Supporting Information

Synthesis of 1-naphthols via Cp*Co(III)-catalyzed C–H activation and cyclization of sulfoxonium ylides with alkynes

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Table of Contents

1. General information............................................................................................................. S2
2. Experimental section ........................................................................................................ S2
3. Characterization data of products....................................................................................... S9
4. NMR spectrum.................................................................................................................. S20
1. General information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The Cp*Co(CO)I₂¹ and sulfoxonium ylides² were prepared according to the previous reports. Products were purified by column chromatography on 200-300 mesh silica gel, SiO₂. ¹H and ¹³C NMR spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shifts are given in δ relative to TMS, and the coupling constants are given in Hertz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; qui, quintet; sxt, sextet. The high-resolution mass spectra (HRMS) analyses were conducted using a TOF MS instrument with an ESI source. Melting points were measured by a melting point instrument and were uncorrected.

2. Experimental section

2.1 General procedure for Cp*Co(III)-catalyzed C–H functionalization to form 1-naphthols.

Sulfoxonium ylide 1 (0.2 mmol, 1.0 equiv), alkyne 2 (0.22 mmol, 1.1 equiv), Cp*Co(CO)I₂ (9.5 mg, 0.02 mmol, 10 mol %), AgOTf (12.8 mg, 0.05 mmol, 25 mol %), KOAc (3.9 mg, 0.04 mmol, 20 mol %) and DCE (1.0 mL) were added to a 35 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and stirred at 140 °C for 12 h. It was then cooled to room temperature, the solvent was removed in vacuum and the product was isolated through column chromatography to afford the desired product 3.

2.2 Procedure for the larger-scale synthesis of 3aa.
Sulfoxonium ylide 1a (392.1 mg, 2.0 mmol, 1.0 equiv), diphenylacetylene 2a (392.2 mg, 2.2 mmol, 1.1 equiv), Cp*Co(CO)I\(_2\) (95.0 mg, 0.2 mmol, 10 mol %), AgOTf (128.0 mg, 0.5 mmol, 25 mol %), KOAc (39.2 mg, 0.4 mmol, 20 mol %) and DCE (10 mL) were added to a 50 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and stirred at 140 °C for 12 h. It was then cooled to room temperature, the solvent was removed in vacuum. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) to afford the product 3aa (450.1 mg, 76% yield).

2.3 Procedure for the derivatization of 3aa.

Under N\(_2\), a 25 mL Schlenk flask was charged successively with 3aa (296.1 mg, 1.0 mmol, 1.0 equiv), dry DCM (3.0 mL) and pyridine (0.12 mL, 1.5 mmol, 1.5 equiv). The solution was cooled to 0 °C in an ice bath, and treated with dropwise addition of triflic anhydride (0.2 mL, 1.2 mmol, 1.2 equiv). The resulting mixture was slowly warmed up to 25 °C and kept stirred for additional 5 hours. At the end of the reaction (monitored by TLC), the mixture was concentrated on a rotary evaporator and the residue was purification by column chromatography on silica gel (eluent: petroleum
ether:ethyl acetate=100:1, v/v) to afford 4 (389.5 mg, 91% yield).

A solution of 4 (85.7 mg, 0.2 mmol, 1 equiv), Pd(PPh3)4 (11.5 mg, 0.01 mmol, 5 mol %), phenylboronic acid (29.3 mg, 0.24 mmol, 1.2 equiv), and Cs2CO3 (78.2 mg, 0.24 mmol, 1.2 equiv) in 1,4-dioxane (0.75 mL) and H2O (0.19 mL) was stirred at 80 ºC for 6 h, after which time TLC showed that the reaction was complete. The cooled mixture was diluted with Et2O (2 mL) and filtered through a short pad of silica gel, which then was washed with more Et2O (3 × 10 mL). The combined filtrates were dried by Na2SO4 and evaporated under reduced pressure. The residue was purification by column chromatography on silica gel (eluent: pure petroleum ether) to afford 5 (68.4 mg, 96% yield).

