

Supporting Information

Construction of Contiguous Quaternary Carbon Centers Enabled by Dearomatization of Phenols with 3-Bromooxindoles

Hui Li,^{a†} Xi Wang,^{a†} Minhong Chang,^a Mengbo Wu,^a Xinyu Yuan,^a Xiangyu Hui,^a
Hongbo Wei,^{a*} Juyun Xi^{b,*} and Weiqing Xie^{a,c*}

^aShaanxi Key Laboratory of Natural Products & Chemical Biology, College of Chemistry &
Pharmacy, Northwest A&F University, 22 Xinong Road, Yangling, 712100, Shaanxi,
China.

^bDepartment of General Surgery, Nanping People's Hospital, Nanping, 35300, China.

^cKey Laboratory of Botanical Pesticide R&D in Shaanxi Province, Yangling, 712100,
Shaanxi, China.

Table of Contents

1. General Information.....	1
2. General Procedure for the Synthesis of 6.	2
3. Derivatization of 6r.....	15
4. Reference	18
5. NMR Data for Substrate Scope and Derivatization.....	19

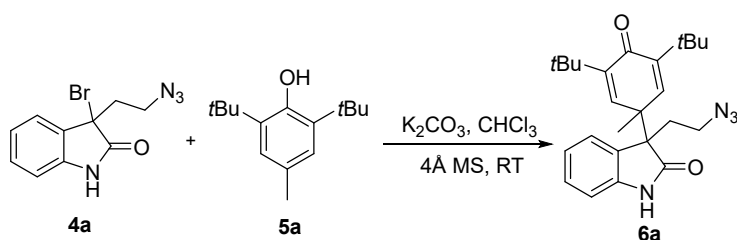
1. General Information

Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reaction was conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvent was treated as follow: tetrahydrofuran was distilled from sodium under argon atmosphere, dichloromethane and toluene were distilled from calcium hydride under argon atmosphere. Anhydrous ethyl acetate, chloroform, 1,2-dichloroethane, *N,N*-Dimethylformamide, 1,4-dioxane were commercially available (Adamas, SafeDry, with molecular sieves).

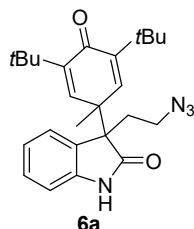
Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 μm , 200-400 mesh, Silicycle P60). NMR data including ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE III 500MHz. The chemical shifts (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvents (CHCl_3 @ 7.26 ppm ^1H NMR, 77.16 ppm ^{13}C NMR). Coupling constants are given in Hz.

High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (ESI).

2. General Procedure for the Synthesis of 6.



A 5 mL reaction tube was charged with oxindole **1** (0.10 mmol), phenol **2** (0.15 mmol), base (0.15 mmol) and 4Å MS molecular sieves (34 mg), then anhydrous CHCl_3 (1.0 mL) was added. The reaction mixture was stirred at room temperature until TLC showed the starting material was no longer consumed. The reaction mixture was directly concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:40 to 1:8) to yield the desired product **3**.

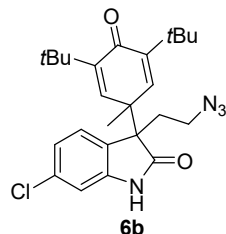


This compound was prepared according to the general procedure as a white solid (42.0 mg, 99% yield in 0.10 mmol scale). R_f = 0.45 (ethyl acetate/petroleum ether = 1/5, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.76 (s, 1H), 7.02 (d, J = 4.5 Hz, 2H), 6.95 (dd, J = 13.0, 5.3 Hz, 2H), 6.49 (d, J = 3.0 Hz, 1H), 2.93 – 2.77 (m, 2H), 2.30 (dt, J = 13.5, 8.2 Hz, 1H), 1.96 – 1.83 (m, 1H), 1.29 (s, 9H), 1.18 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.8, 179.5, 148.7, 148.4, 141.7, 141.7, 141.3, 129.2, 127.8, 125.5, 122.2, 110.2, 57.7, 48.0, 43.7, 35.4, 35.2, 30.9, 29.60, 29.55, 20.2.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{N}_4\text{O}_2$ 421.2598; Found 421.2593.



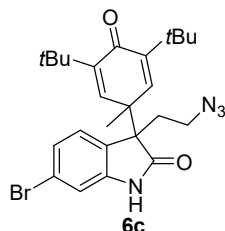
This compound was prepared according to the general procedure as a white solid (33.4 mg, 73% yield in 0.10 mmol scale). R_f = 0.45 (ethyl acetate/petroleum ether = 1/5, v/v).

^1H NMR (400 MHz, CDCl_3) δ 8.44 (s, 1H), 7.01 (dd, J = 8.0, 1.9 Hz, 1H), 6.95 – 6.89 (m, 3H),

6.41 (d, $J = 3.0$ Hz, 1H), 2.96 – 2.81 (m, 2H), 2.30 (dt, $J = 13.7, 8.1$ Hz, 1H), 1.86 (ddd, $J = 13.8, 7.5, 4.9$ Hz, 1H), 1.29 (s, 9H), 1.18 (s, 3H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 185.7, 179.2, 149.0, 148.8, 142.7, 141.2, 140.8, 135.0, 126.3, 126.2, 122.2, 110.8, 57.3, 47.9, 43.7, 35.4, 35.2, 30.8, 29.6, 29.5, 20.2.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{ClN}_4\text{O}_2$ 455.2208; Found 455.2207.

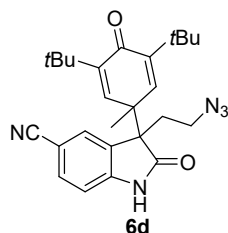


This compound was prepared according to the general procedure as a white solid (36.4 mg, 73% yield in 0.10 mmol scale). $R_f = 0.45$ (ethyl acetate/petroleum ether = 1/5, v/v).

^1H NMR (500 MHz, CDCl_3) δ 9.10 – 8.99 (m, 1H), 7.17 (dd, $J = 7.9, 1.8$ Hz, 1H), 7.12 (d, $J = 1.7$ Hz, 1H), 6.88 (dd, $J = 10.6, 5.5$ Hz, 2H), 6.41 (d, $J = 3.0$ Hz, 1H), 2.93 (ddd, $J = 12.6, 7.9, 4.7$ Hz, 1H), 2.84 (dt, $J = 12.3, 7.8$ Hz, 1H), 2.29 (dt, $J = 13.8, 8.0$ Hz, 1H), 1.86 (ddd, $J = 13.0, 7.4, 4.7$ Hz, 1H), 1.29 (s, 9H), 1.18 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.7, 179.6, 149.0, 148.7, 143.0, 141.2, 140.8, 126.7, 126.5, 125.1, 122.7, 113.7, 57.5, 47.9, 43.6, 35.4, 35.2, 30.7, 29.6, 29.5, 20.2.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{BrN}_4\text{O}_2$ 499.1703; Found 499.1708.

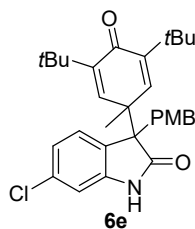


This compound was prepared according to the general procedure as a white solid (43.9 mg, 99% yield in 0.10 mmol scale). $R_f = 0.25$ (ethyl acetate/petroleum ether = 1/1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.63 (s, 1H), 7.59 (dd, $J = 8.1, 1.5$ Hz, 1H), 7.23 (s, 1H), 7.00 (d, $J = 8.2$ Hz, 1H), 6.76 (d, $J = 3.0$ Hz, 1H), 6.34 (d, $J = 3.0$ Hz, 1H), 3.04 (ddd, $J = 12.2, 7.3, 4.7$ Hz, 1H), 2.85 (ddd, $J = 12.5, 8.6, 6.7$ Hz, 1H), 2.42 (dt, $J = 15.2, 8.0$ Hz, 1H), 2.00 – 1.92 (m, 1H), 1.29 (d, $J = 5.6$ Hz, 12H), 1.10 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.4, 149.5, 149.4, 145.4, 140.1, 139.9, 134.1, 129.1, 128.7, 118.7, 110.5, 105.6, 57.2, 48.0, 43.9, 35.4, 35.1, 30.6, 30.3, 29.6, 29.4, 19.8.

HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{26}H_{32}N_5O_2$ 446.2551; Found 446.2557.

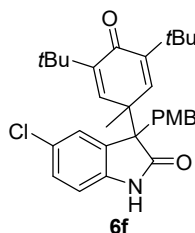


This compound was prepared according to the general procedure as a pale yellow solid (39.6 mg, 89% yield in 0.10 mmol scale). R_f = 0.45 (ethyl acetate/petroleum ether = 1/5, v/v).

1H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.13 – 7.05 (m, 2H), 6.97 (dd, J = 8.1, 2.0 Hz, 1H), 6.72 – 6.63 (m, 3H), 6.54 – 6.46 (m, 3H), 3.63 (d, J = 1.5 Hz, 3H), 3.23 (d, J = 13.4 Hz, 1H), 2.79 (d, J = 13.3 Hz, 1H), 1.33 (s, 9H), 1.23 (s, 3H), 1.18 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 185.9, 179.0, 158.2, 148.7, 148.4, 142.5, 142.0, 141.5, 134.2, 131.1, 127.5, 127.3, 126.7, 121.6, 113.3, 110.2, 60.9, 55.1, 43.8, 37.0, 35.4, 35.2, 29.7, 29.6, 20.6.

HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{31}H_{37}ClNO_3$ 506.2456; Found 506.2456.

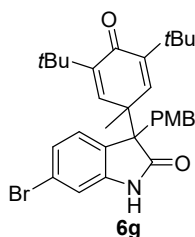


This compound was prepared according to the general procedure as a white solid (26.8 mg, 53% yield in 0.10 mmol scale). R_f = 0.45 (ethyl acetate/petroleum ether = 1/5, v/v).

1H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.14 (d, J = 2.1 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.71 (d, J = 8.3 Hz, 2H), 6.56 (d, J = 8.2 Hz, 1H), 6.50 (dd, J = 16.9, 5.6 Hz, 3H), 3.63 (s, 3H), 3.28 (d, J = 13.3 Hz, 1H), 2.82 (d, J = 13.3 Hz, 1H), 1.35 (s, 9H), 1.31 (s, 3H), 1.14 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 185.8, 178.6, 158.3, 148.7, 148.6, 141.7, 141.4, 139.7, 131.2, 131.0, 128.4, 127.2, 127.1, 126.1, 113.3, 110.3, 61.2, 55.1, 43.9, 37.0, 35.4, 35.1, 29.7, 29.5, 20.4.

HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{31}H_{37}ClNO_3$ 506.2456; Found 506.2458.



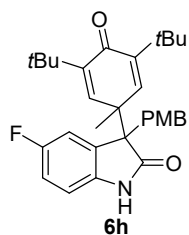
This compound was prepared according to the general procedure as a white solid (31.9 mg, 58%

yield in 0.10 mmol scale). $R_f = 0.45$ (ethyl acetate/petroleum ether = 1/5, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.77 (s, 1H), 7.15 – 7.07 (m, 2H), 7.03 (d, $J = 8.1$ Hz, 1H), 6.81 (d, $J = 1.8$ Hz, 1H), 6.68 (d, $J = 8.3$ Hz, 2H), 6.54 – 6.47 (m, 3H), 3.64 (s, 3H), 3.23 (d, $J = 13.4$ Hz, 1H), 2.79 (d, $J = 13.3$ Hz, 1H), 1.34 (s, 9H), 1.24 (s, 3H), 1.18 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.9, 178.6, 158.3, 148.8, 148.5, 142.6, 142.0, 141.4, 131.2, 128.1, 127.3, 127.1, 124.5, 122.0, 113.4, 112.9, 61.0, 55.1, 43.8, 37.0, 35.4, 35.2, 29.7, 29.6, 20.6.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{37}\text{BrNO}_3$ 550.1951; Found 550.1945.

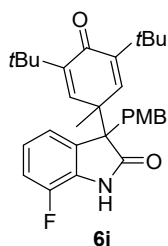


This compound was prepared according to the general procedure as a white solid (41.5 mg, 85% yield in 0.10 mmol scale). $R_f = 0.45$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.59 (s, 1H), 7.09 (d, $J = 3.0$ Hz, 1H), 6.91 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.82 (td, $J = 8.7, 2.6$ Hz, 1H), 6.74 – 6.67 (m, 2H), 6.57 – 6.47 (m, 4H), 3.64 (s, 3H), 3.28 (d, $J = 13.3$ Hz, 1H), 2.81 (d, $J = 13.3$ Hz, 1H), 1.34 (s, 9H), 1.30 (s, 3H), 1.15 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.9, 178.7, 158.3, 158.2 (d, $J = 240.7$ Hz), 148.6 (d, $J = 18.9$ Hz), 141.6 (d, $J = 58.0$ Hz), 131.2, 127.3, 114.9 (d, $J = 23.9$ Hz), 113.8 (d, $J = 25.2$ Hz), 113.3, 109.8 (d, $J = 8.8$ Hz), 61.5, 55.1, 43.9, 37.2, 35.3 (d, $J = 34$ Hz), 29.6 (d, $J = 12.6$ Hz), 20.5.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{37}\text{FNO}_3$ 490.2752; Found 490.2778.

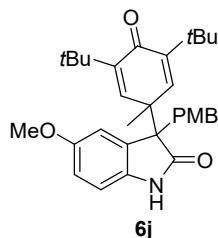


This compound was prepared according to the general procedure as a white solid (29.3 mg, 60% yield in 0.10 mmol scale). $R_f = 0.45$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.51 (s, 1H), 7.12 (d, $J = 3.0$ Hz, 1H), 7.01 – 6.86 (m, 3H), 6.72 – 6.66 (m, 2H), 6.56 – 6.49 (m, 3H), 3.65 (s, 3H), 3.25 (d, $J = 13.3$ Hz, 1H), 2.82 (d, $J = 13.3$ Hz, 1H), 1.34 (s, 9H), 1.26 (s, 3H), 1.17 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 186.0, 178.3, 158.3, 148.5 (d, *J* = 32.8 Hz), 146.9 (d, *J* = 244.4 Hz), 141.8 (d, *J* = 32.8 Hz), 131.9 (d, *J* = 2.52 Hz), 128.9 (d, *J* = 12.6 Hz), 122.1 (d, *J* = 6.3 Hz), 121.7 (d, *J* = 3.78 Hz), 115.6 (d, *J* = 16.4 Hz), 115.5, 113.3, 61.8, 55.1, 43.8, 37.2, 35.3 (d, *J* = 31.5 Hz), 29.6 (d, *J* = 7.56 Hz), 20.6.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₃₁H₃₇FNO₃ 490.2752; Found 490.2757.

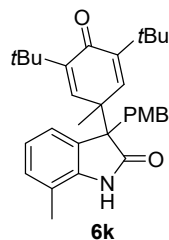


This compound was prepared according to the general procedure as a pale yellow solid (35.0 mg, 70% yield in 0.10 mmol scale). *R_f* = 0.45 (ethyl acetate/petroleum ether = 1/4, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.95 (s, 1H), 7.20 (d, *J* = 2.9 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.74 – 6.64 (m, 3H), 6.61 (d, *J* = 3.0 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 2H), 3.78 (s, 3H), 3.61 (s, 3H), 3.18 (d, *J* = 13.4 Hz, 1H), 2.76 (d, *J* = 13.4 Hz, 1H), 1.34 (s, 9H), 1.20 (d, *J* = 8.0 Hz, 12H).

¹³C NMR (126 MHz, CDCl₃) δ 186.2, 178.9, 158.1, 155.1, 148.4, 148.1, 142.7, 142.0, 135.0, 131.2, 130.4, 127.7, 113.6, 113.2, 113.1, 109.8, 61.7, 56.1, 55.1, 43.7, 37.2, 35.4, 35.2, 29.7, 29.7, 20.8.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₃₂H₄₀NO₄ 502.2952; Found 502.2954.

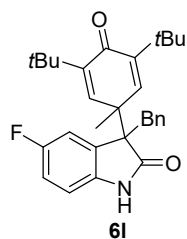


This compound was prepared according to the general procedure as a pale yellow solid (37.3 mg, 77% yield in 0.10 mmol scale). *R_f* = 0.45 (ethyl acetate/petroleum ether = 1/4, v/v).

¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 7.20 (d, *J* = 2.9 Hz, 1H), 7.03 (dd, *J* = 7.2, 1.5 Hz, 1H), 6.98 – 6.87 (m, 2H), 6.72 – 6.66 (m, 2H), 6.62 (d, *J* = 2.9 Hz, 1H), 6.52 – 6.45 (m, 2H), 3.63 (s, 3H), 3.18 (d, *J* = 13.3 Hz, 1H), 2.79 (d, *J* = 13.3 Hz, 1H), 2.12 (s, 3H), 1.33 (s, 9H), 1.20 (s, 9H), 1.18 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 186.1, 180.3, 158.1, 148.4, 148.0, 142.9, 142.2, 140.8, 131.1, 129.9, 128.4, 128.0, 123.5, 121.6, 119.0, 113.1, 62.0, 55.1, 43.7, 37.2, 35.4, 35.3, 29.7, 20.8, 16.5.

HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{32}H_{40}NO_3$ 486.3003; Found 486.3005.

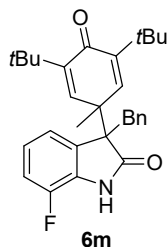


This compound was prepared according to the general procedure as a white solid (45.5 mg, 99% yield in 0.10 mmol scale). R_f = 0.45 (ethyl acetate/petroleum ether = 1/4, v/v).

1H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.11 (d, J = 3.0 Hz, 1H), 7.00 (dd, J = 5.0, 1.9 Hz, 3H), 6.92 (dd, J = 8.5, 2.6 Hz, 1H), 6.84 – 6.78 (m, 3H), 6.55 – 6.49 (m, 2H), 3.34 (d, J = 13.1 Hz, 1H), 2.85 (d, J = 13.1 Hz, 1H), 1.35 (s, 9H), 1.31 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 185.9, 179.0, 158.2 (d, J = 241.9 Hz), 148.7 (d, J = 30.2 Hz), 141.6 (d, J = 64.3 Hz), 137.3 (d, J = 2.52 Hz), 130.6 (d, J = 7.6 Hz), 128.0, 126.7, 115.0 (d, J = 22.7 Hz), 113.9 (d, J = 25.2 Hz), 109.9 (d, J = 3.8 Hz), 61.5, 43.8, 38.0, 35.3 (d, J = 29.0 Hz), 29.6 (d, J = 8.8 Hz), 20.5.

HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{30}H_{35}FNO_2$ 460.2646; Found 460.2676.

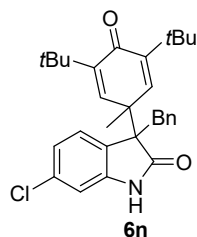


This compound was prepared according to the general procedure as a yellow solid (24.0 mg, 52% yield in 0.10 mmol scale). R_f = 0.5 (ethyl acetate/petroleum ether = 1/4, v/v).

1H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 8.2 Hz, 1H), 7.16 (d, J = 3.0 Hz, 1H), 7.01 – 6.88 (m, 6H), 6.81 – 6.74 (m, 2H), 6.57 (d, J = 3.0 Hz, 1H), 3.30 (d, J = 13.2 Hz, 1H), 2.86 (d, J = 13.1 Hz, 1H), 1.34 (s, 9H), 1.24 (s, 3H), 1.20 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 186.0, 178.4, 148.6 (d, J = 40.3 Hz), 146.9 (d, J = 245.7 Hz), 141.7 (d, J = 66.8 Hz), 135.4, 131.7 (d, J = 2.5 Hz), 128.9 (d, J = 12.6 Hz), 122.1 (d, J = 5.0 Hz), 121.8 (d, J = 3.8 Hz), 115.6 (d, J = 17.6 Hz), 61.8, 43.8, 38.1, 35.5 (d, J = 27.7 Hz), 29.6 (d, J = 5.0 Hz), 20.6.

HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{30}H_{35}FNO_2$ 460.2646; Found 460.2654.

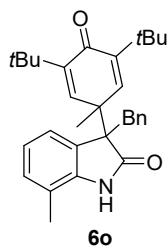


This compound was prepared according to the general procedure as a yellow solid (38.2 mg, 80% yield in 0.10 mmol scale). $R_f = 0.4$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.10 (s, 1H), 7.14 – 7.06 (m, 2H), 6.98 (q, $J = 7.4, 5.3$ Hz, 4H), 6.81 – 6.71 (m, 2H), 6.67 (t, $J = 2.0$ Hz, 1H), 6.52 (d, $J = 3.2$ Hz, 1H), 3.29 (dd, $J = 13.1, 3.5$ Hz, 1H), 2.84 (dd, $J = 13.2, 3.5$ Hz, 1H), 1.34 (d, $J = 3.5$ Hz, 9H), 1.24 (s, 3H), 1.20 (d, $J = 3.5$ Hz, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.9, 179.0, 148.8, 148.5, 142.5, 142.0, 141.4, 135.4, 134.2, 130.1, 128.0, 127.3, 126.9, 126.7, 121.6, 110.1, 60.9, 43.9, 37.9, 35.4, 35.2, 29.7, 29.6, 20.6.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{35}\text{FNO}_2$ 476.2351; Found 476.2361.

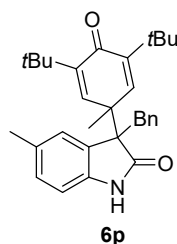


This compound was prepared according to the general procedure as a pale yellow solid (26.1mg, 57% yield in 0.10mmol scale). $R_f = 0.4$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (500 MHz, CDCl_3) δ 9.16 (s, 1H), 7.26 – 7.22 (m, 1H), 7.06 (d, $J = 7.3$ Hz, 1H), 6.94 (dtd, $J = 14.6, 7.4, 2.8$ Hz, 5H), 6.77 (d, $J = 6.8$ Hz, 2H), 6.66 (d, $J = 2.9$ Hz, 1H), 3.22 (d, $J = 13.2$ Hz, 1H), 2.81 (d, $J = 13.2$ Hz, 1H), 2.17 (s, 3H), 1.33 (s, 9H), 1.24 (s, 9H), 1.16 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 186.1, 180.0, 148.5, 148.0, 142.9, 142.2, 140.6, 136.0, 130.1, 129.9, 128.2, 127.7, 126.4, 123.6, 121.6, 119.0, 61.9, 43.7, 38.1, 35.4, 35.3, 29.7, 29.7, 20.8, 16.5.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{38}\text{NO}_2$ 456.2897; Found 456.2900.



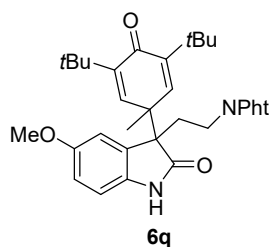
This compound was prepared according to the general procedure as a pale yellow solid (34.9 mg,

77% yield in 0.10 mmol scale). $R_f = 0.45$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.69 (s, 1H), 7.17 (d, $J = 3.0$ Hz, 1H), 7.00 – 6.93 (m, 4H), 6.90 (dt, $J = 8.0, 1.1$ Hz, 1H), 6.80 – 6.76 (m, 2H), 6.57 (d, $J = 3.0$ Hz, 1H), 6.50 (d, $J = 7.8$ Hz, 1H), 3.29 (d, $J = 13.1$ Hz, 1H), 2.85 (d, $J = 13.1$ Hz, 1H), 2.31 (s, 3H), 1.36 (s, 9H), 1.27 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 186.1, 178.7, 148.3, 148.2, 142.5, 142.2, 138.8, 135.9, 131.0, 130.2, 128.9, 128.8, 127.8, 126.7, 126.5, 109.1, 60.9, 43.9, 38.0, 35.4, 35.1, 29.7, 29.5, 21.4, 20.6.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{38}\text{NO}_2$ 456.2897; Found 456.2897.

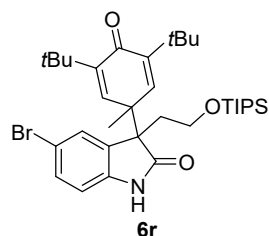


This compound was prepared according to the general procedure as a pale yellow solid (54.9 mg, 99% yield in 0.10 mmol scale). $R_f = 0.35$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.60 (s, 1H), 7.71 – 7.56 (m, 4H), 6.97 (s, 1H), 6.69 (d, $J = 8.5$ Hz, 1H), 6.52 (d, $J = 16.2$ Hz, 2H), 6.39 (d, $J = 8.6$ Hz, 1H), 3.60 – 3.38 (m, 5H), 2.34 (ddd, $J = 33.4, 14.3, 7.9$ Hz, 2H), 1.28 (s, 9H), 1.14 (s, 12H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.9, 178.9, 167.9, 155.1, 148.5, 148.2, 142.0, 141.6, 135.0, 133.8, 131.9, 129.9, 123.0, 113.1, 112.0, 110.6, 58.4, 55.5, 43.8, 35.3, 35.1, 34.8, 30.3, 29.7, 29.6, 28.8, 20.3.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{34}\text{H}_{39}\text{N}_2\text{O}_5$ 555.2853; Found 555.2848.



