Supporting Information

Ruthenium(II)-Catalyzed Cyclization of Azabenzonorbornadienes with Alkynes

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Contents

Part I: General Information	page S2
Part II: Preparation of Azanorbornadienes (8b , 8d) and Alkyne 9f	page S3-S5
Part III: Ru-Catalyzed Cyclizations	page S5-S15
Part IV: ^1H and ^{13}C NMR Spectra	page S16-S39

Part I: 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 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 a Bruker Avance-300 and 400 spectrometers. 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).

Reagents: Unless stated otherwise, commercial reagents were used without purification. THF was purified by distillation under dry nitrogen from potassium/benzophenone. Alkyne **9b** was purchased from Aldrich and [Cp*Ru(CH₃CN)₃]PF₆ was purchased from Strem Chemicals. Azanorbornadienes **8a**,² **8c**,² **8e**,² **8f**,³ **8g**,⁴ alkynes **9a**,⁵ **9c**,⁶ **9d**,⁷ **9e**,⁸ Cp*Ru(COD)Cl,⁹ Cp*Ru(COD)Br¹⁰ and Cp*Ru(COD)I¹⁰ were prepared according to literature procedures.

Special Note: For some of the azabicyclic alkenes, some of the ¹³C NMR signals (especially the 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 or HSQC spectra were obtained in which the “missing peaks” can be detected.¹¹

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

² Hodgson, D.M.; Bebbington, M.W.P.; Willis, P. *Org. Biomol. Chem.* **2003**, *1*, 3787.

³ Lautens, M.; Fagnou, K.; Zunic, V. *Org. Lett.* **2002**, *4*, 3465.

⁴ Keana, J. F. W.; Heo, G. S.; Mann, J. S.; Van Nice, F. L.; Lex, L.; Prabhu, V. S.; Ferguson, G. *J. Org. Chem.* **1988**, *53*, 2268.

⁵ Jordan, R. W.; Villeneuve, K.; Tam, W. *J. Org. Chem.* **2006**, *71*, 5830.

⁶ Bellina, F.; Carpita, A.; De Santis, M.; Rossi, R. *Tetrahedron* **1994**, *50*, 12029.

⁷ Jones, P. S.; Ley, S. V.; Simpkins, N. S.; Whittle, A. J. *Tetrahedron* **1986**, *42*, 6519.

⁸ Krafft, M. E.; Cheung, Y. Y.; Abboud, K. A. *J. Org. Chem.* **2001**, *66*, 7443.

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

¹⁰ Villeneuve, K.; Tam, W. *Organometallics* **2006**, *25*, 843.

¹¹ For detail explanations and the use of 2-D NMR spectra to solve this problem, see: Robinson, V., J.; Bain, A. D. *Magnetic Resonance in Chemistry* **1993**, *31*, 865.

Part II: Preparation of Azanorbornadienes (8b, 8d) and Alknyne 9f

Azanorbornadiene 8b. To an oven-dried round bottom flask was added tetrabromobenzene (1.02 g, 2.59 mmol), toluene (25 mL), and *tert*-butyl-1-pyrrole carboxylate (0.55 mL, 3.29 mmol). The mixture was purged with argon and cooled to $-25\text{ }^{\circ}\text{C}$. A solution of *n*-butyllithium in hexanes (1.0 M, 2.80 mL) was added dropwise over 20 minutes. The mixture was warmed to room temperature slowly and stirred for 23 h then quenched with water. The aqueous phase was extracted three times with diethyl ether. The combined organic layers were washed with water then brine, dried with anhydrous magnesium sulfate, filtered, and concentrated using rotary evaporation. The crude product was purified using column chromatography (1:9 EtOAc:hexanes, $R_f = 0.24$) to provide the product **8b** as a light orange solid (414.8 mg, 1.03 mmol, 40%). Mp $120\text{--}123^{\circ}\text{C}$; IR (NaCl, cm^{-1}) 2976 (w), 2931 (w), 1708 (m), 1392 (m), 1368 (m), 1313 (w), 1253 (m), 1163 (m), 1084 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.48 (br s, 2H), 6.94 (br s, 2H), 5.43 (br s, 2H), 1.38 (s, 9H); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 154.5, 149.5, 127.5, 126.1, 120.6, 81.1, 65.7, 28.1; HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{15}\text{Br}_2\text{O}_2$ (M^+): 399.9548; found: 399.9541. See also the “special note” in the General Information section concerning ^{13}C NMR.

Azanorbornadiene 8d. To a flame-dried RB flask, azanorbornadiene **8a**² (1.50 g, 6.20 mmol) was added and dissolved in CH_2Cl_2 (40 mL). The flask was purged with N_2 and trifluoroacetic acid (TFA, 8.25 mL, 110.9 mmol) was added dropwise and the mixture was stirred for 1 h. Solvent was removed by rotary evaporation and the crude mixture was diluted with toluene (50 mL) and concentrated by rotary evaporation. This process was repeated 3 times to azeotropically remove excess TFA. Upon removal of the last portion of toluene, a brown salt was formed. The salt was dissolved in acetone (35 mL) and K_2CO_3 (5.57g, 40.3 mmol) was added. A condenser was attached and benzyl chloroformate (4.37 mL, 31.0 mmol) was added dropwise while heating. After the addition of benzyl chloroformate,

the temperature was raised to 65°C and refluxed for 18 h. The mixture was then quenched with water and partitioned in diethyl ether. The aqueous layer was extracted with diethyl ether (2 × 50mL) and the combined organic layers were washed with 10% NaOH solution (50 mL) and brine (50 mL). The organic layer was dried with MgSO₄, filtered and concentrated. The crude product was purified by column chromatography (EtOAc:Hexanes = 1.5: 8.5) and then recrystallized in hexanes to provide the product **8d** as an off white solid (525 mg, 1.89 mmol, 31%). *R_f* 0.54 (EtOAc:hexanes = 3:7); mp 74-77°C; IR (CH₂Cl₂) ν_{max} (cm⁻¹) 3032 (m), 2955 (w), 1711 (m), 1499 (m), 1442 (m), 1393 (m), 1315 (m), 1242 (m), 813 (m), 739 (m), 694 (m); ¹H NMR (CDCl₃, 300MHz): δ 7.30 (m, 7H), 6.98 (m, 4H), 5.61 (s, 2H), 5.08 (s, 2H), ¹³C NMR (APT, CDCl₃, 75MHz): δ 148.1 (2), 142.7, 136.2, 128.4, 128.0, 127.7, 125.1, 121.1, 120.9, 120.8, 67.2, 66.2 (2). See also the “specical note” in the General Information section concerning ¹³C NMR.