2.4 Procedure for the synthesis of 6 via one-pot, two-fold C–H functionalizations.

Sulfoxonium ylide 1a (39.2 mg, 0.2 mmol, 1.0 equiv), diphenylacetylene 2a (78.4 mg, 0.44 mmol, 2.2 equiv), Cp*Co(CO)I2 (14.3 mg, 0.03 mmol, 15 mol %), AgOTf (12.8 mg, 0.05 mmol, 25 mol %), KOAc (3.9 mg, 0.04 mmol, 20 mol %) and DCE (1.0 mL) were added to a 35 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and stirred at 140 ºC for 12 h, it was then cooled to room temperature. After that, CuO (31.8 mg, 0.4 mmol, 2.0 equiv), NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv) and DCE (0.4 mL) were added to the mixture. Then the flask was sealed under N2 and stirred at 80 ºC for 24 h. It was then
cooled to room temperature, the solvent was removed in vacuum. Purification by column chromatography on silica gel (eluent: pure petroleum ether) to afford the product 6 (20.7 mg, 22% yield).

2.5 Control experiments.

2.5.1 H/D exchange experiment.

Sulfoxonium ylide 1a (39.2 mg, 0.2 mmol, 1.0 equiv), Cp*Co(CO)I₂ (9.5 mg, 0.02 mmol, 10 mol %), AgOTf (12.8 mg, 0.05 mmol, 25 mol %), KOAc (3.9 mg, 0.04 mmol, 20 mol %), CD₃OD (36.0 mg, 1.0 mmol, 5.0 equiv) and DCE (1.0 mL) were added to a 35 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and stirred at 140 °C for 1 h. It was then cooled to room temperature, the solvent was removed in vacuum and then the reaction mixture was passed through a short pad of silica gel (eluent: pure ethyl acetate). The \(^1\)H NMR of the isolated product shows deuterium incorporation of about 10% in ortho position with respect to carbonyl of 1a.
2.5.2 Intermolecular competition experiment between different Sulfoxonium ylides with 2a.

Sulfoxonium ylide 1i (50.4 mg, 0.2 mmol, 1.0 equiv), sulfoxonium ylide 1m (52.8 mg, 0.2 mmol, 1.0 equiv), diphenylacetylene 2a (35.7 mg, 0.2 mmol, 1.0 equiv), Cp*Co(CO)I₂ (9.5 mg, 0.02 mmol, 10 mol %), AgOTf (12.8 mg, 0.05 mmol, 25 mol %), KOAc (3.9 mg, 0.04 mmol, 20 mol %) and DCE (1.0 mL) were added to a 35 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and stirred at 140 °C for 12 h. It was then cooled to room temperature, the solvent was removed in vacuum and then the crude mixture was purified by column chromatography (eluent: petroleum ether:ethyl acetate=20:1, v/v).
on silica gel to afford the mixture of 3ia and 3ma. The ratio of 3ia and 3ma (3ia:3ma = 5:1) was calculated by $^1$H NMR analysis.

2.5.3 Intermolecular KIE experiment.

Intermolecular competition KIE experiment. Sulfoxonium ylide 1a (39.2 mg, 0.2 mmol), [D$_5$]-1a (40.2 mg, 0.2 mmol), diphenylacetylene 2a (78.4 mg, 0.44 mmol), Cp*Co(CO)$_2$ (19.0 mg, 0.04 mmol), AgOTf (25.6 mg, 0.10 mmol), KOAc (7.8 mg, 0.08 mmol) and DCE (2.0 mL) were added to a 35 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and stirred at 140 °C for 5 min. It was then cooled to room temperature, the solvent was
removed in vacuum and the product was isolated through column chromatography (eluent: petroleum ether:ethyl acetate=20:1, v/v) to afford the desired product less than 10% yield. The KIE value was calculated as $k_H:k_D = 4.26$.

