Supporting Information

Divergent cyclodimerizations of styrylnaphthols under aerobic visible-light irradiation and Brønsted acid catalysis

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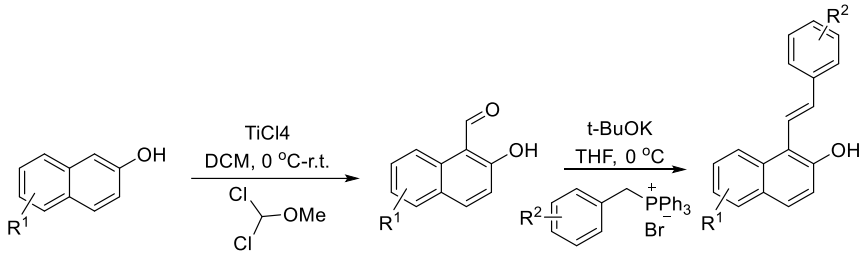
1. Materials and General information.

Solvents were distilled by standard methods using the appropriate drying agent and stored over molecular sieves under argon. All other reagents were obtained from commercial suppliers and directly used unless otherwise noted. Flash column chromatography was carried out using 40-63 µm particle sized silica gel with air pressure. Analytical thin layer chromatography (TLC) plates (silica gel 60 F254) were visualized either with a UV lamp (254 nm), or by submersion in potassium permanganate. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer and the characteristic IR absorption frequencies are reported in cm^{-1}. Proton ^{1}H NMR spectra were recorded on a Bruker Avance 500 MHz or 300 MHz and proton-decoupled carbon ^{13}C NMR spectra were recorded either at 126 MHz or 75 MHz. NMR experiments were carried out in deuterochloroform ($CDCl_3$) or in trideuteroacetonitrile (CD_3CN). Proton-decoupled fluorine ^{19}F NMR spectra were recorded at 282 MHz. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent as an internal reference (^{1}H: 7.26 ppm, ^{13}C: 77.16 ppm for $CHCl_3/CDCl_3$ and ^{1}H: 1.94 ppm, ^{13}C: 1.32 ppm for CHD_2CN/CD_3CN). The following abbreviations are used for the multiplicities: s: singlet; d: doublet; t: triplet; q: quadruplet; quint: quintuplet; m: multiplet or overlap of non-equivalent resonances; br s: broad singlet; app: apparent; rot: rotamer. Coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra were determined on an AEI MS-9 using electrospray ionization (ESI) and a time-of-flight (TOF) analyzer. Photochemical reactions were carried out in a EvoluChem™ PhotoRedox mono box equipped with a EvoluChem™ 405 nm LED lamp (with the fan switched on) and placed on a stirrer plate (relative irradiance in the photoredox box: 28 $mW.cm^{-2}$) .

2. Preparation of substrates 1

General compound **1** were prepared according to literature procedures.[1,2,3]

2.1. Synthetic procedure



2.1.1. Substituted 2-hydroxy-1-naphthaldehyde.

A solution of $TiCl_4$ (18 mmol, 2 equiv) and dichloromethyl methyl ether (9 mmol, 1 equiv) in anhydrous dichloromethane (10 mL) was stirred at 0 °C for 15 min. A solution of the required substituted naphthol (9 mmol, 1 equiv) in CH_2Cl_2 (30 mL) was added dropwise, and the reaction was warmed to room temperature. The reaction was allowed to stir overnight after which it was quenched by adding 1 N HCl (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), and the organic layers were then combined, dried with Na_2SO_4, and reduced to dryness to afford a residue which was further purified by silica gel column chromatography to yield the pure aldehyde (ethyl acetate/petroleum ether 1:10).

2.1.2. Substituted (E)-1-styrylnaphthalen-2-ol

A mixture of methyl triphenylphosphonium bromide (3 mmol, 1.5 equiv) in THF (4 mL) was treated with potassium *ter*t-butoxide (5 mmol, 2.5 equiv). After stirring for 10 min at room temperature, a solution of 2-hydroxy-1-naphthaldehyde (2 mmol, 1 equiv) in THF (2 mL) was added dropwise to the above suspension, and the resulting mixture was stirred at room temperature for 60 min. After completion (monitored by TLC), the resulting solution was quenched with aqueous saturated NH_4Cl solution (10 mL), and concentrated in vacuum to remove THF. The concentrated mixture was extracted with CH_2Cl_2 (40 mL). The organic layer was washed with brine (3 × 40 mL) and dried over $MgSO_4$, filtered and concentrated. The residue was purified by

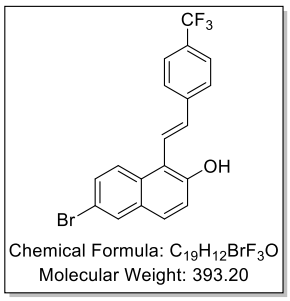
[1] Yang, D-J.; Zhu, Y-F.; Yang, Na.; Jiang, Q-Q. and Liu, R-H. *Adv. Synth. Catal.* **2016**, *358*, 1731-1735.

[2] Niim, K.; Mori, H.; Miyazaki, E.; Osaka, I.; Kakizoe, H.; Takimiya, K. and Adachi, C. *Chem. Commun.*, **2012**, *48*, 5892-5894.

[3] Yang, H.; Sun, H-R.; Xue, R-D.; Wu, Z-B.; Gou, B-B.; Lei, Y-b.; Chen, J. and Zhou, L. *Org. Lett.* **2019**, *21*, 24, 9829-9835.

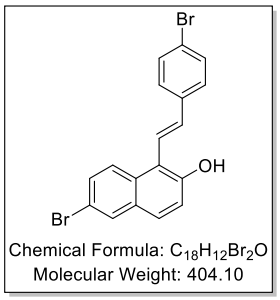
silica gel column chromatography (ethylacetate/petroleum ether 1:20).

2.1.3. Characterization of unknown substrates 1.



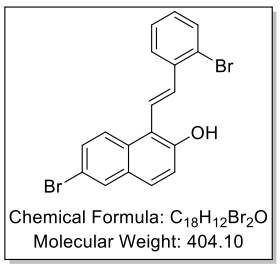
(E)-6-bromo-1-(4-(trifluoromethyl)styryl)naphthalen-2-ol

IR 1615, 1589, 1499, 1463, 1416, 1383, 1263, 1212, 1416, 1383, 1359, 1263, 1213, 1200, 1187, 1163, 1120, 1109, 1066, 1015, 973, 951, 891, 868, 808, 756, 737, 723, 703, 670 cm^{-1}; mp: 137 °C; $^{1}H\{^{13}C\}$ NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 2.1 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.68 (s, 4H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.54 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.49 (d, *J* = 16.7 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.09 (d, *J* = 16.7 Hz, 1H), 5.71 (s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, Chloroform-*d*) δ 151.2, 140.1, 135.0, 131.4, 130.5, 130.3, 130.2, 129.0, 126.9, 126.0 (q, $^{1}J_{C\text{-}F}$= 7.0, 3.4 Hz), 125.5, 124.2, 119.0, 117.6, 116.6. HRMS (ESI^{+}/Q-TOF)*m*/*z* $[M + H]^{+}$ calc for $C_{18}H_{13}Br_2O_1$: 393.0102; found: 393.0100.



(E)-6-bromo-1-(4-bromostyryl)naphthalen-2-ol

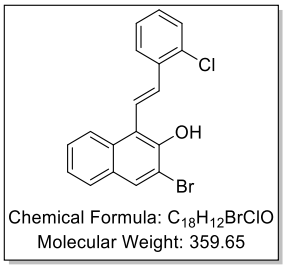
IR 1632, 1610, 1587, 1501, 1487, 1459, 1411, 1398, 1381, 1361, 1342, 1306, 1284, 1264, 1213, 1186, 1154, 1130, 1072, 1008, 989, 951, 908, 891, 864, 874, 853, 782, 762, 737, 702, 673 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.7 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 8.9 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 16.7 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 6.97 (d, *J* = 16.7 Hz, 1H), 5.74 (s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 151.1, 135.5, 135.4, 132.2, 131.4, 130.5, 130.3, 130.1, 128.7, 128.2, 125.6, 122.6, 122.2, 119.0, 117.5, 116.9. HRMS (ESI^{+}/Q-TOF) *m*/*z* $[M + H]^{+}$ calcd for $C_{18}H_{13}Br_2O_1$: 400.9177; found: 400.9196.



(E)-6-bromo-1-(2-bromostyryl)naphthalen-2-ol

IR 1612, 1499, 1464, 1437, 1411, 1384, 1359, 1344, 1304, 1266, 1250, 1211, 1199, 1142, 1080, 1046, 1023, 974, 950, 891, 878, 811, 747, 730, 673, 659 cm^{-1}; mp: 150 °C; $^{1}H\{^{13}C\}$ NMR (500 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.44 – 7.35 (m, 2H), 7.29 (s, 1H), 7.27 – 7.16 (m, 2H), 5.91 (s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 151.3, 137.0, 135.5, 133.4, 131.5, 130.6, 130.3, 130.2, 129.9, 129.0, 128.1,

127.4, 125.7, 124.9, 124.2, 119.2, 117.6, 116.8. HRMS (ESI$^+$/Q-TOF)*m*/*z* [M + H]$^+$ calcd for $C_{18}H_{13}Br_2O_1$: 400.9177; found: 400.9159.



(E)-3-bromo-1-(2-chlorostyryl)naphthalen-2-ol

IR 1616, 1580, 1499, 1469, 1450, 1440, 1425, 1385, 1367, 1340, 1302, 1262, 1206, 1155, 1143, 1124, 1079, 1050, 1037, 985, 967, 898, 878, 848, 796, 780, 771, 689, 704 cm^{-1}; mp: 116 ^{o}C; ^{1}H{^{13}C} NMR (500 MHz, $CDCl_3$) δ 7.93 (t, *J* = 10.3 Hz, 1H), 7.79 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 9.3 Hz, 1H), 7.46 (s, 1H), 7.32 (dd, *J* = 15.8, 8.4 Hz, 2H), 7.25 (d, *J* = 5.7 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (dd, *J* = 11.3, 3.9 Hz, 1H), 5.93 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.1, 135.8, 133.6, 132.4, 132.1, 131.1, 129.9, 129.6, 129.0, 127.7, 127.2, 127.1, 126.8, 124.6, 124.3, 124.0, 118.5, 112.8. HRMS (ESI$^+$/Q-TOF)*m*/*z* [M + H]$^+$ calcd for $C_{18}H_{13}Br_2O_1$: 358.9838; found: 358.9838.

3. Cycloaddition reactions

3.1. General procedure A for visible light-mediated (1+1+4+4) cycloaddition

A solution of **1** (0.1 mmol) in CH_2Cl_2 (1.5 mL) was stirred under air atmosphere and purple light irradiation (405 nm). After full consumption of the starting material (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc= 20:1 to 10:1) to yield the desired cycloaddduct **5**.

Procedure on 1 mmol scale

A solution of **1a** (1 mmol, 0.25 g) in CH_2Cl_2 (15 mL) was stirred under air atmosphere and purple light irradiation (405 nm). After full consumption of the starting material (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc= 20:1 to 10:1) to yield the desired cycloaddduct **5a** (115 mg) in 46% yield as a corlorless oil.

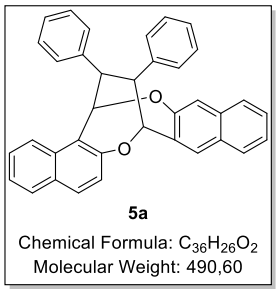
3.2. General procedure B for Bronsted acid-catalyzed (4+2) cycloaddition

A solution of **1** (0.1 mmol), TsOH (0.01 mmol) in dichloroethane or toluene (1.5 mL) was stirred at 50 °C in an oil bath under air atmosphere. After full consumption of the starting material (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/DCM/EtOAc=10:4:1) to yield the corresponding product **3**.

Procedure on 1 mmol scale

A solution of **1a** (1 mmol, 0.25 g), TsOH (0.1 mmol, 0.017 g) in toluene (15 mL) was stirred at 50 °C in an oil bath under air atmosphere stir for 3 days. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (petroleum ether/DCM/EtOAc=10:4:1) to yield the corresponding product **6a** (152 mg) in 61% yield.

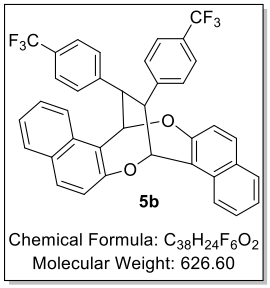
3.3. Characterization of cycloadducts 5 and 6



17,18-diphenyl-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5] dioxocine (5a)

Following the general procedure **A**, **5a** was obtained from (*E*)-1-styrylnaphthalen-2-ol (0.025 g, 0.1 mmol) as a colorless oil (0.012 g) in 50% yield. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.48 – 7.39 (m, 6H), 7.31 – 7.15 (m, 10H), 6.41 (s, 2H), 3.97 (s, 2H).

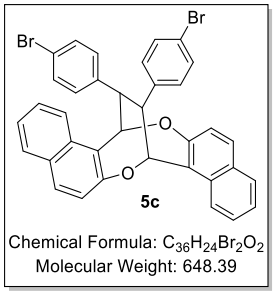
These data matched those reported in the literature.[3]



17,18-bis(4-(trifluoromethyl)phenyl)-8H,16H-8,16-ethanodinaphtho-[2,1-b:2',1'-f][1,5]dioxocine (5b)

Following the general procedure **A**, **5b** was obtained from (*E*)-1-(4-(trifluoromethyl)styryl)naphthalen-2-ol (0.031 g, 0.1 mmol) as a colorless oil (0.009 g) in 29% yield. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.53 (s, 7H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.16 (d, *J* = 8.9 Hz, 2H), 6.35 (s, 2H), 4.02 (s, 2H).

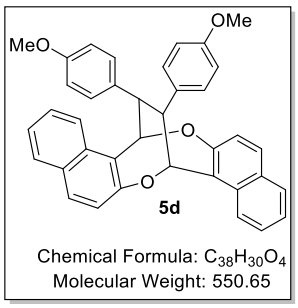
These data matched those reported in the literature.[3]



17,18-bis(4-bromophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',1'-f] [1,5]dioxocine (5c)

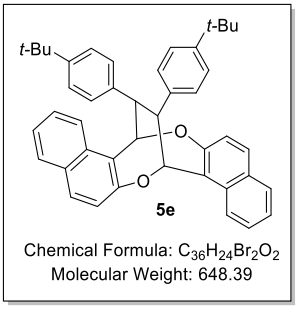
Following the general procedure **A**, **5c** was obtained from (*E*)-1-(4-bromostyryl)naphthalen-2-ol (0.032 g, 0.1 mmol) as a colorless oil (0.013 g) in 41% yield. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.28 (dd, *J* = 14.7, 6.2 Hz, 6H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.33 (s, 2H), 3.85 (s, 2H).

These data matched those reported in the literature.[3]



17,18-bis(4-methoxyphenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2-',1'-f][1,5]- dioxocine (5d)

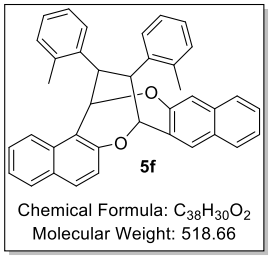
Following the general procedure **A**, **5d** was obtained from (*E*)-1-(4-methoxystyryl)naphthalen-2-ol (0.028 g, 0.1 mmol) as a colorless oil (0.012 g) in 42% yield. IR 1620, 1610, 1598, 1582, 1510, 1465, 1433, 1399, 1314, 1302, 1263, 1246, 1226, 1213, 1178, 1159, 1141, 1109, 1068, 1032, 1001, 952, 923, 859, 826, 816, 783, 767, 702 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 4H), 7.28 (s, 2H), 7.15 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 4H), 6.35 (s, 2H), 3.86 (s, 2H), 3.77 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 158.5, 157.2, 136.0, 133.1, 130.8, 129.9, 129.4, 128.3, 127.2, 123.8, 122.4, 120.9, 117.8, 113.9, 83.1, 56.0, 55.3. HRMS (ESI^+/Q-TOF)*m*/*z* $[M + H]^+$ calcd for $C_{38}H_{31}O_4$: 551.2222; found: 551.2222.



17,18-bis(4-(*tert*-butyl)phenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',1'-f] [1,5]dioxocine (5e)

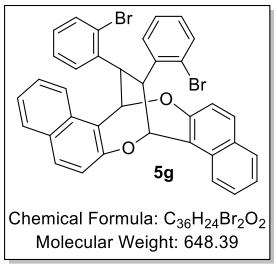
Following the general procedure **A**, **5e** was obtained from (*E*)-1-(4-(*tert*-butyl)styryl)naphthalen-2-ol (0.030 g, 0.1 mmol) as a colorless oil (0.010 g) in 33% yield. $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.7 Hz, 2H), 7.62 – 7.52 (m, 2H), 7.49 (d, J = 8.9 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.27 (d, J = 8.4 Hz, 4H), 7.23 – 7.17 (m, 7H), 7.08 (d, J = 8.8 Hz, 3H), 6.28 (s, 2H), 3.93 (s, 2H), 1.23 (s, 18H).

These data matched those reported in the literature.[3]



17,18-di-*o*-tolyl-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'f][1,5]dioxocine (5f)

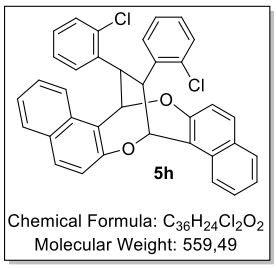
Following the general procedure **A**, **5f** was obtained from the (*E*)-1-(2-methylstyryl)naphthalen-2-ol (0.026 g, 0.1 mmol) as a colorless oil (0.011 g) in 42% yield. IR 1622, 1598, 1512, 1490, 1464, 1433, 1399, 1378, 1305, 1261, 1228, 1213, 1065, 952, 924, 855, 740, 703 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.6 Hz, 2H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 8.9 Hz, 2H), 7.45 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.18 – 7.07 (m, 4H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.31 (s, 2H), 4.41 (s, 2H), 1.80 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 157.1, 141.8, 135.9, 132.9, 130.8, 130.3, 129.9, 128.3, 128.0, 127.1, 126.9, 126.5, 123.8, 122.4, 121.0, 118.0, 83.1, 50.5, 20.0. HRMS (ESI^+/Q-TOF)*m/z* $[M - H]^-$ calcd for $C_{38}H_{29}O_2$: 517.2168; found: 517.2166.



17,18-bis(2-bromophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2-',1'-f][1,5]di-oxocine (5g)

Following the general procedure **A**, **5g** was obtained from (*E*)-1-(2-bromostyryl)naphthalen-2-ol (0.032 g, 0.1 mmol) as a colorless oil (0.019 g) in 58% yield. $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.52 – 7.43 (m, 4H), 7.31 (dt, *J* = 26.2, 7.5 Hz, 4H), 7.10 (t, *J* = 8.3 Hz, 4H), 6.24 (s, 2H), 4.89 (s, 2H).

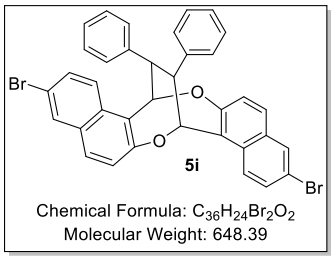
These data matched those reported in the literature.[3]



17,18-bis(2-chlorophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2-',1'-f][1,5]di-oxocine (5h)

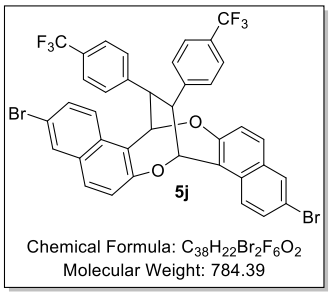
Following the general procedure **A**, **5h** was obtained from (*E*)-1-(2-chlorostyryl)naphthalen-2-ol (0.028 g, 0.1 mmol) as a colorless oil (0.011 g) in 39% yield. $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 4H), 7.56 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.38 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 2H), 7.26 – 7.19 (m, 6H), 7.12 – 7.07 (m, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.18 (s, 2H), 4.81 (s, 2H).

These data matched those reported in the literature.[3]



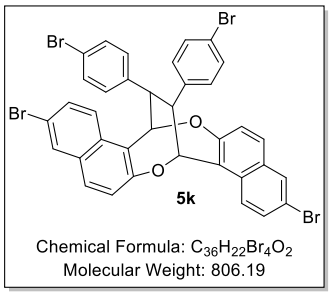
2,11-dibromo-17,18-diphenyl-8H,16H-8,16-ethanodinaphtho[2,-1-b:2',1'-f][1,5]dioxocine (5i)

Following the general procedure **A**, **5i** was obtained from (*E*)-6-bromo-1-styrylnaphthalen-2-ol (0.032 g, 0.1 mmol) as a colorless oil (0.010 g) in 31% yield. $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.2 Hz, 2H), 7.78 (d, *J* = 1.9 Hz, 2H), 7.53 – 7.45 (m, 4H), 7.38 (d, *J* = 6.9 Hz, 4H), 7.26 – 7.18 (m, 6H), 7.16 (d, *J* = 8.9 Hz, 2H), 6.32 (s, 2H), 3.93 (s, 2H). These data matched those reported in the literature.[3]



2,11-dibromo-17,18-bis(4-(trifluoromethyl)phenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',1'-f][1,5]dioxocine (5j)

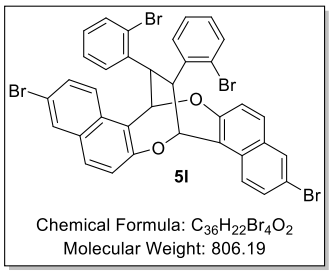
Following the general procedure **A**, **5j** was obtained from (*E*)-6-bromo-1-(4-(trifluoromethyl)styryl)naphthalen-2-ol (0.039 g, 0.1 mmol) as a colorless oil (0.019 g) in 49% yield. IR1618, 1589, 1498, 1463, 1421, 1399, 1355, 1323, 1263, 1227, 1191, 1164, 1122, 1110, 1066, 1018, 1003, 949, 927, 879, 865, 838, 807, 700 cm^{-1}; $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.2 Hz, 2H), 7.80 (d, *J* = 1.9 Hz, 2H), 7.53 (q, *J* = 8.5 Hz, 12H), 7.19 – 7.13 (m, 2H), 6.28 (s, 2H), 4.00 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.2, 146.5, 131.5, 131.4, 130.9, 130.6, 130.5, 130 (q, $^2J_{C\text{-}F}$=32.8 Hz), 128.8, 126.0 (q, $^3J_{C\text{-}F}$=3.8 Hz), 124.0, 124.3 （q, $^1J_{C\text{-}F}$=272.2 Hz）, 122.0, 118.2, 117.6, 82.3, 56.3. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$) δ -62.50 (s, 6F). HRMS (ESI$^+$/Q-TOF) *m*/*z* [M - H]$^-$ calcd for $C_{38}H_{21}Br_2F_6O_2$: 780.9812; found: 780.9822.



3,11-dibromo-17,18-bis(4-bromophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',1'-f][1,5]dioxocine (5k)

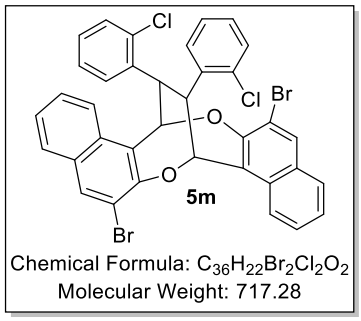
Following the general procedure **A**, **5k** was obtained from (*E*)-6-bromo-1-(4-bromostyryl)naphthalen-2-ol (0.040 g, 0.1 mmol) as a colorless oil (0.020 g) in 50% yield. IR 1615, 1589, 1486, 1463, 1398, 1308, 1287, 1262, 1226, 1213, 1190, 1156, 1069, 1010, 950, 924, 878, 821 cm^{-1}; $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.2 Hz, 2H), 7.78 (d, *J* = 1.7 Hz, 2H), 7.55 – 7.46 (m, 4H), 7.40 (d, *J* = 8.4 Hz, 4H), 7.25 (d, *J* = 8.4 Hz, 4H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.25 (s, 2H), 3.83 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.1, 141.8, 131.9, 131.4, 131.2,

130.7, 130.4, 130.3, 130.1, 124.0, 121.9, 121.4, 118.0, 117.6, 82.3, 56.0. HRMS (ESI$^+$/Q-TOF)*m*/*z* [M + Cl]$^-$ calcd for $C_{36}H_{22}Br_4O_2Cl$: 836.8042; found: 836.8068.



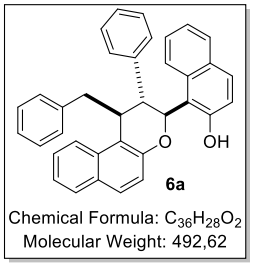
3,11-dibromo-17,18-bis(2-bromophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',1'-f][1,5]dioxocine (5l)

Following the general procedure **A**, **5l** was obtained from the (*E*)-6-bromo-1-(2-bromostyryl)naphthalen-2-ol (0.040 g, 0.1 mmol) as a colorless oil (0.015 g) in 38% yield. IR 1615, 1588, 1597, 1468, 1438, 1399, 1355, 1321, 1300, 1262, 1226, 1213, 1191, 1157, 1103, 1069, 1021, 1002, 949, 929, 878, 804, 756, 704 cm^{-1}; $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.2 Hz, 2H), 7.79 (d, *J* = 5.9 Hz, 4H), 7.52 (d, *J* = 8.1 Hz, 4H), 7.46 (s, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.10 (dd, *J* = 17.4, 8.4 Hz, 4H), 6.17 (s, 2H), 4.87 (s, 2H). $^{13}C\{^1H\}$ (126 MHz,$CDCl_3$) δ 157.1, 140.5, 133.3, 131.3, 131.2, 130.6, 130.4, 130.2, 129.4, 129.0, 128.1, 125.4, 124.0, 121.9, 118.1, 117.9, 82.3, 51.2. HRMS (ESI$^+$/Q-TOF) *m*/*z* [M + H]$^+$ calcd for $C_{36}H_{23}Br_4O_2$: 802.8431; found: 802.8431.



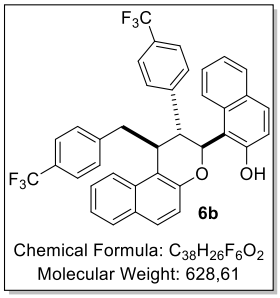
2,11-dibromo-17,18-bis(2-chlorophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',1'-f][1,5]dioxocine (5m)

Following the general procedure **A**, **5m** was obtained from (*E*)-3-bromo-1-(2-chlorostyryl)naphthalen-2-ol (0.036 g, 0.1 mmol) as a colorless oil (0.013 g) in 36% yield. IR 1618, 1584, 1501, 1447, 1430, 1258, 1330, 1071, 1006, 864, 739 cm^{-1}; $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2H), 8.01 – 7.93 (m, 2H), 7.89 (s, 2H), 7.58 – 7.46 (m, 4H), 7.37 – 7.28 (m, 6H), 7.22 – 7.14 (m, 2H), 6.40 (s, 2H), 4.90 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 138.9, 134.1, 134.1, 132.0, 130.6, 129.7, 128.7, 127.7, 127.6, 127.4, 125.2, 122.8, 119.3, 115.2, 83.7, 48.7. HRMS (ESI$^+$/Q-TOF)*m*/*z* [M + H]$^+$ calcd for $C_{36}H_{23}Br_2Cl_2O_2$: 714.9442; found: 714.9441.



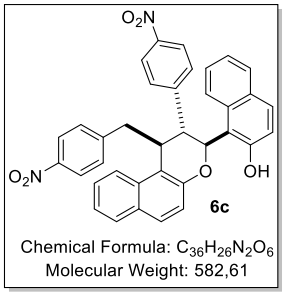
1-(1-benzyl-2-phenyl-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6a)

Following the general procedure **B** with toluene as solvent, **6a** was obtained from (*E*)-1-styrylnaphthalen-2-ol (0.025 g, 0.1 mmol) as a colorless oil (0.025 g) in 99% yield. IR 1622, 1599, 1512, 1494, 1473, 1466, 1435, 1394, 1348, 1303, 1263, 1229, 1156, 1142, 1073, 1036, 999, 964, 859, 815, 699 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (500 MHz, CD_3CN) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 5.9 Hz, 1H), 7.60 (dd, *J* = 17.2, 9.1 Hz, 3H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 22.3 Hz, 3H), 7.12 – 6.83 (m, 10H), 6.73 – 6.49 (m, 2H), 5.84 (d, *J* = 11.4 Hz, 1H), 4.39 (s, 1H), 4.25 (dd, *J* = 11.0, 7.6 Hz, 1H), 3.32 (s, 1H), 2.97 (d, *J* = 12.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 154.5, 153.7, 141.2, 138.1, 132.1, 131.9, 130.9, 130.4, 129.9, 129.3, 128.8, 128.4, 128.2, 128.1, 127.0, 126.7, 126.5, 125.8, 124.4, 122.9, 122.7, 121.8, 119.5, 119.2, 115.6, 81.2, 51.2, 41.55, 41.1. HRMS (ESI^+/Q-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{37}H_{29}O_2$: 493.2168; found: 493.2130.



