

Chromium-Mediated Synthesis of Polycyclic Aromatic Compounds from Halobiaryls

Ken-ichiro Kanno, Yuanhong Liu, Atsushi Iesato, Kiyohiko Nakajima[†], and Tamotsu Takahashi*

Catalysis Research Center, and Graduate School of Pharmaceutical Sciences, Hokkaido University, and SORST, Japan Science and Technology Agency (JST), Sapporo 001-0021, Japan; [†]Department of Chemistry, Aichi University of Education, Igaya, Kariya, Aichi 448-8542, Japan

tamotsu@cat.hokudai.ac.jp

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General Information. All reactions were carried out with standard Schlenk techniques under nitrogen. Tetrahydrofuran, hexane were distilled over sodium and benzophenone. Chromium(III) chloride was purchased from Soekawa Rikagaku Co. Ltd. 2,2-Dibromobiphenyl,¹ 2-bromobiphenyl,² 2-iodo-4'-methylbiphenyl,³ and 1-(2-iodophenyl)naphthalene² were prepared according to the literatures. All other reagents were commercially available and used without further purification. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or benzene-*d*₆ (containing 1% TMS) solutions on a Bruker-ARX400 or JEOL JNM-AL300 NMR spectrometers. GC analyses were performed on SHIMADZU GC-14A equipped with fused silica capillary column SHIMADZU CBP1-M25-025 and SHIMADZU C-R6A-Chromatopac integrator.

General Procedure for the Synthesis of Phenanthrene Derivatives using Chromium(III) Chloride: To a solution of 2,2'-dibromobiphenyl **1** (312 mg, 1.0 mmol) in THF at -78 °C, *n*-butyllithium (1.28 mL, 1.56 M, 2.0 mmol) was added and stirred for 1 h. Then the mixture was added with chromium(III) chloride (158 mg, 1.0 mmol) and warmed to room temperature. After 1 h, an alkyne (2 mmol) was added and the mixture was heated to 50 °C. The mixture was quenched by addition of 3 N HCl(aq.) and extracted with ethyl acetate. The organic layer was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding phenanthrene.

9,10-Diethylphenanthrene (2a): This compound was prepared from 2,2'-dibromobiphenyl and 3-hexyne. GC yield: 95%, Isolated yield: 75%, colorless solid, mp = 107-109 °C (lit.⁴ 105-107 °C); ¹H NMR (400 MHz, CDCl₃): δ 1.44 (t, *J* = 7.5 Hz, 6 H), 3.28 (q, *J* = 7.6 Hz, 4 H), 7.63-7.70 (m, 4 H), 8.19 (d, *J* = 8.5 Hz, 2 H), 8.77 (d, *J* = 7.2 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 15.37, 22.45, 123.31, 124.91, 125.72, 126.91, 130.21, 131.41, 135.15; HRMS calcd for C₁₈H₁₈: 234.1409, found: 234.1420.

9,10-Diphenylphenanthrene (2b): This compound was prepared from 2,2'-dibromobiphenyl and diphenylacetylene. Isolated yield: 48%, colorless solid, mp = 236-237 °C (lit.⁵ 238.5-239.0 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.14-7.25 (m, 10 H), 7.46-7.50 (m, 2 H), 7.55-7.57 (m, 2 H), 7.64-7.68 (m, 2 H), 8.80 (d, *J* = 8.3 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ 122.83, 126.73, 126.81, 126.96, 127.92, 128.18, 130.32, 131.38, 132.21, 137.53, 139.90; HRMS calcd for C₂₄H₁₈: 330.1409, found: 330.1420.

9-Methyl-10-phenylphenanthrene (2c): This compound was prepared from 2,2'-dibromobiphenyl and 1-phenyl-1-propyne. GC yield: 75%, Isolated yield: 58%, colorless solid, mp = 100-101 °C (lit.⁶ 99-100 °C); ¹H NMR (300 MHz, CDCl₃): δ 2.40 (s, 3 H), 7.18-7.66 (m, 10 H), 8.08-8.12 (m, 1 H), 8.66-8.74 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 17.31, 122.31, 122.85, 125.07, 125.60, 126.19, 126.33, 126.80, 127.02, 127.42, 128.39, 129.33, 129.936, 130.35, 131.88, 132.30, 137.06, 140.70; HRMS calcd for C₂₁H₁₆: 268.1252, found: 268.1241.

