m), 1464 (w), 1448 (m), 1331 (w), 1287

(m), 1246 (s), 1221 (s), 1205 (s), 1143 (m), 1103 (m), 1086 (w), 1021 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (m, 2H), 7.34-7.41 (m, 3H), 5.12 (dt, 0.42H, *J* = 9.9, 4.1 Hz), 5.08 (dt, 0.58H, *J* = 9.9, 4.1 Hz), 4.25 (q, 0.84H, *J* = 7.1 Hz), 4.24 (q, 1.16H, *J* = 7.1 Hz), 3.36 (d, 0.58H, *J* = 3.5 Hz), 3.28 (d, 0.42H, *J* = 3.5 Hz), 2.94 (d, 0.42H, *J* = 3.5 Hz), 2.83 (d, 0.58H, *J* = 3.5 Hz), 2.58 (s, 1H), 2.30 (d, 0.58H, *J* = 4.1 Hz), 2.28 (d, 0.42H, *J* = 4.1 Hz), 2.18-2.24 (m, 1H), 2.10 (s, 1.74H), 2.08 (s, 1.26H), 1.47 (dm, 1H, *J* = 11.3 Hz), 1.33 (t, 3H, *J* = 7.1 Hz), 1.18 (d, 1H, *J* = 11.2 Hz), 1.04 (dt, 0.58H, *J* = 13.0, 3.5 Hz), 1.01 (dt, 0.42H, *J* = 12.2, 3.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3f**: δ 171.12, 162.7, 154.8, 132.3, 130.04, 128.8, 128.3, 128.2, 75.45, 60.00, 45.0, 39.0, 38.56, 35.4, 34.2, 29.6, 21.1, 14.3; visible peaks for minor isomer **4f**: δ 171.07, 162.8, 154.9, 129.96, 127.6, 75.47, 60.02, 45.6, 38.59, 38.0, 35.5, 34.7, 29.5.

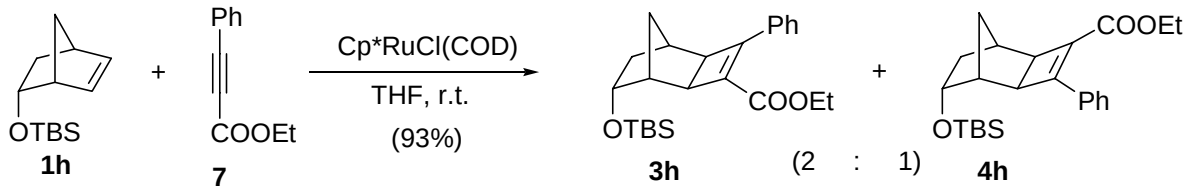
Gradient elution (EtOAc:hexanes=0:1, 1:19, 1:9) of the above mixture by column chromatography afforded a pure sample of **3f** as white crystals. The regiochemistry of **3f** was characterized through the use NMR experiments (^1H NMR, APT, and NOESY). R_f 0.40 (EtAcO:hexanes=1:9); mp 106 ºC; IR (CH_2Cl_2) 2969 (s), 1737 (s), 1733 (s), 1704 (s), 1699 (s), 1615 (m), 1558 (w), 1492 (m), 1464 (w), 1448 (m), 1331 (w), 1287 (m), 1246 (s), 1221 (s), 1205 (s), 1143 (m), 1103 (m), 1086 (w), 1021 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.01 (m, 2H), 7.35-7.41 (m, 3H), 4.25 (q, 2H, *J* = 7.1 Hz), 3.36 (d, 1H, *J* = 3.6 Hz), 2.84 (d, 1H, *J* = 3.6 Hz), 2.58 (d, 1H, *J* = 4.1 Hz), 2.31 (d, 1H, *J* = 4.1 Hz), 2.21 (m, 1H), 2.11 (s, 3H), 1.48 (dm, 1H, *J* = 11.2 Hz), 1.34 (t, 3H, *J* = 7.1 Hz), 1.18 (dm, 1H, *J* = 11.2 Hz), 1.04 (dt, 1H, *J* = 13.2, 3.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.2, 162.7, 154.8, 132.3, 130.1, 128.8, 128.3, 128.2, 75.5, 60.1, 45.0, 39.0, 38.6, 35.4, 34.3, 29.6, 21.2, 14.3. Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found C, 73.28; H, 6.82.



