Supporting Information-1

Ruthenium-Catalyzed [2+2] Cycloadditions of Ynamides

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General Information: All reactions were carried out in an atmosphere of dry nitrogen at ambient temperature unless otherwise stated. Standard column chromatography was performed on 230-400 mesh silica gel (obtained from Silicycle) using flash column chromatography techniques.¹ Analytical thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F₂₅₄ plates. All glassware was flame dried under an inert atmosphere of dry nitrogen. Infrared spectra were taken on a Bomem MB-100 FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded on Bruker Avance-300, 400 or 600 spectrometer. Chemical shifts for ¹H 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 ¹³C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuteriochloroform: δ 77.0 ppm). High resolution mass spectra were done by McMaster Regional Centre for Mass Spectrometry at McMaster University, Hamilton, Ontario. 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 CaH₂ (pyridine); from sodium (toluene); and from potassium/benzophenone (THF). Ynamides **10a,d**,² compound **12**,³ compound **14**,⁴ and Cp*RuCl(COD)⁵ were prepared according to literature procedures.

Special Note: For some of the acyclic ynamides as well as their corresponding [2+2] cycloadducts, some of the ¹³C NMR signals (especially those of acetylenic, olefinic and carbonyl carbons which are directly attached to the nitrogen) are severely broadened and virtually lost (or very hard to detect) in 1-D ¹³C NMR spectra. This is due to the system undergoing chemical exchange near the coalescence point, and in these cases, 2-D HMBC spectra were obtained in which the “missing peaks” can be detected.⁶

¹ W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.

² Frederick, M. O.; Mulder, J. A.; Tracey, M. R.; Hsung, R. P.; Huang, J.; Kurtz, K. C. M.; Shen, L.; Douglas, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 2368.

³ Sibi, M. P.; Rutherford, D.; Sharma, R. *J. Chem. Soc. Perkin Trans. 1* **1994**, 1675.

⁴ Heesing, A.; Herdering, W. *Chem. Ber.* **1983**, *116*, 1081.

⁵ P. J. Fagan, W. S. Mahoney, J. C. Calabrese, I. D. Williams, *Organometallics*. **1990**, *9*, 1843.

⁶ For detail explanations and the use of 2-D HMQC NMR to solve this problem, see: Robinson, V., J.; Bain, A. D. *Magnetic Resonance in Chemistry*, **1993**, *31*, 865.

Part I: Preparation of Ynamides

General Procedure (A) for the Synthesis of the Ynamides. A mixture of the amide (1.0 eq), alkynyl halide (2.0 eq), copper iodide (0.2 eq), 1,10-phenanthroline (0.25 eq), and toluene (~0.6 M w.r.t. the amide) was prepared in an oven-dried round-bottomed flask, equipped with a condenser, under nitrogen. The mixture was heated at 90°C and potassium bis(trimethylsilyl)amide (KHMDs, 1.2 eq, 0.5 M in toluene) was added slowly via a syringe pump over 3-4 hours. The reaction mixture was stirred at 90°C for 12 h under nitrogen. The reaction mixture was diluted with diethyl ether and subsequently washed three times with 2:1 mixture of saturated sodium chloride solution and concentrated NH₄OH. The aqueous layer was extracted three times with diethyl ether and the combined organic layers were washed with saturated sodium chloride, dried over MgSO₄, filtered, and concentrated using rotary evaporation. The crude product was then purified by column chromatography (hexanes or ethyl acetate/hexanes mixture) using silica gel pre-treated with triethylamine.

General Procedure (B) for the Synthesis of the Ynamides. To a cold solution (0°C) of the amide (1.0 eq) in pyridine (0.4 M) was added dropwise potassium bis(trimethylsilyl)amide (KHMDs, 1 eq, 0.5 M in toluene). The reaction was stirred for 15 min then a solution of copper iodide (1.0 eq) in pyridine was added via a cannula. The resulting mixture was allowed to warm up to 25°C and stirred for 2 h. A solution of alkynyl halide (2.0 eq) in THF was added via cannula over 30 min and the resulting mixture was stirred at room temperature for 20 h. The reaction mixture was diluted with diethyl ether and washed three times with 2:1 mixture of saturated sodium chloride solution and concentrated NH₄OH. The aqueous layer was extracted three times with diethyl ether and the combined organic layers were washed with saturated sodium chloride, dried over MgSO₄, filtered, and concentrated using rotary evaporation. The crude product was then purified by column chromatography (hexanes or ethyl acetate/hexanes mixture) using silica gel treated with triethylamine.

N-Cyclohexyl-N-phenylethynylcarbamic acid methyl ester (3a). Following the above general procedure (A) with bromoethynylbenzene **1a** (298.9 mg, 1.651 mmol) and *N*-cyclohexylcarbamic acid methyl ester **2a** (127.4 mg, 0.8106 mmol), copper iodide (8.9 mg, 0.047 mmol), 1,10-phenanthroline

(20.7 mg, 0.115 mmol), and KHMDS (0.5 M in toluene, 2.0 mL, 1.0 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:49) to provide **3a** (89.3 mg, 0.347 mmol, 43%) as a yellow oil. R_f 0.47 (EtOAc:hexanes=1:4); ^1H NMR (CDCl_3 , 400 MHz) δ 7.40–7.43 (m, 2H), 7.24–7.35 (m, 3H), 3.99 (br t, 1H, J = 12.0 Hz), 3.84 (s, 3H), 1.82–1.89 (m, 4H), 1.58–1.68 (m, 3H), 1.33–1.43 (m, 2H), 1.11–1.19 (m, 1H); ^{13}C NMR (APT, CDCl_3 , 100 MHz) δ 155.4, 131.1, 128.2, 127.4, 123.4, 80.6, 72.3, 56.5, 53.9, 30.5, 25.3, 25.1. This is a known compound and the spectral data are identical to those reported in the literature.⁷

***N*-Phenethyl-*N*-phenylethynylcarbamic acid methyl ester (3b).** Following the above general procedure (A) with bromoethynylbenzene **1a** (662 mg, 3.657 mmol) and *N*-phenylcarbamic acid methyl ester **2b** (209.5 mg, 1.169 mmol), copper iodide (16.7 mg, 0.088 mmol), 1,10-phenanthroline (24.7 mg, 0.137 mmol), and KHMDS (2.8 mL, 1.4 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:99) to provide **3b** (171 mg, 0.6121 mmol, 52%) as an orange oil. R_f 0.43 (EtOAc:hexanes=1:9); ^1H NMR (CDCl_3 , 400 MHz) δ 7.26–7.47 (m, 10H), 3.87 (t, 2H, J = 7.8 Hz), 3.84 (s, 3H), 3.09 (t, 2H, J = 7.8 Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 155.5, 137.9, 131.3, 128.9, 128.5, 128.2, 127.6, 126.6, 123.1, 82.7, 71.0, 54.0, 51.3, 34.1. This is a known compound and the spectral data are identical to those reported in the literature.²

***N*-Benzyl-*N*-phenylethynylcarbamic acid methyl ester (3c).** Following the above general procedure (A) with bromoethynylbenzene **1a** (476 mg, 2.623 mmol) and *N*-benzylcarbamic acid methyl ester **2c** (208.7 mg, 1.263 mmol), copper iodide (47.6 mg, 0.250 mmol), 1,10-phenanthroline (59.8 mg, 0.332 mmol), and KHMDS (3.0 mL, 1.5 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:49) to provide **3c** (205.7 mg, 0.7753 mmol, 61%) as a yellow oil. R_f 0.31 (EtOAc:hexanes=1:9); ^1H NMR (CDCl_3 , 400 MHz) δ 7.25–7.42 (m, 10H), 4.71 (s, 2H), 3.85 (s, 3H);

⁷ Dunetz, J. R.; Danheiser, R. L. *Organic Letters* **2003**, 5, 4011.

