o-Dihaloarenes as Aryne Precursors for Nickel-Catalyzed Cycloaddition with Alkynes and Nitriles: a Novel Method to Polysubstituted Naphthalene, Phenanthridine and Triphenylene Derivatives

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Supporting Information

General. All reactions were conducted under nitrogen atmosphere on a dual-manifold Schlenk line unless otherwise mentioned and in oven-dried glass wares. All solvents were dried according to known methods and distilled prior to use. Substituted benzene precursors were synthesized according to the literature procedures (see refs 1 and 2 in the main text). Other reagents were commercially available and used as purchased.

General procedure for the cyclotrimerization and reductive cyclization of diiodoarenes with acetylenes and nitrile:

To a screw-capped sealed tube were added NiBr$_2$(dppe) (31 mg, 0.050 mmol), dppe (20 mg, 0.050 mmol) and zinc powder (96 mg, 1.5 mmol). The tube was sealed with septum and flushed several times with nitrogen. o-Diiodoarene$_1$-$^2$ (0.5 mmol), alkyne$_3$ (3.0 mmol) (or diyne (1.5 mmol)) and acetonitrile (1.0 mL) were injected into the reaction system via a syringe (Solid diiodoarene and alkyne could be added to the tube immediately after the addition of catalyst.). The septum was removed, and the tube was sealed with a screw cap quickly under nitrogen. The reaction mixture was stirred at 100 °C for 48 h. The crude reaction mixture was diluted with CH$_2$Cl$_2$, filtered through a thin Celite pad, and concentrated in vacuo. The residue was
chromatographed on a silica gel column using a mixture of hexane and EA as the eluent to give the desired pure product.

Products 3a-p, and 5a-m, were prepared according to this procedure.

For the synthesis of phenanthridines 6a-e, the procedure is similar to that described above except that no extra dppe was used and the amount of solvent acetonitrile used was 2.5 ml.

The synthesis of triphenylene derivatives 7a-c also followed a similar procedure using THF (2 ml) as the solvent and NiBr₂(PPh₃)₂ as the catalyst. Spectral data for all of these compounds are listed below.

1,2,3,4-Tetraethynaphthalene (3a):⁴

Colorless oil; ¹H NMR (500 MHz, CDCl₃): δ 1.24 (t, J = 6.5 Hz, 6 H), 1.30 (t, J = 6.5 Hz, 6 H), 2.84 (q, J = 6.5 Hz, 4 H), 3.11 (q, J = 4.5 Hz, 4 H), 7.41 (dd, J₁ = 8.0 Hz, J₂ = 3.0 Hz, 2 H), 8.03 (dd, J₁ = 8.0 Hz, J₂ = 3.0 Hz, 2 H); ¹³C NMR (125 MHz, CDCl₃): δ 15.5, 15.8, 21.7, 22.8, 124.5, 124.5, 131.0, 135.4, 137.7; HRMS: C₁₈H₂₄ calculated 240.1878, found 240.1882. Registry Number: [177327-40-1]

1,2,3,4-Tetrapropylnaphthalene (3b):⁵

Colorless oil; ¹H NMR (500 MHz, CDCl₃): δ 1.05 (t, J = 7.0 Hz, 6 H), 1.10 (t, J =
7.0 Hz, 6 H), 1.58 (sextet, \( J = 7.0 \) Hz, 4 H), 1.67 (sextet, \( J = 7.0 \) Hz, 2 H), 2.74 (t, \( J = 7.0 \) Hz, 4 H), 3.01 (t, \( J = 7.0 \) Hz, 4 H), 7.40 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 3.0 \) Hz, 2 H), 7.80 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 3.0 \) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 14.9, 15.1, 24.5, 24.8, 31.3, 32.6, 124.4, 124.5, 131.1, 134.1, 136.7; HRMS: C\(_{22}\)H\(_{32}\) calculated 296.2504, found 296.2503. Registry Number: [42101-99-5]

