Ring Closing Olefin Metathesis of 2,2'-divinylbiphenyls: a Novel and General Approach to Phenanthrenes

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Supporting Information

General

¹H and ¹³C NMR spectra were recorded on a NMR Varian Gemini 200 or on a Varian VXR-300 in CDCl₃ or acetone-d₆, as specified in each case using TMS as internal standard. The following abbreviations were used: s=singlet; d=doublet; dd=doublet doublet; t=triplet; m=multiplet.

TLC analyses were performed on silica gel plates Macherey-Nagel 60 F_{254} . Chromatographic purifications were carried out using silica gel Marcherey-Nagel, 70-230 or 230-400 for flash chromatography. Melting points were taken using a Kofler Reichert-Jung apparatus (heating rate=4°C/min) and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of the University of Pisa.

THF was refluxed over sodium-benzophenone and distilled before use. Acetonitrile, dichloromethane, N,N-dimethylformammide were distilled from CaH₂.

2,2'-diformyl-4,4'-dinitrobiphenyl (2) and 2,2'-diformyl-4,6'-dinitrobiphenyl (3)

Concentrated H_2SO_4 (5,0 ml), concentrated HNO₃ (0.8 ml) 2,2'-diformylbiphenyl (1 g 4.76 mmol) were introduced in a round bottomed flask kept at 0°C. The reaction mixture was stirred at rt. overnight and then quenched with ice. The solid was extracted with AcOEt and the organic layer was washed with 10% NaHCO₃, then water and dried over anhydrous Na₂SO₄. After removing the solvent under reduced pressure, 1.04 g of a mixture of 2,2'-diformyl-4,4'-dinitrobiphenyl and 2,2'-diformyl-4,6'-dinitrobiphenyl was obtained.

2,2'-diformyl-5,5',6,6'-tetramethoxybiphenyl (8)

A solution of 2,2'-dibromo-5,5',6,6'-tetramethoxybiphenyl (1 g, 2.31 mmol) in dry THF (30 ml) was cooled to -78°C and a 1.6 M solution of n-BuLi in hexane (6.88 ml, 11 mmol) was slowly added to it. The reaction mixture was stirred for 5 h at -78°C, then DMF (1.18 ml, 14.78 mmol) was added. After stirring at -50°C for 1h, HCl was added and the mixture was vigorously stirred for 10 minutes at rt., then extracted with CH_2Cl_2 (3 x 50 ml). The collected organic layers were washed with water, then dried (anhydrous Na_2SO_4). After removing the solvent under reduced pressure, chemically pure 2,2'-diformyl-5,5',6,6'-tetramethoxybiphenyl (0.70 g, 2.12 mmol) was obtained in 92% yield. m.p. 120°C

¹H-NMR. (200 MHz, CDCl₃, δ): 3.62 (s, 6H, OMe); 4.00 (s, 6H, OMe); 7.19 (d, 2H, 4 and 4' protons, J=8.4 Hz); 7.81 (d, 2H, 3 and 3' protons, J=8.4 Hz); 9.64 (s, 2H, CHO).

¹³C-NMR (50 MHz, CDCl₃, δ): 56.3, 56.6, 114.5, 123.5, 124.4, 128.9, 147.0, 153.9, 190.0.

Anal. Calcd. for C₁₈H₁₈O₆: C, 65.45; H, 5.49; O, 29.06. Found: C, 65.38; H, 5.50.

Synthesis of the 2,2'-divinylbiphenyls: general procedure

A 1.6M solution of n-BuLi in hexane (7.31 mmol) was added to a suspension of methyltriphenylphosphonium bromide (7.31 mmol) in dry THF (40 ml). The deep orange solution was stirred at rt. for 30 min then a solution of the di-aldehyde (3.33 mmol) in dry THF (15 ml) was added dropwise . The mixture was stirred at rt. for 24 h, then quenched with a saturated solution of NH₄Cl. The aqueous layer was extracted with CHCl₃ and the organic phases were washed with brine, then dried (anhydrous Na₂SO₄). After removing the solvent under vacuum, the crude product was purified by column chromatography.

