Divergent synthesis of oxindole derivatives via controllable reaction of isatin-derived *para*-quinone methides with sulfur ylides

Yong You,*[a] Bao-Xue Quan,[b] Zhen-Hua Wang,[a] Jian-Qiang Zhao,[a] and Wei-Cheng Yuan*[a,b]

[a]Institute for Advanced Study, Chengdu University, Chengdu 610106, China

[b]Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, China

youyong@cdu.edu.cn, yuanwc@cioc.ac.cn

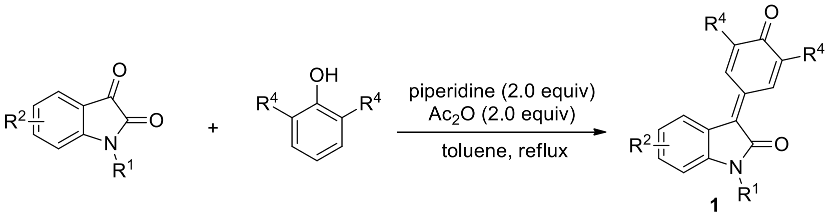
Supporting Information

Table of Contents

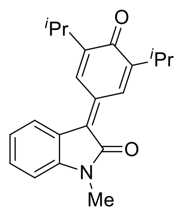
1. General Information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$. ^1H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm). HRMS was recorded on Bruker Q TOF. Melting points were recorded on a Büchi Melting Point B-545.

2. General procedure for the synthesis of isatin-derived *p*-QMs 1



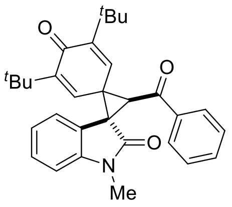
Isatin-derived *p*-QMs **1** were prepared according to the reference[1], isatins (10 mmol) and substituted phenols (10 mmol) were dissolved in toluene (20 mL). Piperidine (20 mmol) was added slowly over 1 h to the mixture at the reflux temperature. Then the mixture continued to reflux for 3 h. After cooling just below the boiling point of toluene, acetic anhydride (20 mmol) was added in one portion, and then the solution was stirred for another 15 min. After cooling to room temperature, the mixture was diluted by EtOAc (30 mL), washed with water (20 mL) and brine (20 mL) sequentially. After that, the resulting product was dried over Na_2SO_4, filtered, concentrated by rotary evaporators. The residues were purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the *p*-QMs **1** as red to reddish black solid.



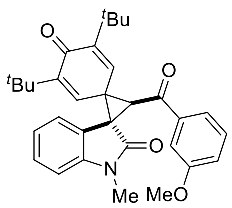
3-(3,5-diisopropyl-4-oxocyclohexa-2,5-dien-1-ylidene)-1-methylindolin-2-one (1i): reddish black solid, 3% yield, mp 136.5–138.3 ℃. ^1H NMR (300 MHz, $CDCl_3$) δ 9.07 (d, *J* = 1.5 Hz, 1H), 7.81 (d, *J* = 2.6 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 3.28–3.12 (m, 5H), 1.21 (t, *J* = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.7, 168.1, 150.3, 149.0, 145.1, 137.8, 131.5, 129.3, 128.5, 127.8, 126.4, 122.7, 116.5, 108.8, 27.5, 27.4, 26.0, 22.3, 22.2; HRMS (ESI-TOF) calcd. for $C_{21}H_{23}NNaO_2$ $[M + Na]^+$ 344.1621; found: 344.1613.

3. General procedure for the synthesis of spirocyclopropyl oxindoles 3

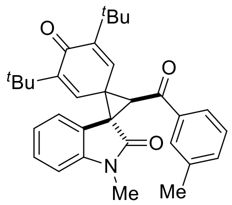
In an ordinary vial equipped with a magnetic stirring bar, the sulfur ylides **2** (0.12 mmol, 1.2 equiv) were added to a solution of isatin-derived *p*-QMs **1** (0.10 mmol, 1.0 equiv) in ethyl acetate (1.0 mL) at 25 ^oC. And then, the mixture was stirred at the same temperature for specified time. After completion of the reaction, as indicated by TLC, the ethyl acetate was evaporated under vacuum at 30 ^oC and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15/1～10/1) to afford the spirocyclopropyl oxindoles **3**.



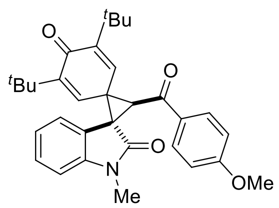
3a: off-white solid; 42.5 mg, 91% yield; 16:1 dr; mp 188.9–190.5 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92–7.80 (m, 2H), 7.58–7.48 (m, 3H), 7.43 (t, J = 7.6 Hz, 2H), 7.35–7.27 (m, 2H), 7.08 (t, J = 7.7 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 4.38 (s, 1H), 3.31 (s, 3H), 1.30 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 185.4, 172.0, 151.0, 150.8, 144.4, 137.0, 136.1, 134.1, 133.4, 129.0, 128.6, 128.5, 125.8, 122.9, 122.5, 108.8, 47.5, 45.4, 42.8, 36.0, 35.8, 29.6, 29.3, 27.1; HRMS (ESI-TOF) calcd. for $C_{31}H_{33}NNaO_3$ $[M + Na]^+$ 490.2353; found: 490.2346.



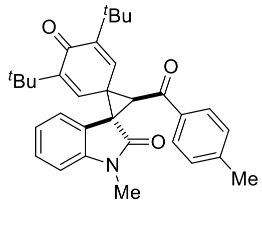
3b: off-white solid; 48.0 mg, 97% yield; 15:1 dr; mp 160.2–161.9 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.46 (m, 2H), 7.46-7.40 (m, 1H), 7.39–7.32 (m, 2H), 7.32–7.27 (m, 1H), 7.24 (d, J = 2.9 Hz, 1H), 7.14–7.04 (m, 2H), 6.90 (d, J = 7.8 Hz, 1H), 4.35 (s, 1H), 3.79 (s, 3H), 3.31 (s, 3H), 1.29 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 185.4, 172.0, 160.0, 151.0, 150.8, 144.4, 138.2, 136.2, 133.5, 130.0, 128.6, 125.8, 122.8, 122.4, 121.2, 121.1, 112.3, 108.8, 55.5, 47.4, 45.6, 42.8, 36.0, 35.8, 29.5, 29.3, 27.1; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_4$ $[M + Na]^+$ 520.2458; found: 520.2450.



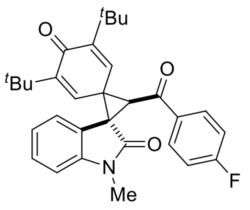
3c: off-white solid; 47.1 mg, 98% yield; 20:1 dr; mp 166.5–168.0 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 1H), 7.61 (s, 1H), 7.54 (d, J = 2.9 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.41–7.27 (m, 3H), 7.22 (d, J = 2.8 Hz, 1H), 7.12–7.02 (m, 1H), 6.90 (d, J = 7.8 Hz, 1H), 4.34 (s, 1H), 3.31 (s, 3H), 2.35 (s, 3H), 1.31 (s, 9H), 1.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 185.4, 172.0, 151.0, 150.8, 144.4, 138.8, 136.9, 136.2, 134.9, 133.6, 129.2, 128.9, 128.6, 125.9, 125.7, 122.9, 122.4, 108.8, 47.3, 45.5, 42.8, 35.9, 35.8, 29.6, 29.3, 27.1, 21.4; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_3$ $[M + Na]^+$ 504.2509; found: 504.2490.



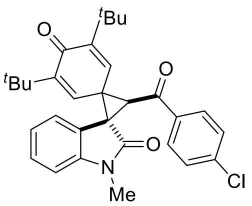
3d: off-white solid; 47.7 mg, 96% yield; 18:1 dr; mp 190.2–193.5 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.9 Hz, 2H), 7.55–7.46 (m, 2H), 7.35–7.26 (m, 2H), 7.06 (t, J = 7.7 Hz, 1H), 6.89 (d, J = 8.9 Hz, 3H), 4.34 (s, 1H), 3.84 (s, 3H), 3.30 (s, 3H), 1.29 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 185.4, 172.1, 164.3, 150.8, 150.5, 144.4, 136.3, 133.9, 131.0, 130.0, 128.5, 125.7, 123.0, 122.4, 114.1, 108.8, 55.7, 47.4, 45.4, 42.7, 35.9, 35.8, 29.6, 29.3, 27.1; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_4$ $[M + Na]^+$ 520.2458; found: 520.2455.



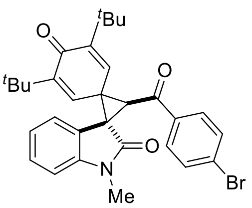
3e: off-white solid; 48.3 mg, 99% yield; 19:1 dr; mp 149.4–151.1 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.56–7.47 (m, 2H), 7.35–7.27 (m, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.07 (t, J = 7.7 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 4.36 (s, 1H), 3.30 (s, 3H), 2.38 (s, 3H), 1.30 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 185.4, 172.1, 150.9, 150.7, 145.2, 144.4, 136.2, 134.6, 133.6, 129.7, 128.7, 128.5, 125.8, 123.0, 122.4, 108.8, 47.5, 45.5, 42.8, 36.0, 35.8, 29.6, 29.3, 27.1, 21.8; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_3$ $[M + Na]^+$ 504.2509; found: 504.2489.



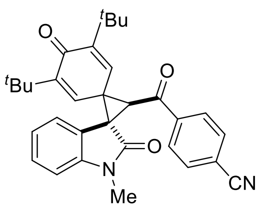
3f: off-white solid; 39.9 mg, 82% yield; 16:1 dr; mp 152.5–154.3 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.83 (m, 2H), 7.54–7.45 (m, 2H), 7.35–7.27 (m, 2H), 7.15–7.03 (m, 3H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.33 (s, 1H), 3.31 (s, 3H), 1.29 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 185.3, 172.0, 166.4 (d, *J* = 255.4 Hz, 1C), 151.1, 150.9, 144.4, 135.9, 133.2, 131.3 (d, *J* = 9.5 Hz, 1C), 128.7, 125.7, 122.7, 122.5, 122.2 (d, *J* = 20.3 Hz, 1C), 116.2 (d, *J* = 22.5 Hz, 1C), 108.9, 47.4, 45.3, 42.7, 36.0, 35.8, 29.6, 29.3, 27.1; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}FNNaO_3$ $[M + Na]^+$ 508.2258; found: 508.2271.



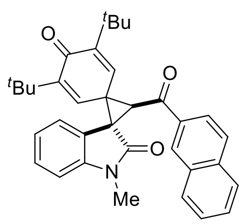
3g: off-white solid; 46.0 mg, 92% yield; 16:1 dr; mp 136.5–138.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84–7.76 (m, 2H), 7.53–7.45 (m, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.34–7.28 (m, 2H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.33 (s, 1H), 3.31 (s, 3H), 1.29 (s, 9H), 1.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.5, 185.3, 171.9, 151.0, 150.9, 144.4, 140.8, 135.9, 135.3, 133.1, 129.9, 129.4, 128.7, 125.7, 122.7, 122.5, 108.9, 47.5, 45.2, 42.7, 36.0, 35.8, 29.6, 29.3, 27.1; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}ClNNaO_3$ $[M + Na]^+$ 524.1963; found: 524.1953.



3h: off-white solid; 47.8 mg, 82% yield; 16:1 dr; mp 147.6–149.4 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.7 Hz, 2H), 7.61–7.56 (m, 2H), 7.52–7.45 (m, 2H), 7.36–7.28 (m, 2H), 7.11–7.04 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.32 (s, 1H), 3.31 (s, 3H), 1.29 (s, 9H), 1.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 185.3, 171.9, 151.1, 151.0, 144.4, 135.9, 135.7, 133.1, 132.36, 130.0, 129.6, 128.7, 125.7, 122.6, 122.5, 109.0, 47.5, 45.2, 42.7, 35.8, 30.4, 29.6, 29.4, 27.1; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}BrNNaO_3$ $[M + Na]^+$ 568.1458; found: 568.1439.

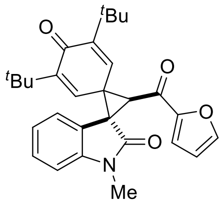


3i: off-white solid; 34.4 mg, 70% yield; 14:1 dr; mp 164.1–165.7 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 2.9 Hz, 1H), 7.37–7.29 (m, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.34 (s, 1H), 3.32 (s, 3H), 1.28 (s, 9H), 1.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 185.2, 171.7, 151.3, 144.4, 139.8, 135.5, 132.8, 132.5, 128.9, 128.8, 125.6, 122.6, 122.4, 117.7, 117.3, 109.1, 47.6, 45.2, 42.7, 36.0, 35.8, 29.5, 29.3, 27.2; HRMS (ESI-TOF) calcd. for $C_{32}H_{32}N_2NaO_3$ $[M + Na]^+$ 515.2305; found: 515.2299.

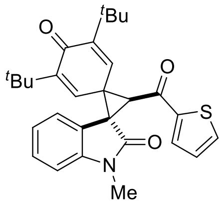


3j: off-white solid; 48.9 mg, 95% yield; 19:1 dr; mp 164.8–166.5 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.8 Hz, 1H), 7.96 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 3H), 7.65–7.50 (m, 4H), 7.36–7.27 (m, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 4.51 (s, 1H), 3.33 (s, 3H), 1.35 (s, 9H), 1.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 185.4, 172.1, 151.0, 150.8, 144.4, 136.2, 136.0, 134.2, 133.6, 132.5, 131.0, 129.8, 129.2, 128.9, 128.6, 127.9, 127.2, 125.9, 123.6, 122.9, 122.5, 108.9, 47.4, 45.5, 42.9, 35.9, 35.8, 29.6, 29.3, 27.1; HRMS (ESI-TOF) calcd. for $C_{35}H_{35}NNaO_3$ [M +

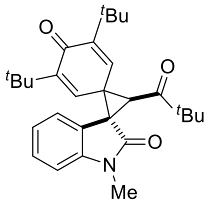
Na]+ 540.2509; found: 540.2497.



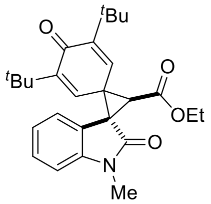
3k: off-white solid; 39.7 mg, 87% yield; >20:1 dr; mp 166.0–167.9 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 2.8 Hz, 1H), 7.61 (d, *J* = 1.5 Hz, 1H), 7.47 (d, *J* = 2.8 Hz, 1H), 7.34–7.26 (m, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.55 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.38 (s, 1H), 3.28 (s, 3H), 1.27 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.6, 181.2, 172.0, 152.9, 150.7, 150.4, 147.6, 144.4, 136.3, 132.8, 128.6, 126.4, 122.8, 122.6, 118.9, 113.0, 108.7, 48.0, 44.6, 42.7, 36.1, 35.7, 29.5, 29.4, 27.1; HRMS (ESI-TOF) calcd. for $C_{29}H_{31}NNaO_4$ $[M + Na]^+$ 480.2145; found: 480.2137.



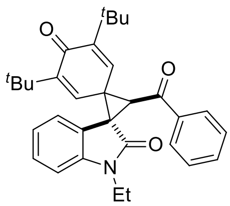
3l: off-white solid; 42.7 mg, 91% yield; >20:1 dr; mp 148.5–150.2 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75–7.64 (m, 3H), 7.52 (d, *J* = 2.9 Hz, 1H), 7.47 (d, *J* = 2.9 Hz, 1H), 7.31 (td, *J* = 7.8, 1.2 Hz, 1H), 7.14–7.05 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 4.33 (s, 1H), 3.29 (s, 3H), 1.28 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.5, 185.2, 172.0, 150.7, 150.6, 144.5, 144.4, 136.1, 135.5, 133.5, 133.1, 128.6, 126.1, 122.8, 122.6, 108.8, 47.8, 45.6, 42.7, 36.0, 35.7, 29.5, 29.4, 27.1; HRMS (ESI-TOF) calcd. for $C_{29}H_{31}NNaO_3S$ $[M + Na]^+$ 496.1917; found: 496.1910.



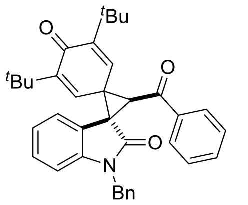
3m: off-white solid; 30.9 mg, 69% yield; >20:1 dr; mp 168.8–170.5 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 1H), 7.38 (s, 2H), 7.31 (td, *J* = 7.7, 1.1 Hz, 1H), 7.10 (td, *J* = 7.7, 1.1 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.98 (s, 1H), 3.27 (s, 3H), 1.25 (s, 9H), 1.22 (s, 9H), 1.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 185.4, 172.0, 150.7, 150.6, 144.3, 136.3, 133.1, 128.6, 126.4, 123.0, 122.5, 108.7, 47.7, 45.5, 44.5, 42.6, 36.0, 35.7, 29.5, 29.5, 27.0, 26.1; HRMS (ESI-TOF) calcd. for $C_{29}H_{37}NNaO_3$ $[M + Na]^+$ 470.2666; found: 470.2667.



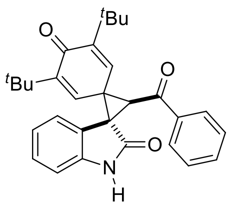
3n: off-white solid; 29.6 mg, 68% yield; >20:1 dr; mp 164.3–165.7 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 2.9 Hz, 1H), 7.39–7.27 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.60 (s, 1H), 3.27 (s, 3H), 1.31–1.24 (m, 12H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.6, 171.9, 167.3, 150.8, 150.3, 144.6, 136.4, 132.6, 128.6, 126.1, 122.8, 122.5, 108.7, 61.9, 46.4, 42.3, 40.9, 36.1, 35.7, 29.5, 27.0, 14.3; HRMS (ESI-TOF) calcd. for $C_{27}H_{33}NNaO_4$ $[M + Na]^+$ 458.2302; found: 458.2300.



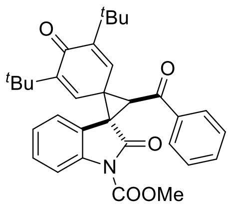
3o: off-white solid; 51.8 mg, 99% yield; >20:1 dr; mp 202.1–203.8 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92–7.79 (m, 2H), 7.62–7.49 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33–7.26 (m, 2H), 7.12–7.01 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 4.38 (s, 1H), 3.86 (q, *J* = 7.2 Hz, 2H), 1.35–1.23 (m, 12H), 1.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.7, 185.4, 171.6, 151.0, 150.8, 143.5, 137.0, 136.2, 134.1, 133.4, 129.0, 128.5, 126.0, 123.0, 122.2, 108.9, 47.5, 45.4, 42.8, 36.0, 35.8, 35.7, 29.6, 29.3, 12.9; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_3$ $[M + Na]^+$ 504.2509; found: 504.2505.



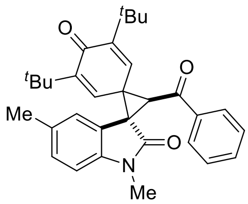
3p: off-white solid; 42.9 mg, 88% yield; 12:1 dr; mp 163.4–165.2 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.62–7.55 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.37–7.27 (m, 6H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.7 Hz, 1H), 5.08 (d, *J* = 15.7 Hz, 1H), 4.95 (d, *J* = 15.5 Hz, 1H), 4.47 (s, 1H), 1.32 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 185.3, 172.3, 151.2, 150.9, 143.5, 136.9, 136.0, 135.7, 134.2, 133.3, 129.0, 128.8, 128.5, 128.4, 128.0, 127.4, 125.8, 122.9, 122.5, 109.6, 47.6, 45.6, 44.6, 43.0, 36.0, 35.8, 29.6, 29.3; HRMS (ESI-TOF) calcd. for $C_{37}H_{38}NO_3$ $[M + H]^+$ 544.2846; found: 544.2841.



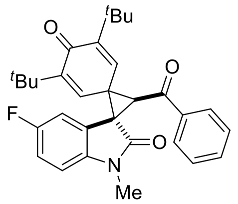
3q: off-white solid; 27.1 mg, 60% yield; 15:1 dr; mp 190.7–192.3 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.94–7.82 (m, 2H), 7.62–7.54 (m, 1H), 7.54–7.39 (m, 4H), 7.30 (d, *J* = 2.8 Hz, 1H), 7.26–7.20 (m, 1H), 7.11–7.01 (m, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 4.38 (s, 1H), 1.29 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 185.3, 174.2, 151.1, 151.0, 141.5, 136.9, 135.8, 134.2, 133.3, 129.0, 128.6, 128.5, 126.1, 123.3, 122.6, 110.6, 47.9, 45.4, 43.0, 36.0, 35.8, 29.6, 29.3; HRMS (ESI-TOF) calcd. for $C_{30}H_{32}NO_3$ $[M + H]^+$ 454.2377; found: 454.2365.



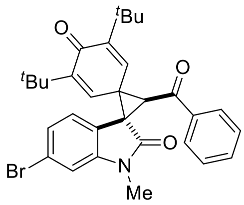
3r: off-white solid; 47.5 mg, 93% yield; 9:1 dr; mp 159.1–160.7 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.89–7.81 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 3H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.26–7.20 (m, 2H), 7.20–7.13 (m, 1H), 4.40 (s, 1H), 4.05 (s, 3H), 1.29 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 185.0, 170.4, 151.7, 151.3, 151.2, 140.1, 136.6, 134.8, 134.4, 132.8, 129.1, 129.0, 128.6, 125.0, 124.6, 122.0, 115.4, 54.3, 47.8, 45.7, 44.0, 36.0, 35.8, 29.6, 29.3; HRMS (ESI-TOF) calcd. for $C_{32}H_{33}NNaO_5$ $[M + Na]^+$ 534.2251; found: 534.2252.



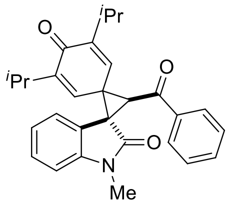
3s: off-white solid; 32.5 mg, 68% yield; 15:1 dr; mp 176.9–178.6 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91–7.51 (m, 2H), 7.62–7.53 (m, 1H), 7.49 (d, *J* = 2.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (s, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 4.38 (s, 1H), 3.29 (s, 3H), 2.36 (s, 3H), 1.29 (s, 9H), 1.15 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 185.4, 171.9, 150.8, 150.6, 142.1, 137.0, 136.2, 134.1, 133.7, 131.9, 129.0, 128.9, 128.5, 126.7, 122.9, 108.5, 47.7, 45.5, 42.7, 36.0, 35.8, 29.6, 29.3, 27.1, 21.5; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_3$ $[M + Na]^+$ 504.2509; found: 504.2515.



3t: off-white solid; 26.4 mg, 54% yield; >20:1 dr; mp 173.1–174.7 °C (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92–7.83 (m, 2H), 7.63–7.55 (m, 1H), 7.52–7.42 (m, 3H), 7.38 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.21 (d, *J* = 2.9 Hz, 1H), 7.07–6.99 (m, 1H), 6.81 (dd, *J* = 8.6, 4.4 Hz, 1H), 4.41 (s, 1H), 3.30 (s, 3H), 1.29 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 185.3, 171.8, 158.9 (d, *J* = 238.3 Hz, 1C), 151.4, 151.3, 140.5, 137.0, 135.7, 134.2, 132.5, 129.1, 128.6, 124.4 (d, *J* = 9.0 Hz, 1C), 114.9 (d, *J* = 23.2 Hz, 1C), 114.3 (d, *J* = 27.8 Hz, 1C), 109.0 (d, *J* = 8.2 Hz, 1C), 47.7, 45.3, 43.0, 36.0, 35.8, 29.6, 29.3, 27.2; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}FNNaO_3$ $[M + Na]^+$ 508.2258; found: 508.2253.



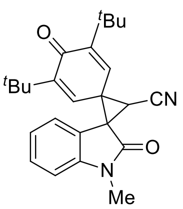
3u: off-white solid; 46.8 mg, 86% yield; 20:1 dr; mp 180.0–181.7 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89–7.81 (m, 2H), 7.62–7.54 (m, 1H), 7.49–7.38 (m, 4H), 7.24–7.17 (m, 2H), 7.04 (d, *J* = 1.9 Hz, 1H), 4.38 (s, 1H), 3.29 (s, 3H), 1.29 (s, 9H), 1.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 185.2, 171.9, 151.3, 151.2, 145.7, 136.8, 135.6, 134.3, 132.7, 129.0, 128.5, 127.0, 125.2, 122.4, 121.8, 112.3, 47.3, 45.3, 43.0, 36.0, 35.8, 29.5, 29.3, 27.2; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}BrNNaO_3$ $[M + Na]^+$ 568.1458; found: 568.1456.



3v: pale yellow solid; 10.5 mg, 24% yield; 15:1 dr; mp 137.4–139.2 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91–7.81 (m, 2H), 7.62-7.53 (m, 2H), 7.49 (d, *J* = 2.9 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35–7.27 (m, 2H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 4.44 (s, 1H), 3.31 (s, 3H), 3.10 (p, *J* = 6.8 Hz, 1H), 2.99 (p, *J* = 6.8 Hz, 1H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 1.8 Hz, 3H), 0.94 (d, *J* = 1.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 184.1, 172.0, 149.2, 144.5, 137.0, 136.2, 134.2, 133.4, 129.0, 128.7, 128.6, 126.0, 122.8, 122.5, 108.8, 47.8, 45.6, 42.7, 27.4, 27.3, 27.1, 22.2, 22.1, 22.0, 21.9; HRMS (ESI-TOF) calcd. for $C_{29}H_{29}NNaO_3$ $[M + Na]^+$ 462.2040; found: 462.2030.

4. Procedure for the synthesis of spirocyclopropyl oxindole 5

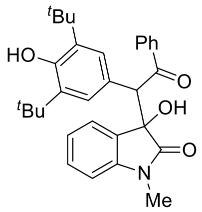
In an ordinary vial equipped with a magnetic stirring bar, the (cyanomethyl)dimethylsulfonium bromide **4** (0.3 mmol, 3.0 equiv) were added to a solution of isatin-derived *p*-QMs **1** (0.10 mmol, 1.0 equiv) and K_2CO_3 (0.3 mmol, 3.0 equiv) in CH_2Cl_2 (1.0 mL) at 25 °C. And then, the mixture was stirred at the same temperature for 14 h. Then, the CH_2Cl_2 was evaporated under vacuum at 30 °C and the residues was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15/1～10/1) to afford the spirocyclopropyl oxindole **5**.



5: white solid; 18.2 mg, 47% yield; >20:1 dr; mp 130.1–131.5 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 2.9 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.99–6.93 (m, 2H), 3.39 (s, 1H), 3.28 (s, 3H), 1.27–1.23 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.1, 170.6, 153.0, 151.6, 144.6, 133.4, 131.2, 129.6, 123.9, 123.0, 121.5, 114.4, 109.4, 39.0, 36.2, 35.8, 30.4, 29.4, 29.3, 27.2, 26.7; HRMS (ESI-TOF) calcd. for $C_{25}H_{28}N_2NaO_2$ $[M + Na]^+$ 411.2043; found: 411.2038.

5. Procedure for the synthesis of 3-hydroxy oxindole 6

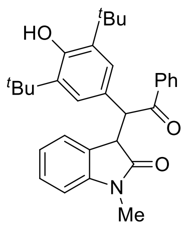
To a solution of **3a** (0.1 mmol, 1.0 equiv) in acetone (2.0 mL) were added *p*-toluenesulfonic acid (TsOH) (0.1 mmol, 1.0 equiv) and H_2O (0.1 mmol, 1.0 equiv) at 25 °C. And then, the mixture was stirred at the same temperature for 2 h. Then H_2O (5 mL) was added and extracted with DCM (5 mL×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8/1～5/1) to afford the 3-hydroxy oxindole **6.**



3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethyl)-3-hydroxy-1-methylindolin-2-one (6): white solid; 30.6 mg, 63% yield; >20:1 dr; mp 157.3–159.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32–7.26 (m, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.83 (s, 2H), 6.56 (d, *J* = 7.8 Hz, 1H), 5.09 (s, 1H), 4.97 (s, 1H), 4.84 (s, 1H), 2.96 (s, 3H), 1.26 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 176.5, 153.6, 143.6, 137.1, 135.7, 133.3, 129.6, 129.0, 128.6, 128.4, 127.3, 126.8, 123.0, 122.6, 107.8, 79.8, 58.3, 34.3, 30.3, 26.0; HRMS (ESI-TOF) calcd. for $C_{31}H_{35}NNaO_4$ $[M + Na]^+$ 508.2458; found: 508.2477.

6. Procedure for the synthesis of oxindole 7

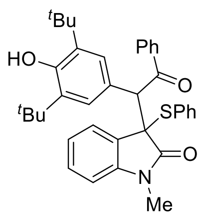
A mixture of **3a** (0.1 mmol) and 10% Pd/C (4.7 mg, 10% w/w) in MeOH (2 mL) was stirred vigorously under an atmosphere of hydrogen at 25 ^{o}C for 2 h. Then, the mixture was filtered through a Celite plug and the filter cake was washed by CH_2Cl_2 (10 mL). Next, it was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to furnish oxindole **7**.



3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethyl)-1-methylindolin-2-one (7): white solid; 41.2 mg, 88% yield; 3:2 dr; mp 155.0–156.6 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87–7.71 (m, 2H), 7.46–7.36 (m, 1H), 7.35–7.27 (m, 2H), 7.26–7.20 (m, 1H), 6.97 (s, 2H), 6.90–6.76 (m, 2H), 6.26 (d, *J* = 7.4 Hz, 1H), 5.49 (d, *J* = 5.3 Hz, 1H), 5.20 (s, 1H), 3.81 (d, *J* = 5.3 Hz, 1H), 3.23 (s, 3H), 1.36 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 176.8, 153.4, 145.1, 136.7, 136.4, 134.7, 132.7, 129.0, 128.4, 127.8, 127.0, 126.3, 124.8, 121.5, 108.0, 55.0, 49.4, 34.6, 30.4, 26.4; HRMS (ESI-TOF) calcd. for $C_{31}H_{35}NNaO_3$ $[M + Na]^+$ 492.2509; found: 492.2514.

7. Procedure for the synthesis of oxindole 8

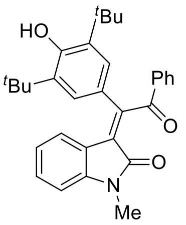
In an oven-dried ordinary vial equipped with a magnetic stirring bar, the thiophenol (0.2 mmol, 2.0 equiv) were added to a solution of compound **3a** (0.10 mmol, 1.0 equiv) and $Zn(OTf)_2$ (0.01 mmol, 0.1 equiv) in CH_2Cl_2 (1.0 mL) at 25 ^{o}C under Ar atmosphere. And then, the mixture was stirred at the same temperature for 2 h. Then, the CH_2Cl_2 was evaporated under vacuum and the residues was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) to afford the oxindole **8**.



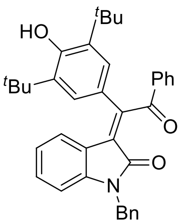
3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethyl)-1-methyl-3-(phenylthio)indolin-2-one (8): white solid; 35.9 mg, 62% yield; >20:1 dr; mp 189.2–190.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55–8.42 (m, 1H), 8.12–7.94 (m, 2H), 7.56–7.45 (m, 1H), 7.44–7.32 (m, 2H), 7.21–7.07 (m, 5H), 7.06–6.96 (m, 2H), 6.83 (s, 2H), 6.32–6.18 (m, 1H), 5.54 (s, 1H), 4.96 (s, 1H), 2.59 (s, 3H), 1.18 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.9, 175.1, 153.4, 143.5, 137.5, 136.8, 135.5, 133.0, 130.1, 129.4, 129.2, 129.1, 128.6, 128.5, 128.2, 126.8, 125.4, 123.4, 122.6, 107.1, 63.0, 57.9, 34.2, 30.3, 25.8; HRMS (ESI-TOF) calcd. for $C_{37}H_{39}NNaO_3S$ $[M + Na]^+$ 600.2543; found: 600.2529.

8. General procedure for the synthesis of *β,β*-disubstituted 3-ylideneoxindoles 9

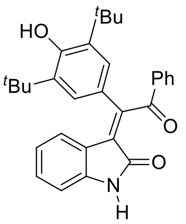
In an ordinary vial equipped with a magnetic stirring bar, the sulfur ylides **2** (0.15 mmol, 1.5 equiv) were added to a solution of isatin-derived *p*-QMs **1** (0.10 mmol, 1.0 equiv) in methanol (1.0 mL) at 25 °C. And then, the mixture was stirred at the same temperature for specified time. After completion of the reaction, as indicated by TLC, the methanol was evaporated under vacuum at 40 °C and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8/1～5/1) to afford the *β*,*β*-disubstituted 3-ylideneoxindoles **9**.



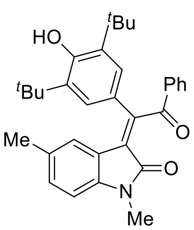
(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethylidene)-1-methylindolin-2-one (9a): yellow solid; 45.8 mg, 98% yield; mp 265.6–267.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11–8.00 (m, 2H), 7.58–7.49 (m, 1H), 7.49–7.40 (m, 4H), 7.30–7.23 (m, 2H), 6.89–6.77 (m, 2H), 5.52 (s, 1H), 3.16 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 166.9, 155.8, 150.9, 144.8, 136.6, 136.1, 133.2, 129.9, 129.1, 128.8, 125.9, 124.7, 124.5, 123.0, 121.7, 121.2, 108.4, 34.7, 30.3, 26.0; HRMS (ESI-TOF) calcd. for $C_{31}H_{34}NO_3$ $[M + H]^+$ 468.2533; found: 468.2526.



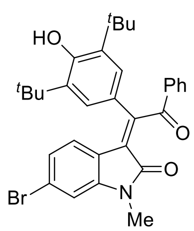
(*Z*)-1-benzyl-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethylidene)indolin-2-one (9b): yellow solid; 53.2 mg, 98% yield; mp 155.8–157.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18–8.03 (m, 2H), 7.59–7.52 (m, 1H), 7.48 (d, *J* = 7.0 Hz, 4H), 7.31–7.25 (m, 6H), 7.15 (td, *J* = 7.8, 1.2 Hz, 1H), 6.81 (td, *J* = 7.7, 1.1 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.53 (s, 1H), 4.88 (brs, 2H), 1.42 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 166.9, 155.8, 151.2, 143.9, 136.6, 136.1, 136.0, 133.3, 129.8, 129.2, 128.8, 128.7, 127.7, 127.6, 125.9, 124.6, 124.5, 123.1, 121.7, 121.3, 109.4, 43.7, 34.7, 30.4; HRMS (ESI-TOF) calcd. for $C_{37}H_{38}NO_3$ $[M + H]^+$ 544.2846; found: 544.2859.



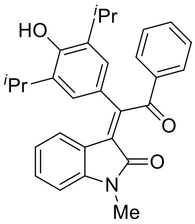
(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethylidene)indolin-2-one (9c): yellow solid; 43.0 mg, 95% yield; mp 158.4–160.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.12–7.98 (m, 2H), 7.58–7.49 (m, 1H), 7.49–7.39 (m, 4H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.14 (td, *J* = 7.7, 1.0 Hz, 1H), 6.78 (td, *J* = 7.7, 0.9 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 5.52 (s, 1H), 1.40 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 168.8, 155.8, 150.9, 142.5, 136.6, 136.2, 133.2, 129.9, 129.2, 128.7, 125.9, 125.3, 124.6, 123.2, 121.7, 121.5, 110.5, 34.7, 30.3; HRMS (ESI-TOF) calcd. for $C_{30}H_{31}NNaO_3$ $[M + Na]^+$ 476.2196; found: 476.2207.



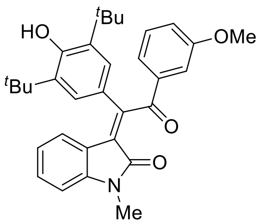
(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethylidene)-1,5-dimethylindolin-2-one (9d): yellow solid; 46.6 mg, 97% yield; mp 247.5–249.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.57–7.37 (m, 5H), 7.17 (s, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 5.52 (s, 1H), 3.13 (s, 3H), 2.21 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 167.0, 155.8, 150.5, 142.6, 136.5, 136.2, 133.2, 130.9, 130.3, 129.1, 128.8, 126.1, 124.8, 124.5, 123.9, 121.1, 108.1, 34.7, 30.3, 26.1, 21.2; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_3$ $[M + Na]^+$ 504.2509; found: 504.2512.



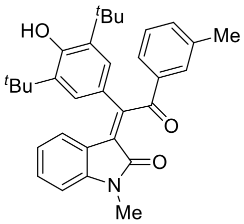
(*Z*)-6-bromo-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethylidene)-1-methylindolin-2-one (9e): yellow solid; 53.5 mg, 98% yield; mp 249.2–251.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12–7.95 (m, 2H), 7.57–7.50 (m, 1H), 7.49–7.40 (m, 4H), 7.15–7.08 (m, 1H), 7.01–6.91 (d, *J* = 7.6 Hz, 2H), 5.55 (s, 1H), 3.14 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 166.7, 156.0, 151.8, 145.8, 136.8, 135.9, 133.4, 129.1, 128.8, 125.9, 124.5, 124.3, 124.0, 123.7, 123.6, 120.1, 111.8, 34.7, 30.3, 26.2; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}BrNNaO_3$ $[M + Na]^+$ 568.1458; found: 568.1482.



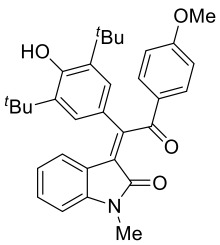
(*Z*)-3-(1-(4-hydroxy-3,5-diisopropylphenyl)-2-oxo-2-phenylethylidene)-1-methylindolin-2-one (9f): yellow solid; 28.9 mg, 66% yield; mp 129.1–130.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15–7.94 (m, 2H), 7.55–7.46 (m, 1H), 7.46–7.37 (m, 2H), 7.35 (s, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.88–6.73 (m, 2H), 5.26 (s, 1H), 3.30–2.96 (m, 5H), 1.22 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 166.9, 152.0, 150.8, 144.8, 135.9, 134.7, 133.2, 130.0, 129.2, 128.8, 125.5, 124.9, 124.5, 123.2, 121.7, 121.3, 108.3, 27.4, 26.0, 22.8; HRMS (ESI-TOF) calcd. for $C_{29}H_{29}NNaO_3$ $[M + Na]^+$ 462.2040; found: 462.2024.