^{13}C NMR (CDCl_3 , 100 MHz) δ 155.5, 135.8, 131.1, 128.5, 128.1, 128.0, 127.5, 123.0, 82.9, 71.1, 54.1. This is a known compound and the spectral data are identical to those reported in the literature.⁸

***N*-Benzyl-*N*-phenylethynylcarbamic acid *tert*-butyl ester (3d).** Following the above general procedure (A) with bromoethynylbenzene **1a** (342 mg, 1.889 mmol) and *N*-benzylcarbamic acid *tert*-butyl ester **2d** (232.4 mg, 1.121 mmol), copper iodide (43.0 mg, 0.226 mmol), 1,10-phenanthroline (45.6 mg, 0.253 mmol), and KHMDS (2.3 mL, 1.2 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:49) to provide **3d** (235.3 mg, 0.7654 mmol, 68%) as a yellow oil. R_f 0.44 (EtOAc:hexanes=1:9); ^1H NMR (CDCl_3 , 400 MHz) δ 7.28–7.49 (m, 10H), 4.74 (s, 2H), 1.60 (s, 9H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.7, 136.3, 130.5, 128.4, 128.2, 128.1, 127.8, 127.0, 123.5, 84.0, 70.9, 53.0, 27.9. This is a known compound and the spectral data are identical to those reported in the literature.²

***N*-Phenyl-*N*-phenylethynylcarbamic acid methyl ester (3e).** Following the above general procedure (A) with bromoethynylbenzene **1a** (478.1 mg, 2.641 mmol) and *N*-phenylcarbamic acid methyl ester **2a** (209.2 mg, 1.384 mmol), copper iodide (57.3 mg, 0.301 mmol), 1,10-phenanthroline (60.9 mg, 0.338 mmol), and KHMDS (3.2 mL, 1.6 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:49) to provide **3e** (225.6 mg, 0.8978 mmol, 65%) as a yellow oil. R_f 0.32 (EtOAc:hexanes=1:9); ^1H NMR (CDCl_3 , 400 MHz) δ 7.26–7.56 (m, 10H), 3.92 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 154.8, 139.5, 131.4, 129.0, 128.2, 127.8, 127.0, 124.6, 122.8, 82.7, 70.1, 54.4. This is a known compound and the spectral data are identical to those reported in the literature.⁹

⁸ Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. M. C.; Vera, E. L. *Org. Lett.* **2004**, 6, 1151.

⁹ Raap, R. *Canadian Journal of Chemistry* **1971**, 49, 1792.

***N*-Phenyl-*N*-*p*-tolylethynylcarbamic acid methyl ester (**3f**).** Following the above general procedure (A) with 1-bromoethynyl-4-methylbenzene **1b** (596 mg, 3.040 mmol) and *N*-phenylcarbamic acid methyl ester **2e** (231 mg, 1.528 mmol), copper iodide (64.2 mg, 0.337 mmol), 1,10-phenanthroline (74.9 mg, 0.416 mmol), and KHMDS (3.6 mL, 1.8 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:24) to provide **3f** (196.1 mg, 0.7391 mmol, 48%) as an orange solid (m.p. 59-63°C). R_f 0.39 (EtOAc:hexanes=1:9); IR (CH₂Cl₂, NaCl) 3045 (w), 2955 (w), 2252 (m), 1738 (s), 1595 (w), 1492 (m), 1439 (m), 1362 (m), 1289 (s), 1124 (w), 1052 (w), 738 (s); ¹H NMR (CDCl₃, 400 MHz) δ 7.61–7.63 (m, 2H), 7.40–7.47 (m, 4H), 7.32 (m, 1H), 7.15–7.17 (m, 2H), 3.93 (s, 3H), 2.37 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 154.6, 139.5, 137.7, 131.2, 128.9, 128.8, 126.7, 124.4, 119.5, 81.9, 70.0, 54.1, 21.2; HRMS calcd. For C₁₇H₁₅NO₂: m/z 265.1103, found m/z 265.1113. Anal. calcd. For C₁₇H₁₅NO₂: C, 76.96; H, 5.70. Found C, 76.80; H, 5.86.

***N*-Phenyl-*N*-*o*-tolylethynylcarbamic acid methyl ester (**3g**).** Following the above general procedure (A) with 1-bromoethynyl-2-methylbenzene **1c** (321.4 mg, 1.648 mmol) and *N*-phenylcarbamic acid methyl ester **2e** (129.6 mg, 0.8579 mmol), copper iodide (36.4 mg, 0.191 mmol), 1,10-phenanthroline (40.9 mg, 0.227 mmol), and KHMDS (2.0 mL, 1.0 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:24) to provide **3g** (89.5 mg, 0.337 mmol, 39%) as an orange oil. R_f 0.39 (EtOAc:hexanes=1:9); IR (CH₂Cl₂, NaCl) 3054 (w), 2987 (w), 2305 (w), 2250 (w), 1738 (m), 1491 (w), 1439 (w), 1360 (w), 1266 (s), 896 (w), 739 (s); ¹H NMR (CDCl₃, 400 MHz) δ 7.43–7.46 (m, 2H), 7.25–7.30 (m, 3H), 7.15 (m, 1H), 6.99–7.06 (m, 3H), 3.77 (s, 3H), 2.30 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 154.7, 139.5, 139.5, 131.1, 129.3, 128.9, 127.6, 126.9, 125.4, 124.4, 122.6, 86.6, 69.3, 54.3, 20.6; HRMS calcd. For C₁₇H₁₅NO₂: m/z 265.1103, found m/z 265.1109.

***N*-(*m*-Fluorophenylethynyl)-*N*-phenylcarbamic acid methyl ester (**3h**).** Following the above general procedure (A) with 1-bromoethynyl-3-fluorobenzene **1d** (335 mg, 1.683 mmol) and *N*-phenylcarbamic acid methyl ester **2e** (133.7 mg, 0.8851 mmol), copper iodide (37.5 mg, 0.197 mmol), 1,10-phenanthroline (44.8 mg, 0.249 mmol), and KHMDS (2.0 mL, 1.0 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:19) to provide **3h** (129.4 mg, 0.4805 mmol, 54%) as an orange solid (m.p. 26-27°C). *R*_f 0.37 (EtOAc:hexanes=1:9); IR (CH₂Cl₂, NaCl) 3065 (w), 2955 (w), 2252 (s), 1738 (s), 1579 (m), 1490 (m), 1439 (m), 1363 (m), 1290 (s), 1053 (w), 940 (w), 738 (s); ¹H NMR (CDCl₃, 400 MHz) δ 6.80–7.39 (m, 9H), 3.75 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.3 (d, *J* = 246.2 Hz), 154.5, 139.2, 129.7 (d, *J* = 8.7 Hz), 129.0, 127.1, 127.0 (d, *J* = 2.4 Hz), 124.7, 124.6, 117.9 (d, *J* = 22.8 Hz), 114.9 (d, *J* = 21.2 Hz), 83.7, 69.1 (d, *J* = 3.0 Hz), 54.4; HRMS calcd. For C₁₆H₁₂NO₂F: *m/z* 269.0852, found *m/z* 269.0845. Anal. calcd. For C₁₆H₁₂NO₂F: C, 71.37; H, 4.49. Found C, 71.48; H, 4.30.

***N*-[3-(*tert*-Butyldimethylsilyloxy)-1-propynyl]-*N*-phenylcarbamic acid methyl ester (**3j**).** Following the above general procedure (A) with (3-bromoprop-2-ynloxy)-*tert*-butyldimethylsilane **1e** (146.4 mg, 0.5874 mmol) and *N*-phenylcarbamic acid methyl ester **2e** (120.6 mg, 0.7984 mmol), copper iodide (49.7 mg, 0.261 mmol), 1,10-phenanthroline (49.6 mg, 0.275 mmol), and KHMDS (2.0 mL, 1.0 mmol). The crude product was purified by column chromatography (Et₂O:pentane=1:9) to provide **3j** (51.4 mg, 0.161 mmol, 35%) as an orange oil. R_f 0.48 (EtOAc:hexanes=1:4); IR (CH₂Cl₂, NaCl) 3054 (w), 2987 (w), 2955 (w), 2859 (w), 2305 (w), 2253 (w), 1739 (m), 1596 (w), 1440 (w), 1266 (s), 1075 (w), 896 (w), 735 (s); ¹H NMR (CDCl₃, 400 MHz) δ 7.44–7.46 (m, 2H), 7.35–7.41 (m, 2H), 7.26 (m, 1H), 4.49 (s, 2H), 3.86 (s, 3H), 0.91 (s, 9H), 0.12 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 154.9, 139.3, 128.8, 127.0, 124.6, 78.4, 68.9, 54.1, 51.8, 25.8, 18.2, -5.2; HRMS calcd. For C₁₇H₂₅NO₃Si: m/z 319.1604, found m/z 319.1611.

