SUPPORTING INFORMATION

Carbopalladation of Nitriles: Synthesis of 2,3-Diarylindenones and Polycyclic Aromatic Ketones by the Pd-Catalyzed Annulation of Alkynes and Bicyclic Alkenes by 2-Iodoarenenitriles

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General. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz or 400 and 100 MHz, respectively. Thin-layer chromatography was performed using commercially prepared 60-mesh silica gel plates (Whatman K6F), and visualization was effected with short wavelength UV light (254 nm) and basic KMnO_4 solution [3 g of KMnO_4 + 20 g of K_2CO_3 + 5 mL of NaOH (5%) + 300 mL of H_2O]. All melting points are uncorrected. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. IR spectra were measured on a Bomem Michelson MB-102 FT-IR spectrometer. All reagents were used directly as obtained commercially unless otherwise noted. $\text{Pd}(\text{OAc})_2$ was donated by Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. PPh_3 was also donated by Kawaken Fine Chemicals Co., Ltd. $\text{Pd}(\text{dba})_2$ was prepared according to a published procedure.¹ 2-Iodobenzonitrile was obtained from Trans World Chemicals, Inc. Diphenylacetylene, acenaphthylene, norbornene, 2,2,6,6-tetramethylpiperidine, 5-nitroanthranilonitrile, indole-2-carboxylic acid, ethyl indole-2-carboxylate, indole-3-carbonitrile, 4-methoxy-2-nitroaniline, triethylamine, 4-octyne, 2,2,7,7-tetramethyl-3,5-octadiyne, 1-cyanonaphthalene, 9-cyanophenanthrene, 3-methoxybenzonitrile, 1,2-dicyanobenzene, 1,4-dicyanobenzene, and 3-cyanopyridine were obtained from Aldrich Chemical Co., Inc. Bicyclo[2.2.2]octene was obtained from Wiley Organics. Tetra-*n*-butylammonium chloride, (2-iodophenyl)acetonitrile, 4,4-dimethyl-2-pentyne, and thiophene-3-carbonitrile were obtained from Lancaster Synthesis, Inc. 1-Phenyl-1-propyne and 2-methyl-4-phenyl-3-butyn-2-ol were obtained from Farchan Laboratories, Inc.

Starting materials. Dimethyl *cis,endo*-5-norbornene-2,3-dicarboxylate,² benzonorbornadiene,³ and 2-iodoindole⁴ were prepared according to published procedures.

General Procedure for the Preparation of 2-Iodoarene carbonitriles via Nitrile-Directed *o*-Lithiation - Iodination. To a solution of 2,2,6,6-tetramethylpiperidine (0.85 g, 6.0 mmol) in 25 mL of anhydrous THF at 0 °C under Ar was added 4 mL of 1.5 M solution of MeLi (6 mmol) in hexane. The resulting solution was stirred at 0 °C for 30 min, cooled to -78 °C, and 6 mmol of an aromatic nitrile (as a solution in THF, if solid) was added slowly. The dark solution was stirred for 35-60 min at -78 °C, after which a solution of I_2 (1.68 g, 6.6 mmol) in 2.5 mL of THF was added. After stirring for 2 h at -78 °C, the mixture was allowed to warm up to room temperature and stirred for 1 h. Then, 20 mL of ice-water was added, the mixture was extracted with ether, the ethereal extracts were combined, and washed with dilute HCl, water, aq $\text{Na}_2\text{S}_2\text{O}_3$, and brine. After drying over MgSO_4 , the ether was removed, and the product was purified by column chromatography or recrystallization.

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The following compounds, prepared by the above procedure, have been previously reported: 1-cyano-2-iodonaphthelene (**19**),⁵ 9-cyano-10-iodophenanthrene (**20**),⁶ 1,4-dicyano-2-iodobenzene (**22**),⁷ and 2-iodothiophene-3-carbonitrile (**26**).⁸

2-Iodo-3-methoxybenzonitrile (21). Obtained in a 50% yield from 3-methoxybenzonitrile under the indicated conditions after recrystallization from hexanes: white solid, mp 121-122 °C (hexanes); ¹H NMR (CDCl₃) δ 3.93 (s, 3H), 7.00 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 56.8, 91.1, 114.4, 119.4, 122.1, 126.3, 129.9, 159.1; IR (neat) 2228, 2840, 3082 cm⁻¹; HRMS *m/z* 258.94988 (calcd for C₈H₆INO, 258.94942).

2,3-Dicyano-1,4-diiodobenzene (23). Obtained in a 74% yield from two consecutive lithiations of 1,2-dicyanobenzene under the indicated conditions after recrystallization from acetone: light yellow solid, mp (dec.) 230-232 °C (acetone); ¹H NMR (CDCl₃) δ 7.80 (s, 2H); ¹³C NMR (CDCl₃) δ 98.6, 115.8, 125.5, 143.5; IR (neat) 2225 cm⁻¹; HRMS *m/z* 379.83123 (calcd for C₈H₂I₂N₂, 379.83075).

