Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Microwave-Assisted Copper Catalytic Decarboxylative Reductive Coupling of *para*-Quinone Methides with 3-Indoleacetic Acids: Rapid Access to Polycyclic Spiroindolequinone derivatives

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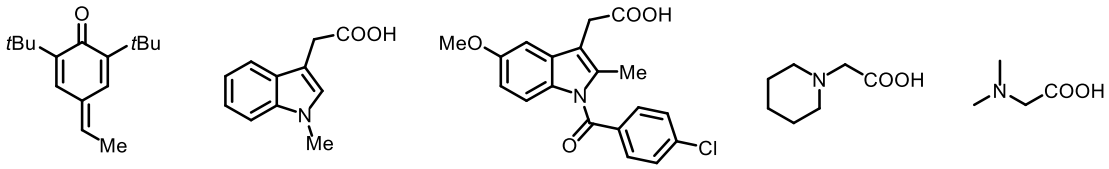
1. General Information

^{1}H and ^{13}C NMR were recorded on a Biotage 400 spectrometer. ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), relative intensity. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ). HPLC-MS analyses were performed on a Shimadzu-2020 LC-MS instrument using the following conditions: Shim-pack VP-ODS C18 column (reverse phase, 50 x 4.6 mm); a linear gradient from 10% water and 90% acetonitrile to 95% acetonitrile and 5% water over 4.0 min; flow rate of 1 mL/min; UV photodiode array detection from 200 to 300 nm. The products were purified by Biotage Isolera™ Spektra Systems and Petroleum Ether/EtOAc solvent systems. All reagents and solvents were obtained from commercial sources and used without further purification. Melting points (m.p.) were determined on a micro melting point apparatus (WRX-4) and were uncorrected.

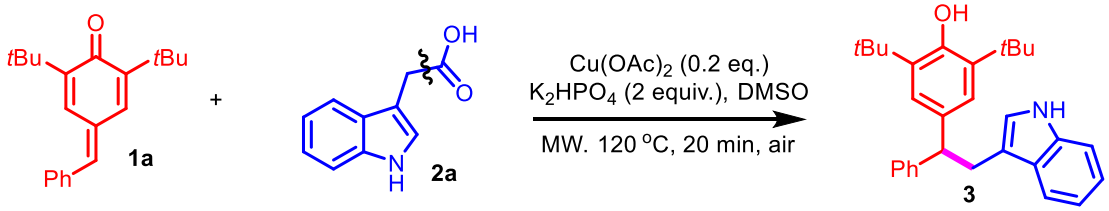
2. Microwave Irradiation Experiments

All microwave irradiation experiments were carried out in a Biotage® Initiator Classic microwave apparatus with continuous irradiation power from 0 to 400W with utilization of the standard absorbance level of 250W maximum power. The reactions were carried out in 10 mL glass tubes, sealed with microwave cavity. The reaction was irradiated at a required ceiling temperature using maximum power for the stipulated time. Then it was cooled to 50 ^{o}C with gas jet cooling.

2. Unsuccessful substrates

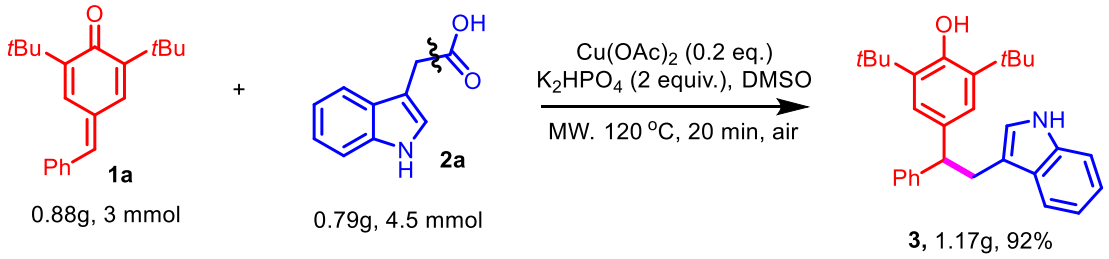


3. General Procedure for Synthesis of Indolylated Diarylethanes



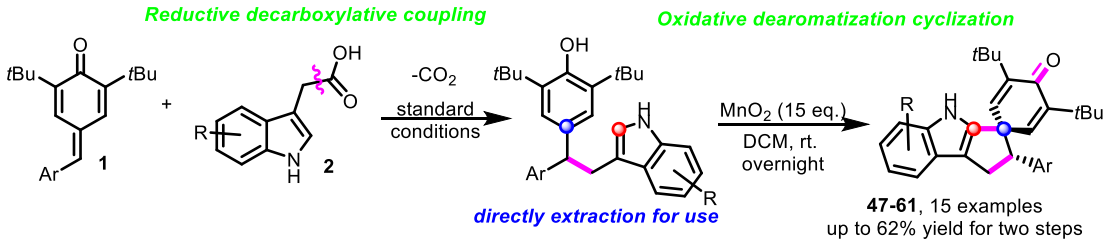
In an oven-dried glass tubes *p*-QM[1] **1a** (60 mg, 0.2 mmol, 1.0 eq.), 3-indoleacetic acids **2a** (53 mg, 0.3 mmol, 1.5 eq.), K_2HPO_4 (70 mg, 0.4 mmol, 2.0 eq.), and $Cu(OAc)_2$ (8 mg, 0.04 mmol, 0.2 equiv.)were dissolved in DMSO (2 mL) and the reaction mixture was stirred at **MW** 120 °C for 20 min by microwave irradiation and monitored by TLC. Then the reaction mixture was extracted using EtOAc/H_2O and concentrated under reduced pressure followed by column chromatography over silica gel using petroleum / EtOAc = 20/1 as eluent to afford the desired product **3** (79 mg, 93% yield).

4. Gram Scale-up Experiment



In an oven-dried glass tubes *p*-QM **1a** (880 mg, 3 mmol, 1.0 eq.), 3-indoleacetic acids **2a** (790 mg, 4.5 mmol, 1.5 eq.), K_2HPO_4 (1045 mg, 6 mmol, 2.0 eq.), and $Cu(OAc)_2$ (120 mg, 0.6 mmol, 0.2 equiv.) were dissolved in DMSO (20 mL) and the reaction mixture was stirred at **MW** 120 °C for 20 min by microwave irradiation and monitored by TLC. Then the reaction mixture was extracted using EtOAc/H_2O and concentrated under reduced pressure followed by column chromatography over silica gel using petroleum / EtOAc = 20/1 as eluent to afford the desired product **3** (1170 mg, 92% yield).

5. General Procedure for Synthesis of Polycyclic Spiroindolequinones



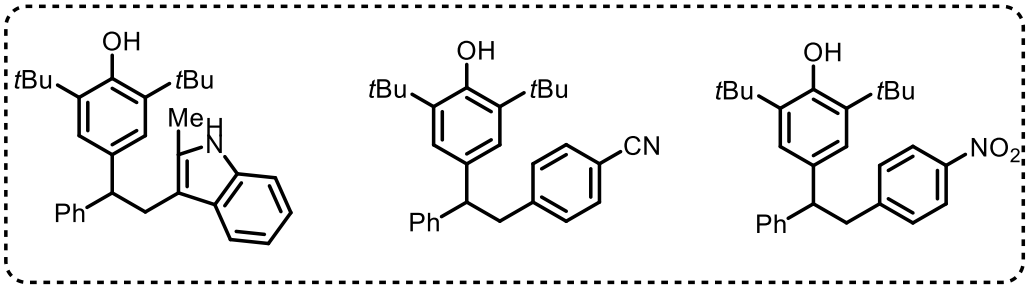
Procedure 1: synthesis of indolylated diarylethanes

p-QMs **1** (0.2 mmol, 1.0 equiv.), 3-indoleacetic acids **2** (0.3 mmol, 1.5 equiv.), K_2HPO_4 (70 mg, 1.2 mmol, 2.0 equiv.), and $Cu(OAc)_2$ (8 mg, 0.04 mmol, 0.2 equiv.) were dissolved in DMSO (2 mL) in a screw capped vial equipped with a magnetic stir bar and the reaction mixture was stirred at **MW** 120 ^oC for 20 min by microwave irradiation and monitored by TLC. The crude product could be directly used by extraction using EtOAc/H_2O and concentrated under reduced pressure.

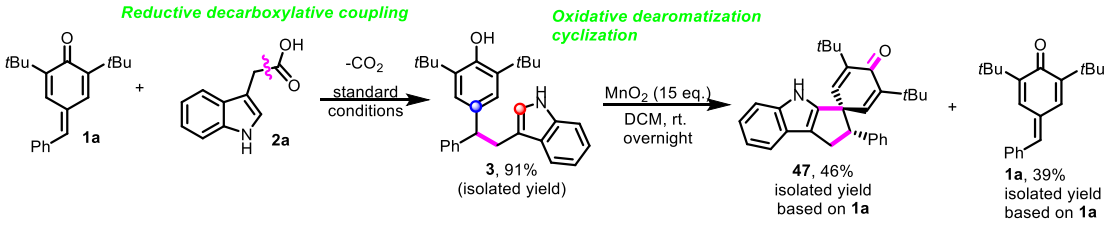
Procedure 2: synthesis of polycyclic spiroindolequinones

The solution of indolylated diarylethane crude product (ca. 0.18 mmol, ca. 88% yield, 1.0 eq.) in DCM (2mL) was added MnO_2 (2.7 mmol, 235 mg, ca. 15 eq) in a flame-dried Schlenk flask containing a stirring bar. The reaction mixture was stirred at room temperature overnight and monitored by TLC. After completion of the reaction, the mixture was purified by chromatography on silica gel (EtOAc/ n-hexane = 3% as eluent) to afford the polycyclic spiroindolequinones **47-61**.

Unsuccessful substrates



Analysis of reaction by-products



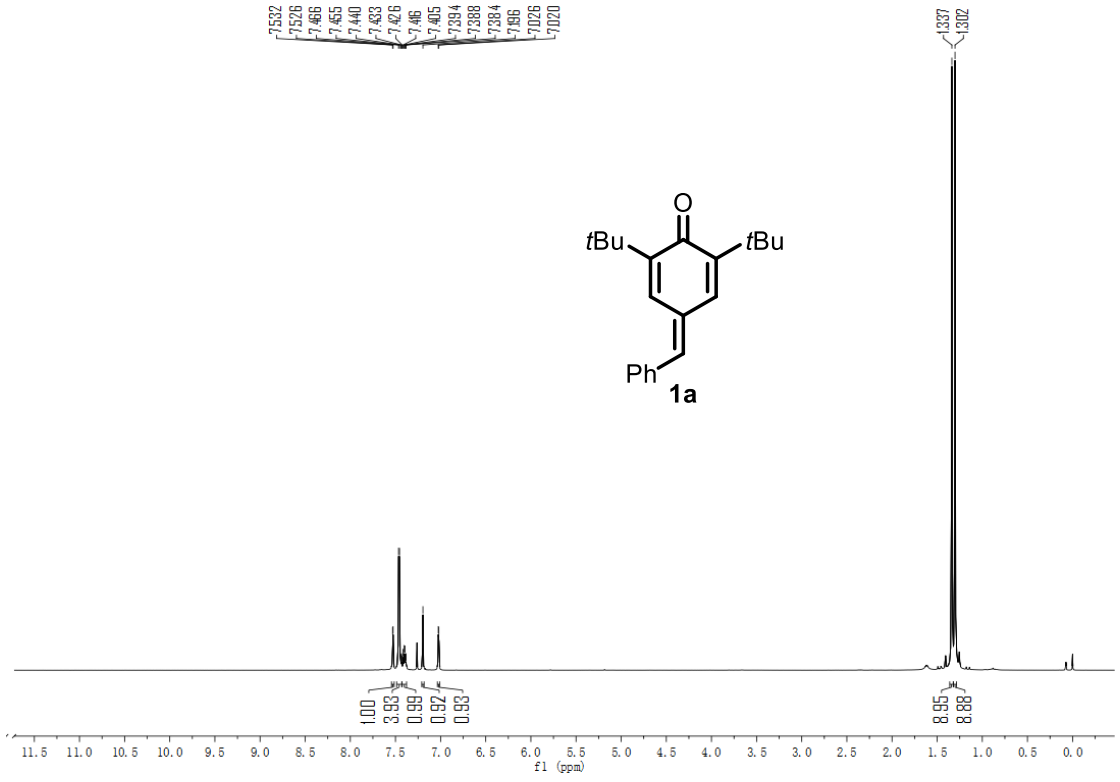
Procedure 1: synthesis of indolylated diarylethanes

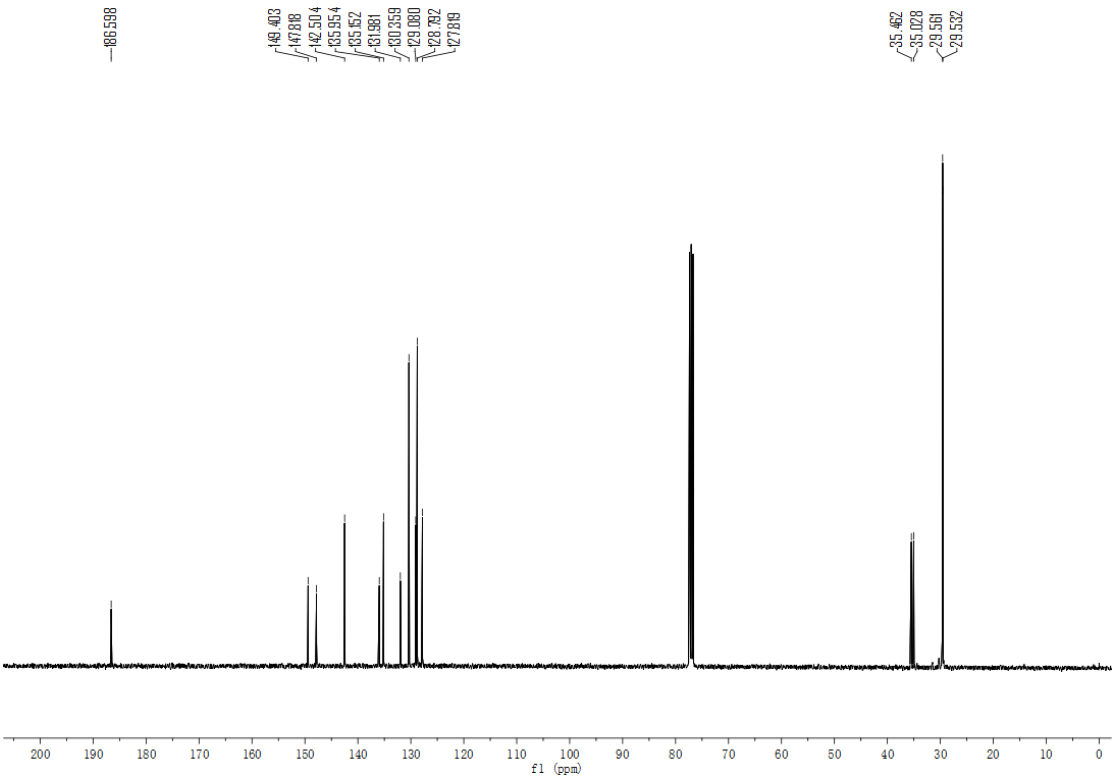
In an oven-dried glass tubes *p*-QM **1a** (60 mg, 0.2 mmol, 1.0 eq.), 3-indoleacetic acids **2a** (53 mg, 0.3 mmol, 1.5 eq.), K_2HPO_4 (70 mg, 0.4 mmol, 2.0 eq.), and $Cu(OAc)_2$ (8 mg, 0.04 mmol, 0.2 equiv.)were dissolved in DMSO (2 mL) and the reaction mixture was stirred at **MW** 120 ^oC for 20 min by microwave irradiation and monitored by TLC. Then the reaction mixture was extracted using EtOAc/H_2O and concentrated under reduced pressure followed by column chromatography over silica

gel using petroleum / EtOAc = 20/1 as eluent to afford the desired product **3** (77 mg, 91% yield).

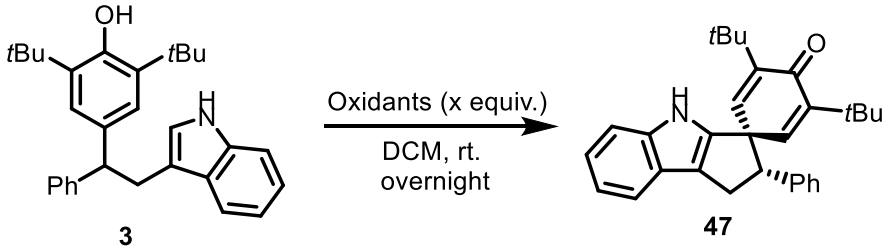
Procedure 2: synthesis of polycyclic spiroindolequinones

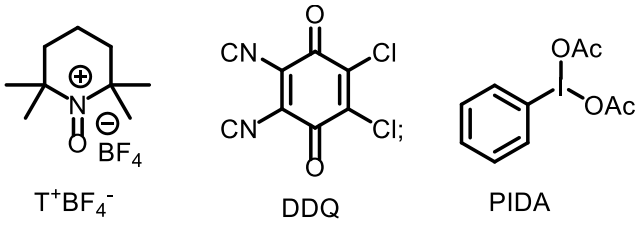
The solution of indolylated diarylethane product (77 mg, 0.18 mmol, 1.0 eq.) in DCM (2mL) was added MnO_2 (2.7 mmol, 235 mg, 15 eq) in a flame-dried Schlenk flask containing a stirring bar. The reaction mixture was stirred at room temperature overnight and monitored by TLC. After completion of the reaction, the mixture was purified by chromatography on silica gel (EtOAc/ n-hexane = 3% as eluent) to afford the polycyclic spiroindolequinones **47** (39 mg, 46% yield based **1a** 0.2 mmol) and **1a** (23 mg, 39%. yield based **1a** 0.2 mmol).





Other oxidant attempts

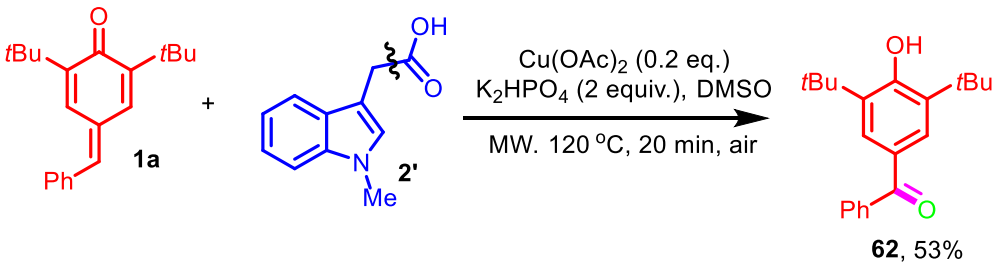




Entry	Oxidant	Equiv.	Conversion of 3	Yield of 47
1	$T^+BF_4^-$	2	100%	N.D.
2	DDQ	2	0%	N.D.
3	PIDA	2	56%	Mess
4	MnO_2	5	42%	<10%
5	MnO_2	15	100%	46%

6. Experimental Studies on the Reaction Mechanism

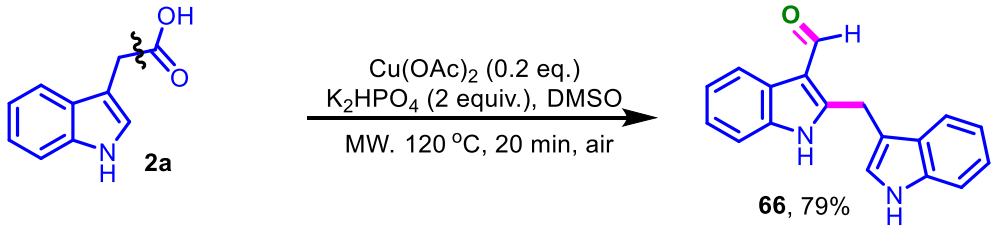
6.1 Trapping the diarylmethyl radical with O_2



Experimental procedure:

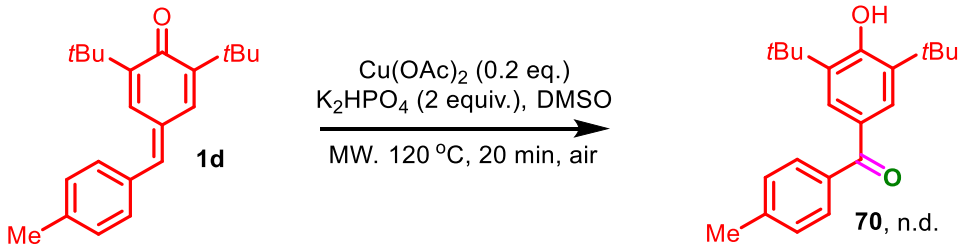
In an oven-dried glass tubes *p*-QM **1a** (60 mg, 0.2 mmol, 1.0 eq.), 3-indoleacetic acids **2'** (57 mg, 0.3 mmol, 1.5 eq.), K_2HPO_4 (70 mg, 0.4 mmol, 2.0 eq.), and $Cu(OAc)_2$ (8 mg, 0.04 mmol, 0.2 equiv.) were dissolved in DMSO (2 mL) and the reaction mixture was stirred at **MW** 120 °C for 20 min by microwave irradiation and monitored by TLC. Then the reaction mixture was concentrated under reduced pressure followed by column chromatography over silica gel using petroleum / EtOAc = 20/1 as eluent to afford the desired product **62** (33 mg, 53% yield).

6.2 Trapping the indole-3-methyl radical with O_2



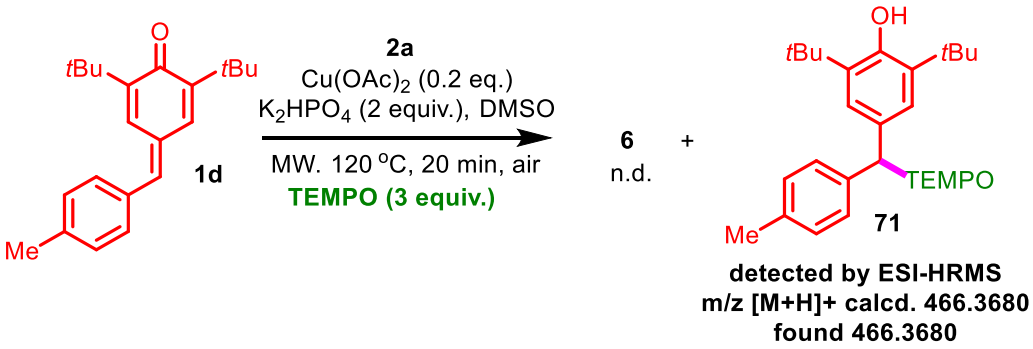
In an oven-dried glass tubes 3-indoleacetic acids **2a** (53 mg, 0.3 mmol, 1.5 eq.), K_2HPO_4 (70 mg, 0.4 mmol, 2.0 eq.), and $Cu(OAc)_2$ (8 mg, 0.04 mmol, 0.2 equiv.) were dissolved in DMSO (2 mL) and the reaction mixture was stirred at **MW** 120 °C for 20 min by microwave irradiation and monitored by TLC. Then the reaction mixture was concentrated under reduced pressure followed by column chromatography over silica gel using petroleum / EtOAc = 10/3 as eluent to afford the desired product **66** (65 mg, 79% yield).

6.3 Control experiments

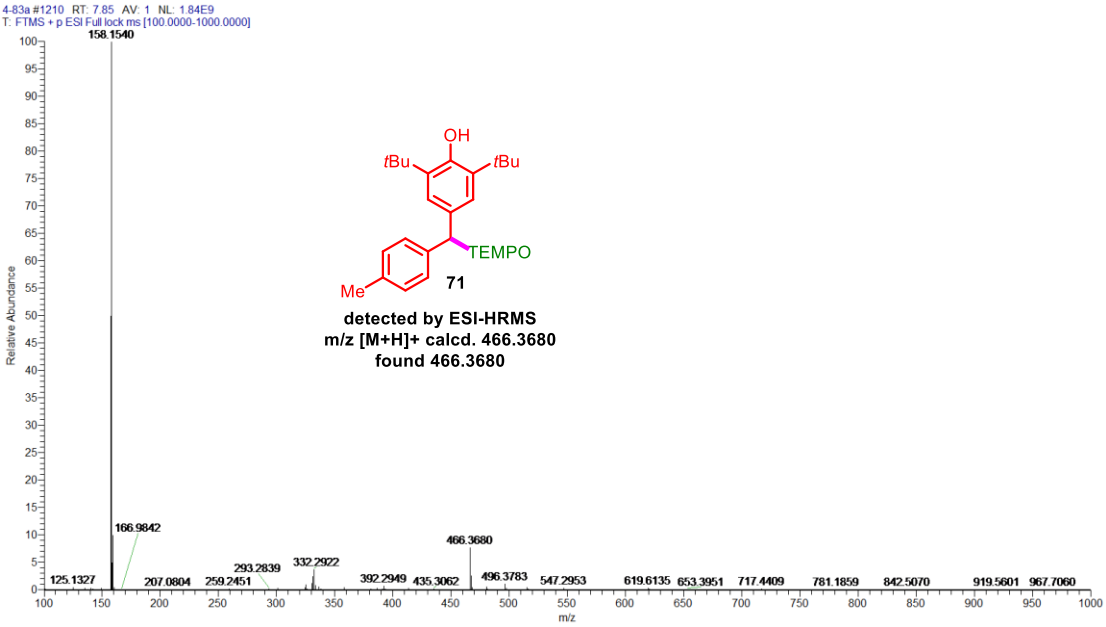


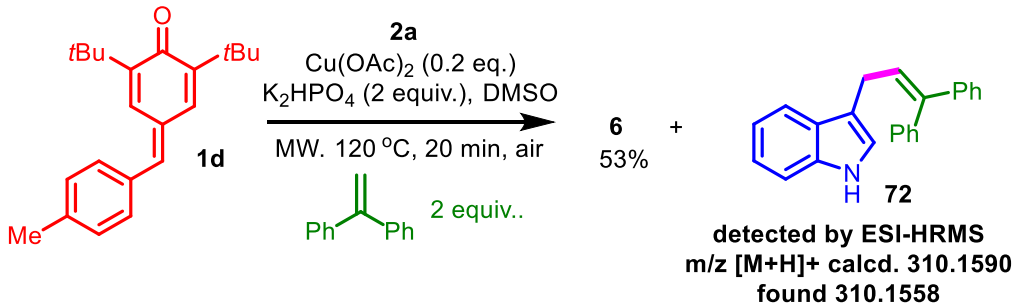
In an oven-dried glass tubes *p*-QM **1d** (62 mg, 0.2 mmol, 1.0 eq.), K_2HPO_4 (70 mg, 0.4 mmol, 2.0 eq.), and $Cu(OAc)_2$ (8 mg, 0.04 mmol, 0.2 equiv.) were dissolved in DMSO (2 mL) and the reaction mixture was stirred at **MW** 120 °C for 20 min by microwave irradiation and monitored by TLC. No

diarylmethane radical O_2-adduct **70** was generated.



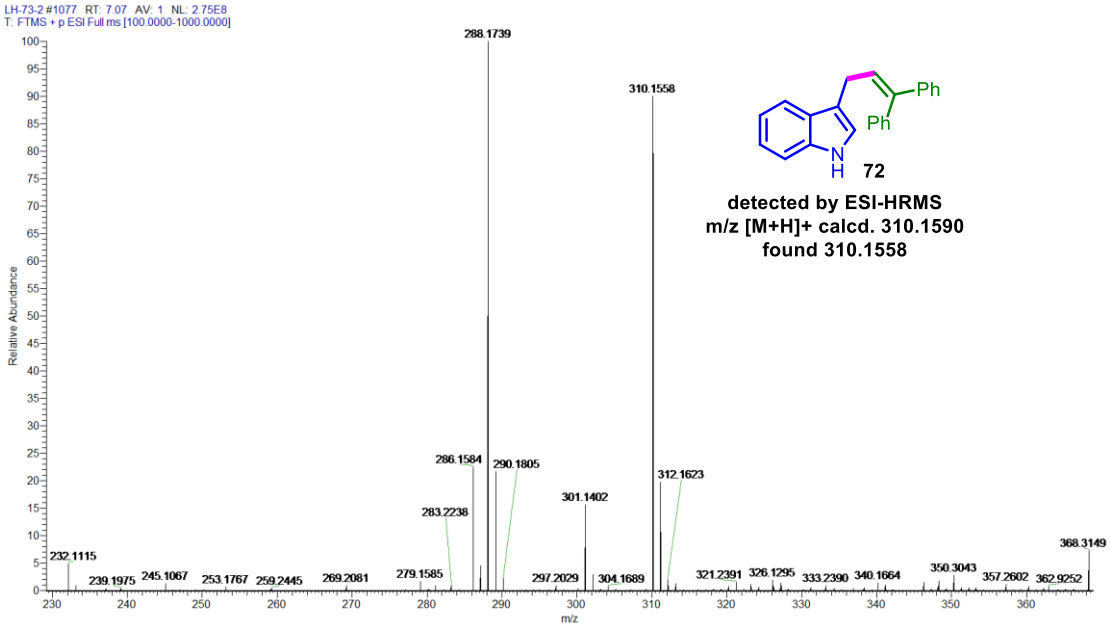
In an oven-dried glass tubes *p*-QM **1d** (62 mg, 0.2 mmol, 1.0 eq.), 3-indoleacetic acids **2a** (53 mg, 0.3 mmol, 1.5 eq.), K_2HPO_4 (70 mg, 0.4 mmol, 2.0 eq.), TEMPO (94 mg, 0.6 mmol, 3 eq.), and $Cu(OAc)_2$ (8 mg, 0.04 mmol, 0.2 equiv.) were dissolved in DMSO (2 mL) and the reaction mixture was stirred at **MW** 120°C for 20 min. After which, the ESI-MS analysis of the crude reaction mixture was carried out. The mass for diarylmethyl radical trapping product **71** could be detected. The mass for **71** is $C_{31}H_{48}NO_2^+$ $[M+H]^+$ calcd. 466.3680, found 466.3680.





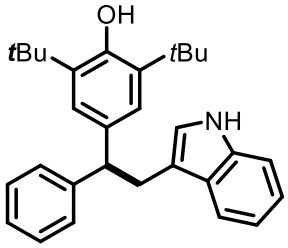
In an oven-dried glass tubes *p*-QM **1d** (62 mg, 0.2 mmol, 1.0 eq.), 3-indoleacetic acids **2a** (53 mg, 0.3

mmol, 1.5 eq.), K_2HPO_4 (70 mg, 0.4 mmol, 2.0 eq.), 1,1-diphenylethylene (71 uL, 0.4 mmol, 2 eq.), and $Cu(OAc)_2$ (8 mg, 0.04 mmol, 0.2 equiv.) were dissolved in DMSO (2 mL) and the reaction mixture was stirred at **MW** 120 °C for 20 min. After which, the ESI-MS analysis of the crude reaction mixture was carried out. The mass for indole-3-methyl radical trapping product **72** could be detected. The mass for **72** is $C_{23}H_{20}N^+$ $[M+H]^+$ calcd. 310.1590, found 310.1558. Then the reaction residue was extracted using EtOAc/H_2O and concentrated under reduced pressure followed by column chromatography over silica gel using petroleum / EtOAc = 20/1 as eluent to afford the desired product **6** (46 mg, 53% yield).



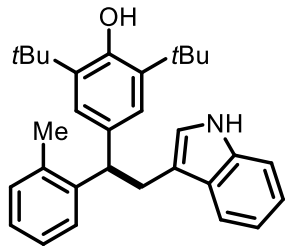
7. Characterization data of compounds

***4-(2-(1H-indol-3-yl)-1-phenylethyl)-2,6-di-tert-butylphenol* (3)**



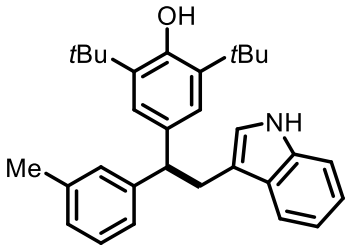
Yellow solid, m. p. 149-153 °C, 79 mg, 93% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.14 (m, 5H), 7.08 (ddd, *J* = 7.8, 5.4, 2.3 Hz, 2H), 7.04 – 6.97 (m, 1H), 6.96 (s, 2H), 6.46 (d, *J* = 2.1 Hz, 1H), 4.95 (s, 1H), 4.19 (t, *J* = 7.7 Hz, 1H), 3.54 – 3.11 (m, 2H), 1.29 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 145.4, 135.9, 135.8, 135.4, 128.2, 128.2, 127.8, 125.9, 124.5, 122.2, 121.7, 119.1, 118.8, 115.0, 110.9, 51.8, 34.4, 32.3, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{36}NO^+$ $(M+H)^+$ 426.2791, found *m/z* 426.2790.

***4-(2-(1H-indol-3-yl)-1-(o-tolyl)ethyl)-2,6-di-tert-butylphenol* (4)**



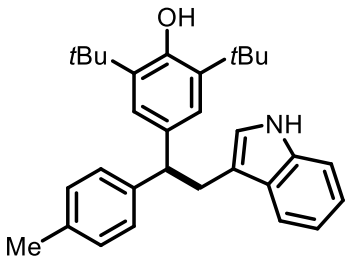
Colorless oil, 80 mg, 91% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.47 (dd, *J* = 10.6, 7.9 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 5.6 Hz, 1H), 7.13 (dd, *J* = 13.4, 5.9 Hz, 1H), 7.06 (dt, *J* = 15.7, 5.4 Hz, 3H), 6.95 (s, 2H), 6.52 (d, *J* = 1.8 Hz, 1H), 4.98 (s, 1H), 4.44 (t, *J* = 7.6 Hz, 1H), 3.69 – 3.22 (m, 2H), 2.16 (s, 3H), 1.34 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 143.4, 136.4, 135.9, 135.3, 135.2, 130.3, 127.9, 126.7, 125.9, 125.7, 124.7, 122.1, 121.7, 119.1, 118.8, 115.1, 110.9, 47.2, 34.3, 32.4, 30.3, 20.0 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO^+$ $(M+H)^+$ 440.2948, found *m/z* 440.2950.

***4-(2-(1H-indol-3-yl)-1-(m-tolyl)ethyl)-2,6-di-tert-butylphenol* (5)**



Yellow solid, m. p. 139-142 °C, 79 mg, 90% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.12 – 6.97 (m, 5H), 6.95 (s, 2H), 6.89 (d, *J* = 6.8 Hz, 1H), 6.43 (s, 1H), 4.92 (s, 1H), 4.13 (t, *J* = 7.6 Hz, 1H), 3.35 (qd, *J* = 14.7, 7.7 Hz, 2H), 2.20 (s, 3H), 1.28 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 145.4, 137.7, 136.0, 135.9, 135.4, 129.2, 128.2, 127.8, 126.7, 125.0, 124.5, 122.3, 121.7, 119.1, 118.9, 115.1, 110.9, 51.9, 34.4, 32.4, 30.4, 21.6 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO^+$ $(M+H)^+$ 440.2948, found *m/z* 440.2951.

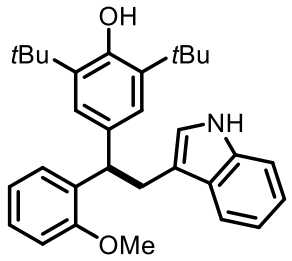
***4-(2-(1H-indol-3-yl)-1-(p-tolyl)ethyl)-2,6-di-tert-butylphenol* (6)**



Yellow soild, m. p. 146-148 °C, 84 mg, 96% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.22 (m, 4H), 7.20 – 7.13 (m, 5H), 6.61 (d, *J* = 1.3 Hz, 1H), 5.11 (d, *J* = 5.5 Hz, 1H), 4.34 (t, *J* = 7.5 Hz, 1H), 3.70 – 3.40 (m, 2H), 2.40 (s, 3H),

1.49 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 142.5, 136.2, 135.9, 135.5, 135.3, 129.0, 128.0, 127.9, 124.5, 122.3, 121.7, 119.1, 118.9, 115.0, 111.0, 51.5, 34.4, 32.4, 30.4, 21.1 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO^+$ $(M+H)^+$ 440.2948, found *m/z* 440.2956.

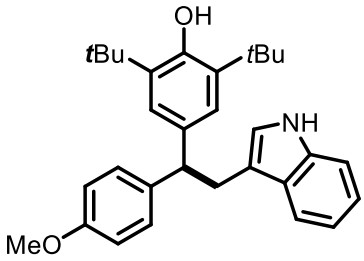
***4-(2-(1H-indol-3-yl)-1-(2-methoxyphenyl)ethyl)-2,6-di-tert-butylphenol* (7)**



Yellow solid, m. p. 153-156 ^oC, 78 mg, 86% yield, Rf = 0.3 (ethyl acetate/hexane = 10%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.05 (dd, *J* = 13.2, 6.0 Hz, 4H), 7.01 – 6.96 (m, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.51 (s, 1H), 4.90 (s, 1H), 4.70 (t, *J* = 7.8 Hz, 1H), 3.62 (s, 3H), 3.35 (ddd, *J* = 39.1, 14.8, 7.8 Hz, 2H), 1.29 (s, 18H).

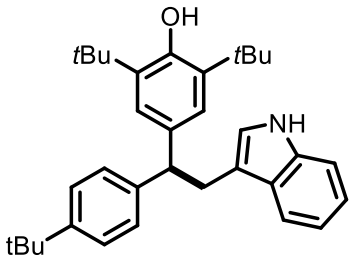
ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 151.8, 135.9, 135.3, 135.1, 134.2, 128.0, 128.0, 126.8, 124.9, 122.0, 121.6, 120.5, 119.0, 119.0, 115.4, 110.8, 110.7, 55.4, 43.7, 34.4, 31.1, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO_2^+$ $(M+H)^+$ 456.2897, found *m/z* 456.2896.

***4-(2-(1H-indol-3-yl)-1-(4-methoxyphenyl)ethyl)-2,6-di-tert-butylphenol* (8)**



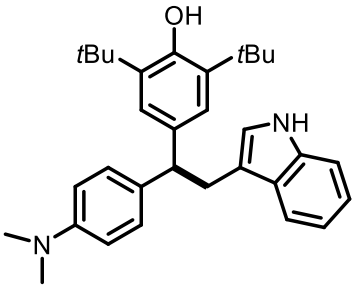
Yellow solid, m. p. 165-169 ^oC, 75 mg, 82% yield, Rf = 0.2 (ethyl acetate/hexane = 10%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 7.9 Hz, 1H), 7.10 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 7.8 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.94 (s, 2H), 6.72 (d, J = 8.6 Hz, 2H), 6.46 (d, J = 1.7 Hz, 1H), 4.93 (s, 1H), 4.14 (t, J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.34 (d, J = 7.7 Hz, 2H), 1.29 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 151.9, 137.7, 136.23, 136.0, 135.5, 129.0, 127.8, 124.4, 122.3, 121.7, 119.1, 118.8, 115.1, 113.6, 110.9, 55.2, 50.9, 34.4, 32.6, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO_2^+$ $(M+H)^+$ 456.2897, found *m/z* 456.2897.

***2,6-di-tert-butyl-4-(1-(4-(tert-butyl)phenyl)-2-(1H-indol-3-yl)ethyl)phenol* (9)**



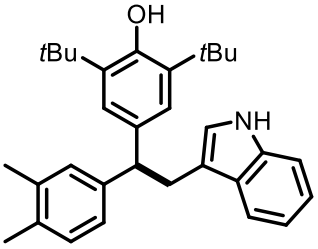
Yellow solid, m. p. 171-173 °C, 89 mg, 92% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ
7.59 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.11 (m, 5H), 7.04 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.02 – 6.92 (m, 3H), 6.45 (s, 1H), 4.92 (s, 1H), 4.13 (t, *J* = 7.6 Hz, 1H), 3.36 (qd, *J* = 14.7, 7.8 Hz, 2H), 1.29 (s, 18H), 1.21 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.08, 148.6, 142.5, 136.0, 135.9, 135.4, 127.9, 127.6, 125.2, 124.6, 122.3, 121.7, 119.1, 118.9, 115.2, 110.9, 51.5, 34.4, 32.5, 31.5, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{34}H_{44}NO^+$ $(M+H)^+$ 482.3417, found *m/z* 482.3417.

2,6-di-tert-butyl-4-(1-(4-(dimethylamino)phenyl)-2-(1H-indol-3-yl)ethyl)phenol **(10)**



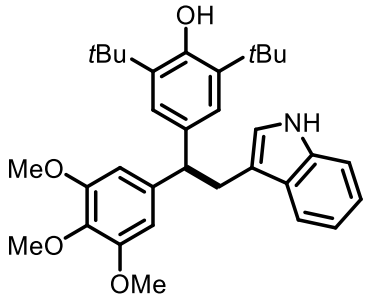
Brown solid, m. p. 182-185 °C, 81 mg, 86% yield, Rf = 0.2 (ethyl acetate/hexane = 15%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.06 (dd, *J* = 11.4, 8.1 Hz, 3H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.96 (s, 2H), 6.59 (d, *J* = 8.7 Hz, 2H), 6.45 (d, *J* = 2.0 Hz, 1H), 4.91 (s, 1H), 4.09 (t, *J* = 7.6 Hz, 1H), 3.33 (t, *J* = 8.1 Hz, 2H), 2.81 (s, 6H), 1.29 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 149.0, 136.6, 135.9, 135.3, 133.9, 128.7, 127.9, 124.4, 122.3, 121.6, 119.0, 118.9, 115.3, 112.9, 110.9, 50.9, 40.9, 34.4, 32.5, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{32}H_{41}N_2O^+$ $(M+H)^+$ 469.3213, found *m/z* 469.3211.

2,6-di-tert-butyl-4-(1-(3,4-dimethylphenyl)-2-(1H-indol-3-yl)ethyl)phenol **(11)**



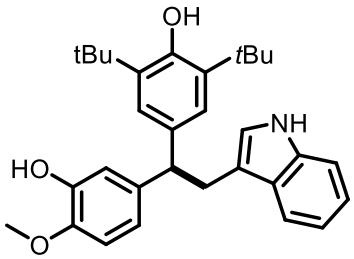
Slight yellow solid, m. p. 135-137 °C, 81 mg, 89% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.51 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.03 (t, *J* = 7.3 Hz, 1H), 7.01 – 6.90 (m, 6H), 6.42 (s, 1H), 4.90 (s, 1H), 4.09 (t, *J* = 7.6 Hz, 1H), 3.34 (qd, *J* = 14.7, 7.7 Hz, 2H), 2.11 (s, 6H), 1.28 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 143.0, 136.3, 136.2, 135.9, 135.4, 134.0, 129.7, 129.6, 127.9, 125.2, 124.5, 122.3, 121.7, 119.1, 118.9, 115.2, 111.0, 51.6, 34.4, 32.4, 30.4, 20.0, 19.5 ppm; **HRMS (ESI)** m/z calcd for $C_{32}H_{40}NO^+$ $(M+H)^+$ 454.3104, found *m/z* 454.3101.

4-(2-(1H-indol-3-yl)-1-(3,4,5-trimethoxyphenyl)ethyl)-2,6-di-tert-butylphenol **(12)**



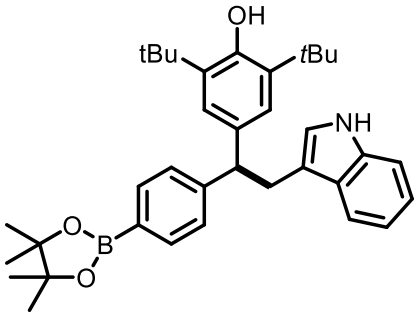
Slight yellow solid, m. p. 177-179 ^{o}C, 83 mg, 80% yield, Rf = 0.3 (ethyl acetate/hexane = 20%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.17 – 7.09 (m, 3H), 6.65 (d, *J* = 2.1 Hz, 1H), 6.55 (s, 2H), 5.13 (s, 1H), 4.23 (d, *J* = 7.6 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 6H), 3.48 (d, *J* = 7.6 Hz, 2H), 1.46 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.9, 152.2, 141.2, 136.1, 136.0, 135.5, 135.5, 127.8, 124.4, 122.5, 121.7, 119.1, 118.8, 114.7, 111.1, 105.2, 60.9, 56.0, 52.4, 34.4, 32.9, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{33}H_{42}NO_4^+$ $(M+H)^+$ 516.3108, found *m/z* 516.3110.

2,6-di-tert-butyl-4-(1-(3-hydroxy-4-methoxyphenyl)-2-(1H-indol-3-yl)ethyl)phenol **(13)**



Yellow solid, m. p. 161-164 ^{o}C, 76 mg, 81% yield, Rf = 0.4 (ethyl acetate/hexane = 20%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.96 (s, 2H), 6.78 – 6.68 (m, 2H), 6.63 (d, *J* = 1.3 Hz, 1H), 6.50 (d, *J* = 2.1 Hz, 1H), 5.37 (s, 1H), 4.95 (s, 1H), 4.11 (t, *J* = 7.7 Hz, 1H), 3.67 (s, 3H), 3.33 (d, *J* = 7.6 Hz, 2H), 1.30 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 146.2, 143.7, 137.4, 136.0, 135.9, 135.4, 127.8, 124.4, 122.3, 121.7, 120.6, 119.1, 118.8, 115.0, 114.0, 111.1, 110.9, 55.8, 51.5, 34.4, 32.7, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO_3^+$ $(M+H)^+$ 472.2846, found *m/z* 472.2846.

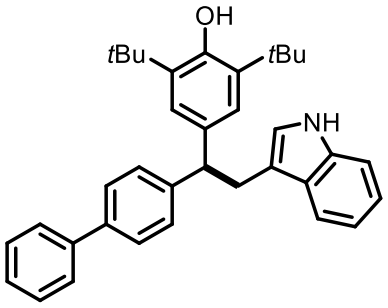
4-(2-(1H-indol-3-yl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)-2,6-di-tert-butyl phenol **(14)**



Slight yellow solid, m. p. 183-185 ^{o}C, 91 mg, 83% yield, Rf = 0.3 (ethyl acetate/hexane = 10%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* =

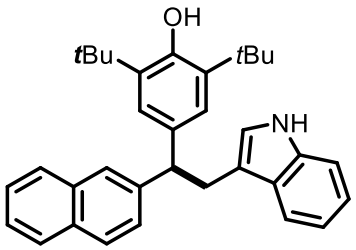
7.8 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 3.7 Hz, 2H), 6.43 (d, *J* = 1.7 Hz, 1H), 4.93 (s, 1H), 4.19 (t, *J* = 7.6 Hz, 1H), 3.50 – 3.22 (m, 2H), 1.28 (s, 18H), 1.24 (s, 12H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 148.8, 135.9, 135.6, 135.5, 134.8, 127.8, 127.7, 124.5, 122.3, 121.7, 119.1, 118.8, 114.8, 111.0, 83.7, 52.0, 34.4, 32.1, 30.4, 24.9, 24.9 ppm; **HRMS (ESI)** m/z calcd for $C_{36}H_{47}BNO_3^+$ $(M+H)^+$ 552.3644, found *m/z* 552.3649.

4-(1-([1,1'-biphenyl]-4-yl)-2-(1H-indol-3-yl)ethyl)-2,6-di-tert-butylphenol **(15)**



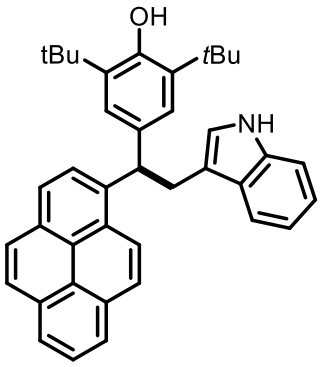
Slight yellow solid, m. p. 159-161 °C, 84 mg, 84% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.51 – 7.38 (m, 5H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.14 (m, 4H), 7.06 (dd, *J* = 16.3, 9.3 Hz, 1H), 7.02 – 6.95 (m, 3H), 6.46 (s, 1H), 4.95 (s, 1H), 4.22 (t, *J* = 7.6 Hz, 1H), 3.39 (dd, *J* = 14.4, 7.7 Hz, 2H), 1.29 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 144.7, 141.1, 138.7, 136.0, 135.8, 135.6, 128.8, 128.6, 127.8, 127.1, 127.0, 127.0, 124.6, 122.4, 121.8, 119.2, 118.9, 114.9, 111.0, 51.6, 34.4, 32.4, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{36}H_{40}NO^+$ $(M+H)^+$ 502.3104, found *m/z* 502.3108.

4-(2-(1H-indol-3-yl)-1-(naphthalen-2-yl)ethyl)-2,6-di-tert-butylphenol **(16)**



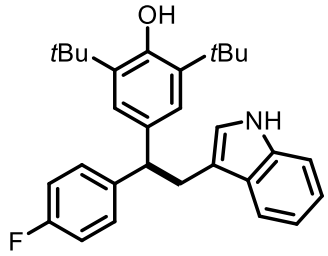
Yellow solid, m. p. 145-148 °C, 84 mg, 88% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.74 (m, 4H), 7.65 (d, *J* = 6.6 Hz, 2H), 7.56 – 7.45 (m, 3H), 7.37 – 7.27 (m, 1H), 7.26 – 7.03 (m, 4H), 6.56 (s, 1H), 5.12 (s, 1H), 4.52 (t, *J* = 7.3 Hz, 1H), 3.98 – 3.19 (m, 2H), 1.46 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 143.0, 136.0, 135.8, 135.6, 133.6, 132.2, 127.8, 127.8, 127.6, 127.1, 126.4, 125.8, 125.2, 124.6, 122.4, 121.8, 119.2, 118.8, 114.8, 111.0, 51.9, 34.4, 32.2, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{34}H_{38}NO^+$ $(M+H)^+$ 476.2948, found *m/z* 476.2955.

4-(2-(1H-indol-3-yl)-1-(pyren-1-yl)ethyl)-2,6-di-tert-butylphenol **(17)**



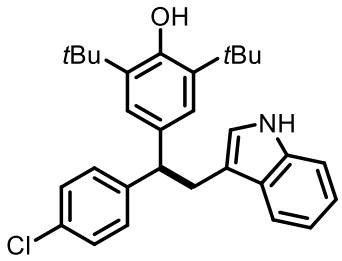
Yellow solid, m. p. 163-166 ^{o}C, 78 mg, 71% yield, Rf = 0.3 (ethyl acetate/hexane = 10%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 9.4 Hz, 1H), 8.09 (s, 2H), 8.04 (dd, *J* = 13.2, 7.6 Hz, 2H), 7.97 – 7.91 (m, 2H), 7.88 (dd, *J* = 12.6, 5.1 Hz, 2H), 7.58 – 7.49 (m, 2H), 7.16 (t, *J* = 3.9 Hz, 1H), 7.10 – 6.96 (m, 4H), 6.33 (d, *J* = 1.5 Hz, 1H), 5.36 (t, *J* = 7.6 Hz, 1H), 4.92 (s, 1H), 3.79 – 3.55 (m, 2H), 1.25 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 139.3, 135.9, 135.9, 135.5, 131.4, 130.8, 129.6, 129.0, 127.9, 127.6, 127.1, 126.7, 125.7, 125.1, 125.1, 125.0, 124.9, 124.8, 124.7, 124.6, 123.5, 122.2, 121.8, 119.2, 118.7, 114.95, 110.9, 46.5, 34.3, 32.8, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{40}H_{40}NO^{+}$ $(M+H)^{+}$ 550.3104, found *m/z* 550.3102.

2,6-di-tert-butyl-4-(1-(4-fluorophenyl)-2-(1H-indol-3-yl)ethyl)phenol **(18)**



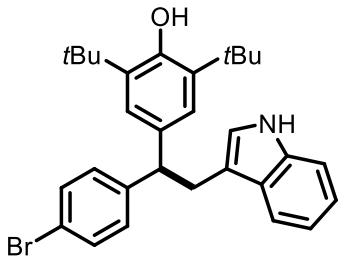
Slight yellow oil, m. p. 149-153 ^{o}C, 77 mg, 87% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.10 (dt, *J* = 11.2, 6.8 Hz, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.93 (s, 2H), 6.85 (t, *J* = 8.7 Hz, 2H), 6.48 (d, *J* = 1.2 Hz, 1H), 4.97 (s, 1H), 4.18 (t, *J* = 7.7 Hz, 1H), 3.45 – 3.24 (m, 2H), 1.30 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 160.0, 152.1, 141.0 (d, *J* = 2.9 Hz), 135.9, 135.7, 135.5, 129.5 (d, *J* = 7.7 Hz), 127.7, 124.4, 122.2, 121.8, 119.2, 118.8, 115.0, 114.8, 114.7, 111.0, 50.9, 34.4, 32.5, 30.3ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ-117.68 (dd, *J* = 9.9, 4.4 Hz, 1F) ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{35}FNO^{+}$ $(M+H)^{+}$ 444.2697, found *m/z* 444.2698.

2,6-di-tert-butyl-4-(1-(4-chlorophenyl)-2-(1H-indol-3-yl)ethyl)phenol **(19)**



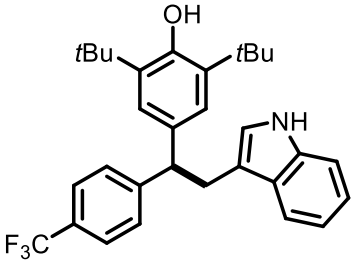
White solid, m. p. 151-153 ^{o}C, 85 mg, 92% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.14 – 7.04 (m, 5H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.93 (s, 2H), 6.45 (s, 1H), 4.97 (s, 1H), 4.16 (t, *J* = 7.6 Hz, 1H), 3.48 – 3.26 (m, 2H), 1.30 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.2, 143.9, 136.0, 135.6, 135.4, 131.5, 129.6, 128.3, 127.67, 124.4, 122.3, 121.9, 119.2, 118.8, 114.5, 111.0, 51.1, 34.4, 32.3, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{35}ClNO^{+}$ $(M+H)^{+}$ 460.2402, found *m/z* 460.2411.

4-(1-(4-bromophenyl)-2-(1H-indol-3-yl)ethyl)-2,6-di-tert-butylphenol **(20)**



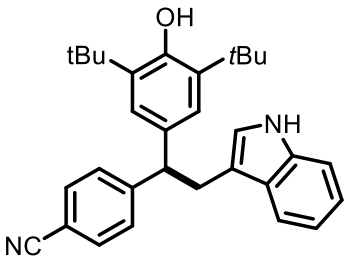
Yellow solid, m. p. 156-159 ^{o}C, 92 mg, 91% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.09 – 6.96 (m, 4H), 6.93 (s, 2H), 6.43 (s, 1H), 4.97 (s, 1H), 4.14 (t, *J* = 7.6 Hz, 1H), 3.43–3.21 (m, 2H), 1.29 (s, 18H)ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.0, 143.3, 134.8, 134.5, 134.1, 130.1, 128.8, 126.5, 123.2, 121.2, 120.7, 118.5, 118.1, 117.6, 113.3, 109.9, 50.0, 33.3, 31.1, 29.2 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{35}BrNO^{+}$ $(M+H)^{+}$ 504.1897, found *m/z* 504.1898.

4-(2-(1H-indol-3-yl)-1-(4-(trifluoromethyl)phenyl)ethyl)-2,6-di-tert-butylphenol **(21)**



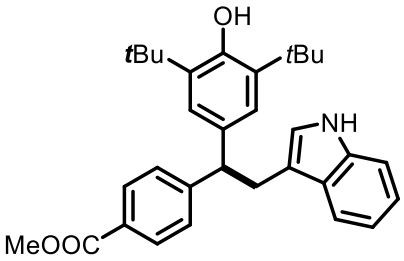
Slight yellow oil, 83 mg, 84% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.65 (s, 1H), 7.40 (t, *J* = 8.0 Hz, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.95 (s, 2H), 6.44 (d, *J* = 1.2 Hz, 1H), 4.99 (s, 1H), 4.24 (t, *J* = 7.6 Hz, 1H), 3.56 – 3.20 (m, 2H), 1.30 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) 152.3, 149.6, 136.0, 135.8, 134.9, 128.4, 127.6, 125.5 (q, J = 219.4 Hz), 125.2 (q, *J* = 3.9 Hz)., 124.4, 122.3, 121.9, 119.3, 118.7, 114.3, 111.1, 51.7, 34.4, 32.1, 30.3 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.11 (s) ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{35}F_3NO^{+}$ $(M+Na)^{+}$ 494.2665, found *m/z* 494.2665.

4-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1H-indol-3-yl)ethyl)benzonitrile **(22)**



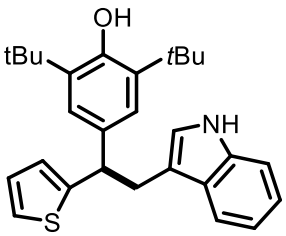
Yellow solid, m. p. 147-151 ^{o}C, 63 mg, 70% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.42 (t, *J* = 7.9 Hz, 3H), 7.23 (t, *J* = 8.6 Hz, 3H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.92 (s, 2H), 6.49 (d, *J* = 2.2 Hz, 1H), 5.02 (s, 1H), 4.26 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.38 (qd, *J* = 14.5, 7.8 Hz, 2H), 1.31 (s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 151.1, 136.0, 135.9, 134.2, 132.0, 129.0, 127.5, 124.4, 122.2, 122.0, 119.3, 119.2, 118.6, 114.0, 111.1, 109.6, 51.8, 34.4, 32.0, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{35}N_2O^+$ $(M+H)^+$ 451.2744, found *m/z* 451.2752.

***methyl -4-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1H-indol-3-yl)ethyl)benzoate* (23)**



Yellow solid, m. p. 142-145 ^{o}C, 75 mg, 78% yield, Rf = 0.2 (ethyl acetate/hexane = 20%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.74 (s, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.07 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.94 (s, 2H), 6.45 (d, *J* = 2.2 Hz, 1H), 4.98 (s, 1H), 4.25 (t, *J* = 7.7 Hz, 1H), 3.80 (d, *J* = 7.2 Hz, 3H), 3.38 (d, *J* = 7.7 Hz, 2H), 1.29 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3, 152.2, 151.0, 136.0, 135.7, 135.0, 129.6, 128.3, 127.8, 127.7, 124.5, 122.3, 121.8, 119.2, 118.7, 114.4, 111.0, 52.0, 51.8, 34.4, 32.1, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{32}H_{38}NO_3^+$ $(M+H)^+$ 484.2846, found *m/z* 484.2850.

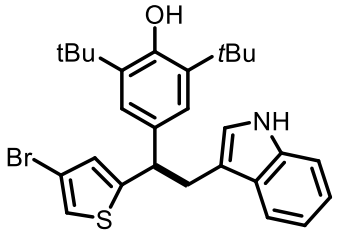
4-(2-(1H-indol-3-yl)-1-(thiophen-2-yl)ethyl)-2,6-di-tert-butylphenol (24)



Yellow solid, m. p. 133-135 ^{o}C, 71 mg, 82% yield, Rf = 0.4 (ethyl acetate/hexane = 10%); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.65 (s, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 1H), 7.09 – 7.02 (m, 2H), 7.01 – 6.93 (m, 3H), 6.80 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.73 (d, *J* = 3.3 Hz, 1H), 6.54 (d, *J* = 2.2 Hz, 1H), 4.96 (s, 1H), 4.39 (t, *J* = 7.5 Hz, 1H), 3.37 (ddd, *J* = 46.0, 14.5, 7.5 Hz, 2H), 1.29 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 149.8, 135.9, 135.6, 135.3, 127.8, 126.4, 124.4, 124.2, 123.3, 122.4,

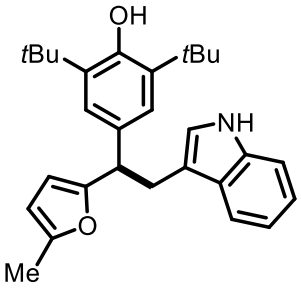
121.8, 119.2, 118.8, 114.5, 111.0, 47.8, 34.5, 34.4, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{28}H_{34}NOS^+$ $(M+H)^+$ 432.2356, found *m/z* 432.2349.

***4-(1-(4-bromothiophen-2-yl)-2-(1H-indol-3-yl)ethyl)-2,6-di-tert-butylphenol* (25)**



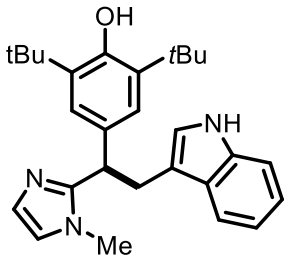
White solid, m. p. 139-142 ^oC, 82 mg, 80% yield, Rf = 0.4 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ
7.72 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.96 – 6.89 (m, 3H), 6.64 (s, 1H), 6.58 (d, *J* = 2.1 Hz, 1H), 5.00 (s, 1H), 4.32 (t, *J* = 7.5 Hz, 1H), 3.34 (ddd, *J* = 21.5, 14.5, 7.5 Hz, 2H), 1.30 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 151.2, 136.0, 135.8, 134.4, 127.6, 126.9, 124.3, 122.5, 121.9, 120.7, 119.3, 118.7, 114.0, 111.0, 108.8, 47.8, 34.4, 33.9, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{28}H_{33}BrNOS^+$ $(M+H)^+$ 510.1461, found *m/z* 510.1455.

***4-(2-(1H-indol-3-yl)-1-(5-methylfuran-2-yl)ethyl)-2,6-di-tert-butylphenol* (26)**



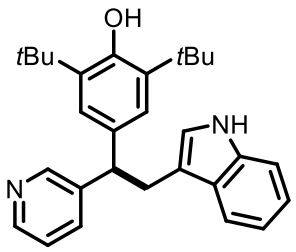
Yellow solid, m. p. 135-138 ^oC, 74 mg, 86% yield, Rf = 0.4 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.89 (s, 2H), 6.58 (d, *J* = 2.2 Hz, 1H), 5.88 (d, *J* = 3.1 Hz, 1H), 5.78 (d, *J* = 2.1 Hz, 1H), 4.94 (s, 1H), 4.09 (t, *J* = 7.6 Hz, 1H), 3.41 (dd, *J* = 14.5, 7.9 Hz, 1H), 3.13 (dd, *J* = 14.5, 7.4 Hz, 1H), 2.19 (s, 3H), 1.27 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.3, 152.2, 150.4, 135.9, 135.4, 133.7, 127.8, 124.4, 122.2, 121.7, 119.1, 118.8, 114.6, 110.8, 106.3, 105.8, 46.2, 34.3, 31.7, 30.3, 13.7ppm; **HRMS (ESI)** m/z calcd for $C_{29}H_{36}NO_2^+$ $(M+H)^+$ 430.2741, found *m/z* 430.2744.

***4-(2-(1H-indol-3-yl)-1-(1-methyl-1H-imidazol-2-yl)ethyl)-2,6-di-tert-butylphenol* (27)**



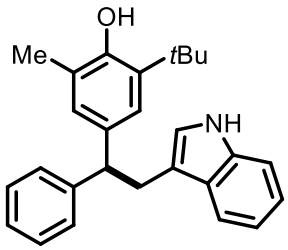
Slight yellow solid, m. p. 147-149 °C, 63 mg, 73% yield, Rf = 0.3 (ethyl acetate/hexane = 30%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.05 (dd, *J* = 11.1, 3.9 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.84 (s, 2H), 6.62 (dd, *J* = 5.4, 1.5 Hz, 2H), 4.97 (s, 1H), 4.09 (t, *J* = 7.5 Hz, 1H), 3.71 (dd, *J* = 14.2, 8.1 Hz, 1H), 3.29 (dd, *J* = 14.3, 7.0 Hz, 1H), 3.17 (s, 3H), 1.25 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 150.1, 136.0, 135.7, 132.6, 127.7, 126.8, 124.4, 122.8, 121.5, 120.4, 119.1, 118.6, 114.4, 111.0, 44.7, 34.3, 32.6, 32.1, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{28}H_{36}N_3O^+$ $(M+H)^+$ 430.2853, found *m/z* 430.2851.

***4-(2-(1H-indol-3-yl)-1-(pyridin-3-yl)ethyl)-2,6-di-tert-butylphenol* (28)**



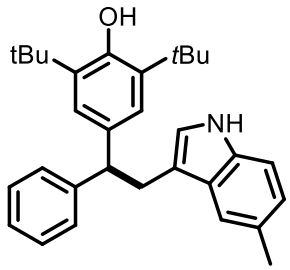
Yellow solid, m. p. 146-148 °C, 68 mg, 80% yield, Rf = 0.4 (ethyl acetate/hexane = 20%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.30 (d, *J* = 4.3 Hz, 1H), 7.98 (s, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 6.7 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.97 (s, 2H), 6.50 (s, 1H), 5.05 (s, 1H), 4.60 – 3.93 (m, 1H), 3.39 (qd, *J* = 14.5, 7.9 Hz, 2H), 1.31 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 149.8, 147.2, 140.7, 136.1, 135.9, 135.5, 134.5, 127.5, 124.4, 123.3, 122.4, 121.9, 119.2, 118.9, 114.0, 111.1, 49.3, 34.4, 32.1, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{29}H_{35}N_2O^+$ $(M+H)^+$ 427.2744, found *m/z* 427.2745.

***4-(2-(1H-indol-3-yl)-1-phenylethyl)-2-(tert-butyl)-6-methylphenol* (29)**



Slight yellow oil, m. p. 135-138 °C, 62 mg, 81% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.17 (dd, *J* = 5.5, 2.7 Hz, 5H), 7.10 – 7.04 (m, 2H), 7.01 (dd, *J* = 10.9, 4.0 Hz, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.79 (d, *J* = 1.7 Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 4.51 (s, 1H), 4.18 (t, *J* = 7.7 Hz, 1H), 3.50 – 3.30 (m, 2H), 2.06 (s, 3H), 1.27 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 145.6, 136.4, 136.0, 135.3, 128.3, 128.1, 127.8, 127.7, 126.0, 124.9, 122.8, 122.3, 121.8, 119.2, 118.8, 114.8, 111.0, 51.2, 34.6, 32.1, 29.8, 16.2 ppm; **HRMS (ESI)** m/z calcd for $C_{27}H_{30}NO^+$ $(M+H)^+$ 384.2322, found *m/z* 384.2322.

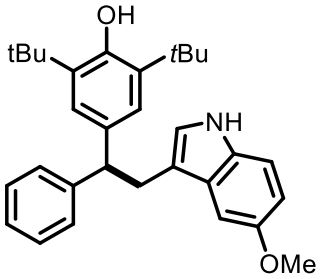
***2,6-di-tert-butyl-4-(2-(5-methyl-1H-indol-3-yl)-1-phenylethyl)phenol* (30)**



White solid, m. p. 151-153 °C, 79 mg, 90% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ

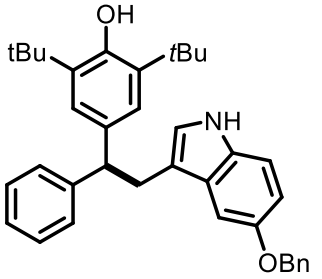
7.46 (s, 1H), 7.23 – 7.17 (m, 3H), 7.11 (s, 1H), 7.06 (ddd, *J* = 16.1, 7.4, 3.8 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.39 (s, 1H), 4.94 (d, *J* = 8.7 Hz, 1H), 4.14 (t, *J* = 7.6 Hz, 1H), 3.33 (dd, *J* = 7.5, 3.2 Hz, 2H), 2.32 (s, 3H), 1.28 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 145.7, 136.0, 135.5, 134.3, 128.2, 128.1, 125.9, 124.6, 123.3, 122.4, 118.6, 114.5, 110.6, 52.0, 34.4, 32.4, 30.4, 21.6 ppm; **^{1}HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO^+$ $(M+H)^+$ 440.2948, found *m/z* 440.2949.

***2,6-di-tert-butyl-4-(2-(5-methoxy-1H-indol-3-yl)-1-phenylethyl)phenol* (31)**



Yellow solid, m. p. 145-147 °C, 84 mg, 92% yield, Rf = 0.3 (ethyl acetate/hexane = 10%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.39 – 7.31 (m, 4H), 7.23 (dd, *J* = 14.2, 7.8 Hz, 2H), 7.12 (s, 2H), 6.59 (d, *J* = 2.2 Hz, 1H), 5.11 (s, 1H), 4.32 (t, *J* = 7.6 Hz, 1H), 3.87 (s, 3H), 3.63 – 3.23 (m, 2H), 1.45 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.8, 152.0, 145.5, 136.0, 135.5, 131.1, 128.3, 128.2, 128.2, 126.0, 124.6, 123.2, 114.8, 112.0, 111.7, 100.7, 55.9, 51.9, 34.5, 34.4, 32.5, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO_2^+$ $(M+H)^+$ 456.2897, found *m/z* 456.2894.

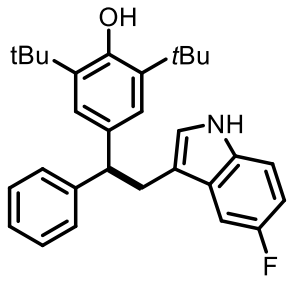
***4-(2-(5-(benzyloxy)-1H-indol-3-yl)-1-phenylethyl)-2,6-di-tert-butylphenol* (32)**



Yellow solid, m. p. 154-157 °C, 93 mg, 88% yield, Rf = 0.4 (ethyl acetate/hexane = 10%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.38 (d, *J* = 7.1 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.20 – 7.11 (m, 4H), 7.11 – 7.04 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.93 (s, 2H), 6.86 (d, *J* = 2.3 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 1H), 4.93 (s, 3H), 4.13 (t, *J* = 7.6 Hz, 1H), 3.46 – 3.02 (m, 2H), 1.27 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 152.0, 145.6, 137.8, 135.9, 135.5, 131.4, 128.5, 128.3, 128.2, 127.8, 127.7, 126.0, 124.6, 123.2, 114.8, 112.7, 111.6, 102.5,

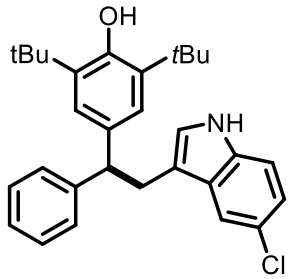
71.0, 51.9, 34.4, 32.5, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{37}H_{42}NO_2^+$ $(M+H)^+$ 532.3210, found *m/z* 532.3210.

***2,6-di-tert-butyl-4-(2-(5-fluoro-1H-indol-3-yl)-1-phenylethyl)phenol* (33)**



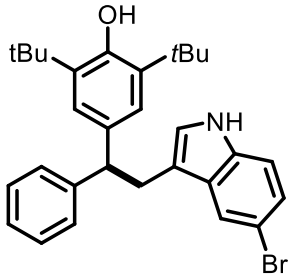
Colorless oil, 74 mg, 84% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.26 – 7.14 (m, 4H), 7.10 – 7.01 (m, 2H), 6.97 – 6.88 (m, 3H), 6.77 (td, *J* = 9.0, 2.2 Hz, 1H), 6.50 (s, 1H), 4.93 (s, 1H), 4.11 (t, *J* = 7.7 Hz, 1H), 3.69 – 2.56 (m, 2H), 1.27 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9, 156.6, 152.1, 145.3, 135.6, 132.4, 128.3, 128.2, 128.1, 126.0, 124.5, 124.1, 115.3, 115.2, 111.5, 111.4, 110.1, 109.9, 103.9, 103.7, 52.0, 34.4, 32.4, 30.4 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -125.17 (td, *J* = 9.5, 4.1 Hz) ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{35}FNO^+$ $(M+H)^+$ 444.2697, found *m/z* 444.2693.