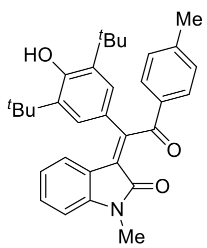
(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(3-methoxyphenyl)-2-oxoethylidene)-1-methylindolin-2-one (9g): yellow solid; 48.0 mg, 97% yield; mp 249.6–251.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68–7.54 (m, 2H), 7.46 (s, 2H), 7.38–7.28 (m, 1H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.11–7.03 (m, 1H), 6.89–6.74 (m, 2H), 5.51 (s, 1H), 3.84 (s, 3H), 3.16 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 166.9, 160.0, 155.8, 150.9, 144.8, 137.4, 136.6, 129.9, 129.8, 125.9, 124.8, 124.6, 123.1, 122.2, 121.7, 121.2, 120.3, 112.5, 108.4, 55.5, 34.7, 30.4, 26.0; HRMS (ESI-TOF) calcd. for $C_{32}H_{36}NO_4$ $[M + H]^+$ 498.2639; found: 498.2647.



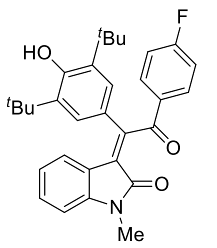
(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-(m-tolyl)ethylidene)-1-methylindolin-2-one (9h): yellow solid; 45.5 mg, 95% yield; mp 289.1–290.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.87–7.78 (m, 1H), 7.46 (s, 2H), 7.39–7.29 (m, 2H), 7.29–7.19 (m, 2H), 6.91–6.75 (m, 2H), 5.50 (s, 1H), 3.16 (s, 3H), 2.38 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 166.9, 155.7, 151.2, 144.8, 138.5, 136.6, 136.1, 134.1, 129.9, 129.6, 128.6, 126.6, 125.9, 124.7, 123.1, 121.7, 121.3, 108.3, 34.7, 30.4, 26.0, 21.5; HRMS (ESI-TOF) calcd. for $C_{32}H_{36}NO_3$ $[M + H]^+$ 482.2690; found: 482.2698.



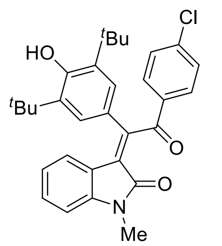
(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-2-oxoethylidene)-1-methylindolin-2-one (9i): yellow solid; 46.0 mg, 93% yield; mp 241.8–243.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.45 (s, 2H), 7.29–7.18 (m, 2H), 6.92 (d, *J* = 7.3 Hz, 2H), 6.87–6.72 (m, 2H), 5.49 (s, 1H), 3.83 (s, 3H), 3.15 (s, 3H), 1.40 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 166.9, 163.7, 155.8, 151.3, 144.7, 136.6, 131.4, 129.8, 129.3, 125.9, 124.9, 124.4, 123.0, 121.6, 121.3, 114.1, 108.3, 55.6, 34.7, 30.4, 26.0; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_4$ $[M + Na]^+$ 520.2458; found: 520.2475.



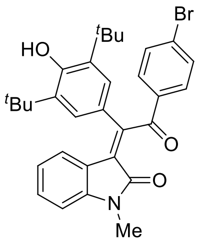
(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-(p-tolyl)ethylidene)-1-methylindolin-2-one (9j): yellow solid; 44.0 mg, 92% yield; mp 291.8–293.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.47 (s, 2H), 7.33–7.18 (m, 4H), 6.92–6.74 (m, 2H), 5.50 (s, 1H), 3.16 (s, 3H), 2.38 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3, 166.9, 155.8, 151.2, 144.8, 144.0, 136.6, 133.7, 129.8, 129.5, 129.2, 125.9, 124.7, 124.5, 123.0, 121.6, 121.3, 108.3, 34.7, 30.4, 26.0, 21.9; HRMS (ESI-TOF) calcd. for $C_{32}H_{35}NNaO_3$ $[M + Na]^+$ 504.2509; found: 504.2511.



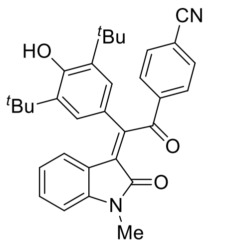
(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4-fluorophenyl)-2-oxoethylidene)-1-methylindolin-2-one (9k): yellow solid; 41.7 mg, 86% yield; mp 298.7–300.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.45 (s, 2H), 7.32–7.22 (m, 2H), 7.11 (t, *J* = 8.6 Hz, 2H), 6.92–6.74 (m, 2H), 5.53 (s, 1H), 3.16 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.2, 167.5, 165.5 (d, *J* = 205.4 Hz, 1C), 155.9, 150.4, 144.8, 136.7, 132.7 (d, *J* = 2.2 Hz, 1C), 131.7 (d, *J* = 9.0 Hz, 1C), 130.0, 125.9, 124.8, 124.4, 123.1, 121.8, 121.1, 116.0 (d, *J* = 22.5 Hz, 1C), 108.4, 34.7, 30.3, 26.0; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}FNNaO_3$ $[M + Na]^+$ 508.2258; found: 508.2269.



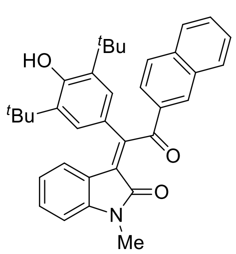
(*Z*)-3-(2-(4-chlorophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxoethylidene)-1-methylindolin-2-one (9l): yellow solid; 44.2 mg, 88% yield; mp 281.9–283.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.50–7.35 (m, 4H), 7.32–7.22 (m, 2H), 6.84 (q, *J* = 7.8 Hz, 2H), 5.54 (s, 1H), 3.16 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 166.9, 156.0, 150.2, 144.9, 139.6, 136.8, 134.6, 130.4, 130.1, 129.2, 125.9, 124.9, 124.3, 123.1, 121.8, 121.1, 108.5, 34.7, 30.4, 26.0; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}ClNNaO_3$ $[M + Na]^+$ 524.1963; found: 524.1986.



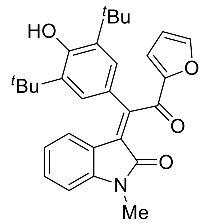
(*Z*)-3-(2-(4-bromophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxoethylidene)-1-methylindolin-2-one (9m): yellow solid; 55.0 mg, 99% yield; mp 275.3–276.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.44 (s, 2H), 7.33–7.21 (m, 2H), 6.84 (q, *J* = 7.8 Hz, 2H), 5.54 (s, 1H), 3.16 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.7, 166.9, 156.0, 150.1, 144.8, 136.8, 135.0, 132.2, 130.5, 130.1, 128.4, 125.9, 124.9, 124.2, 123.1, 121.8, 121.0, 108.5, 34.7, 30.4, 26.1; HRMS (ESI-TOF) calcd. for $C_{31}H_{32}BrNNaO_3$ $[M + Na]^+$ 568.1458; found: 568.1464.



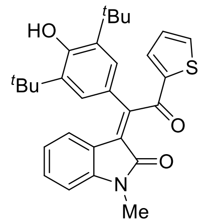
(*Z*)-4-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(1-methyl-2-oxoindolin-3-ylidene)acetyl)benzonitrile (9n): yellow solid; 46.0 mg, 94% yield; mp 195.3–197.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.44 (s, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 6.93–6.77 (m, 2H), 5.57 (s, 1H), 3.15 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 167.0, 156.2, 149.2, 145.0, 139.2, 137.0, 132.7, 130.4, 129.3, 126.0, 125.4, 123.6, 123.1, 122.0, 120.8, 118.3, 116.2, 108.6, 34.7, 30.3, 26.1; HRMS (ESI-TOF) calcd. for $C_{32}H_{32}N_2NaO_3$ $[M + Na]^+$ 515.2305; found: 515.2321.



(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(naphthalen-2-yl)-2-oxoethylidene)-1-methylindolin-2-one (9o): yellow solid; 45.4 mg, 88% yield; mp 284.6–285.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.98–7.77 (m, 3H), 7.61–7.43 (m, 4H), 7.38–7.23 (m, 2H), 6.94–6.75 (m, 2H), 5.51 (s, 1H), 3.15 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.7, 166.9, 155.8, 151.1, 144.9, 136.7, 135.9, 133.7, 132.8, 131.2, 130.0, 129.8, 128.8, 128.4, 127.9, 126.6, 126.0, 124.8, 124.7, 124.5, 123.1, 121.7, 121.3, 108.4, 34.7, 30.4, 26.0; HRMS (ESI-TOF) calcd. for $C_{35}H_{35}NNaO_3$ $[M + Na]^+$ 540.2509; found: 540.2511.

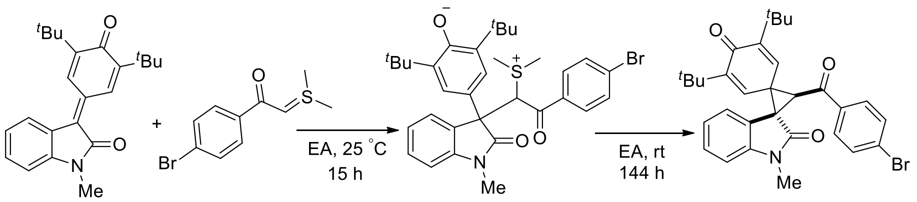


(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(furan-2-yl)-2-oxoethylidene)-1-methylindolin-2-one (9p): yellow solid; 43.3 mg, 95% yield; mp 278.4–279.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61–7.54 (m, 1H), 7.42 (s, 2H), 7.30–7.21 (m, 1H), 7.20–7.11 (m, 2H), 6.86–6.75 (m, 2H), 6.51 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.51 (s, 1H), 3.17 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.7, 166.9, 155.8, 152.5, 148.9, 146.8, 144.8, 136.6, 130.1, 125.9, 125.4, 124.5, 123.2, 121.7, 121.2, 118.3, 112.5, 108.4, 34.7, 30.4, 26.0; HRMS (ESI-TOF) calcd. for $C_{29}H_{31}NNaO_4$ $[M + Na]^+$ 480.2145; found: 480.2152.

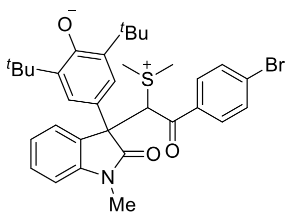


(*Z*)-3-(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-(thiophen-2-yl)ethylidene)-1-methylindolin-2-one (9q): yellow solid; 43.0 mg, 94% yield; mp 306.5–308.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 11.9, 4.3 Hz, 2H), 7.46 (s, 2H), 7.32–7.23 (m, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 4.3 Hz, 1H), 6.88–6.74 (m, 2H), 5.52 (s, 1H), 3.17 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.0, 166.7, 155.8, 149.9, 144.8, 143.7, 136.7, 133.9, 133.3, 130.1, 128.2, 125.9, 124.8, 124.7, 123.2, 121.7, 121.2, 108.4, 34.7, 30.4, 26.0; HRMS (ESI-TOF) calcd. for $C_{29}H_{31}NNaO_3S$ $[M + Na]^+$ 496.1917; found: 496.1918.

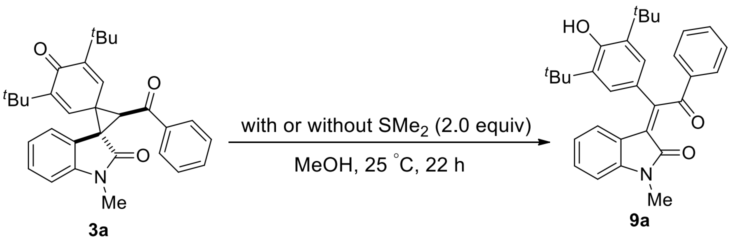
9. Control experiments



In an ordinary vial equipped with a magnetic stirring bar, the sulfur ylides **2h** (0.12 mmol, 1.2 equiv) were added to a solution of isatin-derived *p*-QMs **1a** (0.10 mmol, 1.0 equiv) in ethyl acetate (1.0 mL) at 25 °C. And the mixture was stirred at the same temperature for 15 h. Then, the reaction mixture was filtered and the cake was washed with cold ethyl acetate (2 mL) to give the zwitterionic intermediate **10** as white solid. Next, suspending intermediate 9 in fresh ethyl acetate (0.5 mL) at 25 °C continued to stir for 144 h. Then, the ethyl acetate was evaporated under vacuum at 30 °C and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15/1～10/1) to afford the spirocyclopropyl oxindole **3h**.



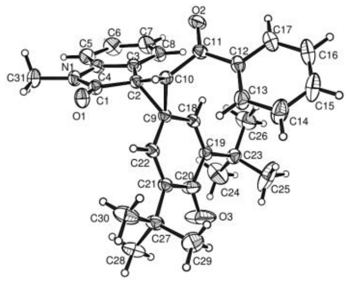
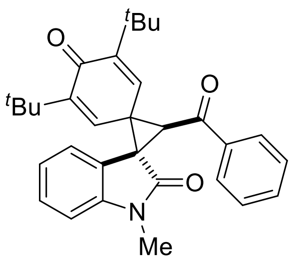
4-(3-(2-(4-bromophenyl)-1-(dimethylsulfonio)-2-oxoethyl)-1-methyl-2-oxoindolin-3-yl)-2,6-di-*tert*-butylphenolate (10): white solid; 46.8 mg, 77% yield; mp 170.2–171.5 ℃ (decomposition); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 4.2 Hz, 2H), 7.21–7.09 (m, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 2H), 6.49 (d, *J* = 7.8 Hz, 1H), 5.17 (s, 1H), 3.07 (s, 3H), 3.04 (s, 3H), 2.76 (s, 3H), 1.36 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.8, 179.0, 153.2, 142.7, 142.5, 135.8, 135.4, 132.2, 129.9, 128.6, 127.7, 125.0, 124.8, 122.2, 121.2, 108.4, 75.1, 59.4, 34.7, 30.4, 27.2, 26.9, 26.2; HRMS (ESI-TOF) calcd. for $C_{33}H_{38}BrNO_3S$ $[M + H]^+$ 608.1829; found: 608.1834.

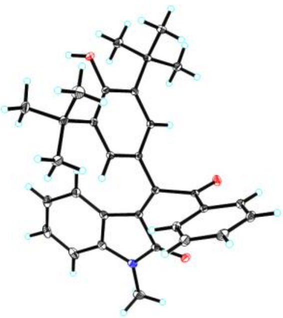
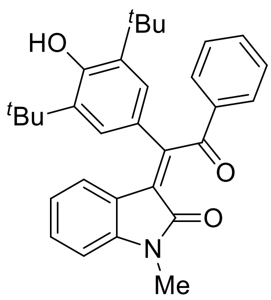


Without SMe_2: In an ordinary vial equipped with a magnetic stirring bar, the compound **3a** (0.05 mmol) were suspended in methanol (0.5 mL) at 25 °C. And the mixture was stirred at the same temperature for 22 h. Monitored by ^{1}H-NMR showed that the transformation was every slow and only 4 percent of **3a** was converted into **9a**.

With SMe_2: In an ordinary vial equipped with a magnetic stirring bar, SMe_2 (0.1 mmol, 2.0 equiv) was added to a solution of compound **3a** (0.05 mmol, 1.0 equiv) in methanol (0.5 mL) at 25 °C. And the mixture was stirred at the same temperature for 22 h. Monitored by ^{1}H-NMR showed that 91 percent of **3a** was transformed into **9a**.

10. X-ray crystal data for compound 3a and 9a

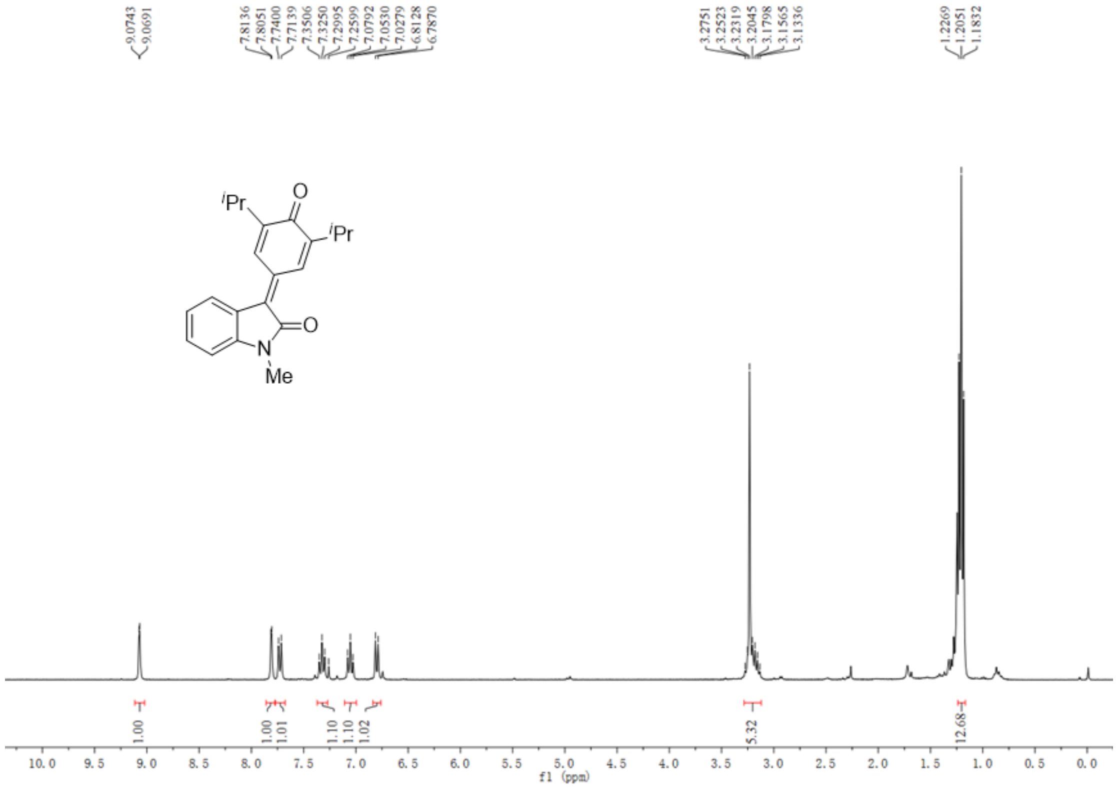
	
Identification code	**3a**
Empirical formula	$C_{31}H_{33}NO_3$
Formula weight	467.58
Temperature/K	290(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.00370(10)
b/Å	20.2706(2)
c/Å	13.21220(10)
α/°	90
β/°	92.2310(10)
γ/°	90
Volume/Å^3	2677.15(4)
Z	4
ρ_{calc}g/cm^3	1.160
μ/mm^{-1}	0.582
F(000)	1000.0

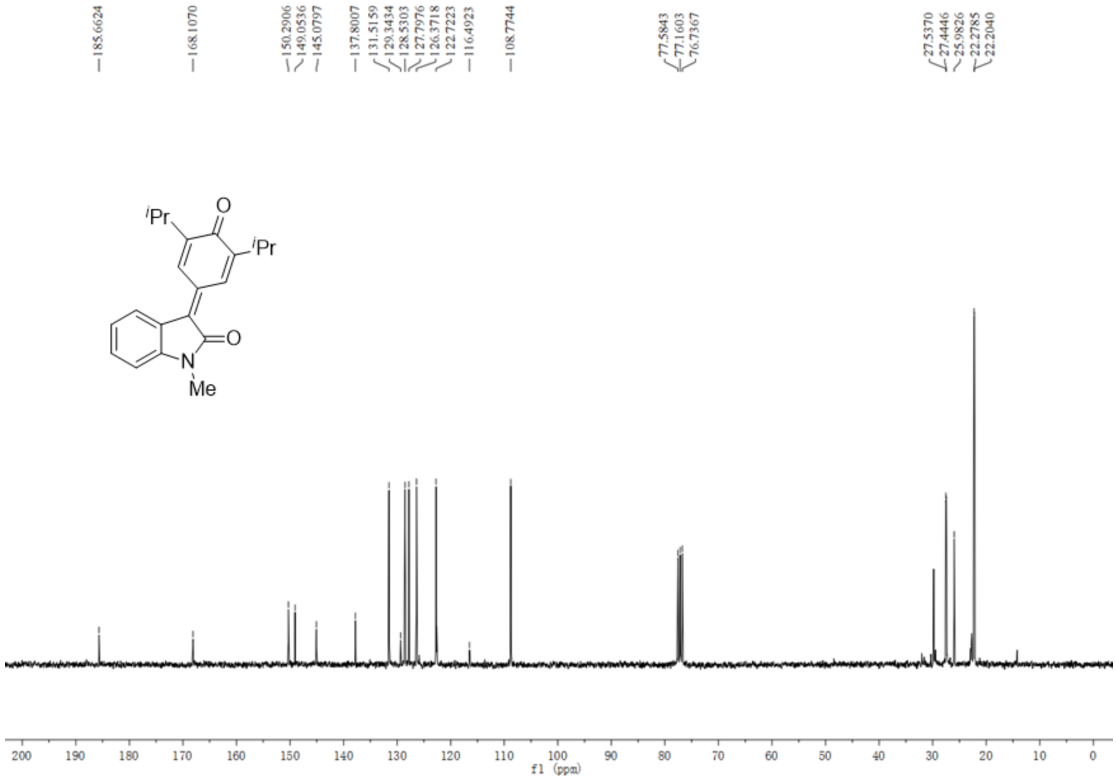
Crystal size/mm^3	0.290 × 0.270 × 0.230
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.992 to 142.428
Index ranges	-8 ≤ h ≤ 12, -19 ≤ k ≤ 24, -15 ≤ l ≤ 16
Reflections collected	10760
Independent reflections	5046 [R_{int} = 0.0209, R_{sigma} = 0.0243]
Data/restraints/parameters	5046/7/324
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0585, wR_2 = 0.1632
Final R indexes [all data]	R_1 = 0.0633, wR_2 = 0.1690
Largest diff. peak/hole / e Å^{-3}	0.62/-0.37
	
Identification code	**9a**
Empirical formula	$C_{31}H_{33}NO_3$
Formula weight	467.58
Temperature/K	100(2)
Wavelength/Å	1.54178
Crystal system	Triclinic
Space group	P-1
a/Å	9.4791(2)
b/Å	9.7988(2)
c/Å	15.5180(4)
α/°	83.6440(10)
β/°	83.3400(10)
γ/°	62.8550(10)
Volume/Å^3	1271.23(5)
Z	2
Density (calculated)/Mg/cm^3	1.222
μ/mm^{-1}	0.613
F(000)	500.0

Crystal size/mm^3	0.360 × 0.290 × 0.260
2Θ range for data collection/°	2.87 to 72.33
Index ranges	-11<=h<=10, -12<=k<=12, -19<=l<=19
Reflections collected	22434
Independent reflections	4956 [R(int) = 0.0279]
Completeness to theta = 72.33 °	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.86 and 0.76
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4956/0/325
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0389, wR_2 = 0.0931
Final R indexes [all data]	R_1 = 0.0403, wR_2 = 0.0940
Largest diff. peak/hole / e $Å^{-3}$	0.284/-0.211

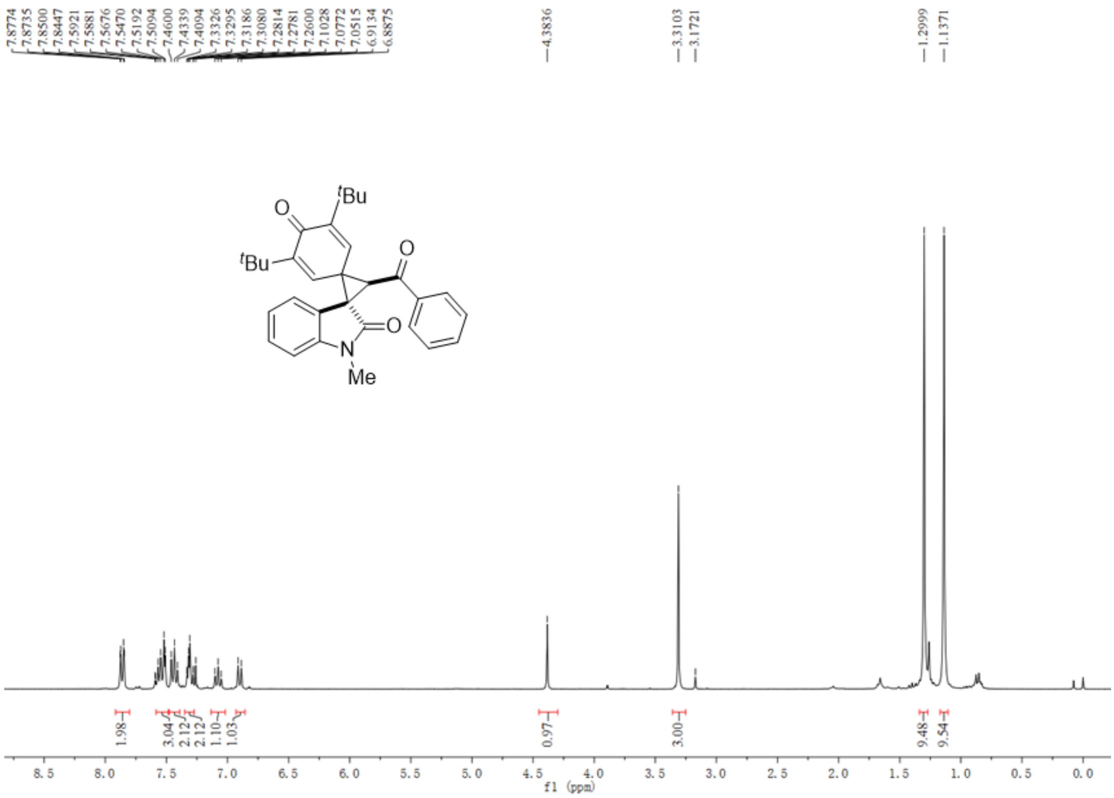
11. The copies of ^{1}H NMR and ^{13}C NMR spectra for compounds 1i, 3, 5, 6, 7, 8, 9 and 10

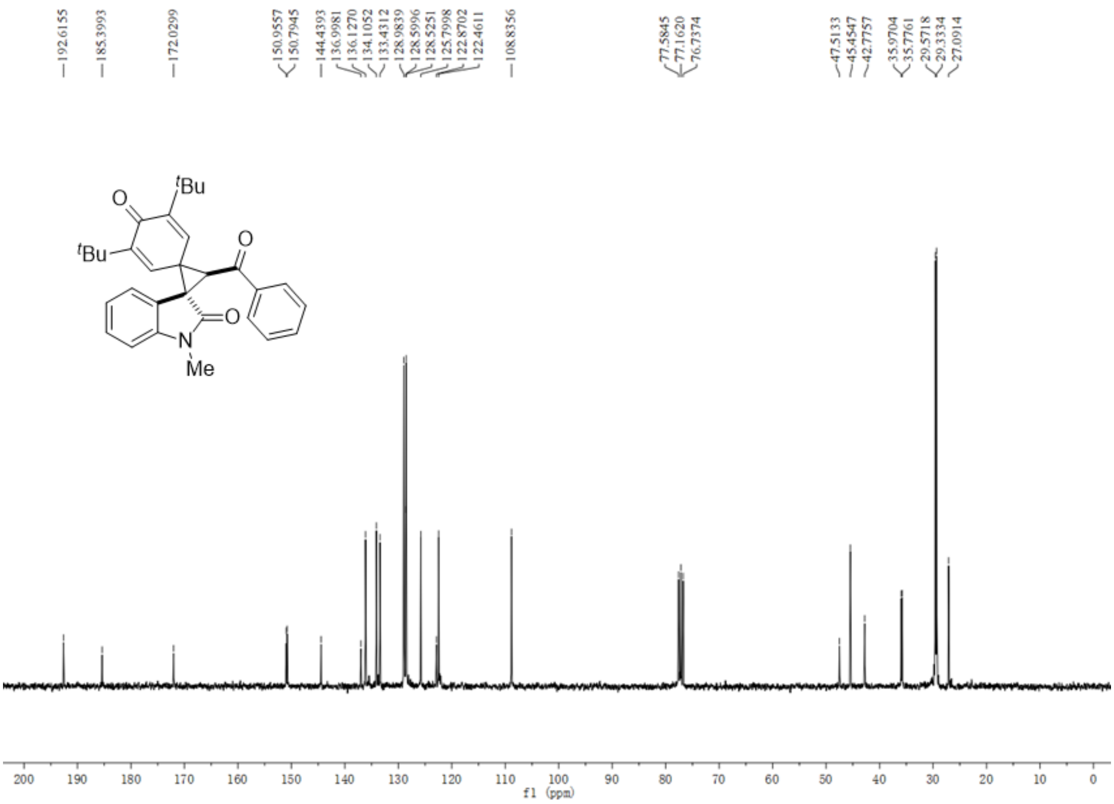
^{1}H NMR and ^{13}C NMR spectra of **1i**



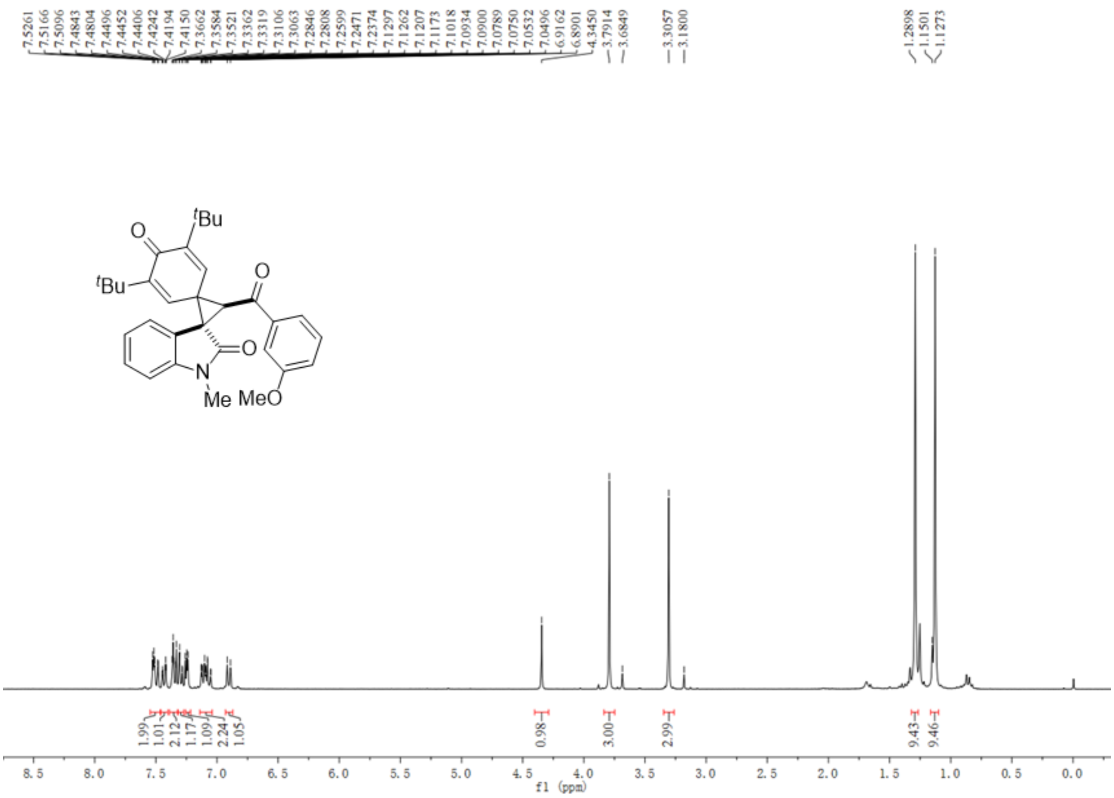


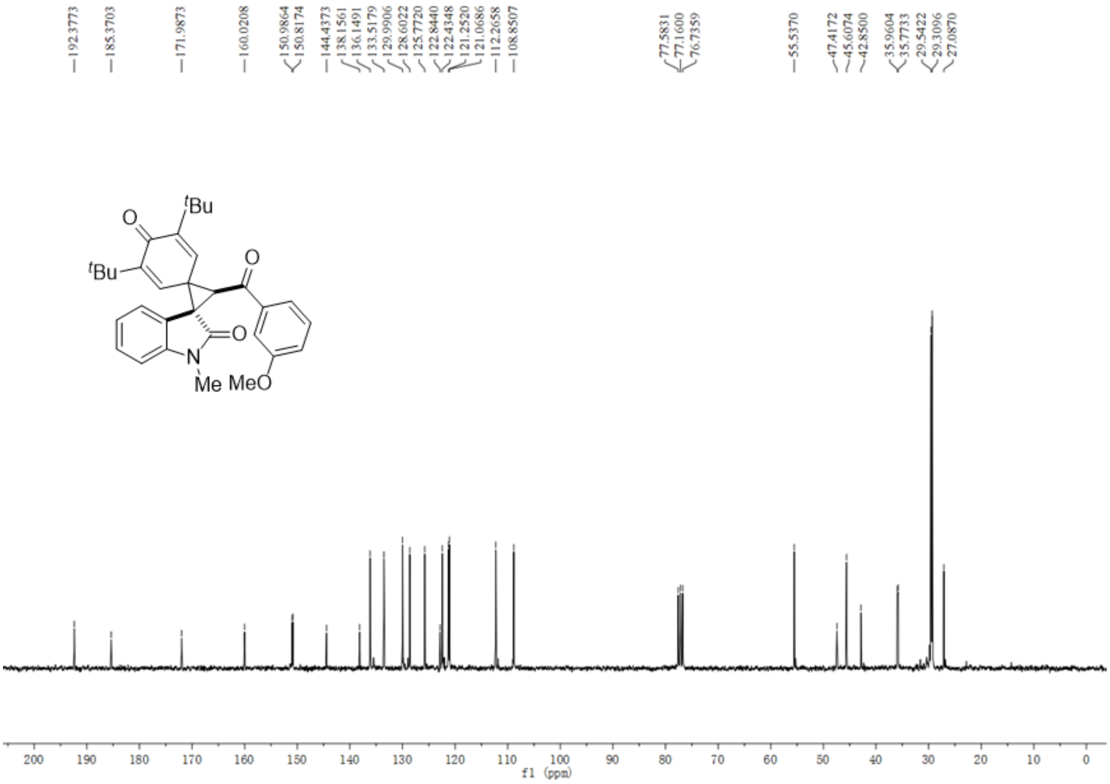
^{1}H NMR and ^{13}C NMR spectra of **3a**



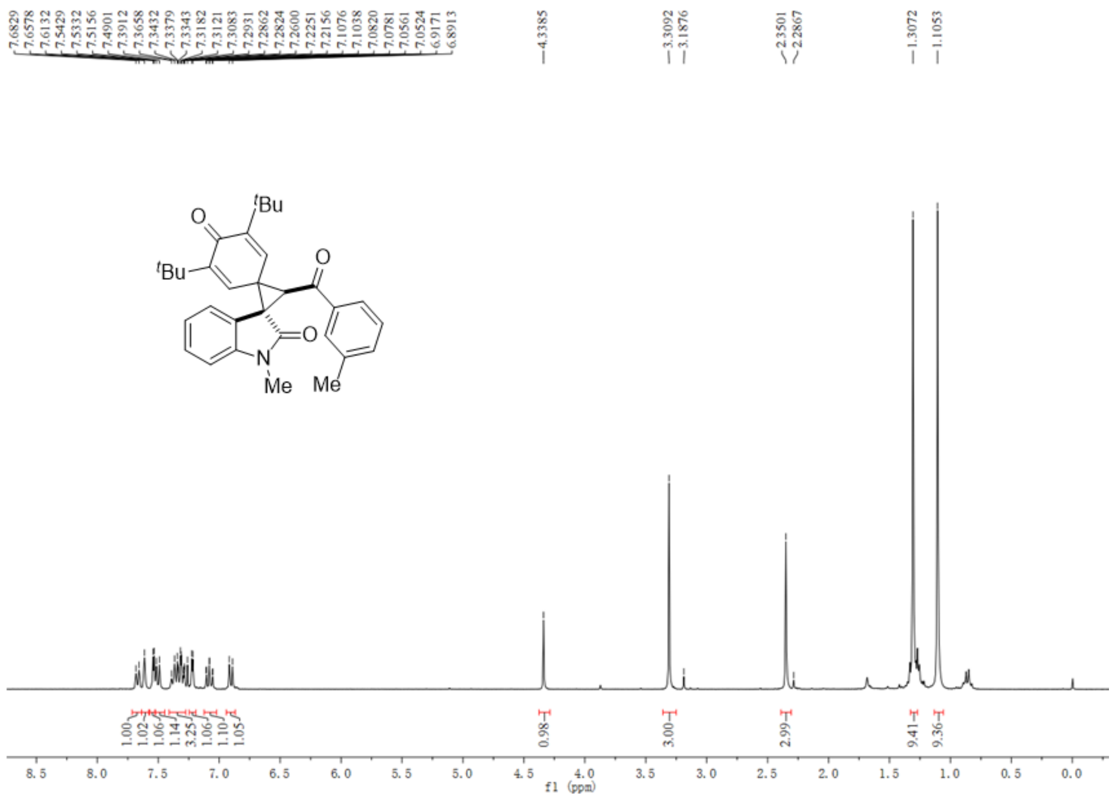


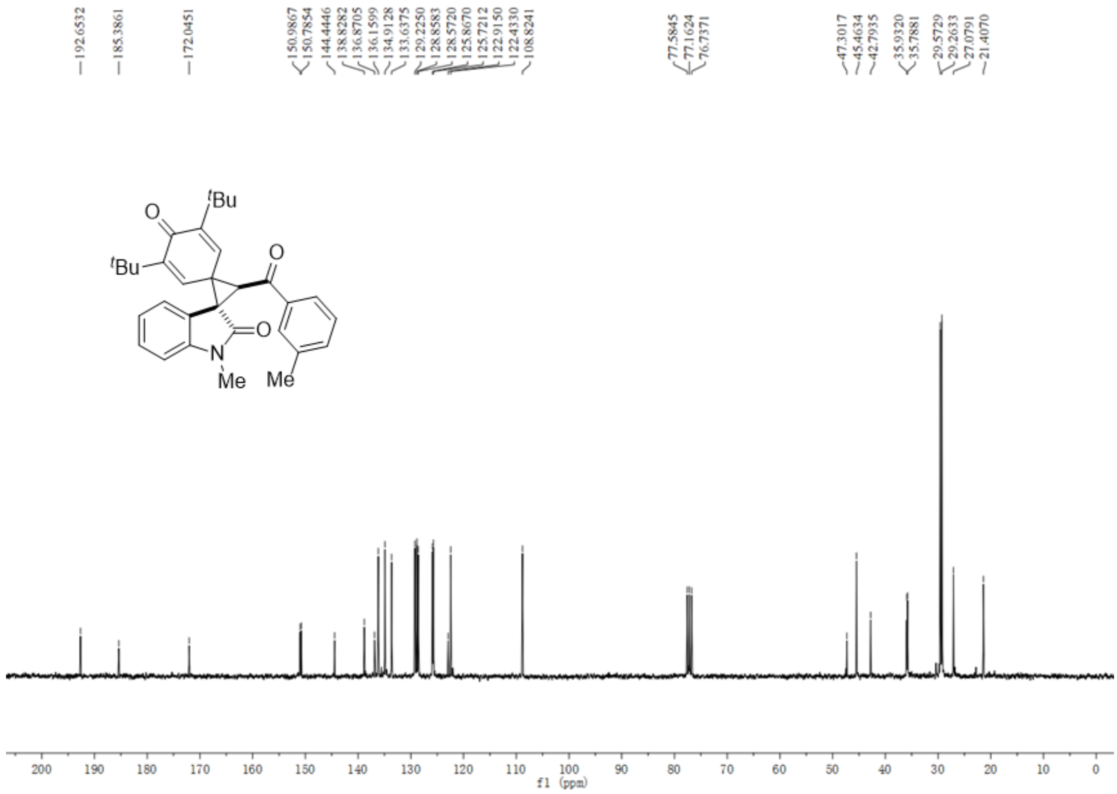
[1]H NMR and [13]C NMR spectra of **3b**



