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Supporting Information

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Supporting Information

Efficient Helicene Synthesis: Friedel–Crafts-type Cyclizations of 1,1-Difluoro-1-alkenes

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General: NMR spectra were obtained on JEOL GSX 270, AL 400, A 500, Bruker DRX 500, or AVANCE 500 spectrometers at the indicated field strengths. Chemical shift values were given in ppm relative to internal Me_4Si (for ^{1}H NMR: δ 0.00), $CDCl_3$ (for ^{13}C NMR: δ 77.0), and C_6F_6 (for ^{19}F NMR: δ 0.00). IR spectra were recorded on a Horiba FT 300S by ATR method or a Shimazu IR 408 spectrometer using KBr pellets. High-resolution mass spectra were obtained with a JEOL MS-700P mass spectrometer. Elemental analyses were carried out at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, the University of Tokyo. Tetrahydrofuran and diethyl ether were purchased from Kanto Chemical Co., Inc and used without purification. Hexamethylphosphoric triamide (HMPA) was distilled from CaH_2, and stored over molecular sieves 4Å. 1,1,1,3,3,3-Hexafluoropropan-2-ol was distilled from molecular sieves 4Å, and stored over molecular sieves 4Å. Column chromatography and preparative thin-layer chromatography (PTLC) were performed on silica gel (Kanto Chemical Co. Inc., Silica Gel 60 and Wako Pure Chemical Industries, Ltd., B5-F), respectively.

4-Phenyl-2-(trifluoromethyl)but-1-ene (**2**)

Method A: 2-Phenylethylmagnesium bromide was prepared from 2-bromoethylbenzene (50.0 g, 0.27 mmol) and magnesium (7.88 g, 0.32 mmol) in Et_2O (80 mL). The Grignard reagent was added dropwise to a solution of ethyl trifluoroacetate (35.1 mL, 0.30 mmol) in Et_2O (360 mL) at –78 °C. The reaction mixture was stirred for 0.5 h at the same temperature and allowed to warm to room temperature. Then aq. NH_4Cl was added to quench the reaction. Organic materials were extracted with pentane three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by distillation to give 1,1,1-trifluoro-4-phenylbutan-2-one (45.4 g, 83%) as a colorless liquid. IR (neat): 3056, 1761, 1205, 1170, 1156, 1114, 1049, 988, 749, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.00 (2H, t, J = 6.9 Hz), 3.06 (2H, t, J = 6.9 Hz), 7.20 (2H, dd, J = 7.3, 1.5 Hz), 7.23 (1H, tt, J = 7.3, 1.5 Hz), 7.31 (2H, dd, J = 7.3, 7.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.2, 38.0, 115.5 (q, J_{CF} = 292 Hz), 126.6, 128.2, 128.7, 139.2, 190.6 (q, J_{CF} = 35 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 82.5 (s). HRMS (FAB): *m/z* calcd for $C_{10}H_9F_3O$ ($[M+H]^+$): 203.0684; found: 203.0682.

A solution of methyltriphenylphosphonium iodide (95.1 g, 235 mmol) and *t*-BuOK (26.4 g, 235 mmol) in THF (600 mL) was stirred for 0.5 h at room temperature and cooled to –78 °C before the addition of 1,1,1-trifluoro-4-phenylbutan-2-one (45.4 g, 225 mmol). The reaction mixture was stirred and allowed to warm to room temperature over 1.5 h. The reaction mixture was then poured into aq. HCl (0.5 M, 500 mL), and organic materials were extracted with pentane three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (pentane) to give **2** (38.4 g, 85%) as a colorless liquid.

Method B: [2-(Trifluoromethyl)allyl]trimethylsilane (0.11 mL, 0.55 mmol) was added to a solution of benzyl bromide (0.071 mL, 0.60 mmol), cesium fluoride (91 mg, 0.60 mmol) and molecular sieves 4Å (15 mg) in *N*,*N*-dimethylformamide at room temperature under argon. After the mixture was stirred for 7 h at 60 °C, phosphate buffer (pH 7) was added to quench the reaction. The mixture was filtered, and organic materials were extracted with Et_2O three times. The combined extracts were washed with water twice, brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (pentane) to give **2** (110 mg, quant.) as a colorless liquid.

IR (neat): 3030, 2933, 1331, 1163, 1110, 941, 746, 696 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.52 (2H, t, J = 7.9 Hz), 2.84 (2H, t, J = 7.9 Hz), 5.29 (1H, q, J_{HF} = 1.2 Hz), 5.67 (1H, q, J_{HF} = 0.7 Hz), 7.20 (2H, dd, J = 7.9, 0.9 Hz), 7.21 (1H, tt, J = 7.9, 0.9 Hz), 7.30 (2H, dd, J = 7.9, 7.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 31.3, 33.8, 118.1 (q, J_{CF} = 6 Hz), 123.7 (q, J_{CF} = 273 Hz), 126.2, 128.3, 128.4, 137.7 (q, J_{CF} = 29 Hz), 140.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ 93.3 (br s). Anal. Calcd for $C_{11}H_{11}F_3$: C, 65.99; H, 5.54. Found: C, 66.19; H, 5.71.

1,1-Difluoro-2-(2-phenylethyl)-4-phenylbut-1-ene (1a)

Butyllithium (3.54 mL, 1.58 M in hexane, 5.6 mmol) was added to a solution of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA, 0.84 mL, 5.6 mmol) in toluene (5.97 mL, 56 mmol) at room temperature under argon. The reaction mixture was stirred for 30 min at room temperature and cooled to –78 °C before the addition of 4-phenyl-2-(trifluoromethyl)but-1-ene (1.12 g, 5.6 mmol) in THF (3.0 mL). After stirring for 1 h at the same temperature, the mixture was warmed to room temperature, and stirred for 1 h. The reaction was quenched with aqueous ammonium chloride (aq. NH_4Cl). Organic materials were extracted with AcOEt three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane–AcOEt, 100:1) to give **1a** (1.22 g, 80%) as a colorless liquid. IR (neat): 3028, 2929, 1749, 1454, 1209, 1061, 748, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.77 (4H, tdd, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz), 2.69 (4H, t, J = 8.0 Hz), 7.16 (4H, d, J = 7.6 Hz), 7.20 (2H, t, J = 7.6 Hz), 7.28 (4H, dd, J = 7.6, 7.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.2 (dd, J_{CF} = 2, 2 Hz), 34.0 (dd, J_{CF} = 3, 3 Hz), 88.1 (dd, J_{CF} = 17, 17 Hz), 126.1, 128.3, 128.4, 141.2, 153.7 (dd, J_{CF} = 285, 284 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 67.0 (br s). Anal. Calcd for $C_{18}H_{18}F_2$: C, 79.39; H, 6.66. Found: C, 79.61; H, 6.77.

