Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

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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1. General information

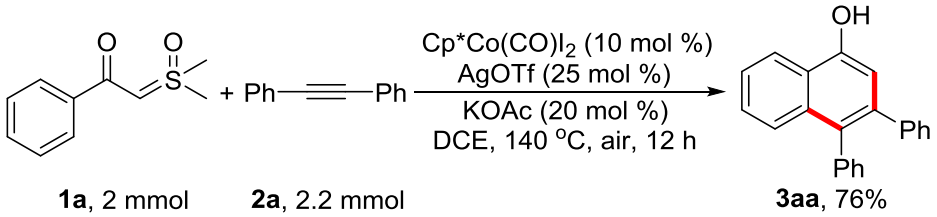
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The Cp*Co(CO)I_2[1] and sulfoxonium ylides[2] were prepared according to the previous reports. Products were purified by column chromatography on 200-300 mesh silica gel, SiO_2. ^1H and ^{13}C 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.

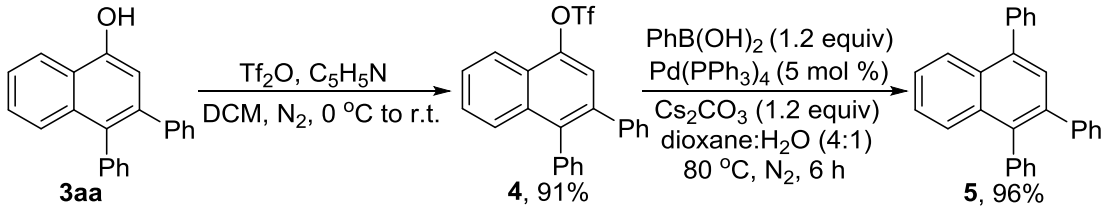
Sulfoxonium ylide **1** (0.2 mmol, 1.0 equiv), alkyne **2** (0.22 mmol, 1.1 equiv), Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), AgOTf (12.8 mg, 0.05 mmol, 25 mol %), KOAc (3.9 mg, 0.04 mmol, 20 mol %) and DCE (1.0 mL) were added to a 35 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. Then the flask was sealed under air and stirred at 140 ^oC 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.

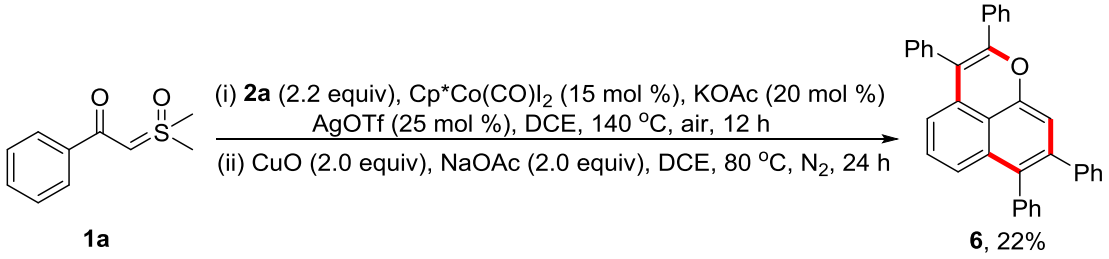


Under N_2, a 25 mL Schlenk flask was charged successively with **3aa** (296.1 mg, 1.0 mmol, 1.0 equiv), dry DCM (3.0 mL) and pyridine (0.12 mL, 1.5 mmol, 1.5 equiv). The solution was cooled to 0 °C in an ice bath, and treated with dropwise addition of triflic anhydride (0.2 mL, 1.2 mmol, 1.2 equiv). 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), $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 5 mol %), phenylboronic acid (29.3 mg, 0.24 mmol, 1.2 equiv), and Cs_2CO_3 (78.2 mg, 0.24 mmol, 1.2 equiv) in 1,4-dioxane (0.75 mL) and H_2O (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 Et_2O (2 mL) and filtered through a short pad of silica gel, which then was washed with more Et_2O (3 × 10 mL). The combined filtrates were dried by Na_2SO_4 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.



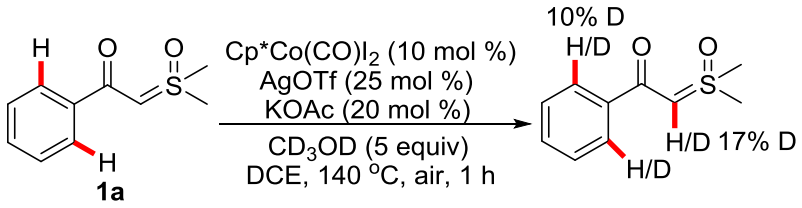
1a **6**, 22%

Sulfoxonium ylide **1a** (39.2 mg, 0.2 mmol, 1.0 equiv), diphenylacetylene **2a** (78.4 mg, 0.44 mmol, 2.2 equiv), $Cp^*Co(CO)I_2$ (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 N_2 and stirred at 80 ^oC for 24 h. It was then

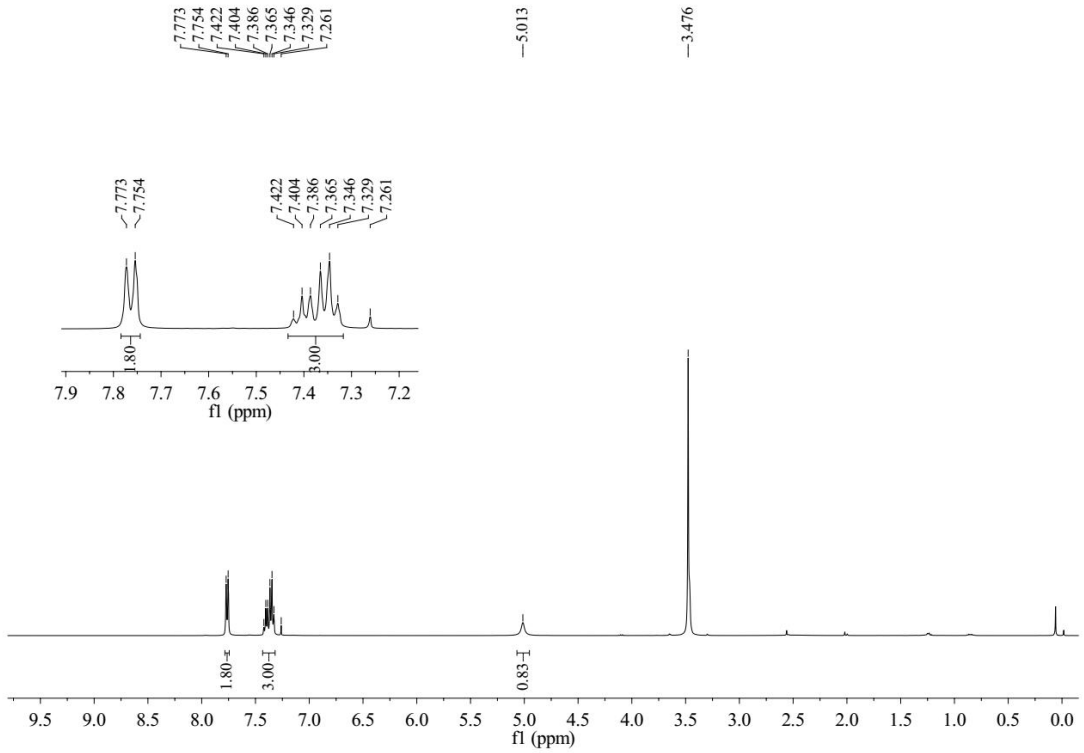
cooled to room temperature, the solvent was removed in vacuum. Purification by column chromatography on silica gel (eluent: pure petroleum ether) to afford the product **6** (20.7 mg, 22% yield).

2.5 Control experiments.

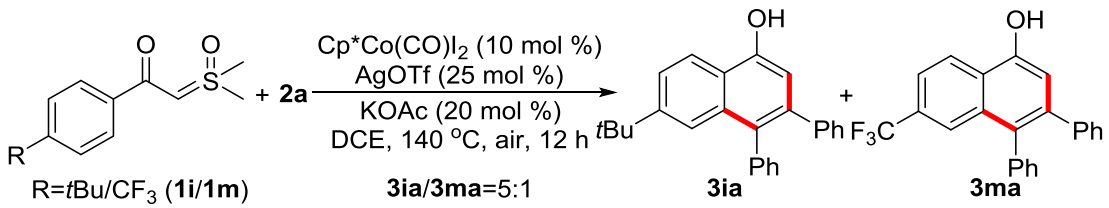
2.5.1 H/D exchange experiment.



Sulfoxonium ylide **1a** (39.2 mg, 0.2 mmol, 1.0 equiv), Cp*Co(CO)I_2 (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 %), CD_3OD (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 ^oC 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 ^1H NMR of the isolated product shows deuterium incorporation of about 10% in *ortho* position with respect to carbonyl of **1a**.

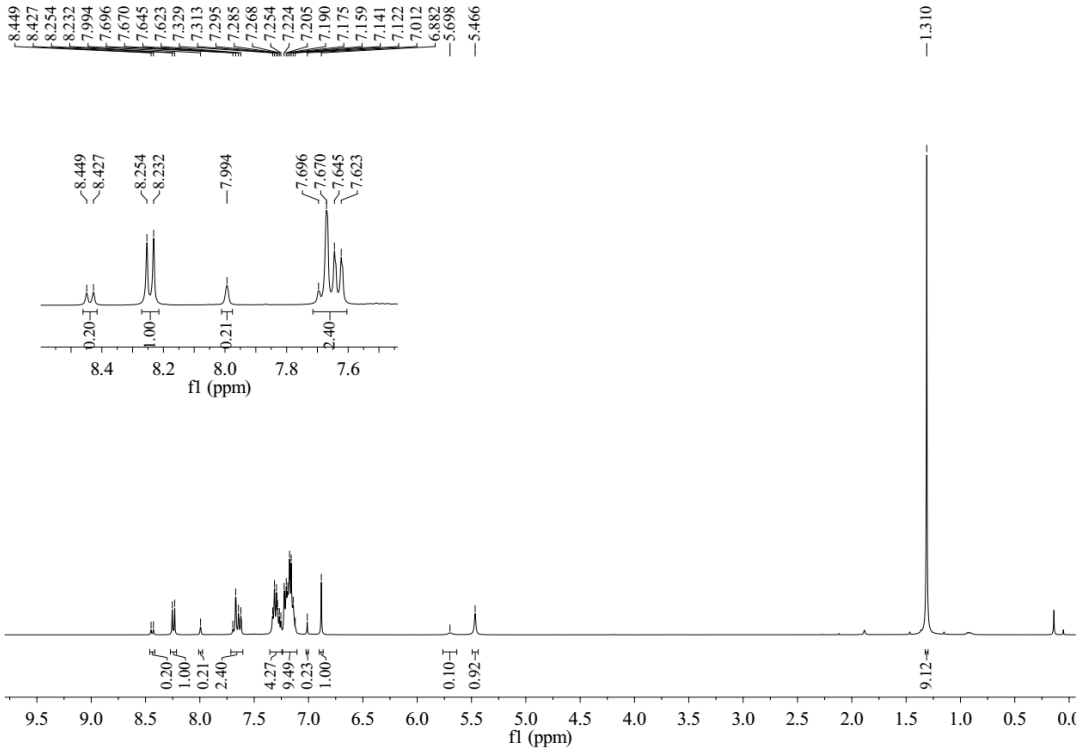


2.5.2 Intermolecular competition experiment between different Sulfoxonium ylides with 2a.

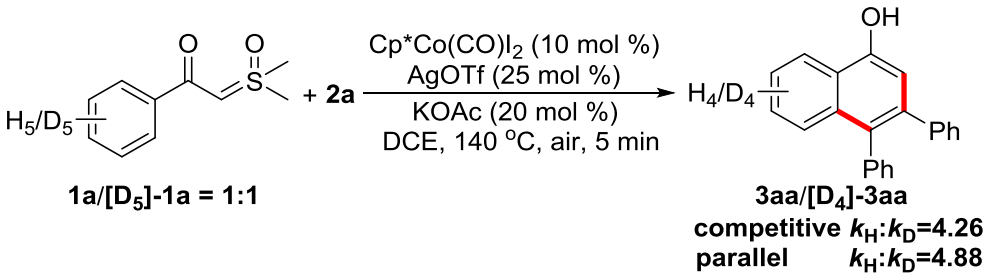


Sulfoxonium ylide **1i** (50.4 mg, 0.2 mmol, 1.0 equiv), sulfoxonium ylide **1m** (52.8 mg, 0.2 mmol, 1.0 equiv), diphenylacetylene **2a** (35.7 mg, 0.2 mmol, 1.0 equiv), Cp*Co(CO)I_2 (9.5 mg, 0.02 mmol, 10 mol %), AgOTf (12.8 mg, 0.05 mmol, 25 mol %), KOAc (3.9 mg, 0.04 mmol, 20 mol %) and DCE (1.0 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 ^{o}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.



1a/[D$_5$]-1a = 1:1

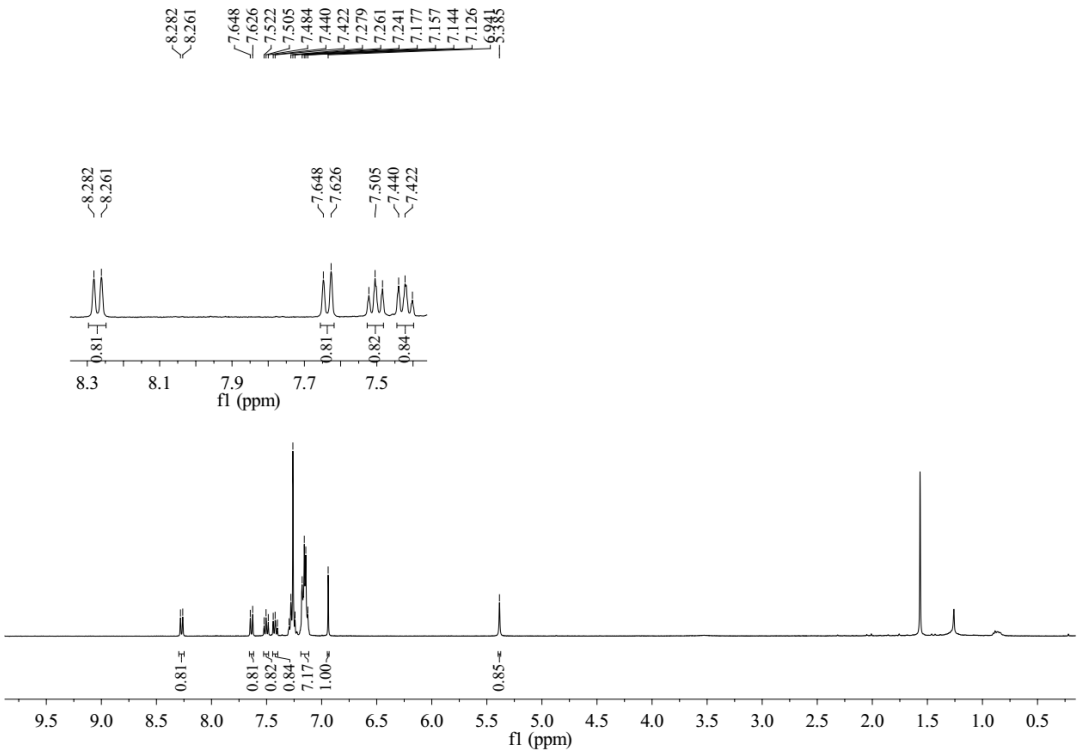
3aa/[D$_4$]-3aa

competitive k_H:k_D=4.26

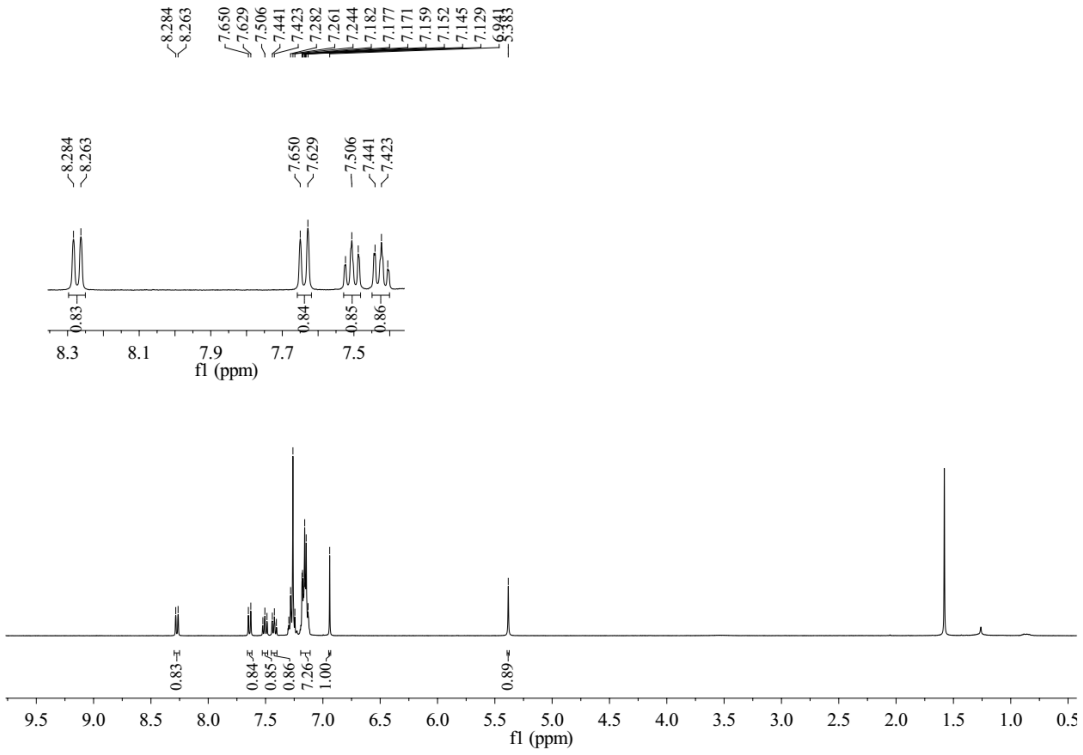
parallel k_H:k_D=4.88

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)I$_2$ (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)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 ^oC 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-Diphenylnaphthalen-1-ol (**3aa**)*[2]. 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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), 7.33-7.27 (m, 3H), 7.21-7.14 (m, 7H), 6.93 (s, 1H), 5.59 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 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-diphenylnaphthalen-1-ol (**3ba**)*[2]. 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ -121.8.

8-Methyl-3,4-diphenylnaphthalen-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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-diphenylnaphthalen-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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-diphenylnaphthalen-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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ

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-diphenylnaphthalen-1-ol (**3fa**)*[2]. 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-Triphenylnaphthalen-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 ^{o}C; ^{1}H NMR (400 MHz, acetone-d_6): δ 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): δ 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-diphenylnaphthalen-1-ol (**3ha**)*[2]. 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-diphenylnaphthalen-1-ol (***3ia***)[2]. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded **3ia** as a white solid (59.9 mg, 85% yield); mp 144-146 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-diphenylnaphthalen-1-ol (***3ja***)[2]. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded **3ja** as a white solid (59.4 mg, 91% yield); mp 197-199 ^oC; ^1H NMR (400 MHz, acetone-d_6): δ 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): δ 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-diphenylnaphthalen-1-ol (***3ka***)[2]. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded **3ka** as a white solid (45.9 mg, 73% yield); mp 185-187 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ -112.9.

*6-Chloro-3,4-diphenylnaphthalen-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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ -62.3.

*6-Nitro-3,4-diphenylnaphthalen-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 ^{o}C; ^{1}H NMR (400 MHz, acetone-d_6): δ 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): δ 153.6, 147.2, 142.4, 142.2,

138.9, 133.8, 132.7, 131.7, 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-diphenylnaphthalen-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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 $C_{22}H_{13}Cl_2O$ $[M - H]^-$ 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-tolylnaphthalen-1-ol (**3ab**)*[2]. 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-tolylnaphthalen-1-ol (**3ac**)*[2]. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=20:1, v/v) afforded **3ac** as a white solid (49.9 mg, 77% yield); mp 156-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 150.4, 139.0, 138.3, 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 (**3ad**)*[2]. Purification by column chromatography on silica gel (eluent: petroleum ether:ethyl acetate=15:1, v/v) afforded **3ad** as a white solid (60.5 mg, 85% yield); mp 197-199 ^{o}C; ^{1}H NMR (400 MHz, acetone-d_6): δ 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): δ 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 (**3ae**)*[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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{22}H_{13}Cl_2O$ $[M - H]^-$ 363.0349, found 363.0350.

*3,4-Bis(4-(trifluoromethyl)phenyl)naphthalen-1-ol (**3ag**)*[2]. 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ -62.4, -62.5.

*[2,1':2',2''-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 ^{o}C; ^{1}H NMR (400 MHz, acetone-d_6): δ 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): δ 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 $C_{30}H_{19}O$ $[M - H]^-$ 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 ^{o}C; ^{1}H NMR (400 MHz, acetone-d_6): δ 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): δ 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 $C_{24}H_{20}NO_3S$ $[M - H]^-$ 402.1169, found 402.1172.