Alkyne 9f. To an oven-dried 100mL round bottom flask was added 3-butyn-(1)-ol (2.0mL, 0.026mol), Tetrahydrofuran (30 mL) and pyridinium *p*-toluene sulfonate (0.675g, 0.0026mol). The mixture was purged with N₂ and Dihydropyran (3.85mL, 0.042mol) was added dropwise via syringe over a 10 minute period. The mixture stirred at room temperature for 1.5 hours. The mixture was quenched with water (30 mL) and extracted with ethyl acetate (50 mL). The organic layer was washed with brine (2 x 50 mL), dried over MgSO₄, filtered and concentrated using rotary evaporation. The crude product was transferred to an oven-dried 250mL round bottom flask and 30 mL of tetrahydrofuran was added. The mixture was purged with N₂ and brought to 0°C with an ice-water bath. ⁿButyl lithium (11.5 mL, 2.5 M in hexanes, 0.029mol) was added dropwise at a rate to keep the temperature at 0°C (45 minutes). The mixture was transferred to a 250mL round bottom flask that was purged with N₂ and contained ethyl chloroformate (2.75mL, 0.029mol) and tetrahydrofuran (30mL) at 0°C via cannula. The mixture then stirred for 2.5 hours while warming up to room temperature. The mixture was quenched with water (50 mL) and extracted with ethyl acetate (150 mL). The organic layer was washed with brine (2 x 50mL), dried over magnesium sulfate, filtered and concentrated by rotary evaporation. The crude product was transferred to a 250 mL round bottom flask containing a condenser, then ethanol (50 mL) and pyridinium *p*-toluene sulfonate (0.675g, 0.0026mol) was added. The mixture refluxed for 2 hours at 55-65°C. The solvent was evaporated by rotary evaporation and the product was purified by column

chromatography (2.5:7.5 to 4:6 EtOAc:hexanes) to provide **9f** as a yellow oil (1.52g, 0.011mol, 40%). IR (CH₂Cl₂) ν_{max} (cm⁻¹) 3412 (m), 2983 (m), 2893 (m), 2239 (s), 1712 (s), 1368 (m), 1254 (s), 1074 (s), 751 (m); ¹H NMR (CDCl₃, 300MHz): δ 4.20 (q, 2H, *J* = 7.1 Hz), 3.79 (t, 2H, *J* = 6.3 Hz), 2.59 (t, 2H, *J* = 6.3 Hz), 2.37 (br.s, 1H), 1.29 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (APT, CDCl₃, 75MHz): δ 153.4, 86.1, 74.4, 62.0, 60.0, 23.0, 14.0.

Part III: Ru-Catalyzed Cyclizations

General Procedure for the Ru-catalyzed cyclizations. A mixture of an azabicyclic alkene (0.34 mmol, 1.25 equiv), an alkyne (0.27 mmol, 1 equiv) and THF (0.5 mL) in an oven-dried vial was added via a cannula to an oven-dried screw-cap vial containing Cp*Ru(COD)Cl or [Cp*Ru(CH₃CN)₃]PF₆ (weighed out from a dry box, 0.013 mmol, 5 mol%) under nitrogen. The reaction mixture was stirred in the dark at room temperature for 72 h. The crude product was purified by column chromatography (EtOAc—hexanes mixtures) to give the dihydrobenz[g]indole and/or the [2+2] cycloaddition product.

Dihydrobenz[g]indole 10a (Table 1, entry 1). Following the above general procedure, with azanorbornadiene **8a** (84.0 mg, 0.343 mmol), alkyne **9a** (35.0 mg, 0.273 mmol), THF (0.5 mL), and Cp*RuCl(COD) (5 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1.5:8.5) to provide the dihydrobenz[g]indole **10a** (79.0 mg, 0.213 mmol, 78%) as a pale brown solid. The structure and relative stereochemistry was determined by NMR experiments (1D ¹H, ¹³C and GOESY; 2D COSY and HSQC).^{12,13} *R_f* 0.48 (EtOAc:hexanes = 3:7); mp 81-86°C; IR (CH₂Cl₂) ν_{max} (cm⁻¹) 3460 (s), 2980 (m), 1685 (s), 1621 (m), 1453 (w), 1367 (m), 1253 (s), 1160 (s), 1029 (m), 737 (m); ¹H NMR (CDCl₃, 300MHz): δ 7.32 (m, 1H), 7.20 (m, 2H), 7.00 (m, 1H), 6.39 (d, 1H, *J* = 9.8 Hz), 6.12 (dd, 1H, *J* = 9.8, 5.7 Hz), 5.57 (d, 1H, *J* = 10.0 Hz), 4.90 (dd, 1H, *J* = 13.7, 8.9

¹² HCOSY: ¹H–¹H Correlated Spectroscopy; HSQC: Heteronuclear Single Quantum Coherence; see: Crews, P.; Rodriguez, J.; Jaspars, M. *Organic Structure Analysis*; Oxford University Press: Oxford, 1998.

H_z), 4.66 (dd, 1H, *J* = 13.7, 6.0 Hz), 4.40 (m, 1H), 4.21 (m, 2H), 4.01 (m, 1H), 1.57 (s, 9H), 1.30 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (APT, CDCl₃, 75MHz): δ 165.0, 153.5, 153.4, 132.3, 131.6, 128.2, 127.8, 127.1, 126.61, 126.57, 123.9, 115.3, 83.2, 60.7, 60.5, 56.0, 41.0, 28.2, 14.2. HRMS (CI) calcd. for C₂₁H₂₅NO₅ (M⁺): 371.1733; found: 371.1736.

