

Supporting Information

Palladium-Catalyzed Rearrangement Reaction to Access 1-Phenanthrol Derivatives

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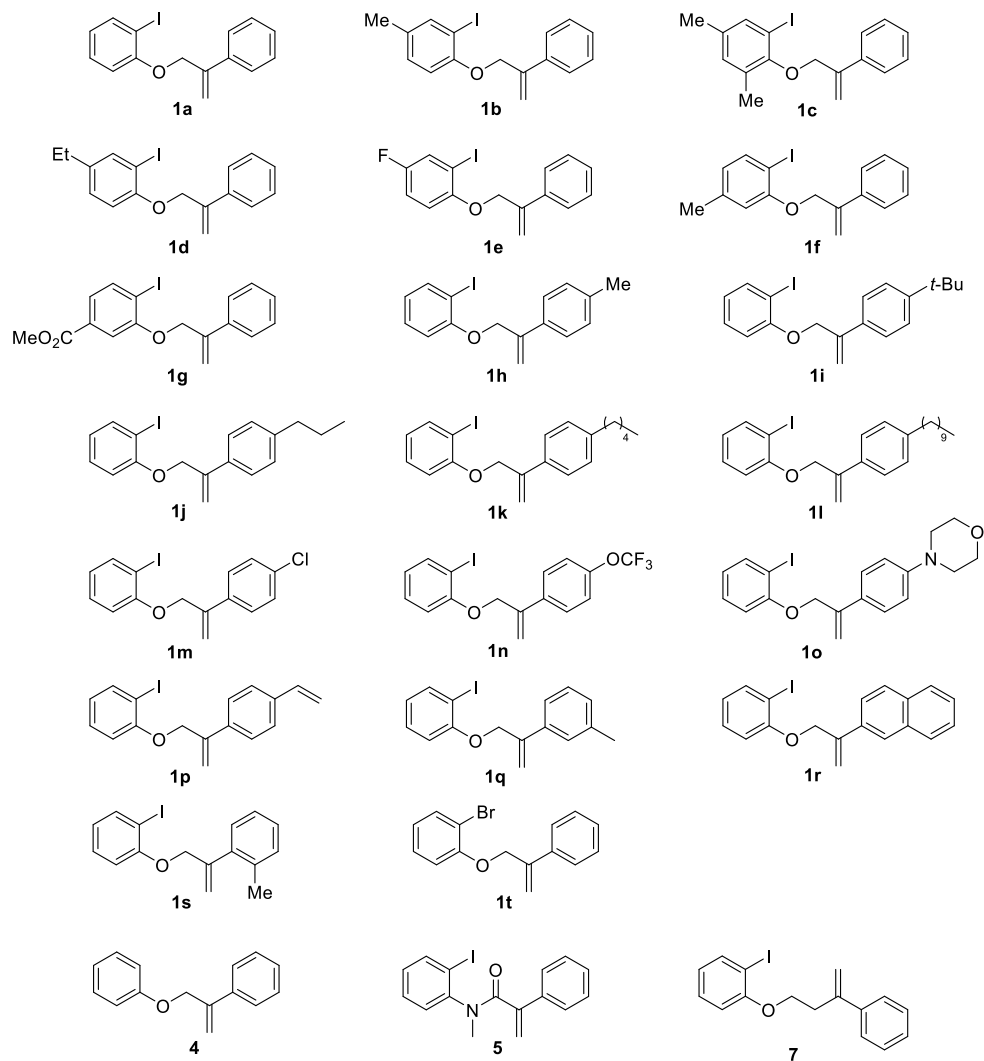
1 General Information

General Procedures. Unless otherwise noted, reactions were performed under a nitrogen atmosphere. Plastic syringes were used to transfer air- and moisture-sensitive reagents. Solvent was freshly distilled/degassed prior to use unless otherwise noted. Analytical TLC was performed with silica gel GF254 plates. For column chromatography, a 200-300 mesh silica gel was employed. Organic solutions were concentrated under reduced pressure using a rotary evaporator. Room temperature is 23-25 °C.

Materials. Commercial reagents were purchased from Acros, Accela, Adamas, Alfa, Ark, Aladdin, or TCI, and used as received with the following exceptions. Ethylene glycol dimethyl ether (DME) and toluene were dried over Na with benzophenone-ketyl intermediate as indicator. Acetonitrile (CH₃CN) was distilled over P₂O₅. *N,N*-Dimethylformamide (DMF) and *N,N*-Dimethylacetamide (DMA) was distilled under reduced pressure. Other commercially available reagents and solvents were used without further purification.

Instrumentation. Deuterated solvents were purchased from Cambridge Isotope Laboratories. ¹H NMR spectra were recorded on Bruker AVANCE III 400, Agilent Mercury plus 300 BB and INOVA instruments with 400, 300, and 600 MHz frequencies, and ¹³C NMR spectra were recorded on a Bruker AVANCE III 400 instrument with a ¹³C operating frequency of 100 MHz. ¹⁹F NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer with a ¹⁹F operating frequency of 376 MHz. Chemical shifts (δ) were reported in ppm relative to the residual solvent signal (CDCl₃ δ = 7.26 for ¹H NMR and δ = 77.0 for ¹³C NMR; DMSO-*d*₆ δ = 2.50 for ¹H NMR and δ = 40.0 for ¹³C NMR; CD₃OD δ = 3.31 for ¹H NMR and δ = 49.0 for ¹³C NMR). Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), or m (multiplet). HRMS was obtained using a Q-TOF instrument equipped with an ESI source. Data collection for crystal structure was performed at room temperature using Mo K α radiation on a Bruker APEXII diffractometer.

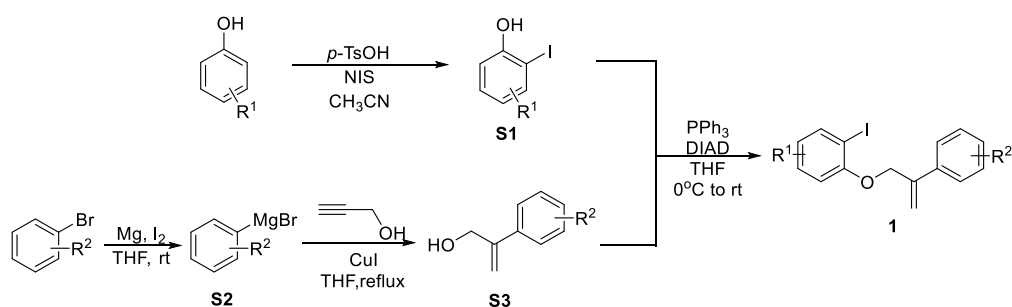
2 Structures



3 Experimental Section

3.1 Preparation of Allyloxy-tethered Aryl Iodides

The substrates **1a**¹, **1b**¹, **1e**¹, **1h**¹, **1i**¹, **1m**¹, **1r**², **1s**¹, **1t**³, **4**⁴, **5**⁵, and **7**⁶ synthesized are reported in previous literature.



(1) General procedure for the synthesis of substituted-2-iodophenols **S1**⁷

p -TsOH (10 mmol) was added to a stirred solution (solvent = 50 mL CH_3CN) containing the phenol (10 mmol) at r.t. After 5 min, 1.1 eq. of NIS (11 mmol) was added and the mixture was stirred overnight. The reaction was monitored by GC-MS until completion and the product composition was determined by GC-MS. The major products were isolated by silica gel column chromatography (petroleum ether (PE)/ethyl acetate (EA), 20/1-10/1) and characterised by GC-MS.

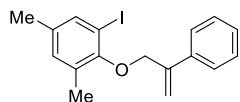
(2) General procedure for the synthesis of allylic alcohols **S3**⁸

Grignard reactions (**S2**) were performed with thoroughly dried glass apparatus. Under N_2 atmosphere, to a magnetically stirred mixture of Mg turnings (55 mmol, 1.1 eq.), a catalytic amount of iodine I_2 (~10 mg) was added and a solution of bromobenzene (50 mmol) in dry THF (120 mL) dropwise during 30 min and allowed to stir at r.t. for 3 h.

CuI (0.57 g, 3.0 mmol) was added to the solution of $ArMgBr$ **S2** (50 mmol) in 120 mL of THF. The mixture was stirred at r.t. for 0.5 h, and then a solution of propargyl alcohol (1.12g, 20 mmol) in 20 mL of THF was added slowly over 0.5 h. After the addition was complete, the reaction mixture was refluxed for 24 h. After cooling to r.t., an aqueous solution of saturated NH_4Cl was added slowly. The organic layer was separated, and aqueous layer was extracted with THF. The organic layer was combined, dried over anhydrous Na_2SO_4 . After removal of the volatiles, the residue was purified by column chromatography (silica gel, PE/EA, 10/1-5/1) to give allylic alcohol **S3**.

(3) General procedure for the synthesis of substrates **1**¹

To a flame-dried flask were added PPh_3 (15 mmol, 1.5 eq.), aryl iodide (1.05 eq.), allylic alcohol (10 mmol, 1 eq.) and dry THF (40 mL) sequentially under N_2 atmosphere at r.t. A solution of DIAD (diisopropyl azodiformate, 15 mmol, 1.5 eq.) in 10 mL of dry THF was added dropwise via addition funnel at $0^\circ C$. The resulting mixture was allowed to warm to r.t. naturally with stirring. After the reaction was complete as monitored by TLC, the reaction mixture was concentrated on a rotary evaporator and the residue was purified by chromatography on silica gel (eluent: PE/EA = 100/1 to 50/1) to afford the desired product **1**.



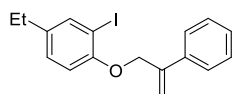
1-iodo-3,5-dimethyl-2-((2-phenylallyl)oxy)benzene (1c)

Light yellow liquid; yield: 75 % (eluent: PE/EA: 100/1)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 2H), 7.44 (d, J = 2.0 Hz, 1H), 7.38 – 7.28 (m, 3H), 6.94 (d, J = 2.1 Hz, 1H), 5.66 – 5.60 (m, 2H), 4.72 (d, J = 1.1 Hz, 2H), 2.26 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8 , 143.4 , 138.6 , 137.4 , 135.6 , 132.3 , 132.0 , 128.4 , 127.9 , 126.1 , 114.5 , 91.7 , 73.8 , 20.2 , 17.1 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{IO}$ 365.0397; Found 365.0394.



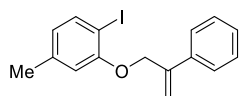
4-ethyl-2-iodo-1-((2-phenylallyl)oxy)benzene (1d)

Light yellow liquid; yield: 70 % (eluent: PE/EA: 100/1)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 2.1 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 – 7.28 (m, 3H), 7.07 (dd, J = 8.4, 2.1 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 5.62 – 5.57 (m, 2H), 4.87 (d, J = 1.3 Hz, 2H), 2.53 (q, J = 7.6 Hz, 2H), 1.18 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1 , 142.4 , 138.8 , 138.7 , 138.3 , 128.6 , 128.4 , 127.9 , 126.0 , 114.5 , 112.4 , 86.5 , 70.5 , 27.5 , 15.6 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{17}\text{IONa}$ 387.0216; Found 387.0212.



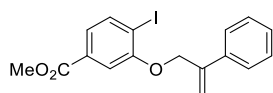
1-iodo-4-methyl-2-((2-phenylallyl)oxy)benzene (1f)

Light yellow liquid; yield: 74 % (eluent: PE/EA: 100/1)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, J = 7.9 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.40 – 7.30 (m, 3H), 6.68 (d, J = 1.8 Hz, 1H), 6.56 (dd, J = 7.9, 1.8 Hz, 1H), 5.63 (dd, J = 11.2, 1.4 Hz, 2H), 4.90 (s, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.9 , 142.4 , 139.7 , 139.0 , 138.4 , 128.5 , 128.0 , 126.1 , 123.7 , 114.6 , 113.6 , 82.5 , 70.3 , 21.4 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{IO}$ 351.0240; Found 351.0237.



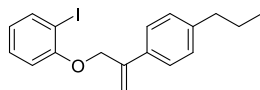
methyl 4-iodo-3-((2-phenylallyl)oxy)benzoate (1g)

Light yellow liquid; yield: 68 % (eluent: PE/EA: 50/1)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, J = 8.1 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.41 – 7.29 (m, 4H), 5.67 – 5.61 (m, 2H), 4.99 (s, 2H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4 , 157.1 , 142.2 , 139.6 , 138.1 , 131.5 , 128.5 , 128.1 , 126.2 , 123.5 , 115.0 , 112.6 , 93.3 , 70.6 , 52.3 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{IO}_3$ 395.0139; Found 395.0135.



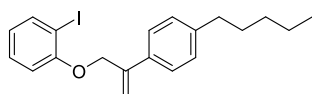
1-iodo-2-((2-(4-propylphenyl)allyl)oxy)benzene (1j)

Light yellow liquid; yield: 80 % (eluent: PE/EA: 100/1)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.30 – 7.25 (m, 1H), 7.17 (d, $J = 8.2$ Hz, 2H), 6.86 (dd, $J = 8.2, 1.3$ Hz, 1H), 6.73 – 6.69 (m, 1H), 5.58 (dd, $J = 2.8, 1.4$ Hz, 2H), 4.92 (s, 2H), 2.61 – 2.57 (m, 2H), 1.67 – 1.62 (m, 2H), 0.94 (d, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1, 142.7, 142.1, 139.5, 135.6, 129.3, 128.6, 125.9, 122.7, 113.8, 112.6, 86.6, 70.5, 37.7, 24.5, 13.8.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{IO}$ 379.0553; Found 379.0557.



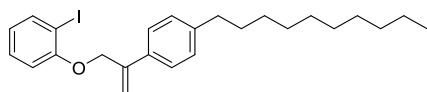
1-iodo-2-((2-(4-pentylphenyl)allyl)oxy)benzene (1k)

Light yellow liquid; yield: 81 % (eluent: PE/EA: 100/1)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.39 (d, $J = 8.1$ Hz, 2H), 7.29 – 7.24 (m, 1H), 7.17 (d, $J = 8.1$ Hz, 2H), 6.85 (d, $J = 8.2$ Hz, 1H), 6.73 – 6.68 (m, 1H), 5.58 (d, $J = 2.9$ Hz, 2H), 4.91 (s, 2H), 2.62 – 2.57 (m, 2H), 1.65 – 1.58 (m, 2H), 1.35 – 1.29 (m, 4H), 0.88 (d, $J = 7.0$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1, 142.9, 142.1, 139.5, 135.6, 129.3, 128.5, 125.9, 122.7, 113.7, 112.5, 86.6, 70.5, 35.6, 31.5, 31.1, 22.5, 14.0.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{24}\text{IO}$ 407.0866; Found 407.0869.



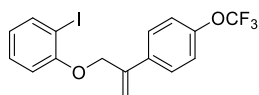
1-((2-(4-decylphenyl)allyl)oxy)-2-iodobenzene (1l)

Light yellow liquid; yield: 72 % (eluent: PE/EA: 100/1)

^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.39 (d, $J = 8.2$ Hz, 2H), 7.30 – 7.25 (m, 1H), 7.17 (d, $J = 8.1$ Hz, 2H), 6.89 – 6.84 (m, 1H), 6.74 – 6.69 (m, 1H), 5.58 (d, $J = 3.5$ Hz, 2H), 4.92 (s, 2H), 2.63 – 2.58 (m, 2H), 1.64 – 1.57 (m, 2H), 1.26 (s, 14H), 0.88 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1, 143.0, 142.1, 139.5, 135.6, 129.3, 128.5, 125.9, 122.7, 113.8, 112.6, 86.6, 70.5, 35.6, 31.9, 31.4, 29.6, 29.6, 29.5, 29.3, 22.7, 14.1.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{34}\text{IO}$ 477.1649; Found 477.1647.



1-iodo-2-((2-(4-(trifluoromethoxy)phenyl)allyl)oxy)benzene (1n)

Light yellow liquid; yield: 77 % (eluent: PE/EA: 100/1)

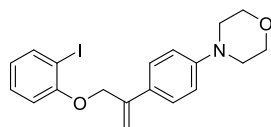
^1H NMR (300 MHz, Chloroform-*d*) δ 7.82 – 7.75 (m, 1H), 7.55 – 7.47 (m, 2H), 7.34 – 7.16 (m, 3H), 6.86 (dd, $J = 8.2, 1.3$ Hz, 1H), 6.73 (td, $J = 7.6, 1.3$ Hz, 1H), 5.67 – 5.57 (m, 2H), 4.90 (d, $J = 1.4$ Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.2, 149.2, 141.6, 139.9, 137.2, 129.6, 127.9, 123.2,

121.1 , 116.3 , 112.8 , 86.9 , 70.8 .

^{19}F NMR (282 MHz, Chloroform-*d*) δ -58.2 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{IO}_2$ 420.9907; Found 420.9914.



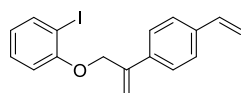
4-(4-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)morpholine (1o)

Brown solid; m.p. = 78-80 °C; yield: 66 % (eluent: PE/EA: 50/1)

^1H NMR (300 MHz, Chloroform-*d*) δ 7.78 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.45 – 7.37 (m, 2H), 7.32 – 7.23 (m, 1H), 6.93 – 6.81 (m, 3H), 6.75 – 6.67 (m, 1H), 5.58 – 5.45 (m, 2H), 4.91 (d, $J = 1.3$ Hz, 2H), 3.90 – 3.80 (m, 4H), 3.22 – 3.12 (m, 4H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.4 , 151.2 , 141.8 , 139.8 , 129.8 , 129.6 , 127.1 , 123.0 , 115.4 , 112.8 , 112.8 , 86.9 , 70.8 , 67.1 , 49.2 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{21}\text{INO}_2$ 422.0611; Found 422.0609.



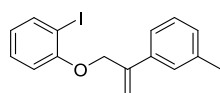
1-iodo-2-((2-(4-vinylphenyl)allyl)oxy)benzene (1p)

Light yellow liquid; yield: 68 % (eluent: PE/EA: 100/1)

^1H NMR (300 MHz, Chloroform-*d*) δ 7.77 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.41 (q, $J = 8.6$ Hz, 4H), 7.31 – 7.22 (m, 1H), 6.84 (dd, $J = 8.2, 1.4$ Hz, 1H), 6.76 – 6.62 (m, 2H), 5.75 (dd, $J = 17.6, 0.9$ Hz, 1H), 5.68 – 5.56 (m, 2H), 5.25 (dd, $J = 10.9, 0.9$ Hz, 1H), 4.90 (d, $J = 1.4$ Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.3 , 142.1 , 139.8 , 137.8 , 137.6 , 136.6 , 129.7 , 126.6 , 126.5 , 123.1 , 114.9 , 114.4 , 112.8 , 86.9 , 70.7 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{IO}$ 363.0240; Found 363.0237.



