SUPPORTING INFORMATION

Ruthenium-Catalyzed [3+2] Intramolecular Cycloaddition of Alk-5-ynylidenecyclopropanes Promoted by the First-Generation Grubbs Carbene Complex

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General. All dry solvents were freshly distilled under argon from an appropriate drying agent before use. THF was distilled from sodium/benzophenone, CH_2Cl_2 and Et_3N were distilled from CaH_2 and toluene was distilled from sodium. Pd_2dba_3 was prepared according to known literature methods.¹ Grubbs catalyst, $\text{Cl}_2(\text{Cy}_3\text{P})_2\text{Ru}=\text{CHPh}$, was purchased from Strem and used without further purification. Its purity was proved by NMR to be higher than 98%. All reactions were conducted in dry solvents under argon atmosphere unless otherwise stated. External bath temperatures were used to record all reaction temperatures. Thin-layer chromatography (TLC) was performed on silica gel plates and components were visualised by observation under UV light, or by treating the plates with either *p*-anisaldehyde or cerium nitrate reagents followed by heating. Flash chromatography was carried out in silica gel unless otherwise stated. Drying was performed with anhydrous MgSO_4 . Concentrations were carried out in a rotary evaporator. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 , at 250 MHz and 62.9 MHz, respectively, and in some cases at 300 or 500 MHz (75.461 or 125.7 for ^{13}C). Carbon types were determined from DEPT- NMR experiments. ^{31}P NMR spectra were recorded in a Varian spectrometer at 121.47 MHz. The following abbreviations are used to indicate signal multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra were acquired using a Chemical Ionization technique. GC-MS was carried out using the Agilent Technologies 6896N, Network GC System, equipped with the HP 190915-433 column and the Agilent 5976 Network Mass Selective Detector switched to the Chemical Ionization Mode.

Preparation of precursors 2a-g.² (Exemplified for 2b).

A solution of compound **11b**³ (1.25 g, 6.3 mmol) in THF (3 mL) was added to an ice-cooled suspension of NaH (250 mg, 6.25 mmol) in THF (3 mL). After stirring at rt for 20 min the solution was transferred via cannula over a

¹ Ishii, Y.; Hasegawa, S.; Kimura, S.; Itoh, K. *J. Organomet. Chem.* **1974**, 73 (3), 411.

² (a) Stolle, A.; Becker, H.; Salaün, J.; de Meijere, A. *Tetrahedron Lett.* **1994**, 35, 3517. (b) Stolle, A.; Ollivier J.; Piras, P.; Salaün, J.; de Meijere, A. *J. Am. Chem. Soc.* **1992**, 114, 4051.

³ Malonate precursors **11**, were prepared according to known procedures: (a) Lawrence W. L.; Woo, H.; Smith, J.; Barrell, K. J.; Nicholls, P. J. *J. Chem. Soc. Perkin Trans I*, **1993**, 3492. (b) Brumond H. M.; Chen H.; Fisher K. D.; Kerekes A. D.; Richards B.; Still P. C.; Geib S. J. *Org. Lett.* **2002**, 4, 1931.

mixture of tosylate **12**⁴ (570 mg, 2.3 mmol), Pd₂dba₃ (24 mg, 2 mol %) and 1,2-bis(diphenylphosphino)ethane (dppe, 2 mol%) in THF (5 mL), previously stirred for 15 min at room temperature. The reaction mixture was allowed to stir for 10 min at rt, poured into water and extracted with ether. The combined organic layers were dried, filtered and concentrated and the crude product was purified by flash chromatography (1 to 5 % Et₂O / hexanes) to give **2b** [542 mg, 86%, colorless oil].