Dihydrobenz[g]indole 10b (Table 1, entry 2). Following the above general procedure, with azanorbornadiene **8b** (79.0 mg, 0.195 mmol), alkyne **9a** (20.0 mg, 0.156 mmol), THF (0.3 mL), and Cp*RuCl(COD) (3 mg, 0.008 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1.5:8.5) to provide the dihydrobenz[g]indole **10b** (48.5 mg, 0.092 mmol, 59%) as a white solid. *R_f* 0.56 (EtOAc:hexanes = 3:7); mp 130-132°C; IR (CH₂Cl₂) *v*_{max} (cm⁻¹) 3488 (w), 2979 (w), 1711 (s), 1687 (s), 1621 (w), 1366 (m), 1271 (s), 1251 (s), 1160 (s), 1146 (s), 1030 (m), 737 (w); ¹H NMR (CDCl₃, 300MHz): δ 7.63 (s, 1H), 7.26 (s, 1H), 6.29 (d, 1H, *J* = 9.9 Hz), 6.21 (dd, 1H, *J* = 9.8, 5.4 Hz), 5.47 (d, 1H, *J* = 9.8 Hz), 4.90 (dd, 1H, *J* = 13.6, 9.1 Hz), 4.67 (dd, 1H, *J* = 13.6, 6.4 Hz), 4.32 (m, 1H), 4.24 (m, 2H), 4.03 (dd, 1H, *J* = 10.0, 5.3 Hz), 1.59 (s, 9H), 1.30 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (APT, CDCl₃, 75MHz): δ 164.7, 153.5, 153.0, 133.0, 132.6, 132.4, 131.1, 126.1, 124.6, 124.3, 123.2, 114.9, 83.9, 60.7, 59.6, 55.8, 40.8, 28.2, 14.2. HRMS (CI) calcd. for C₂₁H₂₃Br₂NO₅ (M⁺): 526.9943; found: 526.9939.

Dihydrobenz[g]indole 10c (Table 1, entry 3). Following the above general procedure, with azanorbornadiene **8c** (68.0mg, 0.341 mmol), alkyne **9a** (35.0 mg, 0.273 mmol), THF (0.5 mL), and Cp*RuCl(COD) (5 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=3:7) to provide the dihydrobenz[g]indole **10c** (67.8 mg, 0.210 mmol, 77%) as a pale

¹³ GOESY: Gradient enhanced nuclear Overhauser enhancement spectroscopy, see: (a) Stonehouse, J.; Adell, P.; Keeler, J.; Shaka, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 6037. (b) Stott, K.; Stonehouse, J.; Keeler, J.; Hwang, T.-L.; Shaka, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4199. (c) Dixon, A. M.; Widmalm, G.; Bull, T. E. *J. Magn. Reson.* **2000**, *147*, 266.

brown oil.); R_f 0.19 (EtOAc:hexanes = 3:7); IR (CH₂Cl₂) $\nu_{\max}$ (cm⁻¹) 3489 (w), 2981 (w), 1712 (s), 1686 (s), 1624 (m), 1416 (m), 1259 (s), 1133 (m), 1028 (m), 757 (m); ¹H NMR (CDCl₃, 300MHz): δ 7.26 (m, 1H), 7.21 (m, 2H), 7.01 (m, 1H), 6.40 (d, 1H, J = 9.8 Hz), 6.09 (dd, 1H, J = 9.8, 5.5 Hz), 5.60 (d, 1H, J = 9.9 Hz), 4.91 (dd, 1H, J = 13.5, 8.8 Hz), 4.70 (dd, 1H, J = 13.4, 6.5 Hz), 4.22 (m, 3H), 4.01 (m, 1H), 3.87 (s, 3H), 1.30 (t, 3H, J = 7.1 Hz); ¹³C NMR (APT, CDCl₃, 75MHz): δ 164.8, 154.8, 153.0, 132.3, 130.8, 128.4, 127.7, 127.5, 126.6 (2), 123.8, 115.8, 60.8, 60.6, 55.7, 53.4, 41.1, 14.2. HRMS (CI) calcd. for C₁₈H₁₉NO₅ (M⁺): 329.1263; found: 329.1277.

Dihydrobenz[g]indole 10d (Table 1, entry 4). Following the above general procedure, with azanorbornadiene **8d** (53.7 mg, 0.194 mmol), alkyne **9a** (35.0 mg, 0.273 mmol), THF (0.5 mL), and Cp*RuCl(COD) (5 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=2:8) to provide the dihydrobenz[g]indole **10d** (62.8 mg, 0.155 mmol, 80%) as a brown solid. R_f 0.27 (EtOAc:hexanes = 3:7); mp 65-70°C; IR (CH₂Cl₂) $\nu_{\max}$ (cm⁻¹) 3473 (s), 2982 (m), 1690 (s), 1624 (m), 1443 (s), 1364 (m), 1261 (s), 1041 (m), 779 (m); ¹H NMR (CDCl₃, 300MHz): δ 7.37 (s, 5H), 7.20 (m, 2H), 7.08 (m, 1H), 7.00 (d, 1H, J = 7.2 Hz), 6.39 (d, 1H, J = 9.8 Hz), 6.09 (dd, 1H, J = 9.8, 5.4 Hz), 5.64 (d, 1H, J = 9.9 Hz), 5.29 (s, 2H), 4.93 (dd, 1H, J = 13.5, 8.9 Hz), 4.71 (dd, 1H, J = 13.6, 6.4 Hz), 4.22 (m, 3H), 4.00 (m, 1H), 1.30 (t, 3H, J = 7.1 Hz); ¹³C NMR (APT, CDCl₃, 75MHz): δ 164.8, 154.1, 152.9, 134.9, 132.3, 130.7, 128.7 (2), 128.6, 128.3, 127.7, 127.6, 126.6, 126.5, 123.8, 115.9, 68.5, 60.8, 60.5, 55.7, 41.1, 14.2.