2,6-di-tert-butyl-4-(2-(5-chloro-1H-indol-3-yl)-1-phenylethyl)phenol (34)



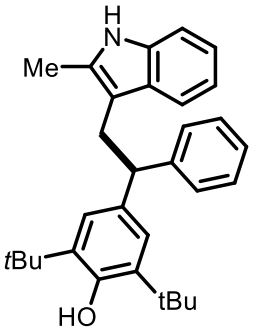
Yellow solid, m. p. 152-155 °C, 79 mg, 86% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.34 (t, *J* = 5.1 Hz, 5H), 7.27 – 7.21 (m, 1H), 7.20 – 7.16 (m, 1H), 7.15 – 7.10 (m, 1H), 7.06 (d, *J* = 4.3 Hz, 2H), 6.65 (s, 1H), 5.09 (d, *J* = 4.3 Hz, 1H), 4.25 (td, *J* = 7.5, 4.4 Hz, 1H), 3.46 (dt, *J* = 11.4, 5.7 Hz, 2H), 1.43 (d, *J* = 4.4 Hz, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 145.3, 135.7, 135.5, 134.2, 129.0, 128.3, 128.1, 126.0, 125.0, 124.5, 123.7, 122.0, 118.5, 115.0, 111.9, 52.2, 34.4, 32.3, 30.34 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{35}ClNO^+$ $(M+H)^+$ 460.2402, found *m/z* 460.2402.

4-(2-(5-bromo-1H-indol-3-yl)-1-phenylethyl)-2,6-di-tert-butylphenol (35)



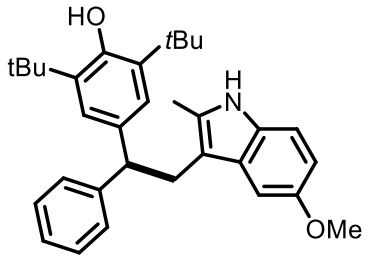
Yellow solid, m. p. 158-161 °C, 90 mg, 89% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.49 (d, *J* = 3.5 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.25 (ddd, *J* = 11.7, 5.3, 3.5 Hz, 2H), 7.14 (dd, *J* = 8.5, 5.0 Hz, 1H), 7.06 (d, *J* = 5.1 Hz, 2H), 6.63 (d, *J* = 2.1 Hz, 1H), 5.09 (d, *J* = 5.1 Hz, 1H), 4.48 – 4.03 (m, 1H), 3.45 (dd, *J* = 13.3, 6.5 Hz, 2H), 1.43 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1, 145.3, 135.7, 135.5, 134.5, 129.7, 128.3, 128.1, 126.1, 124.5, 123.5, 121.6, 114.9, 112.6, 112.3, 52.2, 34.4, 32.3, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{35}BrNO+$ $(M+H)^+$ 504.1897, found *m/z* 504.1895.

***2,6-di-tert-butyl-4-(2-(2-methyl-1H-indol-3-yl)-1-phenylethyl)phenol* (36)**



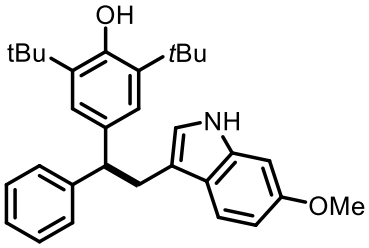
Yellow solid, m. p. 146-149 °C, 72 mg, 82% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.05 (m, 6H), 7.03 – 6.91 (m, 2H), 6.79 (s, 2H), 4.90 (s, 1H), 4.06 (dd, *J* = 16.0, 8.3 Hz, 1H), 3.52 – 2.61 (m, 2H), 1.64 (s, 3H), 1.25 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 145.5, 135.6, 135.3, 135.2, 132.0, 129.0, 128.3, 128.1, 125.9, 124.8, 120.7, 119.0, 118.1, 110.2, 110.0, 51.5, 34.3, 32.0, 30.3, 11.0 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO^+$ $(M+H)^+$ 440.2948, found *m/z* 440.2948. This coumpound is known.[2]

2,6-di-tert-butyl-4-(2-(5-methoxy-2-methyl-1H-indol-3-yl)-1-phenylethyl)phenol (37)



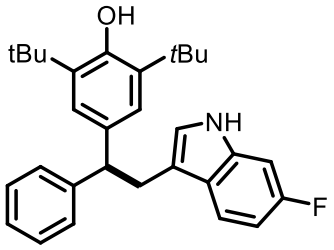
Yellow solid, m. p. 155-158 °C, 81 mg, 86% yield, Rf = 0.3 (ethyl acetate/hexane = 15%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.21 – 7.12 (m, 4H), 7.11 – 7.04 (m, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.79 (s, 2H), 6.73 – 6.58 (m, 2H), 4.92 (s, 1H), 4.12 – 3.85 (m, 1H), 3.70 (s, 3H), 3.19 (qd, *J* = 13.7, 7.6 Hz, 2H), 1.64 (s, 3H), 1.24 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.8, 152.0, 145.6, 135.7, 135.3, 133.0, 130.4, 129.4, 128.4, 128.1, 125.9, 124.8, 110.6, 110.3, 110.1, 100.6, 56.0, 51.4, 34.3, 32.1, 30.3, 11.1 ppm; **HRMS (ESI)** m/z calcd for $C_{32}H_{40}NO_2^+$ $(M+H)^+$ 470.3054, found *m/z* 470.3050.

***2,6-di-tert-butyl-4-(2-(6-methoxy-1H-indol-3-yl)-1-phenylethyl)phenol* (38)**



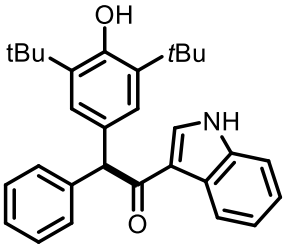
Yellow solid, m. p. 152-154 ^{o}C, 82 mg, 90% yield, Rf = 0.3 (ethyl acetate/hexane = 15%); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.45 (s, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.16 (q, *J* = 8.1 Hz, 4H), 7.06 (dd, *J* = 9.2, 4.3 Hz, 1H), 6.95 (s, 2H), 6.74 – 6.59 (m, 2H), 6.33 (d, *J* = 1.6 Hz, 1H), 4.93 (s, 1H), 4.15 (t, *J* = 7.6 Hz, 1H), 3.70 (s, 3H), 3.44 – 3.04 (m, 2H), 1.28 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 152.0, 145.5, 136.7, 135.9, 135.5, 128.2, 128.2, 125.9, 124.5, 122.4, 121.1, 119.4, 114.9, 109.1, 94.7, 55.7, 51.9, 34.4, 32.5, 30.4 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{38}NO_2^+$ $(M+H)^+$ 456.2897, found *m/z* 456.2898.

***2,6-di-tert-butyl-4-(2-(6-fluoro-1H-indol-3-yl)-1-phenylethyl)phenol* (39)**



Colorless oil, 77 mg, 87% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.22 (dd, *J* = 8.6, 5.3 Hz, 1H), 7.20 – 7.13 (m, 4H), 7.10 – 7.02 (m, 1H), 6.92 (s, 2H), 6.81 (dd, *J* = 9.7, 2.2 Hz, 1H), 6.76 – 6.65 (m, 1H), 6.42 (d, *J* = 1.6 Hz, 1H), 4.93 (s, 1H), 4.13 (t, *J* = 7.7 Hz, 1H), 3.47 – 3.12 (m, 2H), 1.28 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 158.7, 152.1, 145.4, 135.9, 135.7, 135.7, 135.6, 128.3, 128.1, 126.0, 122.5 (d, *J* = 3.7 Hz), 122.5, 122.5, 119.5 (d, *J* = 10.3 Hz) 115.1, 107.8 (d, *J* = 24.6 Hz), 97.2 (d, *J* = 26.0 Hz) 52.0, 34.4, 32.3, 30.4 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.82 (td, *J* = 9.5, 5.4 Hz) ppm; **HRMS (ESI)** m/z calcd for : $C_{30}H_{35}FNO^+$ $(M+H)^+$ 444.2697, found *m/z* 444.2700.

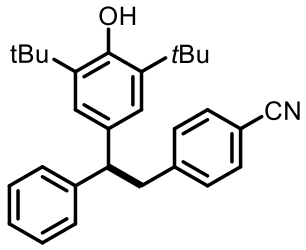
***2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(1H-indol-3-yl)-2-phenylethan-1-one* (40)**



Yellow solid, m. p. 150-153 ^{o}C, 68 mg, 78% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.50 – 8.31 (m, 1H), 7.74 (d, *J* = 3.1 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.17 (ddd, *J* = 14.2, 9.4, 5.9 Hz, 4H), 7.06 (s, 2H), 5.66 (s, 1H), 5.02 (s,

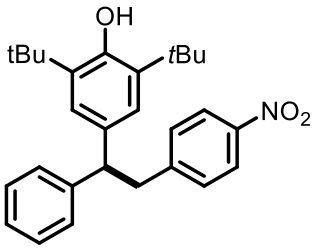
1H), 1.30 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.6, 152.7, 140.7, 136.2, 135.7, 131.7, 130.4, 129.0, 128.5, 126.7, 126.1, 125.8, 123.7, 122.8, 122.7, 118.0, 111.3, 60.9, 34.4, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{34}NO_2^+$ $(M+H)^+$ 440.2584, found *m/z* 440.2588.

4-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylethyl)benzonitrile **(41)**



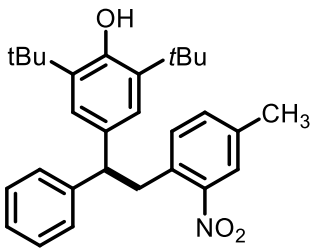
Colorless oil, 58 mg, 71% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.14 (m, 2H), 7.10 (dd, *J* = 7.7, 3.1 Hz, 3H), 6.96 (d, *J* = 8.1 Hz, 2H), 6.84 (s, 2H), 4.98 (s, 1H), 4.01 (t, *J* = 7.9 Hz, 1H), 3.27 (t, *J* = 7.4 Hz, 2H), 1.29 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.2, 146.5, 143.9, 135.7, 134.2, 131.8, 129.9, 128.4, 128.0, 126.3, 124.4, 119.1, 109.7, 52.9, 43.0, 34.3, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{29}H_{34}NO^+$ $(M+H)^+$ 412.2635, found *m/z* 412.2638.

2,6-di-tert-butyl-4-(2-(4-nitrophenyl)-1-phenylethyl)phenol **(42)**



Colorless oil, 56 mg, 65% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.10 (dd, *J* = 7.8, 4.0 Hz, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 2H), 4.98 (s, 1H), 4.04 (t, *J* = 7.9 Hz, 1H), 3.32 (dd, *J* = 7.8, 3.8 Hz, 2H), 1.29 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 148.7, 143.8, 135.8, 134.1, 129.9, 128.4, 127.9, 126.4, 124.3, 123.5, 123.2, 52.9, 42.7, 34.3, 30.3 ppm; **HRMS (ESI)** m/z calcd for $C_{28}H_{34}NO_3^+$ $(M+H)^+$ 432.2533, found *m/z* 432.2533.

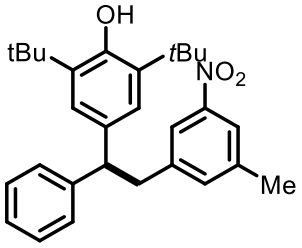
2,6-di-tert-butyl-4-(2-(4-methyl-2-nitrophenyl)-1-phenylethyl)phenol **(43)**



Colorless oil, 61 mg, 68% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.1 Hz, 1H), 7.72 (d, *J* = 2.2 Hz, 1H), 7.39 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.26 – 7.03 (m, 5H),

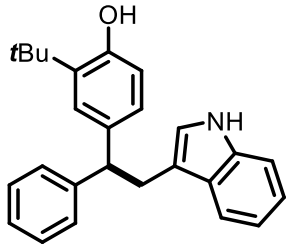
6.79 (d, *J* = 9.0 Hz, 3H), 4.97 (s, 1H), 4.05 (t, *J* = 7.9 Hz, 1H), 3.52 (qd, *J* = 13.3, 7.9 Hz, 2H), 2.49 (s, 3H), 1.28 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 143.4, 135.7, 134.1, 1334.0, 133.8, 133.4, 133.0, 132.5, 132.2, 132.0, 128.4, 128.0, 126.5, 124.7, 124.6, 124.4, 52.1, 39.0, 34.3, 30.2, 30.2, 19.9 ppm; **HRMS (ESI)** m/z calcd for $C_{29}H_{36}NO_3^+$ $(M+H)^+$ 446.2690, found *m/z* 446.2689.

***2,6-di-tert-butyl-4-(2-(3-methyl-5-nitrophenyl)-1-phenylethyl)phenol* (44)**



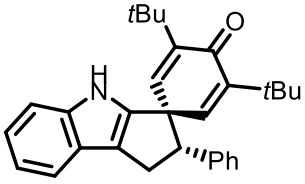
Colorless oil, 68 mg, 76% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.97 (d, *J* = 1.8 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.44 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.31 (dd, *J* = 12.5, 5.4 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 6.90 (s, 2H), 6.85 (d, *J* = 8.3 Hz, 1H), 5.10 (s, 1H), 4.18 (t, *J* = 7.8 Hz, 1H), 3.65 (dt, *J* = 17.4, 8.7 Hz, 2H), 2.58 (s, 3H), 1.40 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 150.2, 143.4, 135.9, 135.7, 135.1, 134.6, 134.2, 134.1, 133.4, 132.5, 128.4, 128.0, 127.5, 127.3, 126.5, 124.6, 119.8, 119.7, 52.0, 39.1, 34.3, 30.3, 20.0 ppm; **HRMS (ESI)** m/z calcd for $C_{29}H_{36}NO_3^+$ $(M+H)^+$ 446.2690, found *m/z* 446.2692.

***4-(2-(1H-indol-3-yl)-1-phenylethyl)-2-(tert-butyl)phenol* (46)**



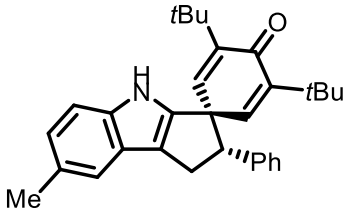
Colorless oil, 57 mg, 77% yield, Rf = 0.3 (ethyl acetate/hexane = 10%); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.67 (s, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.18 (dd, *J* = 4.8, 3.5 Hz, 4H), 7.12 – 7.06 (m, 2H), 7.02 (dd, *J* = 10.9, 4.3 Hz, 2H), 6.85 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.47 (dd, *J* = 7.3, 5.2 Hz, 2H), 4.56 (s, 1H), 4.22 (t, *J* = 7.7 Hz, 1H), 3.37 (dd, *J* = 7.6, 4.3 Hz, 2H), 1.25 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 145.5, 137.1, 136.0, 135.7, 128.3, 128.1, 127.7, 127.1, 126.0, 126.0, 122.3, 121.8, 119.2, 118.8, 116.4, 114.8, 110.9, 51.2, 34.5, 32.1, 29.6 ppm; **HRMS (ESI)** m/z calcd for $C_{26}H_{28}NO^+$ $(M+H)^+$ 370.2165, found *m/z* 370.2162.

***3,5-di-tert-butyl-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one* (47)**



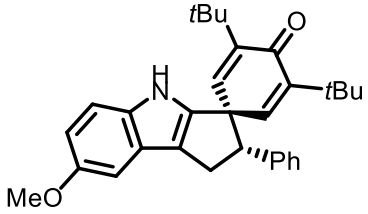
Yellow solid, m. p. 138-140 °C, 36 mg, 43% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.60 (dd, *J* = 6.1, 2.6 Hz, 1H), 7.35 (dd, *J* = 6.3, 2.5 Hz, 1H), 7.25 – 7.12 (m, 7H), 6.81 (d, *J* = 2.7 Hz, 1H), 6.32 (d, *J* = 2.7 Hz, 1H), 4.36 (t, *J* = 8.7 Hz, 1H), 3.57 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.37 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.30 (s, 9H), 0.88 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9, 148.8, 146.3, 142.3, 141.7, 140.7, 140.4, 138.2, 128.0, 128.0, 127.3, 124.7, 121.8, 120.1, 119.1, 119.0, 111.9, 62.6, 52.4, 35.1, 34.7, 29.6, 28.9, 28.4 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{34}NO^+$ $(M+H)^+$ 424.2635, found *m/z* 424.2633.

3,5-di-tert-butyl-7'-methyl-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (48)



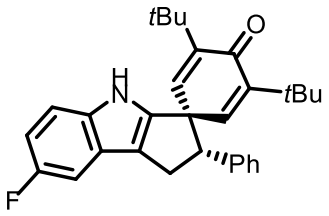
White solid, m. p. 141-143 °C, 34 mg, 39% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.40 (dd, *J* = 24.2, 7.8 Hz, 2H), 7.21 (dd, *J* = 11.9, 7.4 Hz, 3H), 7.14 (d, *J* = 7.1 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 2.6 Hz, 1H), 6.31 (d, *J* = 2.7 Hz, 1H), 4.33 (t, *J* = 8.6 Hz, 1H), 3.53 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.33 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.48 (s, 3H), 1.30 (s, 9H), 0.88 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9, 148.7, 146.3, 142.4, 141.8, 140.8, 138.7, 138.3, 129.5, 128.0, 128.0, 127.3, 124.9, 123.3, 118.8, 118.6, 111.5, 62.6, 52.5, 35.0, 34.6, 29.6, 28.9, 28.3, 21.5 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{36}NO^+$ $(M+H)^+$ 438.2791, found *m/z* 438.2790.

3,5-di-tert-butyl-7'-methoxy-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (49)



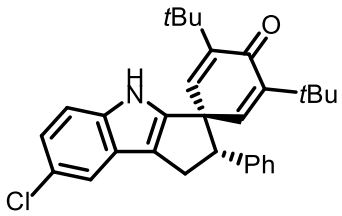
Yellow solid, m. p. 136-139 °C, 49 mg, 54% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.23 (dd, *J* = 12.5, 3.7 Hz, 4H), 7.15 (d, *J* = 7.0 Hz, 2H), 7.06 (d, *J* = 2.2 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.80 (d, *J* = 2.7 Hz, 1H), 6.32 (d, *J* = 2.7 Hz, 1H), 4.34 (t, *J* = 8.6 Hz, 1H), 3.89 (s, 3H), 3.55 (dd, *J* = 14.2, 9.5 Hz, 1H), 3.34 (dd, *J* = 14.3, 7.8 Hz, 1H), 1.30 (s, 9H), 0.88 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.8, 154.5, 148.7, 146.3, 142.5, 142.3, 140.6, 138.2, 135.4, 128.0, 127.3, 125.0, 118.8, 112.5, 111.7, 101.3, 62.6, 56.0, 52.5, 35.1, 34.7, 29.6, 28.9, 28.3 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{36}NO_2^+$ $(M+H)^+$ 454.2741, found *m/z* 454.2746.

3,5-di-tert-butyl-7'-fluoro-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (50)



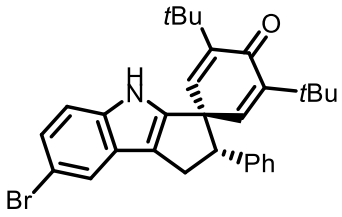
Brown oil, 41 mg, 46% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.27 – 7.19 (m, 5H), 7.16 – 7.11 (m, 2H), 6.79 (d, *J* = 2.7 Hz, 1H), 6.29 (d, *J* = 2.7 Hz, 1H), 4.60 – 4.10 (m, 1H), 3.53 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.32 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.30 (s, 14H), 0.88 (s, 11H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.8, 159.3, 156.9, 148.9, 146.5, 143.7, 141.9, 140.3, 138.0, 136.8, 128.0, 128.0, 127.4, 124.9 (d, *J* = 9.9 Hz), 124.2 (d, *J* = 48.8 Hz), 119.1 (d, *J* = 4.4 Hz), 112.3 (d, *J* = 9.5 Hz), 109.9 (d, *J* = 26.0 Hz), 104.2 (d, *J* = 23.5 Hz), 62.6, 52.4, 35.1, 34.7, 29.6, 28.9, 28.2 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.74 (dd, *J* = 9.2, 4.4 Hz) ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{33}FNO^+$ $(M+H)^+$ 442.2541, found *m/z* 442.2540.

3,5-di-tert-butyl-7'-chloro-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (51)



Yellow solid, m. p. 143-146 °C, 52 mg, 57% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.85 (s, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.31 – 7.21 (m, 4H), 7.18 – 7.09 (m, 3H), 6.79 (d, *J* = 2.7 Hz, 1H), 6.30 (d, *J* = 2.7 Hz, 1H), 4.34 (t, *J* = 8.6 Hz, 1H), 3.53 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.32 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.30 (s, 9H), 0.88 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.7, 149.0, 146.6, 143.4, 141.8, 140.2, 138.7, 137.9, 128.0, 128.0, 127.4, 125.8, 125.7, 122.0, 118.7, 118.7, 112.7, 62.6, 52.4, 35.1, 34.7, 29.6, 28.9, 28.2 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{33}ClNO^+$ $(M+H)^+$ 458.2245, found *m/z* 458.2249.

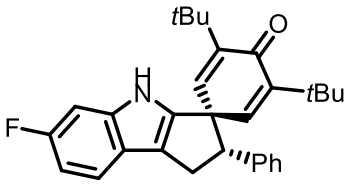
7'-bromo-3,5-di-tert-butyl-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (52)



White solid, m. p. 146-148 °C, 55 mg, 55% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.31 – 7.21 (m, 4H), 7.18 – 7.09 (m, 2H), 6.79 (d, *J* = 2.7 Hz, 1H), 6.30 (d, *J* = 2.7 Hz, 1H), 4.34 (t, *J* = 8.6 Hz, 1H), 3.53 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.32 (dd, *J* = 14.4, 7.8 Hz, 1H), 1.30 (s, 9H), 0.88 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.7, 149.0, 146.6, 143.2, 141.8, 140.2, 139.0, 137.9, 128.1, 128.0, 127.4, 126.3, 124.5, 121.8, 118.6, 113.4, 113.2,

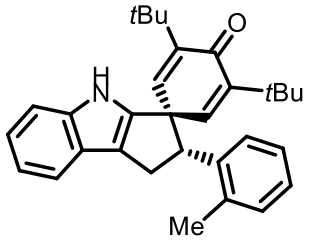
62.6, 52.4, 35.1, 34.7, 29.6, 28.9, 28.2 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{33}BrNO^+$ $(M+H)^+$ 502.1740, found *m/z* 502.1746.

3,5-di-tert-butyl-6'-fluoro-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (53)



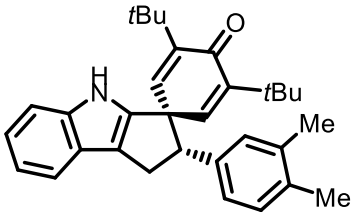
Yellow oil, 41 mg, 47% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.49 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.28 – 7.18 (m, 3H), 7.16 – 7.12 (m, 2H), 7.03 (dd, *J* = 9.7, 2.3 Hz, 1H), 6.98 – 6.90 (m, 1H), 6.79 (d, *J* = 2.8 Hz, 1H), 6.31 (d, *J* = 2.7 Hz, 1H), 4.54 – 4.29 (m, 1H), 3.55 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.34 (dd, *J* = 14.4, 7.9 Hz, 1H), 1.30 (s, 9H), 0.88 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.8, 160.8, 158.5, 148.9, 146.5, 142.2, 140.5, 138.0, 128.0, 128.0, 127.4, 124.5, 124.0, 121.3, 119.6 (d, *J* = 10.3 Hz), 108.7 (d, *J* = 24.2 Hz), 98.5 (d, *J* = 26.0 Hz), 62.7, 52.5, 35.1, 34.7, 29.6, 28.9, 28.3 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.87 (td, *J* = 9.5, 5.4 Hz) ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{33}FNO^+$ $(M+H)^+$ 442.2541, found *m/z* 442.2537.

3,5-di-tert-butyl-2'-(o-tolyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (54)



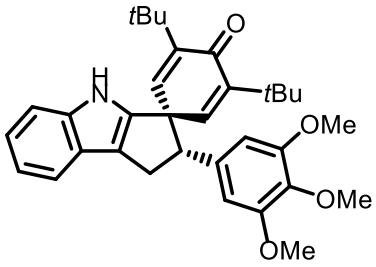
Brown oil, 39 mg, 45% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.60 (dd, *J* = 5.9, 2.6 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.24 – 7.15 (m, 2H), 7.11 (ddd, *J* = 13.7, 6.4, 3.3 Hz, 3H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.29 (d, *J* = 2.7 Hz, 1H), 4.68 (dd, *J* = 8.0, 6.1 Hz, 1H), 3.45 (ddd, *J* = 20.8, 14.9, 7.1 Hz, 2H), 2.19 (s, 3H), 1.25 (s, 9H), 0.94 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.7, 146.3, 146.2, 143.4, 141.7, 141.5, 140.8, 139.1, 136.2, 130.5, 127.9, 126.9, 125.9, 124.5, 124.5, 121.8, 120.1, 119.9, 119.2, 111.8, 57.1, 52.0, 34.9, 34.8, 31.2, 29.4, 29.0, 20.4 ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{36}NO^+$ $(M+H)^+$ 438.2791, found *m/z* 438.2795.

3,5-di-tert-butyl-2'-(3,4-dimethylphenyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (55)



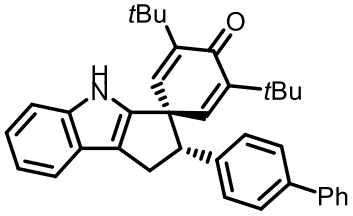
Yellow solid, m. p. 133-136 °C, 40 mg, 44% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.64 – 7.55 (m, 1H), 7.34 (dd, *J* = 7.3, 5.3 Hz, 1H), 7.22 – 7.10 (m, 2H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 6.2 Hz, 2H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.31 (d, *J* = 2.4 Hz, 1H), 4.30 (t, *J* = 8.7 Hz, 1H), 3.54 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.33 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.41 – 1.97 (m, 6H), 1.30 (s, 9H), 0.87 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9, 148.7, 146.1, 142.5, 141.9, 141.1, 140.3, 135.9, 135.5, 135.5, 129.3, 129.2, 125.2, 124.7, 121.7, 120.1, 119.1, 119.1, 111.8, 62.4, 52.6, 35.0, 34.6, 29.6, 28.8, 28.3, 19.7, 19.3 ppm; **HRMS (ESI)** m/z calcd for $C_{32}H_{38}NO^+$ $(M+H)^+$ 452.2948, found *m/z* 452.2955.

3,5-di-tert-butyl-2'-(3,4,5-trimethoxyphenyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (56)



Yellow solid, m. p. 151-154 °C, 51 mg, 50% yield, Rf = 0.3 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.67 – 7.54 (m, 1H), 7.34 (dd, *J* = 6.6, 2.2 Hz, 1H), 7.23 – 7.14 (m, 2H), 6.83 (d, *J* = 2.7 Hz, 1H), 6.39 (s, 2H), 6.32 (d, *J* = 2.7 Hz, 1H), 4.36 (t, *J* = 8.6 Hz, 1H), 3.79 (s, 6H), 3.77 (s, 3H), 3.54 (dd, *J* = 14.4, 9.2 Hz, 1H), 3.40 (dd, *J* = 14.4, 8.1 Hz, 1H), 1.32 (s, 9H), 0.93 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 186.1, 152.9, 148.5, 146.3, 142.9, 141.4, 140.9, 140.5, 137.4, 134.5, 124.6, 121.9, 120.2, 119.0, 118.7, 111.9, 105.1, 62.1, 60.8, 56.2, 52.3, 35.0, 34.7, 29.8, 29.1, 28.7 ppm; **HRMS (ESI)** m/z calcd for $C_{33}H_{40}NO_4^+$ $(M+H)^+$ 514.2952, found *m/z* 514.2947.

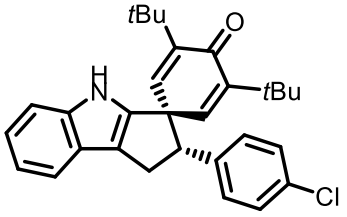
2'-([1,1'-biphenyl]-4-yl)-3,5-di-tert-butyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (57)



Yellow solid, m. p. 146-148 °C, 49 mg, 49% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.65 – 7.59 (m, 1H), 7.53 – 7.50 (m, 2H), 7.47 (t, *J* = 6.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.20 (ddd, *J* = 9.2, 7.9, 2.0 Hz, 4H), 6.83 (d, *J* = 2.8 Hz, 1H), 6.34 (d, *J* = 2.7 Hz, 1H), 4.40 (t, *J* = 8.6 Hz, 1H), 3.61 (dd, *J* = 14.3, 9.4 Hz, 1H), 3.40 (dd, *J* = 14.3, 7.8 Hz, 1H), 1.32 (s, 9H), 0.88 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.8, 148.8, 146.5, 142.3, 141.7, 140.9, 140.7, 140.4, 140.4, 137.4, 128.8, 128.3, 127.2, 127.1, 126.8, 124.7, 121.9, 120.2, 119.1, 119.0, 111.9, 62.4, 52.6, 35.1, 34.7, 29.6, 29.6, 28.9, 28.4 ppm; **HRMS (ESI)** m/z calcd for $C_{36}H_{38}NO^+$ $(M+H)^+$ 500.2948, found *m/z* 500.2943.

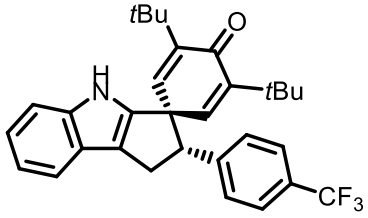
3,5-di-tert-butyl-2'-(4-chlorophenyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-

2,5-dien-4-one (58)



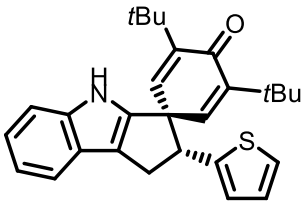
Yellow solid, m. p. 144-147 ^{o}C, 54 mg, 59% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.63 – 7.56 (m, 1H), 7.34 (dd, *J* = 6.5, 2.1 Hz, 1H), 7.19 (ddd, *J* = 7.8, 6.4, 5.0 Hz, 4H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 2.7 Hz, 1H), 6.29 (d, *J* = 2.7 Hz, 1H), 4.31 (t, *J* = 8.6 Hz, 1H), 3.50 (dd, *J* = 14.3, 9.4 Hz, 1H), 3.36 (dd, *J* = 14.3, 7.8 Hz, 1H), 1.30 (s, 9H), 0.91 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.7, 149.1, 146.8, 142.0, 141.5, 140.4, 140.2, 136.8, 133.0, 129.3, 128.1, 124.6, 121.9, 120.2, 119.1, 118.8, 111.9, 61.9, 52.4, 35.1, 34.8, 29.6, 29.0, 28.5 ppm; **HRMS (ESI)** m/z calcd for $C_{30}H_{33}ClNO^{+}$ $(M+H)^{+}$ 458.2245, found *m/z* 458.2249.

3,5-di-tert-butyl-2'-(4-(trifluoromethyl)phenyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (59)



Yellow oil, 61 mg, 62% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.65 – 7.59 (m, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 6.8 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.14 (m, 2H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.27 (d, *J* = 2.7 Hz, 1H), 4.40 (t, *J* = 8.6 Hz, 1H), 3.58 (dd, *J* = 14.3, 9.3 Hz, 1H), 3.40 (dd, *J* = 14.3, 7.8 Hz, 1H), 1.31 (s, 9H), 0.87 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.6, 149.2, 146.9, 142.5, 141.9, 141.3, 140.5, 140.0, 129.6 (q, *J* = 32.5 Hz), 128.2, 128.1, 125.4, 125.0 (q, *J* = 270.3 Hz), 124.9 (q, *J* = 3.8 Hz), 124.5, 124.0, 122.7, 122.0, 120.3, 119.1, 118.7, 111.9, 62.0, 52.3, 35.1, 34.7, 29.6, 28.9, 28.3 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.56 (s) ppm; **HRMS (ESI)** m/z calcd for $C_{31}H_{33}F_3NO^{+}$ $(M+H)^{+}$ 492.2509, found *m/z* 492.250.

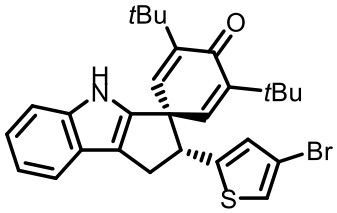
3,5-di-tert-butyl-2'-(thiophen-2-yl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (60)



Yellow oil, 33 mg, 38% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.62 – 7.57 (m, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.15 – 7.08 (m, 1H), 6.91 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.80 (d, *J* = 3.4 Hz, 1H), 6.75 (d, *J* = 2.7 Hz, 1H), 6.34 (d, *J* = 2.7 Hz, 1H), 4.56 (t, *J* = 8.7 Hz, 1H), 3.50 (dd, *J* = 8.8, 2.0 Hz, 2H), 1.28 (s, 9H), 0.94 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.9, 149.7, 147.1, 146.9, 141.8, 141.7, 141.4, 140.3,

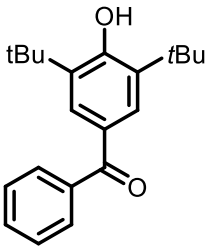
139.9, 126.5, 124.6, 124.5, 124.5, 124.0, 123.8, 121.9, 120.2, 119.1, 119.1, 119.1, 118.6, 111.9, 57.4, 52.4, 35.2, 34.7, 30.7, 29.6, 29.0 ppm; **HRMS (ESI)** m/z calcd for $C_{28}H_{32}NOS^+$ $(M+H)^+$ 430.2199, found *m/z* 430.2203.

2'-(4-bromothiophen-2-yl)-3,5-di-tert-butyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (61)



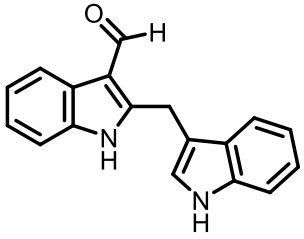
White solid, m. p. 134-137 ^oC, 52 mg, 51% yield, Rf = 0.5 (ethyl acetate/hexane = 5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.56 (dd, *J* = 8.4, 6.7 Hz, 1H), 7.34 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.19 (tt, *J* = 7.2, 5.8 Hz, 2H), 7.01 (d, *J* = 1.1 Hz, 1H), 6.73 (s, 1H), 6.71 (d, *J* = 2.8 Hz, 1H), 6.30 (d, *J* = 2.7 Hz, 1H), 4.60 – 4.26 (m, 1H), 3.45 (qd, *J* = 14.2, 8.7 Hz, 2H), 1.33 (s, 9H), 0.98 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.7, 150.1, 147.3, 143.2, 141.4, 140.9, 140.3, 139.3, 127.5, 124.4, 122.1, 120.9, 120.3, 119.1, 118.3, 111.9, 109.2, 57.1, 52.4, 35.2, 34.8, 30.1, 29.6, 29.0 ppm; **HRMS (ESI)** m/z calcd for $C_{28}H_{31}BrNOS^+$ $(M+H)^+$ 508.1304, found *m/z* 508.1300.

***(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methanone* (62)**



Colorless oil, 33 mg, 53% yield, Rf = 0.4 (ethyl acetate/hexane =5%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.65 (s, 2H), 7.48 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 5.66 (s, 1H), 1.38 (s, 18H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 158.1, 138.6, 135.6, 131.7, 129.8, 128.9, 128.2, 128.1, 34.4, 30.2 ppm; **HRMS (ESI)** m/z calcd for $C_{21}H_{27}O_2^+$ $(M+H)^+$ 311.2006, found *m/z* 311.2010.

***2-((1H-indol-3-yl)methyl)-1H-indole-3-carbaldehyde* (66)**



Slight yellow oil, 65 mg, 79% yield, Rf = 0.4 (ethyl acetate/hexane = 40%); **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 9.81 (s, 1H), 8.37 (s, 1H), 8.25 (dd, *J* = 6.2, 2.3 Hz, 1H), 7.58 (s, 1H), 7.48 (dd, *J* = 6.4, 2.0 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.32 – 7.23 (m, 2H), 7.20 – 7.17 (m, 1H), 7.15 (dd, *J* = 4.2, 1.7 Hz, 1H), 7.05 (dd, *J* = 11.1, 4.0 Hz, 1H), 5.42 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.7, 138.2, 137.5, 136.5, 126.3, 125.7, 124.2, 124.0, 123.1, 123.0, 122.2, 120.6, 118.4, 118.0, 111.7, 110.2, 109.6, 42.5 ppm; **HRMS (ESI)** m/z calcd for $C_{18}H_{15}N_2O^+$ $(M+H)^+$ 275.1179, found *m/z* 275.1183.

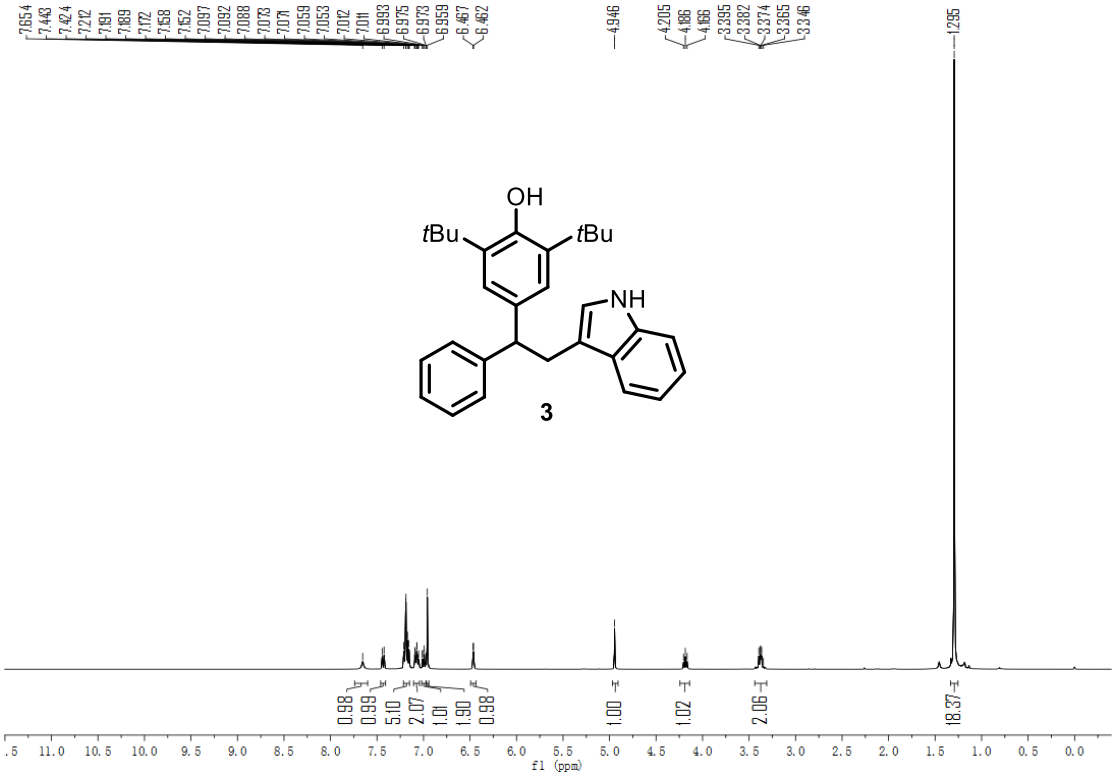
8. Reference

(1) (a) Sharma, M. B.; Rathod, J.; Gonnade, R. G.; Kumar, P.; *J. Org. Chem.* **2018**, *83*, 9353. (b) Shirsath, S. R.; Shinde, G. H.; Shaikh A. C.; Muthukrishnan, M.; *J. Org. Chem.* **2018**, *83*, 12305. (c) Gao, S.; Xu, G.; Yuan, Z.; Zhou, H.; Yao, H.; Lin, A.; *Eur. J. Org. Chem*. **2016**, 3006. (d) Zhao, K.; Zhi, Y.; Shu, T.; Valkonen, A.; Rissanen, K.; Enders, D.; *Angew. Chem. Int. Ed.* **2016**, *55*, 12104.

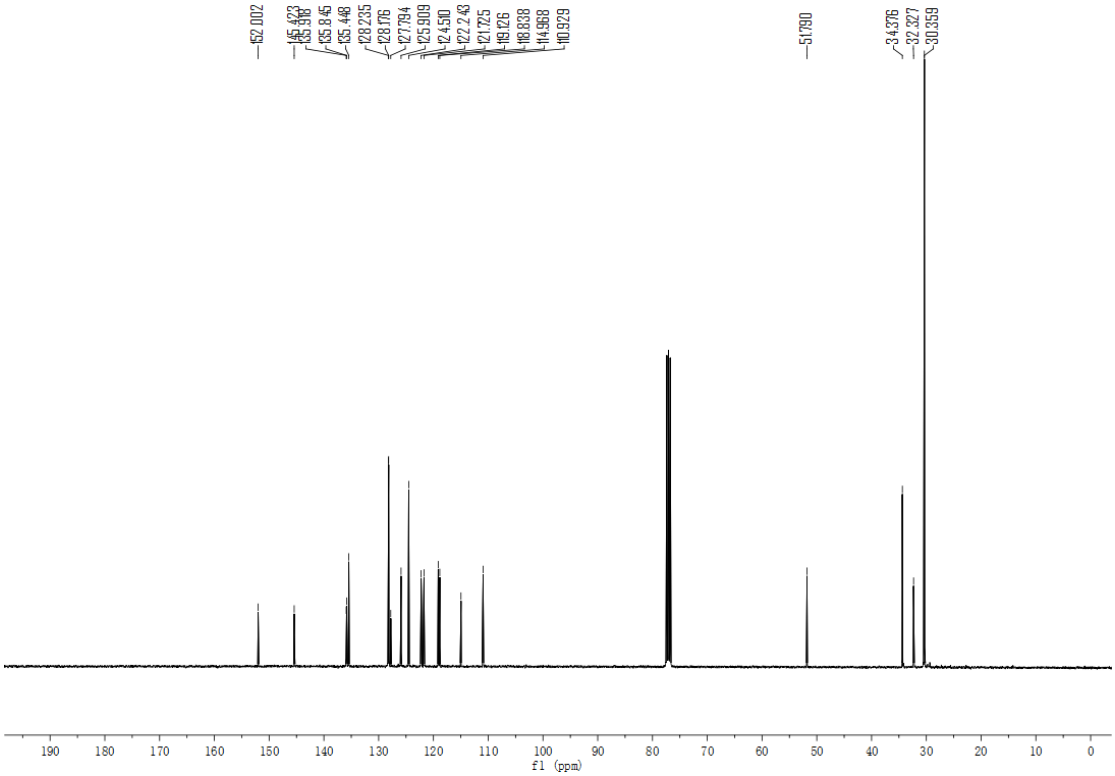
9. Copies ^{1}H NMR, ^{13}C NMR, ^{19}F NMR

4-(2-(1H-indol-3-yl)-1-phenylethyl)-2,6-di-tert-butylphenol (3)

^{1}H NMR (400 MHz, $CDCl_3$):

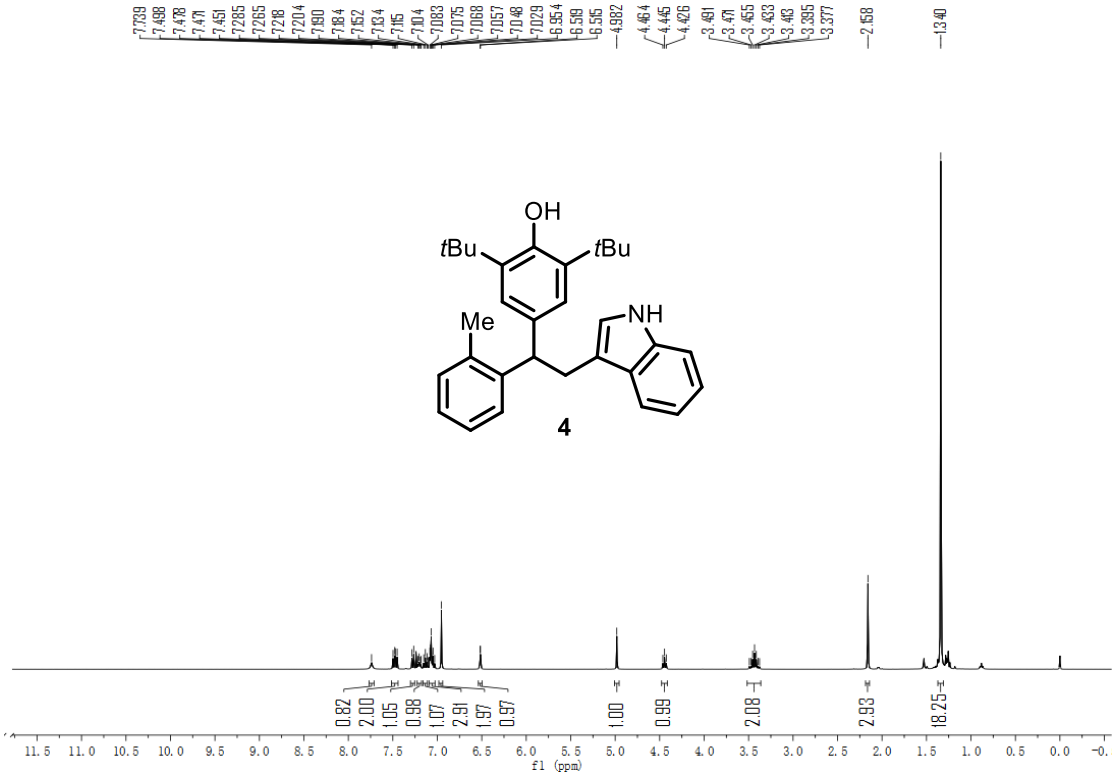


^{13}C NMR (100 MHz, $CDCl_3$):

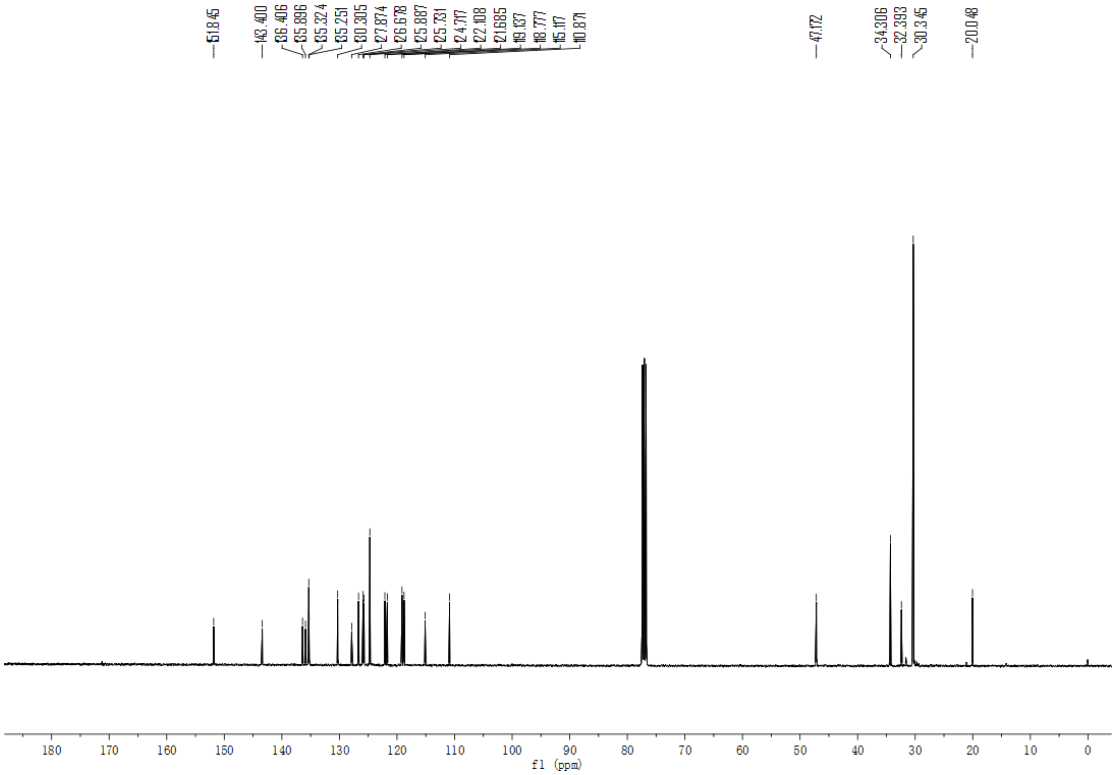


4-(2-(1H-indol-3-yl)-1-(o-tolyl)ethyl)-2,6-di-tert-butylphenol (4)

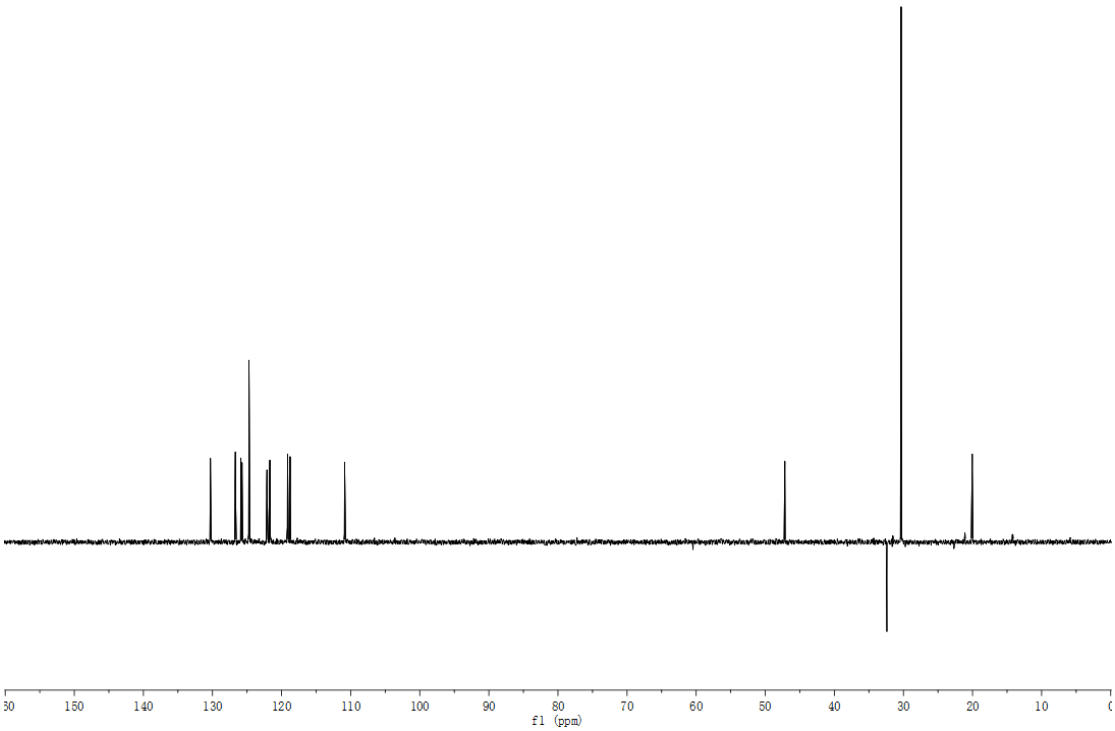
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

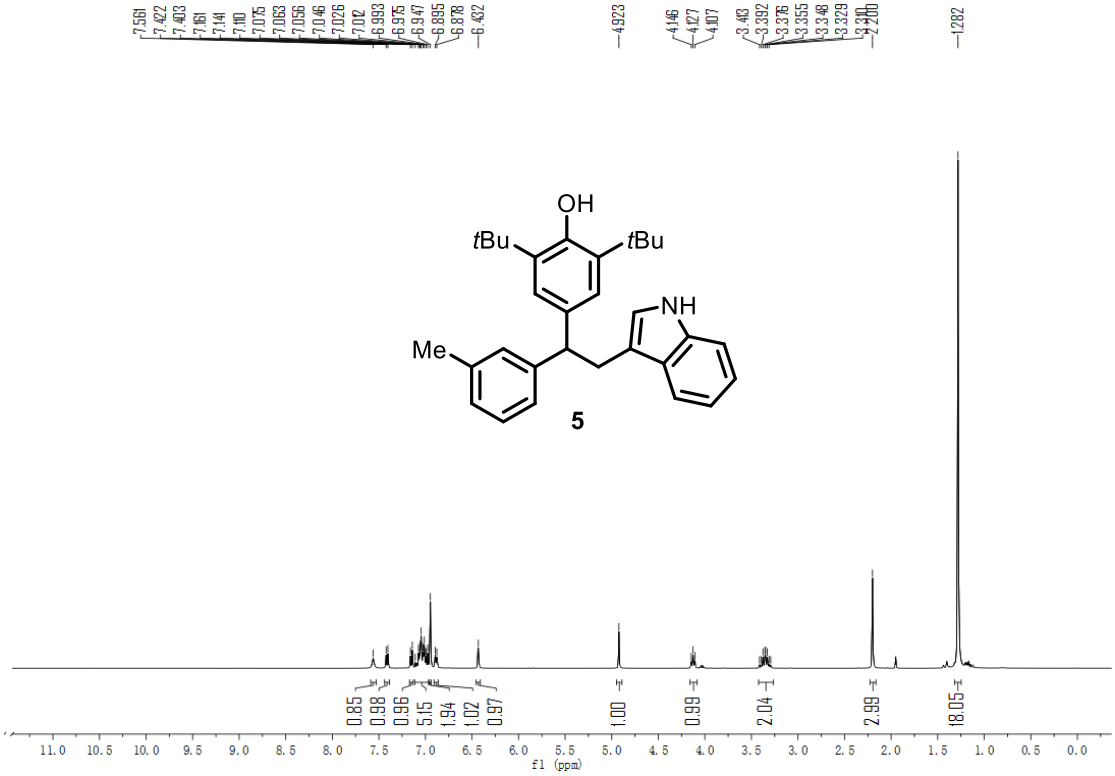


DEPT

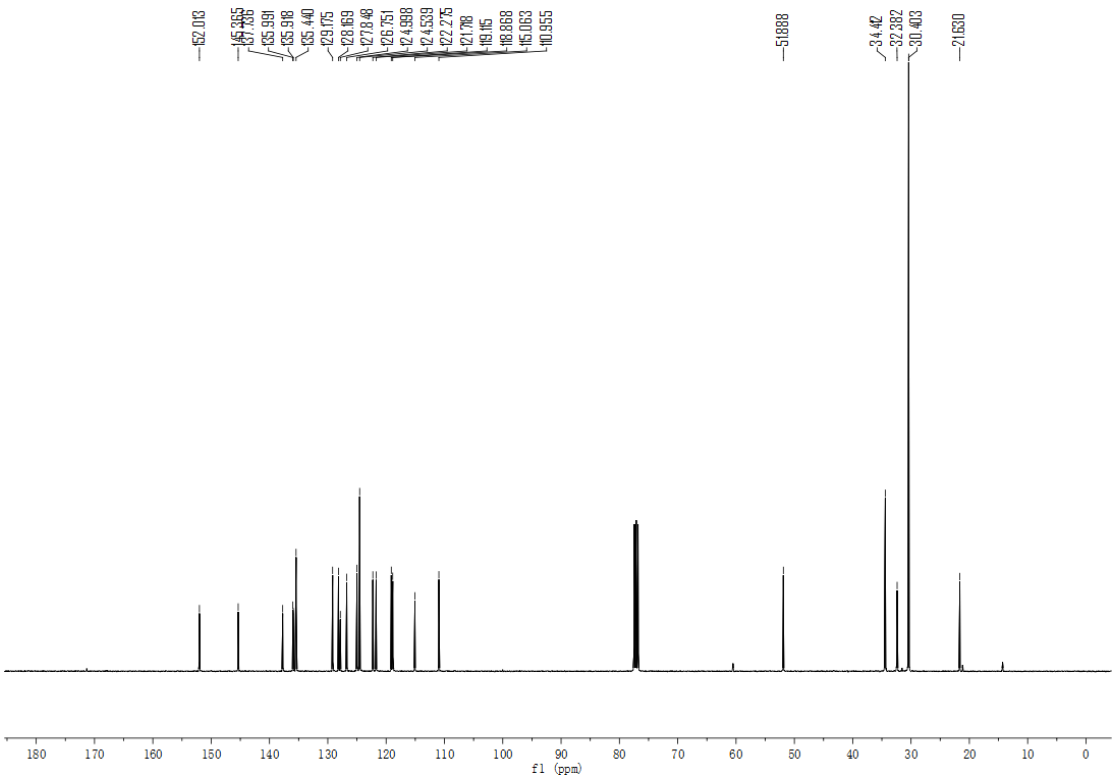


4-(2-(1H-indol-3-yl)-1-(m-tolyl)ethyl)-2,6-di-tert-butylphenol (5)

^{1}H NMR (400 MHz, $CDCl_3$):

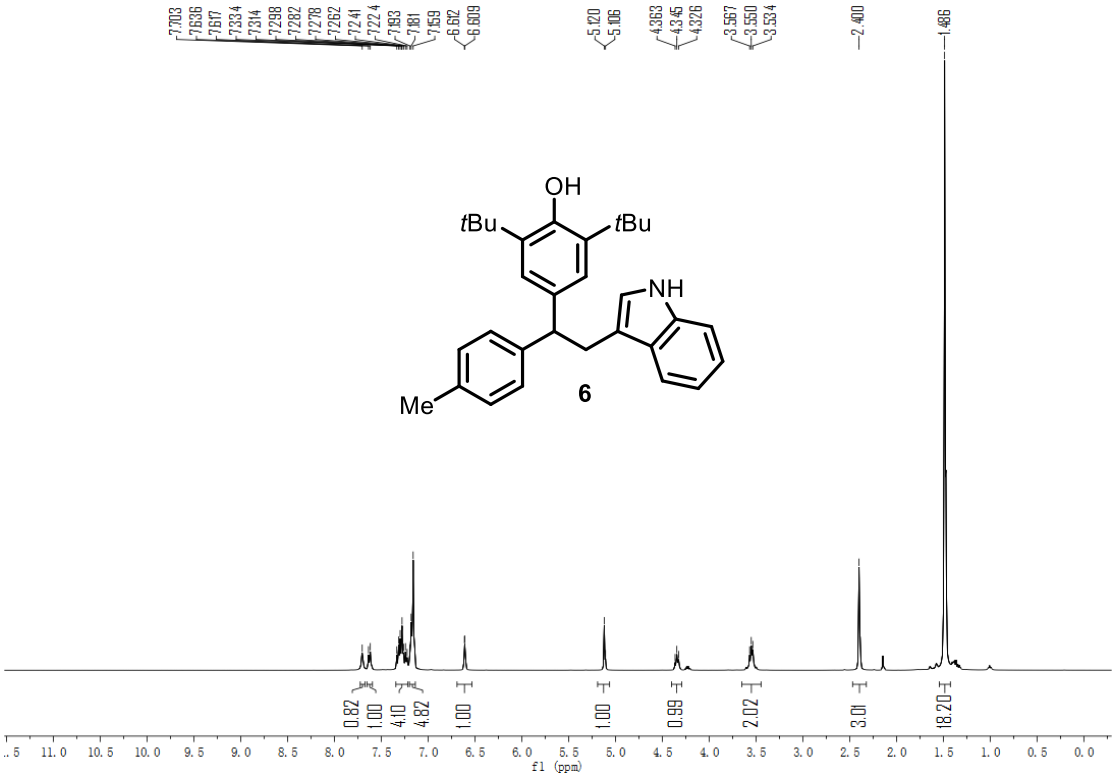


^{13}C NMR (100 MHz, $CDCl_3$):

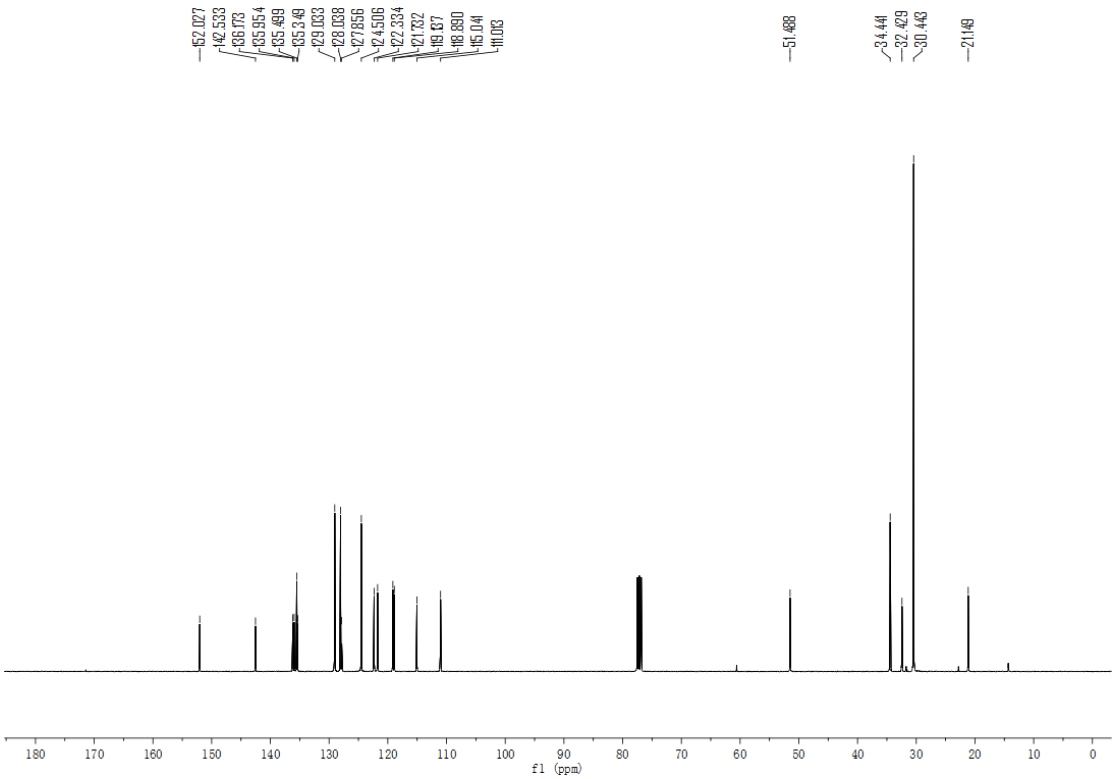


4-(2-(1H-indol-3-yl)-1-(p-tolyl)ethyl)-2,6-di-tert-butylphenol (6)

^{1}H NMR (400 MHz, $CDCl_3$):

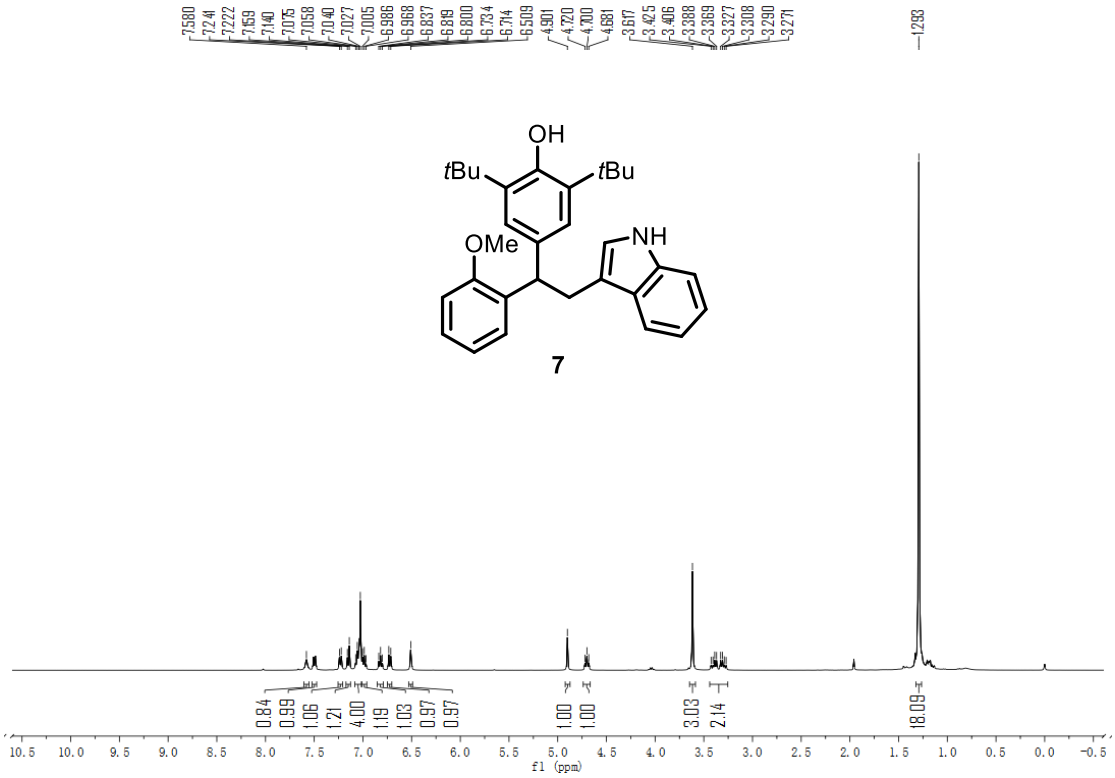


^{13}C NMR (100 MHz, $CDCl_3$):

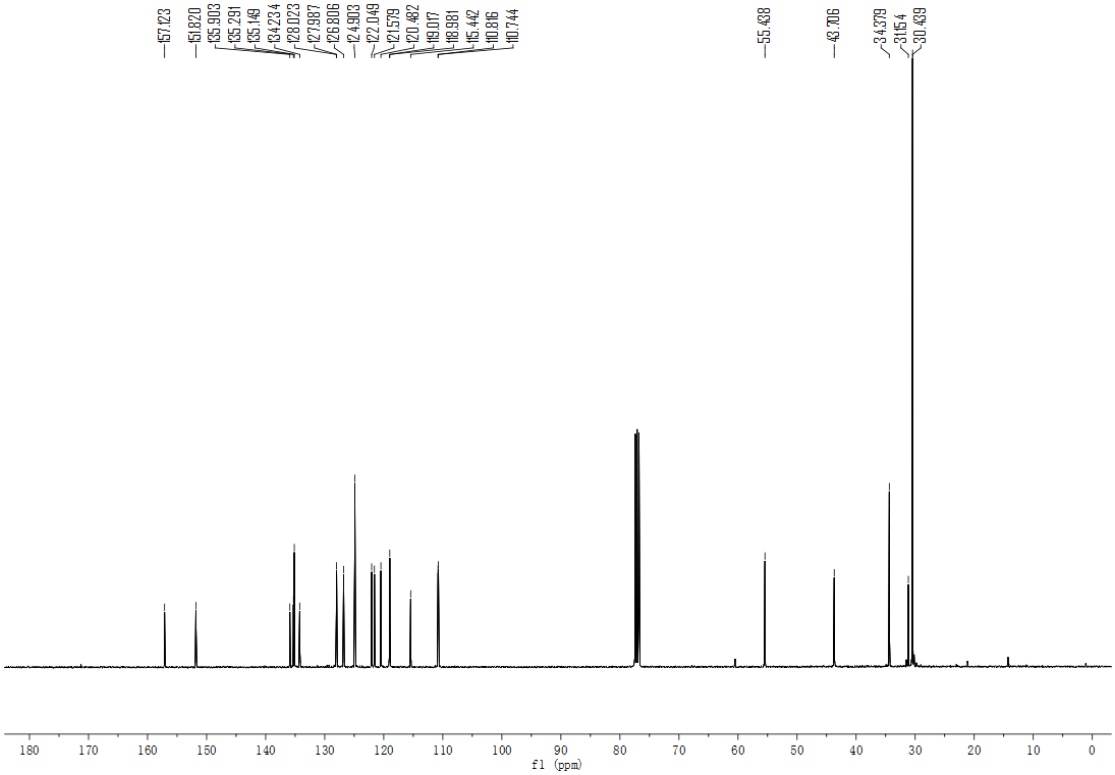


4-(2-(1H-indol-3-yl)-1-(2-methoxyphenyl)ethyl)-2,6-di-tert-butylphenol (7)

^{1}H NMR (400 MHz, $CDCl_3$):

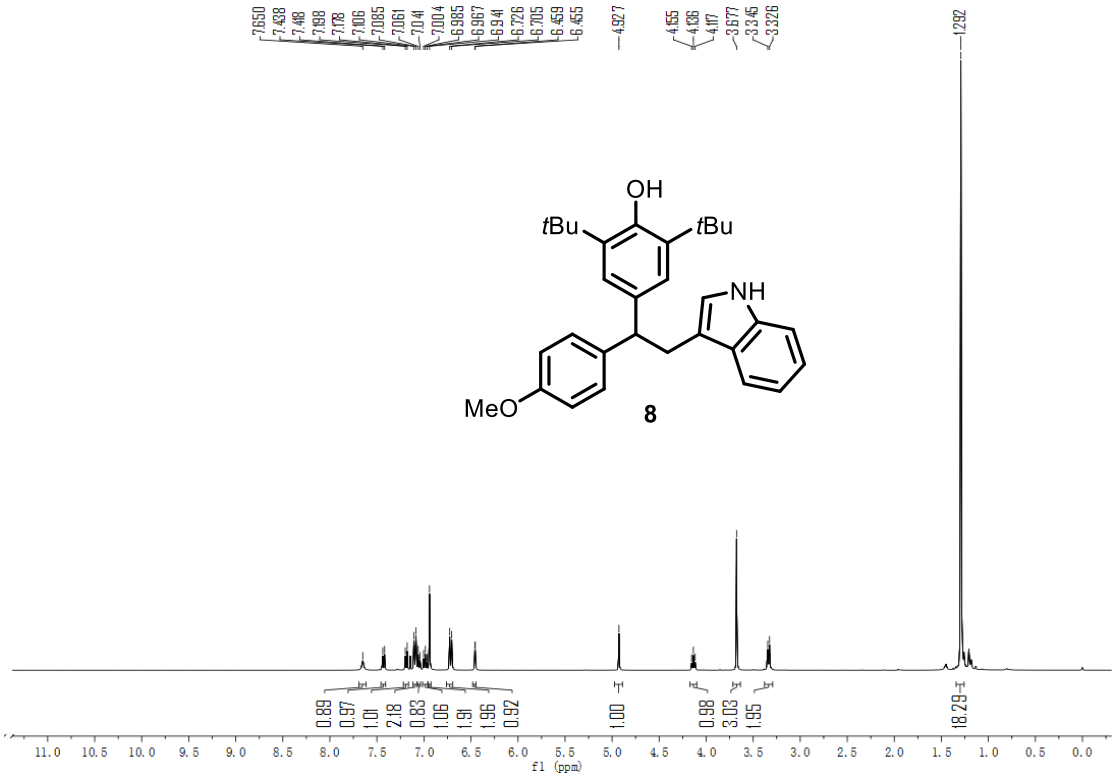


^{13}C NMR (100 MHz, $CDCl_3$):

