Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Direct dilithiation of *N*-aryl heterocycles for the construction of condensed *N*-heterocycles

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Table of Contents

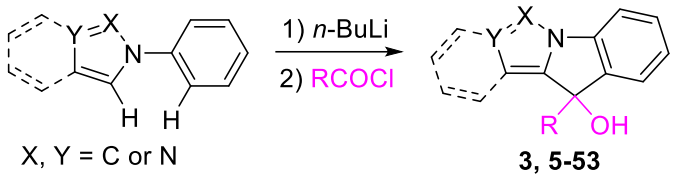
1. General information

All reagents and solvents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros and Meryer. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300 − 400 mesh). ^{1}H NMR and ^{13}C NMR spectra were measured on a 500 MHz Bruker AVANCE spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, 470 MHz for ^{19}F), using DMSO-*d6* or $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.5 ppm) were referenced to $CDCl_3$, Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in Hz. Analysis of crude reaction mixture was done on the Varian 4000 GC/MS and Agilent 7890A/5975C. High-resolution mass spectra were recorded on a micrOTOF-Q II 10410 mass spectrometer.

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Starting materials such as acyl chlorides, *N*-arylpyrazoles and *N*-phenyl imidazole were obtained commercially. 2-Aryl-2*H*-indazoles were prepared according to corresponding literature procedures.[1]

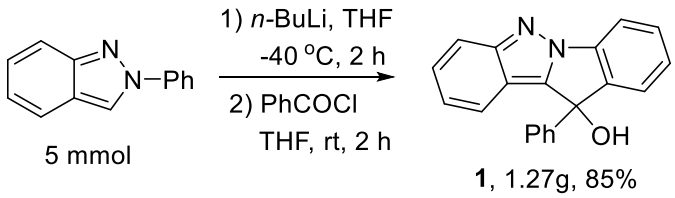
2. General Experimental Procedures

2.1 General experimental procedures for the formation of products 3, 5-53



A 25 mL Schlenk tube equipped with a stir bar was charged with *N*-aryl heterocycles (0.2 mmol) and dry THF (2.0 mL) under nitrogen atmosphere. The reaction mixture was cooled to -40 °C and stirred for 5 minutes, followed by dropwise addition of *n*-butyl lithium (5 equiv) via a syringe. The resulting solution was stirred at -40 °C for 20 minutes, and then acyl chlorides (2.0 equiv) was added dropwise via a syringe. After stirring at -40 °C for one minute, the reaction was quenched by NH_4Cl (aq). The reaction solution was extracted by 30 mL of ethyl acetate in three times, then concentrated with ethyl acetate layer under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding products.

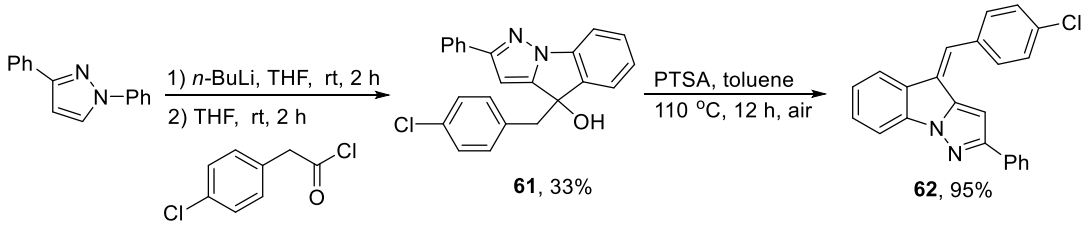
2.2 General experimental procedure for the gram-scale reaction



A 100 mL Schlenk tube equipped with a stir bar was charged with 2-phenyl-2H-indazole (5 mmol) and dry THF (20 mL) under nitrogen atmosphere. The reaction mixture was cooled to -40 °C and stirred for 2 h, followed by dropwise addition of *n*-butyl lithium (5 equiv) via a syringe. The resulting solution was heated to room temperature, and then benzoyl chloride (2.0 equiv) was added dropwise via a syringe. After stirring at room temperature for 2 h, the reaction was quenched by NH_4Cl (aq). The reaction solution was extracted by 100 mL of ethyl acetate in three times, then concentrated with ethyl acetate layer under reduced pressure. The residue was then

purified by flash chromatography on silica gel to provide the corresponding product 1 (1.27 g, 85%).

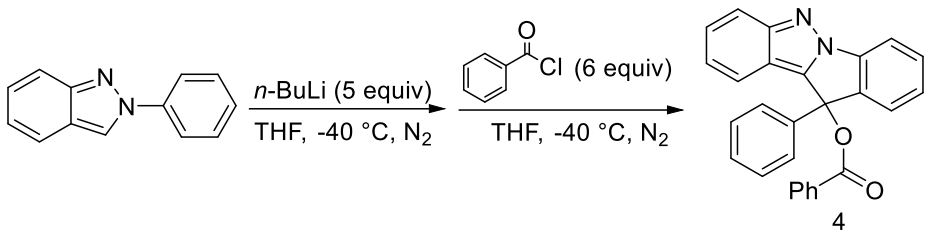
2.3 General experimental procedure for the synthesis of 62

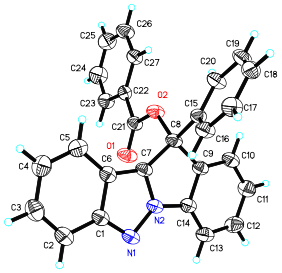


A 25 mL Schlenk tube equipped with a stir bar was charged with 1,3-diphenyl-1*H*-pyrazole (1 mmol) and dry THF (10 mL) under nitrogen atmosphere, followed by dropwise addition of *n*-butyl lithium (5 equiv) via a syringe at room temperature. The resulting solution was stirred at room temperature for 2 h, and then *p*-chlorophenylacetyl chloride (2.0 equiv) was added dropwise via a syringe. After stirring at room temperature for 2 h, the reaction was quenched by NH_4Cl (aq). The reaction solution was extracted by 60 mL of ethyl acetate in three times, then concentrated with ethyl acetate layer under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product **61** (123 mg, 33%).

A 25 mL Schlenk tube equipped with a stir bar was charged with **61** (0.2 mmol), *p*-toluenesulfonic acid (PTSA, 0.4 mmol) and toluene (2 mL) under air atmosphere. The reaction mixture was heated to 110 °C and stirred for 12 h, and then 20 mL of saturated $NaHCO_3$ aqueous solution was added. The reaction solution was extracted by 20 mL of ethyl acetate in three times, then concentrated with ethyl acetate layer under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product **62** (67 mg, 95%).

3. Crystal data and structure refinement of products





4

Single crystals of **4** were grown in ethyl acetate and petroleum ether. Ethyl acetate (1.0 mL) was added to **4** (20 mg in a 20 mL vial) followed by petroleum ether (4.0 mL). The 20 mL vial was not capped and placed at room temperature in the experimental cabinet for 5 days, whereupon crystals formed. A colorless block shaped crystal of **4** was used for the X-ray crystallographic analysis. The crystal data of **4** have been deposited in CCDC with number 2119726 and have been displayed at 50% ellipsoid contour probability level.

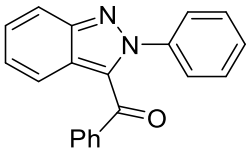
Table 1. Crystal data and structure refinement for 2119726

CCDC	2119726
Empirical formula	$C_{27}H_{18}N_2O_2$
Formula weight	402.43
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 9.4100(4) Å a= 90°. b=12.8983(6)Å b= 90°. c=16.8059(6)Å g = 90°.
Volume	2039.78(15) $Å^3$
Z	4
Density (calculated)	1.310 Mg/m^3
Absorption coefficient	0.084 mm^{-1}
F(000)	840

Crystal size	0.180 x 0.150 x 0.110 mm^3
Theta range for data collection	2.893 to 25.997°.
Index ranges	-9<=h<=11, -15<=k<=15, -20<=l<=20
Reflections collected	10315
Independent reflections	3989 [R(int) = 0.0312
Completeness to theta = 25.242°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6685
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3989 / 0 / 281
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0779
R indices (all data)	R1 = 0.0513, wR2 = 0.0863
Absolute structure parameter	-0.3(7)
Extinction coefficient	0.032(4)
Largest diff. peak and hole	0.128 and -0.117 e.$Å^{-3}$

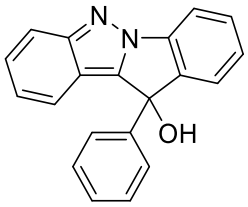
4. Characterization of products in details

phenyl(2-phenyl-2*H*-indazol-3-yl)methanone (2)[2]



White solid (42 mg, 71% yield); PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.91 (d, *J*=8.5 Hz, 1H), 7.82 (d, *J*=7.5 Hz, 2H), 7.70-7.67 (m, 1H), 7.58 (d, *J*=8 Hz, 2H), 7.54-7.49 (m, 2H), 7.49-7.43 (m, 4H), 7.25-7.24 (m, 2H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 186.0, 148.3, 140.6, 137.9, 134.2, 132.5, 130.0, 129.5, 129.4, 129.2, 127.6, 125.1, 125.6, 124.0, 120.6, 118.8.

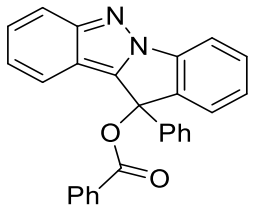
11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (3)[3]



White solid (55 mg, 92% yield); PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.8 1 (d, *J*=8 Hz, 1H), 7.73 (d, *J*=8.5 Hz, 1H), 7.51-7.45 (m, 3H), 7.39 (d, *J*=7.5 Hz, 2H), 7.33-7.21 (m, 5H), 7.07 (s, 1H), 7.04-7.01 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6)

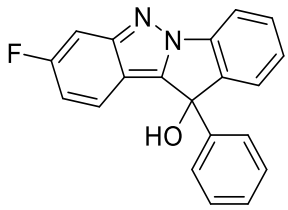
δ 152.8, 144.1, 142.8, 141.7, 138.5, 129.7, 128.5, 127.8, 127.4, 125.4, 125.4, 125.2, 1 22.5, 119.6, 118.4, 116.4, 111.9, 77.0.

11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-yl benzoate (4)



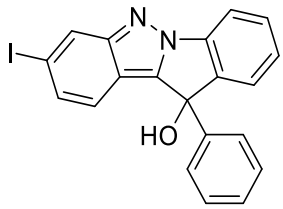
White solid (26 mg, 32% yield); mp 253.4-253.9 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.52 (d, *J*=7.5 Hz, 2H), 7.93 (d, *J*=7.5 Hz, 1H), 7.84 (d, *J*=9 Hz, 1H), 7.77-7.73 (m, 2H), 7.71-7.68 (m, 1H), 7.65-7.62 (m, 1H), 7.55-7.53 (m, 4H), 7.46-7.40 (m, 4H), 7.37-7.34 (m, 1H), 7.16-7.13 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 167.8, 164.3, 153.4, 139.6, 139.1, 138.2, 137.7, 134.5, 133.3, 131.2, 129.9, 129.7, 129.4, 129.4, 129.3, 129.0, 128.2, 127.2, 125.9, 125.6, 124.0, 120.4, 119.2, 118.1, 112.8, 82.2. **HRMS (ESI)**: calculated for $C_{27}H_{19}N_2O_2$ $[M+H]^+$ 403.1441, found 403.1439.

8-fluoro-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (5)



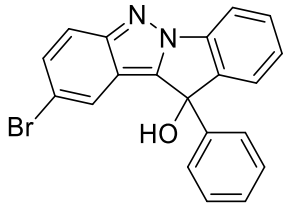
White solid (35 mg, 56% yield), mp 215.3-215.7 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.86 (d, *J*=7.5 Hz, 1H), 7.65-7.57 (m, 3H), 7.54 (d, *J*=7.5 Hz, 1H), 7.45-7.32 (m, 6H), 7.18 (s, 1H), 7.08-7.04 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 161.2 (d, *J* = 240.0 Hz), 152.6 (d, *J* = 13.8 Hz), 143.8, 143.6, 141.5, 138.5, 129.8, 128.6, 127.9, 127.5, 125.4, 125.2, 121.8 (d, *J* = 11.3 Hz), 113.9, 113.7 (d, *J* = 6.3 Hz), 111.9, 101.7 (d, *J* = 23.8 Hz), 77.1. **^{19}F NMR** (470 MHz, DMSO-d_6) δ -113.0 (s, 1F). **HRMS (ESI)**: calculated for $C_{20}H_{14}FN_2O$ $[M+H]^+$ 317.1085, found 317.1077.

8-iodo-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (6)



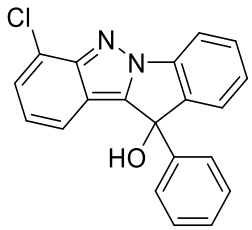
White solid (32 mg, 38% yield), mp 210.5-210.9 °C; PE/THF = 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.82 (d, *J*=7.5 Hz, 1H), 7.75 (d, *J*=8.5 Hz, 1H), 7.53-7.47 (m, 3H), 7.40 (d, *J*=7.5 Hz, 2H), 7.35-7.31 (m, 1H), 7.29-7.23 (m, 3H), 7.07-7.03 (m, 2H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.8, 144.1, 142.9, 141.7, 138.5, 129.7, 128.5, 127.8, 127.4, 125.4, 125.4, 125.2, 122.5, 119.6, 118.4, 116.4, 111.9, 77.0. **HRMS (ESI)**: calculated for $C_{20}H_{14}IN_2O$ $[M+H]^+$ 425.0146, found 425.0139.

9-bromo-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (7)



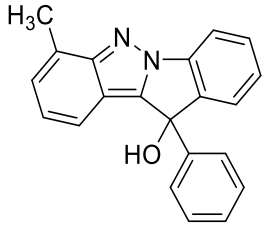
White solid (54 mg, 72% yield), mp 203.4-204.1°C; PE/THF = 3/1; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.91 (d, *J*=6 Hz, 1H), 7.84 (d, *J*=7.2 Hz, 1H), 7.77 (s, 1H), 7.64-7.61 (m, 1H), 7.56 (d, *J*=6 Hz, 1H), 7.48-7.45 (m, 4H), 7.42-7.37 (m, 3H), 7.20 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 151.1, 143.9, 142.6, 141.4, 138.2, 129.9, 129.5, 128.6, 127.9, 127.8, 125.4, 125.1, 121.4, 120.8, 117.4, 115.3, 112.2, 77.0. **HRMS (ESI)**: calculated for $C_{20}H_{13}BrN_2ONa$ $[M+Na]^+$ 399.0109, found 399.0101.

7-chloro-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (8)



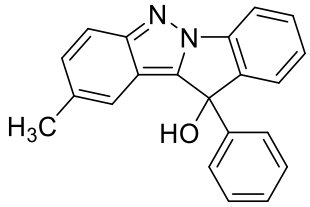
White solid (47 mg, 71% yield), mp 236.1-236.7 °C; PE/THF = 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.95 (d, *J*=8 Hz, 1H), 7.61-7.58 (m, 1H), 7.53 (d, *J*=8 Hz, 2H), 7.46-7.41 (m, 4H), 7.36-7.29 (m, 3H), 7.19 (s, 1H), 7.10-7.07 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 149.8, 144.4, 144.0, 141.2, 138.2, 129.9, 128.6, 127.9, 127.8, 125.9, 125.4, 125.2, 123.0, 122.4, 118.8, 117.7, 112.3, 77.2. **HRMS (ESI)**: calculated for $C_{20}H_{14}ClN_2O$ $[M+H]^+$ 333.0789, found 333.0778.

7-methyl-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (9)



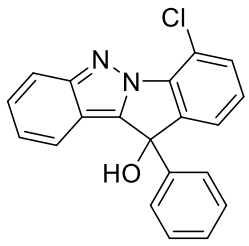
White solid (54 mg, 86% yield), mp 235.4-235.9 °C; PE/THF = 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.85 (d, *J*=8 Hz, 1H), 7.53-7.50 (m, 1H), 7.48 (d, *J*=7.5 Hz, 1H), 7.40 (d, *J*=7.5 Hz, 2H), 7.35-7.24 (m, 5H), 7.06-7.05 (m, 2H), 6.97-6.94 (m, 1H), 2.59 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.2, 144.1, 143.2, 141.9, 138.7, 129.7, 128.5, 128.0, 127.7, 127.2, 125.4, 125.3, 125.2, 122.7, 117.0, 116.2, 111.9, 77.0, 17.0. **HRMS (ESI)**: calculated for $C_{21}H_{16}N_2ONa$ $[M+Na]^+$ 335.1161, found 335.1159.

9-methyl-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (10)



White solid (52 mg, 83% yield), mp 237.6-238.1°C; PE/THF = 3/1; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.79 (d, *J*=7.6 Hz, 1H), 7.66 (d, *J*=9.2 Hz, 1H), 7.53-7.49 (m, 1H), 7.46 (d, *J*=7.6 Hz, 1H), 7.39 (d, *J*=7.2 Hz, 2H), 7.35-7.26 (m, 5H), 7.14-7.12 (m, 1H), 7.03(s, 1H), 2.3(s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 151.8, 144.1, 141.9, 141.8, 138.6, 131.5, 129.6, 129.2, 128.5, 127.7, 127.2, 125.3, 125.2, 118.2, 117.6, 116.6, 111.7, 76.9, 21.3. **HRMS (ESI)**: calculated for $C_{21}H_{16}N_2ONa$ $[M+Na]^+$ 335.1161, found 335.1147.

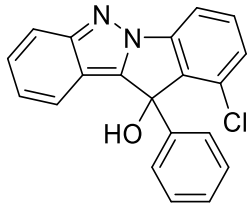
4-chloro-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (11)



White solid (48 mg, 72% yield), mp 235.3-235.9°C; PE/THF=3/1; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.84 (d, *J*=8.8 Hz, 1H), 7.62 (d, *J*=8 Hz, 1H), 7.52 (d, *J*=8.4Hz, 1H), 7.46-7.40 (m, 4H), 7.38-7.33 (m, 4H), 7.15 (s, 1H), 7.13-7.09 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.1, 146.9, 143.7, 141.2, 134.9, 131.0, 128.6, 128.5, 127.9,

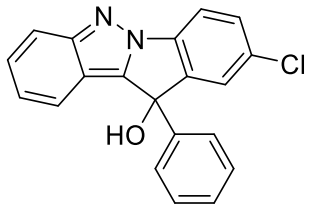
125.8, 125.2, 124.2, 123.0, 119.4, 118.7, 118.0, 115.7, 76.3. **HRMS (ESI**): calculated for $C_{20}H_{14}ClN_2O$ $[M+H]^+$ 333.0789, found 333.0778.

1-chloro-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (12)



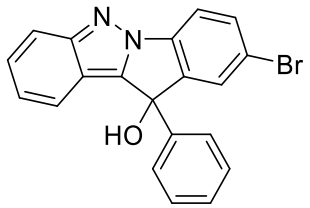
White solid (56 mg, 85% yield)), mp 237.5-237.9°C; PE/THF = 3/1; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.86 (d, *J*=8 Hz, 1H), 7.75 (d, *J*=8.8 Hz, 1H), 7.64-7.60 (m, 1H), 7.48-7.38 (m, 4H), 7.35-7.28 (m, 4H), 7.12 (s, 1H), 7.07-7.04 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.1, 143.6, 140.7, 139.6, 139.4, 131.9, 130.8, 128.4, 128.3, 127.7, 125.8, 125.1, 122.7, 119.4, 118.4, 115.7, 110.8, 77.4. **HRMS (ESI)**: calculated for $C_{20}H_{14}ClN_2O$ $[M+H]^+$ 333.0789, found 333.0774.

2-chloro-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (13)



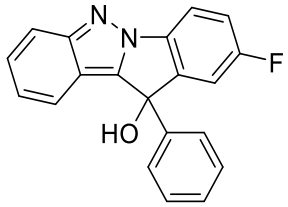
White solid (46 mg, 69% yield)), mp 232.4-232.8 °C; PE/THF = 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.88 (d, *J*=8.5 Hz, 1H), 7.80 (d, *J*=9 Hz, 1H), 7.65-7.63 (m, 1H), 7.55-7.54 (m, 2H), 7.46-7.44 (m, 2H), 7.39-7.32 (m, 4H), 7.24 (s, 1H), 7.14-7.11 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.1, 146.1, 142.9, 141.0, 137.4, 131.6, 129.8, 128.6, 128.0, 125.7, 125.5, 125.2, 122.8, 119.5, 118.5, 116.5, 113.4, 77.0. **HRMS (ESI)**: calculated for $C_{20}H_{14}ClN_2O$ $[M+H]^+$ 333.0789, found 333.0783.

2-bromo-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (14)



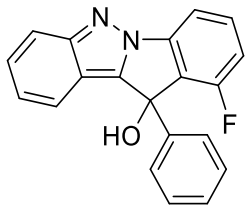
White solid (28 mg, 37% yield); mp 313.6-313.8 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.88 (d, *J*=8 Hz, 1H), 7.81 (d, *J*=8.5 Hz, 1H), 7.61-7.58 (m, 1H), 7.56-7.53 (m, 1H), 7.46-7.32 (m, 7H), 7.14-7.11 (m, 1H), 7.10 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.8, 144.1, 142.9, 141.7, 138.6, 129.7, 128.5, 127.8, 127.4, 125.4, 125.4, 125.2, 122.5, 119.6, 118.4, 116.4, 111.9, 77.0. **HRMS (ESI)**: calculated for $C_{20}H_{13}BrN_2ONa$ $[M+Na]^+$ 399.0109, found 399.0101.

2-fluoro-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (15)



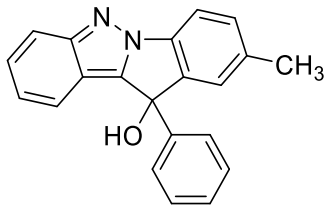
White solid (54.9 mg, 87% yield); mp 243.3-243.7 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.87-7.84 (m, 1H), 7.76 (d, *J*=9 Hz, 1H), 7.52 (d, *J*=8.5 Hz, 1H), 7.43-7.36 (m, 4H), 7.34-7.27 (m, 4H), 7.21 (s, 1H), 7.08-7.05 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 161.3 (d, *J* = 243.8 Hz), 152.8, 146.5 (d, *J* = 7.5 Hz), 142.9, 141.2, 134.9, 128.6, 128.0, 125.5, 125.2, 122.6, 119.5, 118.4, 116.7, 116.3 (d, *J* = 23.8 Hz), 113.3, 113.2 (d, *J* = 15.0 Hz), 77.0. **^{19}F NMR** (470 MHz, DMSO-d_6) δ -114.0 (s, 1F). **HRMS (ESI)**: calculated for $C_{20}H_{14}FN_2O$ $[M+H]^+$ 317.1085, found 317.1077.

1-fluoro-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (16)



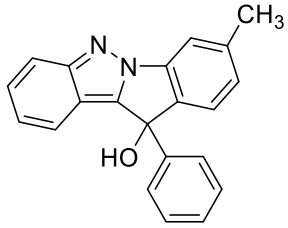
White solid (58 mg, 91% yield); mp 271.2-271.6 °C; PE /THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.76 (d, *J*=8.5 Hz, 1H), 7.72 (d, *J*=8 Hz, 1H), 7.66-7.62 (m, 1H), 7.50 (d, *J*=8.5 Hz, 1H), 7.45 (d, *J*=7.5 Hz, 2H), 7.36-7.29 (m, 4H), 7.26 (s, 1H), 7.21-7.17 (m, 1H), 7.09-7.06 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 158.0 (d, *J* = 250.0 Hz), 153.1, 143.2, 140.6 (d, *J* = 8.8 Hz), 140.1, 132.8 (d, *J* = 7.5 Hz), 129.1 (d, *J* = 18.8 Hz), 128.5, 128.0, 125.8, 125.0, 122.8, 119.5, 118.5, 116.0, 115.2 (d, *J* = 20.0 Hz), 108.5 (d, *J* = 2.5 Hz), 76.8. **^{19}F NMR** (470 MHz, DMSO-d_6) δ -117.1 (s, 1F). **HRMS (ESI)**: calculated for $C_{20}H_{14}FN_2O$ $[M+H]^+$ 317.1085, found 317.1089.

2-methyl-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (17)



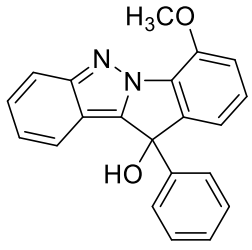
White solid (52 mg, 83% yield); mp 236.0-236-5 °C; PE /THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.77 (d, *J*=9 Hz, 1H), 7.73 (d, *J*=8 Hz, 1H), 7.52 (d, *J*=8 Hz, 1H), 7.42 (d, *J*=7.5 Hz, 2H), 7.36-7.27 (m, 6H), 7.09-7.05 (m, 2H), 2.36 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.7, 144.3, 142.7, 141.9, 137.1, 136.4, 129.9, 128.5, 127.7, 125.2, 125.9, 125.2, 122.3, 119.5, 118.3, 116.4, 111.6, 77.0, 20.9. **HRMS (ESI)**: calculated for $C_{21}H_{16}N_2ONa$ $[M+Na]^+$ 335.1161, found 335.1159.

3-methyl-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (18)



White solid (43 mg, 69% yield); mp 236.7-237.2 °C; PE/THF= 3/1. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.78 (d, *J*=8.8 Hz, 1H), 7.69 (s, 1H), 7.55 (d, *J*=8.4 Hz, 1H), 7.43-7.39 (m, 2H), 7.37-7.28 (m, 5H), 7.20 (d, *J*=7.2 Hz, 1H), 7.11-7.08 (m, 1H), 7.03 (s, 1H), 2.47 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.7, 143.2, 141.9, 141.3, 139.7, 138.7, 128.5, 127.8, 127.7, 125.3, 125.2, 125.1, 122.4, 119.6, 118.4, 116.3, 112.4, 76.8, 21.1. **HRMS (ESI)**: calculated for $C_{21}H_{16}N_2ONa$ $[M+Na]^+$ 335.1161, found 335.1159.

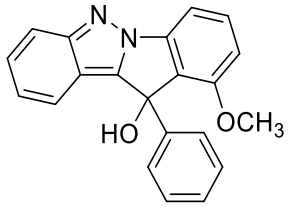
4-methoxy-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (19)



White solid (57 mg, 87% yield); mp 250.8-251.3 °C; PE/THF= 2/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.78 (d, *J*=8.5 Hz, 1H), 7.49 (d, *J*=8.5 Hz, 1H), 7.38 (d, *J*=7.5 Hz, 2H), 7.33-7.29 (m, 3H), 7.27-7.24 (m, 3H), 7.06-7.03 (m, 2H), 7.01 (s, 1H), 4.03 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.9, 147.3, 146.2, 142.5, 142.0, 128.5,

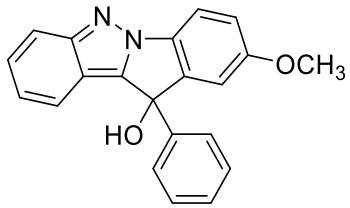
127.7, 125.5, 125.8, 125.2, 122.3, 119.2, 118.5, 117.3, 115.7, 114.1, 76.6, 56.3. **HRMS (ESI)**: calculated for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ 329.1285, found 329.127989.

1-methoxy-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (20)



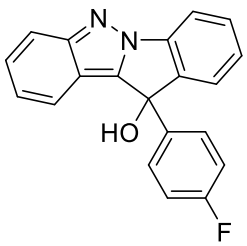
White solid (51 mg, 78% yield); mp 236.5-236.9 °C; PE/THF= 2/1; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.74 (d, *J*=8.8 Hz, 1H), 7.60-7.56 (m, 1H), 7.51-7.47 (m, 2H), 7.42 (d, *J*=7.2 Hz, 2H), 7.33-7.24 (m, 4H), 7.06-7.03 (m, 2H), 6.81 (s, 1H), 3.74 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 156.3, 152.7, 143.6, 140.8, 140.1, 131.9, 128.5, 128.1, 127.4, 125.3, 125.2, 122.3, 119.5, 118.3, 115.8, 111.5, 104.5, 77.2, 55.7. **HRMS (ESI)**: calculated for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ 329.1285, found 329.1281.

2-methoxy-11-phenyl-11*H*-indolo[1,2-*b*]indazol-11-ol (21)



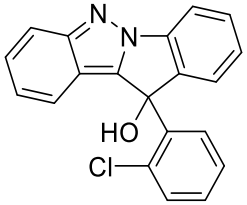
White solid (59 mg, 90% yield); mp 234.6-235.2 °C; PE /THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.75-7.72 (m, 2H), 7.51 (d, *J*=8 Hz, 1H), 7.41-7.39 (m, 2H), 7.32-7.26 (m, 4H), 7.14 (s, 1H), 7.09-7.04 (m, 3H), 3.78 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 159.0, 152.5, 145.6, 142.3, 141.8, 132.1, 128.5, 127.8, 125.9, 125.2, 122.2, 119.3, 118.2. 116.5, 114.1, 112.7, 111.9, 77.1, 55.8. **HRMS (ESI)**: calculated for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ 329.1285, found 329.1279.

11-(4-fluorophenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (23)[2]



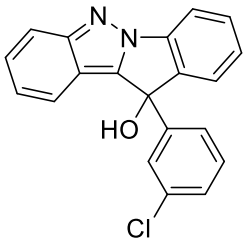
White solid (44 mg, 69% yield); PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.85 (d, *J*=7.5 Hz, 1H), 7.79 (d, *J*=9 Hz, 1H), 7.59-7.53 (m, 2H), 7.51 (d, *J*=7 Hz, 1H), 7.47-7.44 (m, 2H), 7.41-7.38 (m, 1H), 7.34-7.31 (m, 1H), 7.19-7.16 (m, 2H), 7.14 (s, 1H), 7.12-7.09 (m,1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 161.7 (d, *J* = 242.5 Hz), 152.9, 143.9, 142.6, 138.5, 137.9 (d, *J* = 3.8 Hz), 129.8, 127.5, 127.4 (d, *J* = 8.8 Hz), 125.5, 125.3, 122.6, 119.5, 118.5, 116.3, 115.3 (d, *J* = 21.3 Hz), 111.9, 76.6. **^{19}F NMR** (470 MHz, DMSO-d_6) δ -114.7 (s, 1F).

11-(2-chlorophenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (24)



White solid (60 mg, 91% yield); mp 262.9-263.4 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO- d_6) δ 8.52 (d, *J*=9 Hz, 1H), 7.81 (d, *J*=8 Hz, 1H), 7.76 (d, *J*=9 Hz, 1H), 7.60-7.58 (m, 1H), 7.55-7.52 (m, 1H), 7.39-7.35 (m, 1H), 7.31-7.20 (m, 6H), 7.01-6.98 (m, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.7, 142.6, 141.3, 139.9, 138.0, 130.4, 130.3, 129.8, 129.7, 128.8, 127.3, 127.2, 125.3, 124.5, 122.3, 119.1, 118.4, 116.4, 111.7, 74.6. **HRMS (ESI)**: calculated for $C_{20}H_{14}ClN_2O$ $[M+H]^+$ 333.0789, found 333.0778.

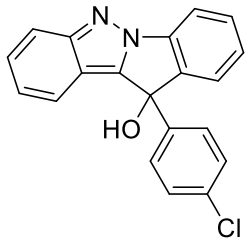
11-(3-chlorophenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (25)



White solid (54 mg, 82% yield); mp 233.5-233.9 °C; PE/THF= 3/1. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.87 (d, *J*=7.5 Hz, 1H), 7.80 (d, *J*=9 Hz, 1H), 7.60-7.51 (m, 4H),

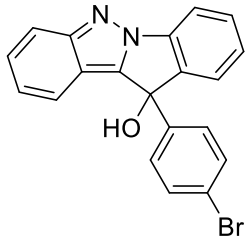
7.41-7.38 (m, 2H), 7.36-7.32 (m, 2H), 7.26 (s, 1H), 7.22 (d, *J*=6.5 Hz, 1H), 7.13-7.10 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.9, 144.3, 143.5, 142.2, 138.6, 133.3, 130.5, 130.0, 127.9, 127.5, 125.5, 125.3, 125.0, 124.0, 122.8, 119.4, 118.5, 116.3, 112.0, 76.5. **HRMS (ESI)**: calculated for $C_{20}H_{14}ClN_2O$ $[M+H]^+$ 333.0789, found 333.0778.

11-(4-chlorophenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (26)



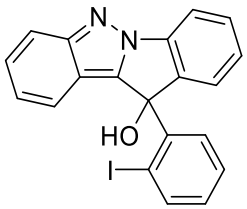
White solid (57 mg, 86% yield); mp 238.7-239.3 °C; PE/THF= 3/1. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.83 (d, *J*=8 Hz, 1H), 7.76 (d, *J*=8.8 Hz, 1H), 7.57-7.46 (m, 3H), 7.39-7.35 (m, 5H), 7.32-7.28 (m, 1H), 7.18 (s, 1H), 7.10-7.06 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.9, 143.7, 142.4, 140.8, 138.5, 132.5, 129.9, 128.5, 127.5, 127.2, 125.5, 125.3, 122.7, 119.4, 118.5, 116.3, 112.0, 76.5. **HRMS (ESI)**: calculated for $C_{20}H_{14}ClN_2O$ $[M+H]^+$ 333.0789, found 333.0778.

11-(4-bromophenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (27)



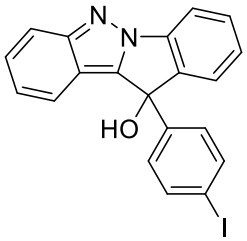
White solid (65 mg, 87% yield); mp 213.3-213.8 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.84 (d, *J*=7.5 Hz, 1H), 7.77 (d, *J*=9 Hz, 1H), 7.58-7.51 (m, 4H), 7.48 (d, *J*=7.5 Hz, 1H), 7.40-7.30 (m, 4H), 7.19 (s, 1H), 7.11-7.08 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.8, 143.6, 142.3, 141.2, 138.5, 131.5, 129.9, 127.5, 125.5, 125.3, 122.7, 121.0, 119.4, 118.5, 116.3, 112.0, 76.6. **HRMS (ESI)**: calculated for $C_{20}H_{13}BrN_2ONa$ $[M+Na]^+$ 399.0109, found 399.0101.

11-(2-iodophenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (28)



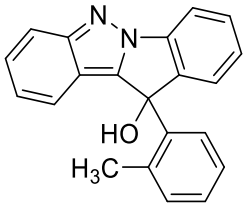
White solid (68 mg, 80% yield); mp 210.7-211.5 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.54-8.53 (m, 1H), 7.81-7.77 (m, 3H), 7.70-7.67 (m, 1H), 7.59-7.56 (m, 1H), 7.34-7.29 (m, 2H), 7.22 (s, 1H), 7.20-7.10 (m, 3H), 7.05-7.02 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.6, 142.3, 141.7, 141.3, 141.1, 140.7, 129.9, 129.8, 128.7, 128.2, 127.2, 125.2, 124.7, 122.3, 119.1, 118.4, 117.2, 111.8, 94.0, 76.8. **HRMS (ESI)**: calculated for $C_{20}H_{13}IN_2ONa$ $[M+Na]^+$ 446.9971, found 446.9983.

11-(4-iodophenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (29)



White solid (69 mg, 81% yield); mp 224.7-225.3 °C; PE/THF= 3/1; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.83 (d, *J*=7.6 Hz, 1H), 7.76 (d, *J*=8.8 Hz, 1H), 7.69 (d, *J*=8.4 Hz, 2H), 7.57-7.45 (m, 3H), 7.38-7.34 (m, 1H), 7.32-7.28 (m, 1H), 7.20-7.18 (m, 2H), 7.15 (s, 1H), 7.09-7.06 (m, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.9, 143.7, 142.3, 141.6, 138.5, 137.3, 129.9, 127.6, 127.5, 125.5, 125.3, 122.7, 119.5, 118.5, 116.3, 112.0, 94.0, 76.7. **HRMS (ESI)**: calculated for $C_{20}H_{13}IN_2ONa$ $[M+Na]^+$ 446.9971, found 446.9974.

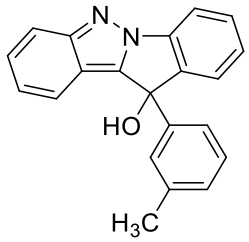
11-(o-tolyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (30)



White solid (59 mg, 94% yield); mp 271.2-271.6 °C; PE/THF=3/1; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.29 (d, *J*=7.6 Hz, 1H), 7.80 (d, *J*=7.6 Hz, 1H), 7.72 (d, *J*=8.8 Hz, 1H), 7.52-7.48 (m, 1H), 7.38-7.34 (m, 1H), 7.29-7.16 (m, 5H), 7.00 (s, 1H), 6.96-6.89

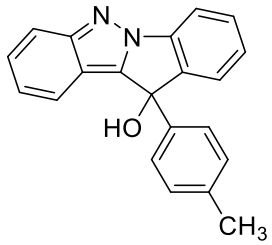
(m, 2H), 1.04 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.8, 143.2, 142.1, 139.3, 138.7, 134.0, 131.5, 129.8, 127.8, 127.5, 125.5, 125.4, 125.1, 124.8, 122.4, 119.2, 118.4, 116.3, 111.8, 75.3, 18.3. **HRMS (ESI)**: calculated for $C_{21}H_{16}N_2ONa$ $[M+Na]^+$ 335.1161, found 335.1164.

11-(*m*-tolyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (31)



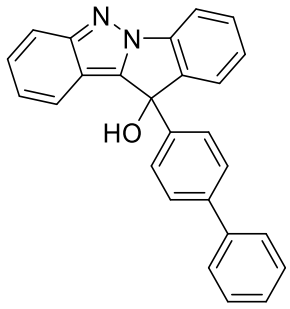
White solid (57 mg, 92% yield); mp 203.7-204.4 °C; PE/THF=3/1; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.84 (d, *J*=7.6 Hz, 1H), 7.77 (d, *J*=8.8 Hz, 1H), 7.57-7.53 (m, 2H), 7.50 (d, *J*=7.2 Hz, 1H), 7.39-7.36 (m, 1H), 7.33-7.27 (m, 2H), 7.23-7.16 (m, 2H), 7.11-7.07 (m, 2H), 7.05 (s, 1H), 2.25 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.8, 144.2, 143.0, 141.7, 138.6, 137.7, 129.7, 128.5, 128.4, 127.3, 125.4, 125.7, 125.4, 122.5, 122.3, 119.6, 118.4, 116.4, 111.9, 77.0, 21.1. **HRMS (ESI)**: calculated for $C_{21}H_{16}N_2ONa$ $[M+Na]^+$ 335.1161, found 335.1159.

11-(*p*-tolyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (32)[2]



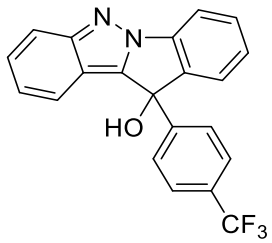
White solid (58 mg, 93% yield); PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.83 (d, *J*=8 Hz, 1H), 7.76 (d, *J*=8.5 Hz, 1H), 7.54-7.51 (m, 2H), 7.48 (d, *J*=7.5 Hz, 1H), 7.36-7.33 (m, 1H), 7.30-7.28 (m, 3H), 7.13-7.11 (m, 2H), 7.08-7.05 (m, 1H), 7.01 (s, 1H), 2.23 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.9, 144.3, 143.0, 138.8, 138.6, 137.0, 129.6, 129.1, 127.3, 125.4, 125.3, 125.2, 122.4, 119.7, 118.4, 116.4, 111.8, 77.0, 20.6.

11-([1,1'-biphenyl]-4-yl)-11*H*-indolo[1,2-*b*]indazol-11-ol (33)



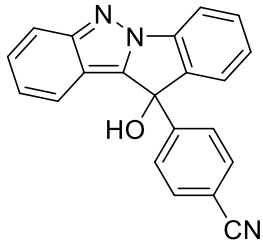
White solid (59 mg, 79% yield); mp 242.6-243.1 °C; PE/THF= 3/1; **^{1}H NMR** (500 M Hz, DMSO-d_6) δ 7.87 (d, *J*=8 Hz, 1H), 7.80 (d, *J*=8.5 Hz, 1H), 7.65-7.62 (m, 4H), 7.6 0-7.54 (m, 3H), 7.50 (d, *J*=8.5 Hz, 2H), 7.46-7.39 (m, 3H), 7.37-7.31 (m, 2H), 7.15 (s, 1H), 7.12-7.09 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.9, 144.1, 142.8, 140. 9, 139.7, 139.6, 138.6, 129.8, 128.9, 127.5, 127.4, 125.9, 125.6, 125.5, 125.8, 125.4, 1 22.6, 119.6, 118.5, 116.4, 111.9, 76.9. **HRMS (ESI)**: calculated for $C_{26}H_{18}N_2ONa$ [M +Na]$^+$ 397.1317, found 397.1320.

12-(4-(trifluoromethyl)phenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (34)



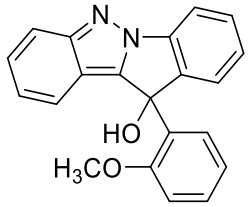
White solid (64 mg, 87% yield); mp 255.6-255.9 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.89 (d, *J*=7.5 Hz, 1H), 7.81 (d, *J*=8.5 Hz, 1H), 7.74 (d, *J*=8 Hz, 2H), 7.64-7.59 (m, 3H), 7.54-7.50 (m, 2H), 7.43-7.40 (m, 1H), 7.36-7.32 (m, 2H), 7.13-7.10 (m. 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.9, 146.4, 143.5, 142.2, 138.6, 130.1, 128.4 (q, *J* = 31.3 Hz), 127.6, 126.5, 126.1, 125.5 (q, *J* = 3.8 Hz), 125.4, 125.2, 123.0, 122.8, 119.3, 118.5, 116.4, 112.0,76.7. **^{19}F NMR** (470 MHz, DMSO-d_6) δ -61.1 (s, 3F); **HRMS (ESI)**: calculated for $C_{21}H_{13}F_3N_2ONa$ [M+Na]$^+$ 389.0878, found 389.0874.

4-(11-hydroxy-11*H*-indolo[1,2-*b*]indazol-11-yl)benzonitrile (35)



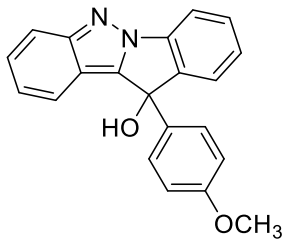
White solid (58 mg, 90% yield); mp 217.7-218.3 °C; PE/THF= 3/1; **^{1}H NMR** (500 M Hz, DMSO-d_6) δ 7.86 (d, *J*=7.5 Hz, 1H), 7.81-7.77 (m, 3H), 7.59-7.56 (m, 3H), 7.50-7.46 (m, 2H), 7.39-7.29 (m, 3H), 7.10-7.07 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.9, 147.2, 143.2, 141.9, 138.6, 132.6, 130.1, 127.6, 125.5, 125.3, 125.3, 122.8, 119.3, 118.5, 118.4, 116.4, 112.1, 110.7, 76.7. **HRMS (ESI)**: calculated for $C_{21}H_{14}N_3O$ $[M+H]^+$ 324.1132, found 324.1135.

11-(2-methoxyphenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (36)



White solid (58 mg, 88% yield); mp 252.7-253.2 °C; PE/THF= 3/1; **^{1}H NMR** (400 M Hz, DMSO-d_6) δ 8.23 (d, *J*=9.5 Hz, 1H), 7.81 (d, *J*=7.5 Hz, 1H), 7.74 (d, *J*=9 Hz, 1H), 7.53-7.50 (m, 1H), 7.34-7.23 (m, 5H), 7.20-7.16 (m, 1H), 7.00-6.97 (m, 1H), 6.93 (s, 1H), 6.79 (d, *J*=7.5 Hz, 1H), 2.94 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 155.8, 152.5, 144.4, 143.0, 139.5, 129.7, 129.1, 129.0, 125.9, 125.7, 125.0, 123.8, 121.6, 120.6, 119.4, 118.2, 115.8, 112.4, 111.1, 73.8, 55.6. **HRMS (ESI)**: calculated for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ 329.1285, found 329.1282.

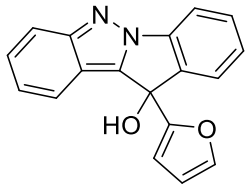
11-(4-methoxyphenyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (37)



White solid (59 mg, 90% yield); mp 246.5-246.9 °C; PE/THF= 3/1; **^{1}H NMR** (400 M Hz, DMSO-d_6) δ 7.81 (d, *J*=8 Hz, 1H), 7.75 (d, *J*=8.8 Hz, 1H), 7.55-7.47 (m, 3H), 7.37-7.27 (m, 4H), 7.09-7.05 (m, 1H), 7.00 (s, 1H), 6.88 (d, *J*=8.4 Hz, 2H), 3.68 (s, 3H).

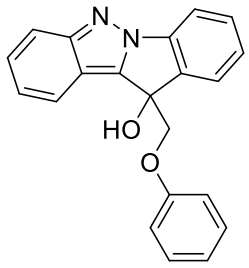
^{13}C NMR (125 MHz, DMSO-d_6) δ 158.8, 152.8, 144.3, 143.0, 138.5, 133.5, 129.6, 12 7.3, 125.5, 125.4, 125.3, 122.4, 119.7, 118.4, 116.3, 113.9, 111.8, 76.8, 55.0. **HRMS (ESI)**: calculated for $C_{21}H_{17}N_2O_2$ $[M+H]^+$ 329.1285, found 329.1287.

11-(furan-2-yl)-11*H*-indolo[1,2-*b*]indazol-11-ol (38)



White solid; (45 mg, 78% yield); mp 219.3-219.8 °C; PE/THF=3/1; **^{1}H NMR** (500 M Hz, DMSO-d_6) δ 7.86 (d, *J*=8.5 Hz, 1H), 7.82 (d, *J*=7.5 Hz, 1H), 7.78 (d, *J*=9 Hz, 1H), 7.71-7.70 (m, 1H), 7.60-7.57 (m, 1H), 7.46-7.43 (m, 1H), 7.36-7.33 (m, 1H), 7.21-7.1 8 (m, 1H), 7.17 (s, 1H), 6.41-6.40 (m, 1H), 6.32-6.31 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.8, 143.8, 140.7, 140.4, 138.4, 130.2, 127.3, 125.5, 125.8, 122.8, 120. 0, 118.4, 116.9, 111.9, 110.4, 107.7, 72.7. **HRMS (ESI)**: calculated for $C_{18}H_{13}N_2O_2$ $[M+H]^+$ 389.0972, found 329.0978.

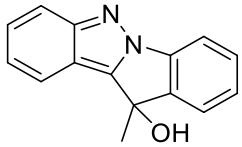
11-(phenoxymethyl)-11*H*-indolo[1,2-*b*]indazol-11-ol (39)



White solid (47 mg, 71% yield); mp 203.6-204.1 °C; PE/THF=3/1; **^{1}H NMR** (500 M Hz, DMSO-d_6) δ 8.05 (d, *J*=8.5 Hz, 1H), 7.86-7.82 (m, 2H), 7.77 (d, *J*=8.5 Hz, 1H), 7. 63-7.60 (m, 1H), 7.47-7.44 (m, 1H), 7.36-7.33 (m, 1H), 7.29-7.26 (m, 2H), 7.22-7.19 (m, 1H), 7.00 (d, *J*=8 Hz, 2H), 6.95-6.92 (m, 1H), 6.76 (s, 1H), 4.71 (d, *J* = 9.5 Hz, 1 H), 4.33 (d, *J* = 9.5 Hz, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 158.3, 152.7, 140.7,

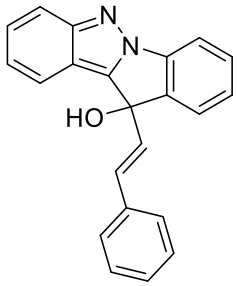
140.2, 139.1, 130.1, 129.4, 127.0, 125.3, 125.4, 122.3, 120.9, 120.8, 118.2, 117.6, 114.6, 111.7, 75.6, 71.6. **HRMS (ESI)**: calculated for $C_{21}H_{16}N_2O_2Na$ $[M+Na]^+$ 351.1110, found 351.1106.

11-methyl-11*H*-indolo[1,2-*b*]indazol-11-ol（40）



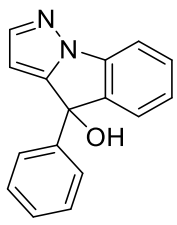
White solid (21 mg, 45% yield); mp 170.3-170.9 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.86 (d, *J*=8.5 Hz, 1H), 7.74-7.69 (m, 3H), 7.54-7.51 (m, 1H), 7.42-7.39 (m, 1H), 7.33-7.30 (m, 1H), 7.16-7.13 (m, 1H), 6.28 (s, 1H), 1.85 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.1, 144.4, 143.8, 138.7, 129.9, 127.6, 126.8, 124.7, 122.5, 120.3, 118.7, 116.6, 112.1, 73.4, 26.0. **HRMS(ESI)**: calculated for $C_{15}H_{13}N_2O$ $[M+H]^+$ 237.1023, found 237.1019.

(*E*)-11-styryl-11*H*-indolo[1,2-*b*]indazol-11-ol (41)



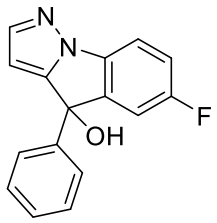
White solid (58 mg, 89% yield); mp 220.8-221.5 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.82 (d, *J*=8 Hz, 1H), 7.75 (d, *J*=9 Hz, 2H), 7.70 (d, *J*=7.5 Hz,1H), 7.59-7.55 (m, 1H), 7.46-7.42 (m, 3H), 7.36-7.28 (m, 3H), 7.25-7.22 (m, 1H), 7.18-7.15 (m, 1H), 6.85-6.82 (m, 2H), 6.76-6.72 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.2, 143.0, 141.7, 138.9, 136.4, 130.3, 129.6, 129.5, 129.1, 128.4, 127.8, 127.1, 126.9, 125.8, 123.0, 120.3, 118.9, 117.4, 112.4, 76.3. **HRMS(ESI)**: calculated for $C_{22}H_{17}N_2O$ $[M+H]^+$ 325.1336, found 325.1340.

4-phenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (42)



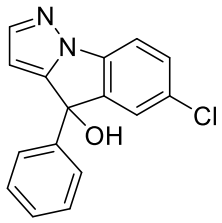
White solid (39 mg, 80% yield); mp 186.6-187.2 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.74 (s, 1H), 7.54 (d, *J*=7.5 Hz, 1H), 7.44-7.41 (m, 1H), 7.35-7.26 (m, 6H), 7.21-7.18 (m, 1H), 6.88 (s, 1H), 6.35 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.2, 144.8, 143.3, 143.2, 138.7, 129.9, 128.8, 128.0, 125.9, 125.9, 125.6, 110.4, 102.3, 76.5. **HRMS (ESI)**: calculated for $C_{16}H_{13}N_2O$ $[M+H]^+$ 249.1023, found 249.1018.

6-fluoro-4-phenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (43)



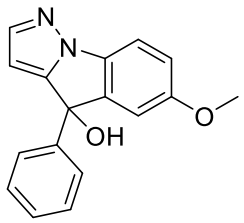
White solid (37 mg, 71% yield); mp 196.3-196.8 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.73 (s, 1H), 7.58-7.55 (m, 1H), 7.37-7.27 (m, 6H), 7.22-7.20 (m, 1H), 7.02 (s, 1H), 6.37 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 160.5 (d, *J* = 252.0 Hz), 152.2, 145.5 (d, *J* = 7.3Hz), 144.8, 142.6, 135.1, 128.9, 128.3, 125.7, 116.4 (d, *J* = 25.2Hz), 113.6 (d, *J* = 25.2Hz), 111.6 (d, *J* = 8.7), 102.7, 76.5. **^{19}F NMR** (470 MHz, DMSO-d_6) δ -116.8 (s, 1F). **HRMS** (ESI): calculated for $C_{16}H_{12}FN_2O$ $[M+H]^+$ 267.0928, found 267.0924.