3-Cyano-4-iodopyridine (24) and 3-cyano-2-iodopyridine (25). Obtained in a 50% combined yield from the reaction of 3-cyanopyridine under the indicated conditions. The mixture of **24** and **25** was partially separated by column chromatography using 1:2 hexanes/EtOAc. Nitrile **24**: light yellow solid, mp (dec.) 114-119 °C (hexanes/EtOAc); ¹H NMR (CDCl₃) δ 7.91 (d, *J* = 5.6 Hz, 1H), 8.39 (d, *J* = 5.2 Hz, 1H), 8.73 (s, 1H); ¹³C NMR (CDCl₃) δ 109.6, 115.3, 134.0, 141.1, 152.1, 153.1; IR (neat) 2231 cm⁻¹; HRMS *m/z* 229.93441 (calcd for C₆H₃IN₂, 229.93410). Nitrile **25**: beige solid, mp (dec.) 120-122 °C (hexanes/EtOAc); ¹H NMR (CDCl₃) δ 7.43 (m, 1H), 7.82 (m, 1H), 8.54 (dd, *J* = 4.8, 2.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 117.7, 119.9, 121.0, 122.5, 141.2, 152.9; IR (neat) 2228 cm⁻¹; HRMS *m/z* 229.93441 (calcd for C₆H₃IN₂, 229.93410).

3-Iodoindole-2-carbonitrile (27a). *From indole-2-carboxylic acid:* the acid was converted to indole-2-carbonitrile by a published procedure.⁹ To a cooled solution of indole-2-carboxylic acid (2.0 g, 12.4 mmol) in 60 mL of anhydrous Et₂O was added 1.9 mL of SOCl₂ (26 mmol). After stirring for 40 min at room temperature, the ether was removed under reduced pressure at a temperature not exceeding 35 °C. The obtained acyl chloride was dissolved in 40 mL of anhydrous Et₂O and the resulting solution was added immediately to a stirred solution of liquid ammonia in 80 mL of Et₂O. The reaction mixture was stirred at room temperature for 24 h. The solvent was then evaporated under reduced pressure, and the white indole-

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2-carboxamide was crystallized from 50% aq EtOH and dried in air, after which it was dissolved in POCl₃ and heated under reflux for 5 min. The cooled solution was poured onto crushed ice and aq NH₄OH was added to maintain a basic pH. The aqueous mixture was extracted with Et₂O, the extracts were dried over Na₂SO₄ and evaporated. The brown indole-2-carbonitrile (68% overall yield from indole-2-carboxylic acid) was recrystallized from 33% aq EtOH, dried, and iodinated according to the procedure of Chashi *et al.*¹⁰ A cold solution of I₂ (0.72 g, 2.8 mmol) in 6 mL of DMF was added to a solution of indole-2-carbonitrile (0.4 g, 2.8 mmol) and powdered KOH (0.56 g, 10 mmol) in 6 mL of DMF. After stirring at room temperature for 4 h, the reaction mixture was poured into 600 mL of water containing 40 mL of 30% aq NH₄OH. The precipitate was collected by filtration and dried to afford 0.56 g (75%) of **27a**, whose spectral properties matched those previously reported.¹¹

3-Iodoindole-2-carbonitrile (27a). From *ethyl indole-2-carboxylate*: the ester (1.5 g, 7.93 mmol) was quantitatively reduced with LiAlH₄ (0.553 g, 14.55 mmol) in ether at room temperature, and the resulting 2-(hydroxymethyl)indole was oxidized to indole-2-carbaldehyde with MnO₂.¹² The aldehyde was converted into indole-2-carbonitrile as follows:¹³ a solution of the crude indole-2-carbaldehyde (0.9 g, 6.2 mmol) and H₂NNMe₂ (1.116 g, 18.6 mmol) in 35 mL of dry benzene was refluxed with a Dean-Stark separator for 4 h, concentrated to half the volume with the trap open, cooled to room temperature, and MeI (1.16 mL, 18.6 mmol) was added. The reaction mixture was refluxed for 2 h, cooled, diluted with Et₂O and filtered to collect the white precipitate, which was dried in a dessicator and added to a freshly prepared solution of NaOMe (made from 6.52 mmol of Na and 20 mL of MeOH). The resulting mixture was refluxed for 4 h, after which MeOH was evaporated to afford crude indole-2-carbonitrile (66% yield), which was converted into **27a** as described above.¹⁰

N-Methyl-3-iodoindole-2-carbonitrile (27b). A solution of **27a** (1.03 g, 3.83 mmol) in 1 mL of DMF was slowly added to a suspension of NaH (0.184 g, 7.66 mmol) in 2 mL of DMF at 0 °C under Ar. After stirring for 30 min at room temperature, MeI (0.36 mL, 5.75 mmol) was added over a few minutes. The mixture was then stirred for 1 h at room temperature, cooled in ice, diluted with aq NH₄OH and extracted with Et₂O. The ethereal extracts were combined, dried over Na₂SO₄, evaporated and chromatographed (2:1 hexanes-EtOAc) to afford **27b** in 84% yield: light yellow solid, mp 106-107 °C (hexanes-EtOAc); ¹H NMR (CDCl₃) δ 3.88 (s, 3H), 7.23-7.29 (m, 2H), 7.41-7.45 (m, 2H); ¹³C NMR (CDCl₃) δ 32.4, 69.1, 110.3,

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113.1, 122.1, 122.7, 126.7, 129.2, 137.6 (1 sp^2 carbon missing due to overlap); IR (neat) 2219, 2926, 3065 cm^{-1} ; HRMS m/z 281.96592 (calcd for $\text{C}_{10}\text{H}_7\text{IN}_2$, 281.96540).