1,1-Difluoro-2-(2-phenylpropyl)-4-phenylpent-1-ene (1b)

Butyllithium (23.0 mL, 1.70 M in hexane, 39.1 mmol) was added to a THF (48 mL) solution of 2,2,2-trifluoroethyl 4-methylbenzenesulfonate (4.71 g, 18.5 mmol) at –78 °C over 10 min under argon. The reaction mixture was stirred for 20 min at –78 °C, and then tris(2-phenylpropyl)borane [Borane–THF complex (20.2 mL, 1.01 M in THF, 20.4 mmol) was added to a solution of isopropenylbenzene (7.27 g, 61.6 mmol) in THF (20 mL) at 0 °C, and the mixture was stirred for 3 h at room temperature.] was added at –78 °C. After being stirred for 30 min, MeONa (3.00 g, 55.6 mmol) was added, and then the reaction mixture was warmed to room temperature and stirred for an additional 3 h. The resulting solution was cooled to –78 °C and treated with bromine (8.90 g, 55.6 mmol) in CH_2Cl_2 (20 mL) over 1 h. After reaction mixture was stirred at room temperature for 1 h, aq. $Na_2S_2O_3$ was added to quench the reaction. The mixture was filtered, and organic materials were extracted with Et_2O three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (pentane) to give **1b** (4.18 g, 75%) as a colorless liquid. (*meso* : *dl* = 1:1) IR (neat): 1745 cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ 1.20 (6H, d, J = 8.0 Hz), 1.98–2.20 (4H, m), 2.58–3.02 (2H, m), 6.98–7.36 (10H, m). ^{13}C NMR (68 MHz, $CDCl_3$): δ 21.1, 21.5, 34.5, 34.6, 37.7, 37.8, 86.6 (dd, J_{CF} = 17, 17 Hz), 86.7 (dd, J_{CF} = 17, 17 Hz), 126.2, 126.8, 128.4, 146.4, 146.5, 154.5 (dd, J_{CF} = 284, 284 Hz), 154.6 (dd, J_{CF} = 284, 284 Hz). ^{19}F NMR (94 MHz, $CDCl_3$): δ 67.5 (br s). HRMS: *m/z* calcd for $C_{20}H_{22}F_2$ (M^+): 300.1688; found: 300.1696.

1,1-Difluoro-2-(2-phenylethyl)-4-(2-methylphenyl)but-1-ene (1c)

Compound **1c** was prepared by the method described for **1a** in 74% yield as a colorless liquid. IR (neat): 3026, 2931, 1745, 1496, 1456, 1205, 774, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.21 (2H, tdd, J = 8.3 Hz, J_{HF} = 2.2, 2.2 Hz), 2.32 (2H, tdd, J = 8.0 Hz, J_{HF} = 2.2, 2.2 Hz), 2.32 (3H, s), 2.68 (2H, t, J = 8.3 Hz), 2.72 (2H, t, J = 8.0 Hz), 7.09–7.16 (4H, m), 7.18 (2H, dd, J = 7.5, 1.5 Hz), 7.20 (1H, tt, J = 7.5, 1.5 Hz), 7.29 (2H, dd, J = 7.5, 7.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.1, 27.1 (dd, J_{CF} = 2, 2 Hz), 28.4 (dd, J_{CF} = 2, 2 Hz), 31.6 (dd, J_{CF} = 3, 3 Hz), 34.0 (dd, J_{CF} = 3, 3 Hz), 88.3 (dd, J_{CF} = 17, 17 Hz), 126.1, 126.1, 126.3, 128.3, 128.4, 128.8, 130.3, 135.8, 139.4, 141.2, 153.6 (dd, J_{CF} = 285, 285 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.4 (1F, br d, J_{FF} = 3 Hz), 66.4 (1F, br d, J_{FF} = 3 Hz). Anal. Calcd for $C_{19}H_{20}F_2$: C, 79.69; H, 7.04. Found: C, 79.57; H, 7.23.

1,1-Difluoro-2-(2-phenylethyl)-4-(3-methylphenyl)but-1-ene (1d)

Compound **1d** was prepared by the method described for **1a** in 76% yield as a colorless liquid. IR (neat): 2925, 2864, 1745, 1454, 1205, 1065, 773, 696 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.27 (2H, tdd, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz), 2.29 (2H, tdd, J = 8.1 Hz, J_{HF} = 2.0, 2.0 Hz), 2.33 (3H, s), 2.66 (2H, t, J = 8.1 Hz), 2.70 (2H, t, J = 8.0 Hz), 6.97 (1H, d, J = 8.0 Hz), 6.98 (1H, s), 7.02 (1H, d, J = 8.0 Hz), 7.17 (2H, d, J = 8.0 Hz), 7.18 (1H, dd, J = 8.0, 8.0 Hz), 7.20 (1H, t, J = 8.0 Hz), 7.29 (2H, dd, J = 8.0, 8.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.4, 28.2 (dd, J_{CF} = 2, 2 Hz), 28.2 (dd, J_{CF} = 2, 2 Hz), 33.9 (dd, J_{CF} = 3, 3 Hz), 33.9 (dd, J_{CF} = 3, 3 Hz), 88.1 (dd, J_{CF} = 17, 17 Hz), 125.3, 126.1, 126.8, 128.3, 128.3, 128.4, 129.1, 138.0, 141.2, 141.2, 153.6 (dd, J_{CF} = 284, 284 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.4 (1F, br d, J_{FF} = 3 Hz), 66.4 (1F, br d, J_{FF} = 3 Hz). Anal. Calcd for $C_{19}H_{20}F_2$: C, 79.69; H, 7.04. Found: C, 79.64; H, 7.19.

1,1-Difluoro-2-(2-phenylethyl)-4-(4-methylphenyl)but-1-ene (1e)

Compound **1e** was prepared by the method described for **1a** in 76% yield as a colorless liquid. IR (neat): 3026, 2926, 2862, 1745, 1454, 1207, 1065, 806, 748, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26 (2H, tdd, J = 8.1 Hz, J_{HF} = 2.0, 2.0 Hz), 2.28 (2H, tdd, J = 8.1 Hz, J_{HF} = 2.0, 2.0 Hz), 2.32 (3H, s), 2.66 (2H, t, J = 8.1 Hz), 2.70 (2H, t, J = 8.1 Hz), 7.06 (2H, d, J = 7.7 Hz), 7.10 (2H, d, J = 7.7 Hz), 7.17 (2H, d, J = 7.7 Hz), 7.20 (1H, t, J = 7.7 Hz), 7.29 (2H, dd, J = 7.7, 7.7 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.1, 28.2 (dd, J_{CF} = 2, 2 Hz), 28.3 (dd, J_{CF} = 2, 2 Hz), 33.6 (dd, J_{CF} = 3, 3 Hz), 34.0 (dd, J_{CF} = 3, 3 Hz), 88.1 (dd, J_{CF} = 17, 17 Hz), 126.0, 128.1, 128.2, 128.3, 129.0, 135.5, 138.0, 141.1, 153.5 (dd, J_{CF} = 284, 284 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.8 (br s). Anal. Calcd for $C_{19}H_{20}F_2$: C, 79.69; H, 7.04. Found: C, 79.72; H, 7.20.