6-chloro-4-phenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (44)



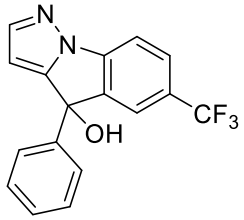
White solid (34 mg, 60% yield); mp 171.4-171.8 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.77 (s, 1H), 7.57 (d, *J*=8.5 Hz, 1H), 7.49 (d, *J*=8.5 Hz, 1H), 7.36-7.34 (m, 6H), 7.03 (s, 1H), 6.38 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.1, 145.3, 142.5, 137.5, 129.9, 129.0, 128.3, 125.9, 125.6, 112.0, 102.8, 76.5. **HRMS (ESI)**: calculated for $C_{16}H_{12}ClN_2O$ $[M+H]^+$ 283.0633, found 283.0628.

6-methoxy-4-phenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (45)



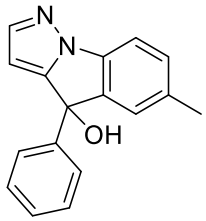
White solid (37 mg, 68% yield); mp 197.9-198.3 °C; PE /THF= 3/1; **^{1}H NMR** (500 M Hz, DMSO-d_6) δ 7.66 (s, 1H), 7.46 (d, *J*=8.5 Hz, 1H), 7.33-7.32 (m, 5H), 6.97 (d, *J*=7. 5 Hz, 1H), 6.89-6.87 (m, 2H), 6.30 (s, 1H), 2.5 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 157.9, 151.8, 144.9, 143.9, 143.3, 132.5, 128.8, 128.0, 125.6, 114.1, 112.5, 111.0, 102.2, 76.6, 56.1. **HRMS (ESI)**: calculated for $C_{17}H_{15}N_2O_2$ $[M+H]^+$ 279.1128, found 279.1133.

4-phenyl-6-(trifluoromethyl)-4*H*-pyrazolo[1,5-*a*]indol-4-ol (46)



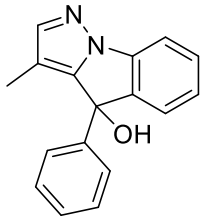
White solid (35 mg, 55% yield); mp 198.4-198.9 °C; PE /THF=3/1; **^{1}H NMR** (500 M Hz, DMSO-d_6) δ 7.87-7.84 (m, 2H), 7.77 (d, *J*=8 Hz, 1H), 7.63 (s, 1H), 7.41-7.31 (m, 5H), 7.14 (s, 1H), 6.46 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.0, 146.3, 144. 4, 142.2, 141.5, 129.0, 128.4, 128.1 (q, *J* =3.75 Hz), 126.3 (q, *J* =31.3 Hz), 125.6,123. 5, 123.3 (q, *J* = 3.75 Hz), 111.2, 103.2, 76.4. **^{19}F NMR** (470 MHz, DMSO-d_6) δ -60.2 (s,3F). **HRMS (ESI)**: calculated for $C_{17}H_{12}F_3N_2O$ $[M+H]^+$ 317.0896, found 317.0889.

6-methyl-4-phenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (47)



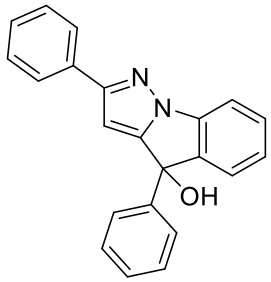
White solid (50 mg, 95% yield); mp 215.6-215.9 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.70 (s, 1H), 7.44 (d, *J*=8 Hz, 1H), 7.37-7.31 (m, 4H),7.28-7.27 (m, 1H), 7.23 (d, *J*=7.5 Hz, 1H), 7.15 (s, 1H), 6.84 (s, 1H), 6.32 (s, 1H), 2.29 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 151.6, 143.8, 143.0, 142.9, 136.2, 134.7, 129.5, 128.3, 127.4, 125.8, 125.1, 109.6, 101.6, 76.0, 20.7. **HRMS (ESI)**: calculated for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1179, found 263.1184.

3-methyl-4-phenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (48)



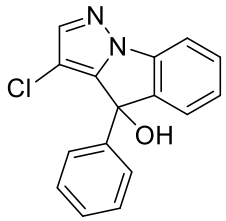
White solid (38 mg, 73% yield); mp 229.5-230.1 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.52 (s, 1H), 7.47 (d, *J*=7.5 Hz, 1H), 7.41-7.38 (m, 1H), 7.33-7.27 (m, 6H), 7.17-7.14 (m, 1H), 6.75 (s, 1H), 1.88 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 148.3, 145.3, 143.4, 142.3, 138.8, 129.8, 128.8, 127.9, 125.7, 125.5, 125.5, 112.4, 110.1, 76.5, 8.3. **HRMS (ESI)**:calculated for $C_{17}H_{15}N_2O$ $[M+H]^+$ 263.1179, found 263.1184.

2,4-diphenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (49)



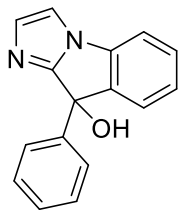
White solid (53 mg, 82% yield); mp 195.1-195.7 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J*=7.5 Hz, 2H), 7.47-7.42 (m, 3H), 7.39-7.36 (m, 2H), 7.32-7.24 (m, 6H), 7.14 (d, *J*=7.5 Hz, 1H), 6.96-6.93 (m, 1H), 6.42 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.9, 152.3, 141.2, 141.1, 138.2, 132.7, 129.6, 128.6, 128.5, 128.3, 128.2, 128.0, 125.8, 125.6, 125.4, 125.2, 110.7, 99.5. **HRMS (ESI)**: calculated for $C_{22}H_{17}N_2O$ $[M+H^+$ 325.1336, found 325.1334.

3-chloro-4-phenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (50)



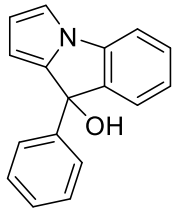
White solid (30 mg, 53% yield); mp 192.1-192.6 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.83 (s, 1H), 7.57 (d, *J*=8 Hz, 1H), 7.48-7.45 (m, 1H), 7.35-7.23 (m, 7H), 7.01 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 146.7, 143.1, 142.8, 140.9, 138.3, 130.2, 128.9, 128.3, 125.7, 125.9, 125.6, 110.6, 106.4, 77.1. **HRMS (ESI)**: calculated for $C_{16}H_{12}ClN_2O$ $[M+H]^+$ 283.0633, found 283.0629.

9-phenyl-9*H*-imidazo[1,2-*a*]indol-9-ol (51)[4]



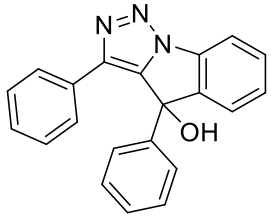
White solid (42 mg, 85% yield); PE /THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.73 (s, 1H), 7.54 (d, *J*=8 Hz, 1H), 7.44-7.41 (m, 1H), 7.35-7.25 (m, 6H), 7.21-7.18 (m, 1H), 6.87 (s, 1H), 6.34 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 152.1, 144.8, 143.3, 138.7, 129.9, 128.8, 128.0, 125.9, 125.9, 125.6, 110.4, 102.3, 76.5.

9-phenyl-*9H*-pyrrolo[1,2-*a*]indol-9-ol (52)



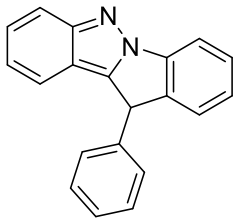
White solid (25 mg, 51% yield); mp 180.6-181.4 °C; PE /THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.50 (d, *J*=8 Hz, 1H), 7.35-7.33 (m, 4H), 7.31-7.26 (m, 2H), 7.22 (d, *J*=7.5Hz, 2H), 7.07-7.04 (m, 1H), 6.46 (s, 1H), 6.28 (s, 1H), 6.02 (s, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 145.5, 143.7, 143.0, 139.4, 129.3, 128.5, 127.4, 125.8, 125.6, 124.4, 113.8, 112.0, 110.6, 104.2, 77.0. **HRMS (ESI)**: calculated for $C_{17}H_{14}NO$ $[M+H]^+$ 248.1070, found 248.1076.

3,4-diphenyl-4*H*-[1,2,3]triazolo[1,5-*a*]indol-4-ol (53)



White solid (36 mg, 55% yield), mp 204.3-204.9 °C; PE/THF= 3/1; **^{1}H NMR** (500 M Hz, DMSO-d_6) δ 7.93 (d, *J*=7.5 Hz, 1H), 7.84 (d, *J*=7.5 Hz, 2H), 7.58- 7.55 (m, 1H), 7.43-7.34 (m, 7H), 7.32-7.25 (m, 4H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 145.5, 142. 8, 141.5, 140.2, 135.1, 130.4, 130.0, 129.2, 129.1, 128.9, 128.7, 128.4, 126.6, 126.4, 1 25.3, 112.7, 76.2. **HRMS (ESI)**: calculated for $C_{21}H_{16}N_3O$ $[M+H]^+$ 326.1293, found 3 26.1297.

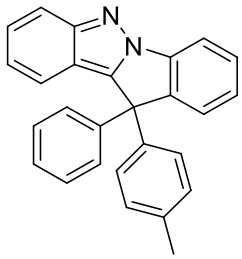
11-phenyl-11*H*-indolo[1,2-*b*]indazole (54)



Green solid (40 mg, 71% yield); mp 105.0-105.6 °C; PE/THF= 3/1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J*=7.6 Hz, 1H), 7.85 (d, *J*=8.8 Hz, 1H), 7.50-7.45 (m, 2H), 7.42 (d, *J*=7.6 Hz, 1H), 7.32-7.31 (m, 5H), 7.21 (d, *J*=7.6 Hz, 2H), 7.07-7.03 (m, 1H), 5.46 (s, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 153.2, 141.0, 140.2, 139.6, 138.4,

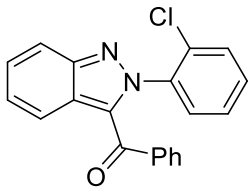
129.6, 129.5, 129.3, 128.2, 128.1, 128.1, 127.3, 126.8, 126.7, 122.2, 120.1, 118.7, 117.0, 112.4, 46.4. **HRMS (ESI)**: calculated for $C_{20}H_{15}N_2$ $[M+H]^+$ 283.1230, found 283.1226.

11-phenyl-11-(*p*-tolyl)-11*H*-indolo[1,2-*b*]indazole (55)



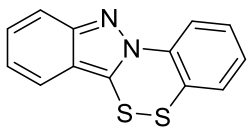
White solid (50 mg, 67% yield); mp 83.9-84.2 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.95 (d, *J*=8 Hz, 1H), 7.80-7.75 (m, 2H), 7.66 (d, *J*=8.5 Hz, 1H), 7.63-7.60 (m, 1H), 7.47-7.44 (m, 1H), 7.35-7.28 (m, 4H), 7.26-7.24 (m, 2H), 7.13-7.10 (m, 5H), 2.24 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 153.3, 143.0, 142.7, 142.7, 139.6, 138.8, 137.3, 129.9, 129.8, 129.3, 128.0, 128.0, 127.9, 127.7, 127.4, 127.0, 123.0, 120.2, 119.0, 117.1, 112.9, 60.2,21.0. **HRMS (ESI)**: calculated for $C_{27}H_{21}N_2$ $[M+H]^+$ 373.1699, found 373.1694.

(2-(2-chlorophenyl)-2*H*-indazol-3-yl)(phenyl)methanone (56)



Light yellow solid (37 mg, 55% yield); mp 110.4-110.9 °C; PE/THF=3/1; **^{1}H NMR** (500MHz, DMSO-d_6) δ 7.09-7.85 (m, 2H), 7.82-7.78 (m, 2H), 7.46 (d, *J*=9 Hz, 2H), 7.42 (d, *J*=7.5 Hz, 2H), 7.37-7.34 (m, 1H), 7.28-7.23 (m, 3H), 7.10-7.07 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 194.2, 148.2, 136.5, 136.4, 136.3, 133.2, 132.2, 130.6, 130.5, 128.8, 128.3, 128.0, 127.9, 123.4, 120.7, 119.1, 119.0, 118.1. **HRMS (ESI)**: calculated for $C_{20}H_{14}ClN_2O$ $[M+H]^+$ 333.0789, found 333.0793.

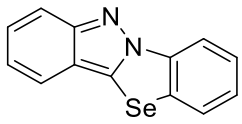
benzo[5,6][1,2,4]dithiazino[4,3-*b*]indazole (57)



Yellow solid (40 mg, 78% yield); mp 145.2-145.8 °C; PE/THF=3/1; **^{1}H NMR** (500MHz, DMSO-d_6) δ 8.15 (d, *J*=8 Hz, 1H), 7.76 (d, *J*=8.5 Hz, 2H), 7.69 (d, *J*=8.5 Hz, 1H),

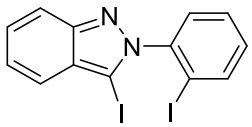
7.65-7.62 (m, 1H), 7.50-7.47 (m, 1H), 7.42-7.39 (m, 1H), 7.21-7.18 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 148.9, 137.9, 130.6, 130.1, 128.7, 128.6, 127.6, 124.5, 123.9, 123.2, 121.3, 120.4, 118.3. **HRMS (ESI)**: calculated for $C_{13}H_9N_2S_2$ $[M+H]^+$ 257.0202, found 257.0208.

benzo[4,5][1,3]selenazolo[3,2-*b*]indazole and benzo[5,6][1,2,4]diselenazino[4,3-*b*]indazole (58 and 59)



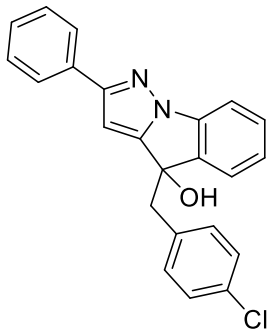
Red solid (50 mg, 71% yield); mp 152.7-153.4 °C; PE/THF=3/1; **^{1}H NMR** (500MHz, DMSO-d_6) δ 8.05 (d, *J*=8.5, 1H), 7.86 (m, *J*=7.5, 1H), 7.71 (d, *J*=9, 1H), 7.68 (d, *J*=8.5, 1H), 7.58-7.55 (m, 1H), 7.43-7.36 (m, 2H), 7.16-7.13 (m,1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 149.1, 140.3, 133.2, 130.2, 128.4, 128.2, 125.4, 124.8, 123.7, 123.2, 121.6, 119.4, 118.1. **HRMS (ESI)**: calculated for $C_{13}H_9N_2Se_2$ $[M+H]^+$ 352.9091, found 352.9086.

3-iodo-2-(2-iodophenyl)-2*H*-indazole (60)



Yellow solid (53 mg, 60% yield), mp 198.2-198.9 °C; PE/THF= 3/1; **^{1}H NMR**(500 MHz, DMSO-d_6) δ 8.10 (d, *J*=8 Hz, 1H), 7.73 (d, *J*=8.5 Hz, 1H), 7.66-7.63 (m, 1H), 7.57-7.52 (m, 2H), 7.42-7.38 (m, 2H), 7.23-7.20 (m, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 149.7, 143.7, 139.6, 132.3, 129.7, 129.6, 127.9, 127.5,123.3, 121.5, 118.5, 98.9, 83.7. **HRMS (ESI)**: calculated for $C_{13}H_9I_2N_2$ $[M+H]^+$446.8855, found 446.8849.

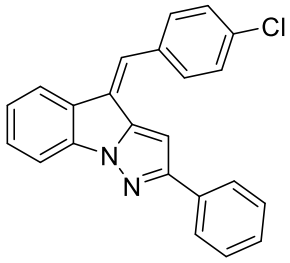
4-(4-chlorobenzyl)-2-phenyl-4*H*-pyrazolo[1,5-*a*]indol-4-ol (61)



White solid (123 mg, 33%), mp 197.4-198.1 °C; PE/THF= 3/1; **^{1}H NMR**(500 MHz, DMSO-d_6) δ 7.87 (d, *J*=8 Hz, 2H), 7.55 (d, *J*=7.5 Hz, 1H), 7.46-7.41 (m, 4H), 7.36-7.

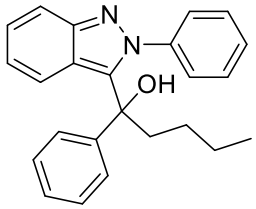
34 (m, 1H), 7.26 (s, 1H), 7.19 (d, *J*=8 Hz, 2H), 7.04 (d, *J*=8.5 Hz, 2H), 6.71 (s, 1H), 6.46 (s, 1H), 3.43 (d, *J*=13.5 Hz, 1H), 3.28 (d, *J*=13 Hz, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 155.4, 151.6, 141.1, 138.7, 135.1, 133.6, 132.7, 131.7,130.0, 129.2, 128.4, 127.9, 125.8, 125.5, 125.4, 110.0, 100.0, 76.1, 44.2. **HRMS (ESI)**: calculated for $C_{23}H_{18}ClN_2O$ $[M+H]^+$373.1107, found 373.1104.

(*Z*)-4-(4-chlorobenzylidene)-2-phenyl-4*H*-pyrazolo[1,5-*a*]indole (62)



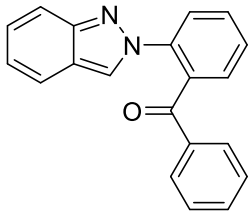
Green solid (67 mg, 95% yield), mp 174.7.3-175.5 °C; PE/THF= 3/1; **^{1}H NMR**(500 MHz, DMSO-d_6) δ 8.03 (d, *J*=7.5 Hz, 1H), 7.99 (d, *J*=8 Hz, 2H), 7.87 (d, *J*=8 Hz, 2H), 7.82 (s, 1H), 7.67-7.63 (m, 3H), 7.52-7.45 (m, 3H), 7.40-7.37 (m, 1H), 7.35-7.32 (m, 1H), 7.26 (s, 1H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 155.8, 141.7, 137.6, 134.6, 134.1, 133.2, 131.7, 131.4, 130.0, 129.6, 129.2, 128.7, 127.6, 126.0, 125.3, 123.9, 122.3, 110.3, 100.7. **HRMS (ESI)**: calculated for $C_{23}H_{16}ClN_2$ $[M+H]^+$355.1002, found 355.1009.

1-phenyl-1-(2-phenyl-2*H*-indazol-3-yl)pentan-1-ol (63)



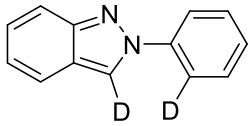
White solid (30 mg, 58% yield); mp 214.6-215.6 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.97 (d, *J*=8.5 Hz, 1H), 7.58 (d, *J*=8.5, 1H), 7.39-7.36 (m, 1H), 7.30-7.25 (m, 3H), 7.16-7.15 (m, 3H), 7.09-7.07 (m, 3H), 6.93-6.92 (d, *J*=6.93 Hz, 1H), 5.91 (s, 1H), 2.38-2.32 (m, 1H), 2.27-2.22 (m, 1H), 1.24-1.11 (m, 4H), 0.78-0.75 (m, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 147.9, 146.5, 142.1, 142.0, 128.9, 128.0, 127.9, 127.8, 127.0, 126.3, 126.2, 123.4, 121.7, 120.6, 117.7, 76.1, 41.5, 25.7, 22.8, 14.4. **HRMS(ESI)**: calculated for $C_{24}H_{25}N_2O$ $[M+H]^+$ 357.1967, found 357.1971.

(2-(2*H*-indazol-2-yl)phenyl)(phenyl)methanone (64)



White solid (55 mg, 64% yield); mp 191.4-192.3 °C; PE/THF= 3/1; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.68 (d, *J*=7.5 Hz, 1H), 7.61-7.56 (m, 4H), 7.51-7.48 (m, 2H), 7.45(d, *J*=8.5 Hz, 1H), 7.21-7.18 (m, 1H), 7.13-7.09 (m, 3H), 6.94-6.91 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.4, 149.5, 139.0, 136.6, 134.9, 132.7, 131.3, 129.8, 128.6, 128.5, 128.0, 126.6, 124.4, 123.6, 122.5, 122.4, 120.2, 117.7. **HRMS(ESI)**: calculated for $C_{20}H_{15}N_2O$ $[M+H]^+$ 299.1184, found 299.11778.

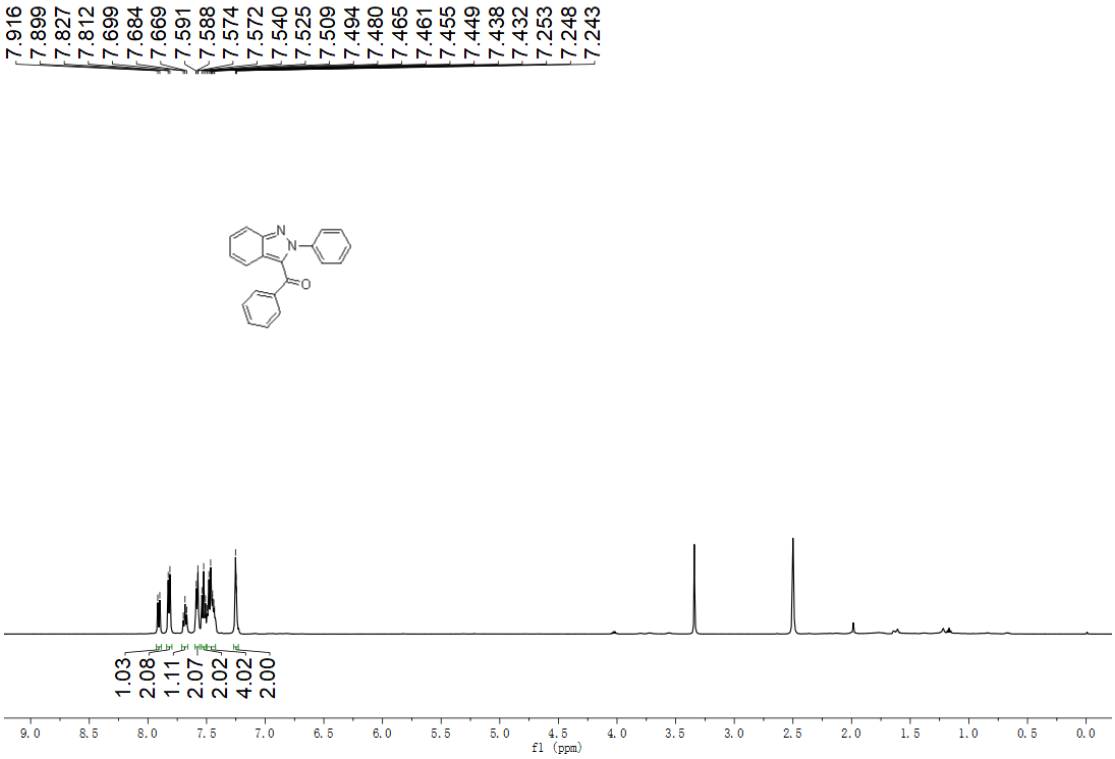
2-(phenyl-2-*d*)-2*H*-indazole-3-*d* (1-d_2)



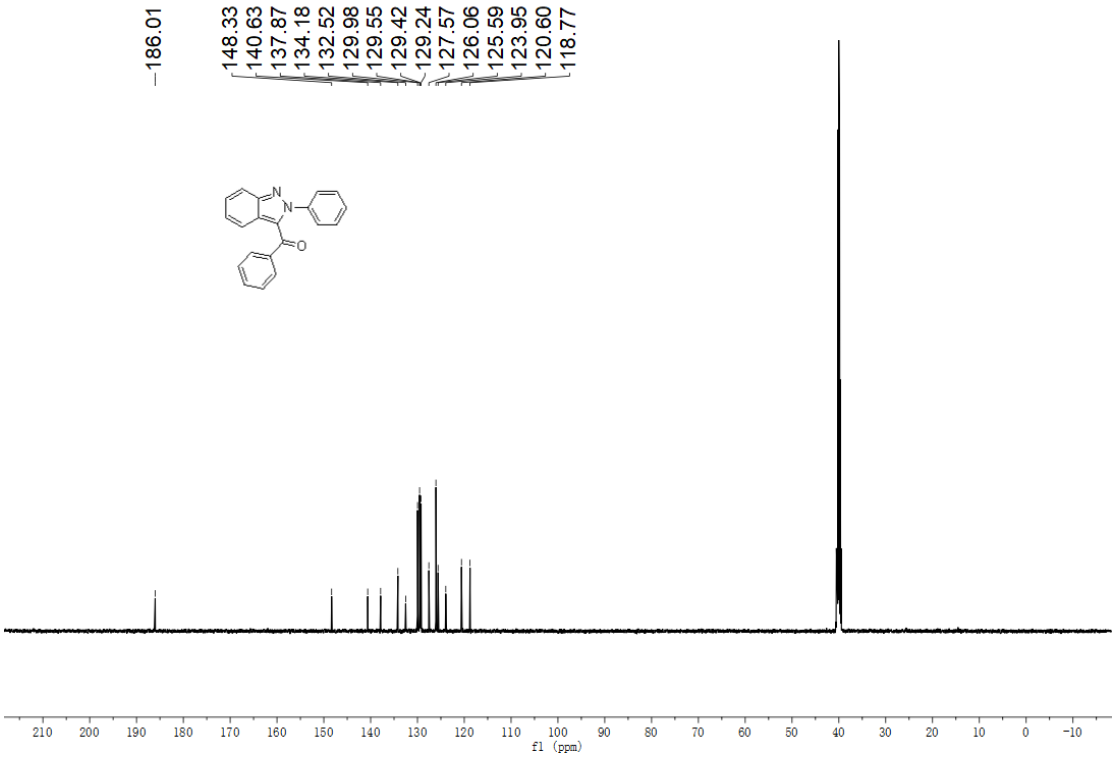
White solid (38 mg, 96% yield); mp 82.6-82.9 °C; PE/THF=3/1; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.14 (d, *J*=8 Hz, 1H), 7.80 (d, *J*=8.5 Hz, 1H), 7.77 (d, *J*=8.5 Hz, 1H)，7.63-7.60 (m, 2H), 7.48-7.45 (m, 1H), 7.36-7.33 (m, 1H), 7.15-7.12 (m, 1H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 149.5, 140.4, 140.3, 130.1, 130.0, 128.3, 127.2, 123.0, 122.6, 121.4, 118.0. **HRMS (ESI)**: calculated for $C_{13}H_9D_2N_2$ $[M+H]^+$197.1043, found 197.1039.

5. ^{1}H, ^{13}C and ^{19}F NMR spectra of products

^{1}H and ^{13}C NMR spectra of compound 2.

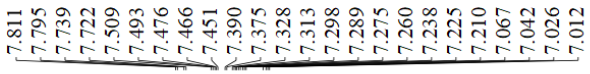


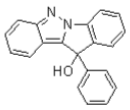
(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

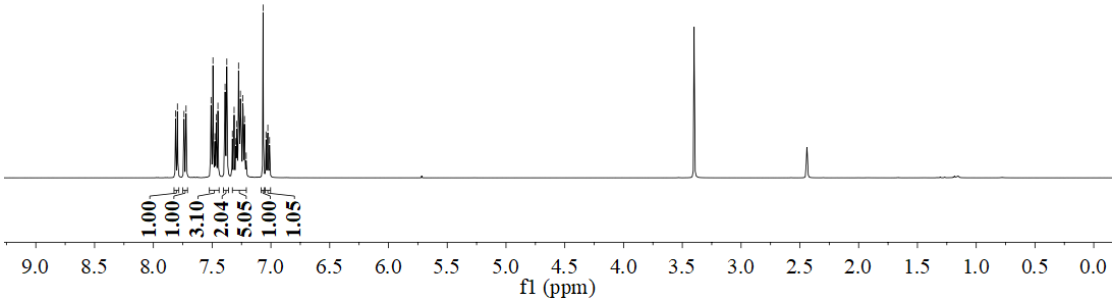


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

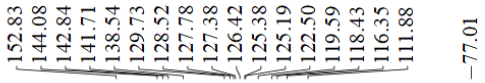
^{1}H and ^{13}C NMR spectra of compound 3.

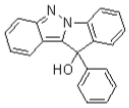






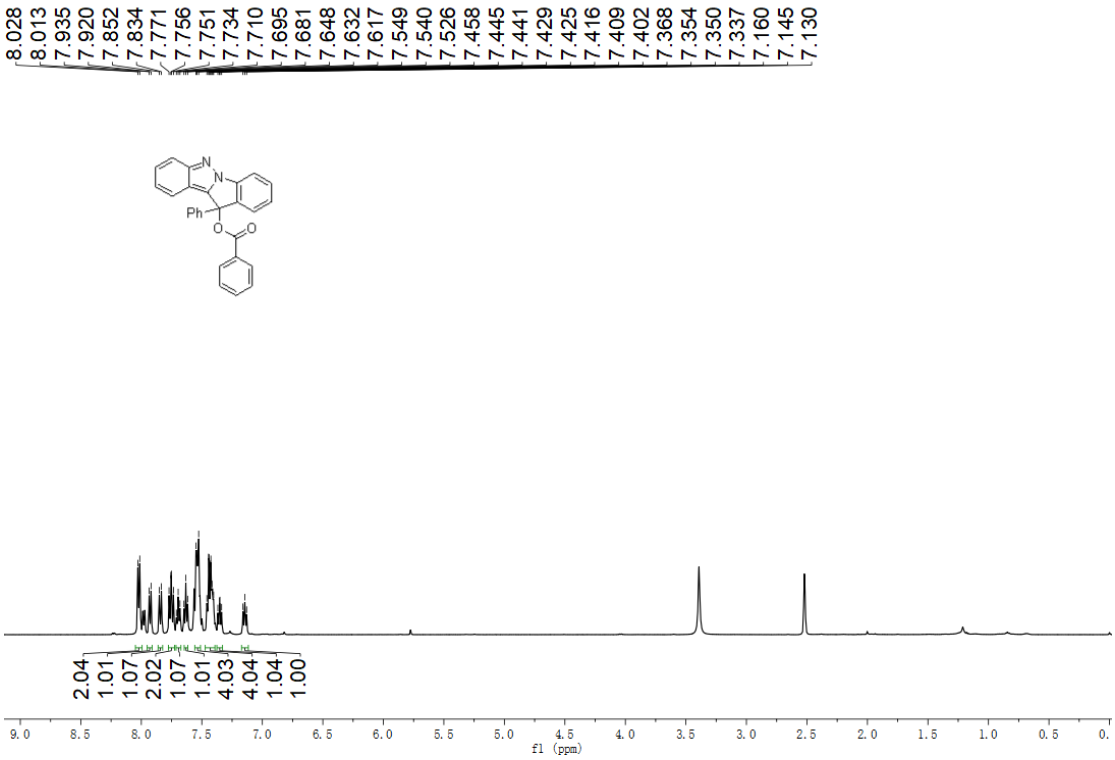
(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)



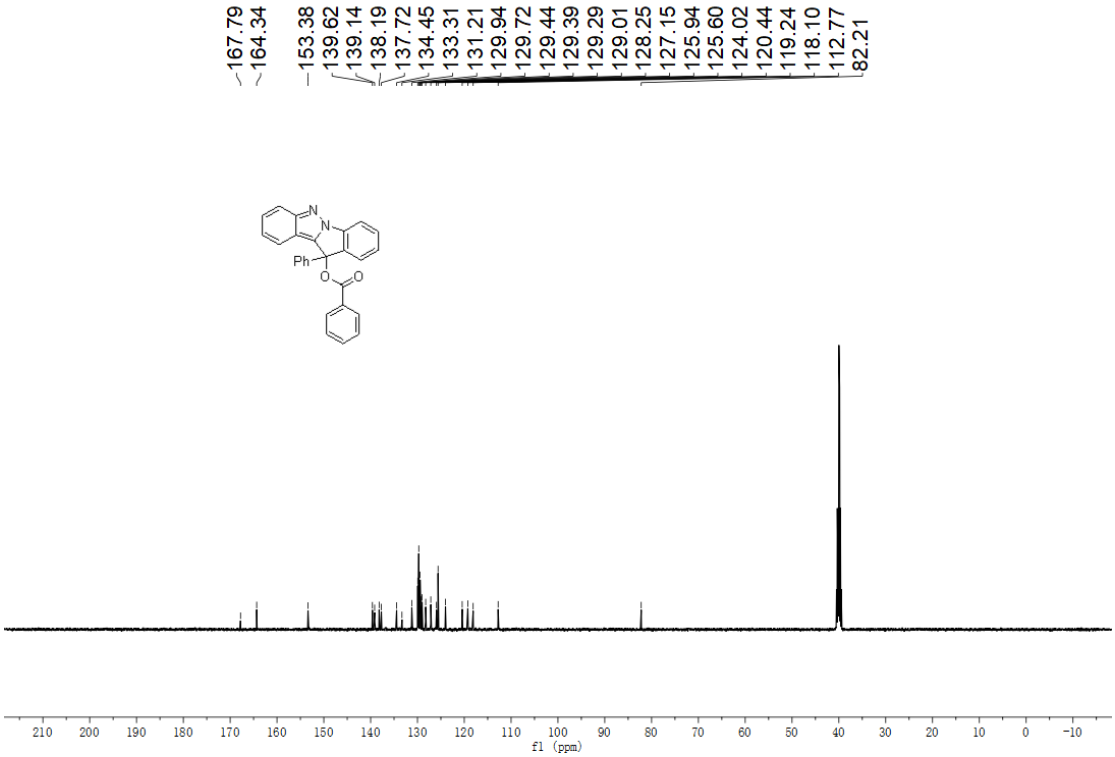


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 4.

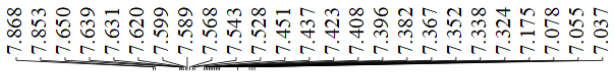


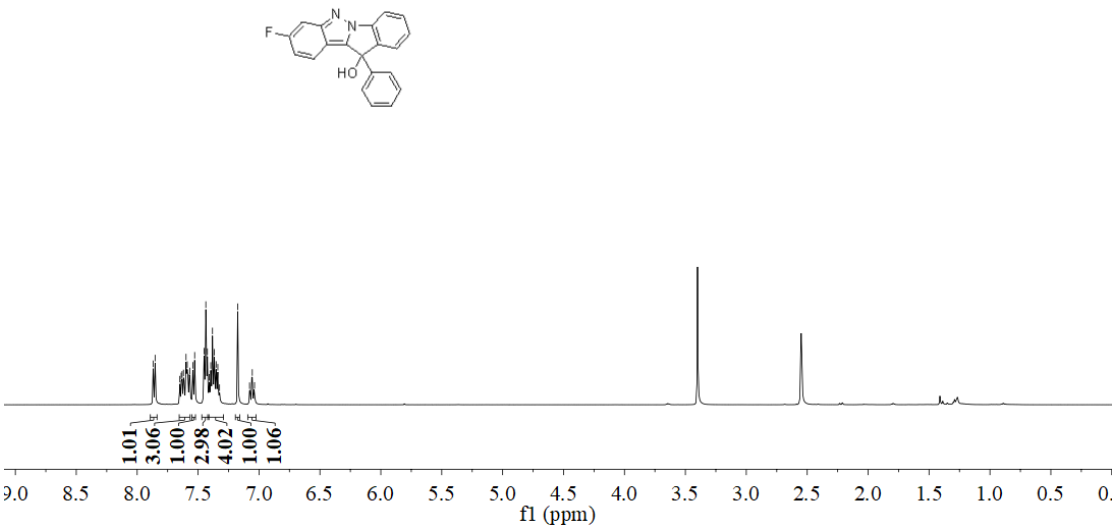
(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)



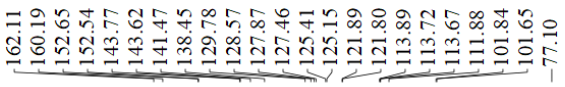
(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

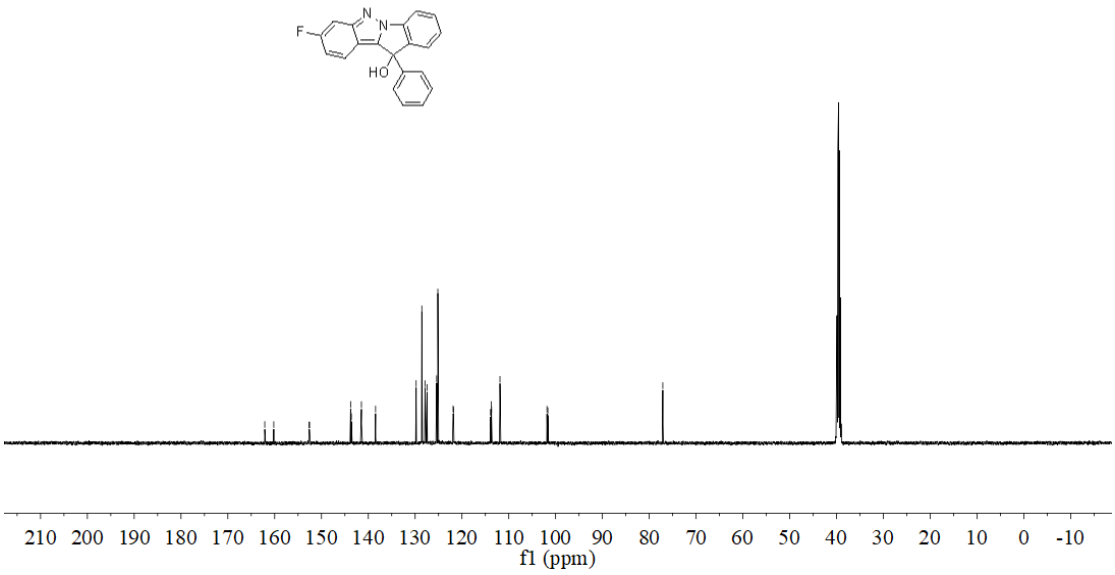
^{1}H ,^{13}C and ^{19}F NMR spectra of compound 5.



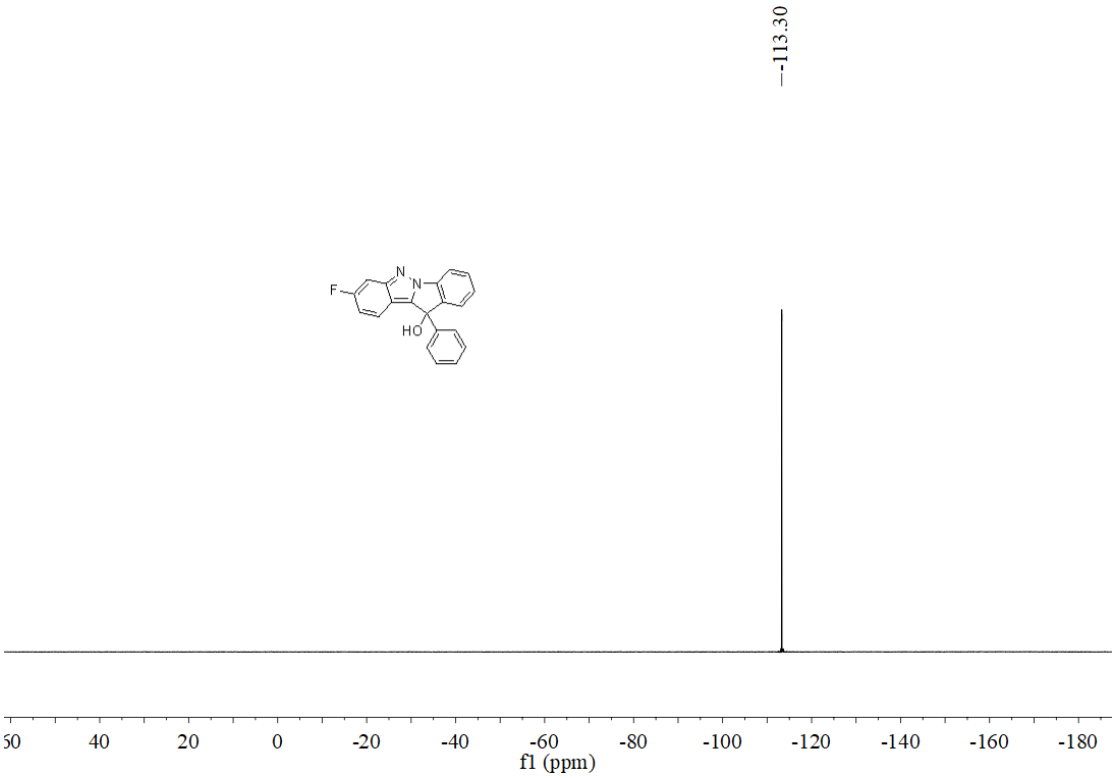


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)



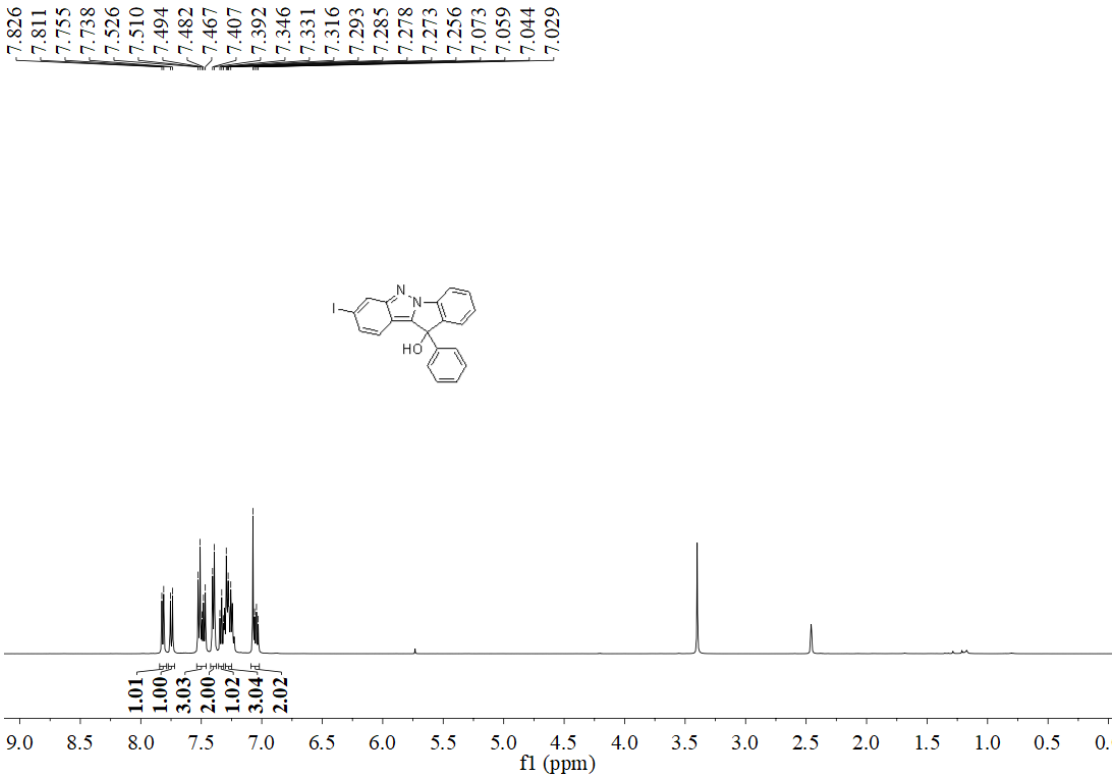


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

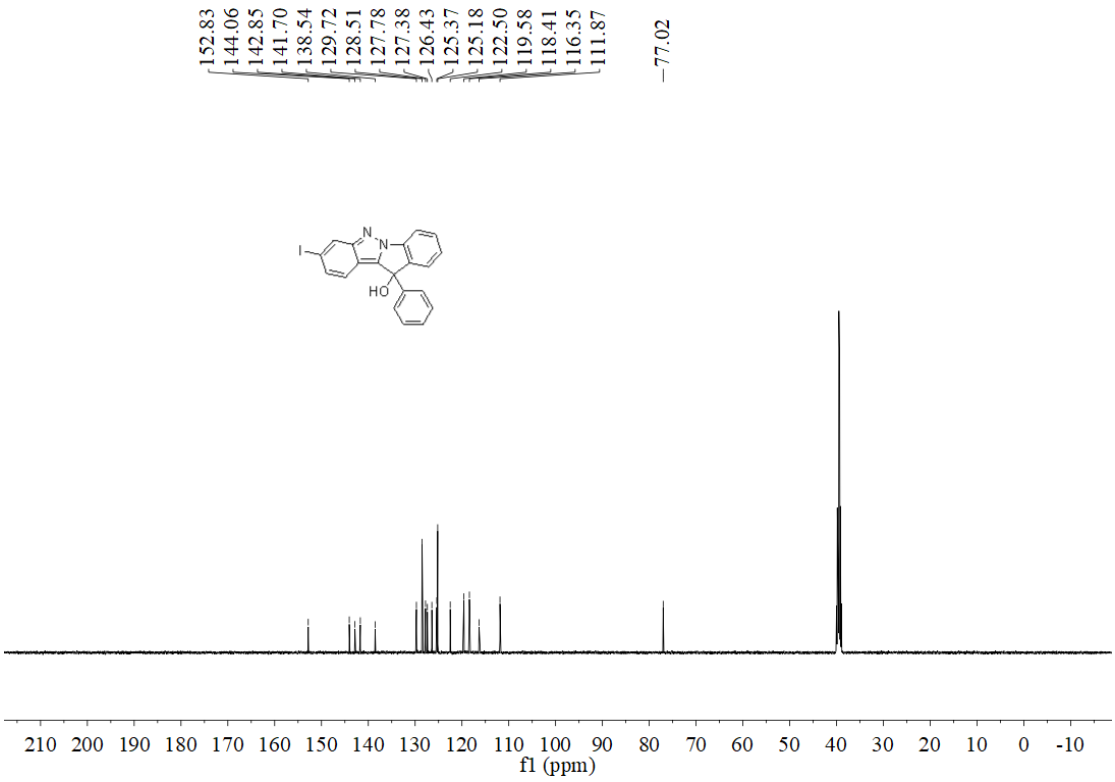


(470 MHz for ^{19}F NMR with DMSO-*d*$_6$ as solvent)

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

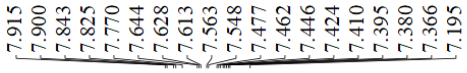


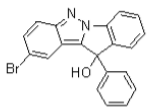
(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

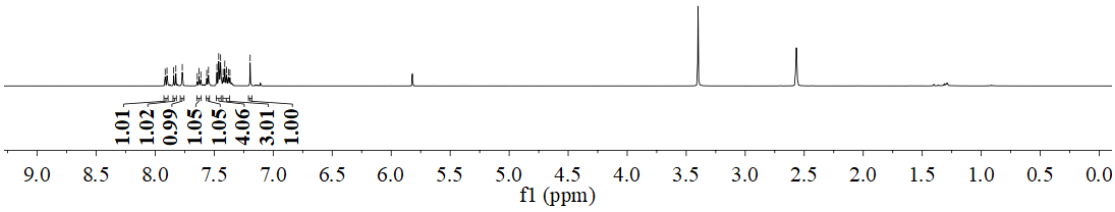


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

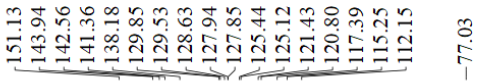
^{1}H and ^{13}C NMR spectra of compound 7.