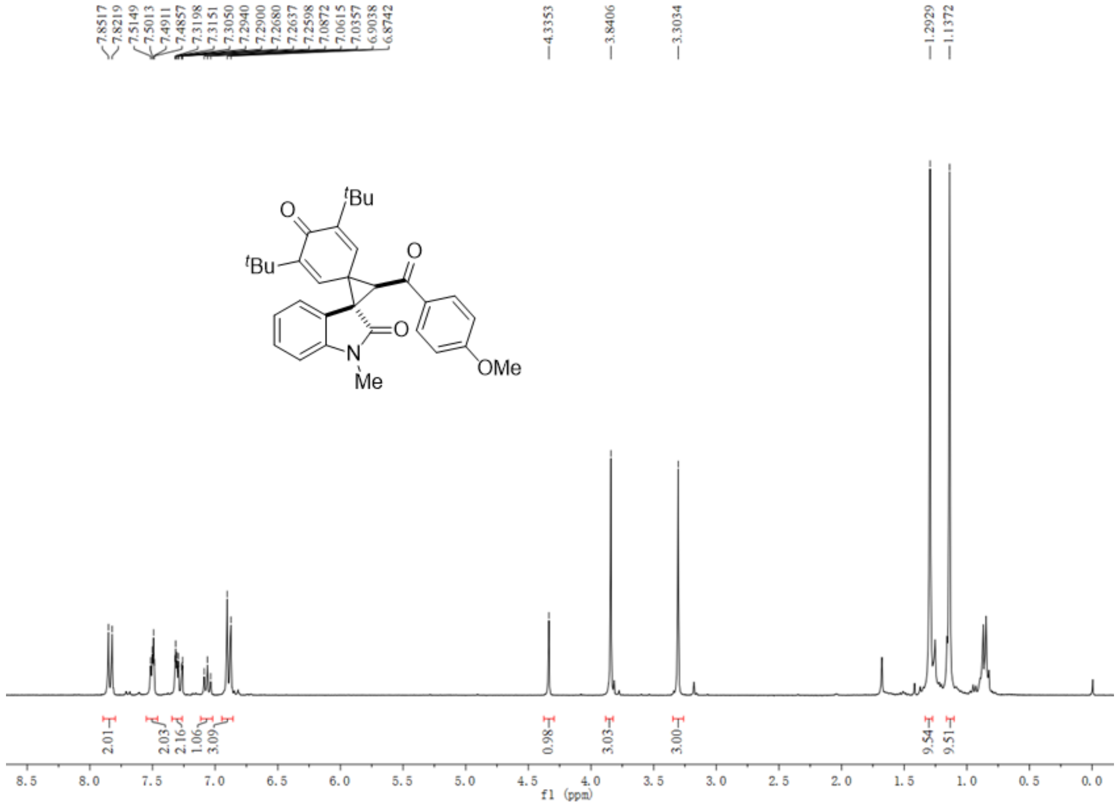


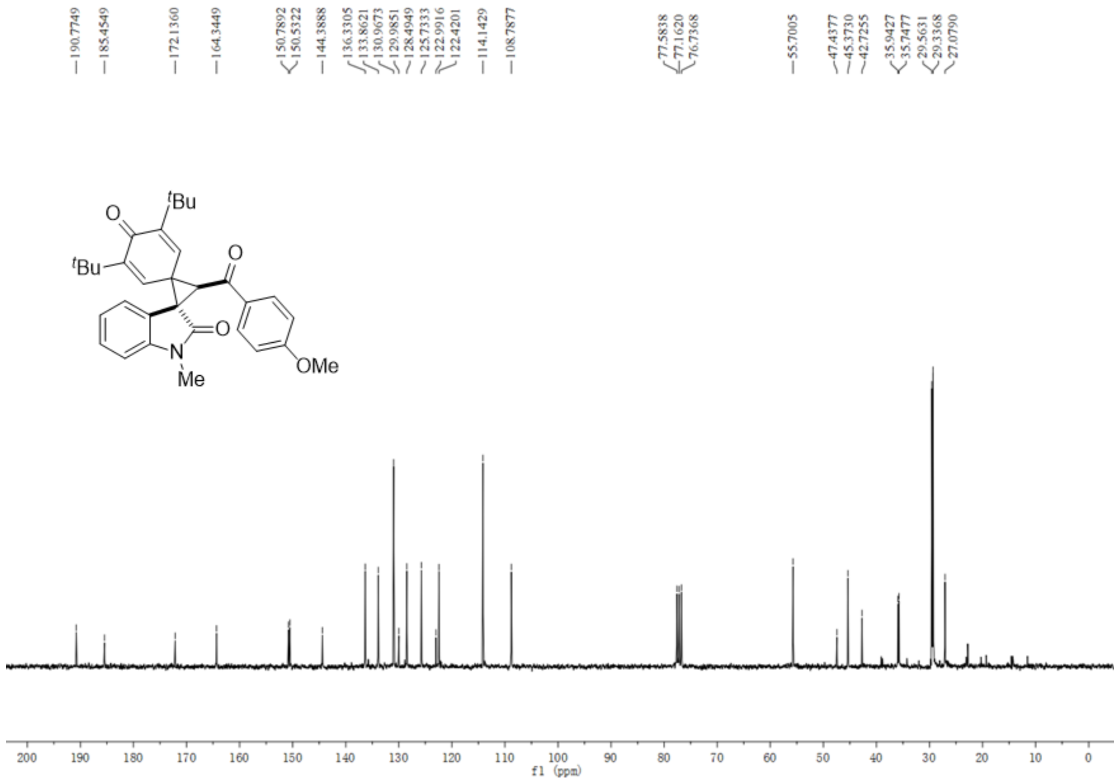
^{1}H NMR and ^{13}C NMR spectra of **3c**



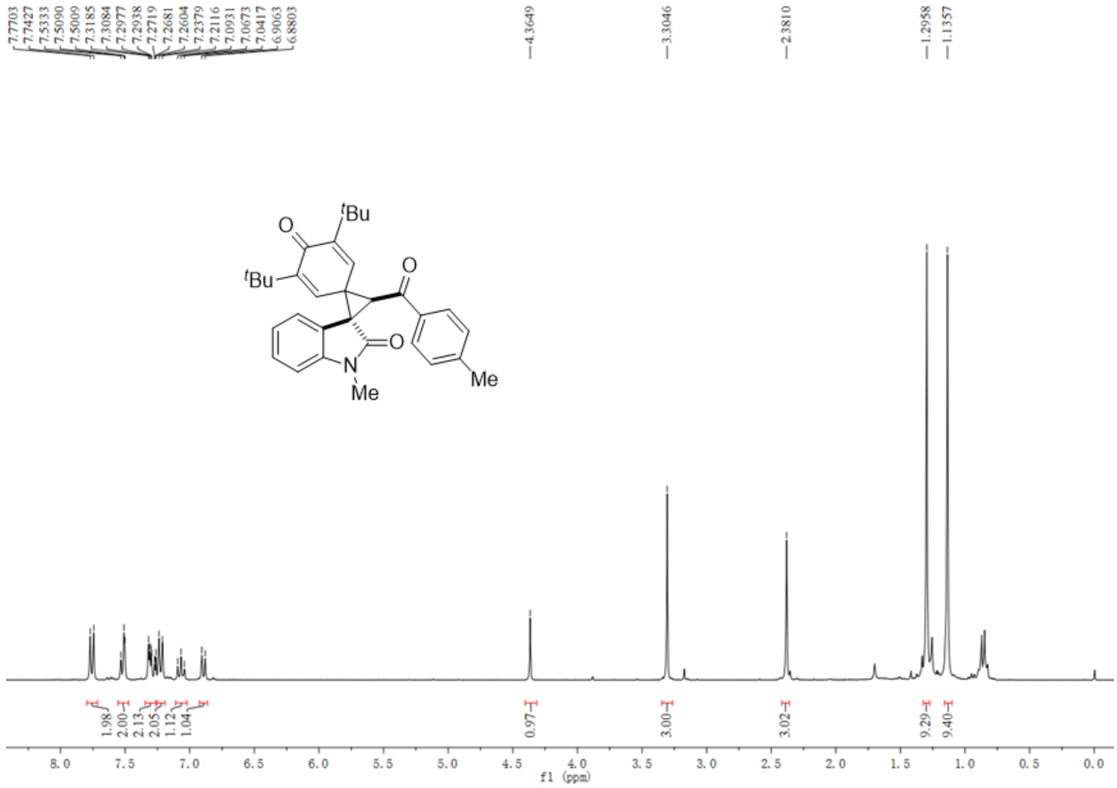


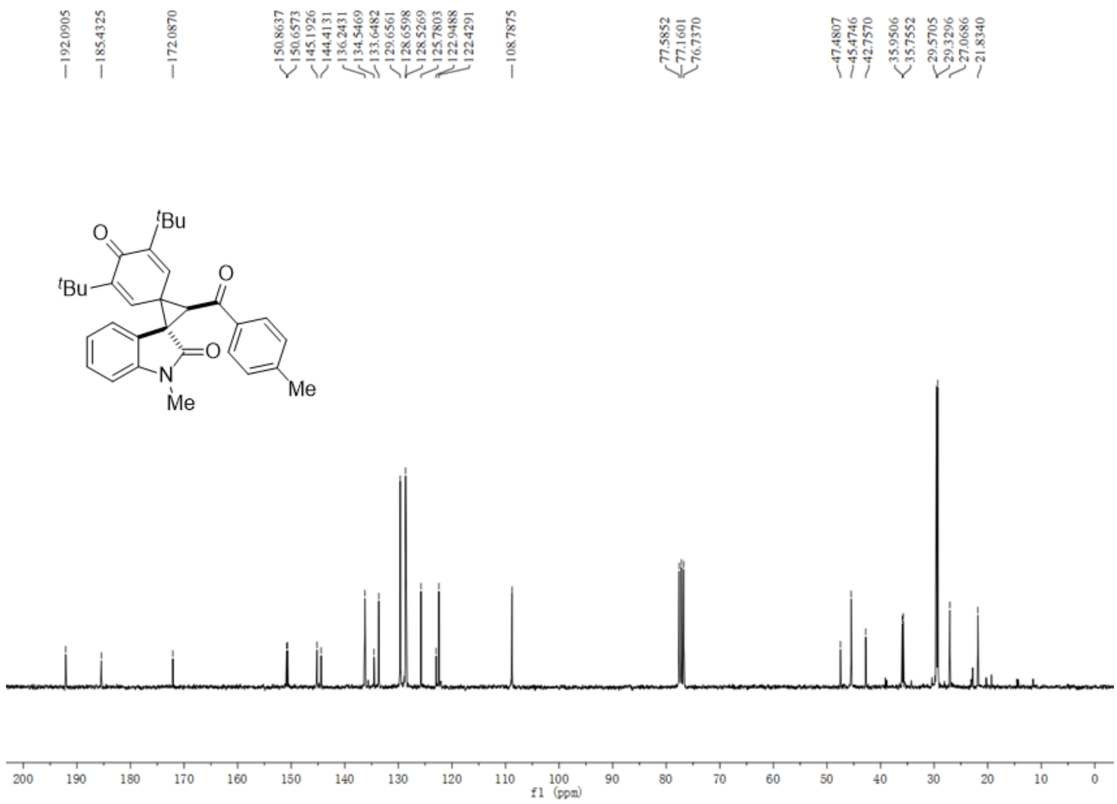
[1]H NMR and [13]C NMR spectra of **3d**



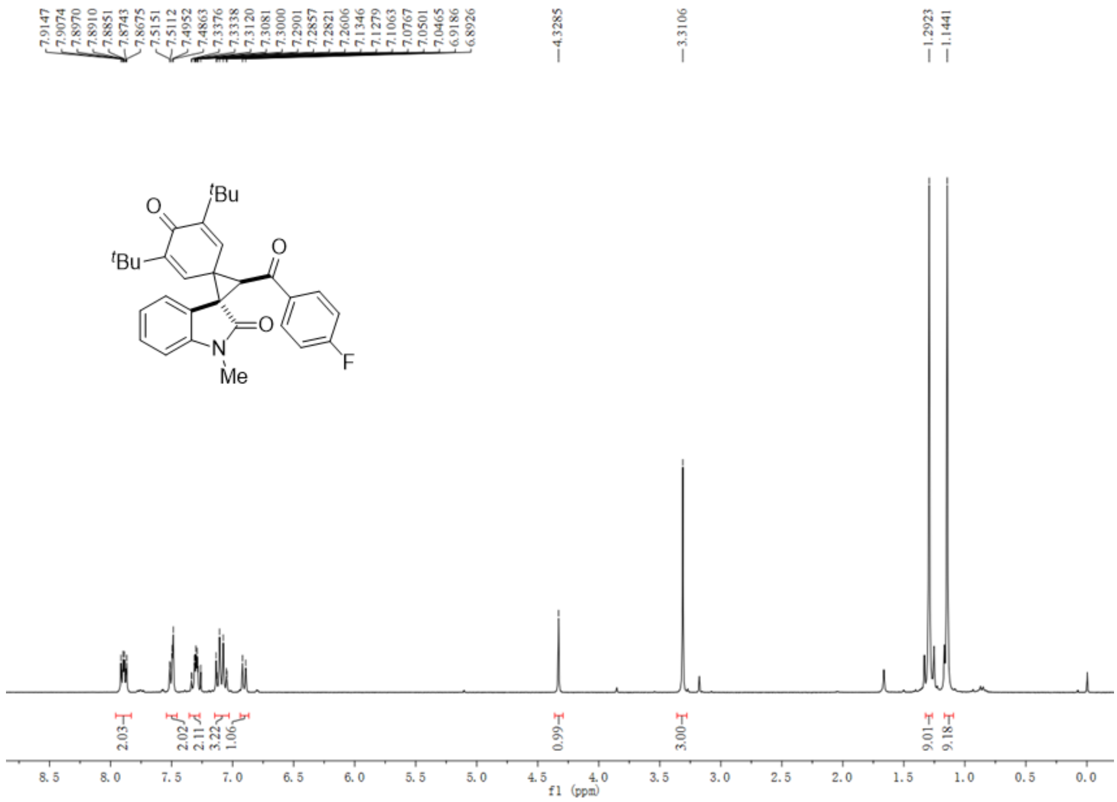


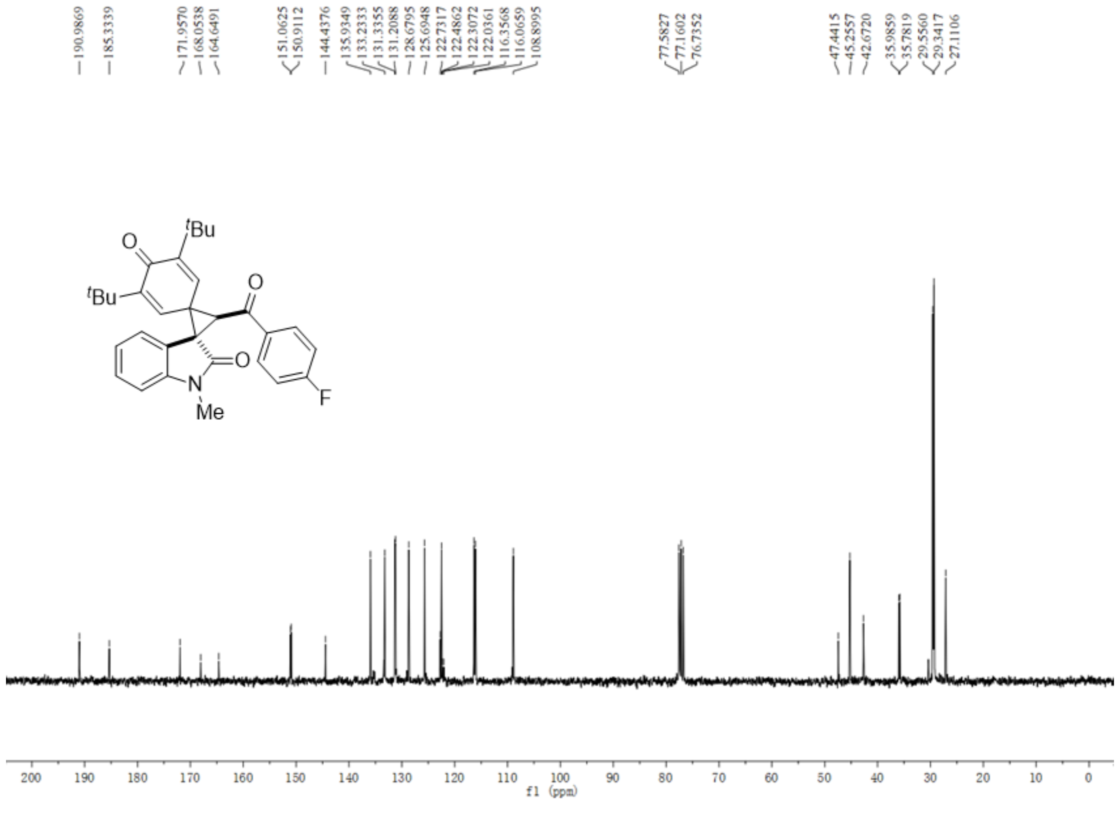
^{1}H NMR and ^{13}C NMR spectra of **3e**



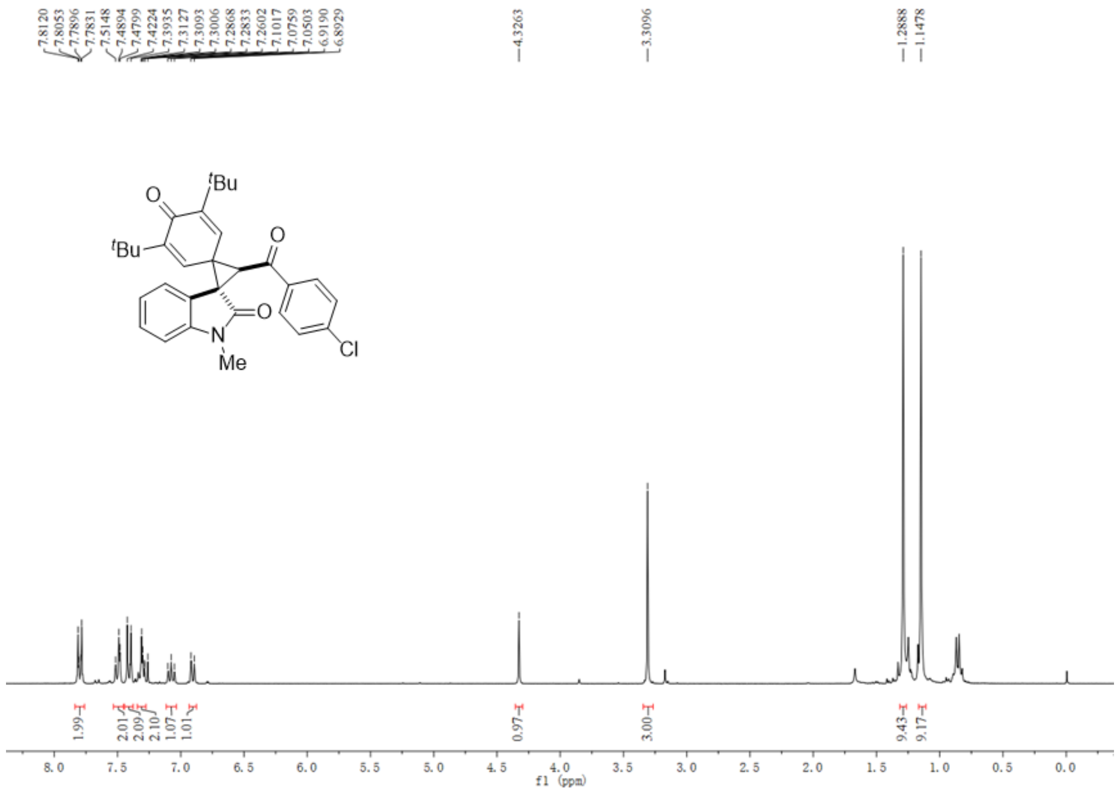


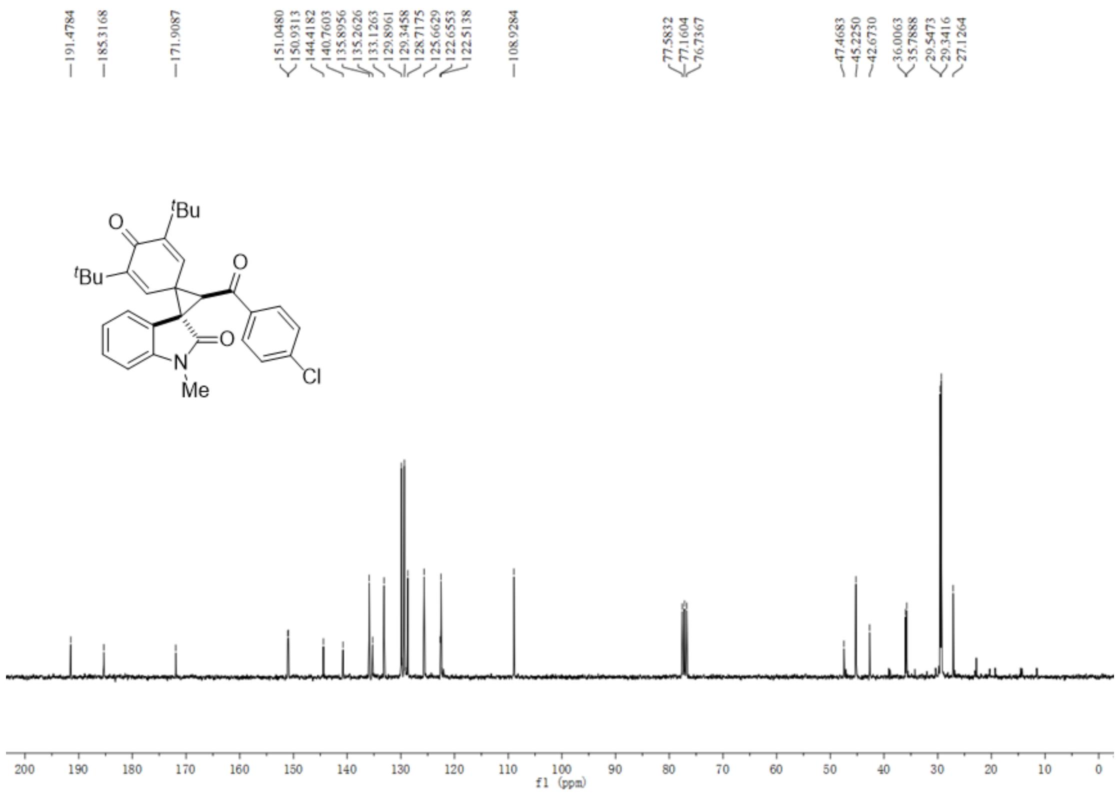
^{1}H NMR and ^{13}C NMR spectra of **3f**



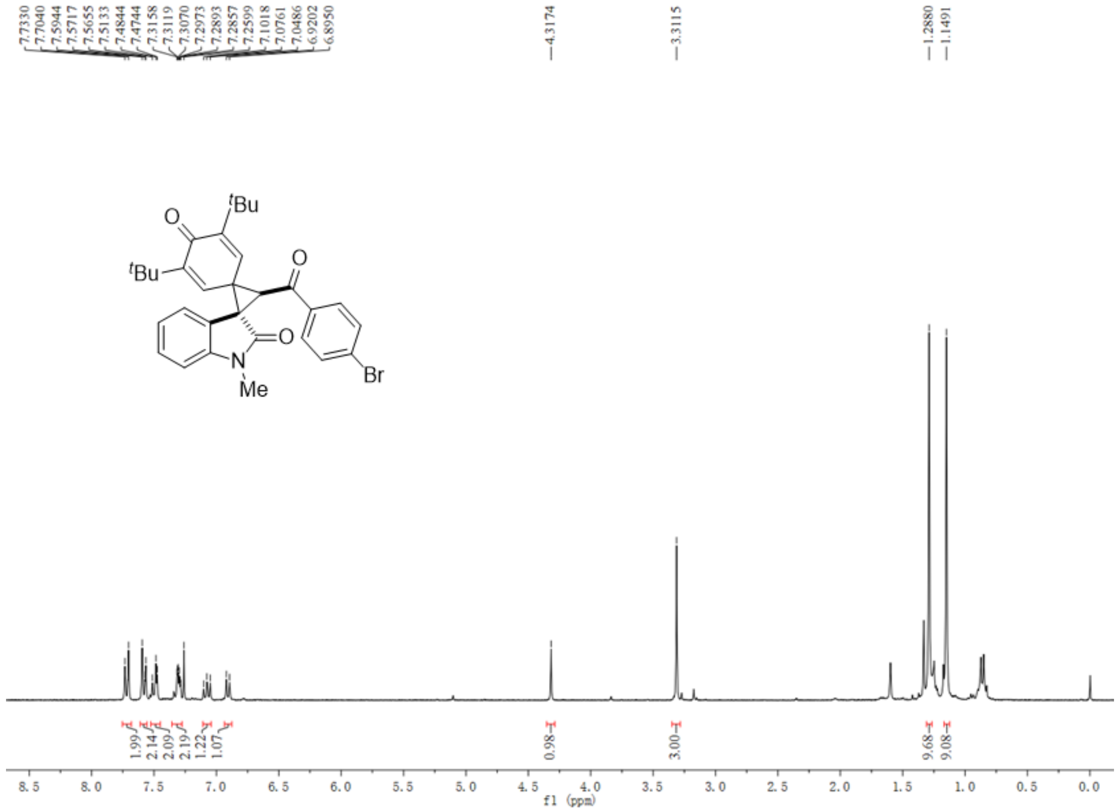


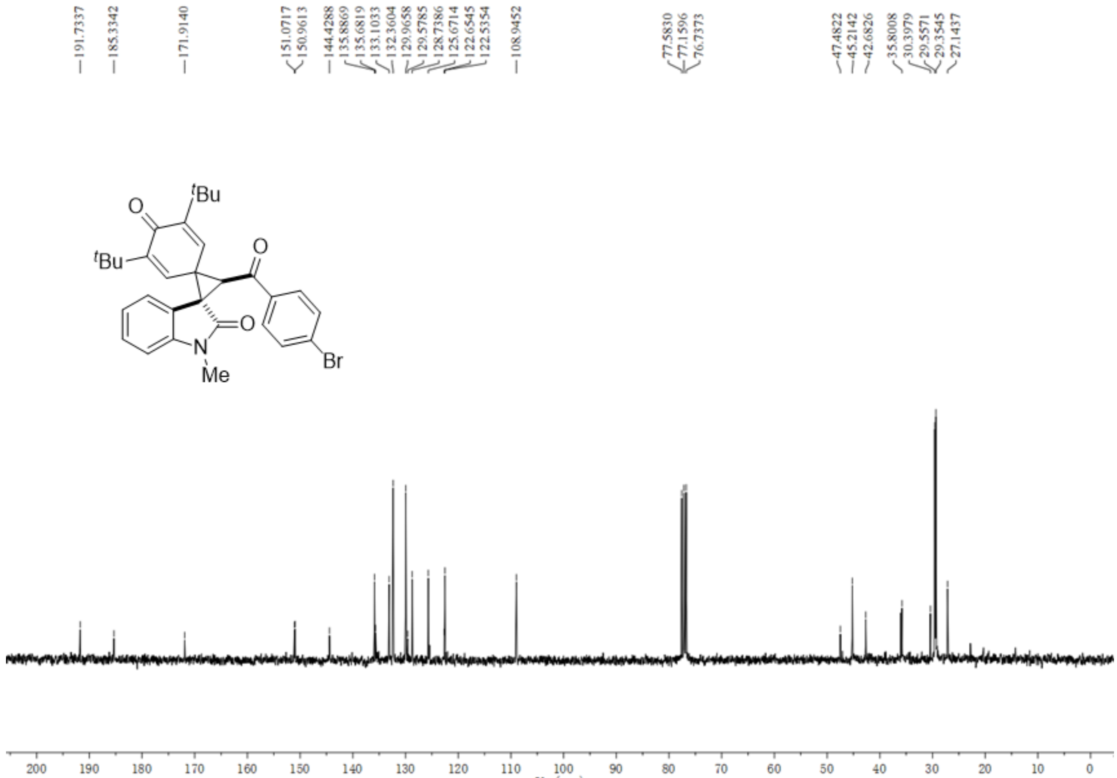
[1]H NMR and [13]C NMR spectra of **3g**



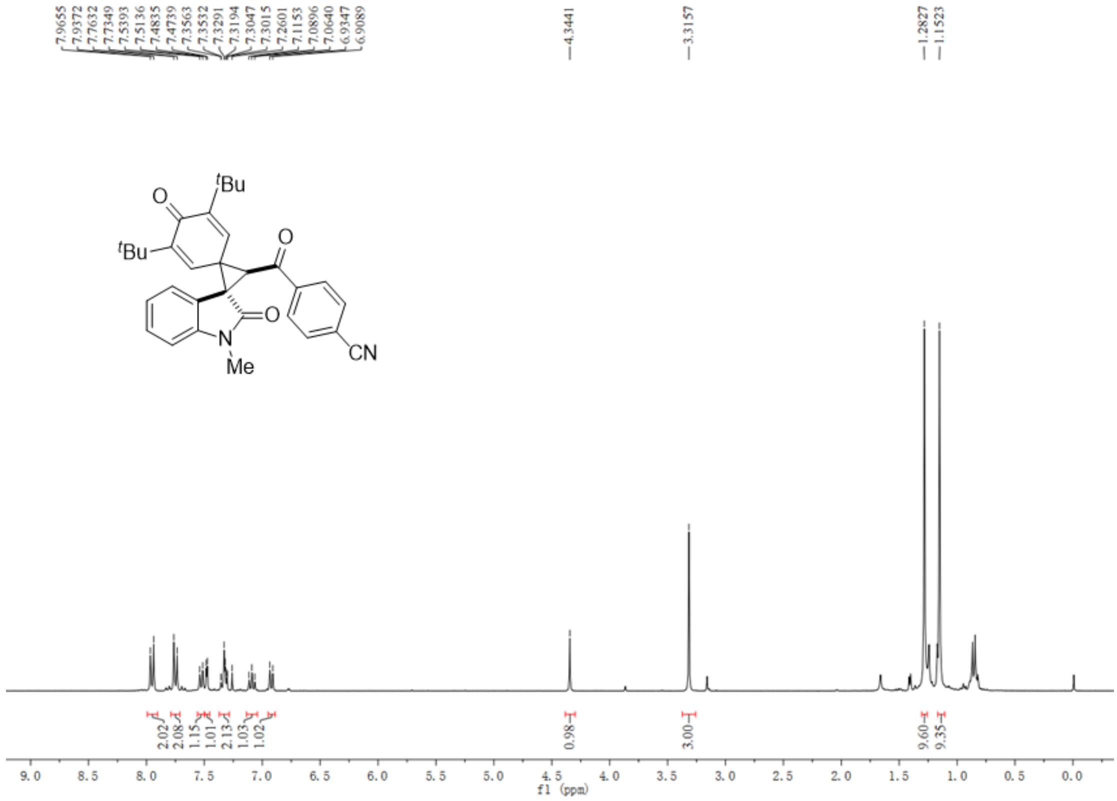


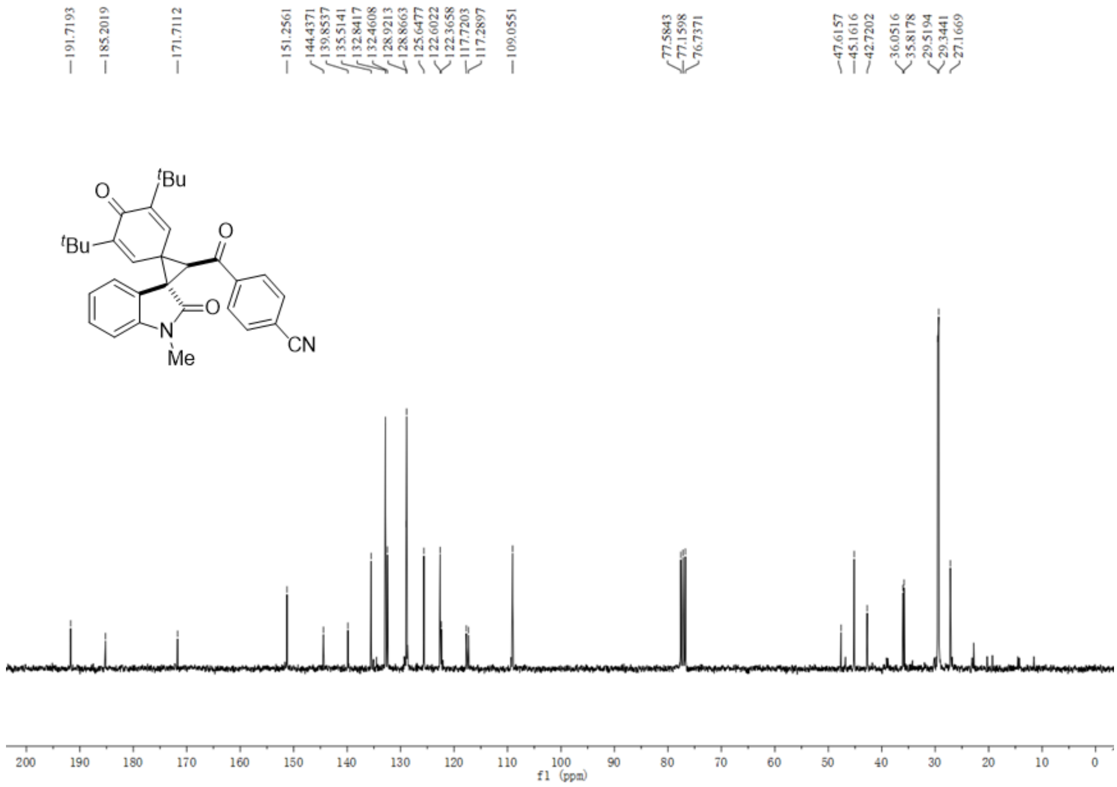
^{1}H NMR and ^{13}C NMR spectra of **3h**