9-Butylphenanthrene (2d): This compound was prepared from 2,2'-dibromobiphenyl and 1-hexyne. GC yield: 75%, Isolated yield: 58%, colorless solid mp = 78-79 °C (lit.⁷ 79.5-80.5 °C); ¹H NMR (300 MHz, CDCl₃): δ 0.95 (t, *J* = 7 Hz, 3 H), 1.43 (qt, *J* = 7, 7 Hz, 2 H), 1.74 (tt, *J* = 7, 7 Hz, 2 H), 3.03 (t, *J* = 7 Hz, 2 H), 7.50-7.56 (m, 5 H), 7.74 (m, 1 H), 8.04 (d, *J* = 7 Hz, 1 H), 8.55 (d, *J* = 4 Hz, 1 H), 8.63 (d, *J* = 4 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 14.04, 22.91, 32.36, 33.13, 122.41, 123.18, 124.45, 125.79, 125.91, 126.02, 126.39, 126.50, 127.98, 129.62, 130.72, 131.36, 131.98, 136.90; HRMS calcd for C₁₈H₁₈: 234.1409, found: 234.1394.

9-Phenylphenanthrene (2e): This compound was prepared from 2,2'-dibromobiphenyl and phenylacetylene. GC yield: 63%, Isolated yield: 45%, colorless solid, mp = 86-87 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.28-7.55 (m, 10 H), 7.73-7.82 (m, 2 H), 8.55 (dd, *J* = 8.08 Hz, 1 H), 8.61 (d, *J* = 8.26 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 122.50, 122.87, 126.41, 126.47, 126.54, 126.80, 126.89, 127.32, 127.49, 128.27, 128.63, 129.93, 130.04, 130.60, 131.10, 131.53, 138.74, 140.77; HRMS calcd for C₂₀H₁₄: 254.1096, found: 254.1098.

9-(1-Butynyl)-10-ethylphenanthrene (2f): This compound was prepared from 2,2'-dibromobiphenyl and 3,5-octadiyne. GC yield: 67%, Isolated yield: 47%, colorless solid, mp = 92-93 °C; ¹H NMR (300 MHz, CDCl₃): δ 1.38 (t, *J* = 7.6 Hz, 3 H), 1.41 (t, *J* = 7.5 Hz, 3 H), 2.66 (q, *J* = 7.5 Hz, 2 H), 4.43 (q, *J* = 7.5 Hz, 2 H), 7.58-7.67 (m, 4

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H), 8.10-8.14 (m, 1 H), 8.48-8.51 (m, 1 H), 8.63-8.72 (m, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.65, 14.27, 14.39, 24.88, 77.17, 100.59, 118.55, 122.36, 123.09, 124.88, 126.11, 126.48, 126.73, 126.83, 127.01, 129.12, 130.11, 130.33, 131.52, 142.18; HRMS calcd for $\text{C}_{20}\text{H}_{18}$: 258.1409, found: 258.1421.

9-Phenyl-10-phenylethynylphenanthrene (2g): This compound was prepared from 2,2'-dibromobiphenyl and 1,4-diphenyl-1,3-butadiyne. Isolated yield: 45%, colorless solid, mp = 146-147 °C (lit.⁸ 143-144 °C); ^1H NMR (300 MHz, CDCl_3): δ 7.19-7.24 (m, 5 H), 7.44-7.71 (m, 10 H), 8.62-8.72 (m, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 87.76, 98.21, 119.03, 122.60, 122.63, 123.47, 126.72, 127.02, 127.14, 127.27, 127.34, 127.46, 127.74, 128.02, 128.12, 128.21, 129.68, 130.19, 130.66 (2C), 131.33, 131.40, 139.76, 142.94; HRMS calcd for $\text{C}_{28}\text{H}_{18}$: 354.1409, found: 354.1404.

9-Phenyl-10-trimethylsilylphenanthrene (2h): This compound was prepared from 2,2'-dibromobiphenyl and 1-phenyl-2-trimethylsilylacetylene, and purified by Kugelrohr distillation followed by recrystallization from pentane. GC yield: 88%, Isolated yield: 75%, colorless solid, mp = 172-173 °C; ^1H NMR (300 MHz, CDCl_3): δ 0.12 (s, 9 H), 7.37-7.50 (m, 3 H), 7.60-7.69 (m, 7 H), 8.33 (d, J = 7.7 Hz, 1 H), 8.73-8.81 (d, 2 H); HRMS calcd for $\text{C}_{23}\text{H}_{22}\text{Si}$: 326.1491, found: 326.1502.

9-Ethoxycarbonyl-10-methylphenanthrene (2i): This compound was prepared from 2,2'-dibromobiphenyl and ethyl 2-butynoate. GC yield: 46%, Isolated yield: 31%, colorless solid, mp = 88-89 °C (lit.⁹ 74 °C); ^1H NMR (300 MHz, CDCl_3): δ 1.40 (t, J = 7.2 Hz, 3 H), 2.62 (s, 3 H), 4.47 (q, J = 7.1 Hz, 2 H), 7.48-7.69 (m, 5 H), 8.02-8.05 (dd, 1 H), 8.58-8.61 (d, 1 H), 8.63 (d, J = 2.2 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.36, 17.06, 61.47, 122.70, 122.94, 125.08, 125.17, 126.39, 127.00, 127.12, 127.23, 128.13, 129.40, 129.56, 130.37, 130.39, 130.95, 170.35; HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2$: 264.1150, found: 264.1132.