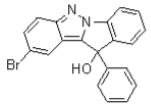


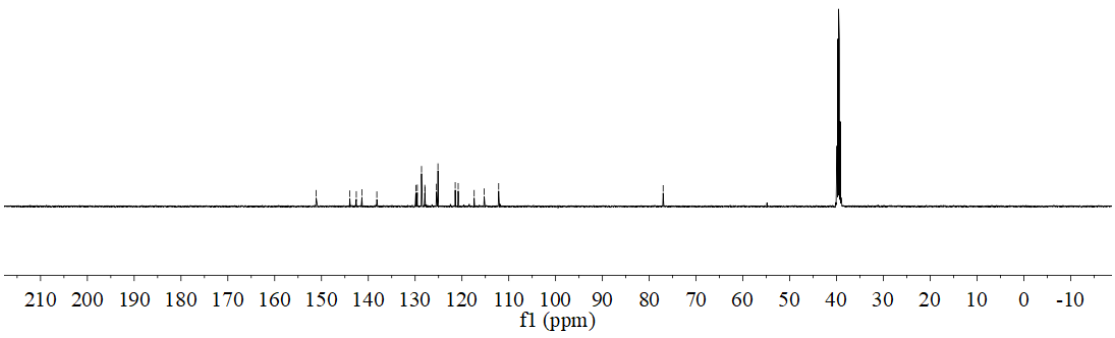




(400 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

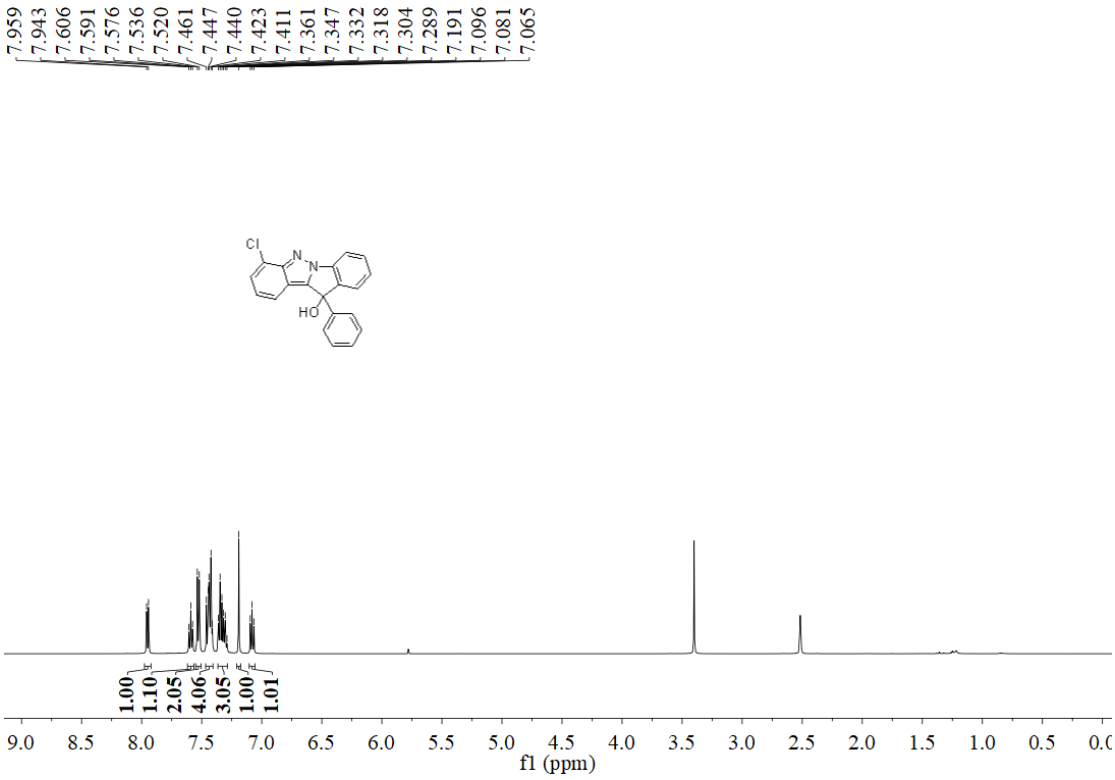




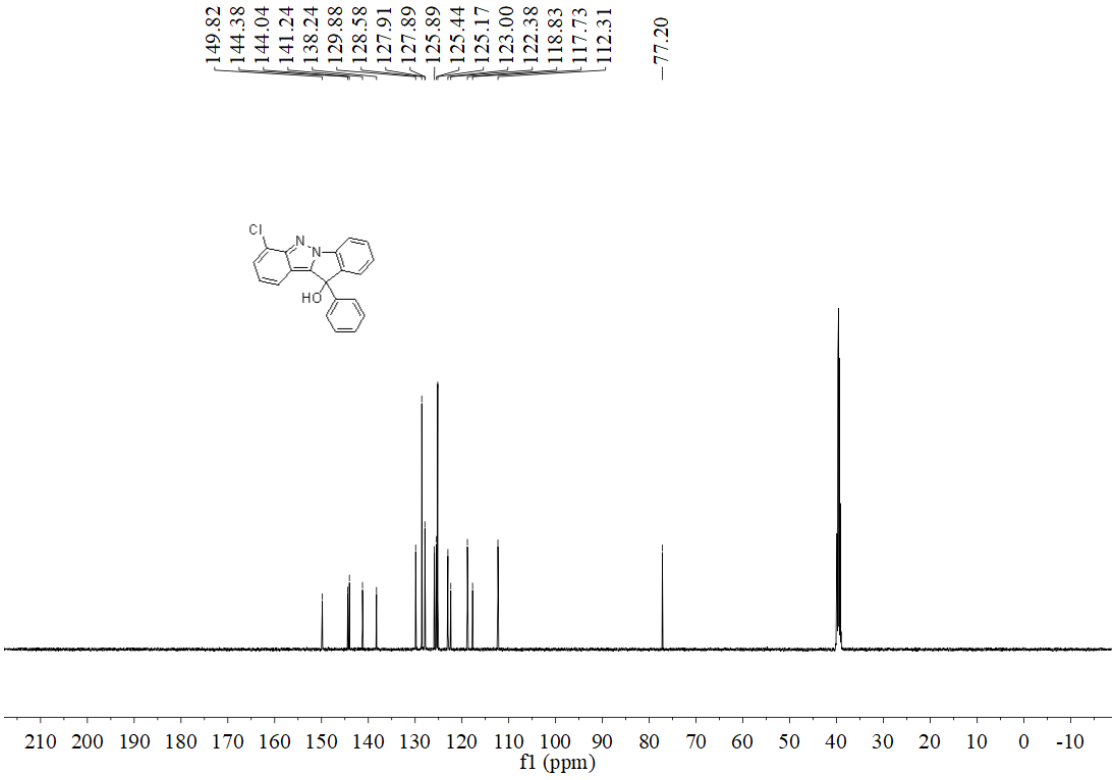


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

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

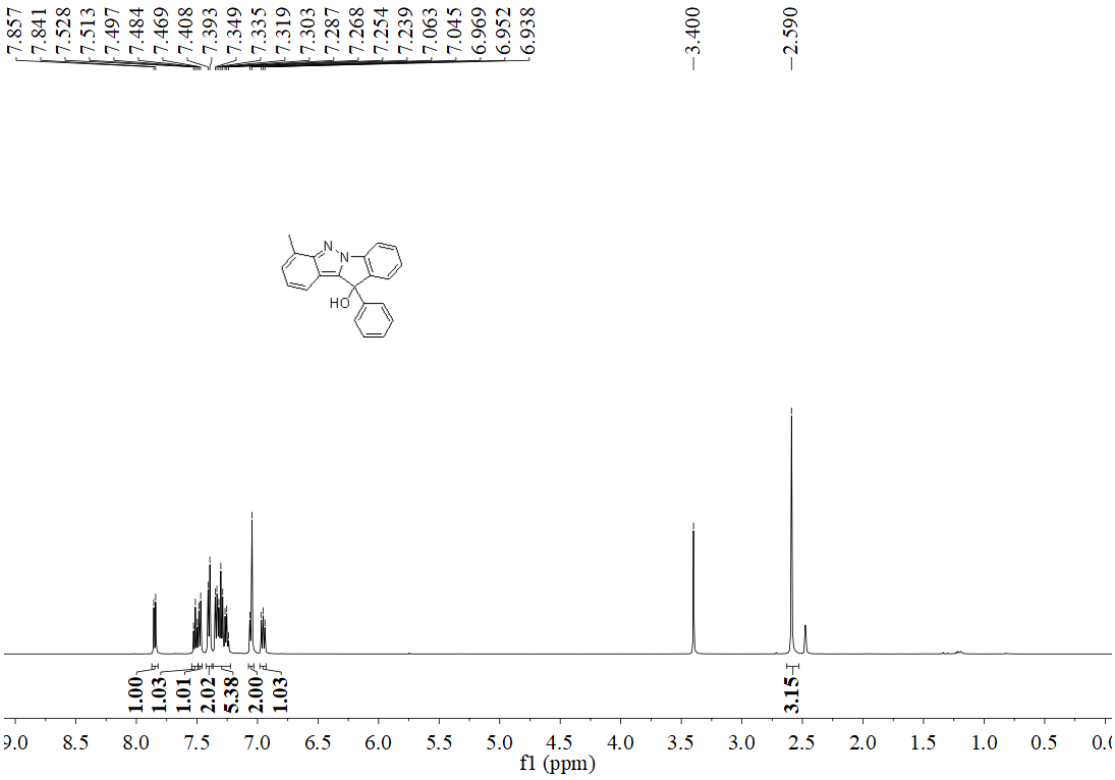


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

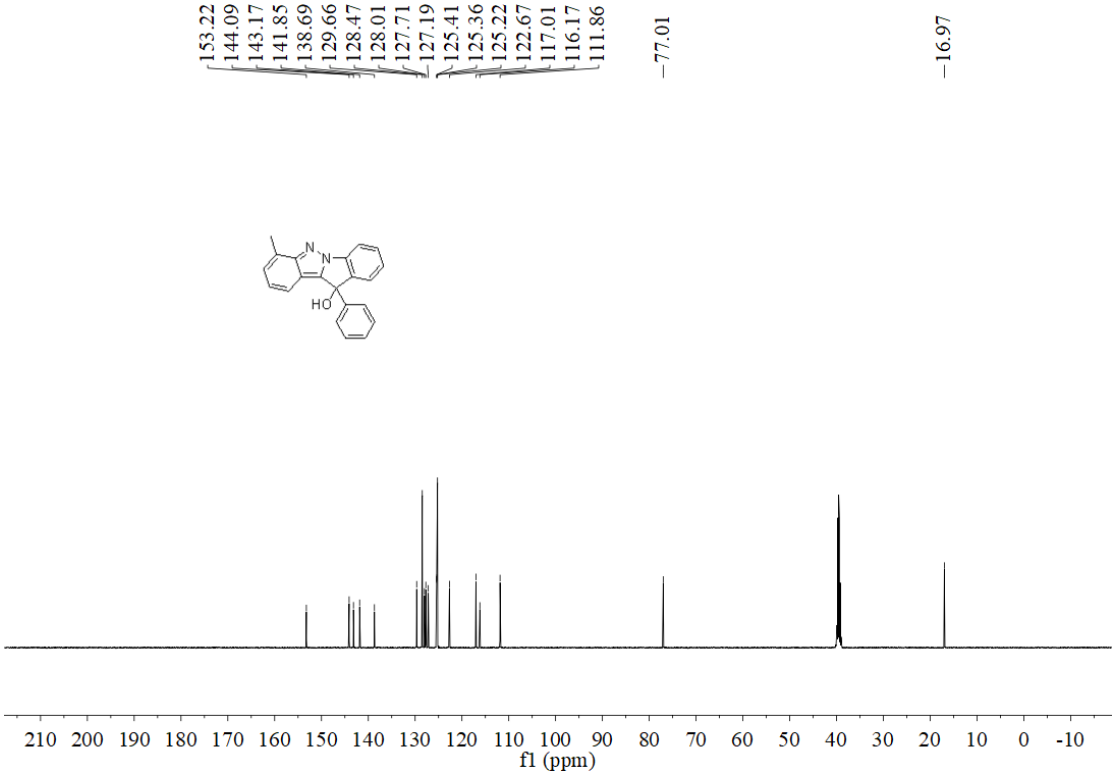


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 9.

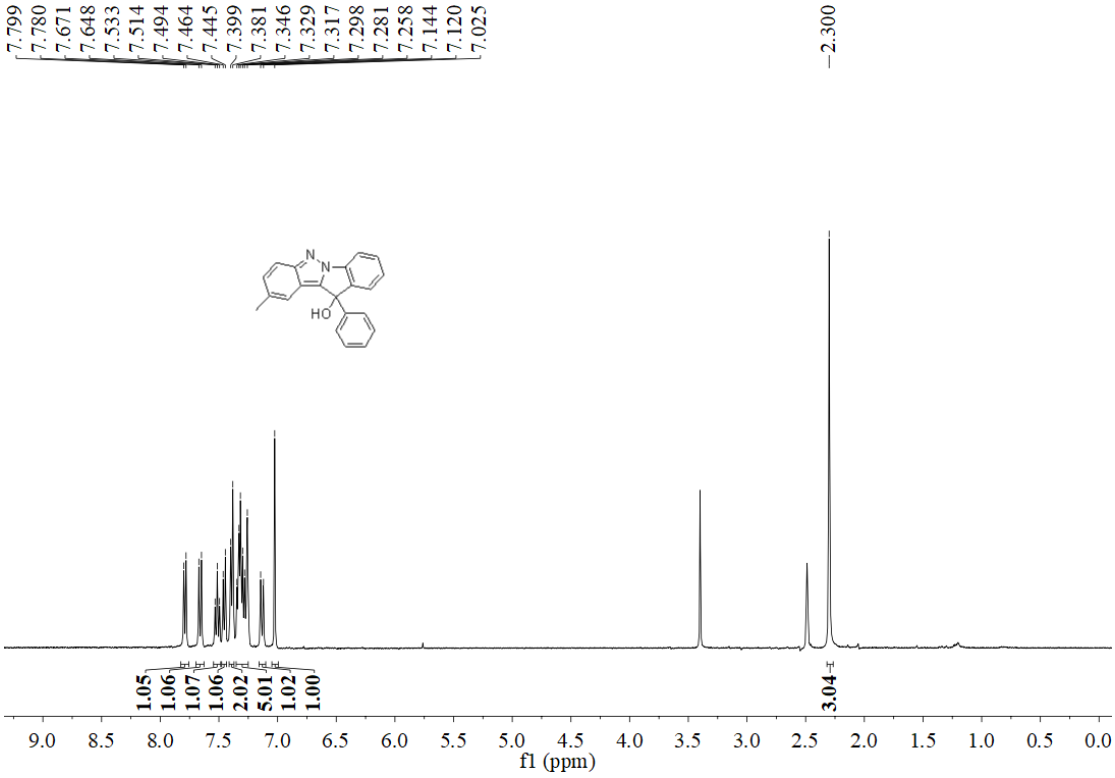


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

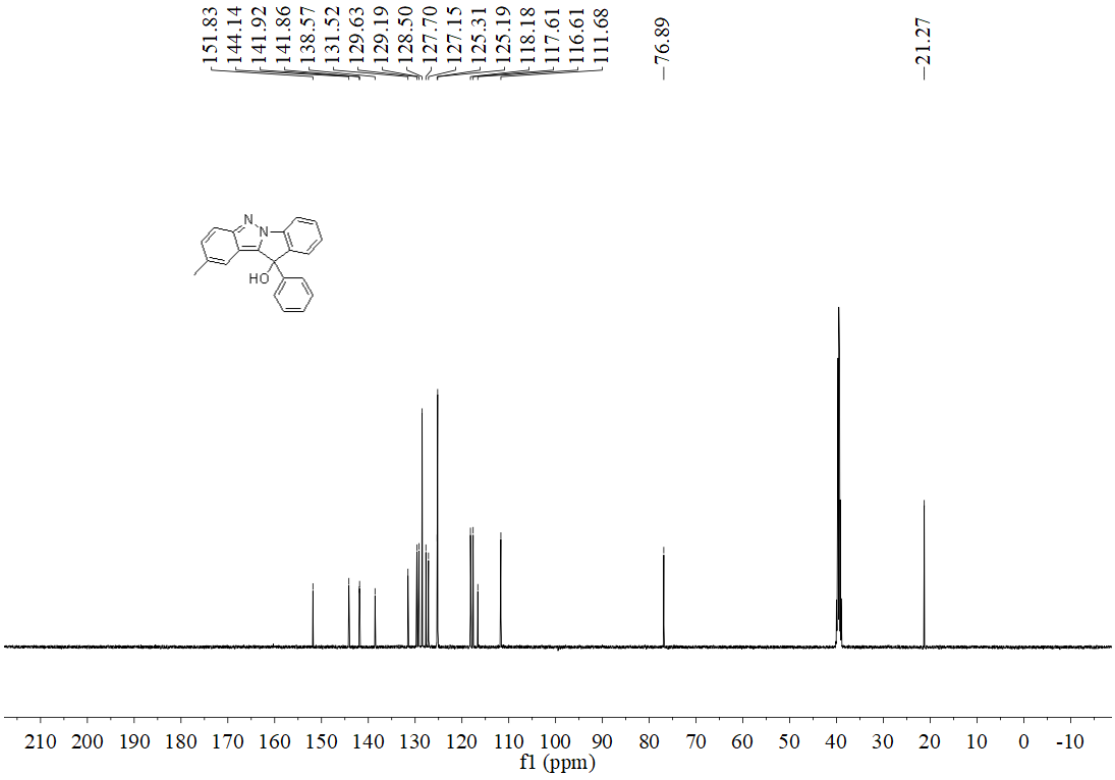


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

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

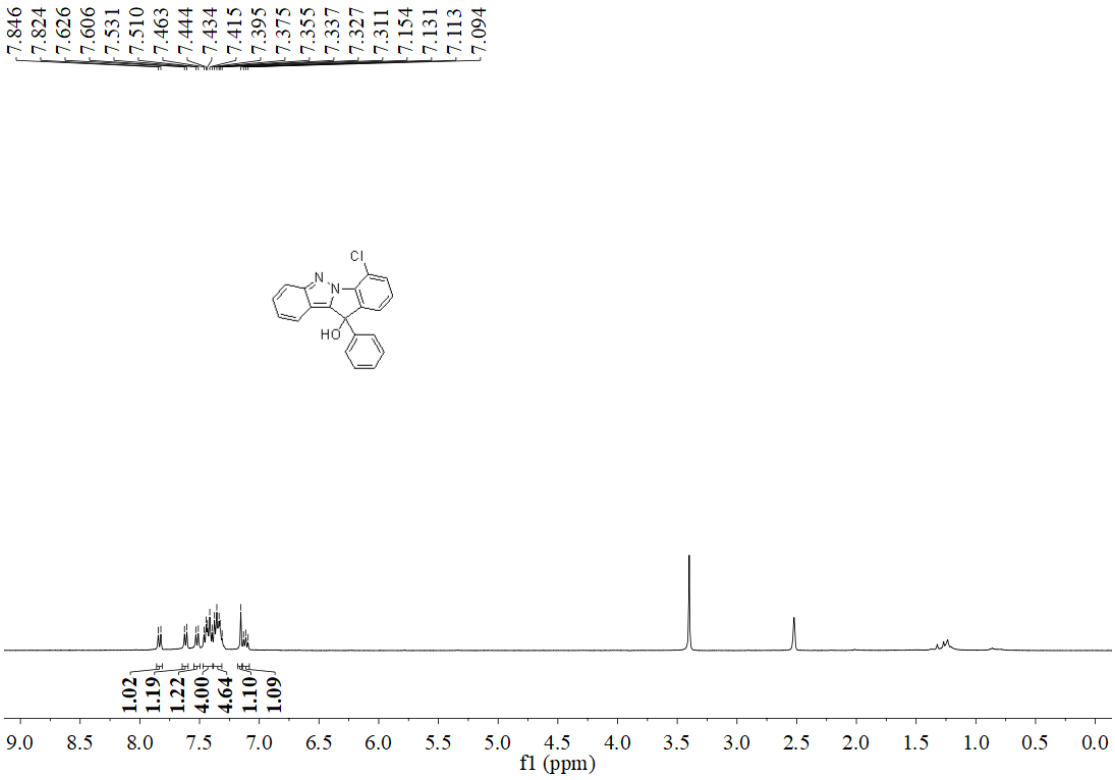


(400 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

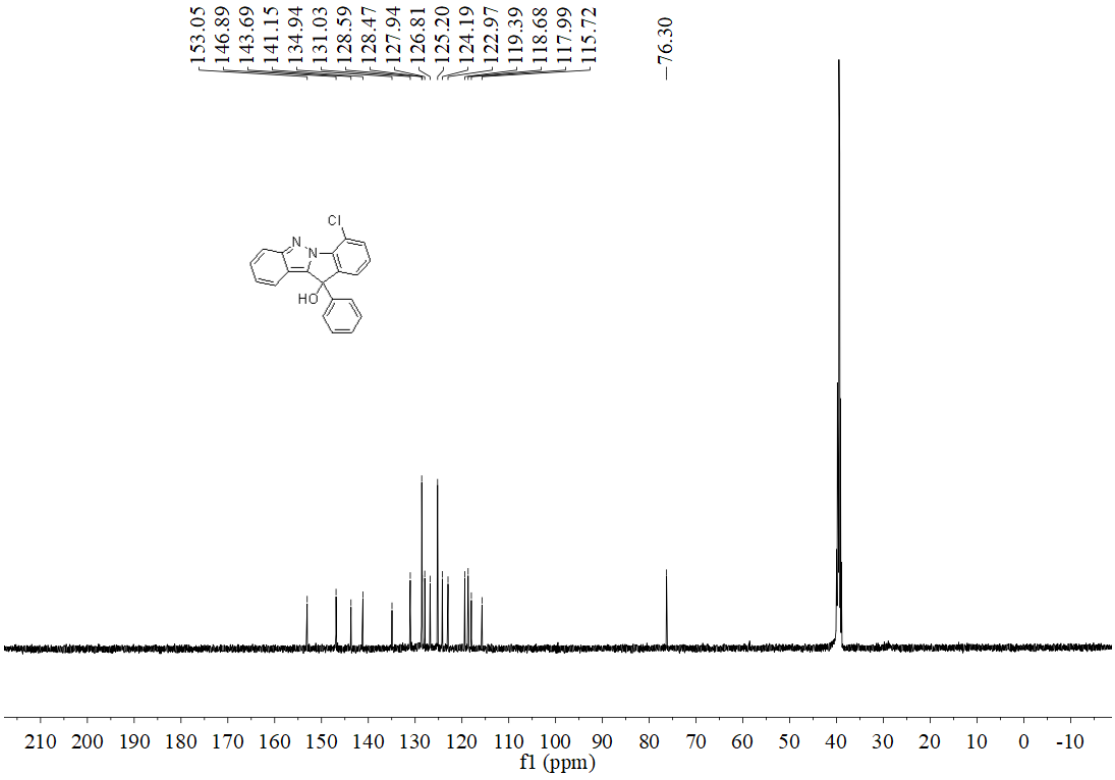


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 11.

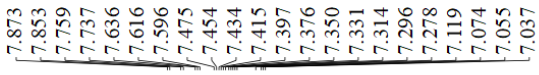


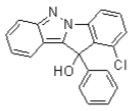
(400 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

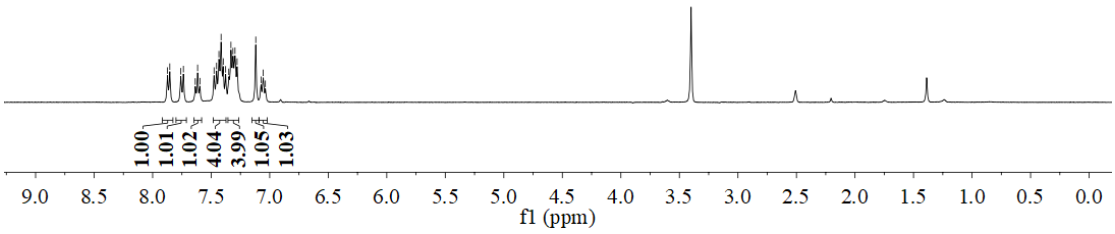


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

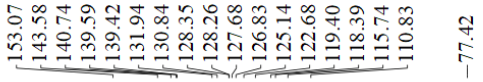
^{1}H and ^{13}C NMR spectra of compound 12.

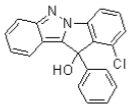


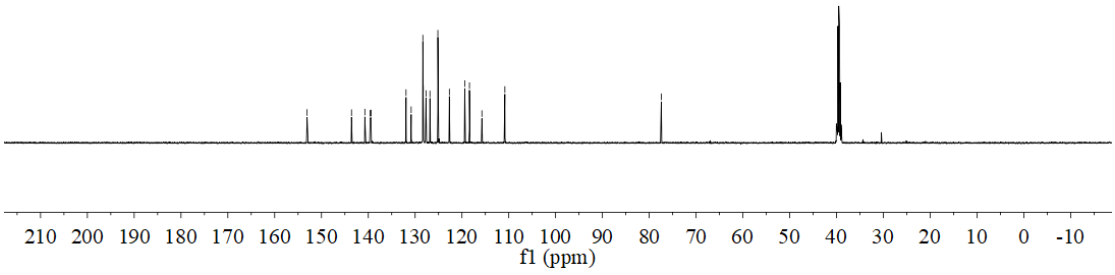




(400 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

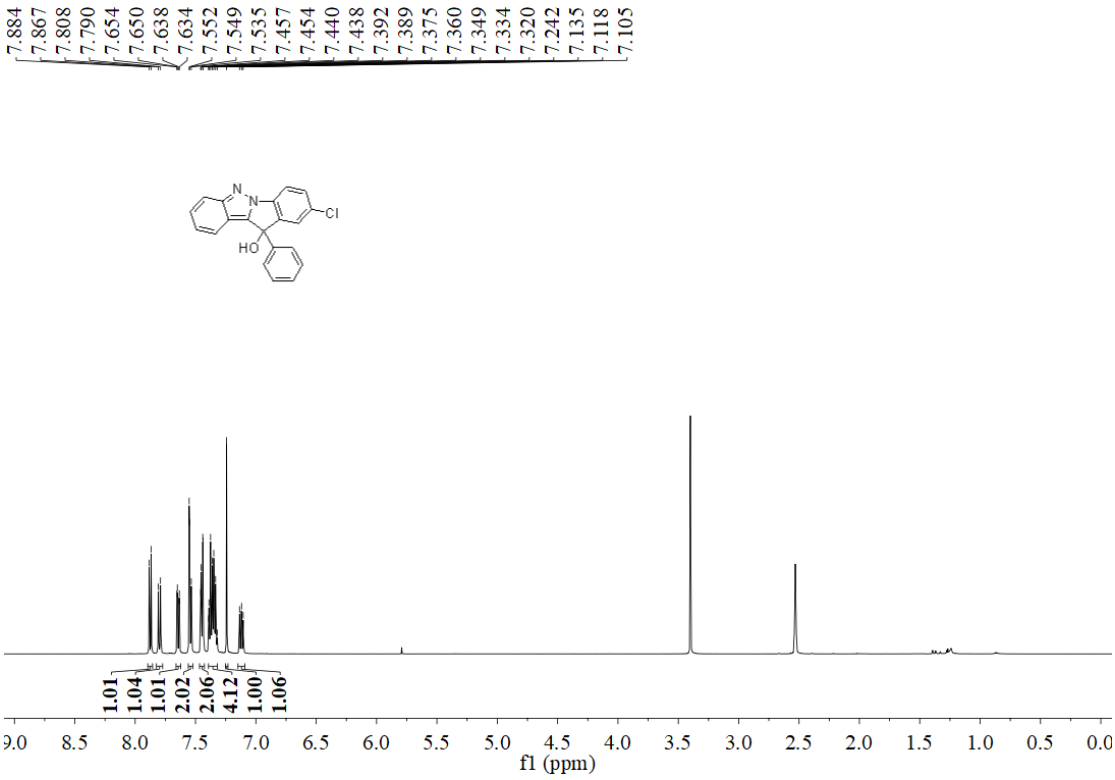




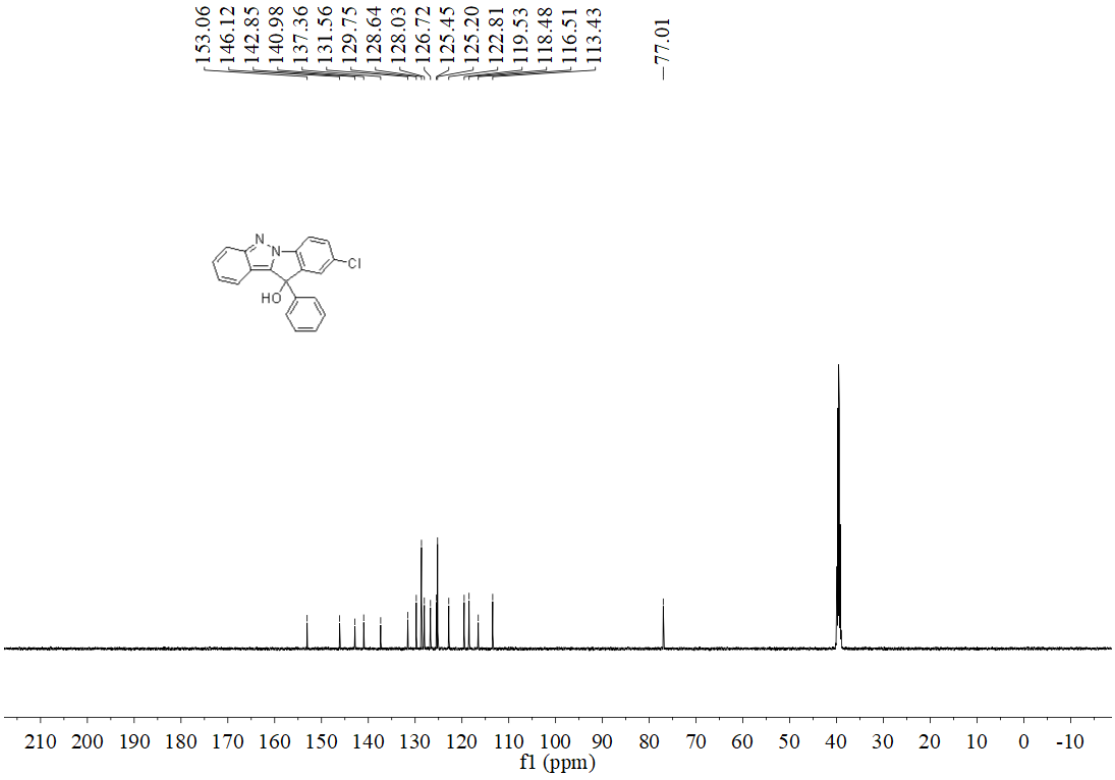


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 13.

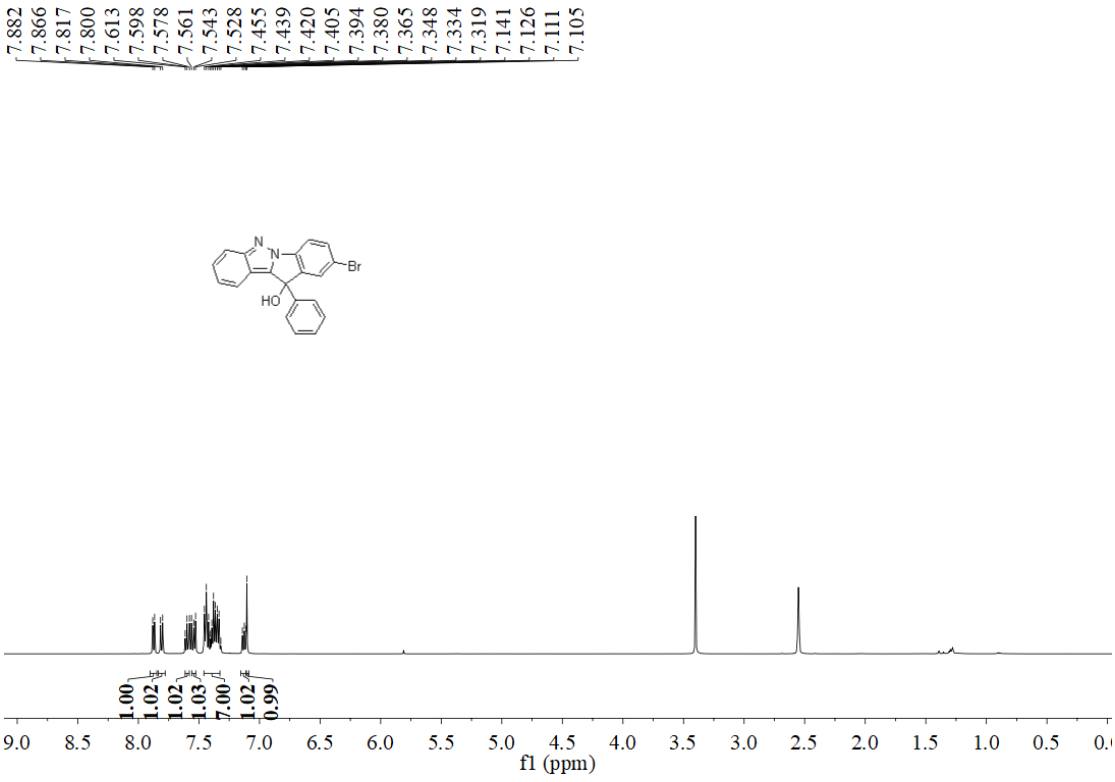


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

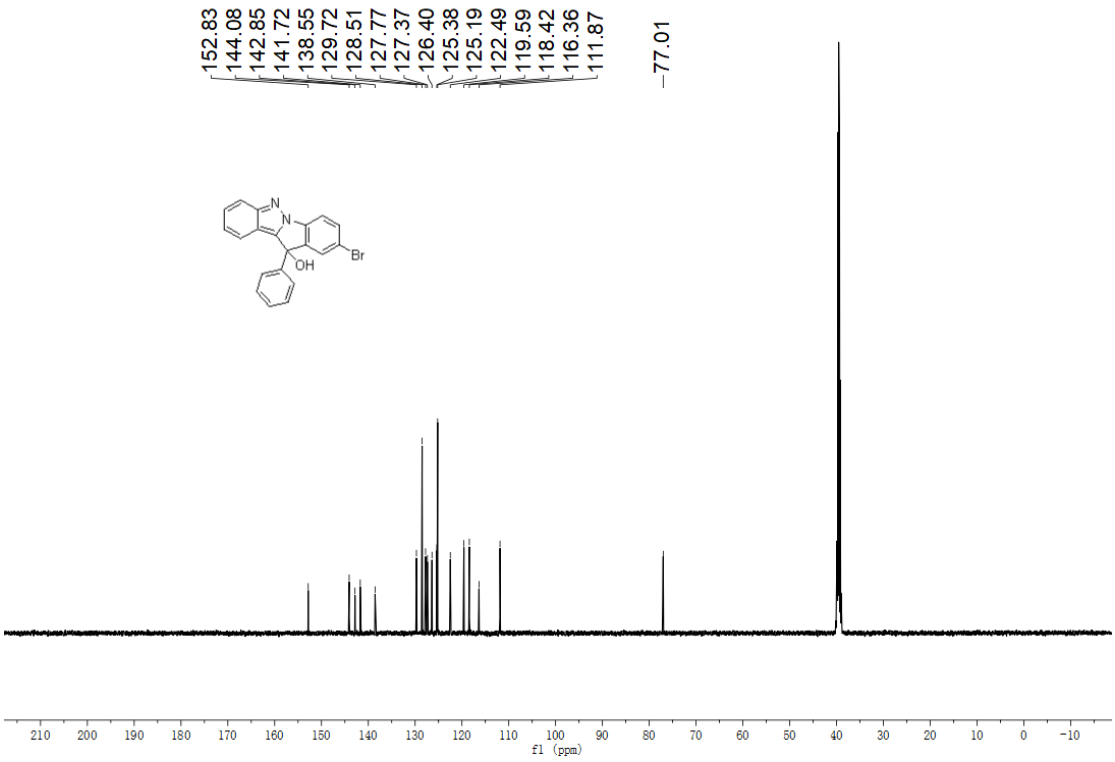


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 14.

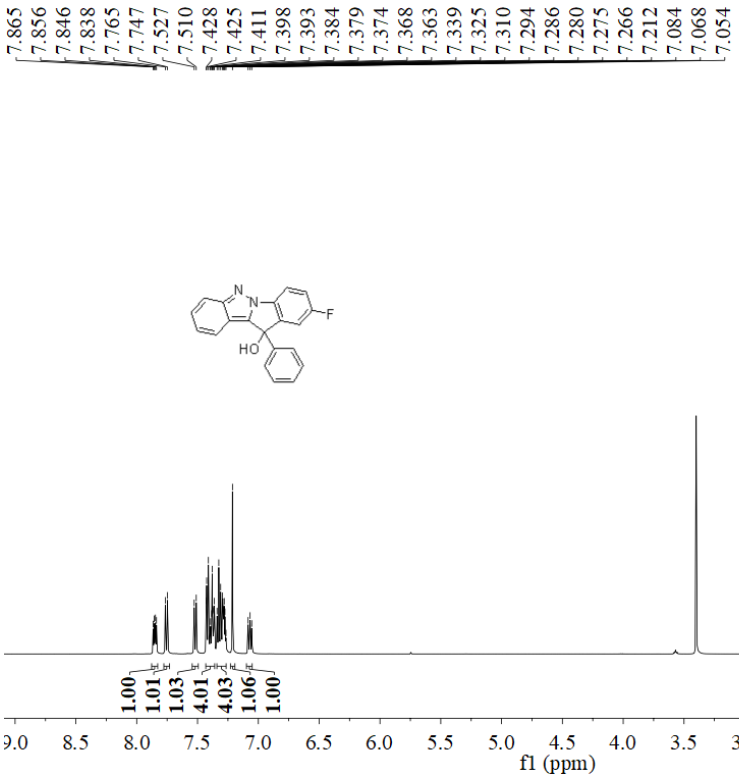


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

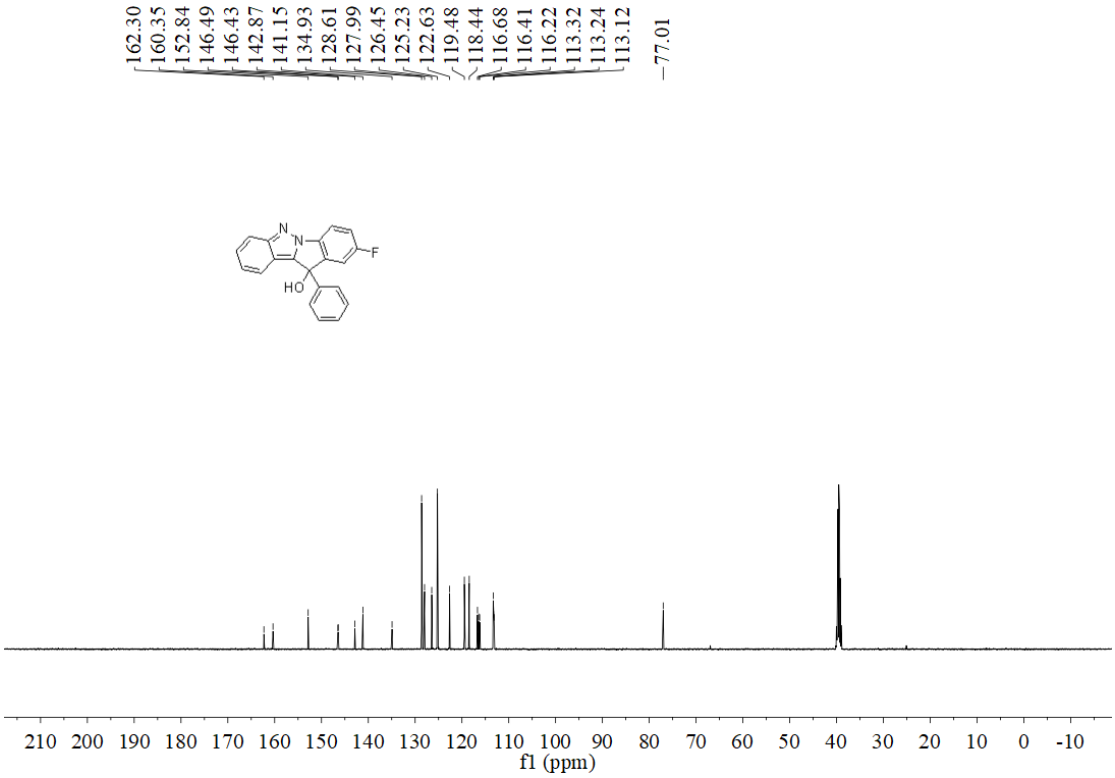


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

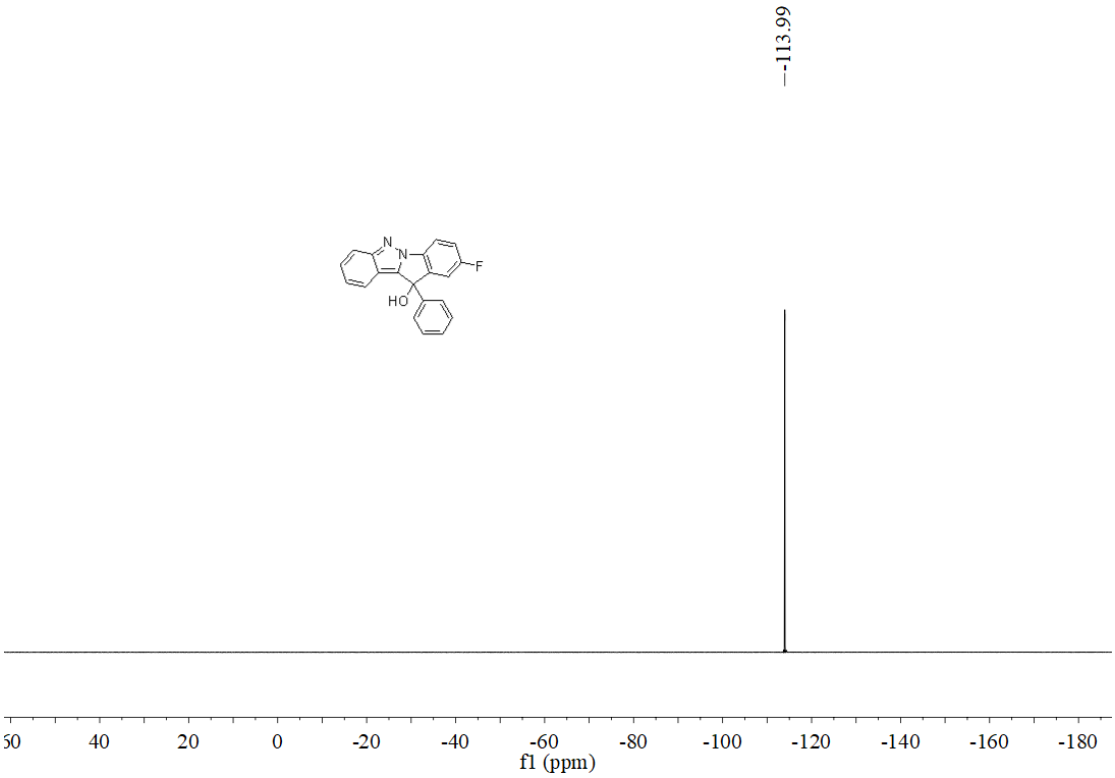
^{1}H ,^{13}C and ^{19}F NMR spectra of compound 15.



(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

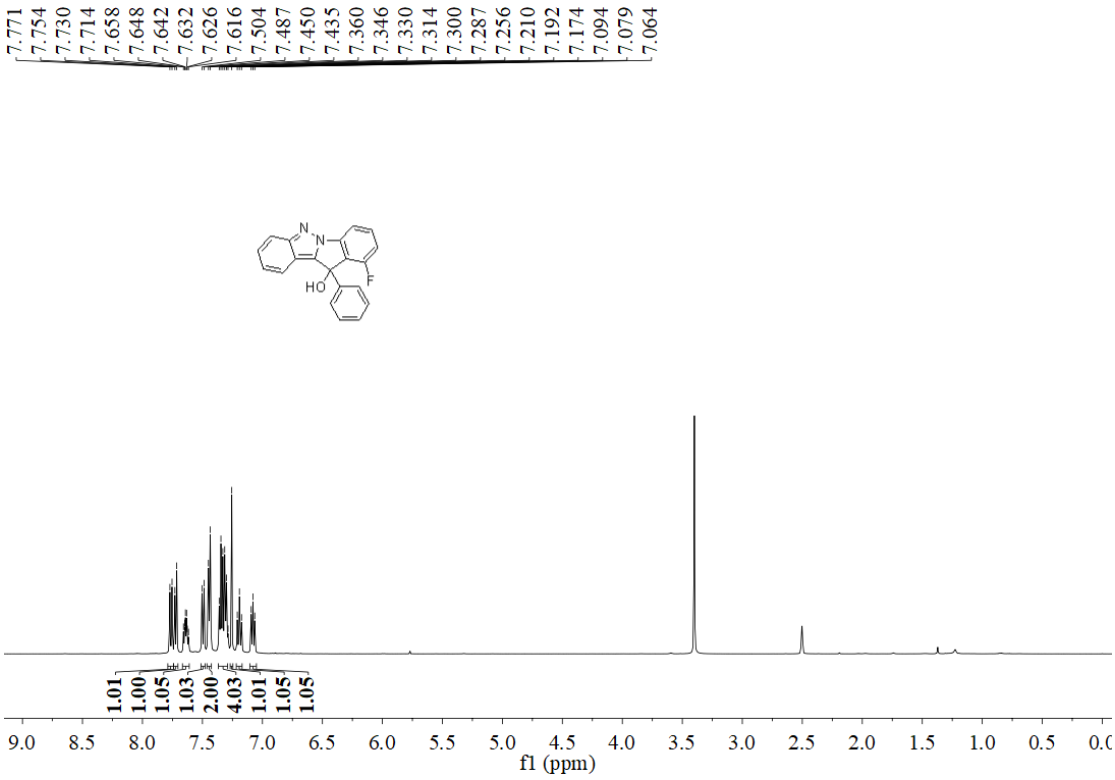


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

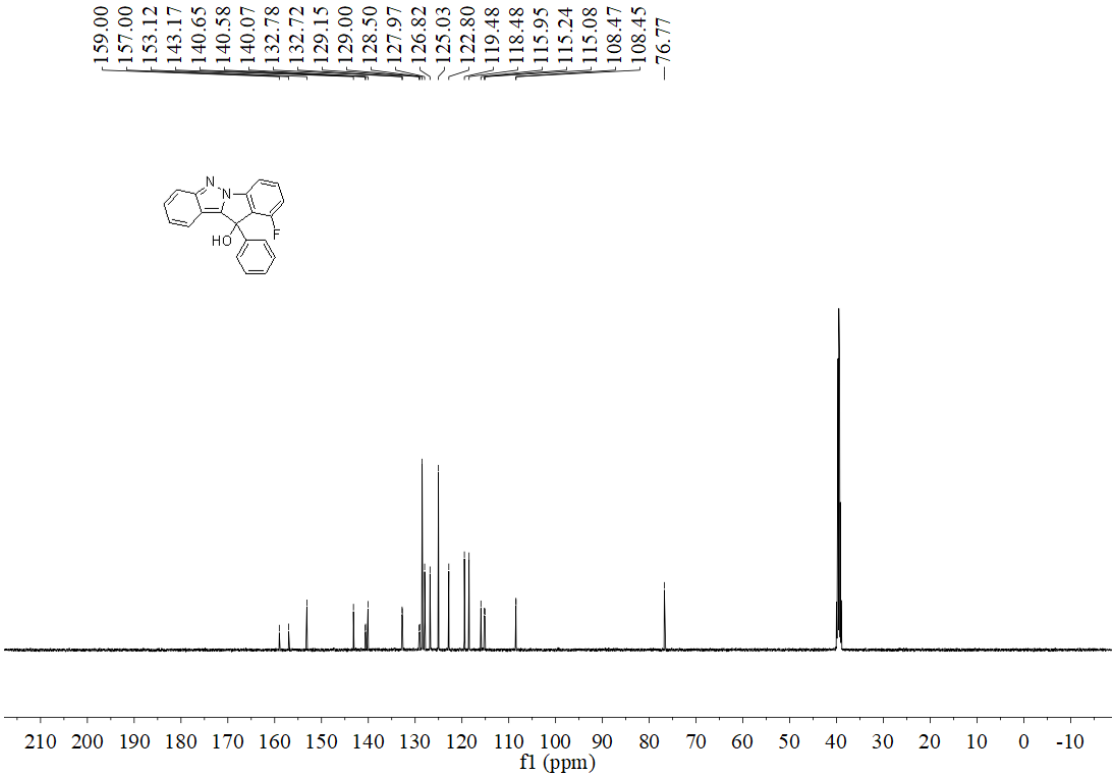


(470 MHz for ^{19}F NMR with DMSO-*d*$_6$ as solvent)

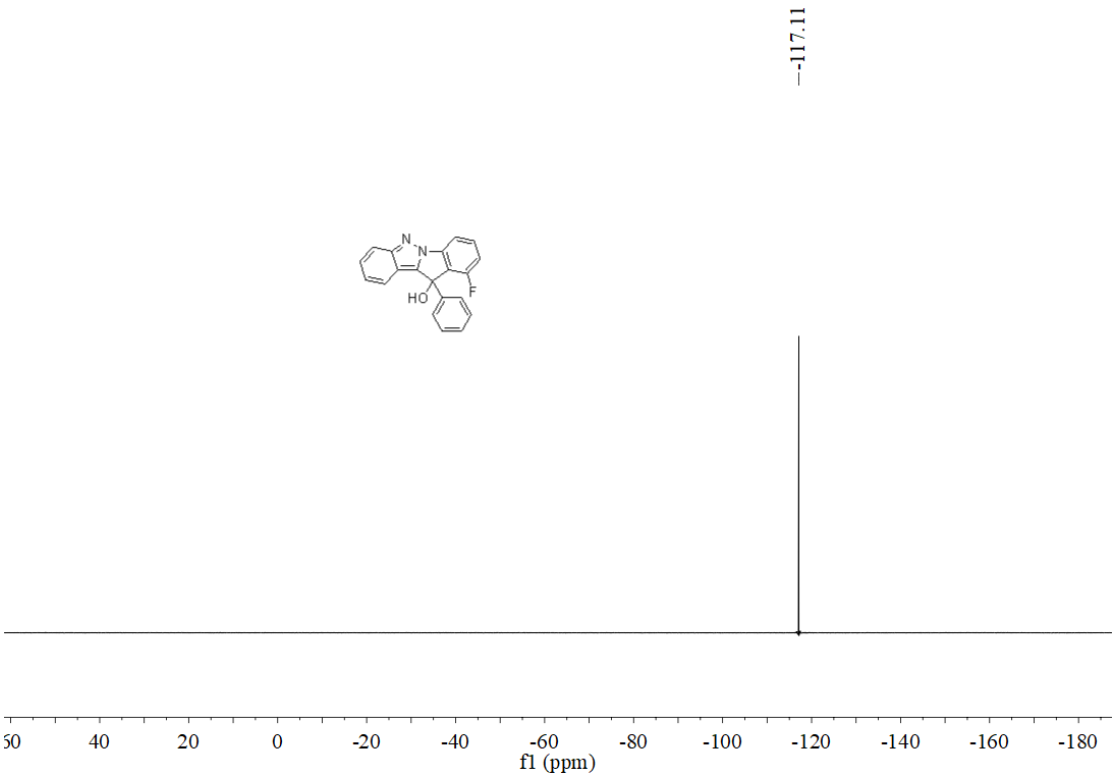
^{1}H and ^{13}C NMR spectra of compound 16.



(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

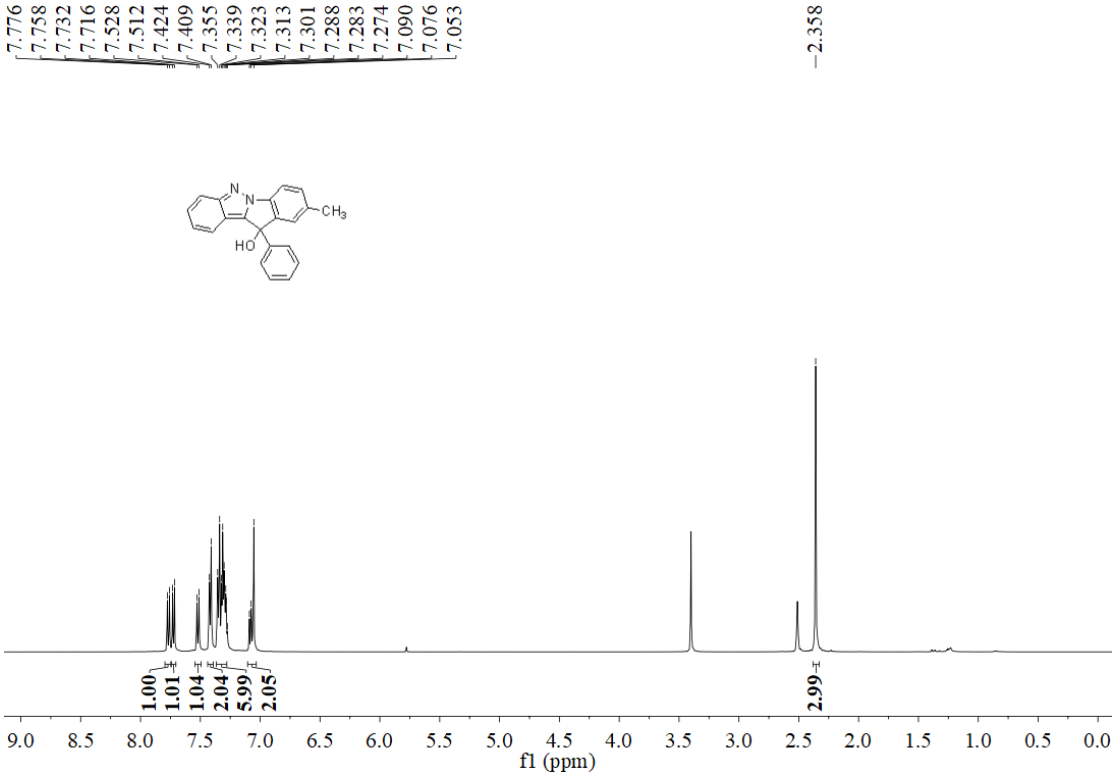


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

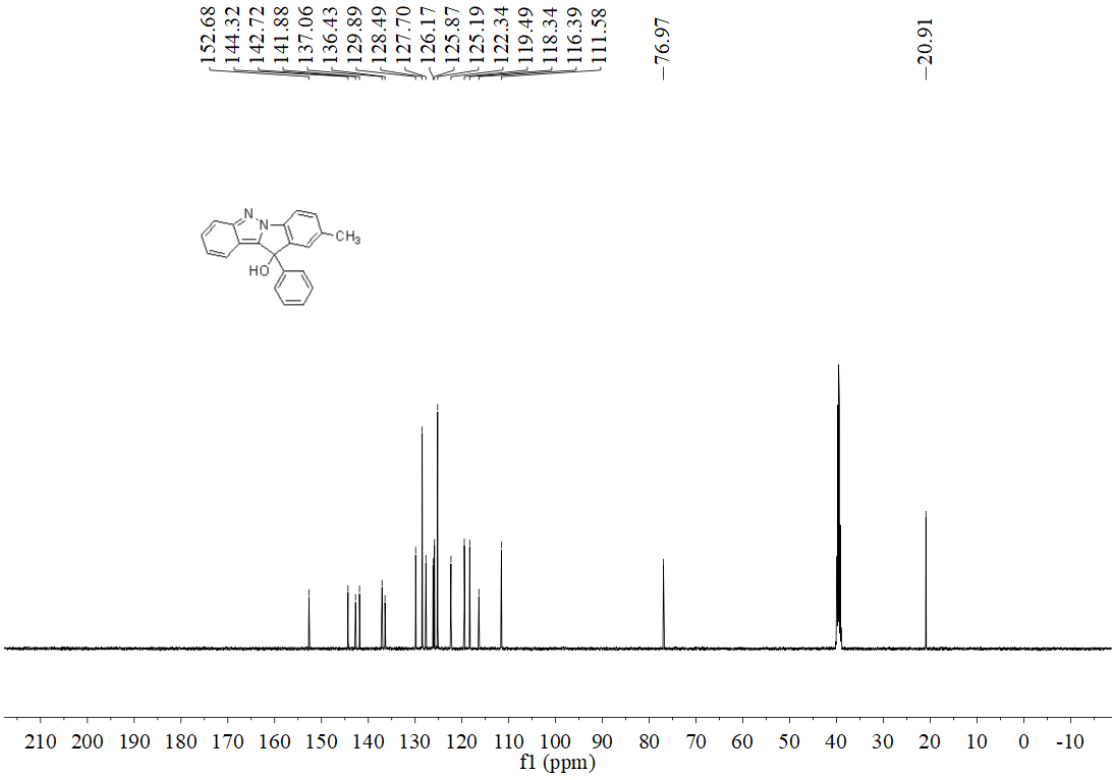


(470 **MHz for ^{19}F NMR with DMSO-*d*$_6$ as solvent)**

^{1}H and ^{13}C NMR spectra of compound 17.