***N*-(3-Hydroxy-1-propynyl)-*N*-phenylcarbamic acid methyl ester (**3i**).** A solution of **3j** (79.4 mg, 0.249 mmol) in THF (0.5 mL) was cooled to -78°C under nitrogen in a dry round-bottom flask. A solution of TBAF (1M in THF, 0.46 mL, 0.46 mmol) was added dropwise and the resulting mixture was stirred for 1 hour. The reaction was quenched with water at -20°C and the aqueous layer was extracted with ethyl acetate three times. The organic layers were combined, dried over MgSO_4 , filtered, and concentrated to dryness. The crude product was purified using flash chromatography (EtOAc:hexanes=2:3) to provide **3i** (33.4 mg, 0.163 mmol, 65%) as a white solid (m.p. $81\text{--}84^{\circ}\text{C}$). R_f 0.48 (EtOAc:hexanes=2:3); IR (CH_2Cl_2 , NaCl) 3052 (w), 2987 (w), 2305 (w), 2253 (w), 1740 (m), 1487 (w), 1442 (w), 1266 (s), 1016 (w), 888 (w), 739 (s); ^1H NMR (CDCl_3 , 400 MHz) δ 7.36–7.45 (m, 4H), 7.28 (m, 1H), 4.43 (s, 2H), 3.85 (s, 3H), 2.11 (br s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 155.0, 139.2, 129.0, 127.2, 124.8, 79.4, 68.6, 54.4, 51.1; HRMS calcd. For $\text{C}_{11}\text{H}_{11}\text{NO}_3$: m/z 205.0739, found m/z 207.0745.

***N*-[4-(*tert*-Butyldimethylsilyloxy)-1-butynyl]-*N*-phenylcarbamic acid methyl ester (**3k**).** Following the above general procedure (A) with **1f** (156.1 mg, 0.5930 mmol) and *N*-phenylcarbamic acid methyl ester **2e** (66.1 mg, 0.438 mmol), copper iodide (20.8 mg, 0.109 mmol), 1,10-phenanthroline (18.4 mg, 0.102 mmol), and KHMDS (0.75 mL, 0.38 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:24) to provide **3k** (37.8 mg, 0.113 mmol, 26%) as a yellow oil. R_f 0.38 (EtOAc:hexanes=1:9); IR (CH_2Cl_2 , NaCl) 3054 (w), 2956 (w), 2930 (w), 2857 (w), 1737 (m), 1492 (w), 1440 (m), 1298 (m), 1266 (s), 1104 (w), 838 (w), 740 (s); ^1H NMR (CDCl_3 , 400 MHz) δ 7.39 (m, 2H), 7.30 (m, 2H), 7.19 (m, 1H), 3.78 (s, 3H), 3.67 (t, 2H, $J = 7.0$ Hz), 2.48 (t, 2H, $J = 7.0$ Hz), 0.81 (s, 9H), -0.02 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 155.2, 139.8, 128.8, 126.7, 124.6, 74.6, 66.8, 62.0, 54.1, 25.8, 22.9, 18.3, -5.3 ; HRMS calcd. For $\text{C}_{18}\text{H}_{27}\text{NO}_3\text{Si}$: m/z 333.1760, found m/z 333.1752.

***N*-Phenyl-*N*-triisopropylsilylethynylcarbamic acid methyl ester (**3l**).** Following the above general procedure (A) with bromoethynyltriisopropylsilane **1g** (2.9332 g, 11.226 mmol) and *N*-phenylcarbamic acid methyl ester **2e** (1.4324 g, 9.4823 mmol), copper iodide (0.5808 g, 3.050 mmol), 1,10-phenanthroline (615.7 mg, 3.417 mmol), and KHMDS (24.0 mL, 12.0 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:24) to provide **3l** (2.8186 g, 8.5017 mmol, 90%) as a yellow oil. R_f 0.53 (EtOAc:hexanes=1:9); IR (CH₂Cl₂, NaCl) 3052 (w), 2949 (m), 2865 (m), 2305 (w), 2178 (m), 1740 (m), 1596 (w), 1492 (w), 1440 (m), 1266 (s), 1055 (w), 881 (w), 740 (s); ¹H NMR (CDCl₃, 400 MHz) δ 7.56 (m, 2H), 7.41 (m, 2H), 7.29 (m, 1H), 3.90 (s, 3H), 1.14 (s, 21H); ¹³C NMR (CDCl₃, 100 MHz) δ 154.8, 139.2, 128.7, 126.5, 123.9, 96.2, 68.9, 54.0, 18.5, 11.3; HRMS calcd. For C₁₉H₂₉NO₂Si: m/z 331.1968, found m/z 331.1977. Anal. calcd. For C₁₉H₂₉NO₂Si: C, 68.83; H, 8.82. Found C, 68.72; H, 8.99.

***N*-Ethynyl-*N*-phenylcarbamic acid methyl ester (**3m**).** A solution of **3l** (2.6024 g, 7.8497 mmol) in THF (15 mL) was cooled to -78°C under nitrogen in a dry round-bottom flask. A solution of TBAF (1 M in THF, 15.0 mL, 15.0 mmol) was added dropwise and the resulting mixture was stirred for 1 hour. The reaction was quenched with water at -20°C and the aqueous layer was extracted with ethyl acetate three times. The organic layers were combined, dried over MgSO₄, filtered, and concentrated to dryness. The crude product was purified using flash chromatography (EtOAc:hexanes=1:24) to provide **3m** (1.0451 g, 5.9658 mmol, 76%) as a white solid (m.p. 48-50°C). R_f 0.38 (EtOAc:hexanes=1:9); IR (CH₂Cl₂, NaCl) 3312 (w), 3055 (w), 2987 (w), 2306 (w), 2148 (w), 1742 (w), 1493 (w), 1440 (w), 1299 (w), 1266 (s), 896 (w), 738 (s), 705 (m); ¹H NMR (CDCl₃, 400 MHz) δ 7.47 (m, 2H), 7.34 (m, 2H), 7.29 (m, 1H), 3.89 (s, 3H), 2.92 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 154.8, 138.8, 129.0, 127.2, 124.6, 76.2, 58.5, 54.4; HRMS calcd. For C₁₀H₉NO₂: m/z 175.0633, found m/z 175.0631.

***N*-Ethoxycarbonylethynyl-*N*-phenylcarbamic acid methyl ester (3n).** In a dry round-bottom flask, at -78°C and under a flow of nitrogen, LiHMDS (1 M in THF, 1.85 mL, 1.85 mmol) was added dropwise to a solution of **1m** (186.4 mg, 1.064 mmol) in THF (8.5 mL). The reaction mixture was allowed to warm slowly to -40°C and then stirred for 1 hour. The reaction mixture was then added to a solution of ethyl chloroformate (0.165 mL, 1.73 mmol) in THF (2.9 mL) at -40°C via a cannula. The reaction was quenched with a saturated NH_4Cl solution and the aqueous layer was extracted three times with ethyl acetate. The organic layers were combined, dried over MgSO_4 , filtered, and concentrated to dryness. The crude product was purified using flash chromatography (EtOAc:hexanes=1:9) to provide **3n** (29.1 mg, 0.118 mmol, 11%) as a white solid (m.p. $82\text{--}84^{\circ}\text{C}$). R_f 0.36 (EtOAc:hexanes=1:4); IR (CH_2Cl_2 , NaCl) 3056 (w), 2981 (w), 2955 (w), 2237 (s), 1754 (s), 1705 (s), 1595 (w), 1492 (w), 1440 (m), 1288 (m), 1266 (s), 1197 (m), 1158 (m), 1025 (w), 896 (w), 740 (s); ^1H NMR (CDCl_3 , 400 MHz) δ 7.39–7.45 (m, 4H), 7.34 (m, 1H), 4.24 (q, 2H, $J = 7.1$ Hz), 3.93 (s, 3H), 1.30 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 154.2, 154.0, 137.7, 129.3, 128.1, 125.0, 81.4, 65.8, 61.7, 55.0, 14.1; HRMS calcd. For $\text{C}_{13}\text{H}_{13}\text{NO}_4$: m/z 247.0845, found m/z 247.0852.