1g **7** **3g** (1.2 : 1) **4g**

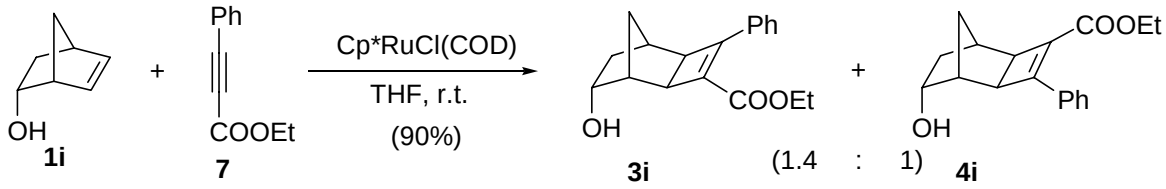
Cycloadducts 3g and 4g. A mixture of norbornene **1g** (235 mg, 1.17 mmol), acetylene **7** (40.5 mg, 0.233 mmol) and THF (0.23 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 4.2 mg, 0.011 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19, 1:9) to give an inseparable mixture of cycloadducts **3g** and **4g** (80.3 mg, 0.214 mmol, 92%, **3g**:**4g** = 1.2:1 measured by ^1H NMR) as a colourless oil. R_f 0.47 (EtOAc:hexanes=1:9); IR (neat) 3064 (m), 3030 (m), 2958 (s), 2863 (m), 1699

(s), 1694 (s), 1613 (m), 1571 (w), 1492 (m), 1463 (w), 1448 (m), 1349 (m), 1330 (m), 1284 (m), 1220 (s), 1204 (s), 1149 (m), 1112 (s), 1085 (m), 1073 (m), 1026 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.06 (m, 1H), 7.97 (m, 1H), 7.31-7.45 (m, 8H), 4.61 (d, 0.45H, *J* = 11.7 Hz), 4.58 (s, 1.10 H), 4.47 (d, 0.45H, *J* = 11.7 Hz), 4.28 (q, 0.90H, *J* = 7.2 Hz), 4.26 (q, 1.10H, *J* = 7.2 Hz), 4.13 (m, 1H), 3.50 (d, 0.55H, *J* = 3.2 Hz), 3.41 (d, 0.45H, *J* = 3.2 Hz), 3.00 (d, 0.45H, *J* = 3.2 Hz), 2.89 (d, 0.55H, *J* = 3.2 Hz), 2.62 (d, 0.45H, *J* = 3.2 Hz), 2.46 (d, 0.55H, *J* = 3.2 Hz), 2.284 (s, 1H), 2.283 (d, 1H, *J* = 10.8 Hz), 2.10 (m, 2H), 1.46 (td, 1H, *J* = 11.1, 1.5 Hz), 1.38 (t, 1.35H, *J* = 7.2 Hz), 1.36 (t, 1.65H, *J* = 7.2 Hz), 1.10-1.15 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3g**: δ 162.8, 155.5, 138.6, 132.5, 129.9, 128.80, 128.4, 128.27, 128.0, 127.8, 127.6, 80.4, 71.8, 59.9, 45.4, 38.9, 38.2, 35.62, 34.2, 29.6, 14.3; visible peaks for minor isomer **4g**: δ 163.0, 154.8, 138.5, 129.8, 128.79, 128.3, 128.25, 127.99, 127.7, 127.5, 80.2, 71.2, 46.0, 38.5, 37.3, 35.59, 34.7. Anal. Calcd. for $C_{25}H_{26}O_3$: C, 80.18; H, 7.00. Found C, 79.88; H, 7.11.