2,2'-divinylbiphenyl (6)

0.45 g (2.20 mmol, 67%) after column chromatography (SiO₂, light petroleum/CH₂Cl₂ 70/30). m.p. 71°C.

¹H-NMR. (200 MHz, CDCl₃, δ): 5.01 (d, 2H, <u>H</u>CH=, J=11.0 Hz); 5.56 (d, 2H, HC<u>H</u>=, J=18.0 Hz); 6.33 (dd, 2H, -CH=, J₁=18.0 Hz J₂=11.0 Hz); 7.06 (dd, 2H, aromatics, J₁=8.2 Hz, J₂=2.6 Hz); 7.19-7.30 (m, 4H, aromatics); 7.58 (dd, 2H, aromatics, J₁=8.0 Hz, J₂=2.5 Hz). ¹³C-NMR (50 MHz, CDCl₃, δ): 112.3, 126.7, 127.3, 127.5, 128.2, 133.8, 134.3, 135.8 Anal.Calcd. for C₁₆H₁₄: C, 93.16; H, 6.84. Found: C, 93.22; H, 6.82

4,4'-dinitro-2,2'-divinylbiphenyl (4)

0.41 g (1.50 mmol, 45%) from the mixture of aldehydes **2** and **3** after chromatographic purification (SiO₂, AcOEt/hexane 20/80)

m.p.225°C

¹H-NMR (200 MHz, CDCl₃, δ): 5.34 (d, 2H, <u>H</u>CH=, J=10.4 Hz); 5.85 (d, 2H, HC<u>H</u>=, J=17.2 Hz); 6.30 (dd 2H, -CH=, J₁=17.2 Hz J₂=10.4 Hz); 7.31 (d, 2H, 6 and 6' protons, J=8.4 Hz); 8.17 (dd, 2H, 5 and 5' protons, J₁=8.4 Hz, J₂=2.2 Hz); 8.52 (d, 2H 3 and 3' protons, J=2,2 Hz);

¹³C-NMR (50 MHz, CDCl₃, δ): 119.0, 120.4, 122.1, 131.0, 132.4, 137.8, 143.4, 148.3.

Anal. Calcd. for C₁₆H₁₂N₂O₄: C, 64.86; H, 4.08; N, 9.46, O, 21.60. Found: C, 64.83; H, 4.08; N, 9.44.

4,6'-dinitro-2,2'-divinylbiphenyl (5)

0.272g (1 mmol, 30%) from the mixture of aldehydes 2 and 3 after chromatographic purification (SiO₂, AcOEt/hexane 20/80) as a viscous oil.

¹H-NMR (200 MHz, CDCl₃, δ): 5.30 (d, 1H, <u>H</u>CH=, J=10.6 Hz); 5.34 (d, 1H, <u>H</u>CH=, J= 11.2 Hz); 5.75 (d, 1H, HC<u>H</u>=, J=17.0 Hz); 5.85 (d, 1H, HC<u>H</u>=, J=17.4 Hz); 6.20 (dd, 1H, -CH=, J₁=10.6 Hz, J₂=17.0 Hz); 6.30 (dd, 1H, -CH=, J₁=11.2 Hz, J₂= 17.4 Hz); 7.23 (d, 1H, 6 proton, J=8.4 Hz); 7.60 (dd, 1H, 4' proton, J₁=8.1Hz, J₂= 2.6 Hz); 7.85 (d, 1H, 3' proton, J=8.2 Hz); 7.95 (d, 1H, 5' proton, J=8.4 Hz); 8.14 (dd, 1H, 5 proton, J₁= 8.2 Hz, J₂= 2.6 Hz); 8.49 (d, 1H, 3 proton, J=2.1 Hz);

¹³C-NMR (50 MHz, CDCl₃, δ): 119.1, 119.3, 120.6, 122.5, 123.7, 129.6, 130.2, 130.5, 132.5, 132.9, 138.7, 139.3, 140.8, 146.9, 148.5, 149.6.