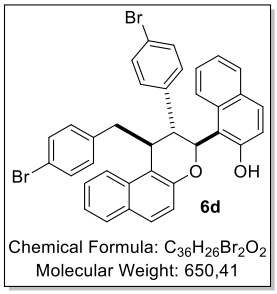
1-(1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6b)

Following the general procedure **B** with 1,2-Dichloroethane as solvent, **6b** was obtained from (*E*)-1-(4-(trifluoromethyl)styryl)naphthalen-2-ol (0.031 g, 0.1 mmol) as white solid (0.028 g) in 90% yield. IR 1618, 1390, 1500, 1488, 1462, 1389, 1344, 1307, 1263, 1231, 1155, 1071, 1009, 961, 880, 814, 703 cm^{-1}; mp: 207 °C; $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 1H), 8.05 – 7.88 (m, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.59 (dt, *J* = 48.1, 7.3 Hz, 4H), 7.34 – 7.20 (m, 7H), 7.17 – 6.79 (m, 7H), 5.73 (d, *J* = 10.8 Hz, 1H), 4.48 (br s, 1H), 3.95 (br s, 1H), 3.32 (br s, 1H), 3.09 (s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 145.0, 142.3, 131.8, 131.7, 131.0, 130.8, 130.0, 129.5, 129.2, 129.2, 129.0 (q, $^{3}J_{C\text{-}F}$= 57.9 Hz), 128.4, 127.3, 126.2, 125.1, 125.0 (q, $^{3}J_{C\text{-}F}$=3.8 Hz), 124.7, 123.1, 122.5, 121.2 (q, $^{1}J_{C\text{-}F}$= 199.1 Hz), 119.3, 115.0, 81.0, 52.0, 42.4, 41.0. $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) δ -62.56 (s, 3F), -62.80 (s, 3F). HRMS (ESI^+/Q-TOF)*m*/*z* $[M + H]^+$ calcd for $C_{38}H_{27}F_6O_2$: 629.1915; found: 629.1907.



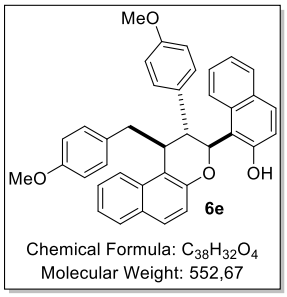
1-(1-(4-bromobenzyl)-2-(4-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6c)

Following the general procedure **B** with toluene as solvent, **6c** was obtained from (*E*)-1-(4-bromostyryl)naphthalen-2-ol (0.032 g, 0.1 mmol) as a yellow foam (0.027 g) in 91% yield. IR 1622, 1597, 1514, 1466, 1436, 1395, 1341, 1255, 1229, 1109, 1079, 1007, 907, 854, 815, 809 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.97 (dd, *J* = 12.3, 8.3 Hz, 3H), 7.89 – 7.62 (m, 5H), 7.61 – 7.48 (m, 2H), 7.39 (br s, 1H), 7.23 (d, *J* = 8.7 Hz, 3H), 7.17 – 6.82 (m, 6H), 5.76 (d, *J* = 10.8 Hz, 1H), 4.60 – 4.32 (m, 1H), 4.07 (br s, 1H), 3.27 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 154.8, 154.6, 148.1, 146.9, 146.8, 145.6, 131.7, 131.5, 131.1, 130.9, 130.6, 129.7, 129.5, 129.3, 128.7, 127.5, 126.4, 124.8, 123.4, 122.3, 121.1, 119.6, 119.2, 114.7, 80.2, 51.4, 41.6, 40.8.



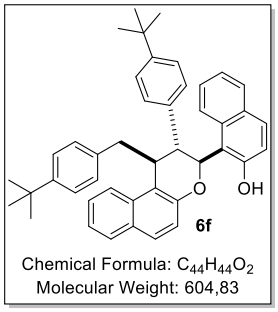
1-(1-(4-bromobenzyl)-2-(4-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6d)

Following the general procedure **B** with toluene as solvent, **6d** was obtained from (*E*)-1-(4-bromostyryl)naphthalen-2-ol (0.032 g, 0.1 mmol) as a colorless oil (0.023 g) in 71% yield. IR 1599, 1487, 1464, 1411, 1288, 1258, 1075, 1008, 864, 798, 740, 702 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (500 MHz, CD_3CN) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.62 (dd, *J* = 14.9, 7.7 Hz, 3H), 7.47 (dd, *J* = 20.5, 13.2 Hz, 1H), 7.31 – 7.18 (m, 4H), 7.18 – 7.05 (m, 3H), 6.87 (d, *J* = 7.9 Hz, 3H), 6.60 – 6.44 (m, 2H), 5.79 (d, *J* = 11.4 Hz, 1H), 4.36 (s, 1H), 4.15 – 4.05 (m, 1H), 3.21 (s, 1H), 3.01 (d, *J* = 11.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 140.0, 136.9, 132.5, 132.0, 131.8, 131.6, 131.4, 131.2, 130.8, 130.6, 130.3, 129.3, 128.7, 128.5, 128.3, 127.1, 126.1, 124.5, 123.6, 123.0, 122.5, 121.4, 120.6, 120.5, 119.5, 119.2, 119.1, 115.2, 80.8, 50.8, 41.1, 40.9. HRMS (ESI^+/Q-TOF) *m*/*z* $[M - H]^-$ calcd for $C_{36}H_{25}Br_2O_2$: 647.0221; found: 647.0219.



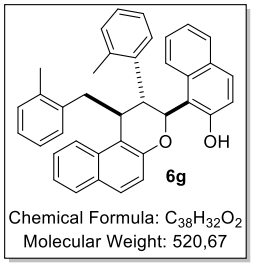
1-(1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-2,3-dihydro-1H-benz-o[f]chromen-3-yl)naphthalen-2-ol (6e)

Following the general procedure **B** with toluene as solvent, **6e** was obtained from (*E*)-1-(4-methoxystyryl)naphthalen-2-ol (0.028 g, 0.1 mmol) as a colorless oil (0.009 g) in 32% yield. IR 1621, 1610, 1599, 1465, 1439, 1394, 1346, 1301, 1246, 1230, 1176, 1142, 1033, 814, 736 cm^{-1}**;** $^1H\{^{13}C\}$ NMR (500 MHz, CD_3CN) δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.74 – 7.64 (m, 4H), 7.54 – 7.41 (m, 1H), 7.33 – 7.13 (m, 2H), 7.12 – 6.99 (m, 2H), 7.00 – 6.82 (m, 3H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.61 – 6.40 (m, 4H), 5.79 (d, *J* = 11.4 Hz, 1H), 4.36 – 4.22 (m, 1H), 4.22 – 4.07 (m, 1H), 3.72 (s, 3H), 3.63 (s, 3H), 3.35 – 3.19 (m, 1H), 2.98 – 2.82 (m, 1H). $^{13}C\{^1H\}$ (126 MHz, $CDCl_3$) δ 158.4, 158.2, 154.5, 153.7, 133.4, 132.2, 132.0, 130.8, 130.5, 130.3, 130.2, 129.8, 129.3, 128.6, 128.3, 128.2, 125.9, 125.0, 124.4, 122.9, 122.8, 121.9, 119.5, 119.2, 113.9, 113.7, 113.6, 113.4, 81.3, 55.3, 55.3, 50.3, 41.4, 40.5. HRMS (ESI^+/Q-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{32}NaO_4$: 575.2198; found: 575.2218.



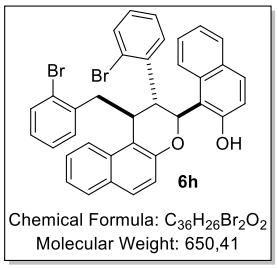
1-(1-(4-(tert-butyl)benzyl)-2-(4-(tert-butyl)phenyl)-2,3-dihydro-1H -benzo[f]c- hromen-3-yl)naphthalen-2-ol (6f)

Following the general procedure **B** with 1,2-dichloroethane as solvent, **6f** was obtained from from (*E*)-1-(4-(*tert*-butyl)styryl)naphthalen-2-ol (0.030 g, 0.1 mmol) as a colorless oil (0.018 g) in 60% yield. IR 1622, 1599, 1514, 1466, 1394, 1363, 1261, 1229, 1076, 1009, 964, 862, 795, 739, 704 cm^{-1}; $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.80 (dd, *J* = 22.1, 8.6 Hz, 1H), 7.69 – 7.47 (m, 5H), 7.23 (dd, *J* = 22.3, 13.5 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.03 – 6.96 (m, 1H), 6.96 – 6.78 (m, 4H), 6.72 (dd, *J* = 16.7, 8.0 Hz, 4H), 5.63 (d, *J* = 11.0 Hz, 1H), 4.49 (dd, *J* = 12.2, 5.4 Hz, 1H), 3.89 (s, 1H), 3.21 (dd, *J* = 13.7, 4.5 Hz, 1H), 3.13 – 3.05 (m, 1H), 1.23 (s, 9H), 1.09 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.4, 153.7, 149.6, 149.3, 138.3, 135.4, 132.3, 132.1, 131.0, 130.4, 129.5, 129.3, 128.5, 128.4, 128.0, 126.9, 125.7, 125.0, 124.9, 124.5, 123.0, 122.8, 122.6, 122.0, 119.6, 119.3, 115.9, 82.1, 51.8, 42.3, 41.1, 34.5, 34.4, 31.6, 31.4. HRMS (ESI^+/Q-TOF)*m*/*z* $[M + Na]^+$ calcd for $C_{44}H_{44}NaO_2$: 627.3239; found: 627.3229.



1-(1-(2-methylbenzyl)-2-(o-tolyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6g)

Following the general procedure **B** with toluene as solvent, **6g** was obtained from (*E*)-1-(2-methylstyryl)naphthalen-2-ol (0.026 g, 0.1 mmol) as a colorless oil (0.025 g) in 98% yield. IR 2921, 2852, 1622, 1599, 1465, 1393, 1264, 1230, 1072, 1001, 964, 815, 764, 704 cm^{-1}; $^1H\{^{13}C\}$ NMR (500 MHz, CD_3CN) δ 8.10 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.83 (t, *J* = 8.7 Hz, 1H), 7.68 (dd, *J* = 20.5, 13.3 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.31 (t, *J* = 10.4 Hz, 1H), 7.18 (s, 1H), 7.08 (dd, *J* = 13.6, 7.4 Hz, 3H), 6.98 (q, *J* = 7.1 Hz, 2H), 6.84 (dt, *J* = 43.8, 18.0 Hz, 2H), 6.44 (d, *J* = 6.8 Hz, 1H), 5.74 (d, *J* = 11.2 Hz, 1H), 4.55 (dt, *J* = 14.5, 4.8 Hz, 1H), 4.44 – 4.30 (m, 1H), 3.14 (ddd, *J* = 25.2, 14.7, 7.8 Hz, 2H), 2.22 (s, 3H), 2.16 (S, 3H).$^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN) δ 142.7, 138.6, 137.9, 137.5, 133.0, 131.7, 131.3, 131.1, 130.9. 130.0, 129.9, 129.4, 129.2, 128.9, 127.8, 127.3, 127.2, 127.0, 126.9, 126.6, 125.2, 123.8, 123.3, 120.3, 119.5, 117.2, 82.9, 47.6, 42.5, 42.1, 20.2, 18.3. HRMS (ESI^+/Q-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{32}NaO_2$: 543.2300; found: 543.2298.

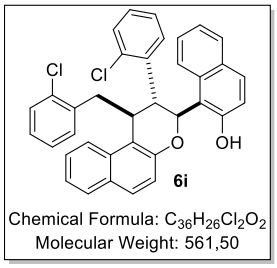


1-(1-(2-bromobenzyl)-2-(2-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6h)

Following the general procedure **B** with 1,2-dichloroethane as solvent, **6h** was obtained from (*E*)-1-(2-bromostyryl)naphthalen-2-ol (0.032 g, 0.1 mmol) as a colorless oil (0.025 g) in 77% yield. IR 1625, 1598, 1578, 1466, 1399, 1257, 1098, 1010, 864, 792, 764, 661 cm^{-1}**;** $^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) mixture of rotamers[4] δ 8.36 (d, *J* = 8.4 Hz, 0.7H), 8.07 (dd, *J* = 17.7, 10.5 Hz, 1H), 7.95 – 7.86 (m, 1H), 7.85 – 7.70 (m, 2H), 7.67 – 7.57 (m, 1.4H), 7.55 – 7.39 (m, 3.3H), 7.36 (d, *J* = 8.6 Hz, 1.4H), 7.30 (dd, *J* = 8.8, 6.3 Hz, 1H), 7.24 (d, *J* = 3.2 Hz, 0.6H), 7.17 (t, *J* = 7.5 Hz, 0.7H), 7.12 – 6.97 (m, 3H), 6.97 – 6.83 (m, 3H), 6.83 – 6.73 (m, 1H), 6.63 (t, *J* = 7.7 Hz, 0.4H), 6.34 (d, *J* = 11.7 Hz, 0.3H), 6.29 (t, *J* = 7.4 Hz, 0.3H), 5.77 – 5.70 (m, 1H), 5.17 (dt, *J* = 10.5, 5.3 Hz, 0.4H), 4.70 – 4.50 (m, 1.4H), 4.09 (dd, *J* = 11.7, 5.3 Hz, 0.4H), 3.56 (dd, *J* = 13.8, 5.2 Hz, 0.4H), 3.37 (dd, *J* = 14.0, 6.3 Hz, 0.7H), 3.21 (dd, *J* = 13.9, 9.6 Hz, 0.7H), 2.92 (dd, *J* = 13.7, 10.5 Hz, 0.4H). $^1H\{^{13}C\}$ NMR (500 MHz, DMSO-d_6, 363 K) δ 9.15 (s, 1H), 8.43 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.33 (m, 6H), 7.27 (d, *J* = 8.2 Hz, 3H), 6.94 (d, *J* =

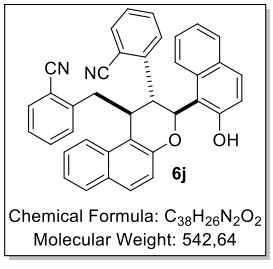
[4] At high temperature, the spectrum simplifies. As such, the obtained isomers were established as rotamers.

29.2 Hz, 6H), 5.99 – 5.74 (m, 1H), 4.95 – 4.73 (m, 1H), 4.63 – 4.32 (m, 1H), 3.55 – 3.16 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 154.3, 153.9, 141.7, 138.3, 137.8, 133.9, 133.8, 132.9, 132.8, 132.8, 132.7, 132.6, 132.3, 131.6, 131.0, 130.7, 130.4, 129.6, 129.1, 129.0, 128.7, 128.4, 128.2, 128.2, 128.0, 128.0, 127.8, 127.5, 127.2, 126.9, 126.8, 126.5, 126.0, 125.8, 125.7, 125.1, 124.6, 124.6, 124.0, 123.5, 122.8, 122.7, 121.6, 121.3, 119.8, 119.7, 119.4, 119.1, 115.2, 84.0, 77.9, 54.4, 50.7, 45.1, 44.8, 40.0, 36.5. HRMS (ESI^+/Q-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{36}H_{27}Br_2O_2$: 649.0402; found: 649.0378.



1-(1-(2-chlorobenzyl)-2-(2-chlorophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6i)

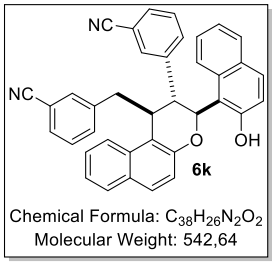
Following the general procedure **B** with toluene as solvent, **6i** was obtained from the corresponding (*E*)-1-(2-chlorostyryl)naphthalen-2-ol (0.028 g, 0.1 mmol) as a colorless oil (0.021 g) in 75% yield. IR 1622, 1598, 1513, 1467, 1261, 1228, 1077, 1050, 1009, 964, 813, 793, 682 cm^{-1}**;** $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) mixture of rotamers δ 8.32 (d, *J* = 8.4 Hz, 0.4H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.00 (s, 0.4H), 7.96 – 7.89 (m, 1H), 7.80 (t, *J* = 9.7 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 0.7H), 7.68 – 7.58 (m, 1.4H), 7.57 – 7.43 (m, 2.8H), 7.41 – 7.27 (m, 1.5H), 7.24 (s, 1H), 7.09 (dd, *J* = 16.0, 7.8 Hz, 3.4H), 7.03 – 6.77 (m, 4.6H), 6.72 (t, *J* = 7.3 Hz, 0.4H), 6.61 (d, *J* = 7.9 Hz, 0.6H), 6.28 (dd, *J* = 15.4, 9.4 Hz, 1H), 5.76 (dd, *J* = 19.2, 8.7 Hz, 1H), 5.16 – 4.97 (m, 0.4H), 4.66 (d, *J* = 8.1 Hz, 1H), 4.05 (dd, *J* = 11.4, 5.1 Hz, 0.4H), 3.59 (dd, *J* = 13.6, 4.6 Hz, 0.4H), 3.49 (dd, *J* = 13.9, 4.6 Hz, 0.6H), 3.08 – 2.99 (m, 0.6H), 2.93 – 2.80 (m, 0.4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 154.0, 153.8, 153.6, 139.5, 137.1, 136.6, 136.1, 134.9, 134.4, 133.1, 132.7, 132.5, 132.3, 132.3, 132.1, 131.6, 131.2, 131.1, 130.7, 130.4, 130.3, 129.6, 129.4, 129.3, 129.1, 128.7, 128.3, 128.1, 128.0, 127.7, 127.0, 126.8, 126.6, 126.0, 125.8, 124.6, 124.6, 123.8, 123.5, 123.2, 122.9, 122.8, 122.7, 121.4, 119.7, 119.6, 119.4, 119.2, 116.1, 115.0, 83.1, 77.8, 53.7, 47.5, 42.7, 42.5, 39.6, 36.5. HRMS (ESI^+/Q-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{36}H_{27}Cl_2O_2$: 561.1388; found: 561.1399.



2-(1-(2-cyanobenzyl)-3-(2-hydroxynaphthalen-1-yl)-2,3-dihydro-1H-benzo[f]chromen-2-yl)benzonitrile (6j)

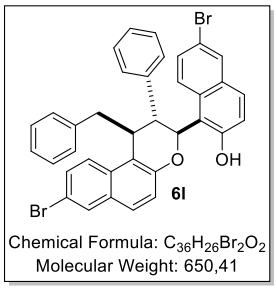
Following the general procedure **B** with 1,2-Dichloroethane as solvent, **6j** was obtained from (*E*)-1-(2-cyanostyryl)naphthalen-2-ol (0.027 g, 0.1 mmol) as a colorless oil (0.025 g) in 94% yield. IR 1622, 1598, 1512, 1467, 1446,

1395, 1264, 1229, 1075, 1008, 964, 815, 715 cm^{-1}**;** $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$) δ 8.60 (br s, 1H), 8.09 (br s, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.81 – 7.64 (m, 3H), 7.64 – 7.30 (m, 8H), 7.14 (t, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 15.2 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 3H), 6.72 (s, 1H), 5.73 (d, *J* = 10.7 Hz, 1H), 4.97 (br s, 1H), 4.40 (br s, 1H), 3.89 (d, *J* = 14.3 Hz, 1H), 2.94 (br s, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 153.9, 144.0, 142.1, 133.9, 133.0, 132.7, 132.6, 132.3, 131.9, 131.5, 131.1, 129.2, 128.9, 128.5, 127.5, 127.2, 127.1, 126.1, 124.9, 123.3, 122.8, 121.4, 120.9, 120.4, 119.1, 119.0, 116.1, 113.5, 112.1, 110.2, 81.3, 50.1, 43.2, 39.9. HRMS (ESI^+/Q-TOF) *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{26}N_2NaO_2$: 565.1892; found: 565.1906.



2-(1-(2-cyanobenzyl)-3-(2-hydroxynaphthalen-1-yl)-2,3-dihydro-1H-benzo[f]chromen-2-yl)benzonitrile (6k)

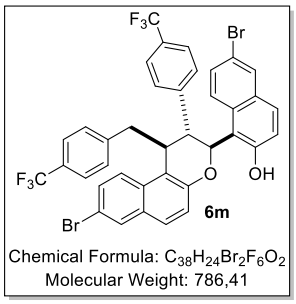
Following the general procedure **B** with 1,2-Dichloroethane as solvent, **6k** was obtained from (*E*)-1-(2-cyanostyryl)naphthalen-2-ol (0.027 g, 0.1 mmol) as a red oil (0.025 g) in 92% yield. IR 2230, 1623, 1599, 1583, 1512, 1436, 1395, 1269, 1231, 1079, 1010, 910, 816**;** $^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 1H), 8.08 – 7.92 (m, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.75 – 7.62 (m, 2H), 7.62 – 7.51 (m, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.26 – 6.81 (m, 12H), 5.71 (d, *J* = 10.9 Hz, 1H), 4.45 (br s, 1H), 3.89 (s, 1H), 3.29 (d, *J* = 13.9 Hz, 1H), 3.11 (br s, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 154.2, 153.6, 142.1, 139.4, 134.2, 133.3, 133.1, 131.9, 131.7, 131.0, 130.9, 130.6, 130.4, 129.6, 129.2, 129.0, 128.8, 128.6, 127.4, 126.3, 124.7, 123.1, 122.4, 121.1, 119.5, 119.1, 118.5, 118.4, 112.2, 112.1, 79.7, 51.4, 41.5, 40.6.



1-(1-benzyl-8-bromo-2-phenyl-2,3-dihydro-1H-benzo[f]chromen-3-yl)-6-bromonaphthalen-2-ol (6l)

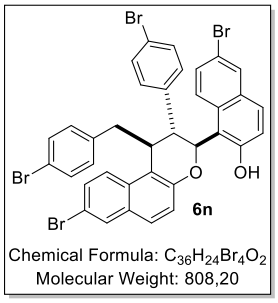
Following the general procedure **B** with toluene as solvent, **6l** was obtained from (*E*)-6-bromo-1-styrylnaphthalen-2-ol (0.032 g, 0.1 mmol) as a colorless oil (0.014 g) in 43% yield. IR 1590, 1496, 1455, 1390, 1260, 1233, 1088, 1016, 961, 874, 800, 700, 661 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.7 Hz, 1H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.73 – 7.64 (m, 3H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.28 (m, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.15 – 7.04 (m, 3H), 7.03 – 6.82 (m, 7H),

6.67 (s, 2H), 5.62 (d, *J* = 10.9 Hz, 1H), 4.43 (d, *J* = 5.0 Hz, 1H), 4.06 – 3.88 (m, 1H), 3.18 (s, 1H), 3.08 (d, *J* = 10.1 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 154.6, 153.9, 140.6, 138.1, 137.6, 132.3, 131.3, 130.7, 130.4, 130.2, 130.1, 129.9, 129.6, 129.0, 128.7, 128.4, 128.2, 127.6, 127.1, 126.7, 124.7, 123.5, 122.1, 120.8, 120.3, 118.4, 115.7, 81.2, 51.1, 41.5, 41.1. HRMS (ESI^+/Q-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{36}H_{27}Br_2O_2$: 649.0188; found: 649.0178.



6-bromo-1-(8-bromo-1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluor-omethyl)phenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthale-n-2-ol (6m)

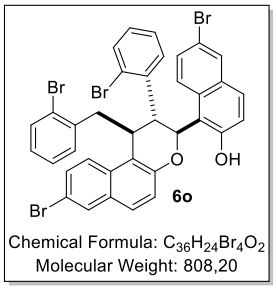
Following the general procedure **B** with toluene as solvent, **6m** was obtained from (*E*)-6-bromo-1-(4-(trifluoromethyl)styryl)naphthalen-2-ol (0.039 g, 0.1 mmol) as a colorless oil (0.037 g) in 94% yield. IR 1618, 1589, 1498, 1463, 1421, 1399, 1323, 1263, 1227, 1191, 1164, 1122, 1110, 1066, 1018, 1003, 949, 927, 879, 838, 807, 700 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (400 MHz, CDCl3) δ 8.04 (d, *J* = 2.1 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.77 – 7.56 (m, 3H), 7.44 (d, *J* = 32.8 Hz, 2H), 7.30 – 7.00 (m, 8H), 6.98 – 6.60 (s, 6H), 5.59 (br s, 1H), 4.35 (d, *J* = 7.5 Hz, 1H), 3.85 (br s, 1H), 3.10 (d, *J* = 60.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.3, 153.9, 144.4, 141.8, 132.2, 132.1, 131.4, 130.5, 130.4, 130.0, 129.7 (q, $^{2}J_{C\text{-}F}$ = 34.0 Hz), 129.6 (q, $^{2}J_{C\text{-}F}$ = 34.0 Hz), 129.3, 129.1, 128.9, 128.1, 125.2, 124.3, 122.9, 122.0 (q, $^{1}J_{C\text{-}F}$ = 270.9 Hz), 121.7 (q, $^{1}J_{C\text{-}F}$= 274.7 Hz), 120.8, 120.4, 118.6, 116.8, 115.0, 80.6, 51.7, 42.1, 40.9$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) δ -62.59 (s, 3F), -62.80 (s, 3F). HRMS (ESI^+/Q-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{38}H_{25}Br_2F_6O_2$: 785.0125; found: 785.0095.



6-bromo-1-(8-bromo-1-(4-bromobenzyl)-2-(4-bromophenyl)-2,3-dih-ydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6n)

Following the general procedure **B** with toluene as solvent, **6n** was obtained from (*E*)-6-bromo-1-(4-bromostyryl)naphthalen-2-ol (0.040 g, 0.1 mmol) as a colorless oil (0.032 g) in 79% yield. IR 1616, 1589, 1496, 1487, 1462, 1389, 1343, 1262, 1230, 1155, 1071, 1009, 960, 880, 814, 703 cm^{-1}**;** $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.94 (d, *J* = 9.4 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.72 – 7.65 (m, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 9.0 Hz, 1H), 7.68 – 7.50 (m, 2H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 16.9 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.14 – 7.02 (m, 2H), 6.98 (d, *J* = 16.8 Hz, 1H), 6.73 (d, *J* = 7.1 Hz, 2H), 6.54 (s, 1H), 5.61 (br s, 1H), 4.30 (d, *J* = 5.2 Hz, 1H), 3.87 (br

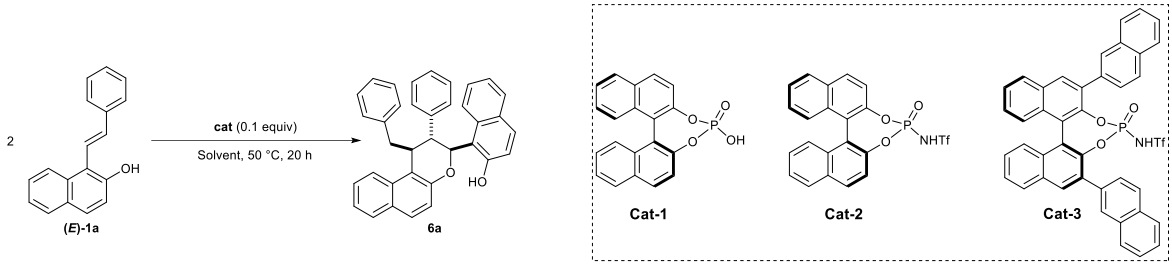
s, 1H), 3.04 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 154.0, 153.9, 139.5, 136.5, 132.1, 132.0, 131.9, 131.8, 131.7, 131.5, 131.4, 131.2, 131.1, 130.9, 130.8, 130.4, 130.3, 129.8, 129.4, 127.9, 124.4, 123.2, 121.1, 120.8, 120.3, 118.5, 116.8, 80.7, 50.7, 40.9. HRMS (ESI^+/Q-TOF) *m*/*z* $[M - H]^-$ calcd for $C_{36}H_{23}Br_4O_2$: 802.8431; found: 802.8434.



6-bromo-1-(8-bromo-1-(2-bromobenzyl)-2-(2-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6o)

Following the general procedure **B** with toluene as solvent, **6o** was obtained from (*E*)-6-bromo-1-(2-bromostyryl)naphthalen-2-ol (0.040 g, 0.1 mmol) as a colorless oil (0.026 g) in 64% yield. IR 1620, 1600, 1513, 1466, 1436, 1420, 1396, 1263, 1229, 1163, 1112, 1067, 1016, 832, 814, 739, 664 cm^{-1}; $^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$) mixture of rotamers δ 8.18 (d, *J* = 9.0 Hz, 0.7H), 8.04 (d, *J* = 14.0 Hz, 1H), 7.97 (s, 0.4H), 7.88 (d, *J* = 9.0 Hz, 0.7H), 7.78 (s, 0.7H), 7.74 – 7.62 (m, 2.5H), 7.55 (d, *J* = 8.9 Hz, 0.4H), 7.49 (d, *J* = 9.0 Hz, 2.7H), 7.41 – 7.27 (m, 3.2H), 7.18 (t, *J* = 7.4 Hz, 1.2H), 7.09 – 7.00 (m, 1.2H), 6.95 (dd, *J* = 10.6, 5.3 Hz, 3.6H), 6.85 (t, *J* = 7.5 Hz, 0.8H), 6.69 (t, *J* = 7.4 Hz, 0.9H), 6.34 (t, *J* = 7.4 Hz, 0.4H), 6.24 (d, *J* = 11.7 Hz, 0.4H), 5.72 (d, *J* = 7.5 Hz, 0.4H), 5.63 (d, *J* = 10.3 Hz, 0.7H), 5.07 (dt, *J* = 10.3, 5.2 Hz, 0.4H), 4.62 (dd, *J* = 10.3, 2.9 Hz, 0.7H), 4.52 (t, *J* = 7.7 Hz, 0.7H), 4.03 (dd, *J* = 11.7, 5.2 Hz, 0.4H), 3.47 (dd, *J* = 13.8, 5.4 Hz, 0.4H), 3.31 (dd, *J* = 13.9, 6.6 Hz, 0.7H), 3.19 (dd, *J* = 13.8, 9.3 Hz, 0.7H), 2.89 (dd, *J* = 13.6, 10.4 Hz, 0.4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) mixture of rotamers δ 154.4, 154.1, 153.6, 141.2, 137.9, 137.8, 137.5, 134.0, 133.7, 133.0, 132.9, 132.8, 132.7, 132.6, 132.4, 132.2, 131.0, 130.9, 130.6, 130.6, 130.3, 130.2, 130.1, 130.0, 129.9, 129.6, 129.6, 129.3, 129.2, 129.0, 128.6, 128.5, 128.3, 128.0, 127.9, 127.6, 127.5, 127.3, 126.7, 125.6, 125.2, 125.0, 124.6, 124.3, 123.4, 123.1, 122.8, 121.0, 120.9, 120.5, 120.2, 118.6, 118.6, 116.6, 116.5, 116.2, 115.3, 83.9, 77.9, 54.4, 50.8, 45.3, 45.0, 40.1, 36.5. HRMS (ESI^+/Q-TOF) *m*/*z* $[M + H]^+$ calcd for $C_{36}H_{25}Br_4O_2$: 804.8588; found: 804.8548.

