Electronic Supplementary Information

Visible Light-Mediated Intramolecular C–H Arylation of Diazonium Salts of \( N-(2\text{-aminoaryl})\)benzoimines: A Facile Synthesis of 6-ArylPhenanthridines

Palani Natarajan*, Naveen Kumar and Manjeet Sharma

Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh - 160 014, India

pnataraj@pu.ac.in

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**General Aspects:** All solvents and precursors, respectively, were dried and recrystallized following the purification procedure described in the literature. All reactions were carried out in an inert atmosphere with standard Schlenk techniques. Reactions were monitored by analytical thin layer chromatography on silica gel with visualization under UV light or iodine chamber. Column chromatography was performed on silica gel or neutral alumina. All NMR spectra were recorded on a Bruker Avance (300 MHz) spectrometer in CDCl₃: chemical shifts are expressed in parts per million (ppm) and were calibrated using the residual protonated solvent peak. IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrometer.

**General procedure for the synthesis of 6-arylphenanthridine:** To an oven-dried Schlenk tube equipped with a magnetic stir bar was charged with tris(2,2′-bipyridyl)ruthenium(II) chloride (1 mol%), \(N\)-(2-aminophenyl)benzoimine (1.0 equiv.), tert-butyl nitrite (1.3 equiv.), and dry DMSO. The mixture was degassed by the freeze-pump-thaw procedure, and then the Schlenk tube was irradiated under a 5W Blue LED bulb at a distance of 5 cm. After stirring at 25 °C for 6 h, the solvent was removed under reduced pressure and the residue was then diluted with water. The aqueous solution was extracted (3 times) with ethyl acetate. The combined organic phases were dried over Na₂SO₄ and filtered. The filtrate was evaporated under reduced pressure to get the crude product, which was purified by column chromatography using hexane-ethyl acetate mixtures. The purity of the compound was confirmed by melting point, \(^1\)H- and \(^{13}\)C NMR measurements, vide infra.

**Experimental characterization data for products**

![Image of 6-phenylphenantridine (PHE1)]

**6-phenylphenantridine (PHE1):** Pale yellow solid (93% yield); mp 104-106 °C; \(R_f\) 0.21 in ethyl acetate–hexane (25:75); IR (neat, cm⁻¹): ν 3057, 3016, 2913, 2852, 1609, 1566, 1483, 1456, 1359, 1327, 1304, 1226, 1136, 957, 782, 726, 701; \(^1\)H NMR (CDCl₃, 300 MHz) \(δ\) 8.69 (d, \(J = 8.4\) Hz, 1H), 8.61 (d, \(J = 8.4\) Hz, 1H), 8.26 (d, \(J = 8.0\) Hz, 1H), 8.11 (d, \(J = 8.4\) Hz, 1H), 7.88-7.82 (m, 1H), 7.79-7.72 (m, 3H), 7.69-7.64 (m, 1H), 7.62-7.51 (m, 4H); \(^{13}\)C-NMR (CDCl₃, 75 MHz) \(δ\) 161.3, 143.6, 139.6, 133.6, 130.6, 130.3, 129.8, 129.1, 128.8, 128.7, 128.4, 127.3, 127.1, 125.5, 123.7, 122.3, 122.0.
2-methyl-6-phenylphenanthridine (PHE2): 3 Pale yellow solid (94% yield); mp 160-163 °C; $R_f$
0.20 in ethyl acetate–hexane (25:75); IR (neat, cm$^{-1}$): $\nu$ 3061, 3007, 2849, 1619, 1567, 1465,
1360, 1306, 1141, 957, 752, 700; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.67 (d, $J = 8.2$ Hz, 1H), 8.37 (s,
1H), 8.13 (d, $J = 8.2$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.81-7.76 (m, 1H), 7.74-7.68 (m, 2H),
7.57-7.46 (m, 5H), 2.56 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 160.6, 142.1, 139.7, 136.5, 133.2,
130.7, 130.3, 130.0, 129.6, 128.9, 128.6, 128.4, 127.0, 125.2, 123.4, 122.2, 121.4, 22.2.