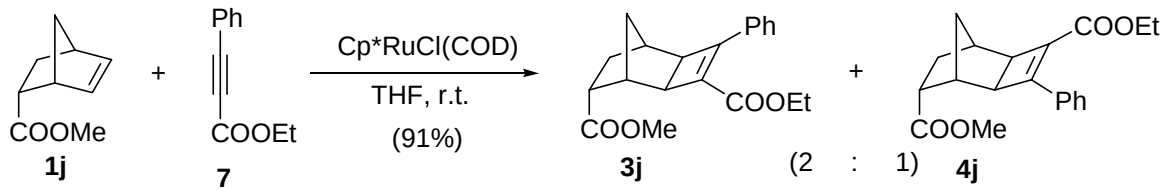


Cycloadducts 3h and 4h. A mixture of norbornene **1h** (249 mg, 1.11 mmol), acetylene **7** (38.3 mg, 0.220 mmol) and THF (0.22 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 8.1 mg, 0.021 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19, 1:9) to give an inseparable mixture of cycloadducts **3h** and **4h** (81.7 mg, 0.205 mmol, 93%, **3h**:**4h** = 2:1 measured by ^1H NMR) as a thick colourless oil. R_f 0.61 (EtOAc:hexanes=1:9); IR (neat) 3066 (w), 2956 (s), 2930 (s), 2884 (m), 2857 (m), 1705 (s), 1615 (m), 1573 (w), 1492 (m), 1471 (m), 1463 (m), 1388 (w), 1366 (m), 1283 (m), 1218 (m), 1204 (s), 1148 (m), 1113 (s), 1073 (s), 1024 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (m. 2H), 7.32-7.42 (m, 3H), 4.33 (m, 1H), 4.24 (q, 1.34H, *J* = 7.1 Hz), 4.23 (q, 0.66H, *J* = 7.1 Hz), 3.56 (d, 0.67H, *J* = 3.5 Hz), 3.42 (d, 0.33H, *J* = 3.5 Hz), 2.93 (d, 0.33H, *J* = 3.5 Hz), 2.82 (d, 0.67H, *J* = 3.5 Hz), 2.20-2.30 (m, 2H), 2.01 (m, 1H), 1.37 (m, 1H), 1.33 (t, 3H, *J* = 7.1 Hz), 1.11 (d, 0.33H, *J* = 11.1 Hz), 1.08 (d, 0.67H, *J* = 11.1 Hz), 0.93 (s, 6.03H), 0.92 (s, 2.97H), 0.87 (m, 1H), 0.11 (s, 2.01H), 0.10 (s, 0.99H), 0.071 (s, 2.01H), 0.068 (s, 0.99H); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3h**: δ 162.9, 156.0, 132.8, 129.8, 128.81, 128.3, 128.1, 73.2, 59.9, 45.4, 41.3, 39.0, 38.60, 34.81, 29.59, 25.89, 18.1,

14.4, -4.7, -4.8; visible peaks for minor isomer **4h**: δ 163.1, 154.8, 132.7, 129.7, 128.78, 128.5, 73.6, 46.0, 40.7, 38.56, 38.5, 35.2, 29.63, 25.92, 18.2, 14.2, -4.9. Anal. Calcd. for $C_{24}H_{34}SiO_3$: C, 72.32; H, 8.60. Found C, 72.61; H, 8.38.