1-iodo-2-((2-(m-tolyl)allyl)oxy)benzene (1q)

Light yellow liquid; yield: 81 % (eluent: PE/EA: 100/1)

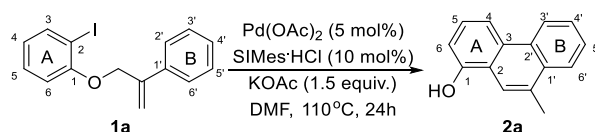
^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.31 – 7.24 (m, 4H), 7.13 (d, $J = 6.7$ Hz, 1H), 6.89 – 6.84 (m, 1H), 6.75 – 6.69 (m, 1H), 5.62 – 5.58 (m, 2H), 4.92 (s, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1 , 142.4 , 139.5 , 138.3 , 138.0 , 129.3 , 128.8 , 128.4 , 126.9 , 123.2 , 122.7 , 114.4 , 112.6 , 86.6 , 70.5 , 21.5 .

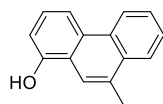
HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{16}\text{IO}$ 351.0240; Found 351.0237.

3.2 General Procedure for Synthesis of Products

3.2.1 Synthesis of phenanthrols 2



General procedure: An oven-dried Schlenk tube under a nitrogen atmosphere was charged with aryl iodide **1** (0.2 mmol, 1.0 eq.), Pd(OAc)₂ (5 mol%), SIMes·HCl (10 mol%) and KOAc (1.5 eq.) in DMF (1 mL). The mixture was stirred at 110 °C in an oil bath for 24 h. The resulting mixture was cooled to room temperature and filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate and the combined filtrate was washed with water. Then the organic layer was dried with Na₂SO₄ before concentration. Then the residue was purified by flash chromatography on silica gel (PE/EA :20/1-10/1) to afford pure product.



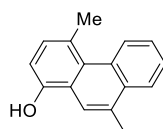
9-methylphenanthren-1-ol (**2a**)

White solid; m.p. = 112-114 °C; yield: 70 % (eluent: PE/EA: 16/1).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.72 – 8.65 (m, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 8.09 – 8.03 (m, 1H), 7.97 (s, 1H), 7.68 – 7.60 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.24 (s, 1H), 2.78 – 2.72 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 151.3, 132.1, 131.9, 131.2, 130.2, 126.7, 126.2, 125.7, 124.7, 123.5, 121.7, 119.5, 115.4, 110.6, 20.3.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₂O 209.0961; Found 209.0961.



4,9-dimethylphenanthren-1-ol (**2b**)

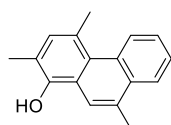
Orange solid; m.p. = 136-138 °C; yield: 39 % (eluent: PE/EA: 16/1).

¹H NMR (400 MHz, Methanol-*d*₄) δ 8.91 – 8.84 (m, 1H), 8.10 – 8.01 (m, 2H), 7.62 – 7.52 (m, 2H), 7.24 – 7.18 (m, 1H), 6.88 (d, *J* = 7.9 Hz, 1H), 4.91 (s, 1H), 2.96 (s, 3H), 2.68 (d, *J* = 1.1 Hz, 3H).

¹³C NMR (101 MHz, Methanol-*d*₄) δ 151.4, 133.3, 131.7, 130.2, 130.2, 127.4, 125.4, 125.2, 124.3, 123.9, 123.1, 120.8, 109.5, 25.7, 19.0.

¹³C NMR (101 MHz, Methanol-*d*₄) δ 151.4, 133.3, 131.7, 130.2, 130.2, 130.1, 127.4, 125.4, 125.2, 124.3, 123.9, 123.1, 120.8, 109.5, 25.7, 19.0.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄O 223.1117; Found 223.1118.



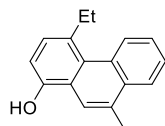
2,4,9-trimethylphenanthren-1-ol (**2c**)

Yellow solid; m.p. = 70-72 °C; yield: 41 % (eluent: PE/EA: 20/1).

^1H NMR (400 MHz, DMSO- d_6) δ 8.84 (d, J = 10.8 Hz, 2H), 8.13 (s, 1H), 8.04 (dd, J = 6.3, 3.4 Hz, 1H), 7.62 (dd, J = 6.4, 3.3 Hz, 2H), 7.20 (s, 1H), 2.93 (s, 3H), 2.68 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 148.8 , 133.8 , 132.8 , 131.9 , 130.7 , 128.3 , 127.6 , 126.0 , 125.7 , 125.6 , 124.7 , 124.3 , 121.8 , 120.6 , 26.8 , 20.5 , 16.8 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{O}$ 237.1274; Found 237.1275.



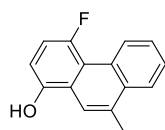
4-ethyl-9-methylphenanthren-1-ol (2d)

Orange solid; m.p. = 92-94 °C; yield: 22 % (eluent: PE/EA: 16/1).

^1H NMR (600 MHz, Chloroform- d) δ 8.77 (dd, J = 8.2, 1.4 Hz, 1H), 8.08 (dd, J = 7.9, 1.8 Hz, 1H), 8.03 (d, J = 1.3 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.30 (d, J = 7.9 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.15 (s, 1H), 3.40 (q, J = 7.4 Hz, 2H), 2.74 (d, J = 1.1 Hz, 3H), 1.48 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform- d) δ 149.4 , 133.7 , 133.4 , 131.4 , 131.0 , 130.3 , 128.4 , 127.7 , 126.0 , 125.0 , 124.4 , 122.9 , 120.4 , 110.5 , 30.6 , 20.2 , 15.7 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{O}$ 237.1274; Found 237.1275.



4-fluoro-9-methylphenanthren-1-ol (2e)

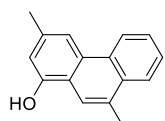
Orange solid; m.p. = 124-126 °C; yield: 68 % (eluent: PE/EA: 16/1).

^1H NMR (400 MHz, DMSO- d_6) δ 10.17 (s, 1H), 9.05 – 8.96 (m, 1H), 8.14 – 8.07 (m, 1H), 8.04 – 7.96 (m, 1H), 7.71 (dd, J = 6.5, 3.1 Hz, 2H), 7.27 (dd, J = 14.6, 8.5 Hz, 1H), 7.00 (dd, J = 8.6, 3.7 Hz, 1H), 2.70 (s, 3H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 154.2 (d, J = 241.2 Hz), 149.8 (d, J = 2.2 Hz), 132.5 (d, J = 24.9 Hz), 128.3 (d, J = 5.8 Hz), 127.8 , 127.5 , 127.5 , 127.2 (d, J = 2.6 Hz), 125.0 , 123.3 (d, J = 4.3 Hz), 120.9 (d, J = 2.3 Hz), 118.8 (d, J = 9.6 Hz), 113.0 (d, J = 26.4 Hz), 110.5 (d, J = 9.4 Hz), 20.5 .

^{19}F NMR (376 MHz, DMSO- d_6) δ -121.7 .

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{11}\text{FO}$ 227.0867; Found 227.0870.



3,9-dimethylphenanthren-1-ol (2f)

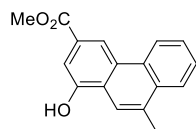
Yellow solid; m.p. = 118-120 °C; yield: 62 % (eluent: PE/EA: 16/1).

^1H NMR (400 MHz, DMSO- d_6) δ 9.92 (s, 1H), 8.66 – 8.58 (m, 1H), 7.94 – 7.82 (m, 3H), 7.56 – 7.47 (m, 2H), 6.79 (d, J = 1.3 Hz, 1H), 2.56 (d, J = 1.1 Hz, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 153.6 , 136.2 , 132.2 , 131.0 , 130.1 , 129.7 , 127.0 , 126.5 ,

125.0 , 124.0 , 120.8 , 120.1 , 113.7 , 112.4 , 22.4 , 20.3 .

HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{16}H_{14}O$ 223.1117; Found 223.1119.



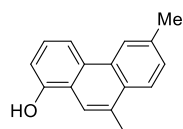
methyl 1-hydroxy-9-methylphenanthrene-3-carboxylate (2g)

Yellow solid; m.p. = 138-140 °C; yield: 38 % (eluent: PE/EA: 10/1).

1H NMR (400 MHz, DMSO- d_6) δ 10.57 (s, 1H), 8.83 – 8.76 (m, 2H), 8.12 – 8.07 (m, 1H), 8.00 (s, 1H), 7.76 – 7.69 (m, 2H), 7.57 (d, J = 1.4 Hz, 1H), 3.93 (s, 3H), 2.72 (d, J = 1.1 Hz, 3H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 167.1 , 153.9 , 134.3 , 132.2 , 130.4 , 130.2 , 127.8 , 127.6 , 127.6 , 125.3 , 125.1 , 123.9 , 120.4 , 115.6 , 109.9 , 52.7 , 20.5 .

HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{17}H_{15}O_3$ 267.1016; Found 267.1015.



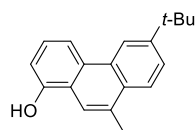
6,9-dimethylphenanthren-1-ol (2h)

Light yellow solid; m.p. = 106-108 °C; yield: 66 % (eluent: PE/EA: 16/1).

1H NMR (400 MHz, Chloroform- d) δ 8.47 – 8.43 (m, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.45 (dd, J = 8.4, 1.7 Hz, 1H), 7.36 (dd, J = 8.4, 7.6 Hz, 1H), 6.89 (dd, J = 7.6, 0.9 Hz, 1H), 5.42 (s, 1H), 2.71 (d, J = 1.1 Hz, 3H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 151.2 , 135.8 , 131.8 , 130.9 , 130.1 , 130.0 , 128.3 , 125.4 , 124.5 , 123.2 , 121.8 , 118.6 , 115.2 , 110.5 , 21.9 , 20.3 .

HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{16}H_{14}O$ 223.1117; Found 223.1118.



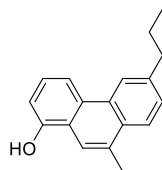
6-(tert-butyl)-9-methylphenanthren-1-ol (2i)

Orange liquid; yield: 68 % (eluent: PE/EA: 16/1).

1H NMR (400 MHz, Methanol- d_4) δ 8.66 (d, J = 2.0 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.98 – 7.87 (m, 2H), 7.65 (dd, J = 8.6, 2.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 6.97 – 6.91 (m, 1H), 4.90 (s, 1H), 2.67 (s, 3H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, Methanol- d_4) δ 153.2 , 148.4 , 131.2 , 130.2 , 129.9 , 129.9 , 125.5 , 124.3 , 124.0 , 122.3 , 119.3 , 118.6 , 113.2 , 109.5 , 34.5 , 30.6 , 18.9 .

HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{19}H_{20}O$ 265.1587; Found 265.1588.



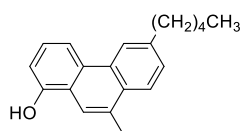
9-methyl-6-propylphenanthren-1-ol (2j)

Orange solid; m.p. = 118-120 °C; yield: 63 % (eluent: PE/EA: 16/1).

^1H NMR (400 MHz, Methanol- d_4) δ 8.50 – 8.43 (m, 1H), 8.15 (d, J = 8.4 Hz, 1H), 8.00 – 7.87 (m, 2H), 7.42 (dd, J = 8.4, 1.7 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 6.97 – 6.90 (m, 1H), 4.89 (s, 1H), 2.81 (t, J = 7.6 Hz, 2H), 2.68 (d, J = 1.1 Hz, 3H), 1.76 (h, J = 7.4 Hz, 2H), 0.99 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Methanol- d_4) δ 153.1, 140.2, 130.9, 130.4, 130.3, 130.2, 127.1, 125.5, 124.1, 122.3, 122.2, 119.2, 113.3, 109.6, 38.0, 24.6, 19.0, 12.8.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{O}$ 251.1430; Found 251.1432.



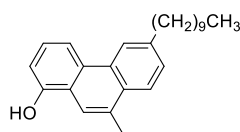
9-methyl-6-pentylphenanthren-1-ol (2k)

Orange solid; m.p. = 68-70 °C; yield: 62 % (eluent: PE/EA: 16/1).

^1H NMR (400 MHz, Methanol- d_4) δ 8.42 (d, J = 1.7 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.95 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.39 – 7.31 (m, 2H), 6.94 (d, J = 7.6 Hz, 1H), 4.91 (s, 1H), 2.76 (t, J = 7.7 Hz, 2H), 2.68 – 2.62 (m, 3H), 1.73 – 1.62 (m, 2H), 1.38 – 1.28 (m, 4H), 0.91 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, Methanol- d_4) δ 153.1, 140.4, 130.9, 130.4, 130.3, 130.2, 127.0, 125.5, 124.1, 122.2, 119.2, 113.3, 109.6, 35.9, 31.3, 31.2, 22.3, 19.0, 13.1.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$ 279.1743; Found 279.1745.



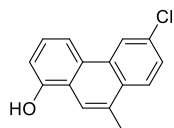
6-decyl-9-methylphenanthren-1-ol (2l)

Orange solid; m.p. = 64-66 °C; yield: 60 % (eluent: PE/EA: 16/1).

^1H NMR (400 MHz, Methanol- d_4) δ 8.43 (d, J = 1.6 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.97 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 6.95 (dd, J = 7.7, 0.8 Hz, 1H), 4.92 (s, 1H), 2.77 (t, J = 7.7 Hz, 2H), 2.67 (d, J = 1.2 Hz, 3H), 1.71 – 1.62 (m, 2H), 1.32 – 1.17 (m, 15H), 0.86 (t, J = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Methanol- d_4) δ 153.1, 140.3, 131.0, 130.3, 130.3, 130.2, 127.0, 125.5, 124.1, 122.2, 119.2, 113.4, 109.6, 35.9, 31.7, 31.5, 29.4, 29.4, 29.3, 29.1, 29.0, 22.4, 19.1, 13.1.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{O}$ 349.2526; Found 349.2527.



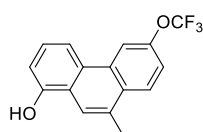
6-chloro-9-methylphenanthren-1-ol (2m)

Yellow solid; m.p. = 140-142 °C; yield: 71 % (eluent: PE/EA: 16/1).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.23 (s, 1H), 8.77 (d, *J* = 2.2 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.03 – 7.95 (m, 2H), 7.61 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 2.64 (d, *J* = 1.2 Hz, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 153.7 , 131.8 , 131.8 , 130.5 , 130.5 , 130.1 , 127.2 , 127.2 , 127.1 , 123.3 , 122.5 , 121.3 , 114.1 , 111.5 , 20.2 .

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₁ClO 243.0571; Found 243.0572.



9-methyl-6-(trifluoromethoxy)phenanthren-1-ol (2n)

Orange solid; m.p. = 132-134 °C; yield: 70 % (eluent: PE/EA: 10/1).

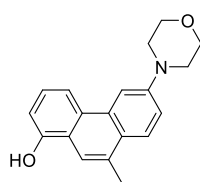
¹H NMR (400 MHz, Methanol-*d*₄) δ 8.43 (dd, *J* = 2.3, 1.1 Hz, 1H), 8.02 – 7.95 (m, 3H), 7.46 – 7.38 (m, 1H), 7.36 (t, *J* = 8.1 Hz, 1H), 6.97 (dd, *J* = 7.7, 0.8 Hz, 1H), 4.91 (s, 1H), 2.62 (s, 2H).

¹³C NMR (101 MHz, Methanol-*d*₄) δ 154.7 , 148.5 , 132.8 , 131.9 , 131.7 , 131.3 , 127.7 , 127.6 , 123.9 , 122.2 , 120.4 , 116.1 , 114.6 , 111.8 , 20.2 .

¹³C NMR (101 MHz, Methanol-*d*₄) δ 154.7 , 148.5 , 132.8 , 131.9 , 131.7 , 131.3 , 127.7 , 127.6 , 123.9 , 123.4 , 122.2 , 120.9 , 120.4 , 116.1 , 114.6 , 111.8 , 20.2 .

¹⁹F NMR (376 MHz, Methanol-*d*₄) δ -59.09 .

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₁F₃O₂ 293.0784; Found 293.0786.



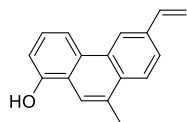
9-methyl-6-morpholinophenanthren-1-ol (2o)

Orange solid; m.p. > 150 °C; yield: 65 % (eluent: PE/EA: 5/1).

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.99 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 2.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.76 (s, 1H), 7.38 – 7.32 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 3.84 – 3.79 (m, 4H), 3.35 – 3.28 (m, 4H), 2.63 (d, *J* = 1.1 Hz, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 153.6 , 149.8 , 131.5 , 130.7 , 130.7 , 126.1 , 125.9 , 125.7 , 122.6 , 117.8 , 117.4 , 114.1 , 110.6 , 107.2 , 66.6 , 49.1 , 20.3 .

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₁₉NO₂ 294.1489; Found 294.1491.



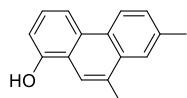
9-methyl-6-vinylphenanthren-1-ol (2p)

White solid; m.p. = 146-148 °C; yield: 36 % (eluent: PE/EA: 16/1).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.14 (s, 1H), 8.77 (d, *J* = 1.9 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.03 – 7.94 (m, 2H), 7.83 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.07 – 6.97 (m, 2H), 6.08 (d, *J* = 17.6 Hz, 1H), 5.39 (d, *J* = 11.0 Hz, 1H), 2.68 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 153.7, 137.4, 135.4, 131.7, 131.1, 130.7, 130.5, 126.9, 125.4, 124.2, 122.6, 122.3, 120.9, 115.3, 114.0, 110.9, 20.3.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₇H₁₄O 235.1117; Found 235.1119.



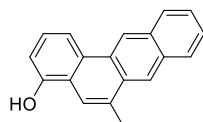
7,9-dimethylphenanthren-1-ol (2q)

White solid; m.p. = 136-138 °C; yield: 59 % (eluent: PE/EA: 16/1).

¹H NMR (400 MHz, Methanol-*d*₄) δ 8.46 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.00 – 7.94 (m, 1H), 7.77 – 7.71 (m, 1H), 7.37 – 7.28 (m, 2H), 6.92 (dd, *J* = 7.7, 0.9 Hz, 1H), 4.92 (s, 1H), 2.63 (d, *J* = 1.2 Hz, 3H), 2.48 (s, 3H).

¹³C NMR (101 MHz, Methanol-*d*₄) δ 153.1, 135.8, 132.1, 131.1, 130.2, 128.1, 127.3, 125.6, 123.7, 123.0, 121.7, 120.0, 113.2, 109.3, 20.4, 19.1.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄O 223.1117; Found 223.1118.



6-methyltetraphen-4-ol (2r)

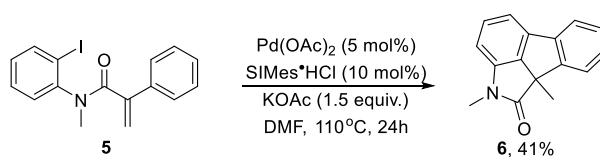
White solid; m.p. > 150 °C; yield: 61 % (eluent: PE/EA: 16/1).

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.06 (s, 1H), 9.28 (s, 1H), 8.50 (s, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.15 – 8.05 (m, 2H), 7.84 (s, 1H), 7.52 – 7.45 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 7.7, 0.8 Hz, 1H), 2.68 (d, *J* = 1.2 Hz, 3H).