9,10-Bis(methoxycarbonyl)phenanthrene (2j): This compound was prepared from 2,2'-dibromobiphenyl and dimethyl acetylenedicarboxylate. GC yield: 54%, Isolated yield: 43%, colorless solid, mp = 129-130 °C (lit.¹⁰ 130 °C); ^1H NMR (300 MHz, CDCl_3): δ 4.02 (s, 6 H), 7.60-7.71 (m, 4 H), 8.12 (d, J = 8.1 Hz, 2 H), 8.63 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 52.73, 122.77, 126.75, 126.91, 127.55, 128.38, 129.77, 130.93, 168.28; HRMS calcd for $\text{C}_{18}\text{H}_{14}\text{O}_4$: 294.0892, found 294.0871.

Synthesis of 1-Butyl-2,3,4-triphenylnaphthalene (3): *Trans*-1-lithio-2-*o*-lithiophenyl-1-phenyl-1-hexene was prepared from diphenylacetylene (178 mg, 1.0 mmol) and *n*-butyllithium (1.28 mL, 1.56 M, 2.0 mmol) in hexane and TMEDA according to the literatures.¹¹ The mixture was added with chromium(III) chloride (158 mg, 1.0 mmol) and stirred at room temperature for 1 h. After addition of diphenylacetylene (356 mg, 2.0 mmol), the mixture was heated to 50 °C for 6 h. The mixture was quenched by addition of 3 N HCl solution and extracted with ethyl acetate. The combined organic layer was dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel (hexane as eluent) to afford 1-butyl-2,3,4-triphenylnaphthalene **3**. GC yield: 99%, Isolated yield: 87%, colorless solid, ^1H NMR (300 MHz, CDCl_3): δ 0.80 (t, J = 7.3 Hz, 3 H), 1.25-1.36 (m, 2 H), 1.60-1.71 (m, 2 H), 2.91 (t, J = 8.3 Hz, 2 H), 6.74-6.84 (m, 5 H), 7.04-7.23 (m, 10 H), 7.34-7.39 (m, 1 H), 7.51-7.55 (m, 1 H), 7.59 (d, J = 8.3 Hz, 1 H), 8.16 (d, J = 8.4 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.71, 23.17, 30.05, 33.42, 124.51, 125.13, 125.52, 125.82, 125.97, 126.19, 126.40, 127.18, 127.037, 127.71, 130.37, 131.07, 131.15, 131.30, 132.33, 136.32, 136.83, 139.06, 139.08, 139.70, 140.80, 141.15; HRMS calcd for $\text{C}_{32}\text{H}_{28}$: 412.2191, found: 412.2197.

General procedure for the synthesis of phenanthrene derivatives from monohalogenated biaryls: To a THF solution of monohalobiphenyl (1.0 mmol), *n*-butyllithium (1.28 mL, 1.56 M, 2.0 mmol) was added at -78 °C and stirred for 1 h. Then the mixture was added with chromium(III) chloride (158 mg, 1.0 mmol) and warmed to room temperature. After 1 h, an alkyne (2 mmol) was added and the mixture was heated to 50 °C. The mixture was quenched by addition of 3 N HCl solution and extracted with ethyl acetate. The organic layer was separated, dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel which afforded the corresponding phenanthrene.

9,10-Diethylphenanthrene (2a): This compound was obtained from 2-bromobiphenyl and 3-hexyne in 69% GC yield. The spectral data were shown above.

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2-Methyl-9,10-diethylphenanthrene (5a): This compound was prepared from 2-iodo-4'-methylbiphenyl and 3-hexyne. GC yield: 68%, Isolated yield: 58%, colorless solid, mp = 109-110 °C; ¹H NMR (300 MHz, CDCl₃): δ 1.29 (t, *J* = 7.5 Hz, 6 H), 2.52 (s, 3 H), 3.08-3.15 (m, 4 H), 7.36 (d, *J* = 8.4 Hz, 1 H), 7.47-7.53 (m, 2 H), 7.82 (s, 1 H), 8.02-8.05 (m, 1 H), 8.51 (d, *J* = 8.4 Hz, 1 H), 8.59-8.62 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 15.03 (2C), 21.99, 22.02, 22.09, 122.75, 122.89, 124.24, 124.52, 125.28, 126.12, 127.06, 127.67, 129.89, 130.66, 131.16, 134.52, 134.81, 136.11; HRMS calcd for C₁₉H₂₀: 248.1565, found: 248.1572.