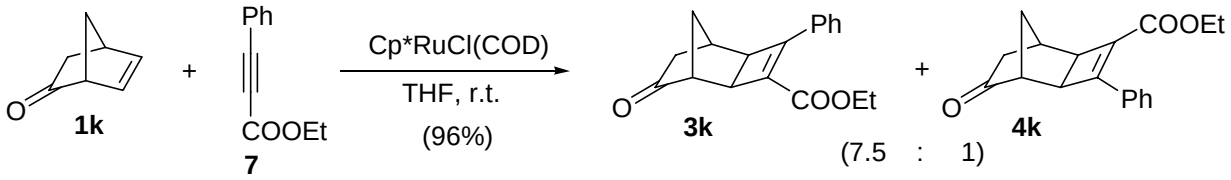


Cycloadducts 3i and 4i. A mixture of norbornene **1i** (129 mg, 1.17 mmol), acetylene **7** (40.4 mg, 0.232 mmol) and THF (0.23 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 6.2 mg, 0.016 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:9, 1:4, 3:7, 2:3) to give an inseparable mixture of cycloadducts **3i** and **4i** (59.4 mg, 0.209 mmol, 90%, **3i**:**4i** = 1.4:1 measured by ^{1}H NMR) as a thick yellow oil. R_f 0.17 (EtOAc:hexanes=1:4); IR (neat) 3391 (br. s), 3066 (m), 2957 (s), 2884 (s), 2251 (w), 1896 (w), 1704 (s), 1683 (s), 1615 (s), 1573 (m), 1558 (w), 1492 (s), 1476 (m), 1391 (m), 1135 (s), 1084 (s), 1051 (s), 1010 (m), 987 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (m, 2H), 7.33-7.41 (m, 3H), 4.40-4.47 (m, 1H), 4.24 (q, 2H, *J* = 7.1 Hz), 3.56 (d, 0.58H, *J* = 3.6 Hz), 3.42 (d, 0.42H, *J* = 3.6 Hz), 2.97 (d, 0.42H, *J* = 3.6 Hz), 2.86 (d, 0.58H, *J* = 3.6 Hz), 2.40 (d, 0.42H, *J* = 3.6 Hz), 2.36 (d, 0.58H, *J* = 3.6 Hz), 2.27 (d, 0.58H, *J* = 4.6 Hz), 2.25 (d, 0.42H, *J* = 4.6 Hz), 2.11-2.18 (m, 1H), 1.89 (br. s, 1H), 1.42 (m, 1H), 1.33 (t, 3H, *J* = 7.1 Hz), 1.14 (d, 1H, *J* = 10.9 Hz), 0.90-0.96 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3i**: δ 162.8, 155.5, 132.5, 129.9, 128.84, 128.25, 127.96, 73.0, 59.97, 45.3, 40.7, 38.5, 38.09, 34.9, 29.9, 14.3; visible peaks for minor isomer **4i**: δ 163.0, 154.9, 132.4, 129.8, 128.78, 128.27, 127.86, 73.3, 60.01, 45.9, 40.3, 38.06, 37.8, 35.3, 30.0. Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found C, 76.28; H, 6.93.



Cycloadducts 3j and 4j. A mixture of norbornene **1j** (177 mg, 1.16 mmol), acetylene **7** (40.2 mg, 0.231 mmol) and THF (0.23 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 7.1 mg, 0.019 mmol) under nitrogen.

The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (EtOAc:hexanes=0:1, 1:19, 1:9) to give an inseparable mixture of cycloadducts **3j** and **4j** (68.9 mg, 0.211 mmol, 91%, **3j**:**4j** = 2:1 measured by ^{1}H NMR) as white crystals. R_f 0.46 (EtOAc:hexanes=1:9); IR (CH_2Cl_2) 3066 (w), 2964 (s), 2882 (w), 1733 (s), 1701 (s), 1698 (s), 1615 (m), 1572 (w), 1492 (m), 1448 (m), 1435 (m), 1367 (w), 1310 (w), 1275 (m), 1205 (s), 1172 (s), 1140 (s), 1116 (m), 1083 (w), 1036 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (m, 2H), 7.34-7.41 (m, 3H), 4.235 (q, 1.34H, *J* = 7.1 Hz), 4.240 (q, 0.66H, *J* = 7.1 Hz), 3.76 (s, 2.01H), 3.73 (s, 0.99H), 2.88-2.95 (m, 2H), 2.80 (d, 0.67H, *J* = 3.6 Hz), 2.78 (d, 0.33H, *J* = 3.6 Hz), 2.63 (d, 0.33H, *J* = 4.1 Hz), 2.60 (d, 0.67H, *J* = 4.1 Hz), 2.35 (d, 0.67H, *J* = 4.1 Hz), 2.31 (d, 0.33H, *J* = 4.1 Hz), 1.85-1.92 (m, 1H), 1.68-1.73 (m, 1H), 1.56 (dm, 1H, *J* = 10.7 Hz), 1.33 (t, 3H, *J* = 7.1 Hz), 1.20 (d, 1H, *J* = 10.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) major isomer **3j** δ 174.6, 162.7, 154.7, 132.25, 130.0, 128.77, 128.5, 128.3, 60.0, 51.7, 45.3, 45.1, 42.0, 38.3, 34.6, 32.1, 30.4, 14.29; visible peaks for minor isomer **4j**: δ 174.7, 162.8, 155.1, 132.28, 129.97, 128.83, 127.6, 51.6, 45.7, 45.5, 41.6, 38.0, 35.0, 32.3, 14.26. Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79. Found C, 73.34; H, 6.84.