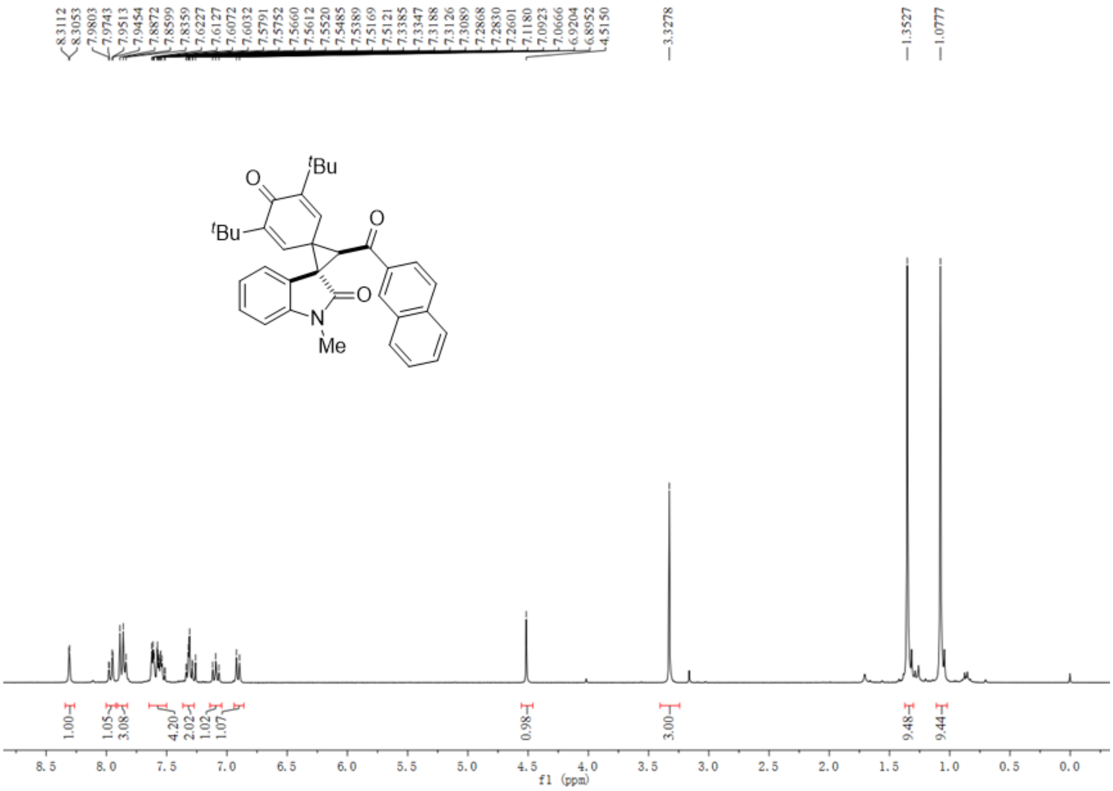


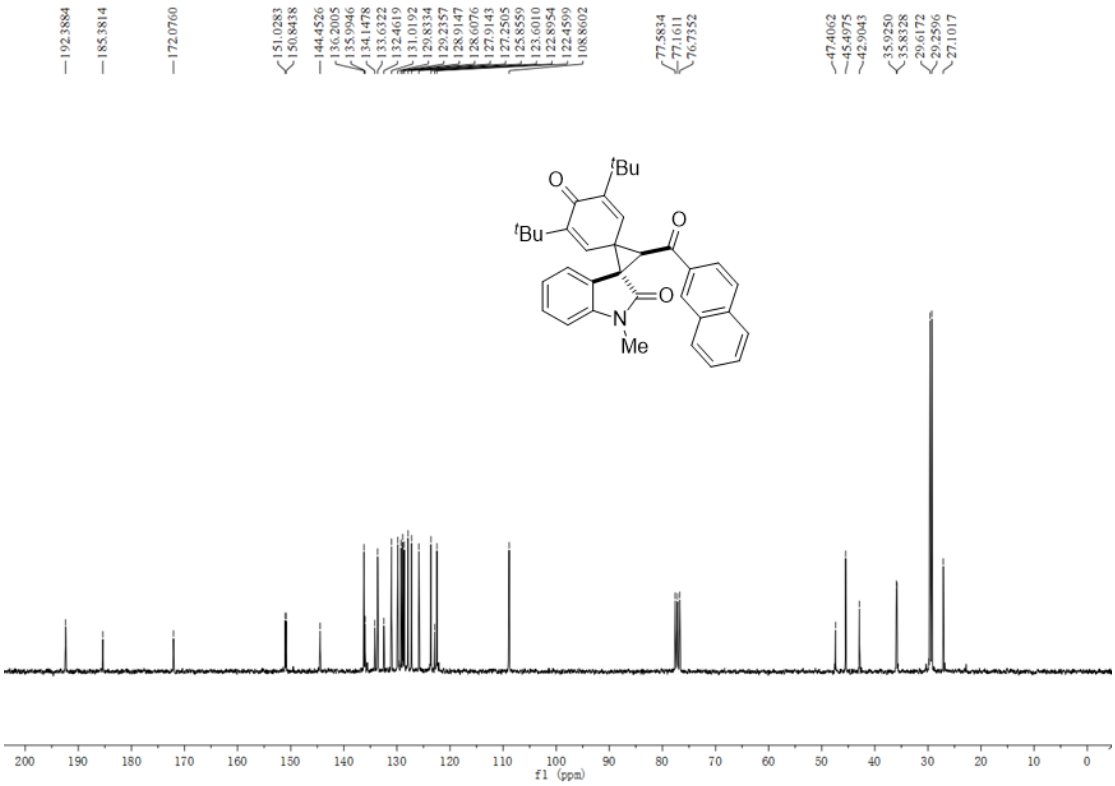
^{1}H NMR and ^{13}C NMR spectra of **3i**



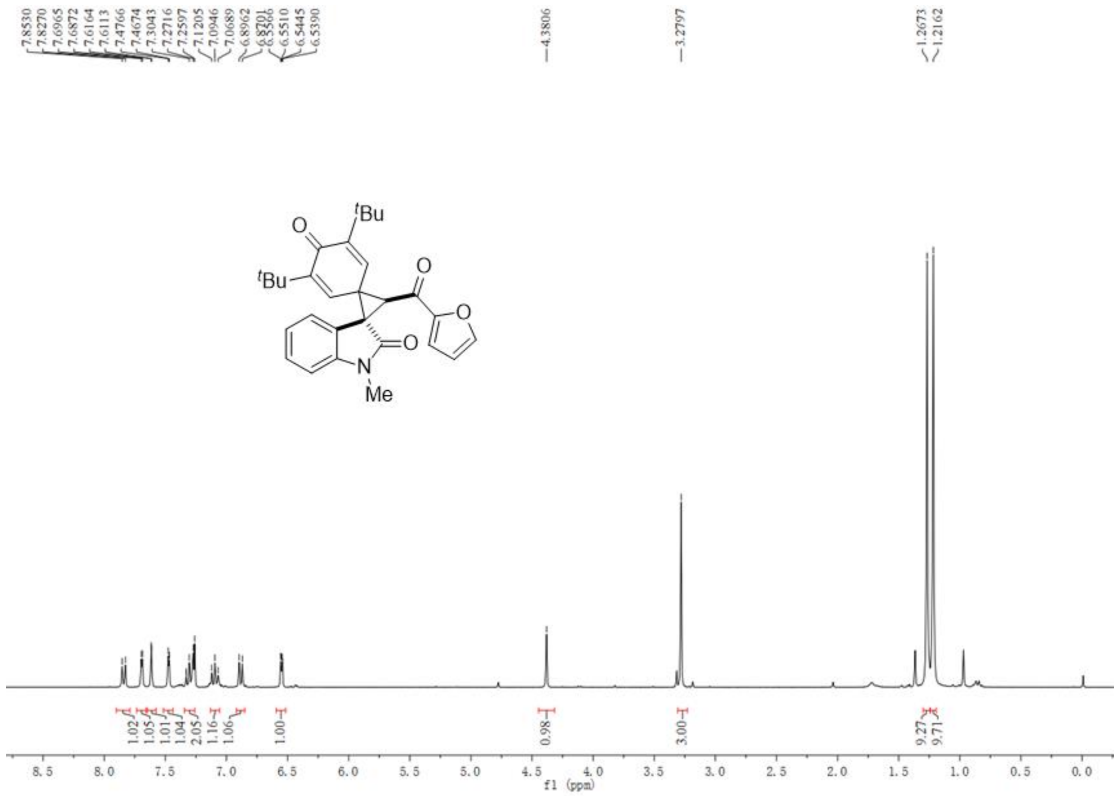


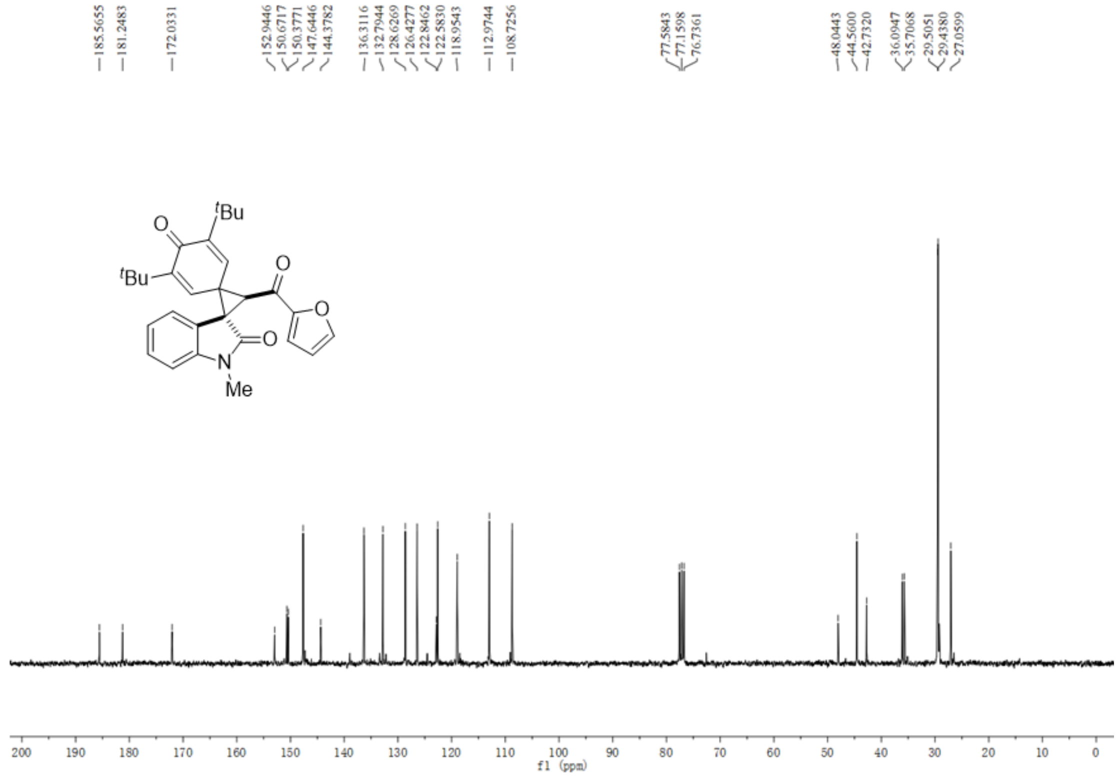
^{1}H NMR and ^{13}C NMR spectra of **3j**



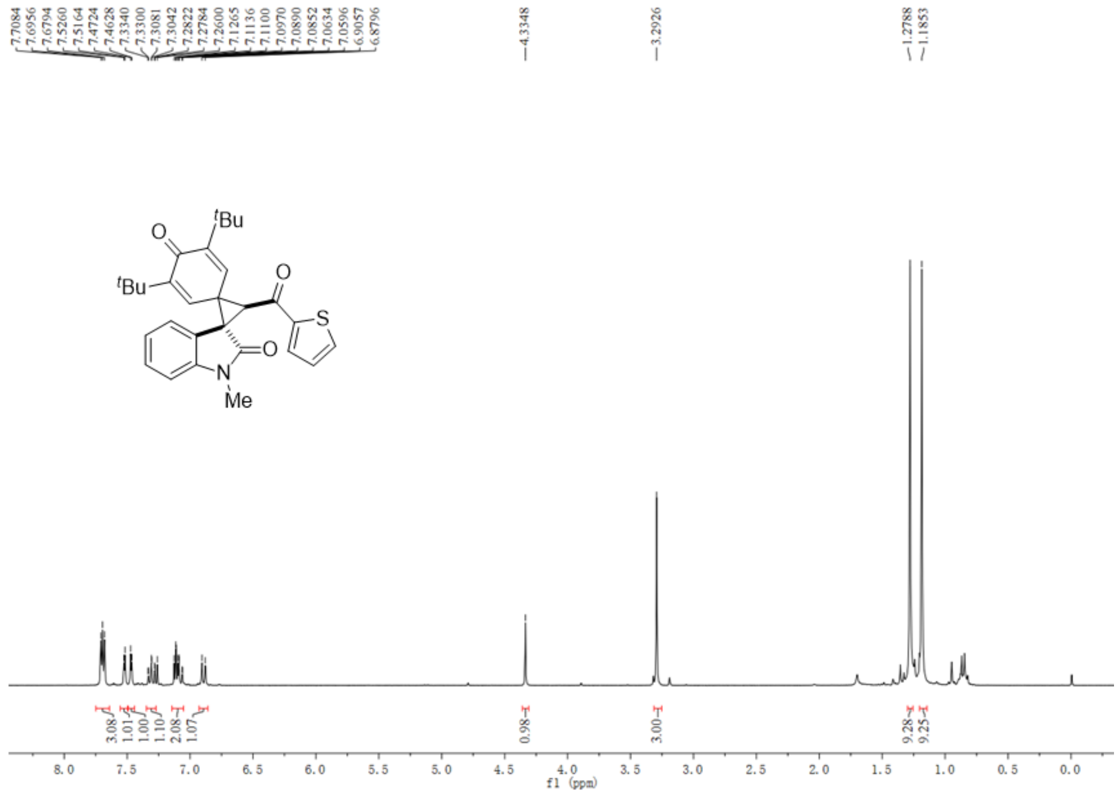


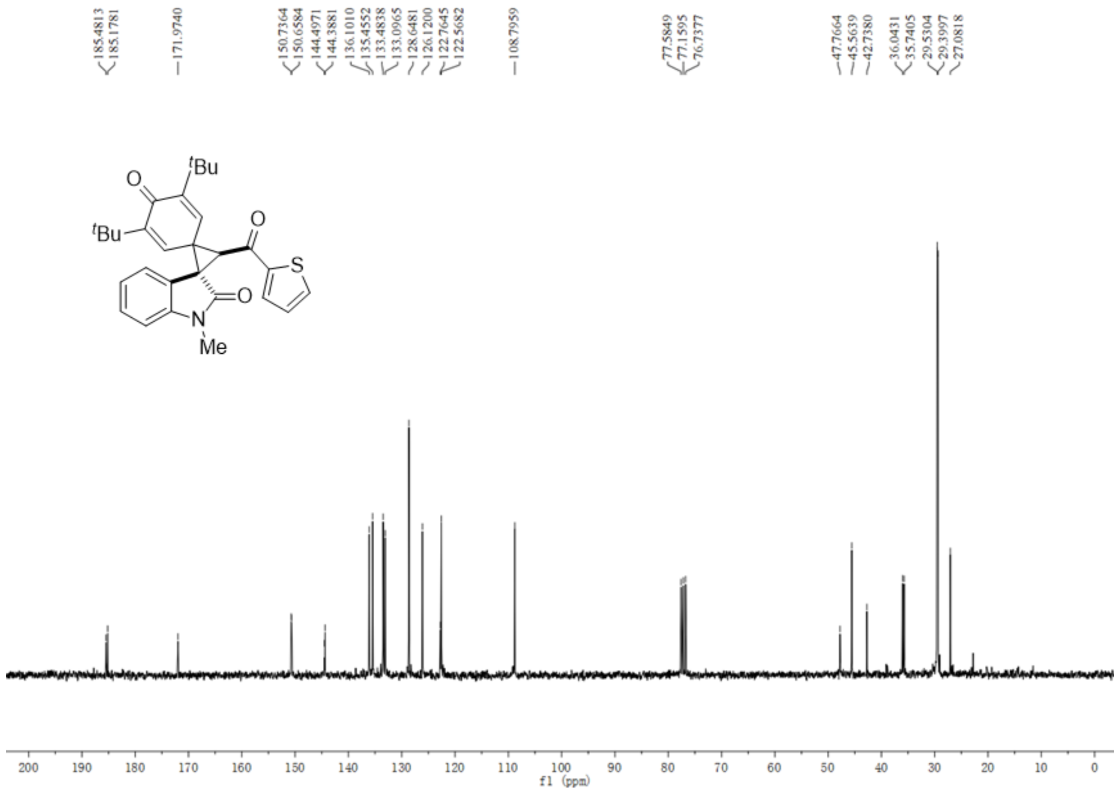
^{1}H NMR and ^{13}C NMR spectra of **3k**



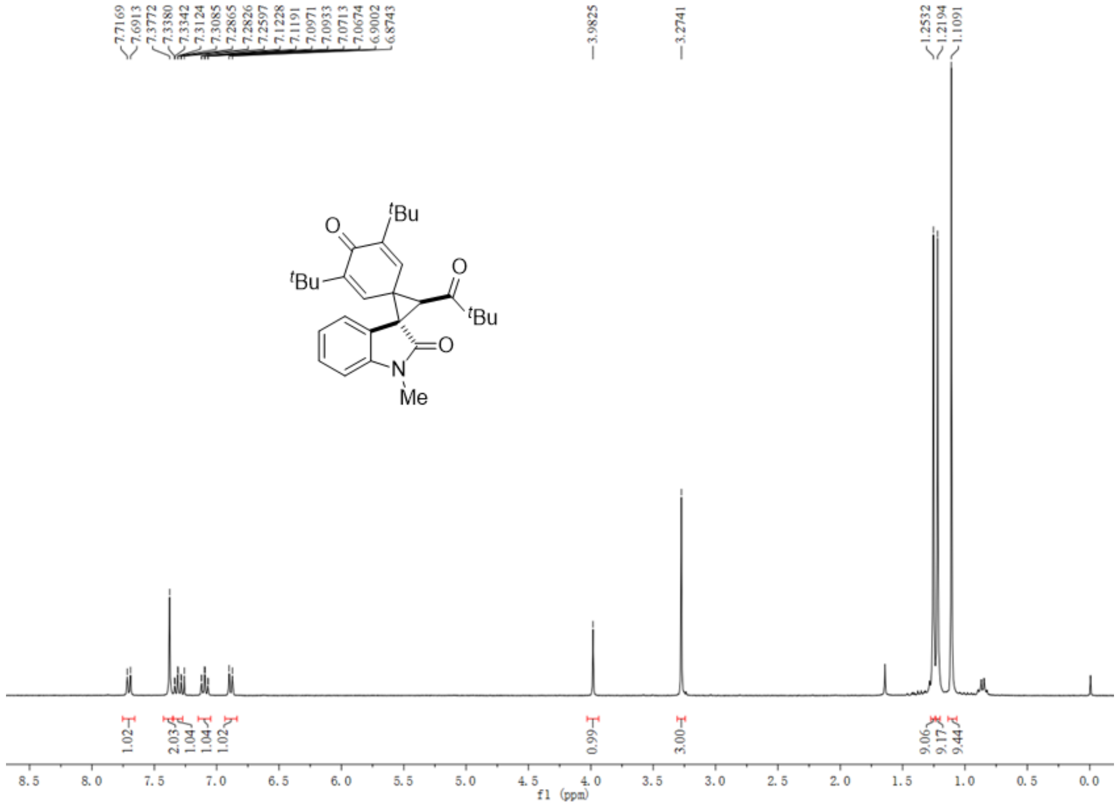


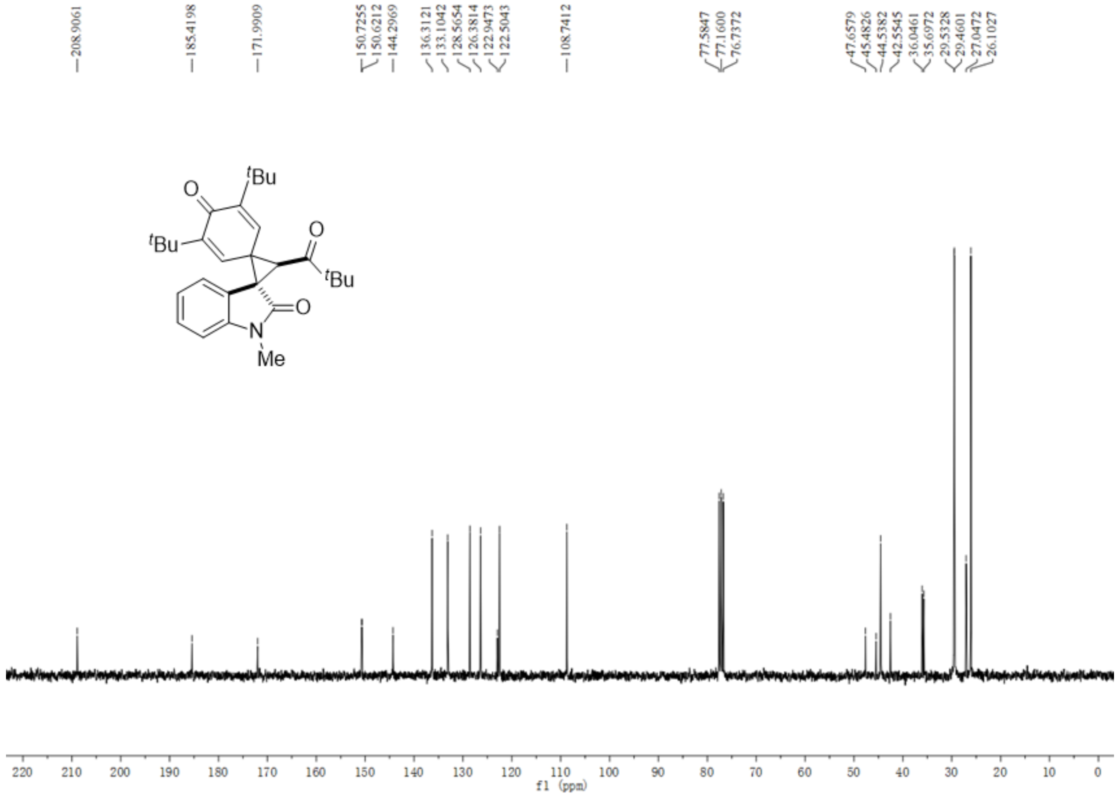
[1]H NMR and [13]C NMR spectra of **3l**



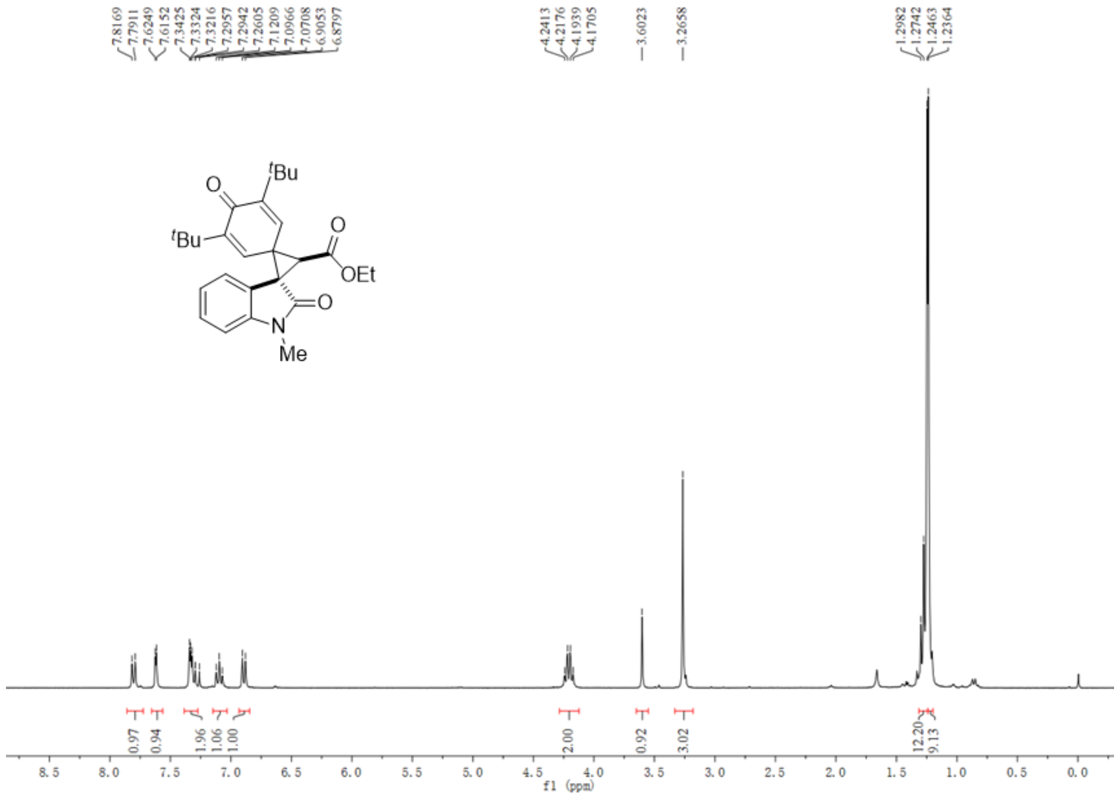


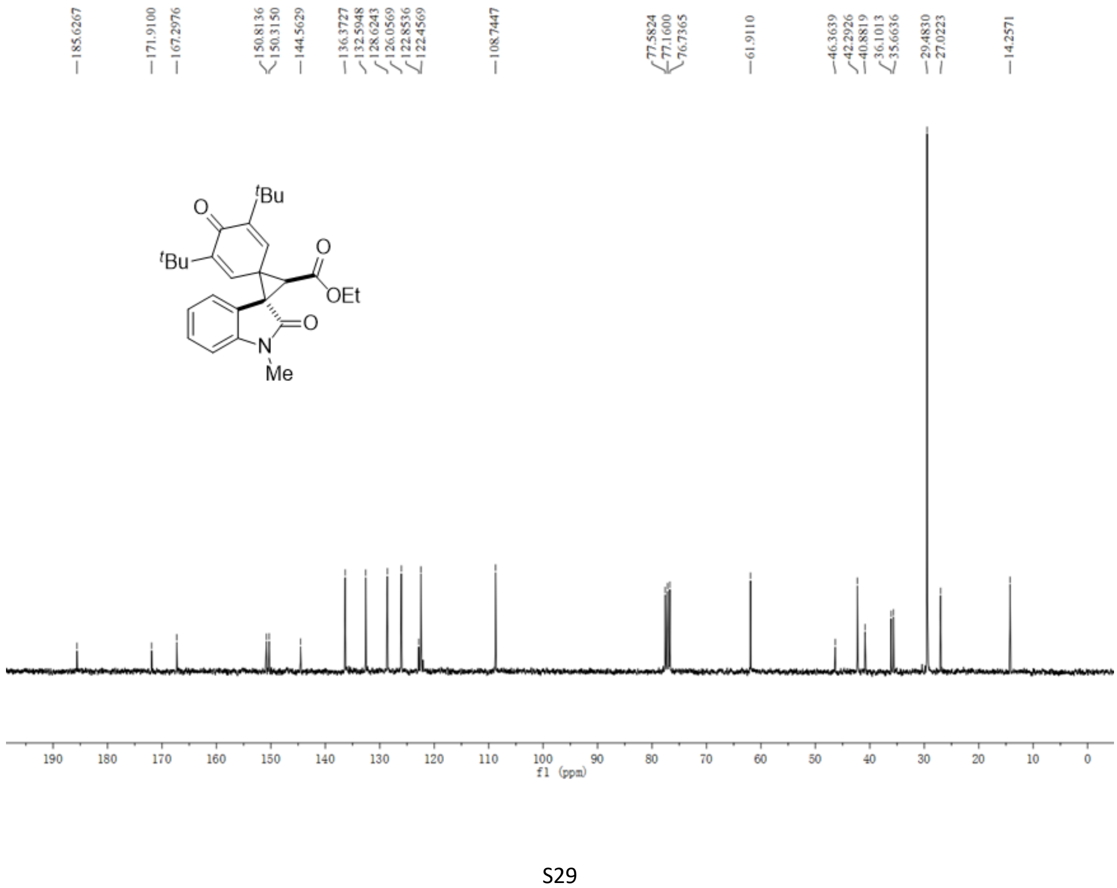
[1]H NMR and [13]C NMR spectra of **3m**



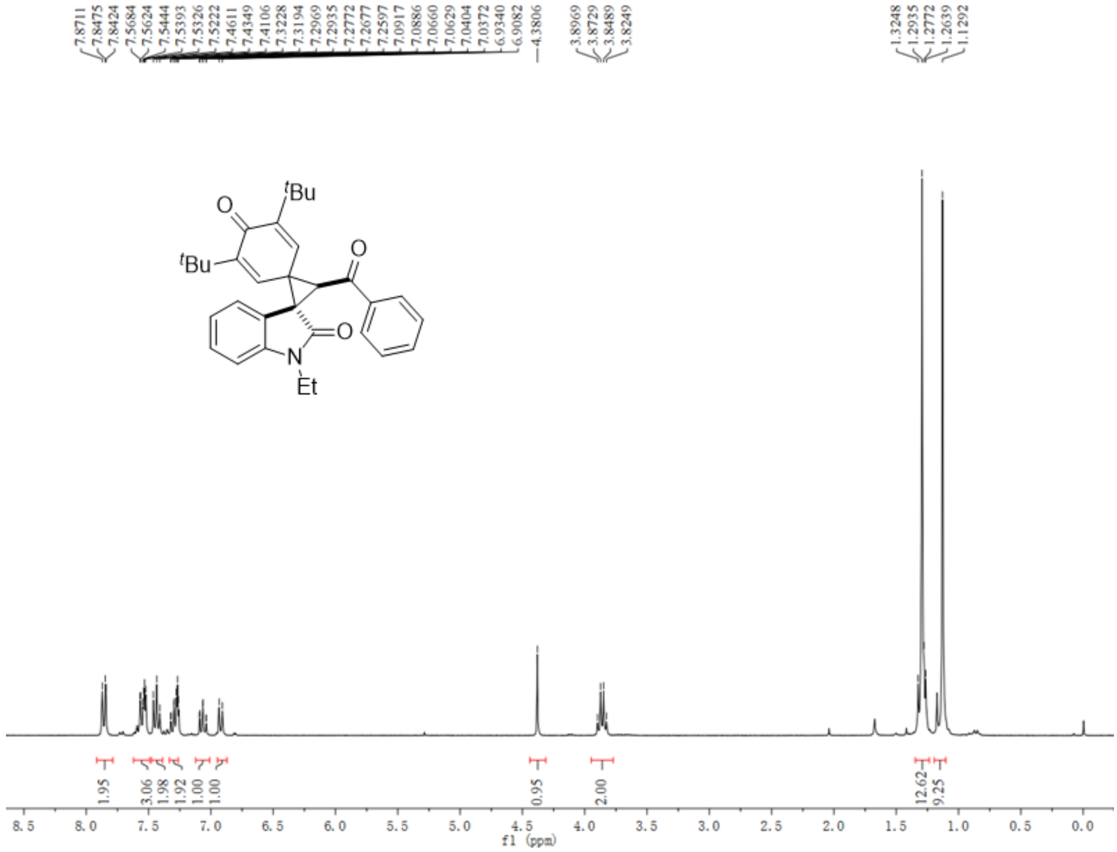


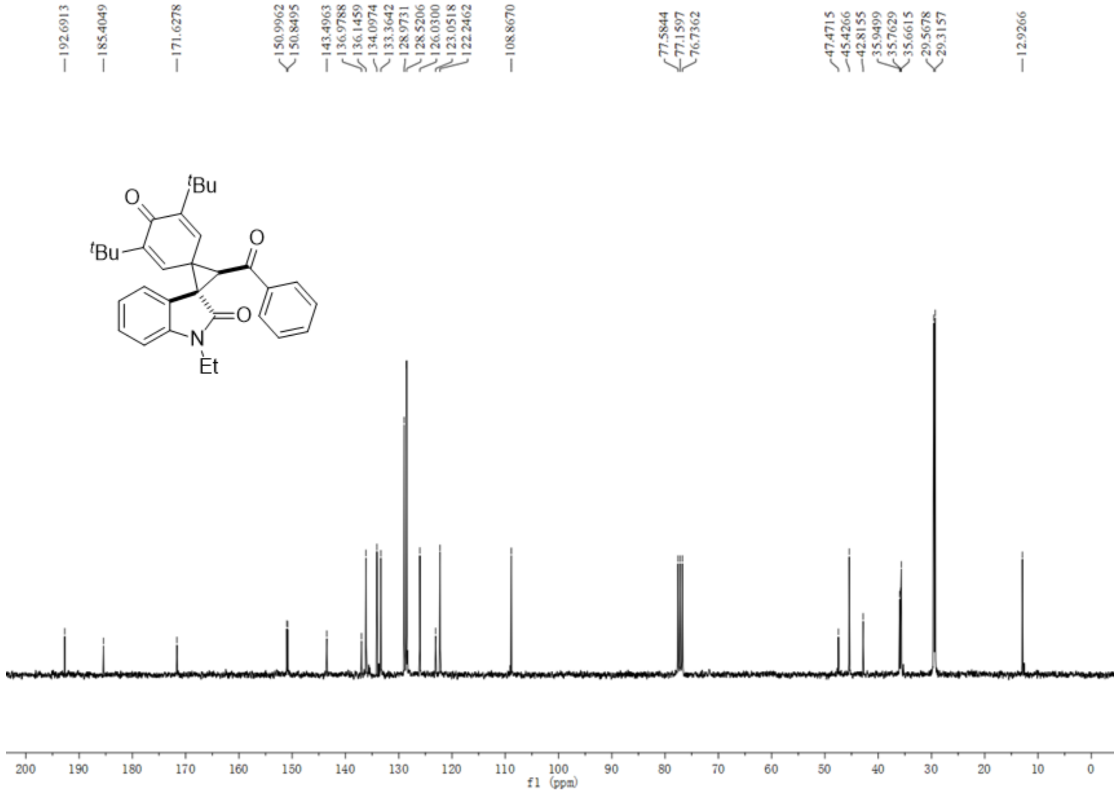
[1]H NMR and [13]C NMR spectra of **3n**



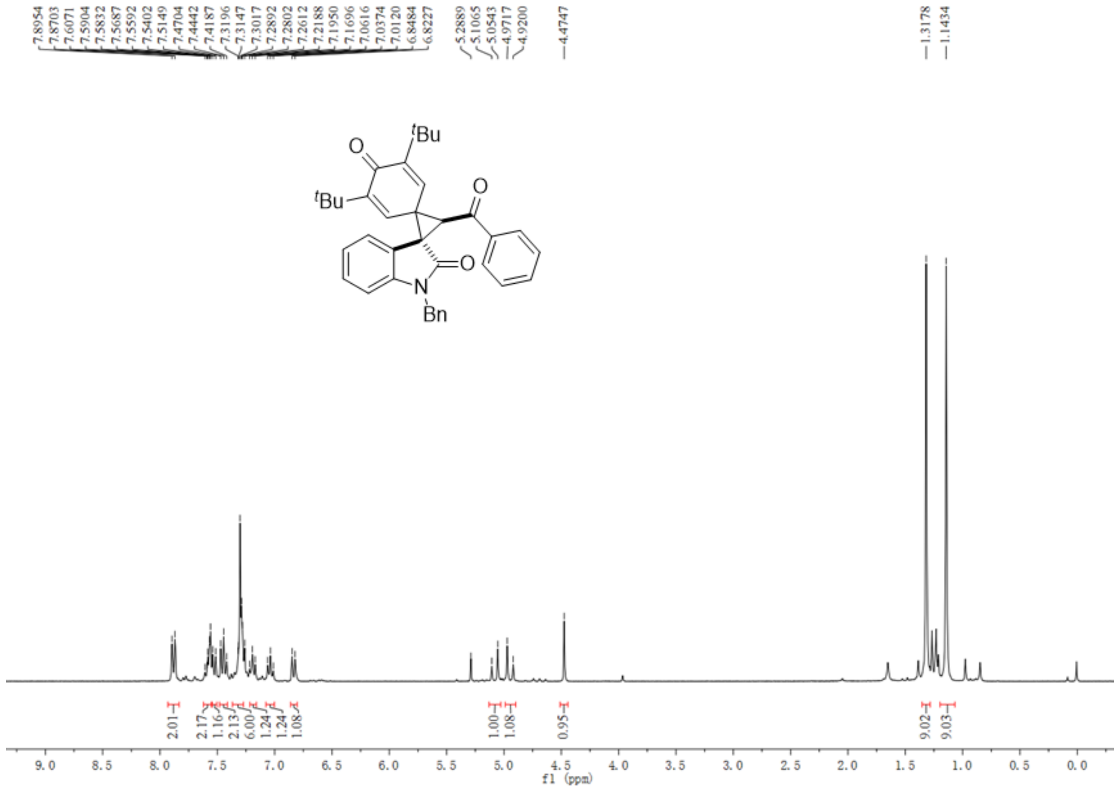


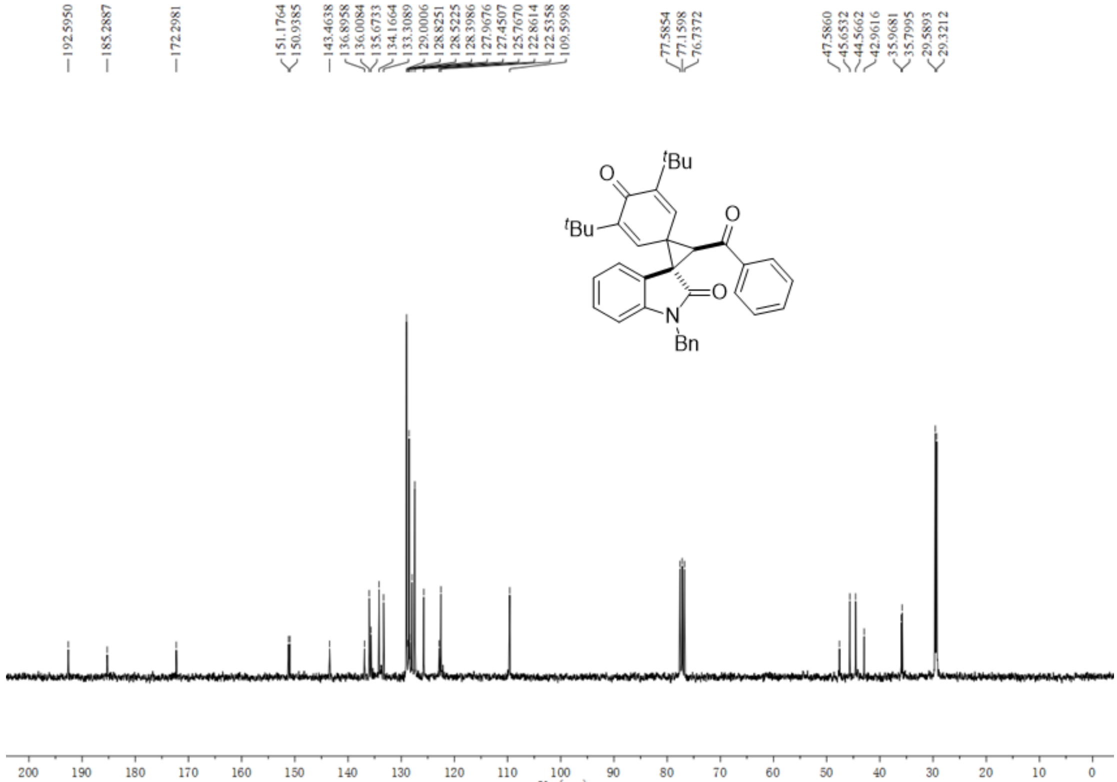
^{1}H NMR and ^{13}C NMR spectra of **3o**



