

Supporting Information

Divergent oxidative dearomatization coupling reactions to construct polycyclic cyclohexadienones

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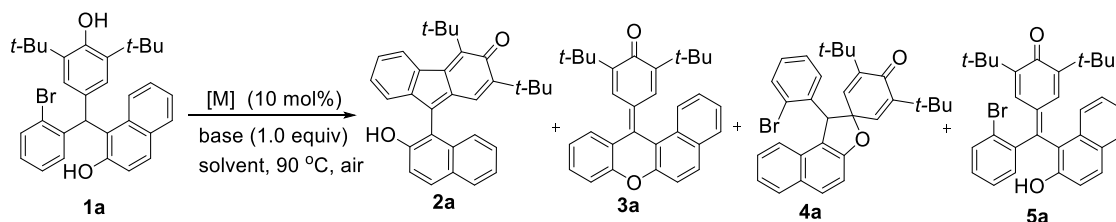
1. General Methods

Various functional groups substituted ortho-hydroxyphenylsubstituted *p*-QMs **1** were prepared according to literature method¹. Commercial grade solvents were dried and purified by standard procedures as specified in Purification of Laboratory Chemicals, 4th Ed (Armarego, W. L. F.; Perrin, D. D. Butterworth Heinemann: 1997). ¹H NMR spectra were recorded on commercial instruments (600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃, δ = 7.26). Spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. ¹³C NMR spectra were collected on commercial instruments (150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl₃, δ = 77.0). Reactions were monitored by TLC and visualized with ultraviolet light. Mass spectra were recorded on Xevo G2-S QToF tandem mass spectrometer.

References

1. K. Zhao, Y. Zhi, T. Shu, A. Valkonen, K. Rissanen, D. Enders. *Angew. Chem. Int. Ed.* **2016**, *55*, 12104-12108.

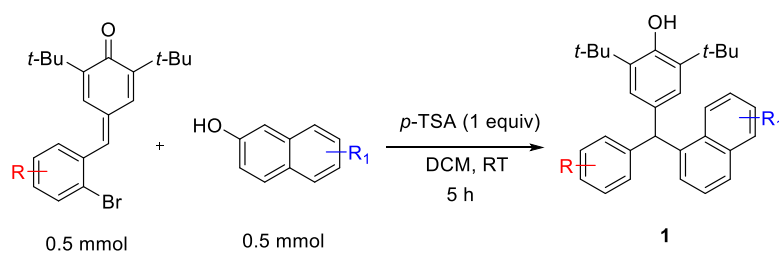
2. Optimization of other reaction conditions^a



Entry	Metal Complex	Base	solvent	Time (h)	Yield of 2a/3a/4a/5a (%) ^b
1	Pd ₂ (dba) ₃	<i>t</i> -BuOK	toluene	3	95/-/-/trace
2	Pd ₂ (dba) ₃	<i>t</i> -BuOK	CH ₃ CN	18	10/-/-/trace
3	Pd ₂ (dba) ₃	<i>t</i> -BuOK	DMF	18	92/-/-/trace
4	Cu(OAc) ₂ H ₂ O	Cs ₂ CO ₃	toluene	72	-/91/trace/-
5	Cu(OTf) ₂	Cs ₂ CO ₃	toluene	72	-/83/trace/-
6	CuI	Cs ₂ CO ₃	toluene	72	-/82/trace/-
7	Cu(OAc) ₂ H ₂ O	KOH	toluene	18	-/99/-/-
8	Cu(OAc) ₂ H ₂ O	KOH	CH ₃ CN	18	-/95/-/-
9	Cu(OAc) ₂ H ₂ O	KOH	DMF	18	-/82/-/-

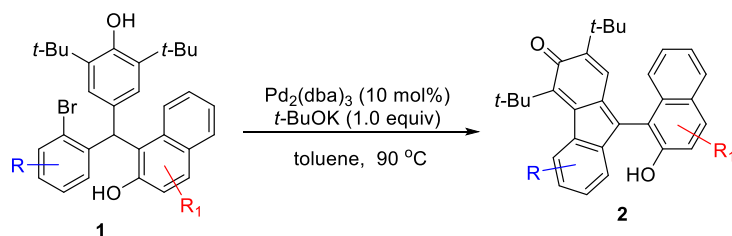
^a Unless otherwise noted, reactions were conducted with 0.1 mmol **1a**, 10 mol % [M], 1.0 equiv base in 1.0 mL solvent, 90 °C, air. ^b Isolated yields.

3. General procedure for the synthesis of **1**



To a solution of *p*-QMs (0.5 mmol, 1 equiv) and β-Naphthol (0.5 mmol, 1 equiv) in DCM(5 mL), *p*-TSA(0.5 mmol, 1 equiv) was added. The reaction mixture was stirred for 5 hours at rt. Next, the solvent was removed under vacuum directly and the crude product was purified by silica gel column chromatography with ethyl acetate (EA) and petroleum ether (Pet) as eluent to afford the product **1**.

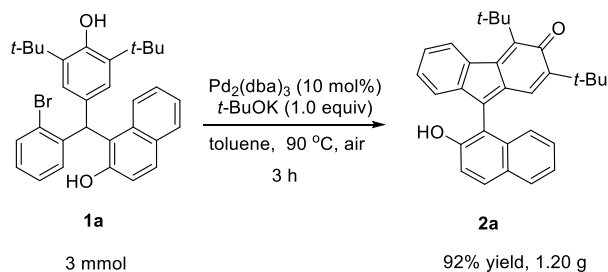
4. General procedure for the C-H oxidative dearomatization/Heck coupling reaction



To a 10 mL test tube were added **1** (0.1 mmol, 1.0 equiv), *t*-BuOK (0.1 mmol, 1.0 equiv), Pd₂(dba)₃ (10 mol%), toluene (1.0 mL). The mixture was then stirred at 90 °C for 3-12 hours (oil bath). After being cooled to room temperature, The solvent

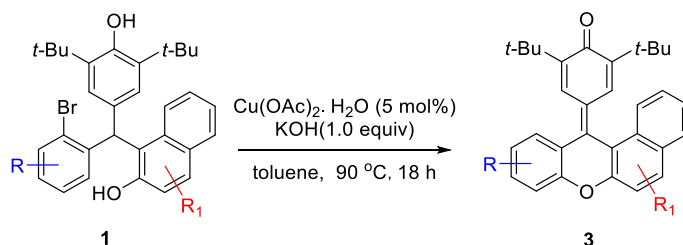
was removed under vacuum directly and the crude product was purified by silica gel column chromatography to afford the product **2**.

Scaled-up version of the reaction



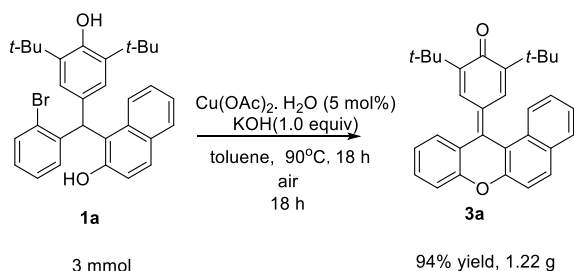
To a 10 mL test tube were added **1a** (3.0 mmol, 1.0 equiv), *t*-BuOK (3.0 mmol, 1.0 equiv), Pd₂(dba)₃ (10 mol%), toluene (30.0 mL). The mixture was then stirred at 90 °C for 3 hours (oil bath). After being cooled to room temperature, The solvent was removed under vacuum directly and the crude product was purified by silica gel column chromatography to afford the product **2a** (92% yield, 1.20 g).

5. General procedure for the C-H oxidative dearomatization/Ullman coupling reaction



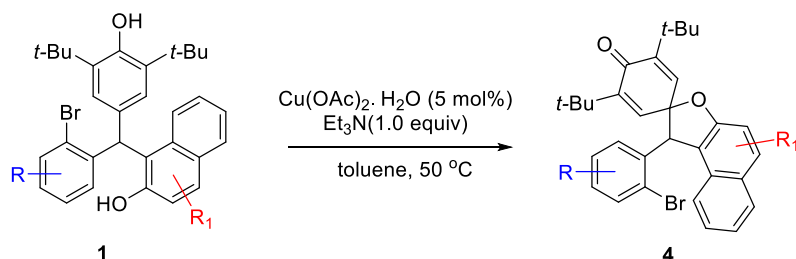
To a 10 mL test tube were added **1** (0.1 mmol, 1.0 equiv), KOH (0.1 mmol, 1.0 equiv), Cu(OAc)₂ (5 mol%), toluene (1.0 mL). The mixture was then stirred at 90 °C for 18 hours (oil bath). After being cooled to room temperature, The solvent was removed under vacuum directly and the crude product was purified by silica gel column chromatography to afford the product **3**.

Scaled-up version of the reaction



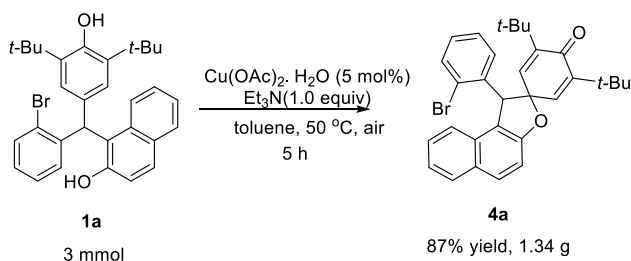
To a 10 mL test tube were added **1a** (3.0 mmol, 1.0 equiv), KOH (3.0 mmol, 1.0 equiv), $\text{Cu}(\text{OAc})_2$ (5 mol%), toluene (30.0 mL). The mixture was then stirred at 90 °C for 18 hours (oil bath). After being cooled to room temperature, The solvent was removed under vacuum directly and the crude product was purified by silica gel column chromatography to afford the product **3a** (94% yield, 1.22 g).

6. General procedure for the oxidative dearomatization coupling reaction



To a 10 mL test tube were added **1** (0.1 mmol, 1.0 equiv), Et_3N (0.1 mmol, 1.0 equiv), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (5 mol%), toluene (1.0 mL). The mixture was then stirred at 50 °C for 5-7 hours (oil bath). After being cooled to room temperature, The solvent was removed under vacuum directly and the crude product was purified by silica gel column chromatography to afford the product **4**.

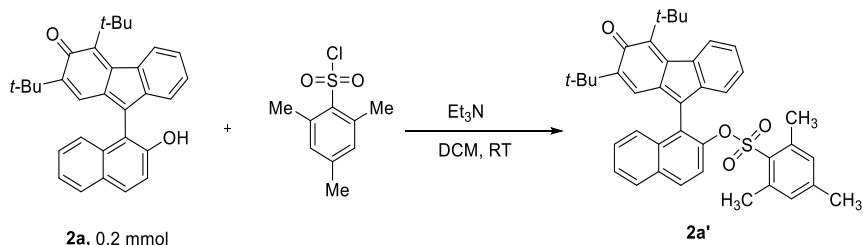
Scaled-up version of the reaction



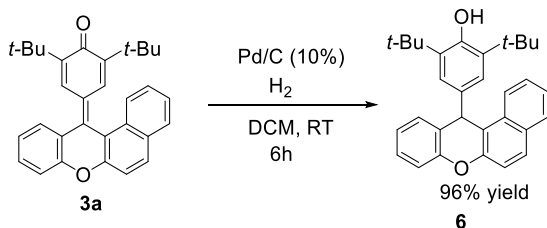
To a 10 mL test tube were added **1a** (3.0 mmol, 1.0 equiv), Et_3N (3.0 mmol, 1.0 equiv), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (5 mol%), toluene (30.0 mL). The mixture was then stirred at 50 °C for 5 hours (oil bath). After being cooled to room temperature, The solvent was

removed under vacuum directly and the crude product was purified by silica gel column chromatography to afford the product **4a** (87% yield, 1.34 g).

7. Experimental procedure for the synthesis of **2a'** and **6**

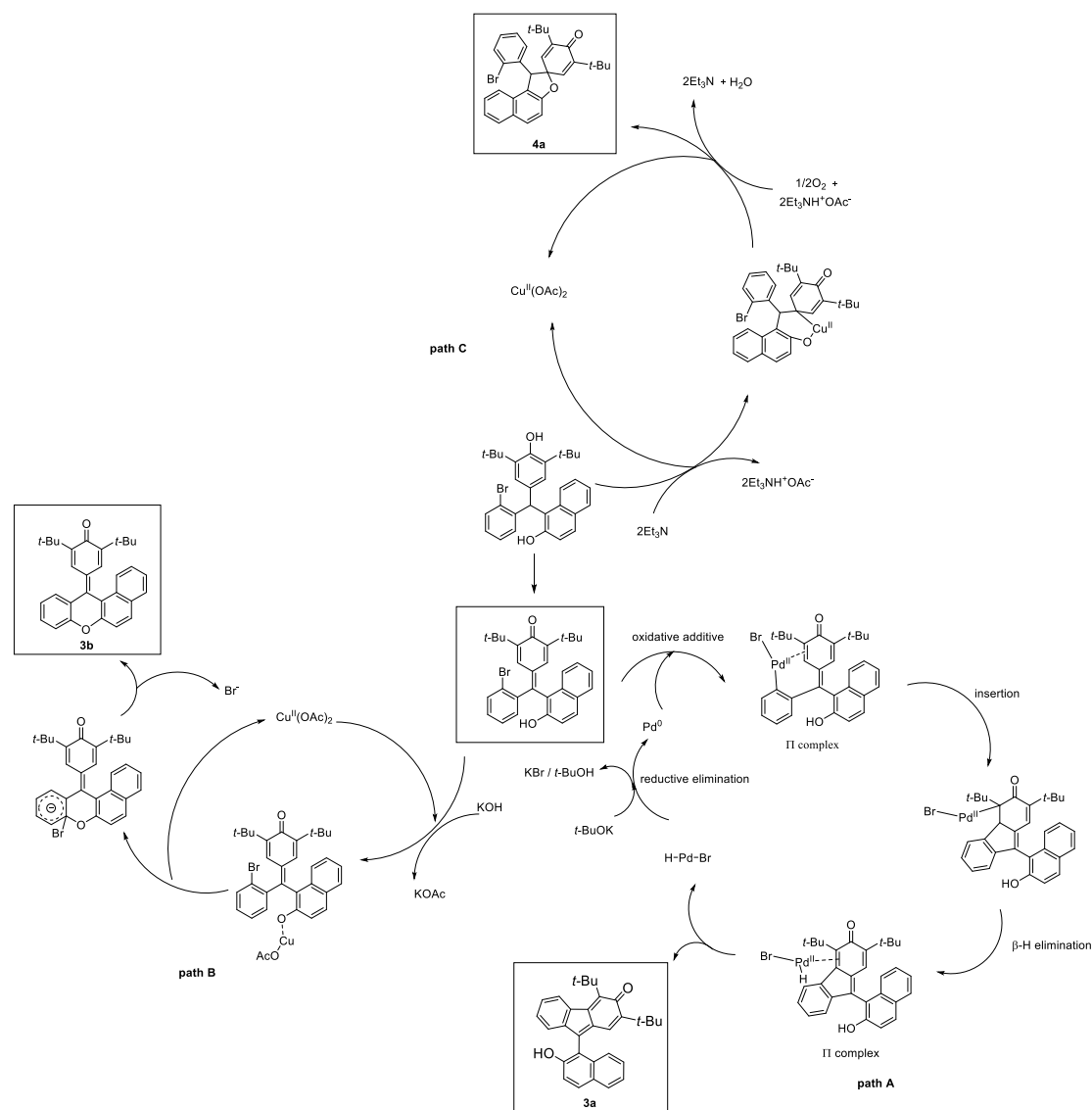


To a 10 mL test tube were added **2a** (0.2 mmol, 1.0 equiv) dissolved in DCM (5.0 mL), drop slowly Mesitylene-2-sulfonyl chloride (0.31 mmol, 1.1 equiv) and Et₃N (0.31 mmol, 1.1 equiv). The mixture was then stirred at rt for about 2 hours. The crude product was recrystallized in the freezer by dissolving in CH₃CN (1.0 mL) and overlaying with Toluene (2.0 mL). The product **2a'** was isolated as a red solid with 96% yield.



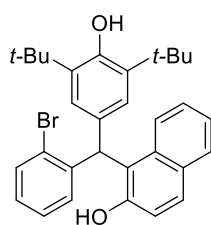
To a solution of **3a** (0.2 mmol, 1 equiv) in CH₂Cl₂ (1 mL) was added Pd on carbon (6.0 mg, 10 wt%). The reaction mixture was degassed by a hydrogen balloon for 10 mins. Then the reaction was allowed to stir at room temperature for about 6 hours. Next, the solvent was removed under vacuum directly and the crude product was purified by silica gel column chromatography to afford the product **6** (96% yield, 83.7 mg).

8. Proposed reaction mechanism



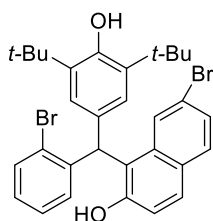
9. Characterization Data of 1, 2, 2a', 3, 4, 5 and 6

1-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-bromophenyl)methyl)naphthalen-2-ol (1a).



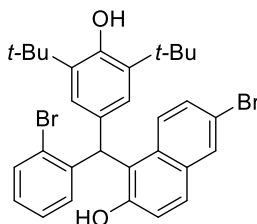
White solid; 51.10 mg, 99% yield (petroleum ether/ethyl acetate =10:1) ; mp 182.5-183.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.81 (d, *J* = 8.64 Hz, 1H), 7.64 (m, 2H), 7.56 (d, *J* = 8.94 Hz, 1H), 7.22 (m, 1H), 7.07-6.97 (m, 5H), 6.81 (s, 2H), 6.46 (s, 1H), 5.42 (s, 1H), 5.15 (s, 1H), 1.23 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 152.6, 152.3, 139.9, 136.8, 136.1, 132.5, 132.1, 129.7, 128.7, 128.5, 127.6, 127.5, 127.2, 127.0, 125.9, 124.3, 124.2, 122.1, 121.9, 118.9, 118.5, 47.7, 33.4, 29.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₄BrO₂ 517.1742; Found 517.1748.

7-bromo-1-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1b).



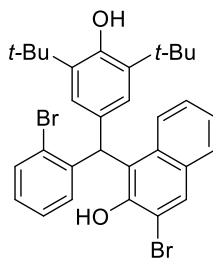
White solid; 54.92 mg, 92% yield (petroleum ether/ethyl acetate =30:1); mp 178.0-180.0 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.01 (s, 1H), 7.58 (d, *J* = 1.74 Hz, 2H), 7.53 (m, 1H), 7.32 (m, 1H), 7.05-6.97 (m, 4H), 6.81 (s, 2H), 6.35 (s, 1H), 5.47 (s, 1H), 5.15 (s, 1H), 1.24 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 153.3, 152.4, 139.5, 136.1, 133.9, 132.4, 129.6, 129.1, 128.5, 127.8, 127.0, 126.9, 125.5, 124.5, 124.2, 120.5, 119.3, 118.1, 47.7, 33.4, 29.1. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₃Br₂O₂ 597.0827; Found 597.0822.

6-bromo-1-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1c).



White solid; 55.44 mg, 93% yield (petroleum ether/ethyl acetate =30:1); mp 170.0-172.0 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.82 (s, 1H), 7.57 (m, 1H), 7.54 (m, 2H), 7.40 (m, 1H), 7.17-6.99 (m, 4H), 6.80 (s, 2H), 6.38 (s, 1H), 5.42 (s, 1H), 5.15 (s, 1H), 1.24 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 152.8, 152.4, 139.7, 136.2, 132.3, 131.1, 129.6, 129.4, 129.1, 128.6, 127.7, 127.0, 124.2, 124.2, 123.8, 120.1, 118.7, 115.9, 47.8, 33.4, 29.1. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₃Br₂O₂ 597.0827; Found 597.0822.

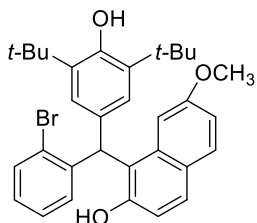
3-bromo-1-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1d).



White solid; 53.65 mg, 90% yield (petroleum ether/ethyl acetate =30:1); mp 146.3-147.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.98 (s, 1H), 7.80 (m, 1H), 7.53 (m, 2H), 7.25 (m, 2H), 7.11-7.02 (m, 3H), 6.82 (s, 2H), 6.47 (s, 1H), 5.88 (s, 1H), 5.12 (s, 1H), 1.24 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 152.2, 148.2, 140.2, 135.8, 132.1, 131.8, 131.0, 130.0, 128.9, 128.7, 127.5, 126.7, 126.1, 124.5, 124.2, 123.1, 122.4, 120.7, 112.7, 48.4, 33.4, 29.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₃Br₂O₂

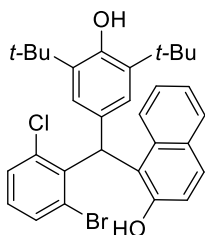
597.0827; Found 597.0820.

1-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-7-methoxynaphthalen-2-ol (1e).



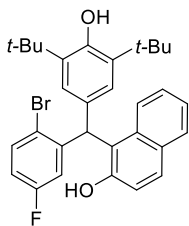
White solid; 49.16 mg, 90% yield (petroleum ether/ethyl acetate =30:1); mp 168.0-170.0 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.57 (m, 3H), 7.55 (m, 3H), 7.02 (m, 1H), 6.88 (m, 1H), 6.82 (m, 3H), 6.39 (s, 1H), 5.37 (s, 1H), 5.14 (s, 1H), 3.75 (s, 3H), 1.24 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 157.5, 153.1, 152.3, 140.0, 136.1, 133.9, 131.9, 129.9, 128.9, 128.3, 127.5, 127.1, 124.3, 124.2, 123.7, 117.8, 116.3, 114.4, 101.2, 54.3, 48.0, 33.4, 29.2. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₂H₃₆BrO₃ 547.1848; Found 547.1839.

1-((2-bromo-6-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1f).



White solid; 52.90 mg, 96% yield (petroleum ether/ethyl acetate =30:1); mp 181.3-182.7 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.65 (d, *J* = 7.56 Hz, 1H), 7.60 (d, *J* = 8.88 Hz, 1H), 7.49 (d, *J* = 8.52 Hz, 2H), 7.19 (m, 2H), 7.13 (m, 2H), 6.96 (m, 2H), 6.84 (s, 1H), 6.70 (s, 1H), 5.47 (s, 1H), 5.21 (s, 1H), 1.30 (d, *J* = 16.56 Hz, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 153.9, 152.7, 139.3, 135.3, 132.6, 128.7, 128.4, 127.7, 126.5, 125.6, 122.0, 121.6, 119.3, 115.5, 33.6, 33.5, 29.8, 29.3, 29.2. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₃BrClO₂ 551.1352; Found 551.1351.

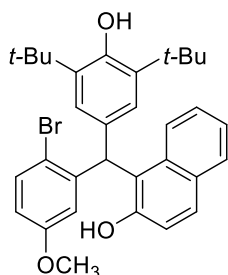
1-((2-bromo-5-fluorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1g).



White solid; 48.16 mg, 90% yield (petroleum ether/ethyl acetate =30:1); mp 136.2-137.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.66 (m, 1H), 7.37 (m, 3H), 7.36 (m, 1H), 7.24 (m, 1H), 6.98 (m, 1H), 6.78-6.76 (m, 4H), 6.41 (s, 1H), 5.34 (s, 1H), 5.16 (s, 1H), 1.25 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 162.2, 160.5, 152.6, 152.4, 142.4, 142.4, 136.2, 132.4, 129.0, 128.6, 128.3, 127.7, 126.0, 124.1, 122.3, 121.6, 119.1, 118.3, 118.3,

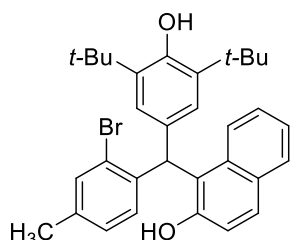
117.9, 117.0, 116.9, 114.9, 114.7, 47.8, 33.4, 29.1. ^{19}F NMR (CDCl_3 , 377 MHz) δ -113.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{33}\text{BrFO}_2$ 535.1648; Found 535.1636.

1-((2-bromo-5-methoxyphenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1h).

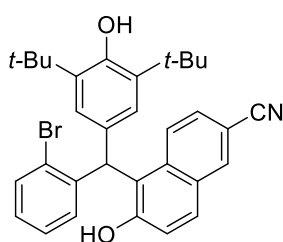


White solid; 49.31 mg, 93% yield (petroleum ether/ethyl acetate =30:1) ; mp 114.0-116.0 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 7.82 (d, $J = 8.64$, 1H), 7.69 (d, $J = 8.04$, 1H), 7.64 (d, $J = 8.88$, 1H), 7.36 (m, 2H), 7.23 (m, 1H), 6.98 (m, 1H), 6.84 (s, 2H), 6.59 (m, 2H), 6.39 (s, 1H), 5.39 (s, 1H), 5.13 (s, 1H), 3.52 (s, 3H), 1.25 (s, 18H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 158.3, 152.6, 152.3, 141.1, 136.0, 132.6, 132.6, 128.8, 128.7, 128.5, 127.6, 125.9, 124.2, 122.1, 121.9, 119.0, 118.4, 115.7, 114.7, 113.0, 54.2, 47.8, 33.4, 29.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{36}\text{BrO}_3$ 547.1848; Found 547.1839.

1-((2-bromo-4-methylphenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1i).



White solid; 47.81 mg, 90% yield (petroleum ether/ethyl acetate =30:1) ; mp 124.6-125.2 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 7.82 (d, $J = 8.64$ Hz, 1H), 7.69-7.62 (m, 2H), 7.39 (m, 2H), 7.16 (m, 1H), 6.97-6.90 (m, 3H), 6.84 (s, 2H), 6.40 (s, 1H), 5.40 (s, 1H), 5.12 (s, 1H), 2.21 (s, 3H), 1.24 (s, 18H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 158.3, 152.6, 152.3, 141.1, 137.5, 136.8, 136.0, 132.6, 132.5, 129.4, 129.3, 128.6, 128.5, 127.8, 127.6, 125.9, 124.3, 124.0, 122.1, 121.9, 118.9, 118.7, 118.4, 115.7, 114.7, 113.0, 54.2, 47.8, 33.4, 29.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{32}\text{H}_{36}\text{BrO}_2$ 531.1899; Found 531.1887.

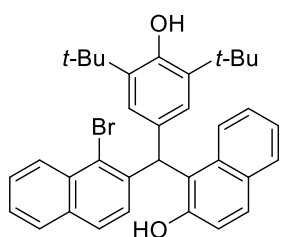


5-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-6-hydroxy-2-naphthonitrile (1j).

White solid; 53.03 mg, 98% yield (petroleum ether/ethyl acetate =30:1) ; mp 161.1-162.5 °C. ^1H NMR (CDCl_3 , 600 MHz) δ 8.06

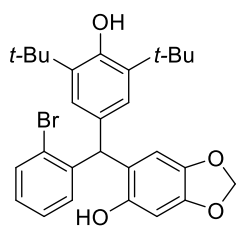
(m, 1H), 7.85 (m, 1H), 7.70 (m, 1H), 7.49 (m, 2H), 7.12-7.06 (m, 3H), 6.98 (m, 1H), 6.80 (s, 2H), 6.40 (s, 1H), 5.69 (s, 1H), 5.18 (s, 1H), 1.25 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 155.2, 152.6, 139.4, 136.4, 134.4, 1335.5, 132.4, 129.4, 129.2, 128.1, 127.9, 127.5, 127.1, 126.7, 124.2, 124.2, 123.1, 120.8, 118.9, 118.4, 105.5, 47.8, 33.4, 29.1. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₂H₃₃BrNO₂ 542.1616; Found 542.1615.

1-((1-bromonaphthalen-2-yl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1k).



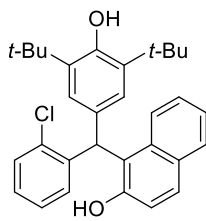
White solid; 53.88 mg, 95% yield (petroleum ether/ethyl acetate =30:1) ; mp 138.6-139.2 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.33 (d, *J* = 8.58 Hz, 1H), 7.86 (d, *J* = 8.64 Hz, 1H), 7.69 (m, 3H), 7.41 (m, 2H), 7.29 (m, 1H), 7.16 (m, 3H), 7.00 (d, *J* = 8.88 Hz, 1H), 6.88 (s, 2H), 6.78 (s, 1H), 5.49 (s, 1H), 5.13 (s, 1H), 1.21 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 152.6, 152.3, 138.2, 136.2, 132.7, 132.7, 131.6, 129.0, 128.8, 128.5, 127.6, 127.1, 126.4, 126.0, 125.3, 124.3, 123.9, 122.2, 122.0, 119.0, 118.7, 49.0, 33.4, 29.2. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₅H₃₆BrO₂ 567.1899; Found 567.1896.

6-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)benzo[d][1,3]dioxol-5-ol (1l).



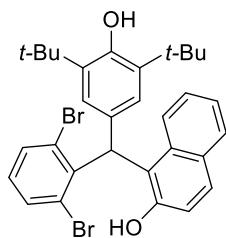
White solid; 46.00 mg, 90% yield (petroleum ether/ethyl acetate =30:1) ; mp 160.0-162.0 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.50 (m, 1H), 7.13 (m, 1H), 7.02 (m, 1H), 6.89 (m, 1H), 6.81 (s, 2H), 6.35 (s, 1H), 6.12 (s, 1H), 5.79 (m, 2H), 5.72 (s, 1H), 5.05 (s, 1H), 4.37 (s, 1H), 1.28 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 151.7, 147.3, 145.6, 141.6, 140.4, 135.1, 132.1, 129.8, 129.8, 127.1, 126.3, 124.9, 124.4, 120.9, 108.3, 100.0, 97.9, 49.4, 33.3, 29.3. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₂₈H₃₂BrO₄ 511.1484; Found 511.1479.

1-((2-chlorophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1m).



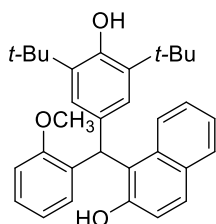
White solid; 43.06 mg, 91% yield (petroleum ether/ethyl acetate =30:1); mp 116.0-118.0 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.83 (m, 1H), 7.82-7.68 (m, 2H), 7.64 (m, 2H), 7.25 (m, 1H), 7.10 (m, 3H), 6.99 (m, 1H), 6.83 (s, 2H), 6.52 (s, 1H), 5.39 (s, 1H), 5.13 (s, 1H), 1.24 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 152.6, 152.3, 138.3, 136.1, 133.3, 132.5, 129.6, 129.1, 128.7, 128.5, 127.6, 127.3, 126.3, 125.9, 124.1, 122.1, 121.7, 119.0, 118.4, 45.0, 33.4, 29.2. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₄ClO₂ 473.2247; Found 473.2236.

1-((3,5-di-tert-butyl-4-hydroxyphenyl)(2,6-dibromophenyl)methyl)naphthalen-2-ol (In).



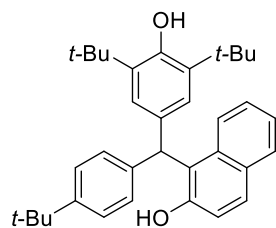
White solid; 55.34 mg, 93% yield (petroleum ether/ethyl acetate =30:1); mp 227.8-228.3 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.64-7.60 (m, 2H), 7.51-7.50 (m, 2H), 7.42 (d, *J* = 8.64, 1H), 7.23-7.09 (m, 4H), 6.88-6.82 (m, 2H), 6.69 (s, 1H), 5.48 (s, 1H), 5.22 (s, 1H), 1.31 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 154.1, 152.7, 140.5, 132.5, 128.8, 128.4, 128.0, 127.7, 126.4, 125.6, 122.1, 121.6, 119.3, 115.4, 51.5, 33.5, 29.2. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₃Br₂O₂ 595.0847; Found 595.0835.

1-((3,5-di-tert-butyl-4-hydroxyphenyl)(2-methoxyphenyl)methyl)naphthalen-2-ol (Io).



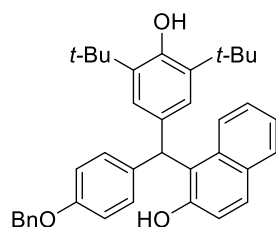
White solid; 45.05 mg, 96% yield (petroleum ether/ethyl acetate =30:1); mp 134.2-135.7 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.92 (d, *J* = 8.64 Hz, 1H), 7.59 (m, 2H), 7.20 (m, 1H), 7.13 (m, 4H), 6.77 (m, 4H), 6.52 (s, 1H), 5.51 (s, 1H), 5.06 (s, 1H), 3.69 (s, 3H), 1.23 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 156.0, 152.4, 151.9, 135.6, 132.7, 130.3, 129.2, 128.9, 128.5, 128.0, 127.5, 127.2, 125.4, 124.1, 122.1, 121.8, 120.1, 119.4, 118.9, 109.8, 54.7, 41.0, 33.4, 29.2. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₂H₃₇O₃ 469.2743; Found 469.2744.

1-((4-(tert-butyl)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (Ip).



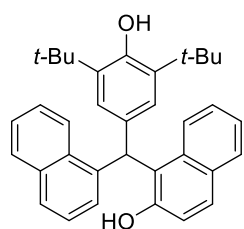
White solid; 45.00 mg, 91% yield (petroleum ether/ethyl acetate =30:1) ; mp 168.2-169.7 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.98 (d, *J* = 8.64 Hz, 1H), 7.69 (m, 1H), 7.63 (m, 1H), 7.35 (m, 1H), 7.26-7.22 (m, 3H), 7.08 (m, 3H), 6.94 (s, 2H), 6.18 (s, 1H), 5.31 (s, 1H), 5.09 (s, 1H), 1.25 (s, 18H), 1.21 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 152.0, 151.9, 148.8, 138.0, 135.5, 132.5, 130.8, 128.5, 128.3, 127.6, 127.5, 125.6, 124.8, 124.6, 122.0, 121.9, 119.5, 118.9, 47.0, 33.4, 30.3, 29.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₅H₄₃O₂ 495.3263; Found 495.3260.

1-((4-(benzyloxy)phenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)naphthalen-2-ol (1q).



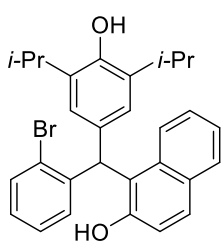
White solid; 51.16 mg, 94% yield (petroleum ether/ethyl acetate =30:1) ; mp 116.3-117.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.94 (d, *J* = 8.64 Hz, 1H), 7.62 (m, 2H), 7.33-7.23 (m, 7H), 7.09 (m, 2H), 6.98 (m, 3H), 6.85-6.83 (m, 2H), 6.15 (s, 1H), 5.35 (s, 1H), 5.11 (s, 1H), 4.95 (s, 2H), 1.25 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 156.7, 152.1, 152.0, 136.1, 135.8, 133.4, 132.5, 131.1, 129.0, 128.6, 128.3, 127.5, 126.9, 126.4, 125.6, 124.6, 122.0, 121.9, 119.5, 118.9, 114.3, 69.1, 46.8, 33.4, 29.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₈H₄₁O₃ 545.3056; Found 545.3044.

1-((3,5-di-tert-butyl-4-hydroxyphenyl)(naphthalen-1-yl)methyl)naphthalen-2-ol (1r).



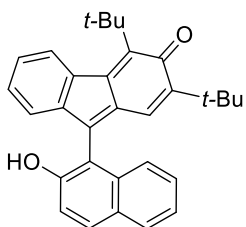
White solid; 44.03 mg, 90% yield (petroleum ether/ethyl acetate =30:1) ; mp 178.0-179.0 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.86 (m, 1H), 7.80 (d, *J* = 8.70 Hz, 2H), 7.71 (t, *J* = 6.96 Hz, 2H), 7.64 (d, *J* = 8.88 Hz, 1H), 7.38-7.28 (m, 5H), 7.22 (m, 1H), 7.06-6.80 (m, 4H), 5.51 (s, 1H), 5.09 (s, 1H), 1.20 (s, 18H); ¹³C NMR (CDCl₃, 150 MHz) δ 153.0, 152.0, 137.3, 135.7, 133.1, 132.3, 130.8, 130.4, 128.6, 128.4, 127.9, 127.7, 127.1, 125.8, 125.4, 124.8, 124.7, 123.0, 122.0, 121.7, 118.8, 118.8, 44.9, 33.3, 29.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₅H₃₇O₂ 489.2794; Found 489.2784.

1-((2-bromophenyl)(4-hydroxy-3,5-diisopropylphenyl)methyl)naphthalen-2-ol (1s).



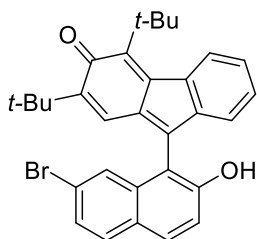
White solid; 46.36 mg, 95% yield (petroleum ether/ethyl acetate =10:1); mp 116.9-117.3 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.79 (m, 1H), 7.70-7.64 (m, 2H), 7.57 (d, *J* = 7.98 Hz, 1H), 7.23 (m, 2H), 7.07 (m, 3H), 6.97 (m, 1H), 6.69 (s, 2H), 6.48 (s, 1H), 5.44 (s, 1H), 4.75 (s, 1H), 2.96-3.03 (m, 2H), 1.02-1.06 (m, 12H); ¹³C NMR (CDCl₃, 150 MHz) δ 152.7, 148.5, 139.7, 134.0, 132.5, 132.2, 130.6, 129.7, 128.7, 128.5, 127.6, 127.0, 126.0, 124.3, 122.8, 121.8, 119.0, 118.4, 47.7, 26.3, 21.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₉H₃₀BrO₂ 489.1429; Found 489.1426.

2,4-di-tert-butyl-9-(2-hydroxynaphthalen-1-yl)-3H-fluoren-3-one (2a).



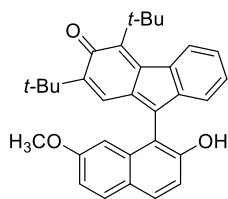
Red solid; 41.25 mg, 95% yield (petroleum ether/ethyl acetate =10:1); mp 96.3-97.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.81-7.78 (m, 2H) 7.76 (m, 1H), 7.64 (d, *J* = 7.74 Hz, 1H), 7.52 (m, 2H), 7.21 (m, 1H), 7.05 (m, 1H), 6.90 (m, 1H), 6.57 (d, *J* = 7.32 Hz, 1H), 6.37 (s, 1H), 5.20 (s, 1H), 1.52 (s, 9H), 1.08 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.8, 164.0, 154.0, 150.1, 147.2, 143.7, 140.8, 139.1, 136.4, 135.0, 131.8, 130.1, 127.8, 127.7, 127.2, 125.8, 124.1, 122.8, 122.2, 116.7, 110.3, 34.8, 34.0, 29.7, 28.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₁O₂ 435.2324; Found 435.2334.

9-(7-bromo-2-hydroxynaphthalen-1-yl)-2,4-di-tert-butyl-3H-fluoren-3-one (2b).



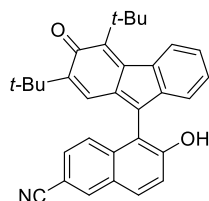
Red solid; 47.12 mg, 92% yield (petroleum ether/ethyl acetate =10:1); mp 106.6-107.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.76 (d, *J* = 8.94 Hz, 1H), 7.66-7.63 (m, 4H), 7.22 (m, 1H), 7.07 (m, 1H), 6.93 (m, 1H), 6.57 (d, *J* = 7.44 Hz, 1H), 6.32 (s, 1H), 5.27 (s, 1H), 1.53 (s, 9H), 1.09 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.7, 154.3, 151.0, 147.5, 143.2, 140.7, 137.9, 136.4, 135.3, 133.0, 130.0, 128.9, 127.8, 126.6, 126.3, 126.2, 123.9, 121.9, 120.4, 117.2, 109.7, 34.9, 34.0, 29.7, 28.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀BrO₂ 513.1429; Found 513.1421.

2,4-di-tert-butyl-9-(2-hydroxy-7-methoxynaphthalen-1-yl)-3H-fluoren-3-one (2c).



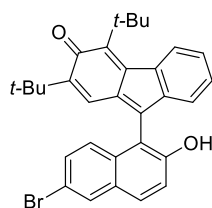
Red solid; 42.71 mg, 92% yield (petroleum ether/ethyl acetate =10:1); mp 178.3-179.3 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.71 (d, *J* = 8.82 Hz, 1H), 7.67-7.63 (m, 2H), 7.05-6.93 (m, 4H), 6.80 (s, 1H), 6.65 (m, 1H), 6.41 (s, 1H), 5.19 (s, 1H), 3.63 (s, 3H), 1.52 (s, 9H), 1.09 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.9, 157.4, 153.8, 150.8, 147.1, 143.2, 140.9, 139.4, 136.5, 134.8, 133.1, 129.8, 128.8, 127.6, 126.4, 124.4, 123.4, 122.3, 114.8, 114.2, 109.5, 103.7, 54.3, 34.9, 33.9, 29.7, 28.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₂H₃₃O₃ 465.2430; Found 465.2433.

5-(2,4-di-tert-butyl-3-oxo-3H-fluoren-9-yl)-6-hydroxy-2-naphthonitrile (2d).

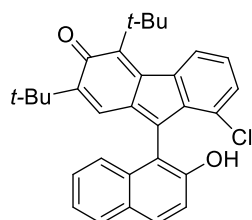


Red solid; 42.24 mg, 92% yield (petroleum ether/ethyl acetate =10:1); mp 121.2-122.2 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.15 (s, 1H), 7.86 (m, 1H), 7.58 (m, 2H), 7.43 (m, 1H), 7.34 (m, 1H), 7.08 (m, 1H), 6.92 (m, 1H), 6.51 (d, *J* = 7.38 Hz, 1H), 6.27 (s, 1H), 5.63 (s, 1H), 1.51 (s, 9H), 1.08 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.7, 154.7, 152.8, 147.8, 143.2, 140.6, 137.2, 135.5, 133.6, 133.3, 130.5, 127.8, 127.0, 126.7, 126.4, 125.4, 123.5, 121.8, 118.7, 118.2, 110.9, 106.2, 34.9, 34.0, 29.6, 28.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₂H₃₀NO₂ 460.2277; Found 460.2283.

9-(6-bromo-2-hydroxynaphthalen-1-yl)-2,4-di-tert-butyl-3H-fluoren-3-one (2e).



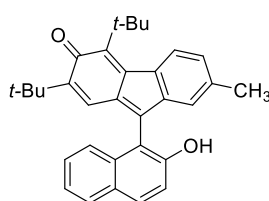
Red solid; 45.58 mg, 89% yield (petroleum ether/ethyl acetate =10:1); mp 177.8-178.8 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.92 (s, 1H), 7.64 (m, 2H), 7.38 (m, 2H), 7.08 (m, 1H), 6.94 (m, 1H), 6.91 (m, 1H), 6.54 (d, *J* = 7.32 Hz, 1H), 6.32 (s, 1H), 5.25 (s, 1H), 1.52 (s, 9H), 1.08 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.7, 154.3, 150.4, 147.6, 143.4, 140.7, 138.2, 136.3, 135.2, 130.3, 129.0, 127.7, 126.6, 126.0, 123.8, 122.0, 117.9, 116.6, 110.6, 34.9, 34.0, 29.7, 28.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀BrO₂ 513.1429; Found 513.1432.



2,4-di-tert-butyl-8-chloro-9-(2-hydroxynaphthalen-1-yl)-3H-fluoren-3-one (2f).

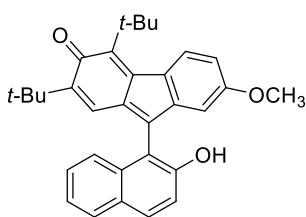
Red solid; 40.26 mg, 86% yield (petroleum ether/ethyl acetate =10:1); mp 209.4-210.4 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.80-7.75 (m, 2H), 7.45 (m, 2H), 7.31 (m, 2H), 7.16 (s, 1H), 6.99 (m, 1H), 6.88 (d, *J* = 8.04 Hz, 1H), 6.24 (s, 1H), 5.06 (s, 1H), 1.51 (s, 9H), 1.04 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.8, 155.2, 149.6, 147.6, 139.6, 139.5, 138.8, 137.7, 137.1, 132.6, 129.8, 129.8, 128.8, 127.0, 126.2, 126.0, 123.9, 123.5, 122.7, 116.4, 112.0, 35.0, 33.9, 29.7, 28.4. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀ClO₂ 469.1934; Found 469.1944.

2,4-di-tert-butyl-9-(2-hydroxynaphthalen-1-yl)-7-methyl-3H-fluoren-3-one (2g).



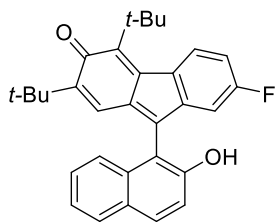
Red solid; 40.34 mg, 90% yield (petroleum ether/ethyl acetate =10:1); mp 187.0-188.0 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.81-7.76 (m, 2H), 7.51 (m, 1H), 7.51 (s, 1H), 7.29 (m, 2H), 7.21 (m, 1H), 6.72 (d, *J* = 7.56 Hz, 1H), 6.46 (d, *J* = 7.56 Hz, 1H), 6.35 (s, 1H), 5.20 (s, 1H), 2.29 (s, 3H), 1.52 (s, 9H), 1.08 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.7, 153.7, 150.0, 146.8, 141.0, 141.0, 139.4, 136.9, 136.6, 134.4, 131.8, 130.0, 129.1, 127.2, 125.7, 124.3, 122.8, 122.0, 116.7, 110.4, 34.8, 33.9, 29.7, 28.5, 20.9. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₂H₃₃O₂ 449.2481; Found 449.2491.

2,4-di-tert-butyl-9-(2-hydroxynaphthalen-1-yl)-7-methoxy-3H-fluoren-3-one (2h).



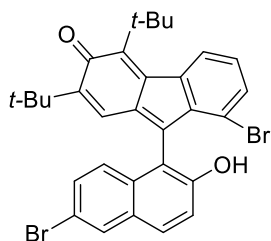
Red solid; 41.78 mg, 90% yield (petroleum ether/ethyl acetate =10:1); mp 201.9-202.9 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.81-7.76 (m, 2H), 7.51 (m, 2H), 7.31-7.28 (m, 2H), 7.21 (m, 1H), 6.54 (d, *J* = 8.46 Hz, 1H), 6.31 (s, 1H), 6.13 (s, 1H), 5.21 (s, 1H), 3.56 (s, 3H), 1.50 (s, 9H), 1.07 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.7, 159.4, 151.7, 150.1, 147.4, 145.7, 140.6, 138.4, 136.3, 131.8, 130.0, 128.5, 127.2, 125.8, 124.0, 122.8, 116.7, 110.2, 110.1, 109.1, 54.4, 34.6, 33.9, 29.6, 28.5. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₂H₃₃O₃ 465.2430; Found 465.2440.

2,4-di-tert-butyl-7-fluoro-9-(2-hydroxynaphthalen-1-yl)-3H-fluoren-3-one (2i).



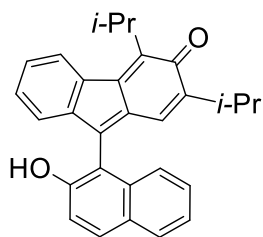
Red solid; 41.15 mg, 91% yield (petroleum ether/ethyl acetate =10:1); mp 114.7-115.7 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.82-7.77 (m, 2H), 7.48 (m, 2H), 7.35-7.29 (m, 2H), 7.20 (m, 1H), 6.73 (m, 1H), 6.35 (s, 1H), 6.27 (d, *J* = 8.04 Hz, 1H), 5.19 (s, 1H), 1.50 (s, 9H), 1.07 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.7, 163.1, 163.0, 161.4, 153.7, 150.1, 147.7, 146.4, 146.4, 139.8, 137.8, 137.8, 136.5, 132.0, 131.9, 131.6, 130.3, 128.6, 127.4, 126.0, 124.0, 124.0, 123.0, 116.7, 112.3, 112.2, 109.8, 109.7, 109.7, 34.8, 34.0, 29.7, 28.5. ¹⁹F NMR (CDCl₃, 377 MHz) δ -112.7. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀FO₂ 453.2230; Found 453.2220.

8-bromo-9-(6-bromo-2-hydroxynaphthalen-1-yl)-2,4-di-tert-butyl-3H-fluoren-3-one (2j).



Red solid; 53.31 mg, 90% yield (petroleum ether/ethyl acetate =10:1); mp 96.5-97.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.91 (s, 1H), 7.60 (m, 4H), 7.20 (s, 1H), 7.09 (d, *J* = 8.04 Hz, 1H), 6.93 (t, *J* = 7.92 Hz, 1H), 6.18 (s, 1H), 5.10 (s, 1H), 1.50 (s, 9H), 1.04 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.8, 155.6, 150.2, 148.0, 140.8, 139.0, 137.6, 137.6, 133.2, 131.4, 129.1, 128.9, 127.2, 126.8, 125.3, 117.6, 116.9, 116.6, 112.0, 35.0, 34.0, 29.7, 28.5, 28.4. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₂₉Br₂O₂ 593.0514; Found 593.0519.

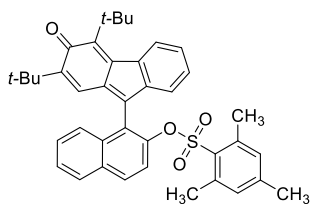
9-(2-hydroxynaphthalen-1-yl)-2,4-diisopropyl-3H-fluoren-3-one (2k).



Red solid; 34.53 mg, 85% yield (petroleum ether/ethyl acetate =10:1); mp 134.2-135.3 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.82 (m, 2H), 7.60 (m, 2H), 7.53 (m, 3H), 7.08 (m, 1H), 6.93 (m, 1H), 6.63 (d, *J* = 7.32 Hz, 1H), 6.46 (s, 1H), 5.24 (s, 1H), 3.61-3.56 (m, 1H), 2.91-2.87 (m, 1H), 1.43-1.41 (m, 6H), 0.92-0.86 (m, 6H); ¹³C NMR (CDCl₃, 150 MHz) δ 187.3, 150.0, 145.0, 143.9, 143.1, 142.3, 141.2, 136.7, 134.2, 131.7, 130.2, 128.3, 127.7, 127.3, 125.8, 124.5, 124.2, 122.9, 122.7, 116.8, 110.3, 28.7, 25.7, 21.0, 20.9, 19.8. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₉H₂₇O₂ 407.2011; Found 407.2020.

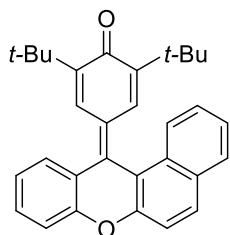
1-(2,4-di-tert-butyl-3-oxo-3H-fluoren-9-yl)naphthalen-2-yl

2,4,6-trimethylbenzenesulfonate (2a').



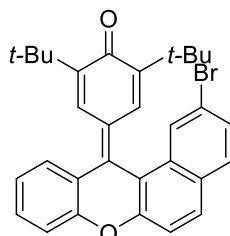
Red solid; 58.17 mg, 96% yield (petroleum ether/ethyl acetate) =30:1; mp 118.4-119.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.93 (d, *J* = 9.00 Hz, 1H), 7.86 (d, *J* = 8.16 Hz, 1H), 7.69 (m, 1H), 7.46-7.43 (m, 3H), 7.34-7.32 (m, 1H), 6.95 (t, *J* = 7.62 Hz, 1H), 6.76 (t, *J* = 7.38 Hz, 1H), 6.45 (s, 2H), 6.25 (d, *J* = 7.32 Hz, 1H), 6.18 (s, 1H), 2.18 (s, 6H), 2.02 (s, 3H), 1.49 (s, 9H), 1.06 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 193.6, 152.8, 138.6, 135.4, 134.1, 131.2, 131.1, 130.5, 129.5, 127.3, 127.2, 127.0, 125.9, 125.5, 125.4, 125.0, 122.5, 121.9, 121.0, 34.6, 33.8, 28.4, 21.7, 20.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₄₀H₄₁O₄S 617.2726; Found 617.2736.

4-(12H-benzo[a]xanthen-12-ylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (3a).



Orange solid; 42.98 mg, 99% yield (petroleum ether/ethyl acetate =30:1); mp 248.8-249.8 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.00 (d, *J* = 8.40 Hz, 1H), 7.78 (m, 2H), 7.68 (m, 2H), 7.38-7.28 (m, 6H), 7.01 (d, *J* = 2.10 Hz, 1H), 1.25 (s, 9H), 0.93 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.8, 153.0, 151.9, 146.9, 146.1, 134.9, 130.8, 129.7, 128.4, 127.1, 127.1, 125.7, 124.8, 124.0, 122.6, 117.7, 115.8, 115.8, 34.6, 34.2, 28.7, 28.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₁O₂ 435.2324; Found 435.2321.

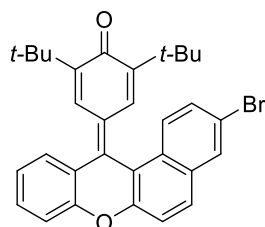
4-(2-bromo-12H-benzo[a]xanthen-12-ylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (3b).



Orange solid; 47.11 mg, 92% yield (petroleum ether/ethyl acetate =30:1); mp 237.4-237.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.14 (s, 1H), 7.76 (m, 1H), 7.67-7.63 (m, 3H), 7.38-7.29 (m, 5H), 6.99 (s, 1H), 1.25 (s, 9H), 0.99 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.6, 152.8, 152.6, 147.2, 146.6, 133.9, 130.9, 129.6, 128.7, 127.4, 127.3, 127.1, 125.0, 123.8, 122.8, 121.5, 120.5, 116.5, 116.4, 115.7, 34.6, 34.3, 28.6, 28.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀BrO₂ 513.1429; Found

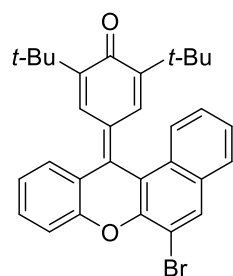
513.1432.

4-(3-bromo-12H-benzo[a]xanthen-12-ylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (3c).



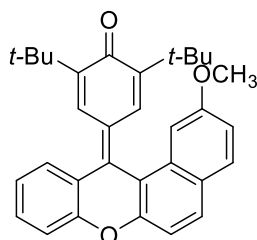
Orange solid; 47.62 mg, 93% yield (petroleum ether/ethyl acetate =30:1); mp 242.9-243.9 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.94 (m, 2H), 7.73-7.65 (m, 3H), 7.44-7.28 (m, 5H), 6.92 (d, *J* = 2.58 Hz, 1H), 1.25 (s, 9H), 0.95 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.7, 152.9, 152.1, 147.2, 146.5, 134.1, 130.8, 130.2, 128.8, 128.3, 127.1, 126.7, 125.0, 123.8, 122.8, 117.7, 117.4, 117.1, 115.8, 34.6, 34.3, 28.6, 28.3. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀BrO₂ 513.1429; Found 513.1426.

4-(6-bromo-12H-benzo[a]xanthen-12-ylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (3d).



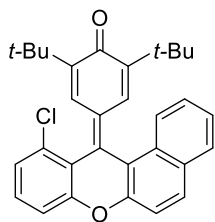
Orange solid; 48.65 mg, 95% yield (petroleum ether/ethyl acetate =30:1); mp 183.4-184.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.10 (s, 1H), 7.94 (m, 1H), 7.67 (m, 3H), 7.42-7.30 (m, 5H), 6.90 (s, 1H), 1.25 (s, 9H), 0.92 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.8, 152.9, 148.1, 147.4, 146.5, 133.8, 132.1, 130.1, 128.3, 126.2, 125.6, 124.9, 123.9, 123.1, 118.9, 116.2, 109.8, 34.6, 34.3, 28.6, 28.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀BrO₂ 513.1429; Found 513.1426.

2,6-di-tert-butyl-4-(2-methoxy-12H-benzo[a]xanthen-12-ylidene)cyclohexa-2,5-dien-1-one (3e).



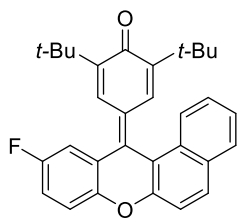
Orange solid; 41.78 mg, 90% yield (petroleum ether/ethyl acetate =30:1); mp 205.6-206.8 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.73-7.67 (m, 4H), 7.28 (m, 5H), 7.09-7.04 (m, 2H), 3.75 (s, 3H), 1.25 (s, 9H), 0.95 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.7, 157.7, 152.9, 152.6, 146.8, 146.0, 135.5, 131.1, 130.8, 128.8, 128.5, 127.1, 125.1, 124.3, 124.1, 122.5, 116.4, 115.8, 113.3, 104.0, 54.4, 34.6, 34.3, 28.6, 28.3. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₂H₃₃O₃ 465.2430; Found 465.2433.

2,6-di-tert-butyl-4-(11-chloro-12H-benzo[a]xanthen-12-ylidene)cyclohexa-2,5-dien-1-one (3f).