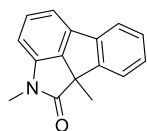
¹³C NMR (101 MHz, DMSO-*d*₆) δ 153.9, 131.9, 131.7, 131.4, 130.9, 130.9, 129.1, 128.6, 128.4, 127.2, 126.4, 126.2, 123.5, 122.9, 121.4, 120.8, 114.3, 112.1, 20.6.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₉H₁₄O 259.1117; Found 259.1119.

3.2.2 Synthesis of fused polycycle **5**



An oven-dried Schlenk tube under a nitrogen atmosphere was charged with aryl iodide **5** (0.2 mmol, 1.0 eq.), Pd(OAc)₂ (5 mol%), SiMes₃•HCl (10 mol%) and KOAc (1.5 eq.) in DMF (1 mL). The mixture was stirred at 110 °C in an oil bath for 24 h. The resulting mixture was cooled to room temperature and filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate and the combined filtrate was washed with water. Then the organic layer was dried with Na₂SO₄ before concentration. Then the residue was purified by flash chromatography on silica gel to afford pure product.



2,9b-dimethyl-2,9b-dihydro-1H-indeno[1,2,3-cd]indol-1-one (6)

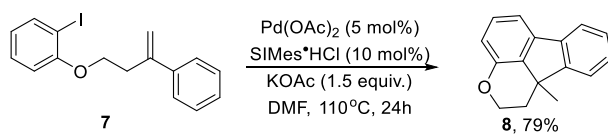
Light yellow liquid; yield: 41 % (eluent: PE/EA: 20/1).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.30 – 7.16 (m, 3H), 6.60 (d, *J* = 7.5 Hz, 1H), 3.13 (s, 3H), 1.79 (s, 3H).

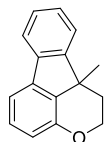
¹³C NMR (101 MHz, Chloroform-*d*) δ 181.8, 150.3, 146.7, 145.0, 142.7, 142.7, 131.5, 128.0, 126.9, 125.0, 122.1, 115.7, 106.9, 57.2, 26.9, 26.8.

HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₃NO 236.1070; Found 236.1070.

3.2.3 Synthesis of fused polycycle **7**



An oven-dried Schlenk tube under a nitrogen atmosphere was charged with aryl iodide **7** (0.2 mmol, 1.0 eq.), Pd(OAc)₂ (5 mol%), SIMes•HCl (10 mol%) and KOAc (1.5 eq.) in DMF (1 mL). The mixture was stirred at 110 °C in an oil bath for 24 h. The resulting mixture was cooled to room temperature and filtered through a thin pad of silica gel. The filter cake was washed with ethyl acetate and the combined filtrate was washed with water. Then the organic layer was dried with Na₂SO₄ before concentration. Then the residue was purified by flash chromatography on silica gel to afford pure product.



10b-methyl-1,10b-dihydro-2H-indeno[1,2,3-de]chromene (8)

White solid; m.p. = 50-52 °C; yield: 79 % (eluent: PE/EA: 50/1).

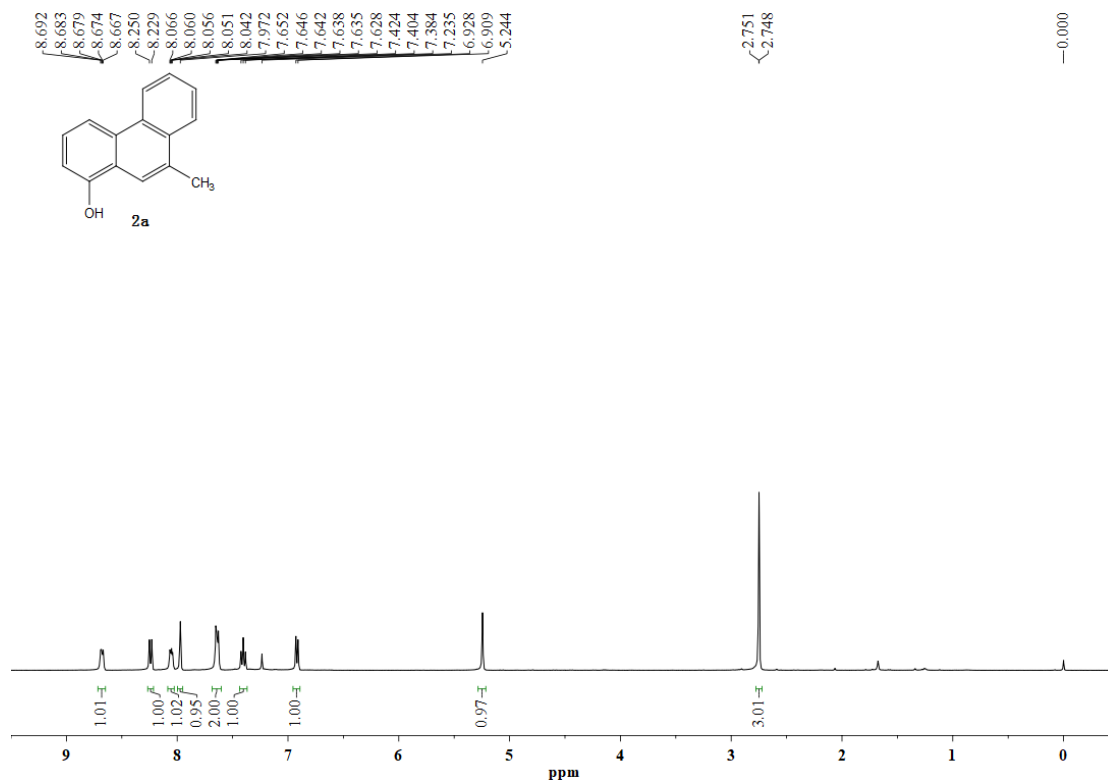
¹H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.19 (m, 3H), 6.72 (t, *J* = 4.4 Hz, 1H), 4.70 – 4.58 (m, 1H), 4.58 – 4.49 (m, 1H), 2.29 (dd, *J* = 13.1, 3.9 Hz, 1H), 1.64 (td, *J* = 13.1, 6.2 Hz, 1H), 1.44 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 153.7, 152.8, 140.5, 140.2, 134.7, 129.4, 127.4, 127.0, 123.0, 121.1, 113.6, 112.4, 65.5, 42.5, 30.9, 25.5.

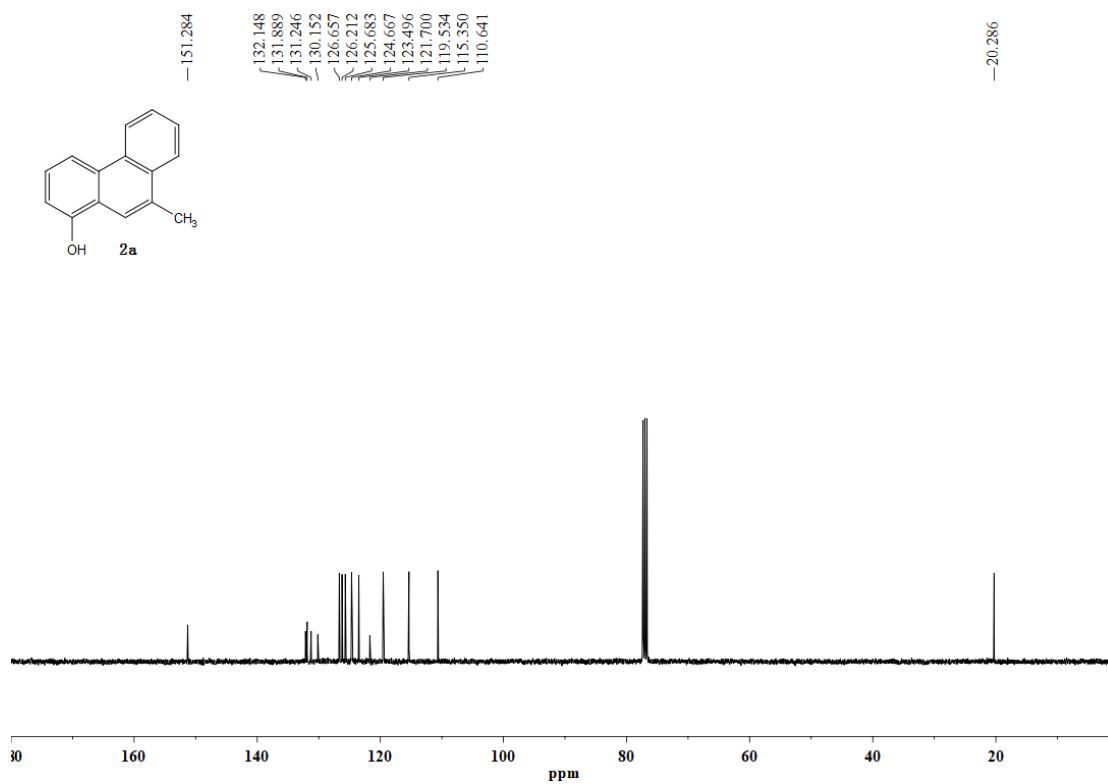
HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₆H₁₄O 223.1117; Found 223.1118.

4 NMR Spectra

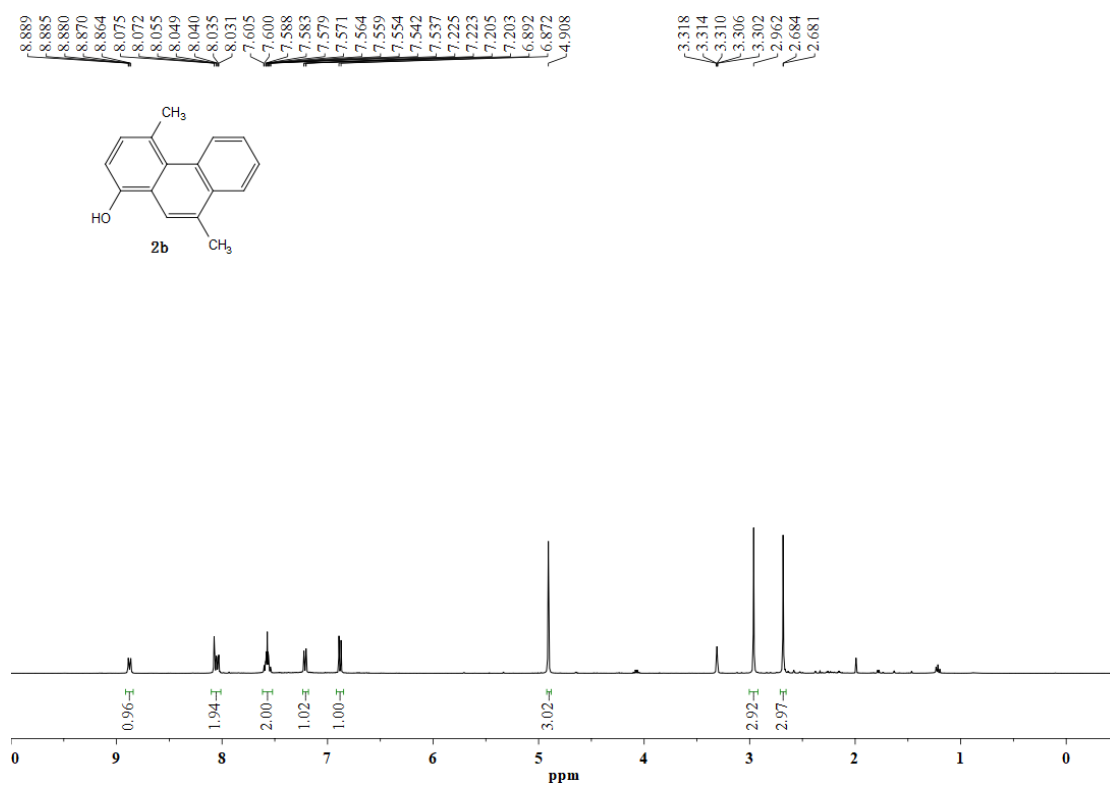
^1H NMR (400 MHz, Chloroform-*d*)



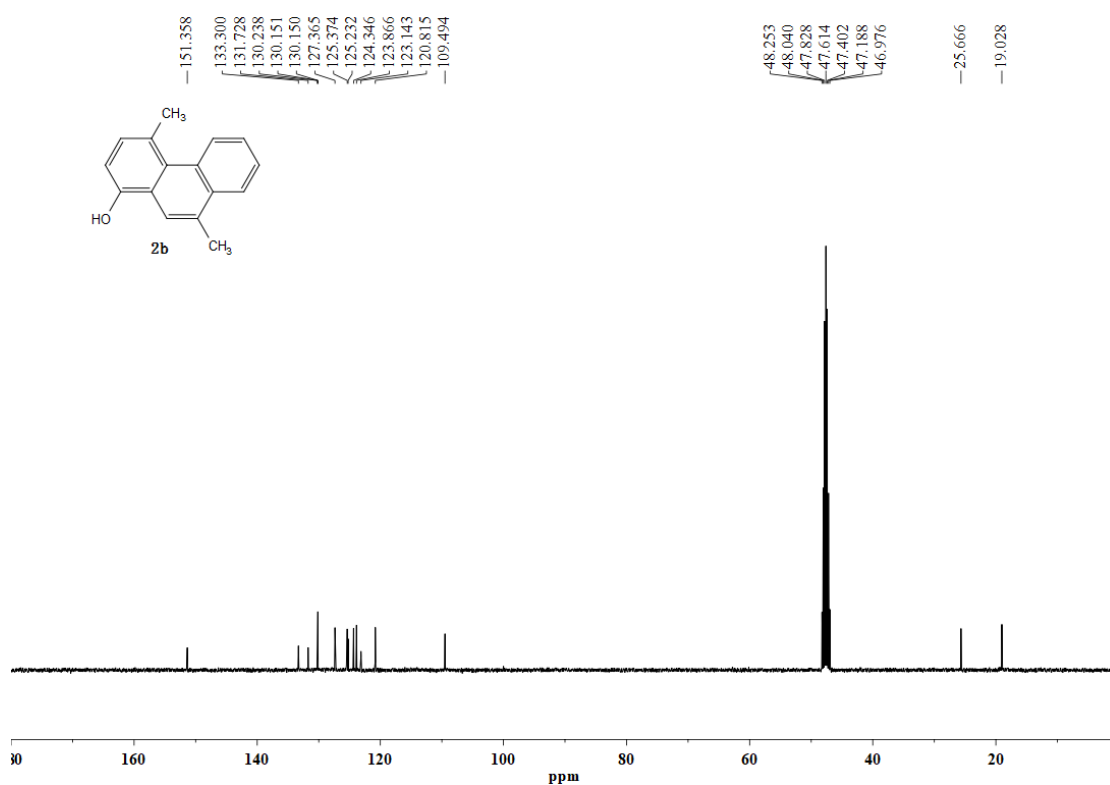
^{13}C NMR (101 MHz, Chloroform-*d*)



¹H NMR (400 MHz, Methanol-d₄)



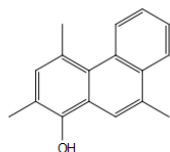
¹³C NMR (101 MHz, Methanol-d₄)



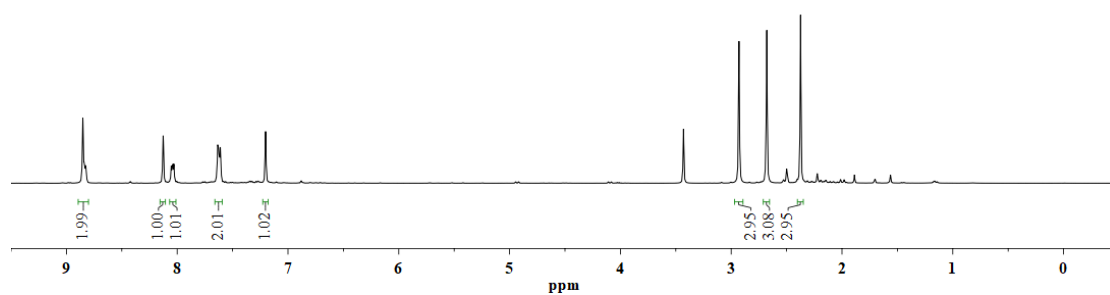
¹H NMR (400 MHz, DMSO-*d*₆)

8.852
8.841
8.833
8.825
8.127
8.054
8.045
8.038
8.029
7.635
7.626
7.619
7.610
7.202

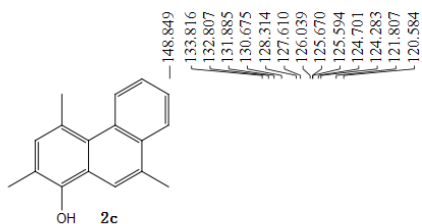
-3.431
2.930
2.679
2.501
2.374



2c



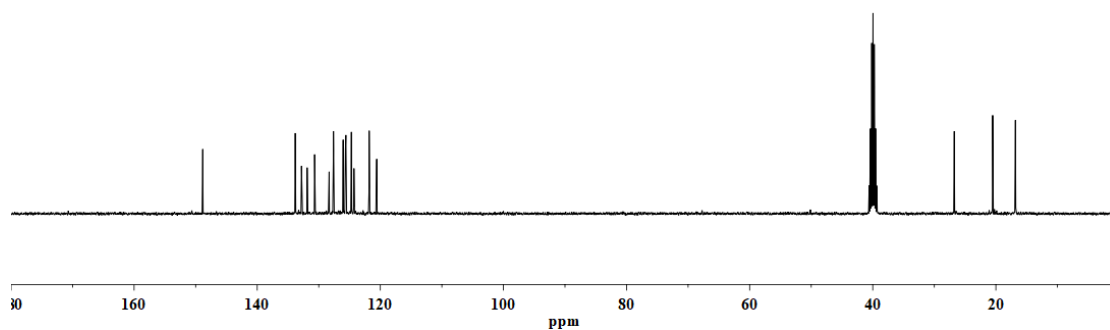
¹³C NMR (101 MHz, DMSO-*d*₆)