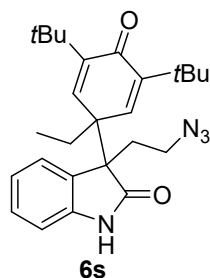
This compound was prepared according to the general procedure as a white solid (40.8 mg, 65% yield in 0.10 mmol scale; 0.7480 g, 59% yield in gram scale). $R_f = 0.65$ (acetone/petroleum ether = 1/2, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.32 (dd, $J = 8.2, 2.0$ Hz, 1H), 7.10 (d, $J = 1.9$ Hz, 1H), 6.90 (d, $J = 3.0$ Hz, 1H), 6.71 (d, $J = 8.2$ Hz, 1H), 6.42 (d, $J = 2.9$ Hz, 1H), 3.34 (dd, $J = 7.8, 5.3$

Hz, 2H), 2.37 (dt, $J = 13.5, 7.7$ Hz, 1H), 1.89 – 1.80 (m, 1H), 1.30 (s, 9H), 1.22 (s, 3H), 1.12 (s, 9H), 0.89 (s, 21H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.7, 179.0, 148.6, 148.5, 141.6, 141.4, 140.5, 131.3, 131.1, 128.8, 114.3, 110.8, 60.0, 57.2, 43.8, 35.3, 35.1, 34.5, 29.7, 29.5, 19.9, 18.0, 17.9, 12.0.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{34}\text{H}_{53}\text{BrNO}_3\text{Si}$ 630.2973; Found 630.2974.

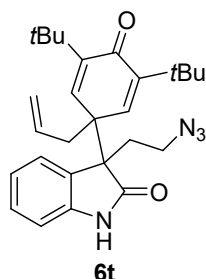


This compound was prepared according to the general procedure as a white solid (36.5mg, 84% yield in 0.10 mmol scale). $R_f = 0.5$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (400 MHz, CDCl_3) δ 9.14 (s, 1H), 7.28 – 7.23 (m, 1H), 7.07 – 7.01 (m, 2H), 6.98 – 6.89 (m, 2H), 6.43 (d, $J = 3.0$ Hz, 1H), 2.90 – 2.77 (m, 2H), 2.25 (dt, $J = 13.7, 8.1$ Hz, 1H), 1.88 – 1.82 (m, 1H), 1.80 – 1.69 (m, 1H), 1.60 (dd, $J = 13.6, 7.2$ Hz, 1H), 1.29 (s, 9H), 1.19 (s, 9H), 0.48 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 186.2, 180.0, 151.0, 150.5, 141.9, 140.9, 140.4, 129.1, 128.0, 125.5, 122.18, 110.4, 58.1, 48.6, 47.8, 35.5, 35.5, 31.1, 29.7, 25.5, 8.5.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{35}\text{N}_4\text{O}_2$ 435.2755; Found 435.2750.



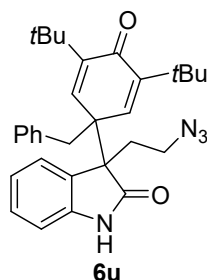
This compound was prepared according to the general procedure as a white solid (24 mg, 54% yield in 0.10 mmol scale). $R_f = 0.6$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (400 MHz, CDCl_3) δ 8.66 (s, 1H), 7.27 (dd, $J = 8.1, 4.3$ Hz, 1H), 7.03 (d, $J = 4.5$ Hz, 2H), 6.98 (d, $J = 3.0$ Hz, 1H), 6.93 (d, $J = 7.8$ Hz, 1H), 6.46 (d, $J = 3.0$ Hz, 1H), 5.26 – 5.12 (m, 1H),

4.84 (dd, $J = 13.8, 2.3$ Hz, 2H), 2.90 – 2.77 (m, 2H), 2.45 (dd, $J = 13.3, 7.1$ Hz, 1H), 2.40 – 2.22 (m, 2H), 1.88 (ddd, $J = 13.3, 7.6, 4.9$ Hz, 1H), 1.28 (s, 9H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 186.3, 179.4, 150.4, 150.1, 141.7, 140.4, 134.0, 132.1, 129.3, 127.6, 125.6, 122.3, 118.4, 110.3, 57.6, 47.8, 47.4, 37.3, 35.5, 35.4, 31.1, 29.6.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{35}\text{N}_4\text{O}_2$ 447.2755; Found 447.2749.

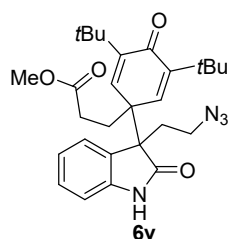


This compound was prepared according to the general procedure as a white solid (41 mg, 83% yield in 0.10 mmol scale). $R_f = 0.45$ (ethyl acetate/petroleum ether = 1/4, v/v).

^1H NMR (400 MHz, CDCl_3) δ 8.95 (s, 1H), 7.31 (ddd, $J = 7.8, 6.7, 2.2$ Hz, 1H), 7.17 (d, $J = 3.0$ Hz, 1H), 7.12 – 7.07 (m, 2H), 7.05 – 6.98 (m, 4H), 6.82 – 6.76 (m, 2H), 6.58 (d, $J = 3.0$ Hz, 1H), 3.03 (d, $J = 12.7$ Hz, 1H), 3.00 – 2.82 (m, 3H), 2.36 (dt, $J = 13.8, 8.2$ Hz, 1H), 1.94 (ddd, $J = 13.1, 7.5, 5.0$ Hz, 1H), 1.19 (s, 9H), 1.00 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 185.6, 179.8, 179.7, 149.7, 149.5, 141.8, 140.1, 139.7, 135.6, 130.2, 129.4, 127.7, 127.2, 127.2, 126.8, 125.6, 122.4, 110.5, 57.7, 48.9, 47.9, 39.5, 35.4, 35.2, 31.4, 29.3, 29.2, 29.1, 29.1.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{31}\text{H}_{37}\text{N}_4\text{O}_2$ 497.2911; Found 497.2906.

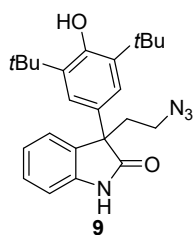


This compound was prepared according to the general procedure as a white solid (38.4 mg, 78% yield in 0.10 mmol scale). $R_f = 0.4$ (ethyl acetate/petroleum ether = 1/4, v/v).

¹H NMR (500 MHz, CDCl₃) δ 8.53 (s, 1H), 7.27 (s, 1H), 7.03 (d, *J* = 5.8 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.44 (d, *J* = 3.0 Hz, 1H), 3.58 (s, 3H), 2.85 (d, *J* = 2.4 Hz, 2H), 2.34 – 2.23 (m, 1H), 2.15 – 1.97 (m, 2H), 1.92 – 1.83 (m, 3H), 1.29 (s, 9H), 1.18 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 185.6, 179.1, 173.4, 151.4, 151.0, 141.7, 139.9, 139.4, 129.4, 127.5, 125.5, 122.3, 110.5, 57.9, 51.9, 47.8, 47.6, 35.6, 35.5, 31.1, 29.6, 29.6, 29.0, 27.3.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₈H₃₇N₄O₂ 493.2809; Found 493.2813.

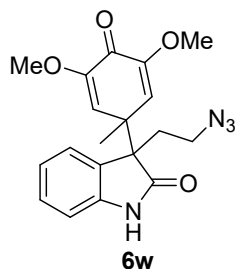


This compound was prepared according to the general procedure as a white solid (31.2 mg, 77% yield in 0.10 mmol scale). *R_f* = 0.5 (ethyl acetate/petroleum ether = 1/4, v/v).

¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 7.33 – 7.21 (m, 2H), 7.18 (s, 2H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 1H), 3.24 – 2.99 (m, 2H), 2.74 (ddd, *J* = 13.5, 9.4, 6.8 Hz, 1H), 2.40 (ddd, *J* = 13.9, 9.4, 4.9 Hz, 1H), 1.37 (s, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 180.4, 153.3, 140.9, 135.8, 131.6, 129.8, 128.6, 125.2, 123.5, 122.7, 110.3, 55.1, 47.9, 36.9, 34.6, 30.3, 30.3, 29.8.

HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₄H₃₁N₄O₂ 407.2442; Found 407.2436.

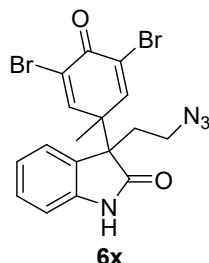


This compound was prepared according to the general procedure as a white solid (18.5 mg, 50% yield in 0.10 mmol scale). *R_f* = 0.45 (ethyl acetate/petroleum ether = 1/4, v/v).

¹H NMR (500 MHz, CDCl₃) δ 9.49 (s, 1H), 7.12 (tt, *J* = 7.7, 1.1 Hz, 1H), 6.94 – 6.81 (m, 2H), 6.74 (tt, *J* = 7.6, 1.0 Hz, 1H), 6.14 (t, *J* = 0.7 Hz, 2H), 3.72 (ddd, *J* = 12.4, 9.7, 5.3 Hz, 1H), 3.64 (d, *J* = 0.7 Hz, 6H), 3.53 (ddd, *J* = 12.1, 9.5, 6.3 Hz, 1H), 2.56 – 2.39 (m, 2H), 2.16 (d, *J* = 0.8 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 153.4, 141.5, 134.4, 131.6, 130.0, 125.9, 125.4, 125.4, 121.9, 110.4, 105.41, 83.1, 55.6, 46.4, 37.2, 22.0.

HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₉H₂₁N₄O₂ 369.1557; Found 369.1554.

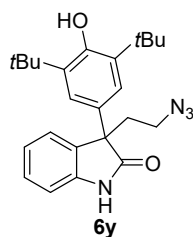


This compound was prepared according to the general procedure as a white solid (44 mg, 94% yield in 0.10 mmol scale). R_f = 0.5 (ethyl acetate/petroleum ether = 1/4, v/v).

¹H NMR (400 MHz, CDCl₃) δ 9.26 (s, 1H), 7.23-7.18 (m, 1H), 7.17 (dd, *J* = 1.7, 0.8 Hz, 2H), 6.93 – 6.89 (m, 1H), 6.85 – 6.78 (m, 2H), 3.66-3.63 (m, 1H), 3.60 – 3.49 (m, 1H), 3.01-2.93 (m, 1H), 2.61 – 2.46 (m, 1H), 2.17 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 177.0, 148.7, 141.417, 137.137, 133.4, 133.1, 130.9, 125.9, 125.139, 122.8, 119.9, 111.0, 84.9, 45.9, 38.9, 20.2.

HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₁₇H₁₅N₄O₂Na 486.9376; Found 486.9370.

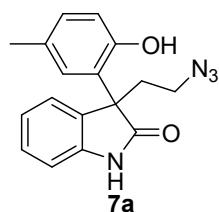


This compound was prepared according to the general procedure as a white solid (31.2 mg, 77% yield in 0.10 mmol scale). R_f = 0.5 (ethyl acetate/petroleum ether = 1/4, v/v).

¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 1H), 7.33 – 7.21 (m, 2H), 7.18 (s, 2H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 5.18 (s, 1H), 3.24 – 2.99 (m, 2H), 2.74 (ddd, *J* = 13.5, 9.4, 6.8 Hz, 1H), 2.40 (ddd, *J* = 13.9, 9.4, 4.9 Hz, 1H), 1.37 (s, 18H).

¹³C NMR (101 MHz, CDCl₃) δ 180.4, 153.3, 140.9, 135.8, 131.6, 129.8, 128.6, 125.2, 123.5, 122.7, 110.3, 55.1, 47.9, 36.9, 34.6, 30.3, 30.3, 29.8.

HRMS (ESI) m/z: [M + H]⁺ Calcd for C₂₄H₃₁N₄O₂ 407.2442; Found 407.2436.

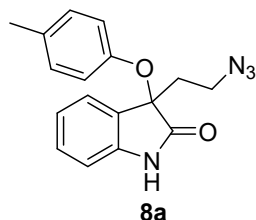


This compound was prepared according to the general procedure as a white solid (12 mg, 39% yield in 0.10 mmol scale). $R_f = 0.45$ (ethyl acetate/petroleum ether = 1/2, v/v).

^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H), 8.75 (s, 1H), 7.35 (td, $J = 7.6, 1.4$ Hz, 1H), 7.32 – 7.28 (m, 1H), 7.22 (dd, $J = 7.5, 1.1$ Hz, 1H), 7.02 (dt, $J = 7.7, 0.8$ Hz, 1H), 7.01 – 6.96 (m, 1H), 6.90 (d, $J = 8.1$ Hz, 1H), 6.77 (d, $J = 2.1$ Hz, 1H), 3.32 – 3.16 (m, 1H), 3.07 (dd, $J = 8.0, 6.3$ Hz, 2H), 2.39 – 2.32 (m, 1H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 183.4, 154.1, 140.4, 130.4, 129.9, 129.8, 129.2, 128.5, 126.3, 123.6, 123.5, 120.1, 111.3, 56.4, 47.7, 33.9, 20.7.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_4\text{O}_2$ 331.1171; Found 331.1201.



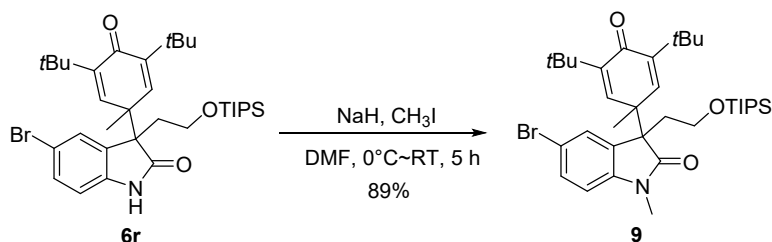
This compound was prepared according to the general procedure as a white solid (5.8 mg, 19% yield in 0.10 mmol scale). $R_f = 0.6$ (ethyl acetate/petroleum ether = 1/2, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.35 – 7.31 (m, 1H), 7.28 (td, $J = 7.7, 1.3$ Hz, 1H), 7.07 (td, $J = 7.6, 1.0$ Hz, 1H), 6.90 – 6.79 (m, 3H), 6.66 – 6.57 (m, 2H), 3.55 (qdd, $J = 12.5, 8.8, 6.1$ Hz, 2H), 2.49 (ddd, $J = 13.9, 8.9, 6.7$ Hz, 1H), 2.39 (s, 1H), 2.17 (s, 3H)..

^{13}C NMR (101 MHz, CDCl_3) δ 176.7, 153.1, 140.1, 132.9, 130.4, 129.8, 127.4, 125.0, 123.4, 119.6, 110.9, 82.1, 45.9, 37.7, 20.7.

HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_2\text{Na}$ 331.1171; Found 331.1173.

3. Derivatization of 6r



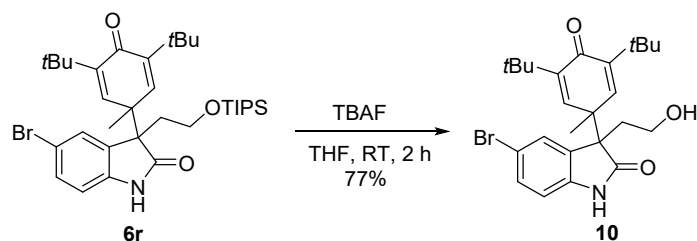
The compound **9** was synthesized by a slight modification of literature known procedure^[3]. A solution of **6r** (50.0 mg, 0.079 mmol) in dry DMF (0.32 mL) was added to a suspension of NaH (60% in mineral oil, 3.8 mg, 0.159 mmol) in DMF (0.64 mL) at 0 °C under nitrogen atmosphere. After the mixture was stirred at the same temperature for 10 min, MeI (7 μ L, 0.119 mmol) was added under the same conditions. This solution was stirred at room temperature after 5 h, the reaction mixture was quenched with water and extracted with EA. The extract was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with ethyl acetate– petroleum ether (1:8) as an eluent to give **9** (45.6 mg, 89%) as a white solid.

This compound was prepared according to the general procedure as a white solid (45.6 mg, 89% yield). R_f = 0.45 (ethyl acetate/petroleum ether = 1/2, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.36 (dd, J = 8.3, 1.9 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 6.90 (d, J = 3.0 Hz, 1H), 6.64 (d, J = 8.2 Hz, 1H), 6.30 (d, J = 3.0 Hz, 1H), 3.28 (ddd, J = 10.2, 8.3, 5.5 Hz, 2H), 3.16 (s, 3H), 2.38 (dt, J = 14.5, 7.5 Hz, 1H), 1.85 (dt, J = 13.7, 5.3 Hz, 1H), 1.29 (s, 9H), 1.17 (s, 3H), 1.07 (s, 9H), 0.86 (t, J = 2.1 Hz, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 185.5, 176.8, 148.3, 143.4, 141.6, 141.3, 131.0, 130.3, 128.3, 114.1, 109.0, 59.9, 56.6, 43.9, 35.1, 34.8, 34.1, 29.5, 29.3, 26.1, 19.6, 17.8, 17.8, 11.8.

HRMS (ESI) m/z : $[M + H]^+$ Calcd for C₃₅H₅₅BrNO₃Si 644.3129; Found 644.3126.



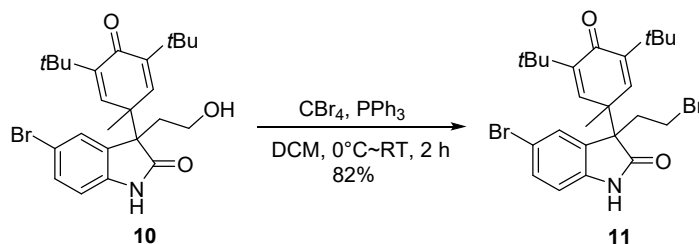
The compound **10** was synthesized by a slight modification of literature known procedure^[1]. A reaction tube was charged with **6r** (50.0 mg, 0.079 mmol). THF (0.20 mL) and TBAF (0.24 mL, 1

M solution in THF) were added. After stirring at room temperature for 2 h, The reaction mixture was directly concentrated under reduced pressure and was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1:2 to 1:1) to give **10** as a white solid (29.0 mg, 77%). This compound was prepared according to the general procedure as a white solid (29.0 mg, 77% yield). R_f = 0.35 (ethyl acetate/petroleum ether = 1/1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.68 (d, J = 20.7 Hz, 1H), 7.32 (dd, J = 8.3, 1.9 Hz, 1H), 7.09 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 2.9 Hz, 1H), 6.73 (dd, J = 8.2, 1.5 Hz, 1H), 6.40 (d, J = 3.0 Hz, 1H), 3.40 (ddd, J = 10.6, 6.5, 3.7 Hz, 1H), 3.13 (q, J = 9.9 Hz, 1H), 2.35 (ddd, J = 13.8, 9.6, 6.5 Hz, 1H), 1.86 (dt, J = 14.0, 4.6 Hz, 1H), 1.29 (s, 9H), 1.20 (s, 3H), 1.12 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.7, 180.5, 148.8, 148.6, 141.4, 141.1, 140.8, 131.6, 130.9, 128.5, 114.5, 111.4, 59.5, 57.5, 43.6, 35.3, 35.1, 34.4, 29.7, 29.5, 20.0.

HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{33}\text{BrNO}_3$ 474.1638; Found 474.1632.



The compound **11** was synthesized by a slight modification of literature known procedure^[2]. In a reaction tube, **10** (43.0 mg, 0.091 mmol) and triphenylphosphine (28.5 mg, 0.109 mmol) was dissolved in dry CH_2Cl_2 (0.20 mL). In an addition funnel, carbon tetrabromide (36.1 mg, 0.109 mmol) dissolved in dry CH_2Cl_2 (60 μL) was added drop-wise under nitrogen atmosphere at 0 °C until the addition was completed. The reaction was allowed to stir at room temperature for an additional 3h, or until complete disappearance of starting materials by TLC. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:8) to yield **11** as a white solid (40.8 mg, 82%).

This compound was prepared according to the general procedure as a white solid (40.8 mg, 82% yield). R_f = 0.45 (ethyl acetate/petroleum ether = 1/2, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.33 (s, 1H), 7.37 (dd, J = 8.3, 1.9 Hz, 1H), 7.12 (d, J = 1.9 Hz, 1H), 6.80 – 6.75 (m, 2H), 6.36 (d, J = 3.0 Hz, 1H), 2.93 (ddd, J = 11.0, 9.6, 5.7 Hz, 1H), 2.76 (ddd, J =

10.9, 9.6, 4.6 Hz, 1H), 2.63 (ddd, J = 13.4, 11.0, 5.7 Hz, 1H), 2.23 (ddd, J = 13.3, 11.1, 4.6 Hz, 1H), 1.30 (s, 9H), 1.29 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 185.4, 178.2, 149.2, 149.0, 140.5, 140.4, 140.2, 132.1, 130.0, 128.4, 115.1, 111.3, 59.2, 44.0, 35.4, 35.0, 29.8, 29.7, 29.4, 27.1, 20.0.

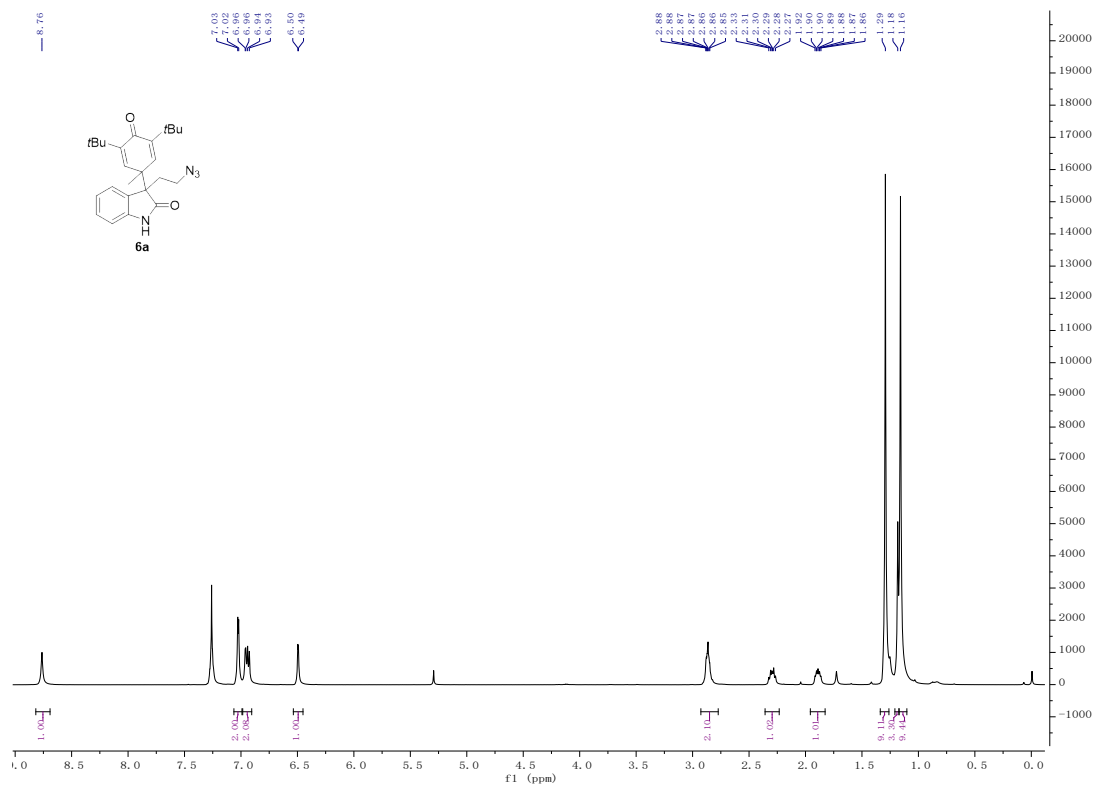
HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{Br}_2\text{NO}_2$ 536.0794; Found 536.0783.

4. Reference

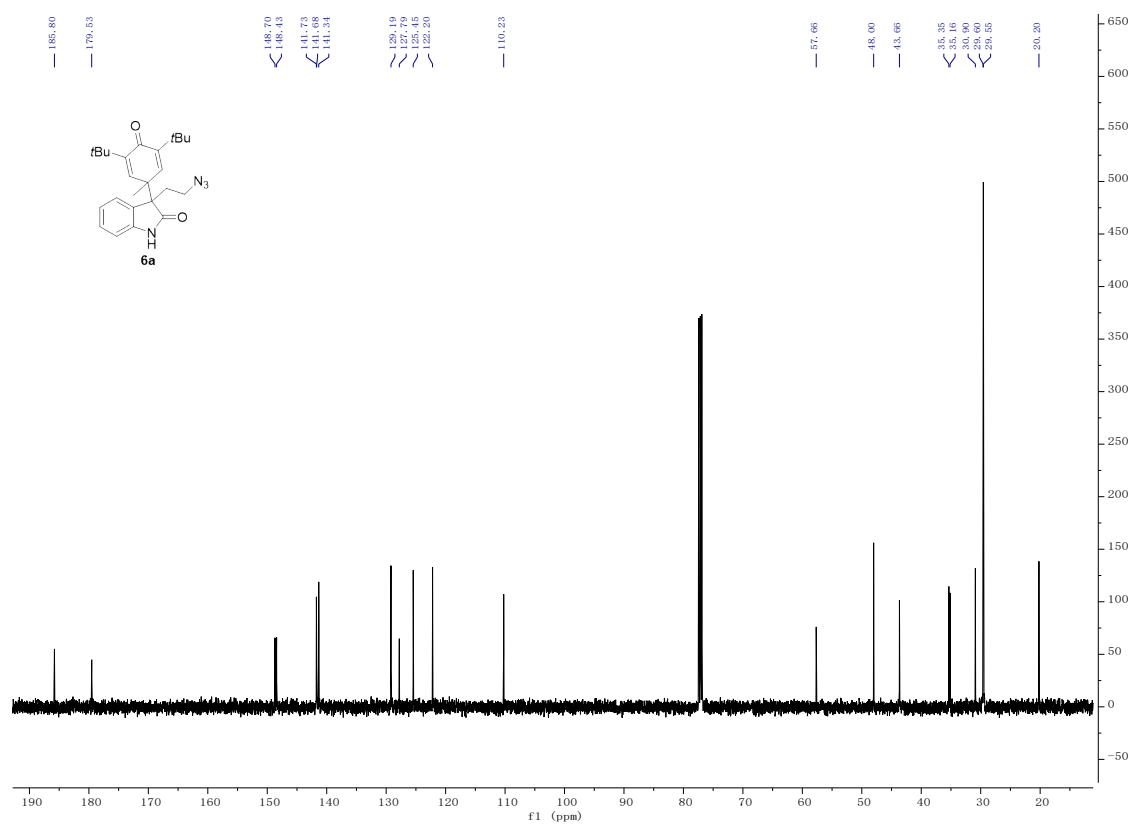
- [1] Zeng, Z.; Yang, L.-Q.; Xiao, Z.-J.; Chen, L.; Zhong, Z.-W.; Wang, F.; Liu, X.-H.; Dong, S.-X.; Feng, X.-M. A Remarkable Influence of La (III)/N, N'-Dioxide Structure on Asymmetric Formal Substitution of 3-Bromo-3-substituted Oxindoles with TMSCN [J]. *ACS. Catal.* **2024**, *14* (5), 2908-2916.
- [2] Doa, Q. T.; Nguyena, G. T.; Celisa, V.; Phillips, R. S. Inhibition of Escherichia coli tryptophan indole-lyase by tryptophan homologues [J]. *Arch. Biochem. Biophys.* **2014**, *560*, 20-26.
- [3] Kawasaki, T.; Shinada, M.; Ohzono, M.; Ogawa, A.; Terashima, R.; Sakamoto, M. Total synthesis of (±)-flustramines A and C, (±)-flustramide A, and (-)- and (+)-debromoflustramines A [J]. *J. Org. Chem.* **2008**, *73* (15), 5959-5964.