![Image of 1,2,3,4-Tetrakis(methoxymethyl)naphthalene (3c):](image)

**1,2,3,4-Tetrakis(methoxymethyl)naphthalene (3c):**

Yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 3.46 (s, 6 H), 3.47 (s, 6 H), 4.74 (s, 4 H), 4.97 (s, 4 H), 7.52 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 3.0 \) Hz, 2 H), 8.19 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 3.0 \) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 58.3, 58.5, 67.7, 68.3, 125.1, 126.5, 132.9, 134.1, 134.4; HRMS: C\(_{18}\)H\(_{24}\)O\(_4\) calculated 304.1675, found 304.1678.

![Image of Tetramethyl naphthalene-1,2,3,4-tetracarboxylate (3d):](image)

**Tetramethyl naphthalene-1,2,3,4-tetracarboxylate (3d):**

Yellow solid, mp: 129-131 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 3.90 (s, 6 H), 4.99 (s, 6 H), 7.69 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 3.0 \) Hz, 2 H), 8.06 (dd, \( J_1 = 8.0 \) Hz, \( J_2 = 3.0 \) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 53.2, 53.2, 126.2, 128.2, 129.7, 130.0, 133.9, 166.7, 167.2; HRMS: C\(_{18}\)H\(_{16}\)O\(_8\) calculated 360.0845, found 360.0842. Registry Number: [36063-07-7]
Tetraethyl naphthalene-1,2,3,4-tetracarboxylate (3e):\(^7\)

Yellow oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.34 (t, \(J = 7.0\) Hz, 6 H), 1.40 (t, \(J = 7.0\) Hz, 6 H), 4.34 (q, \(J = 7.0\) Hz, 4 H), 4.48 (q, \(J = 7.0\) Hz, 4 H), 7.68 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 3.0\) Hz, 2 H), 8.06 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 3.0\) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 13.9, 14.0, 62.3, 62.3, 126.1, 127.6, 129.5, 129.9, 133.9, 166.3, 166.8; HRMS: C\(_{22}\)H\(_{24}\)O\(_8\) calculated 416.1471, found 416.1475. Registry Number: [107002-74-4]

1,2,3,4-Tetraphenylnapthalene (3f):\(^6\)

White solid, mp: 157-159 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 6.83-6.87 (m, 10 H), 7.20-7.27 (m, 10 H), 7.40 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 3.0\) Hz, 2 H), 7.66 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 3.0\) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 125.3, 125.8, 126.4, 126.5, 126.9, 127.5, 131.3, 132.0, 138.4, 138.8, 139.5, 140.5; HRMS: C\(_{32}\)H\(_{24}\) calculated 432.1878, found 432.1881. Registry Number: [751-38-2]
1,2,3,4-Tetra-tolynaphthalene (3g):\(^8\)

Yellow solid, mp: 117-119 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 2.09 (s, 6 H), 2.31 (s, 6 H), 6.65 (d, \(J = 7.5\) Hz, 4 H), 6.71 (d, \(J = 7.5\) Hz, 4 H), 7.04 (d, \(J = 7.5\) Hz, 4 H), 7.08 (d, \(J = 7.5\) Hz, 4 H), 7.35 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 3.0\) Hz, 2 H), 7.62 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 3.0\) Hz, 2 H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 21.1, 21.2, 125.5, 126.9, 127.2, 128.2, 131.1, 132.2, 134.3, 135.6, 136.8, 137.8, 138.3, 139.1; HRMS: C\(_{38}\)H\(_{32}\) calculated 488.2504, found 488.2504. Registry Number: [1003853-52-8]

1,2,3,4-Tetraethyl-6,7-dimethylnaphthalene (3h):