Anal. Calcd. for C₁₆H₁₂N₂O₄: C, 64.86; H, 4.08; N, 9.46, O, 21.60. Found: C, 64.82; H, 4.09; N, 9.43.

2,2'-divinyl-5,5',6,6'-tetramethoxybiphenyl (9)

1.08 g (3.33 mmol, 100%) after chromatographic purification (SiO₂,CH₂Cl₂/acetone 90/10), as a viscous oil.

¹H-NMR. (200 MHz, CDCl₃, δ): 3.58 (s, 6H, OMe); 3.90 (s, 6H, OMe); 4.95 (d, 2H, <u>H</u>CH=, J= 11.1Hz); 5.48 (d, 2H, HC<u>H</u>=, J= 18.2 Hz); 6.18 (dd, 2H, -CH=, J₁= 11.2 Hz, J₂=18.0); 6.95 (d, 2H, 4 and 4' protons, J=8.2 Hz); 7.41 (d, 2H, 5 and 5' protons, J=8.2 Hz);

¹³C-NMR (50 MHz, CDCl₃, δ): 56.6, 60.6, 112.2, 120.0, 126.2, 128.7, 131.6, 146.8, 147.7, 149.0. Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79; O, 19.61. Found: C, 73.72; H, 6.77.

2-formyl-3'-methoxybiphenyl (10)

Pd(PPh₃)₄ (0.094 mmol) was added to a solution of 2-iodobenzaldehyde (9.40 mmol) in dry THF (85 ml). After stirring the reaction mixture under nitrogen for 20 min, K_2CO_3 (9.40 mmol), 3-methoxyphenylboronic acid (9.40 mmol) and water (24 ml) were added. The mixture was refluxed for 24h, then cooled to rt., extracted with diethylether, and the organic extracts were dried over anhydrous Na₂SO₄. After removing the solvent under reduced pressure, the crude product was purified by flash chromatography (SiO₂, CH₂Cl₂/ light petroleum 80/20) affording 1.50 g (8.46 mmol, 90 %) of 2-formyl-3'-methoxy-biphenyl as viscous liquid.

¹H-NMR (200 MHz, CDCl₃, δ): 3.73 (s, 3H, OMe); 7.10-7.80 (m, 8H, aromatic); 9.72 (s, 1H, CHO);

¹³C-NMR (50 MHz, CDCl₃, δ): 56.0, 114.2, 114.6, 121.1, 127.9, 130.2, 135.2, 130.8, 130.5, 134.8, 162.0, 190.0.

Anal. Calcd. for C₁₄H₁₂O₂: C, 79.22; H, 5.70; O, 15.08. Found: C, 79.30; H, 5.69

2-bromo-2'-formyl-5-methoxybiphenyl (11)

Benzyltrimethylammonium tribromide(BTMA·Br3) (1.50 g, 8.46 mmol) was added to a solution of 2-formyl-3'-methoxybiphenyl (4.13 g, 9.58 mmol) in CH_2Cl_2 (62 ml) and MeOH (40 ml). The mixture was stirred until a colorless solution was obtained. After addition of a saturated solution of Na₂S₂O₃ the mixture was extracted with CH_2Cl_2 and the organic extracts were dried over anhydrous Na₂SO₄. After removing the solvent under reduced pressure, pure 2-bromo-2'-formyl-5-methoxybiphenyl (1.80 g 6.17 mmol) was obtained in 73% yield as a viscous oil.