4. Attempts with chiral Brønsted acids for the (4+2)-cyclodimerization



entry	**cat**[a]	solvent	T °C	**6a**[b]	*ee*
1	CF_3COOH (12)[5]	DCE	50 °C	0	-
2	TsOH (8.5)[5]	DCE	50 °C	85%	-
3	TsOH (8.5)[5]	toluene	50 °C	100%	-
4	**cat-1** (13.3)[6]	toluene	50 °C	0%	-
5	**cat-2** (6.4)[6]	toluene	50 °C	100%	0%
6	**cat-3**	toluene	50 °C	100%	0%
7	**cat-3**	toluene	rt	0%	-

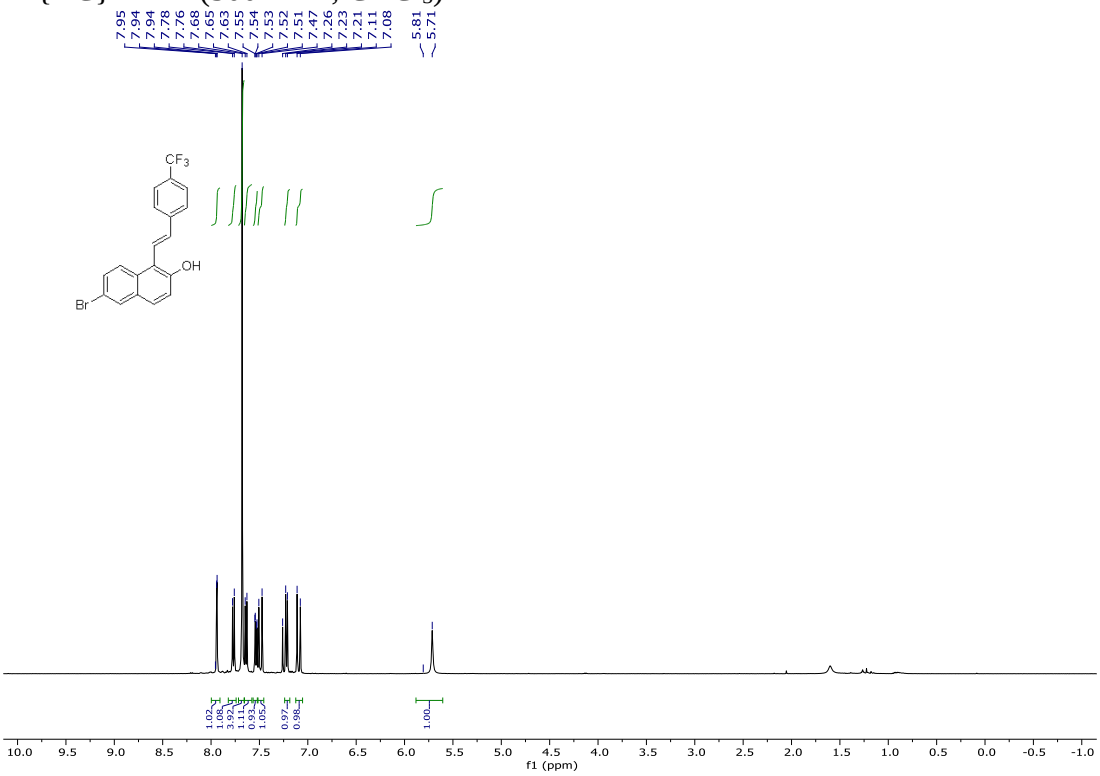
[a] pK_a values in acetonitrile between brackets. [b] NMR yield using 1,2-dibromoethane as internal standard

The starting material was totally recovered when BINOL-derived phosphoric acid **cat-1** was used as catalyst (entry 4). This might be explain by its lower acidity compared to TsOH (entries 1 and 4 *vs* 2 and 3). Although good yields were obtained with the more acidic N-triflylphosphoramide catalysts (**cat-2** and **cat-3**), the product was obtained under its racemic form.

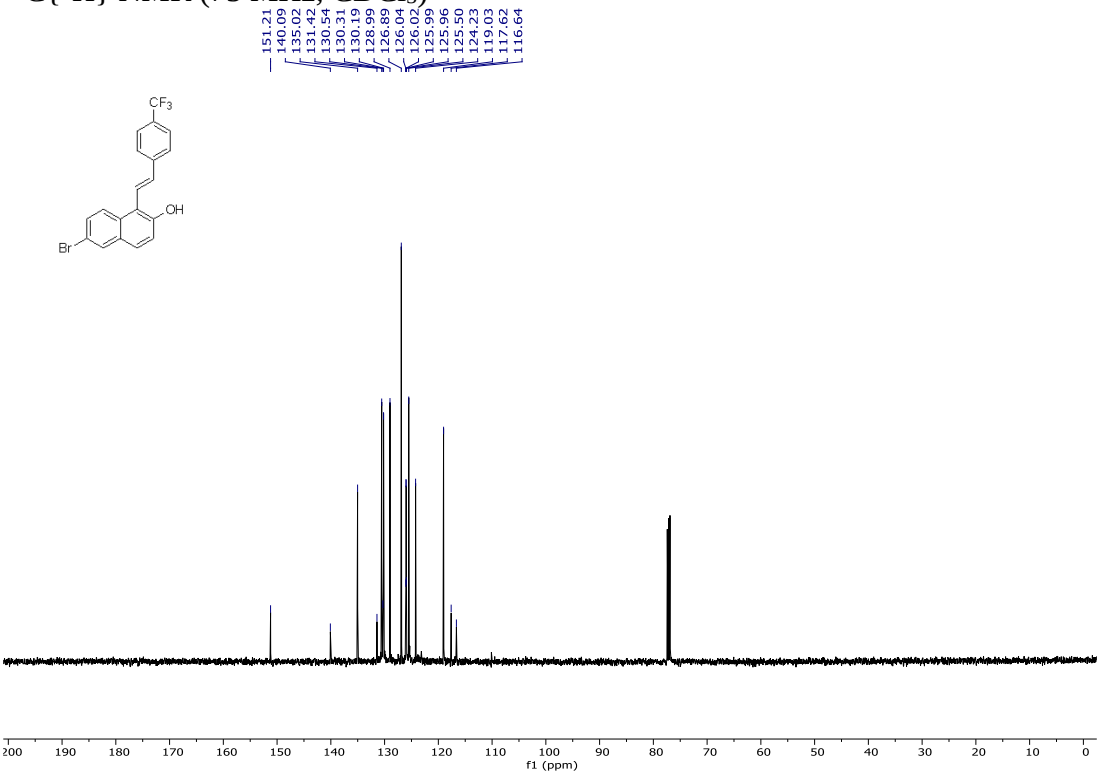
[5] Eckert, F.; Leito, I.; Kaljurand, I.; Kütt, A.; Klamt, A.; Diedenhofen, M. *J. Comp. Chem.* **2009**, *30*, 799.
[6] Parmar, D.; Sugiono, E.; Raja, S.; Rueping, M. *Chem. Rev.* **2014**, *114*, 9047.

(E)-6-bromo-1-(4-(trifluoromethyl)styryl)naphthalen-2-ol

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

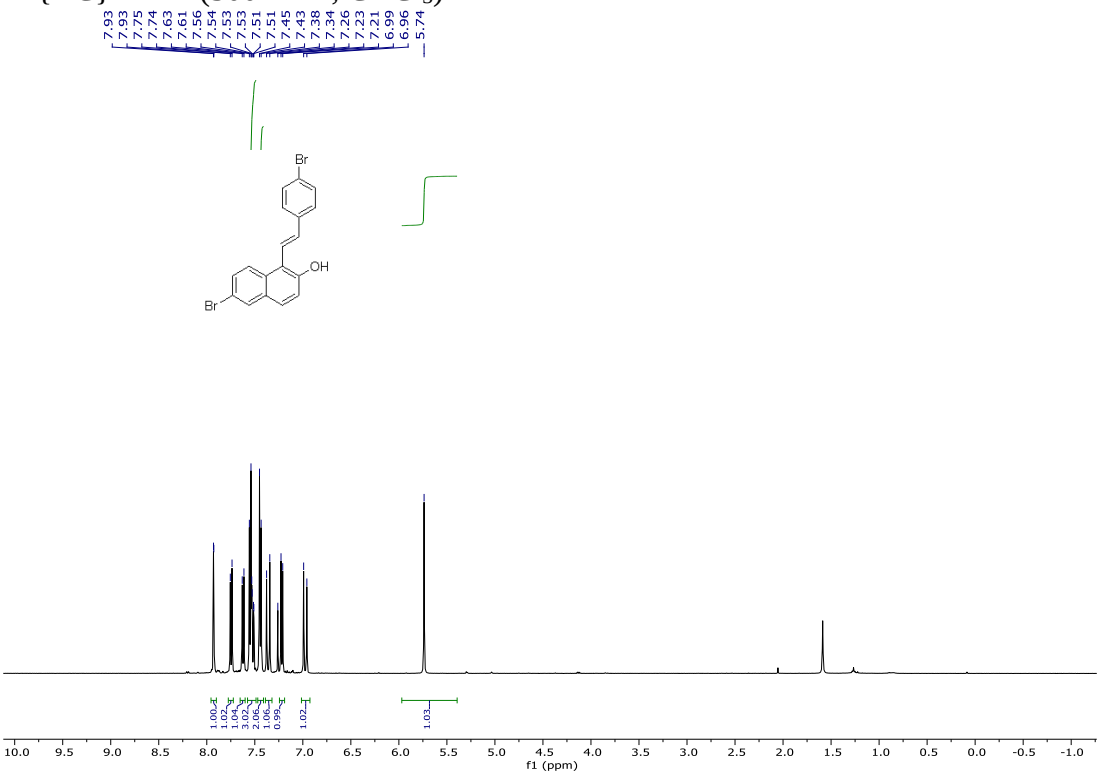


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

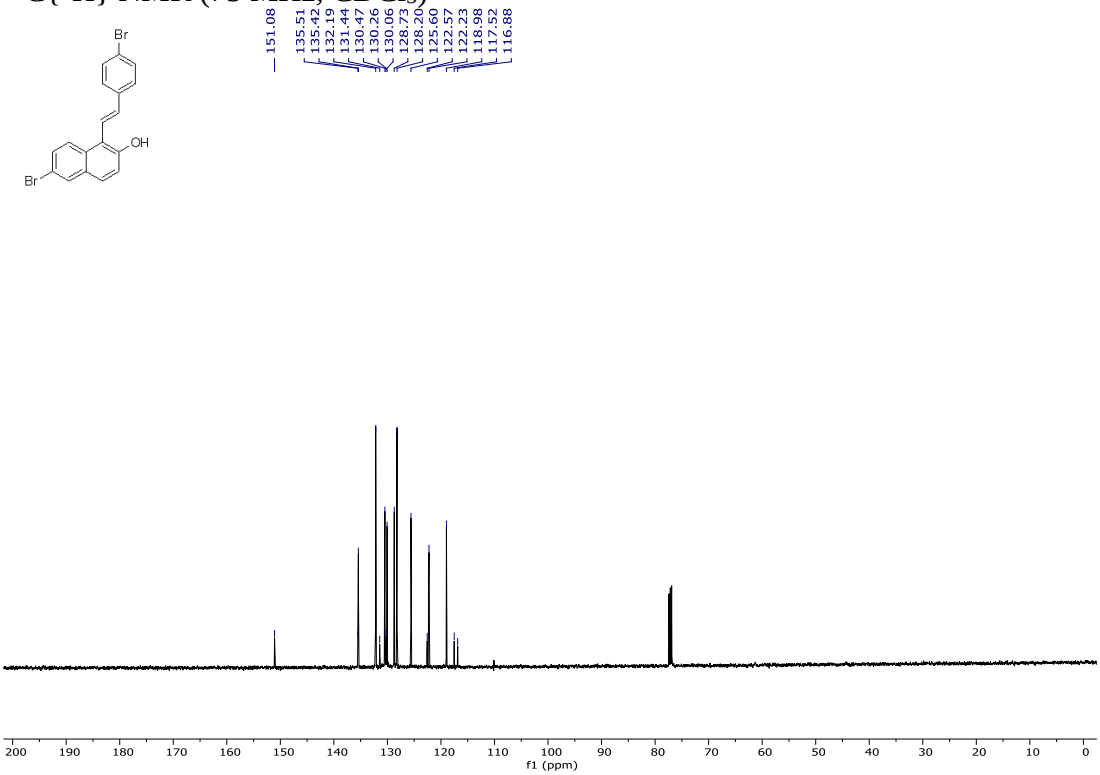


(E)-6-bromo-1-(4-bromostyryl)naphthalen-2-ol

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

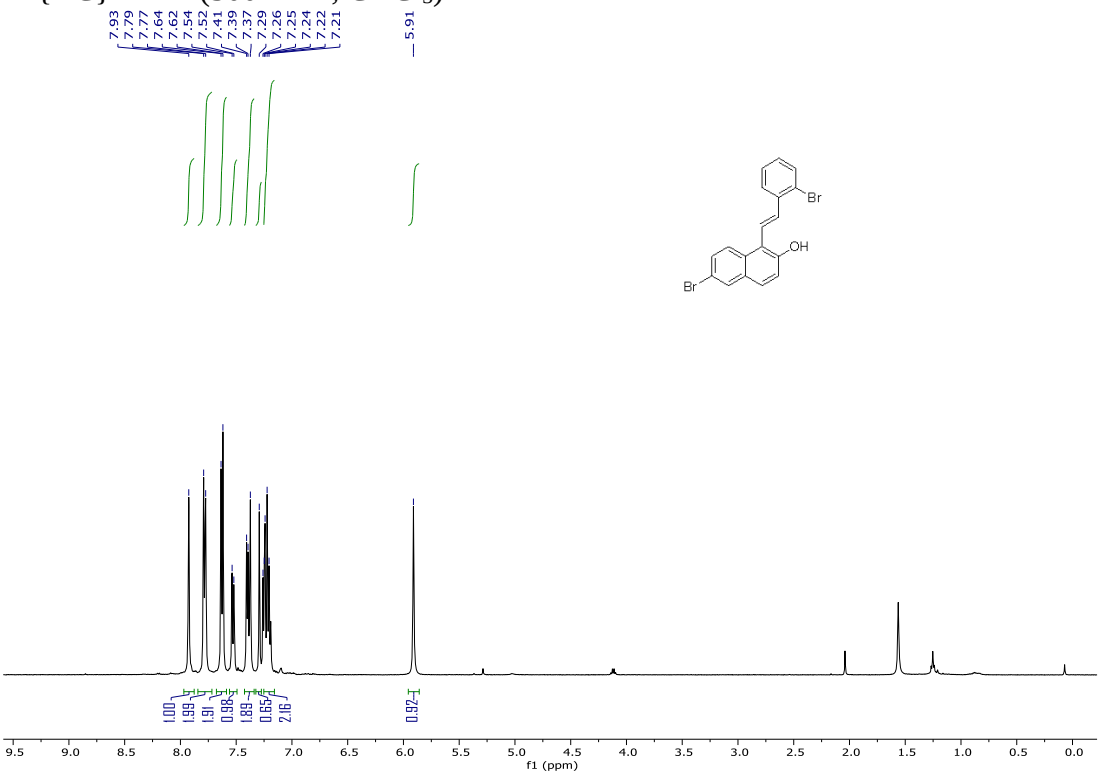


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

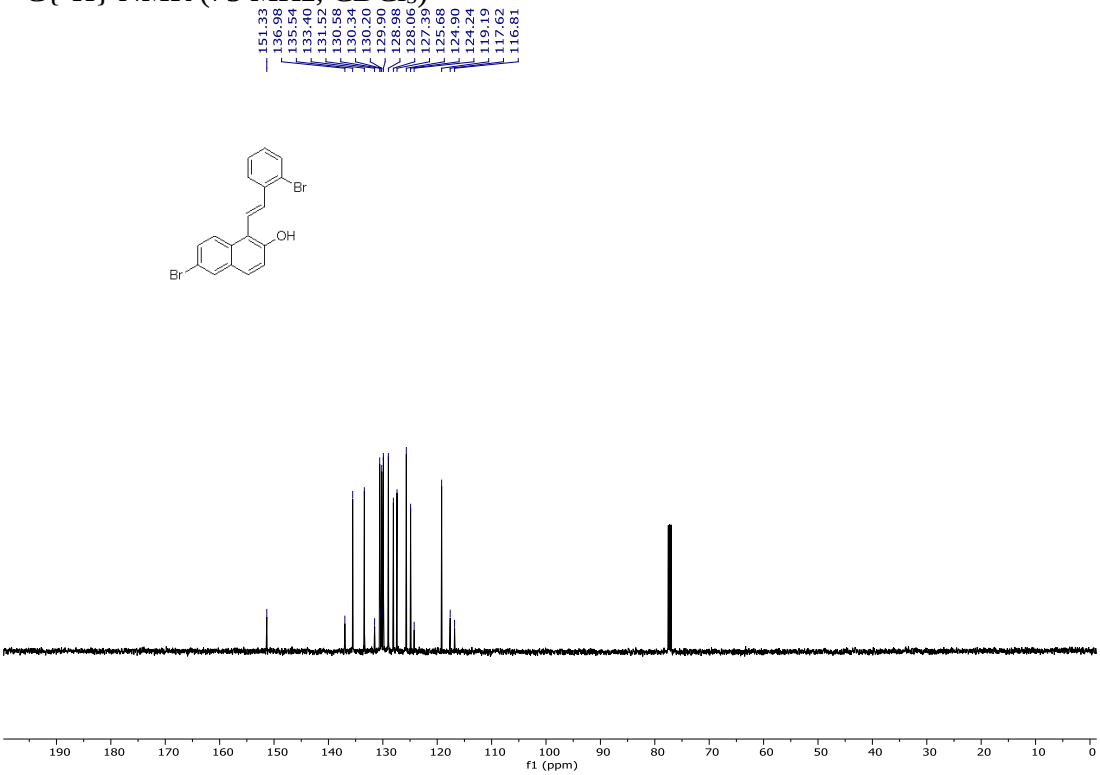


(*E*)-6-bromo-1-(2-bromostyryl)naphthalen-2-ol

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

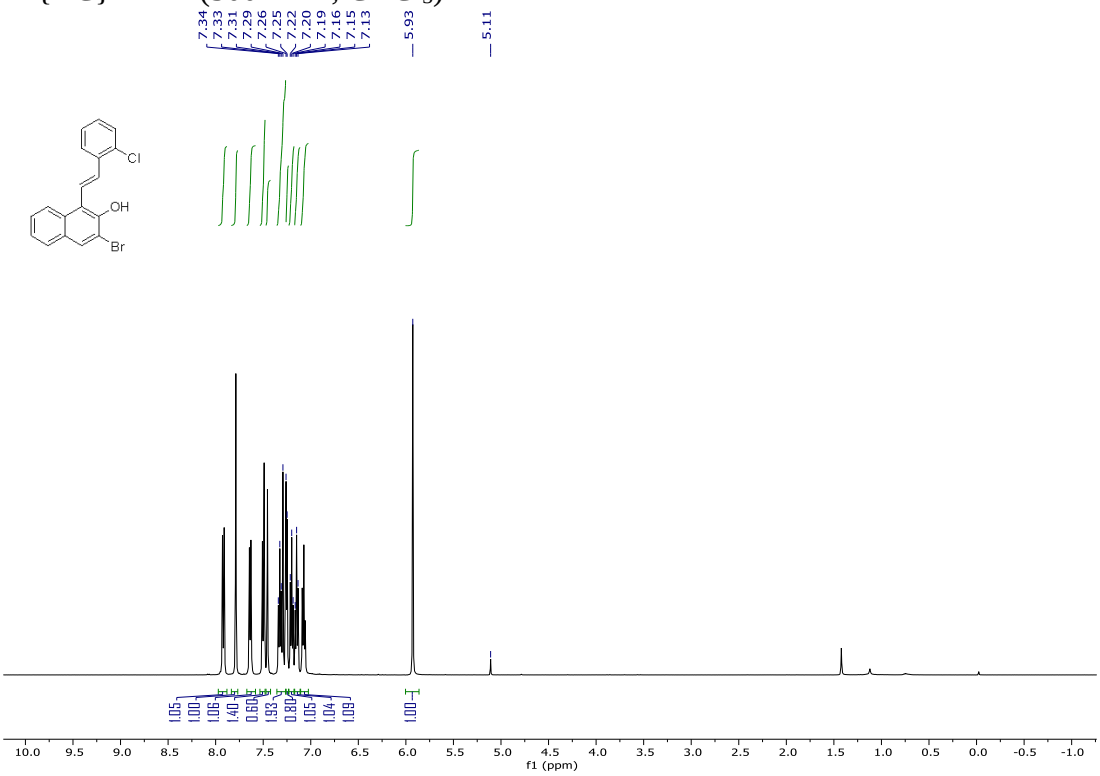


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

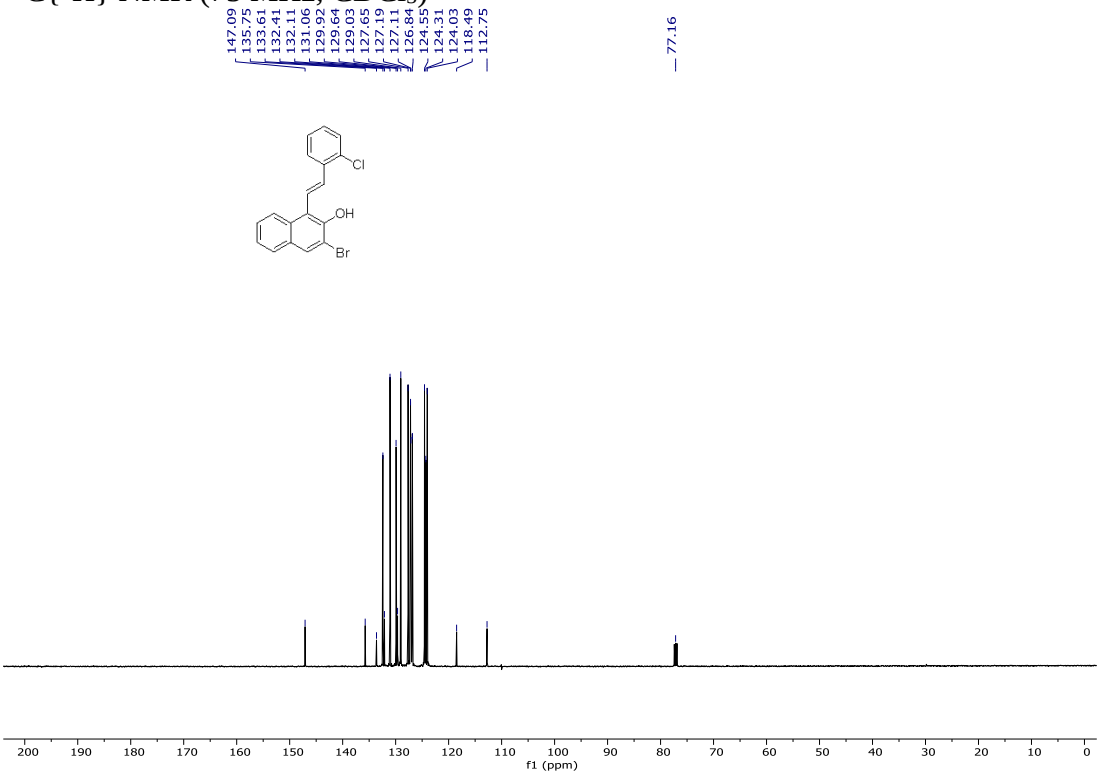


(*E*)-3-bromo-1-(2-chlorostyryl)naphthalen-2-ol

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

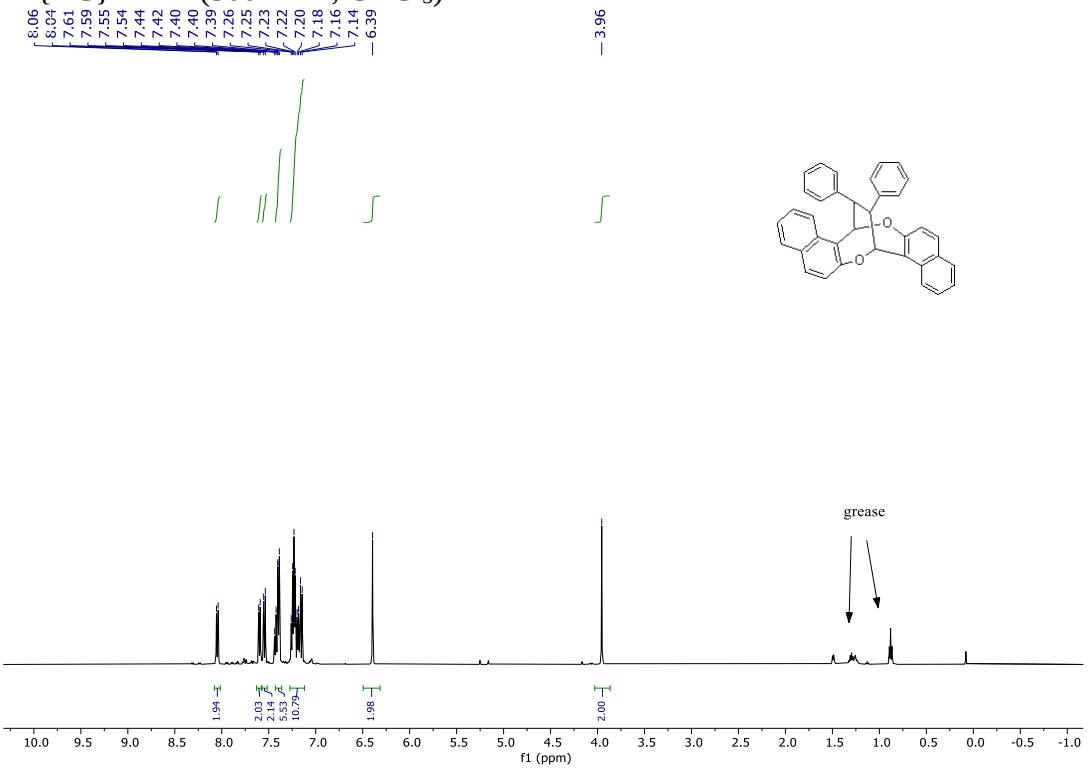


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



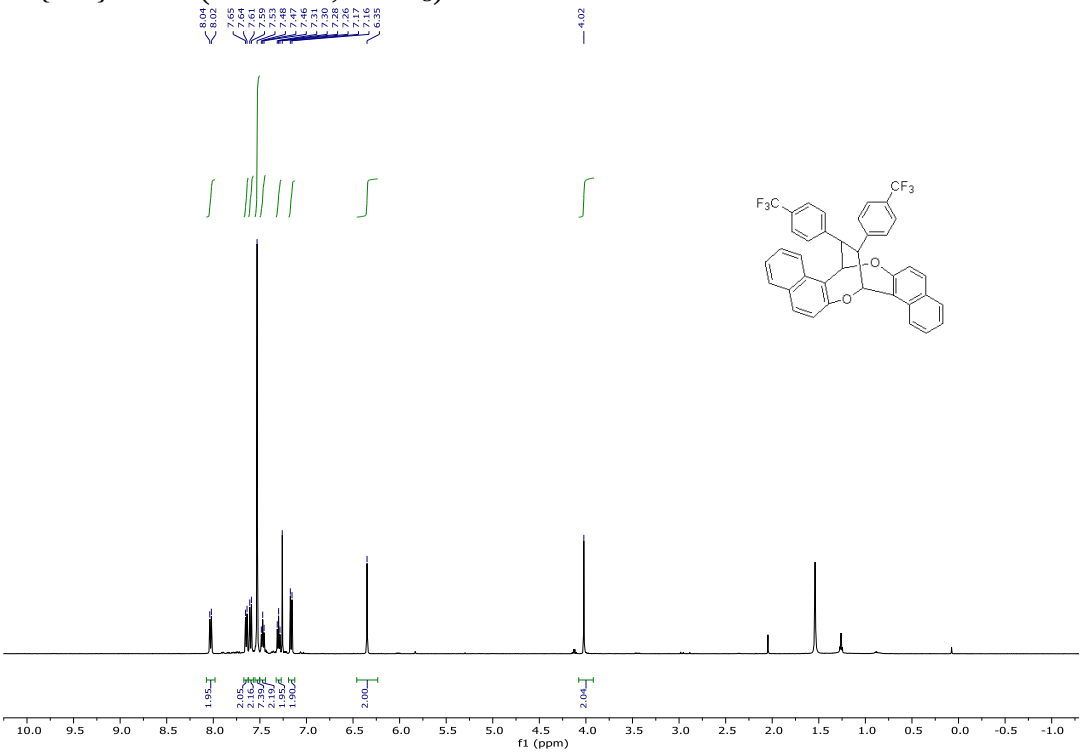
17,18-diphenyl-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5a)

