Sonogashira Coupling Using Bulky Palladium- Phenanthryl Imidazolium Carbene Catalysis

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Supporting Information

General Procedure for Sonogashira Reaction:

To a flame dried flask under nitrogen containing anhydrous THF (5 mL) were added the aryl halide (0.100 mmol), the terminal alkyne (0.140 mmol), followed by PdCl₂(PPh₃)₂ (2.1 mg, 0.003 mmol, 3 mol %) and dihydroimidazolium hexafluorophosphate salt ligand (0.85 mg, 0.006 mmol, 6 mol %), 18-crown-6 (39.65 mg, 0.150 mmol) and KO-*t*-Bu (16.8 mg, 0.150 mmol). The resulting suspension was stirred at rt (for aryl iodides) or heated at reflux with stirring (for aryl bromides) for the time indicated. The progression of the reaction was followed by TLC. To the reaction mixture was added water (5 mL) and the mixture was extracted with ethyl acetate (3 mL, 2X). The ethyl acetate solution was washed 3 times with aqueous brine and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation and the crude material was purified by silica gel chromatography (EtOAc/hexanes, 0-10 %). The known compounds, with the isolated yields indicated, were adequately characterized by the individual data listed below:

Diphenylacetylene: *R_f*: 0.37 (hexanes); ¹H NMR (CDCl₃, 300 MHz) δ 7.23-7.34 (m, 6H), 7.41-7.56 (m, 4H); MS (EI) *m/z* 178.

4-(Phenylethynyl) toluene: R_f : 0.33 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.21-7.67 (m, 9H), 2.41 (s, 3H); MS (EI) m/z 192.

2-(Phenylethynyl) toluene: R_f : 0.33 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.21-7.69 (m, 9H), 2.14 (s, 3H); MS (EI) m/z 192.

2,6-Dimethylphenyl phenyl acetylene: R_f : 0.25 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.17-7.60(m, 8H), 2.50 (s, 6H); MS (EI) m/z 206.

4-(Phenylethynyl) anisole: R_f : 0.36 (hexanes/EtOAc, 95:5); ^1H NMR (CDCl_3 , 300 MHz) δ 7.25-7.39 (m, 7H), 6.78 (d, 2H, J = 6.2 Hz), 3.78 (s, 3H); MS (EI) m/z 208.

2-(Phenylethynyl) anisole: R_f : 0.36 (hexanes/EtOAc, 95:5); ^1H NMR (CDCl_3 , 300 MHz) δ 6.81-7.39 (m, 9H), 3.78 (s, 3H); MS (EI) m/z 208.

4-(Phenylethynyl) acetophenone: R_f : 0.30 (hexanes/EtOAc, 90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.29-7.87 (m, 9H), 2.71 (s, 3H); MS (EI) m/z 220.

4-(Phenylethynyl) nitrobenzene: R_f : 0.50 (hexanes/EtOAc, 90:10); ^1H NMR (CDCl_3 , 300 MHz) 8.13 (d, 2H, J =6.4 Hz), δ 7.36-7.77 (m, 7H); MS (EI) m/z 223.

2-(Phenylethynyl) thiophene: R_f : 0.60 (hexanes/EtOAc, 95:5); ^1H NMR (CDCl_3 , 300 MHz) δ 6.95-7.37 (m, 8H); MS (EI) m/z 184.

Cyclohex-1-enyl-phenylacetylene: R_f : 0.40 (hexanes/EtOAc, 95:5); ^1H NMR (CDCl_3 , 300 MHz) δ 7.15-7.32(m, 5H), 6.43(s, 1H), 6.21(s, 1H), 2.07-2.37(m, 4H), 1.20-1.67(m, 4H); MS (EI) m/z 182.

1-Phenyl-1-octyne: R_f : 0.37 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.19-7.38 (m, 5H), 2.40-2.47(m, 2H) 1.21-1.73(m, 8H), 0.80 (s, 3H); MS (EI) m/z 186.