5. NMR Data for Substrate Scope and Derivatization

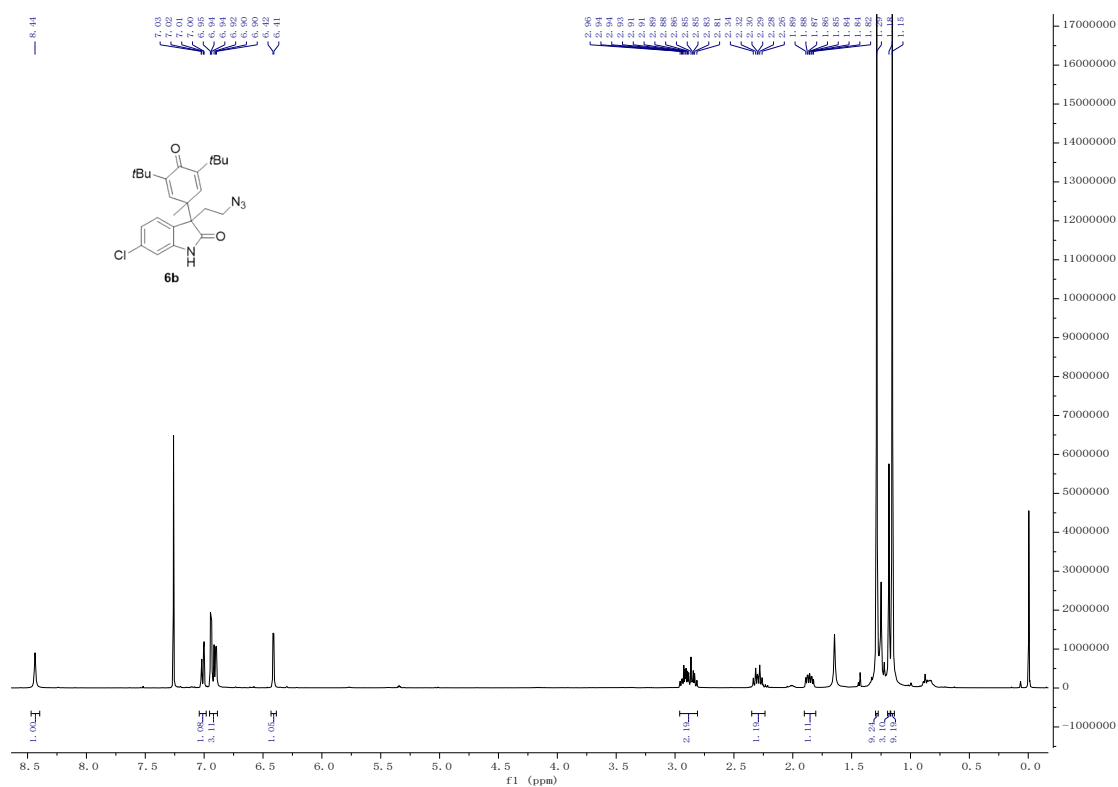
^1H NMR Spectrum of **6a** (500 MHz, CDCl_3)



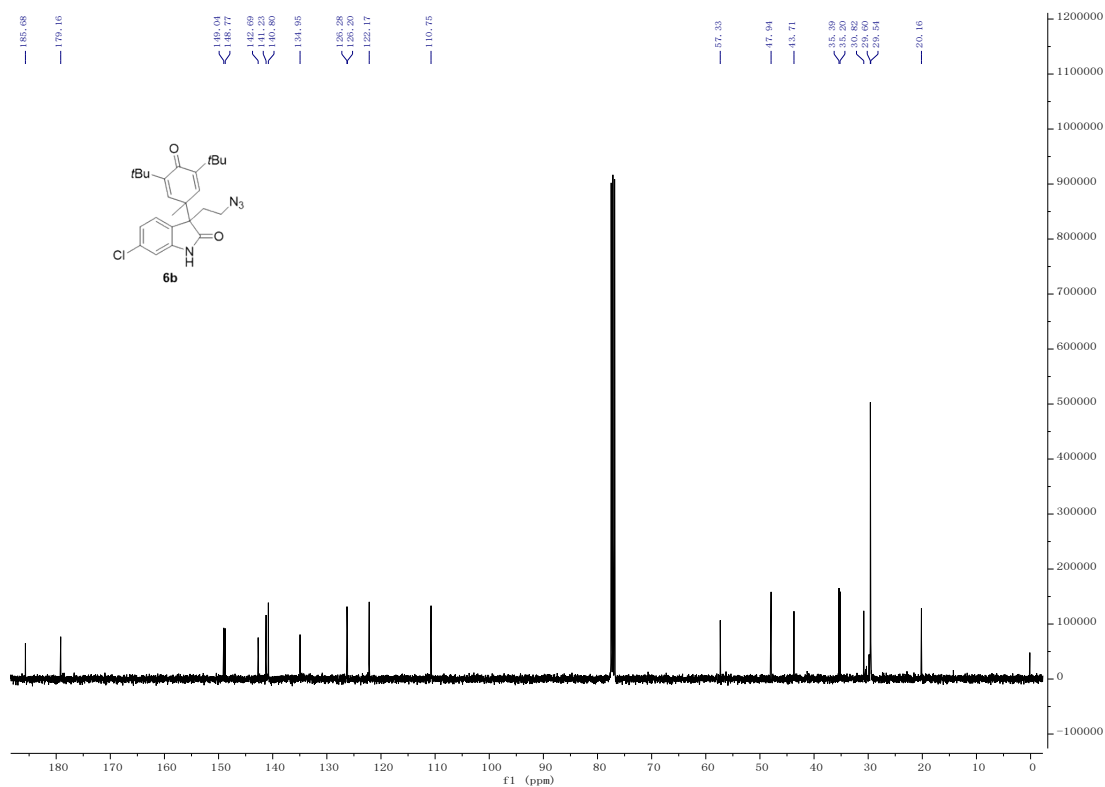
^{13}C NMR Spectrum of **6a** (126 MHz, CDCl_3)



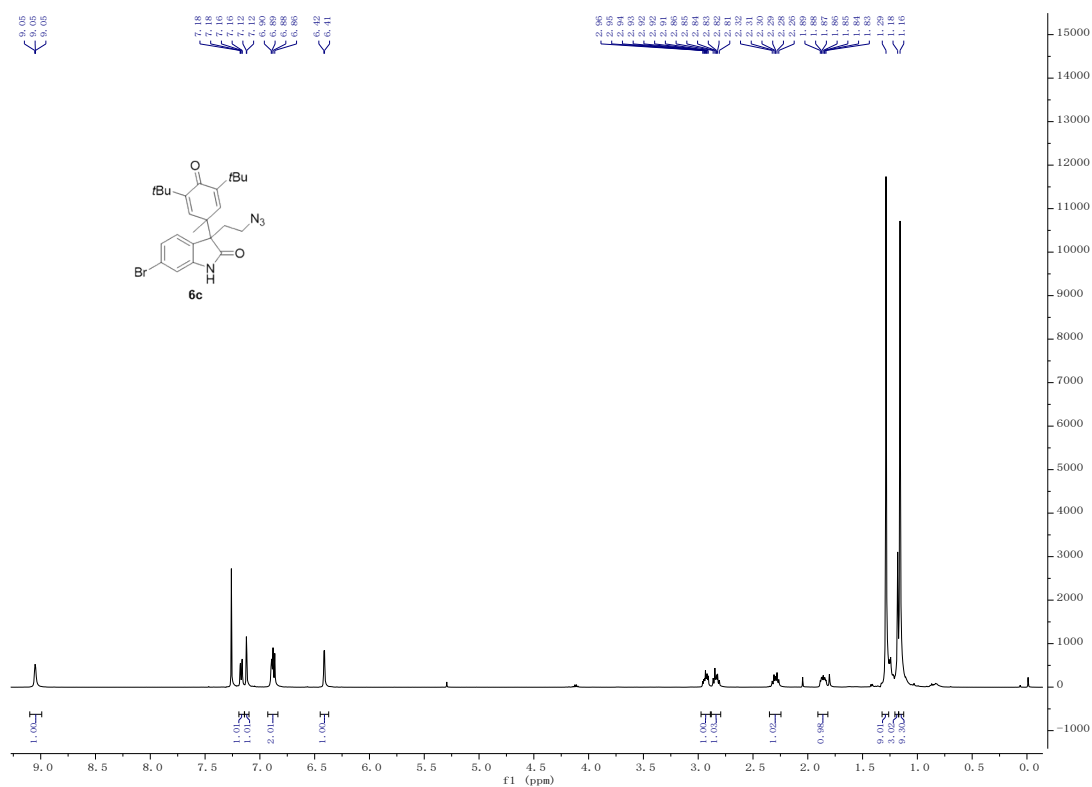
¹H NMR Spectrum of **6b** (400 MHz, CDCl₃)



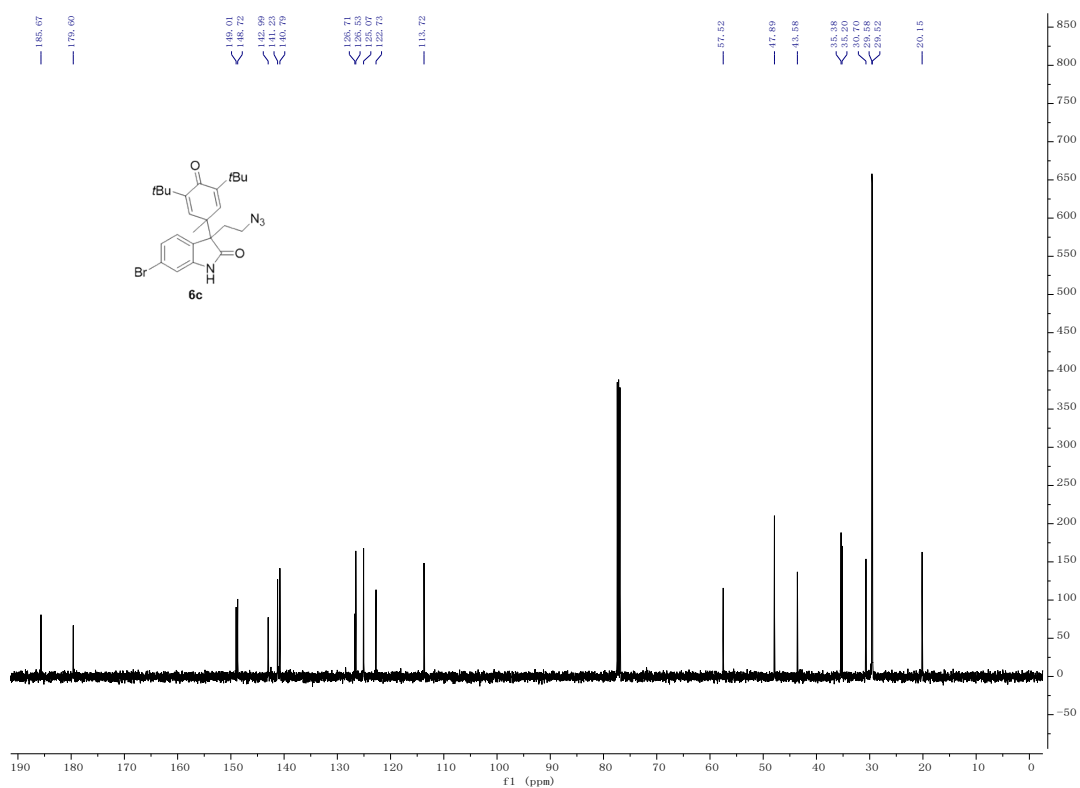
¹³C NMR Spectrum of **6b** (101 MHz, CDCl₃)



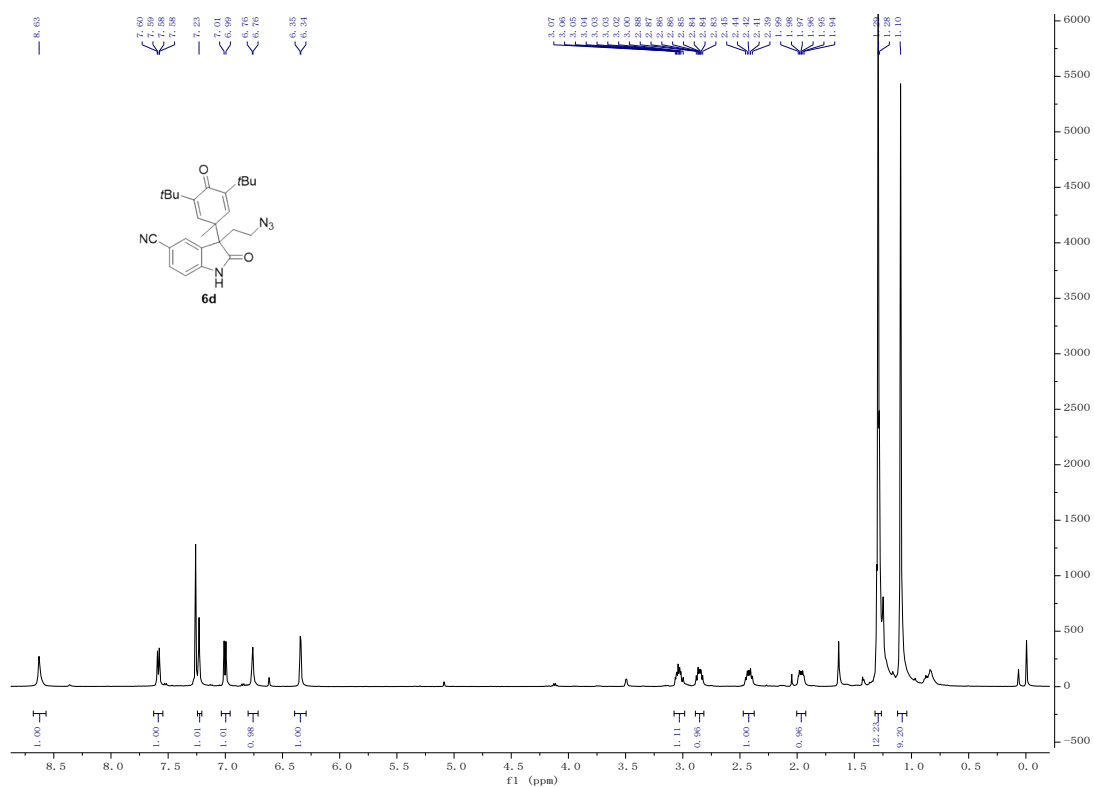
¹H NMR Spectrum of **6c** (500 MHz, CDCl₃)



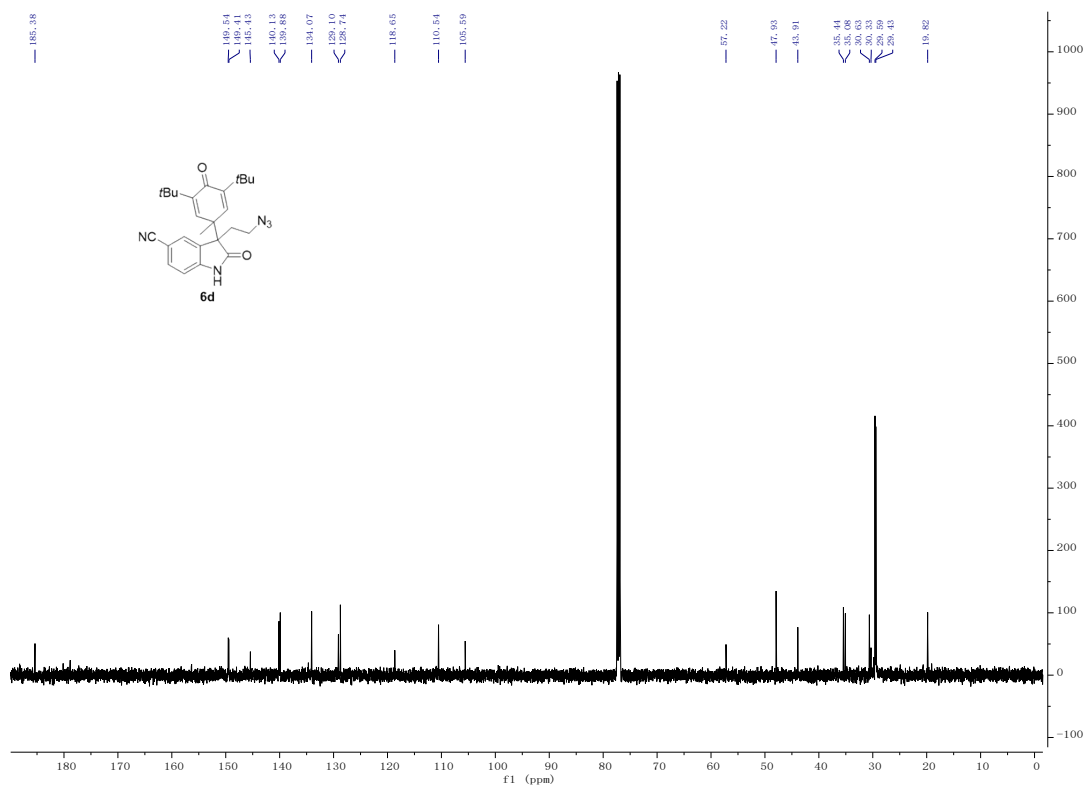
¹³C NMR Spectrum of **6c** (126 MHz, CDCl₃)



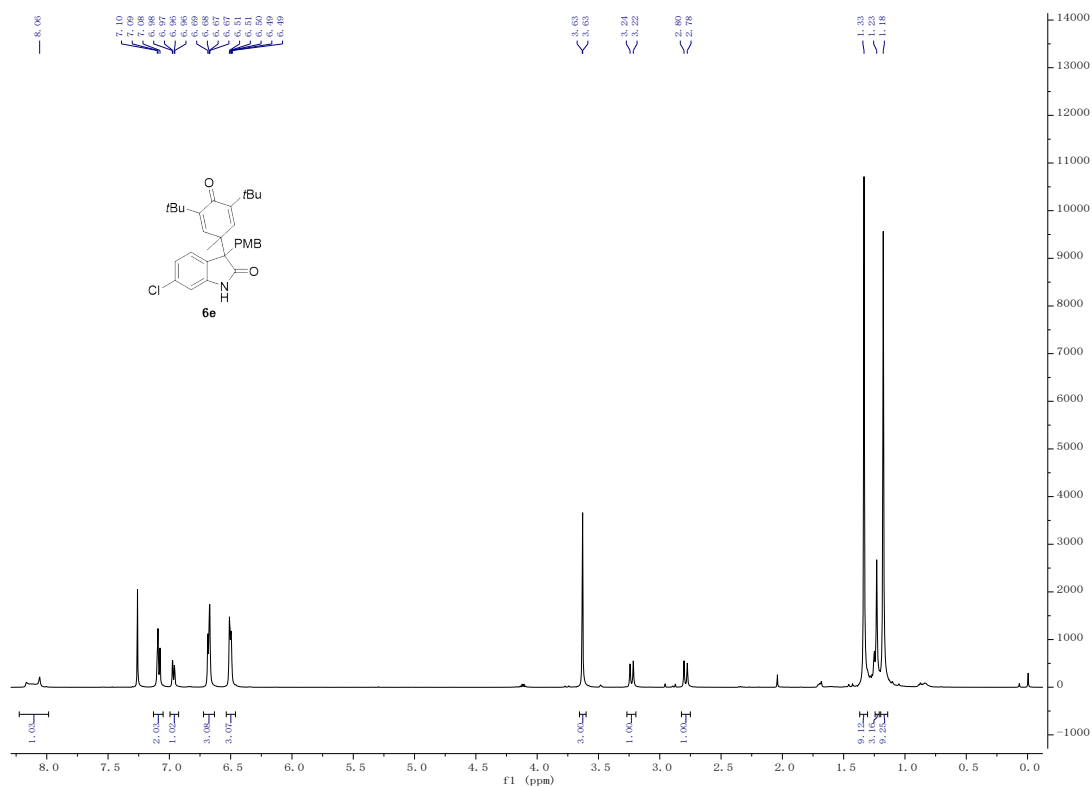
¹H NMR Spectrum of **6d** (500 MHz, CDCl₃)



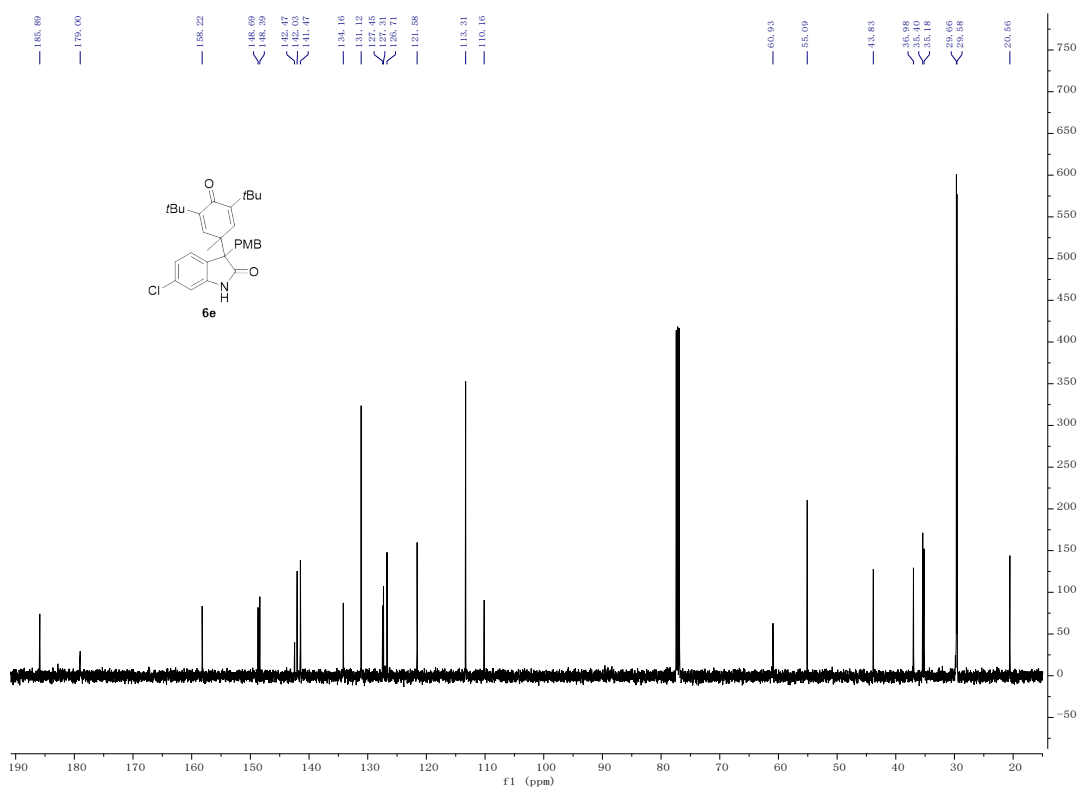
¹³C NMR Spectrum of **6d** (126 MHz, CDCl₃)



