Metal-Catalyzed Cotrimerization of Arynes and AlkenesIago Quintana, Arnold J. Boersma,[†] Diego Peña,* Dolores Pérez,* and Enrique Guitián*Departamento de Química Orgánica, Universidad de Santiago de Compostela,**15782 Santiago de Compostela, Spain**godpena@usc.es, qodolopm@usc.es**Org. Lett.***SUPPORTING INFORMATION****CONTENTS**

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Experimental details

All reactions were performed under argon atmosphere using oven-dried glassware and standard Schlenk techniques. Solvents were dried by distillation from a drying agent before use: MeCN from CaH₂ and toluene from Na.

TLC was performed on Merck silica gel 60 F₂₅₄; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ¹H and ¹³C NMR spectra were recorded at 250.13 and 62.83 MHz (Bruker DPX-250 instrument), 300 and 75 MHz (Varian Mercury-300 instrument) or 400 and 100 MHz (Varian Mercury-400 instrument), respectively. Low-resolution electron impact mass spectra (EI-LRMS) were determined at 70 eV on a HP-5988A instrument. High-resolution mass spectra (HRMS) were obtained on a Micromass Autospec spectrometer. Melting points were measured on a Gallenkamp instrument. IR spectra were recorded on a Mattson Cygnus 100 spectrophotometer. GC/MS analyses were performed on a Agilent 6890N/5973inert instrument with a HP-5MS capillary column.

Triflates **1**,¹ **5a**,² **5b**,³ **13a**^{1b} and **13b**,⁴ Pd(PPh₃)₄⁵ and deuterium-labeled methyl acrylate (β,β -d₂-**2a**)⁶ were prepared following published procedures. Commercial reagents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification.

Figure S1

General procedure for the metal-catalyzed cotrimerization of arynes and alkenes

The aryne precursor (**1**, **5a,b** or **13a,b**, 0.5 mmol approx.) was added to a suspension of finely powdered anhydrous CsF (2 equiv), the corresponding alkene (**2a-f**, 3 equiv) and the metal catalyst (0.1 equiv) in 1:1 MeCN/toluene (5 mL). The mixture was stirred under argon at 60 °C for 16 h. The solvent was evaporated and the residue was purified by column chromatography to isolate dihydrophenanthrenes (**3a-f** or **6a,b**) and *o*-olefinated biaryls (**4a-f** or **7a,b**).

In all the experiments dihydrophenanthrenes and *o*-olefinated biaryls were first isolated as a mixture, in order to determine the combined yield and the mole ratio (¹H NMR). Further careful separation of these products by column chromatography led to pure samples for spectroscopic characterization.

Figure S2

The solvent mixture (1:1 MeCN/toluene) had a crucial influence in the ratio of products (**3**:**4**). For instance, the higher was the proportion of MeCN, the higher was the selectivity in favour of **3**. However, the use of a more polar solvent mixture increases the rate of benzyne generation, so its cyclotrimerization product (triphenylene) was isolated in undesirable notable amounts.

¹ (a) Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211. (b) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Synthesis* **2002**, 1454.

² Yoshida, H.; Ikadai, J.; Shudo, M.; Ohshita, J.; Kunai, A. *J. Am. Chem. Soc.* **2003**, 125, 6638.

³ Sato, Y.; Tamura, T.; Mori, M. *Angew. Chem. Int. Ed.* **2004**, 43, 2436.

⁴ Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, 121, 5827.

⁵ Hegedus, L. S. *Palladium in Organic Synthesis*. In *Organometallics in Synthesis: A Manual*; Schlosser, M., Ed.; John Wiley & Sons: New York, 1994.

⁶ Meltzer, A. D.; Tirrell, D. A.; Jones, A. A.; Inglefield, P. T. *Macromolecules* **1992**, 25, 4549.

The cotrimerization of benzyne and acrylonitrile (**2b**) was particularly interesting. Using an excess of alkene (6 equiv) in MeCN, **3b** evolved *in situ* in a tandem α C-H activation–Michael addition to acrylonitrile (Scheme S1). Consequently, compound **17** was isolated by a cascade sequence, resulting from the overall reaction of two benzynes and two alkenes, in a one pot process with the formation of four C-C bonds. Apparently, the α C-H activation of **3b** is promoted by CsF, since in the absence of palladium catalyst **3b** also evolved to afford compound **17**.