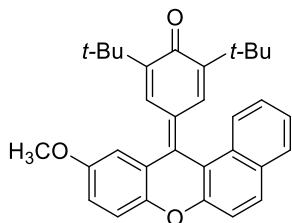
Orange solid; 41.66 mg, 89% yield (petroleum ether/ethyl acetate =30:1); mp 251.3-252.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.06 (d, *J* = 8.46 Hz, 1H), 7.80-7.79 (m, 2H), 7.47 (m, 3H), 7.29-7.25 (m, 3H), 7.16 (m, 1H), 6.96 (d, *J* = 2.58 Hz, 1H), 1.22 (s, 9H), 0.92 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.9, 154.8, 151.3, 146.6, 146.5, 131.2, 129.7, 129.4, 128.4, 126.8, 126.1, 124.7, 124.3, 123.5, 118.2, 115.6, 114.2, 34.4, 34.3, 28.5, 28.3. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀ClO₂ 469.1934; Found 469.1940.

2,6-di-tert-butyl-4-(10-fluoro-12H-benzo[a]xanthen-12-ylidene)cyclohexa-2,5-dien-1-one (3g).



Orange solid; 42.05 mg, 93% yield (petroleum ether/ethyl acetate =30:1); mp 213.4-214.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.96 (m, 1H), 7.84-7.68 (m, 2H), 7.68 (d, *J* = 2.70 Hz, 1H), 7.38 (m, 4H), 7.28 (m, 1H), 7.10-7.07 (m, 1H), 6.96 (d, *J* = 2.64 Hz, 1H), 1.27 (s, 9H), 0.92 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.7, 158.5, 156.9, 152.1, 149.2, 149.2, 147.4, 146.4, 133.5, 130.6, 130.1, 129.7, 129.7, 127.8, 127.1, 125.8, 125.2, 125.1, 125.3, 124.8, 124.1, 117.0, 116.9, 116.6, 115.2, 113.3, 113.1, 34.6, 34.3, 28.6, 28.2. ¹⁹F NMR (CDCl₃, 377 MHz) δ -118.9. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₁H₃₀FO₂ 453.2230; Found 453.2239.

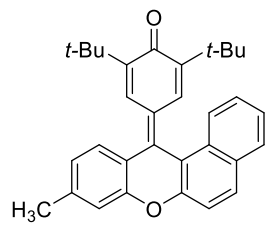
2,6-di-tert-butyl-4-(10-methoxy-12H-benzo[a]xanthen-12-ylidene)cyclohexa-2,5-dien-1-one (3h).



Orange solid; 42.71 mg, 92% yield (petroleum ether/ethyl acetate =30:1); mp 228.5-229.8 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.99 (d, *J* = 8.40 Hz, 1H), 7.80 (m, 3H), 7.76-7.35 (m, 3H), 7.25 (m, 2H), 7.00-6.94 (m, 2H), 3.83 (s, 3H), 1.27 (s, 9H), 0.92 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.7, 154.8, 152.3, 147.4, 146.9, 145.0, 137.7, 135.1, 130.9, 129.6, 128.1, 127.0, 125.7, 124.9, 124.7, 124.4, 123.9, 116.8, 116.6, 115.9, 115.7, 110.4, 54.9, 54.7, 34.6, 34.2, 28.8, 28.2. HRMS (ESI-TOF)

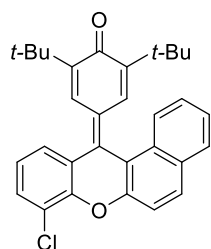
m/z: [M+H]⁺ Calcd for C₃₂H₃₃O₃ 465.2430; Found 465.2419.

2,6-di-tert-butyl-4-(9-methyl-12H-benzo[a]xanthen-12-ylidene)cyclohexa-2,5-dien-1-one (3i).



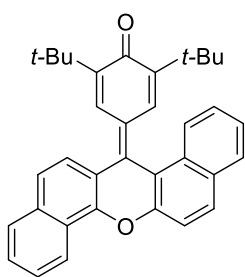
Orange solid; 41.24 mg, 92% yield (petroleum ether/ethyl acetate =30:1); mp 271.3-272.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.00 (d, *J* = 8.40 Hz, 1H), 7.78 (m, 3H), 7.56 (m, 1H), 7.40-7.35 (m, 3H), 7.16 (s, 1H), 7.09 (d, *J* = 7.86 Hz, 1H), 7.00 (s, 1H), 2.39 (s, 3H), 1.26 (s, 9H), 0.92 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.8, 152.9, 151.9, 146.7, 145.8, 139.2, 135.3, 130.9, 129.6, 128.7, 127.0, 126.8, 125.6, 125.0, 124.3, 123.9, 123.7, 121.4, 117.3, 116.1, 115.8, 34.6, 34.2, 28.7, 28.2, 20.4. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₂H₃₃O₂ 449.2481; Found 449.2487.

2,6-di-tert-butyl-4-(8-chloro-12H-benzo[a]xanthen-12-ylidene)cyclohexa-2,5-dien-1-one (3j).



Orange solid; 43.54 mg, 93% yield (petroleum ether/ethyl acetate =30:1); mp 258.2-259.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.97 (d, *J* = 8.34 Hz, 1H), 7.84 (d, *J* = 7.84 Hz, 1H), 7.78 (d, *J* = 7.98 Hz, 1H), 7.61 (m, 3H), 7.38 (m, 3H), 7.18 (m, 1H), 6.98 (s, 1H), 1.24 (s, 9H), 0.92 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.8, 151.7, 148.9, 147.3, 146.5, 133.7, 130.5, 130.1, 130.0, 128.8, 128.1, 127.2, 125.8, 125.6, 125.5, 124.9, 124.3, 122.7, 121.5, 117.1, 115.9, 34.6, 34.3, 28.6, 28.2. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₀ClO₂ 469.1934; Found 469.1924.

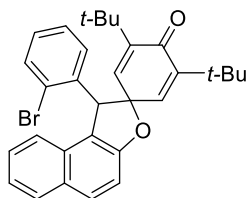
2,6-di-tert-butyl-4-(14H-dibenzo[a,h]xanthen-14-ylidene)cyclohexa-2,5-dien-1-one (3k).



Orange solid; 44.07 mg, 91% yield (petroleum ether/ethyl acetate =30:1); mp 266.7-267.8 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.49 (d, *J* = 8.16 Hz, 1H), 8.09 (d, *J* = 8.40 Hz, 1H), 7.78 (m, 6H), 7.58-7.51 (m, 3H), 7.38 (m, 2H), 7.08 (d, *J* = 2.58 Hz, 1H), 1.25 (s, 9H), 0.94 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.4, 151.8, 148.9, 146.9, 145.9, 130.8, 129.7, 129.6, 128.8, 127.1, 126.8, 126.6, 125.8, 125.7, 125.1, 124.3, 124.2, 124.1, 122.8, 122.2, 121.1, 118.6, 117.4, 115.8, 34.6, 34.3,

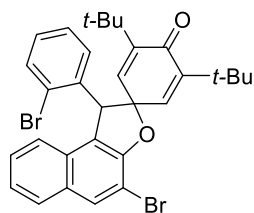
28.7, 28.2. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₅H₃₃O₂ 485.2481; Found 485.2487.

1'-(2-bromophenyl)-3,5-di-tert-butyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4a).



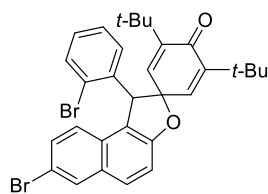
White solid; 50.90 mg, 99% yield (petroleum ether/ethyl acetate =30:1); mp 157.8-158.8 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.80 (d, *J* = 8.76 Hz, 2H), 7.50 (m, 1H), 7.21 (m, 3H), 7.06-7.00 (m, 3H), 6.70 (d, *J* = 2.94 Hz, 1H), 6.53 (m, 1H), 5.98 (d, *J* = 2.88 Hz, 1H), 5.46 (s, 1H), 1.18 (s, 9H), 0.89 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.6, 155.7, 146.0, 144.8, 137.2, 137.2, 136.0, 132.0, 130.0, 129.2, 129.0, 127.9, 126.5, 126.3, 124.6, 122.5, 122.1, 118.4, 111.6, 84.7, 54.5, 33.8, 33.7, 28.4, 28.0. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₂BrO₂ 515.1586; Found 515.1596.

4'-bromo-1'-(2-bromophenyl)-3,5-di-tert-butyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4b).



White solid; 55.65 mg, 94% yield (petroleum ether/ethyl acetate =30:1); mp 166.5-167.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.02 (m, 1H), 7.72 (m, 1H), 7.50 (m, 1H), 7.24 (m, 2H), 7.02 (m, 3H), 6.69 (m, 1H), 6.53 (d, *J* = 5.82 Hz, 1H), 6.00 (s, 1H), 5.56 (s, 1H), 1.19 (s, 9H), 0.89 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.4, 152.8, 146.1, 145.0, 136.8, 136.7, 135.7, 132.1, 131.9, 129.9, 129.1, 128.1, 127.0, 126.6, 126.5, 124.5, 123.4, 122.3, 119.9, 104.4, 85.4, 55.5, 33.8, 30.0, 28.4, 28.0. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₁Br₂O₂ 595.0670; Found 595.0686.

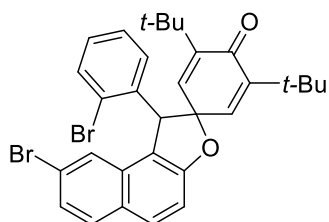
7'-bromo-1'-(2-bromophenyl)-3,5-di-tert-butyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4c).



White solid; 57.43 mg, 97% yield (petroleum ether/ethyl acetate =30:1); mp 183.5-184.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.95 (s, 1H), 7.70 (m, 1H), 7.50 (m, 1H), 7.20 (m, 2H), 6.92 (m, 3H), 6.68 (m, 1H), 6.48 (m, 1H), 5.96 (d, *J* = 3.12 Hz, 1H), 5.44 (s, 1H), 1.18 (s, 9H), 0.88 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.5,

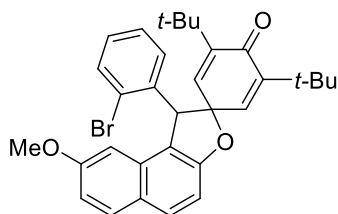
156.0, 146.1, 145.0, 136.9, 136.9, 135.7, 132.1, 129.5, 129.1, 129.0, 127.9, 126.5, 124.6, 123.8, 118.8, 116.1, 112.7, 84.9, 54.4, 33.8, 28.4, 28.0. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₁Br₂O₂ 595.0670; Found 595.0686.

8'-bromo-1'-(2-bromophenyl)-3,5-di-tert-butyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4d).

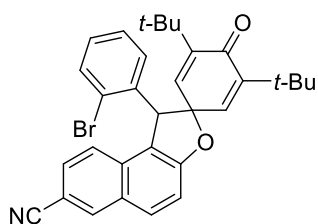


White solid; 58.61 mg, 99% yield (petroleum ether/ethyl acetate =30:1); mp 165.4-166.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.75 (d, *J* = 8.88 Hz, 1H), 7.64 (d, *J* = 8.76 Hz, 1H), 7.51 (m, 1H), 7.50 (m, 1H), 7.19 (m, 2H), 7.02 (m, 2H), 6.65 (m, 1H), 6.49 (m, 1H), 5.92 (d, *J* = 3.12 Hz, 1H), 5.39 (s, 1H), 1.18 (s, 9H), 0.89 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.4, 156.5, 146.2, 145.0, 136.8, 136.6, 135.6, 132.2, 130.1, 128.9, 128.1, 127.3, 126.6, 126.0, 124.6, 124.1, 120.8, 117.7, 112.0, 85.0, 54.2, 33.8, 28.7, 28.4, 28.0. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₁Br₂O₂ 595.0670; Found 595.0686.

1'-(2-bromophenyl)-3,5-di-tert-butyl-8'-methoxy-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4e).



White solid; 52.24 mg, 96% yield (petroleum ether/ethyl acetate =30:1); mp 136.7-137.7 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.71-7.67 (m, 2H), 7.49 (m, 1H), 6.99 (m, 3H), 6.89 (m, 1H), 6.87 (m, 1H), 6.58 (m, 1H), 6.29 (d, *J* = 2.22 Hz, 1H), 6.01 (d, *J* = 3.06 Hz, 1H), 5.41 (s, 1H), 3.55 (s, 3H), 1.18 (s, 9H), 0.88 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.6, 157.6, 156.2, 145.9, 144.8, 137.4, 136.8, 136.2, 131.9, 130.7, 129.2, 127.9, 126.5, 124.5, 124.2, 117.7, 114.7, 108.9, 100.9, 84.6, 54.6, 54.0, 33.8, 33.7, 28.4, 28.0. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₂H₃₄BrO₃ 545.1691; Found 545.1697.

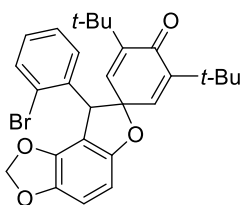


1'-(2-bromophenyl)-3,5-di-tert-butyl-4-oxo-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-diene-7'-carbonitrile (4f).

White solid; 51.76 mg, 96% yield (petroleum ether/ethyl

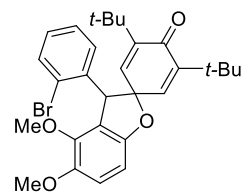
acetate =30:1); mp 133.4-134.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 8.17 (s, 1H), 7.86 (d, *J* = 8.94 Hz, 1H), 7.51 (m, 1H), 7.36-7.30 (m, 2H), 7.01 (m, 3H), 6.66 (d, *J* = 3.12 Hz, 1H), 6.47 (m, 1H), 5.95 (d, *J* = 3.12 Hz, 1H), 5.47 (s, 1H), 1.19 (s, 9H), 0.88 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.3, 158.2, 146.4, 145.3, 136.5, 136.4, 135.2, 134.0, 132.3, 130.8, 128.9, 128.3, 127.8, 126.9, 126.6, 124.7, 123.3, 119.2, 118.3, 113.6, 105.8, 85.5, 54.1, 33.9, 33.8, 30.0, 28.4, 28.0. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₂H₃₁BrNO₂ 540.1538; Found 540.1528.

8'-(2-bromophenyl)-3,5-di-tert-butyl-8'H-spiro[cyclohexane-1,7'-[1,3]dioxolo[4,5-e]benzofuran]-2,5-dien-4-one (4g).



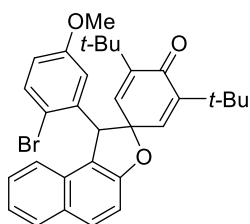
White solid; 49.80 mg, 98% yield (petroleum ether/ethyl acetate =30:1); mp 145.6-146.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.43 (d, *J* = 7.92 Hz, 1H), 7.16 (m, 1H), 7.01 (m, 1H), 6.68 (m, 2H), 6.45 (d, *J* = 3.48 Hz, 2H), 5.91 (m, 3H), 5.04 (s, 1H), 1.18 (s, 9H), 0.85 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.5, 152.4, 147.6, 145.8, 144.9, 141.6, 138.0, 137.2, 135.7, 131.9, 129.4, 127.9, 126.4, 124.8, 118.2, 104.6, 100.5, 92.7, 84.8, 55.1, 33.8, 33.7, 28.7, 28.3, 27.9. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₈H₃₀BrO₄ 509.1327; Found 509.1332.

3-(2-bromophenyl)-3',5'-di-tert-butyl-4,5-dimethoxy-3H-spiro[benzofuran-2,1'-cyclohexane]-2',5'-dien-4'-one (4h).



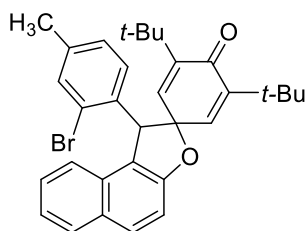
White solid; 51.37 mg, 98% yield (petroleum ether/ethyl acetate =30:1); mp 188.0-189.3 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.44 (d, *J* = 7.92 Hz, 1H), 7.05 (m, 1H), 7.02 (m, 1H), 6.68 (m, 2H), 6.55 (s, 1H), 6.51 (s, 1H), 5.91 (d, *J* = 3.06 Hz, 1H), 5.10 (s, 1H), 3.85 (s, 3H), 3.72 (s, 3H), 1.19 (s, 9H), 0.86 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.5, 152.0, 149.5, 145.8, 144.8, 143.4, 138.2, 137.4, 135.9, 131.9, 129.5, 127.9, 126.4, 124.8, 116.9, 108.1, 94.4, 84.7, 55.7, 55.4, 55.1, 33.8, 33.7, 28.3, 27.9. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₉H₃₄BrO₄ 525.1640; Found 525.1650.

1'-(2-bromo-5-methoxyphenyl)-3,5-di-tert-butyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4i).



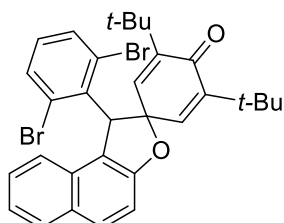
White solid; 53.33 mg, 98% yield (petroleum ether/ethyl acetate =30:1); mp 170.2-171.5 °C. ¹H NMR (CDCl₃, 600 MHz) 7.78 (d, *J* = 9.00 Hz, 2H), 7.38-7.17 (m, 4H), 7.09 (d, *J* = 8.70 Hz, 1H), 6.67 (s, 1H), 6.57 (m, 1H), 6.08 (d, *J* = 3.06 Hz, 1H), 6.03 (d, *J* = 3.12 Hz, 1H), 5.38 (s, 1H), 3.44 (s, 3H), 1.17 (s, 9H), 0.92 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.6, 158.0, 155.6, 146.1, 144.8, 138.2, 137.2, 135.9, 132.5, 130.1, 129.5, 128.9, 127.9, 126.3, 122.4, 122.1, 118.3, 115.6, 115.0, 112.9, 111.6, 84.7, 54.5, 54.3, 33.8, 33.7, 28.7, 28.4, 28.0. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₂H₃₄BrO₃ 545.1691; Found 545.1697.

1'-(2-bromo-4-methylphenyl)-3,5-di-tert-butyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4j).



White solid; 49.65 mg, 94% yield (petroleum ether/ethyl acetate =30:1); mp 122.7-123.8 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.78 (d, *J* = 8.82 Hz, 2H), 7.32-7.17 (m, 4H), 7.07 (m, 2H), 6.68 (s, 1H), 6.40 (d, *J* = 7.92 Hz, 1H), 6.00 (d, *J* = 2.70 Hz, 1H), 5.42 (s, 1H), 2.19 (s, 3H), 1.17 (s, 9H), 0.90 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.6, 155.6, 145.9, 144.7, 138.1, 137.3, 136.2, 134.0, 132.3, 129.9, 128.9, 128.8, 127.3, 126.2, 124.3, 122.4, 122.1, 118.6, 111.6, 84.8, 54.2, 33.8, 33.7, 28.4, 28.0, 19.6. HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₃₂H₃₄BrO₂ 529.1742; Found 529.1748.

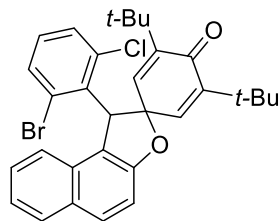
3,5-di-tert-butyl-1'-(2,6-dibromophenyl)-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4k).



White solid; 55.65 mg, 94% yield (petroleum ether/ethyl acetate =30:1); mp 149.3-150.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.77 (d, *J* = 8.70 Hz, 2H), 7.54 (m, 1H), 7.22 (m, 3H), 7.11 (m, 1H), 6.95 (m, 1H), 6.87-6.85 (m, 1H), 6.76-6.73 (m, 2H), 5.99 (s, 1H), 1.19 (s, 9H), 0.88 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.7, 156.9, 146.7, 144.4, 138.0, 136.3, 135.2, 133.8, 131.8, 129.9, 129.7, 128.4, 127.4, 126.2, 123.7, 122.3, 121.0, 118.1, 111.6, 84.7, 56.3, 33.8, 28.3, 28.1. HRMS

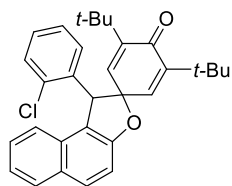
(ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₁Br₂O₂ 595.0670; Found 595.0673.

1'-(2-bromo-6-chlorophenyl)-3,5-di-tert-butyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4l).



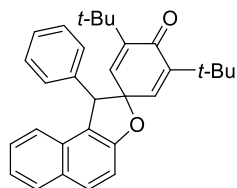
White solid; 52.62 mg, 96% yield (petroleum ether/ethyl acetate =30:1); mp 142.6-143.6 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.78-7.50 (m, 2H), 7.21 (m, 3H), 7.12 (m, 2H), 6.98-6.94 (m, 2H), 6.75-6.70 (m, 2H), 5.98-5.94 (m, 1H), 1.18 (s, 9H), 0.87 (d, *J* = 3.84 Hz, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.7, 156.8, 156.3, 146.7, 146.6, 144.4, 138.1, 138.0, 136.1, 134.9, 134.4, 133.8, 133.0, 131.1, 129.5, 127.9, 126.9, 126.1, 123.7, 122.3, 121.0, 120.8, 118.2, 117.8, 111.6, 111.6, 84.8, 55.5, 53.3, 33.8, 28.3, 28.0. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₁BrClO₂ 549.1196; Found 549.1186.

3,5-di-tert-butyl-1'-(2-chlorophenyl)-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4m).



White solid; 45.14 mg, 96% yield (petroleum ether/ethyl acetate =30:1); mp 141.3-142.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.79 (d, *J* = 8.70 Hz, 2H), 7.24 (m, 4H), 7.06 (m, 2H), 6.95 (m, 1H), 6.70 (d, *J* = 3.12 Hz, 1H), 6.55 (d, *J* = 9.12 Hz, 1H), 5.99 (s, 1H), 5.47 (s, 1H), 1.18 (s, 9H), 0.87 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.6, 155.7, 145.9, 144.8, 137.3, 135.9, 135.4, 133.7, 130.0, 128.9, 128.9, 128.7, 127.9, 127.6, 126.2, 125.9, 122.4, 122.1, 117.9, 111.6, 84.8, 52.2, 33.7, 28.7, 28.3, 27.9. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₁H₃₂ClO₂ 471.2091; Found 471.2099.

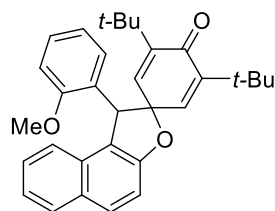
3,5-di-tert-butyl-1'-phenyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4n).



White solid; 41.88 mg, 96% yield (petroleum ether/ethyl acetate =30:1); mp 174.2-175.2 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.78 (d, *J* = 8.40 Hz, 2H), 7.22-7.15 (m, 9H), 6.74 (d, *J* = 3.06 Hz, 1H), 6.09 (d, *J* = 3.00 Hz, 1H), 4.89 (s, 1H), 1.20 (s, 9H), 0.82 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 185.1, 155.5, 145.6, 145.3, 138.0, 137.2, 136.8, 129.8, 129.8, 129.0, 127.9, 127.6, 127.0, 126.6, 125.9, 122.3, 118.5, 111.7, 85.4, 57.3, 33.8,

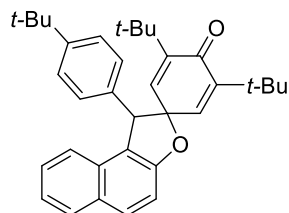
33.5, 28.4, 27.8, 27.7. HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{31}H_{33}O_2$ 437.2481; Found 437.2487.

3,5-di-tert-butyl-1'-(2-methoxyphenyl)-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4o).



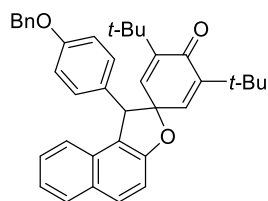
White solid; 46.16 mg, 99% yield (petroleum ether/ethyl acetate =30:1); mp 80.3-81.3 °C. 1H NMR ($CDCl_3$, 600 MHz) δ 7.79-7.75 (m, 2H), 7.22-7.09 (m, 5H), 7.09 (m, 2H), 6.61 (m, 1H), 6.48 (d, J = 5.94 Hz, 1H), 6.05 (d, J = 3.06 Hz, 1H), 5.44 (s, 1H), 3.61 (s, 3H), 1.21 (s, 9H), 0.85 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 185.8, 155.9, 155.7, 144.7, 143.9, 138.3, 136.9, 129.8, 129.5, 128.8, 127.3, 125.8, 122.5, 122.1, 119.1, 117.9, 111.5, 108.8, 85.0, 53.8, 49.1, 33.6, 33.5, 28.4, 28.0, 27.9, 27.3. HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{32}H_{35}O_3$ 467.2586; Found 467.2595.

3,5-di-tert-butyl-1'-(4-(tert-butyl)phenyl)-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4p).



White solid; 47.75 mg, 97% yield (petroleum ether/ethyl acetate =30:1); mp 202.2-203.2 °C. 1H NMR ($CDCl_3$, 600 MHz) δ 7.79-7.77 (m, 2H), 7.23-7.17 (m, 7H), 6.73 (d, J = 3.00 Hz, 2H), 6.06 (d, J = 3.00 Hz, 1H), 4.88 (s, 1H), 1.20 (s, 9H), 1.18 (s, 9H), 0.79 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 185.1, 155.5, 149.6, 145.3, 145.2, 138.0, 137.5, 133.7, 129.8, 129.7, 128.9, 127.8, 125.8, 124.5, 122.5, 122.2, 118.6, 111.6, 85.5, 56.9, 33.7, 33.5, 33.4, 30.3, 28.4, 27.8. HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{35}H_{41}O_2$ 493.3107; Found 493.3117.

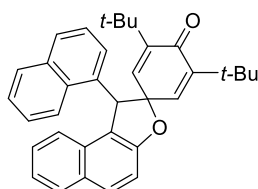
1'-(4-(benzyloxy)phenyl)-3,5-di-tert-butyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4q).



White solid; 53.14 mg, 98% yield (petroleum ether/ethyl acetate =30:1); mp 161.5-162.8 °C. 1H NMR ($CDCl_3$, 600 MHz) δ 7.77 (m, 2H), 7.22-7.16 (m, 10H), 6.72 (m, 4H), 6.09 (d, J = 3.00 Hz, 1H), 4.93 (s, 1H), 4.84 (s, 2H), 1.19 (s, 9H), 0.84 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 186.2, 158.3, 156.4, 146.6, 146.3, 139.2, 139.0, 138.7, 138.1, 136.9, 130.8, 130.7, 130.3, 130.0, 128.9, 128.5, 127.9, 127.3,

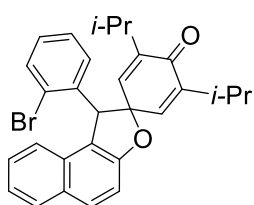
126.8, 123.4, 123.3, 123.2, 119.8, 115.0, 112.8, 112.6, 86.6, 70.0, 57.5, 34.6, 29.4, 29.0. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₈H₃₉O₃ 543.2899; Found 543.2893.

3,5-di-tert-butyl-1'-(naphthalen-1-yl)-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4r).

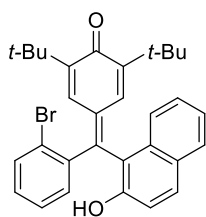


White solid; 46.19 mg, 95% yield (petroleum ether/ethyl acetate =30:1); mp 103.5-104.7 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.84-7.77 (m, 4H), 7.64 (d, *J* = 8.16 Hz, 1H), 7.34 (m, 4H), 7.17 (m, 2H), 7.04 (m, 1H), 6.87 (s, 1H), 6.73 (s, 1H), 5.92 (d, *J* = 2.52 Hz, 1H), 5.80 (s, 1H), 1.27 (s, 9H), 0.38 (s, 9H); ¹³C NMR (CDCl₃, 150 MHz) δ 184.4, 155.8, 145.3, 145.1, 137.5, 136.3, 133.4, 132.9, 131.3, 129.8, 129.0, 127.8, 126.9, 126.0, 124.9, 124.2, 122.5, 122.3, 122.3, 118.2, 111.6, 84.9, 51.7, 51.1, 33.9, 33.2, 28.6, 28.3, 27.5, 27.3. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₃₅H₃₅O₂ 487.2637; Found 487.2640.

1'-(2-bromophenyl)-3,5-diisopropyl-1'H-spiro[cyclohexane-1,2'-naphtho[2,1-b]furan]-2,5-dien-4-one (4s).



White solid; 44.24 mg, 91% yield (petroleum ether/ethyl acetate =30:1); mp 125.1-125.3 °C. ¹H NMR (CDCl₃, 600 MHz) δ 7.81-7.79 (m, 2H), 7.48 (m, 1H), 7.26-7.18 (m, 3H), 7.06-6.99 (m, 3H), 6.67 (s, 1H), 6.55 (t, *J* = 7.26 Hz, 1H), 5.95 (s, 1H), 5.47 (s, 1H), 3.01-2.94 (m, 1H), 2.84-2.77 (m, 1H), 1.04 (d, *J* = 6.84 Hz, 3H), 0.99 (d, *J* = 6.90 Hz, 3H), 0.76 (d, *J* = 6.84 Hz, 3H), 0.58 (d, *J* = 6.90 Hz, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 183.6, 155.7, 144.4, 142.8, 137.3, 137.0, 135.6, 132.1, 130.0, 129.3, 129.0, 127.9, 126.3, 124.6, 122.5, 122.1, 118.4, 111.7, 84.3, 54.2, 25.4, 25.1, 21.2, 20.4, 20.3. HRMS (ESI-TOF) m/z: [M+H]⁺ Calcd for C₂₉H₂₈BrO₂ 487.1273; Found 487.1265.

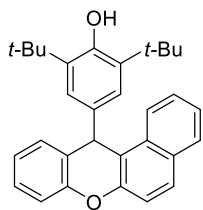


2,6-di-tert-butyl-4-((2-bromophenyl)(2-hydroxynaphthalen-1-yl)methylene)cyclohexa-2,5-dienone (5a).

Yellow solid; 43.30 mg, 92% yield (petroleum ether/ethyl acetate =30:1); mp 210.4-211.5 °C. ¹H NMR (CDCl₃, 600 MHz) δ

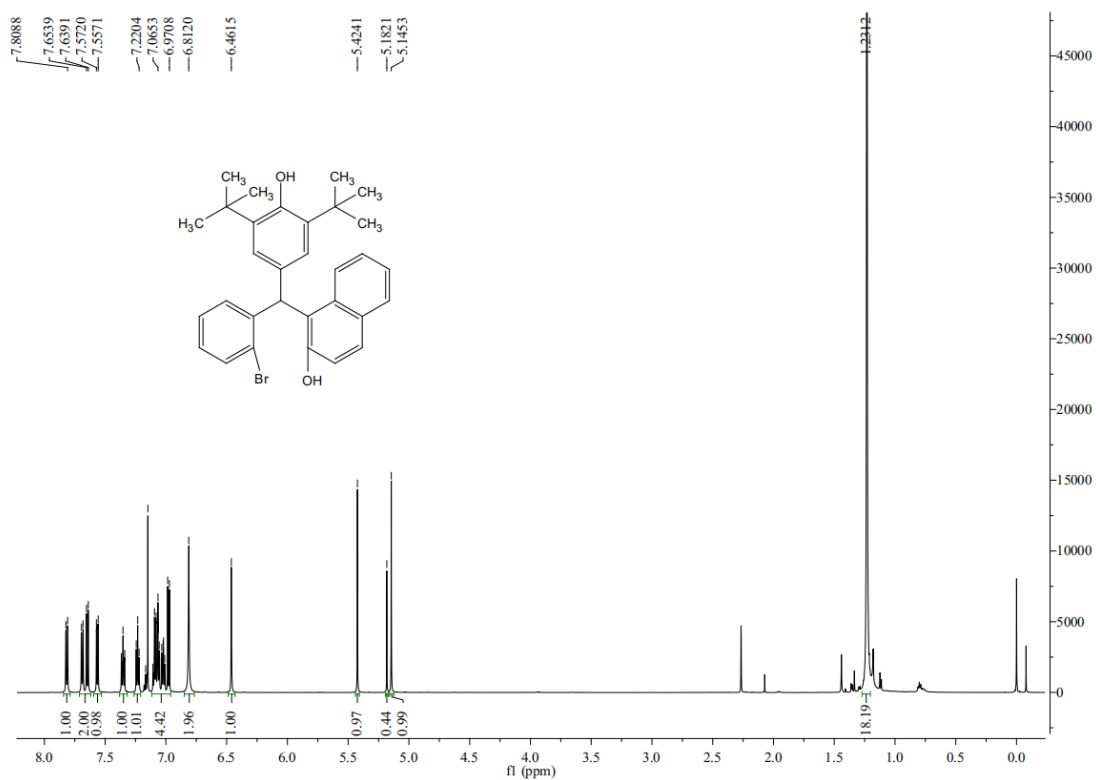
7.74-7.58 (m, 5H), 7.23-6.98 (m, 6H), 6.60 (s, 1H), 5.54 (s, 1H), 1.20 (s, 9H), 1.05 (s, 3H), 0.93 (s, 6H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 185.5, 151.2, 149.6, 148.8, 148, 147.7, 147.3, 141.8, 138.4, 130.7, 128.7, 126.4, 122.1, 118.5, 117.9, 117.1, 116.5, 34.4, 34.1, 28.5, 28.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{32}\text{BrO}_2$ 515.1586; Found 515.1595.

2,6-di-tert-butyl-4-(12H-benzo[a]xanthen-12-yl)phenol (6).

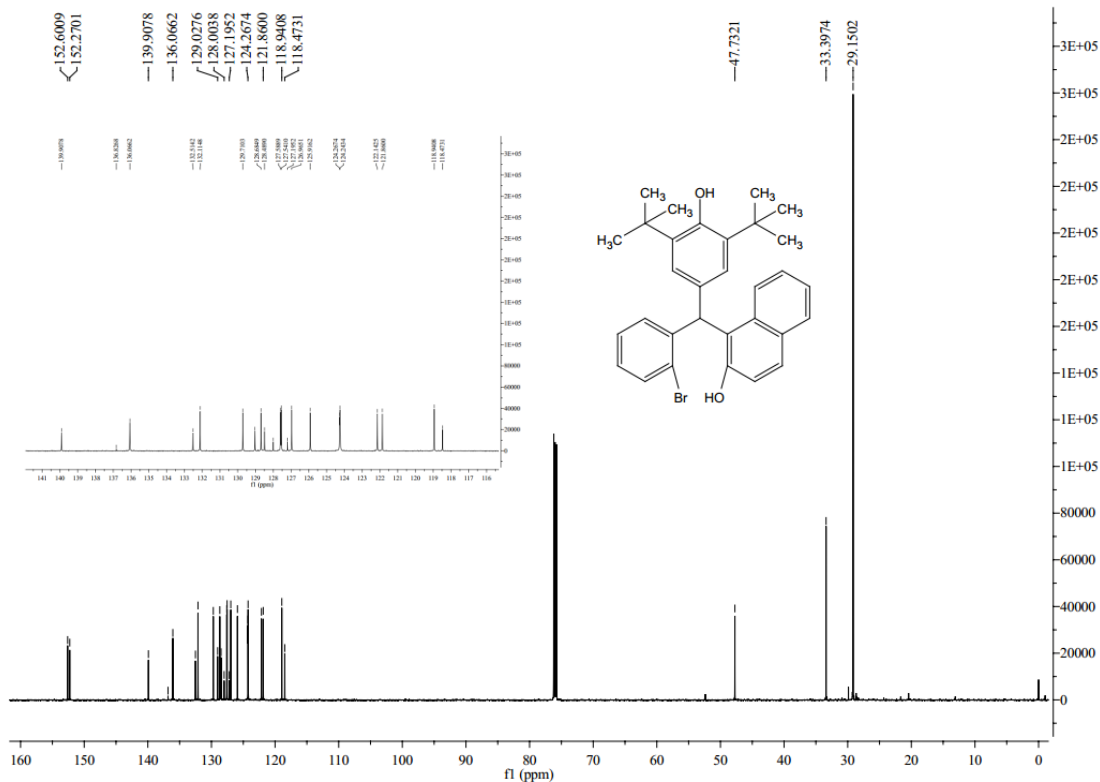


White solid; 41.88 mg, 96% yield (petroleum ether); mp 115.2-116.5 $^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 600 MHz) δ 7.95 (d, $J = 8.52$ Hz, 1H), 7.67 (m, 2H) 7.31 (m, 4H), 7.14-7.09 (m, 2H), 6.99-6.96 (m, 3H), 5.64 (s, 1H), 4.85 (s, 1H), 1.21 (s, 18H); ^{13}C NMR (CDCl_3 , 150 MHz) δ 151.1, 149.9, 148.6, 135.7, 134.7, 130.7, 129.8, 128.2, 127.6, 127.5, 126.3, 125.4, 125.1, 122.9, 122.8, 122.6, 122.1, 117.0, 116.2, 115.5, 40.6, 33.2, 29.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{33}\text{O}_2$ 437.2481; Found 437.2487.

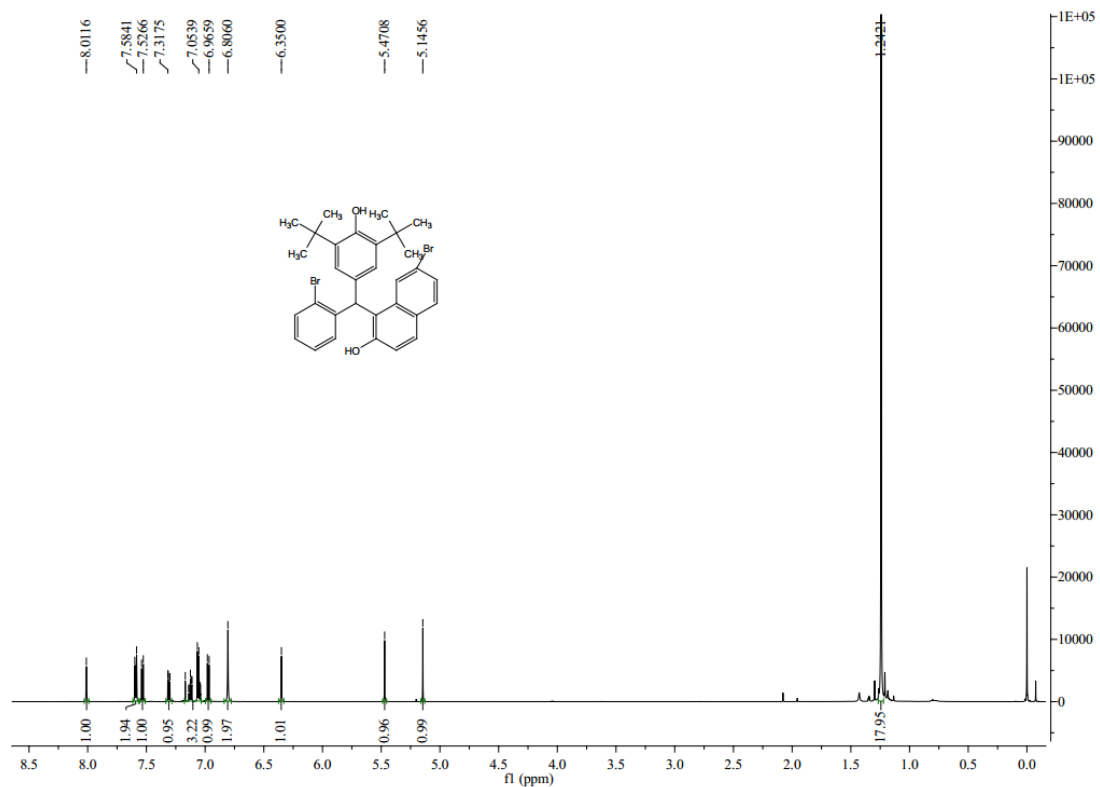
10. NMR Spectra



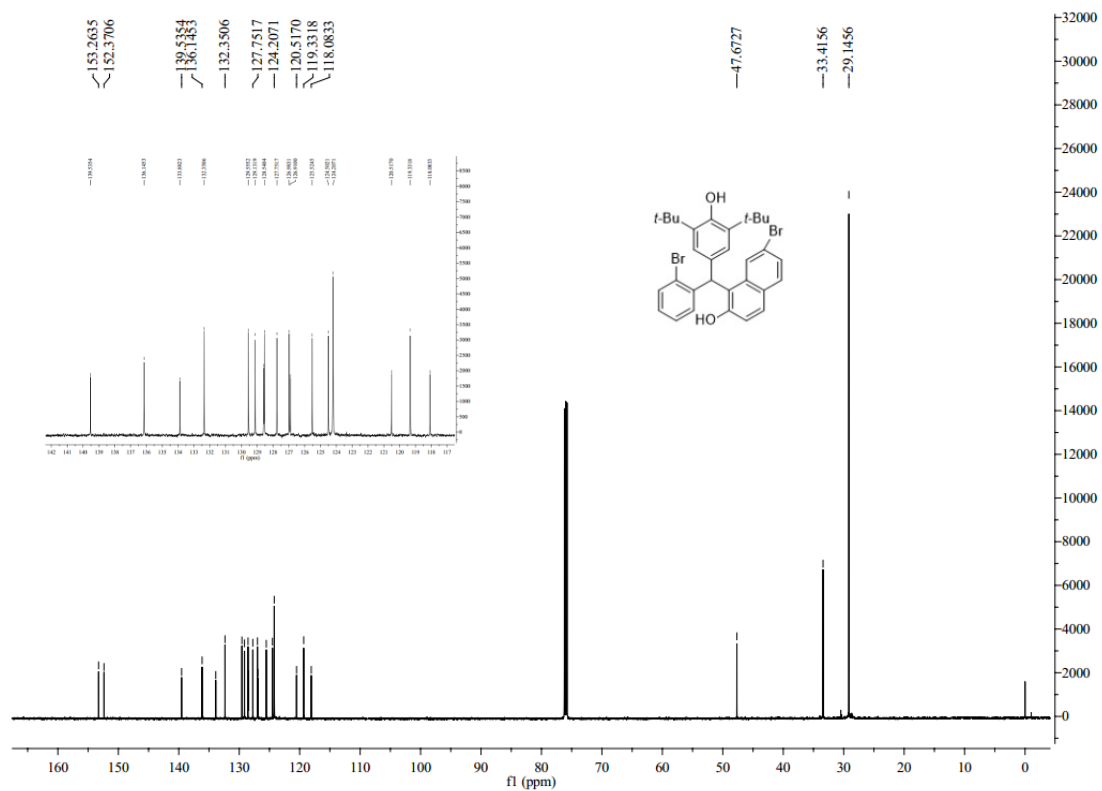
¹H NMR Spectrum of **1a** (CDCl₃, 600 MHz)



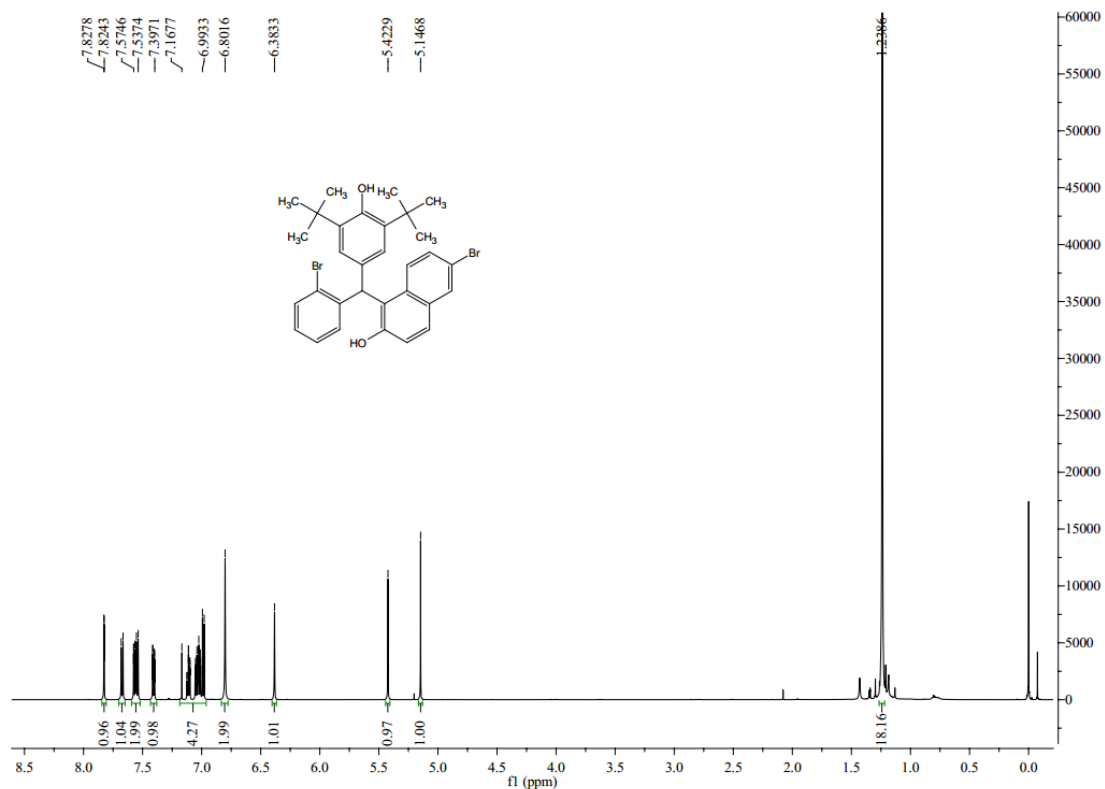
¹³C NMR Spectrum of **1a** (CDCl₃, 150 MHz)



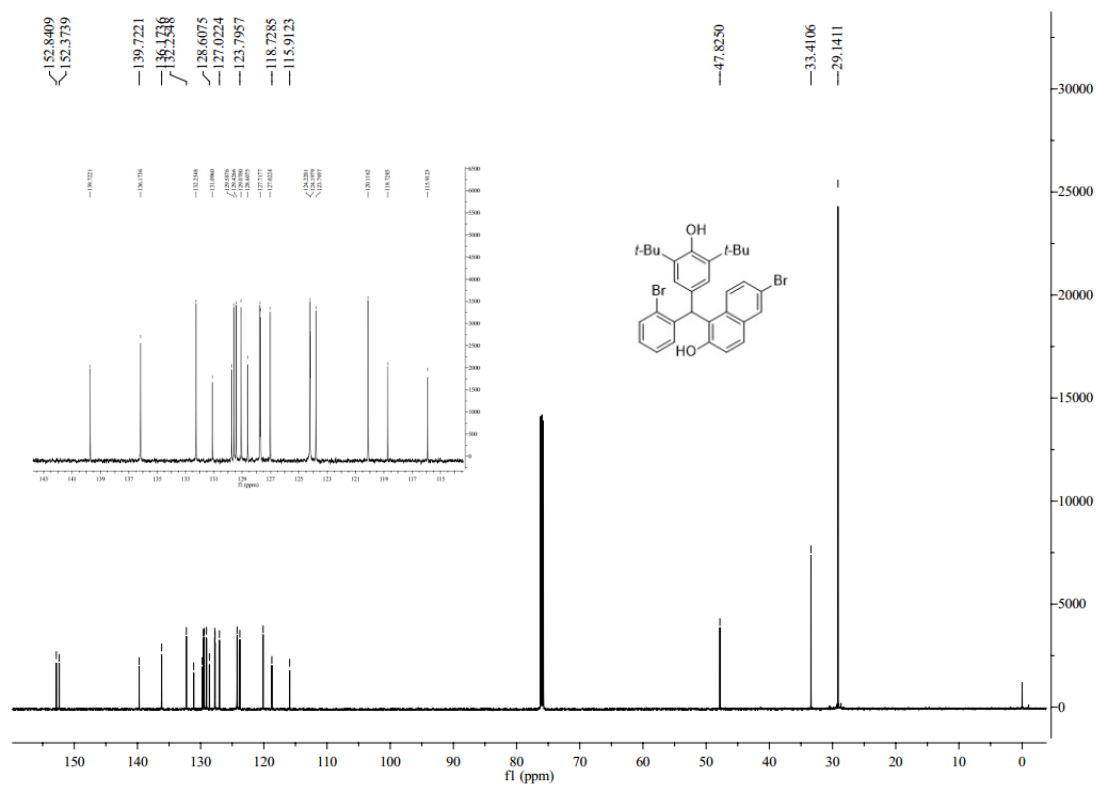
¹H NMR Spectrum of **1b** (CDCl₃, 600 MHz)



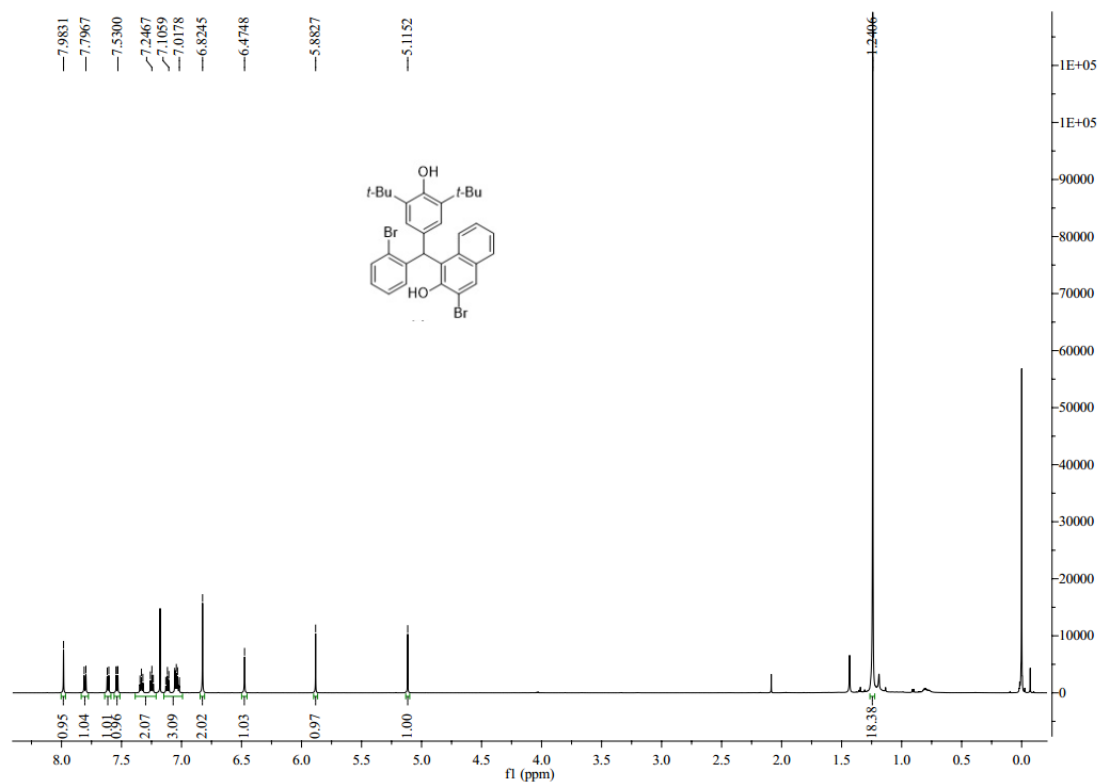
¹³C NMR Spectrum of **1b** (CDCl₃, 150 MHz)



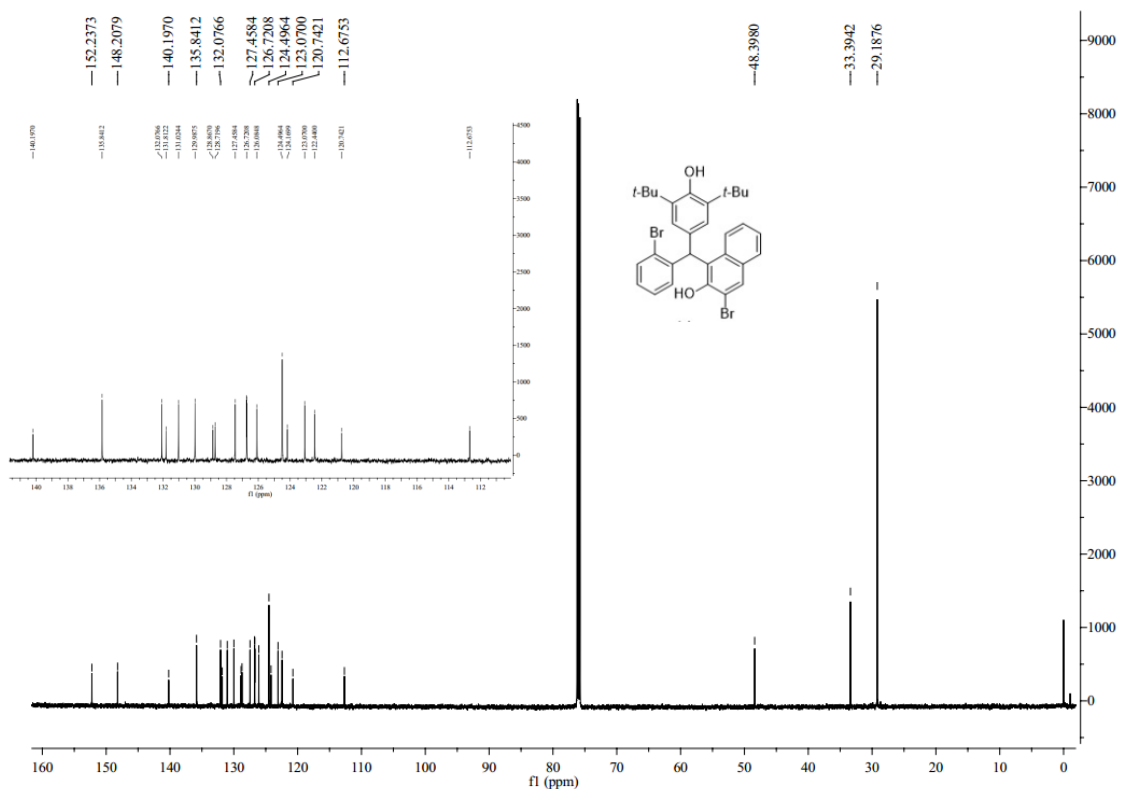
¹H NMR Spectrum of **1c** (CDCl₃, 600 MHz)



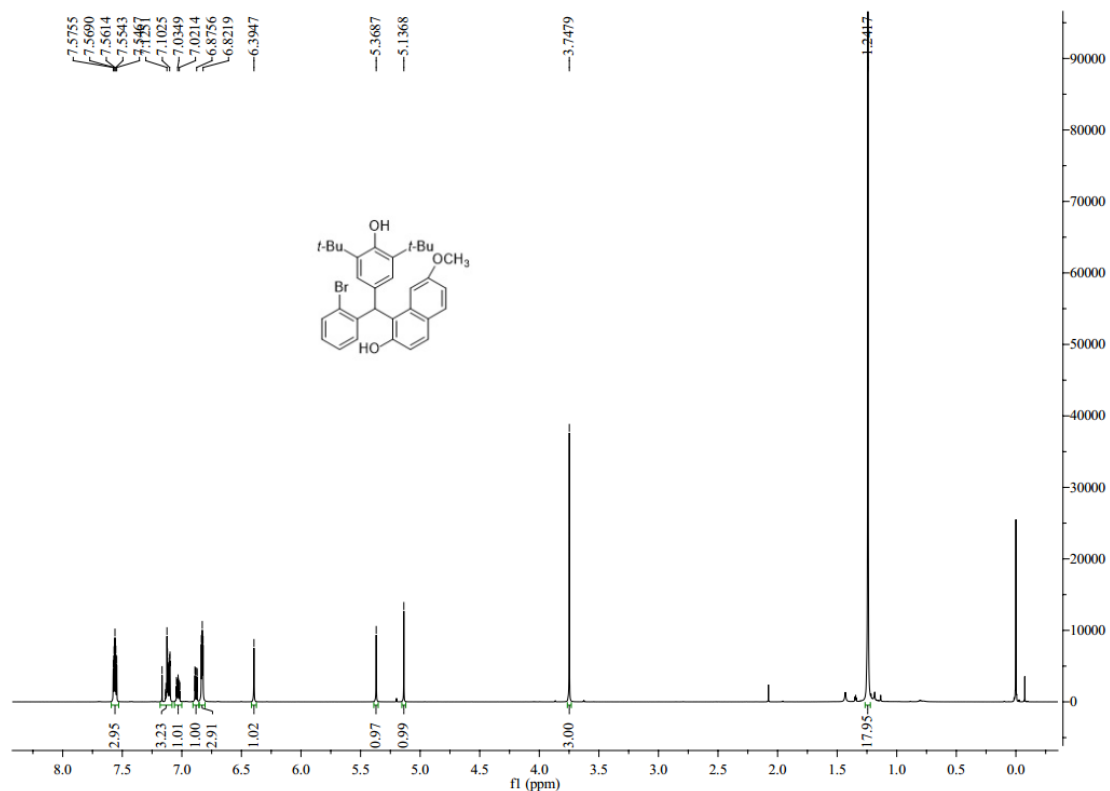
¹³C NMR Spectrum of **1c** (CDCl₃, 150 MHz)