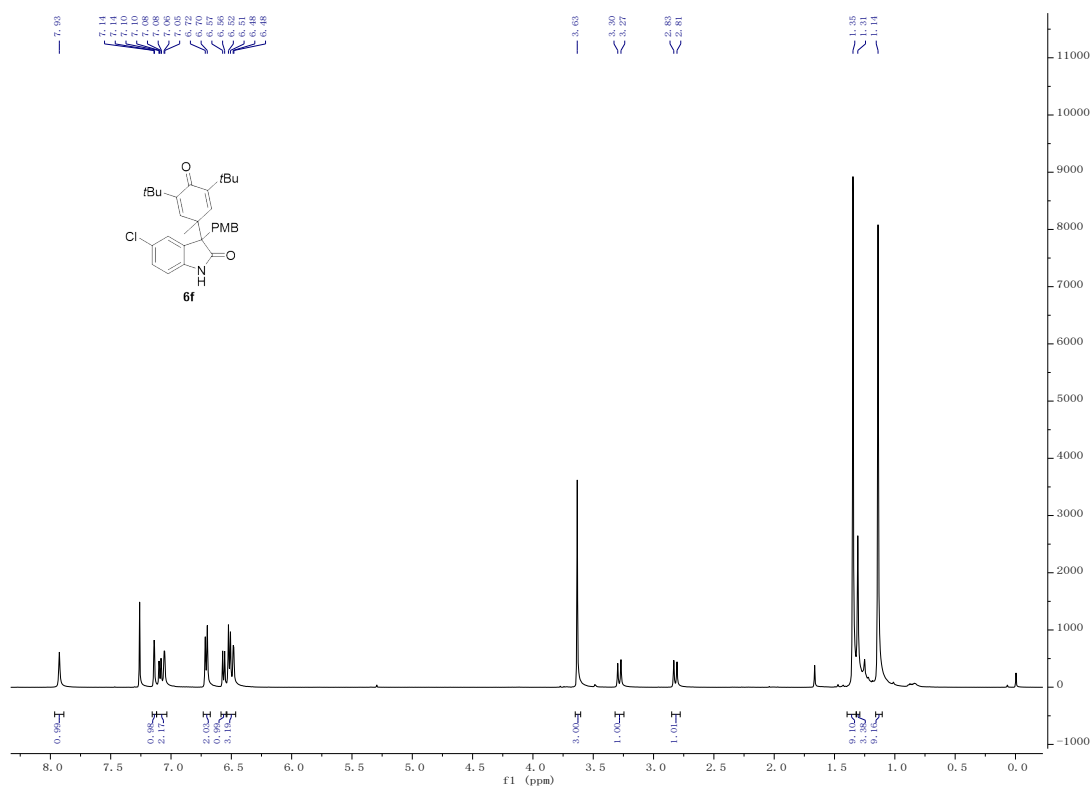
¹H NMR Spectrum of **6e** (500 MHz, CDCl₃)



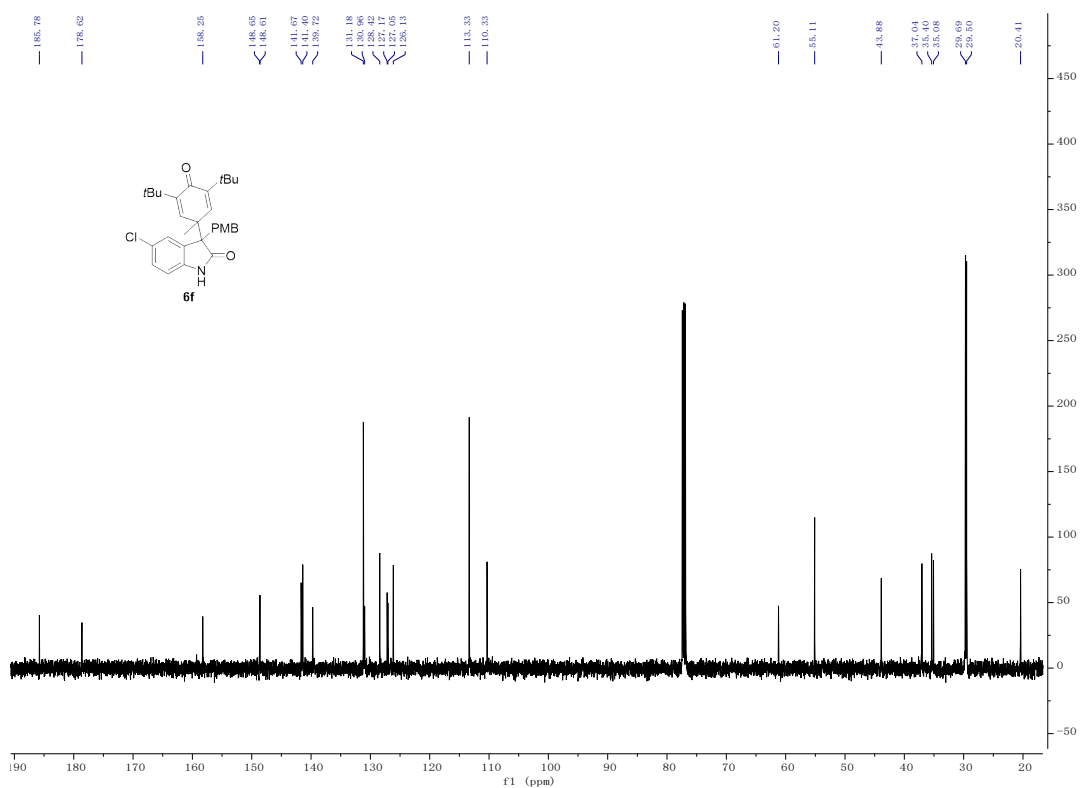
¹³C NMR Spectrum of **6e** (126 MHz, CDCl₃)



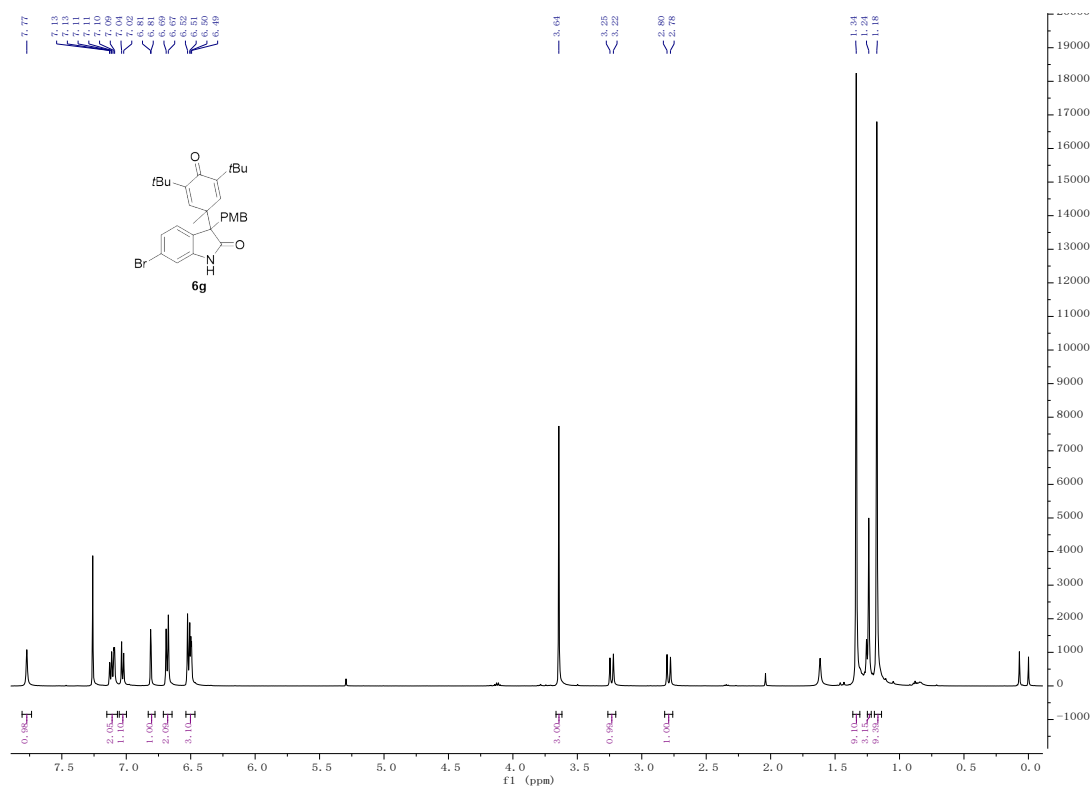
¹H NMR Spectrum of **6f** (500 MHz, CDCl₃)



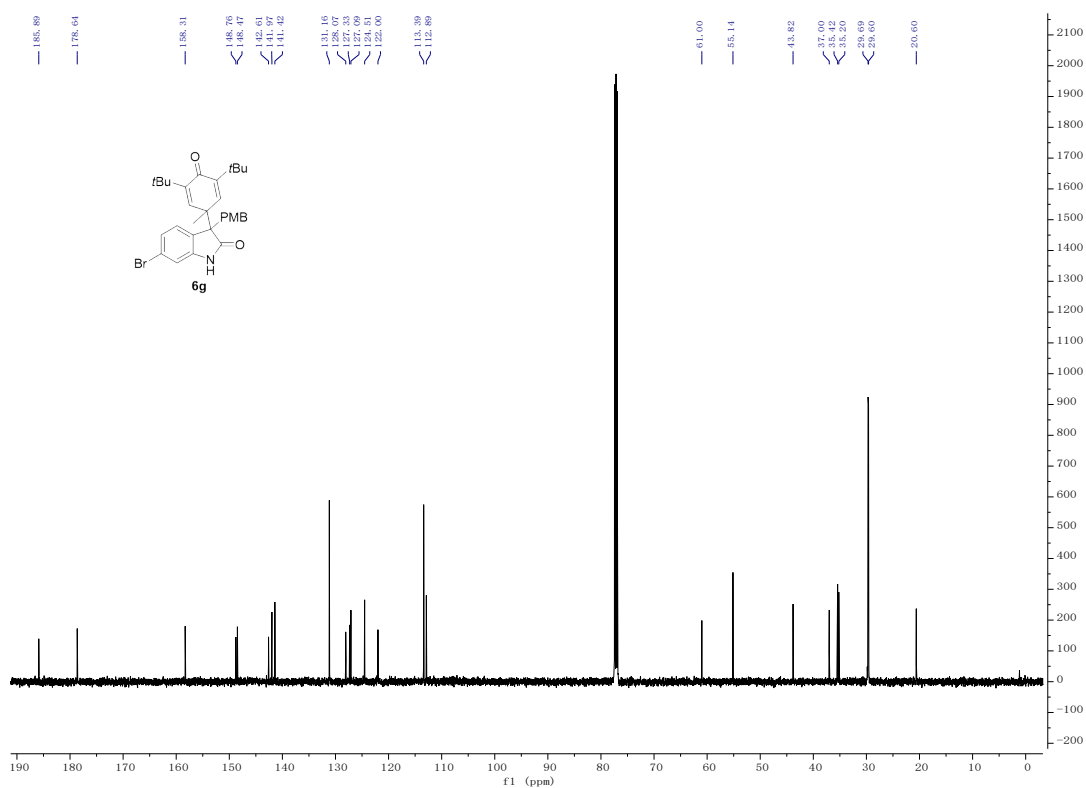
¹³C NMR Spectrum of **6f** (126 MHz, CDCl₃)



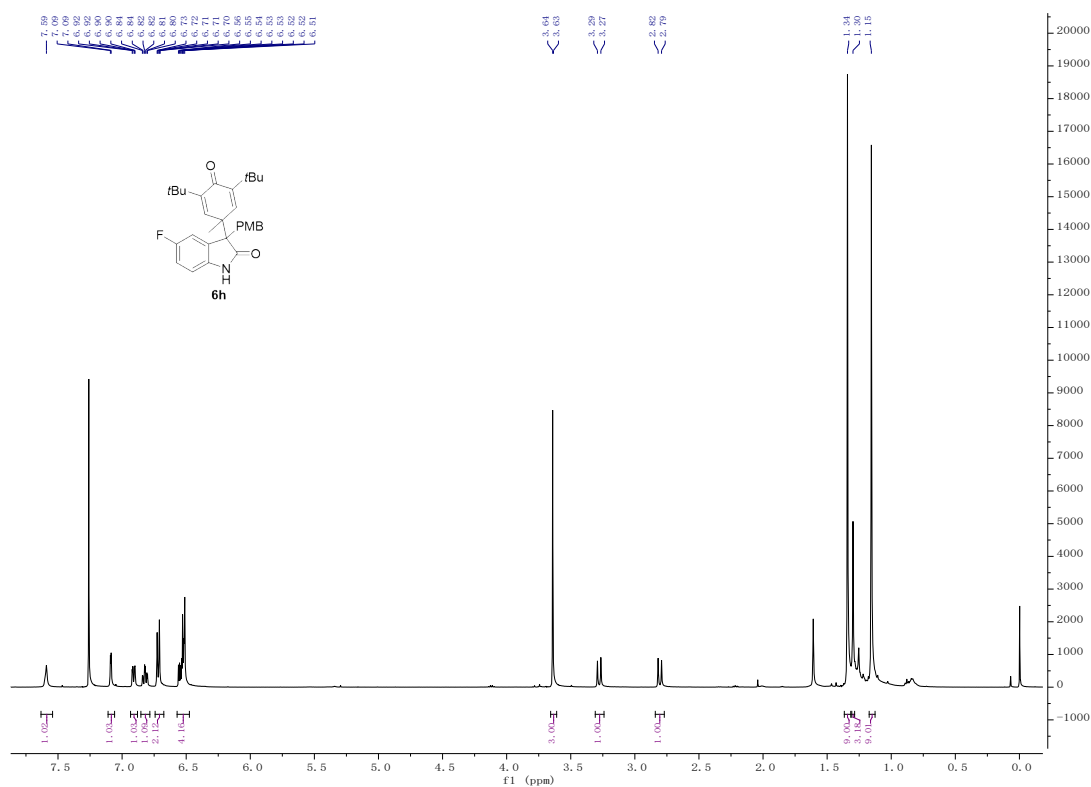
¹H NMR Spectrum of **6g** (500 MHz, CDCl₃)



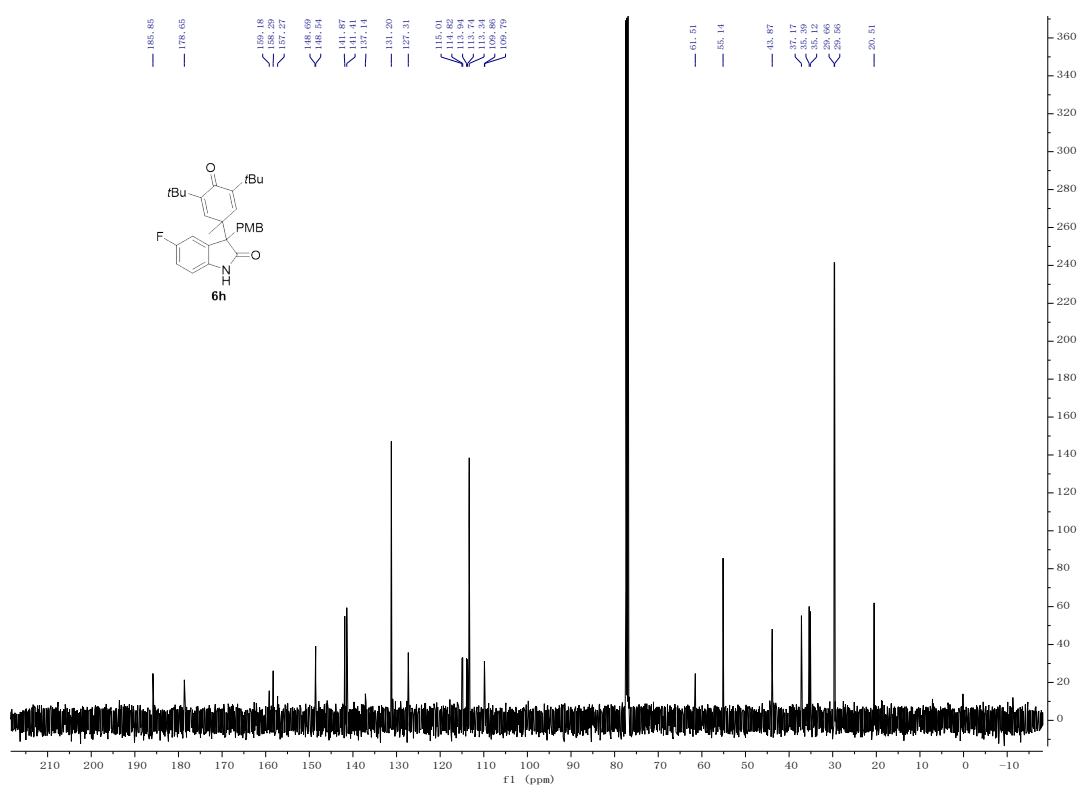
¹³C NMR Spectrum of **6g** (126 MHz, CDCl₃)



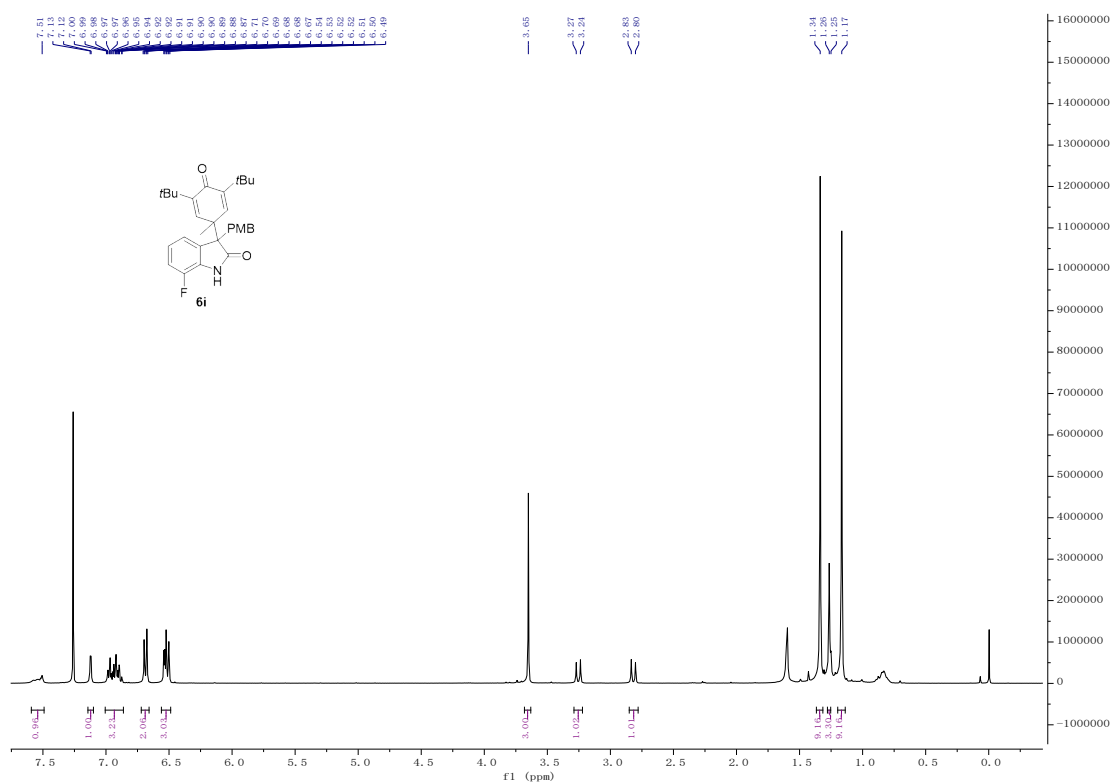
¹H NMR Spectrum of **6h** (500 MHz, CDCl₃)



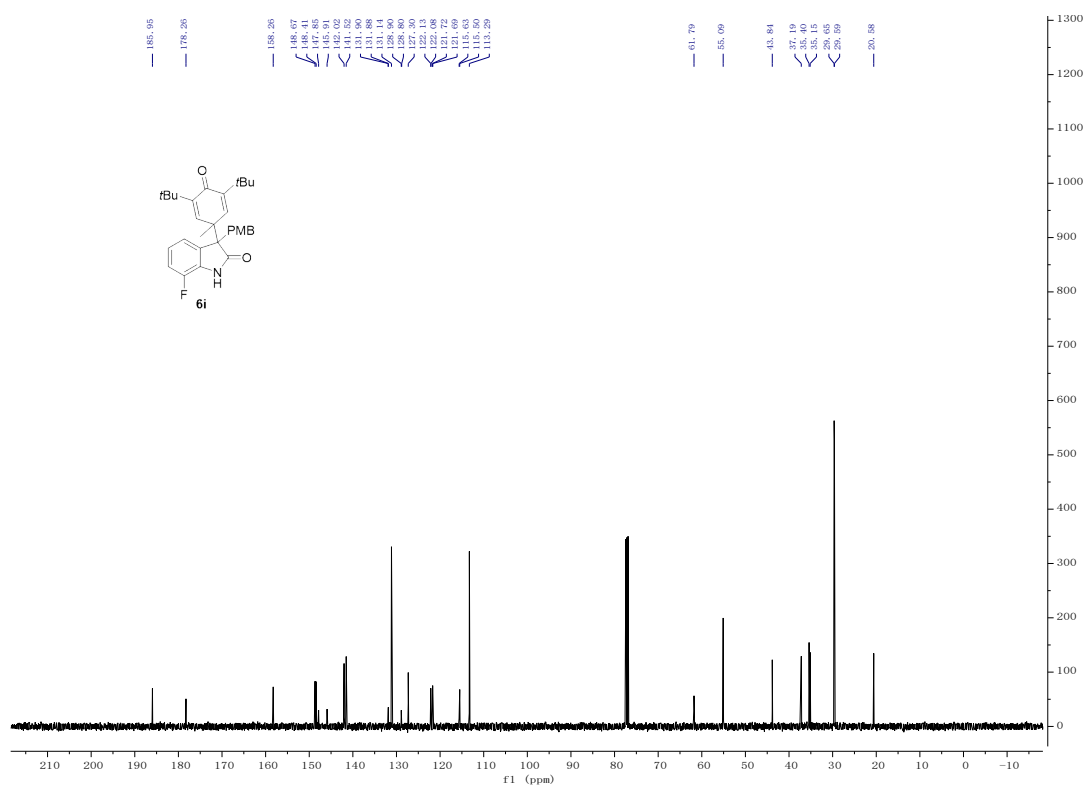
¹³C NMR Spectrum of **6h** (126 MHz, CDCl₃)



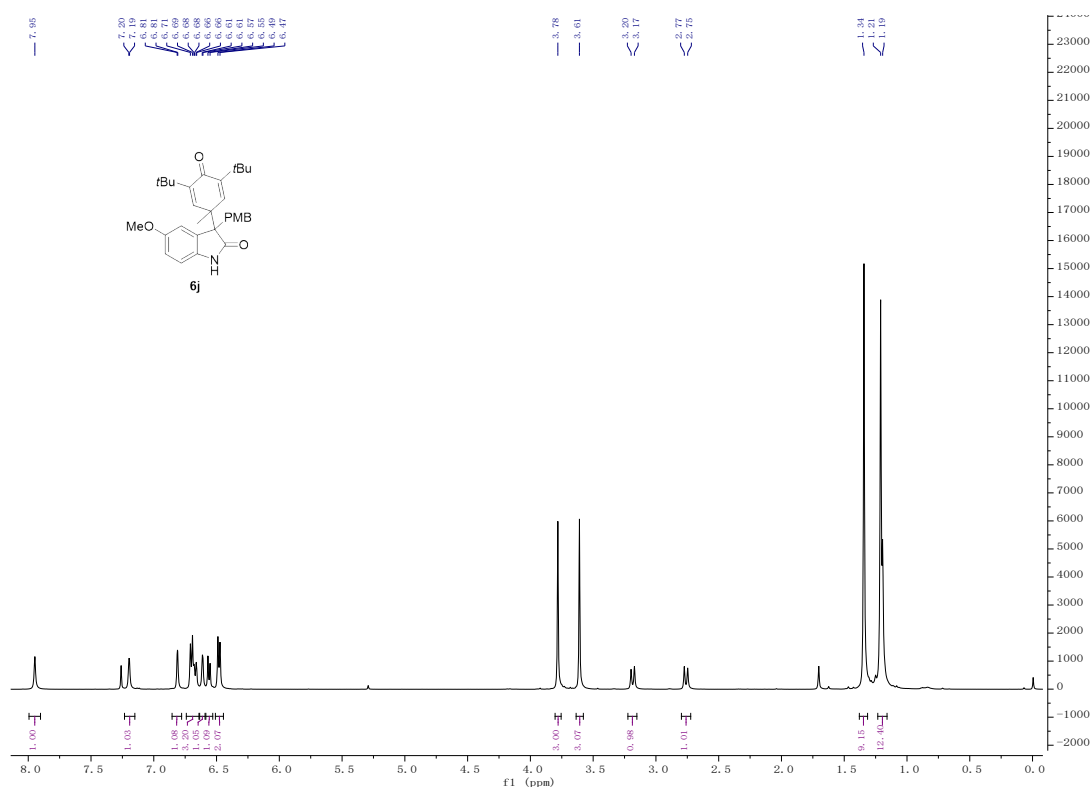
¹H NMR Spectrum of **6i** (400 MHz, CDCl₃)



