## SUPPORTING INFORMATION

# Divergent Reaction Pathways for Phenol Arylation by Arynes: Synthesis of Helicenes and 2-Arylphenols

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**General considerations**:

For helicene synthesis, reactions were performed in 2-dram vials using screw caps with 17 mm hole and white silicone septum with white teflon face (from SUPELCO). For phenol arylation, reactions were run in 2-dram vials using 17 mm screw caps with PTFE/Liner (from SUPELCO). Column chromatography was performed on 60Å silica gel (Sorbent Technologies). Purification by preparative HPLC was performed on a Shimadzu Prominence LC (LC-20AB) equipped with a SPD-20A UV-Vis detector and a Varian Dynamax (250 mm x 21.4 mm) column. GC-MS analyses were performed on a Shimadzu GCMS-QP5000 chromatograph equipped with a Restek column (Rtx-XLB, 30 m x 0.25 mm I.D.). The $^{1}$H and $^{13}$C NMR were recorded on JEOL EC-400 or JEOL EC-500 spectrometers using residual solvent peak as a reference. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. IR spectra were obtained on a ThermoNicolet Avatar 370 FT-IR instrument. Analytical thin layer chromatography was performed on silica gel IB-F (Baker-flex) by J. T. Baker. All procedures were performed under nitrogen atmosphere unless otherwise noted.

Room temperature: 25 $^{o}$C.

**Materials**. The following starting materials were obtained from commercial sources and were used without further purification: phenol, 2-*tert*-butylphenol, 3-*tert*-butylphenol, 2,3-dimethylphenol, 2,6-diisopropylphenol, 2-hydroxybenzotrifluoride, 4-hydroxybiphenyl, 1-naphthol, 2-naphthol, 7-methoxy-2-naphthol, 4-hydroxybenzophenone, chlorobenzene, 2-chloroanisole, 3-chloro-1-fluorobenzene, 3-chlorobenzonitrile 1-chloronaphthalene, 3-chlorobenzotrifluoride, 1,1'-binaphthyl-2,2'-diol (racemic), silver acetate, *tert*-butyl-3-bromobenzoate, 2,2,6,6-tetramethylpiperidine (TMPH), iodomethane, *m*-cresol, (R)-(+)-1,1'-bi(2-naphthol). 3-(*tert*-Butyldimethylsilyloxy) phenol was synthesized according to literature.[1]

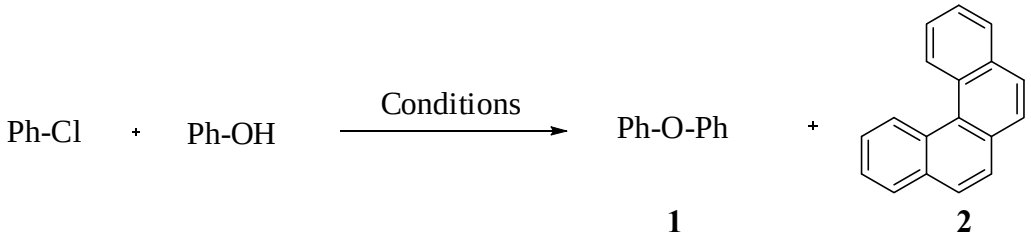
**TMPLi**: A 250 mL oven-dried flask equipped with a magnetic stirring bar and a septum was evacuated and backfilled with nitrogen 5 times. TMPH (15.5 g, 18.5 mL, 110 mmol) was added via syringe, followed by anhydrous pentane to give approximately 100 mL of solution. The mixture was cooled to -73 °C (dry ice-acetone bath) and stirred for 10 minutes. *n*-BuLi (2.5 M in hexanes, 40.0 mL, 100 mmol) was added dropwise and reaction mixture was stirred for 30 minutes at -73 °C, then warmed up to room temperature (25 °C) and stirred overnight. The

reaction mixture was vacuumed to remove all solvent and dried under vacuum for at least 5 hours. A light yellow powder of solid TMPLi was obtained.

**TMPLi 1 M in pentane/hexanes:** A 50 mL oven-dried flask equipped with a magnetic stirring bar and a septum was evacuated and backfilled with argon 5 times. TMPH (4.64 g, 33.0 mmol) was added, followed by anhydrous pentane to give 30 mL of solution (marked the flask at the level of solution). The mixture was cooled to -73 °C (dry ice-acetone) and stirred for 5 minutes. *n*-BuLi (2.5 M in hexanes, 12.0 mL, 30 mmol) was added dropwise and reaction mixture was stirred for 30 minutes at -73 °C, then warmed up to room temperature and stirred overnight. The reaction mixture was vacuumed to give 30 mL (at the marked level) of TMPLi suspension.

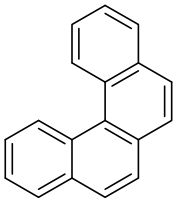
**General procedure for synthesis of helicenes**: A 2 dram vial equipped with a magnetic stir bar was charged with appropriate phenol (0.5 mmol) and ArCl (3 – 4 equiv). The vial was flushed with nitrogen and capped. To this mixture was added the appropriate base solution or suspension (3.7 – 4.7 equiv) at the specified reaction temperature by injecting through the septum by 1 mL syringe. The base suspension was stirred vigorously during the time being withdrawn by syringe. Tetrahydrofuran (THF) or diethyl ether was then promptly added. The vial was flushed with nitrogen (20 seconds) and then stirred at specified temperature for indicated time. Unless otherwise stated, reaction mixture was quenched with anhydrous MeOH (0.5 mL), evacuated to volume of 1 mL and subjected to column chromatography on silica gel in hexanes or pentane followed by appropriate solvent to elute the product. After concentrating the fractions containing the product, the residue was dried under reduced pressure.

**Optimization of conditions of helicene synthesis:** All reactions were carried out following the general procedure. Phenol (x mmol), chlorobenzene (y mmol), TMPLi [1M suspention in pentane/hexanes, 1.2*(x + y) mmol], 24 hours. Conversions and **1**/**2** ratio were calculated by GC analysis. Conversions are presented in Table S1 and show the amount of product **1** and **2** formed (e.g. 70 % means that 70 % of starting limiting reagent is converted to **1** and **2**). Mixture with exact molar amounts of pure **1** and pure **2** was used as the standard to determine the ratio **2**/**1**.




**1** **2**

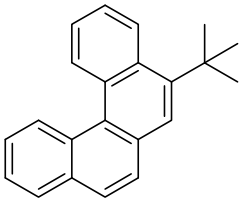
| Entry | PhOH /PhCl | Base/T ($^{o}$C) | Solvent | Conversion | **2/1** |
|---|---|---|---|---|---|
| 1 | 1/2 | TMPLi/ 25 $^{o}$C | THF | 32 | 1/4 |
| 2 | 1/2 | TMPLi/ 25 $^{o}$C | $Et_2O$ | 21 | 1/3 |
| 3 | 1/2 | LDA/ 25 $^{o}$C | $Et_2O$ | 27 | < 1/50 |
| 3 | 1/2 | TMPLi/ 40 $^{o}$C | Pentane | 35 | 7/1 |
| 4 | 2/1 | TMPLi/ 40 $^{o}$C | Pentane | 17 | 1/2 |
| 5 | 1/2 | TMPLi/ 25 $^{o}$C | Pentane/THF (10/1) | 40 | 8/1 |
| 6 | 1/2 | TMPLi/ 25 $^{o}$C | Pentane/THF (8/1) | 34 | 7/1 |
| 7 | 1/2 | TMPLi/ 25 $^{o}$C | Pentane/THF (20/1) | 52 | 40/1 |
| 8 | 1/2 | TMPLi/ 25 $^{o}$C | Pentane/THF (36/1) | 61 | > 50/1 |
| 9 | 1/2 | TMPLi/ 25 $^{o}$C | Pentane/THF (50/1) | 65 | > 50/1 |
| 10 | 1/4 | TMPLi/ 25 $^{o}$C | Pentane/THF (50/1) | 80 | > 50/1 |



**Benzophenanthrene (2) (Table 2, Entry 1)**

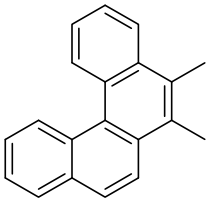
Chlorobenzene (225 mg, 2.0 mmol), phenol (48 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.7 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 76 mg (67 %) of a light yellow solid was obtained.

Chlorobenzene (112.5 mg, 1.0 mmol), benzocyclooctenone-5(6H) (85 mg, 0.5 mmol), TMPLi in pentane (1M, 1.8 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 102 mg (90 %) of a light yellow solid was obtained. $R_f$ = 0.24 (hexanes/$CH_2Cl_2$ 90/10). This compound is known.[2] $^1$H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 8.4 Hz, 2H), 8.03 (dd, *J* = 8.0 Hz, 1.3 Hz, 2H), 7.93 – 7.90 (m, 2H), 7.85 – 7.82 (m, 2H), 7.71 – 7.61 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 133.6, 131.1, 130.4, 128.6, 128.0, 127.6, 127.4, 127.0, 126.2, 126.0.



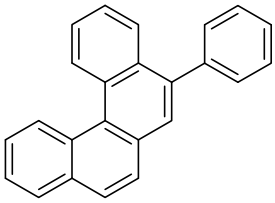
**5-*tert*-Butylbenzophenanthrene (3) (Table 2, Entry 2)**

Chlorobenzene (225 mg, 2.0 mmol), 2-*tert*-butylphenol (75 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.7 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 68 mg (48 %) of a colorless oil was obtained. $R_f$ = 0.35 (hexanes/$CH_2Cl_2$ 90/10). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.17 – 9.14 (m, 1H), 9.04 (d, *J* = 8.5 Hz, 1H), 8.69 – 8.66 (m, 1H), 8.01 (dd, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.91 – 7.80 (m, 3H), 7.69 – 7.59 (m, 5H), 1.76 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 144.6, 133.6, 132.0, 131.9, 130.4, 129.9, 129.3, 128.6, 128.2, 127.6, 127.1, 127.0, 126.7, 126.2, 125.6, 124.8, 124.7, 124.3, 36.0, 32.1. FT-IR (neat, $cm^{-1}$) 2965, 1599, 1368, 887. Anal calcd for $C_{22}H_{20}$ (284.16 g/mol): C, 92.91; H, 7.09; Found. C, 92.51; H, 7.15.



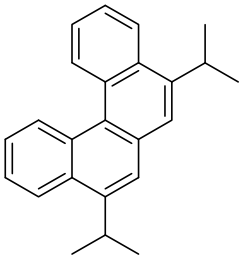
**5,6-Dimethylbenzophenanthrene (4) (Table 2, Entry 3)**

Chlorobenzene (225 mg, 2.0 mmol), 2,3-dimethylphenol (61 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.7 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 74 mg (58 %) of a white solid was obtained. $R_f$ = 0.27 (hexanes/$CH_2Cl_2$ 90/10). This compound is known.[3] $^1$H NMR (400 MHz, $CDCl_3$) δ 9.03 – 9.01 (m, 2H), 8.24 (dd, *J* = 8.2 Hz, 1.5 Hz, 1H), 8.12 (d, *J* = 9.1 Hz, 1H), 8.02 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H), 7.93 (d, *J* = 9.1 Hz, 1H), 7.68 – 7.59 (m, 4H), 2.81 (s, 3H), 2.80 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 133.2, 132.7, 130.7, 130.2, 130.0, 129.6, 129.1, 128.8, 128.7, 128.2, 127.2, 126.8, 126.0, 125.9, 125.6, 124.7, 124.1, 122.8, 16.4, 16.2.