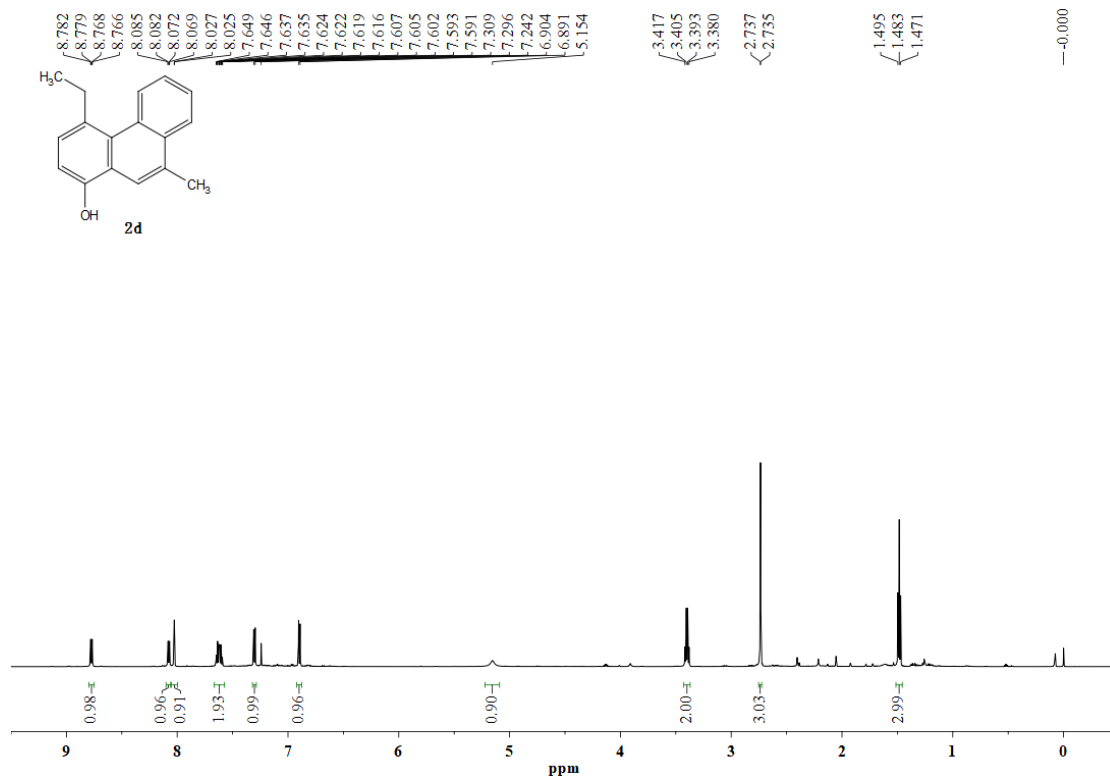
2c

148.849
133.816
132.807
131.885
130.675
128.314
127.610
126.039
125.670
125.594
124.701
124.283
121.807
120.584

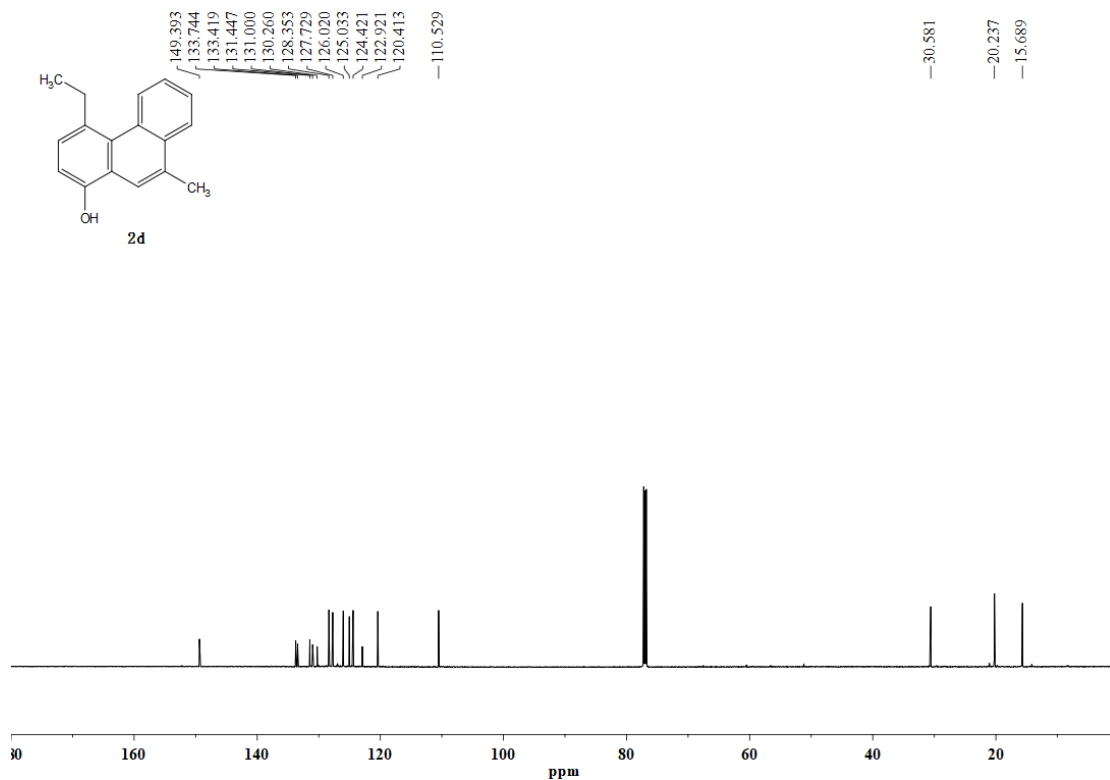
26.759
20.519
16.826



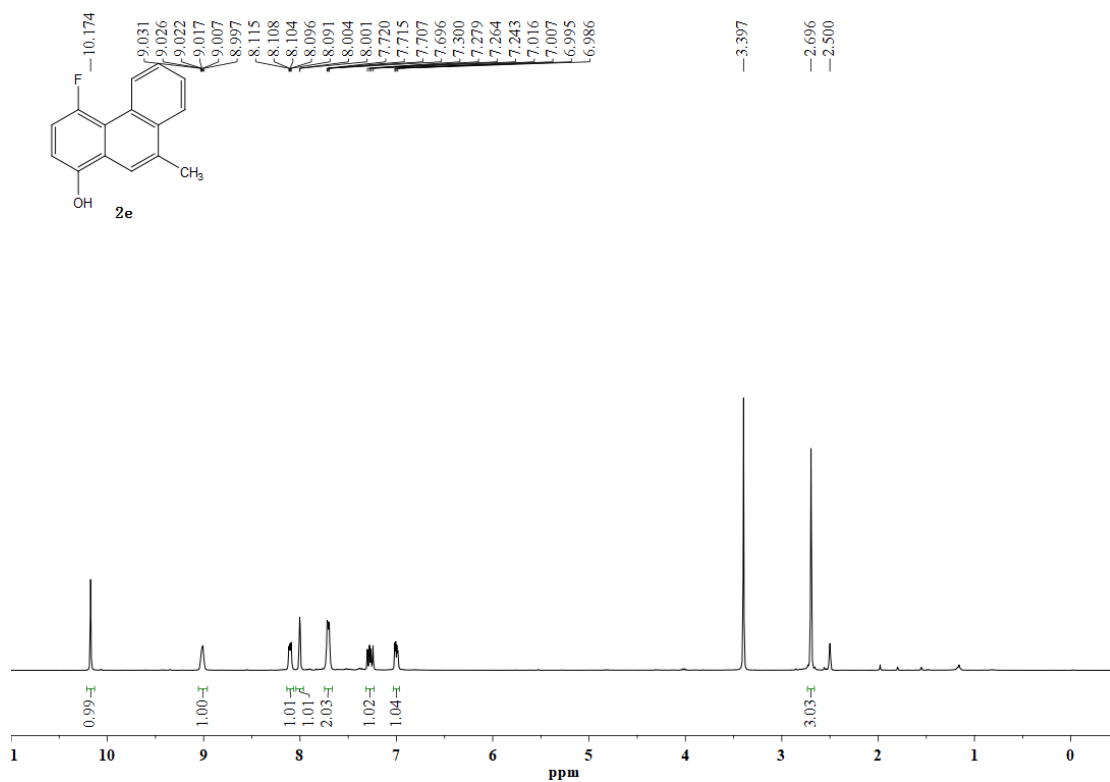
¹H NMR (600 MHz, Chloroform-*d*)



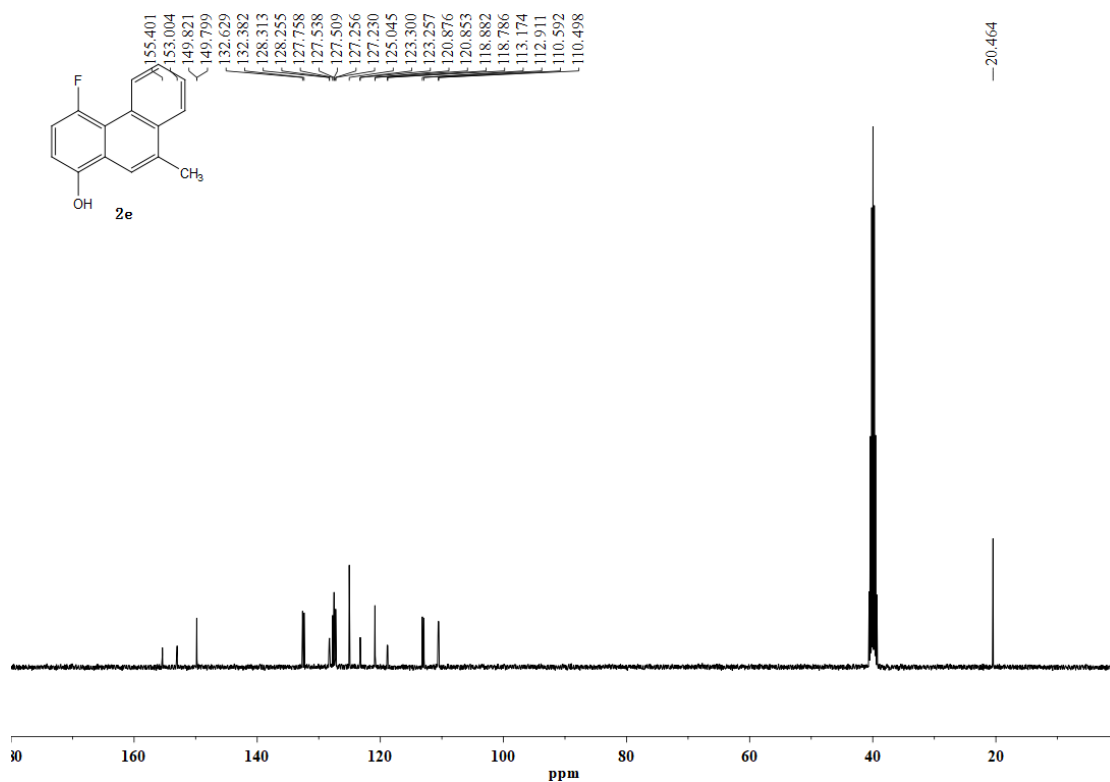
¹³C NMR (151 MHz, Chloroform-*d*)



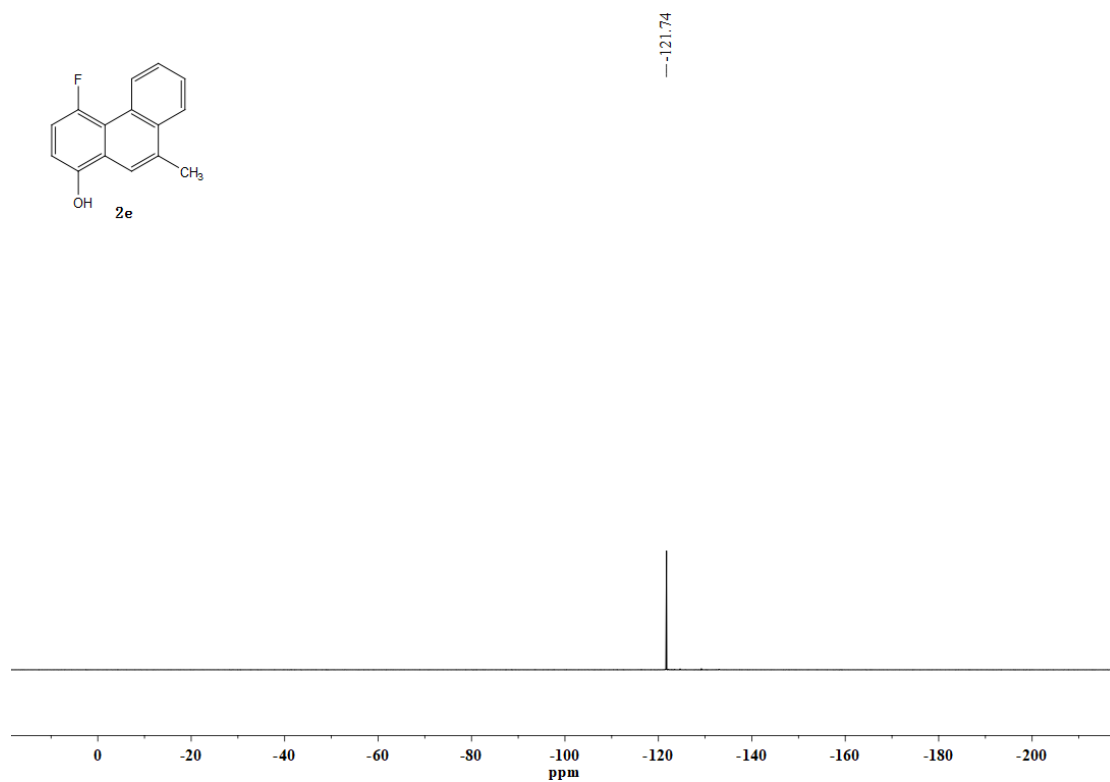
¹H NMR (400 MHz, DMSO-*d*₆)



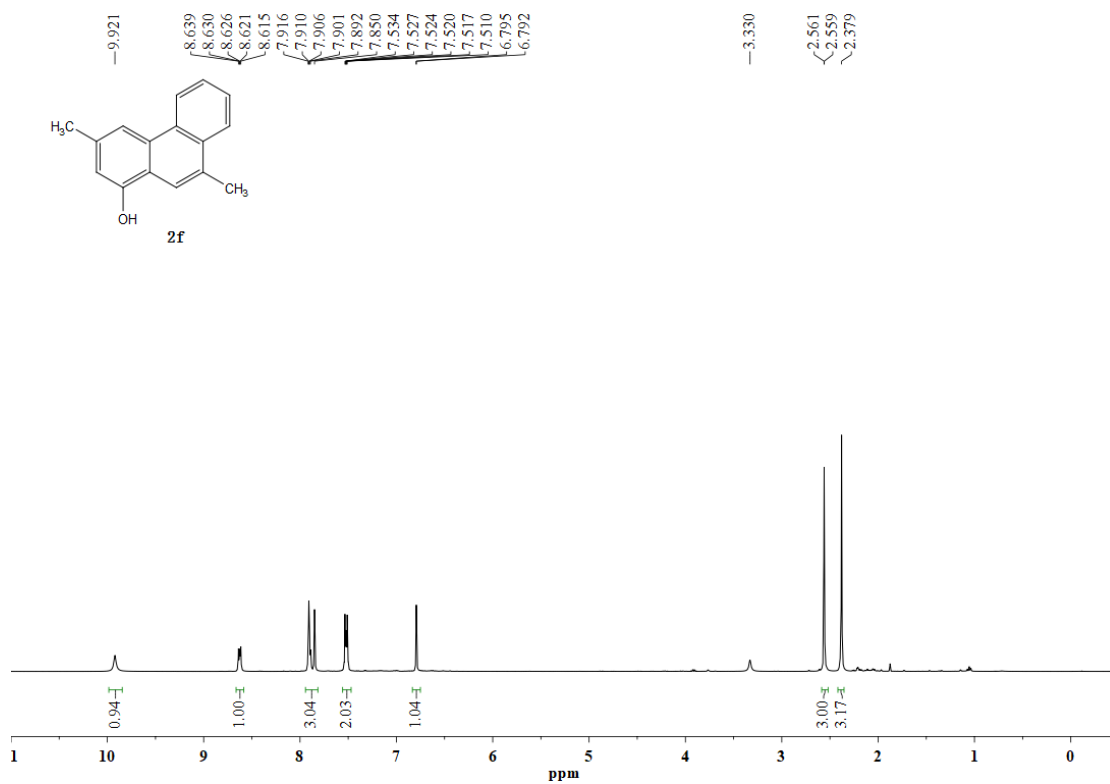
¹³C NMR (101 MHz, DMSO-*d*₆)



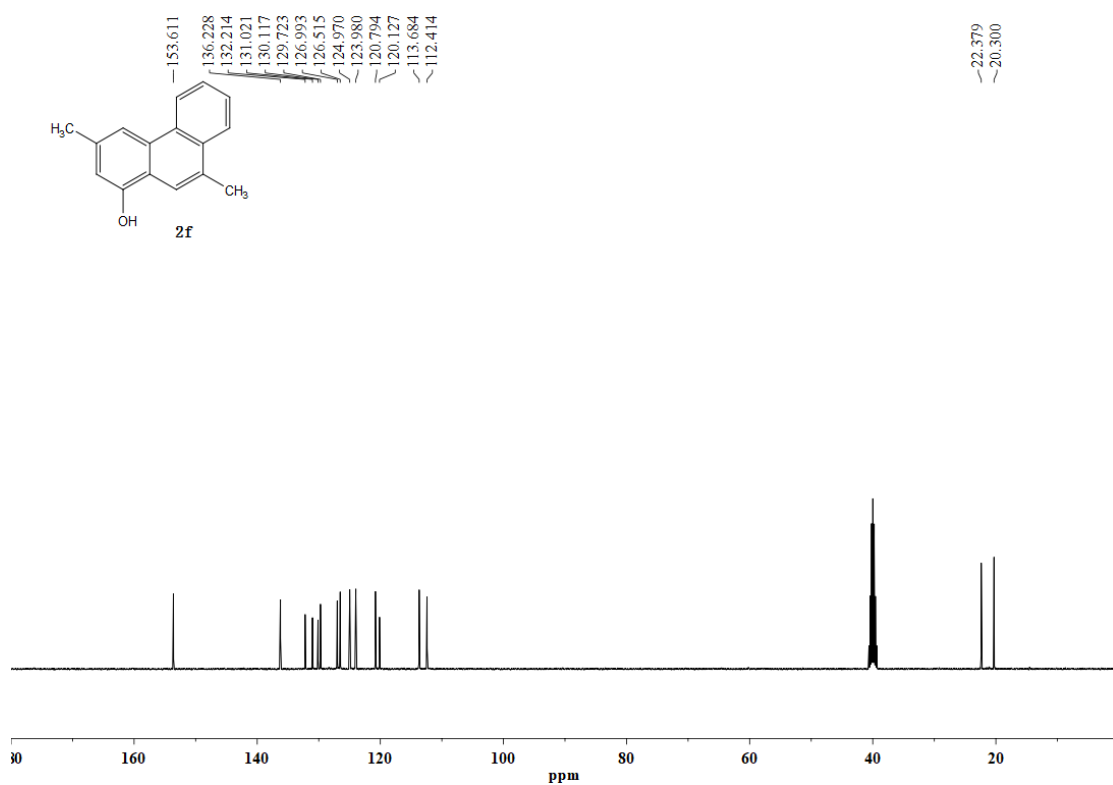
^{19}F NMR (376 MHz, $\text{DMSO-}d_6$)