*4-Methyl-3-phenylnaphthalen-1-ol (**3aj**)*[2]. 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 ^{o}C; ^{1}H NMR (400 MHz, acetone-d_6): δ 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): δ 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-Phenylnaphthalen-1-ol (**3ak**)*[3]. 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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-Diphenylnaphthalen-1-yl trifluoromethanesulfonate (**4**).*[2] 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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-Triphenylnaphthalene (**5**).*[4] 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 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 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).

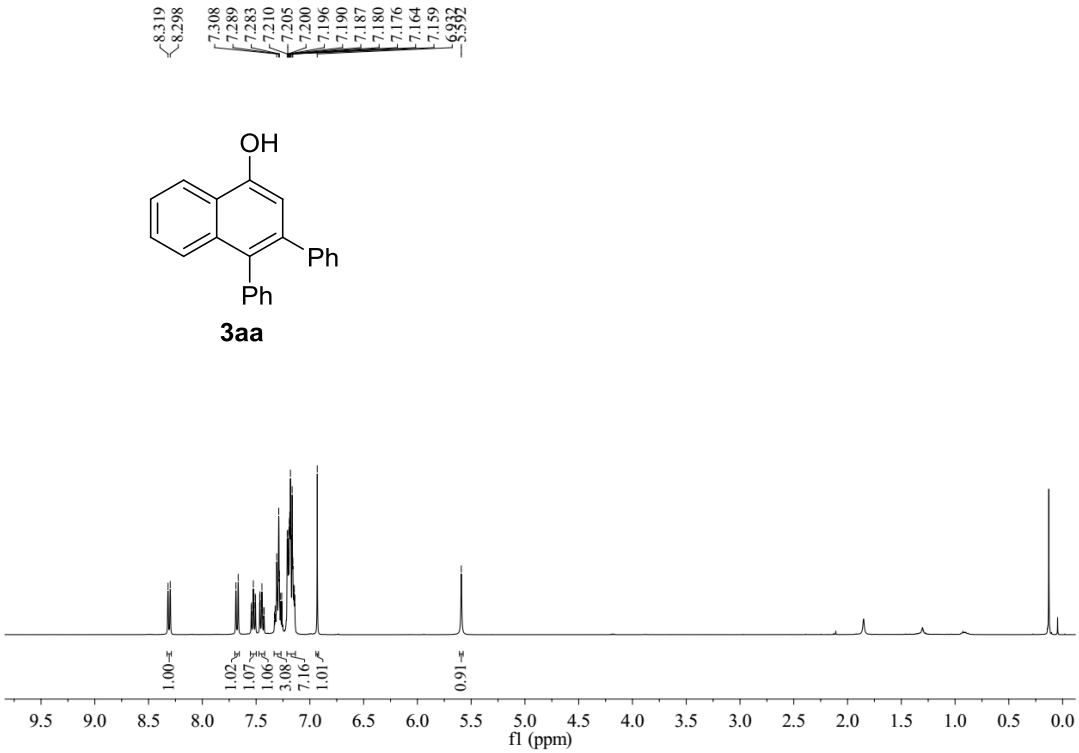
*2,3,7,8-Tetraphenylbenzo[de]chromene (**6**).*[5] Purification by column chromatography on silica gel (eluent: pure petroleum ether) afforded **6** as a yellow solid (20.7 mg, 22% yield); mp 249-251 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.38 (m, 2H), 7.36-7.32 (m, 3H), 7.29-7.25 (m, 5H), 7.22-7.14 (m, 11H), 7.11-7.07 (m, 1H), 7.04 (s, 1H), 6.49 (d, J = 7.2 Hz, 1H).

References

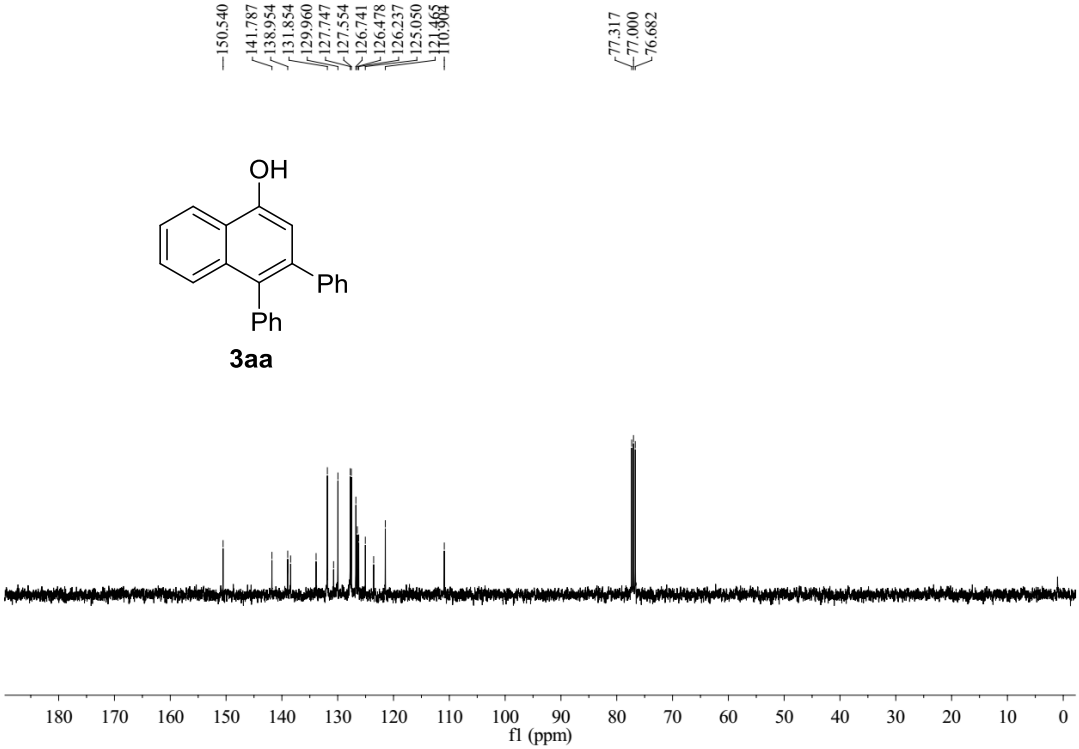
1. B. Sun, T. Yoshino, S. Matsunaga and M. Kanai, *Adv. Synth. Catal*., 2014, **356**, 1491.
2. Y. Xu, X. Yang, X. Zhou, L. Kong and X. Li, *Org. Lett.*, 2017, **19**, 4307.
3. Z. Lou, S. Zhang, C. Chen, X. Pang, M. Li and L. Wen, *Adv. Synth. Catal.*, 2014, **356**, 153.
4. D. Wei, T.-J. Hu, C.-G. Feng and G.-Q. Lin, *Chin. J. Chem.*, 2018, **36**, 743.
5. Q. Wang, Y. Xu, X. Yang, Y. Li and X. Li, *Chem. Commun.*, 2017, **53**, 9640.