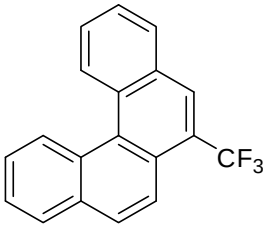
**5-Phenylbenzophenanthrene (5) (Table 2, Entry 4)**

Chlorobenzene (225 mg, 2.0 mmol), 2-phenylphenol (85 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.7 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 98 mg (65 %) of a light yellow solid was obtained. $R_f$ = 0.19 (hexanes/$CH_2Cl_2$ 90/10). This compound is known.[4] $^1$H NMR (400 MHz, $CDCl_3$) δ 9.25 (d, *J* = 8.6 Hz, 1H), 9.21 (d, *J* = 8.6 Hz, 1H), 8.14 (dd, *J* = 8.0 Hz, 1.1 Hz, 1H), 8.08 (dd, *J* = 8.0 Hz, 1.1 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.84 (s, 1H), 7.77 – 7.72 (m, 2H), 7.69 – 7.66 (m, 3H), 7.61 – 7.57 (m, 3H), 7.55 – 7.52 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 140.7, 139.2, 133.7, 132.4, 130.9, 130.5, 130.3, 128.8, 128.6, 128.4, 128.1, 128.0, 127.6, 127.1, 127.0, 126.9, 126.4, 126.2, 126.1, 126.0. Signals for two carbons could not be located.



**5,8-Diisopropylbenzophenanthrene (6) (Table 2, Entry 5)**

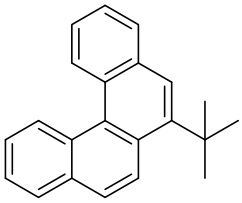
Chlorobenzene (225 mg, 2.0 mmol), 2.6-diisopropylphenol (89 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.7 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 62 mg (40 %) of a white solid was obtained. $R_f$ = 0.34 (hexanes/$CH_2Cl_2$ 90/10), mp 91 – 93 $^oC$ (from hexane). $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.07 – 9.04 (m, 2H), 8.31 – 8.29 (m, 2H), 7.73 (s, 2H), 7.67 – 7.62 (m, 4H), 3.84 (heptet, *J* = 6.5 Hz, 2H), 1.52 (d, *J* = 6.5 Hz, 12H). $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) δ 143.2, 131.7, 130.6, 130.5, 128.9, 125.5, 125.4, 125.1, 123.7, 122.5, 28.6, 23.5. FT-IR (neat, $cm^{-1}$) 2963, 1603, 1521, 893. Anal calcd for $C_{24}H_{24}$ (312.19 g/mol): C, 92.26; H, 7.74; Found. C, 92.55; H, 7.32.




**6-(Trifluoromethyl)benzophenanthrene (7) (Table 2, Entry 6)**

Chlorobenzene (225 mg, 2.0 mmol), 3-hydroxybenzotrifluoride (81 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.7 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 59 mg (40 %) of a white solid was obtained. $R_f$ = 0.31 (hexanes/$CH_2Cl_2$ 90/10), mp 78 – 80 $^oC$ (from hexane). $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.06 – 9.01 (m, 2H), 8.31 (s, 1H), 8.18 – 8.15 (m, 1H), 8.08 – 8.02 (m, 2H), 7.98 (d, *J* = 9.1 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.70 – 7.65 (m, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) δ 133.2, 131.6, 131.0, 130.0, 129.6, 129.5, 129.1, 128.4, 128.3, 128.2, 127.0 (q, *J* = 6.7 Hz), 126.9, 126.8, 126.5, 126.0, 124.9 (q, *J* = 273 Hz), 124.5, (q, *J* = 30.8 Hz), 122.2 (q, *J* = 2.7 Hz).

Signal for one carbon could not be located. FT-IR (neat, $cm^{-1}$) 3680, 2967, 1328, 1110, 1054, 1032. Anal calcd for $C_{19}H_{11}F_3$ (296.08 g/mol): C, 77.02; H, 3.74; Found. C, 77.41; H, 3.72.



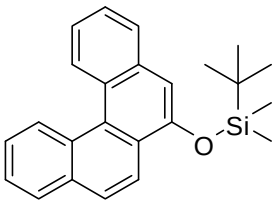
**6-*tert*-Butylbenzophenanthrene (8) (Table 2, Entry 7)**

Chlorobenzene (225 mg, 2.0 mmol), 3-*tert*-butylphenol (75 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 3.0 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 72 mg (51 %) of a light yellowish oil was obtained.

6-*tert*-Butyl-6a,12b-dihydrobenzophenanthren-12b-ol (**12**) (151 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 1.0 mL), followed by THF (0.03 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 127 mg (90 %) of a light yellowish oil was obtained.

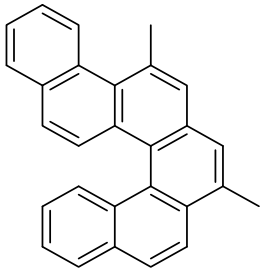
Chlorobenzene (112.5 mg, 1.0 mmol), (7E,9Z)-7-tert-butylbenzo[8]annulen-5(6H)-one **(11)** (113 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.5 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 82 mg (58 %) of a light yellow oil was obtained.

$R_f$ = 0.34 (hexanes/$CH_2Cl_2$ 90/10). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.01 – 8.99 (m, 1H), 8.94 – 8.92 (m, 1H), 8.51 (d, *J* = 9.1 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.90 (s, 1H), 7.87 (d, *J* = 9.1 Hz, 1H), 7.62 – 7.56 (m, 4H), 1.72 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 143.9, 132.9, 132.3, 130.7, 129.8, 129.6, 129.2, 129.1, 128.4, 128.2, 127.7, 126.0, 125.6, 125.5, 125.3, 125.2, 124.5, 36.1, 32.3. Signal for one carbon could not be located. FT-IR (neat, $cm^{-1}$) 2960, 1487, 1367, 889. Anal calcd for $C_{22}H_{20}$ (284.16 g/mol): C, 92.91; H, 7.09; Found. C, 92.76; H, 6.88.

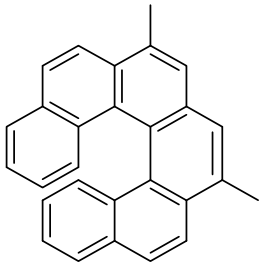



**(Benzo[c]phenanthren-6-yloxy)(tert-butyl)dimethylsilane (9) (Table 2, Entry 8)**

Chlorobenzene (225 mg, 2.0 mmol), 3-(*tert*-butyldimethylsilyloxy) phenol (112 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 3.0 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 93 mg (52 %) of a light yellow oil was obtained. $R_f$ = 0.23 (hexanes/$CH_2Cl_2$ 90/10). $^1$H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, *J* = 8.1 Hz, 1H), 9.08 (d, *J* = 8.1 Hz, 1H), 8.38 (d, *J* = 8.7 Hz, 1H), 8.06 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H), 7.97 (d, *J* = 8.7 Hz, 1H), 7.91 (dd, *J* = 7.9 Hz, 1.4 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.62 – 7.56 (m, 2H), 7.30 (s, 1H), 1.21 (s, 9H), 0.42 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 149.8, 134.2, 133.7, 130.3, 129.3, 128.6, 128.3, 128.1, 127.4, 127.3, 127.2, 126.7, 126.3, 126.2, 126.1, 124.0, 121.0, 112.0, 26.1, 18.7, -4.0.



**7,10-Dimethylnaphtho[2,1-c]chrysene (10)**



**3,6-Dimethylphenanthro[3,4-c]phenanthrene (11)**

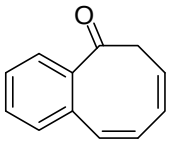
**(Scheme 1)**

1-Chloronaphthalene (335 mg, 2.0 mmol), 2,6-dimethylphenol (62 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.7 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/$CH_2Cl_2$ 90/10), 106 mg (60 %) of a light brown solid (mixture of isomers) was obtained. The isomer ratio was determined to be 2/1 **10**/**9** by $^1$HNMR. The isomers were separated by fractional crystallization from hexanes. Compound **10** crystallized out and was collected by vacuum filtration at - 20 $^o$C. Residue from crystallization contains a mixture of two isomers. White crystalline **10** was obtained (45 mg, 26% yield) and 61 mg of isomer mixture was recovered. Mixture: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.5

Hz), 8.16 – 8.11 (m), 8.05 – 8.03 (m), 7.99 – 7.89 (m), 7.83 – 7.81 (m), 7.75 – 7.72 (m), 7.68 – 7.62 (m), 7.53 – 7.47 (m), 7.43 (d, *J* = 8.8 Hz), 7.21 – 7.17 (m), 6.65 – 6.61 (m), 3.17 (s), 2.90 (s), 2.86 (s).

**3,6-Dimethylphenanthro[3,4-c]phenanthrene (11) (Scheme 1)**

$R_f$ = 0.19 (hexanes/$CH_2Cl_2$ 90/10), mp 240 – 242 $^oC$ (from hexanes). $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.1 Hz, 2H), 7.93 (d, *J* = 9.1 Hz, 2H), 7.80 (dd, *J* = 8.3 Hz, 0.9 Hz, 2H), 7.76 (s, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.19 = 7.15 (m, 2H), 7.65 – 7.60 (m, 2H), 2.90 (s, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) δ 133.2, 132.6, 131.4, 130.2, 130.1, 128.6, 128.2, 127.3, 127.2, 126.8, 125.4, 124.5, 122.2, 122.1, 20.1. FT-IR (neat, $cm^{-1}$) 2380, 2343, 2334. Anal calcd for $C_{28}H_{20}$ (356.16 g/mol): C, 94.34; H, 5.66; Found. C, 93.96; H, 5.64.

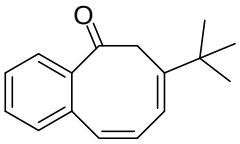



**5(6H)-Benzocyclooctenone (16) (Scheme 3)**

Chlorobenzene (90 mg, 0.8 mmol), phenol (48 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 1.5 mL), followed by THF (0.04 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 70/30), └ 46 mg (55 %) of a colorless oil was obtained.

Chlorobenzene (56 mg, 0.5 mmol), phenol (94 mg, 1.0 mmol), solid TMPLi (265 mg, 1.8 mmol), benzene (1 mL), 45 $^oC$, 24 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 70/30), 53 mg (63 %) of a colorless oil was obtained.

$R_f$ = 0.32 (hexanes/EtOAc 70/30). This compound is known.[5] $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0 Hz, 1.1 Hz, 1H), 7.54 (dt, *J* = 7.5 Hz, 1.6 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.37 (dt, *J* = 7.5 Hz, 1.1 Hz, 1H), 6.87 (d, *J* = 12.9 Hz, 1H), 6.41 (dd, *J* = 12.9 Hz, 4.5 Hz, 1H), 6.30 (dd, *J* = 10.1 Hz, 4.5 Hz, 1H), 5.86 (q, *J* = 10.1 Hz, 1H), 3.42 (d, *J* = 8.1 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$, ppm) δ 193.7, 137.3, 136.7, 134.4, 132.4, 132.1, 131.0, 130.2, 128.8, 128.0, 127.1, 43.8.

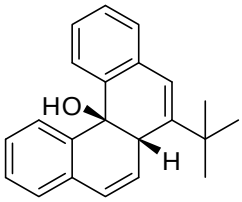



**(7E,9Z)-7-*tert*-Butylbenzo[8]annulen-5(6H)-one (12) (Scheme 2)**

Chlorobenzene (90 mg, 0.8 mmol), 3-*tert*-butylphenol (75 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 1.4 mL), followed by THF (0.03 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 95/5), 69 mg (61 %) of a colorless oil was obtained.

Chlorobenzene (56 mg, 0.5 mmol), 3-*tert*-butylphenol (225 mg, 1.5 mmol), TMPLi in pentane/hexanes (1M, 1.4 mL), followed by $Et_2O$ (0.03 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 95/5), 73 mg (65 %) of a colorless oil was obtained.