Cycloadducts 3k and 4k. A mixture of norbornene **1k** (132 mg, 1.22 mmol), acetylene **7** (42.2 mg, 0.243 mmol) and THF (0.24 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*RuCl(COD) (weighed out from a dry box, 6.6 mg, 0.017 mmol) under nitrogen. The reaction mixture was stirred in the dark at 25 ºC for 67 h. The crude product was purified by column chromatography (Et_20:hexanes=0:1, 1:9, 1:4, 3:7) to give a mixture of cycloadducts **3k** and **4k** (65.5 mg, 0.232 mmol, 96%, **3k**:**4k** = 7.5:1 measured by GC) as white crystals. R_f for major isomer **3k**=0.43 and R_f for minor isomer **4k**=0.35 (EtOAc:hexanes=1:4); GC (HP-1 column): retention time for major isomer **3k**=27.959 min. and retention time for minor isomer **4k**=28.325 min.; IR (CH_2Cl_2) 3066 (m), 2978 (m), 1748 (s), 1704 (s), 1572 (w), 1492 (m), 1448 (m), 1370 (w), 1333 (w), 1296 (m), 1262 (w), 1223 (s), 1203 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 – 8.07 (m, 2H), 7.37-7.42 (m, 3H), 4.27 (q, 1.76H, *J* = 7.1 Hz), 4.23 (q, 0.24H, *J* = 7.1 Hz), 3.10 (d, 0.88H, *J* = 3.5 Hz), 3.08 (d, 0.12H, *J* = 3.5 Hz), 3.00 (d, 0.88H, *J* = 3.5 Hz), 2.98 (d, 0.12H, *J* = 3.5 Hz), 2.73 (s, 0.12H), 2.65 (s, 1.88H), 2.19 (dd, 1H, *J* = 17.3, 4.7 Hz), 1.81 (d, 1H, *J* = 4.6 Hz), 1.74-1.76 (m, 1H), 1.58 (d, 1H, *J* = 11.0 Hz), 1.35 (t, 2.64H, *J* = 7.1 Hz), 1.32 (t, 0.36H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) major

isomer **3k**: δ 215.1, 162.4, 152.1, 131.6, 130.5, 129.1, 128.8, 128.4, 60.30, 48.2, 43.9, 42.02, 39.5, 32.57, 29.54, 14.3; visible peaks for minor isomer **4k**: δ 162.3, 155.8, 130.6, 128.9, 125.4, 60.27, 48.0, 44.3, 42.05, 39.3, 32.61, 29.45, 14.1.

Gradient elution (Et_2O:hexanes=0:1, 1:9, 1:4, 3:7) of the above mixture by column chromatography afforded a pure sample of **3k** as white crystals. The regiochemistry of **4k** was characterized through the use NMR experiments (^{1}H NMR, APT, HSQC, and NOESY). R_f 0.43 (EtOAc:hexanes=1:4); mp 85 ºC; GC (HP-1 column): retention time for major isomer **3k**=27.887 min.; IR (CH_2Cl_2) 3066 (m), 2979 (m), 1748 (s), 1704 (s), 1572 (w), 1492 (m), 1448 (m), 1370 (w), 1333 (w), 1296 (m), 1262 (w), 1223 (s), 1203 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (m, 2H), 7.38-7.42 (m, 3H), 4.28 (q, 2H, *J* = 7.1 Hz), 3.11 (d, 1H, *J* = 3.5 Hz), 3.08 (d, 1H, *J* = 3.5 Hz), 2.66 (s, 2H), 2.20 (dd, 1H, *J* = 17.3, 4.8 Hz), 1.79 (dd, 1H, *J* = 17.3, 4.8 Hz), 1.77 (s, 1H), 1.59 (d, 1H, *J* = 11.1 Hz), 1.36 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 215.2, 162.5, 152.2, 131.6, 130.5, 129.1, 128.8, 128.5, 60.4, 48.2, 43.9, 42.1, 39.5, 32.6, 29.6, 14.3. Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found C, 76.43; H, 6.39.