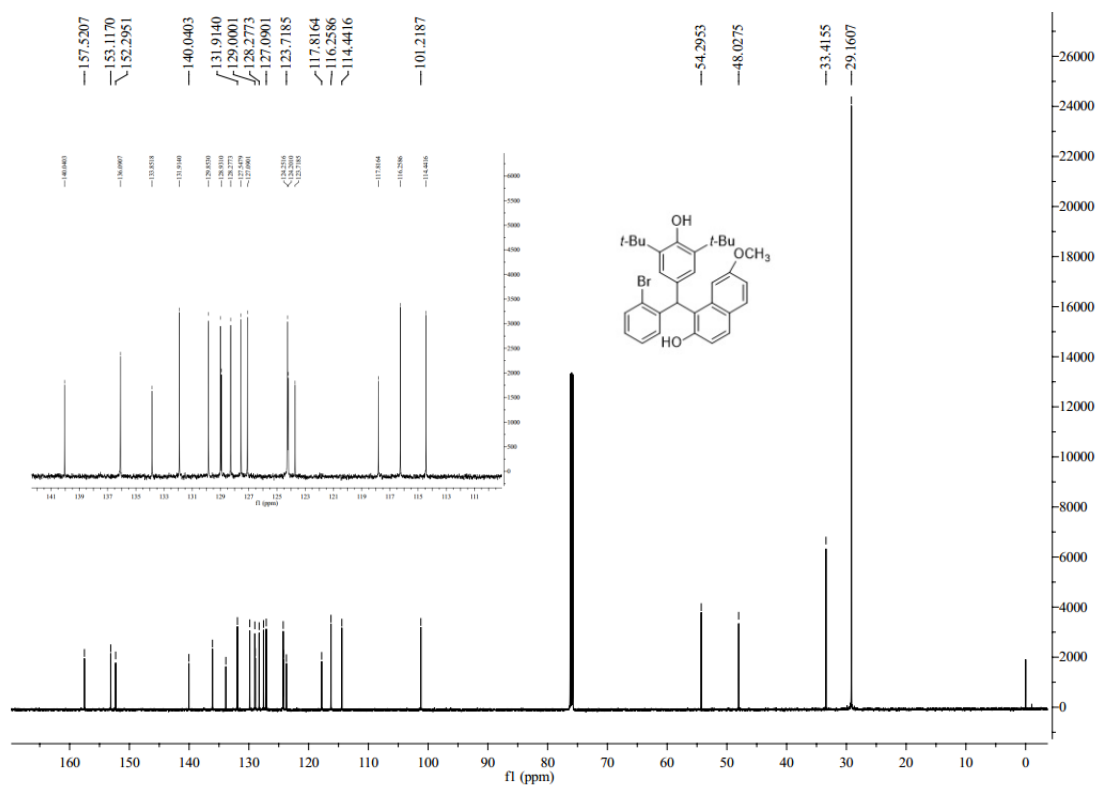
¹H NMR Spectrum of **1d** (CDCl₃, 600 MHz)



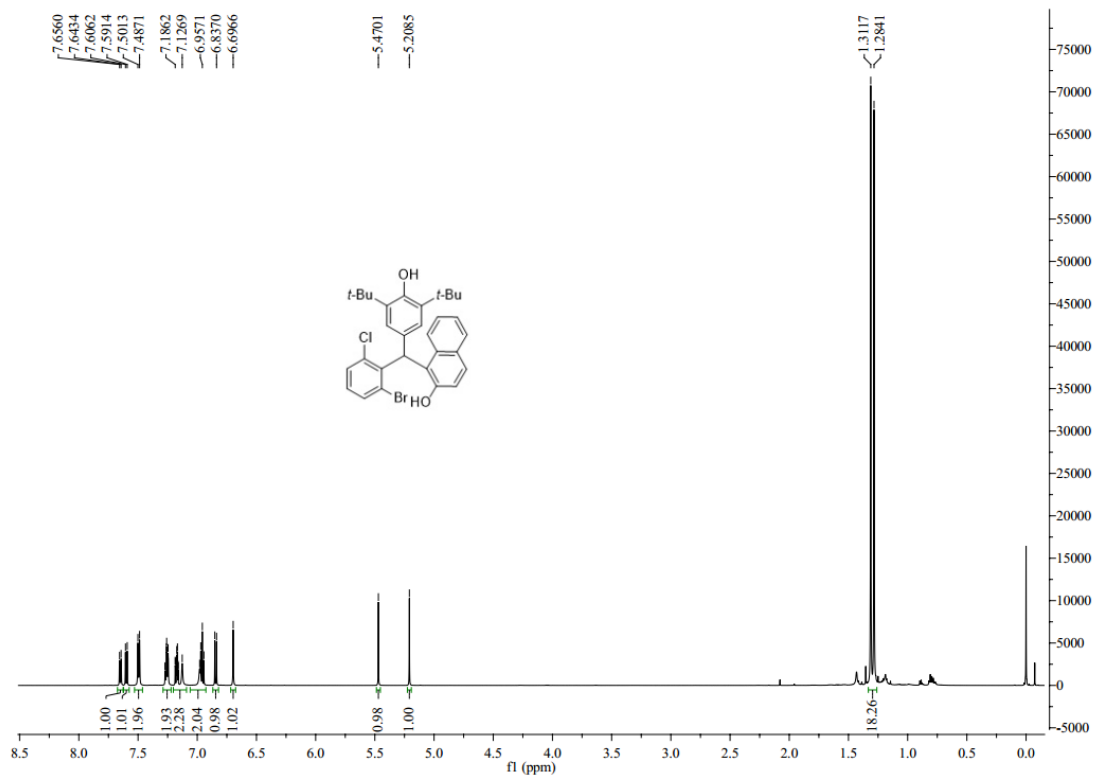
¹³C NMR Spectrum of **1d** (CDCl₃, 150 MHz)



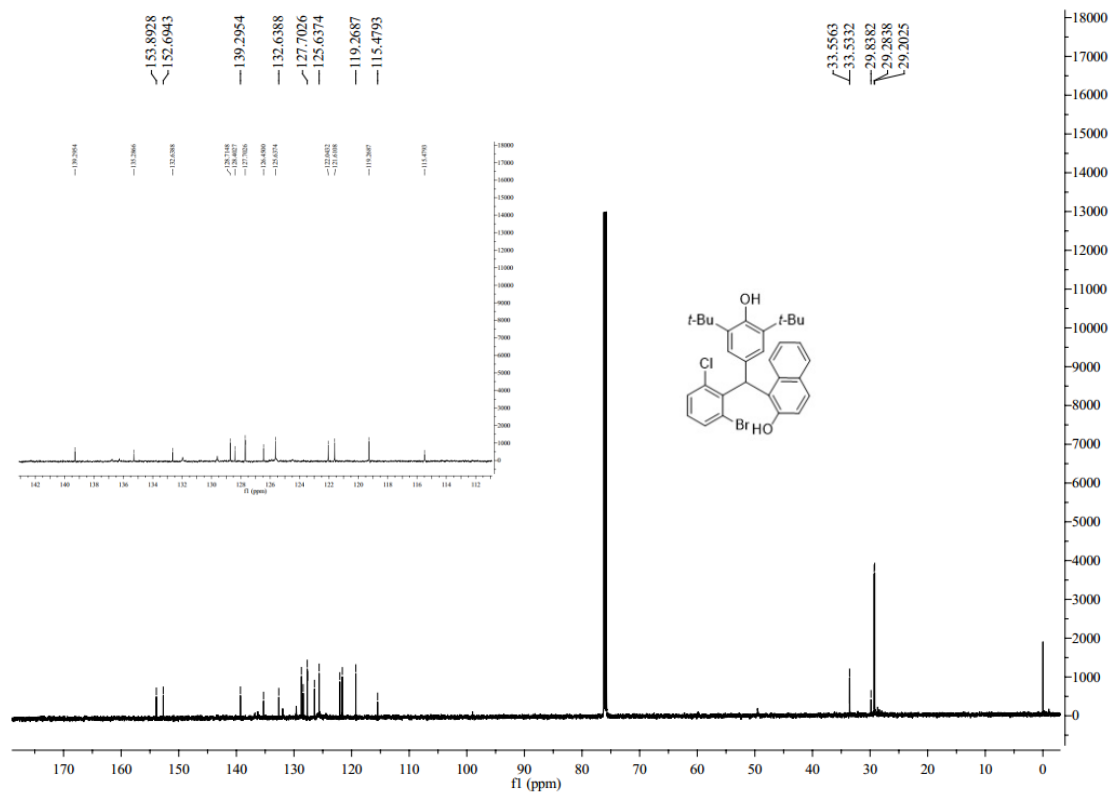
¹H NMR Spectrum of **1e** (CDCl₃, 600 MHz)



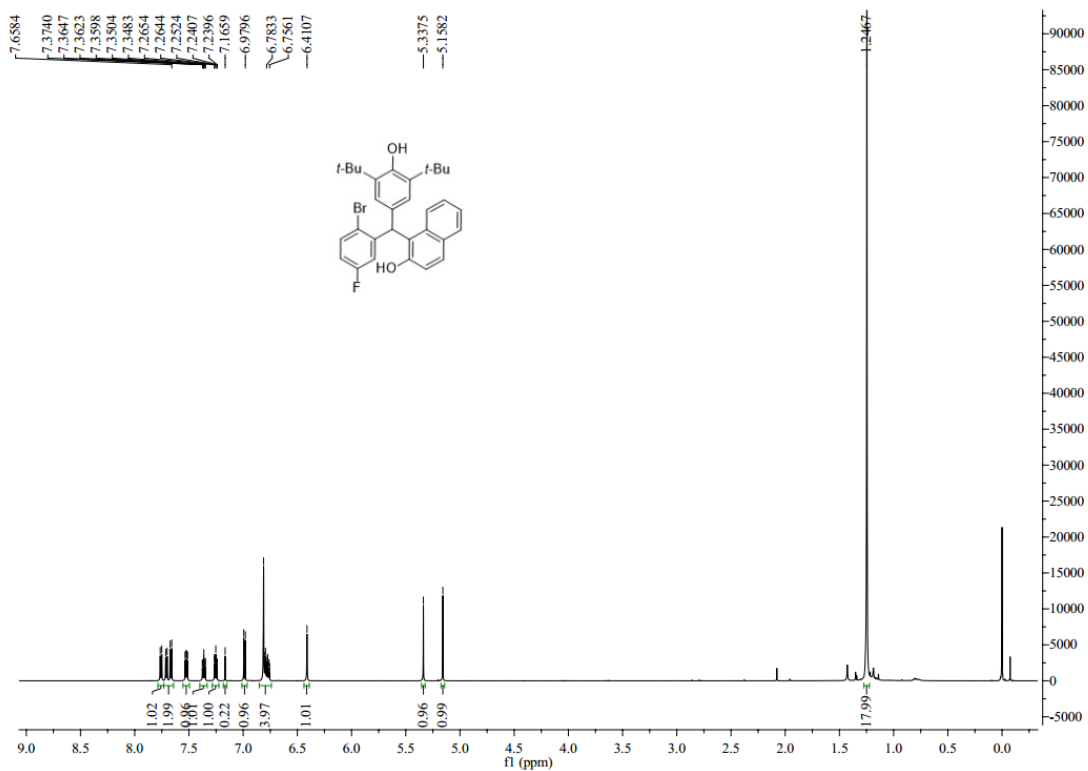
¹³C NMR Spectrum of **1e** (CDCl₃, 150 MHz)



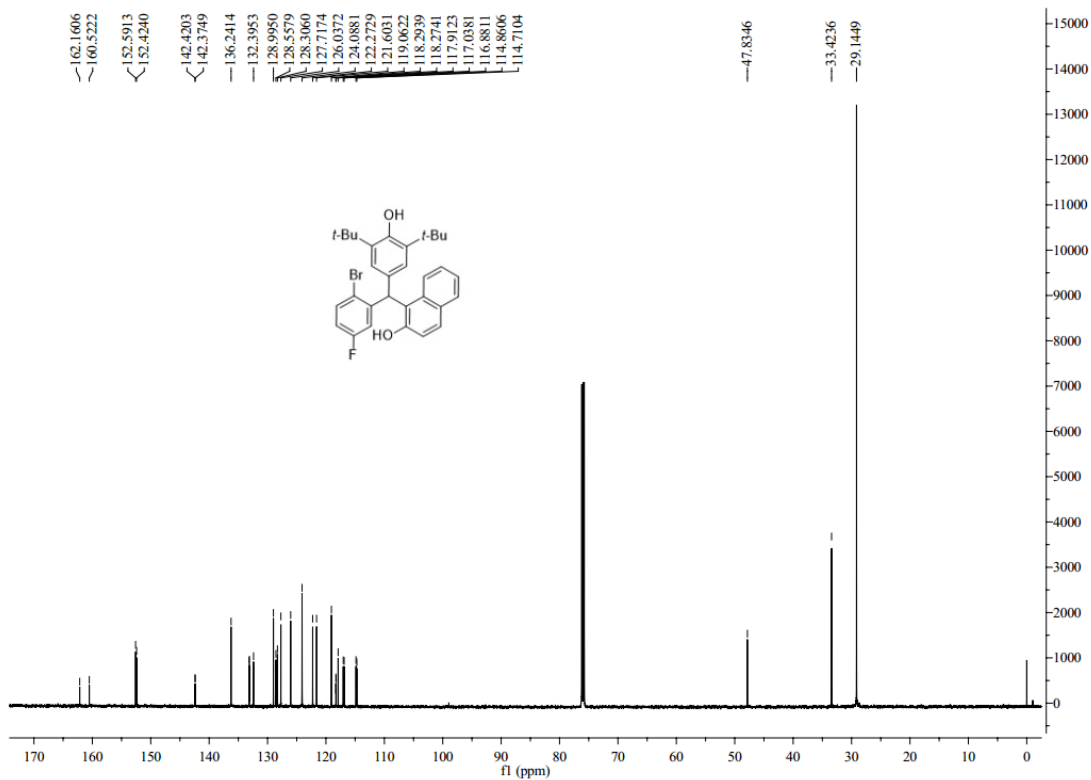
¹H NMR Spectrum of **1f** (CDCl₃, 600 MHz)



¹³C NMR Spectrum of **1f** (CDCl₃, 150 MHz)

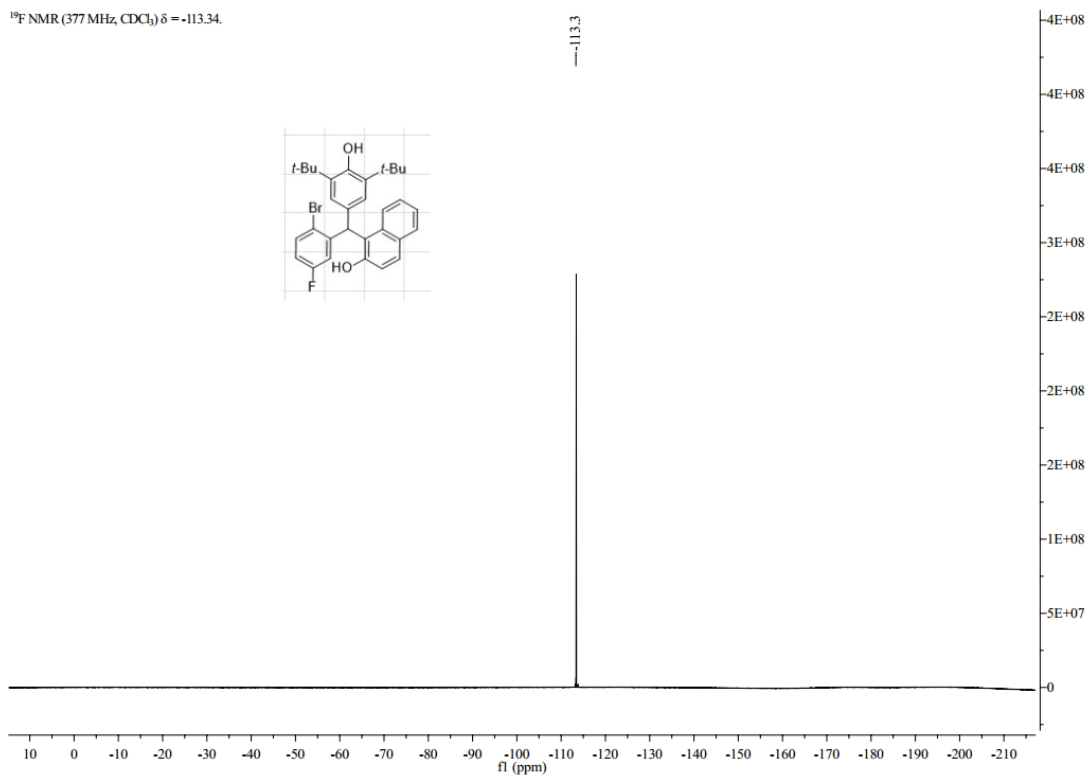


¹H NMR Spectrum of **1g (CDCl₃, 600 MHz)**

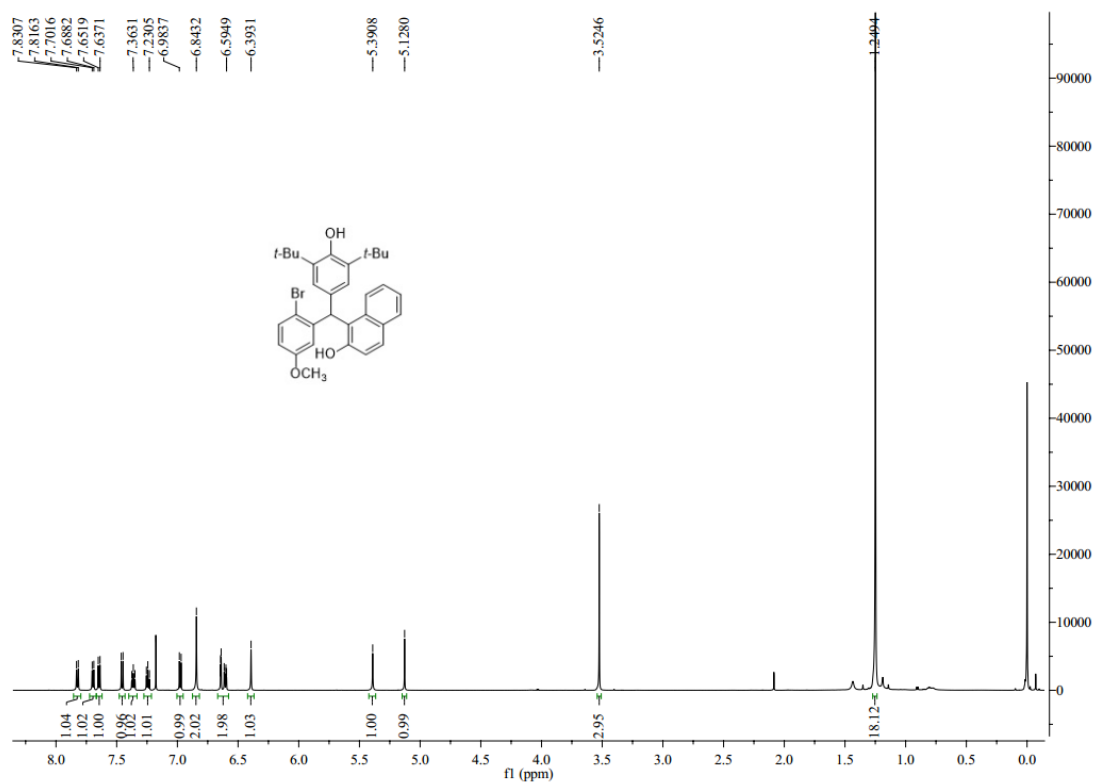


¹³C NMR Spectrum of **1g (CDCl₃, 150 MHz)**

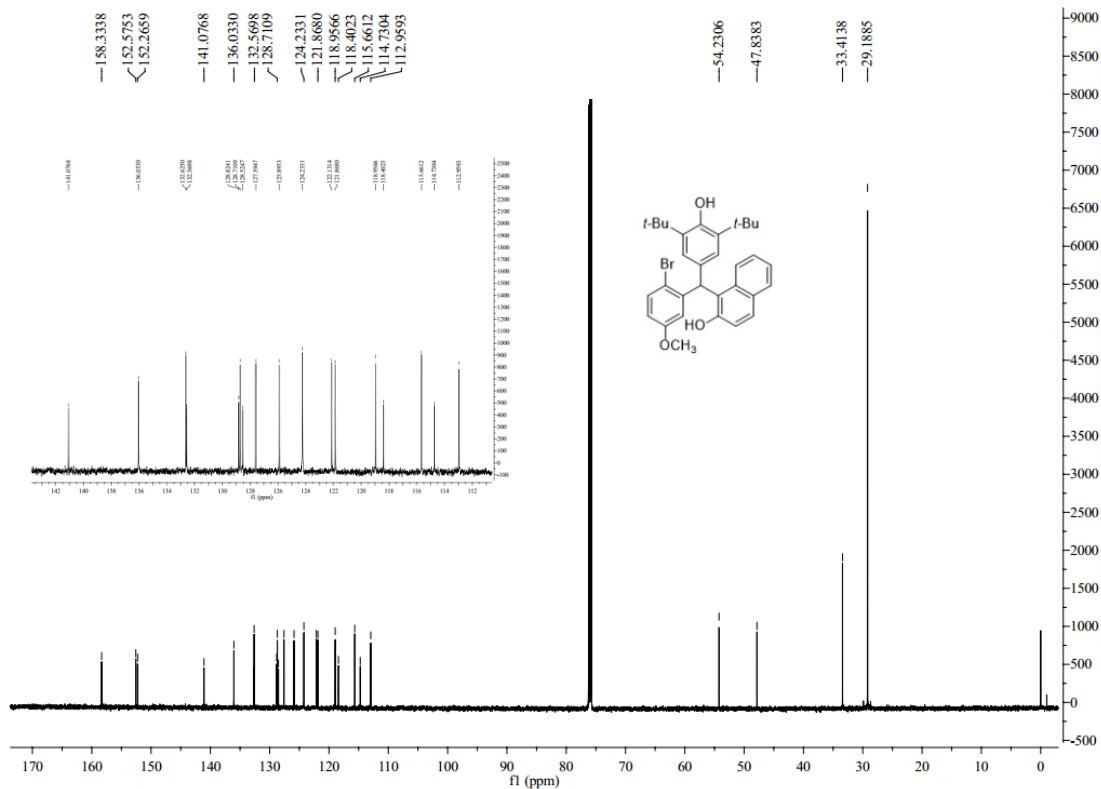
^{19}F NMR (377 MHz, CDCl_3) $\delta = -113.34$.



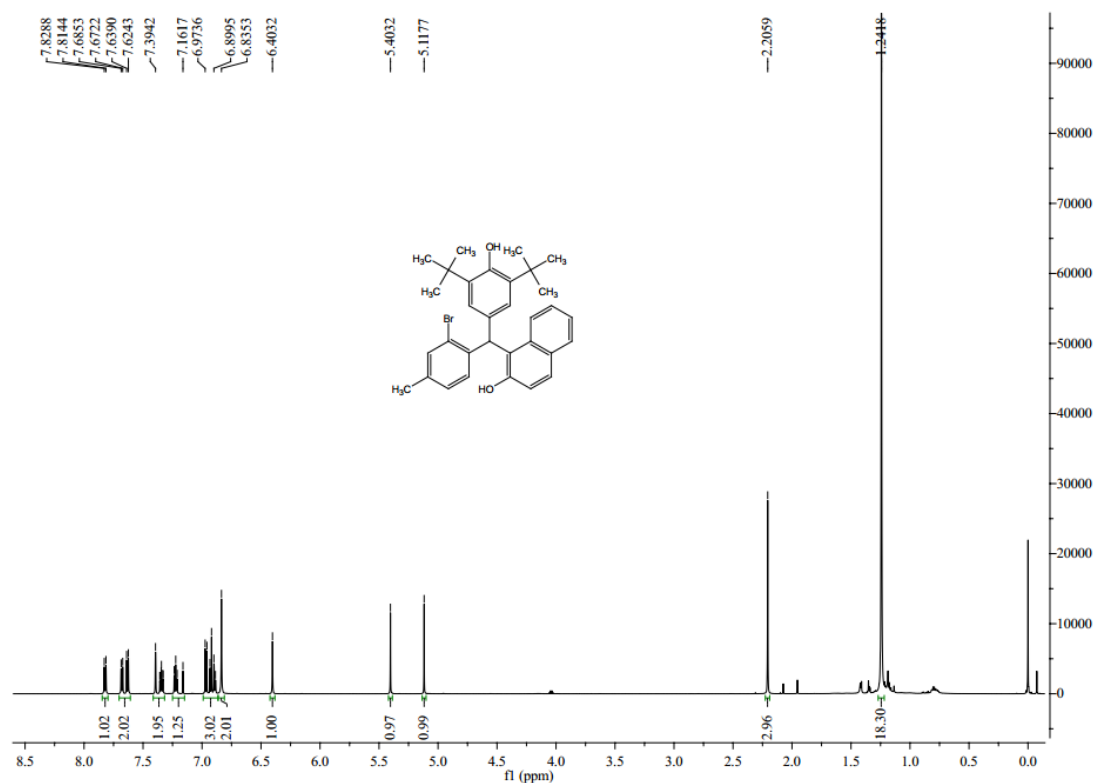
^{19}F NMR Spectrum of **1g** (CDCl_3 , 377 MHz)



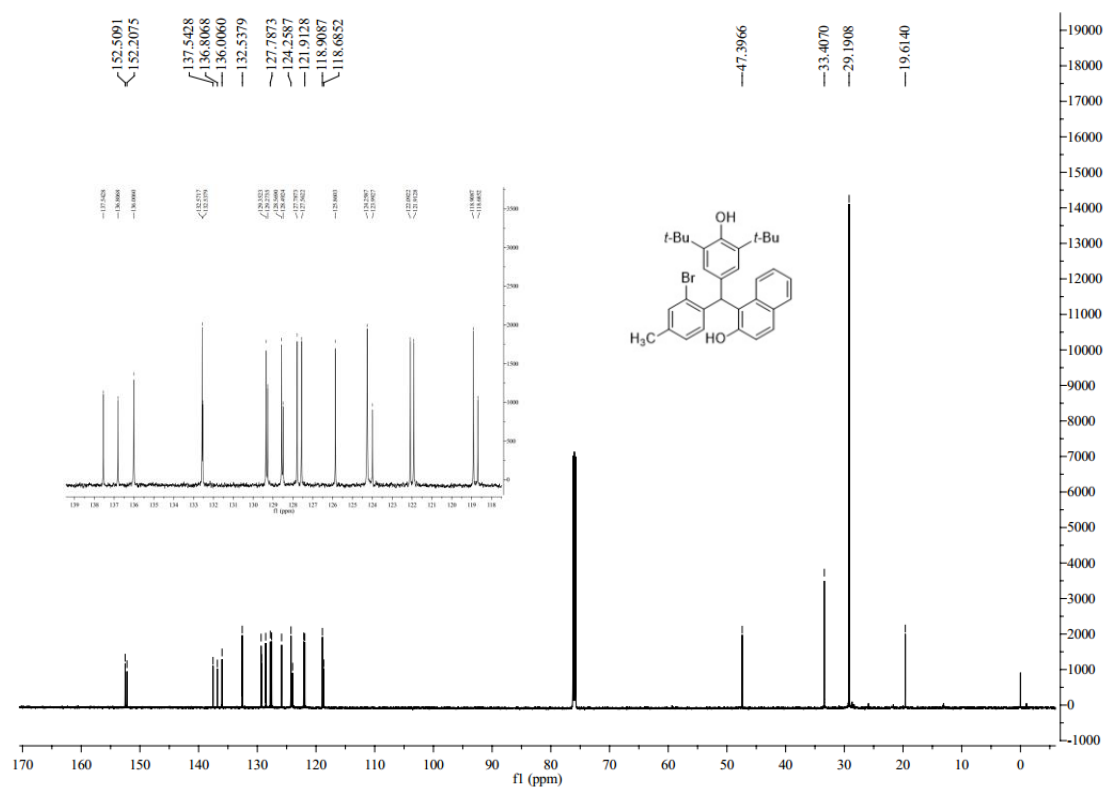
¹H NMR Spectrum of **1h (CDCl₃, 600 MHz)**



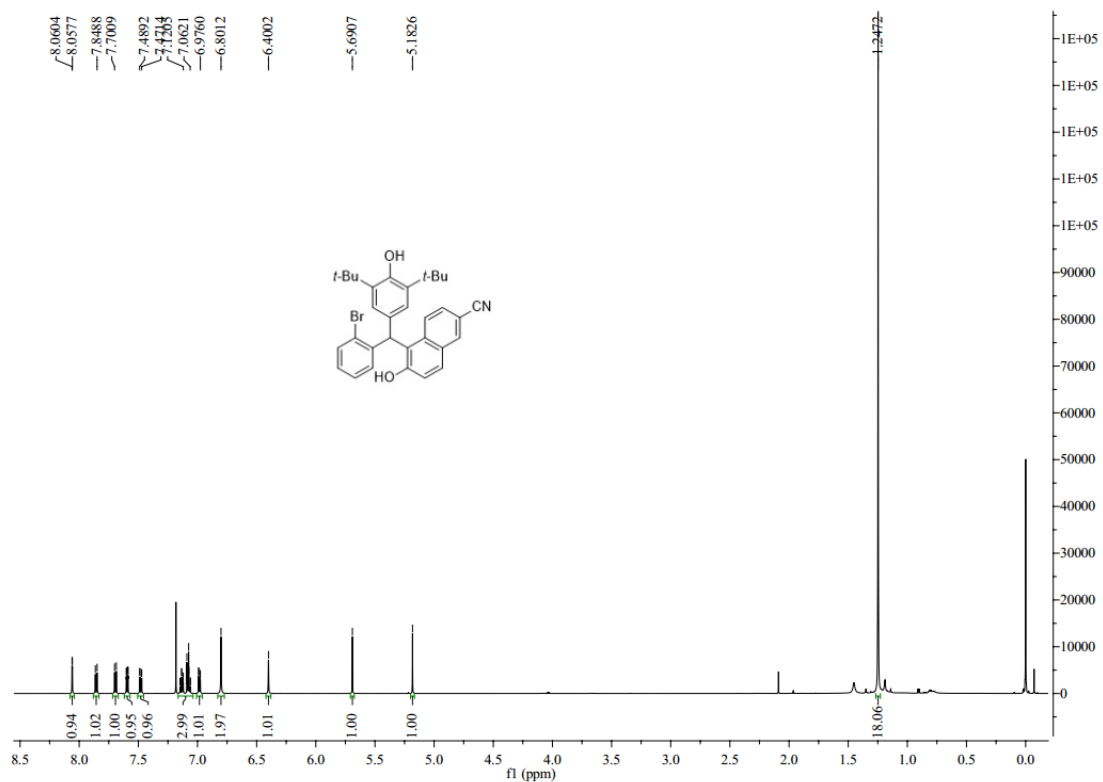
¹³C NMR Spectrum of **1h (CDCl₃, 150 MHz)**



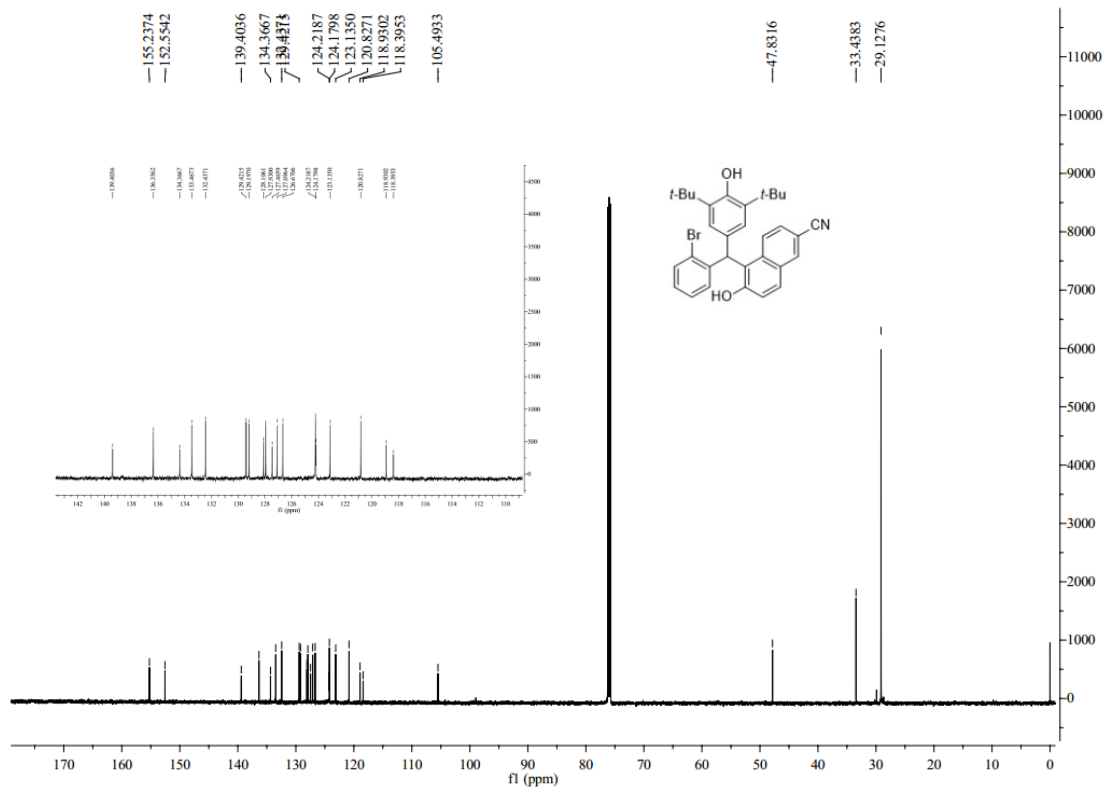
¹H NMR Spectrum of **1i** (CDCl₃, 600 MHz)



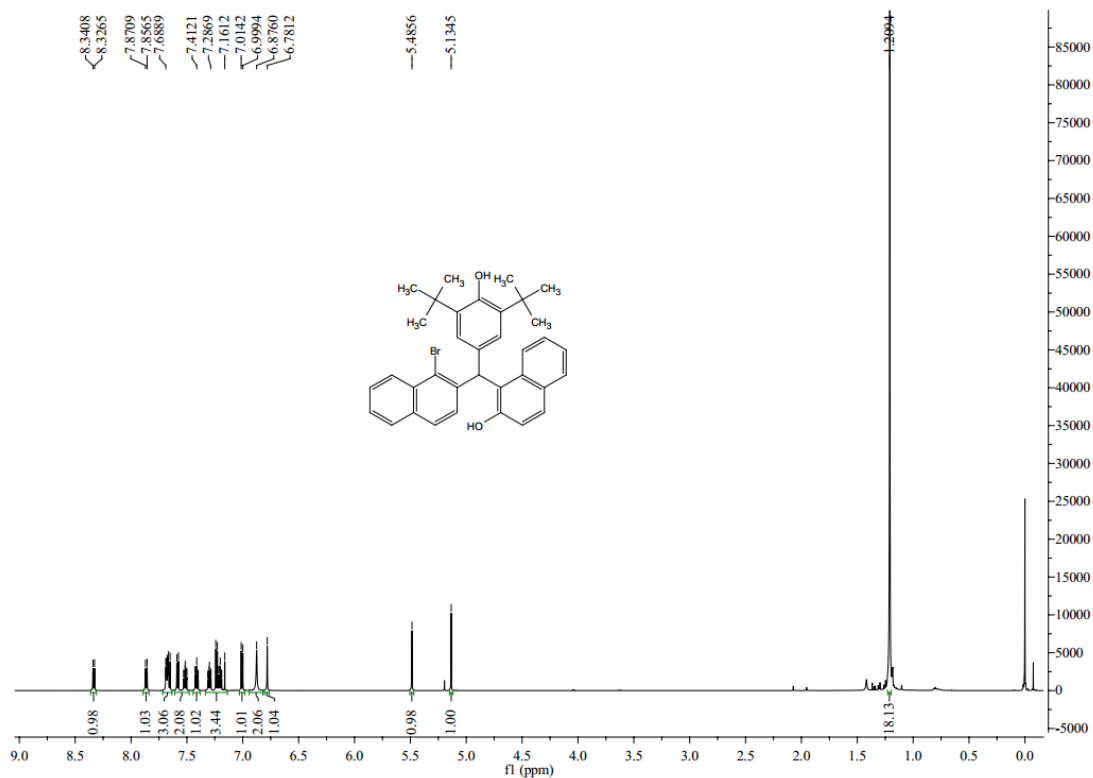
¹³C NMR Spectrum of **1i** (CDCl₃, 150 MHz)



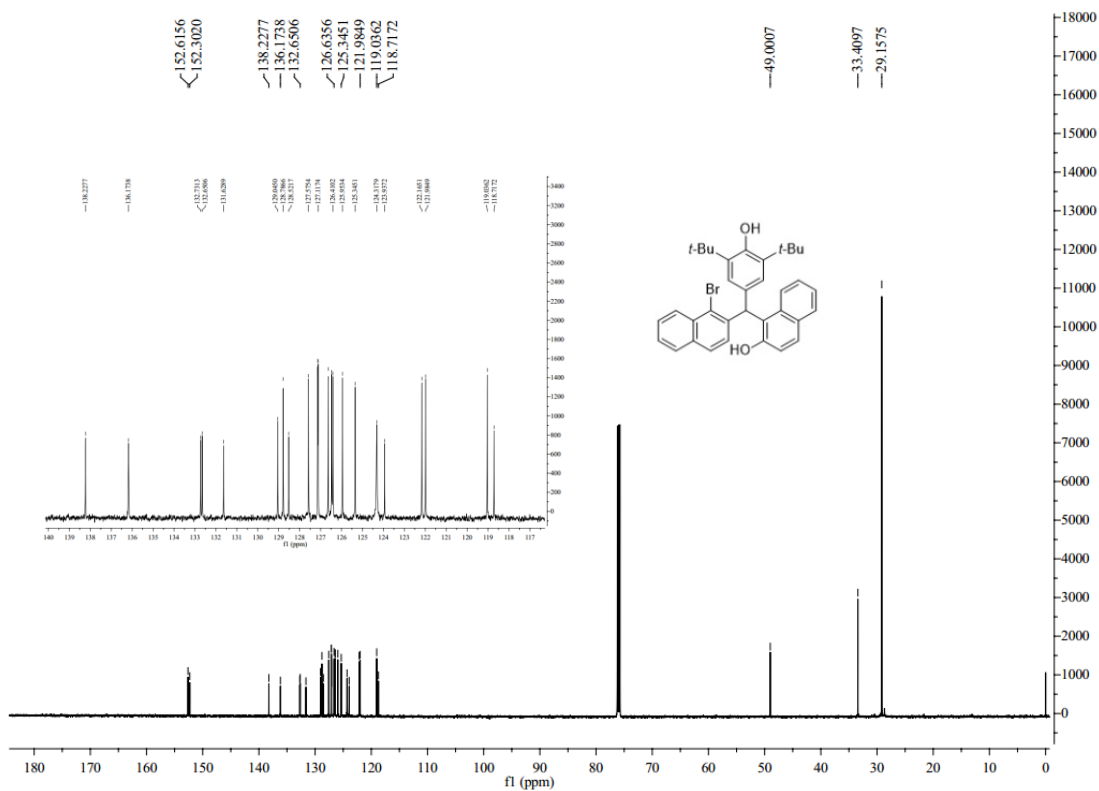
¹H NMR Spectrum of **1j** (CDCl₃, 600 MHz)



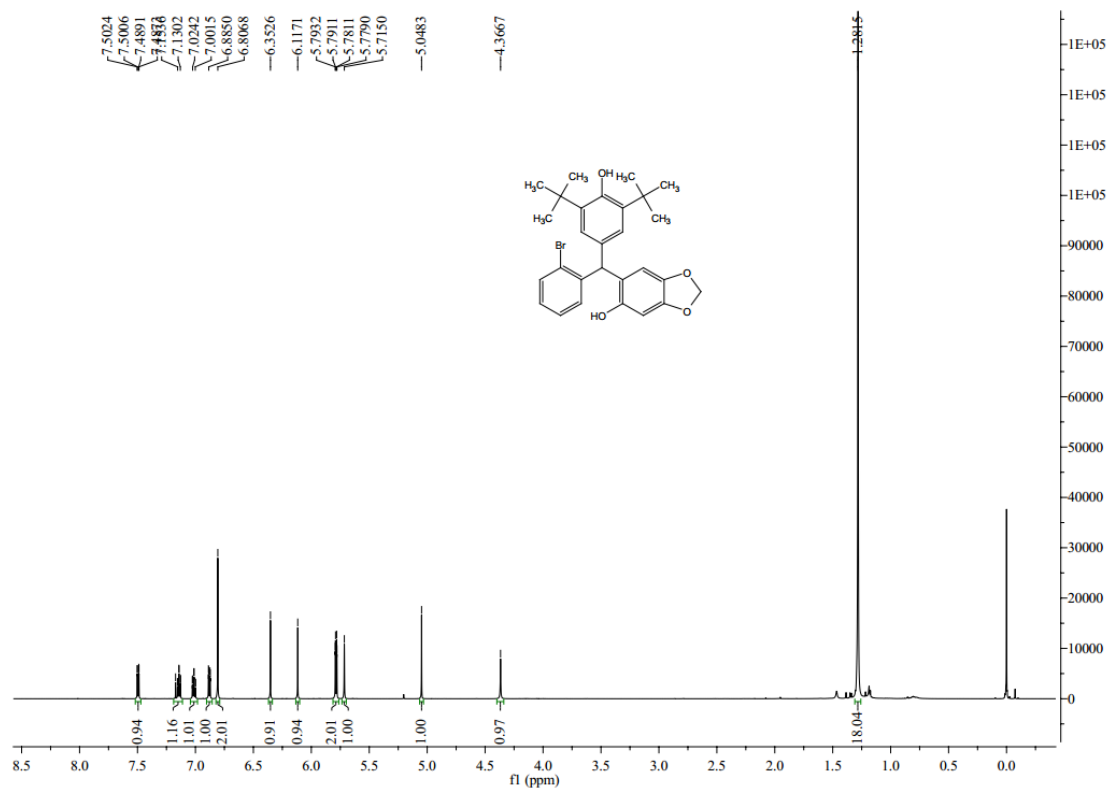
¹³C NMR Spectrum of **1j** (CDCl₃, 150 MHz)



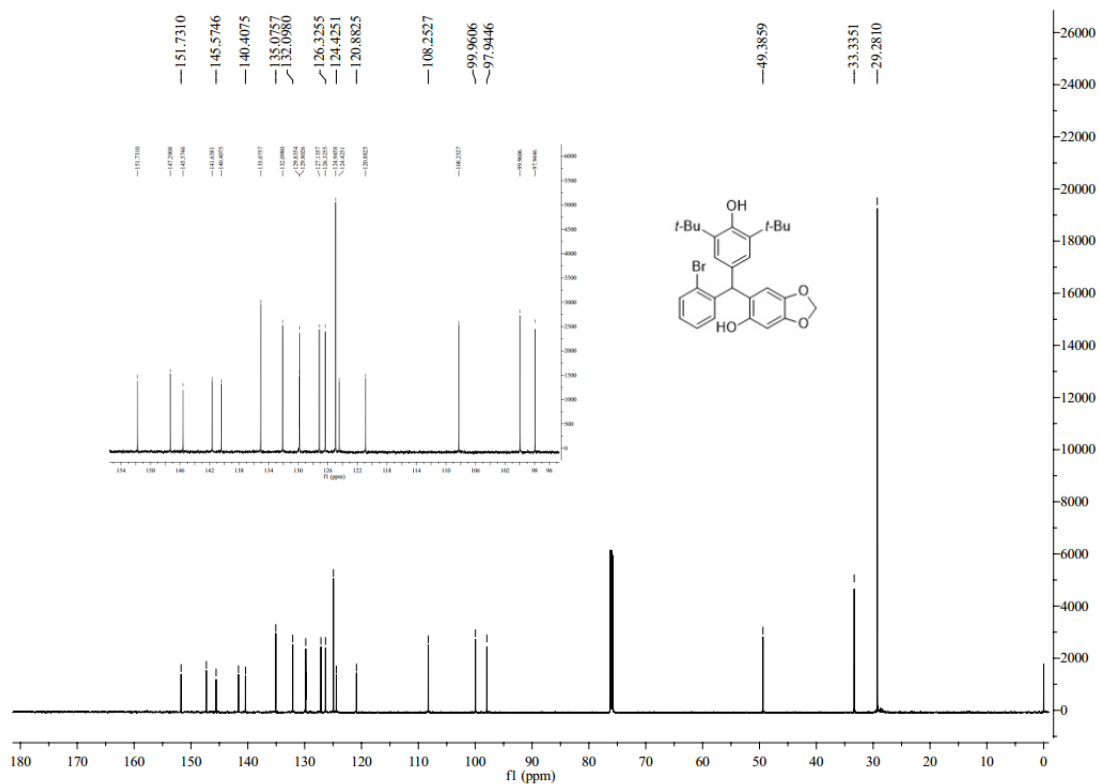
^1H NMR Spectrum of **1k** (CDCl_3 , 600 MHz)



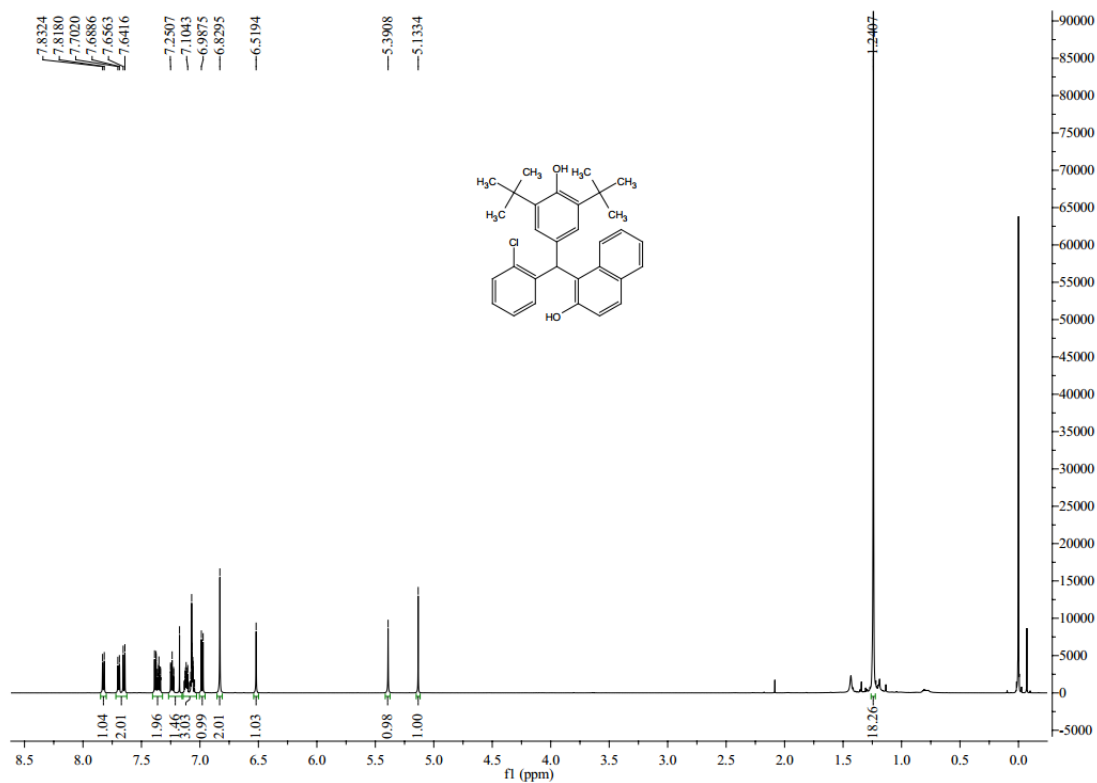
^{13}C NMR Spectrum of **1k** (CDCl_3 , 150 MHz)



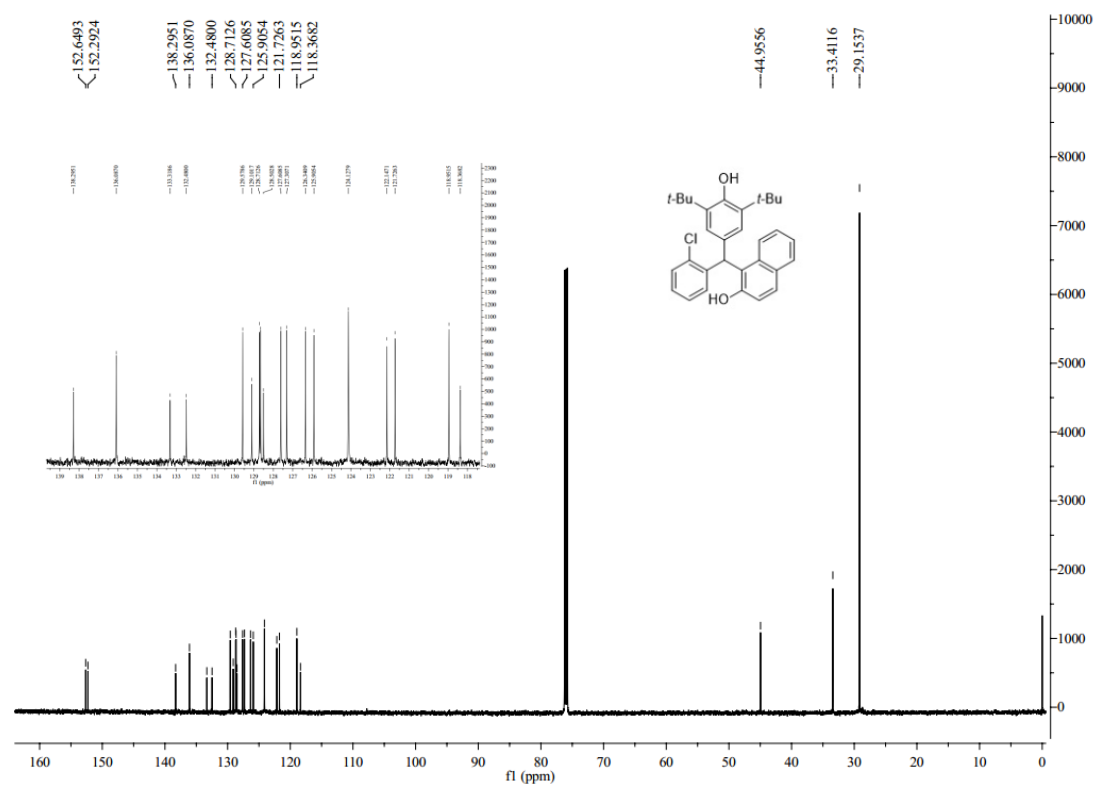
¹H NMR Spectrum of **11** (CDCl₃, 600 MHz)



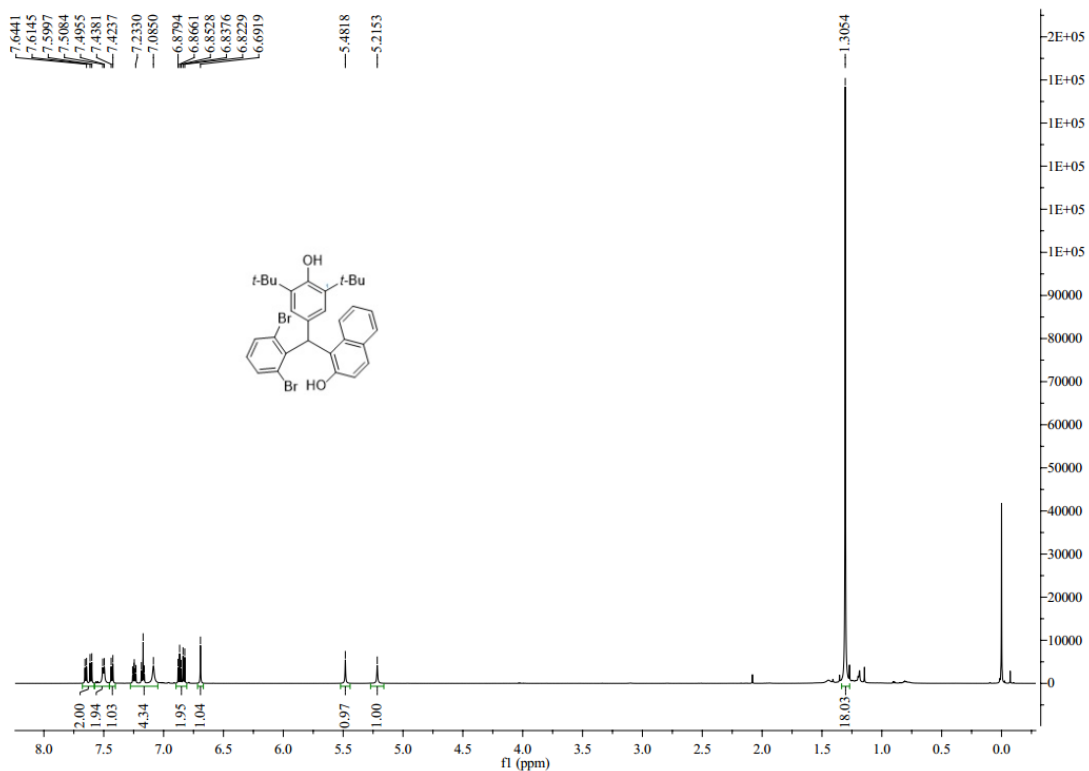
¹³C NMR Spectrum of **11** (CDCl₃, 150 MHz)



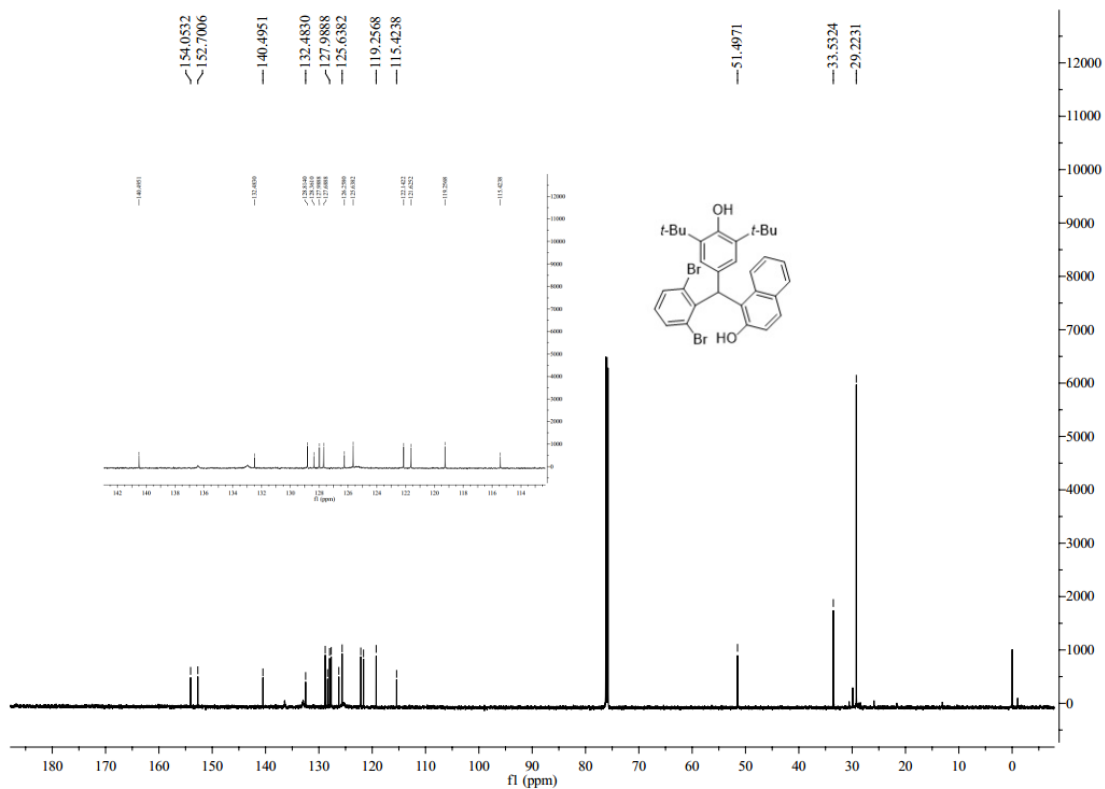
¹H NMR Spectrum of **1m** (CDCl₃, 600 MHz)