***(S)*-4-(*tert*-Butyldimethylsilyloxymethyl)oxazolidin-2-one (13):** To a solution of *(S)*-4-hydroxymethyloxazolidin-2-one **12**³ (1.16 g, 9.91 mmol) in CH_2Cl_2 (15 mL) were successively added triethylamine (1.50 mL, 10.8 mmol), 4-(*N,N*-dimethylamino)pyridine (DMAP, 70.3 mg, 0.575 mmol) and *tert*-Butyl(chloro)dimethylsilane (TBSCl, 2.04 g, 13.5 mmol). The reaction mixture was stirred for 16 h at 25°C under N_2 then quenched with of water (1 mL). Magnesium sulfate was added and the mixture was filtered, and the filtrate was concentrated to dryness. The crude product was purified by column chromatography (EtOAc:hexanes=3:2) to give the product **13** (1.84 g, 7.95 mmol, 80%) as a semi-solid. $[\alpha]_{\text{D}}^{23} = +26$ (c 0.59, CH_2Cl_2); R_f 0.55 (EtOAc); IR (neat) 3327 (s), 2956 (s), 2936 (s), 1748 (s), 1253 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 6.30 (br s, 1H), 4.42 (app t, 1H, $J = 8.6$ Hz), 4.18 (dd, 1H, $J = 8.7, 4.8$ Hz), 3.89–3.92 (m, 1H), 3.59 (d, 2H, $J = 5.4$ Hz), 0.87 (s, 9H), 0.05 (s, 6H); ^{13}C

NMR (APT, CDCl₃, 100 MHz) δ 160.0, 67.1, 64.6, 53.6, 25.7, 18.1, -5.6. HRMS (m/z) for C₁₀H₂₁NO₃Si calc. 231.1291, found 231.1299.

(S)-4-(tert-Butyldimethylsilyloxymethyl)-3-phenylethynloxazolidin-2-one (10b): Following the above general procedure (A) with alkynyl bromide **1a** (1.095 g, 6.049 mmol) and **13** (900.3 mg, 3.891 mmol), copper iodide (303.3 mg, 1.593 mmol), 1,10-phenanthroline (295.7 mg, 1.641 mmol), and KHMDS (0.5 M in toluene, 12.4 mL, 6.2 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1:4) to give the ynamide **10b** (592.6 mg, 1.788 mmol, 46%) as a semi-solid. $[\alpha]_D^{23} = -94$ (c 0.30, CH₂Cl₂); R_f 0.56 (EtOAc:hexanes= 2:3); IR (neat) 2961 (m), 2937 (m), 2251 (m), 1777 (s), 1414 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.43 (m, 2H), 7.30 (m, 3H), 4.48 (app t, 1H, J = 8.6 Hz), 4.43 (dd, 1H, J = 8.5, 5.2 Hz), 4.10-4.13 (m, 1H), 4.04 (dd, 1H, J = 11.3, 3.0 Hz), 3.72 (d, 1H, J = 11.3 Hz), 0.89 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ¹³C NMR (APT, CDCl₃, 100 MHz) δ 155.8, 131.6, 128.2, 128.1, 122.1, 77.8, 72.2, 65.4, 60.5, 58.6, 25.6, 18.0, -5.6. HRMS (m/z) for C₁₈H₂₅NO₃Si calc. 331.1604, found 331.1620.

(S)-4-Hydroxymethyl-3-phenylethynyl-oxazolidin-2-one (10c): To a cold solution (-78°C) of **10b** (500.1 mg, 1.508 mmol) in THF (3 mL) under N₂ was slowly added a solution of tetrabutylammonium fluoride (1M in THF, 3.0 mL, 3.0 mmol). After 30 min, the reaction was quenched with saturated NH₄Cl solution (3 mL) and diluted with EtOAc. Layers were separated and aqueous layer was extracted three times with EtOAc. Organics were combined, dried over sodium sulfate and concentrated. The crude product was purified by column chromatography (EtOAc:hexanes= 2:3) to give ynamide **10c** (142.3 mg, 0.6551 mmol, 48%) as a solid (mp. 109-112°C). $[\alpha]_D^{23} = -63$ (c 0.40, CH₂Cl₂); R_f 0.13 (EtOAc:hexanes= 2:3); IR (neat) 2942 (w), 2978 (w), 2253 (m), 1753 (s), 1414 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.42-7.26 (m, 2H), 7.29-7.33 (m, 3H), 4.46-4.56 (m, 2H), 4.16-4.22 (m, 1H), 4.11 (dd, 1H, J = 12.2, 3.5 Hz), 3.81 (d, 1H, J = 11.8 Hz), 2.06 (br s, 1H); ¹³C NMR (APT, CDCl₃, 100 MHz) δ 156.1, 131.5, 128.3, 121.9, 77.4, 72.5, 65.5, 60.1, 58.6. HRMS (m/z) for C₁₂H₁₁NO₃ calc. 217.0739, found 217.0729.

(+)-3-Phenylethynyl-3,3a,8,8a-tetrahydroindeno[1,2-d]oxazol-2-one (10e): Following the above general procedure (B) with bromoethynylbenzene **1a** (631.2 mg, 3.487 mmol) and amide **14**⁴ (199.3 mg, 1.861 mmol), copper iodide (354.1 mg, 1.859 mmol), and KHMDS (0.5 M in toluene, 3.6 mL, 1.8 mmol). The crude mixture was purified by column chromatography (EtOAc:hexanes= 1:4) affording the ynamide **10e** (181.9 mg, 0.8615 mmol, 46%) as a solid (mp. 73-77 °C). $[\alpha]_{\text{D}}^{23} = +52$ (c 0.37, CH₂Cl₂); R_f 0.45 (EtOAc:hexanes=3:7); IR (neat) 3052 (w), 2987 (w), 2246 (m), 1727 (s), 1397 (s), 1266 (vs) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.36-7.40 (m, 2H), 7.20-7.27 (m, 3H), 4.15 (br s, 1H), 2.85 (m, 1H), 2.03 (dm, 1H, J = 9.9 Hz), 1.81-1.97 (m, 3H), 1.67-1.74 (m, 1H), 1.47 (dm, 1H, J = 9.9 Hz); ¹³C NMR (APT, CDCl₃, 100 MHz) δ 177.7, 131.2, 128.1, 127.6, 122.7, 79.4, 72.2, 64.4, 44.1, 39.0, 27.6, 24.1. HRMS (m/z) for C₁₄H₁₃NO calc. 211.0997, found 211.0991. Anal. Calcd. for C₁₄H₁₃NO = C, 79.59%; H, 6.20%; found C, 79.70%; H, 6.08%.

