Regio- and Diastereoselective Synthesis of Diverse Spirocyclic Indenes by Cyclization with Indene-Dienes as Two Carbon Building Blocks

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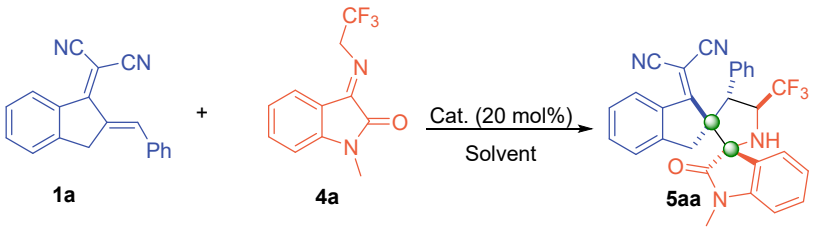
1. General experimental information

Reactions were monitored by TLC and visualization of the developed chromatogram was performed by ultraviolet light. Unless otherwise noted, all reagents including solvents were obtained from commercial supplier without any purification. The forced-flow column chromatography was performed using silica gel eluting with dichloromethane and petroleum ether. NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra of $CDCl_3$ or DMSO-d_6 solutions were recorded either at 400, 376 and 100 MHz or at 500, 471 and 125 MHz (Bruker Avance), respectively and resonances (δ) are given in parts per million (ppm) relatives to tetramethylsilane (TMS). Data for NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. The X-ray crystal-structure determinations of **3ar, 3ab'** and **5aa** were obtained on Bruker APEX DUO and Bruker D8 VENTURE PHOTON II systems. All melting points are determined on a SGW X-4 melting apparatus and are uncorrected.

2. Optimization of the reaction conditions of [3+2] cyclization of indene-dienes with N-2,2,2-trifluoroethylisatin ketimines

Table S1. Optimization of the reaction conditions [a]



Entry	Cat.	Solvent	T (°C)	Cat. Loading (mol%)	Time (days)	Yield (%)
1	DIPEA	DCM	25	20	3	84
2	DABCO	DCM	25	20	3	41

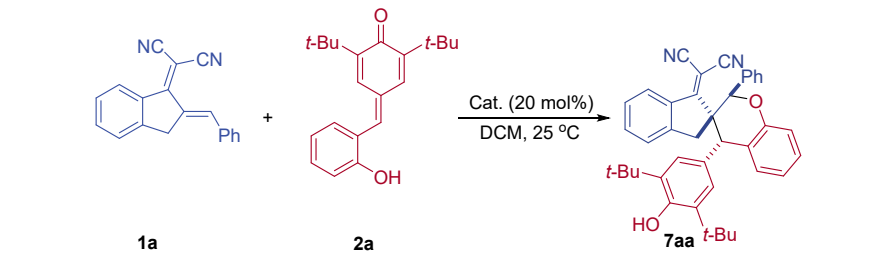
3	PBu_3	DCM	25	20	3	65
4	PPh_3	DCM	25	20	3	43
5	Et_3N	DCM	25	20	3	67
6	K_2CO_3	DCM	25	20	3	64
7	Cs_2CO_3	DCM	25	20	3	65
8	DIPEA	DCE	25	20	3	79
9	DIPEA	THF	25	20	3	78
10	DIPEA	DMF	25	20	3	47
11	DIPEA	DMSO	25	20	3	56
12	DIPEA	PhCl	25	20	3	67
13	DIPEA	MeCN	25	20	3	74
14	DIPEA	MeOH	25	20	3	72
15	DIPEA	PhMe	25	20	3	12
16	DIPEA	$CHCl_3$	25	20	3	17
17	DIPEA	Cyclohecane	40	20	3	71
18	DIPEA	DCM	40	20	3	88
19	DIPEA	DCM	40	5	3	64
20	DIPEA	DCM	40	10	3	82
21	DIPEA	DCM	40	30	3	61

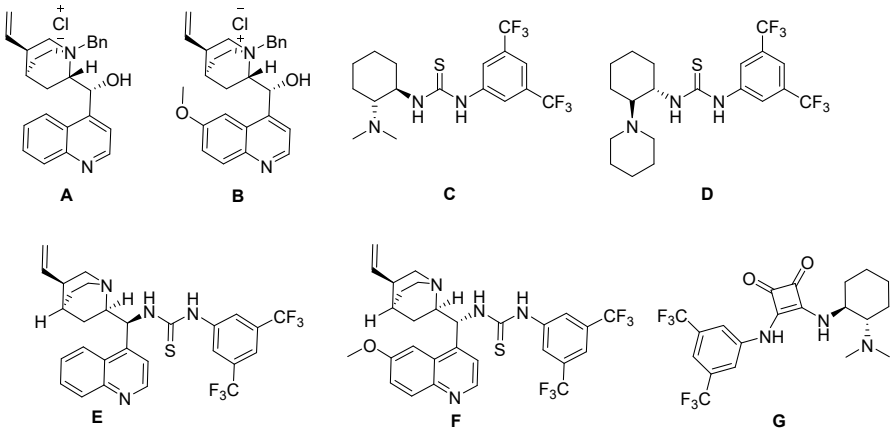
22[c]	DIPEA	DCM	40	20	5	95
23[d]	DIPEA	DCM	40	20	5	84

[a] Reaction conditions: **1a** (0.2 mmol), **4a** (0.2 mmol), catalyst (20 mol%), solvent (2.0 mL), 25 °C, 3 days. [b] Yield of isolated **5aa** after purification by silica gel column chromatography (two isomers). [c] The molar ratios to 1.5:1.0 (**1a**/**4a**). [d] The molar ratios to 2.0:1.0 (**1a**/**4a**).

3. Optimization of the reaction conditions of catalytic asymmetric [3+2] cyclization of indene-dienes with *p*-QM.

Table S2. Optimization of the reaction conditions [a]



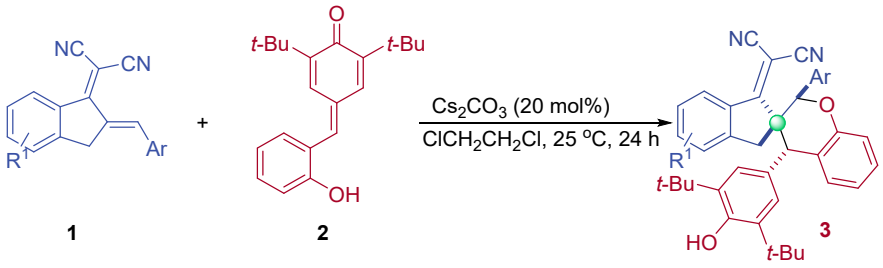


Entry	Cat.	Additive	Time (h)	dr[b]	yield[c] (%)	ee (%)
1	**A**	Na_2CO_3	24	1:2.8	59	40 (n.d.)
2	**B**	Na_2CO_3	48	1:2	52	38 (n.d.)
3	**A**	-	120		N.R.	
4	**B**	-	120		N.R.	
5	**C**	-	120		N.R.	

6	**D**	-	120	N.R.
7	**E**	-	120	N.R.
8	**F**	-	120	N.R.
9	**G**	-	120	N.R.

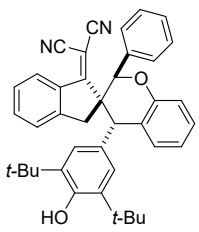
[a] Unless otherwise indicated, the reaction conditions were **1a** (0.10 mmol), **2a** (0.10 mmol) and additive (20 mol%) in the presence of catalyst (20 mol%) in DCM (1.0 mL) at 25 °C. [b] the dr was determined by ^{1}H NMR. [c] Yield of isolated **7aa** after purification by silica gel column chromatography (two isomers).

4. General experimental procedures for synthesis of compounds 3.



A mixture of Cs_2CO_3 (0.03 mmol, 0.2 equiv.), **1** (0.15 mmol, 1.0 equiv.) and **2** (0.30 mmol, 2.0 equiv.) and 1,2 - dichloroethane (1.5 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 25 °C for the 24-36 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:DCM = 3:1-2:1) to afford pure products **3**.

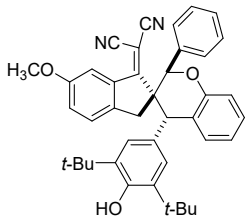
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aa)



3aa

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.40 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 78.0 mg, 90% yield (two isomers), 10:1 dr, reaction time = 24 h, m.p. 226.2-227.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 8.2 Hz, 1H), 7.65 (td, J = 7.5, 1.0 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.35 – 7.32 (m, 3H), 7.28 – 7.24 (m, 1H), 7.10 (dd, J = 8.3, 1.2 Hz, 1H), 6.99 (dd, J = 7.7, 1.7 Hz, 1H), 6.92 (td, J = 7.4, 1.2 Hz, 1H), 6.84 (d, J = 2.2 Hz, 1H), 6.56 (d, J = 2.2 Hz, 1H), 6.09 (s, 1H), 5.29 (s, 1H), 4.03 (d, J = 17.9 Hz, 1H), 3.79 (s, 1H), 3.08 (d, J = 18.0 Hz, 1H), 1.49 (s, 9H), 1.32 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 154.8, 154.0, 148.6, 136.3, 136.2, 134.9, 134.8, 131.7, 129.7, 129.2, 129.0, 128.9, 128.8, 128.8, 128.6, 128.4, 126.8, 126.2, 123.9, 121.6, 116.9, 113.9, 112.4, 80.0, 77.4, 77.2, 76.9, 75.3, 59.2, 56.3, 41.3, 34.5, 34.3, 30.4, 30.1. IR (KBr) υ: 762, 936, 1005, 1151, 1237, 1311, 1441, 1482, 1569, 2220, 2875, 1960, 3033, 3628 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{40}H_{38}N_2O_2$ $[M + H]^+$: 579.3006; Found: 597.3001.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-5'-methoxy-2-phenylspiro[chromane-3,2'-inden]-3'(1'H)-ylidene)malononitrile (3ab)

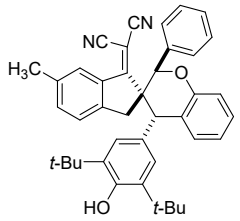


3ab

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.43 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 86.8 mg, 95% yield (two isomers), 6:1 dr, reaction time = 36 h, m.p. 236.5-237.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.3 Hz, 1H), 7.33 (q, *J* = 3.5 Hz, 5H), 7.24 (dt, *J* = 7.7, 1.9 Hz, 2H), 7.08 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.98 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.92 (td, *J* = 7.4, 1.2 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.06 (s, 1H), 5.29 (s, 1H), 3.96 (d, *J* = 17.7 Hz, 1H), 3.90 (s, 3H), 3.78

(s, 1H), 3.00 (d, *J* = 17.6 Hz, 1H), 1.50 (s, 9H), 1.32 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 160.0, 154.8, 154.0, 141.3, 137.3, 136.2, 136.1, 134.8, 131.7, 129.9, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 127.7, 127.4, 124.1, 124.0, 121.6, 117.0, 114.1, 112.4, 108.0, 79.6, 75.3, 60.0, 56.6, 55.8, 40.8, 34.6, 34.3, 30.4, 30.1. IR (KBr) υ: 747, 813, 924, 1014, 1114, 1152, 1239, 1304, 1364, 1439, 1487, 1559, 1596, 2218, 2875, 2960, 3056, 3610 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{41}N_2O_3$ $[M + H]^+$ 609.3112; Found 609.3112.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-5'-methyl-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ac)

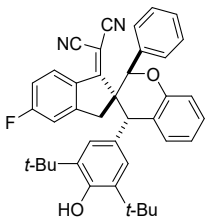


3ac

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.40 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.7 mg, 96% yield (two isomers), 14:1 dr, reaction time = 36 h, m.p. 240.8-241.4 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.49 (dd, J = 7.9, 1.5 Hz, 1H), 7.40 – 7.31 (m, 6H), 7.30 – 7.24 (m, 1H), 7.11 (dd, J = 8.4, 1.2 Hz, 1H), 7.00 (dd, J = 7.7, 1.7 Hz, 1H), 6.93 (td, J = 7.4, 1.2 Hz, 1H), 6.86 (d, J = 2.2 Hz, 1H), 6.60 (d, J = 2.2 Hz, 1H), 6.11 (s, 1H), 5.32 (s, 1H), 4.00 (d, J = 17.8 Hz, 1H), 3.80 (s, 1H), 3.05 (d, J = 17.9 Hz, 1H), 2.52 (s, 3H), 1.52 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 154.8, 154.0, 145.9, 138.7, 136.5, 136.2, 136.1, 134.8, 131.7, 129.8, 129.2, 128.9, 128.7, 128.7, 128.4, 126.5, 126.1, 124.0, 121.6, 116.9, 114.0, 112.5, 79.6, 75.3, 59.4, 56.4, 41.0, 34.5, 34.3, 30.4, 30.1, 21.8. IR (KBr) υ: 744, 814, 905, 1025, 1145, 1237, 1304, 1439, 1486, 1552, 2218, 2875, 2960, 3056, 3610 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{40}N_2O_2$ $[M + H]^+$ 593.3163; Found 593.3170.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-5'-fluoro-2-phenylspiro[chromane-3,2'-

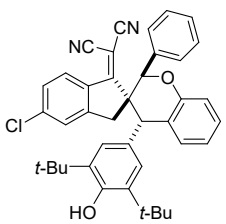
inden]-1'(3'H)-ylidene)malononitrile (3ad)



3ad

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.50 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.5 mg, 95% yield (two isomers), 8:1 dr, reaction time = 36 h, m.p. 214.0-215.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 9.0, 4.9 Hz, 1H), 7.41 – 7.31 (m, 5H), 7.32 – 7.23 (m, 1H), 7.23 (td, *J* = 8.8, 8.2, 2.0 Hz, 1H), 7.15 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.11 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.94 (td, *J* = 7.4, 1.2 Hz, 1H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.09 (s, 1H), 5.32 (s, 1H), 4.03 (d, *J* = 18.2 Hz, 1H), 3.81 (s, 1H), 3.08 (d, *J* = 18.2 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 166.8 (d, *J* = 259.8 Hz), 154.6, 154.1, 151.9 (d, *J* = 9.9 Hz), 136.3, 136.1, 134.9, 132.5 (d, *J* = 2.4 Hz), 131.7, 129.6, 129.1 (d, *J* = 7.2 Hz), 128.8, 128.7, 128.6, 128.6, 128.5, 127.5, 123.6, 121.7, 117.0, 116.8 (d, *J* = 23.3 Hz), 113.8 (d, *J* = 22.3 Hz) 112.3, 79.6, 79.5, 75.1, 59.8, 56.3, 41.2, 41.2, 34.5, 34.3, 30.3, 30.3, 30.1. IR (KBr) υ: 754, 813, 879, 941, 1000, 1116, 1150, 1251, 1322, 1366, 1441, 1483, 1570, 1599, 2220, 2875, 2958, 3032, 3628 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}FN_2O_2$ $[M + H]^+$ 597.2912; Found 597.2917.

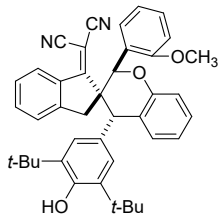
2-(5'-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ae)



3ae

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.50 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 89.4 mg, 97% yield (two isomers), 8:1 dr, reaction time = 36 h, m.p. 215.4-216.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.7 Hz, 1H), 7.51 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.46 (d, *J* = 1.9 Hz, 1H), 7.36 (td, *J* = 7.2, 6.8, 3.8 Hz, 5H), 7.33 – 7.24 (m, 1H), 7.11 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.01 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.95 (td, *J* = 7.4, 1.2 Hz, 1H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.56 (d, *J* = 2.2 Hz, 1H), 6.09 (s, 1H), 5.33 (s, 1H), 4.02 (d, *J* = 18.1 Hz, 1H), 3.80 (s, 1H), 3.07 (d, *J* = 18.2 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 154.6, 154.1, 150.2, 141.5, 136.3, 136.0, 134.9, 134.7, 131.7, 129.5, 129.3, 129.1, 129.0, 128.8, 128.7, 128.6, 127.5, 127.2, 127.0, 123.5, 121.7, 117.0, 113.7, 112.2, 80.3, 75.1, 59.5, 56.3, 41.0, 34.5, 34.3, 30.3, 30.1. IR (KBr) υ: 756, 814, 903, 1001, 1081, 1151, 1235, 1315, 1363, 1440, 1483, 1564, 2221, 2876, 2958, 3030, 3629 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}ClN_2O_2$ $[M + H]^+$ 613.2616; Found 613.2614.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-methoxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3af)

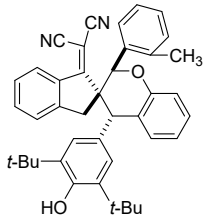


3af

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 88.3 mg, 97% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 265.1-266.0 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.1 Hz, 1H), 7.68 (td, *J* = 7.5, 1.0 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.34-7.31 (m, 1H), 7.27 – 7.20 (m, 1H), 7.08 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.94 (d, *J* = 2.2 Hz, 1H), 6.90 (td, *J* = 7.4, 1.2 Hz, 1H), 6.72 (td, *J* = 7.5, 1.0 Hz, 1H), 6.68 (dd,

J = 7.8, 1.8 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 1H), 6.36 (s, 1H), 5.26 (s, 1H), 4.19 (d, *J* = 18.2 Hz, 1H), 3.85 (s, 3H), 3.78 (s, 1H), 3.18 (d, *J* = 18.3 Hz, 1H), 1.47 (s, 9H), 1.34 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 159.5, 155.7, 153.9, 148.3, 136.6, 135.9, 134.7, 134.6, 131.8, 130.8, 129.9, 129.1, 129.0, 128.6, 128.2, 127.5, 126.9, 126.1, 124.5, 124.2, 121.3, 119.8, 117.0, 114.0, 112.6, 111.3, 79.9, 70.3, 58.6, 57.3, 56.2, 42.3, 34.5, 34.3, 30.4, 30.1. IR (KBr) υ: 759, 938, 1019, 1125, 1153, 1243, 1300, 1373, 1444, 1483, 1570, 1595, 2220, 2873, 2957, 3066, 3617 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{40}N_2O_3$ $[M + H]^+$ 609.3112; Found 609.3107.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(o-tolyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ag)

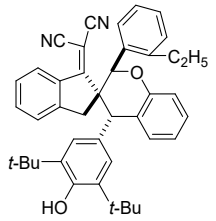


3ag

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.45 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 88.3 mg, 99% yield (two isomers), 14:1 dr, reaction time = 24 h, m.p. 243.1-244.3 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.1 Hz, 1H), 7.70 (td, *J* = 7.5, 1.1 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.07 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.00 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.96-6.92 (m, 2H), 6.87 (d, *J* = 2.2 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 2.1 Hz, 1H), 6.12 (s, 1H), 5.28 (s, 1H), 4.15 (d, *J* = 18.1 Hz, 1H), 3.81 (s, 1H), 3.18 (d, *J* = 18.2 Hz, 1H), 2.57 (s,3H), 1.48 (s,9H), 1.32 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.7, 155.2, 153.9, 148.2, 140.3, 136.5, 136.0, 134.9, 134.7, 133.4, 132.1, 131.9, 129.9, 129.4, 129.1, 128.8, 128.7, 128.5, 127.1, 126.2, 126.0, 125.4, 124.4, 121.8, 116.8, 113.8, 111.7, 79.8, 73.0, 58.5, 57.1, 42.1, 34.5, 34.3, 30.4, 30.1, 19.5. IR (KBr) υ: 762, 935, 1006, 1126, 1149, 1236, 1302, 1356, 1441, 1478, 1569, 2219, 2870,

2961, 3068, 3610 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{40}N_2O_2$ $[M + H]^+$ 593.3163; Found 593.3160.

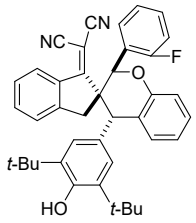
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-ethylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ah)



3ah

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.37 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 80.0 mg, 88% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 266.4-267.3 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.1 Hz, 1H), 7.70 (td, *J* = 7.5, 1.0 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.00 – 6.89 (m, 2H), 6.86 (d, *J* = 2.1 Hz, 1H), 6.63 – 6.55 (m, 2H), 6.21 (s, 1H), 5.28 (s, 1H), 4.15 (d, *J* = 18.2 Hz, 1H), 3.81 (s, 1H), 3.18 (d, *J* = 18.3 Hz, 1H), 3.02-283 (m, 2H), 1.48 (s, 9H), 1.40 (t, *J* = 7.5 Hz, 3H), 1.32 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 155.0, 154.0, 148.3, 145.8, 136.5, 136.0, 134.8, 134.7, 132.8, 131.9, 129.9, 129.9, 129.5, 129.1, 128.8, 128.8, 128.4, 127.1, 126.2, 126.0, 125.1, 124.5, 121.8, 116.8, 113.9, 111.7, 79.9, 72.7, 58.5, 57.0, 42.1, 34.5, 34.3, 30.4, 30.0, 24.9, 14.5. IR (KBr) υ: 767, 938, 1005, 1125, 1148, 1238, 1302, 1366, 1443, 1480, 1570, 2221, 2872, 2961, 3068, 3613 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{42}H_{42}N_2O_2$ $[M + H]^+$ 607.3319; Found 607.3316.

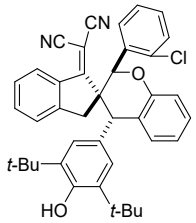
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-fluorophenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ai)



3ai

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.23 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 82.9 mg, 93% yield (two isomers), 8:1 dr, reaction time = 36 h, m.p. 223.5-224.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.36 (q, *J* = 7.3 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.23 – 7.15 (m, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 6.9 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 2H), 6.91 (d, *J* = 2.1 Hz, 1H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.56 (d, *J* = 2.1 Hz, 1H), 6.36 (s, 1H), 5.30 (s, 1H), 4.10 (d, *J* = 18.1 Hz, 1H), 3.81 (s, 1H), 3.19 (d, *J* = 18.1 Hz, 1H), 1.48 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 162.8 (d, *J* = 246.6 Hz), 154.4, 154.1, 148.5, 138.9, 138.8, 136.3, 136.2, 135.0, 134.9, 131.7, 130.2 (d, *J* = 8.2 Hz), 129.6, 129.2, 128.8, 128.6, 126.8, 126.3, 124.2 (d, *J* = 2.8 Hz), 123.8, 121.8, 116.9, 116.2 (d, *J* = 22.4 Hz). 115.9, 113.8, 112.5, 80.1, 74.6, 59.3, 56.2, 41.0, 34.6, 34.3, 30.4, 30.1. IR (KBr) υ: 744, 768, 886, 106, 1119, 1153, 1241, 1313, 1361, 1440, 1482, 1576, 2219, 2874, 2959, 3069, 3630 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}FN_2O_2$ $[M + H]^+$ 597.2912; Found 597.2916.

2-(2-(2-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aj)

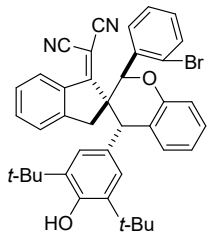


3aj

The compound was prepared according to general procedure with petroleum

ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.23 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.0 mg, 93% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 223.7-224.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.1 Hz, 1H), 7.72 (td, *J* = 7.5, 1.1 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.32 – 7.29 (m, 1H), 7.27 (d, *J* = 5.9 Hz, 1H), 7.11 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.06 (td, *J* = 7.7, 1.3 Hz, 1H), 7.00 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.74 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.33 (s, 1H), 5.30 (s, 1H), 4.12 (d, *J* = 18.2 Hz, 1H), 3.83 (s, 1H), 3.21 (d, *J* = 18.3 Hz, 1H), 1.49 (s, 9H), 1.34 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 155.2, 154.1, 148.1, 137.9, 136.5, 136.1, 135.1, 134.9, 133.1, 131.9, 131.6, 130.6, 129.8, 129.0, 129.0, 129.0, 128.6, 127.7, 127.2, 126.3, 126.3, 124.4, 122.0, 117.0, 113.8, 111.4, 80.0, 73.0, 58.6, 57.3, 42.0, 34.6, 34.4, 30.4, 30.2. IR (KBr) υ: 749, 904, 939, 1009, 1042, 1161, 1237, 1310, 1322, 1440, 1477, 1572, 2223, 2875, 2959, 3069, 3631 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}ClN_2O_2$ $[M + H]^+$ 613.2616; Found 613.2614.

2-(2-(2-bromophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ak)

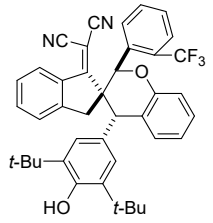


3ak

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.26 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.5 mg, 87% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 227.3-228.4 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.1 Hz, 1H), 7.74 (dd, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.21 (td, *J* = 7.7, 1.6 Hz, 1H), 7.13 – 7.08 (m, 2H), 7.00 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.72 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.56 (d, *J* = 2.2 Hz, 1H),

6.21 (s, 1H), 5.29 (s, 1H), 4.10 (d, *J* = 18.2 Hz, 1H), 3.82 (s, 1H), 3.20 (d, *J* = 18.3 Hz, 1H), 1.48 (s, 9H), 1.34 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 155.1, 154.0, 148.0, 136.4, 136.1, 135.0, 134.9, 134.8, 134.4, 131.8, 130.7, 129.7, 129.0, 128.9, 128.9, 128.5, 128.4, 127.7, 127.1, 126.9, 126.2, 124.4, 121.9, 117.0, 113.8, 111.4, 80.0, 75.0, 58.7, 57.2, 41.9, 34.6, 34.3, 30.4, 30.1. IR (KBr) υ: 749, 871, 1020, 1151, 1235, 1305, 1361, 1440, 1478, 1568, 2219, 2874, 2958, 3070, 3626 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}BrN_2O_2$ $[M + H]^+$ 657.2111; Found 657.2116.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-(trifluoromethyl)phenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3al)

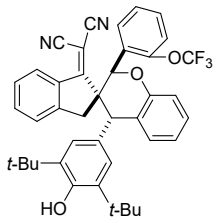


3al

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 91.4 mg, 94% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 220.0-221.1 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.56 (d, *J* = 5.5 Hz, 2H), 5.30 (s, 1H), 4.01 (d, *J* = 18.2 Hz, 1H), 3.81 (s, 1H), 3.18 (d, *J* = 18.2 Hz, 1H), 1.49 (s, 9H), 1.31 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 154.6, 154.1, 148.0, 136.3, 136.1, 135.1, 134.7, 133.9, 131.7, 131.1, 129.7, 129.5, 129.3 (q, *J* = 5.8 Hz) 129.0, 128.9, 128.8, 128.5, 127.2, 127.1, 126.3, 124.2, 122.0, 117.0, 113.8, 111.6, 79.8, 72.2, 72.2, 58.7, 57.0, 41.6, 34.6, 34.2, 30.3, 29.9. IR (KBr) υ: 763, 931, 1035, 1126, 1236, 1304, 1366, 1440, 1480, 1568, 2221,

2875, 1898, 3068, 3632 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{37}F_3N_2O_2$ $[M + H]^+$ 647.2880; Found 647.2880.

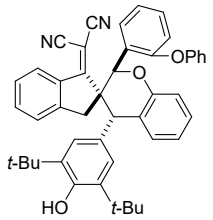
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-(trifluoromethoxy)phenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3am)



3am

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 79.2 mg, 80% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 258.7-259.5 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 4.5 Hz, 2H), 7.32 – 7.22 (m, 1H), 7.12 – 7.03 (m, 2H), 7.00 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 2.2 Hz, 1H), 6.36 (s, 1H), 5.31 (s, 1H), 4.11 (d, *J* = 18.2 Hz, 1H), 3.83 (s, 1H), 3.22 (d, *J* = 18.2 Hz, 1H), 1.49 (s, 9H), 1.33 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 154.9, 154.0, 149.9, 147.9, 136.3, 136.1, 135.0, 134.8, 131.7, 130.9, 129.6, 128.9, 128.9, 128.5, 127.9, 127.5, 127.1, 126.2, 125.7, 124.1, 121.8, 120.5, 116.8, 113.7, 111.4, 79.9, 70.2, 58.1, 57.0, 41.8, 34.6, 34.2, 30.3, 29.9. IR (KBr) υ: 763, 936, 1009, 1172, 1250, 1301, 1360, 1444, 1486, 1571, 2221, 2872, 2960, 3071, 3620 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{37}F_3N_2O_3$ $[M + H]^+$ 663.2829; Found 663.2825.

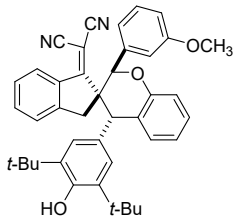
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2-phenoxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3an)



3an

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 97.6 mg, 97% yield (two isomers), 9:1 dr, reaction time = 36 h, m.p. 209.6-210.8 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.32 – 7.25 (m, 1H), 7.17 – 7.09 (m, 4H), 6.94 (td, *J* = 6.5, 5.9, 1.3 Hz, 2H), 6.90 – 6.85 (m, 3H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.57 (d, *J* = 2.1 Hz, 1H), 6.49 (s, 1H), 5.26 (s, 1H), 4.16 (d, *J* = 18.1 Hz, 1H), 3.80 (s, 1H), 3.20 (d, *J* = 18.1 Hz, 1H), 1.49 (s, 9H), 1.22 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 157.6, 157.2, 155.2, 153.9, 148.2, 136.5, 136.0, 134.8, 134.7, 131.6, 130.6, 129.9, 129.6, 129.0, 128.9, 128.7, 128.3, 127.5, 127.0, 126.3, 126.2, 124.3, 123.5, 122.2, 121.5, 119.8, 119.8, 119.0, 116.7, 113.9, 111.5, 79.9, 70.8, 58.4, 57.0, 42.0, 34.6, 34.2, 30.4, 30.3, 29.9. IR (KBr) υ: 747, 863, 1006, 1119, 1156, 1239, 1308, 1372, 1444, 1484, 1575, 2222, 2875, 2958, 3069, 3628 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{46}H_{42}N_2O_3$ $[M + H]^+$ 671.3268; Found 671.3272.

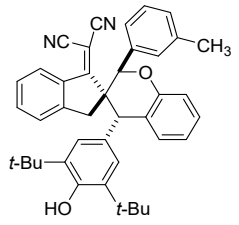
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-methoxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ao)



3ao

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 87.1 mg, 95% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 200.3-201.1 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 7.65 (td, *J* = 7.5, 1.0 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.28 – 7.21 (m, 1H), 7.16 – 7.10 (m, 2H), 7.03 – 6.98 (m, 2H), 6.99 – 6.90 (m, 1H), 6.88 (dd, *J* = 8.1, 2.3 Hz, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.59 (d, *J* = 2.3 Hz, 1H), 6.09 (s, 1H), 5.33 (s, 1H), 4.03 (d, *J* = 17.9 Hz, 1H), 3.80 (s, 1H), 3.75 (s, 3H), 3.08 (d, *J* = 17.9 Hz, 1H), 1.51 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 159.6, 154.6, 154.0, 148.7, 137.8, 136.2, 136.2, 134.9, 134.8, 131.6, 129.7, 129.7, 129.2, 128.8, 128.6, 128.4, 126.7, 126.2, 123.8, 121.6, 120.8, 116.9, 115.1, 114.2, 114.0, 112.5, 80.0, 75.1, 59.4, 56.1, 55.3, 41.2, 34.5, 34.3, 30.3, 30.1. IR (KBr) υ: 743, 768, 952, 1014, 1126, 1150, 1239, 1302, 1350, 1441, 1481, 1571, 2220, 2874, 2956, 3072, 3611 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{40}N_2O_3$ $[M + H]^+$ 609.3112; Found 609.3115.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(m-tolyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ap)

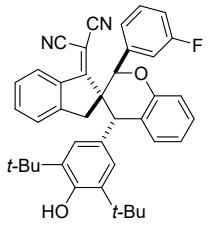


3ap

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.34 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 81.7 mg, 92% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 213.2-214.0 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 7.30 – 7.23 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.4 Hz,1H), 7.11 (d, *J* = 8.3 Hz, 1H),

7.04 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.84 (s, 1H), 6.56 (s, 1H), 6.06 (s, 1H), 5.30 (s, 1H), 4.03 (d, *J* = 17.9 Hz, 1H), 3.78 (s, 1H), 3.07 (d, *J* = 17.9 Hz, 1H), 2.33 (s, 3H), 1.49 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 154.8, 154.0, 148.7, 138.5, 136.3, 136.2, 136.2, 134.8, 131.7, 130.2, 129.8, 129.8, 129.2, 128.8, 128.6, 128.4, 128.4, 128.3, 126.8, 126.2, 125.2, 123.9, 121.5, 117.0, 114.0, 112.4, 80.0, 75.3, 59.3, 56.3, 41.3, 34.5, 34.3, 30.4, 30.1, 21.7. IR (KBr) υ: 739, 768, 903, 1010, 1127, 1147, 1234, 1303, 1356, 1440, 1478, 1556, 2219, 2869, 2690, 3055, 3609 cm^{-1} cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{40}N_2O_2$ $[M + H]^+$ 593.3163; Found 593.3171.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-fluorophenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aq)

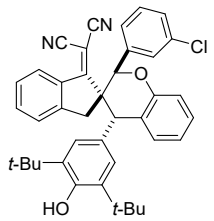


3aq

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.31 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 70.3 mg, 79% yield (two isomers), 7:1 dr, reaction time = 36 h, m.p. 215.0-216.1 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.2 Hz, 1H), 7.65 (td, *J* = 7.5, 1.0 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.18-7.14 (m, 1H), 7.12-7.11 (m, 1H), 7.09 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.04-7.00 (m, 1H), 6.98 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.93 (td, *J* = 7.4, 1.2 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 6.55 (d, *J* = 2.3 Hz, 1H), 6.08 (s, 1H), 5.30 (s, 1H), 3.92 (d, *J* = 17.9 Hz, 1H), 3.77 (s, 1H), 1.48 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 174.7, 162.8 (d, *J* = 246.4 Hz), 154.4, 154.6, 148.5, 138.9, 138.8, 136.4, 136.2, 135.1, 134.9, 131.7, 130.2 (d, *J* = 8.1 Hz), 129.6, 129.2, 128.8, 128.6, 126.8, 126.3, 124.2 (d, *J* = 3.2 Hz), 123.8, 121.8, 116.9, 116.2 (d, *J* = 22.2 Hz). 116.0, 113.8, 112.5, 80.1, 74.6, 59.3,

56.2, 41.0, 34.6, 34.3, 30.4, 30.1 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}FN_2O_2$ $[M + H]^+$ 597.2912; Found 597.2915.

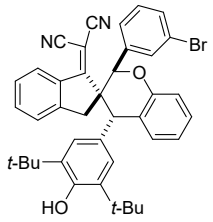
2-(2-(3-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ar)



3ar

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.32 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.9 mg, 94% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 207.2-208.0 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.2 Hz, 1H), 7.65 (td, *J* = 7.5, 0.9 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 6.99 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 2.2 Hz, 1H), 6.56 (d, *J* = 2.2 Hz, 1H), 6.08 (s, 1H), 5.31 (s, 1H), 3.91 (d, *J* = 17.8 Hz, 1H), 3.78 (s, 1H), 3.06 (d, *J* = 17.8 Hz, 1H), 1.49 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 154.3, 154.1, 148.5, 138.5, 136.3, 136.1, 135.1, 134.9, 134.8, 131.6, 129.8, 129.5, 129.5, 129.2, 129.2, 128.7, 128.6, 126.8, 126.3, 126.3, 123.7, 121.8, 116.9, 113.8, 112.5, 80.0, 74.5, 59.3, 56.1, 41.0, 34.5, 34.3, 30.4, 30.1. IR (KBr) υ: 747, 766, 872, 1010, 1119, 1153, 1237, 1308, 1361, 1438, 1478, 1569, 2220, 2875, 2959, 3070, 3624 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}ClN_2O_2$ $[M + H]^+$ 613.2616; Found 613.2618.

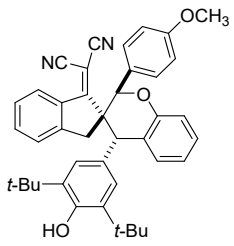
2-(2-(3-bromophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3as)



3as

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.20 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 97.1 mg, 99% yield (two isomers), 17:1 dr, reaction time = 36 h, m.p. 236.5-237.3 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 7.00 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.73 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.33 (s, 1H), 5.30 (s, 1H), 4.12 (d, *J* = 18.2 Hz, 1H), 3.83 (s, 1H), 3.21 (d, *J* = 18.2 Hz, 1H), 1.49 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 155.1, 154.0, 148.0, 137.8, 136.4, 136.0, 134.9, 134.8, 133.0, 131.8, 131.5, 130.5, 129.7, 128.9, 128.9, 128.9, 128.5, 127.6, 127.1, 126.2, 126.2, 124.3, 121.9, 116.9, 113.7, 111.3, 79.9, 72.9, 58.5, 57.2, 41.9, 34.5, 34.3, 30.3, 30.1. IR (KBr) υ: 747, 905, 940, 1008, 1042, 1120, 1237, 1310, 1322, 1440, 1478, 1570, 2223, 2875, 2958, 3069, 3632 cm^{-1}. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{37}BrN_2O_2$ $[M + H]^+$ 657.2111; Found 657.2116.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3at)

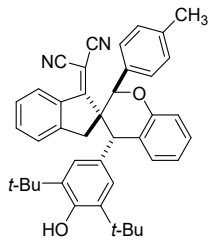


3at

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.20 (petroleum ether/ethyl acetate =

20:1). Yellow solid, 78.7 mg, 86% yield (two isomers), 10:1 dr, reaction time = 36 h, m.p. 211.6-212.7 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.1 Hz, 1H), 7.65 (td, *J* = 7.5, 1.0 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.21 (m, 3H), 7.08 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.98 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.91 (td, *J* = 7.4, 1.2 Hz, 1H), 6.88 – 6.81 (m, 3H), 6.55 (d, *J* = 2.2 Hz, 1H), 6.01 (s, 1H), 5.29 (s, 1H), 4.04 (d, *J* = 17.9 Hz, 1H), 3.77 (s, 4H), 3.07 (d, *J* = 18.0 Hz, 1H), 1.48 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 159.8, 154.9, 154.0, 148.6, 136.4, 136.2, 134.9, 134.8, 131.7, 130.3, 129.8, 129.2, 128.8, 128.6, 128.4, 128.2, 126.8, 126.2, 123.9, 121.5, 117.0, 114.1, 114.0, 112.4, 80.0, 75.0, 59.4, 56.5, 55.4, 41.4, 34.5, 34.3, 30.4, 30.1. IR (KBr) υ: 730, 763, 914, 1001, 1030, 1176, 1234, 1306, 1361, 1442, 1473, 1570, 1610, 2222, 2876, 2960, 3069, 3628 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{40}N_2O_3$ [M + H]$^+$ 609.3112; Found 609.3115.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(p-tolyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3au)

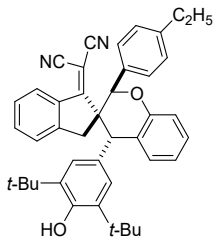


3au

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.35 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 84.6 mg, 95% yield (two isomers), 10:1 dr, reaction time = 36 h, m.p. 220.8-221.7 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.1 Hz, 1H), 7.66 (td, *J* = 7.5, 1.0 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 2.9 Hz, 2H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.99 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.93 (td, *J* = 7.4, 1.2 Hz, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.06 (s, 1H), 5.30 (s, 1H), 4.06 (d, *J* = 17.9 Hz, 1H), 3.79 (s, 1H), 3.08 (d, *J* = 18.0 Hz, 1H), 2.33 (s, 3H), 1.50 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (125

MHz, $CDCl_3$) δ 175.2, 154.9, 154.0, 148.6, 138.8, 136.4, 136.2, 134.8, 134.8, 133.2, 131.7, 129.8, 129.4, 129.2, 128.8, 128.8, 128.6, 128.4, 126.8, 126.2, 123.9, 121.5, 117.0, 114.0, 112.4, 80.0, 75.2, 59.3, 56.4, 41.4, 34.5, 34.3, 30.4, 30.1, 21.3. IR (KBr) υ: 760, 918, 1006, 1124, 1153, 1235, 1309, 1361, 1441, 1479, 1568, 2222, 2875, 2958, 3631 cm^{-1}. IR (KBr) υ: 760, 918, 1006, 1124, 1153, 1235, 1309, 1361, 1441, 1479, 1568, 2222, 2875, 2958, 3631 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{40}N_2O_2$ $[M + H]^+$ 593.3169; Found 593.3170.

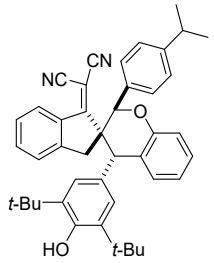
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-ethylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3av)



3av

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 83.6 mg, 92% yield (two isomers), 13:1 dr, reaction time = 36 h, m.p. 222.8-223.5 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.2 Hz, 1H), 7.66 (td, *J* = 7.5, 1.0 Hz, 1H), 7.57 – 7.50 (m, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.13 – 7.07 (m, 1H), 6.99 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.07 (s, 1H), 5.30 (s, 1H), 4.06 (d, *J* = 17.9 Hz, 1H), 3.79 (s, 1H), 3.08 (d, *J* = 17.9 Hz, 1H), 2.63 (q, *J* = 7.7 Hz, 2H), 1.50 (s, 9H), 1.33 (s, 9H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 154.9, 154.0, 148.6, 145.0, 136.4, 136.2, 134.8, 134.8, 133.4, 131.7, 129.8, 129.2, 128.9, 128.8, 128.6, 128.4, 128.3, 126.8, 126.2, 123.9, 121.5, 117.0, 114.0, 112.4, 80.0, 75.2, 59.3, 56.4, 41.4, 34.5, 34.3, 30.4, 30.1, 28.6, 15.3. IR (KBr) υ: 762, 927, 1012, 1125, 1155, 1234, 1309, 1362, 1440, 1477, 1566, 2222, 2960, 3611 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{42}H_{42}N_2O_2$ $[M+H]^+$ 607.3319; Found 607.3320.

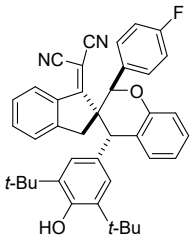
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-isopropylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aw)



3aw

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.50 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 91.0 mg, 98% yield (two isomers), 14:1 dr, reaction time = 36 h, m.p. 242.5-243.1 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.2 Hz, 1H), 7.65 (td, *J* = 7.5, 1.0 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.98 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.92 (td, *J* = 7.4, 1.2 Hz, 1H), 6.84 (d, *J* = 2.3 Hz, 1H), 6.56 (d, *J* = 2.3 Hz, 1H), 6.07 (s, 1H), 5.29 (s, 1H), 4.05 (d, *J* = 17.9 Hz, 1H), 3.78 (s, 1H), 3.08 (d, *J* = 18.0 Hz, 1H), 2.93-2.83 (m, 1H), 1.49 (s, 9H), 1.33 (s, 9H), 1.23 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 154.8, 154.0, 149.6, 148.7, 136.4, 136.2, 134.8, 134.8, 133.4, 131.7, 129.8, 129.2, 128.8, 128.8, 128.6, 128.4, 126.9, 126.8, 126.2, 123.9, 121.5, 117.0, 114.0, 112.4, 80.0, 75.2, 59.3, 56.4, 41.4, 34.5, 34.3, 33.9, 30.4, 30.1, 23.9, 23.9. IR (KBr) υ: 732, 839, 920, 1005, 1149, 1233, 1302, 1355, 1440, 1473, 1568, 2221, 2872, 2959, 3065, 3604 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{43}H_{44}N_2O_2$ $[M + H]^+$ 621.3476; Found 621.3479.

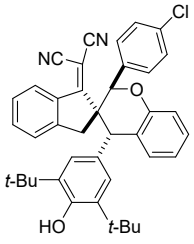
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-fluorophenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ax)



3ax

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.30 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 82.9 mg, 93% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 225.8-226.3 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 – 7.24 (m, 1H), 7.10 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.07 – 6.98 (m, 3H), 6.94 (td, *J* = 7.4, 1.2 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 6.08 (s, 1H), 5.32 (s, 1H), 4.00 (d, *J* = 18.0 Hz, 1H), 3.81 (s, 1H), 3.10 (d, *J* = 18.0 Hz, 1H), 1.50 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 162.8 (d, *J* = 248.9 Hz), 154.6, 154.1, 148.4, 136.3, 136.2, 135.0, 134.9, 132.2 (d, *J* = 3.3 Hz), 131.7, 130.8 (d, *J* = 8.3 Hz), 129.6, 129.2, 128.7, 128.5, 126.8, 126.3, 123.8, 121.7, 116.9, 115.8 (d, *J* = 21.6 Hz), 113.8, 112.5, 80.0, 74.7, 59.3, 56.3, 41.1, 34.5, 34.3, 30.4, 30.1. IR (KBr) υ: 744, 785, 936, 1008, 1154, 1235, 1309, 1360, 1441, 1479, 1563, 2220, 2875, 2959, 3070, 3627 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}FN_2O_2$ $[M + H]^+$ 597.2912; Found 597.2913.

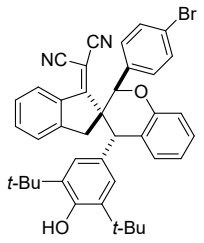
2-(2-(4-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ay)



3ay

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.35 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 80.7 mg, 91% yield (two isomers), 16:1 dr, reaction time = 36 h, m.p. 223.7-224.5 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.2, 2.8 Hz, 1H), 7.65 (dt, *J* = 7.5, 3.7 Hz, 1H), 7.53 (t, *J* = 6.8 Hz, 1H), 7.47 (d, *J* = 6.7 Hz, 1H), 7.31 (t, *J* = 2.4 Hz, 4H), 7.26 (d, *J* = 3.0 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.97 – 6.89 (m, 1H), 6.81 (s, 1H), 6.55 (s, 1H), 6.06 (d, *J* = 2.9 Hz, 1H), 5.31 (d, *J* = 2.9 Hz, 1H), 3.94 (dd, *J* = 18.1, 2.8 Hz, 1H), 3.79 (d, *J* = 2.8 Hz, 1H), 3.07 (dd, *J* = 18.1, 2.8 Hz, 1H), 1.48 (d, *J* = 3.0 Hz, 9H), 1.32 (d, *J* = 3.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 154.5, 154.1, 148.4, 136.3, 136.2, 135.1, 135.0, 134.9, 134.8, 131.7, 130.3, 129.6, 129.2, 129.0, 128.8, 128.7, 128.5, 126.8, 126.3, 123.8, 121.8, 116.9, 113.8, 112.5, 80.0, 74.6, 59.2, 56.2, 41.1, 34.5, 34.3, 30.4, 30.1. IR (KBr) υ: 747, 763, 805, 833, 915, 1010, 1107, 1154, 1235, 1310, 1359, 1441, 1484, 1562, 2220, 2875, 2959, 3070, 3626 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}ClN_2O_2$ $[M + H]^+$ 613.2676; Found 613.2669.

2-(2-(4-bromophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3az)

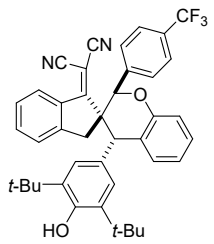


3az

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 94.6 mg, 96% yield (two isomers), 13:1 dr, reaction time = 36 h, m.p. 214.5-215.1 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.2, 2.8 Hz, 1H), 7.66 (td, *J* = 7.5, 2.8 Hz, 1H), 7.54 (td, *J* = 8.0, 2.6 Hz, 1H), 7.47 (dd, *J* = 7.9, 2.6 Hz, 1H), 7.35 – 7.29 (m, 4H), 7.26 (d, *J* = 3.2 Hz, 1H), 7.09 (dd, *J* = 8.3, 2.8 Hz, 1H), 6.99 (d, *J*

= 7.6 Hz, 1H), 6.94 (td, *J* = 7.6, 2.7 Hz, 1H), 6.81 (s, 1H), 6.56 (s, 1H), 6.06 (d, *J* = 2.9 Hz, 1H), 5.31 (d, *J* = 2.9 Hz, 1H), 3.95 (dd, *J* = 18.0, 2.8 Hz, 1H), 3.79 (d, *J* = 2.8 Hz, 1H), 3.07 (dd, *J* = 18.1, 2.8 Hz, 1H), 1.49 (d, *J* = 3.0 Hz, 9H), 1.32 (d, *J* = 3.0 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 154.5, 154.1, 148.4, 136.3, 136.2, 135.4, 135.1, 134.9, 131.9, 131.8, 131.7, 130.5, 129.5, 129.2, 128.8, 128.7, 128.5, 126.8, 126.3, 123.8, 123.2, 121.8, 116.9, 113.8, 112.5, 80.1, 74.7, 59.2, 56.2, 41.1, 34.5, 34.3, 30.4, 30.4, 30.1. IR (KBr) υ: 762, 829, 919, 1008, 1079, 1117, 1233, 1308, 1359, 1443, 1482, 1567, 2222, 2874, 2959, 3070, 3626 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}BrN_2O_2$ $[M + H]^+$ 657.2111; Found 657.2113.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-(trifluoromethyl)phenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3aa')

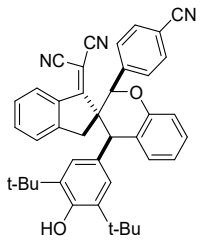


3aa'

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.45 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 97.0 mg, 53% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 257.5-258.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 3H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.00 (dd, 1H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.57 (d, *J* = 2.3 Hz, 1H), 6.16 (s, 1H), 5.32 (s, 1H), 3.93 (d, *J* = 18.0 Hz, 1H), 3.81 (s, 1H), 3.09 (d, *J* = 18.0 Hz, 1H), 1.49 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.6, 154.3, 154.2, 148.3, 140.3, 136.3, 136.1, 135.2, 134.9, 131.7, 129.5, 129.3, 129.2, 128.8, 128.7, 128.6, 126.8, 126.3, 125.7 (q, *J* = 3.6 Hz), 123.7, 121.9, 116.8, 113.7, 112.5, 80.0, 77.5, 77.2, 76.8, 74.6, 59.1, 56.1, 41.0, 34.5, 34.3, 30.4, 30.1.IR (KBr) υ:763, 845, 932, 1010, 1068, 1125, 1165, 1233,

1320, 1362, 1442, 1481, 1566, 2221, 2875, 2959, 3073, 3627 cm^{-1}.HRMS (ESI) m/z: Calcd for $C_{41}H_{37}F_3N_2O_2$ $[M + H]^+$ 647.2880; Found 647.2888.

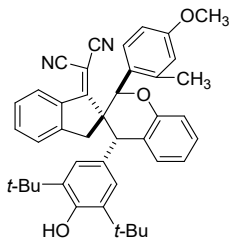
2-(2-(4-cyanophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ab')



3ab'

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.20 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 73.2 mg, 80% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 233.0-234.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 4.6 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 3H), 6.98 (t, *J* = 7.7 Hz, 2H), 6.70 (s, 1H), 6.30 (s, 1H), 5.34 (s, 1H), 4.97 (s, 1H), 3.50 (d, *J* = 18.8 Hz, 1H), 3.26 (d, *J* = 18.8 Hz, 1H), 1.27 (d, *J* = 53.6 Hz, 18H). ^{13}C NMR (125MHz, $CDCl_3$) δ 180.4, 154.4, 153.4, 151.1, 141.5, 136.7, 135.6, 132.4, 130.5, 128.7, 128.3, 127.8, 126.6, 125.6, 124.9, 123.6, 121.8, 118.3, 117.0, 115.0, 113.5, 112.9, 79.0, 76.0, 58.7, 52.5, 34.2, 34.0, 30.2. IR (KBr) υ:763, 1042, 1125, 1231, 1307, 1363, 1438, 1476, 1550, 1707, 2223, 2959, 3074, 3615 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{41}H_{37}N_3O_2$ $[M + H]^+$: 604.2959, found:604.2965.

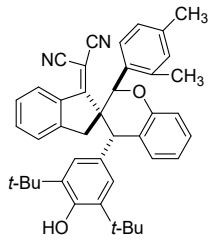
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxy-2-methylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ac')



3ac'

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.30 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 83.6 mg, 90% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 221.1-221.9 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.93 (td, *J* = 7.4, 1.2 Hz, 1H), 6.87 (d, *J* = 2.4 Hz, 2H), 6.57 (d, *J* = 2.0 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 1H), 6.48 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.06 (s, 1H), 5.29 (s, 1H), 4.14 (d, *J* = 18.2 Hz, 1H), 3.81 (s, 1H), 3.76 (s, 3H), 3.17 (d, *J* = 18.2 Hz, 1H), 2.55 (s, 3H), 1.49 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 159.9, 155.2, 153.9, 148.3, 142.1, 136.5, 136.0, 134.8, 134.7, 131.9, 129.9, 129.1, 128.7, 128.4, 127.2, 127.1, 126.2, 125.8, 124.4, 121.7, 117.8, 116.8, 113.9, 111.7, 110.3, 79.9, 72.7, 58.6, 57.2, 55.2, 42.2, 34.5, 34.3, 30.4, 30.1, 19.8. IR (KBr) υ: 732, 763, 807, 909, 998, 1044, 1123, 1156, 1235, 1305, 1360, 1443, 1471, 1572, 1613, 2221, 2876, 2960, 3072, 3631 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{42}H_{42}N_2O_3$ $[M + H]^+$ 623.3268; Found 623.3264.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(2,4-dimethylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ad')

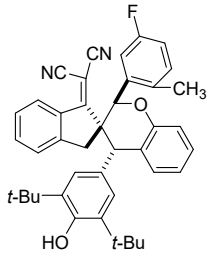


3ad'

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.40 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 86.1 mg, 95% yield (two isomers), 14:1 dr, reaction time = 36 h, m.p. 274.8-275.6 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.12 (s, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 6.8 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H),

6.85 (d, *J* = 1.8 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.56 (d, *J* = 1.8 Hz, 1H), 6.47 (d, *J* = 7.9 Hz, 1H), 6.07 (s, 1H), 5.27 (s, 1H), 4.14 (d, *J* = 18.2 Hz, 1H), 3.79 (s, 1H), 3.16 (d, *J* = 18.2 Hz, 1H), 2.52 (s, 3H), 2.27 (s, 3H), 1.48 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 155.3, 153.9, 148.3, 140.1, 139.2, 136.6, 136.0, 134.8, 134.7, 132.9, 131.9, 130.5, 129.9, 129.1, 128.7, 128.7, 128.4, 127.1, 126.2, 126.0, 125.9, 124.4, 121.7, 116.8, 113.9, 111.7, 79.8, 72.9, 58.6, 57.1, 42.1, 34.5, 34.3, 30.4, 30.1, 21.2, 19.4. IR (KBr) υ: 729, 765, 827, 910, 1003, 1032, 1122, 1161, 1235, 1311, 1374, 1441, 1474, 1569, 2223, 2875, 2960, 3070, 3627 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{42}H_{42}N_2O_2$ $[M + H]^+$ 607.3319; Found 607.3317.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(5-fluoro-2-methylphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ae')

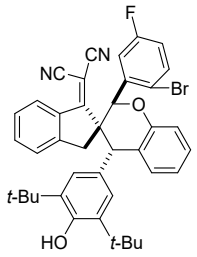


3ae'

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.43 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 91.1 mg, 99% yield (two isomers), >20:1 dr, reaction time = 36 h, m.p. 225.7-226.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.02-6.93 (m, 3H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.58 (d, *J* = 2.2 Hz, 1H), 6.34 (dd, *J* = 10.0, 2.6 Hz, 1H), 6.08 (s, 1H), 5.30 (s, 1H), 4.10 (d, *J* = 18.3 Hz, 1H), 3.82 (s, 1H), 3.19 (d, *J* = 18.3 Hz, 1H), 2.53 (s, 3H), 1.49 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 160.2 (d, *J* = 243.5 Hz), 155.0, 154.0, 147.9, 136.3, 135.9 (d, *J* = 3.2 Hz), 135.2 (d, *J* = 6.8 Hz) 134.8, 133.2 (d, *J* = 7.7 Hz), 131.9, 129.7, 129.1, 129.0, 128.7, 128.5, 127.1, 126.2, 124.3, 122.0, 116.7, 115.9 (d, *J* = 20.4 Hz), 113.7, 113.4 (d, *J* = 22.8 Hz) 111.7, 79.8, 72.7, 72.7, 58.4, 57.2, 41.8, 34.5, 34.3,

30.4, 30.0, 18.8. IR (KBr) υ: 742, 824, 900, 1008, 1122, 1157, 1239, 1310, 1364, 1440, 1473, 1572, 2222, 2875, 2958, 3070, 3632 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{39}FN_2O_2$ $[M + H]^+$ 611.3068; Found 611.3065.

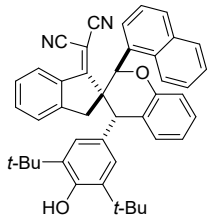
2-(2-(2-bromo-5-fluorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3af')



3af'

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 97.0 mg, 96% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 257.5-258.1 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.00-6.94 (m, 3H), 6.90 (d, *J* = 2.1 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 1H), 6.44 (dd, *J* = 9.3, 2.9 Hz, 1H), 6.16 (s, 1H), 5.30 (s, 1H), 4.04 (d, *J* = 18.2 Hz, 1H), 3.82 (s, 1H), 3.20 (d, *J* = 18.3 Hz, 1H), 1.48 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 160.9 (d, *J* = 247.5 Hz), 154.9, 154.1, 147.7, 136.3 (d, *J* = 6.7 Hz), 136.2, 136.1, 136.0 (d, *J* = 8.0 Hz), 135.2, 134.8, 131.8, 129.5, 129.1, 129.0, 128.9, 128.6, 127.2, 126.3, 124.3, 122.6 (d, *J* = 3.3 Hz), 122.1, 117.7 (d, *J* = 22.1 Hz), 116.9, 115.4 (d, *J* = 24.3 Hz), 113.6, 111.4, 80.0, 74.8, 58.6, 57.3, 41.6, 34.6, 34.4, 30.4, 30.1. IR (KBr) υ: 744, 823, 898, 1027, 1121, 1161, 1237, 1311, 1365, 1441, 1473, 1572, 2222, 2875, 2958, 3070, 3632 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{36}BrFN_2O_2$ $[M + H]^+$ 675.2017; Found 675.2019.

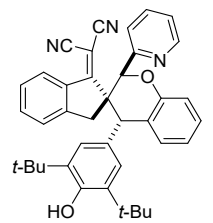
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(naphthalen-1-yl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ag')



3ag'

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.40 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 92.1 mg, 98% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 226.9-227.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.77 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.61 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.48 – 7.41 (m, 1H), 7.33 – 7.26 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.06 – 7.00 (m, 1H), 6.96 (t, *J* = 7.0 Hz, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 6.29 (s, 1H), 5.32 (s, 1H), 4.15 (d, *J* = 17.9 Hz, 1H), 3.84 (s, 1H), 3.14 (d, *J* = 17.9 Hz, 1H), 1.51 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, CDCl3) δ 175.0, 154.7, 154.1, 148.6, 136.3, 134.9, 134.8, 133.7, 133.3, 132.8, 131.7, 129.7, 129.2, 128.8, 128.7, 128.7, 128.6, 128.5, 127.9, 127.6, 126.9, 126.8, 126.6, 126.4, 126.2, 123.9, 121.7, 116.9, 113.9, 112.6, 80.1, 75.3, 59.5, 56.3, 41.3, 34.5, 34.3, 30.4, 30.2. IR (KBr) υ: 740, 812, 863, 898, 1005, 1119, 1157, 1231, 1310, 1362, 1441, 1478, 1567, 2219, 2875, 2959, 3059, 3627 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{44}H_{40}N_2O_2$ $[M + H]^+$ 629.3163; Found 629.3167.

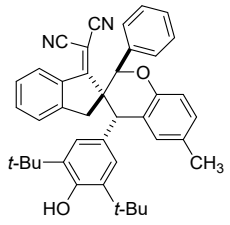
2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(pyridin-2-yl)spiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ah')



3ah'

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.30 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 91.1 mg, 96% yield (two isomers), 11:1 dr, reaction time = 36 h, m.p. 230.6-231.4 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.1 Hz, 1H), 8.31-8.29 (m, 1H), 7.80 – 7.73 (m, 2H), 7.62 (td, *J* = 7.5, 1.1 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.21 (m, 1H), 7.24 – 7.17 (m, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.98 – 6.89 (m, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.56 (d, *J* = 2.3 Hz, 1H), 6.19 (s, 1H), 5.28 (s, 1H), 4.38 (d, *J* = 16.8 Hz, 1H), 3.78 (s, 1H), 2.97 (d, *J* = 16.8 Hz, 1H), 1.49 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 155.9, 154.6, 153.8, 149.7, 148.0, 136.9, 136.7, 135.9, 134.7, 134.3, 131.8, 130.2, 129.0, 128.4, 128.3, 127.9, 126.5, 126.0, 125.9, 124.2, 123.6, 121.7, 116.8, 114.3, 113.0, 77.9, 75.8, 59.0, 55.5, 42.1, 34.5, 34.3, 30.4, 30.1. IR (KBr) υ: 765, 808, 861, 904, 998, 1043, 1123, 1156, 1236, 1305, 1360, 1443, 1488, 1572, 1612, 2224, 2878, 2959, 3070, 3626 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{39}H_{37}N_3O_2$ $[M + H]^+$ 580.2959; Found 580.2956.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methyl-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ba)

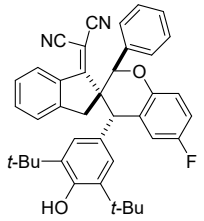


3ba

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 81.1 mg, 83% yield (two isomers), 9:1 dr, reaction time = 36 h, m.p. 236.3-237.0 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.34 (td, *J* = 8.6, 7.0, 4.0 Hz, 5H), 7.06 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 2.0

Hz, 1H), 6.79 (s, 1H), 6.56 (d, *J* = 1.9 Hz, 1H), 6.07 (s, 1H), 5.31 (s, 1H), 4.02 (d, *J* = 18.0 Hz, 1H), 3.74 (s, 1H), 3.07 (d, *J* = 18.0 Hz, 1H), 2.22 (s, 3H), 1.50 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 154.0, 152.6, 148.7, 136.3, 136.3, 136.2, 134.8, 134.8, 131.6, 130.8, 129.8, 129.3, 129.2, 128.9, 128.7, 128.6, 128.6, 127.6, 126.8, 126.2, 123.4, 116.6, 114.0, 112.4, 79.9, 75.2, 59.3, 56.4, 41.3, 34.5, 34.3, 30.4, 30.2, 20.6. IR (KBr) υ: 730, 768, 813, 898, 1008, 1148, 1236, 1305, 1364, 1438, 1492, 1560, 2218, 2874, 2874, 2960, 3627 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{41}H_{40}N_2O_2$ $[M + H]^+$ 593.3163; Found 593.3168.

2-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-fluoro-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ca)

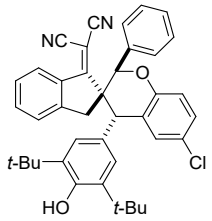


3ca

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.35 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 79.6 mg, 89% yield (two isomers), 13:1 dr, reaction time = 36 h, m.p. 239.8-240.9 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.33 (s, 5H), 7.05 (dd, *J* = 9.1, 4.8 Hz, 1H), 6.97 (td, *J* = 8.9, 8.5, 3.0 Hz, 1H), 6.84 (d, *J* = 2.1 Hz, 1H), 6.70 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 6.06 (s, 1H), 5.31 (s, 1H), 4.02 (d, *J* = 17.9 Hz, 1H), 3.74 (s, 1H), 3.04 (d, *J* = 18.0 Hz, 1H), 1.47 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 157.5 (d, *J* = 240.0 Hz), 154.2, 150.9, 150.9, 148.3, 136.3, 136.2, 136.0, 135.0, 129.2, 129.1, 128.9, 128.8, 128.8, 128.6, 126.9, 126.3, 125.0 (d, *J* = 7.3 Hz), 118.1 (d, *J* = 8.1 Hz), 117.2 (d, *J* = 22.9 Hz), 115.8 (d, *J* = 23.5 Hz) 113.8, 112.4, 80.1, 75.5, 59.0, 56.4, 41.3, 34.6, 34.3, 30.3, 30.1. IR (KBr) υ: 732, 766, 808, 904, 1016, 1145, 1230, 1311, 1373, 1436, 1489, 1554, 1606, 2219, 2876, 2958,

3063, 3600 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}FN_2O_2$ $[M + H]^+$ 597.2912; Found 597.2905.

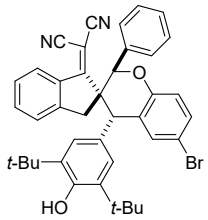
2-(6-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3da)



3da

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 85.7 mg, 93% yield (two isomers), 12:1 dr, reaction time = 36 h, m.p. 248.4-249.1 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.2 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.34 (s, 5H), 7.22 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 6.55 (d, *J* = 1.7 Hz, 1H), 6.10 (s, 1H), 5.34 (s, 1H), 4.01 (d, *J* = 17.9 Hz, 1H), 3.74 (s, 1H), 3.02 (d, *J* = 17.9 Hz, 1H), 1.49 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.6, 154.3, 153.3, 148.2, 136.4, 136.1, 135.8, 135.1, 135.0, 130.9, 129.2, 129.1, 129.0, 128.8, 128.8, 128.8, 128.7, 128.5, 126.8, 126.4, 126.3, 125.4, 118.4, 113.8, 112.3, 80.1, 75.5, 58.9, 56.1, 41.2, 34.5, 34.3, 30.3, 30.2, 30.2, 30.1. IR (KBr) υ: 737, 810, 907, 1014, 1145, 1237, 1309, 1373, 1438, 1479, 1554, 1594, 2217, 2876, 2959, 3064, 3606 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}ClN_2O_2$ $[M + H]^+$ 613.2616; Found 613.2618.

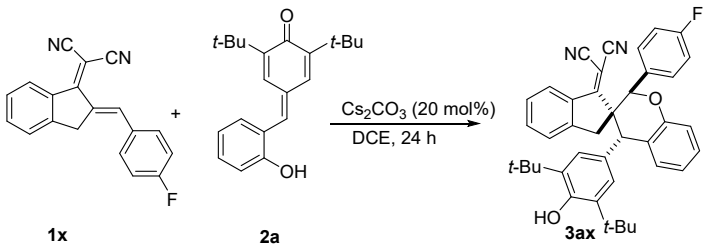
2-(6-bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenylspiro[chromane-3,2'-inden]-1'(3'H)-ylidene)malononitrile (3ea)



3ea

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 3:1-2:1 as eluent. R_f = 0.37 (petroleum ether/ethyl acetate = 20:1). Yellow solid, 82.4 mg, 84% yield (two isomers), 17:1 dr, reaction time = 36 h, m.p. 249.5-250.9 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.2 Hz, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.31 (m, 6H), 7.13 (d, *J* = 2.3 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 1H), 6.10 (s, 1H), 5.34 (s, 1H), 4.00 (d, *J* = 17.9 Hz, 1H), 3.74 (s, 1H), 3.02 (d, *J* = 17.9 Hz, 1H), 1.49 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.5, 154.3, 153.8, 148.2, 136.4, 136.1, 135.8, 135.1, 135.0, 133.9, 131.6, 129.2, 129.1, 128.9, 128.8, 128.8, 128.8, 128.5, 126.8, 126.2, 126.0, 118.8, 113.8, 113.7, 112.3, 80.1, 75.5, 58.9, 56.0, 41.2, 34.5, 34.3, 30.3, 30.1. IR (KBr) υ: 732, 815, 908, 1009, 1121, 1235, 1301, 1359, 1399, 1438, 1470, 1565, 2223, 2874, 2959, 3069, 3616 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{40}H_{37}BrN_2O_2$ $[M + H]^+$ 657.2111; Found 657.2122.

5. Experimental procedure for gram scale synthesis of 3ax

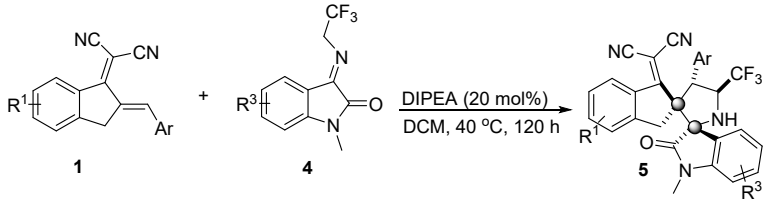


1x **2a** **3ax**

A mixture of Cs_2CO_3 (0.6 mmol, 0.2 equiv.), **1x** (3 mmol, 1.0 equiv.) and **2a** (6 mmol, 2.0 equiv.) and 1,2-dichloroethane (30 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 25 °C in oil bath heating for the 24 h. Upon completion (monitored by TLC), the reaction solution was concentrated in vacuo. The crude product was purified by column

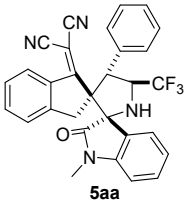
chromatography on silica gel (eluent PE:DCM = 3:1) to afford products **3ax** as a mixture of the major and minor diastereomers of **3ax** in 93% yield (1.66 g).

6. General experimental procedures for synthesis of compounds 5



A mixture of DIPEA (0.02 mmol, 0.2 equiv.), **1** (0.15 mmol, 1.5 equiv.) and **4** (0.10 mmol, 1.0 equiv.) and dichloromethane (1.0 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 40 °C in oil bath heating for the 120 h. Upon completion (monitored by TLC), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:DCM = 1:2 to 1:3) to afford pure products **5**.

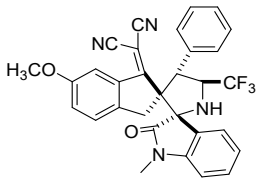
2-(1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5aa)



The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.3 mg, 95% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 197.8-198.7 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.3, 1.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.36 (dt, J = 7.7, 3.8 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.30 – 7.23 (m, 1H), 7.22 (t, J = 7.7 Hz, 1H), 6.57 (dd, J = 7.8, 0.9 Hz, 1H), 5.40 (d, J = 10.5 Hz, 1H), 4.86 – 4.75 (m, 1H), 3.88 (d, J = 15.3 Hz, 1H), 3.20 (d, J = 15.4 Hz, 1H), 3.14 (d, J = 8.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 172.0, 147.9, 141.3, 136.0,

134.7, 133.8, 130.6, 130.4, 129.9, 129.2, 128.5, 127.7, 126.7, 126.4, 125.1, 123.9, 114.9, 113.3, 107.7, 78.9, 76.0, 73.6, 63.4 (q, J = 29.7 Hz) 46.8, 36.0, 25.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.14. IR (KBr) υ: 695, 743, 862, 971, 1020, 1137, 1235, 1286, 1373, 1438, 1561, 1614, 1707, 2219, 2934, 2969, 3065, 3327 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{21}F_3N_4O$ [M + Na]$^+$: 533.1560, found:533.1563.