1-(4'-Methylphenyl)-1-octyne: R_f : 0.37 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.17-7.33 (m, 4H), 2.34-2.46(m, 5H) 1.21-1.73(m, 8H), 0.80 (s, 3H); MS (EI) m/z 200.

1-(2'-Methylphenyl)-1-octyne: R_f : 0.37 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.18-7.33 (m, 4H), 2.31-2.43(m, 5H) 1.21-1.75(m, 8H), 0.81 (s, 3H); MS (EI) m/z 200.

1-(2', 6'-Dimethylphenyl)-1-octyne: R_f : 0.32 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.15-7.30 (m, 3H), 2.32-2.45(m, 8H) 1.20-1.75(m, 8H), 0.82 (s, 3H); MS (EI) m/z 214.

1-(4'-Methoxyphenyl)-1-octyne: R_f : 0.65 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.12-7.36 (abba, 4H), 3.78 (s, 3H), 2.34-2.41(m, 5H) 1.21-1.72(m, 8H), 0.80 (s, 3H); MS (EI) m/z 216.

1-(2'-Methoxyphenyl)-1-octyne: R_f : 0.65 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.26-7.38 (m, 4H), 3.78 (s, 3H), 2.32-2.40(m, 5H) 1.20-1.72(m, 8H), 0.80 (s, 3H); MS (EI) m/z 216.

1-(4'-Acetylphenyl)-1-octyne: R_f : 0.50 (hexanes/EtOAc, 90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.07-7.33 (abba, 4H), 2.70 (s, 3H), 2.34-2.40(m, 5H) 1.19-1.61(m, 8H), 0.80(s, 3H); MS (EI) m/z 228.

1-(4'-Nitrophenyl)-1-octyne: R_f : 0.60 (hexanes/EtOAc, 90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.17-7.43 (abba, 4H), 2.34-2.40(m, 2H) 1.21-1.68(m, 8H), 0.81(s, 3H); MS (EI) m/z 231.

1-(5'-Nitropyridinyl)-1-octyne: R_f : 0.4.5 (hexanes/EtOAc, 90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.54-7.65 (m, 3H), 2.34-2.40(m, 2H) 1.21-1.68(m, 8H), 0.81(s, 3H); MS (EI) m/z 232.

1-Thiophenyl-1-octyne: R_f : 0.30 (hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 7.29-7.41 (m, 3H), 2.40-2.47(m, 2H) 1.21-1.73(m, 8H), 0.80 (s, 3H); MS (EI) m/z 192.

3-Cyclohexenyl-1-octyne: R_f : 0.40 (hexanes/EtOAc, 95:5); ^1H NMR (CDCl_3 , 300 MHz) δ 6.21(s, 1H), 2.11-2.39(m, 6H), 1.21-1.68(m, 12H), 0.81(s, 3H); MS (EI) m/z 190.

Cyclohex-1-enyl-4'-methylphenylacetylene: R_f : 0.40 (hexanes/EtOAc, 95:5); ^1H NMR (CDCl_3 , 300 MHz) δ 7.15-7.30(abba, 4H), 6.21(s, 1H), 2.41(s, 3H), 2.09-2.35(m, 4H), 1.20-1.67(m, 4H); MS (EI) m/z 196.

Cyclohex-1-enyl-2'-methylphenylacetylene: R_f : 0.40 (hexanes/EtOAc, 95:5); ^1H NMR (CDCl_3 , 300 MHz) δ 7.13-7.27(m, 4H), 6.23(s, 1H), 2.11-2.37(m, 7H), 1.20-1.67(m, 4H); MS (EI) m/z 196.

Cyclohex-1-enyl-2', 6'-dimethylphenylacetylene: R_f : 0.40 (hexanes/EtOAc, 95:5); ^1H NMR (CDCl_3 , 300 MHz) δ 7.09-7.21(m, 3H), 6.22(s, 1H), 2.43(s, 6H), 2.09-2.35(m, 4H), 1.20-1.67(m, 4H); MS (EI) m/z 210.