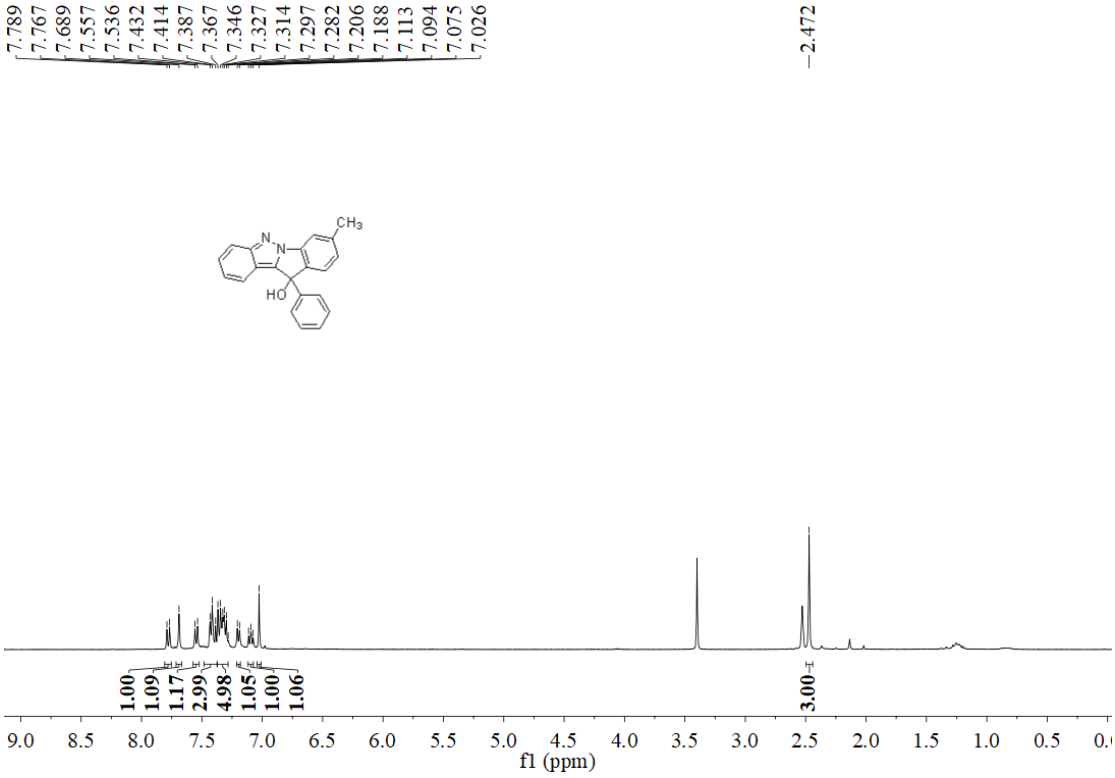


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

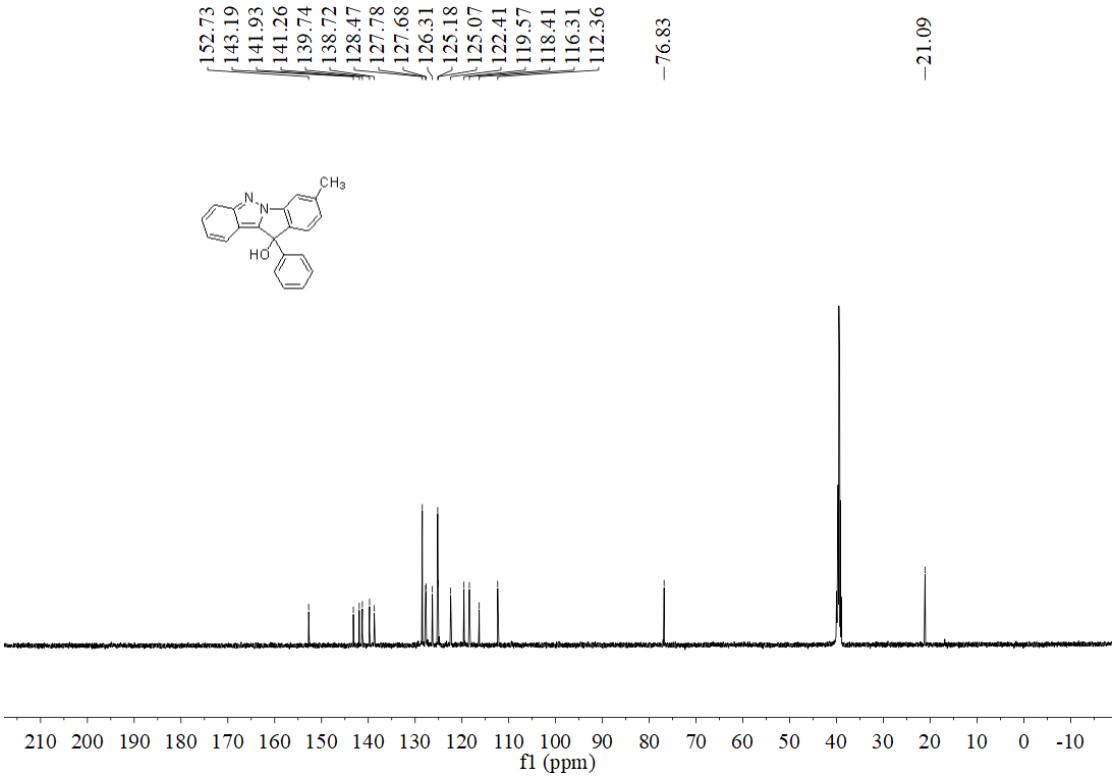


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 18.

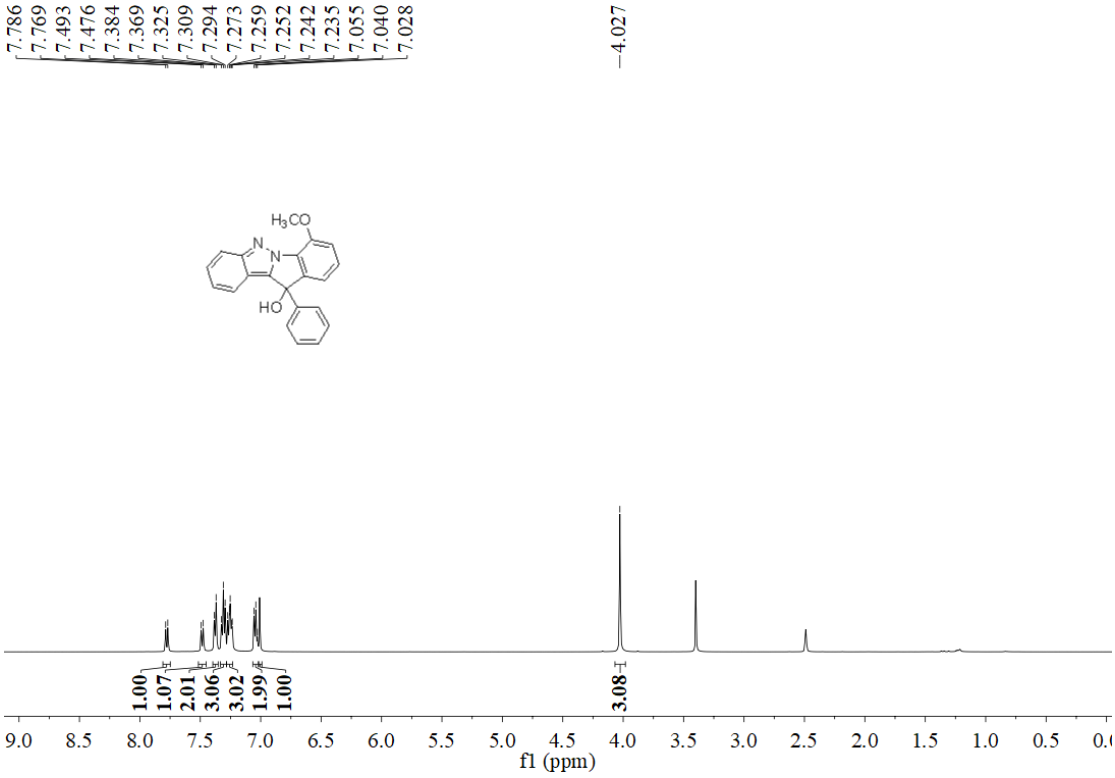


(400 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

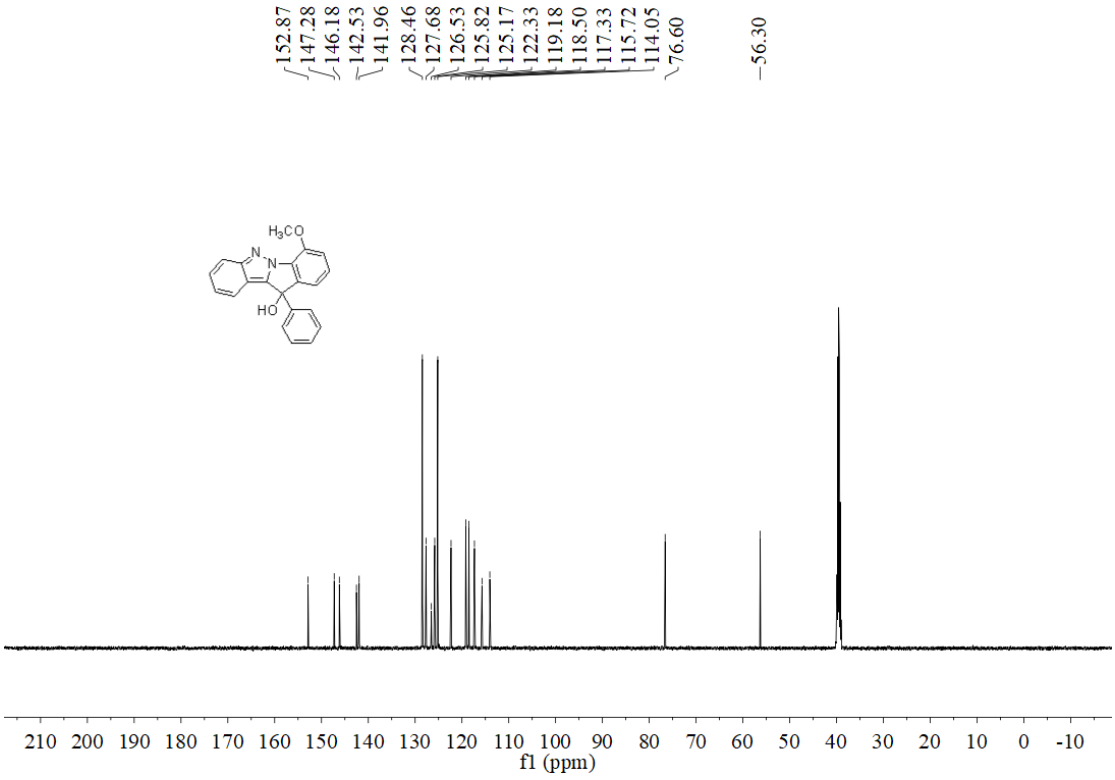


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 19.

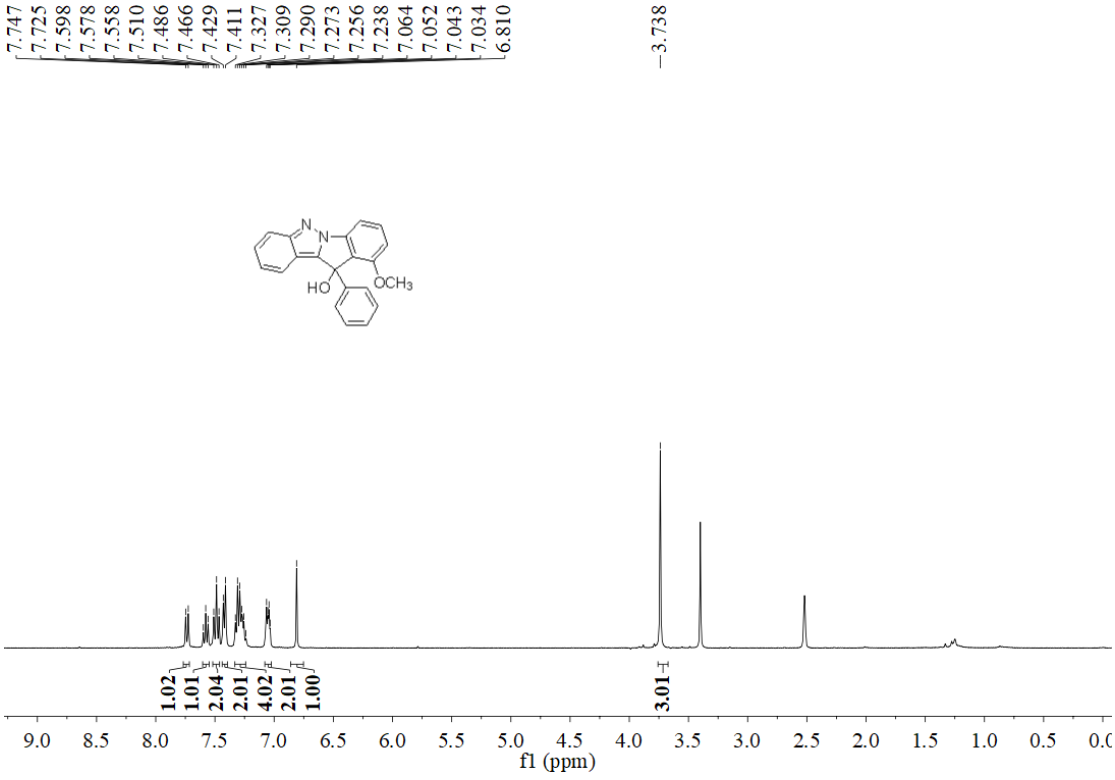


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

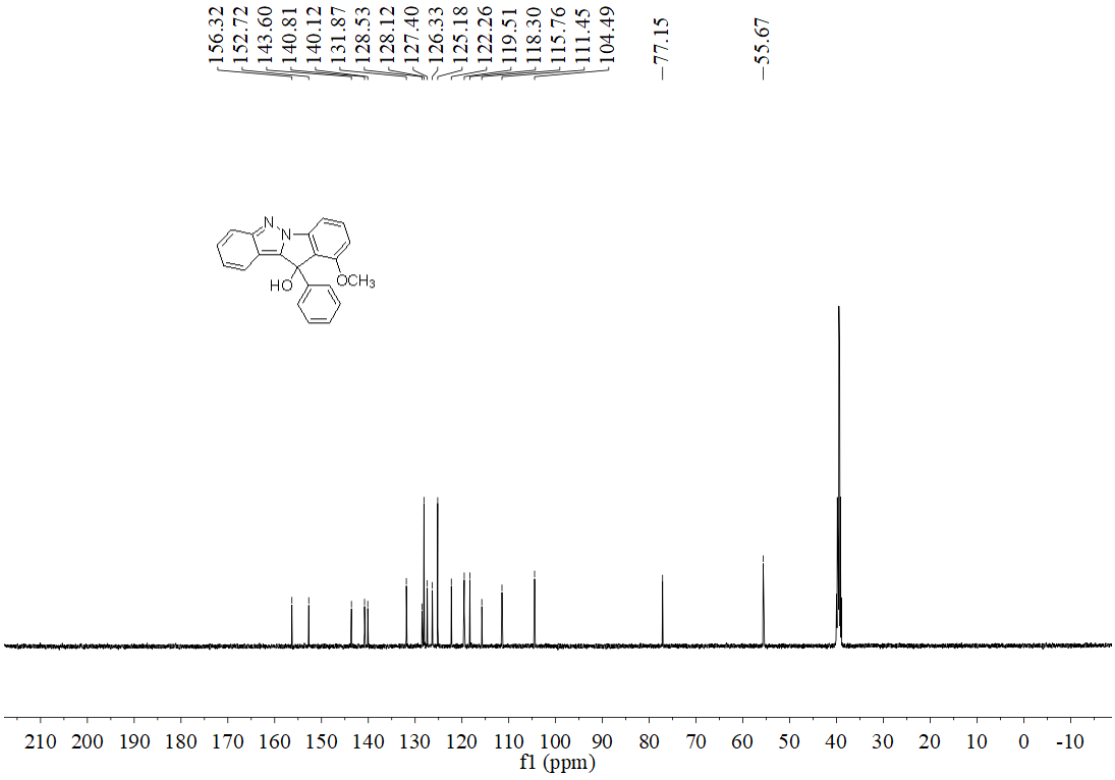


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 20.

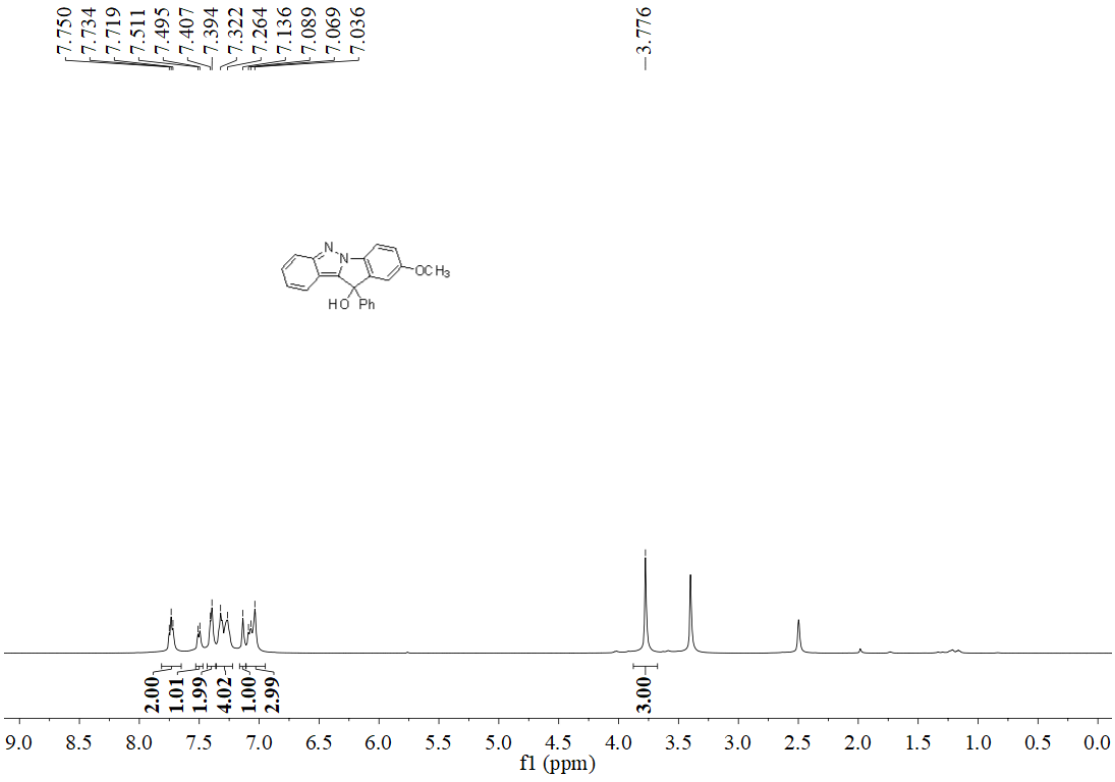


(400 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

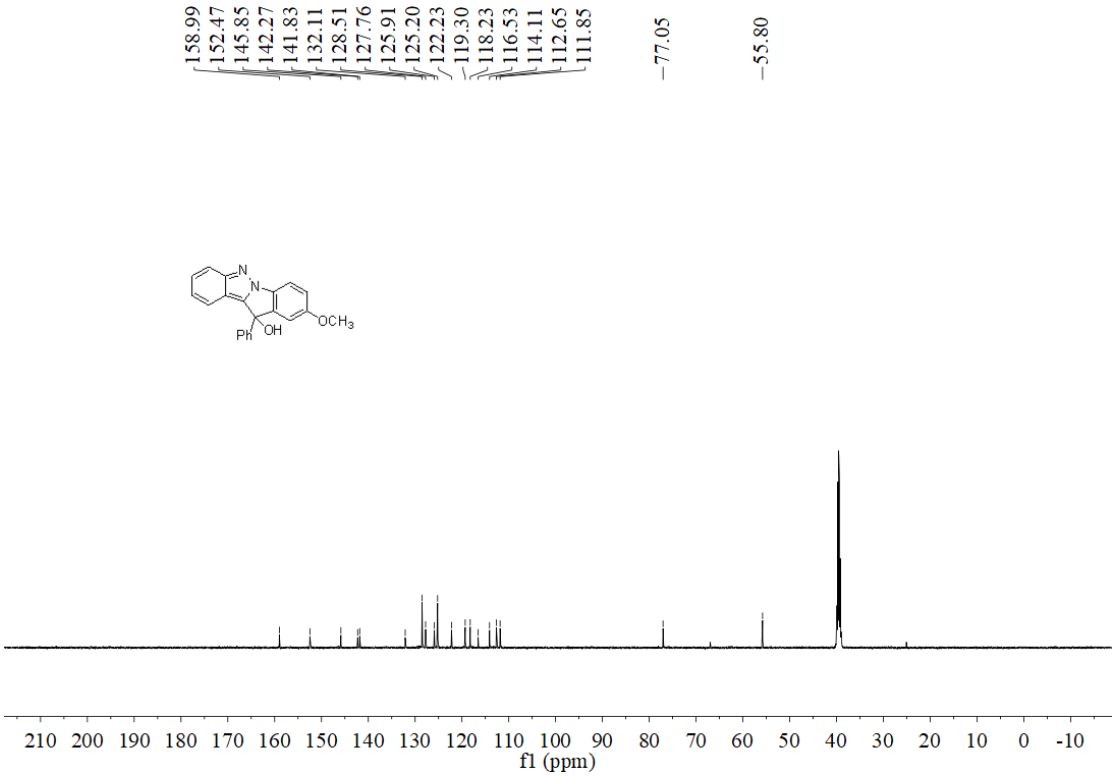


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 21.

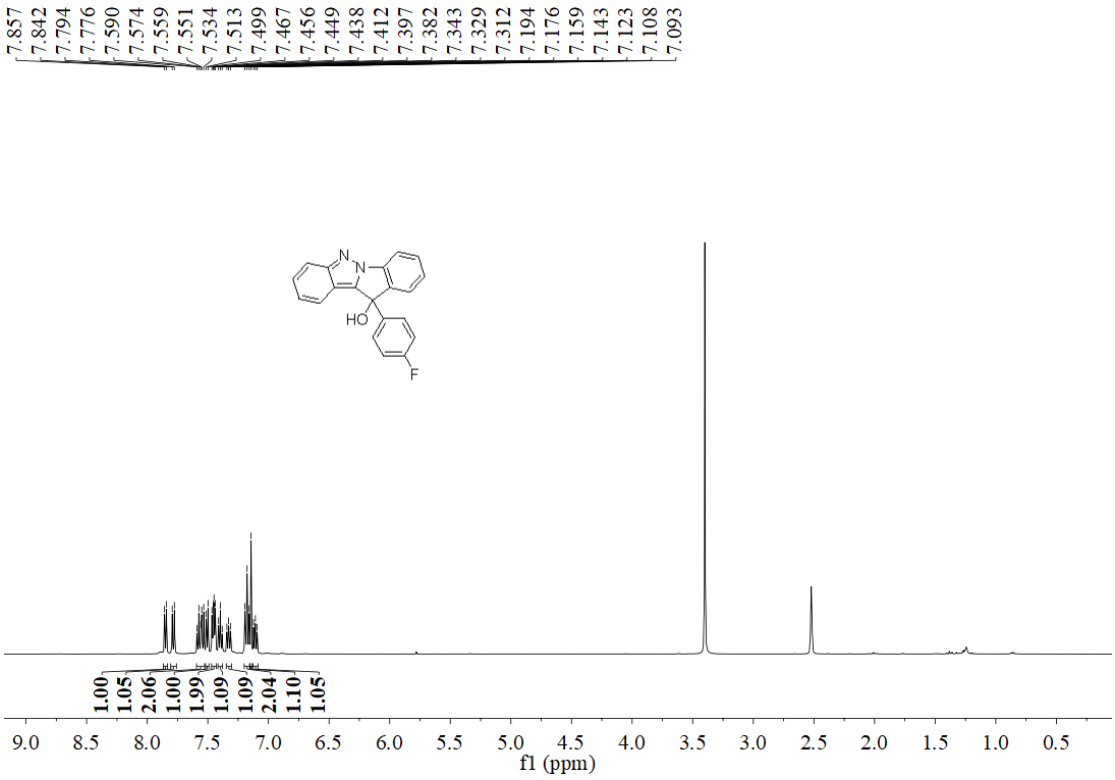


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

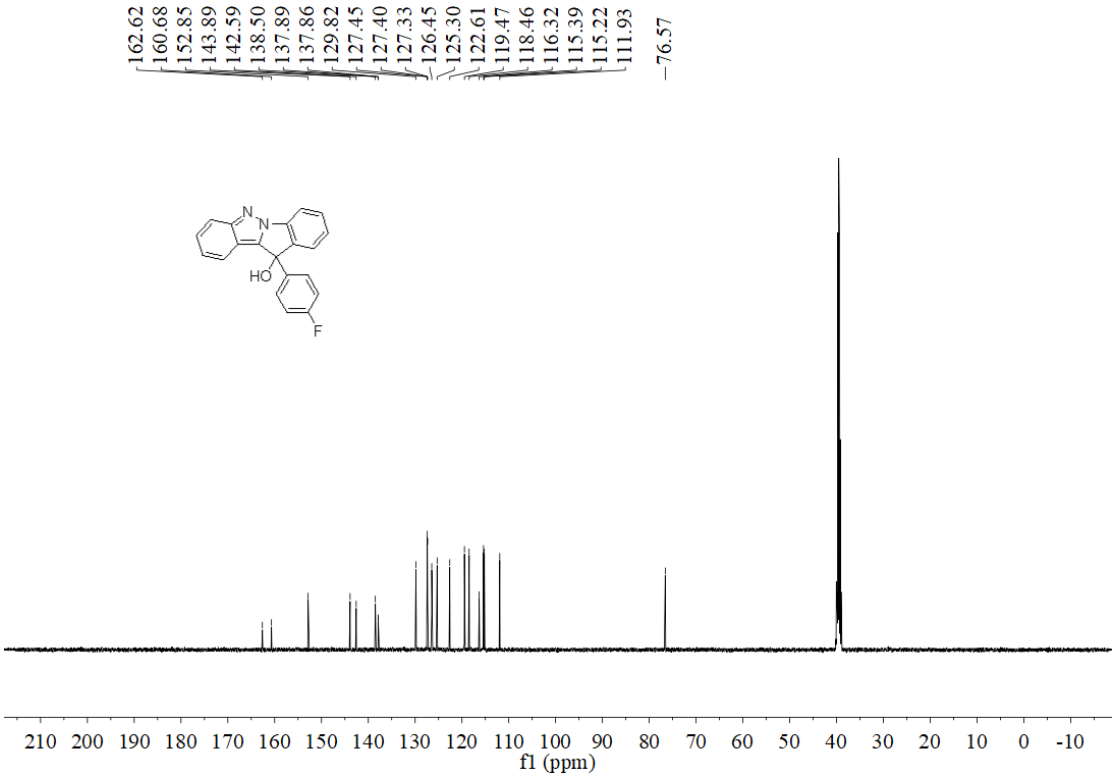


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

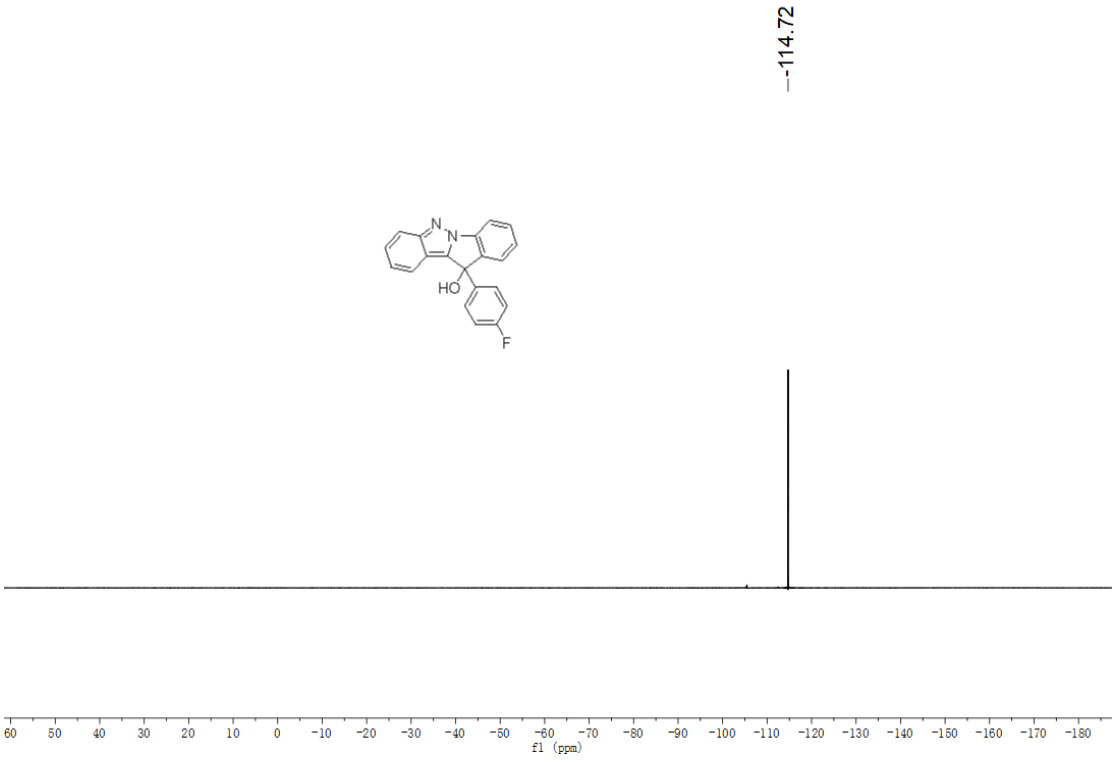
^{1}H ,^{13}C and ^{19}F NMR spectra of compound 23.



(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

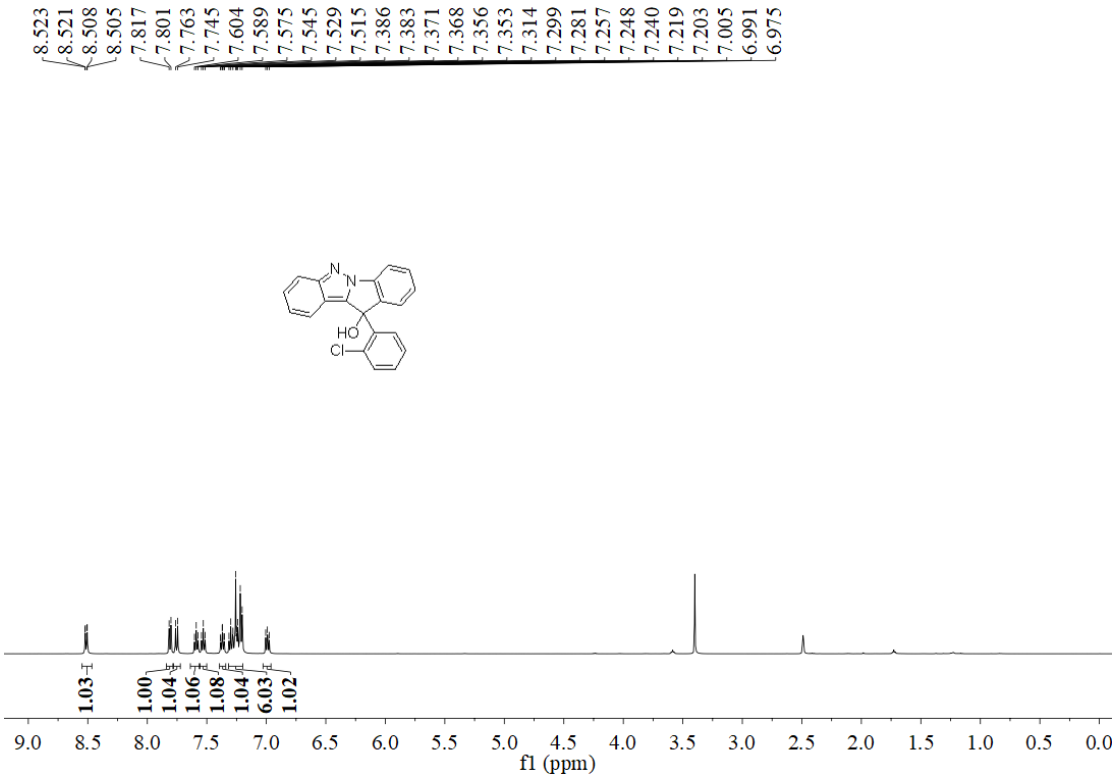


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

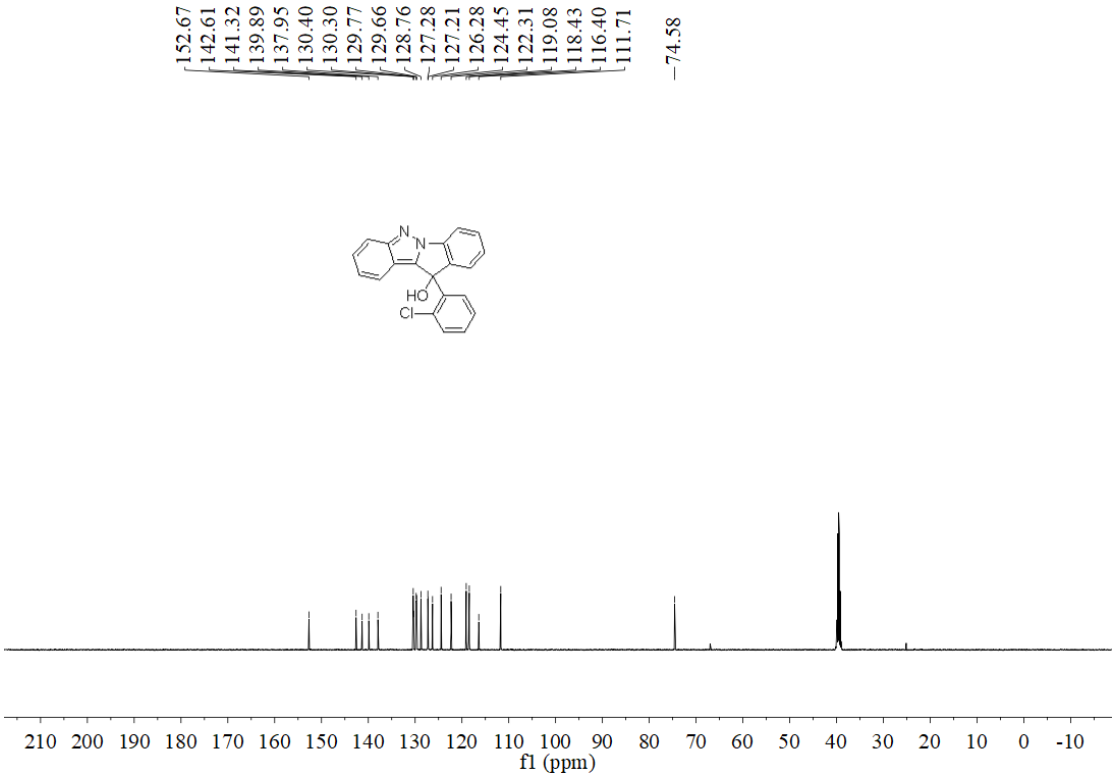


(470 MHz for ^{19}F NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 24.

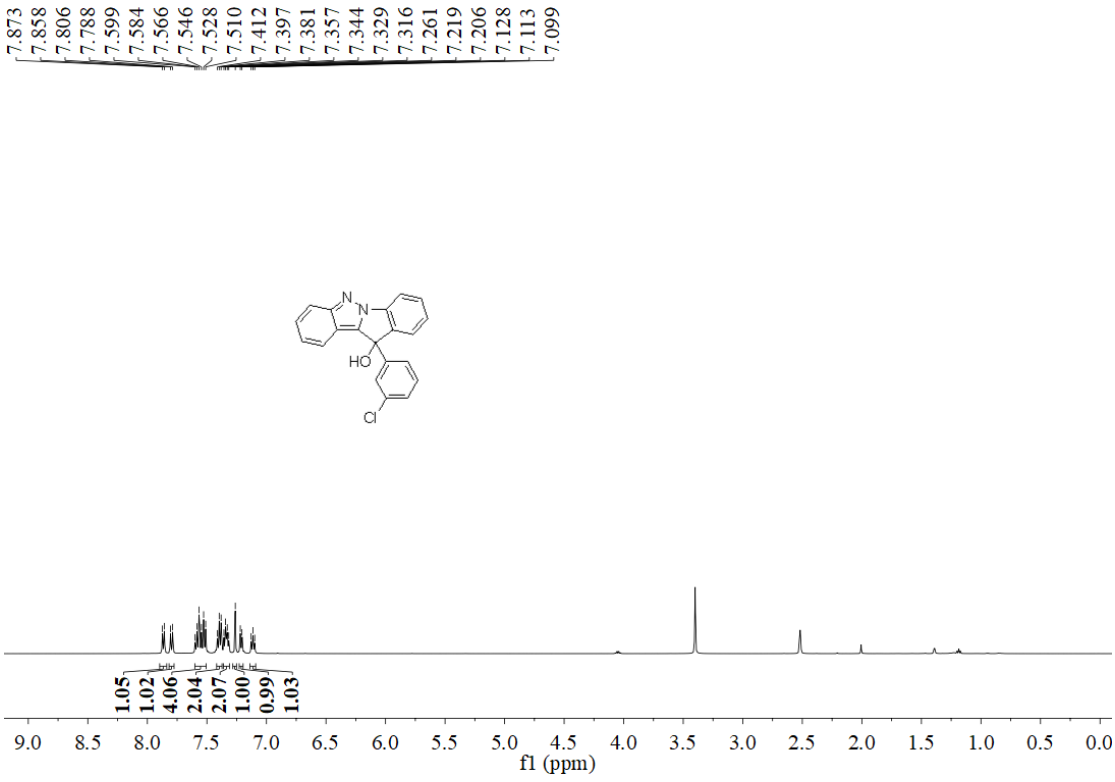


(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

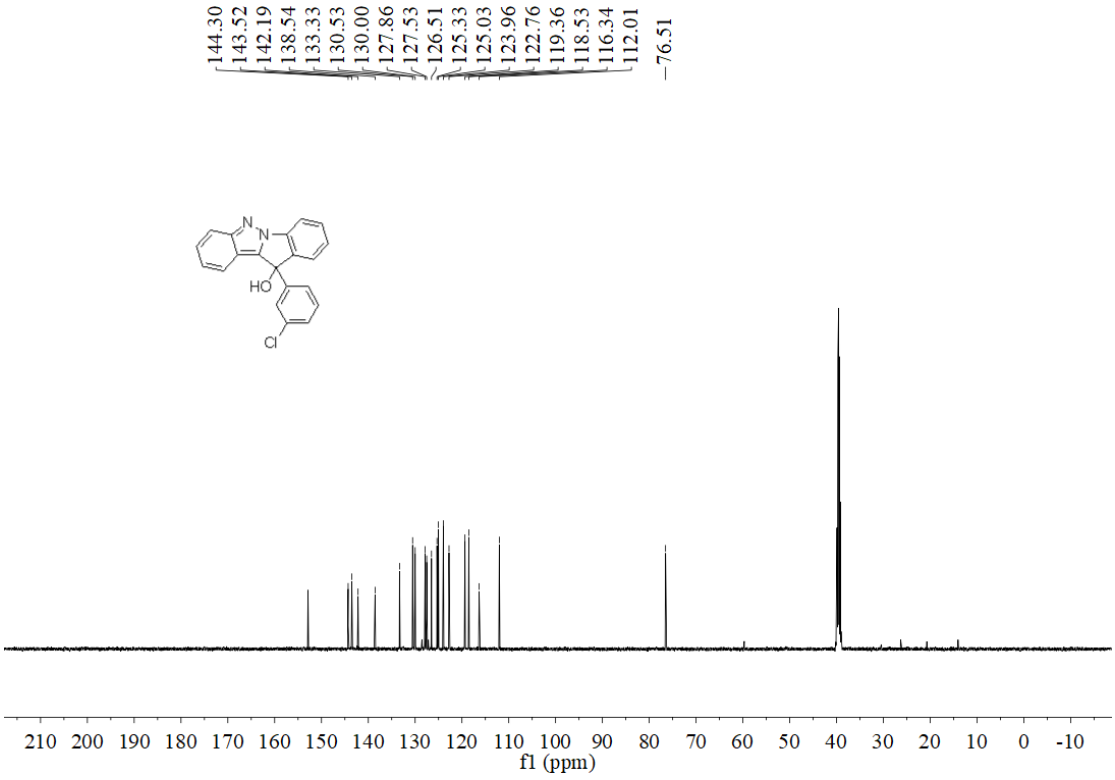


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 25.

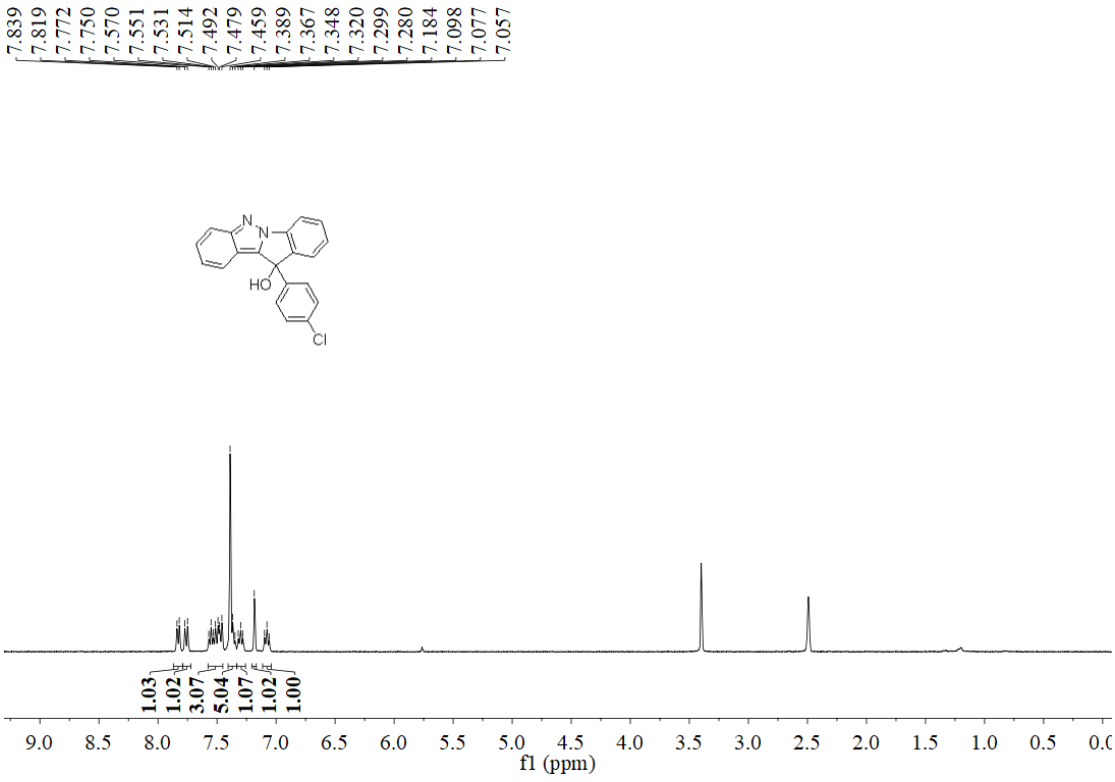


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

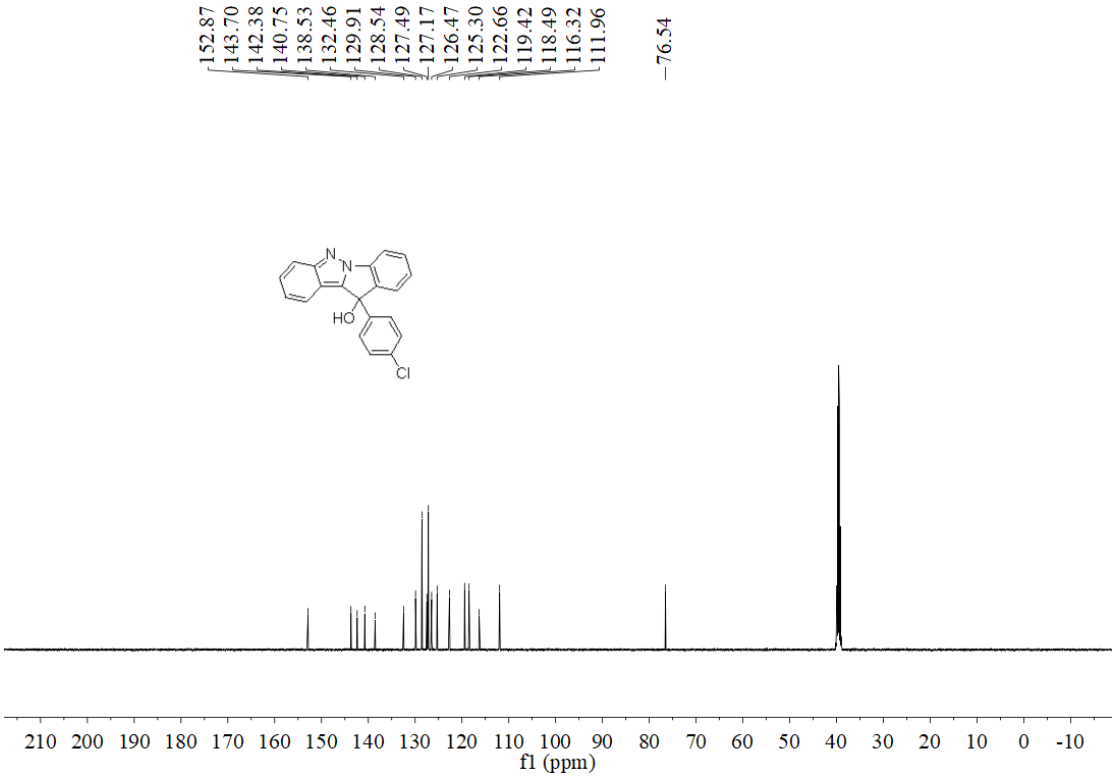


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 26.

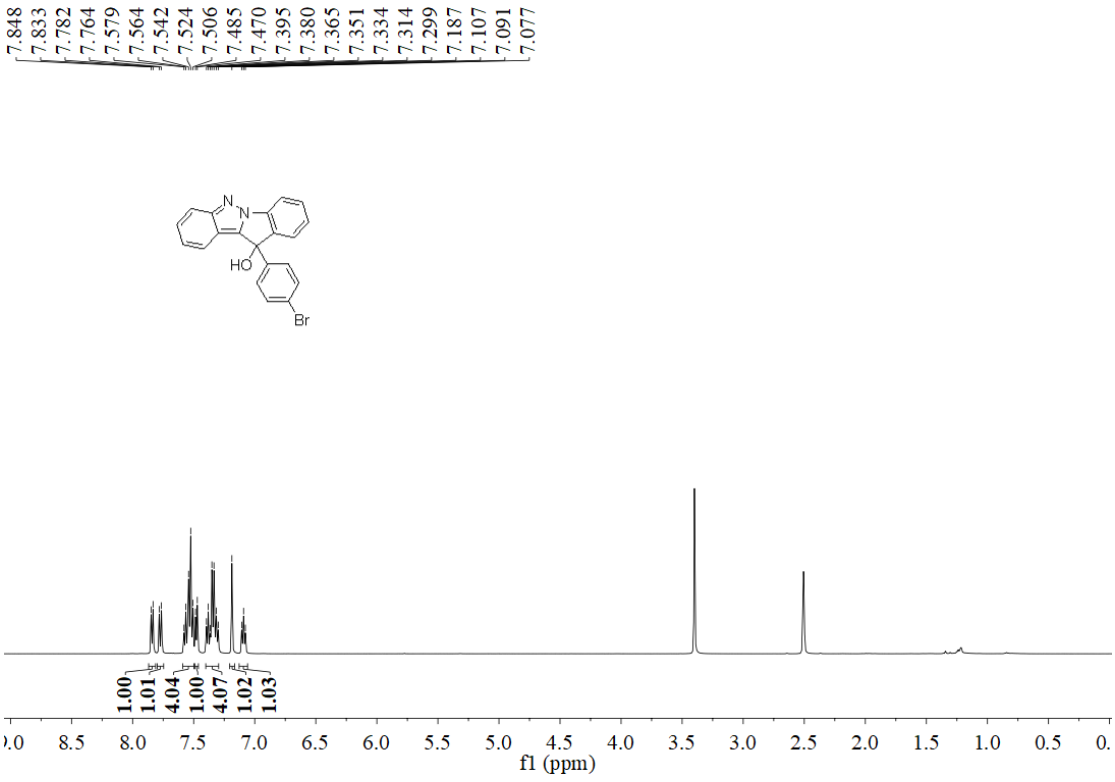


(400 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

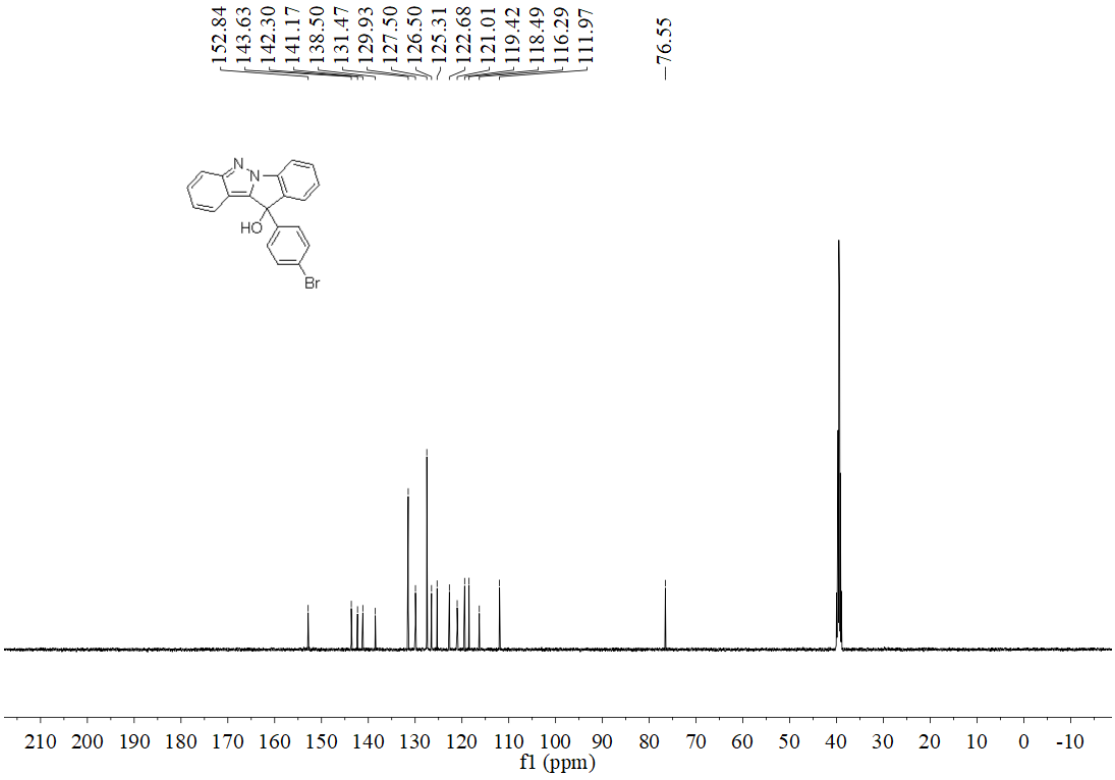


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 27.