Colorless oil; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.19 (t, \(J = 6.5\) Hz, 6 H), 1.28 (t, \(J = 6.5\) Hz, 6 H), 2.42 (s, 6 H), 2.81 (q, \(J = 6.5\) Hz, 4 H), 3.06 (q, \(J = 6.5\) Hz, 4 H), 7.74 (s, 2 H); \(^13\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 15.6, 15.7, 21.6, 22.7, 23.5, 124.2, 127.3, 128.8, 131.2, 137.4; HRMS: C\(_{20}\)H\(_{28}\) calculated 268.2191, found 268.2192.
6,7-Dimethyl-1,2,3,4-tetraphenylnaphthalene (3i): 9
Yellow solid, mp: 266-268 °C; 1H NMR (500 MHz, CDCl3): δ 2.30 (s, 6 H), 6.81-6.84 (m, 10 H), 7.18-7.25 (m, 10 H), 7.38 (s, 2 H); 13C NMR (125 MHz, CDCl3): δ 20.3, 125.1, 126.2, 126.4, 126.4, 127.4, 130.8, 131.3, 131.4, 135.6, 137.5, 138.0, 139.8, 140.8; HRMS: C36H28 calculated 460.2191, found 460.2193. Registry Number: [76054-73-4]

1,2,3,4-Tetraethyl-6,7-dimethoxynaphthalene (3j):
Colorless oil; 1H NMR (500 MHz, CDCl3): δ 1.22 (t, J = 7.0 Hz, 6 H), 1.30 (t, J = 7.0 Hz, 6 H), 2.80 (q, J = 7.0 Hz, 4 H), 3.04 (q, J = 7.0 Hz, 4 H), 3.99 (s, 6 H), 7.28 (s, 2 H); 13C NMR (125 MHz, CDCl3): δ 15.1, 16.0, 22.1, 22.7, 55.7, 103.8, 126.5, 134.0, 136.2, 148.3; HRMS: C20H28O2 calculated 300.3089, found 300.2092.
6,7-Dimethoxy-1,2,3,4-tetraphenylnaphthalene (3k): 

Yellow solid, mp: 305-307 °C; \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 3.73 (s, 6 H), 6.84 (m, 10 H), 6.94 (s, 2 H), 7.21-7.24 (m, 10 H); \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 55.6, 105.7, 125.1, 126.4, 127.6, 127.8, 131.1, 131.4, 137.0, 137.3, 139.9, 140.8, 149.2; HRMS: C\(_{36}\)H\(_{28}\)O\(_2\) calculated 492.2089, found 492.2090. Registry Number: [26002-78-8]

5,6,7,8-Tetraethynaphtho[2,3-d][1,3]dioxole (3l):

Colorless oil; \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 1.20 (t, \( J = 7.0\) Hz, 6 H), 1.26 (t, \( J = 7.0\) Hz, 6 H), 2.78 (q, \( J = 7.0\) Hz, 4 H), 2.98 (q, \( J = 7.0\) Hz, 4 H), 5.99 (s, 2 H), 7.32 (s, 2 H); \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 15.2, 15.9, 22.2, 22.7, 100.7, 101.1, 127.8, 134.7, 136.4, 146.6; HRMS: C\(_{19}\)H\(_{24}\)O\(_2\) calculated 284.1776, found 284.1779.

Tetramethyl naphtho[2,3-d][1,3]dioxole-5,6,7,8-tetracarboxylate (3m):

Yellow solid, mp: 120-122 °C; \( ^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 3.87 (s, 6 H), 3.96 (s, 6 H), 6.12 (s, 2 H), 7.35 (s, 2 H); \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 53.0, 53.1, 102.4, 102.4, 126.4, 128.3, 134.2, 150.7, 166.9, 167.5; HRMS: C\(_{19}\)H\(_{16}\)O\(_{10}\) calculated 404.0743, found 404.0745.
1,2,3,4-Tetraethyl-5,6,7,8-tetrafluoronaphthalene (3n):\(^{11}\)