**Intermolecular parallel KIE experiment.** Sulfoxonium ylide 1a (39.2 mg, 0.2 mmol) or [D$_5$]-1a (40.2 mg, 0.2 mmol), diphenylacetylene 2a (39.2 mg, 0.22 mmol), Cp*Co(CO)$_2$I$_2$ (9.5 mg, 0.02 mmol), AgOTf (12.8 mg, 0.05 mmol), KOAc (3.9 mg, 0.04 mmol) and DCE (1.0 mL) were added to a 35 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and stirred at 140 °C for 5 min. It was then cooled to room temperature, mix the two reaction mixtures together, the solvent was removed in vacuum and the product was isolated through column chromatography (eluent: petroleum ether:ethyl acetate=20:1, v/v) to afford the desired product less than 9% yield. The KIE value was calculated as $k_H:k_D = 4.88$. 
3. Characterization data of products

3,4-Diphenyl-naphthalene-1-ol (3aa). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3aa as a white solid (49.2 mg, 83% yield); mp 146-148 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.31 (d, $J = 8.4$ Hz, 1H), 7.68 (d, $J = 8.8$ Hz, 1H), 7.55-7.51 (m, 1H), 7.47-7.43 (m, 1H), 7.33-7.29 (m, 3H), 7.21-7.14 (m, 7H), 6.93 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.5, 141.8, 139.0, 138.4, 133.9, 131.9, 130.7, 130.0, 127.7, 127.6, 126.7, 126.5, 126.2, 125.1, 123.6, 121.5, 110.9.

8-Fluoro-3,4-diphenyl-naphthalene-1-ol (3ba). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=50:1, v/v) afforded 3ba as a light yellow solid (42.1 mg, 67% yield); mp 147-149 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48 (d, $J = 8.8$ Hz, 1H), 7.33-7.28 (m, 4H), 7.21-7.15 (m, 9H), 7.13 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.7, 150.5, 141.2, 140.9, 138.8, 136.3
(d, $J = 2.4$ Hz), 131.7, 129.9, 127.9, 127.6, 126.7, 126.5, 125.8, 125.7, 124.0, 123.9, 113.7 (d, $J = 2.2$ Hz), 109.4 (d, $J = 22.5$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -121.8.

8-Methyl-3,4-diphenynaphthalen-1-ol (3ca)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ca as a light yellow solid (37.2 mg, 60% yield); mp 178-180 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44 (d, $J = 8.8$ Hz, 1H), 7.27-7.20 (m, 5H), 7.14-7.09 (m, 7H), 6.81 (s, 1H), 5.36 (s, 1H), 3.01 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.0, 141.6, 139.7, 138.3, 135.6, 134.9, 131.9, 131.2, 129.9, 128.0, 127.7, 127.5, 126.4, 126.2, 125.2, 123.0, 112.3, 24.9.

8-Methoxy-3,4-diphenynaphthalen-1-ol (3da). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3da as a white solid (41.1 mg, 63% yield); mp 186-188 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.53 (s, 1H), 7.26-7.22 (m, 5H), 7.16-7.10 (m, 7H), 7.02 (s, 1H), 6.80 (d, $J = 6.8$ Hz, 1H), 4.09 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.2, 153.7, 141.7, 140.6, 139.5, 135.8, 131.9, 129.9, 128.9, 127.8, 127.5, 126.4, 126.2, 125.8, 120.9, 114.3, 112.6, 103.9, 56.3; HRMS (ESI, m/z) calcd for C$_{23}$H$_{17}$O$_2$ [M - H]$^-$ 325.1234, found 325.1230.

7-Methyl-3,4-diphenynaphthalen-1-ol (3ea)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ea as a white solid (50.2 mg, 81% yield); mp 117-119 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03 (s, 1H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.26-7.23 (m, 4H), 7.16-7.09 (m, 7H), 6.87 (s, 1H), 5.38 (s, 1H), 2.52 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$
150.0, 141.9, 139.1, 137.4, 134.8, 132.1, 131.8, 130.6, 130.0, 128.9, 127.7, 127.5, 126.7, 126.4, 126.1, 123.6, 120.4, 111.0, 21.7.

7-Bromo-3,4-diphenynaphthalen-1-ol (3fa). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3fa as a white solid (53.9 mg, 72% yield); mp 181-183 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.44 (d, J = 2.0 Hz, 1H), 7.50-7.44 (m, 2H), 7.27-7.25 (m, 3H), 7.17-7.09 (m, 7H), 6.91 (s, 1H), 5.43 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.7, 141.4, 138.9, 138.4, 132.4, 131.7, 130.8, 130.0, 129.8, 128.6, 127.9, 127.6, 126.7, 126.4, 124.8, 124.1, 119.3, 111.9.