Scheme S1

Spectroscopic data

Methyl 9,10-dihydro-9-phenanthrenecarboxylate (**3a**)⁷

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded **3a** as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.78 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.43-7.24 (m, 6H), 3.89 (t, *J* = 5.8 Hz, 1H), 3.68 (s, 3H), 3.32 (dd, *J* = 15.3, 5.9 Hz, 1H), 3.12 (dd, *J* = 15.3, 5.8 Hz, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 173.5 (C), 134.5 (C), 134.1 (C), 133.8 (C), 133.6 (C), 128.6 (CH), 128.4 (CH), 128.1 (CH), 127.8 (CH), 127.6 (CH), 127.3 (CH), 124.0 (CH), 123.7 (CH), 52.1 (CH₃), 44.6 (CH), 31.7 (CH₂) ppm; MS (EI), *m/z* (%): 238 (14), 179 (100); HRMS (EI) for C₁₆H₁₄O₂, calcd: 238.0994, found: 238.0995; IR (CsI): 1735 cm⁻¹.

Methyl (*E*)-3-(1,1'-biphenyl-2-yl)-2-propenoate [(*E*)-**4a**]

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded (*E*)-**4a** as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.80-7.65 (m, 2H), 7.49-7.23 (m, 8H), 6.40 (d, *J* = 15.9 Hz, 1H), 3.74 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 167.3 (C), 143.9 (CH), 142.9 (C), 139.8 (C), 132.5 (C), 130.5 (CH), 129.85 (CH), 129.75 (2CH), 128.3 (2CH), 127.6 (CH), 127.5 (CH), 126.8 (CH), 118.7 (CH), 51.6 (CH₃) ppm; MS (EI), *m/z* (%): 238 (16), 179 (100); HRMS (EI) for C₁₆H₁₄O₂, calcd: 238.0994, found: 238.0989.

Methyl (*Z*)-3-(1,1'-biphenyl-2-yl)-2-propenoate [(*Z*)-**4a**]

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded (*Z*)-**4a** as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.59-7.51 (m, 2H), 7.45-7.31 (m, 7H), 6.85 (d, *J* = 12.2 Hz, 1H), 5.93 (d, *J* = 12.2 Hz, 1H), 3.69 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 166.8 (C), 144.3 (CH), 141.3 (C), 140.5 (C), 133.6 (C), 129.9 (CH), 129.8 (2CH), 129.4 (CH), 128.9 (CH), 128.1 (2CH), 127.4 (CH), 126.7 (CH), 119.8 (CH), 51.3 (CH₃) ppm; MS (EI), *m/z* (%): 238 (15), 179 (100); HRMS (EI) for C₁₆H₁₄O₂, calcd: 238.0994, found: 238.0984.

9,10-Dihydro-9-phenanthrenecarbonitrile (**3b**)^{7,8}

Column chromatography (SiO₂; 1:50 AcOEt/hexane) yielded **3b** as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.82-7.27 (m, 8H), 4.08 (t, *J* = 7.8 Hz, 1H), 3.21 (d, *J* = 7.9 Hz, 2H) ppm; MS (EI), *m/z* (%): 205 (100), 190 (22).

(*E*)-3-(1,1'-Biphenyl-2-yl)-2-propenenitrile [(*E*)-**4b**]

Column chromatography (SiO₂; 1:50 AcOEt/hexane) yielded (*E*)-**4b** as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.62 (d, *J* = 7.8 Hz, 1H), 7.53-7.25 (m, 9H), 5.85 (d, *J* = 16.6 Hz, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 149.7 (CH), 142.7 (C), 139.2 (C), 131.6 (C), 130.8 (CH), 130.7 (CH), 129.6 (2CH), 128.5 (2CH), 127.9 (CH), 127.8 (CH), 125.8 (CH), 118.2 (C), 96.8 (CH) ppm; MS (EI), *m/z* (%): 205 (100), 190 (35); HRMS (EI) for C₁₅H₁₁N, calcd: 205.0891, found: 205.0884.