4. NMR spectrum

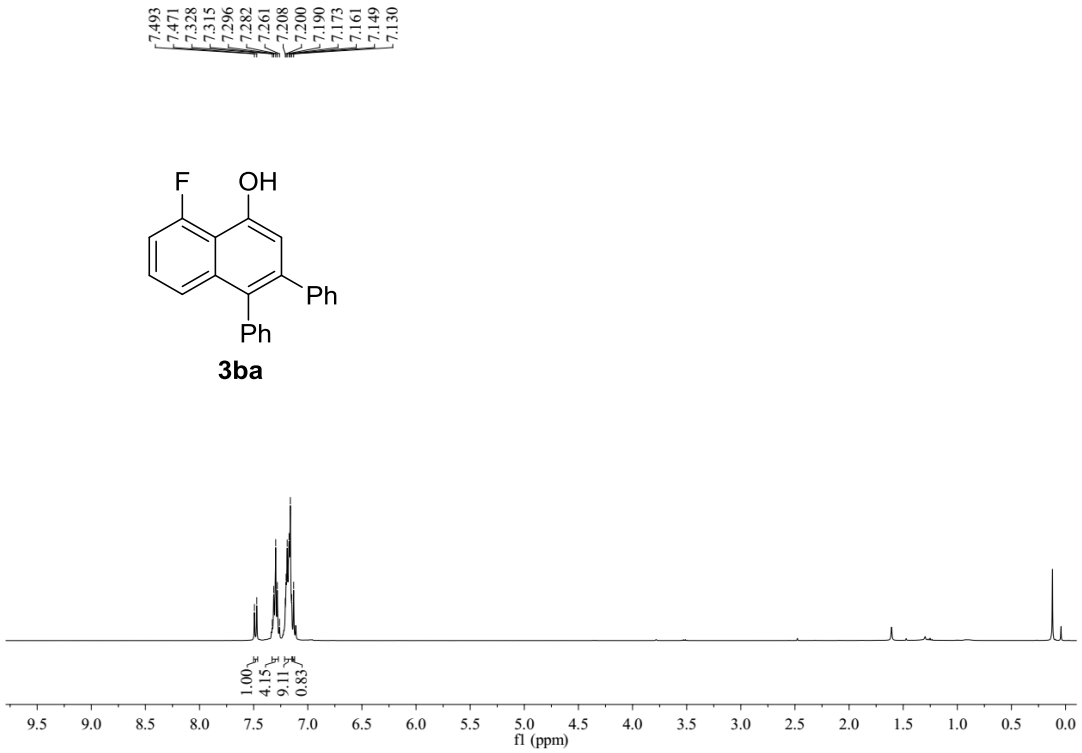
^{1}H NMR spectrum of **3aa**



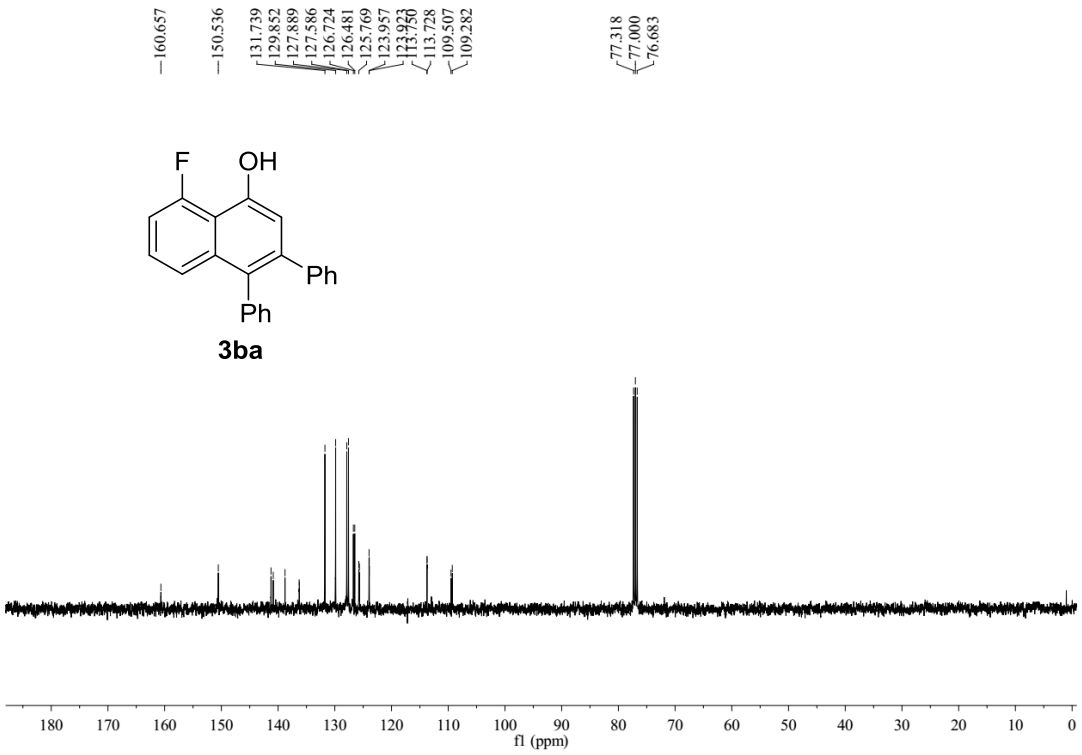
^{13}C NMR spectrum of **3aa**



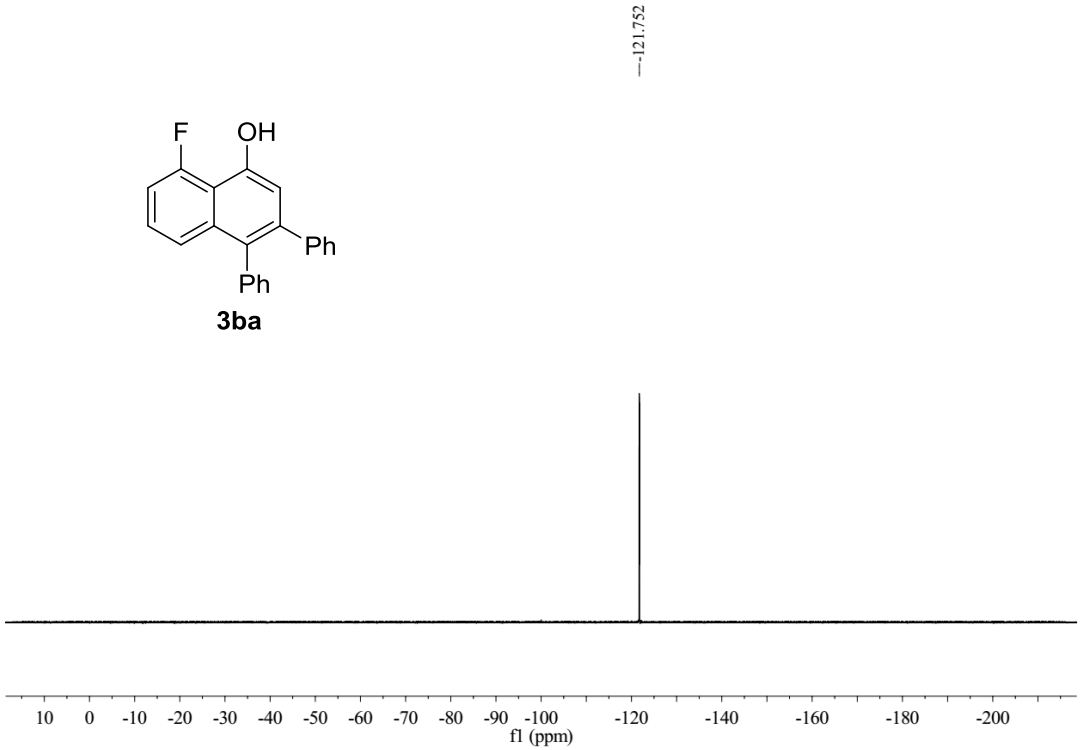
^{1}H NMR spectrum of **3ba**



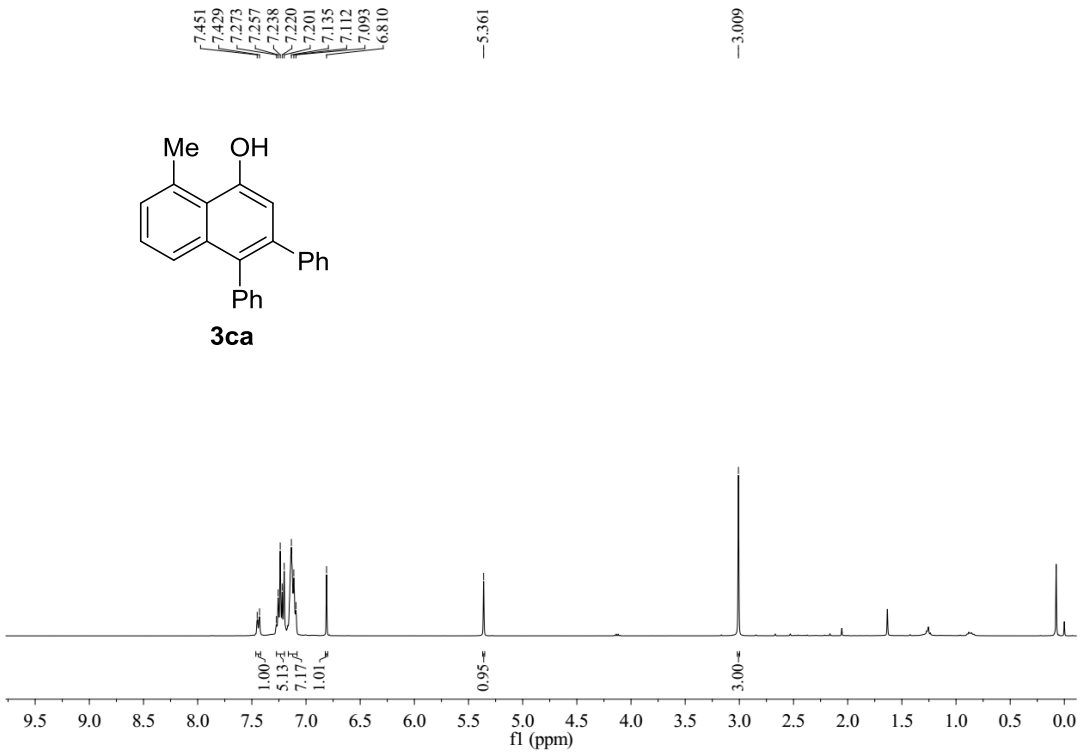
^{13}C NMR spectrum of **3ba**



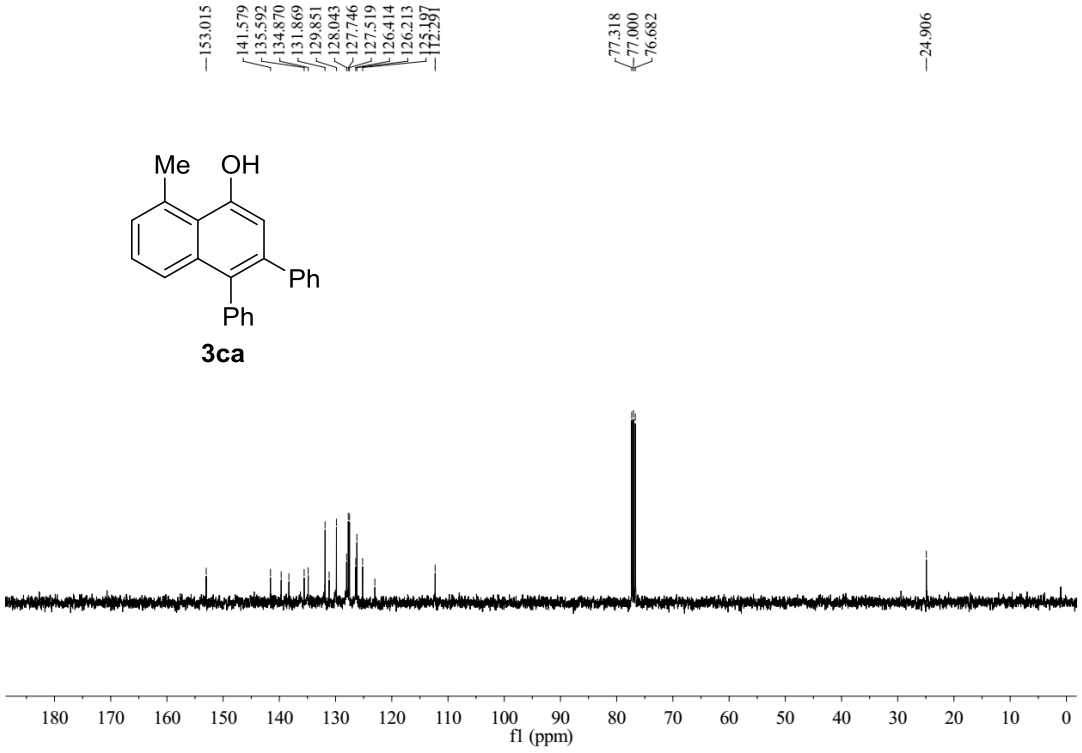
^{19}F NMR spectrum of **3ba**



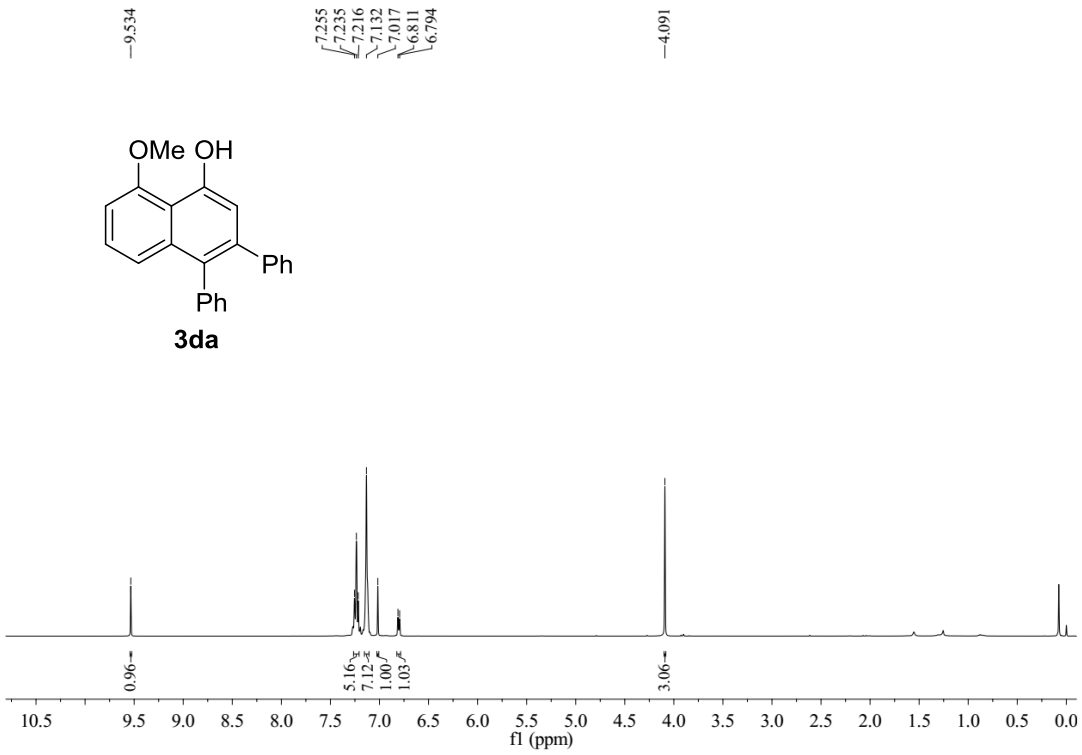
^{1}H NMR spectrum of **3ca**



^{13}C NMR spectrum of **3ca**



^{1}H NMR spectrum of **3da**



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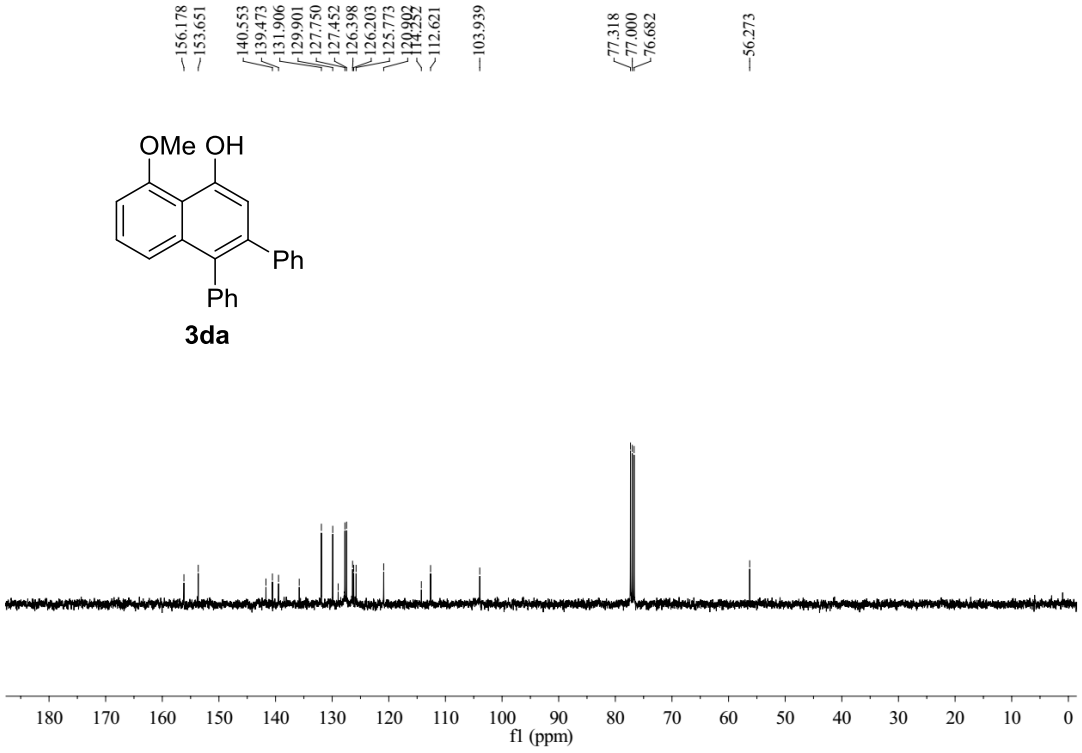

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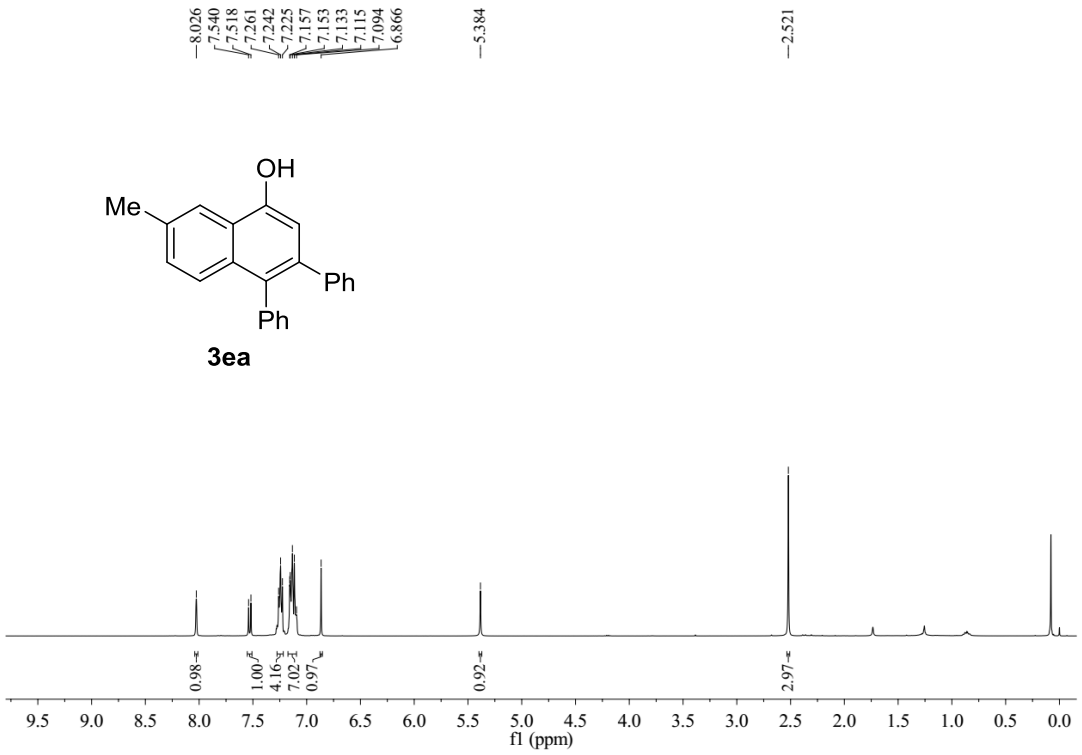

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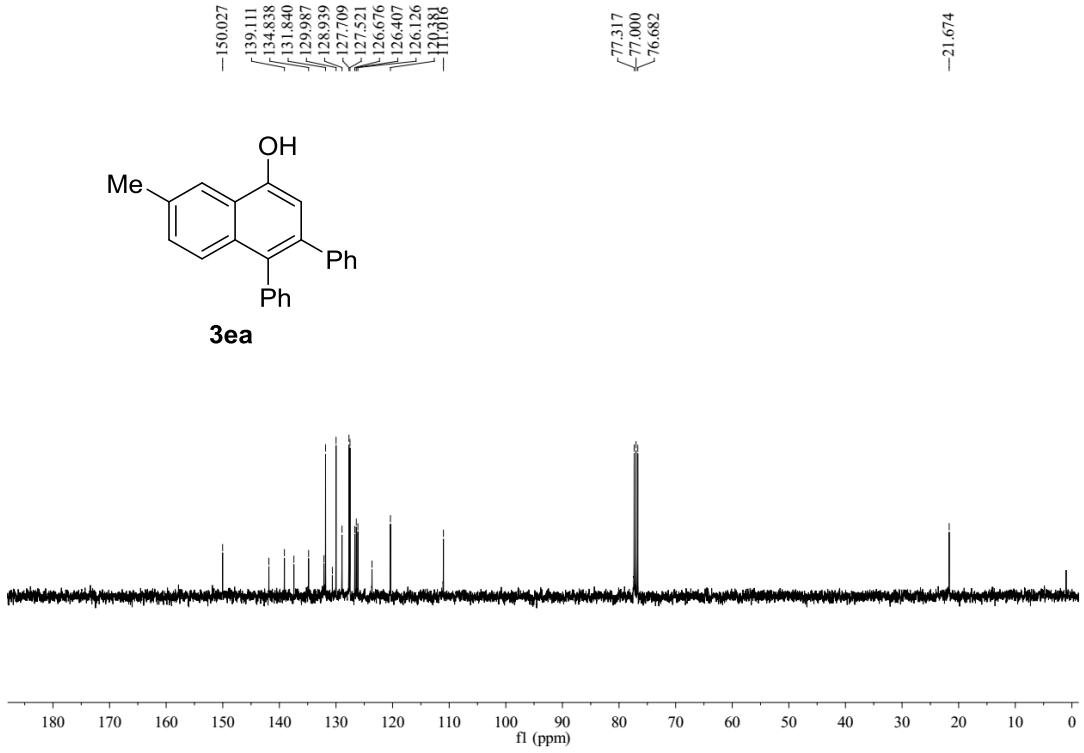
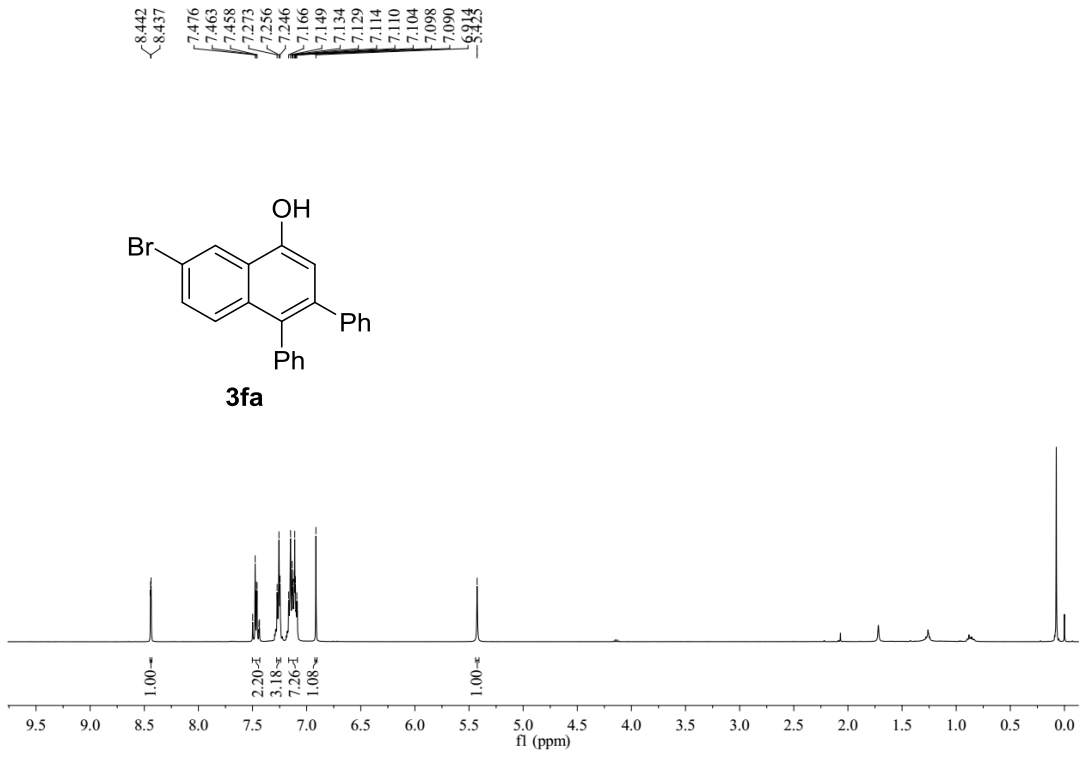
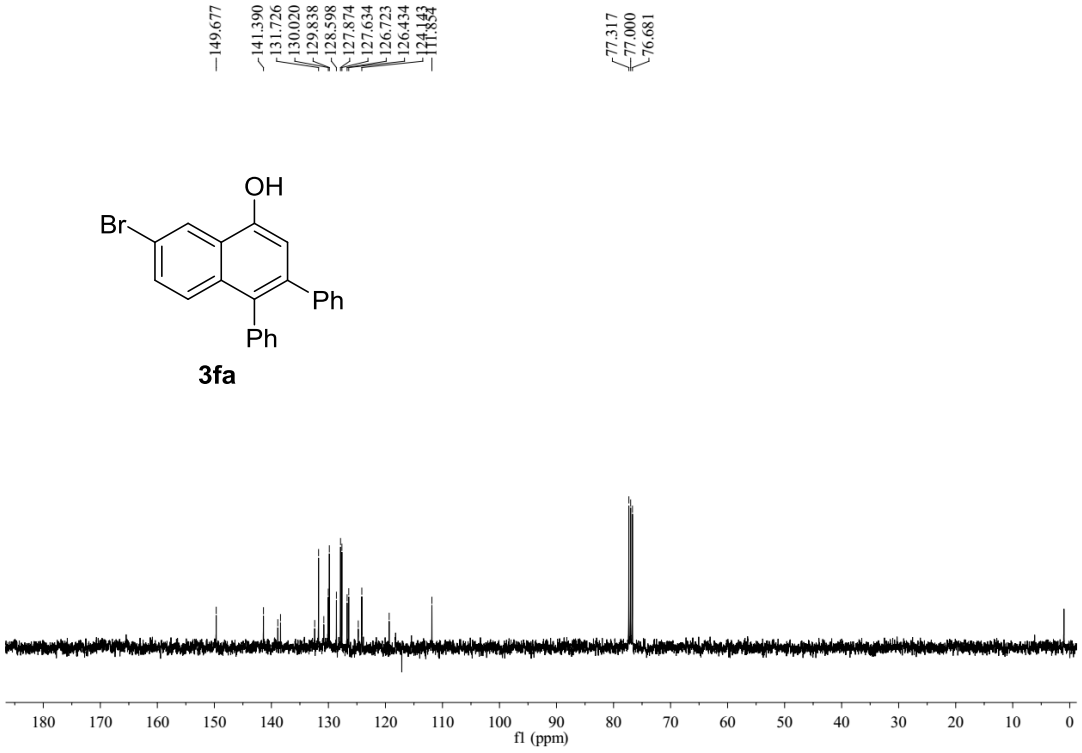