$R_f$ = 0.29 (hexanes/EtOAc 95/5). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.1 Hz, 1.3 Hz, 1H), 7.48 (dt, *J* = 7.4 Hz, 1.3 Hz, 1H), 7.33 – 7.27 (m, 1H), 6.78 (d, *J* = 12.3 Hz, 1H), 6.41 (dd, *J* = 12.3 Hz, 4.5 Hz, 1H), 6.03 (d, *J* = 4.5 Hz, 1H), 3.55 (s, 2H), 1.12 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 199.9, 149.0, 137.5, 137.0, 132.1, 131.9, 131.1, 130.7, 130.6, 127.0, 122.2, 45.9, 37.6, 29.3. . FT-IR (neat, $cm^{-1}$) 2963, 1669, 1595, 1289. Anal calcd for $C_{16}H_{18}O$ (226.14 g/mol): C, 84.91; H, 8.02; Found. C, 84.68; H, 7.85.

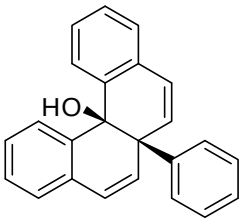



**6-*tert*-Butyl-6a,12b-dihydrobenzophenanthren-12b-ol (13) (Scheme 2)**

Chlorobenzene (168 mg, 1.5 mmol), 3-*tert*-butylphenol (75 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.1 mL), followed by THF (0.04 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 95/15), 98 mg (65 %) of a yellowish oil was obtained.

Chlorobenzene (112.5 mg, 1.0 mmol), (7E,9Z)-7-tert-butylbenzo[8]annulen-5(6H)-one **(11)** (113 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 1.6 mL), followed by THF (0.03 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 95/15), 96 mg (64 %) of a light yellow oil was obtained.

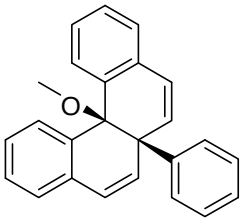
$R_f$ = 0.34 (hexanes/EtOAc 95/5). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd. *J* = 7.8 Hz, 0.8 Hz, 1H), 7.42 (dt, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.34 (dt, *J* = 7.8 Hz, 1.3 Hz, 1H), 7.21 (dt, *J* = 7.5 Hz, 1.3 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.98 (dt, *J* = 7.5 Hz, 1.3 Hz, 1H), 6.55 – 6.52 (m, 2H), 6.42 (dd, *J* = 9.5 Hz, 3.2 Hz, 1H), 5.58 (dd, *J* = 9.5 Hz, 2.2 Hz, 1H), 3.73 (t, *J* = 2.8 Hz, 1H), 2.45 (s, 1H), 1.26 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 147.5, 138.0, 136.9, 133.9, 133.2, 129.5, 129.3, 128.6, 127.9, 127.8, 127.3, 126.9, 126.4, 126.2, 126.0, 119.5, 74.9, 43.9, 36.2, 28.6. FT-IR (neat, $cm^{-1}$) 2950, 1537, 1321. Anal calcd for $C_{22}H_{22}O$ (302.17 g/mol): C, 87.38; H, 7.33; Found. C, 86.98; H, 7.45.




**6a-Phenyl-6a,12b-dihydrobenzophenanthren-12b-ol (14) (Scheme 2)**

Chlorobenzene (225 mg, 2.0 mmol), 4-hydroxybiphenyl (85 mg, 0.5 mmol), TMPLi in pentane/hexanes (1M, 2.7 mL), followed by THF (0.05 mL), rt, 24 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 95/5), 122 mg (70 %) of a white solid was obtained.

$R_f$ = 0.31 (hexanes/EtOAc 90/10). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 3H), 7.30 – 7.22 (m, 6H), 7.17 – 7.14 (m, 4H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.97 (broad singlet, 2H), 1.89 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 137.9, 136.9, 132.8 (broad), 131.7 (broad), 129.4, 128.4, 128.3, 128.1, 127.7, 127.0, 126.5, 51.8. Signals for two carbons could not be located. FT-IR (neat, $cm^{-1}$) 2955, 1544, 1334, 1235. Anal calcd for $C_{24}H_{18}O$ (322.14 g/mol): C, 89.41; H, 5.63; Found. C, 88.97; H, 5.55.



**6a-Phenyl-6a-hydro-12b-methoxybenzophenanthrene (Scheme 2)**

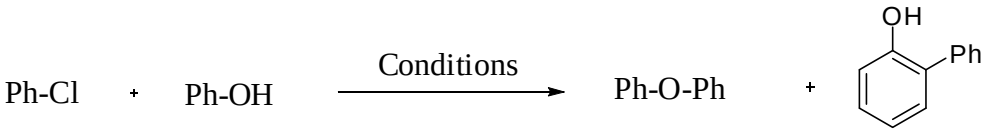
A 2 dram vial equipped with magnetic stirring bar was charged with 6a-phenyl-6a,12b-dihydrobenzophenanthren-12b-ol **(13)** (175 mg, 0.5 mmol), MeI (284 mg, 2.0 mmol). Vial was flushed with nitrogen and taken into glovebox. To this mixture, THF (1 mL) was added, followed by NaH (24 mg, 1.0 mmol). Vial was shaken to release all generated hydrogen. Vial was capped, taken out glovebox and placed in oil bath at 50 $^{o}$C for 4 hours. After completion, vial was allowed to cool down to room temperature and reaction mixture was quenched with $H_2O$ (10 mL). The reaction mixture was diluted with ethyl acetate (30 mL) and washed with brine (1 x 30 mL). The aqueous phase was extracted with ethyl acetate (3 x 15 mL). Combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved EtOAc (1 mL) and subjected to column chromatography on silica gel (hexane followed 95/5 hexane/EtOAc). After concentration of fractions containing product, 173 mg (91 %) of a light yellow solid was obtained.

*Recrystallization procedure*: Vial equipped with magnetic stirring bar was charged with 50 mg of product. Hexane (1.5 mL) was then added. Vial was placed into oil bath at 60 $^{o}$C for an hour. $CH_2Cl_2$ was added to vial dropwise at 40 $^{o}$C until all solid dissolved. Vial was capped and taken out oil bath and allowed to cool down to room temperature to obtain crystals suitable for X-ray analysis.

$R_f$ = 0.33 (hexanes/EtOAc 95/5). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 3H), 7.28 – 7.24 (m, 3H), 7.22 – 7.17 (m, 4H), 7.17 – 7.10 (m, 4H), 6.66 (d, *J* = 9.6 Hz, 2H), 5.98 (broad singlet, 2H), 3.08 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 138.63, 134.0 (broad), 133.5 (broad), 129.3, 128.5, 128.2, 127.9, 127.7, 127.0, 126.0, 81.2, 53.6, 51.5. Signals for two carbons could not be located.

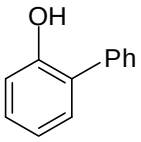
**General procedure for arylation of phenols:** Outside the glovebox a 2-dram vial equipped with a magnetic stirring bar was charged with chloroarene (0.8 – 2.0 mmol), phenol (0.5 mmol), and AgOAc (0 – 1.0 mmol). The vial was flushed with nitrogen, capped and placed inside the glovebox. To this mixture was added dioxane (0.8 – 1.3 mL), *t*-BuONa (1.5 – 3.0 mmol). The sealed vial was taken out the glovebox, stirred at room temperature for 5 minutes, placed in ultrasonic bath for 1 minute, covered with aluminum foil, and then transferred to preheated oil bath for indicated time. Reaction vials were occasionally shaken during first few hours to ensure complete mixing which is important to ensure reproducible yields. The reaction mixture was cooled to room temperature and quenched with 10 % aqueous citric acid (10 mL). The reaction mixture was diluted with ethyl acetate (30 mL) and washed with brine (1 x 30 mL). The aqueous phase was extracted with ethyl acetate (3 x 15 mL). Combined organic phases were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in minimal amount of ethyl acetate and subjected to column chromatography on silica gel in hexane followed by appropriate solvent to elute the products. After concentrating the fractions containing the product, the residue was dried under reduced pressure.

**Optimization of conditions for phenol arylation:** All reactions were carried out following the general procedure. Phenol (x mmol), chlorobenzene (y mmol), base [1.3*(x + y) mmol], solvent (1 mL), 24 hours. Conversions and **3**/**1** ratio were calculated by GC analysis. Conversions are presented in Table S1 and show the amount of product **1** and **3** formed (e.g. 70 % means that 70 % of starting limiting reagent is converted to **1** and **3**). Mixture with exact molar amounts of pure **1** and pure **3** was used as the standard to determine the ratio **3**/**1**.



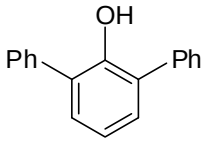

**1** **3**

| Entry | PhOH /PhCl | Base/T ($^{o}$C) | Solvent | Additive/equiv. | Conversion | **3/1** |
|---|---|---|---|---|---|---|
| | 1/2 | TMPLi/25 | Etheral | None | 32 | < 1/50 |
| | 1/2 | TMPLi/25 | Pentane/Etheral | None | 15 | < 1/50 |
| | 1/2 | NaHMDS/50 | THF | None | 95 | < 1/50 |
| | 1/2 | *t*-BuOK/110 | Dioxane | None | 91 | 1/9 |
| | 1/2 | *t*-BuONa/155 | Dioxane | None | 87 | 1/7 |
| | 2/1 | *t*-BuONa/155 | Dioxane | None | 68 | 1/11 |
| | 1/2 | *t*-BuONa/155 | Toluene | None | 45 | 1/10 |
| | 1/2 | *t*-BuONa/155 | Dioxane | AgOAc/1.0 | 87 | 30/1 |
| | 1/2 | *t*-BuONa/155 | Dioxane | AgOAc/0.5 | 79 | 24/1 |
| | 1/2 | *t*-BuONa/155 | Dioxane | AgOAc/0.1 | 65 | 15/1 |
| | 1/2 | *t*-BuONa/155 | Dioxane | $MnCl_2$/1.0 | 32 | 7/1 |
| | 1/2 | *t*-BuONa/155 | Dioxane | $NiCl_2$/1.0 | < 5 | ND |
| | 1/2 | *t*-BuONa/155 | Dioxane | $FeCl_3$/1.0 | 13 | 3/1 |



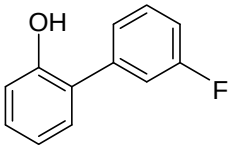

**2-Phenylphenol (Table 4, Entry 1)**

Chlorobenzene (101 mg, 0.9 mmol), phenol (47 mg, 0.5 mmol), AgOAc (42 mg, 0.25 mmol), *t*-BuONa (192 mg, 2.0 mmol), dioxane (0.8 mL), 155 $^{o}$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 90/10), 66 mg (78 %) of a light yellow solid was obtained. $R_f$ = 0.32 (hexanes/EtOAc 90/10). This compound is known.[6] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 4H), 7.45 – 7.40 (m, 1H), 7.32 – 7.27 (m, 2H), 7.06 – 7.00 (m, 2H), 5.30 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 152.5, 137.2, 130.4, 129.5, 129.3, 129.2, 128.3, 128.0, 121.0, 116.0.




**2,6-Diphenylphenol (Table 4, Entry 2)**

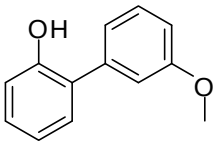
Chlorobenzene (282 mg, 2.5 mmol), phenol (47 mg, 0.5 mmol), AgOAc (125 mg, 0.75 mmol), *t*-BuONa (336 mg, 3.5 mmol), dioxane (1.2 mL), 155 $^{o}$C, 96 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 95/5), 73 mg (60 %) of a white solid was obtained. $R_f$ = 0.27 (hexanes/EtOAc 95/5). This compound is known.[7] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 4H), 7.53 – 7.49 (m, 4H), 7.44 – 7.40 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 5.44 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 149.4, 137.7, 130.1, 129.5, 129.0, 128.9, 127.8, 120.8.