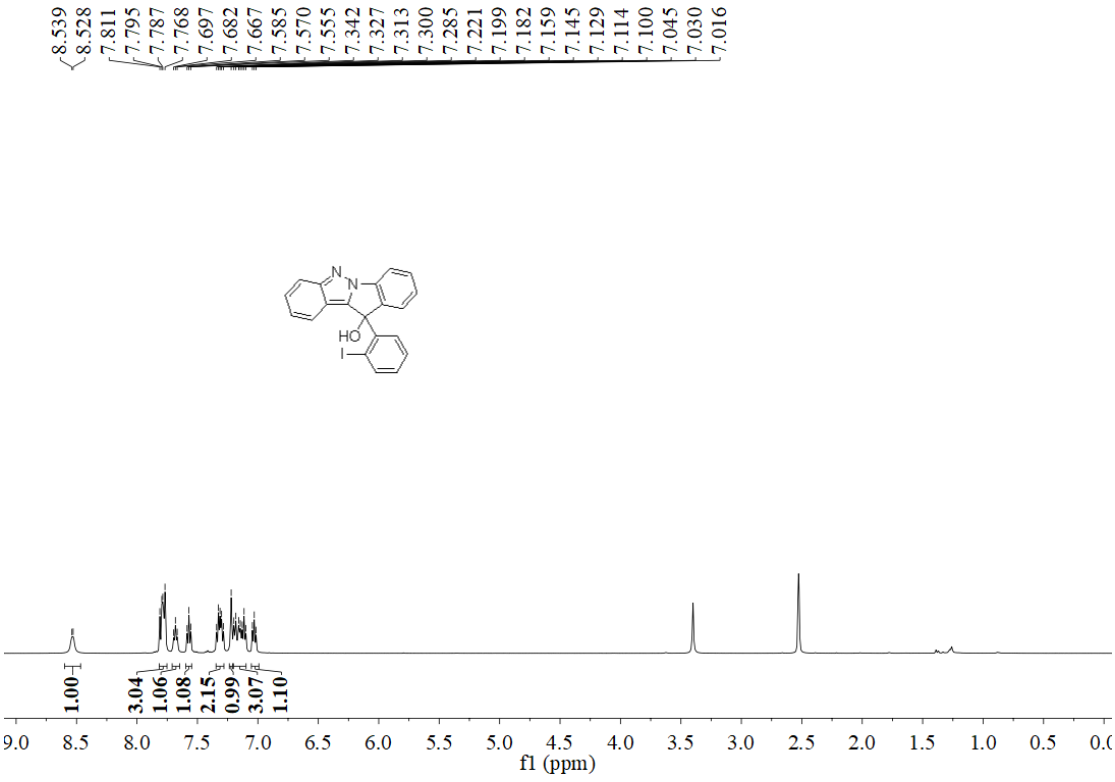


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

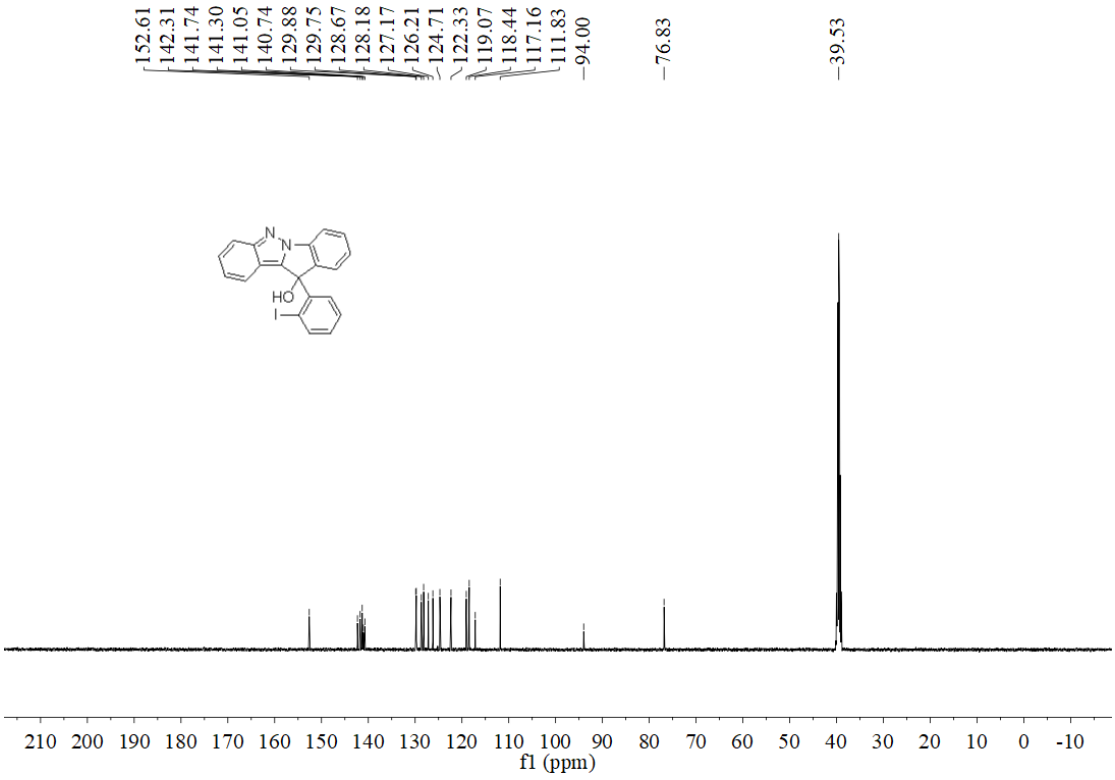


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 28.

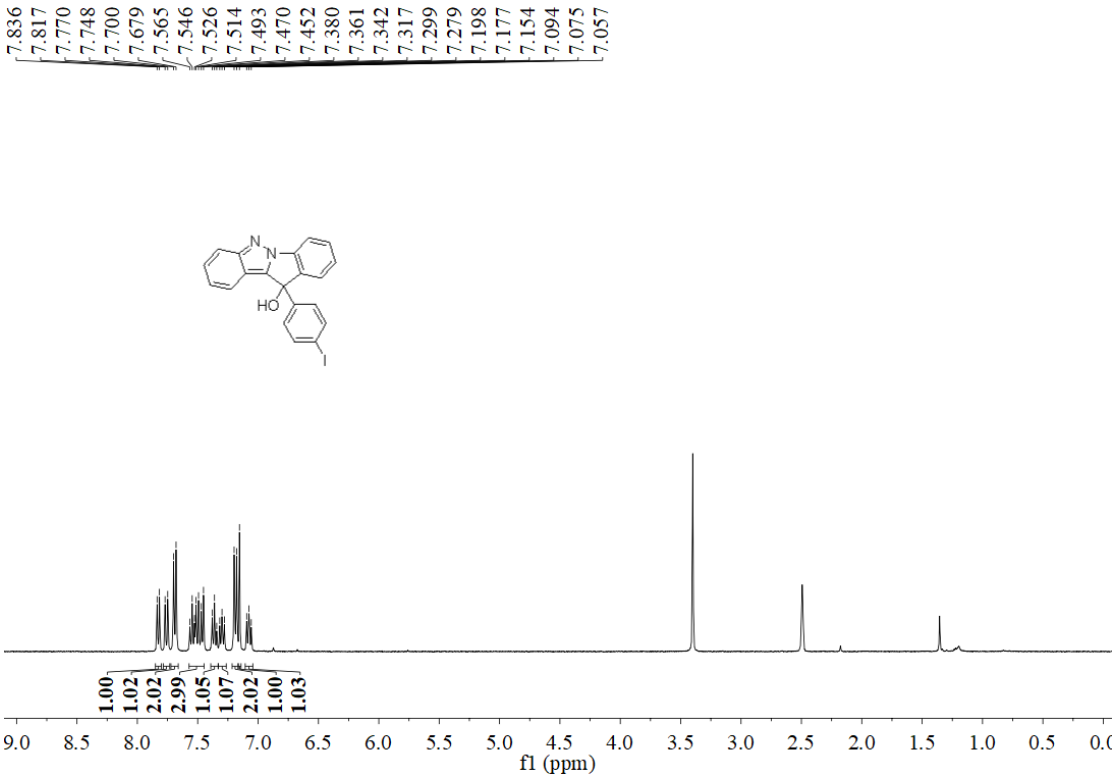


(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

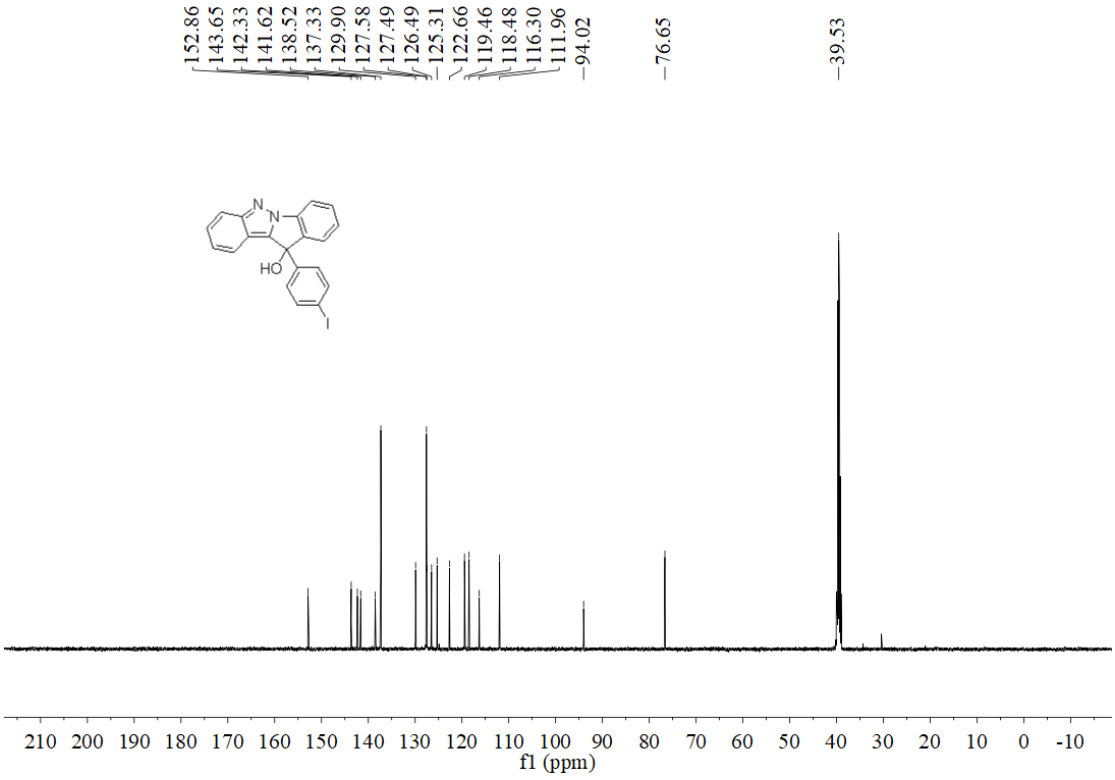


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 29.

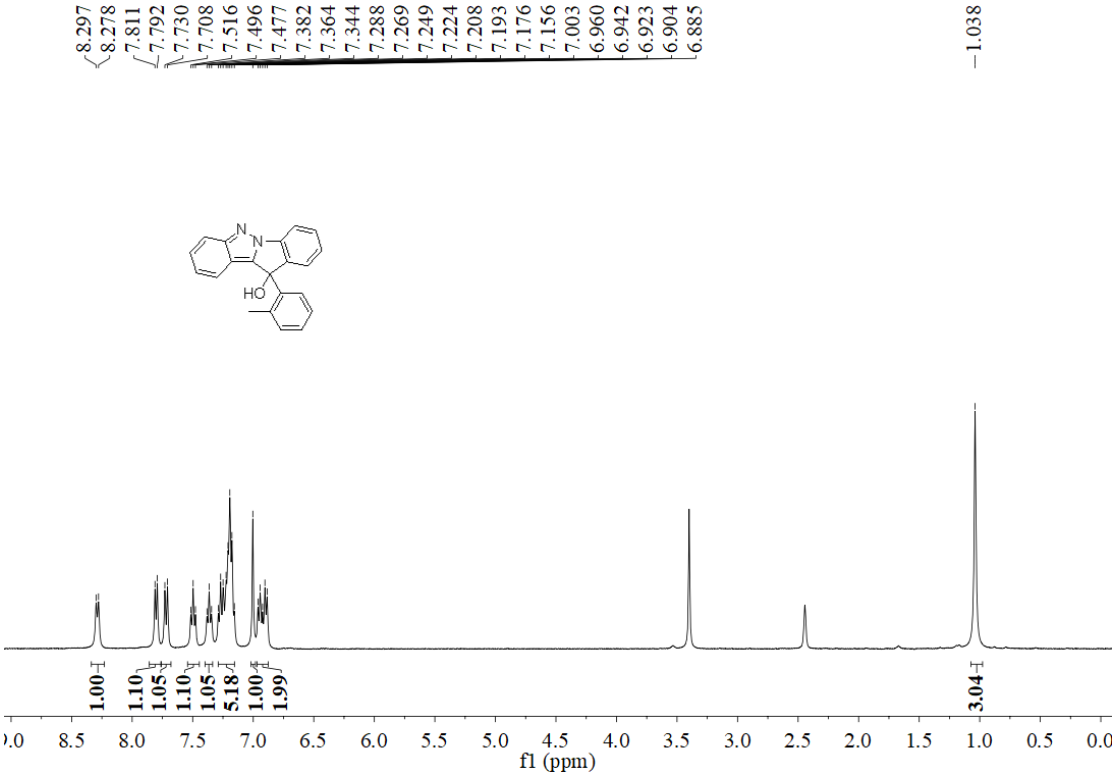


(400 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

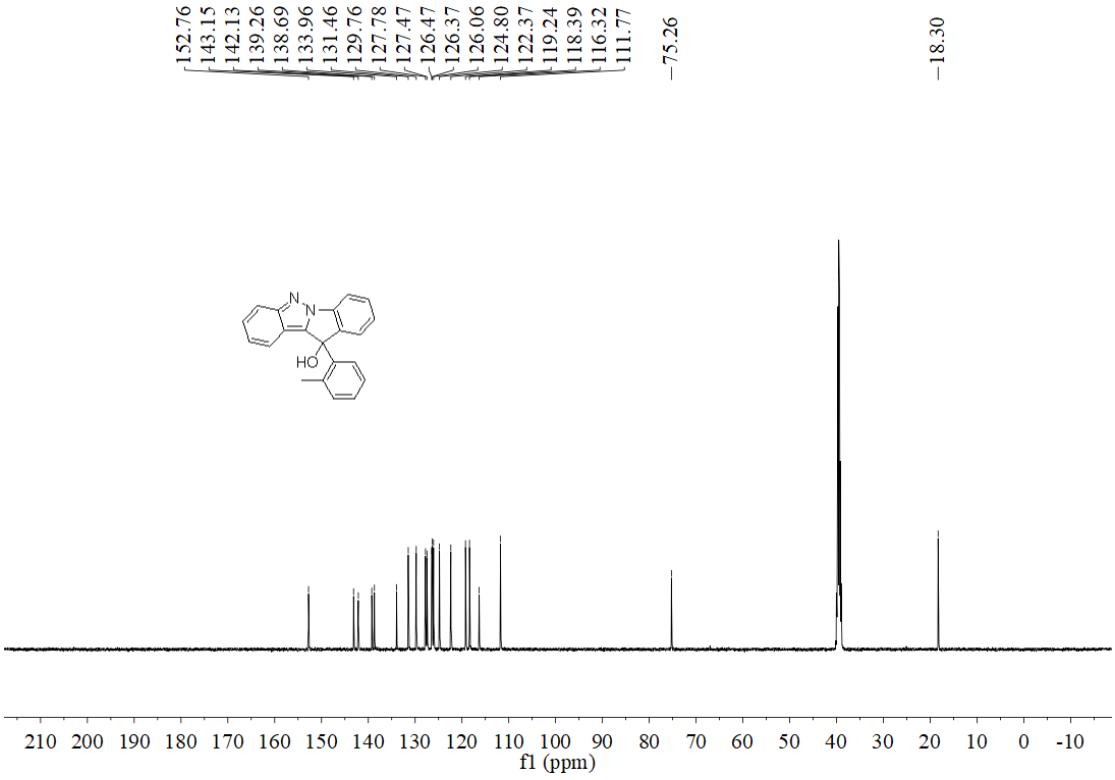


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 30.

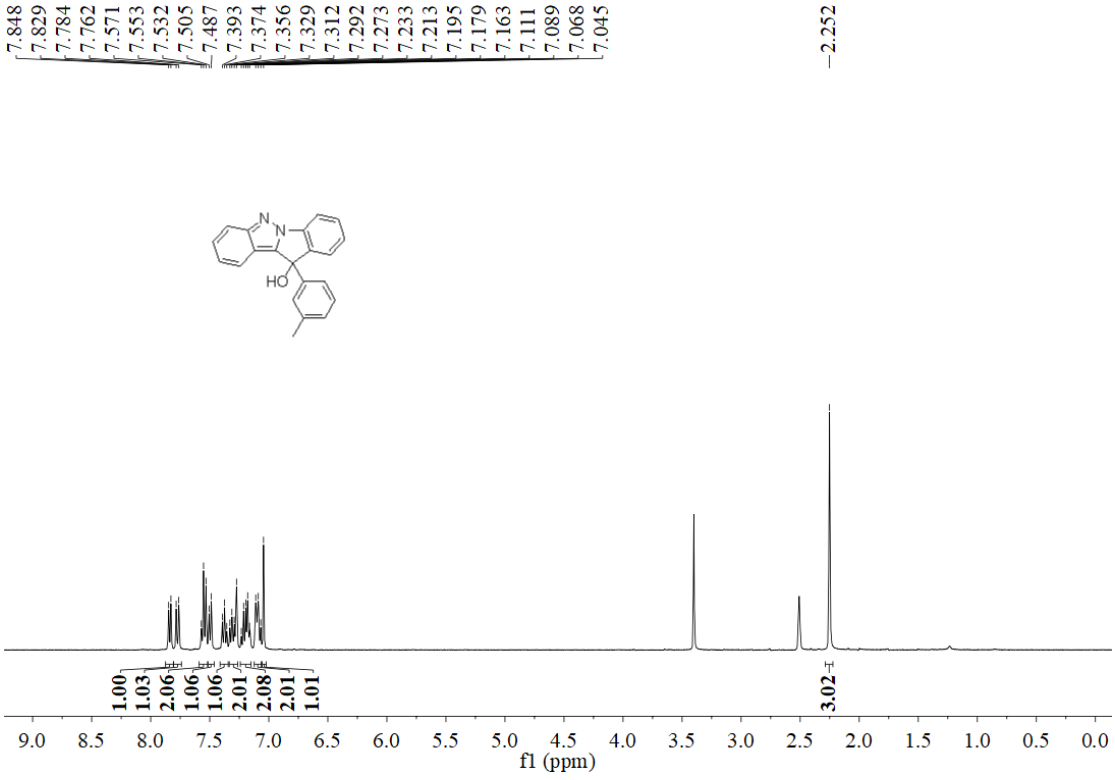


(400 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

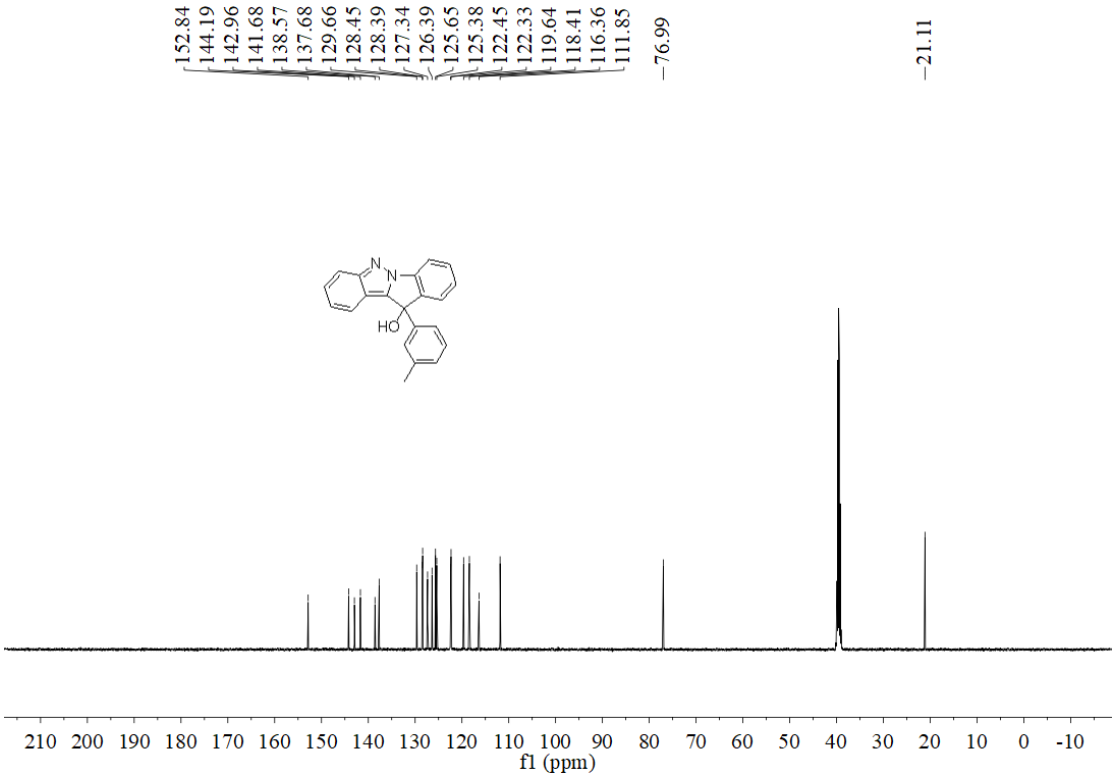


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 31.

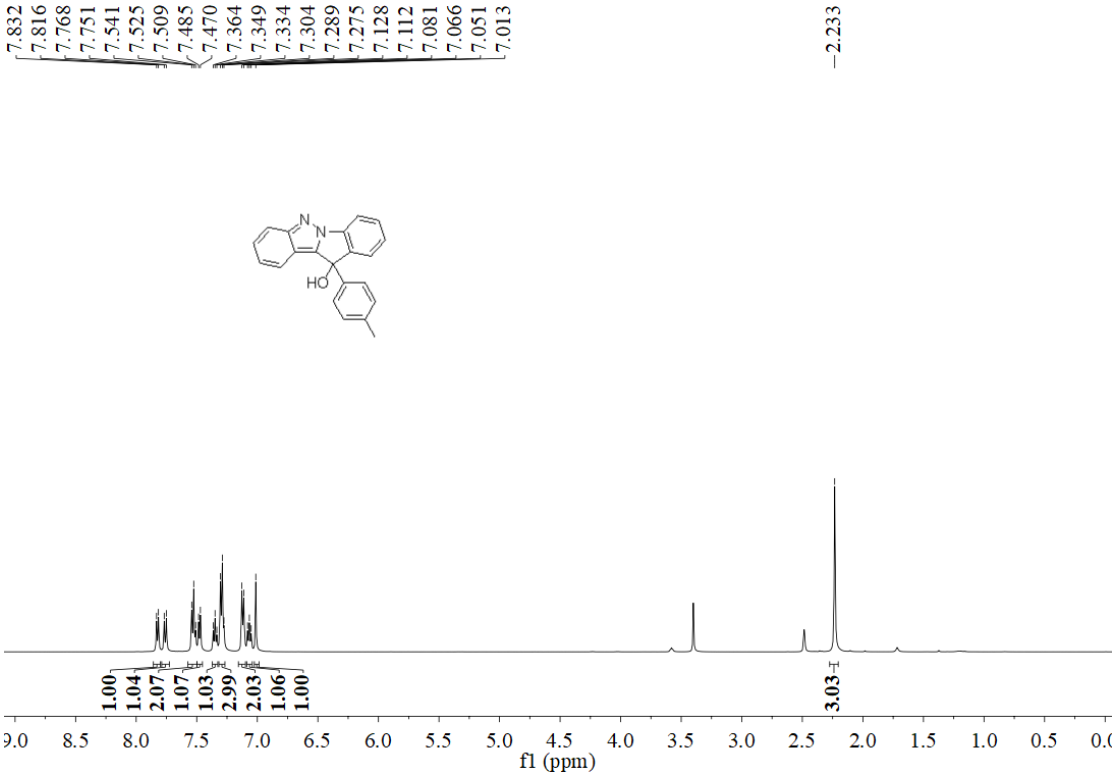


(400 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

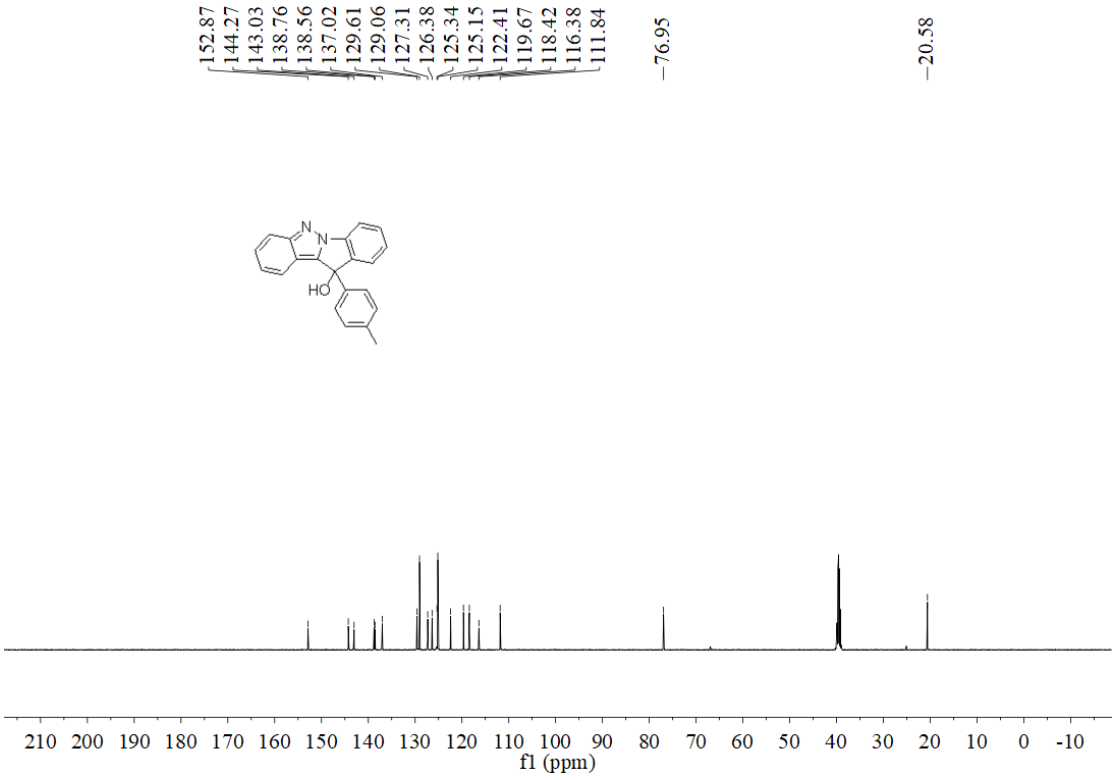


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 32.

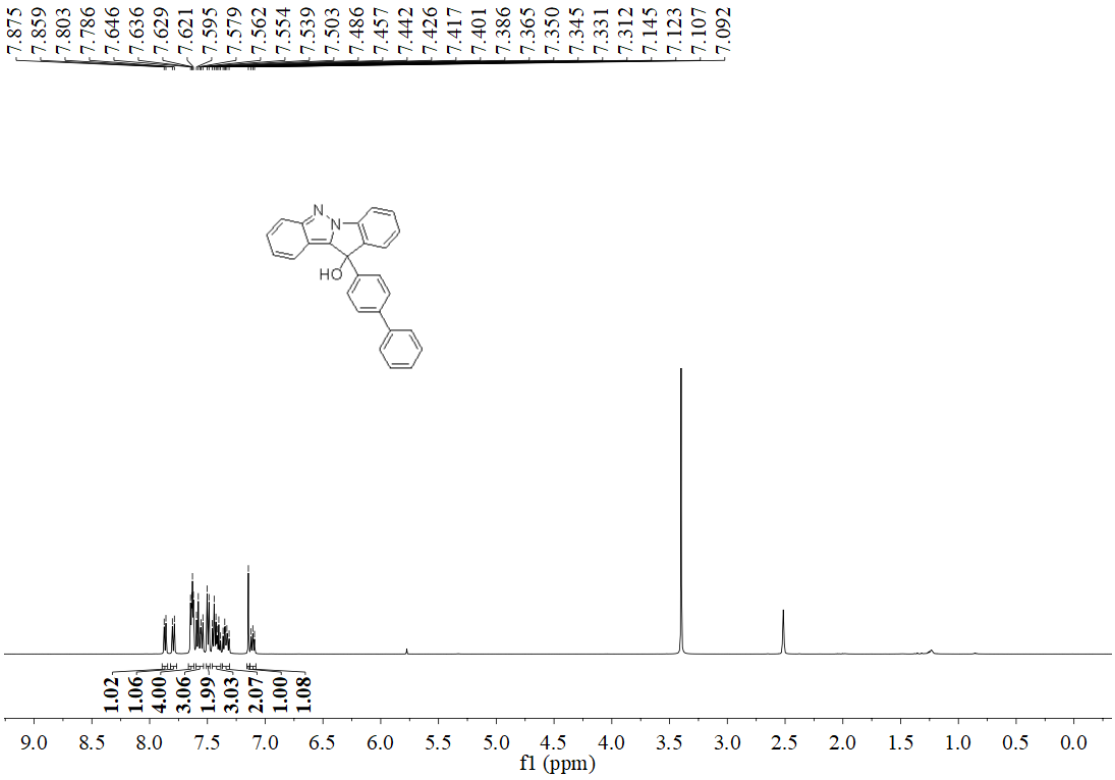


(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

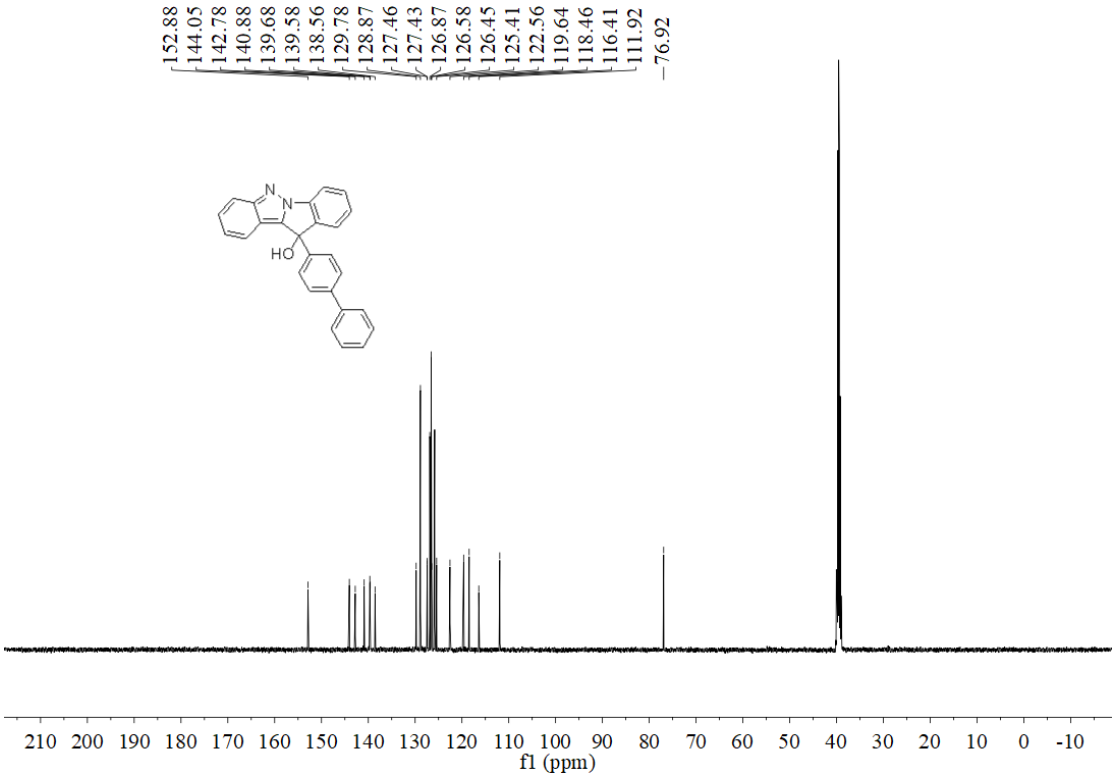


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 33.

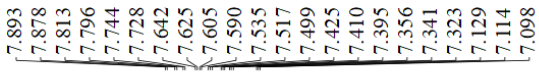


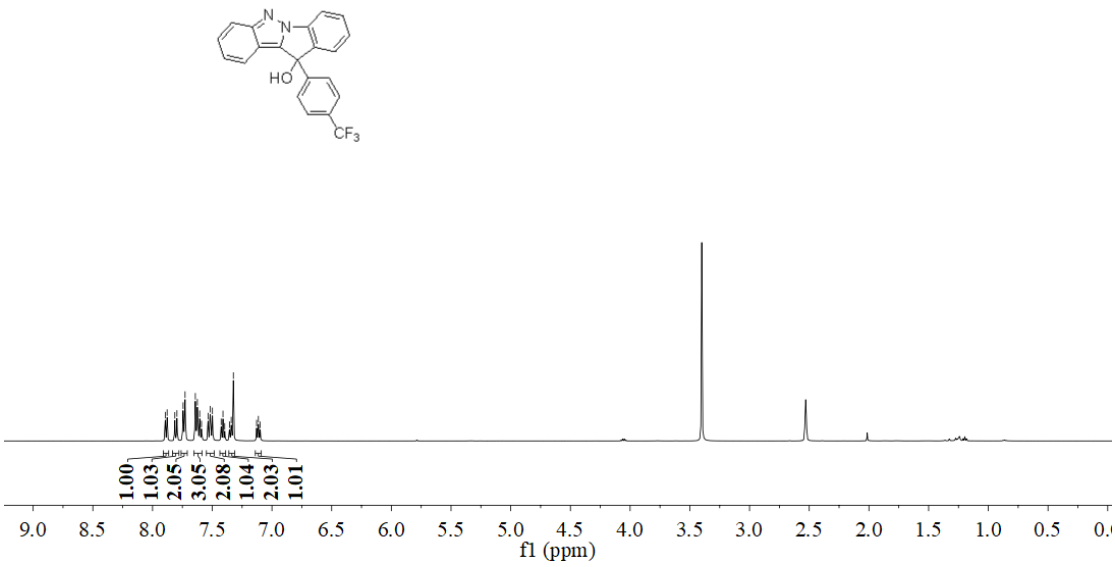
(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)



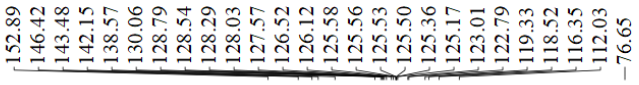
(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

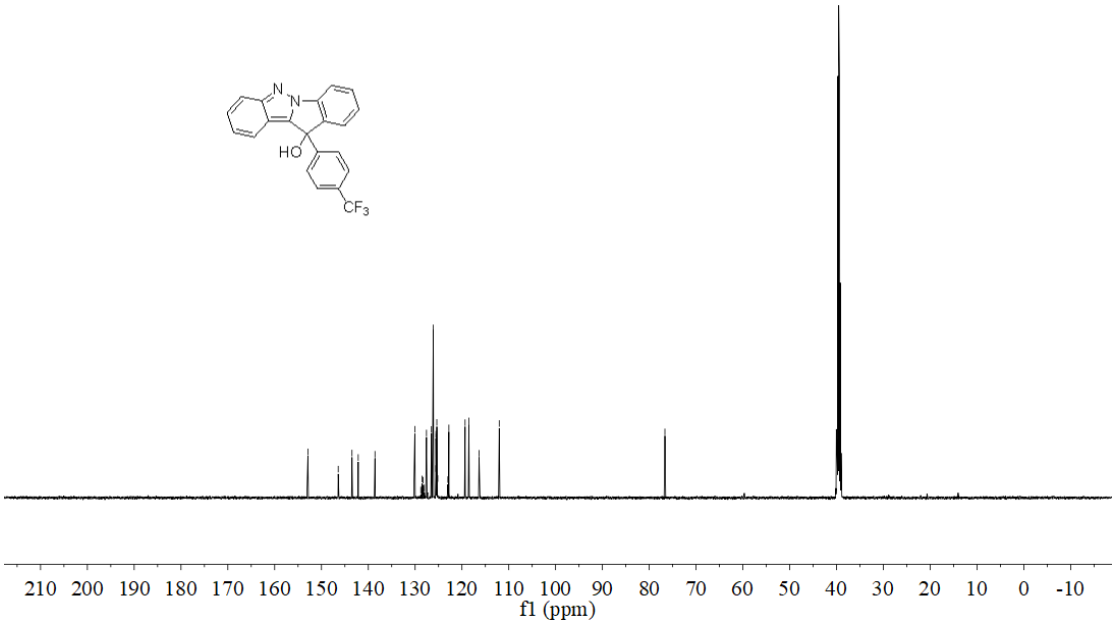
^{1}H , ^{13}C and ^{19}F NMR spectra of compound 34.



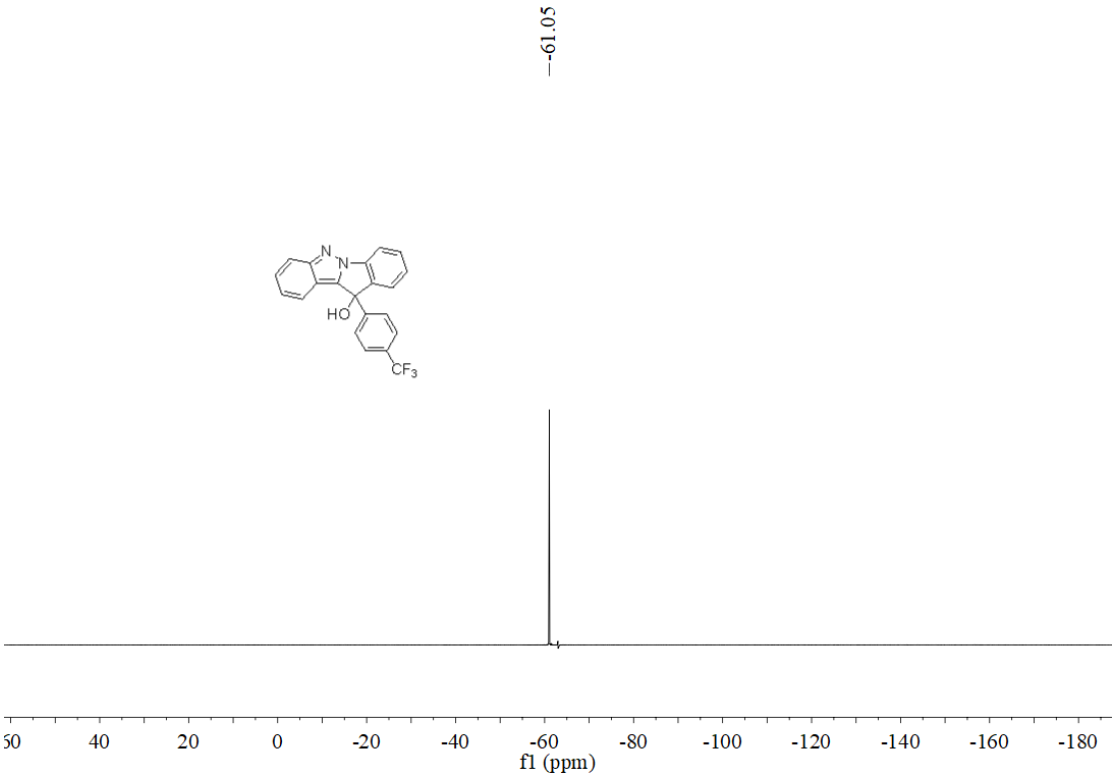


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)



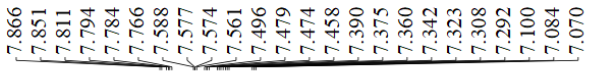


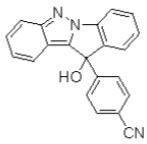
(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

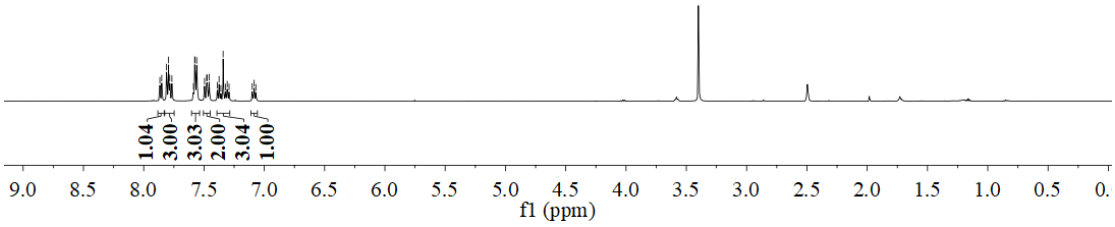


(470 MHz for ^{19}F NMR with DMSO-d_6 as solvent)

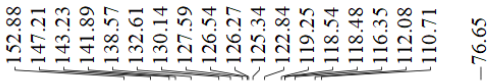
^{1}H and ^{13}C NMR spectra of compound 35.

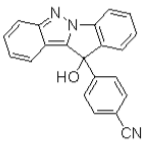


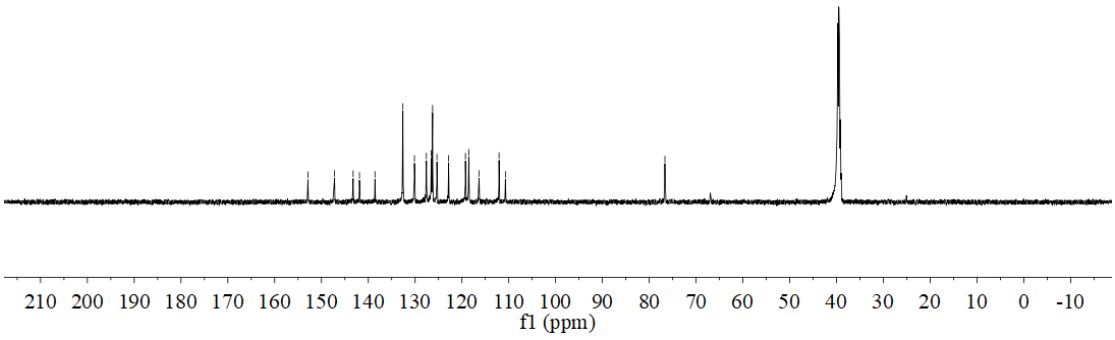




(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

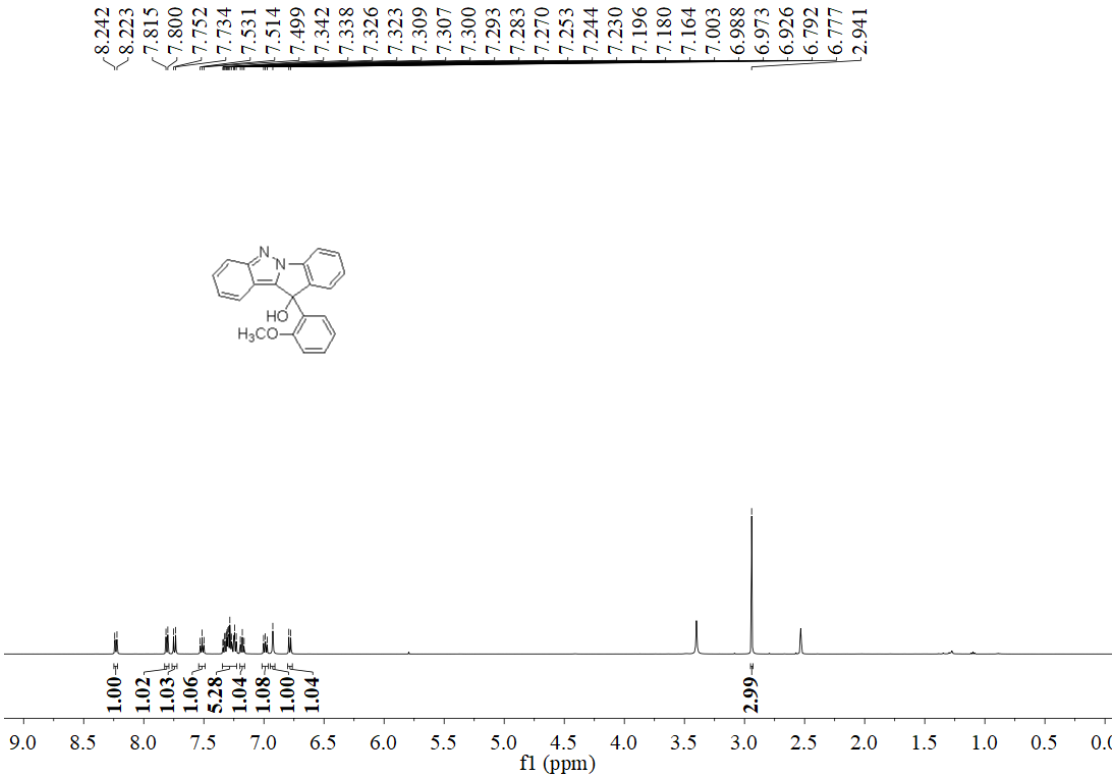




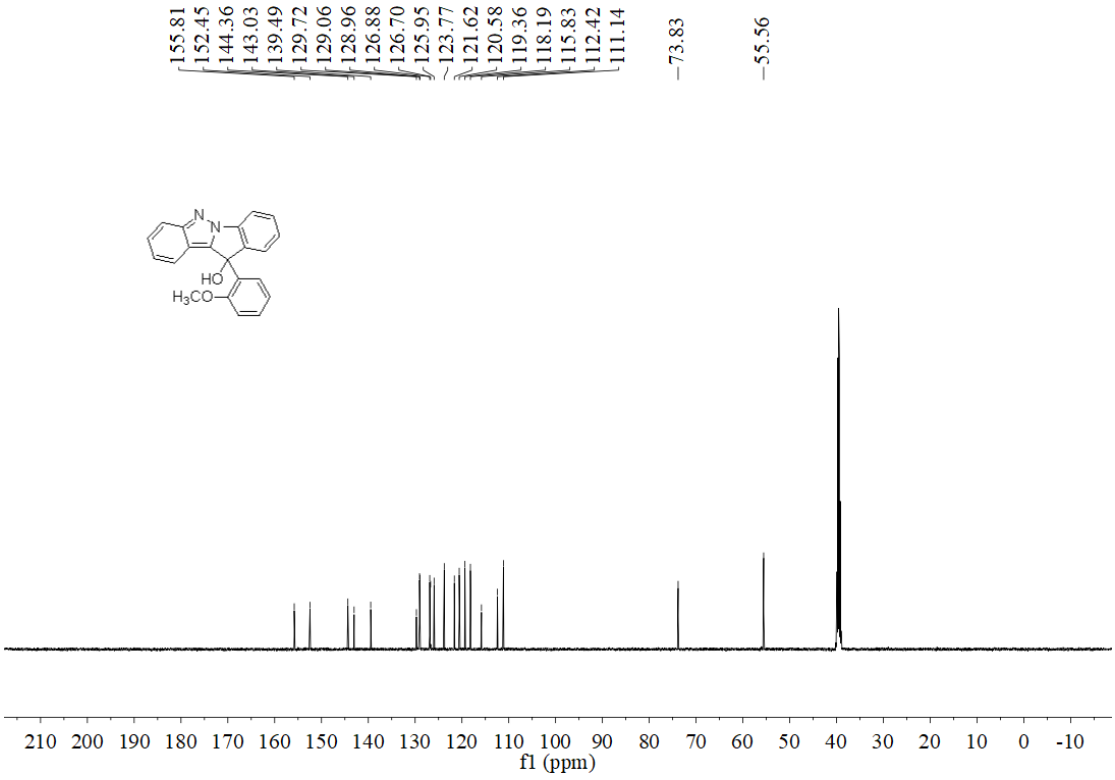


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 36.