[2+2] Cycloadduct 11e (Table 1, entry 5). Following the above general procedure, with azanorbornadiene **8e** (78.0 mg, 0.341 mmol), alkyne **9a** (35.0 mg, 0.273 mmol), THF (0.5 mL), and Cp*RuCl(COD) (5 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=1.5:8.5) to provide the cyclobutene cycloadduct **11e** (79.8 mg, 0.224 mmol, 82%) as

a pale brown oil. R_f 0.25 (EtOAc:hexanes = 4:6); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 3404 (m), 2979 (m), 1712 (s), 1604 (s), 1481 (m), 1425 (m), 1369 (m), 1204 (m), 1116 (m), 1024 (m), 745 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.30 (m, 2H), 7.19 (m, 2H), 5.52 (s, 1H), 5.40 (s, 1H), 4.70 (m, 1H), 4.28 (m, 2H), 4.21 (q, 2H, J = 7.1 Hz), 2.79 (br. s, 1H), 2.73 (m, 1H), 1.31 (t, 3H, J = 7.1 Hz), 1.14 (s, 9H); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 177.7, 163.4, 162.7, 143.1, 142.4, 130.8, 127.1, 126.9, 120.7, 119.8, 61.6, 60.7, 59.9, 58.7, 46.1, 44.8, 39.0, 28.1, 14.3. HSQC experiments confirm the carbon peaks at 61.6 and 46.1

Dihydrobenz[g]indole 10g (Scheme 2). Following the above general procedure, with azanorbornadiene **8g** (105 mg, 0.341 mmol), alkyne **9a** (35.0 mg, 0.273 mmol), THF (0.5 mL), and $\text{Cp}^*\text{RuCl}(\text{COD})$ (5 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=2.5:7.5 to 3.5:6.5) to provide the dihydrobenz[g]indole **10g** (76.2 mg, 0.174 mmol, 63%) as brown oil. R_f 0.12 (EtOAc:hexanes = 3:7); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 3448 (m), 2982 (w), 1719 (s), 1271 (s), 1148 (m); ^1H NMR (CDCl_3 , 400MHz): δ 6.18 (m, 1H), 6.12 (dd, 1H, J = 8.8, 4.1 Hz), 5.32 (d, 1H, J = 8.8 Hz), 4.86 (m, 1H), 4.80 (m, 1H), 4.23 (m, 3H), 3.86 (m, 1H), 3.79 (s, 6H), 1.47 (s, 9H), 1.30 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, CDCl_3 , 100MHz): δ 166.7, 166.3, 164.7, 154.7, 152.1, 132.0, 129.0, 127.7, 120.2, 112.6, 84.1, 60.7, 58.4, 55.7, 52.5, 52.3, 40.4, 27.9, 14.2. HRMS (CI) calcd. for $\text{C}_{21}\text{H}_{27}\text{NO}_9$ (M^+): 437.1686; found: 437.1681.

Dihydrobenz[g]indole 10a'' (Table 2, entry 4). Following general procedure: azanorbornadiene **8a** (84.0 mg, 0.343 mmol), alkyne **9a** (35.0 mg, 0.273 mmol), THF (0.5mL), and $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (6 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 1.5:8.5) to provide the dihydrobenz[g]indole **10a''** (46.5 mg, 0.126 mmol, 46%) as a brown oil. R_f 0.22 (EtOAc:hexanes = 2:8); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2979.42(s), 1731.73(s), 1454.09(m), 1367.80(s), 1162.86(m), 1119.24(m), 1020.79(m), 946.21(m), 770.09(m), 735.97(m); ^1H NMR (CDCl_3 , 400MHz):

δ 9.63 (d, 1H, J = 1.4 Hz), 7.50 (d, 1H, J = 7.6 Hz), 7.26 (m, 1H), 7.17 (m, 1H), 6.98 (d, 1H, J = 7.2 Hz), 6.48 (d, 1H, J = 9.8 Hz), 5.89 (m, 1H), 5.43 (br. s, 1H), 4.31 (m, 1H), 3.77 (m, 1H), 3.64 (t, 1H, J = 7.9 Hz), 3.48 (m, 1H), 3.29 (m, 1H), 1.52 (s, 9H), 0.88 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 201.7, 169.6, 133.7, 129.8, 128.5, 127.5, 127.1, 126.3, 122.9, 81.7, 65.6, 61.1, 58.2, 28.3, 13.6. carbon peaks elucidated by HSQC and HMBC experiments: 131.2, 77.2, ~53.7, ~41.1. HRMS (CI) calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 372.1811; found: 372.1821.

Dihydrobenz[g]indole 10h and [2+2] Cycloadduct 11h (Table 2, entry 5). Following general procedure: azanorbornadiene **8a** (58.0 mg, 0.237 mmol), alkyne **9b** (40.0 mg, 0.354 mmol), THF (0.5 mL), and $\text{Cp}^*\text{Ru}(\text{COD})\text{Cl}$ (5 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 1:9) to give a separable mixture of dihydrobenz[g]indole **10h** (27.2 mg, 0.133 mmol, 35%) as a colourless oil and cycloadduct **11h** (42.9 mg, 0.084 mmol, 56%) as a pale yellow solid.

10h: R_f 0.62 (EtOAc:hexanes = 3:7); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2979 (m), 1694 (s), 1619 (m), 1363 (m), 1251 (s), 1160 (s), 1053 (m), 777 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.40 (m, 1H), 7.20 (m, 2H), 6.99 (m, 1H), 6.36 (d, 1H, J = 9.8 Hz), 6.11 (dd, 1H, J = 9.7, 5.4 Hz), 5.56 (d, 1H, J = 9.9 Hz), 4.20 (m, 2H), 3.95 (m, 1H), 2.49 (s, 3H), 1.55 (s, 9H), 1.29 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 165.7, 153.1, 152.9, 132.4, 132.2, 128.0, 127.9, 127.6, 126.3, 126.0, 125.1, 112.9, 82.1, 60.6, 59.7, 40.4, 28.3, 15.4, 14.4. HRMS (CI) calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_5$ (M^+): 355.1784; found: 355.1766.