**3'-Fluorobiphenyl-2-ol (Table 4, Entry 3)**

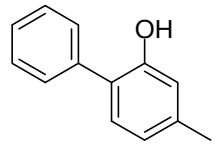
1-Fluoro-3-chlorobenzene (105 mg, 0.8 mmol), phenol (47 mg, 0.5 mmol), AgOAc (58 mg, 0.35 mmol), *t*-BuONa (173 mg, 1.8 mmol), dioxane (1.0 mL), 135 $^{o}$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 90/10), 67 mg (72 %) of a light

yellowish oil was obtained. $R_f$ = 0.29 (hexanes/EtOAc 90/10). This compound is known.[8] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 1H), 7.30 – 7.19 (m, 4H), 7.11 – 7.06 (m, 1H), 7.02 – 6.96 (m, 2H), 5.17 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 163.3 (d, $J_{C-F}$ = 247.7 Hz), 152.4, 139.5 (d, $J_{C-F}$ = 7.8 Hz), 130.7 (d, $J_{C-F}$ = 8.7 Hz), 130.3, 129.7, 127.0, 124.8 (d, $J_{C-F}$ = 2.5 Hz), 121.2, 116.3 (d, $J_{C-F}$ = 21.9 Hz), 116.2, 114.8 (d, $J_{C-F}$ = 21.9 Hz).




**3'-Methoxybiphenyl-2-ol (Table 4, Entry 4)**

2-Chloroanisole (215 mg, 1.5 mmol), phenol (47 mg, 0.5 mmol), *t*-BuONa (240 mg, 2.5 mmol), AgOAc (67 mg, 0.4 mmol), dioxane (1.0 mL), 155 $^o$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 85/15), 64 mg (64 %) of a white solid was obtained. $R_f$ = 0.25 (hexanes/EtOAc 85/15). This compound is known.[9] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.07 – 7.04 (m, 1H), 7.02 – 6.99 (m, 3H), 6.95 (dd, *J* = 8,2 Hz, 2.7 Hz, 1H), 5.39 (s, 1H), 3.85 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 160.4, 152.5, 138.5, 130.5, 130.2, 129.4, 128.0, 121.3, 120.9, 115.9, 114.6, 113.7, 55.4.

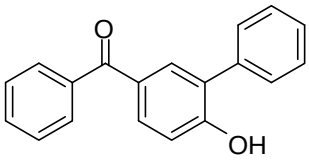



**4-Methylbiphenyl-2-ol (Table 4, Entry 5)**

Chlorobenzene (170 mg, 1.5 mmol), *m*-cresol (54 mg, 0.5 mmol), AgOAc (144 mg, 0.85 mmol), sodium *tert*-pentoxide (336 mg, 3.0 mmol), dioxane (1.0 mL), 155 $^o$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 93/7), 73 mg (80 %) of a colorless oil was obtained. Isomer ratio in crude product was determined to be 9/1 (4-methylbiphenyl-2-ol)/(6-methylbiphenyl-2-ol) by GC analysis.

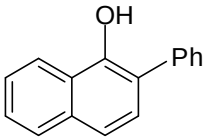
$R_f$ = 0.28 (hexanes/EtOAc 93/7). This compound is known.[10] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 4H), 7.39 – 7.36 (m, 1H), 7.13 (d, J = Hz, 1H), 6.82 – 6.81 (m, 2H), 5.15 (s, 1H), 2.36

(s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 152.3, 139.5, 137.2, 130.1, 129.4, 129.2, 127.8, 125.3, 121.8, 116.5, 21.3.



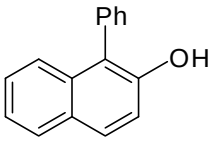

**(6-Hydroxybiphenyl-3-yl)(phenyl)methanone (Table 4, Entry 6)**

Chlorobenzene (225 mg, 2.0 mmol), 4-hydroxybenzophenone (99 mg, 0.5 mmol), *t*-BuONa (338 mg, 3.5 mmol), AgOAc (167 mg, 1.0 mmol), dioxane (1.0 mL), 155 $^{o}$C, 96 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 50/50), 79 mg (58 %) of a white solid was obtained. $R_f$ = 0.31 (hexanes/EtOAc 40/60). This compound is known.[11] $^1$H NMR (400 MHz, DMSO-d6) δ 10.64 (s, 1H), 7.69 – 7.67 (m, 2H), 7.63 – 7.58 (m, 3H), 7.52 – 7.49 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29 (tt, *J* = 7.6 Hz, 2.2 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 1H).$^{13}$C NMR (100 MHz, DMSO-d6, ppm) δ 194.8, 159.5, 138.5, 138.0, 133.5, 132.5, 131.9, 129.8, 129.6, 129.0, 128.8, 128.7, 128.3, 127.6, 116.5.




**1-Phenyl-1-naphthol (Table 4, Entry 7)**

Chlorobenzene (225 mg, 2.0 mmol), 1-naphthol (72 mg, 0.5 mmol), AgOAc (167 mg, 1.0 mmol), *t*-BuONa (384 mg, 4.0 mmol), dioxane (1.0 mL), 155 $^{o}$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 93/7), 90 mg (82 %) of a white solid was obtained. $R_f$ = 0.28 (hexanes/EtOAc 90/10). This compound is known.[12] $^1$H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.29 (m, 1H), 7.84 – 7.81 (m, 1H), 7.58 – 7.54 (m, 4H), 7.53 – 7.48 (m, 3H), 7.47 – 7.42 (m, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 5.84 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 147.8, 137.5, 134.3, 129.7, 129.5, 128.0, 127.7, 127.6, 126.6, 125.7, 124.4, 122.5, 121.3, 120.3.

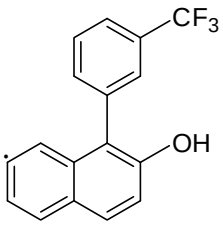



**1-Phenyl-2-naphthol (Table 4, Entry 8)**

Chlorobenzene (225 mg, 2.0 mmol), 2-naphthol (72 mg, 0.5 mmol), *t*-BuONa (384 mg, 4.0 mmol), dioxane (1.0 mL), 155 $^{o}$C, 72 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 93/7), 87 mg (80 %) of a light brown solid was obtained.

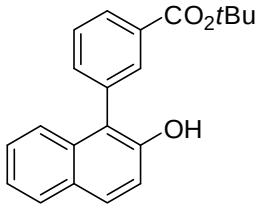
Large scale synthesis: A 50 mL pressure vessel equipped with a stir bar was charged with 2-naphthol (1.44 g, 10.0 mmol) and chlorobenzene (4.5 g, 40.0 mmol). The vessel was flushed with nitrogen, capped and placed inside the glovebox. To this mixture was added dioxane (20 mL) and *t*-BuONa (7.6 g, 80 mmol). The sealed vessel was taken out the glovebox, reaction mixture was stirred at room temperature for 5 minutes, then placed in preheated oil bath at 155 $^{o}$C for 72 hours. The reaction mixture was cooled to room temperature and quenched with 10 % aqueous citric acid (50 mL). The reaction mixture was diluted with ethyl acetate (100 mL) and washed with brine (1 x 50 mL). The aqueous phase was extracted with ethyl acetate (3 x 30 mL). Combined organic phases were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in minimal amount of ethyl acetate and subjected to column chromatography on silica gel in hexane followed by hexanes/EtOAc 93/7 to elute the product. After concentrating the fractions containing the product, 1.69 g (77 %) of a light brown solid was obtained.

$R_f$ = 0.27 (hexanes/EtOAc 90/10). This compound is known.[13] $^{1}$H NMR (400 MHz, $CDCl_3$) δ7.85 – 7.81 (m, 2H), 7.61 – 7.58 (m, 2H), 7.54 – 7.50 (m, 1H), 7.45 – 7.41 (m, 3H), 7.37 – 7.33 (m, 2H), 7.28 (d, *J* = 8.6 Hz, 1H), 5.18 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 150.3, 134.3, 133.3, 131.3, 129.8, 129.6, 129.0, 128.6, 128.2, 126.6, 124.7, 123.4, 121.1, 117.5.



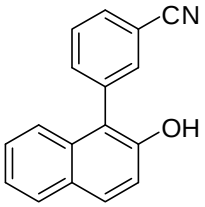

**1-(3-(Trifluoromethyl)phenyl)-2-naphthol (Table 4, Entry 9)**

3-Chlorobenzotrifluoride (360 mg, 2.0 mmol), 2-naphthol (72 mg, 0.5 mmol), *t*-BuONa (384 mg, 4.0 mmol), dioxane (1.0 mL), 135 $^{o}$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 90/10), 106 mg (74 %) of a light brown oil was obtained. $R_f$ = 0.29 (hexanes/EtOAc 90/10). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.80 – 7.78 (m, 1H), 7.75 – 7.70 (m, 2H), 7.65 – 7.63 (m, 1H), 7.41 – 7.31 (m, 3H), 7.27 (d, *J* = 8.8 Hz, 1H), 5.1 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 150.3, 135.6, 134.8, 133.2, 132.0 (q, $J_{C-F}$ = 32 Hz), 130.3, 130.1, 129.1, 128.3, 128.2 (q, $J_{C-F}$ = 3.7 Hz), 127.0, 125.3 (q, $J_{C-F}$ = 3.7 Hz), 124.3, 124.0 (q, $J_{C-F}$ = 272 Hz), 123.7, 119.7, 117.7. FT-IR (neat, cm$^{-1}$) 1331, 1166, 1123. Anal calcd for $C_{17}H_{11}F_3O$ (288.08 g/mol): C, 70.83; H, 3.85; Found. C, 71.12; H, 3.52.




**tert-Butyl 3-(2-hydroxynaphthalen-1-yl)benzoate (Table 4, Entry 10)**

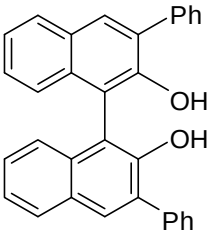
*tert*-Butyl-3-bromobenzoate (385 mg, 1.5 mmol), 2-naphthol (72 mg, 0.5 mmol), *t*-BuONa (384 mg, 4.0 mmol), dioxane (1.0 mL), 150 $^{o}$C, 24 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 90/10), 112 mg of a light yellowish oil containing a mixture of product and 2-naphthol was obtained. NMR analysis showed that the mixture contains 104 mg (66 %) of product. Attempts to completely separate product from starting material by preparative TLC and HPLC failed. $R_f$ = 0.27 (hexanes/EtOAc 90/10). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.15 (td, *J* = 7.8 Hz, 1.4 Hz, 1H), 8.04 (t, *J* = 1.4 Hz, 1H), 7.84 – 7.81 (m, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.58 (td, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.25 (s, 1H), 5.00 (s, 1H), 1.59 (s, 9H) . $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 165.4, 150.3, 135.4, 134.5, 133.5, 133.3, 132.1, 129.9, 129.7, 129.6, 129.0, 128.2, 126.8, 124.5, 123.6, 120.3, 117.5, 81.6, 28.3. FT-IR (neat, cm$^{-1}$) 2965, 1662, 1597, 1289. Anal calcd for $C_{21}H_{20}O_3$ (320.14 g/mol): C, 78.73; H, 6.29; Found. C, 78.24; H, 6.03.




**3-(2-Hydroxynaphthalen-1-yl)benzonitrile (Table 4, Entry 11)**

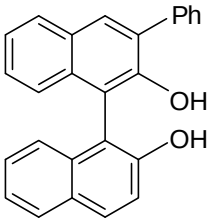
3-Chlorobenzonitrile (205.5 mg, 1.5 mmol), 2-naphthol (72 mg, 0.5 mmol), *t*-BuONa (288 mg, 3.0 mmol), dioxane (1.0 mL), 140 $^{o}$C, 72 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 75/25), 79 mg (65 %) of a brown oil was obtained. $R_f$ = 0.22 (hexanes/EtOAc 75/25). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.81 (m, 2H), 7.79 – 7.74 (m, 2H), 7.69 – 7.67 (m, 2H), 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 1H), 7.25 (d, *J* = 8.7 Hz, 1H), 5.48 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 150.3, 136.6, 136.1, 135.0, 133.1, 131.9, 130.5, 130.3, 129.0, 128.4, 127.2, 124.0, 123.8, 119.1, 118.6, 117.8, 113.5. FT-IR (neat, $cm^{-1}$) 3394, 2232, 1513, 1273. Anal calcd for $C_{17}H_{11}NO$ (245.08 g/mol): C, 83.25; H, 4.52; Found. C, 83.41; H, 4.04.