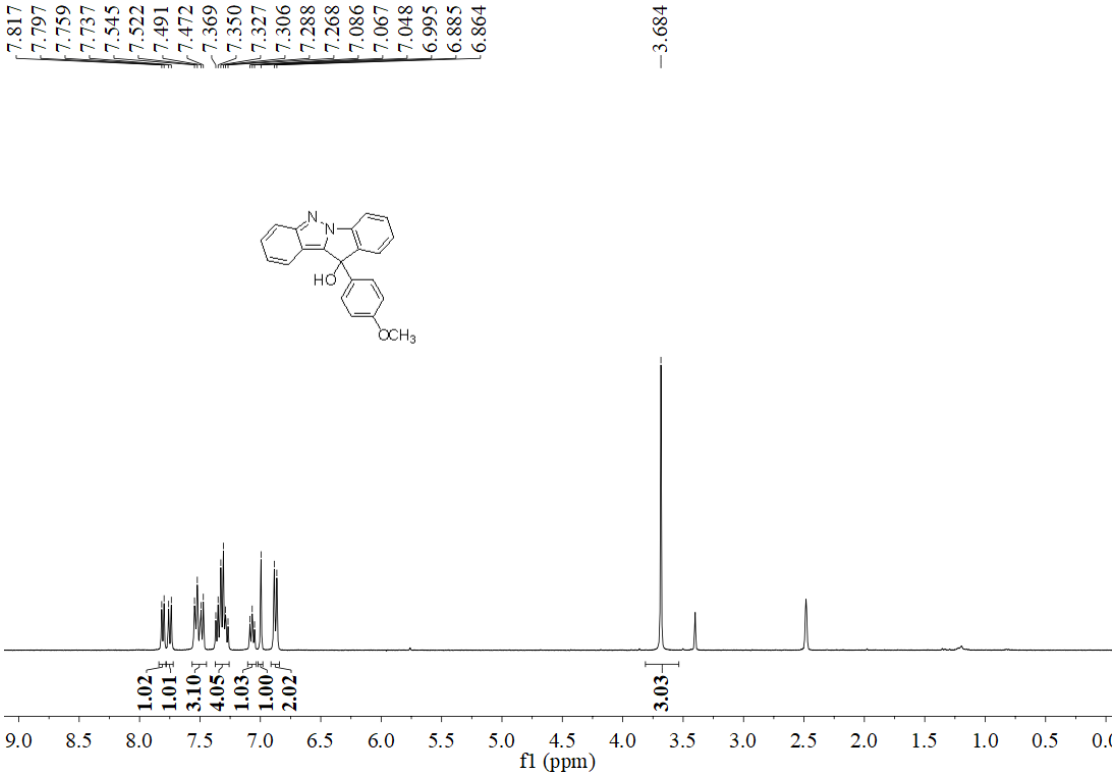


(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

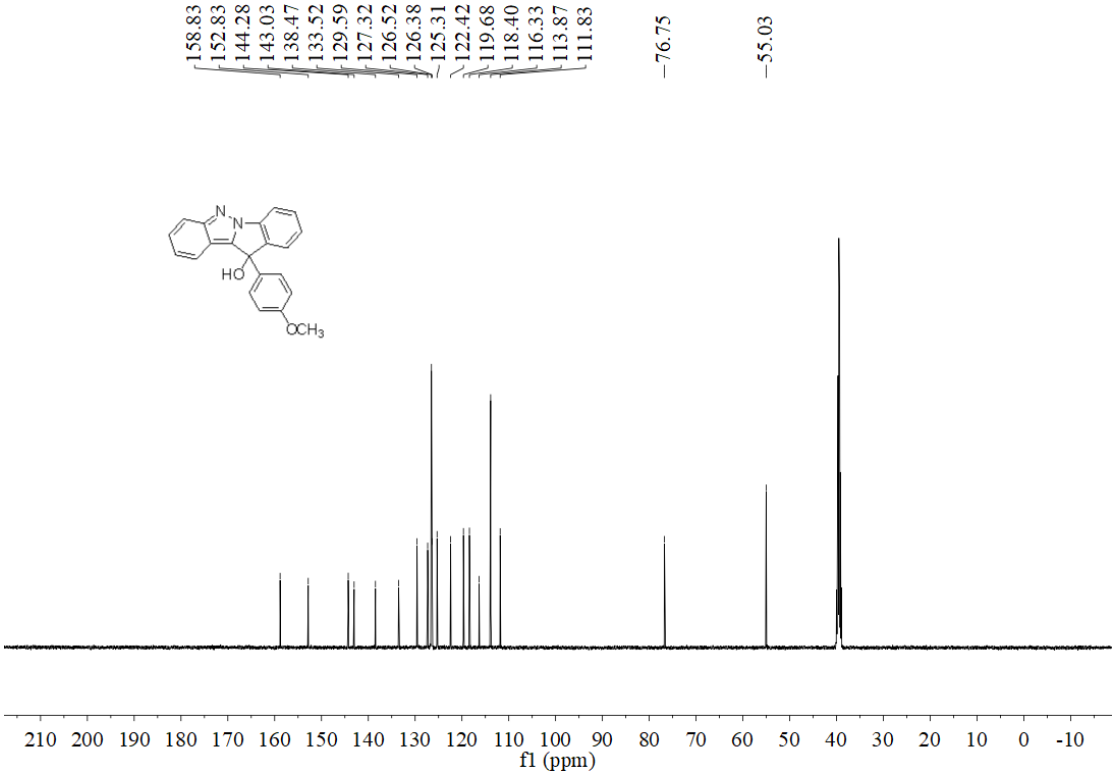


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 37.

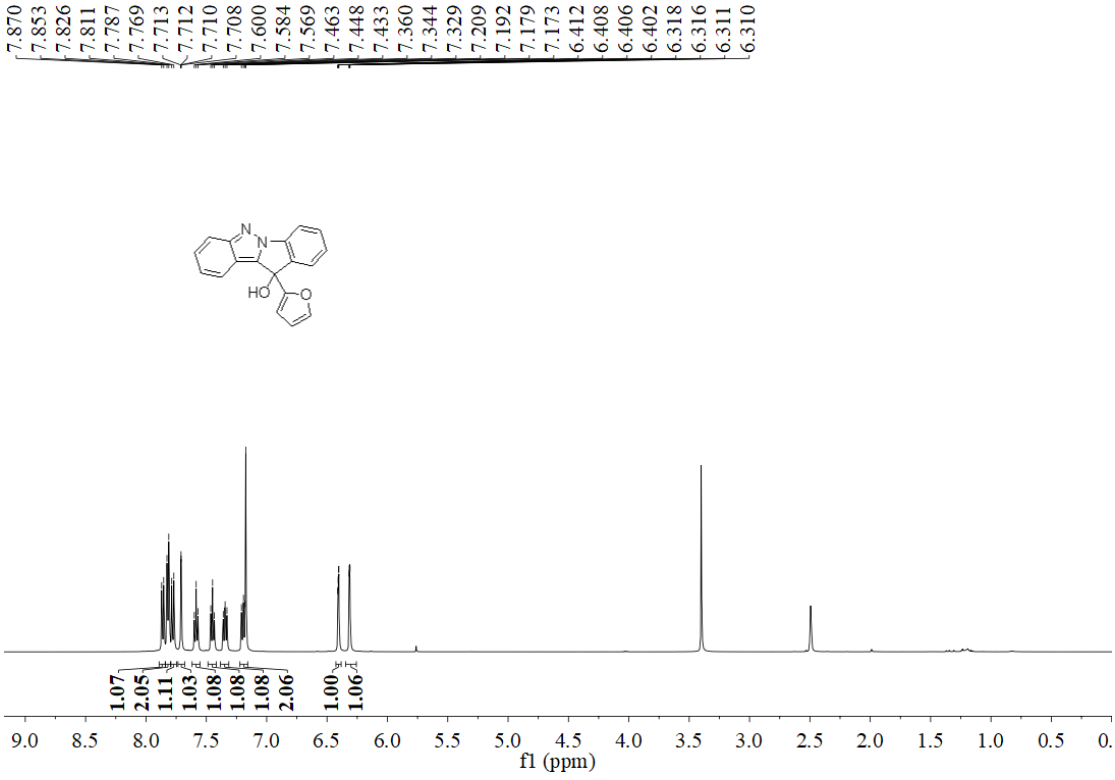


(400 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

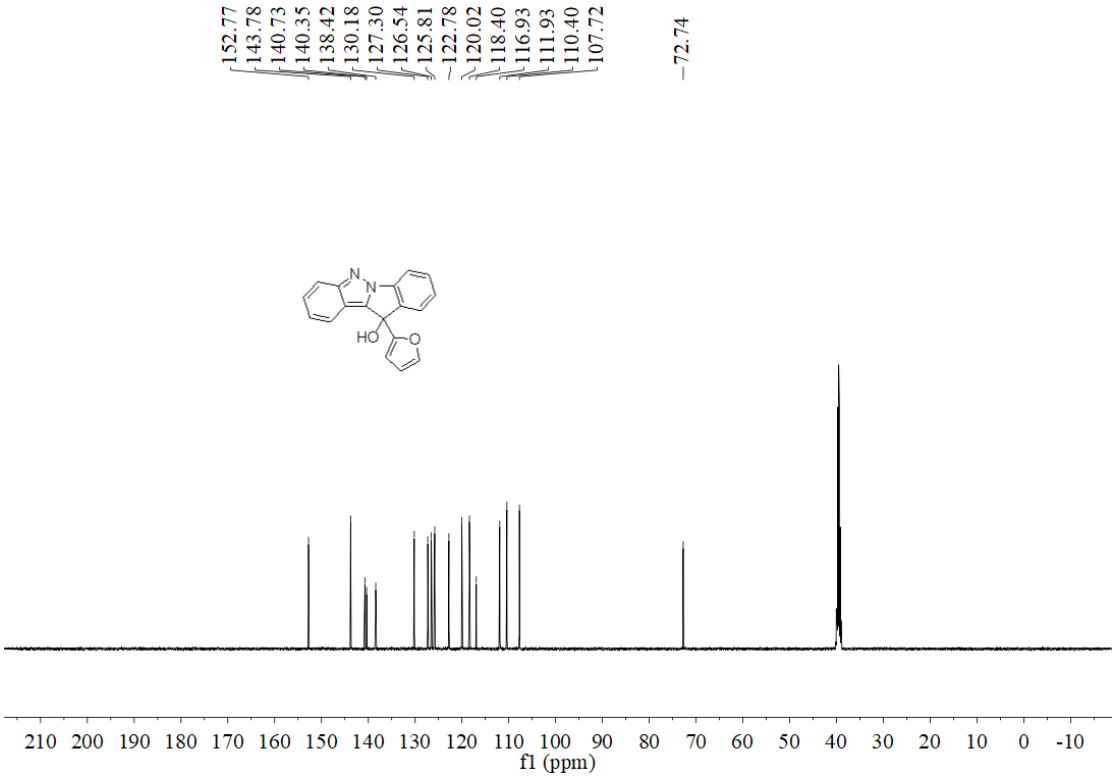


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 38.

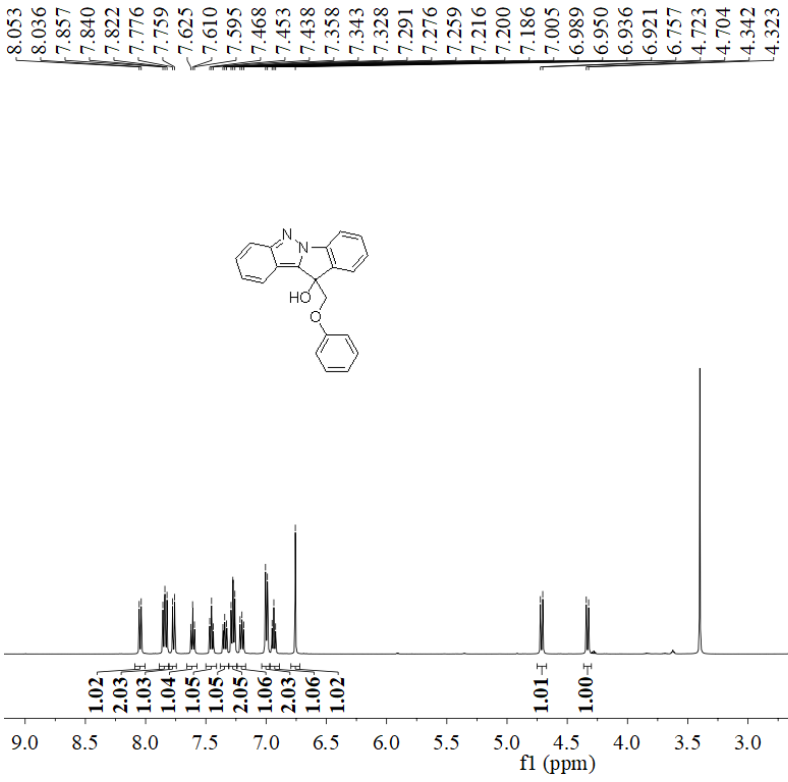


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

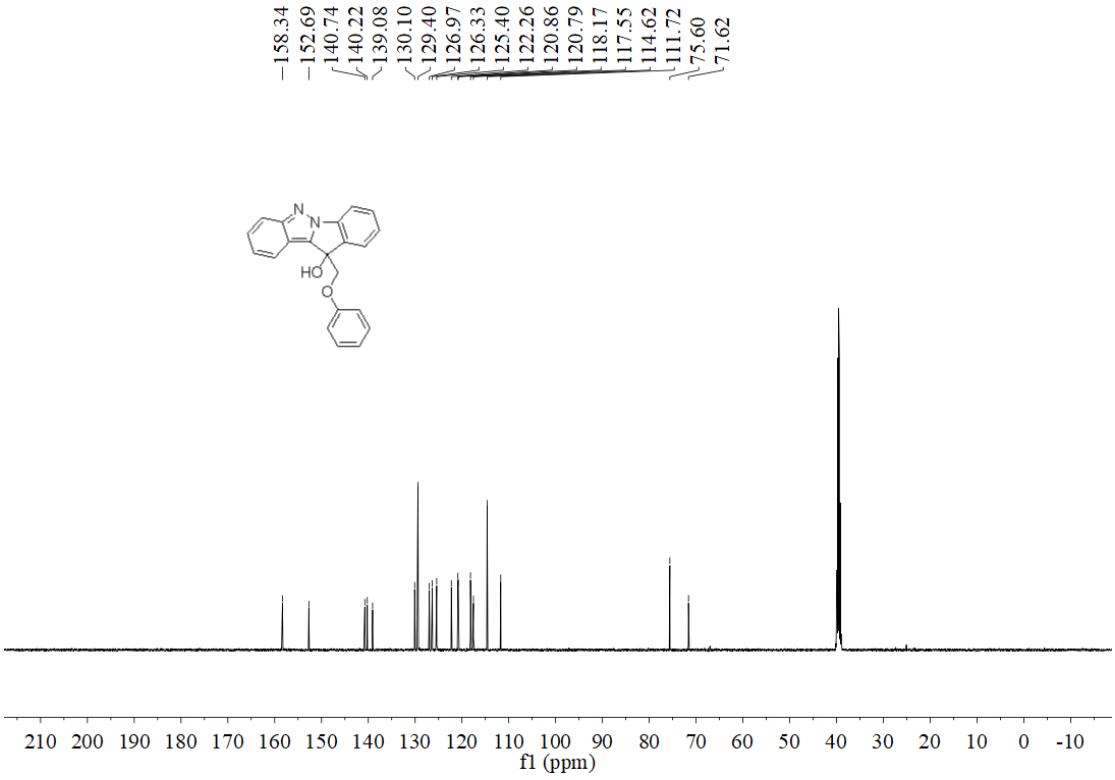


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 39.

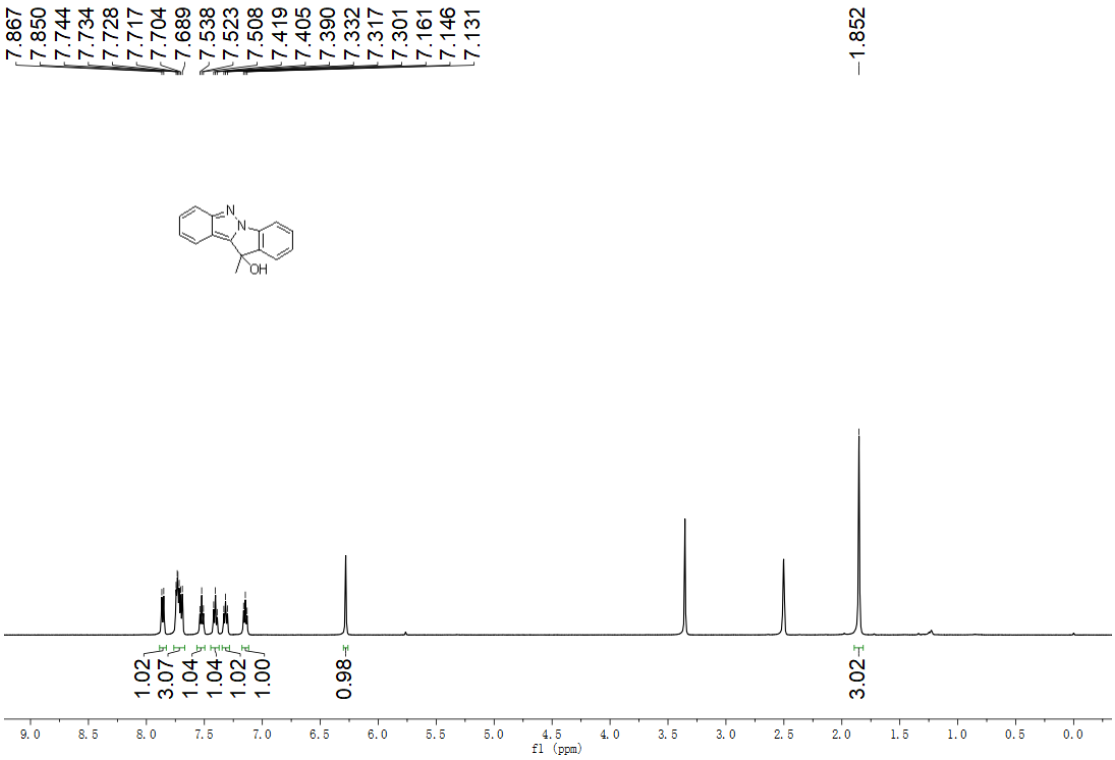


(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

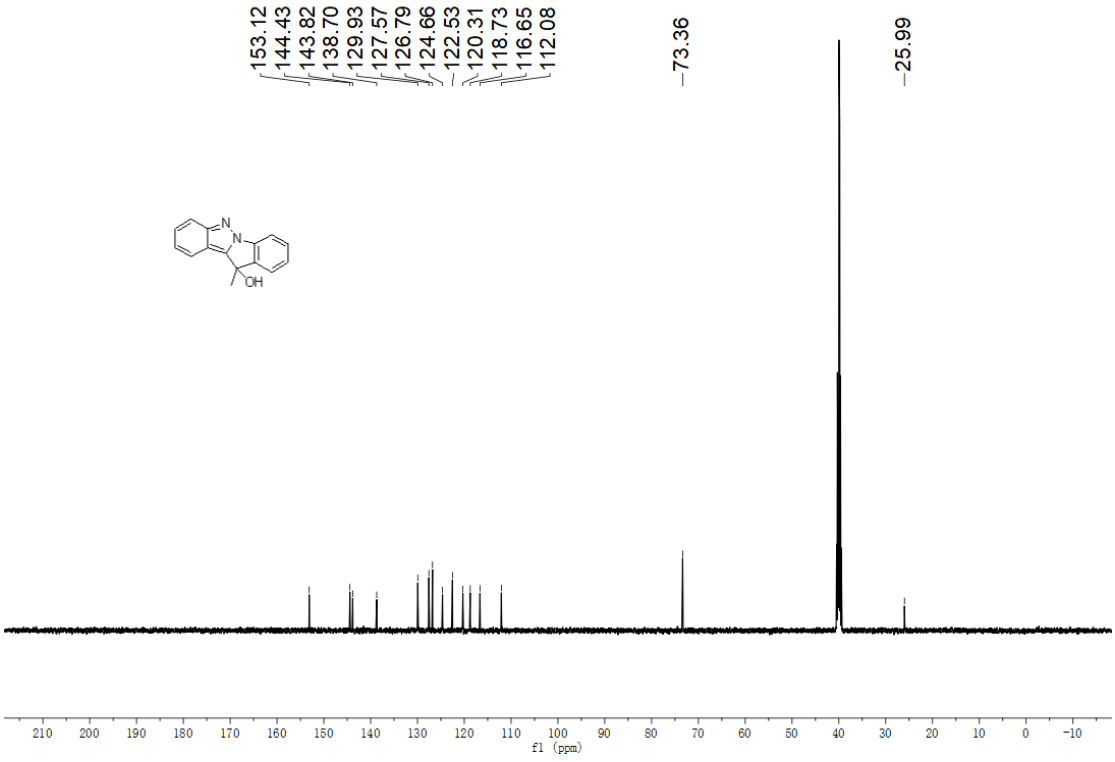


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 40.

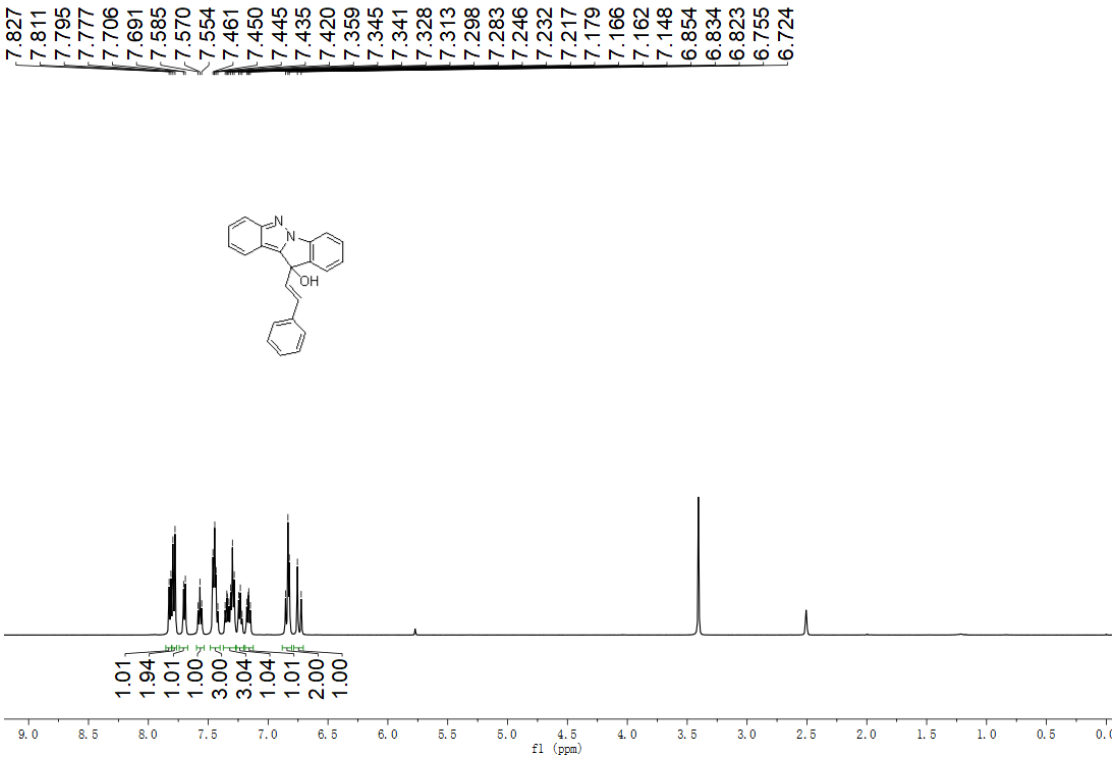


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

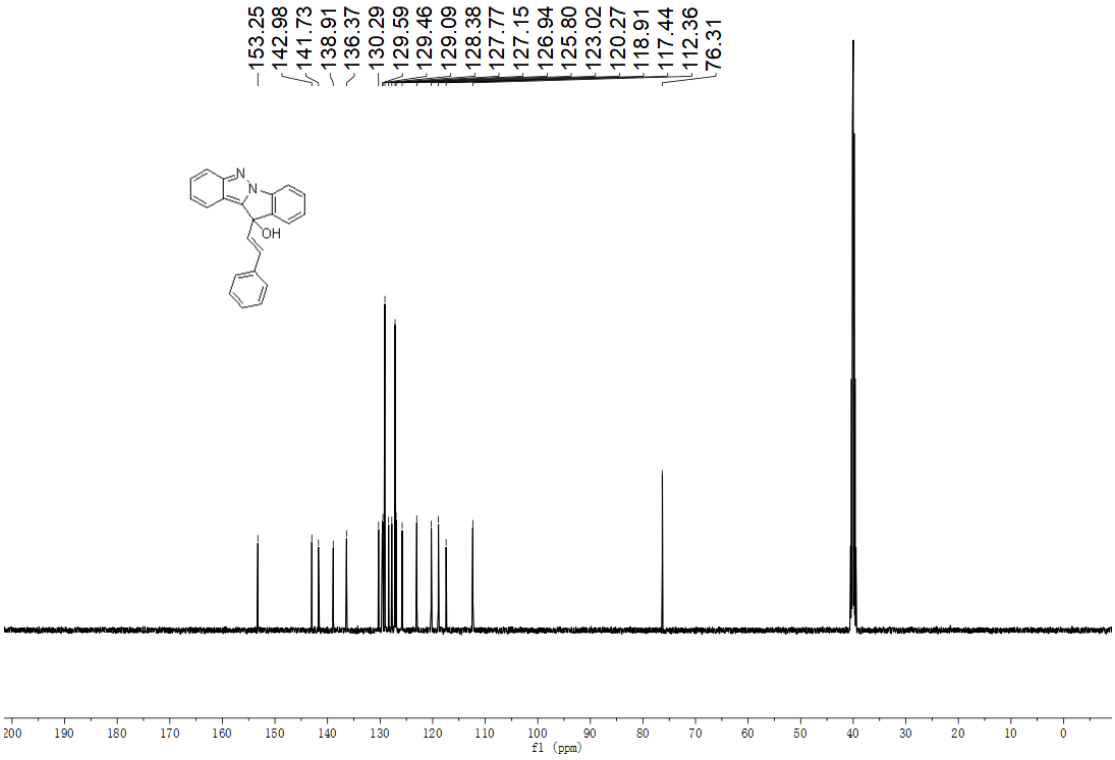


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 41.

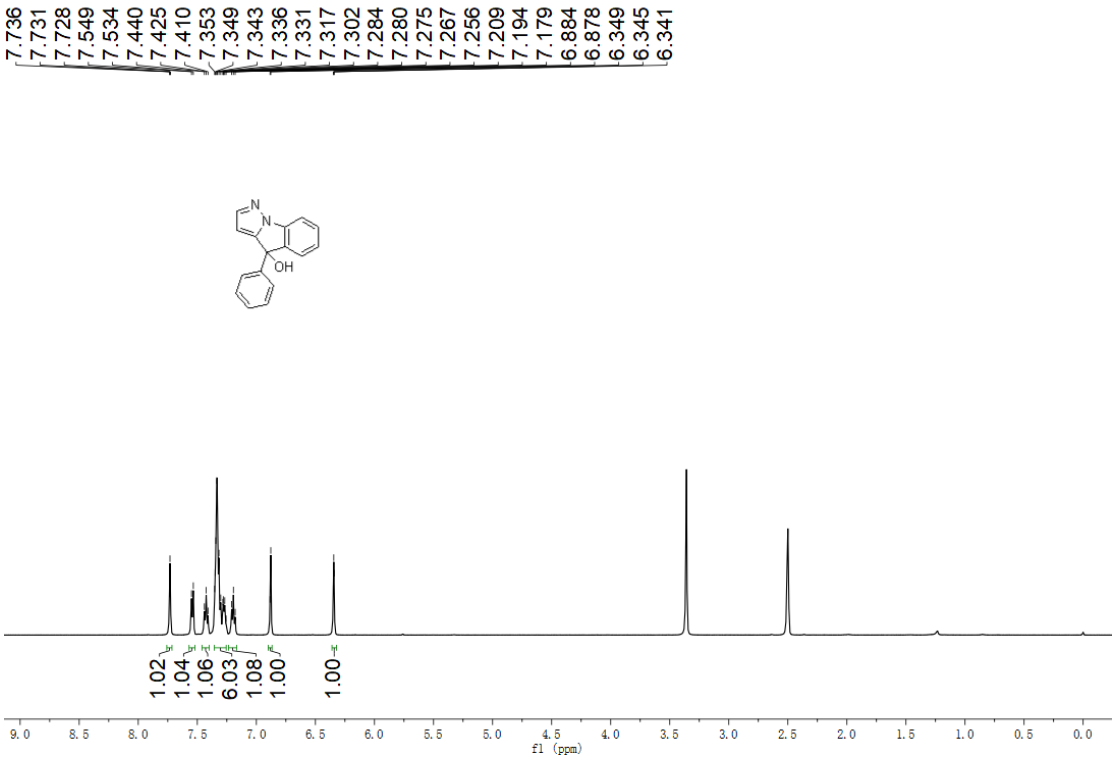


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

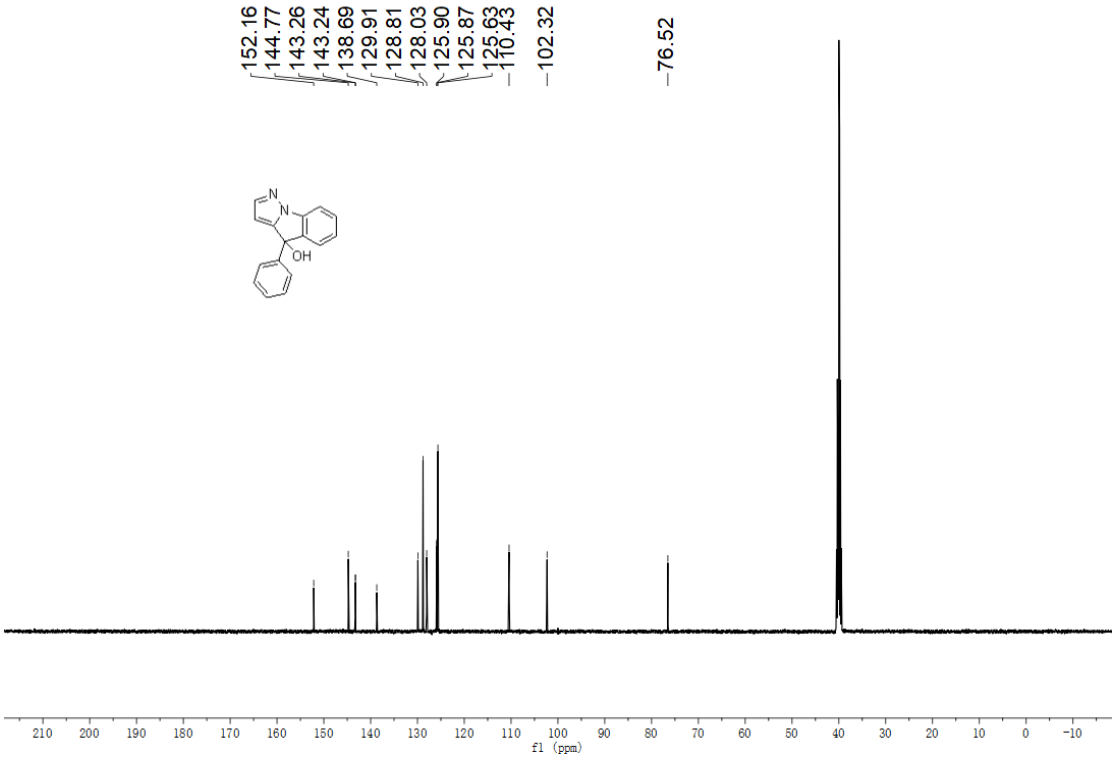


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 42.

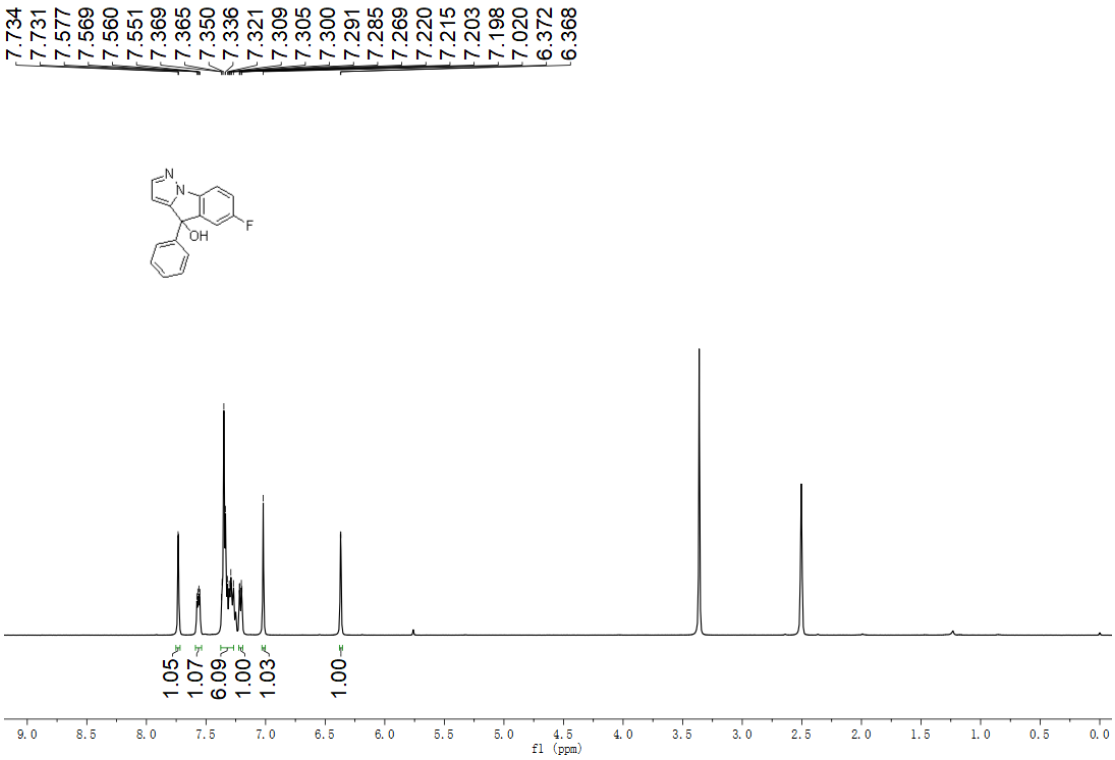


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

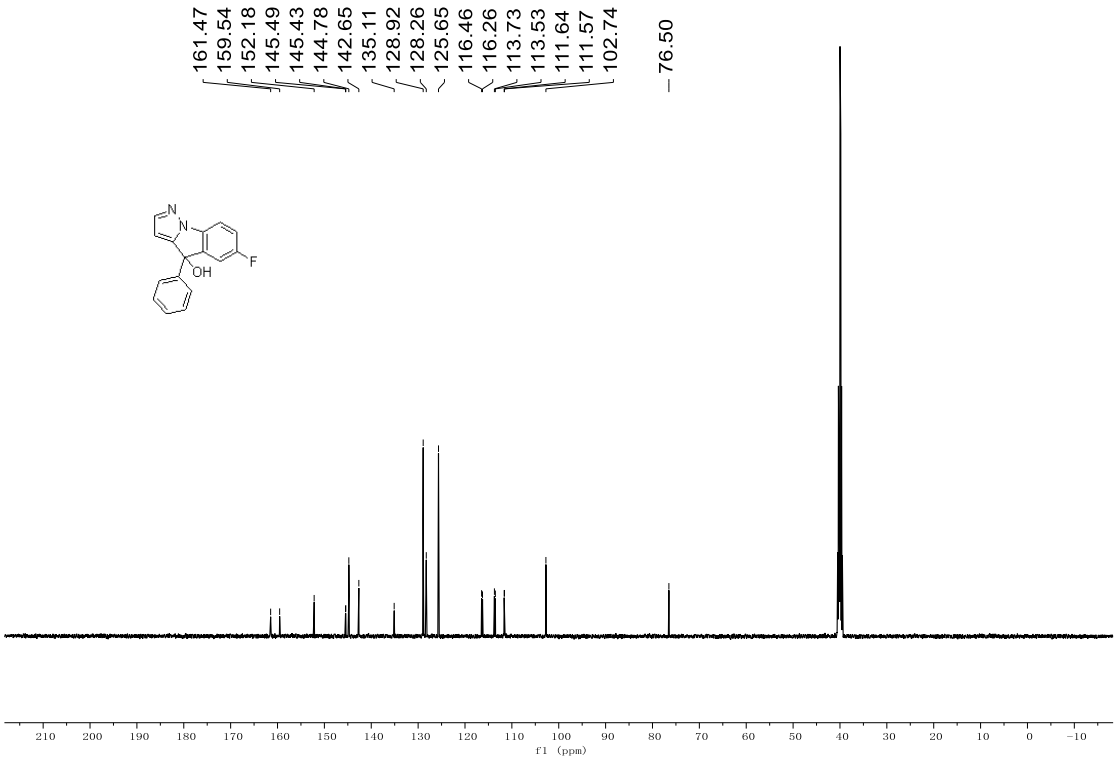


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

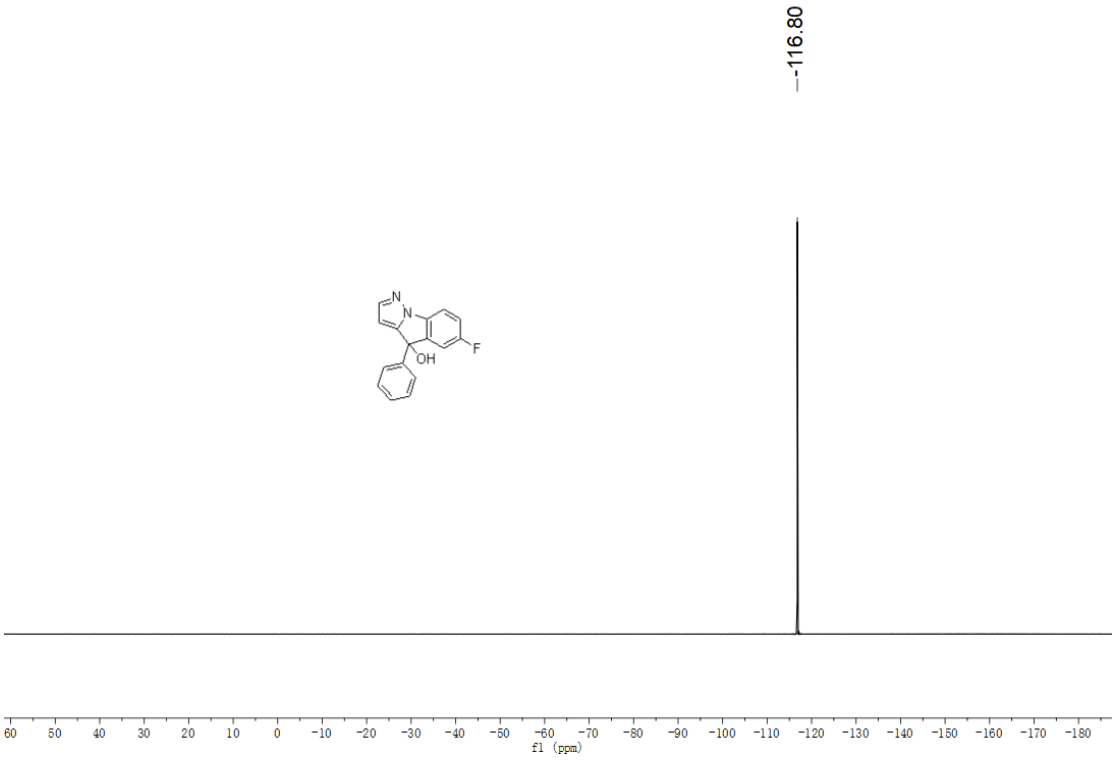
^{1}H , ^{13}C and ^{19}FNMR spectra of compound 43.



(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

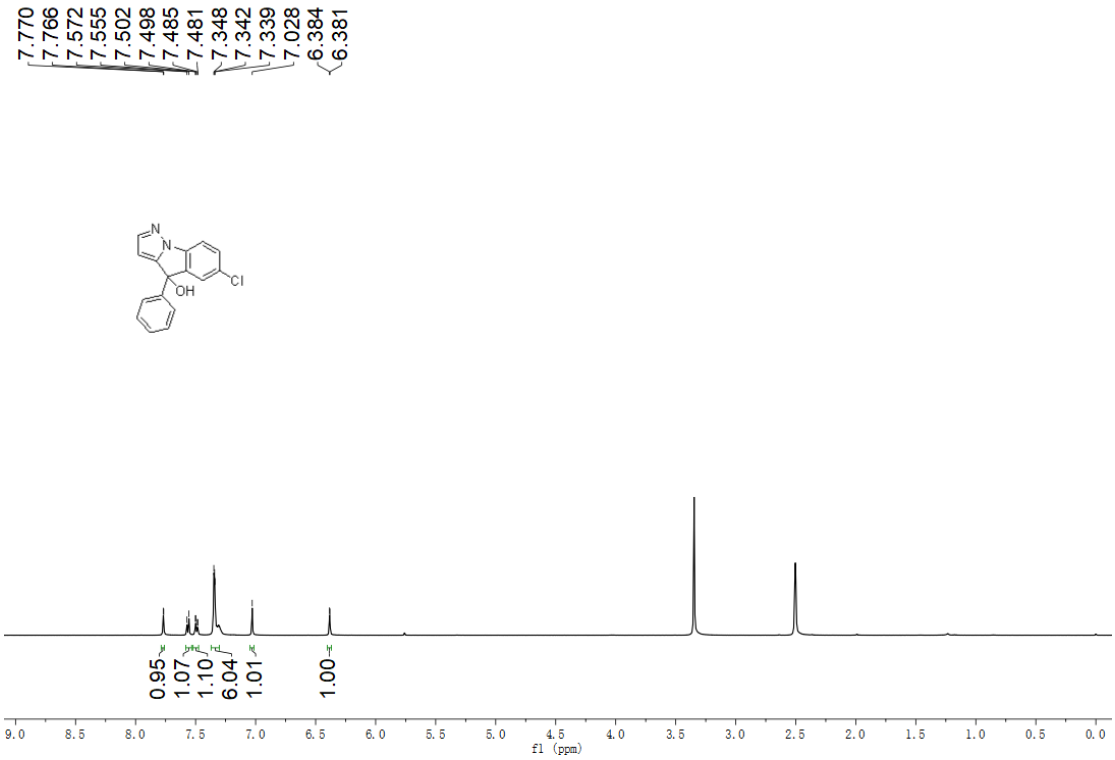


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

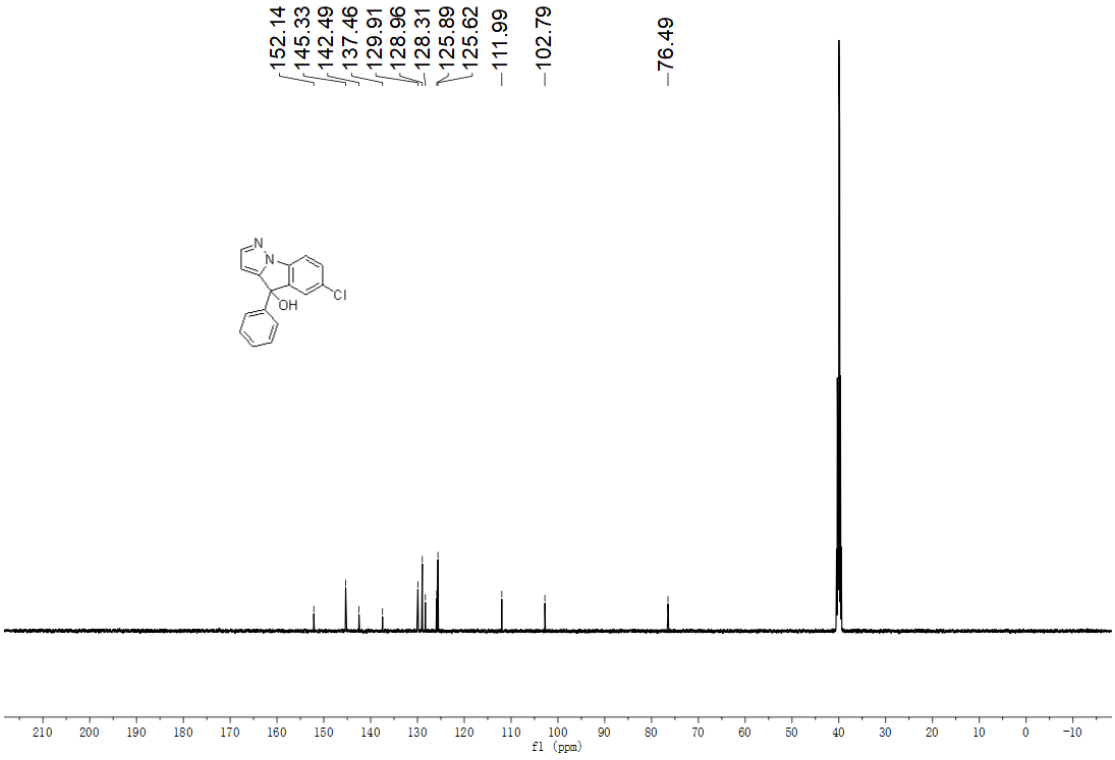


(470MHz for ^{19}F NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 44.

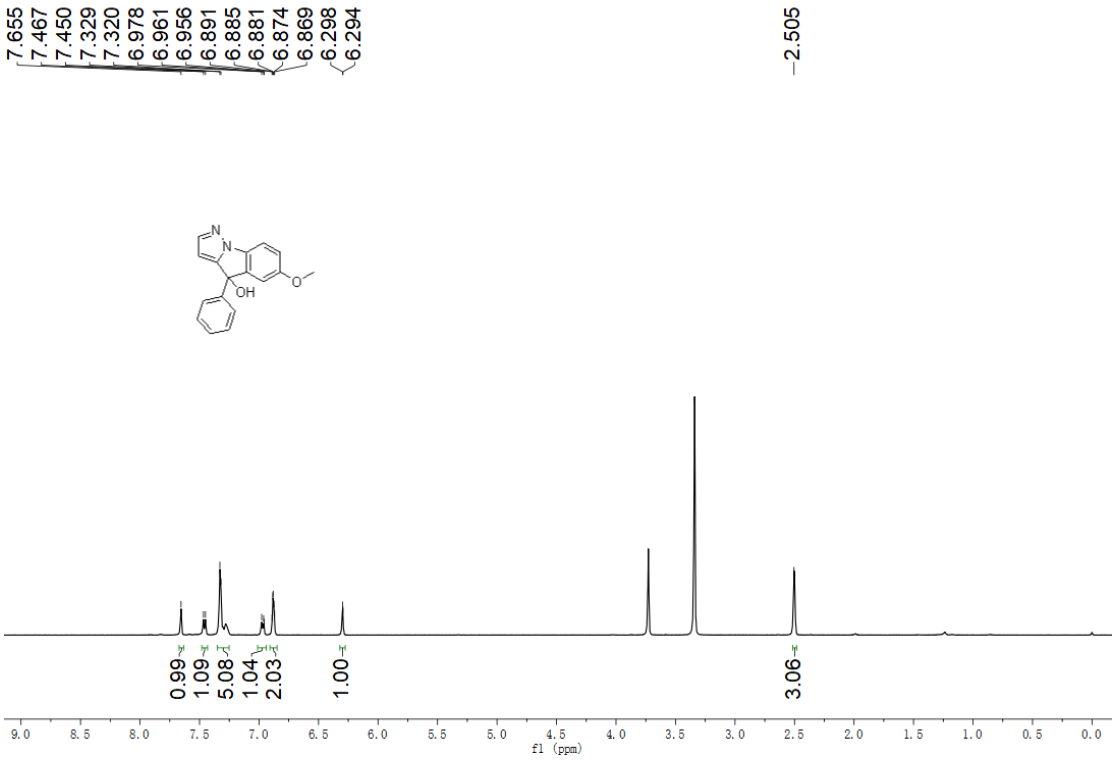


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

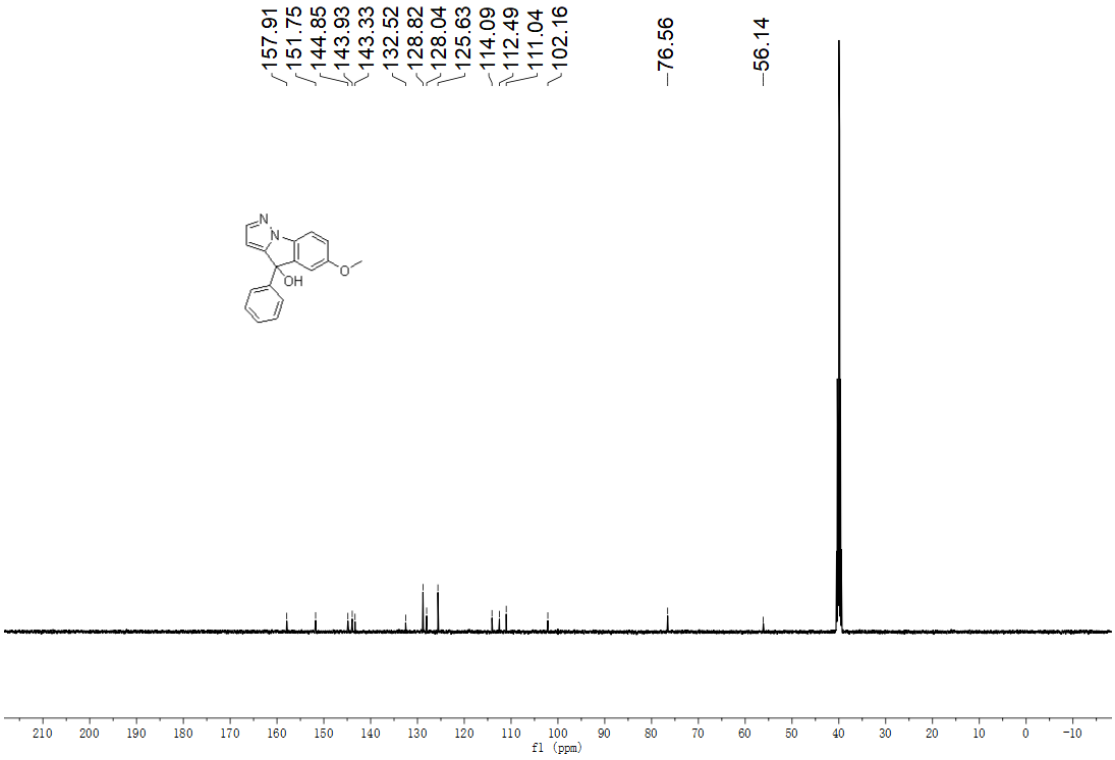


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 45.