Colorless oil; \(^1H\) NMR (500 MHz, CDCl\(_3\)): \(\delta 1.22 \ (t, \ J = 7.0 \ Hz, \ 6 \ H), \ 1.28 \ (t, \ J = 7.0 \ Hz, \ 6 \ H), \ 2.84 \ (q, \ J = 7.0 \ Hz, \ 4 \ H), \ 3.12 \ (broad, \ 4 \ H); \ ^{13}C\) NMR (125 MHz, CDCl\(_3\)): \(\delta 15.5, 15.7, 22.1, 22.3, 118.9, 133.9, 137.8, 140.7 \ (d, \ J = 240.0 \ Hz), \ 143.8 \ (d, \ J = 240.0 \ Hz); \) HRMS: C\(_{18}\)H\(_{20}\)F\(_4\) calculated 312.1501, found 312.1502. Registry Number: [900167-12-6]

**Tetramethyl 5,6,7,8-tetrafluoronaphthalene-1,2,3,4-tetracarboxylate (3o):**

White solid, mp: 174-176 °C; \(^1H\) NMR (500 MHz, CDCl\(_3\)): \(\delta 3.89 \ (s, \ 6 \ H), \ 3.99 \ (s, \ 6 \ H); \ ^{13}C\) NMR (125 MHz, CDCl\(_3\)): \(\delta 53.5, 54.3, 116.7, 129.1, 129.9, 138.4 \ (d, \ J = 245.0 \ Hz), \ 142.7 \ (d, \ J = 245.0 \ Hz), \ 165.2, \ 166.4, \ 143.8; \) HRMS: C\(_{18}\)H\(_{12}\)F\(_4\)O\(_8\) calculated 432.0468, found 432.0466.

1,2,3,4,5,6,7,8-Octaphenylanthracene (3p):\(^{12}\)
Yellow solid, mp: 766-768 °C; (very low solubility) $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.79-6.83 (m, 20 H), 6.96-7.03 (m, 20 H), 7.89 (s, 2 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 125.3, 126.0, 126.5, 127.2, 130.8, 131.0, 131.1, 131.2, 131.3, 138.3, 139.2, 140.6; HRMS: C$_{62}$H$_{42}$ calculated 786.3287, found 786.3283. Registry Number: [100367-30-4]

1,2,3,4-Tetraethyl-6-methylnaphthalene (3q):

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.22 (t, $J$ = 7.0 Hz, 6 H), 1.30 (t, $J$ = 7.0 Hz, 6 H), 2.51 (s, 3 H), 2.83 (q, $J$ = 7.0 Hz, 4 H), 3.09 (q, $J$ = 7.0 Hz, 4 H), 7.25 (d, $J$ = 9.0 Hz, 1 H), 7.78 (s, 1 H), 7.92 (d, $J$ = 9.0 Hz, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 15.5, 15.6, 15.8, 15.8, 21.6, 21.7, 22.1, 22.7, 22.8, 123.6, 124.4, 126.6, 129.1, 131.1, 133.8, 134.7, 135.2, 136.7, 137.8; HRMS: C$_{19}$H$_{26}$ calculated 254.2035, found 254.2037.

6-Methyl-1,2,3,4-tetraphenylnaphthalene (3r):

White solid, mp: 195-197 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.39 (s, 3 H), 6.81-6.87 (m, 10 H), 7.18-7.26 (m, 11 H), 7.41 (s, 1 H), 7.55 (d, $J$ = 8.0 Hz, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.8, 125.2, 125.8, 126.3, 126.5, 126.9, 127.5, 128.1, 130.2, 131.2, 131.3, 131.3, 131.3, 132.1, 135.6, 137.7, 137.9, 138.2, 138.9, 139.7,
2,3-Dihydro-1H-cyclopenta[b]naphthalene (5a):\(^{14}\)

White solid, mp: 84-86 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 2.13 (quintet, \(J = 10\) Hz, 2 H), 3.05 (t, \(J = 7.5\) Hz, 4 H), 7.37 (q, \(J = 6.5\) Hz, 2 H), 7.65 (s, 2 H), 7.75 (q, \(J = 6.5\) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 26.2, 32.6, 122.1, 124.8, 127.4, 132.6, 143.4; HRMS: C\(_{13}\)H\(_{12}\) calculated 168.0939, found 168.0937. Registry Number: [21991-42-4]