5,6-Diethylbenzo[*c*]phenanthrene (7a): This compound was prepared from 1-(2-iodophenyl)naphthalene and 3-hexyne. Isolated yield: 58%, colorless solid, ¹H NMR (300 MHz, CDCl₃): δ 1.35 (t, *J* = 8.1 Hz, 3 H), 1.78 (t, *J* = 8.1 Hz, 3 H), 3.18-3.27 (m, 4 H), 7.51-7.61 (m, 4 H), 7.87 (d, *J* = 9.0 Hz, 1 H), 7.93-7.95 (m, 1 H), 8.05 (d, *J* = 9.0 Hz, 1 H), 8.19 (d, *J* = 7.9 Hz, 1 H), 8.96 (dd, *J* = 7.3 Hz, *J* = 7.5 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 15.20, 15.48, 22.13, 22.32, 122.57, 123.99, 124.45, 125.49, 125.65, 125.88, 127.03, 127.23, 127.85, 128.63, 128.87, 129.42, 129.57, 130.224, 131.98, 132.60, 134.91, 135.33; HRMS calcd for C₂₂H₂₀: 284.1565, found: 284.1590.

5,6-Diphenylbenzo[*c*]phenanthrene (7b): This compound was prepared from 1-(2-iodophenyl)naphthalene and diphenylacetylene. Isolated yield: 28%, colorless solid, ¹H NMR (300 MHz, CDCl₃): δ 7.07-7.17 (m, 10 H), 7.40-7.68 (m, 7 H), 7.88 (d, *J* = 7.7 Hz, 1 H), 9.05 (d, *J* = 8.3 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 125.26, 125.60, 125.98, 126.01, 126.05, 126.50, 126.52, 127.06, 127.37, 127.44, 127.56, 127.59, 128.14, 128.23, 128.52, 129.70, 129.85, 130.11, 131.07, 131.18, 132.74, 133.10, 137.16, 137.51, 139.45, 139.63; HRMS calcd for C₃₀H₂₀: 380.1565, found: 380.1572.

9,10-Diethylbenzo[*g*]chrysene (9): 9-Phenyl-10-trimethylsilylphenanthrene **2h** was converted into 9-iodo-10-phenylphenanthrene **8** by the treatment with iodine monochloride according to the literature.³ Dilithiation of iodophenanthrene **8** (380 mg, 1.0 mmol) was carried out in toluene with *n*-butyllithium (1.28 mL, 1.56 M, 2.0 mmol) at 0 °C for 1 h. The resulting mixture was added with chromium(III) chloride (158 mg, 1.0 mmol) and THF, and stirred at room temperature for 1 h. After addition of 3-hexyne (0.23 mL, 2.0 mmol), the mixture was heated to 50 °C for 12 h. The reaction was quenched by addition of 3 N HCl solution and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel (hexane as eluent) to afford the corresponding benzo[*g*]chrysene **9**. Isolated yield: 22%, colorless solid, ¹H NMR (300 MHz, CDCl₃): δ 1.39 (t, *J* = 7.4 Hz, 3 H), 1.45 (t, *J* = 7.3 Hz, 3 H), 3.35 (q, *J* = 8.1 Hz, 2 H), 3.40 (q, *J* = 7.4 Hz, 2 H), 7.49-7.61 (m, 6 H), 8.20 (d, *J* = 8.1 Hz, 1 H), 8.29 (d, *J* = 7.9 Hz, 1 H), 8.60-8.71 (m, 4 H); ¹³C NMR (75 MHz, CDCl₃): δ 15.45, 16.87, 21.86, 25.49, 123.40, 123.50, 123.95, 124.66, 125.68, 125.85, 126.12, 126.14, 126.46, 128.28, 128.40, 128.60, 128.65, 129.33, 129.74, 129.80, 130.37, 130.54 (2C), 131.76, 134.76, 137.35; HRMS calcd for C₂₆H₂₂: 334.1721, found: 334.1740.

General procedure for the synthesis of pyrrolo[1,2-*a*]quinoline derivatives 11: To a hexane solution of 1-phenylpyrrole **10** (143 mg, 1.0 mmol) was added *n*-butyllithium (1.28 mL, 1.56 M, 2.0 mmol) in the presence of TMEDA (0.30 mL, 2.0 mmol) at -78 °C.¹² Then, the mixture was added chromium(III) chloride (158 mg, 1.0 mmol) and THF and stirred at room temperature. After 1 h, an alkyne (2 mmol) was added and the mixture was heated to 50 °C for 12 h. The reaction was quenched by addition of 3 N HCl solution and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel (hexane as eluent) to afford the corresponding pyrrolo[1,2-*a*]quinoline derivatives **11**.