¹H-NMR. (200 MHz, CDCl₃, δ): 3.82 (s, 3H, OMe), 6.85 (m, 3H, 3, 4 and 6 protons); 7.32 (d, 1H 6' proton); 7.50-7.70 (m, 2H, 4' and 5' protons); 8.00 (dd, 1H, 3' proton, J₁=8.2 Hz J₂=2.4 Hz); 9.80 (s, 1H, CHO)

¹³C-NMR (50 MHz, CDCl₃,): 55.6, 114.2, 115.7, 117.1, 127.2, 128.5, 130.6, 133.3, 133.6. 139.6, 144.5, 158.8, 191.5.

Anal. Calcd. for C₁₄H₁₁BrO₂: C, 57.76; H, 3.81; Br, 27.45; O, 10.99. Found: C, 57.75; H, 3.80; Br, 27.41

2-bromo-2'-vinyl-5-methoxybiphenyl (12)

A 1.6M solution of n-BuLi in hexane (4.24 ml 6.78 mmol) was added to a suspension of methyltriphenylphosphonium bromide (2.42 g, 6.78 mmol) in dry THF (74 ml). The deep orange solution was stirred at rt. for 30 min then a solution of **11** (1.79 g, 6.17 mmol) in anhydrous THF (30 ml) was dropwise added. The mixture was stirred at rt. for 24 h, then quenched with a saturated solution of NH₄Cl. The aqueous layer was extracted with CHCl₃ and the organic phases were washed with brine then dried (anhydrous Na₂SO₄). After removing the solvent under vacuum, the crude product was purified by column chromatography (SiO₂, CH₂Cl₂) giving 2-bromo-2'-vinyl-5-methoxybiphenyl (1.67 g 5.81 mmol) in 94% yield.

¹H-NMR. (200 MHz, CDCl₃, δ): 3.80 (s, 3H, OMe); 5.14 (d, 1H, <u>H</u>CH=, J=10.5 Hz); 5.68 (d, 1H, HC<u>H</u>=, J=17.8 Hz); 6.44 (dd, 1H, -CH=, J₁=10.5 Hz, J₂= 17.8 Hz); 6.77(d, 1H, 6 proton, J=2 Hz); 6.81 (dd, 1H, 4 proton, J₁=8.2 Hz, J₂= 2.2 Hz); 7.15 (dd, 1H, 3' proton, J₁=7.2 Hz, J₂=1.4 Hz); 7.27-7.42 (m, 2H 4' and 5' protons); 7.52 (d, 1H, 3 proton, J= 8.2 Hz); 7.66 (dd, 1H, 6' proton, J₁= 7.6 Hz, J₂= 1.8 Hz).

¹³C-NMR (50 MHz, CDCl₃, δ): 55.5, 114.3, 114.9, 115.1, 116.7, 124.8, 127.3, 128.1, 129.7, 133.1, 134.7, 135.7, 140.0, 142.5, 158.6.

Anal. Calcd. for C₁₅H₁₃BrO: C, 62.30; H, 4.53; Br, 27.63; O, 5.53. Found: C, 62.27; H, 4.54; Br, 27.59

2-formyl-2'-vinyl-5-methoxybiphenyl (13)

A solution of **12** (1.14 g 3.94 mmol) in dry THF (45 ml) was cooled to -78° C and a 1.6M solution of n-BuLi in hexane (5.85 ml 9.36 mmol) was slowly added to it. The reaction mixture was stirred for 5 h at -78° C, then DMF (1.03 ml 13.00 mmol) was added. After stirring at -50° C for 1h, HCl was added and the mixture was vigorously stirred for ten minutes at rt. then extracted with CH₂Cl₂ (3 x 50 ml). The collected organic layers were washed with water then dried (anhydrous Na₂SO₄). After removing the solvent under reduced pressure, chemically pure 2-formyl-2'-vinyl-5-methoxybiphenyl (0.70 g, 2.75 mmol) was obtained in 70% yield.