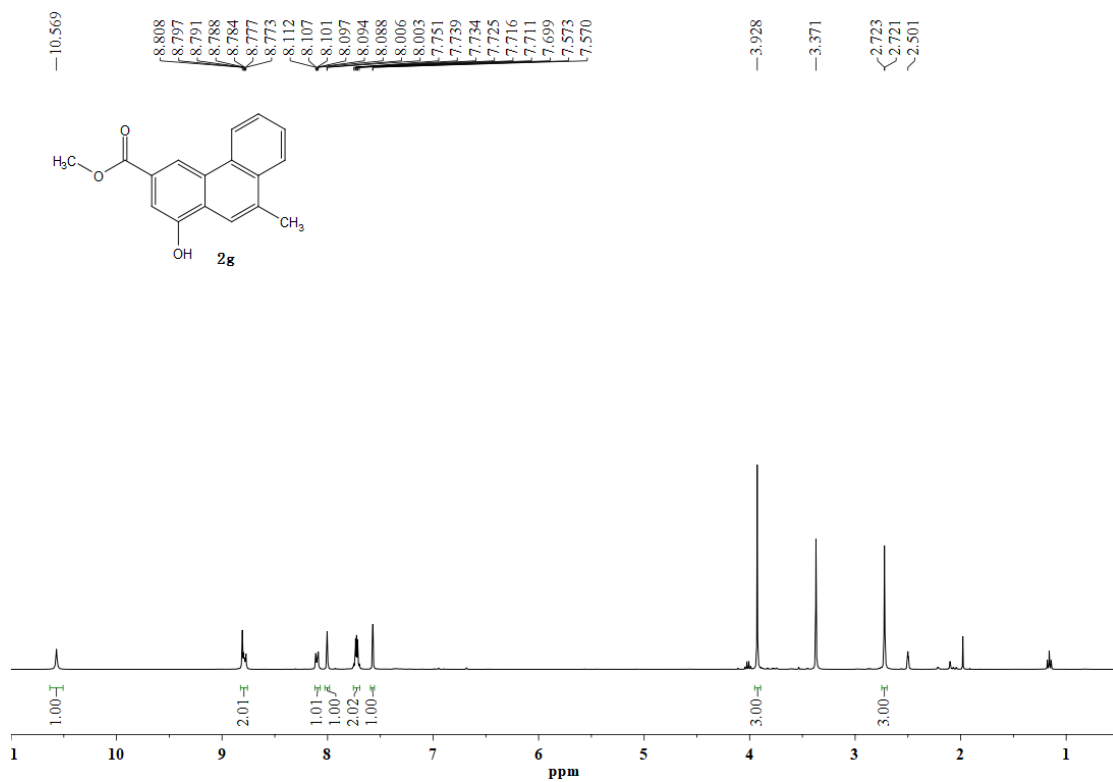
^1H NMR (400 MHz, $\text{DMSO-}d_6$)



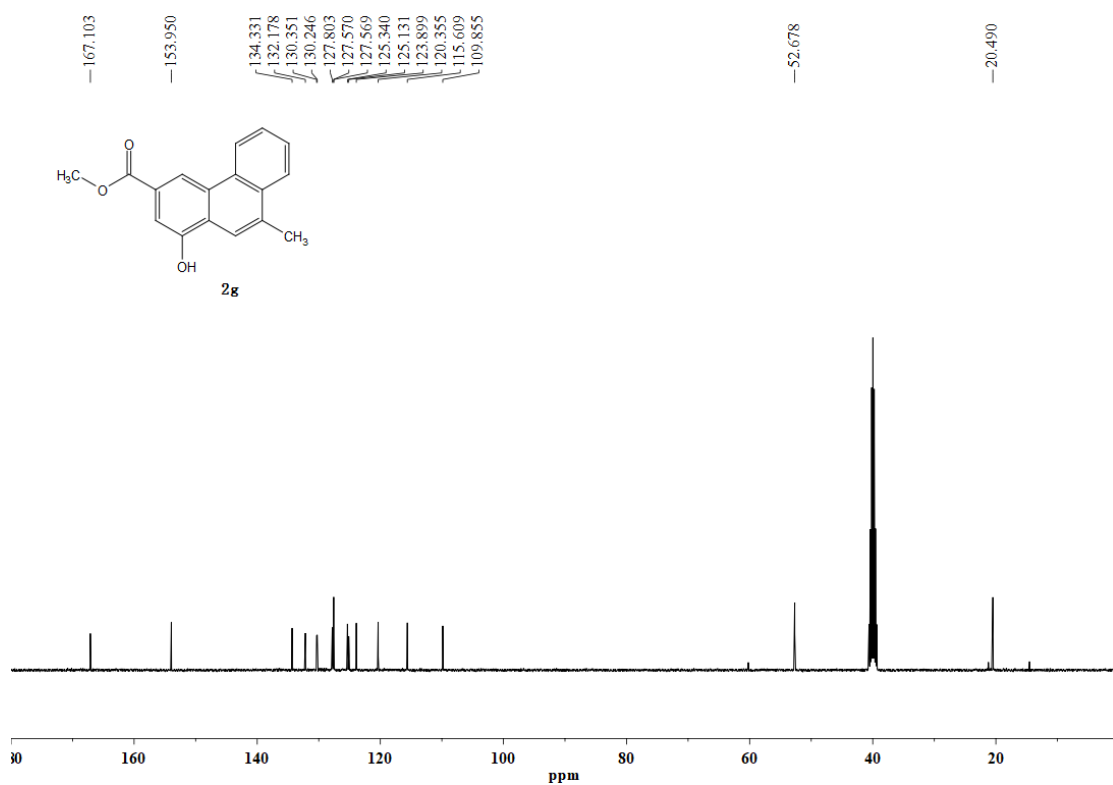
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$)



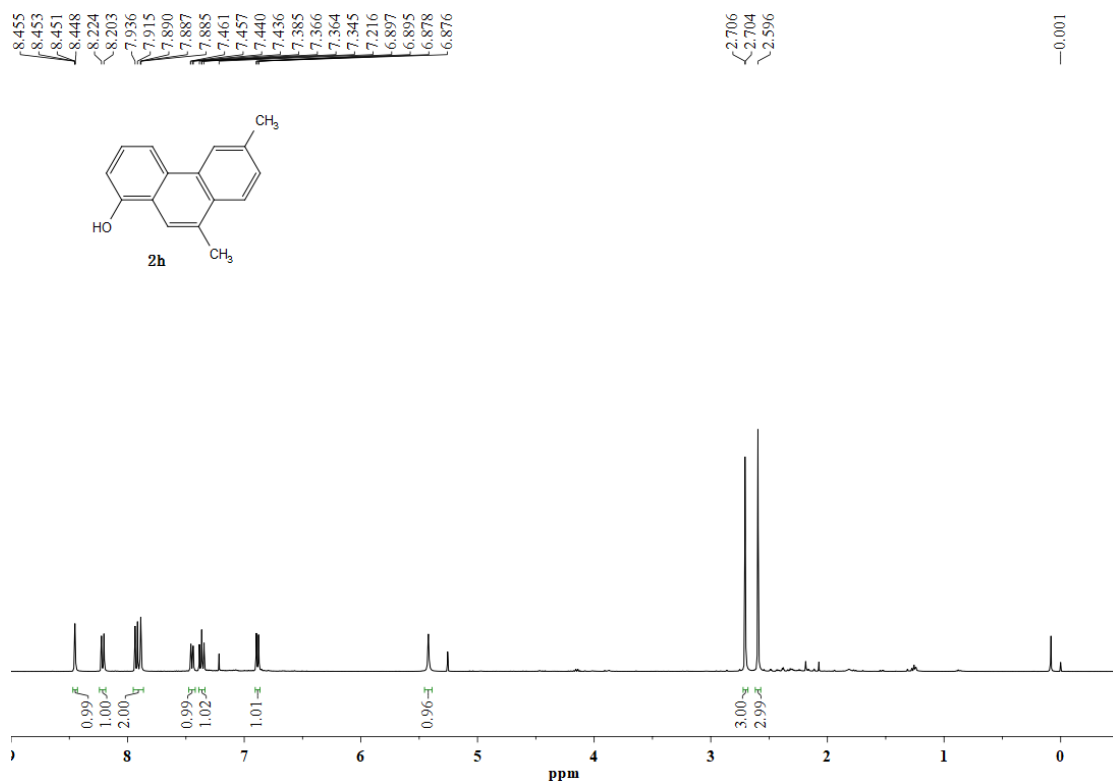
^1H NMR (400 MHz, $\text{DMSO-}d_6$)



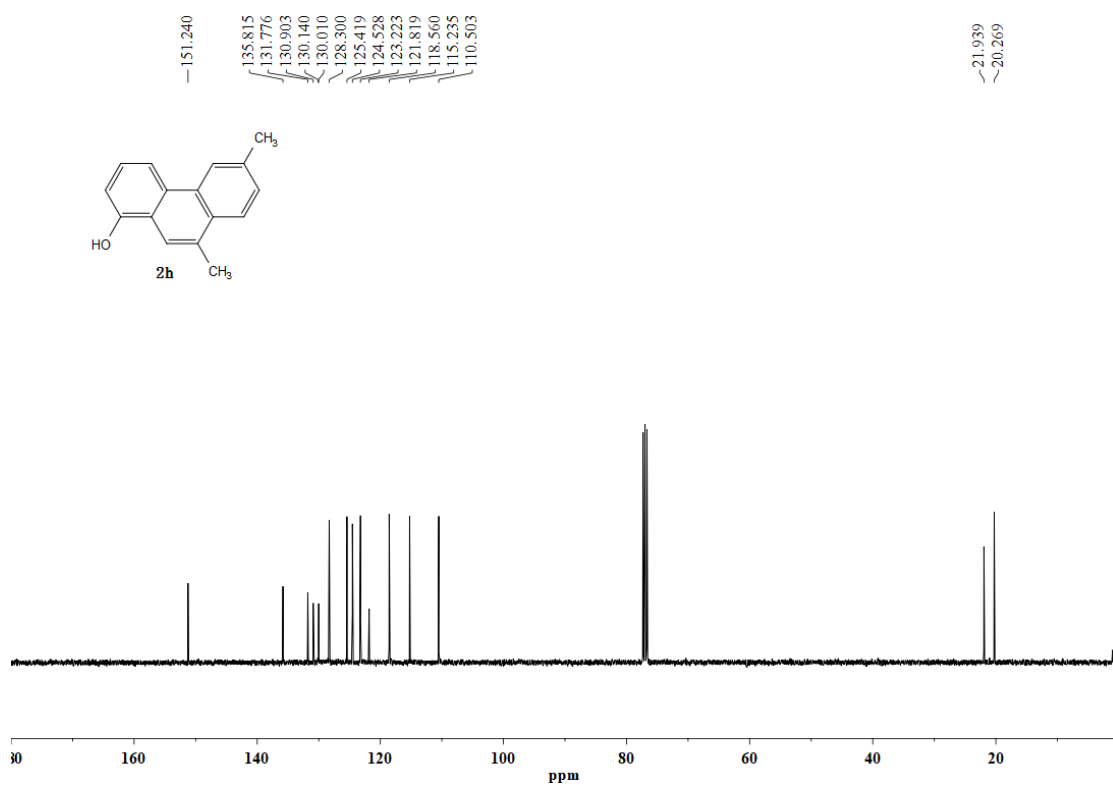
¹³C NMR (101 MHz, DMSO-*d*₆)



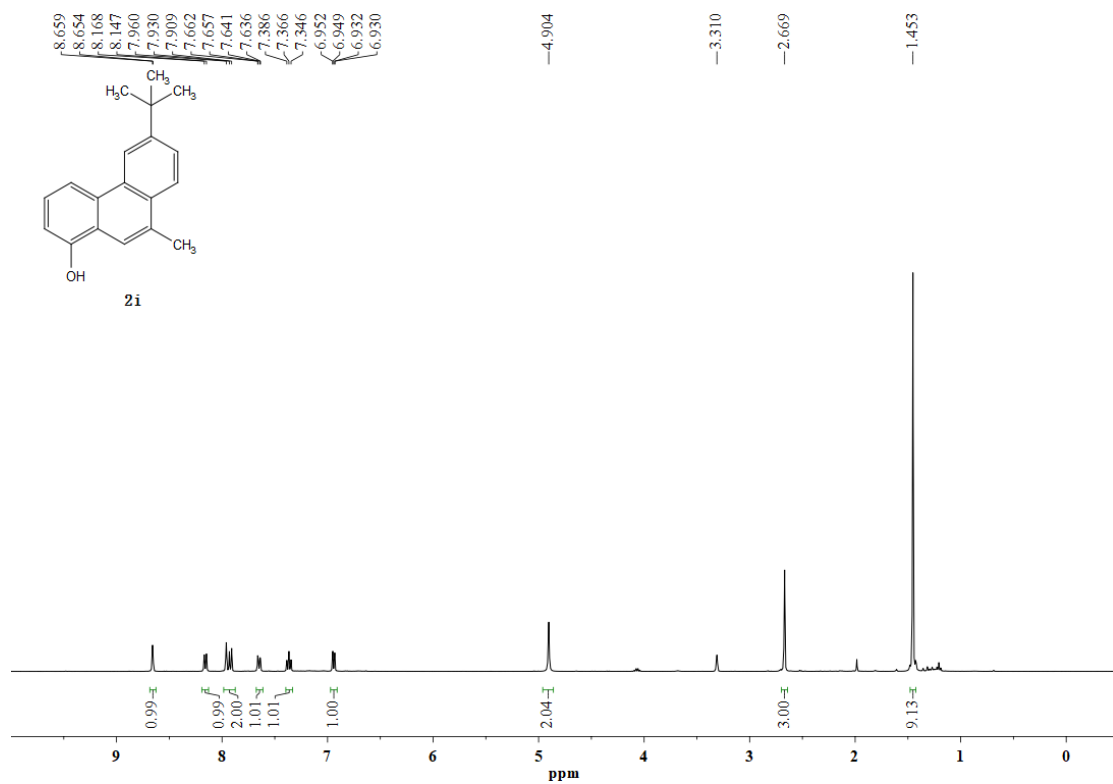
¹H NMR (400 MHz, Chloroform-*d*)



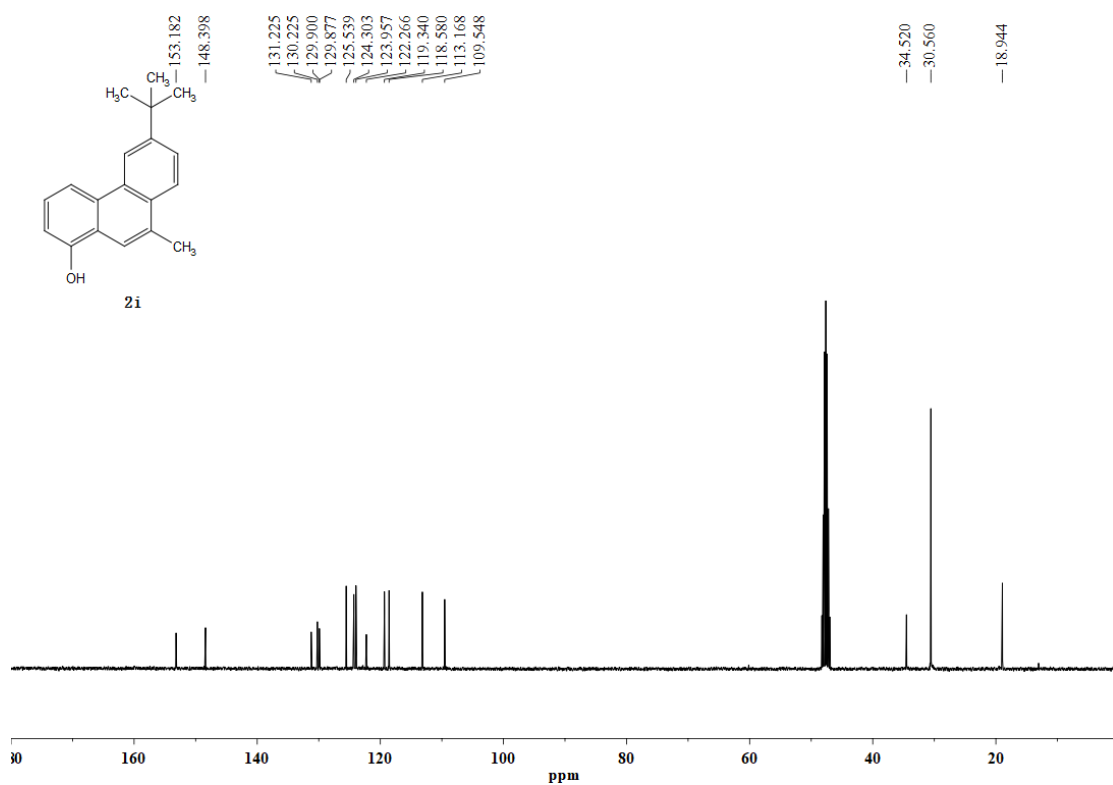
¹³C NMR (101 MHz, Chloroform-*d*)



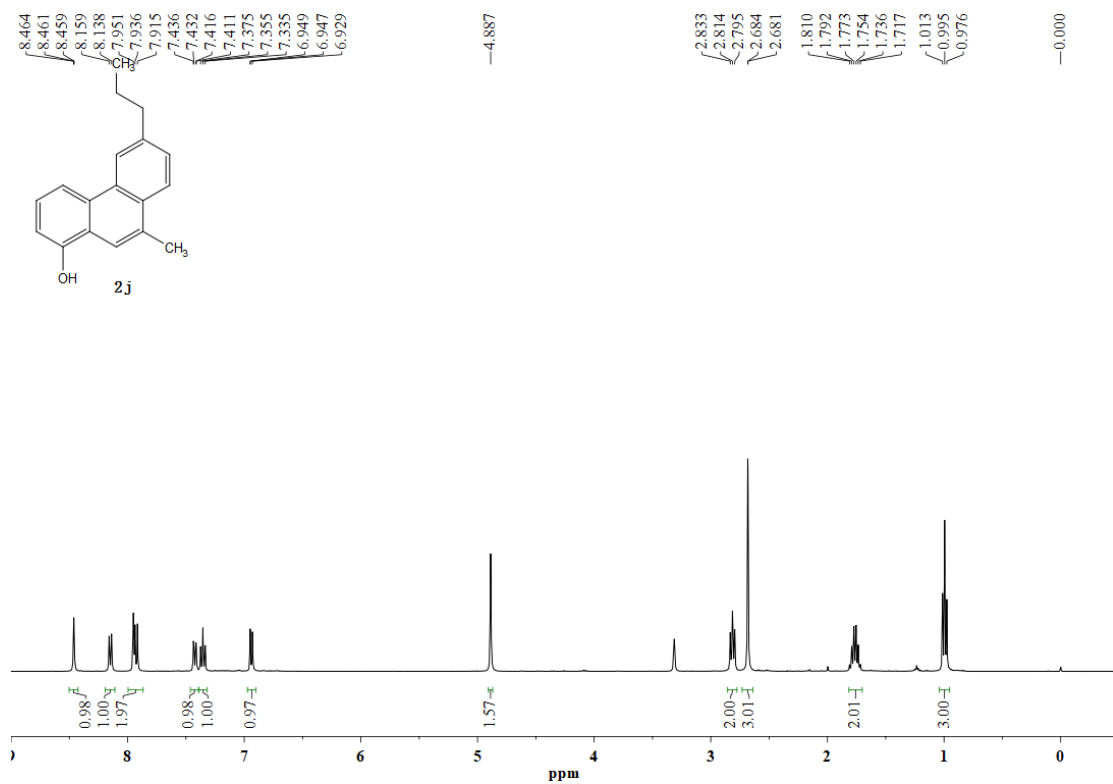
¹H NMR (400 MHz, Methanol-*d*₄)