(-)-10,10-Dimethyl-4-phenylethynyl-3-thia-4-aza-tricyclo[5.2.1.0^{1,5}]decane-3,3-dioxide (10f): Following the above general procedure (B) with bromoethynylbenzene **1a** (69.4 mg, 0.383 mmol) and amide **15** (41.1 mg, 0.191 mmol), copper iodide (37.4 mg, 0.196 mmol), and KHMDS (0.5 M in toluene, 0.38 mL, 0.19 mmol). The crude mixture was purified by column chromatography (EtOAc:hexanes= 1:4) affording the ynamide **10f** (41.5 mg, 0.132 mmol, 69%) as a pale yellow oil. $[\alpha]_{\text{D}}^{23} = -146$ (c 0.52, CH₂Cl₂); R_f 0.41 (EtOAc:hexanes= 3:7); IR (neat) 3058 (w), 3000 (m), 2962 (s), 2237 (s), 1336 (s), 1146 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.40-7.44 (m, 2H), 7.27-7.29 (m, 3H), 3.68 (dd, 1H, J = 8.1, 4.1 Hz), 3.29 (s, 2H), 2.29 (dd, 1H, J = 13.4, 3.0 Hz), 1.98 (m, 1H), 1.89-1.93 (m, 2H), 1.82 (dd, 1H, J = 13.4, 8.2 Hz), 1.43-1.46 (m, 1H), 1.33-1.36 (m, 1H), 1.15 (s, 3H), 0.96 (s, 3H); ¹³C NMR (APT, CDCl₃, 100 MHz) δ 131.7, 128.1, 127.8, 122.6, 76.7, 72.6, 67.2, 51.2, 49.8, 48.0, 44.4, 34.4, 31.6, 27.0, 20.2, 19.9. HRMS (m/z) for C₁₈H₂₁NO₂S calc. 315.1293, found 315.1273. Anal. Calcd. for C₁₈H₂₁NO₂S = C, 68.54%; H, 6.71%; found C, 68.79%; H, 6.66%.

Part II: Ru-catalyzed [2+2] cycloaddition of Ynamides

General Procedure (C) for the Ru-catalyzed [2+2] cycloaddition Between Norbornene (4**) and Ynamides.** A mixture of norbornene **4** (2.5-5 equiv.), ynamide (1 equiv.) and THF (0.2-0.5 M w.r.t. the ynamide) 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, 5-10 mol%) under nitrogen. The reaction mixture was stirred in the dark at 25°C or 65°C for 68-168 h. The crude product was purified by column chromatography to give the cycloadduct.

Cycloadduct 5a (Table 2, entry 1). Following the above general procedure (C) with norbornene **4** (15.8 mg, 0.168 mmol), ynamide **3a** (16.6 mg, 0.0645 mmol), THF (0.3 mL), and Cp*RuCl(COD) (6.2 mg, 0.016 mmol). The reaction mixture was stirred in the dark at 60 °C for 168 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:49) to provide cycloadduct **5a** (12.4 mg, 0.0354 mmol, 55%) as a slightly yellow oil. R_f 0.48 (EtOAc:hexanes= 1:9); IR (CH₂Cl₂, NaCl) 3052 (m), 2987 (w), 2942 (w), 2305 (w), 1693 (m), 1442 (m), 1422 (m), 1266 (s), 894 (w), 740 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.28–7.29 (m, 4H), 7.20 (m, 1H), 3.93 (m, 1H), 3.59 (s, 3H), 2.74 (d, 1H, J = 3.5 Hz), 2.60 (d, 1H, J = 3.5 Hz), 2.30 (br s, 1H), 2.09 (br s, 1H), 1.90 (m, 1H), 1.72–1.82 (m, 4H), 1.51–1.66 (m, 5H), 1.26–1.37 (m, 2H), 1.06–1.19 (m, 3H), 0.99 (m, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 154.7, 136.8, 133.7, 131.3, 128.1, 127.3, 126.4, 57.4, 52.7, 52.4, 43.9, 35.2, 34.2, 32.0, 31.1, 30.8, 28.6, 28.4, 26.0, 25.9, 25.5. HRMS calcd. For C₂₃H₂₉NO₂: m/z 351.2198, found m/z 351.2189.

Cycloadduct 5b (Table 2, entry 2). Following the above general procedure (C) with norbornene **4** (43.4 mg, 0.461 mmol), ynamide **3b** (26.9 mg, 0.0963 mmol), THF (0.3 mL), and Cp*RuCl(COD) (4.5

mg, 0.012 mmol). The reaction mixture was stirred in the dark at 60 °C for 72 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:49) to provide cycloadduct **5b** (26.1 mg, 0.0698 mmol, 73%) as a yellow oil. R_f 0.34 (EtOAc:hexanes= 1:9); IR (CH₂Cl₂, NaCl) 2950 (w), 2865 (w), 1711 (m), 1648 (w), 1493 (w), 1447 (m), 1390 (w), 1313 (w), 1203 (w), 765 (w), 694 (w) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.13–7.34 (m, 10H), 3.80 (m, 1H), 3.68 (s, 3H), 3.60 (m, 1H), 2.83–2.99 (m, 2H), 2.74 (br s, 1H), 2.59 (d, 1H, J = 3.2 Hz), 2.32 (s, 1H), 2.14 (br s, 1H), 1.61–1.70 (m, 3H), 1.07–1.22 (m, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 155.1, 138.6, 134.1, 132.3, 130.7, 128.8, 128.4, 128.0, 126.9, 126.3, 52.6, 50.0, 48.6, 44.0, 35.4, 35.2, 34.5, 30.6, 28.4, 28.2. HRMS calcd. For C₂₅H₂₇NO₂: m/z 373.2042, found m/z 373.2051.

Cycloadduct 5c (Table 2, entry 3). Following the above general procedure (C) with norbornene **4** (31.7 mg, 0.337 mmol), ynamide **3c** (31.9 mg, 0.120 mmol), THF (0.3 mL), and Cp^{*}RuCl(COD) (4.9 mg, 0.013 mmol). The reaction mixture was stirred in the dark at 60 °C for 72 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:49) to provide cycloadduct **5c** (39.4 mg, 0.110 mmol, 91%) as an orange solid (m.p. 55-60 °C). R_f 0.34 (EtOAc:hexanes= 1:9); IR (CH₂Cl₂, NaCl) 3054 (w), 2953 (m), 2871 (w), 2305 (w), 1710 (s), 1648 (m), 1494 (w), 1447 (m), 1265 (s), 974 (w), 896 (w), 738 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.21–7.33 (m, 10H), 4.83 (d, 1H, J = 15.3 Hz), 4.62 (d, 1H, J = 15.4 Hz), 3.70 (s, 3H), 2.71 (br s, 1H), 2.54 (d, 1H, J = 3.4 Hz), 2.26 (s, 1H), 2.00 (br s, 1H), 1.53–1.64 (m, 2H), 1.40 (m, 1H), 1.06–1.17 (m, 2H), 0.91 (m, 1H); ¹³C NMR (CDCl₃, 150 MHz) δ 155.6, 138.1, 134.3, 132.2, 130.5, 128.3, 128.0, 127.4, 127.2, 126.9, 52.9, 50.1, 50.0, 44.1, 35.2, 34.4, 30.4, 28.4, 28.1. HRMS calcd. For C₂₄H₂₅NO₂: m/z 359.1885, found m/z 359.1892.

Cycloadduct 5d (Table 2, entry 5). Following the above general procedure (C) with norbornene **4** (72.6 mg, 0.771 mmol), ynamide **3c** (32.5 mg, 0.106 mmol), THF (0.3 mL), and Cp^{*}RuCl(COD) (4.3

mg, 0.011 mmol). The reaction mixture was stirred in the dark at 25 °C for 168 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:49) to provide cycloadduct **5d** (31.8 mg, 0.0792 mmol, 75%) as a colourless oil. R_f 0.63 (EtOAc:hexanes= 1:4); IR (CH₂Cl₂, NaCl) 2949 (m), 2865 (w), 1698 (s), 1383 (m), 1364 (m), 1313 (m), 1248 (w), 1161 (m), 688 (w) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.13–7.25 (m, 10H), 4.79 (d, 1H, J = 15.0 Hz), 4.46 (d, 1H, J = 15.4 Hz), 2.68 (br s, 1H), 2.43 (br s, 1H), 2.23 (br s, 1H), 1.93 (br s, 1H), 1.50–1.54 (m, 2H), 1.36 (d, 1H, J = 10.1 Hz), 1.28 (s, 9H), 1.02–1.08 (m, 2H), 0.84 (d, 1H, J = 10.1 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 153.8, 138.7, 135.0, 132.6, 129.6, 128.3, 127.8, 127.3, 127.0, 126.6, 80.9, 50.2, 49.4, 44.3, 35.6, 34.3, 30.4, 28.5, 28.2, 28.1. HRMS calcd. For C₂₇H₃₁NO₂: m/z 401.2355, found m/z 401.2330. Anal. calcd. For C₂₇H₃₁NO₂: C, 80.76; H, 7.78. Found C, 80.65; H, 7.89.