11h: (note: signals split into a 2:1 ratio due to the rotational isomers of the BOC group on the nitrogen) R_f 0.55 (EtOAc:hexanes = 3:7); mp 97-100°C; IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2978 (m), 1714 (s), 1391 (s), 1333 (m), 1289 (m), 1246 (m), 1172 (s), 1092 (m), 746 (m), 653 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.27 (m, 2H), 7.15 (m, 2H), 5.04 (m, 2H), 4.23 (m, 2H), 2.80 (br s, 0.33H), 2.73 (br s, 0.66H), 2.50 (br s, 0.66H), 2.47 (br s, 0.33H), 2.13 (s, 1H), 2.09 (s, 2H), 1.42 (s, 3H), 1.37 (s, 6H), 1.35 (m, 3H); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 161.0, 154.2, 144.2, 143.7, 142.9, 132.0, 126.5, 126.4, 120.1, 120.0, 79.6, 60.3, 59.9, 58.0, 48.6, 45.6, 28.0, 15.2, 14.3; visible minor isomer peaks: δ 120.5, 119.6, 61.0, 59.0, 58.6, 48.4, 28.2, 15.7, 14.2.

Dihydrobenz[g]indole 10h (Table 2, entry 8). Following general procedure: azanorbornadiene **8a** (58.0 mg, 0.237 mmol), acetylene **9b** (40.0 mg, 0.354 mmol), THF (0.5 mL), and $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (6 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 1:9) to give an inseparable mixture of dihydrobenz[g]indole **10h** and **10h'** (68.9 mg, 0.194 mmol, 82%) as a colourless oil. R_f 0.62 (EtOAc:hexanes = 3:7); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2979 (m), 1694 (s), 1619 (m), 1363 (m), 1251 (s), 1160 (s), 1053 (m), 777 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.59 (m, 0.89H), 7.41 (m, 0.11H), 7.24(m, 0.22H), 7.20 (m, 1.78H), 6.99 (m, 1H), 6.45 (d, 0.11H, J = 9.7 Hz), 6.37 (d, 1H, J = 9.8 Hz), 6.12 (dd, 0.89H, J = 9.7, 5.4 Hz), 5.85 (dd, 0.11H, J = 9.7, 6.0 Hz), 5.69 (d, 0.11H, J = 10.0 Hz), 5.56 (d, 1H, J = 9.9 Hz), 4.20 (m, 2H), 3.95 (m, 1H), 2.50 (d, 3H, J = 1.8 Hz), 1.55 (s, 8H), 1.38 (s, 1H), 1.29 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 165.7, 153.1, 152.9, 132.4, 132.2, 128.0, 127.9, 127.6, 126.3, 126.0, 125.1, 112.9, 82.1, 60.6, 59.7, 40.4, 28.3, 15.4, 14.4. visible minor isomer peaks at: 128.5, 128.4, 127.7, 121.5, 44.9, 28.1, 14.2, 11.9 HRMS (CI) calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_5$ (M^+): 355.1784; found: 355.1766.

Dihydrobenz[g]indole 10i and [2+2] Cycloadduct 11i (Table 2, entry 9). Following general procedure: azanorbornadiene **8a** (70.0 mg, 0.284 mmol), alkyne **9c** (35.0 mg, 0.227 mmol), THF (0.5mL), and $\text{Cp}^*\text{Ru}(\text{COD})\text{Cl}$ (4 mg, 0.011 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 1:9) to give a separable mixture of dihydrobenz[g]indole **10i** (28.4 mg, 0.073 mmol, 32%) and cyclobutene cycloadduct **11i** (55.9 mg, 0.141 mmol, 62%) as brown oils.

10i: R_f 0.62 (EtOAc:hexanes = 3:7); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2959 (m), 1720 (s), 1693 (s), 1614 (m), 1366 (m), 1249 (s), 1161 (s), 1092 (m), 778 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.33 (m, 1H), 7.18 (m, 2H), 6.98 (m, 1H), 6.35 (d, 1H, J = 9.8 Hz), 6.11 (dd, 1H, J = 9.7, 5.7 Hz), 5.57 (d, 1H, J = 9.7 Hz), 4.15 (m, 2H), 3.93 (m, 1H), 3.16 (m, 1H), 2.96 (m, 1H), 1.56 (s, 9H), 1.38 (m, 2H), 1.28 (t, 3H, J = 7.1

Hz), 1.19 (m, 2H), 0.80 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 165.6, 156.9, 152.9, 152.6, 132.4, 132.3, 127.8, 127.6, 127.3, 126.3, 126.2, 124.9, 113.3, 82.0, 60.9, 59.7, 40.3, 30.1, 28.3, 28.1, 26.7, 22.2, 14.3, 13.8. HRMS (CI) calcd. for $\text{C}_{24}\text{H}_{31}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 398.2331; found: 398.2325

11i: (NOTE: signals split into a 3:1 ratio due to the rotational isomers of the BOC group on the nitrogen). R_f 0.55 (EtOAc:hexanes = 3:7); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2959 (m), 1713 (s), 1391 (s), 1367 (m), 1245 (m), 1172 (m), 1092 (m), 745 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.27 (m, 2H), 7.15 (m, 2H), 5.12 (s, 0.33H), 5.04 (s, 0.66H), 5.01 (s, 0.66H), 4.89 (s, 0.33H), 4.23 (m, 2H), 2.71 (m, 2H), 2.56 (d, 0.66H, $J = 2.7$ Hz), 2.52 (br s, 0.33H), 2.39 (m, 1H), 1.56 (m, 2H), 1.40 (s, 3H), 1.37 (s, 6H), 1.37 (m, 5H), 0.93 (m, 3H); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 165.0, 162.6, 154.1, 144.1, 143.8, 143.1, 131.2, 126.5, 126.4, 120.0 (2), 79.5, 60.2, 59.9, 58.2, 46.7, 45.3, 29.1, 28.7, 28.1, 22.6, 14.3, 13.8; visible minor isomer peaks: δ 128.7, 125.8, 120.6, 119.6, 59.4, 58.6, 29.0, 28.2.