3,4,7-Triphenynaphthalen-1-ol (3ga). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ga as a white solid (55.1 mg, 74% yield); mp 202-204 °C; $^1$H NMR (400 MHz, acetone-d$_6$): $\delta$ 8.61 (d, J = 2.0 Hz, 1H), 7.80 (d, J = 7.2 Hz, 2H), 7.74 (dd, J = 8.8, 2.0 Hz, 1H), 7.60 (d, J = 9.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.30-7.25 (m, 3H), 7.19-7.13 (m, 7H), 7.07 (d, J = 2.4 Hz, 1H); $^{13}$C NMR (100 MHz, acetone-d$_6$): $\delta$ 153.7, 143.2, 141.7, 140.3, 139.9, 137.7, 134.0, 132.7, 130.8, 129.9, 129.7, 128.7, 128.4, 128.2, 127.9, 127.3, 127.0, 126.5, 125.4, 120.6, 111.4; HRMS (ESI, m/z) calcd for C$_{28}$H$_{19}$O [M - H]’ 371.1441, found 371.1437.

6-Methyl-3,4-diphenynaphthalen-1-ol (3ha). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ha as a light yellow solid (47.8 mg, 77% yield); mp 165-167 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.16 (d, J = 8.8 Hz, 1H), 7.39 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.27-7.24 (m, 3H), 7.16-7.10 (m, 7H), 6.84 (s, 1H), 5.36 (s, 1H), 2.39 (s, 3H); $^{13}$C
NMR (100 MHz, CDCl$_3$): $\delta$ 150.6, 142.0, 139.1, 138.6, 136.5, 134.1, 131.9, 130.1, 130.0, 127.7, 127.5, 127.2, 126.4, 126.1, 125.7, 121.7, 121.4, 110.1, 22.0.

6-(Tert-butyl)-3,4-diphenynaphthalen-1-ol ($3\text{i}a$)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded $3\text{i}a$ as a white solid (59.9 mg, 85% yield); mp 144-146 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.24 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 1.2$ Hz, 1H), 7.63 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.33-7.27 (m, 3H), 7.22-7.14 (m, 7H), 6.88 (s, 1H), 5.42 (s, 1H), 1.31 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.4, 149.4, 142.0, 139.1, 138.5, 133.8, 131.9, 130.8, 130.0, 127.6, 127.5, 126.4, 126.1, 123.9, 121.9, 121.7, 121.1, 110.4, 35.0, 31.1.

6-Methoxy-3,4-diphenynaphthalen-1-ol ($3\text{ja}$)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded $3\text{ja}$ as a white solid (59.4 mg, 91% yield); mp 197-199 °C; $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 8.25 (d, $J = 9.2$ Hz, 1H), 7.30-7.22 (m, 3H), 7.16-7.11 (m, 8H), 6.89-6.88 (m, 2H), 3.64 (s, 3H); $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 159.2, 153.5, 143.5, 140.6, 140.5, 136.3, 132.7, 130.7, 128.8, 128.7, 128.3, 127.2, 126.9, 124.8, 120.4, 117.0, 109.2, 106.2, 55.2.

6-Fluoro-3,4-diphenynaphthalen-1-ol ($3\text{ka}$)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded $3\text{ka}$ as a white solid (45.9 mg, 73% yield); mp 185-187 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.34-8.30 (m, 1H), 7.34-7.27 (m, 5H), 7.20-7.13 (m, 7H), 6.87 (s, 1H), 5.47 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.6 (d, $J = 244.2$ Hz), 150.7, 141.5, 139.8, 138.5, 135.3 (d, $J = 9.0$ Hz), 131.7, 130.3 (d, $J = 5.5$ Hz), 129.9, 128.0,
127.6, 126.7, 126.4, 124.4 (d, J = 9.1 Hz), 120.7, 115.1 (d, J = 25.2 Hz), 110.3 (d, J = 22.3 Hz), 110.2; $^{19}$F NMR(376 MHz, CDCl$_3$): $\delta$ -112.9.