1,2,3,4-Tetrahydroanthracene (5b):\(^{14}\)

White solid, mp: 92-94 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.85 (quintet, \(J = 10\) Hz, 4 H), 2.96 (t, \(J = 7.5\) Hz, 4 H), 7.34 (q, \(J = 6.5\) Hz, 2 H), 7.52 (s, 2 H), 7.59 (q, \(J = 6.5\) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 23.4, 29.8, 124.9, 126.6, 126.9, 132.1, 136.2; HRMS: C\(_{14}\)H\(_{14}\) calculated 182.1096, found 182.1095. Registry Number: [1624-26-6]

1,3-Dihydronaphtho-[2,3-c] furan (5c):\(^{14}\)

Yellow solid, mp: 153-155 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 5.12 (s, 4 H), 7.43 (q, \(J = 6.5\) Hz, 2 H), 7.66 (s, 2 H), 7.80 (q, \(J = 6.5\) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 72.8, 119.2, 125.7, 127.9, 133.1, 138.2; HRMS: C\(_{12}\)H\(_{10}\)O calculated 170.0732,
1,3-Dihydrocyclopenta[c]naphthalene-2,2-dicarboxylic acid dimethyl ester (5d): \(^{14}\)
Yellow solid, mp: 120-122 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 3.71\) (s, 4 H), 3.74 (s, 6 H), 7.38 (q, \(J = 6.5\) Hz, 2 H), 7.63 (s, 2 H), 7.74 (q, \(J = 6.5\) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 40.2, 53.0, 60.9, 122.5, 125.3, 127.6, 133.1, 138.8, 171.9\); HRMS: C\(_{17}\)H\(_{16}\)O\(_4\) calculated 284.1049, found 284.1050. Registry Number: [856897-90-0]

1,3-Dihydrocyclopenta[b]naphthalene-2,2-dicarbonitrile (5e): \(^{14}\)
Yellow solid, mp: 161-163 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 3.84\) (s, 4 H), 7.49 (q, \(J = 6\) Hz, 2 H), 7.75 (s, 2 H), 7.80 (q, \(J = 6\) Hz, 2 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta 34.3, 44.2, 116.1, 123.8, 126.6, 127.9, 133.4, 134.1\); HRMS: C\(_{15}\)H\(_{10}\)N\(_2\) calculated 218.0844, found 218.0842. Registry Number: [856897-91-1]

2,3-Dihydro-4,9-diphenyl-1\(H\)-cyclopenta[b]naphthalene (5f): \(^{15}\)
White solid, mp: 169-171 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 2.00\) (quintet, \(J = 8.0\) Hz, 2 H), 2.88 (t, \(J = 8.0\) Hz, 4 H), 7.28 (dd, \(J_1 = 8.0\) Hz, \(J_2 = 3.0\) Hz, 2 H), 7.40 (d, \(J \)
= 8.0 Hz, 4 H), 7.42 (t, J = 8.0 Hz, 2 H), 7.50 (t, J = 8.0 Hz, 4 H), 7.63 (dd, J1 = 8.0 Hz, J2 = 3.0 Hz, 2 H); 13C NMR (125 MHz, CDCl3): δ 25.7, 33.0, 124.7, 125.8, 127.0, 128.3, 130.1, 131.9, 134.1, 139.6, 141.1; HRMS: C25H20 calculated 320.1565, found 320.1566. Registry Number: [1167-64-2]

![Image](image1.png)

2,3-Dihydro-4,9-bis(4-methylphenyl)-1H-cyclopenta[b]napthalene (5g):

White solid, mp: 169-171 °C; 1H NMR (500 MHz, CDCl3): δ 2.00 (quintet, J = 8.0 Hz, 2 H), 2.88 (t, J = 8.0 Hz, 4 H), 2.31 (s, 6 H), 7.05 (d, J = 8.0 Hz, 4 H), 7.10 (d, J = 8.0 Hz, 4 H), 7.27 (dd, J1 = 8.0 Hz, J2 = 3.0 Hz, 2 H), 7.64 (dd, J1 = 8.0 Hz, J2 = 3.0 Hz, 2 H); 13C NMR (125 MHz, CDCl3): δ 21.3, 25.7, 33.1, 55.3, 124.6, 125.9, 128.2, 131.1 131.2, 132.1, 134.1, 139.6, 141.3; HRMS: C27H24 calculated 348.1878, found 348.1881.