¹H-NMR. (200 MHz, CDCl₃, δ): 3.87 (s, 3H, OMe); 5.16 (d, 1H, <u>H</u>CH=, J=10.4 Hz); 5.66 (d, 1H, HC<u>H</u>=, J=17.9 Hz); 6.42 (dd, 1H, -CH=, J₁=10.5 Hz, J₂= 17.8 Hz); 6.77 (d, 1H, 6 proton, J= 2.4 Hz); 7.00 (dd, 1H, 4 proton, J₁= 8.8 Hz, J₂=2.6 Hz); 7.21-7.45 (m, 2H, 4' and 5' protons); 7.52 (dd, 1H, 3' proton, J₁= 8.6 Hz, J₂=2.3 Hz); 7.65 (dd, 1H, 6' proton, J₁=7.2 Hz, J₂=1.8 Hz); 8.00 (d, 1H, 3 proton, J=8.4 Hz); 9.54 (d, 1H, CHO, J=0.8 Hz long range coupling with 3 proton).

¹³C-NMR (50 MHz, CDCl₃, δ): 55.5, 114.1, 115.6, 116.0, 125.2, 127.4, 127.9, 128.5, 128.4, 130.4, 134.6, 136.3, 136.7, 146.9, 163.5, 190.6. Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92; O, 13.43. Found: C, 80.73; H, 5.90

2,2'-divinyl-5-methoxybiphenyl (14)

A 1.6M solution of n-BuLi in hexane (1.88 ml, 3.02 mmol) was added to a suspension of methyltriphenylphosphonium bromide (1.08 g, 3.02 mmol) in dry THF (35 ml). The deep orange solution was stirred at rt. for 30 min then a solution of **13** (0.70 g, 2.75 mmol) in dry THF (15 ml) was dropwise added. The mixture was stirred at rt. for 24 h, then quenched with a saturated solution of NH_4Cl . The aqueous layer was extracted with CHCl₃ and the organic phases were washed with brine then dried (anhydrous Na₂SO₄). After removing the solvent under vacuum, the crude product was purified by column chromatography (SiO₂, CH₂Cl₂) giving 2,2'-divinyl-5-methoxybiphenyl (0.53 g 2.24 mmol) in 81% yield.

¹H-NMR. (200 MHz, CDCl₃): 3.81 (s, 3H, OMe); 4.98 (d, 1H, <u>H</u>CH=, J=10.6 Hz); 5.16 (d, 1H, <u>H</u>CH=, J=11.2 Hz); 5.53 (d, 1H, HC<u>H</u>=, J=17.0 Hz); 5.66 (d, 1H, HC<u>H</u>=, J=17.4 Hz); 6.27-6.53 (two superimposed dd, 2H, -CH=); 6.70 (d, 1H, 6 proton, J = 3 Hz); 6.93 (dd, 1H, 4 proton, J₁= 8.8 Hz, J₂= 2.8 Hz,); 7.15-7.42 (m, 2H, 4' and 5' protons); 7.61 (d, 1H, 3 proton, J= 8.8 Hz); 7.68 (dd, 1H, 6' proton, J₁=7.4 Hz, J₂= 1.8 Hz).

¹³C-NMR (50 MHz, CDCl₃,): 55.6, 112.6, 114.2, 114.9, 115.3, 125.0, 126.2, 127.6, 127.9, 130.6, 134.7, 135.3, 136.4, 136.8, 139.8, 141.2, 159.0.

Anal. Calcd. for C₁₇H₁₆O: C, 86.40; H, 6.82; O, 6.77. Found: C, 86.32; H, 6.84

Synthesis of the phenanthrene derivatives: general procedure

Catalyst **15a** or **15b** (60 mg 5% mol) was added to a solution of the 2,2'-divinylbiphenyl derivative (1.47 mmol) in dry solvent (25 ml). The reaction mixture was stirred at rt. or at reflux of the solvent (see table 1) until conversion was complete or did not proceed further. After removing the solvent under reduced pressure, the crude product was purified by column chromatography.