6-Chloro-3,4-diphenynaphthalen-1-ol (3la)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3la as a light yellow solid (50.2 mg, 76% yield); mp 186-188 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.24 (d, J = 9.2 Hz, 1H), 7.63 (s, 1H), 7.44 (d, J = 8.8 Hz, 1H), 7.31-7.28 (m, 3H), 7.19-7.11 (m, 7H), 6.90 (s, 1H), 5.46 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.6, 141.4, 139.8, 138.2, 134.8, 133.0, 131.7, 130.1, 129.8, 128.0, 127.6, 126.8, 126.5, 125.8, 125.5, 123.5, 121.9, 111.2.

3,4-Diphenyl-6-(trifluoromethyl)naphthalen-1-ol (3ma)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ma as a light yellow solid (51.7 mg, 71% yield); mp 151-153 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.42 (d, J = 8.8 Hz, 1H), 7.97 (s, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.32-7.30 (m, 3H), 7.20-7.12 (m, 7H), 7.03 (s, 1H), 5.57 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.5, 141.2, 140.0, 137.9, 132.9, 131.7, 129.8, 128.2 (q, J = 33.6 Hz), 128.0, 127.7, 127.0, 126.6, 124.8, 124.4 (q, J = 270.7 Hz), 124.3 (q, J = 4.7 Hz), 123.0, 120.6 (q, J = 2.8 Hz), 112.9; $^{19}$F NMR(376 MHz, CDCl$_3$): $\delta$ -62.3.

6-Nitro-3,4-diphenynaphthalen-1-ol (3na)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=15:1, v/v) afforded 3na as a yellow solid (30.7 mg, 45% yield); mp 242-244 °C; $^1$H NMR (400 MHz, acetone-d$_6$): $\delta$ 8.53-8.46 (m, 2H), 8.20 (dd, J = 9.2, 2.0 Hz, 1H), 7.37-7.32 (m, 3H), 7.26 (s, 1H), 7.21-7.17 (m, 7H); $^{13}$C NMR (100 MHz, acetone-d$_6$): $\delta$ 153.6, 147.2, 142.4, 142.2,
138.9, 133.8, 132.7, 130.7, 129.0, 128.6, 128.1, 127.6, 127.4, 125.4, 123.5, 118.4, 114.7.

6,7-Dichloro-3,4-diphenylanthracen-1-ol (3oa). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3oa as a light yellow solid (45.1 mg, 62% yield); mp 199-201 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.40 (s, 1H), 7.72 (s, 1H), 7.30-7.28 (m, 3H), 7.18-7.16 (m, 3H), 7.13-7.10 (m, 4H), 6.92 (s, 1H), 5.57 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 149.7, 141.1, 139.9, 137.9, 133.1, 131.6, 131.4, 130.0, 129.8, 129.5, 128.1, 127.9, 127.7, 127.0, 126.6, 123.3, 122.8, 111.9; HRMS (ESI, m/z) calcd for C$_{22}$H$_{13}$Cl$_2$O [M - H]$^-$ 363.0349, found 363.0344.

3,4-Diphenylanthracen-1-ol (3pa). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3pa as a white solid (47.1 mg, 68% yield); mp 218-220 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.84 (s, 1H), 8.18 (s, 1H), 8.02 (d, $J = 8.4$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.45-7.36 (m, 2H), 7.33-7.29 (m, 3H), 7.24-7.22 (m, 2H), 7.16-7.11 (m, 5H), 6.84 (s, 1H), 5.52 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.5, 141.9, 139.1, 137.3, 132.4, 132.1, 132.0, 130.8, 130.5, 130.0, 128.5, 128.4, 127.9, 127.6, 126.6, 126.2, 125.7, 125.6, 125.5, 123.2, 120.5, 109.2; HRMS (ESI, m/z) calcd for C$_{26}$H$_{17}$O [M - H]$^-$ 345.1285, found 345.1281.

3,4-Di-m-tolynaphthalen-1-ol (3ab). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ab as a white solid (52.5 mg, 81% yield); mp 87-89 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.30 (d, $J =$
8.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.11-6.94 (m, 7H), 6.92 (s, 1H), 5.59 (s, 1H), 2.32 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.4, 141.7, 138.9, 138.4, 137.1, 137.0, 133.9, 132.5, 130.8, 130.7, 128.9, 127.6, 127.3, 127.1, 127.0, 126.9, 126.8, 126.6, 124.9, 123.5, 121.4, 110.9, 21.4, 21.3.