$^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)



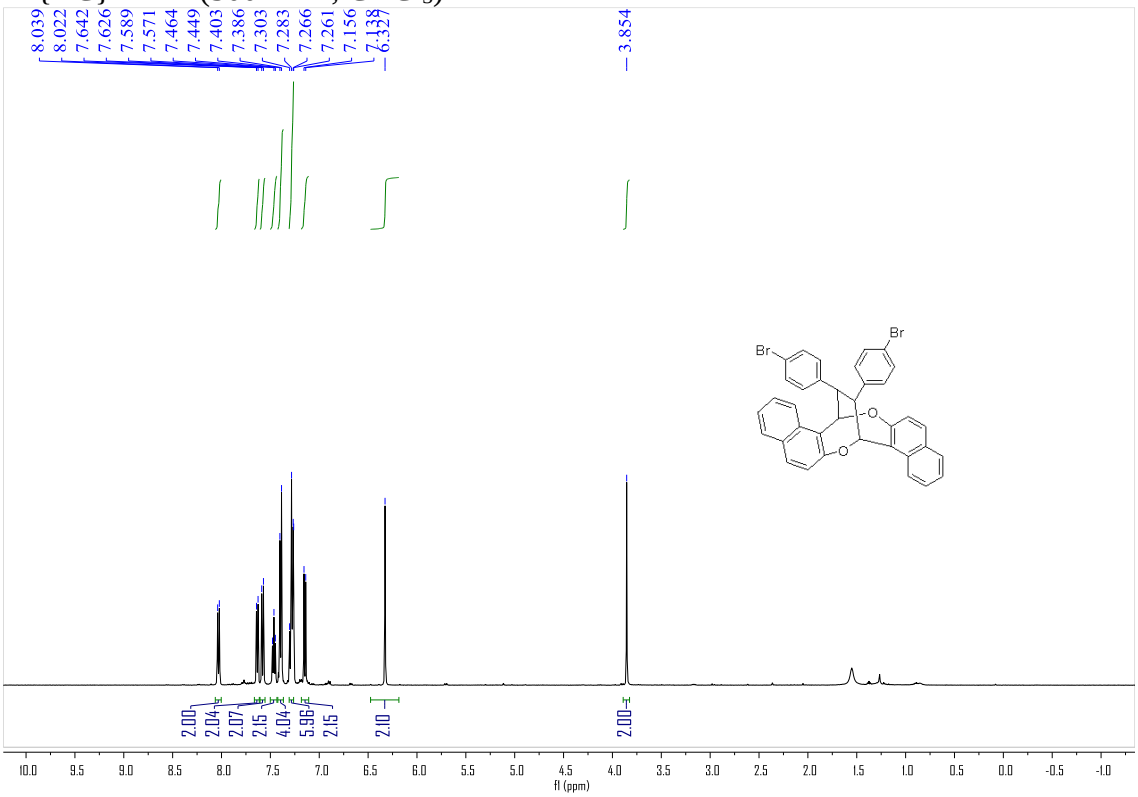
17,18-bis(4-(trifluoromethyl)phenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5b)

$^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)



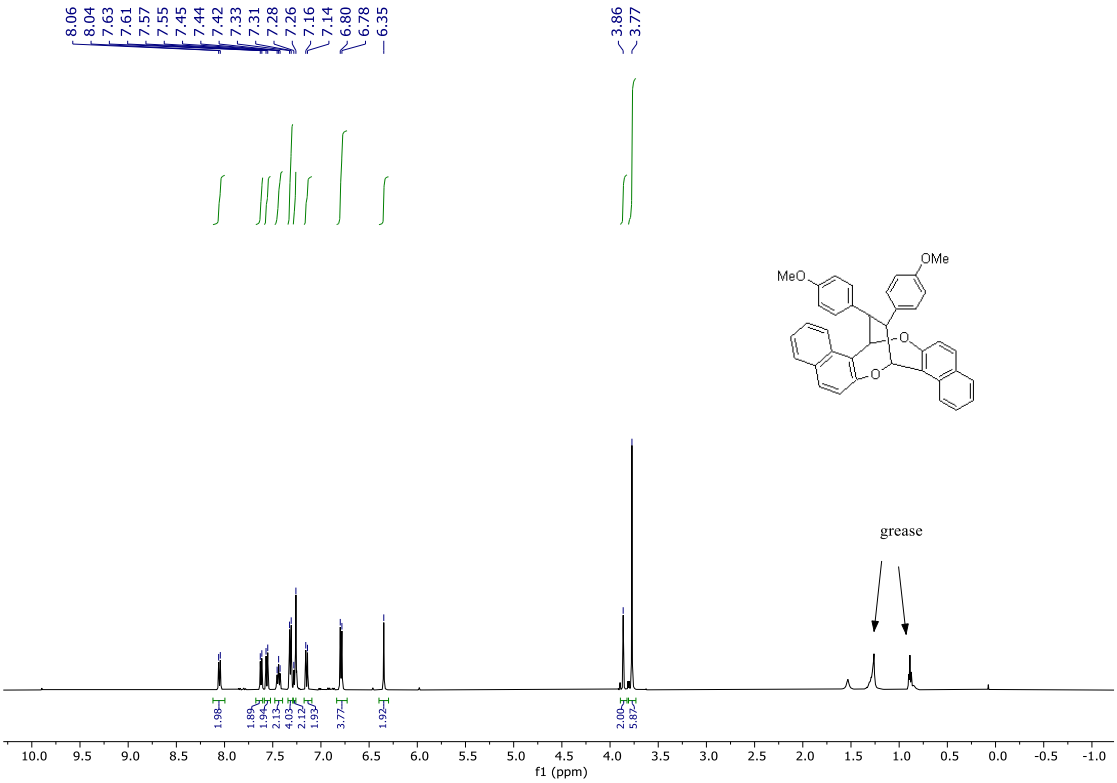
17,18-bis(4-bromophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5c)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

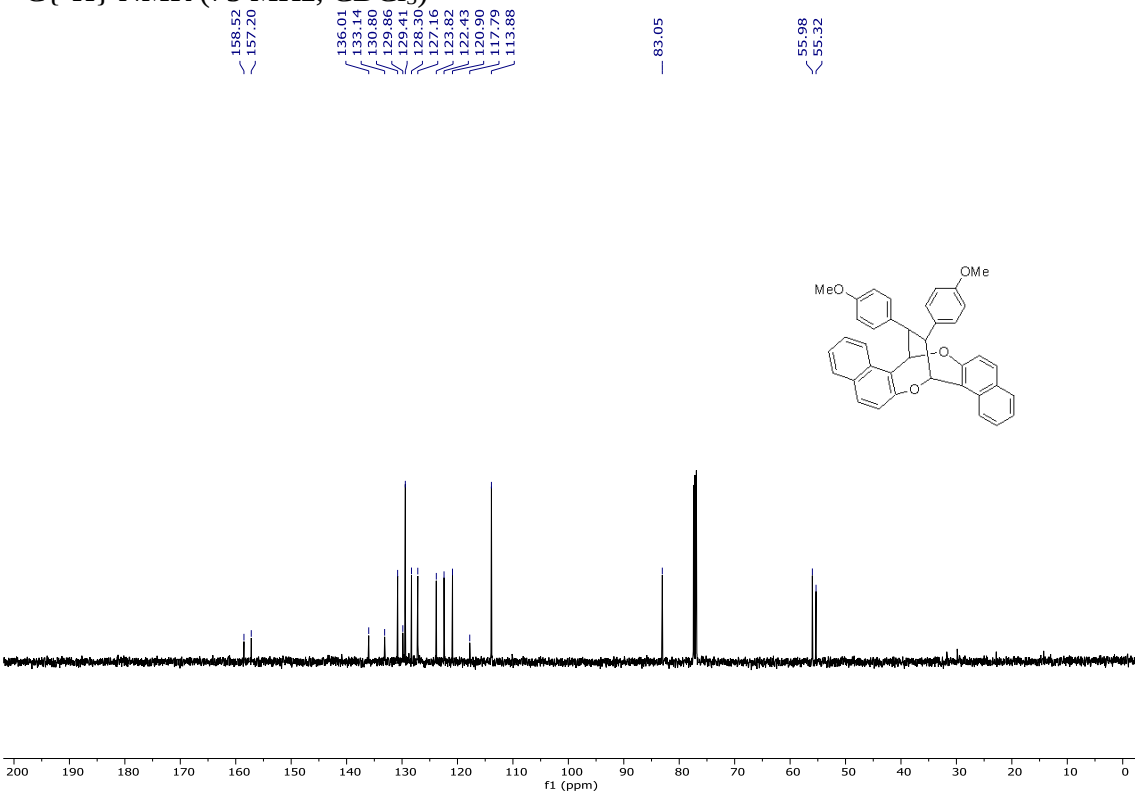


17,18-bis(4-methoxyphenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5d)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

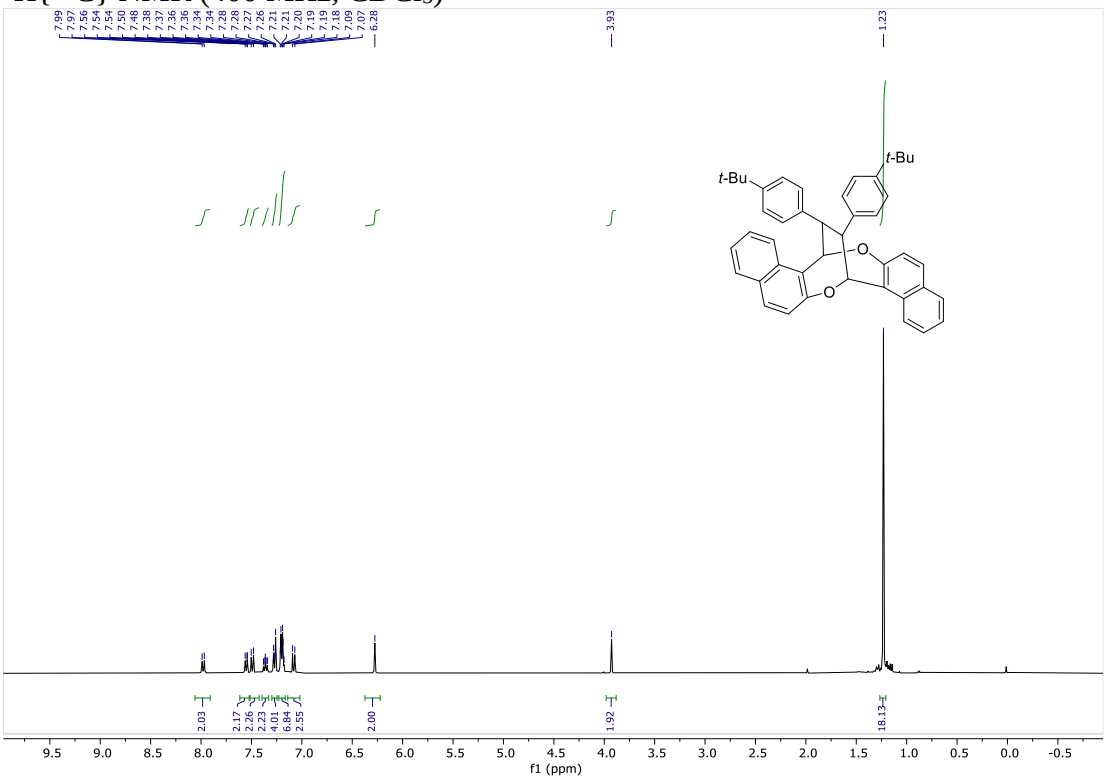


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



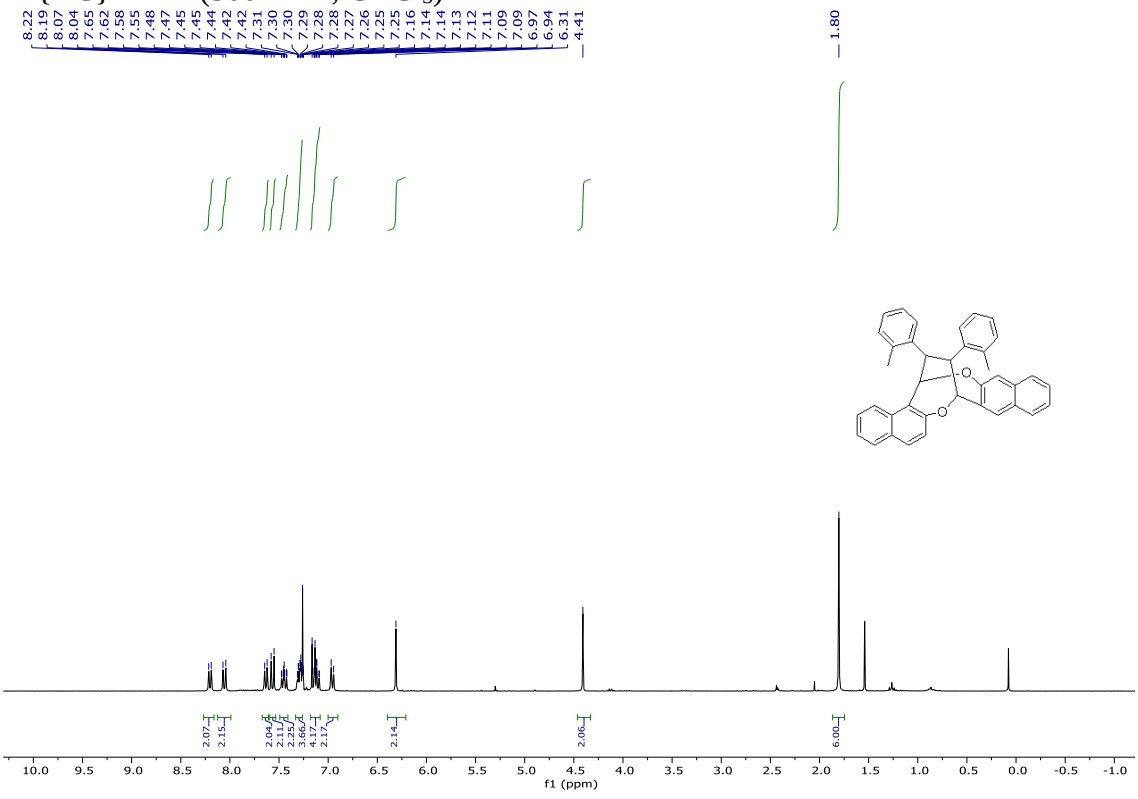
17,18-bis(4-(*t*-butyl)phenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5e)

$^1H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$)

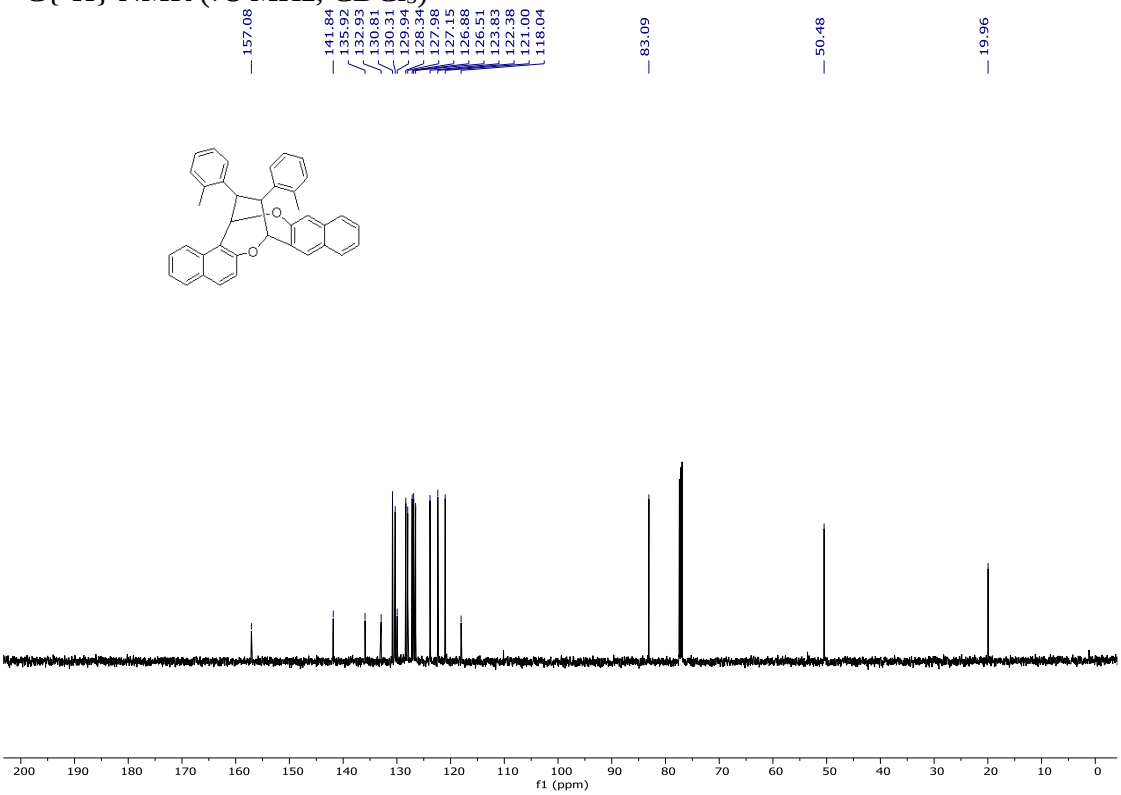


17,18-di-o-tolyl-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5f)

$^1H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

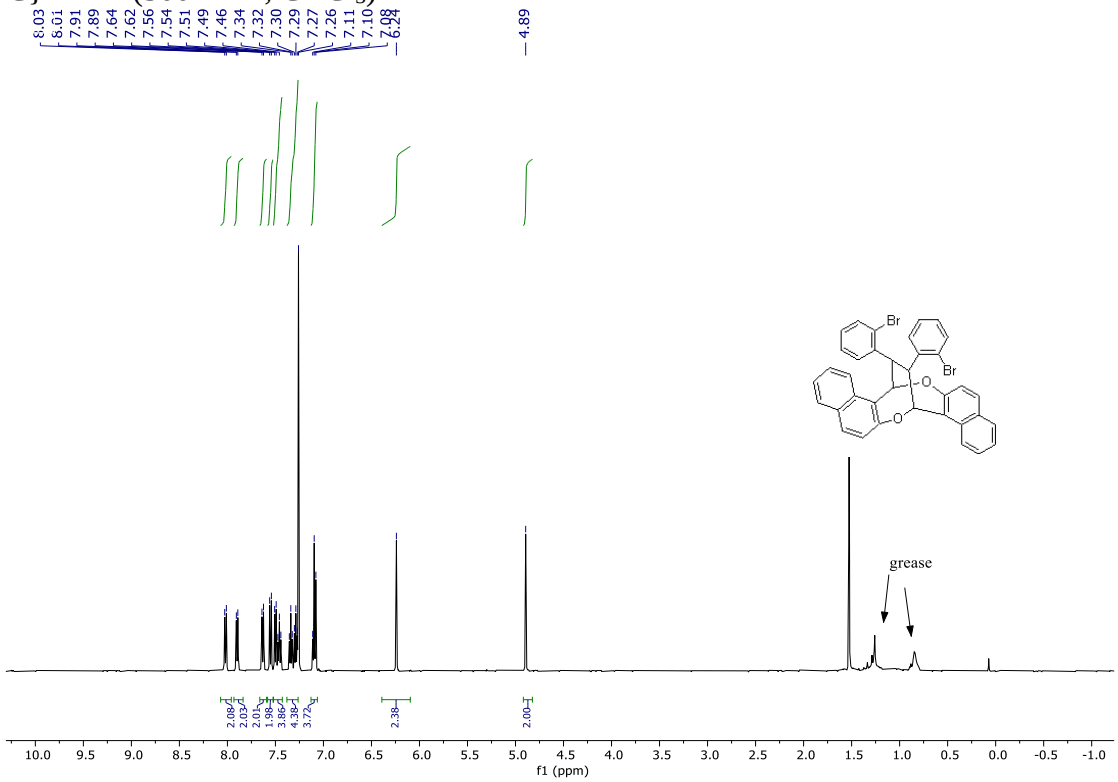


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



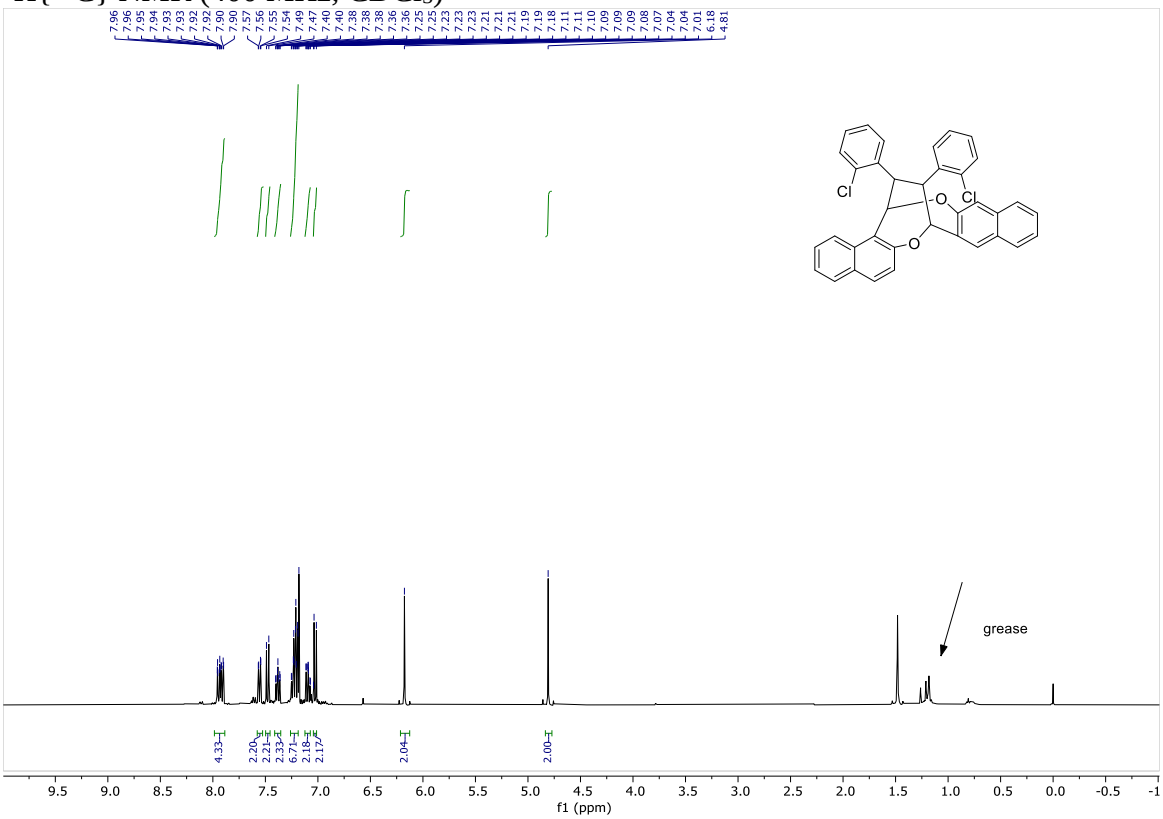
17,18-bis(2-bromophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5g)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)



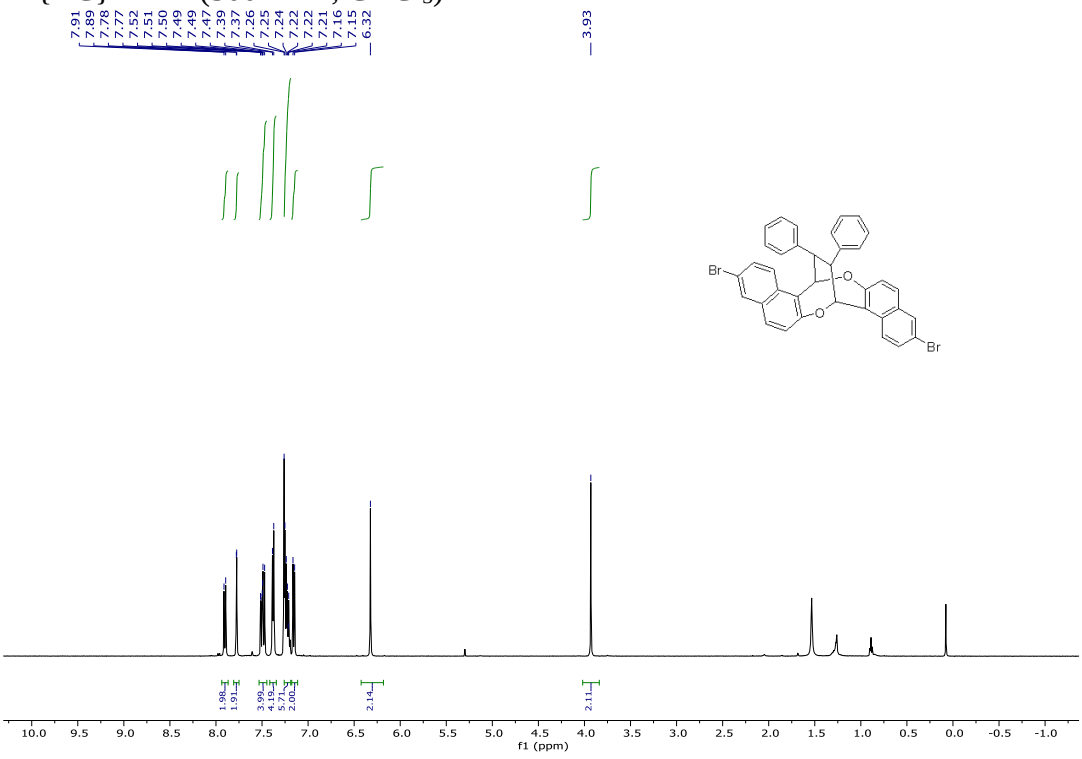
17,18-bis(2-chlorophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5h)

$^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$)



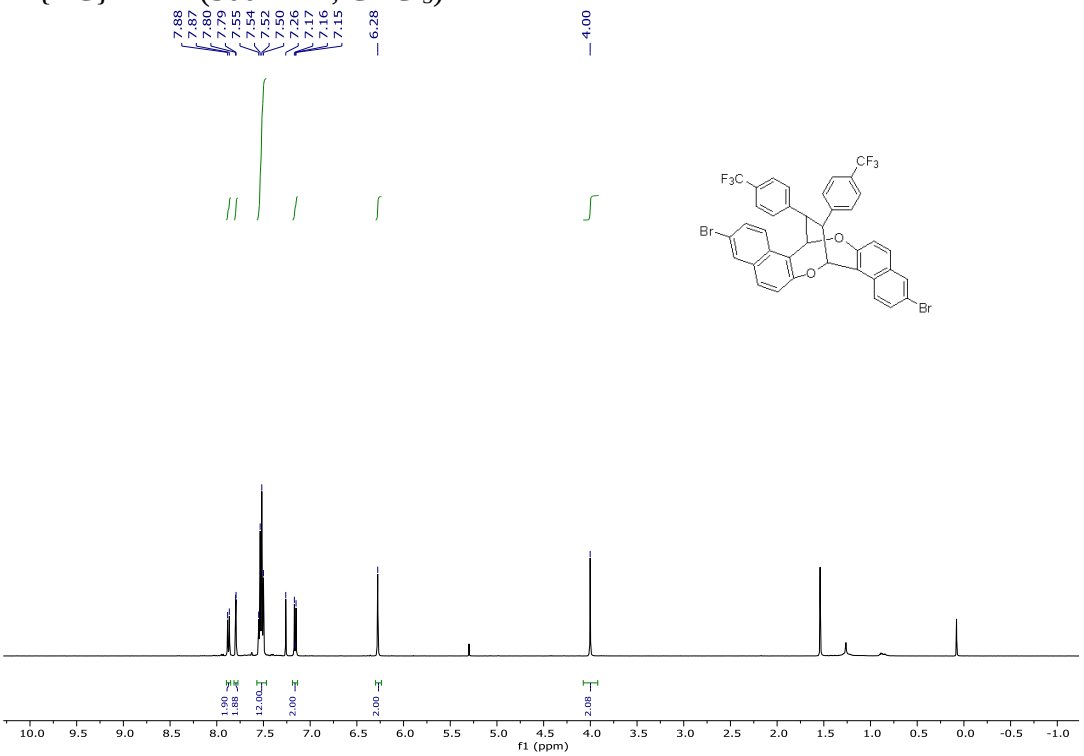
3,11-dibromo-17,18-diphenyl-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5i)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