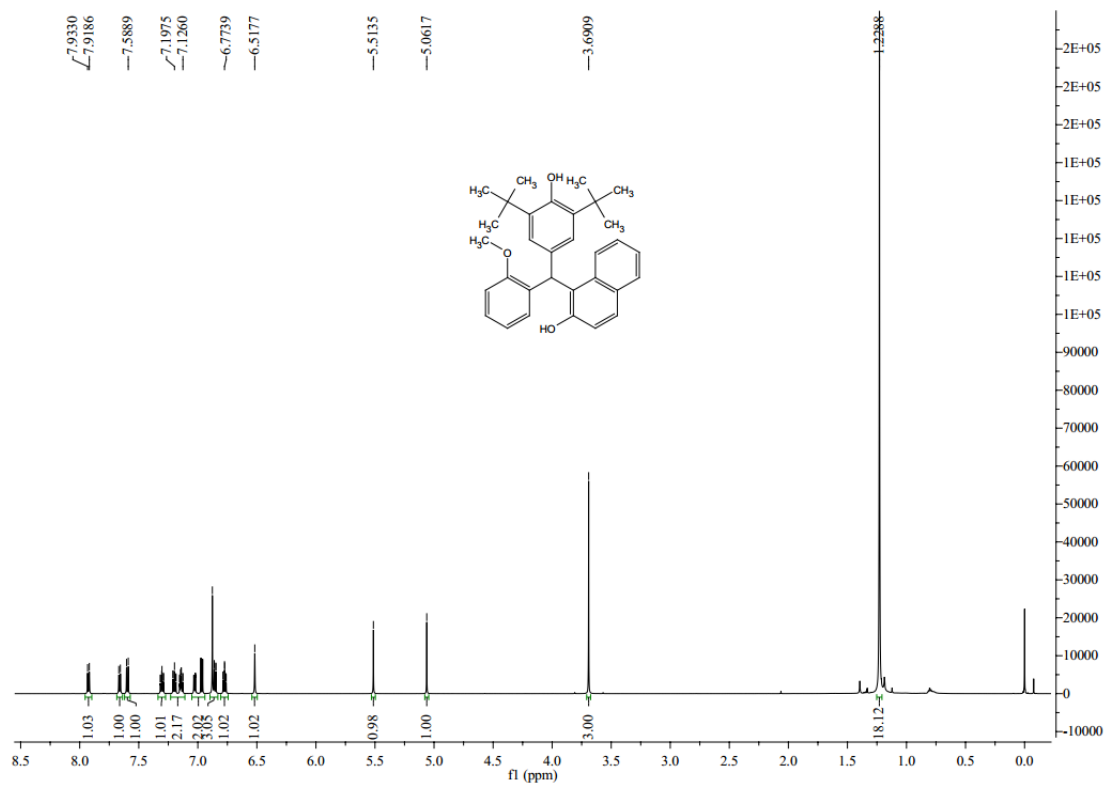
¹³C NMR Spectrum of **1m** (CDCl₃, 150 MHz)



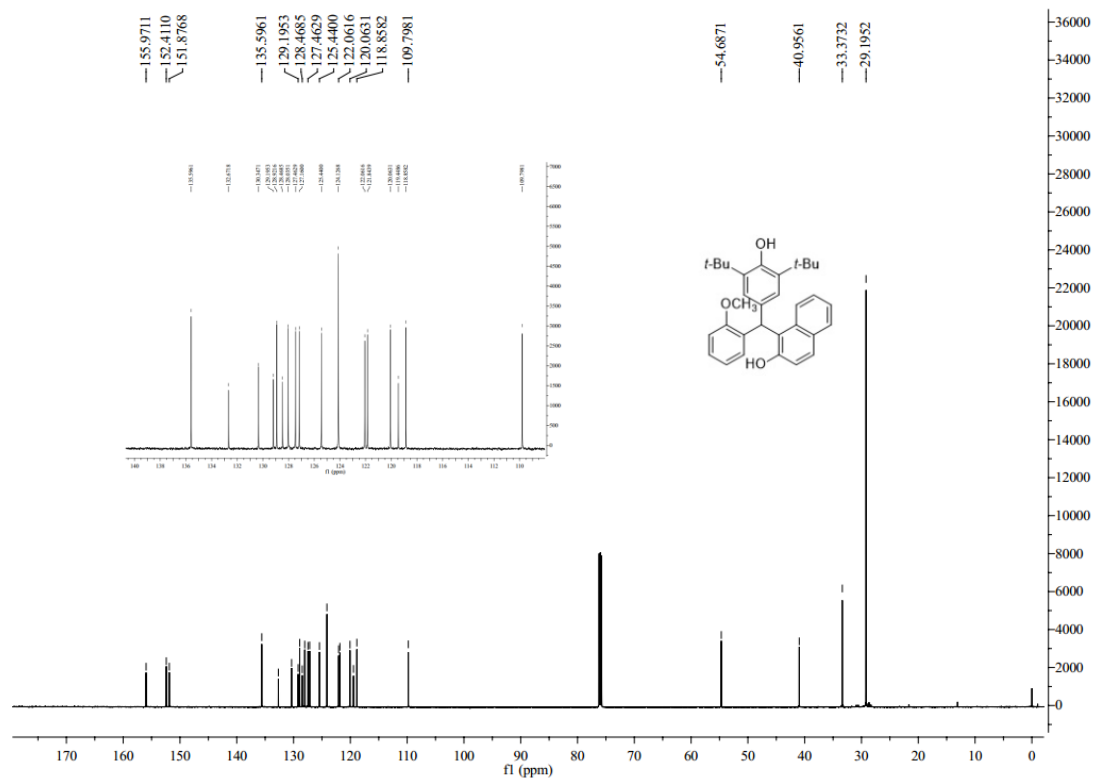
¹H NMR Spectrum of 1n (CDCl₃, 600 MHz)



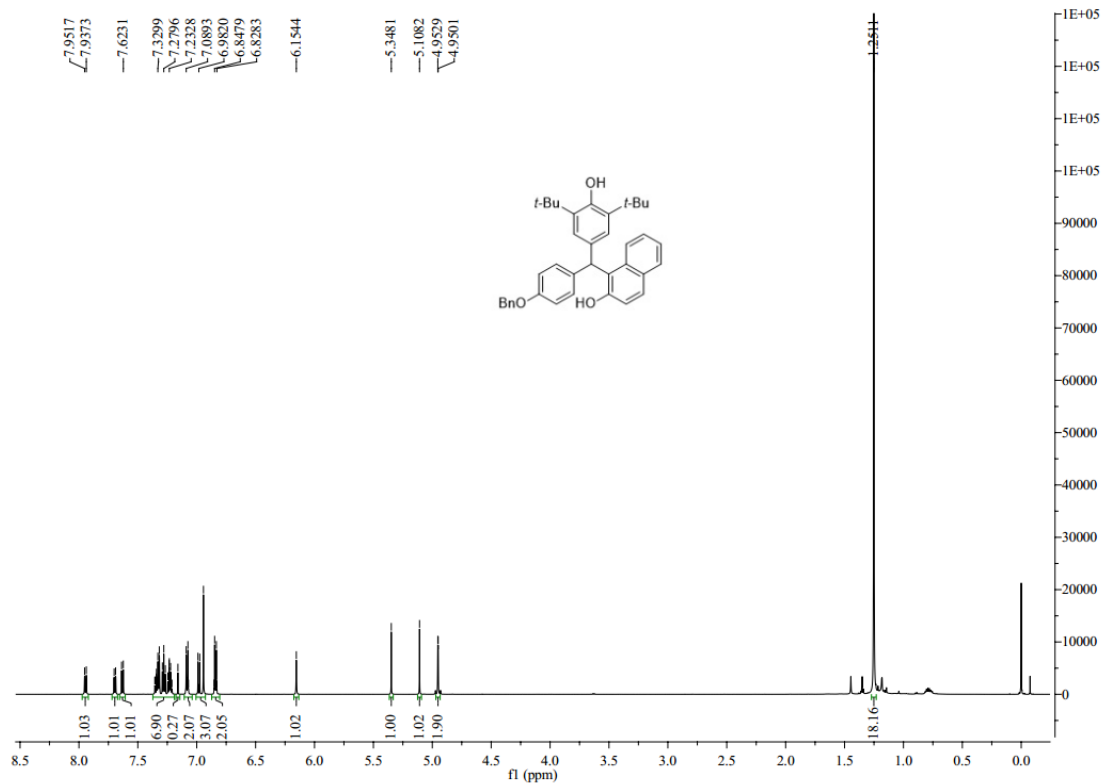
¹³C NMR Spectrum of 1n (CDCl₃, 150 MHz)



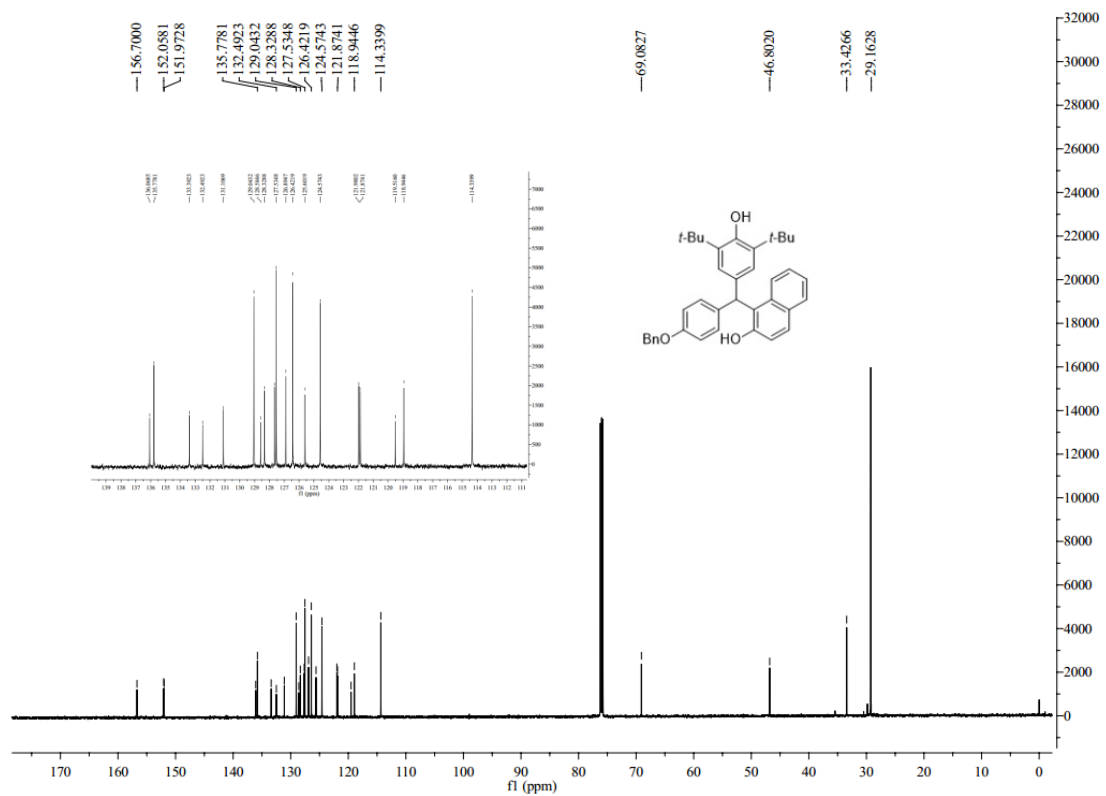
¹H NMR Spectrum of **1o** (CDCl₃, 600 MHz)



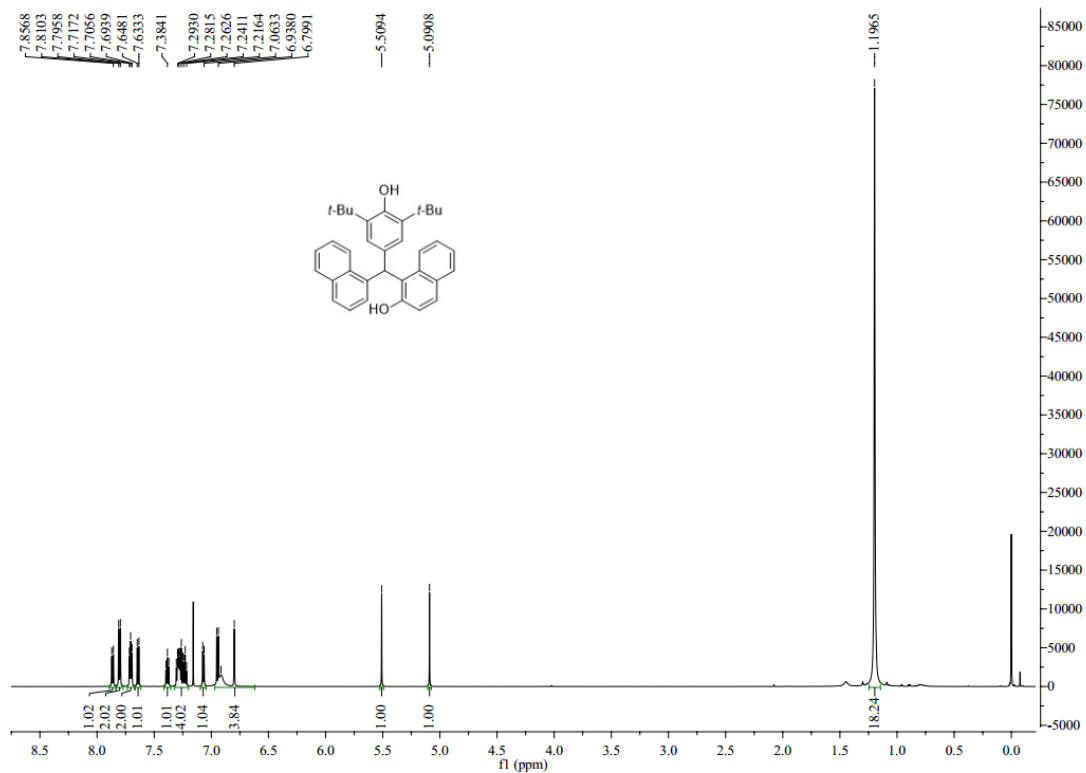
¹³C NMR Spectrum of **1o** (CDCl₃, 150 MHz)



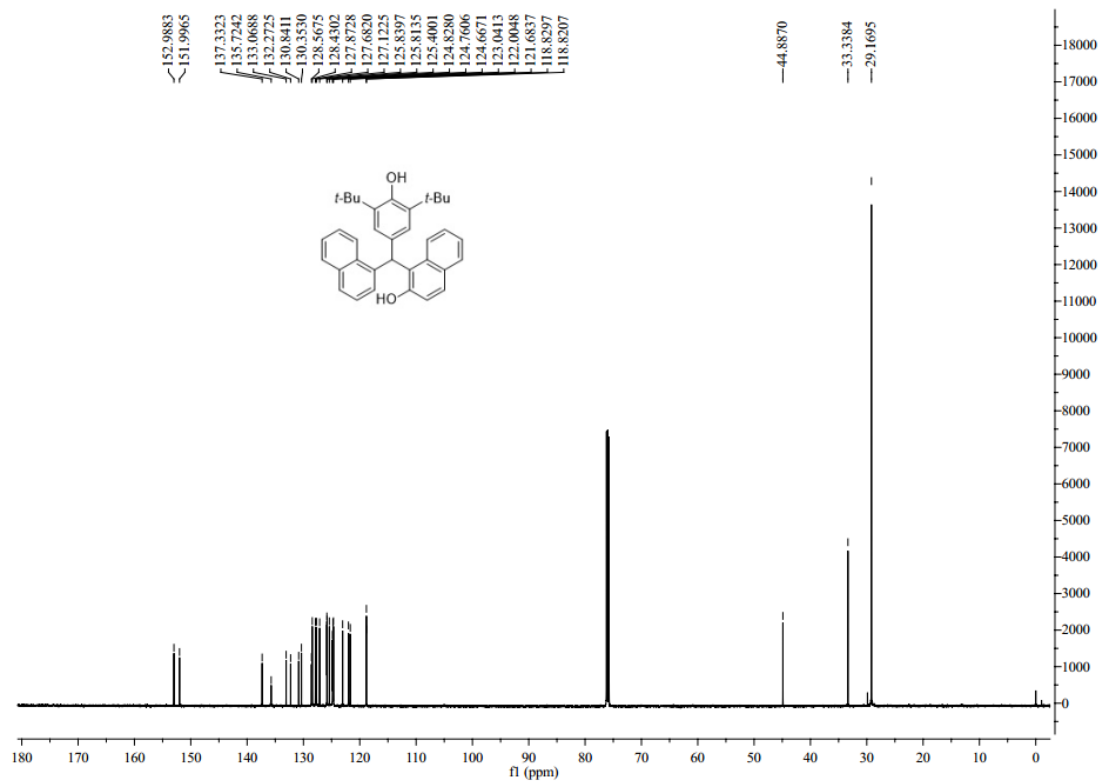
¹H NMR Spectrum of **1q** (CDCl₃, 600 MHz)



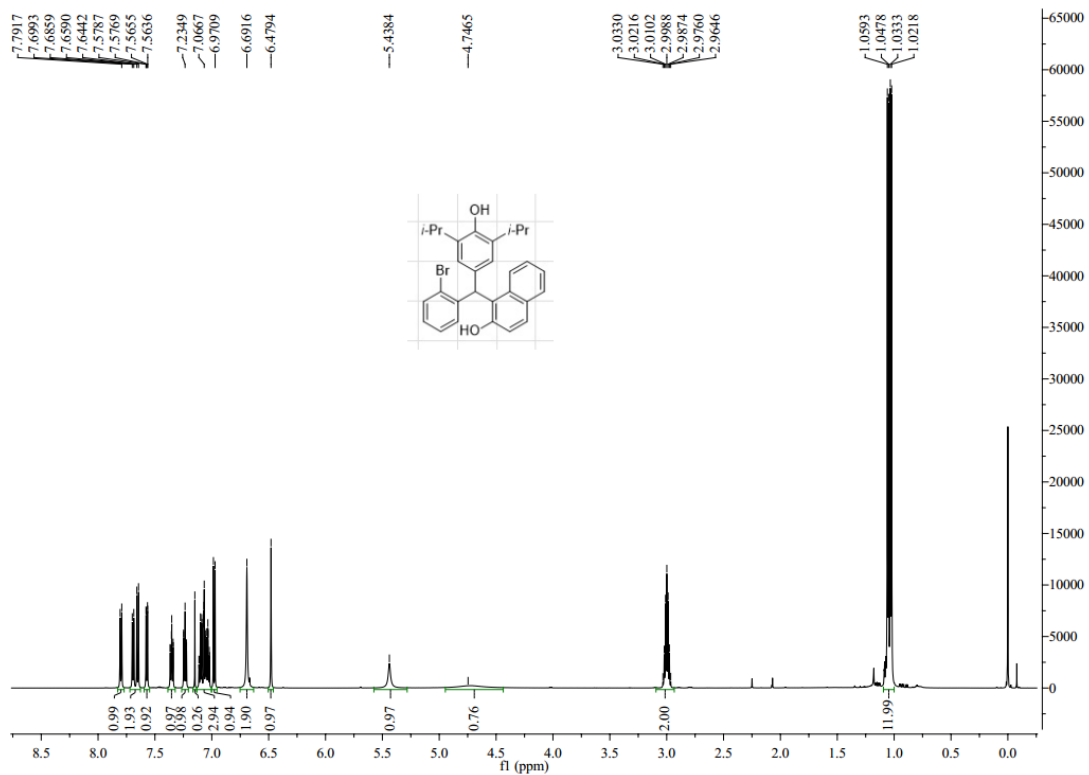
¹³C NMR Spectrum of **1q** (CDCl₃, 150 MHz)



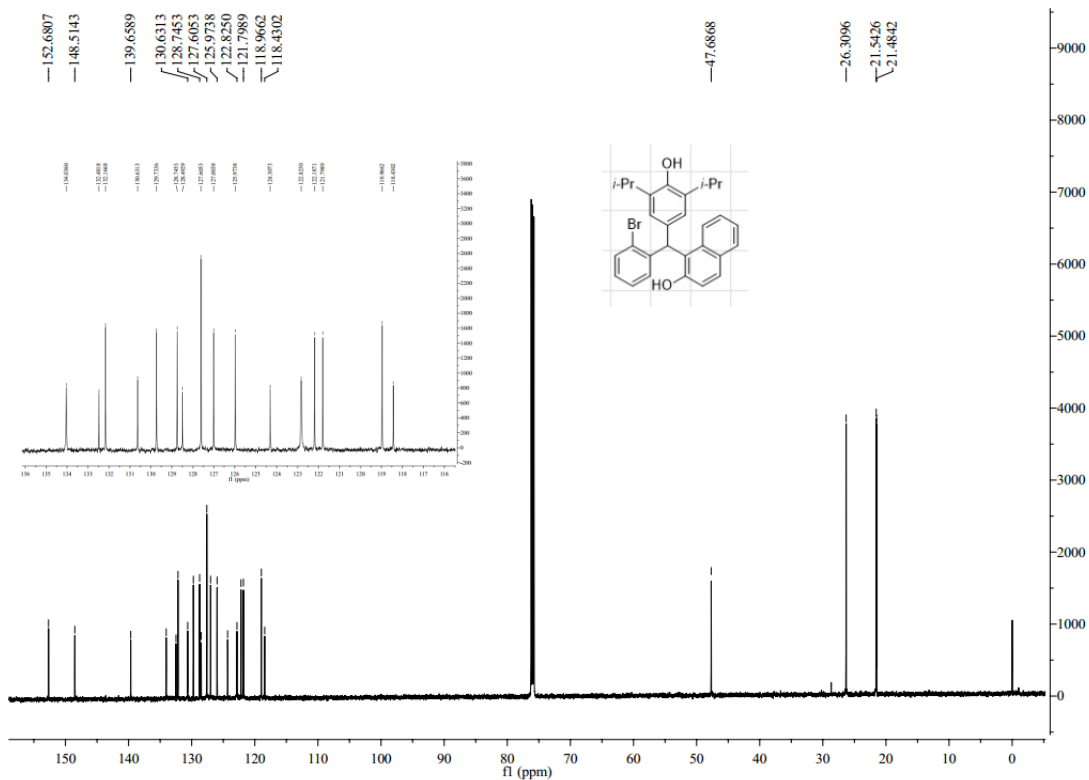
¹H NMR Spectrum of **1r** (CDCl₃, 600 MHz)



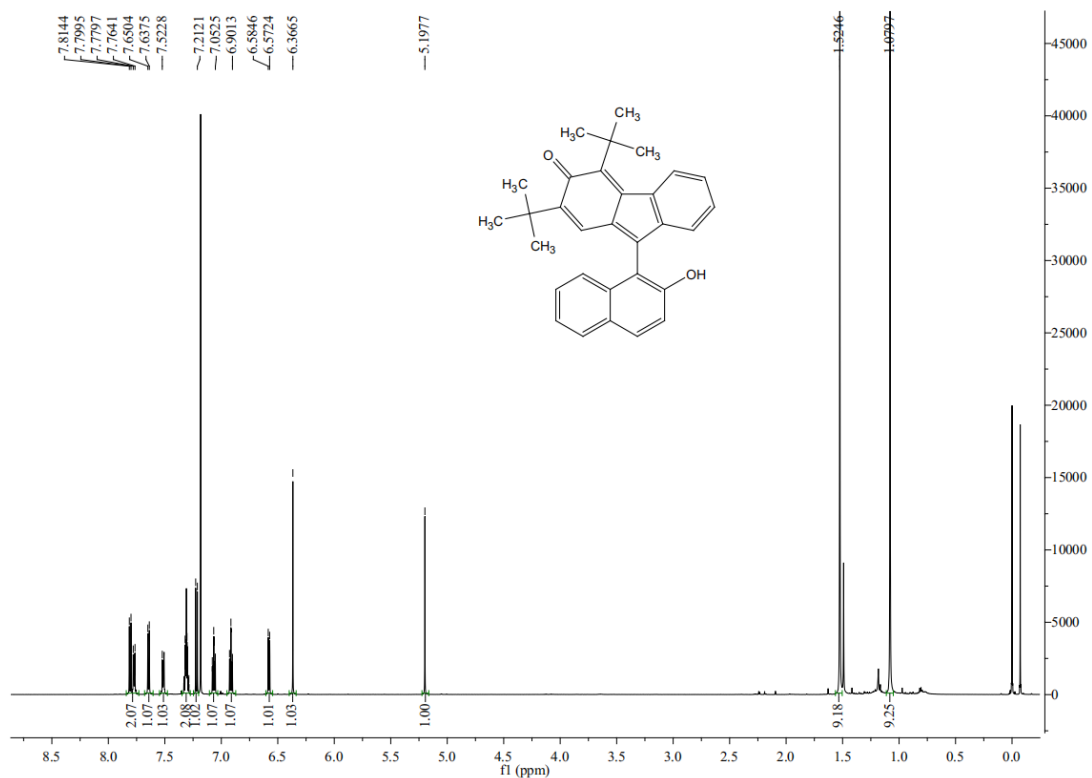
¹³C NMR Spectrum of **1r** (CDCl₃, 150 MHz)



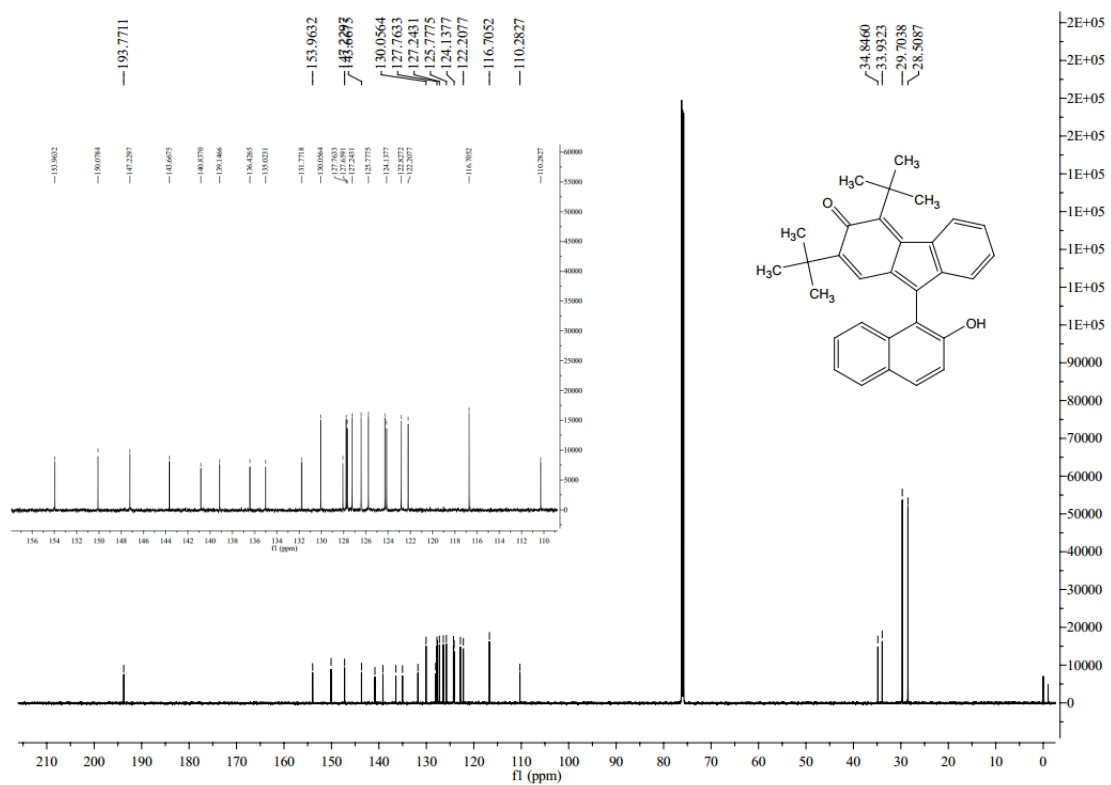
^1H NMR Spectrum of **1s** (CDCl_3 , 600 MHz)



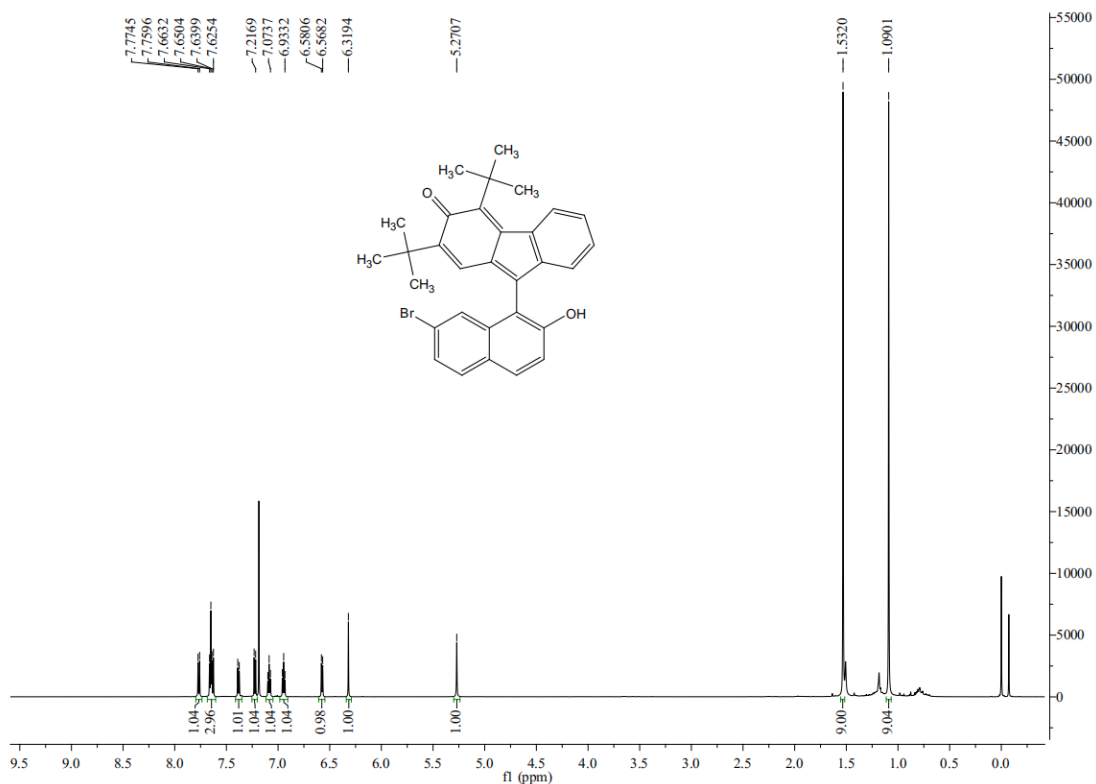
^{13}C NMR Spectrum of **1s** (CDCl_3 , 150 MHz)



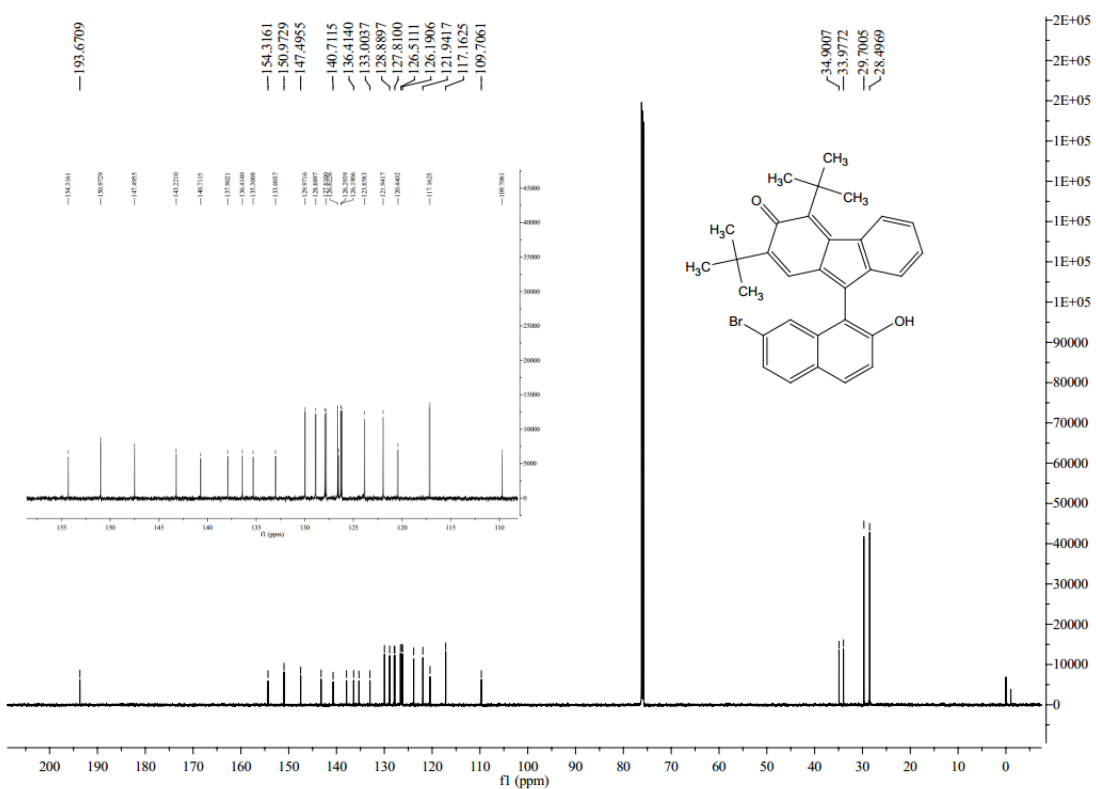
¹H NMR Spectrum of 2a (CDCl₃, 600 MHz)



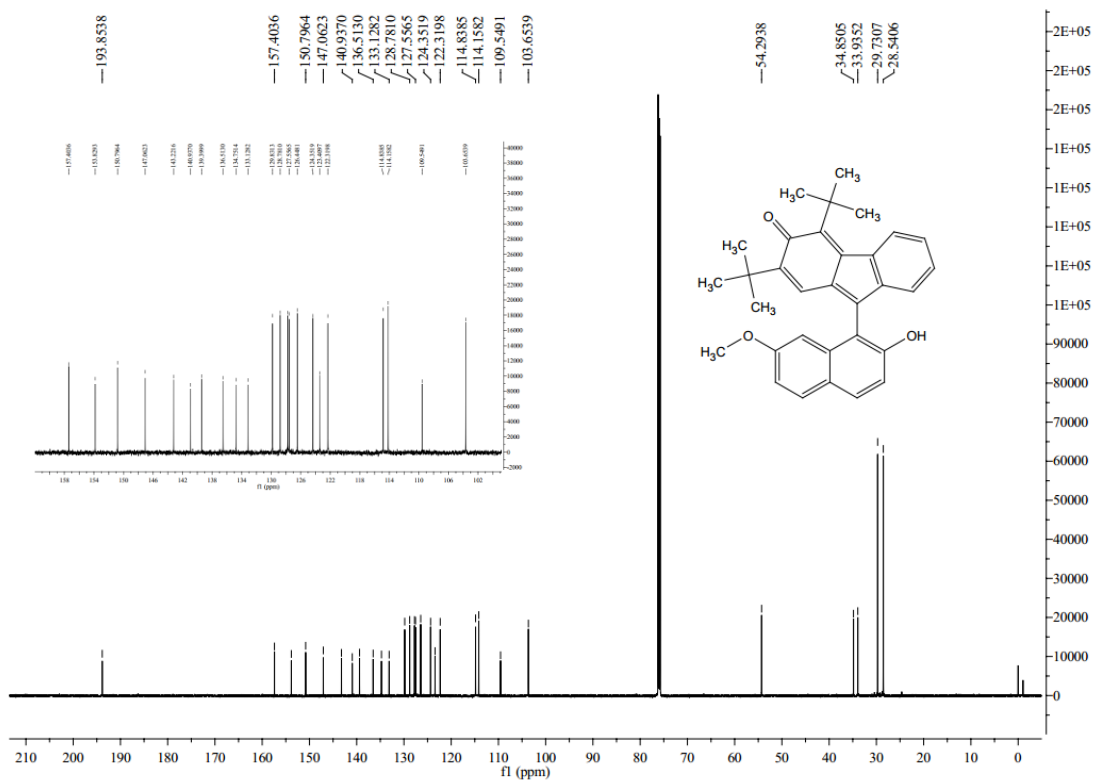
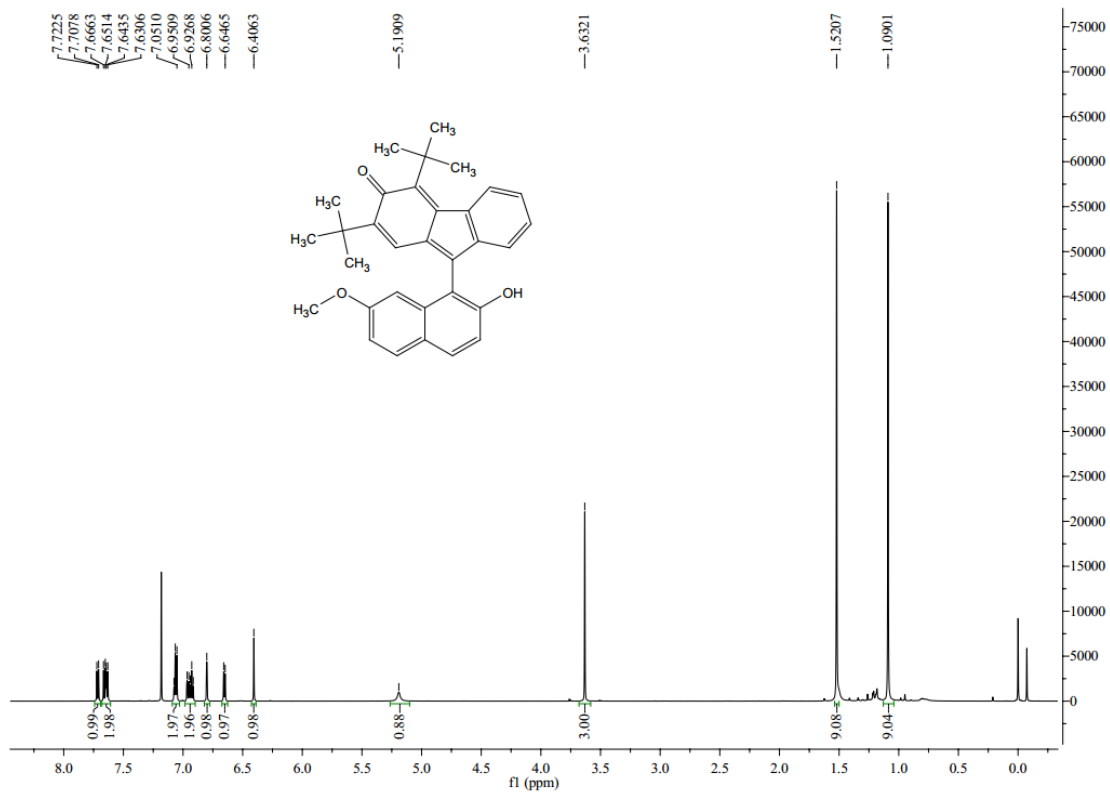
¹³C NMR Spectrum of 2a (CDCl₃, 150 MHz)



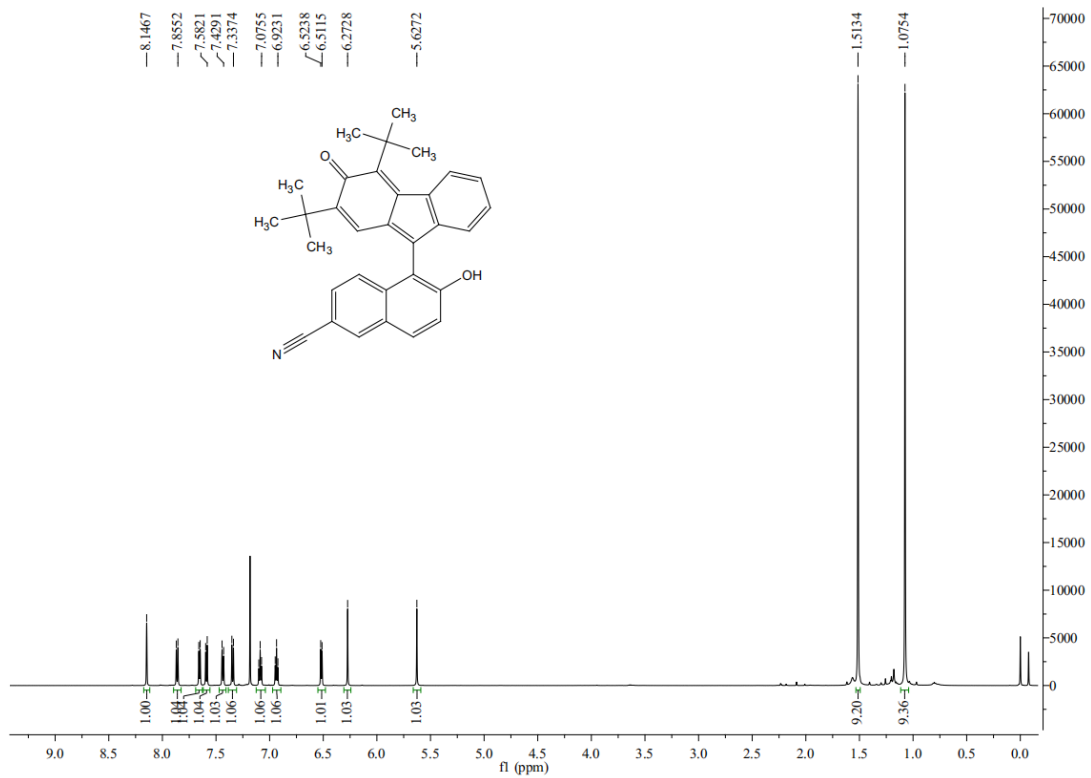
¹H NMR Spectrum of **2b** (CDCl₃, 600 MHz)



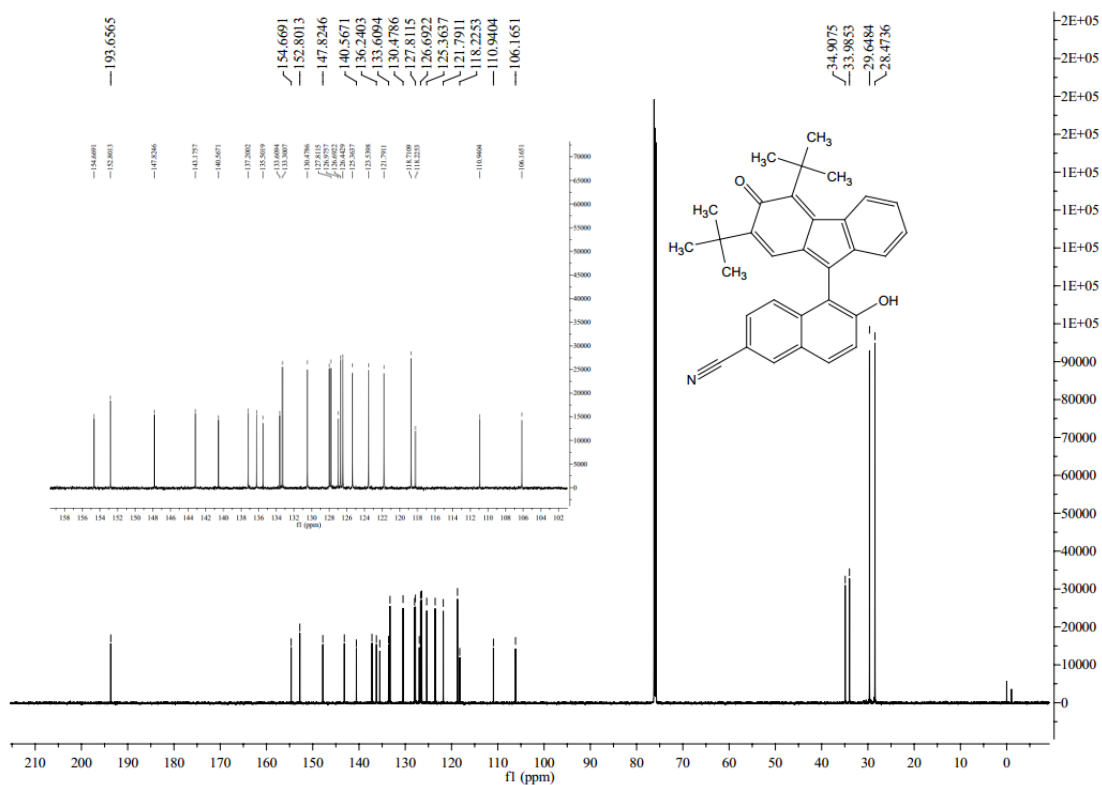
¹³C NMR Spectrum of **2b** (CDCl₃, 150 MHz)



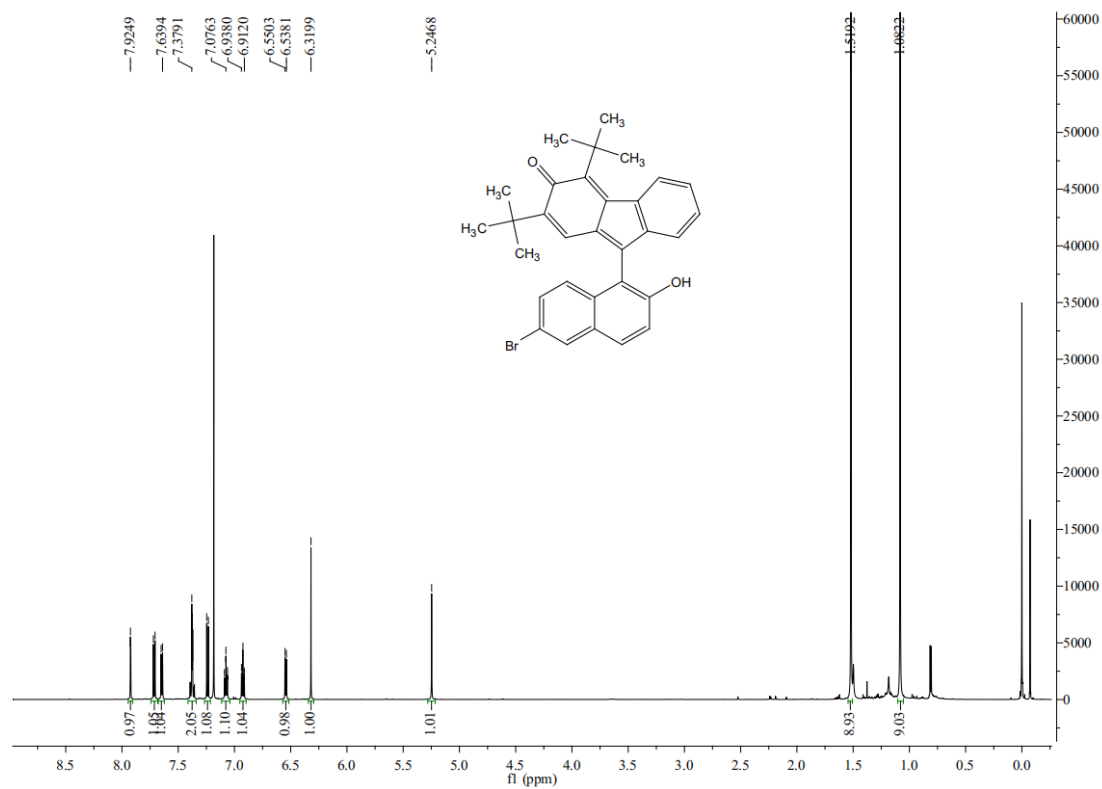
¹³C NMR Spectrum of 2c (CDCl₃, 150 MHz)



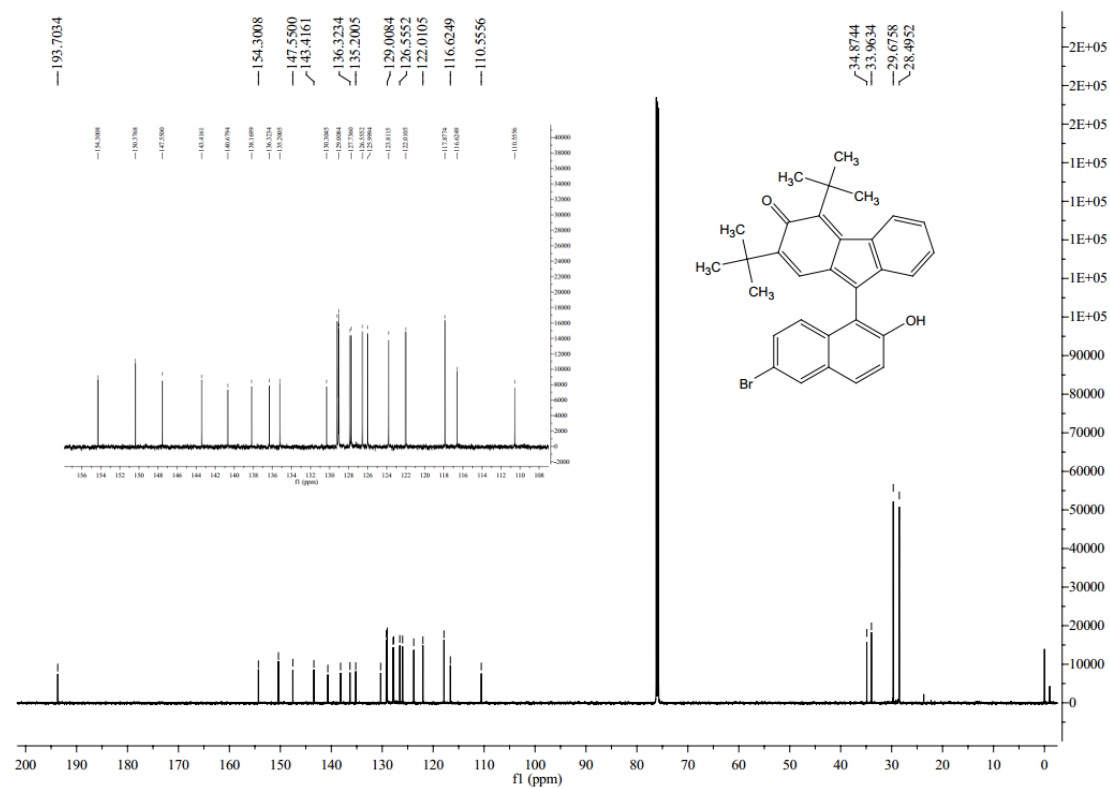
¹H NMR Spectrum of **2d** (CDCl₃, 600 MHz)



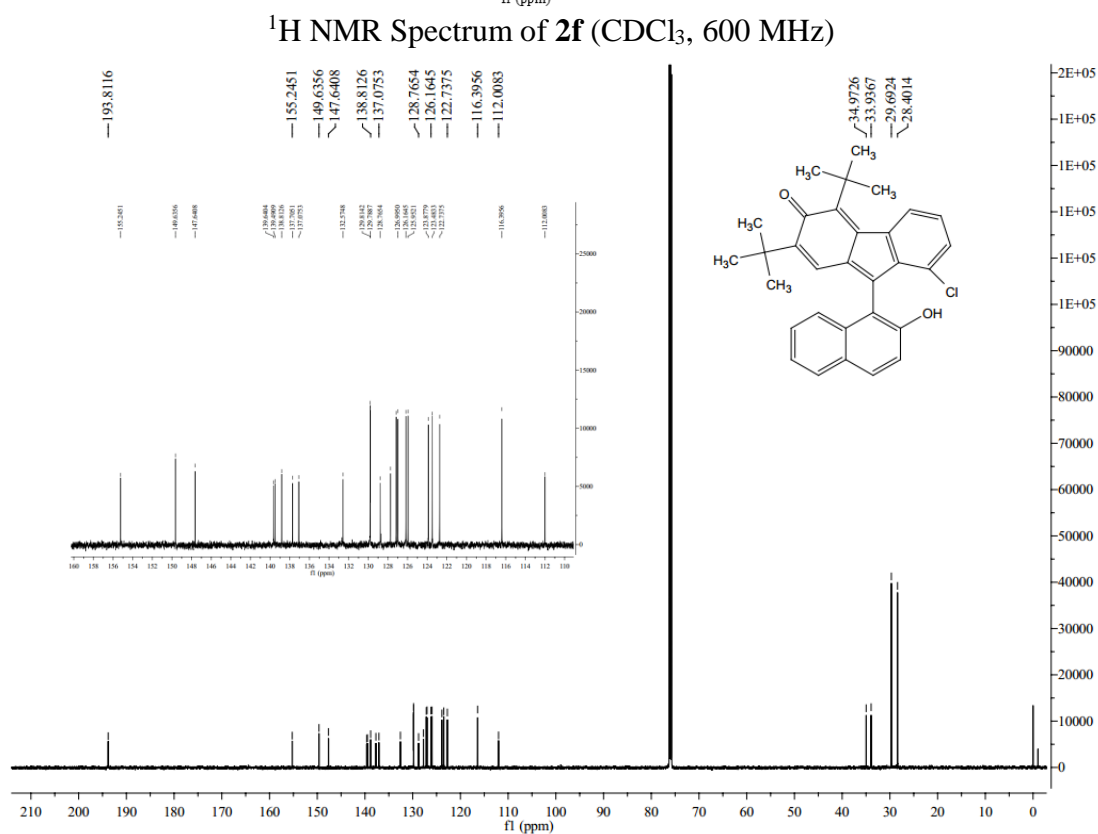
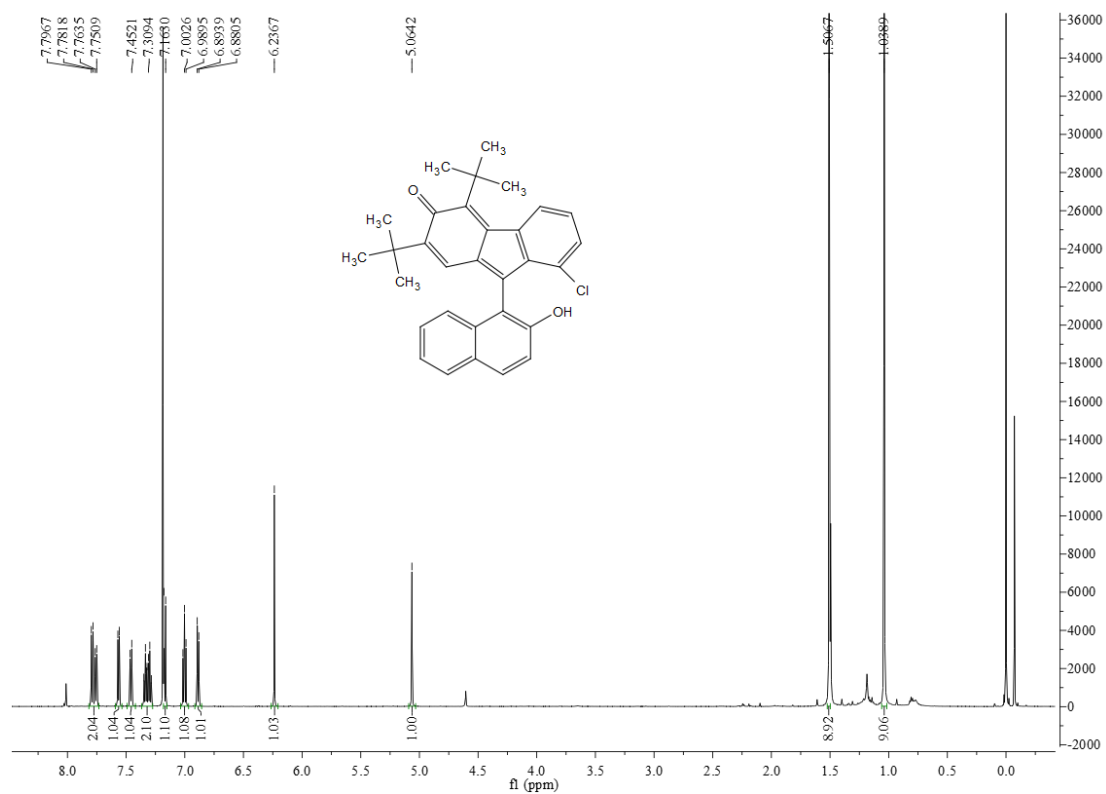
¹³C NMR Spectrum of **2d** (CDCl₃, 150 MHz)