Cycloadduct 5e (Table 2, entry 6). Following the above general procedure (C) with norbornene **4** (36.6 mg, 0.389 mmol), ynamide **3e** (32.5 mg, 0.129 mmol), THF (0.3 mL), and Cp^{*}RuCl(COD) (5.2 mg, 0.014 mmol). The reaction mixture was stirred in the dark at 60 °C for 72 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:49) to provide cycloadduct **5e** (43.3 mg, 0.125 mmol, 97%) as a pale yellow solid (m.p. 66-69 °C). R_f 0.36 (EtOAc:hexanes= 1:9); IR (CH₂Cl₂, NaCl) 3054 (w), 2955 (w), 2865 (w), 2363 (w), 2305 (w), 1715 (m), 1596 (w), 1493 (w), 1442 (w), 1266 (s), 894 (w), 741 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.18–7.38 (m, 10H), 3.73 (s, 3H), 2.70 (d, 1H, J = 3.4 Hz), 2.64 (d, 1H, J = 3.5 Hz), 2.35 (d, 1H, J = 3.6 Hz), 1.95 (d, 1H, J = 3.5 Hz), 1.55–1.73 (m, 2H), 0.92–1.30 (m, 4H); ¹³C NMR (CDCl₃, 150 MHz) δ 158.0, 154.4, 139.6, 133.6, 131.7, 128.9, 127.9, 127.0, 126.8, 126.7, 126.6, 53.0, 49.8, 44.0, 35.5, 34.3, 30.8, 28.4, 28.2. HRMS calcd. For C₂₃H₂₃NO₂: m/z 345.1729, found m/z 345.1722.

Cycloadduct 5f (Table 2, entry 7). Following the above general procedure (C) with norbornene **4** (60.2 mg, 0.639 mmol), ynamide **3f** (41.5 mg, 0.156 mmol), THF (0.3 mL), and Cp*RuCl(COD) (8.7 mg, 0.023 mmol). The reaction mixture was stirred in the dark at 60 °C for 168 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:24) to provide cycloadduct **5f** (48.0 mg, 0.134 mmol, 85%) as a yellow solid (m.p. 69 – 75 °C). R_f 0.36 (EtOAc:hexanes= 1: 9); IR (CH₂Cl₂, NaCl) 3052 (m), 2954 (m), 2871 (m), 2350 (w), 2298 (w), 1714 (s), 1597 (m), 1492 (m), 1440 (m), 1266 (s), 1062 (m), 894 (w), 734 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.24–7.31 (m, 4H), 7.18 (m, 1H), 6.99–7.06 (m, 4H), 3.65 (s, 3H), 2.59 (d, 1H, J = 3.5 Hz), 2.54 (d, 1H, J = 3.6 Hz), 2.26 (s, 3H), 2.25 (br s, 1H), 1.84 (d, 1H, J = 3.6 Hz), 1.43–1.65 (m, 3H), 0.94–1.13 (m, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 154.4, 139.8, 136.9, 132.0, 130.8, 130.6, 128.9, 128.7, 126.7, 126.5, 53.0, 49.7, 43.8, 35.4, 34.3, 30.8, 28.5, 28.2, 21.3. HRMS calcd. For C₂₄H₂₅NO₂: m/z 359.1885, found m/z 359.1896.

Cycloadduct 5g (Table 2, entry 8). Following the above general procedure (C) with norbornene **4** (38.7 mg, 0.411 mmol), ynamide **3g** (38.6 mg, 0.146 mmol), THF (0.3 mL), and Cp*RuCl(COD) (6.3 mg, 0.017 mmol). The reaction mixture was stirred in the dark at 60 °C for 168 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:9) to provide cycloadduct **5g** (26.7 mg, 0.0742 mmol, 51%) as pale yellow oil. R_f 0.53 (EtOAc:hexanes= 1:4); IR (CH₂Cl₂, NaCl) 3054 (m), 2954 (m), 1718 (m), 1597 (w), 1491 (w), 1440 (m), 1348 (m), 1266 (s), 896 (w), 740 (s) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.21–7.25 (m, 2H), 7.13–7.18 (m, 3H), 6.99–7.04 (m, 4H), 3.48 (s, 3H), 2.70 (d, 1H, J = 3.0 Hz), 2.60 (d, 1H, J = 3.4 Hz), 2.25 (s, 3H), 2.17 (br s, 1H), 1.85 (br s, 1H), 1.74 (d, 1H, J = 10.1 Hz), 1.48–1.56 (m, 2H), 1.00–1.07 (m, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 154.4, 139.0, 136.0,

135.4, 132.9, 129.6, 128.6, 127.7, 127.6, 127.0, 126.5, 124.8, 52.7, 49.7, 46.9, 35.6, 34.9, 30.6, 28.2, 28.1, 20.5. HRMS calcd. For $C_{24}H_{25}NO_2$: m/z 359.1885, found m/z 359.1880.

Cycloadduct 5h (Table 2, entry 9). Following the above general procedure (C) with norbornene **4** (35.0 mg, 0.372 mmol), ynamide **3h** (31.0 mg, 0.115 mmol), THF (0.3 mL), and $Cp^*RuCl(COD)$ (5.6 mg, 0.015 mmol). The reaction mixture was stirred in the dark at 60 °C for 168 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:19) to provide cycloadduct **5h** (24.3 mg, 0.0668 mmol, 58%) as a yellow oil. R_f 0.38 (EtOAc:hexanes= 1:9); IR (CH_2Cl_2 , NaCl) 3054 (m), 2954 (m), 2872 (w), 2298 (w), 1718 (m), 1610 (w), 1596 (w), 1581 (w), 1494 (w), 1440 (m), 1348 (m), 1266 (s), 1062 (w), 851 (w), 739 (s) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 7.24–7.28 (m, 2H), 7.14–7.20 (m, 3H), 7.07 (m, 1H), 6.66–6.82 (m, 3H), 3.64 (s, 3H), 2.63 (d, 1H, J = 3.6 Hz), 2.50 (d, 1H, J = 3.6 Hz), 2.22 (d, 1H, J = 3.5 Hz), 1.86 (d, 1H, J = 3.4 Hz), 1.47–1.59 (m, 3H), 0.96–1.10 (m, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 162.5 (d, J = 244.8 Hz), 154.1, 139.4, 135.8 (d, J = 7.2 Hz), 133.1, 129.2 (d, J = 7.4 Hz), 129.0, 128.8, 127.0, 126.9, 122.4, 113.6 (d, J = 21.4 Hz), 113.4 (d, J = 21.7 Hz), 53.1, 50.0, 44.2, 35.5, 34.3, 30.7, 28.4, 28.2. HRMS calcd. For $C_{23}H_{22}NO_2F$: m/z 363.1635, found m/z 363.1643.

