Supporting Information

Palladium-catalyzed carbopalladation and carbocyclization of arynes with aryl halides: a highly efficient route to functionalized triphenylenes

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Experimental Section

General: All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. Acetonitrile was dried with CaH₂ and distilled prior to use. Benzyne precursors 1a-c were synthesized according to the literature procedures.¹ Pd(dba)₂ was prepared by reported procedure.² Other reagents were commercially available and used as purchased.

General Procedure for the Synthesis of Triphenylenes (3): To a solution of Pd(dba)₂ (0.0150 mmol), CsF (2.40 mmol), Tl(OAc) (0.36 mmol) and aryl iodide (2) (0.30 mmol) under one atmosphere of nitrogen was added benzyne precursor (1) (0.60 mmol) and CH₃CN (3.0 mL) via syringes. The reaction mixture was allowed to stir at 85 °C for 8 h. At the end of the reaction, the reaction mixture was diluted with CH₂Cl₂, filtered through Celite and silica gel. The filtrate was concentrated and the residue was purified through a silica gel column using hexane as eluent to give pure 3.

Compounds 3a-h, were prepared by following this procedure. Spectral data of 3a-h are listed below:

References:


1-(Triphenyl-6-yl)ethanone (3a): white solid, mp 152-153 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 2.70 (s, 3H), 7.59-7.63 (m, 4H), 8.01 (dd, $J = 8.5$, $J = 1.7$, 1H), 8.46-8.58 (m, 5H), 9.07 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 26.7, 123.18, 123.20, 123.3, 123.4; 123.8, 123.9, 126.0, 127.3, 127.4, 127.6, 128.2, 128.7, 129.3, 129.7, 130.5 133.1, 134.9, 197.9; HRMS calcd for C$_{20}$H$_{14}$O$_2$ 270.1045, found 270.1051. Registry Number: [74733-00-9]

Ethyl triphenylene-2-carboxylate (3b): white solid, mp 129-130 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 1.48 (t, $J = 7.2$ Hz, 3H), 4.48 (q, $J = 14.4$ Hz, $J = 7.2$ Hz, 2H), 7.64-7.70 (m, 4H), 8.23 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 1H), 8.60-8.64 (m, 4H), 8.70-8.72 (m, 1H); 9.33 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 14.4, 61.13, 123.2 (2C), 123.3(C2), 123.5, 125.3, 127.2, 127.3, 127.4, 127.6, 128.1, 128.7, 128.9, 129.4, 129.8, 130.6, 133.0, 166.7; HRMS calcd for C$_{21}$H$_{16}$O$_2$ 300.1150, found 300.1146. Registry Number: [34177-32-7]

2-Nitrotriphenylene (3c): yellow solid, mp 162-163 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 7.60 (m, 4H), 8.19 (d, $J = 6.3$ Hz, 1H), 8.39-8.43 (m, 3H), 8.50 (t, $J = 9.6$ Hz, 2H), 9.19 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 118.8, 120.6, 123.2, 123.31, 123.32, 124.0, 124.1, 127.6, 127.7, 127.9, 128.3, 128.4, 129.0, 129.7, 129.9, 130.7, 134.0, 146.1; HRMS calcd for C$_{18}$H$_{11}$NO$_2$ 273.0790, found 273.0792. Registry Number: [81316-79-2]

1-(2,3,6,7-Tetramethyltriphenyl-11-yl)ethanone (3d): white solid, mp 236-237 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 2.76 (s, 3H), 2.50-2.49 (m, 12H), 8.07 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 1H), 8.30-8.31 (m, 3H), 8.58 (d, $J = 4.0$ Hz, 2H), 9.16 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 20.2, 20.26, 20.33, 26.8, 29.7, 123.2, 123.6, 123.7, 123.8, 124.5,
125.5, 126.7, 127.4, 128.9, 129.1, 133.1, 134.7, 135.8, 136.0, 136.6, 137.4, 198.2;

HRMS calcd for C$_{24}$H$_{22}$O 326.1671, found 326.1675.

**10-Fluoro-2,3,6,7-tetramethyltriphenylene (3e):** white solid, mp 202-203 °C; $^1$H NMR (400 MHz, CDCl$_3$): δ 2.26 (s, 6H), 2.47 (s, 6H), 7.29-7.24 (m, 1H), 8.14-8.12 (m, 2H), 8.15 (s, 1H), 8.26 (s, 2H), 8.51-8.47 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 20.2, 108.3 (d), 114.5 (d), 123.6 (2C), 123.9, 125.0, 125.1, 125.9, 126.8, 127.2, 127.3, 128.2, 131.3, 131.4, 135.6, 135.7, 136.6, 162.0 (d); HRMS calcd for C$_{22}$H$_{19}$F 302.1471, found 302.1468.

**2,3,6,7-Tetramethyltriphenylene (3f):** white solid, mp 199-200 °C; $^1$H NMR (600 MHz, CDCl$_3$): δ 2.49-2.50 (m, 12H), 7.57 - 7.59 (m, 2H), 8.34 (d, $J$ = 10.2 Hz, 4H), 8.57 - 8.59 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 20.2, 123.0, 123.6, 123.8, 126.4, 127.6, 127.9, 129.5, 135.5, 136.0; HRMS calcd for C$_{22}$H$_{20}$ 284.1565, found 284.1567.

**1-(1,2,3,10,11,12-Hexahydrodicyclopenta[b,h]triphenyen-6-yl)-1-ethanone (3g):** white solid, mp 281-282 °C; $^1$H NMR (400MHz, CDCl$_3$): δ 2.18-2.22 (m, 4H), 2.76 (s, 3H), 3.10-3.16 (m, 8H), 8.07 (d, $J$ = 8.4Hz, 1H), 8.43 (s, 3H), 8.50 (s, 1H), 8.59 (d, $J$ = 8.8 Hz, 1H), 9.12 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 25.8 (2C), 26.8, 32.9, 33.0 (2C), 33.1, 118.3, 118.4, 118.5, 119.0, 123.4, 123.9, 125.5, 127.3, 127.9, 129.1, 129.5, 130.0, 133.5, 134.5, 143.8, 143.9, 144.7, 145.4, 198.2; HRMS calcd for C$_{26}$H$_{22}$O 350.1671, found 350.1677.

**Ethyl 1,2,3,10,11,12-hexahydrodicyclopenta[b,h]triphenylene-6-carboxylate (3h):** white solid, mp 253-255 °C; $^1$H NMR (400MHz, CDCl$_3$): δ 1.49 (t, $J$ = 7.2 Hz, 3H), 2.15-2.26 (m, 4H), 3.06-3.13 (m, 8H), 4.49 (q, $J$ = 14.4 Hz, $J$ = 7.2 Hz, 2H), 8.12 (dd, $J$ =
8.8 Hz, 1H), 8.33 (s, 3H), 8.44 (s, 1H), 8.50 (d, J = 8.8 Hz, 1H), 9.22 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 14.5, 25.7 (2C), 32.8, 32.88, 32.97, 33.0, 61.0, 118.1, 118.2, 118.4, 118.8, 123.0, 125.1, 126.3, 127.3, 127.7, 127.8, 128.9, 129.4, 129.8, 133.2, 143.5, 143.7, 144.3, 145.0, 167.0; HRMS calcd for C$_{27}$H$_{24}$O$_2$ 380.1776, found 380.1772.