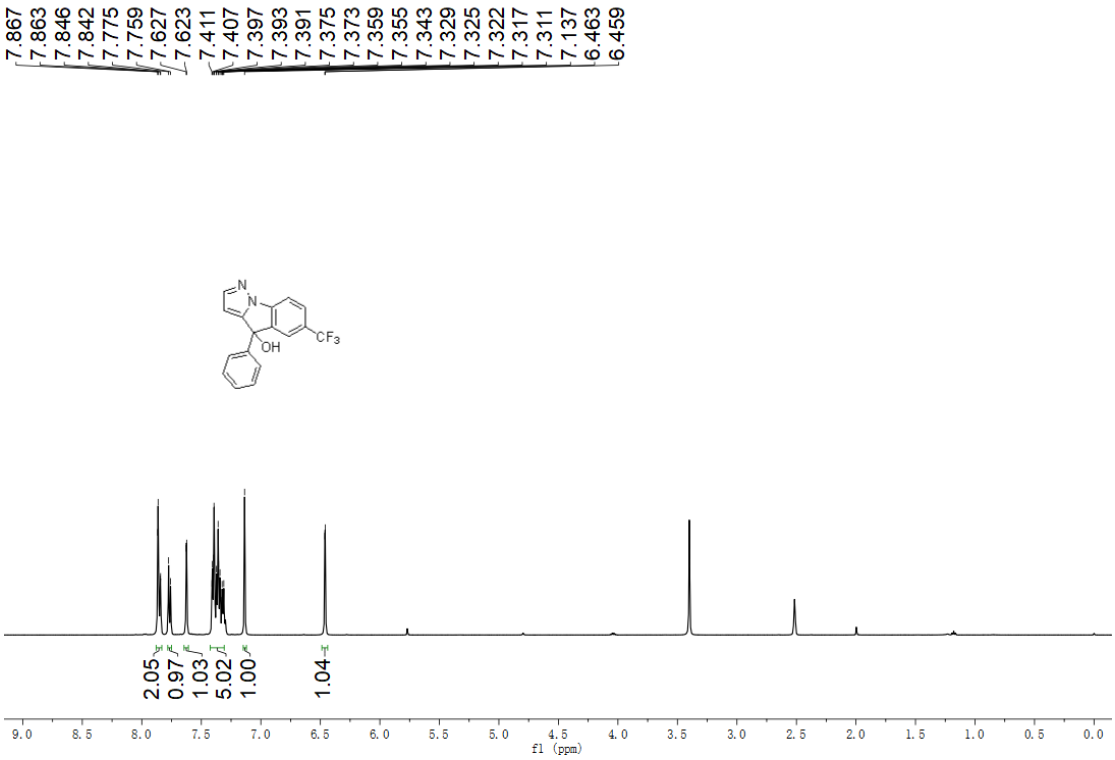


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

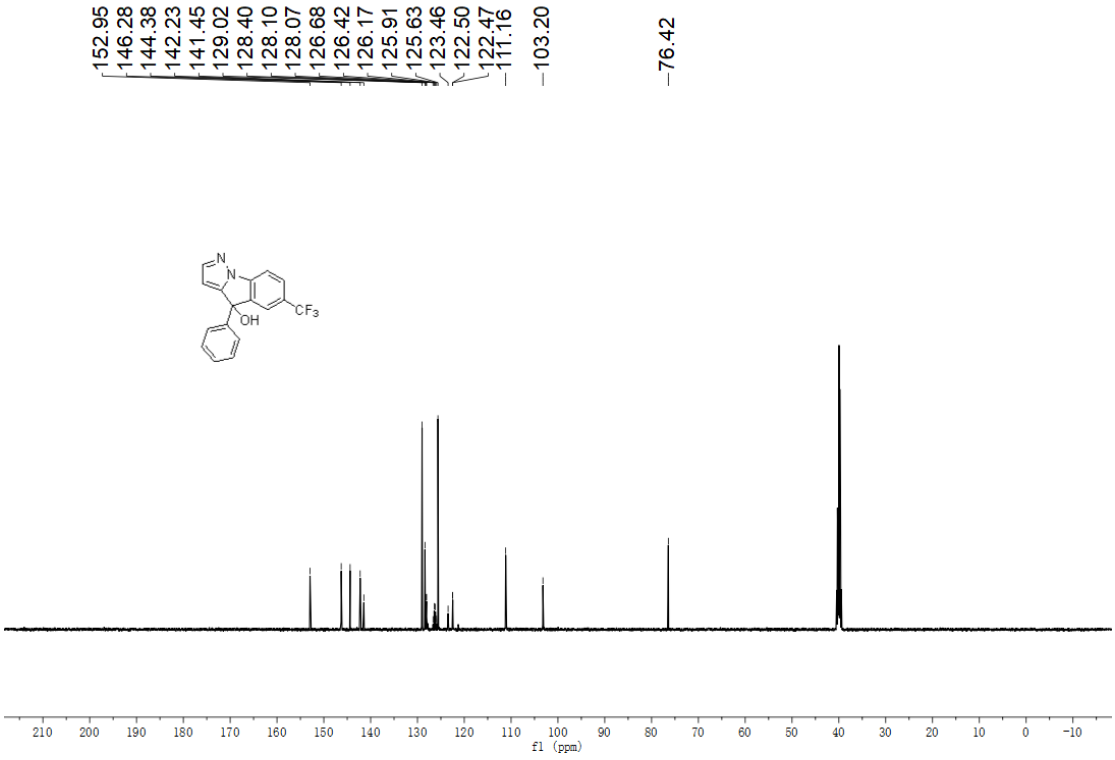


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

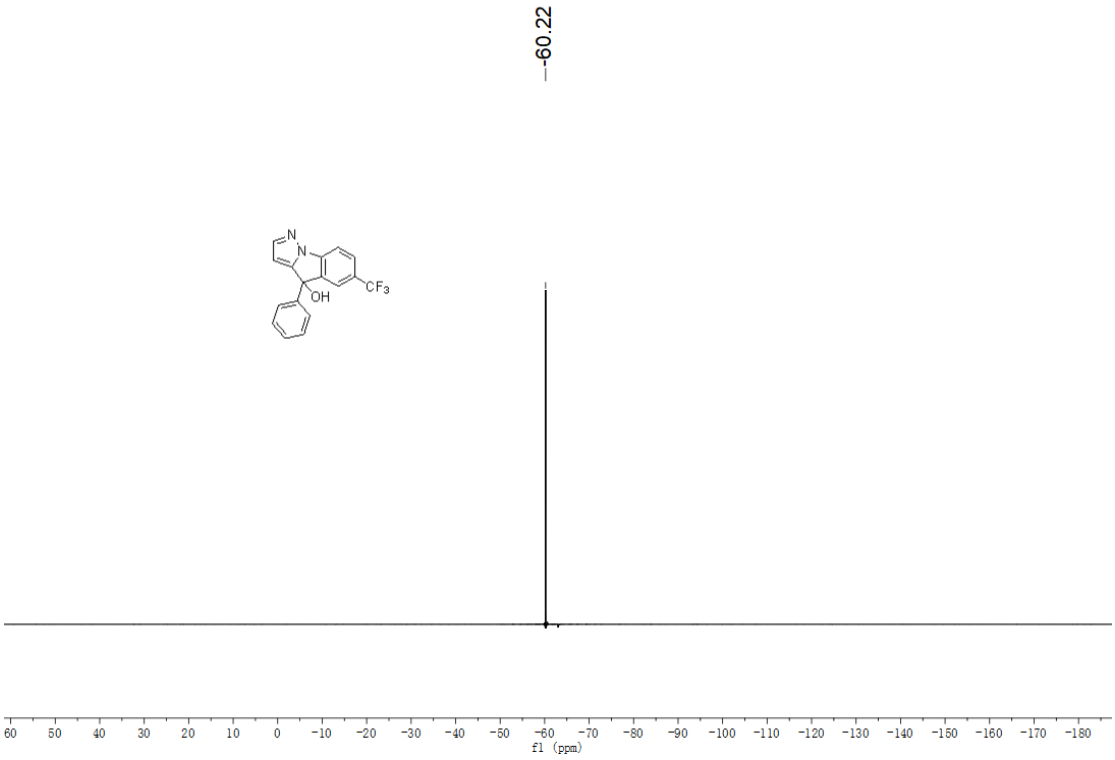
^{1}H ,^{13}C and ^{19}F NMR spectra of compound 46.



(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

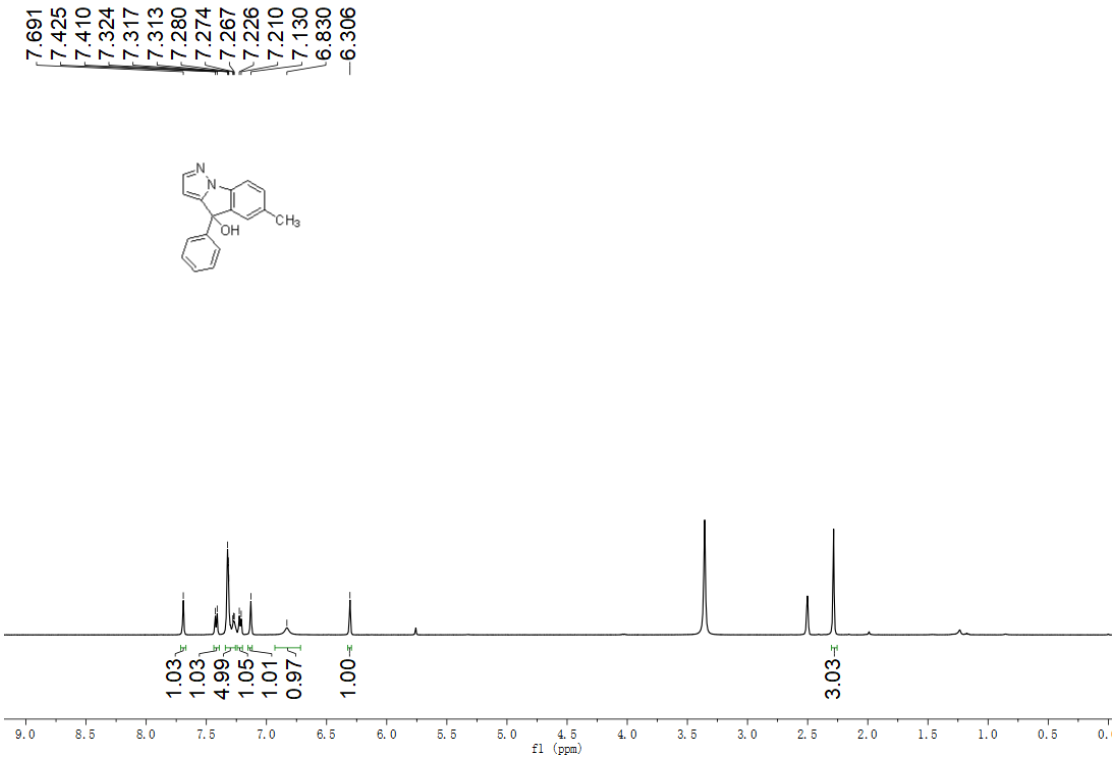


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

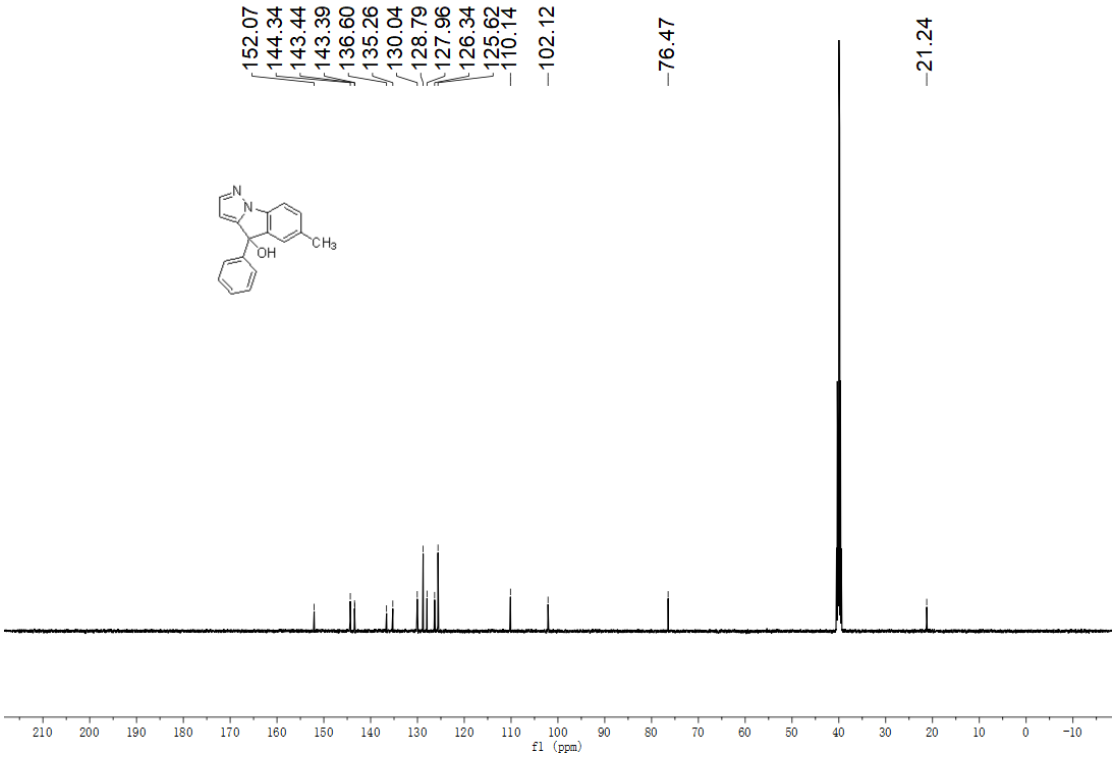


(470 MHz for ^{19}F NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 47.

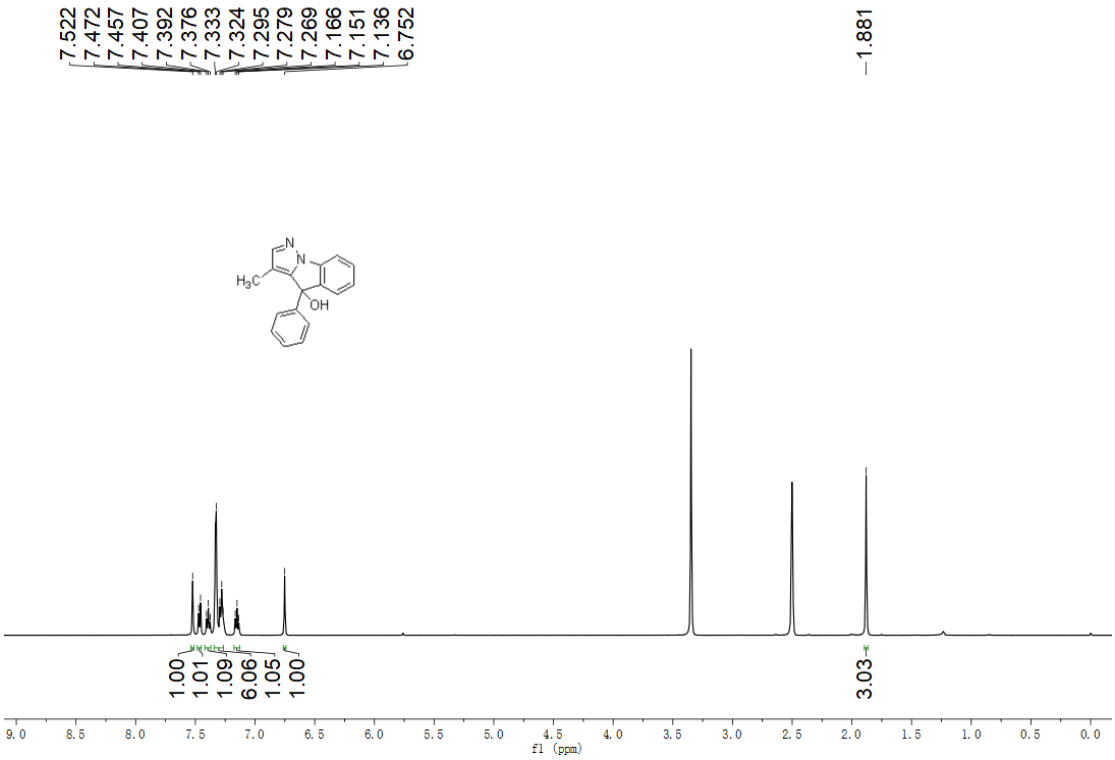


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

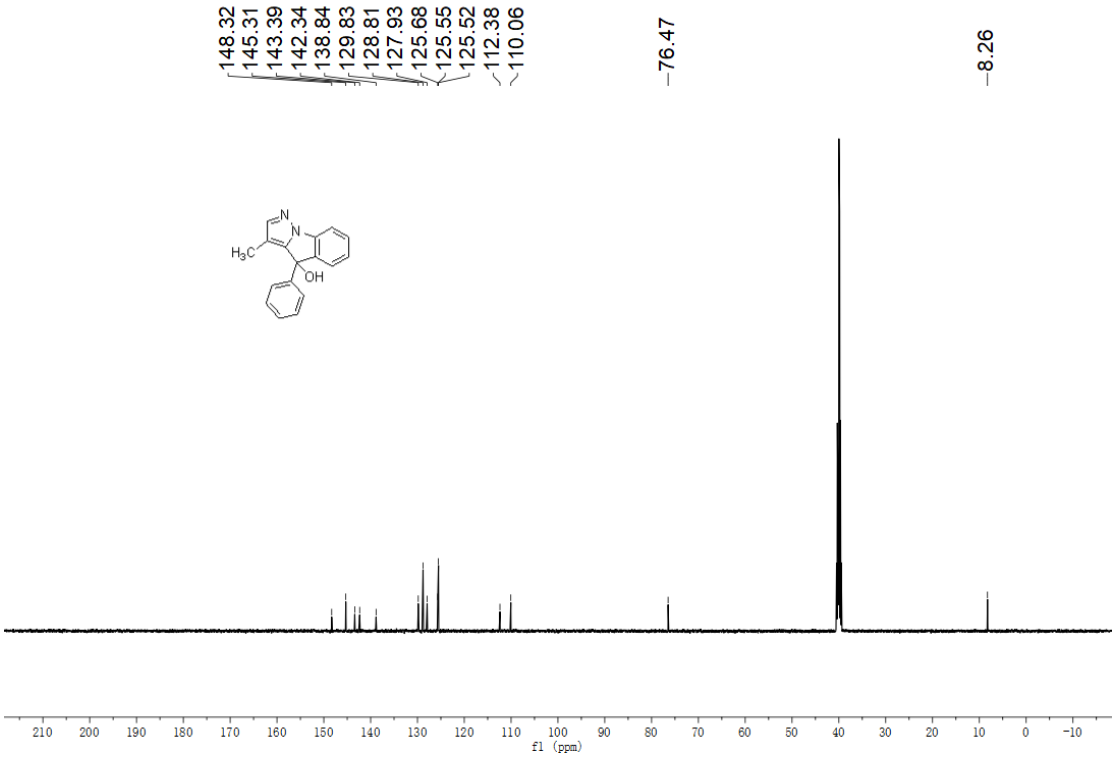


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 48.

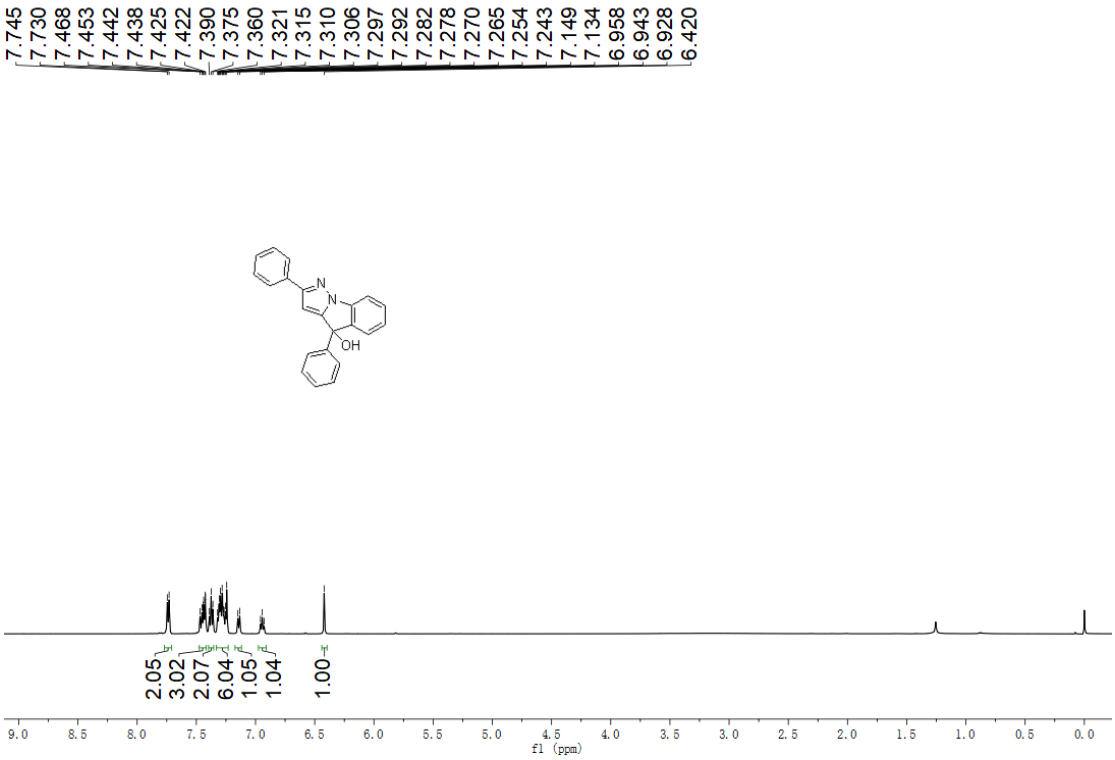


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

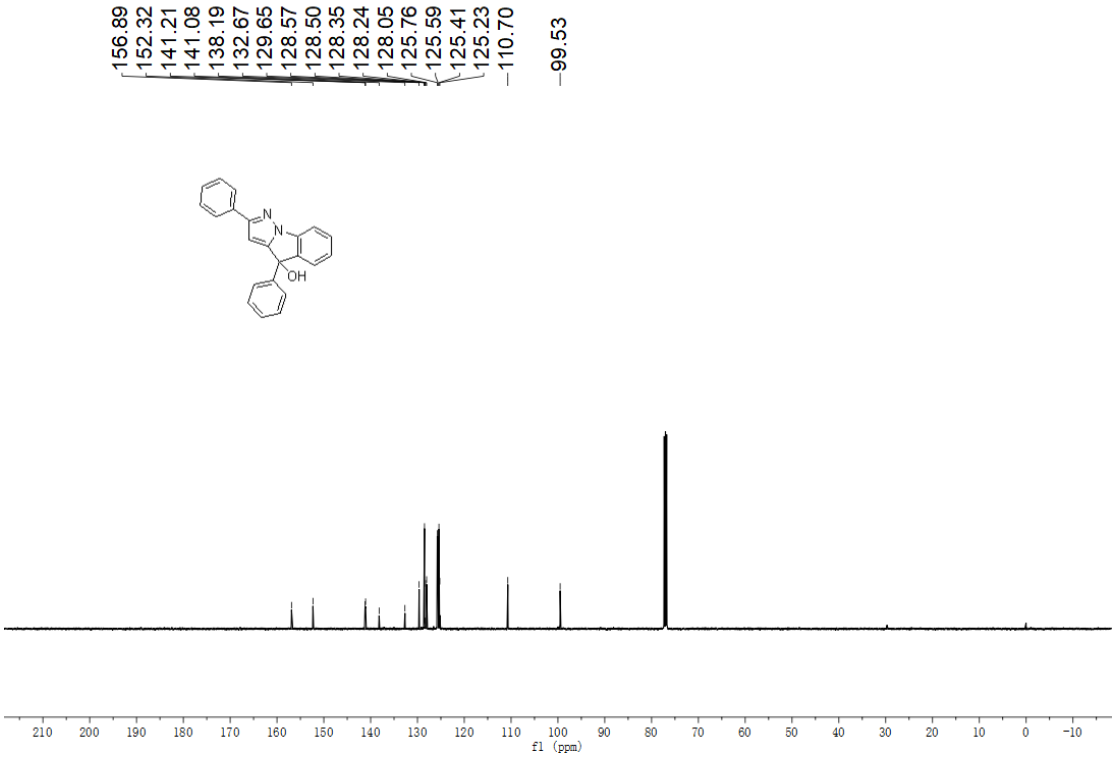


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 49.

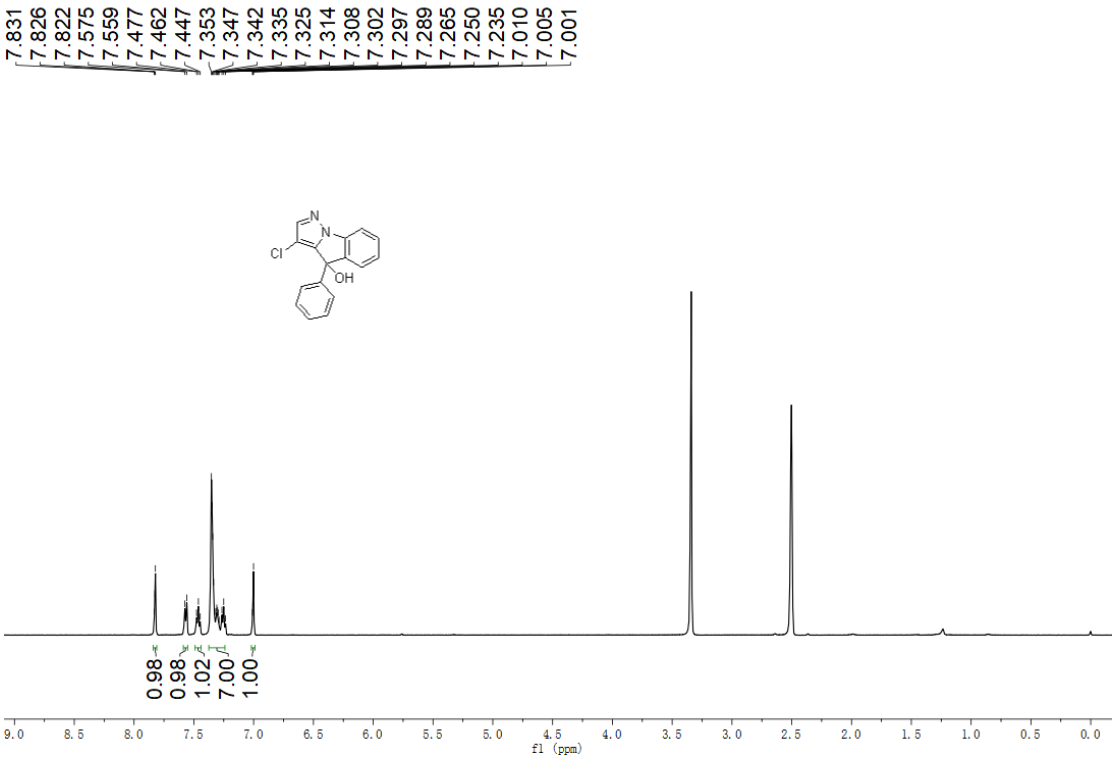


(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

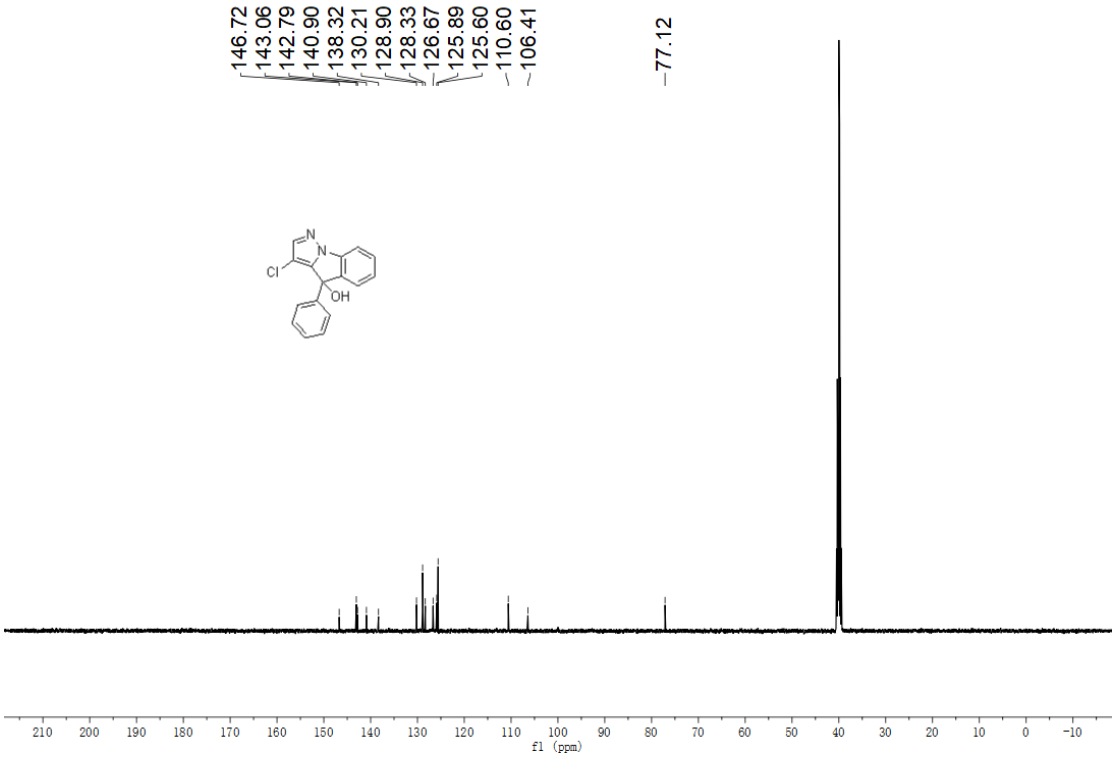


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 50.

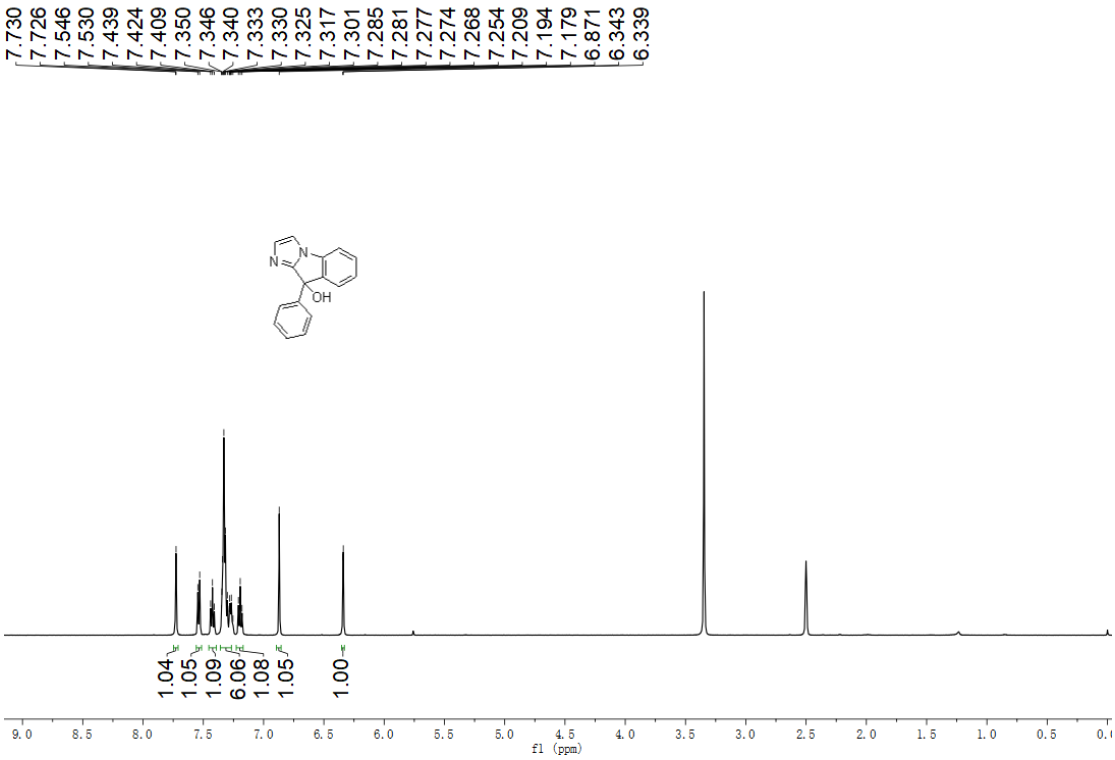


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

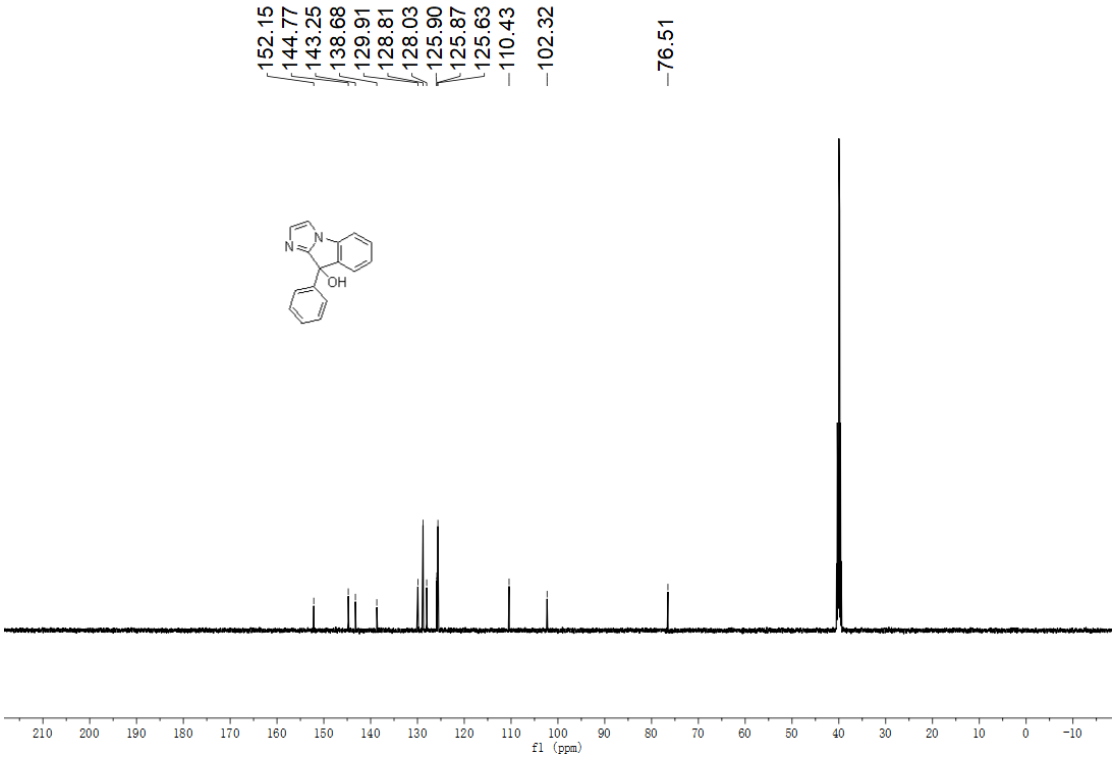


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 51.

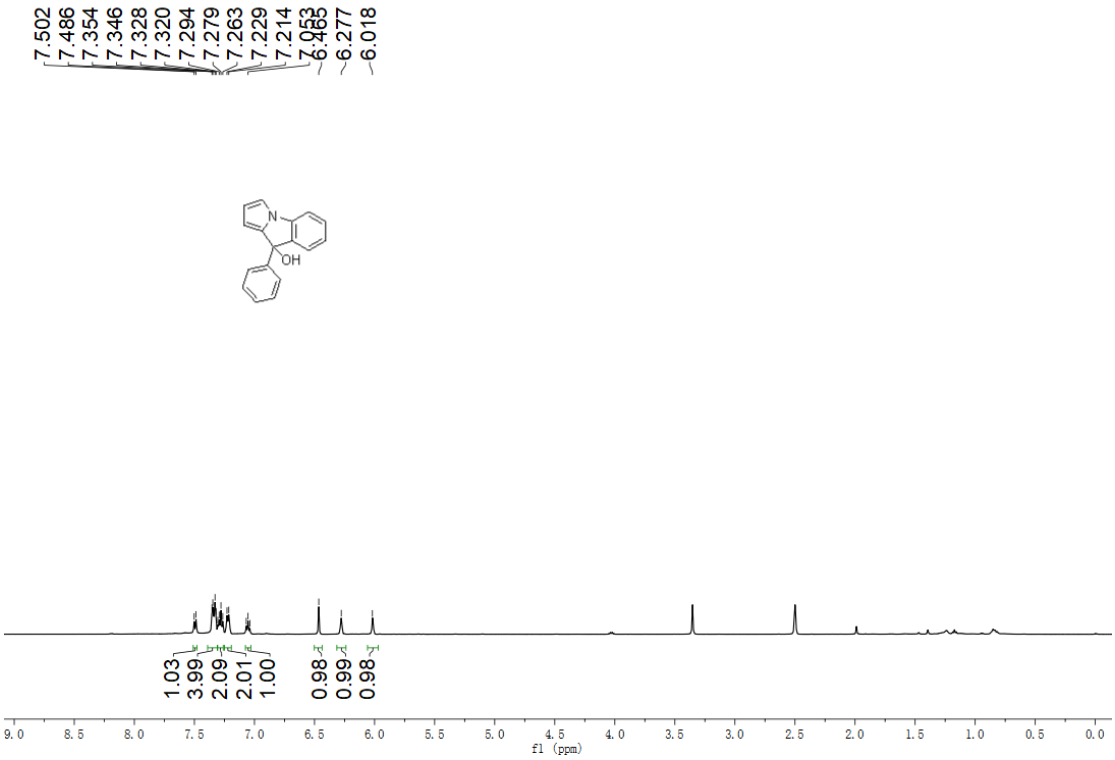


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

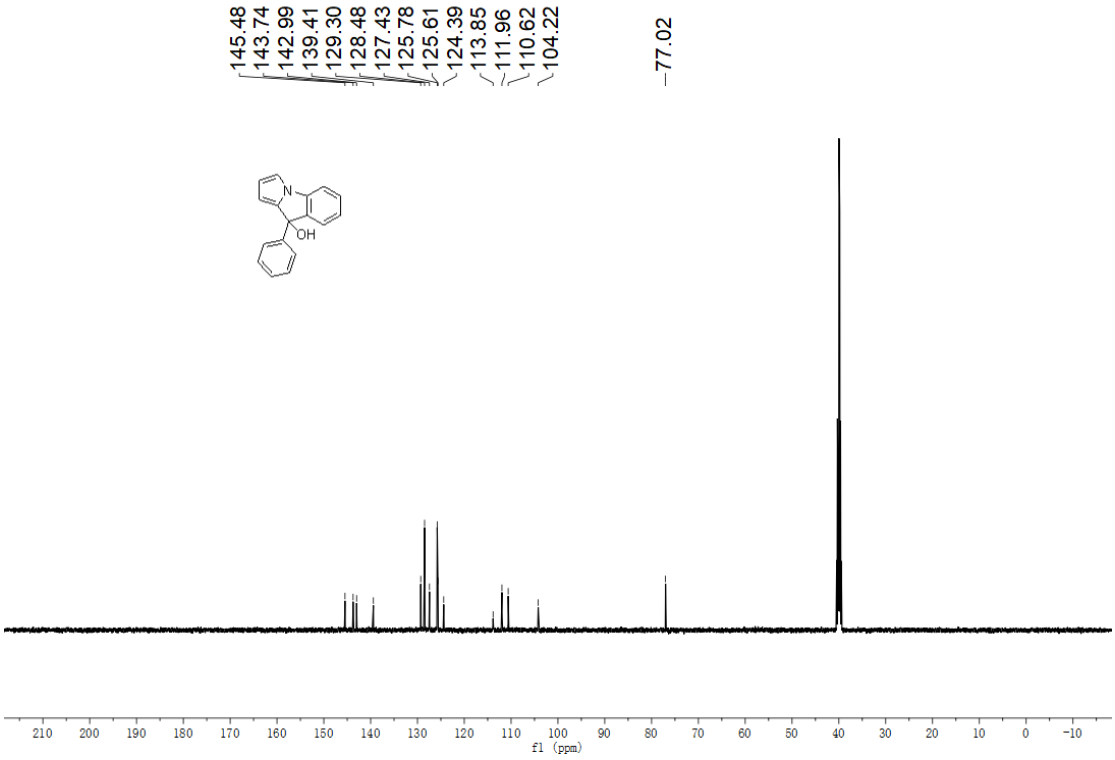


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 52.

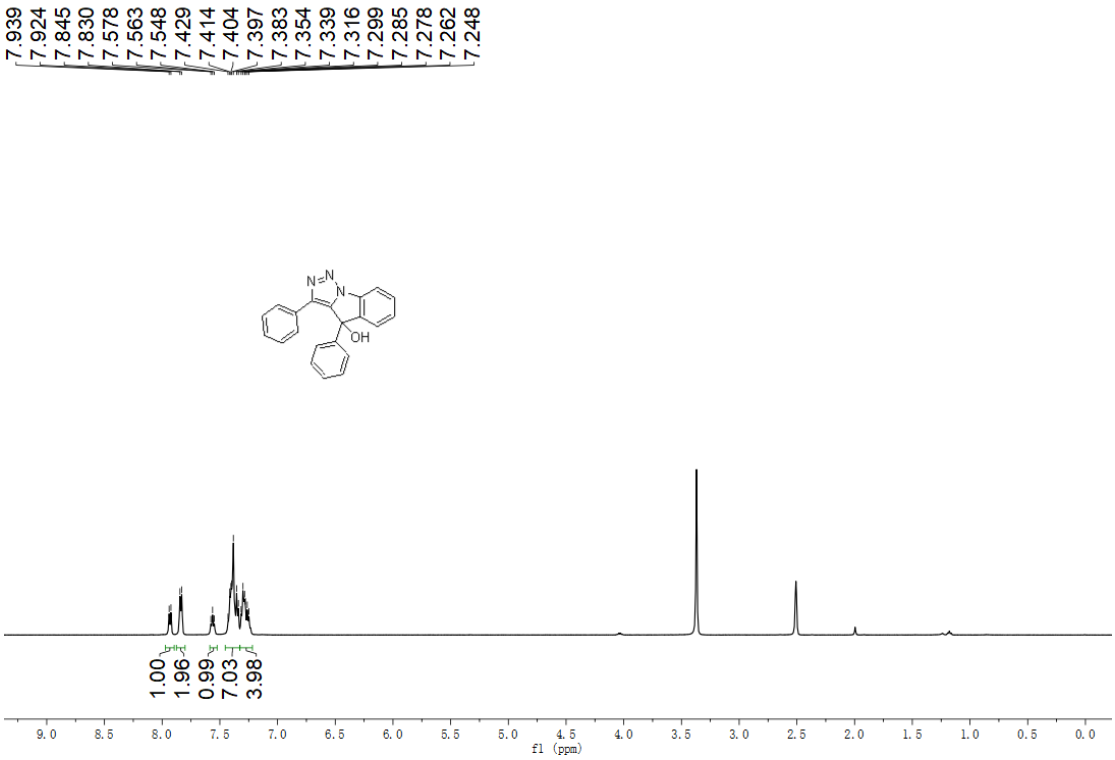


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

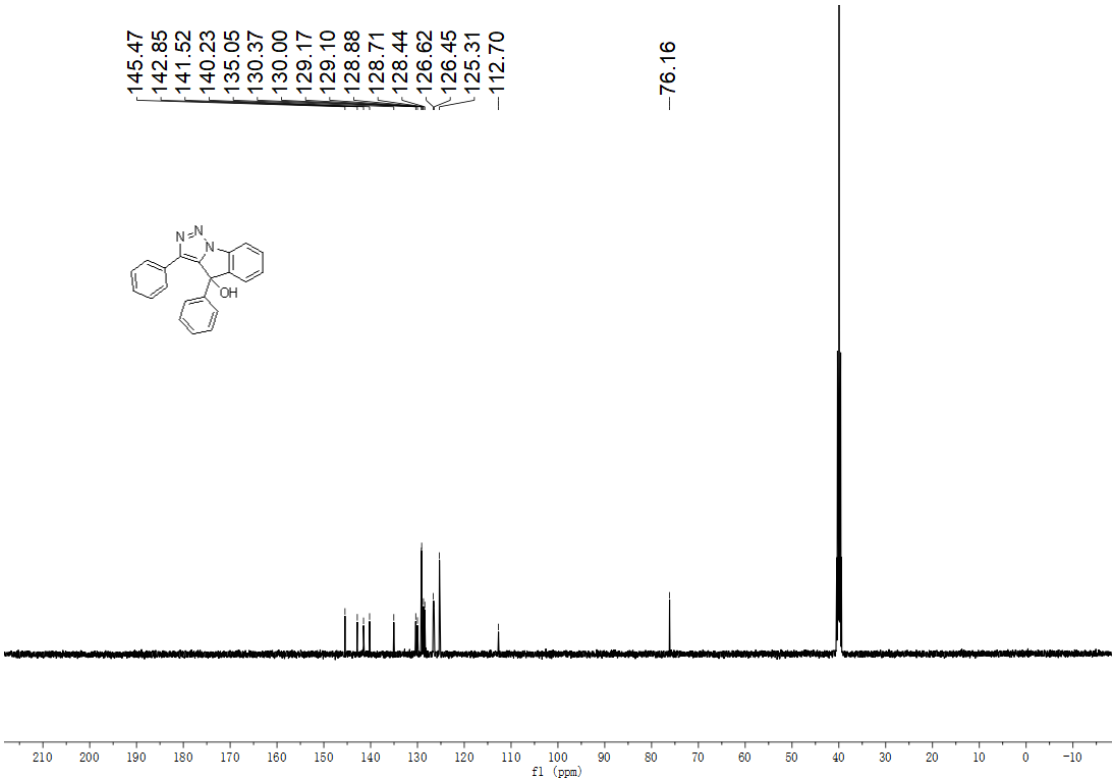


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 53.

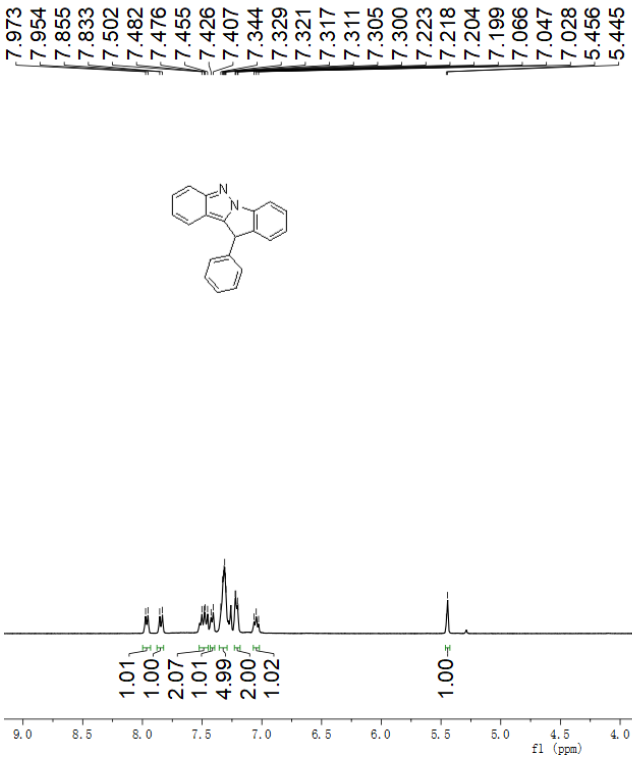


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

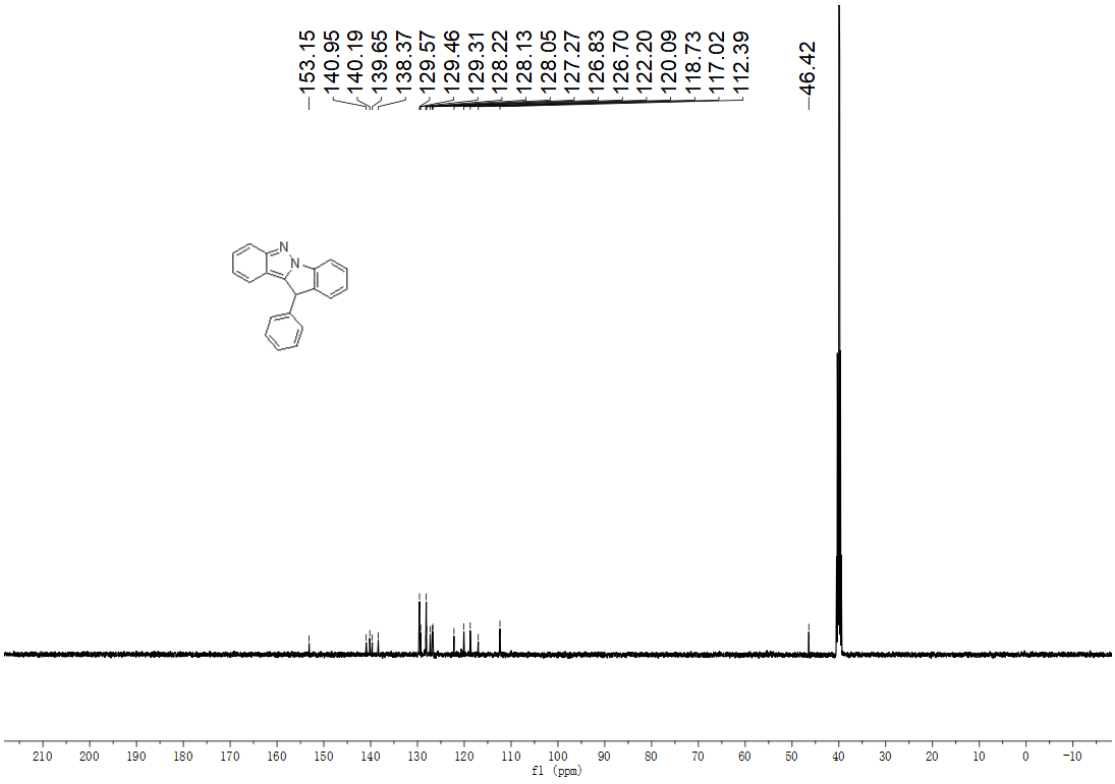


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 54.