Diethyl 2-(2-cyclopropylideneethyl)-2-(prop-2-ynyl)malonate (2b)⁵ (colorless oil, 86% yield) ¹H-NMR δ (ppm): 5.59-5.52 (1H, m), 4.22-4.13 (4H, q, *J* = 7.01 Hz), 2.92 (2H, d, *J* = 7.2 Hz), 2.77-2.75 (2H, m), 1.98 (1H, t, *J* = 2.3 Hz), 1.26-1.19 (6H, t, *J* = 7.22 Hz), 1.03 (4H, br s). **MS**: 265 (*M* + 1, 39%); 191 (*M* - CO₂Et, 85%), 117 (100%).

Diethyl 2-(2-cyclopropylideneethyl)-2-(but-2-ynyl)malonate (2a)⁵ (colorless oil, 81% yield). ¹H-NMR δ (ppm): 5.50-5.43 (1H, m), 4.12-4.01 (4H, m), 2.80 (2H, d, *J* = 8.5 Hz), 2.63-2.58 (2H, m), 1.65-1.61 (3H, t, *J* = 2.5 Hz), 1.11 (6H, t, *J* = 7.2 Hz), 0.91 (4H, br s). **MS**: 263 (*M* - 15, 36%), 191 (94%), 73 (100%).

Diethyl 2-(2-cyclopropylideneethyl)-2-(pent-2-ynyl)malonate (2c) (colorless oil, 89% yield), ¹H-NMR δ (ppm): 5.52 (1H, m), 4.12 (4H, m), 2.85 (2H, d, *J* = 7.3 Hz), 2.65 (2H, m), 2.06 (2H, q, *J* = 7.5 Hz), 1.17 (6H, t, *J* = 7.2 Hz), 0.972 (7H, m). ¹³C-NMR δ (ppm): 170.1 (CO), 126.6 (C), 111.5 (CH), 84.4 (C), 73.8 (C), 61.1 (CH₂), 57.1 (C), 34.3 (CH₂), 22.7 (CH₂), 14.0 (CH₃), 13.9 (CH₃), 12.2 (CH₂), 2.73 (CH₂), 1.70 (CH₂). **MS**: 293 (*M* + 1, 59%), 219 (*M* - CO₂Et, 85%). **HRMS**: calculated for C₁₇H₂₄O₄ 292.1675, found 292.1681.

Diethyl 2-(2-cyclopropylideneethyl)-2-(oct-2-ynyl)malonate (2d) (colorless oil, 67% yield), ¹H-NMR δ (ppm): 5.58 (1H, m), 4.16 (4H, m), 2.89 (2H, d, *J* = 7.4 Hz), 2.71 (2H, s), 2.08 (2H, t, *J* = 6.7 Hz), 1.41 (2H, m), 1.29 (4H, m), 1.21 (6H, t, *J* = 7.1 Hz), 1.01 (4H, m), 0.86 (3H, t, *J* = 6.9 Hz). ¹³C-NMR δ (ppm): 170.2 (C), 126.7 (C), 111.6 (CH), 83.2 (C), 74.5 (C), 61.3 (CH₂), 57.3 (C), 34.4 (CH₂), 30.9 (CH₂), 28.5 (CH₂), 22.8 (CH₂), 22.1 (CH₂), 18.5 (CH₂), 14.0 (CH₃), 13.9 (CH₃), 2.85 (CH₂), 1.82 (CH₂). **MS**: 335 (*M* + 1, 29%), 262 (*M* - CO₂Et, 75%); **HRMS**: calculated for C₂₀H₃₀O₄ 334.2144, found 334.2141.

⁴ (a) Racauchot, S.; Silvestre, I.; Olliver, J.; Kozyrkov, Y.; Pukin, A.; Kulinkovich, O.; Salaün, J. *Eur. J. Org. Chem.* **2002**, 2160. (b) Silvestre, I.; Olliver, J.; Salaün, J. *Tetrahedron. Lett.*, **2001**, 42, 4991.

⁵ Delgado, A.; Rodríguez, J. R.; Castedo, L.; Mascareñas, J. L. *J. Am. Chem. Soc.* **2003**, 125, 9282.