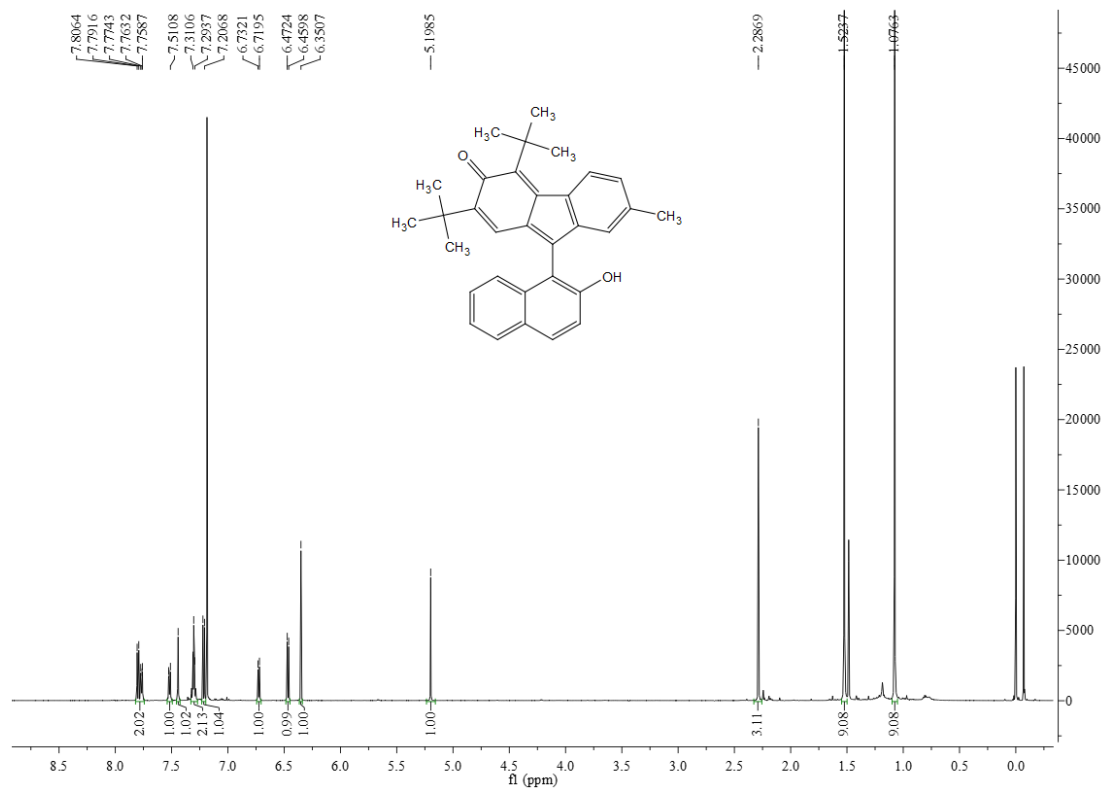


¹H NMR Spectrum of 2e (CDCl₃, 600 MHz)

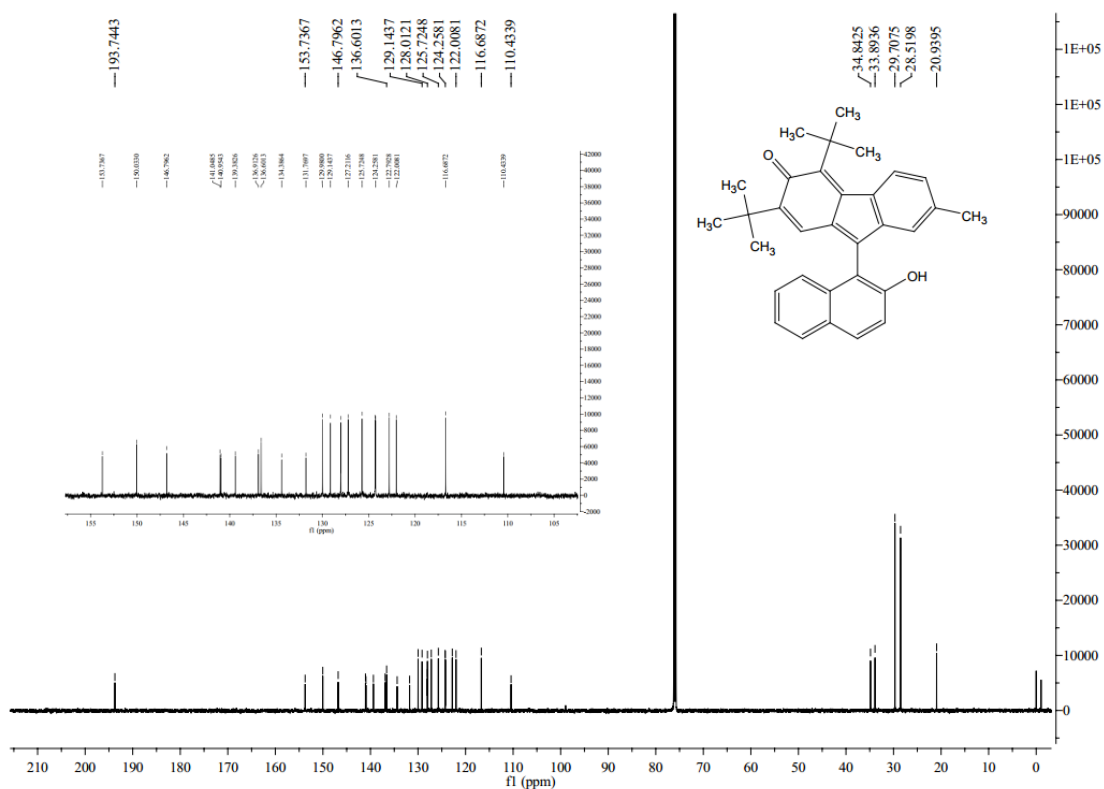


¹³C NMR Spectrum of 2e (CDCl₃, 150 MHz)

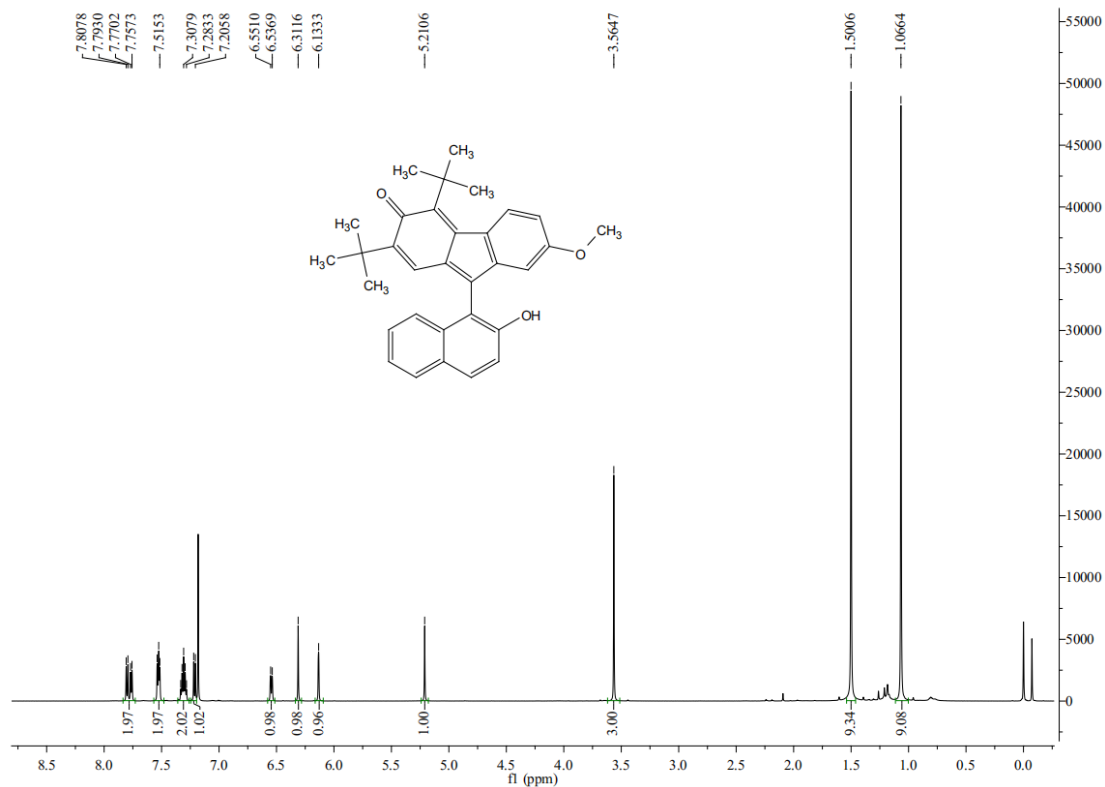




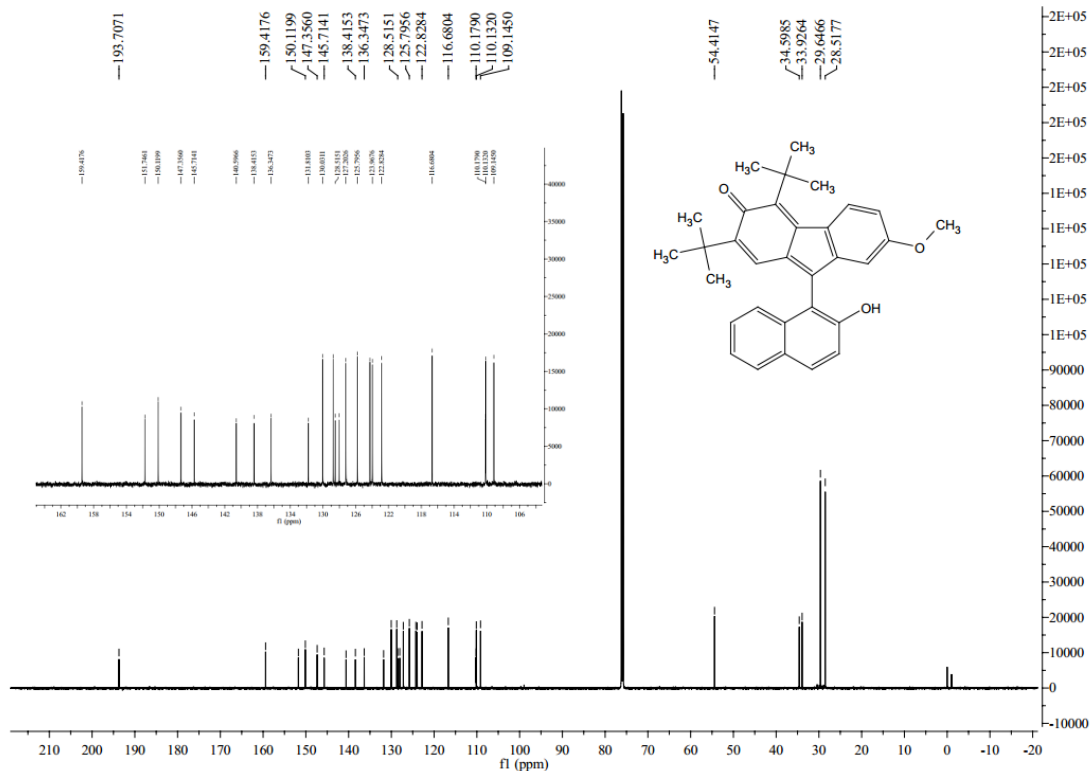
¹H NMR Spectrum of **2g** (CDCl₃, 600 MHz)



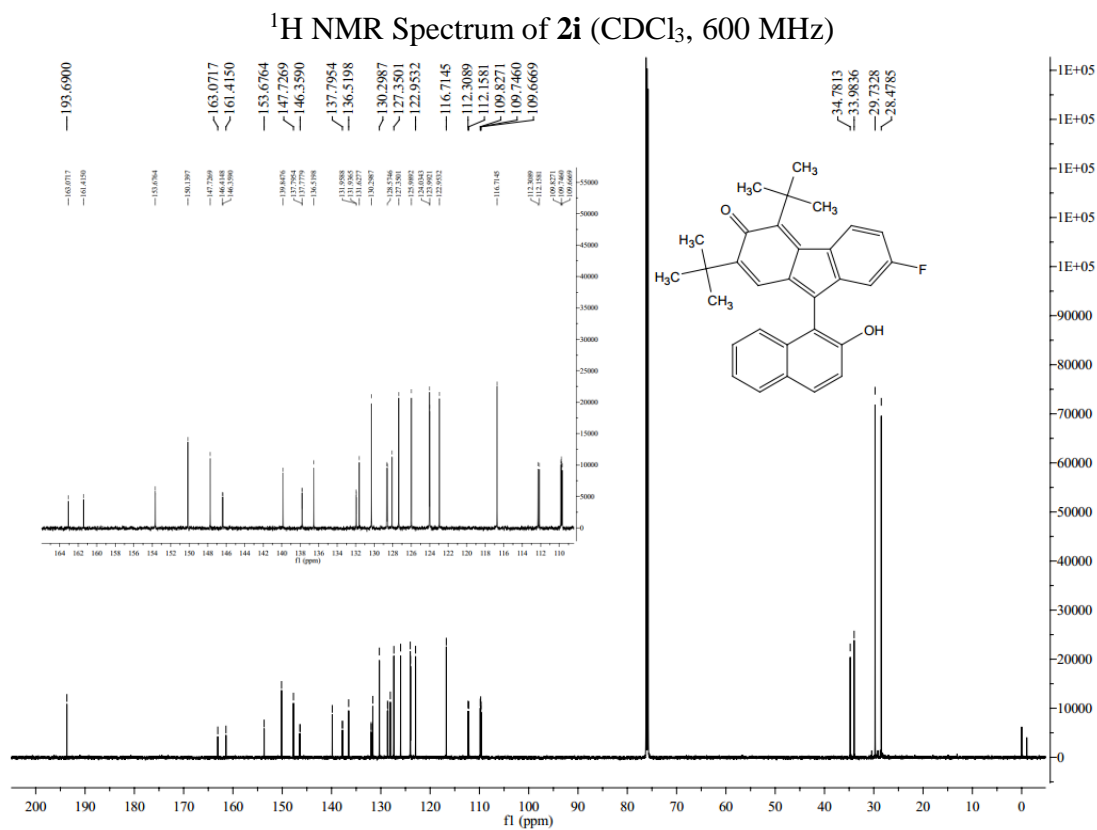
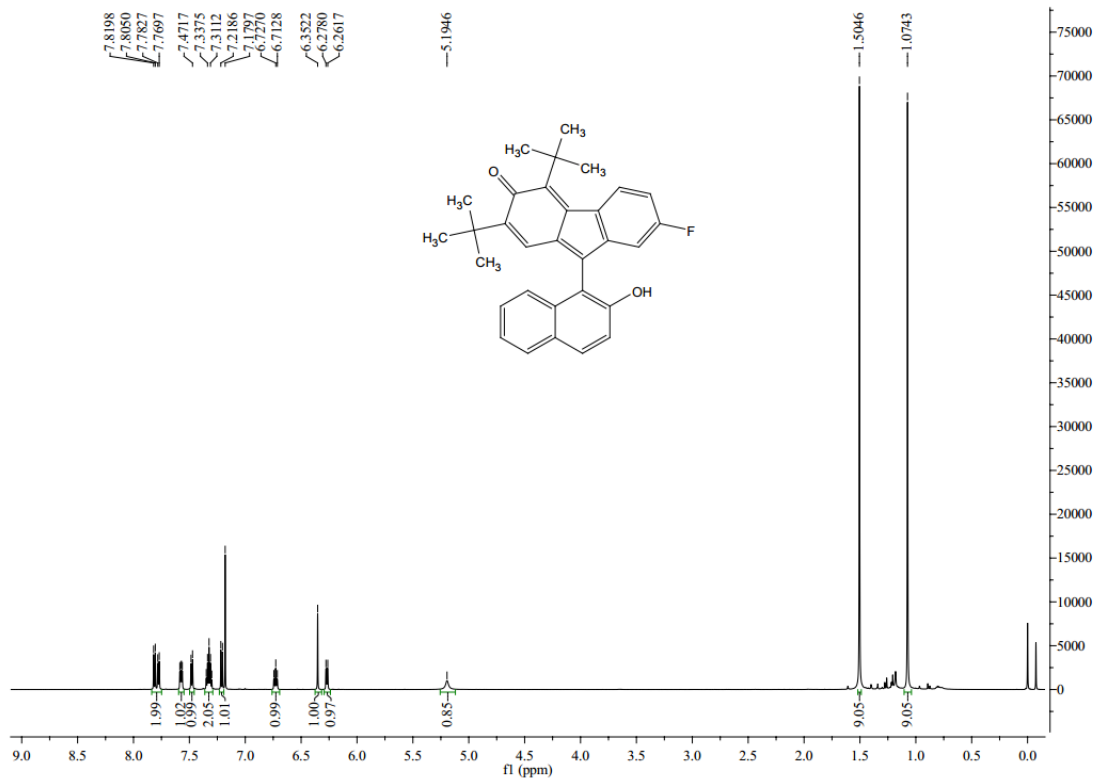
¹³C NMR Spectrum of **2g** (CDCl₃, 150 MHz)



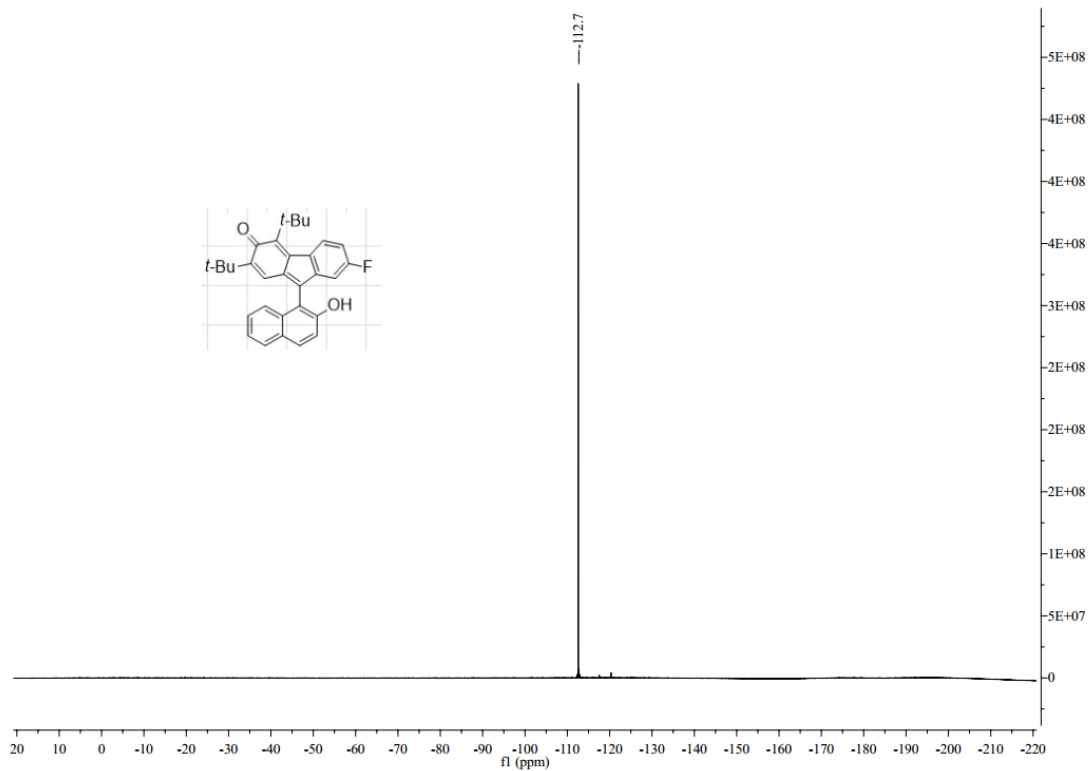
^1H NMR Spectrum of **2h** (CDCl_3 , 600 MHz)



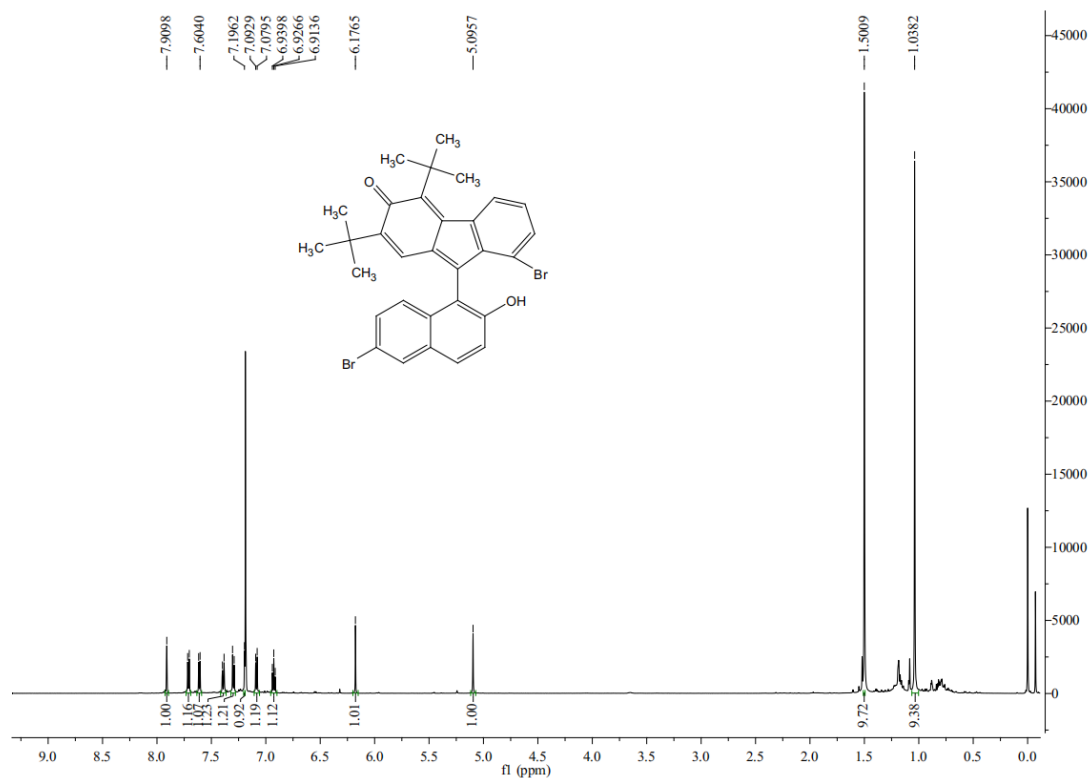
^{13}C NMR Spectrum of **2h** (CDCl_3 , 150 MHz)



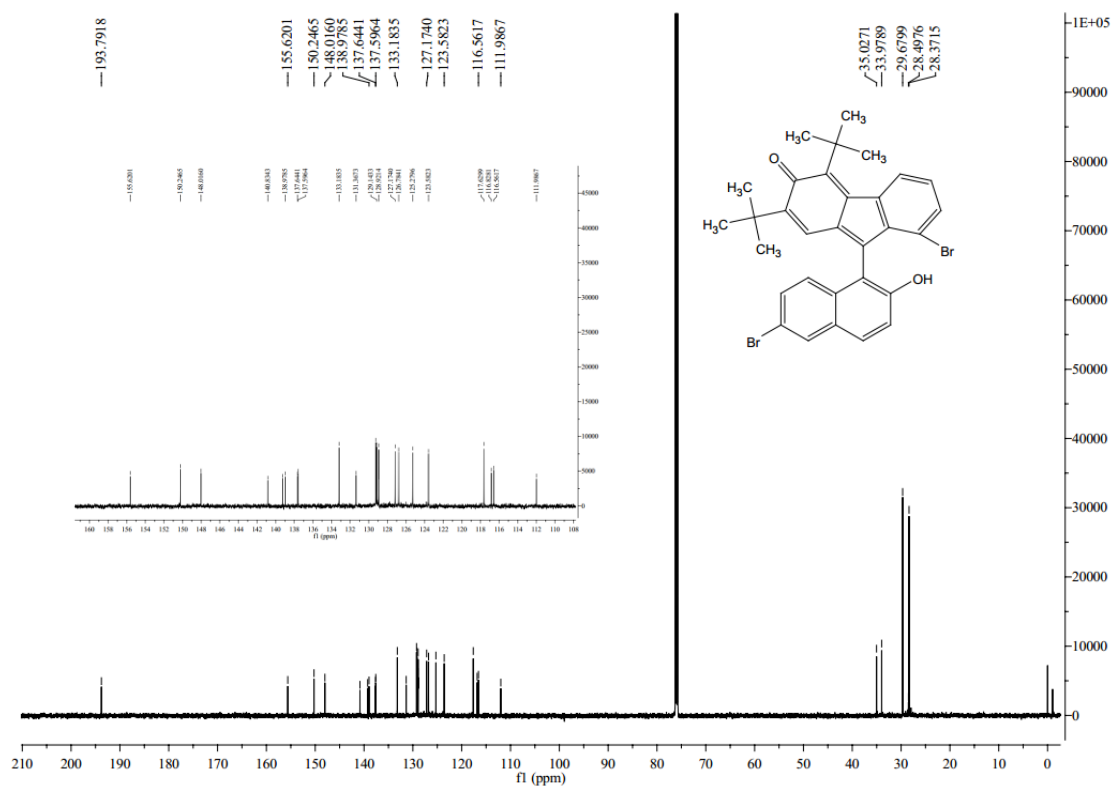
¹³C NMR Spectrum of 2i (CDCl₃, 150 MHz)



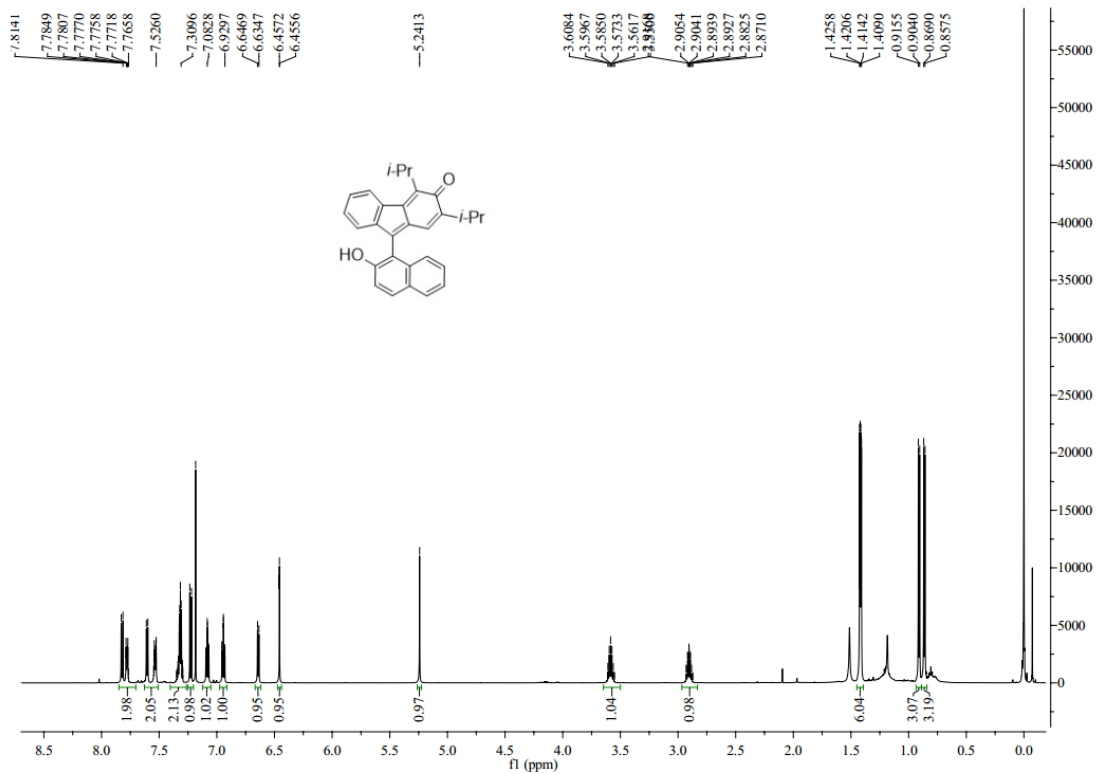
¹⁹F NMR Spectrum of **2i** (CDCl₃, 377 MHz)



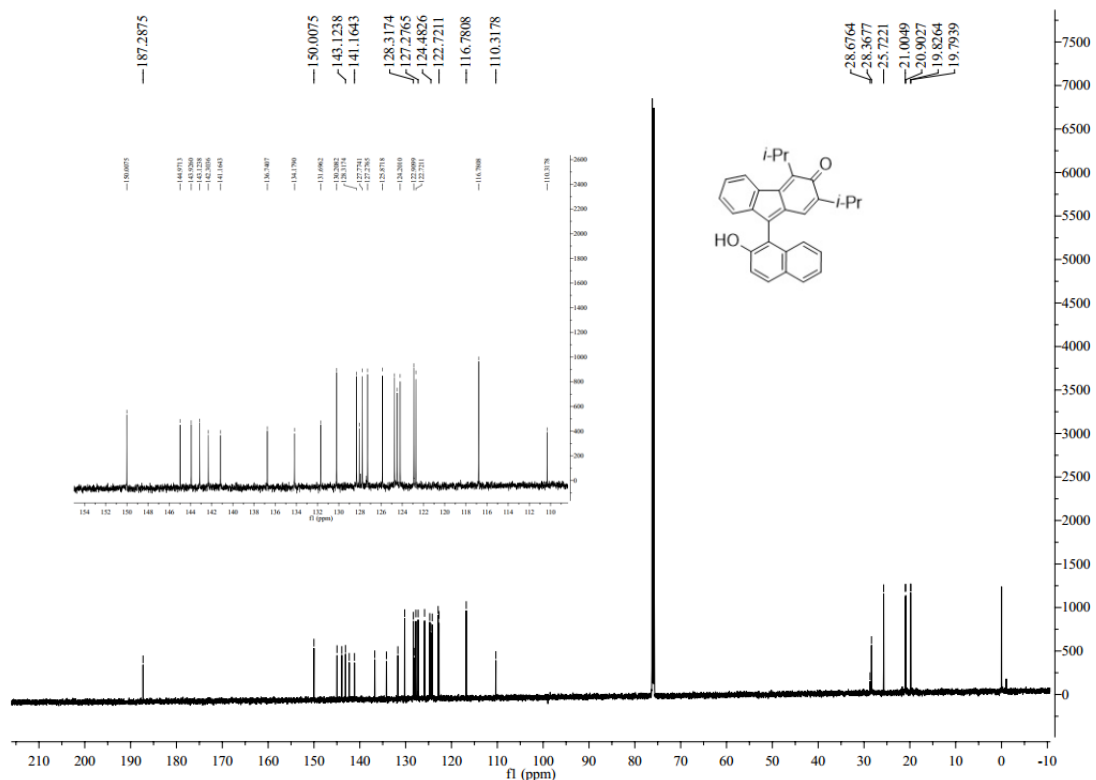
¹H NMR Spectrum of **2j** (CDCl₃, 600 MHz)



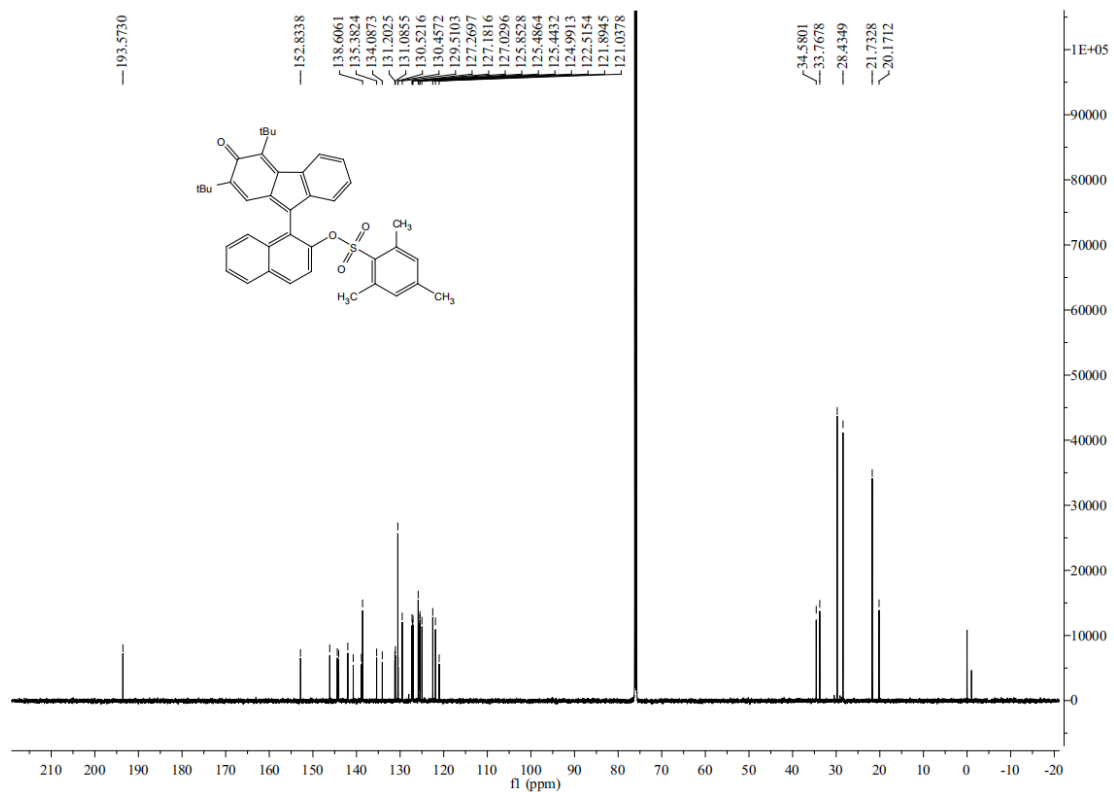
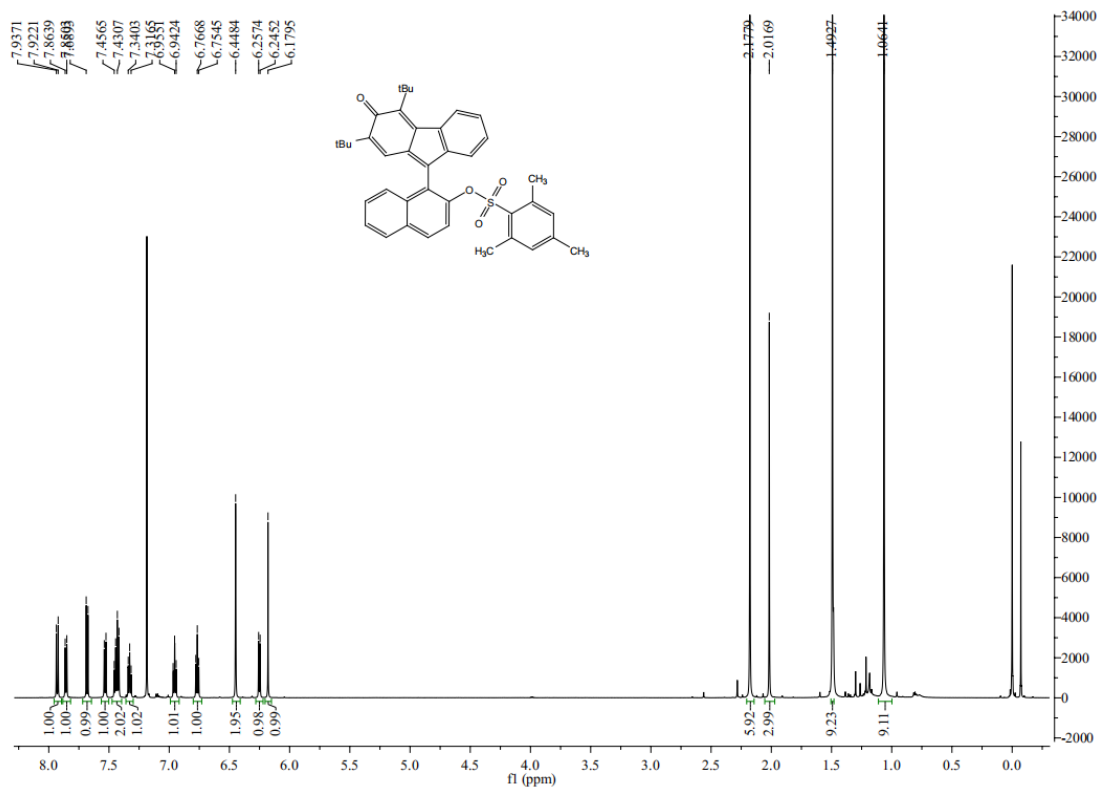
¹³C NMR Spectrum of **2j** (CDCl₃, 150 MHz)



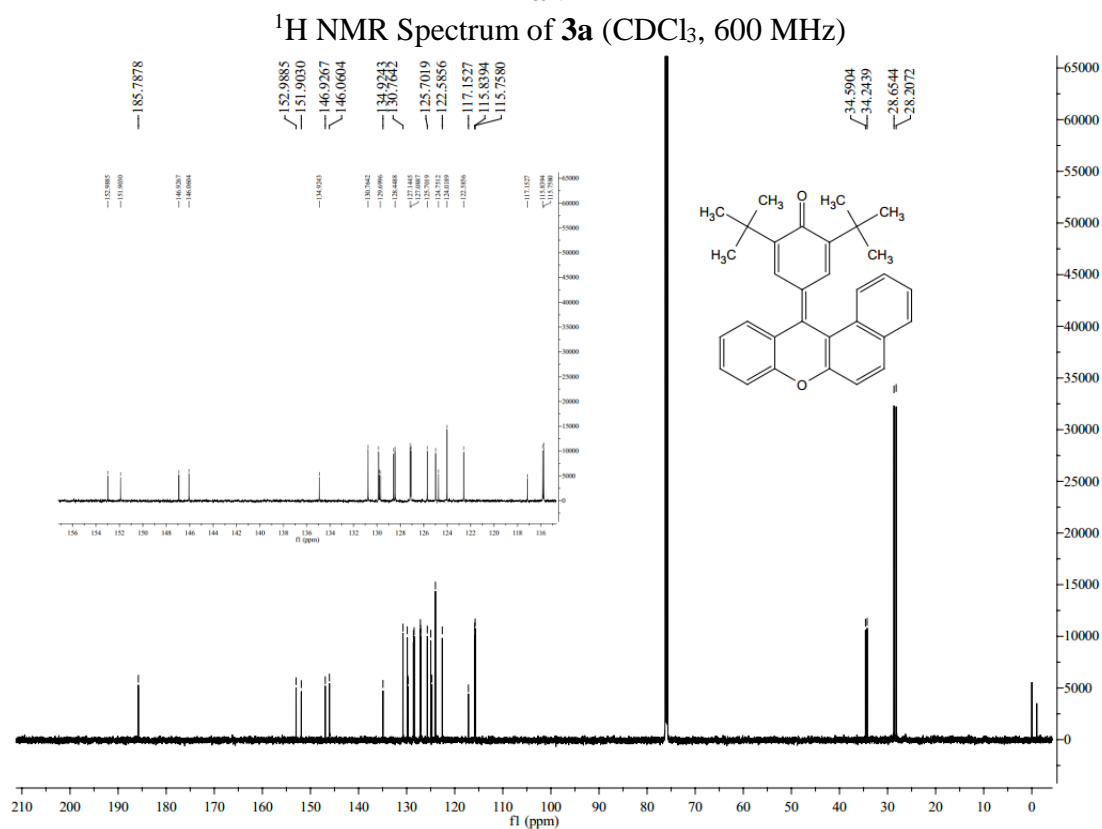
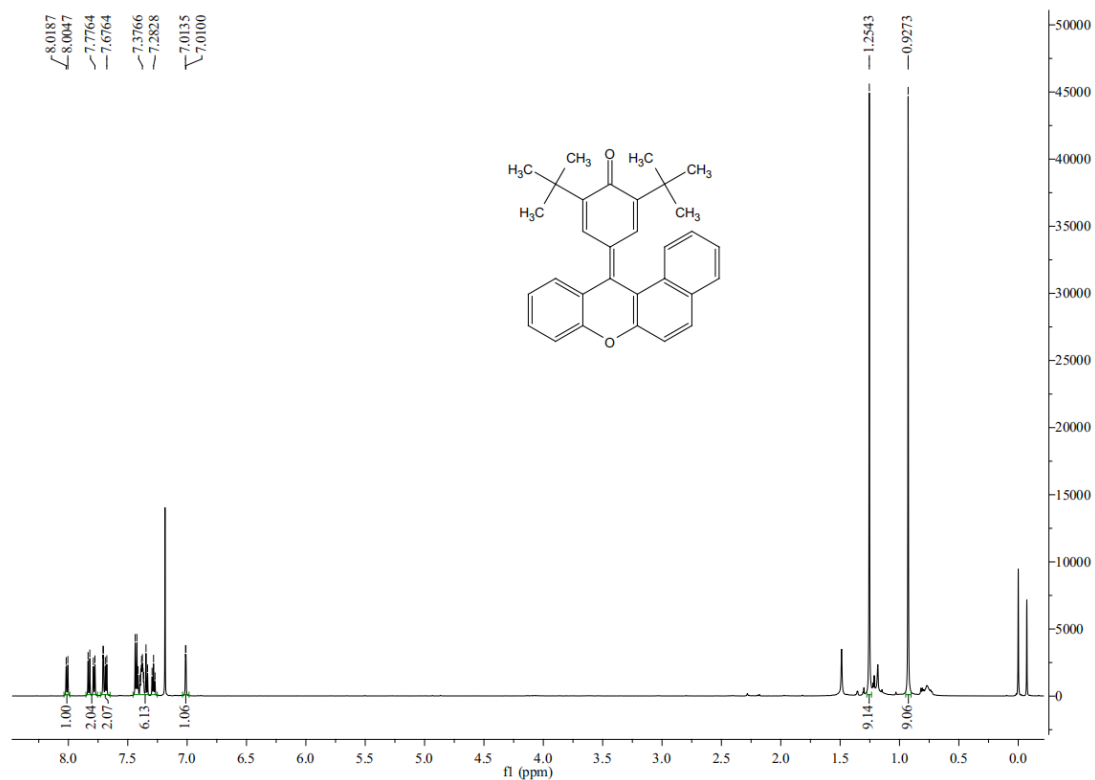
¹H NMR Spectrum of **2k (CDCl₃, 600 MHz)**



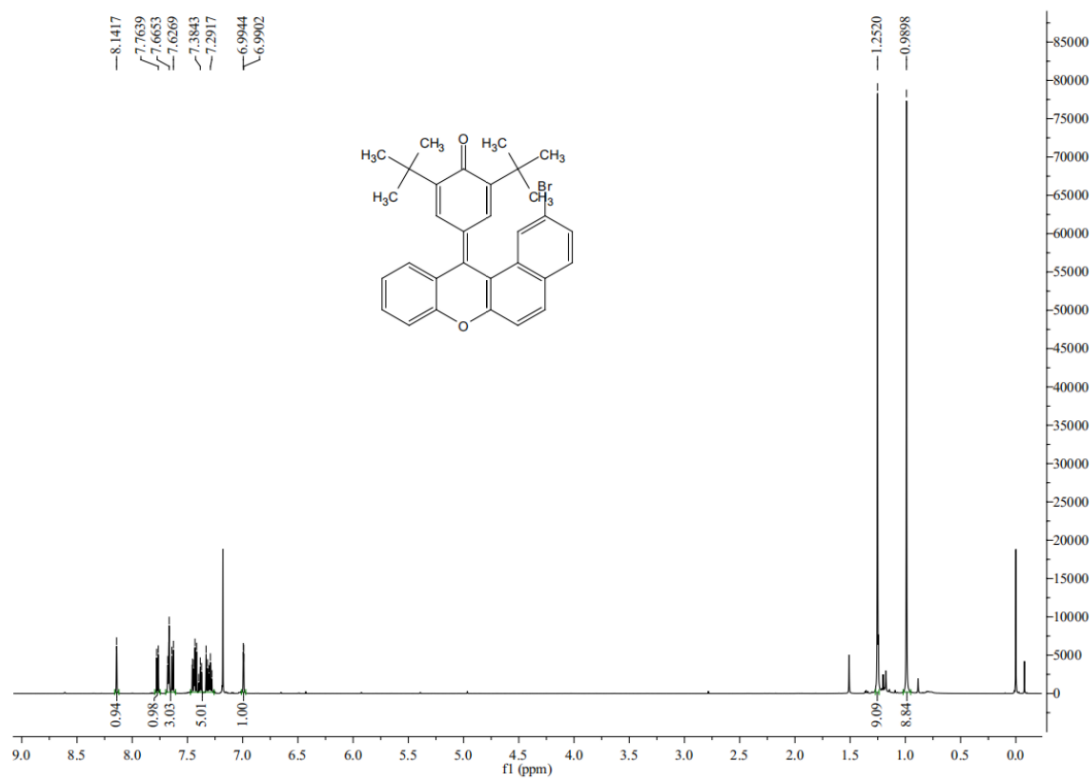
¹³C NMR Spectrum of **2k (CDCl₃, 150 MHz)**



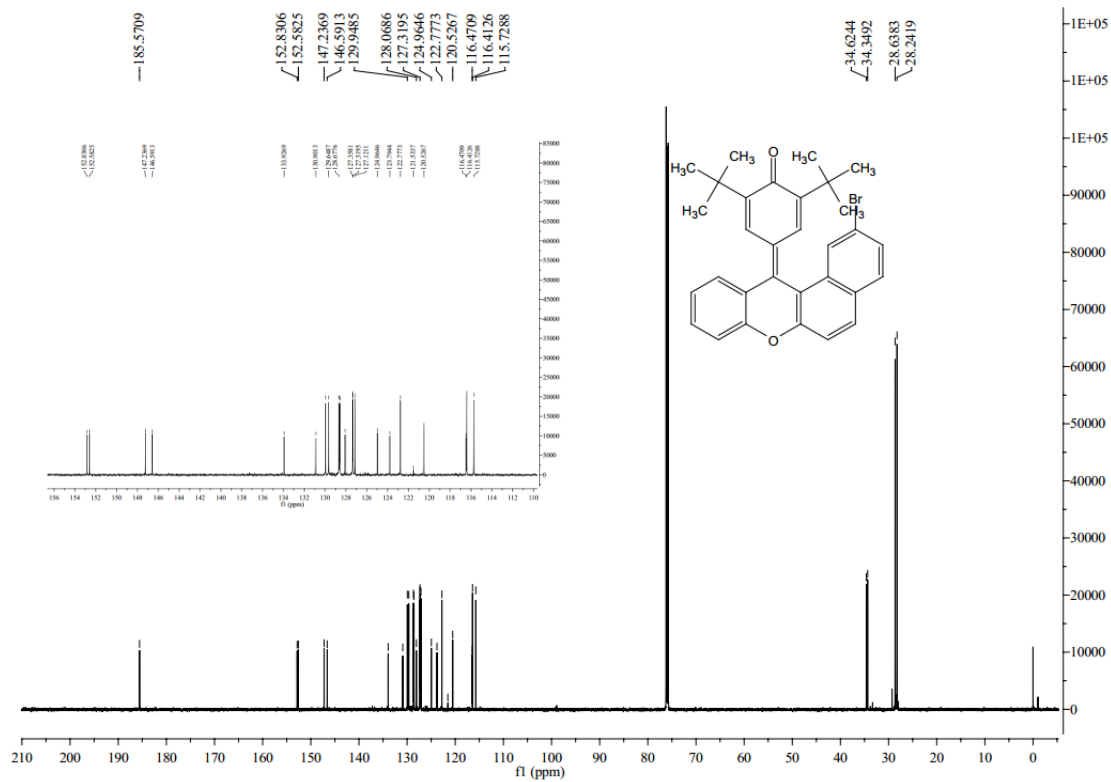
¹³C NMR Spectrum of 2a' (CDCl₃, 150 MHz)



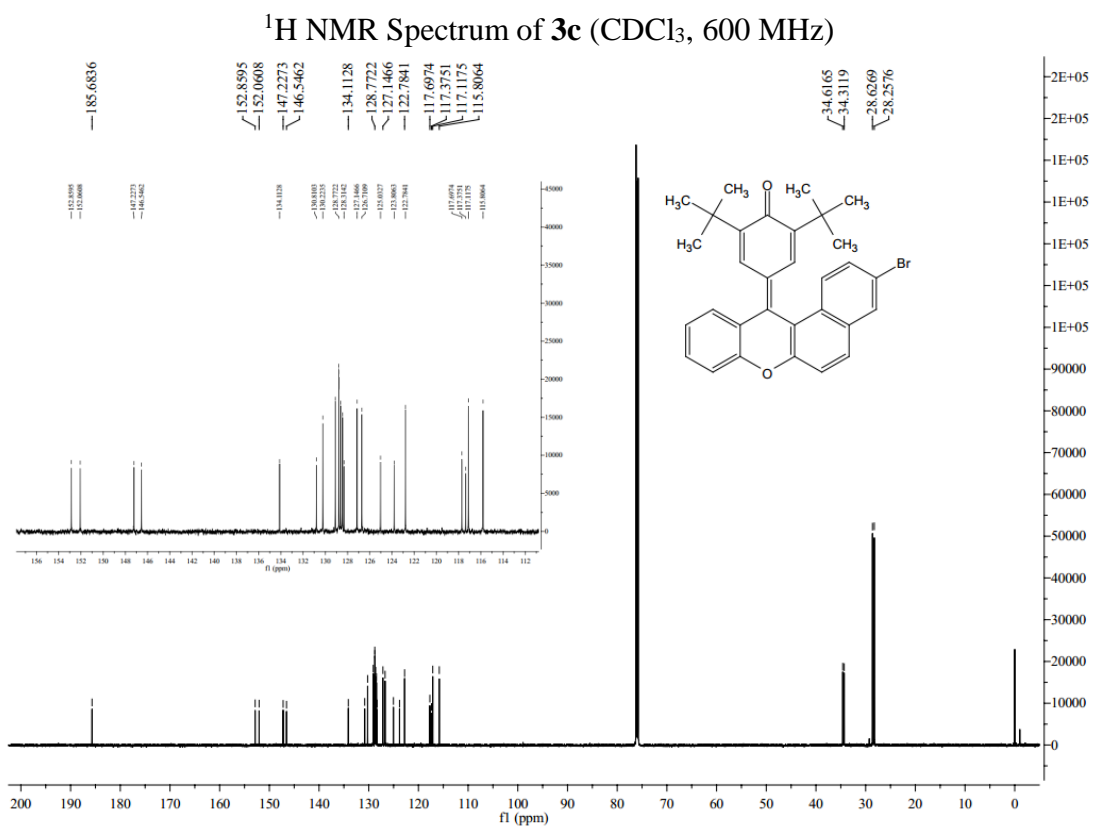
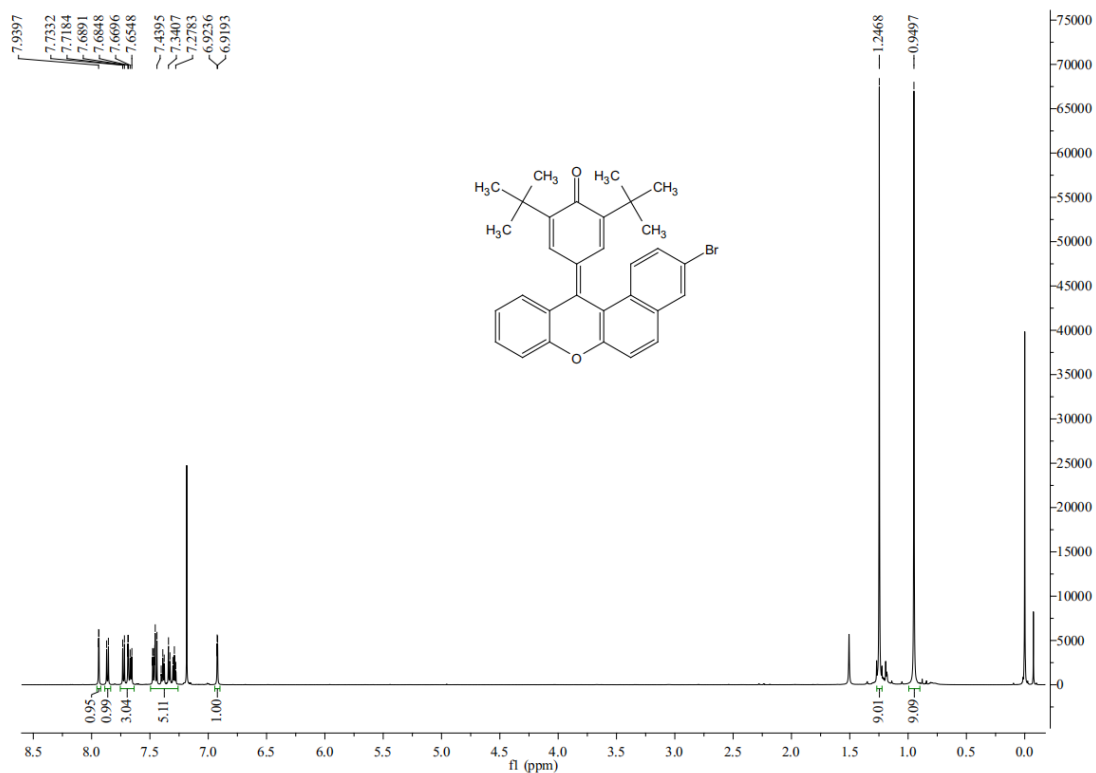
¹³C NMR Spectrum of 3a (CDCl₃, 150 MHz)



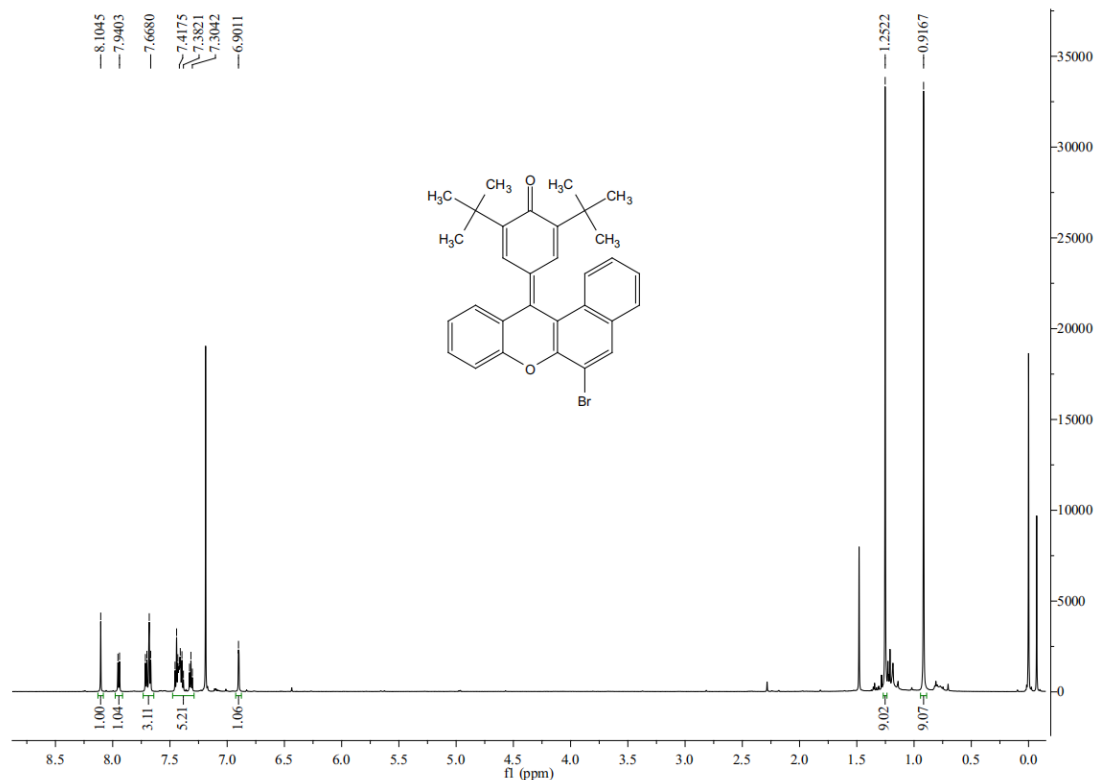
¹H NMR Spectrum of **3b (CDCl₃, 600 MHz)**



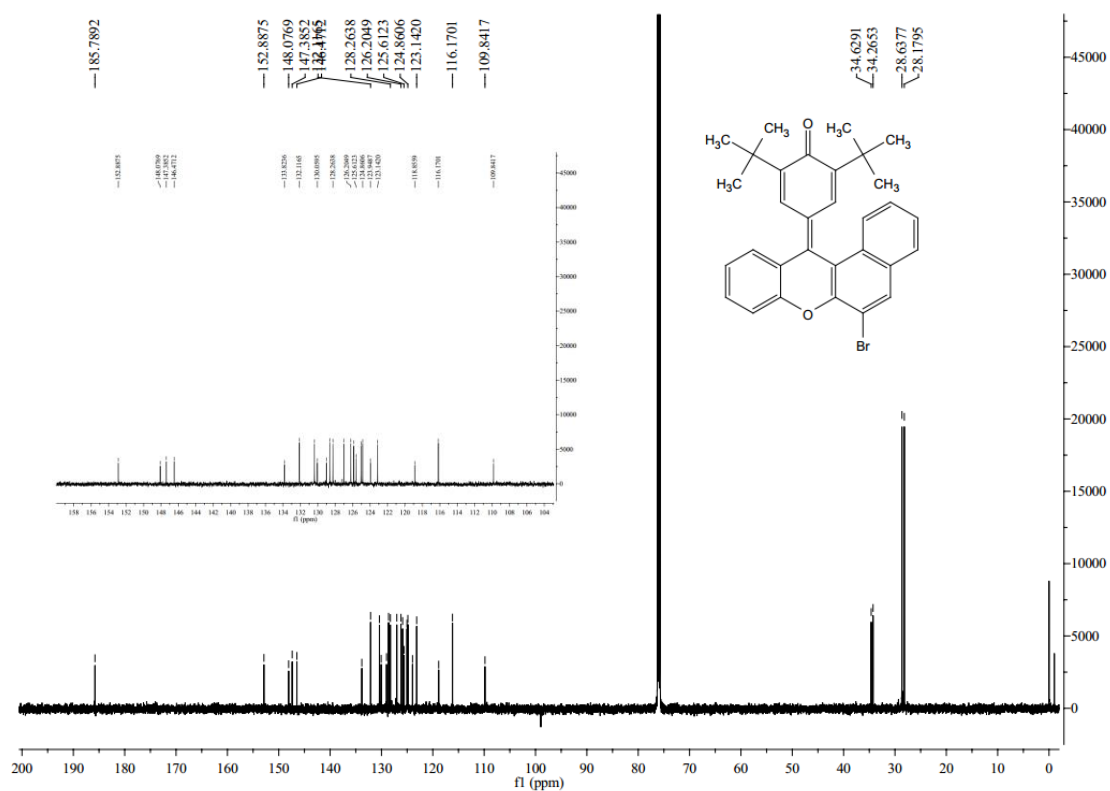
¹³C NMR Spectrum of **3b (CDCl₃, 150 MHz)**