Cyclohex-1-enyl-4'-methoxyphenylacetylene: R_f : 0.40 (hexanes/EtOAc, 90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.16-7.37(abba, 4H), 6.20(s, 1H), 3.78(s, 3H), 2.09-2.35(m, 4H), 1.20-1.67(m, 4H); MS (EI) m/z 212.

Cyclohex-1-enyl-2'-methoxyphenylacetylene: R_f : 0.40 (hexanes/EtOAc, 90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.05-7.26(m, 4H), 6.20(s, 1H), 3.77(s, 3H), 2.09-2.35(m, 4H), 1.20-1.67(m, 4H); MS (EI) m/z 212.

Cyclohex-1-enyl-4'-acetylphenylacetylene: R_f : 0.40 (hexanes/EtOAc, 90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.17-7.39(abba, 4H), 6.21(s, 1H), 2.46(s, 3H), 2.09-2.35(m, 4H), 1.20-1.67(m, 4H); MS (EI) m/z 224.

Cyclohex-1-enyl-4'-nitrophenylacetylene: R_f : 0.35 (hexanes: EtOAc=90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.16-7.41(abba, 4H), 6.20(s, 1H), 2.12-2.37(m, 4H), 1.23-1.71(m, 4H); MS (EI) m/z 227.

Cyclohex-1-enyl-4'-methoxyphenylacetylene: R_f : 0.40 (hexanes: EtOAc=90:10); ^1H NMR (CDCl_3 , 300 MHz) δ 7.16-7.37(abba, 4H), 6.20(s, 1H), 3.78(s, 3H), 2.09-2.35(m, 4H), 1.20-1.67(m, 4H); MS (EI) m/z 212.

2-Methyl-4-phenyl-3-butyn-2-ol: R_f : 0.30 (hexanes: EtOAc=80:20); ^1H NMR (CDCl_3 , 300 MHz) δ 7.45(m, 2H), 7.37(m, 3H), 2.20(s, 1H), 1.67(s, 6H); MS (EI) m/z 160.

1-(*p*-Tolyl)-3-methyl-1-butyn-3-ol: R_f : 0.25(hexanes: EtOAc=80:20); ^1H NMR (CDCl_3 , 300 MHz) δ 7.11-7.45(m, 4H), 2.41(s, 3H), 2.17(s, 1H), 1.67(s, 6H); MS (EI) m/z 174.

1-(*o*-Tolyl)-3-methyl-1-butyn-3-ol: R_f : 0.25(hexanes: EtOAc=80:20); ^1H NMR (CDCl_3 , 300 MHz) δ 7.10-7.43(m, 4H), 2.17(s, 1H), 2.12(s, 3H), 1.65(s, 6H); MS (EI) m/z 174.

1-(2,6-Dimethylphenyl)-3-methyl-1-butyn-3-ol: R_f : 0.25(hexanes: EtOAc=80:20); ^1H NMR (CDCl_3 , 300 MHz) δ 7.12-7.41(m, 3H), 2.27(s, 6H), 2.17(s, 1H), 1.65(s, 6H); MS (EI) m/z 188.

4-(4'-Methoxyphenyl)-2-methyl-3-butyn-2-ol: R_f : 0.25(hexanes/EtOAc, 80:20); ^1H NMR (CDCl_3 , 300 MHz) δ 7.31(m, 2H), 6.80(m, 2H), 3.80(s, 3H), 2.12(s, 1H), 1.63(s, 6H); MS (EI) m/z 190.

4-(2'-Methoxyphenyl)-2-methyl-3-butyn-2-ol: R_f : 0.25(hexanes/EtOAc, 80:20); ^1H NMR (CDCl_3 , 300 MHz) δ 6.91-7.29(m, 4H), 3.79(s, 3H), 2.11(s, 1H), 1.65s, 6H); MS (EI) m/z 190.

4-(4'-Acetylphenyl)-2-methyl-3-butyn-2-ol: R_f : 0.30(hexanes/EtOAc, 70:30); ^1H NMR (CDCl_3 , 300 MHz) δ 7.49-7.81(m, 4H), 2.66(s, 3H), 2.15(s, 1H), 1.67s, 6H); MS (EI) m/z 216.