***N*-Benzenesulfonyl-3-iodoindole-2-carbonitrile (27c).** Obtained in 96% yield following the procedure for **27b** using PhSO_2Cl instead of MeI after extraction with EtOAc and column chromatography with 2:1 hexanes-EtOAc: off-white solid, mp 210-211 $^\circ\text{C}$ (hexanes-EtOAc); ^1H NMR (CDCl_3) δ 7.42-7.44 (m, 2H), 7.50-7.54 (m, 2H), 7.58-7.64 (m, 2H), 8.03-8.05 (m, 2H), 8.20 (d, J = 8.4 Hz, 1H); ^{13}C NMR (CDCl_3) δ 85.6, 112.2, 114.5, 123.6, 125.4, 127.2, 129.7, 129.8, 130.7, 135.0, 135.9, 137.0 (1 sp^2 carbon missing due to overlap); IR (neat) 1184, 1379, 2231, 3086 cm^{-1} ; HRMS m/z 407.94341 (calcd for $\text{C}_{15}\text{H}_9\text{IN}_2\text{O}_2\text{S}$, 407.94295).

2-Iodoindole-3-carbonitrile (28a) was obtained according to a modified procedure of Vorbrüggen.¹⁴ To a solution of 2-iodoindole (0.24 g, 1 mmol) in 2 mL of MeCN, kept in an ice-water bath, was slowly added 0.09 mL (1.05 mmol) of ClSO_2NCO . The reaction mixture was stirred for 2 h at 0 $^\circ\text{C}$, after which Et_3N (0.146 mL, 1.05 mmol) was added dropwise. After stirring for another 2 h at room temperature, the mixture was poured into ice water and extracted with Et_2O . The extracts were dried with Na_2SO_4 and chromatographed using 1:1 hexanes-EtOAc to afford **28a** in 40% yield: white solid, mp 185-186 $^\circ\text{C}$ (hexanes-EtOAc); ^1H NMR (CDCl_3) δ 7.24-7.29 (m, 2H), 7.41-7.43 (m, 1H), 7.68-7.70 (m, 1H), 8.82 (br s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 92.5, 94.0, 112.0, 116.5, 117.5, 121.9, 123.5, 128.2, 138.0; IR (neat) 2217, 3246 cm^{-1} ; HRMS m/z 267.95012 (calcd for $\text{C}_9\text{H}_5\text{IN}_2$, 267.94975).

***N*-Methyl-2-iodoindole-3-carbonitrile (28b).** Indole-3-carbonitrile was methylated according to the procedure for **27b**, and the *N*-methyl derivative was converted into crude **28b** by nitrile-directed *o*-lithiation-iodination as described above. Recrystallization from 2:1 hexanes-EtOAc afforded **28b** in 91% yield: beige solid, mp 148-149 $^\circ\text{C}$ (hexanes-EtOAc); ^1H NMR (CDCl_3) δ 3.76 (s, 3H), 7.18-7.25 (m, 2H), 7.31 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H); ^{13}C NMR (CDCl_3) δ 35.1, 94.9, 95.8, 110.6, 116.2, 118.5, 122.2, 123.8, 128.6, 137.3; IR (neat) 2213, 2932, 3058 cm^{-1} ; HRMS m/z 281.96601 (calcd for $\text{C}_{10}\text{H}_7\text{IN}_2$, 281.96540). Alternatively, **28b** was obtained from **28a** by methylation according to the procedure for **27b**.

***N*-Benzenesulfonyl-2-iodoindole-3-carbonitrile (28c)** was obtained from **28a** by sulfonylation according to the procedure for **27c** and recrystallized from 2:1 hexanes-EtOAc, 95% yield: white solid, mp 191-192 $^\circ\text{C}$ (hexanes-EtOAc); ^1H NMR (CDCl_3) δ 7.35-7.43 (m, 2H), 7.50-7.55 (m, 2H), 7.60-7.68 (m, 2H), 7.97-8.00 (m, 2H), 8.32-8.35 (m, 1H); ^{13}C NMR (CDCl_3) δ 87.0, 114.5, 115.5, 119.1, 125.1, 126.6, 127.4, 129.3, 129.6, 130.1, 135.0, 137.6 (1 sp^2 carbon missing due to overlap); IR (neat) 1194, 1378, 2228 cm^{-1} ; HRMS m/z 407.94341 (calcd for $\text{C}_{15}\text{H}_9\text{IN}_2\text{O}_2\text{S}$, 407.94295). Nitrile-directed *o*-lithiation-iodination of

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N-benzenesulfonyl indole-3-carbonitrile led to a hard-to-separate mixture of **28c**, unreacted starting material, and 2-iodoindole-3-carbonitrile.

2-Iodo-5-nitrobenzonitrile (29) was prepared by the procedure of Clive *et al.*¹⁵ A solution of NaNO₂ (0.56 g, 8.1 mmol) in 2.5 ml of water was added, with stirring, to a cold (0 °C) solution of 5-nitroanthranilonitrile (1.2 g, 7.35 mmol) in 10 ml of concentrated HCl and 15 g of ice. The mixture was stirred at 0 °C for 30 min and the cold solution, maintained at 0 °C, was added dropwise over 20-30 min to a stirred solution (room temperature) of KI (12.2 g, 73 mmol) in 15 ml of water. The resulting mixture was stirred at room temperature overnight and extracted with CH₂Cl₂. The extracts were washed with 10% aq NaOH solution, 5% aq NaHCO₃, and water, and dried over MgSO₄. 2-Iodo-5-nitrobenzonitrile (**29**) was obtained in 65% yield upon column chromatography with 1:1 hexanes-CH₂Cl₂: yellowish solid, mp 116-117 °C (EtOH); ¹H NMR (CDCl₃) δ 8.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.44 (d, *J* = 2.4 Hz, 1H); ¹³C NMR (CDCl₃) δ 106.9, 117.4, 122.2, 127.6, 128.6, 128.9, 141.0; IR (neat) 1360, 1502, 2233 cm⁻¹; HRMS *m/z* 273.92429 (calcd for C₇H₃IN₂O₂, 273.92393).