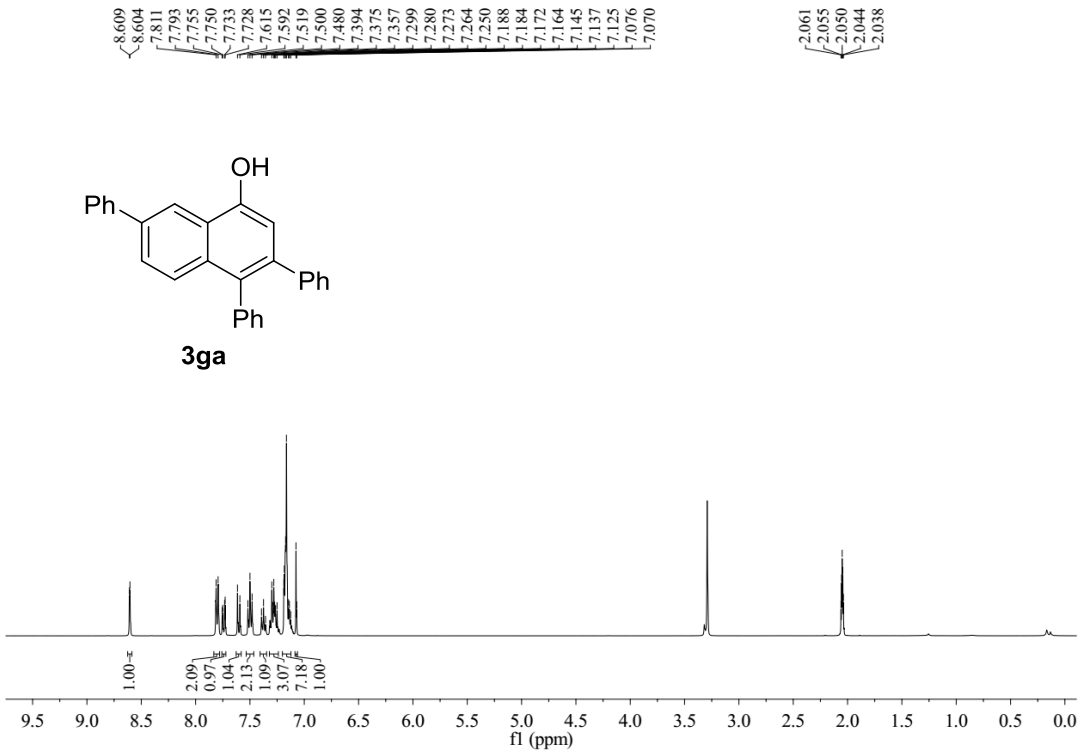
^{1}H NMR spectrum of **3fa**



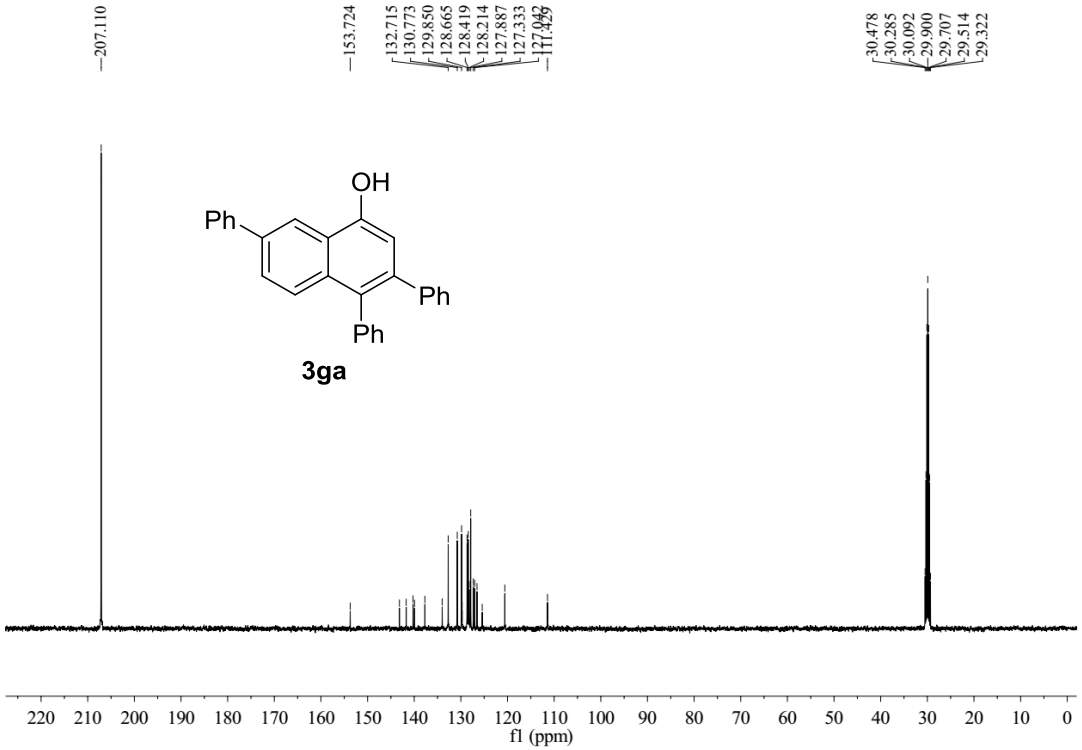
^{13}C NMR spectrum of **3fa**



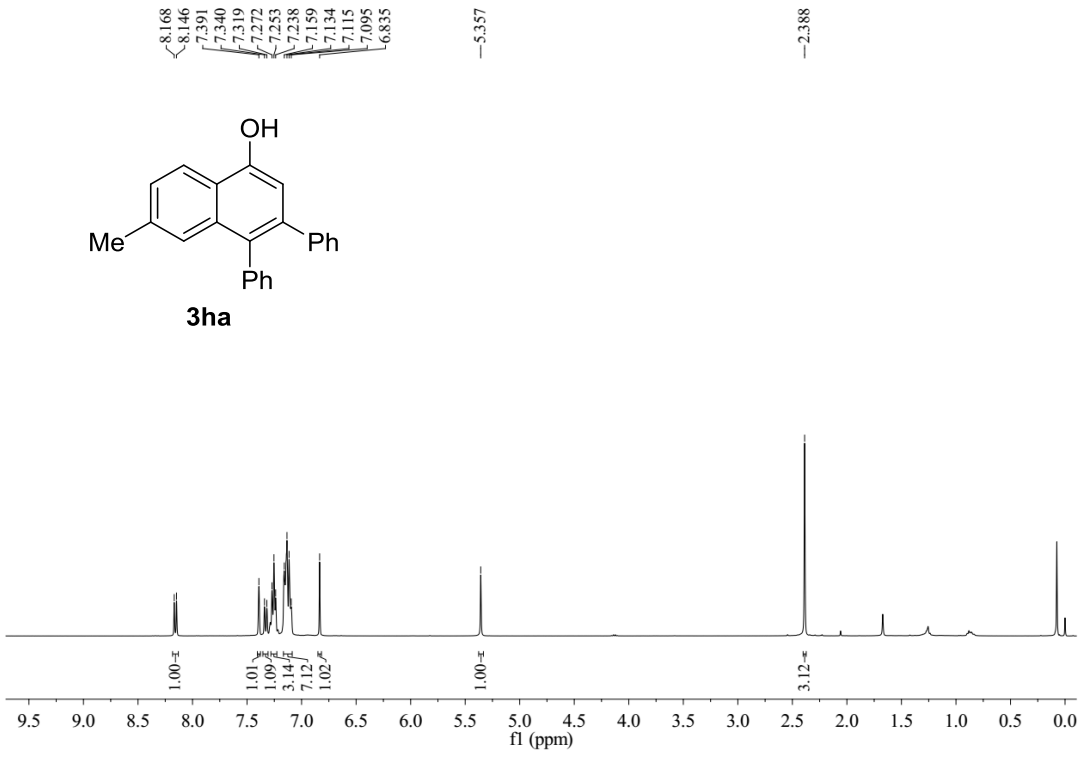
^{1}H NMR spectrum of **3ga**



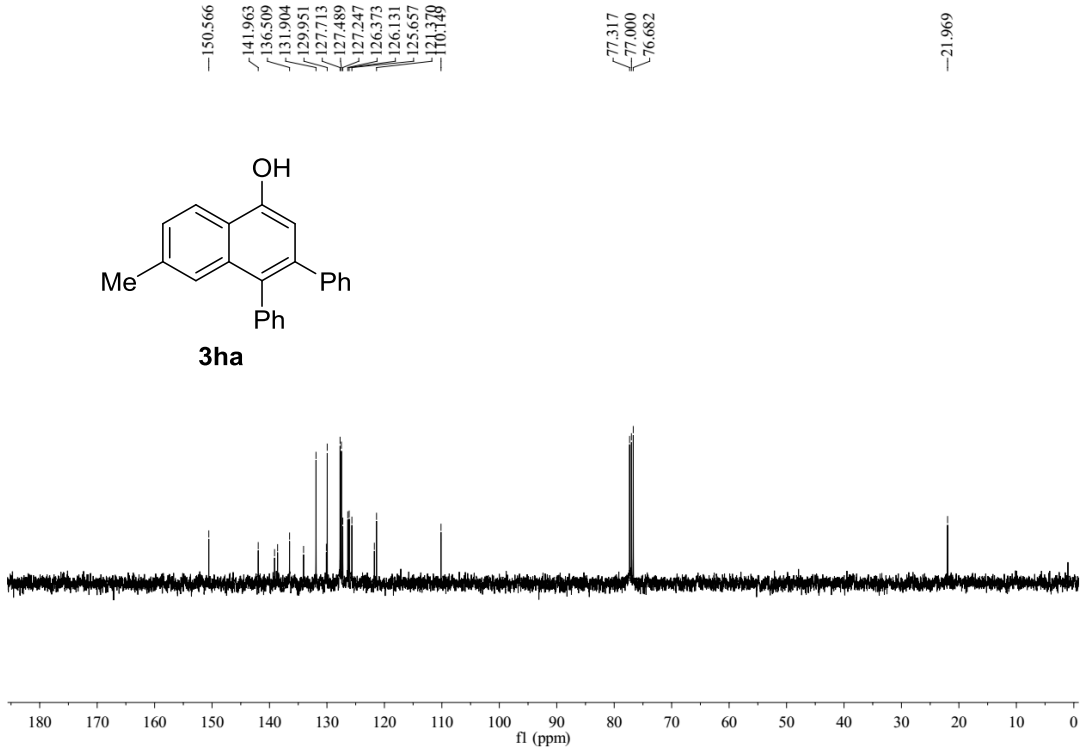
^{13}C NMR spectrum of **3ga**



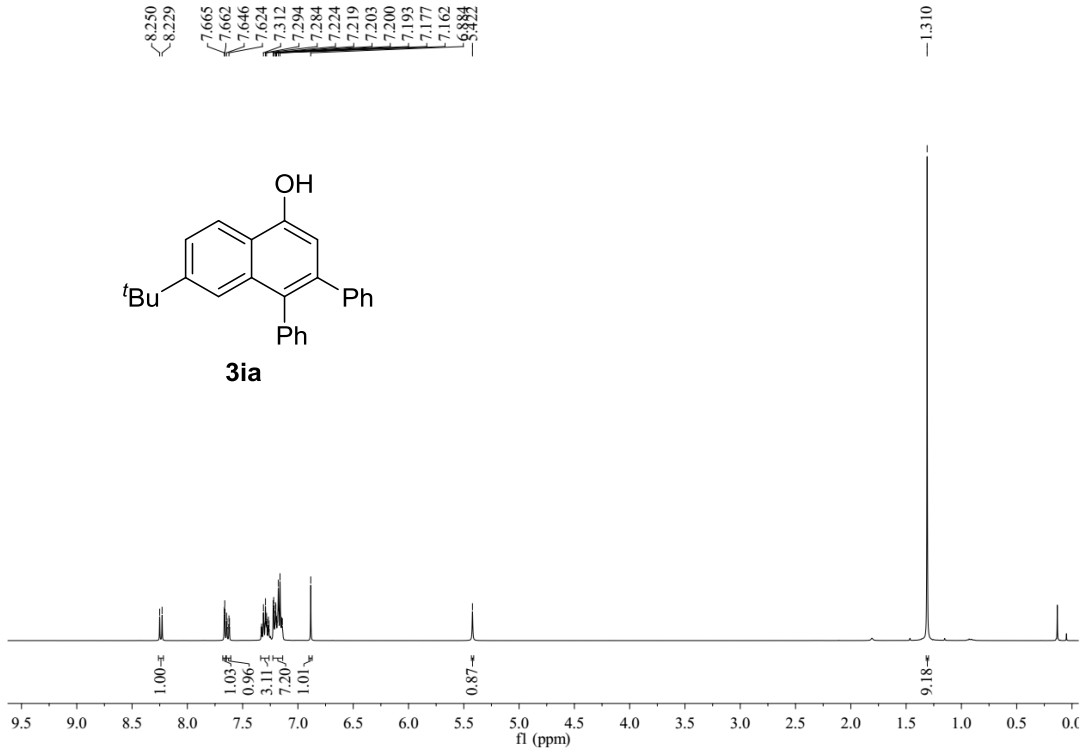
^{1}H NMR spectrum of **3ha**



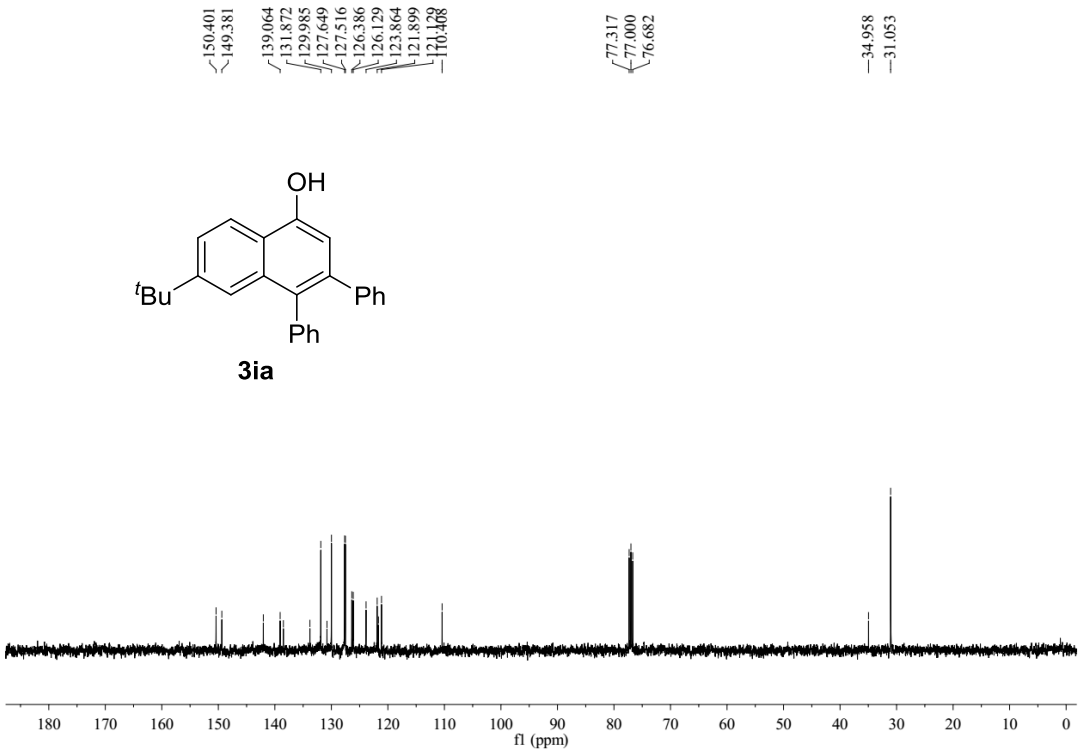
^{13}C NMR spectrum of **3ha**



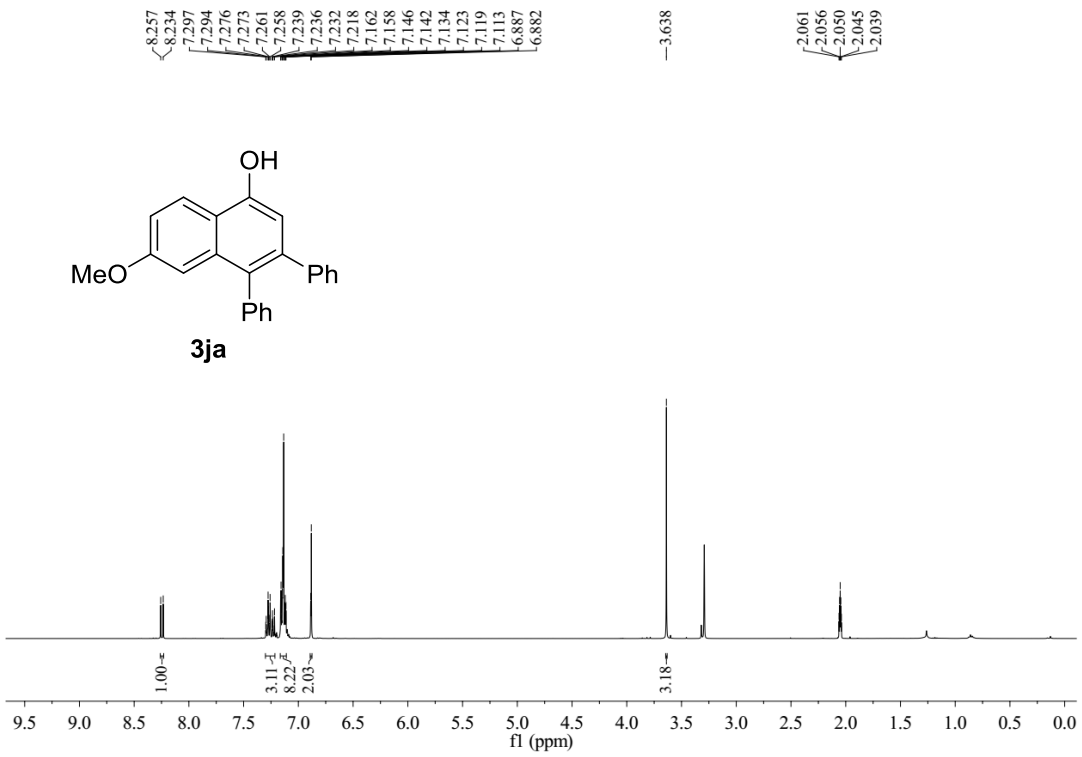
^{1}H NMR spectrum of **3ia**



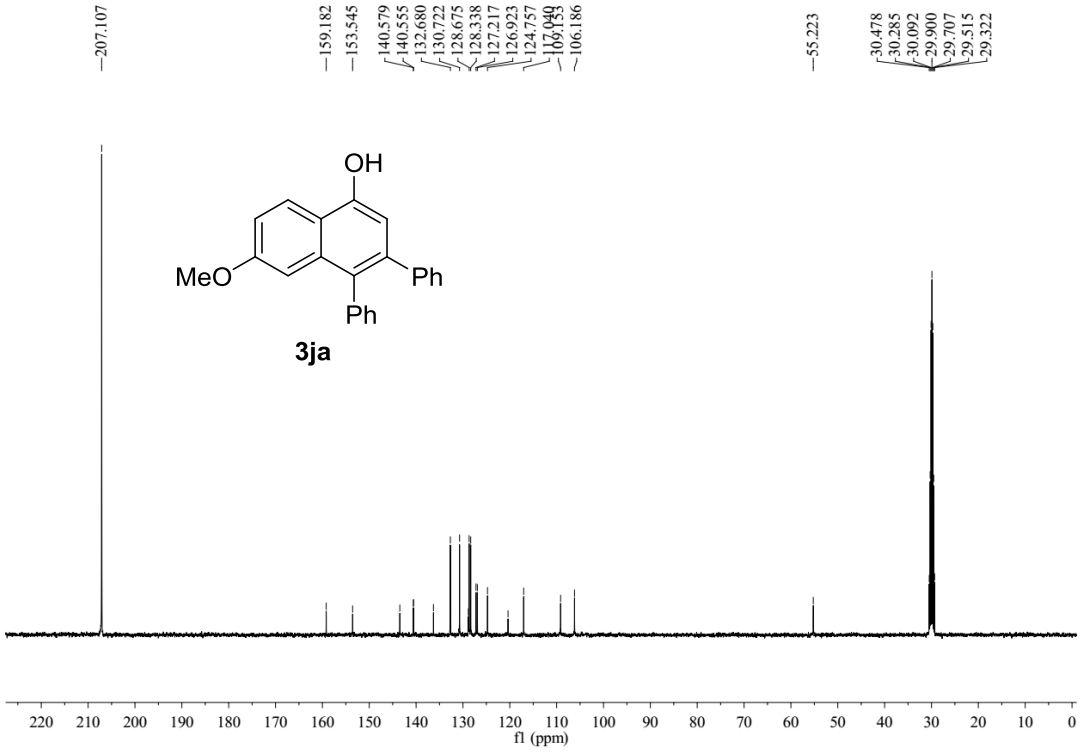
^{13}C NMR spectrum of **3ia**



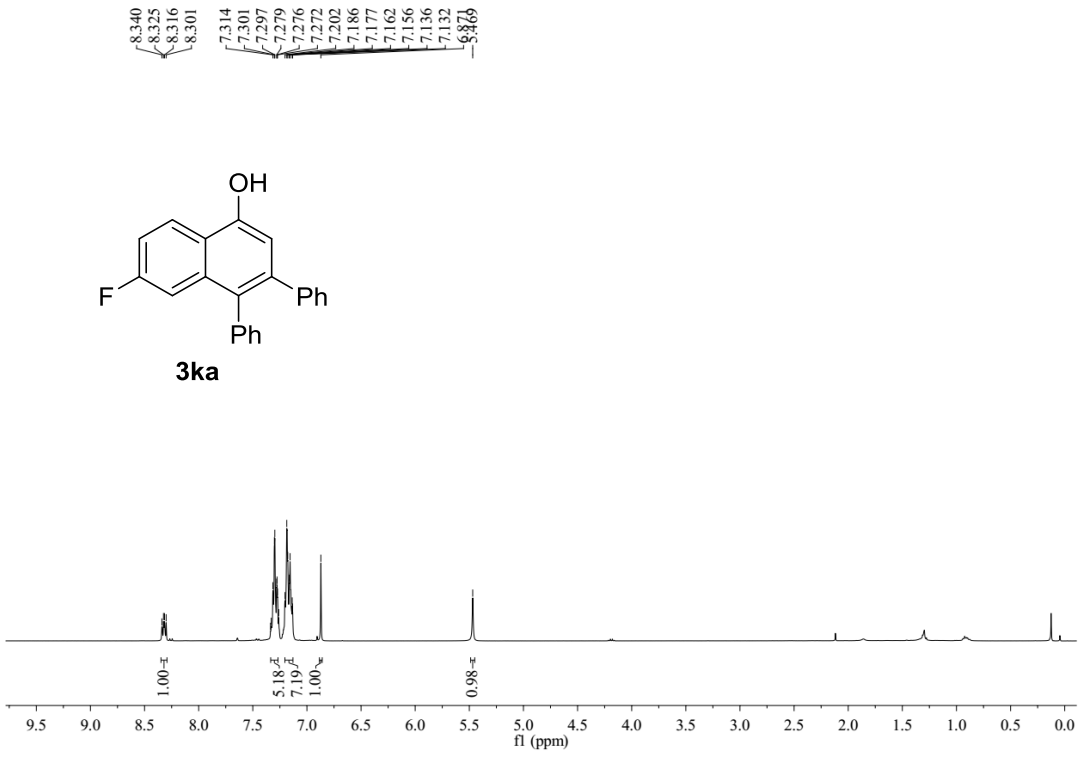
^{1}H NMR spectrum of **3ja**



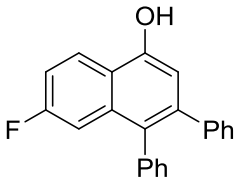
^{13}C NMR spectrum of **3ja**