4-(4'-Nitrophenyl)-2-methyl-3-butyn-2-ol: R_f : 0.25(hexanes/EtOAc, 70:30); ^1H NMR (CDCl_3 , 300 MHz) δ 7.52-7.87(m, 4H), 2.15(s, 1H), 1.67s, 6H); MS (EI) m/z 205.

2-Methyl-4-Thiophenyl-3-butyn-2-ol: R_f : 0.25 (hexanes/EtOAc, 80:20); ^1H NMR (CDCl_3 , 300 MHz) δ 7.27-7.51(m, 3H), 2.20(s, 1H), 1.67(s, 6H); MS (EI) m/z 166.

4-(4'-Nitroipyridinyl)-2-methyl-3-butyn-2-ol: R_f : 0.25(hexanes/EtOAc, 70:30); ^1H NMR (CDCl_3 , 300 MHz) δ 6.77-7.12(m, 3H), 2.12(s, 1H), 1.65s, 6H); MS (EI) m/z 206.

Procedure for the phenanthryl dihydroimidazolium ligand

9-Bromophenanthrene:¹ To a 500 mL round-bottomed flask was added copper (II) bromide on alumina (71.4 g), phenanthrene (5.34 g, 3 mmol) dissolved in 200 mL chlorobenzene. The mixture vigorously stirred at 80 °C for 2 h. The mixture was allowed to cool, and it was filtered, washed with toluene, and recrystallized with hot toluene (75 mL), to give a brown product as solid needles, 7.48 g (97%): mp 98-99 °C; ^1H NMR (CDCl_3) δ 7.42-8.82 (m, 9H); ^{13}C NMR (CDCl_3) δ 138.6 (s), 134.7 (s), 132.1 (s), 129.4 (s), 128.6 (s), 127.5 (d), 127.1 (s), 126.6 (s), 126.1 (s), 124.7 (d), 122.4 (s), 120.0 (s); MS (EI) m/z 257.1.

9-Bromo-10-nitrophenanthrene:² In a 50 mL round-bottomed flask, nitric acid (2.5 mL, con.) was slowly added dropwise to a hot solution of 9-bromophenanthrene (2.0 g, 7.78 mmol) in acetic acid (2.0 mL) and acetic anhydride (0.8 mL). The mixture was heated on the steam-bath for an additional 15 min. The volatiles were removed by rotary evaporation and the dried mixture was recrystallized from toluene/acetone (50:50, 34 mL). A second batch of crystals was also collected from the resultant mother liqueur to give a combined dark yellow solid product 1.2 g (53%): mp 199-202 °C; ^1H NMR (CDCl_3) δ 7.61-8.93 (m, 8H); ^{13}C NMR (CDCl_3) δ 142.6 (s), 134.5 (s), 133.7 (s), 132.1 (s), 129.4 (d), 128.6 (s), 127.5 (s), 127.1 (s), 126.6 (s), 126.1 (s), 124.7 (s), 123.8 (s), 119.2 (s); MS (EI) m/z 289.1.

2, 9-Dibromo-10-nitrophenanthrene: 9-Bromo-10-nitrophenanthrene (2.0 g, 6.92 mmol) was added to acetone (20 mL) and the solution was cooled to -30 °C. A UV lamp placed in close proximity was illuminated. N-bromosuccinimide (1.44 g, 8 mmol) in THF (15 mL) was slowly added dropwise. After stirred 5 h, the solvents were removed and the dried mixture was recrystallized from acetone/toluene (50:50, 35 mL). A second batch of crystals was also collected from the resultant mother liqueur to give a combined brown solid product. LC-MS showed two products (approx. 1:1) both with MS (EI) m/z 397.1.