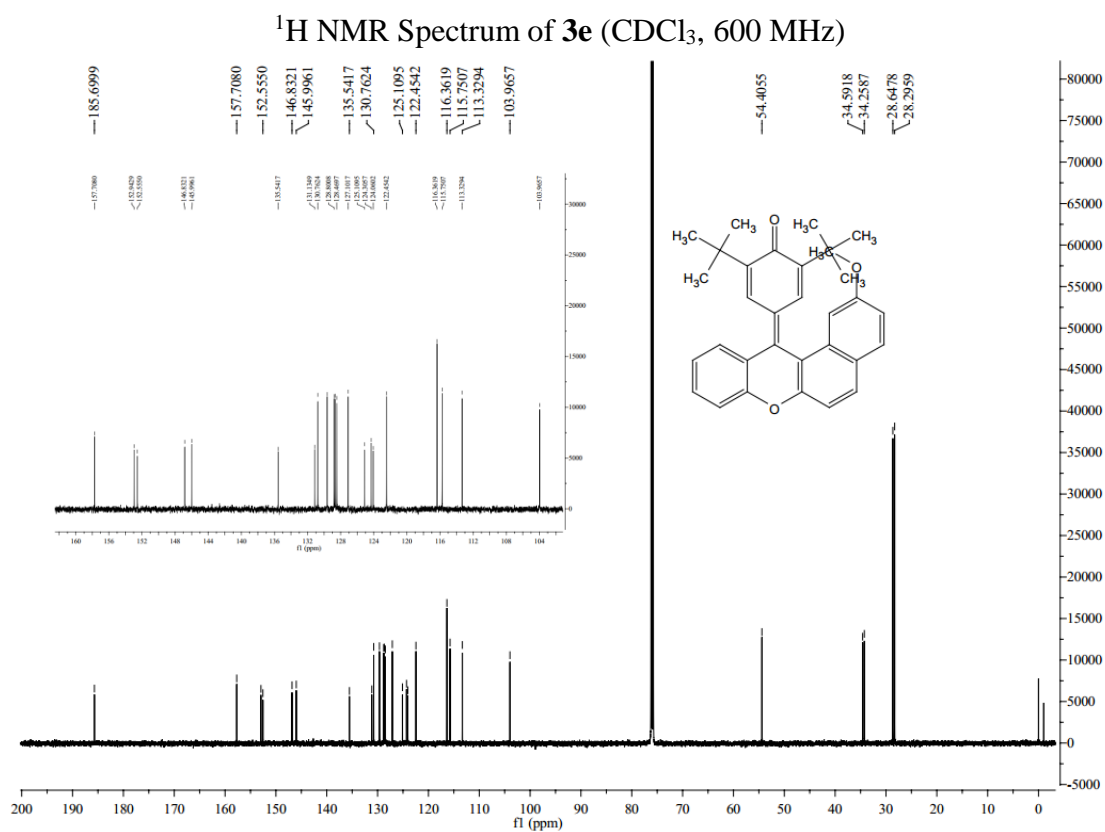
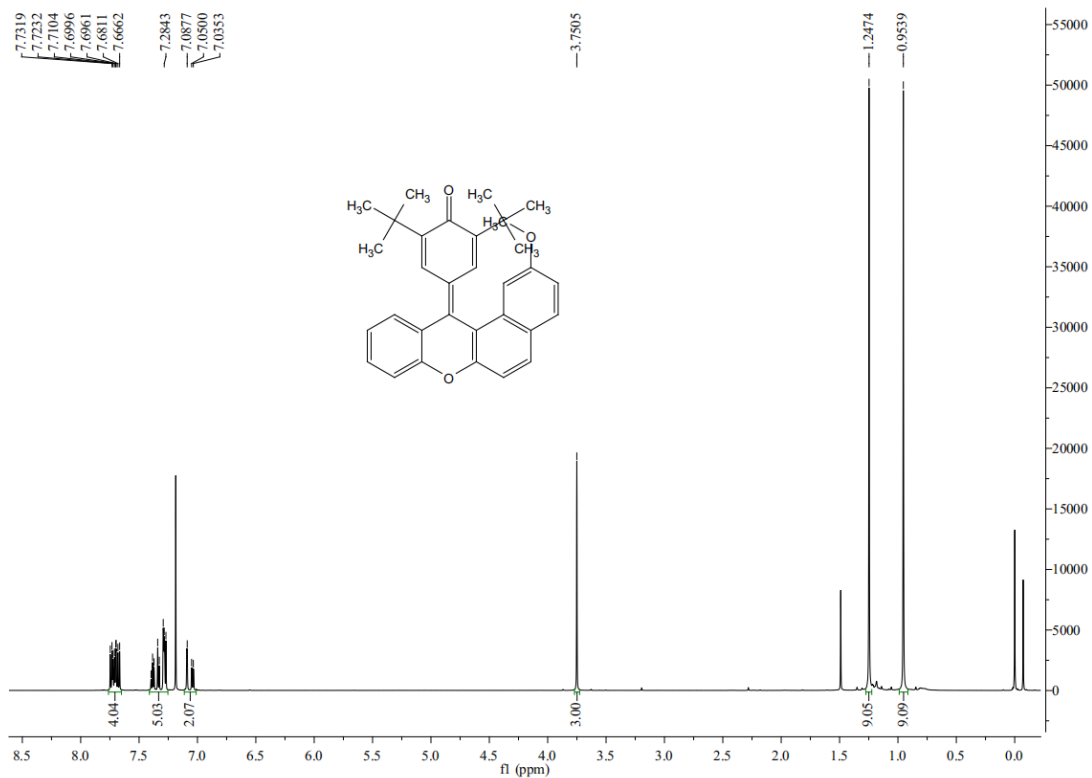
¹³C NMR Spectrum of 3c (CDCl₃, 150 MHz)



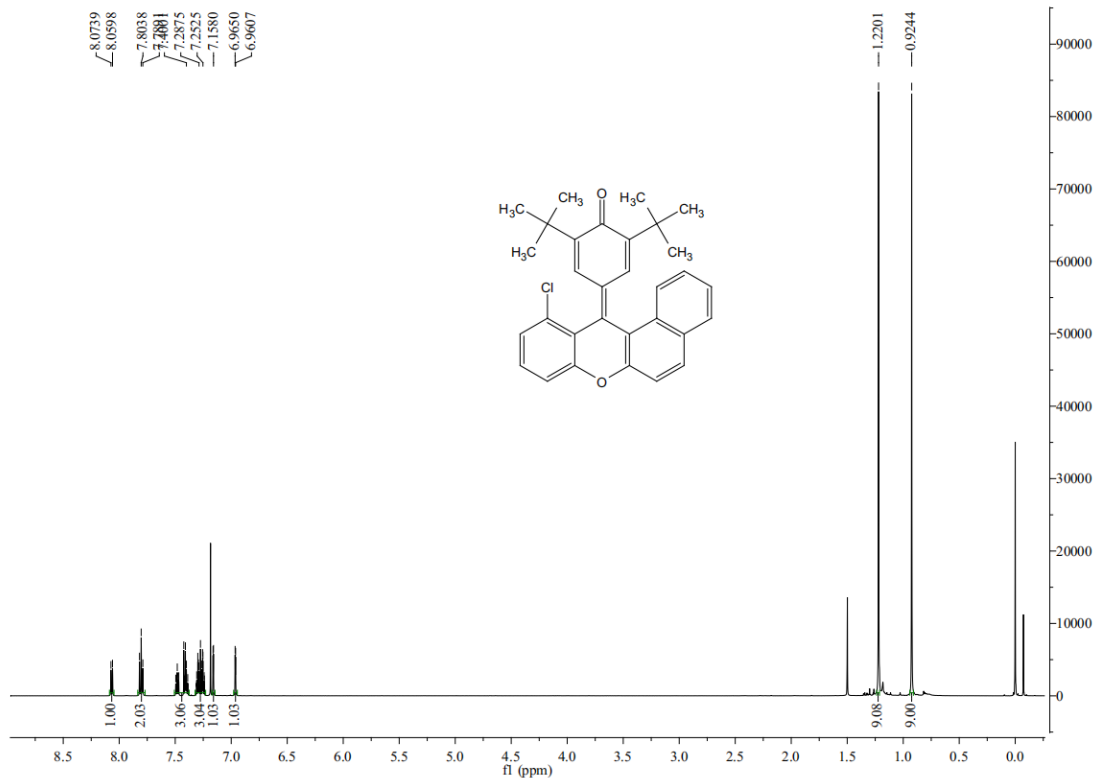
¹H NMR Spectrum of **3d** (CDCl₃, 600 MHz)



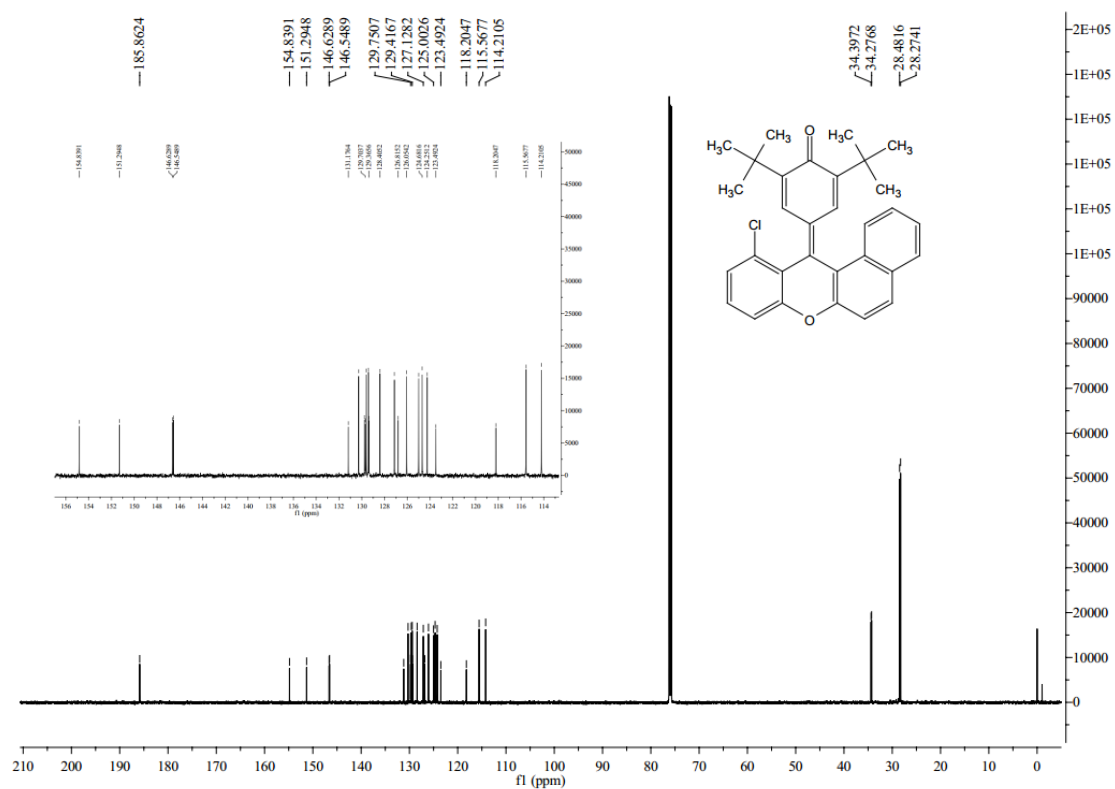
¹³C NMR Spectrum of **3d** (CDCl₃, 150 MHz)



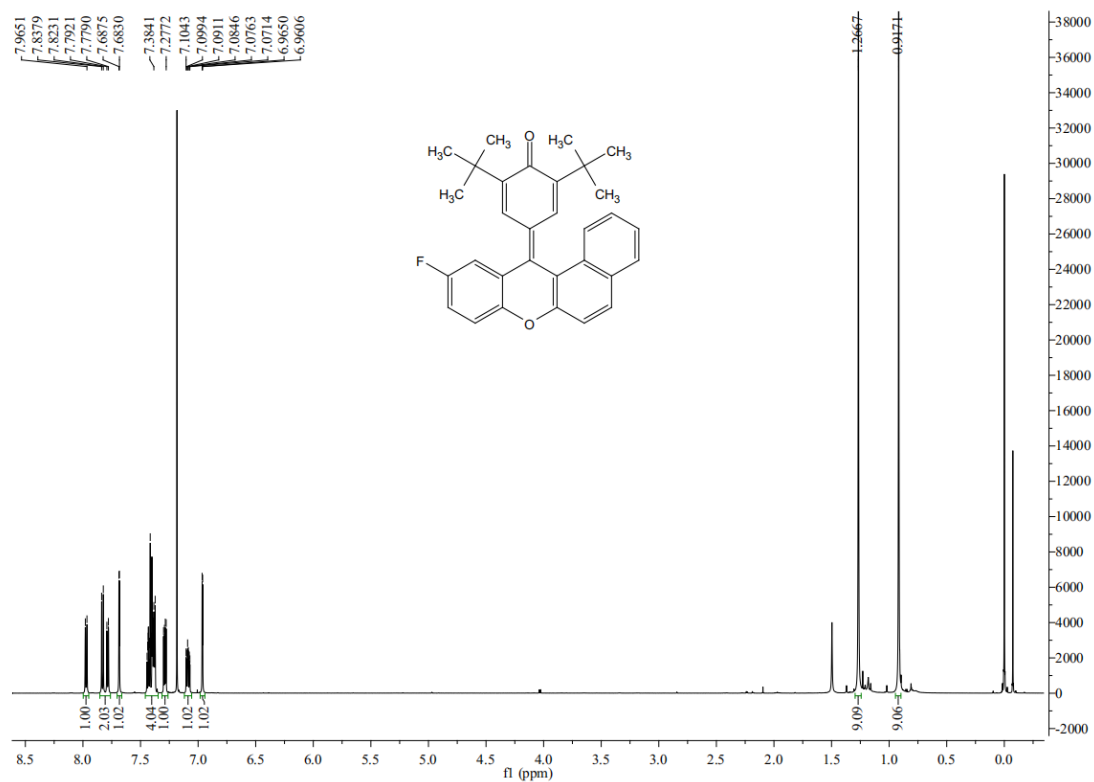
¹³C NMR Spectrum of 3e (CDCl₃, 150 MHz)



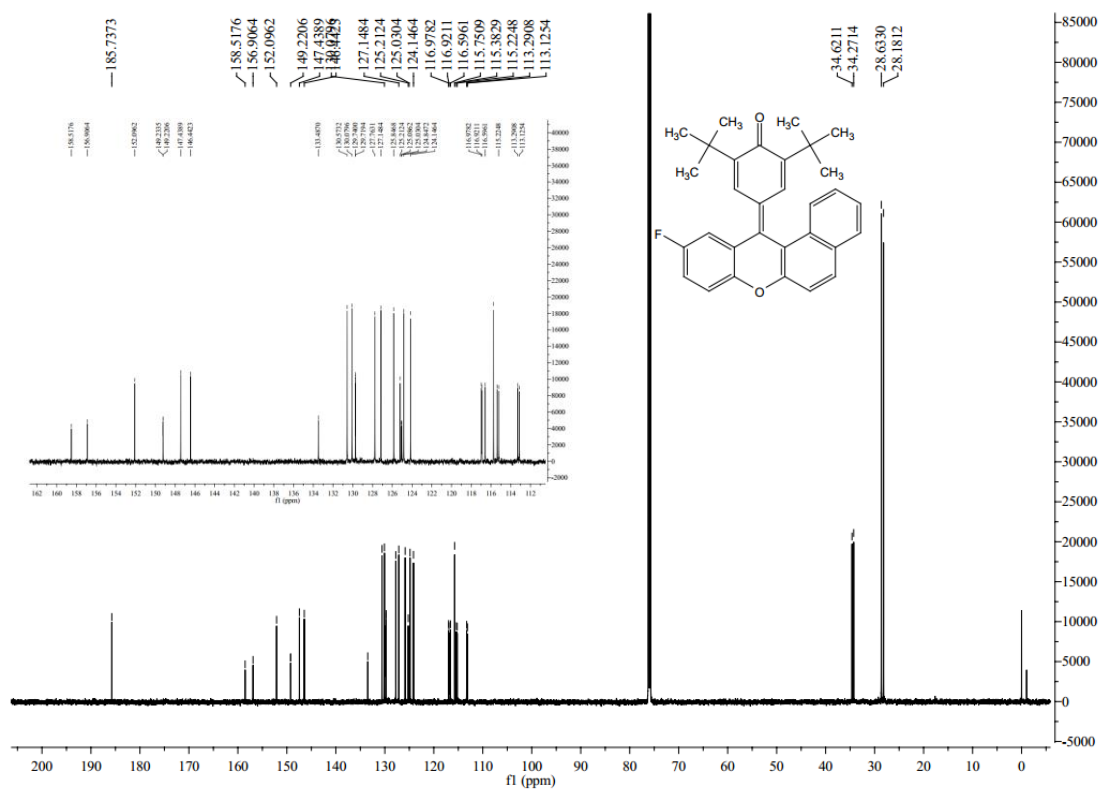
¹H NMR Spectrum of **3f (CDCl₃, 600 MHz)**



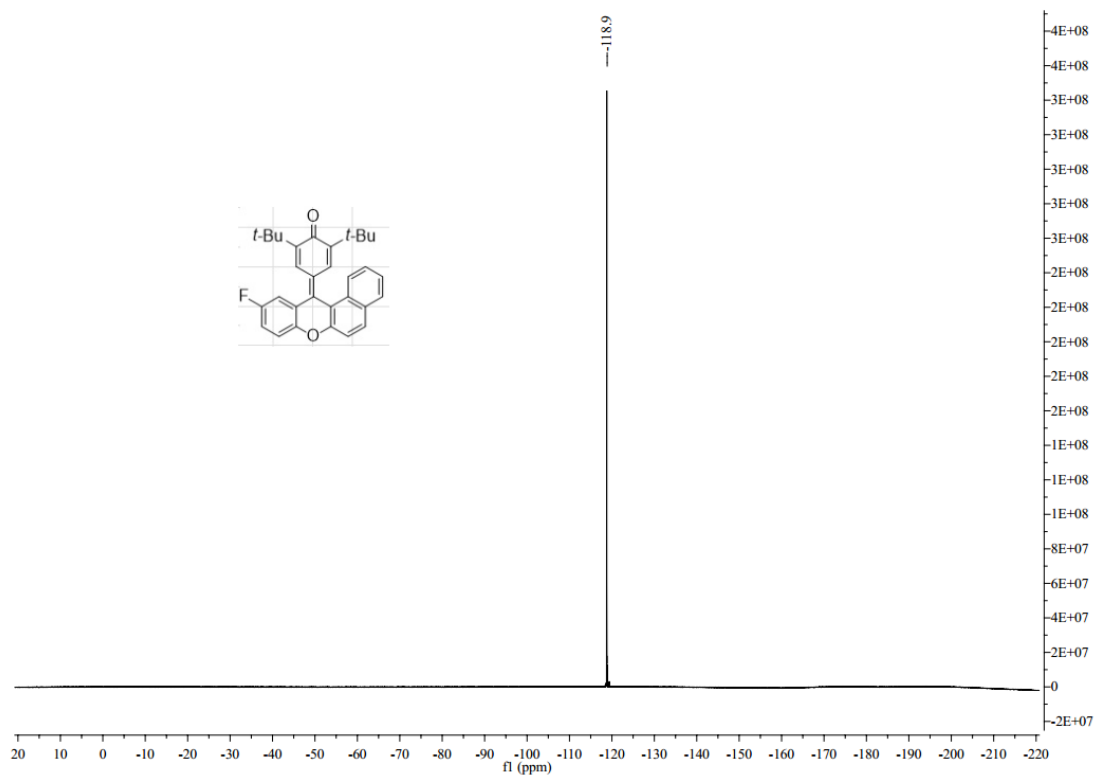
¹³C NMR Spectrum of **3f (CDCl₃, 150 MHz)**



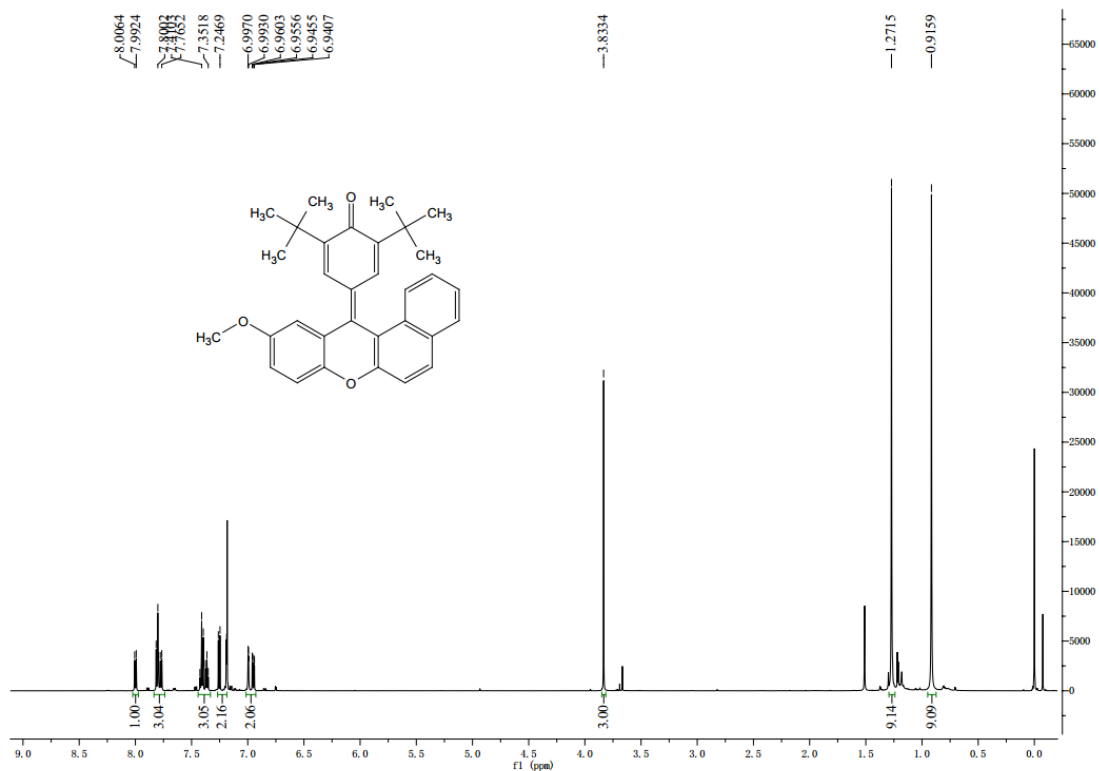
¹H NMR Spectrum of **3g (CDCl₃, 600 MHz)**



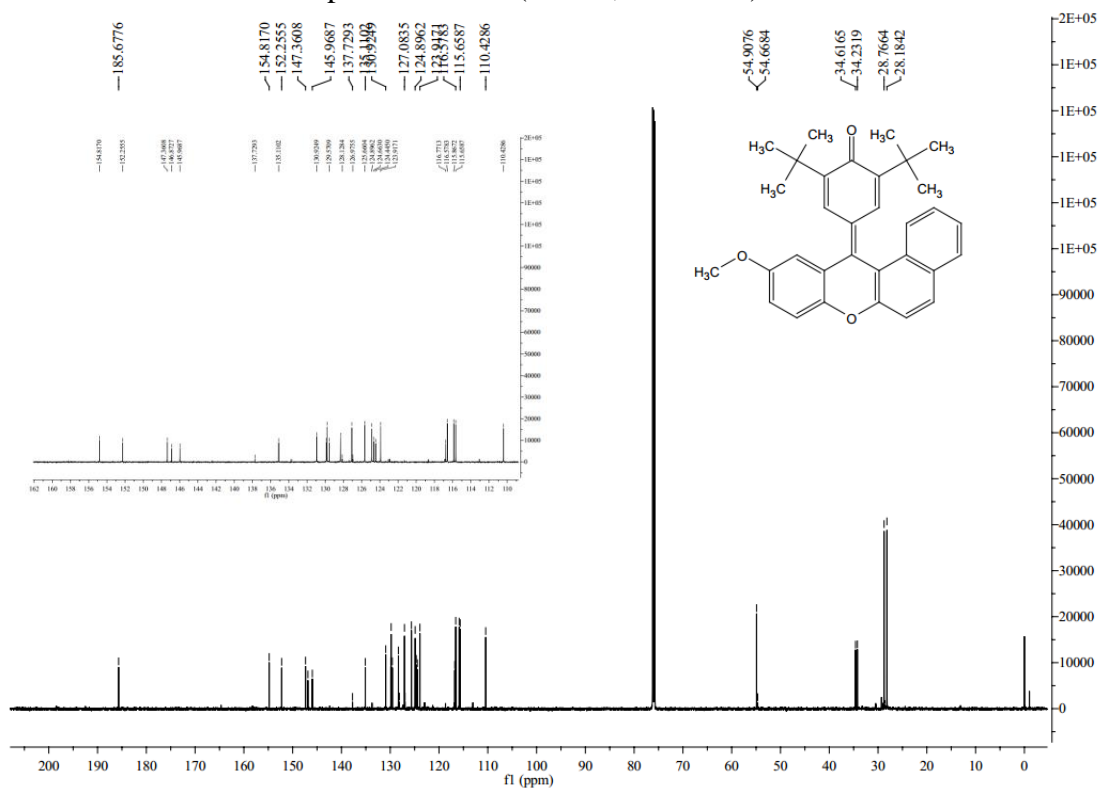
¹³C NMR Spectrum of **3g (CDCl₃, 150 MHz)**



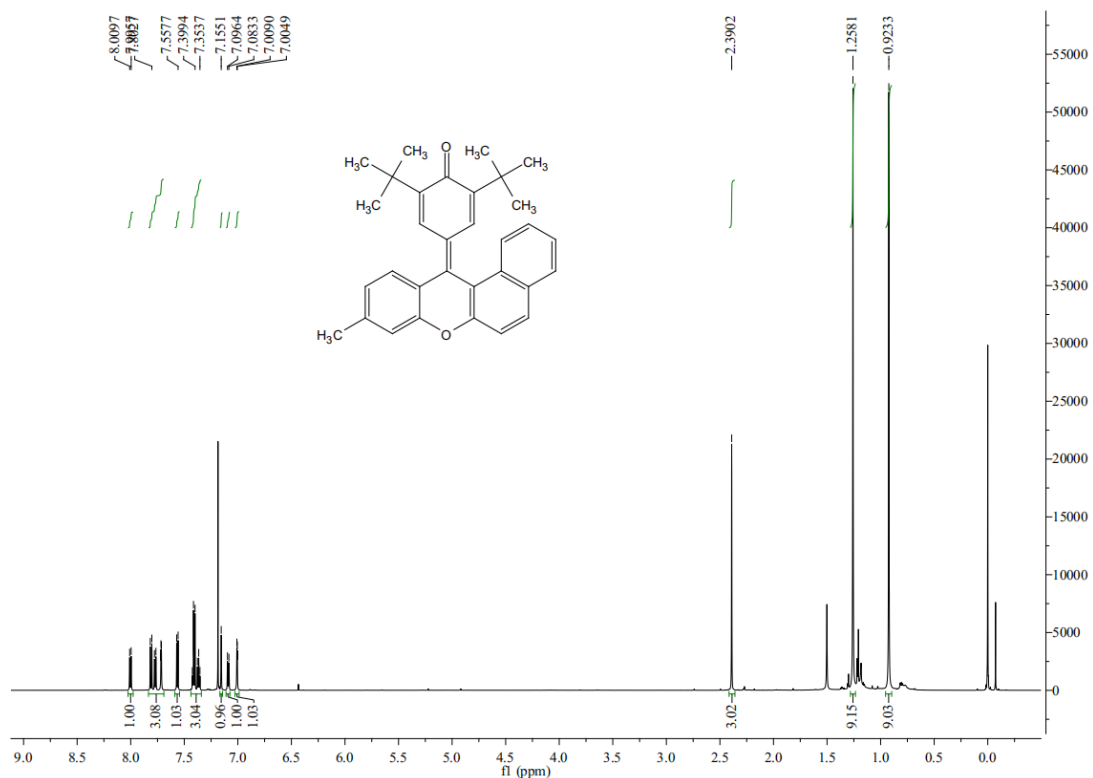
^{19}F NMR Spectrum of **3g** (CDCl_3 , 377 MHz)



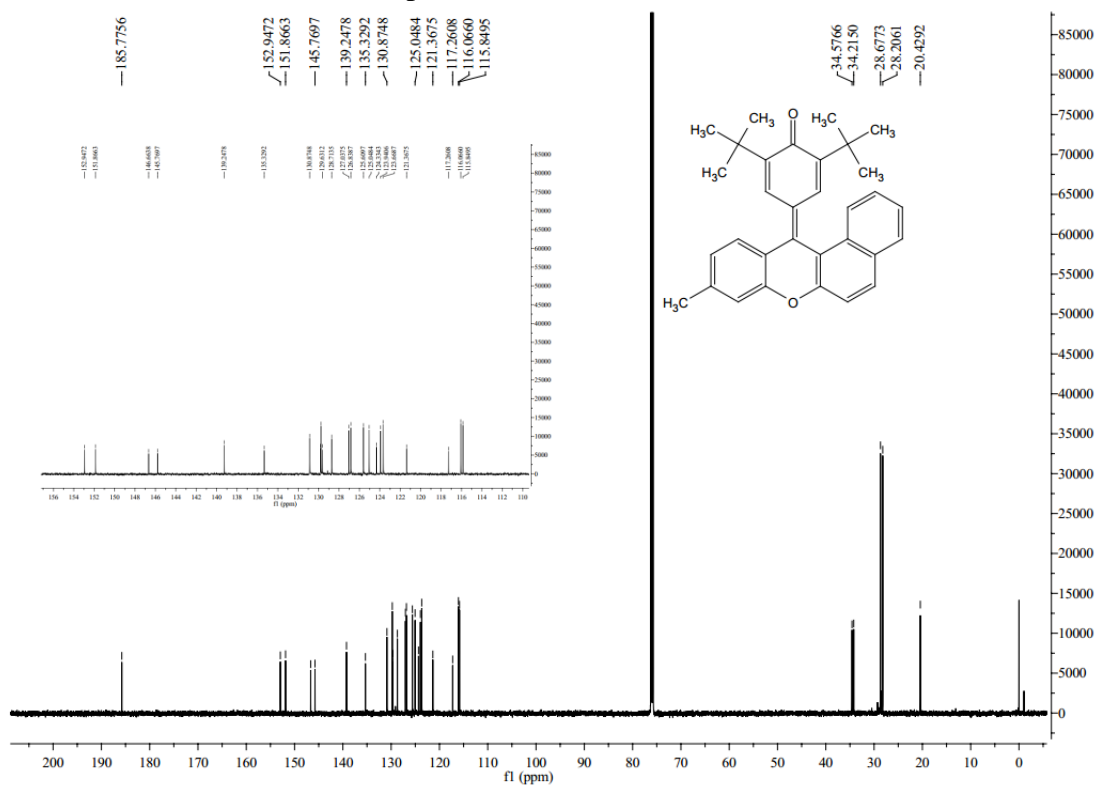
¹H NMR Spectrum of **3h (CDCl₃, 600 MHz)**



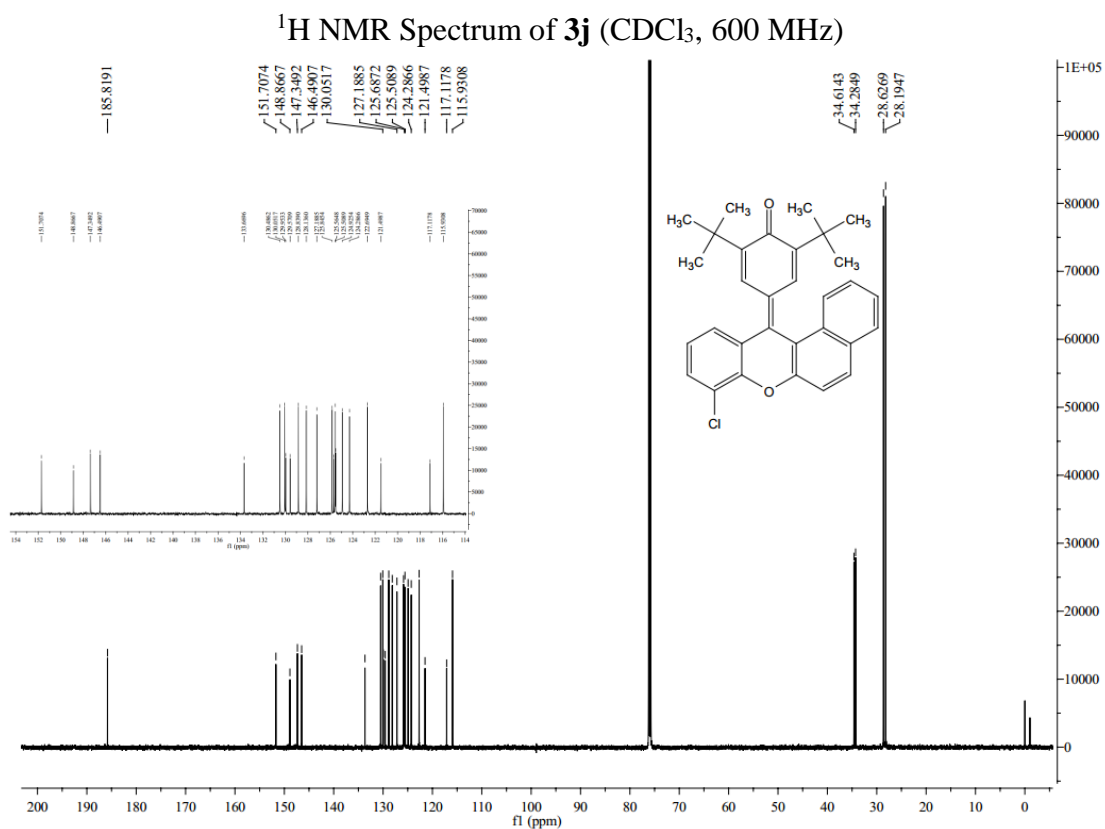
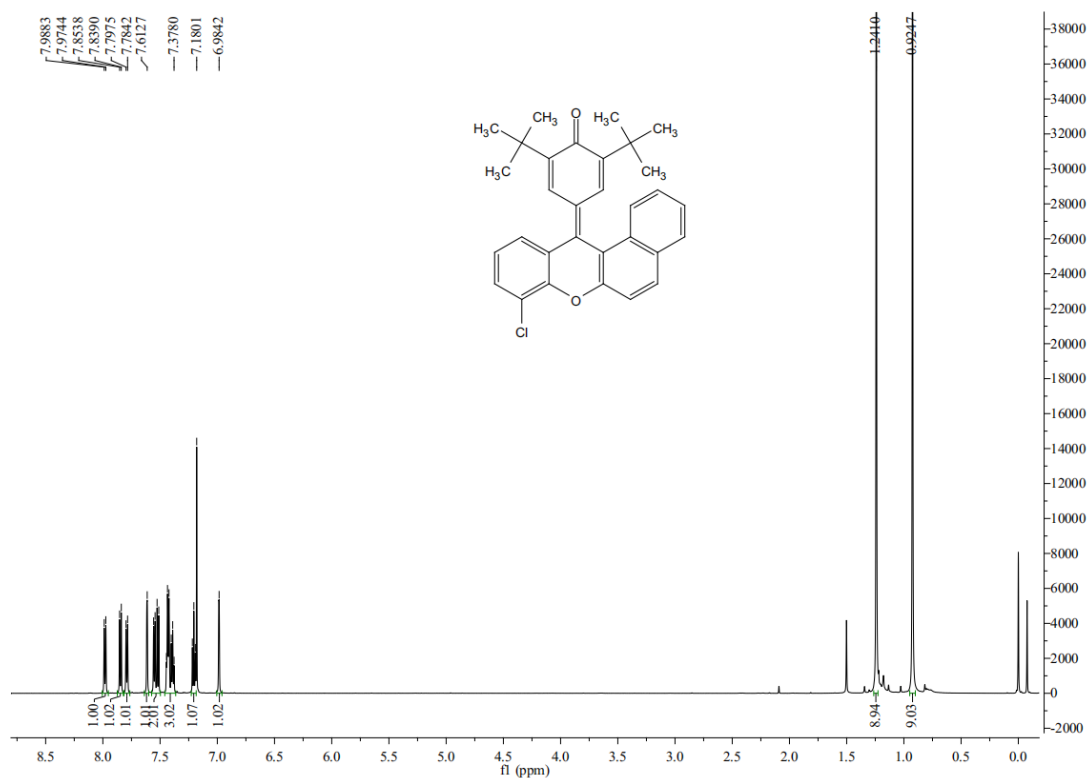
¹³C NMR Spectrum of **3h (CDCl₃, 150 MHz)**



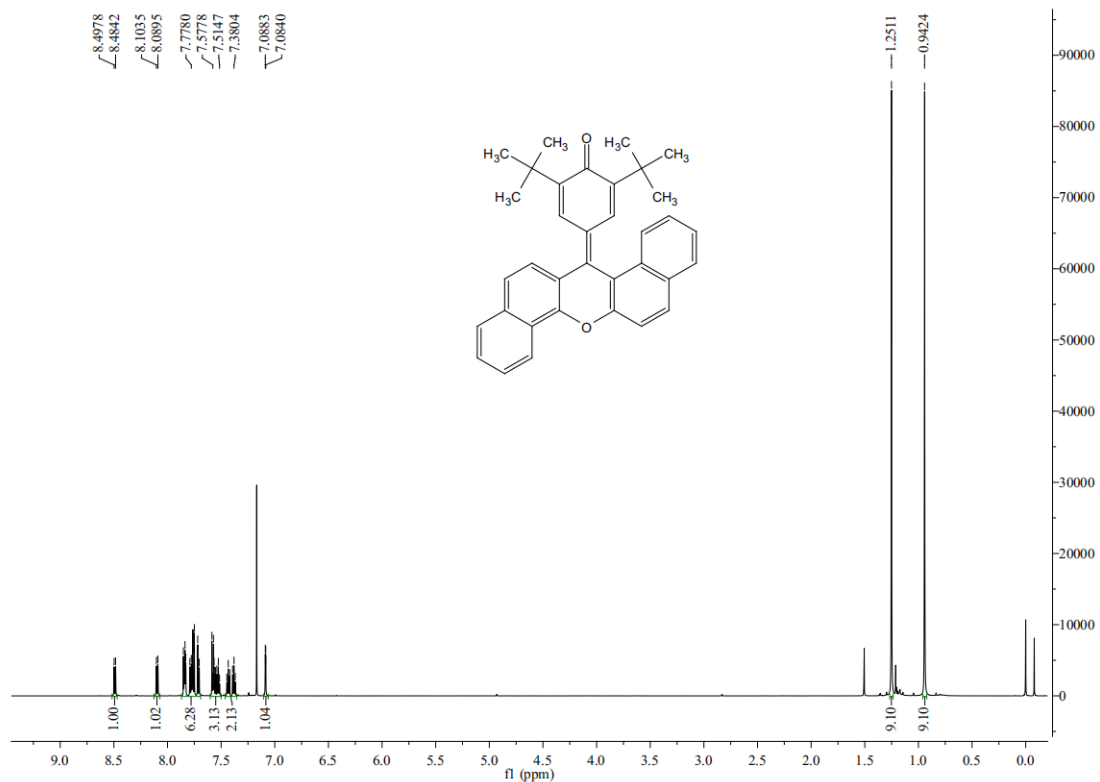
¹H NMR Spectrum of 3i (CDCl₃, 600 MHz)



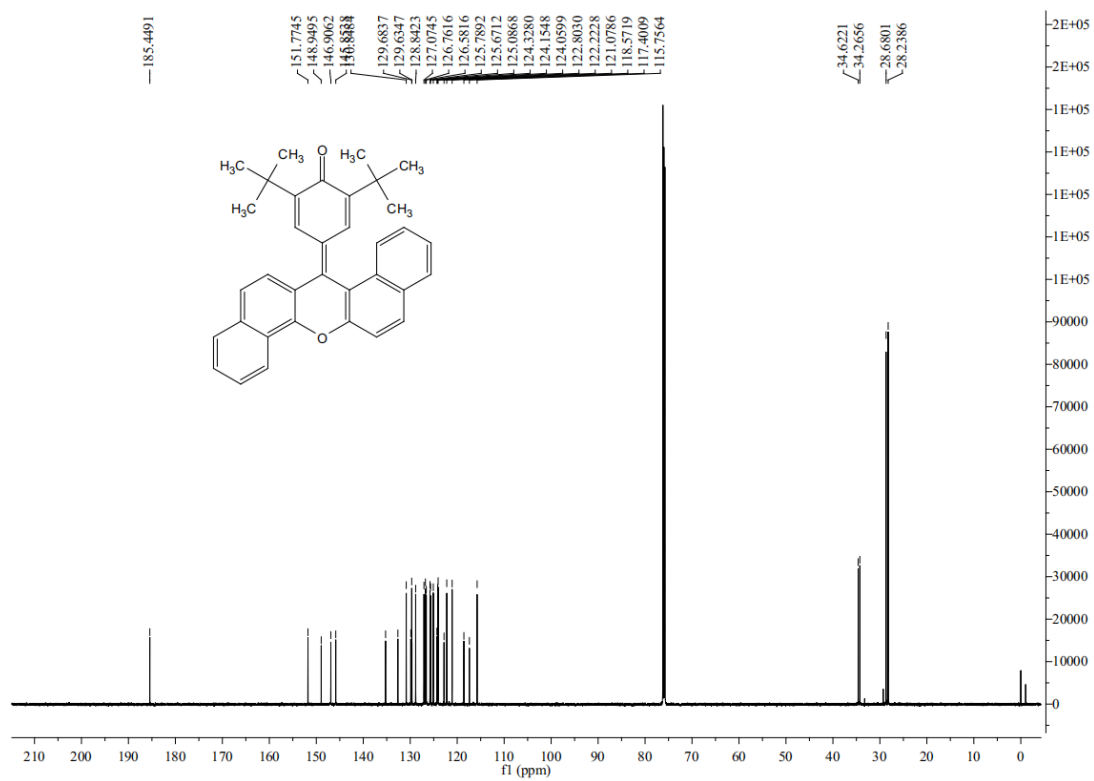
¹³C NMR Spectrum of 3i (CDCl₃, 150 MHz)



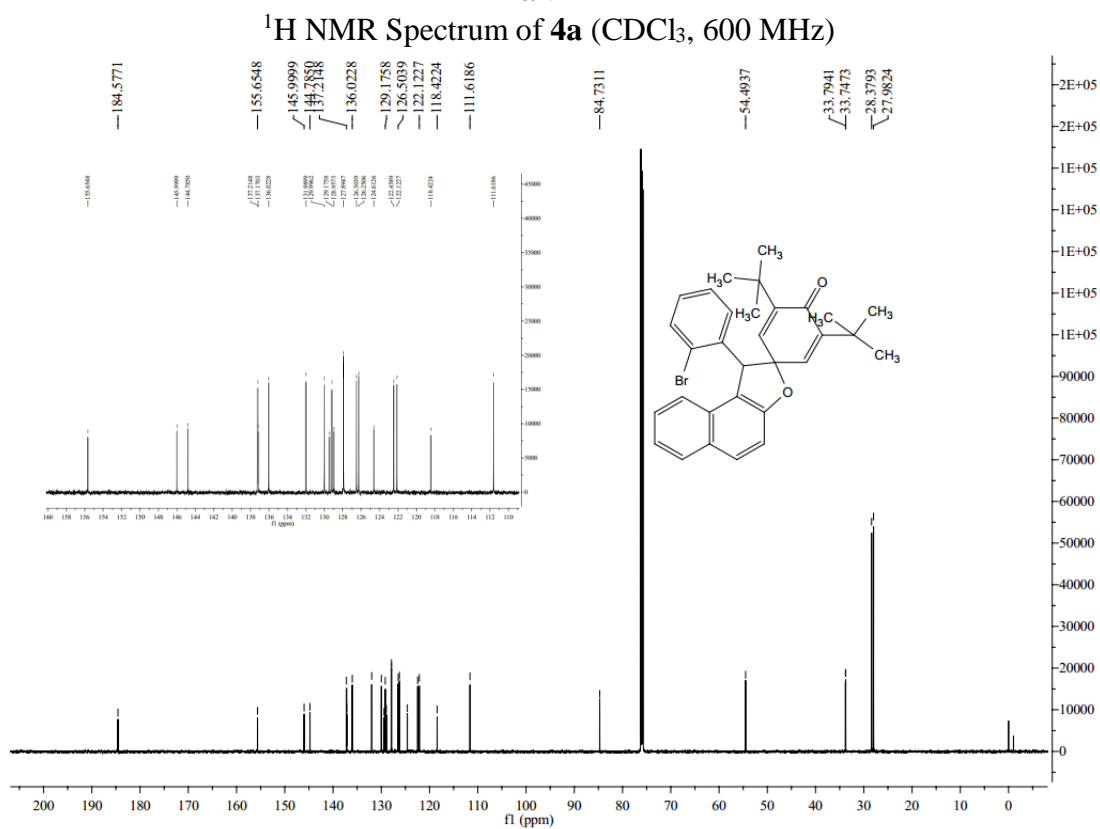
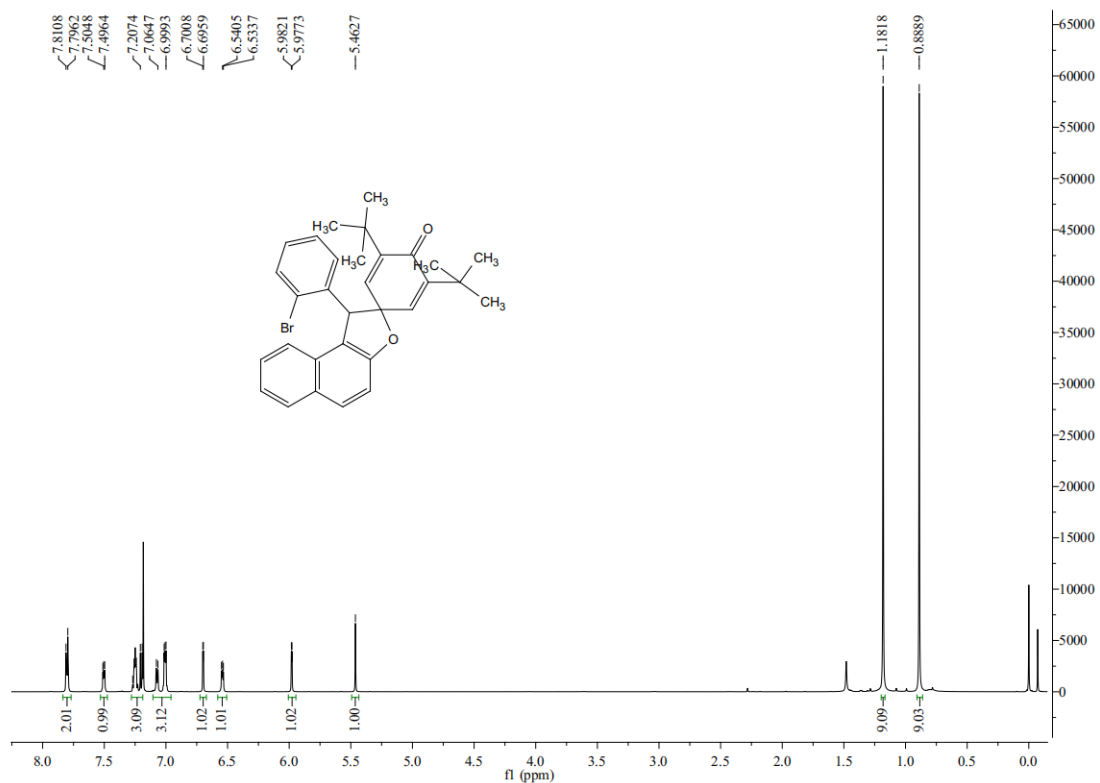
¹³C NMR Spectrum of 3j (CDCl₃, 150 MHz)



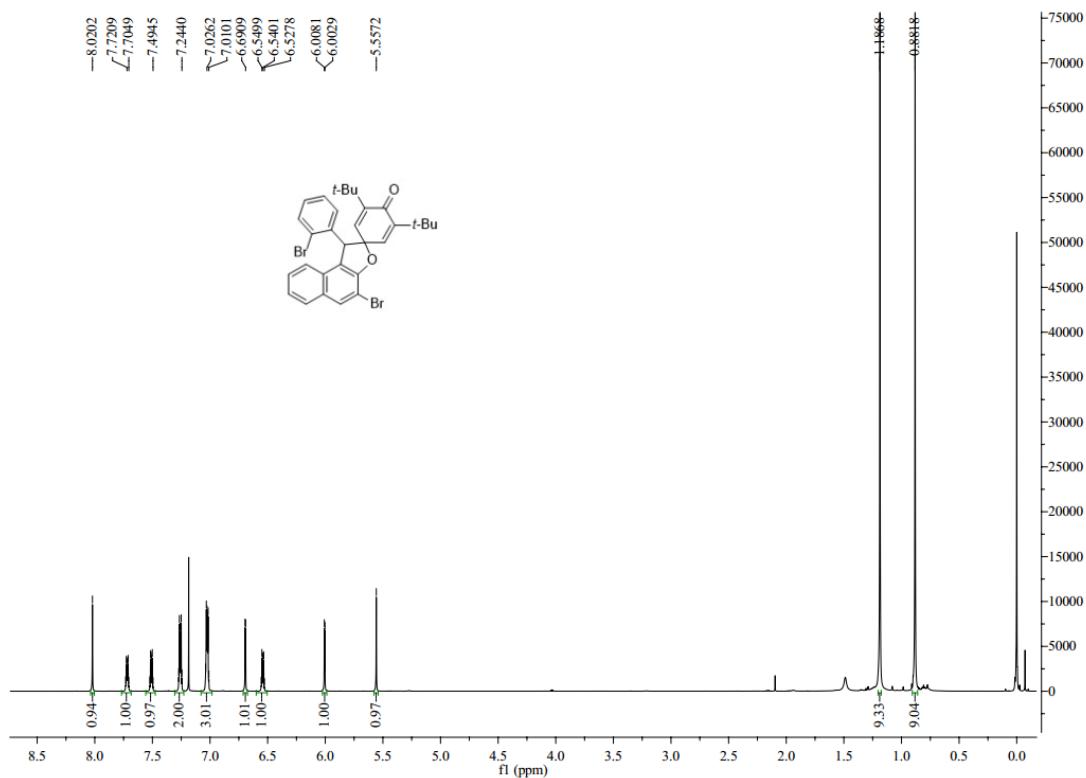
¹H NMR Spectrum of **3k** (CDCl₃, 600 MHz)



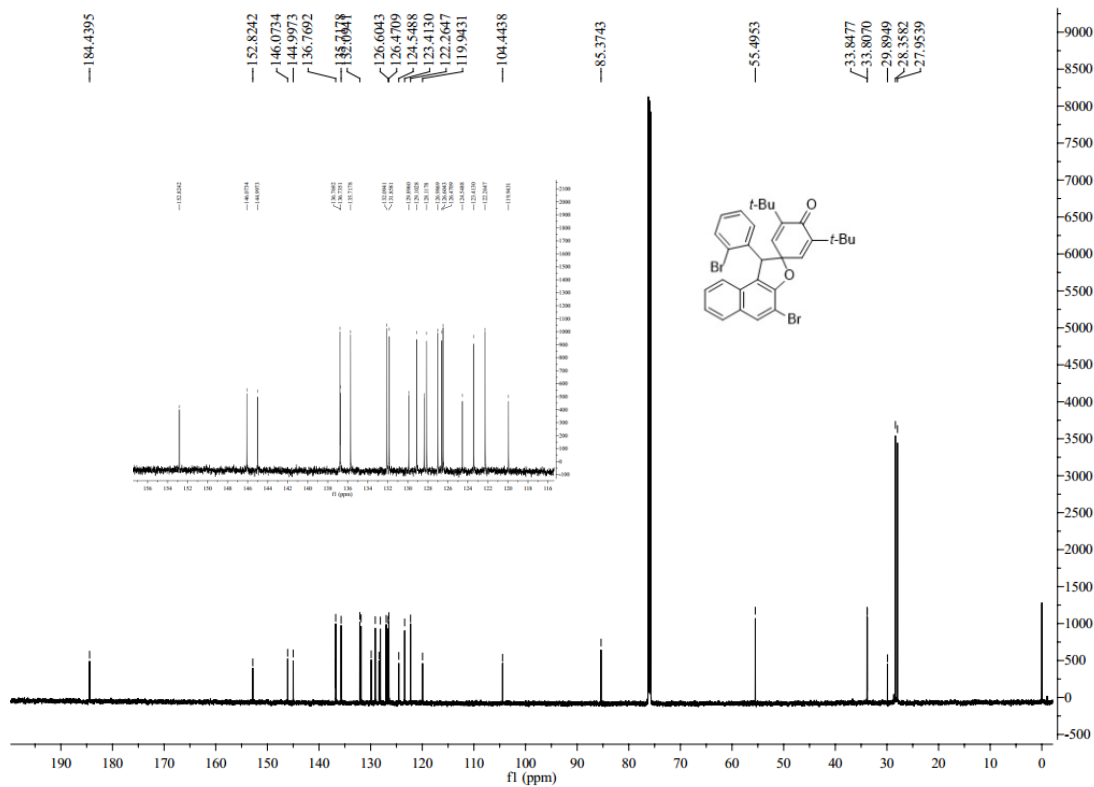
¹³C NMR Spectrum of **3k** (CDCl₃, 150 MHz)