2-Iodo-4-methoxybenzonitrile (30). 2-Nitroanisidine was converted into 4-methoxy-2-nitrobenzonitrile by the procedure of Rapaport.¹⁶ 2-Nitroanisidine (1.68 g, 10 mmol) was diazotized at 0 °C as described in the procedure for **29**. The solution of the resulting diazonium salt was neutralized by addition of solid Na₂CO₃ and added slowly, with stirring, to a suspension of CuCN (0.94 g, 10.5 mmol) and NaCN (1.03 g, 21 mmol) in 6 mL of H₂O at 0 °C. The reaction mixture was stirred for 1 h at room temperature, the precipitate was dissolved in CH₂Cl₂, the aqueous layer was discarded, and the organic layer was washed with water, dried over Na₂SO₄ and evaporated to afford 4-methoxy-2-nitrobenzonitrile (73% yield), which was used without further purification. 4-Methoxy-2-nitrobenzonitrile (0.7 mmol) was dissolved in 3 mL of a 5:4:1 DME-EtOH-AcOH mixture, a solution of SnCl₂ (5.5 mmol) in the same solvent mixture was added dropwise with stirring, the reaction mixture was stirred at room temperature for 5 min, then at 65 °C for 3 h, and worked up to afford a quantitative yield of 2-amino-4-methoxybenzonitrile. Using the procedure for **29**, 2-amino-4-methoxybenzonitrile was converted into **30**, which was obtained in 61% yield after column chromatography with 1:1 hexanes-CH₂Cl₂: yellow solid, mp 76-78 °C (EtOH); ¹H NMR (CDCl₃) δ 3.86 (s, 3H), 6.95 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) δ 55.8, 99.2, 112.1, 114.4, 119.6, 124.9, 135.1, 162.4; IR (neat) 2218, 2841, 3090 cm⁻¹; HRMS *m/z* 258.94988 (calcd for C₈H₆INO, 258.94942).

General Procedure for the Palladium-Catalyzed Annulation of Alkynes and Bicyclic Alkenes with 2-Iodoarenenitriles. Palladium bis(dibenzylideneacetone) (14.4 mg, 0.025 mmol), Et₃N (25.3 mg, 0.25

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mmol), the 2-iodoarenenitrile (0.25 mmol), the alkyne or bicyclic alkene (0.75 mmol), and 5 mL of a 9:1 DMF-water mixture were placed in a 4 dram vial, which was heated in an oil bath at 130 °C for the appropriate period of time. The reaction mixture was cooled, diluted with ether, washed with satd aq NH_4Cl , dried over anhydrous Na_2SO_4 , and filtered. The solvent was evaporated under reduced pressure and the product was isolated by chromatography on a silica gel column.

The following compounds, prepared by the above procedure, have been previously reported by us: indenones **1**, **3-7** and **9**, polycyclic aromatic ketones **11** and **12**, and naphthenone **16**.^{17,18} Also, 2,3-diphenyl-1*H*-benz[*g*]inden-1-one (**31**),¹⁹ 1-oxo-2,3-diphenyl-1*H*-cyclopenta[*l*]phenanthrene (**33**),²⁰ 1-oxo-2,3-dihydro-2,3-diphenyl-1*H*-cyclopenta[*l*]-phenanthrene (**34**),^{20,21} 3,3'-dicyano-2,2'-bithiophene (**39**),²² 4-methoxy-2,3-diphenyl-1-indenone (**45**),²³ and 5-methoxy-2,3-diphenyl-1-indenone (**46**)²³ have been described elsewhere.

3-Phenyl-2-(2-propenyl)-1-indenone (8). Obtained in a 6% yield from the reaction of 2-methyl-4-phenyl-3-butyn-2-ol and 2-iodobenzonitrile according to the general procedure at 100 °C after purification by column chromatography using 20:1 hexanes/EtOAc: orange solid, mp 104-106 °C (hexanes-EtOAc); ^1H NMR (CDCl_3) δ 1.71 (s, 3H), 5.23-5.24 (m, 1H), 5.26-5.28 (m, 1H), 7.05 (d, $J = 7.2$ Hz, 1H), 7.24-7.26 (m, 1H), 7.30-7.33 (m, 1H), 7.45-7.53 (m, 6H); ^{13}C NMR (CDCl_3) δ 22.5, 120.1, 121.1, 122.8, 128.0, 128.5, 128.6, 128.7, 129.2, 130.8, 133.2, 133.3, 134.9, 145.3, 154.5, 196.2; IR (neat) 1703, 2970, 3033 cm^{-1} ; HRMS m/z 246.10475 (calcd for $\text{C}_{18}\text{H}_{14}\text{O}$, 246.10447).