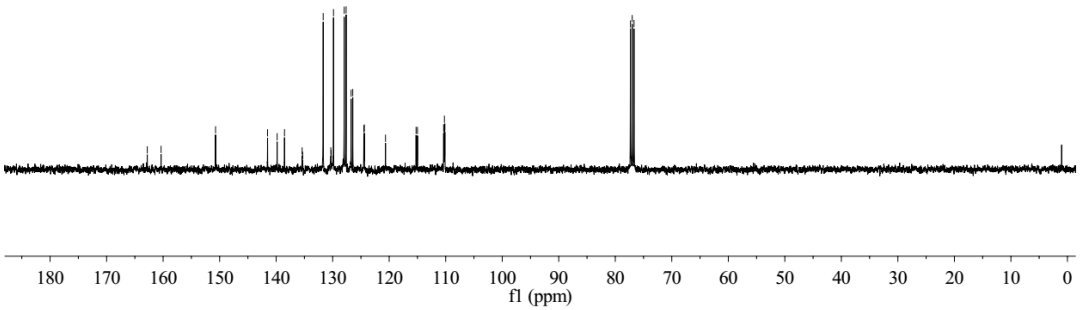
^{1}H NMR spectrum of **3ka**



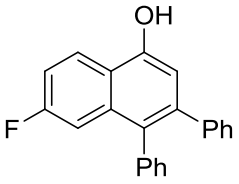
^{13}C NMR spectrum of **3ka**



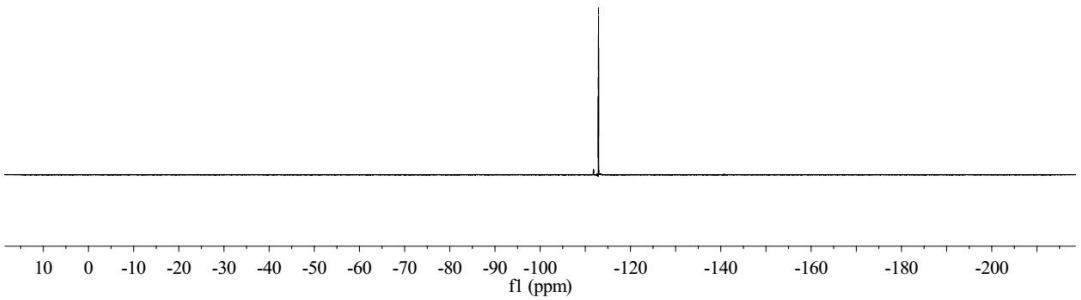
3ka



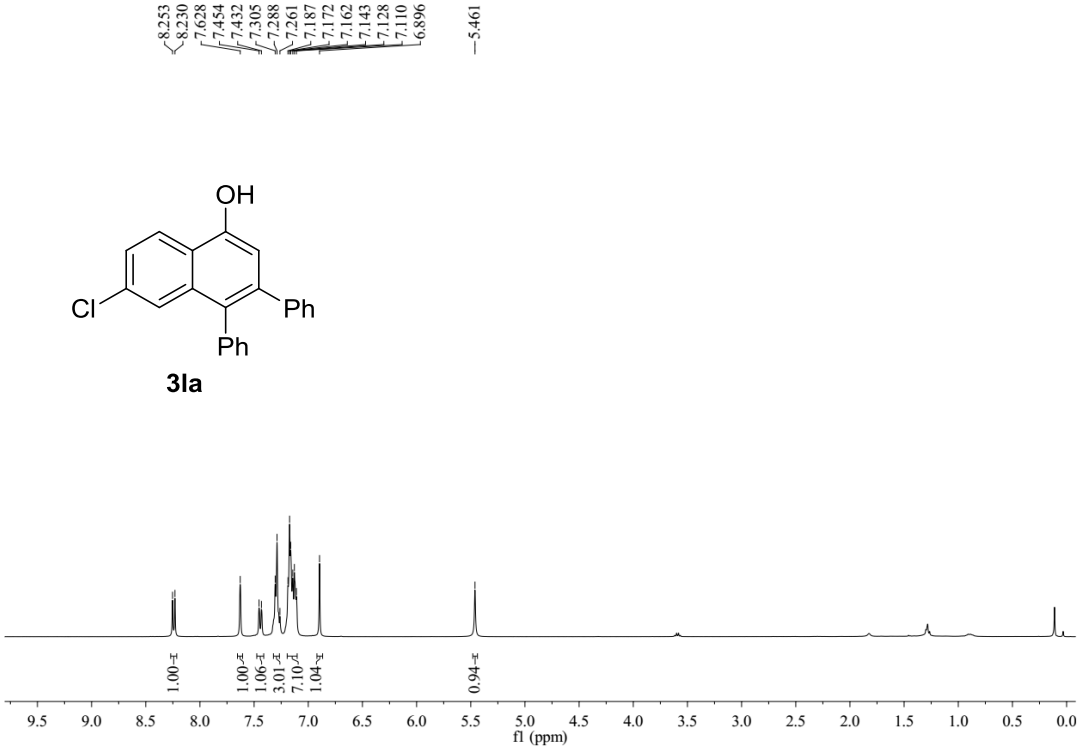
^{19}F NMR spectrum of **3ka**



3ka

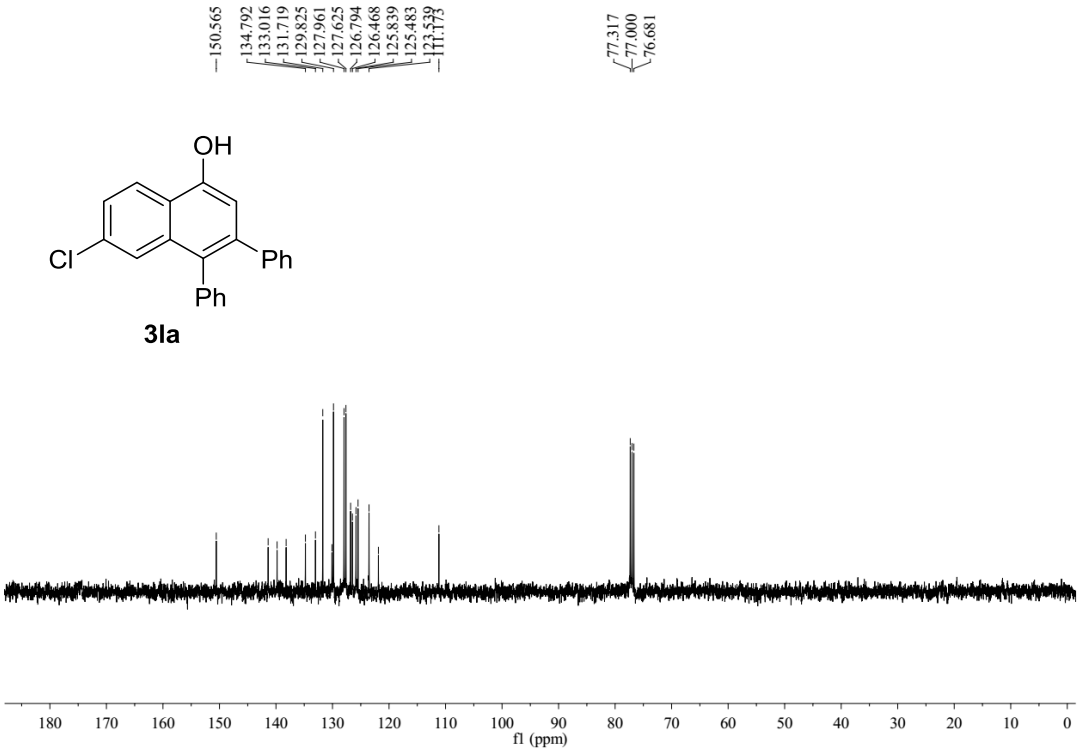


^{1}H NMR spectrum of **3la**



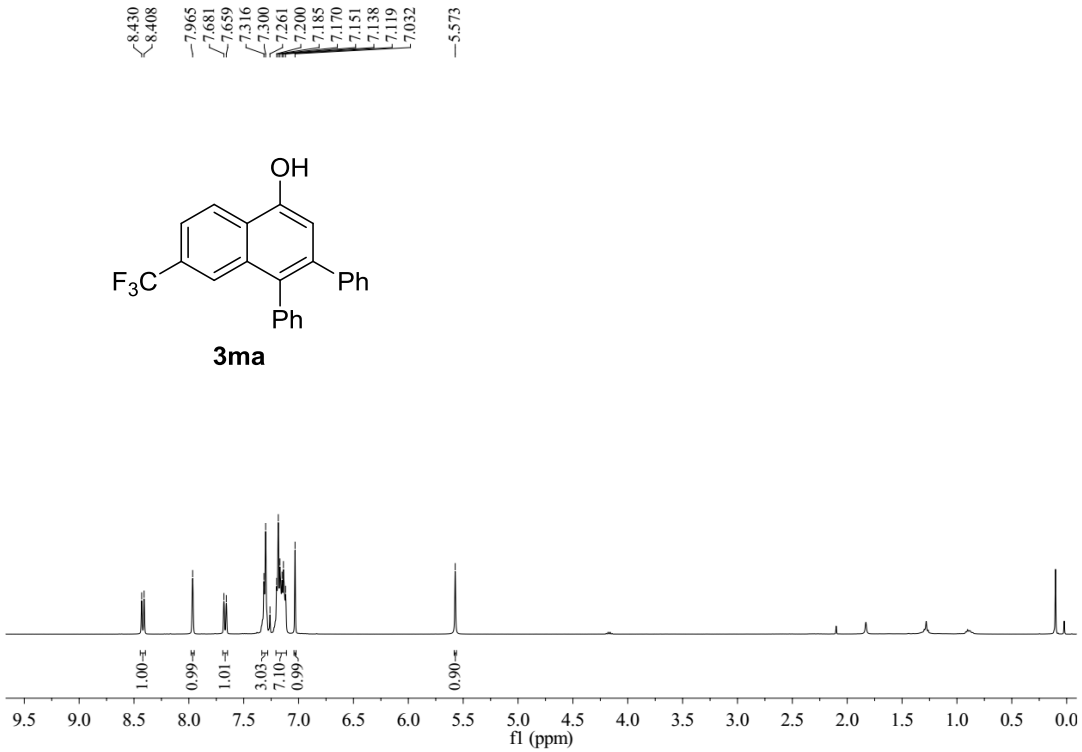
3la

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

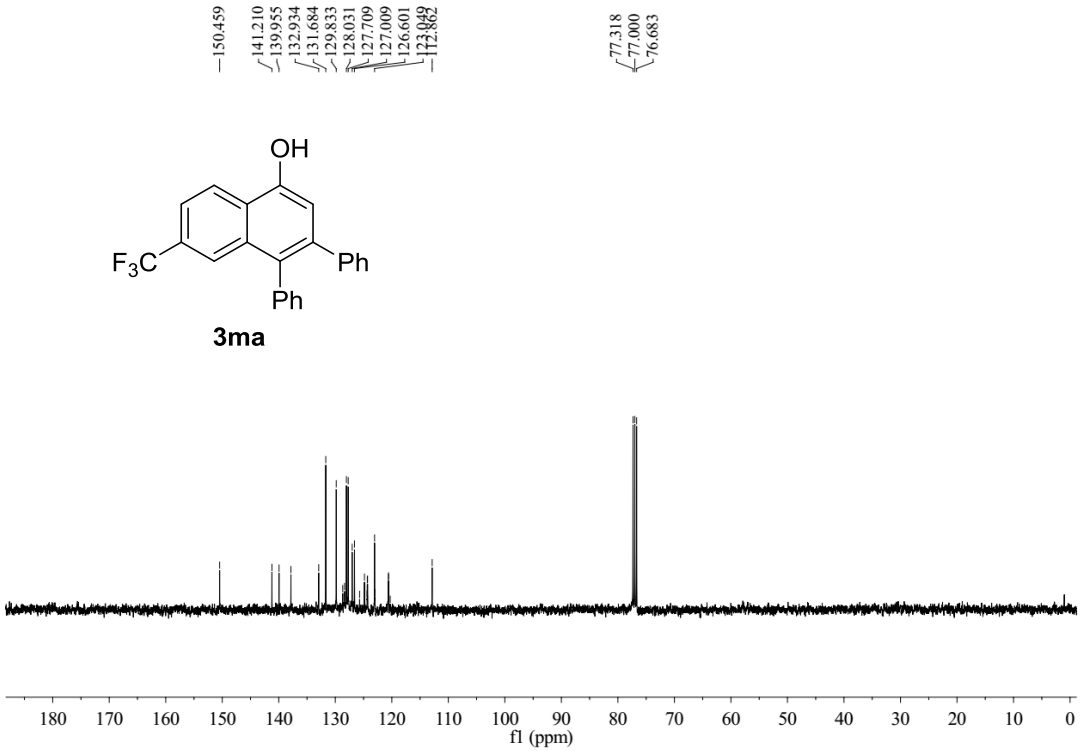


3la

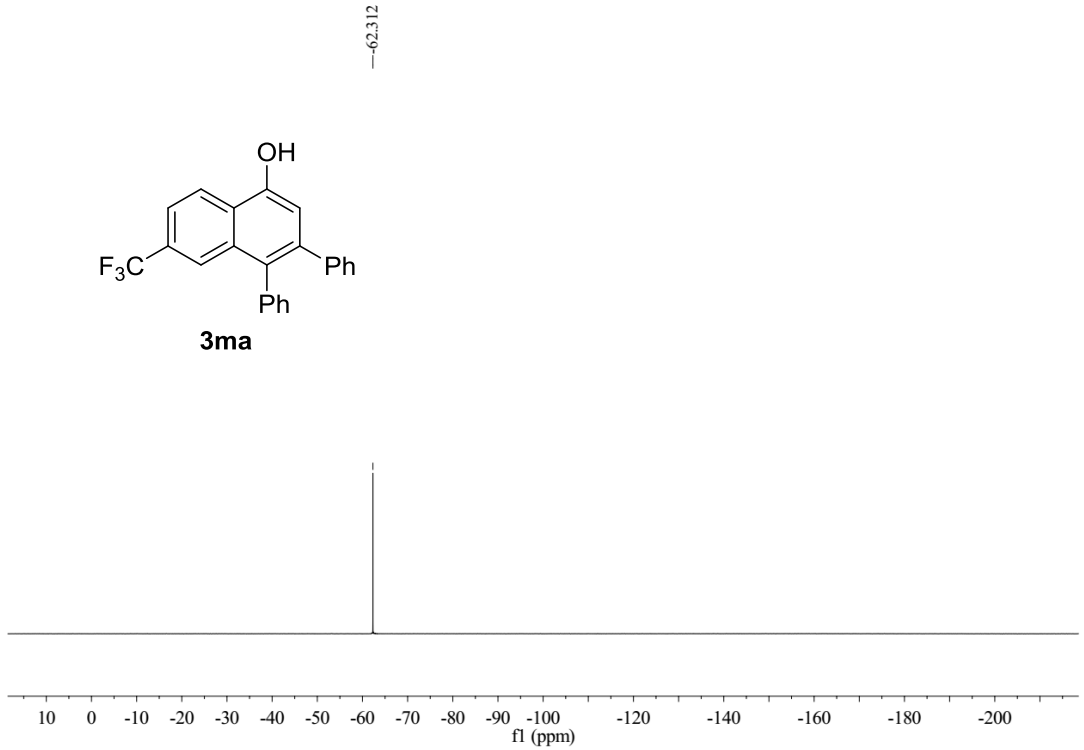
^{1}H NMR spectrum of **3ma**



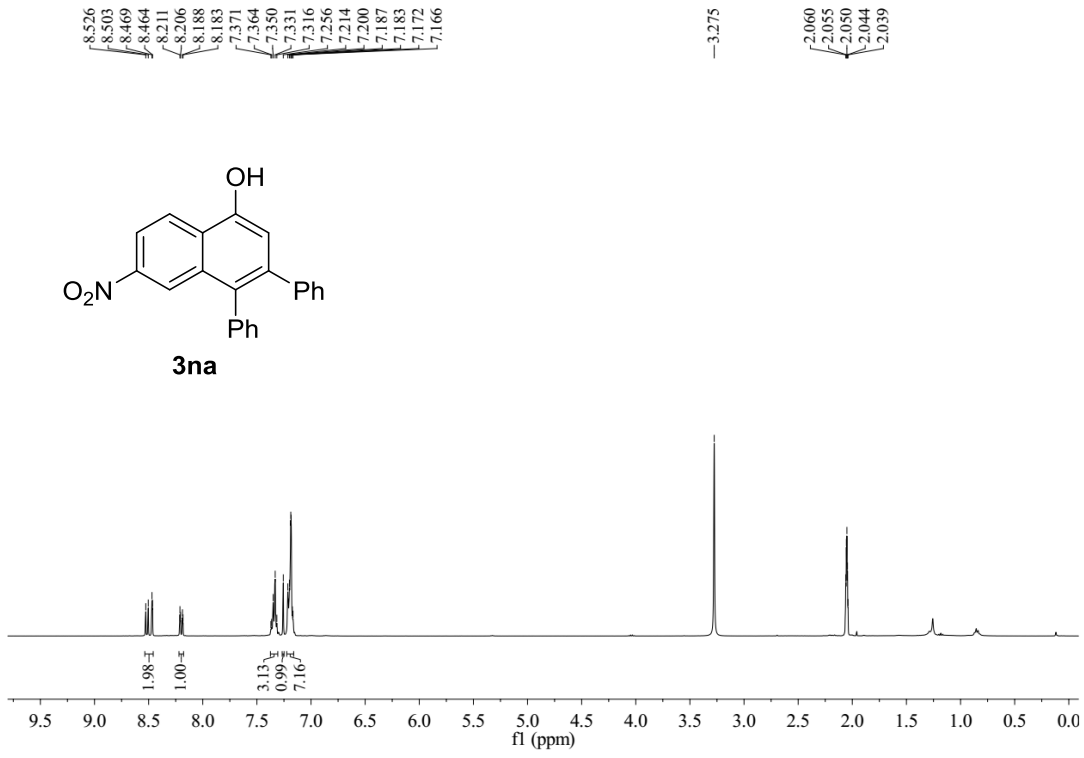
^{13}C NMR spectrum of **3ma**



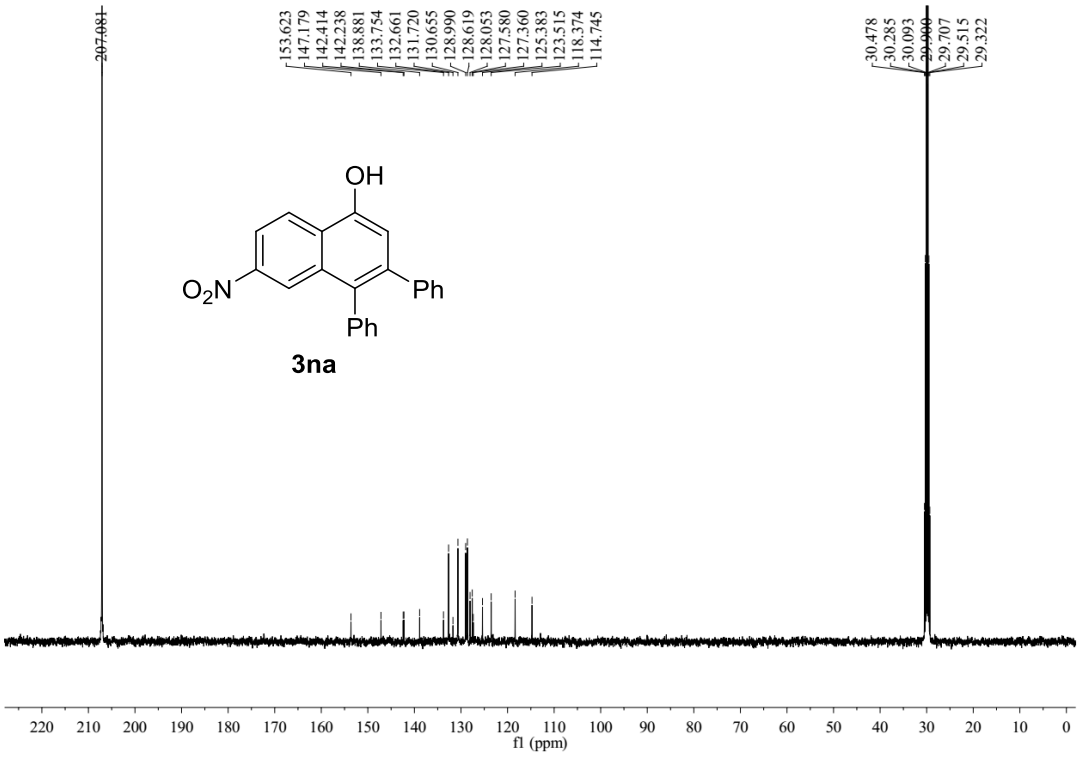
^{19}F NMR spectrum of **3ma**