(*Z*)-3-(1,1'-Biphenyl-2-yl)-2-propenenitrile [(*Z*)-**4b**]

Column chromatography (SiO₂; 1:50 AcOEt/hexane) yielded (*Z*)-**4b** as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ = 8.15 (m, 1H), 7.61-7.19 (m, 8H), 7.11 (d, *J* = 12.1 Hz, 1H), 5.42 (d, *J* = 12.0 Hz, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 148.7 (CH), 142.6 (C), 139.6 (C), 131.6 (C), 130.5 (CH), 130.2 (CH), 129.8 (2CH), 128.3 (2CH), 128.0 (CH), 127.7 (2CH), 117.3 (C), 96.1 (CH); MS (EI), *m/z* (%): 205 (100), 190 (41); HRMS (EI) for C₁₅H₁₁N, calcd: 205.0891, found: 205.0896.

9-Acetyl-9,10-dihydrophenanthrene (**3c**)⁷

Column chromatography (SiO₂; 1:40 AcOEt/hexane) yielded **3c** as a light brown oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.79 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.42-7.21 (m, 6H), 3.73 (dd, *J* = 6.1, 3.6 Hz, 1H), 3.32 (dd, *J* = 15.4, 3.6 Hz, 1H), 3.13 (dd, *J* = 15.4, 6.1 Hz, 1H), 1.96 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 208.6 (C), 134.7 (C), 134.4 (C), 134.3 (C), 133.4 (C), 129.2 (CH), 128.6 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 124.3 (CH), 123.6 (CH), 52.6 (CH), 31.2 (CH₂), 28.6 (CH₃) ppm; MS (EI), *m/z* (%): 222 (11), 179 (100); HRMS (ESI) for C₁₆H₁₄ONa (M⁺ + Na), calcd: 245.0943, found: 245.0940; IR (CsI): 1710 cm⁻¹.

(*E*)-4-(1,1'-Biphenyl-2-yl)-3-buten-2-one [(*E*)-**4c**]

Column chromatography (SiO₂; 1:40 AcOEt/hexane) yielded (*E*)-**4c** as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.75-7.22 (m, 10H), 6.65 (d, *J* = 16.3 Hz, 1H), 2.23 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃)

⁷ Harvey, R. G.; Fu, P. P.; Rabideau, P. W. *J. Org. Chem.* **1976**, *41*, 3722.

⁸ Lewis, F. D.; Zebrowski, B. E.; Correa, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 187.

δ = 198.6 (C), 142.9 (CH), 139.8 (C), 132.5 (C), 130.4 (CH), 130.0 (CH), 129.8 (2CH), 128.9 (C), 128.4 (CH), 128.2 (2CH), 127.7 (CH), 127.6 (CH), 126.7 (CH), 26.9 (CH₃) ppm; MS (EI), m/z (%): 222 (2), 179 (100); HRMS (EI) for C₁₆H₁₄O, calcd: 222.1045, found: 222.1045.

(Z)-4-(1,1'-Biphenyl-2-yl)-3-buten-2-one [(Z)-4c]

Column chromatography (SiO₂; 1:40 AcOEt/hexane) yielded (Z)-4c as a yellow oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.71-7.20 (m, 9H), 6.86 (d, J = 12.3 Hz, 1H), 6.12 (d, J = 12.3 Hz, 1H), 2.14 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 201.1 (C), 141.1 (CH), 140.3 (C), 134.0 (C), 130.2 (CH), 129.8 (CH), 129.75 (CH), 129.6 (2CH), 129.1 (CH), 128.8 (C), 128.1 (2CH), 127.4 (CH), 127.1 (CH), 30.5 (CH₃) ppm; MS (EI), m/z (%): 222(3), 179 (100); HRMS (EI) for C₁₆H₁₄O, calcd: 222.1045, found: 222.1041.