Diethyl 2-(2-cyclopropylideneethyl)-2-(4-tertbutyldimethylsilyloxybut-2-ynyl) malonate (2e)⁵ (colorless oil, 76% yield), ¹H-NMR δ (ppm): 5.60-5.52 (1H, m), 4.24 (2H, t, J = 2.2 Hz), 4.16 (4H, q, J = 6.9 Hz), 2.89 (2H, d, J = 7.2 Hz), 2.79 (2H, t, J = 2.2 Hz), 1.22 (6H, t, J = 7.1 Hz), 1.05-0.98 (4H, bs), 0.87 (9H, s), 0.07 (6H, s). **MS**: 409 (M + 1, 9%); 351 (M - C₄H₉, 34%), 277 (M - OTBS, 100%).

Diethyl 2-(2-cyclopropylideneethyl)-2-(4-hydroxybut-2-ynyl)malonate (2f)⁶ (colorless oil), ¹H-NMR δ (ppm): 5.59-5.52 (1H, m), 4.21-4.12 (6H, m), 2.89 (2H, d, J = 7.2 Hz), 2.78 (2H, s), 1.22 (6H, t, J = 7.1 Hz), 1.02 (br s). **MS**: 295 (M+1, 19%); 277 (M + -H₂O, 100%).

Diethyl 2-(2-cyclopropylideneethyl)-2-(3-trimethylsilyl-prop-2-ynyl)malonate (2g)⁵ (colorless oil, 86% yield), ¹H-NMR δ (ppm): 5.60-5.45 (1H, m), 4.30-4.00 (4H, m), 2.93 (2H, d, J = 8.8 Hz), 2.79 (s, 2H), 1.23 (6H, t, J = 7.06 Hz), 1.05 (4H, br s), 0.12 (9H, s).

Compounds **2a**, **2b**, **2e**, **2f** and **2g** have been previously described.

General procedure for the ruthenium catalyzed cycloaddition of 2 (exemplified for **2a**).

Compound **2a** (60 mg, 0.210 mmol) and ruthenium carbene **4** (18 mg, 0.021 mmol) were dissolved in toluene (2.0 mL) and heated under reflux during 45 min. The solvent was concentrated and the crude residue was chromatographed (0-2% Et₂O/hexanes) to afford 47 mg of bicycle **3a** as a colorless oil.

a, R = CH₃ **d**, R = (CH₂)₄CH₃
b, R = H **e**, R = CH₂OTBS
c, R = CH₂CH₃ **f**, R = CH₂OH

Diethyl-6-(methyl)-4-methylene-1,2,3,3a,4,5-hexahydro-2,2-pentalenedicarboxylate (3a), ¹H-NMR δ (ppm): 4.87 (1H, bs), 4.82 (1H, bs), 4.24-4.12 (4H, m), 3.59-3.34 (2H, m), 2.97- 2.83 (2H, m), 2.75-2.67 (1H, m), 2.60 (1H, dd, J = 7.85 and 4.7 Hz), 1.76 (1H, dd, J = 10.8 and 1.9 Hz), 1.63 (3H, s), 1.27 (6H, q, J = 6.6 Hz). ¹³C-NMR δ (ppm): 172.4 (CO), 171.8 (CO), 152.7 (C), 140.1 (C), 127.8 (C), 106.2 (CH₂), 63.1 (C), 61.5 (CH₂), 61.4 (CH₂), 53.9 (CH), 48.0 (CH₂), 37.9 (CH₂), 31.7 (CH₂), 14.2 (CH₃), 14.1 (CH₃), 14.0 (CH₃). **MS**: 279 (M + 1, 58%), 205 (M - CO₂Et, 100%) **HRMS**: calculated for C₁₆H₂₃O₄ 279.1596, found 279.1602.

⁶ Obtained in 97% yield by treatment of a solution of **2e** in THF at rt with tetrabutyl ammonium fluoride (1.0 M in THF, 1.10 equiv) followed by conventional work up and silica gel chromatography (20% Et₂O/hexanes).