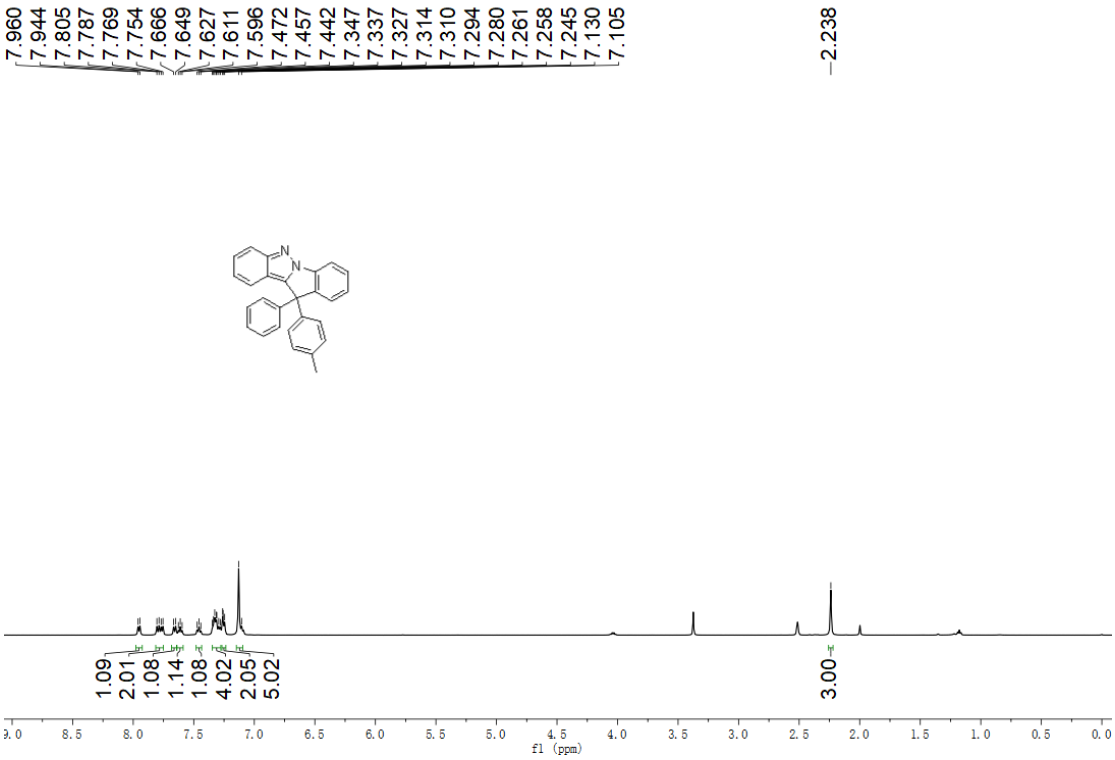


(400 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

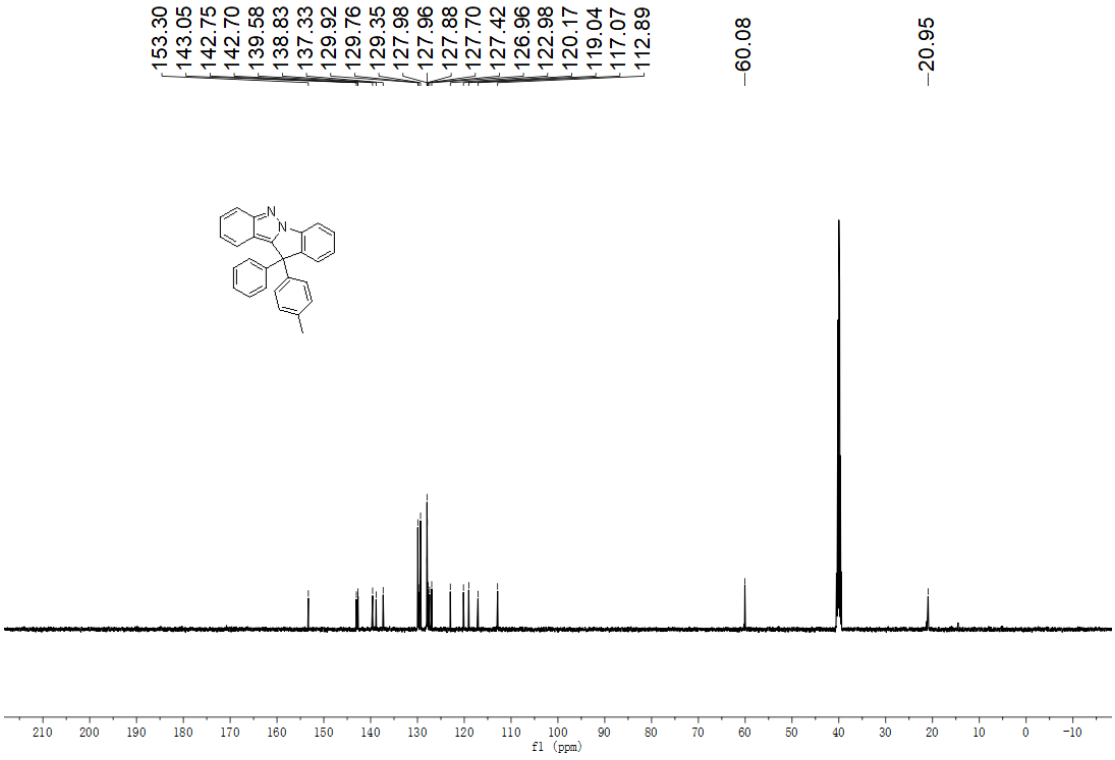


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 55.

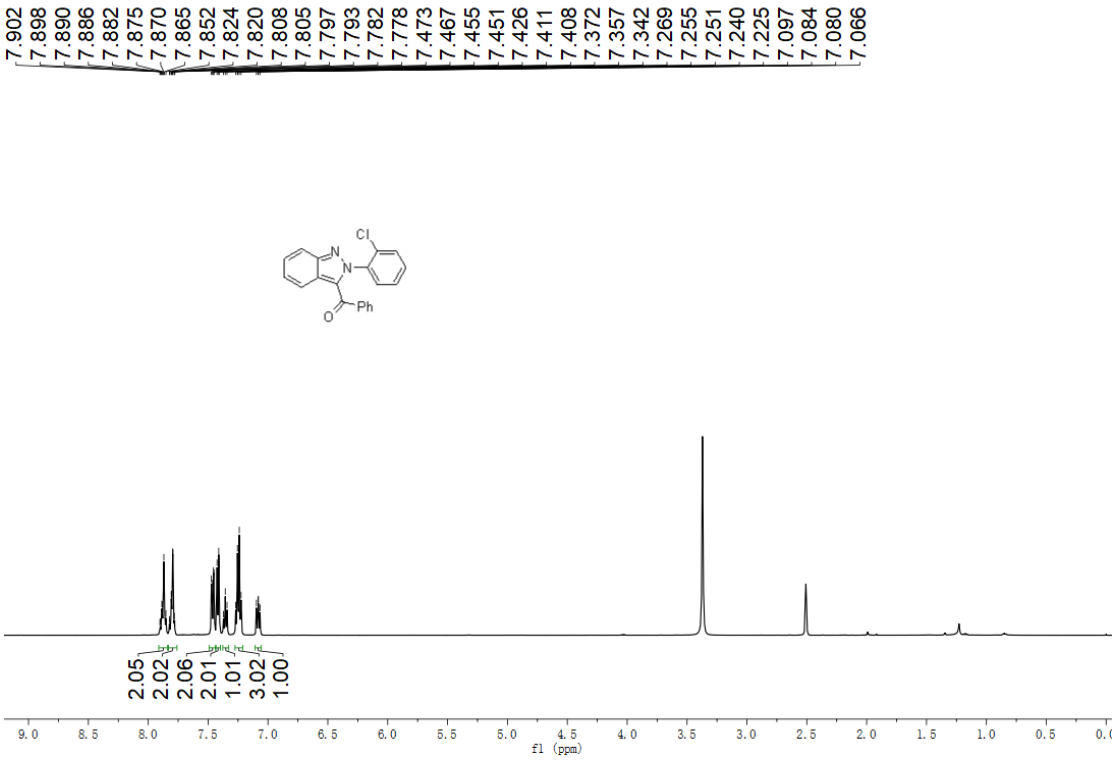


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

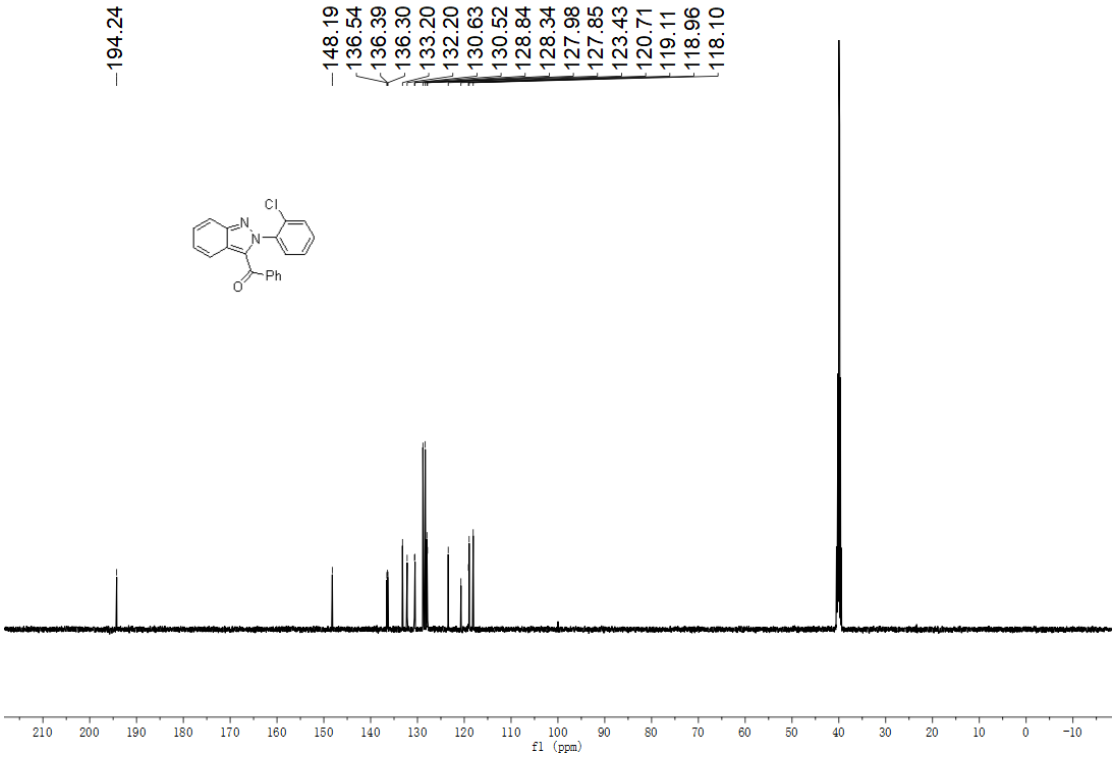


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 56.

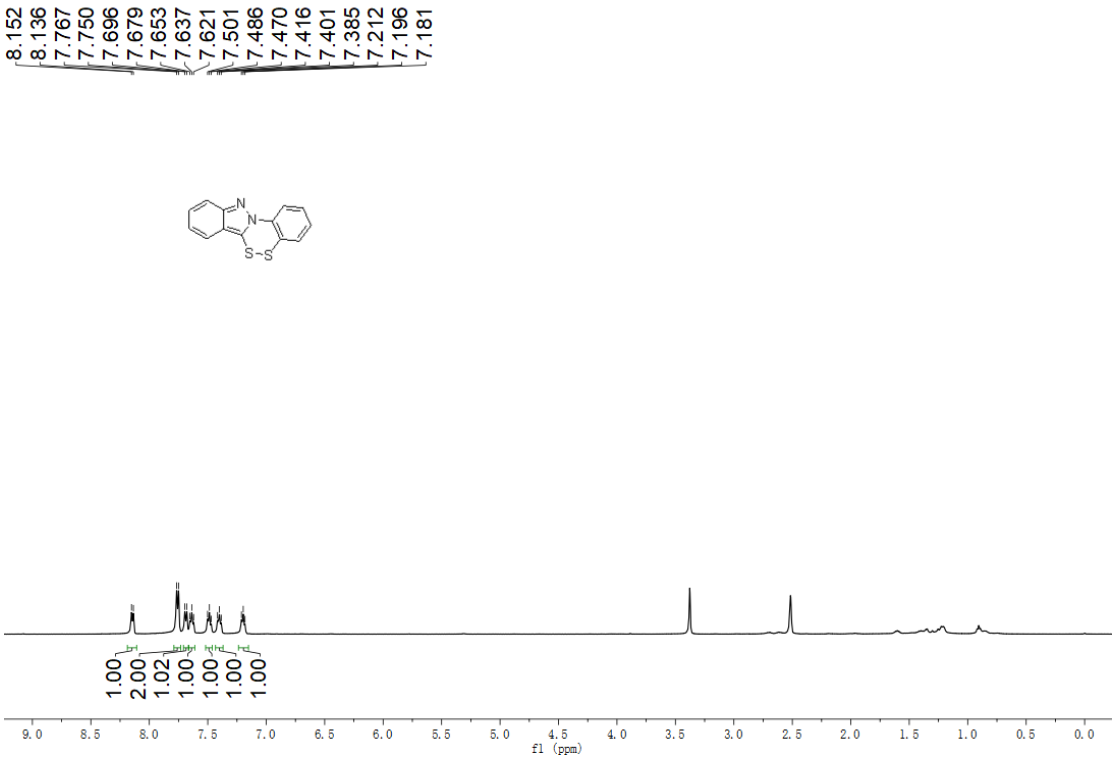


(500 MHz for ^{1}H NMR with DMSO-d_6 as solvent)

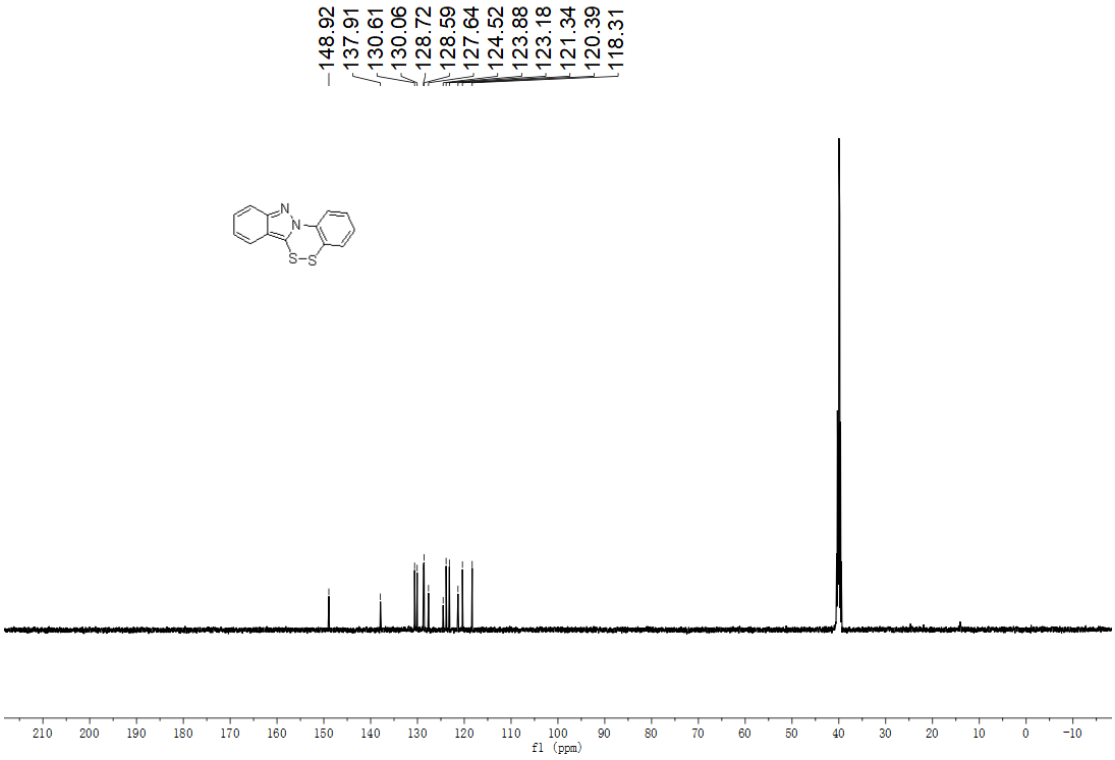


(125 MHz for ^{13}C NMR with DMSO-d_6 as solvent)

^{1}H and ^{13}C NMR spectra of compound 57.

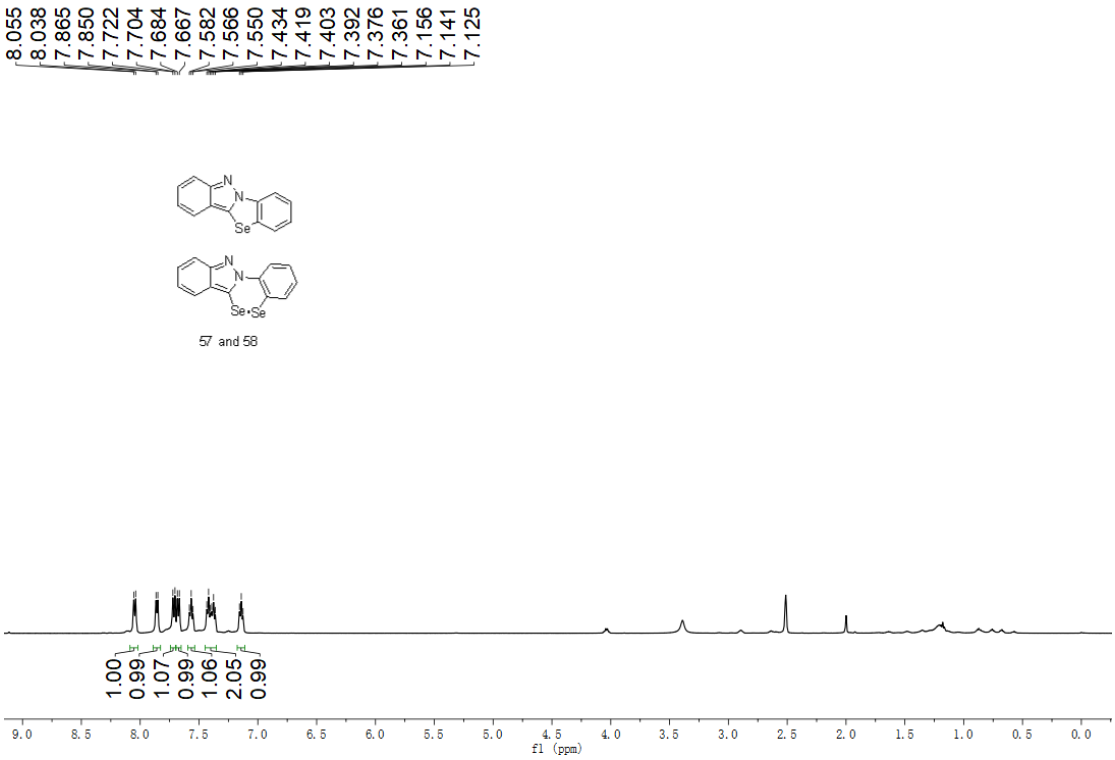


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

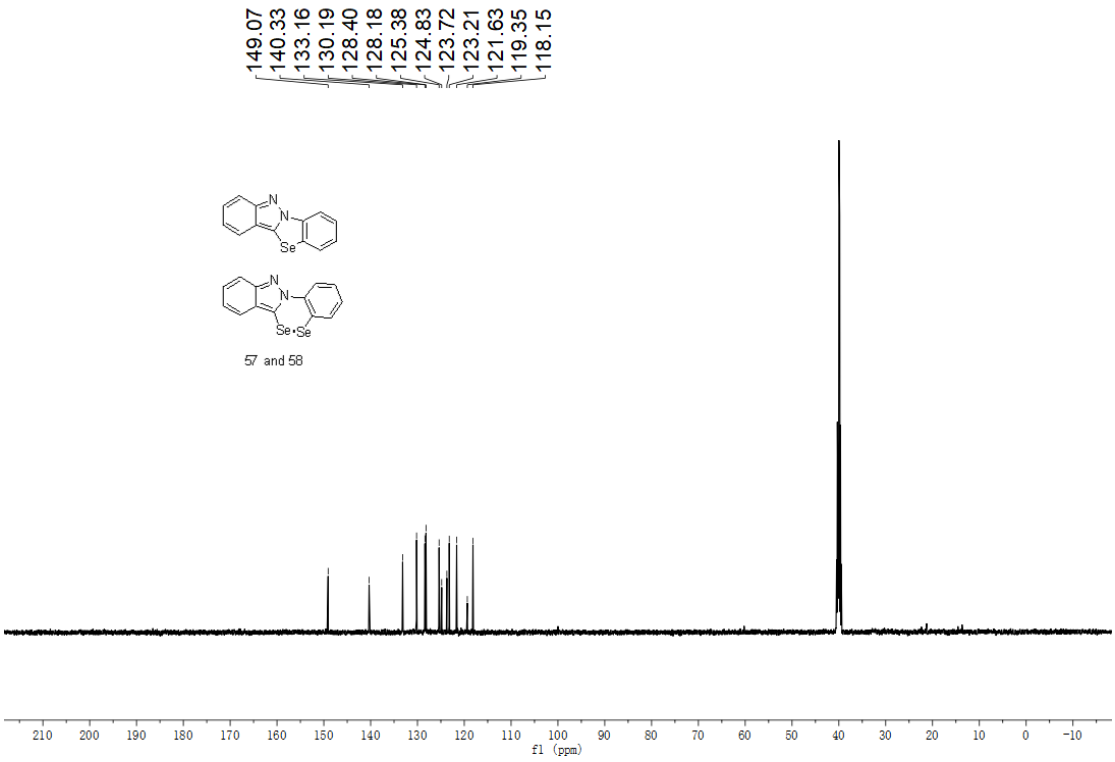


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 58 and 59.

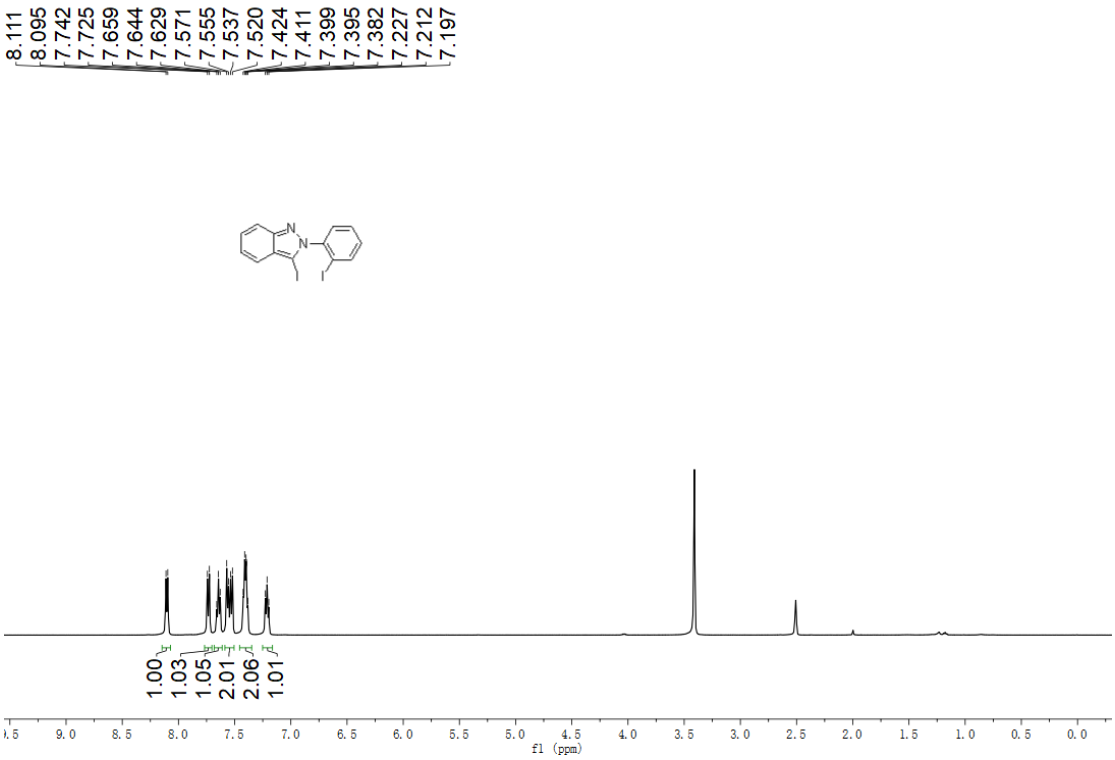


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

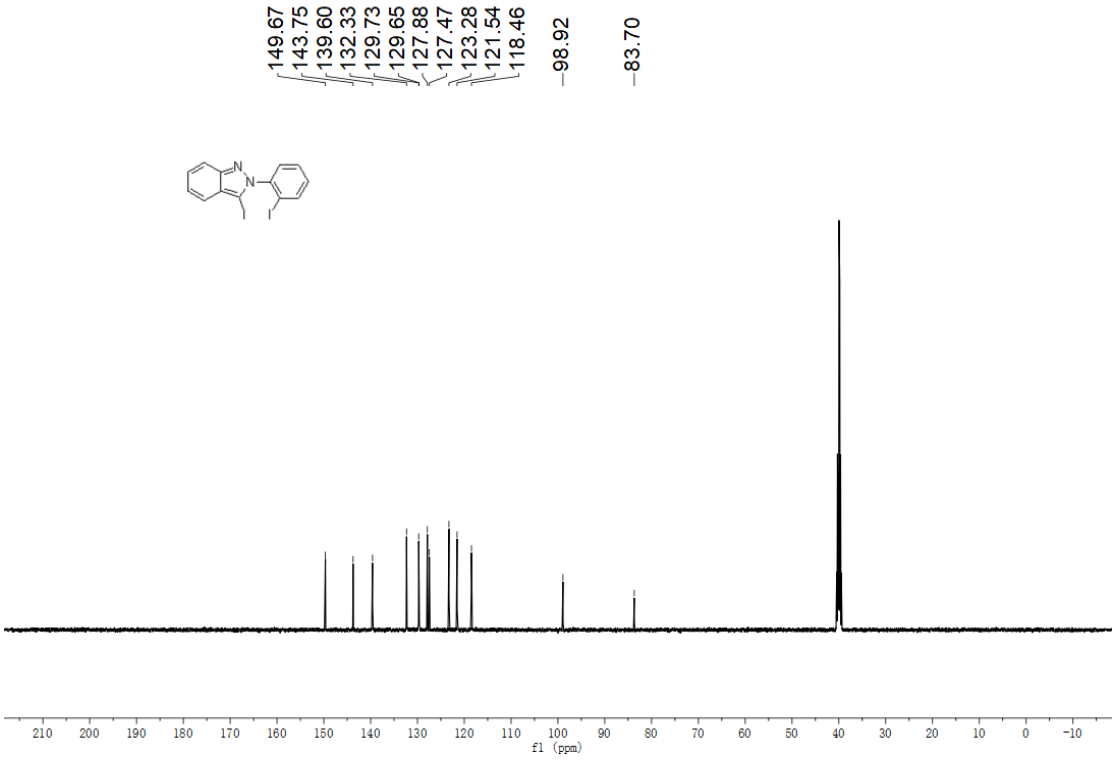


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 60.

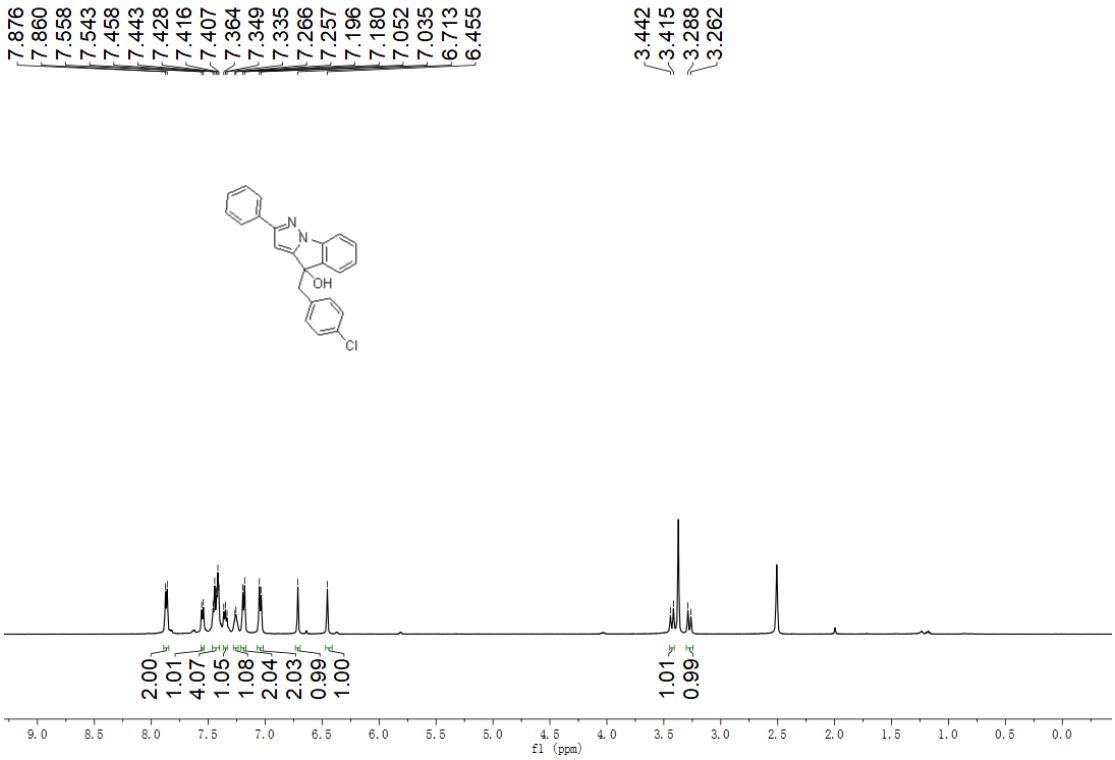


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

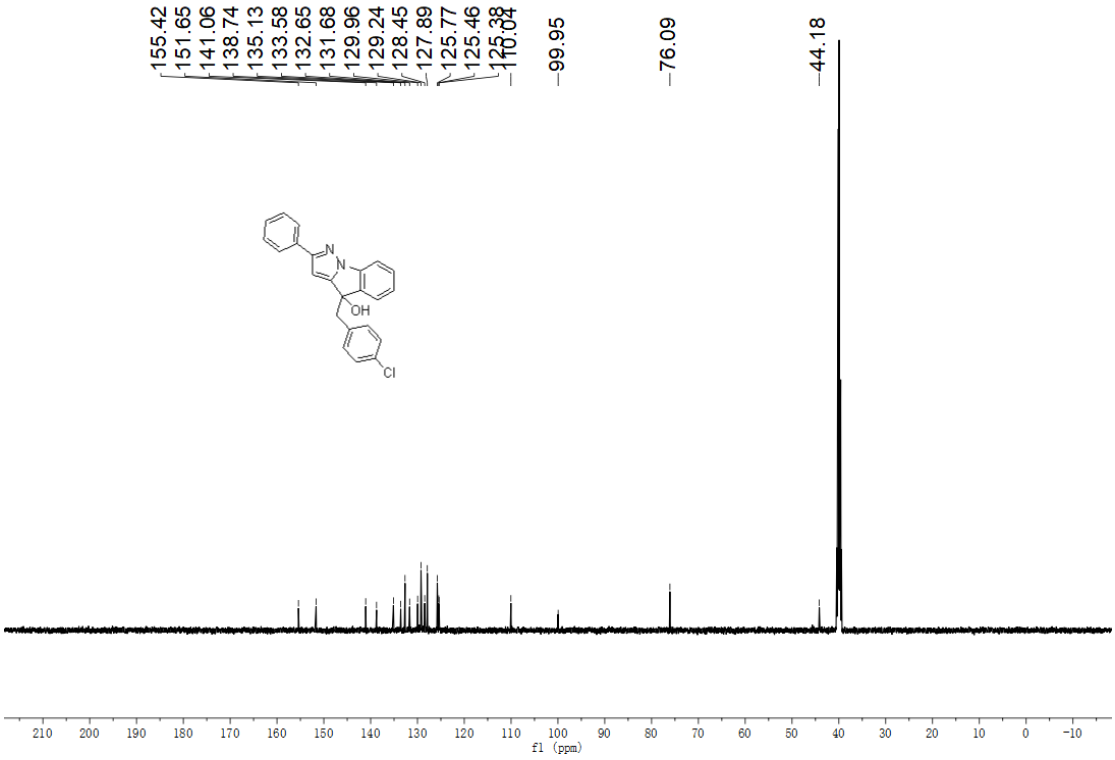


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 61.

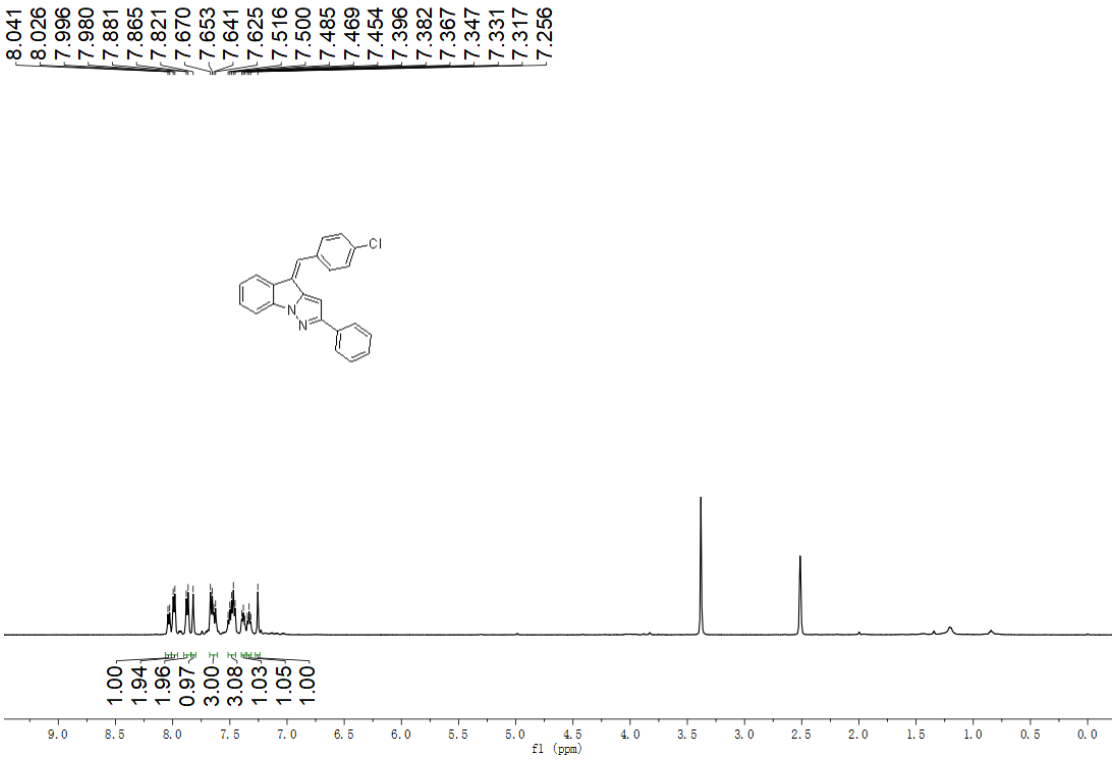


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

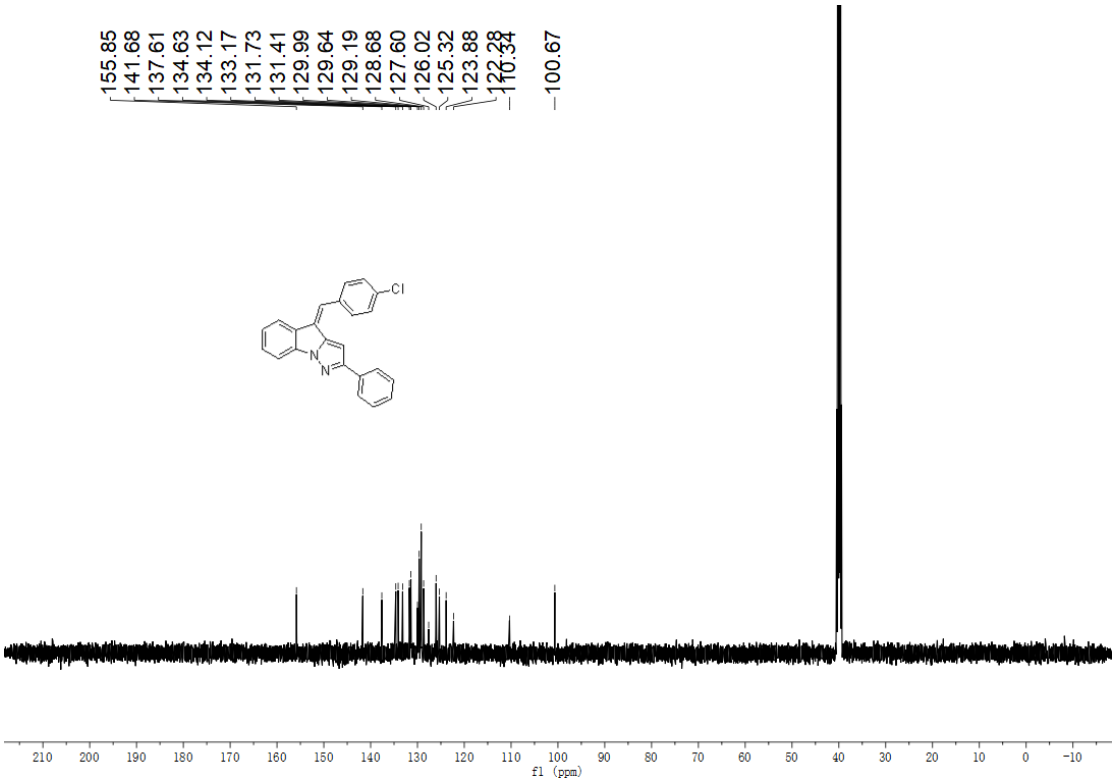


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 62.

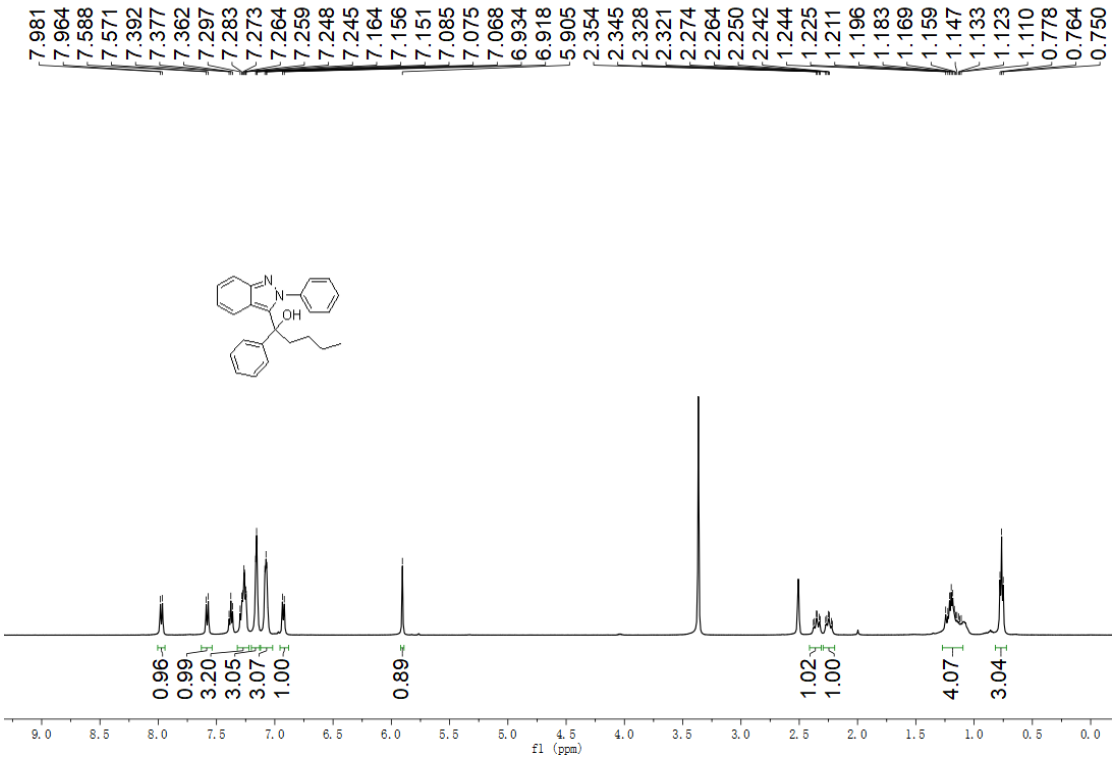


(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

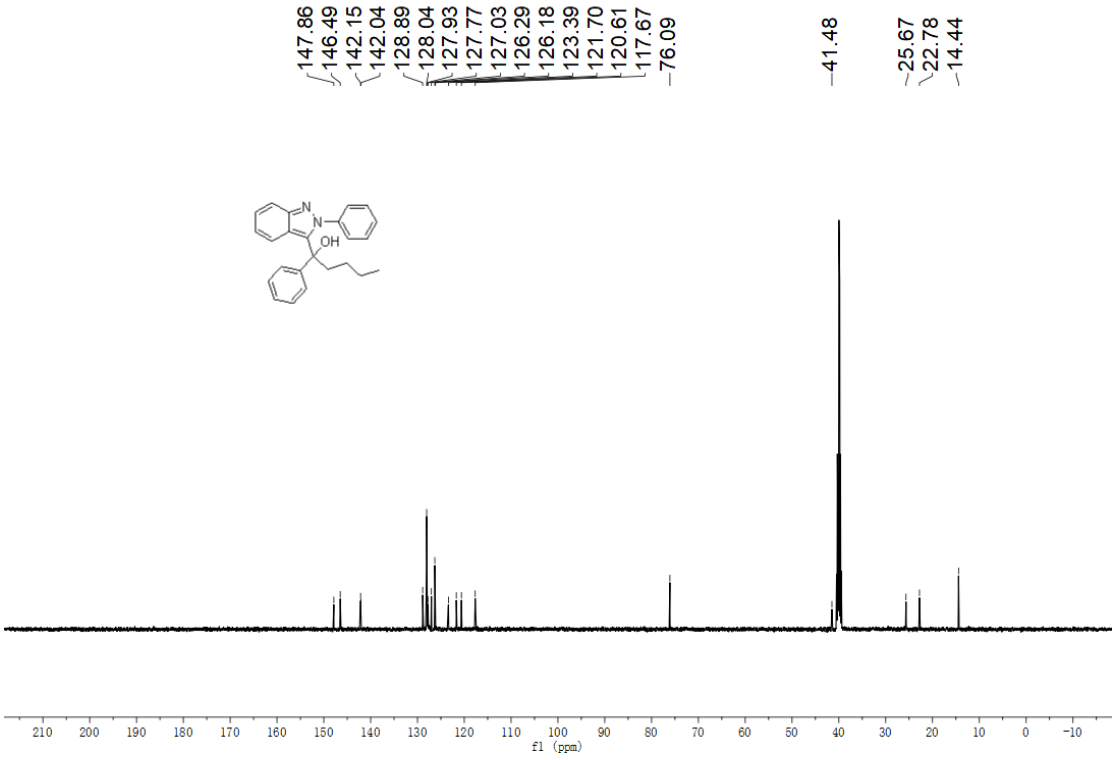


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 63.

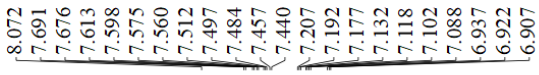


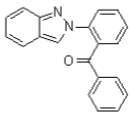
(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)

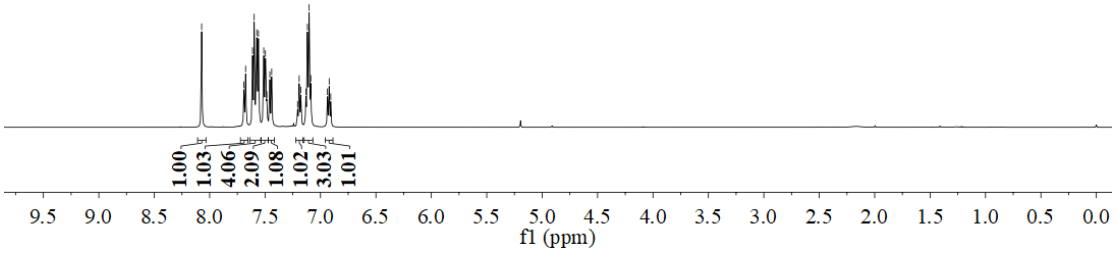


(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

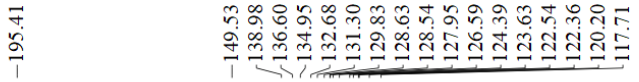
^{1}H and ^{13}C NMR spectra of compound 64.

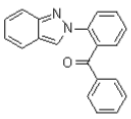


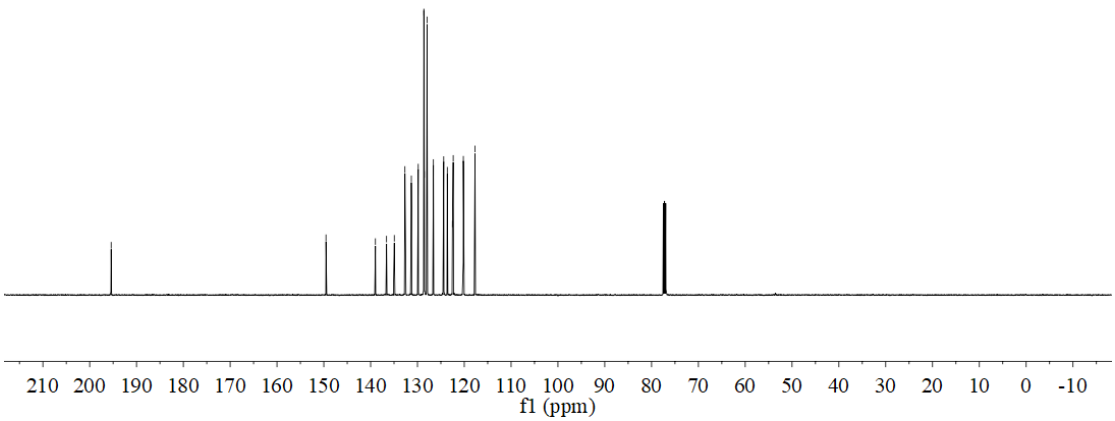




(500 MHz for ^{1}H NMR with $CDCl_3$ as solvent)

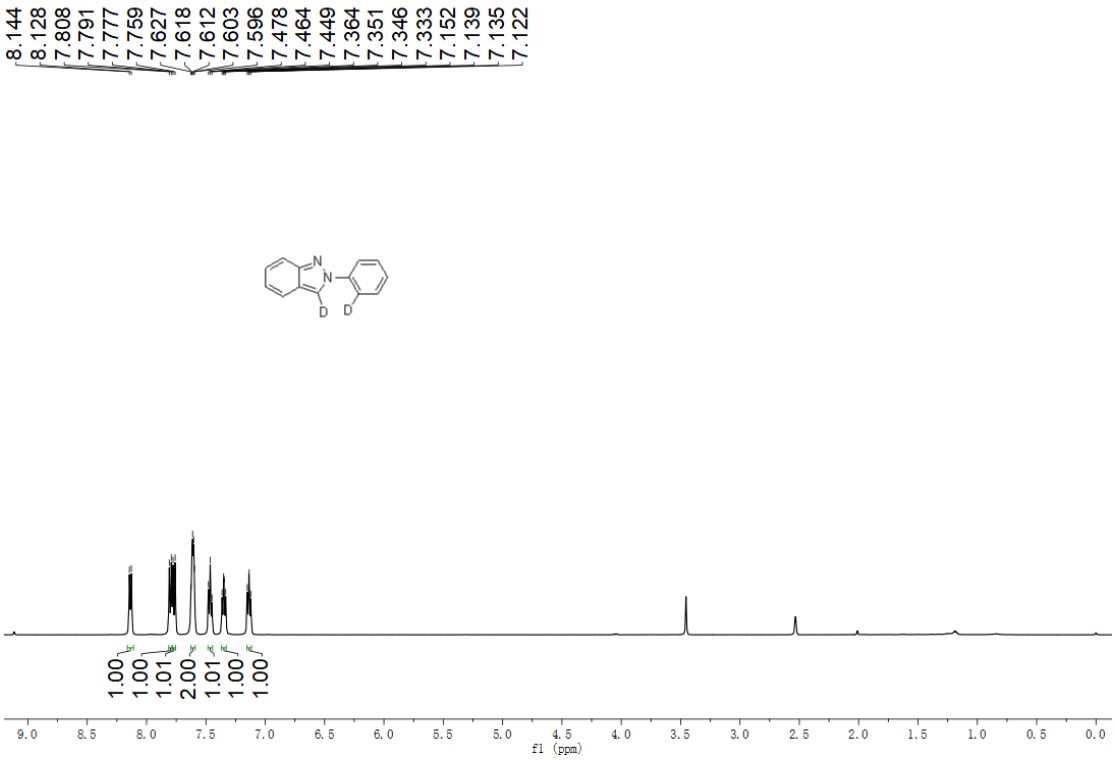




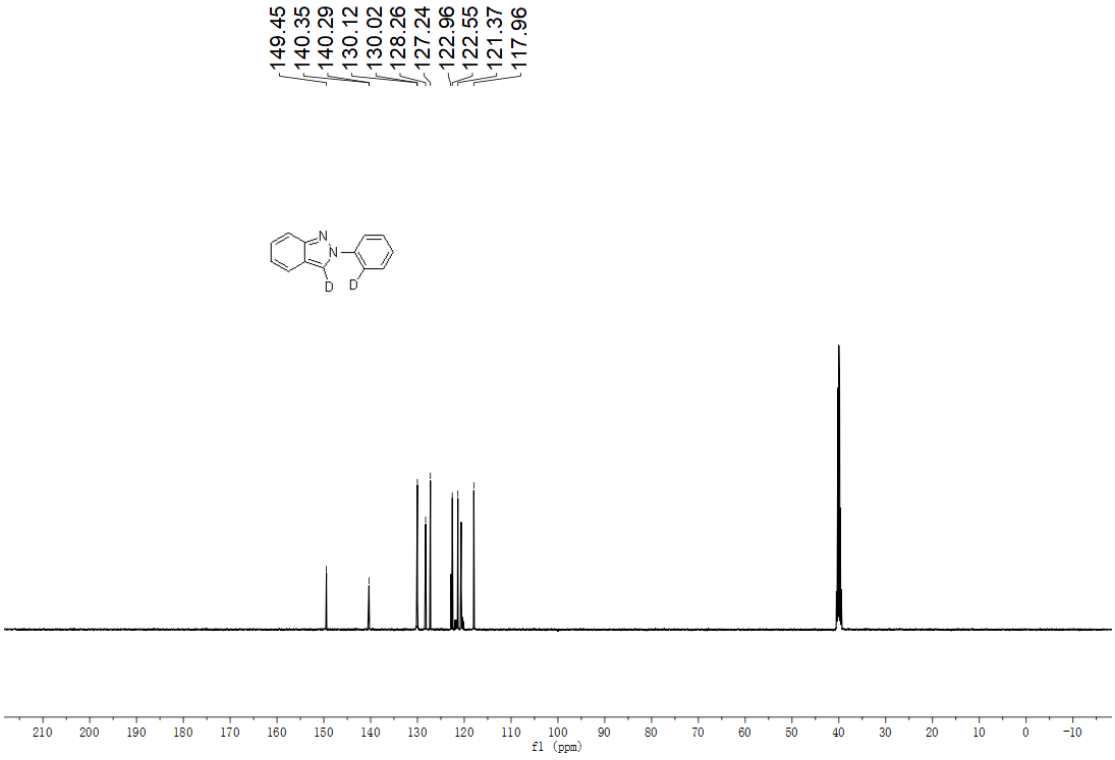


(125 MHz for ^{13}C NMR with $CDCl_3$ as solvent)

^{1}H and ^{13}C NMR spectra of compound 1-*d*$_2$.



(500 MHz for ^{1}H NMR with DMSO-*d*$_6$ as solvent)



(125 MHz for ^{13}C NMR with DMSO-*d*$_6$ as solvent)

6. References

[1] G.-Q. Jin, W.-X. Gao, Y.-B. Zhou, M.-Ch. Liu and H.-Y. Wu, *Chem. Commun.*, 2020, **56**, 14617.

[2] Y.-L. Liu, Y.-L. Pan, G.-J. Li, H.-F. Xu and J.-Z. Chen, *Org. Biomol. Chem.*, 2019, **17**, 8749.

[3] B. Li, S. Mai and Q. Song, *Org. Chem. Front.*, 2018, **5**, 1639.

[4] J. Rosevear and J. Wilshire, *Aust. J. Chem.*, 1991, **44**, 1097.