9-(Methylsulfonyl)-9,10-dihydrophenanthrene (3d)

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded 3d as a dark yellow oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.87 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 8.3 Hz, 1H), 7.43-7.22 (m, 4H), 4.25 (d, J = 6.9 Hz, 1H), 3.72 (dd, J = 17.0, 1.4 Hz, 1H), 3.50 (dd, J = 17.0, 7.0 Hz, 1H), 2.06 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 134.3 (C), 132.9 (C), 131.9 (CH), 131.5 (C), 130.2 (CH), 129.0 (CH), 128.8 (CH), 128.3 (CH), 128.2 (CH), 127.7 (C), 124.1 (CH), 123.8 (CH), 64.6 (CH), 37.7 (CH₃), 29.4 (CH₂) ppm; MS (EI), m/z (%): 178 (M⁺ - HSO₂Me, 100); HRMS (EI) for C₁₄H₁₀ (M⁺ - HSO₂Me), calcd: 178.0782, found: 178.0779; IR (CsI): 1302, 1118 cm⁻¹.

2-[(E)-2-(Methylsulfonyl)-1-ethenyl]-1,1'-biphenyl [(E)-4d]

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded (E)-4d as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.72-7.61 (m, 2H), 7.55-7.37 (m, 6H), 7.33-7.24 (m, 2H), 6.81 (d, J = 15.5 Hz, 1H), 2.96 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 143.5 (C), 143.1 (CH), 139.2 (C), 130.9 (CH), 130.8 (CH), 130.1 (C), 129.6 (2CH), 128.5 (2CH), 127.9 (CH), 127.8 (CH), 127.3 (CH), 127.2 (CH), 43.1 (CH₃) ppm; MS (EI), m/z (%): 178 (M⁺ - HSO₂Me, 100); HRMS (EI) for C₁₄H₁₀ (M⁺ - HSO₂Me), calcd: 178.0782, found: 178.0781.

2-[(Z)-2-(Methylsulfonyl)-1-ethenyl]-1,1'-biphenyl [(Z)-4d]

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded (Z)-4d as a colourless oil. ¹H NMR (250 MHz, CDCl₃) δ = 7.63-7.28 (m, 9H), 7.03 (d, J = 12.0 Hz, 1H), 6.42 (d, J = 12.0 Hz, 1H), 2.91 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 141.9 (CH), 141.7 (C), 139.8 (C), 130.9 (CH), 130.8 (C), 130.3 (CH), 130.1 (CH), 129.7 (CH), 129.5 (2CH), 128.3 (2CH), 127.8 (CH), 127.2 (CH), 42.7 (CH₃) ppm; MS (EI), m/z (%): 178 (M⁺ - HSO₂Me, 100); HRMS (EI) for C₁₄H₁₀ (M⁺ - HSO₂Me), calcd: 178.0782, found: 178.0781.

trans-9,10-Dihydrophenanthrene-9,10-dicarboxylic acid dimethyl ester (trans-3e)⁹

Column chromatography (SiO₂; 1:10 AcOEt/hexane) yielded trans-3e as a white solid. M.p. 119°C; ¹H NMR (250 MHz, CDCl₃) δ = 7.75 (d, J = 7.7 Hz, 2H), 7.44-7.22 (m, 6H), 4.41 (s, 2H), 3.56 (s, 6H) ppm; ¹³C NMR (62.8 MHz, CDCl₃) δ = 171.9 (C), 133.1 (C), 131.4 (C), 129.9 (CH), 128.4 (CH), 127.9 (CH), 123.9 (CH), 52.4 (CH₃), 46.9 (CH) ppm; MS (EI), m/z (%): 296 (4), 236 (42), 178 (100); HRMS (EI) for C₁₈H₁₆O₄, calcd: 296.1048, found: 296.1042.