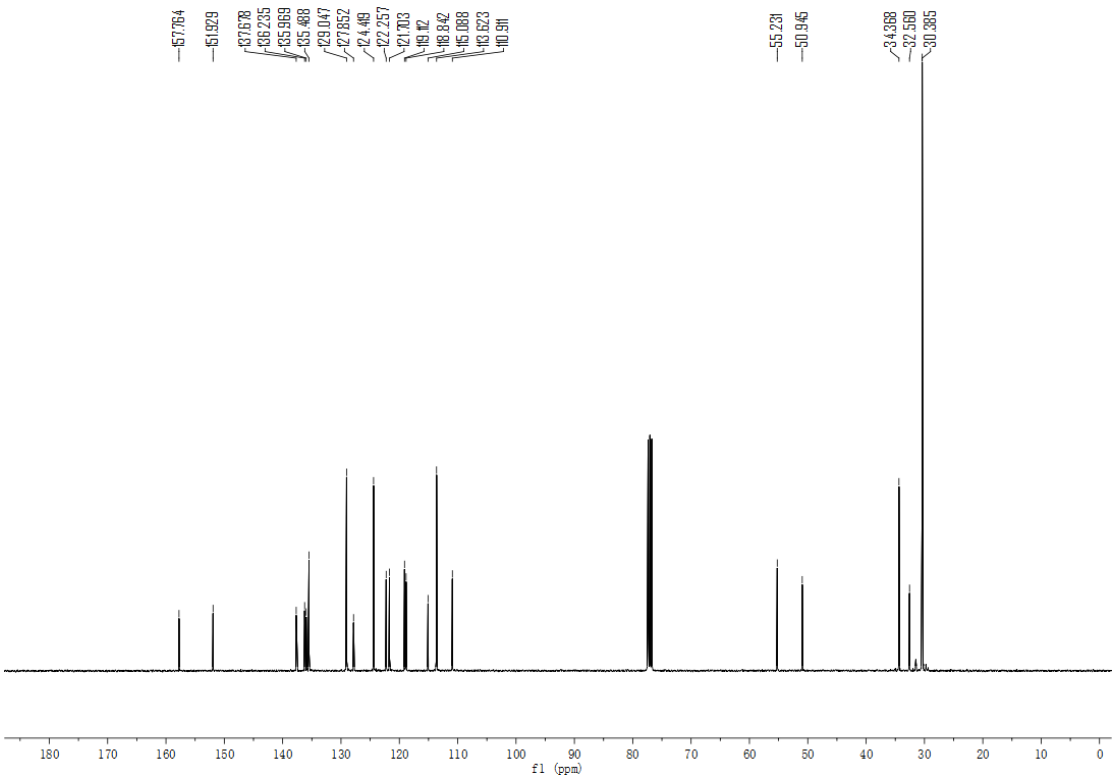


4-(2-(1H-indol-3-yl)-1-(4-methoxyphenyl)ethyl)-2,6-di-tert-butylphenol (8)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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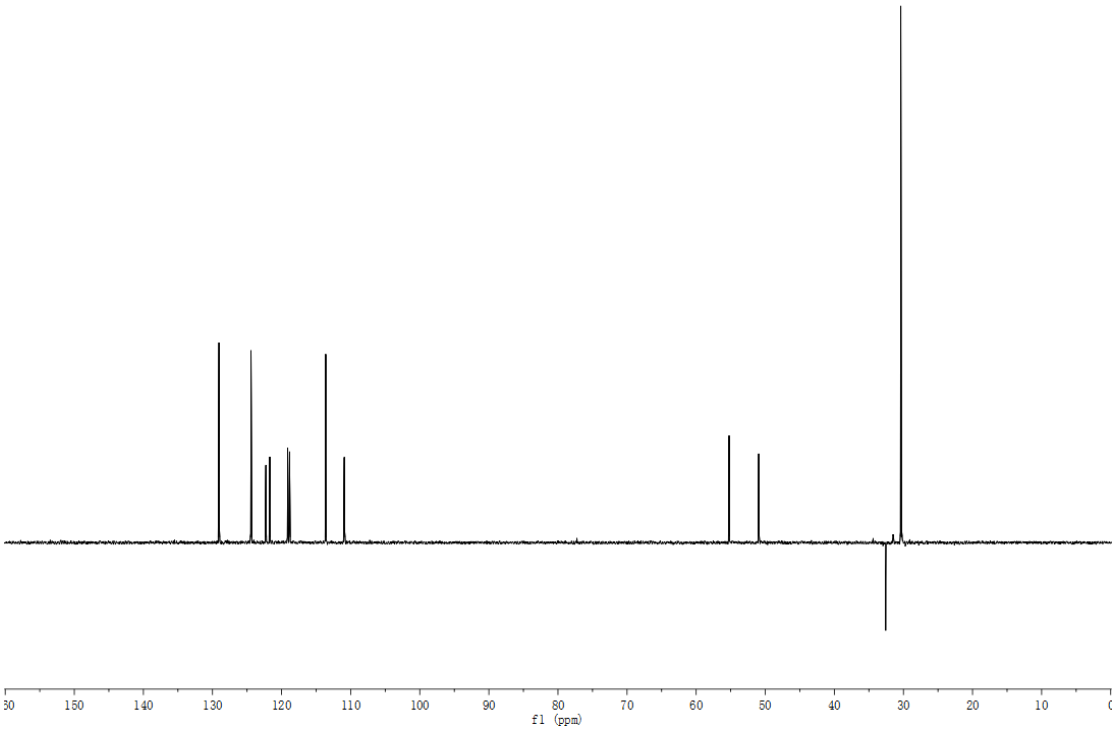
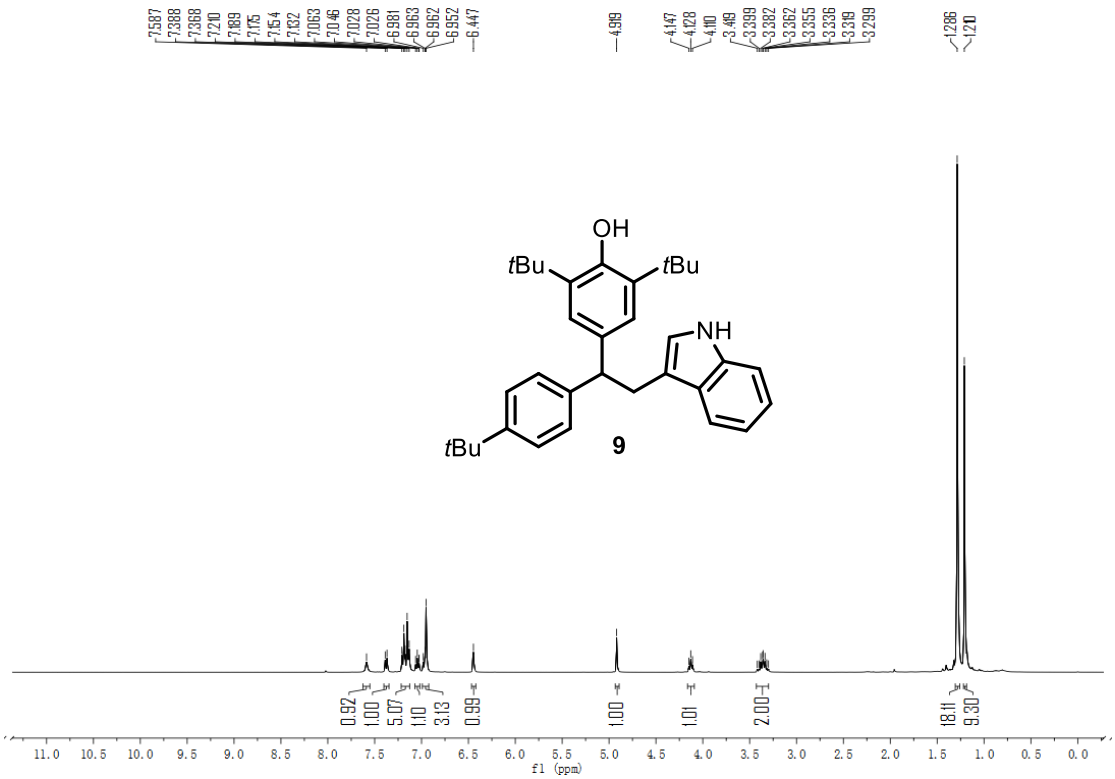
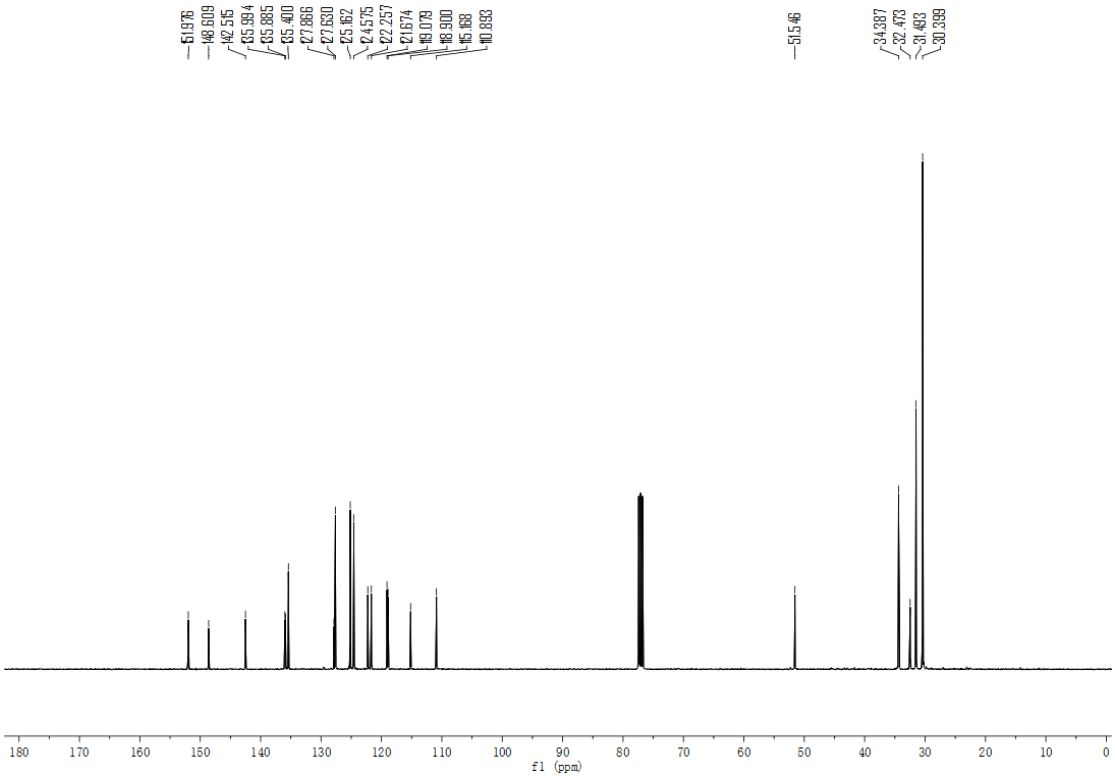


2,6-di-tert-butyl-4-(1-(4-(tert-butyl)phenyl)-2-(1H-indol-3-yl)ethyl)phenol (9)

^{1}H NMR (400 MHz, $CDCl_3$):

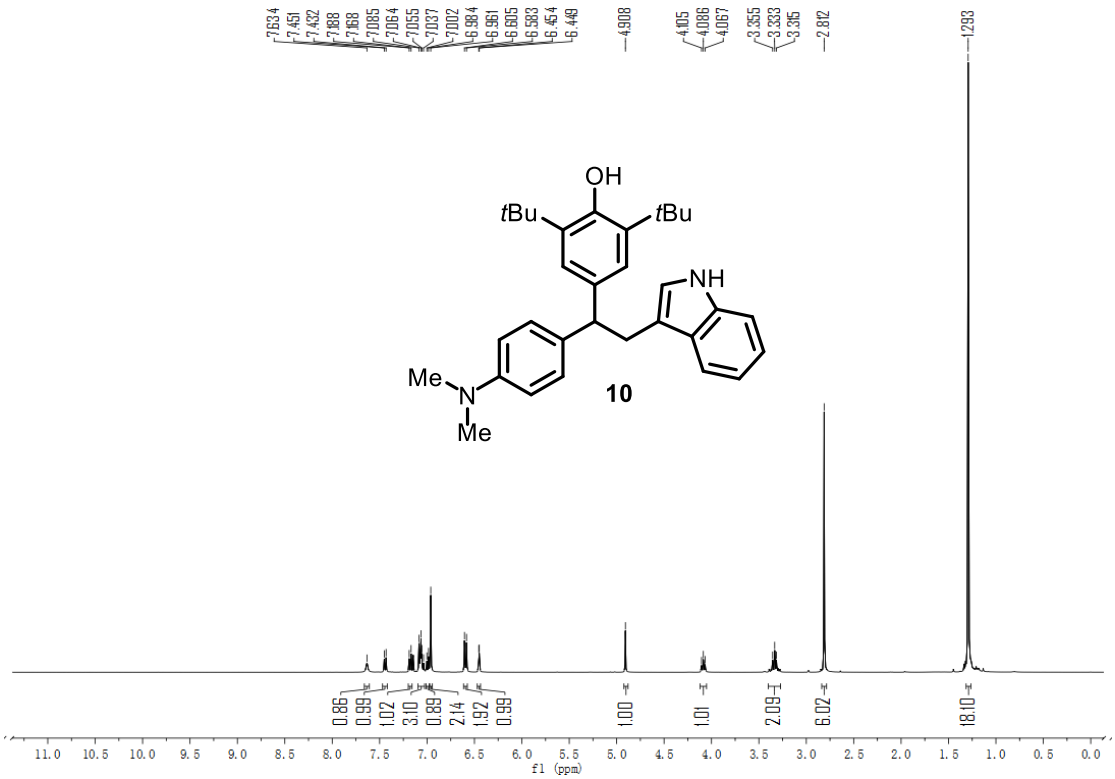


^{13}C NMR (100 MHz, $CDCl_3$):

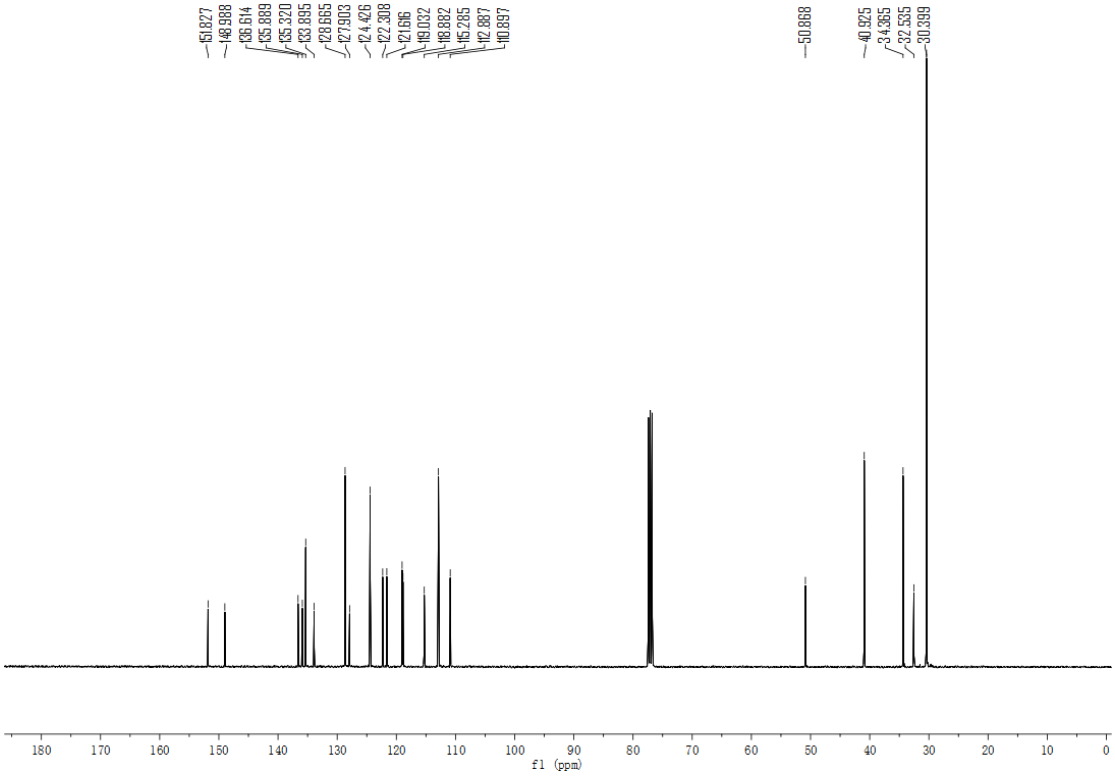


2,6-di-tert-butyl-4-(1-(4-(dimethylamino)phenyl)-2-(1H-indol-3-yl)ethyl)phenol (10)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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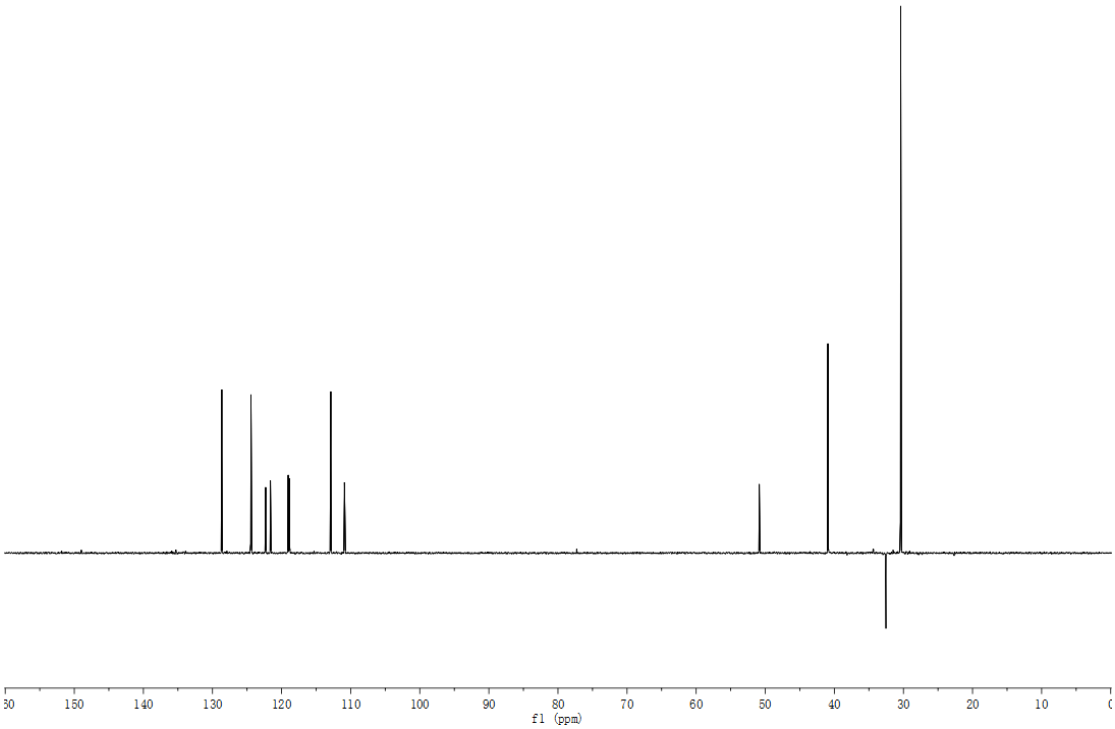
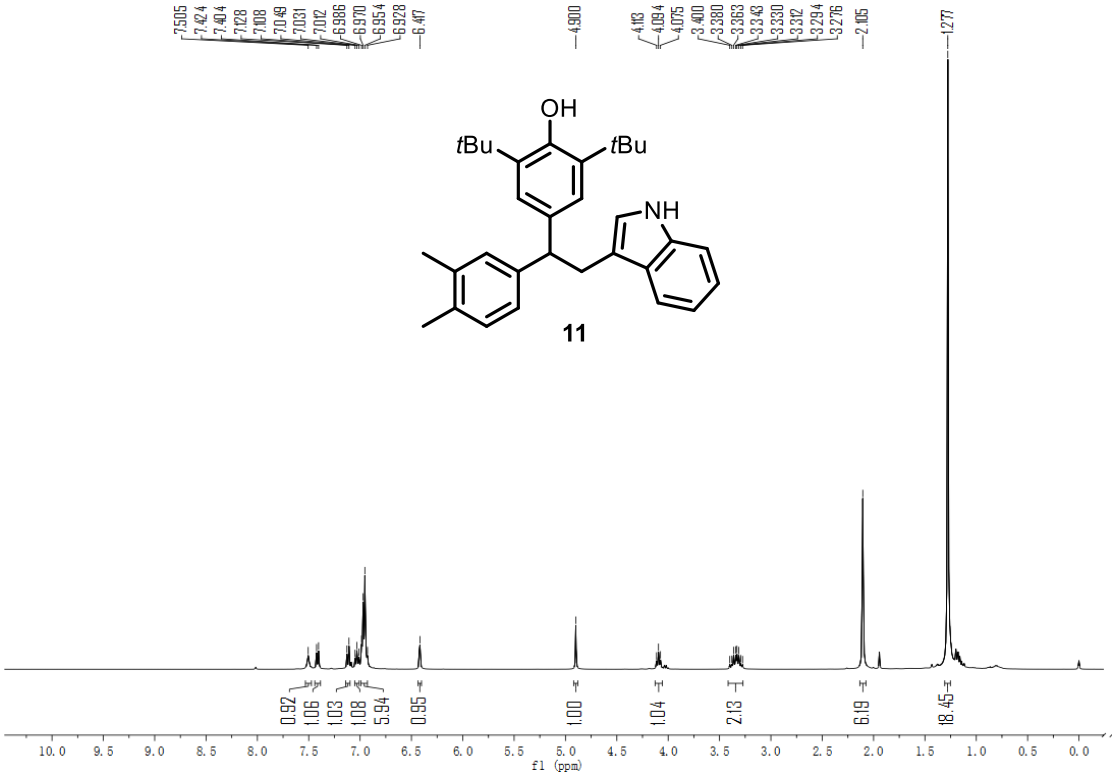
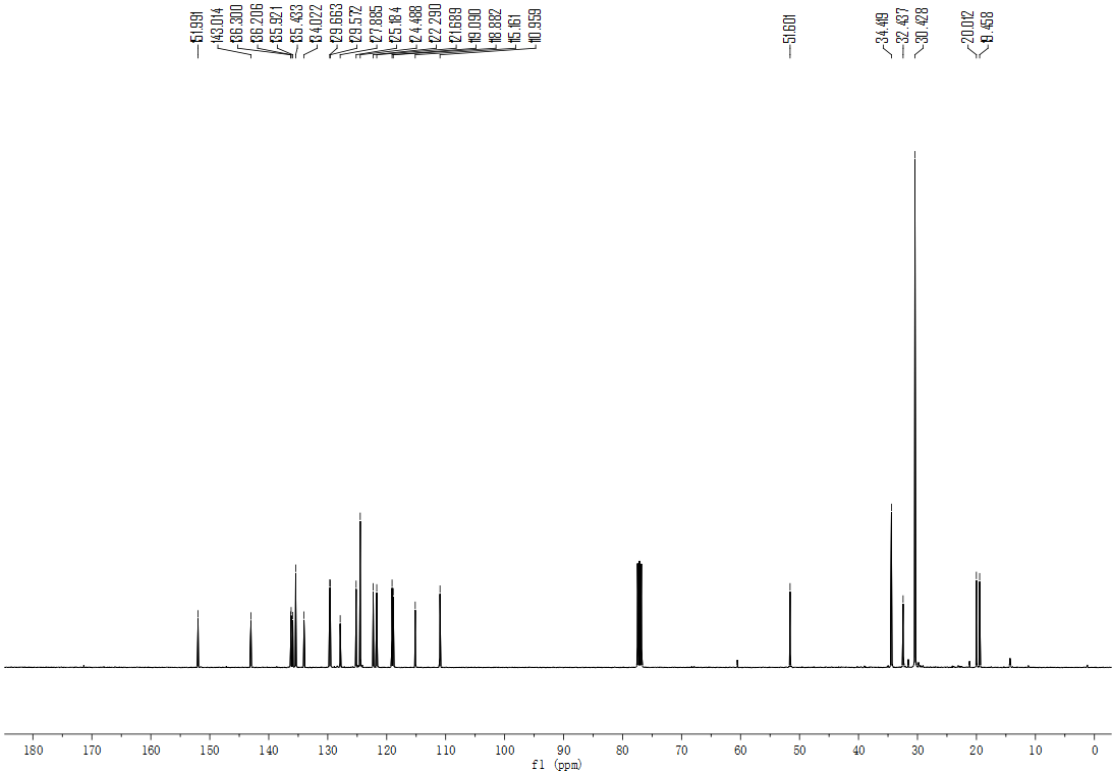


2,6-di-tert-butyl-4-(1-(3,4-dimethylphenyl)-2-(1H-indol-3-yl)ethyl)phenol (11)

^{1}H NMR (400 MHz, $CDCl_3$):

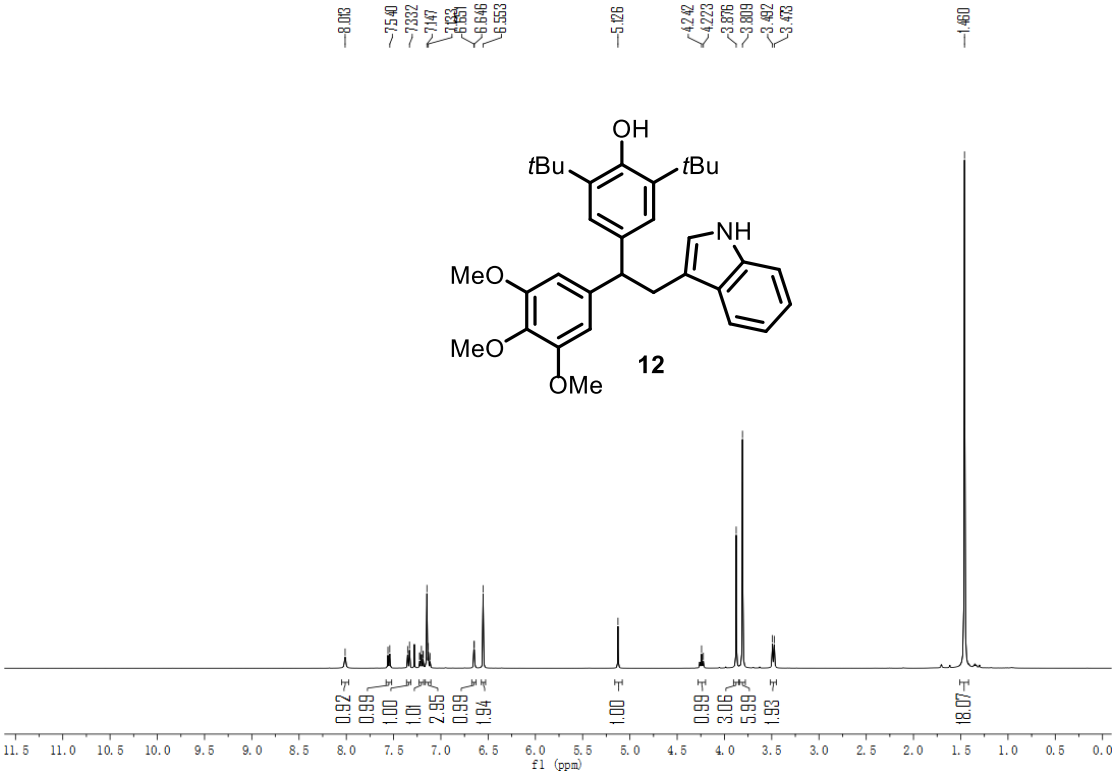


^{13}C NMR (100 MHz, $CDCl_3$):

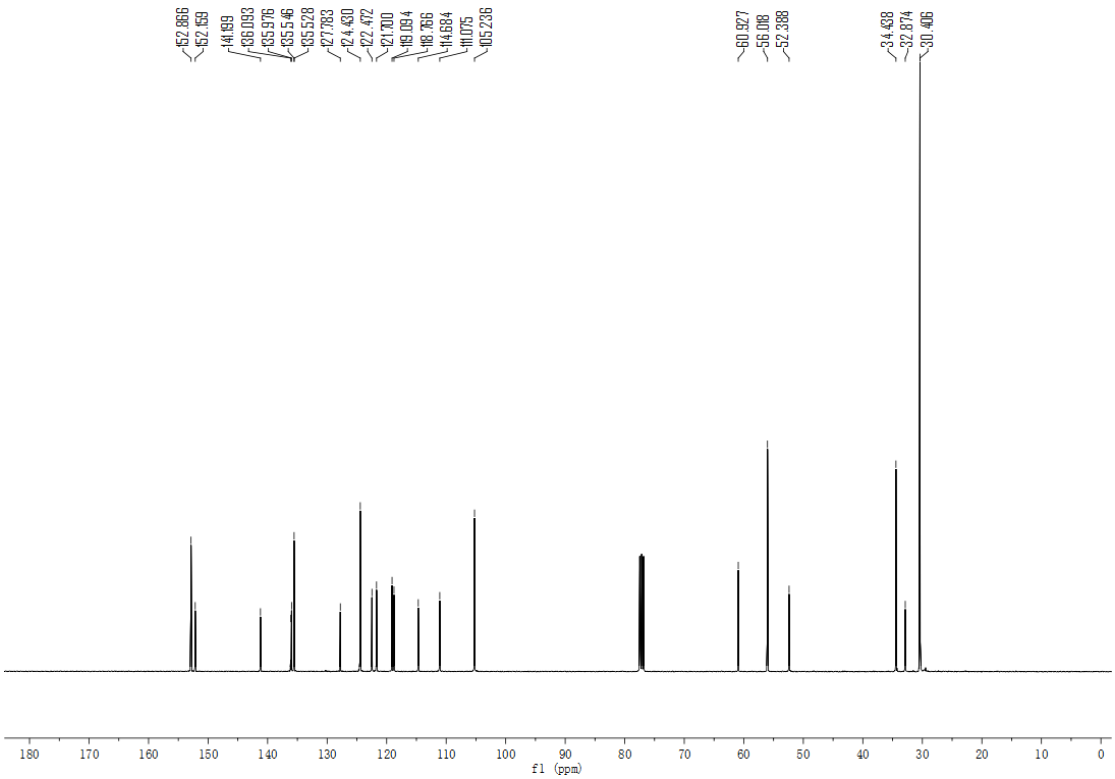


4-(2-(1H-indol-3-yl)-1-(3,4,5-trimethoxyphenyl)ethyl)-2,6-di-tert-butylphenol (12)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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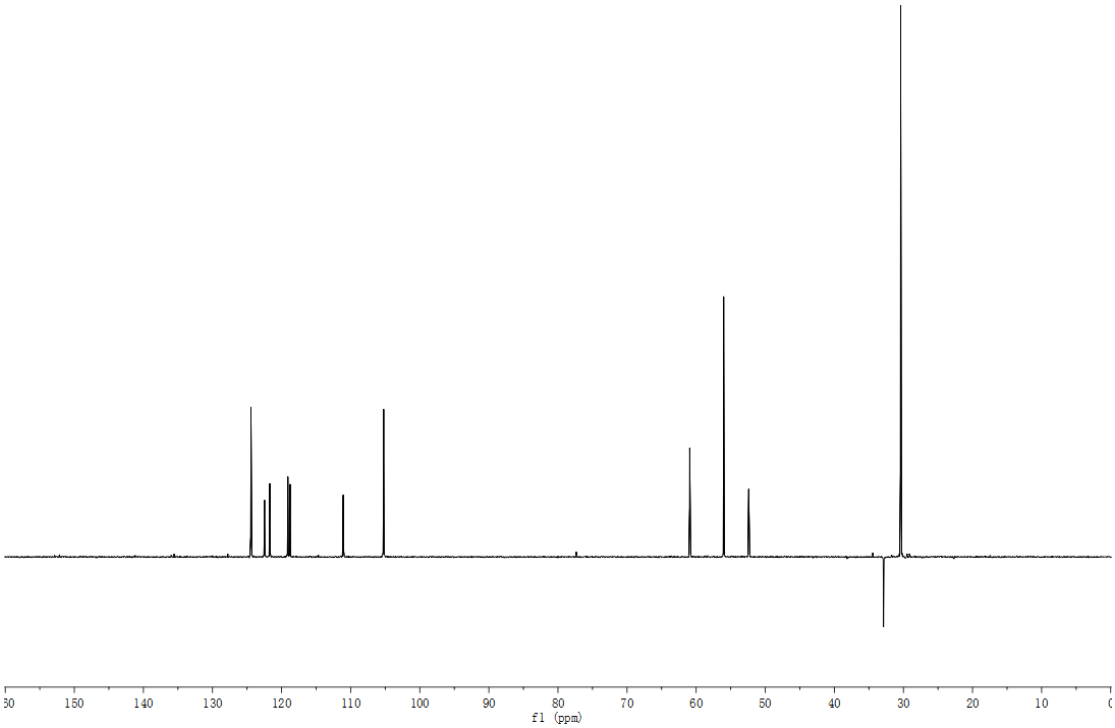
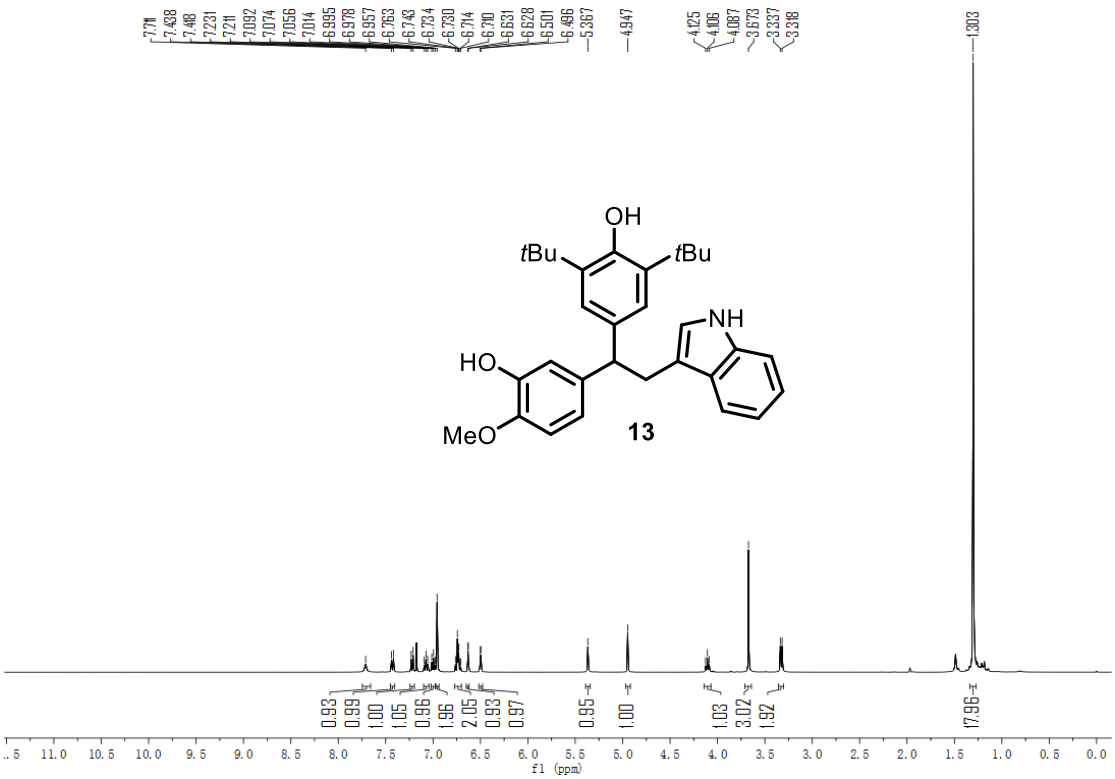
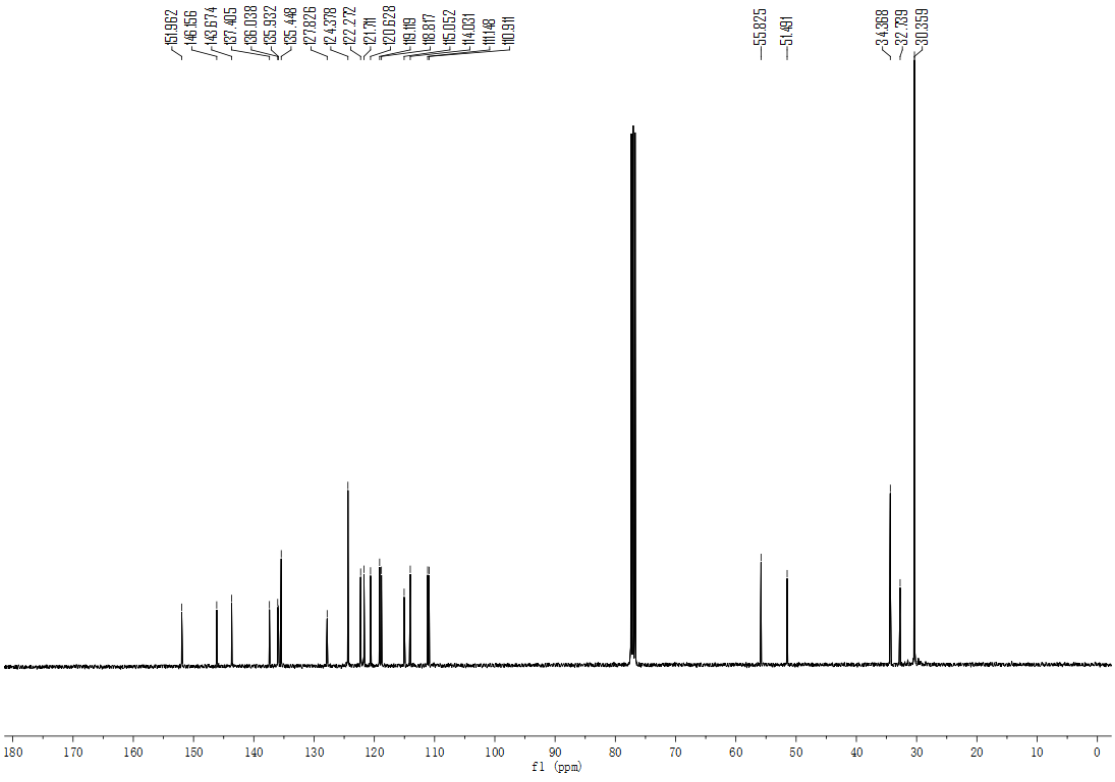


2,6-di-tert-butyl-4-(1-(3-hydroxy-4-methoxyphenyl)-2-(1H-indol-3-yl)ethyl)phenol (13)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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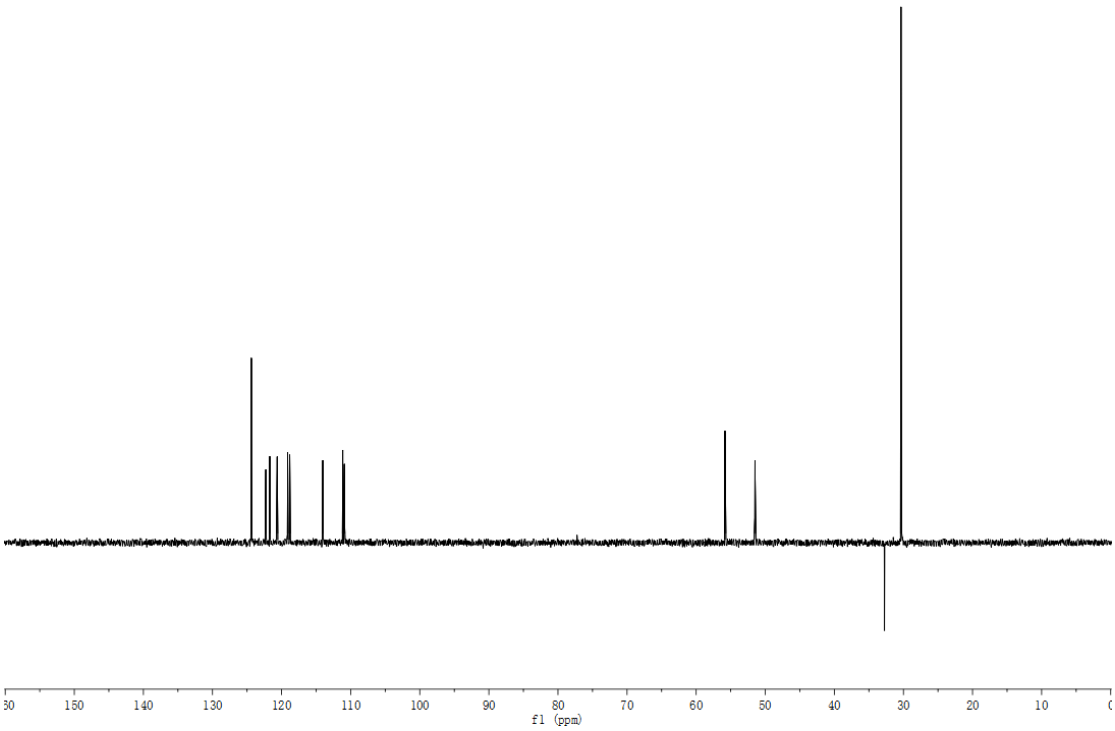
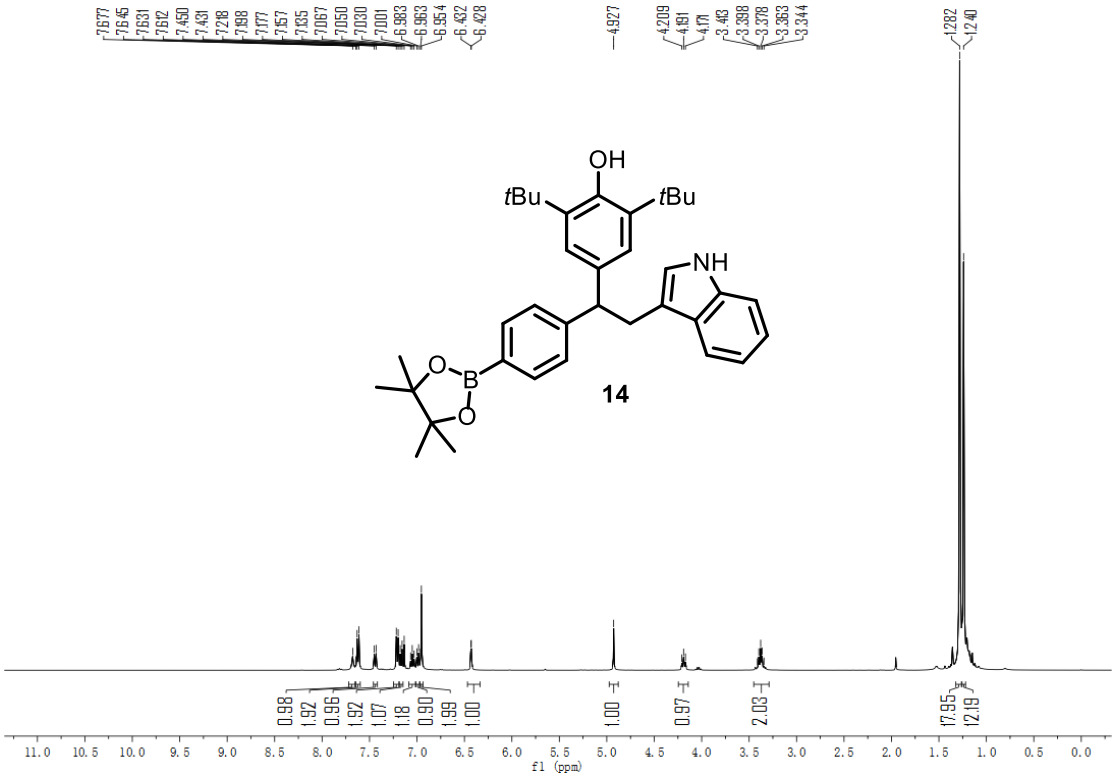
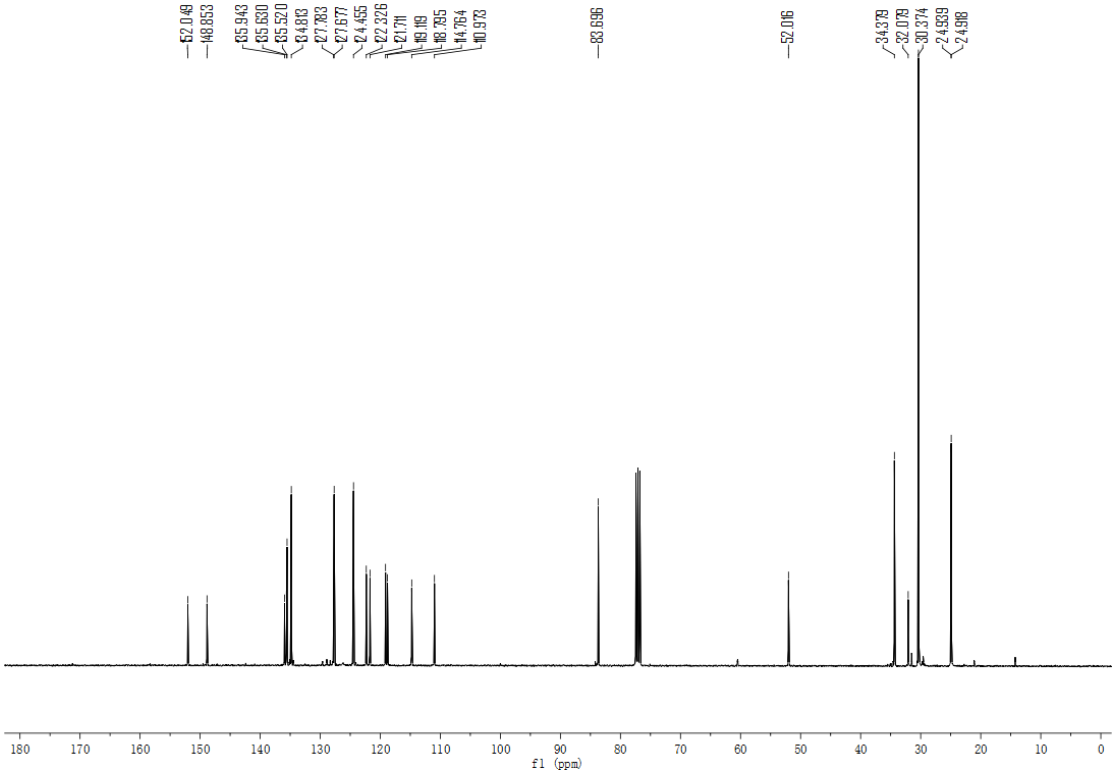


4-(2-(1H-indol-3-yl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)-2,6-di-tert-butylphenol (14)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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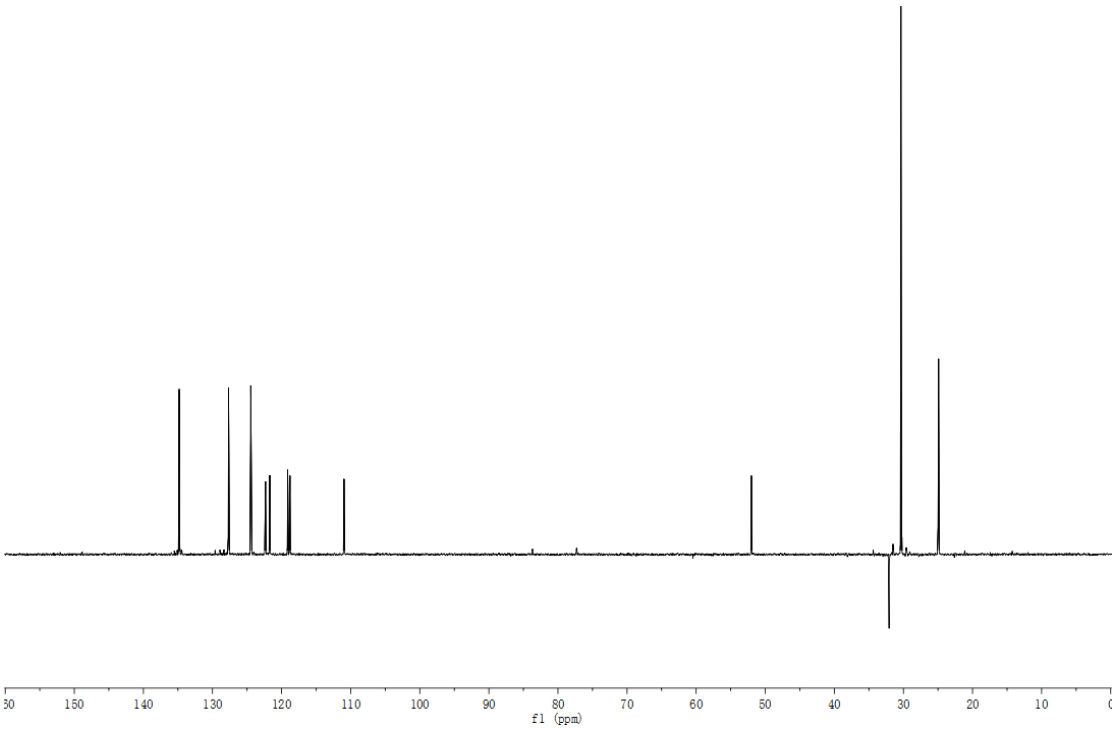
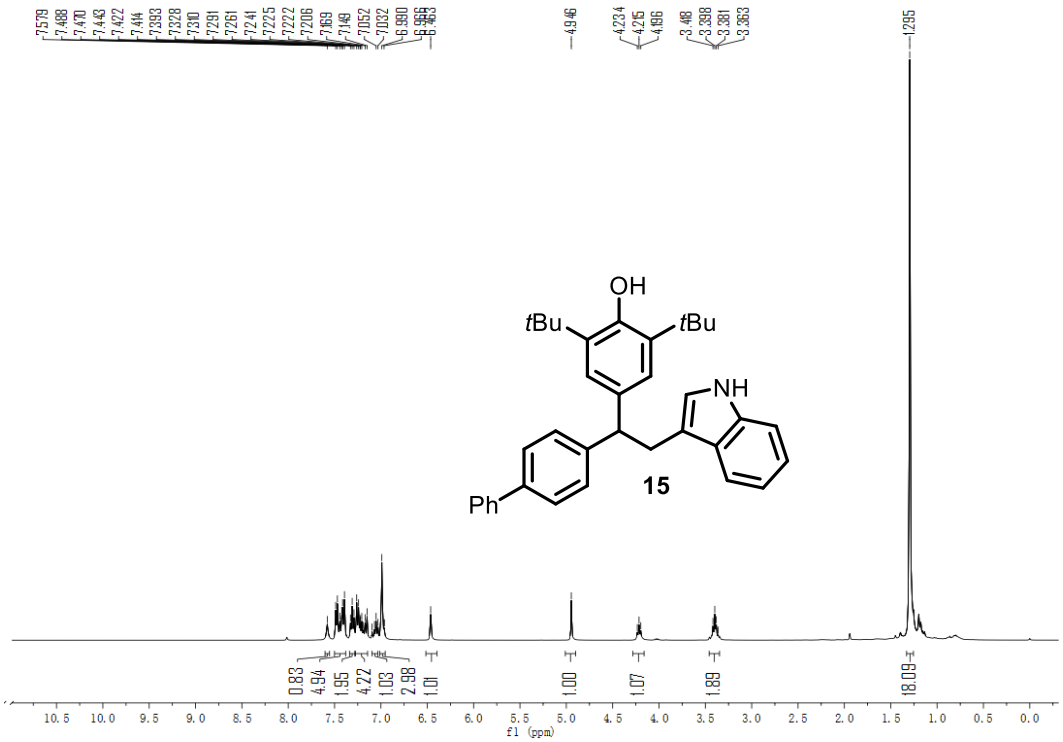
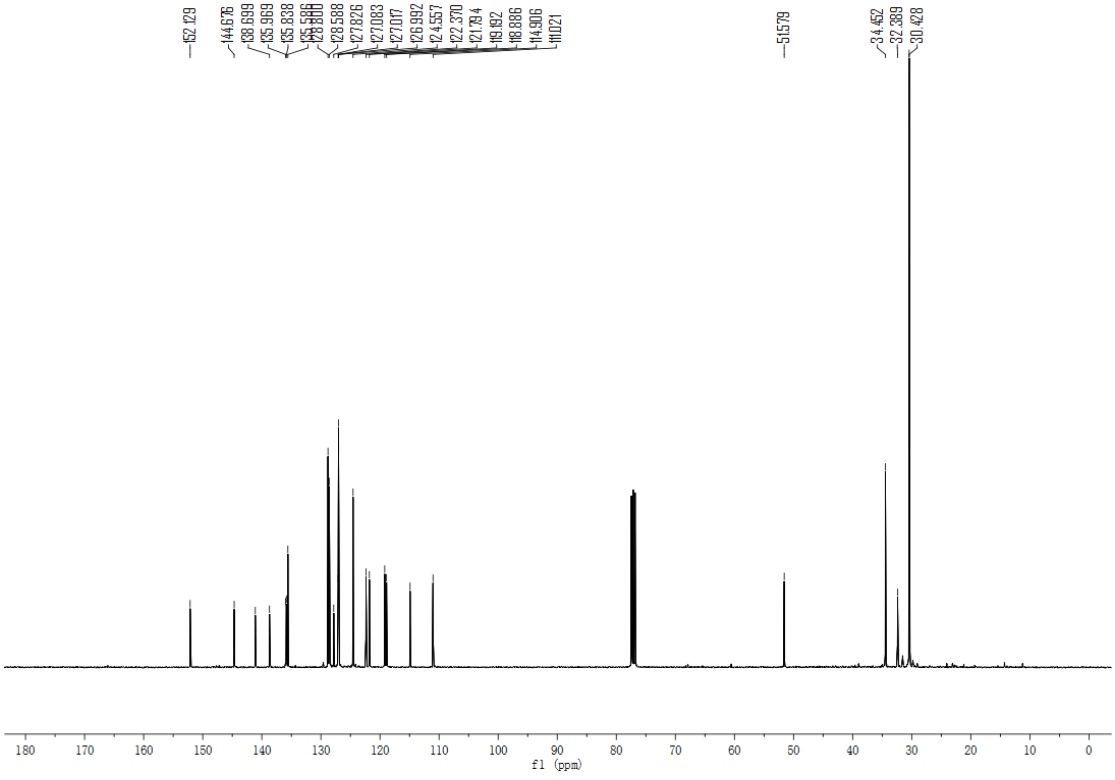


4-(1-([1,1'-biphenyl]-4-yl)-2-(1H-indol-3-yl)ethyl)-2,6-di-tert-butylphenol (15)

^{1}H NMR (400 MHz, $CDCl_3$):

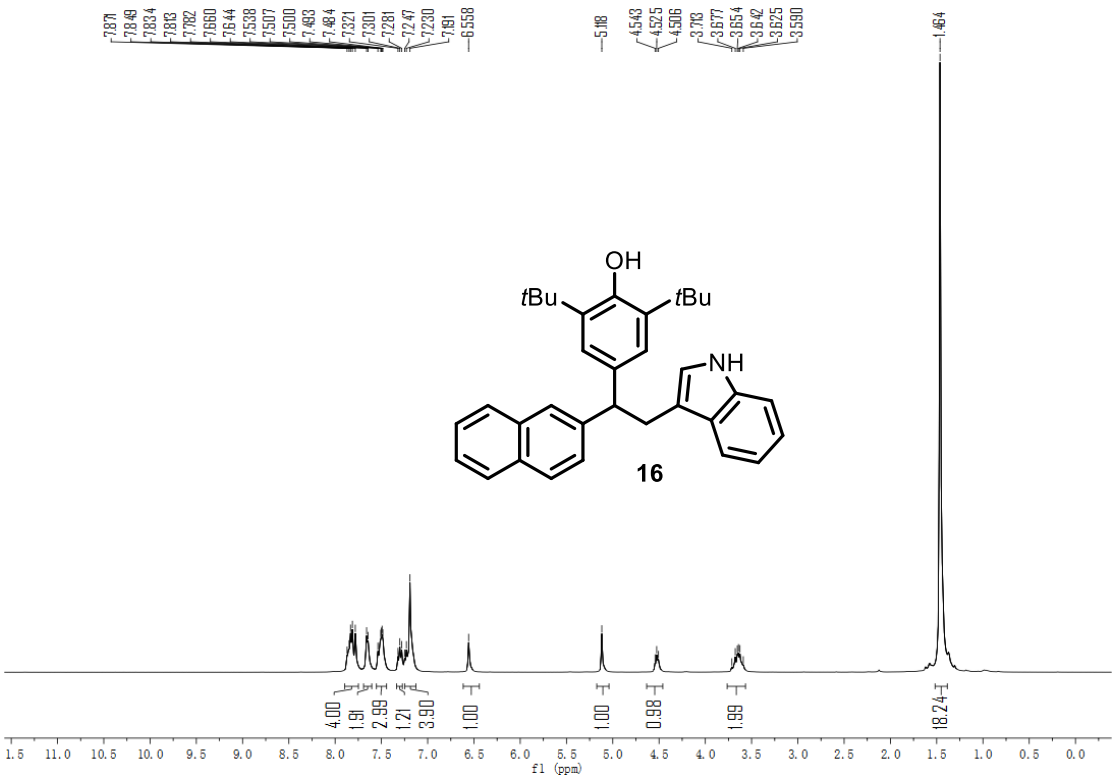


^{13}C NMR (100 MHz, $CDCl_3$):

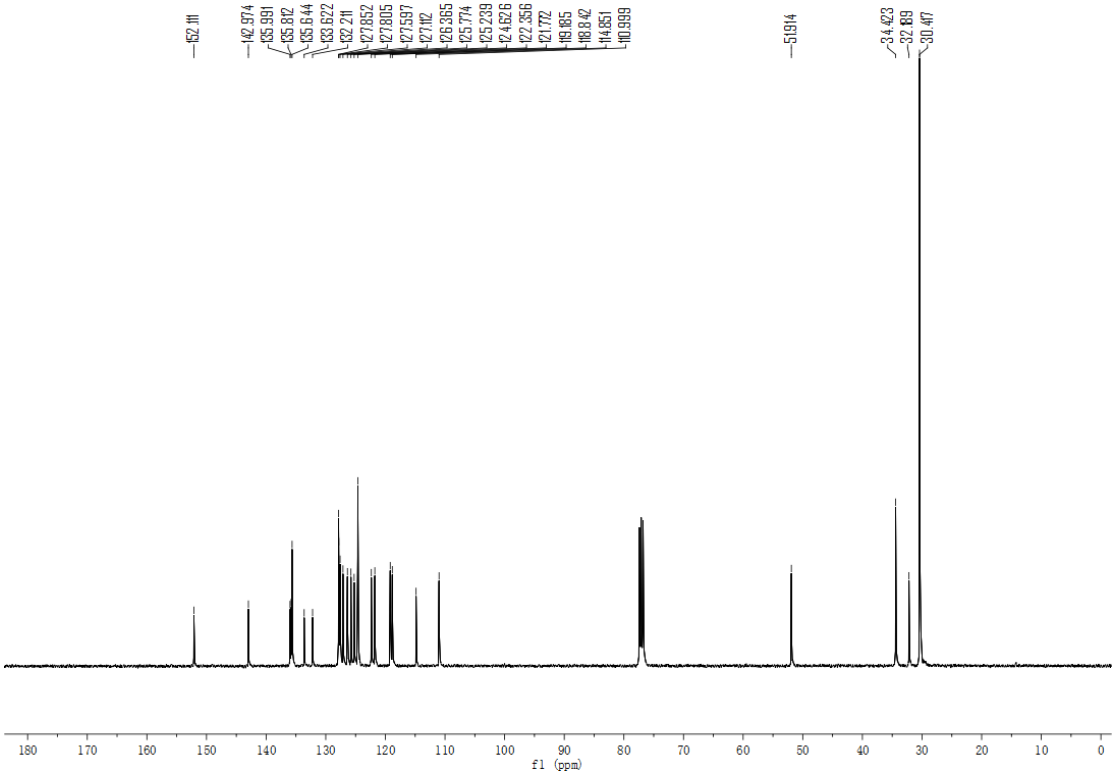


4-(2-(1H-indol-3-yl)-1-(naphthalen-2-yl)ethyl)-2,6-di-tert-butylphenol (16)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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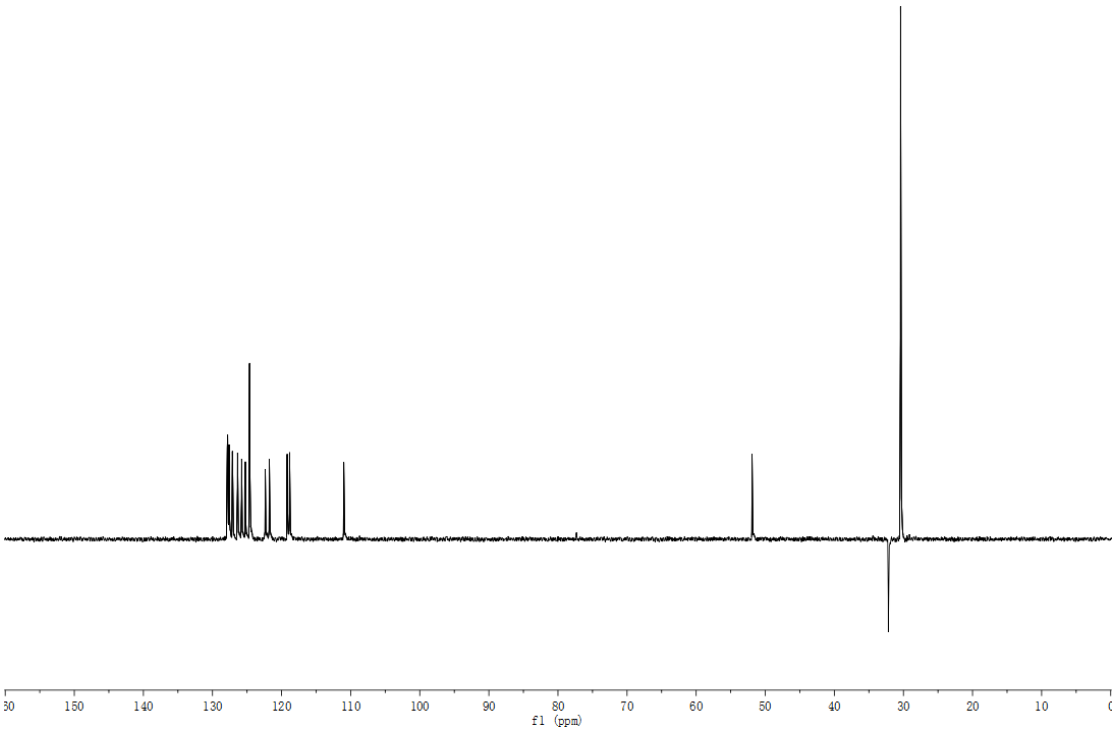
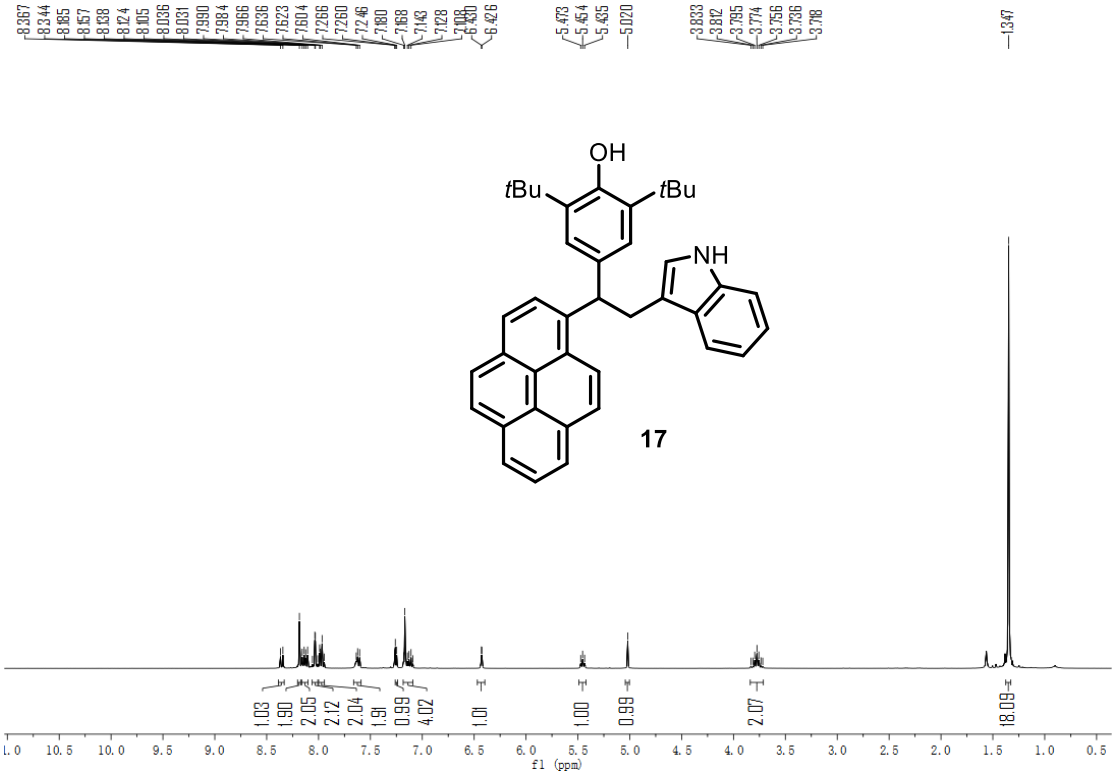
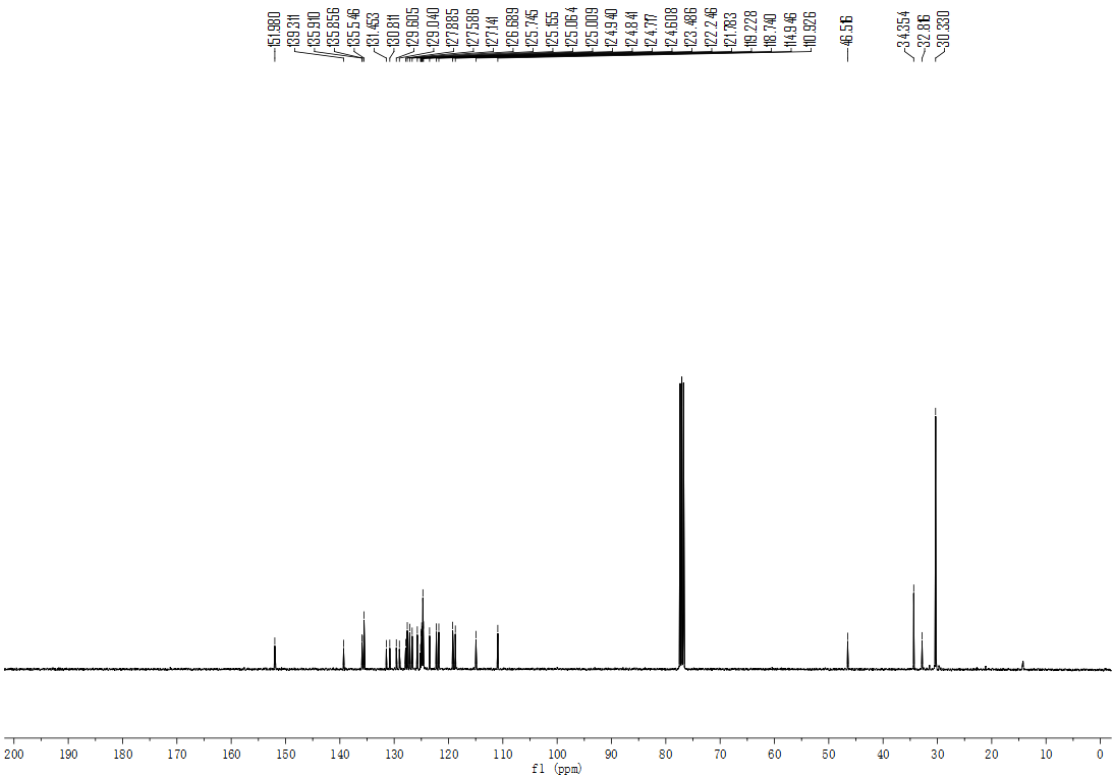