There was no starting material showing at this point by GC. HPLC was used to separate a sample of each of these products for analysis: compound one: mp 251-253 °C; ¹H NMR (CDCl₃) δ 7.58-9.12 (m, 7H); ¹³C NMR (CDCl₃) δ 141.2 (s), 135.1 (s), 134.2 (s), 134.1 (d), 130.8 (d), 129.6 (s), 128.2 (s), 124.8 (s), 124.6 (s), 124.1 (s), 123.9 (s), 123.3 (s), 120.5 (s); single crystal X-ray analysis shows that it is the desired 2, 9-Dibromo-10-nitrophenanthrene. Compound two: mp 245-246 °C, ¹H NMR (CDCl₃) δ 7.37-9.09 (m, 7H); ¹³C NMR (CDCl₃) δ 141.2 (s), 134.8 (s), 134.5 (s), 134.1 (d), 130.8 (d), 129.6 (s), 128.2 (s), 124.8 (s), 124.6 (s), 124.1 (s), 123.9 (s), 123.3 (s), 120.5 (s); X-ray analysis shows that it is 1, 9-Dibromo-10-nitrophenanthrene. This solid mixture was used for the next step shown below.

2, 9-Dicyclohexany-10-nitrophenanthrene: To a flame dried flask under nitrogen containing THF (100 mL) was added cyclohexanyl boronic pinacolato ester (4.20 g, 20.0 mmol) and the mixture of 2,9-dibromo-10-nitrophenanthrene and 1,9-dibromo-10-nitrophenanthrene (3.57 g, 9.3 mmol), followed by Pd(OAc)₂ (101mg, 0.45 mmol, 5 mol %), N,N-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazolium chloride (191 mg, 0.45 mmol, 5 mol %) and NaHCO₃ (20 mL, sat.). The resulting suspension was stirred at 50 °C for 3 hr. The reaction mixture was extracted with ethyl acetate (20x2 mL). The ethyl acetate solution was washed 3 times with aqueous brine and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation and the crude material was purified by silica gel chromatography using ethyl acetate/DCM (10-35%) to give 3.75 g of a solid mixture product. The solid was crystallized from *n*-propanol/chlorobenzene/dichloroethane (1:1:1, 15 mL) two times to give the target compound 0.61 g (17%); ¹H NMR (CDCl₃) δ 7.22-8.61 (m, 7H), 2.87 (m, 1H), 2.53 (m, 1H), 1.86-1.31 (m, 20H); ¹³C NMR (CDCl₃) δ 142.2 (s), 137.1 (d), 132.7 (d), 129.1 (s), 125.6(d), 123.6 (d), 123.1 (d), 120.7 (d), 44.3 (s), 42.2 (s), 36.6 (d), 27.4-26.9 (m); MS (EI) *m/z* 403.5. X-ray analysis shows that it as 2,9-Dicyclohexanyl-10-nitrophenanthrene.

Preparation of 2,9-Dicyclohexany-10-aminophenanthrene: To a dried flask under nitrogen containing methanol (50 mL) was added 2,9-dicyclohexyl-10-nitrophenanthrene (3.0 g, 7.4 mmol) followed by Pd/C (15%, 450 mg) and a balloon of hydrogen gas was attached. After 8 hr, the solution was filtered through the celite (2 g) and the solvent was removed by rotary evaporation to obtain product, 2.71 g (98%); ¹H NMR (CDCl₃), δ 7.06-8.28 (m, 7H), 5.23 (broad, 2H), 2.87 (m, 1H), 2.53 (m, 1H), 1.86-1.31 (m, 20H); ¹³C NMR (CDCl₃) δ 140.7 (s), 134.1 (d), 129.7 (d), 128.3 (s), 127.5 (s), 127.0 (s), 126.8(s), 126.3 (s), 125.6 (s), 124.3 (s), 121.1 (s), 43.8 (d), 36.3 (d), 34.7 (d), 32.5 (d), 28.2 (m), 26.4 (d); MS (EI) *m/z* 373.5.