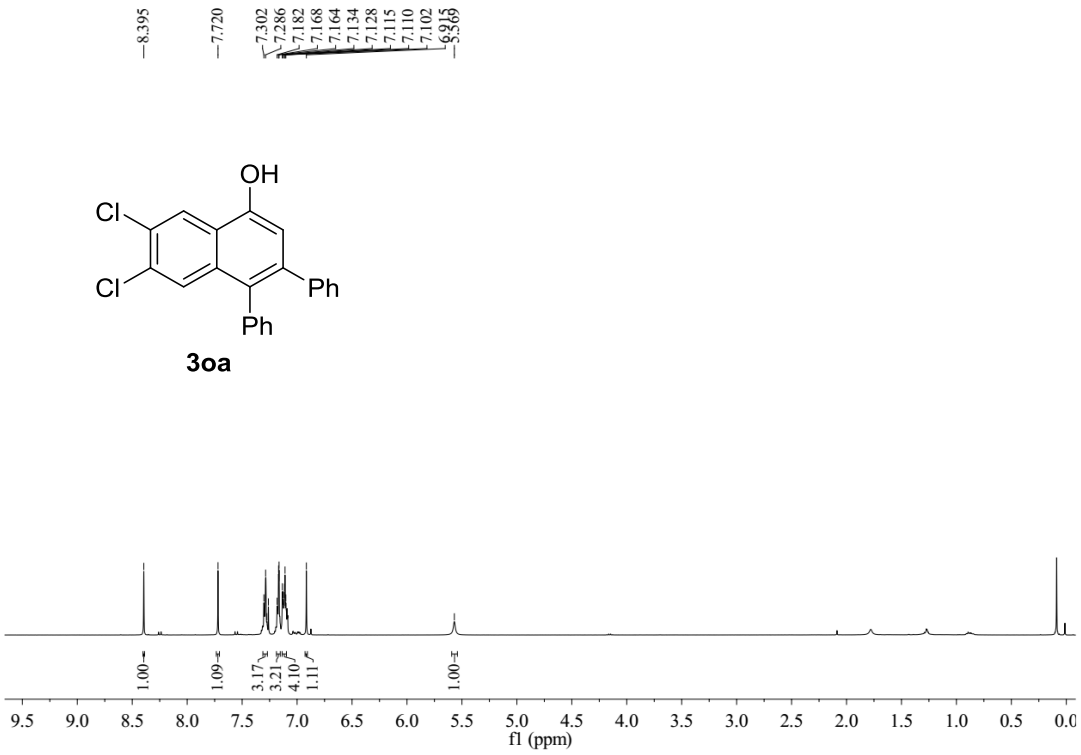
^{1}H NMR spectrum of **3na**



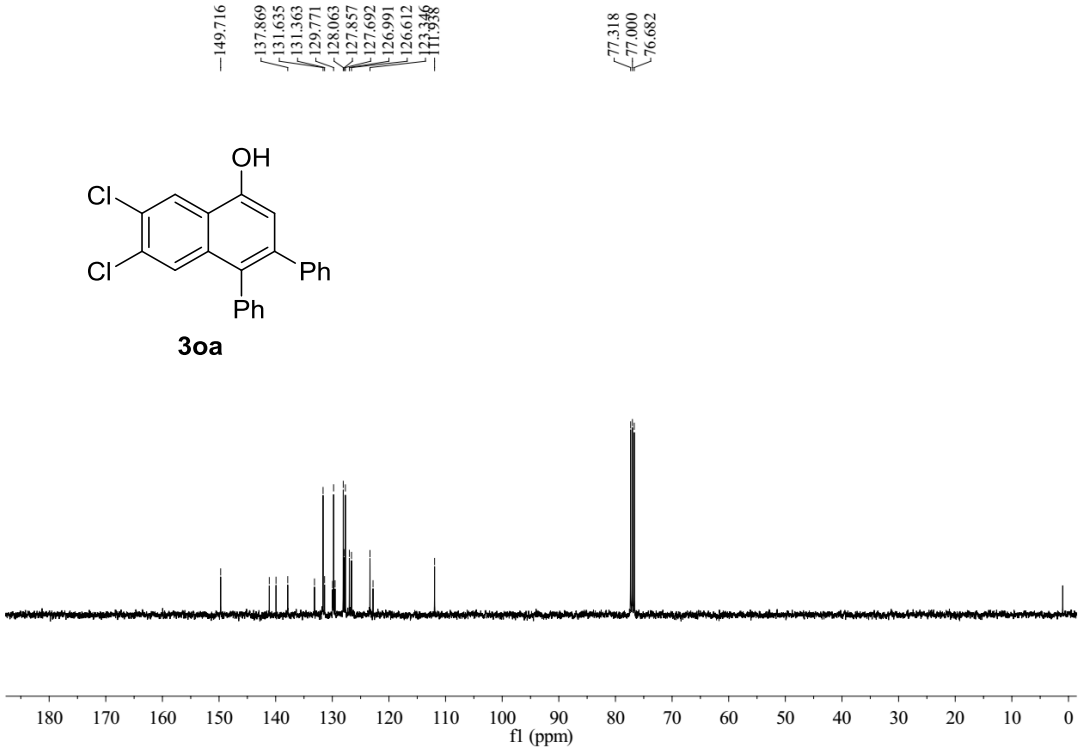
^{13}C NMR spectrum of **3na**



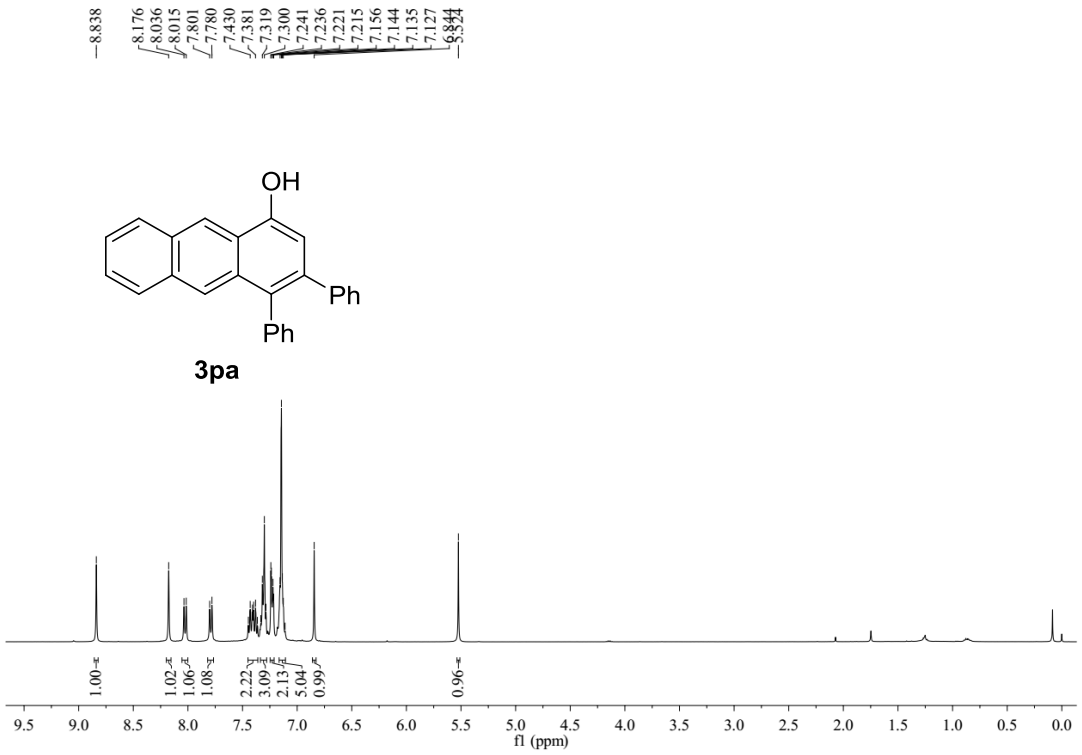
^{1}H NMR spectrum of **3oa**



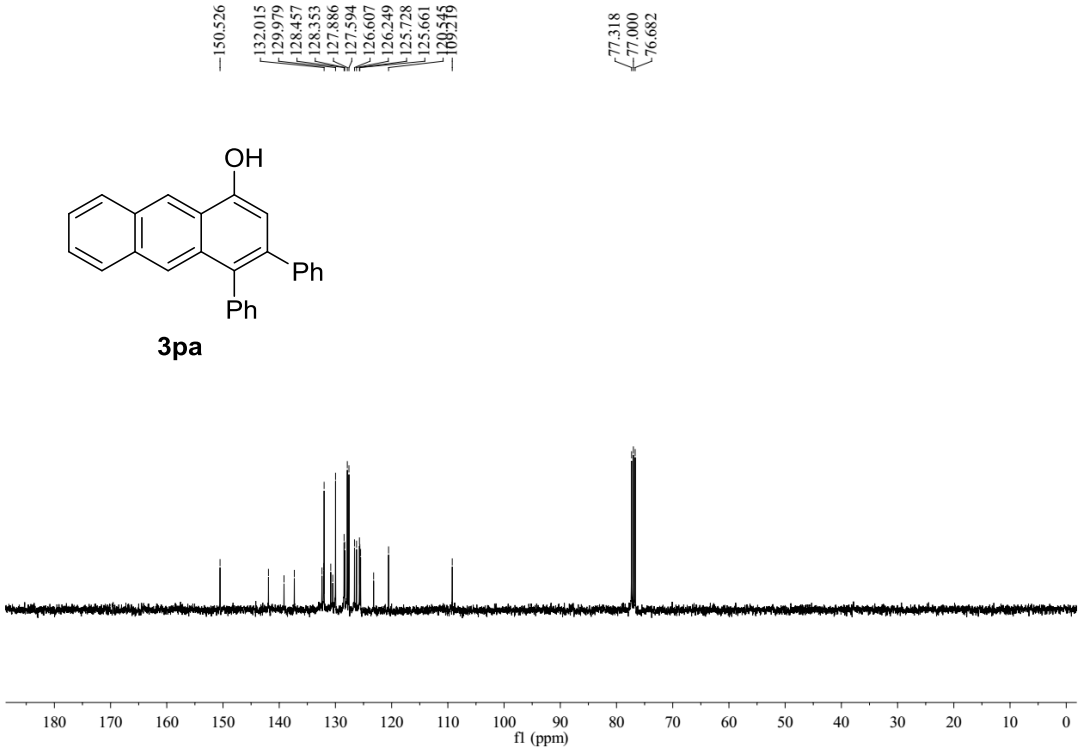
^{13}C NMR spectrum of **3oa**



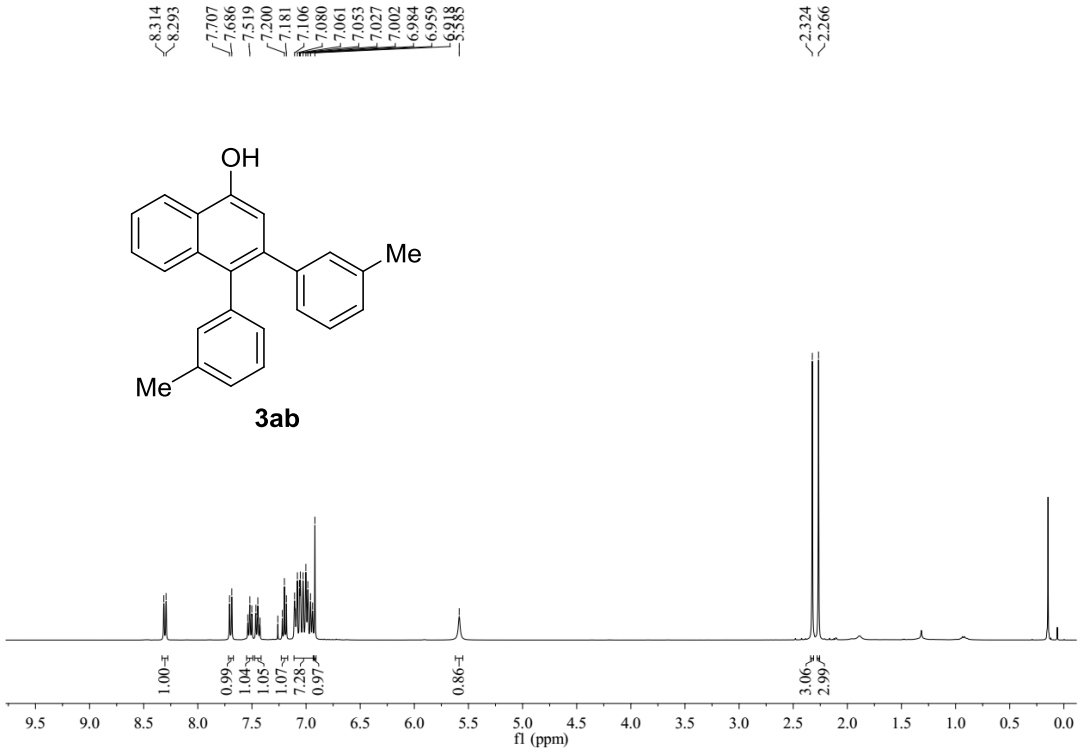
^{1}H NMR spectrum of **3pa**



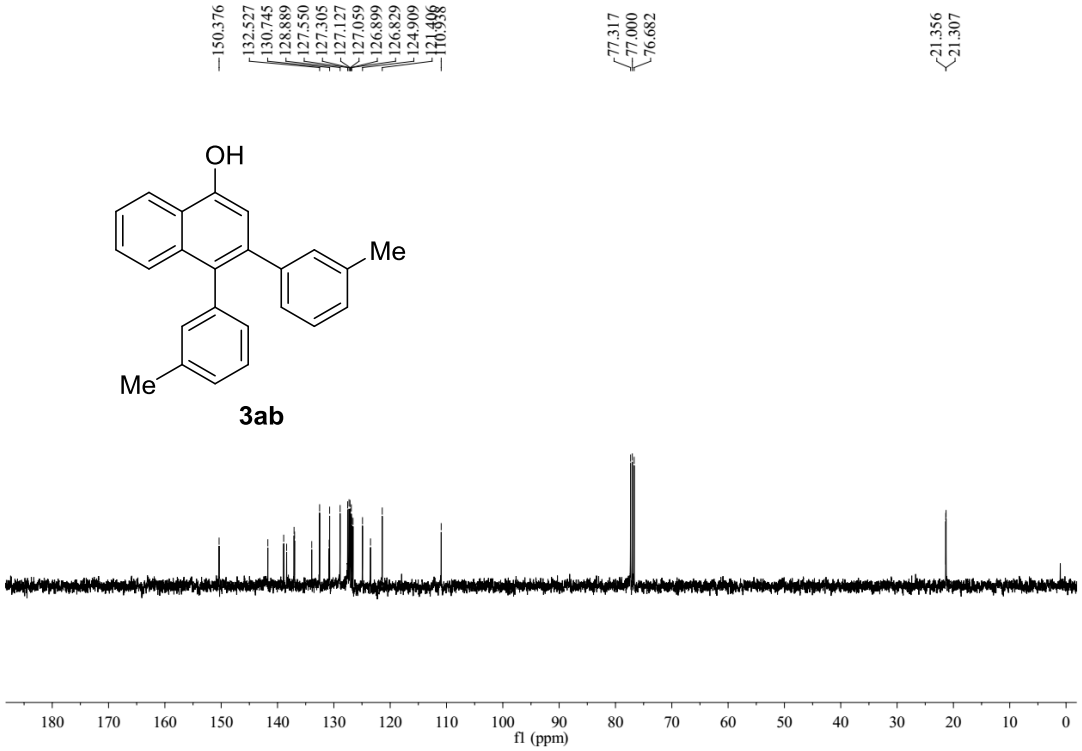
^{13}C NMR spectrum of **3pa**



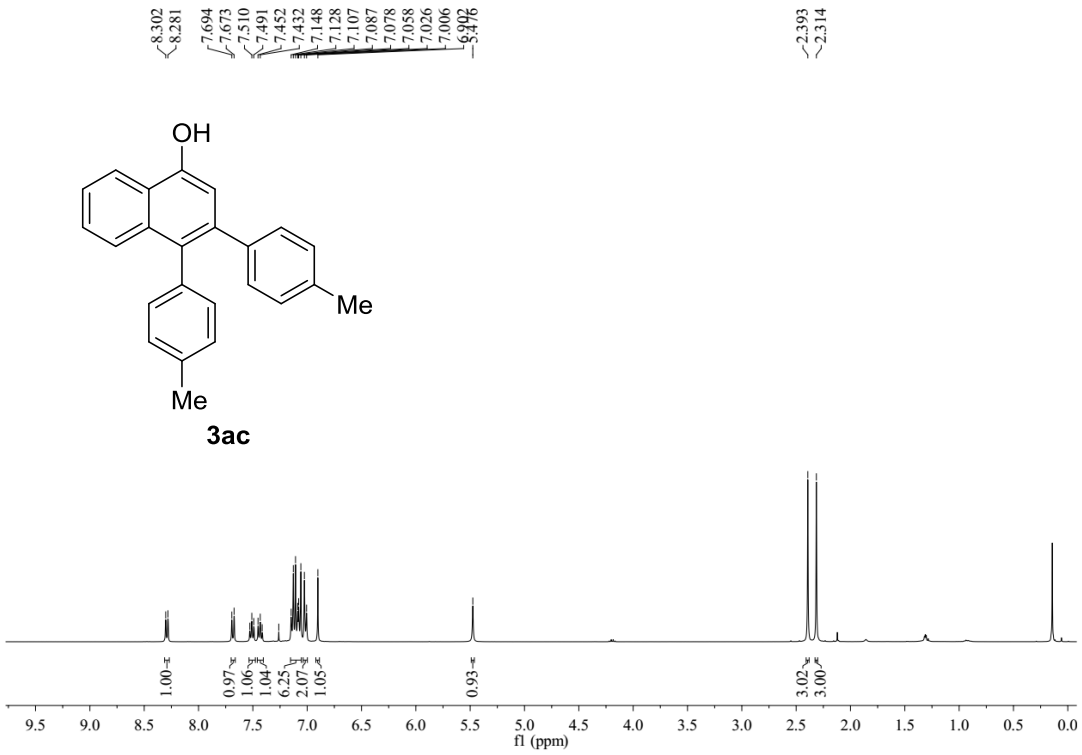
^{1}H NMR spectrum of **3ab**



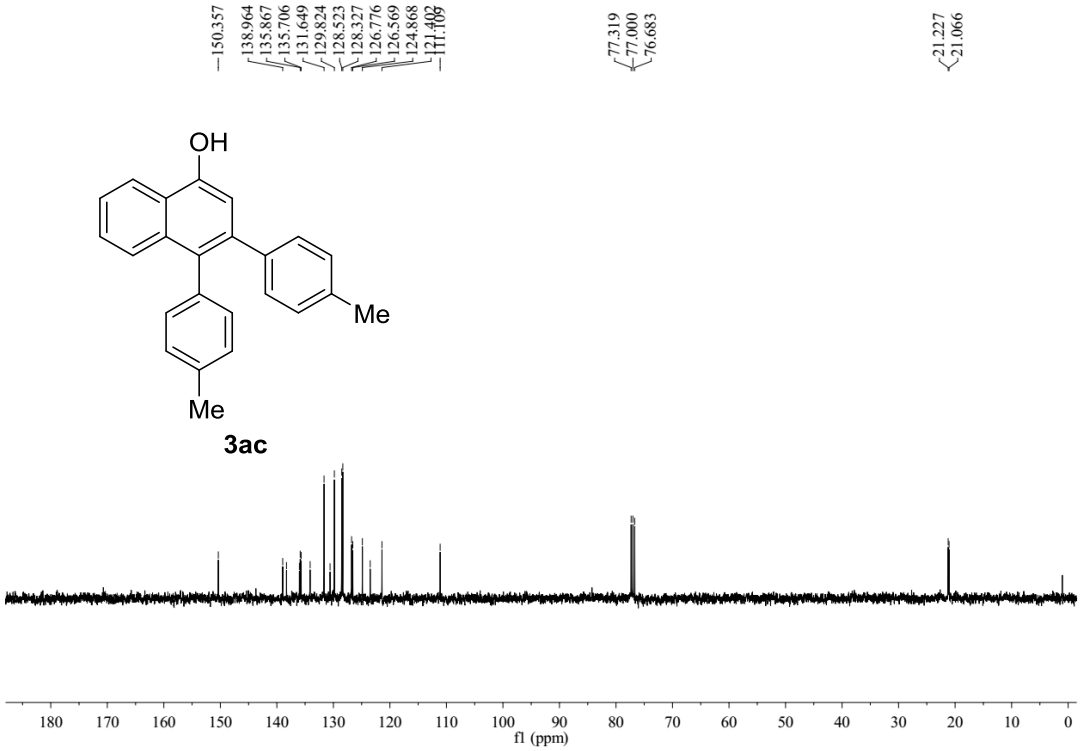
^{13}C NMR spectrum of **3ab**



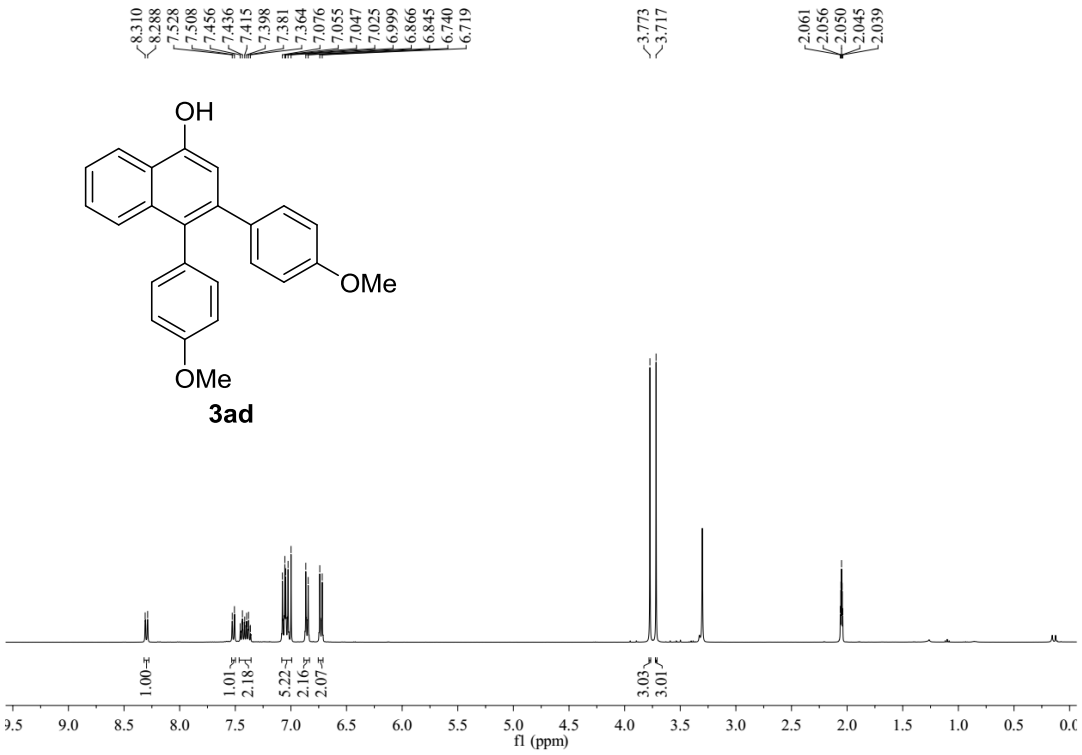
^{1}H NMR spectrum of **3ac**



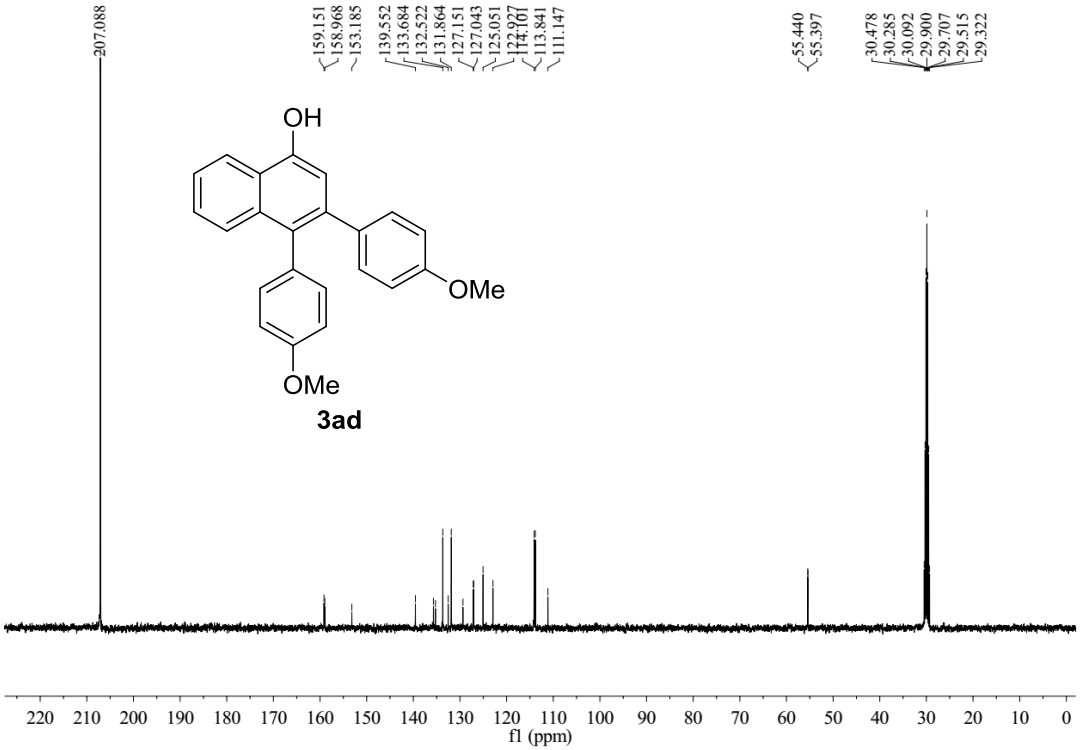