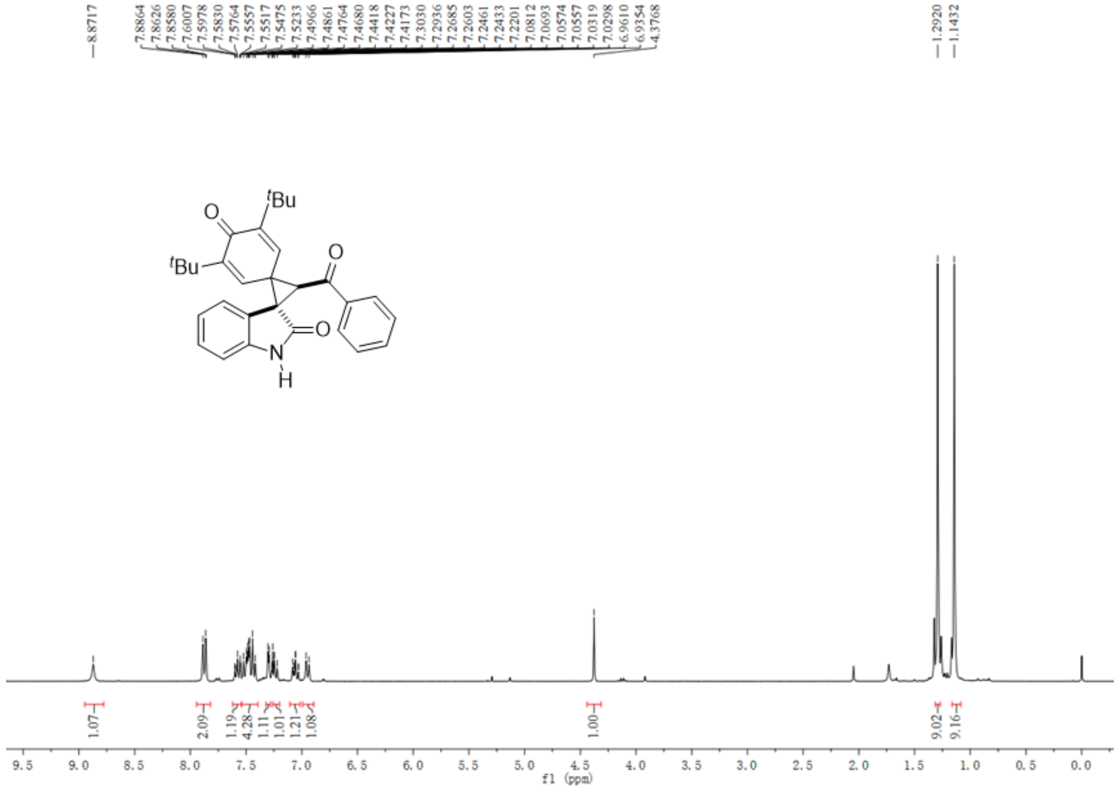


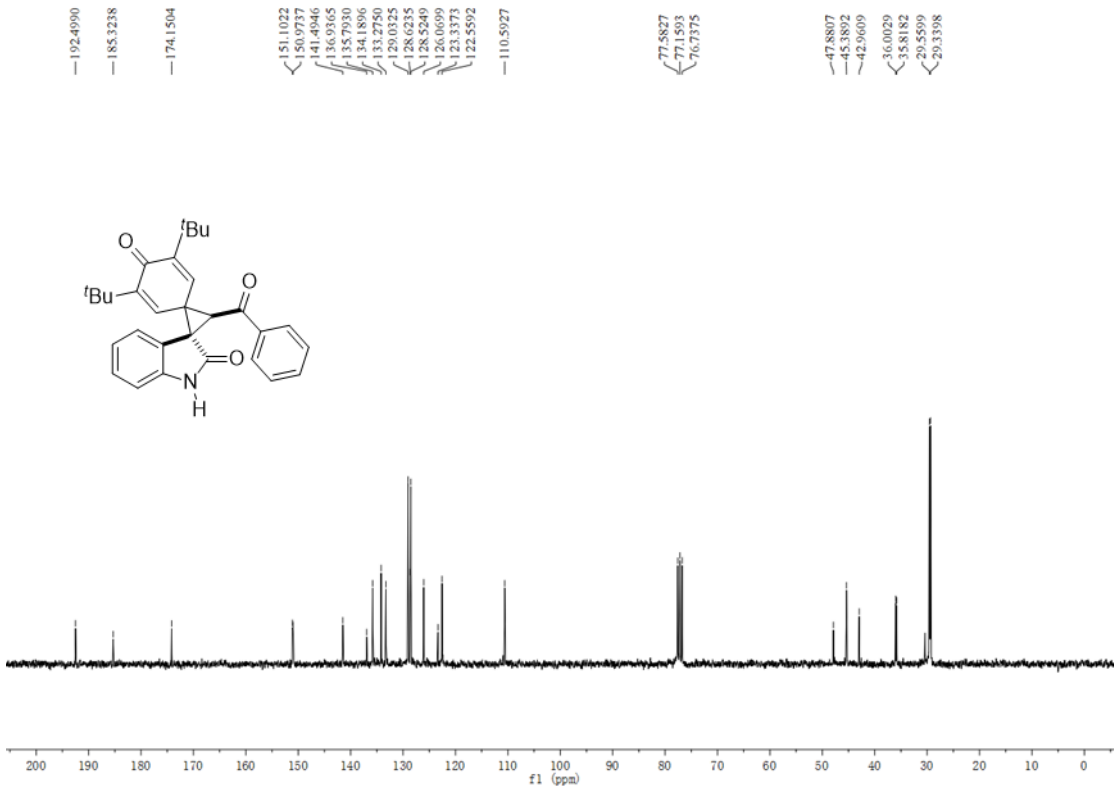
^{1}H NMR and ^{13}C NMR spectra of **3p**



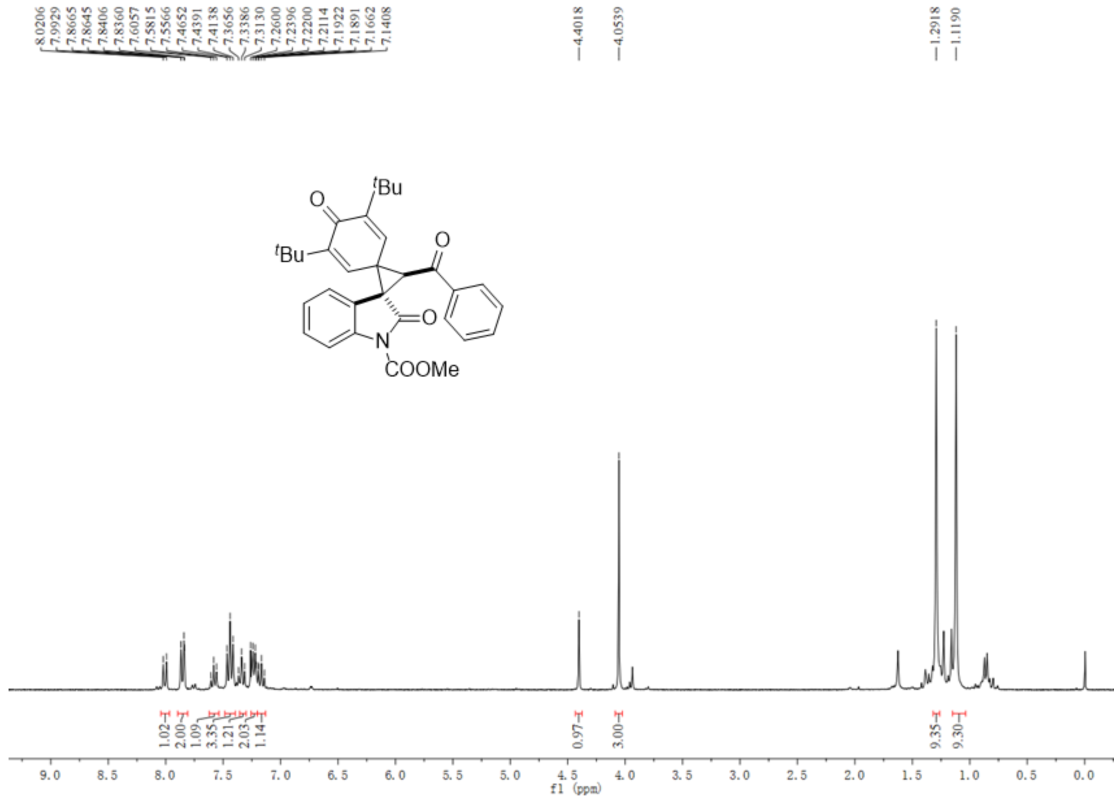


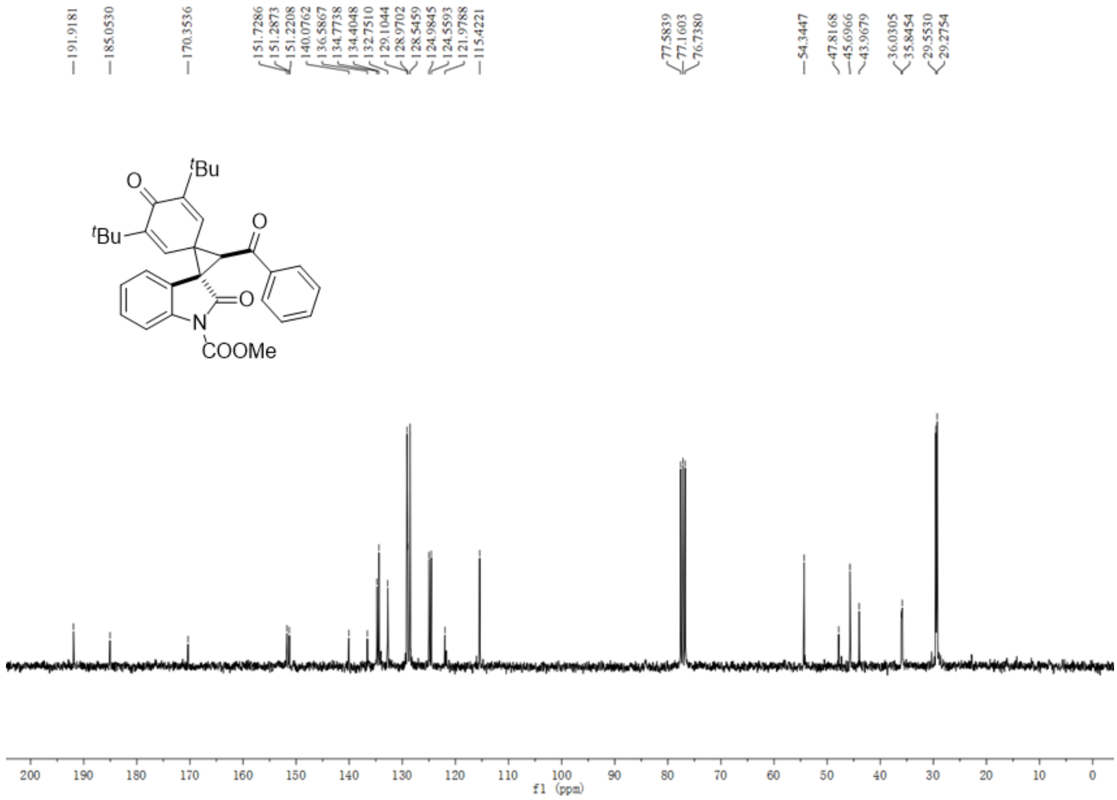
[1]H NMR and [13]C NMR spectra of **3q**



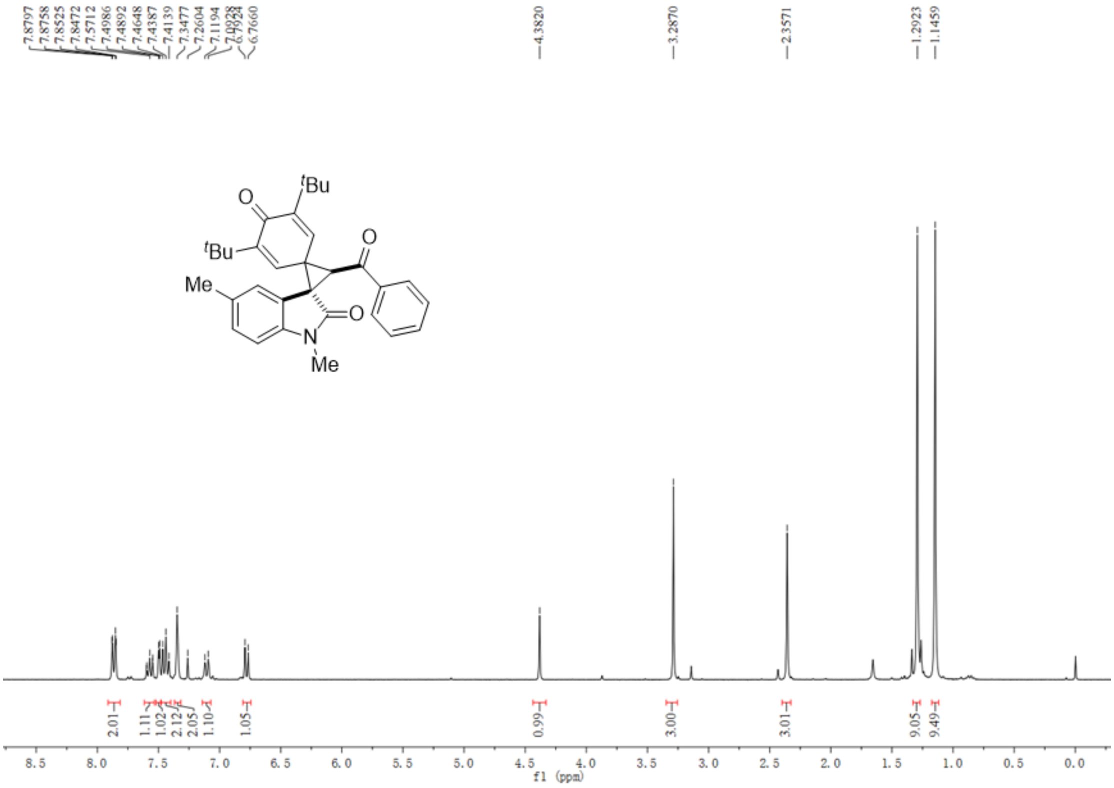


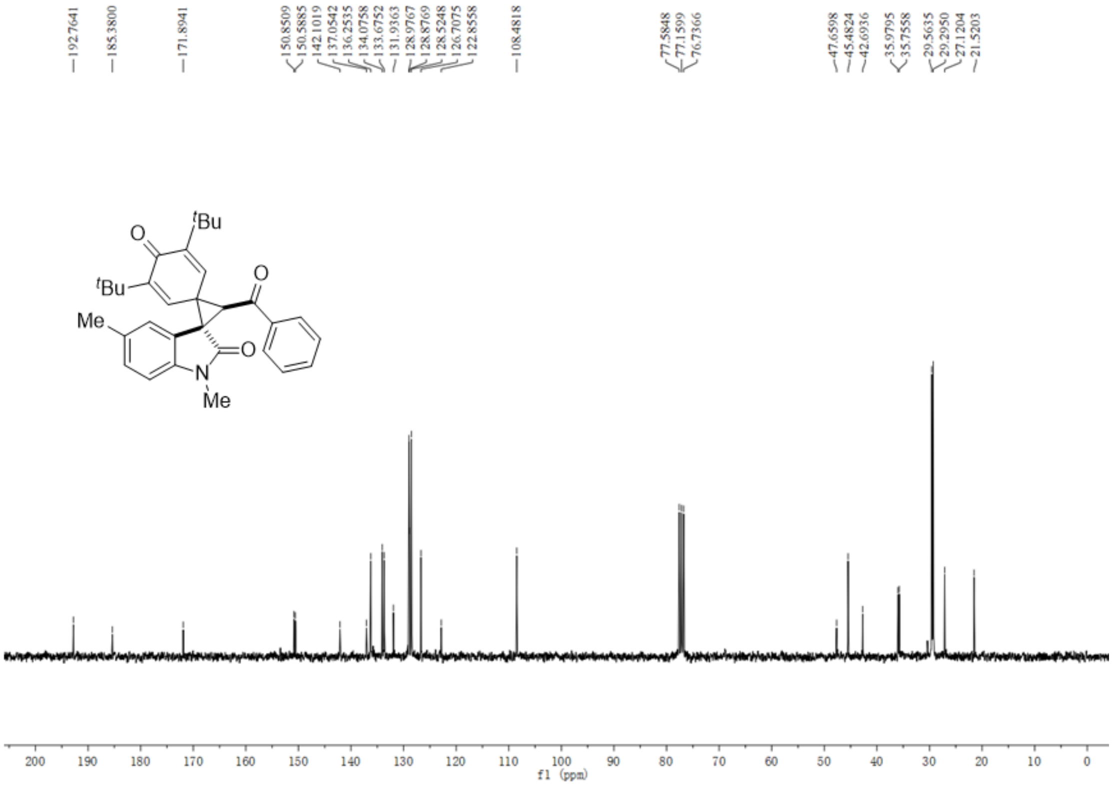
[1]H NMR and [13]C NMR spectra of **3r**



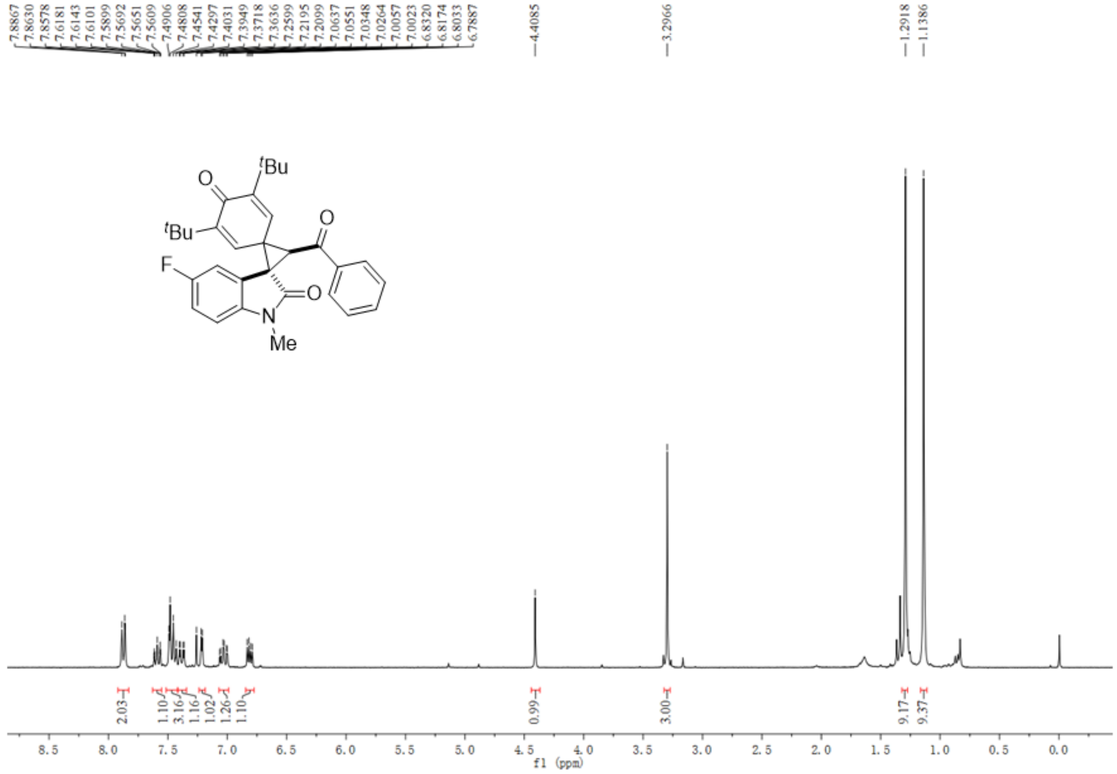


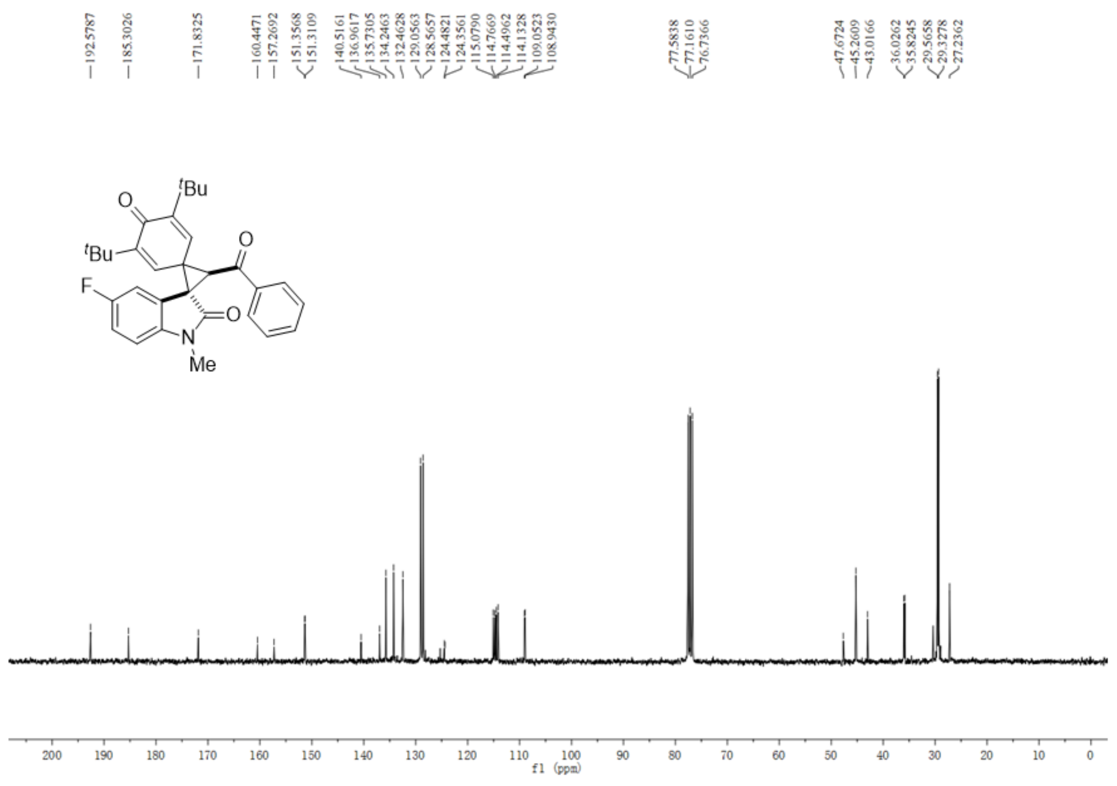
[1]H NMR and [13]C NMR spectra of **3s**



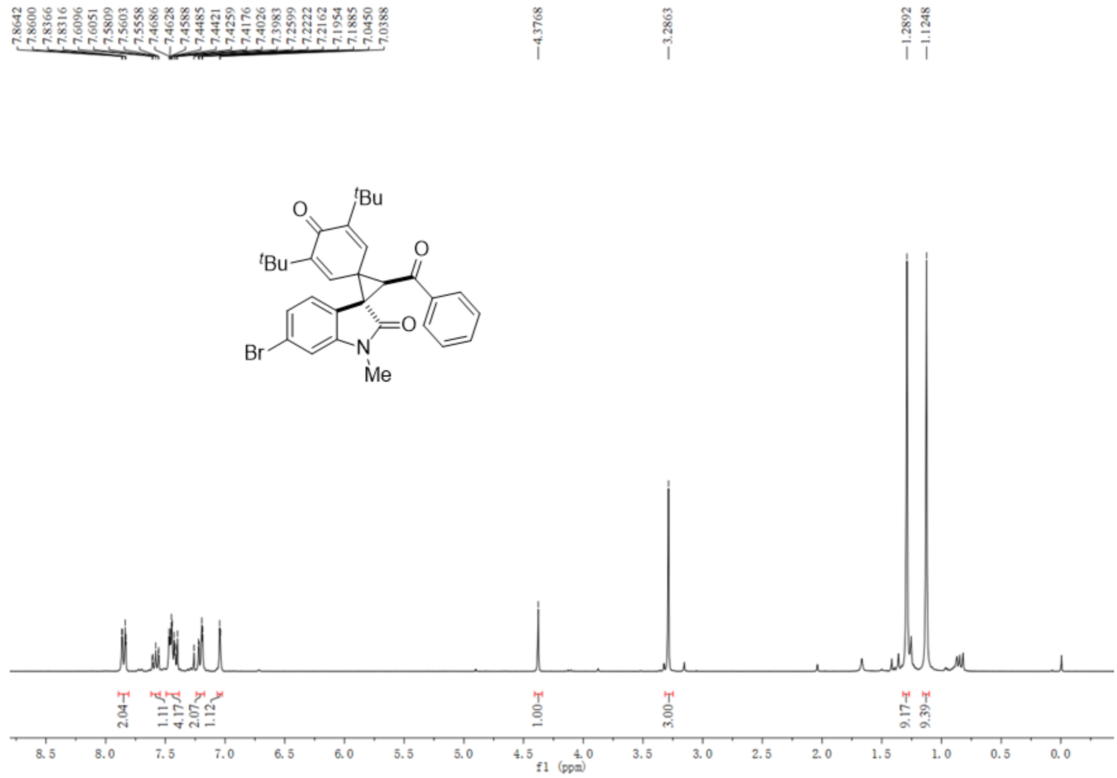


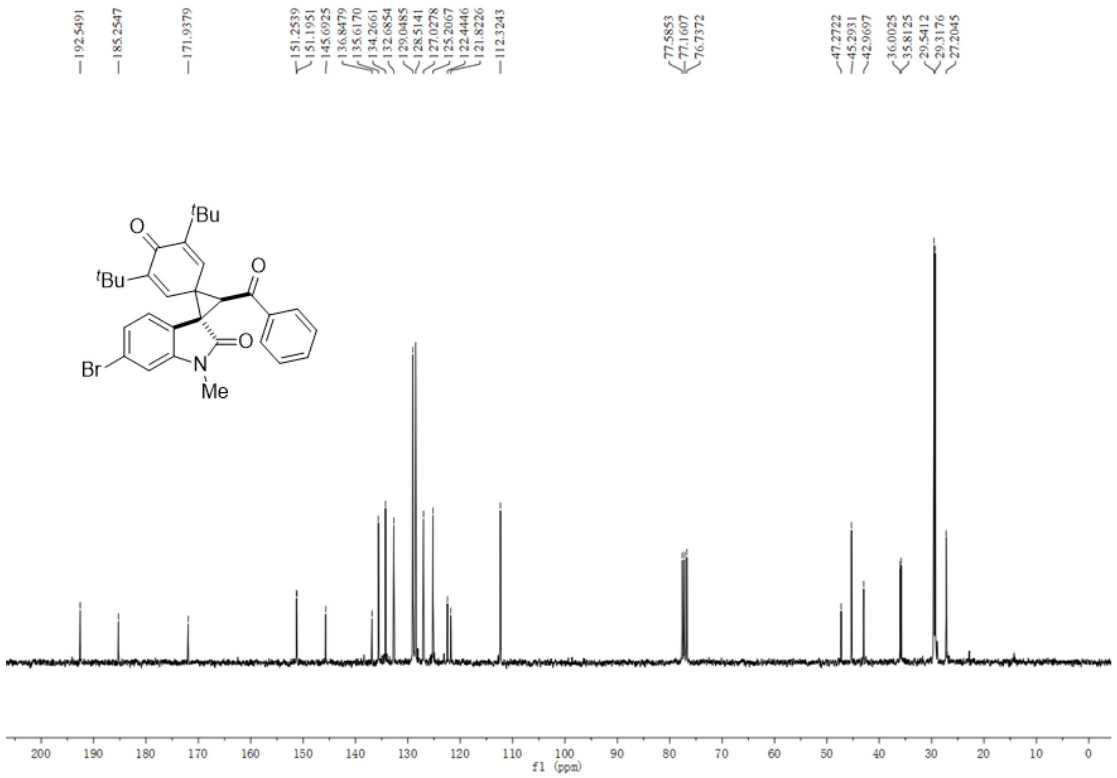
[1]H NMR and [13]C NMR spectra of **3t**



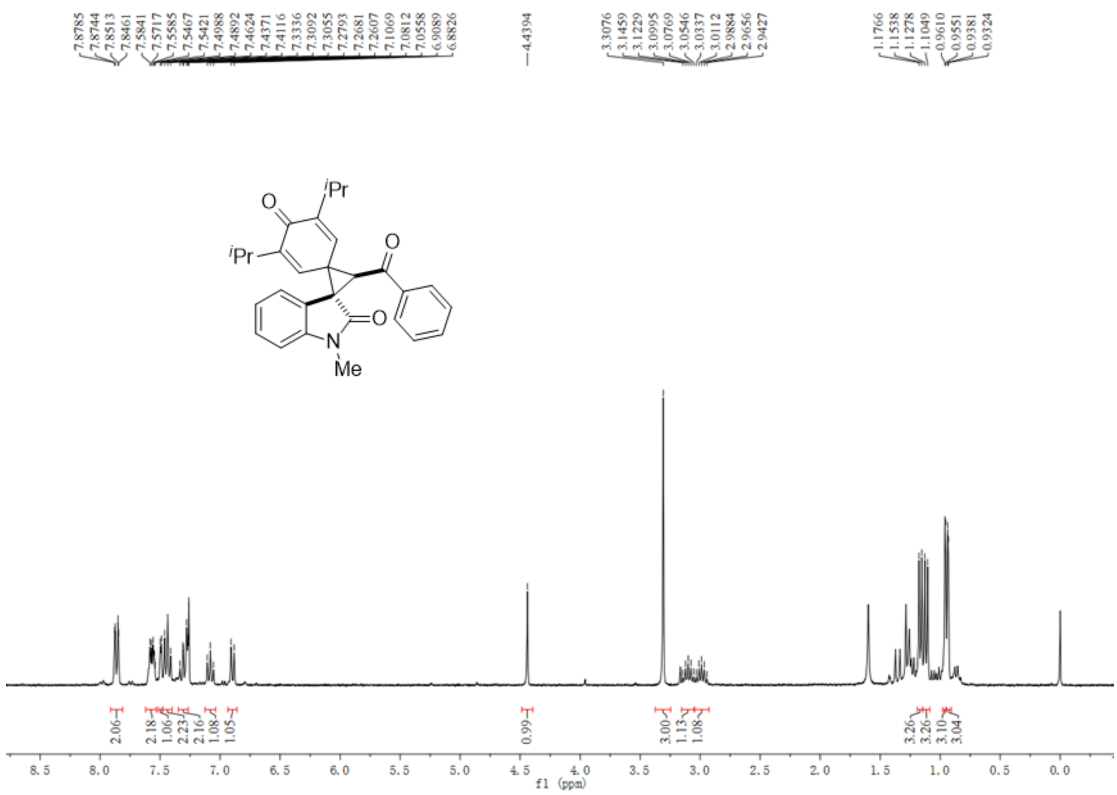


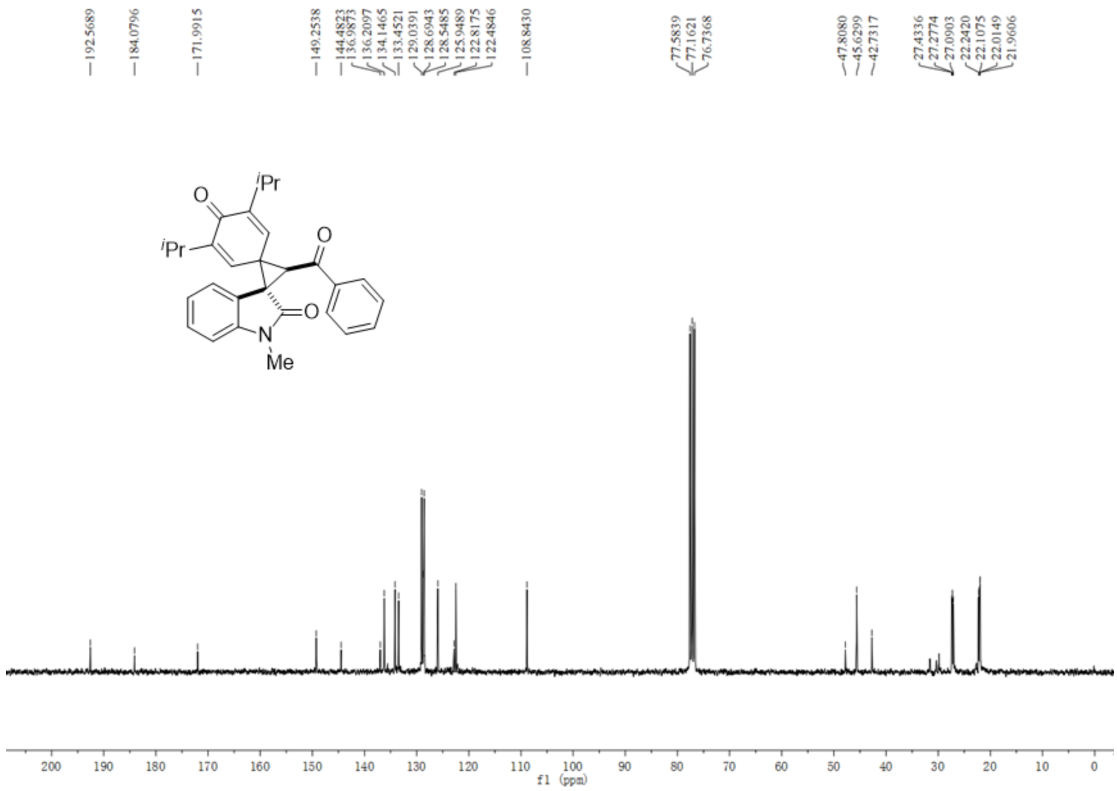
^{1}H NMR and ^{13}C NMR spectra of **3u**



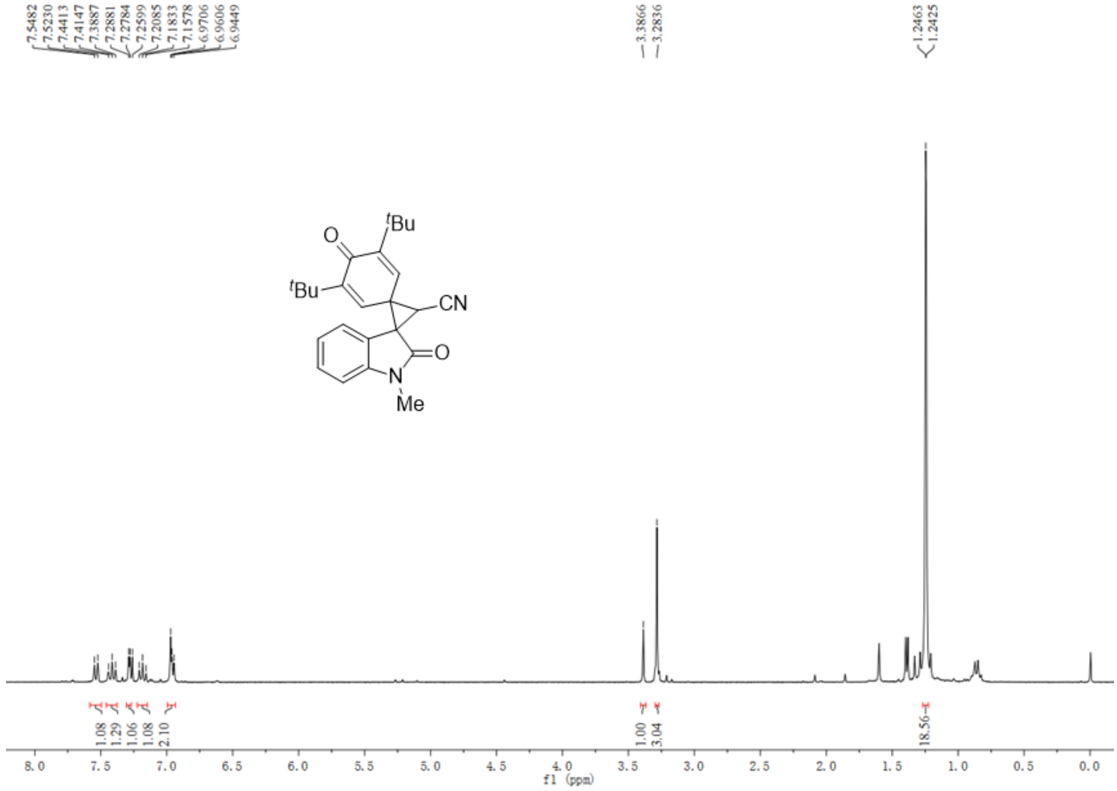


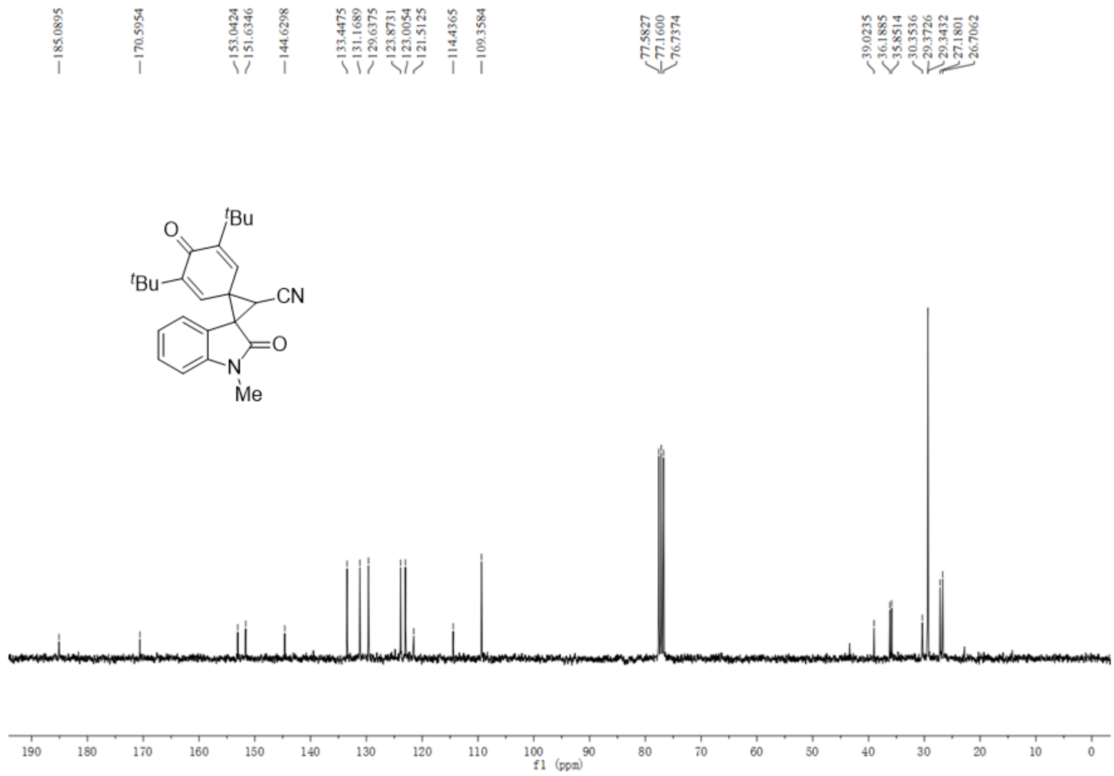
^1H NMR and ^{13}C NMR spectra of **3v**