![Image](image2.png)

2,3-Dihydro-4,9-bis(4-methoxyphenyl)-1H-cyclopenta[b]napthalene (5h):
White solid, mp: 204-206 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.00 (quintet, $J$ = 8.0 Hz, 2 H), 2.87 (t, $J$ = 8.0 Hz, 4 H), 3.89 (s, 6 H), 7.03 (d, $J$ = 8.0 Hz, 4 H), 7.27 (dd, $J_1$ = 8.0 Hz, $J_2$ = 3.0 Hz, 2 H), 7.31 (d, $J$ = 8.0 Hz, 4 H), 7.65 (dd, $J_1$ = 8.0 Hz, $J_2$ = 3.0 Hz, 2 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 25.7, 33.1, 55.3, 113.7, 124.6, 125.9, 131.2, 131.9, 132.2, 133.6, 141.3, 158.6; HRMS: C$_{27}$H$_{24}$O$_2$ calculated 380.1776, found 380.1778.

![Structure of 2,3-Dihydro-4,9-bis(4-acetonphenone)-1H-cyclopenta[b]naphthalene (5i):](image)

2,3-Dihydro-4,9-bis(4-acetonphenone)-1H-cyclopenta[b]naphthalene (5i):

White solid, mp: 265-267 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.02 (quintet, $J$ = 8.0 Hz, 2 H), 2.67 (s, 6 H), 2.85 (t, $J$ = 8.0 Hz, 4 H), 7.31 (dd, $J_1$ = 8.0 Hz, $J_2$ = 3.0 Hz, 2 H), 7.50 (d, $J$ = 8.0 Hz, 4 H), 7.55 (dd, $J_1$ = 8.0 Hz, $J_2$ = 3.0 Hz, 2 H), 8.10 (d, $J$ = 8.0 Hz, 4 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 25.7, 26.7, 32.8, 125.3, 125.6, 128.5, 130.4, 131.5, 132.0, 133.5, 141.1, 144.7, 197.9; HRMS: C$_{29}$H$_{24}$O$_2$ calculated 404.1776, found 404.1778.
2,3-Dihydro-6,7-dimethyl-4,9-diphenyl-1\textit{H}-cyclopenta\textit{b}naphthalene (5j):

White solid, mp: 192-194 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.98 (quintet, $J = 8.0$ Hz, 2 H), 2.27 (s, 6 H), 2.84 (t, $J = 8.0$ Hz, 4 H), 7.37 (s, 2 H), 7.40 (d, $J = 8.0$ Hz, 4 H), 7.42 (t, $J = 8.0$ Hz, 2 H), 7.51 (t, $J = 8.0$ Hz, 4 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 20.1, 25.7, 32.9, 125.4, 126.8, 128.2, 130.1, 130.7, 133.3, 134.2, 140.0, 140.1; HRMS: C$_{27}$H$_{24}$ calculated 348.1878, found 348.1879.

2,3-Dihydro-6,7-dimethoxy-4,9-diphenyl-1\textit{H}-cyclopenta\textit{b}naphthalene (5k):

White solid, mp: 150-152 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.98 (quintet, $J = 8.0$ Hz, 2 H), 2.84 (t, $J = 8.0$ Hz, 4 H), 3.73 (s, 6 H), 6.96 (s, 2 H), 7.40 (d, $J = 8.0$ Hz, 4 H), 7.42 (t, $J = 8.0$ Hz, 2 H), 7.52 (t, $J = 8.0$ Hz, 4 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 25.7, 33.0, 55.5, 104.9, 127.0, 127.4, 128.4, 129.9, 133.0, 139.4, 139.9, 148.4; HRMS: C$_{27}$H$_{24}$O$_2$ calculated 380.1776, found 380.1778.