3,4-Di-p-tolynaphthalen-1-ol ($3_{ac}$)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded $3_{ac}$ as a white solid (49.9 mg, 77% yield); mp 156-158 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.29 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.15-7.06 (m, 6H), 7.02 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 5.48 (s, 1H), 2.39 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.4, 139.0, 138.3, 136.0, 136.0, 135.9, 135.7, 134.1, 131.6, 130.6, 129.8, 128.5, 128.3, 126.8, 126.6, 124.9, 123.5, 121.4, 111.1, 21.2, 21.1.

3,4-Bis(4-methoxyphenyl)naphthalen-1-ol ($3_{ad}$)$^2$. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=15:1, v/v) afforded $3_{ad}$ as a white solid (60.5 mg, 85% yield); mp 197-199 °C; $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 8.30 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.46-7.36 (m, 2H), 7.08-7.00 (m, 5H), 6.86 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 3.72 (s, 3H); $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 159.2, 159.0, 153.2, 139.6, 135.7, 135.3, 133.7, 132.5, 131.9, 129.4, 127.2, 127.0, 125.1, 122.9, 114.1, 113.8, 111.1, 55.4, 55.3.

3,4-Bis(4-(tert-butyl)phenyl)naphthalen-1-ol ($3_{ae}$)$^2$. Purification by column
chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ae as a white solid (67.8 mg, 83% yield); mp 134-136 °C; 1H NMR (400 MHz, CDCl3): δ 8.29 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 6.95 (s, 1H), 5.51 (s, 1H), 1.35 (s, 9H), 1.29 (s, 9H); 13C NMR (100 MHz, CDCl3): δ 150.4, 149.2, 148.9, 138.8, 138.5, 136.0, 133.9, 131.5, 130.8, 129.6, 126.9, 126.5, 124.9, 124.5, 124.3, 123.5, 121.4, 111.0, 34.4, 34.3, 31.4, 31.2.

3,4-Bis(4-chlorophenyl)naphthalen-1-ol (3af). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3af as a white solid (48.8 mg, 67% yield); mp 180-182 °C; 1H NMR (400 MHz, CDCl3): δ 8.28 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 6.8 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.86 (s, 1H), 5.52 (s, 1H); 13C NMR (100 MHz, CDCl3): δ 151.0, 139.9, 137.3, 137.2, 133.7, 133.1, 132.7, 132.6, 131.2, 129.4, 128.2, 128.0, 127.1, 126.4, 125.4, 123.7, 121.6, 110.5; HRMS (ESI, m/z) calcd for C22H13ClO [M - H] 363.0349, found 363.0350.

3,4-Bis(4-(trifluoromethyl)phenyl)naphthalen-1-ol (3ag). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ag as a light yellow solid (53.6 mg, 62% yield); mp 169-171 °C; 1H NMR (400 MHz, CDCl3): δ 8.33 (d, J = 8.4 Hz, 1H), 7.59-7.54 (m, 4H), 7.50-7.45 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.90 (s, 1H), 5.64 (s, 1H); 13C NMR
(100 MHz, CDCl₃): \( \delta \) 151.3, 145.0, 142.5, 137.2, 133.5, 132.1, 130.2, 129.4, 129.1 (q, \( J = 34.4 \) Hz), 127.4, 126.3, 125.7, 125.0 (q, \( J = 2.8 \) Hz), 124.8 (q, \( J = 3.4 \) Hz), 124.2 (q, \( J = 269.4 \) Hz), 124.1 (q, \( J = 272.1 \) Hz), 123.9, 121.8, 110.4; \(^{19}\)F NMR (376 MHz, CDCl₃): \( \delta \) -62.4, -62.5.