Diethyl 4-methylene-1,2,3,3a,4,5-hexahydro-2,2-pentalenedicarboxylate (3b), $^1\text{H-NMR}$ δ . (ppm): 5.37 (1H, br s), 4.89 (1H, bs), 4.83 (1H, bs), 4.24-4.13 (4H, m), 3.61-3.51 (1H, m), 3.43-3.31 (1H, m), 3.18-3.04 (1H, m), 2.99-2.78 (2H, m), 2.62 (1H, dd, $J = 8.1$ Hz, $J = 4.6$ Hz), 1.79 (1H, dd, $J = 10.9$ Hz, $J = 1.8$ Hz), 1.28-1.20 (6H, m). $^{13}\text{C-NMR}$ δ . (ppm): 172.3 (CO), 171.7 (CO), 152.9 (C), 148.3 (C), 118.7 (CH), 106.7 (CH₂), 63.0 (C), 61.5 (CH₂), 61.4 (CH₂), 53.5 (CH), 43.6 (CH₂), 37.6 (CH₂), 32.3 (CH₂), 14.0 (CH₃). **MS**: 265 (M + 1, 18%). **HRMS**: calculated for C₁₅H₂₁O₄ 265.1440, found 265.1437.

Diethyl-6-(ethyl)-4-methylene-1,2,3,3a,4,5-hexahydro-2,2-pentalenedicarboxylate (3c), $^1\text{H-NMR}$ δ . (ppm): 4.85 (1H, s), 4.81 (1H, s), 4.18 (4H, m), 3.57 (1H, t, $J = 8.5$ Hz), 3.42 (1H, d, $J = 19.1$ Hz), 2.95 (2H, m), 2.73 (1H, d, $J = 16.7$ Hz), 2.60 (1H, dd, $J = 12.4$ and 7.7 Hz), 2.07 (2H, m), 1.79 (1H, dd, $J = 12.5$ and 10.4 Hz), 1.27 (6H, m), 1.01 (3H, t, $J = 6.8$ Hz). $^{13}\text{C-NMR}$ δ . (ppm): 172.3 (CO), 171.8 (CO), 152.6 (C), 139.0 (C), 133.3 (C), 106.1 (CH₂), 63.0 (C), 61.5 (CH₂), 61.4 (CH₂), 54.0 (CH), 45.4 (CH₂), 37.6 (CH₂), 31.8 (CH₂), 22.3 (CH₂), 14.0 (CH₃), 12.5 (CH₃). **MS**: 293 (M + 1, 7%). **HRMS**: calculated for C₁₇H₂₄O₄ 292.1675, found 292.1671.

Diethyl-6-(pentyl)-4-methylene-1,2,3,3a,4,5-hexahydro-2,2-pentalenedicarboxylate (3d), $^1\text{H-NMR}$ δ . (ppm): 4.84 (1H, s), 4.80 (1H, s), 4.19 (4H, m), 3.56 (1H, m), 3.38 (1H, d, $J = 19.1$ Hz), 2.93 (2H, m), 2.73 (1H, d, $J = 16.5$ Hz), 2.59 (1H, m), 2.04 (2H, m), 1.78 (1H, m), 1.44-1.21 (12H, m), 0.89 (3H, m). $^{13}\text{C-NMR}$ δ (ppm): 172.4 (C), 171.8 (C), 152.7 (C), 139.8 (C), 132.1 (C), 106.1 (CH₂), 63.0 (C), 61.5 (CH₂), 61.4 (CH₂), 53.9 (CH), 45.8 (CH₂), 37.7 (CH₂), 31.9 (CH₂), 31.6 (CH₂), 29.1 (CH₂), 27.4 (CH₂), 22.4 (CH₂), 14.0 (CH₃). **MS**: 335 (M + 1, 19%). **HRMS**: calculated for C₂₀H₃₀O₄ 334.2144, found 334.2154.