Cycloadduct 5i (Table 2, entry 10). Following the above general procedure (C) with norbornene **4** (44.6 mg, 0.474 mmol), ynamide **3i** (24.5 mg, 0.119 mmol), THF (0.3 mL), and $Cp^*RuCl(COD)$ (7.3 mg, 0.019 mmol). The reaction mixture was stirred in the dark at 60 °C for 72 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:4) to provide cycloadduct **5i** (11.6 mg, 0.0387 mmol, 32%) as a yellow oil. R_f 0.35 (EtOAc:hexanes= 2:3); IR (CH_2Cl_2 , NaCl) 3052 (m), 2955 (m), 2871 (w), 1712 (m), 1596 (w), 1493 (w), 1442 (m), 1313 (m), 1266 (s), 1055 (w), 894 (w),

740 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.32–7.42 (m, 3H), 7.20–7.22 (m, 2H), 3.74 (m, 1H), 3.70 (s, 3H), 3.66 (m, 1H), 2.50 (br s, 1H), 2.27 (d, 1H, $J = 3.3$ Hz), 2.08 (d, 1H, $J = 3.3$ Hz), 1.77 (br s, 1H), 1.43–1.52 (m, 3H), 0.07–1.04 (m, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 154.6, 139.2, 132.9, 129.2, 128.0, 127.9, 125.4, 57.6, 53.3, 49.3, 44.2, 35.0, 34.1, 30.3, 28.1, 27.9. HRMS calcd. For $\text{C}_{18}\text{H}_{21}\text{NO}_3$: m/z 299.1521, found m/z 299.1530.

Cycloadduct 5j (Table 2, entry 11). Following the above general procedure (C) with norbornene **4** (24.8 mg, 0.263 mmol), ynamide **3j** (21.0 mg, 0.0657 mmol), THF (0.3 mL), and $\text{Cp}^*\text{RuCl}(\text{COD})$ (5.9 mg, 0.016 mmol). The reaction mixture was stirred in the dark at 60°C for 72 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:9) to provide cycloadduct **5j** (6.8 mg, 0.016 mmol, 25%) as a yellow oil. R_f 0.58 (EtOAc:hexanes= 1:4); IR (CH_2Cl_2 , NaCl) 3052 (w), 2981 (w), 2949 (w), 2305 (w), 1719 (w), 1442 (w), 1422 (w), 1266 (s), 1036 (w), 894 (w), 740 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.37–7.40 (m, 2H), 7.33 (m, 1H), 7.20–7.22 (m, 2H), 3.70 (s, 3H), 3.48 (d, 1H, $J = 13.6$ Hz), 3.38 (d, 1H, $J = 13.6$ Hz), 2.73 (br s, 1H), 2.29 (d, 1H, $J = 3.1$ Hz), 2.07 (br s, 1H), 2.02 (br s, 1H), 1.51–1.53 (m, 3H), 0.96–1.04 (m, 3H), 0.81 (s, 9H), -0.07 (s, 3H), -0.09 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 154.1, 139.8, 132.3, 130.5, 129.2, 128.1, 127.6, 57.4, 52.9, 49.7, 44.2, 35.3, 34.4, 30.4, 28.1, 28.1, 25.9, 18.3, -5.4. HRMS calcd. For $\text{C}_{24}\text{H}_{35}\text{NO}_3\text{Si}$: m/z 413.2386, found m/z 413.2391.

Cycloadduct 5k (Table 2, entry 12). Following the above general procedure (C) with norbornene **4** (36.0 mg, 0.382 mmol), ynamide **3k** (37.8 mg, 0.113 mmol), THF (0.3 mL), and $\text{Cp}^*\text{RuCl}(\text{COD})$ (4.9 mg, 0.013 mmol). The reaction mixture was stirred in the dark at 60°C for 72 h. The crude product was purified by column chromatography (EtOAc:hexanes= 1:24) to provide cycloadduct **5k** (37.7 mg, 0.0881 mmol, 78%) as a yellow oil. R_f 0.48 (EtOAc:hexanes= 1:9); IR (CH_2Cl_2 , NaCl) 3052 (w),

2954 (m), 2871 (w), 1716 (m), 1442 (m), 1351 (w), 1266 (s), 1087 (w), 1055 (w), 836 (w), 740 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.36–7.39 (m, 2H), 7.29 (m, 1H), 7.21–7.22 (m, 2H), 3.70 (s, 3H), 3.43 (t, 2H, $J = 7.2$ Hz), 2.75 (br s, 1H), 2.18 (d, 1H, $J = 3.1$ Hz), 2.00 (br s, 1H), 1.98 (br s, 1H), 1.48–1.73 (m, 5H), 0.95–1.05 (m, 3H), 0.84 (s, 9H), -0.03 (s, 6H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 154.2, 140.0, 133.4, 129.0, 128.0, 127.3, 125.1, 61.1, 52.8, 50.2, 45.4, 35.1, 34.1, 30.4, 30.4, 28.2, 28.0, 25.9, 18.2, -5.3. HRMS calcd. For $\text{C}_{25}\text{H}_{37}\text{NO}_3\text{Si}$: m/z 427.2543, found m/z 427.2548.

Cycloadduct 11a (Table 3, entry 1). Following the above general procedure (C) with norbornene **4** (54.1 mg, 0.575 mmol), ynamide **10a** (54.6 mg, 0.207 mmol), THF (0.60 mL), and $\text{Cp}^*\text{RuCl}(\text{COD})$ (5.0 mg, 0.013 mmol). The reaction mixture was stirred in the dark at 65°C for 68 h. The crude product was purified by column chromatography ($\text{EtOAc}:\text{hexanes}=3:7$) to give the cycloadducts **11a** as an inseparable mixture of diastereoisomers (60.4 mg, 0.169 mmol, 83%, $\text{dr} = 72 : 28$ measured by 400 MHz ^1H NMR) as pale yellow oil. R_f 0.37 ($\text{EtOAc}:\text{hexanes}=3:7$); IR (neat) 3065 (w), 3032 (w), 2949 (m), 2872 (w), 1762 (s), 1648 (w), 1395 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) 7.18–7.36 (m, 8H), 7.08–7.17 (m, 0.56H), 6.93–6.97 (m, 1.44H), 5.11–5.15 (m, 1H), 4.74 (app t, 0.28H, $J = 8.8$ Hz), 4.73 (app t, 0.72H, $J = 8.8$ Hz), 4.22 (dd, 0.72H, $J = 8.8, 5.8$ Hz), 4.18 (dd, 0.28H, $J = 8.8, 5.8$ Hz), 2.86 (br d, 0.72H, $J = 3.6$ Hz), 2.57 (br d, 0.56H), 2.50 (br d, 0.72H, $J = 3.6$ Hz), 2.18 (br s, 0.72H), 2.06 (br s, 0.72H), 2.02 (br s, 0.56H), 1.46–1.58 (m, 2H), 1.27 (d, 0.28H, $J = 10.4$ Hz), 1.14–1.23 (m, 2H), 0.85 (d, 0.72H, $J = 10.4$ Hz), 0.79 (d, 0.28H, $J = 10.4$ Hz), 0.74 (d, 0.72H, $J = 10.4$ Hz); ^{13}C NMR (APT, CDCl_3 , 75 MHz) δ 154.94, 154.91, 138.6, 134.9, 133.5, 130.3, 129.3, 128.8, 128.7, 128.6, 128.04, 127.97, 127.94, 127.89, 127.84, 127.76, 127.43, 127.35, 127.1, 126.9, 126.5, 126.2, 70.4, 70.2, 59.6, 58.7, 55.9, 48.6, 48.5, 46.3, 44.8, 35.4, 35.0, 34.1, 34.0, 30.3, 29.8, 28.10, 28.07, 28.03, 28.0. HRMS (m/z) for $\text{C}_{24}\text{H}_{23}\text{NO}_2$ calc. 357.1729, found 357.1720. Anal. Calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_2 = \text{C}$, 80.64%; H, 6.49%; found C, 80.78%; H, 6.30%.