3-methyl-6-phenylphenanthridine (PHE3): 4 Pale yellow solid (89% yield); mp 107-108 °C; $R_f$
0.20 in ethyl acetate–hexane (25:75); IR (neat, cm$^{-1}$): $\nu$ 3056, 3014, 2921, 2853, 1611, 1561,
1473, 1456, 1361, 1306, 1138, 774, 766, 751; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.67 (d, $J = 8.2$ Hz,
1H), 8.51 (d, $J = 8.2$ Hz, 1H), 8.11-8.04 (m, 2H), 7.87-7.81 (m, 1H), 7.75-7.71 (m, 2H), 7.60-
7.52 (m, 5H), 2.59 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 161.3, 143.9, 139.8, 139.1, 133.7,
130.6, 129.9, 129.8, 129.0, 128.7, 128.5, 128.3, 126.8, 125.0, 122.1, 121.8, 121.3, 21.6.
2-methoxy-6-phenylphenanthridine (PHE4): Colorless solid (94% yield); mp 179-180 °C; \( R_f \) 0.17 in ethyl acetate–hexane (25:75); IR (neat, cm\(^{-1}\)): \( \nu \) 3057, 3013, 2861, 1614, 1561, 1486, 1459, 1361, 1296, 1141, 773, 768; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 8.62 (d, \( J = 8.4 \) Hz, 1H), 8.17 (d, \( J = 8.4 \) Hz, 1H), 8.12-7.91 (m, 2H), 7.81-7.74 (m, 1H), 7.72-7.66 (m, 2H), 7.62 (d, \( J = 7.8 \) Hz, 1H), 7.55-7.48 (m, 2H), 7.43 (d, \( J = 7.8 \) Hz, 1H), 7.41-7.36 (m, 1H), 4.04 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz): \( \delta \) 158.9, 158.6, 140.2, 139.5, 133.3, 132.2, 130.4, 130.0, 129.2, 128.8, 128.5, 127.5, 125.7, 125.0, 122.5, 119.1, 103.2, 55.8.

3-methoxy-6-phenylphenanthridine (PHE5): Colorless solid (86% yield); mp 138-140 °C; \( R_f \) 0.17 in ethyl acetate–hexane (25:75); IR (neat, cm\(^{-1}\)): \( \nu \) 3074, 3016, 1616, 1564, 1446, 1364, 1306, 1149, 771, 714; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 8.68 (d, \( J = 8.3 \) Hz, 1H), 8.16 (d, \( J = 8.3 \) Hz, 1H), 8.14-7.99 (m, 2H), 7.78 (t, \( J = 7.8 \) Hz, 2H), 7.69-7.65 (m, 2H), 7.61 (t, \( J = 7.8 \) Hz, 2H), 7.53-7.49 (m, 1H), 7.42-7.33 (m, 1H), 4.07 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 159.4, 158.8, 141.3, 139.6, 133.8, 132.4, 130.4, 130.0, 129.6, 129.3, 128.7, 127.9, 127.6, 125.6, 122.8, 118.6, 103.7, 55.7.
2-chloro-6-phenylphenanthridine (PHE6): Colorless solid (92% yield); mp 171-173 °C; $R_f$ 0.22 in ethyl acetate–hexane (25:75); IR (neat, cm$^{-1}$): ν 3094, 3062, 3017, 1617, 1561, 1489, 1364, 1143, 776, 728; $^1$H NMR (CDCl$_3$, 300 MHz) δ 8.64 (d, $J$ = 8.2 Hz, 1H), 8.61 (d, $J$ = 3.8 Hz, 1H), 8.17 (d, $J$ = 8.2 Hz, 1H), 8.12 (d, $J$ = 8.4 Hz, 1H), 7.91-7.86 (m, 1H), 7.73-7.59 (m, 4H), 7.57-7.51 (m, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ: 161.3, 141.9, 139.5, 133.2, 132.4, 131.7, 131.2, 130.0, 129.7, 129.2, 129.0, 128.5, 127.9, 125.4, 124.8, 122.7, 122.1.