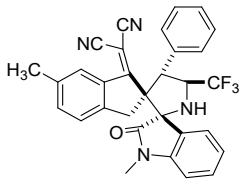
2-(5-methoxy-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-3(1H)-ylidene)malononitrile (5ab)



5ab

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.20 (petroleum ether/ethyl acetate = 2:1). Yellow solid, 44.2 mg, 83% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 106.7-107.5 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.4, 1.1 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.43 – 7.35 (m, 4H), 7.32 (t, J = 7.4 Hz, 1H), 7.26 (t, 3H), 7.24 (d, J = 8.5 Hz, 1H), 7.04 (dd, J = 8.5, 2.4 Hz, 1H), 6.60 (d, J = 7.7 Hz, 1H), 5.38 (d, J = 10.5 Hz, 1H), 4.84 – 4.75 (m, 1H), 3.79 (d, J = 15.0 Hz, 1H), 3.73 (s, 3H), 3.17 – 3.09 (m, 2H), 2.46 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 172.2, 159.2, 141.3, 140.7, 137.0, 133.9, 130.7, 130.4, 129.8, 129.1, 128.4, 127.0, 126.7, 123.8, 123.5, 114.9, 113.5, 107.7, 107.4, 78.5, 76.1, 74.2, 63.4 (q, J = 29.6 Hz), 55.9, 46.8, 35.2, 29.8, 26.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -71.88. IR (KBr) υ: 710, 776, 837, 979, 1031, 1163, 1213, 1290, 1333, 1439, 1487, 1612, 1694, 2436, 2837, 2925, 3020, 3369 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{31}H_{23}F_3N_4O_2$ [M + Na]$^+$: 563.1665, found:563.1659.

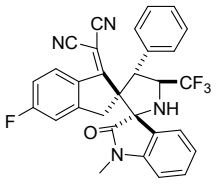
2-(1'',5-dimethyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-3(1H)-ylidene)malononitrile (5ac)



5ac

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.23 (petroleum ether/ethyl acetate = 2:1). Yellow solid, 46.8 mg, 89% yield (two isomers), 10:1 dr, reaction time = 120 h, m.p. 221.5-222.3 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 1H), 7.69 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.24 (d, *J* = 8.1 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 5.39 (d, *J* = 10.5 Hz, 1H), 4.85 – 4.75 (m, 1H), 3.82 (d, *J* = 15.2 Hz, 1H), 3.18 – 3.11 (m, 2H), 2.40 (s, 3H), 2.30 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 172.1, 145.2, 141.3, 137.8, 136.2, 135.9, 133.9, 130.6, 130.4, 129.9, 129.8, 129.1, 128.4, 126.7, 126.1, 124.9, 123.8, 115.0, 113.4, 107.7, 78.4, 76.0, 73.8, 63.4 (q, *J* = 29.9 Hz) 46.8, 35.5, 29.8, 25.8, 21.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.12. IR (KBr) υ: 695, 740, 867, 1021, 1141, 1237, 1285, 1374, 1443, 1491, 1559, 1615, 1704, 2219, 2936, 2974, 3034, 3322 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{31}H_{23}F_3N_4O$ $[M + Na]^+$: 547.1716, found:547.1717.

2-(5-fluoro-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ad)

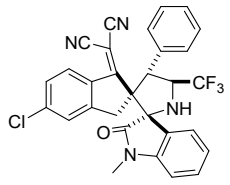


5ad

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.27 (petroleum ether/ethyl acetate = 2:1). Yellow solid, 44.4 mg, 84% yield (two isomers), 5:1 dr, reaction time = 120 h, m.p. 207.6-208.9 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.90 (m, 2H), 7.67 – 7.62

(m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.29 – 7.26 (m, 1H), 7.07 – 7.02 (m, 1H), 6.92 (td, *J* = 8.7, 2.5 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 5.39 (d, *J* = 10.4 Hz, 1H), 4.83 – 4.75 (m, 1H), 3.89 (d, *J* = 15.6 Hz, 1H), 3.18 (d, *J* = 15.6 Hz, 1H), 3.13 (d, *J* = 8.8 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 176.2, 170.4, 166.4 (d, *J* = 260.2 Hz), 151.2 (d, *J* = 10.4 Hz), 141.3, 133.6, 132.2 (d, *J* = 2.4 Hz), 130.6, 130.4, 130.4, 129.8, 129.3, 128.6, 127.5 (d, *J* = 10.1 Hz), 126.8, 124.0, 115.8 (d, *J* = 23.5 Hz), 114.8, 113.4 (d, *J* = 22.7 Hz), 113.3, 107.8, 78.5, 75.9, 73.7, 63.3 (q, *J* = 29.9 Hz), 46.9, 35.9, 26.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.07, -102.45. IR (KBr) υ: 696, 754, 857, 1102, 1150, 1262, 1370, 1480, 1563, 1613, 1711, 2223, 2308, 2898, 2980, 3071, 3326 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}F_4N_4O$ $[M + H]^+$: 529.1646, found:529.1651.

2-(5-chloro-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ae)

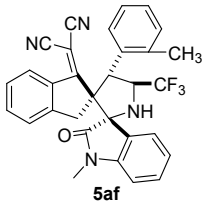


5ae

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.37 (petroleum ether/ethyl acetate = 2:1). Yellow solid, 52.3 mg, 96% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 207.0-208.6 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.3 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.66 – 7.61 (m,2H), 7.42 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.25 (m, 1H), 7.22 – 7.16 (m, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 5.39 (d, *J* = 10.5 Hz, 1H), 4.86 – 4.74 (m, 1H), 3.87 (d, *J* = 15.5 Hz, 1H), 3.16 (d, *J* = 15.6 Hz, 1H), 3.11 (d, *J* = 8.7 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 170.5, 149.5, 141.3, 141.3, 134.5, 133.7, 130.6, 130.5, 129.82, 129.3, 128.7, 128.3, 126.9, 126.5, 126.2, 124.0, 114.7, 113.1, 107.9, 79.3, 76.0, 74.3, 63.4 (q, *J* = 29.8 Hz), 46.9, 35.9, 26.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.16. IR (KBr) υ: 695, 752, 861, 911, 1088, 1152, 1234, 1284, 1368, 1456, 1559, 1609, 1711, 2221, 2886, 2933,

2971, 3325 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}ClF_3N_4O$ $[M + H]^+$: 545.1351, found:545.1350.

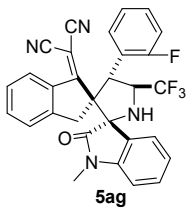
2-(1''-methyl-2''-oxo-4'-(o-tolyl)-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5af)



5af

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.37 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 52.3 mg, 36% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 117.7-118.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.28 – 7.09 (m, 3H), 7.09 – 7.02 (m, 2H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.8 Hz, 1H), 6.25 – 6.19 (m, 1H), 5.52 – 5.43 (m, 1H), 5.30 (d, *J* = 9.6 Hz, 1H), 3.11 (d, *J* = 17.0 Hz, 1H), 2.92 (s, 3H), 2.59 (d, *J* = 4.2 Hz, 1H), 2.51 (d, *J* = 17.0 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.3, 178.8, 146.9, 143.0, 138.5, 137.2, 135.6, 135.2, 134.4, 131.1, 130.1, 129.5, 128.0, 127.7, 126.9, 126.8, 125.6, 124.3, 123.3, 122.9, 114.0, 112.8, 110.1, 107.6, 78.7, 75.9, 70.3, 63.5 (q, *J* = 30.0 Hz), 49.5, 42.8, 24.9, 17.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -71.97. IR (KBr) υ: 690, 742, 873, 957, 1054, 1123, 1288, 1366, 1402, 1467, 1563, 1609, 1686, 2223, 2976, 3067, 3292 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{31}H_{23}F_3N_4O$ $[M + Na]^+$: 547.1716,found:547.1725.

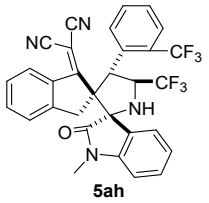
2-(4'-(2-fluorophenyl)-1''-methyl-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ag)



5ag

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.40 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 32.8 mg, 62% yield (two isomers), 5:1 dr, reaction time = 120 h, m.p. 184.3-185.1 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (td, 1H), 7.85 – 7.80 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.10 (m, 2H), 6.50 (d, *J* = 7.7 Hz, 1H), 5.37 (d, *J* = 10.3 Hz, 1H), 5.33 – 5.20 (m, 1H), 3.90 (d, *J* = 15.8 Hz, 1H), 3.08 (d, *J* = 8.1 Hz, 1H), 2.93 (dd, *J* = 15.8, 3.7 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 173.0, 161.3 (d, *J* = 246.6 Hz), 147.9, 141.5, 135.9, 134.6, 132.5 (d, *J* = 3.9 Hz), 130.8, 130.7, 130.4, 130.2, 127.7, 126.1, 125.9, 125.4, 125.4, 125.3, 123.6, 121.6 (d, *J* = 10.3 Hz), 117.1 (d, *J* = 24.2 Hz), 114.6, 113.4, 107.8, 78.8, 75.5, 73.6, 61.2 (d, *J* = 30.0 Hz), 44.9, 37.9, 25.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.56, -105.34. IR (KBr) υ: 691, 752, 880, 1049, 1091, 1234, 1290, 1380, 1454, 1562, 1617, 1708, 2219, 2888, 2974, 3324 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{30}H_{20}F_4N_4O$ $[M + H]^+$ 529.1646; Found 529.1646.

2-(1''-methyl-2''-oxo-5'-(trifluoromethyl)-4'-(2-(trifluoromethyl)phenyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ah)

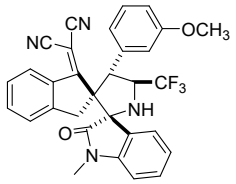


5ah

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 18.7 mg, 32% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 158.2-159.9 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.76 – 7.68 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.22 (td, *J* = 7.5, 0.9 Hz, 1H), 7.09 – 7.03 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.28 – 6.21 (m, 1H), 5.58 – 5.47 (m, 1H), 5.35 (d, *J* = 9.2 Hz, 1H), 3.04 (d, *J* = 16.7 Hz, 1H), 2.96 (s, 3H), 2.64 (d, *J* = 4.3 Hz, 1H), 2.45 (d, *J* = 16.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 175.9, 146.0, 142.9, 136.2, 135.4, 134.1, 132.6, 132.1, 130.3, 128.2, 127.8, 126.6, 126.4 (q, *J* = 5.9 Hz) 125.8, 124.4, 123.1, 123.0, 114.1, 112.3, 107.7, 79.4, 75.4, 70.6, 64.9 (q, *J* = 30.5 Hz), 44.1, 43.3, 25.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -57.66, -71.63. IR (KBr) υ: 683, 758, 874, 1059, 1123, 1160, 1235, 1308, 1360, 1446, 1566, 1610, 1692, 2224, 2869, 2933, 3072, 3295 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{31}H_{20}F_6N_4O$ $[M + H]^+$: 579.1614, found:579.1623.

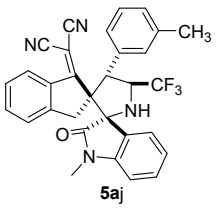
2-(4'-(3-methoxyphenyl)-1''-methyl-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ai)



5ai

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.28 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 53.6 mg, 99% yield (two isomers), >20:1 dr, reaction time = 120 h, m.p. 188.5-189.3 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 11.5, 7.7 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 8.2 Hz, 2H), 6.86 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.35 (d, *J* = 10.5 Hz, 1H), 4.84 – 4.66 (m, 1H), 3.87 (d, *J* = 15.5 Hz, 1H), 3.82 (s, 3H), 3.24 (d, *J* = 15.3 Hz, 1H), 3.13 (d, *J* = 8.9 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ 176.2, 172.1, 160.0, 147.9, 141.3, 136.0, 135.4, 134.7, 130.7, 130.4, 130.0, 127.7, 126.7, 126.7, 126.4, 125.1, 123.9, 121.9, 116.3, 115.0, 113.6, 113.3, 107.7, 78.8, 76.0, 73.6, 63.4 (q, *J* = 29.8 Hz), 55.5, 46.9, 36.1, 25.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.24. IR (KBr) υ: 696, 745, 869, 1046, 1099, 1144, 1168, 1281, 1379, 1466, 1496, 1564, 1608, 1706, 2220, 2926, 2970, 3069, 3321 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{31}H_{23}F_3N_4O_2$ $[M + H]^+$ 541.1846; Found 541.1844.

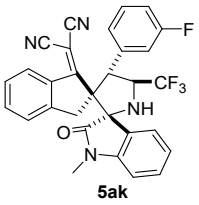
2-(1''-methyl-2''-oxo-4'-(m-tolyl)-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5aj)



5aj

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 51.5 mg, 98% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 181.4-182.1 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.33 – 7.23 (m, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.35 (d, *J* = 10.4 Hz, 1H), 4.85 – 4.73 (m, 1H), 3.87 (d, *J* = 15.4 Hz, 1H), 3.21 (d, *J* = 15.3 Hz, 1H), 3.14 (d, *J* = 8.9 Hz, 1H), 2.39 (d, *J* = 2.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 172.1, 147.9, 141.3, 138.8, 136.0, 134.6, 133.8, 130.7, 130.6, 130.4, 129.2, 128.9, 127.7, 126.9, 126.7, 126.4, 125.1, 123.8, 114.9, 113.4, 107.7, 78.8, 76.0, 73.6, 63.4 (q, *J* = 29.7 Hz), 46.8, 36.1, 25.8, 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.13. IR (KBr) υ: 698, 745, 865, 973, 1050, 1104, 1141, 1168, 1282, 1378, 1467, 1563, 1614, 1709, 2222, 2930, 2973, 3067, 3327 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{31}H_{23}F_3N_4O$ $[M + H]^+$ 525.1897; Found 525.1895.

2-(4'-(3-fluorophenyl)-1''-methyl-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ak)

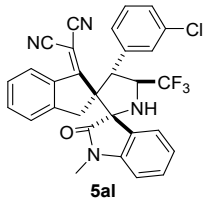


5ak

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.33 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 40.7 mg, 77% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 205.4-207.0 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.4, 1.3 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.43 – 7.33 (m, 4H), 7.29 – 7.25 (m, 1H), 7.25 – 7.21 (m, 1H), 7.07 –

7.00 (m, 1H), 5.39 (d, *J* = 10.5 Hz, 1H), 4.81 – 4.70 (m, 1H), 3.89 (d, *J* = 15.3 Hz, 1H), 3.18 – 3.12 (m, 2H), 2.40 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 171.8, 162.9 (d, *J* = 247.4 Hz), 147.6, 141.3, 136.4 (d, *J* = 7.2 Hz), 135.9, 134.8, 130.8 (d, *J* = 8.4 Hz), 130.5, 130.4, 127.9, 126.6, 126.4, 125.7 (d, *J* = 3.0 Hz), 125.2, 123.9, 117.0 (d, *J* = 22.7 Hz) 115.7 (d, *J* = 20.8 Hz) 114.9, 113.2, 107.8, 78.9, 76.0, 73.3, 63.5 (q, *J* = 30.0 Hz) 46.5, 36.0, 25.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.03, -110.05. IR (KBr) υ: 691, 756, 864, 1020, 1102, 1145, 1238, 1374, 1447, 1489, 1568, 1610, 1707, 2221, 2877, 2937, 2973, 3068, 3338 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}F_4N_4O$ [M + Na]$^+$: 551.1465, found:551.1479.

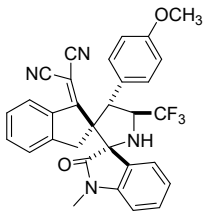
2-(4'-(3-chlorophenyl)-1''-methyl-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5al)



5al

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.35 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 51.2 mg, 94% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 169.7-170.8 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 7.25 – 7.21 (m, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.37 (d, *J* = 10.5 Hz, 1H), 4.83 – 4.66 (m, 1H), 3.89 (d, *J* = 15.3 Hz, 1H), 3.14 (d, *J* = 6.6 Hz, 1H), 3.11 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 171.8, 147.6, 141.3, 136.1, 136.0, 135.1, 134.8, 130.5, 130.5, 130.4, 129.9, 128.9, 128.3, 127.9, 126.6, 126.4, 125.2, 123.9, 114.8, 113.2, 107.8, 78.9, 76.0, 73.3, 63.6 (q, *J* = 30.0 Hz), 46.6, 36.1, 25.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.13. IR (KBr) υ: 693, 750, 797, 862, 1019, 1097, 1138, 1174, 1235, 1281, 1370, 1434, 1473, 1715, 2224, 2855, 2924, 2962, 3066, 3331 cm^{-1}. HRMS (ESI) m/z: Calcd for C30H20ClF3N4O [M + H]$^+$ 545.1351; Found 545.1351.

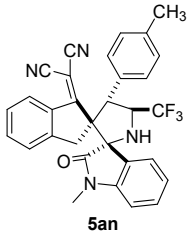
2-(4'-(4-methoxyphenyl)-1''-methyl-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5am)



5am

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.3 mg, 89% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 183.4-185.0 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.46 (td, *J* = 7.5, 1.0 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.29 – 7.19 (m, 2H), 6.98 – 6.87 (m, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.36 (d, *J* = 10.6 Hz, 1H), 4.80 – 4.66 (m, 1H), 3.86 (d, *J* = 15.3 Hz, 1H), 3.79 (s, 3H), 3.22 (d, *J* = 15.4 Hz, 1H), 3.15 (d, *J* = 8.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 172.1, 159.4, 147.9, 141.2, 136.0, 134.7, 131.0, 130.7, 130.4, 127.7, 126.6, 126.4, 125.4, 125.1, 123.8, 114.9, 114.5, 113.3, 107.7, 78.8, 75.9, 73.8, 63.4 (q, *J* = 29.6 Hz) 55.4, 46.2, 35.8, 25.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.95. IR (KBr) υ: 688, 755, 844, 1045, 1141, 1174, 1234, 1272, 1375, 1463, 1518, 1561, 1612, 1711, 2220, 2928, 2973, 3071, 3352 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{31}H_{23}F_3N_4O_2$ $[M + H]^+$: 541.1846, found:541.1849.

2-(1''-methyl-2''-oxo-4'-(p-tolyl)-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5an)

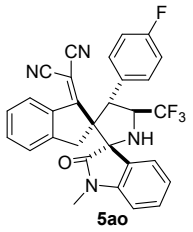


5an

The compound was prepared according to general procedure with petroleum

ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.35 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 49.6 mg, 95% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 195.4-196.1 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.45 (td, *J* = 7.5, 1.0 Hz, 1H), 7.36 (td, *J* = 7.6, 1.4 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.19 (m, 3H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.37 (d, *J* = 10.5 Hz, 1H), 4.84 – 4.72 (m, 1H), 3.87 (d, *J* = 15.4 Hz, 1H), 3.21 (d, *J* = 15.4 Hz, 1H), 3.15 (d, *J* = 8.8 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 172.0, 147.9, 141.2, 138.3, 136.0, 134.6, 130.7, 130.6, 130.4, 129.8, 129.7, 127.7, 126.7, 126.4, 125.1, 123.8, 114.9, 113.3, 107.7, 78.8, 76.0, 73.7, 63.4 (q, *J* = 29.5 Hz), 46.5, 35.9, 25.8, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.18. IR (KBr) υ: 693, 745, 862, 1020, 1137, 1170, 1234, 1284, 1374, 1438, 1465, 1520, 1557, 1614, 1706, 2218, 2930, 2972, 3066, 3328 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{31}H_{23}F_3N_4O$ $[M + H]^+$: 525.1897, found: 525.1890.

2-(4'-(4-fluorophenyl)-1''-methyl-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ao)

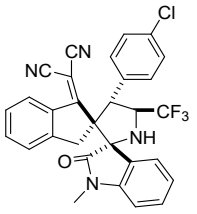


5ao

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.23 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.4 mg, 92% yield (two isomers), 12:1 dr, reaction time = 96 h, m.p. 216.5-217.4 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 2H), 7.68 – 7.61 (m, 2H), 7.47 (td, *J* = 7.5, 1.0 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.27 (d, *J* = 1.0 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.11 (t, *J* = 8.6 Hz, 2H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.39 (d, *J* = 10.5 Hz, 1H), 4.83 – 4.62 (m, 1H), 3.88 (d, *J* = 15.2 Hz, 1H), 3.15 (d, *J* = 15.2 Hz, 1H), 3.11 (d, *J* = 8.7 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 176.2, 171.9, 162.50 (d, *J* = 249.0 Hz), 147.7, 141.3, 136.0, 134.8, 131.6 (d, *J* = 8.0 Hz), 130.5, 130.5,

129.6 (d, J = 3.3 Hz), 127.8, 126.6, 126.4, 125.2, 123.9, 116.2 (d, J = 21.4 Hz), 114.9, 113.2, 107.8, 78.8, 75.9, 73.4, 63.7 (q, J = 29.7 Hz) 46.2, 35.9, 25.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.13, -113.04. IR (KBr) υ: 691, 746, 850, 1020, 1134, 1233, 1286, 1371, 1434, 1468, 1513, 1564, 1614, 1707, 2220, 2871, 2934, 3070, 3329 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}F_4N_4O$ [M + H]$^+$: 529.1646, found:529.1655.

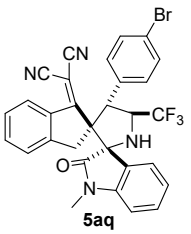
2-(4'-(4-chlorophenyl)-1''-methyl-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ap)



5ap

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 48.6 mg, 89% yield (two isomers), 11:1 dr, reaction time = 96 h, m.p. 198.1-199.3 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dt, J = 8.0, 1.8 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.43 – 7.33 (m, 4H), 7.26 (t, 1H), 7.23 (t, J = 6.9 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 5.38 (d, J = 10.5 Hz, 1H), 4.80 – 4.63 (m, 1H), 3.87 (d, J = 15.2 Hz, 1H), 3.15 – 3.08 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 171.8, 147.6, 141.3, 135.9, 134.8, 134.6, 132.4, 131.2, 130.5, 130.5, 129.4, 127.9, 126.6, 126.4, 125.2, 123.9, 114.9, 113.1, 107.8, 78.8, 75.9, 73.3, 63.5 (q, J = 30.0 Hz), 46.3, 35.9, 25.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.24. IR (KBr) υ: 693, 749, 873, 1049, 1094, 1138, 1232, 1285, 1377, 1440, 1514, 1564, 1613, 1707, 2220, 2925, 2972, 3071, 3329 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}ClF_3N_4O$ [M + Na]$^+$: 567.1170, found:567.1166.

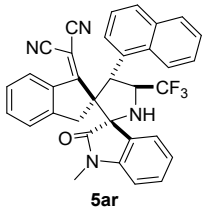
2-(4'-(4-bromophenyl)-1''-methyl-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5aq)



5aq

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 56.4 mg, 96% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 186.4-187.3 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.85 (m, 2H), 7.54 (s, 4H), 7.47 (td, *J* = 7.5, 1.0 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.29 – 7.25 (m, 1H), 7.23 (t, *J* = 6.7 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.36 (d, *J* = 10.5 Hz, 1H), 4.82 – 4.63 (m, 1H), 3.87 (d, *J* = 15.3 Hz, 1H), 3.17 – 3.06 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 171.8, 147.6, 141.3, 136.0, 134.8, 132.9, 132.4, 131.5, 130.5, 130.5, 127.9, 126.7, 126.4, 125.22, 123.9, 122.8, 114.9, 113.1, 107.8, 78.9, 76.0, 73.3, 63.5 (q, *J* = 29.9 Hz), 46.4, 36.0, 25.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.25. IR (KBr) υ: 693, 754, 859, 1012, 1107, 1146, 1232, 1282, 1374, 1460, 1490, 1563, 1609, 1706, 2218, 2934, 2968, 3066, 3324 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}BrF_3N_4O$ $[M + H]^+$: 589.0845, found: 589.0847.

2-(1''-methyl-4'-(naphthalen-1-yl)-2''-oxo-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ar)

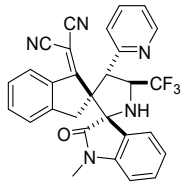


5ar

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.30 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 37.6 mg, 67% yield (two isomers), 10:1 dr, reaction time = 96 h, m.p. 189.2-190.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.9 Hz, 1H), 8.00 (dd,

J = 7.4, 1.3 Hz, 1H),7.90 (dd, *J* = 8.8, 5.1 Hz, 3H), 7.86 – 7.78 (m, 1H), 7.70 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.43 (td, *J* = 7.5, 1.0 Hz, 1H), 7.38 (td, *J* = 7.8, 1.3 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.58 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.59 (d, *J* = 10.4 Hz, 1H), 4.97 (s, 1H), 3.95 (d, *J* = 15.4 Hz, 1H), 3.29 – 3.16 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.3, 172.1, 147.8, 141.3, 136.0, 134.8, 133.3, 132.9, 131.2, 130.6, 130.4, 129.9, 128.7, 128.4, 127.7, 127.6, 127.6, 127.0, 126.9, 126.9, 126.6, 126.5, 126.3, 125.1, 123.9, 115.0, 113.3, 107.8, 78.9, 76.1, 73.8, 63.4 (q, *J* = 28.1 Hz), 47.0, 36.3, 25.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.55. IR (KBr) υ: 693, 756, 878, 1049, 1089, 1145, 1237, 1283, 1376, 1465, 1564, 1610, 1709, 2218, 2892, 2929, 2974, 3063, 3342 cm^{-1}. HRMS (ESI) m/z: Calcd for C34H23F3N4O $[M + H]^+$ 561.1897; Found 561.1894.

2-(1''-methyl-2''-oxo-4'-(pyridin-2-yl)-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5as)

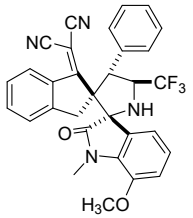


5as

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.40 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 44.7 mg, 87% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 215.7-216.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.8, 1.8 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.71 (td, *J* = 7.7, 1.9 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.34 (m, 2H), 7.31 – 7.18 (m, 3H), 5.47 (d, *J* = 10.1 Hz, 1H), 5.29 – 5.15 (m, 1H), 3.97 (d, *J* = 16.6 Hz, 1H), 3.70 (d, *J* = 16.5 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 171.8, 153.9, 149.3, 148.7, 141.3, 137.4, 136.0, 134.7, 130.6, 130.4, 127.5, 126.7, 126.0, 124.9, 123.9, 123.1, 115.0, 113.3, 107.7, 78.3, 76.5, 74.1, 63.0 (q, *J* = 29.9 Hz), 47.9, 35.3, 25.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.38. IR (KBr) υ: 694, 748, 864, 1021, 1104, 1141, 1233, 1287,

1376, 1438, 1470, 1563, 1615, 1712, 2219, 2943, 3067, 3324 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{29}H_{20}F_3N_5O$ $[M + H]^+$ 512.1693; Found 512.1693.

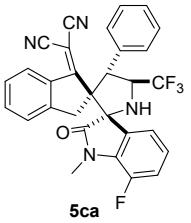
2-(7''-methoxy-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ba)



5ba

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.25 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 53.0 mg, 98% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 187.1-187.9 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.20 – 7.15 (m, 1H), 7.13 (t, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.30 (d, *J* = 10.5 Hz, 1H), 4.78 – 4.67 (m, 1H), 3.80 (d, *J* = 15.3 Hz, 1H), 3.72 (s, 3H), 3.08 (d, *J* = 15.3 Hz, 1H), 3.05 (d, *J* = 8.8 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.4, 172.1, 147.8, 145.0, 136.0, 134.6, 133.9, 132.7, 129.9, 129.1, 128.6, 128.4, 127.7, 126.3, 125.2, 124.6, 119.5, 114.9, 114.6, 113.5, 78.4, 76.0, 73.6, 63.48 (q, *J* = 29.6 Hz), 56.4, 46.7, 36.0, 29.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.89. IR (KBr) υ: 728, 768, 868, 947, 1050, 1143, 1280, 1364, 1462, 1495, 1561, 1607, 1704, 2220, 2846, 2939, 2967, 3072, 3340 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{31}H_{23}F_3N_4O_2$ $[M + H]^+$: 541.1846, found: 541.1847.

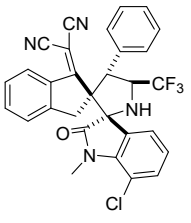
2-(7''-fluoro-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ca)



5ca

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 46.3 mg, 88% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 168.7-168.6 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.25 (m, 1H), 7.21 (td, *J* = 8.0, 4.6 Hz, 1H), 7.10 (dd, *J* = 10.9, 8.7 Hz, 1H), 5.37 (d, *J* = 10.4 Hz, 1H), 4.86 – 4.76 (m, 1H), 3.86 (d, *J* = 15.4 Hz, 1H), 3.20 (d, *J* = 15.3 Hz, 1H), 3.13 (d, *J* = 8.5 Hz, 1H), 2.60 (d, *J* = 2.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 171.8, 147.7, 147.3 (d, *J* = 245.1 Hz), 135.9, 134.9, 133.7 (d, *J* = 1.9 Hz), 133.6, 129.8, 129.2, 128.6, 128.0, 127.6 (d, *J* = 8.3 Hz), 126.4, 125.3, 124.6 (d, *J* = 6.2 Hz), 122.7, 118.5 (d, *J* = 19.1 Hz) 114.8, 113.2, 78.8, 76.0, 73.7, 63.4 (q, *J* = 29.8 Hz, 46.7, 36.0, 28.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.33, -136.27. IR (KBr) υ: 564, 608, 717, 766, 875, 1055, 1137, 1247, 1283, 1345, 1370, 1476, 1603, 1632, 1717, 2222, 2858, 2938, 3067, 3337 cm^{-1}. HRMS (ESI) m/z: Calcd for $C_{30}H_{20}F_4N_4O$ $[M + H]^+$ 529.1646; Found 529.1643.

2-(7''-chloro-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5da)

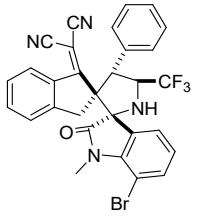


5da

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate =

3:1). Yellow solid, 44.8 mg, 82% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 207.6-208.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.3 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 5.34 (d, *J* = 10.5 Hz, 1H), 4.86 – 4.76 (m, 1H), 3.82 (d, *J* = 15.3 Hz, 1H), 3.18 (d, *J* = 15.3 Hz, 1H), 3.10 (d, *J* = 8.4 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.9, 171.9, 147.6, 137.0, 136.0, 134.9, 133.8, 133.6, 132.5, 129.8, 129.2, 128.6, 128.0, 126.3, 125.3, 125.0, 124.7, 115.4, 114.8, 113.2, 78.7, 75.6, 73.8, 63.4 (q, *J* = 29.9 Hz), 46.6, 36.2, 29.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.29. IR (KBr) υ: 702, 763, 904, 1017, 1063, 1128, 1166, 1282, 1361, 1458, 1561, 1603, 1710, 2219, 2855, 2924, 3064, 3341 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}ClF_3N_4O$ $[M + H]^+$: 545.1351, found: 545.1350.

2-(7''-bromo-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ea)

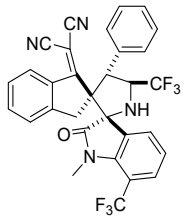


5ea

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.38 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 36.7 mg, 62% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 174.8-175.9 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 6.9 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.11 (t, *J* = 7.8 Hz, 1H), 5.33 (d, *J* = 10.6 Hz, 1H), 4.87 – 4.74 (m, 1H), 3.80 (d, *J* = 15.4 Hz, 1H), 3.17 (d, *J* = 15.4 Hz, 1H), 3.08 (d, *J* = 8.4 Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1, 171.9, 147.5, 138.5, 136.0, 135.8, 134.9, 134.2, 133.6, 129.8, 129.2, 128.6, 128.0, 126.3, 125.5, 125.4, 125.1, 114.8, 113.1,

102.1, 78.7, 75.6, 73.9, 63.4 (q, J = 30.3 Hz), 46.5, 36.3, 29.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.38. IR (KBr) υ: 700, 766, 854, 944, 1013, 1056, 1132, 1173, 1274, 1348, 1455, 1558, 1604, 1714, 2221, 2951, 3004, 3063, 3350 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}BrF_3N_4O$ $[M + H]^+$: 589.0845, found: 589.0845.

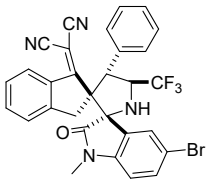
2-(1''-methyl-2''-oxo-4'-phenyl-5',7''-bis(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5fa)



5fa

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.60 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 36.4 mg, 63% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 202.2-203.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 10.2, 8.3 Hz, 3H), 7.48 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.34 (dd, J = 7.8, 4.8 Hz, 3H), 7.30 – 7.24 (m, 1H), 5.36 (d, J = 10.6 Hz, 1H), 4.90 – 4.77 (m, 1H), 3.81 (d, J = 15.4 Hz, 1H), 3.20 (d, J = 15.4 Hz, 1H), 3.10 (d, J = 8.3 Hz, 1H), 2.57 (q, J = 2.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 171.7, 147.3, 139.3, 135.9, 135.1, 133.7, 133.4, 129.8, 129.7, 129.2, 128.7, 128.1, 128.0 (q, J = 5.9 Hz), 126.3, 125.5, 123.3, 114.7, 112.9, 78.9, 74.5, 73.8, 63.2 (q, J = 29.9 Hz), 46.6, 36.2, 28.6, 28.6, 28.5, 28.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.32, -74.28. IR (KBr) υ: 700, 770, 863, 958, 1128, 1174, 1273, 1341, 1458, 1556, 1600, 1737, 2220, 2897, 2973, 3067, 3341 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{31}H_{20}F_6N_4O$ $[M + H]^+$: 579.1646, found: 579.1642.

2-(5''-bromo-1''-methyl-2''-oxo-4'-phenyl-5'-(trifluoromethyl)dispiro[indene-2,3'-pyrrolidine-2',3''-indolin]-1(3H)-ylidene)malononitrile (5ga)



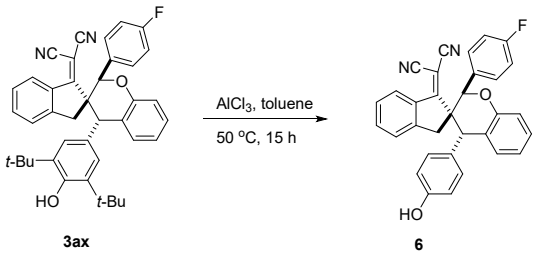
5ga

The compound was prepared according to general procedure with petroleum ether/dichloromethane = 1:1-3:1 as eluent. R_f = 0.13 (petroleum ether/ethyl acetate = 3:1). Yellow solid, 52.6 mg, 89% yield (two isomers), >20:1 dr, reaction time = 96 h, m.p. 196.4-197.2 °C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.51 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.25 (d, *J* = 10.5 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 1H), 5.34 (d, *J* = 10.5 Hz, 1H), 4.83 – 4.73 (m, 1H), 3.85 (d, *J* = 15.4 Hz, 1H), 3.23 (d, *J* = 15.6 Hz, 1H), 3.13 (d, *J* = 8.7 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 171.4, 147.8, 140.3, 135.9, 134.9, 133.4, 133.2, 132.5, 130.0, 129.8, 129.2, 128.6, 127.9, 126.5, 125.1, 116.8, 114.5, 113.2, 109.2, 79.2, 76.1, 73.6, 63.3 (q, *J* = 29.7 Hz), 46.8, 35.8, 26.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.24. IR (KBr) υ: 700, 733, 862, 1052, 1107, 1148, 1231, 1278, 1355, 1419, 1481, 1560, 1608, 1714, 2222, 2928, 2971, 3071, 3327 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{30}H_{20}BrF_3N_4O$ $[M + H]^+$: 589.0845, found: 589.0853.

7. Experimental procedure for gram scale synthesis of 5aa

A mixture of DIPEA (0.6 mmol, 0.2 equiv.), **1** (4.5 mmol, 1.5 equiv.) and **4** (3.0 mmol, 1.0 equiv.) and dichloromethane (30 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred at 40 °C for the 5 days. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:DCM = 1:2 to 1:3) to afford products **5aa** as a mixture of the major and minor diastereomers of **5aa** in 95% yield (1.26 g).

8. Experimental procedures for synthesis of compound 6



3ax **6**

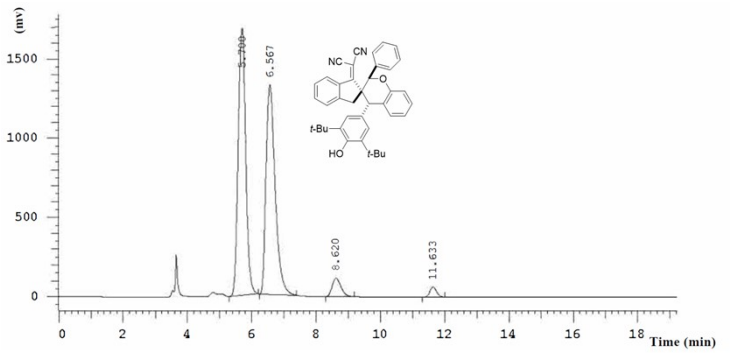
Under a nitrogen atmosphere, $AlCl_3$ (0.5 mmol, 66.5 mg) was added to the solution of **3ax** (0.1 mmol 59.7 mg) in anhydrous toluene (2 mL). Then, the reaction mixture was stirred at 50 °C for 3 hours. Next, another portion of $AlCl_3$ (0.5 mmol, 66.5 mg) was added to the reaction mixture. And the reaction solution was stirred overnight. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was quenched with water (5 mL). Subsequently, the reaction mixture was extracted with ethyl acetate (10 mL) and the organic layer was dried over anhydrous sodium sulfate. The resultant solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent petroleum ether/ethyl acetate = 10:1-5:1) to afford the pure product **6**. R_f = 0.38 (petroleum ether/ethyl acetate = 3:1). Brown solid, 9.7 mg, 20% yield, m.p. 95.5-96.3 °C.^{1}H NMR (500 MHz, DMSO-d_6) δ 10.01 (s, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.58 (dd, J = 7.7, 1.7 Hz, 1H), 7.39-7.31 (m, 2H), 7.30 – 7.21 (m, 4H), 7.12 (td, J = 7.5, 1.2 Hz, 1H), 6.99 (d, J = 8.9 Hz, 1H), 6.92 – 6.90 (m, 2H), 6.87 (t, J = 8.8 Hz, 2H), 5.01 (s, 1H), 4.78 (s, 1H), 3.45 (d, J = 17.1 Hz, 1H), 2.65 (d, J = 16.9 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.2, 161.6 (d, J = 244.2 Hz), 159.8, 156.3, 153.7, 148.9, 135.5, 133.5, 131.9 (d, J = 2.9 Hz), 131.6, 129.9, 129.1, 128.5 (d, J = 8.0 Hz), 127.4, 127.3, 125.4, 124.0, 121.7, 121.6, 116.9, 116.4, 115.0, 114.2 (d, J = 21.3 Hz), 96.3, 72.4, 60.7, 46.0, 35.6. IR (KBr) υ: 762, 830, 998, 1021, 1106, 1164, 1233, 1279, 1380, 1458, 1510, 1550, 1604, 1657, 2215, 2855, 2925, 3440 cm^{-1}. HRMS (ESI, m/z): calculated for $C_{32}H_{22}FN_2O_2$ $[M + H]^+$: 485.1660, found: 485.1661.

9. Experimental procedures for synthesis of compound 7aa

A mixture of chiral catalyst (0.02 mmol, 0.2 equiv.), **1a** (0.10 mmol, 1.0 equiv.) and **2a** (0.10 mmol, 1.0 equiv.) and CH_2Cl_2 (1.0 mL) were added to a sealed reaction tube equipped with a stir bar. The tube was then sealed and the resulting mixture was stirred

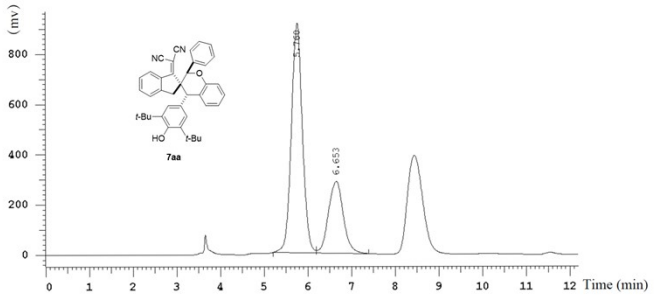
at 25 °C for the 24-120 h. Upon completion (monitored by TLC, visualized by UV light), the reaction solution was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent PE:DCM = 3:1-2:1) to afford pure products **7aa**. Yellow solid. ee as determined by HPLC (Chiralpak IC-H, 99:1 n-hexane/*i*-PrOH, 1.0 mL/min), tr (major) = 5.760 min, tr (minor) = 6.653 min. The ratio of **7aa**-A/**7aa**-B was 0.51:1 as determined by ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$, a mixture of two isomers) δ 8.48 (d, *J* = 8.2 Hz, 1H, isomer A), 7.97 (d, *J* = 8.3 Hz, 1H, isomer B), 7.57 (t, *J* = 7.5 Hz, 1H, isomer A), 7.50 – 7.45 (m, 2H, isomer B), 7.44 (d, *J* = 7.8 Hz, 1H, isomer A), 7.39 (d, *J* = 7.6 Hz, 1H, isomer A), 7.30 – 7.21 (m, 4H, for isomer A and isomer B, overlapped), 7.21 – 7.15 (m, 3H, for isomer A and isomer B, overlapped), 7.04 – 6.96 (m, 3H, for isomer A and isomer B, overlapped), 6.96 – 6.81 (m, 4.5H, for isomer A and isomer B, overlapped), 6.75 (d, *J* = 2.3 Hz, 1H, isomer A), 6.64 (s, 1H, isomer B), 6.47 (d, *J* = 2.2 Hz, 1H, isomer A), 6.19 (s, 1H, isomer B), 6.00 (s, 1H, isomer A), 5.26 (s, 1H, isomer B), 5.21 (S, 1H, isomer A), 4.87 (s, 1H, isomer B), 3.94 (d, *J* = 17.9 Hz, 1H, isomer A), 3.70 (s, 1H, isomer A), 3.66 (s, 1H, isomer B), 3.62 (d, *J* = 18.8 Hz, 1H, isomer B), 3.17 (d, *J* = 18.7 Hz, 1H, isomer B), 2.99 (d, *J* = 18.0 Hz, 1H, isomer A), 1.40 (s, 9H, isomer A), 1.32 – 0.95 (m, 23H, for isomer A and isomer B, overlapped) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, a mixture of two isomers) δ 181.1, 175.0, 154.9, 154.6, 153.9, 153.1, 151.4, 148.5, 136.9, 136.2, 136.2, 136.1, 135.0, 134.8, 134.7, 131.6, 130.4, 129.6, 129.01, 128.9, 128.8, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 127.5, 127.3, 127.0, 126.7, 126.1, 125.4, 124.8, 123.8, 123.7, 121.5, 121.2, 117.0, 116.8, 115.0, 113.8, 113.7, 112.3, 79.9, 79.9, 75.8, 75.2, 59.1, 58.8, 56.2, 52.6, 43.5, 41.2, 34.4, 34.2, 34.1, 30.2, 30.1, 30.0.

HPLC chromatogram of compound 7aa (Chiralpak IC-H, 99:1 n-hexane/i-PrOH, 1.0 mL/min**):**
Racemic:



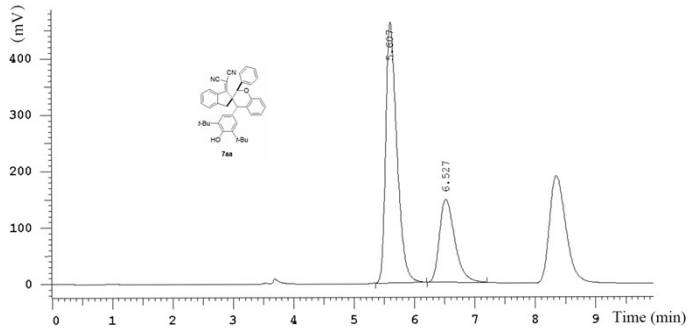
No.	RT	Area	Relative Area (%)
1	5.700	27855362	48.813
2	6.567	26061765	45.670
3	8.620	2232912	3.913
4	11.633	915582	1.604
		57065621	100.000

Enantioselective (A as a catalyst):



No.	RT	Area	Relative Area (%)
1	5.760	15992277	70.132
2	6.653	6810984	29.868
		22803261	100.000

Enantioselective (B as a catalyst):



No.	RT	Area	Relative Area (%)
1	5.607	5914112	69.326
2	6.527	2616724	30.674
		8530836	100.000

10. X-ray crystal structure of compound 3ar

Preparation of the single crystals of **3ar**: pure compound **3ar** (30 mg) was completely dissolved in the solvents of petroleum ether and DCM (20 mL, v/v = 1:2) at 2-8 °C. The bottle was sealed by a parafilm with several tiny holes, allowing slow evaporation of the solvents at room temperature. After a week, several small particles could be observed on the wall and at the bottom of the bottle. Then, the crystals were chosen and subjected to the crystal X-ray diffraction analysis for the determination of the structure of **3ar**. The crystal was kept at 296 K during data collection.

The relative configuration of product **3ar** was determined by X-ray diffraction on Bruker D8 VENTURE PHOTON II diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) at 284(2) K using SAINT and SMART programs. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2270813). Crystallographic data and structure refinements for compound **3ar** are listed in Table S2.

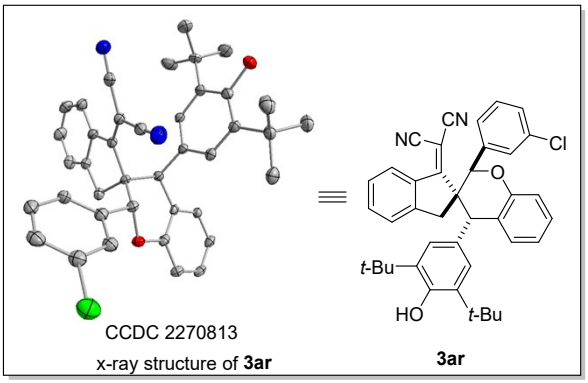


Figure S1. View of a molecule of compound **3ar** with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table S3. Crystal data and structure refinement for compound **3ar**.

Crystal data	**3ar**
Empirical formula	$C_{40}H_{37}ClN_2O_2$
Formula weight	613.33
Temperature/K	296
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.946(5)
b/Å	32.16(2)
c/Å	11.104(6)

α/°	90
β/°	110.730(16)
γ/°	90
Volume/Å^3	3322(3)
Z	1
ρ_{calc}g/cm^3	1.226
μ/mm^{-1}	0.152
F(000)	1296.0
Crystal size/mm^3	0.16 × 0.13 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.122 to 56.928
Index ranges	-12 ≤ h ≤ 12, -39 ≤ k ≤ 34, -13 ≤ l ≤ 13
Reflections collected	26901
Independent reflections	6529 [R_{int} = 0.2271, R_{sigma} = 0.2093]
Data/restraints/parameters	6529/0/414
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0863, wR_2 = 0.1941
Final R indexes [all data]	R_1 = 0.2231, wR_2 = 0.2777
Largest diff. peak/hole / e Å^{-3}	1.08/-0.38

11. X-ray crystal structure of compound 3ab'

Preparation of the single crystals of **3ab'**: pure compound **3ab'** (15 mg) was completely dissolved in the solvents of petroleum ether and DCM (15 mL, v/v = 1:2) at room temperature. The bottle was sealed by a parafilm with several tiny holes, allowing slow evaporation of the solvents at room temperature. After a week, several small particles could be observed on the wall and at the bottom of the bottle. Then, the crystals were chosen and subjected to the crystal X-ray diffraction analysis for the determination of the structure of **3ab'**. The crystal was kept at 100 K during data collection.

The relative configuration of product **3ab'** was determined by X-ray diffraction on a Bruker APEX DUO system. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2268414). Crystallographic data and structure refinements for compound **3ab'** are listed in Table S3.

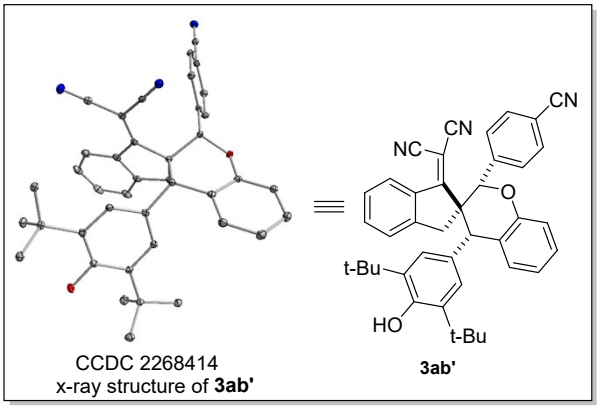


Figure S2. View of a molecule of **3ab'** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.

Table S4. Crystal data and structure refinement for **3ab'**.

Identification code	global	
Empirical formula	C41 H37 N3 O2	
Formula weight	603.73	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.8858(2) Å	α= 90.7900(10)°.
	b = 12.1164(2) Å	β= 90.4010(10)°.
	c = 12.8017(3) Å	γ = 108.7490(10)°.
Volume	1598.63(6) $Å^3$	
Z	2	
Density (calculated)	1.254 Mg/m^3	
Absorption coefficient	0.605 mm^{-1}	
F(000)	640	
Crystal size	0.240 x 0.190 x 0.060 mm^3	
Theta range for data collection	3.45 to 70.18°.	
Index ranges	-11<=h<=13, -14<=k<=14, -15<=l<=15	
Reflections collected	29426	
Independent reflections	6084 [R(int) = 0.0537]	
Completeness to theta = 70.18°	99.7 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.96 and 0.74
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6084 / 0 / 422
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0414, wR2 = 0.1120
R indices (all data)	R1 = 0.0469, wR2 = 0.1157
Largest diff. peak and hole	0.357 and -0.337 e.$Å^{-3}$

12. X-ray crystal structure of compound 5aa

Preparation of the single crystals of **5aa**: pure compound **5aa** (10 mg) was completely dissolved in the solvents of petroleum ether and DCM (20 mL, v/v = 1:3) at room temperature. The bottle was sealed by a parafilm with several tiny holes, allowing slow evaporation of the solvents at room temperature. After a week, several small particles could be observed on the wall and at the bottom of the bottle. Then, the crystals were chosen and subjected to the crystal X-ray diffraction analysis for the determination of the structure of **5aa**. The crystal was kept at 150.01 K during data collection.

The relative configuration of product **5aa** was determined by X-ray diffraction on a Bruker D8 VENTURE PHOTON II diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) at 284(2) K using SAINT and SMART programs. The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2268375). Crystallographic data and structure refinements for compound **5aa** are listed in Table S4.

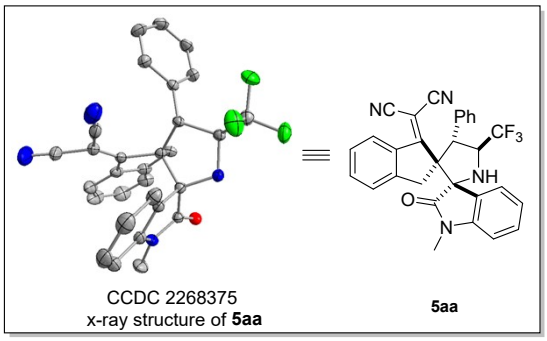


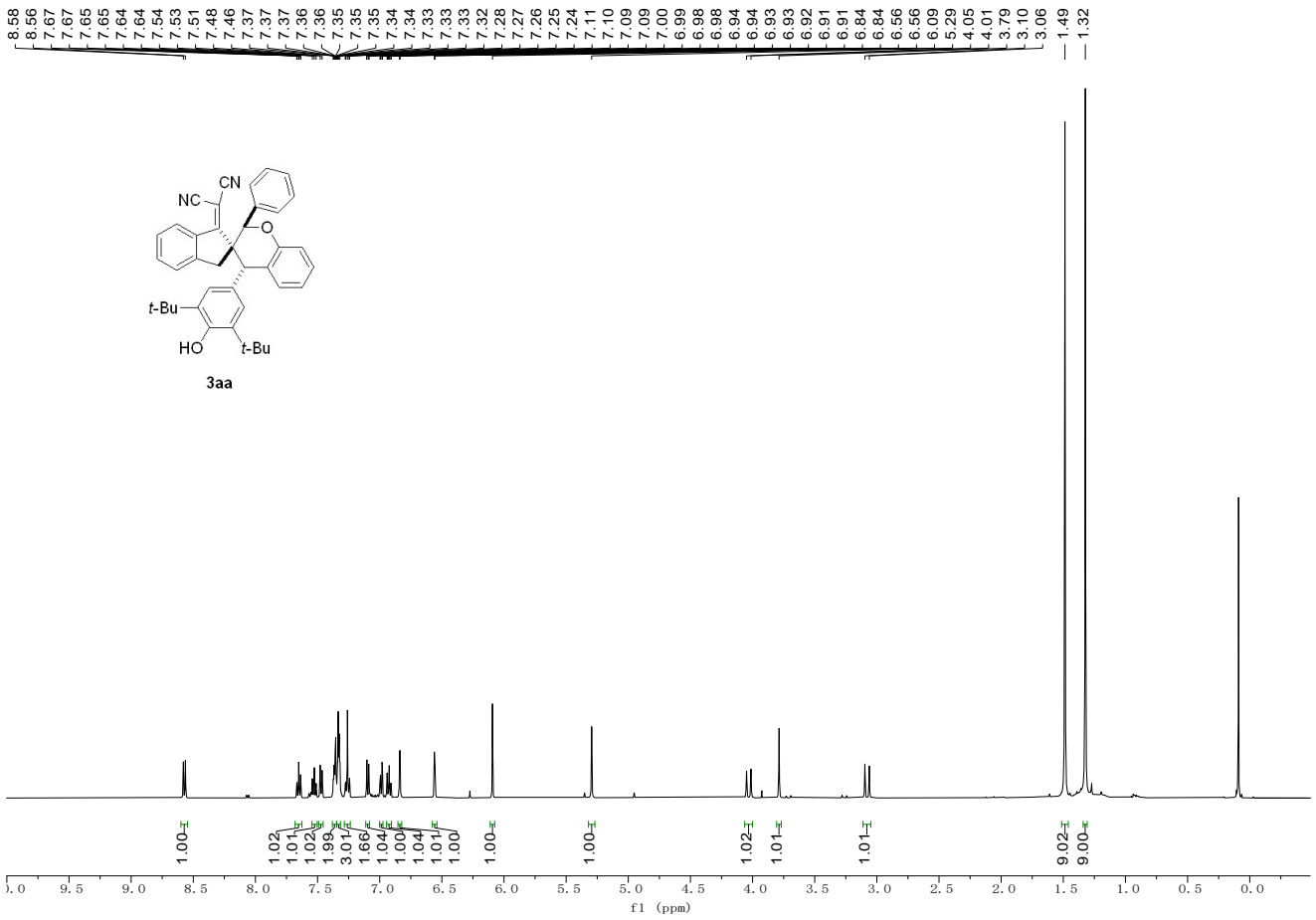
Figure S3. View of a molecule of **5aa** with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table S5. Crystal data and structure refinement for **5aa**.

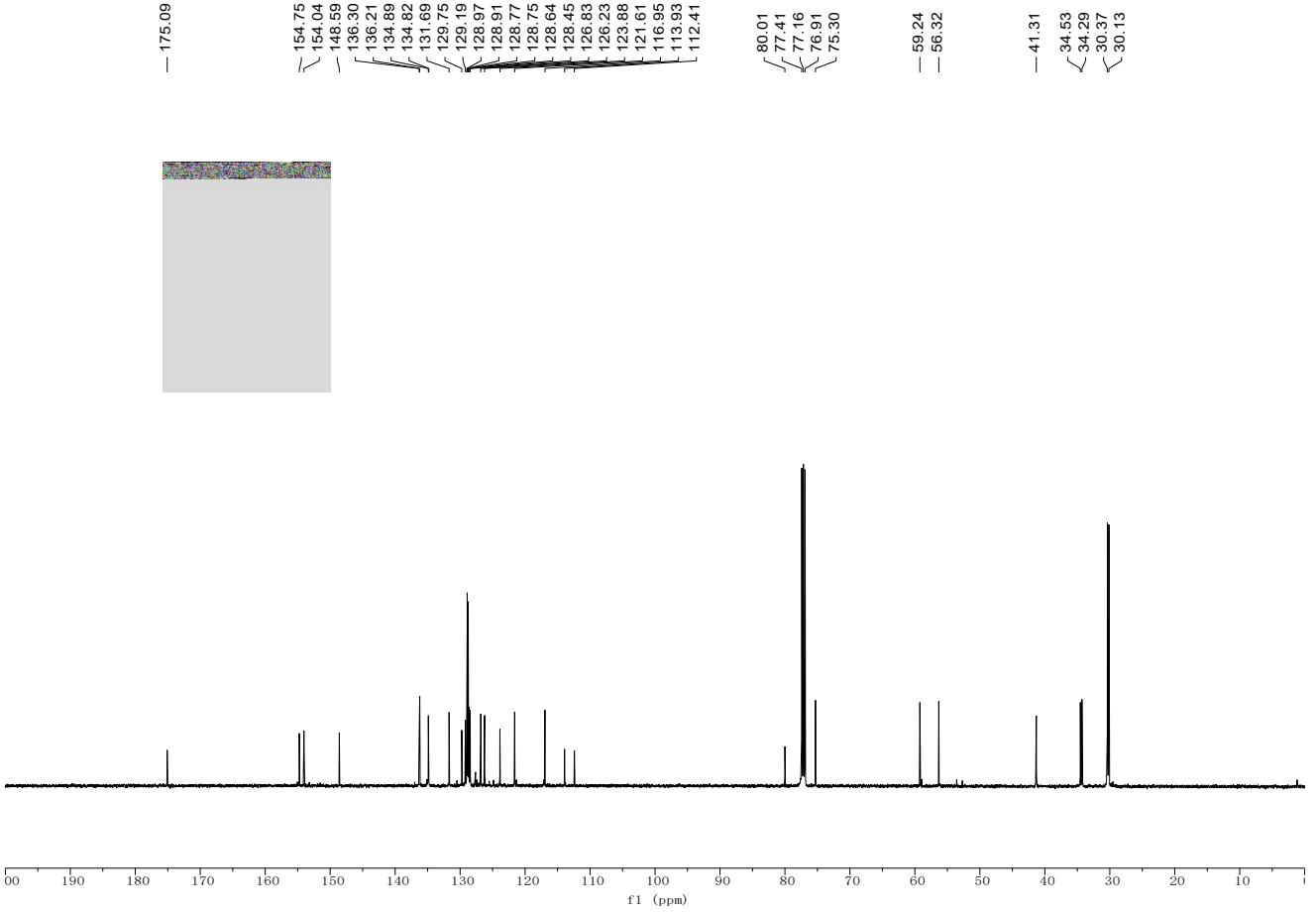
Identification code	**5aa**
Empirical formula	$C_{120}H_{84}F_{12}N_{16}O_4$
Formula weight	2046.06
Temperature/K	150.01
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.7949(5)
b/Å	10.0157(4)
c/Å	20.5833(11)
α/°	90
β/°	90.996(2)
γ/°	90
Volume/Å^3	2431.22(19)
Z	1
ρ_{calc}g/cm^3	1.397
μ/mm^{-1}	0.103
F(000)	1060.0
Crystal size/mm^3	0.16 × 0.12 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.522 to 56.646
Index ranges	$-15 \leq h \leq 15$, $-13 \leq k \leq 13$, $-27 \leq l \leq 25$
Reflections collected	26603
Independent reflections	6050 [R_{int} = 0.0945, R_{sigma} = 0.0835]
Data/restraints/parameters	6050/0/344
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0616, wR_2 = 0.1212
Final R indexes [all data]	R_1 = 0.1268, wR_2 = 0.1525
Largest diff. peak/hole / e Å^{-3}	0.60/-0.58

13. NMR spectra

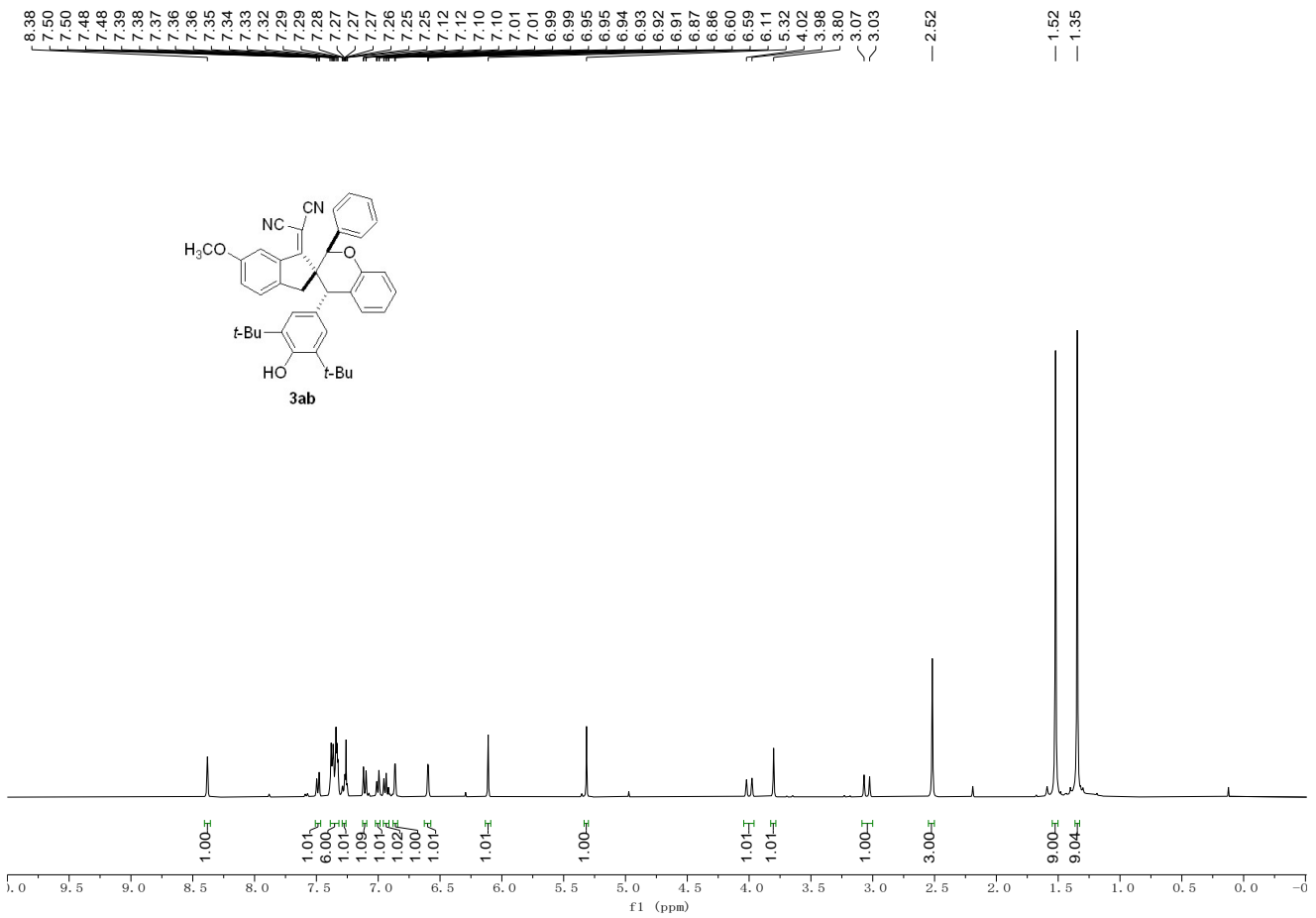
^{1}H NMR spectra for compound **3aa** (500 Hz, $CDCl_3$)



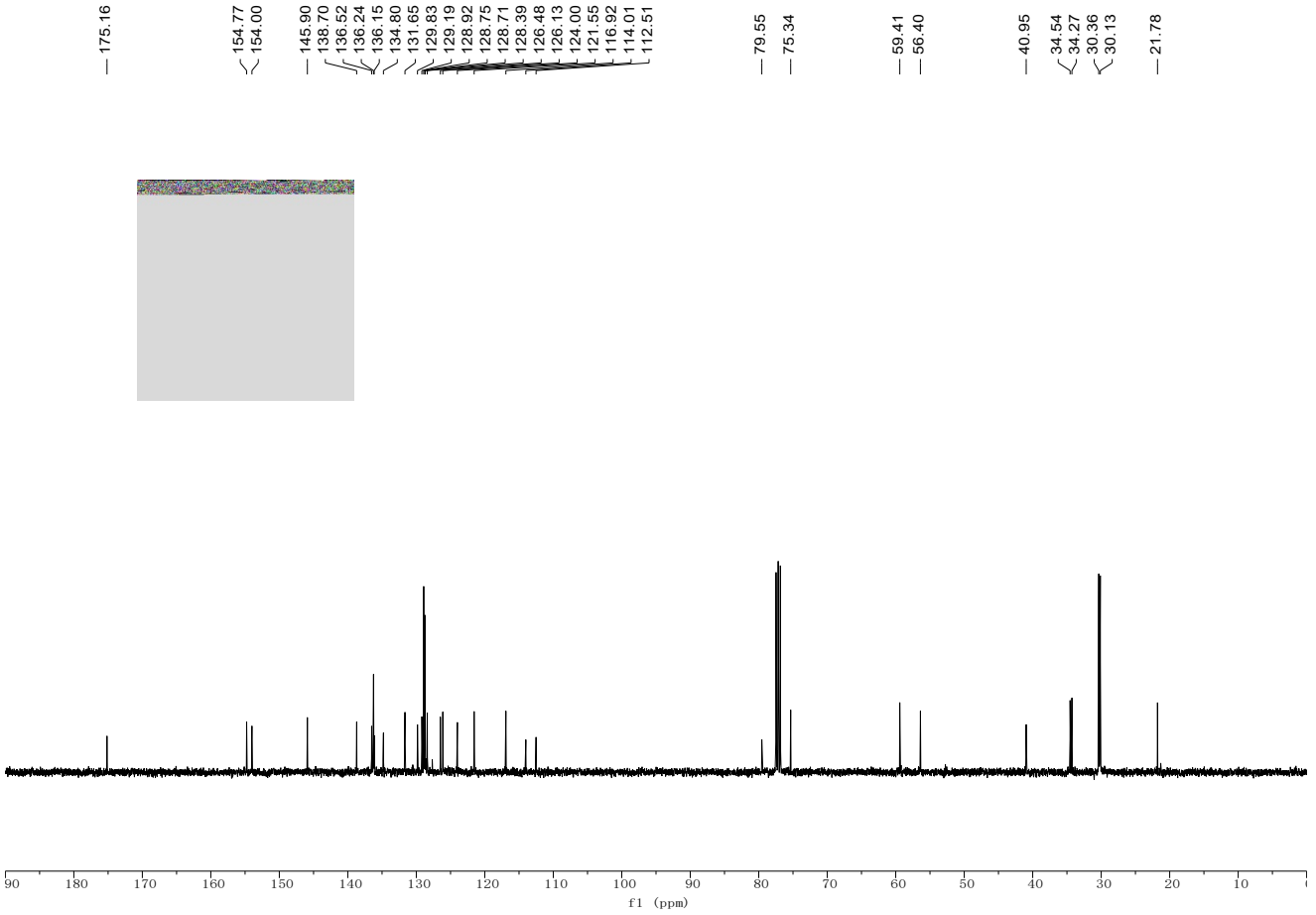
^{13}C NMR spectra for compound **3aa** (125 Hz, $CDCl_3$)



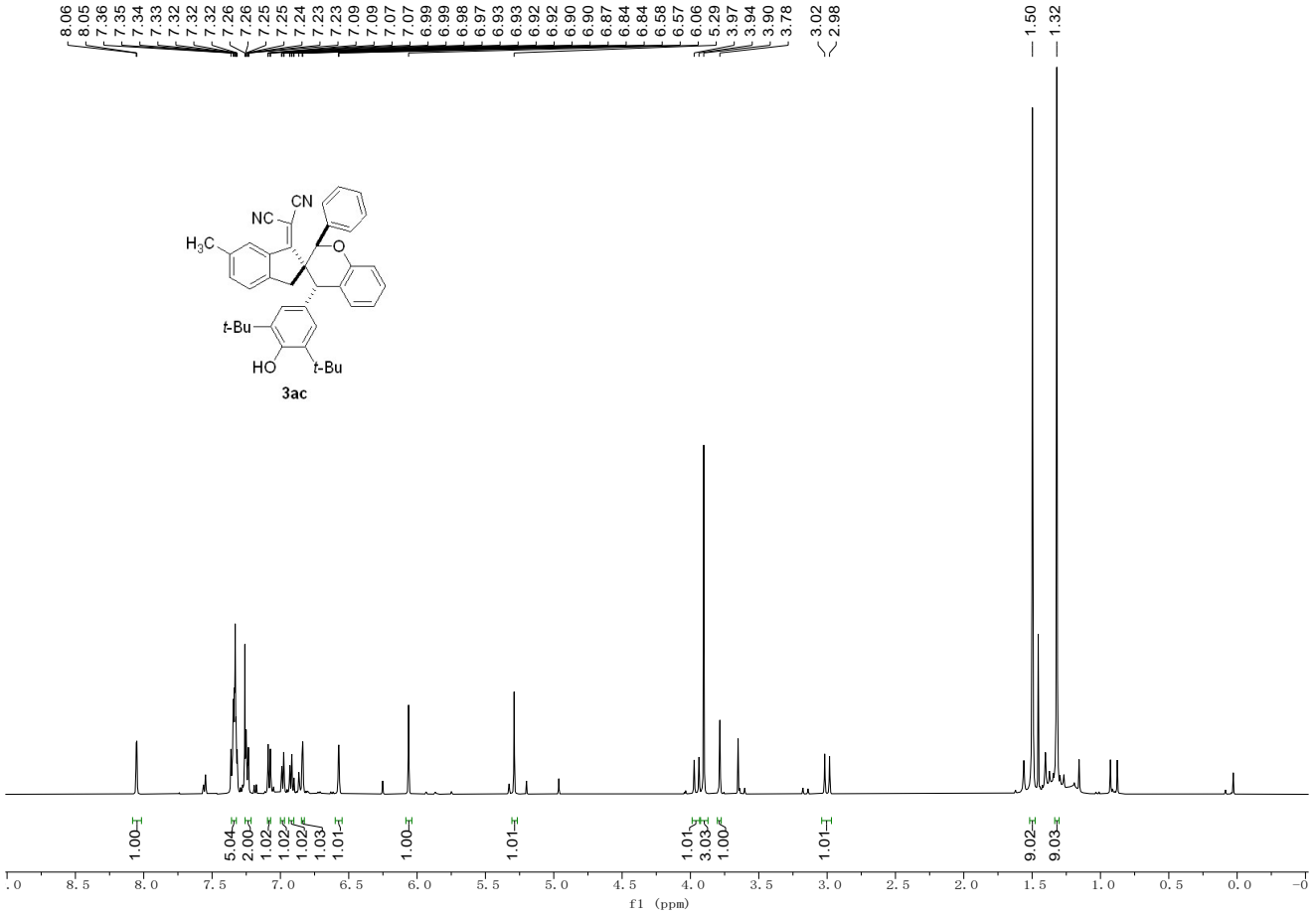
^{1}H NMR spectra for compound **3ab** (500 Hz, $CDCl_3$)