4,5-Diethyl-pyrrolo[1,2-*a*]quinoline (11a): This compound was prepared from 1-phenylpyrrole and 3-hexyne. GC yield: 73%, Isolated yield: 68%, colorless solid, mp = 68-69 °C; ¹H NMR (300 MHz, CDCl₃): δ 1.19 (t, *J* = 7.4 Hz, 3 H), 1.23 (t, *J* = 7.5 Hz, 3 H), 2.78 (q, *J* = 7.5 Hz, 2 H), 2.86 (q, *J* = 7.5 Hz, 2 H), 6.42 (d, *J* = 2.6 Hz, 1 H), 6.68 (t, *J* = 3.2 Hz, 1 H), 7.23-7.39 (m, 2 H), 7.71-7.84 (m, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 14.23, 14.92, 20.35, 22.52, 100.46, 111.47, 112.31, 114.37, 123.32, 123.76, 125.04, 126.22, 126.50, 129.88, 131.79, 132.83; HRMS calcd for C₁₆H₁₇N: 223.1361, found: 223.1364.

4,5-Diphenyl-pyrrolo[1,2-*a*]quinoline (11b): This compound was prepared from 1-phenylpyrrole and diphenylacetylene. GC yield: 99%, Isolated yield: 83%, colorless solid, mp = 210-211 °C; ¹H NMR (300 MHz, CDCl₃): δ 6.24-6.25 (m, 1 H), 6.77-6.80 (dd, *J* = 3.3 Hz, 1 H), 7.15-7.29 (m, 11 H), 7.41-7.44 (m, 1 H), 7.49-7.55 (m, 1

¹² Faigl, F.; Schlosser, M. *Tetrahedron* **1993**, *49*, 10271.

H), 7.96 (d, $J = 8.1$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3): δ 104.27, 112.26, 112.91, 114.04, 123.38, 124.74, 126.71, 126.93, 127.56, 127.69, 127.76, 128.11, 128.41, 130.20, 130.83, 131.47, 131.99, 132.71, 137.60, 137.72; HRMS calcd for $\text{C}_{24}\text{H}_{17}\text{N}$: 319.1361, found: 319.1361.

Synthesis of 9b-azacyclopenta[cd]phenalene derivatives 12: 4,5-Diethyl-pyrrolo[1,2-*a*]quinoline **11a** (234 mg, 1.0 mmol) was dilithiated by the addition of *n*-butyllithium (1.28 mL, 1.56 M, 2.0 mmol) at -78 °C for 1 h in hexane in the presence of TMEDA (0.302 mL, 2.0 mmol). Then, to a solution of the reaction was added chromium(III) chloride (0.158 g, 1.0 mmol) and THF at room temperature. After 1 h, an alkyne (2 mmol) was added and the mixture was heated to 50 °C. The mixture was quenched by addition of 3 N HCl solution and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, and concentrated in vacuo. The residue was purified by a flash column chromatography on silica gel (hexane as eluent) to afford the corresponding 9b-azacyclopenta[cd]phenalene derivatives **12**.

3,4,8,9-Tetraethyl-9b-azacyclopenta[cd]phenalene (12a): This compound was prepared from pyrroloquinoline **11a** and 3-hexyne. Isolated yield: 39%, Yellow solid, mp = 193-194 °C; ^1H NMR (400 MHz, Benzene- d_6): δ 1.18 (t, $J = 7.5$ Hz, 6 H), 1.26 (t, $J = 7.6$ Hz, 6 H), 2.73-2.84 (m, 8 H), 6.97 (s, 2 H), 7.47 (s, 3 H); ^{13}C NMR (100 MHz, Benzene- d_6): δ 13.94, 15.52, 21.65, 23.30, 104.07, 116.72, 124.09, 126.19, 127.79, 128.05, 130.78, 132.65; HRMS calcd for $\text{C}_{22}\text{H}_{25}\text{N}$: 303.1987, found: 303.1984.

3,4-Diethyl-8,9-diphenyl-9b-azacyclopenta[cd]phenalene (12b): This compound was prepared from pyrroloquinoline **11a** and diphenylacetylene. Isolated yield: 55%, Light yellow solid, mp = 225-226 °C; ^1H NMR (400 MHz, Benzene- d_6): δ 1.30 (t, $J = 7.5$ Hz, 3 H), 1.38 (t, $J = 7.5$ Hz, 3 H), 2.84-2.94 (m, 4 H), 6.98-7.01 (m, 2 H), 7.09-7.46 (m, 12 H), 7.53 (d, $J = 7.7$ Hz, 1 H); ^{13}C NMR (100 MHz, Benzene- d_6): δ 13.86, 15.50, 21.68, 23.30, 104.78, 107.31, 117.48, 119.46, 124.14, 125.95, 127.53, 127.68, 127.91, 128.02, 128.32, 128.78, 129.31, 130.02, 131.08, 131.30, 131.86, 132.02, 133.14, 138.91, 139.24; HRMS calcd for $\text{C}_{30}\text{H}_{25}\text{N}$: 399.1987, found: 399.1964.