3,4,5,6-tetramethoxyphenanthrene (16b)

Purified by column chromatography (SiO₂, CH₂Cl₂/ aceton 95/5) m.p. 98°C.

¹H-NMR. (200 MHz, CDCl₃, δ): 3.58 (s, 6H, OMe); 4.00 (s, 6H, OMe); 7.29 (d, 2H, 2 and 7 protons, J=8.8 Hz); 7.35 (s, 2H, 9 and 10 protons); 7.47 (d, 2H,1 and 8 protons, J=8.8 Hz). ¹³C-NMR (50 MHz, CDCl₃, δ): 57.2, 60.9, 114.0, 122.5, 125.0, 129.4, 148.3, 151.5 Anal. Calcd. for C₁₈H₁₈O₄: C, 72.47; H, 6.08; O, 21.45. Found: C 72.50; H, 6.06.

2,7-dinitrophenanthrene (16c)

Crystallized from reaction mixture m.p. 230°C

¹H-NMR (200 MHz, CDCl₃, δ):8.03 (s, 2H, 9 and 10 protons); 8.52 (dd, 2H 3 and 6 protons, J₁=9.2 Hz, J₂=2.2 Hz); 8.86 (d, 2H, 4 and 5 protons, J=8.8 Hz,); 8.86 (d, 2H, 1 and 8 protons, J= 2.6 Hz). ¹³C-NMR (50 MHz, CDCl₃-(CD₃)₂SO, δ):119.2,122.8,124.4, 127.6, 131.1, 131.3, 149.9. Anal. Calcd. for C₁₄H₈N₂O₄ : C, 62.69; H, 3.01; N, 10.44; O, 23.86. Found: C 62.73; H, 3.00; N, 10.41

2,5-dinitrophenanthrene (16d)

Purified by column chromatography (SiO₂, CH₂Cl₂/ aceton 99/1) m.p. 210° C

¹H-NMR (200 MHz, CDCl₃, δ): 8.00 (dd, 1H, 7 proton, J₁=8.0 Hz J₂=8.0 Hz); 8.18-8.52 (m, 6H, 3, 4, 6, 8, 9 and 10 protons); 9.13 (d, 1H, 1 proton, J= 2.6 Hz).

¹³C-NMR (50 MHz, CDCl₃, δ): 119.8, 121.6, 124.7, 125.6, 126.8, 129.4, 129.5, 129.8, 130.3, 133.7, 133.9, 135.4, 146.8, 149.3.

Anal. Calcd. for $C_{14}H_8N_2O_4$: C, 62.69; H, 3.01; N, 10.44; O, 23.86. Found: C 62.65; H, 3.02; N, 10.41

3-methoxyphenanthrene (16e)

Purified by column chromatography (SiO₂, CH₂Cl₂/ light petroleum 80/20) m.p. 95° C

¹H-NMR (200 MHz, CDCl₃, δ): 4.02 (s, 3H, OMe); 7.27 (dd, 1H, 2 proton, J₁=8.6 Hz, J₂=2.6 Hz); 7.60-7.73 (m, 4H, 6,7,9 and 10 protons); 7.82 (d, 1H, 1 proton, J=8.8 Hz); 7.89 (dd, 1H, 8 proton, J₁= 6.6 Hz, J₂=2.6 Hz); 8.07 (d, 1H, 4 proton, J=2.4 Hz); 8.63 (dd, 1H, 5 proton, J₁=7.0 Hz, J₂=2.2 Hz).

¹³C-NMR (50 MHz, CDCl₃, δ): 55.7, 122.9, 124.8, 126.4, 127.1, 127.2, 128.9, 130.1, 130.2, 131.9, 132.7, 153.2.

Anal. Calcd. for C₁₅H₁₂O: C, 86.51; H, 5.81; O, 7.68. Found: C 86.25; H, 5.83