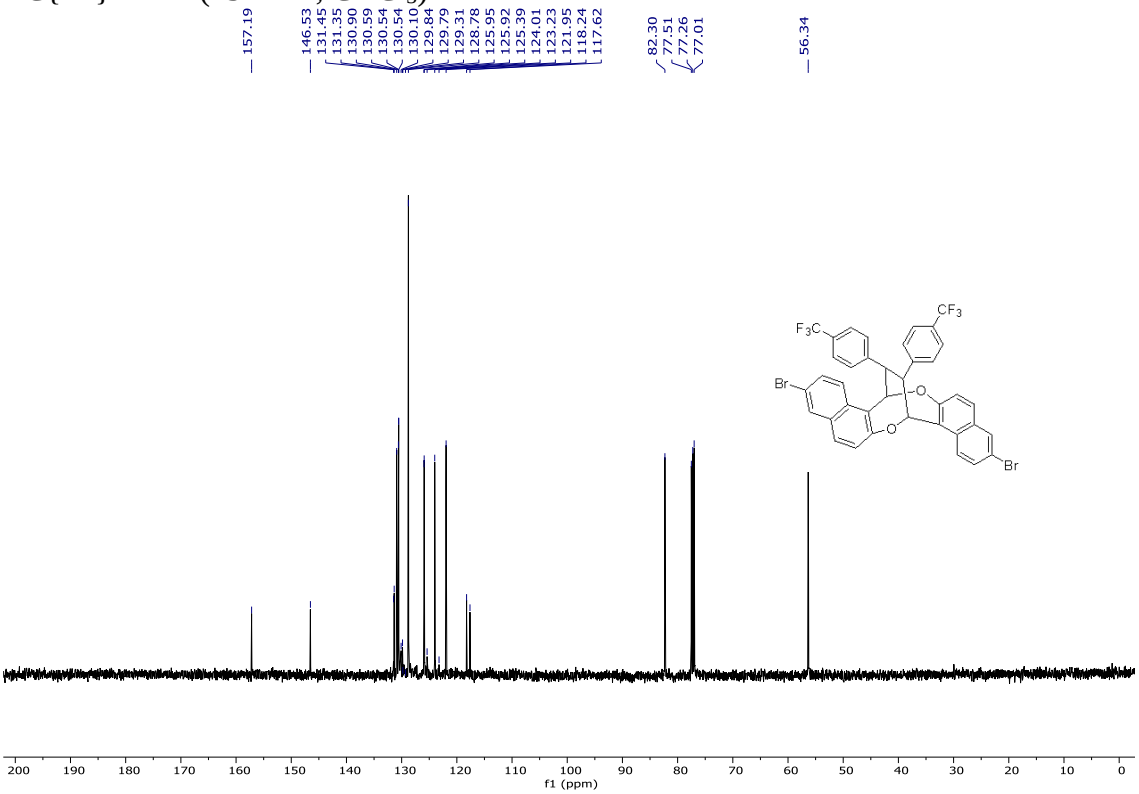


3,11-dibromo-17,18-bis(4-(trifluoromethyl)phenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5j)

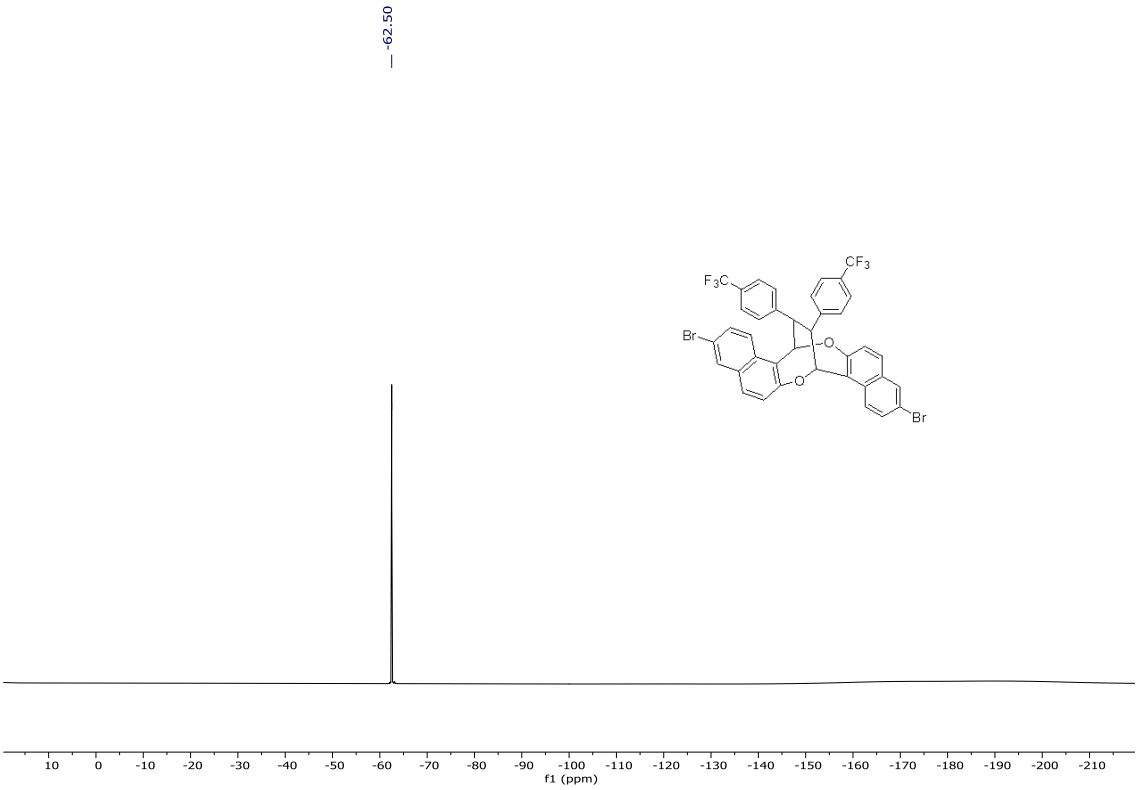
$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

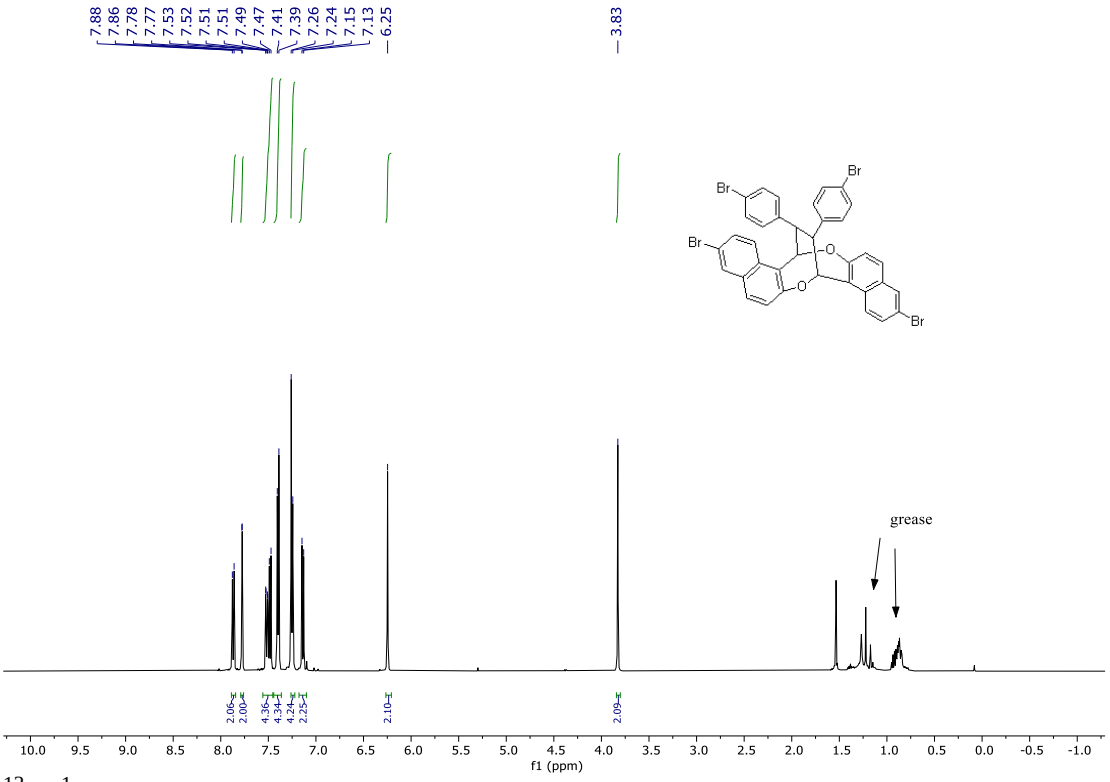


^{19}F NMR (282 MHz, $CDCl_3$)

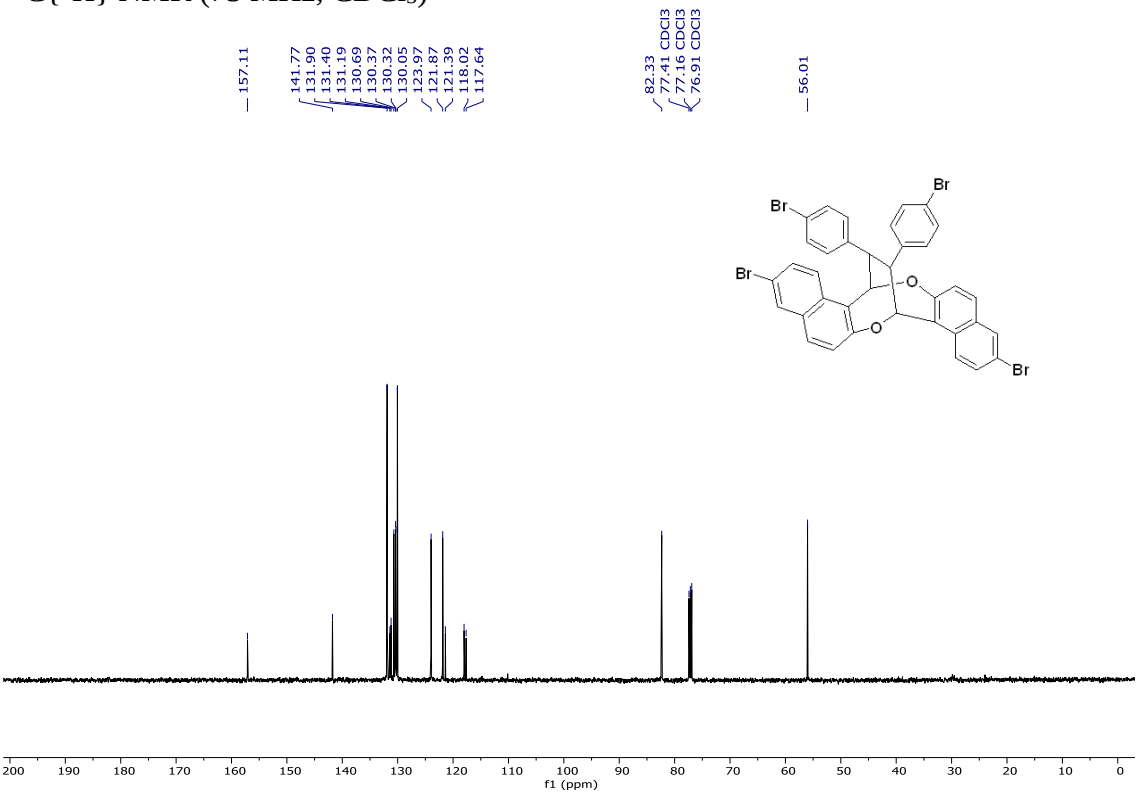


3,11-dibromo-17,18-bis(4-bromophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5k)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

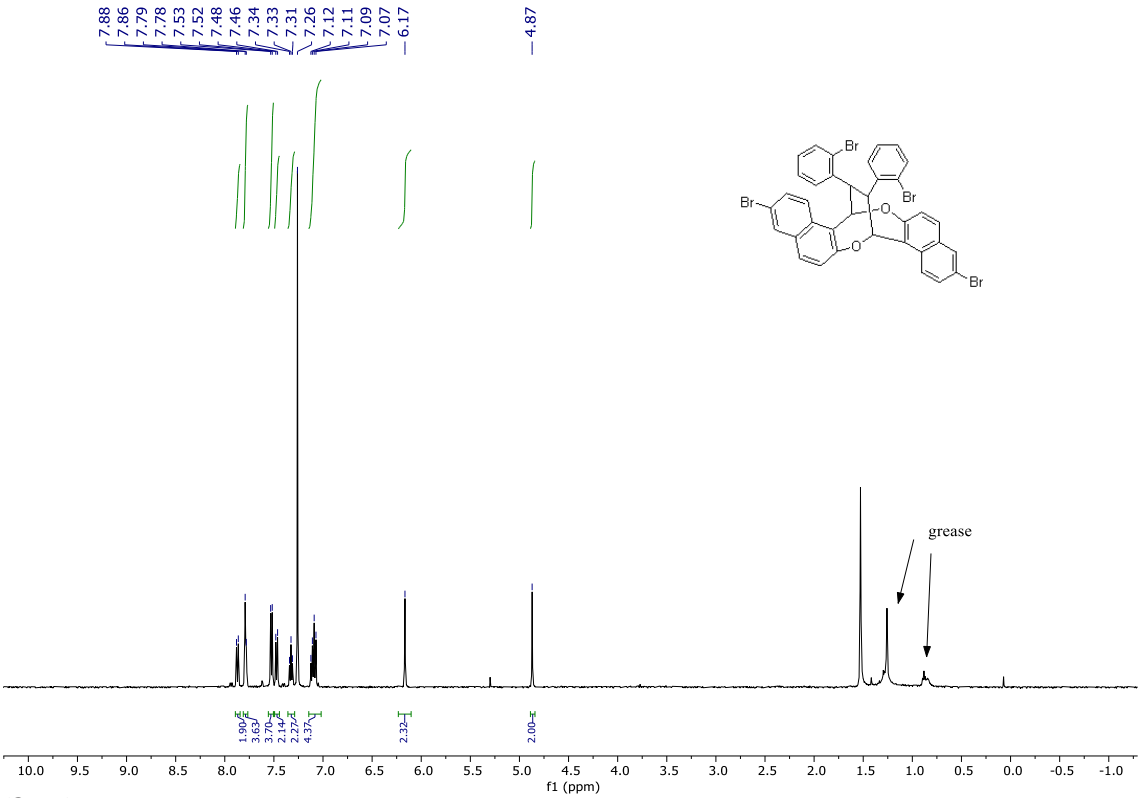


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

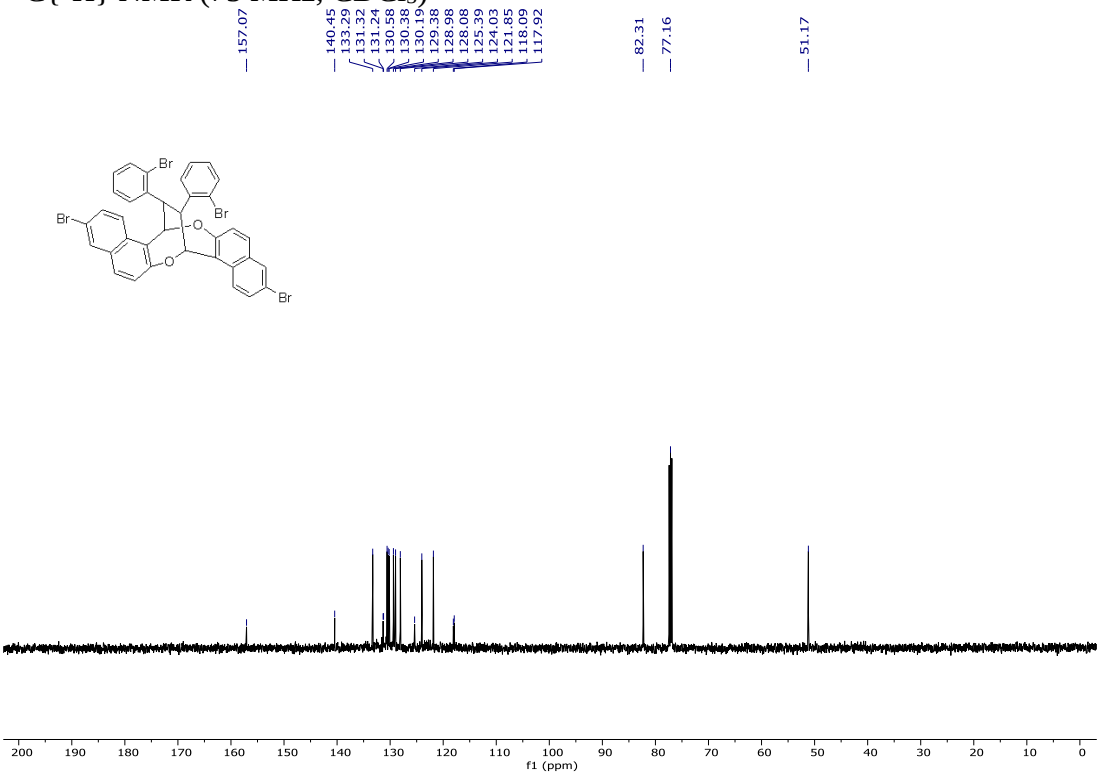


3,11-dibromo-17,18-bis(2-bromophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5l)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

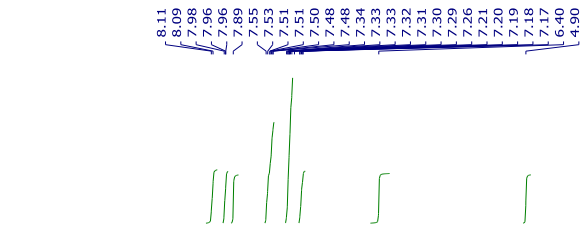


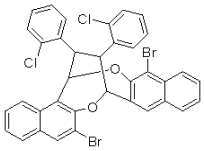
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

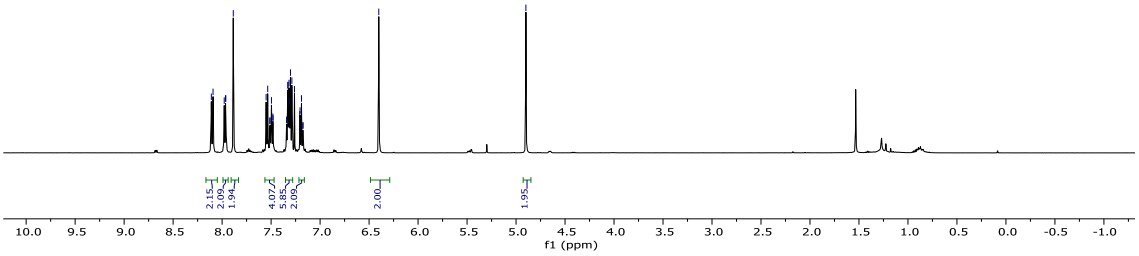


6,14-dibromo-17,18-bis(2-chlorophenyl)-8H,16H-8,16-ethanodinaphtho[2,1-b:2',3'-f][1,5]dioxocine (5m)

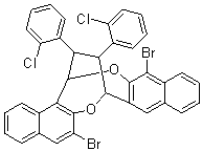
$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

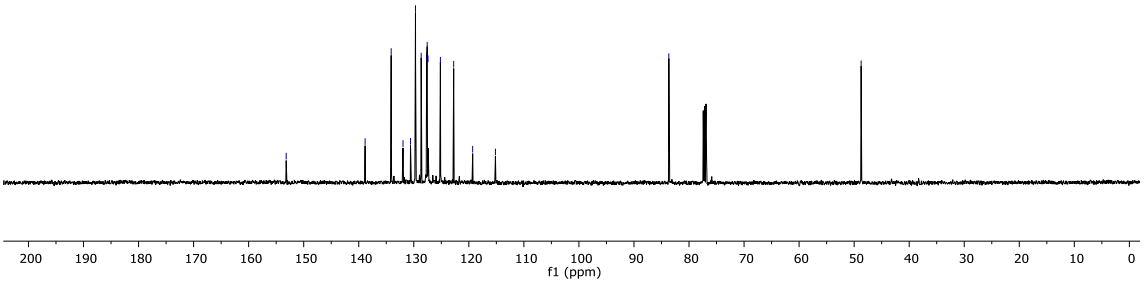






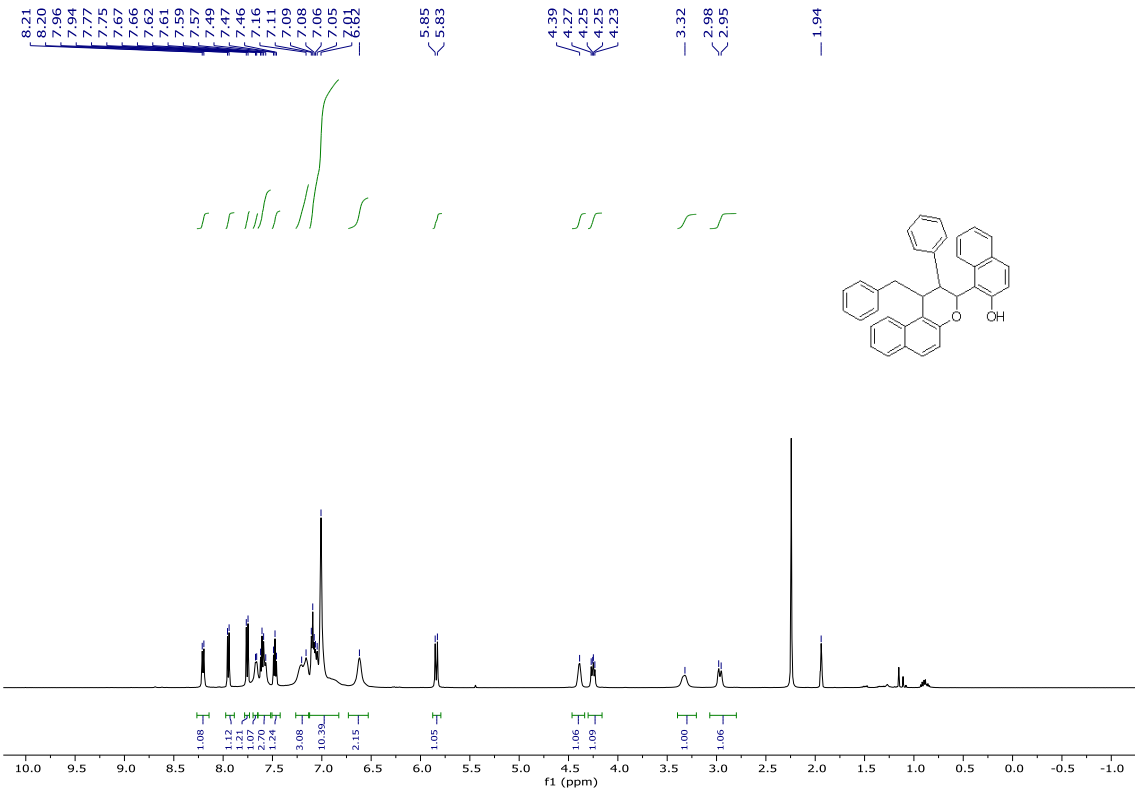
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



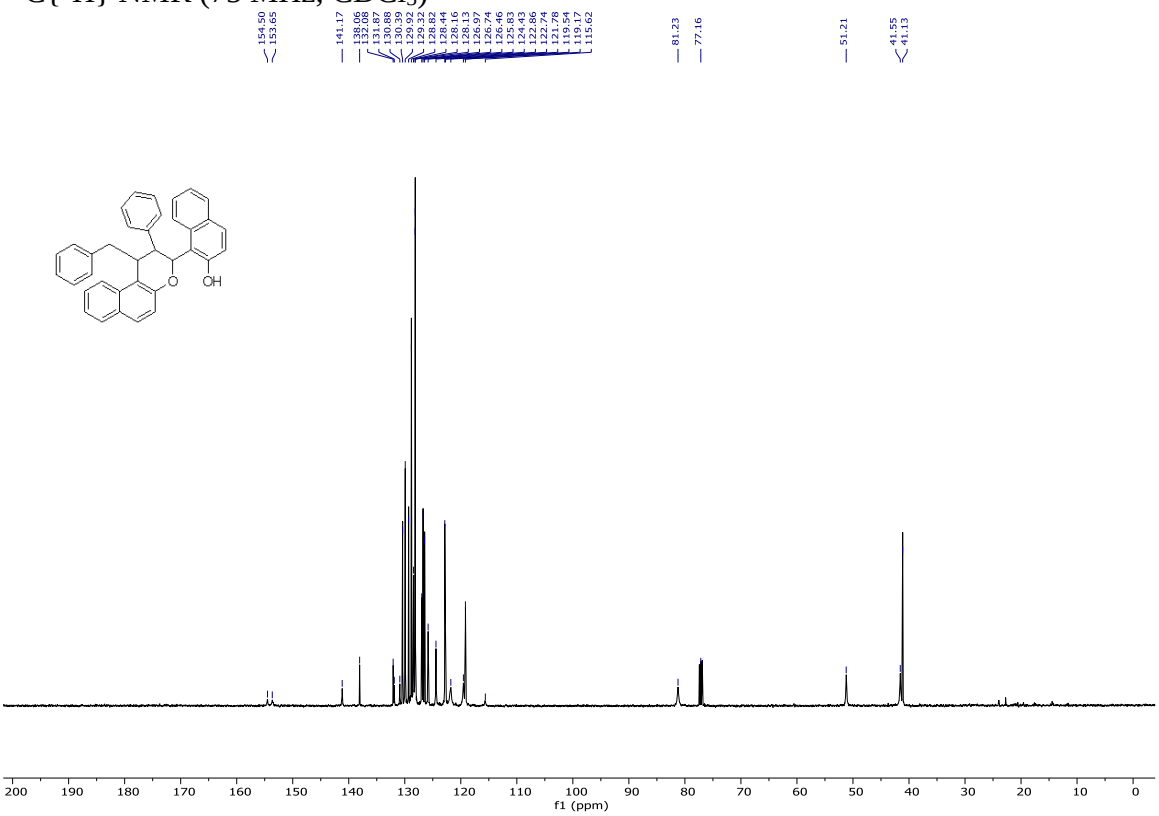


1-(1-benzyl-2-phenyl-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6a)

$^{1}H\{^{13}C\}$ NMR (500 MHz, CD_3CN)

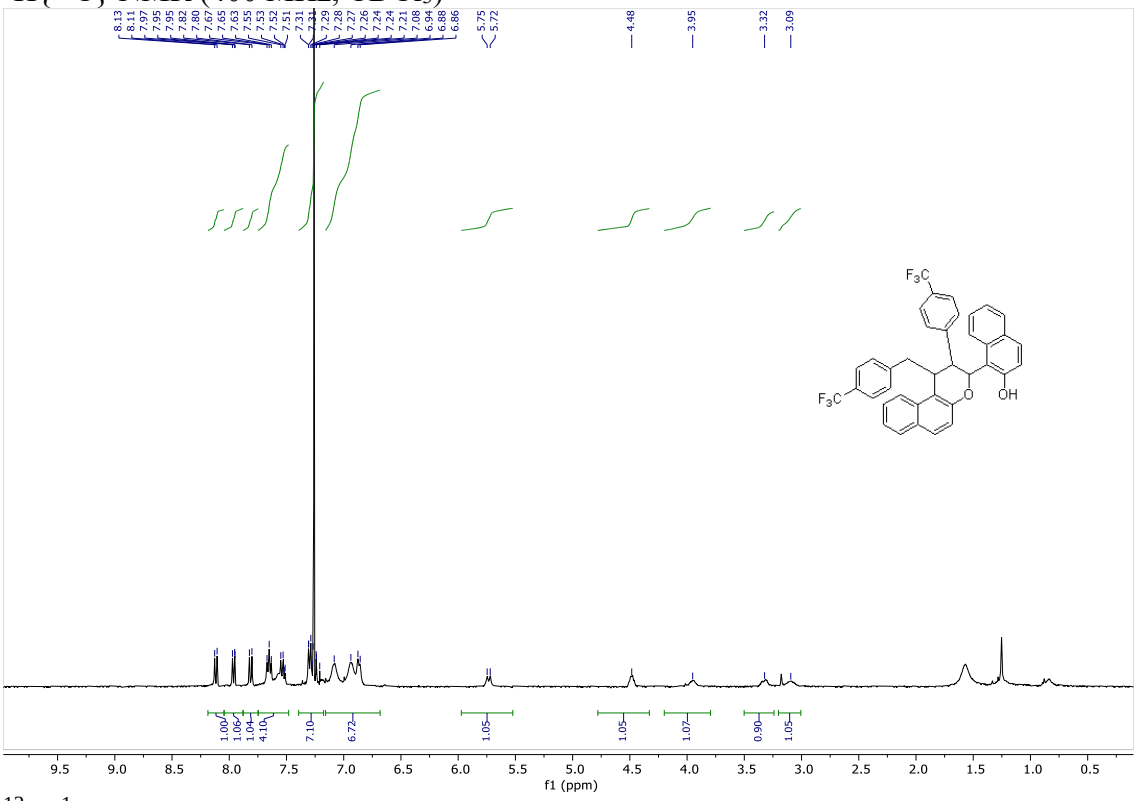


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

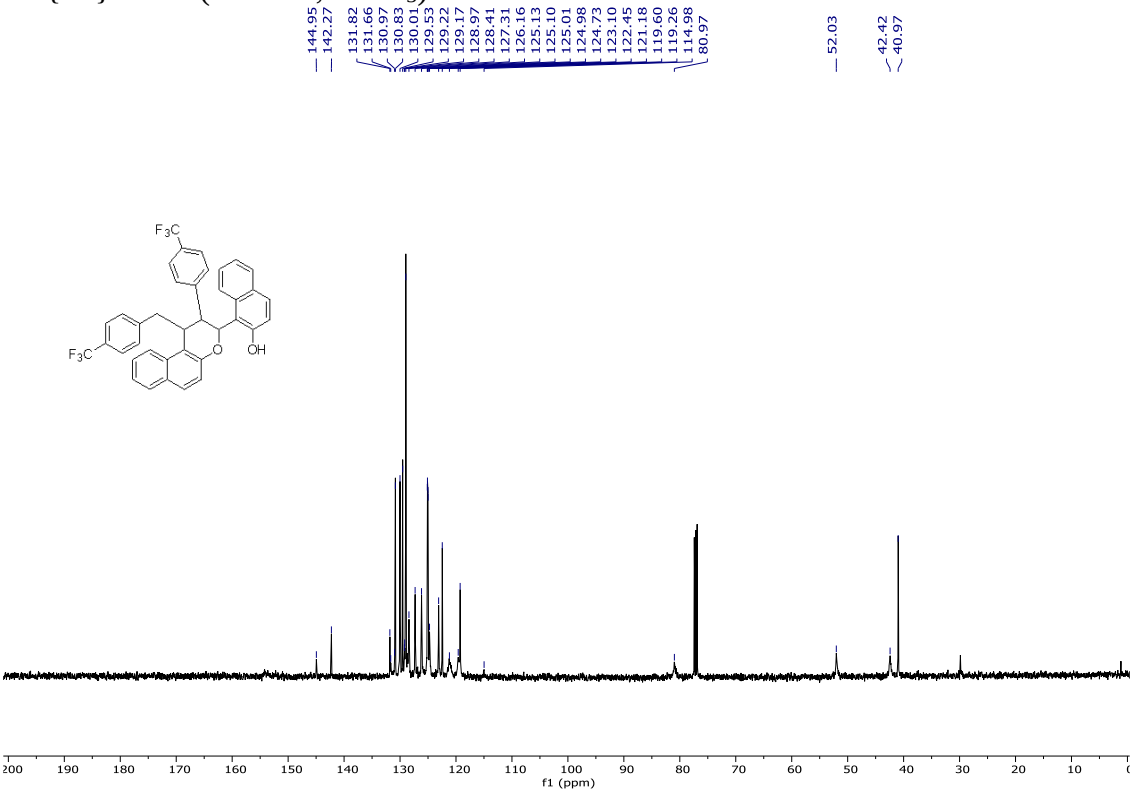


1-(1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6b)