Preparation of bis-(2,9-dicyclohexyl-10-aminophenanthryl)ethane bis-imine: To an *n*-propanol solution (50 mL) were added 2,9-dicyclohexany-10-aminophenanthrene (2.5 g, 6.69 mmol) followed by a 40% aqueous solution of glyoxal (0.5 g, 3.44 mmol of glyoxal). The mixture was stirred for 16 h at rt and then 4 h at 60 °C. Upon addition of water (50 mL), a light yellow solid precipitated which was collected by filtration and dried in vacuum, 3.78 g (75%); mp 259-260 °C; ¹H NMR (CDCl₃) δ 7.01-8.67 (m, 16H), 3.13 (broad, 1H), 2.53 (m, 1H), 2.01-1.28 (m, 20H); ¹³C NMR (CDCl₃) δ 141.2 (d), 137.5 (d), 133.2 (d), 132.8 (d), 130.3 (d), 129.5 (d), 128.2 (d), 127.3 (d), 126.6 (d), 125.0 (d),

123.9 (d), 118.7 (d), 43.5 (d), 36.1 (d), 34.7 (d), 32.1 (d), 28.5 (d), 27.8 (d); MS (EI) m/z 753.1

Preparation of N,N'-bis-(2,9-dicyclohexyl-10-aminophenanthrenyl)ethane

dihydrochloride: To a solution of bis-(2,9-dicyclohexyl-10-aminophenanthryl)ethane bis-imine (3.5 g, 4.65 mmol) in THF (20 mL) at 0 °C was added sodium borohydride (1.0 g, 26.4 mmol) in 0.2 g portions over a period of 60 min. The mixture was allowed to warm to rt, stirred for 16 h, and subsequently refluxed for 3 h. To the reaction mixture was first added ice water (15 mL) over 0.5 h, and then cautiously hydrochloric acid (3M, 20 mL) was added. The off-white solid precipitate was collected by filtration, and dried in vacuum, 3.12 g (81%): ¹H NMR (CDCl₃) δ 8.12-8.47 (m, 4H), 7.11-7.62 (m, 10H), 5.36 (broad, 2H), 3.33 (m, 4H), 2.85 (m, 1H), 2.55 (m, 1H), 1.53-1.97 (m, 20H); ¹³C NMR (CDCl₃) δ 141.2 (s), 135.1 (s), 134.7 (s), 134.1 (d), 130.8 (d), 129.6 (s), 128.2 (s), 124.8 (s), 124.6 (s), 124.1 (s), 123.9 (s), 123.3 (s), 120.5 (s); MS (EI) m/z 757.1

Preparation of N,N'-Bis-(2,9-dicyclohexyl-10-phenanthrenyl)-4,5-

dihydroimidazolium chloride: A mixture of N,N'-bis-(2,9-dicyclohexyl-10-aminophenanthrenyl)ethane dihydrochloride (4.14g, 5.0 mmol), triethyl orthoformate (30 mL), and two drops of formic acid (96%) was refluxed for 60 h. After cooling to rt, an off-white solid precipitated which was collected by filtration and recrystallized from warm toluene/dichloroethane/*n*-propanol (2:1:1, 40 mL), 3.26 g (85 %), mp 300 °C (decomp): ¹H NMR (CDCl₃) δ 9.71 (d, 1H), 6.95-8.21 (m, 14H), 4.69 (d, 4H), 2.85 (m, 1H), 2.51 (m, 1H), 1.29-1.91 (m, 20H); ¹³C NMR (CDCl₃) δ 161.1 (s), 141.2 (s), 134.9 (s), 134.5 (s), 131.2 (d), 130.3 (s), 128.2 (s), 124.8 (s), 124.6 (s), 123.8 (s), 123.1 (s), 120.5 (s), 112.8 (d), 63.5 (s), 45.9 (s), 42.7 (s), 35.6 (d), 34.7 (d), 31.8 (d), 27.3 (d), 26.8 (d); MS (EI) m/z 769.1. The hexafluorophosphate salt was obtained prior to use by treating the title compound with ammonium hexfluorophosphate (5 equiv.) in methanol (2 M), followed by solvent removal and crystallization as above.

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