Diethyl-6-(tertbutylsilyloxymethyl)-4-methylene-1,2,3,3a,4,5-hexahydro-2,2-pentalene dicarboxylate (3e), $^1\text{H-NMR}$ δ . (ppm): 4.89 (1H, bs), 4.82 (1H, bs), 4.23-4.0 (6H, m), 3.6-3.3 (2H, m), 3.05 (2H, m), 2.87-2.75 (1H, m), 2.61-2.53 (1H, dd, $J = 7.5$ and 5.0 Hz), 1.82-1.71 (1H, m), 1.24 (6H, q, $J = 6.6$ Hz), 0.88 (9H, s), 0.04 (6H, s). $^{13}\text{C-NMR}$ δ (ppm): 172.3 (CO), 171.6 (CO), 151.8 (C), 141.5 (C), 130.6 (C), 106.6 (CH₂), 63.1 (C), 61.5 (CH₂), 61.4 (C), 60.7 (CH₂), 54.4 (CH), 44.0 (CH₂), 37.3 (CH₂), 32.0 (CH₂), 25.9 (CH₂), 18.3 (C), 14.0 (CH₃), -5.3 (CH₃), -5.4 (CH₃). **MS**: 409 (M + 1, 1%), 282 (16%), 115 (65%), 75 (100%). **HRMS**: calculated for C₂₂H₃₇O₅Si 409.2410, found 409.2418.

Diethyl-6-(hydroxymethyl)-4-methylene-1,2,3,3a,4,5-hexahydro-2,2-pentalenedicarboxylate (3f), $^1\text{H-NMR}$ δ . (ppm): 4.88 (1H, bs), 4.81 (1H, bs), 4.2-4.0 (6H, m), 3.7-3.4 (2H, m), 3.17-2.97 (2H, m), 2.74 (1H, bs), 2.64 (1H, dd, $J = 8.0$ and 4.7

Hz), 1.75 (1H, dd, $J = 10.8$ and 1.9 Hz), 1.21 (6H, q, $J = 6.91$ Hz). $^{13}\text{C-NMR}$ δ . (ppm): 172.0 (CO), 171.8 (CO), 151.7 (C), 143.1 (C), 130.9 (C), 106.9 (CH₂), 62.7 (C), 61.6 (C), 61.5 (C), 59.8 (CH), 53.9 (CH), 43.7 (CH₂), 37.2 (CH₂), 32.0 (CH₂), 14.0 (CH₃). **MS**: 295 ($M + 1$, 26%), 279 ($M - \text{OH}$, 42%), 235 (50%), 61 (100%). **HRMS**: calculated for C₁₆H₂₃O₅ 295.1545, found 295.1540.

Reaction of ruthenium carbene **4** and malonate **8**

Malonate **8**^{2b} (30 mg, 0.133 mmol) was added over a solution of **4** (100 mg, 0.121 mmol) in CH₂Cl₂ (2 mL) in a schelink tube. After being stirred at rt for 4 h the solvent was removed under vacuum and the crude residue was washed with pentane (2 x 1.25 mL) to afford **9** as a brown solid.⁷ $^1\text{H-NMR}$ δ . (ppm): 2.56 (6H, bs), 2.11–1.02 (60H, m), 0.55 (4H, s). $^{13}\text{C-NMR}$ δ . (ppm): 303.0 (C, t, $J = 10.8$ Hz), 33.3 (CH, t, $J = 9.0$ Hz), 30.1 (CH₂, s), 28.3 (CH₂, t, $J = 5.0$ Hz), 27.0 (CH₂, s), 25.6 (CH₂, s). $^{31}\text{P-NMR}$ δ . (ppm): 31.82 (s).

⁷ All attempts to crystallize this ruthenium complex failed. For the synthesis of related cyclopropylalkylidene ruthenium complexes see: (a) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **1995**, *34*, 2039. (b) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503. (c) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

^{31}P -NMR evolution of **2a** and **9** in (D_8)-toluene from 25 °C to 110 °C