Methyl trans-9,10-dihydro-10-methyl-9-phenanthrenecarboxylate (trans-3f)¹⁰

Column chromatography (SiO₂; 1:50 AcOEt/hexane) yielded trans-3f as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.88-7.65 (m, 2H), 7.39-7.23 (m, 6H), 3.67 (d, J = 2.8 Hz, 1H), 3.52 (s, 3H), 3.50 (m, 1H), 1.15 (d, J = 7.2 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 173.2 (C), 139.6 (C), 133.5 (C), 132.2 (C), 131.7 (C), 130.4 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 127.2 (CH), 123.81 (CH), 123.79 (CH), 52.0 (CH₃), 51.4 (CH), 36.3 (CH), 20.7 (CH₃) ppm; MS (EI), m/z (%): 252 (14), 193 (100); HRMS (EI) for C₁₇H₁₆O₂, calcd: 252.1150, found: 252.1150.

Methyl (E)-3-(1,1'-biphenyl-2-yl)-2-butenate [(E)-4f]

Column chromatography (SiO₂; 1:50 AcOEt/hexane) yielded (E)-4f as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.47-7.14 (m, 9H), 5.96 (q, J = 1.3 Hz, 1H), 3.70 (s, 3H), 2.03 (d, J = 1.3 Hz, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 166.8 (C), 159.6 (C), 142.8 (C), 141.1 (C), 139.6 (C), 130.4 (CH), 128.8 (2CH), 128.5 (CH), 128.3 (3CH), 127.2 (CH), 127.2 (CH), 119.8 (CH), 51.0 (CH₃), 20.6 (CH₃) ppm; MS (EI), m/z (%): 252 (8), 193 (100); HRMS (EI) for C₁₇H₁₆O₂, calcd: 252.1150, found: 252.1150.

⁹ Gawroński, J.; Grycz P.; Kwit, M.; Rychlewska, U. *Chem. Eur. J.* **2002**, *8*, 4210.

¹⁰ Lewis, F. D.; DeVoe, R. J. *J. Org. Chem.* **1982**, *47*, 888.

The conformation of the product (*E*) was determined by NOE experiments. Irradiation of the signal at 2.03 ppm (Me *trans* to the olefinic H) showed NOE with aromatic hydrogens but not with the signal at 5.96 ppm (olefinic H).

Methyl 1,2,3,5,6,8,9,10-octahydrodicyclopenta[*b,h*]phenanthrene-5-carboxylate (6a)

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded **6a** as a colourless oil. ¹H NMR (250 MHz, CDCl₃) δ = 7.64 (s, 1H), 7.60 (s, 1H), 7.10 (s, 2H), 3.82 (t, *J* = 5.8 Hz, 1H), 3.64 (s, 3H), 3.25 (dd, *J* = 15.1, 6.0 Hz, 1H), 3.12-2.85 (m, 9H), 2.19-2.01 (m, 4H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 174.3 (C), 144.4 (C), 143.7 (C), 143.5 (C), 143.4 (C), 133.1 (C), 132.6 (C), 132.5 (C), 131.9 (C), 124.5 (CH), 124.4 (CH), 120.1 (CH), 119.7 (CH), 52.2 (CH₃), 45.3 (CH), 33.0 (2CH₂), 32.9 (CH₂), 32.5 (CH₂), 25.6 (CH₂) ppm; MS (EI), *m/z* (%): 318 (52), 259 (100); HRMS (EI) for C₂₂H₂₂O₂, calcd: 318.1620, found: 318.1617; IR (CsI): 1737 cm⁻¹.

Methyl (*E*)-3-[6-(2,3-dihydro-1*H*-5-indenyl)-2,3-dihydro-1*H*-5-indenyl]-2-propenoate [(*E*)-7a]

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded (*E*)-**7a** as a colourless oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.76 (d, *J* = 15.9 Hz, 1H), 7.57 (s, 1H), 7.30-7.20 (m, 2H), 7.16 (s, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 3.74 (s, 3H), 2.99-2.92 (m, 8H), 2.19-2.07 (m, 4H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 167.6 (C), 146.8 (C), 144.8 (CH), 144.2 (C), 143.5 (C), 143.3 (C), 142.0 (C), 138.2 (C), 130.6 (C), 128.0 (CH), 126.4 (CH), 125.7 (CH), 123.9 (CH), 122.2 (CH), 116.9 (CH), 51.5 (CH₃), 32.9 (CH₂), 32.8 (CH₂), 32.6 (CH₂), 32.5 (CH₂), 25.5 (CH₂), 25.4 (CH₂) ppm; MS (EI), *m/z* (%): 318 (36), 259 (100); HRMS (EI) for C₂₂H₂₂O₂, calcd: 318.1620, found: 318.1625.