4-(2-(1H-indol-3-yl)-1-(pyren-1-yl)ethyl)-2,6-di-tert-butylphenol (17)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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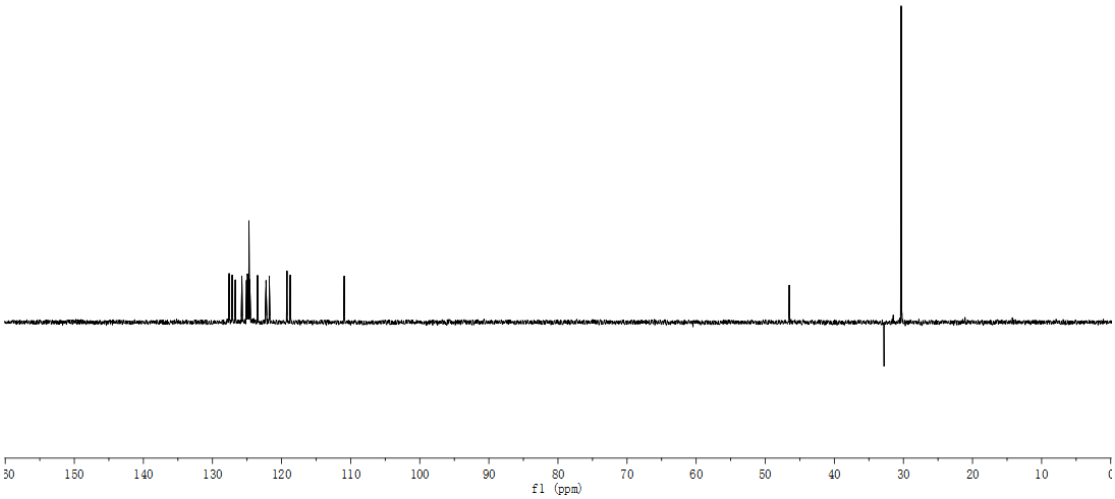
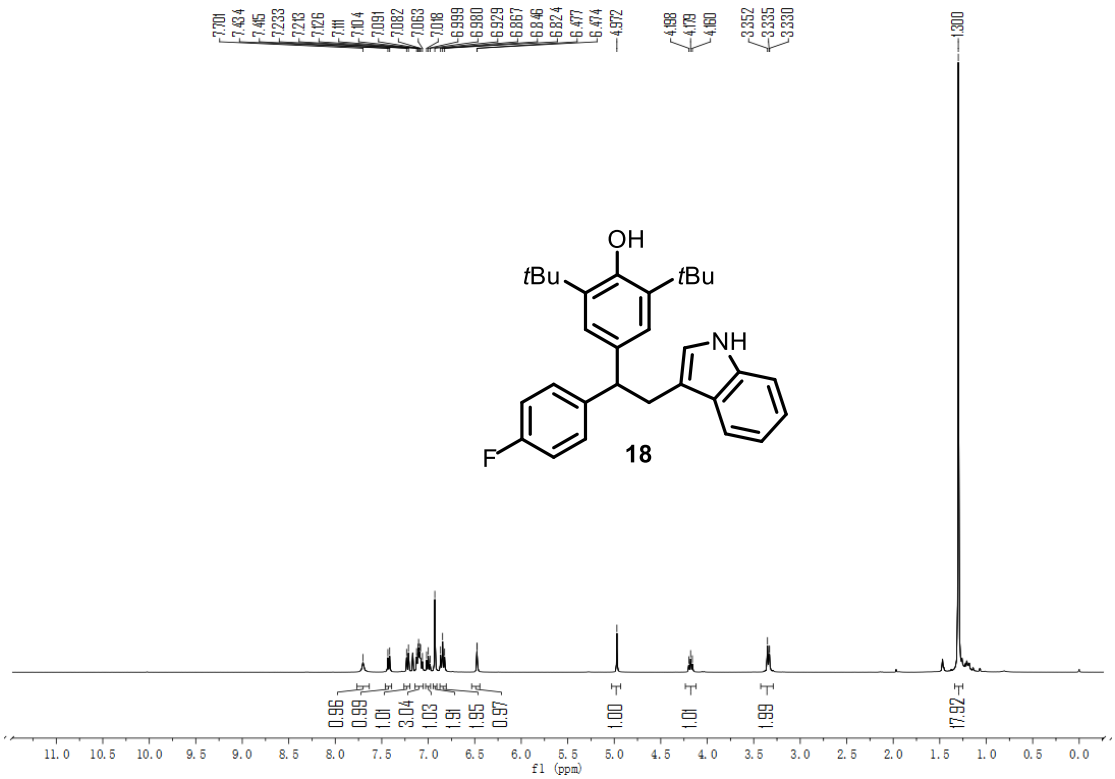
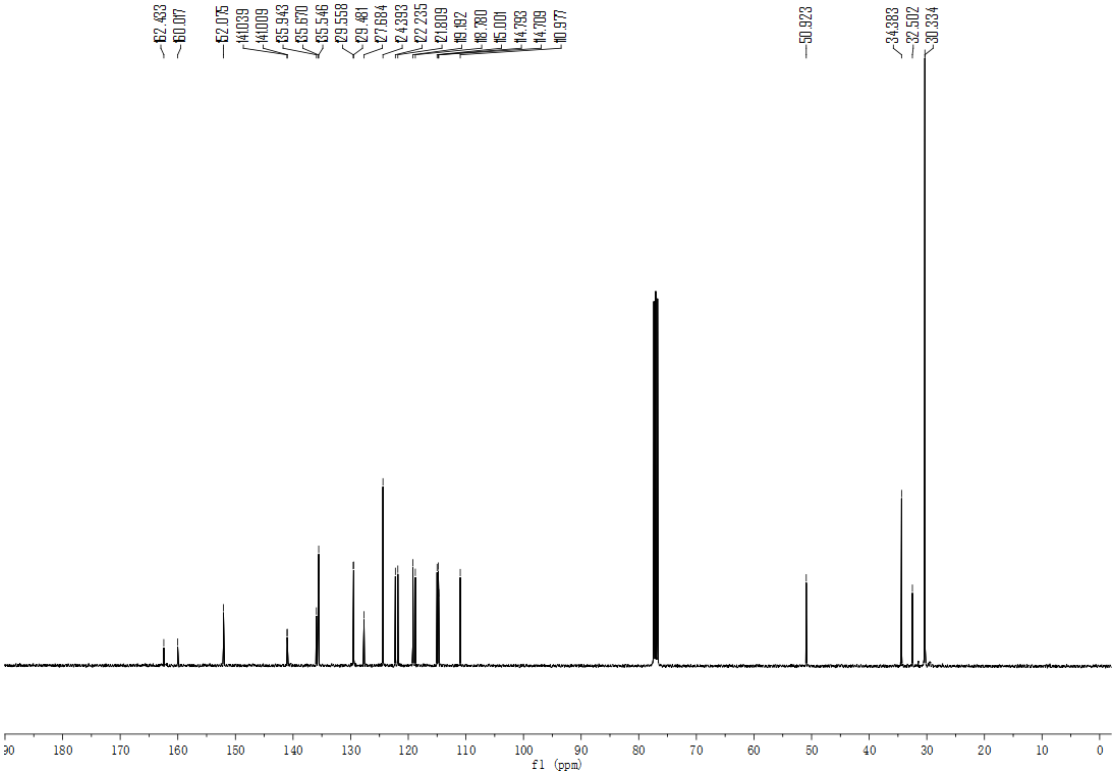


2,6-di-tert-butyl-4-(1-(4-fluorophenyl)-2-(1H-indol-3-yl)ethyl)phenol (18)

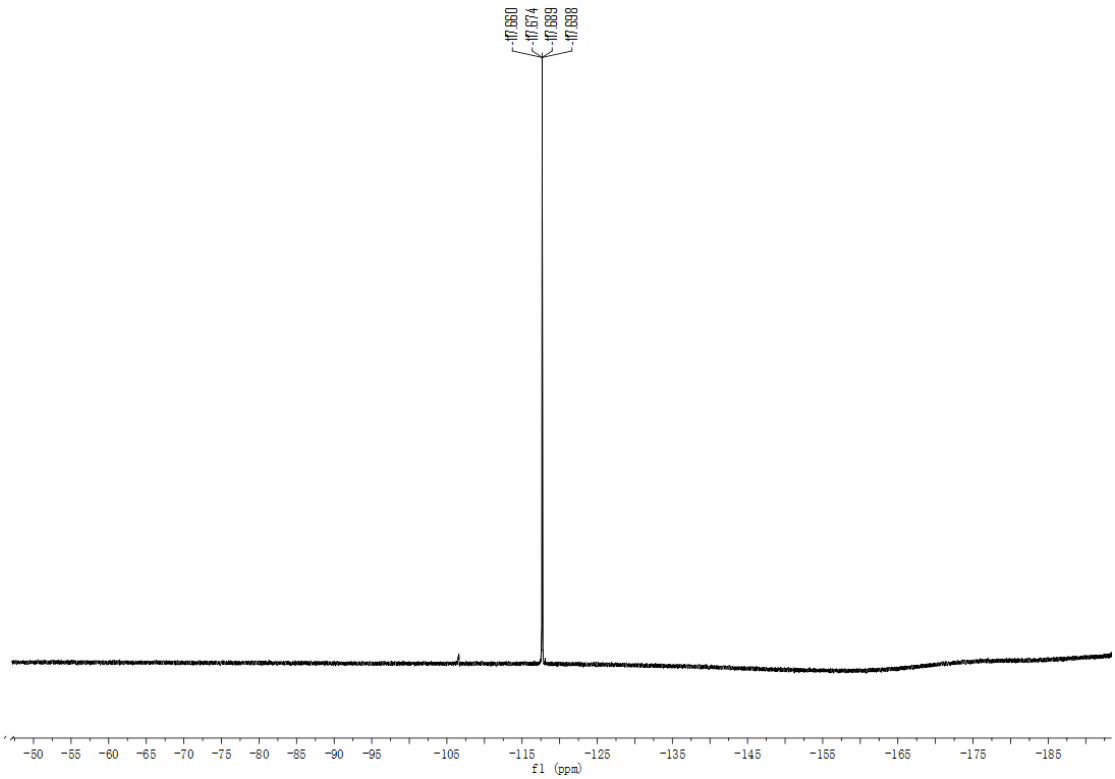
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):



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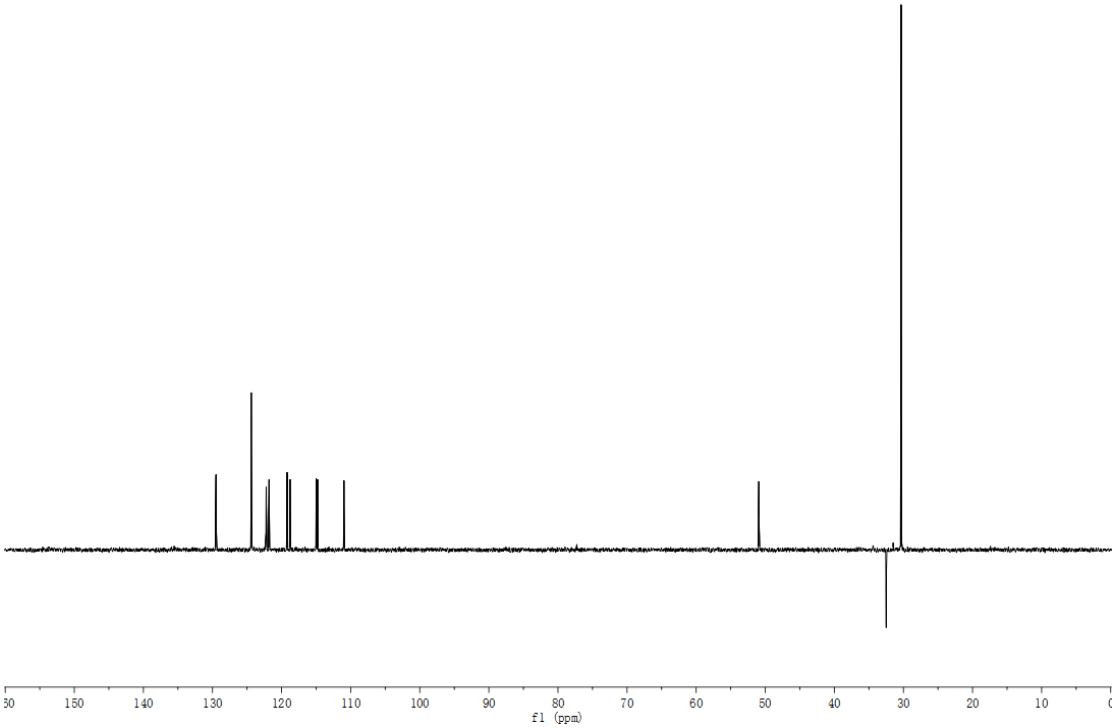
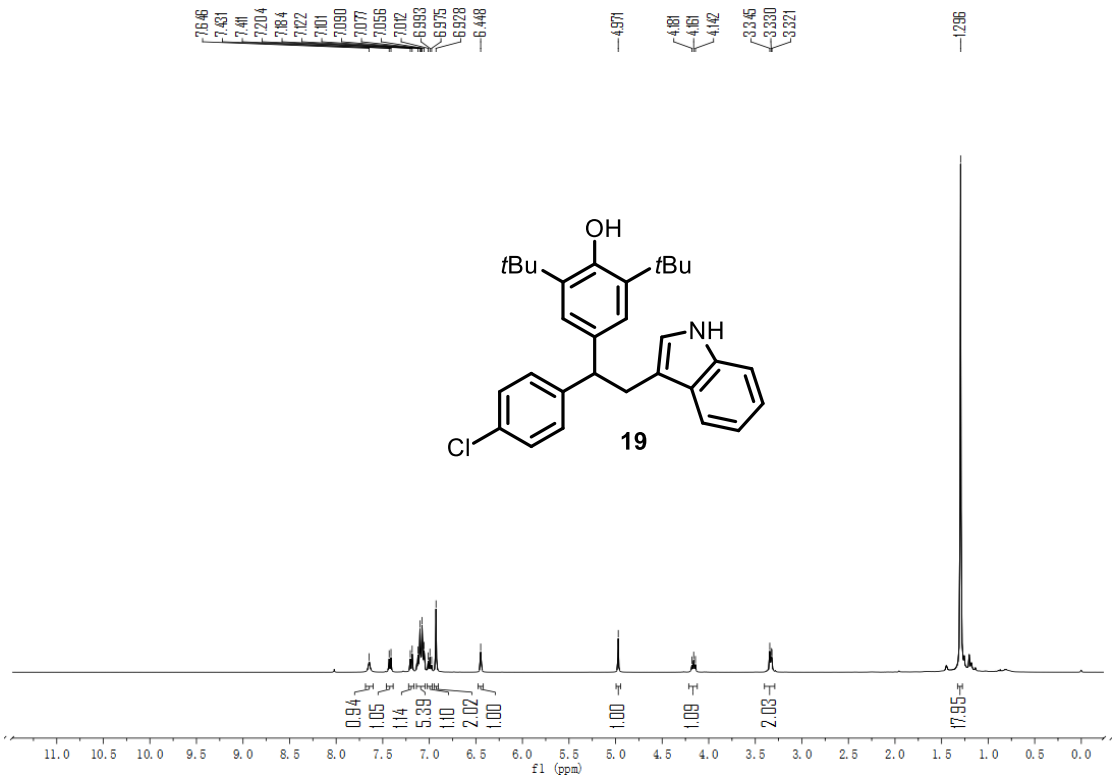
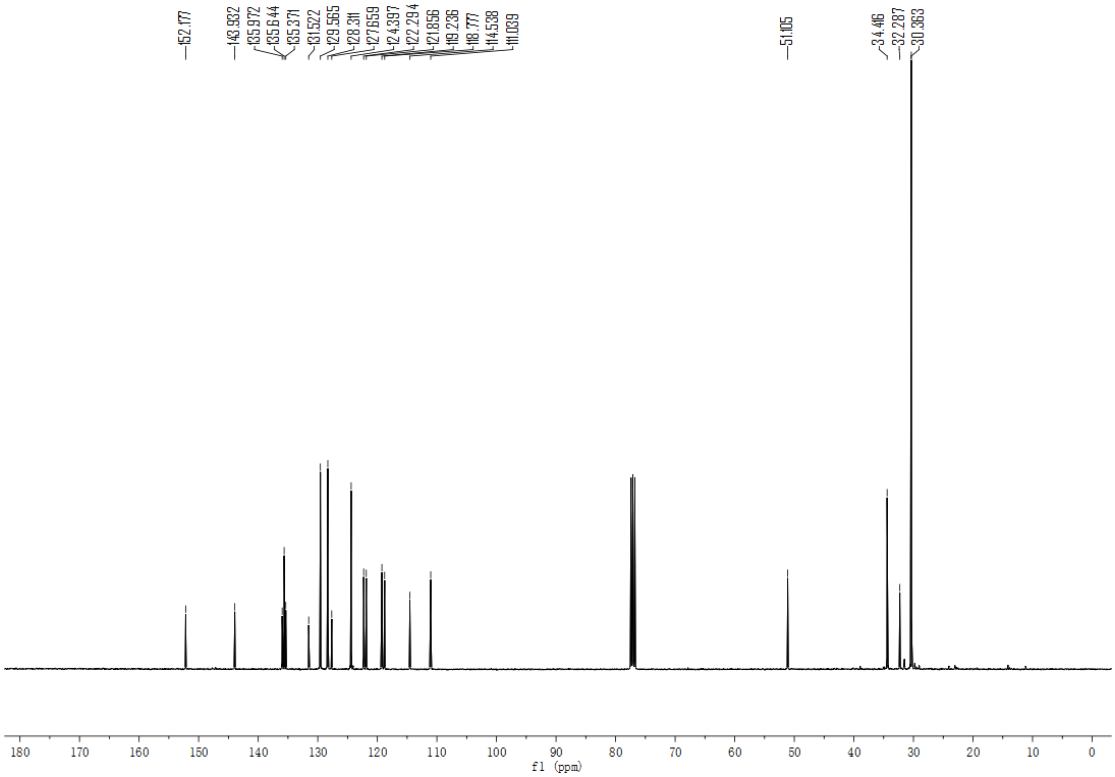


2,6-di-tert-butyl-4-(1-(4-chlorophenyl)-2-(1H-indol-3-yl)ethyl)phenol (19)

^{1}H NMR (400 MHz, $CDCl_3$):

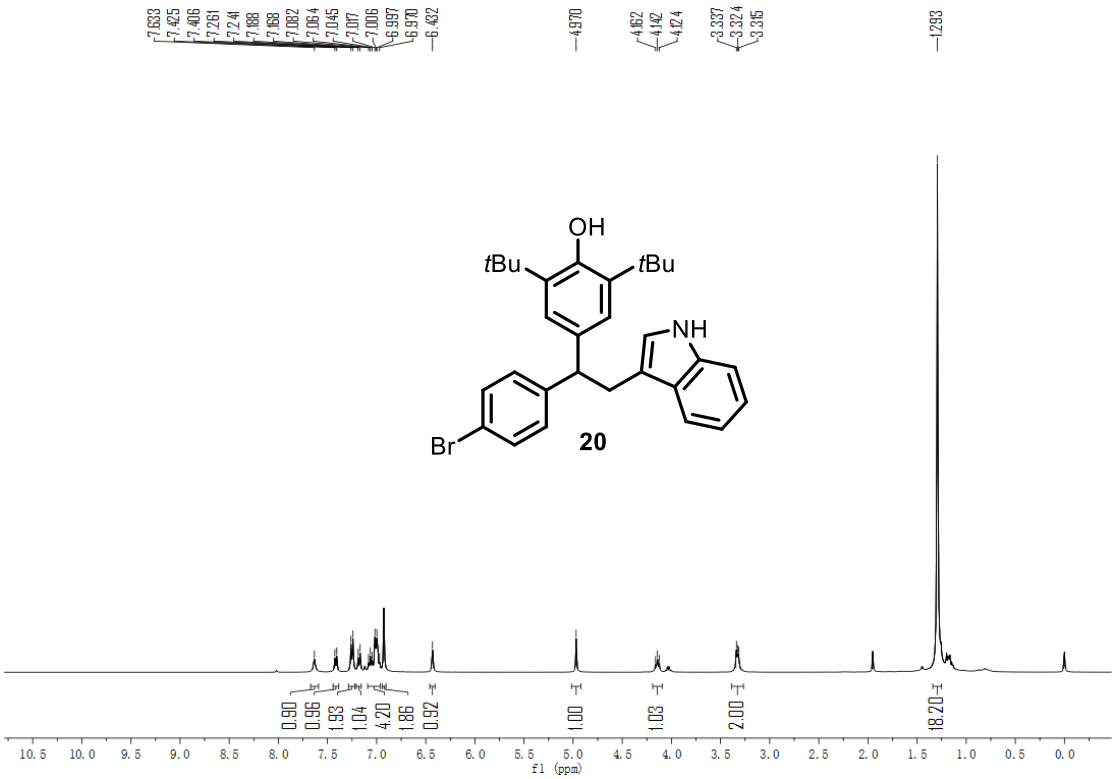


^{13}C NMR (100 MHz, $CDCl_3$):

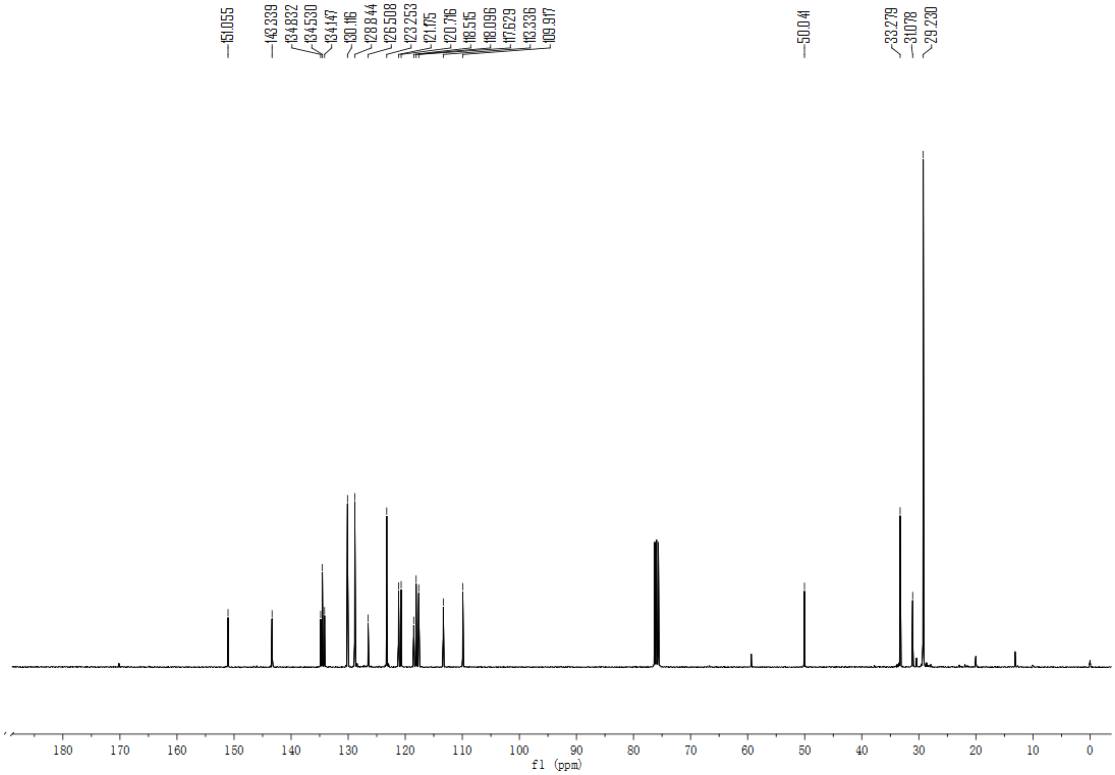


4-(1-(4-bromophenyl)-2-(1H-indol-3-yl)ethyl)-2,6-di-tert-butylphenol (20)

^{1}H NMR (400 MHz, $CDCl_3$):

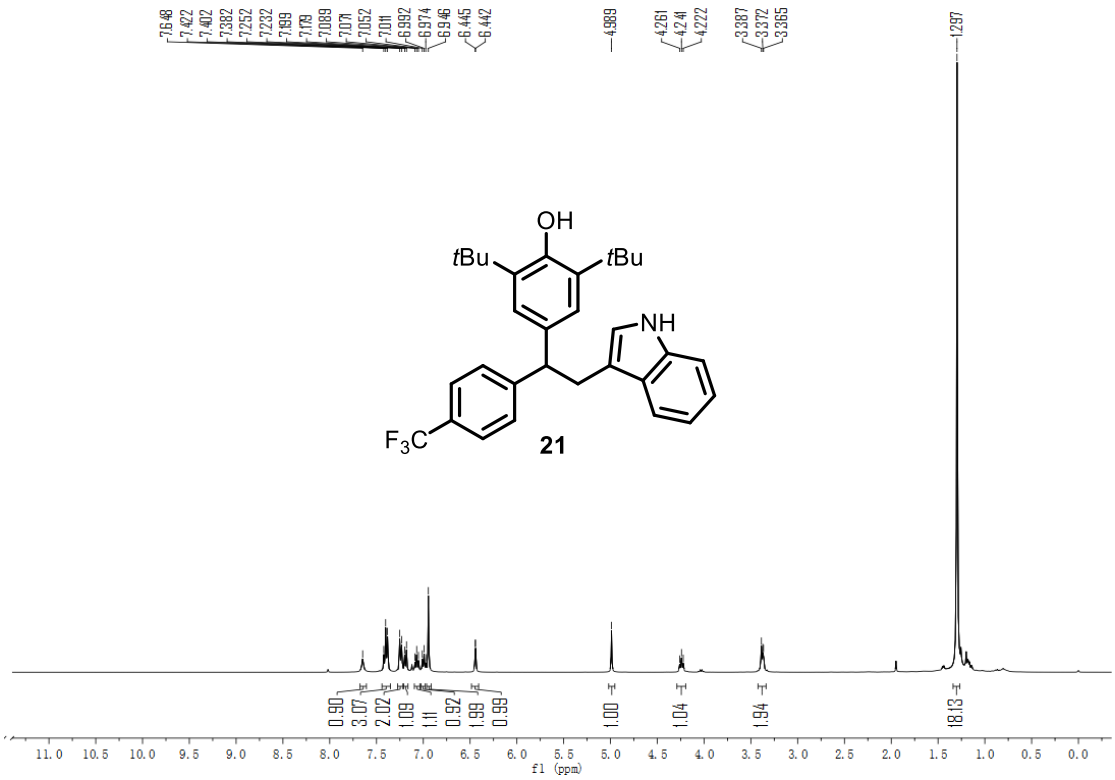


^{13}C NMR (100 MHz, $CDCl_3$):

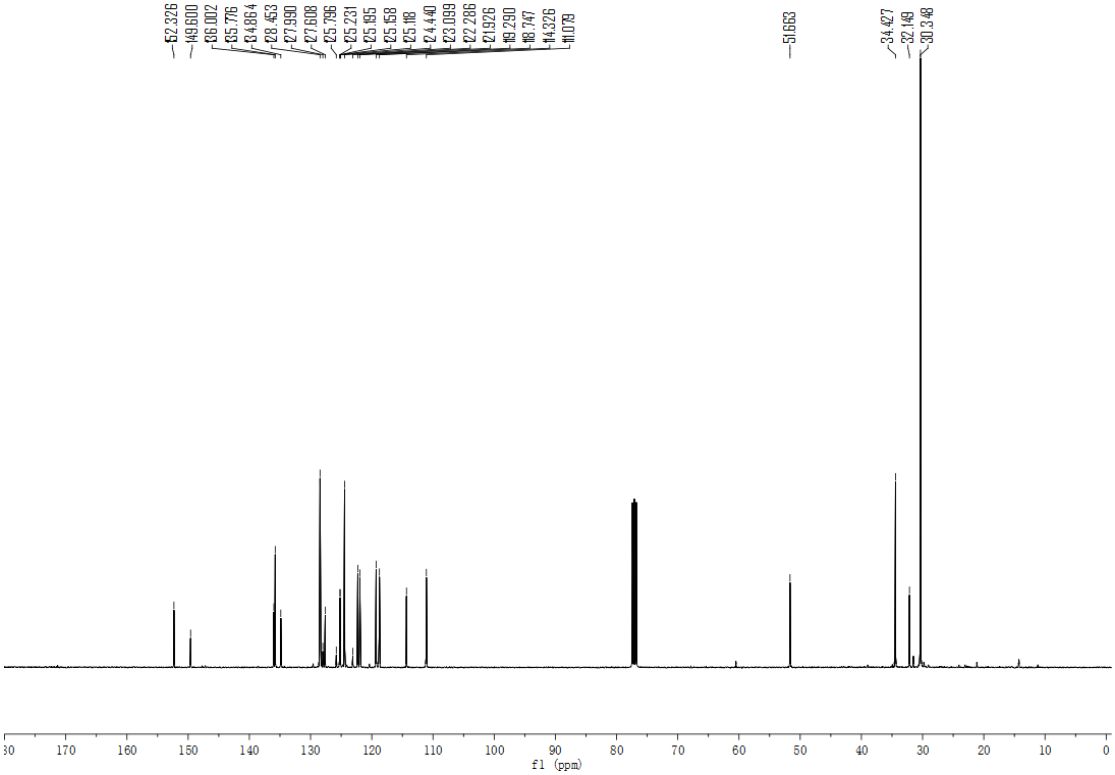


4-(2-(1H-indol-3-yl)-1-(4-(trifluoromethyl)phenyl)ethyl)-2,6-di-tert-butylphenol (21)

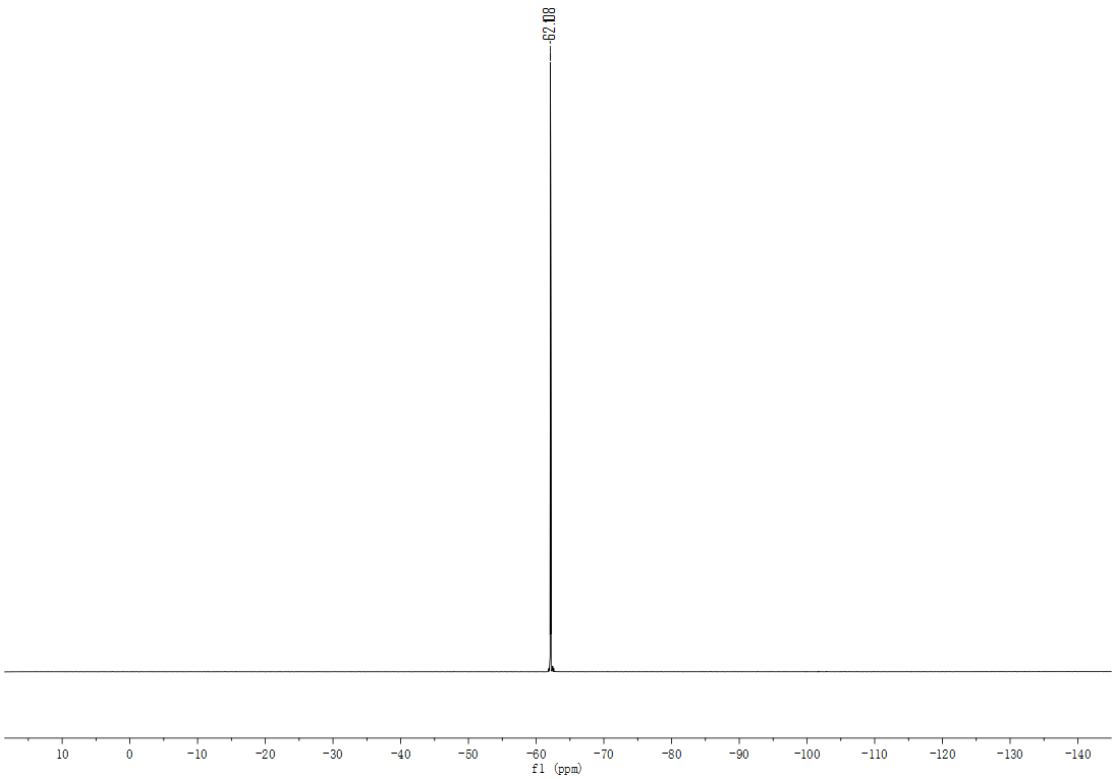
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

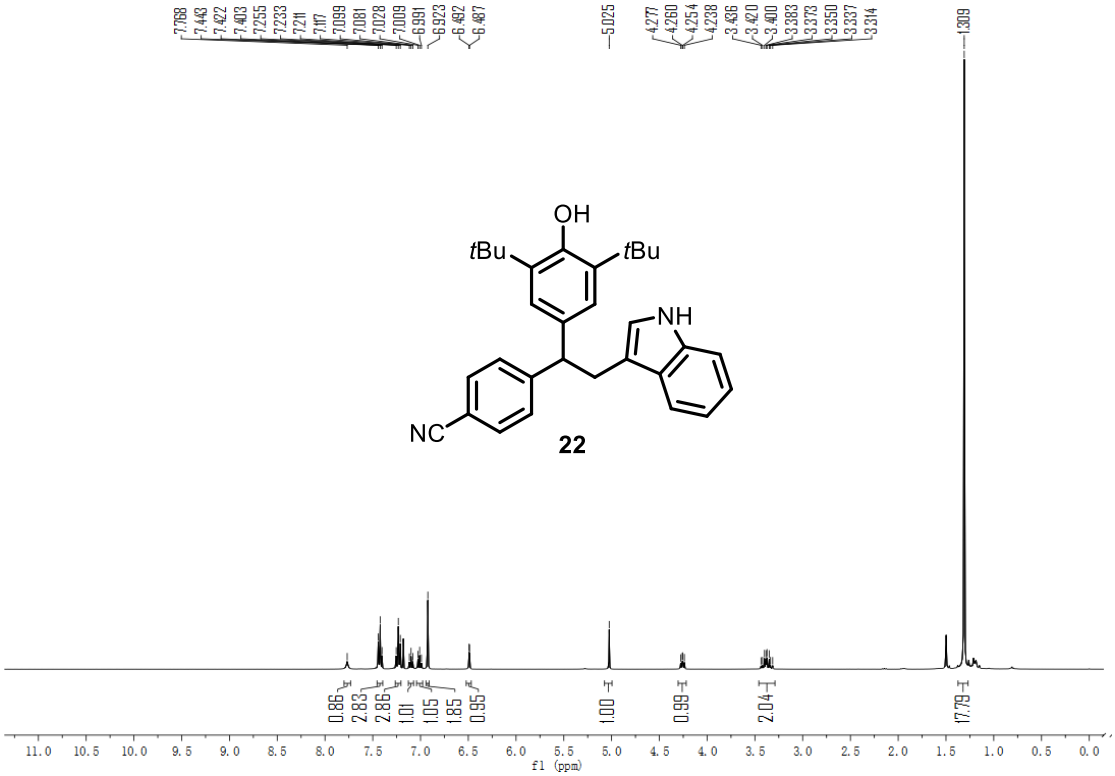


^{19}F NMR (376 MHz, $CDCl_3$):

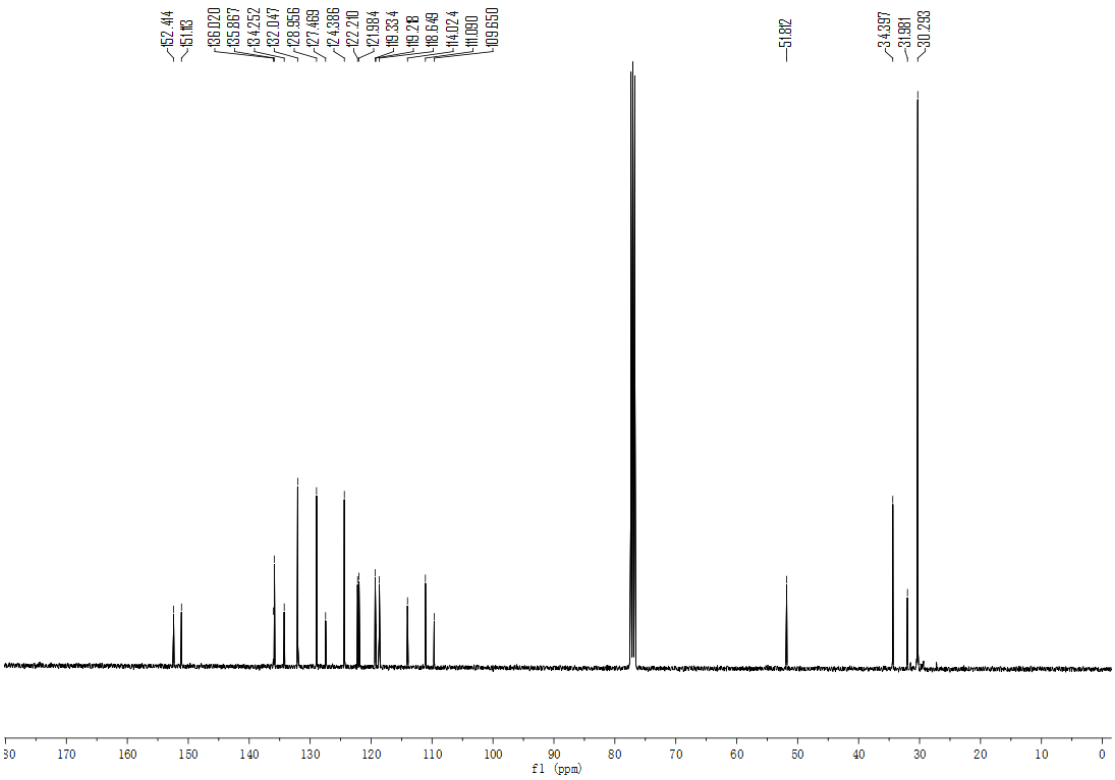


4-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1H-indol-3-yl)ethyl)benzonitrile (22)

^{1}H NMR (400 MHz, $CDCl_3$):

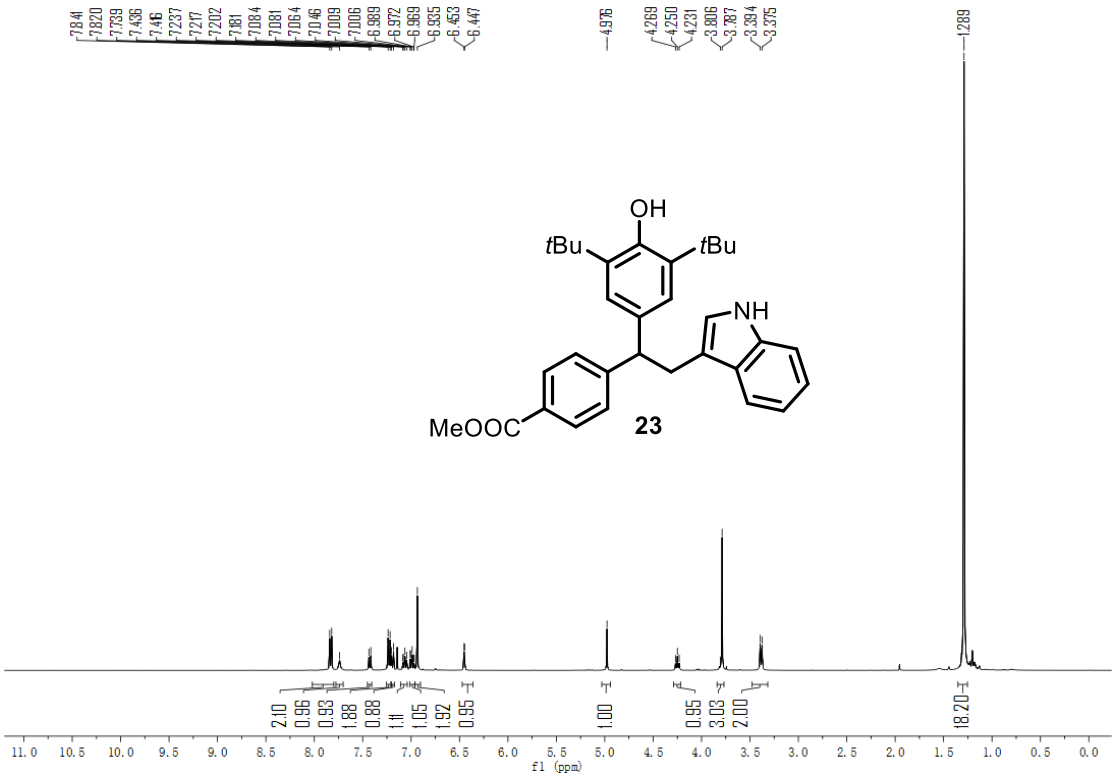


^{13}C NMR (100 MHz, $CDCl_3$):

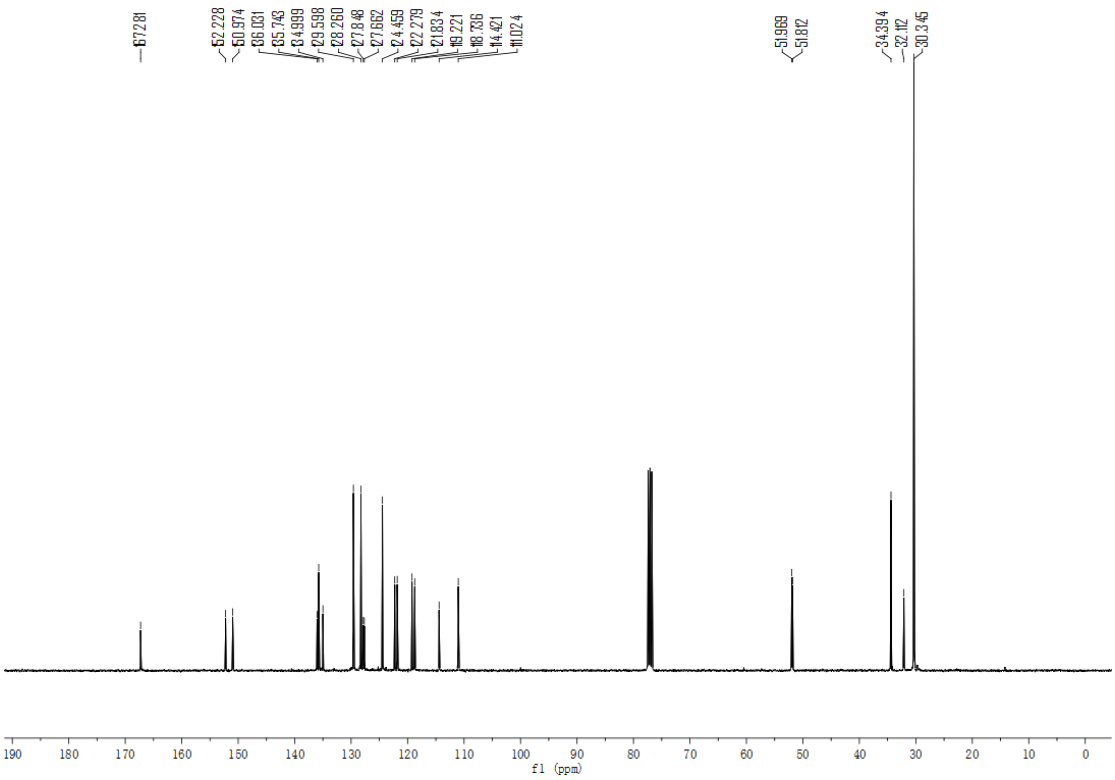


methyl 4-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(1H-indol-3-yl)ethyl)benzoate (23)

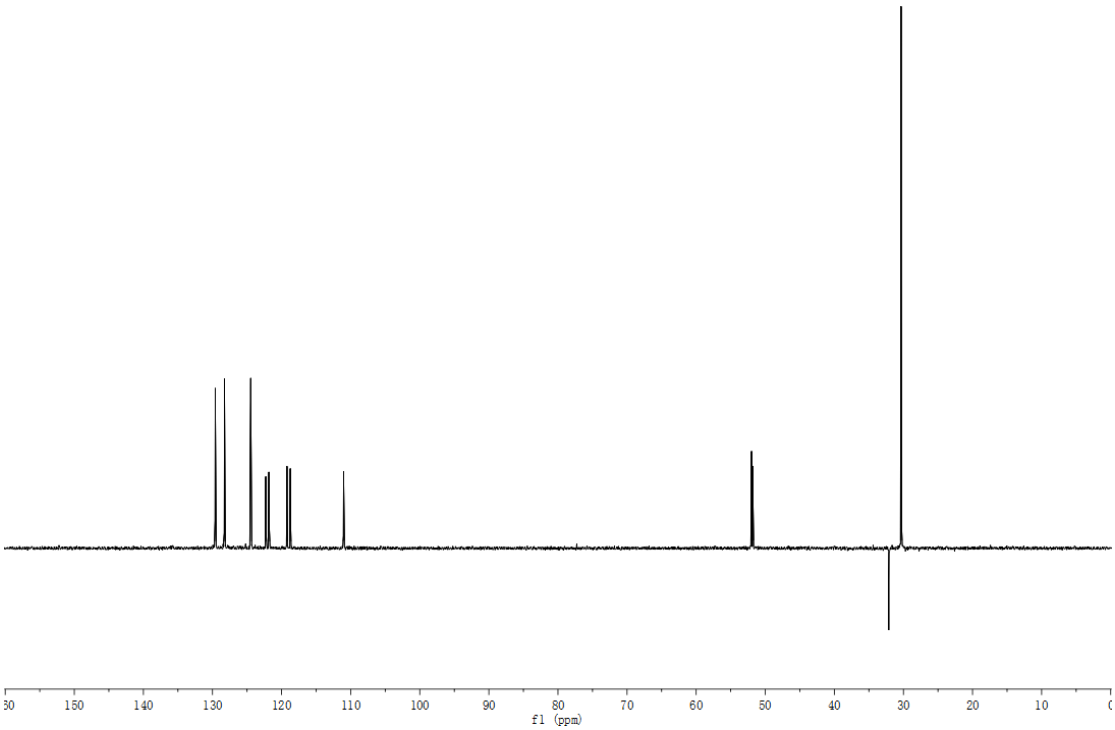
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

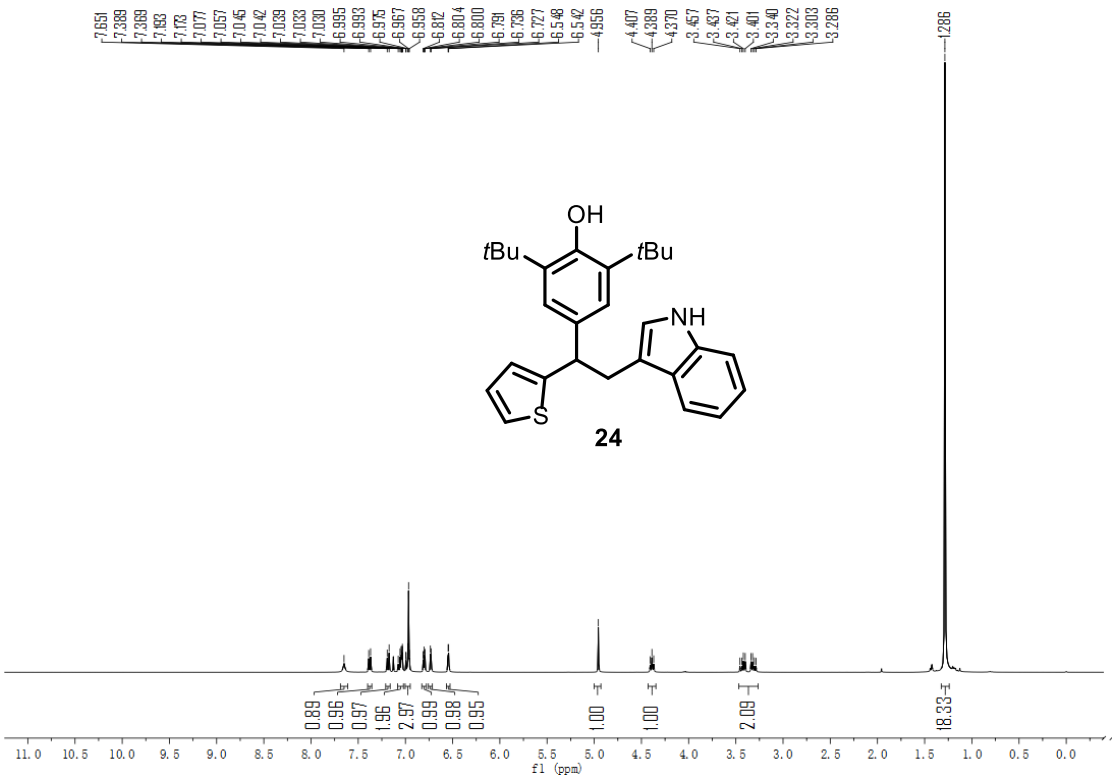


DEPT

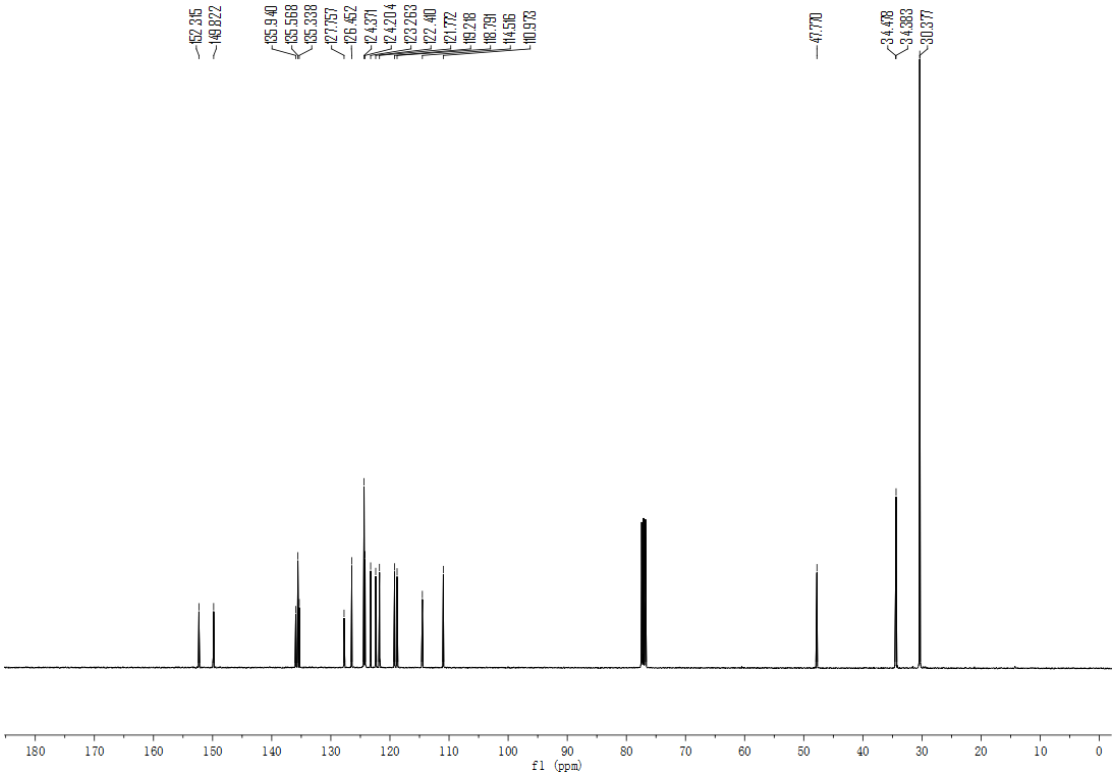


4-(2-(1H-indol-3-yl)-1-(thiophen-2-yl)ethyl)-2,6-di-tert-butylphenol (24)

^{1}H NMR (400 MHz, $CDCl_3$):

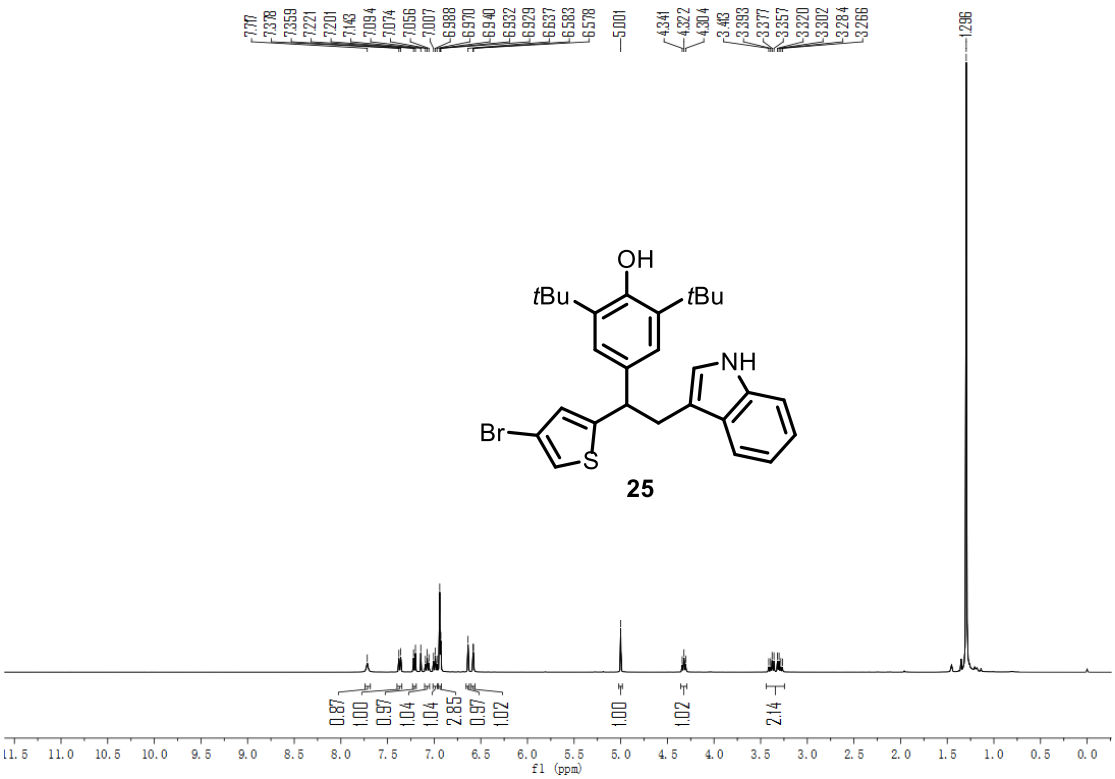


^{13}C NMR (100 MHz, $CDCl_3$):

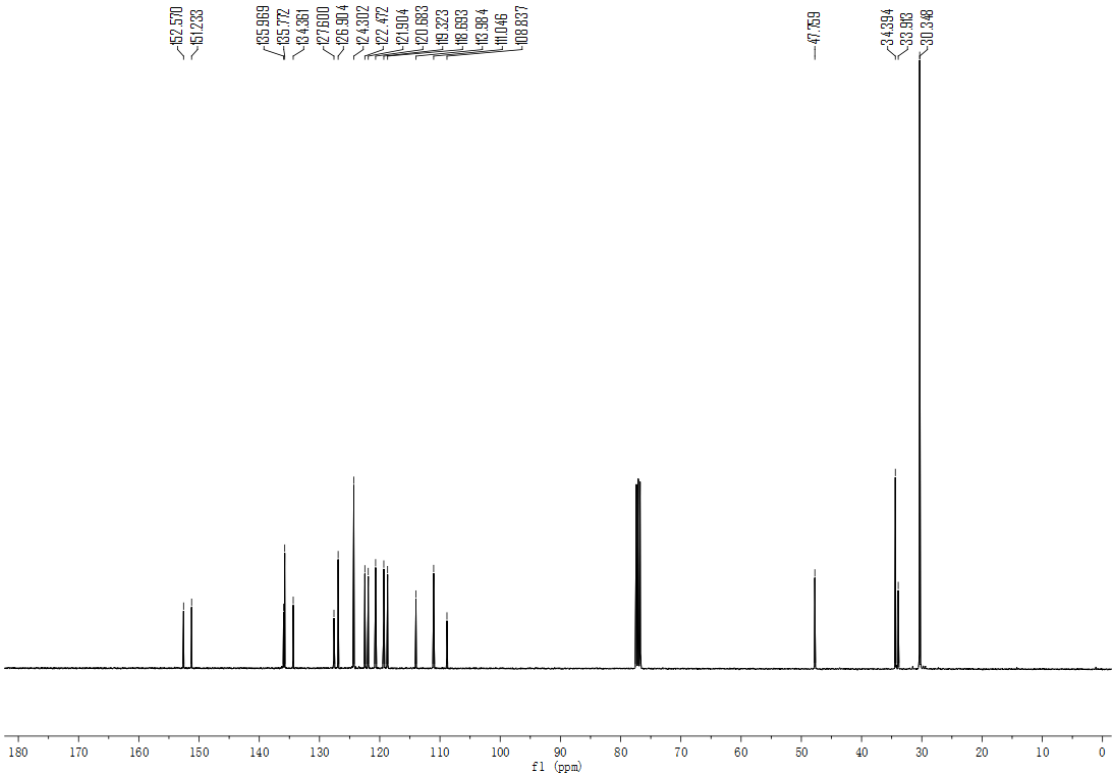


4-(1-(4-bromothiophen-2-yl)-2-(1H-indol-3-yl)ethyl)-2,6-di-tert-butylphenol (25)

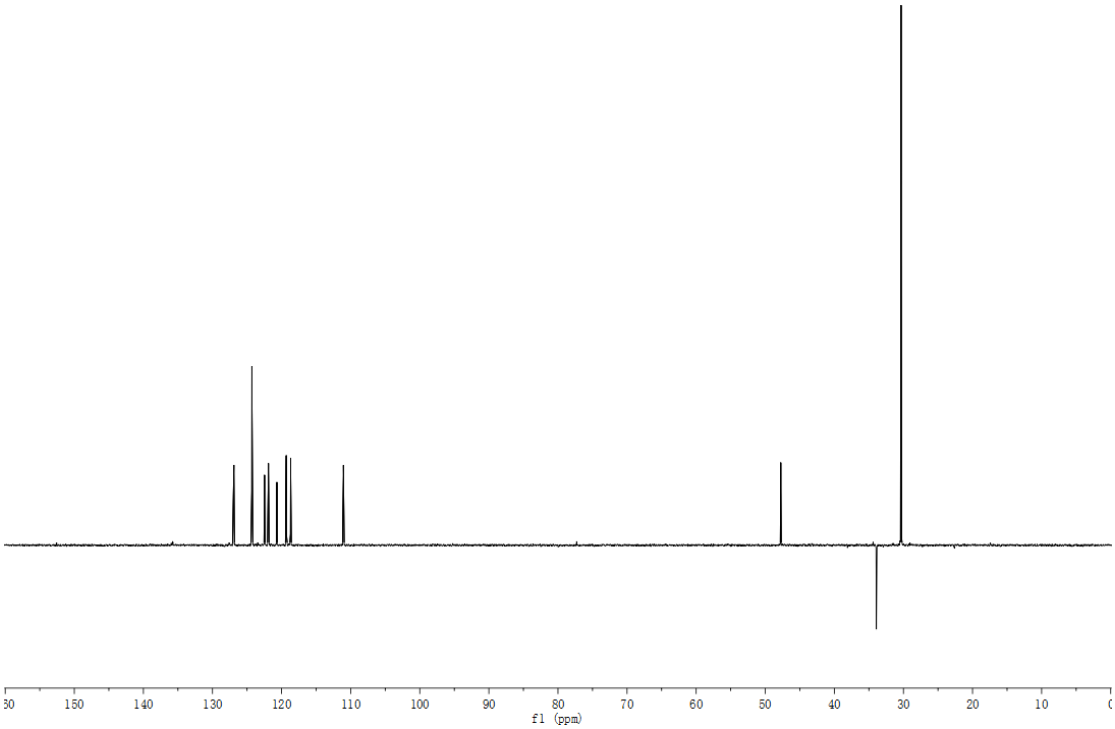
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

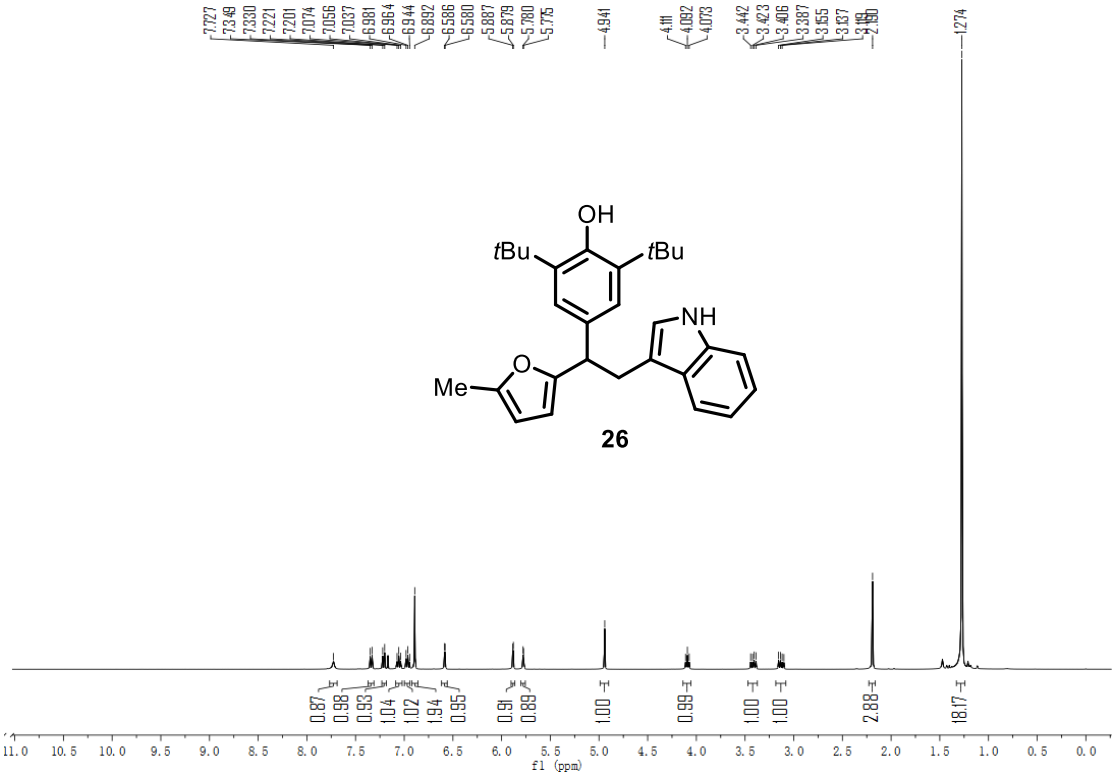


DEPT

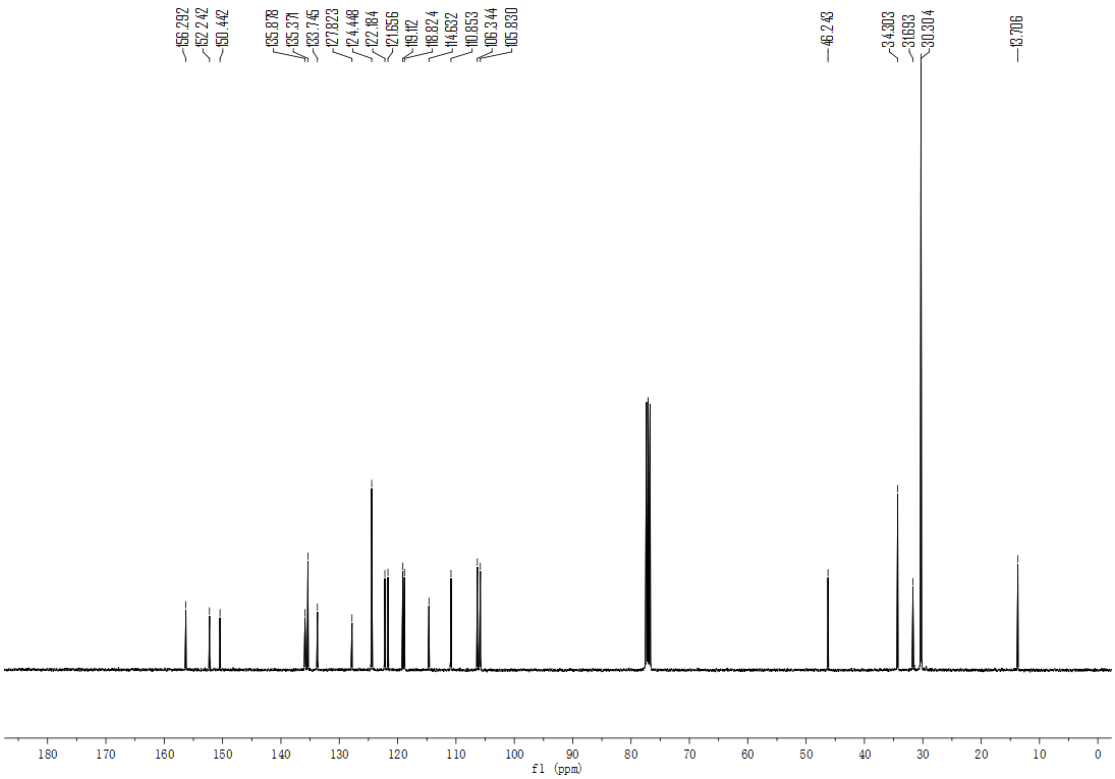


4-(2-(1H-indol-3-yl)-1-(5-methylfuran-2-yl)ethyl)-2,6-di-tert-butylphenol (26)

^{1}H NMR (400 MHz, $CDCl_3$):

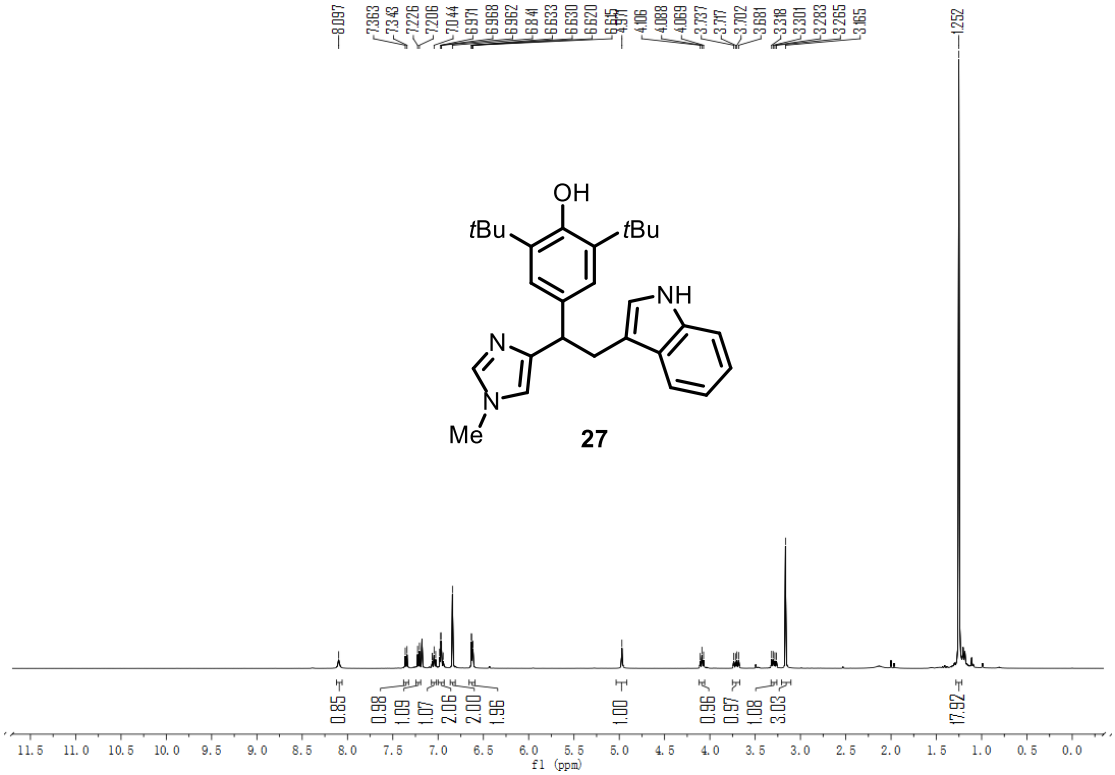


^{13}C NMR (100 MHz, $CDCl_3$):

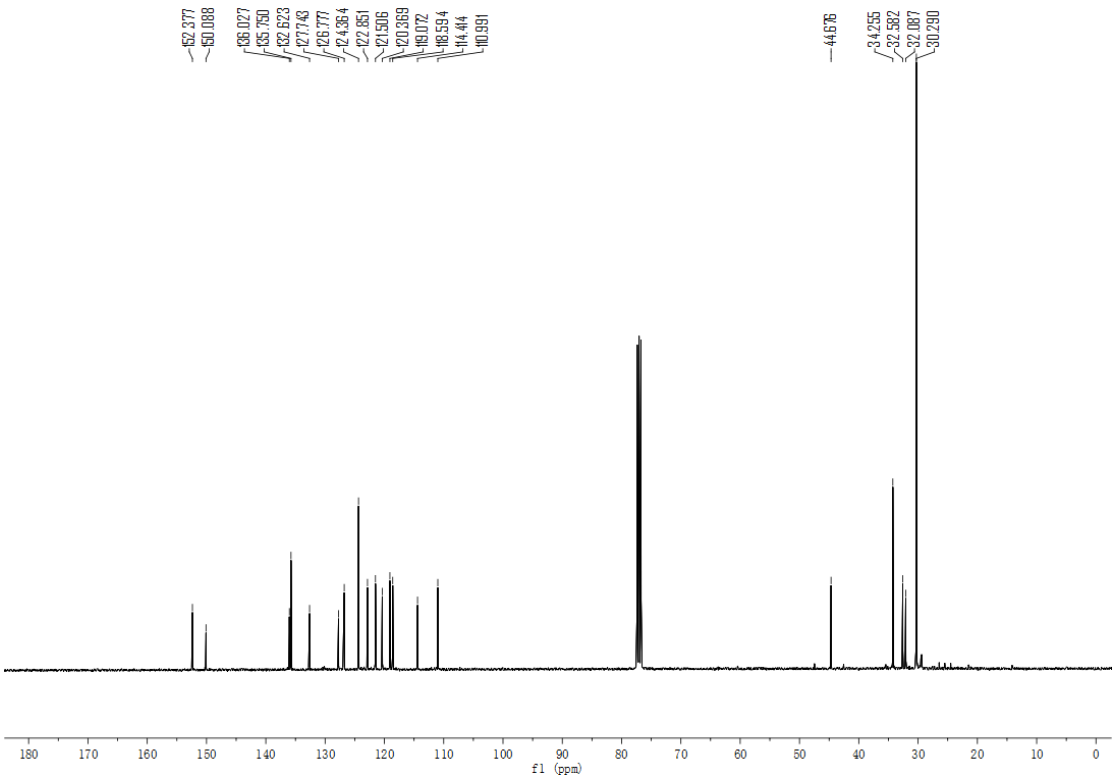


4-(2-(1H-indol-3-yl)-1-(1-methyl-1H-imidazol-4-yl)ethyl)-2,6-di-tert-butylphenol (27)

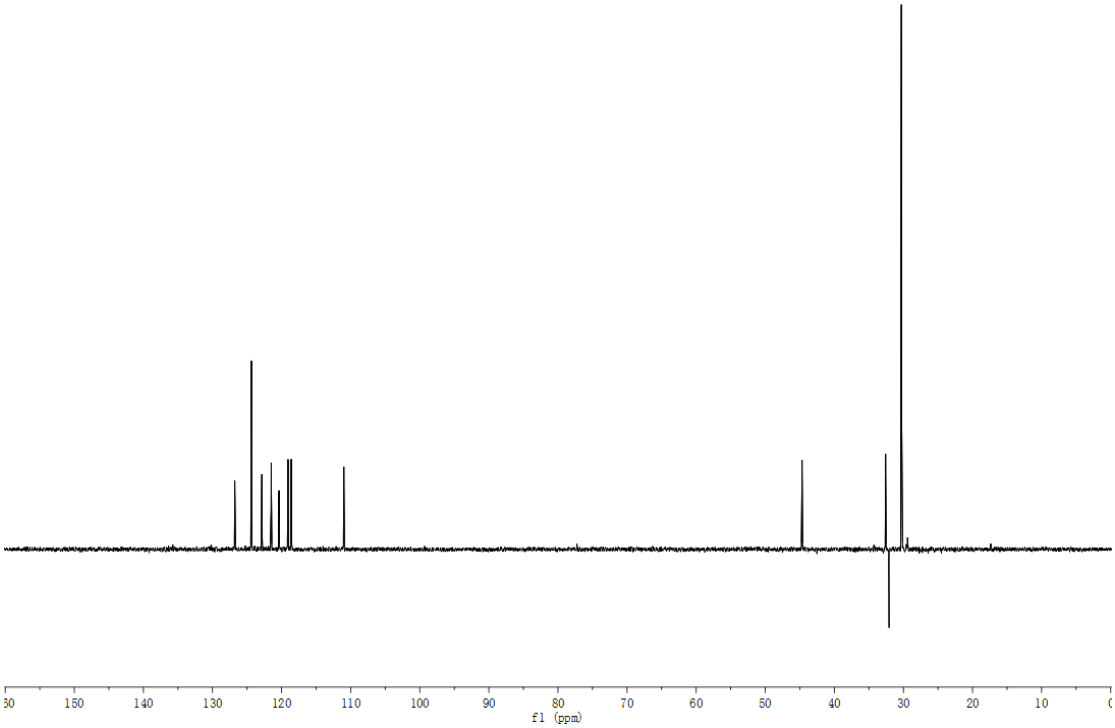
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