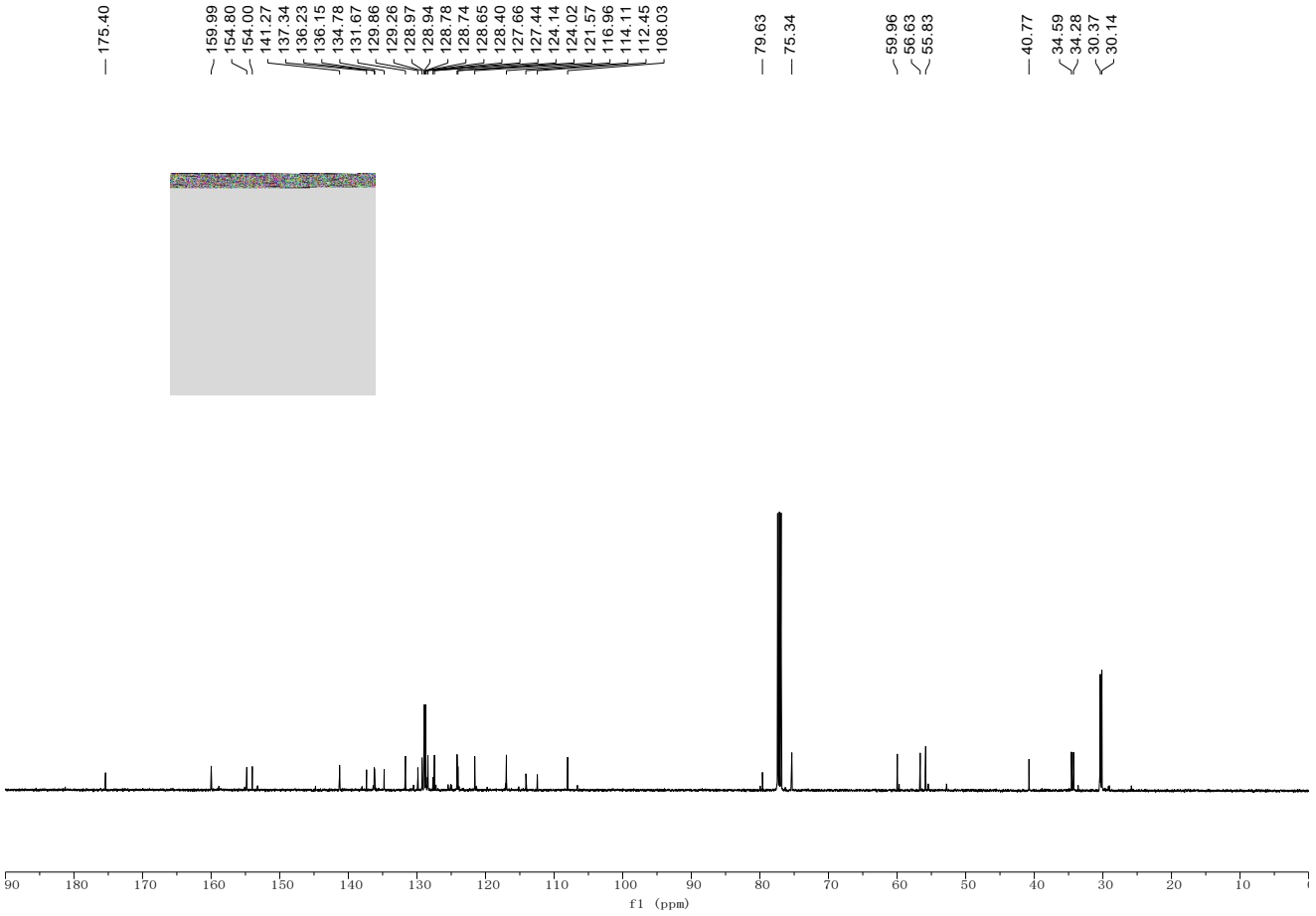
^{13}C NMR spectra for compound **3ab** (125 Hz, $CDCl_3$)



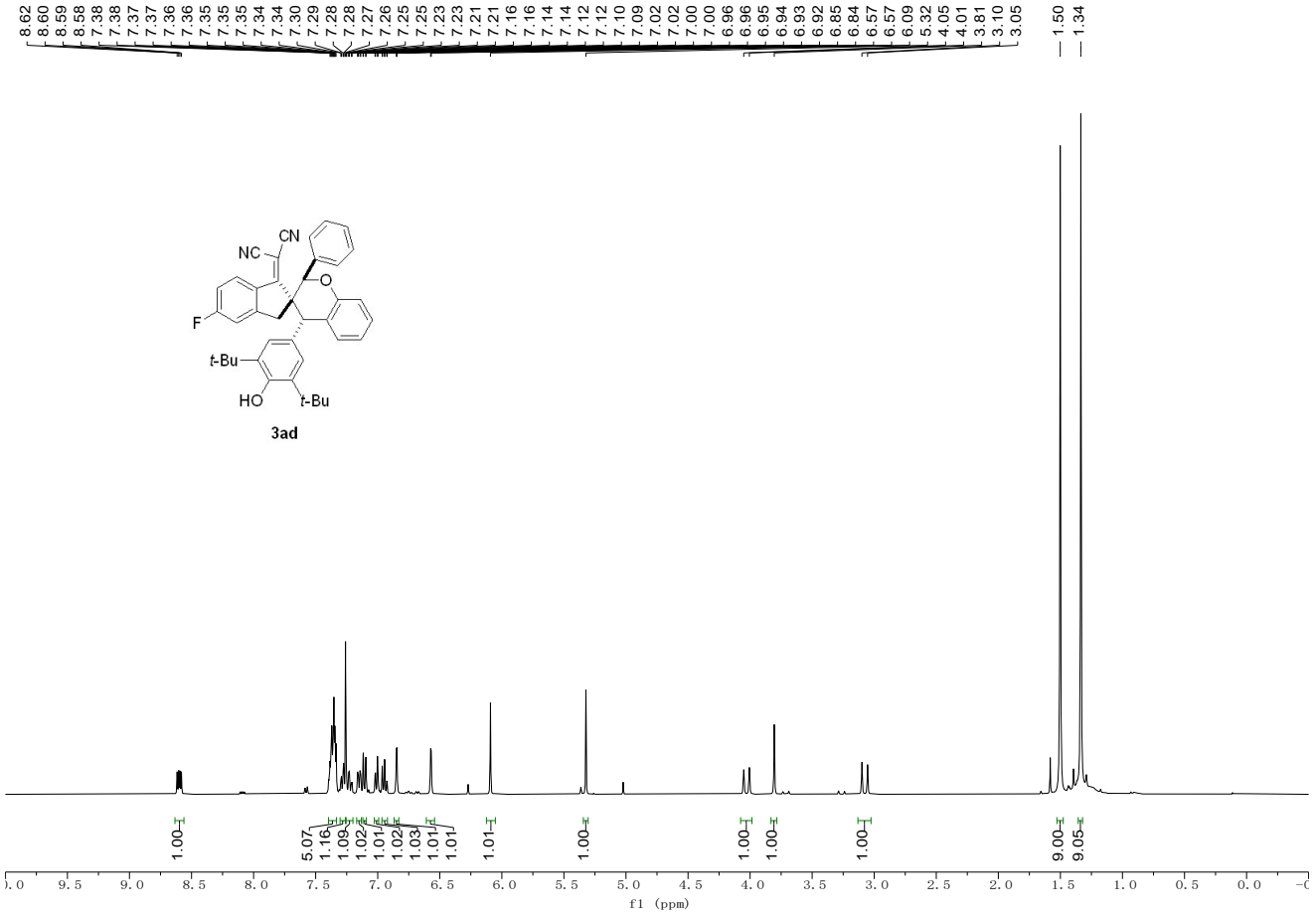
^{1}H NMR spectra for compound **3ac** (400 Hz, $CDCl_3$)



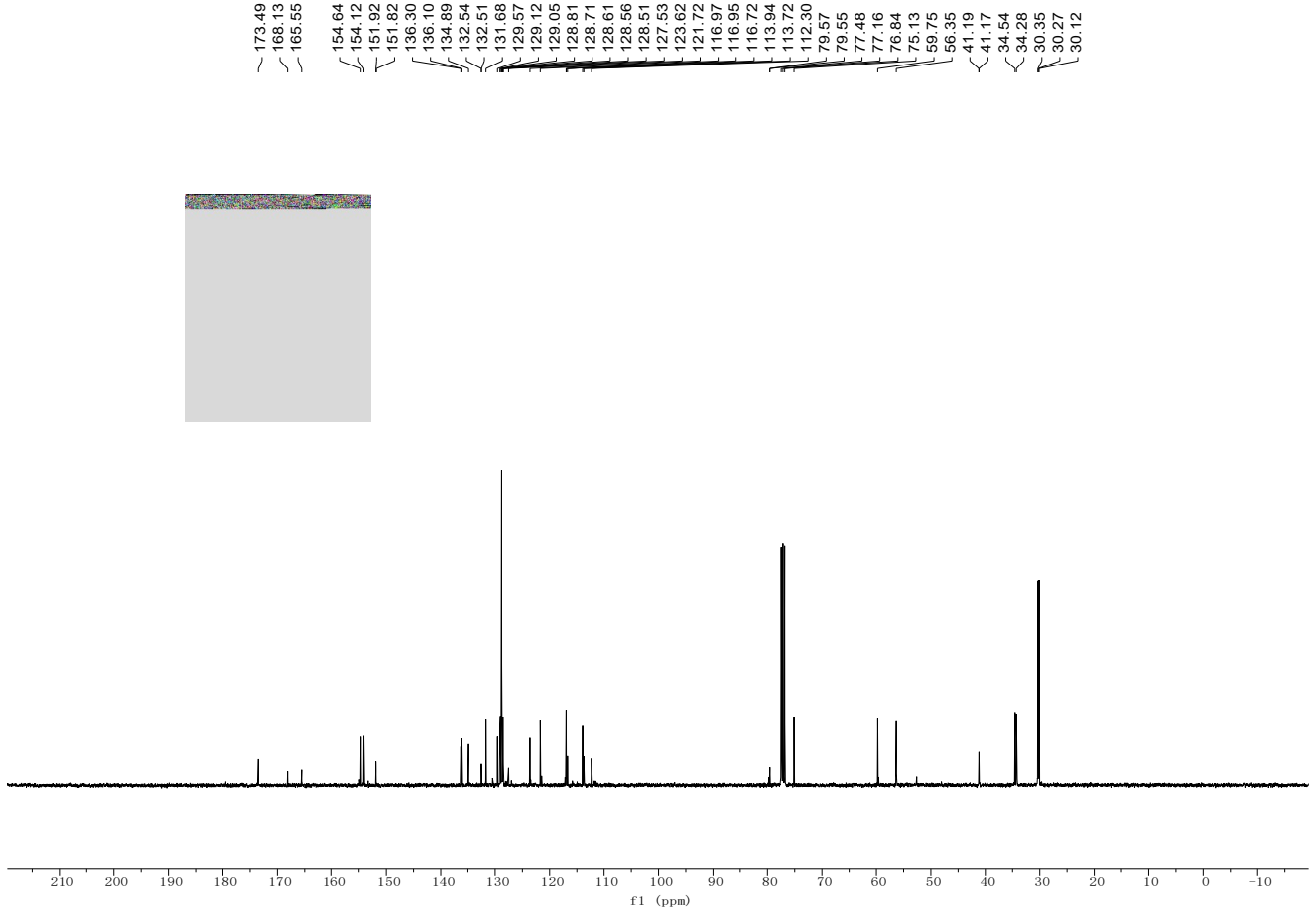
^{13}C NMR spectra for compound **3ac** (100 Hz, $CDCl_3$)



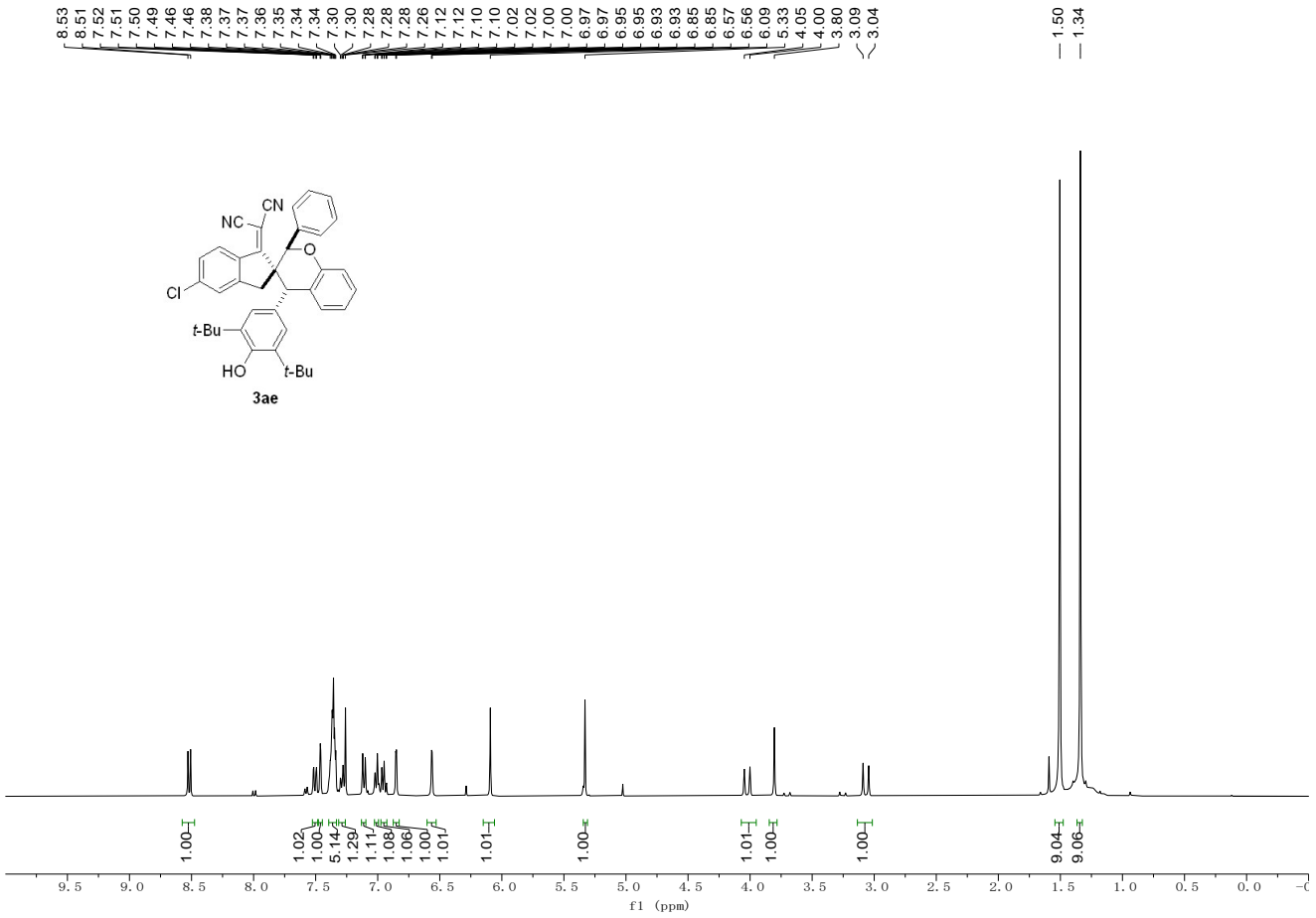
^{1}H NMR spectra for compound **3ad** (400 Hz, $CDCl_3$)



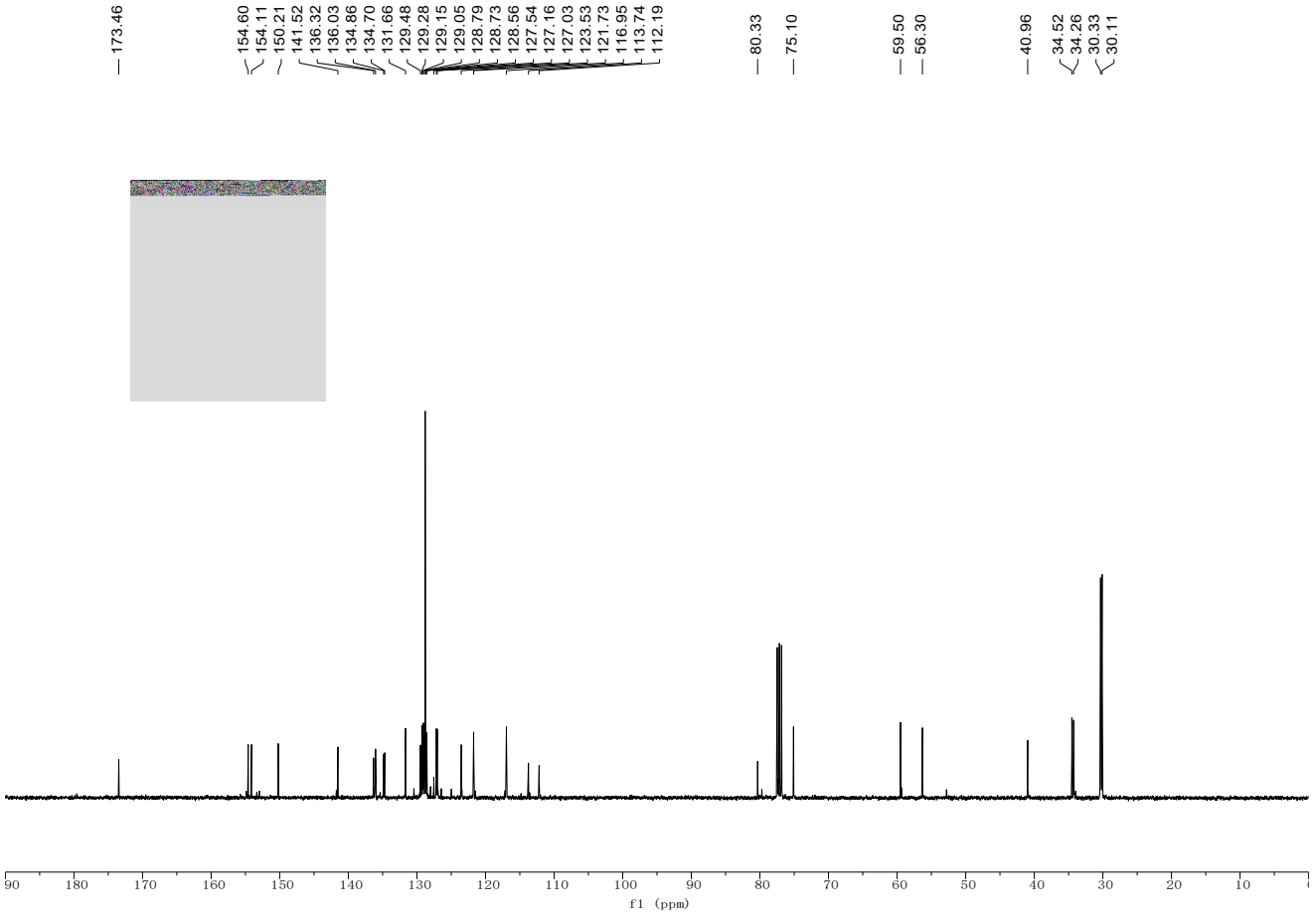
^{13}C NMR spectra for compound **3ad** (100 Hz, $CDCl_3$)



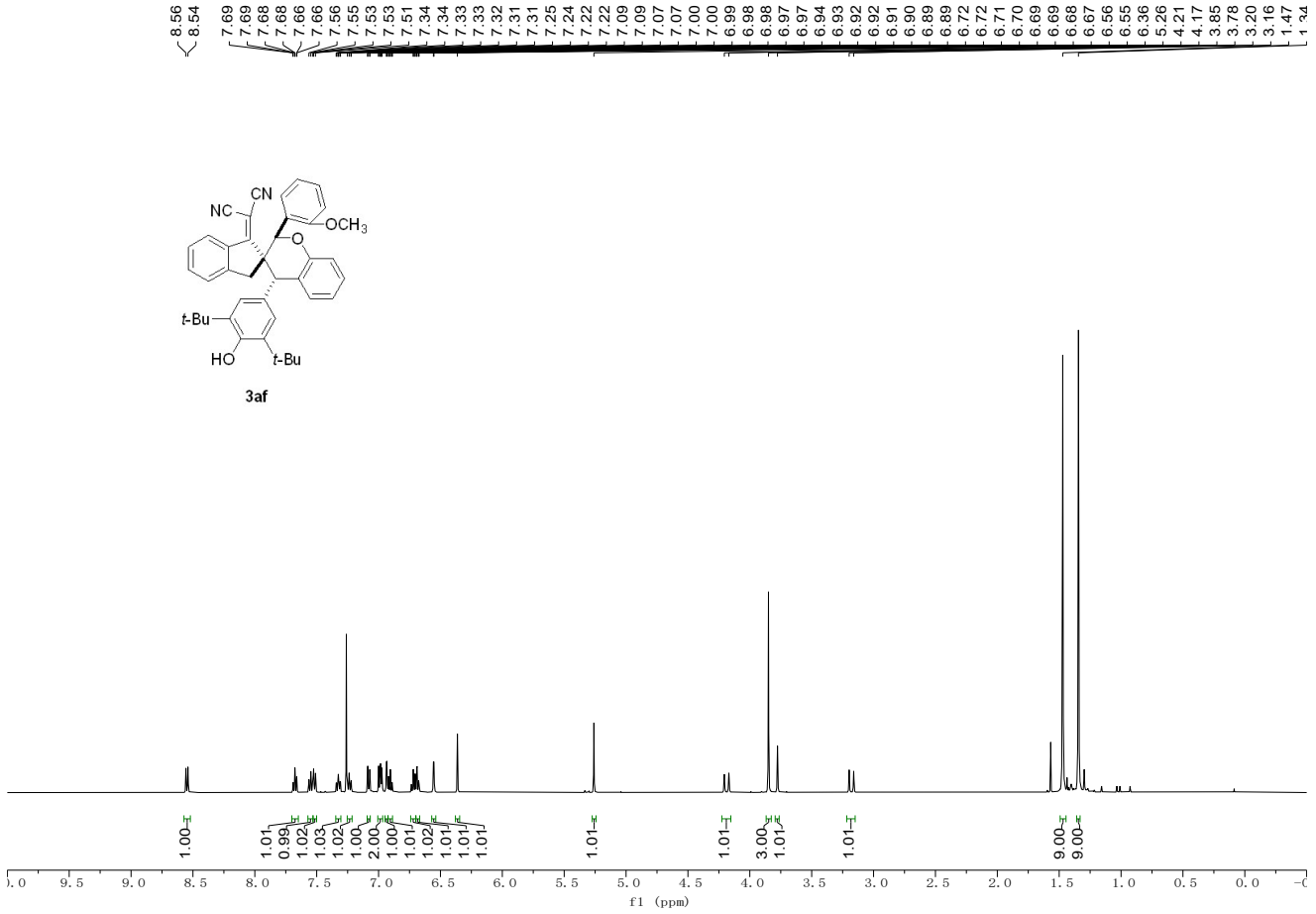
^{1}H NMR spectra for compound **3ae** (400 Hz, $CDCl_3$)



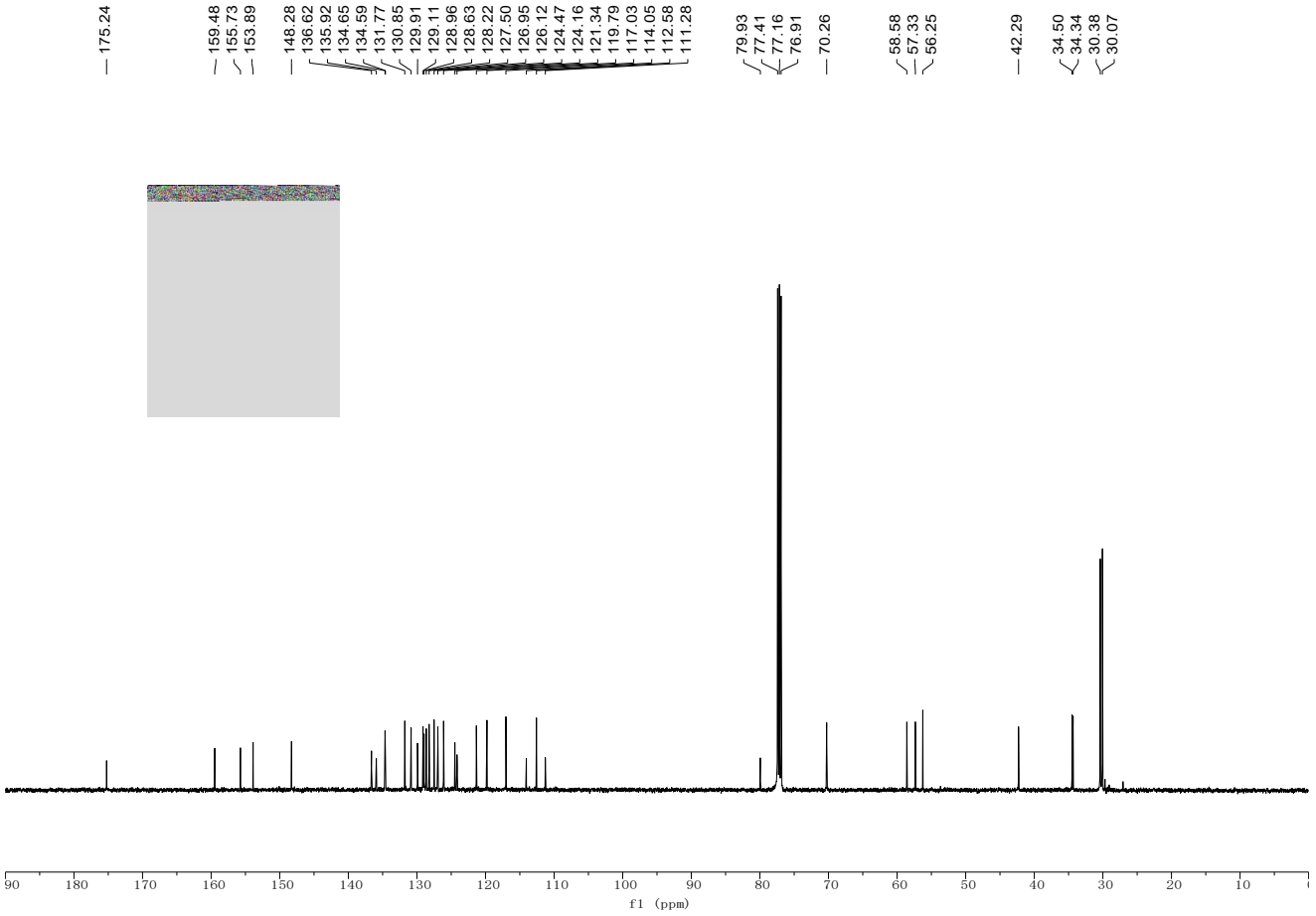
^{13}C NMR spectra for compound **3ae** (100 Hz, $CDCl_3$)



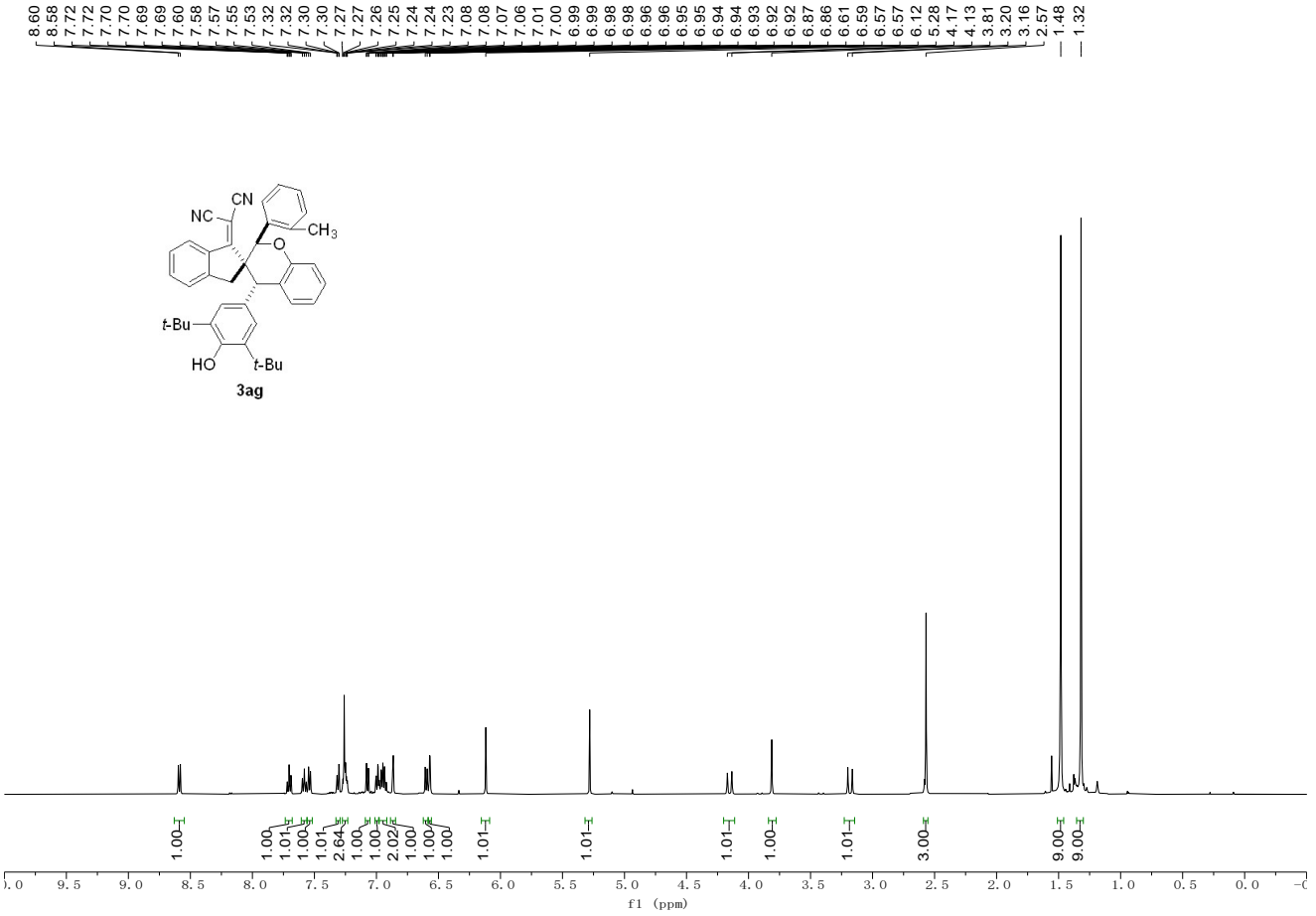
^{1}H NMR spectra for compound **3af** (500 Hz, $CDCl_3$)



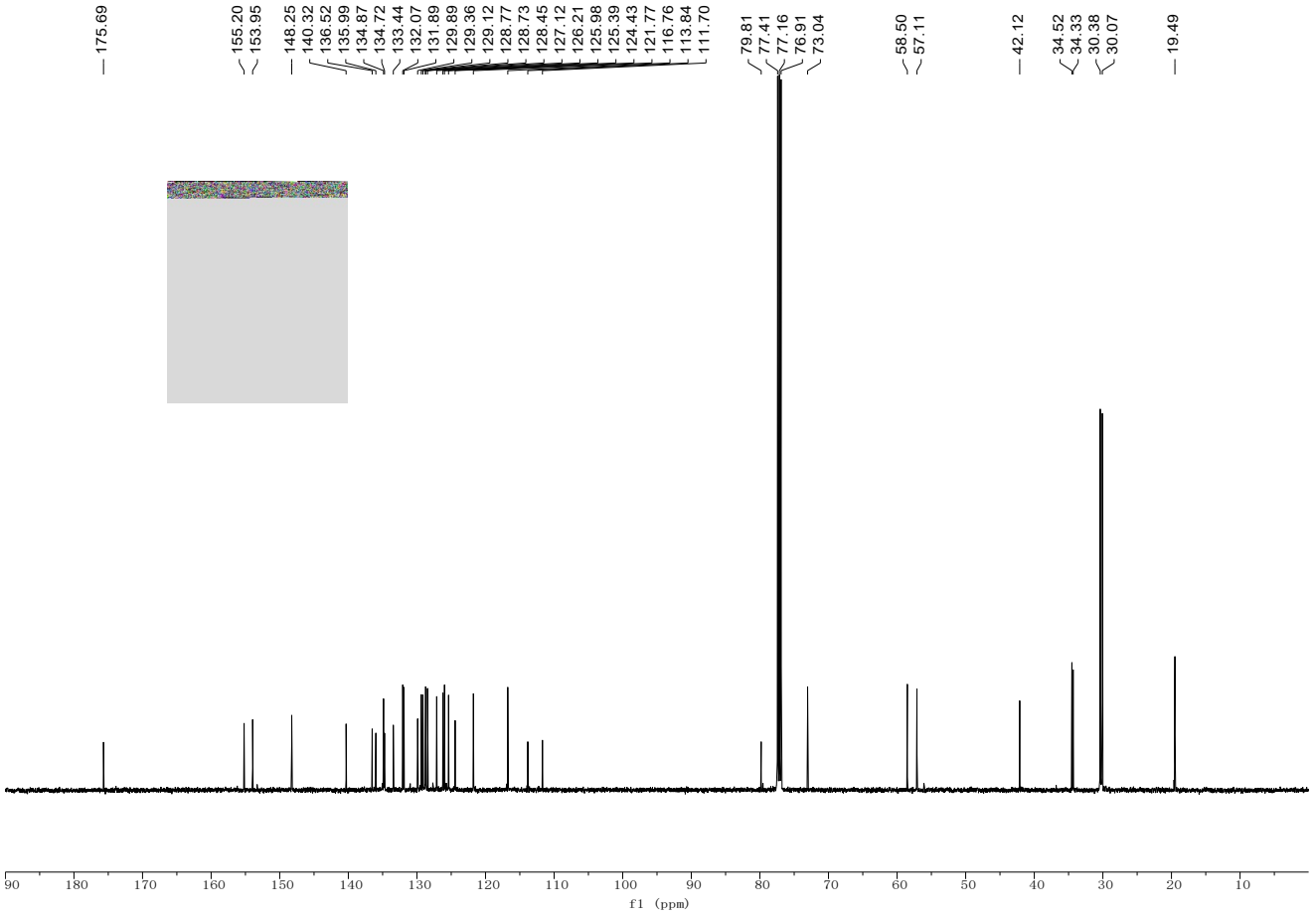
^{13}C NMR spectra for compound **3af** (125 Hz, $CDCl_3$)



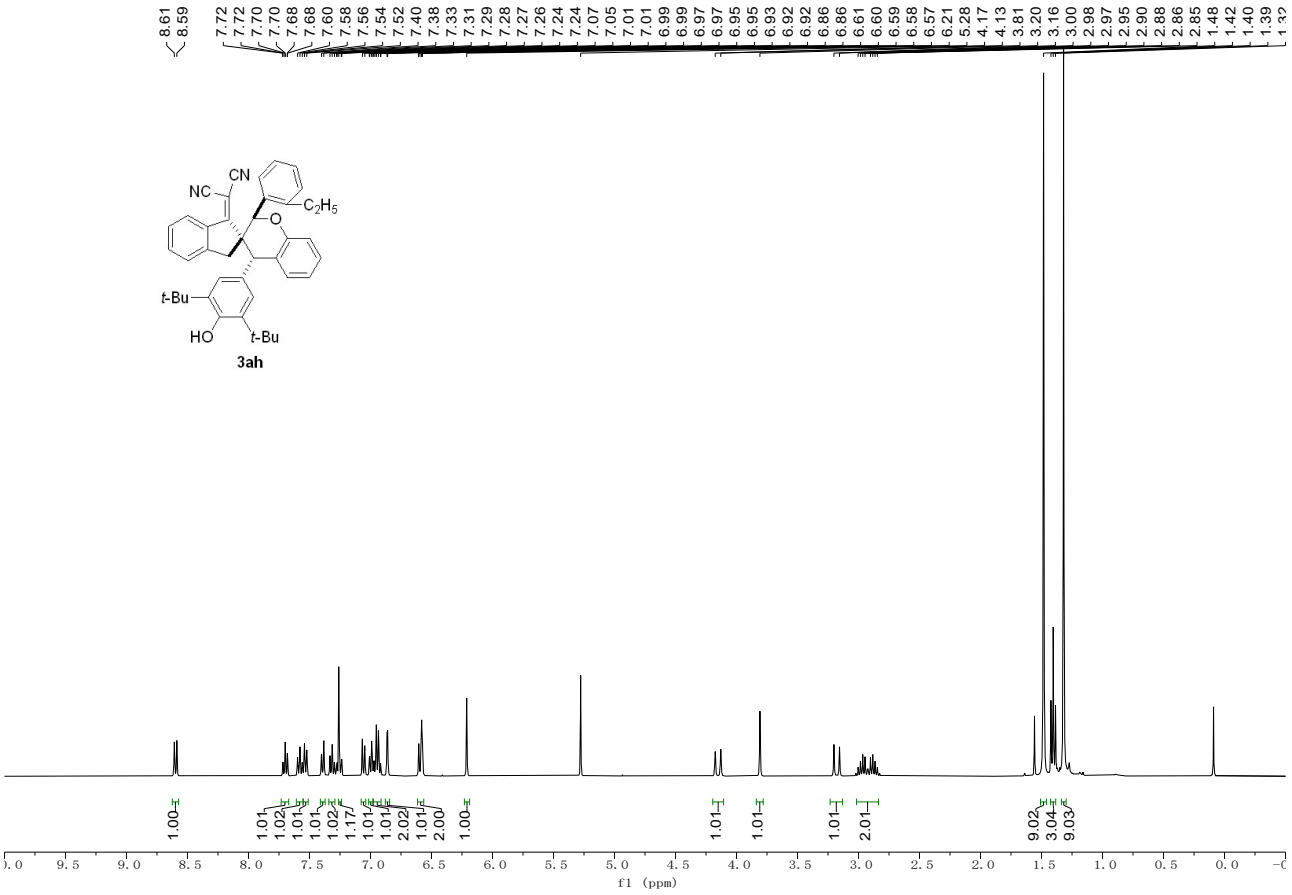
^{1}H NMR spectra for compound **3ag** (500 Hz, $CDCl_3$)



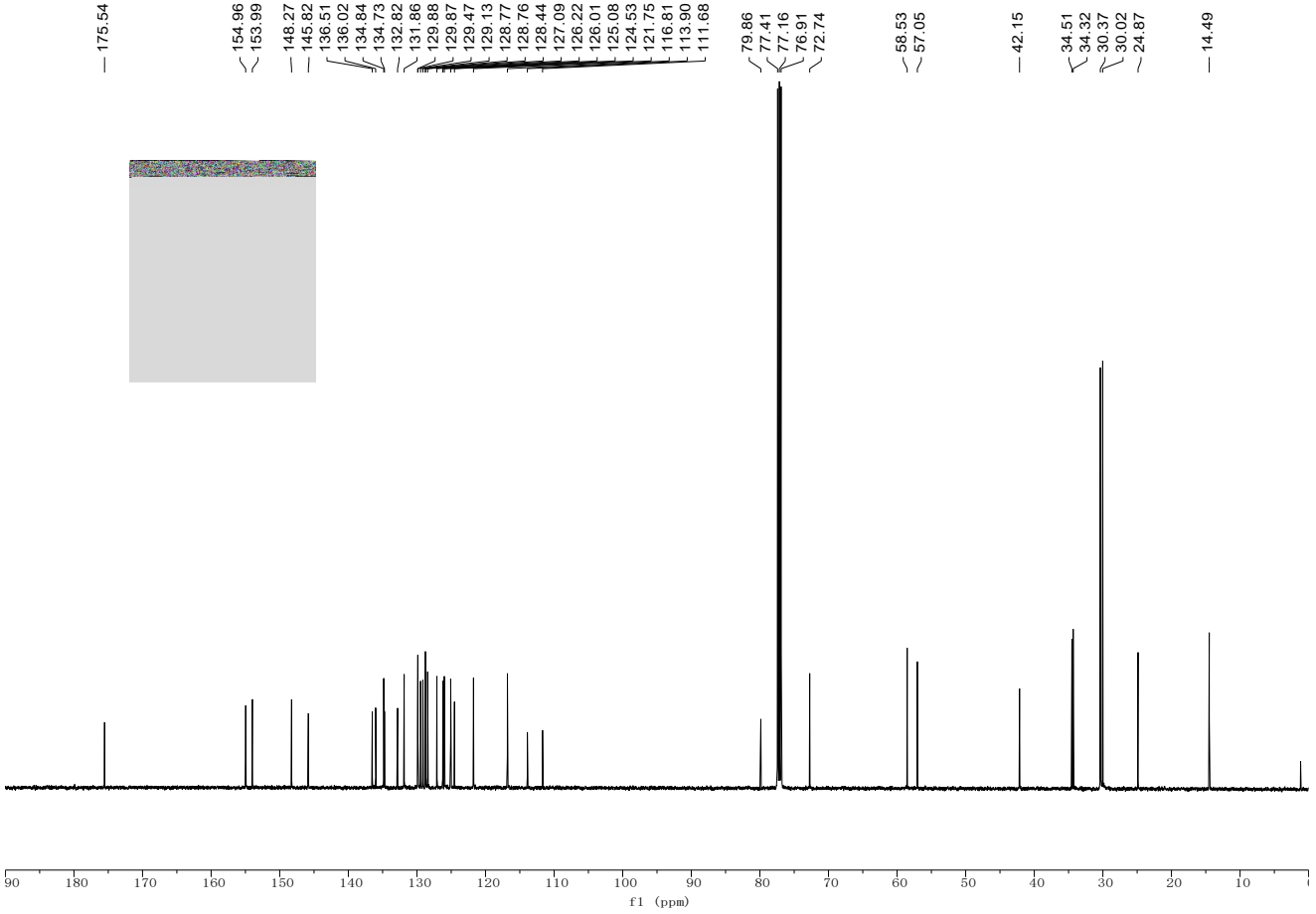
^{13}C NMR spectra for compound **3ag** (125 Hz, $CDCl_3$)



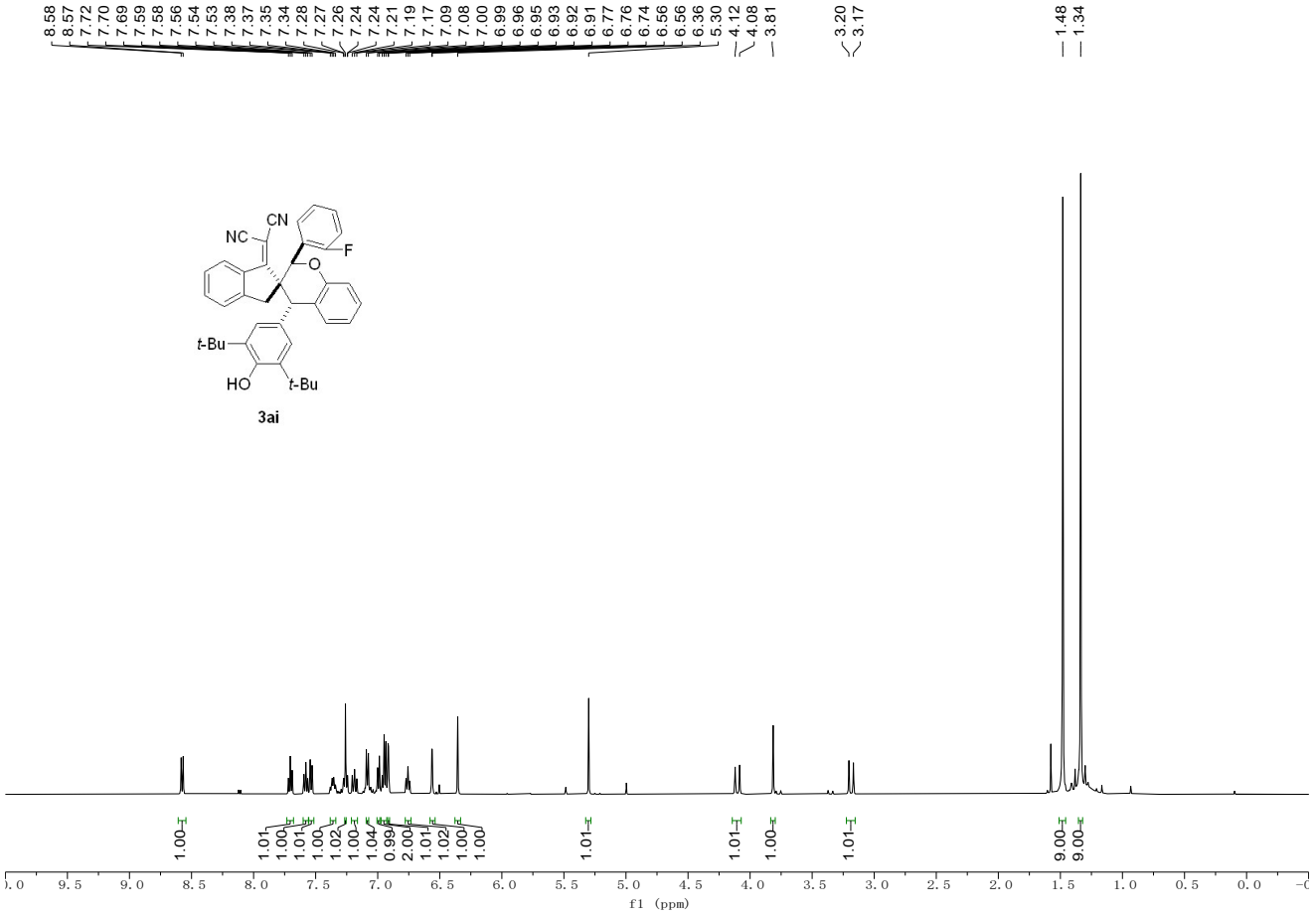
^{1}H NMR spectra for compound **3ah** (400 Hz, $CDCl_3$)



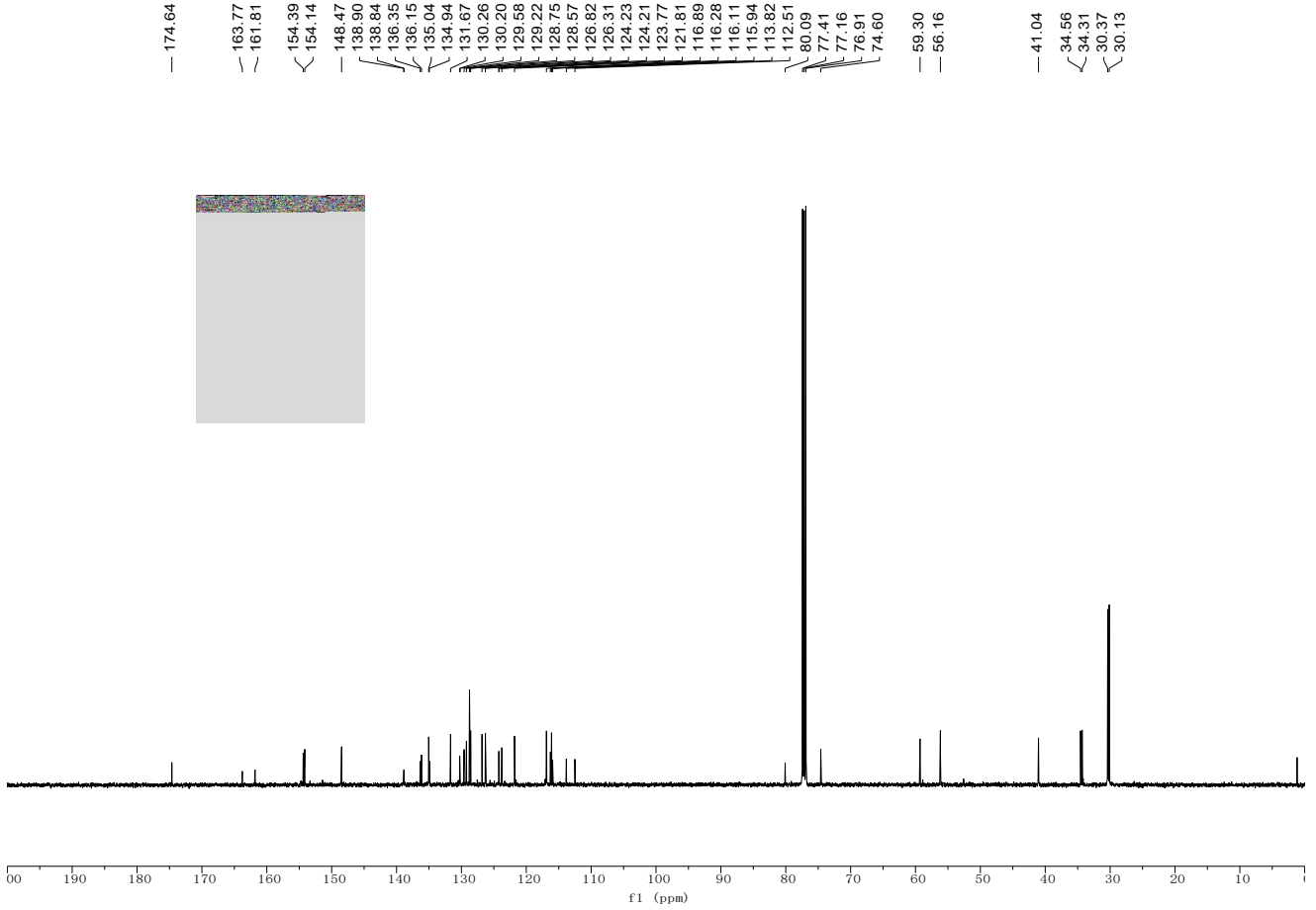
^{13}C NMR spectra for compound **3ah** (125 Hz, $CDCl_3$)



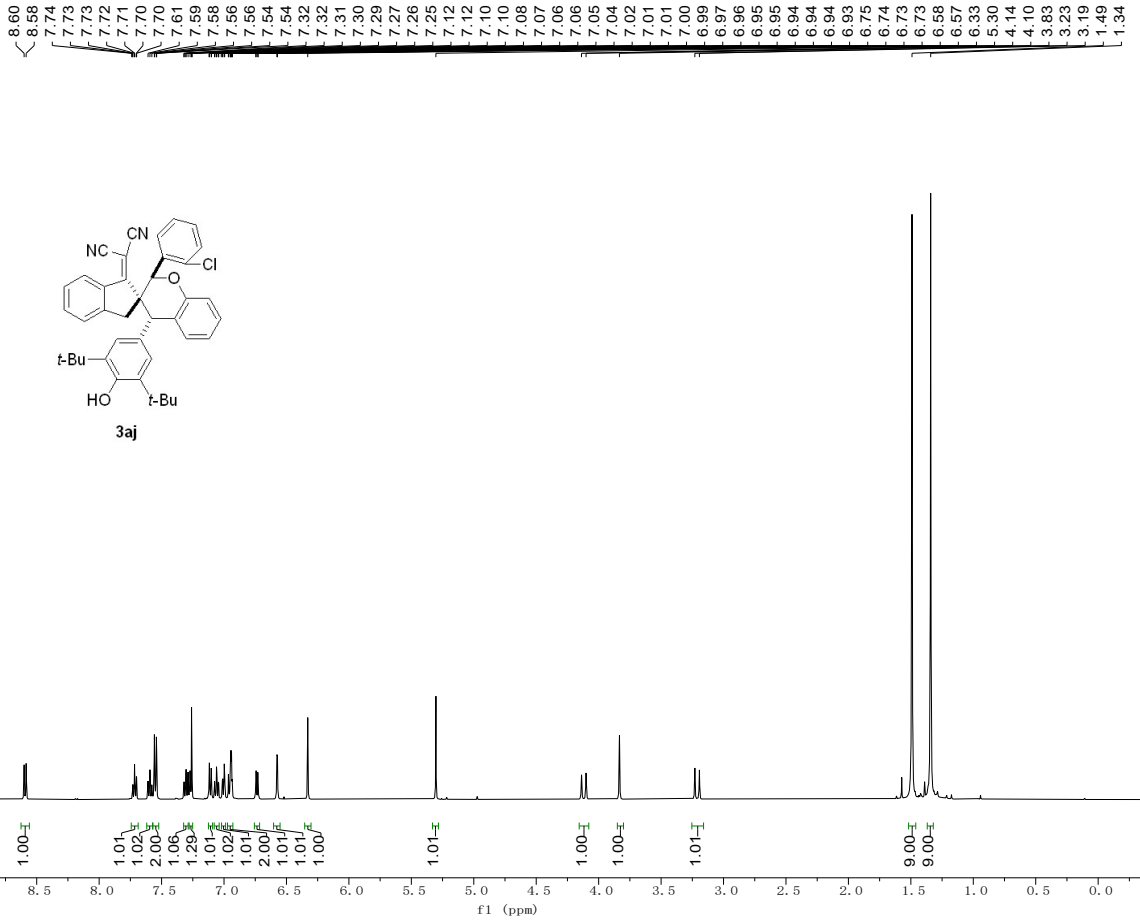
^{1}H NMR spectra for compound **3ai** (500 Hz, $CDCl_3$)



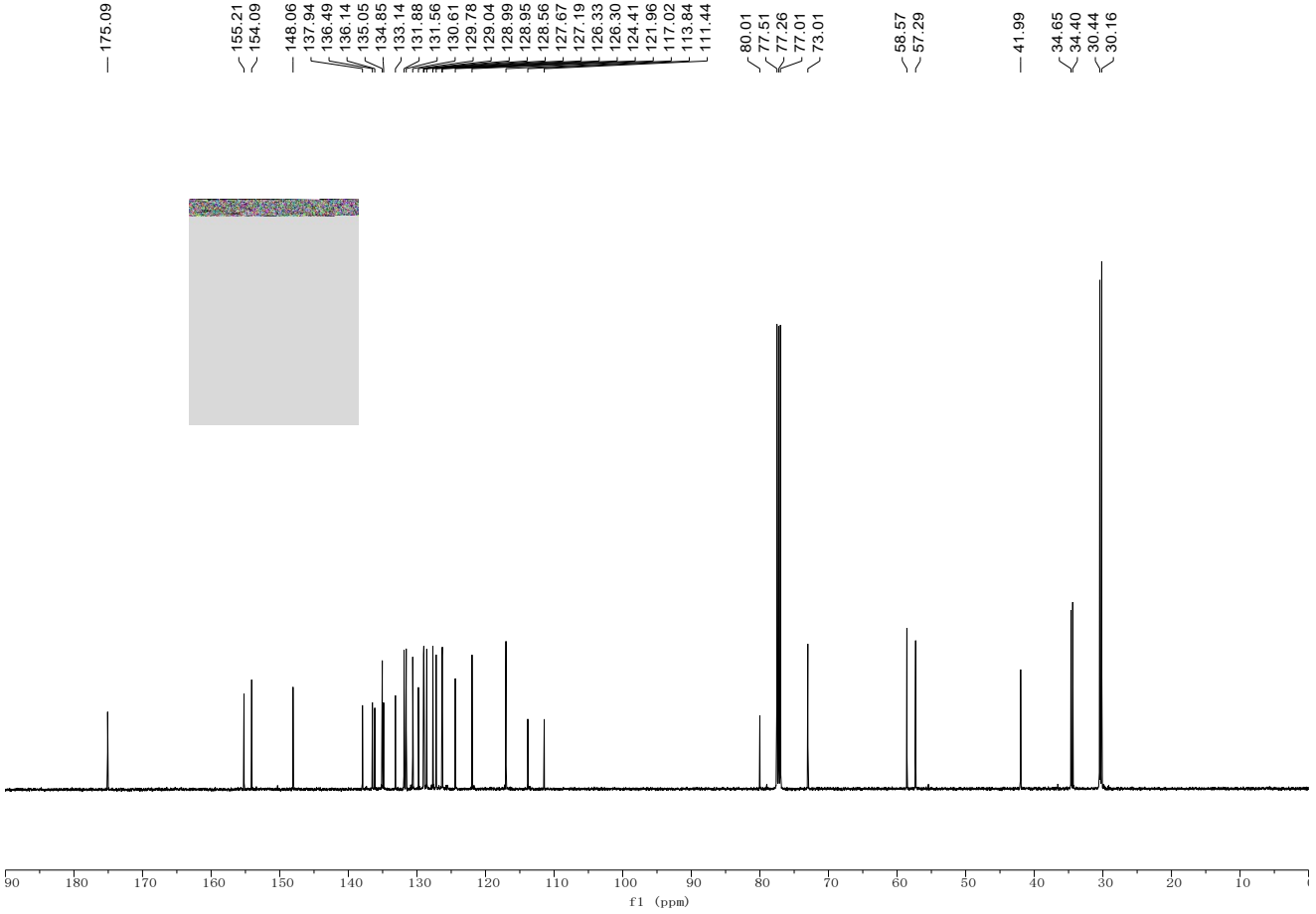
^{13}C NMR spectra for compound **3ai** (125 Hz, $CDCl_3$)



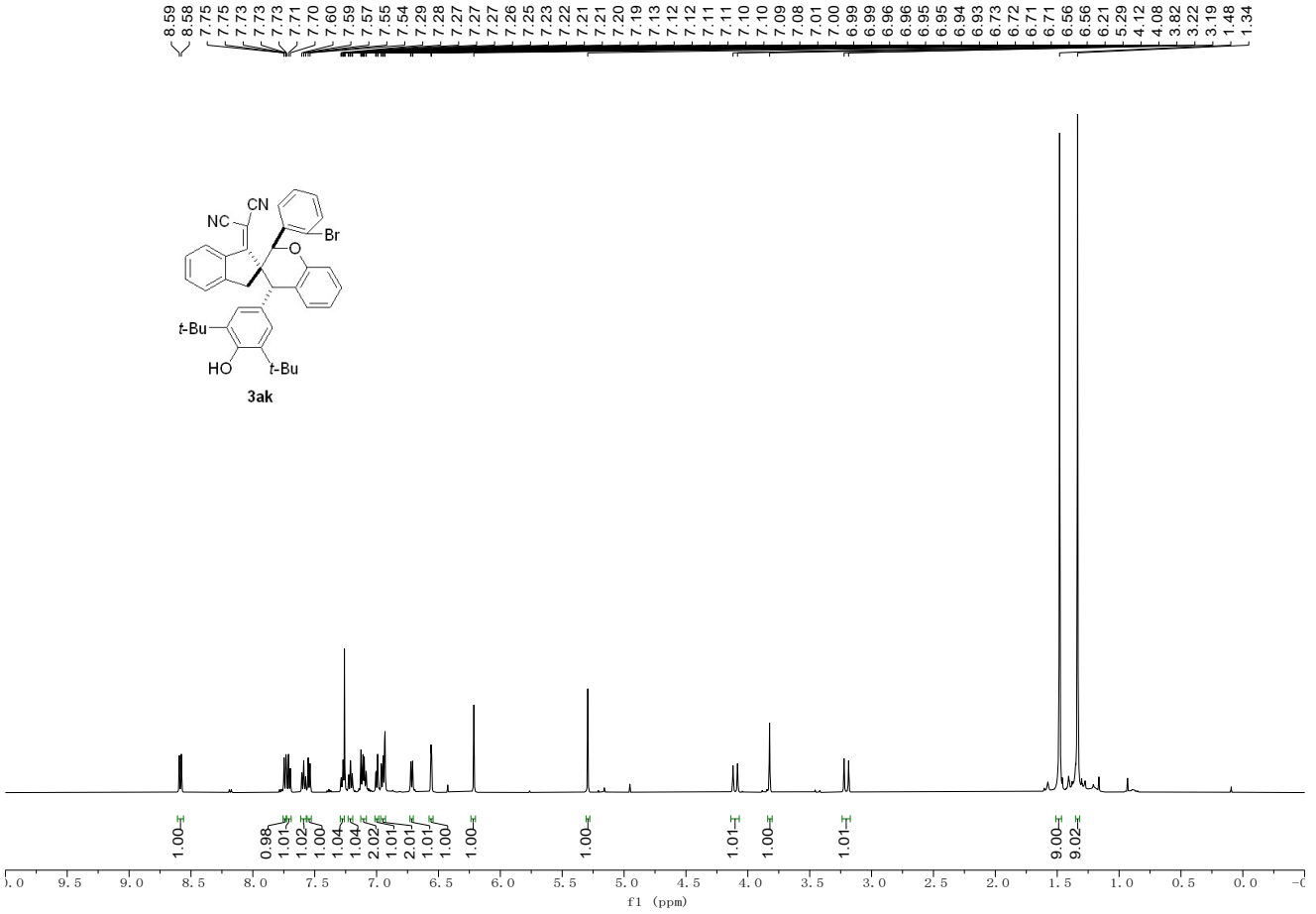
^{1}H NMR spectra for compound **3aj** (500 Hz, $CDCl_3$)



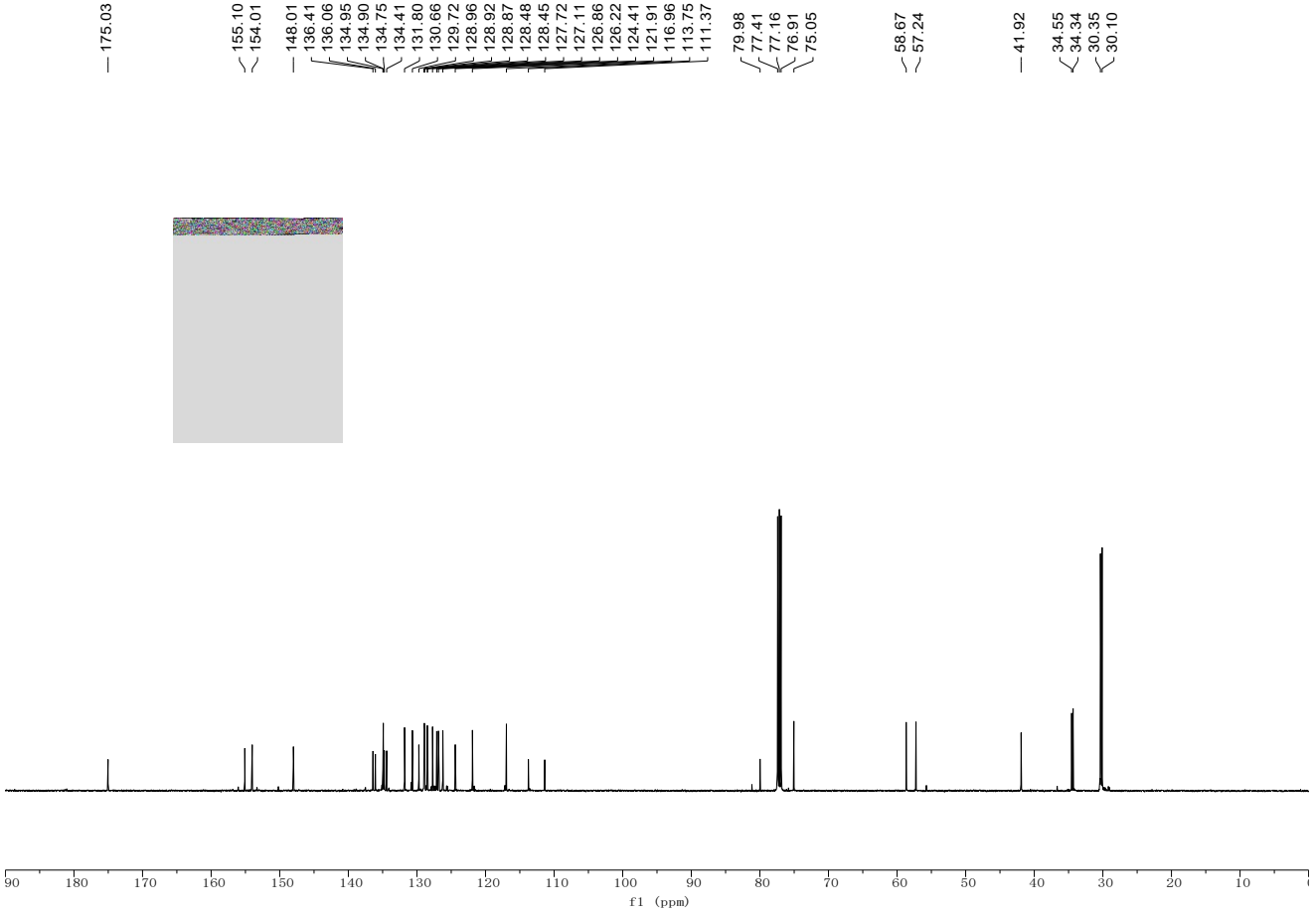
^{13}C NMR spectra for compound **3aj** (125 Hz, $CDCl_3$)



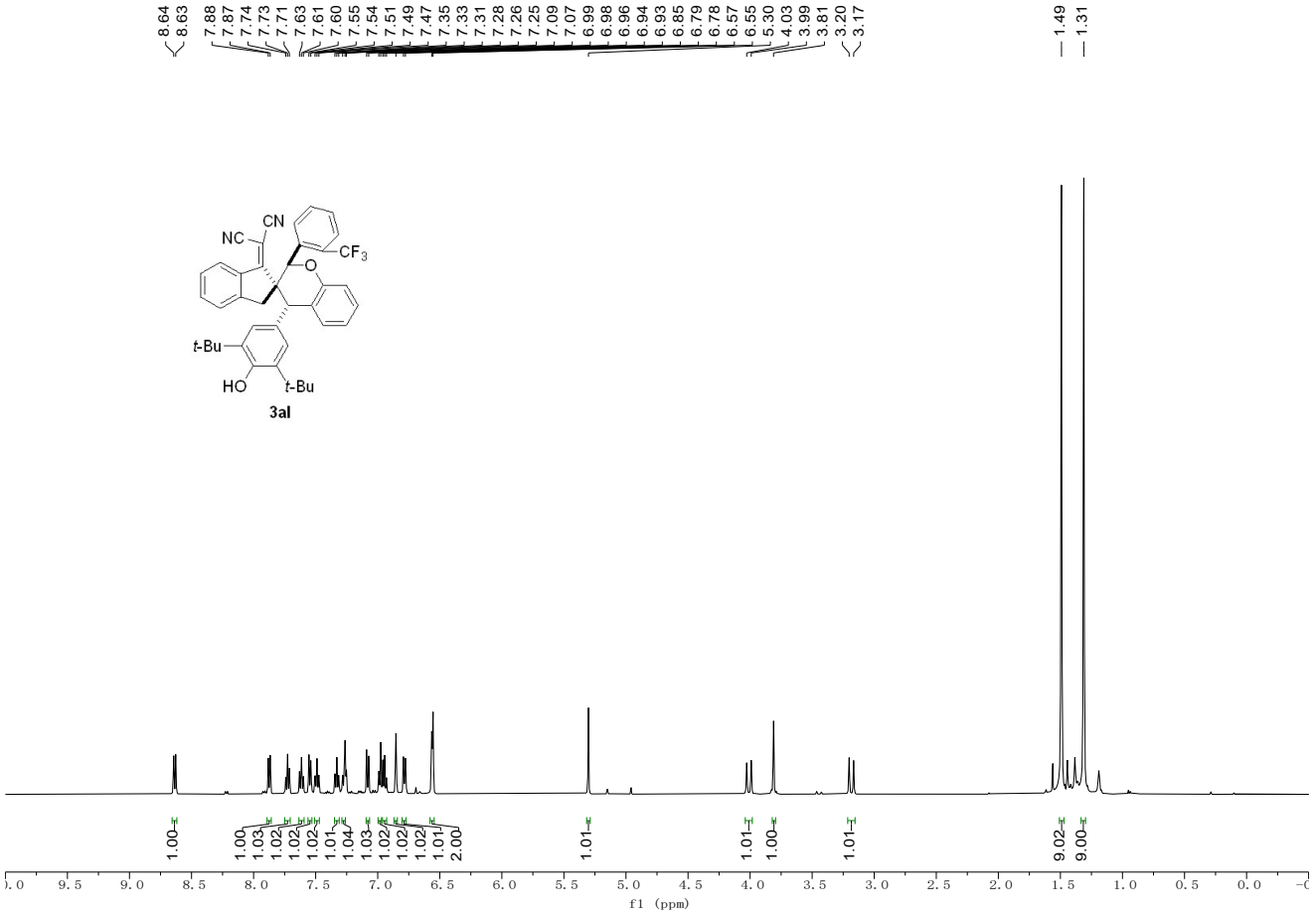
^{1}H NMR spectra for compound **3ak** (500 Hz, $CDCl_3$)