\([2,1':2',2''-\text{Ternaphthalen}]\)-4'-ol (3ah). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ah as a white solid (72.9 mg, 92% yield); mp 208-210 °C; \(^{1}\)H NMR (400 MHz, acetone-\(d_6\)): \( \delta \) 8.41 (d, \( J = 8.4 \) Hz, 1H), 7.82-7.80 (m, 2H), 7.76 (d, \( J = 8.4 \) Hz, 1H), 7.73-7.68 (m, 4H), 7.56-7.48 (m, 3H), 7.42-7.35 (m, 6H), 7.29 (dd, \( J = 8.4 \), 1.6 Hz, 1H), 7.21 (s, 1H); \(^{13}\)C NMR (100 MHz, acetone-\(d_6\)): \( \delta \) 153.7, 140.9, 139.9, 137.9, 135.0, 134.1, 134.0, 133.0, 132.8, 131.5, 131.1, 129.9, 129.5, 129.2, 128.7, 128.6, 128.4, 128.3, 128.1, 127.6, 127.5, 127.1, 126.9, 126.8, 126.7, 126.6, 125.5, 125.3, 123.1, 111.2; HRMS (ESI, m/z) calcd for C₃₀H₁₉O [M - H]⁻ 395.1441, found 395.1441.

N-(4-Hydroxy-1-phenylnaphthalen-2-yl)-N,4-dimethylbenzenesulfonamide (3ai). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=2:1, v/v) afforded 3ai as a white solid (41.1 mg, 51% yield); mp 203-205 °C; \(^{1}\)H NMR (400 MHz, acetone-\(d_6\)): \( \delta \) 8.31-8.28 (m, 1H), 7.84-7.81 (m, 1H), 7.51-7.47 (m, 2H), 7.37-7.33 (m, 5H), 7.18-7.13 (m, 4H), 6.89 (s, 1H), 3.28 (s, 3H), 3.25 (s, 3H); \(^{13}\)C NMR (100 MHz, acetone-\(d_6\)): \( \delta \) 154.1, 143.7, 142.9, 141.9, 138.2, 134.4, 130.1, 129.8, 128.9, 128.3, 128.1, 128.0, 126.3, 125.7, 125.2, 123.6, 112.9, 111.3, 40.1, 21.4; HRMS (ESI, m/z) calcd for C_{24}H_{20}NO_{3}S [M - H]⁻ 402.1169, found 402.1172.

4-Methyl-3-phenylnaphthalen-1-ol (3aj). Purification by column chromatography on
silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3aj as a white solid (22.9 mg, 49% yield); mp 110-112 °C; $^1$H NMR (400 MHz, acetone-$d_6$): $\delta$ 8.29 (d, $J = 8.4$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.59-7.54 (m, 1H), 7.50-7.44 (m, 3H), 7.39-7.35 (m, 3H), 6.85 (s, 1H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, acetone-$d_6$): $\delta$ 152.0, 143.8, 140.1, 135.0, 130.4, 128.9, 127.6, 127.3, 125.5, 125.2, 125.1, 123.4, 121.8, 110.9, 15.8.

3-Phenyl napthalen-1-ol (3ak). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded 3ak as a light yellow solid (15.8 mg, 36% yield); mp 79-81 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.20 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 3H), 7.55-7.46 (m, 4H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.09 (s, 1H), 5.53 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 151.7, 140.9, 138.9, 134.9, 128.8, 128.0, 127.4, 127.3, 126.9, 125.3, 123.5, 121.5, 118.7, 108.4.

3,4-Diphenyl napthalen-1-yl trifluoromethanesulfonate (4). Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=100:1, v/v) afforded 4 as a white solid (389.5 mg, 91% yield); mp 105-107 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.63-7.58 (m, 2H), 7.47 (t, $J = 8.0$ Hz, 1H), 7.31-7.28 (m, 3H), 7.18-7.11 (m, 7H).

1,2,4-Triphenyl naphthalene (5). Purification by column chromatography on silica gel (eluent: pure petroleum ether) afforded 5 as a white solid (68.4 mg, 96% yield); mp 160-162 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.89 (d, $J = 8.8$ Hz, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.49-7.45 (m, 3H), 7.38 (t, $J = 7.2$ Hz, 2H), 7.33-7.28 (m, 3H), 7.22-7.13 (m,
5H), 7.08-7.00 (m, 5H).

2,3,7,8-Tetraphenylbenzo[de]chromene (6). Purification by column chromatography on silica gel (eluent: pure petroleum ether) afforded 6 as a yellow solid (20.7 mg, 22% yield); mp 249-251 °C; 1H NMR (400 MHz, CDCl3): δ 7.41-7.38 (m, 2H), 7.36-7.32 (m, 3H), 7.29-7.25 (m, 5H), 7.22-7.14 (m, 11H), 7.11-7.07 (m, 1H), 7.04 (s, 1H), 6.49 (d, J = 7.2 Hz, 1H).