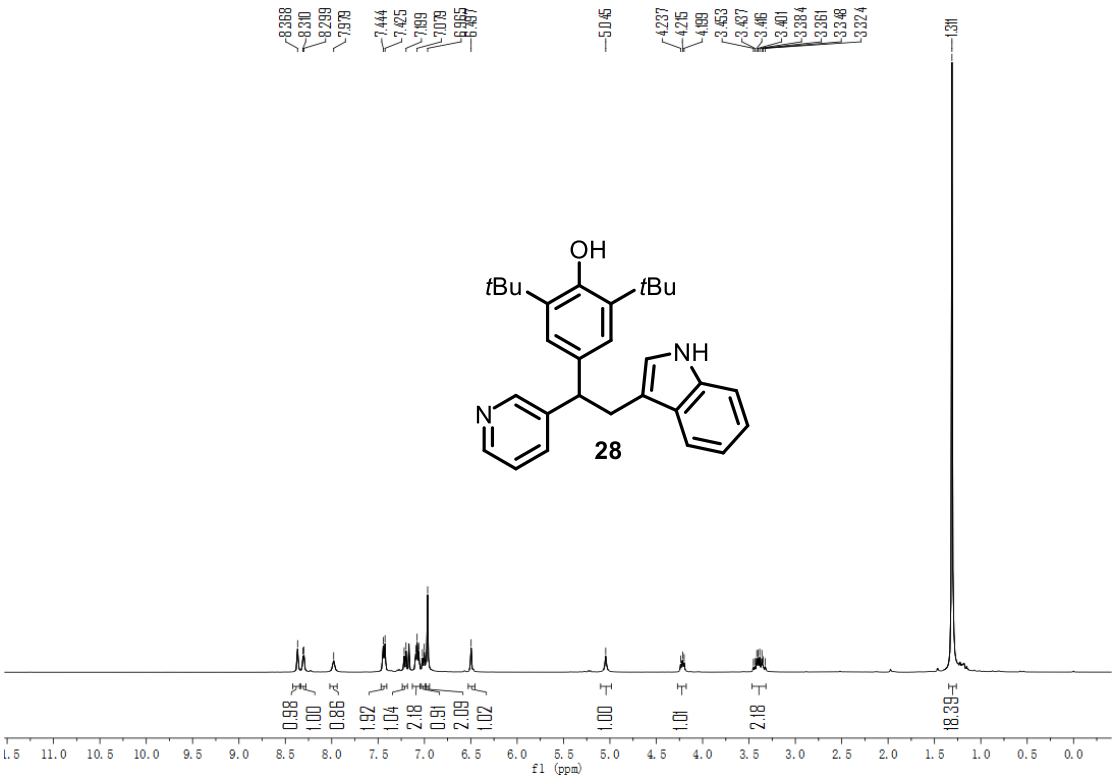


DEPT

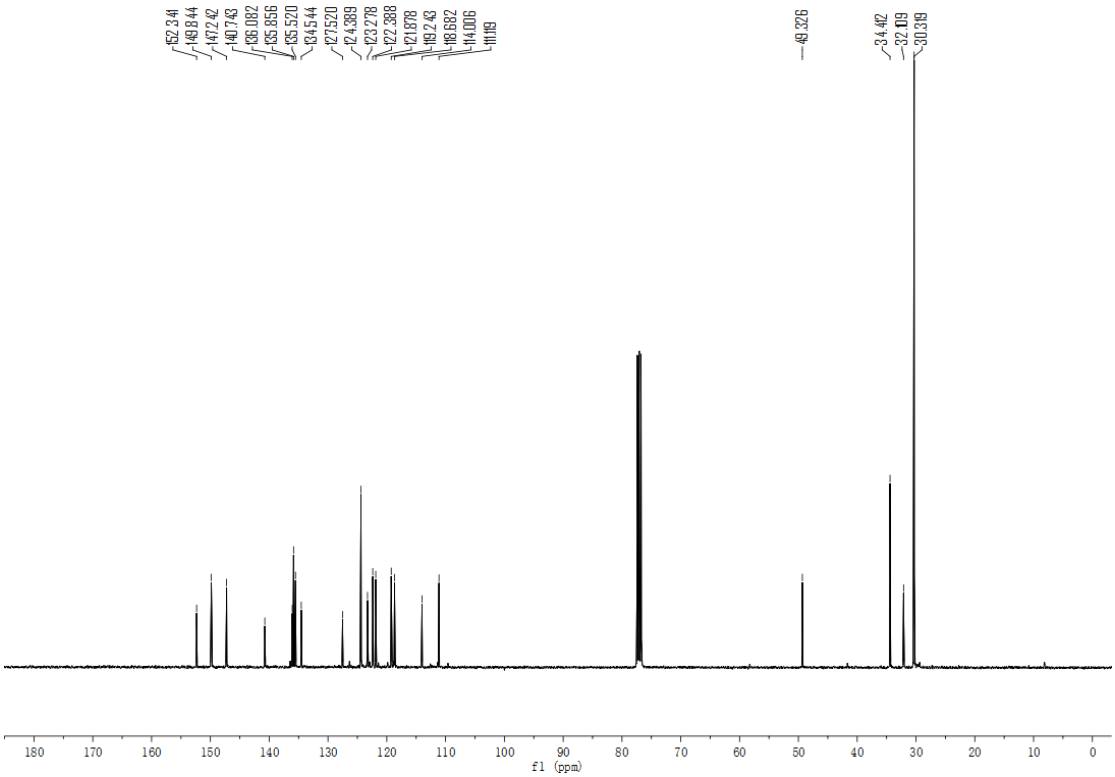


4-(2-(1H-indol-3-yl)-1-(pyridin-3-yl)ethyl)-2,6-di-tert-butylphenol (28)

^{1}H NMR (400 MHz, $CDCl_3$):

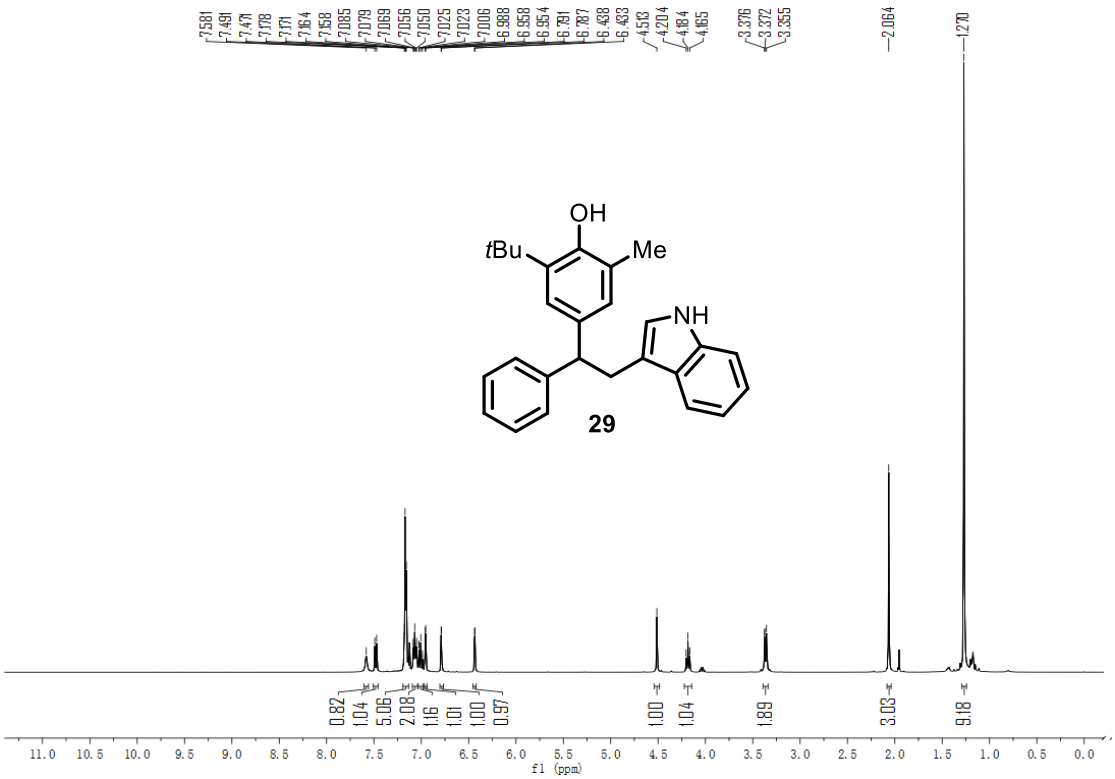


^{13}C NMR (100 MHz, $CDCl_3$):

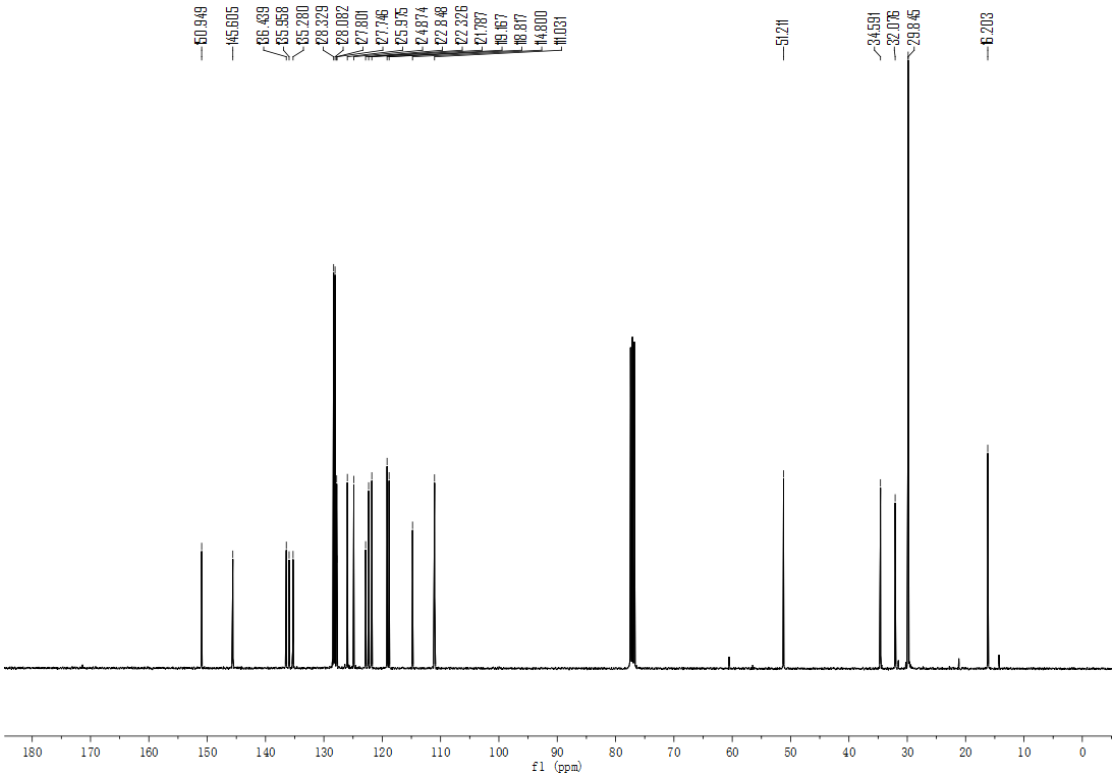


4-(2-(1H-indol-3-yl)-1-phenylethyl)-2-(tert-butyl)-6-methylphenol (29)

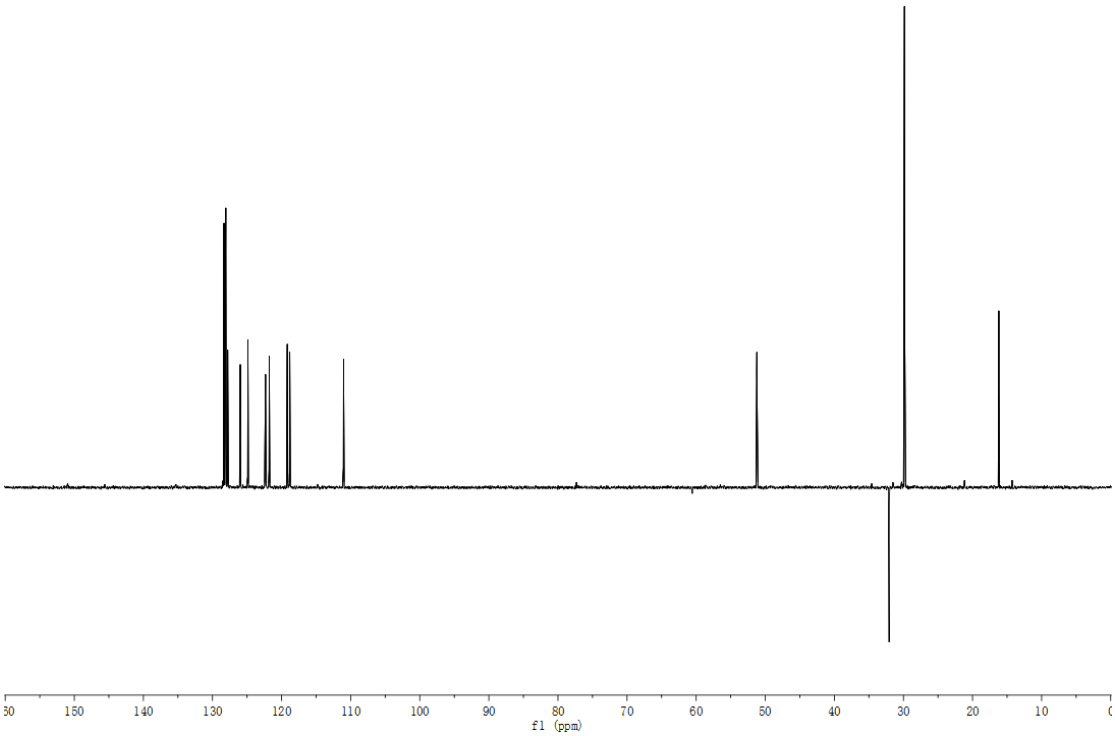
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

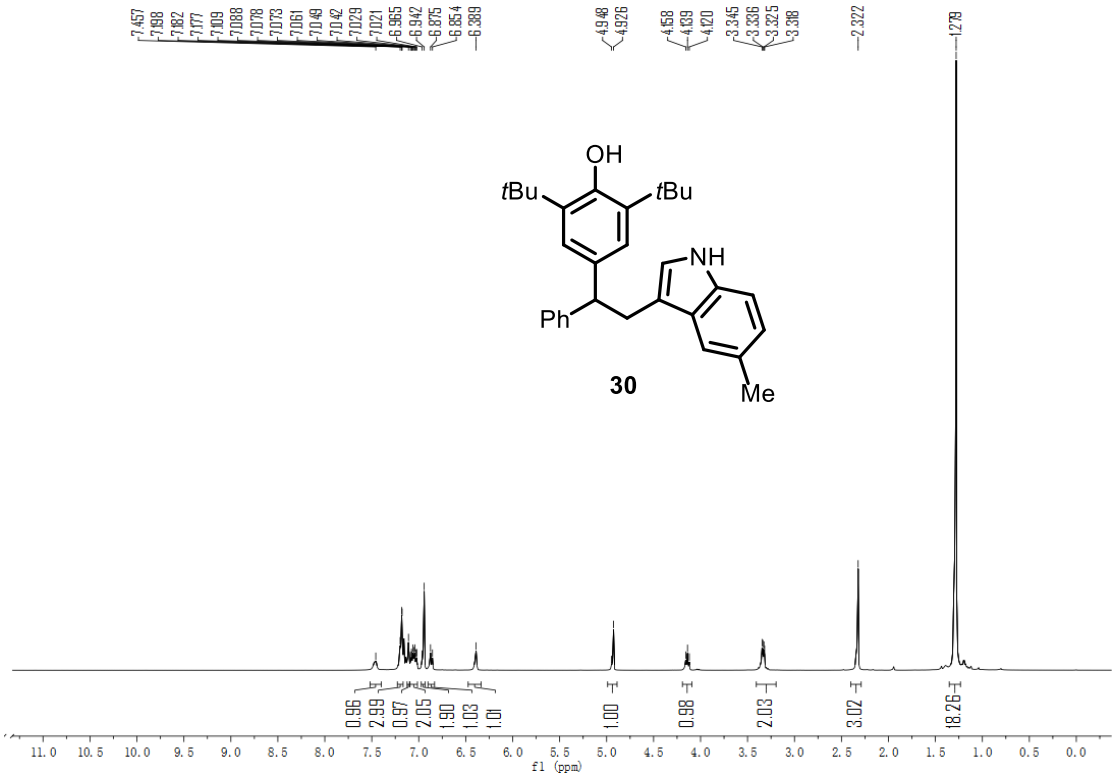


DEPT

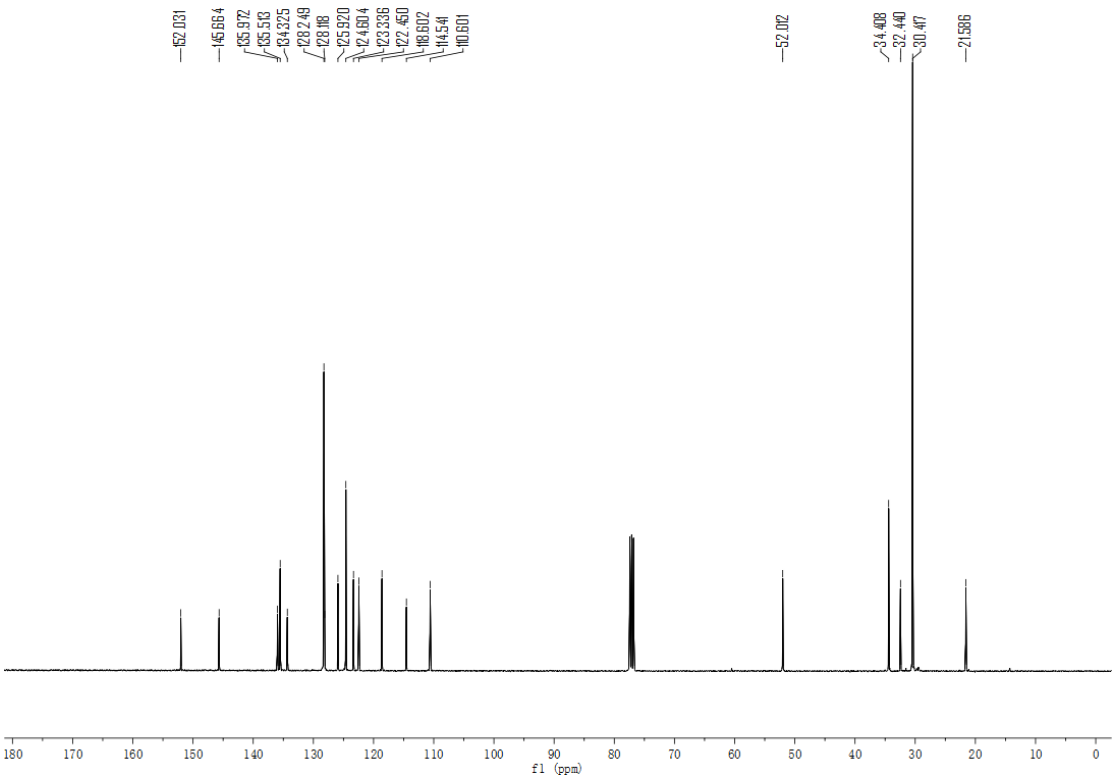


2,6-di-tert-butyl-4-(2-(5-methyl-1H-indol-3-yl)-1-phenylethyl)phenol (30)

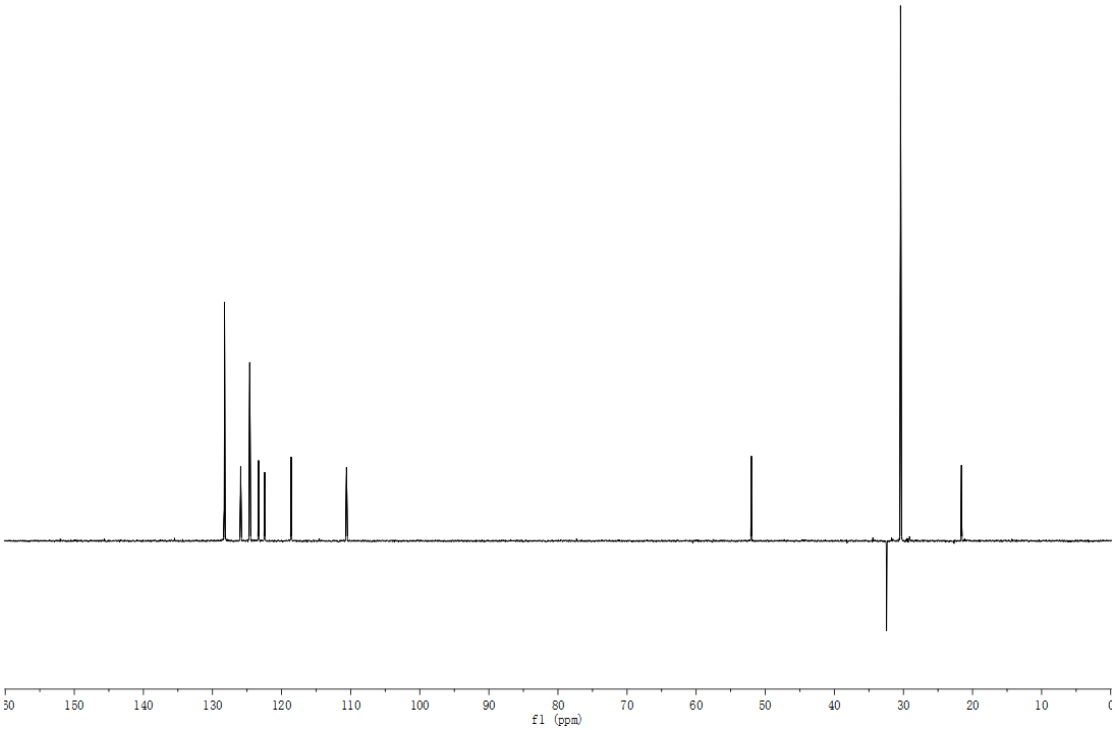
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

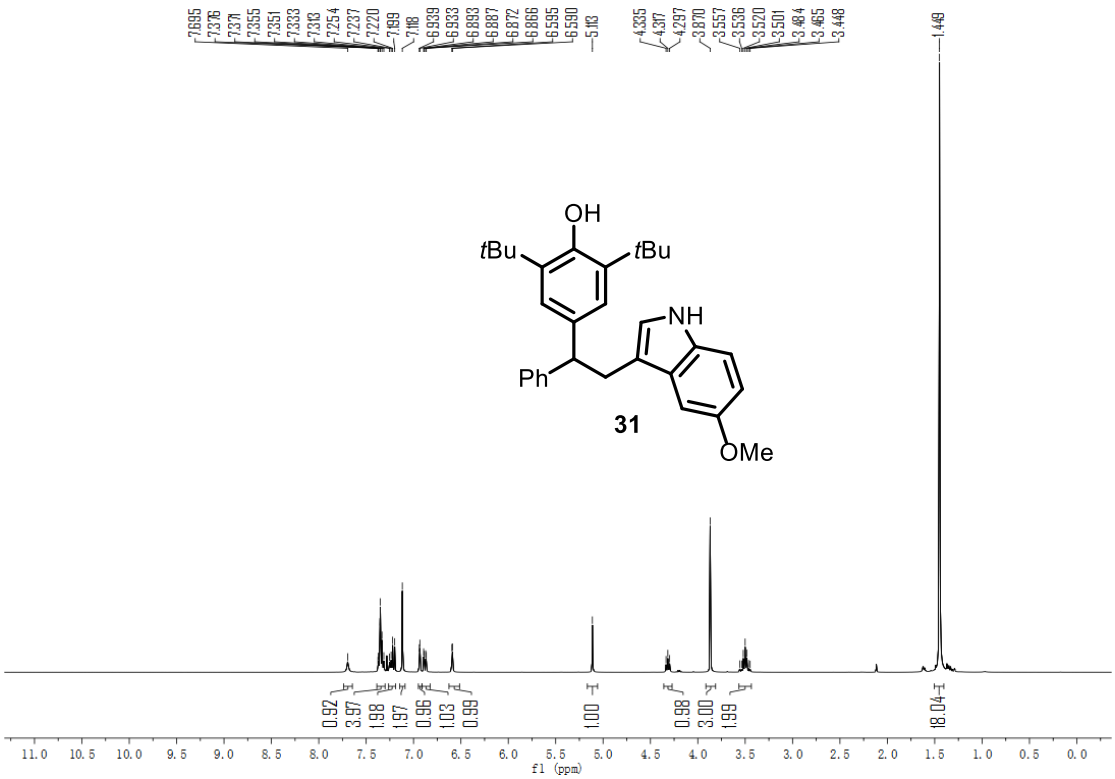


DEPT

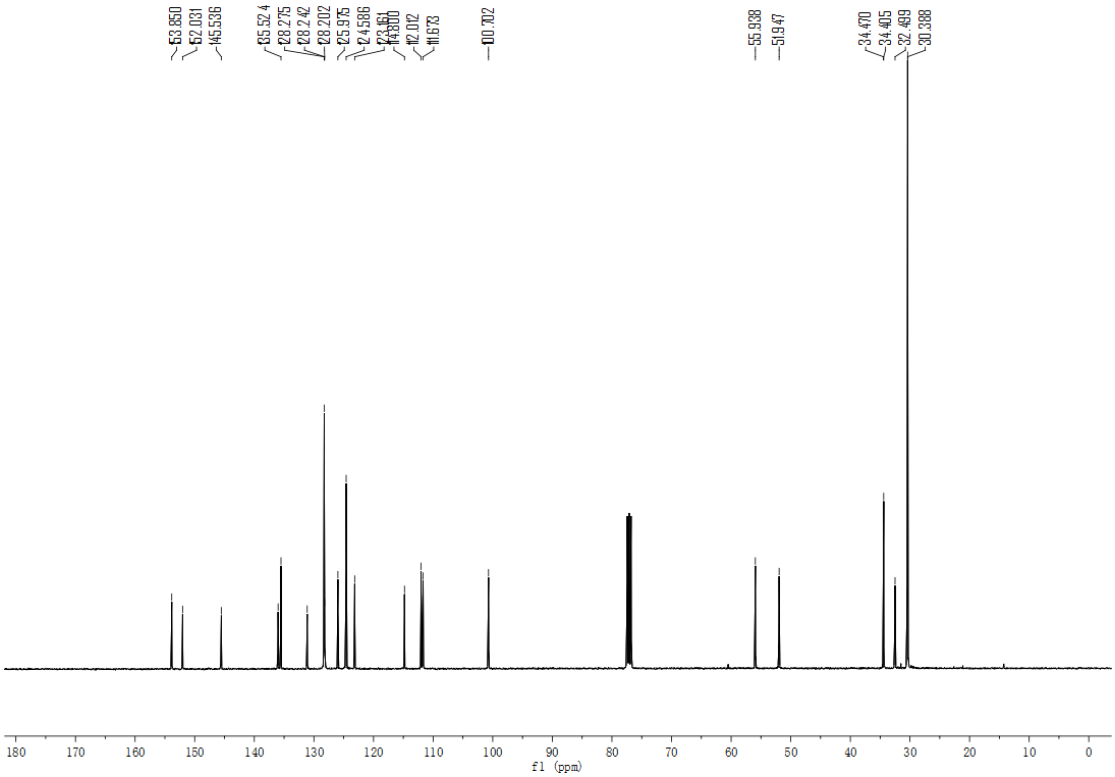


2,6-di-tert-butyl-4-(2-(5-methoxy-1H-indol-3-yl)-1-phenylethyl)phenol (31)

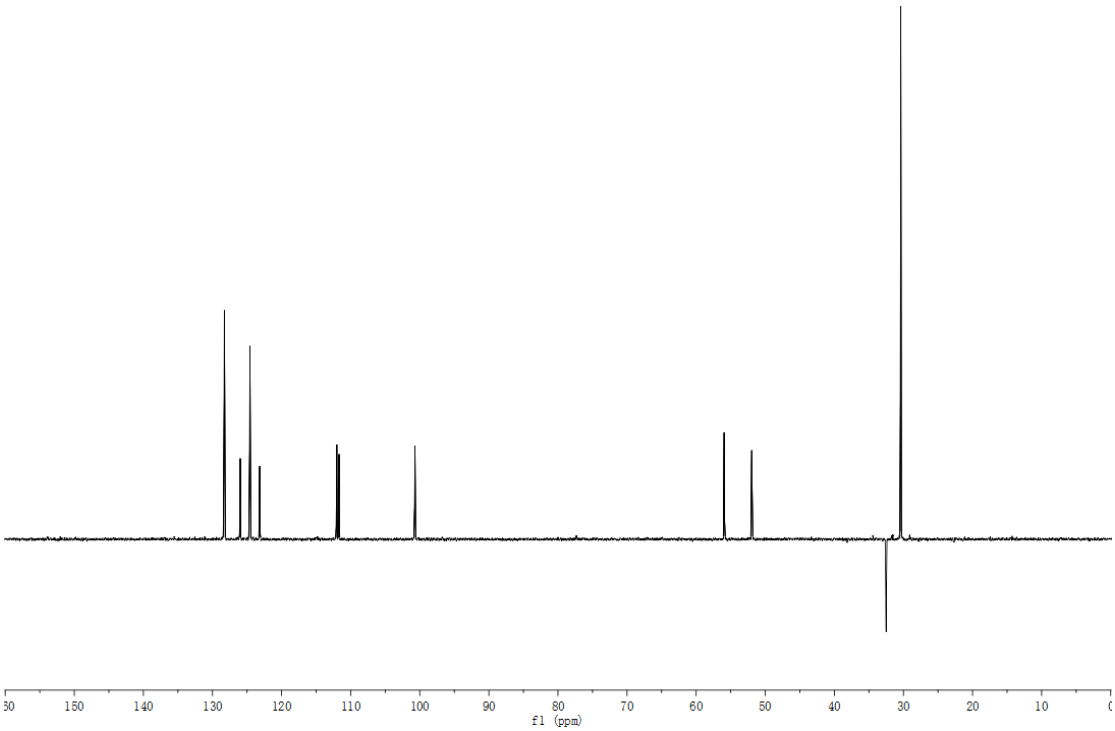
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

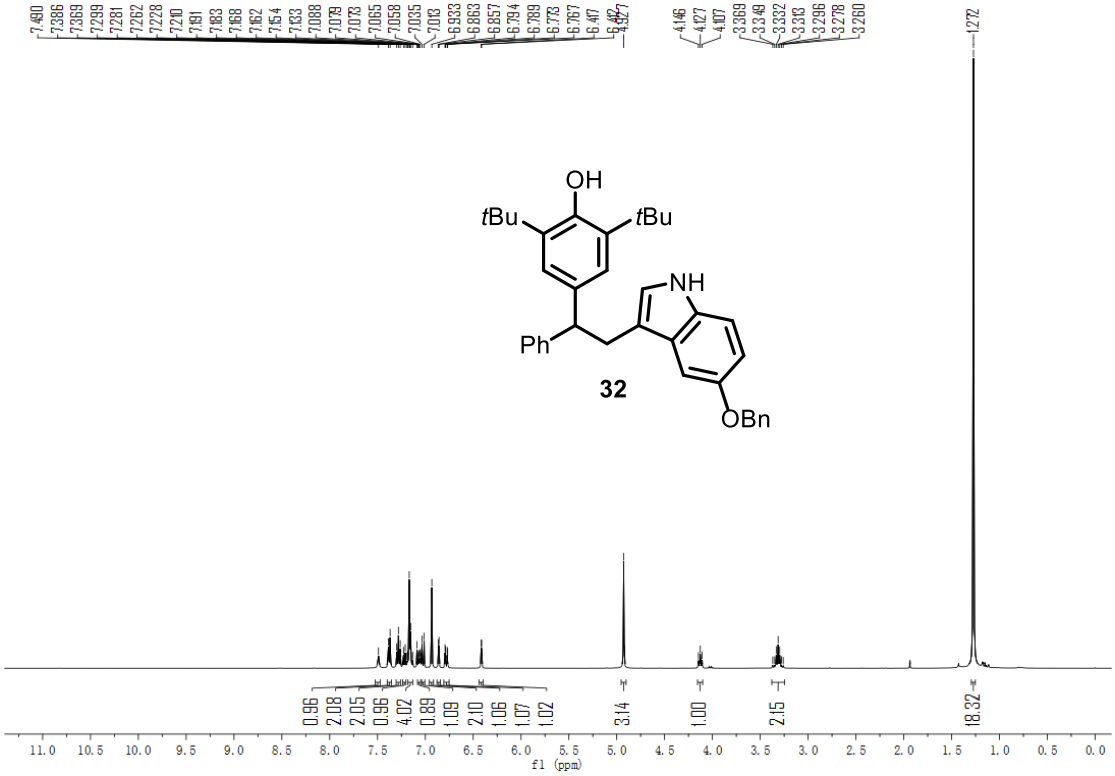


DEPT

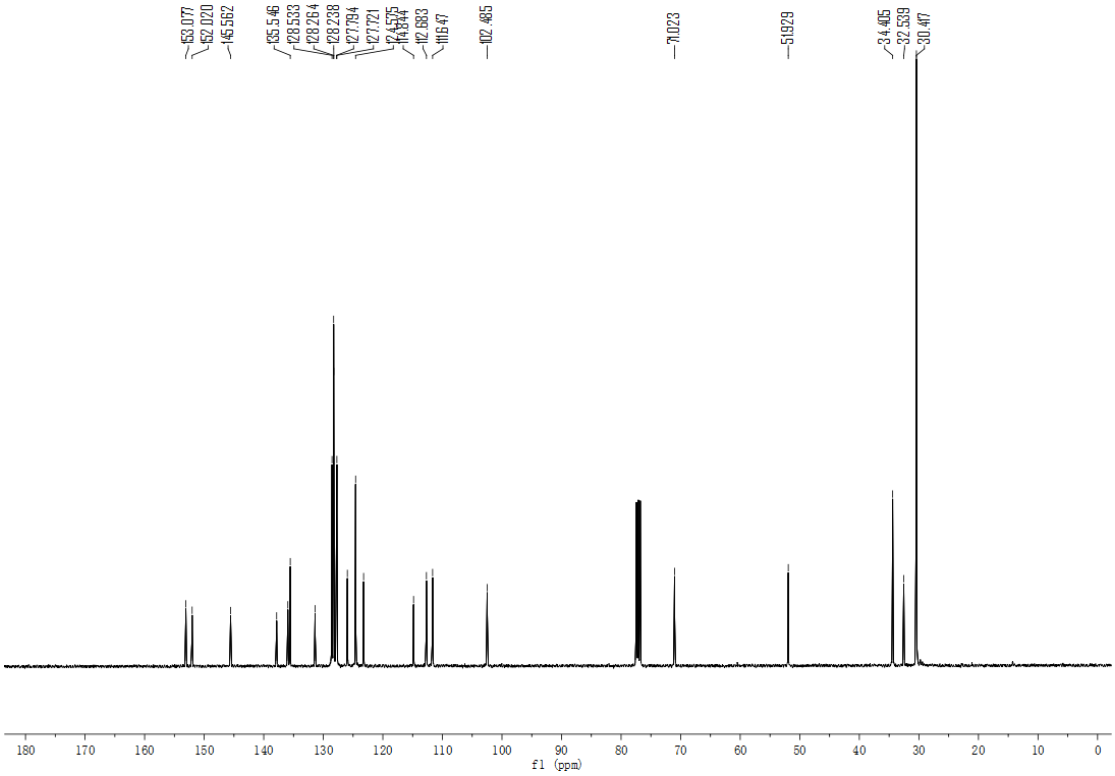


4-(2-(5-(benzyloxy)-1H-indol-3-yl)-1-phenylethyl)-2,6-di-tert-butylphenol (32)

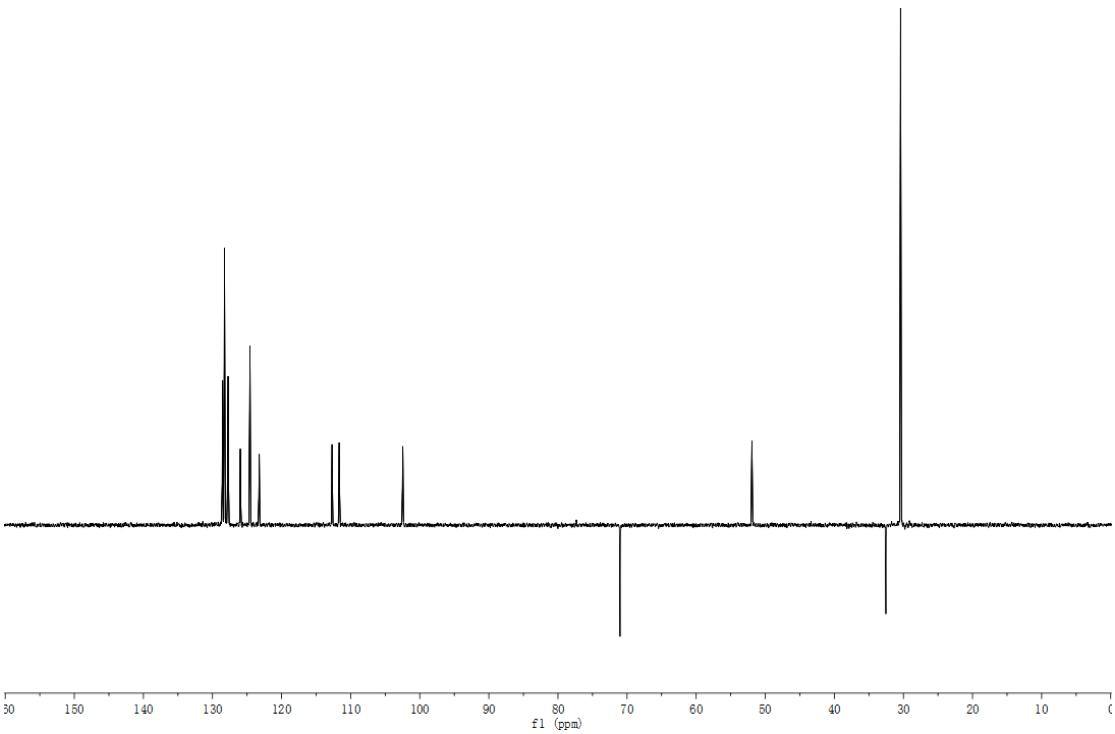
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

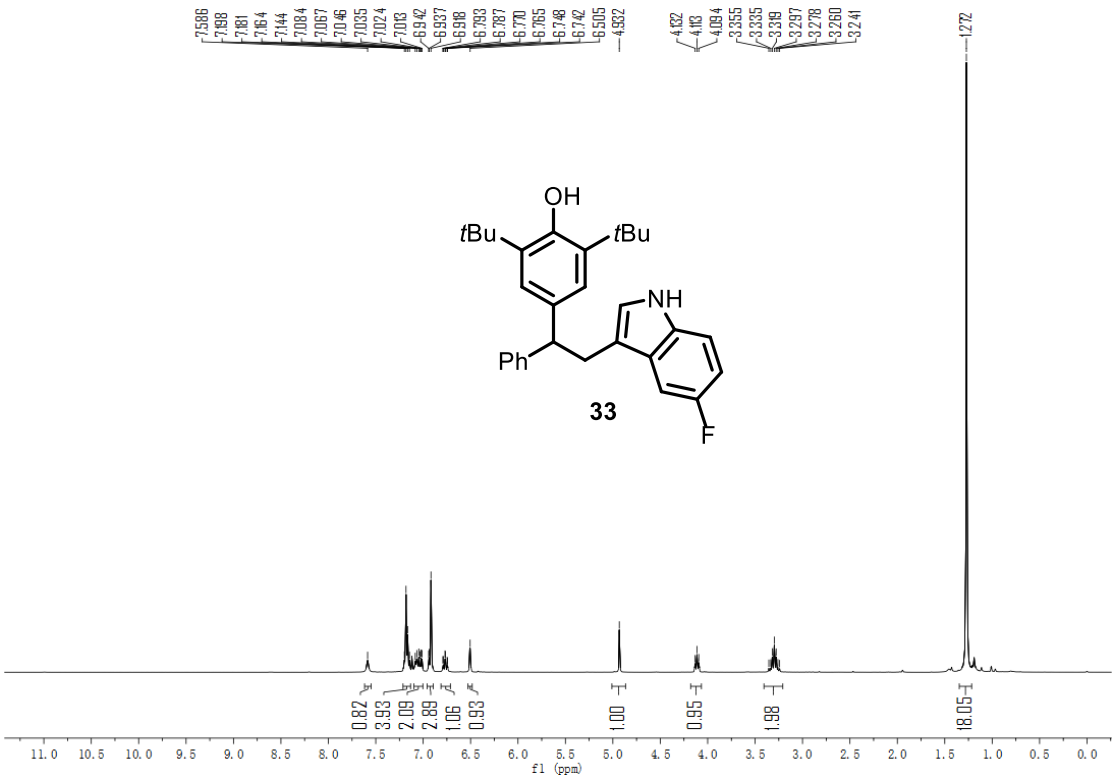


DEPT

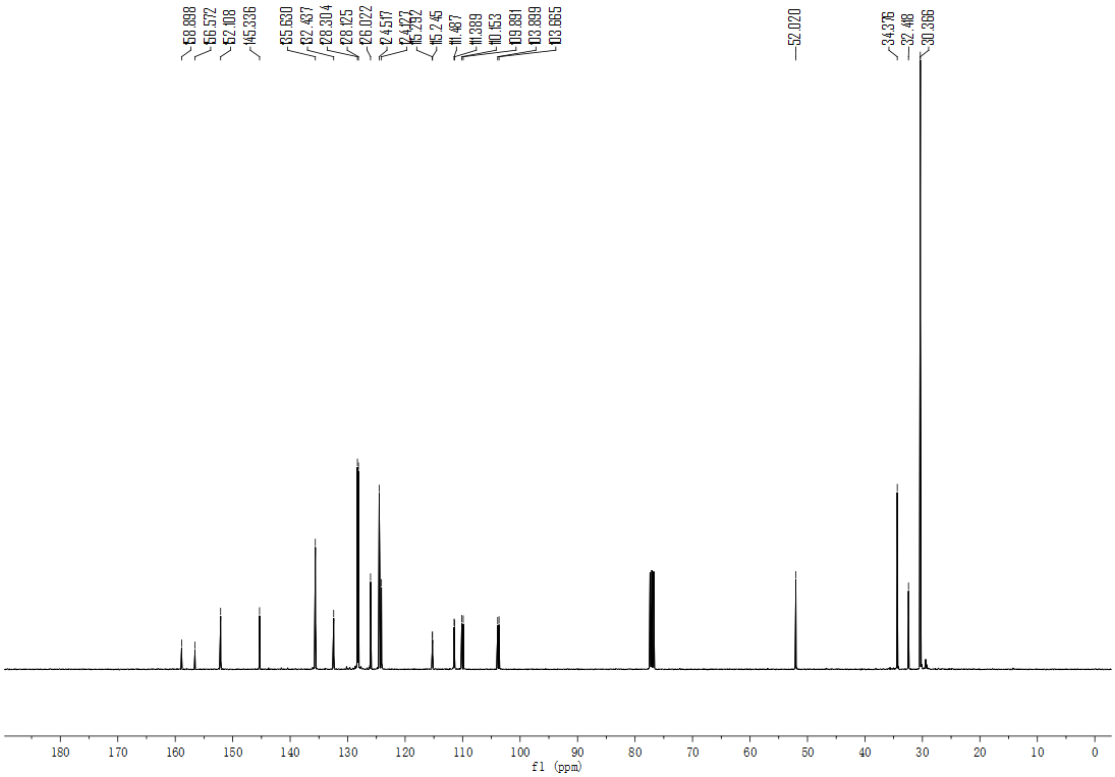


2,6-di-tert-butyl-4-(2-(5-fluoro-1H-indol-3-yl)-1-phenylethyl)phenol (33)

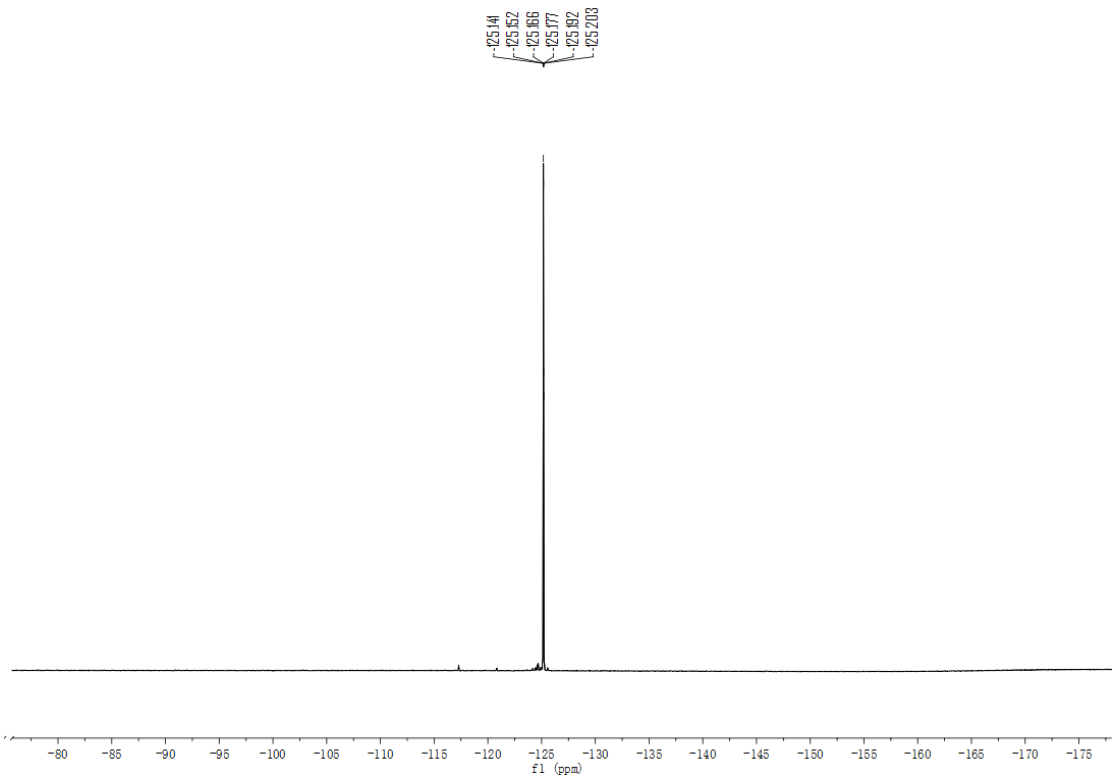
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):



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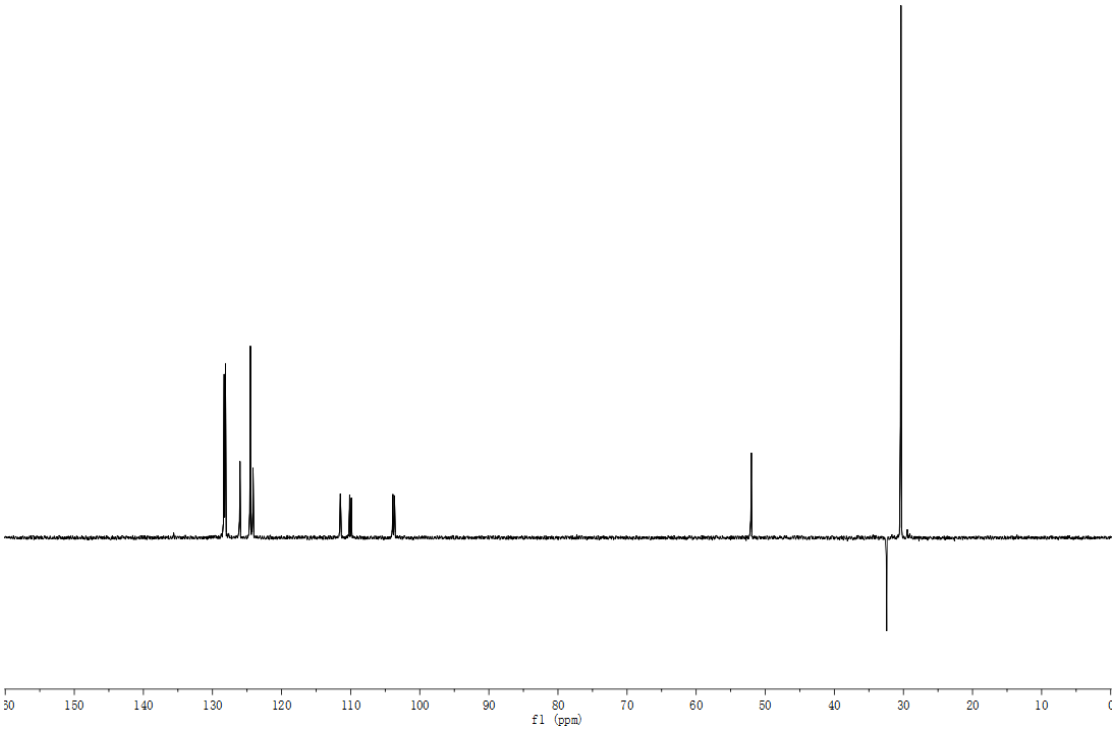
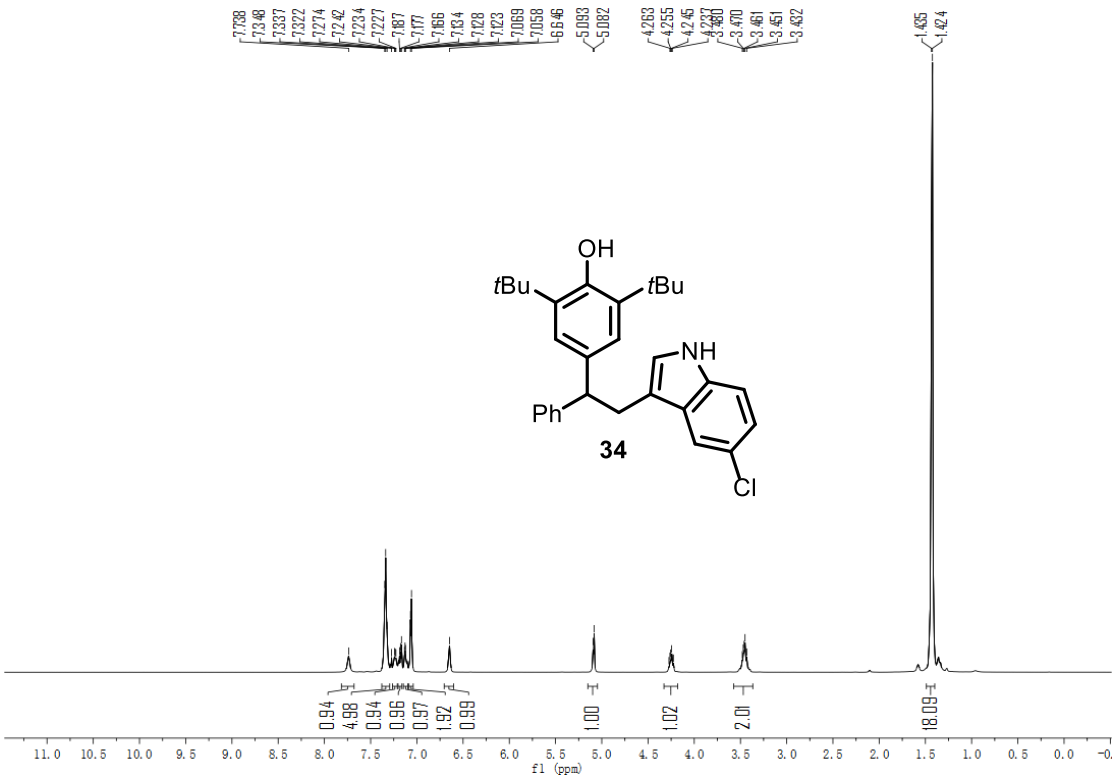
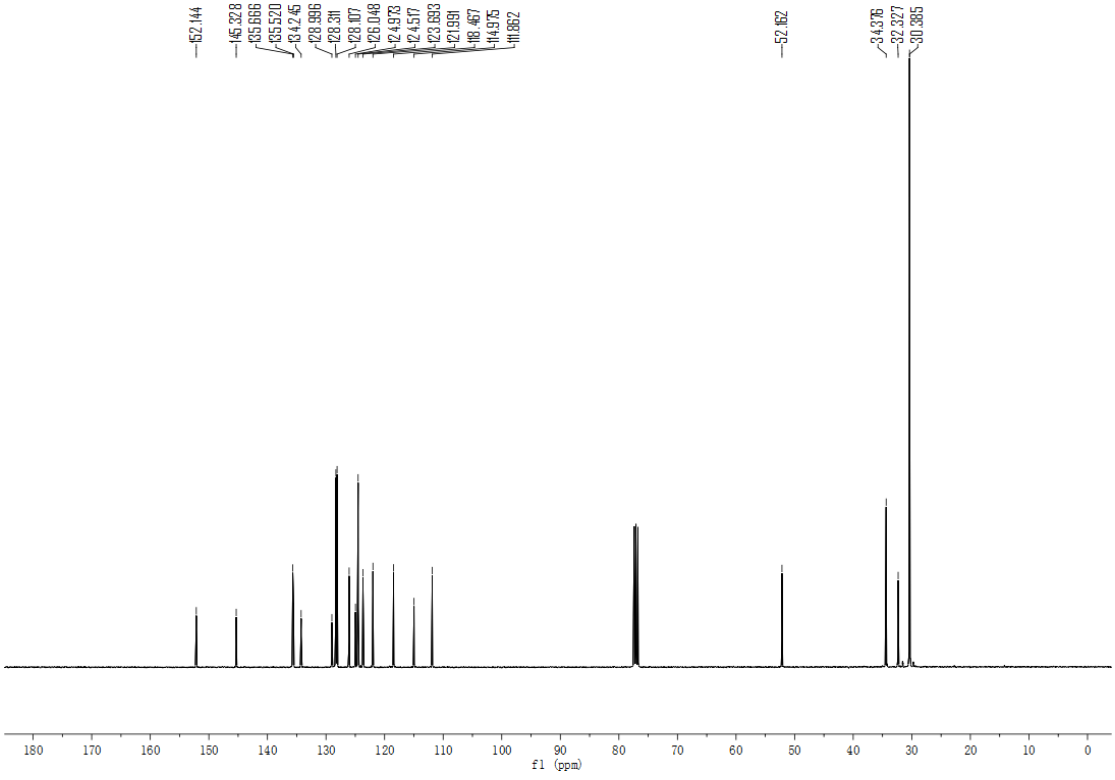


2,6-di-tert-butyl-4-(2-(5-chloro-1H-indol-3-yl)-1-phenylethyl)phenol (34)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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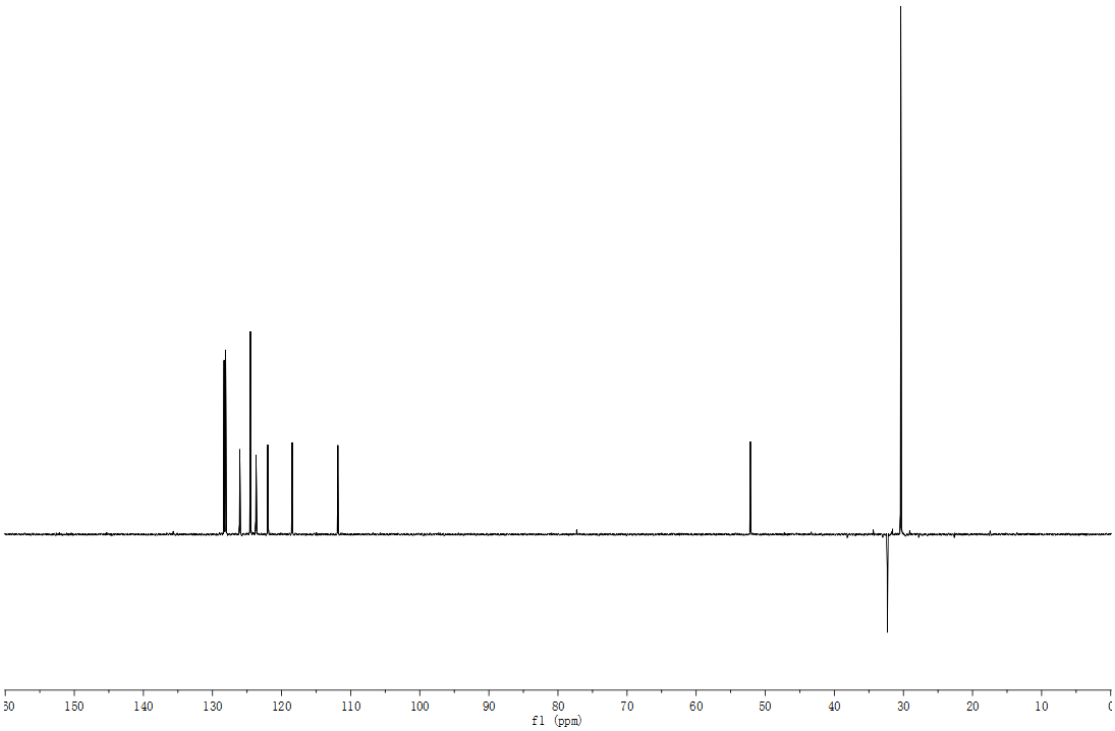
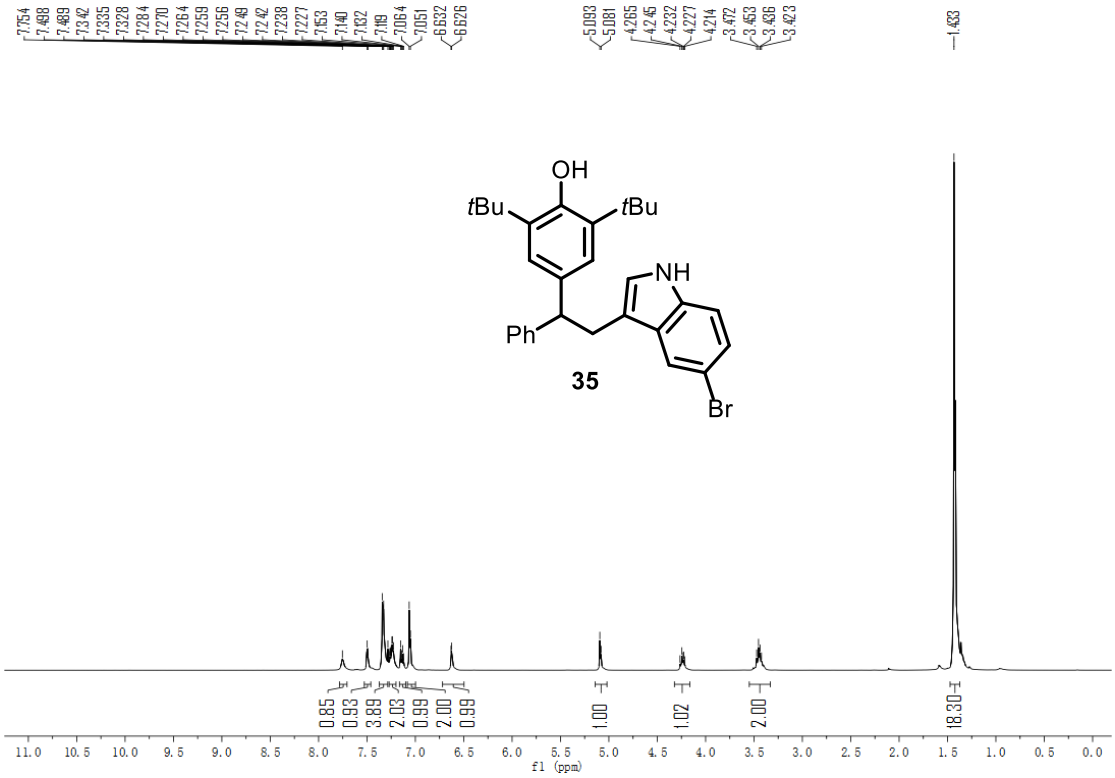
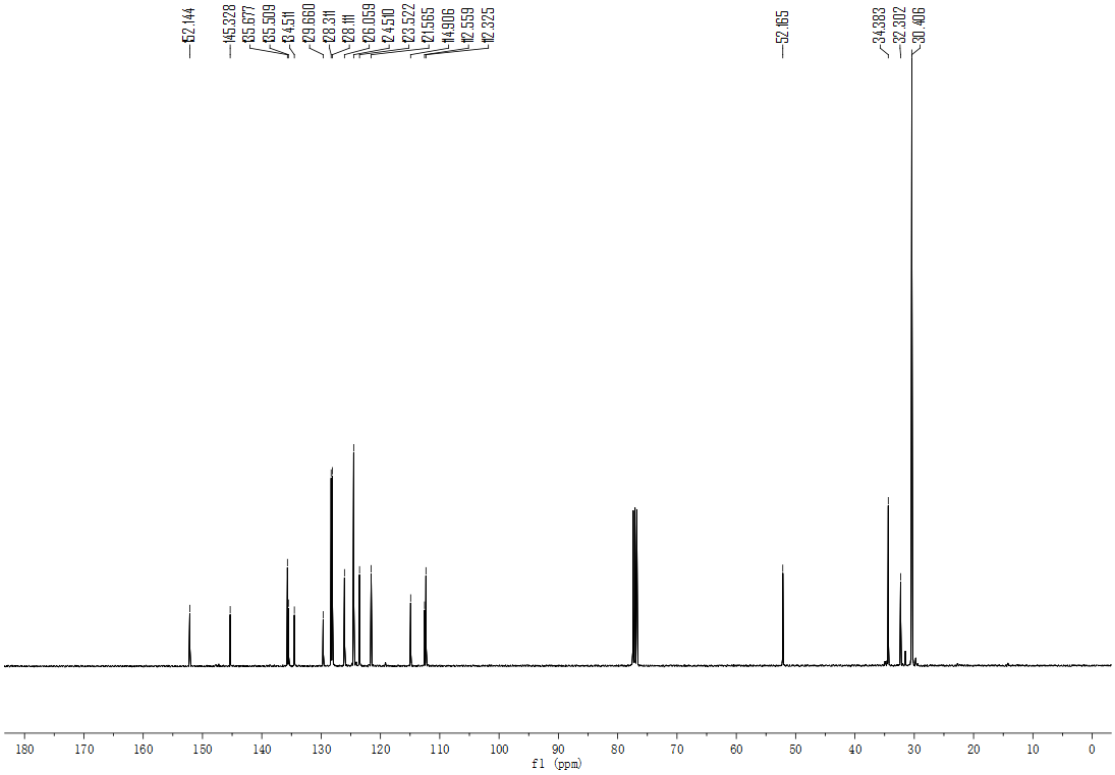


4-(2-(5-bromo-1H-indol-3-yl)-1-phenylethyl)-2,6-di-tert-butylphenol (35)

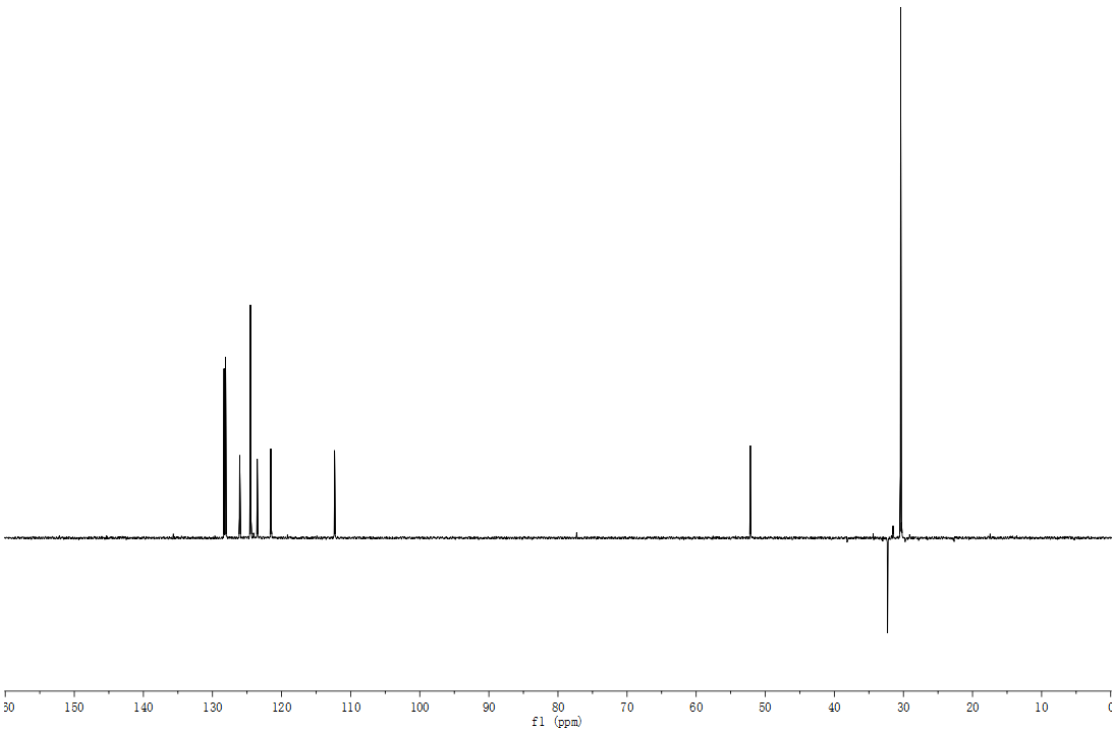
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

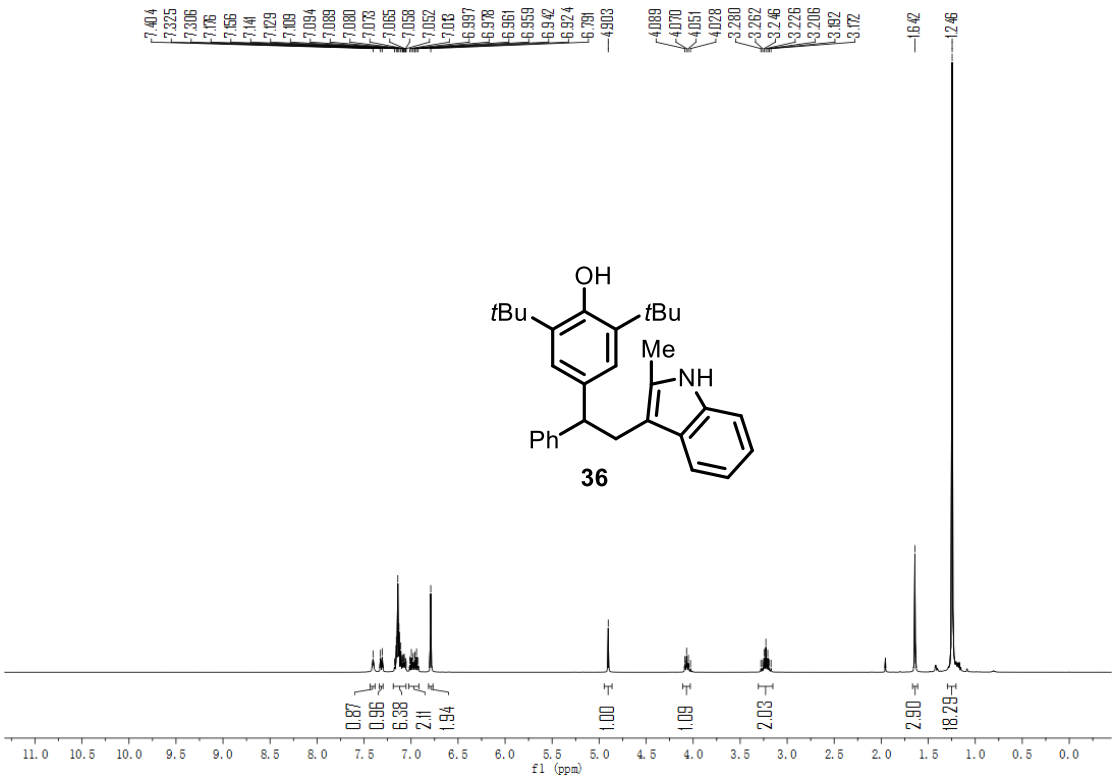


DEPT

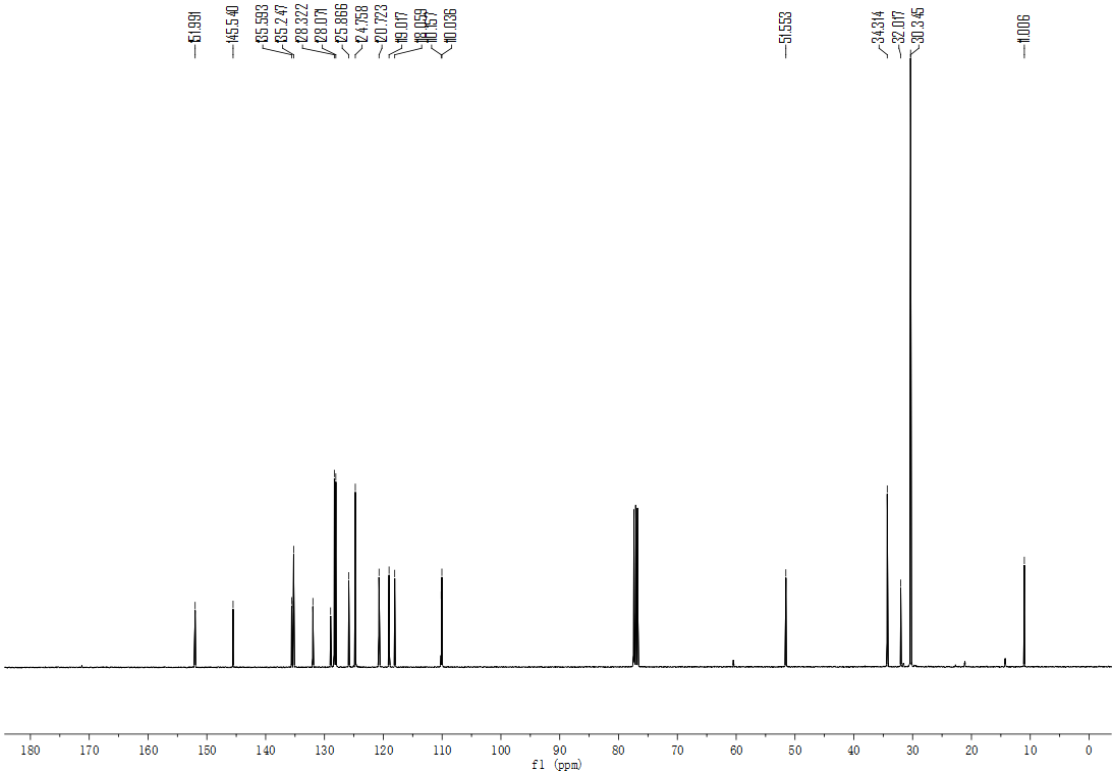


2,6-di-tert-butyl-4-(2-(2-methyl-1H-indol-3-yl)-1-phenylethyl)phenol (36)