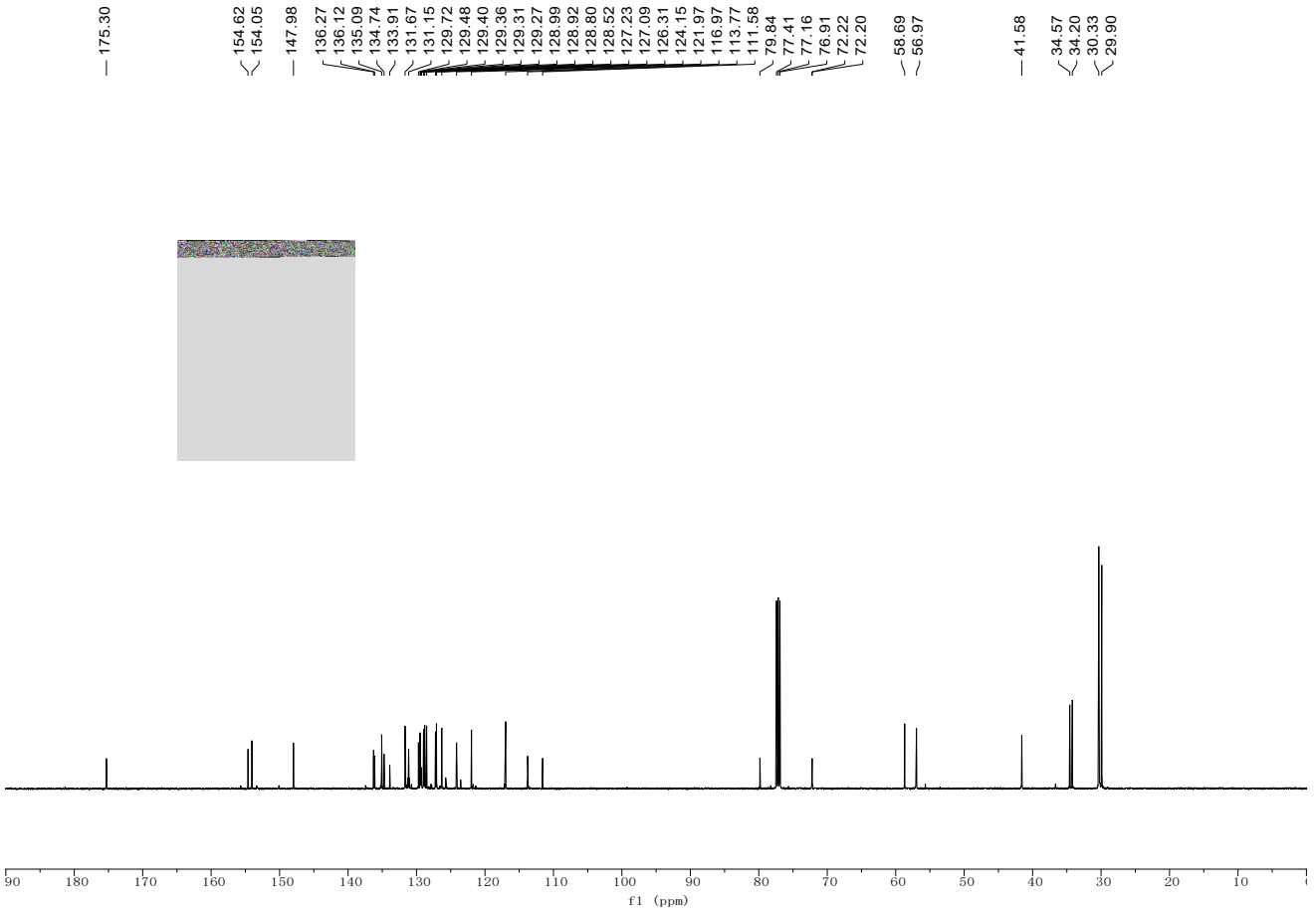
^{13}C NMR spectra for compound **3ak** (125 Hz, $CDCl_3$)



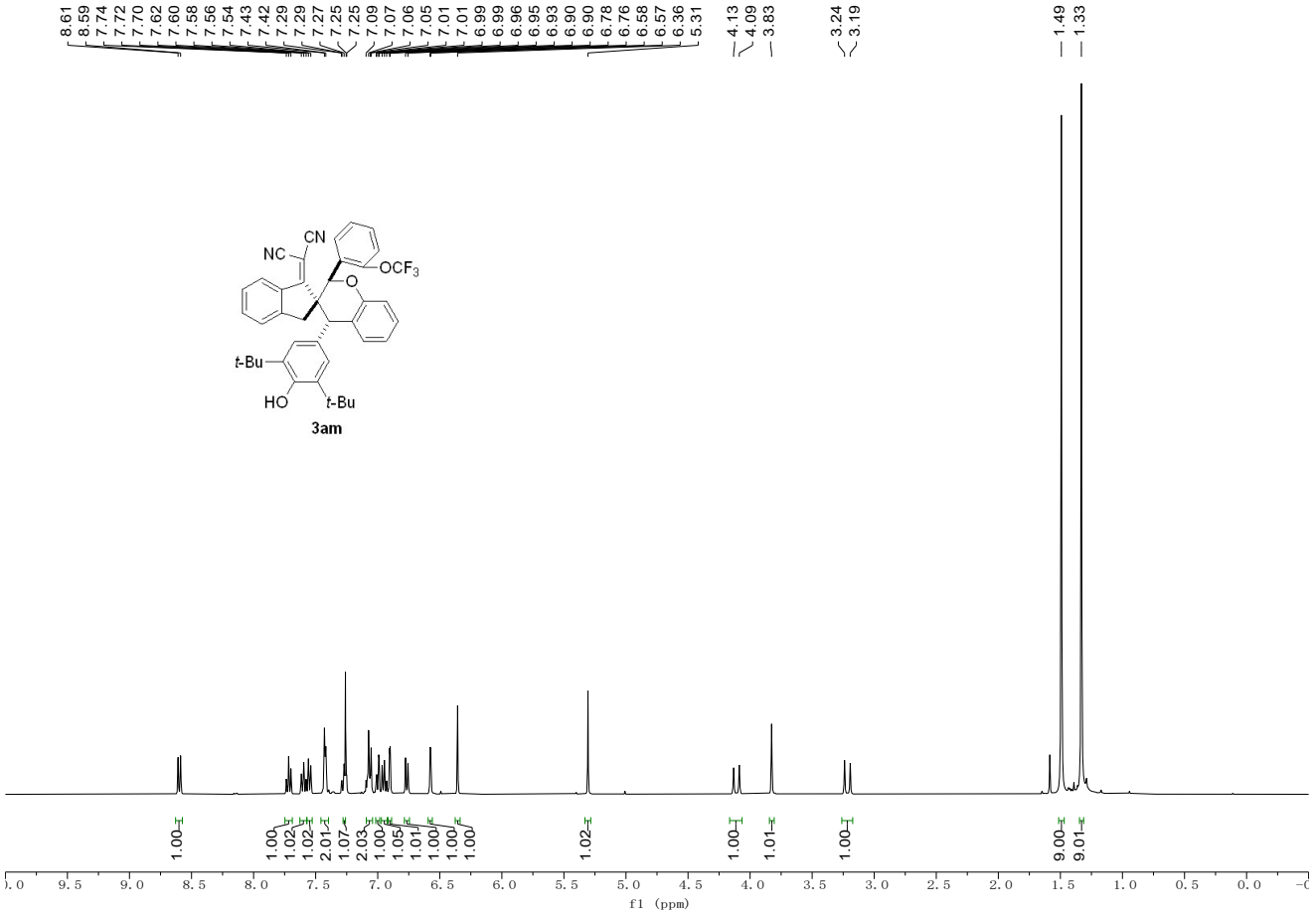
^{1}H NMR spectra for compound **3al** (500 Hz, $CDCl_3$)



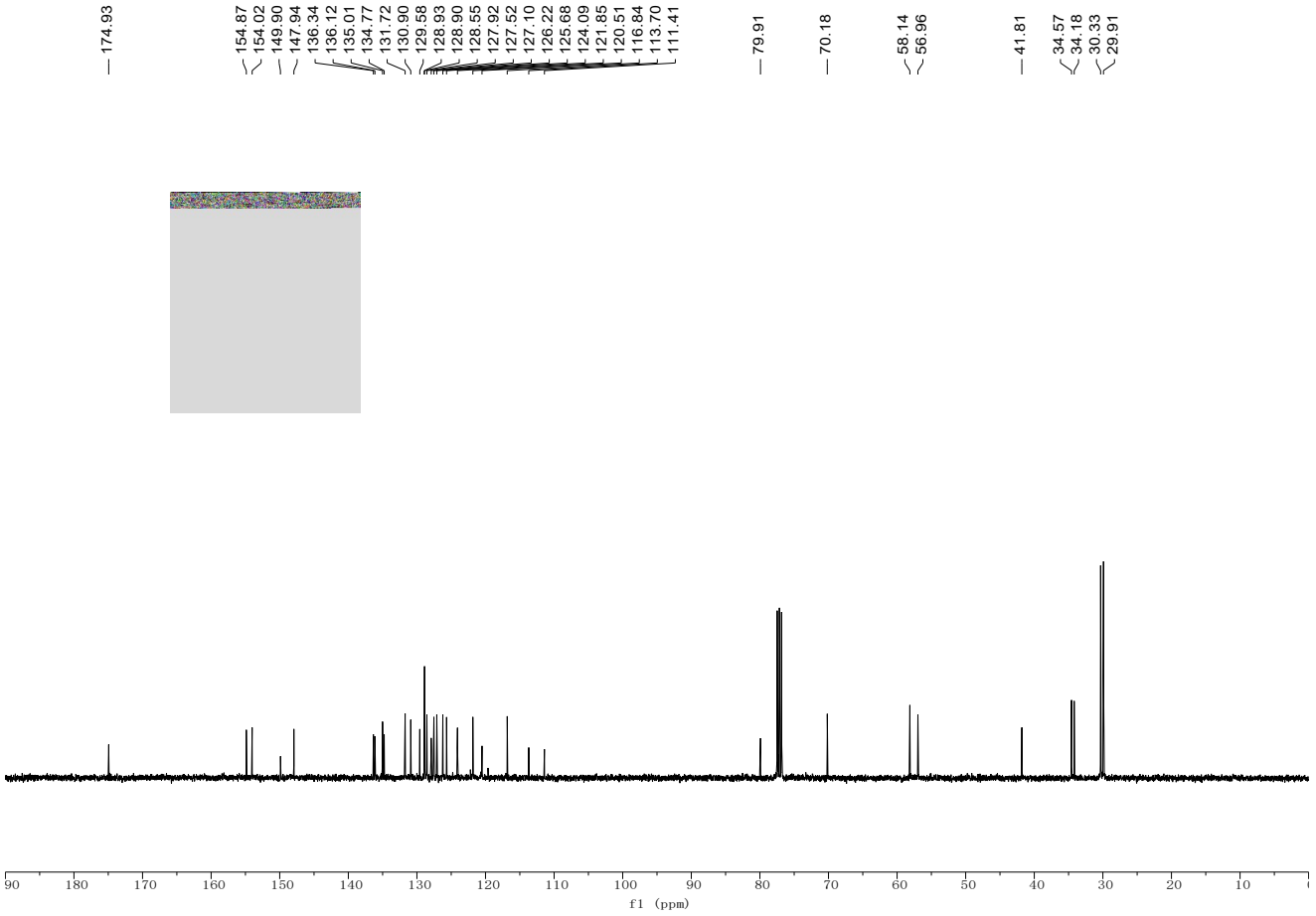
^{13}C NMR spectra for compound **3al** (125 Hz, $CDCl_3$)



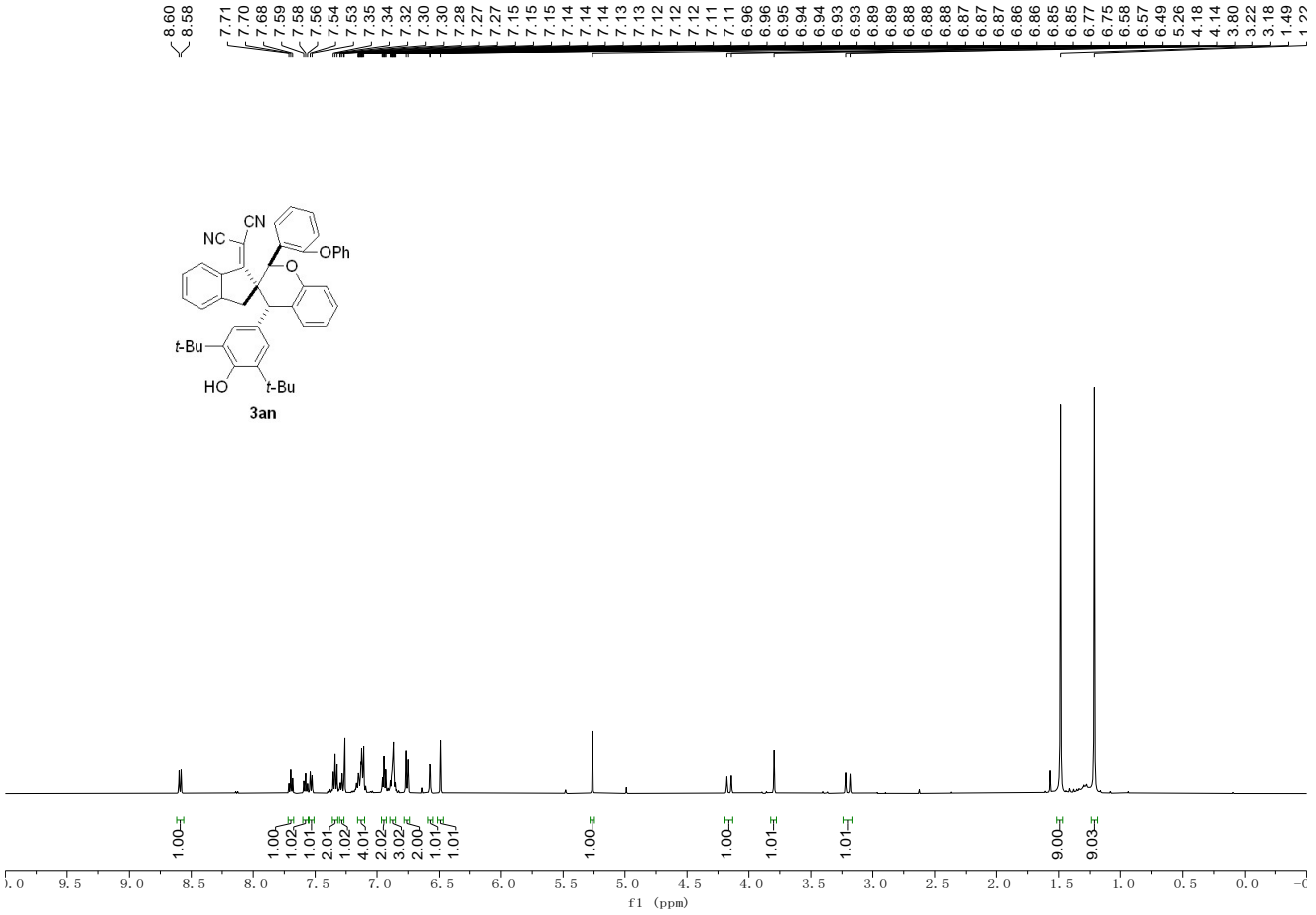
^{1}H NMR spectra for compound **3am** (400 Hz, $CDCl_3$)



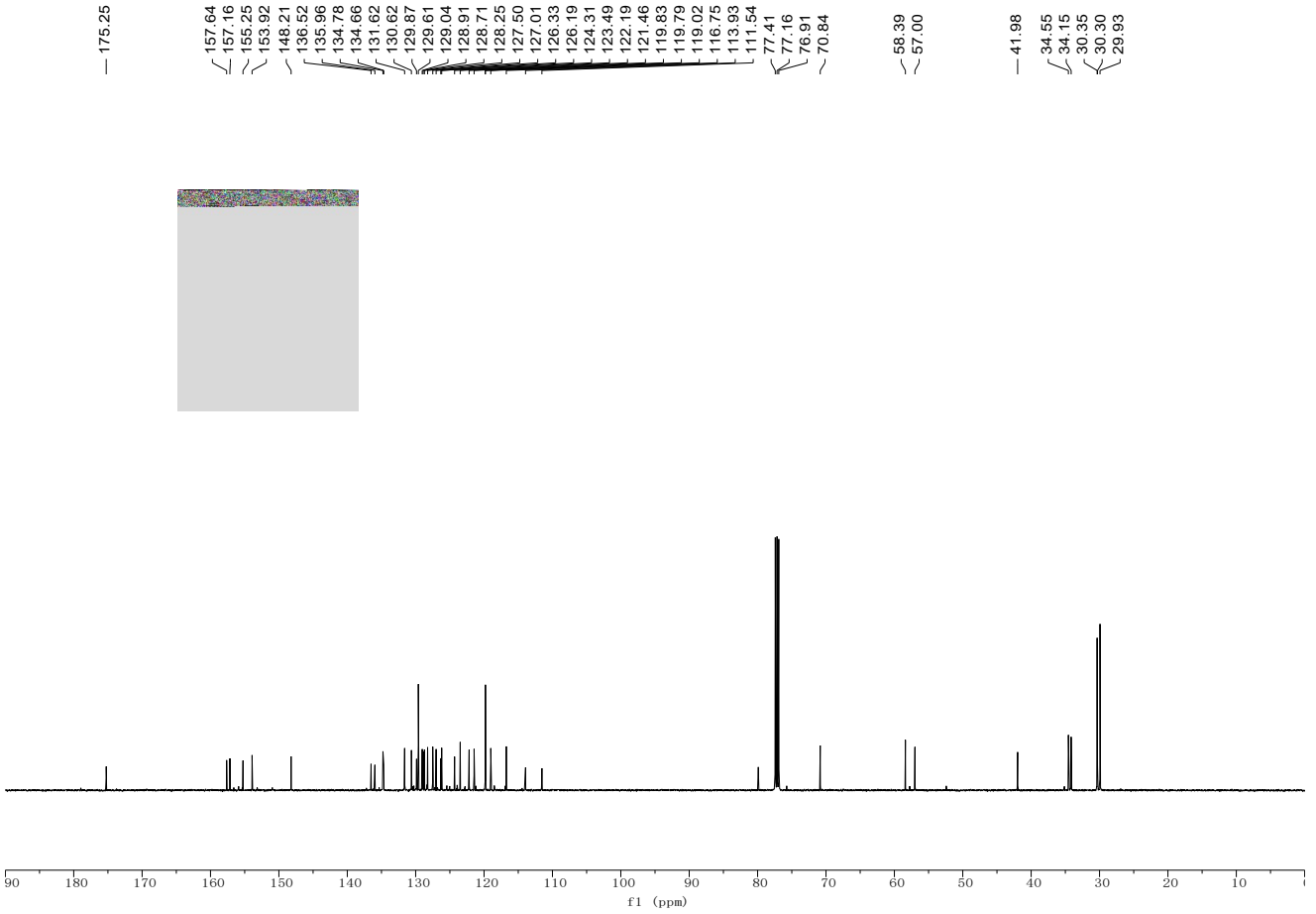
^{13}C NMR spectra for compound **3am** (100 Hz, $CDCl_3$)



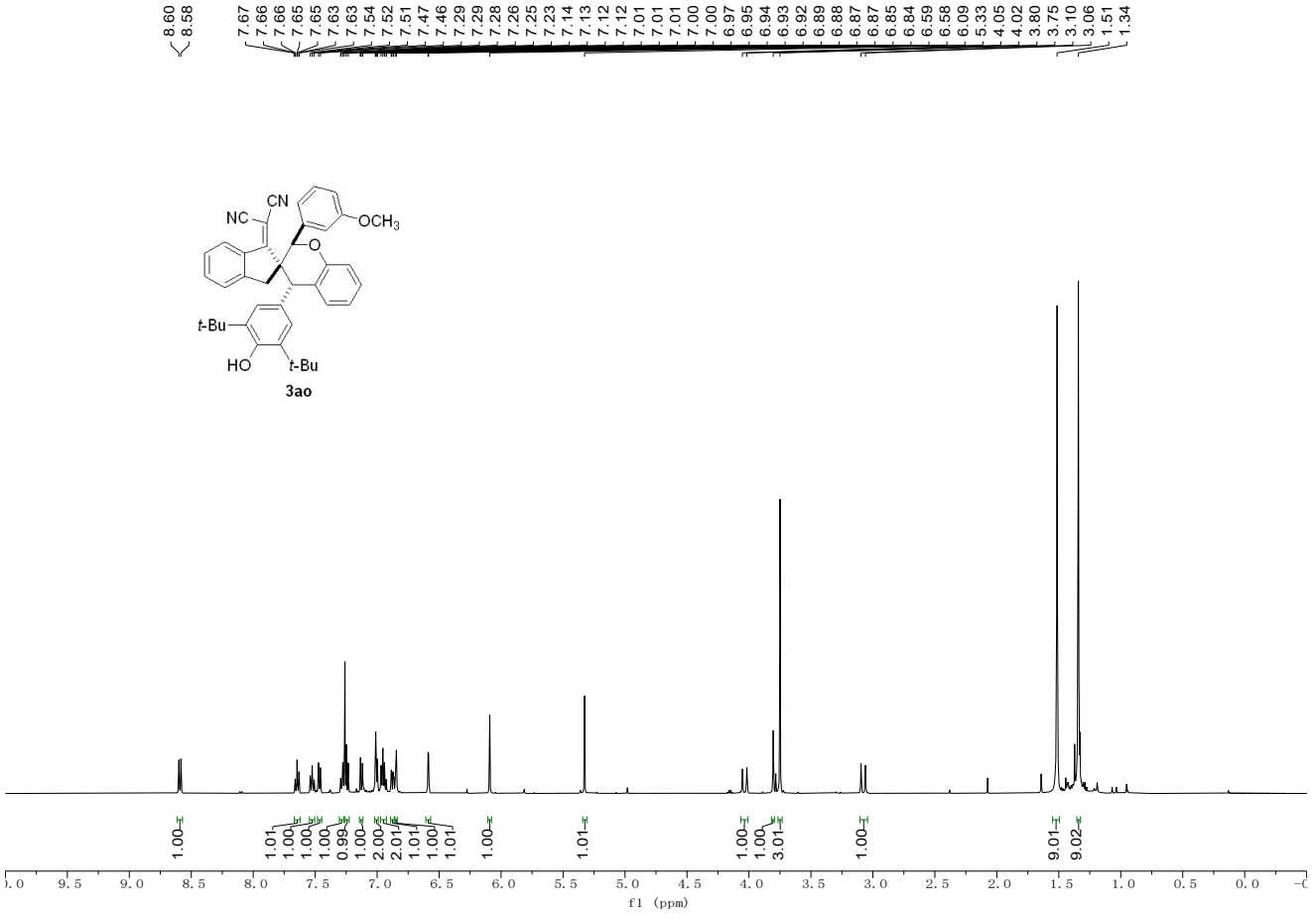
^{1}H NMR spectra for compound **3an** (500 Hz, $CDCl_3$)



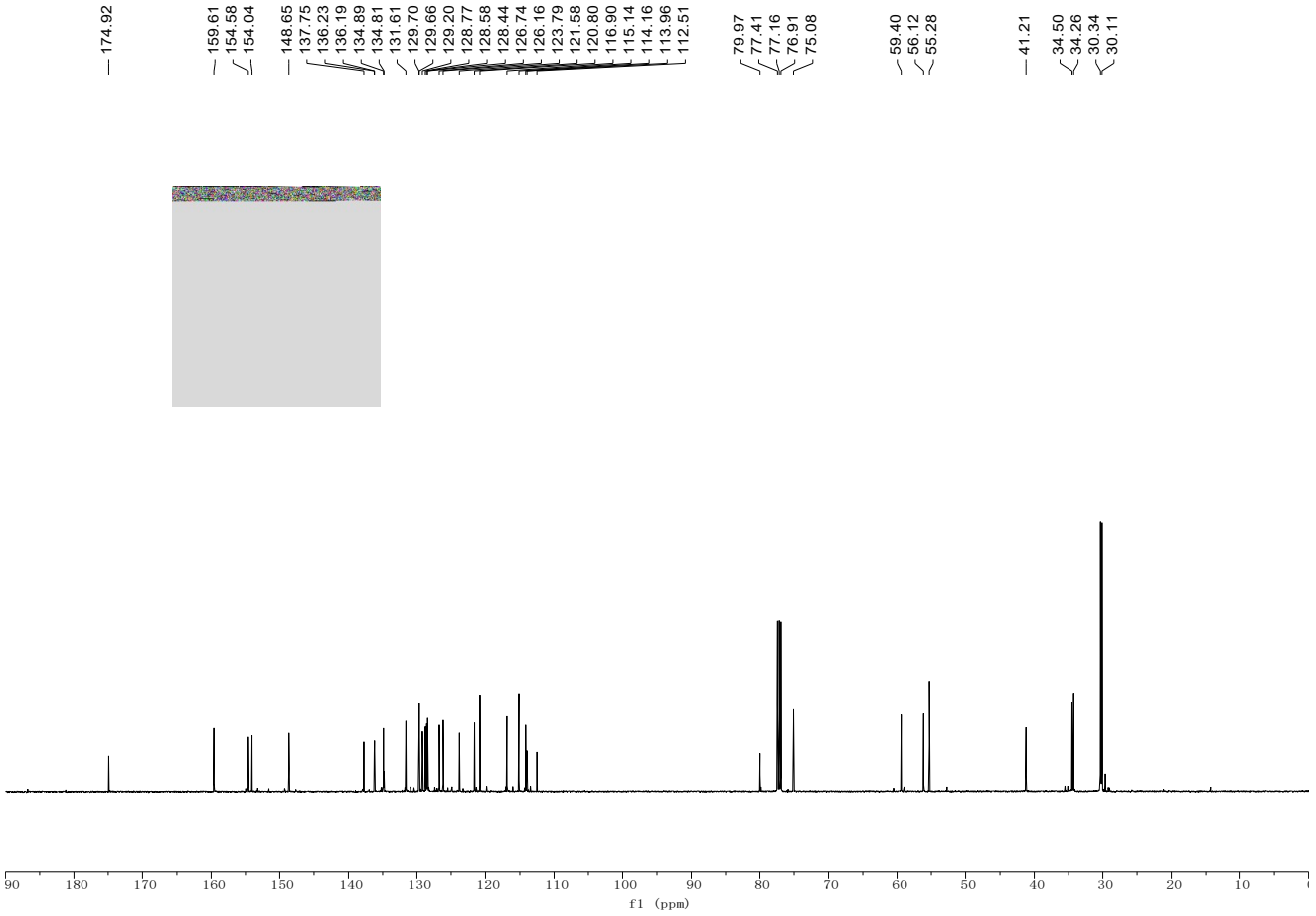
^{13}C NMR spectra for compound **3an** (125 Hz, $CDCl_3$)



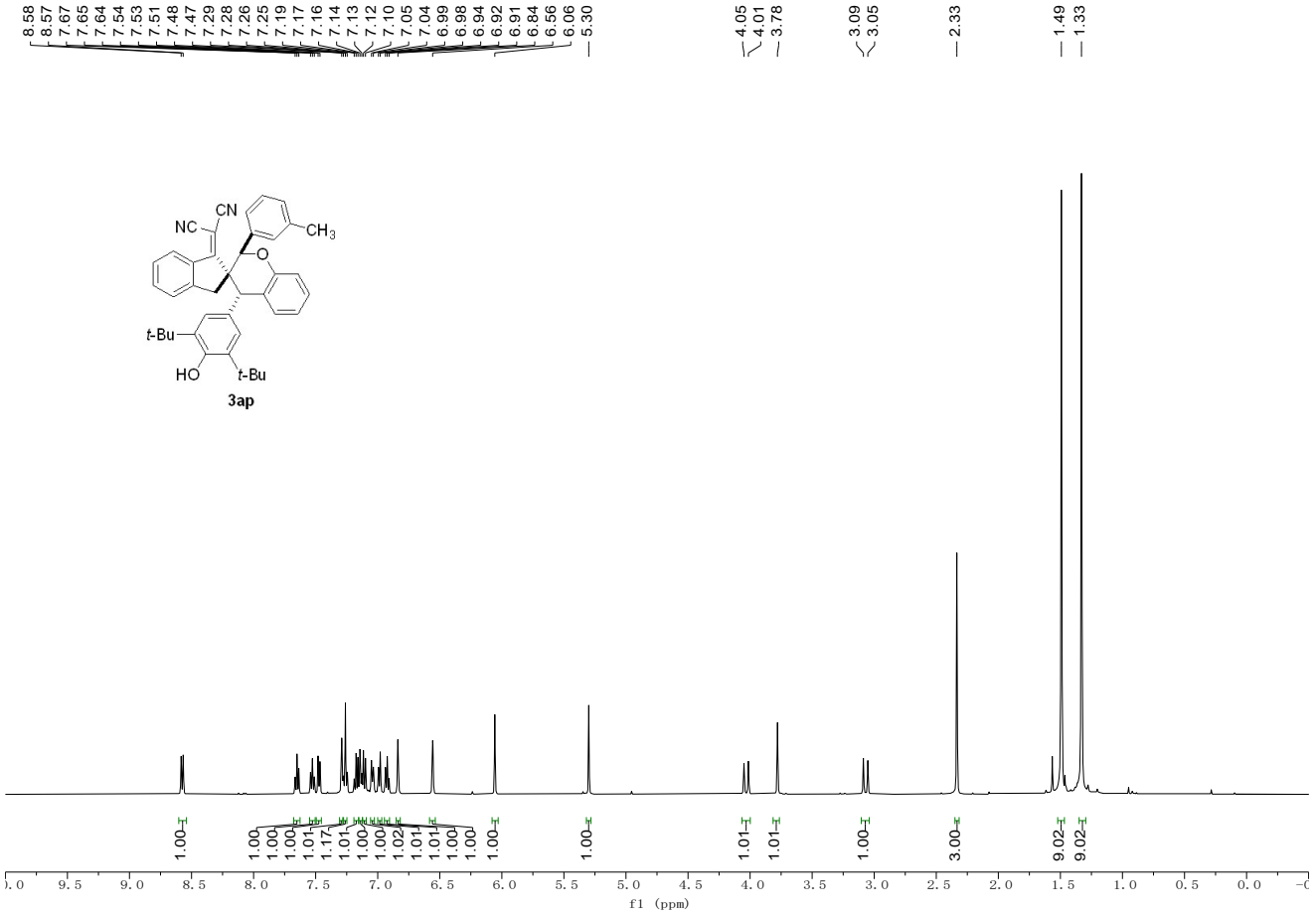
^{1}H NMR spectra for compound **3ao** (500 Hz, $CDCl_3$)



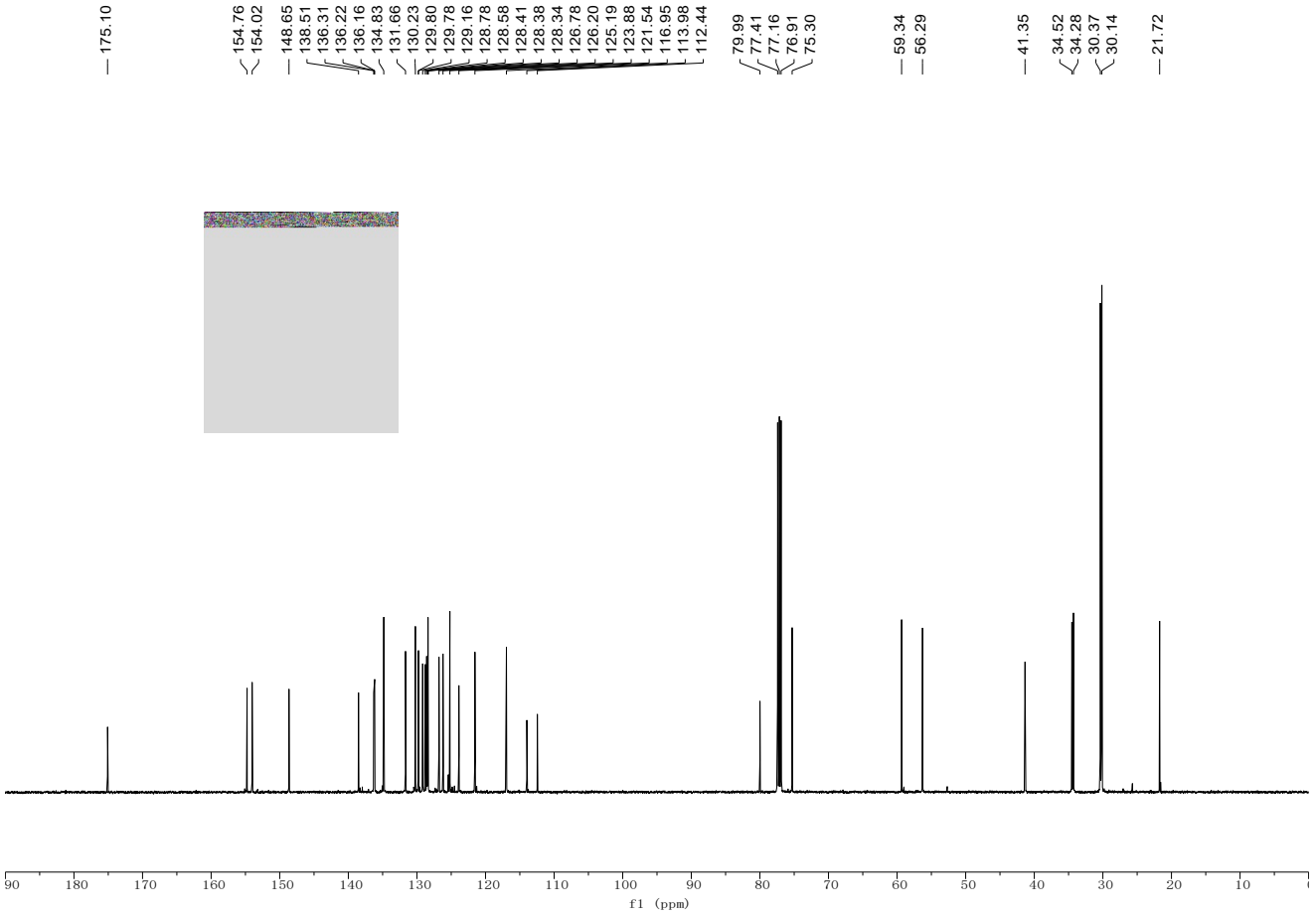
^{13}C NMR spectra for compound **3ao** (125 Hz, $CDCl_3$)



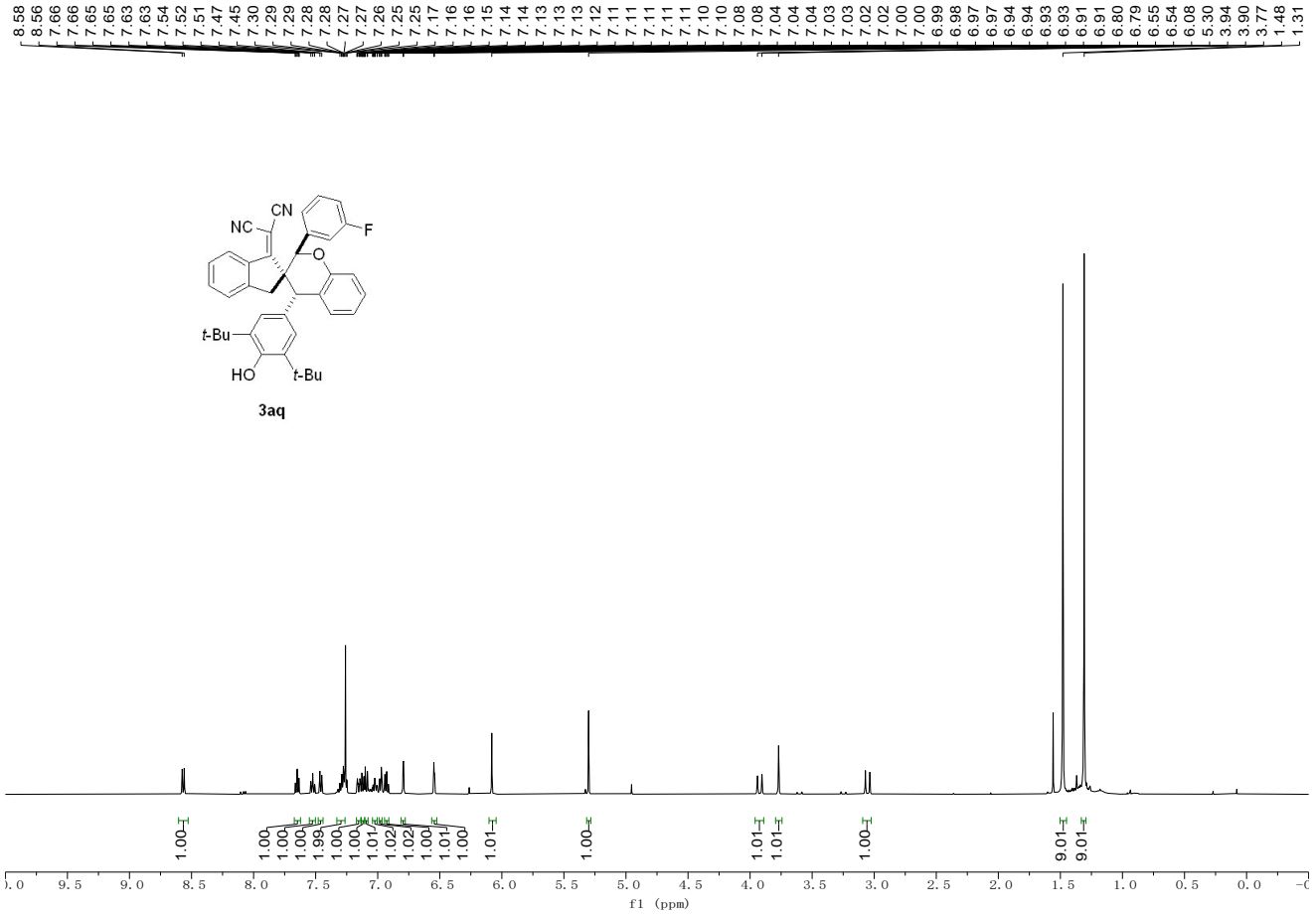
^{1}H NMR spectra for compound **3ap** (500 Hz, $CDCl_3$)



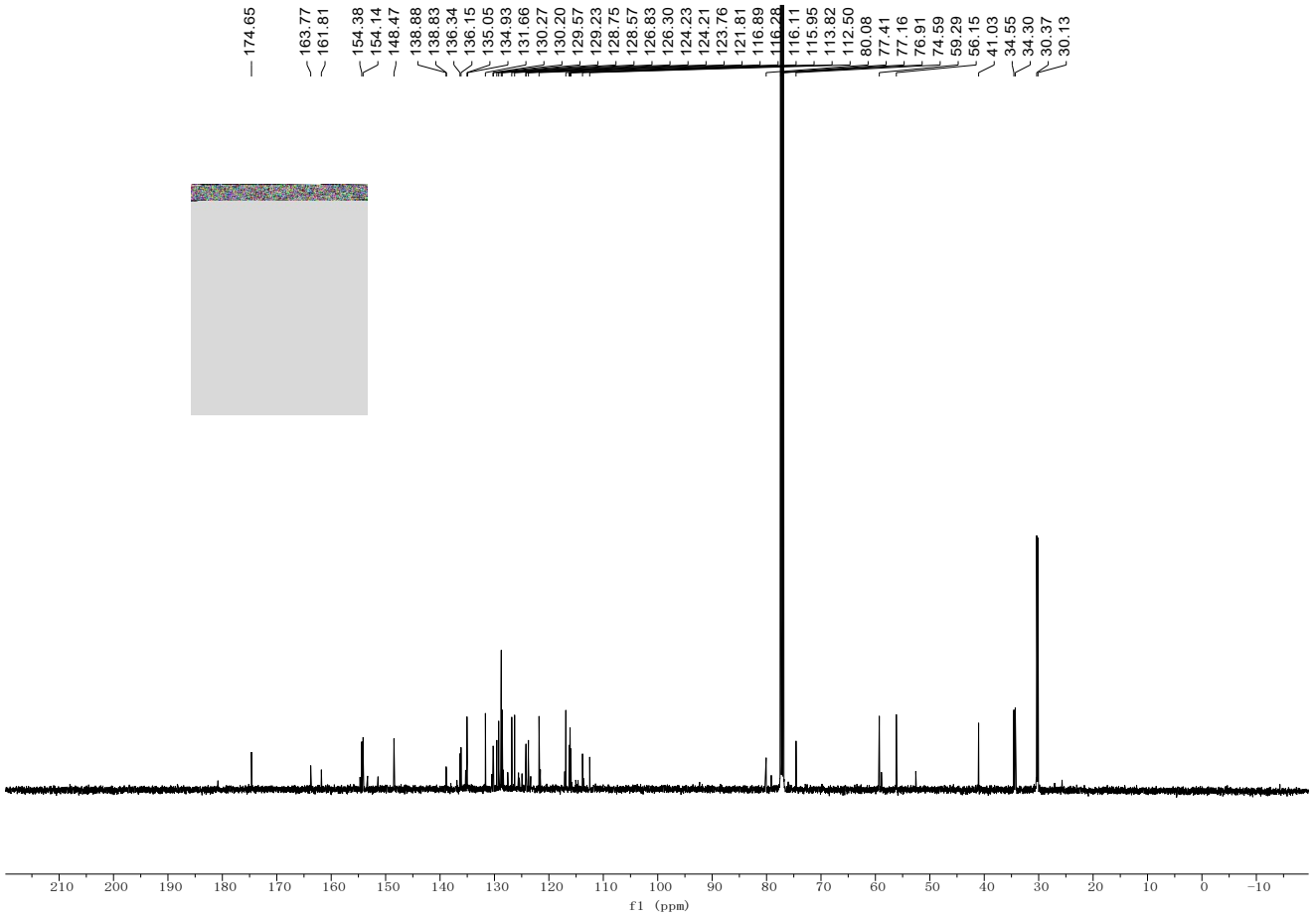
^{13}C NMR spectra for compound **3ap** (125 Hz, $CDCl_3$)



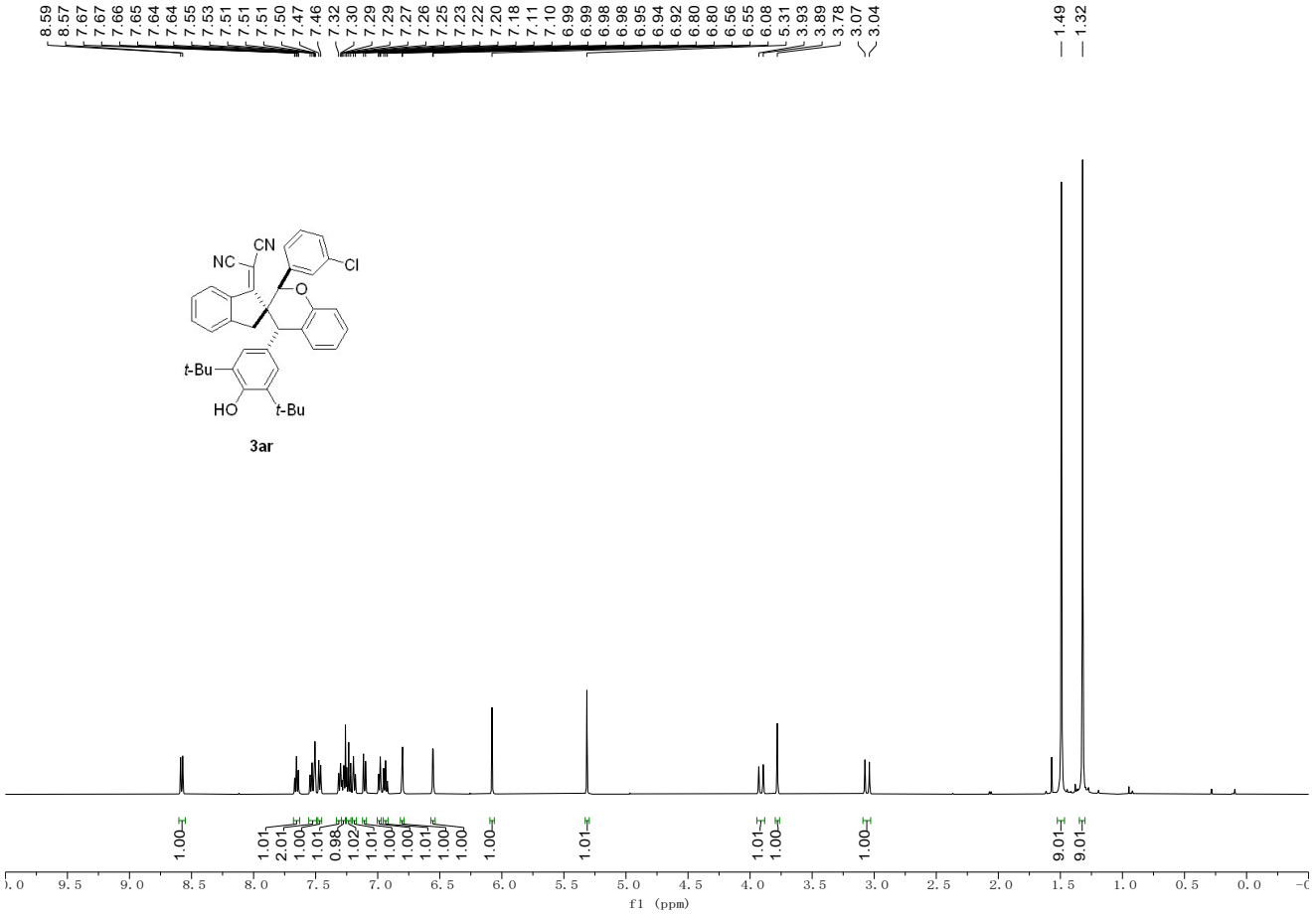
^{1}H NMR spectra for compound **3aq** (500 Hz, $CDCl_3$)



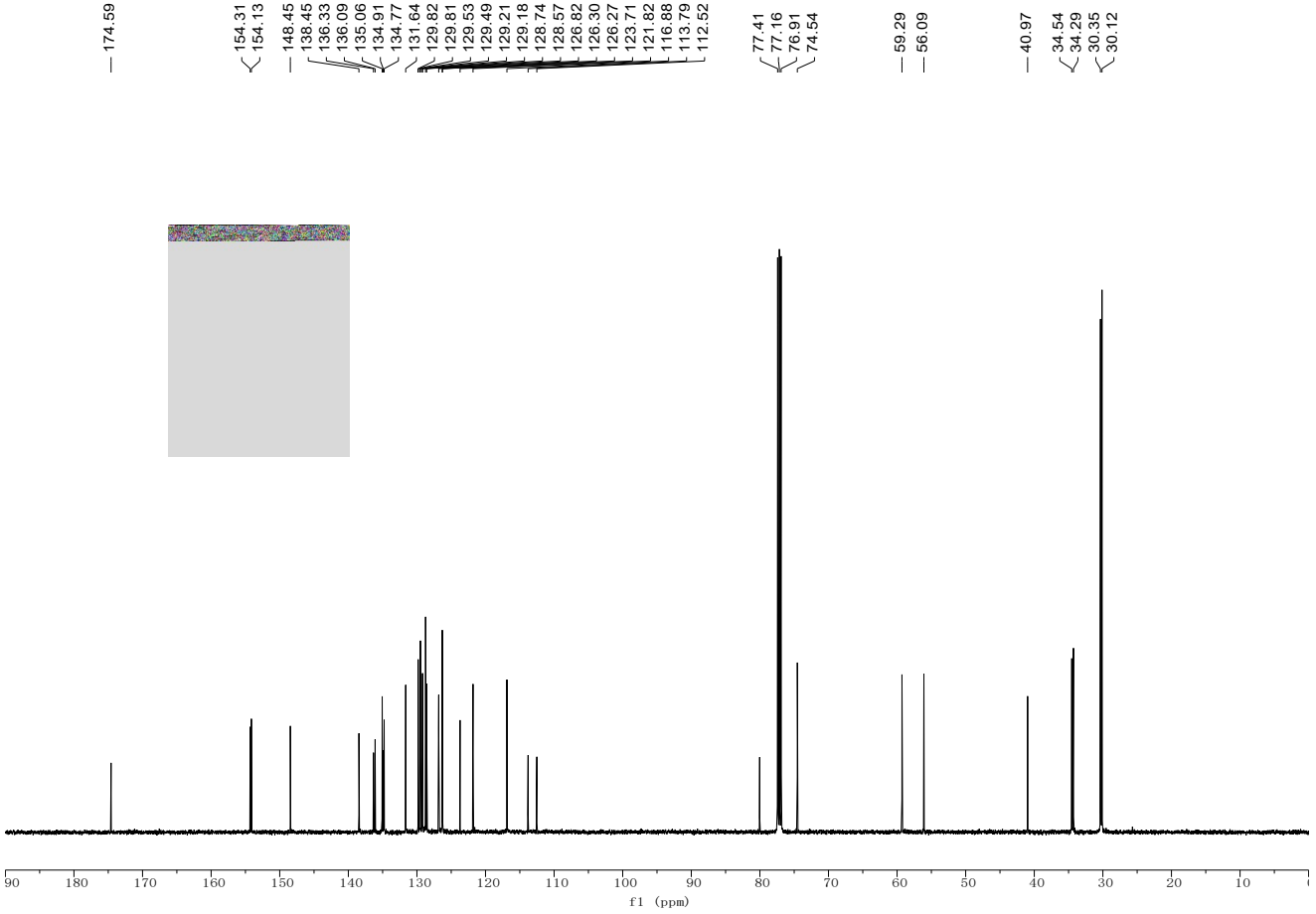
^{13}C NMR spectra for compound **3aq** (125 Hz, $CDCl_3$)



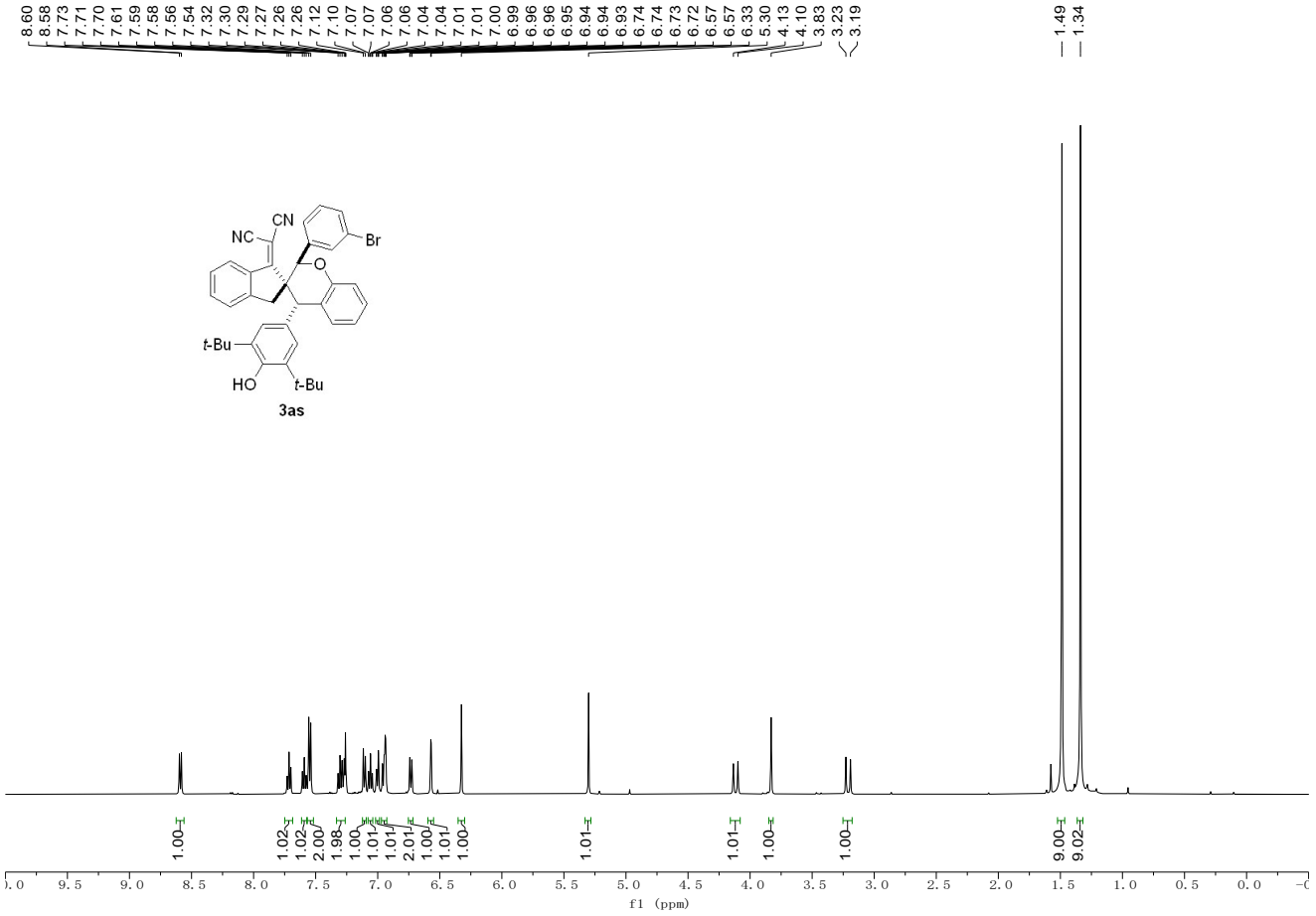
^{1}H NMR spectra for compound **3ar** (500 Hz, $CDCl_3$)



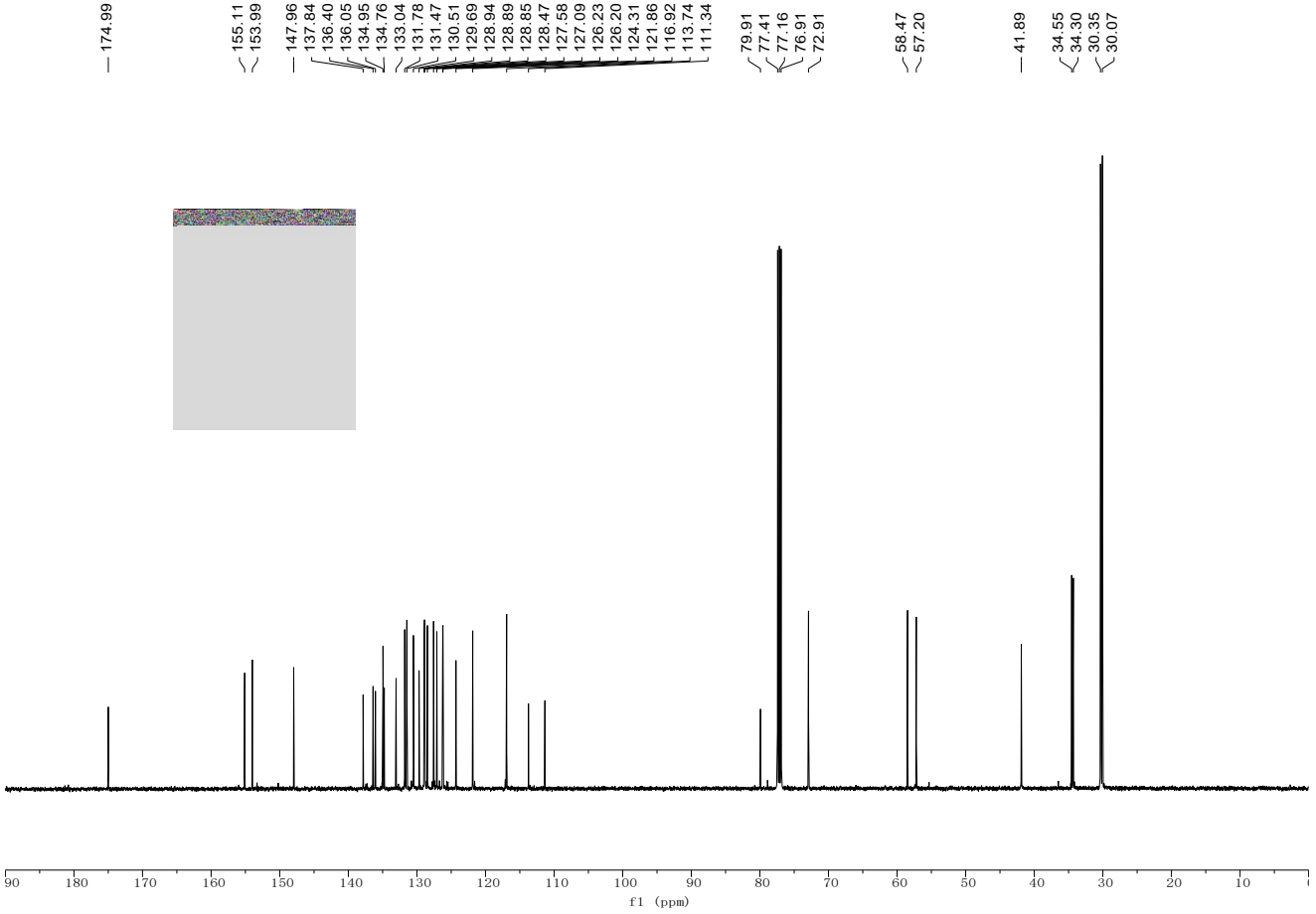
^{13}C NMR spectra for compound **3ar** (125 Hz, $CDCl_3$)



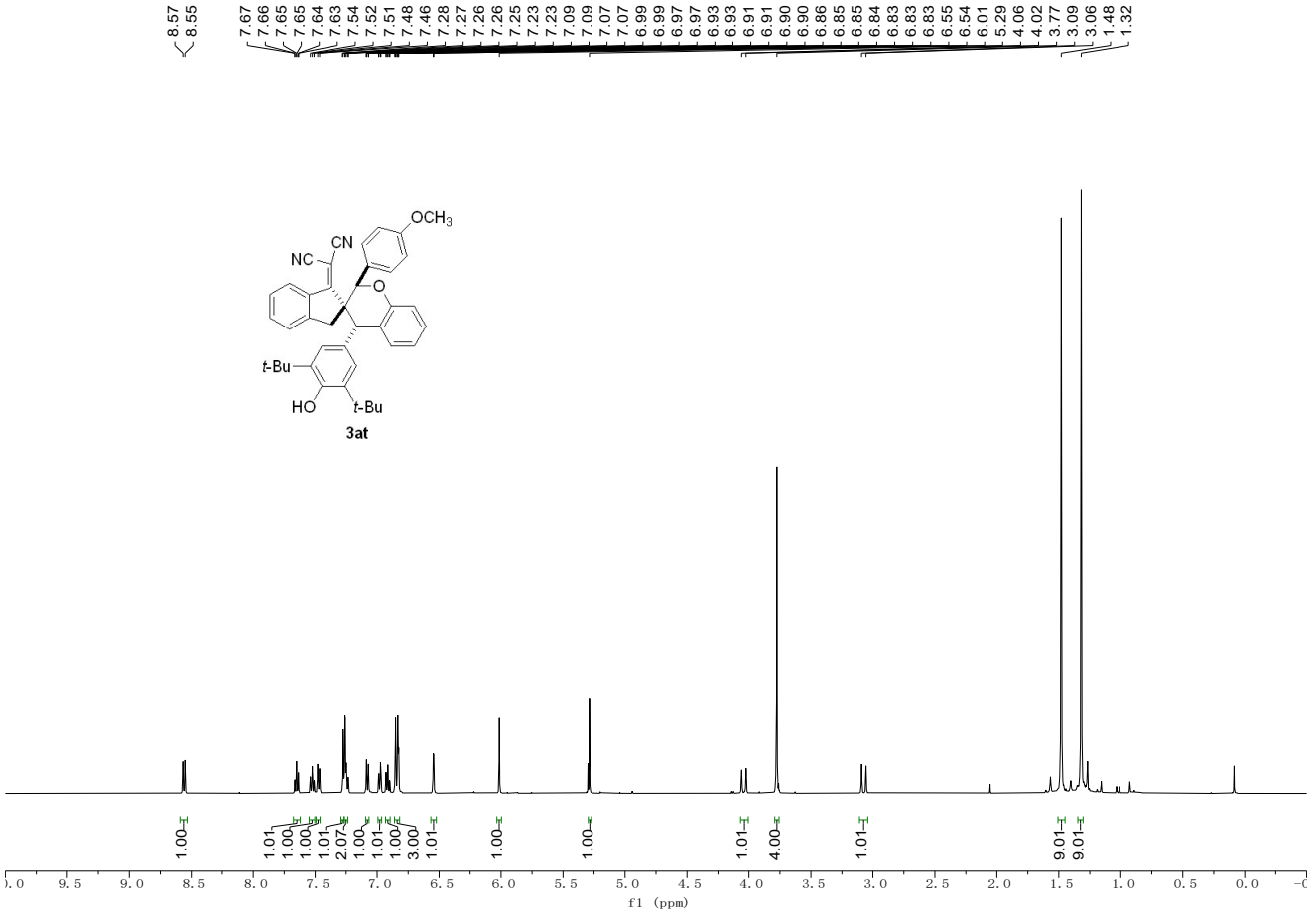
^{1}H NMR spectra for compound **3as** (500 Hz, $CDCl_3$)



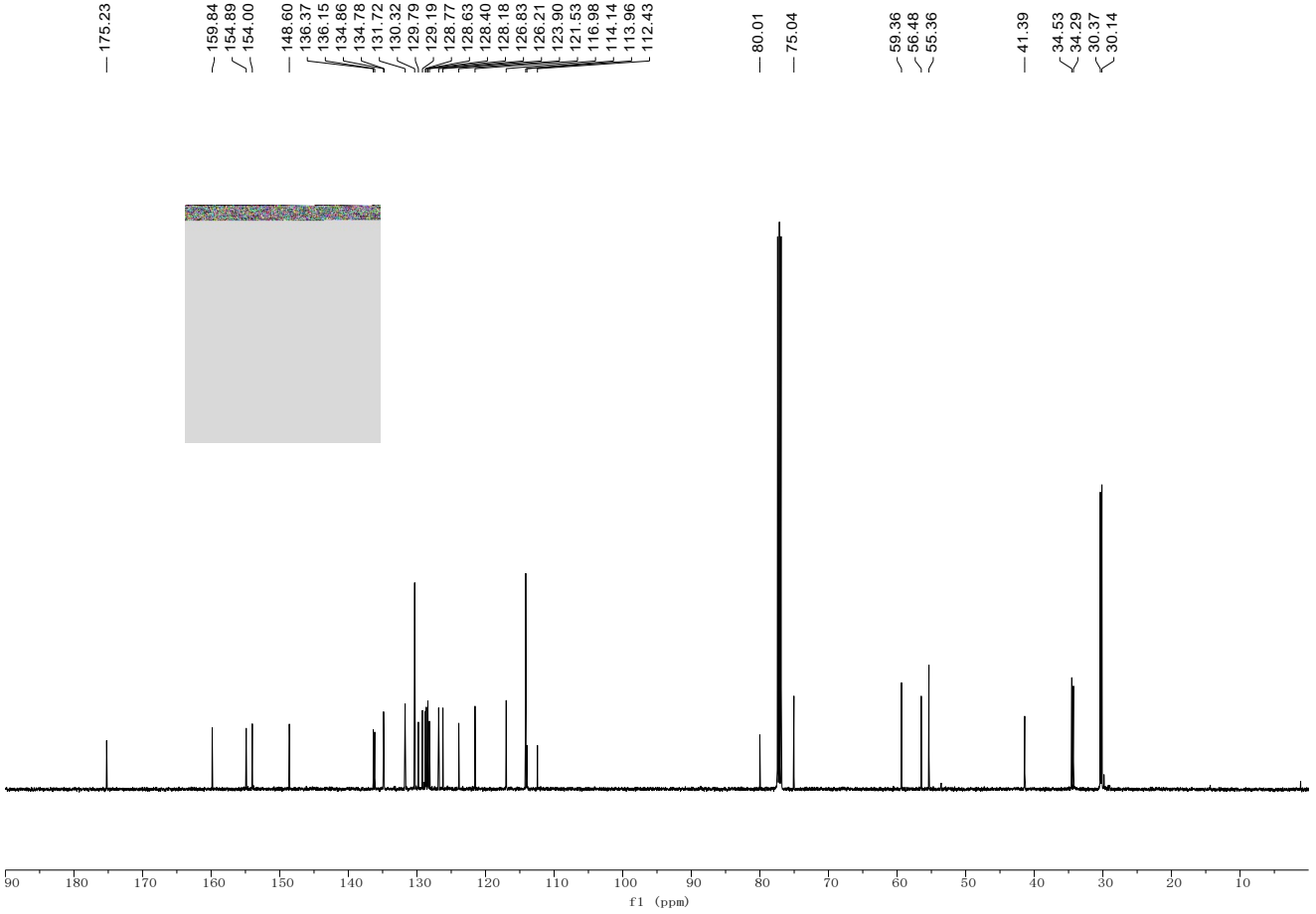
^{13}C NMR spectra for compound **3as** (125 Hz, $CDCl_3$)



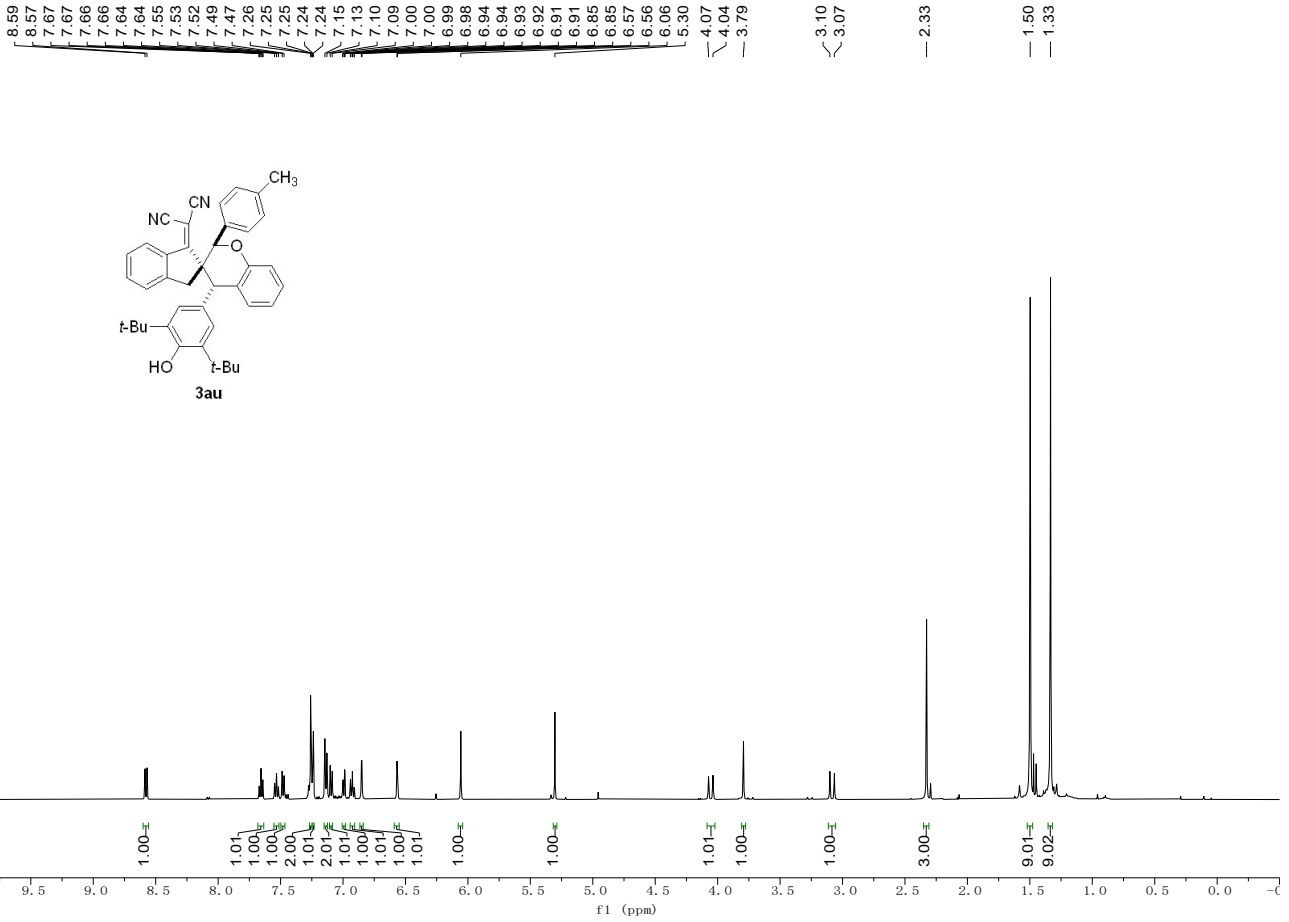
^{1}H NMR spectra for compound **3at** (500 Hz, $CDCl_3$)



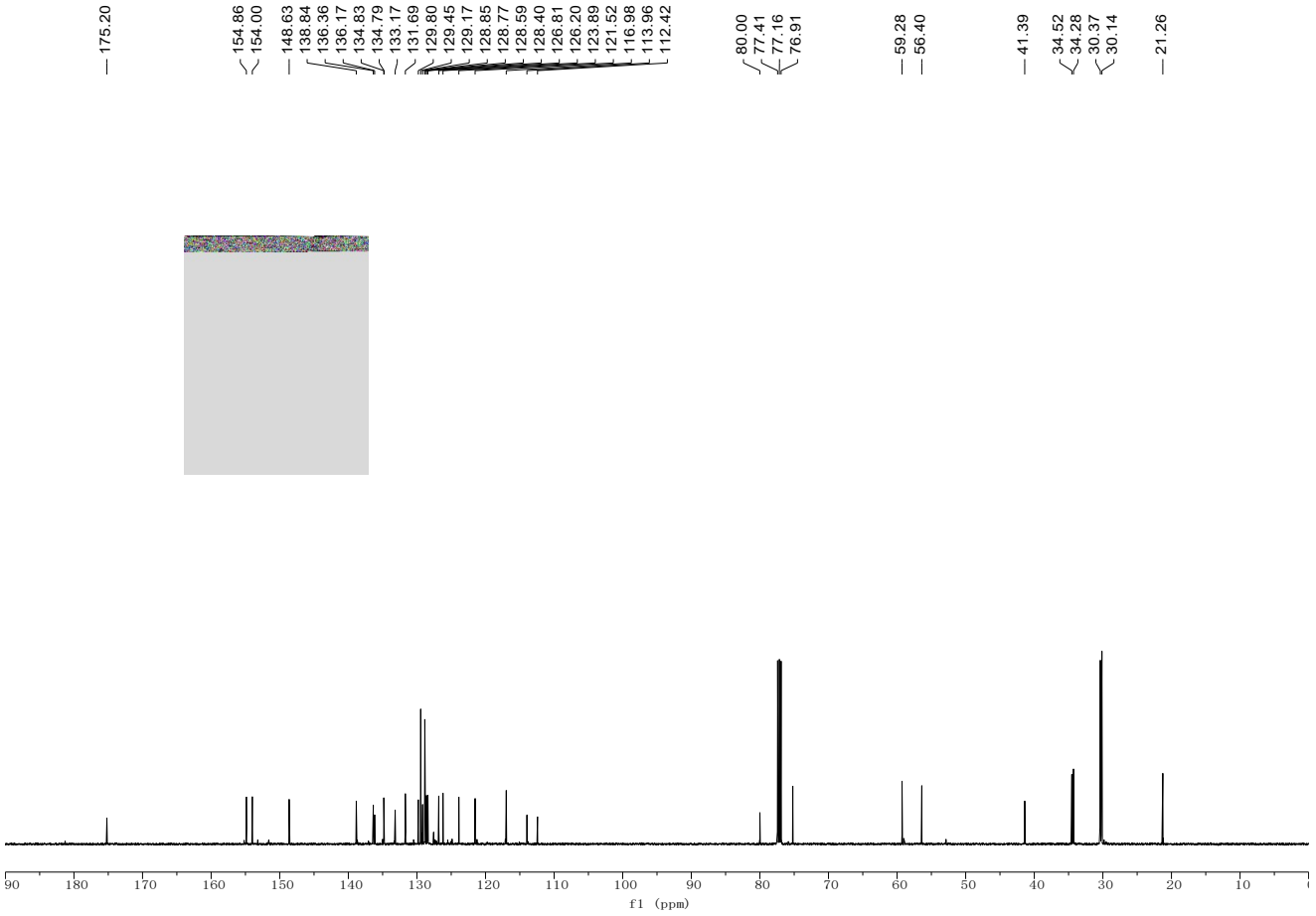
^{13}C NMR spectra for compound **3at** (125 Hz, $CDCl_3$)