^{13}C NMR spectrum of **3ac**



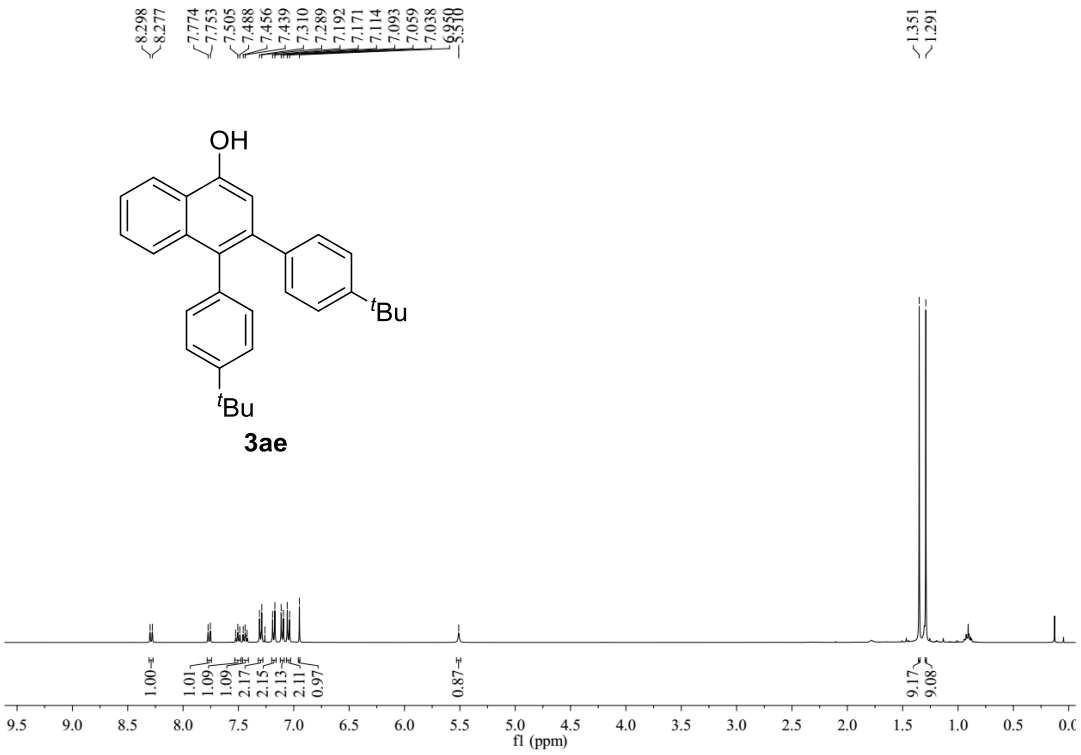
^{1}H NMR spectrum of **3ad**



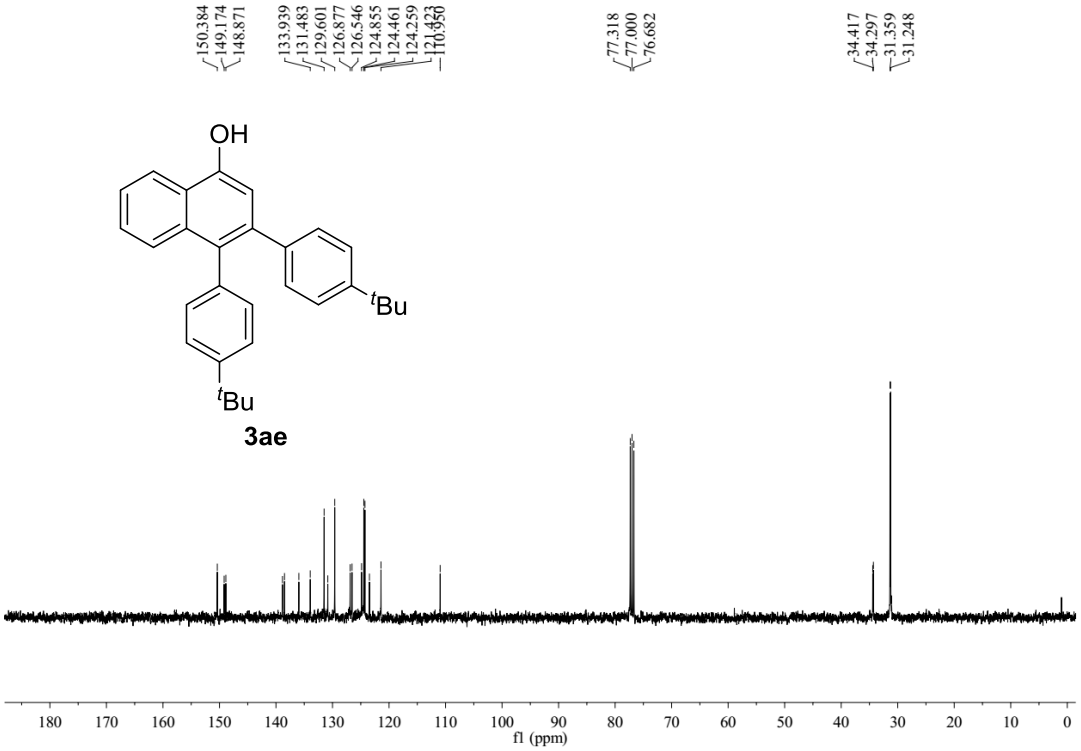
^{13}C NMR spectrum of **3ad**



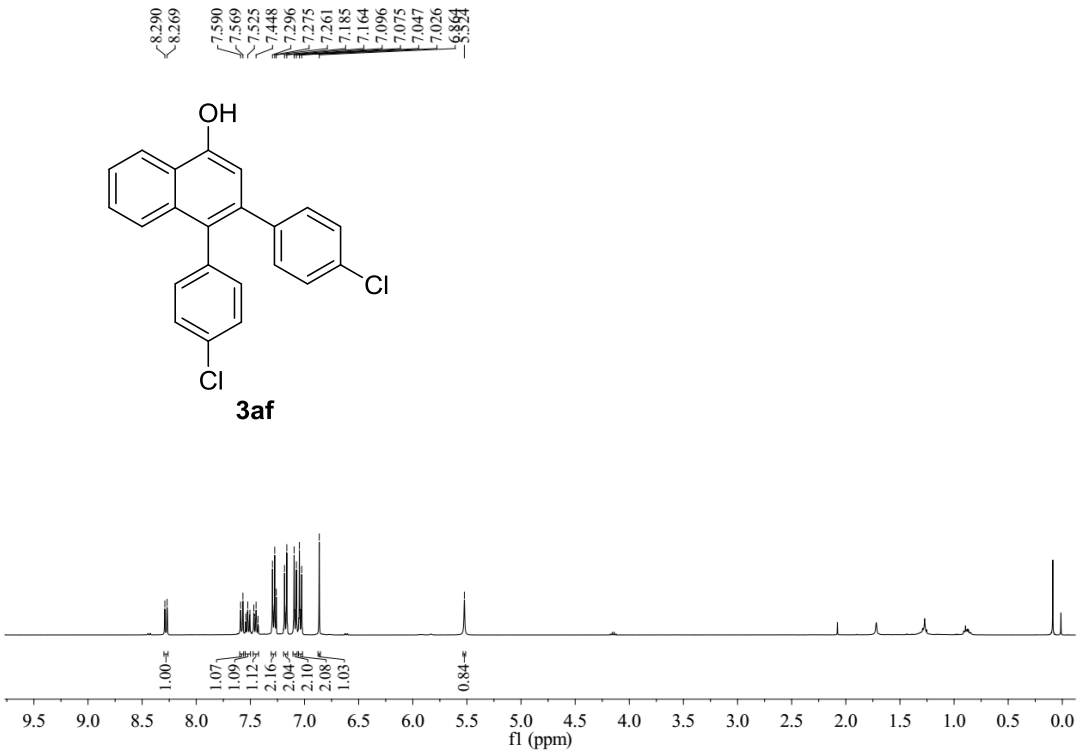
^{1}H NMR spectrum of **3ae**



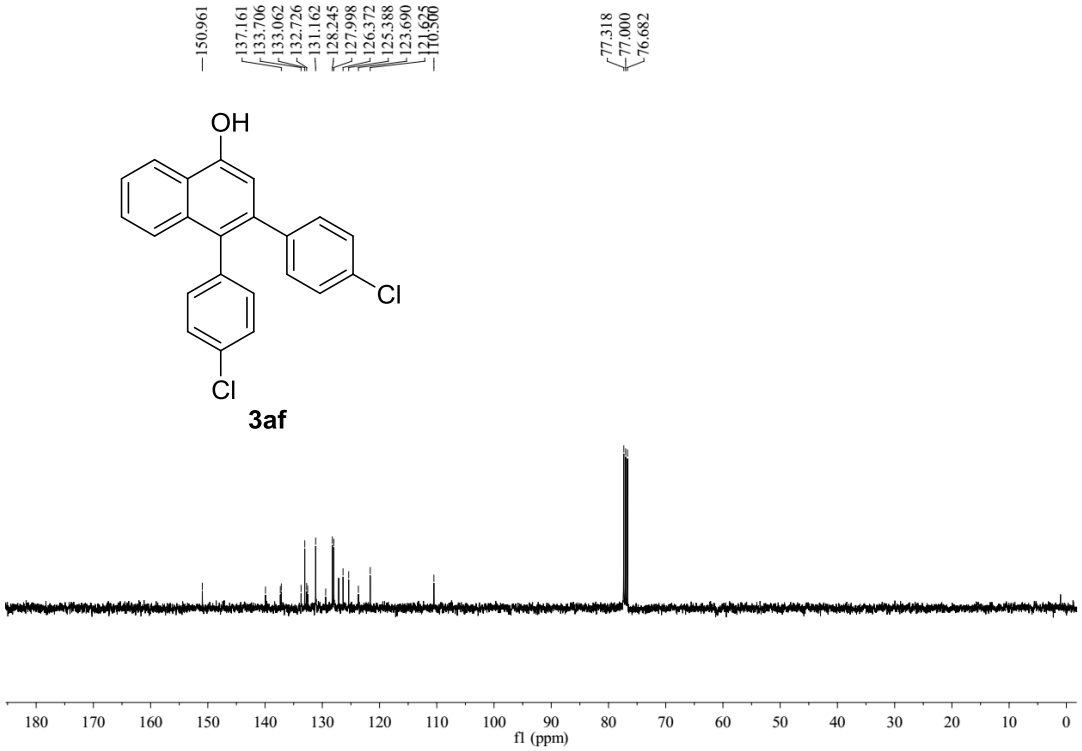
^{13}C NMR spectrum of **3ae**



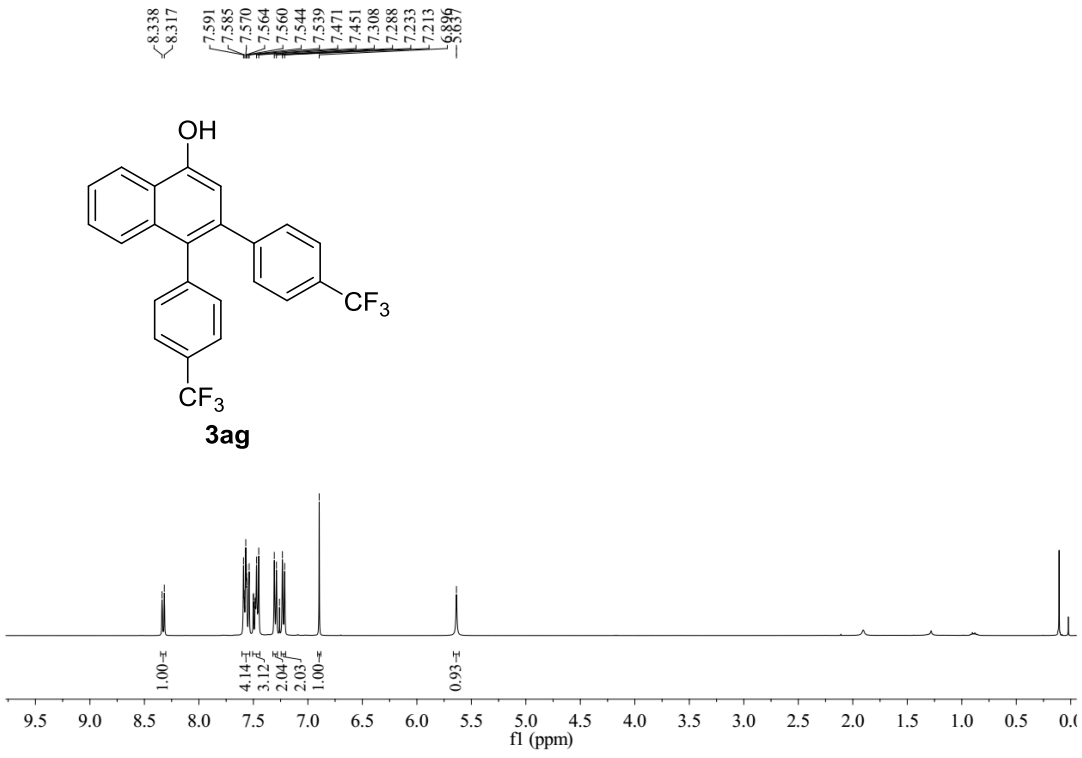
^{1}H NMR spectrum of **3af**



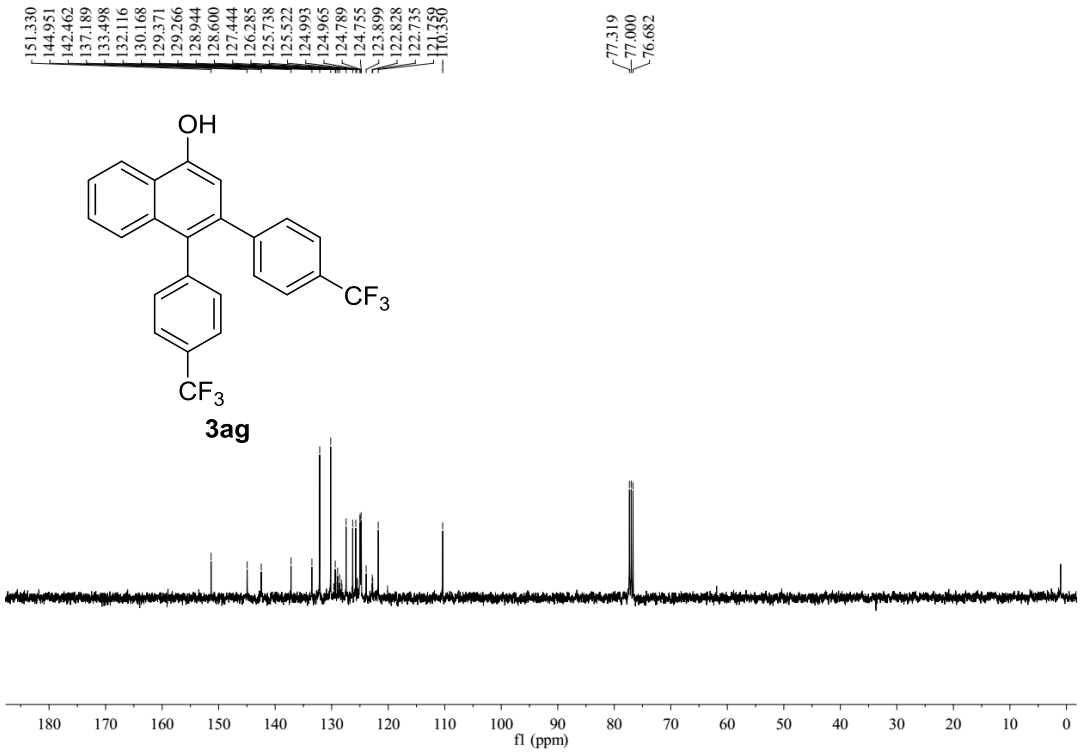
^{13}C NMR spectrum of **3af**



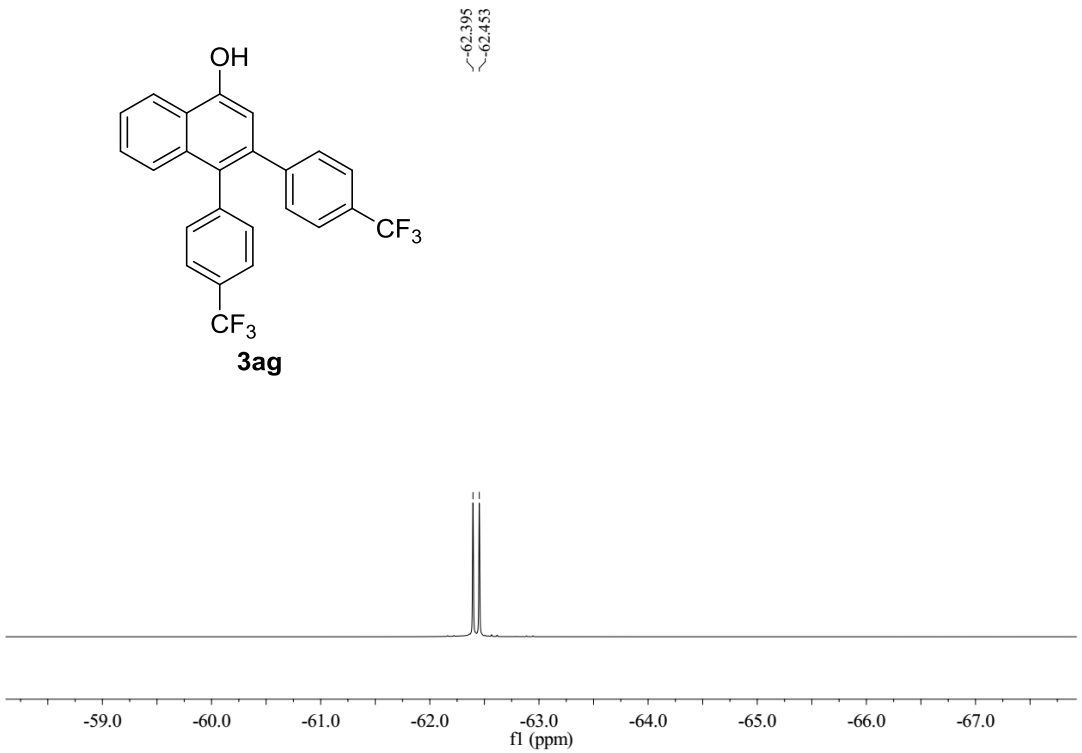
^{1}H NMR spectrum of **3ag**



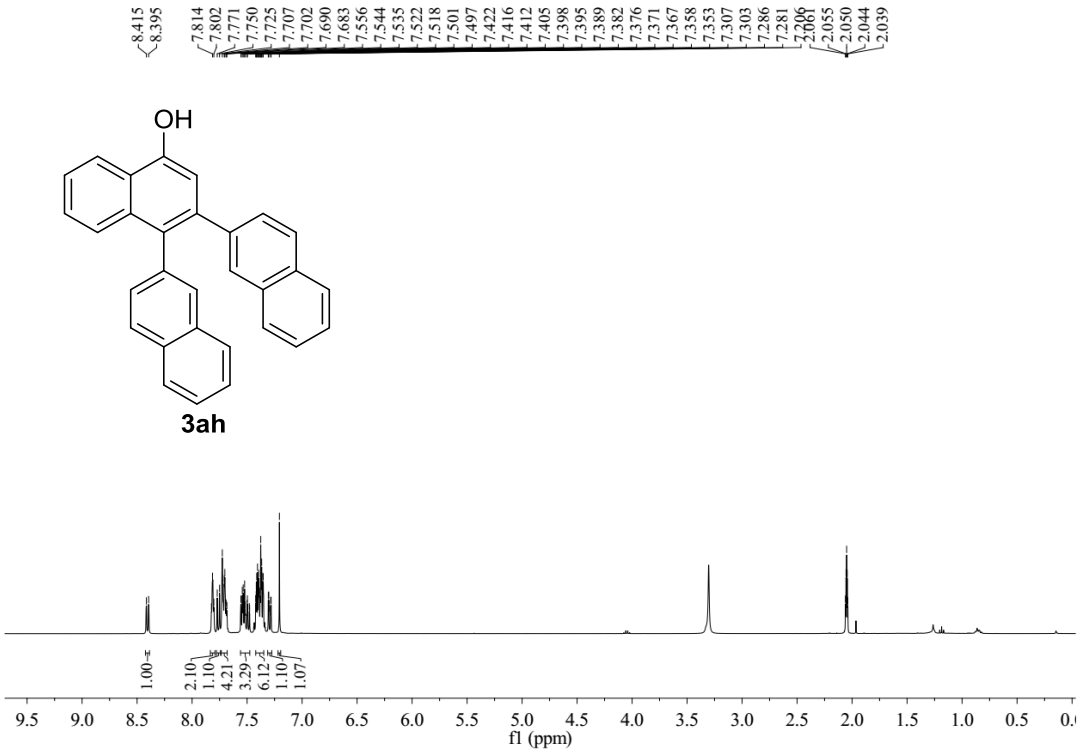
^{13}C NMR spectrum of **3ag**



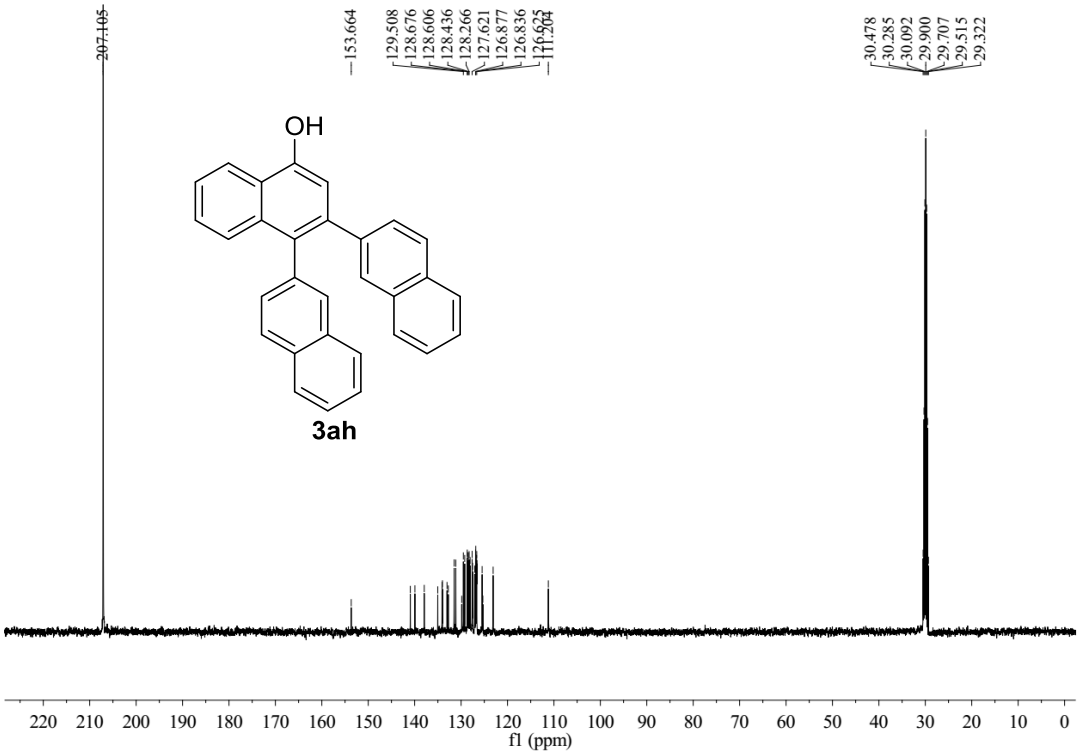
^{19}F NMR spectrum of **3ag**



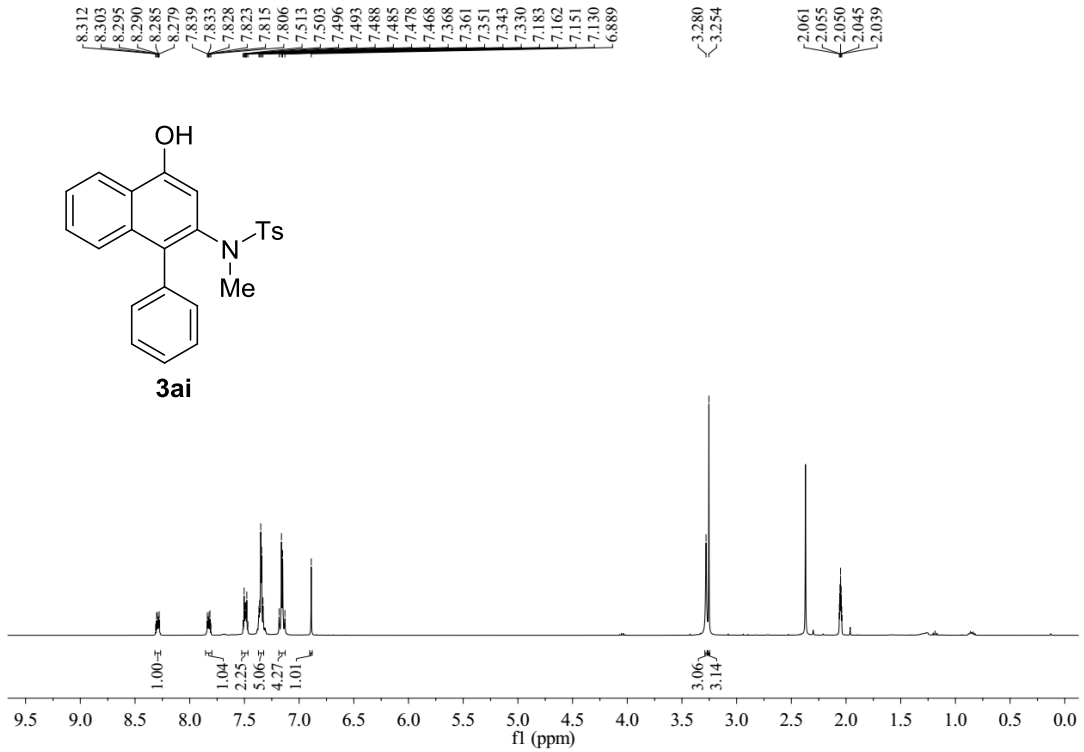