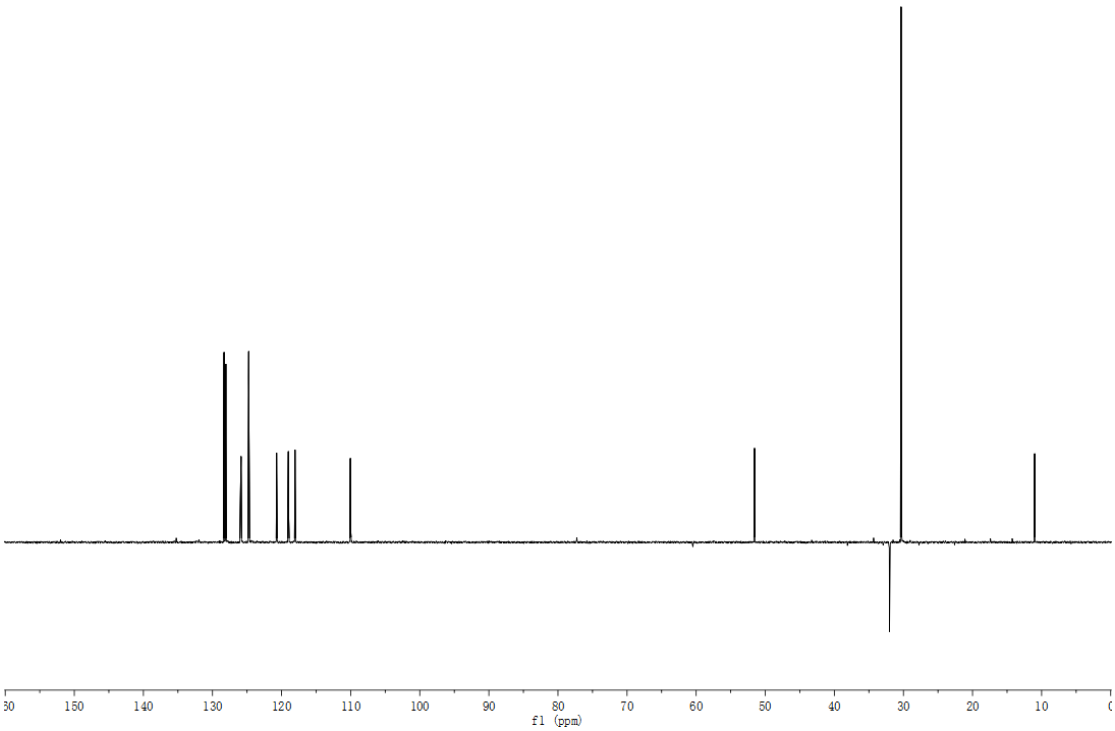
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

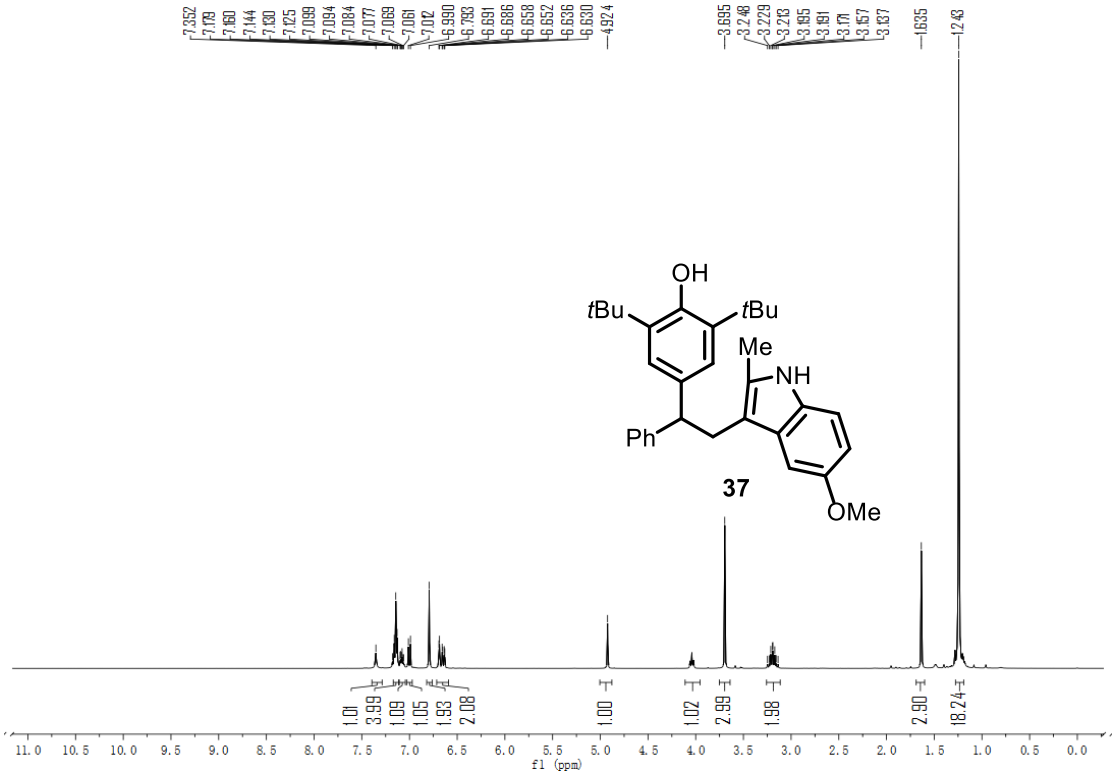


DEPT

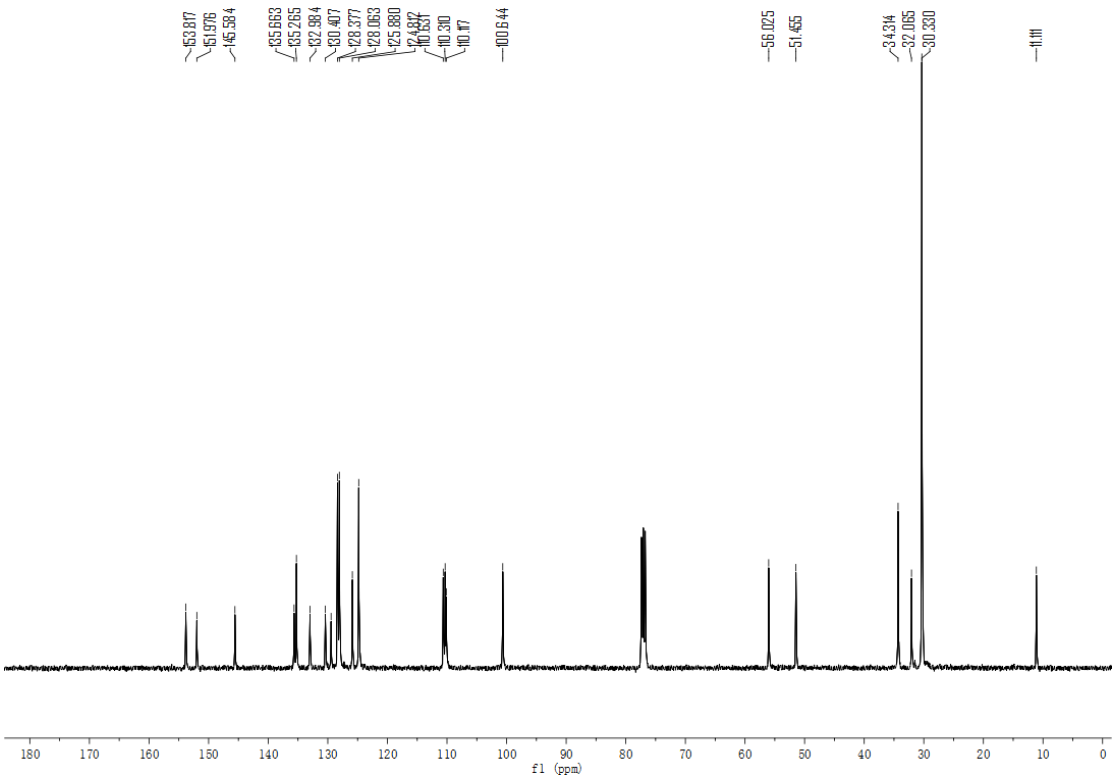


2,6-di-tert-butyl-4-(2-(5-methoxy-2-methyl-1H-indol-3-yl)-1-phenylethyl)phenol (37)

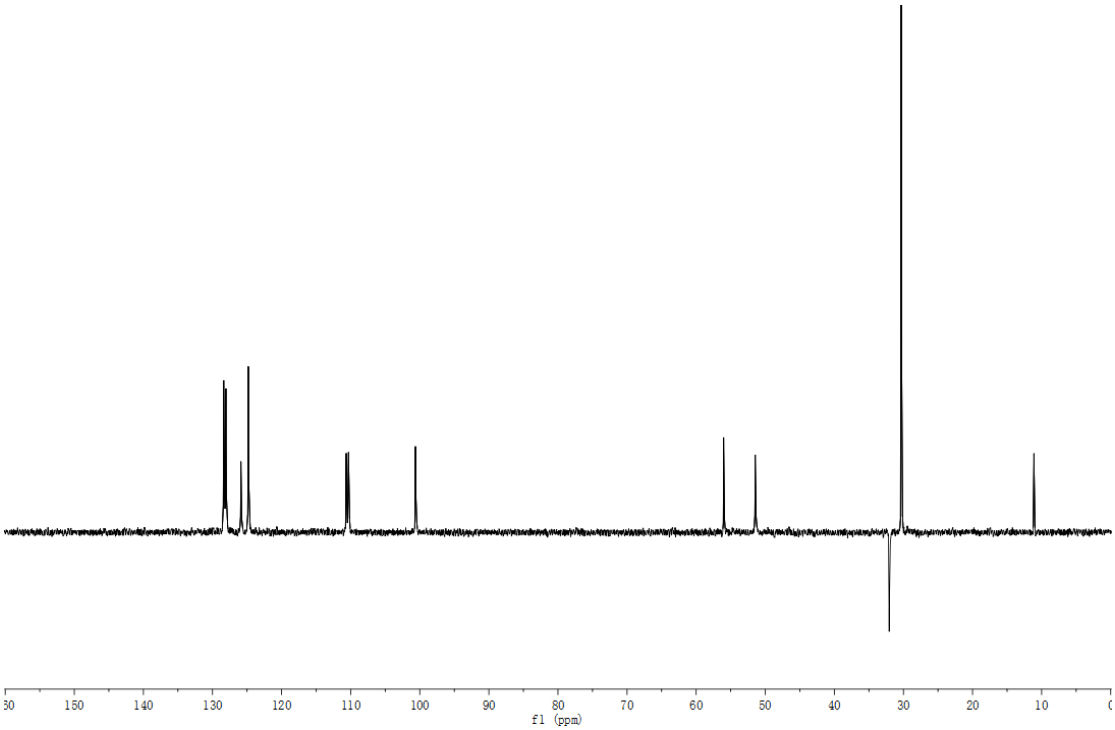
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

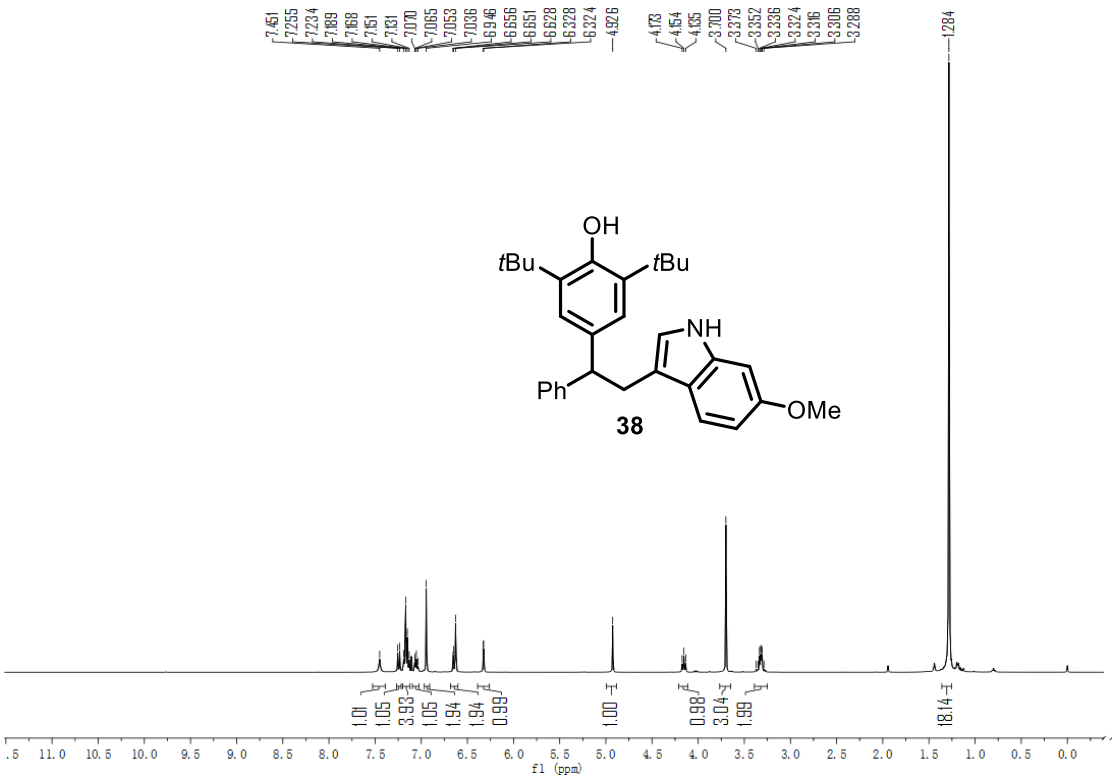


DEPT

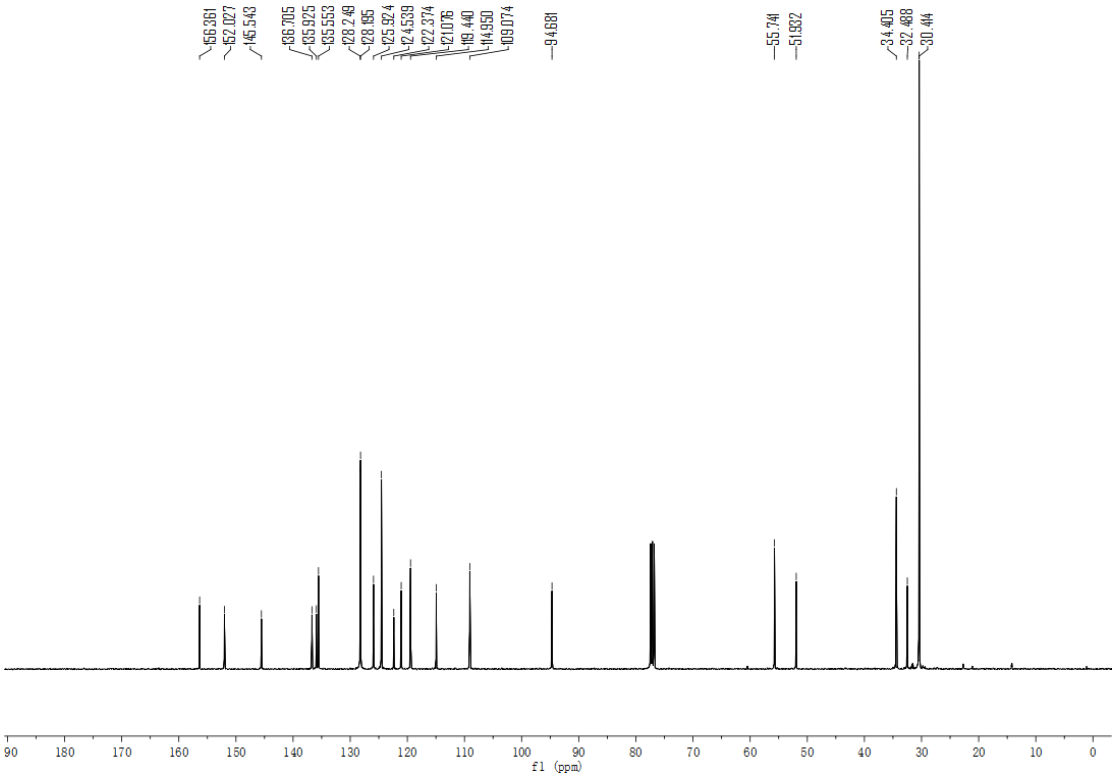


2,6-di-tert-butyl-4-(2-(6-methoxy-1H-indol-3-yl)-1-phenylethyl)phenol (38)

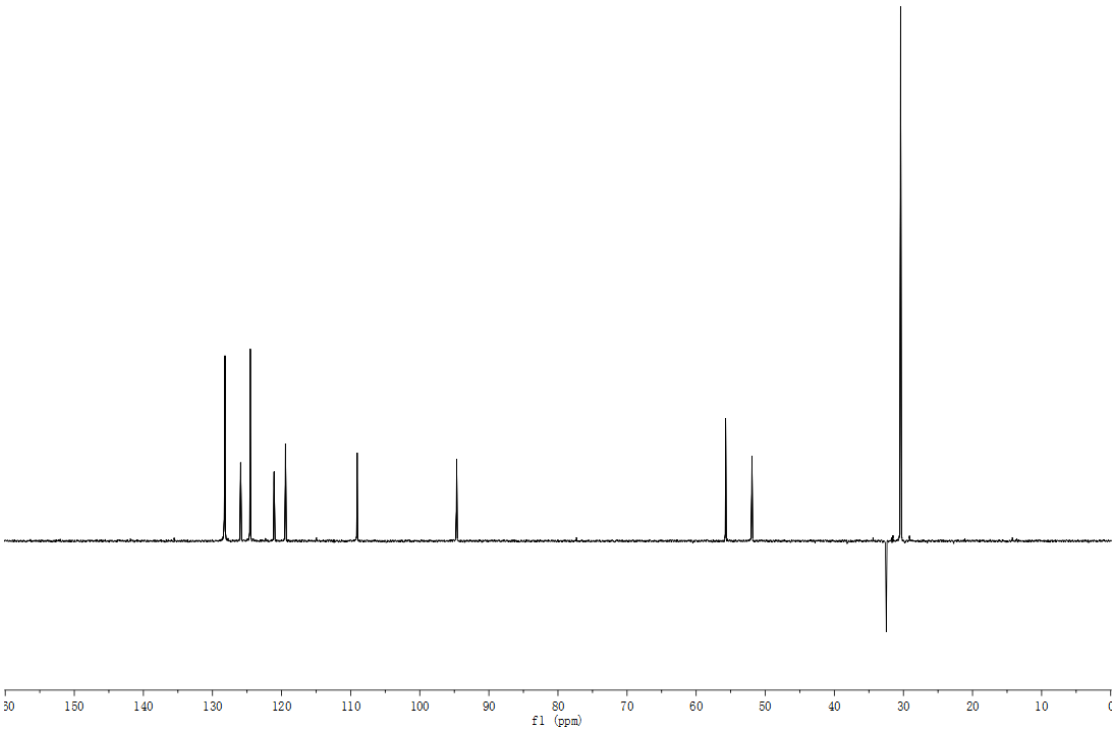
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

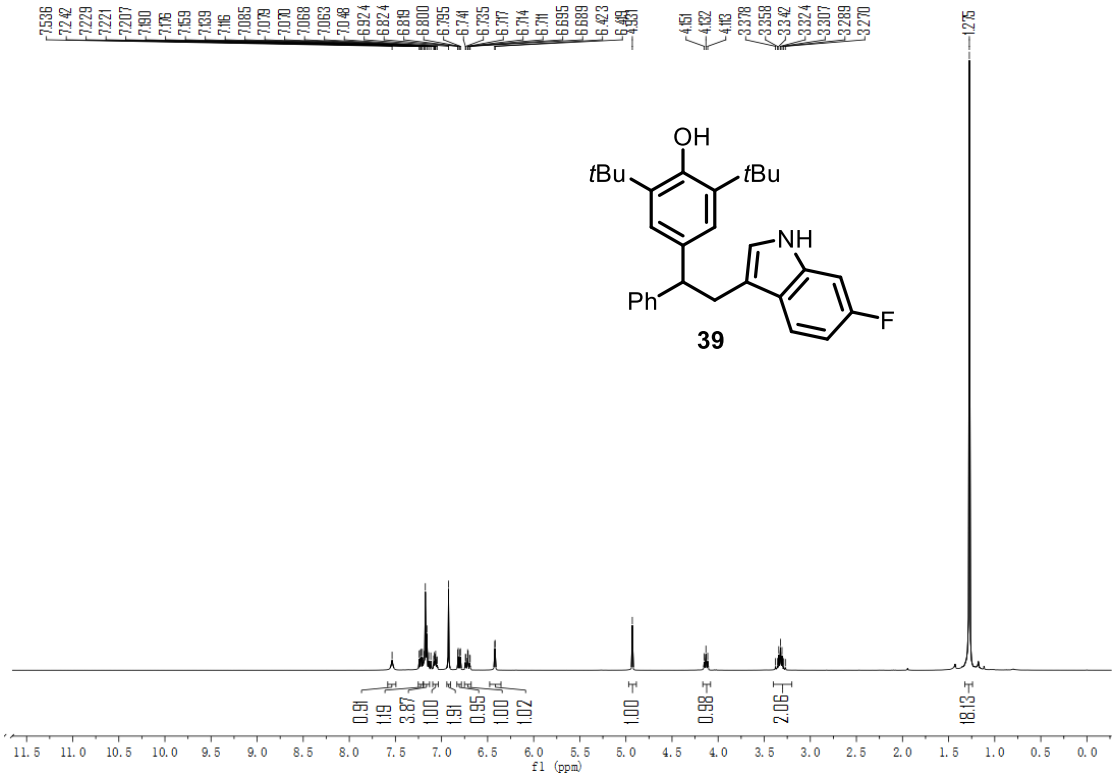


DEPT

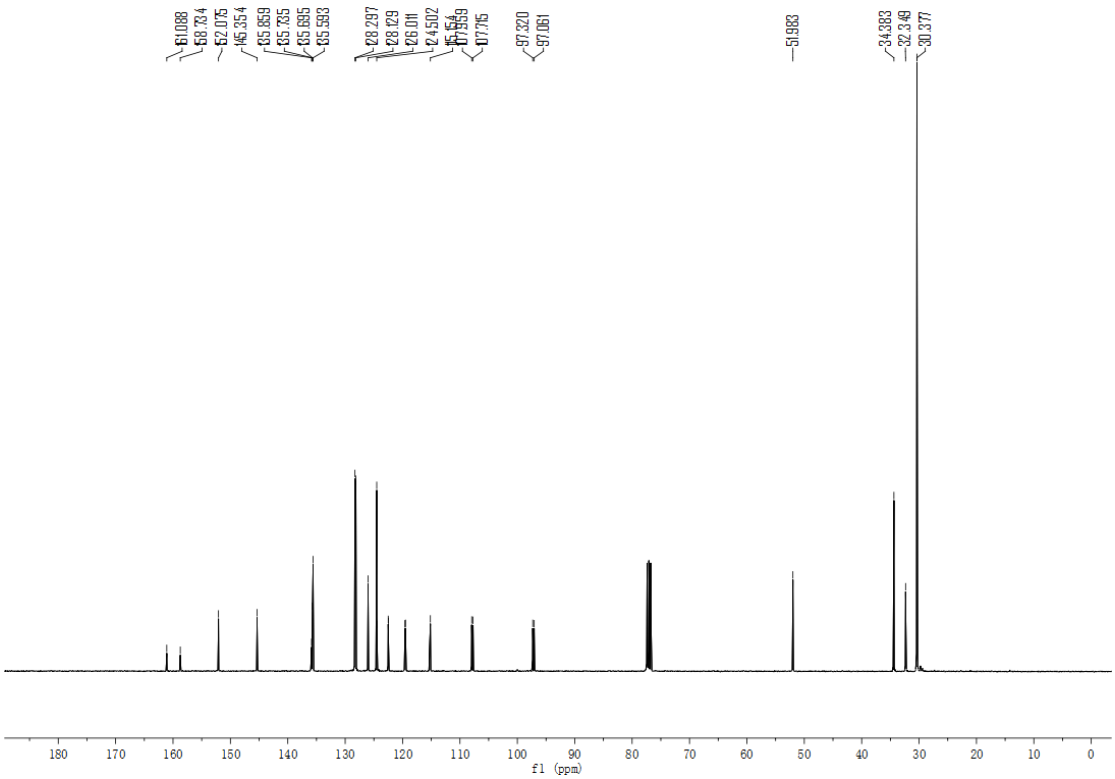


2,6-di-tert-butyl-4-(2-(6-fluoro-1H-indol-3-yl)-1-phenylethyl)phenol (39)

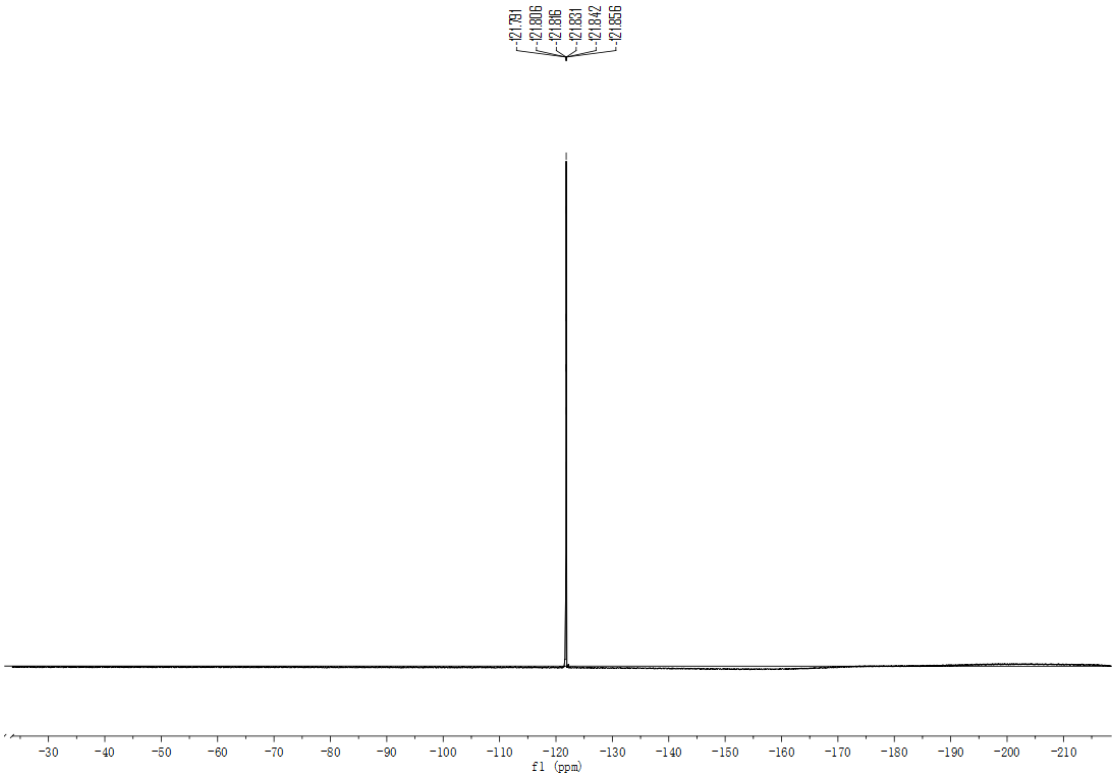
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$):



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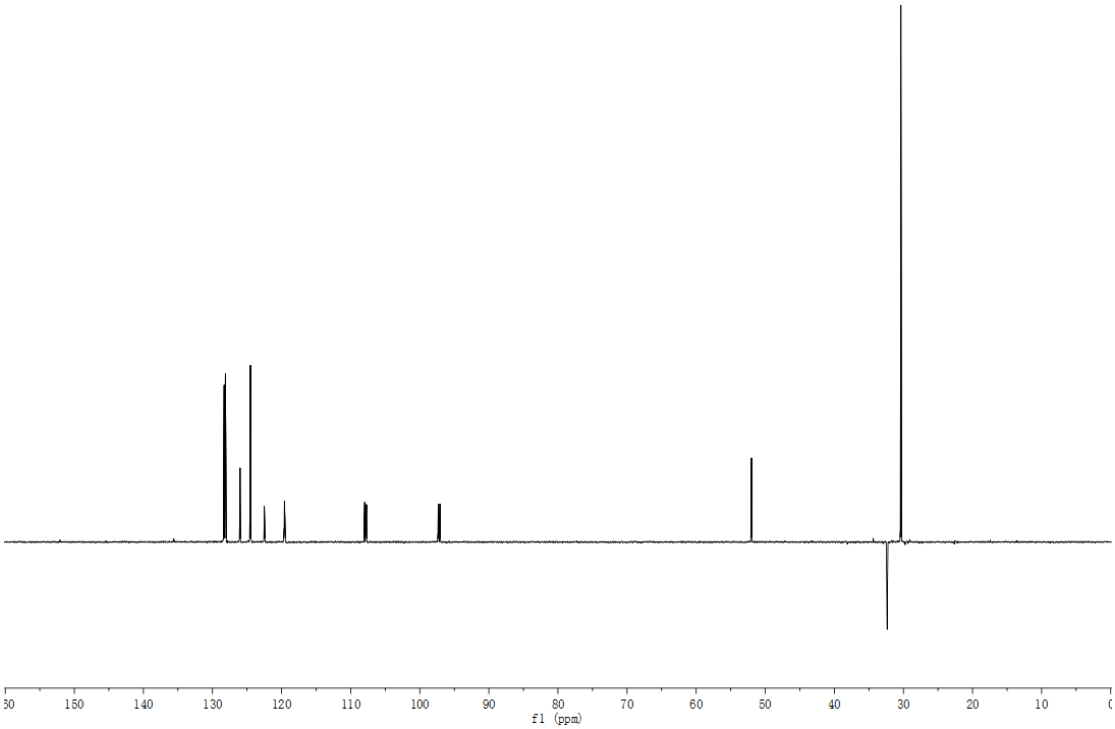
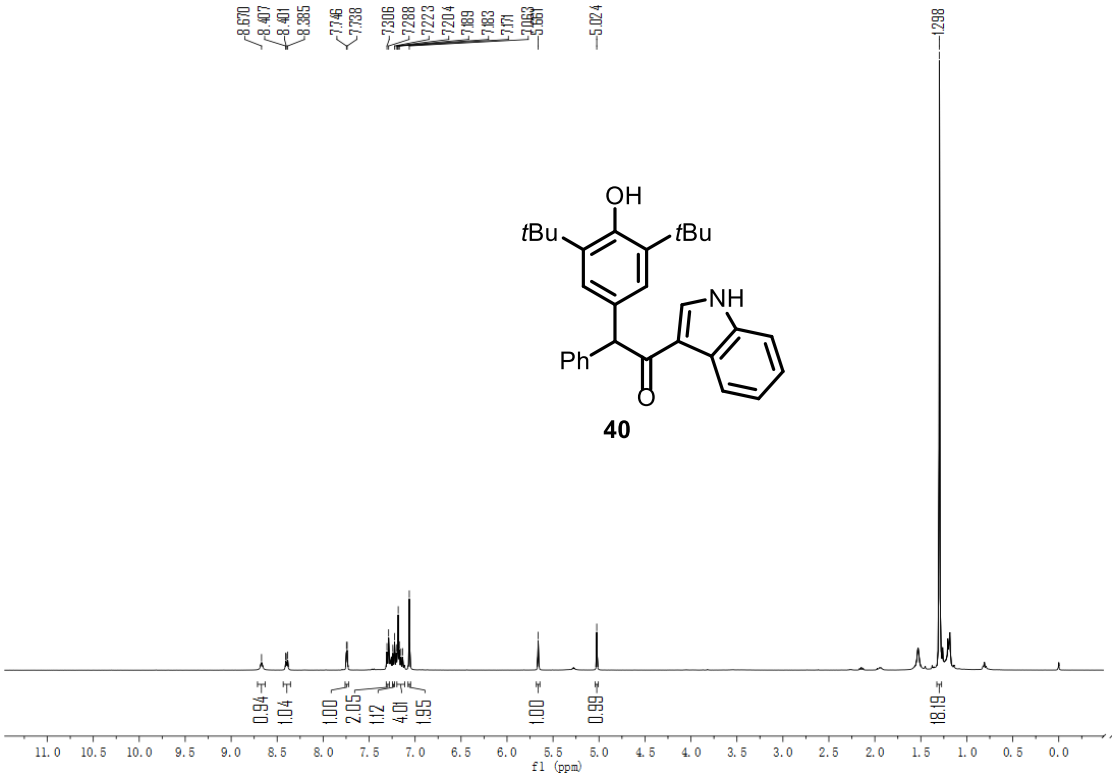
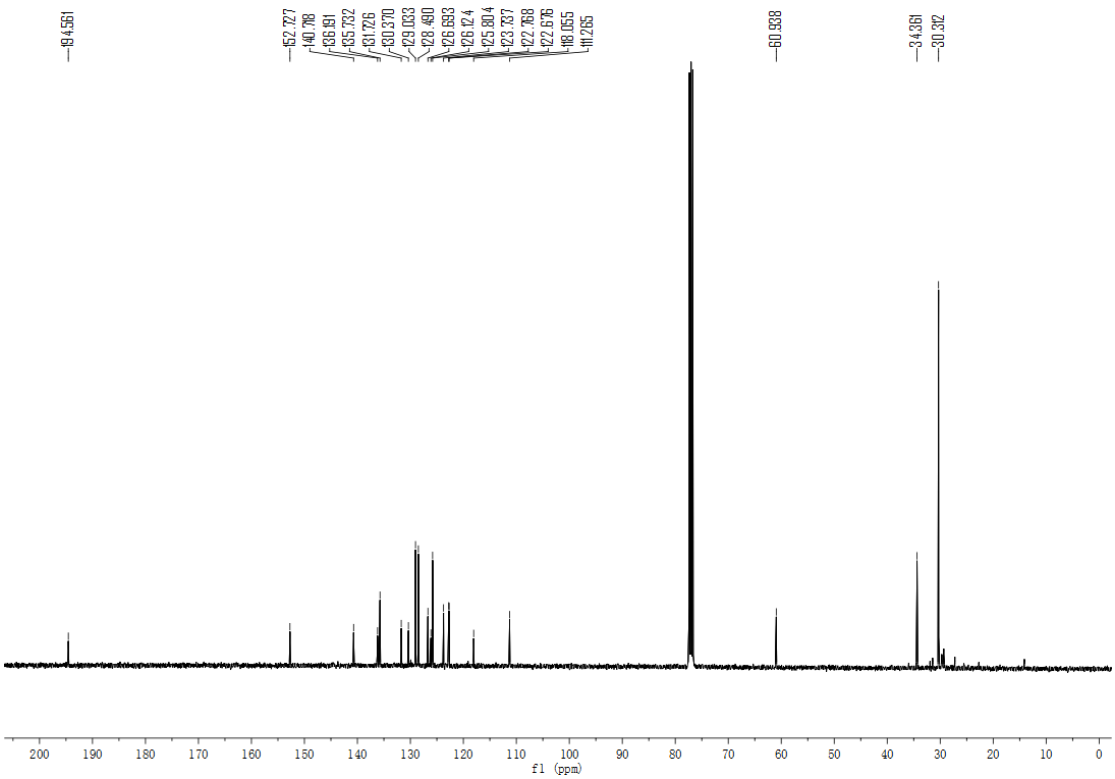


2-(3,5-di-tert-butyl-4-hydroxyphenyl)-1-(1H-indol-3-yl)-2-phenylethan-1-one (40)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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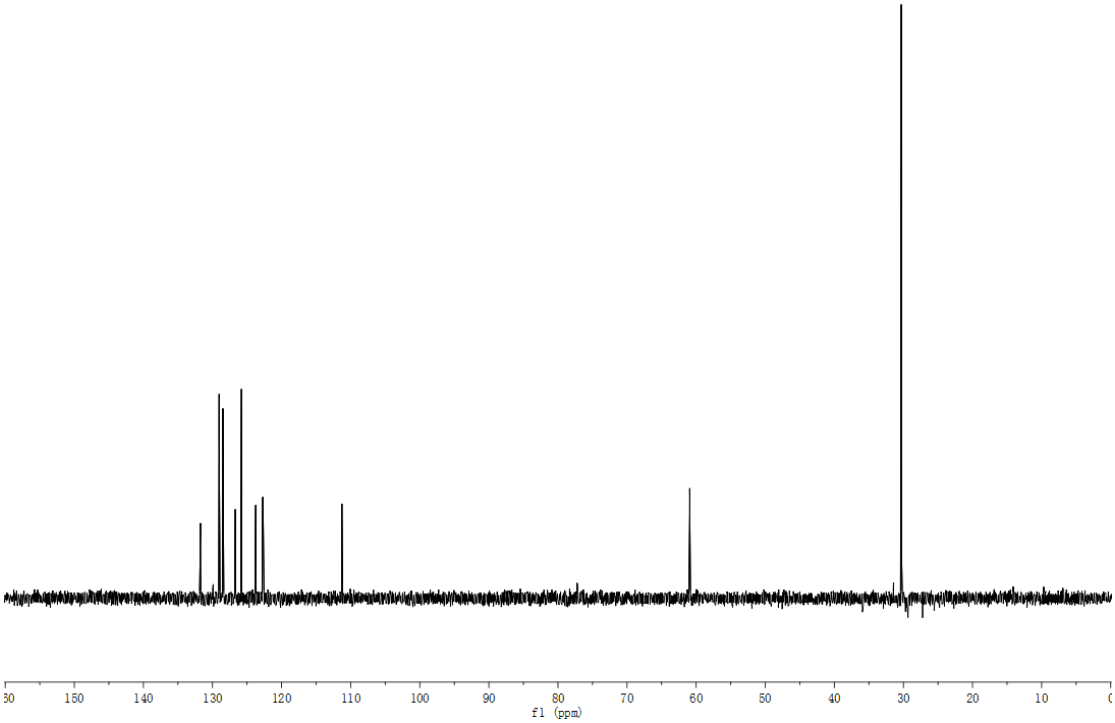
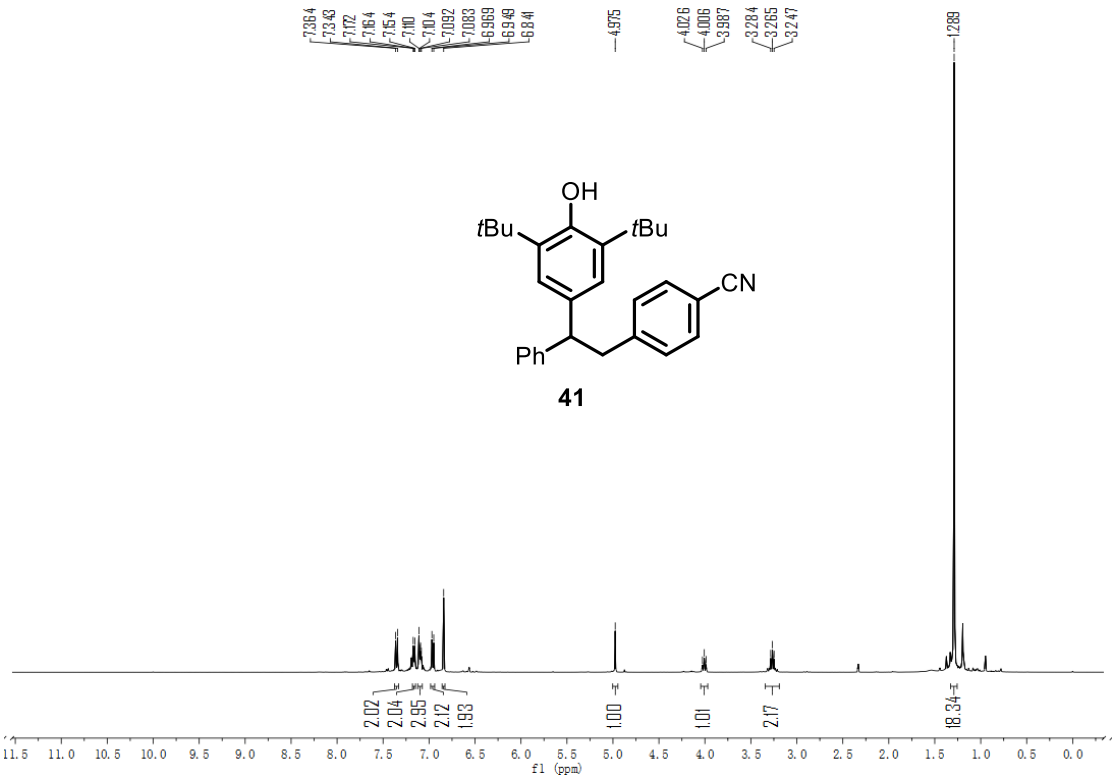
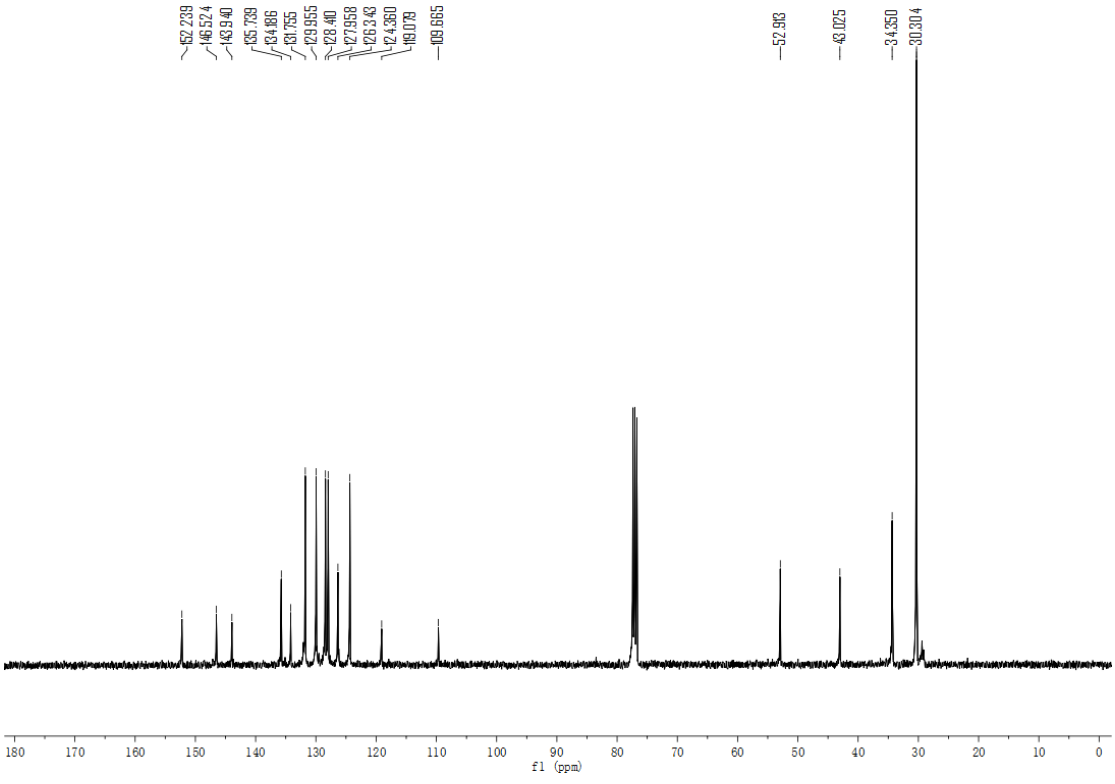


4-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylethyl)benzonitrile (41)

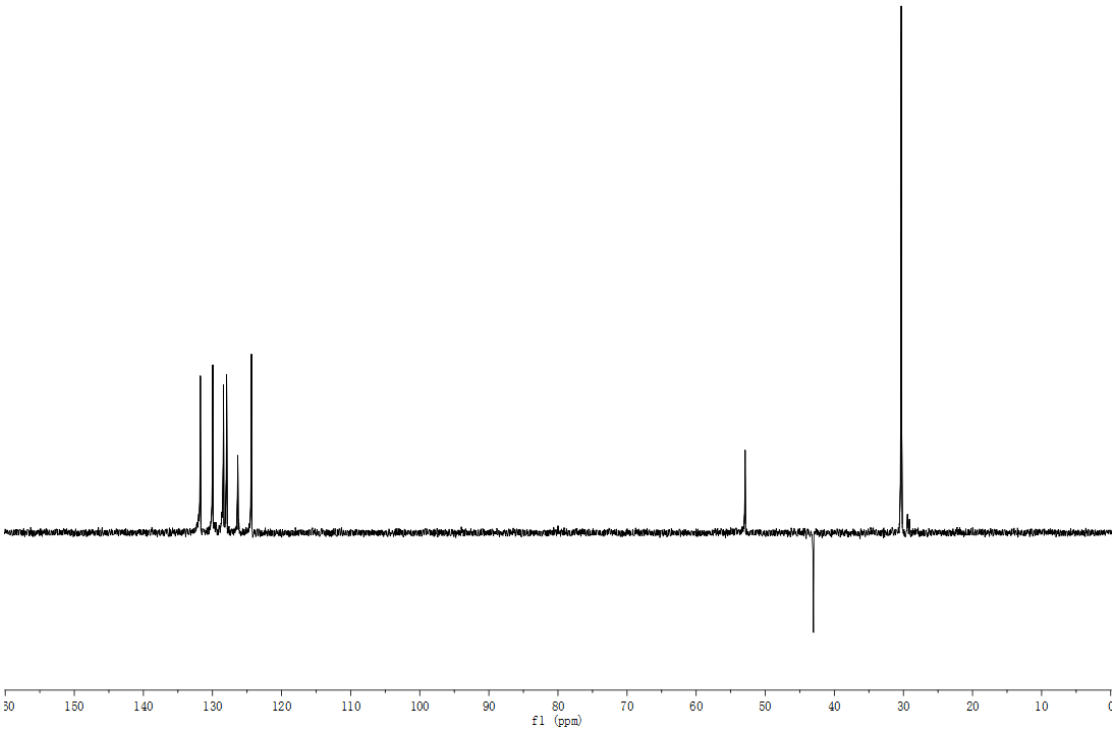
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

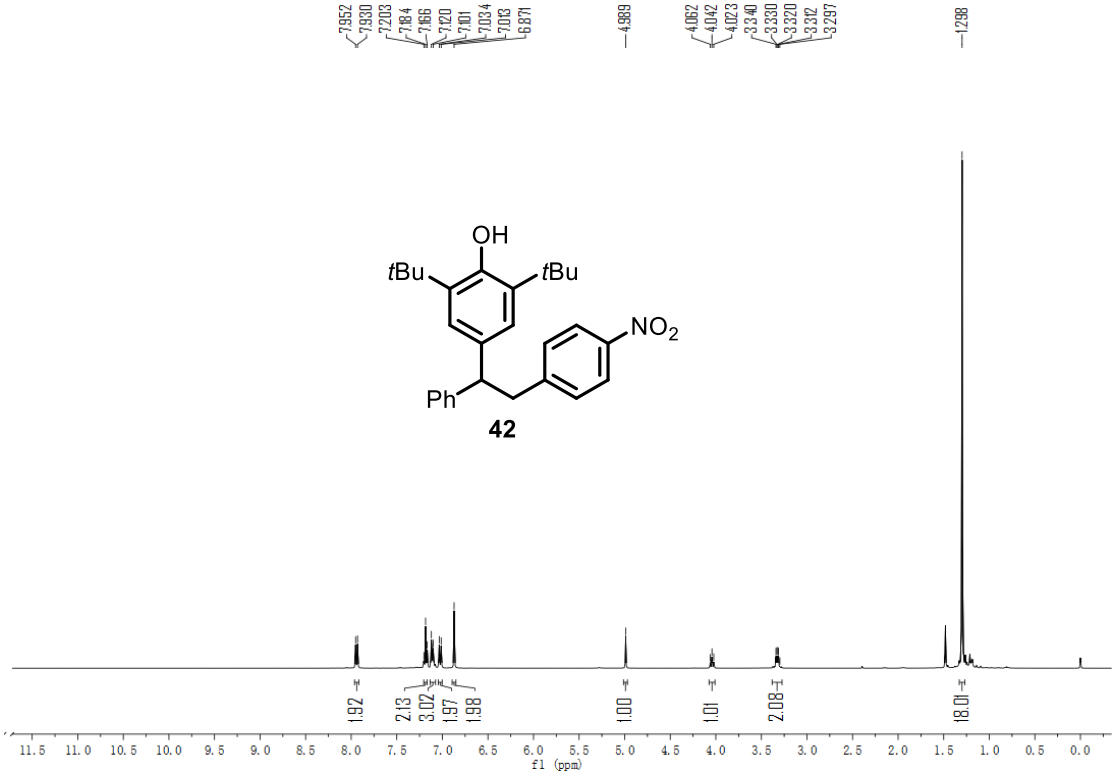


DEPT

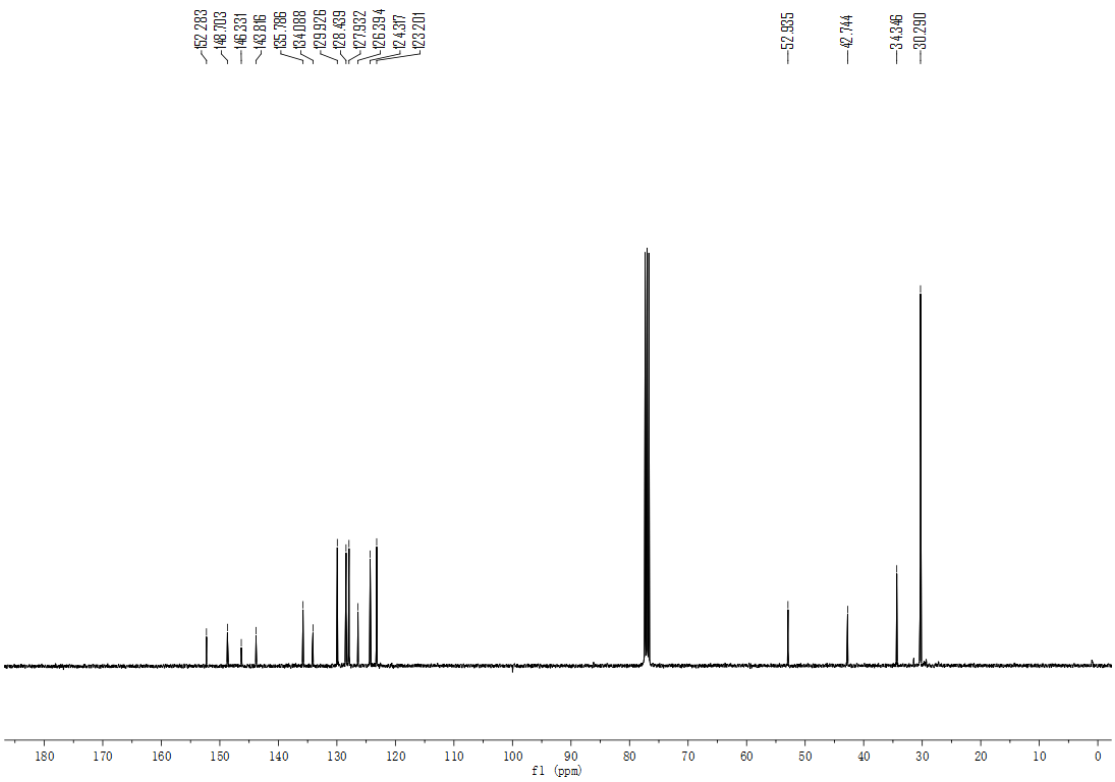


2,6-di-tert-butyl-4-(2-(4-nitrophenyl)-1-phenylethyl)phenol (42)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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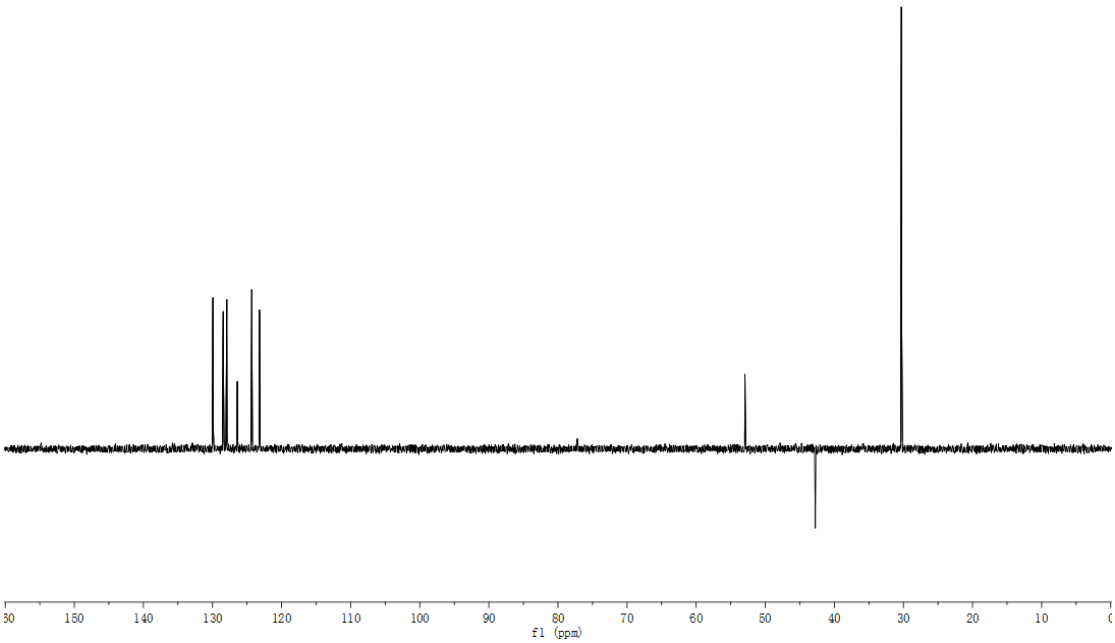
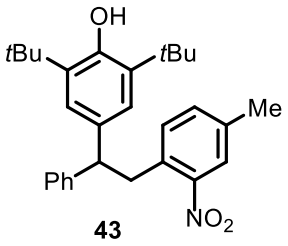
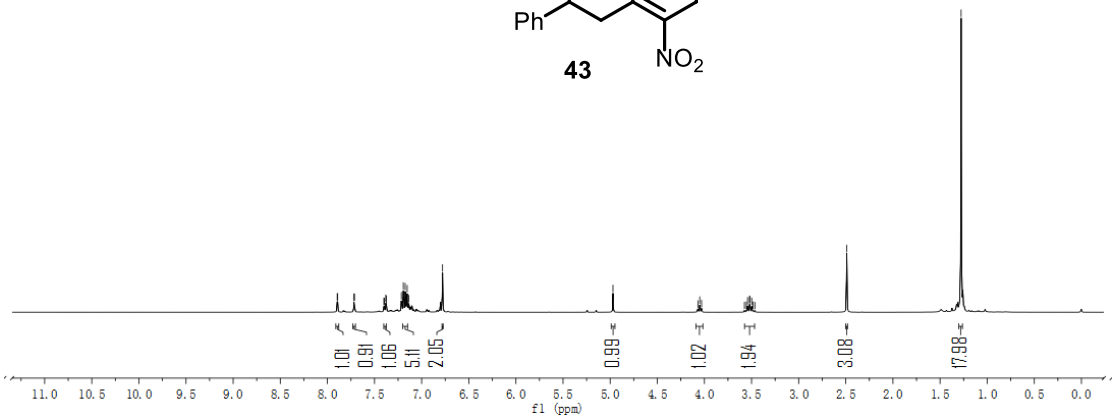


2,6-di-tert-butyl-4-(2-(4-methyl-2-nitrophenyl)-1-phenylethyl)phenol (43)

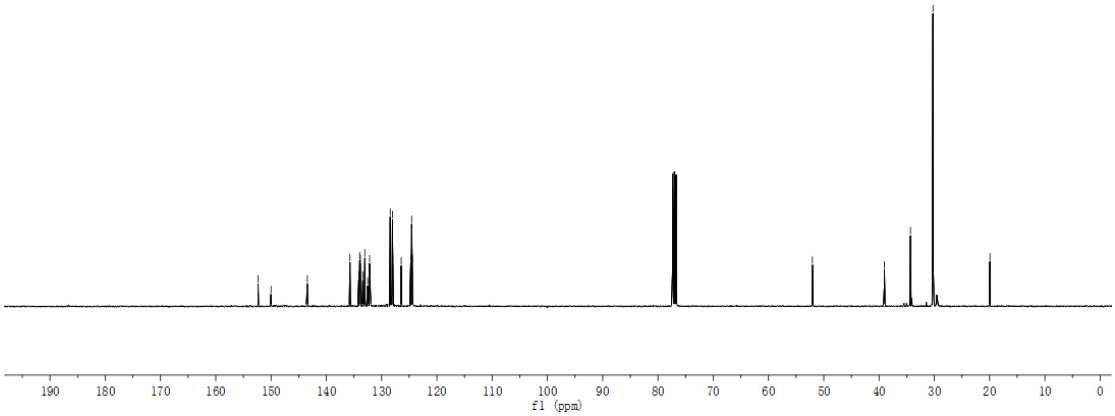
^{1}H NMR (400 MHz, $CDCl_3$):



43



^{13}C NMR (100 MHz, $CDCl_3$):



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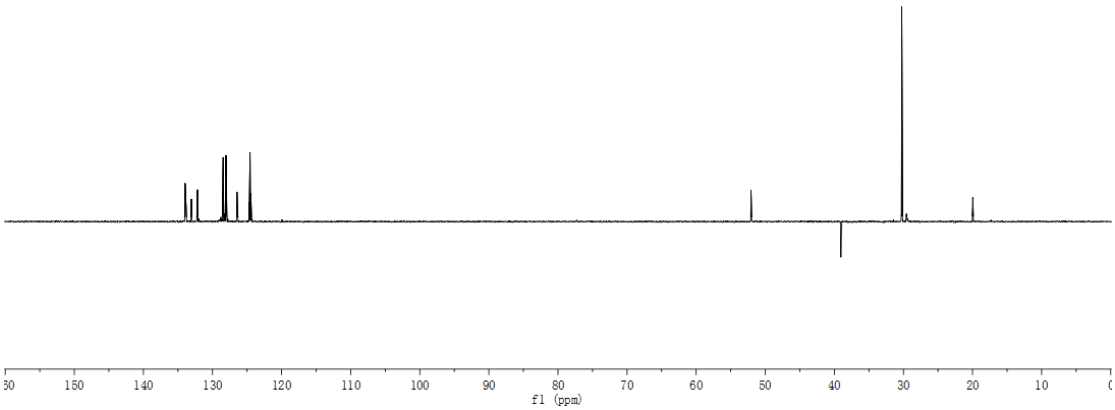
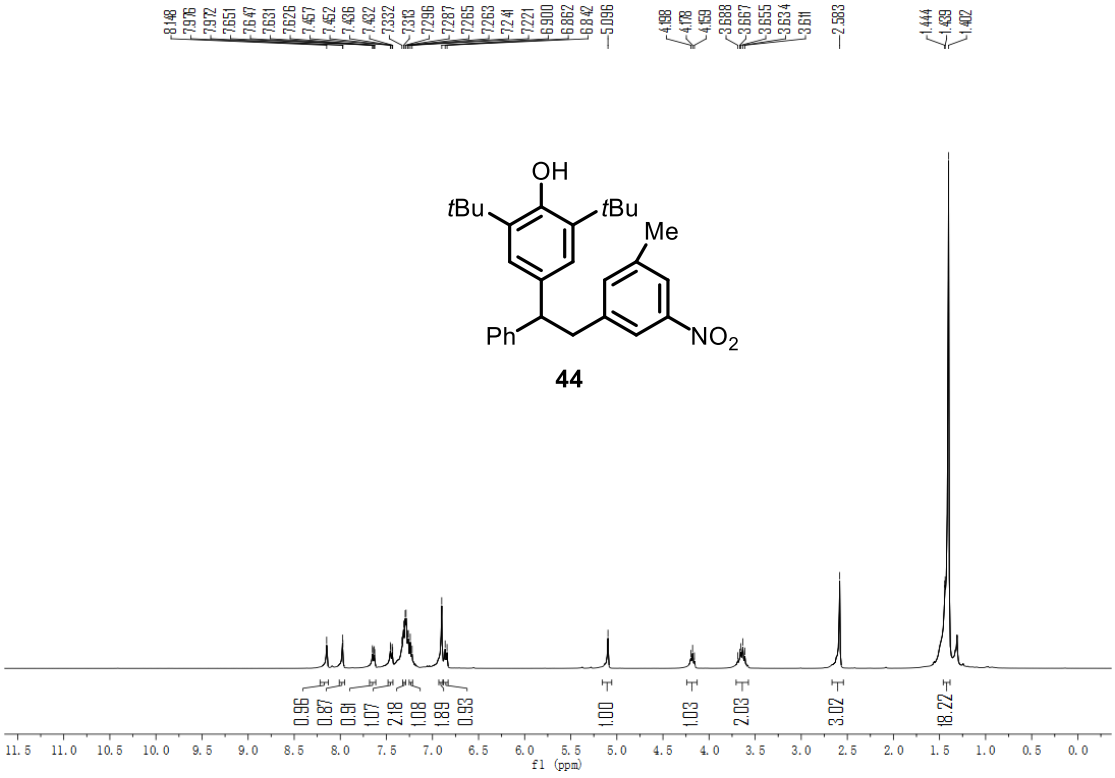
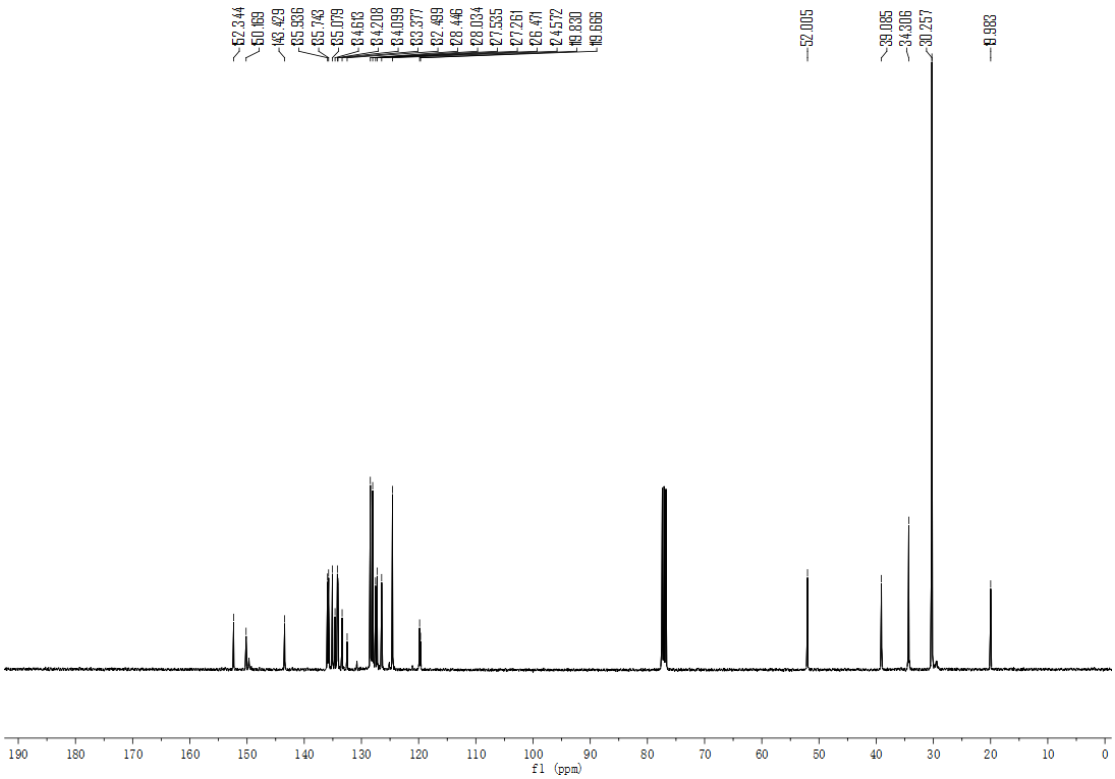


2,6-di-tert-butyl-4-(2-(3-methyl-5-nitrophenyl)-1-phenylethyl)phenol (44)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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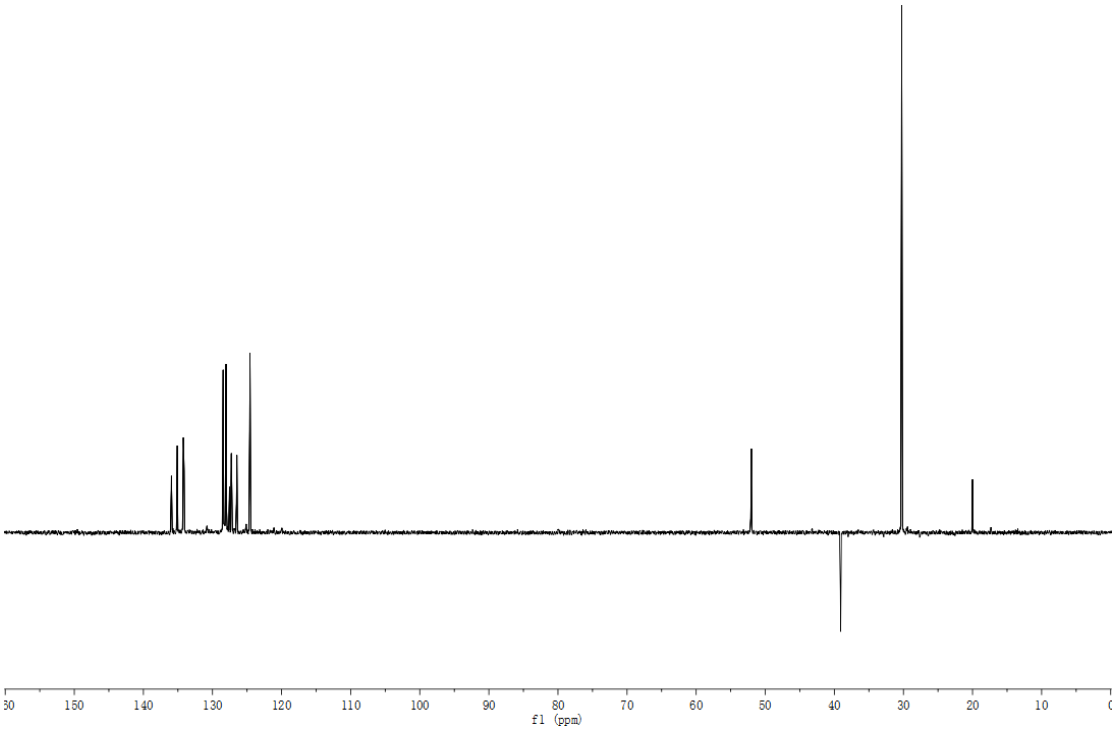
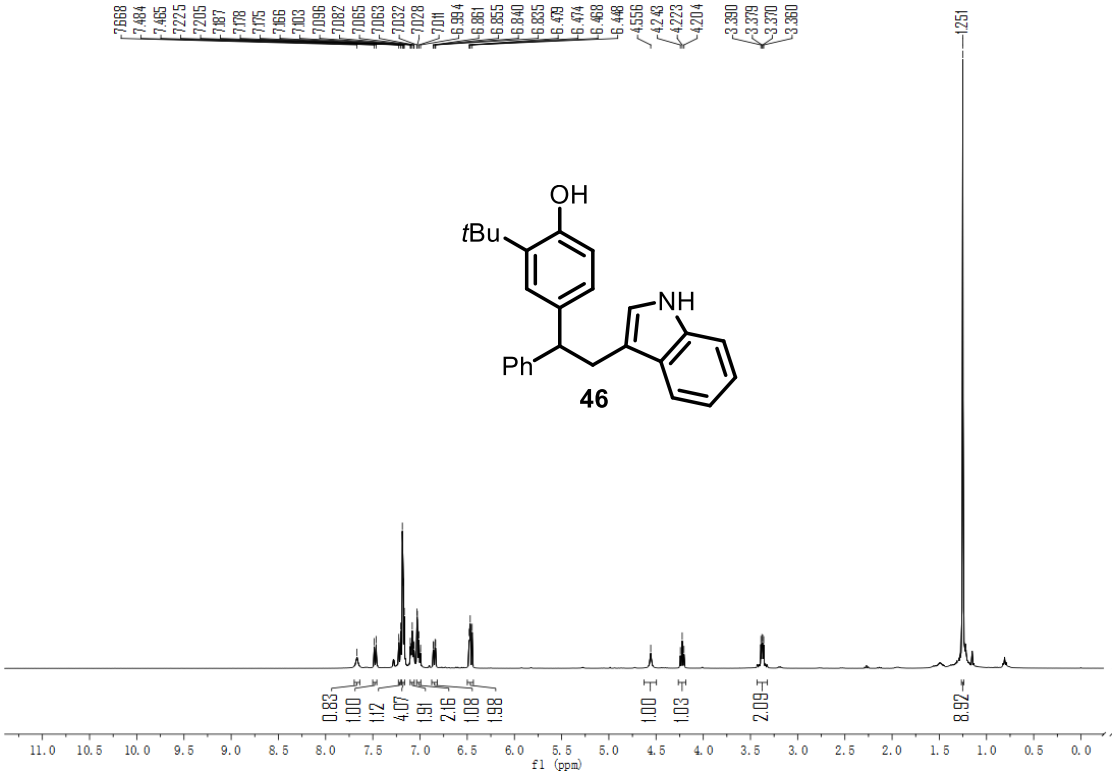
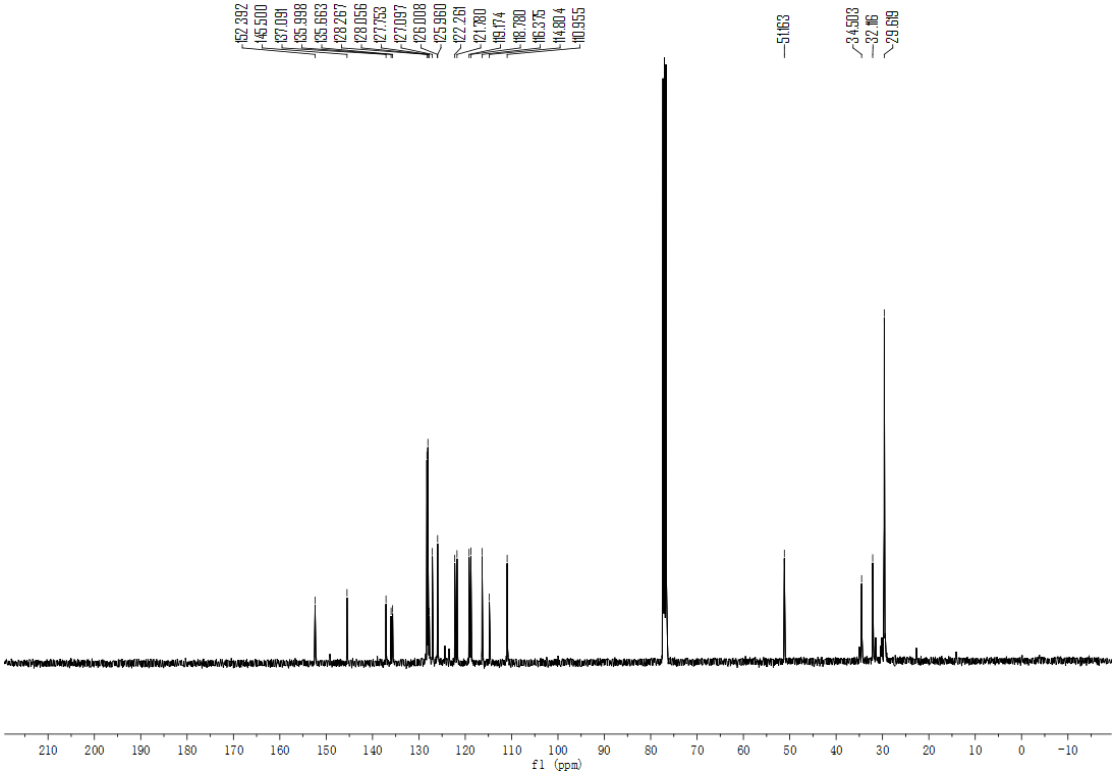