1-(2-Cyanophenyl)acenaphthylene (10). Obtained in a 57% yield from the reaction of acenaphthylene and 2-iodobenzonitrile according to the general procedure at 100 °C after purification by column chromatography using 20:1 hexanes/EtOAc: bright yellow solid, mp 168-170 °C (benzene); ^1H NMR (CDCl_3) δ 7.42-7.48 (m, 1H), 7.50 (s, 1H), 7.57-7.64 (m, 2H), 7.65-7.71 (m, 1H), 7.72-7.84 (m, 4H), 7.86-7.90 (m, 2H); ^{13}C NMR (CDCl_3) δ 111.5, 119.0, 124.3, 125.5, 127.6, 127.7, 128.0, 128.1, 128.3, 128.6, 128.8, 129.9, 130.4, 132.7, 134.3, 138.3, 138.5, 138.9, 139.5; IR (neat) 2223, 3043, 3062 cm^{-1} ; HRMS m/z 253.08946 (calcd for $\text{C}_{19}\text{H}_{11}\text{N}$, 253.08915).

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Dimethyl 1,2,3,4,4a,9a-hexahydro-1,4-methano-9-oxofluorene-*cis,endo*-2,3-dicarboxylate (13).

Obtained in an 89% yield from the reaction of dimethyl *cis,endo*-5-norbornene-2,3-dicarboxylate and 2-iodobenzonitrile according to the general procedure after purification by column chromatography using 2:1 hexanes/EtOAc: off-white solid, mp 142-144 °C (hexanes-EtOAc); ¹H NMR (CDCl₃) δ 0.96-1.04 (m, 2H), 2.63-2.65 (m, 1H), 2.87-2.92 (m, 2H), 3.00-3.06 (m, 1H), 3.13-3.19 (m, 1H), 3.64 (s, 6H), 3.94 (d, *J* = 6.0 Hz, 1H), 7.27-7.32 (m, 1H), 7.49-7.56 (m, 2H), 7.63-7.66 (m, 1H); ¹³C NMR (CDCl₃) δ 33.5, 41.6, 43.8, 44.4, 46.0, 46.7, 50.5, 51.6, 51.9, 123.3, 126.3, 127.5, 135.2, 139.2, 142.6, 156.7, 172.2, 207.3; IR (neat) 1702, 1728, 1743, 2923, 2985, 3078 cm⁻¹; HRMS *m/z* 314.11597 (calcd for C₁₈H₁₈O₅, 314.11542).

4b,5,10,10a-Tetrahydro-5,10-methanobenz[*b*]fluoren-11-one (14). Obtained in a 59% yield from the reaction of benzonorbornadiene and 2-iodobenzonitrile according to the general procedure after purification by column chromatography using 4:1 hexanes/EtOAc: white solid, mp 86-87 °C (hexanes); ¹H NMR (CDCl₃) δ 1.31-1.36 (m, 1H), 1.63-1.67 (m, 1H), 2.70-2.73 (m, 1H), 3.37 (d, *J* = 5.7 Hz, 1H), 3.43 (s, 1H), 3.66 (s, 1H), 7.12-7.15 (m, 2H), 7.26-7.35 (m, 2H), 7.41-7.44 (m, 1H), 7.63-7.68 (m, 2H), 7.77 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (CDCl₃) δ 42.8, 46.8, 48.2, 48.3, 55.5, 121.3, 121.4, 123.7, 126.1, 126.2, 127.9, 135.2, 140.7, 147.3, 148.0, 156.0, 206.7 (1 sp² carbon missing due to overlap); IR (neat) 1703, 2966, 3026 cm⁻¹; HRMS *m/z* 246.10475 (calcd for C₁₈H₁₄O, 246.10447).

2,3-Di(4-methoxyphenyl)-1-indenone (15). Obtained in a 79% yield from the reaction of bis(4-methoxyphenyl)acetylene and 2-iodobenzonitrile according to the general procedure after purification by column chromatography using 4:1 hexanes/EtOAc: dark red solid, mp 118-119 °C (hexanes-EtOAc); ¹H NMR (CDCl₃) δ 3.79 (s, 3H), 3.85 (s, 3H), 6.82 (dd, *J* = 7.2, 2.0 Hz, 2H), 6.94 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.22-7.27 (m, 3H), 7.33-7.37 (m, 3H), 7.55 (dd, *J* = 6.8, 0.4 Hz, 1H); ¹³C NMR (CDCl₃) δ 55.2, 55.3, 113.6, 114.1, 120.9, 122.6, 123.4, 125.0, 128.6, 130.1, 130.9, 131.1, 131.2, 133.2, 145.4, 153.7, 159.0, 160.2, 196.9; IR (neat) 1705, 2834, 2957, 3066 cm⁻¹; HRMS *m/z* 342.12611 (calcd for C₂₃H₁₈O₃, 342.12559).

1,1,3-Trimethyl-4-phenyl-1,2-dihydronaphthalen-2-one (17). Obtained (along with **18**) in an 18% yield from the reaction of 1-phenyl-1-propyne and 2-(2-iodophenyl)-2-methylpropanenitrile according to the general procedure after purification by column chromatography using 20:1 hexanes/EtOAc: pink solid, mp 61-62 °C (hexanes-EtOAc); ¹H NMR (CDCl₃) δ 1.56 (s, 6H), 1.76 (s, 3H), 6.83 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.10 (td, *J* = 8.0, 0.8 Hz, 1H), 7.19-7.20 (m, 2H), 7.32 (td, *J* = 8.0, 0.8 Hz, 1H), 7.41-7.45 (m, 1H), 7.47-7.52 (m, 3H); ¹³C NMR (CDCl₃) δ 13.9, 28.3, 46.8, 125.8, 126.2, 127.7, 128.2, 128.5, 128.6, 128.7, 129.2, 130.8, 137.9, 146.5, 150.9, 204.3; IR (neat) 1657, 2971, 3064 cm⁻¹; HRMS *m/z* 262.13625 (calcd for C₁₉H₁₈O, 262.13577).