Methyl (*Z*)-3-[6-(2,3-dihydro-1*H*-5-indenyl)-2,3-dihydro-1*H*-5-indenyl]-2-propenoate [(*Z*)-7a]

Column chromatography (SiO₂; 1:15 AcOEt/hexane) yielded (*Z*)-**7a** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.49 (s, 1H), 7.25-7.18 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 12.4 Hz, 1H), 5.84 (d, *J* = 12.3 Hz, 1H), 3.71 (s, 3H), 2.16-2.07 (m, 8H), 3.05-2.84 (m, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 167.0 (C), 145.5 (C), 145.2 (CH), 144.0 (C), 143.2 (C), 142.4 (C), 140.4 (C), 138.9 (C), 131.4 (C), 128.0 (CH), 125.8 (CH), 125.6 (CH), 125.4 (CH), 123.7 (CH), 118.1 (CH), 51.2 (CH₃), 32.9 (CH₂), 32.8 (CH₂), 32.6 (CH₂), 32.5 (CH₂), 25.5 (CH₂), 25.4 (CH₂) ppm; MS (EI), *m/z* (%): 318 (29), 259 (100); HRMS (EI) for C₂₂H₂₂O₂, calcd: 318.1620, found: 318.1627.

Methyl 5,6-dihydro[1,3]dioxolo[4',5':6,7]phenanthro[2,3-*d*][1,3]dioxole-5-carboxylate (6b)

Column chromatography (SiO₂; 1:40 AcOEt/hexane) yielded **6b** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.09 (s, 1H), 7.06 (s, 1H), 6.74 (s, 1H), 6.72 (s, 1H), 6.06-5.87 (m, 4H), 3.70 (t, *J* = 5.4 Hz, 1H), 3.61 (s, 3H), 3.18 (dd, *J* = 15.3, 5.0 Hz, 1H), 2.99 (dd, *J* = 15.2, 5.8 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 173.3 (C), 147.7 (C), 147.1 (C), 146.5 (C), 146.4 (C), 128.5 (C), 127.7 (C), 127.6 (C), 126.8 (C), 109.1 (CH), 108.7 (CH), 104.1 (CH), 104.0 (CH), 101.1 (CH₂), 100.9 (CH₂), 52.1 (CH₃), 44.6 (CH), 31.8 (CH₂) ppm; MS (EI), *m/z* (%): 326 (87), 267 (100); HRMS (EI) for C₁₈H₁₄O₆, calcd: 326.0790, found: 326.0791; IR (CsI): 1732 cm⁻¹.

Methyl (*E*)-3-[6-(1,3-benzodioxol-5-yl)-1,3-benzodioxol-5-yl]-2-propenoate [(*E*)-7b]

Column chromatography (SiO₂; 1:40 AcOEt/hexane) yielded (*E*)-**7b** as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.63 (d, *J* = 15.9 Hz, 1H), 7.12 (s, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 6.77 (s, 1H), 6.73 (d, *J* = 1.7 Hz, 1H), 6.68 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.24 (d, *J* = 15.9 Hz, 1H), 6.03 (s, 2H), 6.02 (s, 2H), 3.73 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 167.5 (C), 149.1 (C), 147.5 (C), 147.3 (C), 147.1 (C), 143.5 (CH), 138.3 (C), 133.5 (C), 126.4 (C), 123.5 (CH), 116.4 (CH), 110.3 (CH), 110.2 (CH), 108.1 (CH), 105.6 (CH), 101.6 (CH₂), 101.2 (CH₂), 51.5 (CH₃) ppm; MS (EI), *m/z* (%): 326 (90), 267 (100); HRMS (EI) for C₁₈H₁₄O₆, calcd: 326.0790, found: 326.0783.