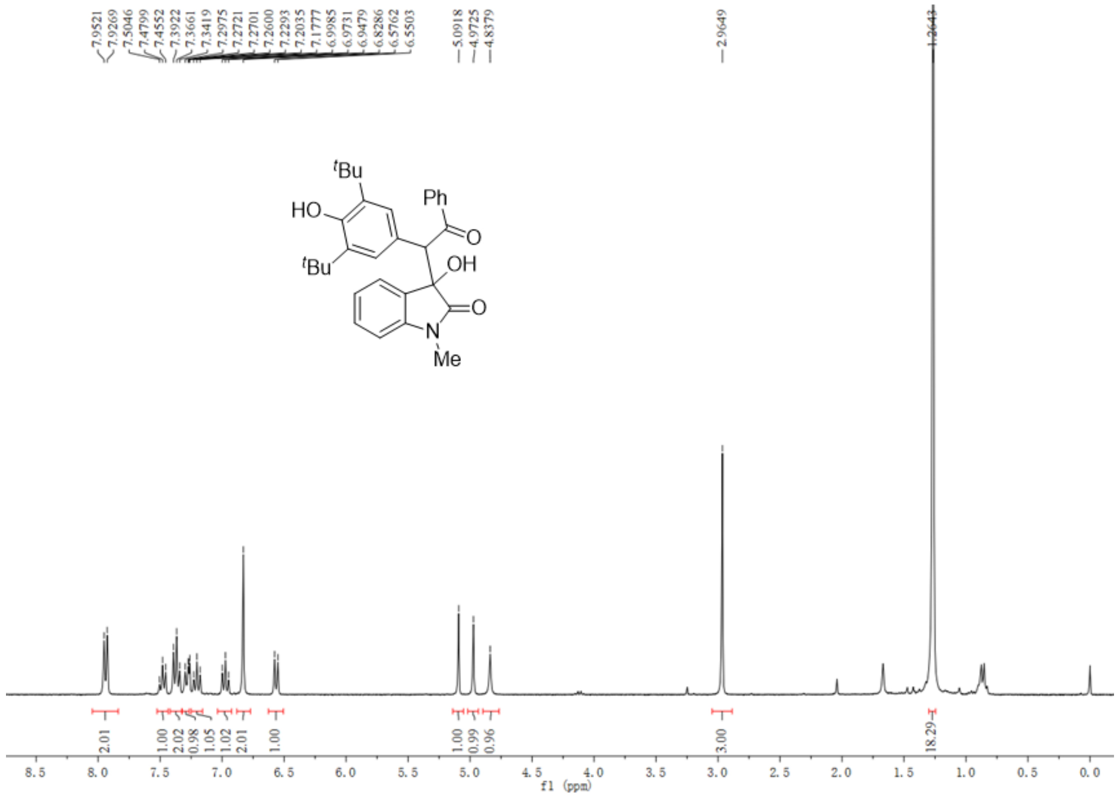


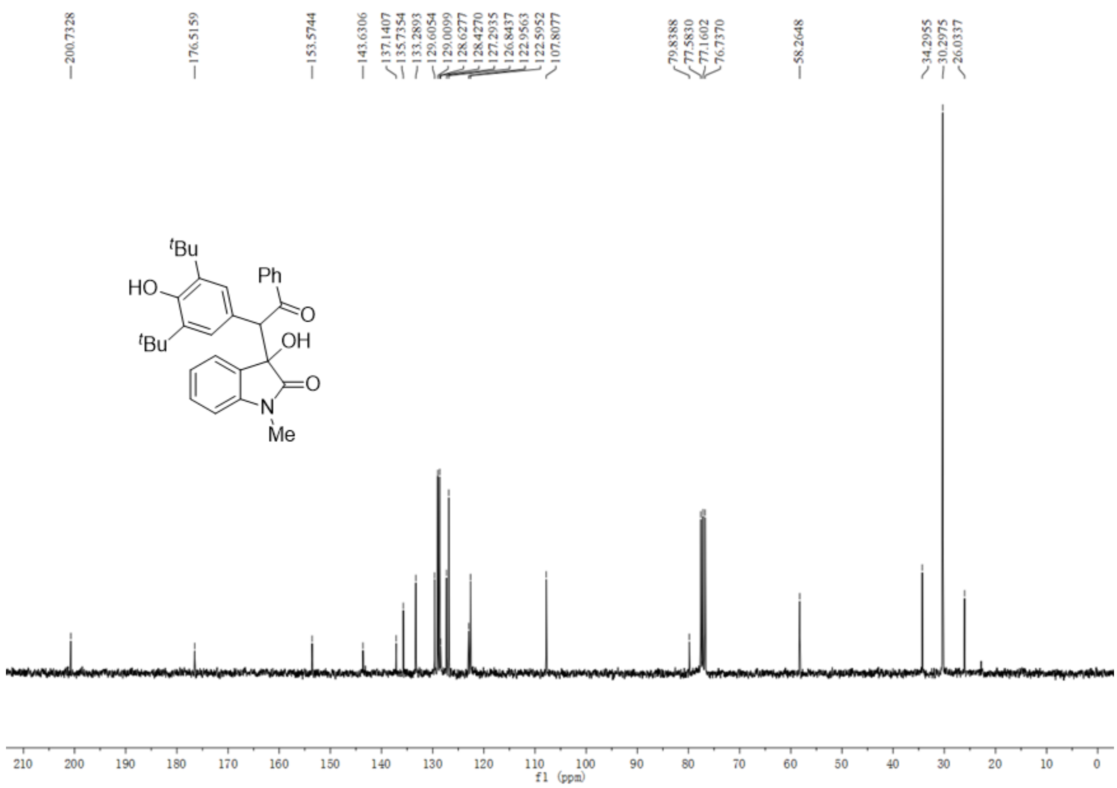
^{1}H NMR and ^{13}C NMR spectra of **5**



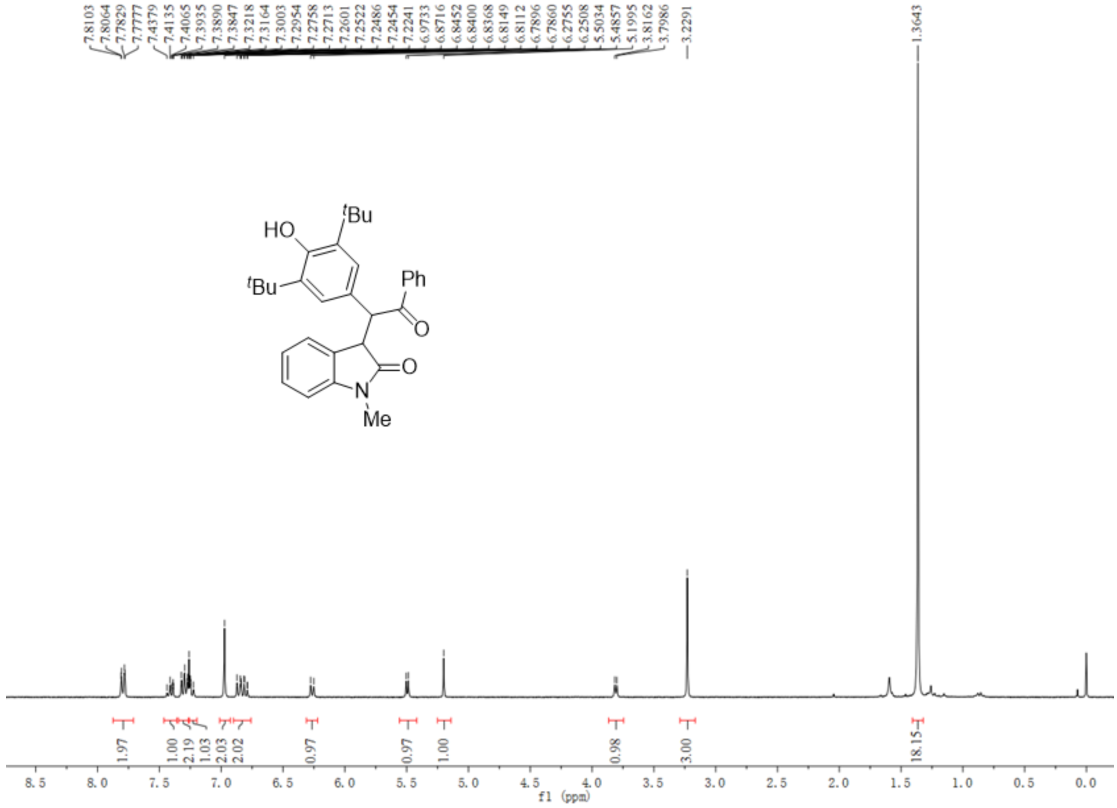


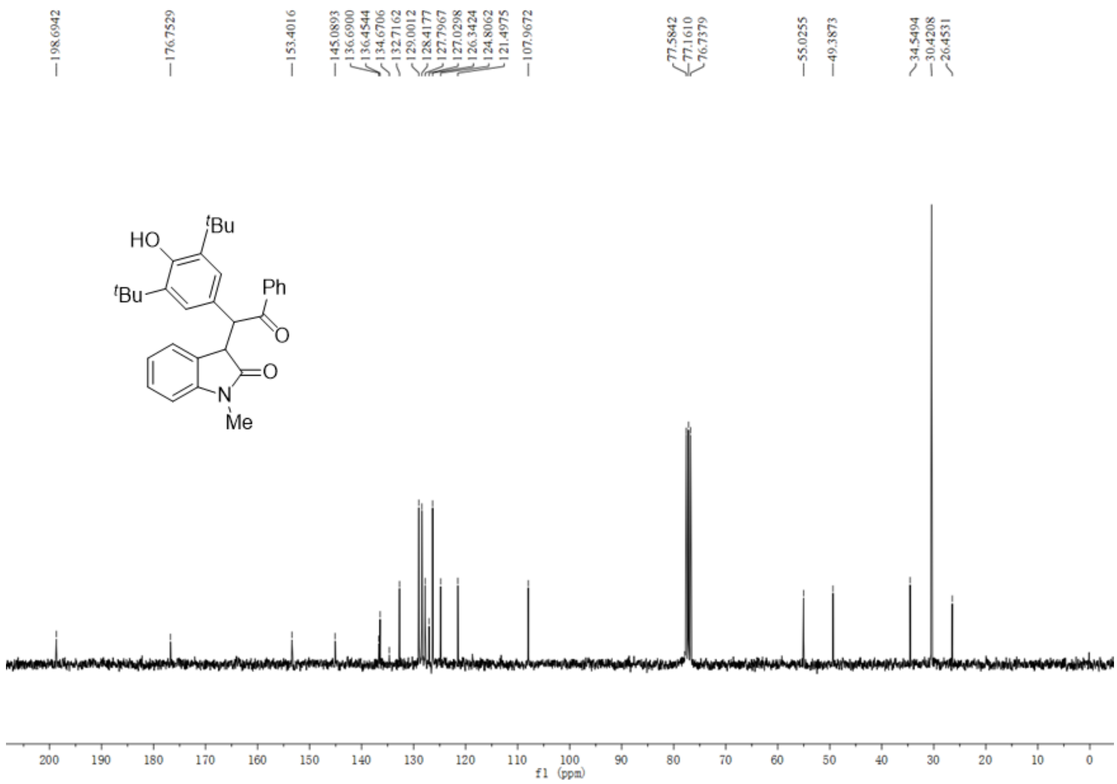
^{1}H NMR and ^{13}C NMR spectra of **6**



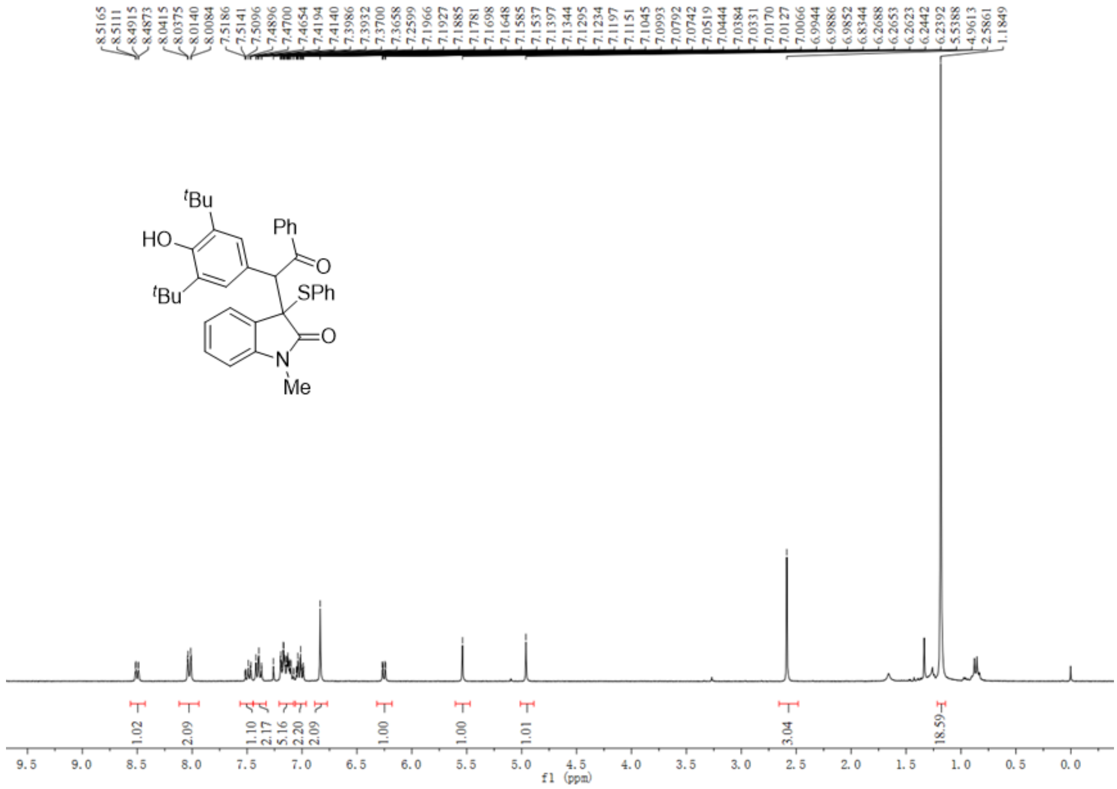


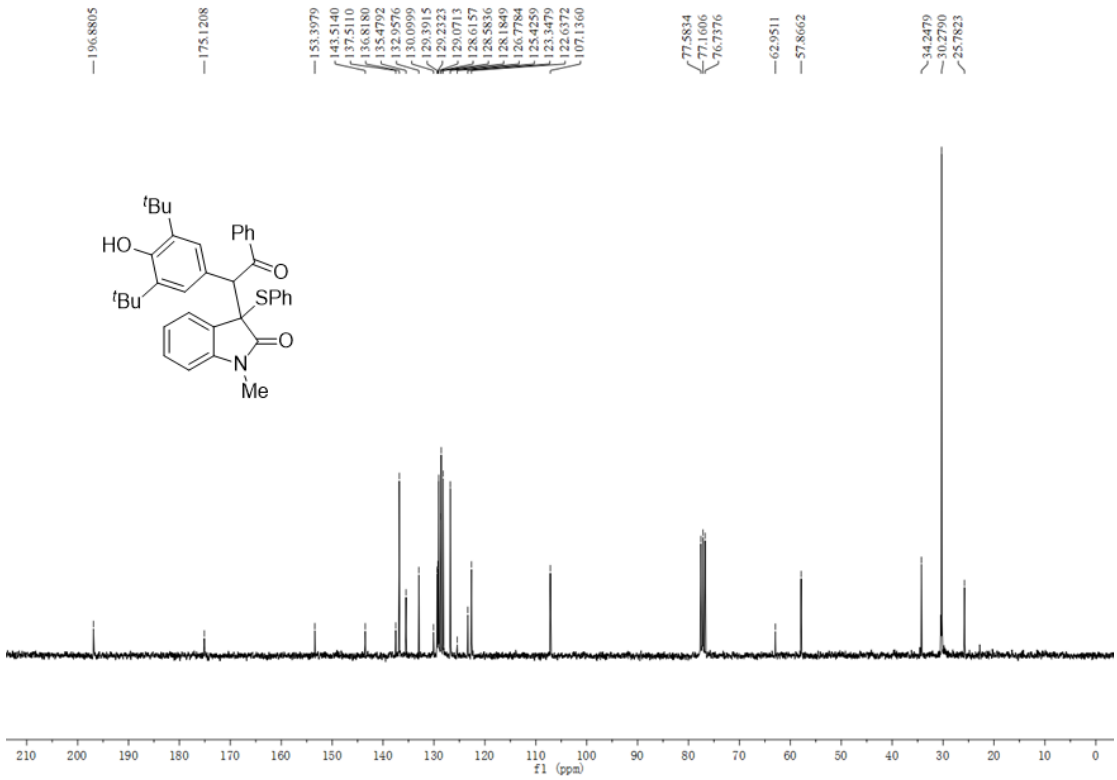
^{1}H NMR and ^{13}C NMR spectra of **7**



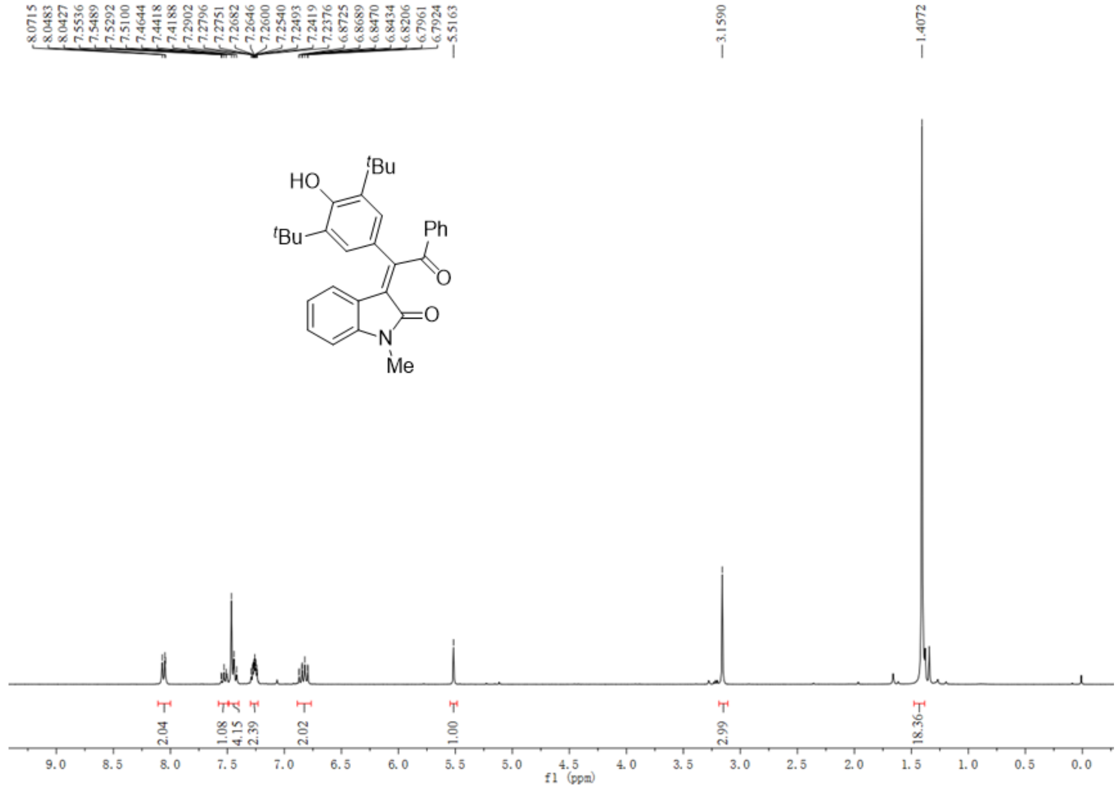


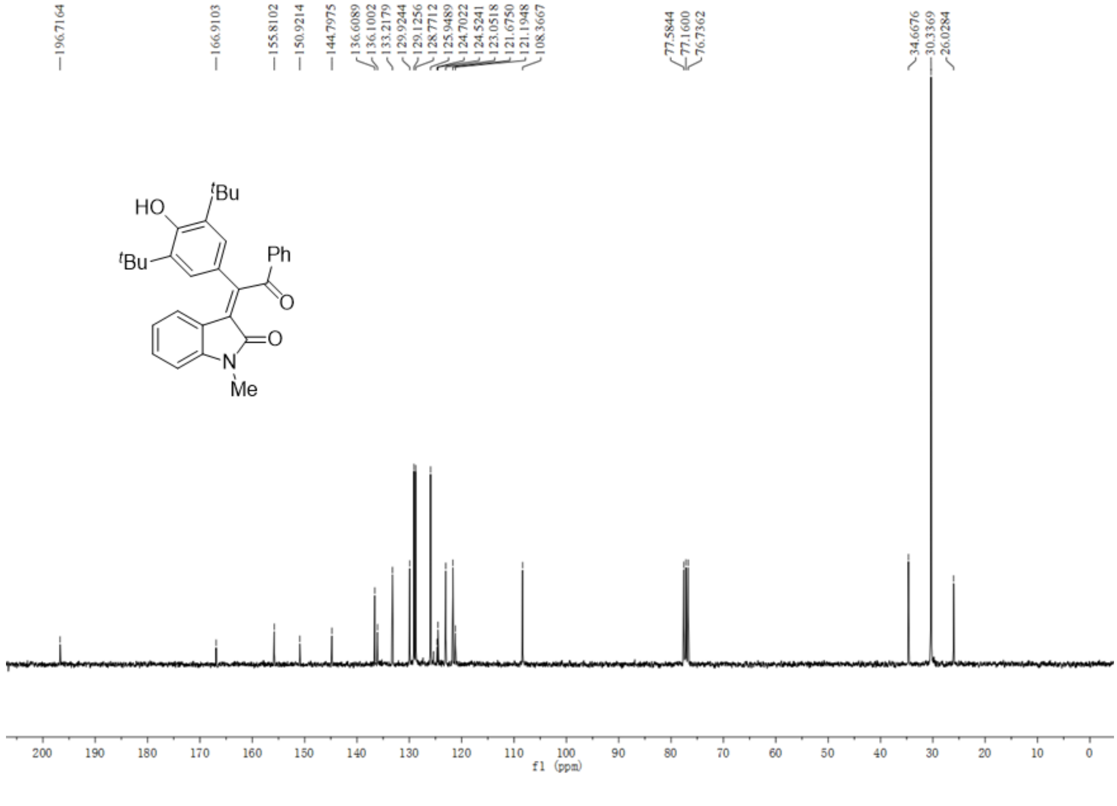
^{1}H NMR and ^{13}C NMR spectra of **8**



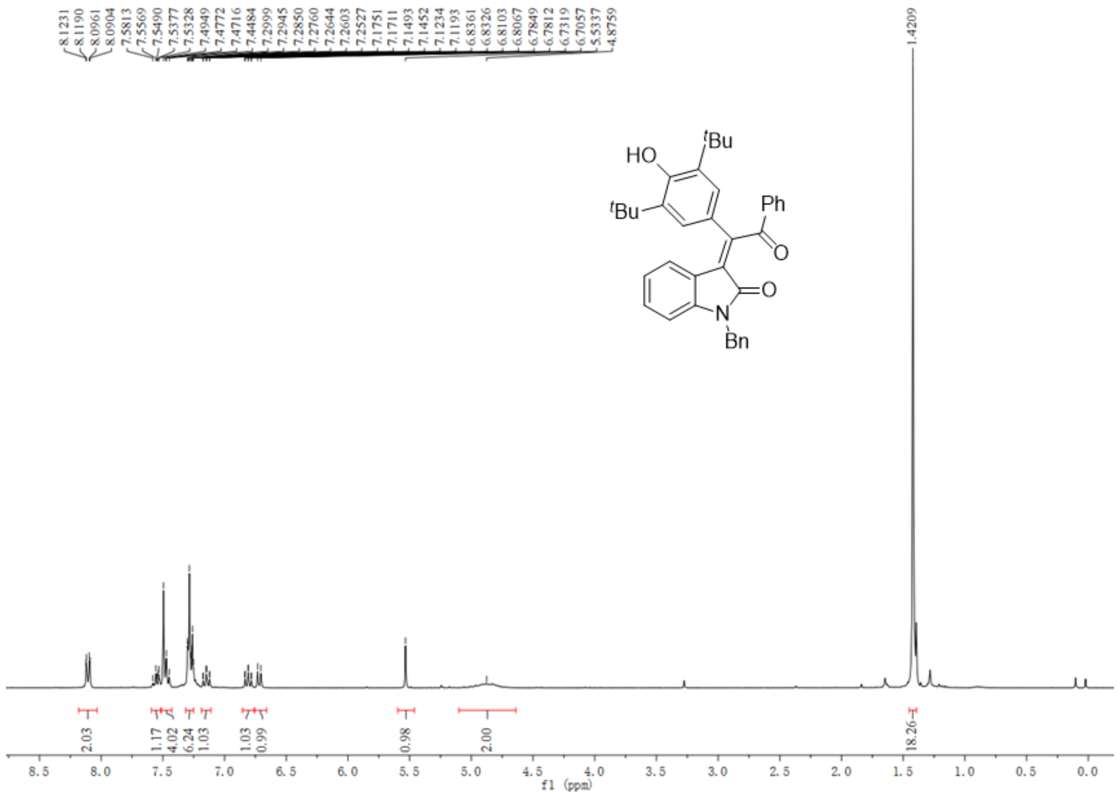


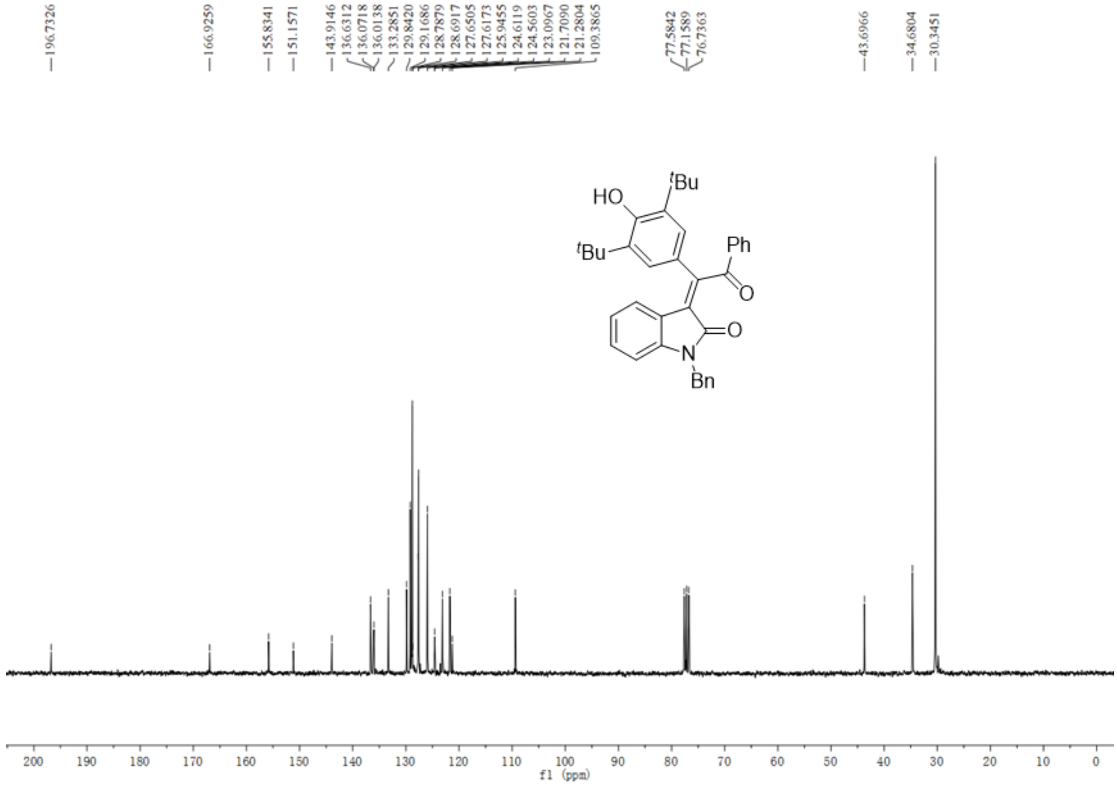
^{1}H NMR and ^{13}C NMR spectra of **9a**



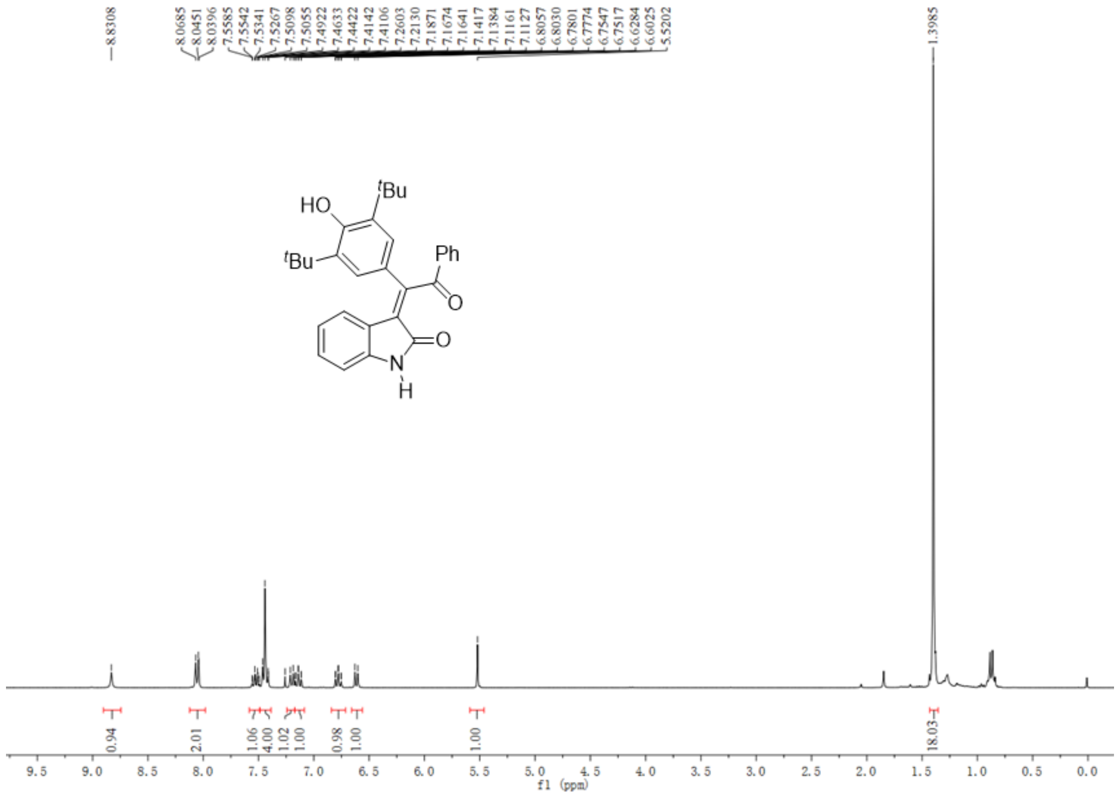


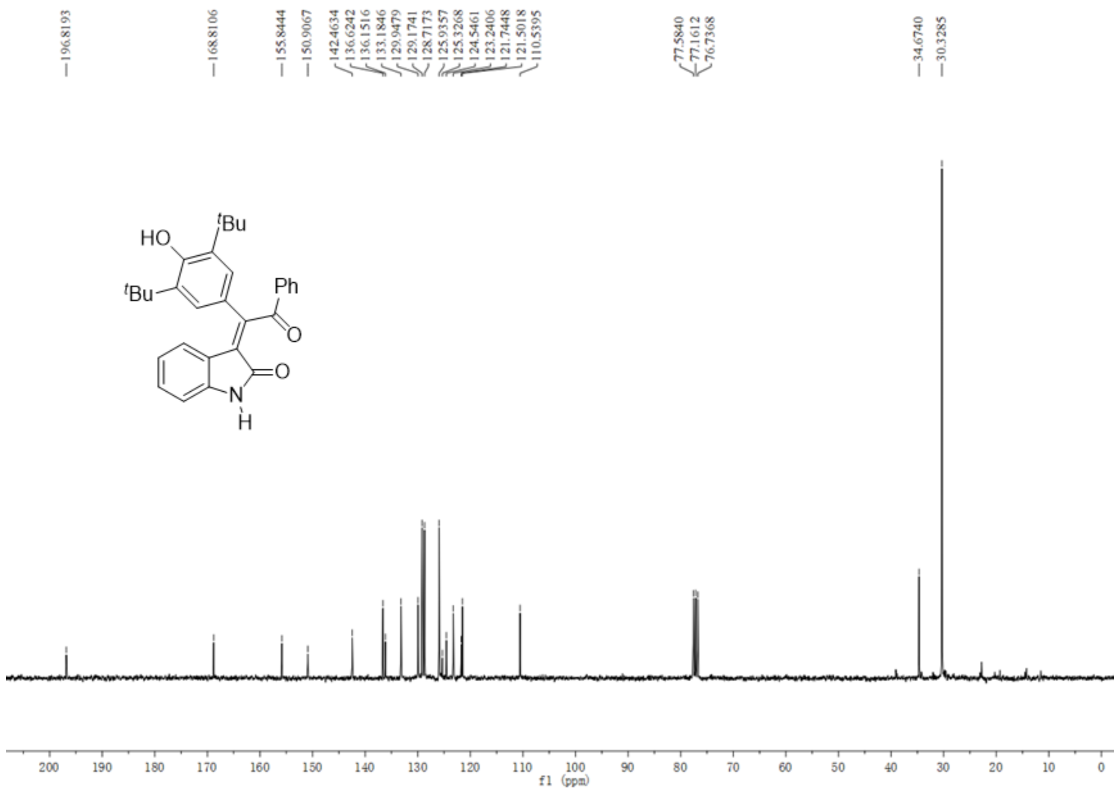
^{1}H NMR and ^{13}C NMR spectra of **9b**



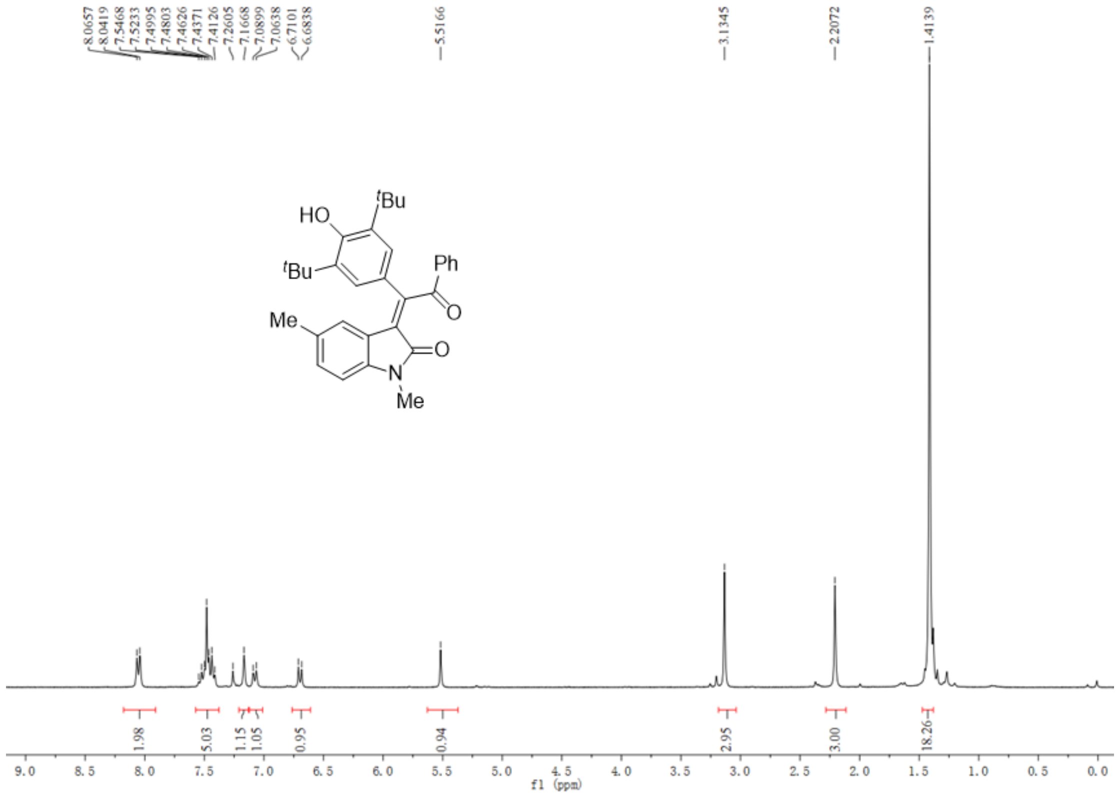


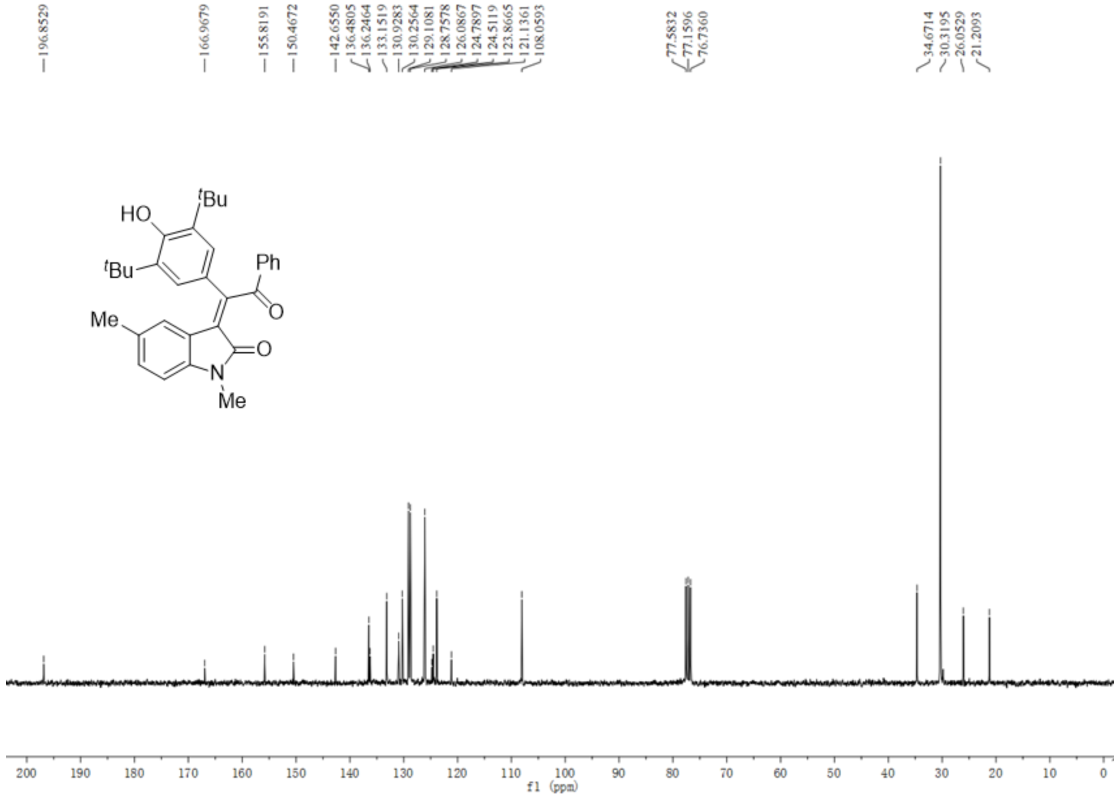
^{1}H NMR and ^{13}C NMR spectra of **9c**