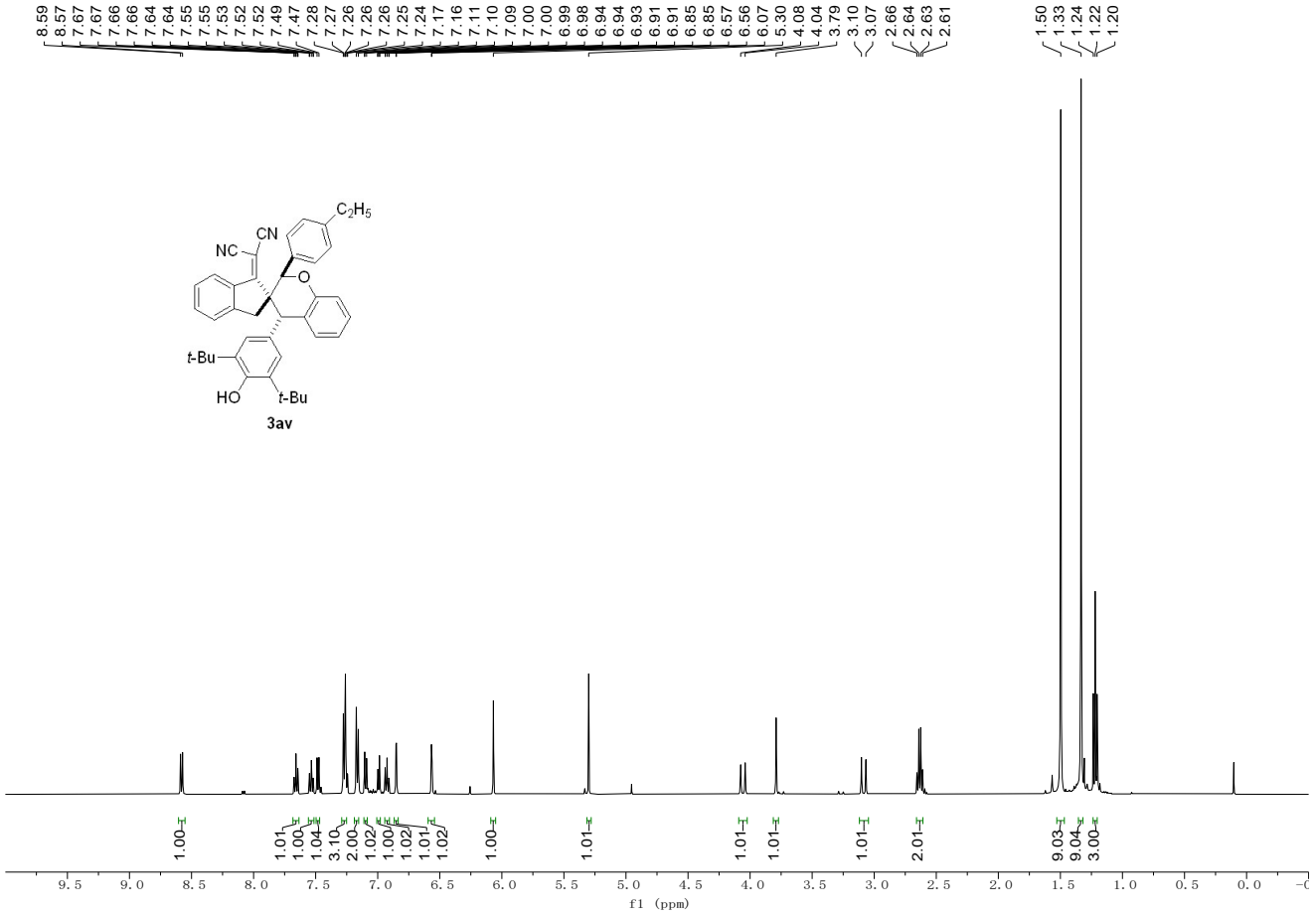
^{1}H NMR spectra for compound **3au** (500 Hz, $CDCl_3$)



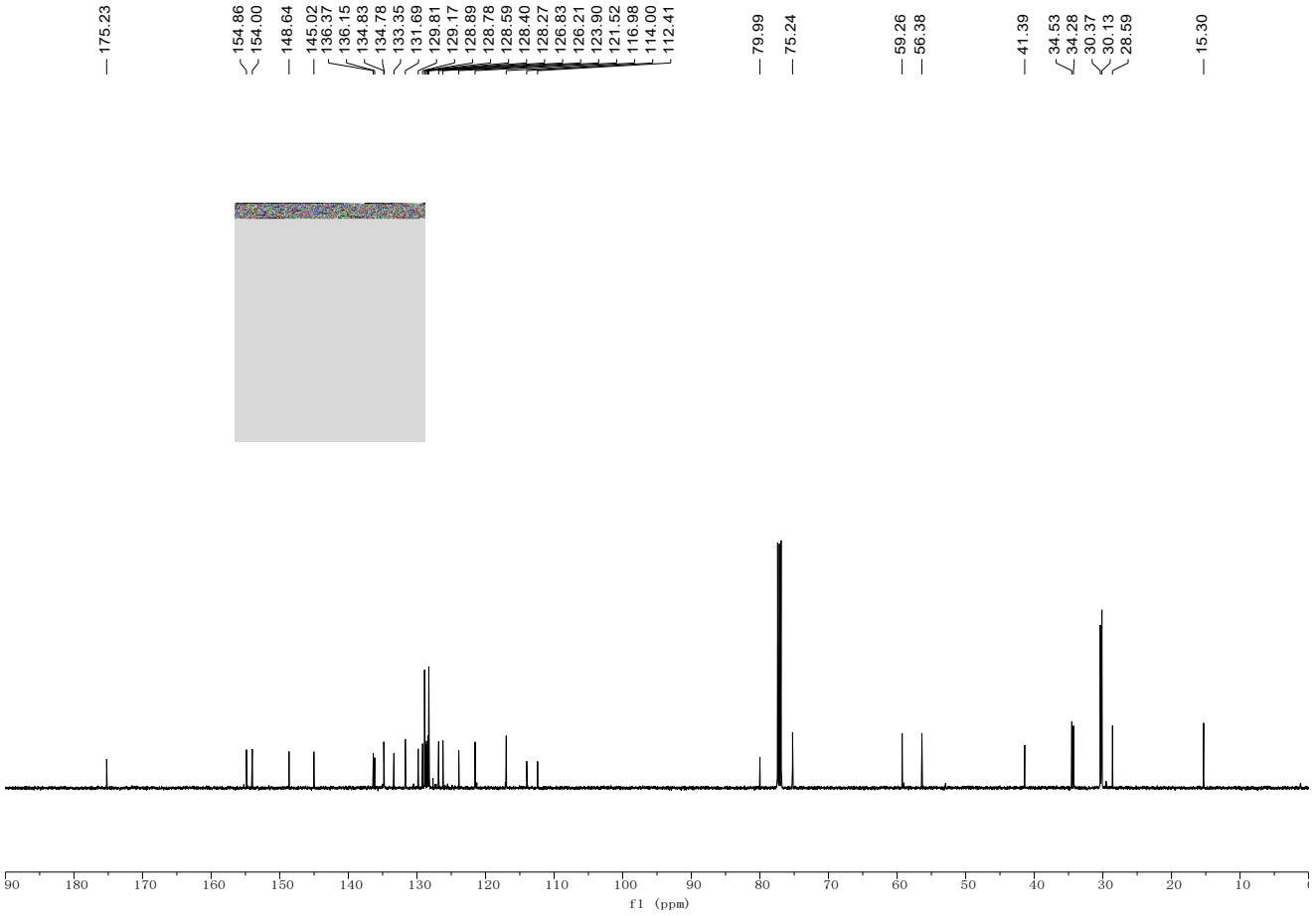
^{13}C NMR spectra for compound **3au** (125 Hz, $CDCl_3$)



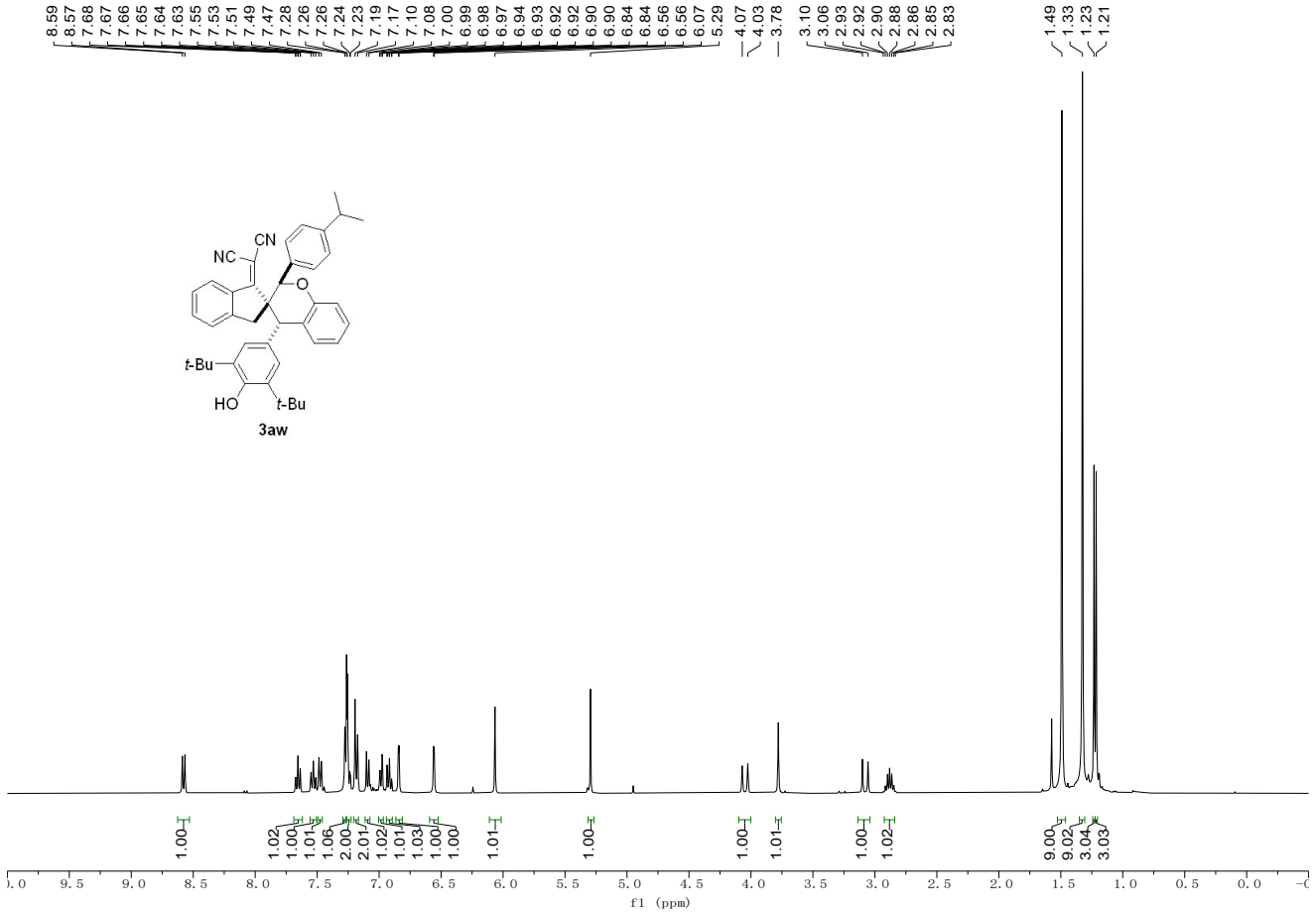
^{1}H NMR spectra for compound **3av** (500 Hz, $CDCl_3$)



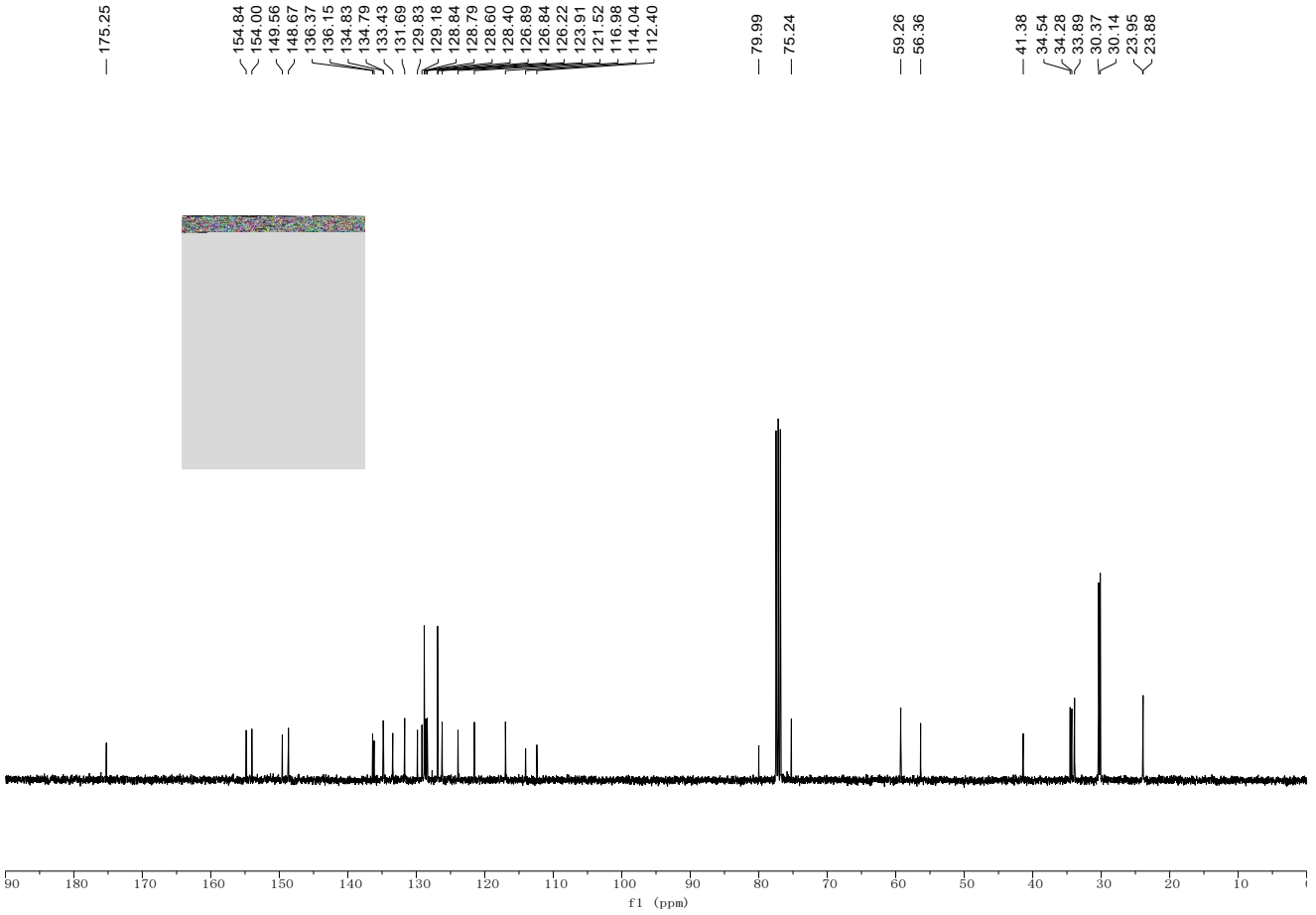
^{13}C NMR spectra for compound **3av** (125 Hz, $CDCl_3$)



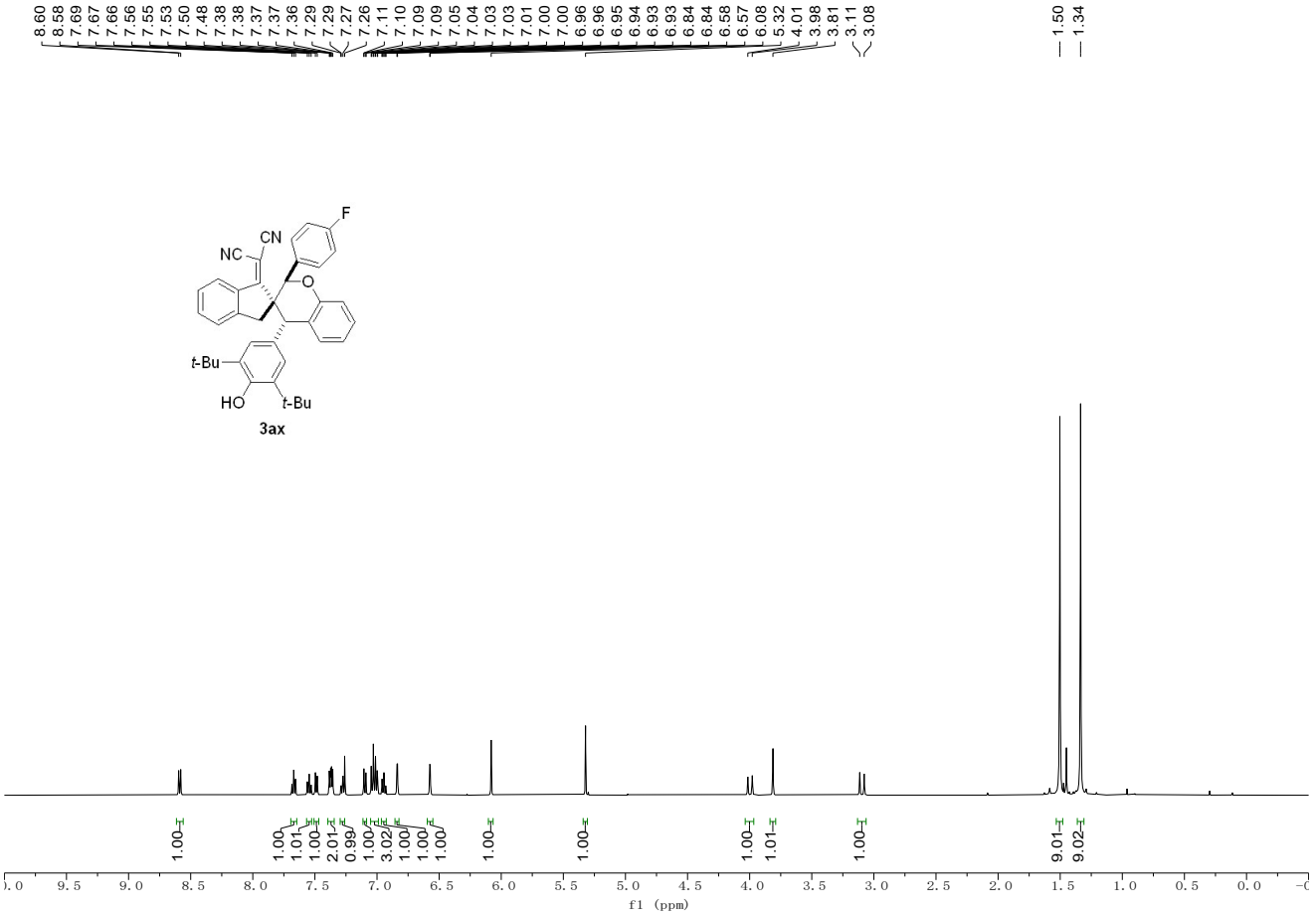
^{1}H NMR spectra for compound **3aw** (400 Hz, $CDCl_3$)



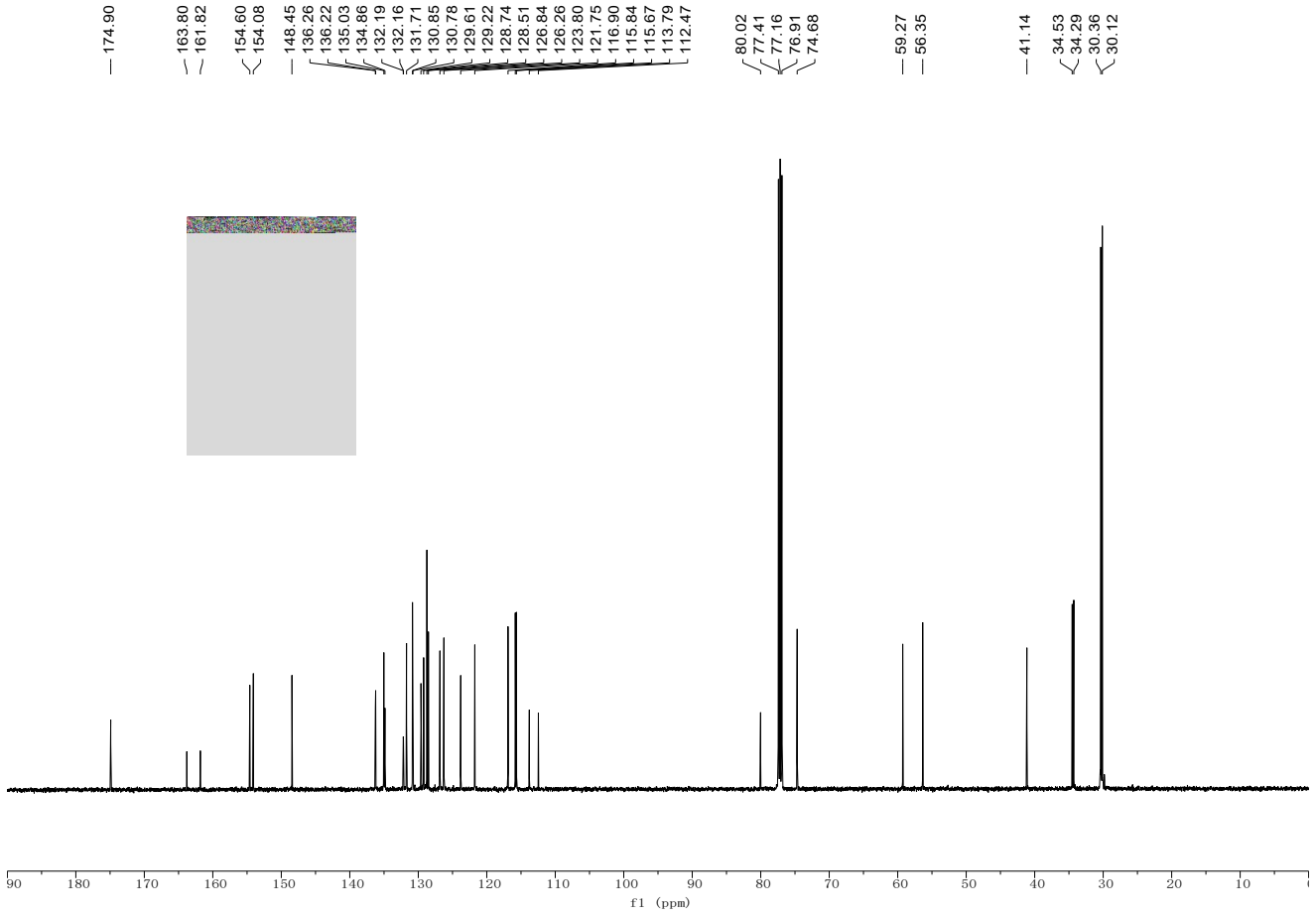
^{13}C NMR spectra for compound **3aw** (100 Hz, $CDCl_3$)



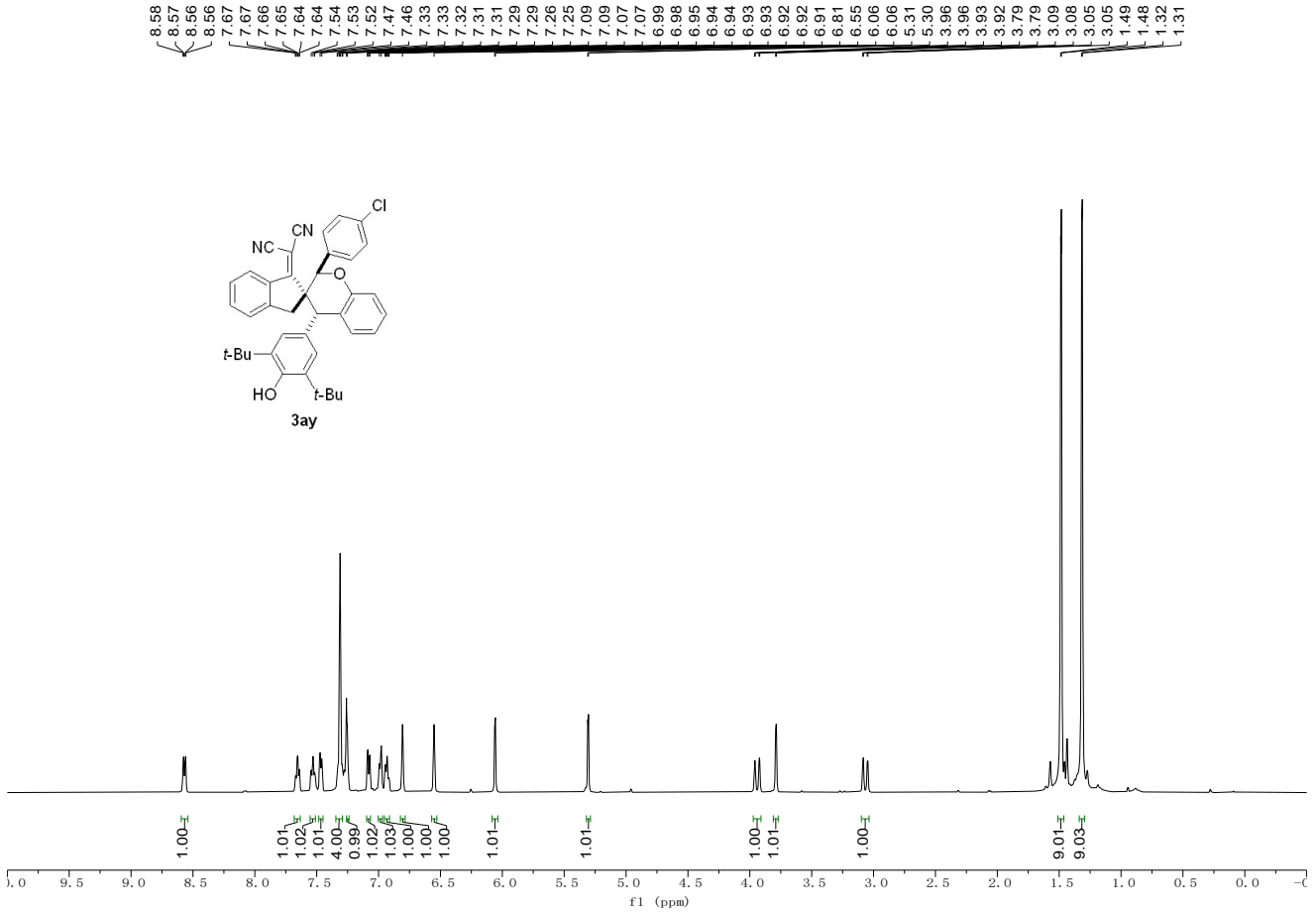
^{1}H NMR spectra for compound **3ax** (500 Hz, $CDCl_3$)



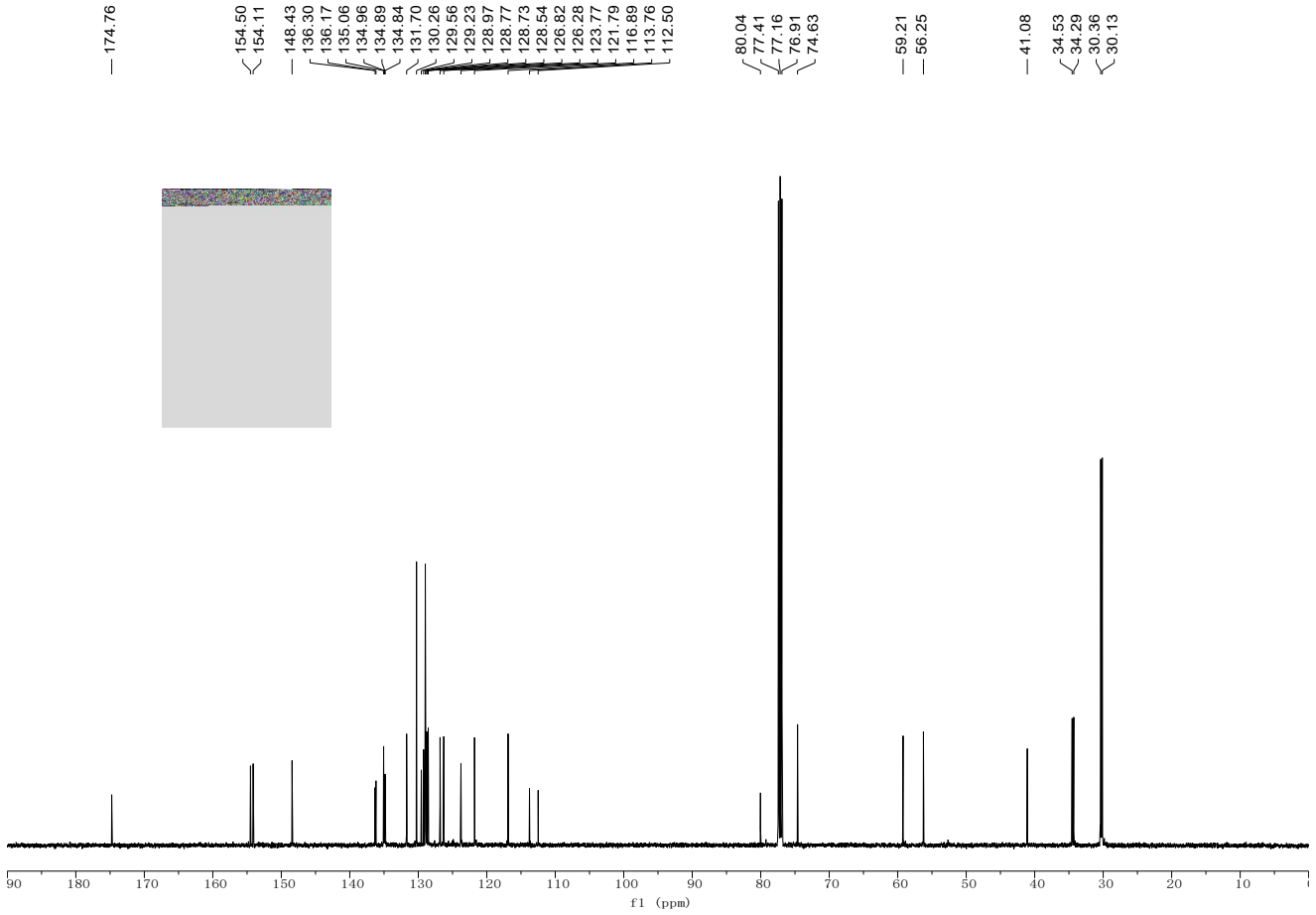
^{13}C NMR spectra for compound **3ax** (125 Hz, $CDCl_3$)



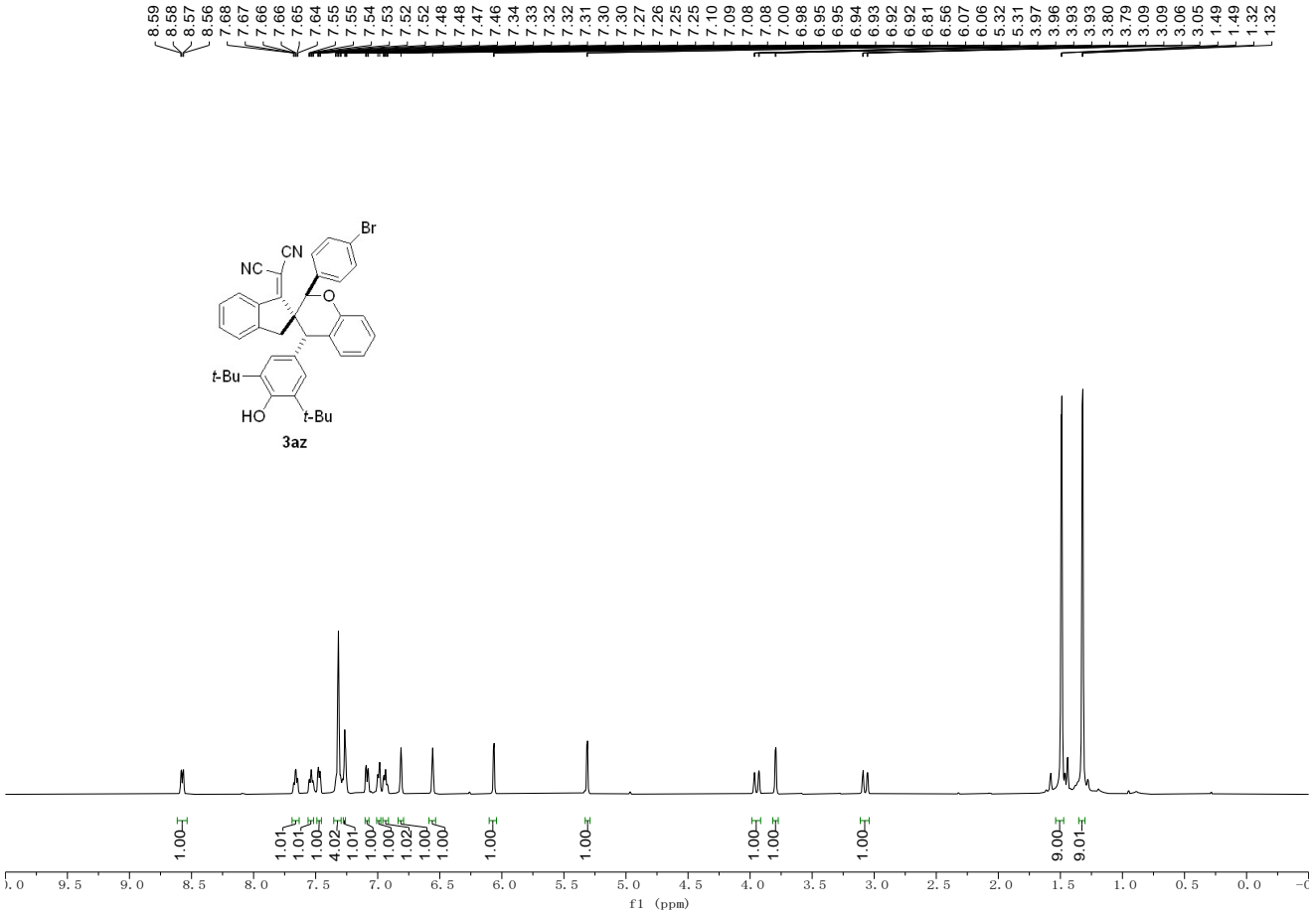
^{1}H NMR spectra for compound **3ay** (500 Hz, $CDCl_3$)



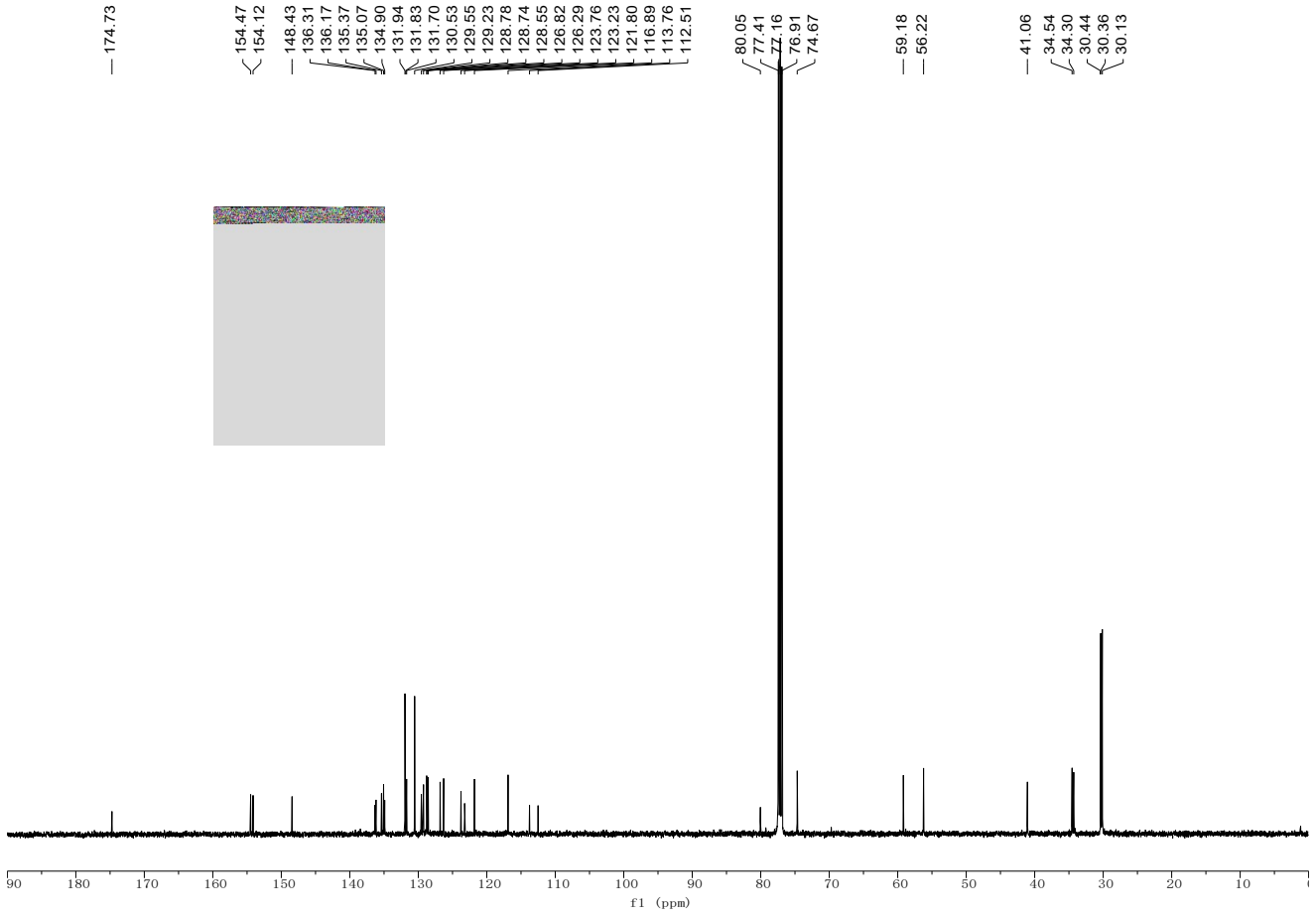
^{13}C NMR spectra for compound **3ay** (125 Hz, $CDCl_3$)



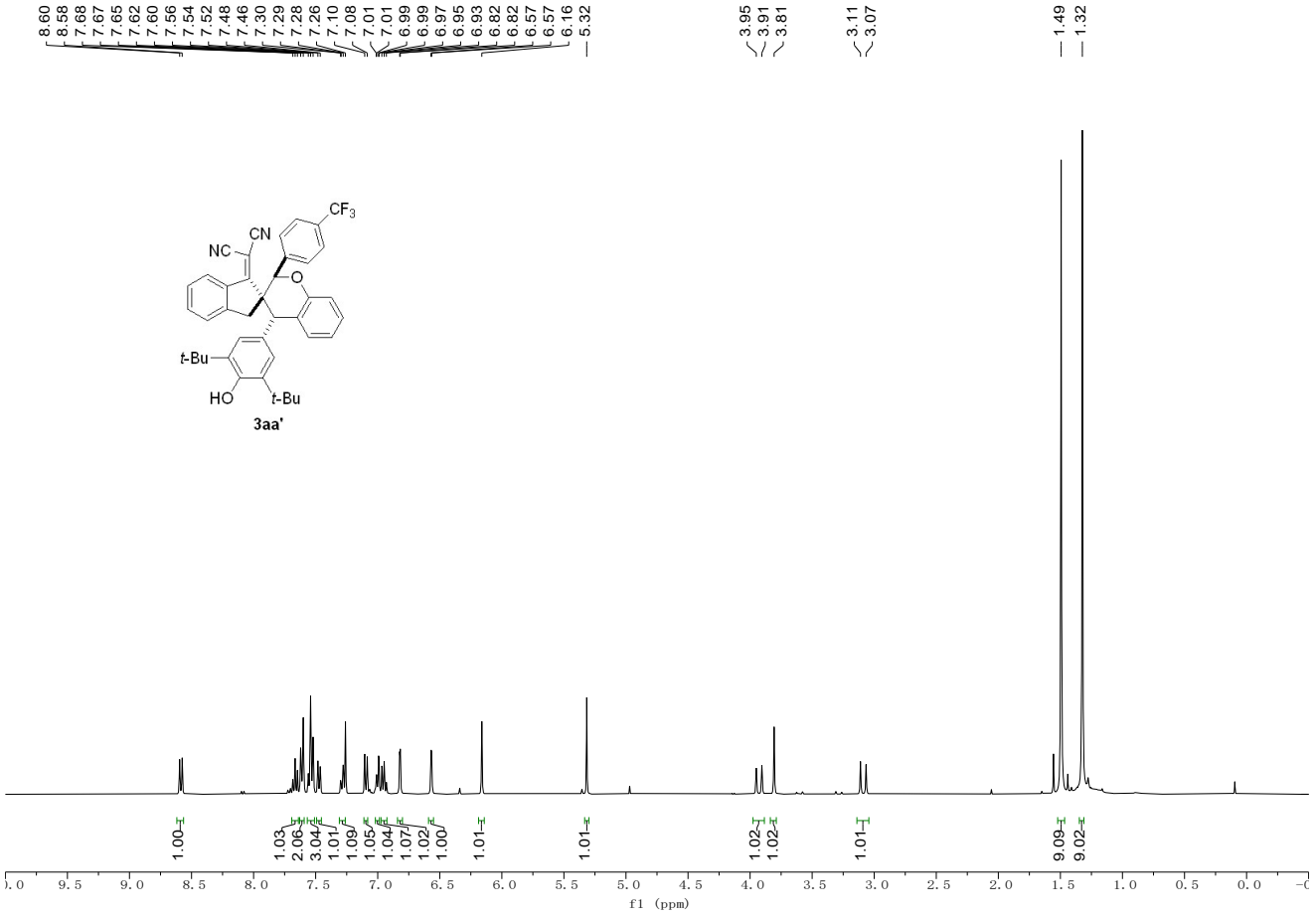
^{1}H NMR spectra for compound **3az** (500 Hz, $CDCl_3$)



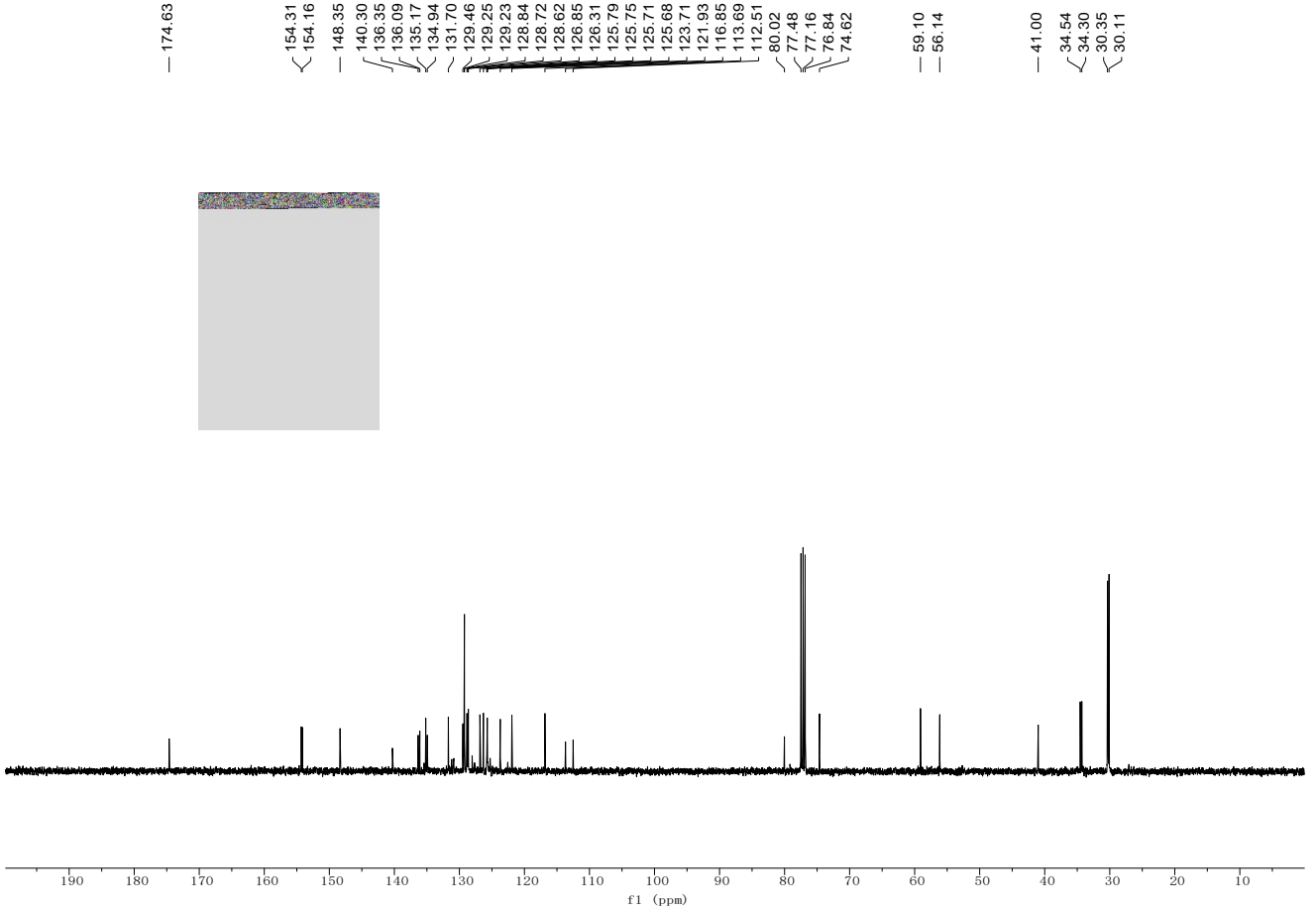
^{13}C NMR spectra for compound **3az** (125 Hz, $CDCl_3$)



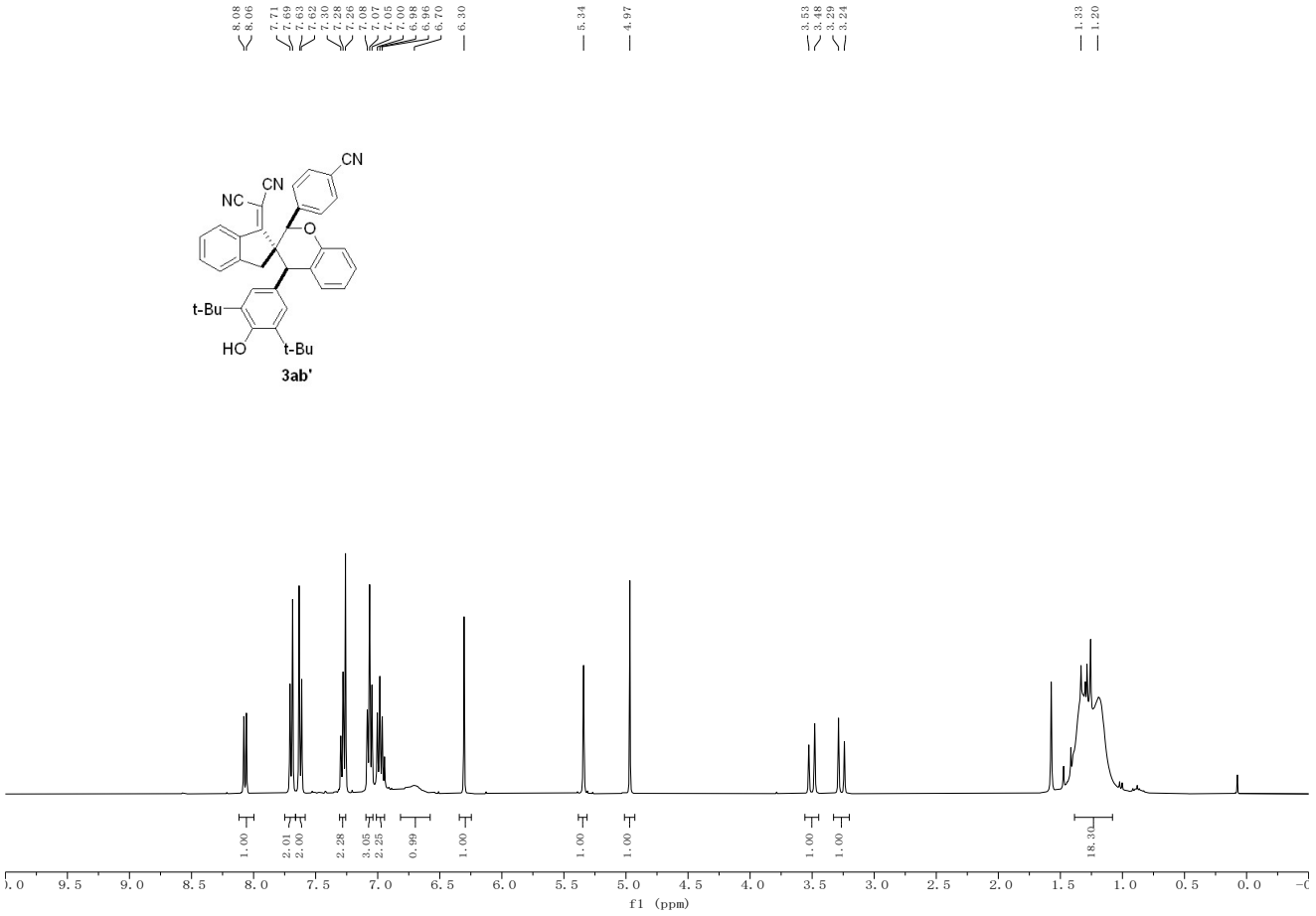
^{1}H NMR spectra for compound **3aa'** (500 Hz, $CDCl_3$)



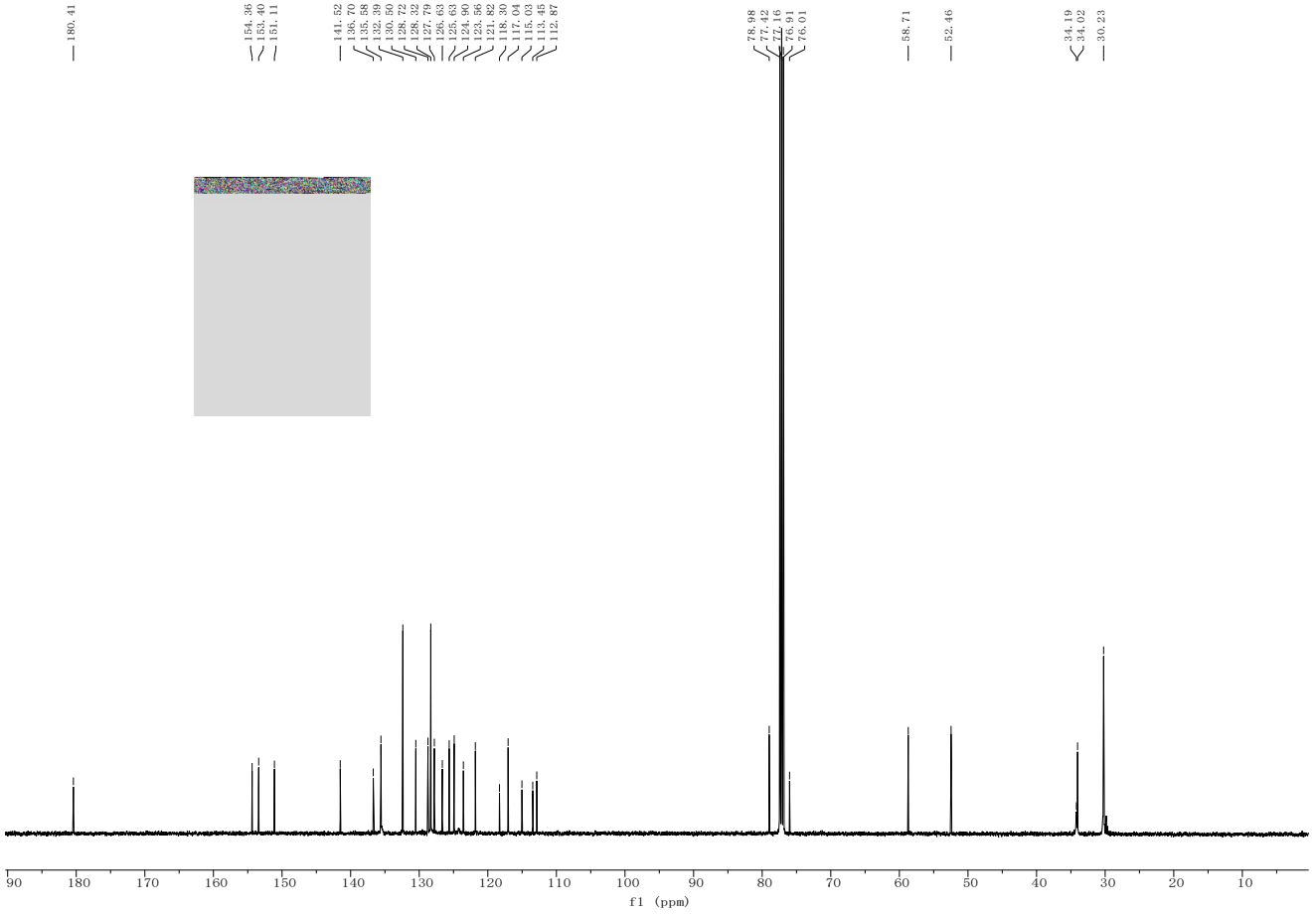
^{13}C NMR spectra for compound **3aa'** (125 Hz, $CDCl_3$)



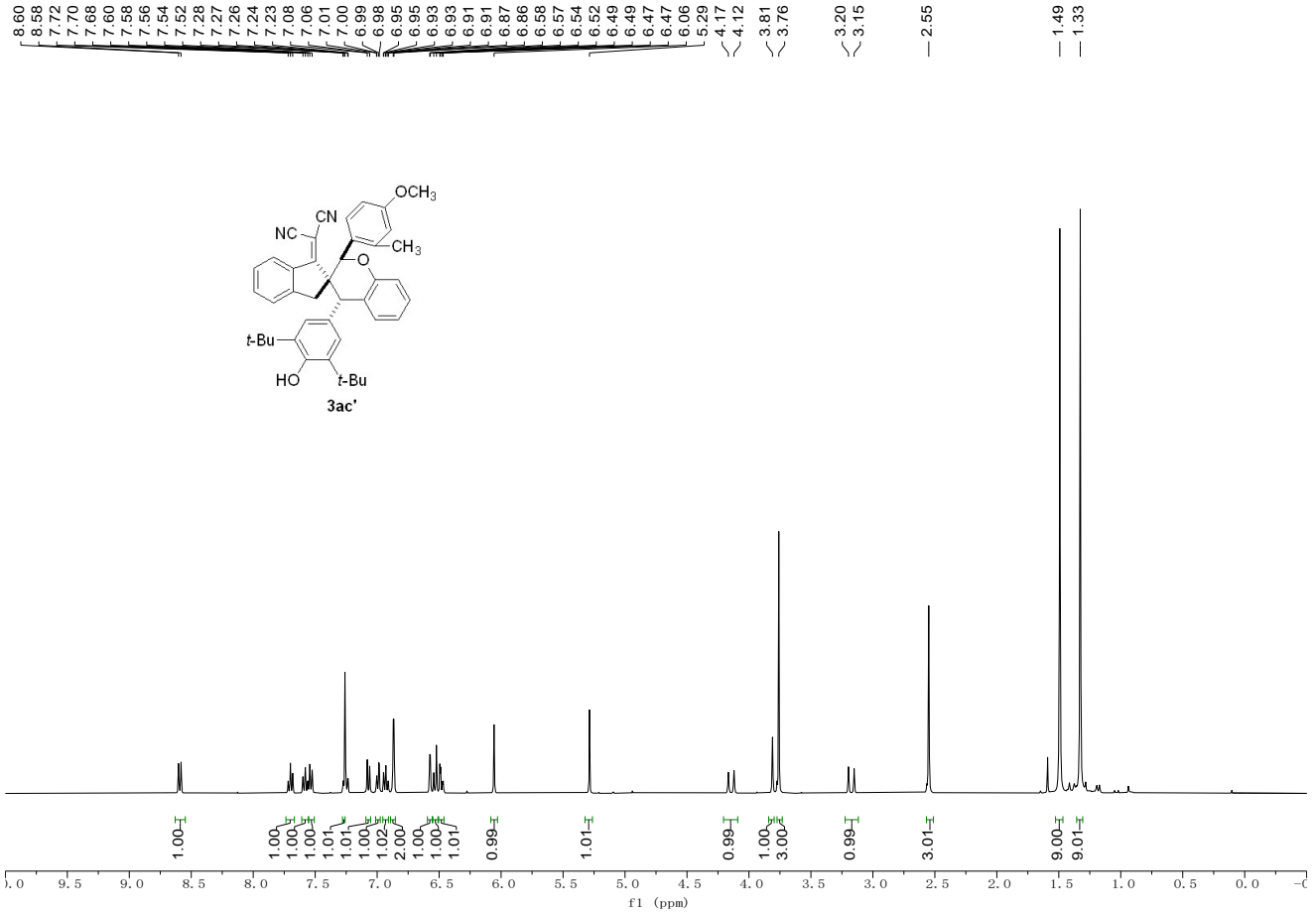
^{1}H NMR spectra for compound **3ab'** (500 Hz, $CDCl_3$)



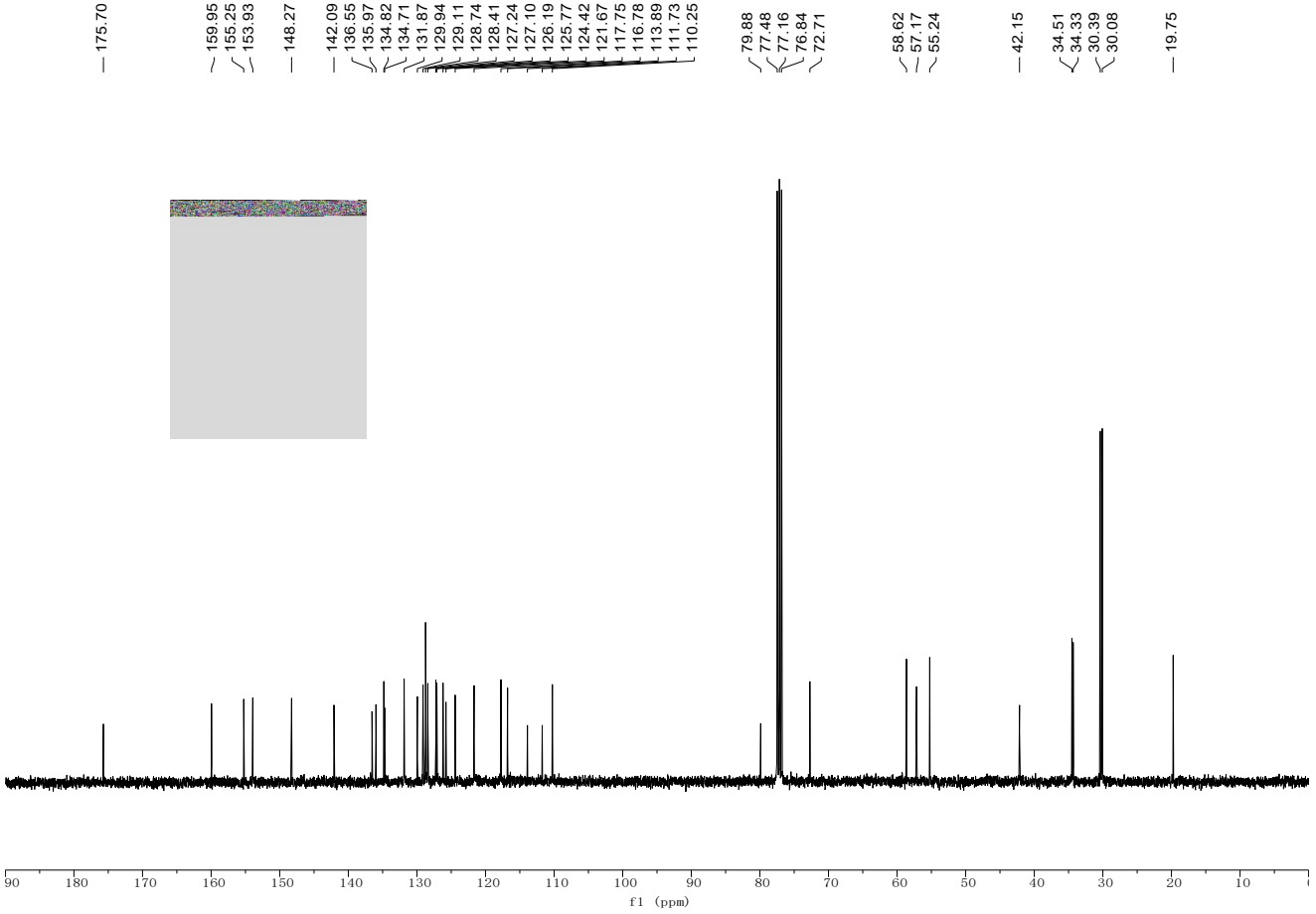
^{13}C NMR spectra for compound **3ab'** (125 Hz, $CDCl_3$)



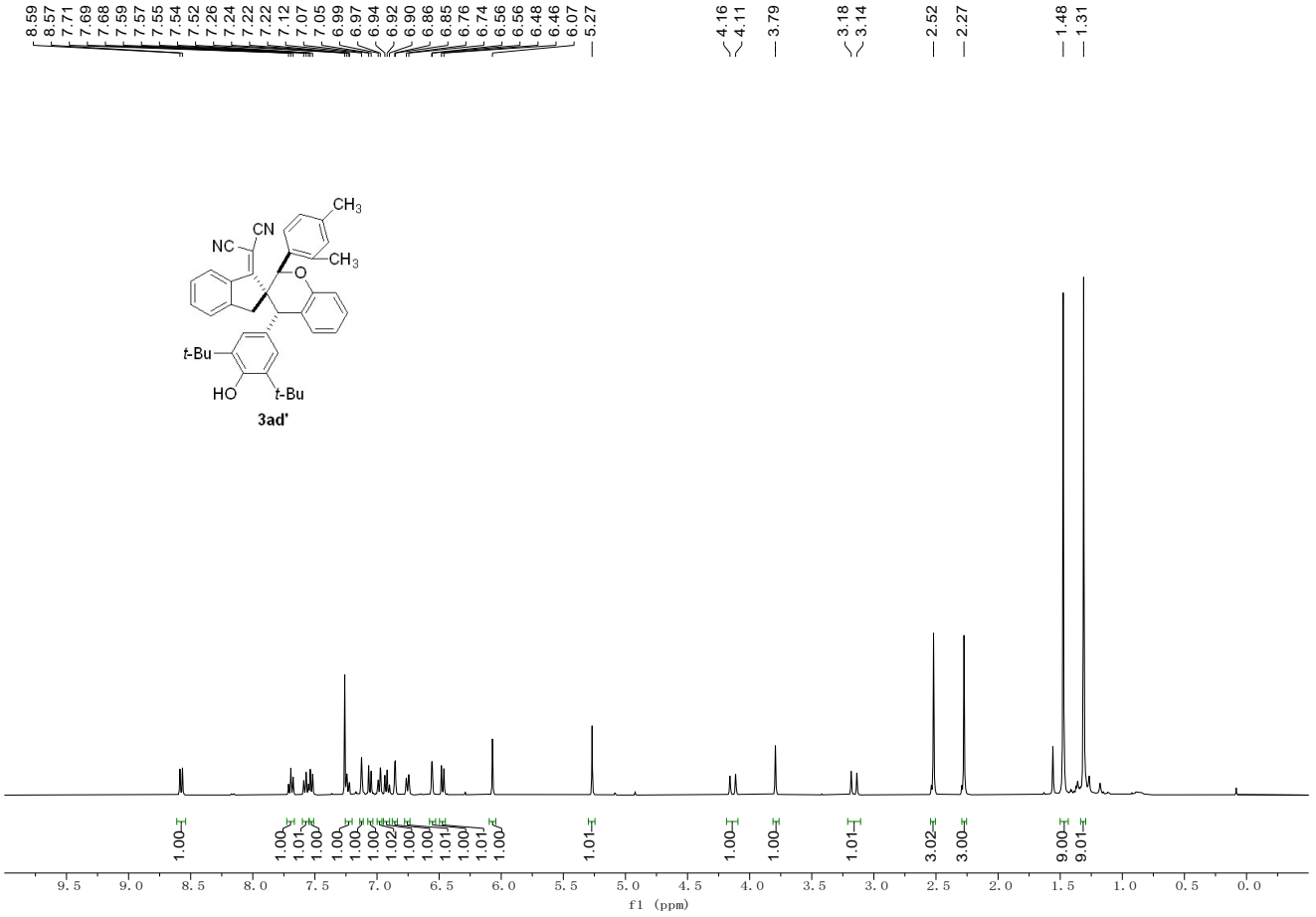
^{1}H NMR spectra for compound **3ac'** (400 Hz, $CDCl_3$)



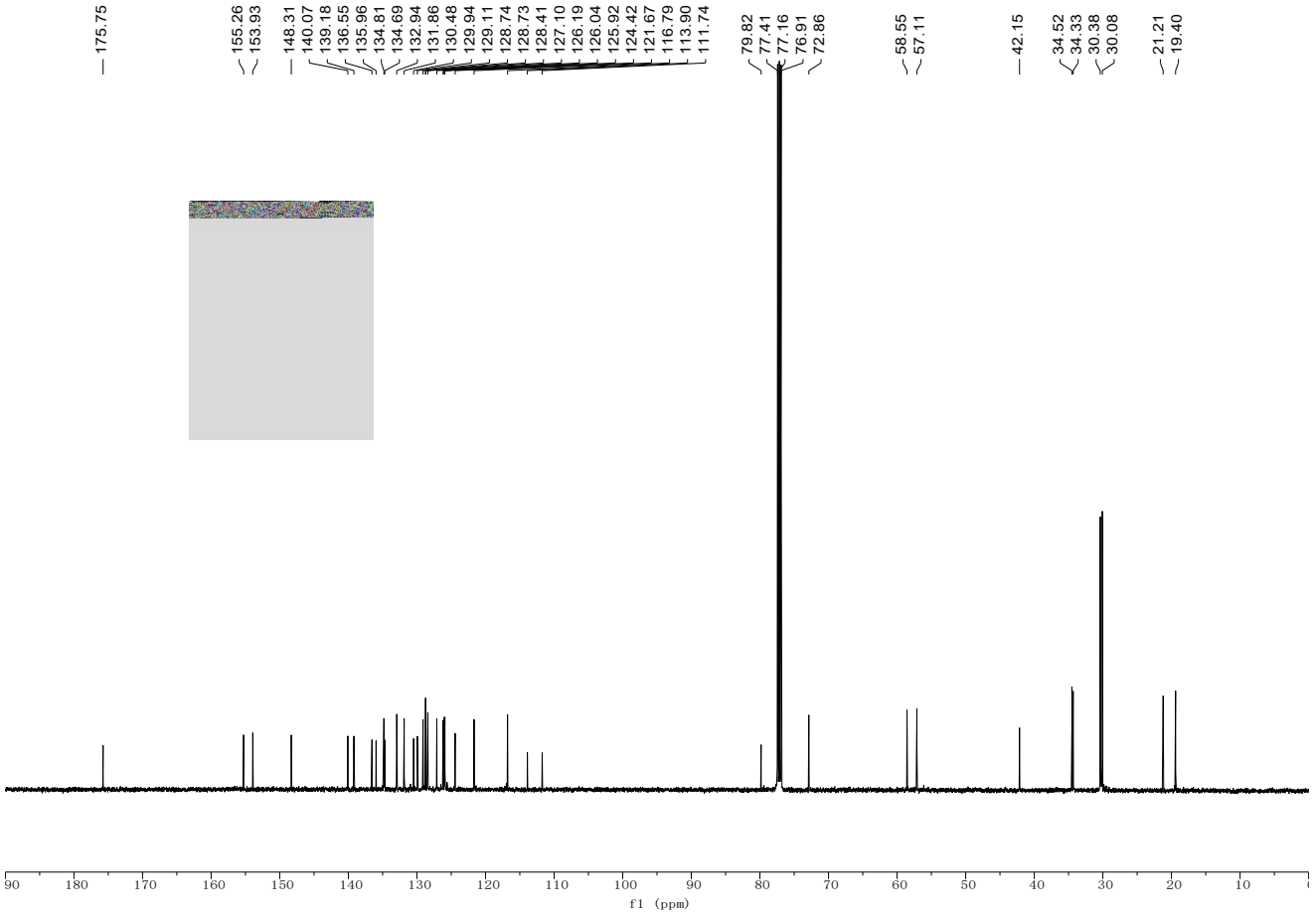
^{13}C NMR spectra for compound **3ac'** (100 Hz, $CDCl_3$)