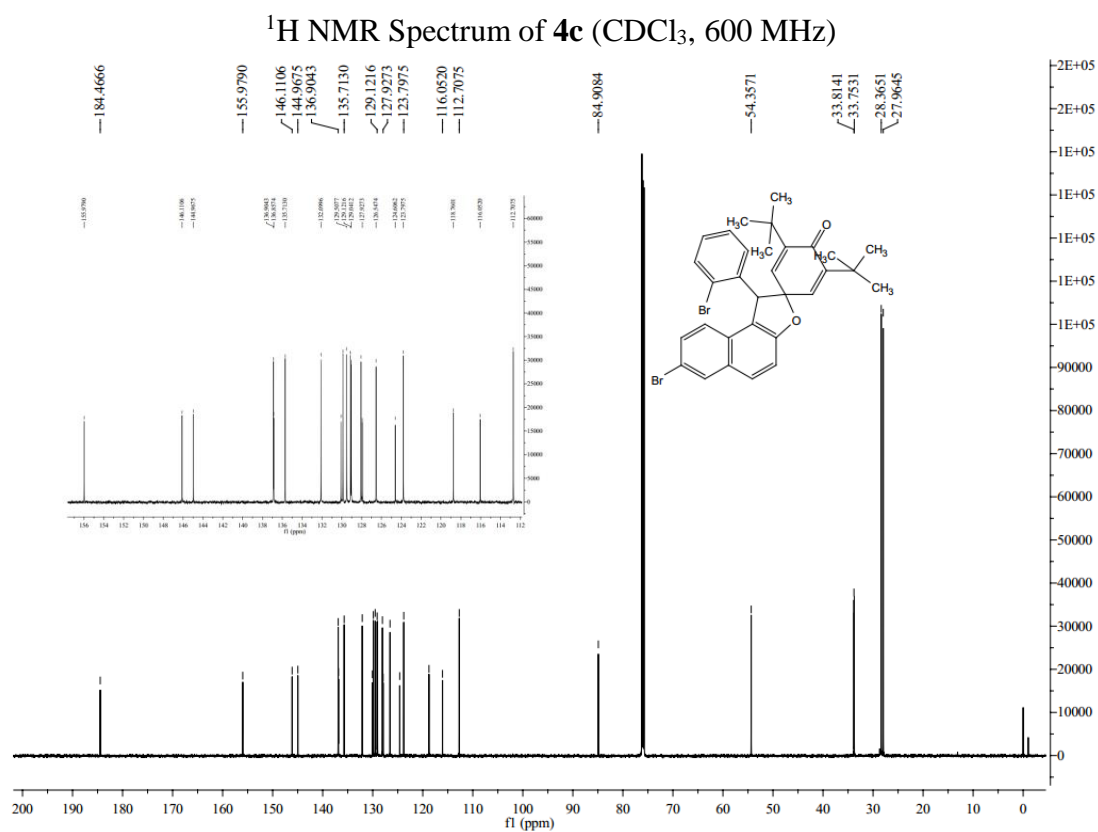
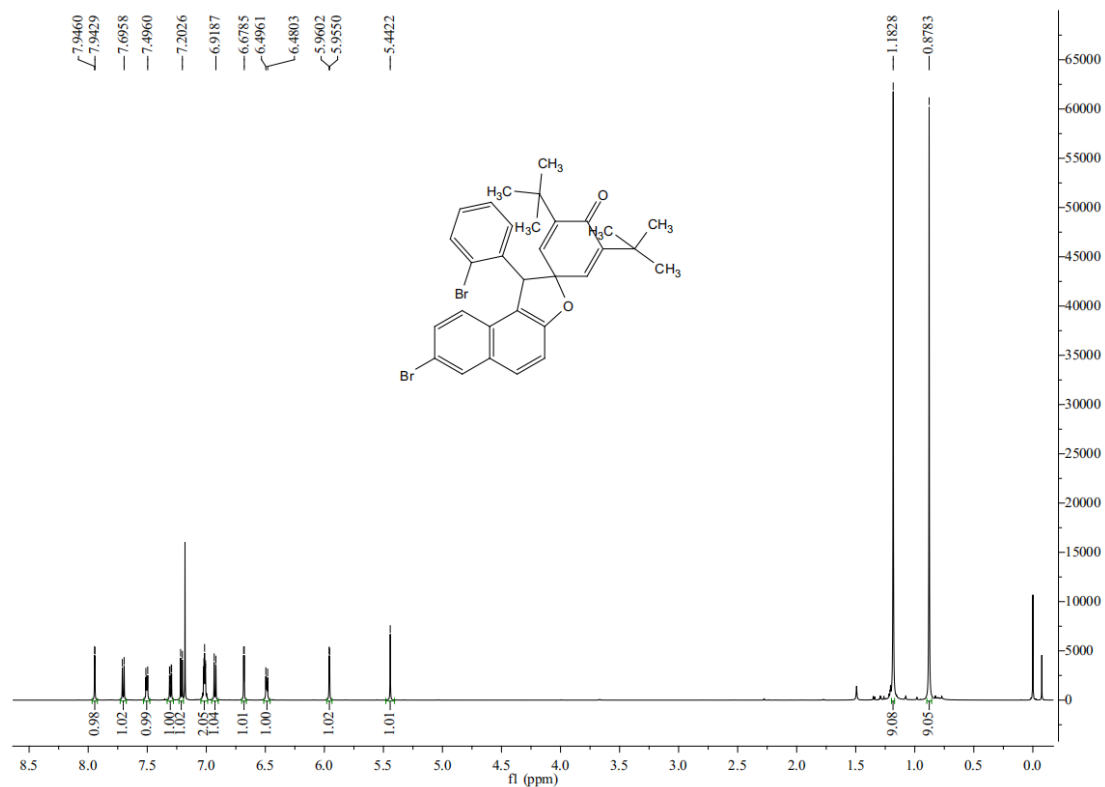
¹³C NMR Spectrum of 4a (CDCl₃, 150 MHz)



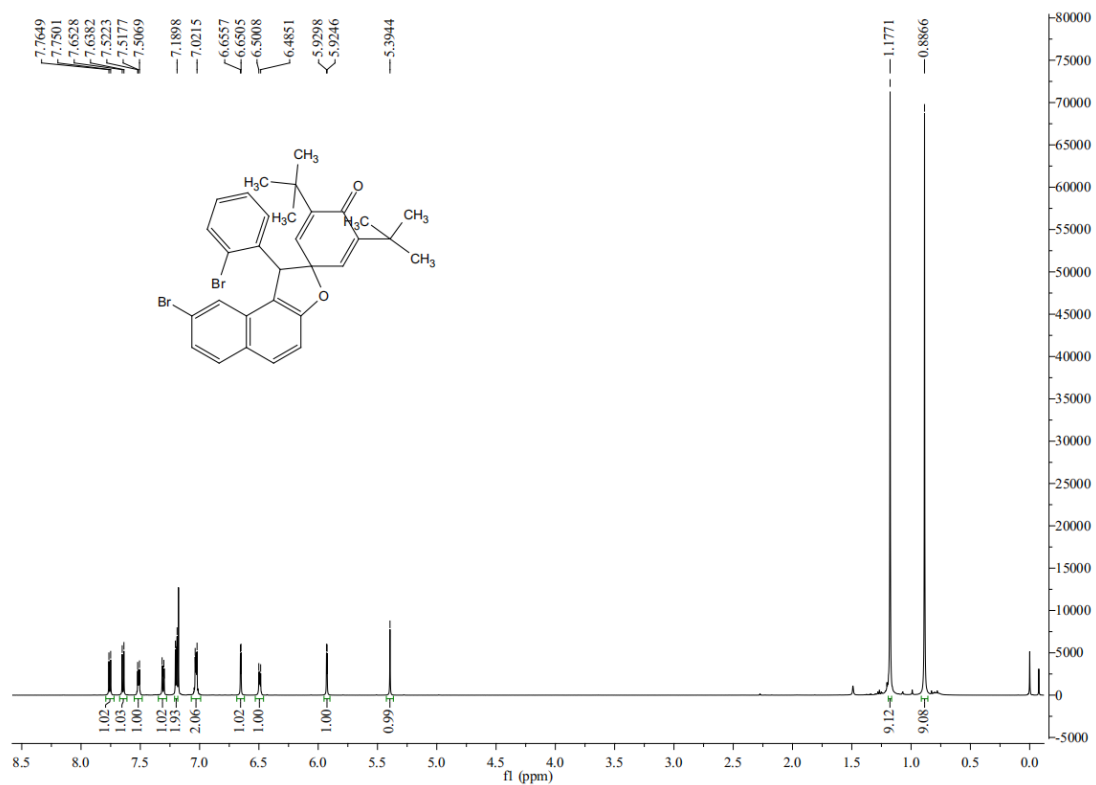
¹H NMR Spectrum of **4b** (CDCl₃, 600 MHz)



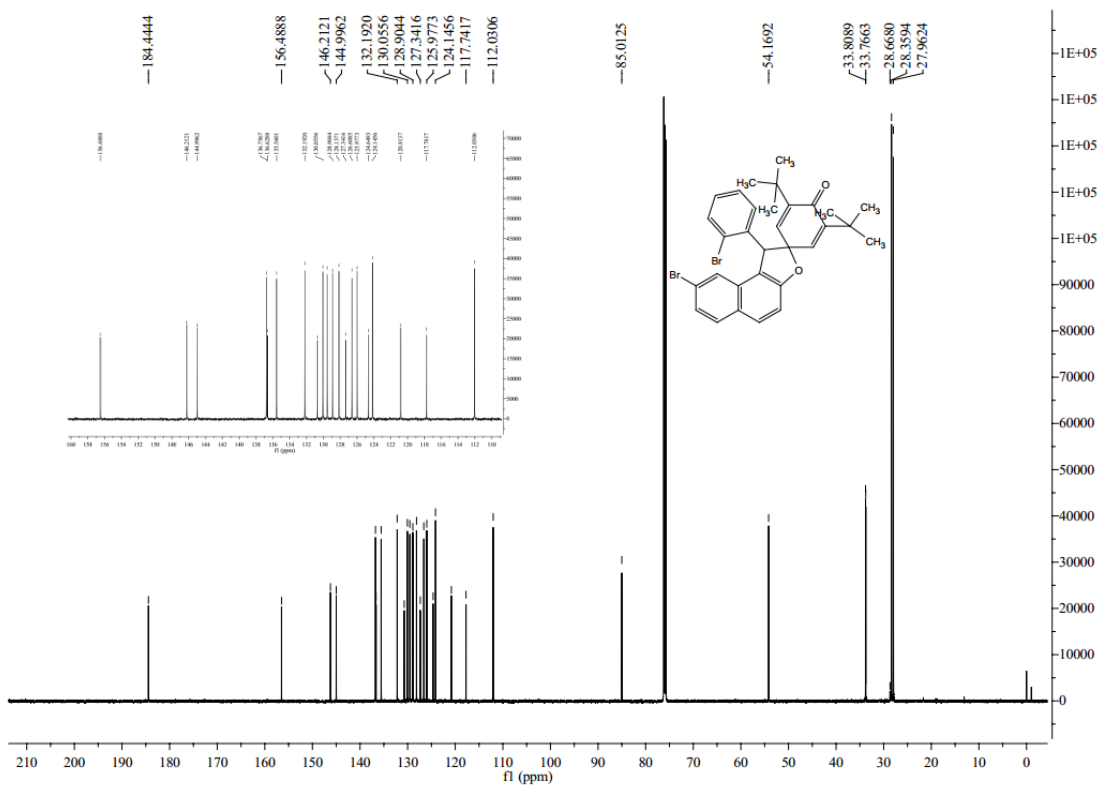
¹³C NMR Spectrum of **4b** (CDCl₃, 150 MHz)



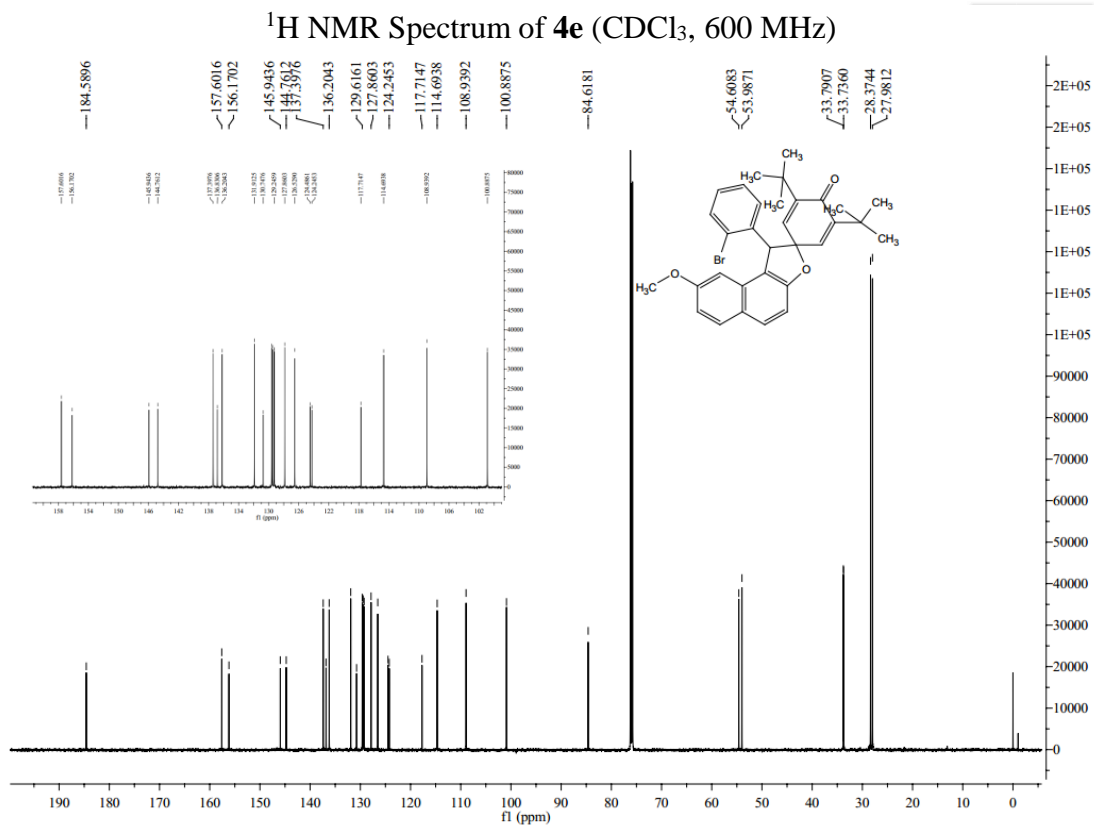
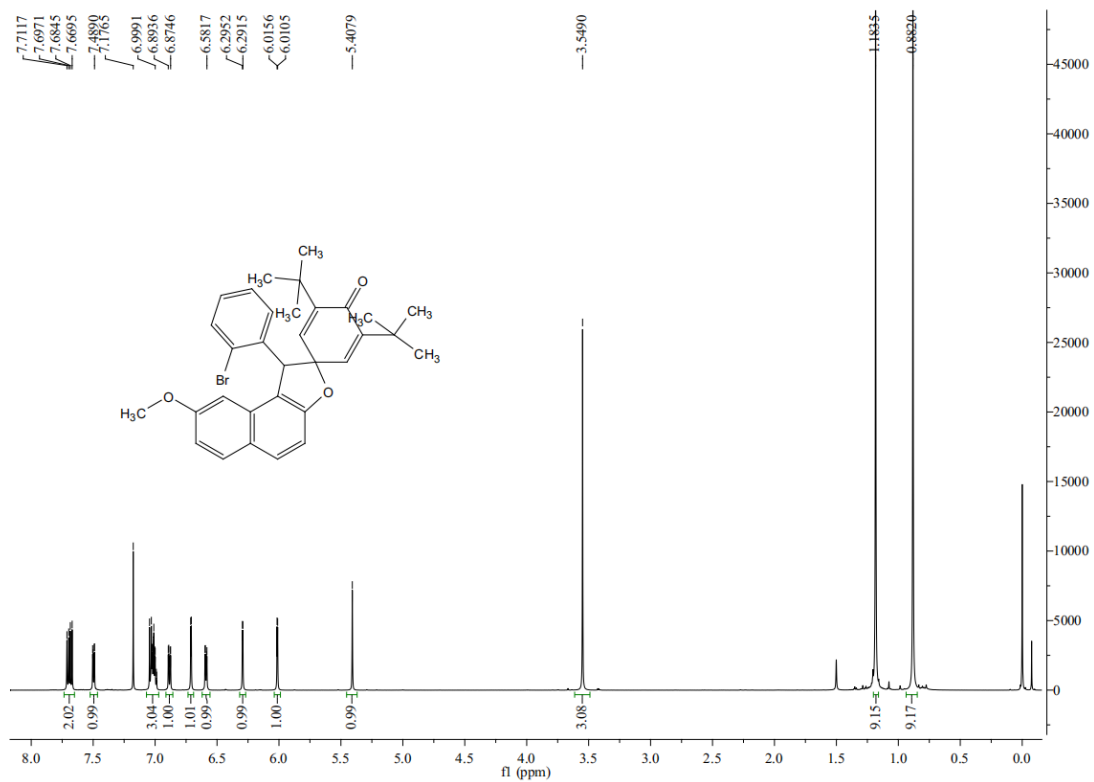
¹³C NMR Spectrum of 4c (CDCl₃, 150 MHz)



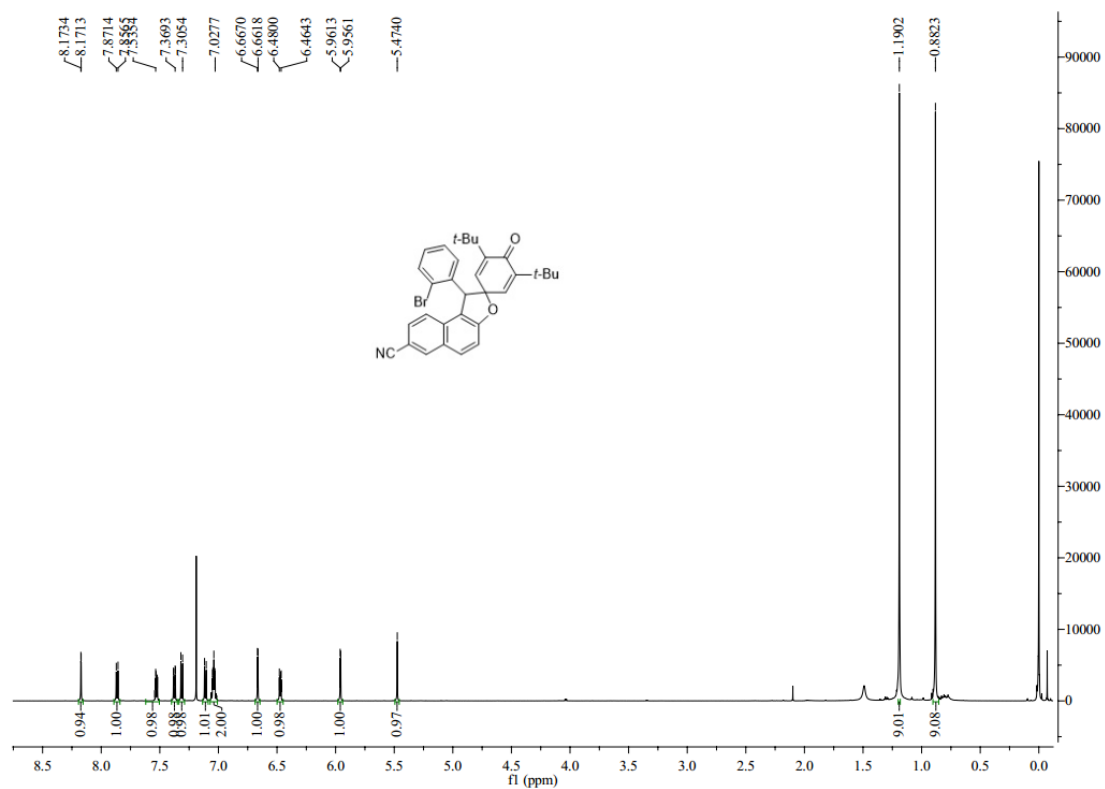
¹H NMR Spectrum of **4d (CDCl₃, 600 MHz)**



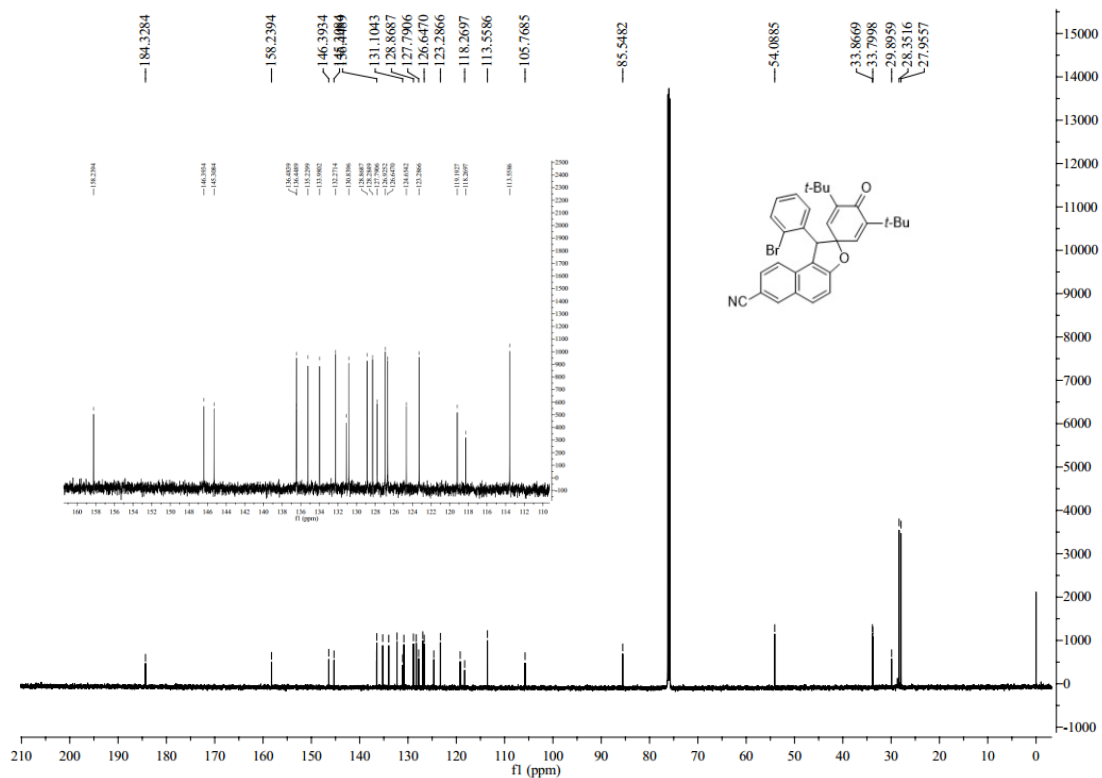
¹³C NMR Spectrum of **4d (CDCl₃, 150 MHz)**

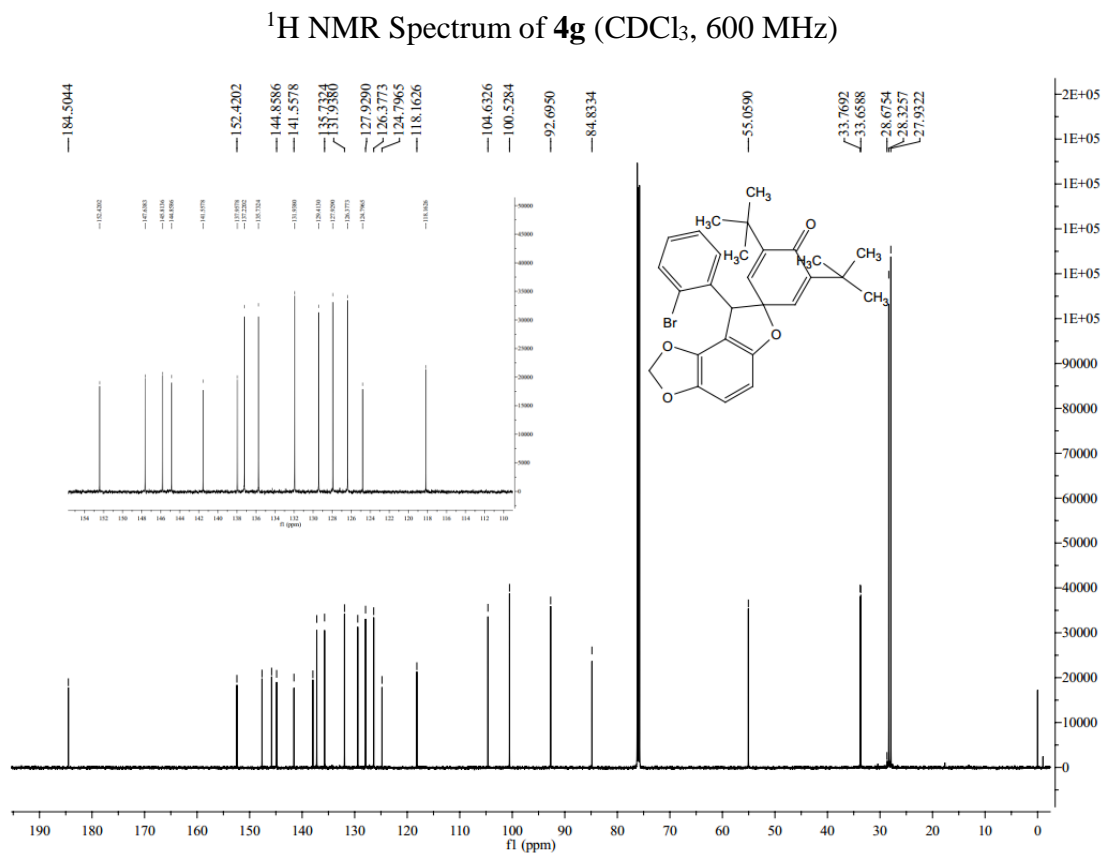
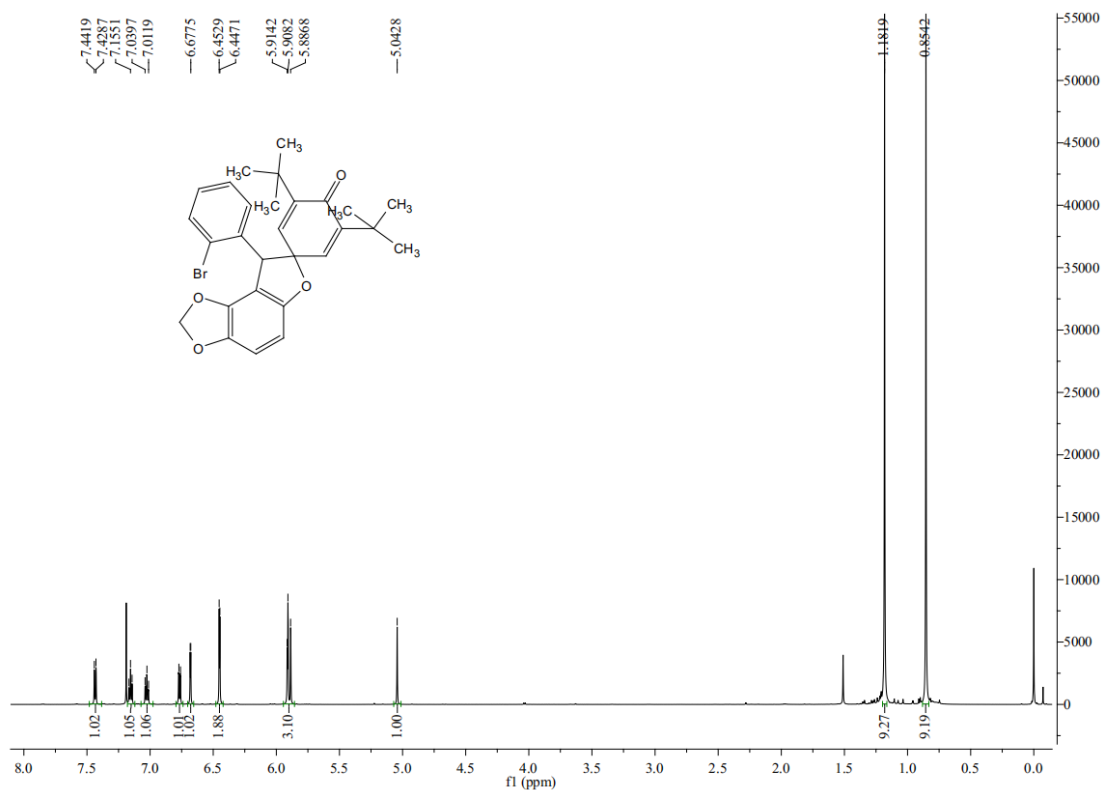


¹³C NMR Spectrum of 4e (CDCl₃, 150 MHz)

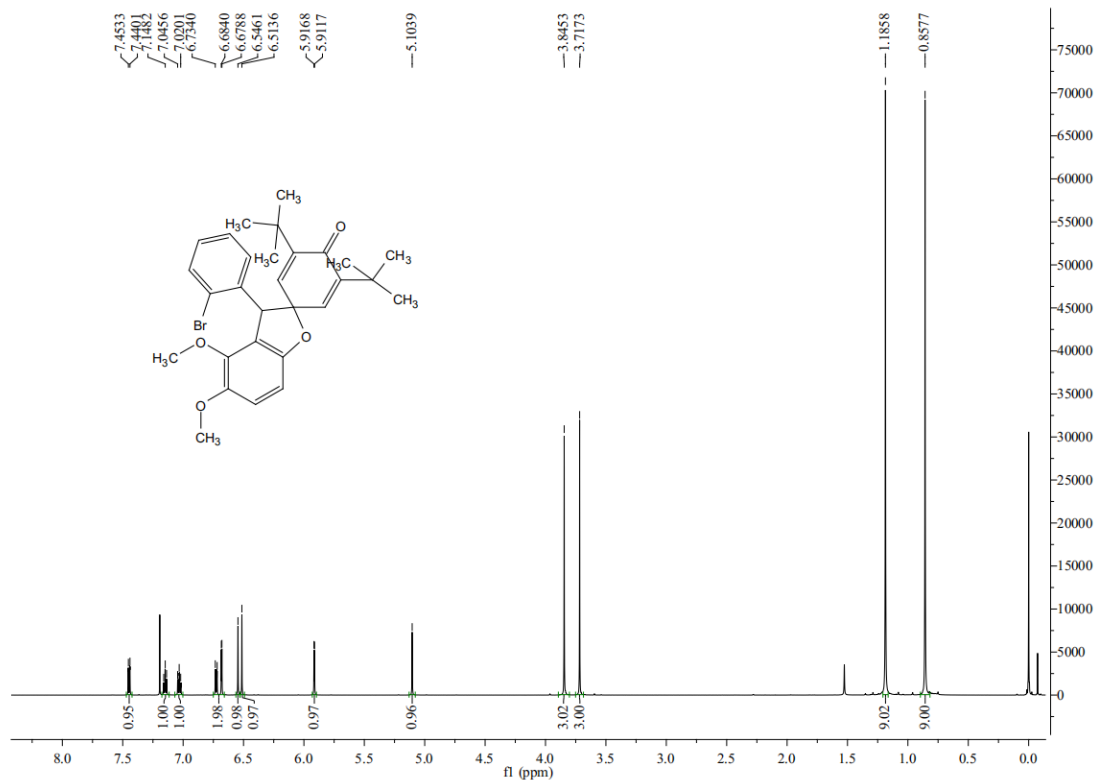


¹H NMR Spectrum of **4f** (CDCl₃, 600 MHz)

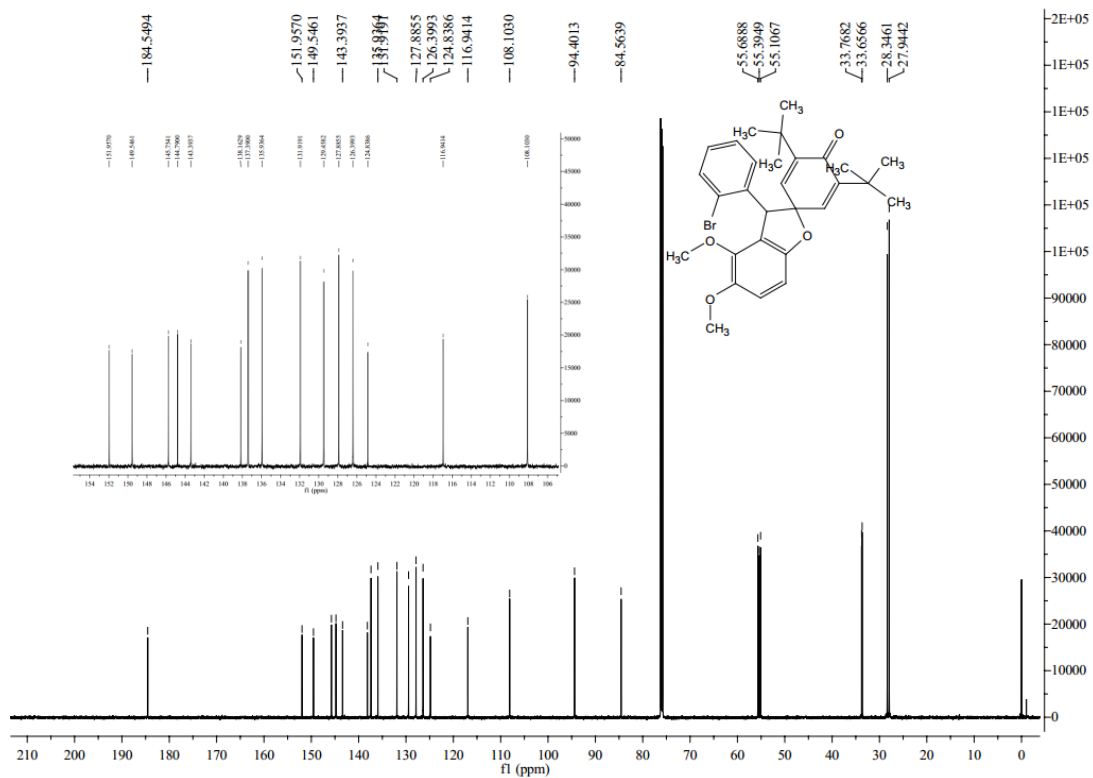




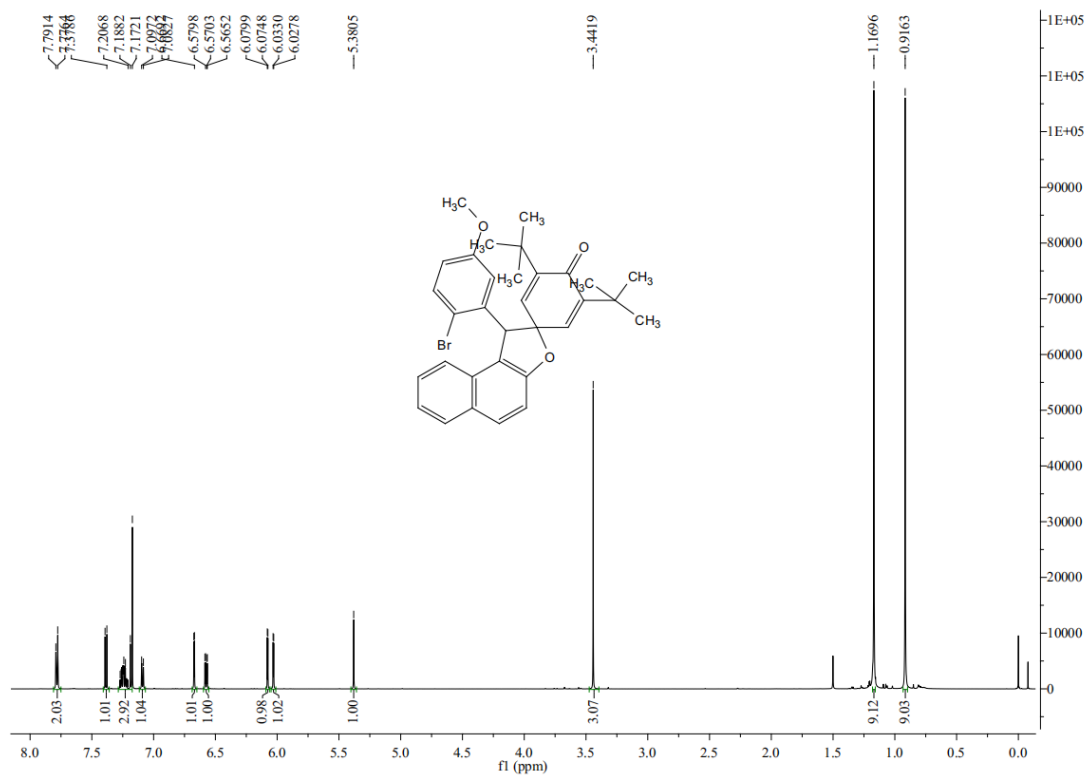
¹³C NMR Spectrum of **4g** (CDCl₃, 150 MHz)



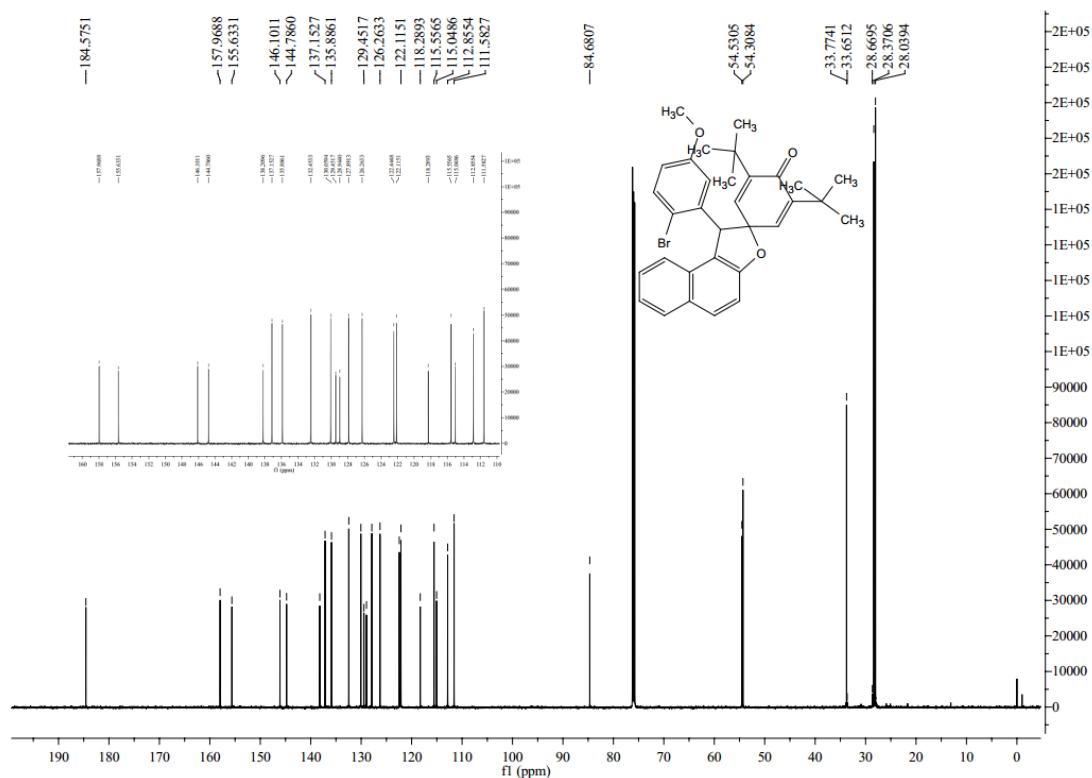
¹H NMR Spectrum of 4h (CDCl₃, 600 MHz)



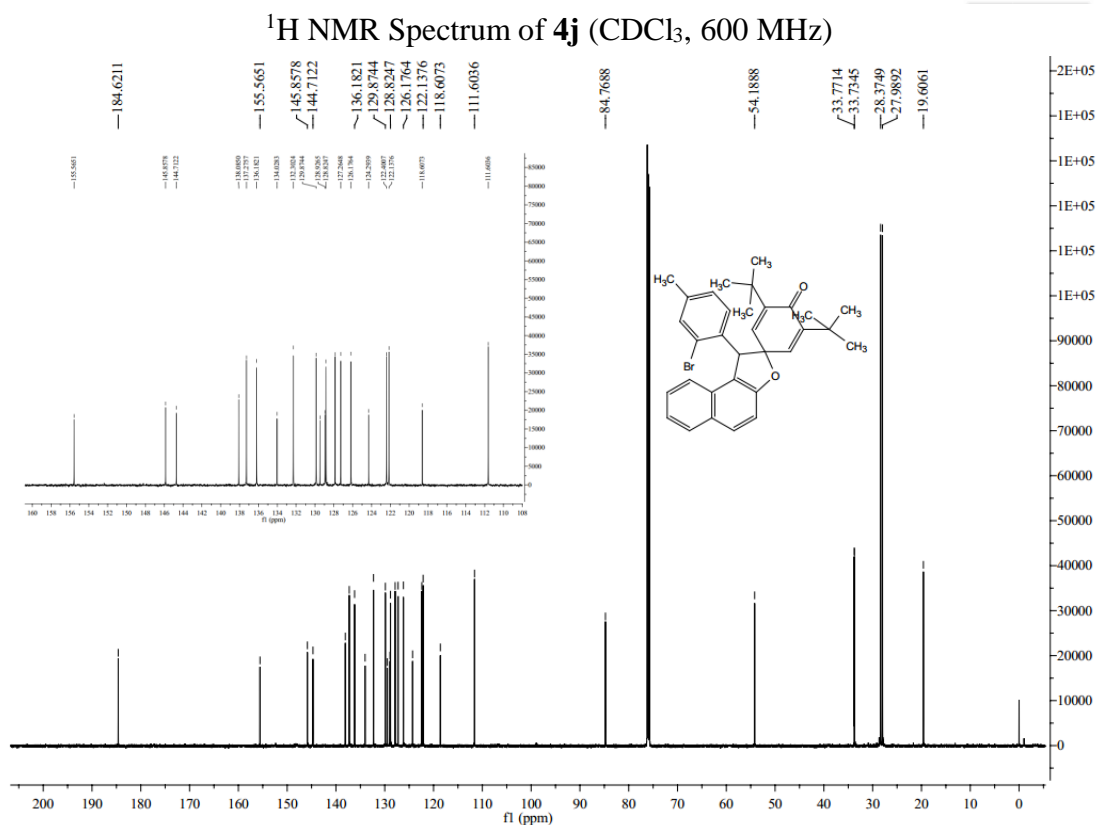
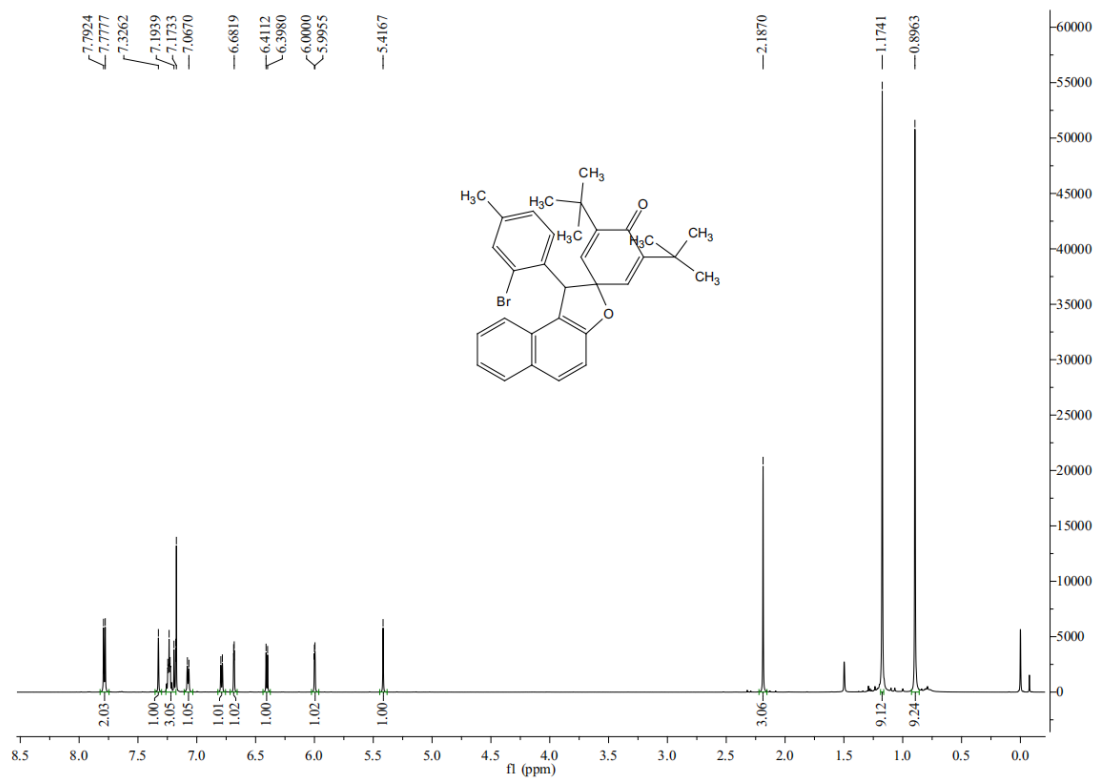
¹³C NMR Spectrum of 4h (CDCl₃, 150 MHz)



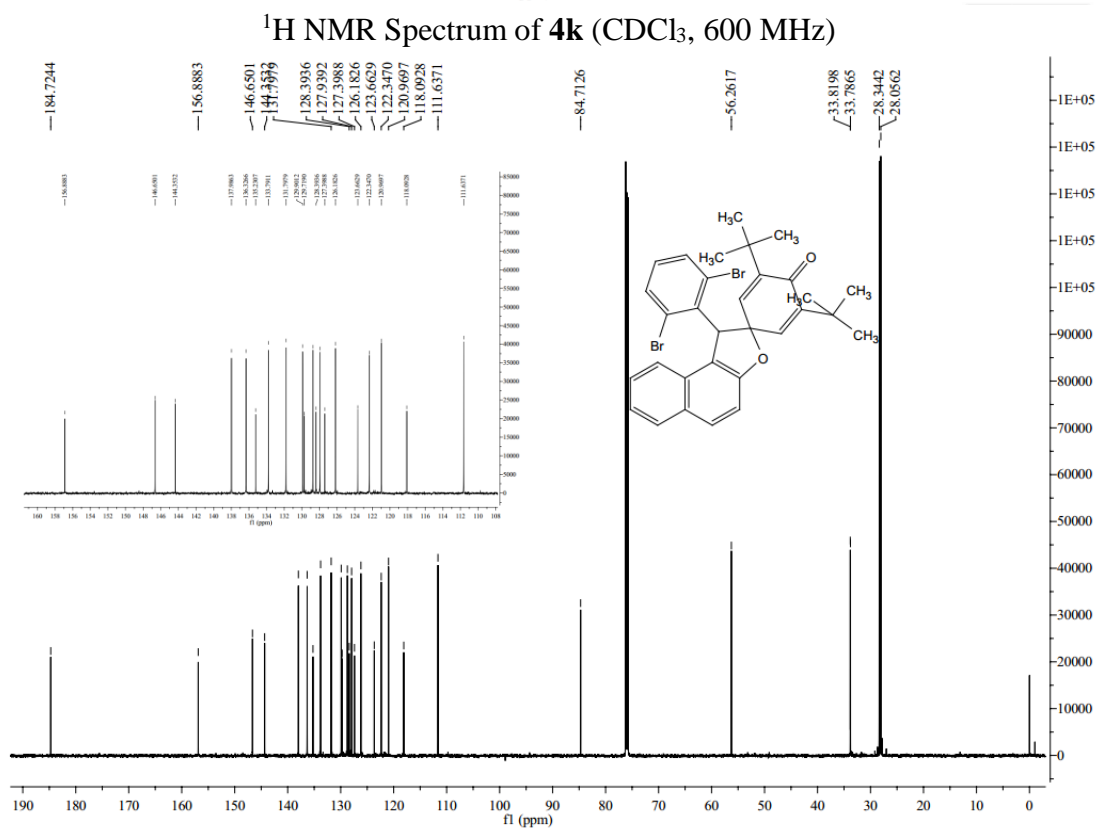
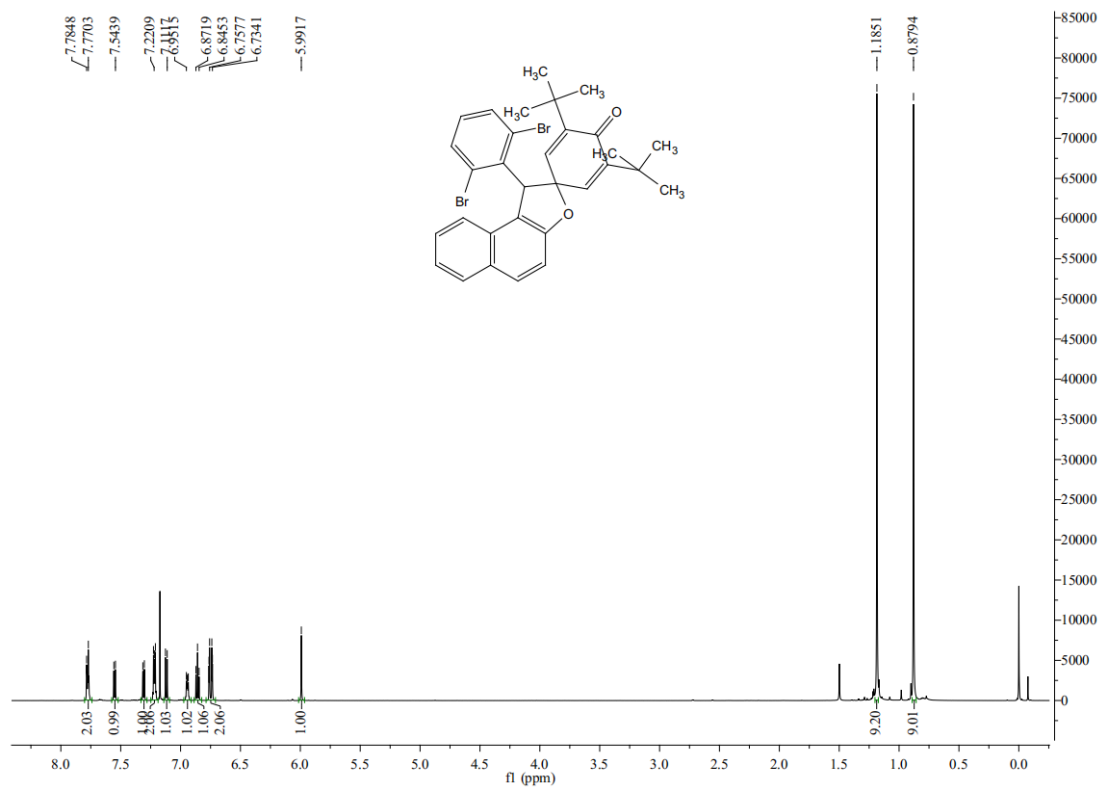
¹H NMR Spectrum of **4i** (CDCl₃, 600 MHz)



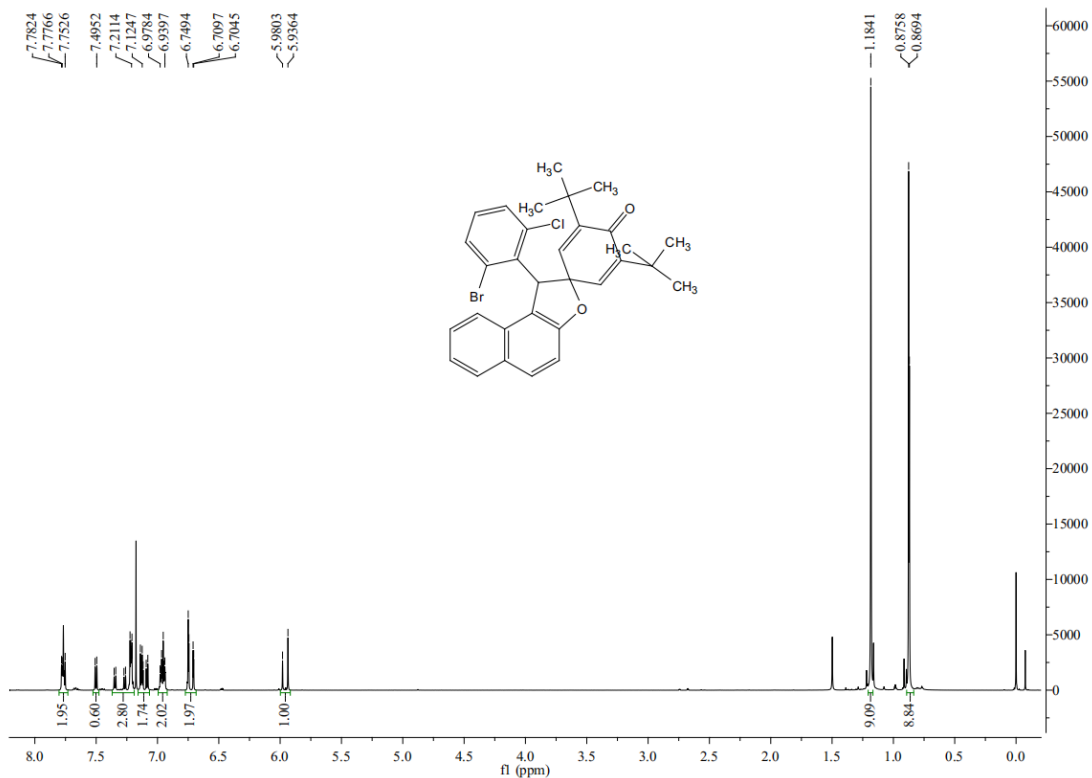
¹³C NMR Spectrum of **4i** (CDCl₃, 150 MHz)



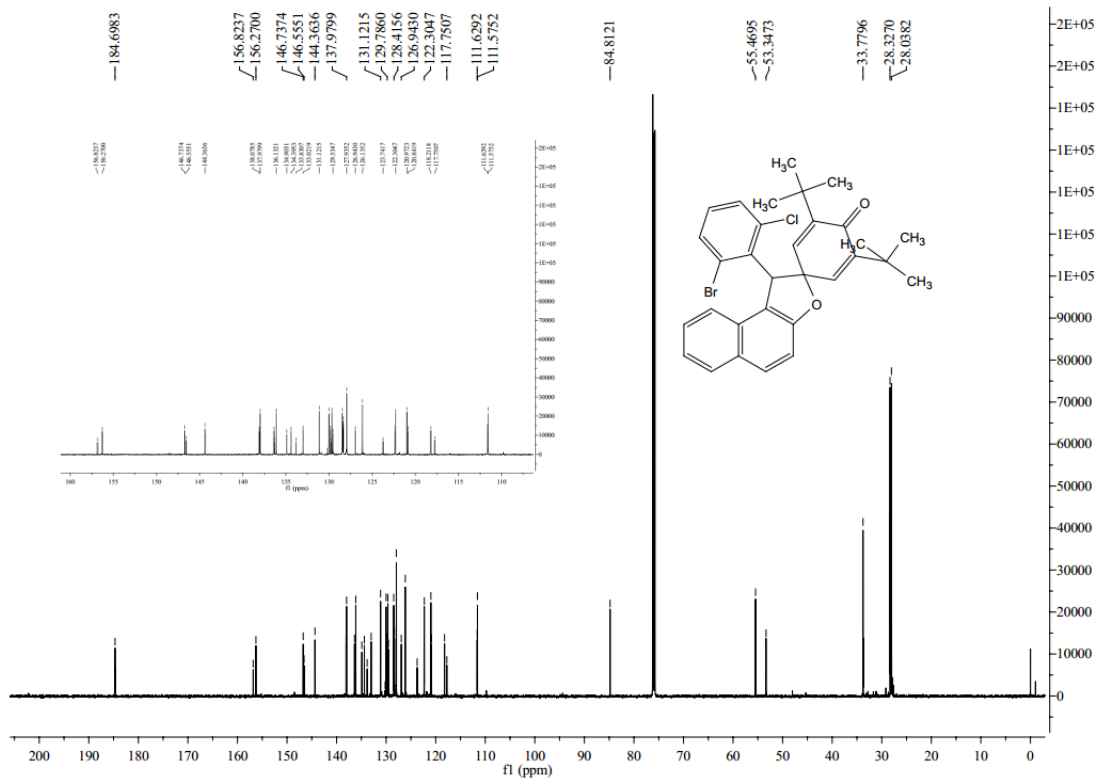
¹³C NMR Spectrum of 4j (CDCl₃, 150 MHz)