References
4. NMR spectrum

$^1$H NMR spectrum of 3aa

$^{13}$C NMR spectrum of 3aa
$^1$H NMR spectrum of 3ba

$^{13}$C NMR spectrum of 3ba
$^{19}$F NMR spectrum of $3_{ba}$

$^1$H NMR spectrum of $3_{ca}$
$^{13}$C NMR spectrum of 3ca

$^1$H NMR spectrum of 3da
$^{13}$C NMR spectrum of 3da

![13C NMR spectrum of 3da](image)

$^{1}$H NMR spectrum of 3ea

![1H NMR spectrum of 3ea](image)
$^{13}$C NMR spectrum of 3ea

3ea

$^1$H NMR spectrum of 3fa

3fa
$^{13}$C NMR spectrum of 3fa

3fa

$^1$H NMR spectrum of 3ga

3ga
$^{13}$C NMR spectrum of 3ga

$^1$H NMR spectrum of 3ha
$^{13}$C NMR spectrum of 3ha

![13C NMR spectrum of 3ha](image)

$^1$H NMR spectrum of 3ia

![1H NMR spectrum of 3ia](image)
$^{13}$C NMR spectrum of 3ia

$^1$H NMR spectrum of 3ja
$^{13}$C NMR spectrum of 3ja

$^1$H NMR spectrum of 3ka
$^{13}$C NMR spectrum of 3ka

![Carbon NMR spectrum of 3ka](image)

$^{19}$F NMR spectrum of 3ka

![Fluorine NMR spectrum of 3ka](image)
$^1$H NMR spectrum of 3la

3la

$^{13}$C NMR spectrum of 3la

3la
$^1$H NMR spectrum of **3ma**

![$^1$H NMR spectrum of **3ma**](image1)

$^{13}$C NMR spectrum of **3ma**

![$^{13}$C NMR spectrum of **3ma**](image2)
$^{19}$F NMR spectrum of 3ma

![19F NMR spectrum of 3ma](image)

$^1$H NMR spectrum of 3na

![1H NMR spectrum of 3na](image)
$^{13}$C NMR spectrum of $3\text{na}$

![$^{13}$C NMR spectrum of $3\text{na}$]

$^1$H NMR spectrum of $3\text{oa}$

![$^1$H NMR spectrum of $3\text{oa}$]

S35
$^{13}$C NMR spectrum of 3oa

![$^{13}$C NMR spectrum of 3oa](image)

$^1$H NMR spectrum of 3pa

![$^1$H NMR spectrum of 3pa](image)
$^{13}$C NMR spectrum of 3pa

3pa

$^1$H NMR spectrum of 3ab

3ab
$^{13}$C NMR spectrum of 3ab

$^1$H NMR spectrum of 3ac
$^{13}$C NMR spectrum of 3ac

![Chemical structure of 3ac and its $^{13}$C NMR spectrum]

$^1$H NMR spectrum of 3ad

![Chemical structure of 3ad and its $^1$H NMR spectrum]
$^{13}$C NMR spectrum of 3ad

$^1$H NMR spectrum of 3ae
$^{13}$C NMR spectrum of 3ae

$^1$H NMR spectrum of 3af
$^{13}$C NMR spectrum of 3af

$^1$H NMR spectrum of 3ag
$^{13}$C NMR spectrum of 3ag

$^{19}$F NMR spectrum of 3ag
$^1$H NMR spectrum of 3ah

13C NMR spectrum of 3ah
$^1$H NMR spectrum of 3ai

$^{13}$C NMR spectrum of 3ai
$^1$H NMR spectrum of 3aj

$^{13}$C NMR spectrum of 3aj
$^1$H NMR spectrum of 3ak

3ak

$^{13}$C NMR spectrum of 3ak

3ak
$^1$H NMR spectrum of 4

$\text{OTf}$

$\text{Ph}$

$\text{4}$

$^1$H NMR spectrum of 5

$\text{Ph}$

$\text{Ph}$

$\text{5}$
$^1$H NMR spectrum of 6

![NMR Spectrum](image-url)