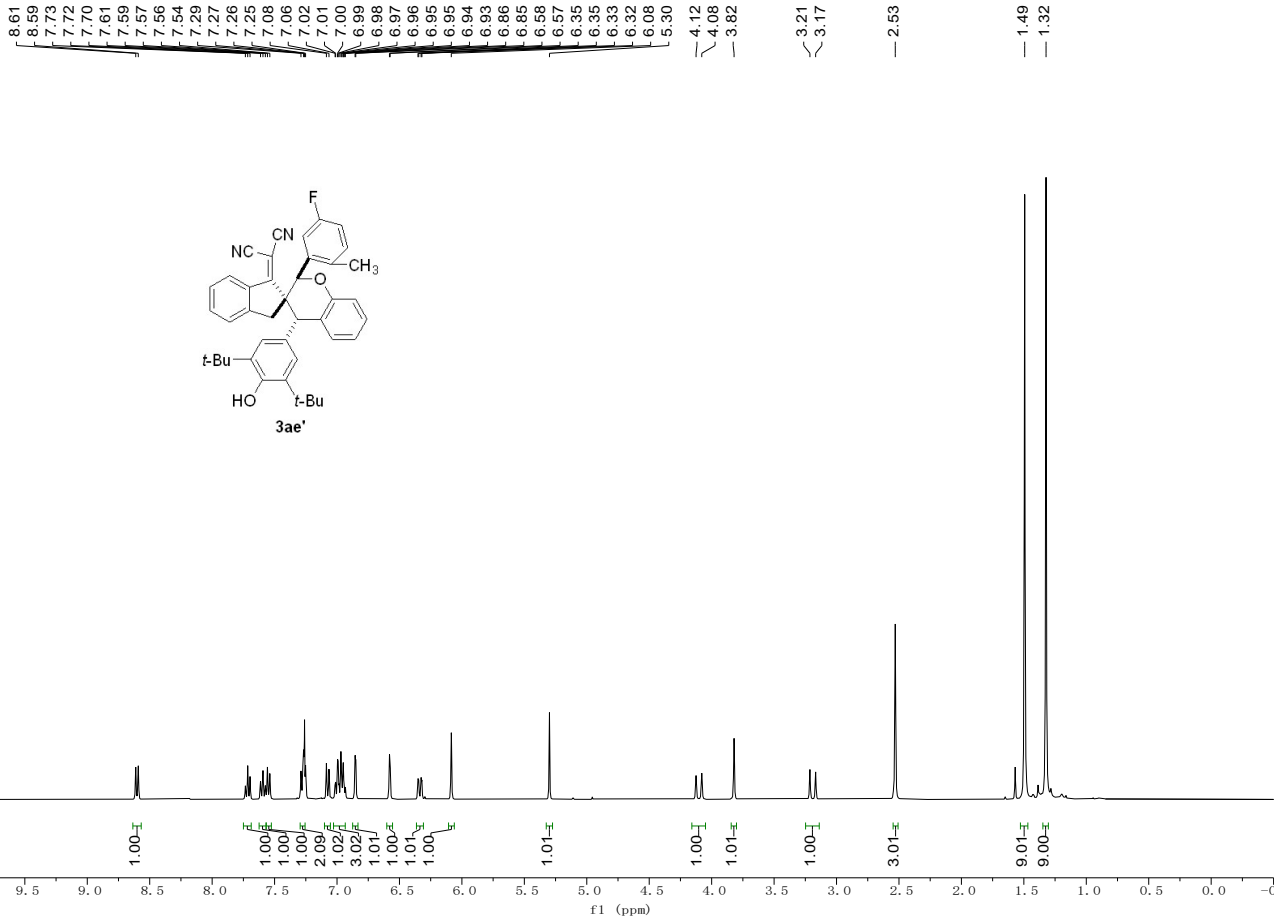
^{1}H NMR spectra for compound **3ad'** (400 Hz, $CDCl_3$)



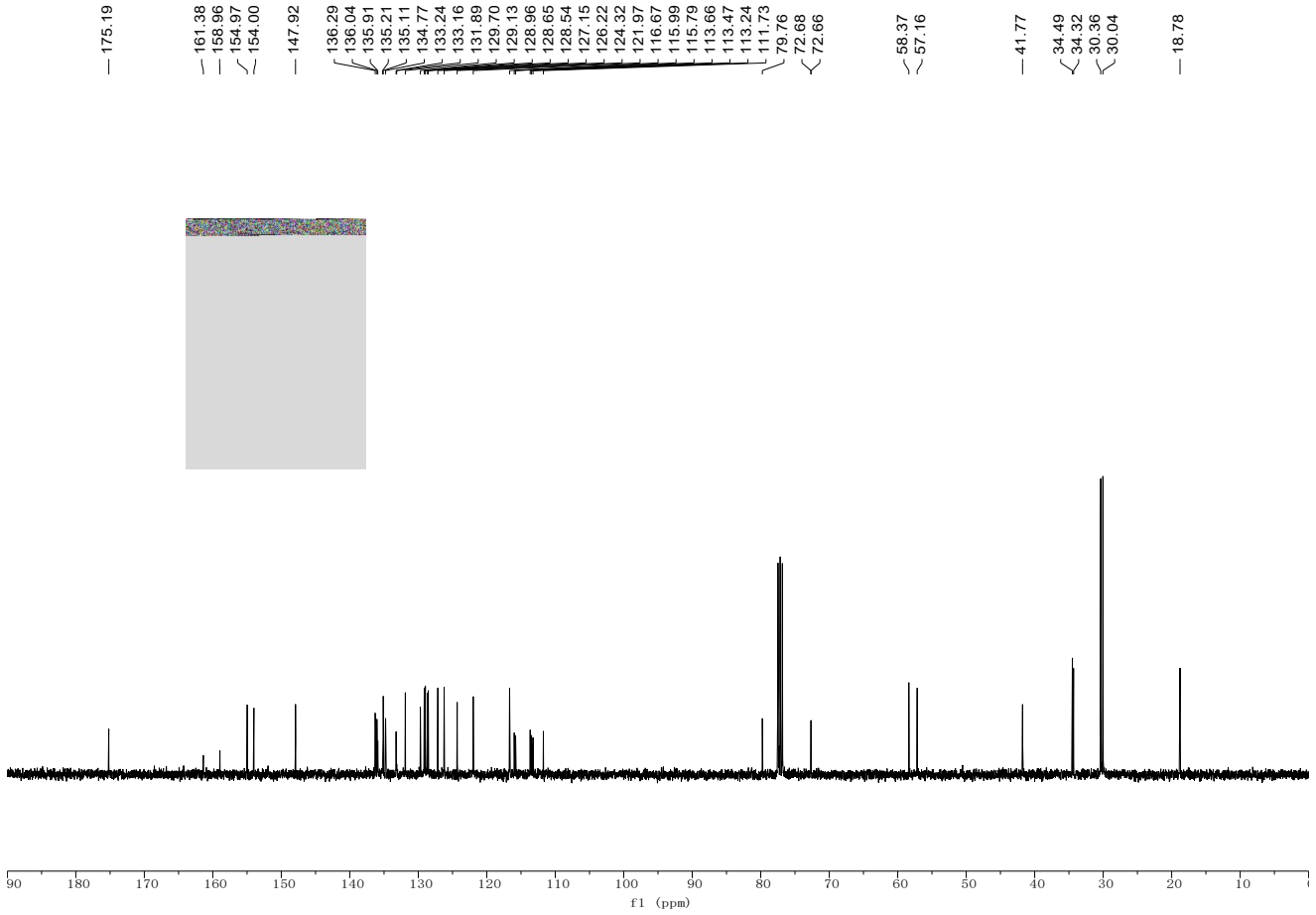
^{13}C NMR spectra for compound **3ad'** (125 Hz, $CDCl_3$)



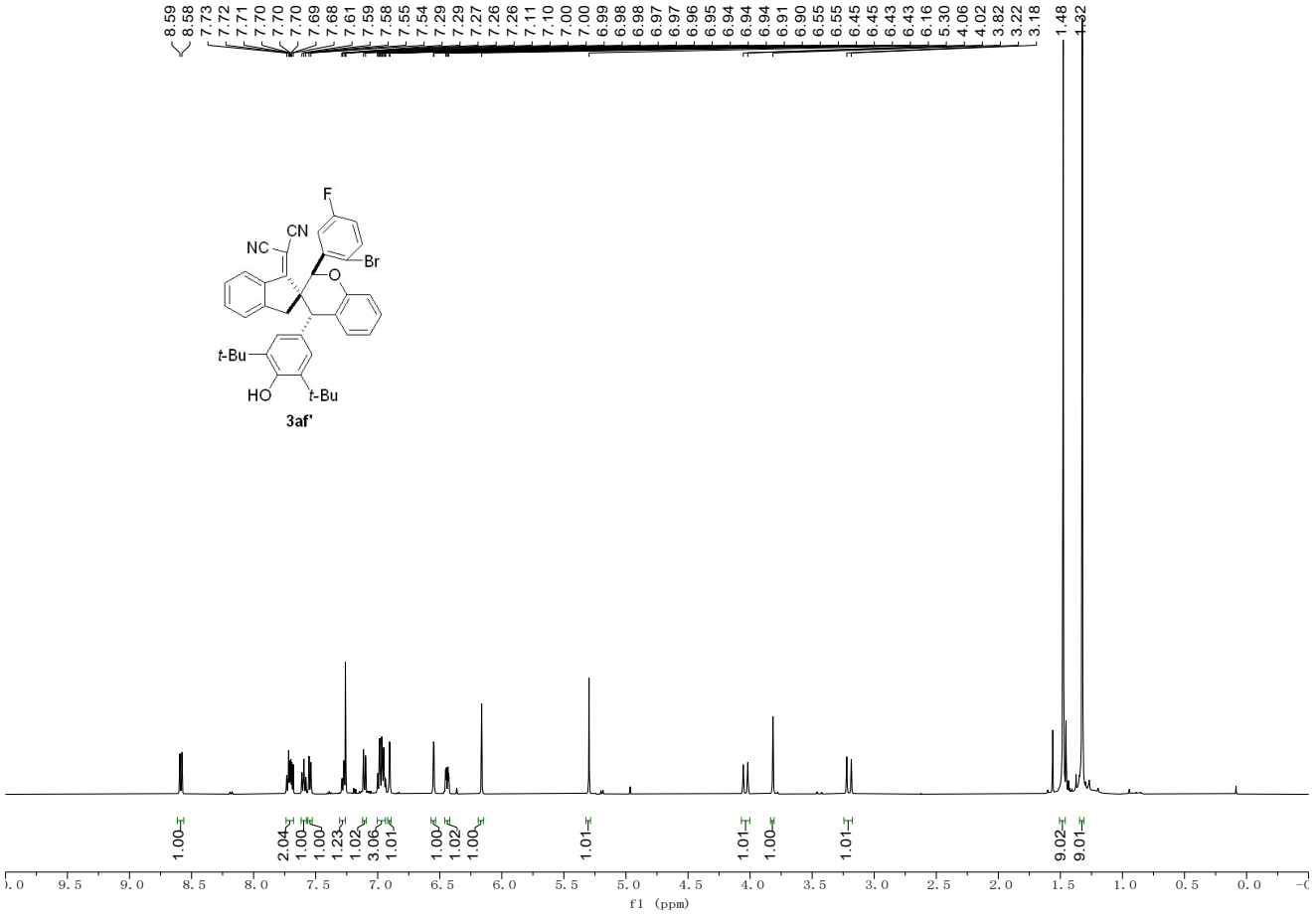
^{1}H NMR spectra for compound **3ae'** (400 Hz, $CDCl_3$)



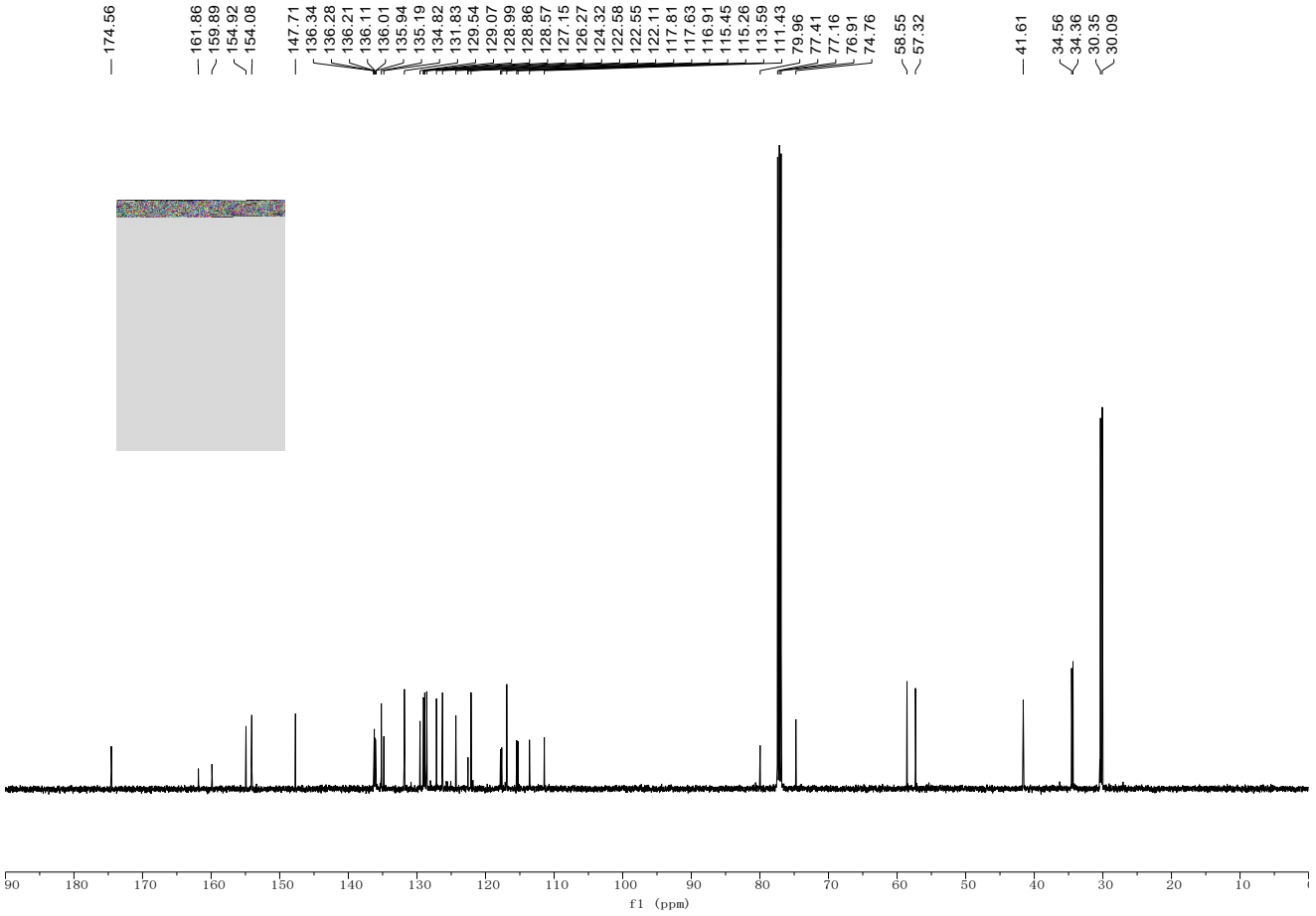
^{13}C NMR spectra for compound **3ae'** (100 Hz, $CDCl_3$)



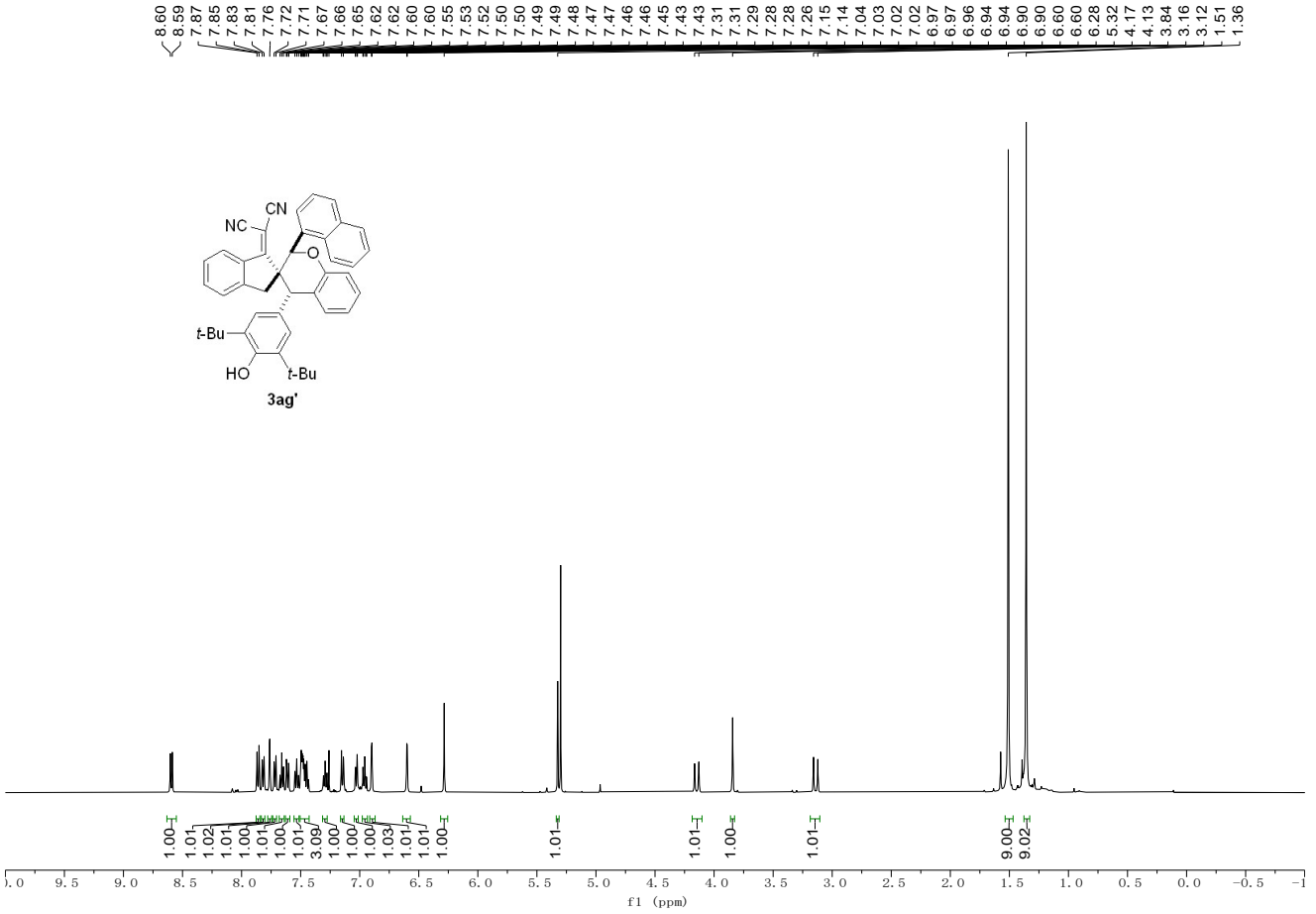
^{1}H NMR spectra for compound **3af'** (500 Hz, $CDCl_3$)



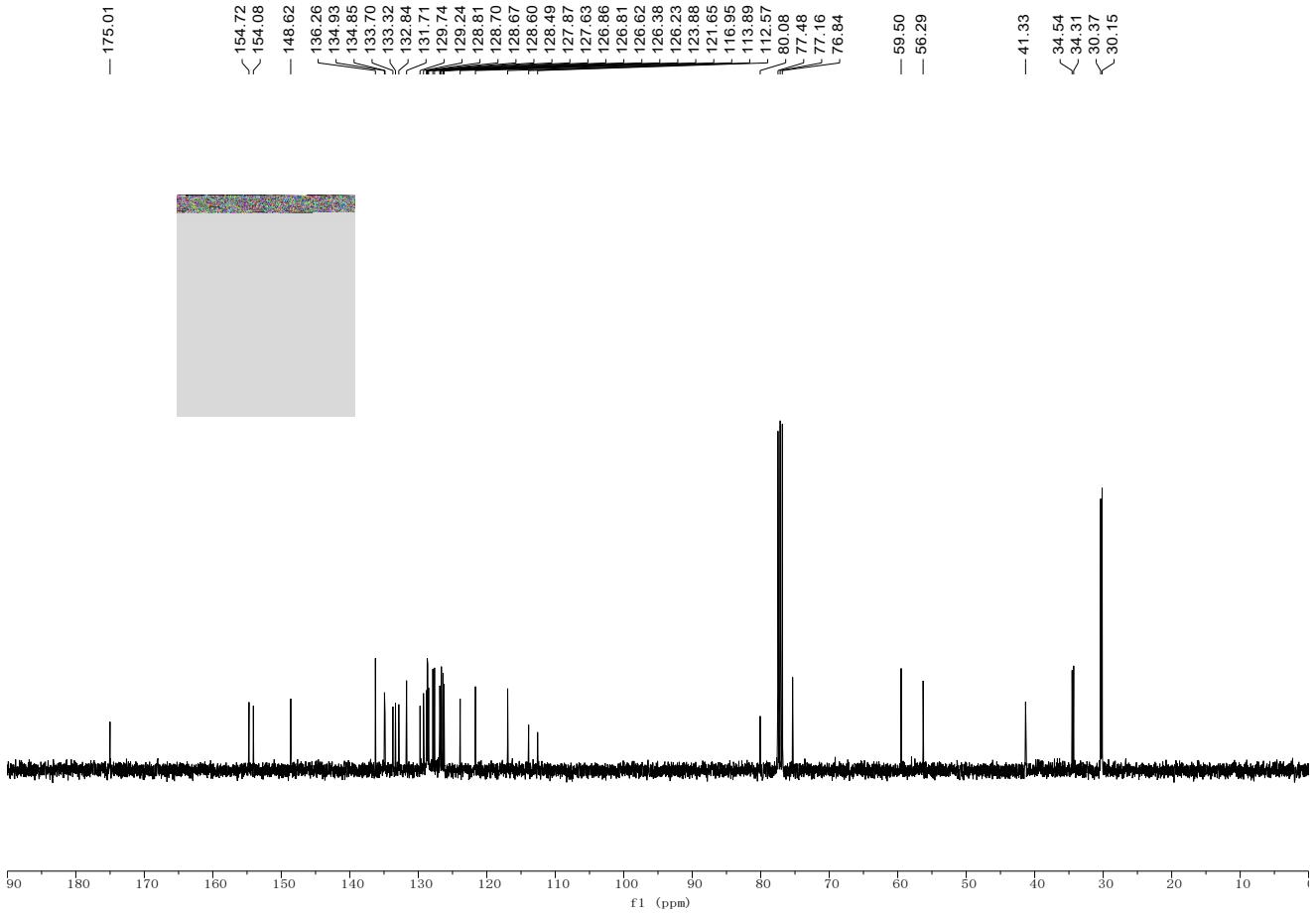
^{13}C NMR spectra for compound **3af'** (125 Hz, $CDCl_3$)



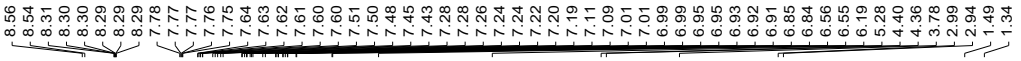
^{1}H NMR spectra for compound **3ag'** (500 Hz, $CDCl_3$)

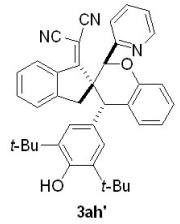


^{13}C NMR spectra for compound **3ag'** (100 Hz, $CDCl_3$)



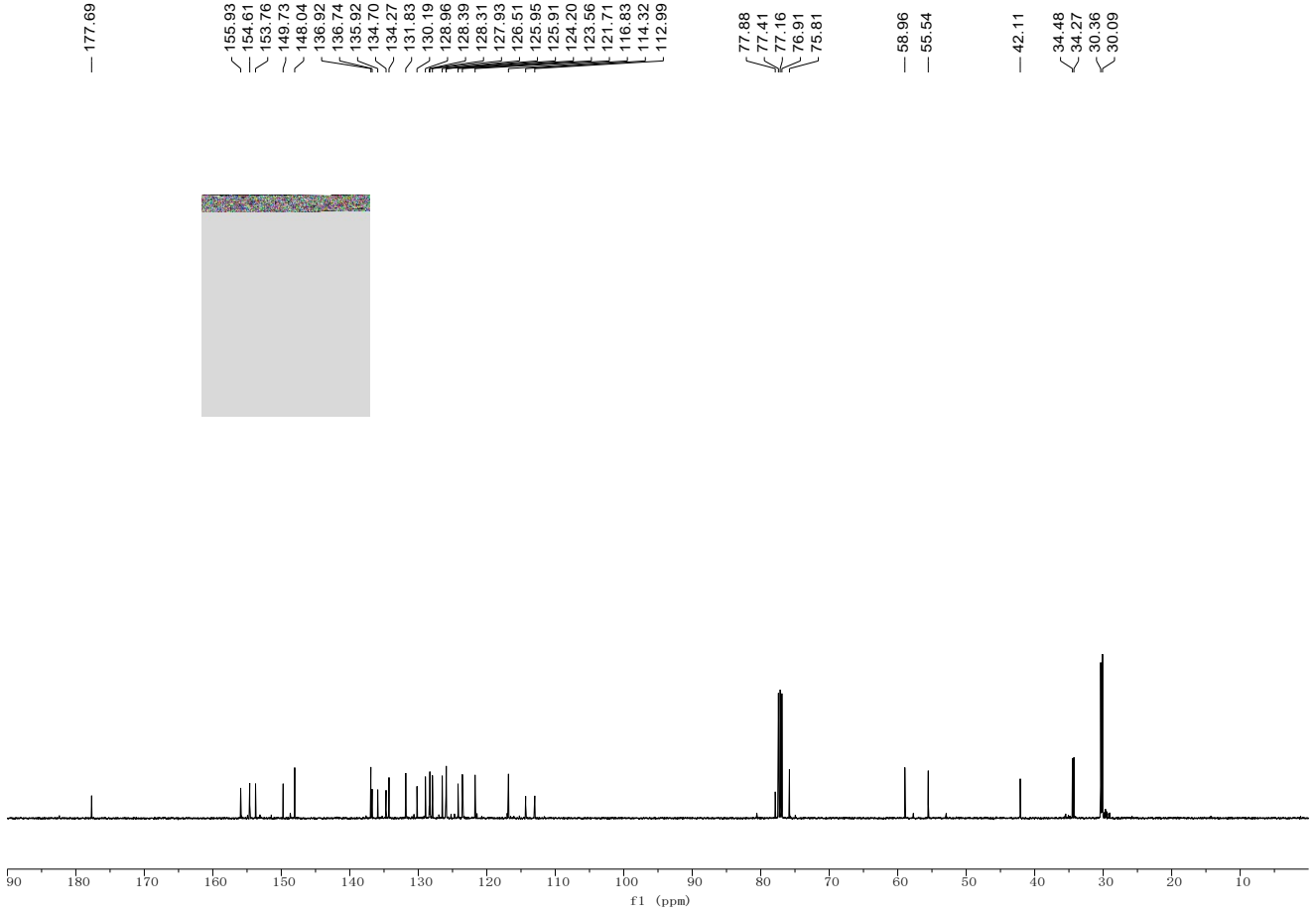
^{1}H NMR spectra for compound **3ah'** (400 Hz, $CDCl_3$)



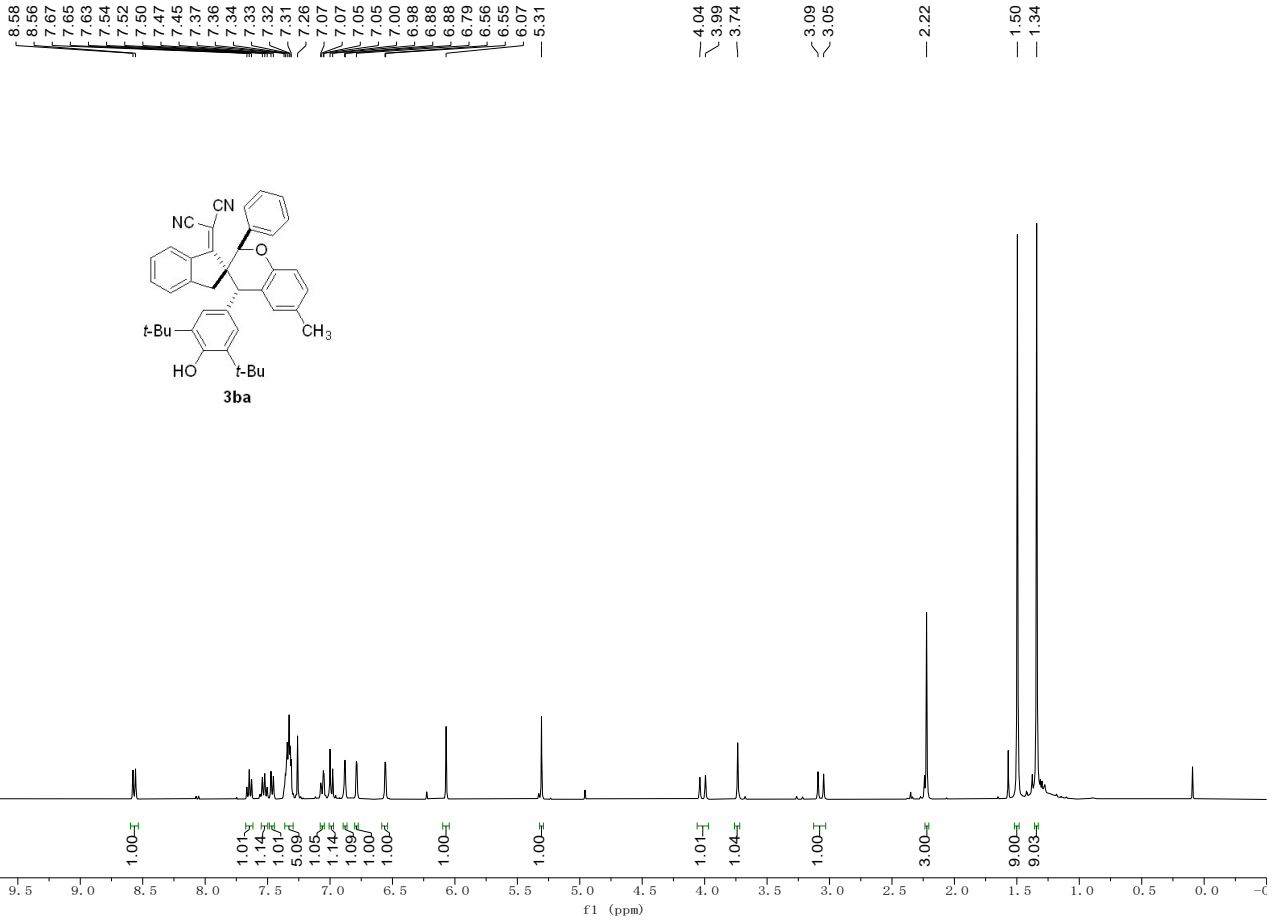


3ah'

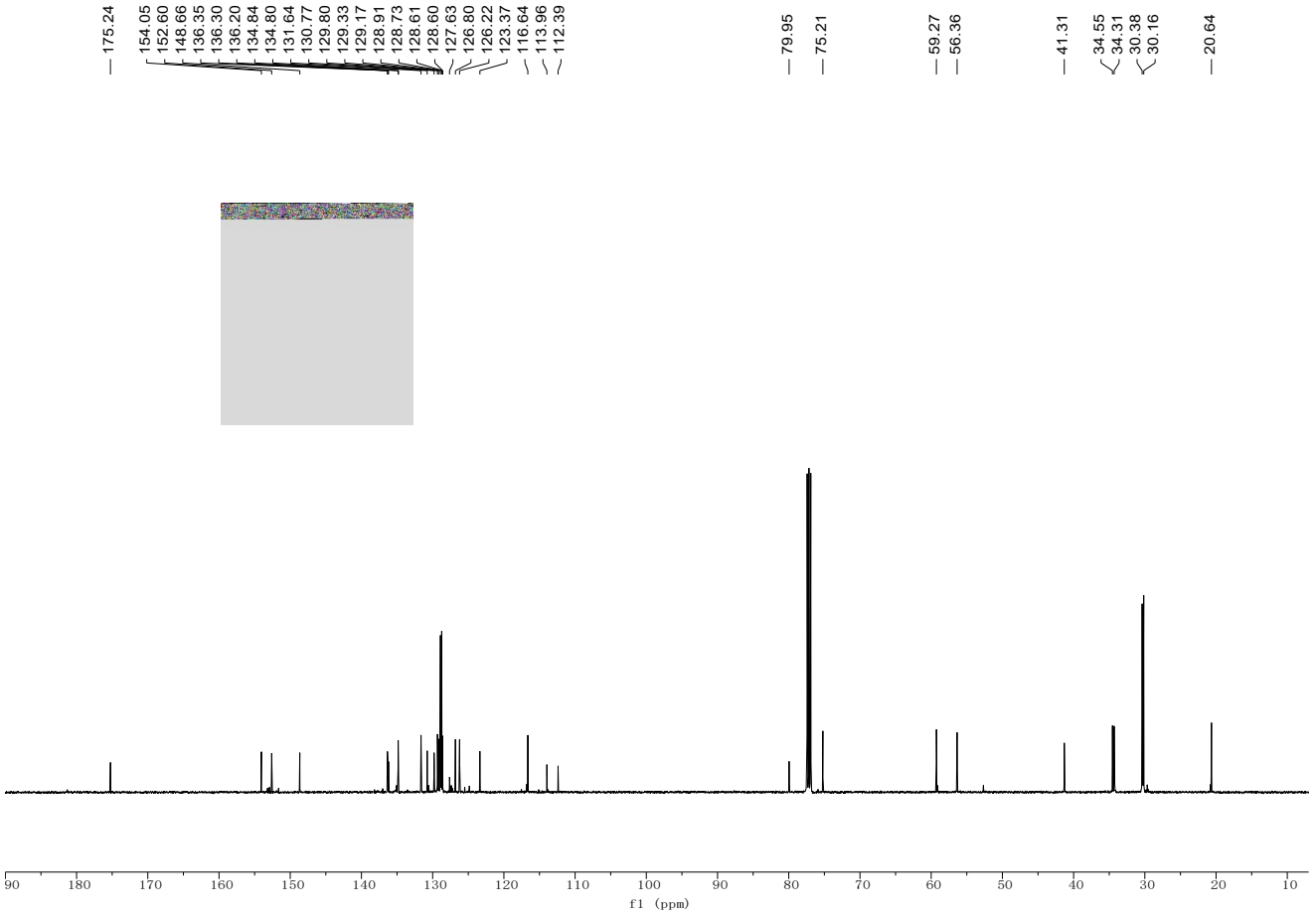
^{13}C NMR spectra for compound **3ah'** (125 Hz, $CDCl_3$)



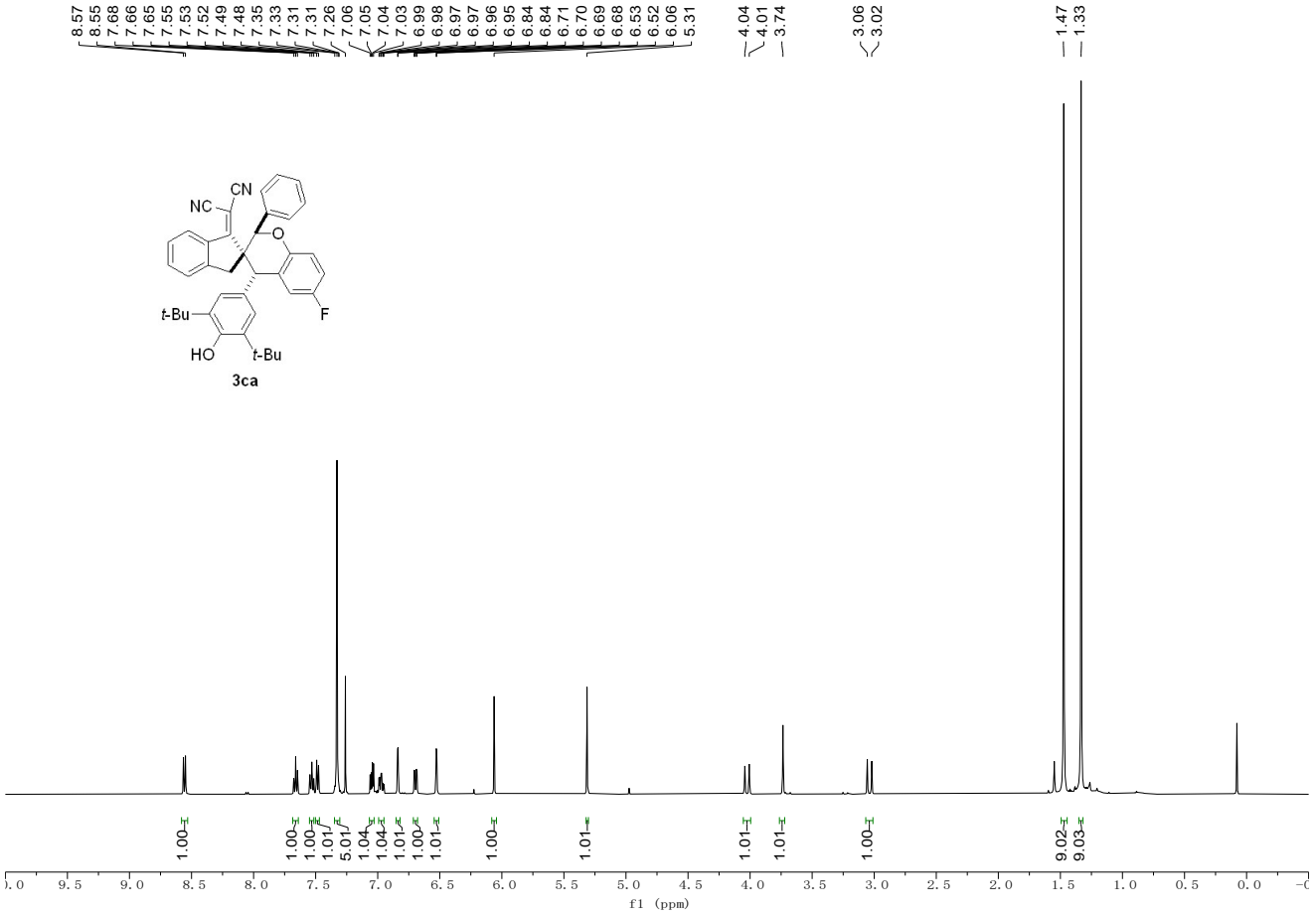
^{1}H NMR spectra for compound **3ba** (400 Hz, $CDCl_3$)



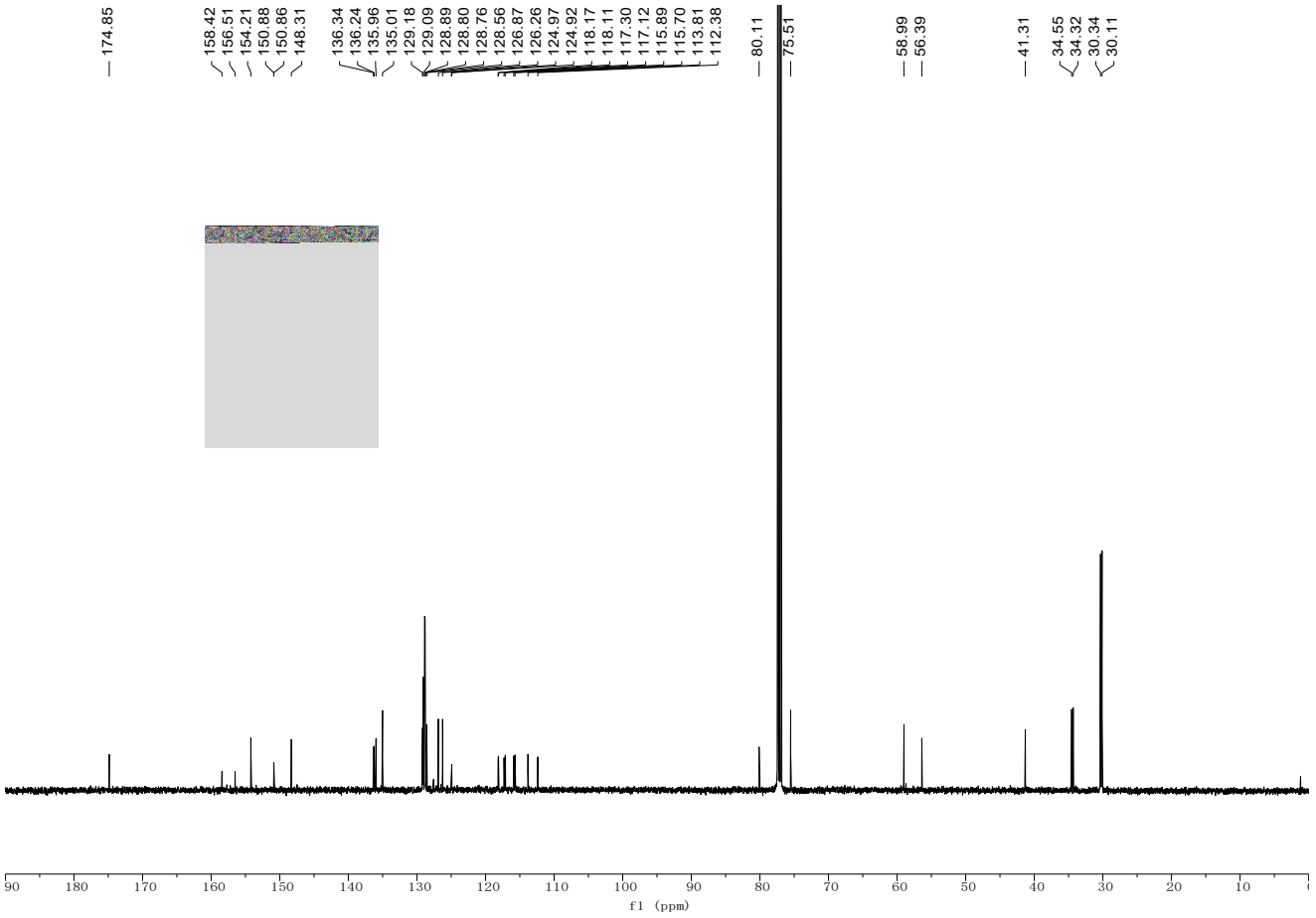
^{13}C NMR spectra for compound **3ba** (125 Hz, $CDCl_3$)



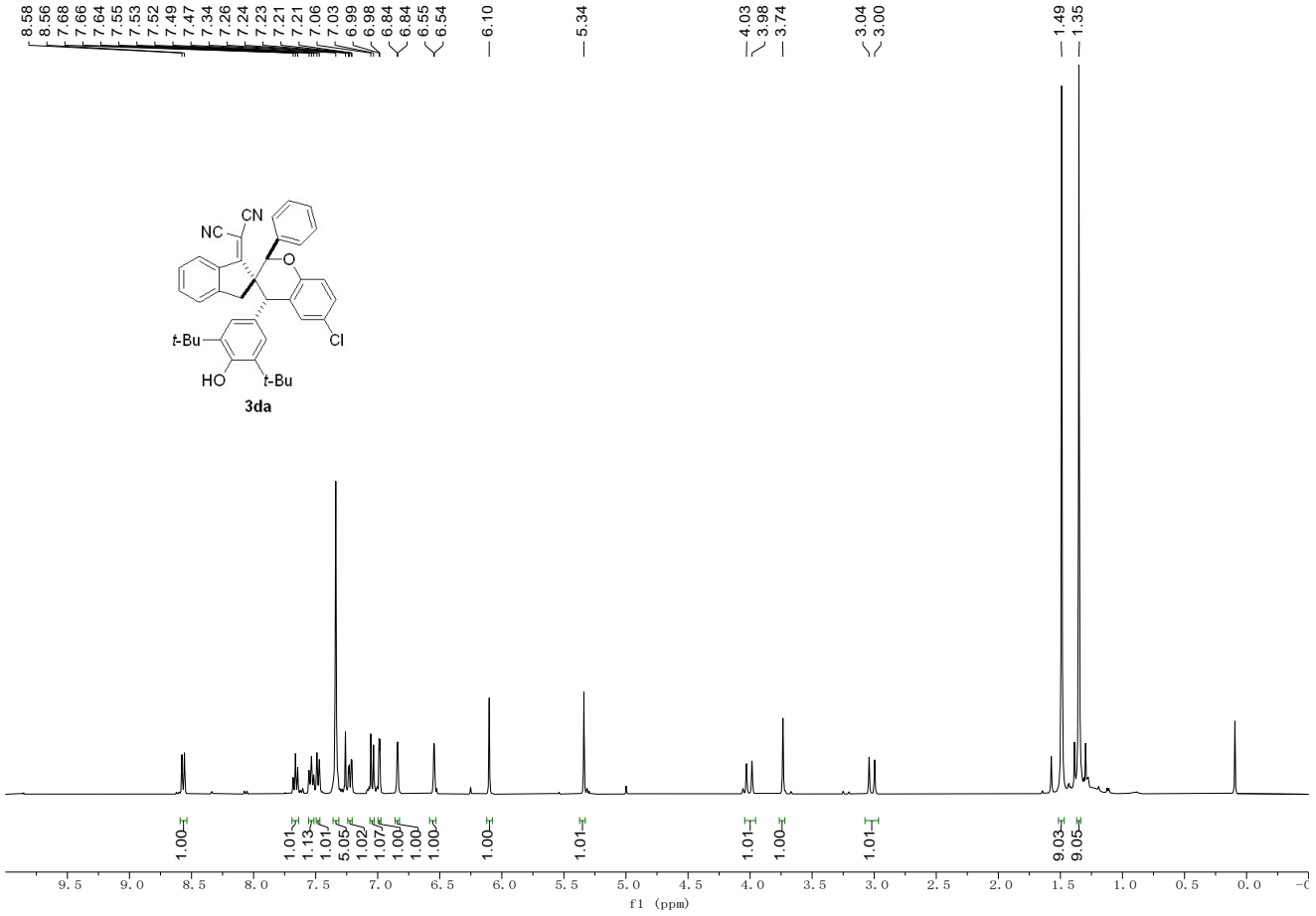
^{1}H NMR spectra for compound **3ca** (500 Hz, $CDCl_3$)



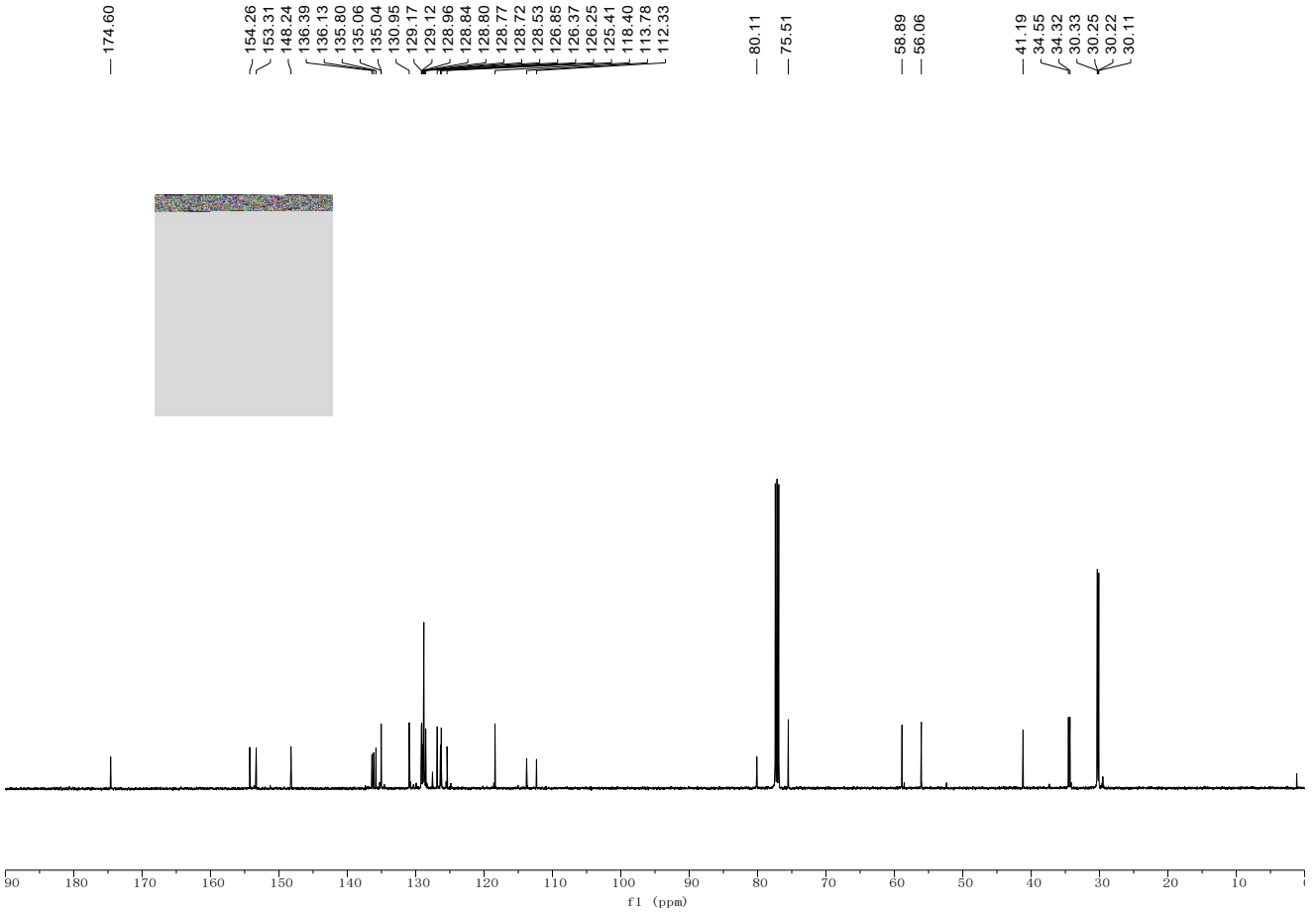
^{13}C NMR spectra for compound **3ca** (125 Hz, $CDCl_3$)



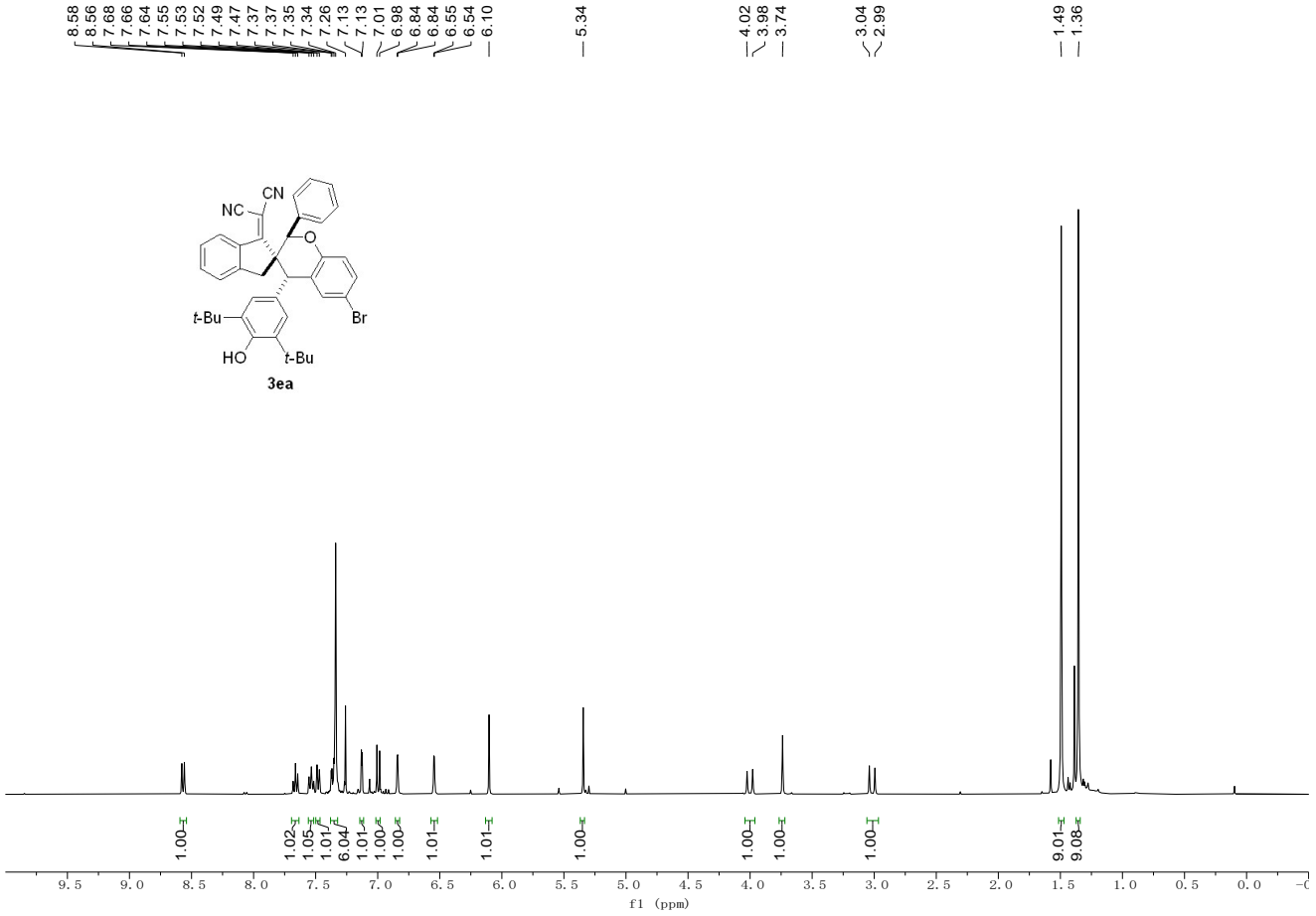
^{1}H NMR spectra for compound **3da** (400 Hz, $CDCl_3$)



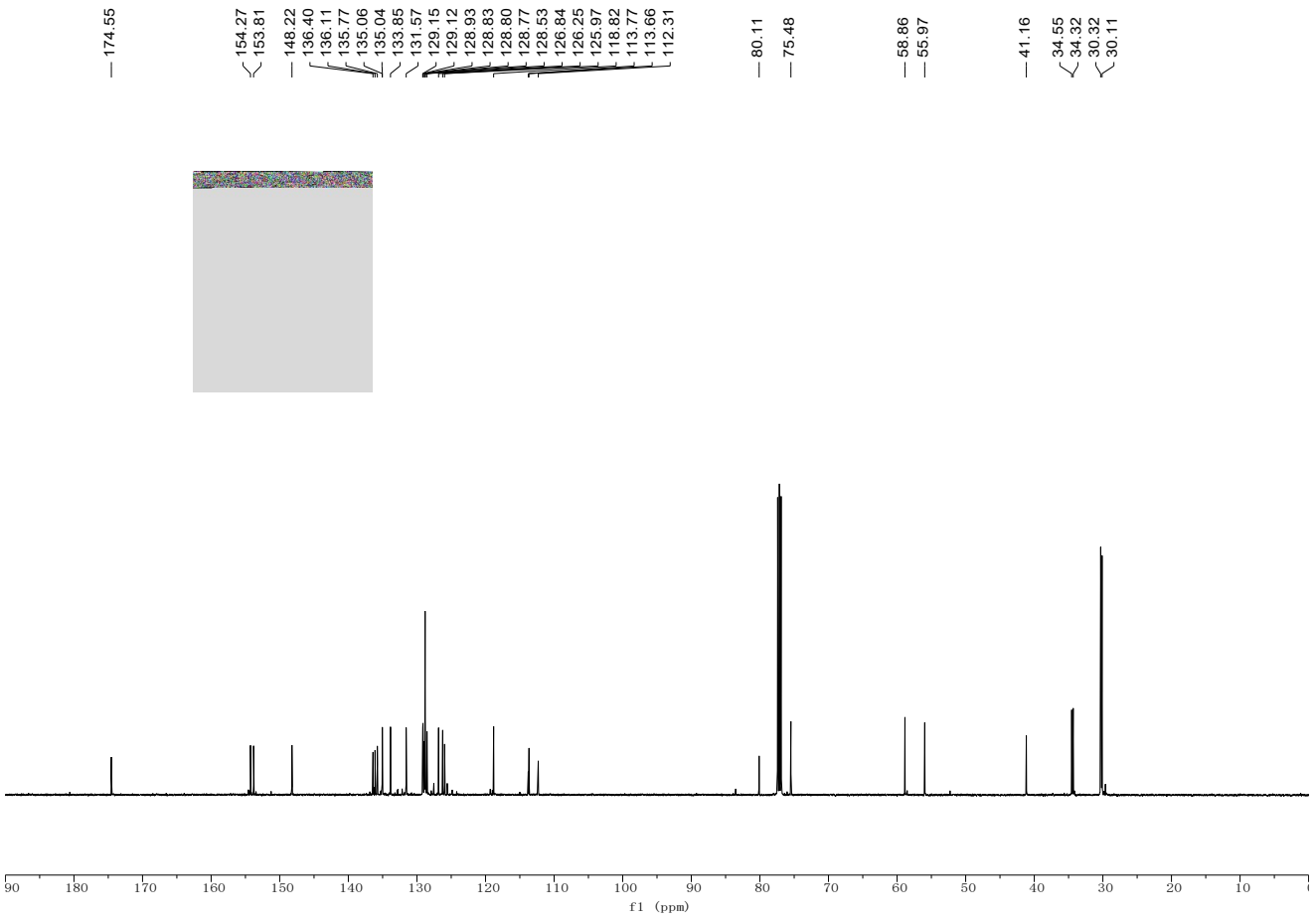
^{13}C NMR spectra for compound **3da** (125 Hz, $CDCl_3$)



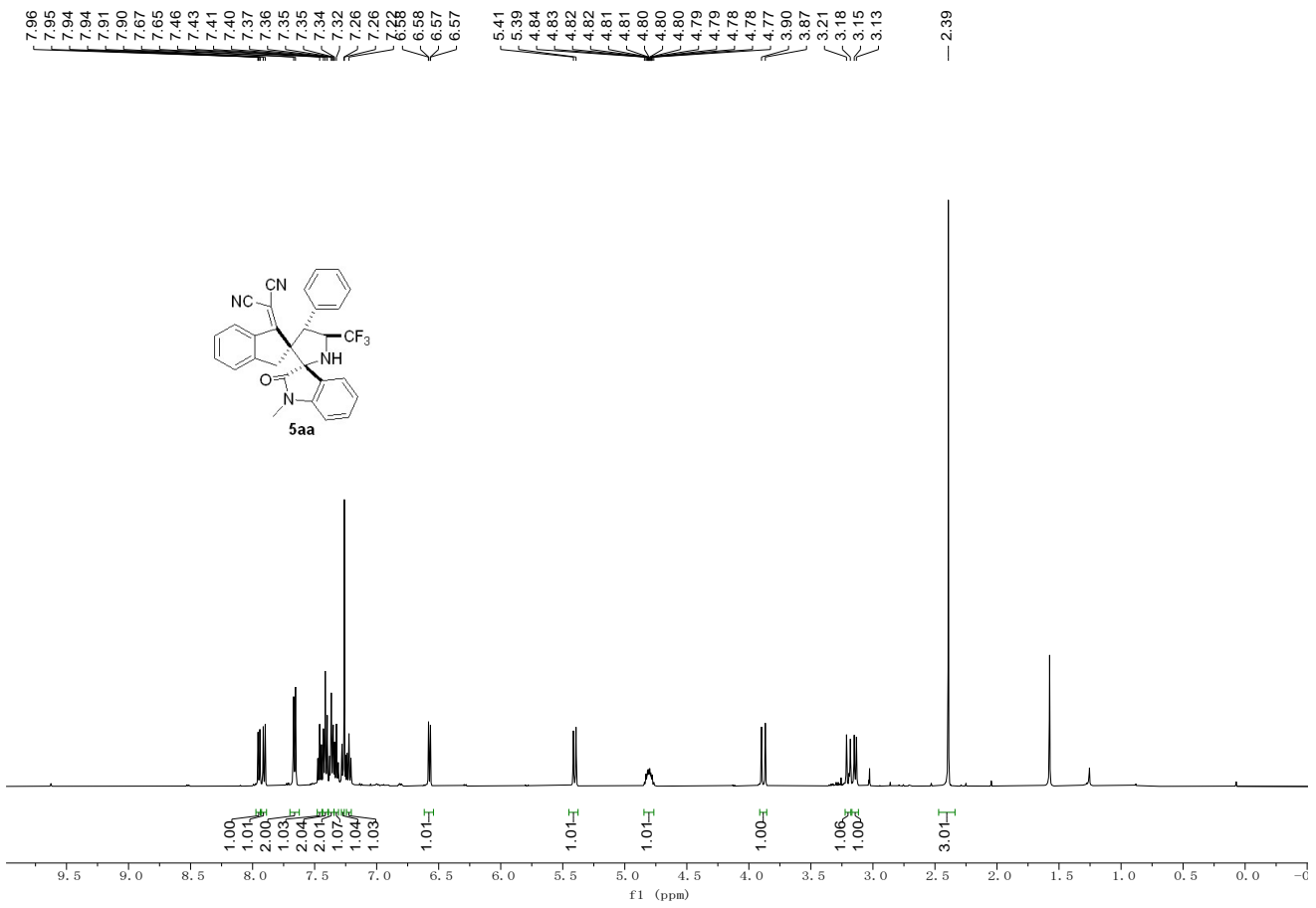
^{1}H NMR spectra for compound **3ea** (400 Hz, $CDCl_3$)



^{13}C NMR spectra for compound **3ea** (125 Hz, $CDCl_3$)



^{1}H NMR spectra for compound **5aa** (500 Hz, $CDCl_3$)


7.96
7.95
7.94
7.94
7.91
7.90
7.67
7.65
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7.41
7.40
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4.84
4.83
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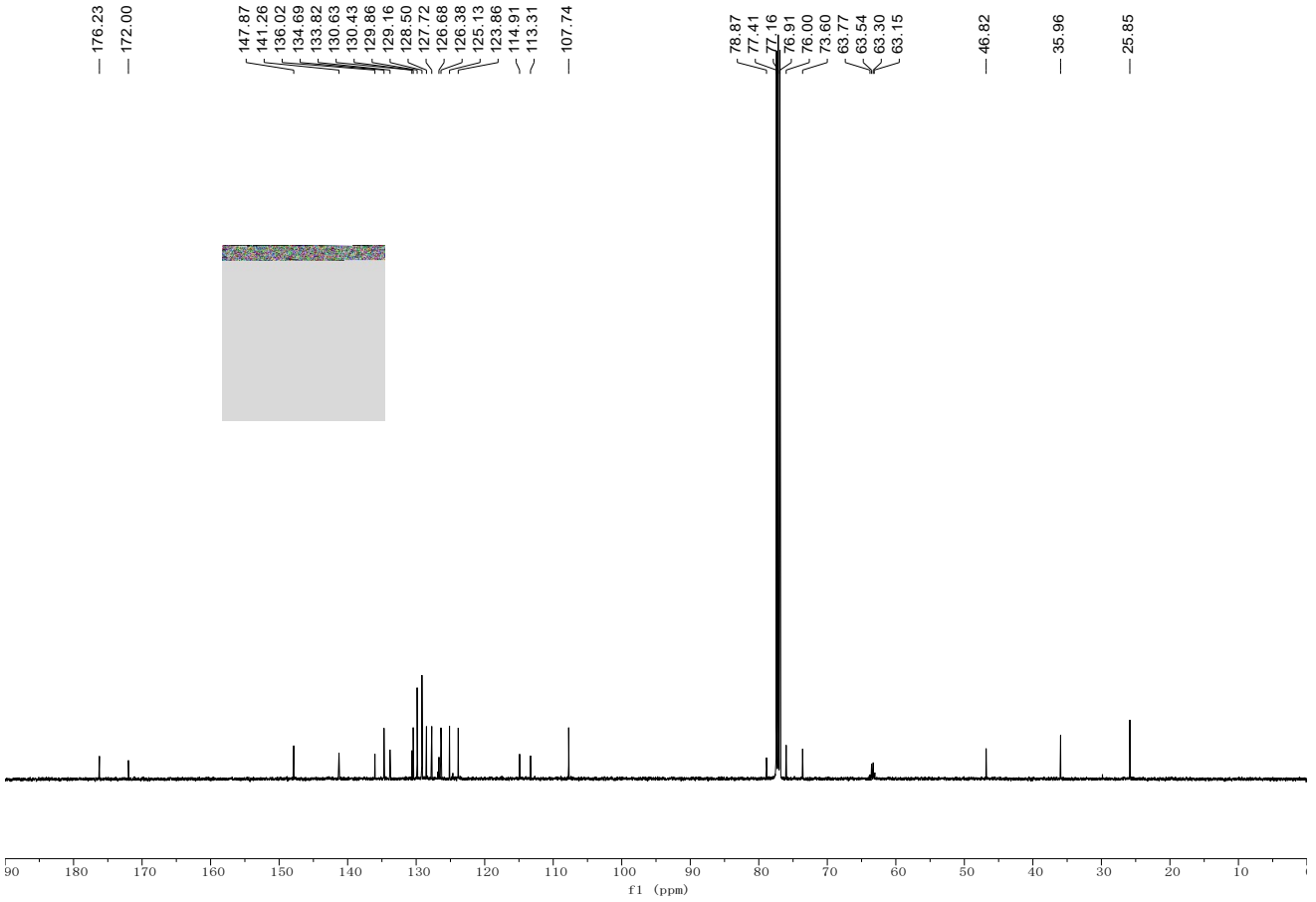
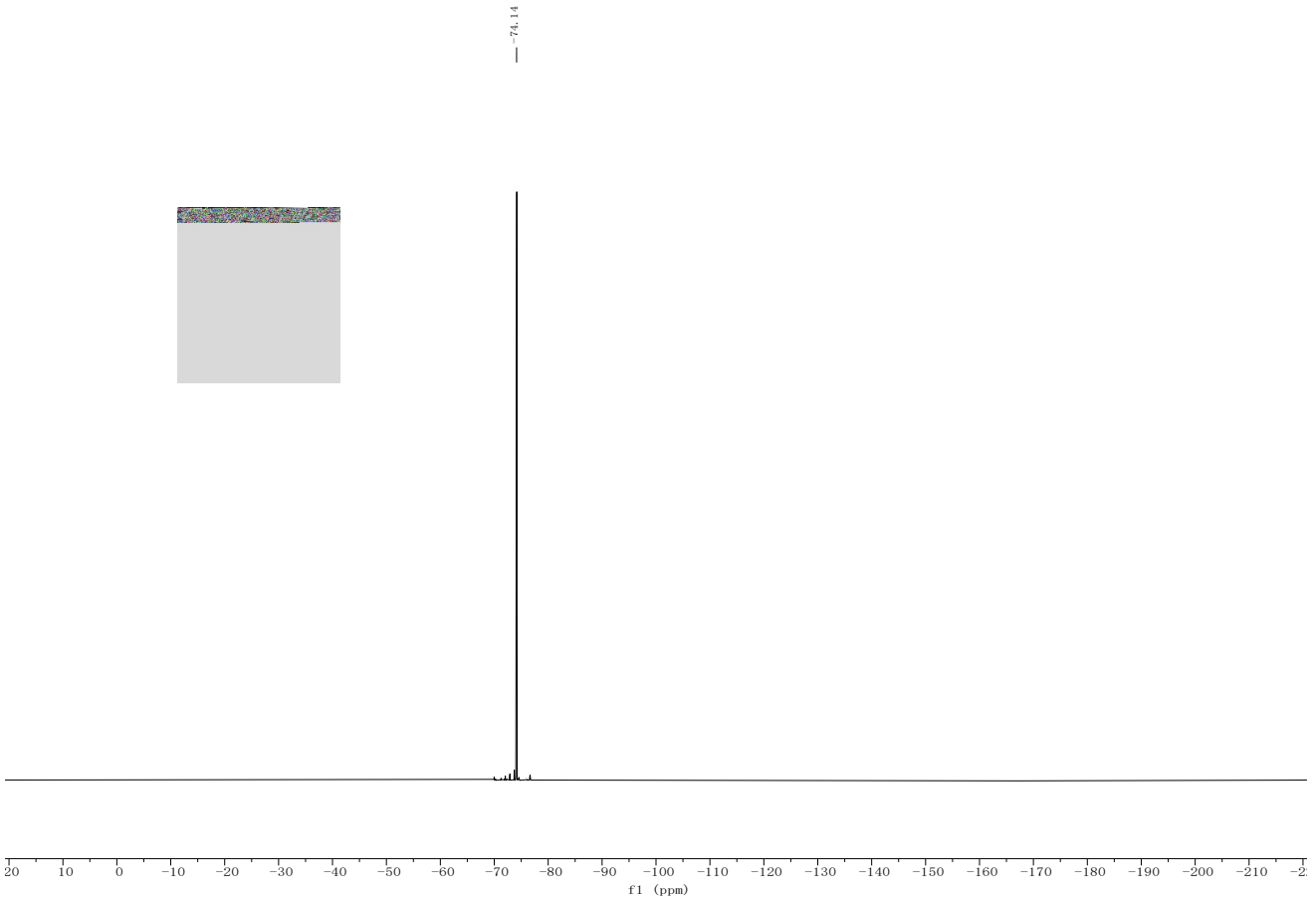
4.80
4.80
4.80
4.79
4.79
4.78
4.78
4.77
3.90
3.87
3.21
3.18
3.15
3.13
2.39
CN
NC
CF3
NH
O
N
5aa
1.00
1.01
2.00
1.03
2.04
2.01
1.07
1.04
1.03
1.01
1.01
1.01
1.00
1.06
1.00
3.01
f1 (ppm)