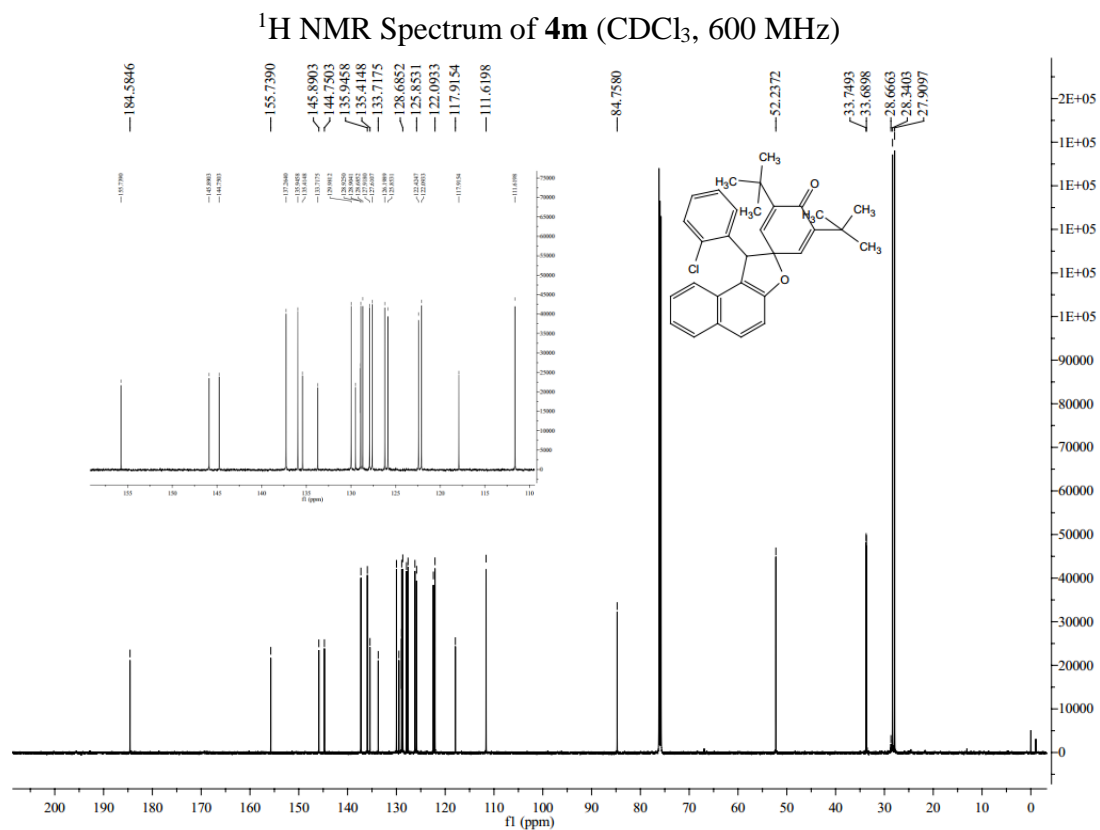
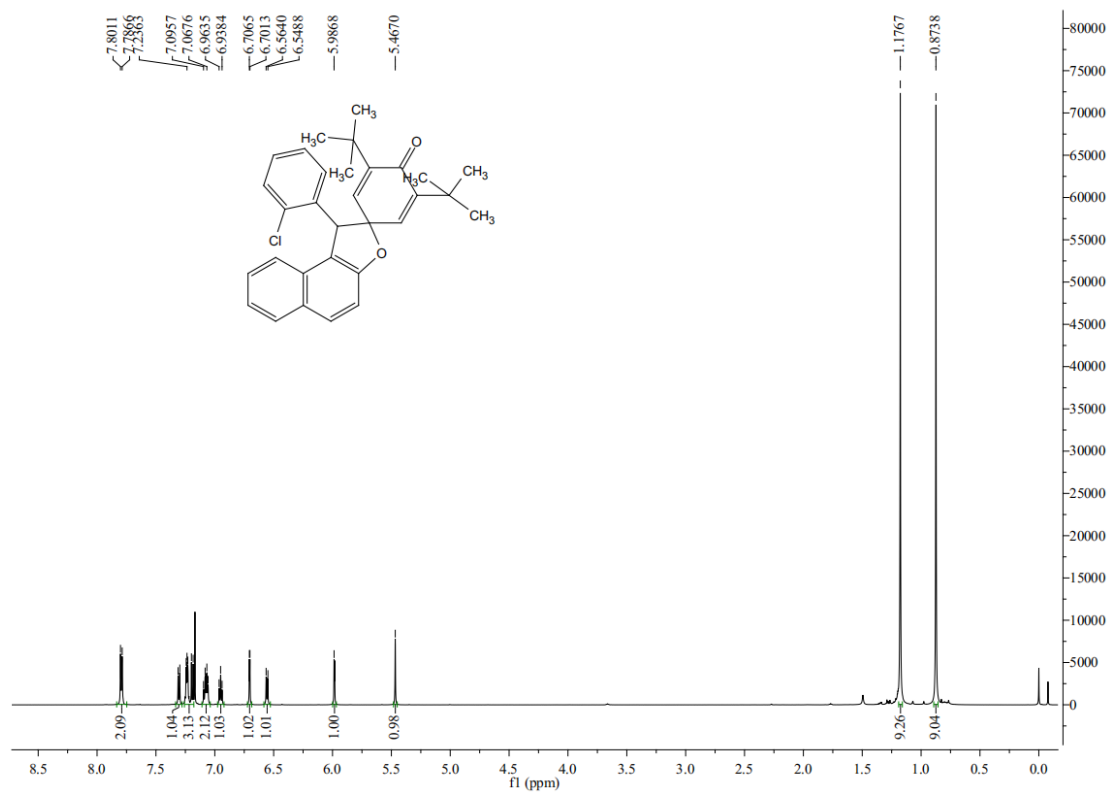
¹³C NMR Spectrum of 4k (CDCl₃, 150 MHz)



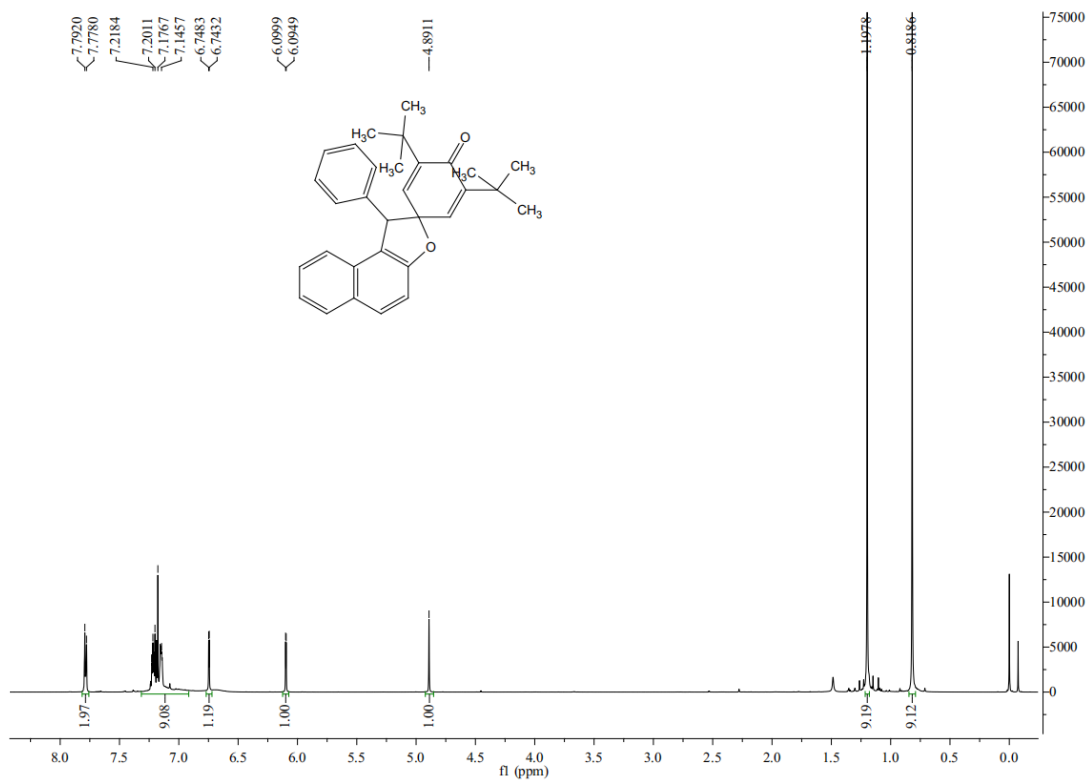
¹H NMR Spectrum of 4l (CDCl₃, 600 MHz)



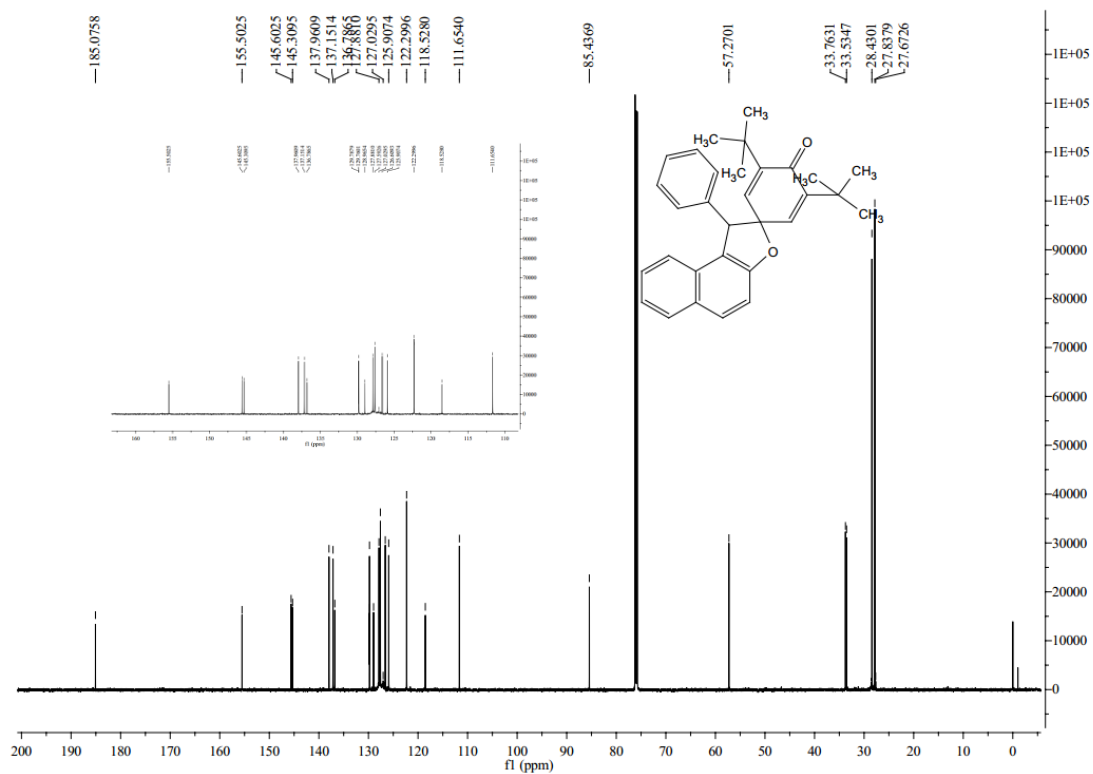
¹³C NMR Spectrum of 4l (CDCl₃, 150 MHz)



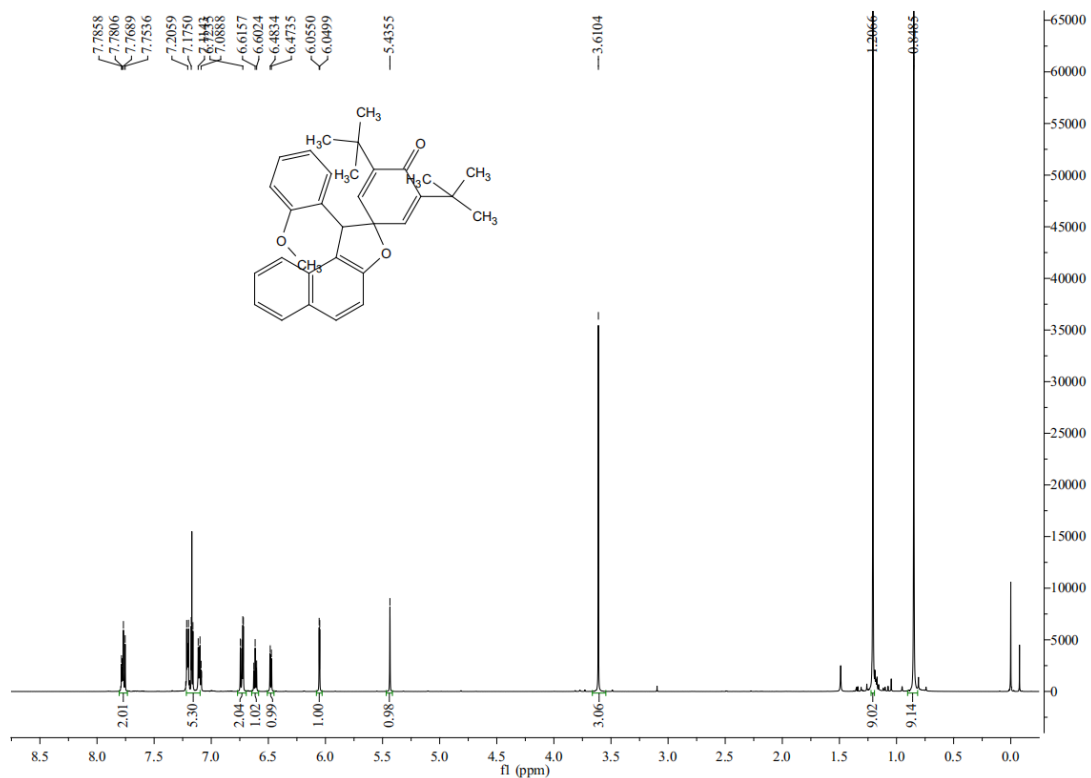
¹³C NMR Spectrum of 4m (CDCl₃, 150 MHz)



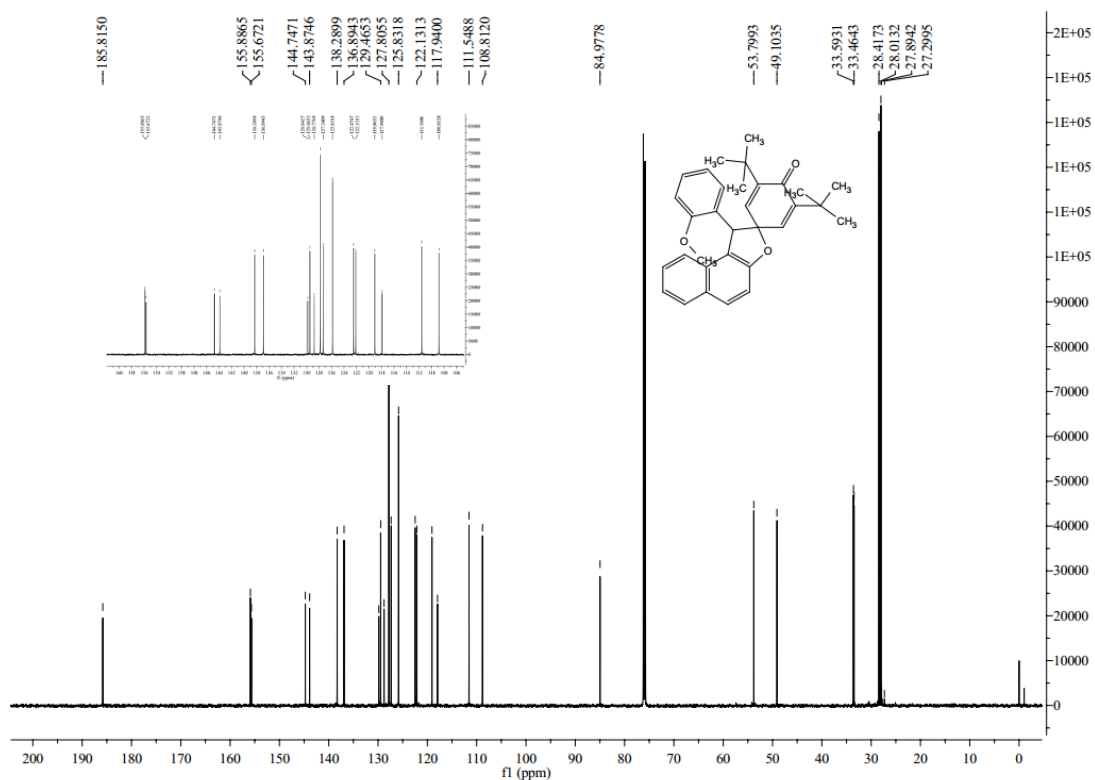
¹H NMR Spectrum of 4n (CDCl₃, 600 MHz)



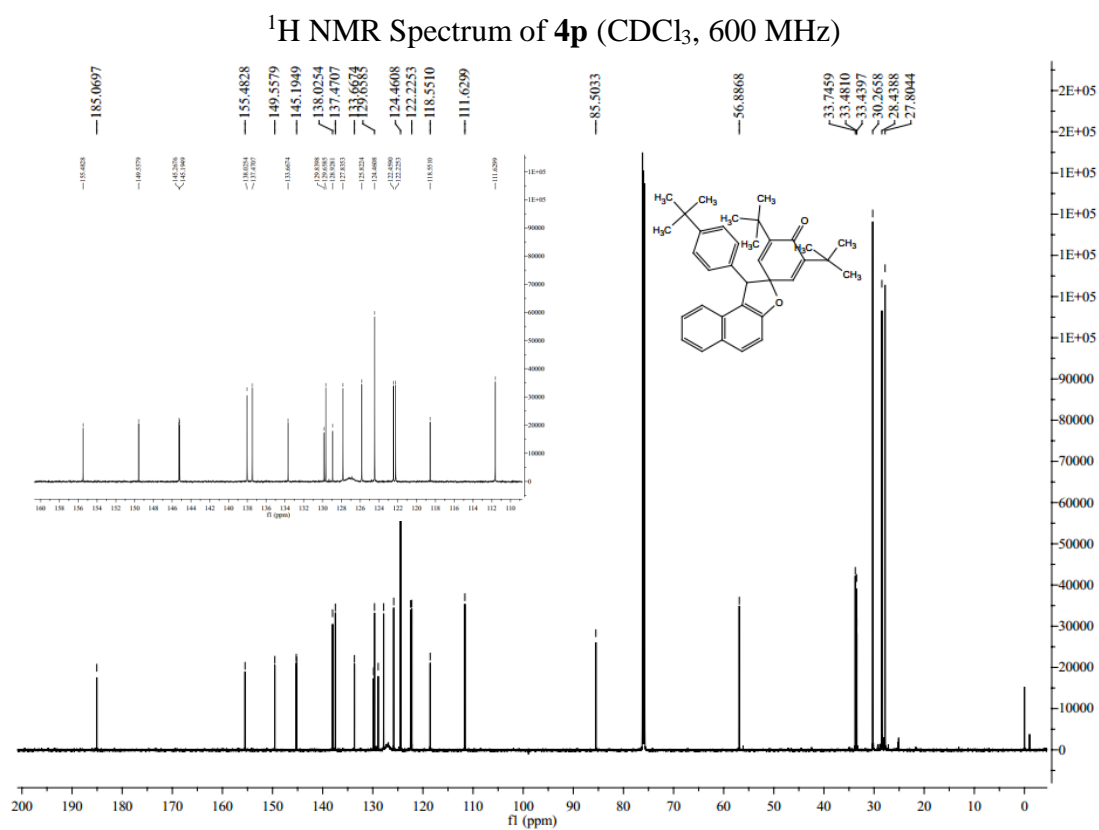
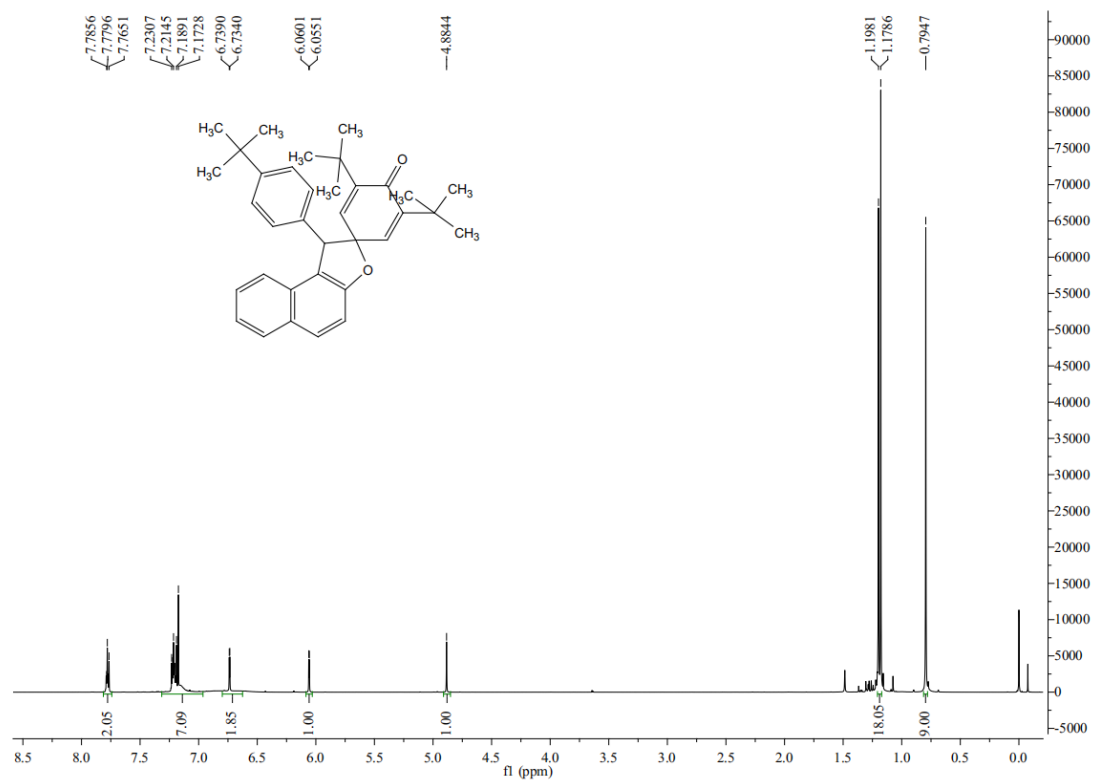
¹³C NMR Spectrum of 4n (CDCl₃, 150 MHz)



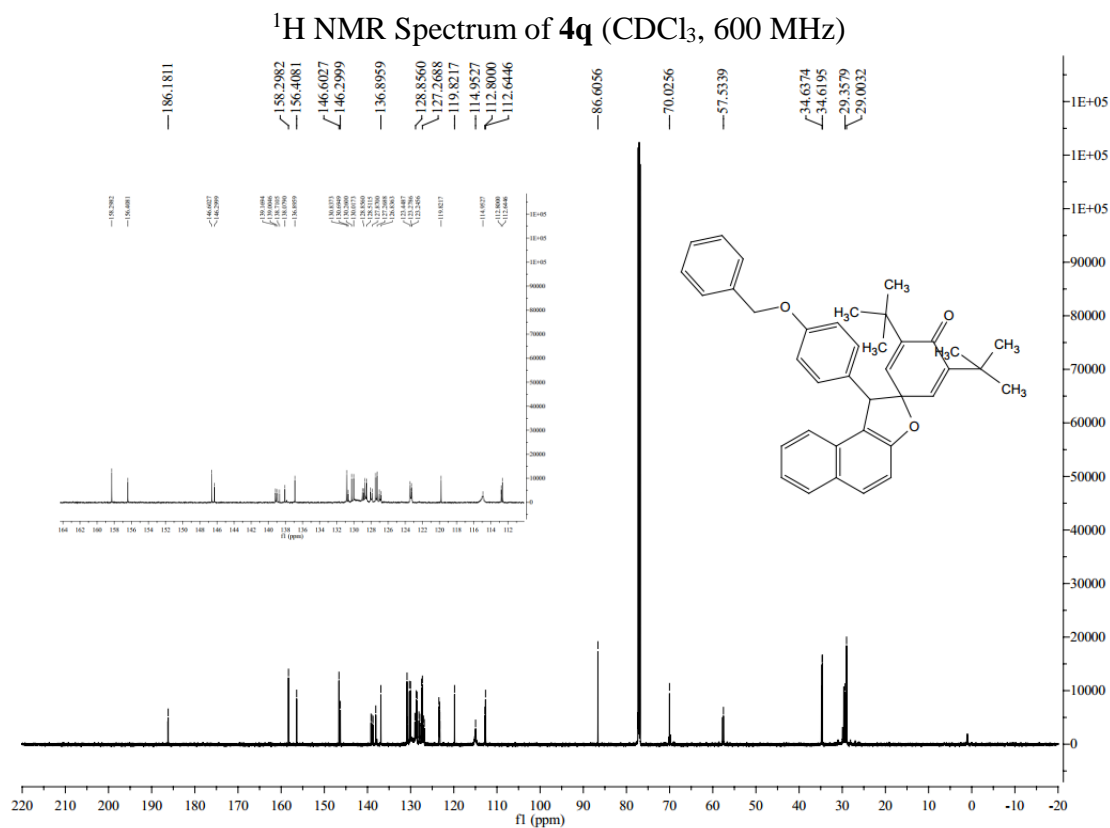
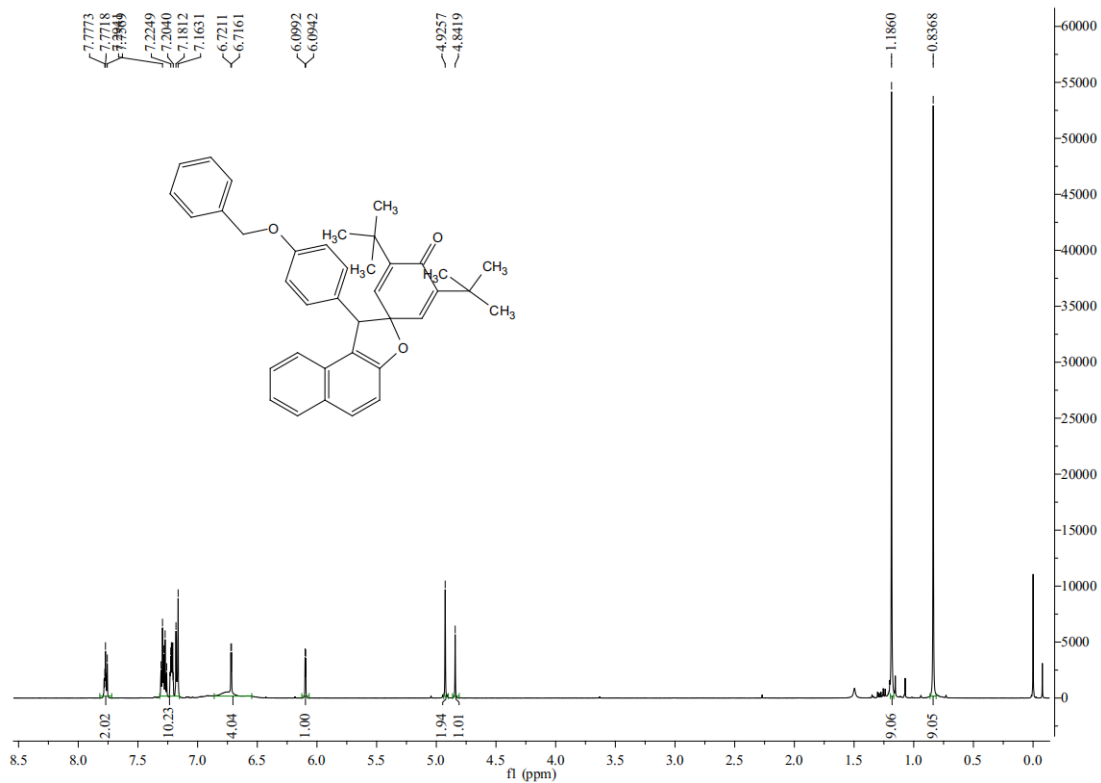
¹H NMR Spectrum of **4o** (CDCl₃, 600 MHz)



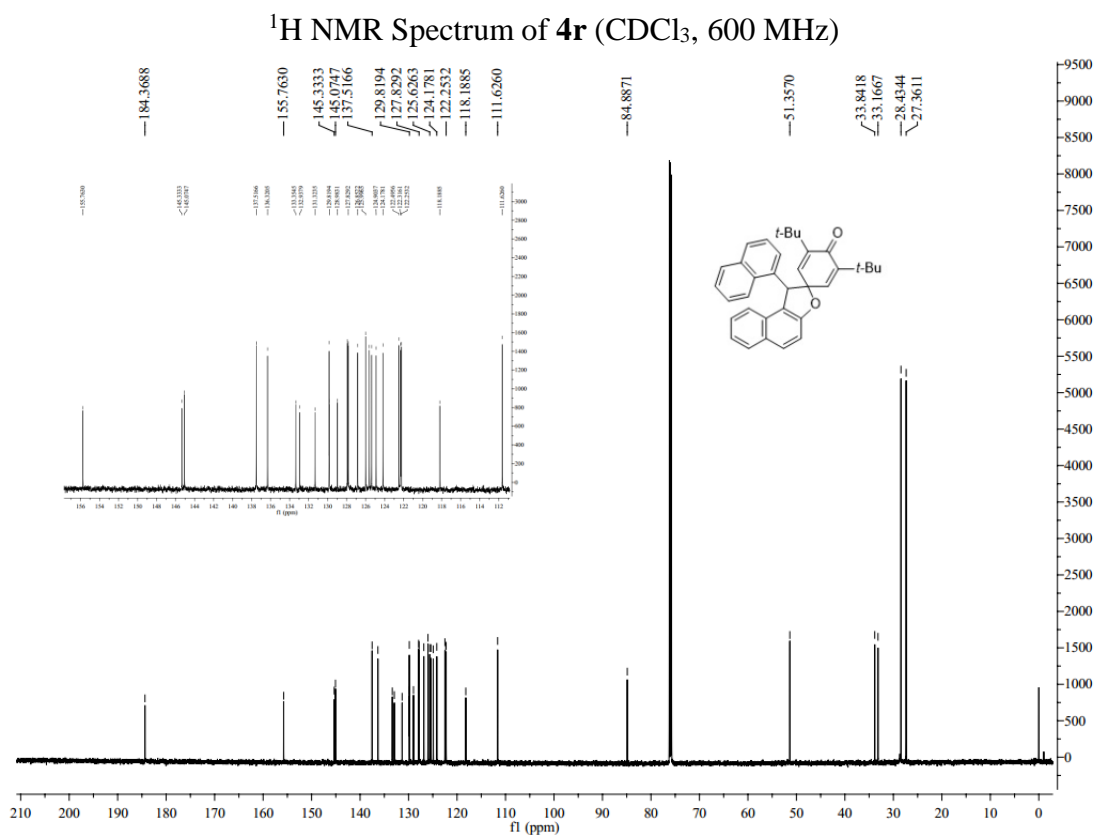
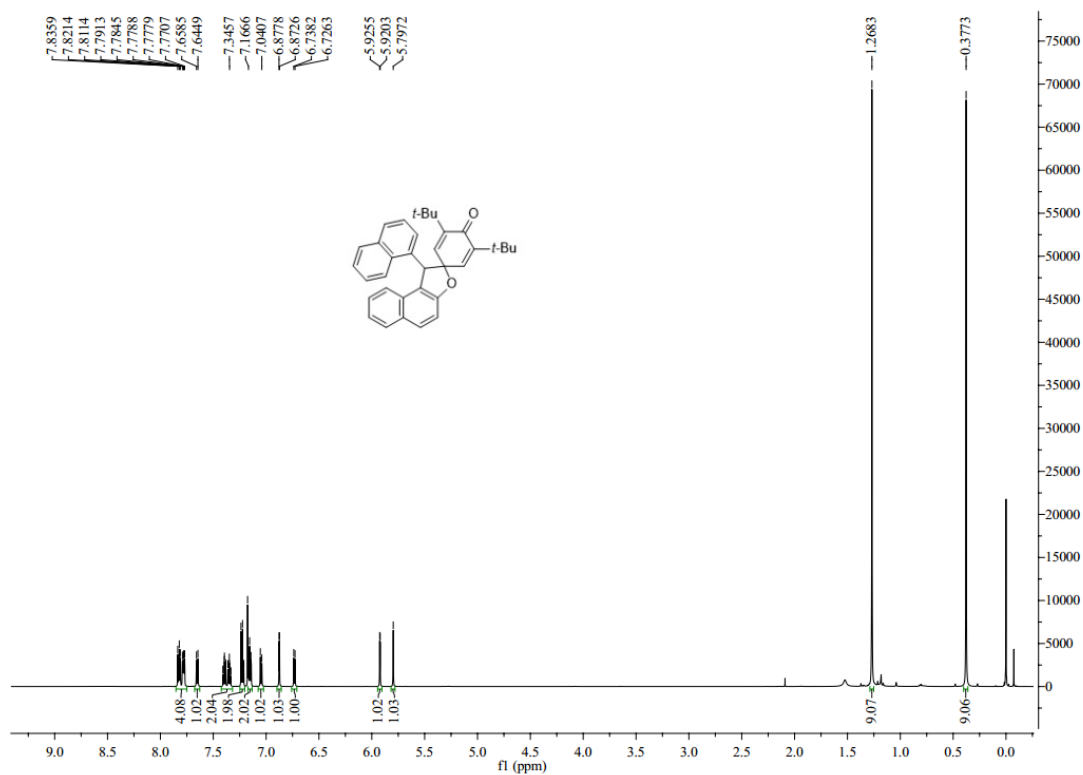
¹³C NMR Spectrum of **4o** (CDCl₃, 150 MHz)



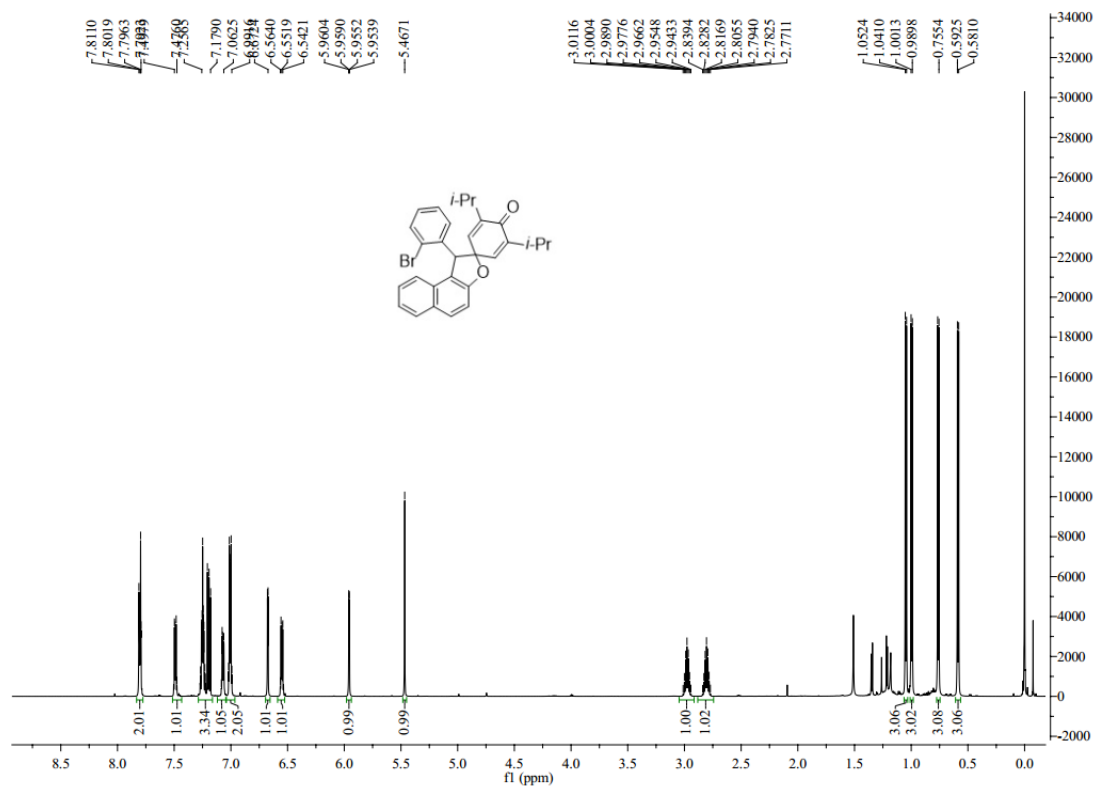
¹³C NMR Spectrum of 4p (CDCl₃, 150 MHz)



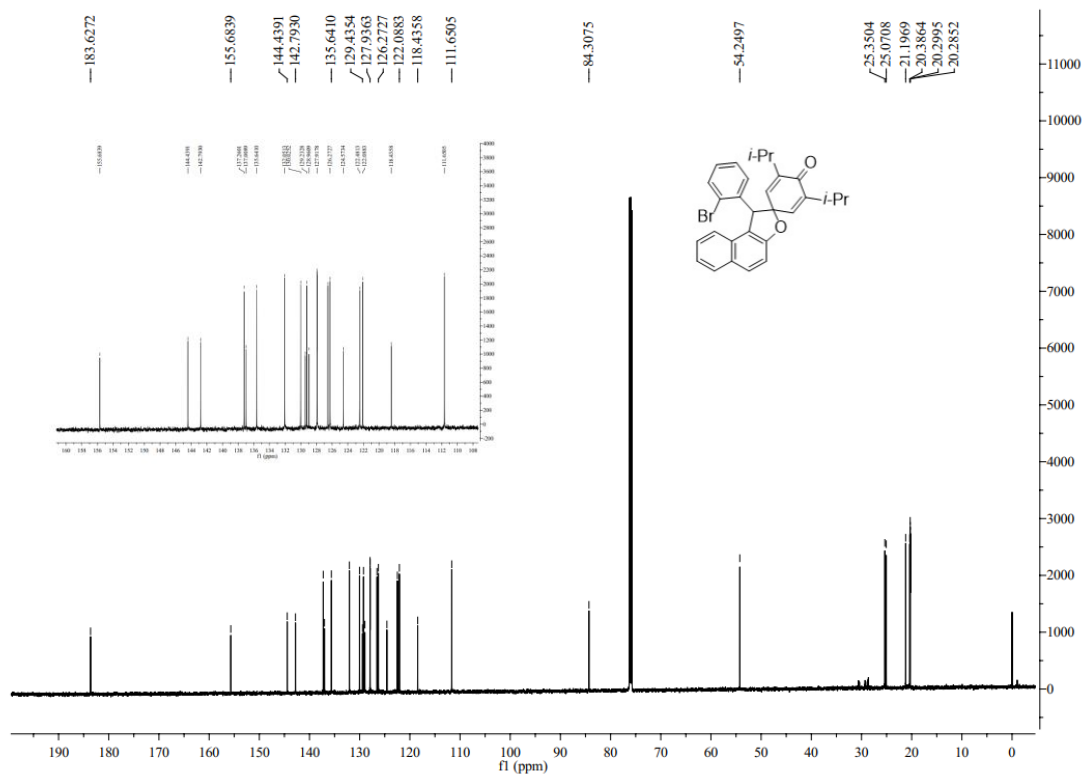
¹³C NMR Spectrum of 4q (CDCl₃, 150 MHz)



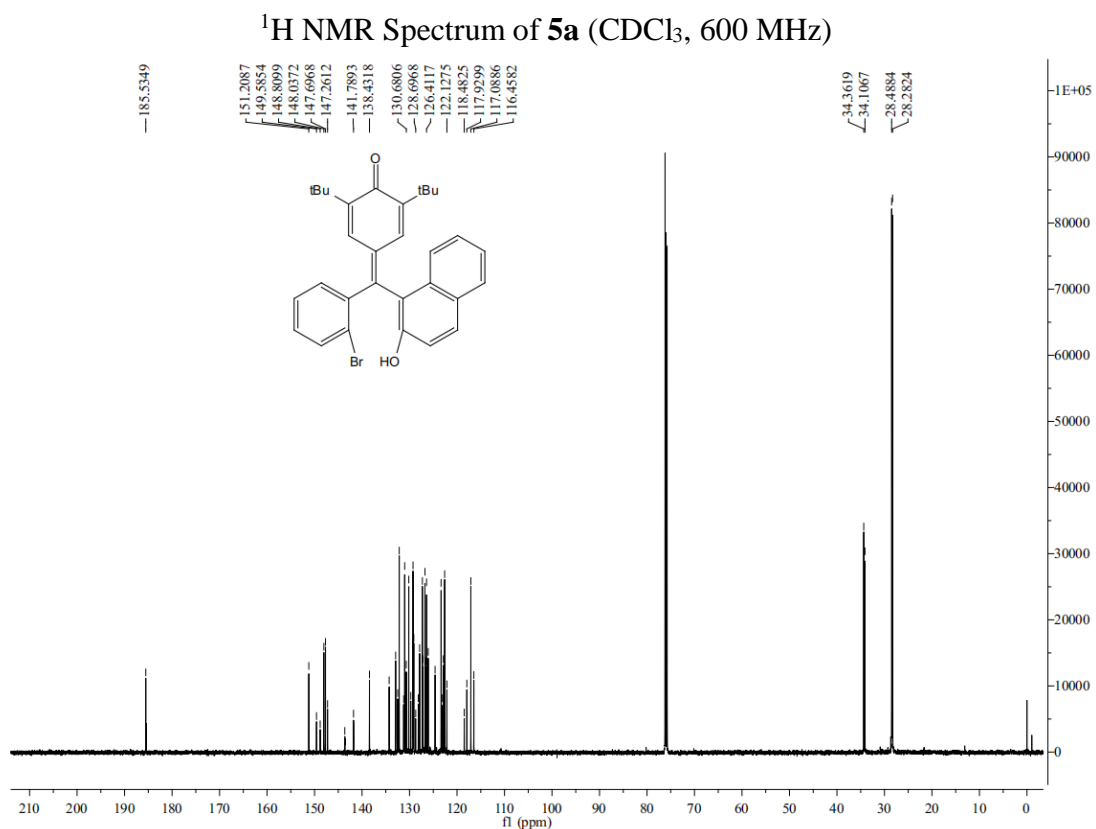
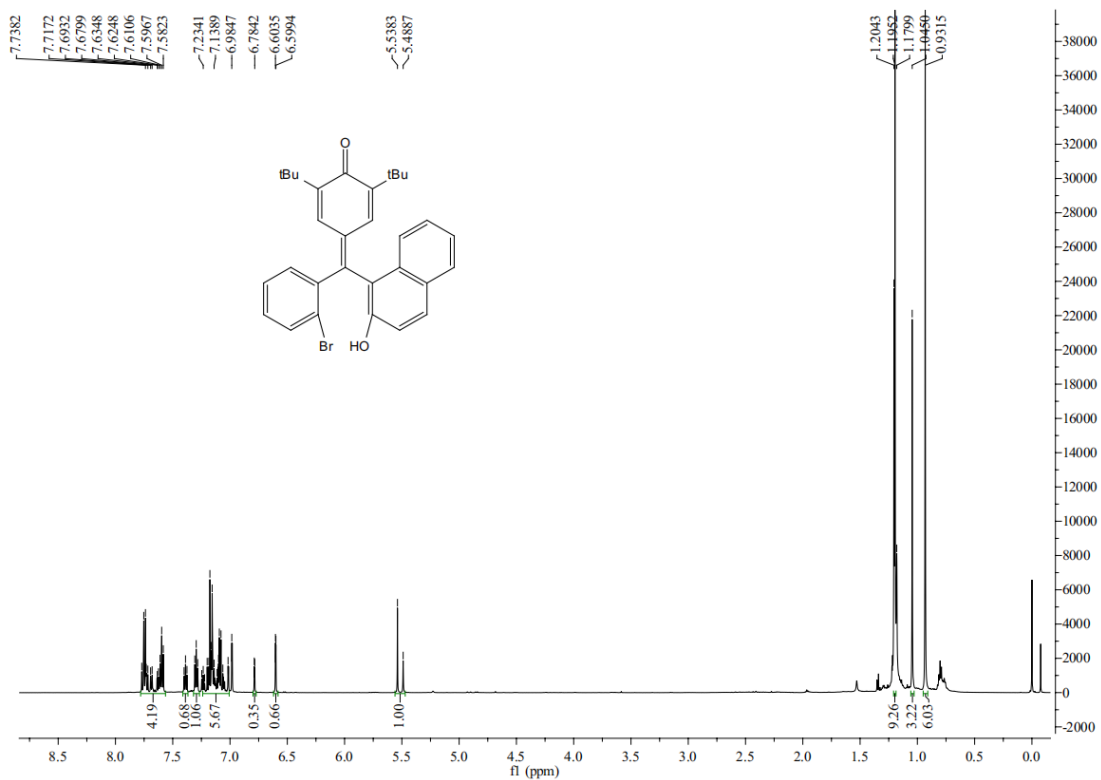
¹³C NMR Spectrum of 4r (CDCl₃, 150 MHz)



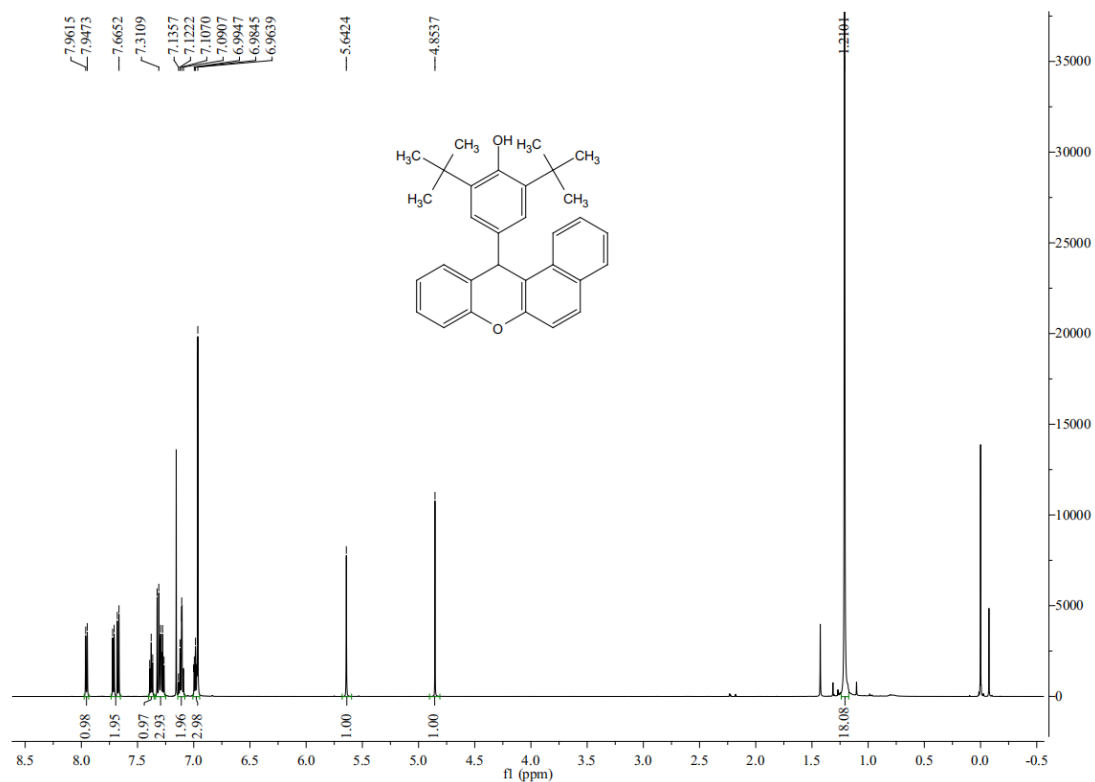
¹H NMR Spectrum of 4s (CDCl₃, 600 MHz)



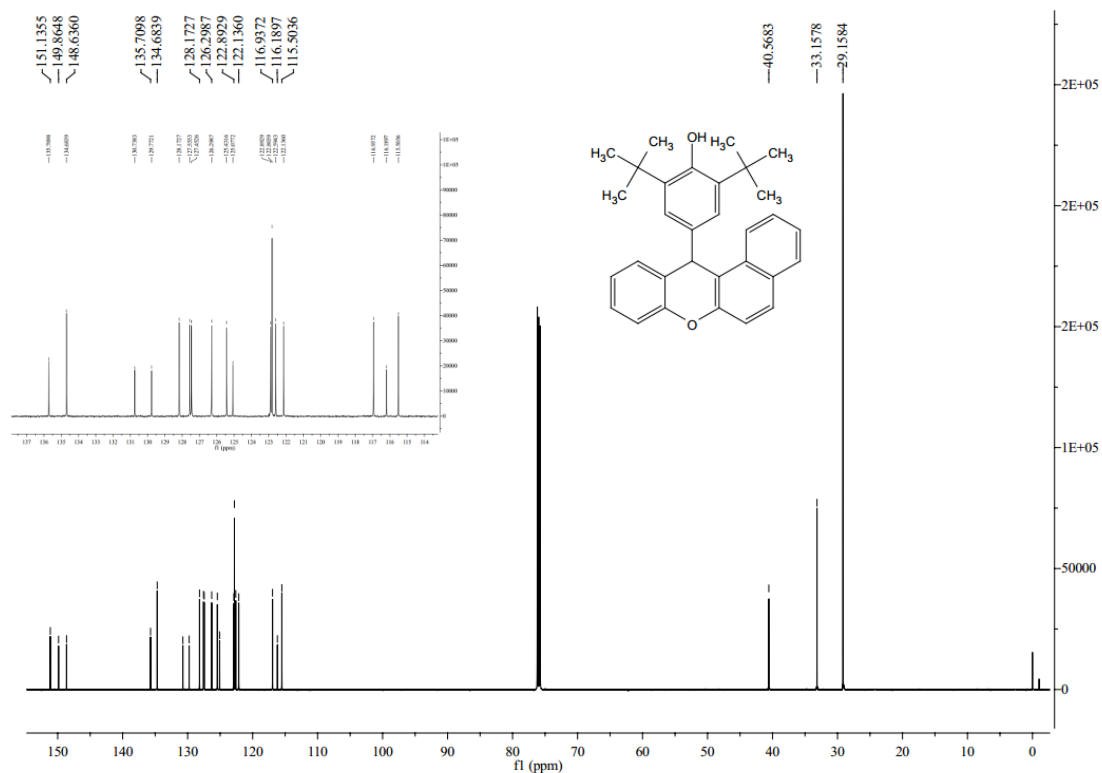
¹³C NMR Spectrum of 4s (CDCl₃, 150 MHz)



¹³C NMR Spectrum of 5a (CDCl₃, 150 MHz)



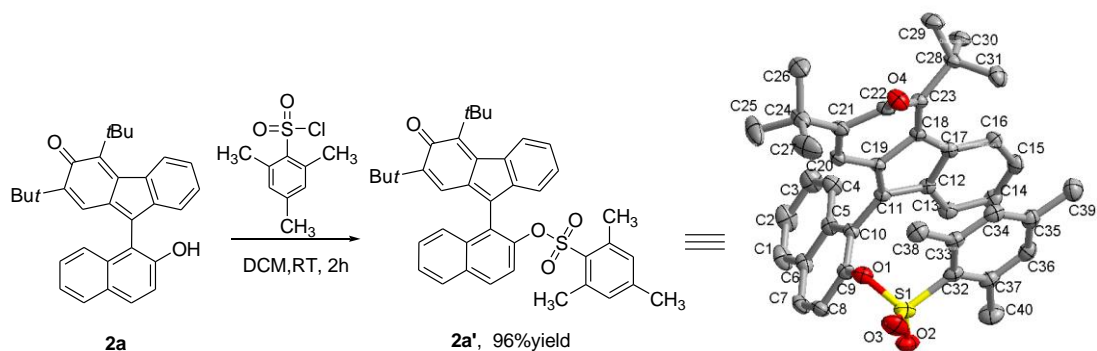
¹H NMR Spectrum of **6** (CDCl₃, 600 MHz)



¹³C NMR Spectrum of **6** (CDCl₃, 150 MHz)

11. Single-Crystal X-ray Crystallography of 2a', 3a, 4a and 5a

Single-Crystal X-ray Crystallography of Product **2a'** (CCDC number: 2116525)



Bond precision: C-C = 0.0026 Å Wavelength=1.54184

Cell: a=17.6560(2) b=12.29932(13) c=17.8070(2)

alpha=90 beta=101.2817(11) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	3792.19(7)	3792.21(8)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C40 H40 O4 S [+ solvent]	C40 H40 O4 S
Sum formula	C40 H40 O4 S [+ solvent]	C40 H40 O4 S
Mr	616.78	616.78
Dx, g cm ⁻³	1.080	1.080
Z	4	4
Mu (mm ⁻¹)	1.035	1.035
F000	1312.0	1312.0
F000'	1316.88	
h,k,lmax	21,14,21	21,14,21
Nref 6762 6753		
Tmin,Tmax	0.851,0.883	0.868,1.000
Tmin'	0.847	

Correction method= # Reported T Limits: Tmin=0.868 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.999

Theta(max)= 67.072

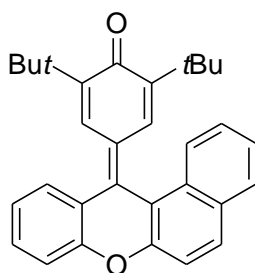
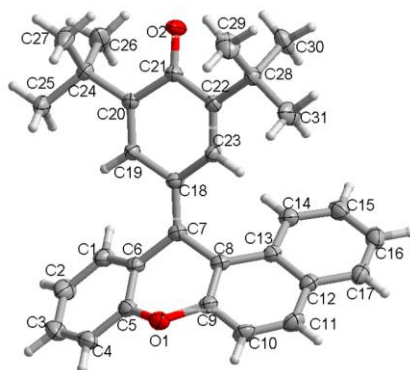
R(reflections)= 0.0449(5440)

wR2(reflections)= 0.1302(6753)

S = 1.031

Npar= 415

Single-Crystal X-ray Crystallography of Product **3a** (CCDC number: 2116523)



Bond precision:

C-C = 0.0027 Å

Wavelength=1.54184

Cell: a=10.8263(3)

b=21.7654(4)

c=11.6633(4)

alpha=90

beta=117.279(4)

gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	2442.67(15)	2442.67(13)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C31 H30 O2	C31 H30 O2
Sum formula	C31 H30 O2	C31 H30 O2
Mr	434.55	434.55
Dx,g cm-3	1.182	1.182
Z	4	4
Mu (mm-1)	0.559	0.559
F000	928.0	928.0
F000'	930.53	
h,k,lmax	12,26,13	12,26,13
Nref	4346	4339
Tmin,Tmax	0.904,0.946	0.549,1.000
Tmin'	0.889	

Correction method= # Reported T Limits: T_{min}=0.549 T_{max}=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.998

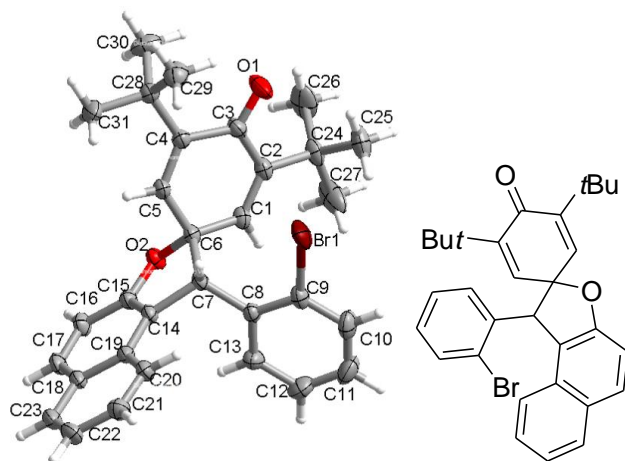
Theta(max)= 67.063

R(reflections)= 0.0429(3487)

wR2(reflections)= 0.1292(4339)

S = 1.060 Npar= 305

Single-Crystal X-ray Crystallography of Product **4a** (CCDC number: 2116524)



Bond precision:

C-C = 0.0034 Å

Wavelength=1.54184

Cell:

a=18.8373(4)

b=11.7899(3)

c=27.1076(7)

alpha=90

beta=105.181(2)

gamma=90

Temperature:

293 K

	Calculated	Reported
Volume	5810.2(3)	5810.3(2)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C31 H31 Br O2 [+ solvent]	C31 H31 Br O2
Sum formula	C31 H31 Br O2 [+ solvent]	C31 H31 Br O2
Mr	515.46	515.47
D _x , g cm ⁻³	1.179	1.179
Z	8	8
Mu (mm ⁻¹)	2.095	2.095
F000	2144.0	2144.0
F000'	2143.63	

h,k,lmax	22,14,32	22,14,32
Nref	5184	5147
Tmin,Tmax	0.767,0.811	0.857,1.000
Tmin'	0.696	

Correction method= # Reported T Limits: Tmin=0.857 Tmax=1.000

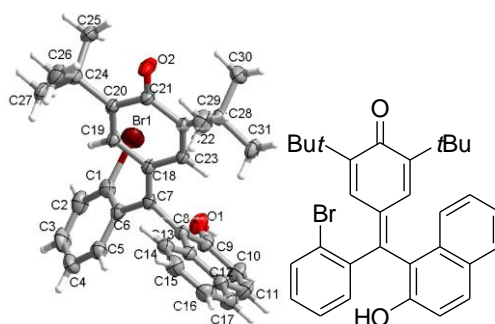
AbsCorr = MULTI-SCAN

Data completeness= 0.993 Theta(max)= 67.075

R(reflections)= 0.0406(4540) wR2(reflections)= 0.1168(5147)

S = 1.022 Npar= 313

Single-Crystal X-ray Crystallography of Product **5a** (CCDC number: 2127166)



Bond precision: C-C = 0.0071 Å Wavelength=1.54184

Cell: a=11.4412(3) b=13.3055(4) c=21.0185(6)
 alpha=107.066(2) beta=90.028(2) gamma=112.861(3)

Temperature: 293 K

	Calculated	Reported
Volume	2794.60(16)	2794.59(14)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C31 H31 Br O2), C H4 O	2(C31 H31 Br O2), C H4 O
Sum formula	C63 H66 Br2 O5	C63 H66 Br2 O5
Mr	1062.96	1062.97
Dx,g cm-3	1.263	1.263
Z	2	2
Mu (mm-1)	2.206	2.206

F000	1108.0	1108.0
F000'	1107.95	
h,k,lmax	13,15,25	13,15,25
Nref	9984	9972
Tmin,Tmax	0.809,0.896	0.962,1.000
Tmin'	0.751	

Correction method= # Reported T Limits: Tmin=0.962 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.999

Theta(max)= 67.078

R(reflections)= 0.0667(7068)

wR2(reflections)=0.2103(9972)

S = 1.009

Npar= 656