Cycloadduct 11b (Table 3, entry 2). Following the above general procedure (C) with norbornene **4** (29.7 mg, 0.315 mmol), ynamide **10b** (28.1 mg, 0.0848 mmol), THF (0.40 mL), and Cp^{*}RuCl(COD) (3.4 mg, 0.0089 mmol). The reaction mixture was stirred in the dark at 65 °C for 68 h. The crude product was purified by column chromatography (EtOAc:hexanes=1:4) to give the cycloadducts **11b** as an inseparable mixture of diastereoisomers (26.1 mg, 0.0611 mmol, 72%, dr = 58 : 42 measured by 400 MHz ¹H NMR) as pale yellow oil. *R*_f 0.49 (EtOAc:hexanes=1:4); IR (neat) 3055 (w), 3026 (w), 2952 (s), 2868 (m), 1760 (vs), 1650 (m), 1404 (vs) cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 7.29-7.34 (m, 2H), 7.21-7.24 (m, 3H), 4.43 (d, 0.42H, *J* = 8.6 Hz), 4.41 (d, 0.58H, *J* = 8.6 Hz), 4.33 (dd, 0.42H, *J* = 8.4, 3.6 Hz), 4.28 (dd, 0.58H, *J* = 8.6, 4.4 Hz), 4.17-4.21 (m, 1H), 3.50 (dd, 0.42H, *J* = 10.4, 5.2 Hz), 3.46 (dd, 0.58H, *J* = 10.6, 4.7 Hz), 3.40 (dd, 0.58H, *J* = 10.4, 3.0 Hz), 3.29 (dd, 0.42H, *J* = 10.6, 2.4 Hz), 3.02 (br d, 0.58H, *J* = 3.5 Hz), 2.79 (br d, 0.42H, *J* = 3.5 Hz), 2.72 (br d, 0.42H, *J* = 3.4 Hz), 2.59 (d, 0.58H, *J* = 3.6 Hz), 2.48 (br s, 0.42H), 2.41 (br s, 0.58H), 2.19 (br s, 0.58H), 2.02 (br s, 0.42H), 1.53-1.64 (m, 3H), 1.12-1.18 (m, 2H), 1.06 (d, 0.58H, *J* = 10.3 Hz), 1.02 (d, 0.42H, *J* = 10.2 Hz), 0.83 (s, 3.78H), 0.81 (s, 5.22H), -0.06 (s, 1.26H), -0.08 (s, 1.74H), -0.09 (s, 1.26H), -0.10 (s, 1.74H); ¹³C NMR (APT, CDCl₃, 100 MHz) major diastereomer: δ 155.0, 134.8, 128.1, 128.0, 127.2, 126.99, 126.3, 65.1, 55.5, 48.8, 46.4, 45.2, 36.3, 34.3, 30.6, 28.26, 28.1, 25.6, -5.6; minor diastereomer: δ 155.1, 133.8, 128.7, 128.2, 127.5, 127.1, 125.2, 65.1, 60.9, 55.9, 48.5, 45.2, 35.5, 34.5, 30.5, 28.35, 27.8, 25.6, -5.8. HRMS (*m/z*) for C₂₅H₃₅NO₃Si calc. 425.2386, found 425.2367. Anal. Calcd. for C₂₅H₃₅NO₃Si = C, 70.55%; H, 8.29%; found C, 70.40%; H, 8.44%.

Cycloadduct 11c (Table 3, entry 3). Following the above general procedure (C) with norbornene **4** (62.6 mg, 0.665 mmol), ynamide **10c** (46.8 mg, 0.215 mmol), THF (0.50 mL), and Cp^{*}RuCl(COD) (7.3 mg, 0.019 mmol). The reaction mixture was stirred in the dark at 65 °C for 68 h. The crude product was purified by column chromatography (EtOAc:hexanes=3:2) to give the cycloadducts **11c** as

an inseparable mixture of diastereoisomers (54.6 mg, 0.174 mmol, 81%, dr = 71 : 29 measured by 400 MHz ^1H NMR) as a pale yellow oil. R_f 0.47 (EtOAc:hexanes=3:2); IR (neat) 3058 (w), 2953 (m), 2870 (m), 1739 (s), 1649 (m), 1409 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 7.24-7.31 (m, 5H), 4.43-4.47 (m, 2H), 4.20-4.23 (m, 1H), 3.50-3.63 (m, 1H), 3.38-3.48 (m, 1H), 2.99 (br s, 0.71H), 2.77 (br s, 0.29H), 2.73 (br s, 0.29H), 2.62 (br s, 0.71H), 2.40 (br s, 1H), 2.16 (br s, 0.71H), 2.08 (br s, 0.29H), 1.99 (br s, 0.29H), 1.89 (br s, 0.71H), 1.52-1.69 (m, 3H), 1.02-1.25 (m, 3H); ^{13}C NMR (APT, CDCl_3 , 75 MHz) major diastereomer: δ 155.1, 134.3, 128.5, 128.2, 127.42, 127.38, 127.1, 64.9, 60.9, 55.6, 48.8, 46.0, 36.0, 34.1, 30.4, 28.2, 28.1; minor diastereomer: δ 155.2, 133.4, 128.3, 128.06, 128.01, 127.34, 127.24, 65.1, 60.8, 56.1, 48.8, 45.1, 35.3, 34.4, 30.5, 28.3, 27.9. HRMS (m/z) for $\text{C}_{19}\text{H}_{21}\text{NO}_3$ calc. 311.1521, found 311.1530. Anal. Calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_3$ = C, 73.29%; H, 6.80%; found C, 73.44%; H, 6.71%.

Cycloadduct 11d (Table 3, entry 4). Following the above general procedure (C) with norbornene **4** (74.3 mg, 0.789 mmol), ynamide **10d** (65.2 mg, 0.237 mmol), THF (0.40 mL), and $\text{Cp}^*\text{RuCl}(\text{COD})$ (5.4 mg, 0.014 mmol). The reaction mixture was stirred in the dark at 65°C for 68 h. The crude product was purified by column chromatography (EtOAc:hexanes=3:7) to give an inseparable mixture cycloadducts **11d** as an inseparable mixture of diastereoisomers (72.0 mg, 0.195 mmol, 82%, dr = 74 : 26 measured by 400 MHz ^1H NMR) as a pale yellow oil. R_f 0.51 (EtOAc:hexanes=3:7); IR (neat) 3065 (m), 2953 (s), 2871 (m), 1751 (s), 1651 (s), 1385 (s), 1266 (m) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) 7.38-7.39 (m, 1H), 7.24-7.33 (m, 5H), 7.18-7.22 (m, 1H), 7.10-7.14 (m, 1H), 7.04-7.06 (m, 1H), 5.58 (d, 0.26H, J = 6.5 Hz), 5.57 (d, 0.74H, J = 7.3 Hz), 5.35-5.41 (m, 1H), 3.33-3.41 (m, 2H), 3.12 (br d, 0.74H, J = 3.6 Hz), 2.86 (br d, 0.26H, J = 3.6 Hz), 2.73 (br d, 0.26H, J = 3.5 Hz), 2.68 (br d, 0.74H, J = 3.6 Hz), 2.60 (br s, 0.26H), 2.48 (br d, 0.74H, J = 3.1 Hz), 2.13 (br d, 0.74H, J = 2.9 Hz), 2.11 (br s, 0.26H), 1.57-1.70 (m, 3H), 1.14-1.23 (m, 2H), 1.08 (d, 0.26H, J = 10.3 Hz), 1.00 (d, 0.74H, J = 10.4 Hz); ^{13}C NMR (APT, CDCl_3 , 75 MHz) δ 154.1, 154.0, 140.04, 139.93, 139.0, 138.6, 134.6, 133.5, 129.5, 129.4, 128.5, 128.2, 127.9, 127.7, 127.63, 127.55, 127.4, 127.3, 127.2, 127.1, 127.0, 126.6,

125.6, 125.33, 125.26, 78.1, 77.8, 63.3, 63.2, 49.1, 49.0, 46.2, 44.9, 38.6, 38.1, 36.2, 35.6, 34.3, 34.1, 30.6, 30.3, 28.3, 28.2, 28.0, 27.8. HRMS (m/z) for $C_{25}H_{23}NO_2$ calc. 369.1729, found 369.1717. Anal. Calcd. for $C_{25}H_{23}NO_2$ = C, 81.27%; H, 6.27%; found C, 81.36%; H, 6.14%.