Dihydrobenz[g]indole 10i (Table 2, entry 11). Following general procedure: azanorbornadiene **8a** (70.0 mg, 0.284 mmol), alkyne **9c** (35.0 mg, 0.227 mmol), THF (0.5 mL), and $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (6 mg, 0.013 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 1:9) to give an inseparable mixture of dihydrobenz[g]indole **10i** and **10i'** (72.7mg, 0.183 mmol, 81%) as a pale brown oil. R_f 0.62 (EtOAc:hexanes = 3:7); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2959 (m), 1720 (s), 1693 (s), 1614 (m), 1366 (m), 1249 (s), 1161 (s), 1092 (m), 778 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.57 (m, 0.10H), 7.34 (m, 0.9H), 7.18 (m, 2H), 6.97 (m, 1H), 6.46 (d, 0.1H, $J = 9.7$ Hz), 6.35 (d, 0.9H, $J = 9.8$ Hz), 6.11 (dd, 0.9H, $J = 9.8, 5.7$ Hz), 5.85 (dd, 0.1H, $J = 9.8, 6.0$ Hz), 5.66 (d, 0.1H, $J = 9.9$ Hz), 5.57 (d, 0.9H, $J = 9.7$ Hz), 4.17 (m, 2H), 3.93 (m, 1H), 3.16 (m, 2H), 2.96 (m, 1H), 1.56 (s, 8.1H), 1.43 (m, 2H), 1.38 (s, 0.9H), 1.27 (t, 3H, $J = 7.1$ Hz), 1.21 (m, 2H), 0.8 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 165.6, 156.9, 152.6, 132.4, 132.3, 127.8, 127.6, 127.3, 126.3, 126.2, 124.9, 133.3, 82.0, 60.9, 59.7, 40.3, 30.1, 28.3, 26.7, 22.2, 14.3, 13.8; visible minor isomer peaks: 14.1. HRMS (CI) calcd. for $\text{C}_{24}\text{H}_{31}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 398.2331; found: 398.2325

Dihydrobenz[g]indole 10j (Table 2, entry 13). Following general procedure: azanorbornadiene **8a** (210 mg, 0.750 mmol), alkyne **9d** (150 mg, 0.600 mmol), THF (1.1 mL), and $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (15 mg, 0.033 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0.5:9.5) to give and a separable mixture of regioisomers dihydrobenz[g]indole **10j** (79.6 mg, 0.162 mmol, 27%) and **10j'** (24.3 mg, 0.048 mmol, 8%) as pale yellow oils.

10j: R_f 0.40 (EtOAc:hexanes = 1:9); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2956 (m), 2856 (m), 1694 (s), 1619 (m), 1472 (w), 1364 (m), 1251 (s), 1161 (m), 1046 (m), 838 (m), 778 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.55 (m, 1H), 7.24 (m, 2H), 7.04 (m, 1H), 6.44 (d, 1H, $J = 9.8$ Hz), 6.15 (dd, 1H, $J = 9.7, 5.6$ Hz), 5.64 (d, 1H, $J = 9.8$ Hz), 5.33 (d, 1H, $J = 13.0$ Hz), 4.87 (dd, 1H, $J = 13.0, 2.3$ Hz), 4.26 (dq, 2H, $J = 7.1, 2.1$ Hz), 4.02 (m, 1H), 1.62 (s, 9H), 1.36 (t, 3H, $J = 7.1$ Hz), 0.88 (s, 9H), 0.00 (s, 3H), -0.21 (s, 3H); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 165.0, 153.7, 152.7, 132.12, 132.09, 128.6, 127.83, 127.78, 126.7, 126.1, 124.1, 113.7, 81.8, 61.0, 60.0, 56.2, 40.8, 28.1, 25.8, 18.1, 14.3, -5.5, -5.7.

10j': (Note: spectra as a 5:1 ratio of **10j':10j**). R_f 0.39 (EtOAc:hexanes = 1:9); IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2955 (m), 2857 (w), 1706 (m), 1367 (m), 1254 (m), 1161 (m), 1061 (m), 838 (m), 777 (m); ^1H NMR (CDCl_3 , 300MHz): δ 7.57 (d, 1H, $J = 7.3$ Hz), 7.22 (m, 2H), 6.97 (d, 1H, $J = 6.9$ Hz), 6.44 (d, 1H, $J = 9.8$ Hz), 6.01 (dd, 1H, $J = 9.7, 5.8$ Hz), 5.67 (d, 1H, $J = 10.0$ Hz), 4.66 (d, 1H, $J = 12.4$ Hz), 4.17 (m, 4H), 1.51 (s, 9H), 1.31 (t, 3H, $J = 7.1$ Hz), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 161.9, 154.2, 135.2, 132.8, 131.6, 128.9, 128.6, 128.4, 128.0, 127.8 (2), 126.3, 122.3, 81.4, 60.8, 60.7, 56.6, 42.9, 28.2, 25.9, 18.2, 14.1, -5.3, -5.4.

Dihydrobenz[g]indole 10k and [2+2] cycloadduct 11k (Table 2, entry 14). Following general procedure: azanorbornadiene **8a** (70.0 mg, 0.250 mmol), alkyne **9e** (50.0 mg, 0.201 mmol), THF (0.5 mL), and $\text{Cp}^*\text{Ru}(\text{COD})\text{Cl}$ (4 mg, 0.010 mmol). The crude product was purified by column

chromatography (EtOAc:hexanes = 0.5:9.5) to give a separable mixture of dihydroindole **10k** (15.3 mg, 0.030 mmol, 15%) as a colourless oil and cycloadduct **11k** (24.7 mg, 0.050 mmol, 25%) as a pale yellow oil.

10k: R_f 0.40 (EtOAc:hexanes = 1:9); IR (CH₂Cl₂) $\nu_{\max}$ (cm⁻¹) 2956 (m), 2856 (m), 1721(s), 1695(s), 1617 (m), 1363 (m), 1247 (s), 1161 (s), 1096 (m), 836 (m), 777 (m); ¹H NMR (CDCl₃, 300MHz): δ 7.34 (m, 1H), 7.18 (m, 2H), 6.98 (m, 1H), 6.36 (d, 1H, J = 9.8 Hz), 6.10 (dd, 1H, J = 9.8, 5.5 Hz), 5.56 (d, 1H, J = 9.8 Hz), 4.20 (m, 2H), 3.93 (m, 1H), 3.65 (m, 2H), 3.35 (m, 2H), 1.55 (s, 9H), 1.28 (t, 3H, J = 7.1 Hz), 0.81 (s, 9H), -0.02 (s, 3H), -0.03 (s, 3H); ¹³C NMR (APT, CDCl₃, 75MHz): δ 165.3, 152.9, 152.7, 132.4, 132.1, 127.9, 127.6(2), 126.3, 126.2, 124.8, 114.6, 82.2, 61.4, 60.8, 59.8, 40.4, 30.8, 28.3, 25.8, 18.2, 14.3, -5.4(2).