3,4-Diethyl-8,9-di-*p*-tolyl-9b-azacyclopenta[cd]phenalene (12c): This compound was prepared from pyrroloquinoline **11a** and di-*p*-tolylacetylene. Isolated yield: 49%, Light yellow solid, mp = 196-197 °C; ^1H NMR (300 MHz, Benzene- d_6): δ 1.21 (t, $J = 7.4$ Hz, 3 H), 1.28 (t, $J = 7.5$ Hz, 3 H), 2.01 (s, 3 H), 2.05 (s, 3 H), 2.74-2.85 (m, 4 H), 6.93-6.99 (m, 5 H), 7.17-7.98 (m, 5 H), 7.29-7.35 (m, 2 H), 7.42-7.47 (m, 1 H); ^{13}C NMR (75 MHz, DMSO- d_6 , 423 K): δ 11.90, 13.36, 19.37, 19.69, 19.71, 20.93, 103.14, 105.14, 115.86, 117.36, 122.51, 123.85, 125.52, 126.24, 126.36, 127.34, 127.51, 128.07, 128.11, 129.03, 129.59, 129.71, 129.88, 130.51, 133.61, 133.95, 135.21, 135.46; HRMS calcd for $\text{C}_{32}\text{H}_{29}\text{N}$: 427.2300, found: 427.2293.

3,4-Diethyl-8,9-di(2-thienyl)-9b-azacyclopenta[cd]phenalene (12d): This compound was prepared from pyrroloquinoline **11a** and bis(2-thienyl)acetylene. Isolated yield: 38%, Light yellow solid, mp = 188-189 °C; ^1H NMR (300 MHz, Benzene- d_6): δ 1.17 (t, $J = 7.8$ Hz, 3 H), 1.25 (t, $J = 7.5$ Hz, 3 H), 2.68-2.79 (m, 4 H), 6.74-4.77 (m, 1 H), 6.82-6.93 (m, 3 H), 6.98 (d, $J = 4.6$ Hz, 1 H), 7.13-7.15 (m, 2 H), 7.27 (dd, $J = 7.9$ Hz, 1 H), 7.36 (d, $J = 7.7$ Hz, 1 H), 7.47 (d, $J = 7.7$ Hz, 1 H); ^{13}C NMR (75 MHz, DMSO- d_6 , 423 K): δ 11.84, 13.29, 19.39, 20.92, 103.76, 106.39, 116.63, 117.60, 121.36, 122.86, 123.75, 125.28, 125.36, 125.48, 125.62, 125.99, 126.10, 126.29, 126.94, 127.88, 128.22, 128.30, 129.67, 130.37, 136.58, 137.25; HRMS calcd for $\text{C}_{26}\text{H}_{21}\text{NS}$: 411.1115, found: 411.1118.

Table 1. Crystallographic Data and Experimental Details of 3,4-Diethyl-8,9-diphenyl-9b-azacyclopenta[*cd*]phenalene (**12b**)

Compound	9b-azacyclopenta[<i>cd</i>]phenalene (12b)
Formula	C ₃₀ H ₂₅ N
<i>M</i>	399.53
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , (Å)	17.979(2)
<i>b</i> , (Å)	10.718(1)
<i>c</i> , (Å)	11.977(1)
β , (°)	104.943(8)
<i>V</i> , (Å ³)	2230.0(4)
<i>Z</i>	4
μ (Mo <i>K</i> α), (cm ⁻¹)	4.854(4)
Crystal color	yellow
Crystal habit	prism
Crystal size, (mm ³)	0.20 x 0.25 x 0.30
D _{calcd} , (g/cm ³)	1.190
<i>F</i> (000)	848
Diffractometer	Rigaku AFC7S
λ (Mo <i>K</i> α), (Å)	1.5418
<i>T</i> , (K)	298.2
Data Images	44 exposures at 4.0 minutes per degree
Oscillation Ranges ($\varphi=0.0^\circ$, $\chi=45.0^\circ$)	ω 130.0 – 190.0° with 5.0° step
Oscillation Ranges ($\varphi=180.0^\circ$, $\chi=45.0^\circ$)	ω 0.0 – 162.0° with 5.0° step
2 θ max, (°)	55
No. of reflections meads	4215(Unique: 4215, <i>R</i> _{int} = 0.035)
No. of reflections obsd [<i>I</i> >2 σ (<i>I</i>)]	2852
No. of parameters refined	281
<i>R</i>	0.0984
<i>R</i> _w	0.1373
<i>S</i> , goodness of fit	3.383
(Δ/δ)max	0.0002
Largest diff peak, (e Å ⁻³)	0.59
Largest diff hole, (e Å ⁻³)	-0.22