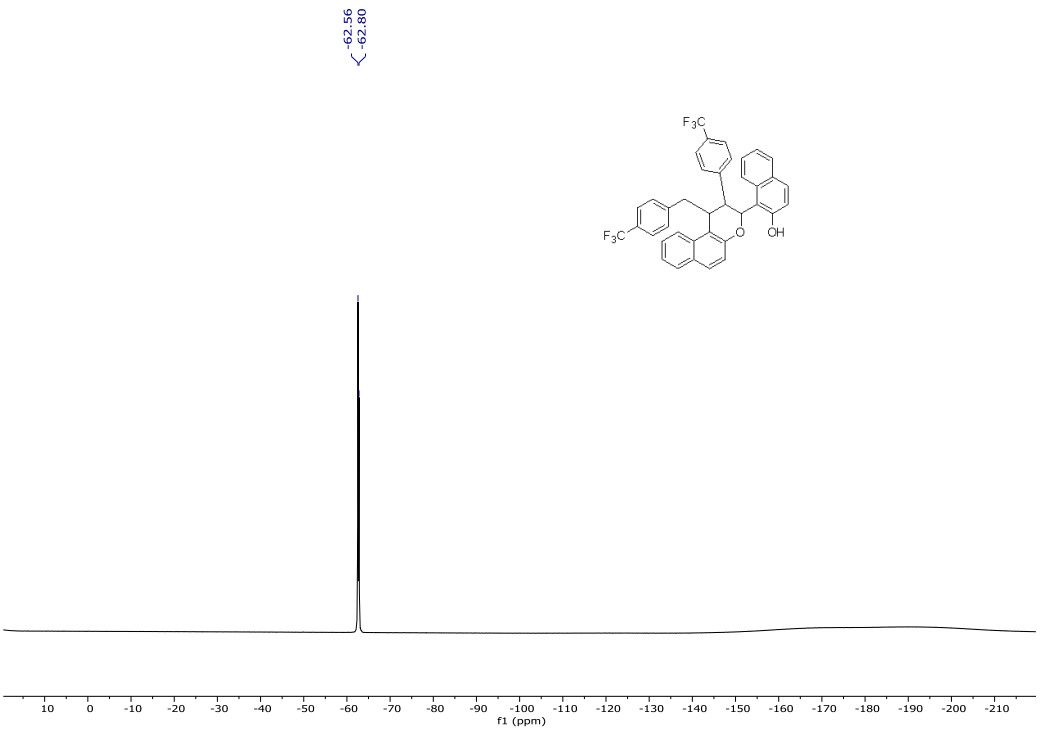
$^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

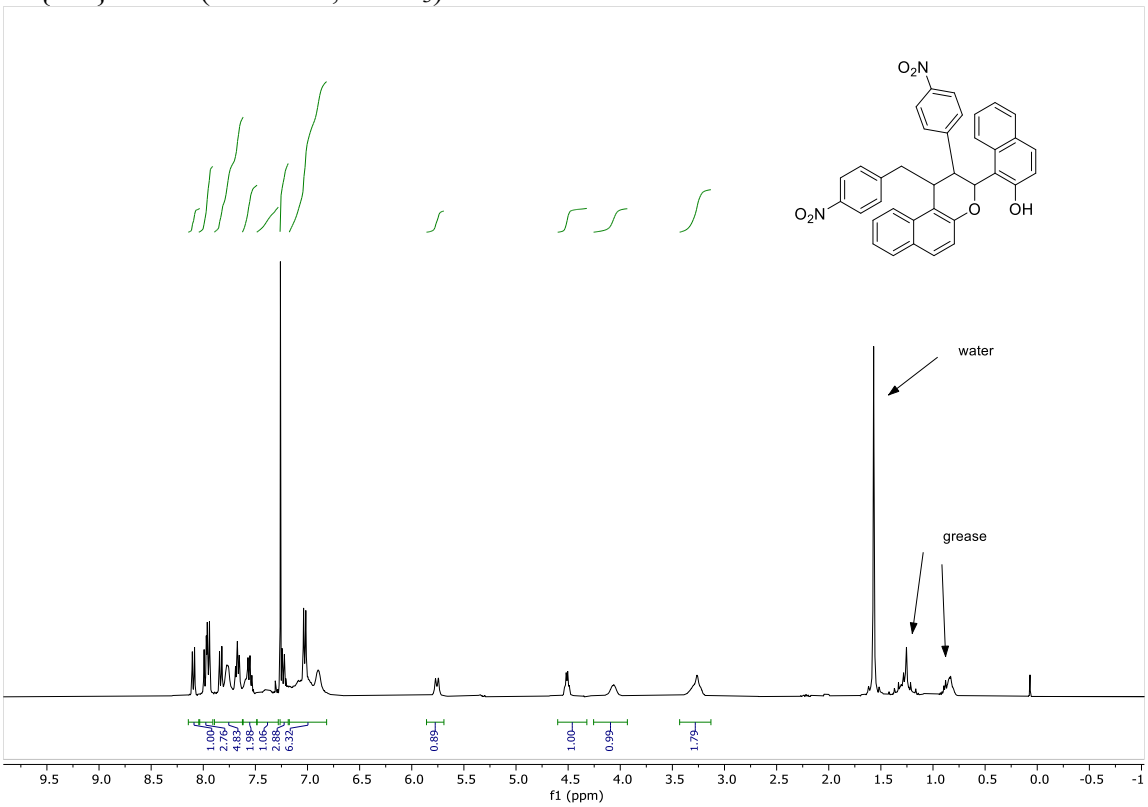


^{19}F NMR (282 MHz, $CDCl_3$)

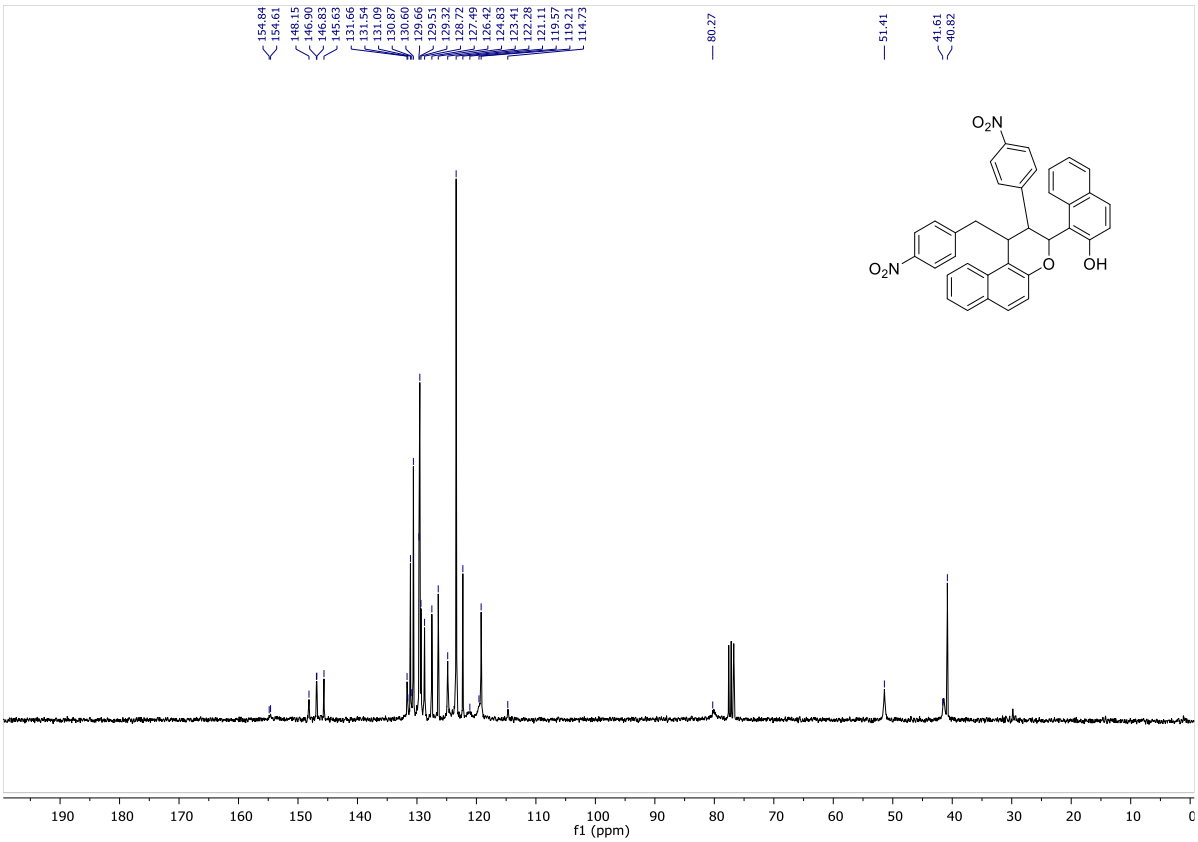


1-(1-(4-nitrobenzyl)-2-(4-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6c)

$^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$)

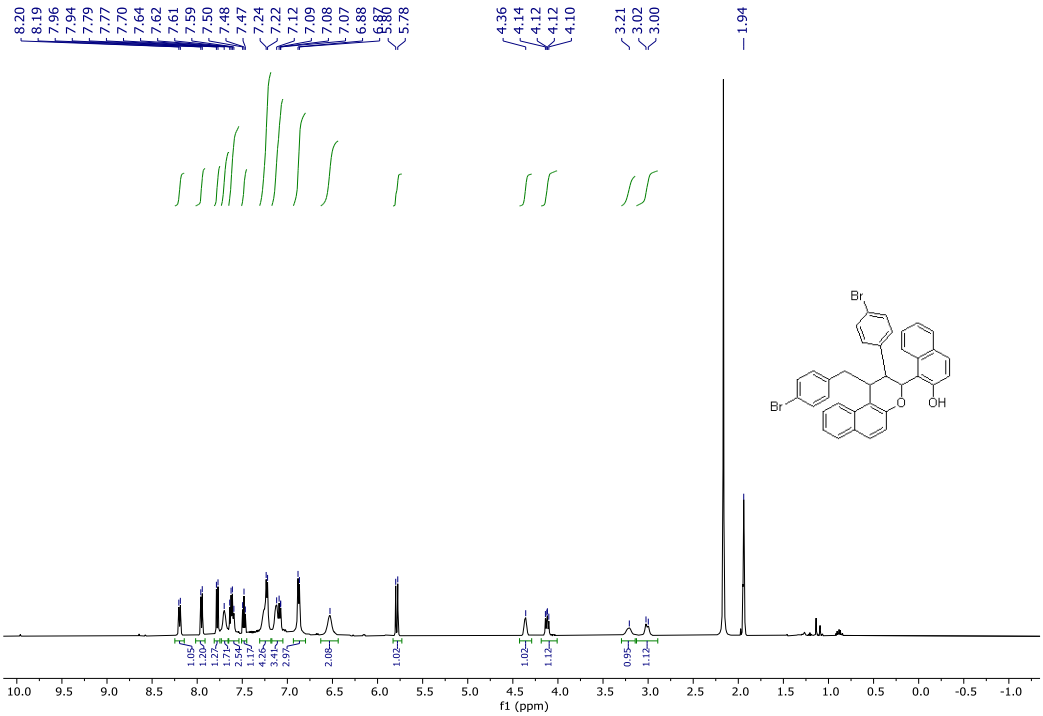


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

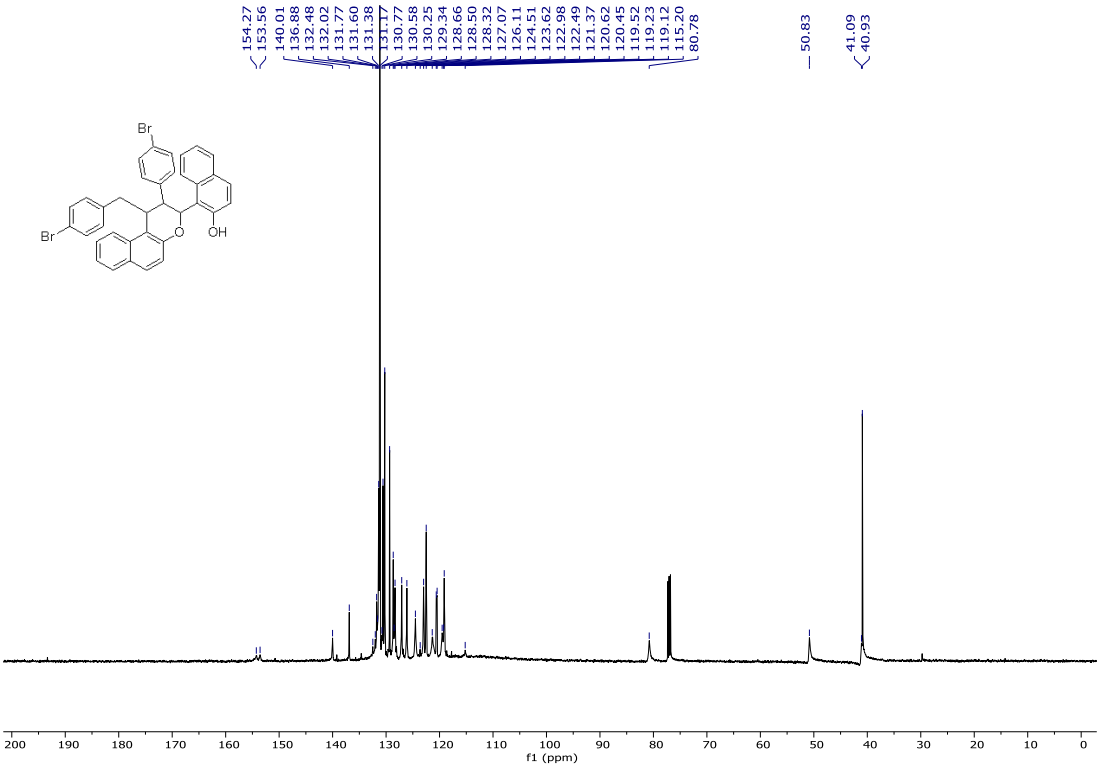


1-(1-(4-bromobenzyl)-2-(4-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6d)

$^{1}H\{^{13}C\}$ NMR (500 MHz, CD_3CN)

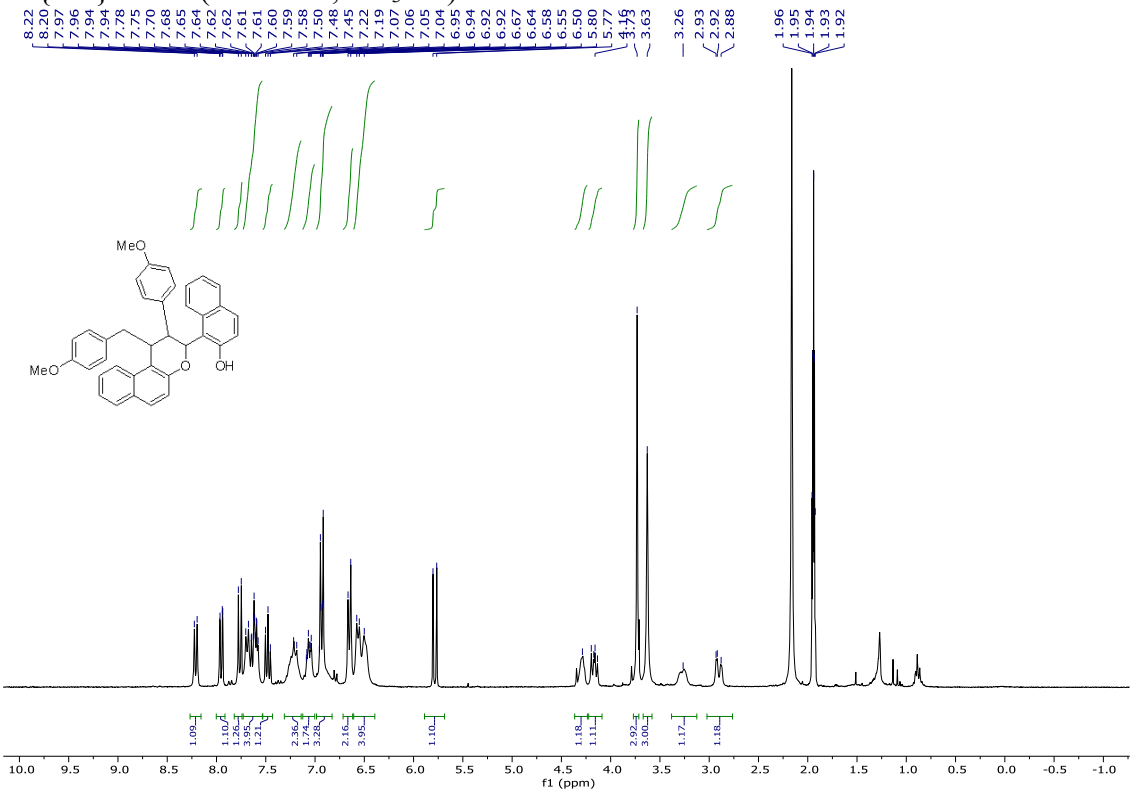


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

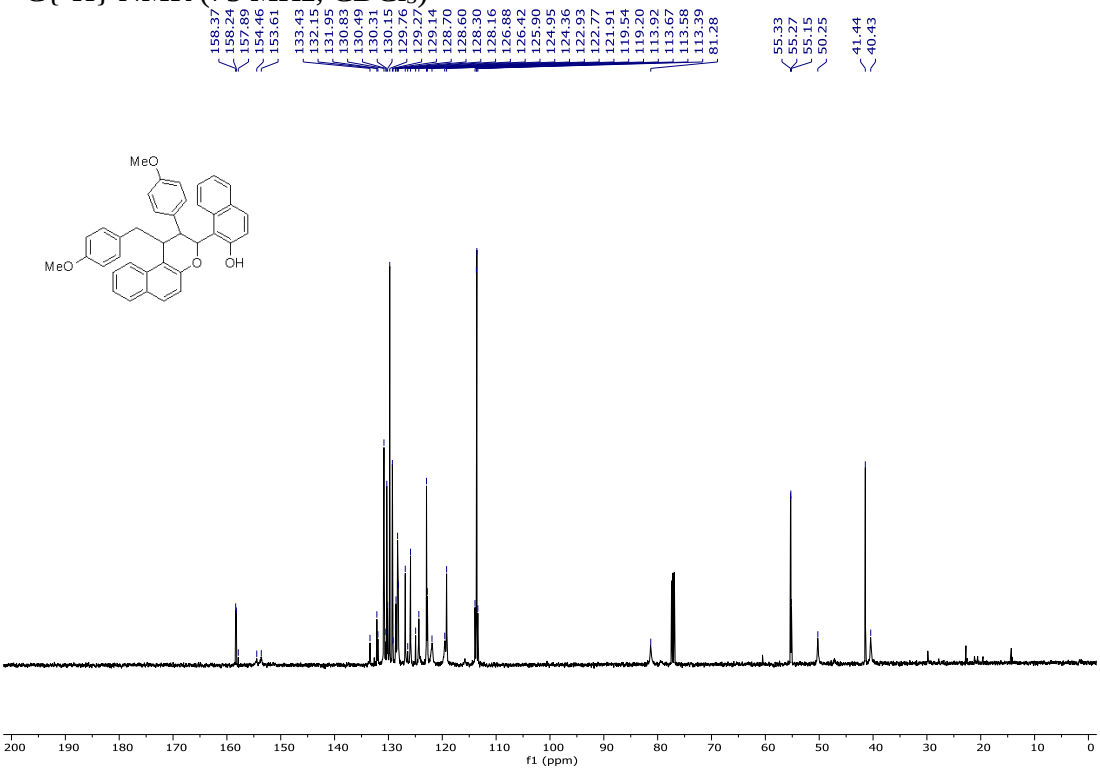


1-(1-(4-methoxybenzyl)-2-(4-methoxyphenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6e)

$^{1}H\{^{13}C\}$ NMR (500 MHz, CD_3CN)

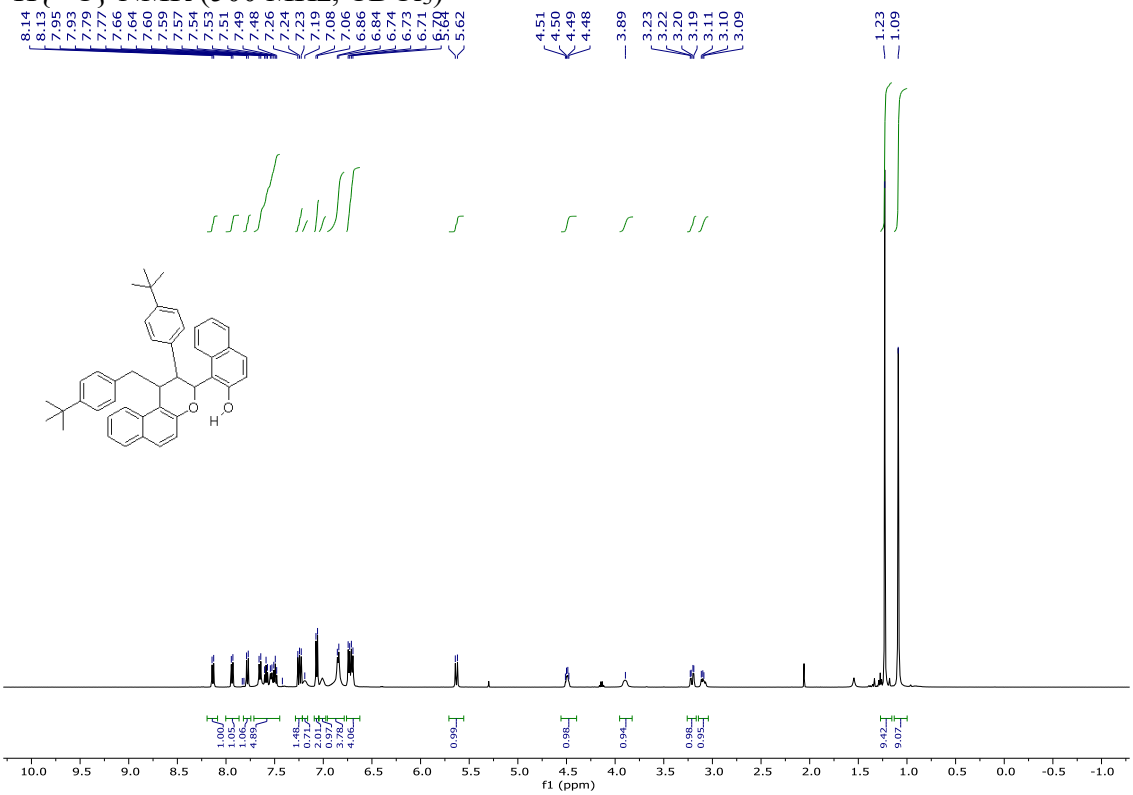


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

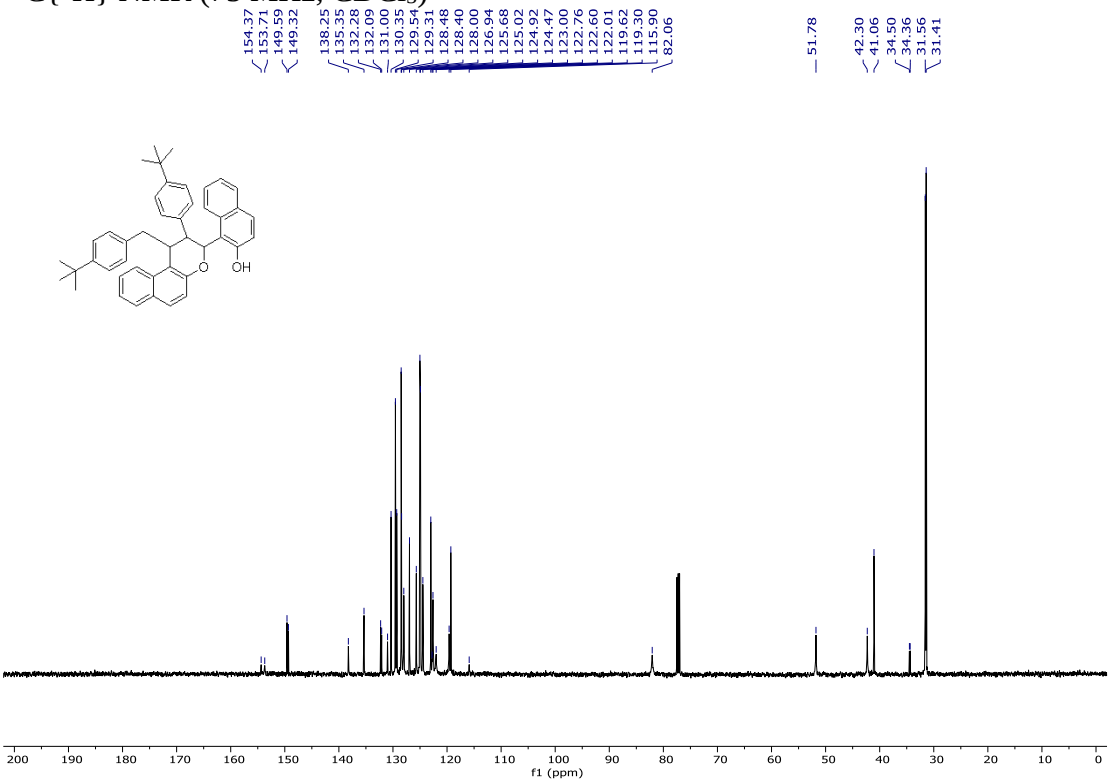


1-(1-(4-(tert-butyl)benzyl)-2-(4-(tert-butyl)phenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6f)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