2,3-Dihydro-4,9-diphenyl-1\textit{H}-cyclopentanaphtho[2,3-d][1,3]dioxole (5l):

White solid, mp: 141-143 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.98 (quintet, $J = 8.0$ Hz, 2 H), 2.84 (t, $J = 8.0$ Hz, 4 H), 5.76 (s, 6 H), 6.99 (s, 2 H), 7.40 (d, $J = 8.0$ Hz, 4
H), 7.42 (t, J = 8.0 Hz, 2 H), 7.52 (t, J = 8.0 Hz, 4 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 25.8, 33.5, 101.0, 102.2, 127.0, 127.8, 128.4, 130.0, 133.0, 140.1, 140.5, 146.7; HRMS: C\(_{26}\)H\(_{20}\)O\(_2\) calculated 364.1463, found 364.1462.

![Image of compound](image)

**2,3-Dihydro-5,6,7,8-tetrafluoro-4,9-diphenyl-1H-cyclopenta[b]naphthalene (5m):**
White solid, mp: 203-205 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 2.00 (quintet, \(J = 8.0\) Hz, 2 H), 2.88 (t, \(J = 8.0\) Hz, 4 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 25.7, 33.0, 119.1, 125.8, 127.0, 128.3, 130.1, 137.9, 143.1(d, \(J = 240.0\) Hz), 145.2, 149.1(d, \(J = 240.0\) Hz); HRMS: C\(_{25}\)H\(_{16}\)F\(_4\) calculated 392.1188, found 392.1190.

![Image of compound](image)

**6-Methylphenanthidine (6a):\(^{16}\)**
Yellow solid, mp: 81-83 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.03 (s, 3 H), 7.61 (t, \(J = 7.0\) Hz, 1 H), 7.67-7.71 (m, 2 H), 7.83 (t, \(J = 8.0\) Hz, 1 H), 8.08 (d, \(J = 8.0\) Hz, 1 H), 8.21 (d, \(J = 8.0\) Hz, 1 H), 8.52 (d, \(J = 8.0\) Hz, 1 H), 8.62 (d, \(J = 8.0\) Hz, 1 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 23.4, 121.9, 122.3, 123.8, 125.9, 126.3, 126.6, 127.3, 128.6, 129.3, 130.5, 132.6, 143.7, 158.9; HRMS: C\(_{14}\)H\(_{11}\)N calculated 193.0891, found 193.0890. Registry Number: [3955-65-5]
6-Ethylphenanthridine (6b):\(^{17}\)

Yellow solid, mp: 55-57 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.50 (t, \(J = 7.5\) Hz, 3 H), 3.40 (q, \(J = 7.5\) Hz, 2 H), 7.61 (t, \(J = 7.0\) Hz, 1 H), 7.67-7.71 (m, 2 H), 7.82 (t, \(J = 8.0\) Hz, 1 H), 8.10 (d, \(J = 8.0\) Hz, 1 H), 8.25 (d, \(J = 8.0\) Hz, 1 H), 8.53 (d, \(J = 8.0\) Hz, 1 H), 8.63 (d, \(J = 8.0\) Hz, 1 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 13.6, 29.4, 121.9, 122.5, 123.7, 125.0, 126.3, 126.3, 127.2, 128.6, 129.5, 130.3, 132.9, 143.7, 163.3; HRMS: C\(_{15}\)H\(_{13}\)N calculated 207.1048, found 207.1051. Registry Number: [13362-58-8]

6-Propylphenanthridine (6c):\(^{17}\)