Note: product contains less than 3 % of another isomer.



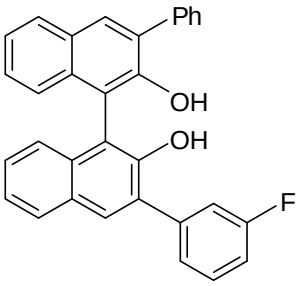

**3,3'-Diphenyl-1,1'-binaphthyl-2,2'-diol (21) (Scheme 4)**

Chlorobenzene (337 mg, 3.0 mmol), 1,1'-binaphthyl-2,2'-diol (143 mg, 0.5 mmol), *t*-BuONa (432 mg, 4.5 mmol), AgOAc (168 mg, 1.0 mmol), dioxane (1.3 mL), 155 $^{o}$C, 96 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 90/10), 111 mg (51 %) of a light yellow solid was obtained. $R_f$ = 0.36 (hexanes/EtOAc 90/10). This compound is known.[14] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.75 – 7.71 (m, 4H), 7.51 – 7.47 (m, 4H), 7.42 – 7.37 (m, 4H), 7.34 – 7.30 (m, 2H), 7.24 (t, *J* = 8.7 Hz, 2H), 5.35 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 150.2, 137.5, 133.0, 131.5, 130.7, 129.7, 129.5, 128.6, 128.5, 127.9, 127.5, 124.4, 124.3, 112.4.




**3-Phenyl-1,1'-binaphthyl-2,2'-diol (22) (Scheme 4)**

Chlorobenzene (192 mg, 1.7 mmol), 1,1'-binaphthyl-2,2'-diol (143 mg, 0.5 mmol), *t*-BuONa (288 mg, 3.0 mmol), AgOAc (144 mg, 0.85 mmol), dioxane (1.0 mL), 155 $^{o}$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 87/13), 120 mg (67 %) of a light yellow solid was obtained. $R_f$ = 0.26 (hexanes/EtOAc 85/15). This compound is known.[15] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.97 (d, *J* = 9.1 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.76 – 7.73 (m, 2H), 7.53 – 7.49 (m, 2H), 7.45 – 7.31 (m, 6H), 7.27 – 7.25 (m, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 5.33 (s, 1H), 5.13 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 152.8, 150.4, 137.5, 133.5, 133.1, 131.6, 131.5, 130.8, 129.7, 129.6, 128.7, 128.6, 128.5, 127.9, 127.6, 124.5, 124.4, 124.3, 124.1, 117.9, 111.9, 111.6. Signals for two carbons could not be located.

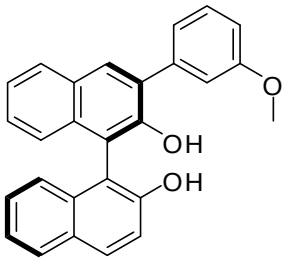



**3-(3-Fluorophenyl)-3'-phenyl-1,1'-binaphthyl-2,2'-diol (23) (Scheme 4)**

1-Chloro-3-fluorobenzene (260 mg, 2.0 mmol), 3-phenyl-1,1'-binaphthyl-2,2'-diol (180 mg, 0.5 mmol), *t*-BuONa (338 mg, 3.5 mmol), AgOAc (168 mg, 1.0 mmol), dioxane (1.0 mL), 135 $^{o}$C, 96 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 93/7), 136 mg (60 %) of a light yellow solid was obtained. $R_f$ = 0.31 (hexanes/EtOAc 90/10), mp 118 – 120 $^{o}$C (from hexanes). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 2.7 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.77 – 7.74 (m, 2H), 7.55 – 7.50 (m, 4H), 7.46 – 7.40 (m, 4H), 7.37 – 7.33 (m, 2H), 7.27 – 7.24 (m, 2H), 7.12 (ddt, *J* = 8.4 Hz, 2.7 Hz, 0.9 Hz, 1H), 5.39 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 162.8 (d, $J_{C\text{-}F}$ = 244.6 Hz), 150.4, 150.0, 139.8 (d, $J_{C\text{-}F}$ = 7.9 Hz), 137.4, 133.2, 133.0,

131.7 (d, $J_{C-F}$ = 10.4 Hz), 130.8, 129.9, 129.8, 129.7, 129.6, 129.5, 128.8, 128.7, 128.6, 128.0, 127.8, 127.6, 125.4 (d, $J_{C-F}$ = 2.8 Hz), 124.6, 124.4, 124.3, 116.8 (d, $J_{C-F}$ = 22.2 Hz), 114.6 (d, $J_{C-F}$ = 22.2 Hz).112.8, 112.0. Signals for two carbons could not be located. FT-IR (neat, $cm^{-1}$) 2956, 1434, 1263, 1121. Anal calcd for $C_{32}H_{21}FO_2$ (456.15 g/mol): C, 84.19; H, 4.64; Found. C, 84.01; H, 4.65.

Note: product contains less than 4 % of another isomer.




**3-(3-Methoxyphenyl)-(R)-(+)-1,1'-binaphthyl-2,2'-diol (24) (Scheme 4)**

3-Chloroanisole (285 mg, 2.0 mmol), (R)-(+)-1,1'-bi(2-naphthol) (143 mg, 0.5 mmol), *t*-BuONa (336 mg, 3.5 mmol), AgOAc (153 mg, 0.9 mmol), dioxane (1.0 mL), 130 $^{o}$C, 36 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 85/15), and then HPLC (hexanes/EtOAc 87/13), 97 mg (50 %) of a light yellow solid was obtained.

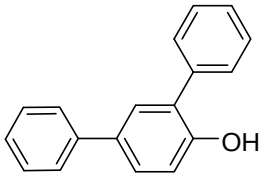
Determination of % ee by HPLC on chiral stationary phase: CHIRALPAK ID, hexanes/isopropanol 95:5, 0.75 mL/min, 95 % ee. Retention time: major, (R) = 31.3 min, (S) = 34.6 min.

$R_f$ = 0.22 (hexanes/EtOAc 85/15). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.97 (d, *J* = 8.9 Hz, 1H), 7.90 (t, *J* = 8.5 Hz, 2H), 7.42 – 7.35 (m, 4H), 7.33 – 7.21 (m, 5H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.96 (ddd, *J* = 8.2 Hz, 2.7 Hz, 0.9 Hz, 1H), 5.16 (broad singlet, 2H), 3.86 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 159.8, 152.8, 152.7, 150.3, 138.8, 133.5, 131.6, 131.5, 131.4, 129.7, 129.6, 128.6, 128.5, 127.6, 127.5, 124.5, 124.4, 124.3, 124.1, 122.0, 117.8, 115.3, 113.6, 111.9, 111.7, 110.9, 55.5. FT-IR (neat, $cm^{-1}$) 2946, 1344, 1363. Anal calcd for $C_{27}H_{20}O_3$ (492.14 g/mol): C, 82.63; H, 5.14; Found. C, 82.11; H, 4.85.

Note: Product contains less than 3 % of 1,1'-bi(2-naphthol).

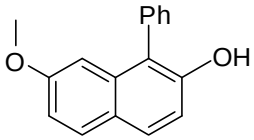
**Control experiment:** Diphenyl ether (78 mg, 0.5 mmol), PhCl (113 mg, 1.0 mmol), AgOAc (170 mg, 1.0 mmol), dioxane (1 mL), 155 $^{o}$C, 48 hours. No detectable amount of 2-phenylphenol was observed by GC and diphenyl ether was recovered.

**Additional examples**



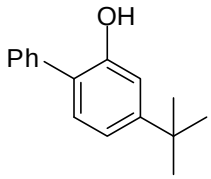

**2,4-Diphenylphenol**

Chlorobenzene (136 mg, 1.2 mmol), 4-phenylphenol (85 mg, 0.5 mmol), AgOAc (42 mg, 0.25 mmol), *t*-BuONa (192 mg, 2.0 mmol), dioxane (1.0 mL), 155 $^{o}$C, 72 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 90/10), 94 mg (77 %) of a white solid was obtained. $R_f$ = 0.25 (hexanes/EtOAc 90/10). This compound is known.[16] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.6 – 7.56 (m ,2H), 7.54 – 7.49 (m, 6H), 7.44 – 7.40 (m, 3H), 7.33 – 7.29 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 5.29 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 152.1, 140.7, 137.1, 134.1, 129.5, 129.3, 129.1, 128.9, 128.5, 128.1, 127.9, 127.0, 126.9, 116.4.




**7-Methoxy-1-phenyl-2-naphthol**

Chlorobenzene (225 mg, 2.0 mmol), 7-methoxy-2-naphthol (87 mg, 0.5 mmol), *t*-BuONa (384 mg, 4.0 mmol), dioxane (1.0 mL), 155 $^{o}$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 85/15), 108 mg (87 %) of a white solid was obtained. $R_f$ = 0.21 (hexanes/EtOAc 85/15). This compound is known.[17] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 2H), 7.61 – 7.57 (m, 2H), 7.52 – 7.48 (m, 1H), 7.46 – 7.43 (m, 2H), 7.13 (d, *J* = 8.7 Hz, 1H), 7.01 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 6.72 (d, *J* = 2.4 Hz, 1H), 5.18 (s, 1H), 3.70 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 158.4, 150.9, 134.7, 134.5, 131.3, 129.8, 129.7, 129.4, 128.6, 124.4, 120.4, 115.4, 115.0, 103.9, 55.2.




**4-*tert*-Butylbiphenyl-2-ol**

Chlorobenzene (136 mg, 1.2 mmol), 3-*tert*-butylphenol (75 mg, 0.5 mmol), AgOAc (42 mg, 0.25 mmol), *t*-BuONa (192 mg, 2.0 mmol), dioxane (1.0 mL), 155 $^{o}$C, 48 hours. After column chromatography (hexanes, followed by hexanes/EtOAc 95/5), 81 mg (72 %) of a white solid was obtained. $R_f$ = 0.33 (hexanes/EtOAc 95/5). This compound is known.[18] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 4H), 7.40 – 7.36 (m, 1H), 7.20 – 7.17 (m, 1H), 7.05 – 7.01 (m, 2H), 5.18 (s, 1H), 1.35 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$, ppm) δ 153.0, 152.1, 137.2, 129.8, 129.4, 129.1, 127.7, 125.2, 118.1, 113.1, 34.7, 31.4.

## X-RAY DATA

All measurements were made with a Siemens SMART platform diffractometer equipped with a 4K CCD APEX II detector. A hemisphere of data (1271 frames at 6 cm detector distance) was collected using a narrow-frame algorithm with scan widths of 0.30\% in omega and an exposure time of 45s/frame. The data were integrated using the Bruker-Nonius SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A psi scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 3030 reflections having I>10\s(I), and these, along with other information pertinent to data collection and refinement, are listed in Table S1. The Laue symmetry was determined to be 2/m, and from the systematic absences noted the space group was shown unambiguously to be P2(1)/c.