3-chloro-6-phenylphenanthridine (PHE7): Colorless solid (91% yield); mp 133-135 °C; $R_f$ 0.22 in ethyl acetate–hexane (25:75); IR (neat, cm$^{-1}$): ν 3061, 3014, 2931, 1610, 1531, 1496, 1462, 1363, 1256, 1171, 773, 738; $^1$H NMR (CDCl$_3$, 300 MHz) δ 8.66 (d, $J$ = 8.2 Hz, 1H), 8.54 (d, $J$ = 8.2 Hz, 1H), 8.28-8.22 (m, 1H), 8.16-8.11 (m, 1H), 7.91-7.83 (m, 1H), 7.75-7.70 (m, 2H), 7.66-7.59 (m, 2H), 7.61-7.53 (m, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 162.3, 144.6, 139.6, 134.5, 133.0, 130.1, 129.8, 129.7, 129.2, 128.9, 128.6, 127.5, 127.3, 125.2, 123.3, 122.4, 122.2.
2-nitro-6-phenylphenanthridine (PHE8): Pale yellow solid (87% yield); mp 192-194 °C; $R_f$ 0.14 in ethyl acetate–hexane (25:75); IR (neat, cm$^{-1}$): $\nu$ 3075, 3024, 2923, 2224, 1610, 1561, 1511, 1479, 1476, 1361, 961, 904, 776, 667, 611; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.94 (m, 1H), 8.64 (d, $J$ = 8.0 Hz, 1H), 8.31 (d, $J$ = 8.0 Hz, 1H), 8.19 (d, $J$ = 8.2 Hz, 1H), 7.98-7.94 (m, 2H), 7.76-7.71 (m, 3H), 7.62-7.59 (m, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 164.4, 145.2, 139.0, 132.6, 131.8, 131.6, 130.2, 129.9, 129.7, 129.3, 128.8, 128.6, 127.3, 125.8, 124.1, 122.2, 120.2; C$_{19}$H$_{12}$N$_2$O$_2$ (300.3): Calcd. C, 75.99; H, 4.03; N, 9.33; Found C, 75.84; H, 4.06; N, 9.32.

3-nitro-6-phenylphenanthridine (PHE9): Pale yellow solid (89% yield); mp 158-160 °C; $R_f$ 0.14 in ethyl acetate–hexane (25:75); IR (neat, cm$^{-1}$): $\nu$ 3052, 3019, 2921, 2226, 1611, 1562, 1514, 1479, 1366, 961, 671, 617; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 8.86 (s, 1H), 8.71 (d, $J$ = 8.2 Hz, 1H), 8.33 (d, $J$ = 8.2 Hz, 1H), 8.14 (d, $J$ = 8.2 Hz, 1H), 7.94-7.89 (m, 2H), 7.80-7.71 (m, 2H), 7.71-7.64 (m, 1H), 7.61-7.53 (m, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 162.3, 142.9, 135.2, 131.3, 131.2, 129.7, 129.3, 128.7, 128.4, 128.2, 128.1, 126.2, 124.6, 122.8, 119.8, 119.4, 119.2; C$_{19}$H$_{12}$N$_2$O$_2$ (300.3): Calcd. C, 75.99; H, 4.03; N, 9.33; Found C, 75.91; H, 4.02; N, 9.29.
1-methyl-6-phenylphenanthridine (PHE10): Colorless solid (85% yield); mp 131-133 °C; \( R_f \) 0.19 in ethyl acetate–hexane (25:75); IR (neat, cm\(^{-1}\)): \( \nu \) 2975, 2924, 2381, 1680, 1564, 1521, 1483, 1471, 1361, 1321, 1130, 1020, 960, 756, 707; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 8.71 (d, \( J = 8.4 \text{ Hz}, 1\text{H} \)), 8.22 (d, \( J = 8.6 \text{ Hz}, 1\text{H} \)), 8.14 (d, \( J = 8.4 \text{ Hz}, 1\text{H} \)), 7.82-7.87 (m, 1H), 7.74-7.77 (m, 2H), 7.61-7.66 (m, 2H), 7.51-7.57 (m, 3H), 7.19 (d, \( J = 7.9 \text{ Hz}, 1\text{H} \)), 2.54 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 161.2, 156.2, 140.2, 135.5, 133.5, 130.6, 130.2, 129.3, 128.9, 128.6, 127.5, 127.3, 125.8, 125.2, 122.9, 114.0, 108.7, 20.8; C\(_{20}\)H\(_{15}\)N (269.3): Calcd. C, 89.19; H, 5.61; N, 5.20; Found C, 89.14; H, 5.78; N, 5.16.