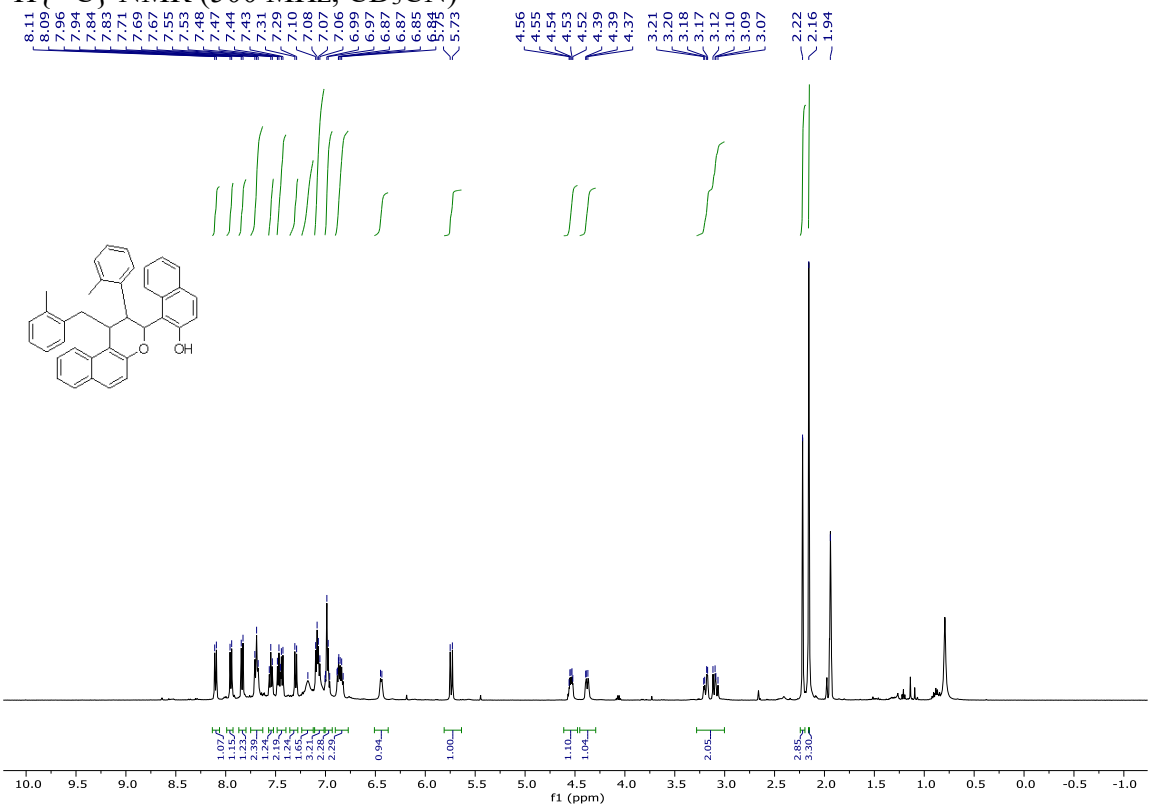


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

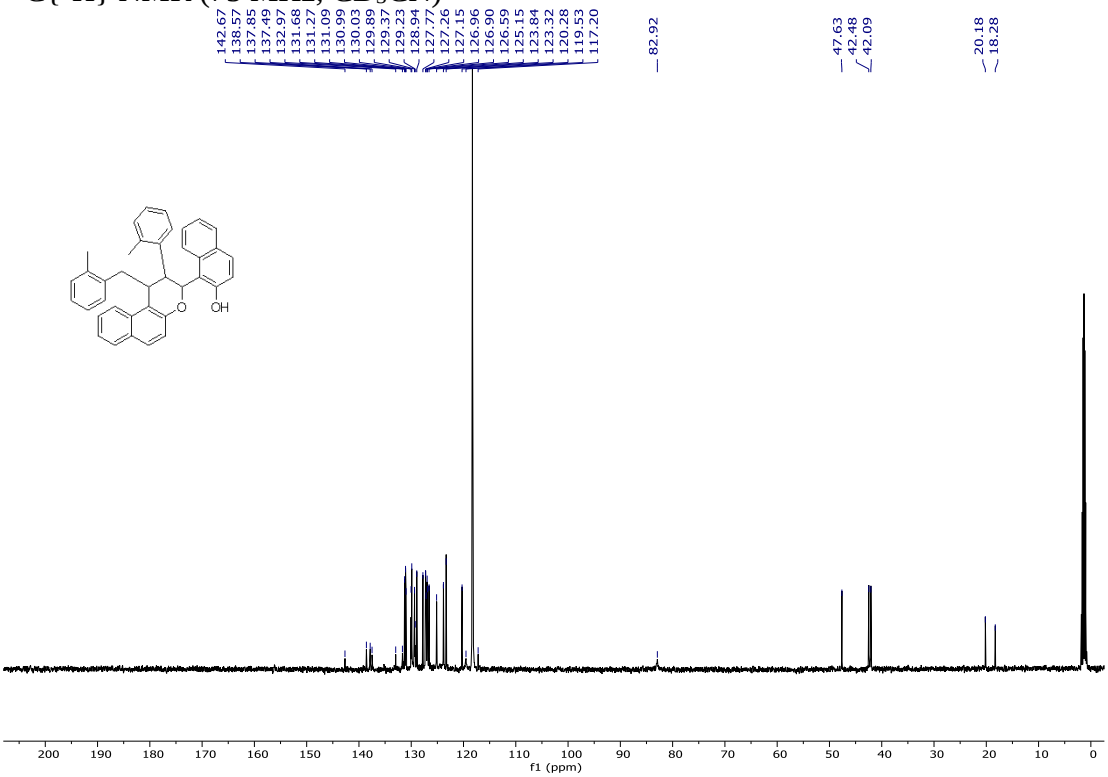


1-(1-(2-methylbenzyl)-2-(o-tolyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6g)

$^{1}H\{^{13}C\}$ NMR (500 MHz, CD_3CN)

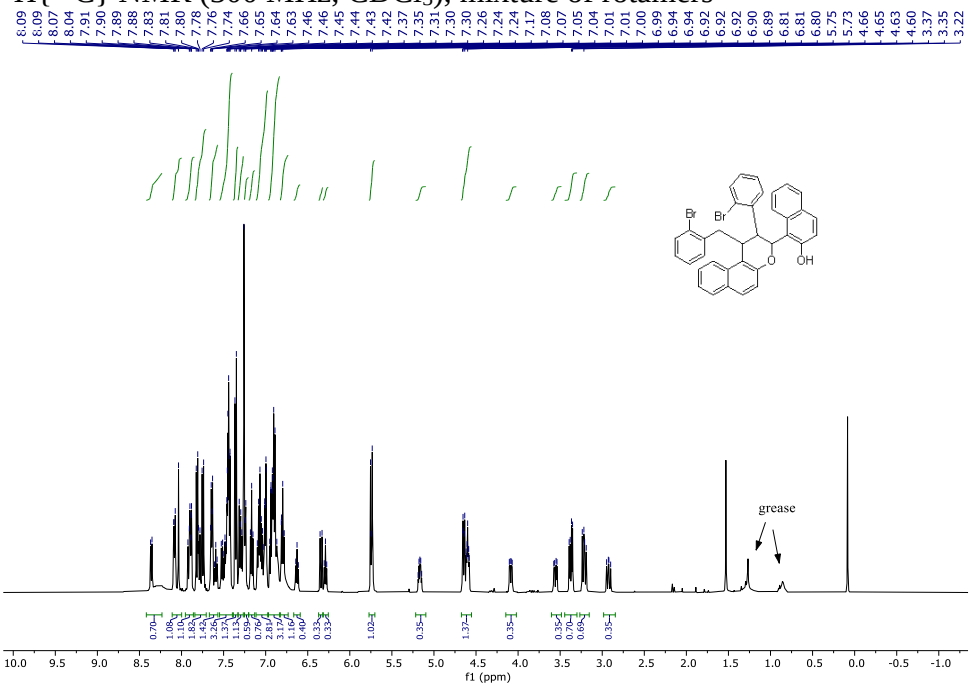


$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN)

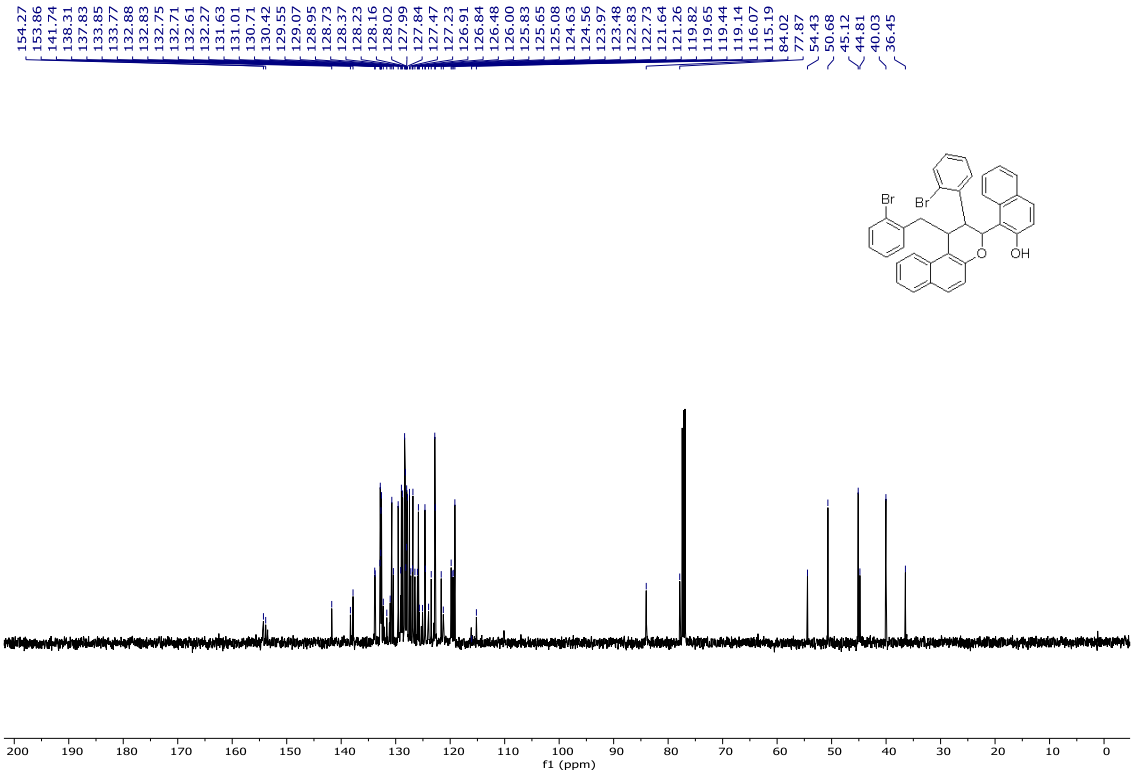


1-(1-(2-bromobenzyl)-2-(2-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6h)

$^{1}H\{^{13}C\}$ NMR (300 MHz, $CDCl_3$), mixture of rotamers

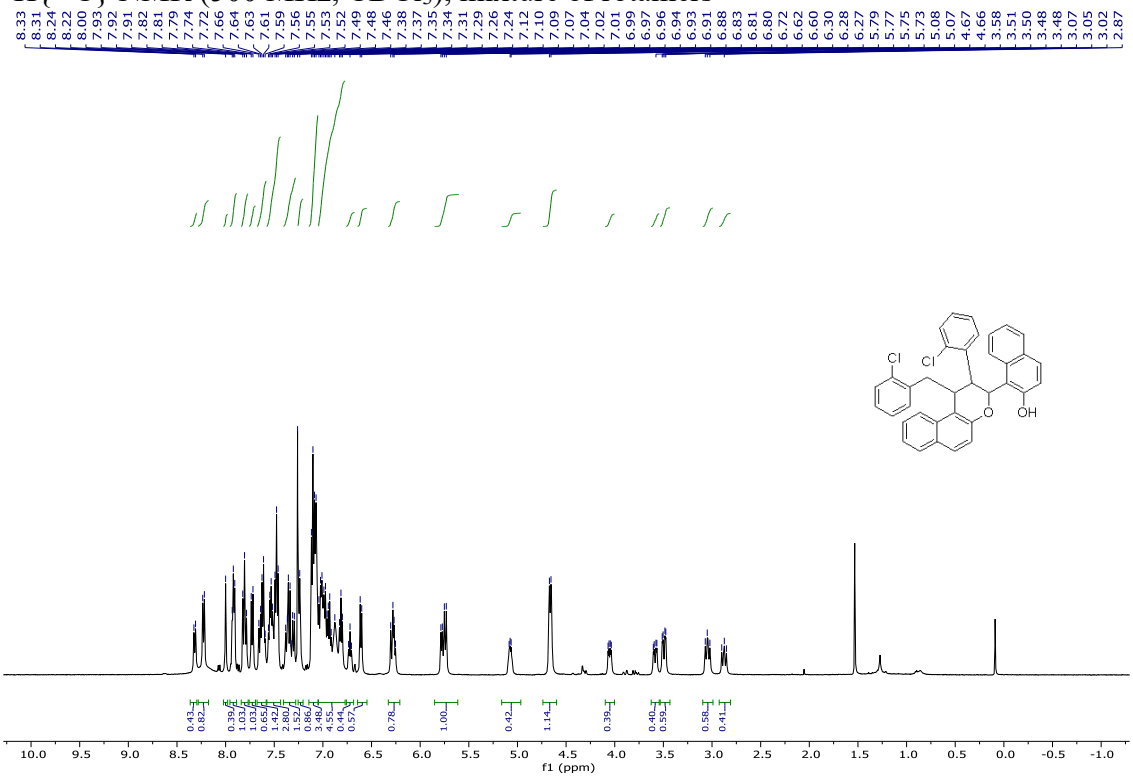


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), mixture of rotamers

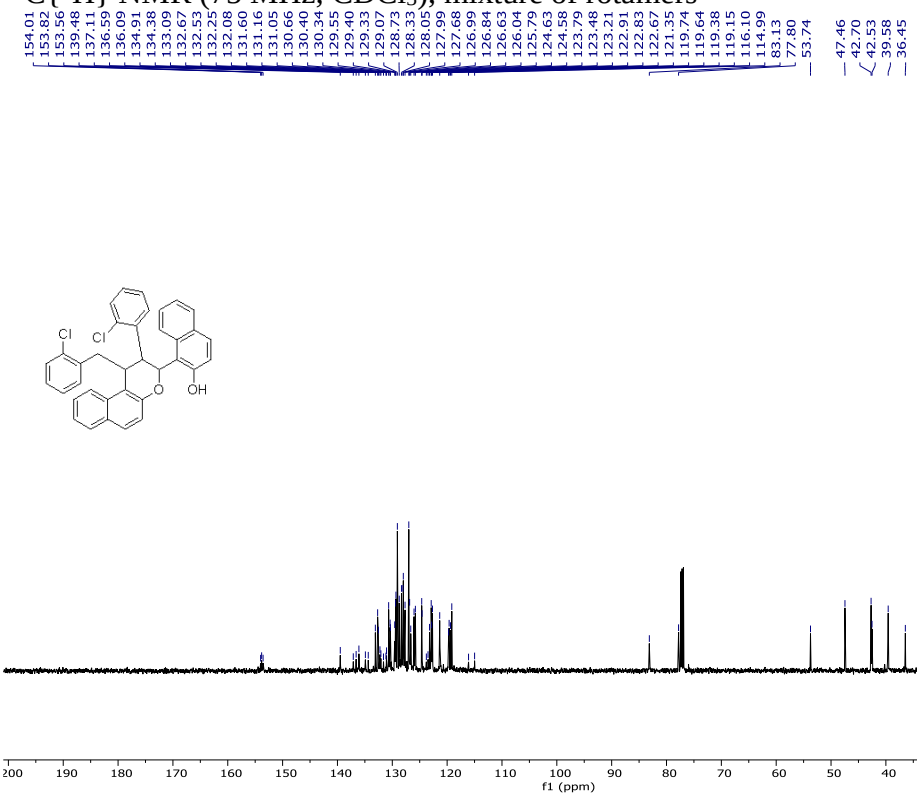


1-(1-(2-chlorobenzyl)-2-(2-chlorophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6i)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$), mixture of rotamers

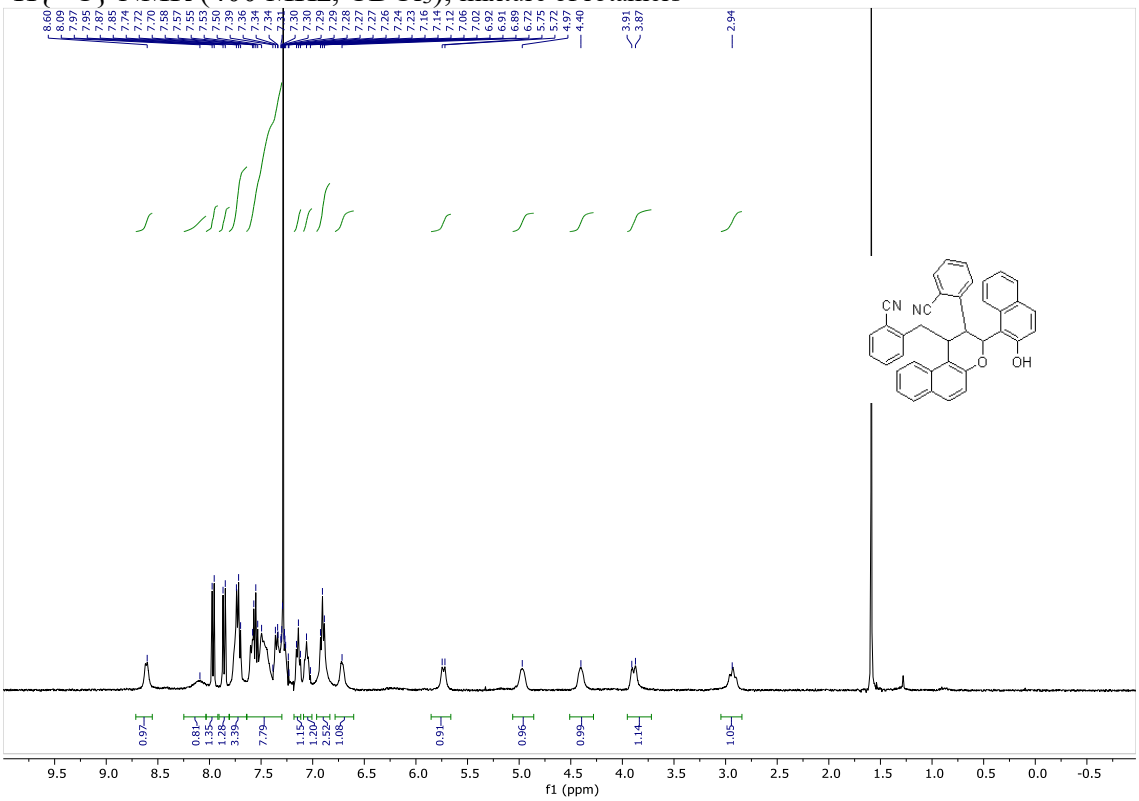


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), mixture of rotamers

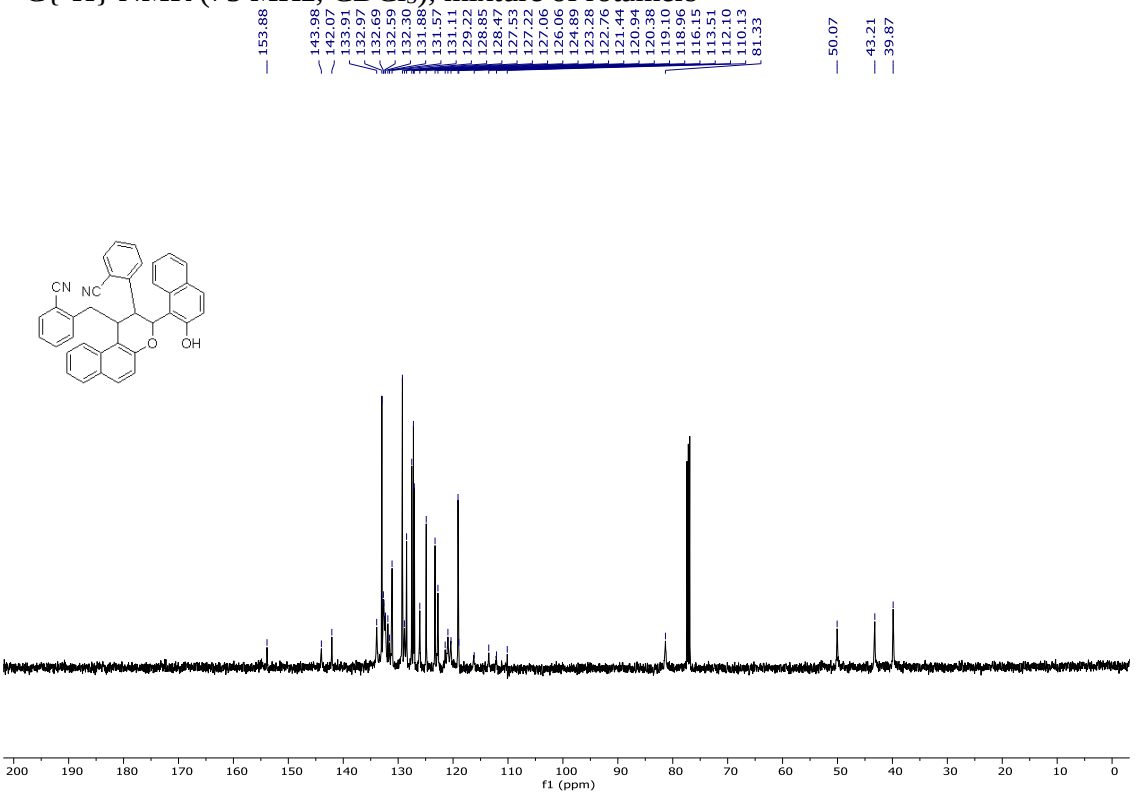


2-(1-(2-cyanobenzyl)-3-(2-hydroxynaphthalen-1-yl)-2,3-dihydro-1H-benzo[f]chromen-2-yl)benzonitrile (6j)

$^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$), mixture of rotamers

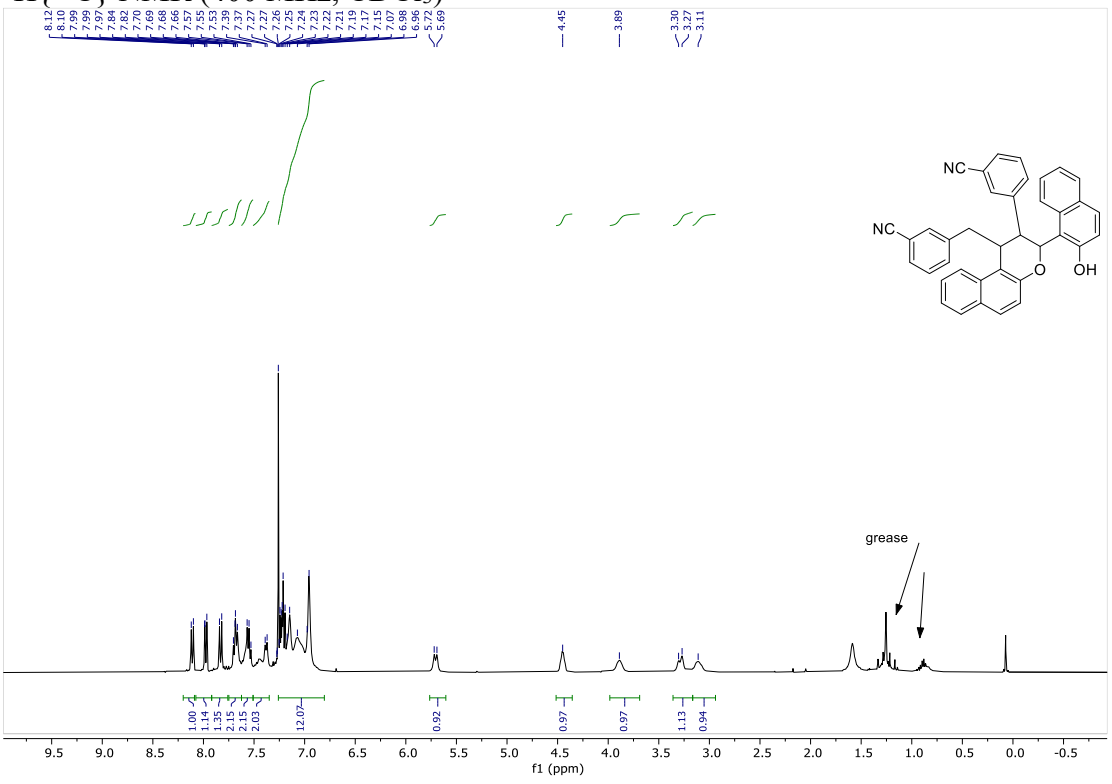


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), mixture of rotamers

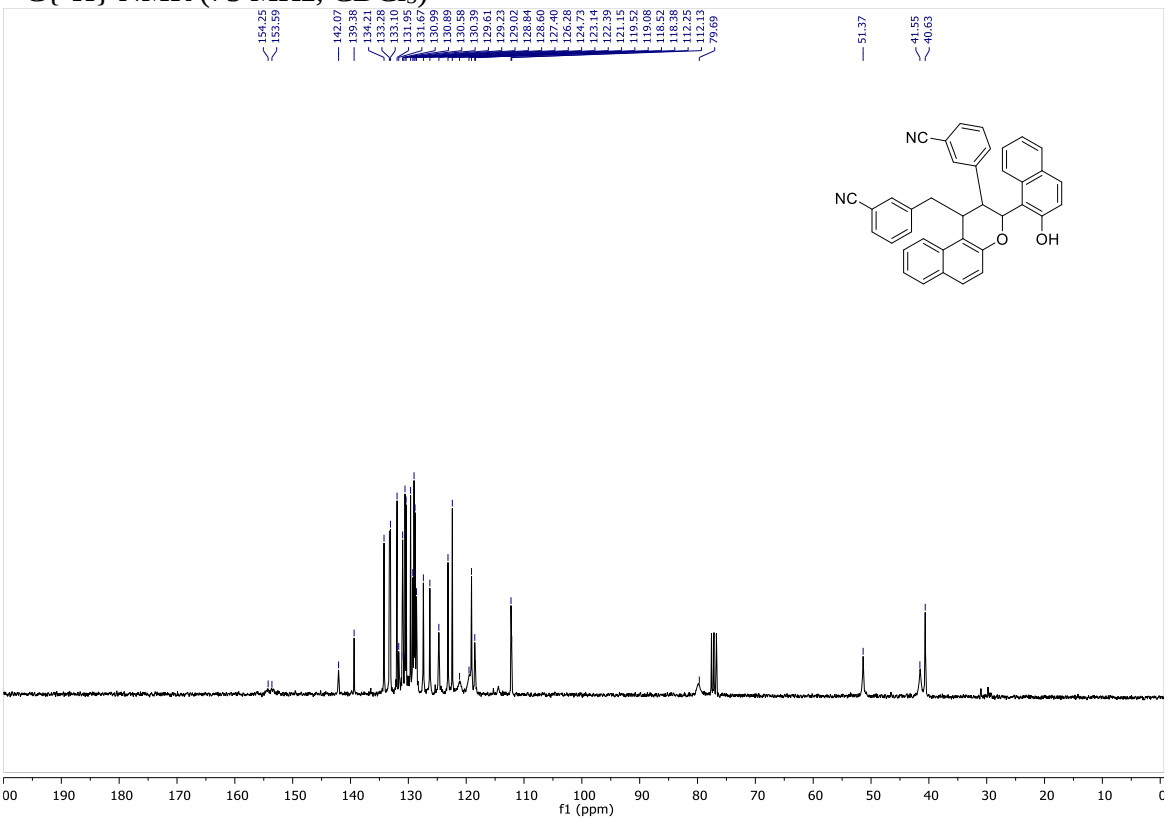


2-(1-(3-cyanobenzyl)-3-(2-hydroxynaphthalen-1-yl)-2,3-dihydro-1H-benzo[f]chromen-2-yl)benzonitrile (6k)

$^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$)

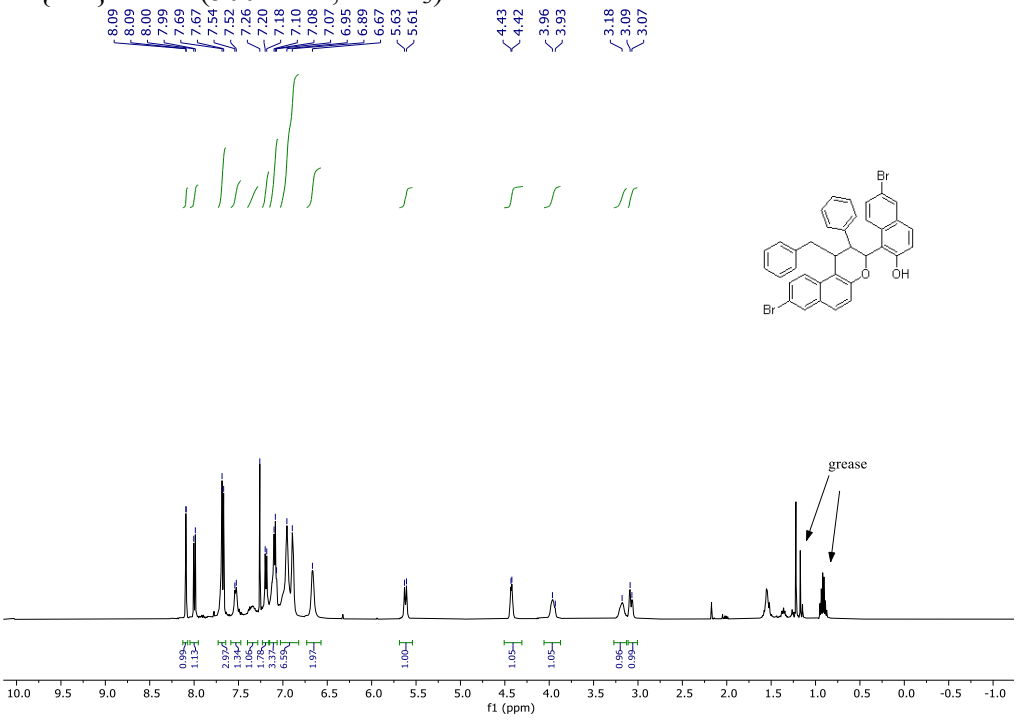


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

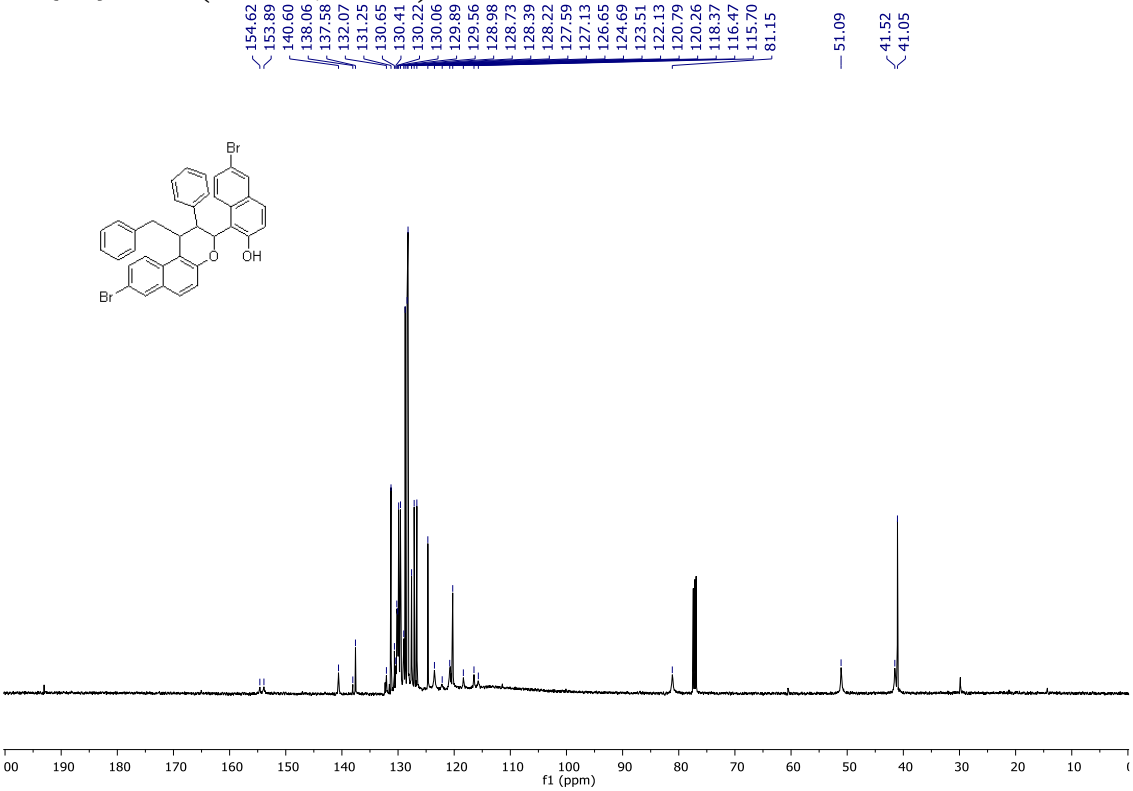


1-(1-benzyl-8-bromo-2-phenyl-2,3-dihydro-1H-benzo[f]chromen-3-yl)-6-bromonaphthalen-2-ol (6l)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