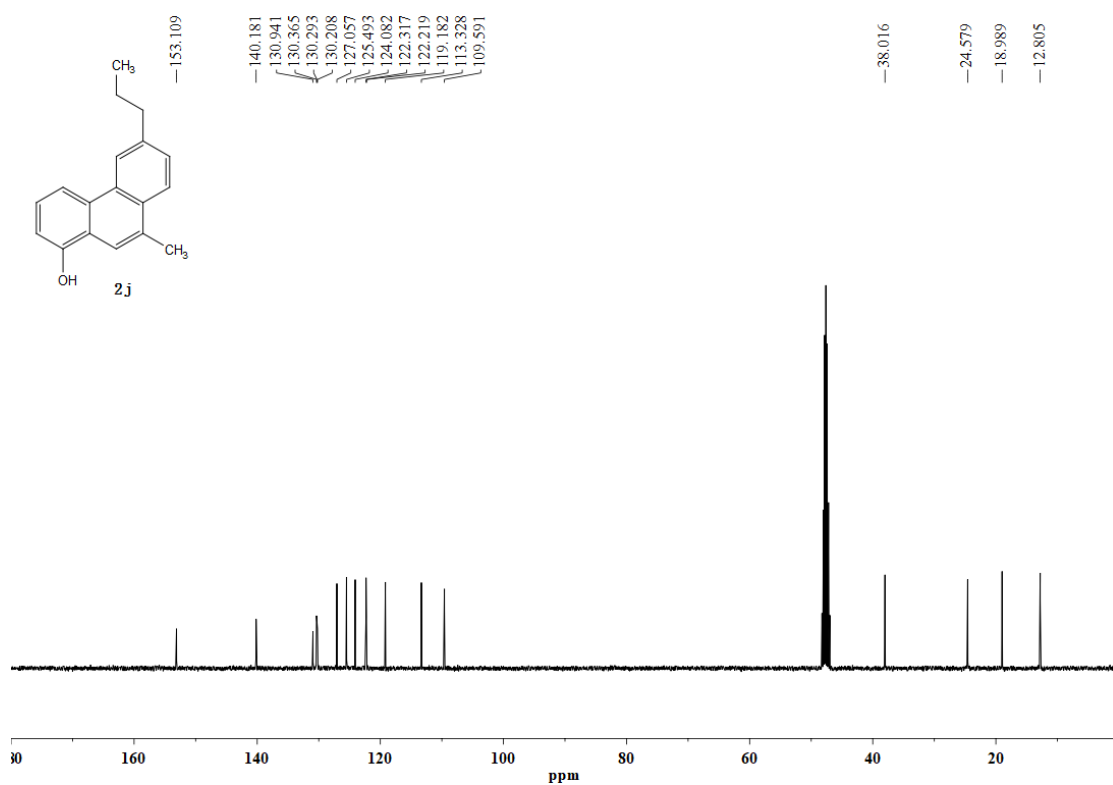
¹³C NMR (101 MHz, Methanol-*d*₄)



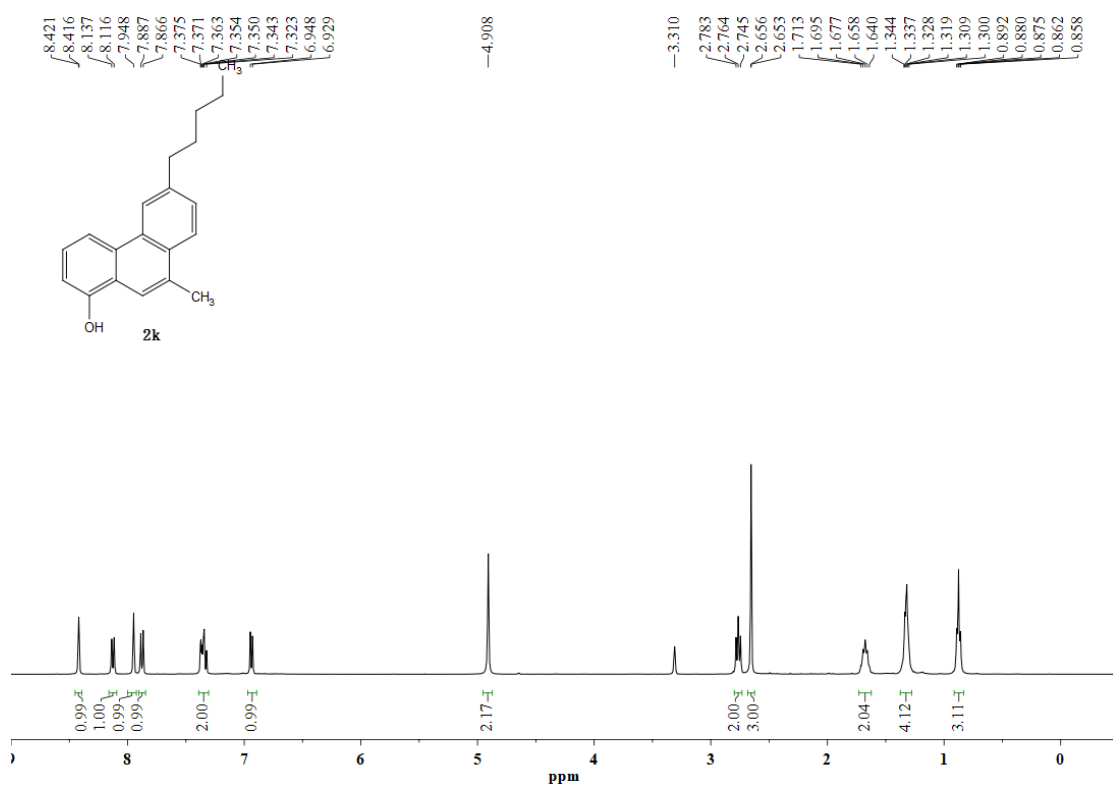
¹H NMR (400 MHz, Methanol-*d*₄)



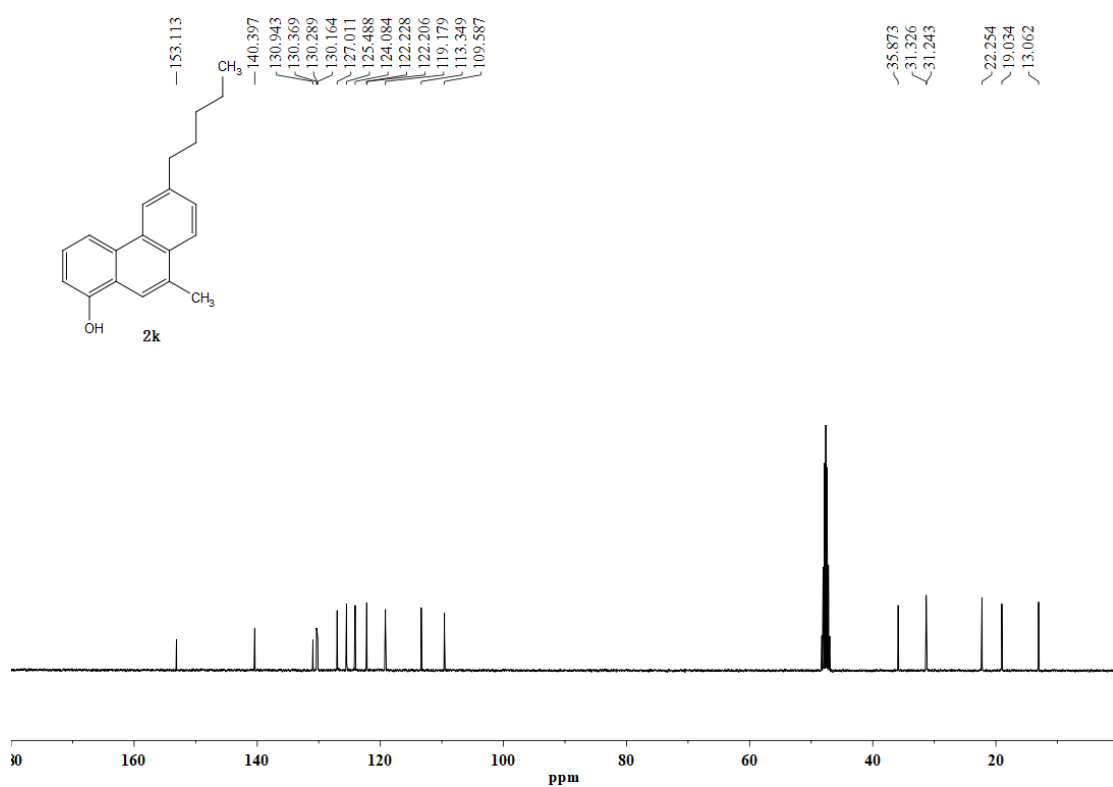
¹³C NMR (101 MHz, Methanol-d₄)



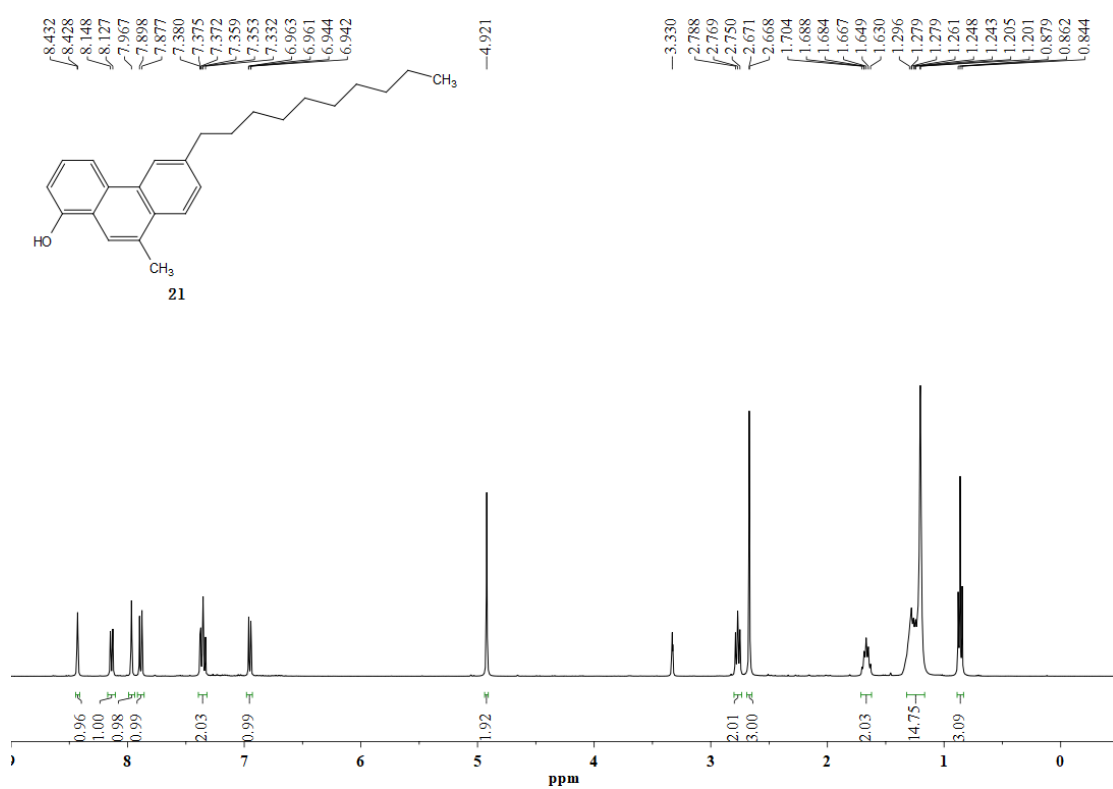
¹H NMR (400 MHz, Methanol-d₄)



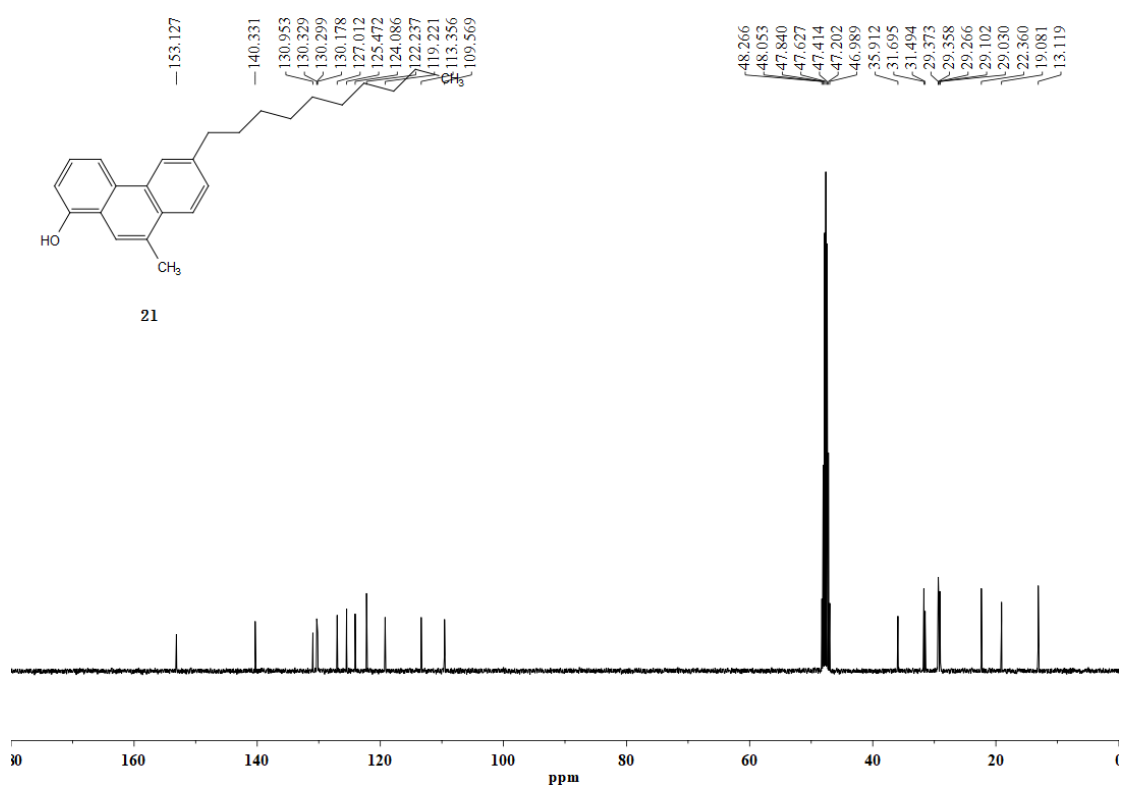
¹³C NMR (101 MHz, Methanol-*d*₄)



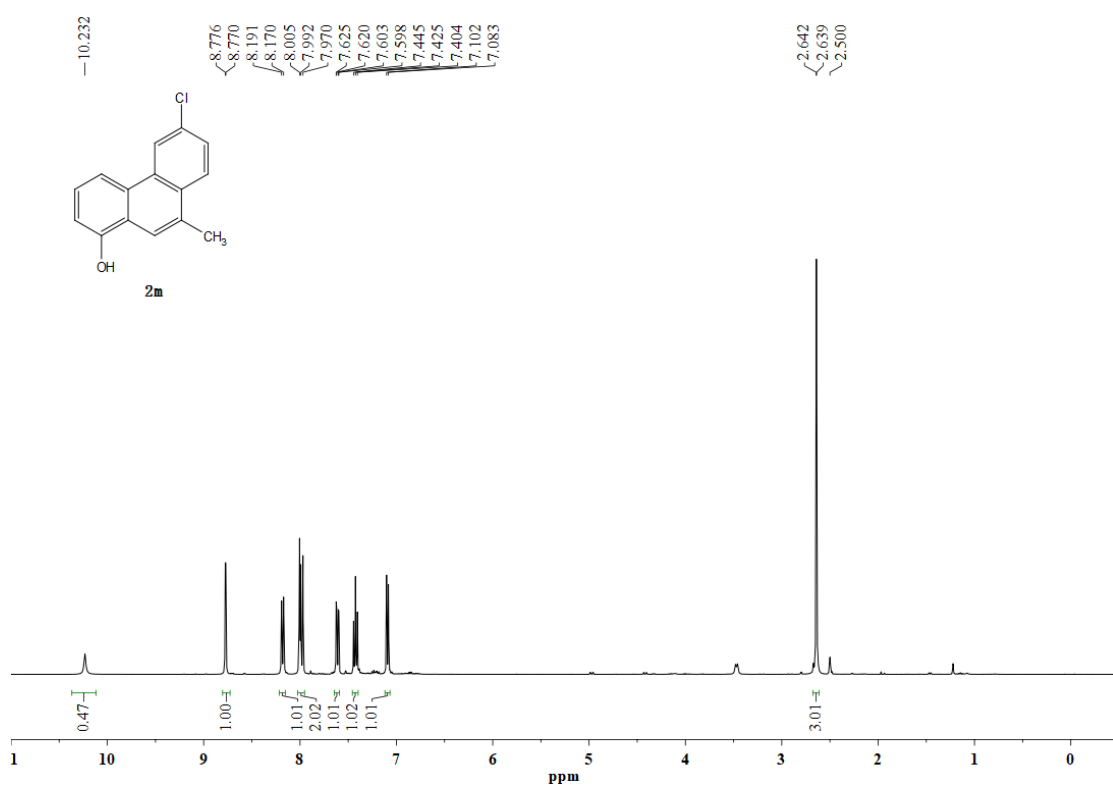
¹H NMR (400 MHz, Methanol-*d*₄)



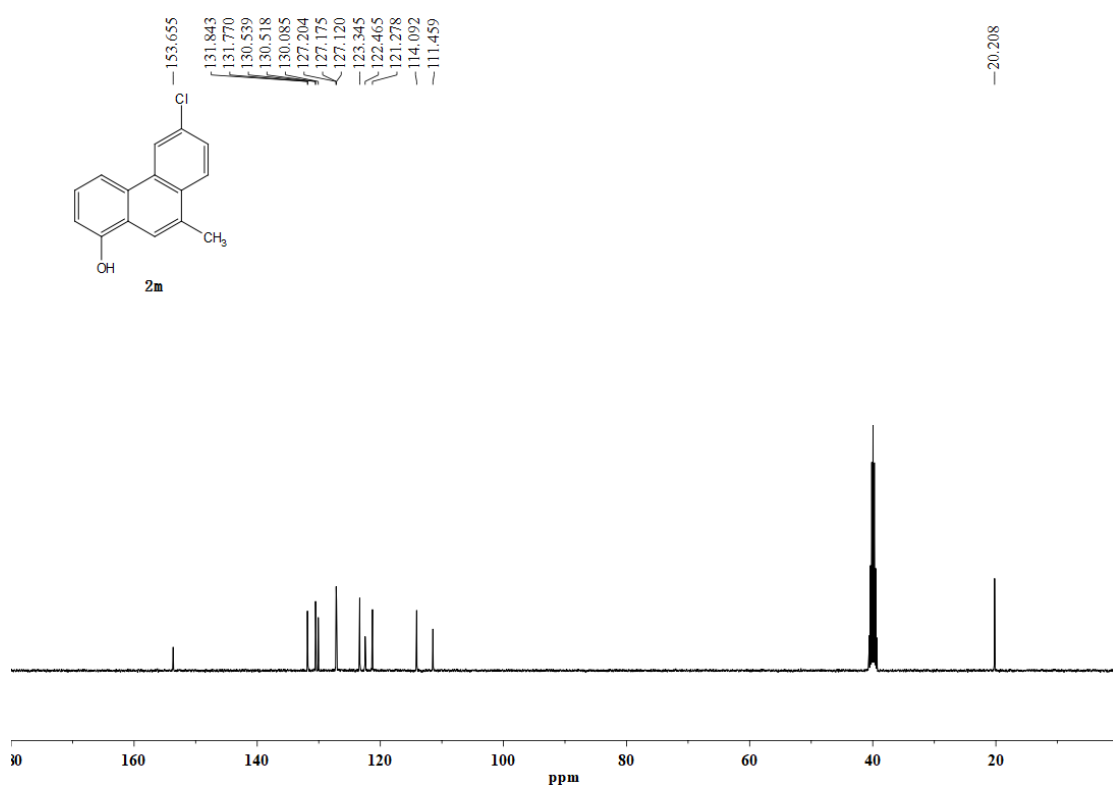
¹³C NMR (101 MHz, Methanol-*d*₄)