2,3-dimethyl-6-phenylphenanthridine (PHE11): Colorless solid (89% yield); mp 54-55 °C; \( R_f \) 0.17 in ethyl acetate–hexane (25:75); IR (neat, cm\(^{-1}\)): \( \nu \) 3060, 2977, 2921, 2357, 1689, 1594, 1561, 1483, 1441, 1360, 1320, 1031, 962, 876, 767; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 8.64 (d, \( J = 8.6 \text{ Hz}, 1\text{H} \)), 8.37 (s, 1H), 8.11 (d, \( J = 8.6 \text{ Hz}, 1\text{H} \)), 8.04 (s, 1H), 7.85 -7.78 (m, 1H), 7.75-7.71 (m, 2H), 7.59-7.50 (m, 4H), 2.58 (s, 3H), 2.52 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 160.1, 143.1, 140.1, 138.7, 136.4, 133.4, 130.6, 129.9, 129.2, 128.7, 128.6, 126.6, 125.3, 122.1, 121.8, 21.3, 20.8.
5-phenylbenzo[b]phenanthridine (PHE13): Yellow solid (86% yield); mp 62-64 °C; \( R_f \) 0.12 in ethyl acetate–hexane (25:75); IR (neat, cm\(^{-1}\)):\( \nu \) 3061, 3016, 2372, 1603, 1501, 1439, 1351, 958, 902, 776, 671; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 9.07 (s, 1H), 8.86 (d, \( J = 8.6 \) Hz, 1H), 8.81 (s, 1H), 8.16-8.07 (m, 3H), 7.93-7.88 (m, 1H), 7.84-7.76 (m, 2H), 7.68-7.52 (m, 6H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 161.9, 141.6, 140.1, 133.7, 132.2, 131.1, 129.9, 129.7, 128.8, 128.7, 128.5, 128.3, 127.5, 126.4, 126.3, 125.5, 123.2, 122.9, 121.1.

References
Figure S1. $^1$H (top) and $^{13}$C (bottom) spectra of 6-phenylphenantridine in CDCl$_3$. 
Figure S2. $^1$H (top) and $^{13}$C (bottom) spectra of 2-methyl-6-phenylphenanthidine in CDCl$_3$. 
Figure S3. $^1$H (top) and $^{13}$C (bottom) spectra of 3-methyl-6-phenylphenanthridine in CDCl$_3$. 
Figure S4. $^1$H (top) and $^{13}$C (bottom) spectra of 2-methoxy-6-phenylphenanthridine in CDCl$_3$. 
**Figure S5.** $^1$H (top) and $^{13}$C (bottom) spectra of 3-methoxy-6-phenylphenanthridine in CDCl$_3$. 
Figure S6. $^1$H (top) and $^{13}$C (bottom) spectra of 2-chloro-6-phenylphenanthidine in CDCl$_3$. 
Figure S7. $^1$H (top) and $^{13}$C (bottom) spectra of 2-nitro-6-phenylphenanthridine in CDCl$_3$. 
Figure S8. $^1$H (top) and $^{13}$C (bottom) spectra of 3-nitro-6-phenylphenanthridine in CDCl$_3$. 
Figure S9. $^1$H (top) and $^{13}$C (bottom) spectra of 1-methyl-6-phenylphenanthridine in CDCl$_3$. 
Figure S10. $^1$H (top) and $^{13}$C (bottom) spectra of 2,3-dimethyl-6-phenylphenanthridine in CDCl$_3$. 
Figure S11. $^1$H (top) and $^{13}$C (bottom) spectra of 5-phenylbenzo[b]phenanthridine in CDCl$_3$. 