1,1-Difluoro-4-(2-methoxyphenyl)-2-(2-phenylethyl)but-1-ene (1f)

Butyllithium (0.97 mL, 1.54 M in hexane, 1.50 mmol) was added to a solution of *t*-BuOK (168 mg, 1.50 mmol) in 1-methoxy-2-methylbenzene (1.86 mL, 15.0 mmol) at room temperature under argon. The reaction mixture was stirred for 30 min at room temperature. To the above mixture was added lithium bromide (LiBr, 130 mg, 1.50 mmol) and hexane (1.00 mL) at the same temperature. After stirring for 3 min, 4-phenyl-2-trifluoromethylbut-1-ene (300 mg, 1.50 mmol) in THF (2.00 mL) was added at –78 °C. The mixture was stirred for 1 h and for an additional 1 h at room temperature. The reaction was quenched with aq. NH_4Cl. Organic materials were extracted with AcOEt three times. The combined extracts were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane–AcOEt, 20:1) to give **1f** (331 mg, 73%) as a colorless liquid. IR (neat): 2935, 1747, 1541, 1495, 1244, 1207, 752, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.26 (2H, tdd, J = 8.1 Hz, J_{HF} = 2.1, 2.1 Hz), 2.28 (2H, tdd, J = 8.1 Hz, J_{HF} = 2.1, 2.1 Hz), 2.70–2.74 (4H, m), 3.84 (3H, s), 6.85 (1H, dd, J = 7.4, 1.4 Hz), 6.89 (1H, ddd, J = 7.4, 7.4, 1.4 Hz), 7.11 (1H, dd, J = 7.4, 1.4 Hz), 7.18–7.22 (4H, m), 7.28–7.31 (2H, m). ^{13}C NMR (126 MHz, $CDCl_3$): δ 26.4 (dd, J_{CF} = 2, 2 Hz), 28.2 (dd, J_{CF} = 2, 2 Hz), 28.7 (dd, J_{CF} = 3, 3 Hz), 33.9 (dd, J_{CF} = 3, 3 Hz), 55.2, 88.4 (dd, J_{CF} = 17, 17 Hz), 110.2, 120.4, 126.2, 127.4, 128.3, 128.4, 129.6, 129.8, 141.5, 153.6 (dd, J_{CF} = 284, 284 Hz), 157.4. ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.3 (br s). Anal. Calcd for $C_{19}H_{20}F_2O$: C, 75.47; H, 6.67. Found: C, 75.59; H, 6.85.

1,1-Difluoro-4-(3-methoxyphenyl)-2-(2-phenylethyl)but-1-ene (1g)

Compound **1g** was prepared by the method described for **1f** in 68% yield as a colorless liquid. IR (neat): 2935, 1747, 1603, 1456, 1259, 1049, 773, 696 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.28 (2H, tdd, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz), 2.28 (2H, tdd, J = 8.0 Hz, J_{HF} = 2.0, 2.0 Hz), 2.65–2.72 (4H, m), 3.80 (3H, s), 6.71–6.77 (3H, m), 7.16–7.22 (4H, m), 7.26–7.30 (2H, m). ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.1 (dd, J_{CF} = 2, 2 Hz), 28.3 (dd, J_{CF} = 2, 2 Hz), 33.9 (dd, J_{CF} = 3, 3 Hz), 34.0 (dd, J_{CF} = 3, 3 Hz), 55.2, 88.0 (dd, J_{CF} = 17, 17 Hz), 111.3, 114.1, 120.7, 126.1, 128.3, 128.4, 129.4, 141.2, 142.8, 153.8 (dd, J_{CF} = 285, 284 Hz), 160.6. ^{19}F NMR (470 MHz, $CDCl_3$): δ 66.5 (br s). Anal. Calcd for $C_{19}H_{20}F_2O$: C, 75.47; H, 6.67. Found: C, 75.31; H, 6.83.

1-[4,4-Difluoro-3-(2-phenylethyl)but-3-en-1-yl]-4-methylnaphthalene (**1h**)

Compound **1h** was prepared by the method described for **1f** in 66% yield as a colorless liquid. IR (neat): 2933, 1745, 1454, 1269, 1205, 754, 698 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.34 (2H, tdd, J = 8.1 Hz, J_{HF} = 2.1, 2.1 Hz), 2.39 (2H, tdd, J = 8.1 Hz, J_{HF} = 2.1, 2.1 Hz), 2.67 (3H, s), 2.72 (2H, t, J = 8.1 Hz), 3.13 (2H, t, J = 8.1 Hz), 7.16 (2H, dd, J = 7.3, 1.1 Hz), 7.20 (1H, tt, J = 7.3, 1.1 Hz), 7.21 (1H, d, J = 7.3 Hz), 7.24 (1H, d, J = 7.3 Hz), 7.29 (2H, dd, J = 7.3, 7.3 Hz), 7.53–7.55 (2H, m), 8.02–8.04 (2H, m). ^{13}C NMR (126 MHz, CDCl$_3$): δ 19.4, 27.8 (dd, J_{CF} = 1, 1 Hz), 28.5 (dd, J_{CF} = 1, 1 Hz), 31.3 (dd, J_{CF} = 3, 3 Hz), 34.1 (dd, J_{CF} = 3, 3 Hz), 88.5 (dd, J_{CF} = 17, 17 Hz), 123.9, 124.9, 125.3, 125.6, 125.7, 126.1, 126.3, 128.3, 128.4, 131.7, 132.9, 133.0, 135.5, 141.2, 153.7 (dd, J_{CF} = 285, 285 Hz). ^{19}F NMR (470 MHz, CDCl$_3$): δ 66.8 (1F, br d, J_{FF} = 54 Hz), 67.1 (1F, br d, J_{FF} = 54 Hz). Anal. Calcd for $C_{23}H_{22}F_2$: C, 82.11; H, 6.59. Found: C, 82.14; H, 6.76.