Yellow oil, \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.08 (t, \(J = 7.5\) Hz, 3 H), 1.96 (quintet, \(J = 7.5\) Hz, 2 H), 3.34 (t, \(J = 7.5\) Hz, 2 H), 7.61 (t, \(J = 8.0\) Hz, 1 H), 7.66-7.71 (m, 2 H), 7.81 (t, \(J = 8.0\) Hz, 1 H), 8.10 (d, \(J = 8.0\) Hz, 1 H), 8.25 (d, \(J = 8.0\) Hz, 1 H), 8.53 (d, \(J = 8.0\) Hz, 1 H), 8.63 (d, \(J = 8.0\) Hz, 1 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 14.4, 23.0, 38.4, 121.9, 122.5, 123.7, 125.3, 126.3, 127.2, 128.6, 129.5, 130.3, 132.9, 143.7, 162.3; HRMS: C\(_{16}\)H\(_{15}\)N calculated 221.1204, found 221.1206. Registry Number: [31150-40-0]

6-Isopropylphenanthridine (6d):\(^{16}\)
Yellow oil, $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.50 (s, s, 6 H), 3.99 (quintet, $J = 6.5$ Hz, 1 H), 7.58 (t, $J = 7.0$ Hz, 1 H), 7.67-7.70 (m, 2 H), 7.80 (t, $J = 8.0$ Hz, 1 H), 8.13 (d, $J = 8.0$ Hz, 1 H), 8.30 (d, $J = 8.0$ Hz, 1 H), 8.53 (d, $J = 8.0$ Hz, 1 H), 8.64 (d, $J = 8.0$ Hz, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 21.9, 31.5, 121.8, 122.6, 123.4, 124.7, 125.7, 126.2, 127.1, 128.4, 129.9, 129.9, 133.0, 143.8, 165.9; HRMS: C$_{16}$H$_{15}$N calculated 221.1204, found 221.1206. Registry Number: [16573-52-7]

![Image of 2,3,6,8,9-pentamethylphenanthridine (6e)]

**2,3,6,8,9-pentamethylphenanthridine (6e):**

White solid, mp: 157-159 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.45 (s, 3 H), 2.48 (s, 6 H), 2.53 (s, 3 H), 2.96 (s, 3 H), 7.82 (s, 1 H), 7.90 (s, 1 H), 8.22 (s, 1 H), 8.31 (s, 1 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 20.1, 20.3 (2 C), 20.7, 23.1, 121.7, 121.9 (2 C), 122.3, 124.3, 124.7, 126.6, 127.8, 129.0, 130.8, 136.1, 137.6, 157.3; HRMS: C$_{18}$H$_{19}$N calculated 249.1517, found 249.1517.

![Image of Triphenylene (7a)]

**Triphenylene (7a):**

White solid, mp: 197-199 °C; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.67 (dd, $J_1 = 7.0$ Hz, $J_2 = 3.0$ Hz, 6 H), 8.65 (dd, $J_1 = 7.0$ Hz, $J_2 = 3.0$ Hz, 6 H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 123.2, 127.1, 129.7; HRMS: C$_{18}$H$_{12}$ calculated 228.0939, found 228.0942. Registry Number: [217-59-4]
2,3,6,7,10,11-Hexamethyltriphenylene (7b):\textsuperscript{19}

White solid, mp: 277-279 °C; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 2.49 (s, 18 H), 8.32 (s, 6 H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 20.3, 123.6, 127.6, 135.3; HRMS: C\textsubscript{24}H\textsubscript{24} calculated 312.1878, found 312.1879. Registry Number: [26146-81-6]

2,3,6,7,10,11-Hexamethoxytriphenylene (7c):\textsuperscript{20}

White solid, mp: 330-332 °C; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \( \delta \) 4.11 (s, 18 H), 7.79 (s, 6 H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \( \delta \) 56.1, 104.3, 123.2, 148.8; HRMS: C\textsubscript{24}H\textsubscript{24}O\textsubscript{6} calculated 408.1573, found 408.1571. Registry Number: [808-57-1]

References

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