1,1,4-Trimethyl-3-phenyl-1,2-dihydronaphthalen-2-one (18). Obtained (along with **17**) in an 11% yield from the reaction of 1-phenyl-1-propyne and 2-(2-iodophenyl)-2-methylpropanenitrile according to the general procedure after purification by column chromatography using 20:1 hexanes/EtOAc: pink solid, mp 67-68 °C (hexanes-EtOAc); ^1H NMR (CDCl_3) δ 1.55 (s, 6H), 2.24 (s, 3H), 7.15 (dd, J = 8.4, 1.6 Hz, 2H), 7.32-7.37 (m, 2H), 7.39-7.45 (m, 3H), 7.51 (dd, J = 7.6, 0.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H); ^{13}C NMR (CDCl_3) δ 18.2, 27.9, 47.2, 125.8, 126.0, 126.6, 127.2, 128.0, 129.4, 130.0, 130.7, 134.9, 136.5, 146.6, 202.5 (1 sp^2 carbon missing due to overlap); IR (neat) 1652, 2924, 2970, 3054 cm^{-1} ; HRMS m/z 262.13625 (calcd for $\text{C}_{19}\text{H}_{18}\text{O}$, 262.13577).

6b,7,8,9,10,10a-Hexahydro-7,10-methano-11H-benz[a]fluoren-11-one (32). Obtained in a 93% yield from the reaction of norbornene and 1-cyano-2-iodonaphthalene (**19**) according to the general procedure after purification by column chromatography using 10:1 hexanes/EtOAc: white solid, mp 79-81 °C (ether); ^1H NMR (CDCl_3) δ 0.83-0.96 (m, 2H), 1.38-1.55 (m, 2H), 1.61-1.80 (m, 2H), 2.46 (d, J = 3.6 Hz, 1H), 2.59 (d, J = 5.7 Hz, 1H), 2.65 (d, J = 3.6 Hz, 1H), 3.19 (d, J = 6.0 Hz, 1H), 7.52-7.58 (m, 2H), 7.63-7.69 (m, 1H), 7.88 (dd, J = 8.1, 0.6 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 9.18 (dd, J = 8.4, 0.6 Hz, 1H); ^{13}C NMR (CDCl_3) δ 28.6, 29.1, 31.8, 40.2, 40.5, 48.0, 56.3, 123.4, 124.1, 126.6, 128.0, 128.9, 129.0, 132.6, 133.1, 136.0, 160.0, 209.2; IR (neat) 1691, 2954, 3056 cm^{-1} ; HRMS m/z 248.120143 (calcd for $\text{C}_{18}\text{H}_{16}\text{O}$, 248.120115).

13-Oxo-1,2,3,4,4a,13a-hexahydro-1,4-methano-1H-indeno[2,1-*l*]phenanthrene (35). Obtained in a 91% yield from the reaction of norbornene and 9-cyano-10-iodophenanthrene (**20**) according to the general procedure after purification by column chromatography using 10:1 hexanes/EtOAc: white solid, mp 195-196 °C (ether); ^1H NMR (CDCl_3) δ 0.90-1.02 (m, 2H), 1.48-1.85 (m, 4H), 2.67-2.69 (m, 3H), 3.51 (d, J = 5.7 Hz, 1H), 7.66-7.73 (m, 3H), 7.78-7.84 (m, 1H), 8.24 (dd, J = 7.8, 0.9 Hz, 1H), 8.62-8.73 (m, 2H), 9.33-9.36 (m, 1H); ^{13}C NMR (CDCl_3) δ 28.6, 29.5, 32.3, 39.5, 40.4, 46.4, 56.3, 122.5, 123.6, 124.9, 126.0, 127.0, 127.1, 127.2, 128.1, 128.6, 129.8, 130.1, 132.1, 133.8, 159.9, 209.2; IR (neat) 1687, 2954, 3087 cm^{-1} ; HRMS m/z 298.136302 (calcd for $\text{C}_{22}\text{H}_{18}\text{O}$, 298.135765).

1,2,3,4,4a,6b,7,8,9,10,10a,12a-Dodecahydro-{1,4},{7,10}-dimethano-11H,12H-indeno[2,1-*a*]fluoren-11,12-dione (36). Obtained in a 33% yield from the reaction of norbornene and 2,3-dicyano-1,4-diiodobenzene (**23**) according to the general procedure (the amount of all reagents except **23** was doubled) after purification by column chromatography using 1:1 hexanes/EtOAc: off-white solid, mp (dec.) 278-280 °C (hexanes-EtOAc); ^1H NMR (CDCl_3) δ 0.79-0.83 (m, 2H), 0.92-0.96 (m, 2H), 1.34-1.50 (m, 4H), 1.59-1.76 (m, 4H), 2.39 (d, J = 3.0 Hz, 2H), 2.53 (d, J = 4.5 Hz, 2H), 2.65 (d, J = 2.4 Hz, 2H), 3.17 (d, J = 4.5 Hz, 2H), 7.72 (s, 2H); ^{13}C NMR (CDCl_3) δ 28.5, 28.9, 31.9, 40.8, 41.3, 48.1, 55.8, 132.2,

136.2, 158.6, 205.8; IR (neat) 1716, 2870, 2949 cm^{-1} ; HRMS m/z 318.162625 (calcd for $\text{C}_{22}\text{H}_{22}\text{O}_2$, 318.161980).