2-[4,4-Difluoro-3-(2-phenylethyl)but-3-en-1-yl]naphthalene (**1i**)

Compound **1i** was prepared by the method described for **1f** in 62% yield as a colorless liquid. IR (neat): 3025, 2929, 1747, 1600, 1454, 1274, 1209, 817, 746 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.31 (2H, tdd, J = 7.9 Hz, J_{HF} = 2.1, 1.8 Hz), 2.37 (2H, tdd, J = 8.2 Hz, J_{HF} = 2.1, 2.1 Hz), 2.72 (2H, t, J = 8.2 Hz), 2.86 (2H, t, J = 7.9 Hz), 7.17 (2H, dd, J = 7.5, 1.5 Hz), 7.20 (1H, tt, J = 7.5, 1.5 Hz), 7.28 (1H, d, J = 7.5 Hz), 7.30 (2H, dd, J = 7.5, 7.5 Hz), 7.42 (1H, ddd, J = 7.5, 7.5, 1.5 Hz), 7.45 (1H, ddd, J = 7.5, 7.5, 1.5 Hz), 7.60 (1H, s), 7.77 (1H, d, J = 7.5 Hz), 7.77 (1H, dd, J = 7.5, 1.5 Hz), 7.81 (1H, dd, J = 7.5, 1.5 Hz). ^{13}C NMR (126 MHz, CDCl$_3$): δ 28.1, 28.2, 34.1 (dd, J_{CF} = 3, 3 Hz), 34.1 (dd, J_{CF} = 3, 3 Hz), 88.1 (dd, J_{CF} = 17, 17 Hz), 125.3, 126.0, 126.1, 126.4, 127.0, 127.4, 127.6, 128.0, 128.3, 128.4, 132.1, 133.6, 138.7, 141.2, 153.7 (dd, J_{CF} = 284, 284 Hz). ^{19}F NMR (470 MHz, CDCl$_3$): δ 67.1 (br s). HRMS: *m*/*z* calcd for $C_{22}H_{20}F_2$ (M$^+$): 322.1533; found: 322.1537.

2-[4,4-Difluoro-3-(2-phenylethyl)but-3-en-1-yl]-3-methylnaphthalene (**1j**)

Compound **1j** was prepared by the method described for **1f** in 41% yield as a colorless liquid. IR (neat): 2931, 2864, 1869, 1273, 1205, 877, 744, 698 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ 2.31 (2H, tdd, J = 8.0 Hz, J_{HF} = 2.4, 2.4 Hz), 2.35 (2H, tdd, J = 8.0 Hz, J_{HF} = 2.4, 2.4 Hz), 2.48 (3H, s), 2.75 (2H, t, J = 8.0 Hz), 2.83 (2H, t, J = 8.0 Hz), 7.18 (2H, d, J = 7.2 Hz), 7.20 (1H, t, J = 7.2 Hz), 7.29 (2H, dd, J = 7.2, 7.2 Hz), 7.36–7.41 (2H, m), 7.56 (1H, s), 7.61 (1H, s), 7.71–7.75 (2H, m). ^{13}C NMR (126 MHz, CDCl$_3$): δ 19.6, 27.2 (dd, J_{CF} = 2, 2 Hz), 28.4 (dd, J_{CF} = 2, 2 Hz), 31.7 (dd, J_{CF} = 3, 3 Hz), 34.1 (dd, J_{CF} = 3, 3 Hz), 88.3 (dd, J_{CF} = 17, 17 Hz), 125.1, 125.3, 126.1, 126.8, 126.8, 127.0, 128.2, 128.3, 128.4, 132.3, 132.4, 134.5, 138.3, 141.1, 153.7 (dd, J_{CF} = 285, 285 Hz). ^{19}F NMR (470 MHz, CDCl$_3$): δ 66.6 (br s). Anal. Calcd for $C_{23}H_{22}F_2$: C, 82.11; H, 6.59. Found: C, 82.23; H, 6.79.

1,1-Difluoro-4-(3-methyl-2-naphthyl)-2-[2-(3-methyl-2-naphthyl)ethyl]but-1-ene (**1k**)

Butyllithium (1.92 mL, 1.44 M in hexane, 2.77 mmol) was added to a THF (7.0 mL) solution of 2,2,2-trifluoroethyl 4-methylbenzenesulfonate (336 mg, 1.32 mmol) at –78 °C over 10 min under argon. The reaction mixture was stirred for 20 min at –78 °C, and then tris[2-(3-methyl-2-naphthyl)ethyl]borane [Borane–THF complex (1.49 mL, 0.98 M in THF, 1.46 mmol) was added to a solution of 2-methyl-3-vinylnaphthalene (734 mg, 4.36 mmol) in THF (2.0 mL) at 0 °C, and the mixture was stirred for 17 h at room temperature.] was added at –78 °C. After being stirred for 30 min, MeONa (221 mg, 4.10 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 2 h, and then heated at reflux for an additional 1 h. The resulting solution was cooled to –78 °C and treated with bromine (637 mg, 3.99 mmol) in CH_2Cl_2 (3.5 mL) over 1 h. After the mixture was stirred for 1 h at –78 °C and for an additional 1 h at room temperature, aq. $Na_2S_2O_3$ was added to quench the reaction. The mixture was filtered, and organic materials were extracted with Et_2O three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt, 50:1) to give **1k** (217 mg, 41%) as a colorless solid. IR (neat): 3055, 2939, 2866, 1745, 1458, 1205, 877, 742 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.39 (4H, tdd, J = 8.2 Hz, J_{HF} = 2.2, 2.2 Hz), 2.49 (6H, s), 2.88 (4H, t, J = 8.2 Hz), 7.38–7.42 (4H, m), 7.57 (2H, s), 7.62 (2H, s), 7.71–7.45 (4H, m). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.6, 27.4 (dd, J_{CF} = 2, 2 Hz), 31.8 (dd, J_{CF} = 3, 3 Hz), 88.6 (dd, J_{CF} = 17, 17 Hz), 125.1, 125.3, 126.8, 126.8, 127.0, 128.2, 132.3, 132.4, 134.5, 138.2, 153.7 (dd, J_{CF} = 286, 286 Hz). ^{19}F NMR (470 MHz, $CDCl_3$): δ 67.1 (br s). Anal. Calcd for $C_{28}H_{26}F_2$: C, 83.97; H, 6.54. Found: C, 83.81; H, 6.66.