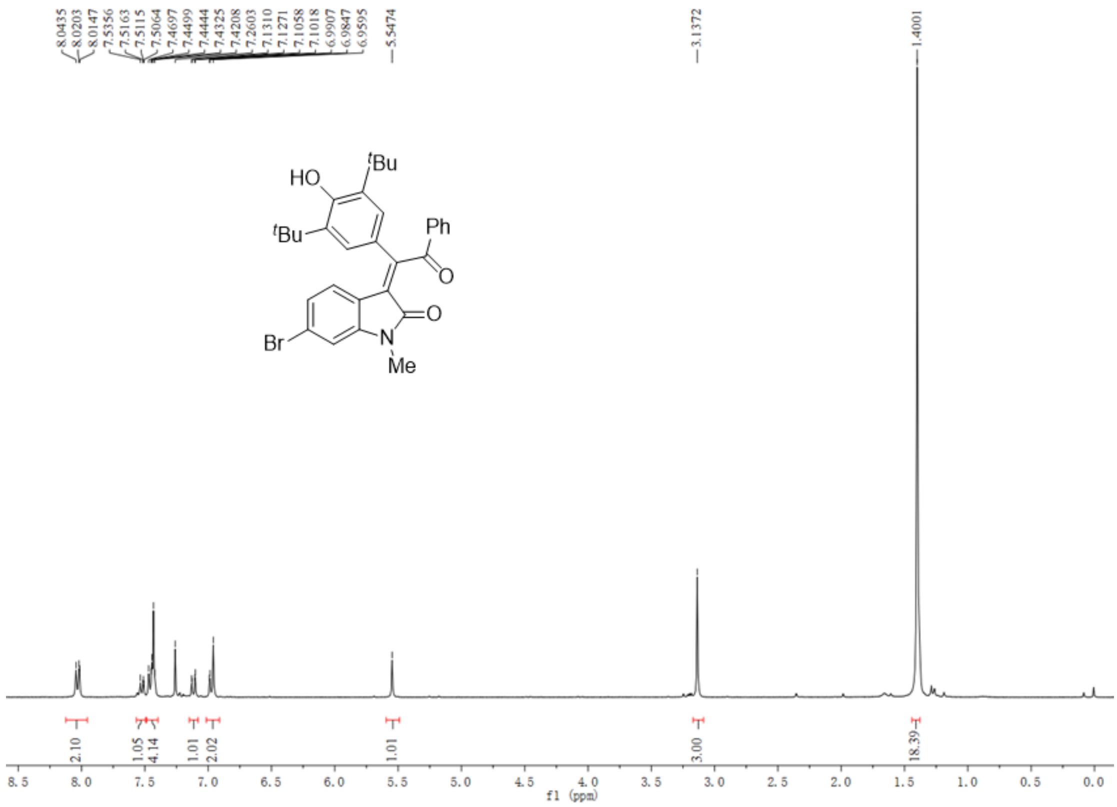


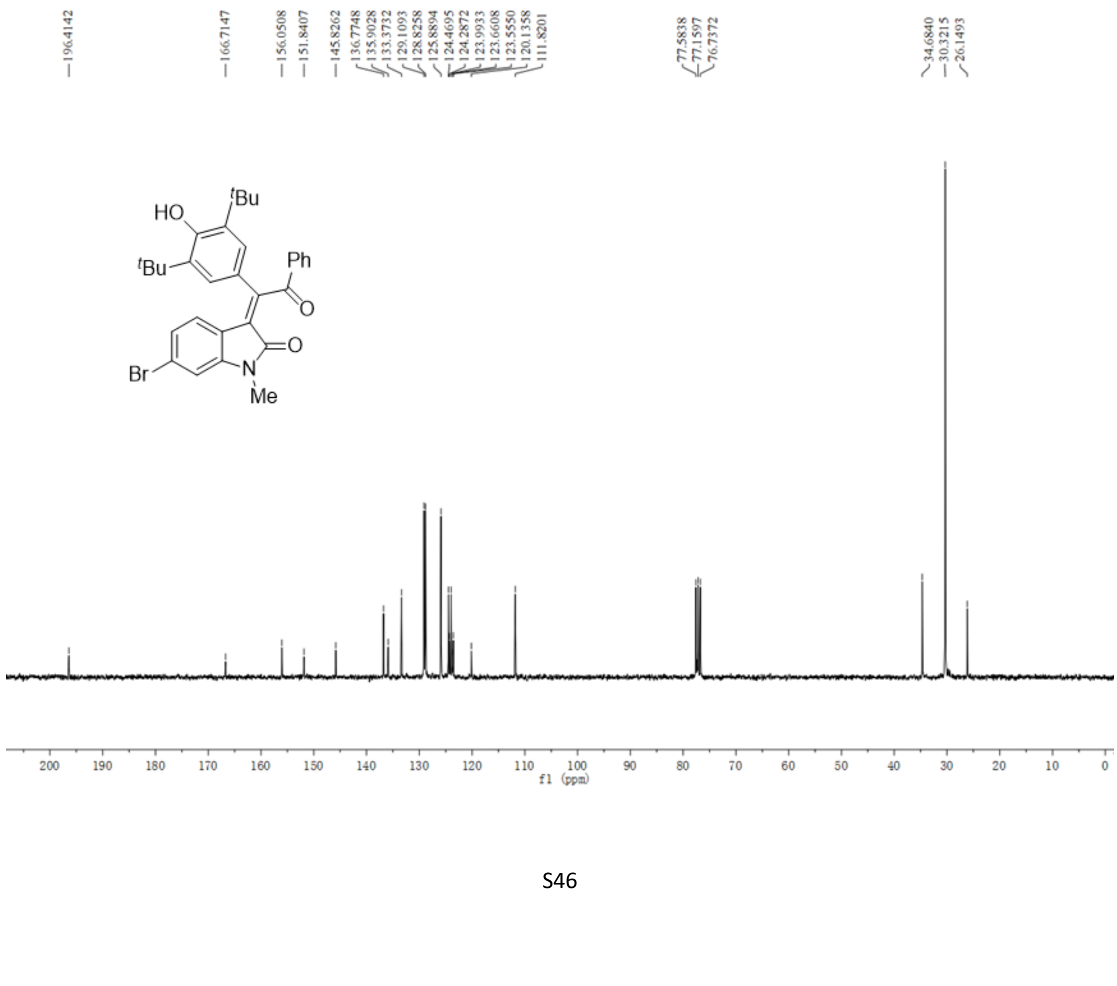
[1]H NMR and [13]C NMR spectra of **9d**



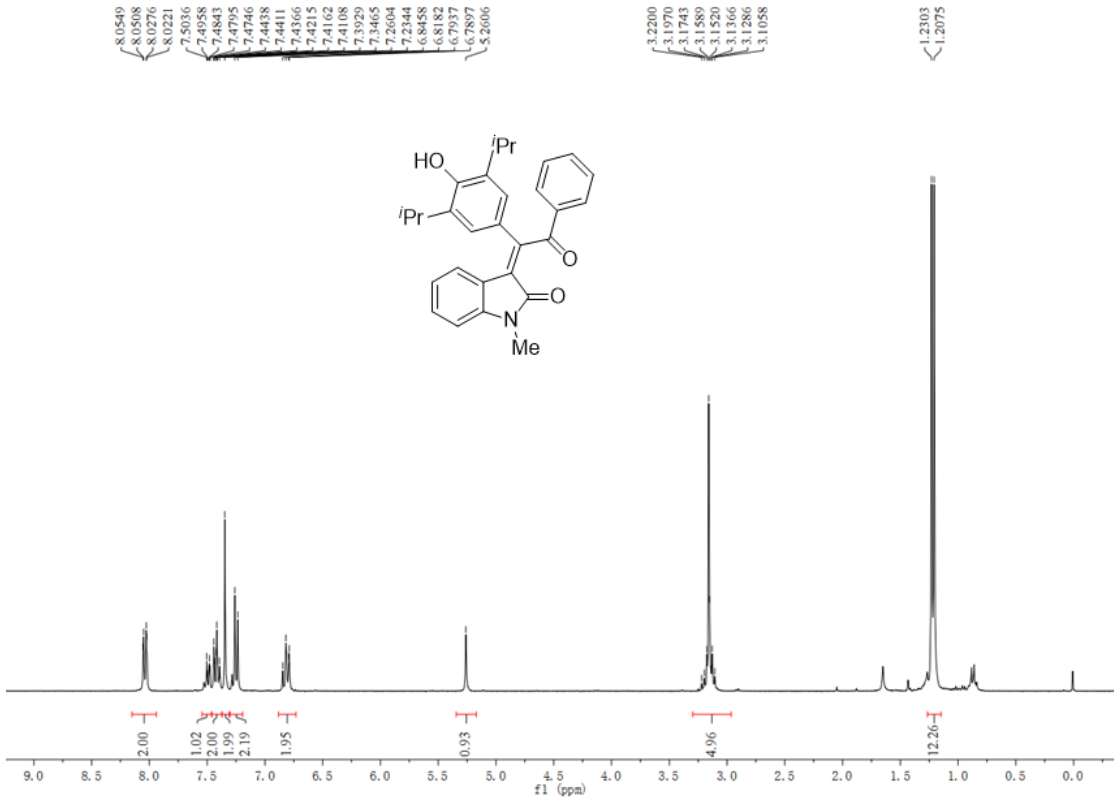


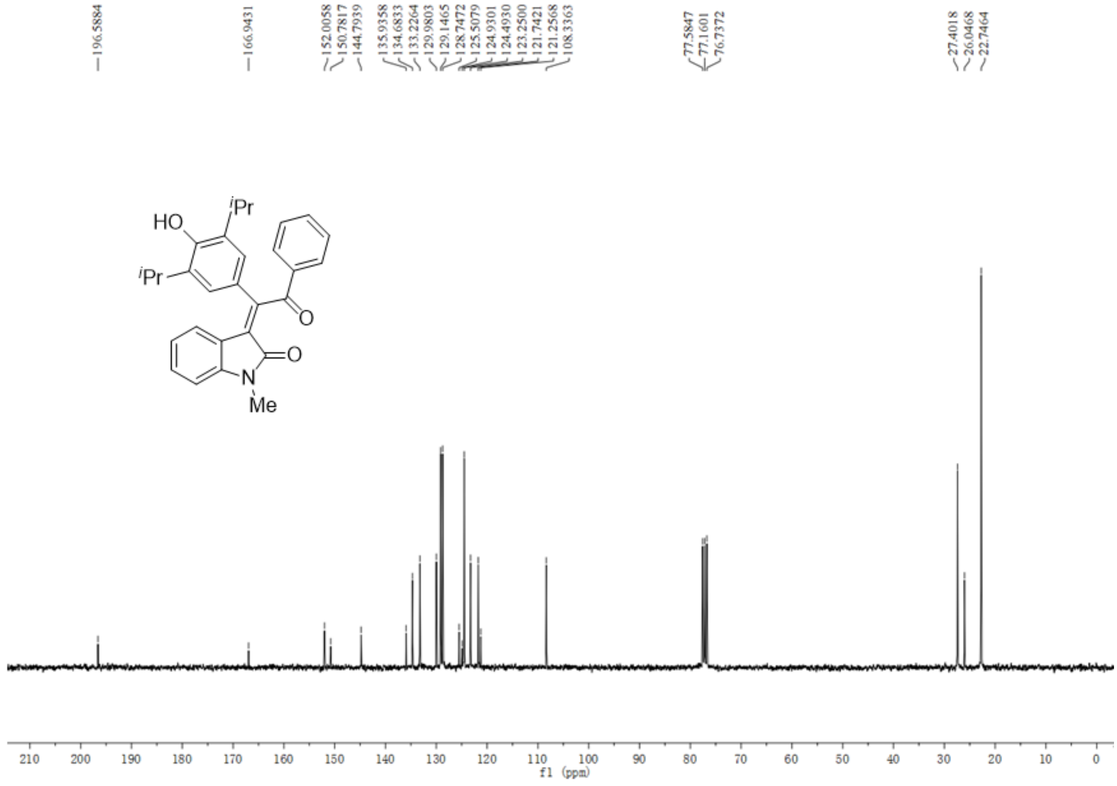
^{1}H NMR and ^{13}C NMR spectra of **9e**



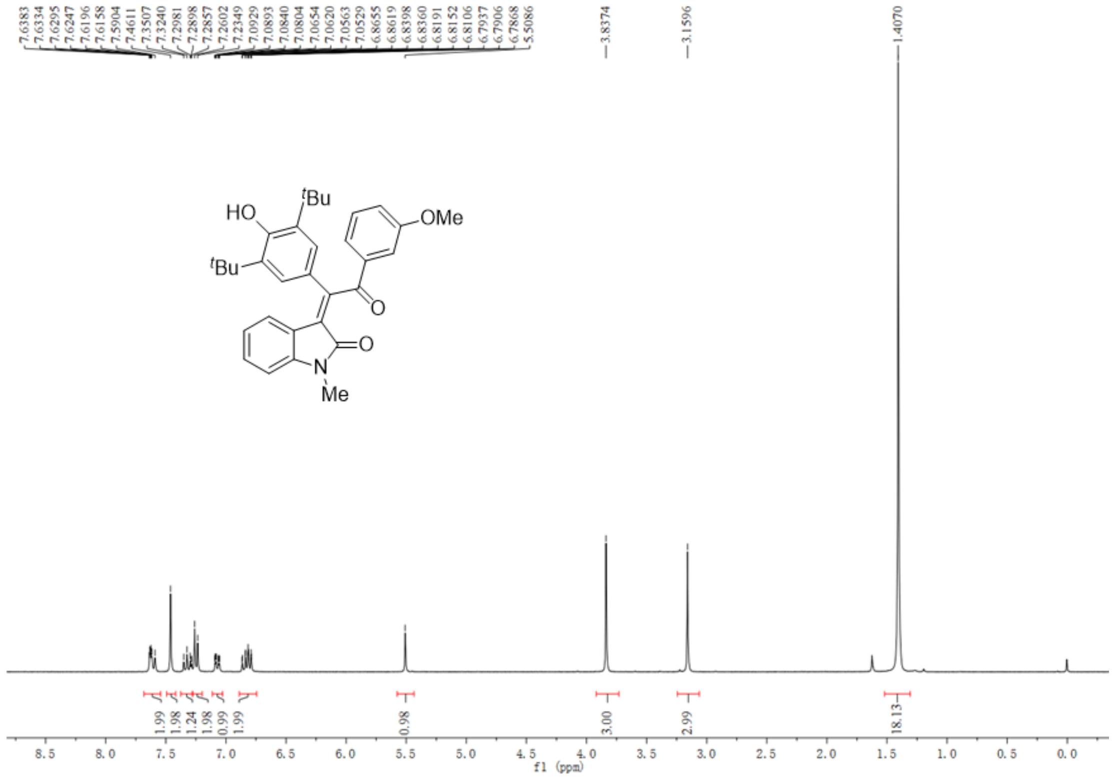


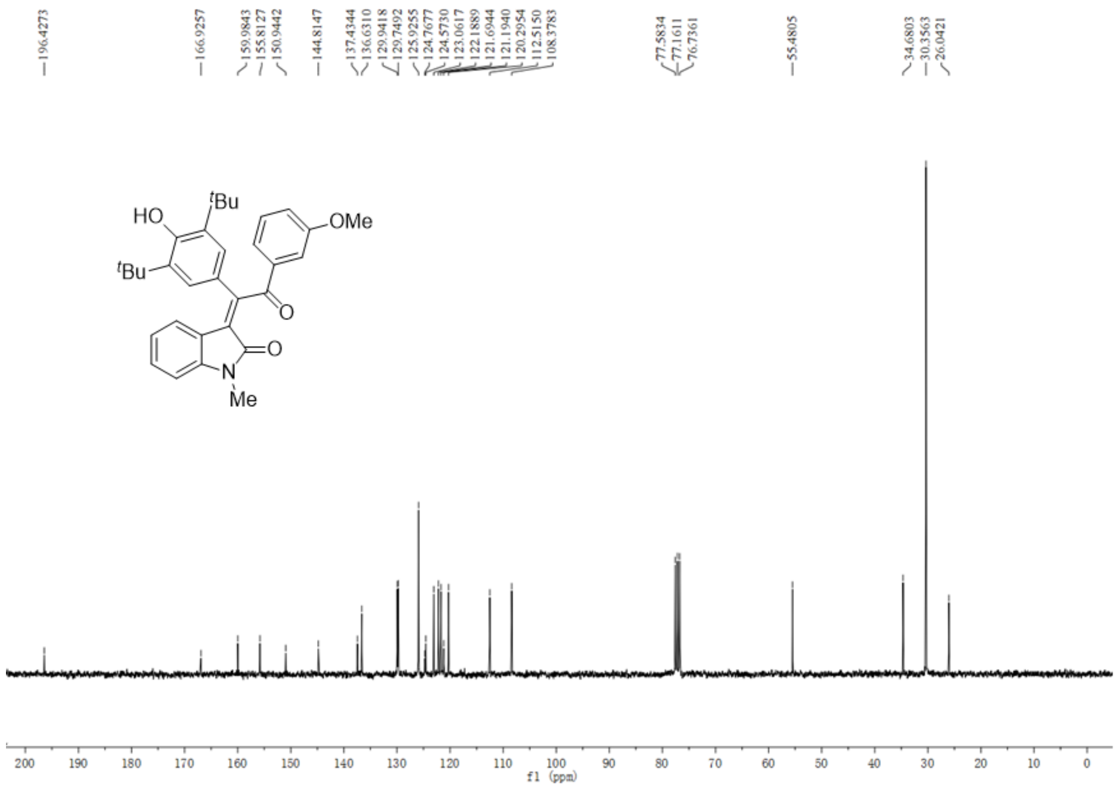
^{1}H NMR and ^{13}C NMR spectra of **9f**



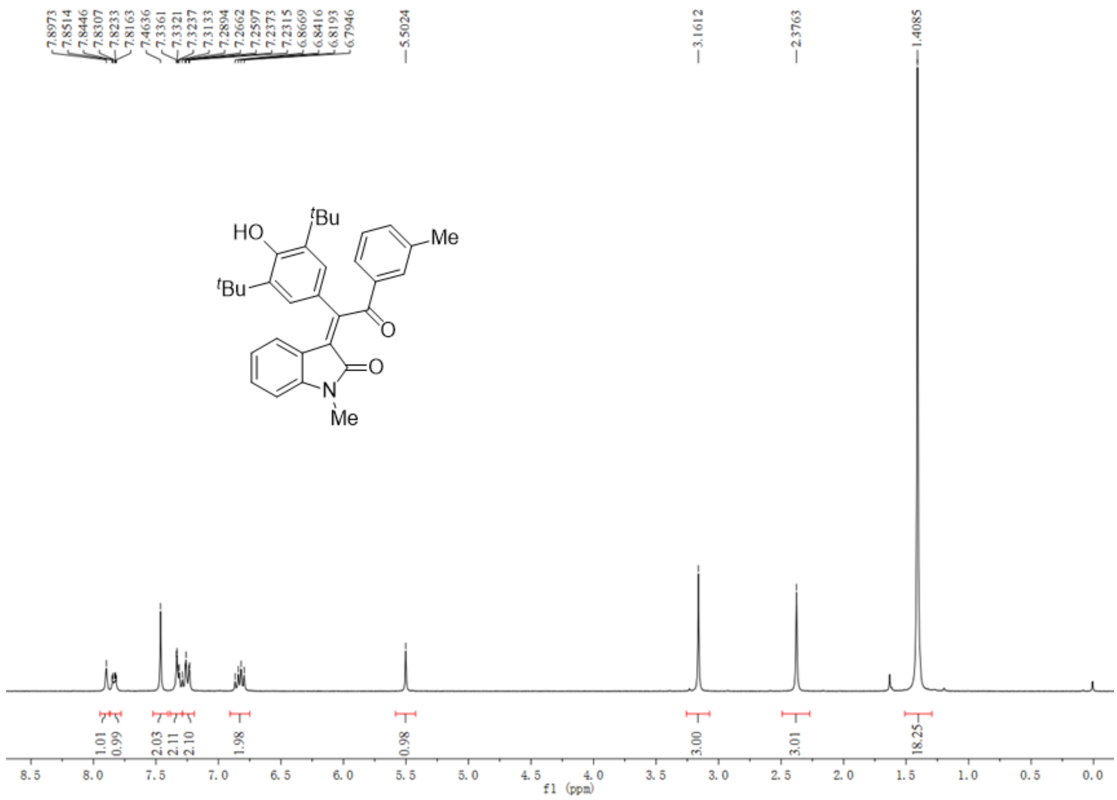


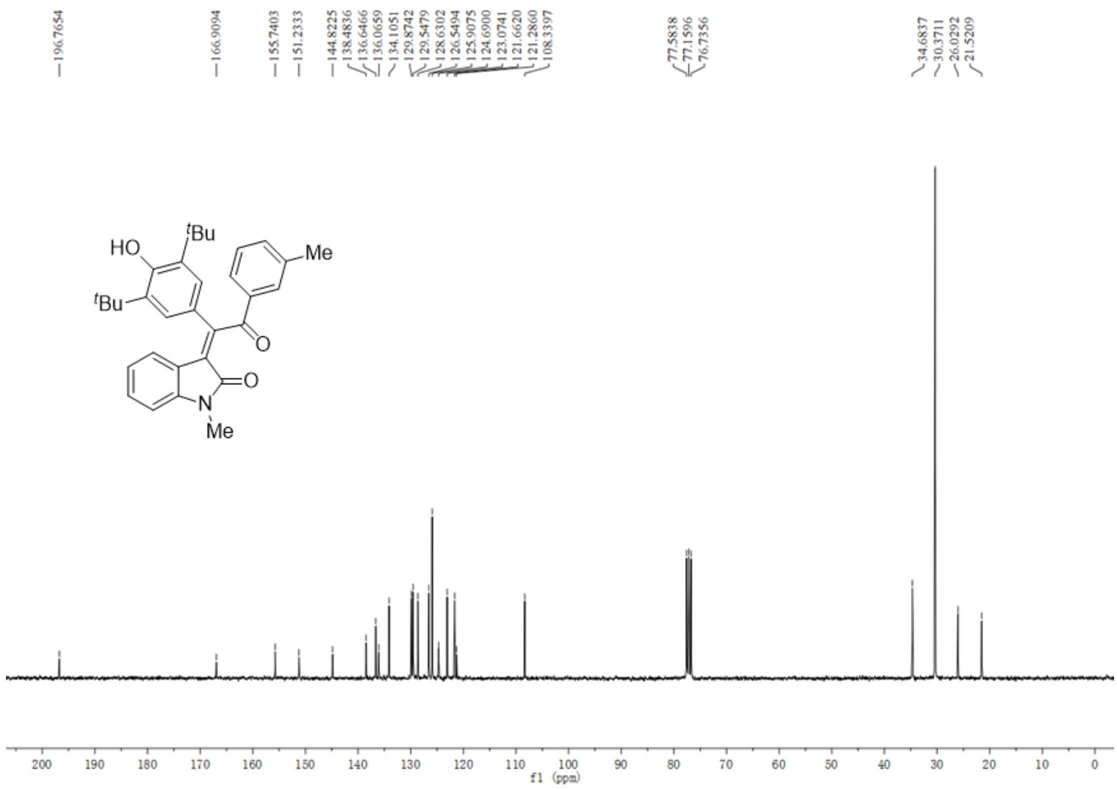
^1H NMR and ^{13}C NMR spectra of **9g**



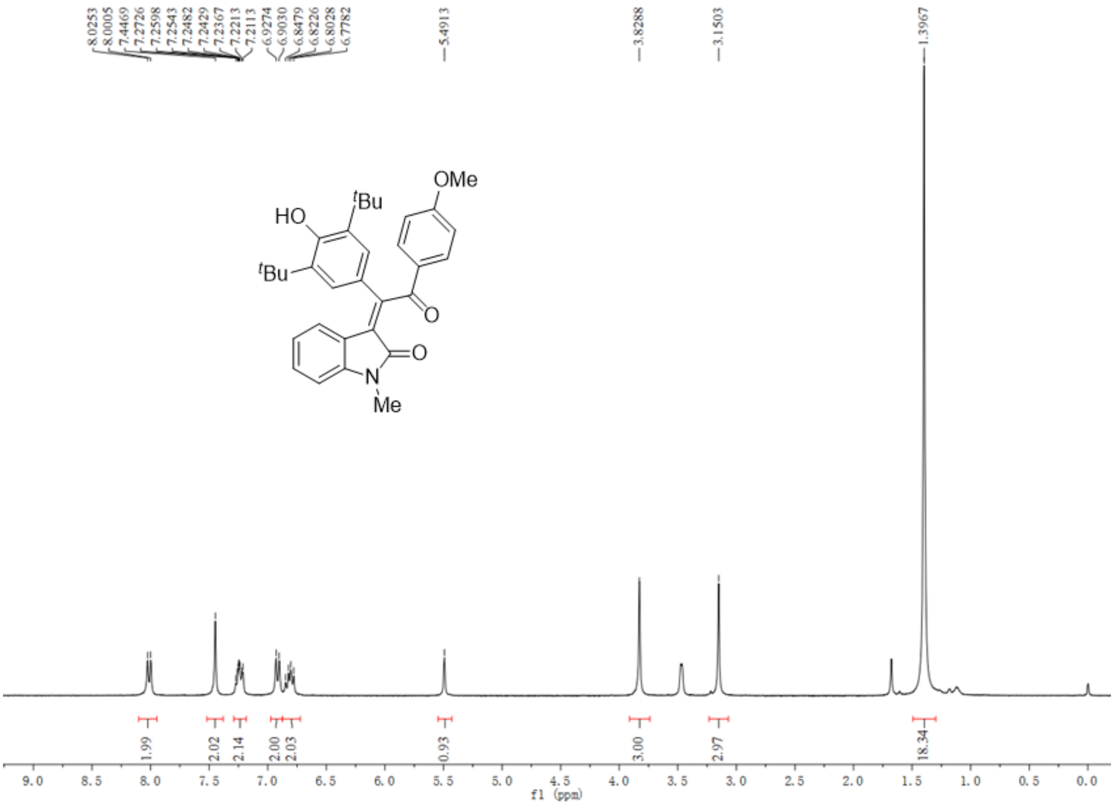


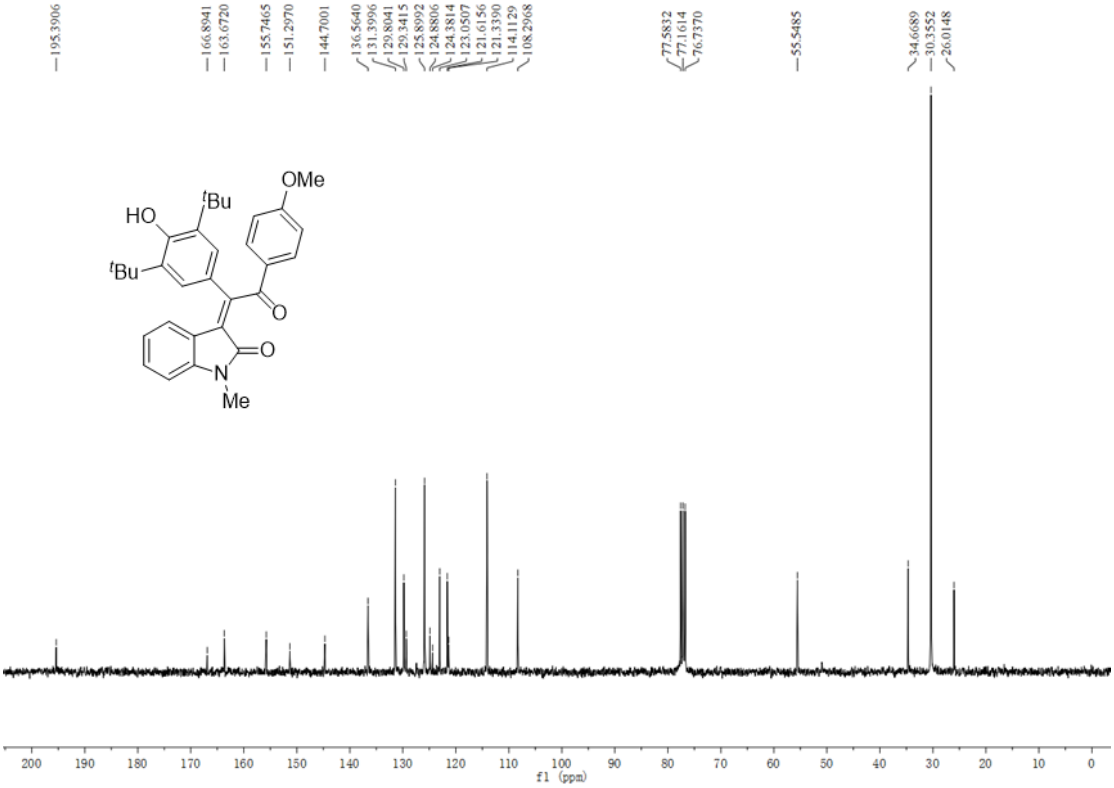
^{1}H NMR and ^{13}C NMR spectra of **9h**



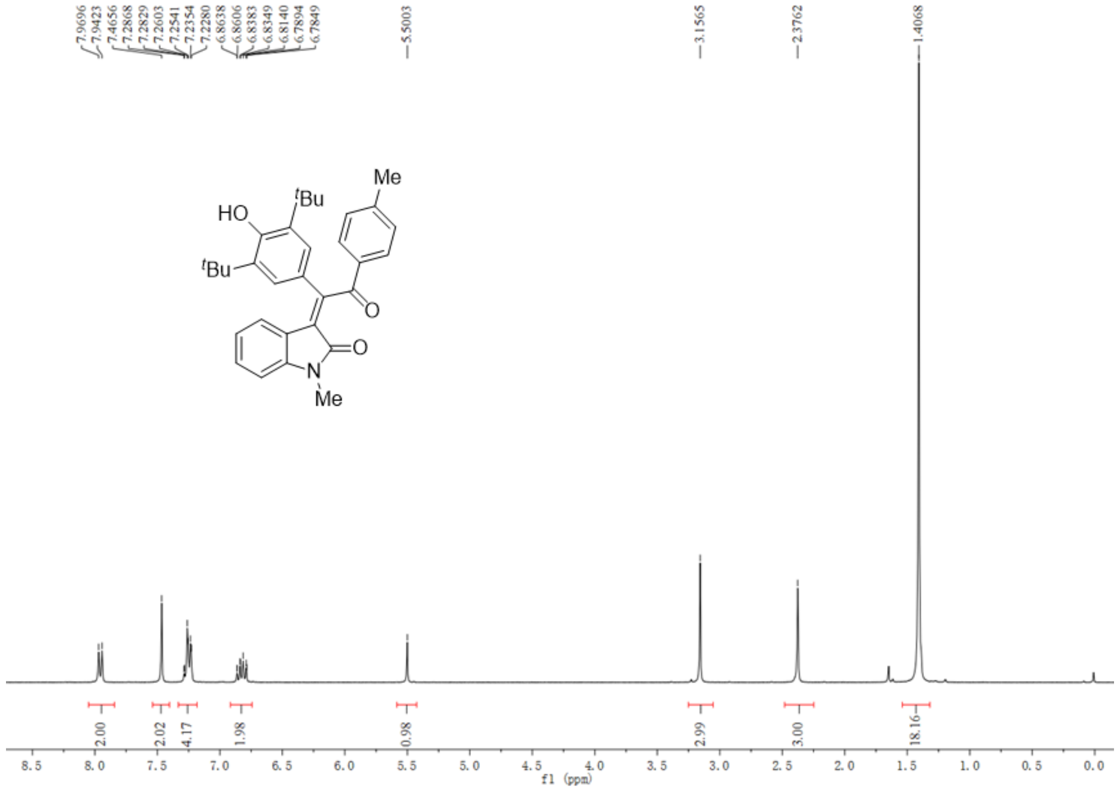


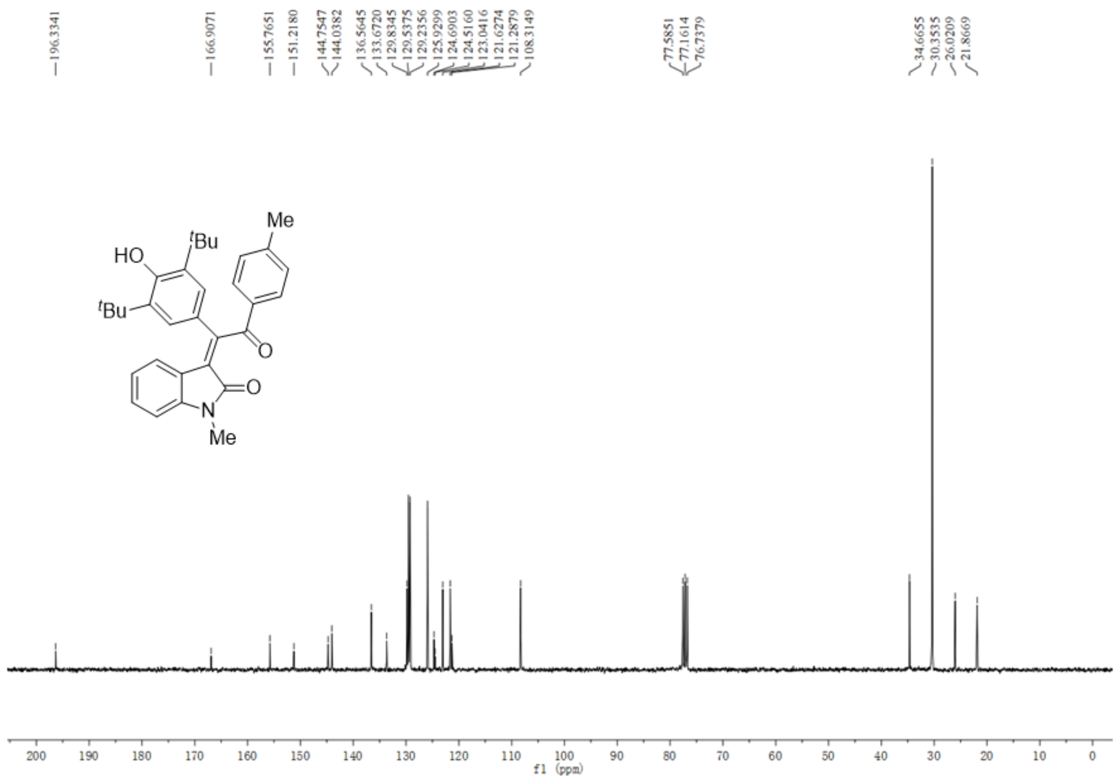
^{1}H NMR and ^{13}C NMR spectra of **9i**