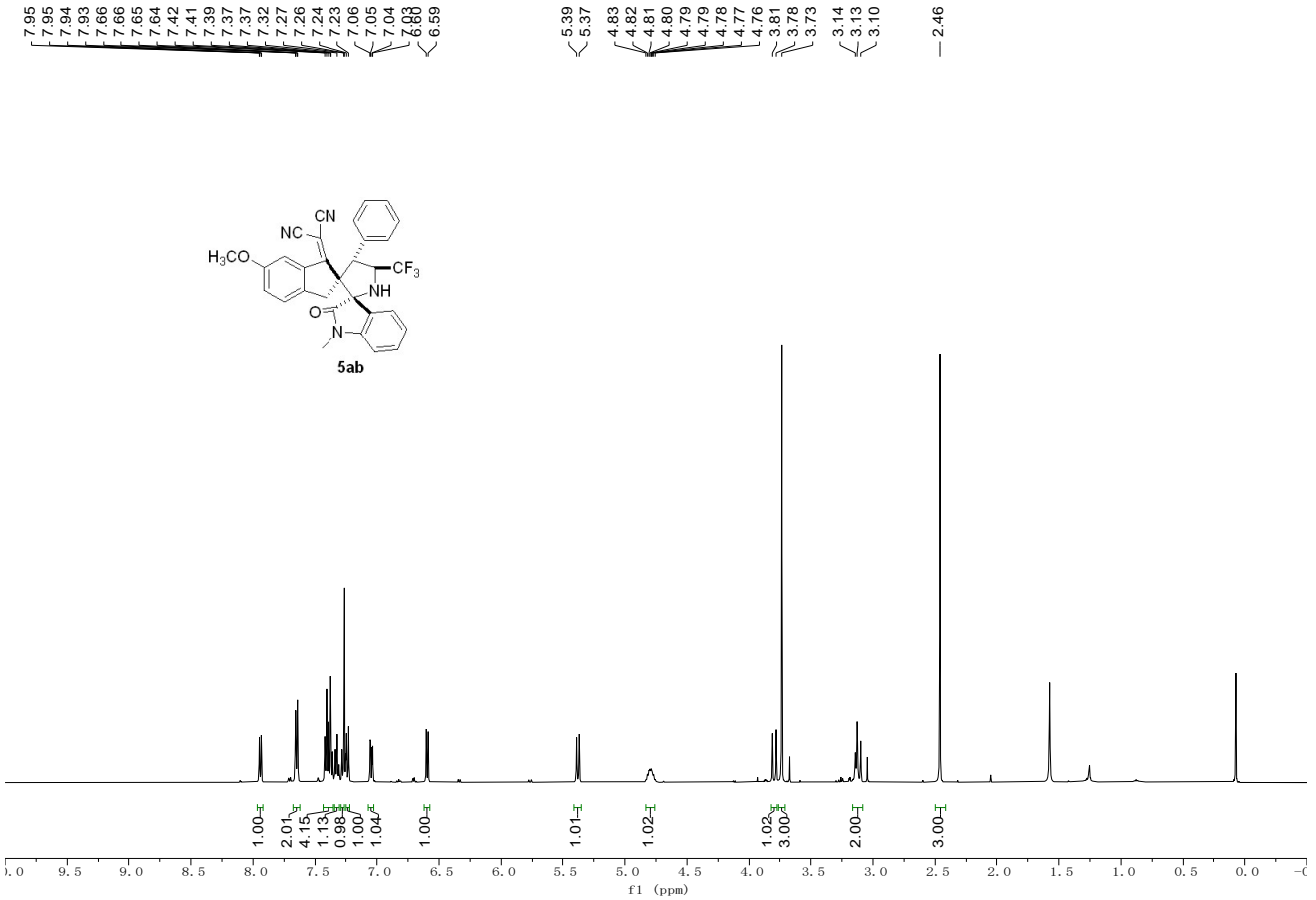
^{13}C NMR spectra for compound **5aa** (125 Hz, $CDCl_3$)



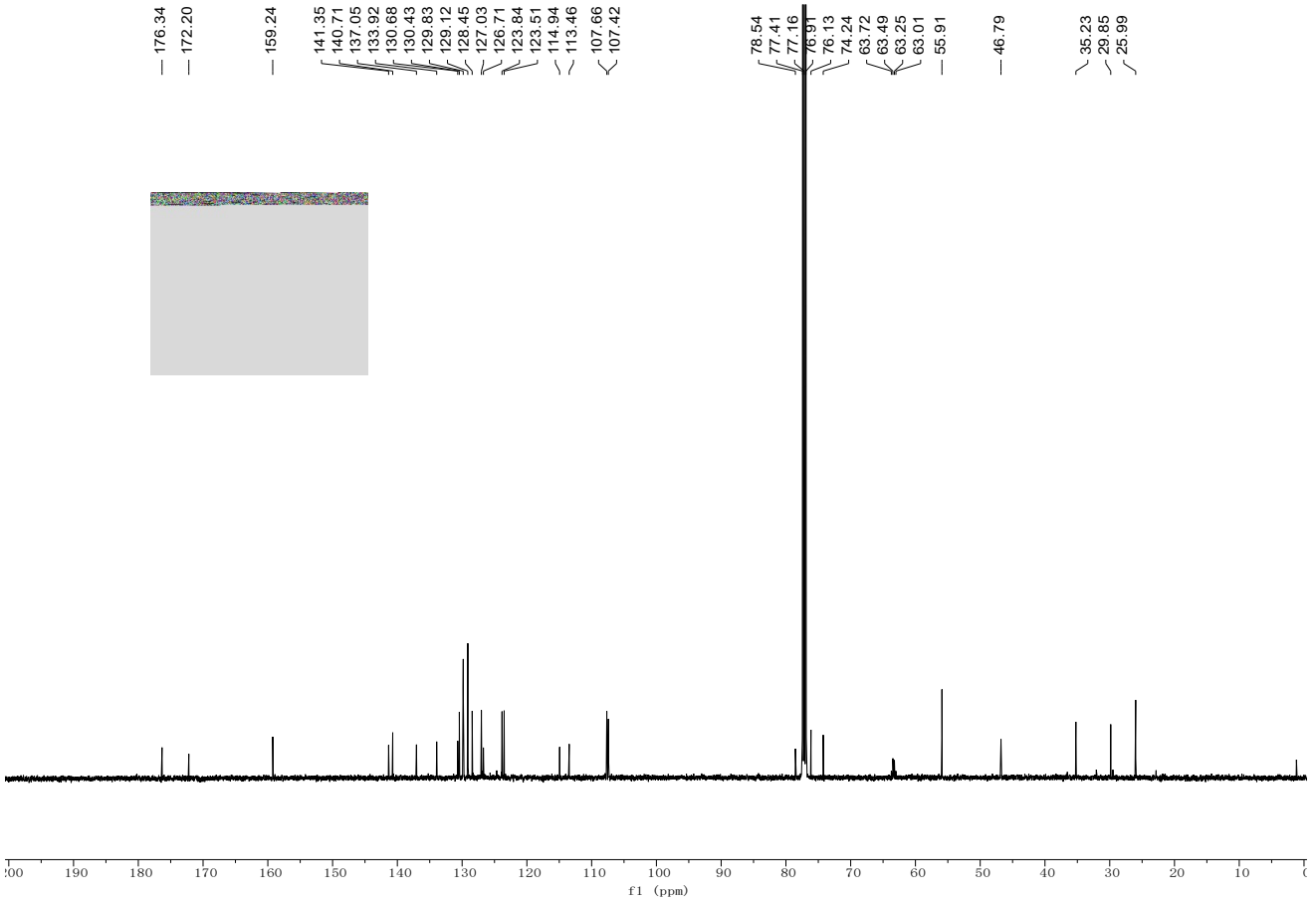
^{19}F NMR spectra for compound **5aa** (471 Hz, $CDCl_3$)



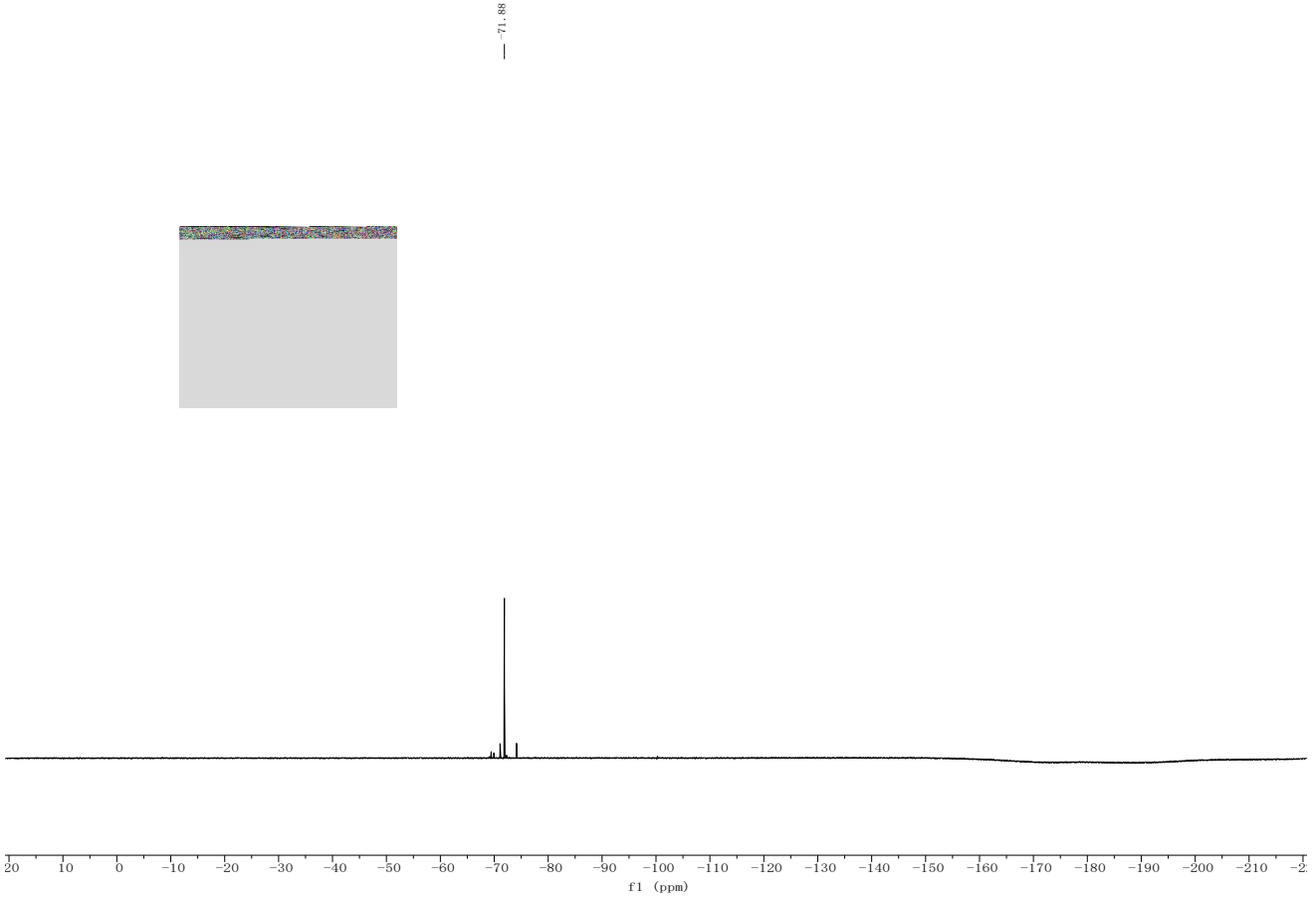
^{1}H NMR spectra for compound **5ab** (500 Hz, $CDCl_3$)



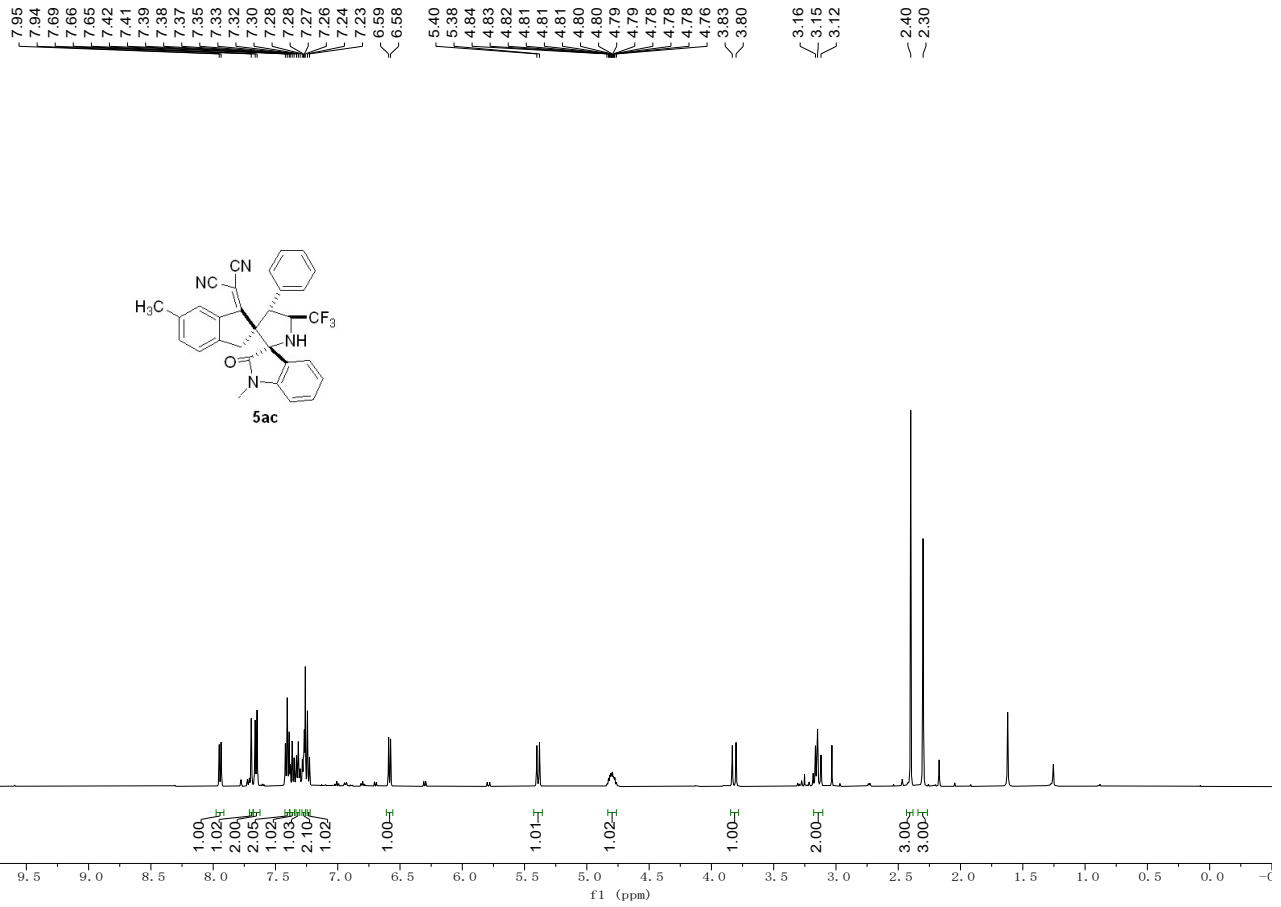
^{13}C NMR spectra for compound **5ab** (125 Hz, $CDCl_3$)



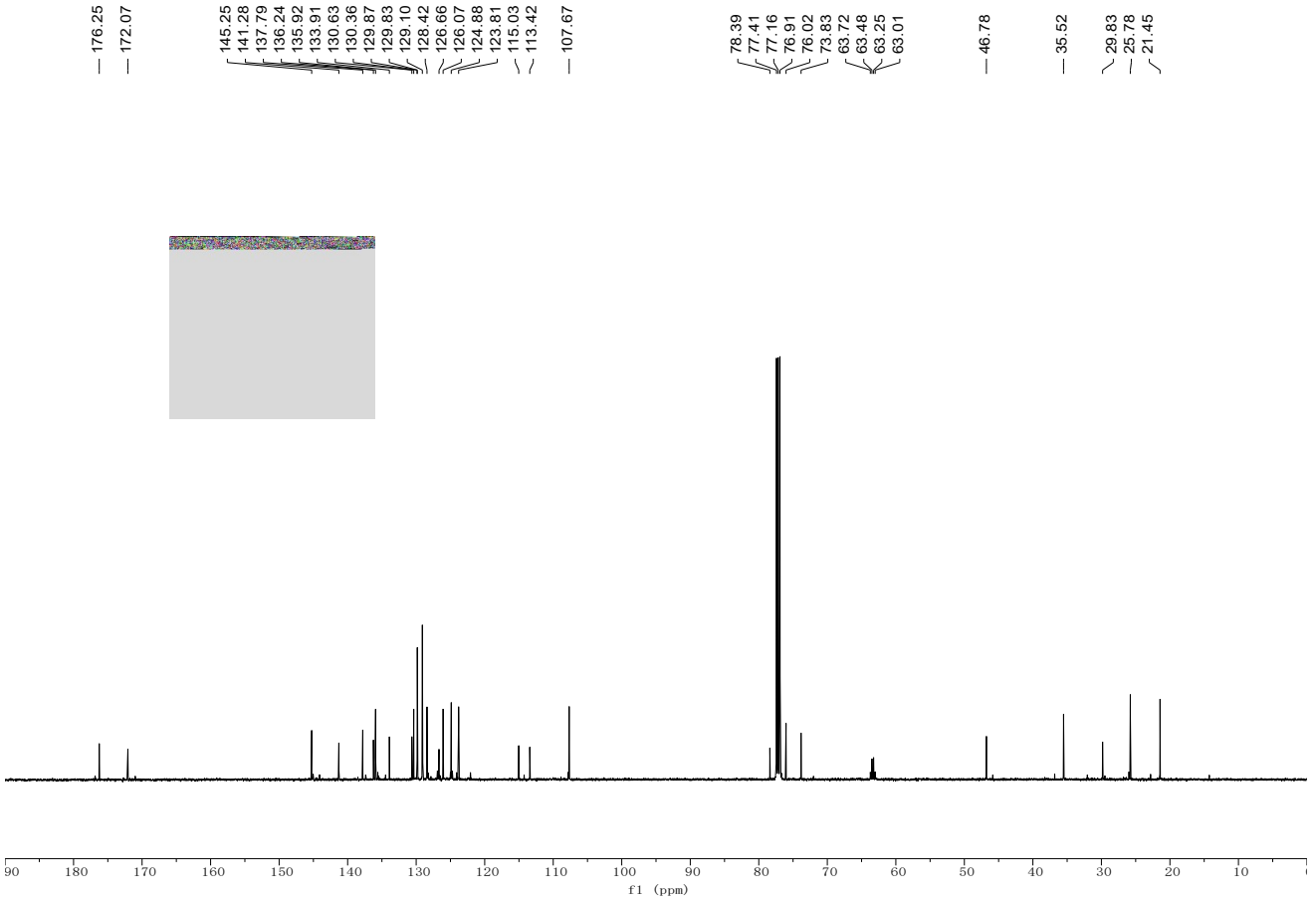
^{19}F NMR spectra for compound **5ab** (471 Hz, $CDCl_3$)



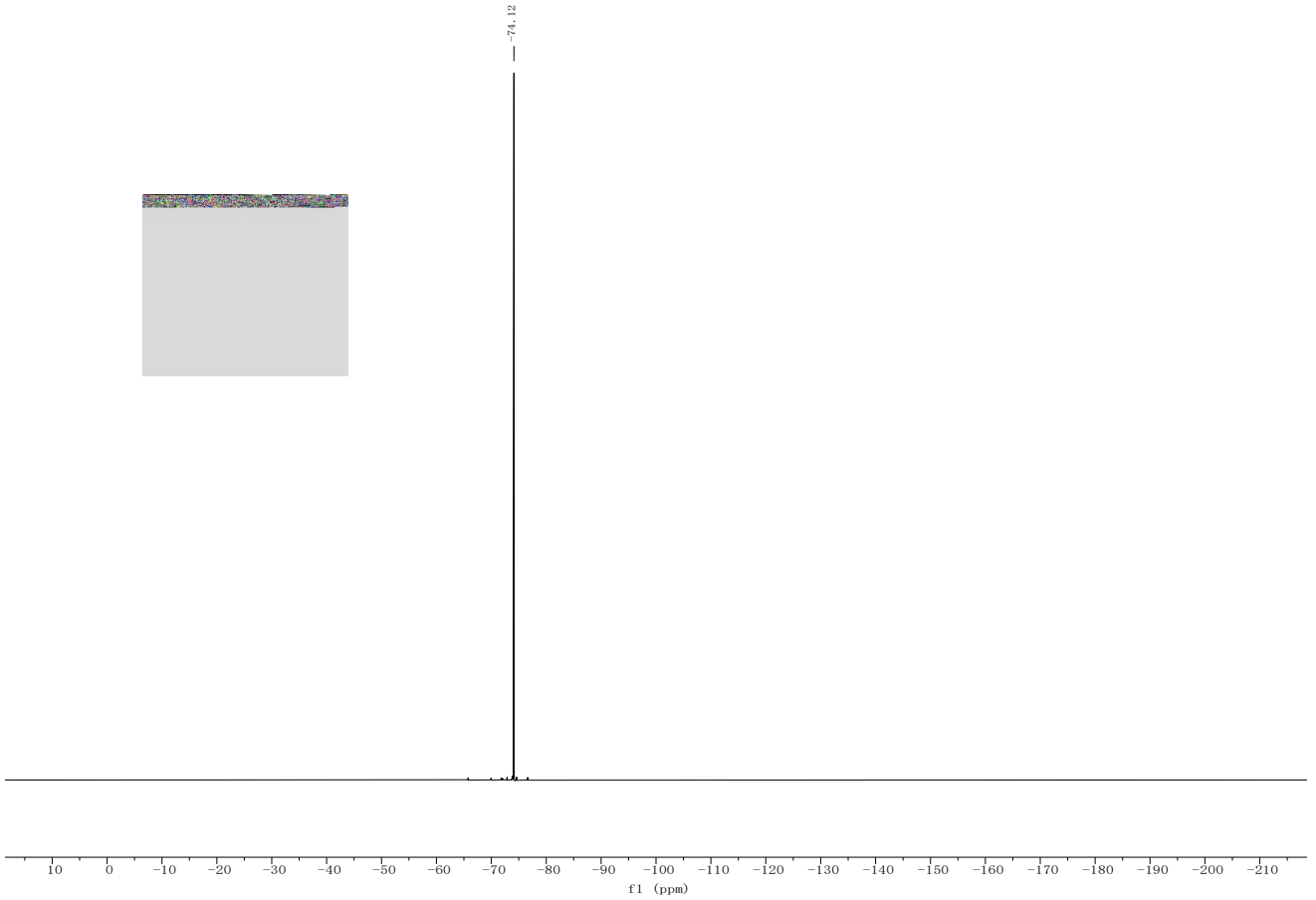
^{1}H NMR spectra for compound **5ac** (500 Hz, $CDCl_3$)



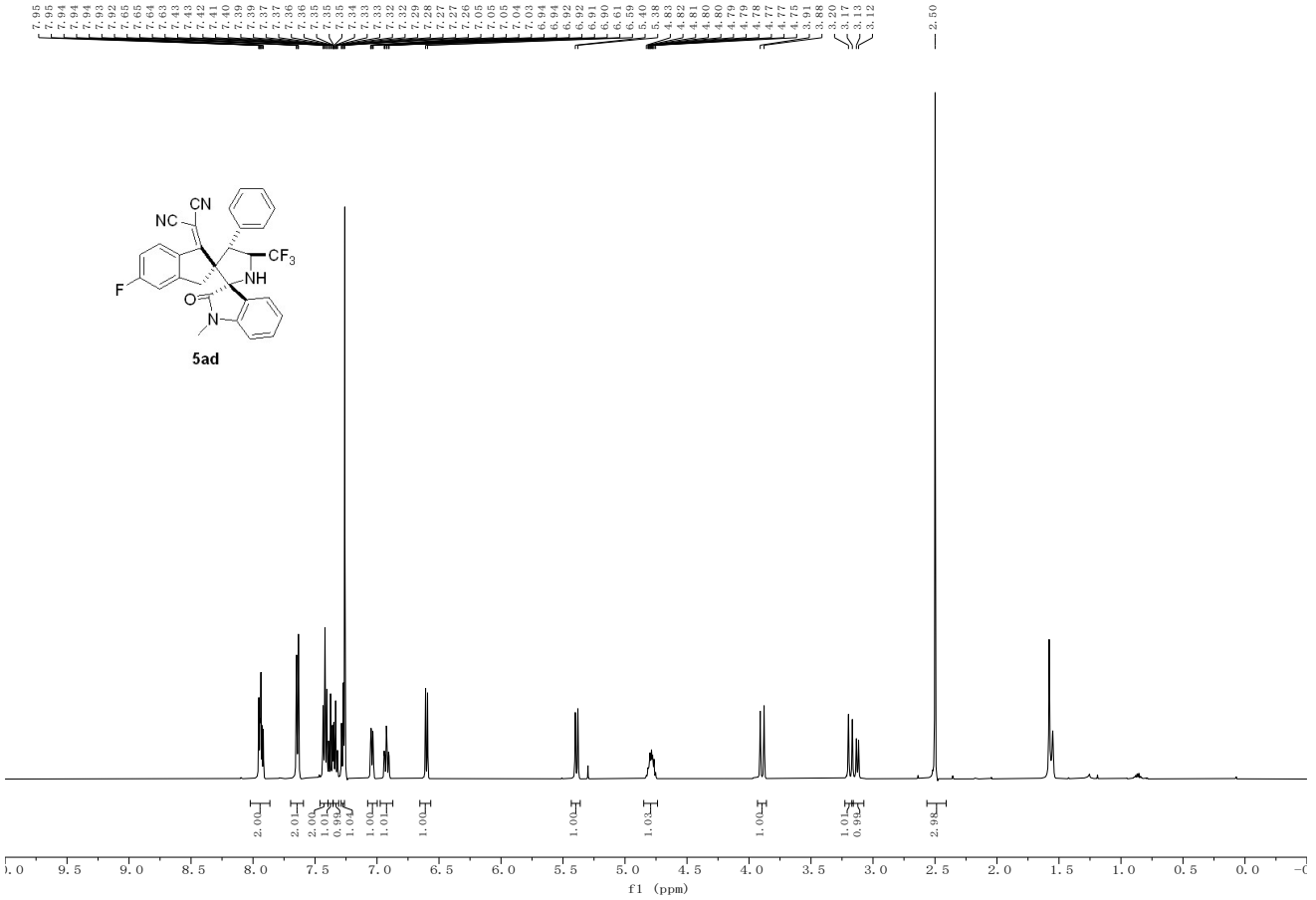
^{13}C NMR spectra for compound **5ac** (125 Hz, $CDCl_3$)



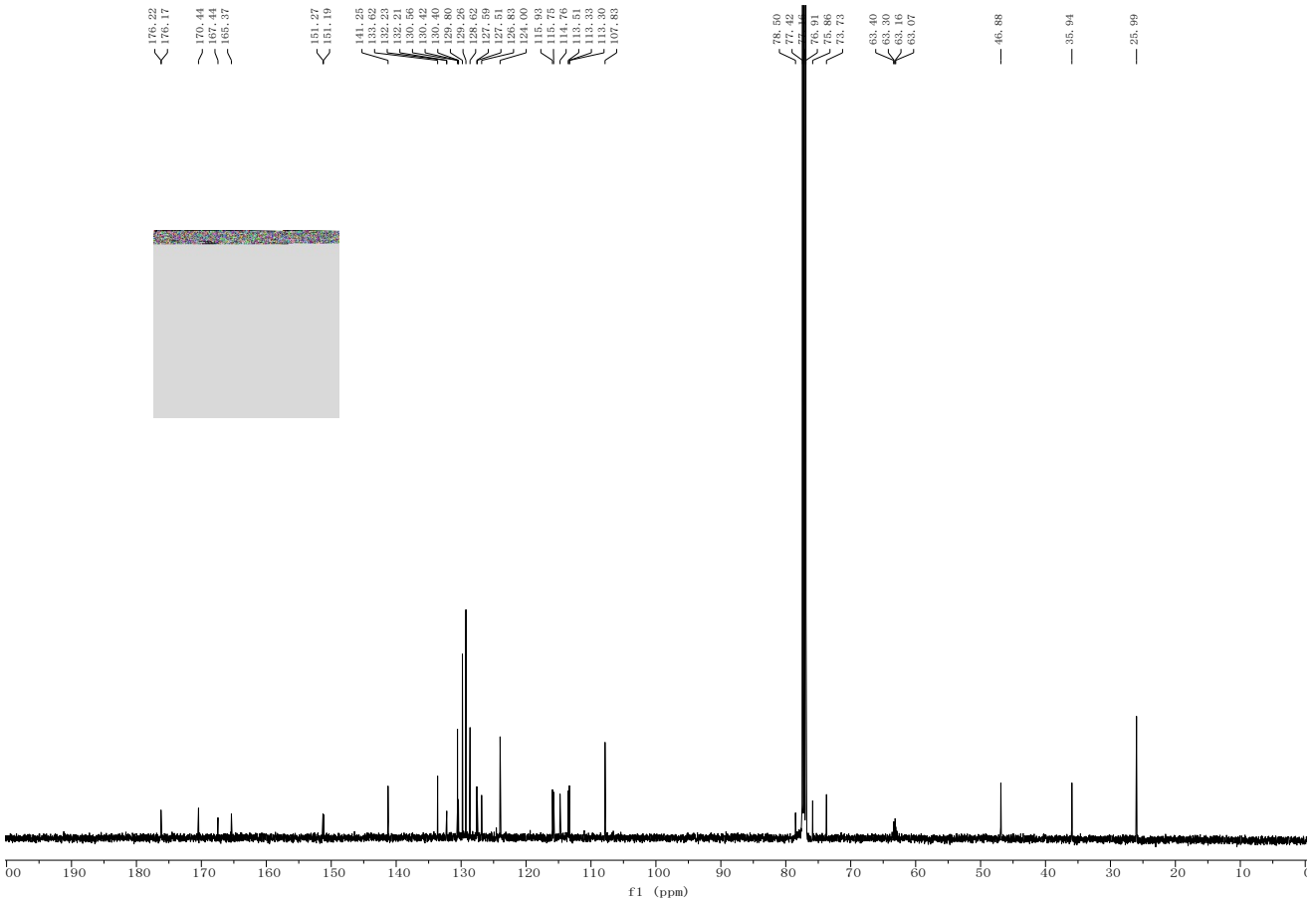
^{19}F NMR spectra for compound **5ac** (376 Hz, $CDCl_3$)



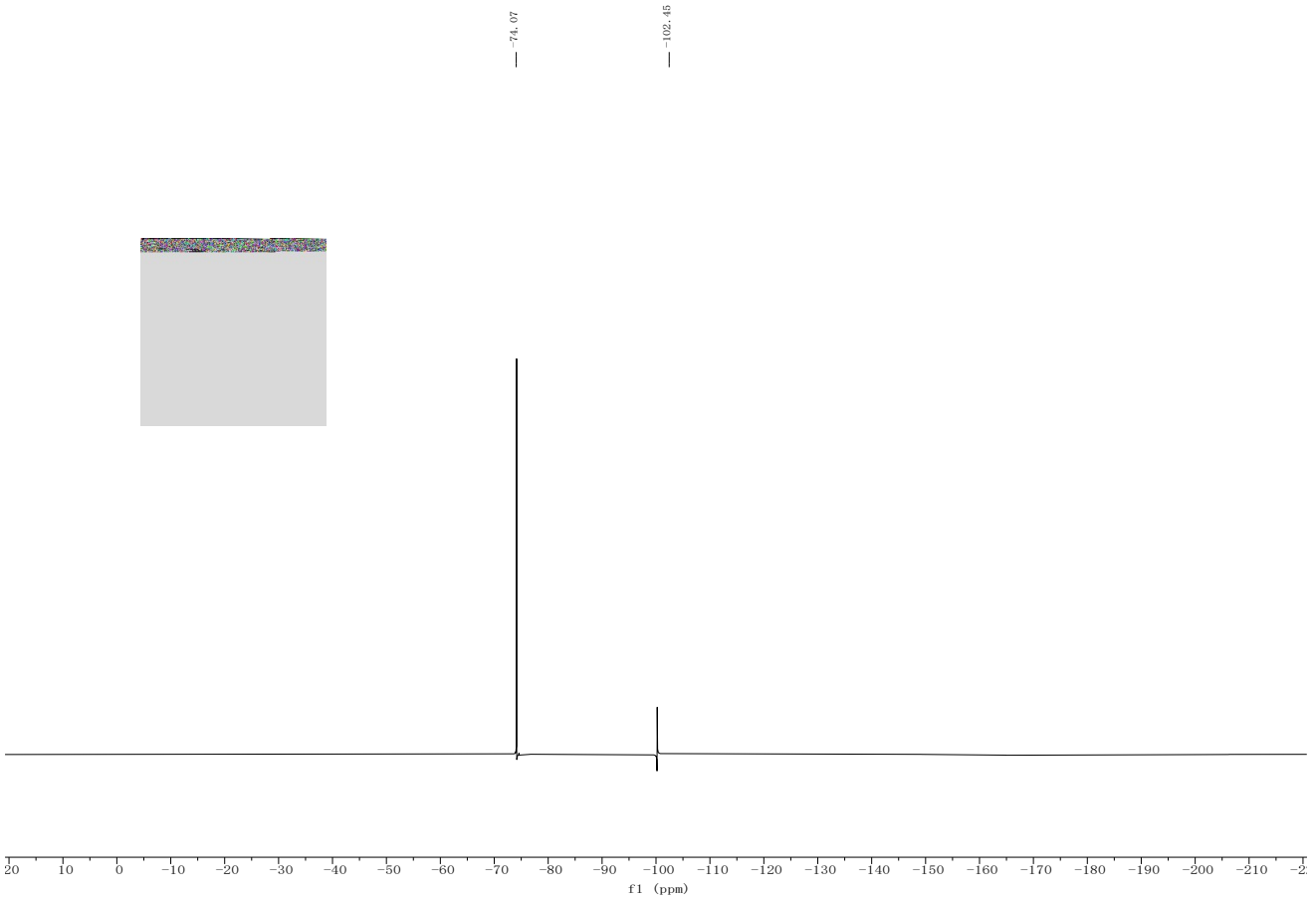
^{1}H NMR spectra for compound **5ad** (500 Hz, $CDCl_3$)



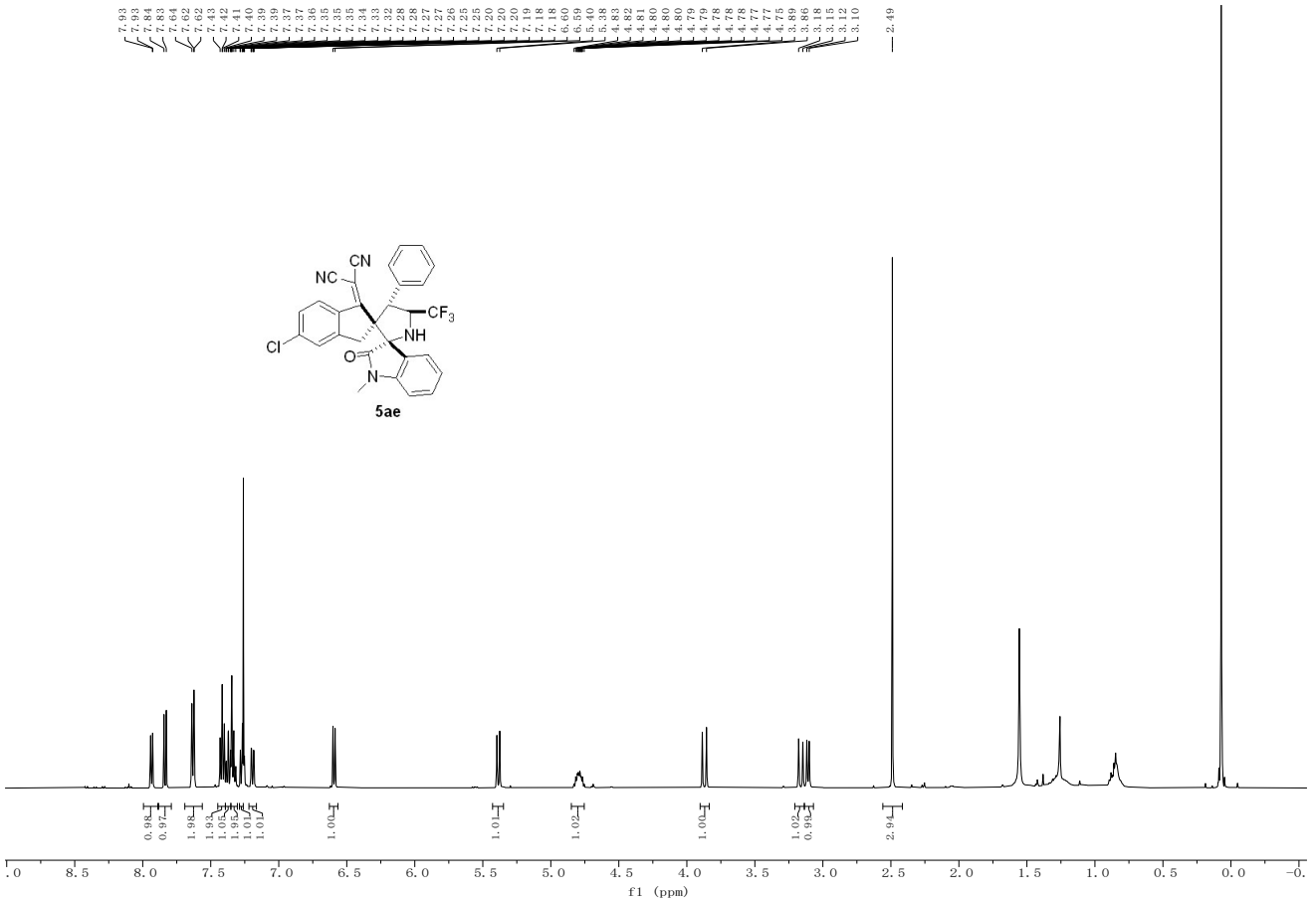
^{13}C NMR spectra for compound **5ad** (125 Hz, $CDCl_3$)



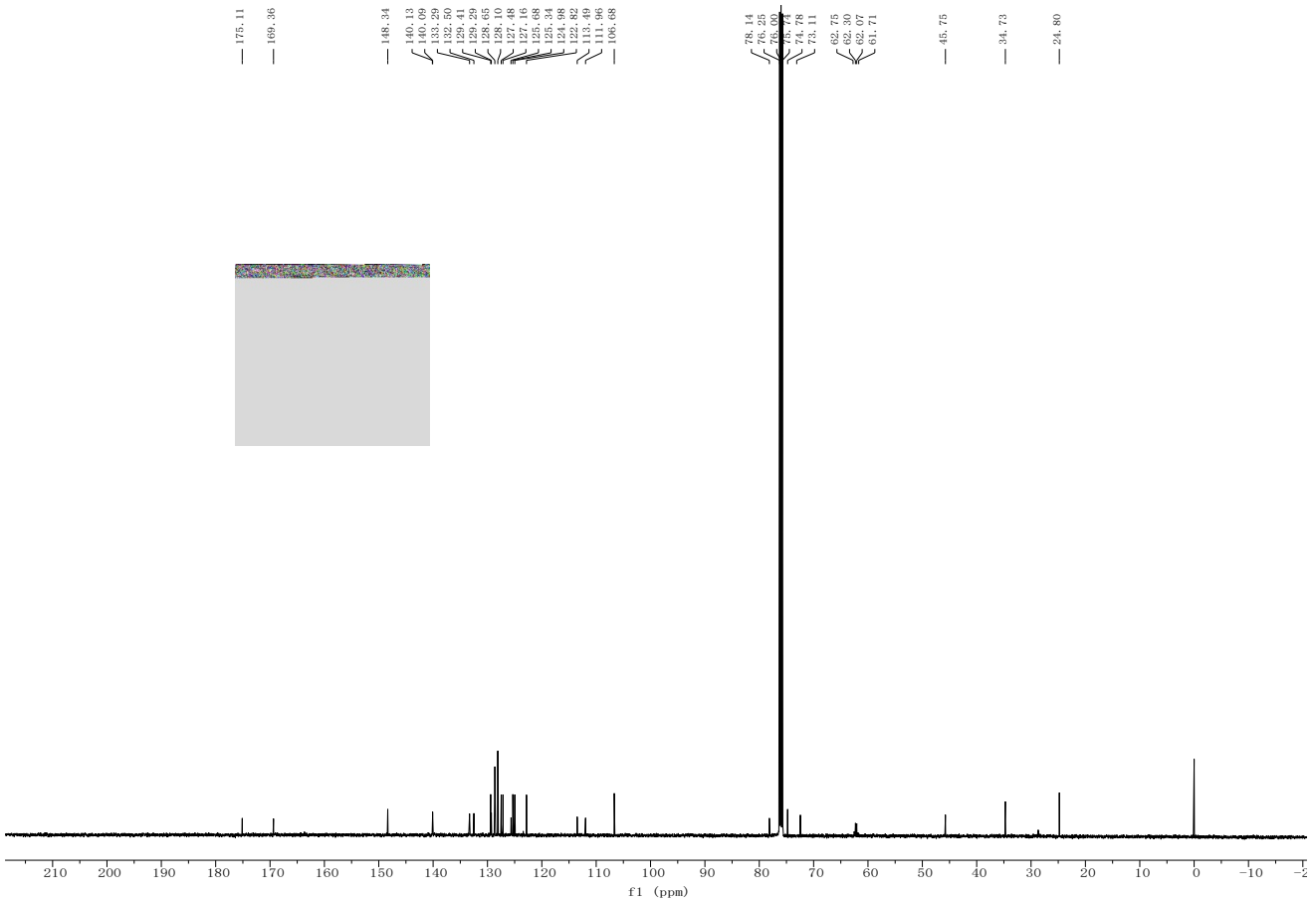
^{19}F NMR spectra for compound **5ad** (471 Hz, $CDCl_3$)



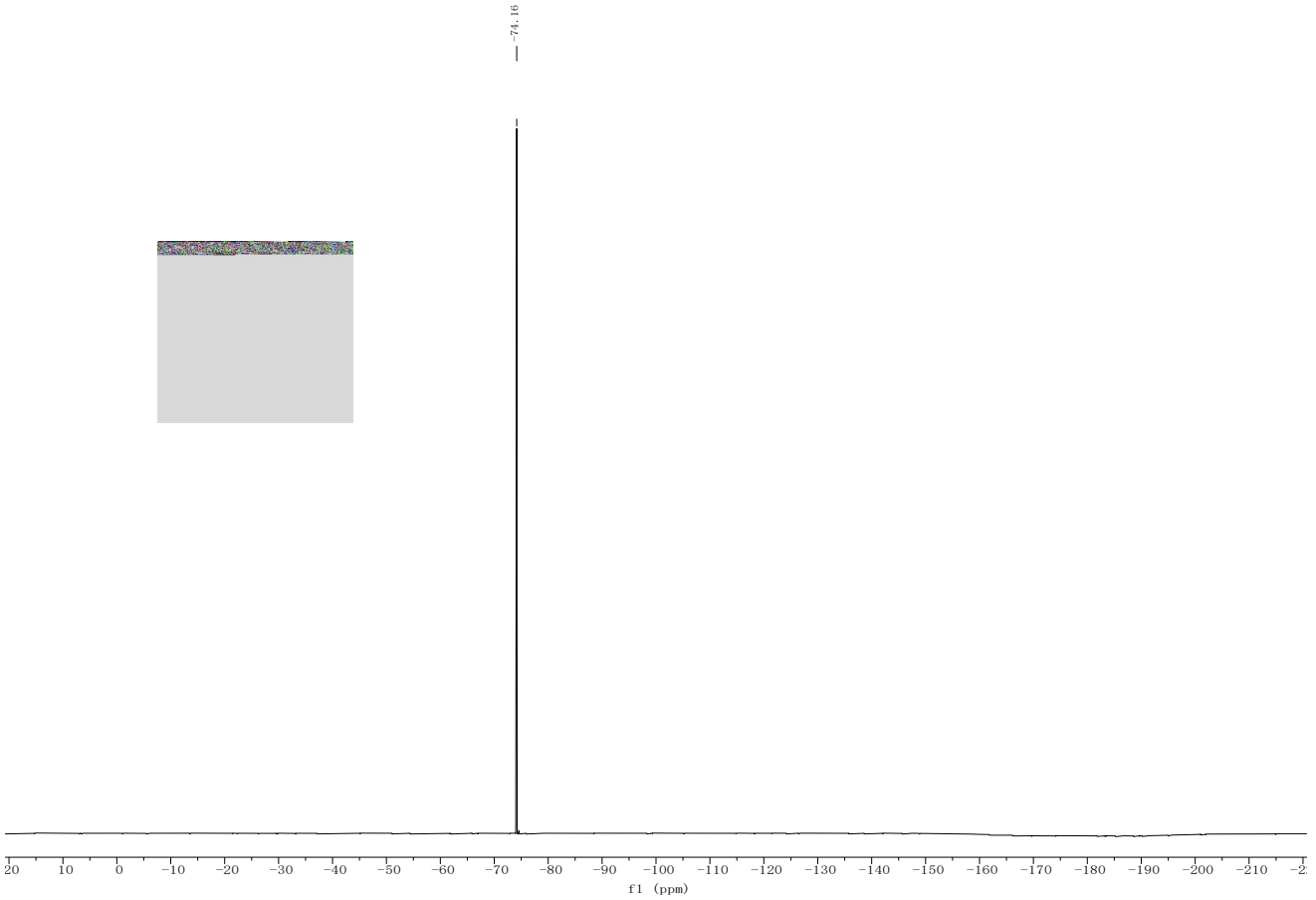
^{1}H NMR spectra for compound **5ae** (500 Hz, $CDCl_3$)



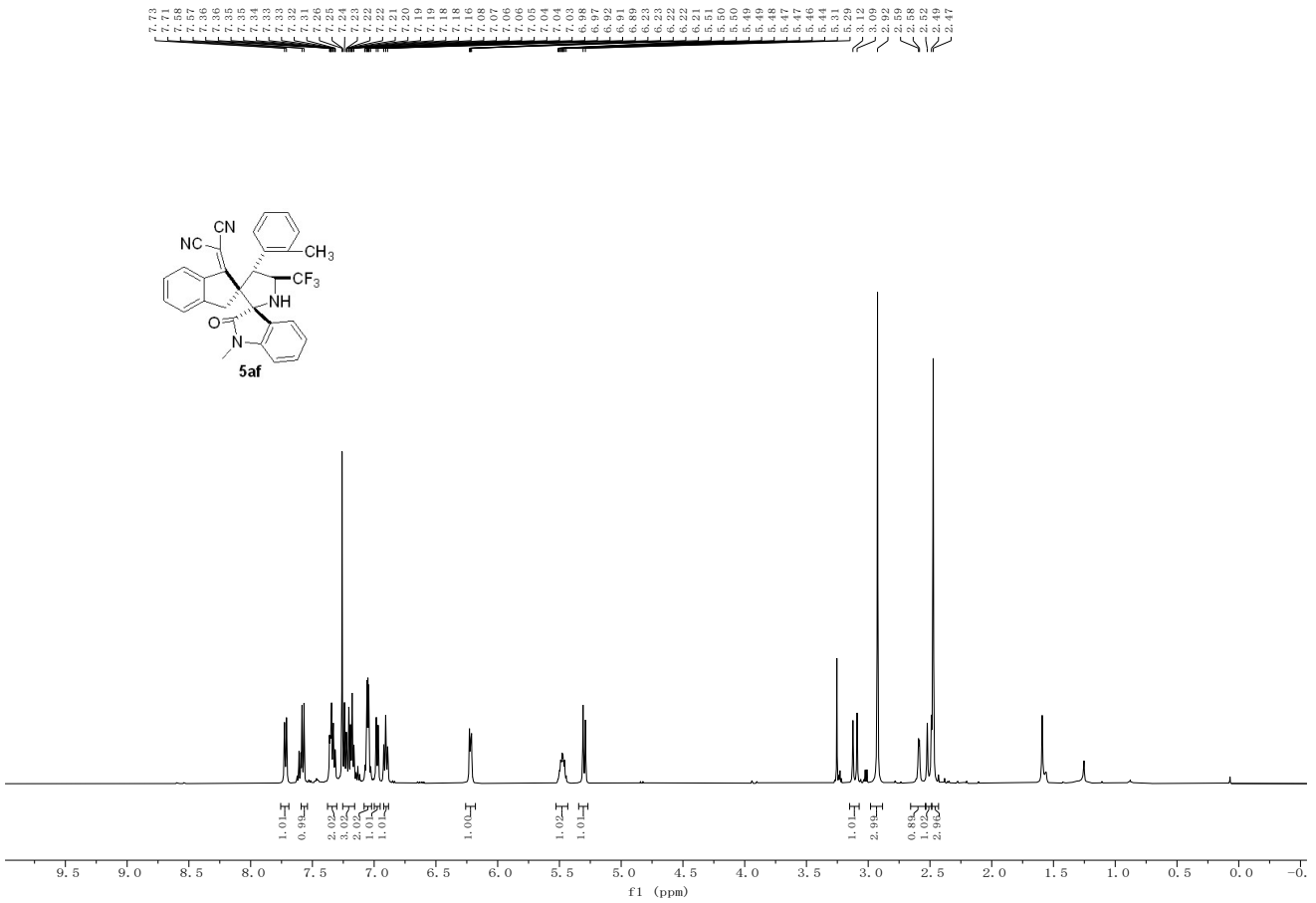
^{13}C NMR spectra for compound **5ae** (125 Hz, $CDCl_3$)



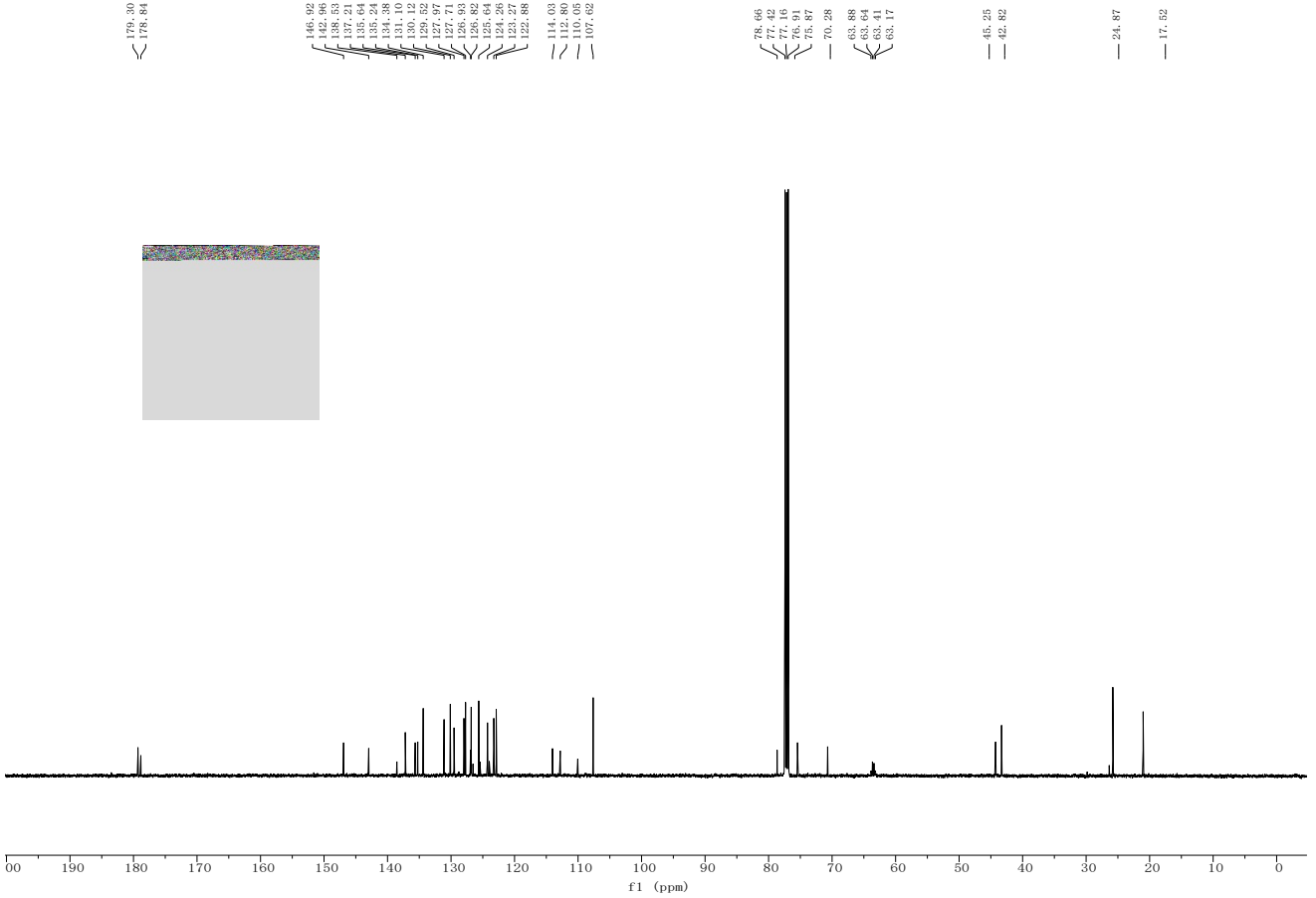
^{19}F NMR spectra for compound **5ae** (471 Hz, $CDCl_3$)



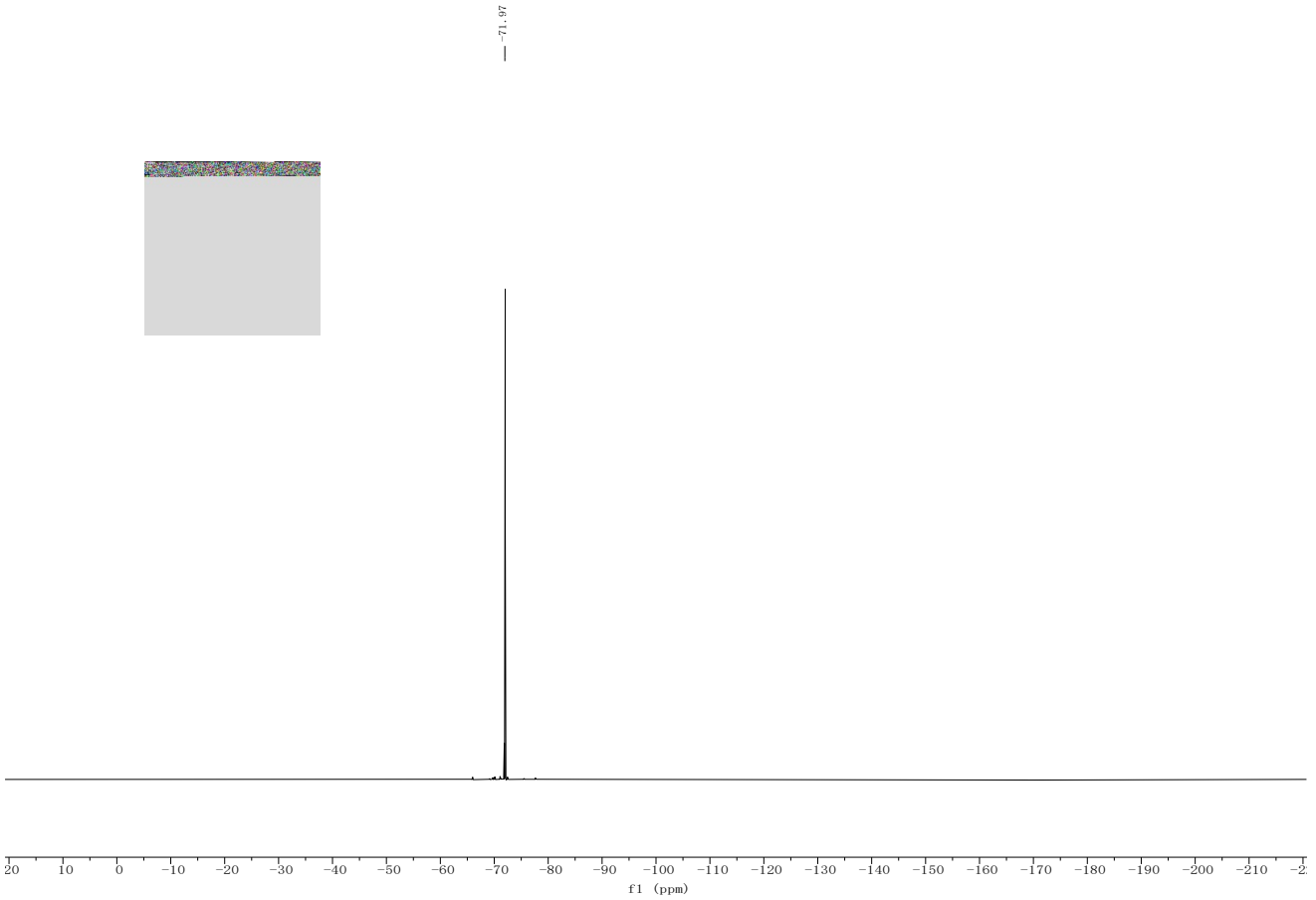
^{1}H NMR spectra for compound **5af** (500 Hz, $CDCl_3$)



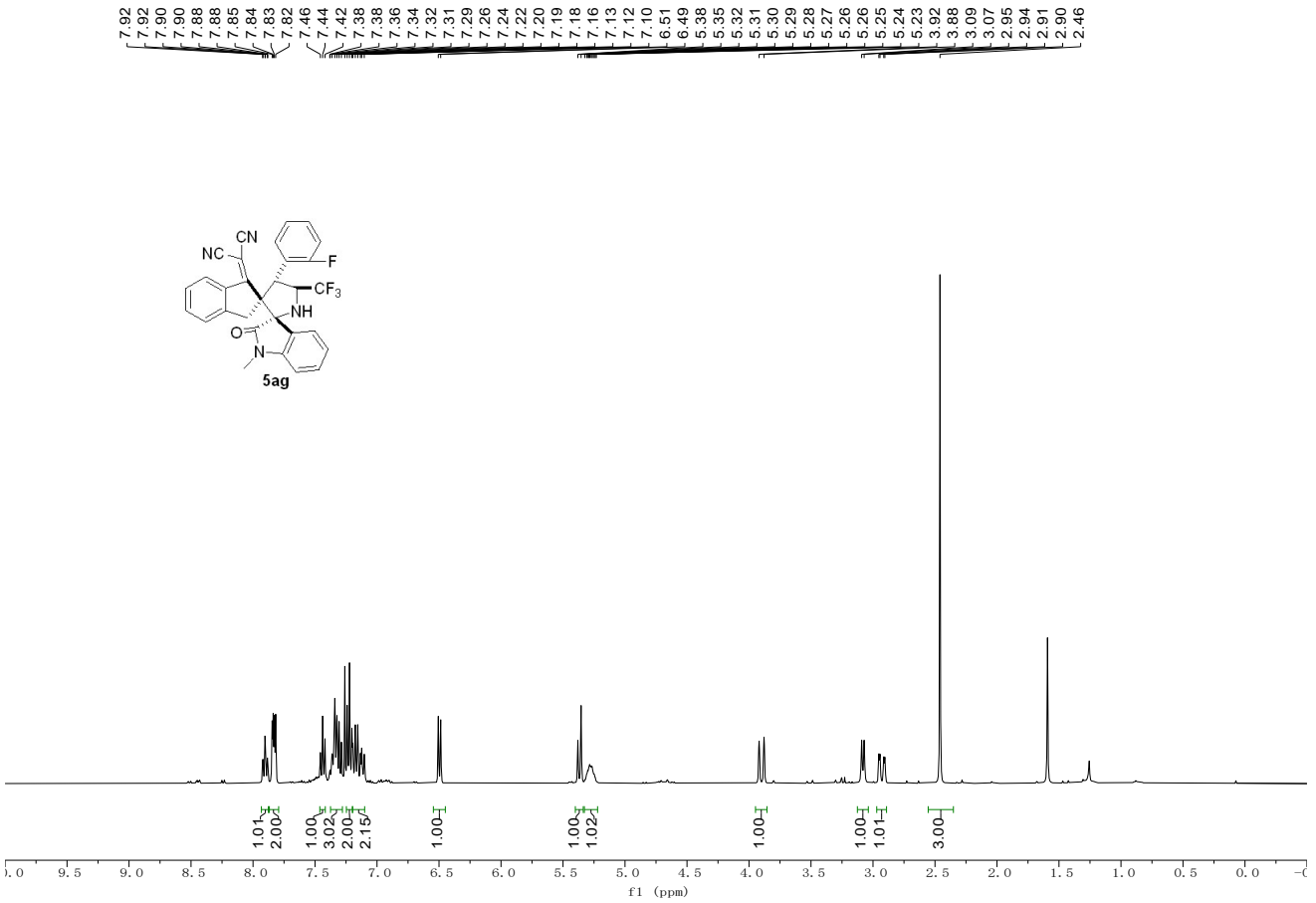
^{13}C NMR spectra for compound **5af** (125 Hz, $CDCl_3$)



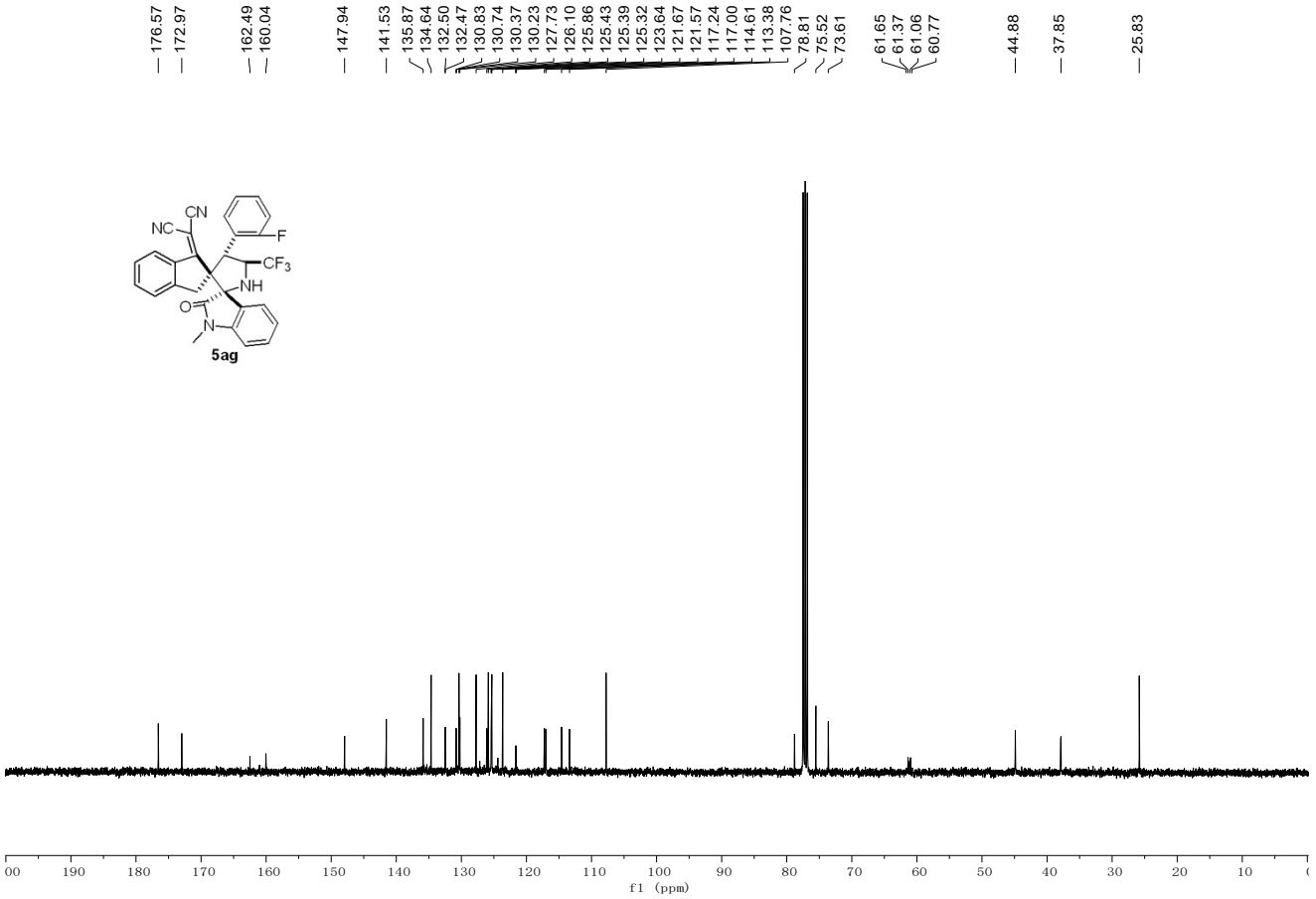
^{19}F NMR spectra for compound **5af** (500 Hz, $CDCl_3$)



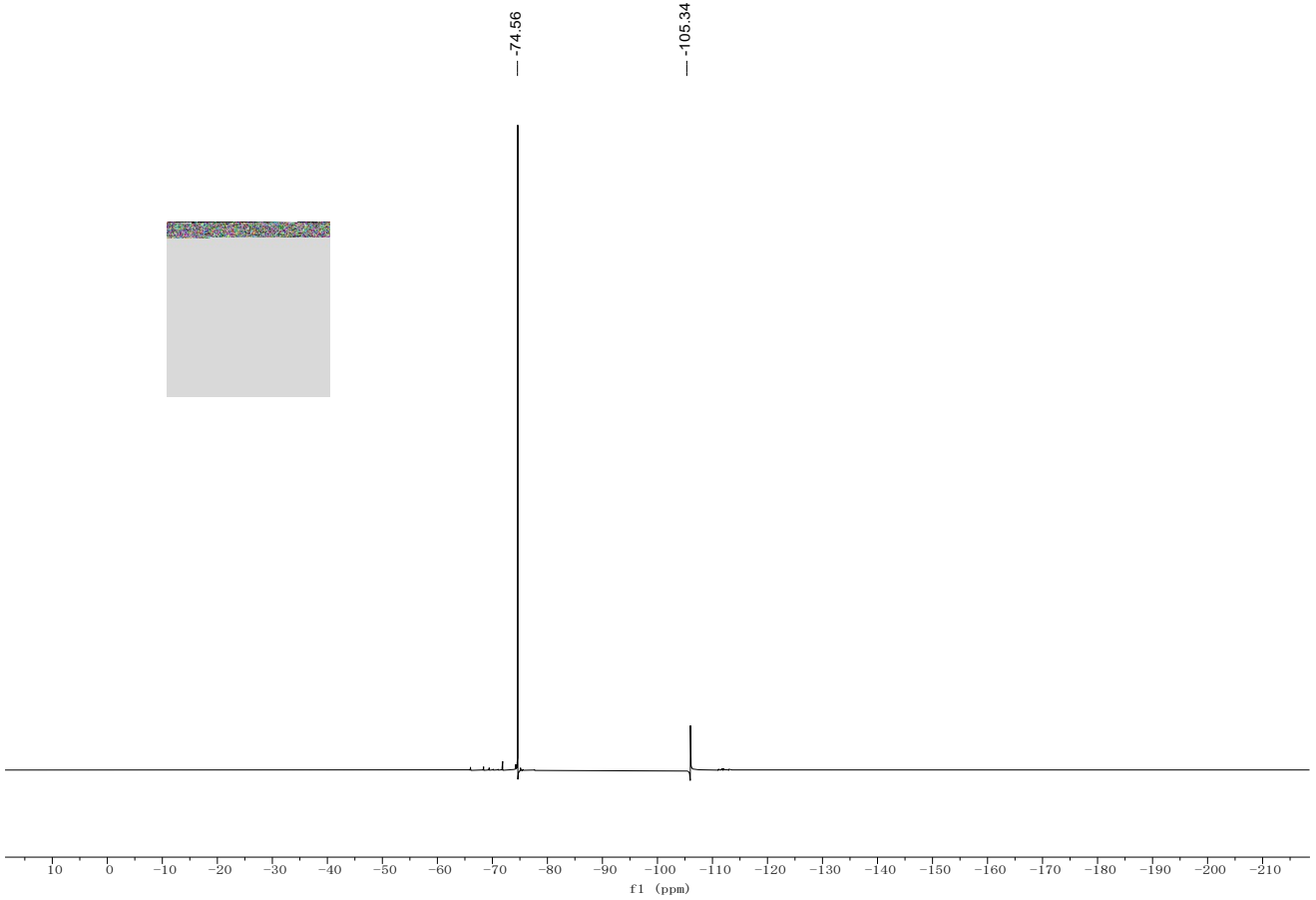
^{1}H NMR spectra for compound **5ag** (400 Hz, $CDCl_3$)



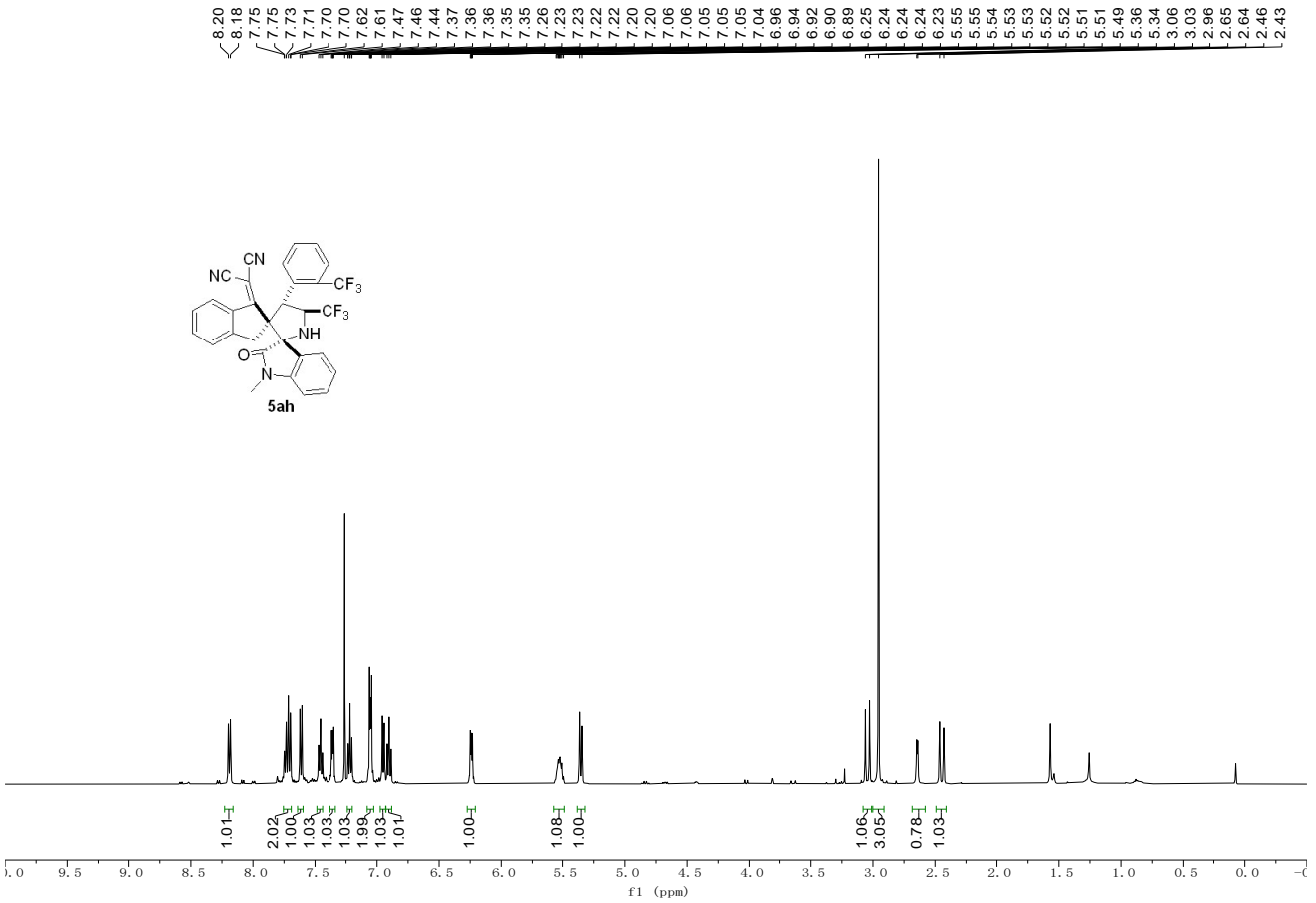
^{13}C NMR spectra for compound **5ag** (100 Hz, $CDCl_3$)