5,6,7,8-Tetrahydrobenzo[*c*]phenanthrene (3a)

To a solution of $FSO_3H \cdot SbF_5$ (437 mg, 1.38 mmol) in $(CF_3)_2CHOH$ (4.0 mL) was added **1a** (150 mg, 0.55 mmol) in $(CF_3)_2CHOH$ (2.0 mL) at 0 °C under argon. After being stirred for 1 h at 0 °C, the mixture was warmed to room temperature. After stirring for 1 h at room temperature, phosphate buffer (pH 7) was added to quench the reaction. Organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **3a** (111 mg, 87%) as a colorless solid. IR (neat): 3026, 2943, 1684, 1599, 1483, 1448, 1227, 1105, 1037, 941, 771 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.36 (4H, t, J = 7.6 Hz), 2.74 (4H, t, J = 7.6 Hz), 7.14–7.24 (6H, m), 7.52 (2H, dd, J = 7.3, 1.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.8, 29.2, 124.8, 125.8, 126.0, 127.6, 129.9, 133.8, 137.4, 139.3. HRMS: *m*/*z* calcd for $C_{18}H_{16}$ (M^+): 232.1252; found: 232.1228.

5,6,7,8-Tetrahydro-5,8-dimethylbenzo[*c*]phenanthrene (3b)

Compound **3b** was obtained by the method described for **3a** in 85% yield as a colorless solid. IR (KBr disk): 2950, 2910, 2870, 2800, 1480, 1455, 1380, 770, 750 cm^{-1}. major: ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (6H, d, J = 7.0 Hz), 2.15 (2H, dd, J = 17.6, 7.8 Hz), 2.46 (2H, dd, J = 17.6, 5.7 Hz), 2.89 (2H, dqd, J = 7.8, 7.0, 5.7 Hz), 7.19–7.22 (4H, m), 7.24–7.28 (2H, m), 7.53–7.57 (2H, m). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.1, 32.5, 37.6, 125.1, 125.7, 125.9, 126.3, 128.7, 133.0, 136.0, 142.1. minor: ^1H NMR (500 MHz, $CDCl_3$): δ 1.26 (6H, d, J = 6.4 Hz), 2.10 (2H, dd, J = 17.5, 8.5 Hz), 2.50 (2H, dd, J = 17.5, 5.2 Hz), 2.89 (2H, dqd, J = 8.5, 6.4, 5.2 Hz), 7.19–7.22 (4H, m), 7.24–7.28

(2H, m), 7.53–7.57 (2H, m). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.0, 32.5, 37.6, 125.1, 125.7, 125.9, 126.3, 128.9, 133.1, 136.4, 142.0. Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found C, 91.99; H, 7.59.

4-Methyl-5,6,7,8-tetrahydrobenzo[*c*]phenanthrene (**3c**)

Compound **3c** was obtained by the method described for **3a** in 84% yield as a colorless solid. IR (neat): 2916, 2829, 1487, 1469, 1450, 789, 764, 739 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.32–2.38 (4H, m), 2.36 (3H, s), 2.70 (2H, t, *J* = 7.7 Hz), 2.75 (2H, t, *J* = 7.5 Hz), 7.06 (1H, d, *J* = 7.4 Hz), 7.11 (1H, dd, *J* = 7.4, 7.4 Hz), 7.15 (1H, ddd, *J* = 7.4, 7.4, 1.6 Hz), 7.18 (1H, ddd, *J* = 7.4, 7.4, 1.6 Hz), 7.24 (1H, dd, *J* = 7.4, 1.6 Hz), 7.38 (1H, d, *J* = 7.4 Hz), 7.47 (1H, dd, *J* = 7.4, 1.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.9, 24.1, 28.8, 28.8, 29.1, 122.9, 125.0, 125.1, 125.8, 125.9, 127.5, 128.2, 130.2, 133.6, 134.1, 134.7, 135.7, 137.4, 138.9. HRMS (FAB): *m*/*z* calcd for $C_{19}H_{19}$ ($[M+H]^+$): 247.1488; found: 247.1467.

3-Methyl-5,6,7,8-tetrahydrobenzo[*c*]phenanthrene (**3d**)

Compound **3d** was obtained by the method described for **3a** in 89% yield as a colorless solid. IR (neat): 2927, 2819, 1485, 1433, 823, 766, 746, 681, 652 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.33–2.36 (4H, m), 2.35 (3H, s), 2.71 (2H, t, *J* = 7.5 Hz), 2.73 (2H, t, *J* = 7.5 Hz), 7.01 (1H, d, *J* = 7.6 Hz), 7.05 (1H, s), 7.15 (1H, ddd, *J* = 7.6, 7.6, 1.4 Hz), 7.19 (1H, ddd, *J* = 7.6, 7.6, 1.4 Hz), 7.22 (1H, dd, *J* = 7.6, 1.4 Hz), 7.41 (1H, d, *J* = 7.6 Hz), 7.51 (1H, dd, *J* = 7.6, 1.4 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.1, 28.8, 28.8, 29.1, 29.2, 124.7, 124.7, 125.8, 125.9, 126.3, 127.5, 128.4, 129.7, 130.9, 133.8, 135.6, 137.4, 137.4, 138.4. HRMS (FAB): *m*/*z* calcd for $C_{19}H_{19}$ ($[M+H]^+$): 247.1488; found: 247.1484.

2-Methyl-5,6,7,8-tetrahydrobenzo[*c*]phenanthrene (**3e**)

Compound **3e** was obtained by the method described for **3a** in 80% yield as a colorless solid. IR (neat): 2927, 2829, 1485, 1450, 1435, 814, 766, 748, 635 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.31 (3H, s), 2.32–2.36 (4H, m), 2.70 (2H, t, *J* = 7.8 Hz), 2.73 (2H, t, *J* = 7.7 Hz), 6.98 (1H, dd, *J* = 7.6, 1.5 Hz), 7.12 (1H, d, *J* = 7.6 Hz), 7.17 (1H, ddd, *J* = 7.6, 7.6, 1.5 Hz), 7.22 (1H, ddd, *J* = 7.6, 7.6, 1.5 Hz), 7.23 (1H, d, *J* = 7.6 Hz), 7.35 (1H, s), 7.53 (1H, dd, *J* = 7.6, 1.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.4, 28.4, 28.8, 29.2, 29.4, 124.8, 125.4, 125.8, 125.9, 126.5, 127.4, 127.5, 129.9, 133.5, 133.7, 134.3, 135.1, 137.4, 139.3. HRMS (FAB): *m*/*z* calcd for $C_{19}H_{19}$ ($[M+H]^+$): 247.1488; found: 247.1483.

4-Methoxy-5,6,7,8-tetrahydrobenzo[*c*]phenanthrene (**3f**)

Compound **3f** was obtained by the method described for **3a** in 27% yield as a colorless solid. IR (neat): 2953, 2831, 1560, 1458, 1437, 1255, 761 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.32 (2H, t, *J* = 7.7 Hz), 2.37 (2H, t, *J* = 7.7 Hz), 2.74 (2H, t, *J* = 7.7 Hz), 2.77 (2H, t, *J* = 7.7 Hz), 3.88 (3H, s), 6.82 (1H, d, *J* = 8.6 Hz), 7.14–7.25 (5H, m), 7.48 (1H, dd, *J* = 8.6, 1.3 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.1, 28.7, 28.8, 29.2, 55.7, 108.9, 118.1, 125.0, 125.8, 125.9, 125.9, 125.9, 127.5, 131.4, 134.0, 135.1, 137.4, 139.7, 156.1. HRMS (FAB): *m*/*z* calcd. for $C_{19}H_{19}O$ ($[M+H]^+$): 263.1437; found: 263.1438.