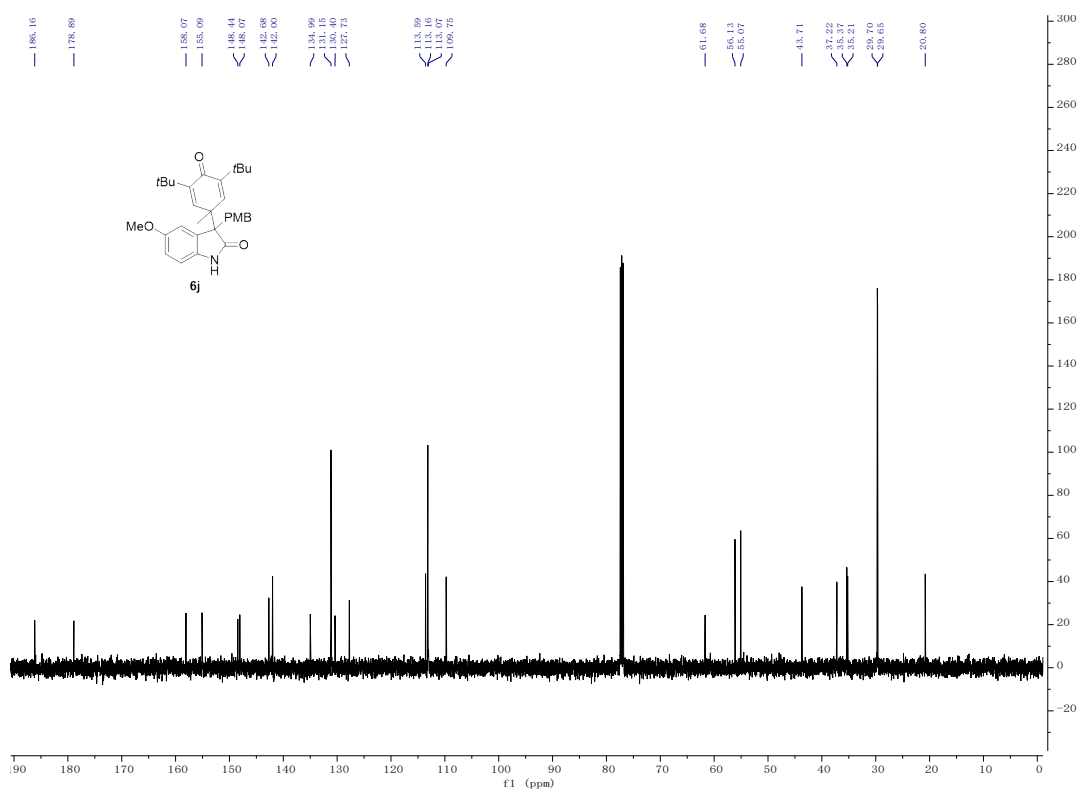
¹³C NMR Spectrum of **6i** (126 MHz, CDCl₃)



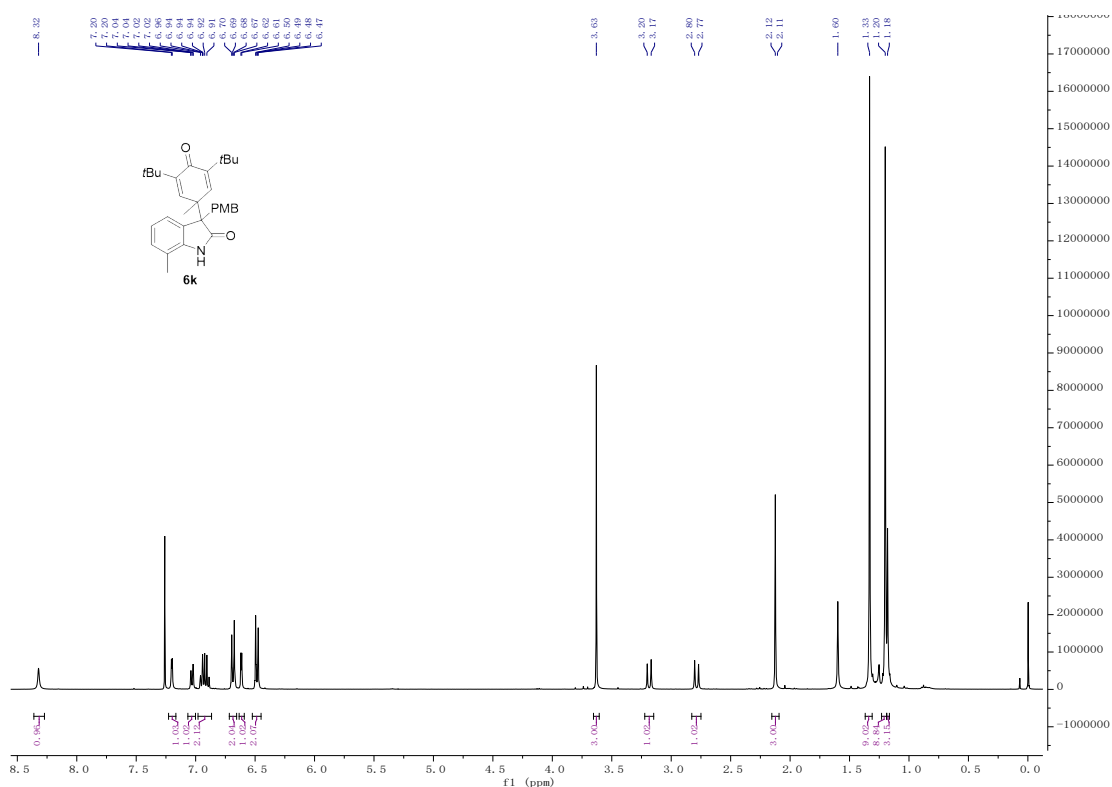
¹H NMR Spectrum of **6j** (500 MHz, CDCl₃)



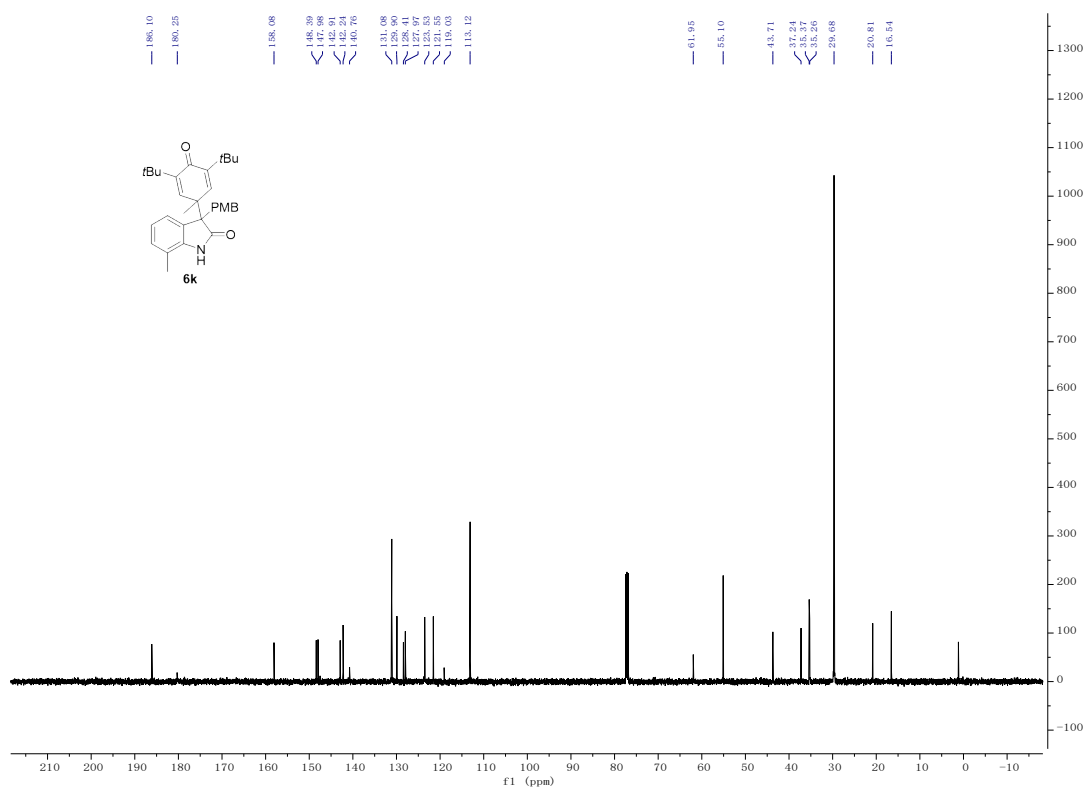
¹³C NMR Spectrum of **6j** (126 MHz, CDCl₃)



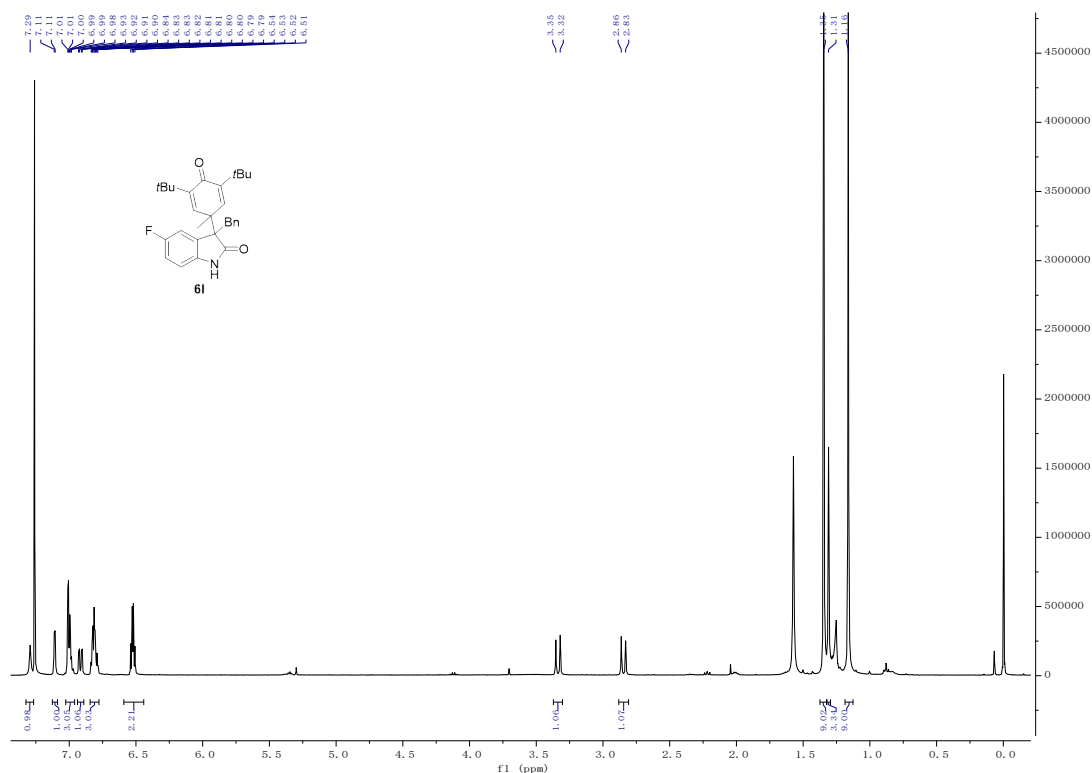
¹H NMR Spectrum of **6k** (400 MHz, CDCl₃)



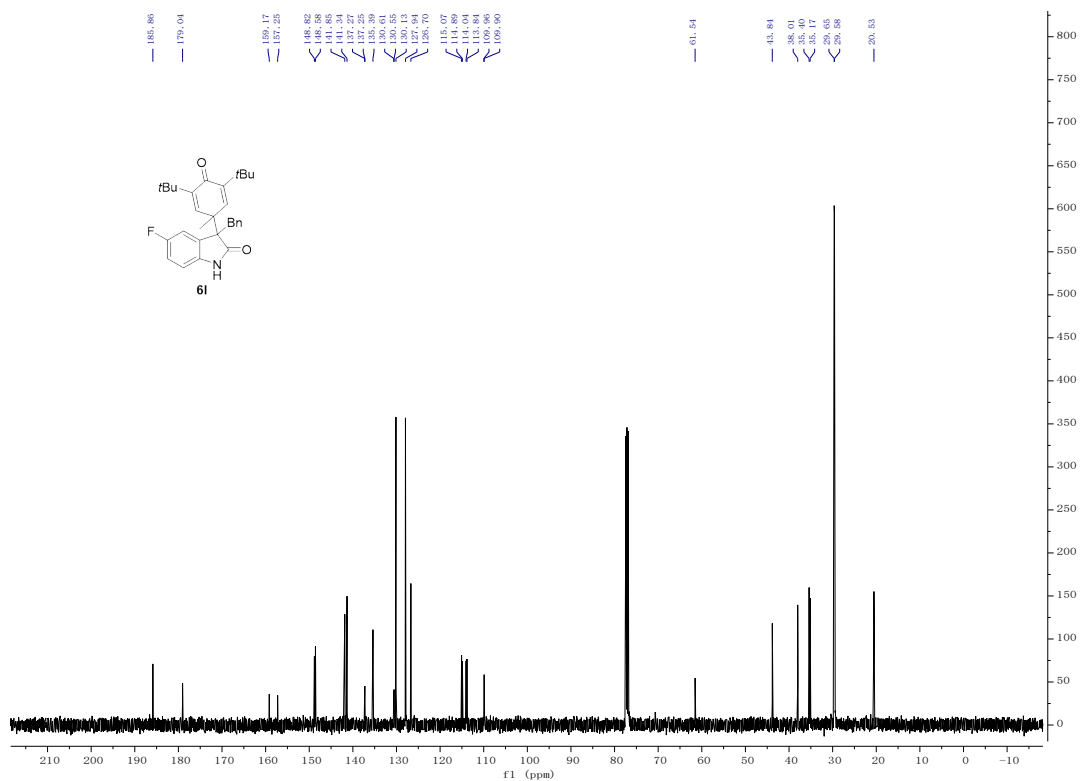
¹³C NMR Spectrum of **6k** (126 MHz, CDCl₃)



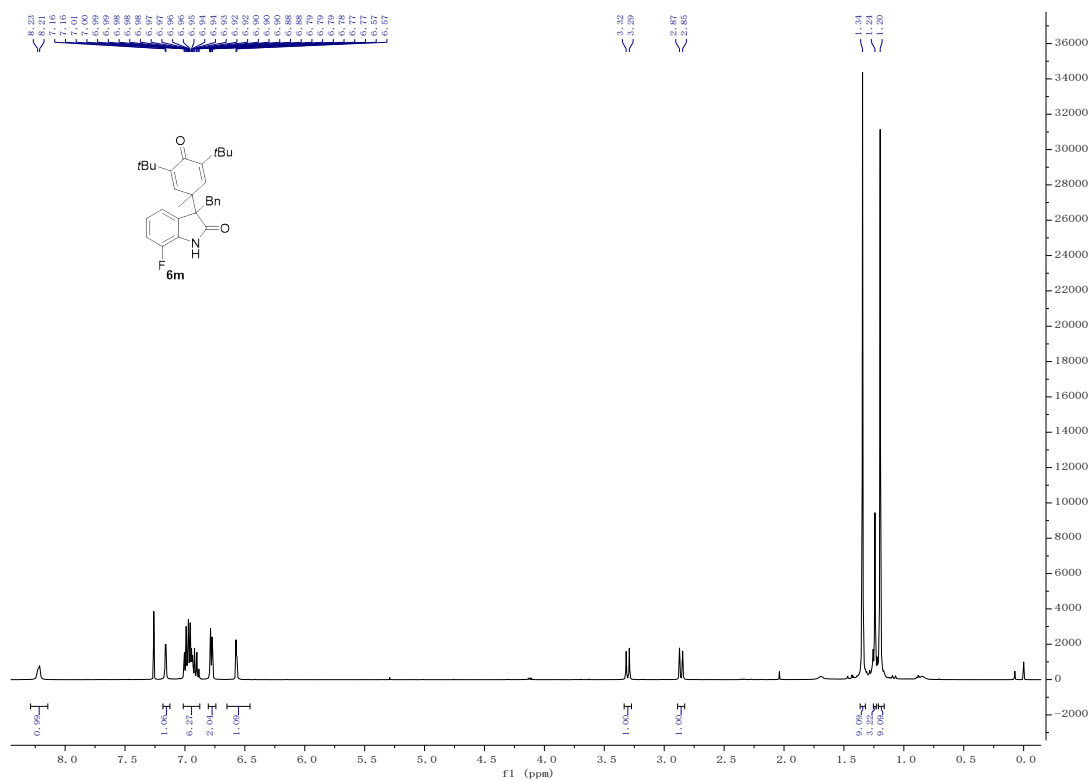
¹H NMR Spectrum of **61** (400 MHz, CDCl₃)



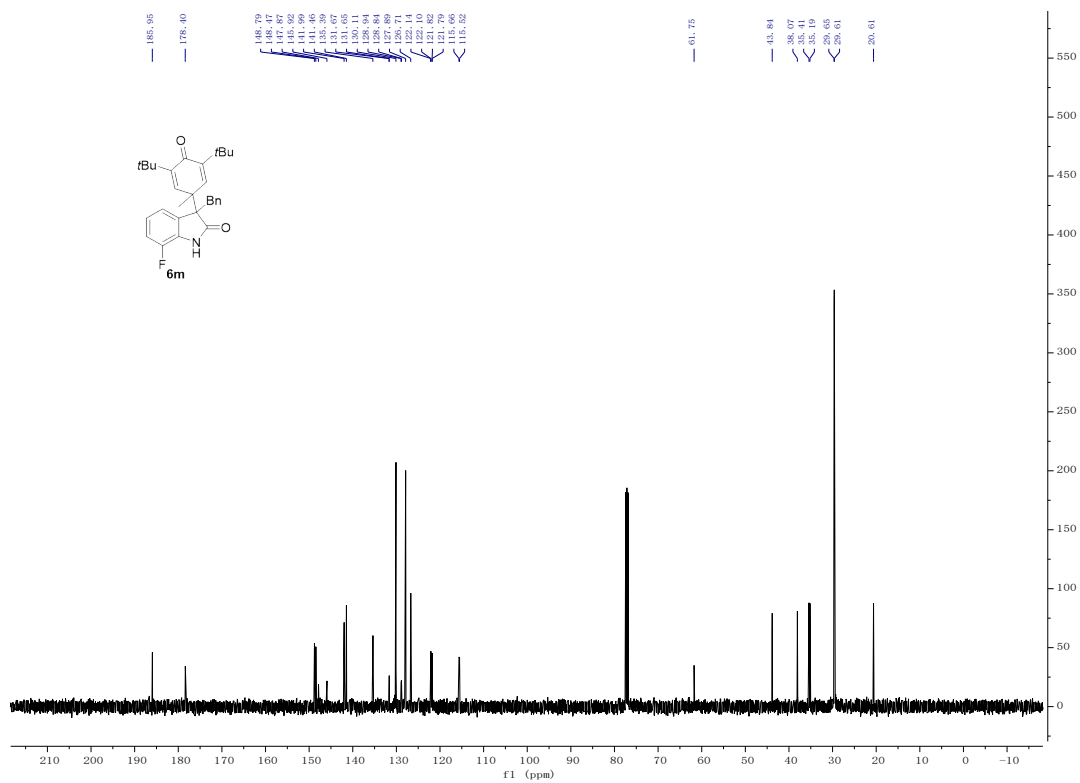
¹³C NMR Spectrum of **61** (126 MHz, CDCl₃)



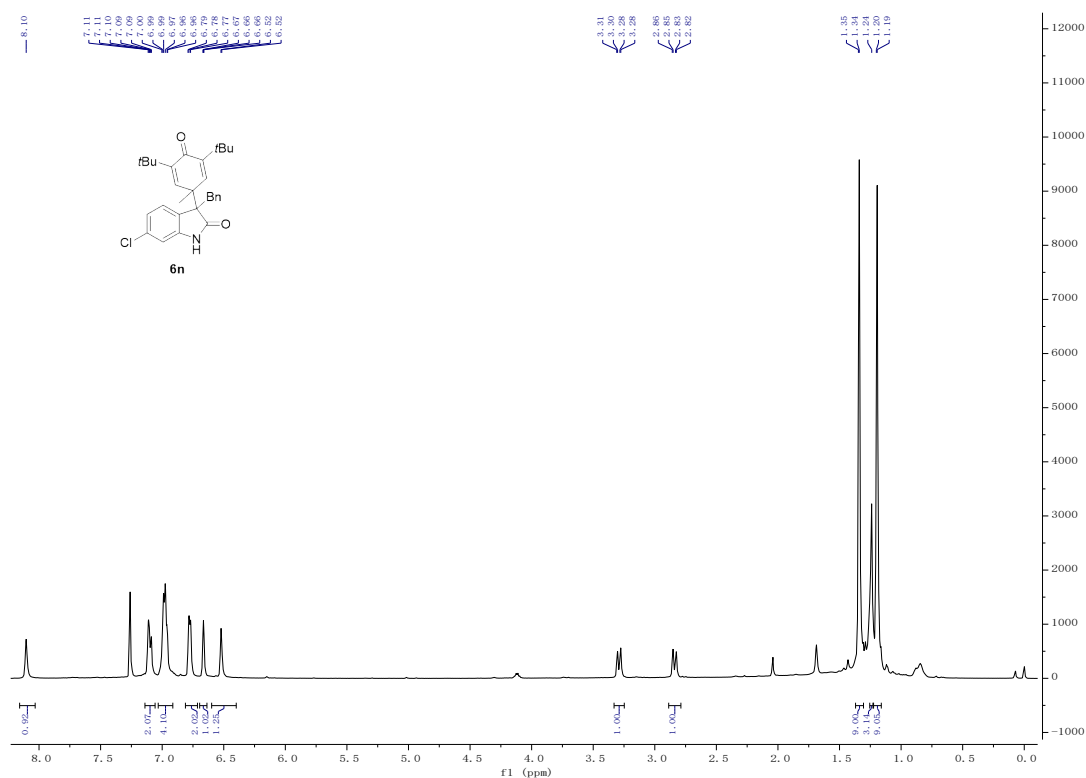
¹H NMR Spectrum of **6m** (500 MHz, CDCl₃)



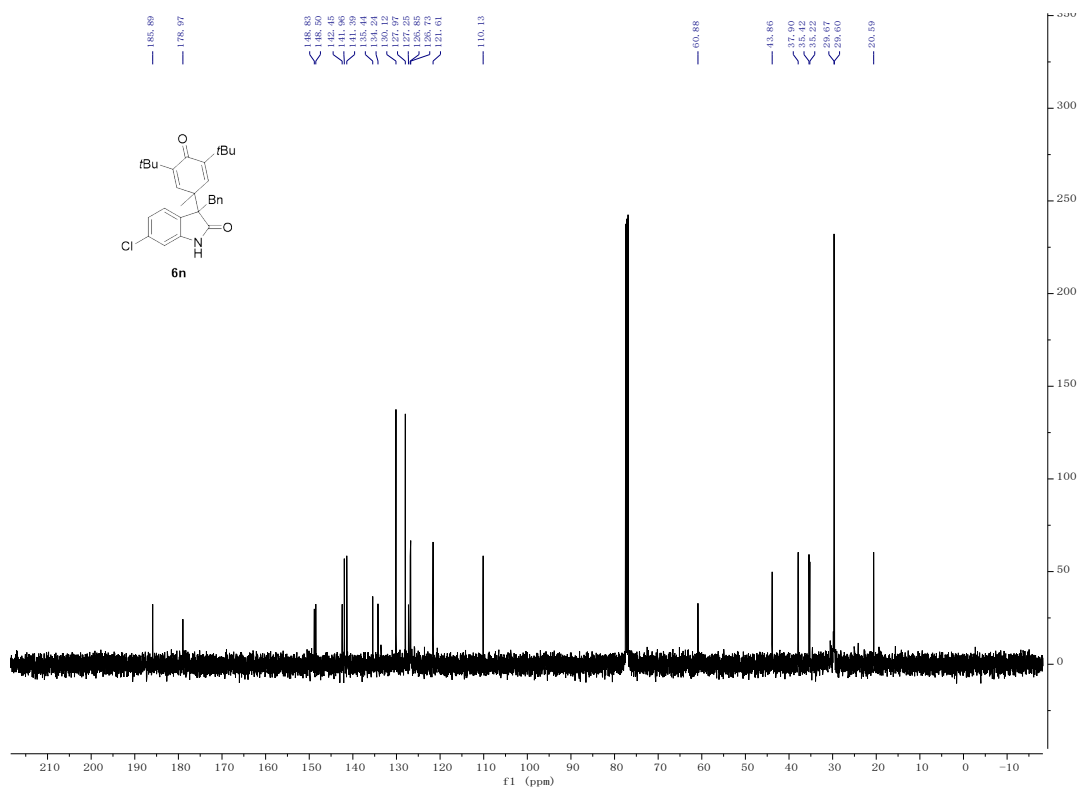
¹³C NMR Spectrum of **6m** (126 MHz, CDCl₃)



¹H NMR Spectrum of **6n** (500 MHz, CDCl₃)



¹³C NMR Spectrum of **6n** (126 MHz, CDCl₃)



Chemical structure of **6o** is shown above the spectrum.

¹H NMR spectrum (CDCl₃) of compound **6o**. The x-axis represents the chemical shift in ppm (f1), ranging from 0.0 to 9.16. The y-axis represents intensity, ranging from -2000 to 25000. Integration values are provided below the baseline.

Chemical shifts (ppm) listed at the top: 9.16, 7.25, 7.23, 7.05, 6.97, 6.96, 6.94, 6.92, 6.91, 6.76, 6.66, 2.23, 2.20, 2.83, 2.80, 2.17, 1.33, 1.31, 1.14.

Integration values (from left to right): 0.97, 1.40, 1.00, 2.00, 0.99, 0.99, 1.00, 3.00, 9.01, 3.04, 3.04, 0.00.