Methyl (*Z*)-3-[6-(1,3-benzodioxol-5-yl)-1,3-benzodioxol-5-yl]-2-propenoate [(*Z*)-7b]

Column chromatography (SiO₂; 1:40 AcOEt/hexane) yielded (*E*)-**7b** as a yellowish oil. ¹H NMR (300 MHz, CDCl₃) δ = 7.17 (s, 1H), 6.83-6.68 (m, 5H), 6.01 (s, 2H), 6.00 (s, 2H), 5.82 (d, *J* = 12.3 Hz, 1H), 3.73 (s, 3H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 166.7 (C), 148.2 (C), 147.3 (C), 147.0 (C), 146.2 (C), 144.1 (CH), 136.4 (C), 134.2 (C), 126.9 (C), 123.6 (CH), 118.0 (CH), 110.3 (CH), 110.0 (CH), 109.3 (CH), 107.9 (CH), 101.3 (CH₂), 101.1 (CH₂), 51.3 (CH₃) ppm; MS (EI), *m/z* (%): 326 (92), 267 (100); HRMS (EI) for C₁₈H₁₄O₆, calcd: 326.0790, found: 326.0790.

9-(2-Cyanoethyl)-9,10-dihydro-9-phenanthrenecarbonitrile (17)

Column chromatography (SiO₂, AcOEt:hexanes 1:5) yielded a yellowish oil; ¹H NMR (400 MHz, CDCl₃) δ = 7.85 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.61 (ddd, *J* = 7.6, 1.4, 0.5 Hz, 1H), 7.50 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.44-7.39 (m, 2H), 7.34 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 3.58 (d, *J* = 15.3 Hz, 1H), 3.18 (d, *J* = 15.3 Hz, 1H), 2.56 (ddd, *J* = 16.7, 10.0, 6.7 Hz, 1H), 2.27 (ddd, *J* = 16.6, 9.4, 6.5 Hz, 1H), 2.02 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 132.3 (C), 132.2 (C), 131.6 (C), 130.1 (C), 129.7 (CH), 129.0 (CH), 128.9 (CH), 128.6 (CH), 128.5 (CH), 126.8 (CH), 125.2 (CH), 124.0 (CH), 121.3 (C), 117.9 (C), 41.6 (C), 38.4 (CH₂), 31.9 (CH₂), 13.8 (CH₂) ppm; MS (EI), *m/z* (%): 258 (26), 204 (100).

Figure S5

The analysis by GC/MS additionally confirmed the isolation of deuterated compounds d_2 -**3a** and d_2 -(*E/Z*)-**4a**, showing a deuterium incorporation > 98%.

Experiment using regioisomeric triflates **13a,b**

Figure S6 shows all the possible isomers that would be expected from the cotrimerization of two molecules of 3-methoxybenzyne (**14**) and one molecule of methyl acrylate (**2a**). Similarly to the reaction with unsubstituted benzyne, it would be expected four regioisomeric dihydrophenanthrenes (**15a-d**) and eight *o*-olefinated biaryls [(*E/Z*)-**16a-d**]. Geminally substituted *o*-olefinated biaryls (i.e. **17**) were not isolated from the reaction of benzyne and acrylate. As proposed in this paper, a mechanism via two molecules of benzyne would produce the same isomers from **13a** and **13b**.

Figure S6

On the contrary, an alternative mechanism initiated by oxidative addition of the aryl triflate to Pd(0) would produce different isomers from **13a** and **13b**, as shown in Scheme S3.¹¹

Scheme S3

Analysis by GC/MS of the reactions of acrylate **2a** and triflates **13a** or **13b**, showed identical mixtures of products with FW = 298 (**15** and **16**), with the same isomer ratios for both reactions (Figure S7).

Figure S7

¹¹ This alternative has been proposed for some Pd-catalyzed cyclizations of *o*-(trimethylsilyl)phenyl triflates with alkynes. See: Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280.

(Z)-4d
[93:7 (Z)-4d/3d]

ppm (t1)

ppm (t1)

ppm (t1)

(E)-7a
(96:4 E/Z)

17