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}}{w}, w = [\sigma^2(F_o) + (p^2/4)|F_o|^2]^{-1}, p = 0.00063$$

$$S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2} \quad (m = \text{no. of used reflections}, n = \text{no. of refined parameters})$$

Table 2. Intramolecular Distances (Å) Involving the Nonhydrogen Atoms of 3,4-Diethyl-8,9-diphenyl-9b-azacyclopenta[*cd*]phenalene (**12b**)

N(1)-C(1)	1.373(5)	C(9)-C(10)	1.379(6)
N(1)-C(9)	1.385(5)	C(10)-C(11)	1.550(10)
N(1)-C(12)	1.378(5)	C(11)-C(12)	1.513(9)
C(1)-C(2)	1.398(5)	C(12)-C(13)	1.427(7)
C(1)-C(6)	1.397(5)	C(13)-C(14)	1.369(7)
C(2)-C(3)	1.360(7)	C(13)-C(27)	1.515(7)
C(2)-C(14)	1.451(7)	C(14)-C(29)	1.510(7)
C(3)-C(4)	1.222(9)	C(15)-C(16)	1.408(6)
C(4)-C(5)	1.318(8)	C(15)-C(20)	1.383(6)
C(5)-C(6)	1.375(6)	C(16)-C(17)	1.363(7)
C(6)-C(7)	1.464(5)	C(17)-C(18)	1.388(8)
C(7)-C(8)	1.365(5)	C(18)-C(19)	1.373(8)
C(7)-C(15)	1.491(5)	C(19)-C(20)	1.404(7)
C(8)-C(9)	1.442(6)	C(21)-C(22)	1.369(7)
C(8)-C(21)	1.507(6)	C(21)-C(26)	1.380(6)

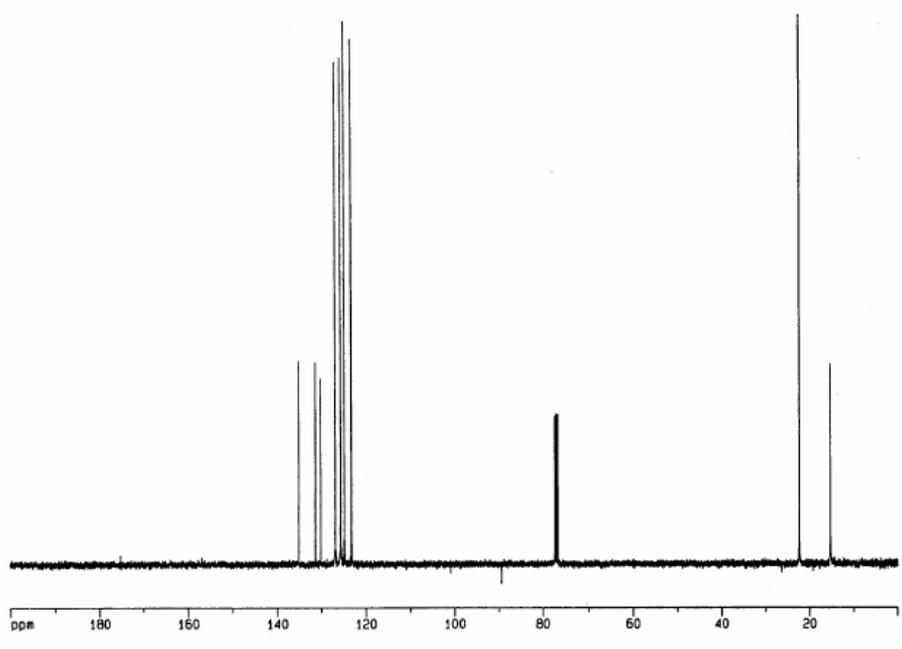
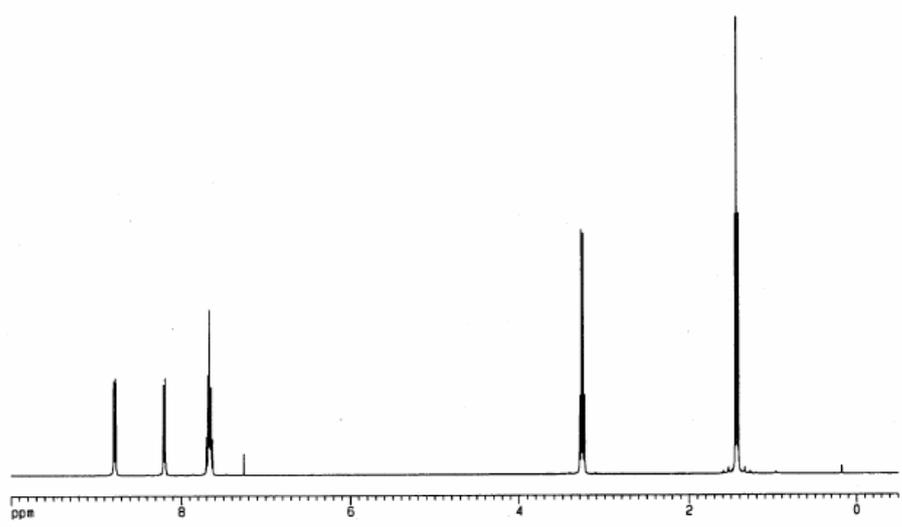
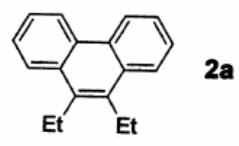
C(22)-C(23)	1.391(7)	C(25)-C(26)	1.373(6)
C(23)-C(24)	1.363(8)	C(27)-C(28)	1.539(9)
C(24)-C(25)	1.371(8)	C(29)-C(30)	1.53(1)