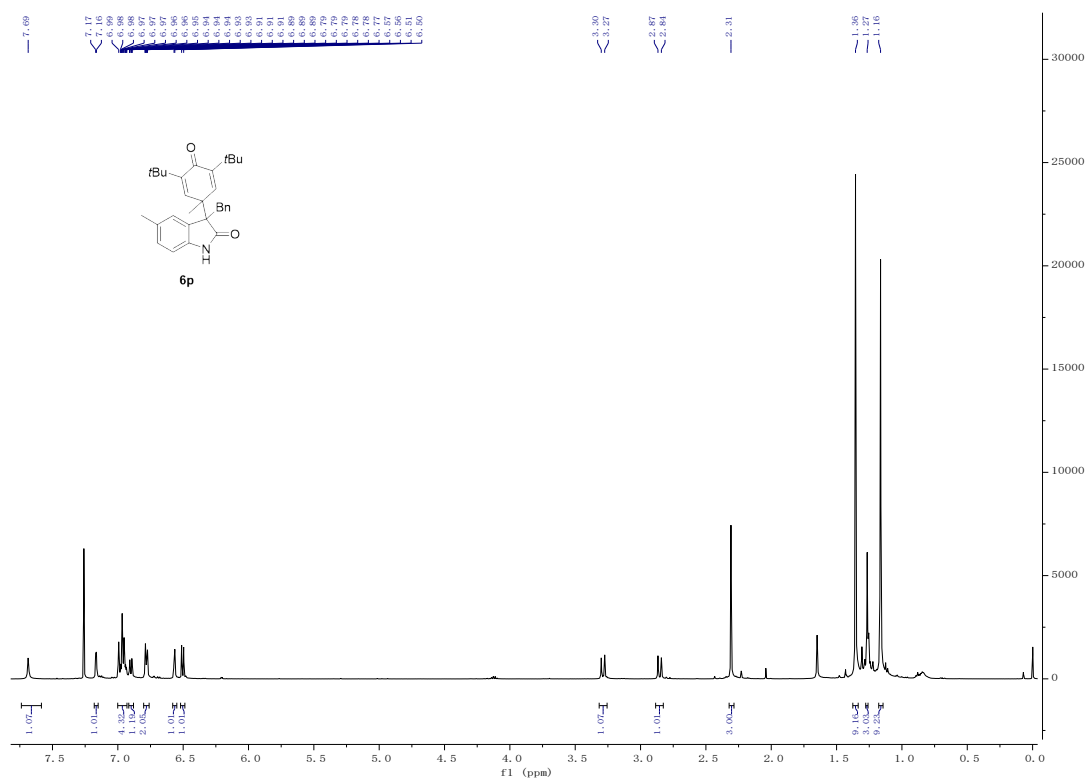
Chemical structure of **6o** is shown as an inset. The structure is a benzimidazole derivative with a 4,6-di-tert-butylphenyl group at position 2, a benzyl group at position 3, and a methyl group at position 4.

¹H NMR spectrum (CDCl₃) of **6o** is displayed. The x-axis represents the chemical shift in ppm (f1), ranging from 0 to 10. The y-axis represents the intensity. The spectrum shows several peaks, with integration values provided below the baseline.

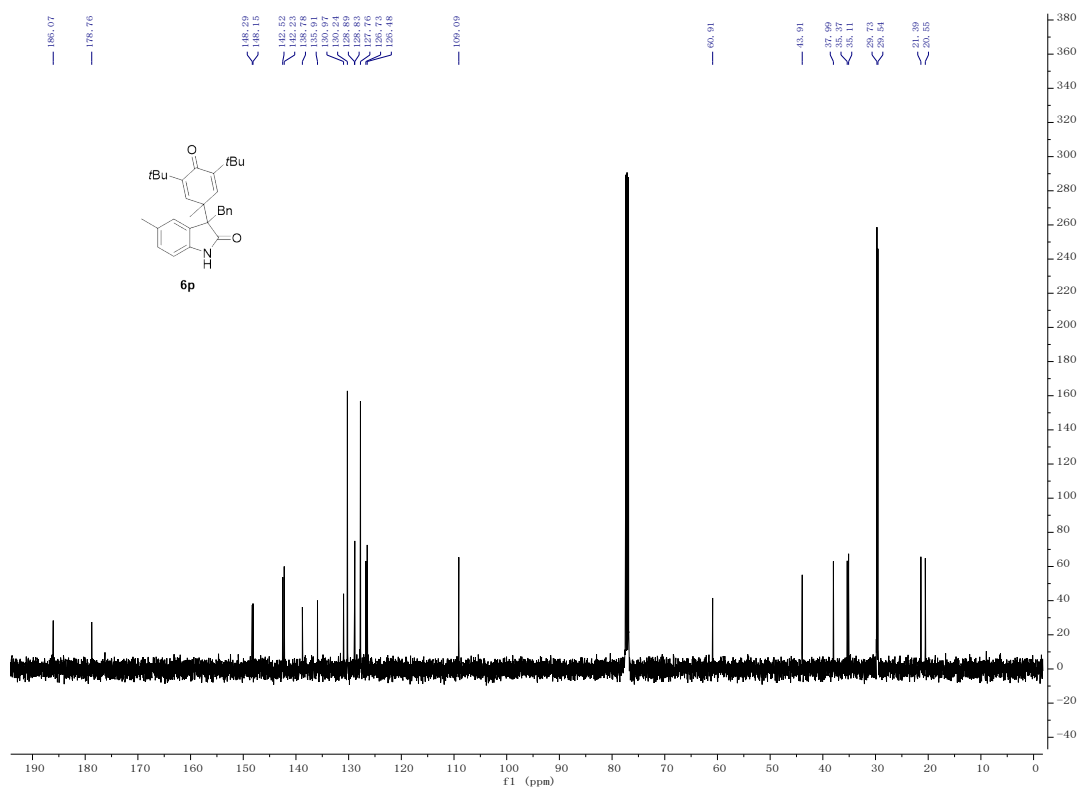
Integration values (from left to right):

- 188.10
- 185.00
- 148.47
- 148.03
- 142.87
- 140.61
- 135.95
- 130.09
- 128.98
- 128.18
- 127.70
- 126.52
- 125.62
- 121.56
- 118.95
- 61.85
- 43.73
- 36.13
- 35.38
- 35.28
- 29.69
- 29.67
- 20.83
- 16.49

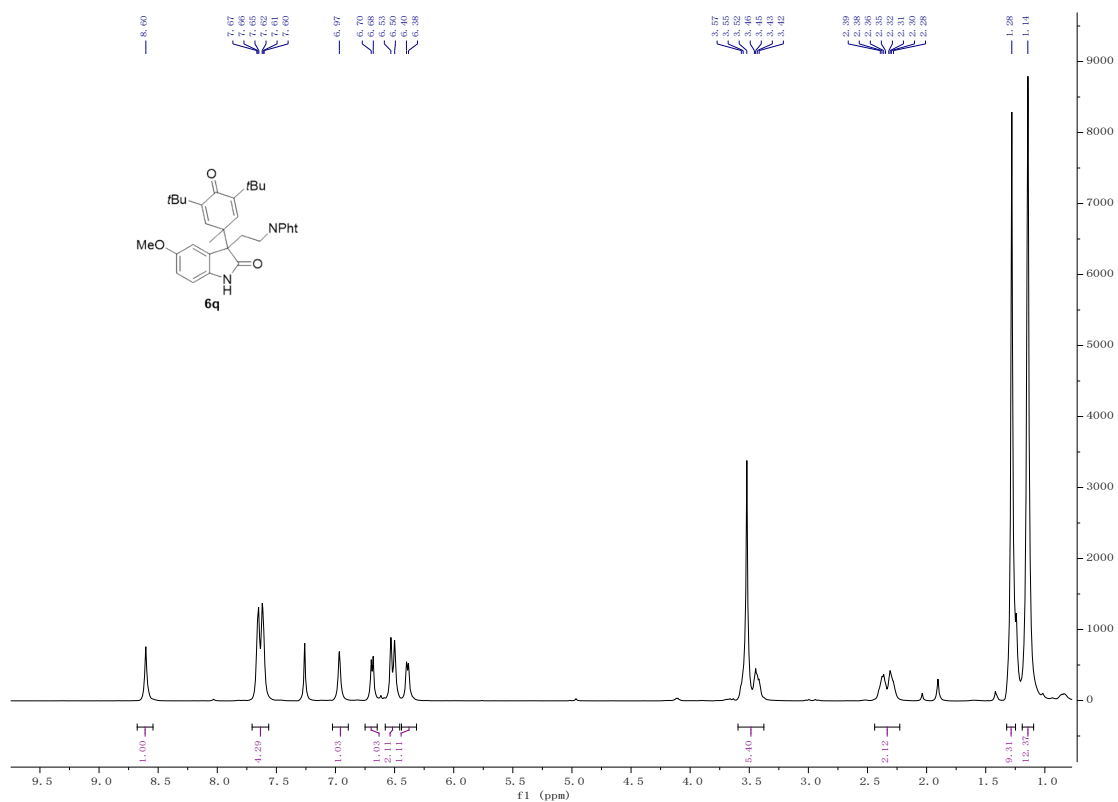
¹H NMR Spectrum of **6p** (500 MHz, CDCl₃)



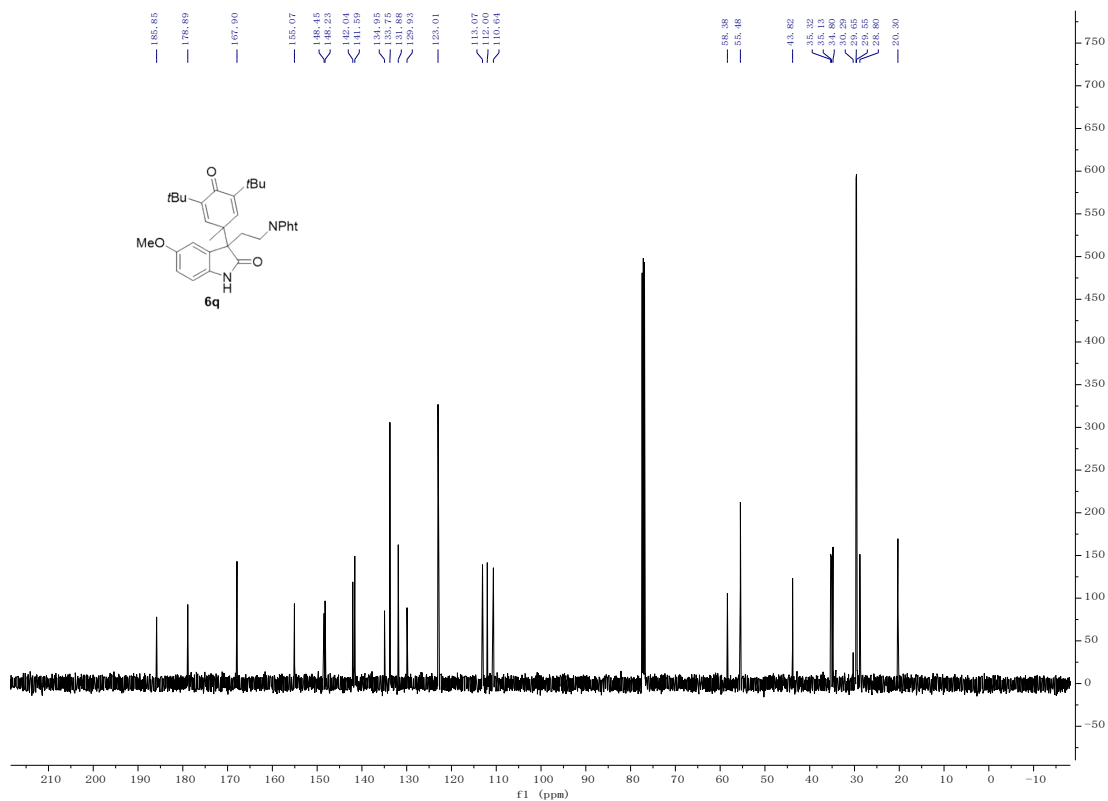
¹³C NMR Spectrum of **6p** (126 MHz, CDCl₃)



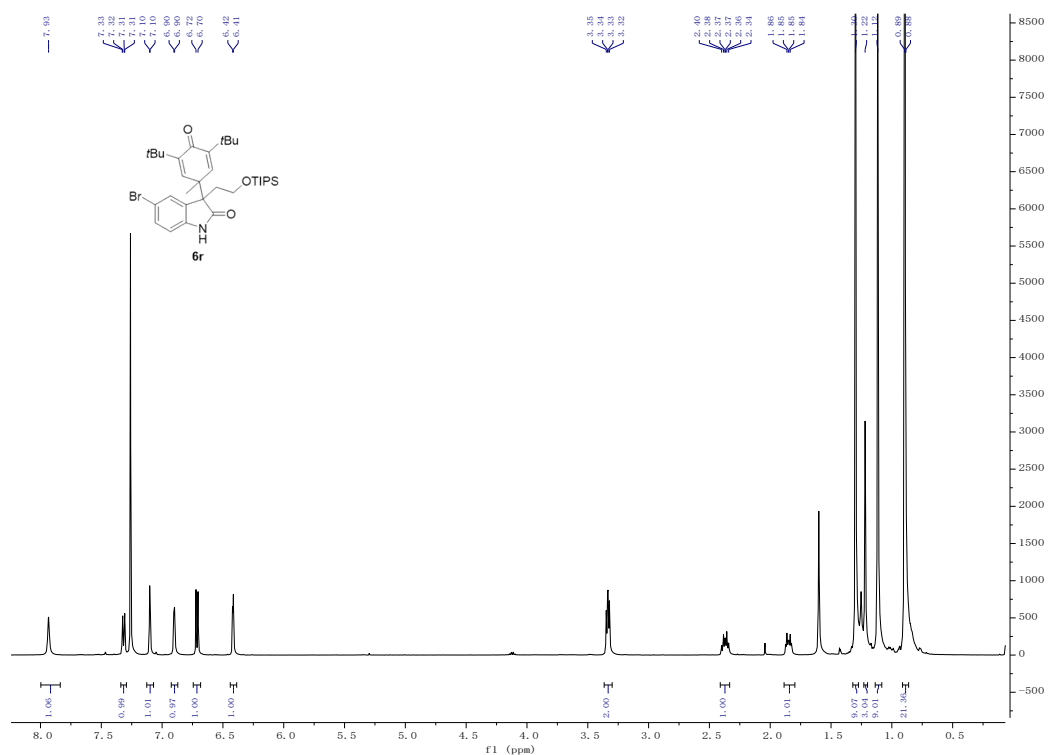
¹H NMR Spectrum of **6q** (500 MHz, CDCl₃)



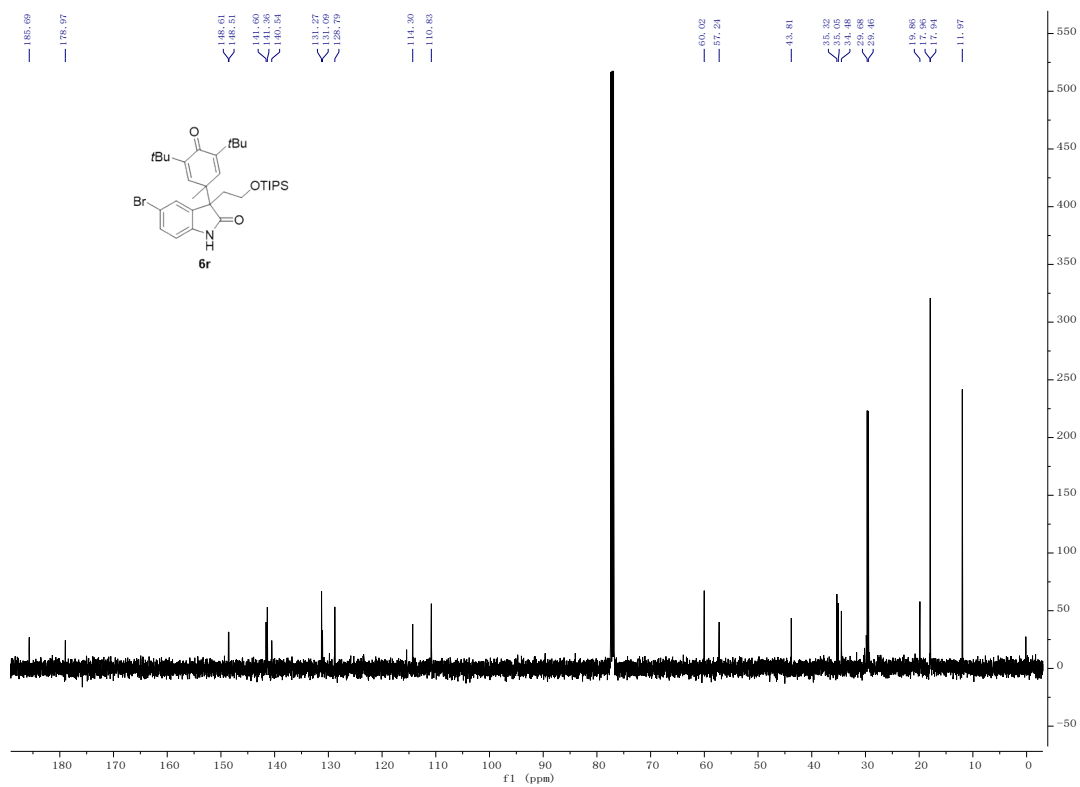
¹³C NMR Spectrum of **6q** (126 MHz, CDCl₃)



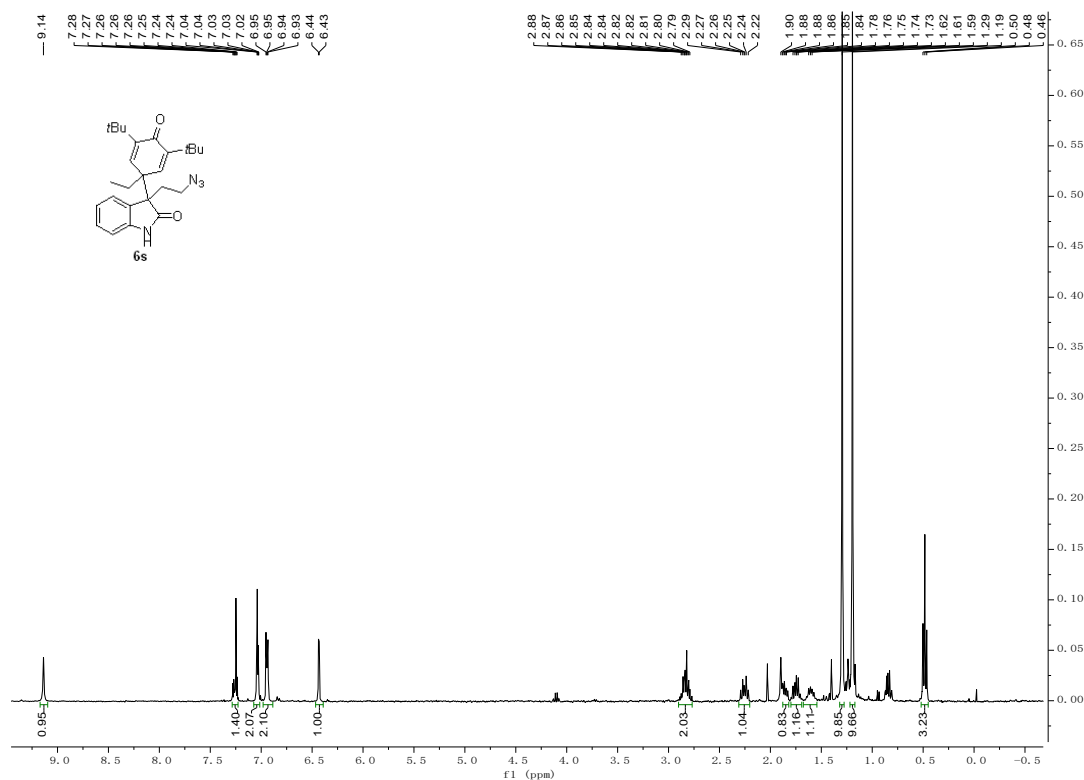
¹H NMR Spectrum of **6r** (500 MHz, CDCl₃)



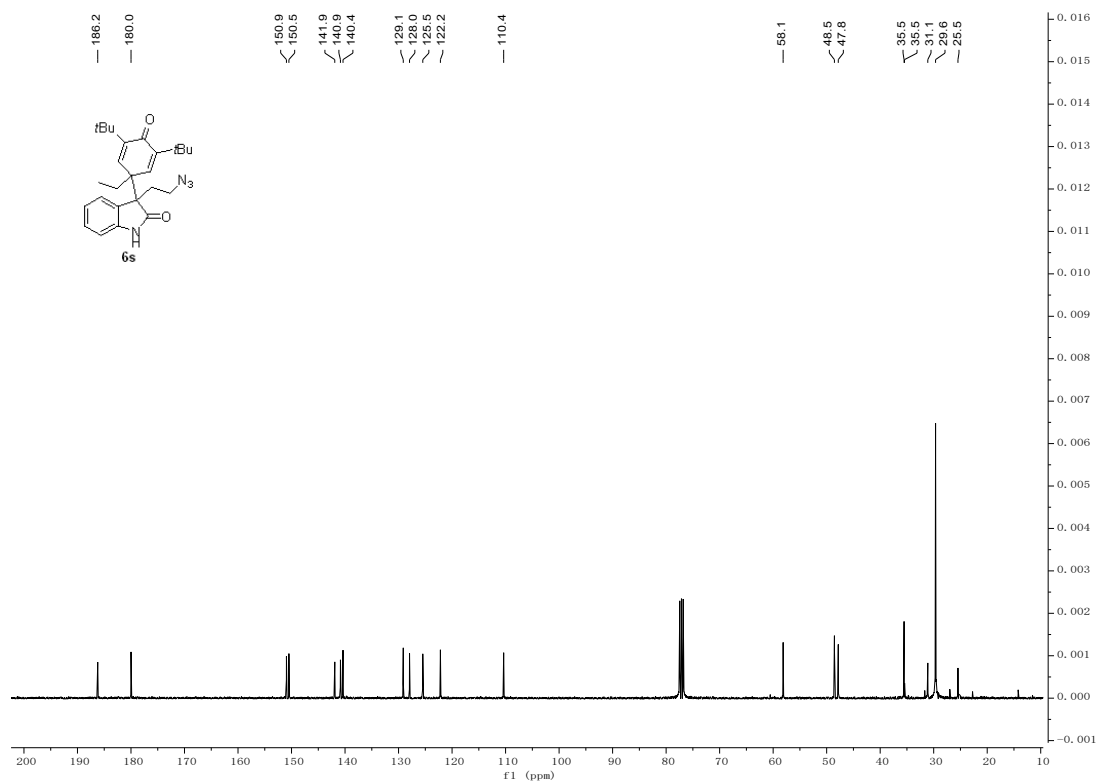
¹³C NMR Spectrum of **6r** (126 MHz, CDCl₃)



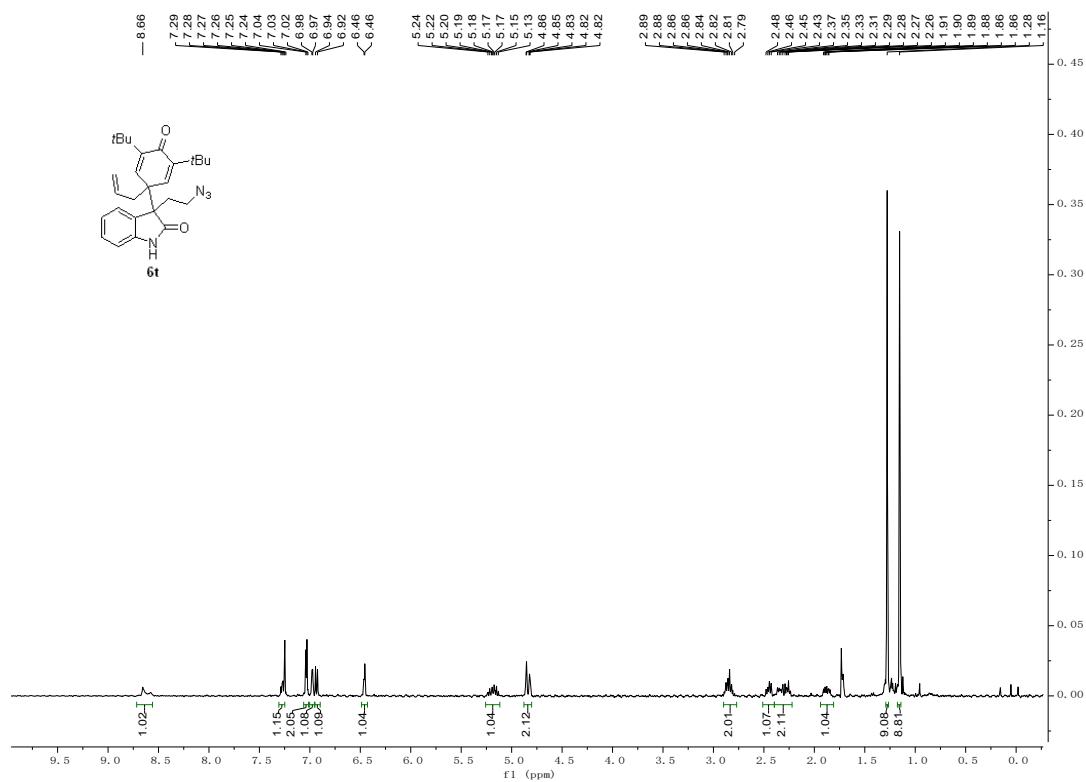
¹H NMR Spectrum of **6s** (400 MHz, CDCl₃)