3-Methoxy-5,6,7,8-tetrahydrobenzo[*c*]phenanthrene (**3g**)

Compound **3g** was obtained by the method described for **3a** in 59% yield as a colorless solid. IR (neat): 2931, 2829, 1606, 1498, 1248, 1039, 766 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.31–2.38 (4H, m), 2.72 (2H, t, *J* = 6.9 Hz), 2.73 (2H, t, *J* = 7.0 Hz), 3.82 (3H, s), 6.74 (1H, dd, *J* = 8.1, 2.6 Hz), 6.80 (1H, d, *J* = 2.6 Hz), 7.14–7.22 (3H, m), 7.45 (1H, d, *J* = 8.1 Hz), 7.50 (1H, d, *J* = 8.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.8, 29.0, 29.1, 29.2, 55.3, 110.4, 113.8, 124.7, 125.8, 125.9, 125.9, 126.7, 127.5, 129.4, 133.9, 137.0, 137.4, 139.2, 157.8. HRMS (FAB): *m*/*z* calcd for $C_{19}H_{19}O$ ($[M+H]^+$): 263.1437; found: 263.1439.

14-Methyl-5,6,7,8-tetrahydrobenzo[*c*]chrysene (**3h**)

Compound **3h** was obtained by the method described for **3a** in 92% yield as a colorless solid. IR (neat): 2927, 2829, 1485, 1450, 1435, 814, 766, 748, 635 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.41–2.47 (4H, m), 2.67 (3H, s), 2.80 (2H, t, *J* = 7.4 Hz), 3.17 (2H, t, *J* = 7.7 Hz), 7.18 (1H, ddd, *J* = 7.3, 7.3, 1.2 Hz), 7.22 (1H, ddd, *J* = 7.3, 7.3, 1.2 Hz), 7.25 (1H, dd, *J* = 7.3, 1.2 Hz), 7.44 (1H, dd, *J* = 7.3, 1.2 Hz), 7.46 (1H, ddd, *J* = 7.3, 7.3, 1.2 Hz), 7.52 (1H, ddd, *J* = 7.3, 7.3, 1.2 Hz), 7.56 (1H, s), 8.00 (1H, dd, *J* = 7.3, 1.2 Hz), 8.12 (1H, dd, *J* = 7.3, 1.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.6, 23.3, 28.9, 28.9, 29.1, 124.1, 124.7, 124.7, 124.7, 125.1, 125.5, 125.9, 126.0, 127.6, 130.5, 130.6, 130.7, 131.2, 131.7, 131.7, 139.0, 137.4, 139.3. HRMS (FAB): *m*/*z* calcd for $C_{23}H_{21}$ ($[M+H]^+$): 297.1643; found: 297.1623.

5,6,7,8-Tetrahydronaphtho[1,2-*a*]anthracene (**3i**)

Compound **3i** was obtained by the method described for **3a** in 62% yield as a pale yellow solid. ^1H NMR (500 MHz, $CDCl_3$): δ 2.41 (2H, t, *J* = 7.5 Hz), 2.45 (2H, t, *J* = 6.9 Hz), 2.79 (2H, t, *J* = 7.5 Hz), 2.93 (2H, t, *J* = 6.9 Hz), 7.20–7.28 (3H, m), 7.38 (1H, ddd, *J* = 7.7, 7.7, 1.2 Hz), 7.41 (1H, ddd, *J* = 7.7, 7.7, 1.2 Hz), 7.65 (1H, s), 7.68 (1H, d, *J* = 7.7 Hz), 7.74 (1H, dd, *J* = 7.7, 1.2 Hz), 7.75 (1H, dd, *J* = 7.7, 1.2 Hz), 7.95 (1H, s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 28.8, 29.4, 29.4, 29.6, 123.0, 125.0, 125.2, 125.3, 125.4, 126.0, 126.2, 126.8, 127.7, 127.9, 130.1, 132.1, 132.3, 132.5, 133.9, 136.6, 137.6, 140.4. HRMS (FAB): *m*/*z* calcd for $C_{22}H_{19}$ ($[M+H]^+$): 283.1487, Found: 283.1497.

2-Methyl-3,4,5,6-tetrahydrodibenzo[*c*,*g*]phenanthrene (**3j**)

Compound **3j** was obtained by the method described for **3a** in 78% yield as a pale yellow solid. IR (neat): 2920, 2879, 2825, 1485, 1215, 875, 746 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.23 (1H, ddd, *J* = 16.2, 5.4, 1.3 Hz), 2.38–2.46 (2H, m), 2.52 (3H, s), 2.54–2.62 (2H, m), 2.82 (1H, ddd, *J* = 14.4, 5.4, 1.2 Hz), 2.93–3.01 (2H, m), 6.60 (1H, dd, *J* = 7.9, 1.2 Hz), 6.94 (1H, ddd, *J* = 7.9, 7.9, 1.2 Hz), 7.08 (1H, ddd, *J* = 7.9, 7.9, 1.2 Hz), 7.09 (1H, ddd, *J* = 7.9, 7.9, 1.2 Hz), 7.24 (1H, d, *J* = 7.9, 1.2 Hz), 7.31 (1H, ddd, *J* = 7.9, 7.9, 1.2 Hz), 7.44 (1H, dd, *J* = 7.9, 1.2 Hz), 7.58 (1H, s), 7.73 (1H, dd, *J* = 7.9, 1.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.6, 25.8, 28.7, 28.8, 29.7, 123.3, 124.4, 125.4, 125.4, 125.6, 127.1, 127.2, 127.3, 127.5, 128.1, 130.3, 130.4, 132.7, 133.2, 135.4, 135.8, 136.8, 142.5. HRMS (FAB): *m*/*z* calcd for $C_{23}H_{21}$ ($[M+H]^+$): 297.1643; found: 297.1632.