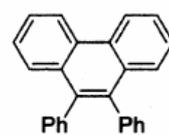
Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Intramolecular Bond Angles (°) Involving the Nonhydrogen Atoms of 3,4-Diethyl-8,9-diphenyl-9b-azacyclopenta[*cd*]phenalene (**12b**)

C(1)-N(1)-C(9)	123.1(3)	N(1)-C(12)-C(13)	120.2(4)
C(1)-N(1)-C(12)	121.7(4)	C(11)-C(12)-C(13)	136.4(5)
C(9)-N(1)-C(12)	115.2(4)	C(12)-C(13)-C(14)	119.2(4)
N(1)-C(1)-C(2)	119.7(4)	C(12)-C(13)-C(27)	116.2(5)
N(1)-C(1)-C(6)	120.4(3)	C(14)-C(13)-C(27)	124.6(5)
C(2)-C(1)-C(6)	120.0(4)	C(2)-C(14)-C(13)	120.0(4)
C(1)-C(2)-C(3)	114.8(5)	C(2)-C(14)-C(29)	117.1(6)
C(1)-C(2)-C(14)	119.2(4)	C(13)-C(14)-C(29)	122.9(6)
C(3)-C(2)-C(14)	126.0(5)	C(7)-C(15)-C(16)	119.9(4)
C(2)-C(3)-C(4)	128.2(7)	C(7)-C(15)-C(20)	121.2(4)
C(3)-C(4)-C(5)	117.2(7)	C(16)-C(15)-C(20)	118.8(4)
C(4)-C(5)-C(6)	125.0(5)	C(15)-C(16)-C(17)	120.9(5)
C(1)-C(6)-C(5)	114.6(4)	C(16)-C(17)-C(18)	120.4(5)
C(1)-C(6)-C(7)	118.0(3)	C(17)-C(18)-C(19)	119.6(5)
C(5)-C(6)-C(7)	127.4(4)	C(18)-C(19)-C(20)	120.6(5)
C(6)-C(7)-C(8)	120.2(4)	C(15)-C(20)-C(19)	119.7(5)
C(6)-C(7)-C(15)	117.8(3)	C(8)-C(21)-C(22)	120.9(4)
C(8)-C(7)-C(15)	122.0(4)	C(8)-C(21)-C(26)	119.5(4)
C(7)-C(8)-C(9)	120.8(4)	C(22)-C(21)-C(26)	119.6(4)
C(7)-C(8)-C(21)	122.1(4)	C(21)-C(22)-C(23)	119.4(5)
C(9)-C(8)-C(21)	117.2(3)	C(22)-C(23)-C(24)	121.0(6)
N(1)-C(9)-C(8)	117.5(3)	C(23)-C(24)-C(25)	119.2(5)
N(1)-C(9)-C(10)	110.2(4)	C(24)-C(25)-C(26)	120.5(5)
C(8)-C(9)-C(10)	132.2(4)	C(21)-C(26)-C(25)	120.3(5)
C(9)-C(10)-C(11)	105.1(4)	C(13)-C(27)-C(28)	112.0(5)
C(10)-C(11)-C(12)	106.1(5)	C(14)-C(29)-C(30)	111.3(6)
N(1)-C(12)-C(11)	103.4(5)		

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.





2b