11k: (NOTE: Spectral signals split into a 2.5:1 ratio of rotational isomers) R_f 0.29 (EtOAc:hexanes = 1:9); IR (CH₂Cl₂) $\nu_{\max}$ (cm⁻¹) 2958 (m), 2856 (m), 1695 (s), 1645 (m), 1458 (m), 1389 (s), 1245 (m), 1172 (m), 1095 (s), 833 (m), 780 (m), 747 (m); ¹H NMR (CDCl₃, 300MHz): δ 7.29 (m, 1H), 7.24 (m, 1H), 7.15 (m, 2H), 5.12 (s, 0.3H), 5.06 (s, 0.7H), 5.04 (s, 0.7H), 4.94 (s, 0.3H), 4.24 (m, 2H), 3.93 (m, 1H), 3.79 (m, 1H), 3.01 (m, 0.3H), 2.86 (m, 0.7H), 2.79 (s, 0.3H), 2.73 (s, 0.7H), 2.67 (m, 0.7H), 2.62 (m, 1.3H), 1.41 (s, 3H), 1.36 (s, 6H), 1.34 (t, 3H, J = 7.3 Hz), 0.90 (br s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ¹³C NMR (APT, CDCl₃, 75MHz): δ 162.8, 162.5, 154.2, 144.1, 143.2, 132.2, 126.4(2), 120.1(2), 79.5, 60.4, 60.2, 60.0, 58.5, 48.0, 45.7, 32.5, 28.1, 25.9, 18.2, 14.3, -5.3; visible minor isomeric peaks: 59.5, 58.7, 28.3.

Dihydrobenz[g]indole 10k (Table 2, entry 15). Following general procedure: azanorbornadiene **8a** (210 mg, 0.750 mmol), alkyne **9e** (150 mg, 0.600 mmol), THF (1.1 mL), and [Cp*Ru(CH₃CN)₃]PF₆ (15 mg, 0.033 mmol). The crude product was purified by column chromatography (EtOAc:hexanes = 0.5:9.5) to give an inseparable mixture of dihydrobenz[g]indole **10k** and **10k'** (122.5 mg, 0.240 mmol, 40%) as colourless oils. R_f 0.40 (EtOAc:hexanes = 1:9); IR (CH₂Cl₂) $\nu_{\max}$ (cm⁻¹) 2956 (m), 2856 (m), 1721(s), 1695(s), 1617 (m), 1363 (m), 1247 (s), 1161 (s), 1096 (m), 836 (m), 777 (m); ¹H NMR (CDCl₃, 300MHz): δ 7.34 (m, 1H), 7.18 (m, 2H), 6.98 (m, 1H), 6.36 (d, 1H, J = 9.8 Hz), 6.10 (dd, 1H, J = 9.8, 5.5 Hz), 5.56 (d, 1H, J = 9.8 Hz), 4.20 (m, 2H), 3.93 (m, 1H), 3.65 (m, 2H), 3.35 (m, 2H), 1.55

(s, 9H), 1.28 (t, 3H, $J = 7.1$ Hz), 0.81 (s, 9H), -0.02 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 165.3, 152.9, 152.7, 132.4, 132.1, 127.9, 127.6(2), 126.3, 126.2, 124.8, 114.6, 82.2, 61.4, 60.8, 59.8, 40.4, 30.8, 28.3, 25.8, 18.2, 14.3, -5.4(2).

Dihydrobenz[g]indole 10f (Table 2, entry 16). Following the above general procedure, with azanorbornadiene **8a** (140.0 mg, 0.568 mmol), alkyne **9f** (70.0 mg, 0.485 mmol), THF (1.0 mL), and $\text{Cp}^*\text{RuCl}(\text{COD})$ (10 mg, 0.025 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=2:8 to 3:7) to provide the dihydrobenz[g]indole **10f** (40.9 mg, 0.107 mmol, 22%) as a pale brown oil and cyclobutene **11f** (135.5 mg, 75%) as a pale brown oil.

10f: R_f 0.21 (EtOAc:hexanes = 3:7). IR (CH_2Cl_2) ν_{max} (cm^{-1}) 3473 (w), 2978 (m), 1687 (s), 1618 (m), 1364 (s), 1250 (s), 1156 (s), 1046 (m), 776 (w); ^1H NMR (CDCl_3 , 400MHz): δ 7.34 (m, 1H), 7.21 (m, 2H), 6.99 (m, 1H), 6.38 (d, 1H, $J = 9.8$ Hz), 6.08 (dd, 1H, $J = 9.8, 5.6$ Hz), 5.55 (d, 1H, $J = 9.7$ Hz), 4.20 (m, 2H), 3.97 (m, 1H), 3.80 (m, 2H), 3.37 (t, 2H, $J = 5.9$ Hz), 2.66 (br.s, 1H), 1.54 (s, 9H), 1.29 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 165.8, 154.3, 152.9, 132.5, 131.6, 128.2, 127.7, 127.3, 126.5, 126.3, 124.6, 114.5, 82.7, 61.5, 61.2, 60.1, 40.3, 30.3, 28.2, 14.3.