^{1}H NMR spectrum of **3ah**



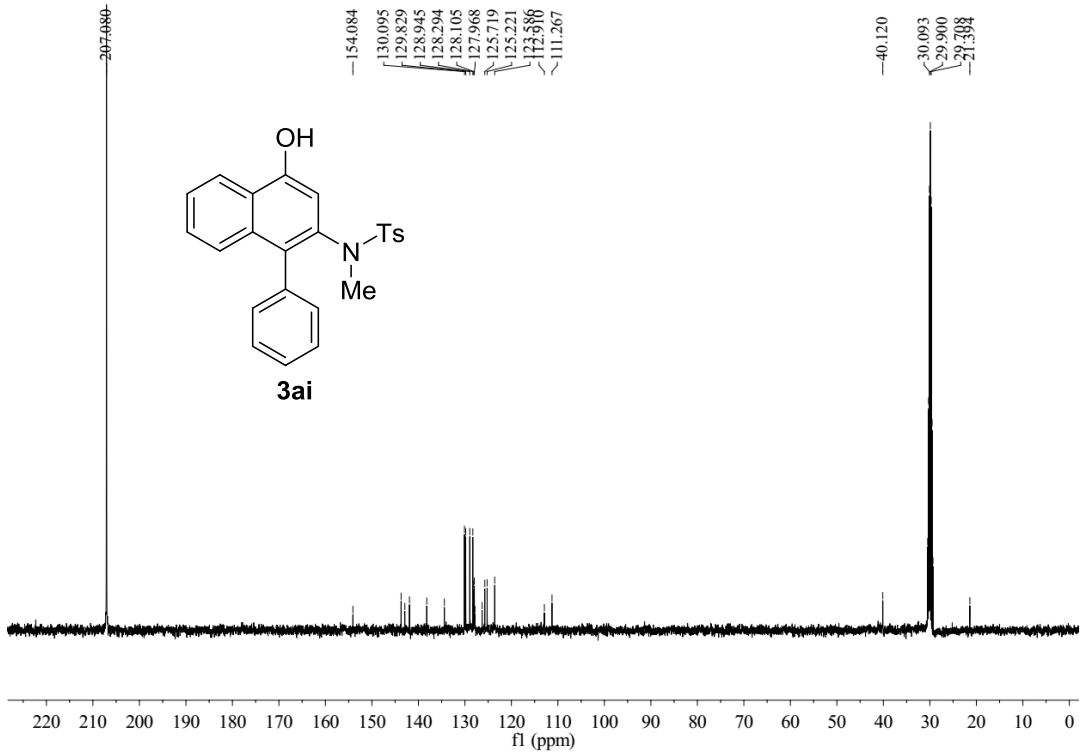
^{13}C NMR spectrum of **3ah**



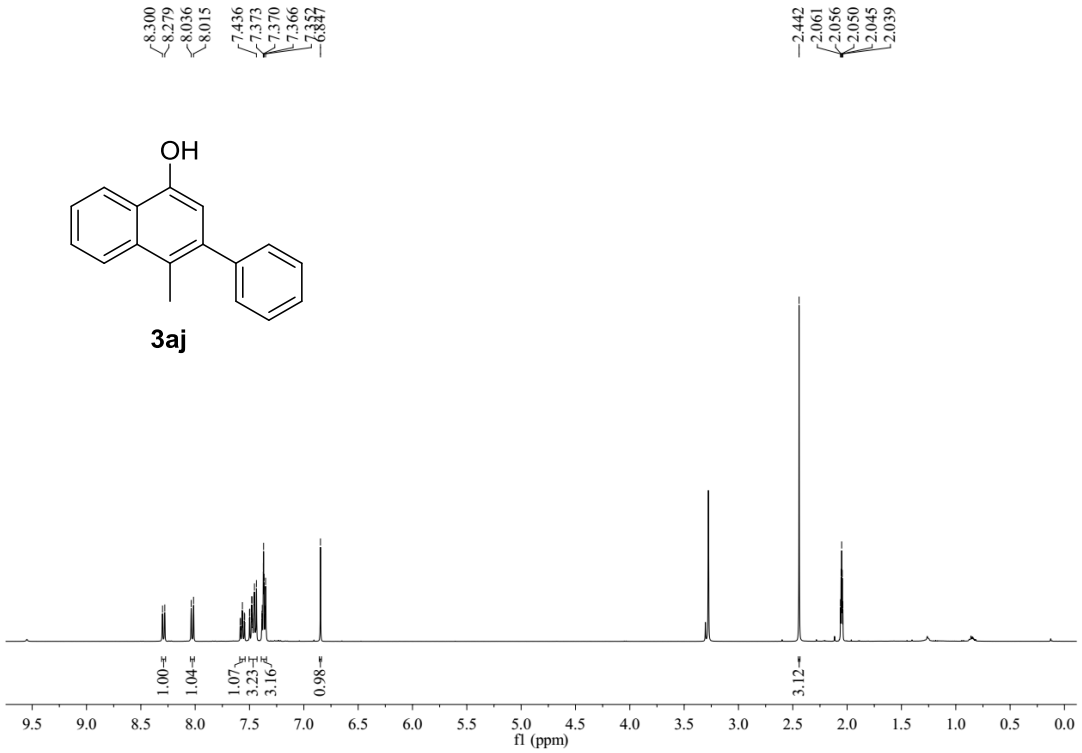
^{1}H NMR spectrum of **3ai**



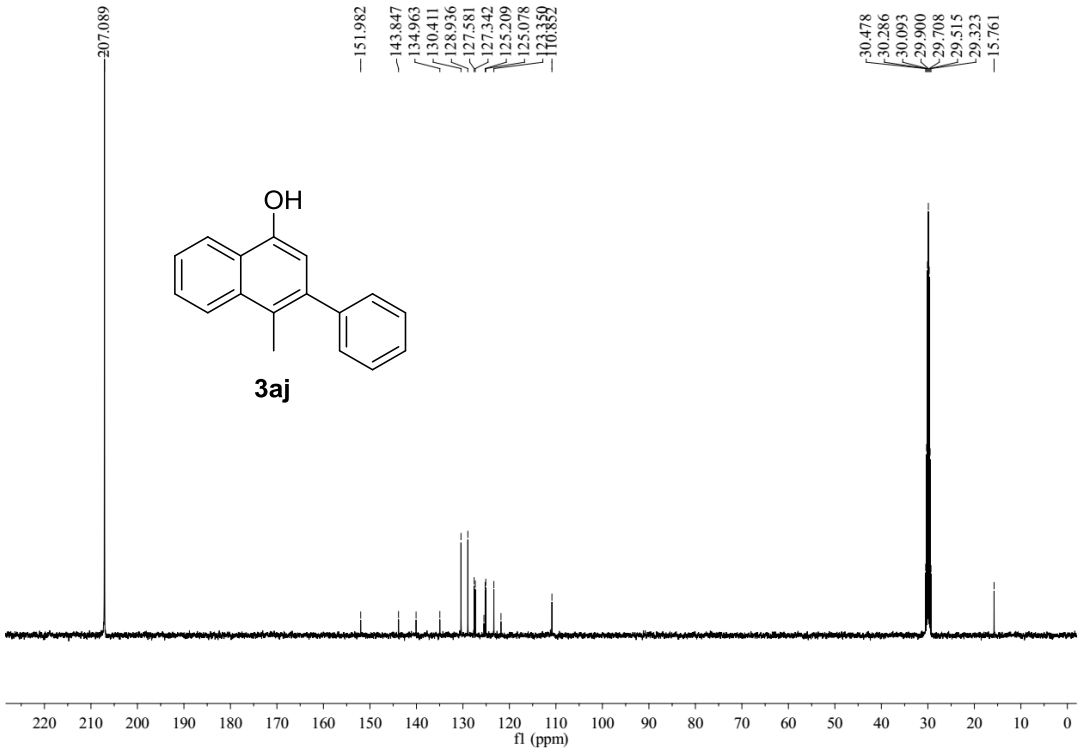
^{13}C NMR spectrum of **3ai**



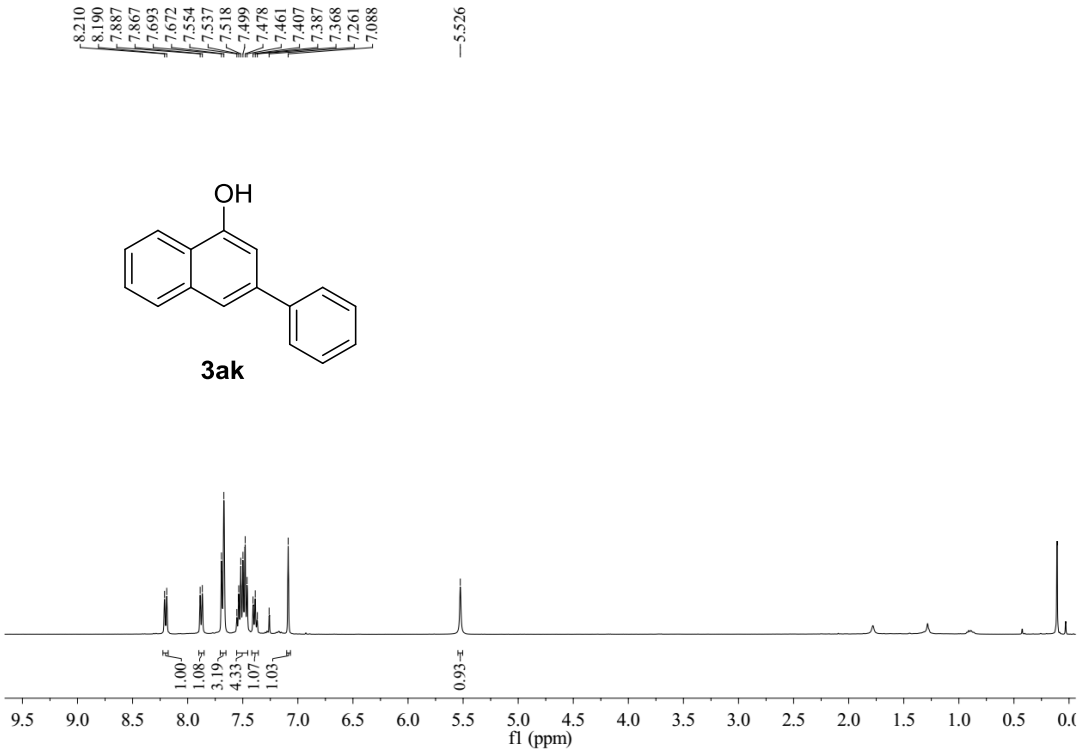
^{1}H NMR spectrum of **3aj**



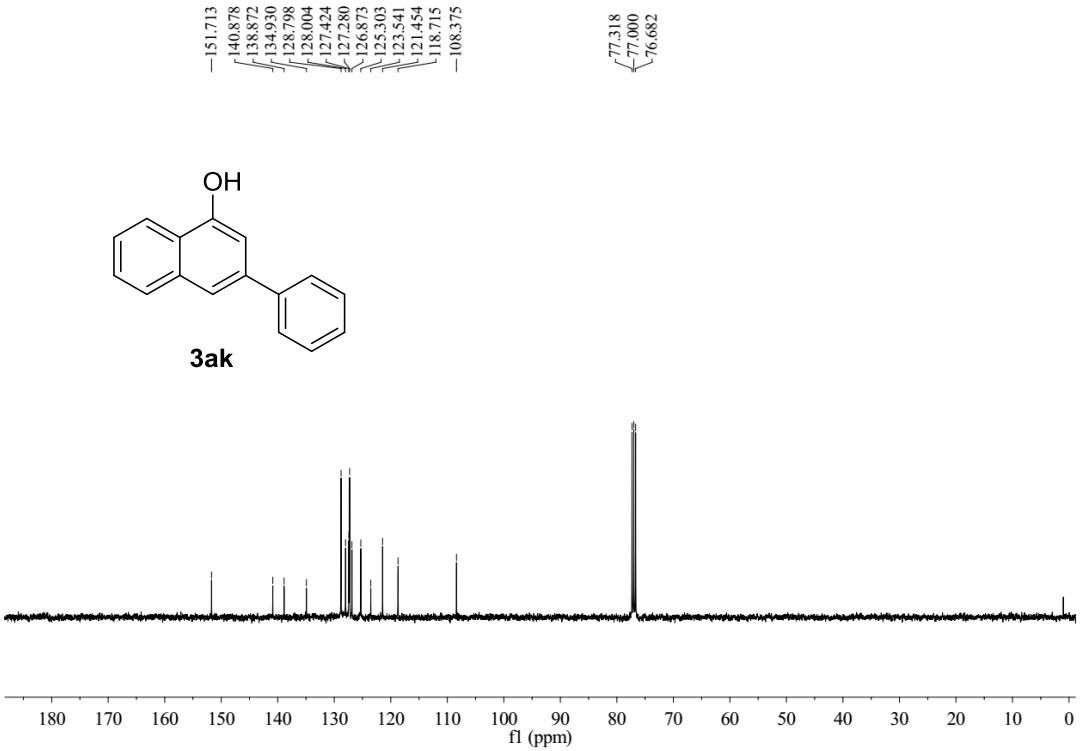
^{13}C NMR spectrum of **3aj**



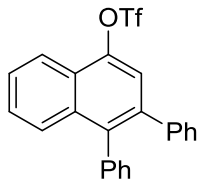
^{1}H NMR spectrum of **3ak**



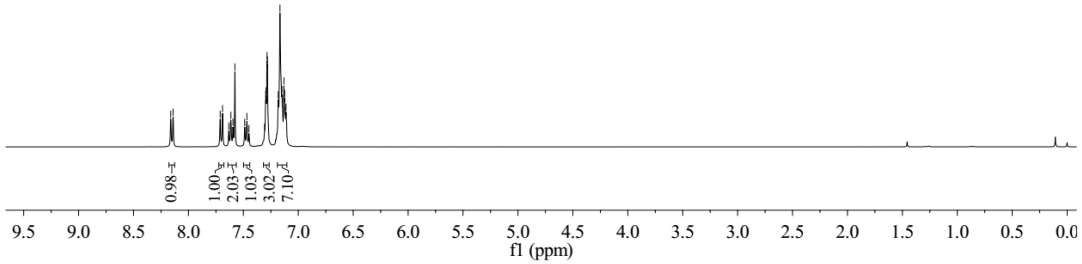
^{13}C NMR spectrum of **3ak**



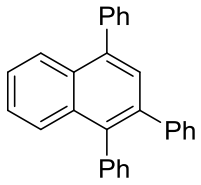
^{1}H NMR spectrum of **4**



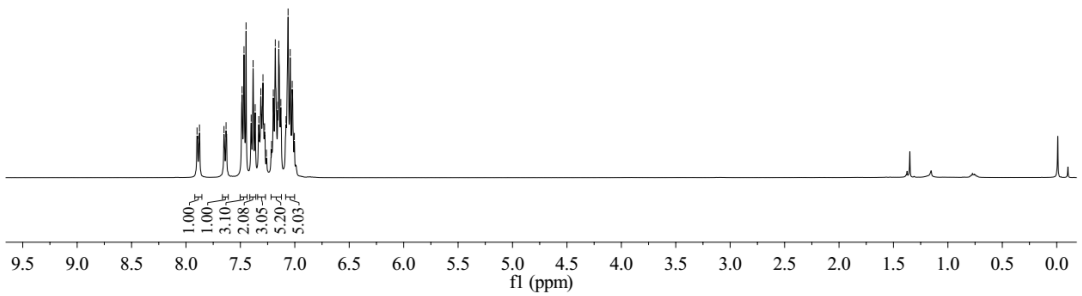
4



^{1}H NMR spectrum of **5**



5



^{1}H NMR spectrum of **6**