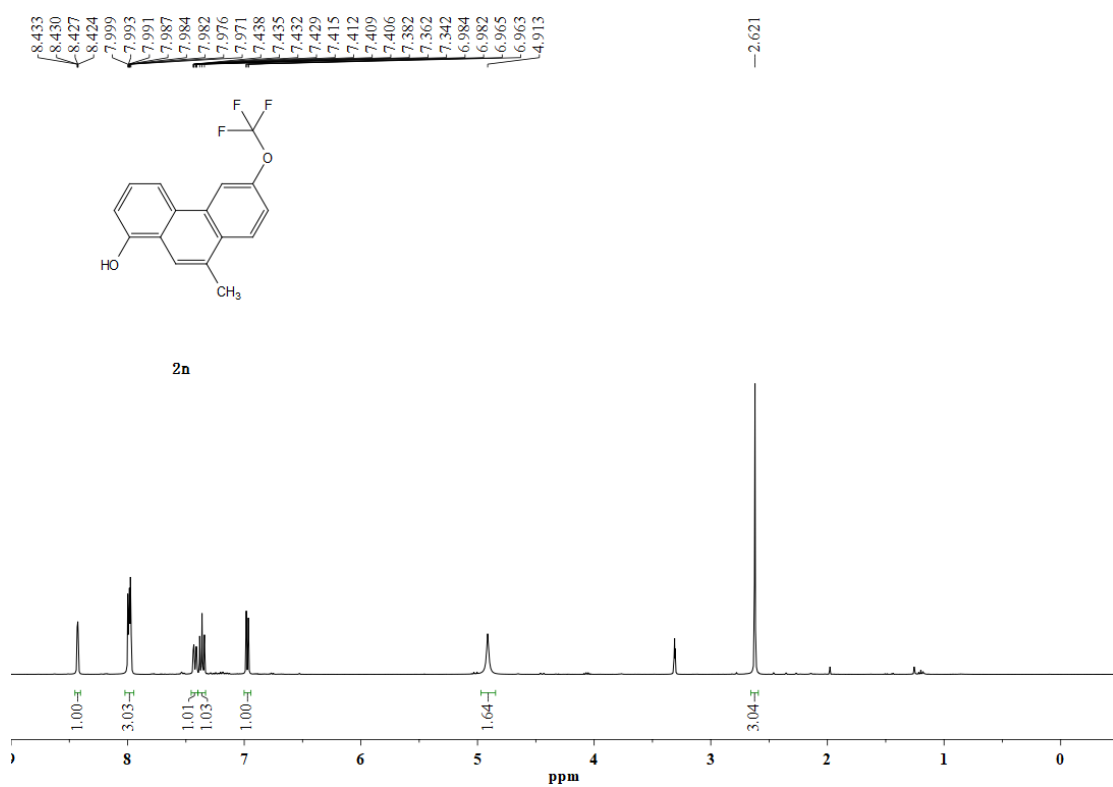
¹H NMR (400 MHz, DMSO-*d*₆)



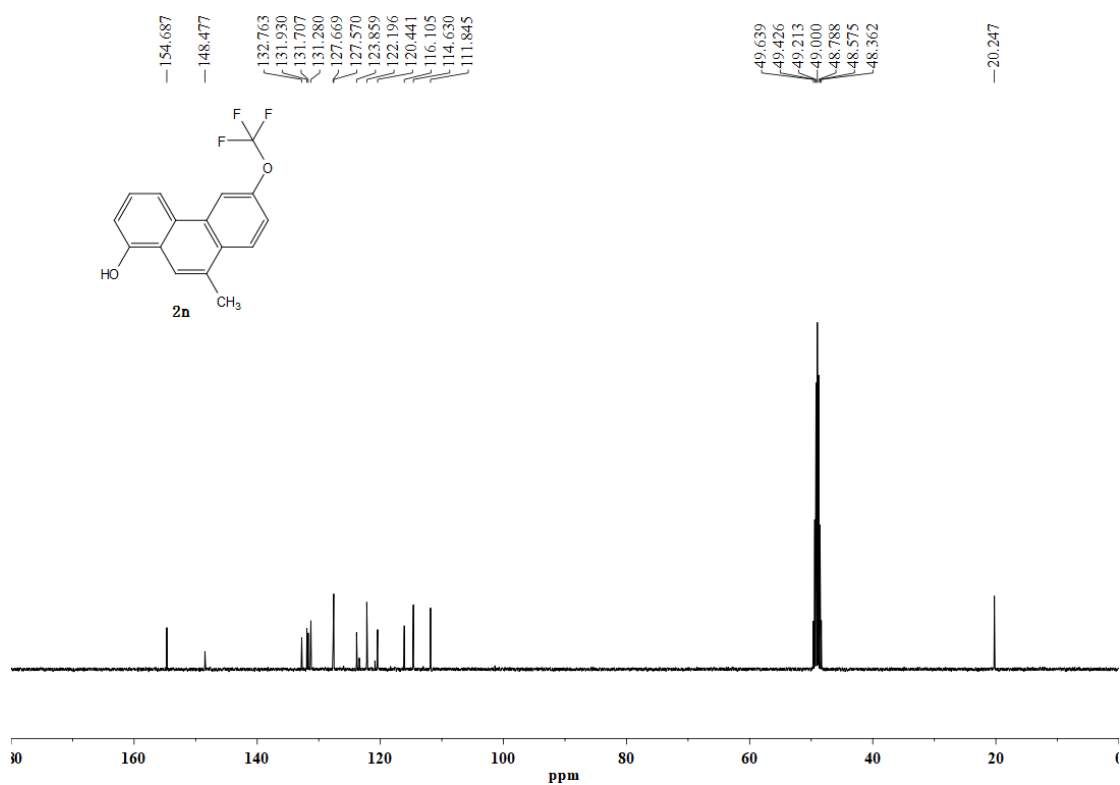
¹³C NMR (101 MHz, DMSO-*d*₆)



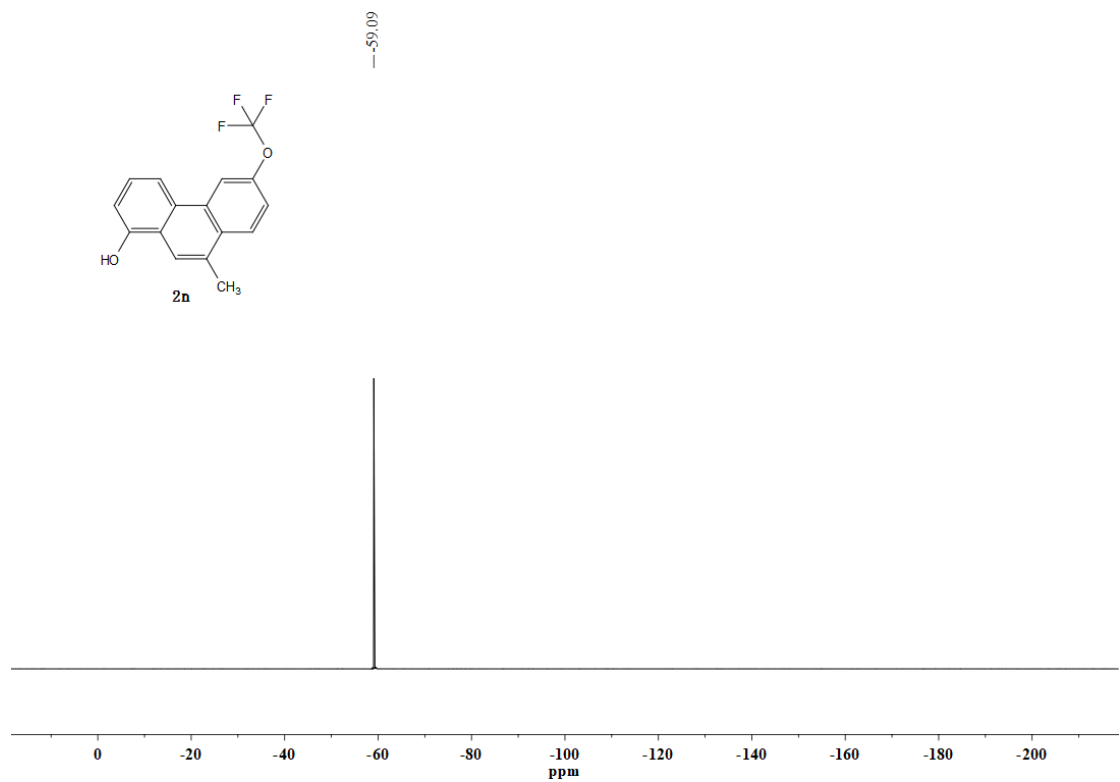
¹H NMR (400 MHz, Methanol-*d*₄)



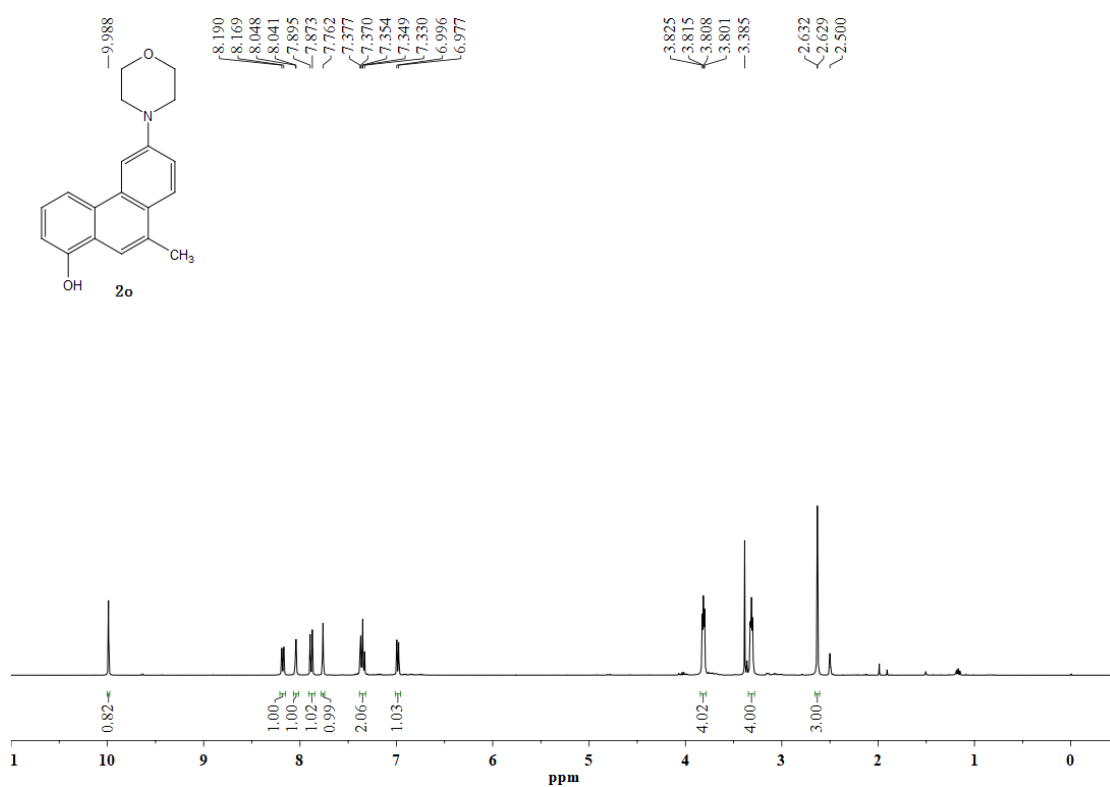
¹³C NMR (101 MHz, Methanol-*d*₄)



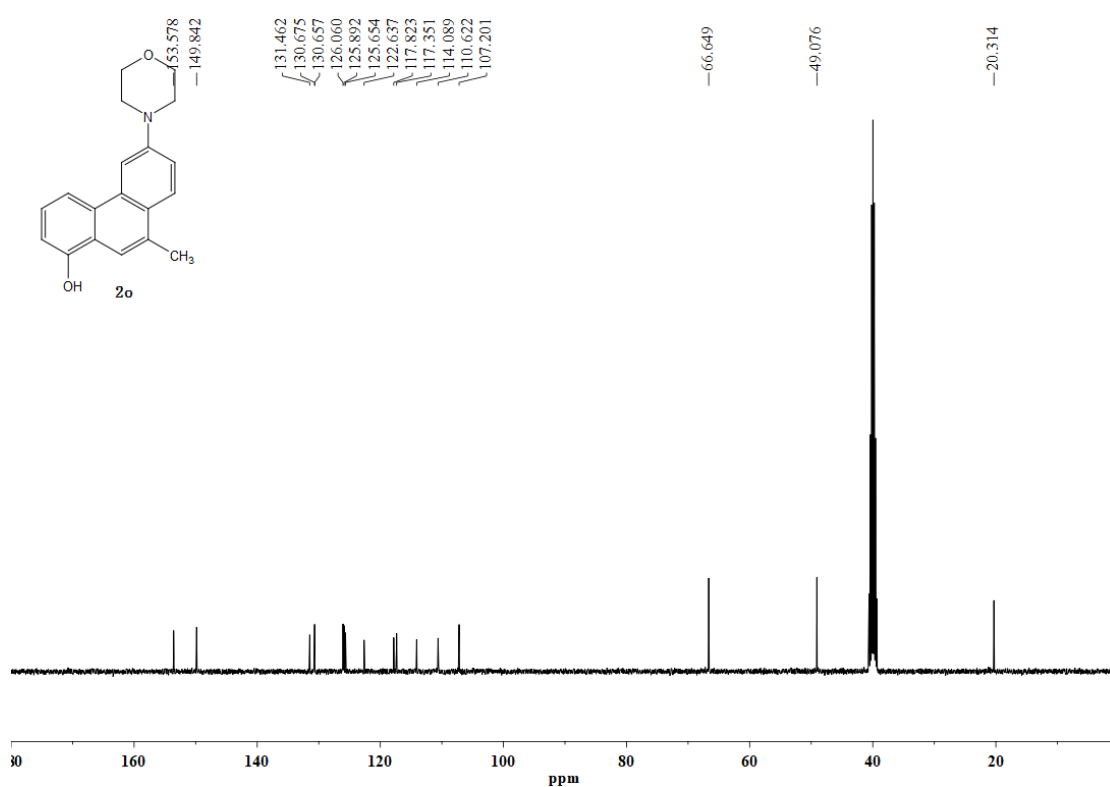
¹⁹F NMR (376 MHz, Methanol-*d*₄)



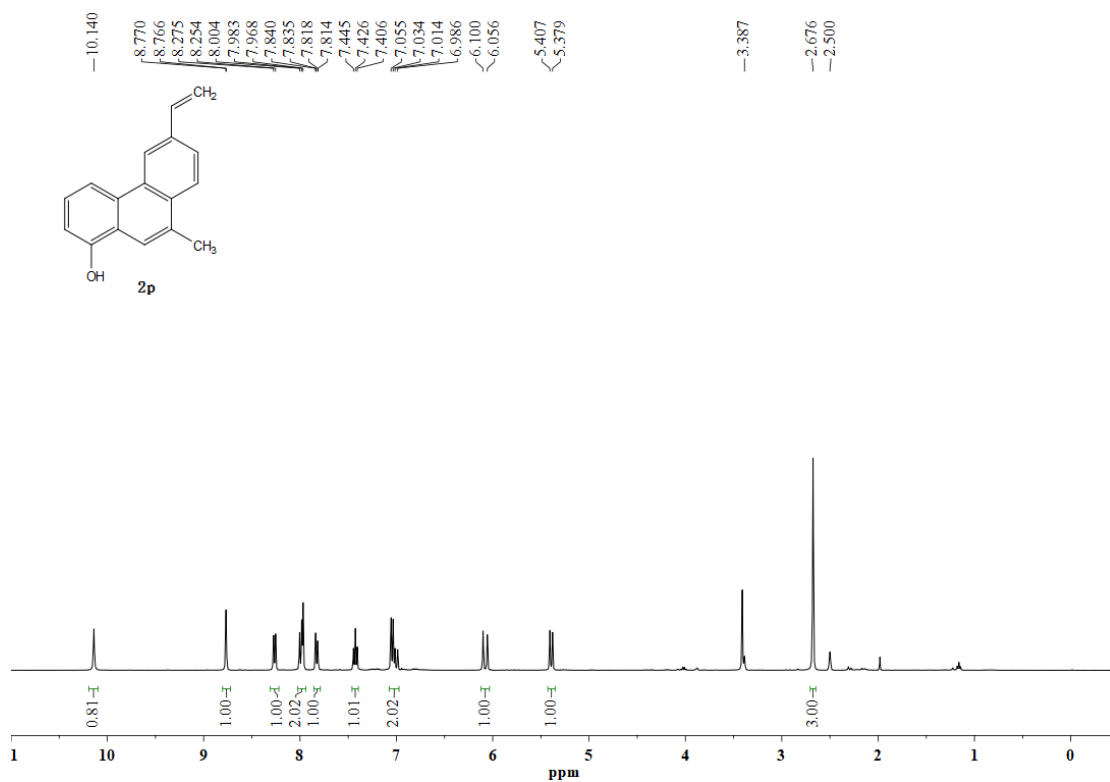
^1H NMR (400 MHz, $\text{DMSO-}d_6$)