11f: R_f 0.12 (EtOAc: hexanes = 3: 7). IR (CH_2Cl_2) ν_{max} (cm^{-1}) 3420 (m), 2978 (m), 1712 (s), 1389 (s), 1295 (m), 1242 (s), 1168 (s), 1091 (m), 1062 (m), 894 (w), 739 (m); ^1H NMR (CDCl_3 , 300MHz): 7.28 (m, 2H), 7.17 (m, 2H), 5.15 (s, 1H), 5.09 (s, 1H), 4.25 (q, 2H, $J = 7.1$ Hz), 3.86 (m, 2H), 2.90 (m, 1H), 2.74 (br.s, 1H), 2.60 (m, 2H), 1.40 (s, 9H), 1.35 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 162.8, 162.5, 154.6, 143.2, 143.0, 133.2, 126.6, 120.0, 80.3, 60.2, 59.8, 59.6, 58.5, 48.0, 45.4, 34.3, 28.1, 14.2.

Dihydrobenz[g]indole lactone 10f' (Table 2, entry 17). Following the above general procedure, with azanorbornadiene **8a** (140.0 mg, 0.568 mmol), alkyne **9f** (70.0 mg, 0.485 mmol), THF (1.0 mL), and $\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_2\text{PF}_6$ (12 mg, 0.025 mmol). The crude product was purified by column chromatography (EtOAc:hexanes=2:8 to 3:7) to provide an unseparable mixture of dihydrobenz[g]indole lactone **10f'** and regioisomeric dihydroindole **10f''** (59.2 mg, 0.175 mmol, 36%) as a pale brown oil and cyclobutene **11f** (54.1 mg, 0.141 mmol, 29%) as a pale brown oil.

10f' and **10f''**: R_f 0.21 (EtOAc:hexanes = 3:7). (NOTE: a 5:1 ratio of lactone **10f'** and regioisomeric dihydroindole **10f''** was isolated as an inseparable mixture). IR (CH_2Cl_2) ν_{max} (cm^{-1}) 2978 (w), 1699 (s), 1630 (m), 1413 (m), 1373 (m), 1283 (m), 1246 (m), 1160 (m), 1140 (m), 1046 (w), 735 (w); ^1H NMR (CDCl_3 , 300MHz): δ 7.53 (d, 1H, J = 6.8 Hz), 7.34 (m, 0.2H), 7.23 (m, 2H), 7.03 (m, 1H), 6.38 (d, 1H, J = 9.8 Hz), 6.21 (dd, 1H, J = 9.7, 5.2 Hz), 6.07 (dd, 0.2H, J = 9.7, 5.5 Hz), 5.75 (d, 1H, J = 10.5 Hz), 5.55 (d, 0.2H, J = 9.7 Hz), 4.38 (m, 1H), 4.20 (m, 1.4H), 4.16 (m, 1H), 3.96 (m, 0.2H), 3.80 (m, 0.4H), 3.37 (t, 0.4H, J = 6.0 Hz), 3.07 (m, 1H), 2.79 (m, 1H), 2.60 (br.s, 0.2H), 1.57 (s, 9H), 1.54 (s, 1.8H), 1.29 (t, 0.6H, J = 7.1 Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 155.9, 152.2, 132.2, 131.1, 128.4 (2), 127.8, 126.9, 126.0, 123.6, 111.2, 83.3, 65.4, 60.8, 39.4, 28.2, 25.9. Visible minor peaks: δ 164.0, 128.1, 127.6, 127.3, 126.5, 126.3, 124.6, 61.5, 61.2, 60.1, 40.3, 30.4.

11f: R_f 0.12 (EtOAc: hexanes = 3: 7). IR (CH_2Cl_2) ν_{max} (cm^{-1}) 3420 (m), 2978 (m), 1712 (s), 1389 (s), 1295 (m), 1242 (s), 1168 (s), 1091 (m), 1062 (m), 894 (w), 739 (m); ^1H NMR (CDCl_3 , 300MHz): 7.28 (m, 2H), 7.17 (m, 2H), 5.15 (s, 1H), 5.09 (s, 1H), 4.25 (q, 2H, J = 7.1 Hz), 3.86 (m, 2H), 2.90 (m, 1H), 2.74 (br.s, 1H), 2.60 (m, 2H), 1.40 (s, 9H), 1.35 (t, 3H, J = 7.1 Hz); ^{13}C NMR (APT, CDCl_3 , 75MHz): δ 162.8, 162.5, 154.6, 143.2, 143.0, 133.2, 126.6, 120.0, 80.3, 60.2, 59.8, 59.6, 58.5, 48.0, 45.4, 34.3, 28.1, 14.2.

(300 MHz ^1H NMR spectrum)

(75 MHz ^{13}C -APT NMR spectrum)

(300 MHz ^1H NMR spectrum)

(75 MHz ^{13}C -APT NMR spectrum)

(400 MHz ^1H NMR spectrum)

(75 MHz ^{13}C -APT NMR spectrum)

(300 MHz ¹H NMR spectrum)

(75 MHz ¹³C-APT NMR spectrum)

(300 MHz ^1H NMR spectrum)

(75 MHz ^{13}C -APT NMR spectrum)

(300 MHz ^1H NMR spectrum)

(75 MHz ^{13}C -APT NMR spectrum)

(300 MHz ^1H NMR spectrum)

(75 MHz ^{13}C -APT NMR spectrum)

(400 MHz ¹H NMR spectrum)

(100 MHz ¹³C-APT NMR spectrum)

(300 MHz ¹H NMR spectrum)

(75 MHz ¹³C-APT NMR spectrum)

(300 MHz ¹H NMR spectrum)

(75 MHz ¹³C-APT NMR spectrum)

(as a 5:1 mixture of **10j'** : **10j**)

(300 MHz ¹H NMR spectrum)

(75 MHz ¹³C-APT NMR spectrum)

(400 MHz ^1H NMR spectrum)

(100 MHz ^{13}C -APT NMR spectrum)

(300 MHz ^1H NMR spectrum)

(75 MHz ^{13}C -APT NMR spectrum)

(note: signals split into a 2:1 ratio due to the rotational isomers of the BOC group on the nitrogen)

(note: signals split into a 3:1 ratio due to the rotational isomers of the BOC group on the nitrogen)

(300 MHz ^1H NMR spectrum)

(75 MHz ^{13}C -APT NMR spectrum)

(note: signals split into a 2.5:1 ratio due to the rotational isomers of the BOC group on the nitrogen)

(300 MHz ¹H NMR spectrum)

(75 MHz ¹³C-APT NMR spectrum)