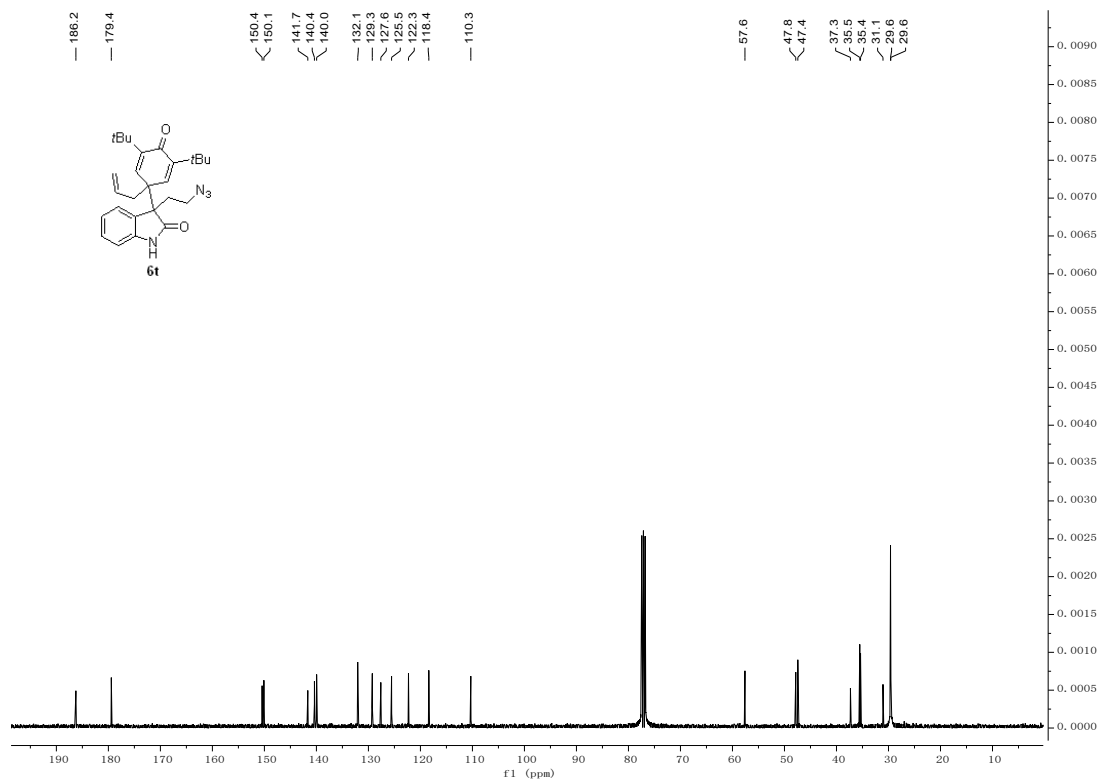
¹³C NMR Spectrum of **6s** (101 MHz, CDCl₃)



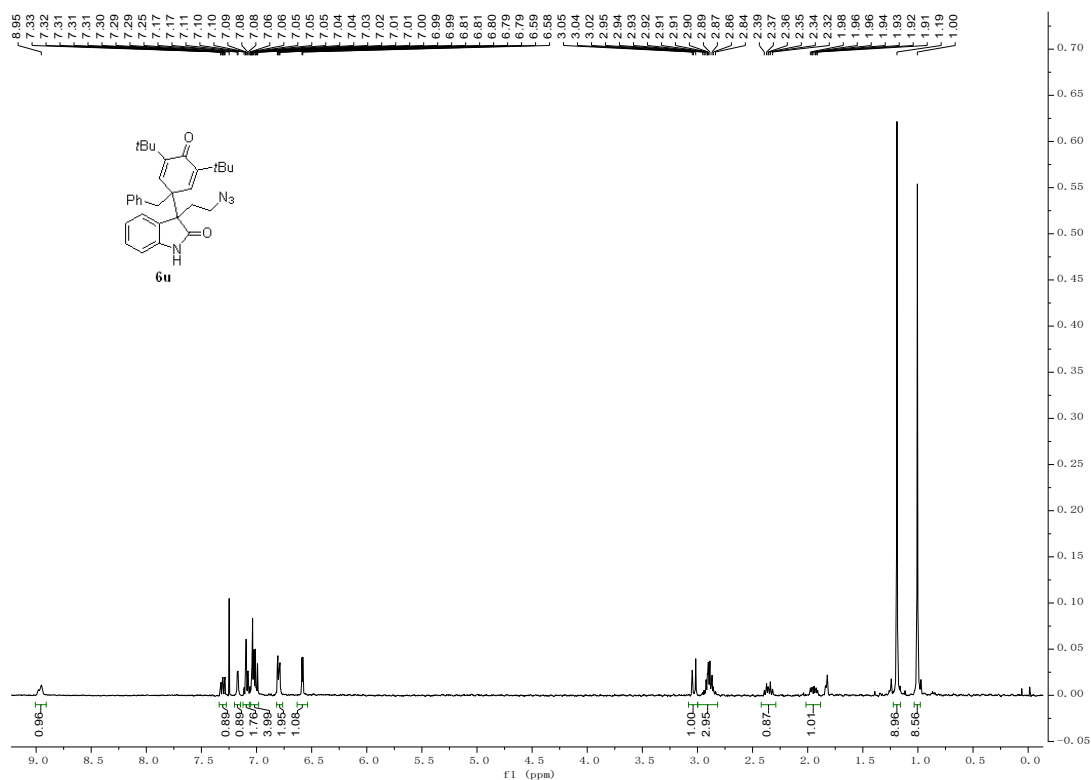
¹H NMR Spectrum of **6t** (400 MHz, CDCl₃)



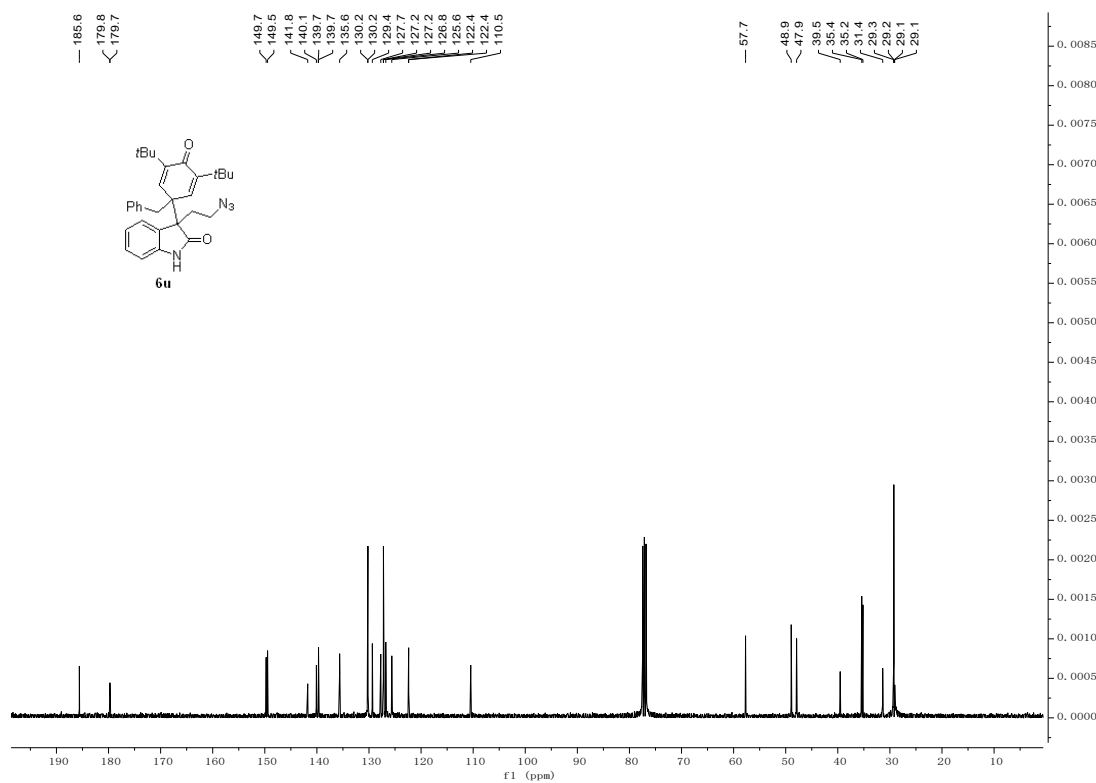
¹³C NMR Spectrum of **6t** (101 MHz, CDCl₃)



¹H NMR Spectrum of **6u** (400 MHz, CDCl₃)



¹³C NMR Spectrum of **6u** (101 MHz, CDCl₃)



Chemical structure of **6v** is shown above the spectrum.

¹H NMR spectrum (CDCl₃) of compound **6v**. The x-axis represents the chemical shift in ppm (f1), ranging from 0.0 to 8.5. The y-axis represents intensity, ranging from -1000 to 11000. Integration values are provided below the baseline, and chemical shifts are listed at the top.

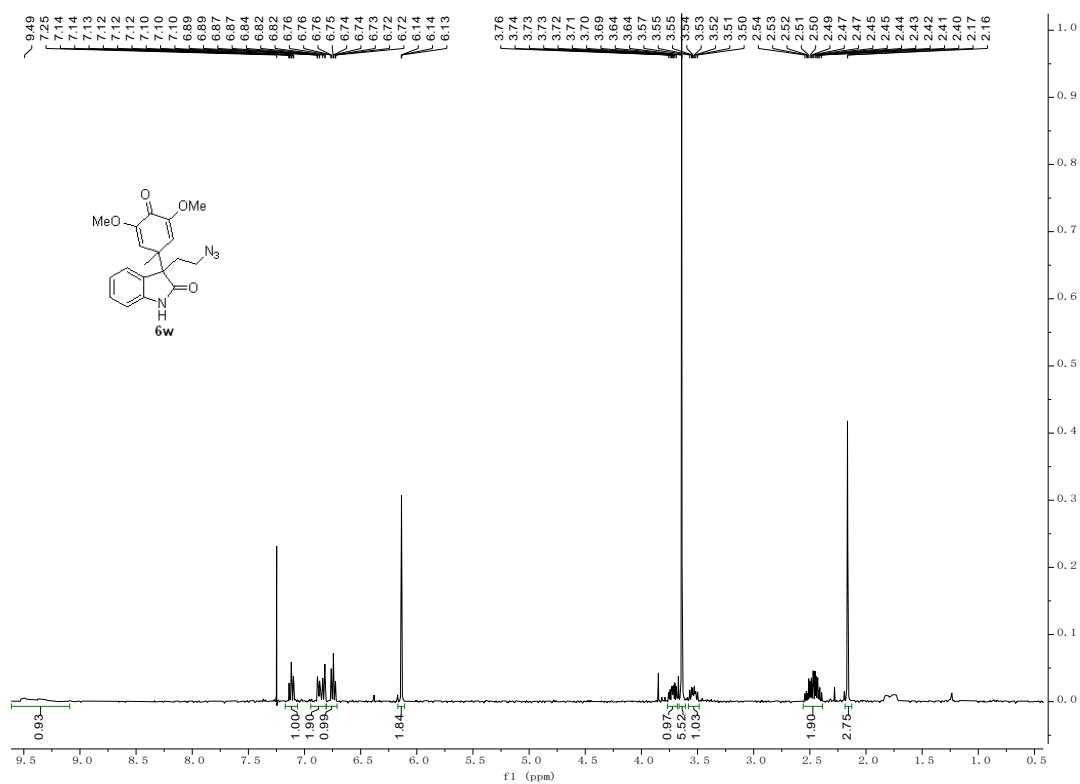
Chemical shifts (ppm) listed at the top: 8.53, 7.27, 7.25, 7.23, 7.04, 7.03, 6.95, 6.93, 5.44, 3.58, 2.85, 2.83, 2.81, 2.79, 2.29, 2.27, 2.25, 2.23, 2.21, 2.13, 2.11, 2.11, 2.09, 2.07, 2.05, 2.02, 1.91, 1.90, 1.89, 1.88, 1.86, 1.85, 1.29, 1.18.

Integration values (from left to right): 1.0, 0.86, 2.03, 2.01, 1.00, 3.00, 2.15, 1.02, 2.25, 3.03, 9.01, 9.32.

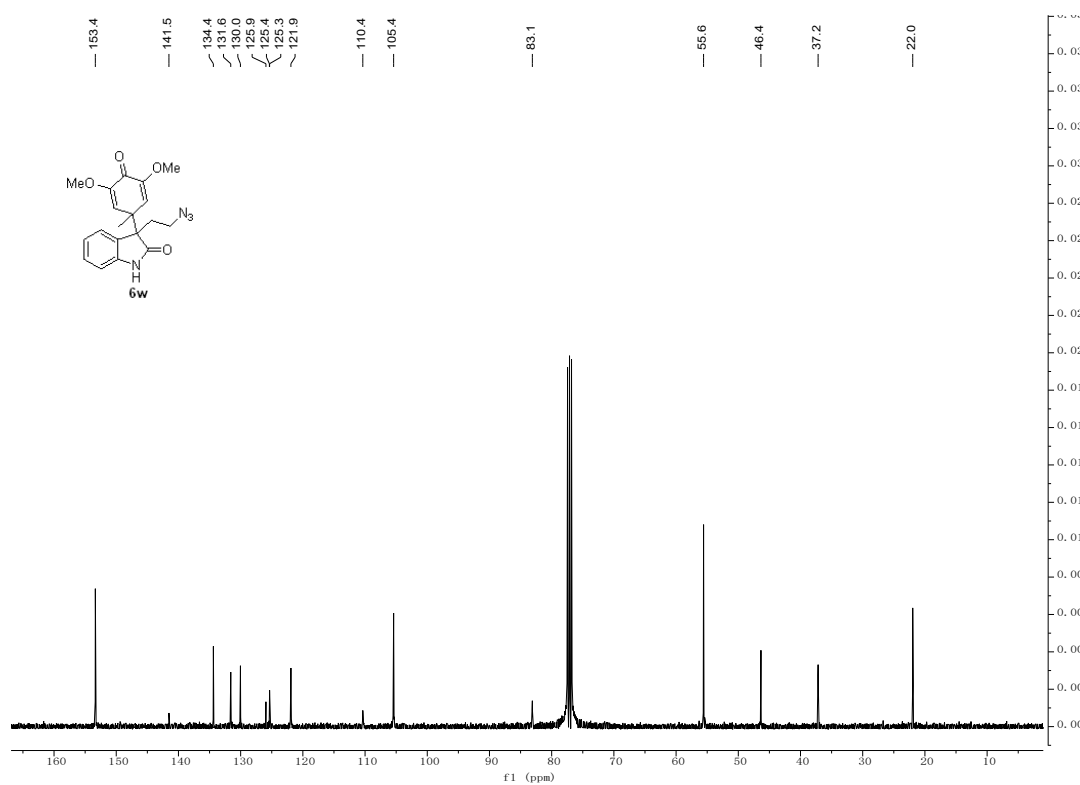
Chemical structure of compound **6v** is shown above the ¹³C NMR spectrum. The spectrum displays peaks corresponding to the carbon atoms in the molecule, with the following chemical shifts (ppm) labeled above the peaks:

- 185.00
- 179.11
- 175.43
- 151.35
- 150.97
- 141.67
- 138.90
- 138.40
- 128.37
- 127.45
- 126.52
- 110.49
- 57.90
- 51.86
- 47.80
- 47.01
- 35.63
- 33.59
- 33.08
- 29.61
- 29.58
- 29.54
- 27.29

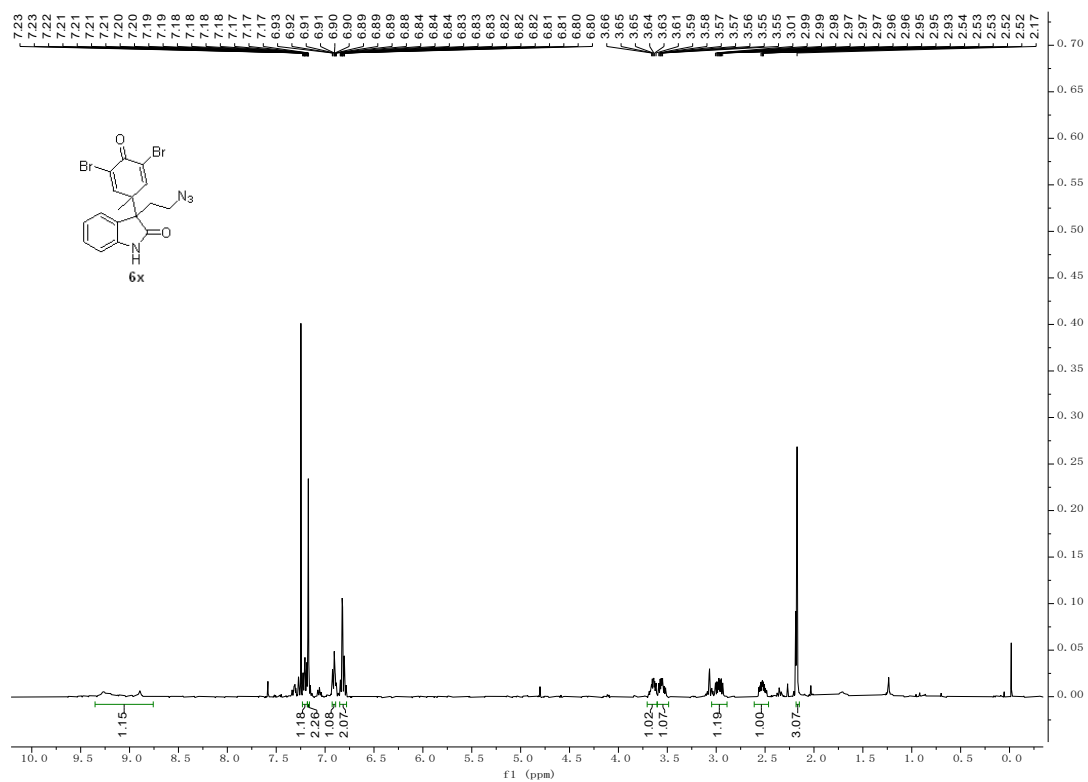
¹H NMR Spectrum of **6w** (400 MHz, CDCl₃)



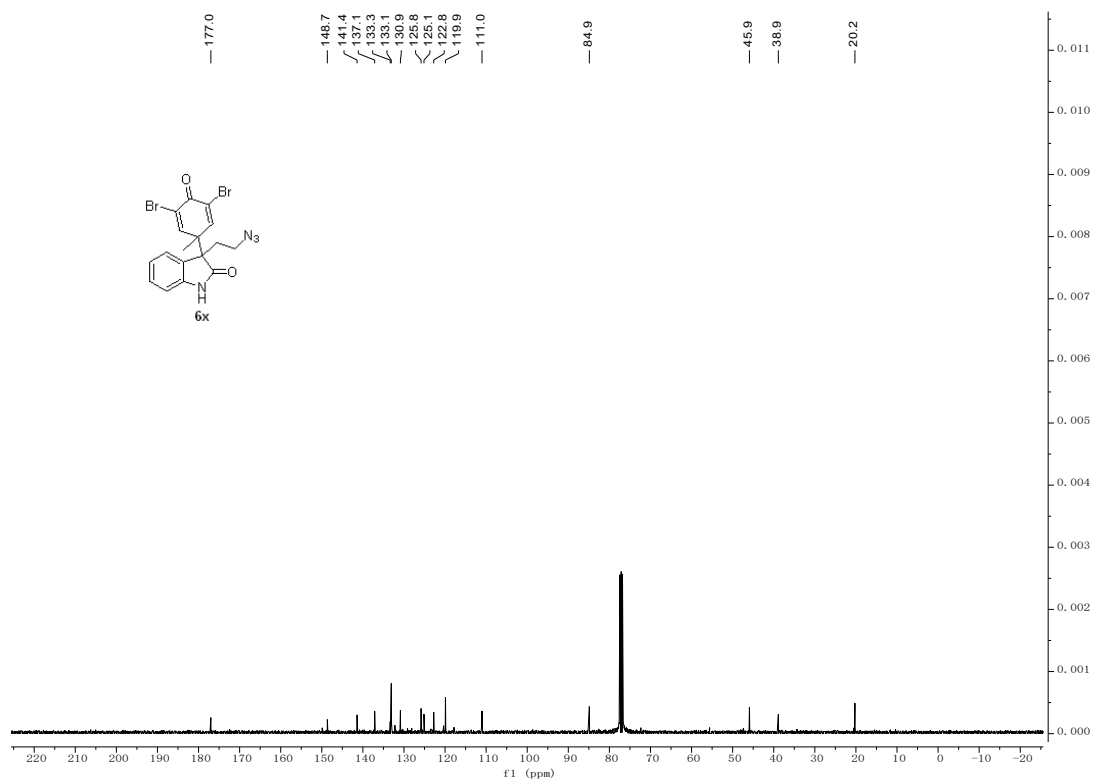
¹³C NMR Spectrum of **6w** (101 MHz, CDCl₃)



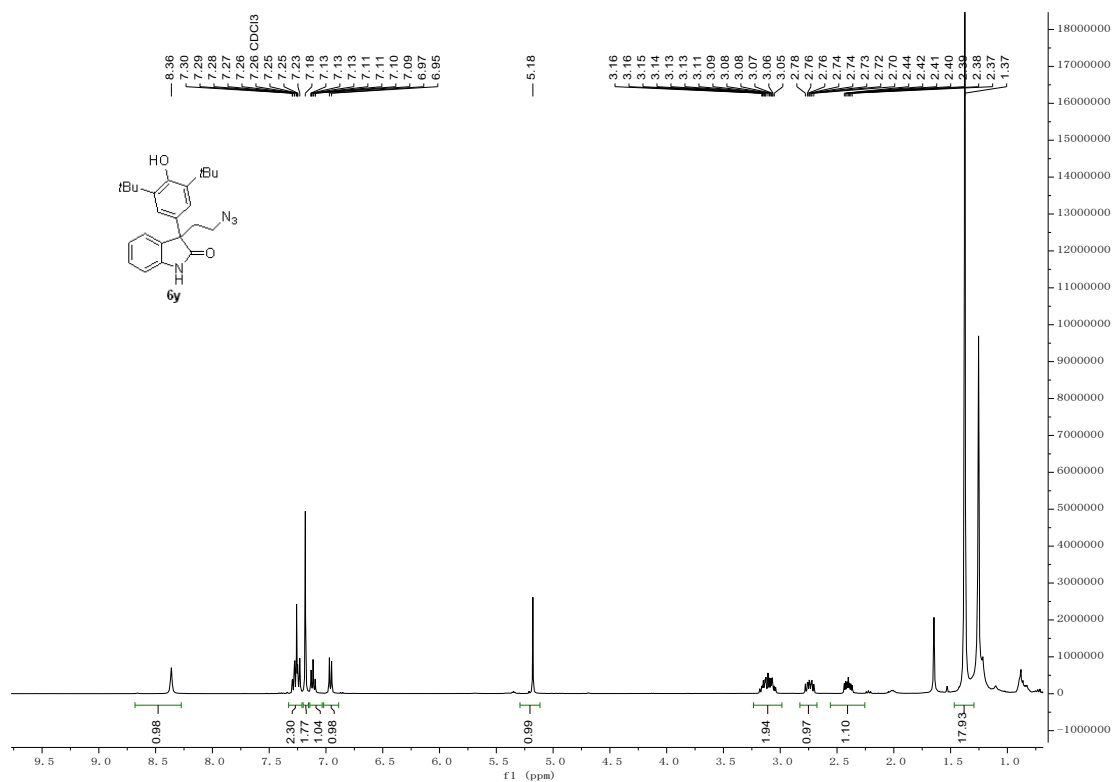
¹H NMR Spectrum of **6x** (400 MHz, CDCl₃)



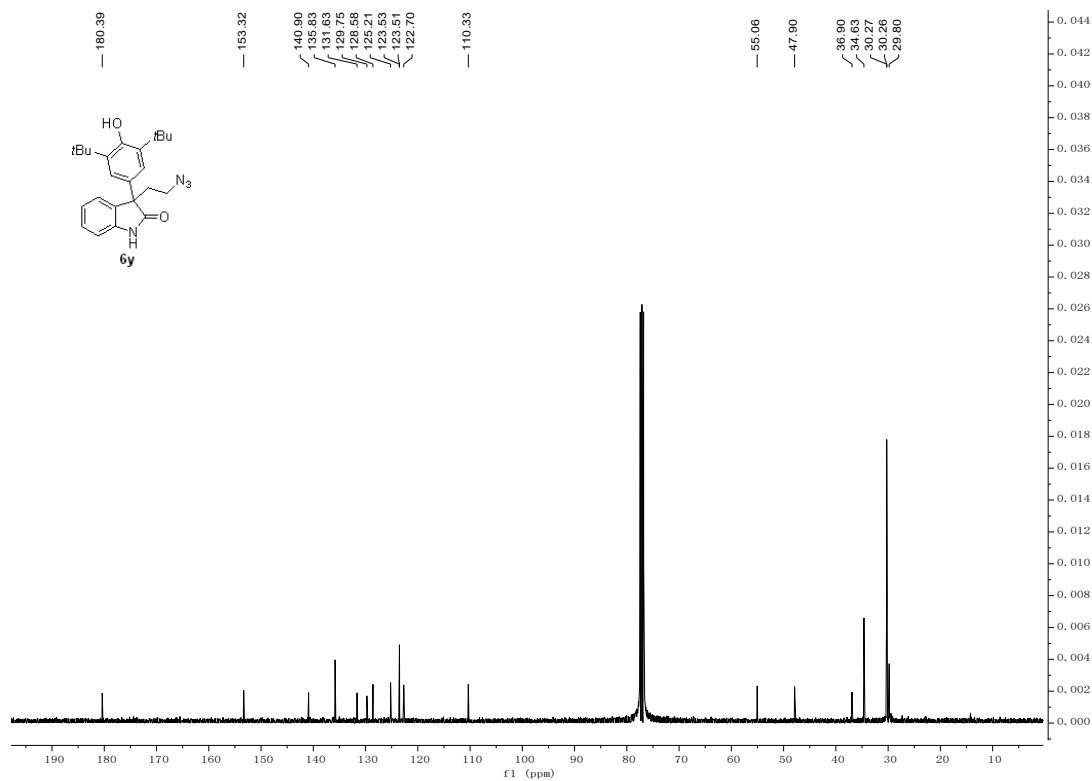
¹³C NMR Spectrum of **6x** (101 MHz, CDCl₃)