exo-2-(2-Norbornyl)pyridine-3-carbonitrile (38). Obtained in a 40% yield from the reaction of norbornene and 3-cyano-2-iodopyridine (**25**) according to the general procedure after purification by column chromatography using 4:1 hexanes/EtOAc: yellow oil; ^1H NMR (CDCl_3) δ 1.14-1.20 (m, 1H), 1.30-1.36 (m, 1H), 1.47-1.75 (m, 4H), 2.13-2.21 (m, 1H), 2.41-2.45 (m, 2H), 3.25-3.30 (m, 1H), 7.17-7.22 (m, 1H), 7.88 (dd, $J = 7.8, 1.8$ Hz, 1H), 8.70 (dd, $J = 4.8, 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 28.9, 30.2, 35.7, 36.7, 43.7, 47.7, 108.9, 117.1, 120.4, 140.2, 151.7, 168.5 (1 sp^3 carbon missing due to overlap); IR (neat) 2228, 2959, 3052 cm^{-1} ; HRMS m/z 198.11606 (calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2$, 198.11570).

N-Benzenesulfonyl-10-oxo-5b,6,7,8,9,9a-hexahydro-6,9-methano-10H-indeno[1,2-b]indole (40). Obtained in a 16% yield from the reaction of norbornene and *N*-benzenesulfonyl-2-iodoindole-3-carbonitrile (**28c**) according to the general procedure after purification by column chromatography using 2:1 hexanes/EtOAc: white solid, mp 175-177 $^\circ\text{C}$ (hexanes); ^1H NMR (CDCl_3) δ 1.06-1.17 (m, 2H), 1.33-1.40 (m, 1H), 1.50-1.57 (m, 1H), 1.64-1.84 (m, 2H), 2.64 (d, $J = 3.6$ Hz, 1H), 2.82 (d, $J = 5.1$ Hz, 1H), 2.89 (d, $J = 3.6$ Hz, 1H), 3.37 (d, $J = 5.1$ Hz, 1H), 7.29-7.39 (m, 2H), 7.47-7.52 (m, 2H), 7.59-7.65 (m, 1H), 7.84-7.93 (m, 3H), 7.96-7.99 (m, 1H); ^{13}C NMR (CDCl_3) δ 28.2, 29.2, 31.8, 39.3, 39.8, 46.3, 61.6, 114.3, 121.3, 122.1, 125.0, 125.8, 126.8, 128.7, 129.7, 134.6, 138.0, 140.7, 167.5, 198.2; IR (neat) 1194, 1356, 1695, 2955 cm^{-1} ; HRMS m/z 377.109143 (calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_3\text{S}$, 377.108386).

N-Benzenesulfonyl-6-oxo-6a,7,8,9,10,10a-hexahydro-7,10-methano-6H-indeno[2,1-b]indole (42). Obtained in a 69% yield from the reaction of norbornene and *N*-benzenesulfonyl-3-iodoindole-2-carbonitrile (**27c**) according to the general procedure after purification by column chromatography using 2:1 hexanes/EtOAc: white solid, mp 147-149 $^\circ\text{C}$ (hexanes); ^1H NMR (CDCl_3) δ 0.79-0.84 (m, 1H), 0.93-0.97 (m, 1H), 1.33-1.43 (m, 2H), 1.63-1.73 (m, 2H), 2.41 (d, $J = 3.0$ Hz, 1H), 2.56 (d, $J = 3.0$ Hz, 1H), 2.79 (d, $J = 5.1$ Hz, 1H), 3.03 (d, $J = 5.1$ Hz, 1H), 7.33-7.39 (m, 1H), 7.42-7.48 (m, 2H), 7.52-7.59 (m, 2H), 7.67-7.71 (m, 1H), 8.08-8.11 (m, 2H), 8.36 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 28.5, 29.0, 31.9, 38.2, 39.3, 41.7, 61.7, 115.9, 121.8, 124.1, 124.6, 127.5, 129.3, 129.4, 134.1, 138.6, 140.3, 143.9, 155.7, 192.0; IR (neat) 1188, 1380, 1699, 2954 cm^{-1} ; HRMS m/z 377.1091428 (calcd for $\text{C}_{22}\text{H}_{19}\text{NO}_3\text{S}$, 377.108566).

6-Nitro-2,3-diphenyl-1-indenone (43). Obtained in a 53% yield from the reaction of diphenylacetylene and 2-iodo-5-nitrobenzonitrile (**29**) according to the general procedure after purification by column chromatography using CH_2Cl_2 : red solid, mp 224-226 $^\circ\text{C}$ (CH_2Cl_2 -hexanes); ^1H NMR (CDCl_3) δ 7.30-7.48 (m, 12H), 8.33 (dd, $J = 7.8, 2.1$ Hz, 1H), 8.39 (d, $J = 2.1$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 117.9, 121.3, 128.3, 128.4, 128.7, 129.2, 129.3, 129.7, 130.0, 131.6, 131.7, 136.2, 148.6, 151.1, 153.9, 193.4 (1

sp² carbon missing due to overlap); IR (neat) 1335, 1519, 1707, 3080 cm⁻¹; HRMS *m/z* 327.0896467 (calcd for C₂₁H₁₃NO₃, 327.089543).