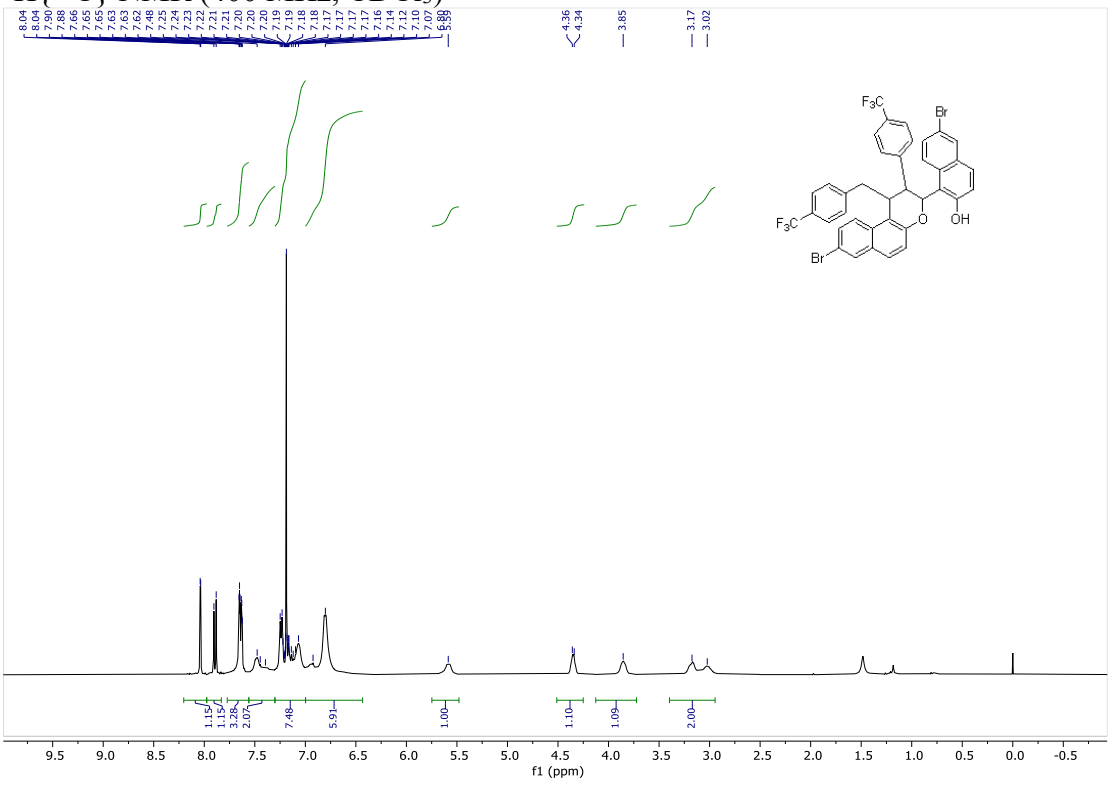


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

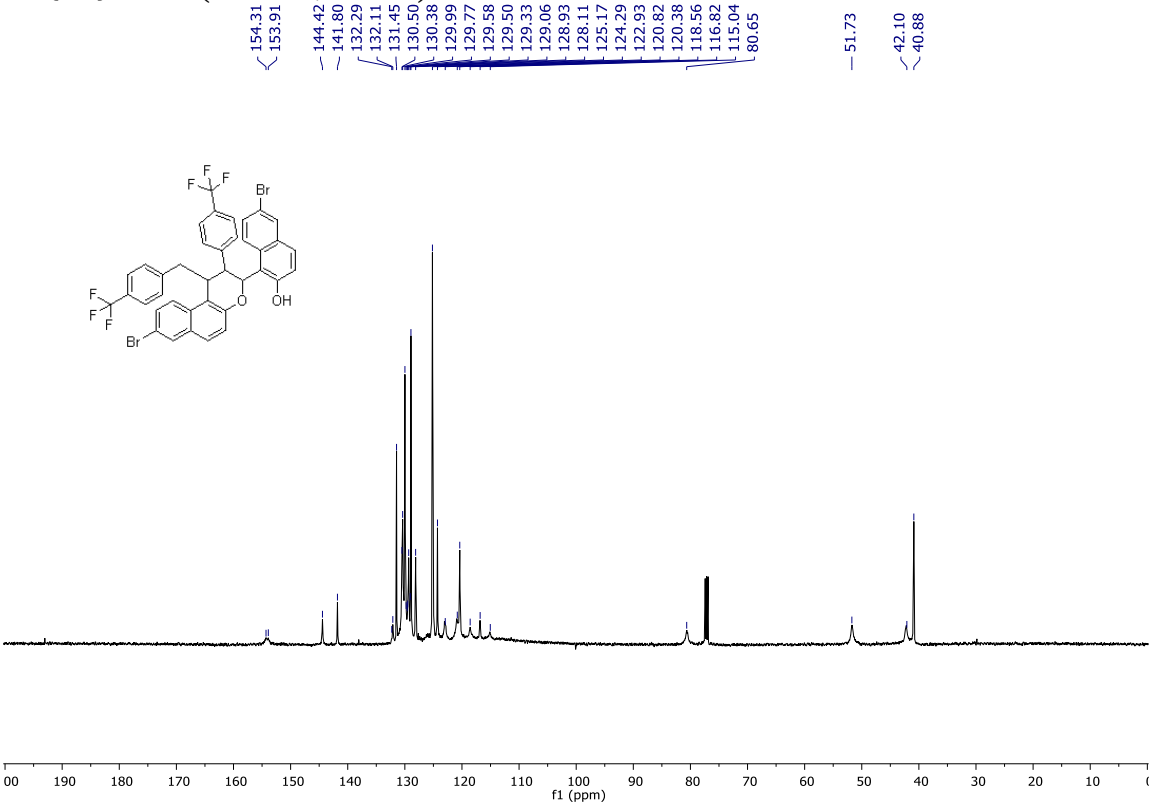


6-bromo-1-(8-bromo-1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6m)

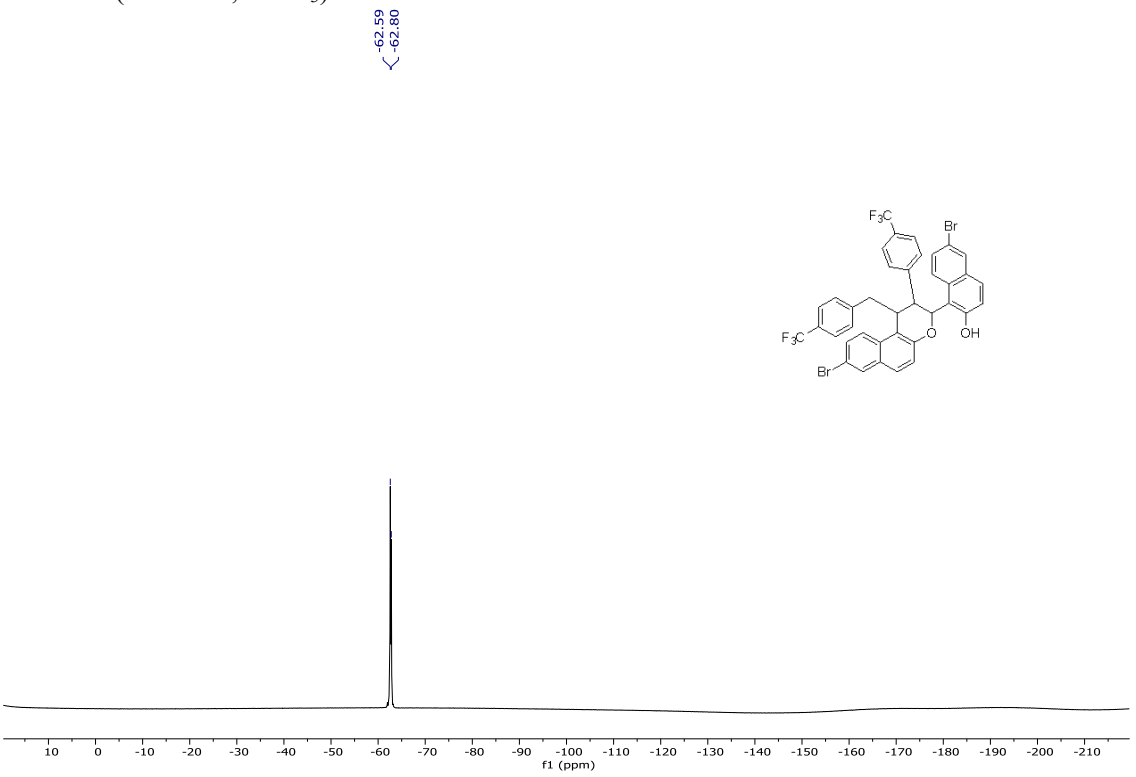
$^{1}H\{^{13}C\}$ NMR (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

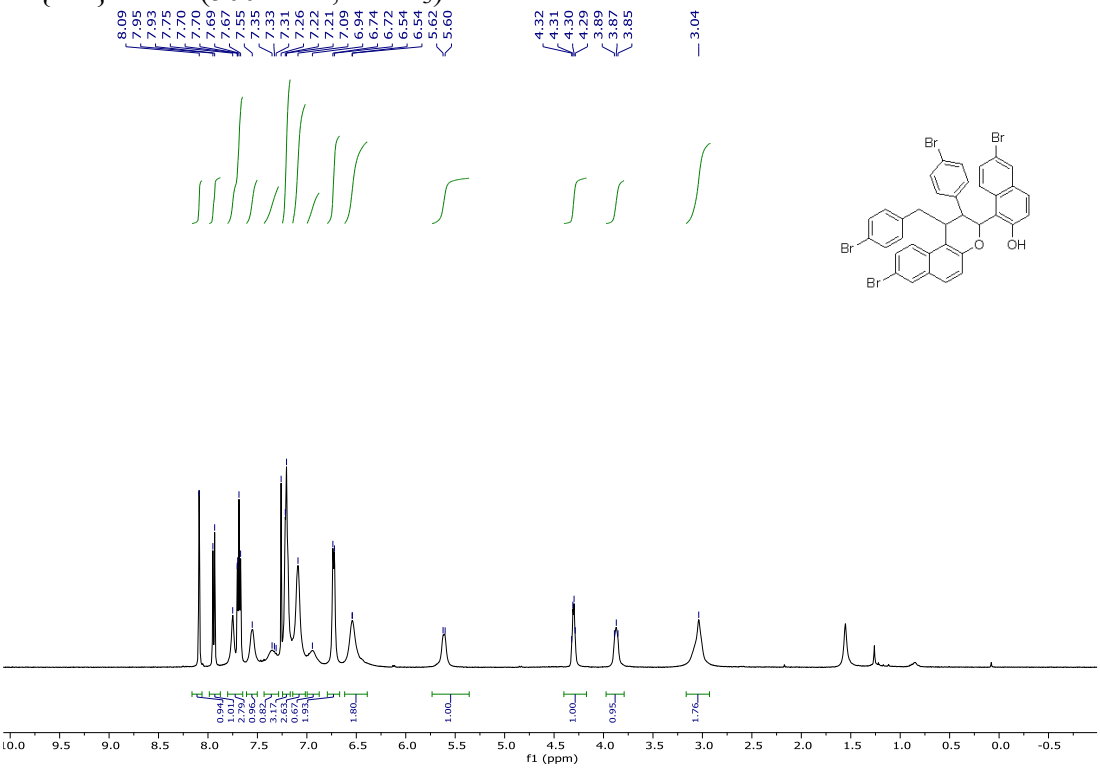


^{19}F NMR (282 MHz, $CDCl_3$)

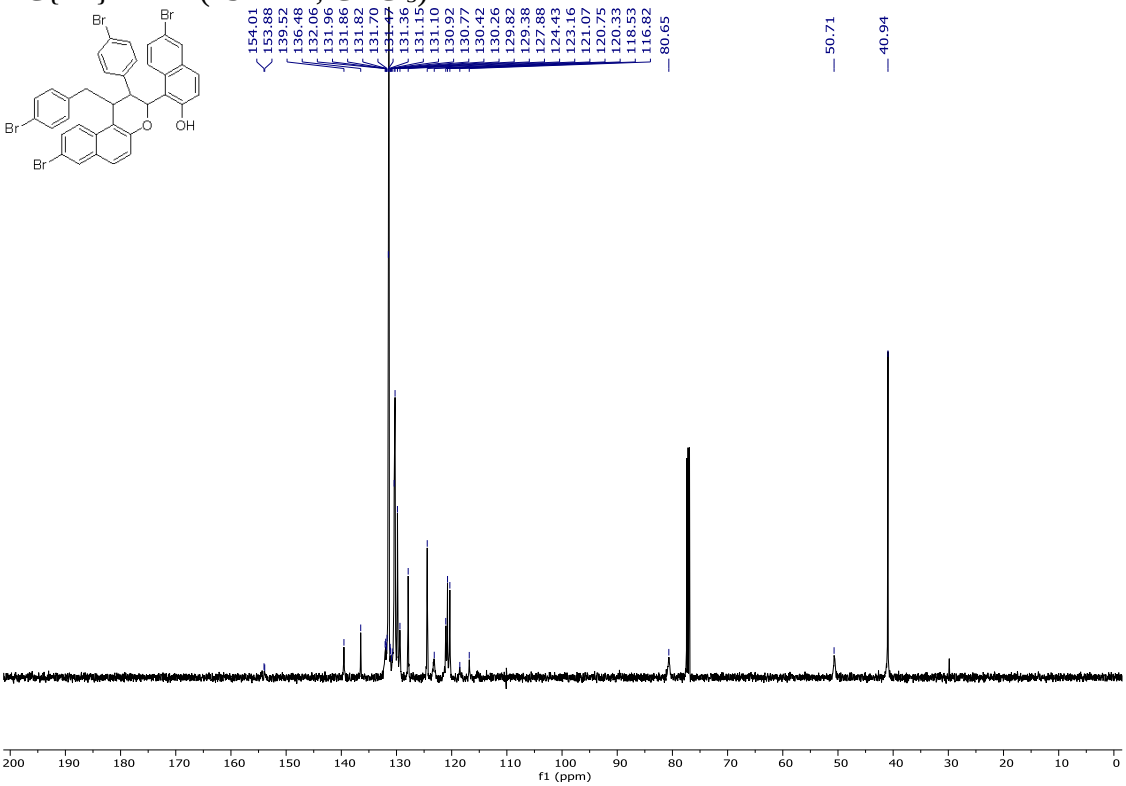


6-bromo-1-(8-bromo-1-(4-bromobenzyl)-2-(4-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6n)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$)

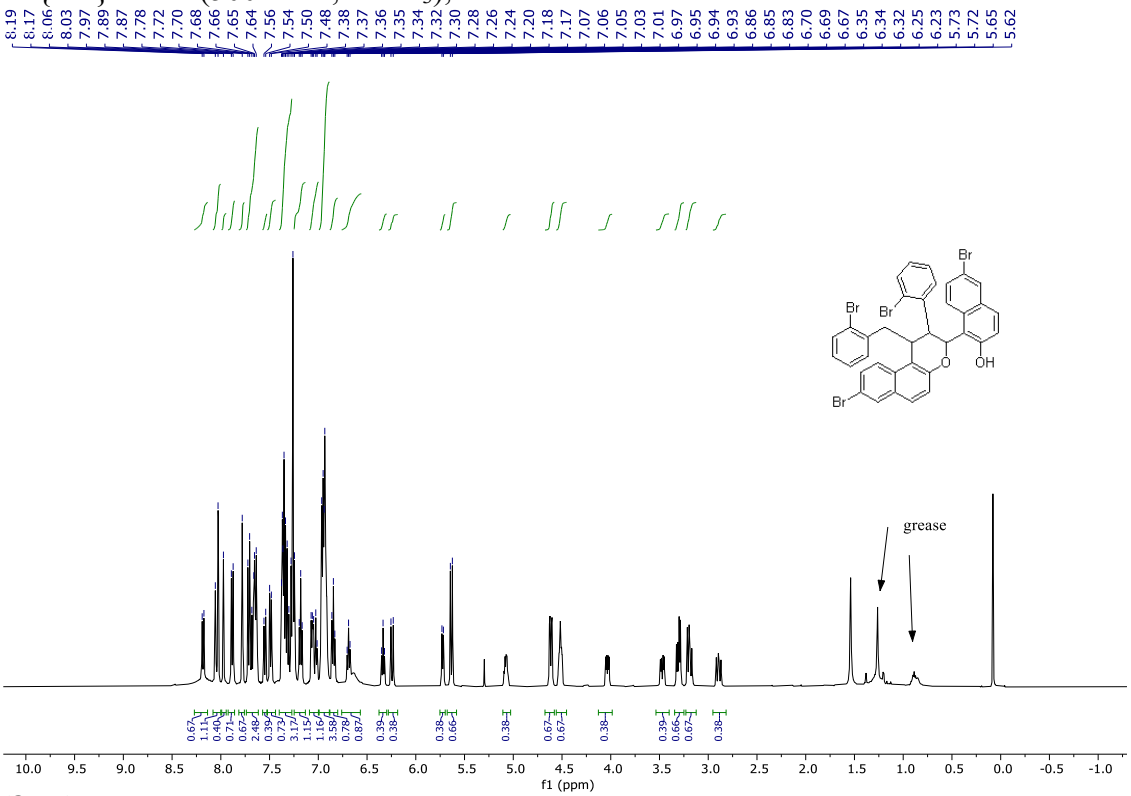


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

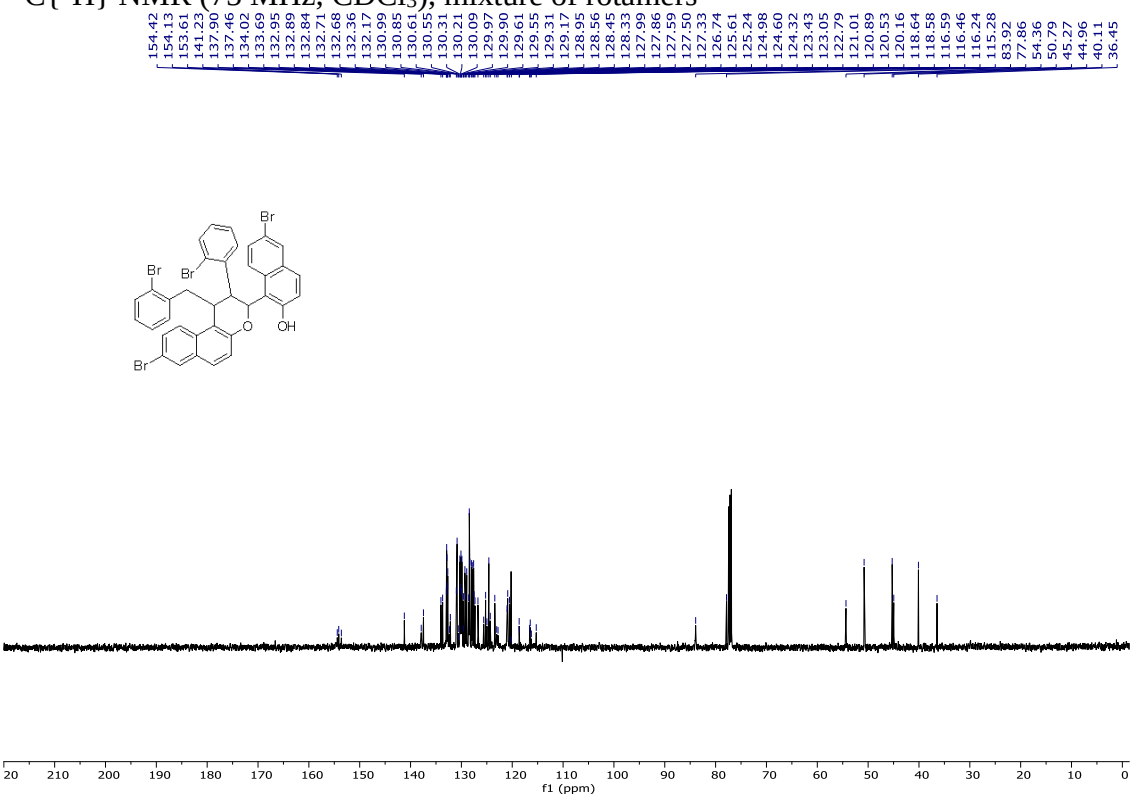


6-bromo-1-(8-bromo-1-(2-bromobenzyl)-2-(2-bromophenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol (6o)

$^{1}H\{^{13}C\}$ NMR (500 MHz, $CDCl_3$), mixture of rotamers



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), mixture of rotamers



4. Crystallographic data collection, structure determination and refinement

Suitable crystal for single crystal X-ray diffraction (SCXRD) analysis was obtained for compound **3b** X-ray diffraction data were measured at room temperature using a RIGAKU *XtaLabPro* diffractometer equipped with a Mo microfocus sealed tube *MM003* generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD *PILATUS3R 200K* detector. *CrysAlisPro 1.171.39.46* [1] was employed for the data processing, with *SCALE3 ABSPACK* scaling algorithm implemented for the empirical absorption correction using spherical harmonics.

The crystal structure (see Fig. 1) was readily solved by intrinsic phasing methods (*SHELXT* program),[2] then refined by full-matrix least-squares methods on F^2 using *SHELX-L*.[3] All non-hydrogen atoms of the molecule of interest improved by anisotropic refinement. Most of their H atoms were clearly identified in difference maps. The H atoms carried by carbons were positioned geometrically and refined with U_{iso} set to $1.2U_{eq}$(C) of the parent carbon atom (or 1.5 for the methyl). The position of the hydroxy hydrogen was freely refined but its U_{iso} was set to $1.5U_{eq}$(O). The F atoms of both CF_3 groups appeared disordered over two orientations 60° apart with refined site occupancies of 0.899(4):0.101(4) for that attached in ortho to the phenyl group and 0.684(5):0.316(5) for that bound to the benzyl one. All the components of the disordered CF_3 groups were restrained to have approximately equal C–F distances by use of the *SHELXL* SADI instruction. Their anisotropies were restrained with the *SHELXL* RIGU and ISOR 0.01 (for few F atoms) instructions. A search of the Cambridge Structural Database (CSD version 5.42, update of February 2021) [4] provided one structure having the bis-naphtalenol assembly in common with refcode CSD MIDYED[5]. Overlay is shown in figure S2. Crystal data, data collection and structure refinement details are summarized in Table S1.

CCDC 2082935 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

1 Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.

2 Sheldrick, G. M. (2015). *Acta Crystallogr.,* **C**71, 3-8.

3 Sheldrick, G. M. (2015). *Acta Crystallogr.,* **A**71, 3-8.

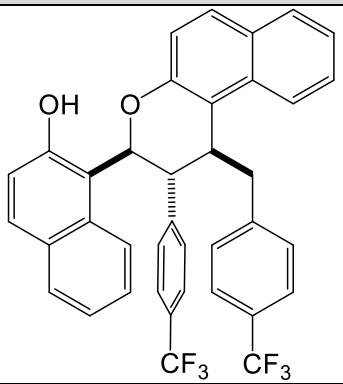
4 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Crystallogr.,*B**72**, 171–179.

5 Rashidi-Ranjbar, P., Mohajeri, A., Mahmoudkhani, A.H. (2001). *J.Phys.Org.Chem.,* 14, 210-216; Bolte, M. (2018), CSD Communication (Private Communication).

6 Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

7 Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453-457.

Table S1 Crystal data, data collection and structure refinement details for **6b**.

Compound	**6b**
	
	1-(1-(4-(trifluoromethyl)benzyl)-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-benzo[f]chromen-3-yl)naphthalen-2-ol
Empirical formula	$C_{38}\ H_{26}\ F_6\ O_2$
Formula weight	628.59
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, P 2_1/n
Unit cell dimensions | (Å) | (°)	10.5131(6) 11.3065(7) 25.1627(17) 90 96.162(6) 90
Volume (Å^3)	2973.7(3)
Z, Calculated density (Mg/m^3)	4, 1.404
Absorption coefficient (mm^{-1})	0.111
F(000)	1296
Crystal size (mm)	0.22 x 0.11 x 0.03
θ range for data collection (°)	1.977 to 25.028
Limiting indices	$-12 \le h \le 11$, $-13 \le k \le 13$, $-29 \le l \le 29$
Reflections collected / unique [R(int)	29061 / 5257 0.039
Completeness to θ_{full} (%)	99.8
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.436
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters		5256 / 210 / 475
Goodness-of-fit on F^2		1.045
Final R indices [$I>2\sigma(I)$]	R1, wR2	0.0561, 0.1412
R indices (all data)	R1, wR2	0.0750, 0.1520
Largest Δ peak and hole (e.Å^{-3})		0.326 and -0.257
CCDC deposit number		2082935

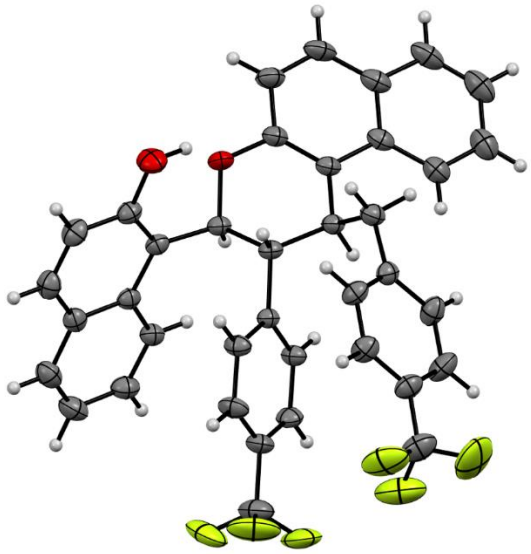


Figure S1

Ortep [6] view of 6b in the asymmetric unit of the title compound with displacement ellipsoids for the non-hydrogen atoms drawn at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radius. The minor components of the disordered CF3 groups were omitted for clarity.

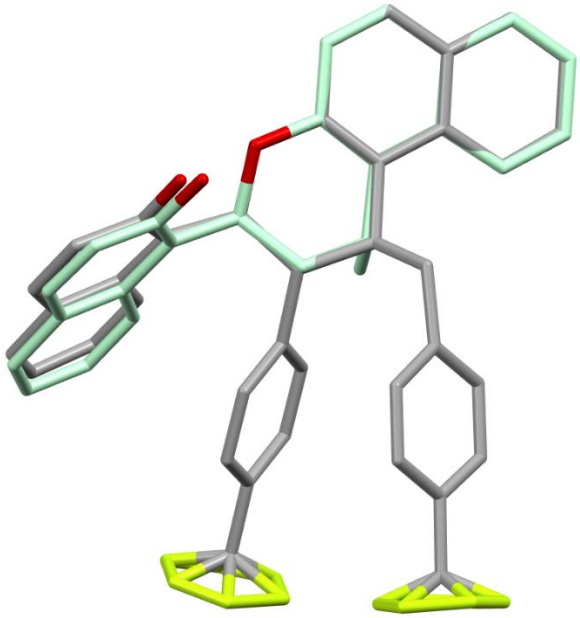


Figure S2

Overlay image [7] of **6b** and MIDYED structures over one common naphtalen group.