**Table S1**. **Crystal Data and Structure Refinement for *O*-methylated 13**

| | |
|---|---|
| Empirical formular | $C_{25}H_{20}O$ |
| Formular weight | 336.41 |
| Temperature | 223 (2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, P-2 |
| Unit cell dimensions | a = 11.7510 (9) Å alpha = 90.00 |
| | b = 7.5332 (6) Å beta = 95.651 (1) |
| | c = 19.9382 (15) Å gamma = 90.00 |
| Volume | 1756.4 (2) Å^ 3 |
| Z, calculated density | 4, 1.272 Mg/m^3 |
| Absorption coefficient | 0.076 mm^-1 |
| F(000) | 712 |
| Crystal color and shape | colorless plate |
| Crystal size | 0.35 x 0.30 x 0.06 mm |
| Theta range for data collection | 1.74 to 25.02 deg. |
| Limiting indices | -13<=h<=13, 0<=k<=8, 0<=l<=23 |

| | |
|---|---|
| Reflections collected/unique | 8948/3346 [R(int) = 0.0277] |
| Completeness to theta 25.02 | 96.2 % |
| Absorption correction | Empirical |
| Max. and min. transmission | 0.9877 and 0.8927 |
| Refinement method | Full-matrix least squares on F^2 |
| Data/restrains/parameter | 3090/0/237 |
| Goodness-of-fit on F^2 | 0.973 |
| Final R indices [I>4sigma(I)] | $R_1$ = 0.0299 and $wR_2$ = 0.0772 |
| R indices (all data) | $R_1$ = 0.0525 and $wR_2$ = 0.0916 |

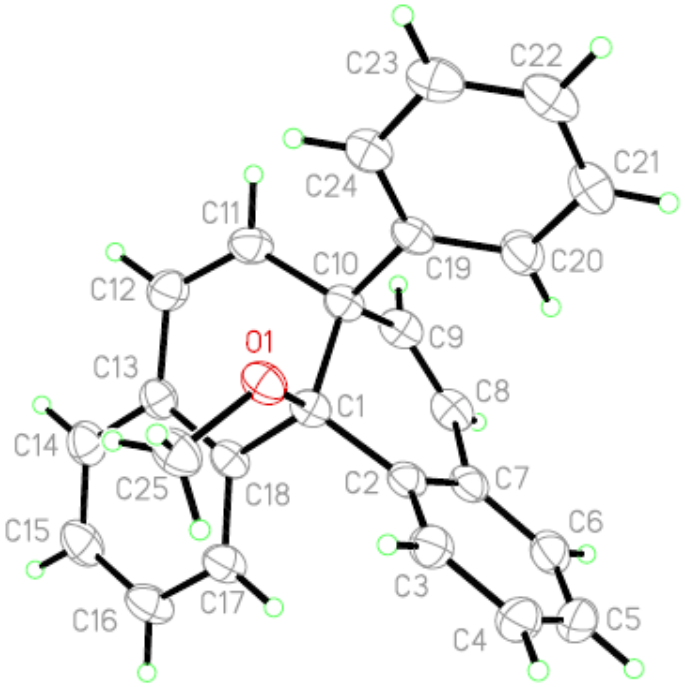



**Figure S1**. ORTEP view of 6a-phenyl-6a-hydro-12b-methoxybenzophenanthrene

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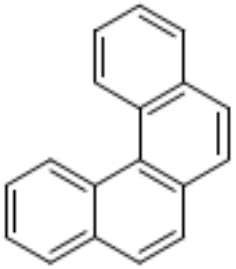

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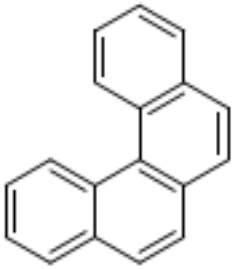

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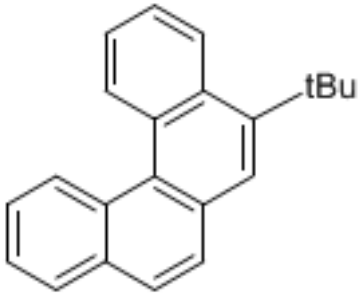


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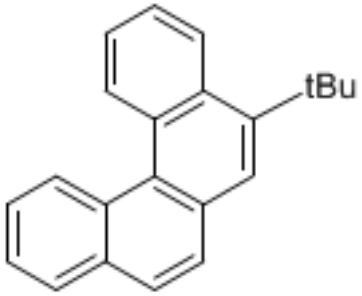


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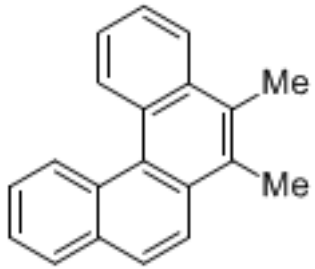


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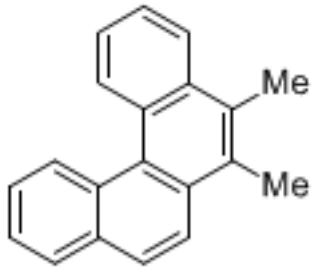


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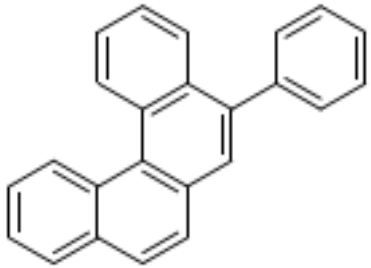

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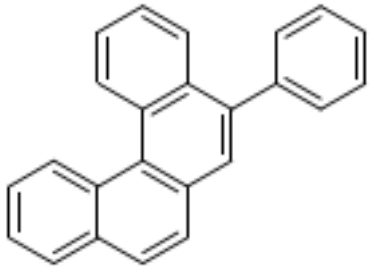

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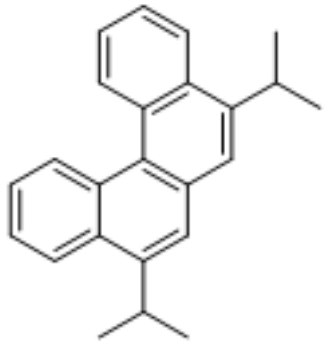

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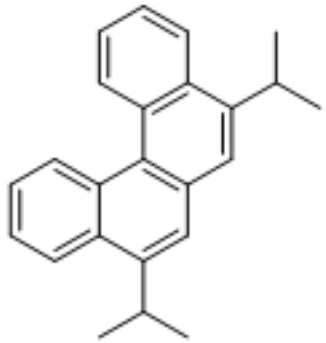

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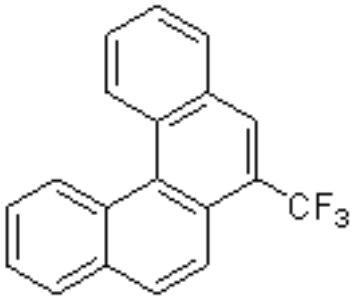


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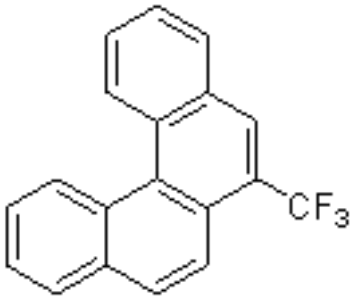


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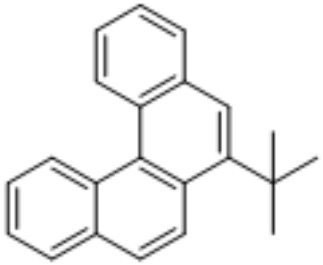

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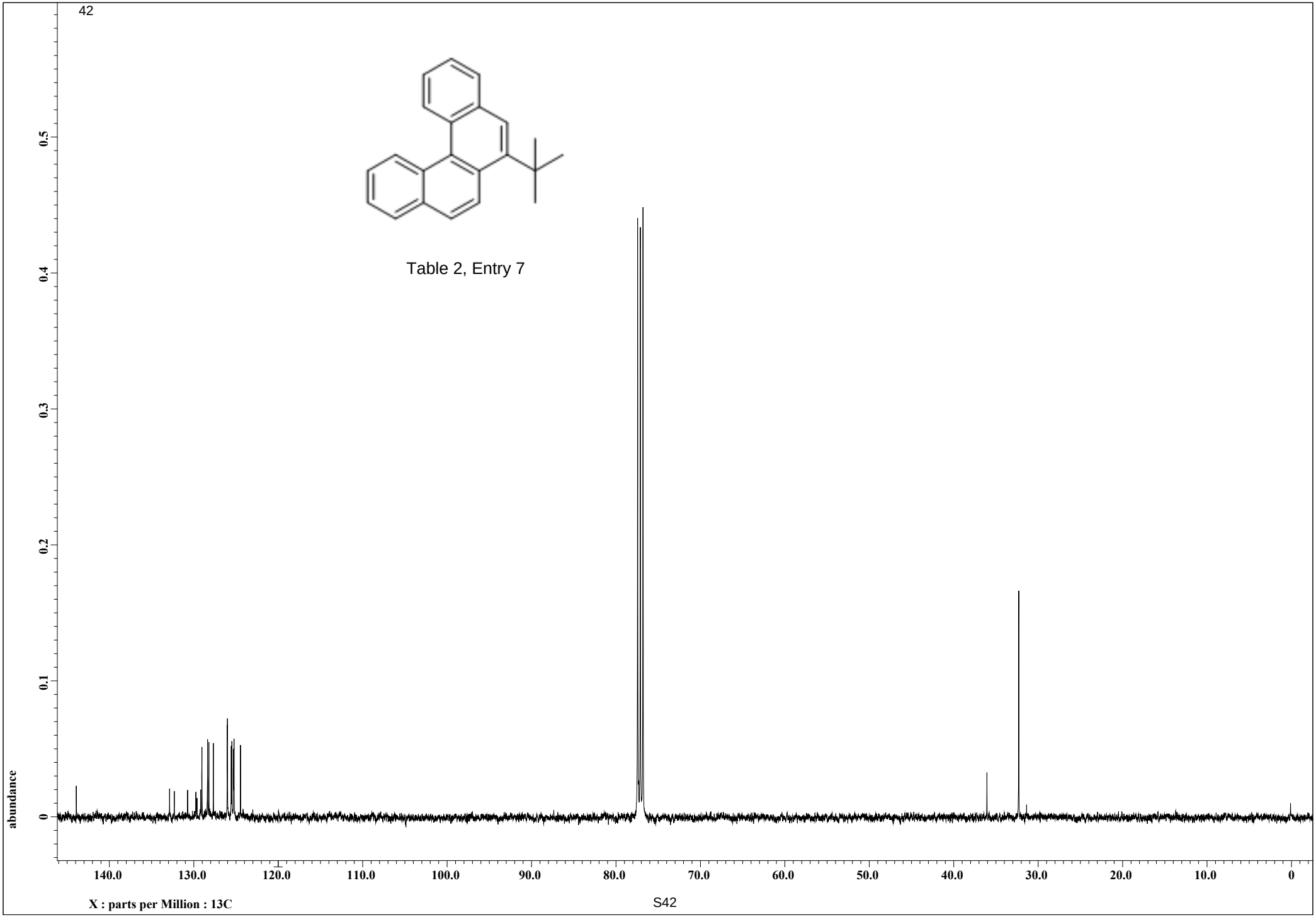