7-Nitro-1,2,3,4,4a,9a-hexahydro-1,4-methanofluoren-9-one (47). Obtained in an 81% yield from the reaction of norbornene and **29** according to the general procedure after purification by column chromatography using 4:1 hexanes/EtOAc: yellow oil; ¹H NMR (CDCl₃) δ 0.76-0.81 (m, 1H), 1.02-1.06 (m, 1H), 1.37-1.50 (m, 2H), 1.52-1.83 (m, 2H), 2.50 (d, *J* = 4.2 Hz, 1H), 2.63-2.68 (m, 2H), 3.28 (d, *J* = 6.0 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 8.45-8.52 (m, 2H); ¹³C NMR (CDCl₃) δ 28.4, 28.8, 32.4, 40.8, 41.4, 48.2, 56.4, 118.5, 127.3, 129.2, 140.0, 147.8, 162.7, 206.6; IR (neat) 1341, 1527, 1718, 2954, 3098 cm⁻¹; HRMS *m/z* 243.089638 (calcd for C₁₄H₁₃NO₃, 243.089543).

6-Cyano-1,2,3,4,4a,9a-hexahydro-1,4-methanofluoren-9-one (48). Obtained in an 85% yield from the reaction of norbornene and 4-cyano-2-iodobenzonitrile (**22**) according to the general procedure (reaction time – 48 h) after purification by column chromatography using 4:1 hexanes/EtOAc: white solid, mp 135-137 °C (hexanes-EtOAc); ¹H NMR (CDCl₃) δ 0.71-0.78 (m, 1H), 0.99-1.05 (m, 1H), 1.37-1.54 (m, 2H), 1.62-1.81 (m, 1H), 2.45 (d, *J* = 3.6 Hz, 1H), 2.58 (d, *J* = 6.0 Hz, 1H), 2.64 (d, *J* = 3.6 Hz, 1H), 3.22 (d, *J* = 6.0 Hz, 1H), 7.62-7.66 (m, 1H), 7.77-7.84 (m, 2H); ¹³C NMR (CDCl₃) δ 28.7, 29.0, 32.6, 41.0, 41.6, 48.1, 56.1, 118.2, 118.4, 124.1, 130.7, 131.3, 142.2, 157.2, 207.6; IR (neat) 1711, 2227, 2965 cm⁻¹; HRMS *m/z* 223.100031 (calcd for C₁₅H₁₃NO, 223.099714).

5-Methoxy-1,2,3,4,4a,9a-hexahydro-1,4-methanofluoren-9-one (49). Obtained in a 75% yield from the reaction of norbornene and 2-iodo-3-methoxybenzonitrile (**21**) according to the general procedure after purification by column chromatography using 4:1 hexanes/EtOAc: beige solid, mp 82-83 °C (hexanes-EtOAc); ¹H NMR (CDCl₃) δ 0.75-0.83 (m, 1H), 0.91-0.96 (m, 1H), 1.36-1.39 (m, 1H), 1.43-1.47 (m, 1H), 1.61-1.70 (m, 2H), 2.46 (d, *J* = 6.0 Hz, 1H), 2.57-2.61 (m, 2H), 3.15 (d, *J* = 6.0 Hz, 1H), 3.92 (s, 3H), 7.02-7.06 (m, 1H), 7.29-7.33 (m, 2H); ¹³C NMR (CDCl₃) δ 28.6, 29.0, 32.3, 38.6, 40.2, 45.6, 55.4, 55.8, 114.8, 115.2, 129.0, 140.7, 145.4, 157.1, 209.2; IR (neat) 1707, 2871, 2959 cm⁻¹; HRMS *m/z* 228.1151534 (calcd for C₁₅H₁₆O₂, 228.115030).

6-Methoxy-1,2,3,4,4a,9a-hexahydro-1,4-methanofluoren-9-one (50). Obtained in an 84% yield from the reaction of norbornene and 2-iodo-4-methoxybenzonitrile (**30**) according to the general procedure after purification by column chromatography (note: the *R_f* of the byproduct, 4-methoxybenzonitrile, is very close to that of **50**) using 4:1 hexanes/EtOAc: colorless oil; ¹H NMR (CDCl₃) δ 0.83-0.86 (m, 1H), 0.93-0.97 (m, 1H), 1.39-1.45 (m, 2H), 1.59-1.75 (m, 2H), 2.40 (d, *J* = 4.0 Hz, 1H), 2.49 (d, *J* = 6.0 Hz, 1H), 2.58 (d, *J* = 4.0 Hz, 1H), 3.09 (d, *J* = 6.0 Hz, 1H), 3.89 (s, 3H), 6.87-6.92 (m, 2H), 7.65 (d, *J* = 8.4 Hz, 1H); ¹³C NMR (CDCl₃) δ 28.8, 32.2, 40.1, 41.3, 48.0, 55.6, 56.2, 109.2, 115.3, 124.9, 132.4, 160.1, 162.8, 165.5, 192.4; IR (neat) 1702, 2871, 2954 cm⁻¹; HRMS *m/z* 228.11549 (calcd for C₁₅H₁₆O₂, 228.11503).

Dimethyl 1,2,3,4,4a,9a-hexahydro-1,4-methano-9-oxofluorene-*cis,endo*-2,3-dicarboxylate (**13**)

0.000

7.263

7.796

2,3-Dicyano-1,4-diiodobenzene (**23**)

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

-0.006

1.582

3-Cyano-4-iodopyridine (24)

7.260

7.907

7.921

8.382

8.395

8.730

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

1.035

1.038

1.000

13-Oxo-1,2,3,4,4a,13a-hexahydro-1,4-methano-1H-indeno[2,1-b]phenanthrene (**35**)

7-Nitro-1,2,3,4,4a,9a-hexahydro-
-1,4-methanofluoren-9-one (**47**)