6,11-Dimethyl-7,8,9,10-tetrahydrohexahelicene (**3k**)

Compound **3k** was obtained by the method described for **3a** in 62% yield as a pale yellow solid. IR (neat): 2958, 2921, 2872, 1418, 1216, 873, 845, 747 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.37–2.56 (4H, m), 2.60 (6H, s), 2.73 (2H, ddd, *J* = 16.3, 15.2, 6.1 Hz), 3.06–3.12 (2H, m), 6.61 (2H, ddd, *J* = 7.8, 7.8, 0.8 Hz), 6.82 (2H, dd, *J* = 7.8, 0.8 Hz), 7.05 (2H, ddd, *J* = 7.8, 7.8, 0.8 Hz), 7.56 (2H, s), 7.58 (2H, dd, *J* = 7.8, 0.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.8, 25.7, 29.0, 123.5, 124.2, 125.5, 126.8, 127.0, 128.1, 130.7, 132.4, 133.0, 133.1, 133.9, 145.7. HRMS (FAB): *m*/*z* calcd for $C_{28}H_{25}$ ($[M+H]^+$): 361.1956; found: 361.1929.

Benzo[*c*]phenanthrene (**4a**)[S1]

Triphenylmethylium tetrafluoroborate (370 mg, 1.12 mmol) and **3a** (76 mg, 0.33 mmol) were dissolved in 1,2-dichloroethane ($ClCH_2CH_2Cl$, 4.0 mL) and heated to reflux for 3 h under argon. The solvent was removed under reduced pressure, and the residue was purified by thin-layer chromatography on silica gel (hexane–AcOEt, 10:1) to give **4a** (60 mg, 80%) as a colorless solid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (2H, dd, *J* = 7.9, 7.9 Hz), 7.69 (2H, dd, *J* = 7.9, 7.9 Hz), 7.84 (2H, d, *J* = 7.9 Hz), 7.91 (2H, d, *J* = 7.9 Hz), 8.03 (2H, d, *J* = 7.9 Hz), 9.14 (2H, d, *J* = 7.9 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 125.9, 126.1, 126.7, 127.4, 127.9, 128.6, 130.3, 131.0, 133.5, 133.5.

5,8-Dimethylbenzo[*c*]phenanthrene (**4b**)

To a solution of **3b** (41 mg, 0.158 mmol) in mesitylene was added palladium on carbon (10 mg, Pd: 10%, 25wt%) under nitrogen. The reaction mixture was heated for 9 h at reflux. The mixture was filtered, and organic materials were extracted with CH_2Cl_2 three times. The combined extracts were washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by thin-layer chromatography on silica gel (hexane) to give **4b** (33 mg, 82%) as a colorless solid. IR (KBr disk): 3074, 2966, 2850, 1606, 1502, 1439, 1407, 1383, 903, 754 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.77 (6H, s), 7.57 (2H, s), 7.60–7.68 (4H, m), 8.14 (2H, dd, *J* = 7.9, 1.8 Hz), 9.05 (2H, dd, *J* = 7.9, 1.8 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.7, 124.4, 125.3, 125.6, 126.7, 128.3, 128.3, 130.3, 130.5, 132.7, 123.0. HRMS: *m*/*z* calcd for $C_{20}H_{16}$ (M^+): 256.1252; found: 256.1262.

4-Methylbenzo[*c*]phenanthrene (**4c**)

Compound **4c** was obtained by the method described for **4a** in 81% yield as a colorless solid. IR (neat): 3047, 2924, 1603, 1423, 831, 750, 669 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.84 (3H, s), 7.48 (1H, dd, *J* = 8.5, 1.2 Hz), 7.57 (1H, dd, *J* = 8.5, 8.5 Hz), 7.62 (1H, ddd, *J* = 8.5, 8.5, 1.2 Hz), 7.67 (1H, ddd, *J* = 8.5, 8.5, 1.2 Hz), 7.83 (1H, d, *J* = 8.5 Hz), 7.87 (1H, d, *J* = 8.5 Hz), 7.90 (1H, d, *J* = 8.5 Hz), 8.02 (1H, dd, *J* = 8.5, 1.2 Hz), 8.12 (1H, d, *J* = 8.5 Hz), 8.99 (1H, dd, *J* = 8.5, 1.2 Hz), 9.10 (1H, dd, *J* = 8.5, 1.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.3, 123.2, 125.5, 125.8, 126.0, 126.4, 126.6, 126.7, 127.0, 127.4, 127.8, 128.3, 128.4, 130.3, 130.4, 130.5, 132.3, 133.5, 134.5. HRMS (FAB): *m*/*z* calcd for $C_{19}H_{15}$ ($[M+H]^+$): 243.1175; found: 243.1193.

3-Methylbenzo[*c*]phenanthrene (**4d**)

Compound **4d** was obtained by the method described for **4a** in 80% yield as a colorless solid. IR (neat): 3045, 1423, 1232, 835, 744, 669 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.61 (3H, s), 7.51 (1H, d, J = 8.1 Hz), 7.62 (1H, ddd, J = 8.1, 8.1, 1.2 Hz), 7.68 (1H, ddd, J = 8.1, 8.1, 1.2 Hz), 7.80 (1H, d, J = 8.1 Hz), 7.82 (1H, s), 7.82 (1H, d, J = 8.1 Hz), 7.83 (1H, d, J = 8.1 Hz), 7.87 (1H, d, J = 8.1 Hz), 8.01 (1H, dd, J = 8.1, 1.2 Hz), 9.03 (1H, d, J = 8.1 Hz), 9.12 (1H, dd, J = 8.1, 1.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.4, 125.7, 126.0, 126.9, 126.9, 127.0, 127.1, 127.3, 127.7, 127.9, 127.9, 128.0, 128.1, 128.3, 128.5, 130.2, 133.4, 133.7, 135.6. HRMS (FAB): *m*/*z* calcd for $C_{19}H_{15}$ ($[M+H]^+$): 243.1175; found: 243.1172.

2-Methylbenzo[*c*]phenanthrene (**4e**)

Compound **4e** was obtained by the method described for **4b** in 96% yield as a colorless solid. IR (neat): 3045, 3008, 2916, 2846, 1614, 1602, 1506, 839, 752 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.66 (3H, s), 7.46 (1H, dd, J = 8.3, 1.2 Hz), 7.62 (1H, ddd, J = 8.3, 8.3, 1.2 Hz), 7.69 (1H, ddd, J = 8.3, 8.3, 1.2 Hz), 7.76 (1H, d, J = 8.3 Hz), 7.81 (1H, d, J = 8.3 Hz), 7.85 (1H, d, J = 8.3 Hz), 7.87 (1H, d, J = 8.3 Hz), 7.92 (1H, d, J = 8.3 Hz), 8.01 (1H, dd, J = 8.3, 1.2 Hz), 8.93 (1H, d, J = 1.2 Hz), 9.14 (1H, dd, J = 8.3, 1.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 22.3, 125.6, 125.9, 125.9, 126.8, 126.9, 127.2, 127.2, 127.3, 127.6, 127.8, 128.3, 128.4, 130.3, 130.4, 131.1, 131.5, 133.4, 135.8. HRMS (FAB): *m*/*z* calcd for $C_{19}H_{15}$ ($[M+H]^+$): 243.1175; found: 243.1148.