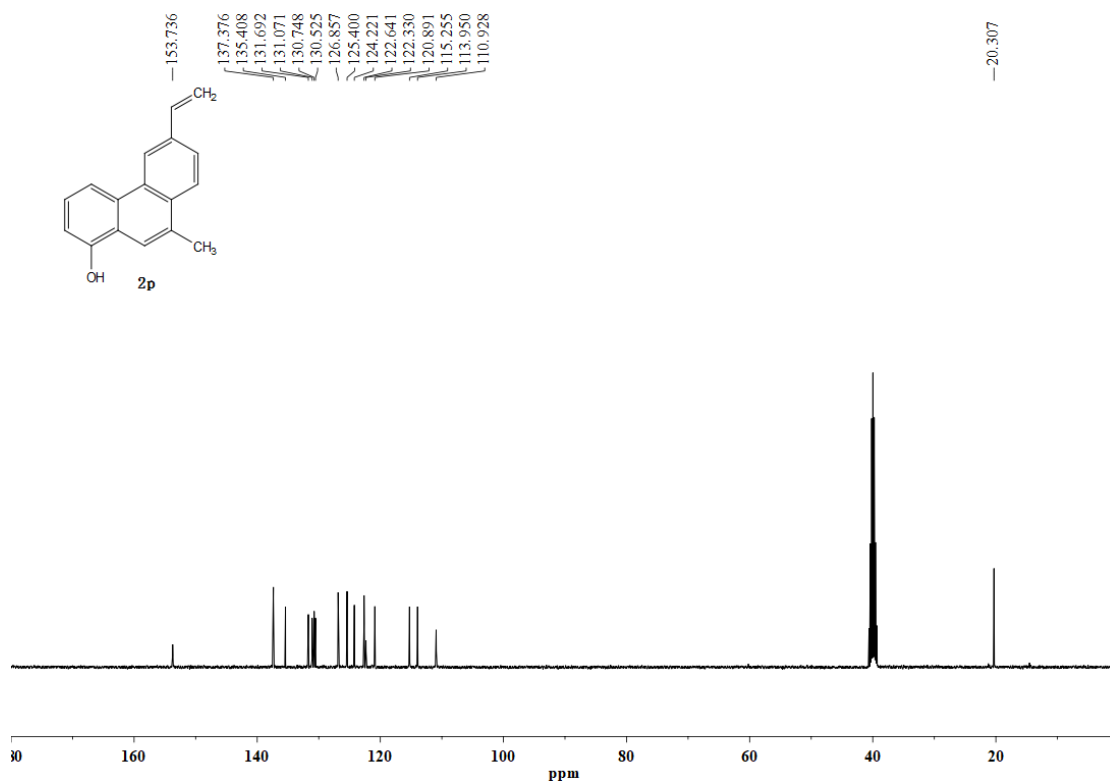
^{13}C NMR (101 MHz, $\text{DMSO-}d_6$)



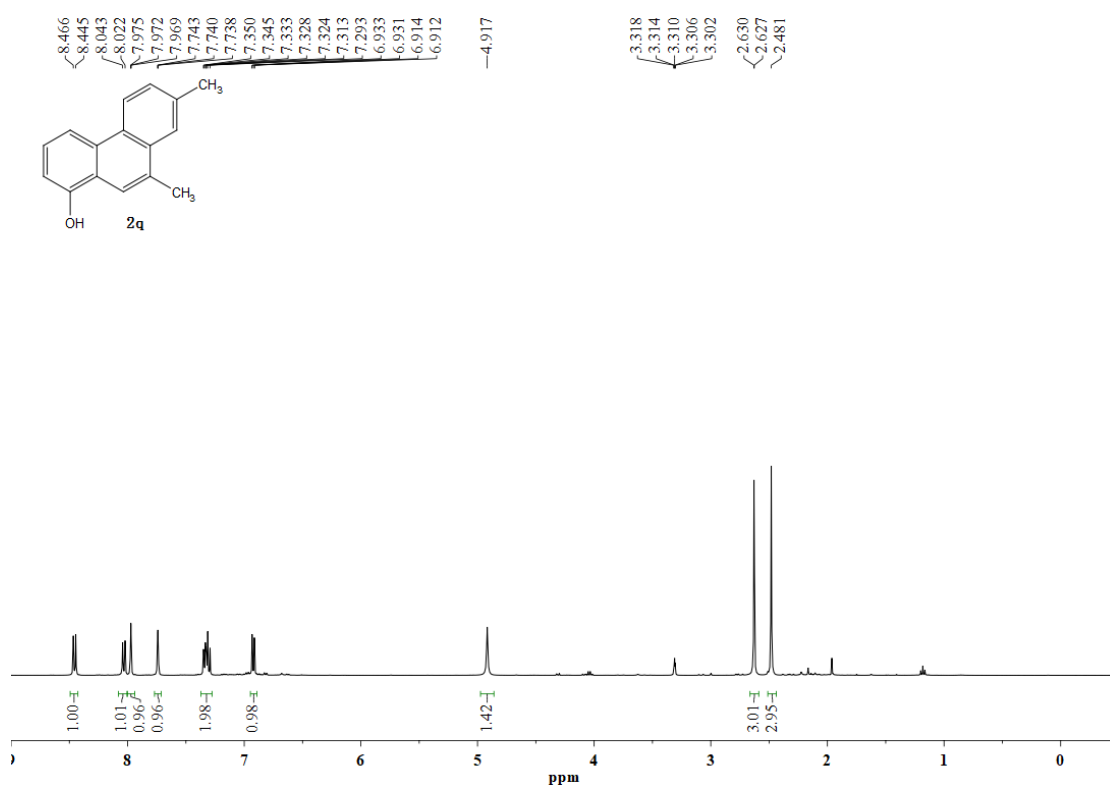
¹H NMR (400 MHz, DMSO-*d*₆)



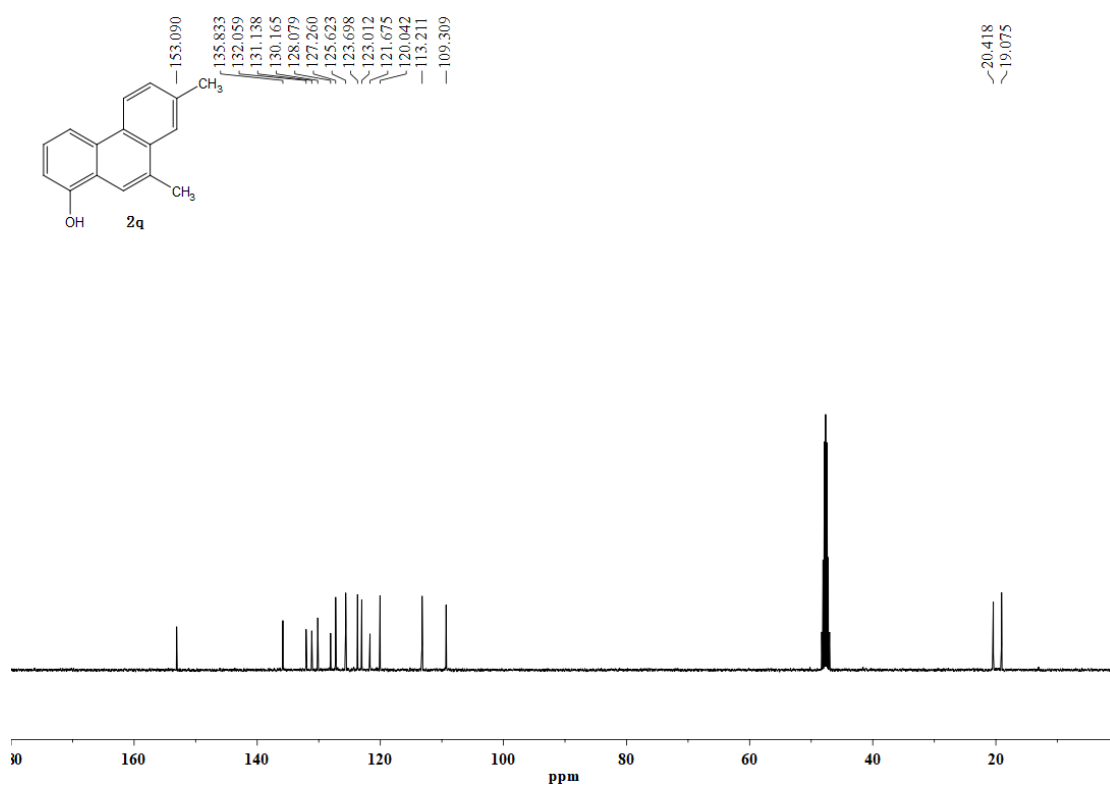
¹³C NMR (101 MHz, DMSO-*d*₆)



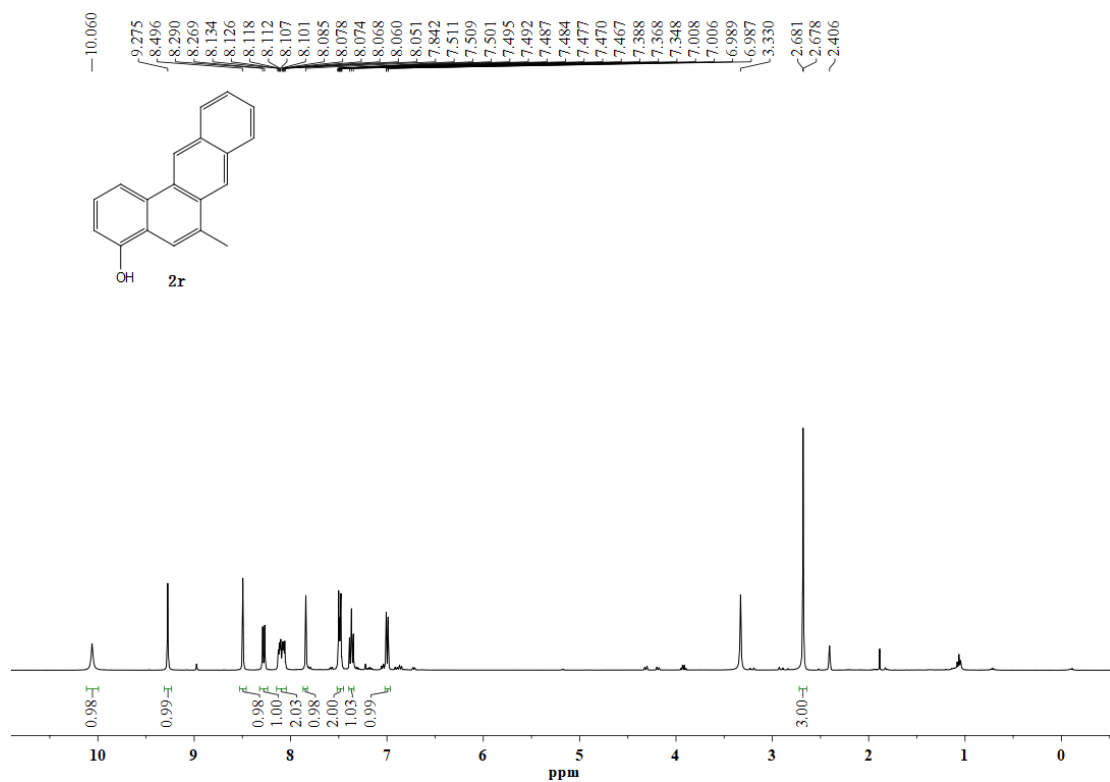
¹H NMR (400 MHz, Methanol-d₄)



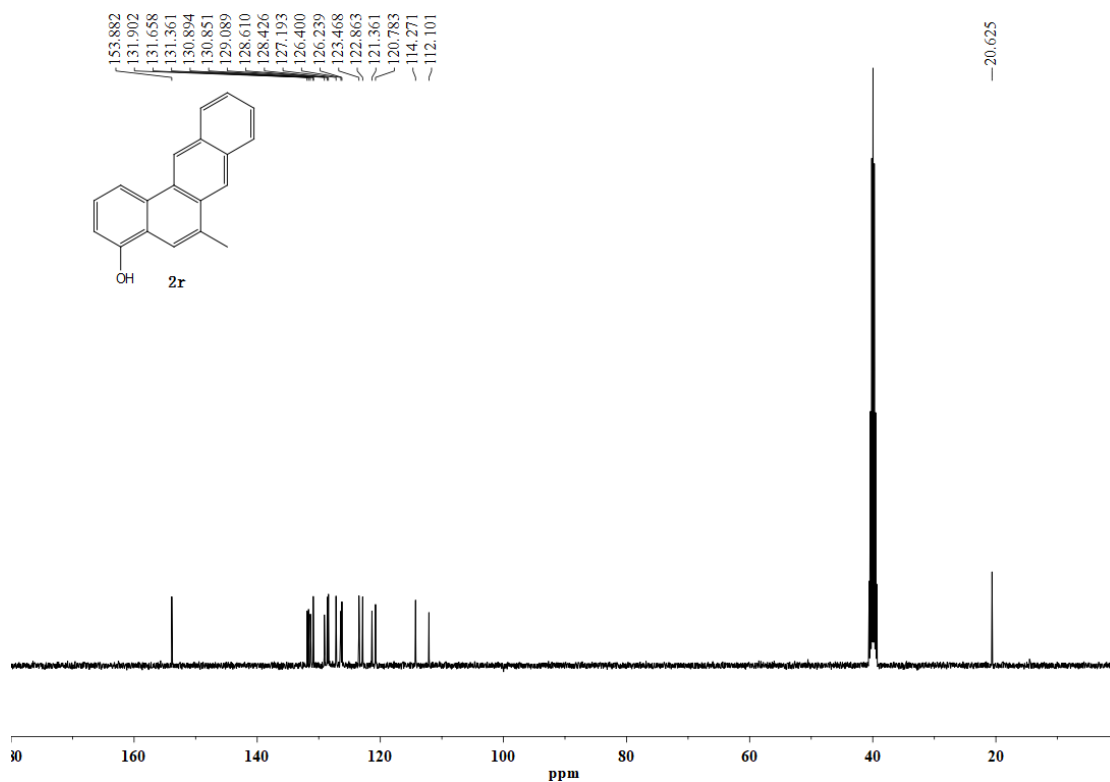
¹³C NMR (101 MHz, Methanol-d₄)



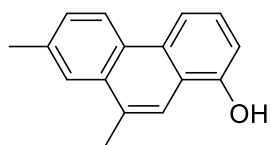
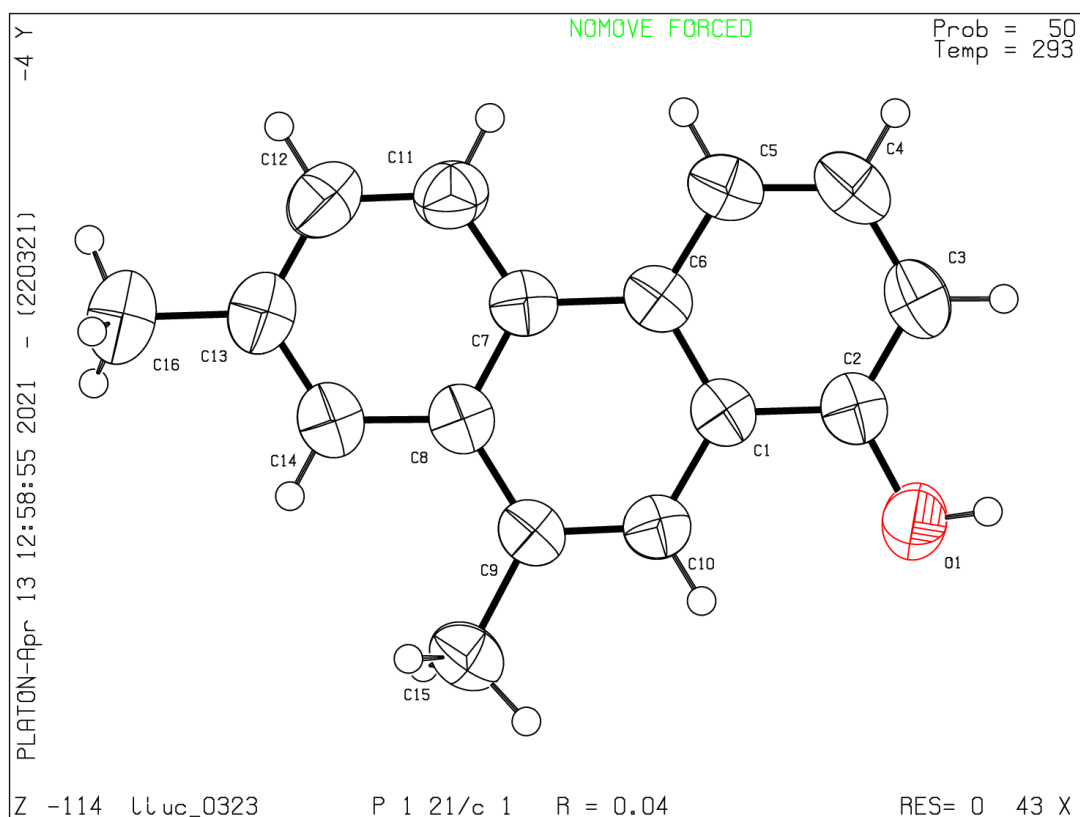
¹H NMR (400 MHz, DMSO-*d*₆)



¹³C NMR (101 MHz, DMSO-*d*₆)



5 X-ray Crystallographic Data of 2q



2q CCDC: 2011205

Thermal ellipsoids are drawn at 50% probability level.

Sample preparation: A solution of compound **2q** (50 mg) in ethyl acetate was placed in a vial (5 mL). Petroleum ether was added to the vial with a dropper until a small amount of solid precipitation, then, added the ethyl acetate until the solution clarification. The single crystal **2q** was obtained by slowly evaporating mixed solvent at room temperature under the air conditions.

Crystal measurement: X-ray crystal structures were determined at 295 K. The crystal was measured on a SuperNova, Dual, Cu at zero, Eos diffractometer.

Bond precision:	C-C = 0.0019 Å	Wavelength=1.54184
Cell:	a=16.9314(10) b=5.2194(3) c=13.7603(8)	
	alpha=90 beta=105.149(6) gamma=90	
Temperature:	293 K	
	Calculated	Reported
Volume	1173.76(12)	1173.76(12)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C16 H14 O	C16 H14 O
Sum formula	C16 H14 O	C16 H14 O
Mr	222.27	222.27
Dx, g cm ⁻³	1.258	1.258
Z	4	4
Mu (mm ⁻¹)	0.597	0.597
F000	472.0	472.0
F000'	473.30	
h,k,lmax	20,6,16	20,6,16
Nref	2088	2086
Tmin,Tmax	0.898,0.931	0.750,1.000
Tmin'	0.898	
Correction method= # Reported T Limits: Tmin=0.750 Tmax=1.000		
AbsCorr = MULTI-SCAN		
Data completeness= 0.999	Theta(max)= 66.599	
R(reflections)= 0.0398(1703)	wR2(reflections)= 0.1244(2086)	
S = 1.046	Npar= 158	

6 Reference

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- (4) Lu, L.; Siu, J. C.; Lai, Y.; Lin, S., *J. Am. Chem. Soc.* **2020**, *142*, 21272.
- (5) Liang, R.-X.; Chen, R.-Y.; Zhong, C.; Zhu, J.-W.; Cao, Z.-Y.; Jia, Y.-X., *Org. Lett.* **2020**, *22*, 3215.
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- (7) Bovonsombat, P.; Leykajarakul, J.; Khan, C.; Pla-on, K.; Krause, M. M.; Khanthapura, P.; Ali, R.; Doowa, N., *Tetrahedron Lett.* **2009**, *50*, 2664.
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