4-(2-(1H-indol-3-yl)-1-phenylethyl)-2-(tert-butyl)phenol (46)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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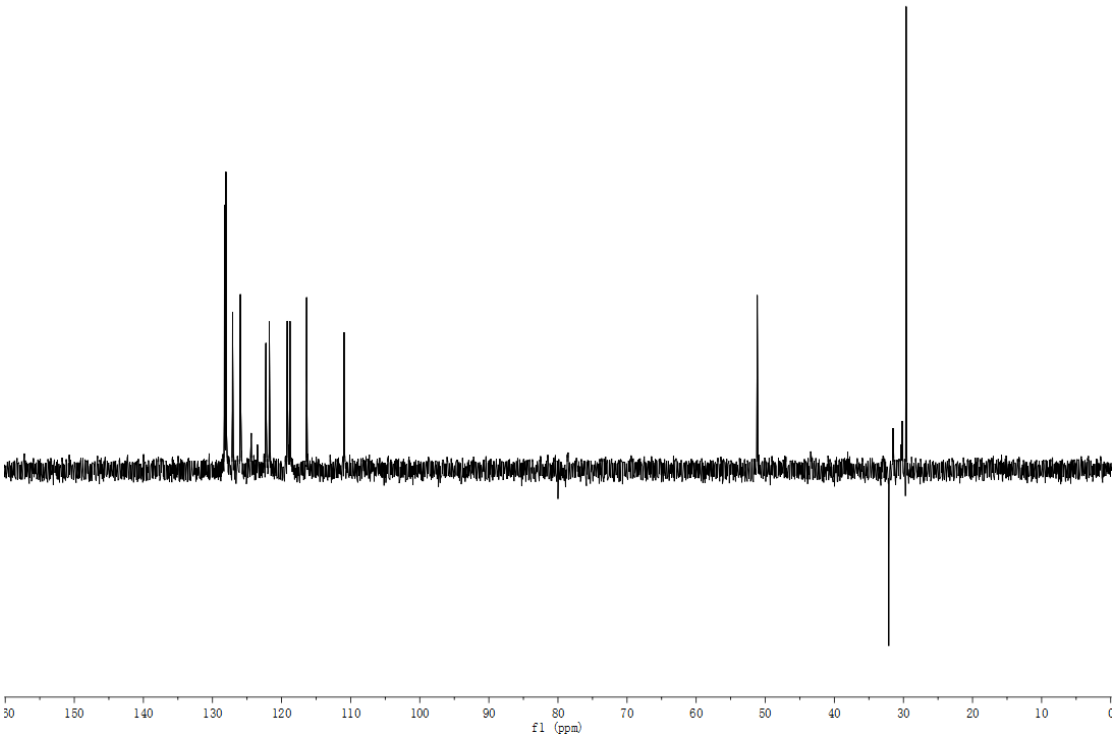
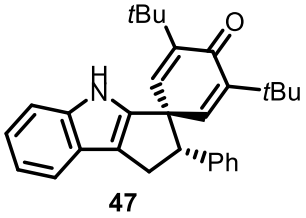


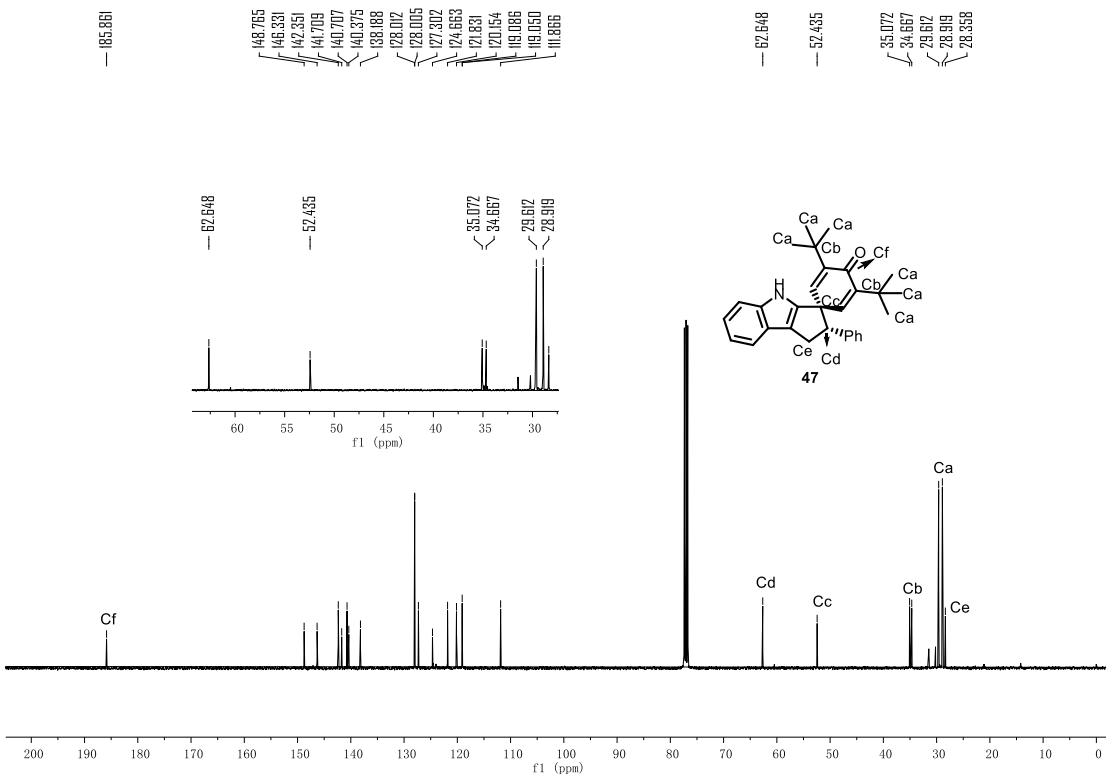
3,5-di-tert-butyl-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (47)

^{1}H NMR (400 MHz, $CDCl_3$):

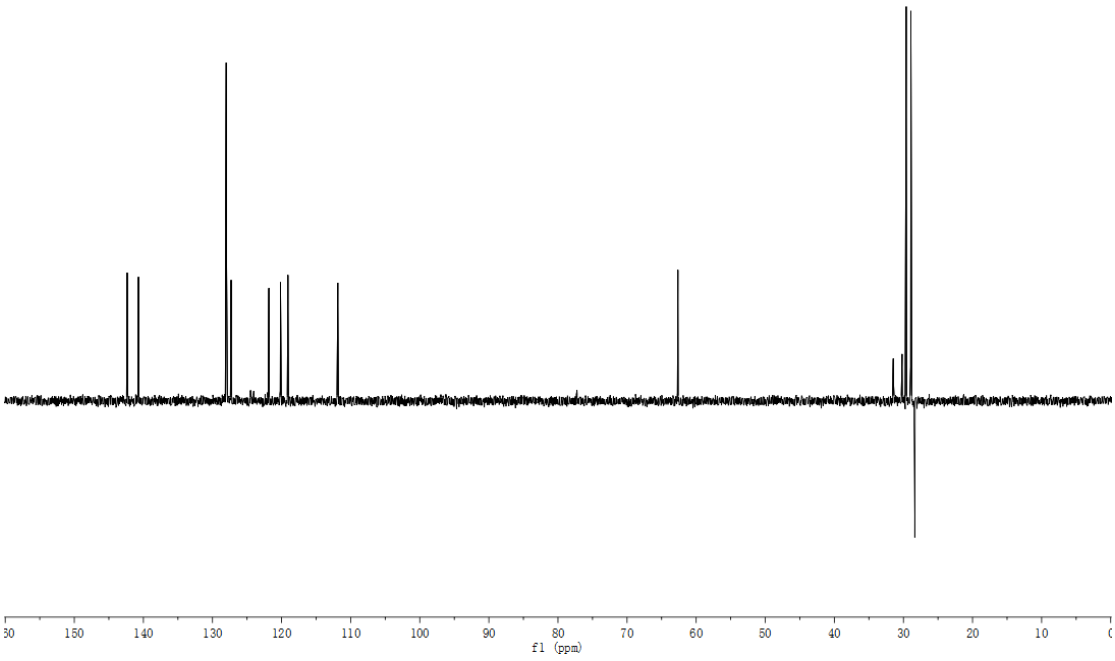


47

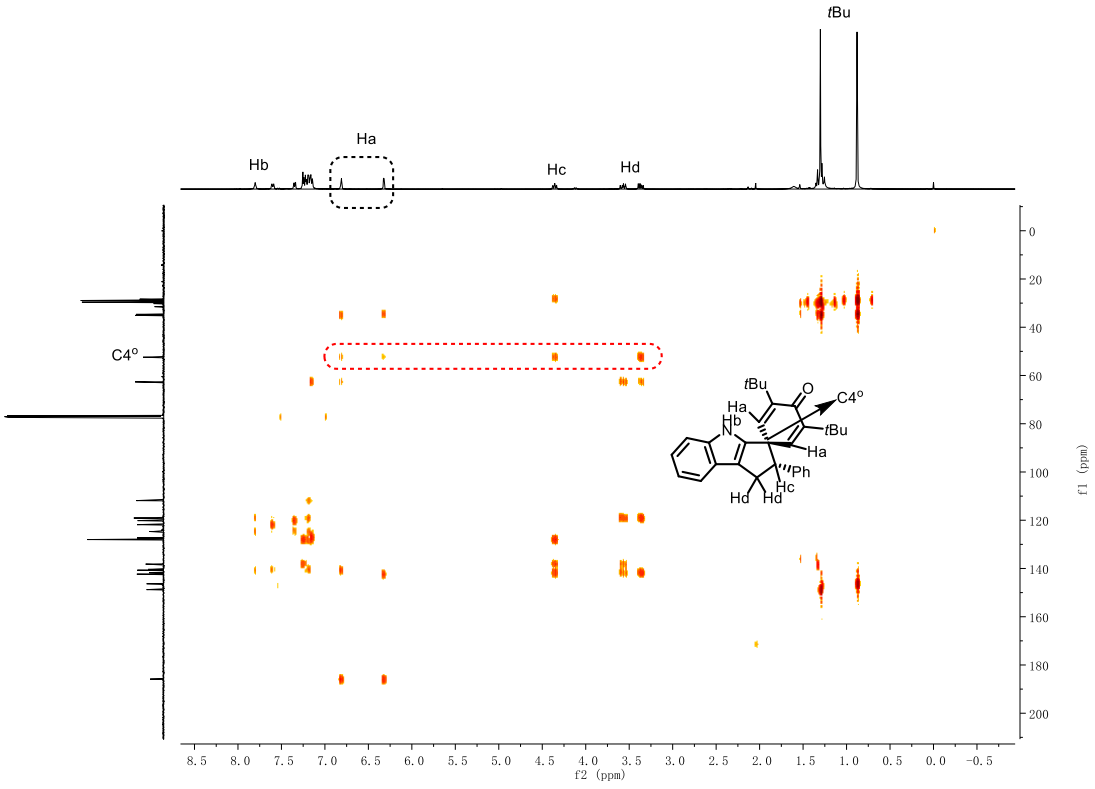
^{13}C NMR (100 MHz, $CDCl_3$):


185.861
148.765
146.331
142.351
141.709
140.707
140.375
138.188
128.012
128.005
127.302
124.663
121.831
120.154
119.086
119.050
111.866
62.648
52.435
35.072
34.667
29.612
28.919
28.358
62.648
52.435
35.072
34.667
29.612
28.919
60 55 50 45 40 35 30
f1 (ppm)
Ca
Ca
Ca
Cb
O
Cf
Ca
Cb
Ca
Ca
Cc
Ph
Ce
Cd
47
Cf
Cd
Cc
Cb
Ca
Ce
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

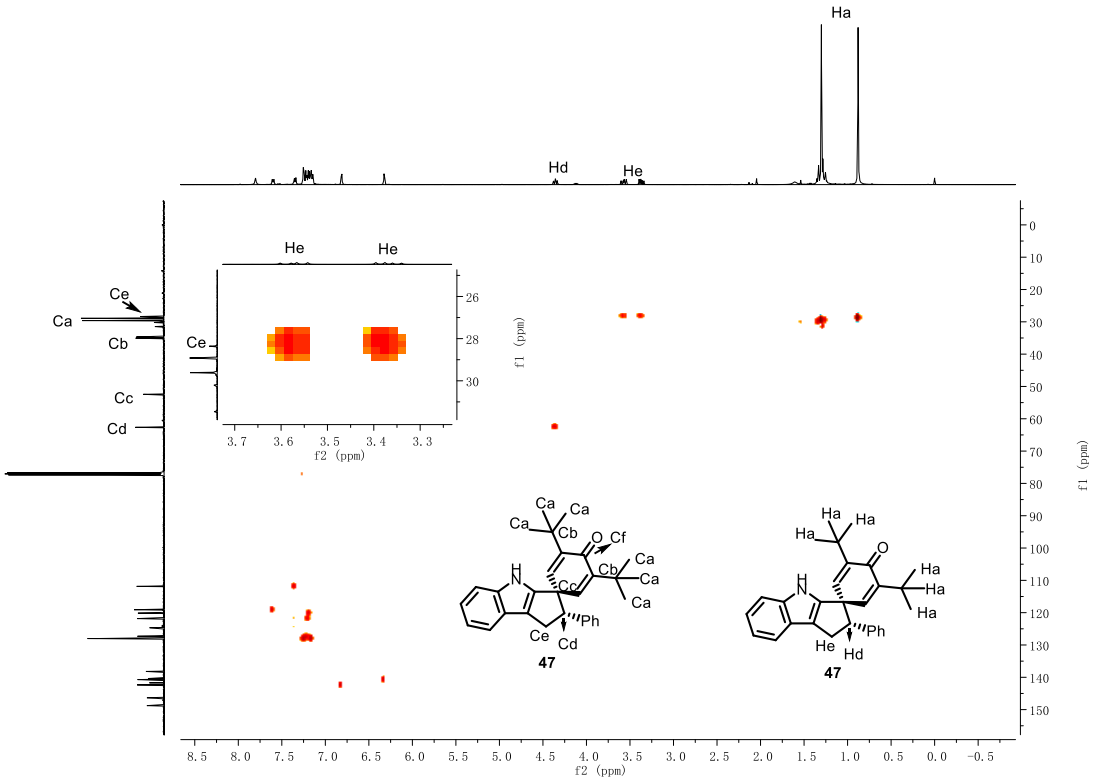
DEPT


150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

HMBC

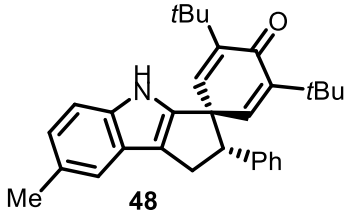


HSQC



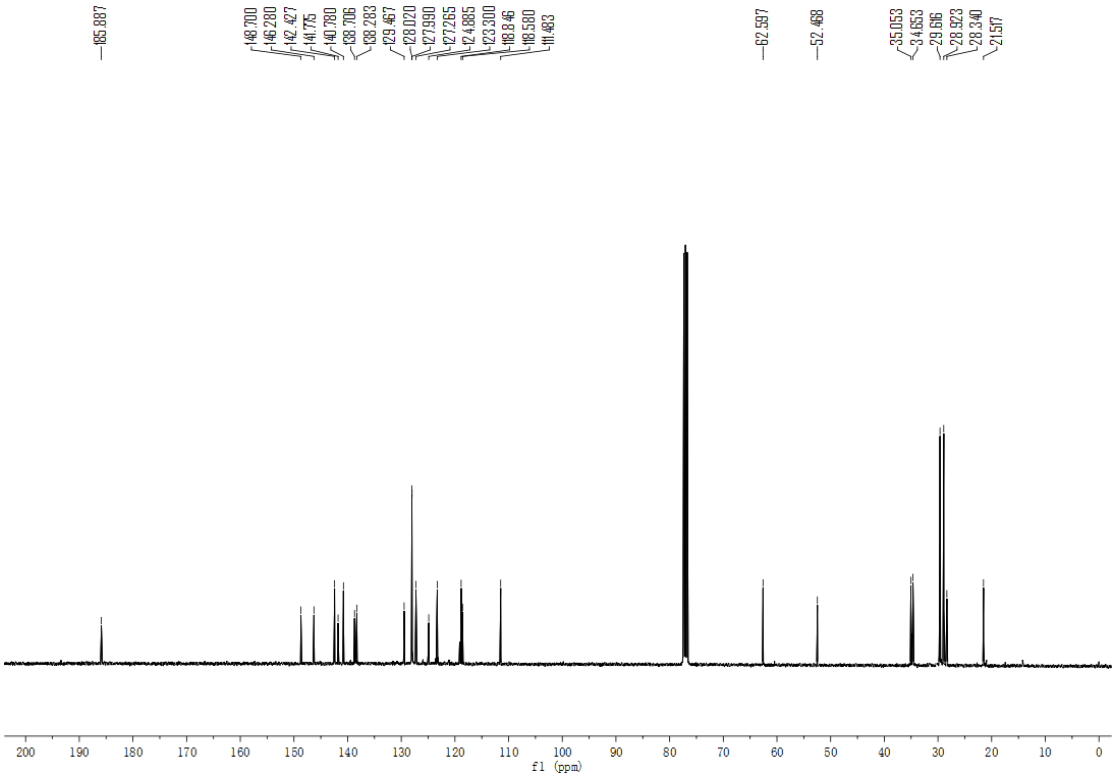
3,5-di-tert-butyl-7'-methyl-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (48)

^{1}H NMR (400 MHz, $CDCl_3$):



48

^{13}C NMR (100 MHz, $CDCl_3$):



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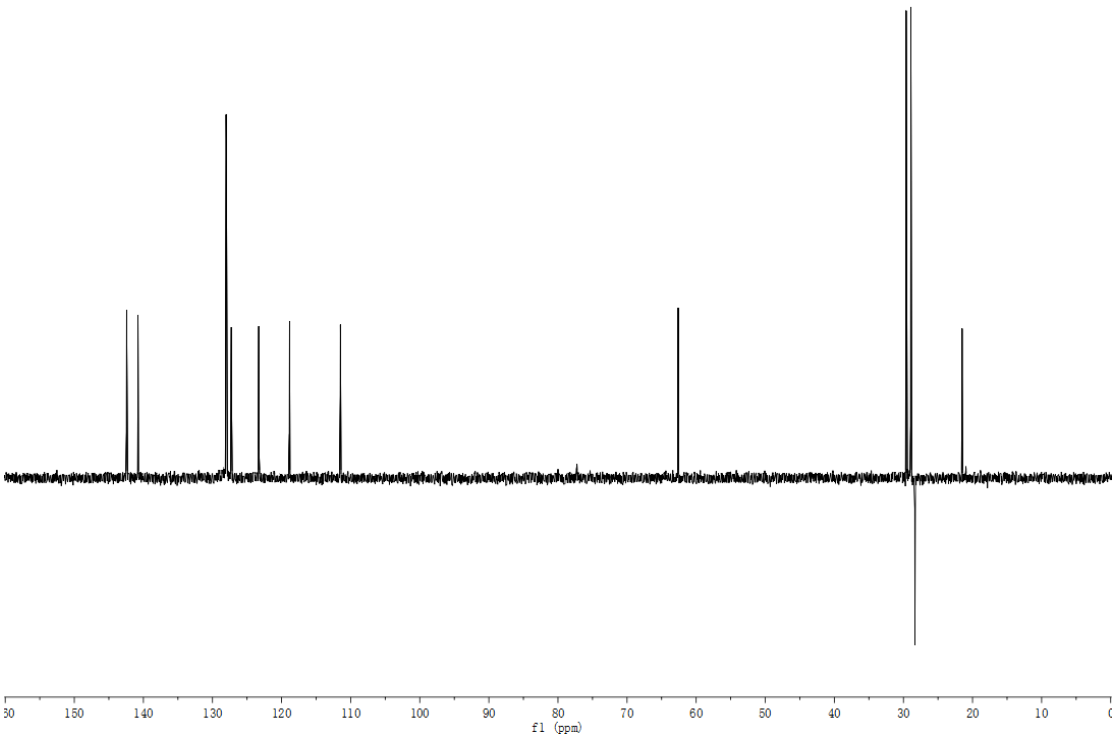
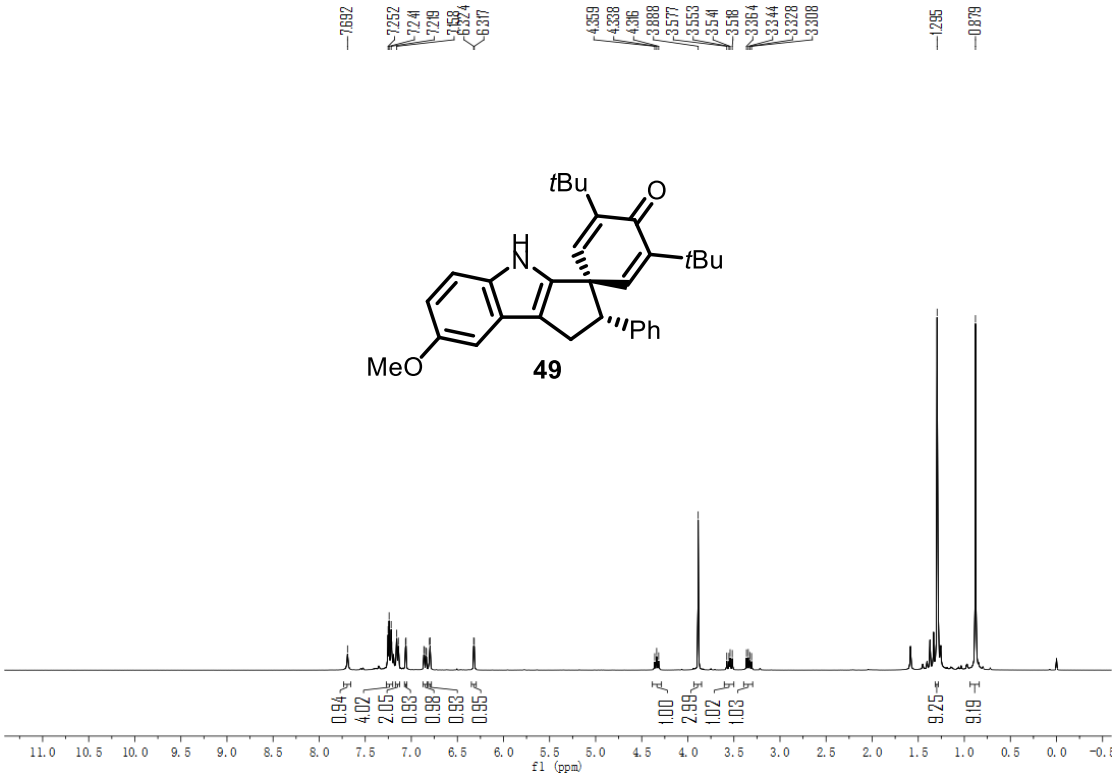
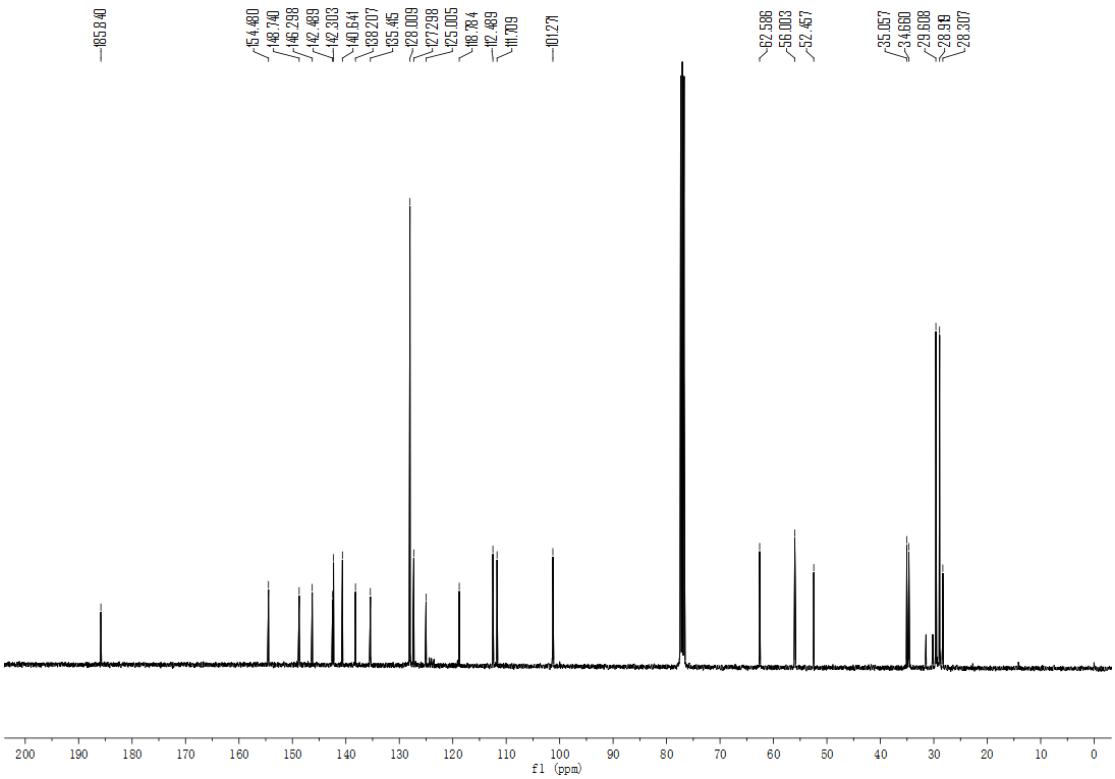


3,5-di-tert-butyl-7'-methoxy-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (49)

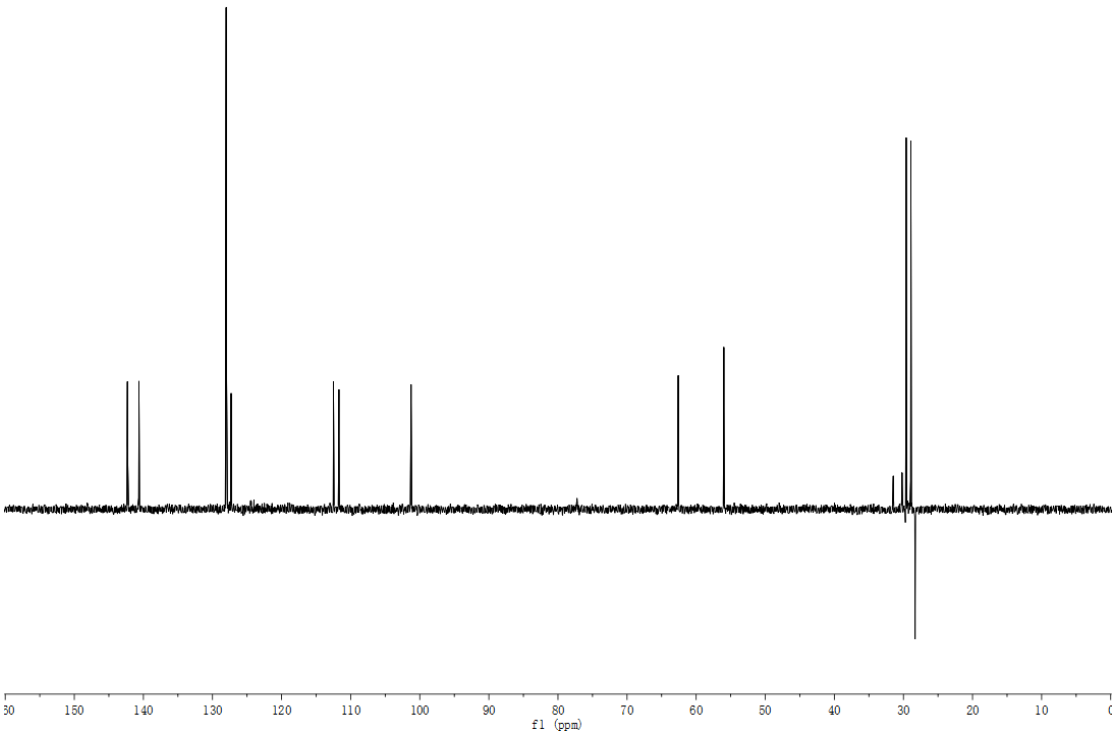
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

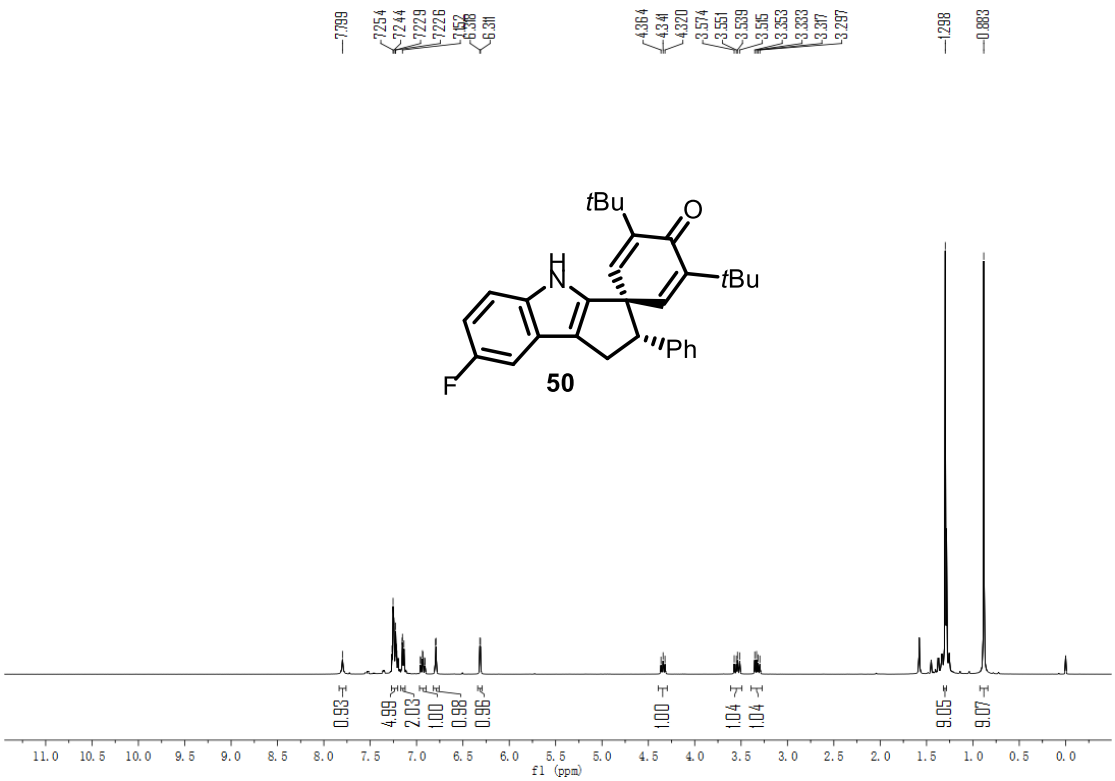


DEPT

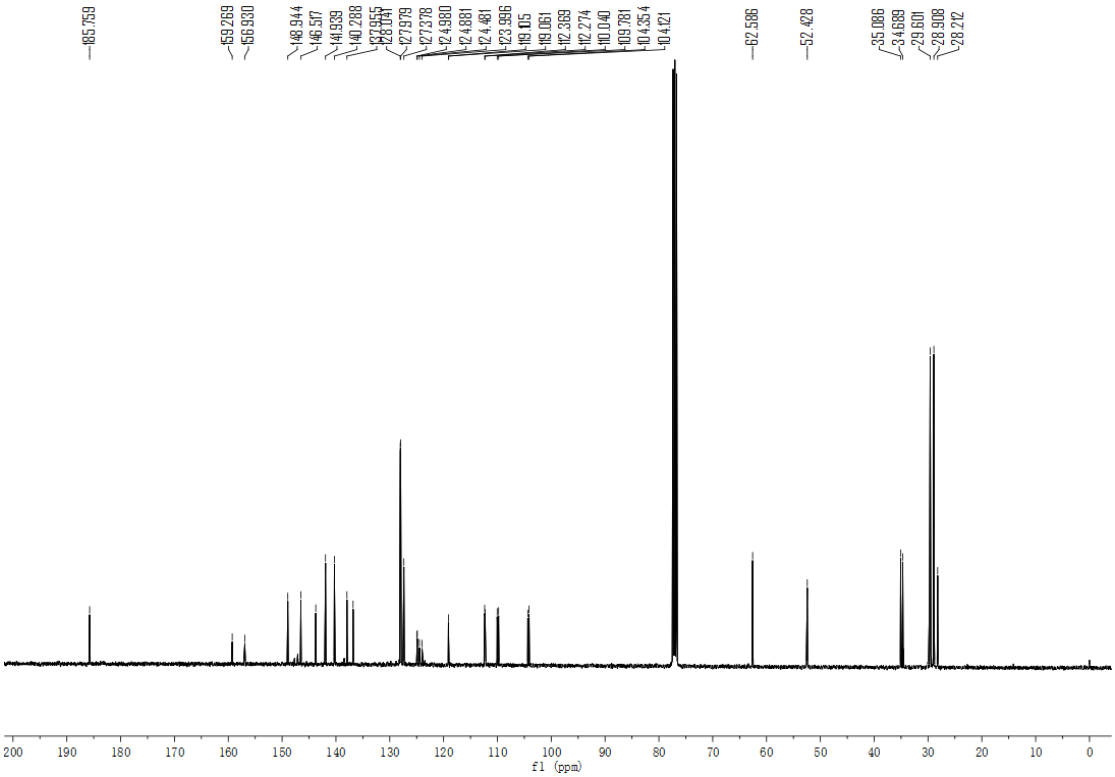


3,5-di-tert-butyl-7'-fluoro-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (50)

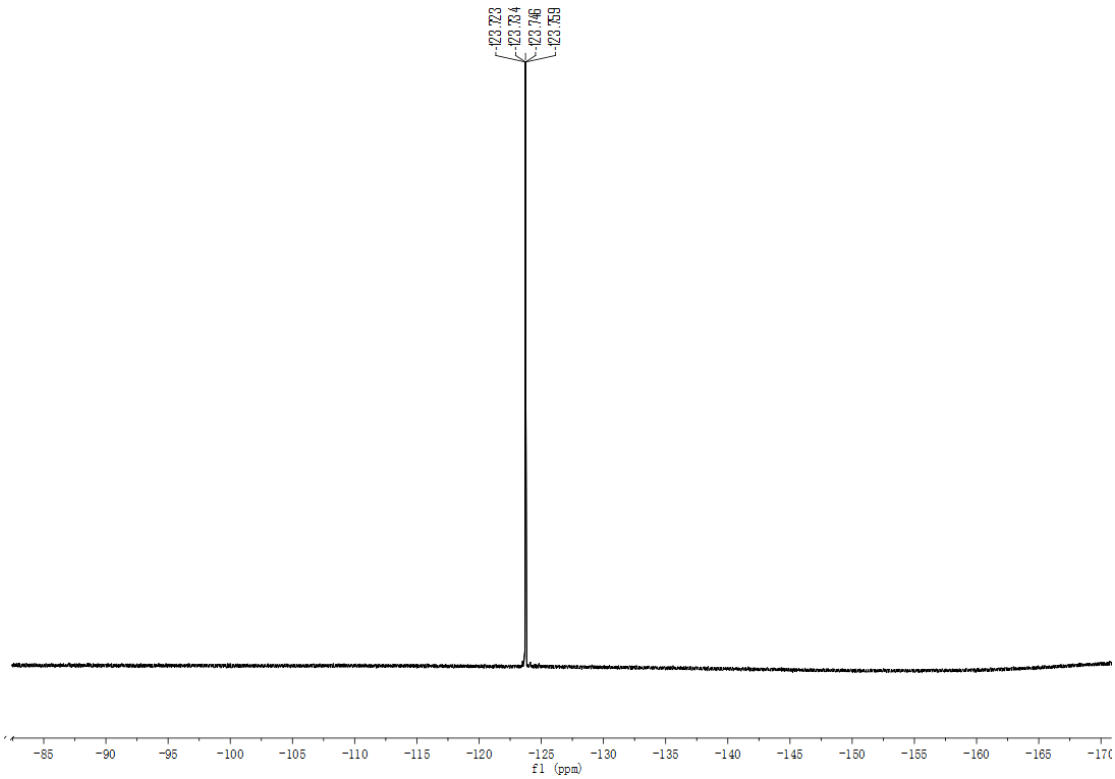
^{1}H NMR (400 MHz, $CDCl_3$):



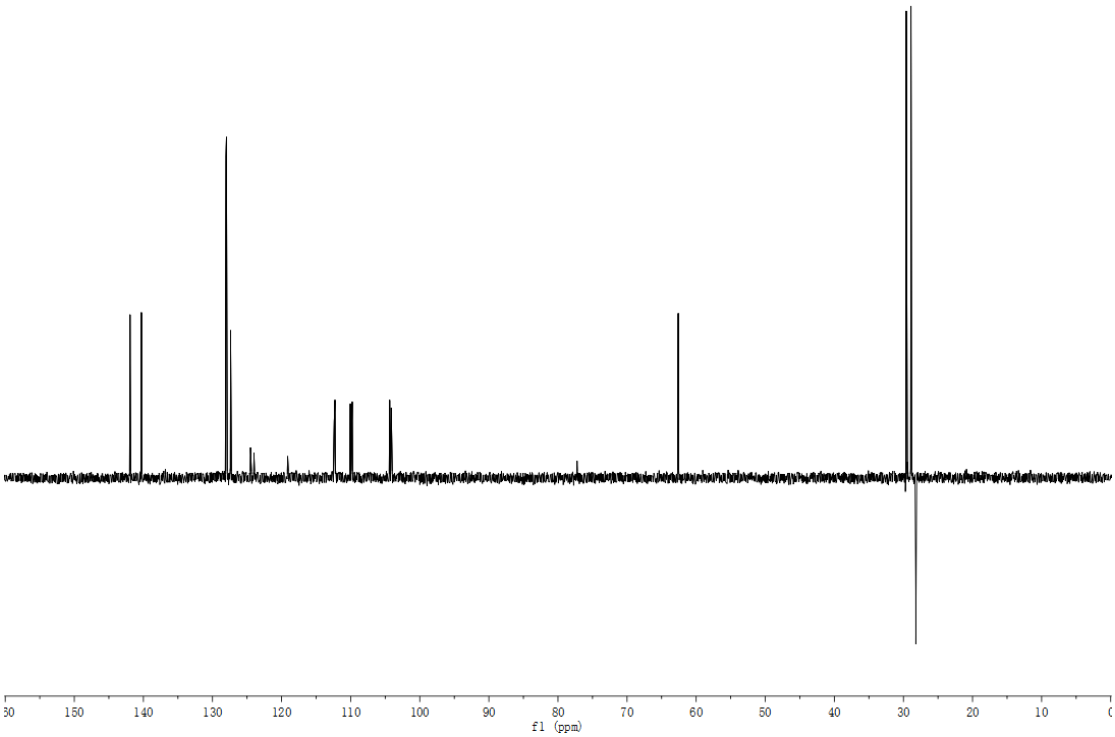
^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$)

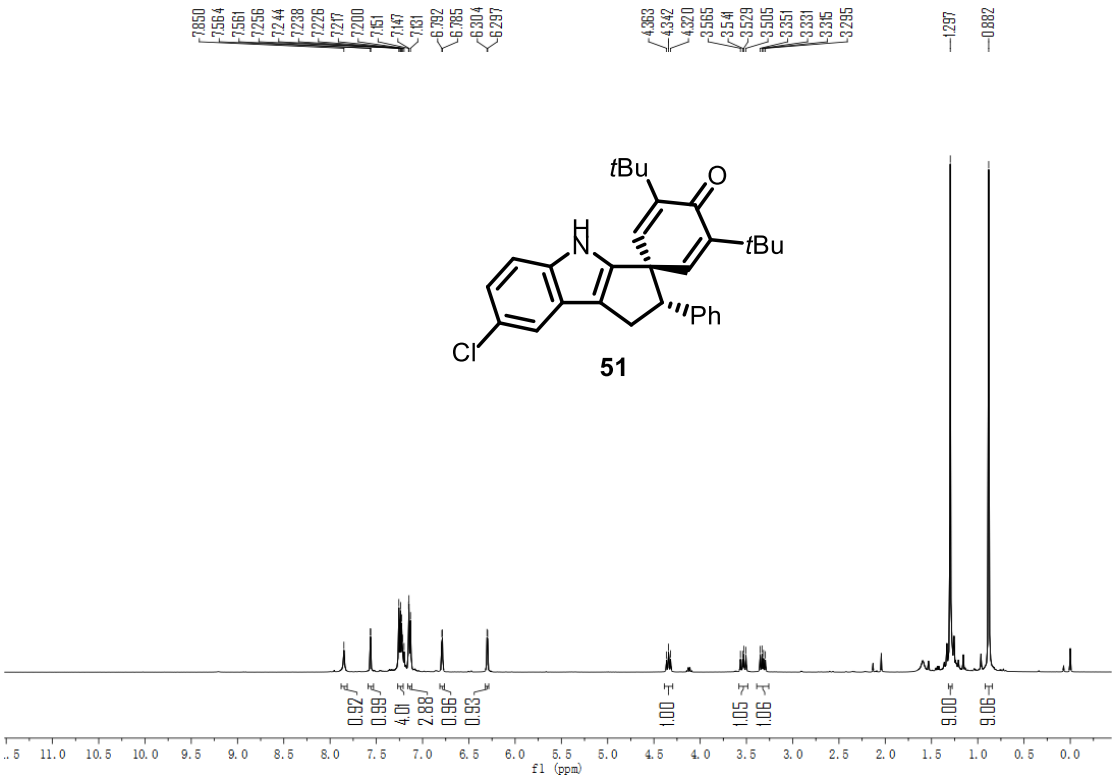


DEPT

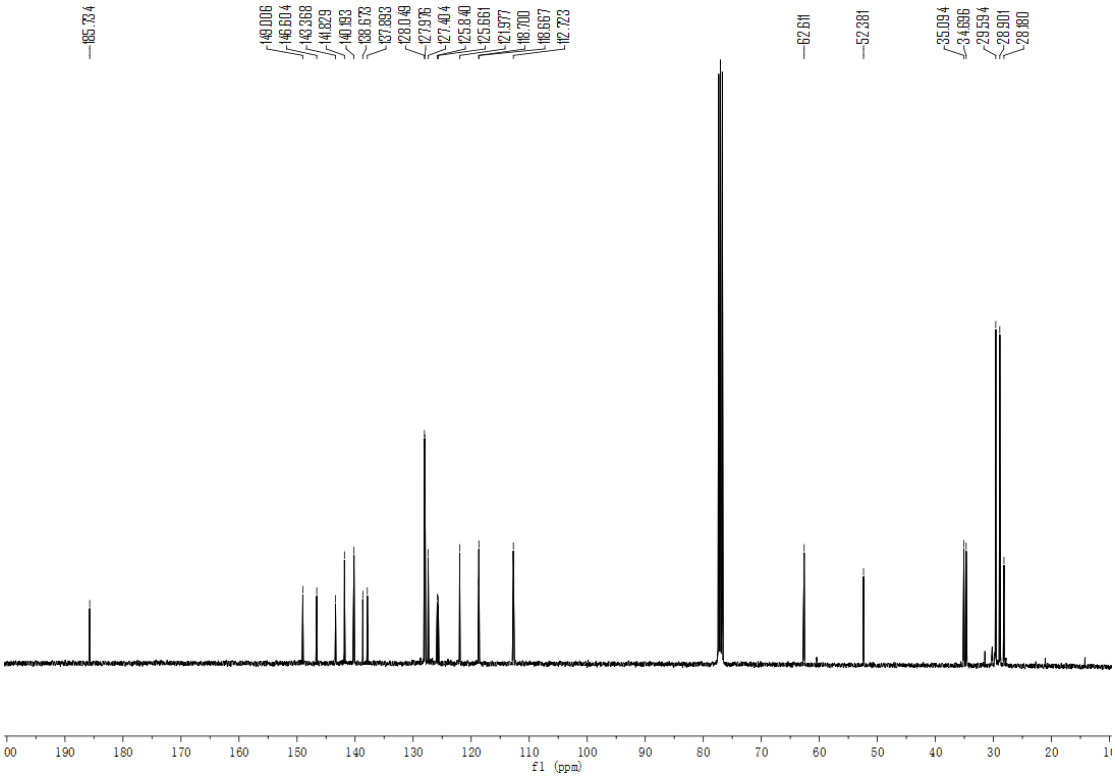


3,5-di-tert-butyl-7'-chloro-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (51)

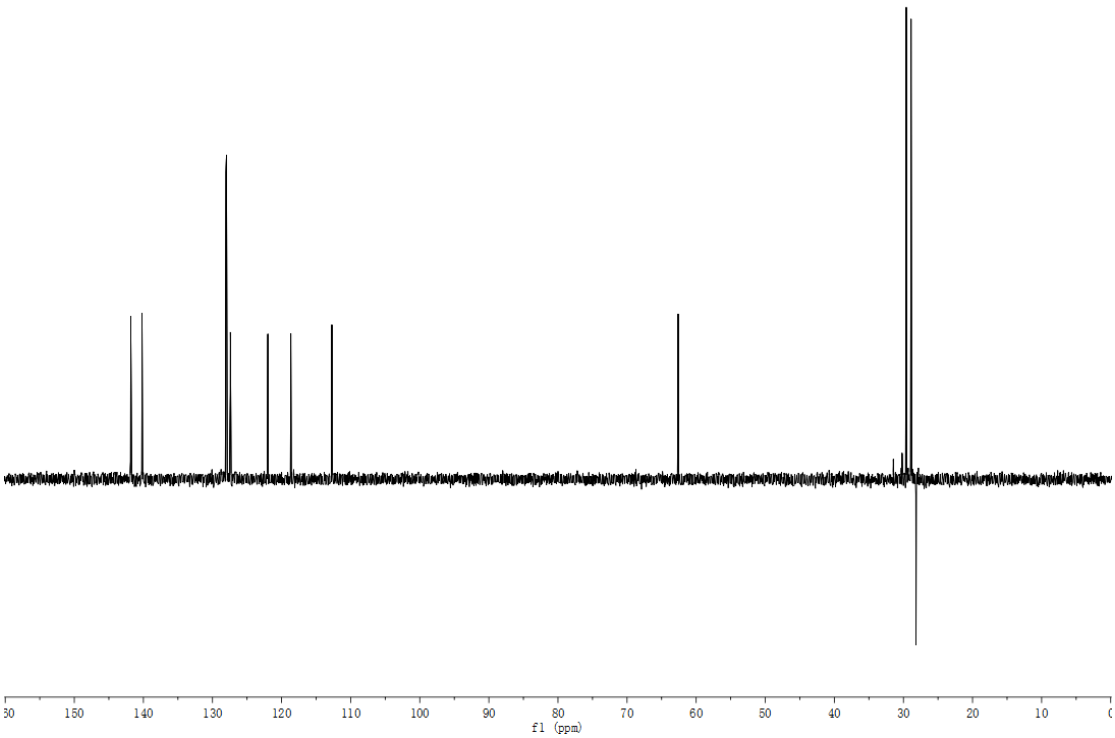
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

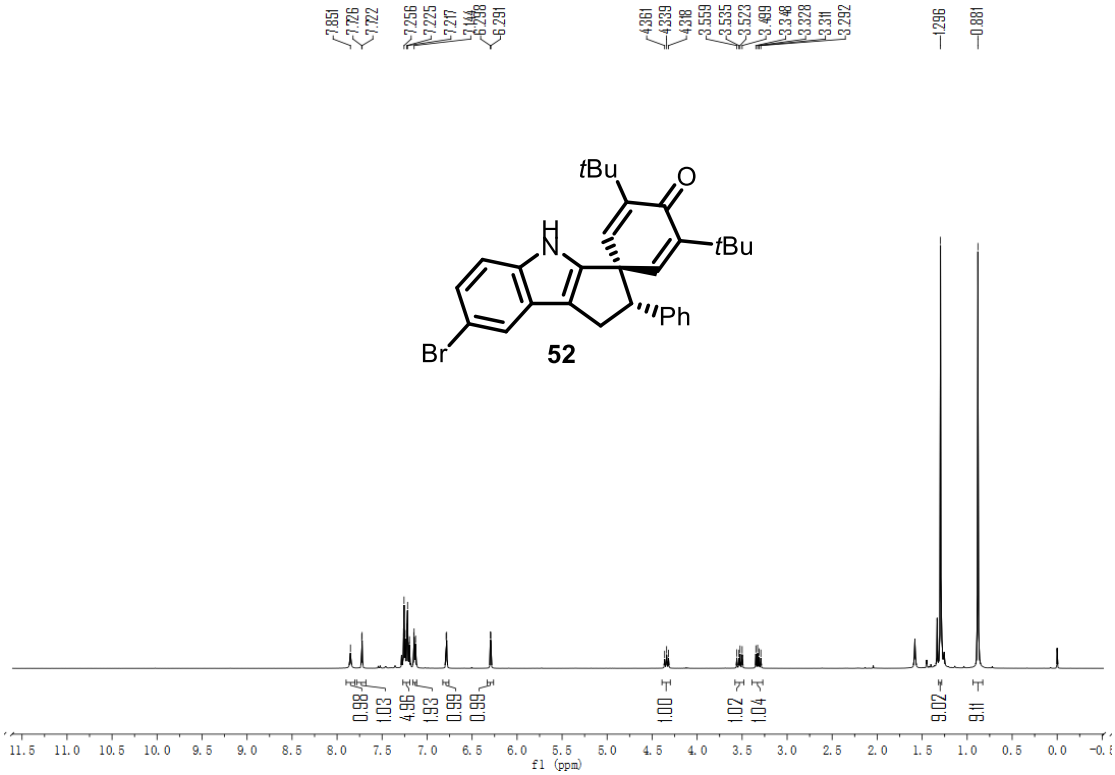


DEPT

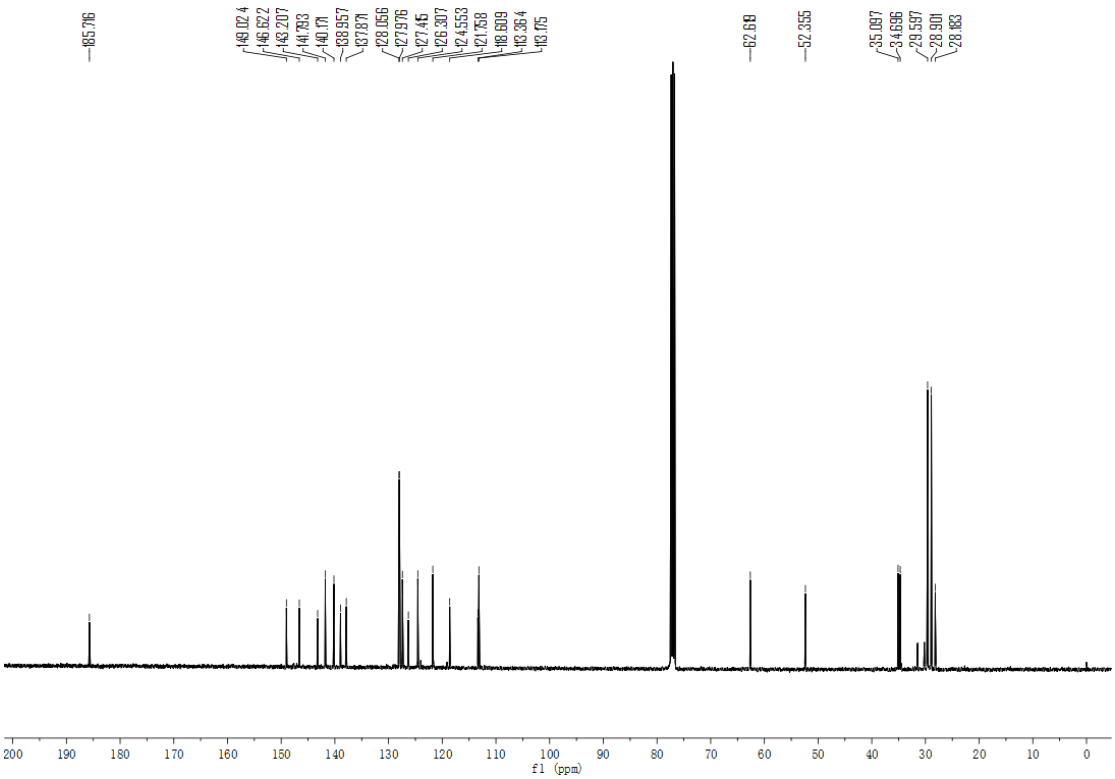


7'-bromo-3,5-di-tert-butyl-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (52)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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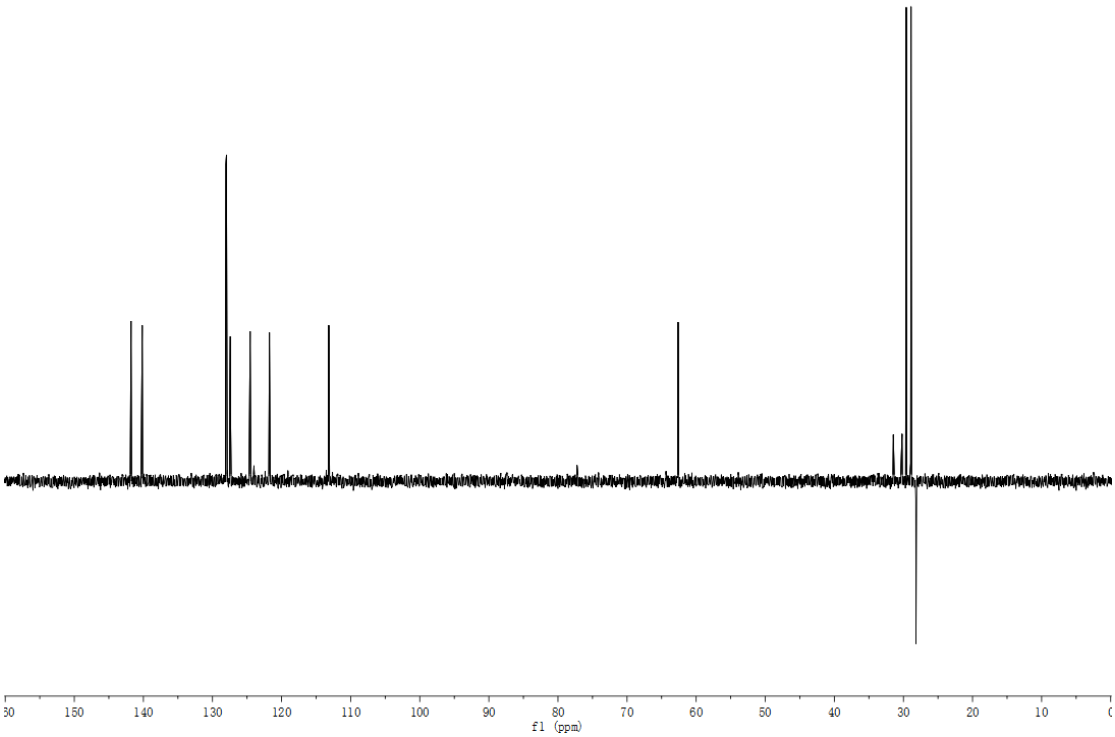
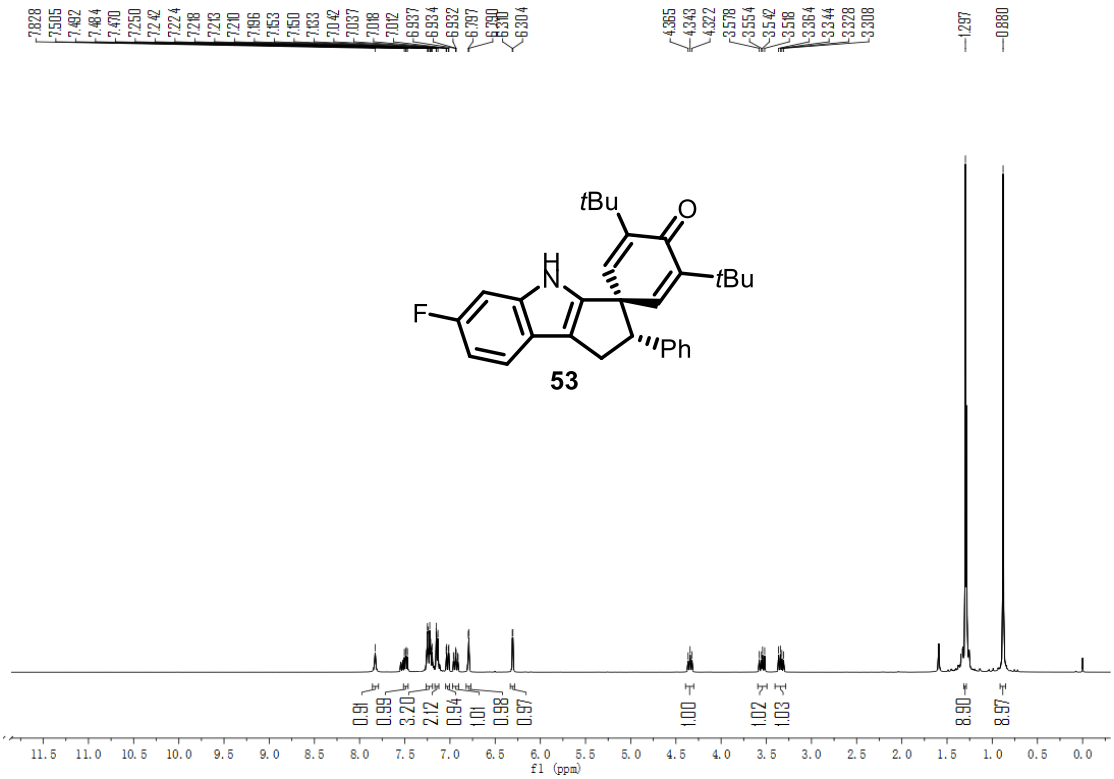
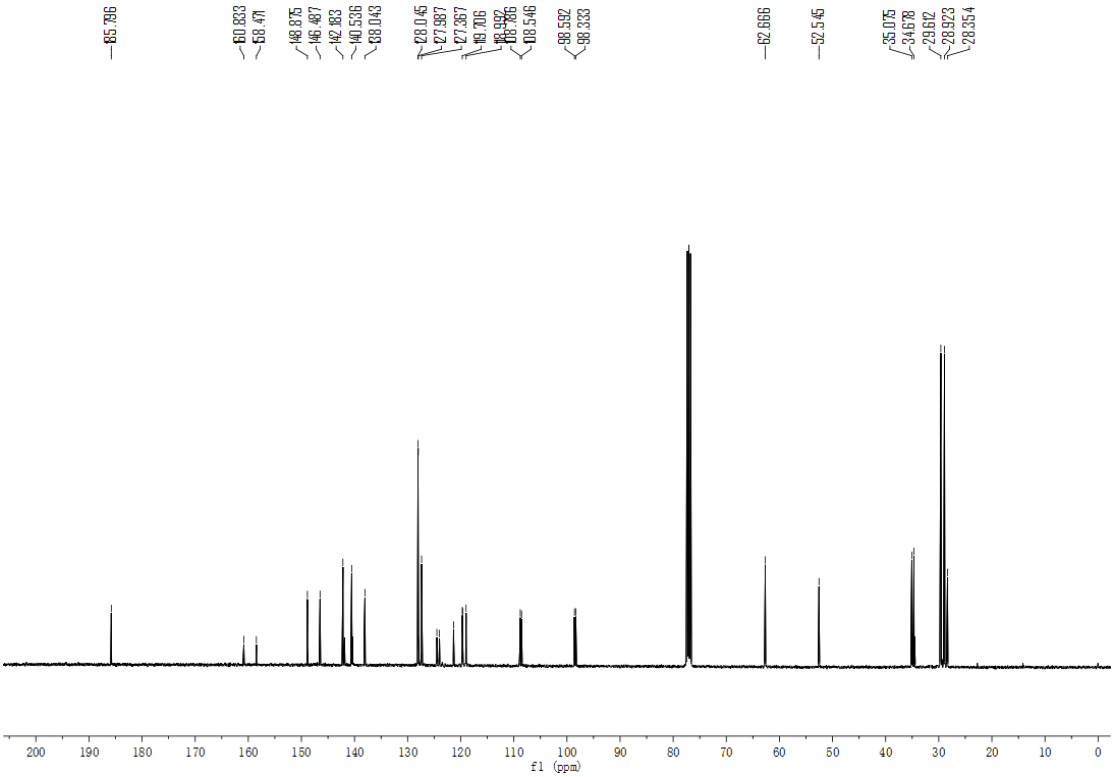


3,5-di-tert-butyl-6'-fluoro-2'-phenyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (53)

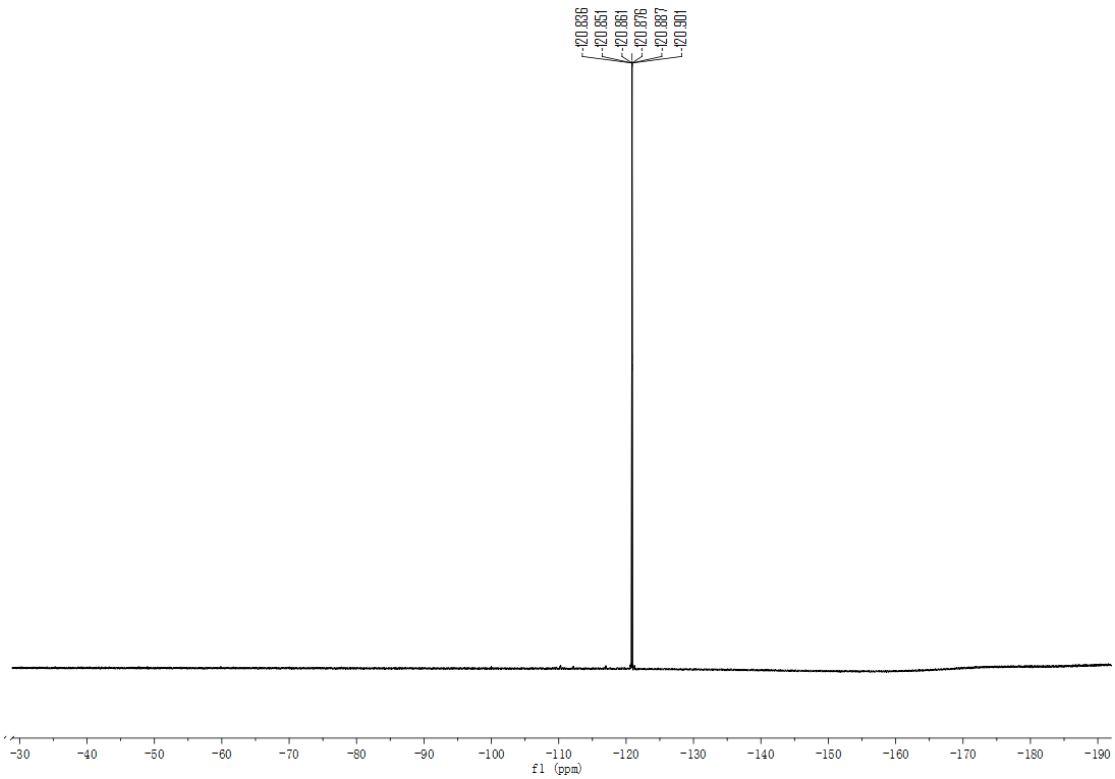
^{1}H NMR (400 MHz, $CDCl_3$):



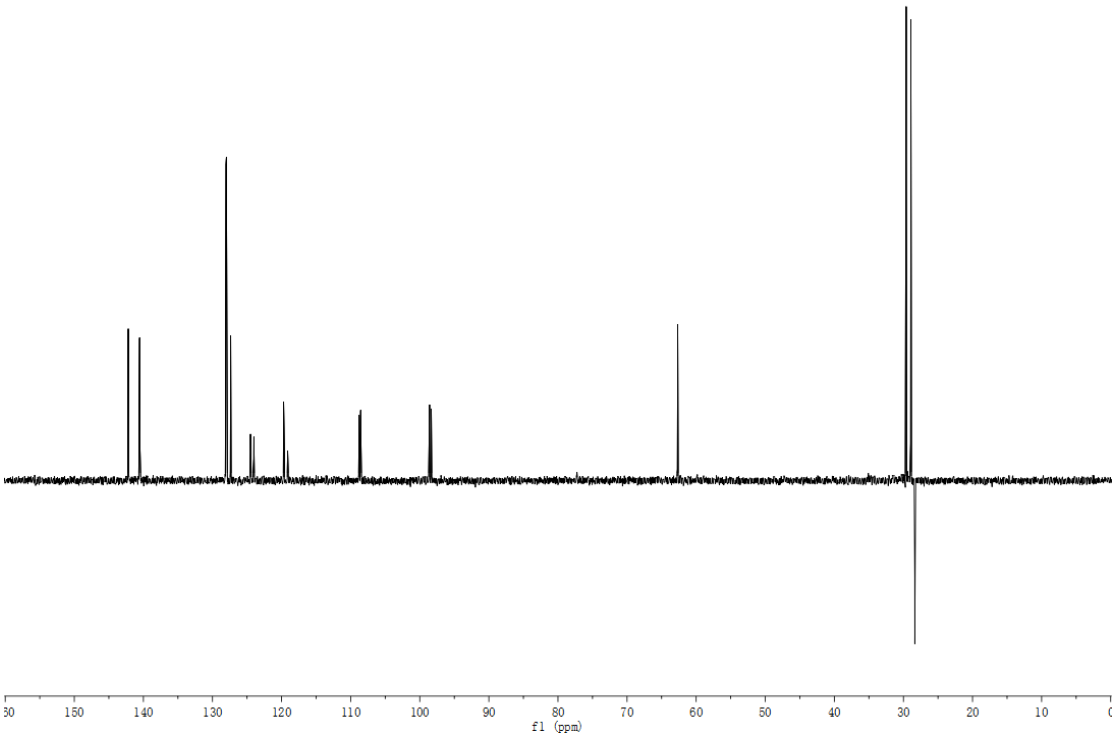
^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (376 MHz, $CDCl_3$)