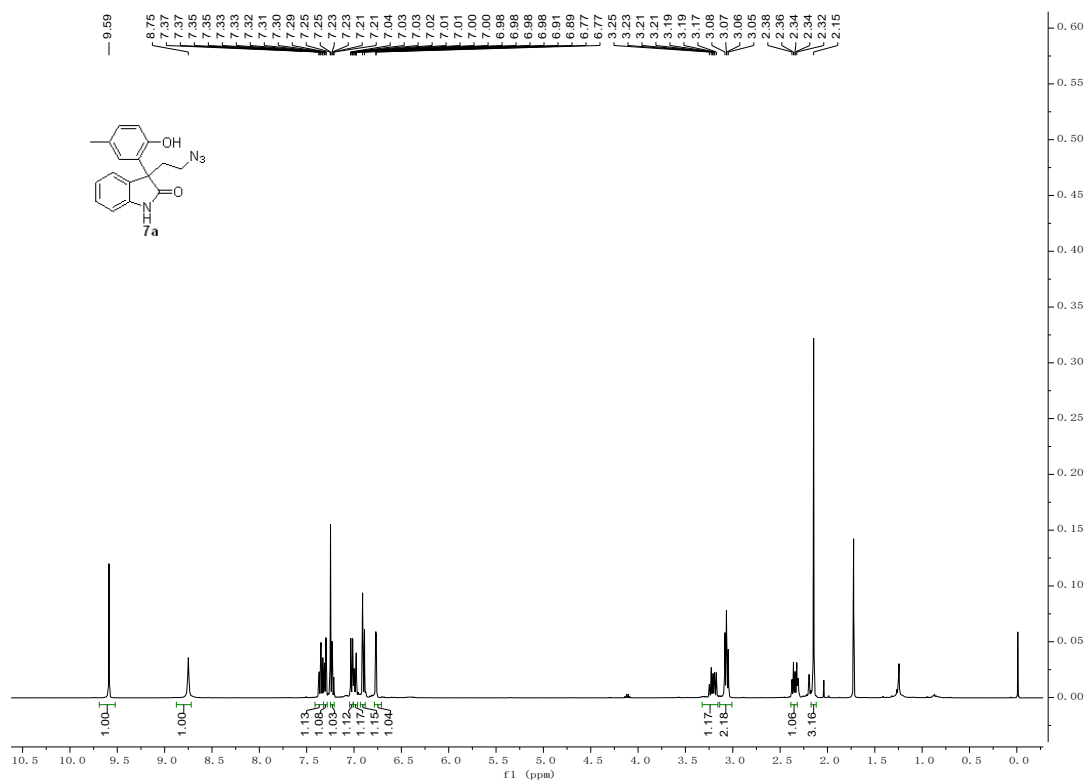
¹H NMR Spectrum of **6y** (400 MHz, CDCl₃)



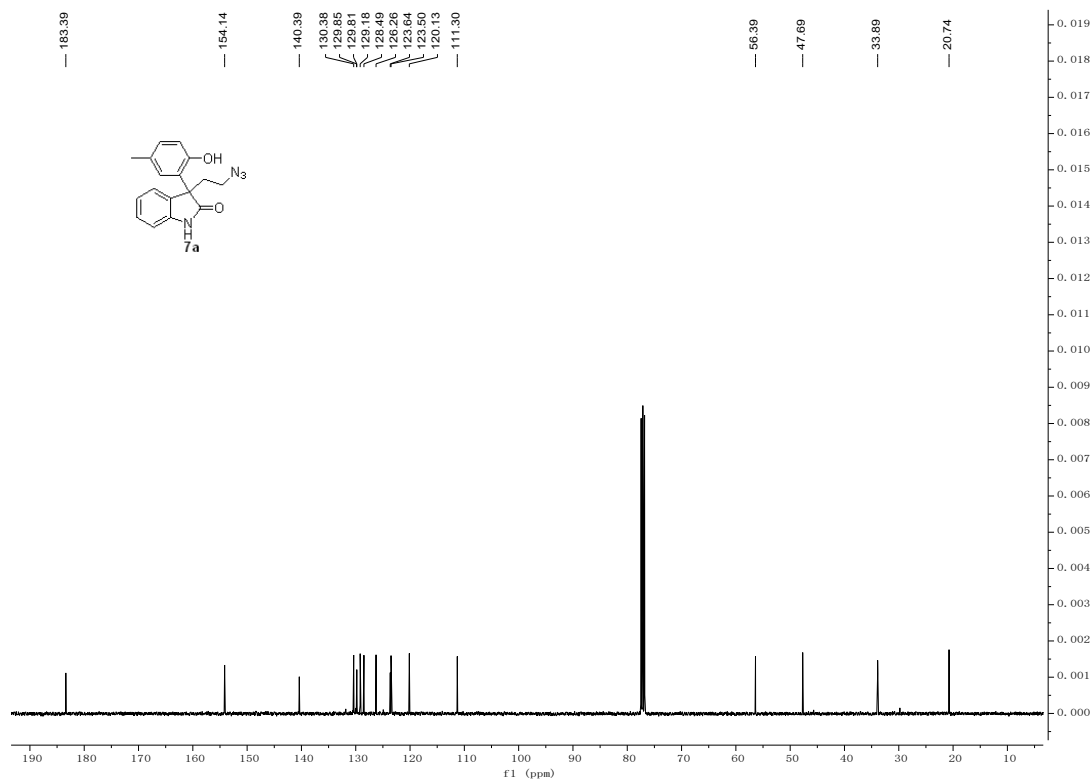
¹³C NMR Spectrum of **6y** (101 MHz, CDCl₃)



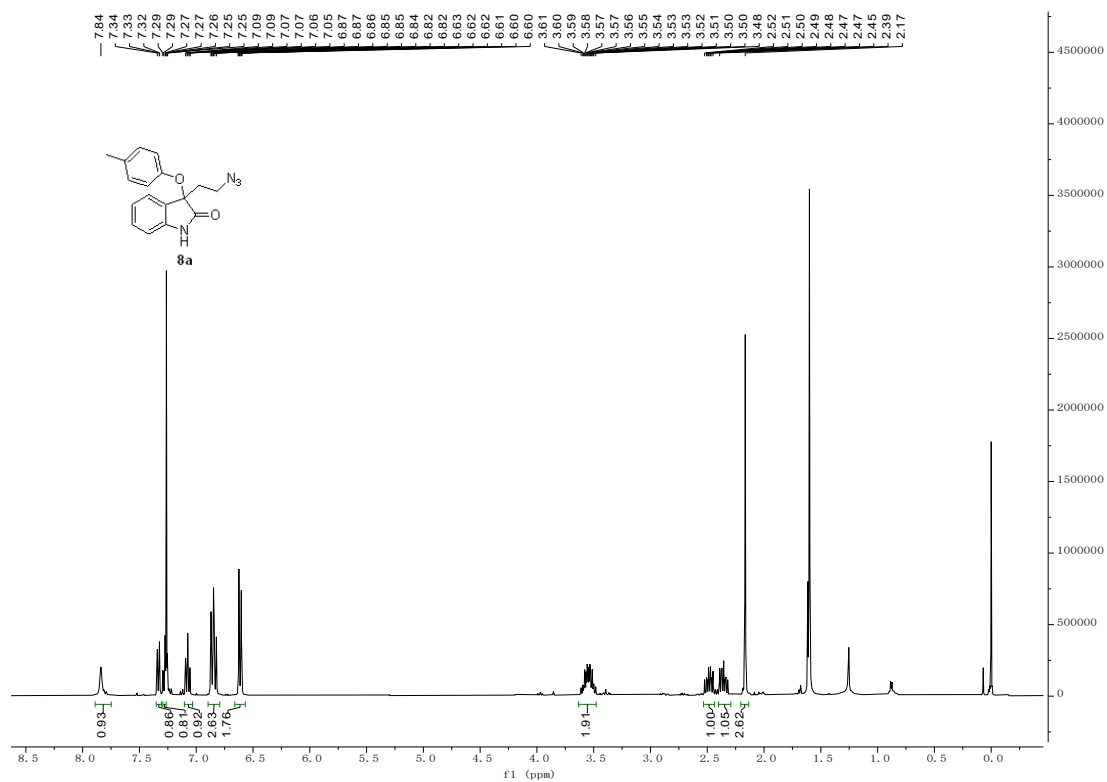
¹H NMR Spectrum of **7a** (400 MHz, CDCl₃)



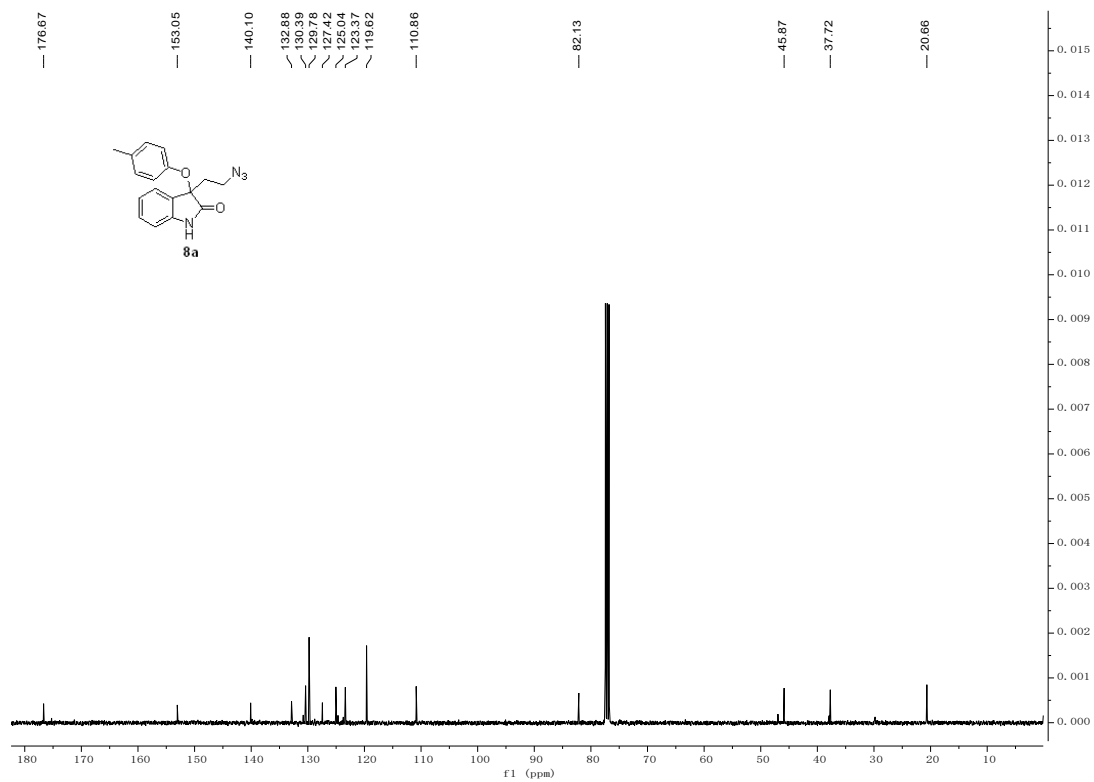
¹³C NMR Spectrum of **7a** (101 MHz, CDCl₃)



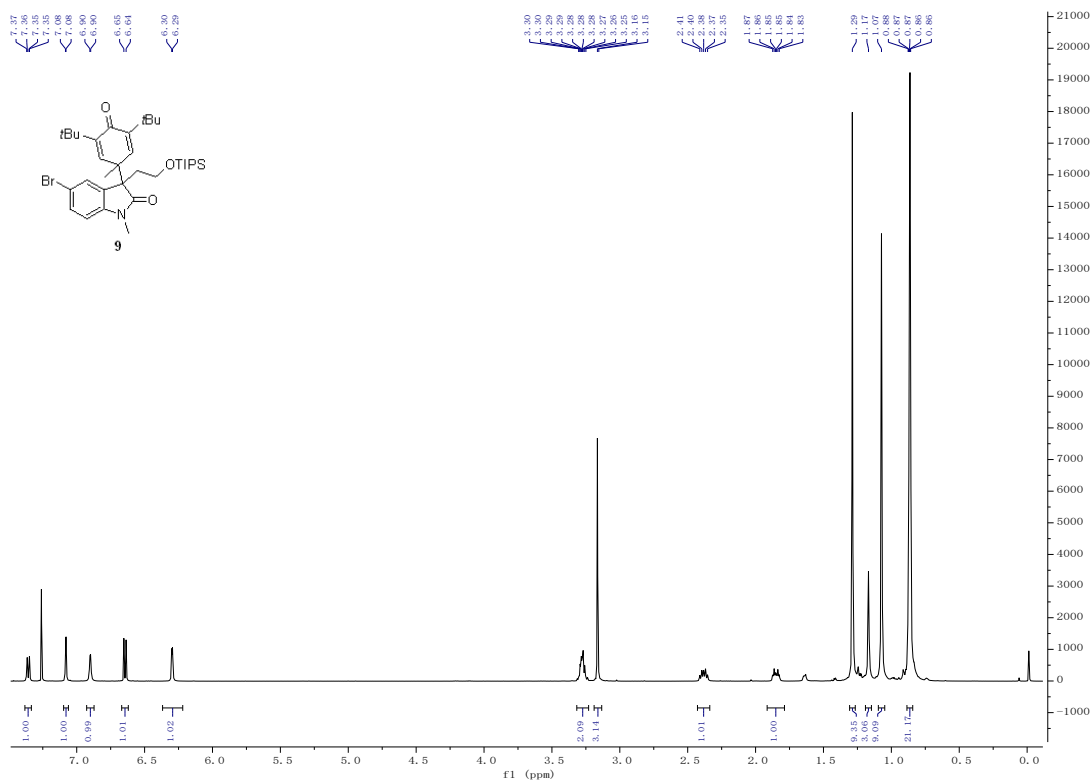
¹H NMR Spectrum of **8a** (400 MHz, CDCl₃)



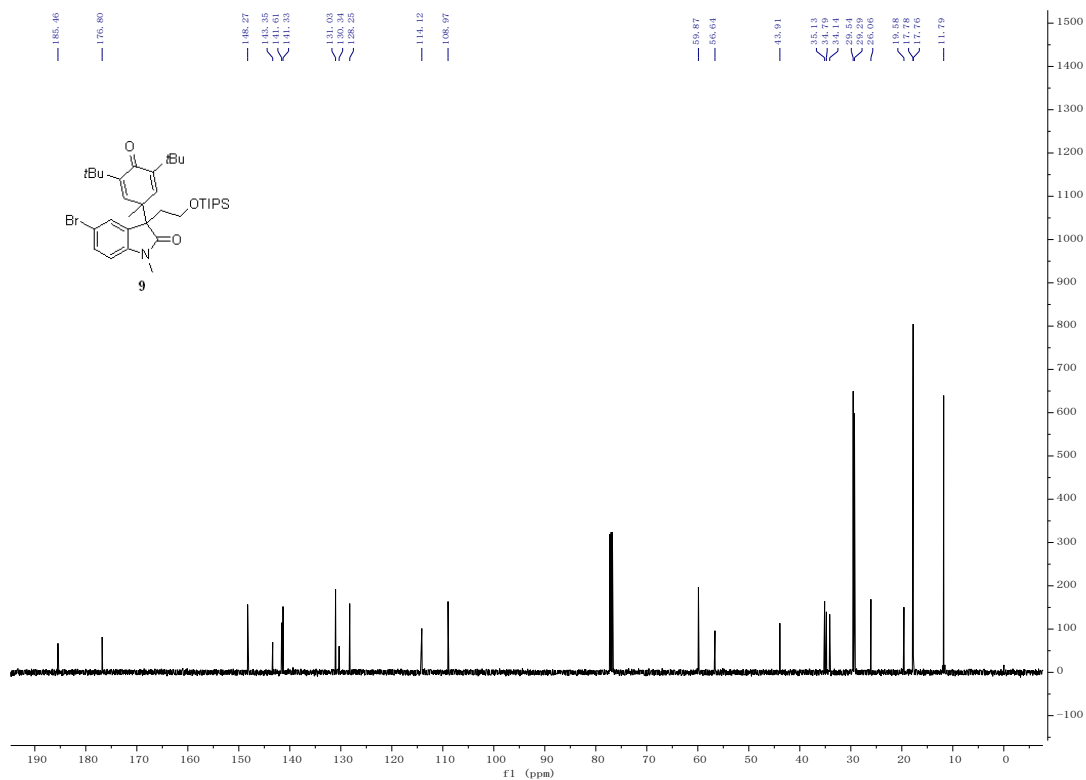
¹H NMR Spectrum of **8a** (400 MHz, CDCl₃)



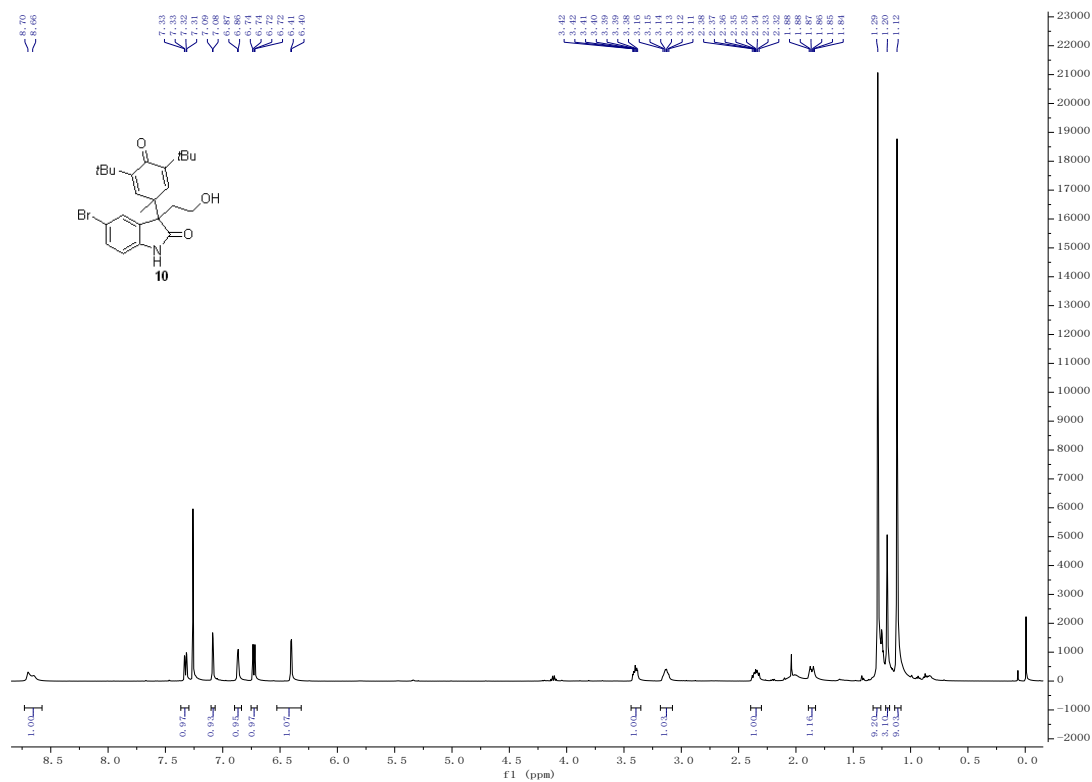
¹H NMR Spectrum of **9** (500 MHz, CDCl₃)



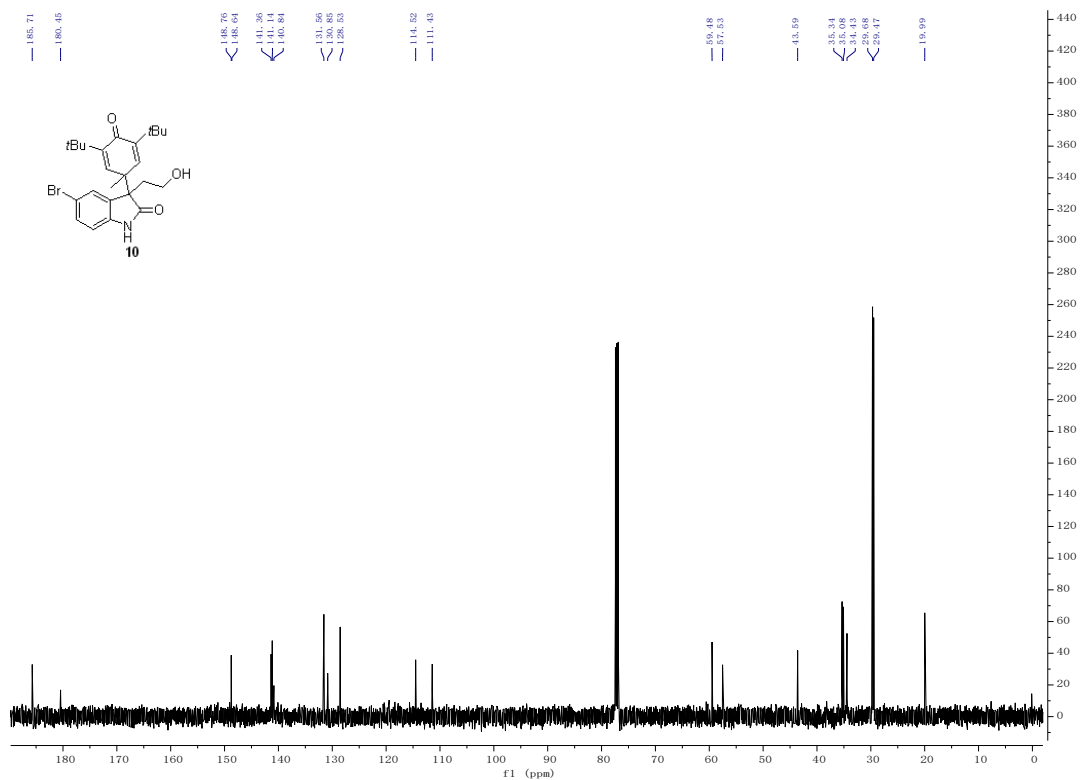
¹³C NMR Spectrum of **9** (126 MHz, CDCl₃)



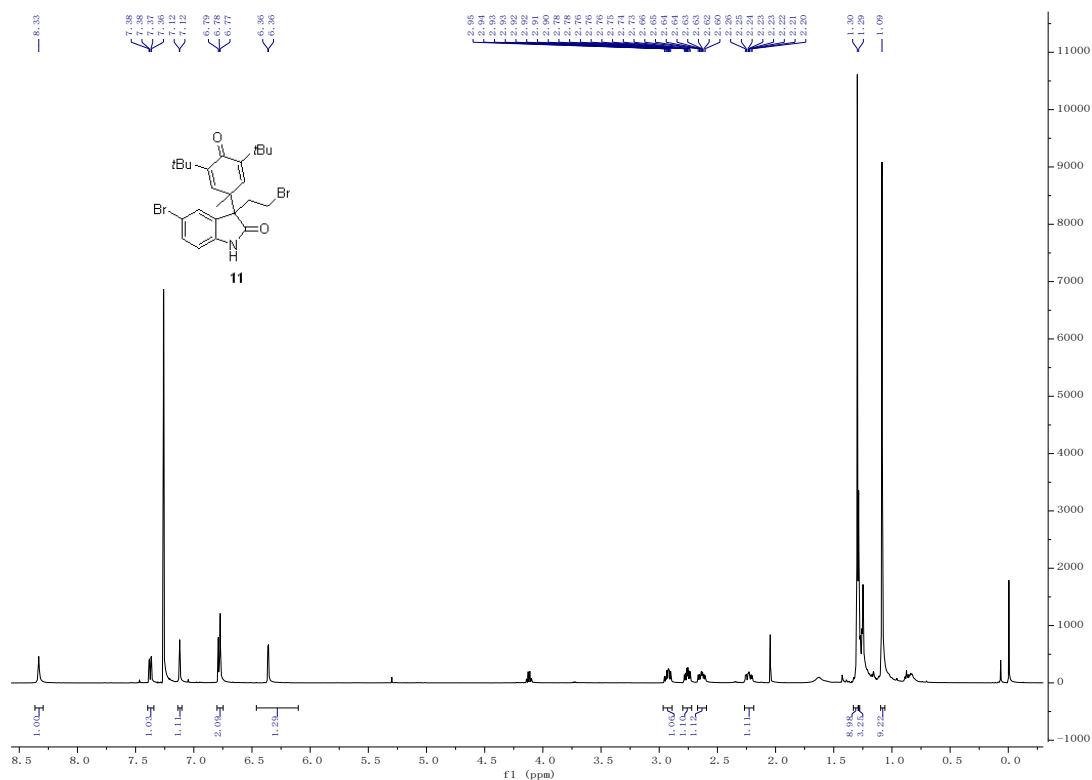
¹H NMR Spectrum of **10** (500 MHz, CDCl₃)



¹³C NMR Spectrum of **10** (126 MHz, CDCl₃)



¹H NMR Spectrum of **11** (500 MHz, CDCl₃)



¹³C NMR Spectrum of **11** (126 MHz, CDCl₃)