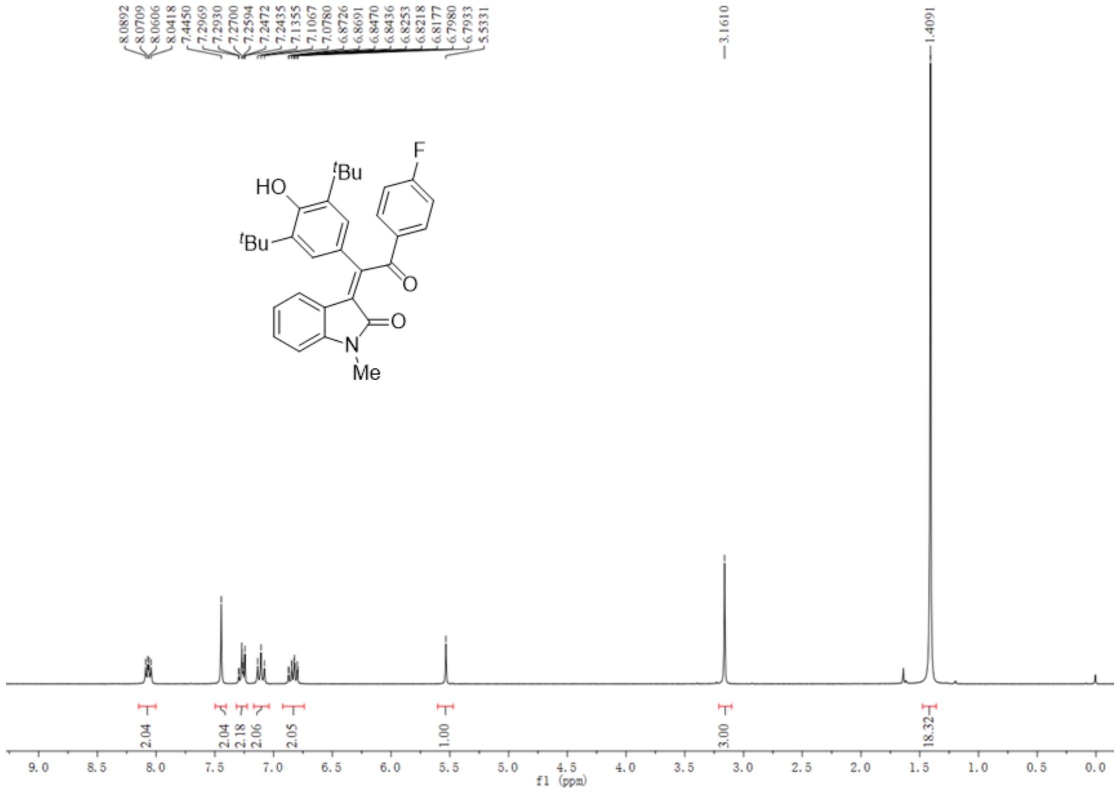


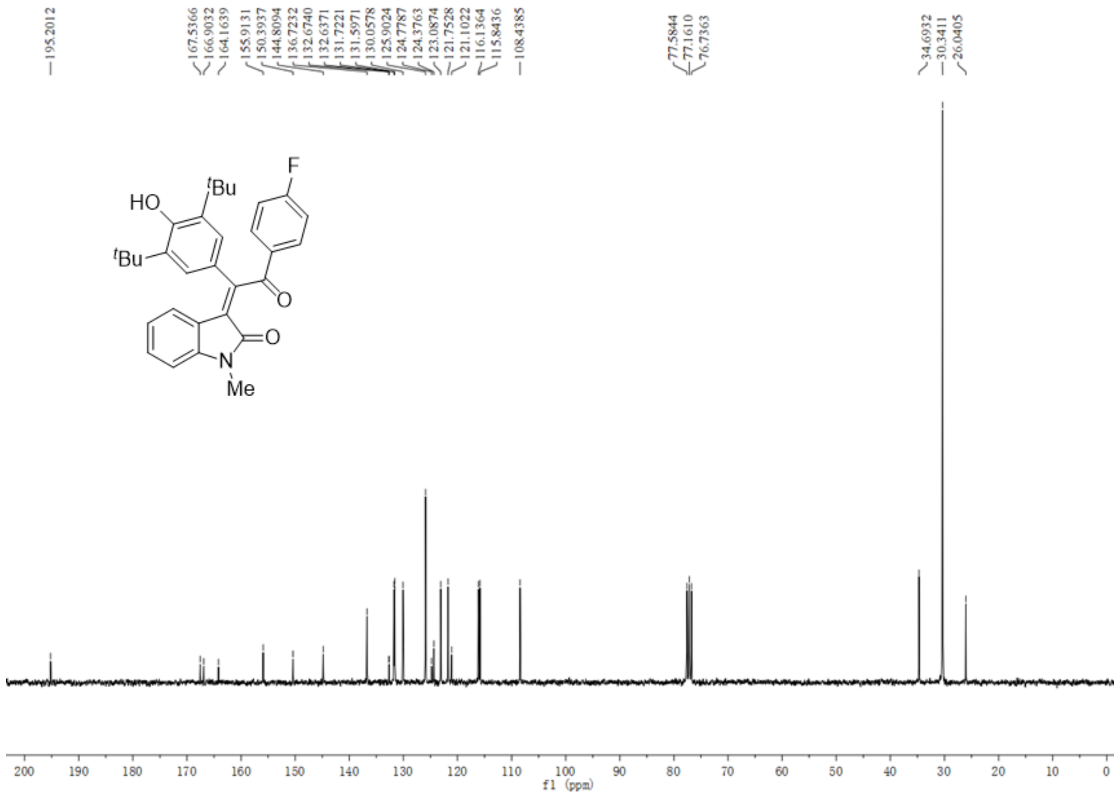
^{1}H NMR and ^{13}C NMR spectra of **9j**



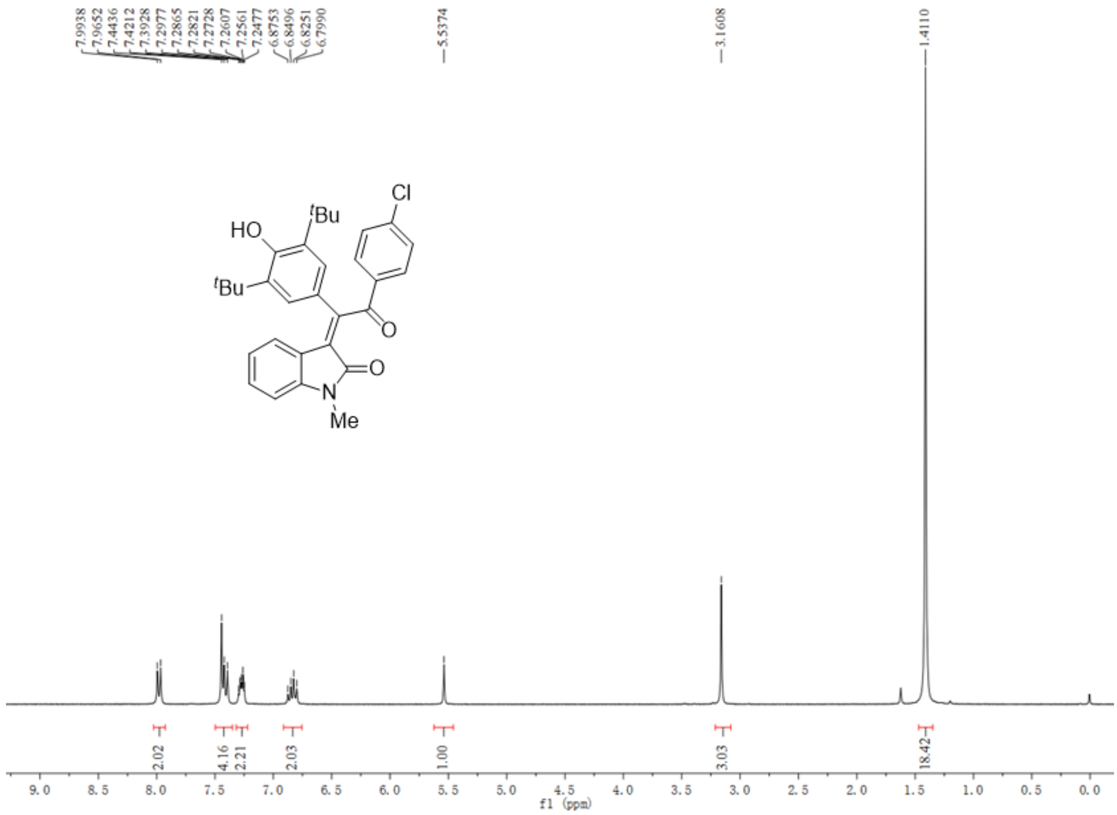


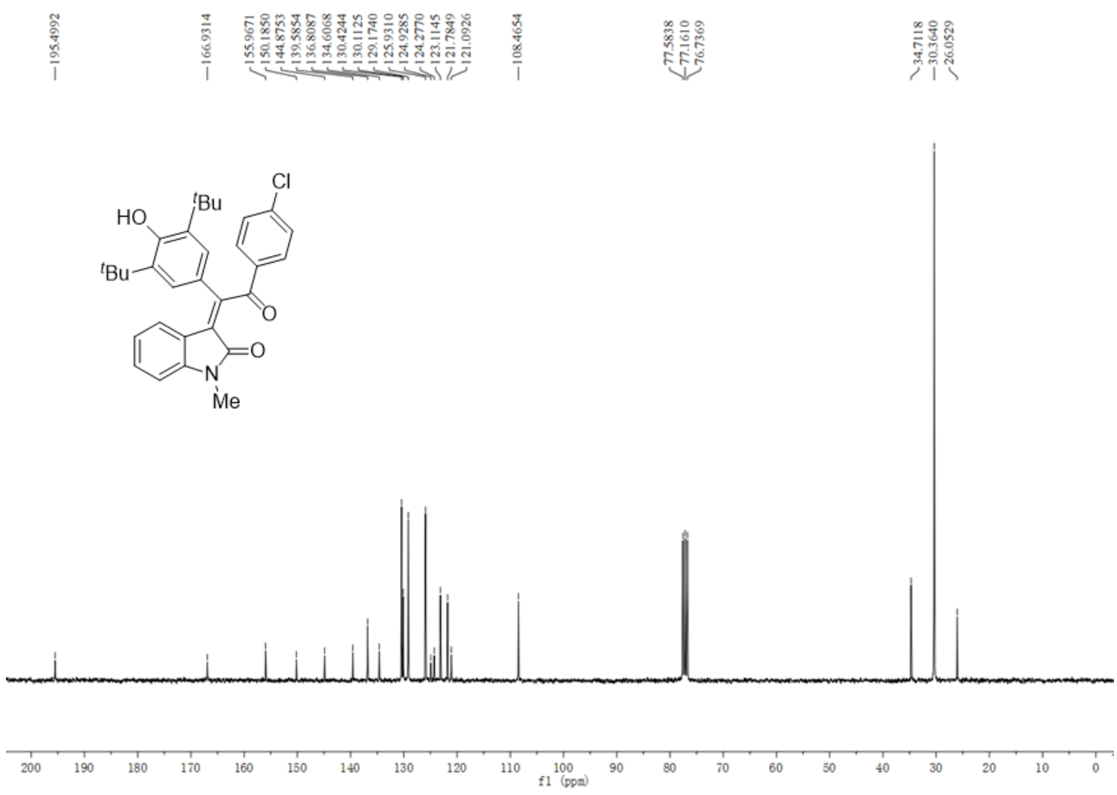
[1]H NMR and [13]C NMR spectra of **9k**



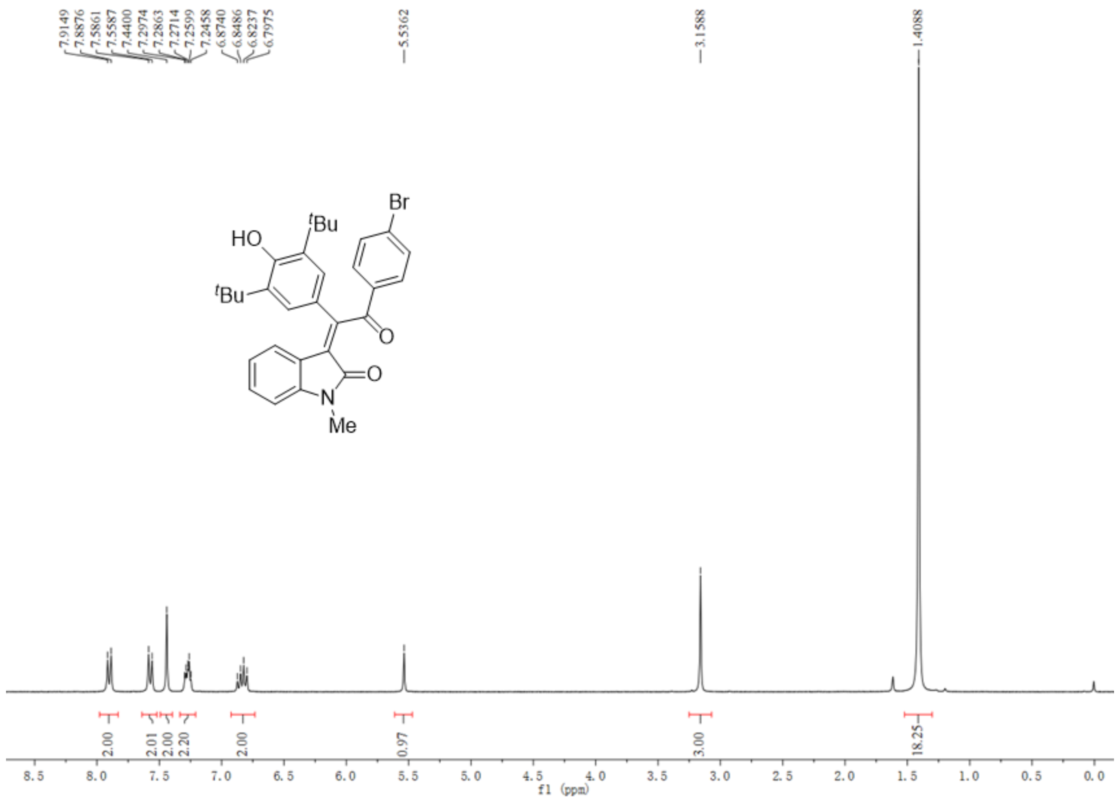


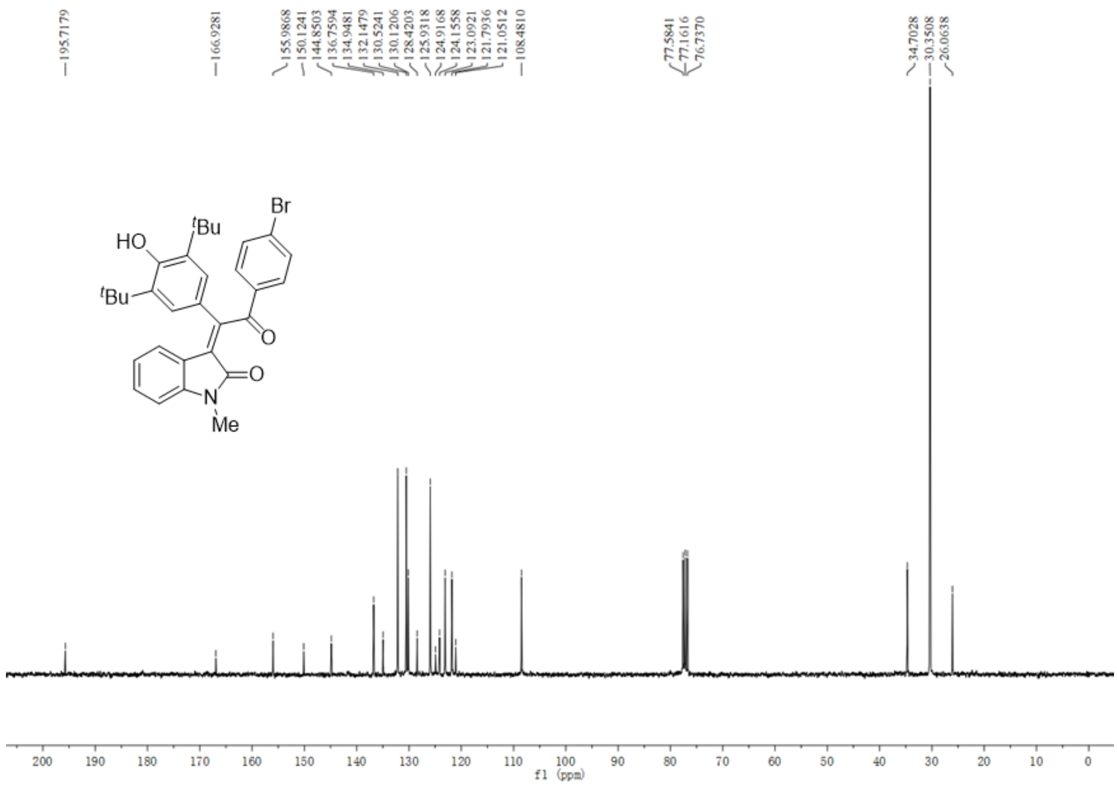
^{1}H NMR and ^{13}C NMR spectra of **9l**



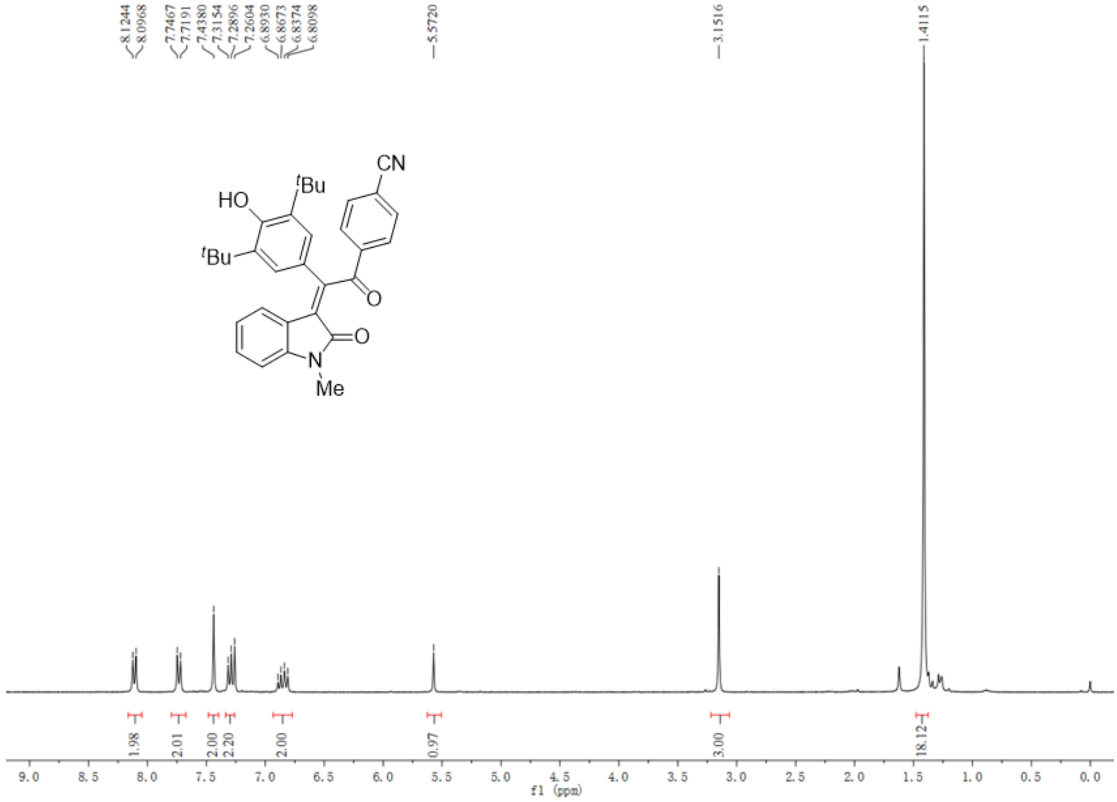


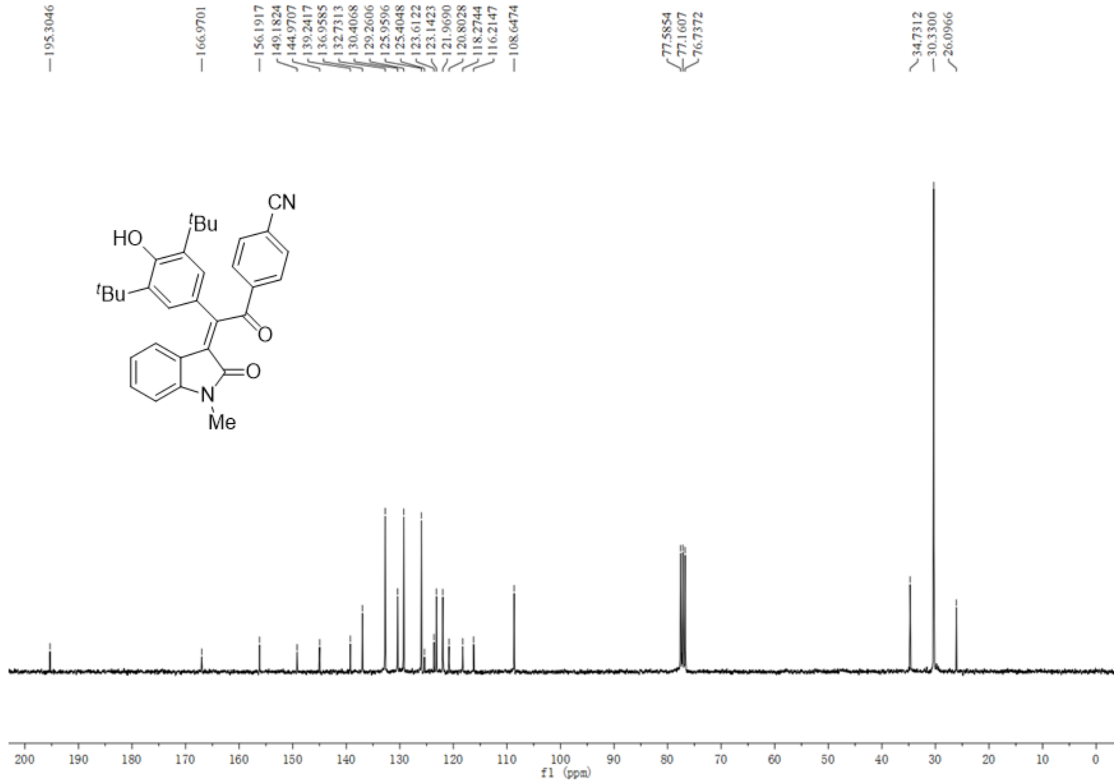
[1]H NMR and [13]C NMR spectra of **9m**



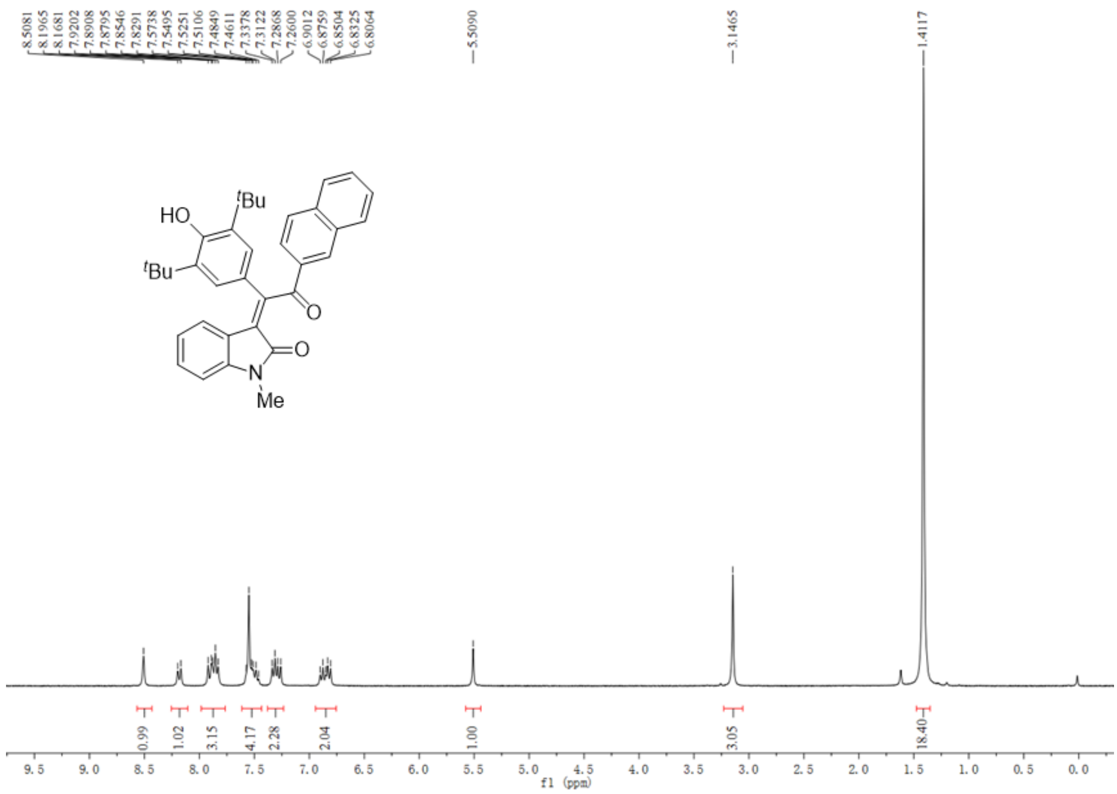


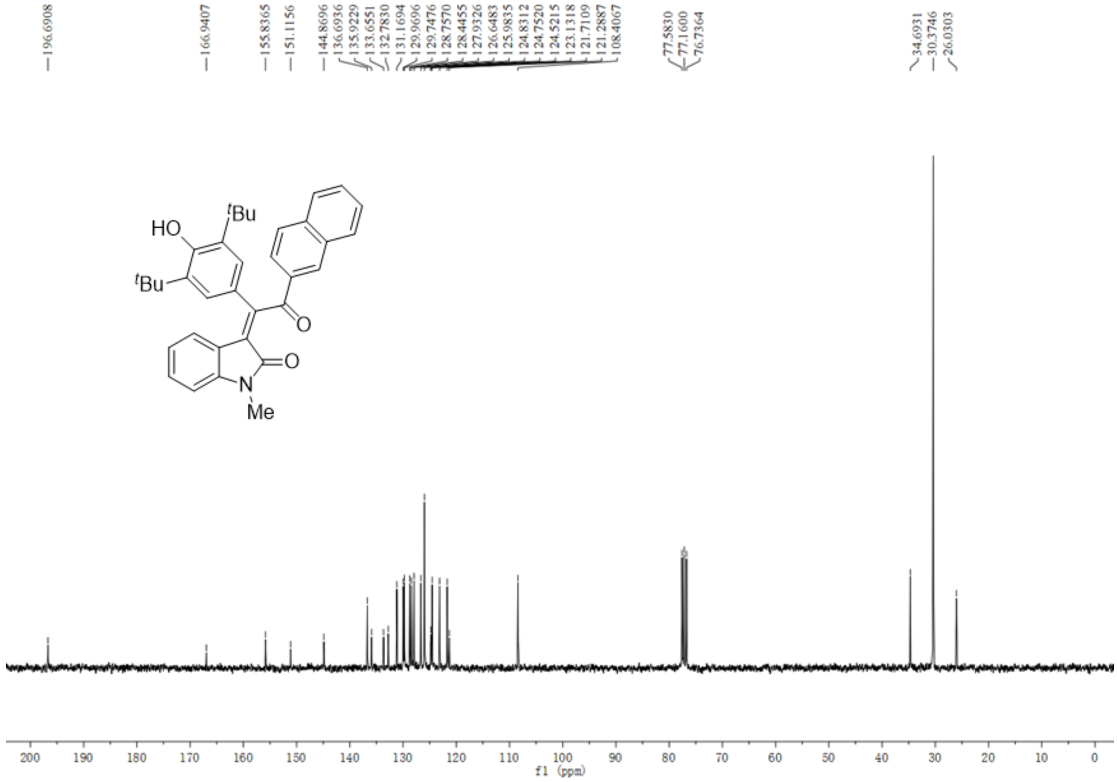
^{1}H NMR and ^{13}C NMR spectra of **9n**



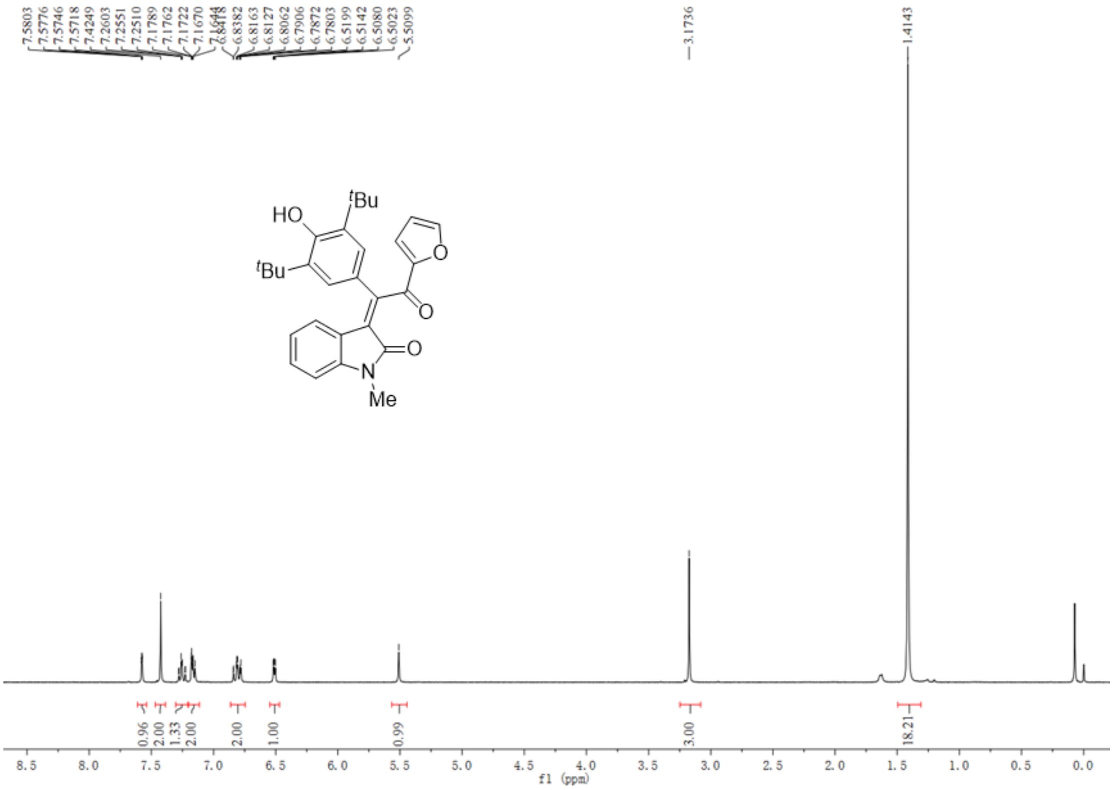


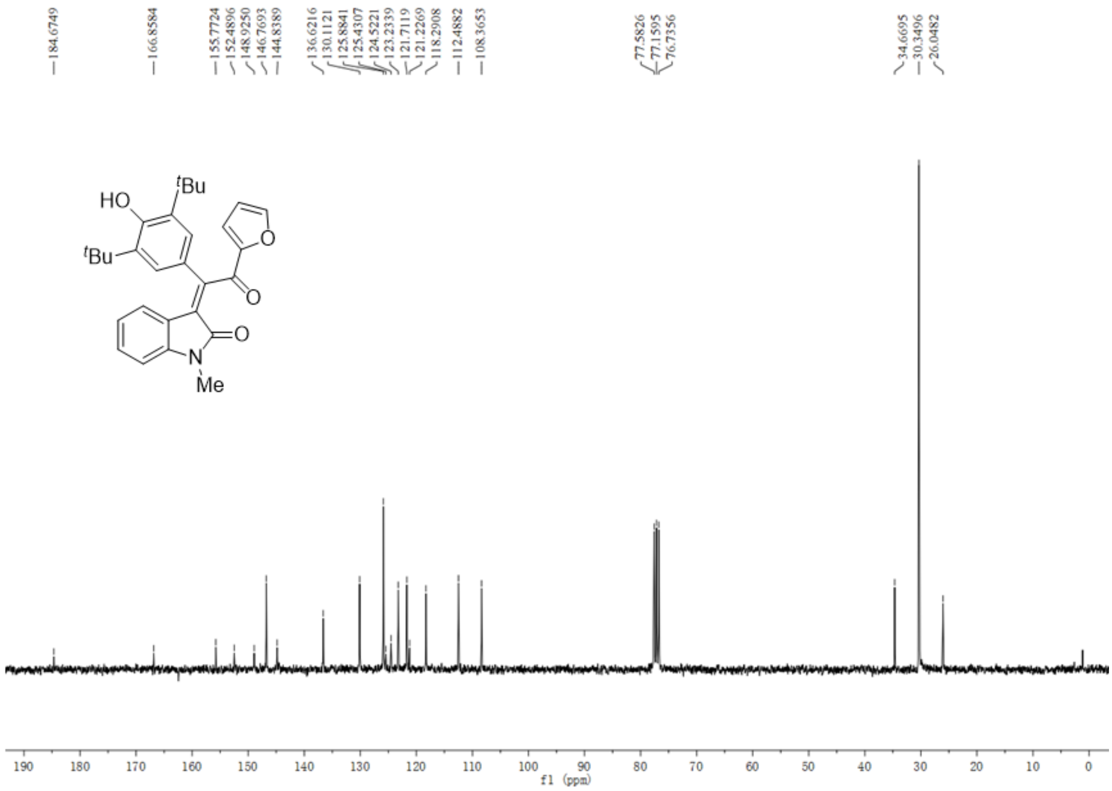
^{1}H NMR and ^{13}C NMR spectra of **9o**



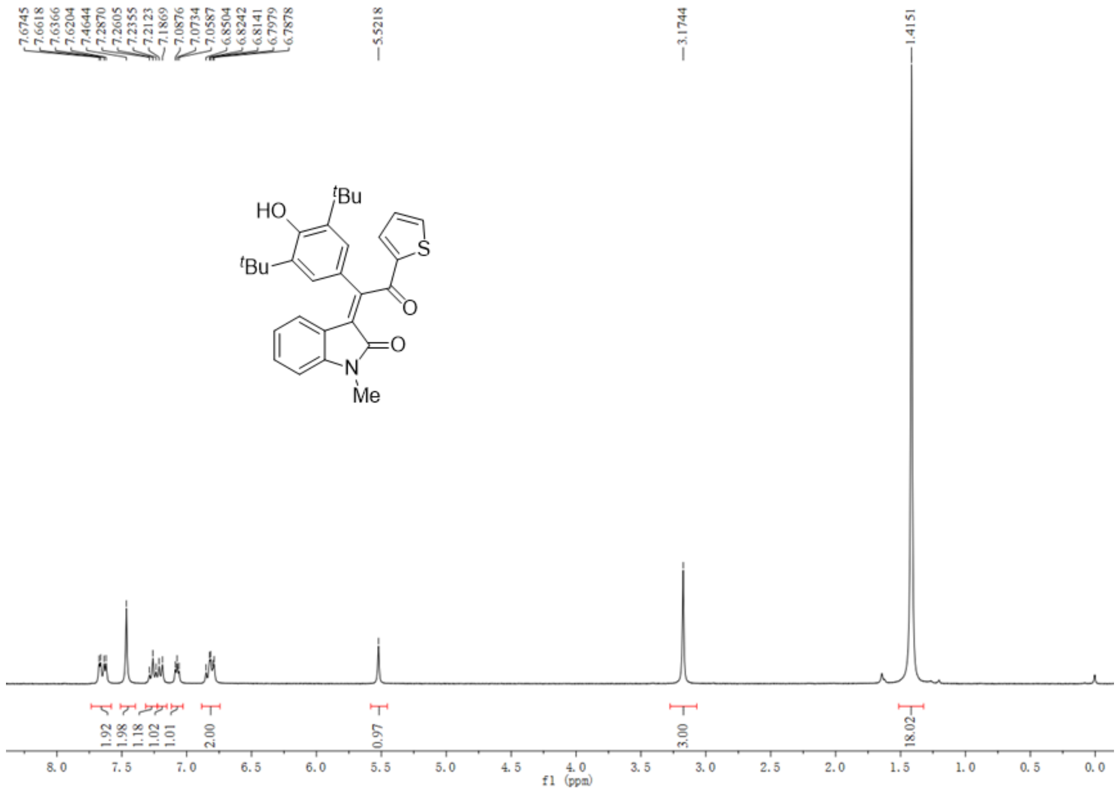


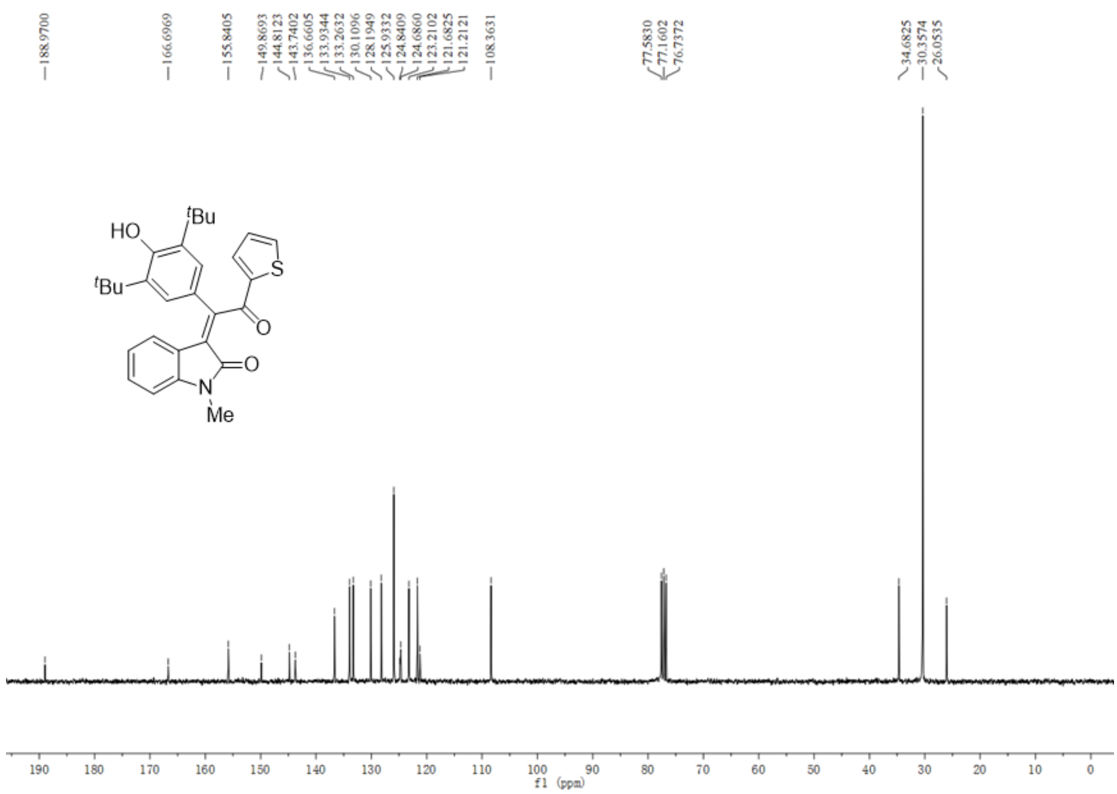
^{1}H NMR and ^{13}C NMR spectra of **9p**





^{1}H NMR and ^{13}C NMR spectra of **9q**





^{1}H NMR and ^{13}C NMR spectra of **10**