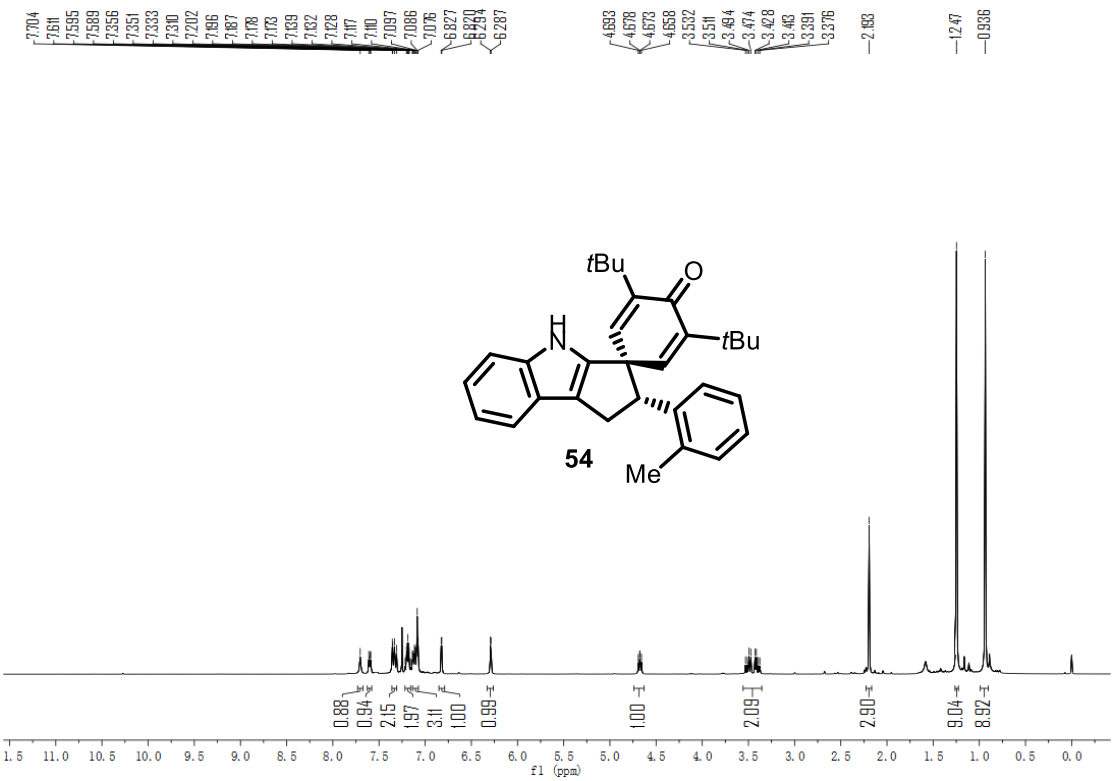


DEPT

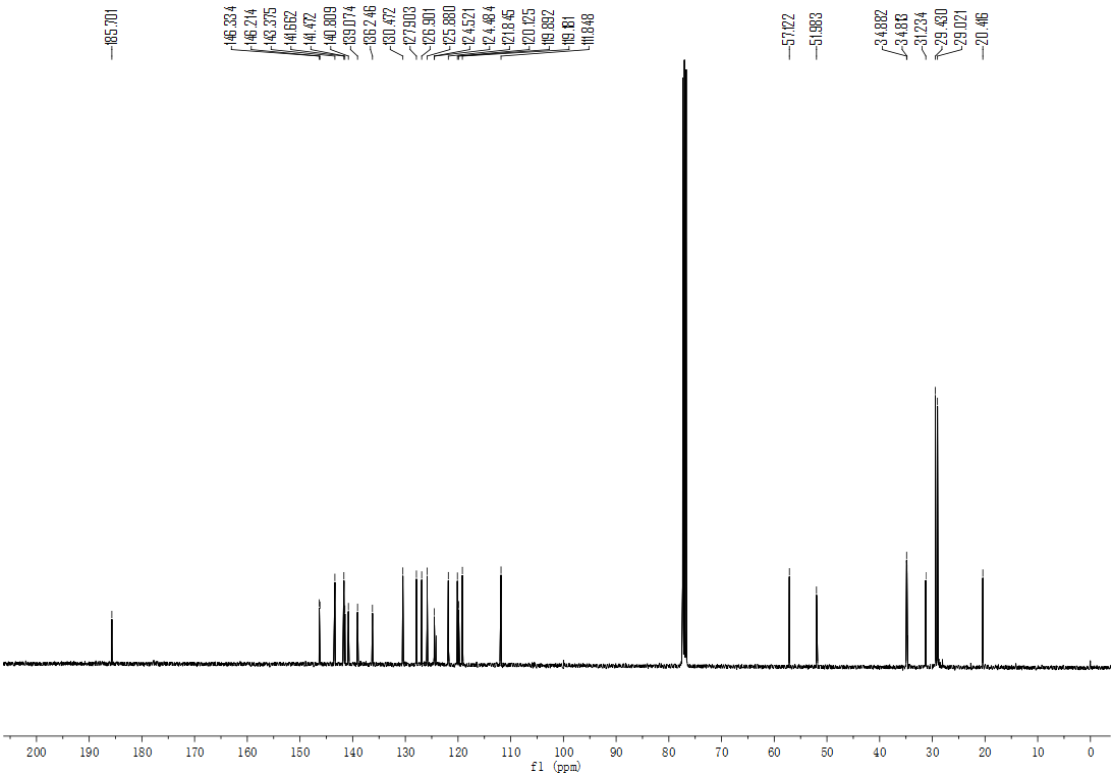


3,5-di-tert-butyl-2'-(o-tolyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (54)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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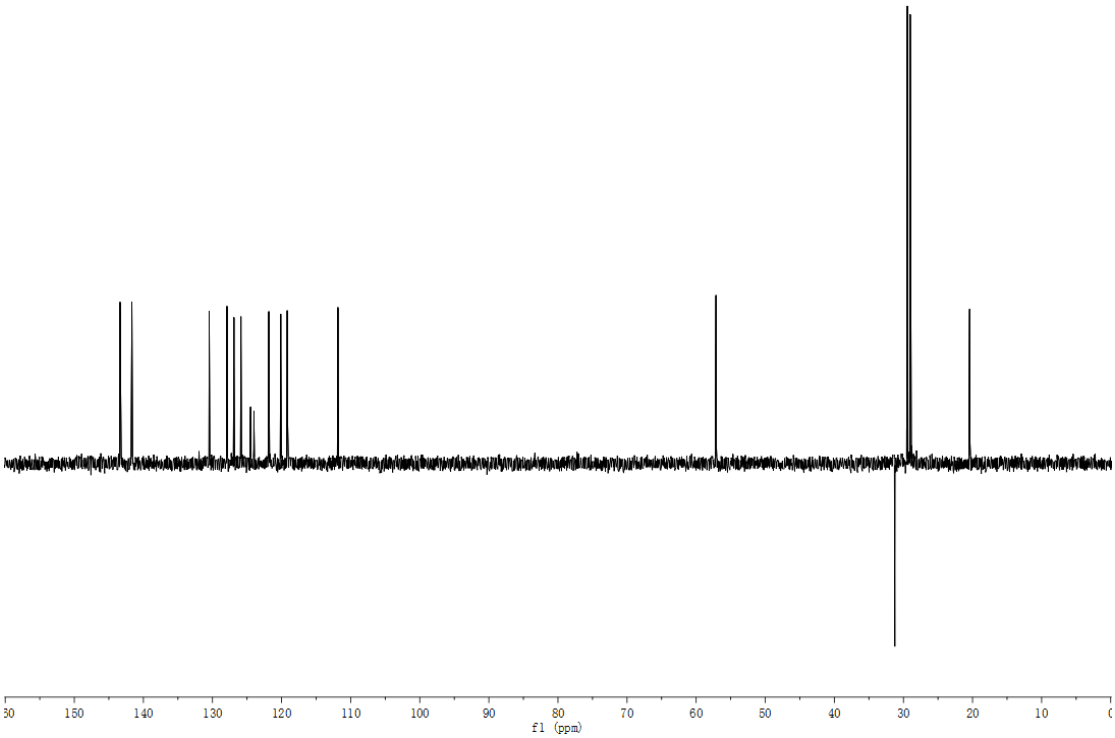
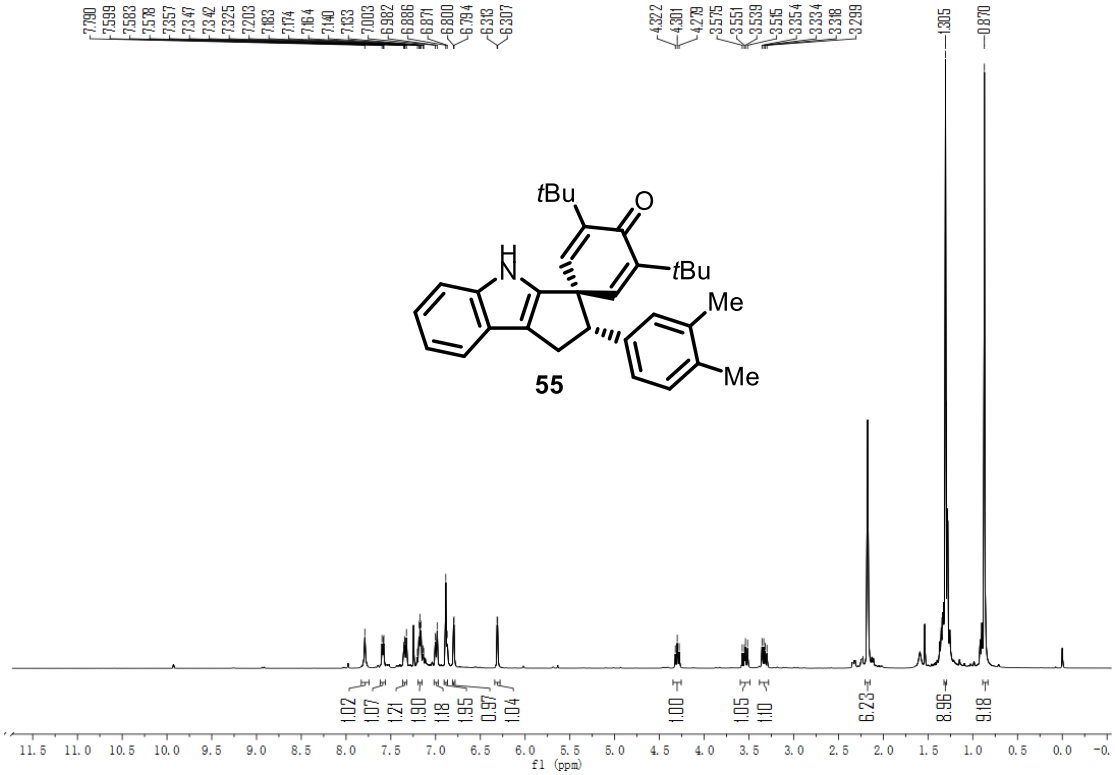
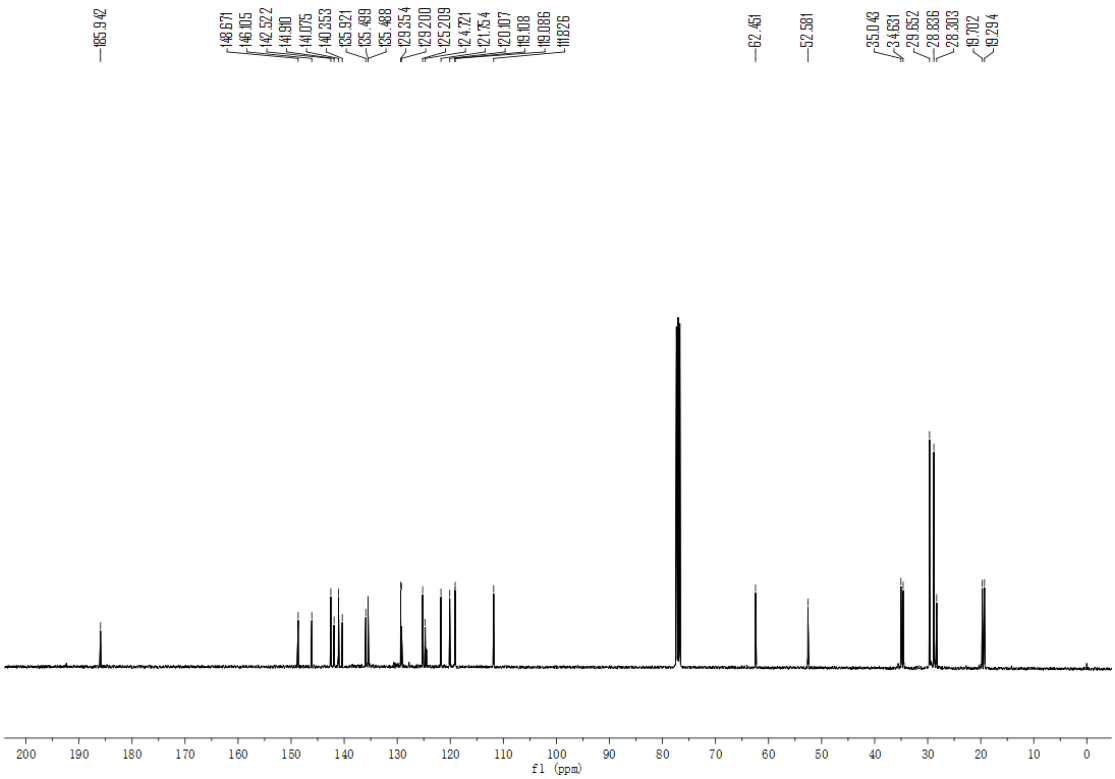


3,5-di-tert-butyl-2'-(3,4-dimethylphenyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (55)

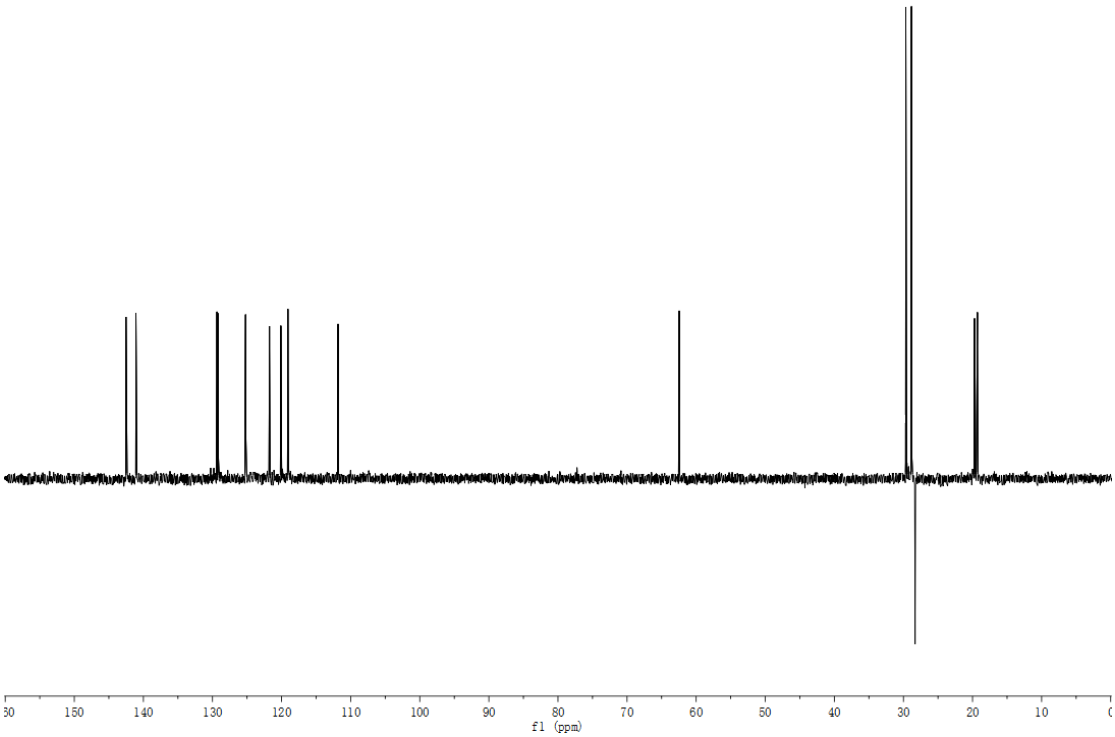
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):

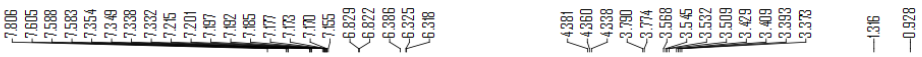


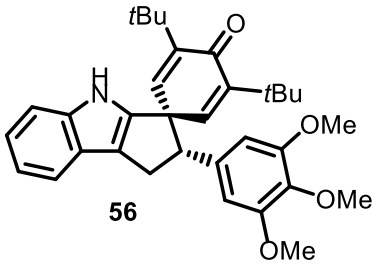
DEPT



3,5-di-tert-butyl-2'-(3,4,5-trimethoxyphenyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1, 3'-cyclopenta[b]indole]-2,5-dien-4-one (56)

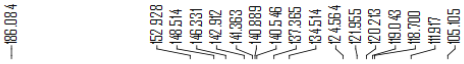
^{1}H NMR (400 MHz, $CDCl_3$):

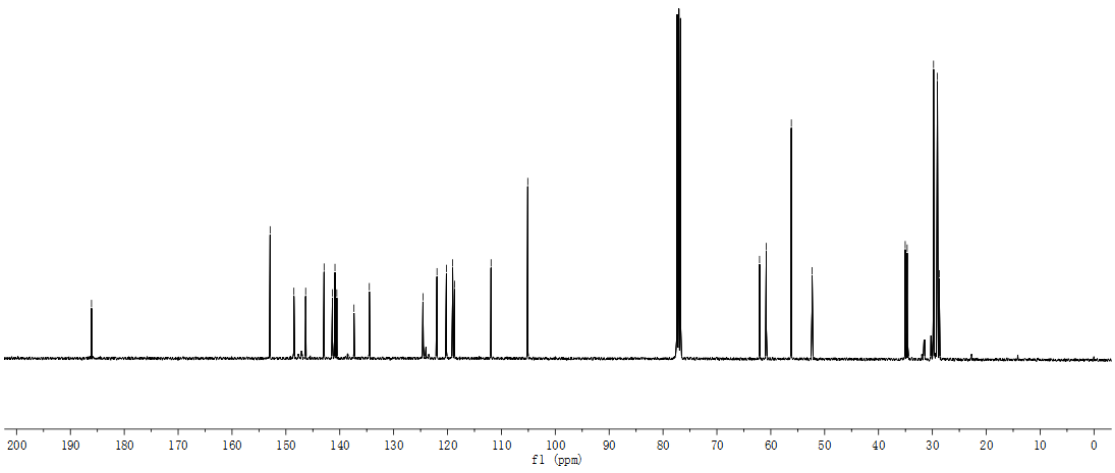




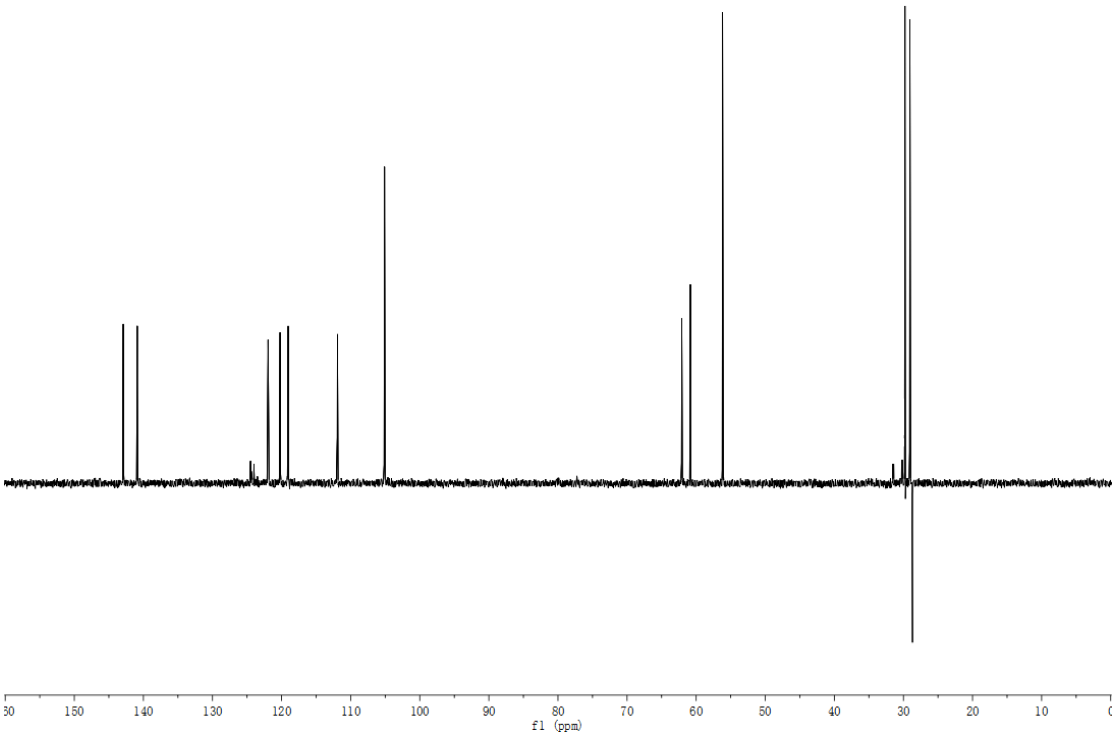
56

^{13}C NMR (100 MHz, $CDCl_3$):



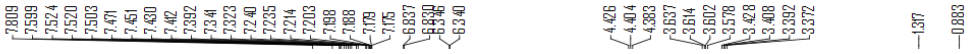


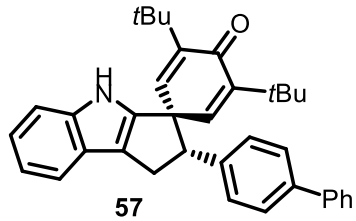
DEPT



2'-([1,1'-biphenyl]-4-yl)-3,5-di-tert-butyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (57)

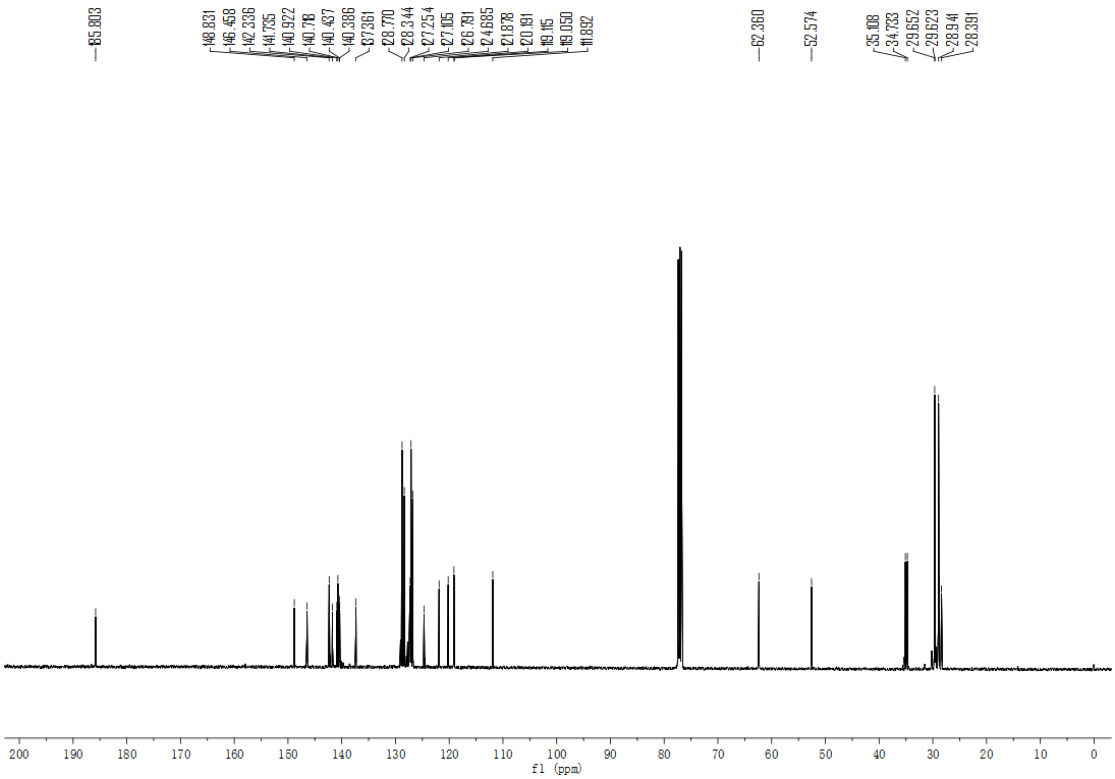
^{1}H NMR (400 MHz, $CDCl_3$):



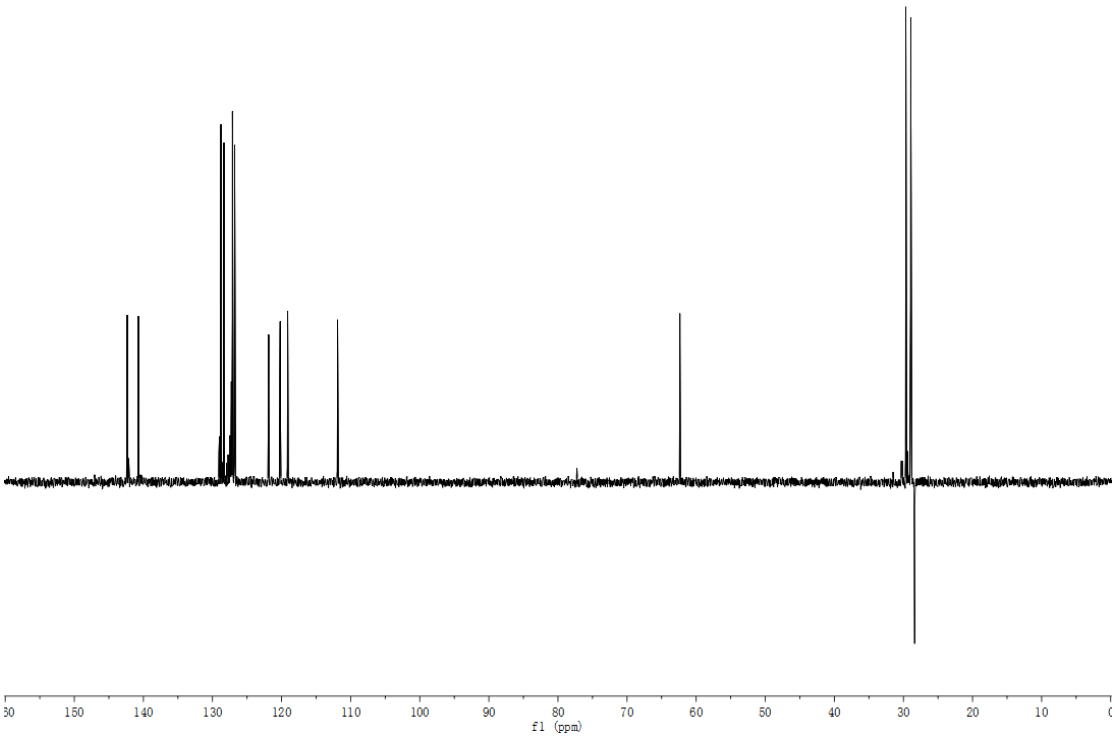


57

^{13}C NMR (100 MHz, $CDCl_3$):

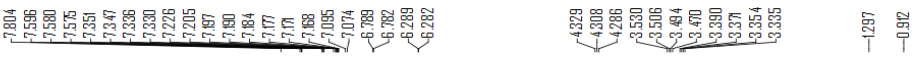


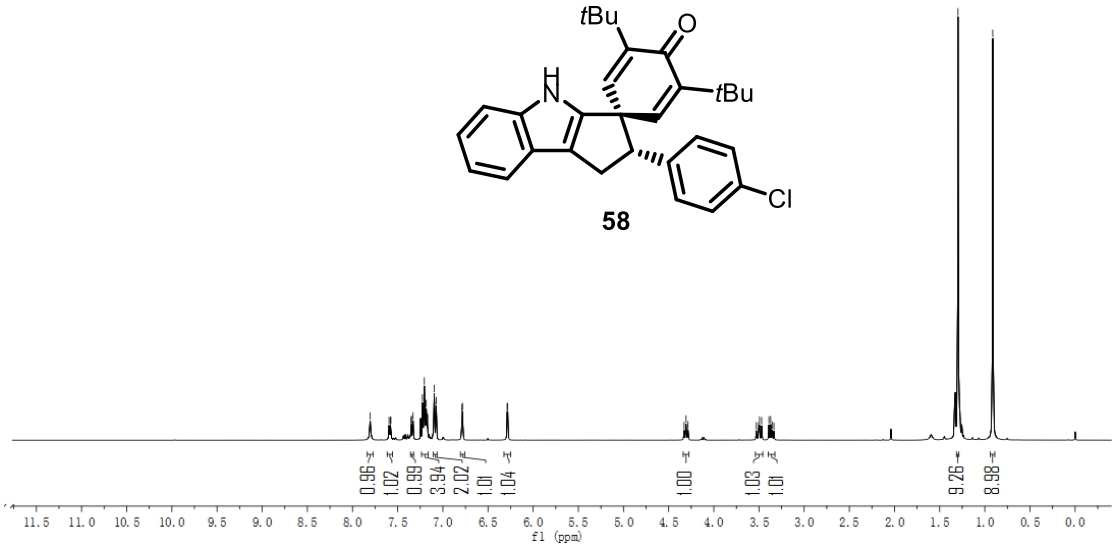
DEPT



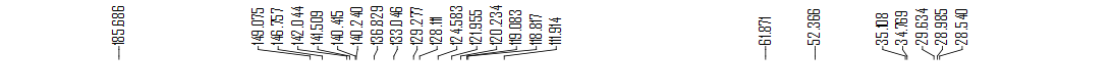
3,5-di-tert-butyl-2'-(4-chlorophenyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (58)

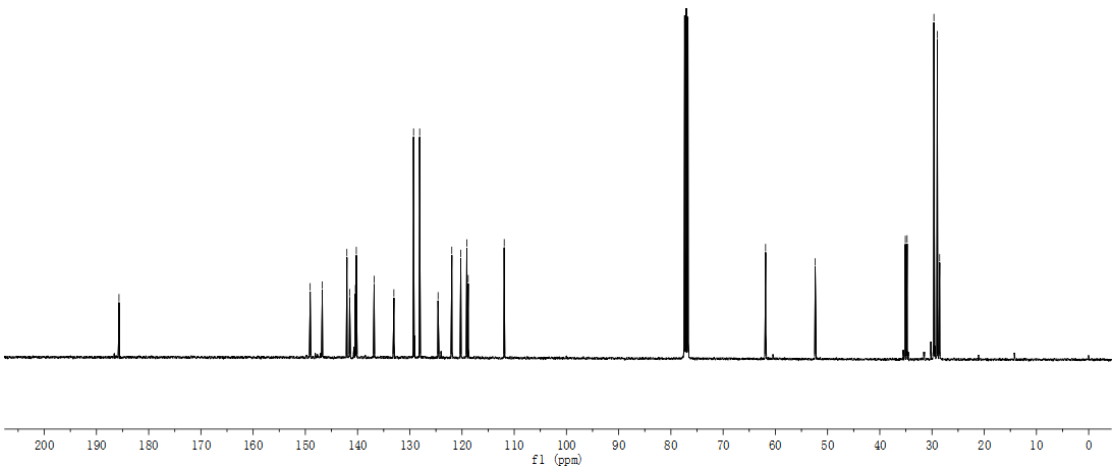
^{1}H NMR (400 MHz, $CDCl_3$):



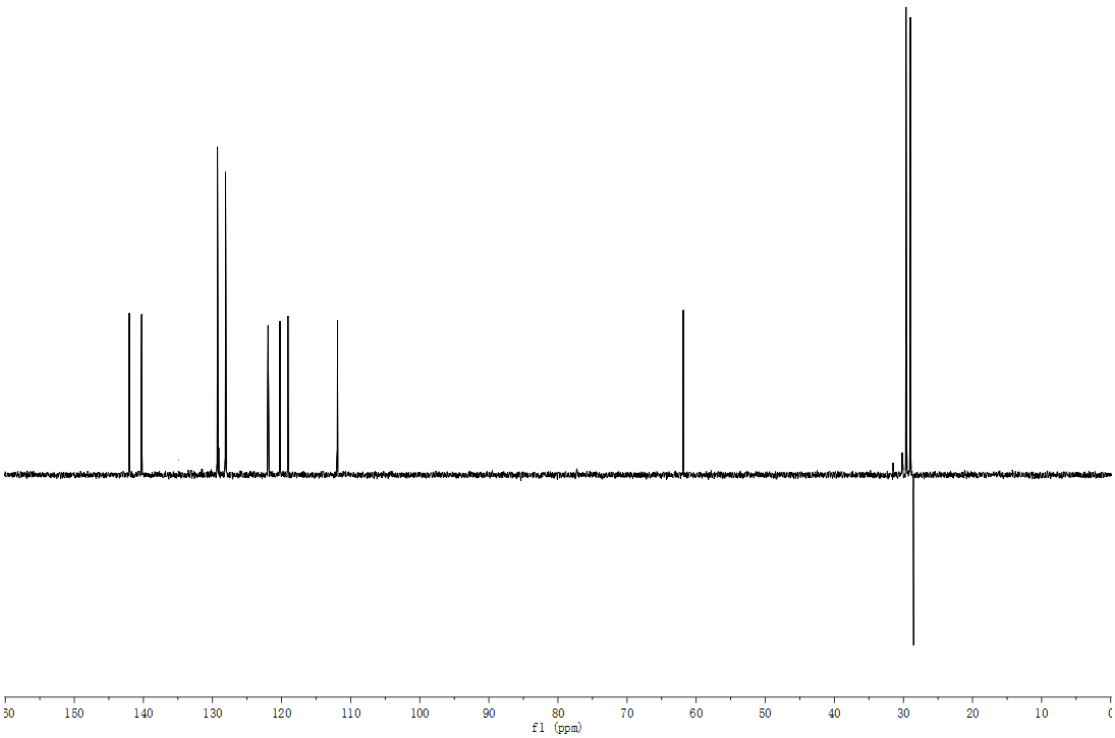


^{13}C NMR (100 MHz, $CDCl_3$):



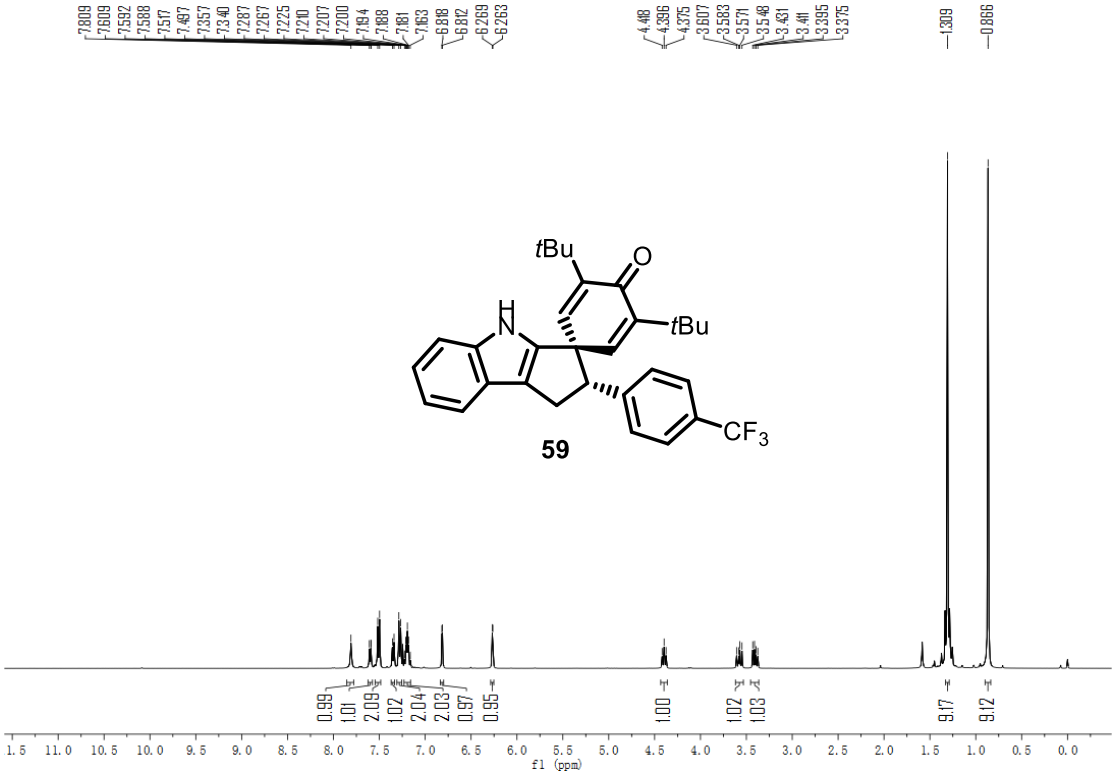


DEPT

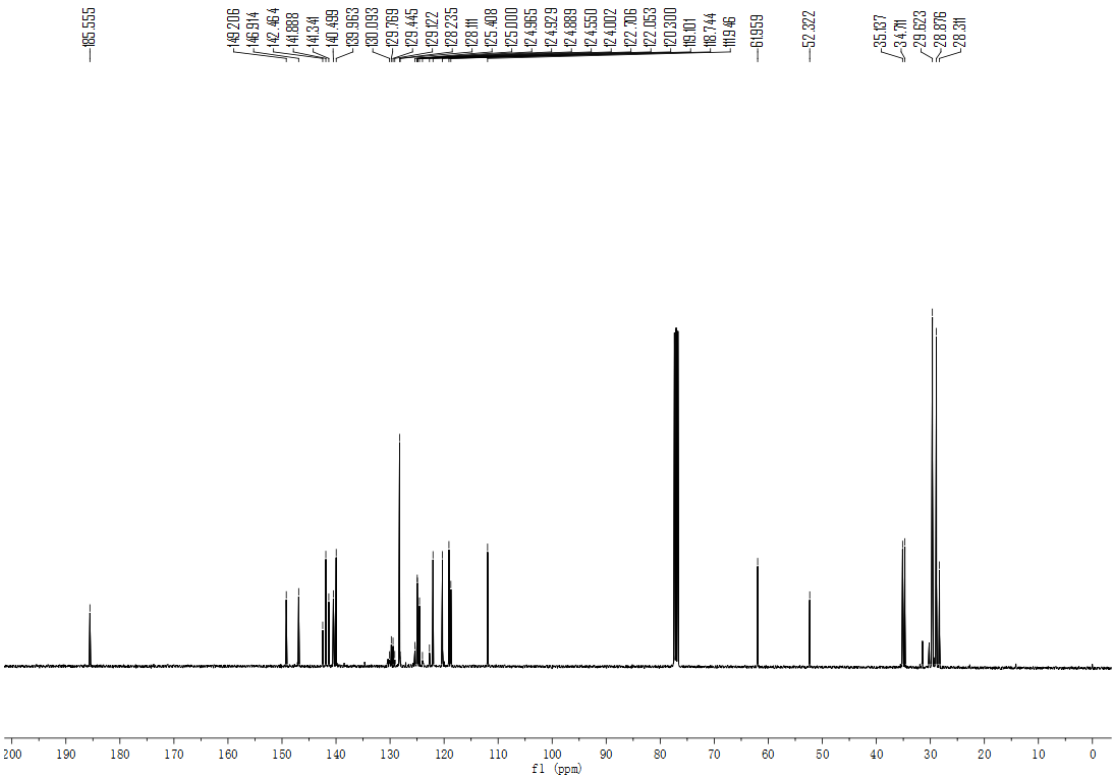


3,5-di-tert-butyl-2'-(4-(trifluoromethyl)phenyl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (59)

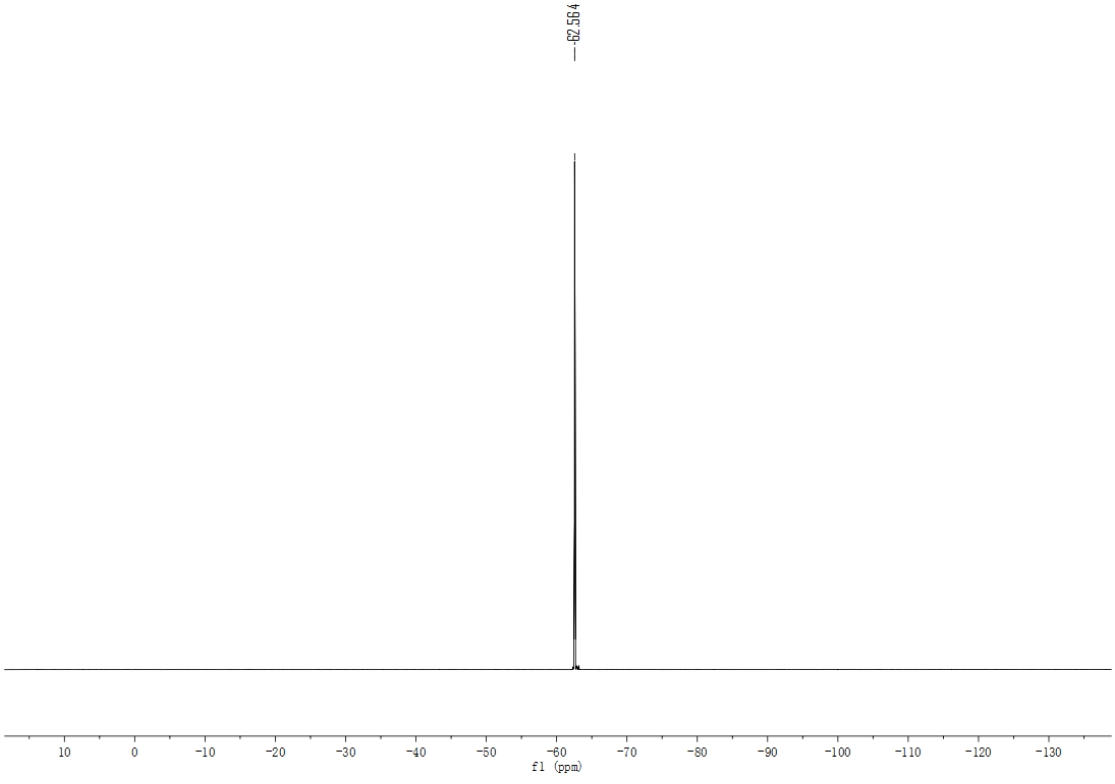
^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



^{19}F NMR (400 MHz, $CDCl_3$):



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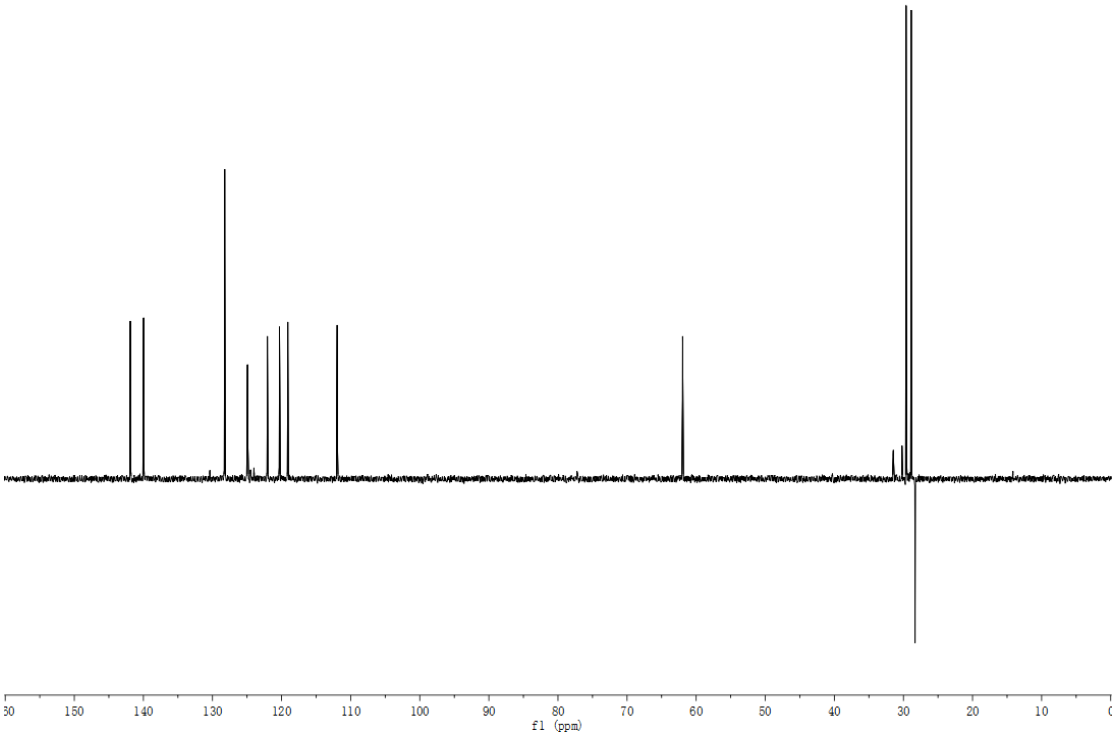
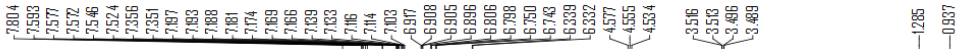
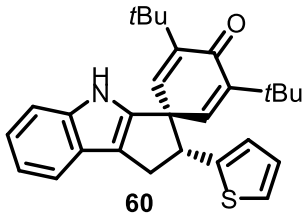


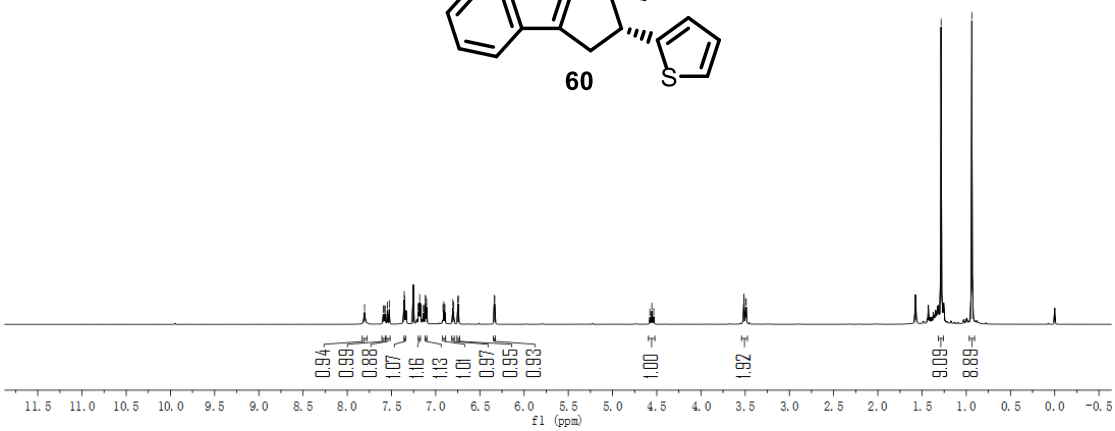
3,5-di-tert-butyl-2'-(thiophen-2-yl)-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (60)

^{1}H NMR (400 MHz, $CDCl_3$):

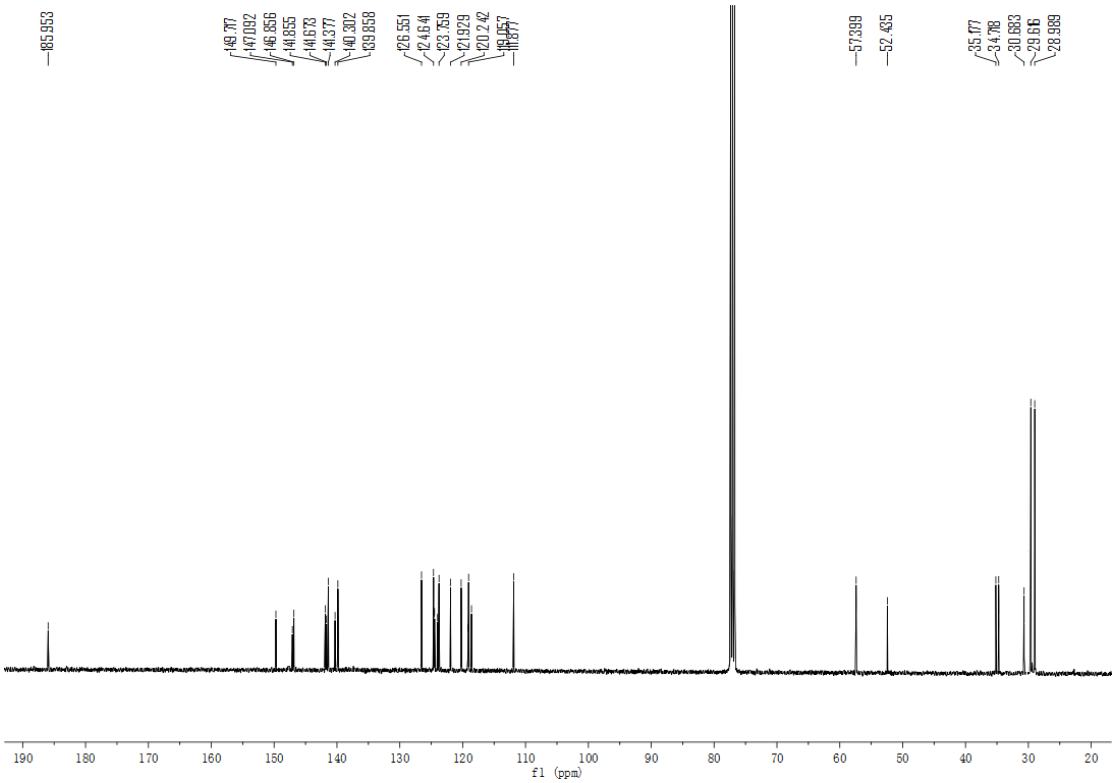




60



^{13}C NMR (100 MHz, $CDCl_3$):



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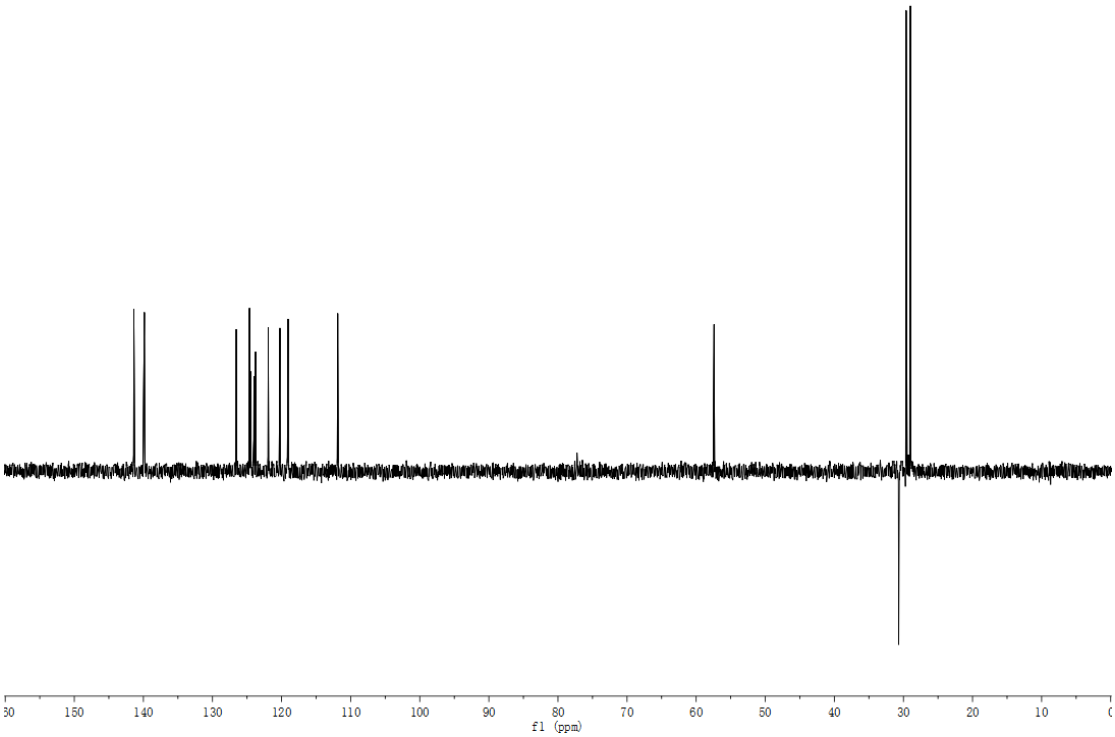
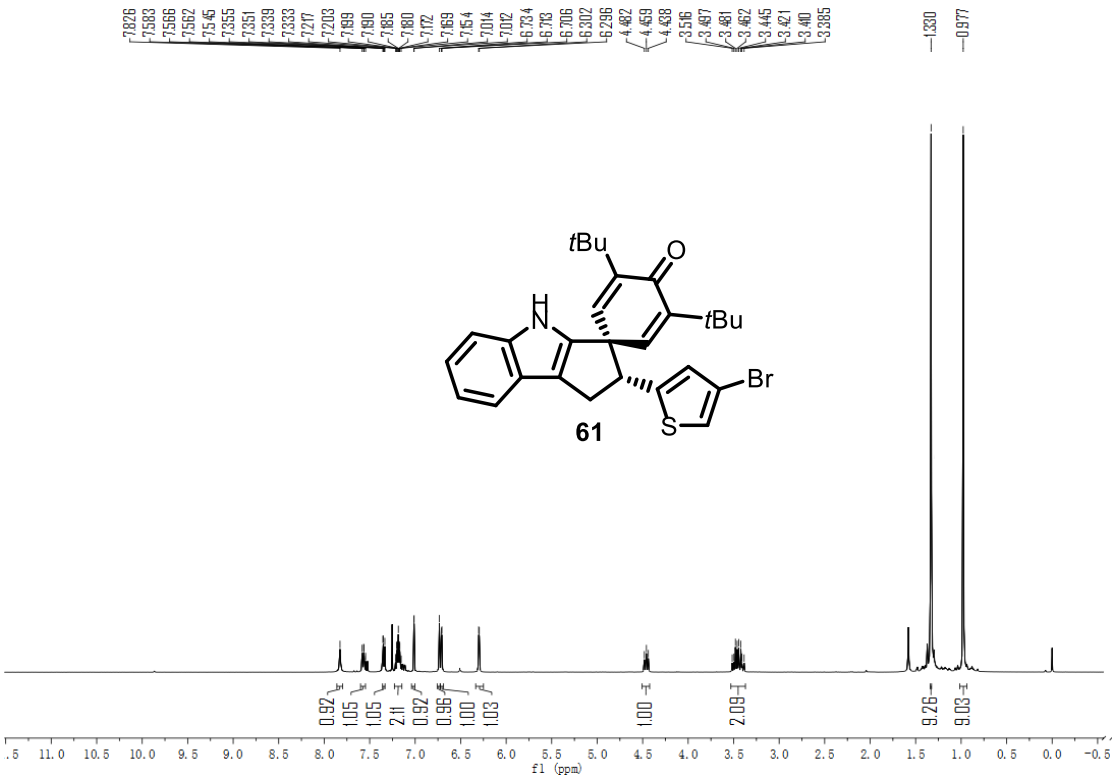
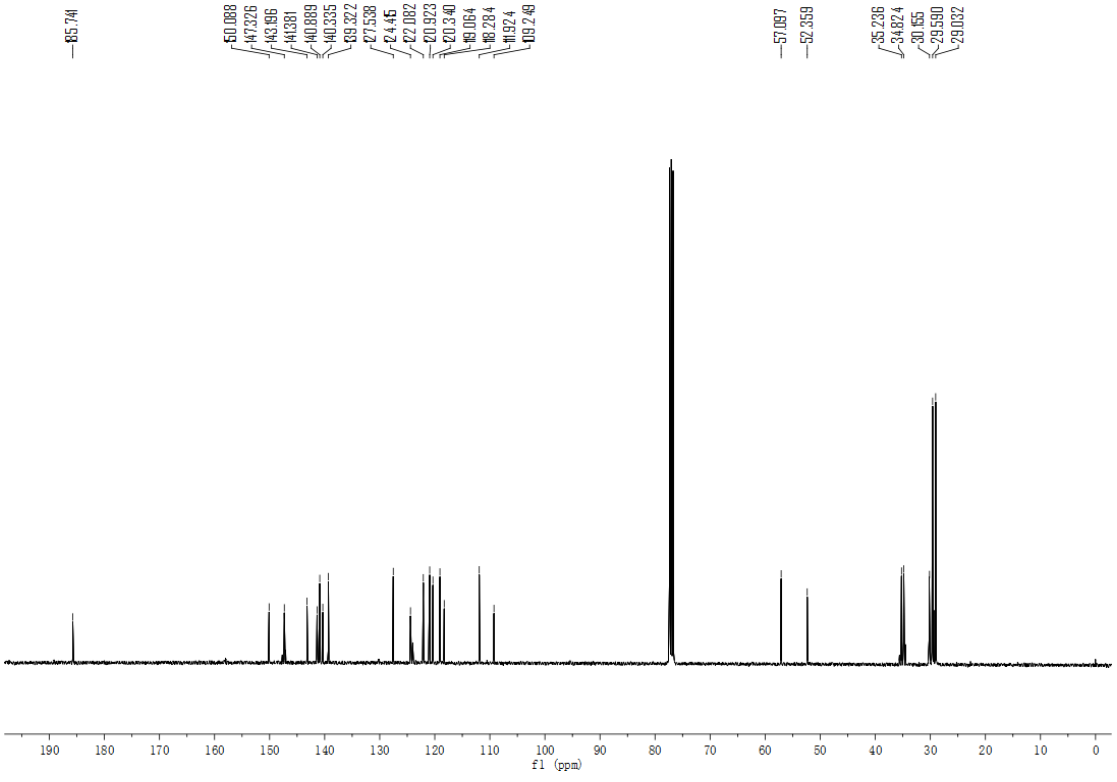


2'-(4-bromothiophen-2-yl)-3,5-di-tert-butyl-1',4'-dihydro-2'H-spiro[cyclohexane-1,3'-cyclopenta[b]indole]-2,5-dien-4-one (61)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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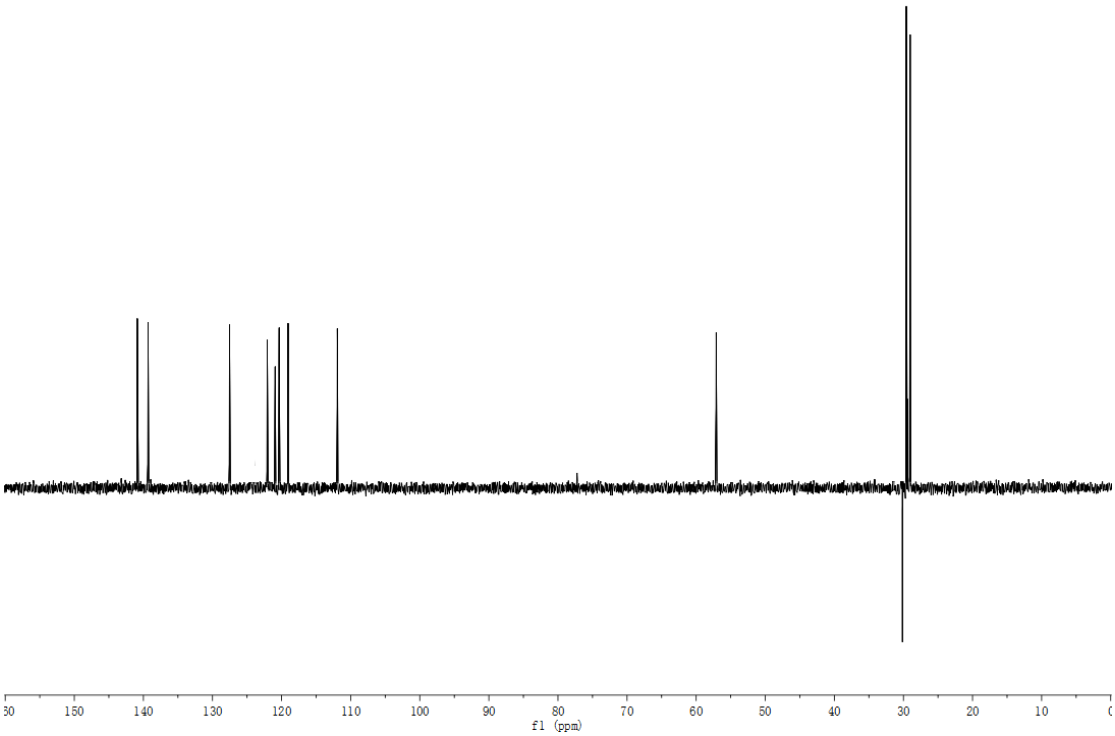
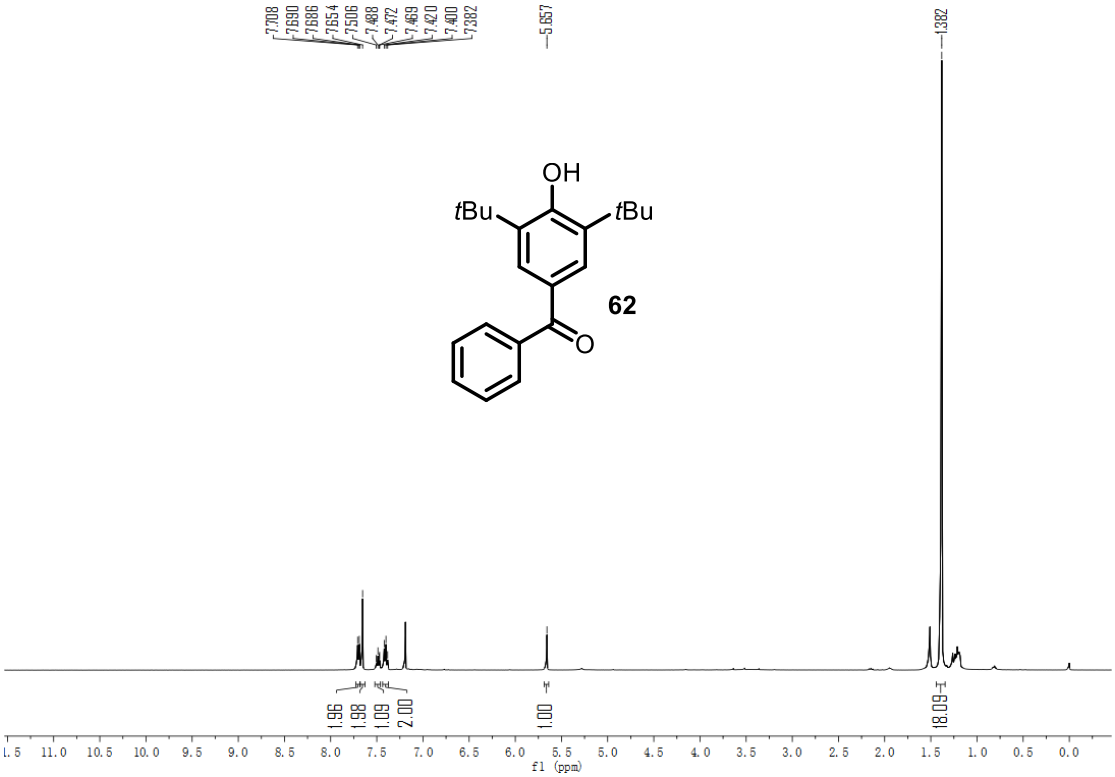
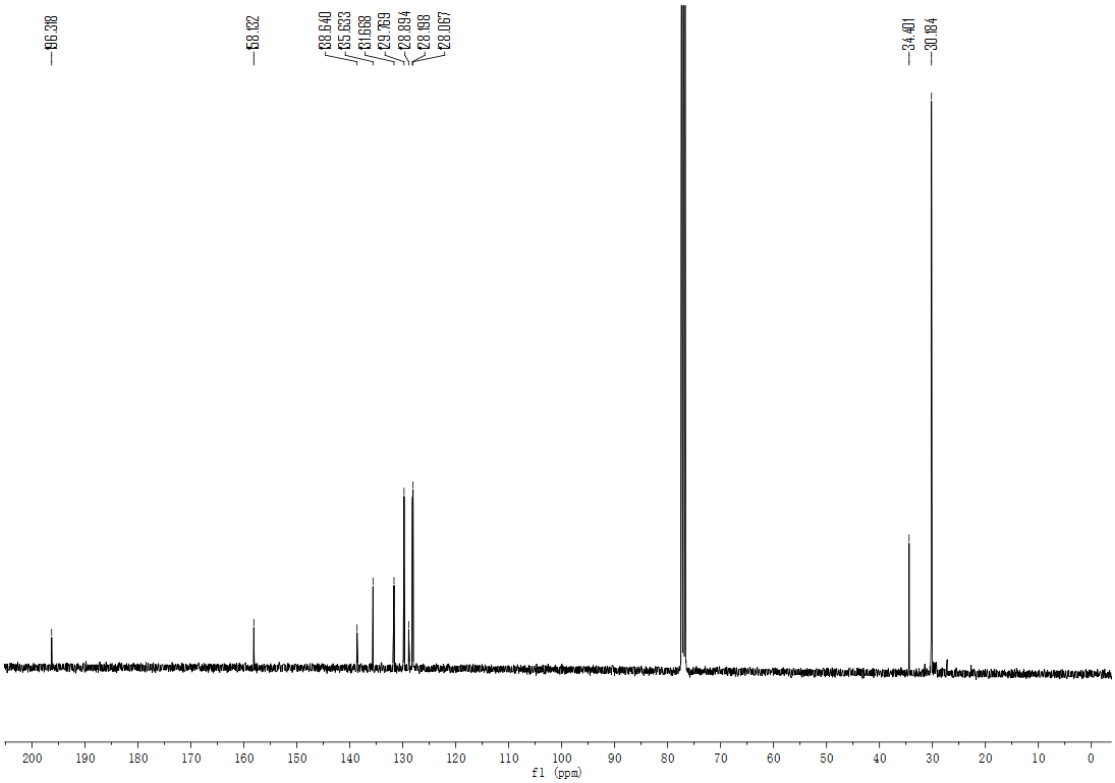


(3,5-di-tert-butyl-4-hydroxyphenyl)(phenyl)methanone (62)

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



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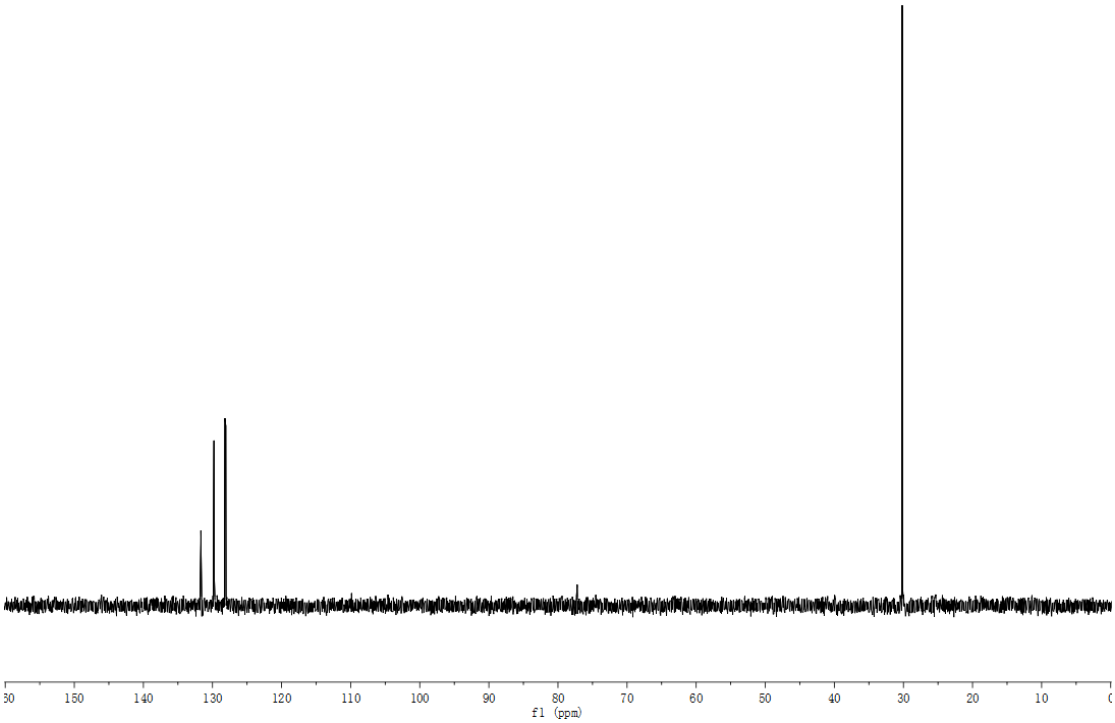
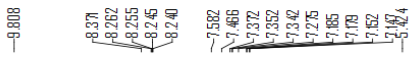
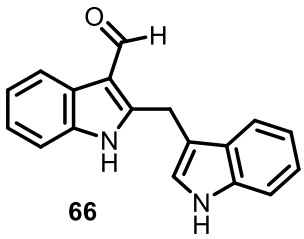


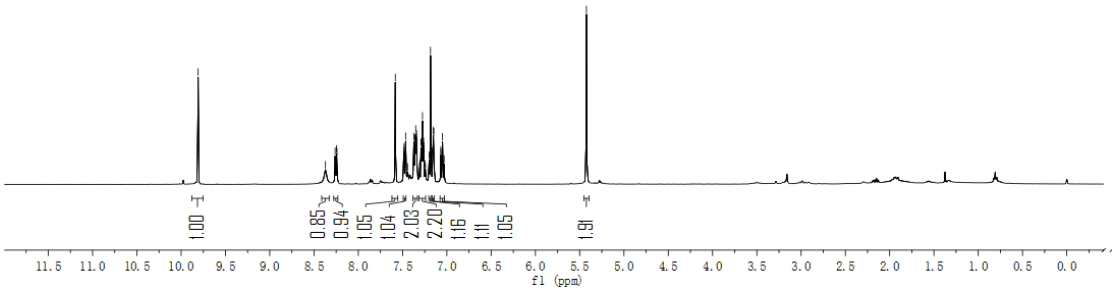
2-((1H-indol-3-yl)methyl)-1H-indole-3-carbaldehyde (66)

^{1}H NMR (400 MHz, $CDCl_3$):

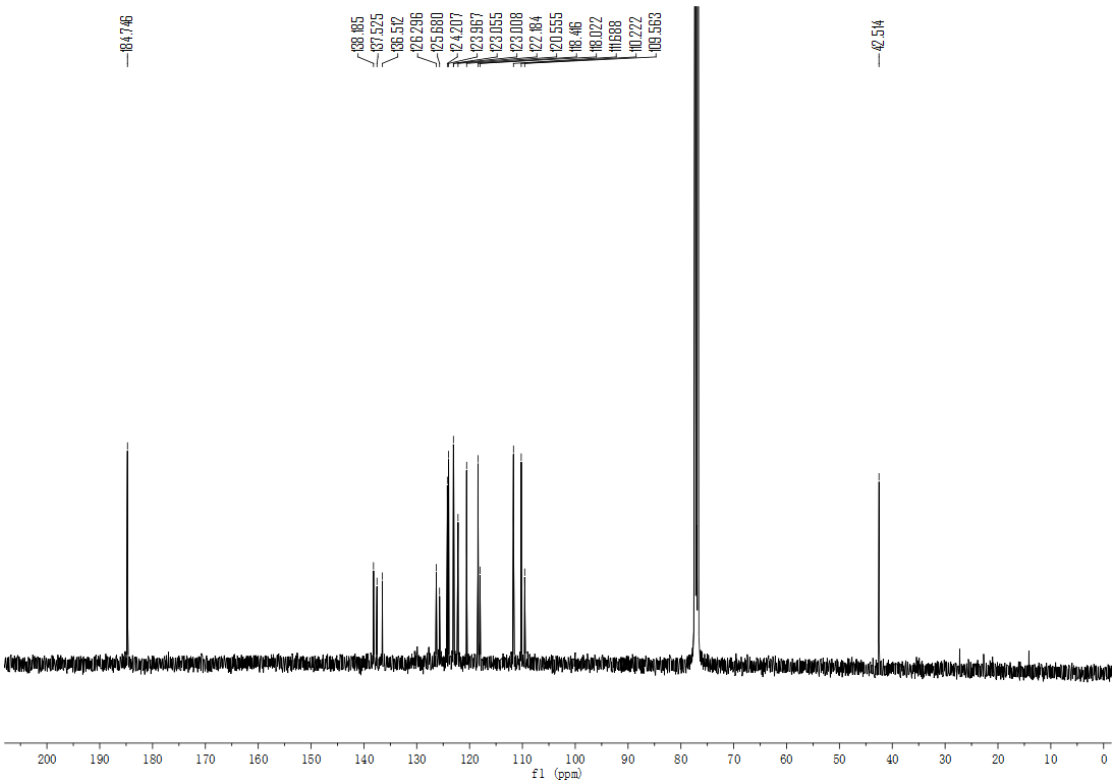




66



^{13}C NMR (100 MHz, $CDCl_3$):



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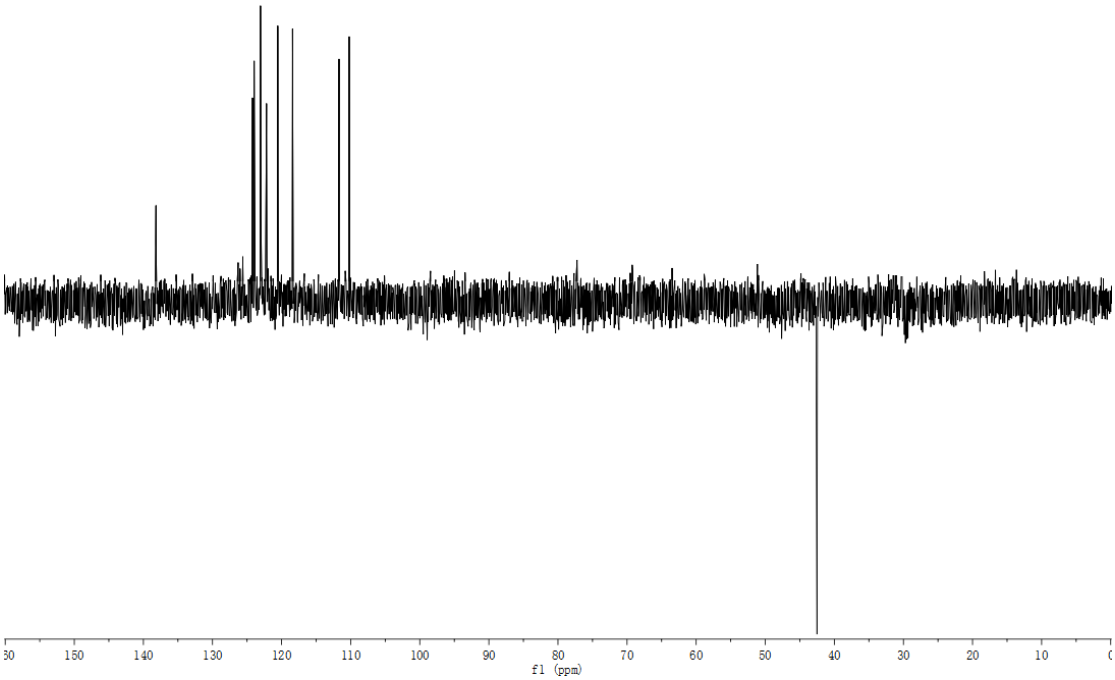
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)