4-Methoxybenzo[*c*]phenanthrene (**4f**)[S2]

Compound **4f** was obtained by the method described for **4a** in 80% yield as a colorless solid. ^1H NMR (500 MHz, $CDCl_3$): δ 4.08 (3H, s), 7.02 (1H, d, J = 8.4 Hz), 7.58 (1H, dd, J = 8.4, 8.4 Hz), 7.60 (1H, ddd, J = 8.4, 8.4, 1.1 Hz), 7.66 (1H, ddd, J = 8.4, 8.4, 1.1 Hz), 7.82 (1H, d, J = 8.4 Hz), 7.83 (1H, d, J = 8.4 Hz), 7.87 (1H, d, J = 8.4 Hz), 8.00 (1H, dd, J = 8.4, 1.1 Hz), 8.41 (1H, d, J = 8.4 Hz), 8.71 (1H, d, J = 8.4 Hz), 9.12 (1H, dd, J = 8.4, 1.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.8, 104.8, 118.6, 120.3, 120.9, 125.7, 125.9, 126.0, 126.0, 126.7, 127.0, 127.5, 128.1, 128.4, 130.5, 131.2, 131.3, 133.4, 155.7.

3-Methoxybenzo[*c*]phenanthrene (**4g**)

Compound **4g** was obtained by the method described for **4a** in 82% yield as a colorless solid. IR (neat): 3047, 1610, 1427, 1265, 1234, 1033, 833, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 4.00 (3H, s), 7.32 (1H, dd, J = 9.2, 2.1 Hz), 7.36 (1H, d, J = 2.1 Hz), 7.58–7.68 (2H, m), 7.78–7.84 (4H, m), 7.99 (1H, dd, J = 9.2, 2.1 Hz), 9.03 (1H, d, J = 9.2 Hz), 9.05 (1H, dd, J = 9.2, 2.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 55.4, 107.9, 117.0, 125.0, 125.7, 125.9, 126.4, 126.7, 126.8, 127.4, 127.5, 127.8, 128.4, 129.4, 129.6, 130.0, 133.5, 135.0, 157.4. HRMS (FAB): *m*/*z* calcd for $C_{19}H_{15}O$ ($[M+H]^+$): 259.1122; found: 259.1126.

14-Methylbenzo[*c*]chrysene (4h)

Compound **4h** was obtained by the method described for **4a** in 82% yield as a pale yellow solid. IR (neat): 3047, 2918, 1606, 1441, 1261, 1213, 835, 769 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.89 (3H, s), 7.65 (1H, ddd, *J* = 8.3, 8.3, 1.1 Hz), 7.71 (1H, ddd, *J* = 8.3, 8.3, 1.1 Hz), 7.72 (1H, ddd, *J* = 8.3, 8.3, 1.1 Hz), 7.75 (1H, ddd, *J* = 8.3, 8.3, 1.1 Hz), 7.88 (1H, d, *J* = 8.3 Hz), 7.89 (1H, d, *J* = 8.3 Hz), 8.01 (1H, d, *J* = 8.3 Hz), 8.03 (1H, dd, *J* = 8.3, 1.1 Hz), 8.16 (1H, dd, *J* = 8.3, 1.1 Hz), 8.81 (1H, d, *J* = 8.3 Hz), 8.86 (1H, dd, *J* = 8.3, 1.1 Hz), 8.91 (1H, s), 9.09 (1H, dd, *J* = 8.3, 1.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.6, 121.8, 123.7, 124.5, 125.8, 125.9, 126.2, 126.3, 126.5, 126.5, 126.7, 127.4, 127.5, 128.4, 128.5, 128.5, 129.2, 130.3, 130.6, 131.1, 131.5, 132.0, 133.6. HRMS (FAB): *m*/*z* calcd for $C_{23}H_{17}$ ([M+H]$^+$): 293.1330; found: 293.1324.

2-Methyldibenzo[*c*,*g*]phenanthrene (4j)

Compound **4j** was obtained by the method described for **4a** in 80% yield as a pale yellow solid. IR (neat): 3047, 2939, 1437, 1215, 881, 833, 748 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.84 (3H, d, *J* = 1.6 Hz), 7.17 (1H, ddd, *J* = 8.1, 8.1, 1.2 Hz), 7.24 (1H, ddd, *J* = 8.1, 8.1, 1.2 Hz), 7.46 (1H, ddd, *J* = 8.1, 8.1, 1.2 Hz), 7.49 (1H, ddd, *J* = 8.1, 8.1, 1.2 Hz), 7.75 (1H, d, *J* = 1.6 Hz), 7.85 (1H, dd, *J* = 8.1, 1.2 Hz), 7.86 (1H, d, *J* = 8.1 Hz), 7.89 (1H, d, *J* = 8.1 Hz), 7.90 (1H, d, *J* = 8.1 Hz), 7.93 (1H, dd, *J* = 8.1, 1.2 Hz), 8.06 (1H, d, *J* = 8.1 Hz), 8.40 (1H, dd, *J* = 8.1, 1.2 Hz), 8.45 (1H, dd, *J* = 8.1, 1.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.2, 123.0, 123.6, 124.3, 126.1, 126.1, 126.2, 127.0, 127.0, 127.0, 127.3, 127.3, 127.4, 127.8, 129.1, 129.3, 130.0, 131.0, 131.7, 131.8, 132.3, 132.3, 132.5. HRMS (FAB): *m*/*z* calcd for $C_{23}H_{17}$ ([M+H]$^+$): 293.1330; found: 293.1308.

6,11-Dimethylhexahelicene (4k)

Compound **4k** was obtained by the method described for **4a** in 86% yield as a pale yellow solid. IR (neat): 3024, 2921, 1439, 1034, 878, 730, 609 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.93 (6H, s), 6.59 (2H, ddd, *J* = 8.1, 8.1, 1.2 Hz), 7.15 (2H, ddd, *J* = 8.1, 8.1, 1.2 Hz), 7.46 (2H, dd, *J* = 8.1, 1.2 Hz), 7.70 (2H, dd, *J* = 8.1, 1.2 Hz), 7.75 (2H, s), 8.04 (2H, d, *J* = 8.1 Hz), 8.18 (2H, d, *J* = 8.1 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.4, 123.1, 123.8, 124.3, 125.5, 126.5, 126.6, 127.7, 127.7, 128.6, 129.3, 131.1, 131.5, 131.7, 132.2. HRMS (FAB): *m*/*z* calcd for $C_{28}H_{21}$ ([M+H]$^+$): 357.1643; found: 357.1638.

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