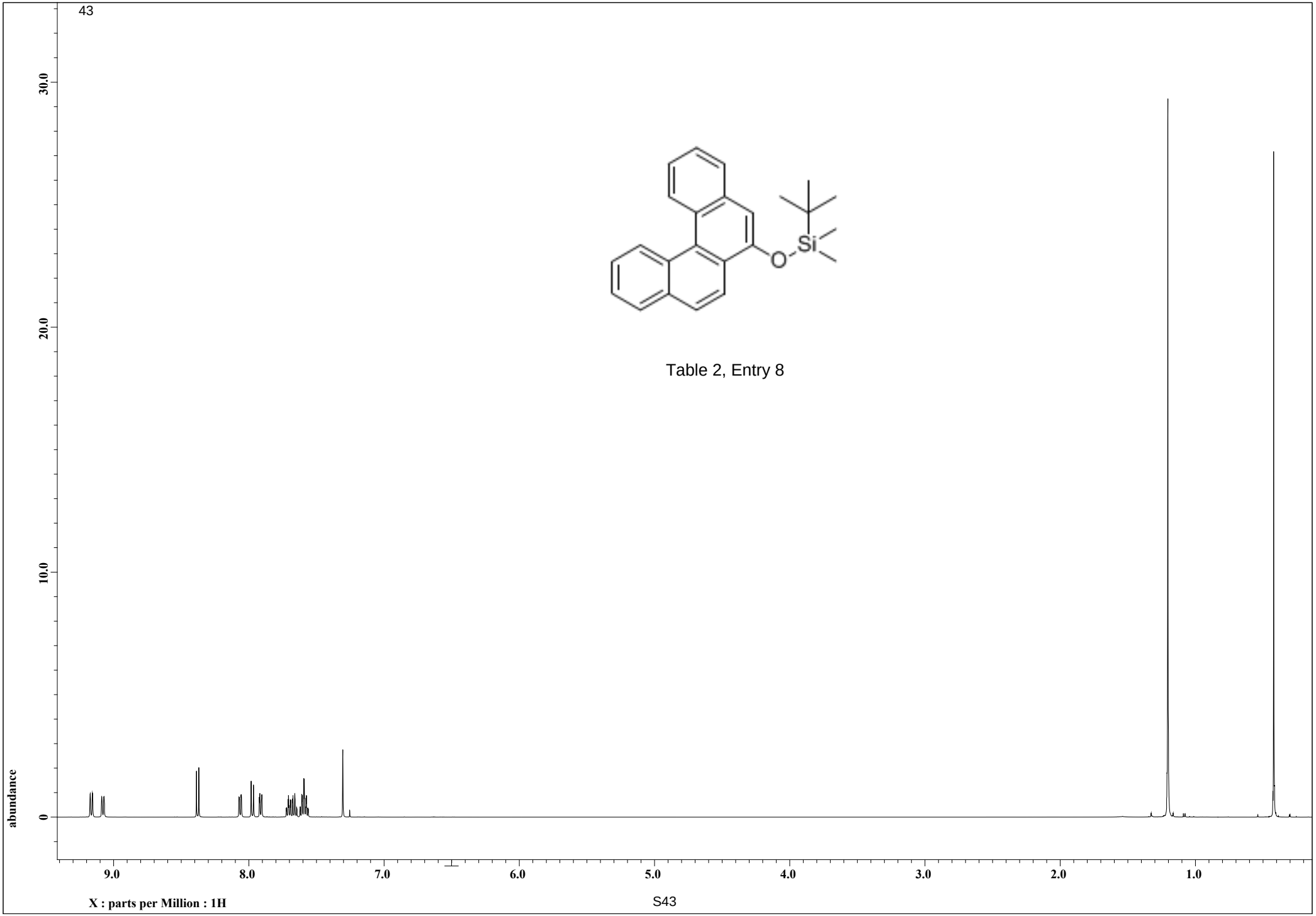


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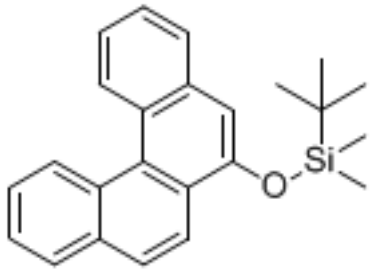


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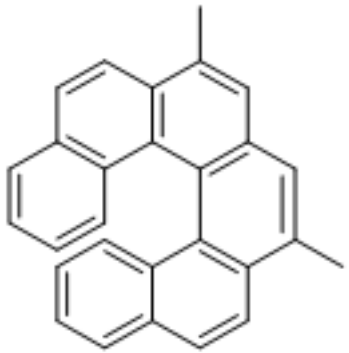
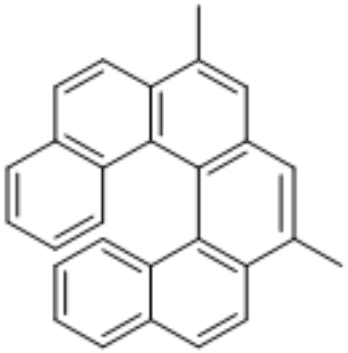


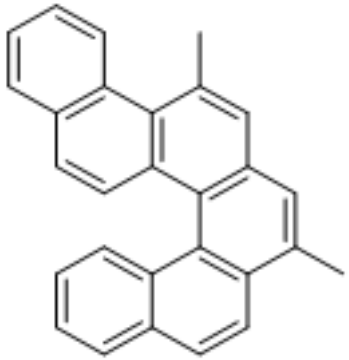
Compound 11, Scheme 1

46



Compound 11, Scheme 1

47



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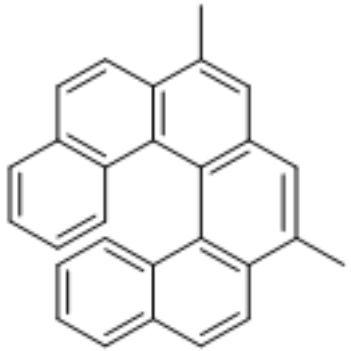
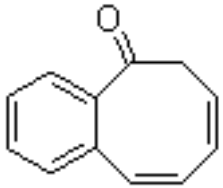


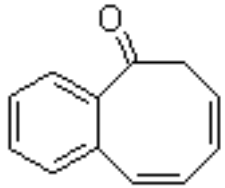
Mixture of compound 10 and 11, Scheme 1

48



Compound 16, Scheme 3

49



Compound 16, Scheme 3

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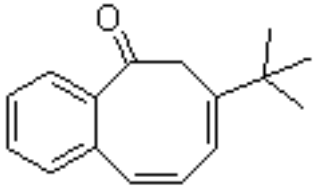
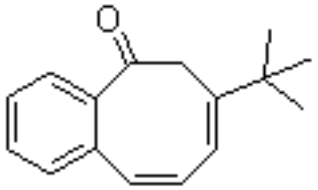


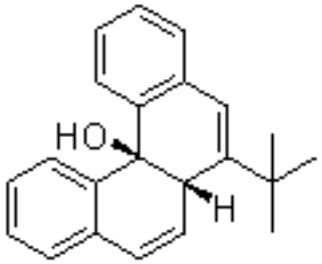
Compound 12, Scheme 2

51



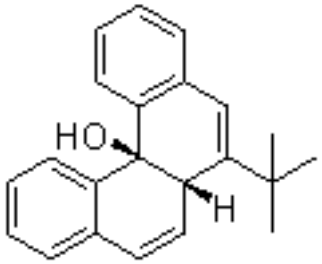
Compound 12, Scheme 2

52



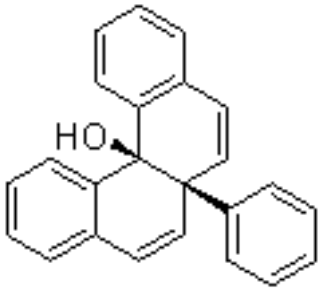

Compound 13, Scheme 2

53



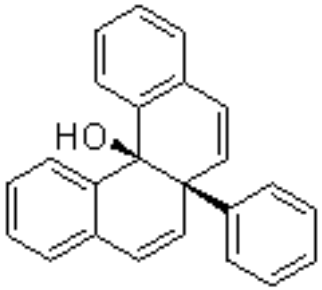

Compound 13, Scheme 2

54




Compound 14, Scheme 2

55




Compound 14, Scheme 2

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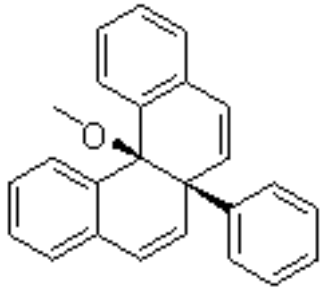
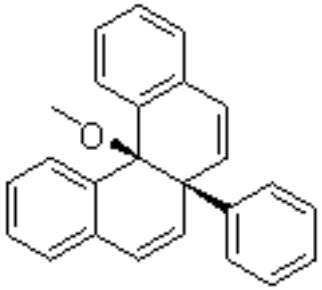


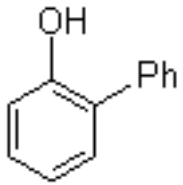

Scheme 2

57




Scheme 2

58

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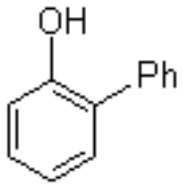


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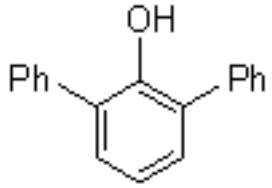


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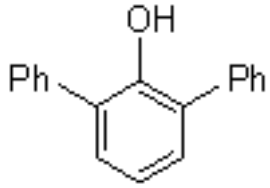


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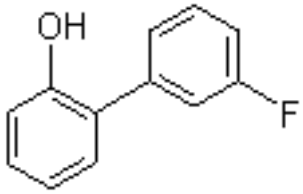


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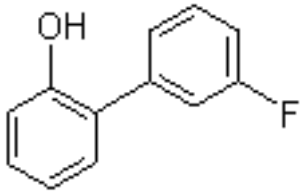


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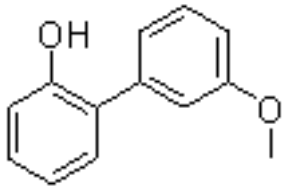


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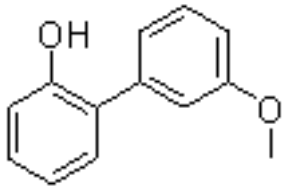


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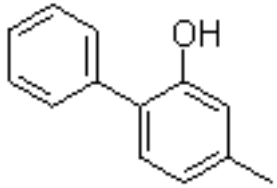


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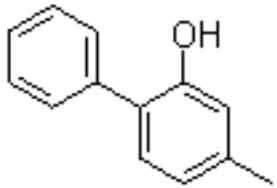


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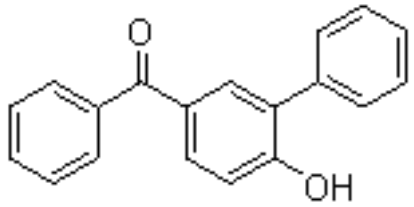


Table 4, Entry 6

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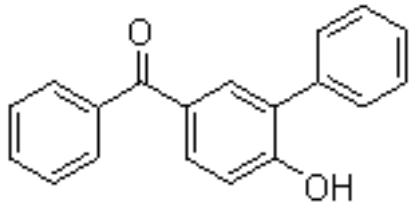


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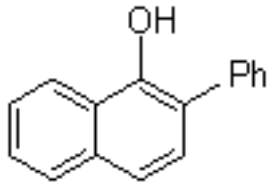


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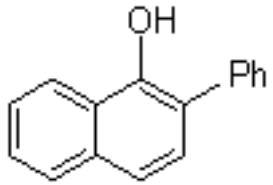


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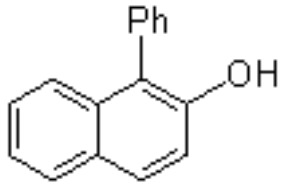


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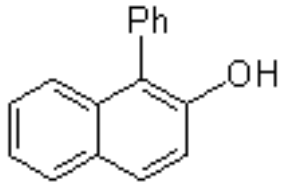


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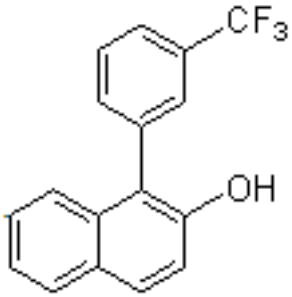


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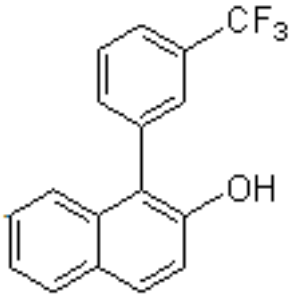


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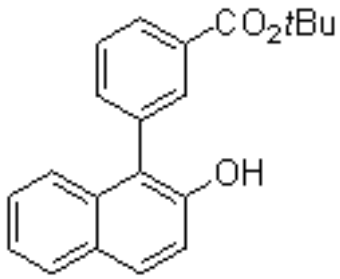


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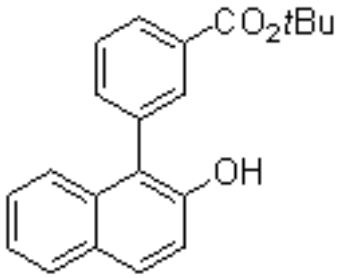


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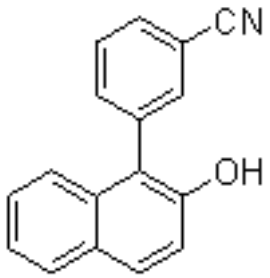


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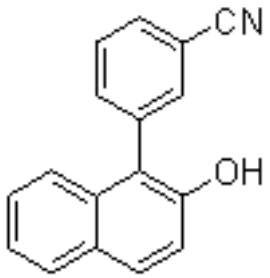


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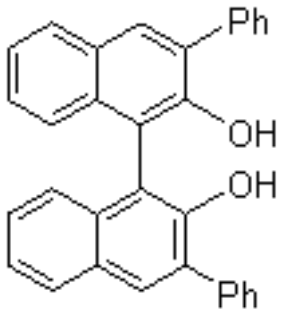
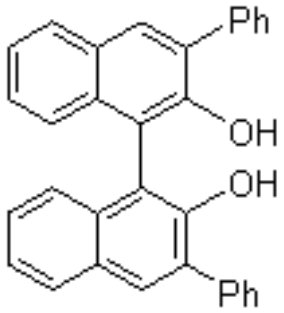


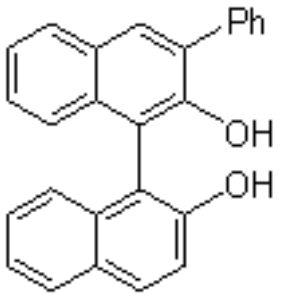

Compound 21, Scheme 4

81



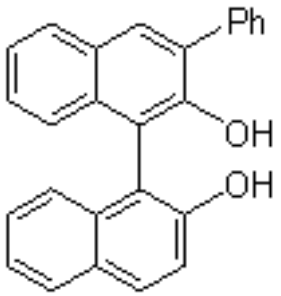

Compound 21, Scheme 4

82



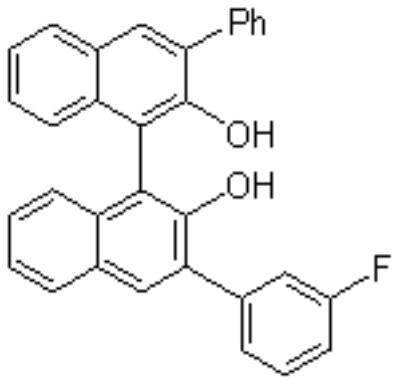

Compound 22, Scheme 4

83



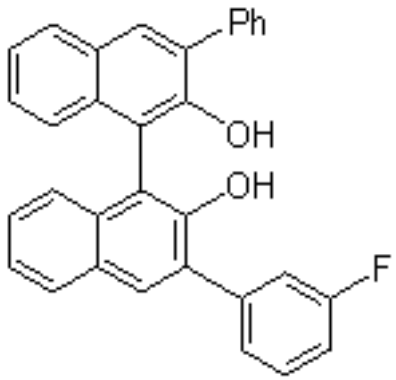

Compound 22, Scheme 4

84



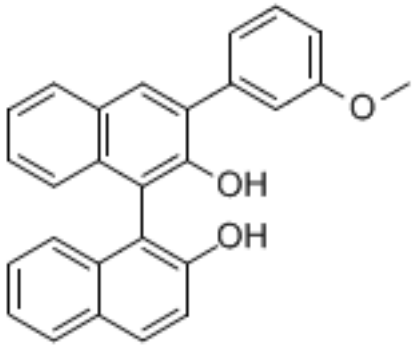

Compound 23, Scheme 4

85



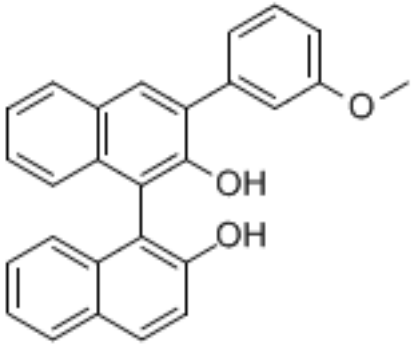

Compound 23, Scheme 4

86

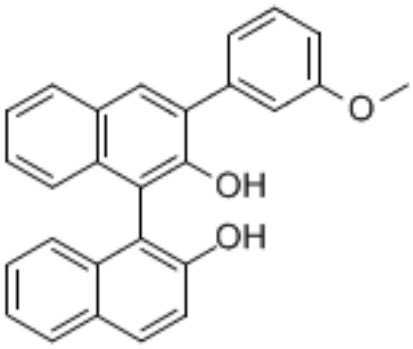



Compound 24, Scheme 4

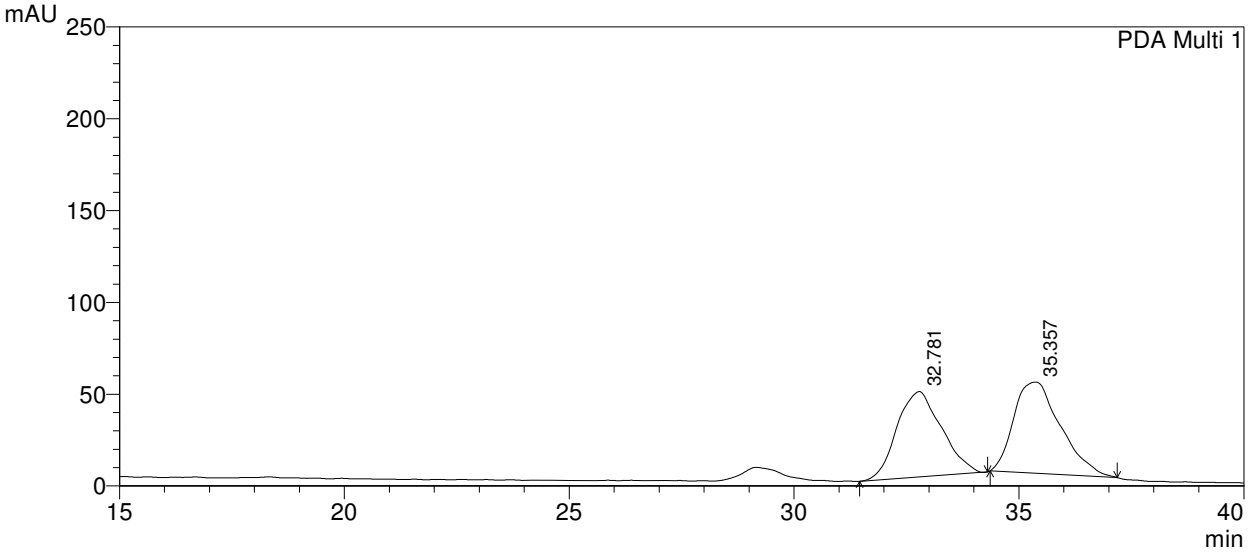
87




Compound 24, Scheme 4



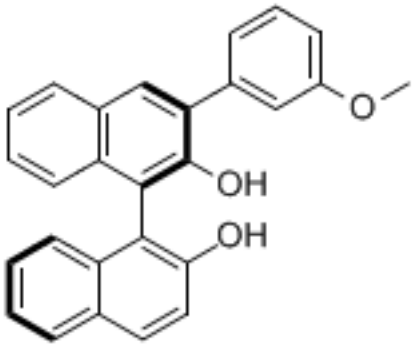

Compound 24, Racemic



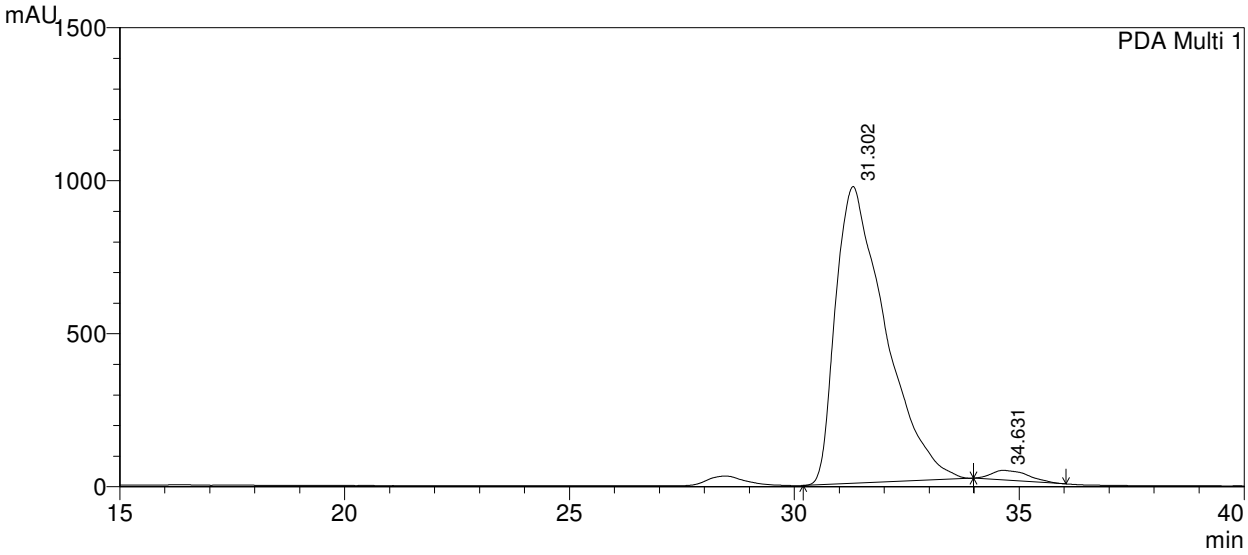

1 PDA Multi 1/254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 32.781 | 3204387 | 46505 | 47.133 | 48.384 |
| 2 | 35.357 | 3594182 | 49611 | 52.867 | 51.616 |
| Total | | 6798569 | 96116 | 100.000 | 100.000 |

89




Compound 24, Scheme 4

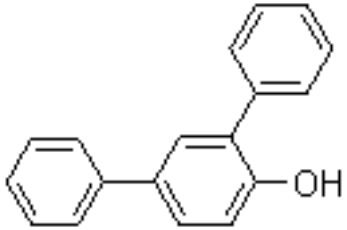



1 PDA Multi 1/254nm 4nm

PDA Ch1 254nm 4nm

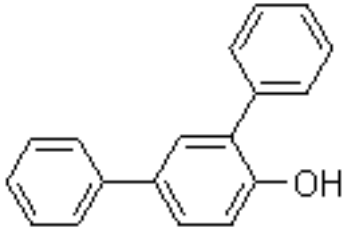
| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 31.302 | 74681702 | 970185 | 97.589 | 96.868 |
| 2 | 34.631 | 1844730 | 31366 | 2.411 | 3.132 |
| Total | | 76526432 | 1001550 | 100.000 | 100.000 |

90



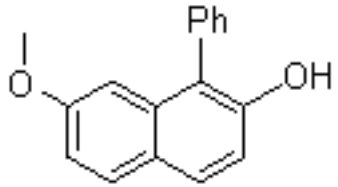

Additional example 1

91



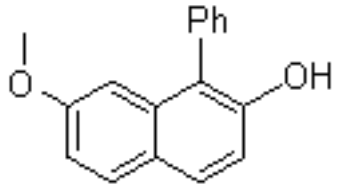

Additional example 1

92



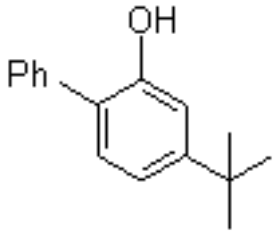

Additional example 2

93



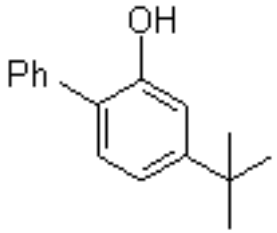

Additional example 2

94




Additional example 3

95




Additional example 3