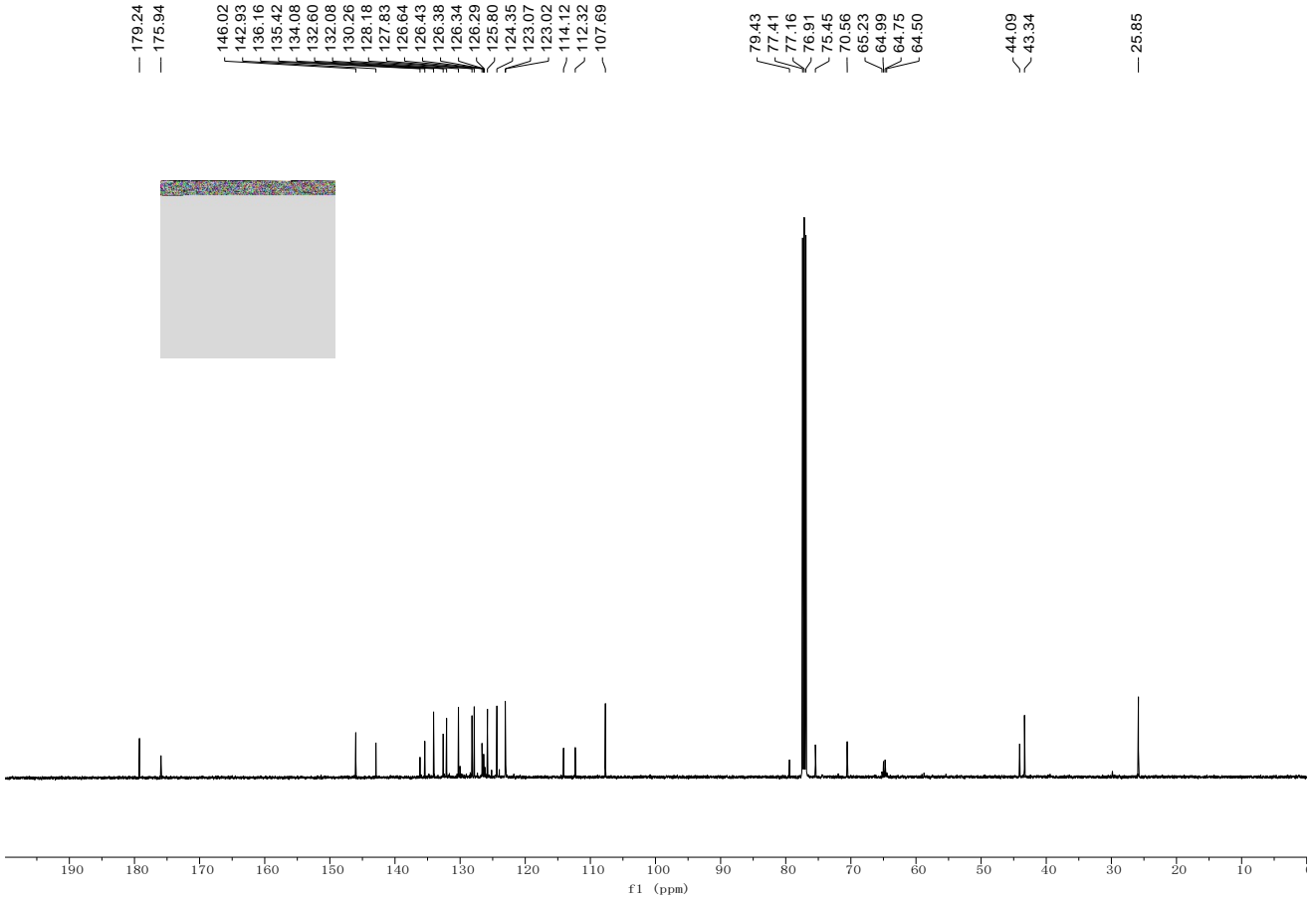
^{19}F NMR spectra for compound **5ag** (376 Hz, $CDCl_3$)



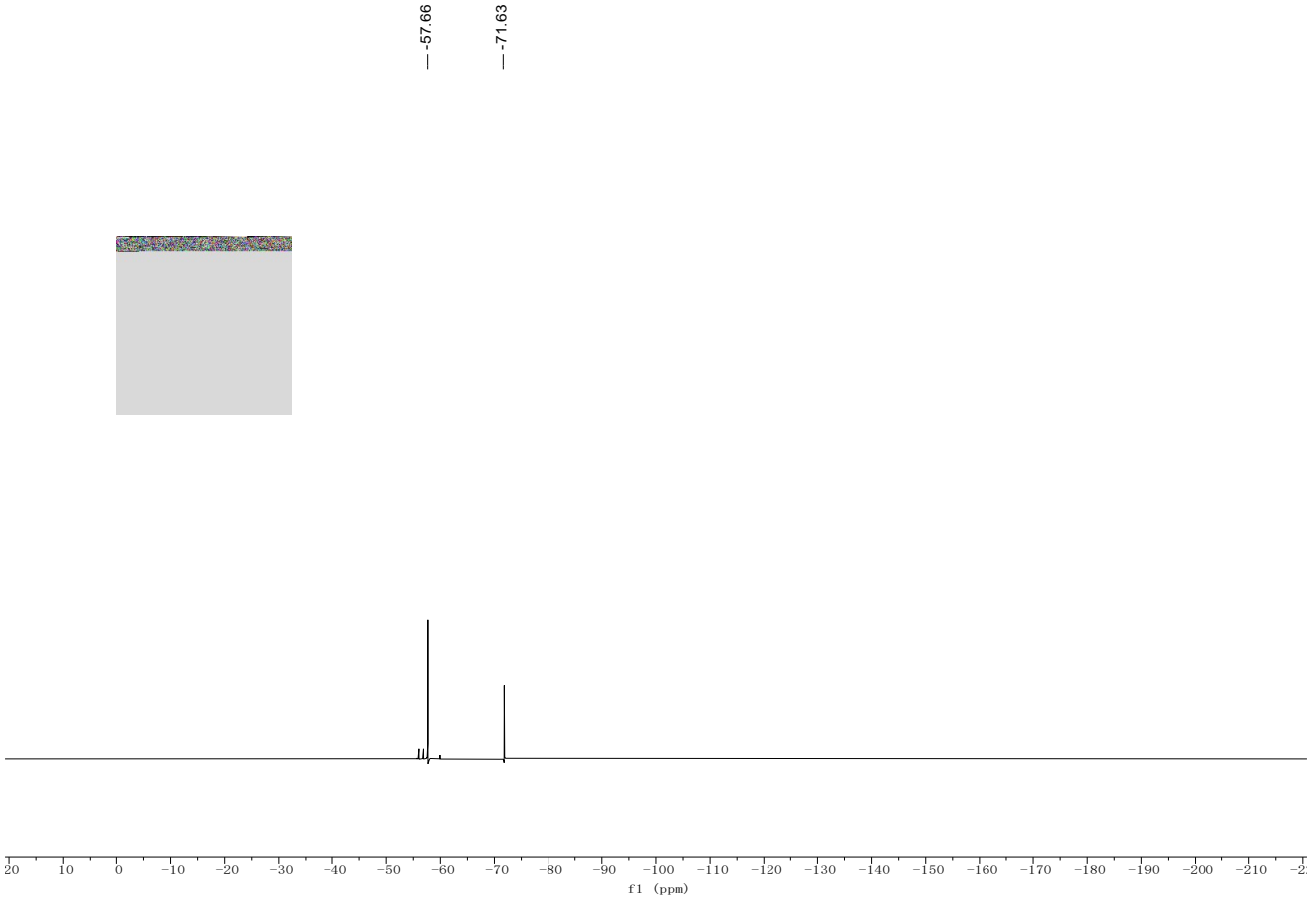
^{1}H NMR spectra for compound **5ah** (500 Hz, $CDCl_3$)



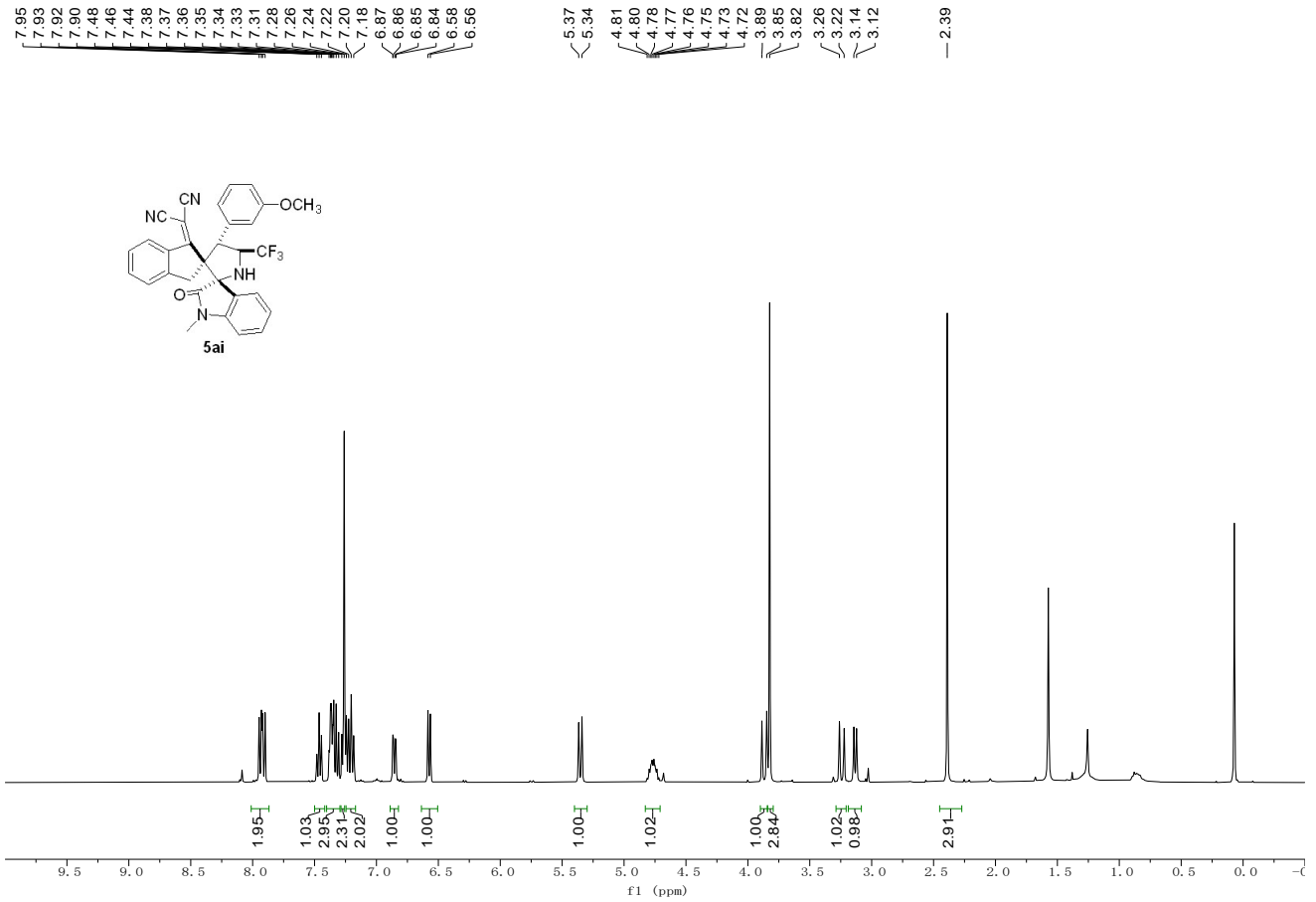
^{13}C NMR spectra for compound **5ah** (125 Hz, $CDCl_3$)



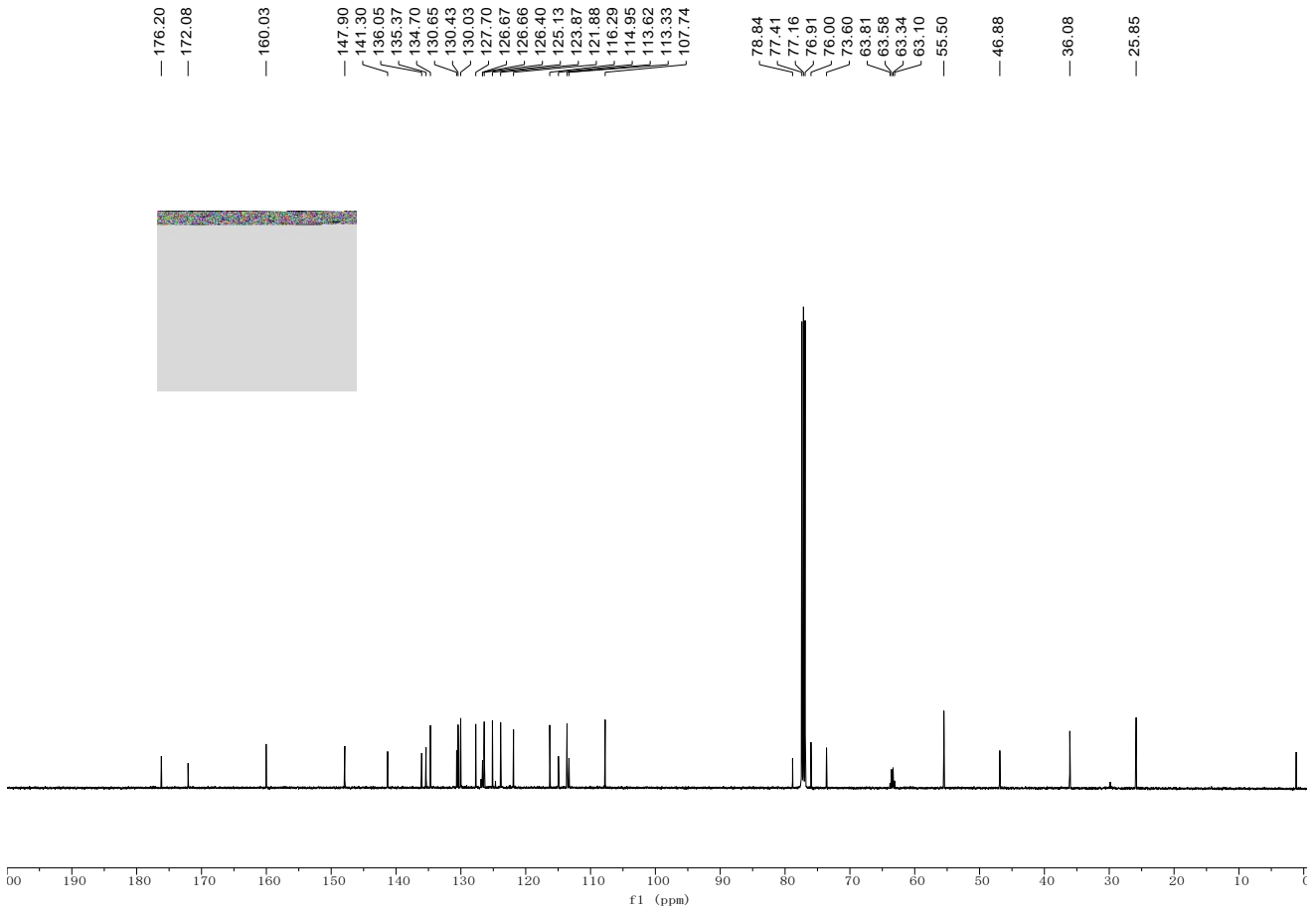
^{19}F NMR spectra for compound **5ah** (471 Hz, $CDCl_3$)



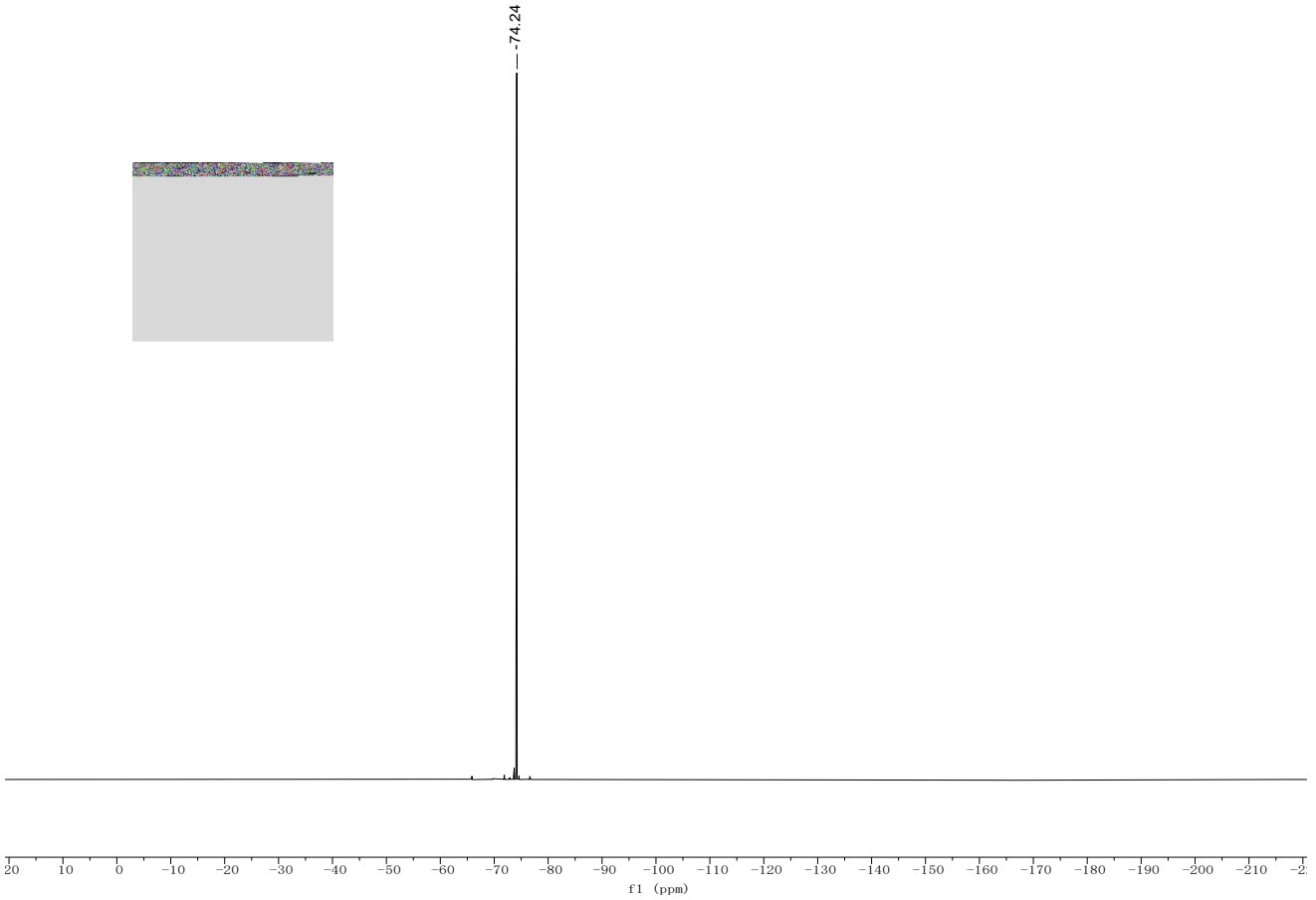
^{1}H NMR spectra for compound **5ai** (500 Hz, $CDCl_3$)



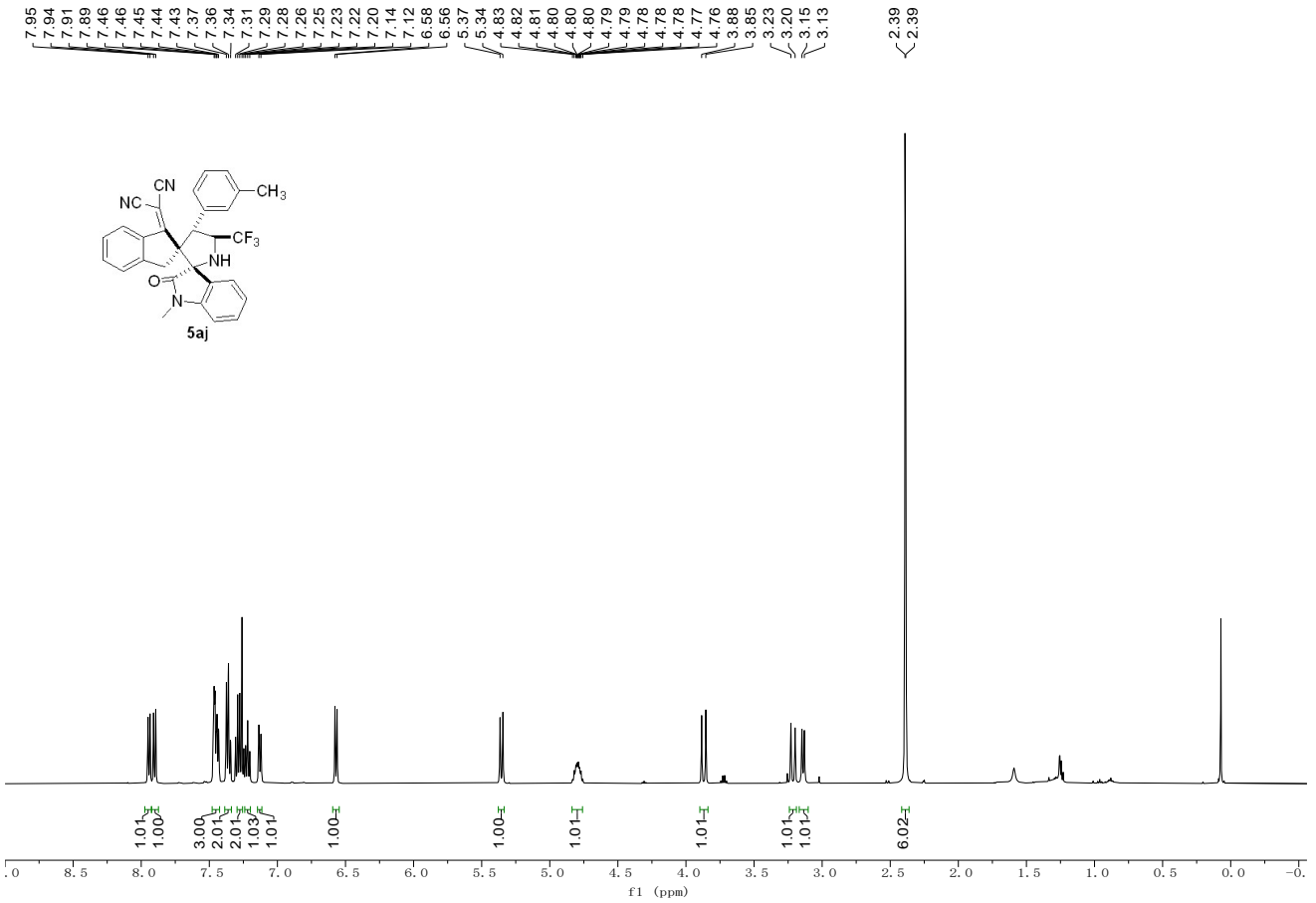
^{13}C NMR spectra for compound **5ai** (125 Hz, $CDCl_3$)



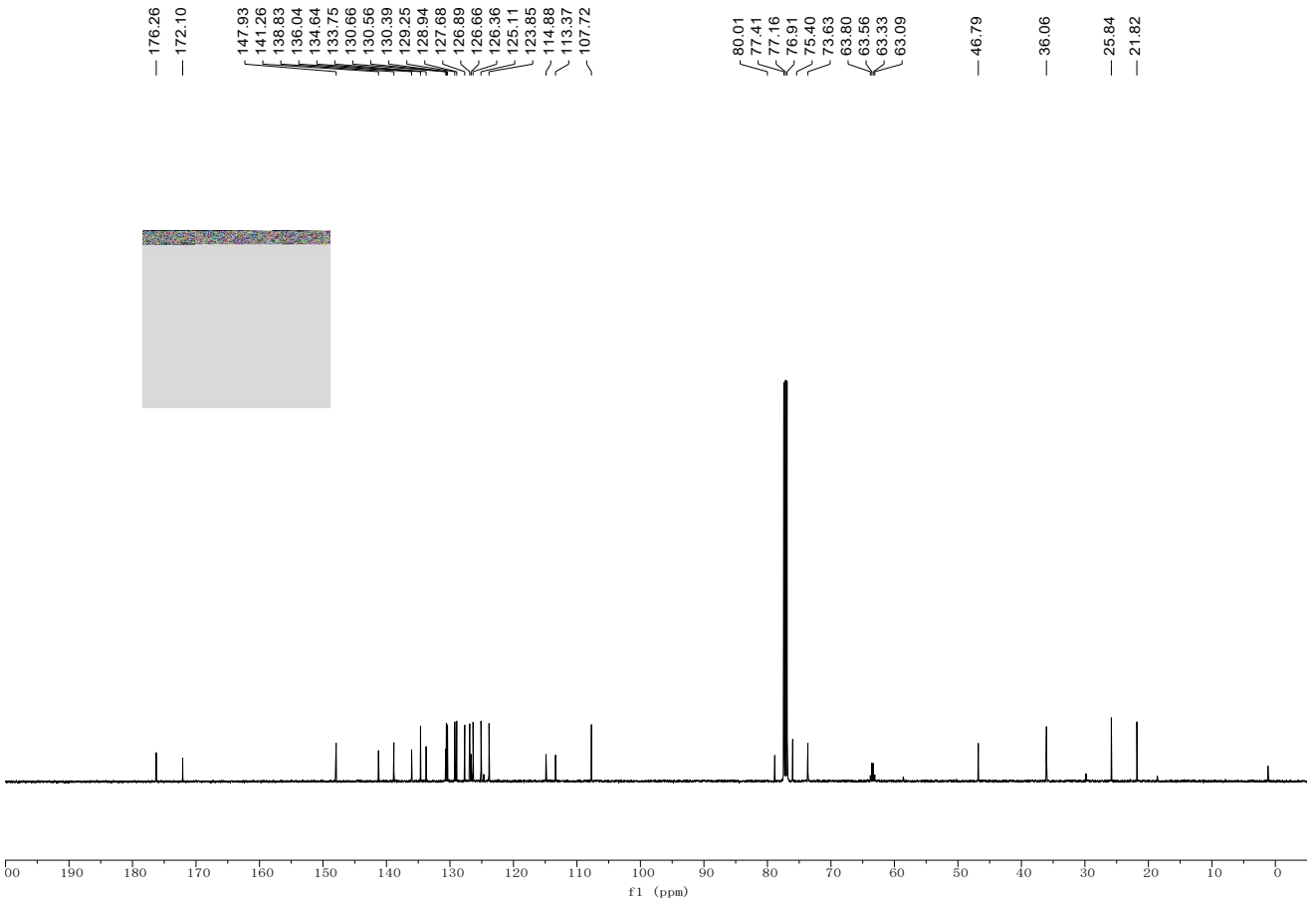
^{19}F NMR spectra for compound **5ai** (471 Hz, $CDCl_3$)



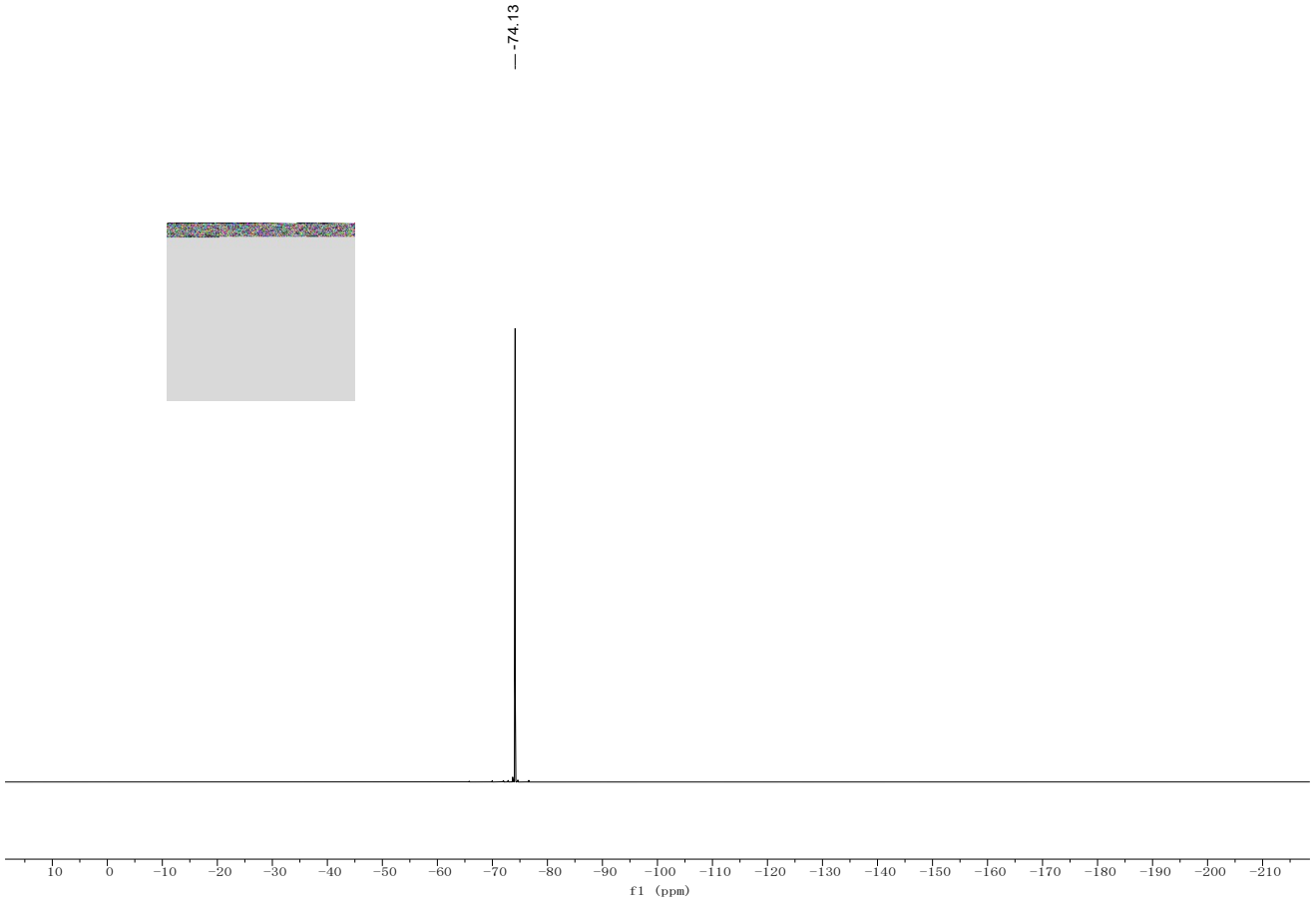
^{1}H NMR spectra for compound **5aj** (500 Hz, $CDCl_3$)



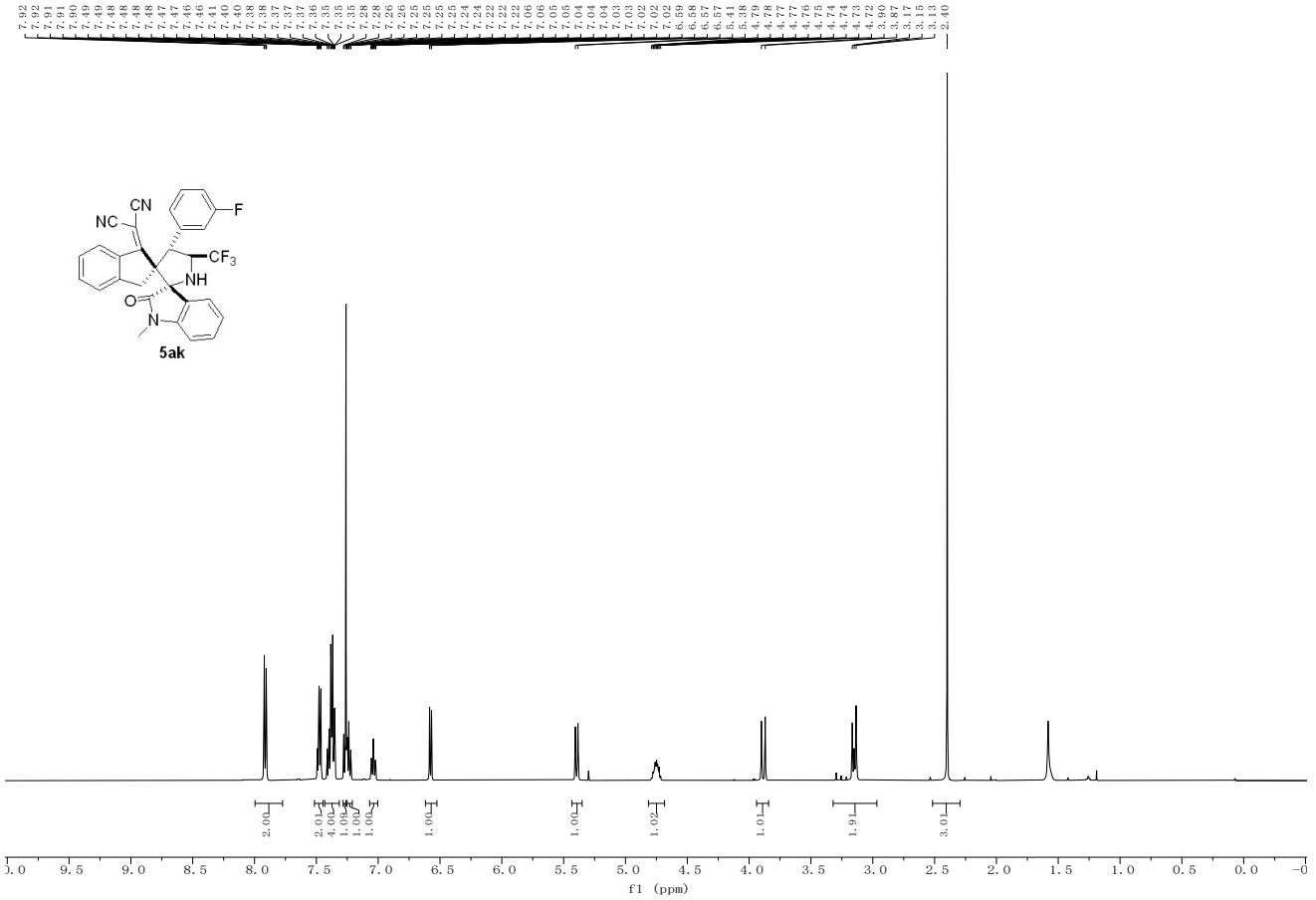
^{13}C NMR spectra for compound **5aj** (125 Hz, $CDCl_3$)



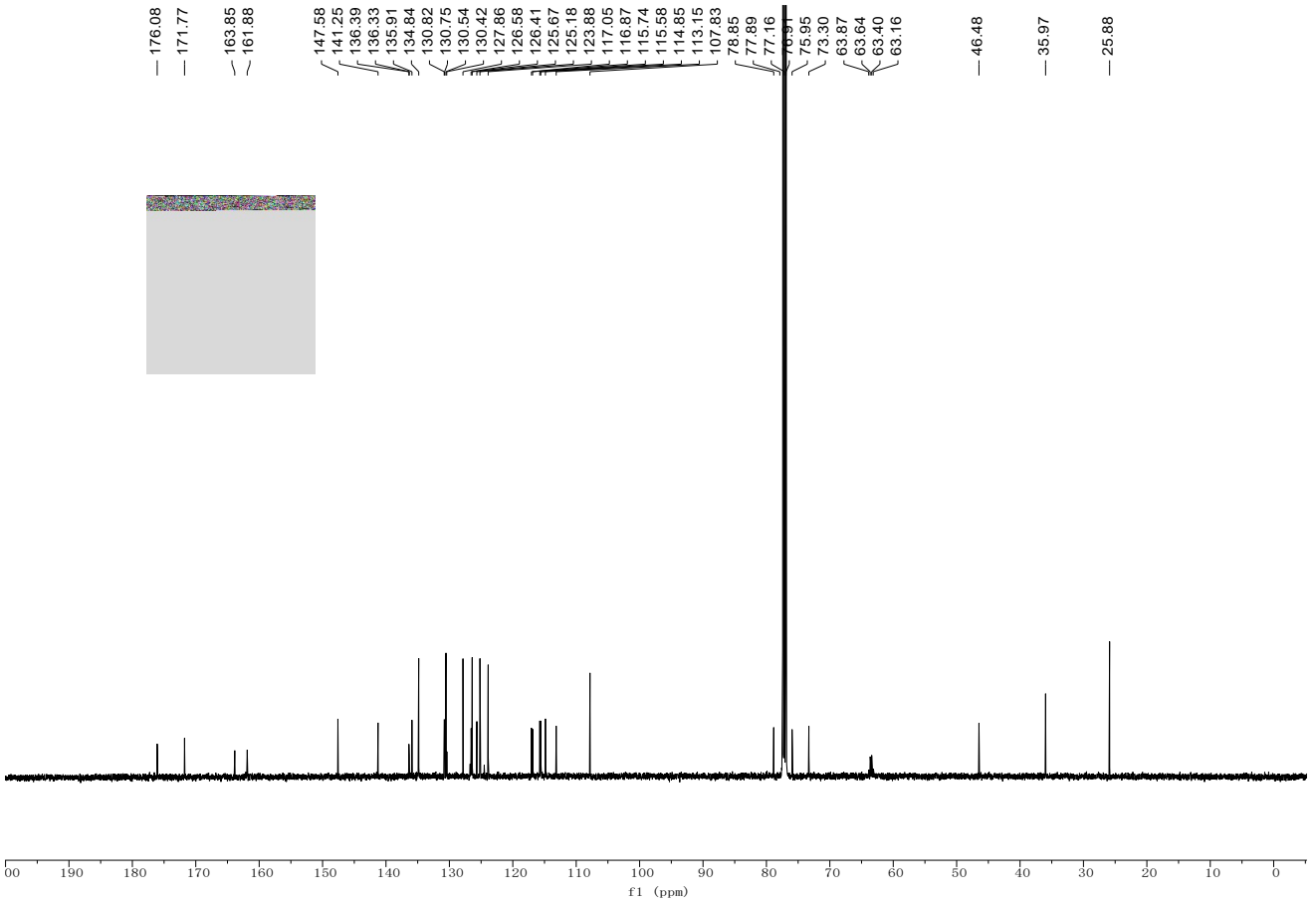
^{19}F NMR spectra for compound **5aj** (376 Hz, $CDCl_3$)



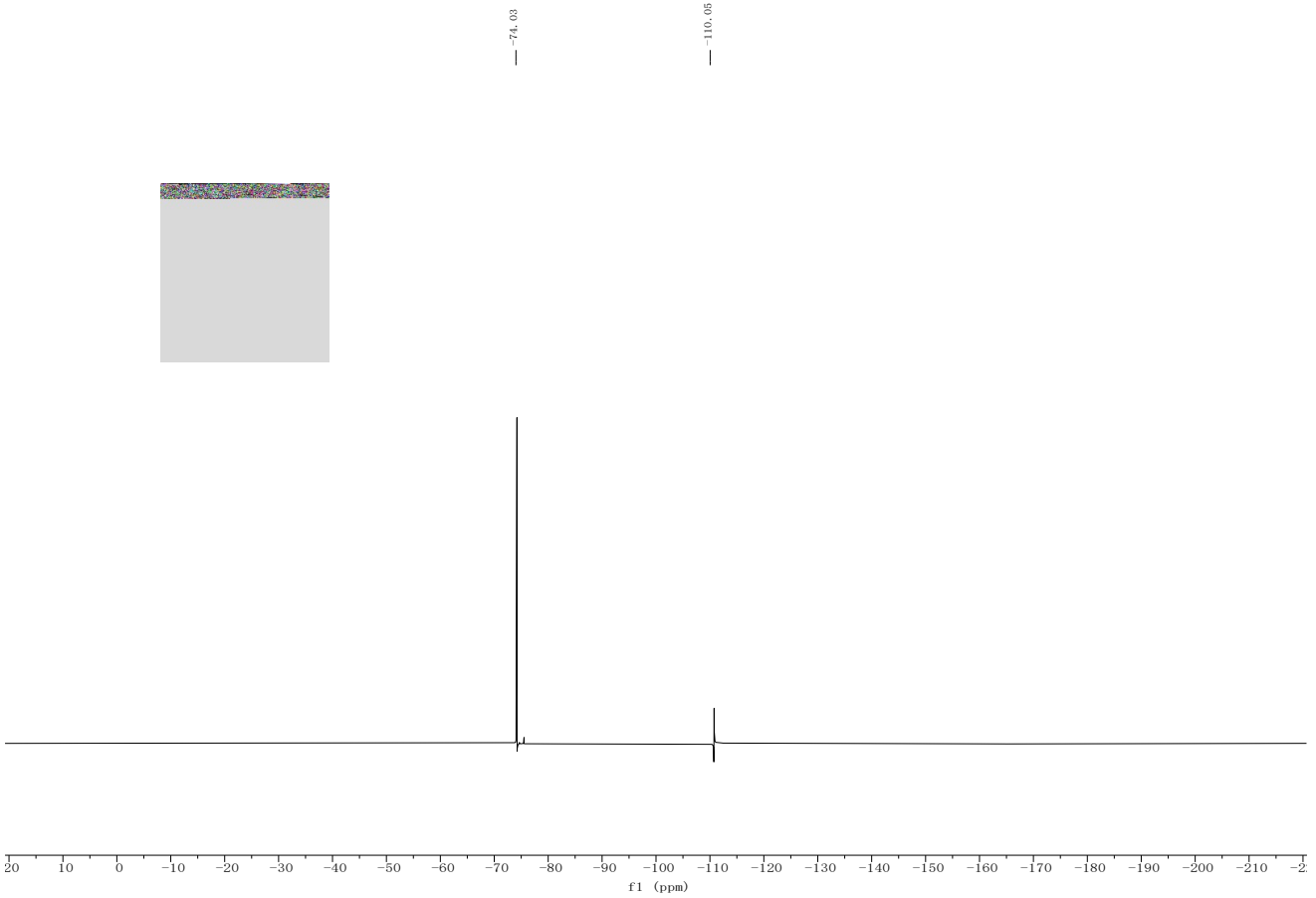
^{1}H NMR spectra for compound **5ak** (500 Hz, $CDCl_3$)



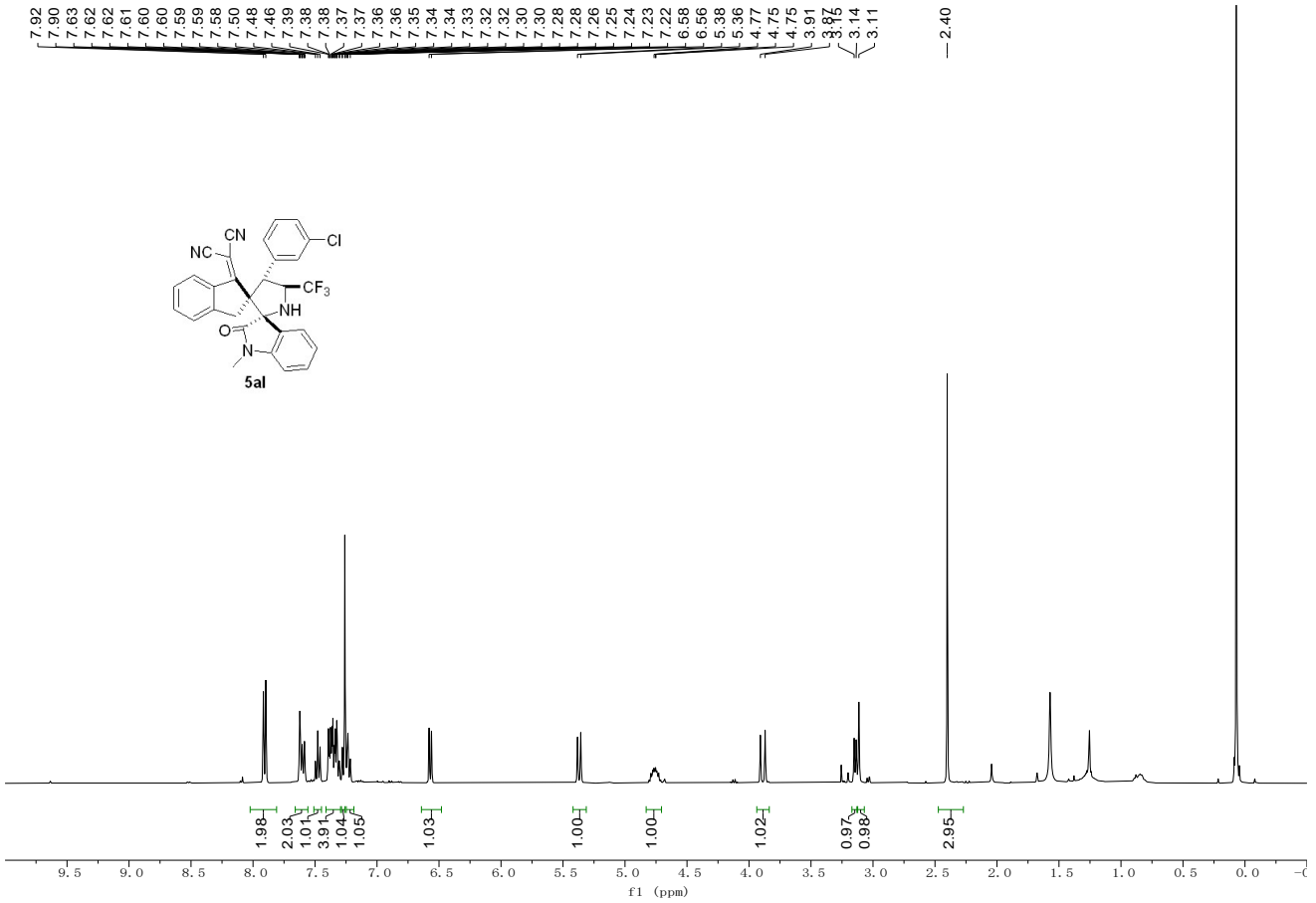
^{13}C NMR spectra for compound **5ak** (125 Hz, $CDCl_3$)



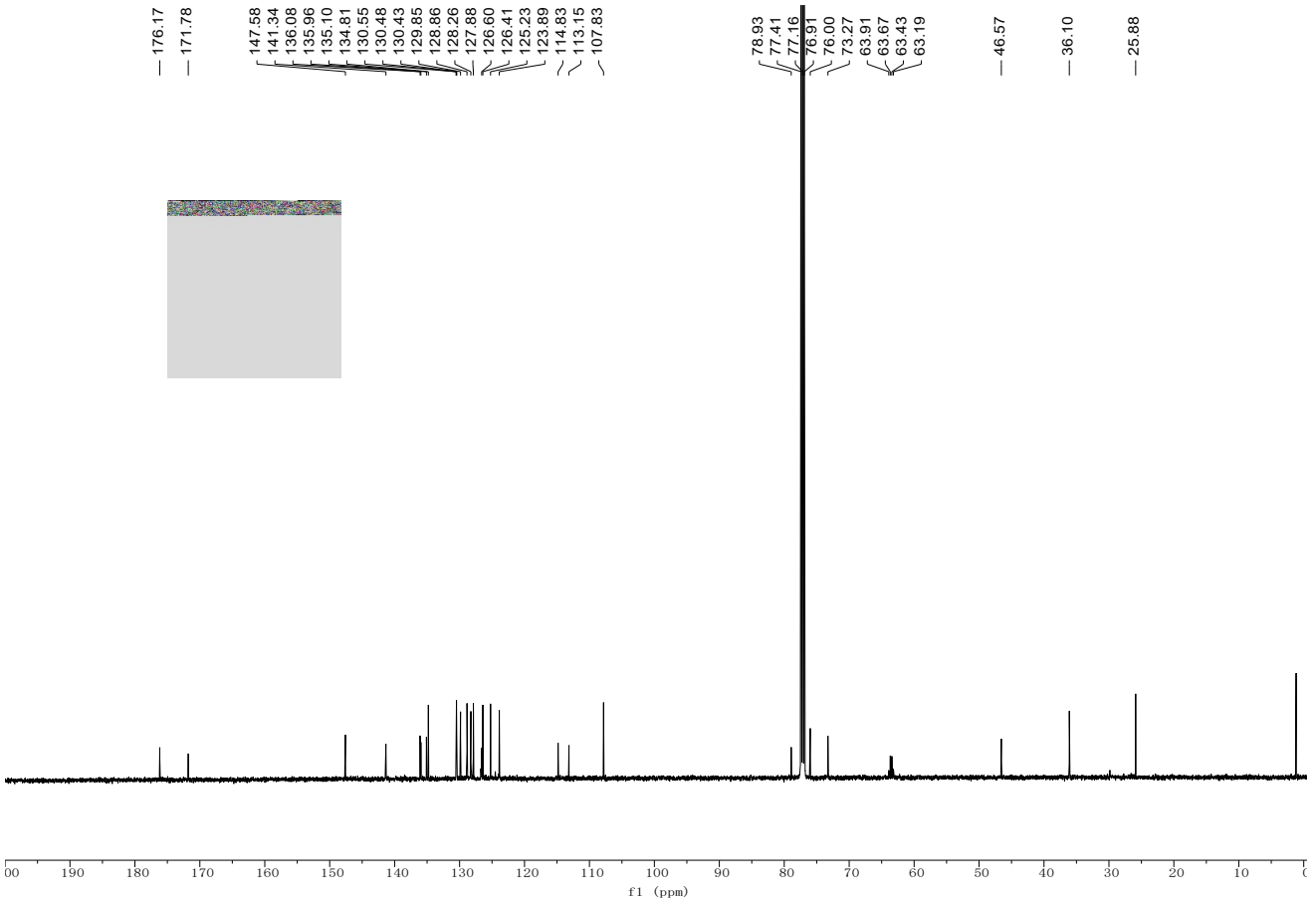
^{19}F NMR spectra for compound **5ak** (471 Hz, $CDCl_3$)



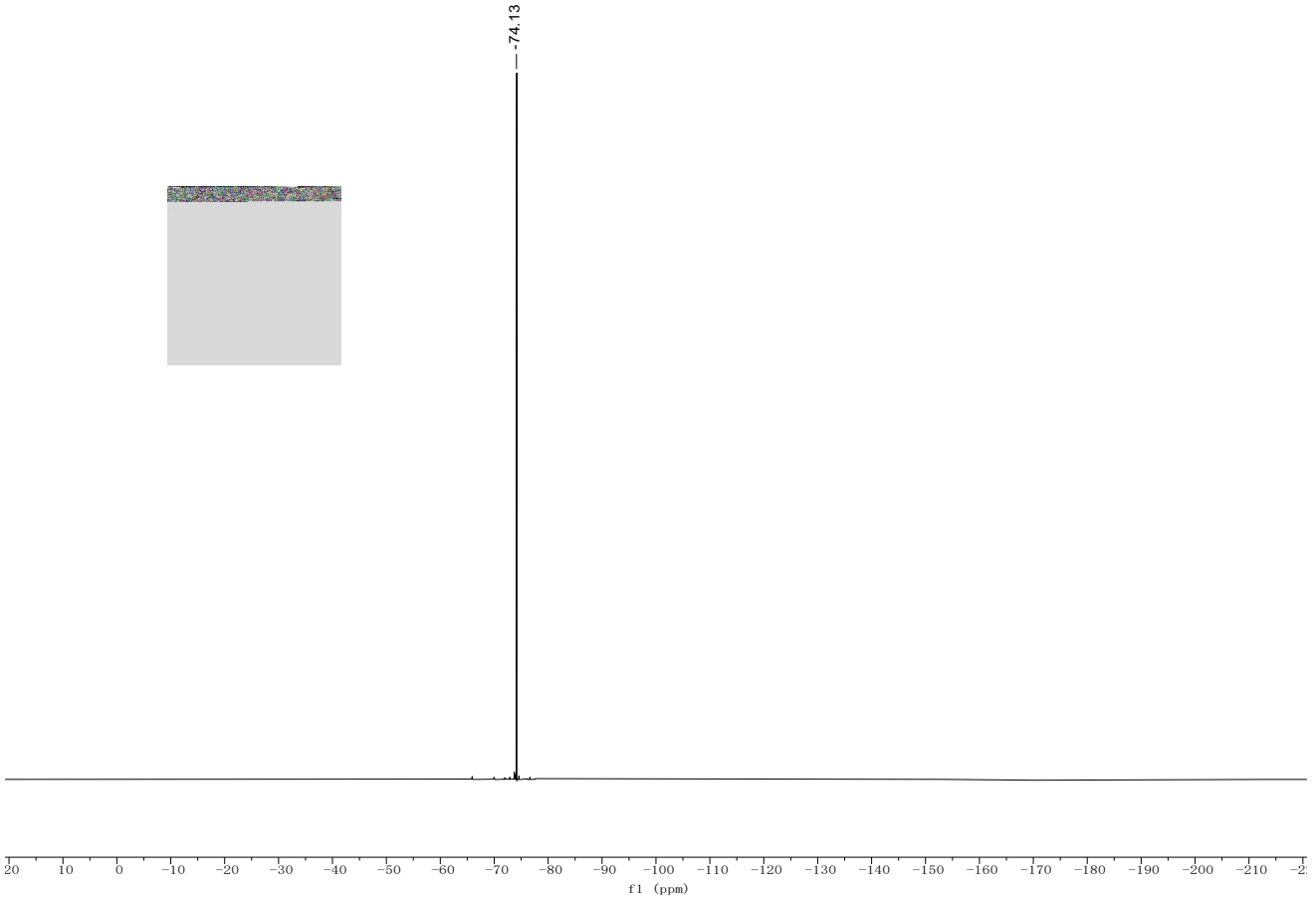
^{1}H NMR spectra for compound **5al** (400 Hz, $CDCl_3$)



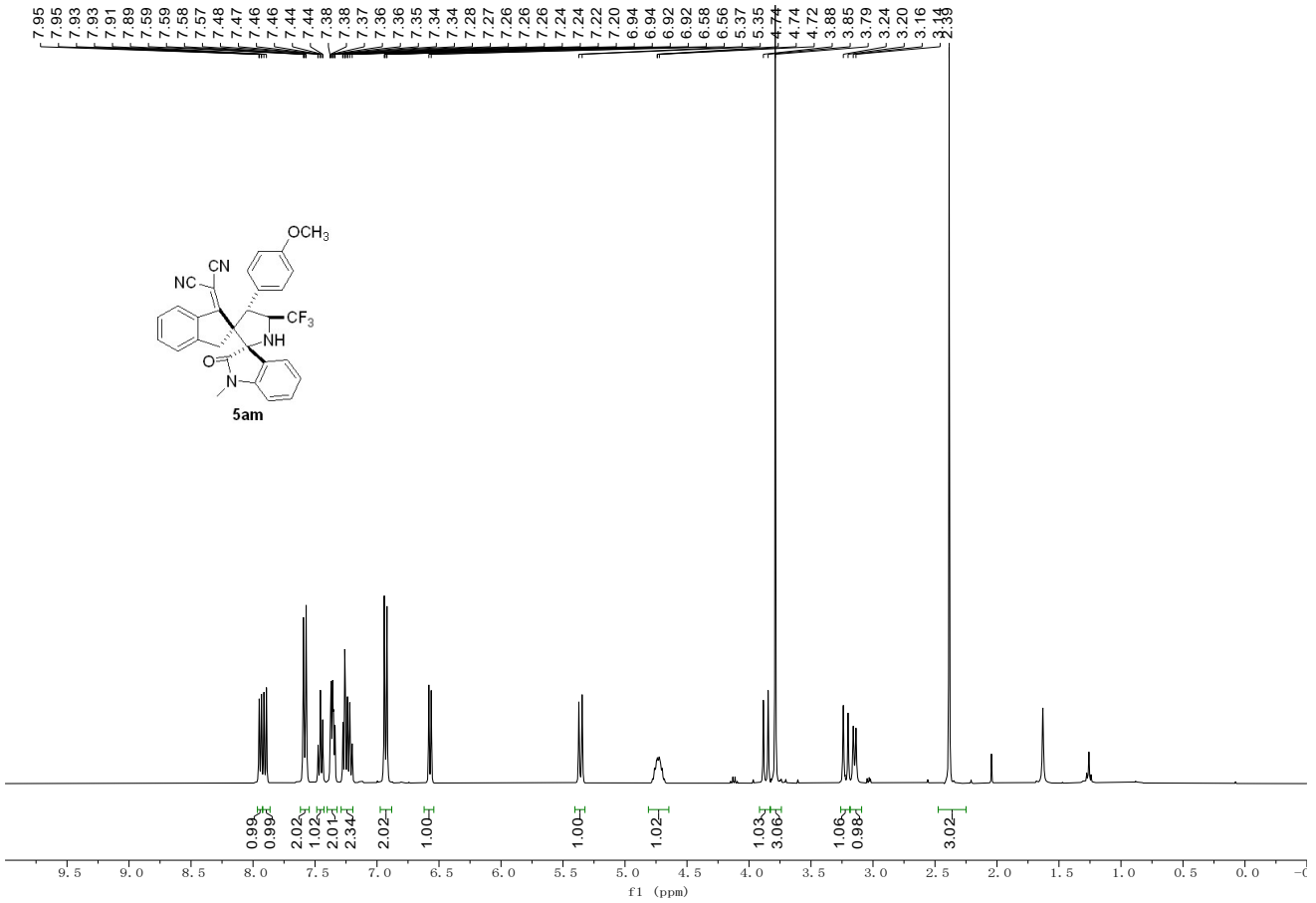
^{13}C NMR spectra for compound **5al** (125 Hz, $CDCl_3$)



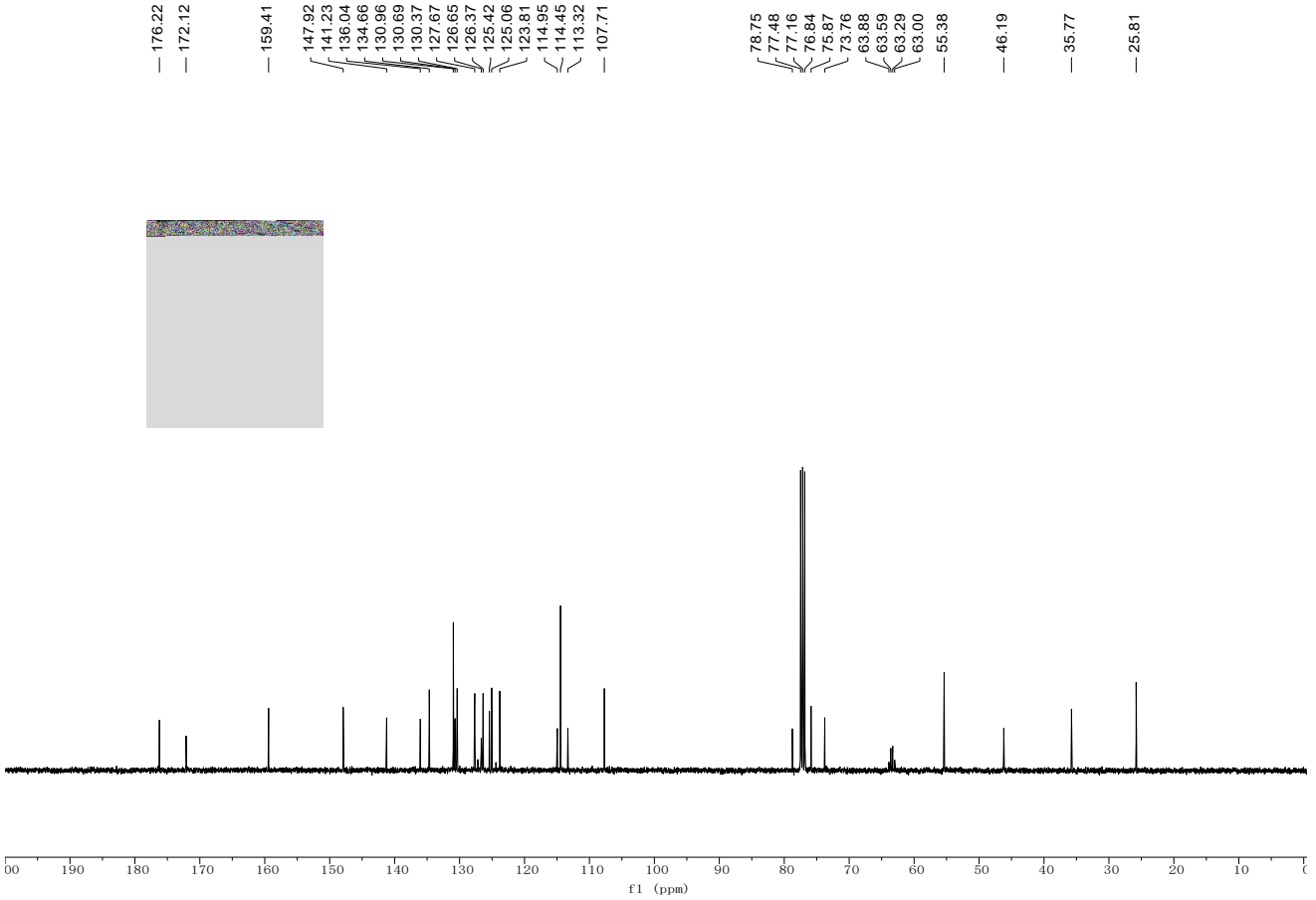
^{19}F NMR spectra for compound **5al** (471 Hz, $CDCl_3$)



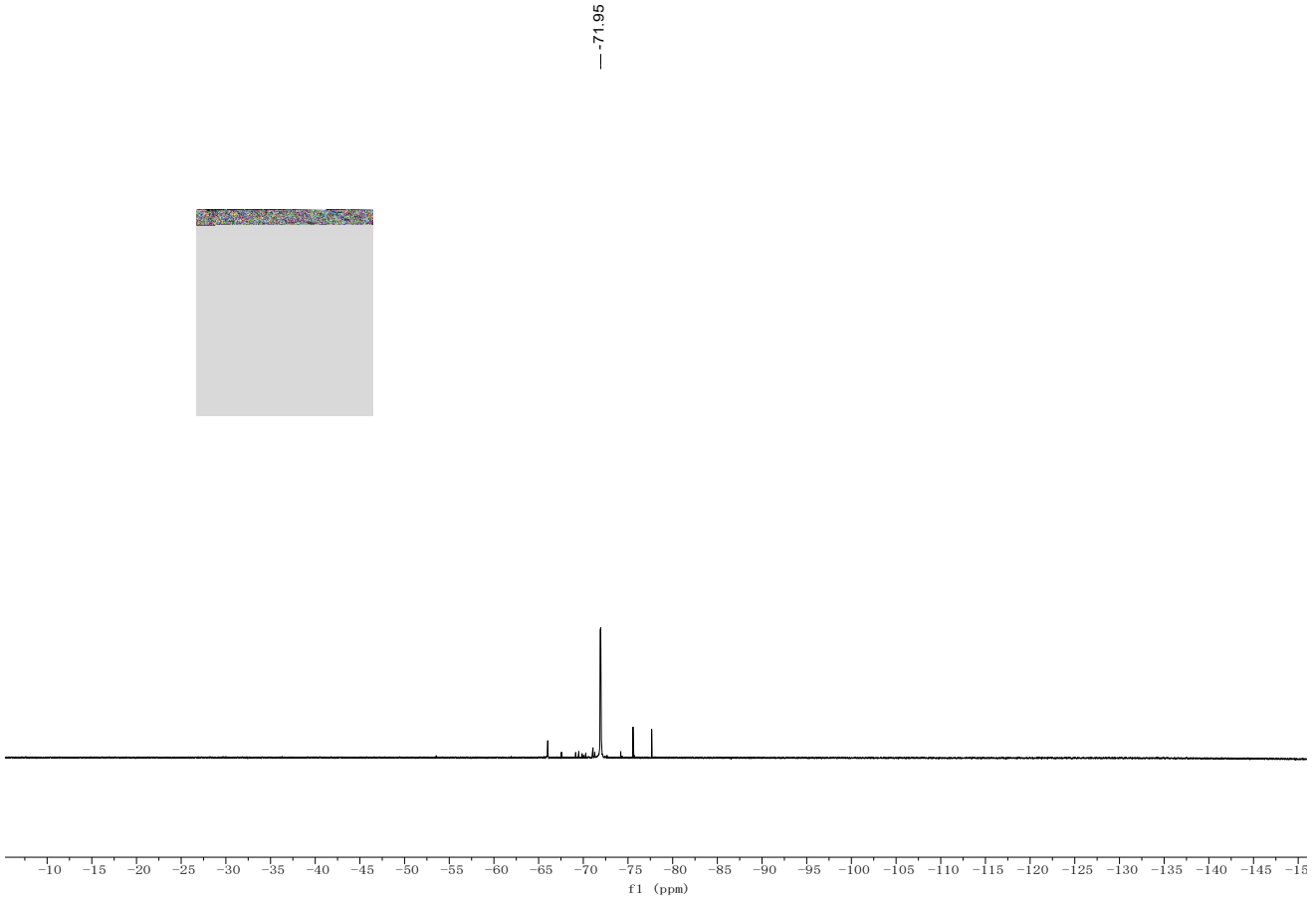
^{1}H NMR spectra for compound **5am** (400 Hz, $CDCl_3$)



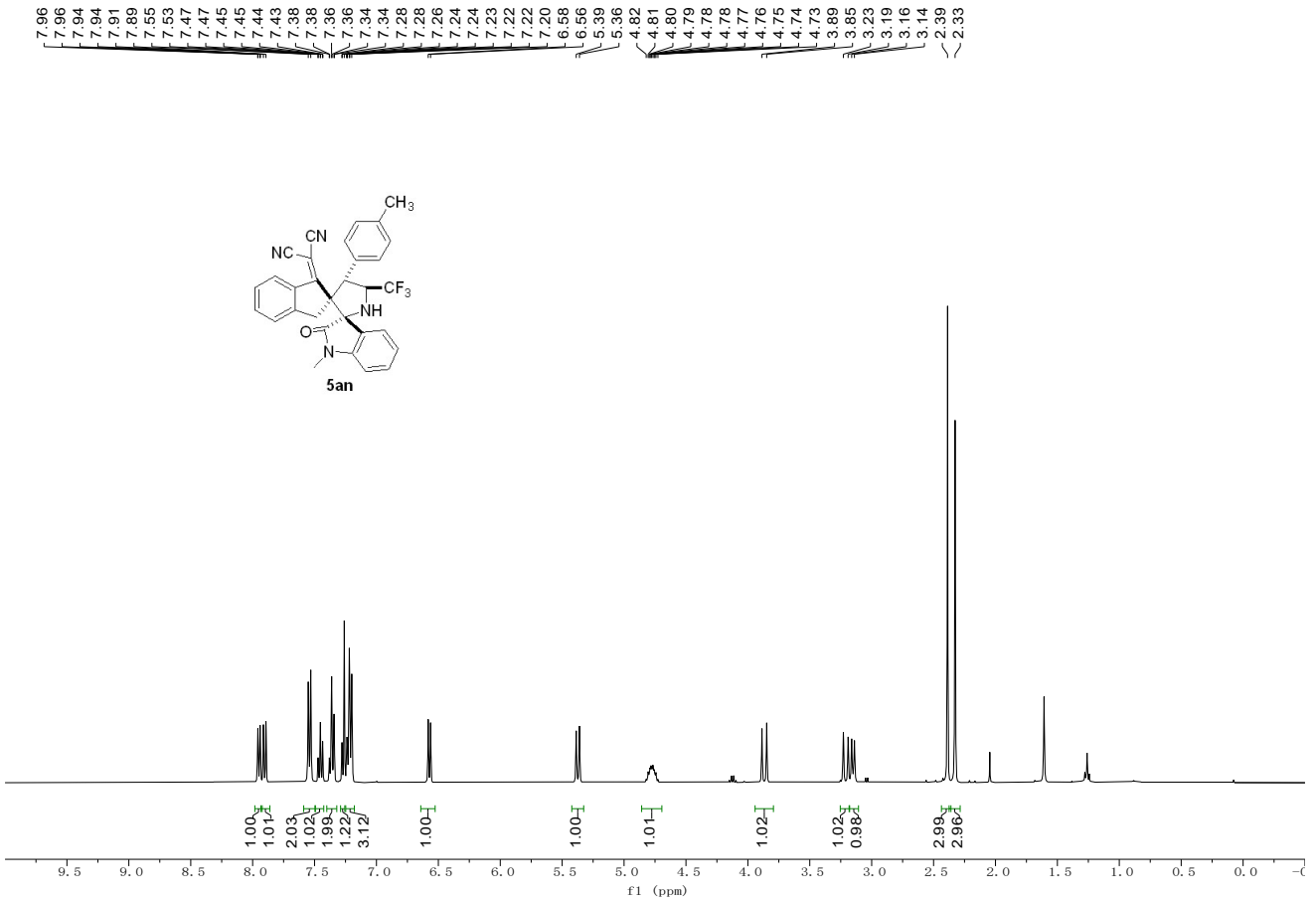
^{13}C NMR spectra for compound **5am** (100 Hz, $CDCl_3$)



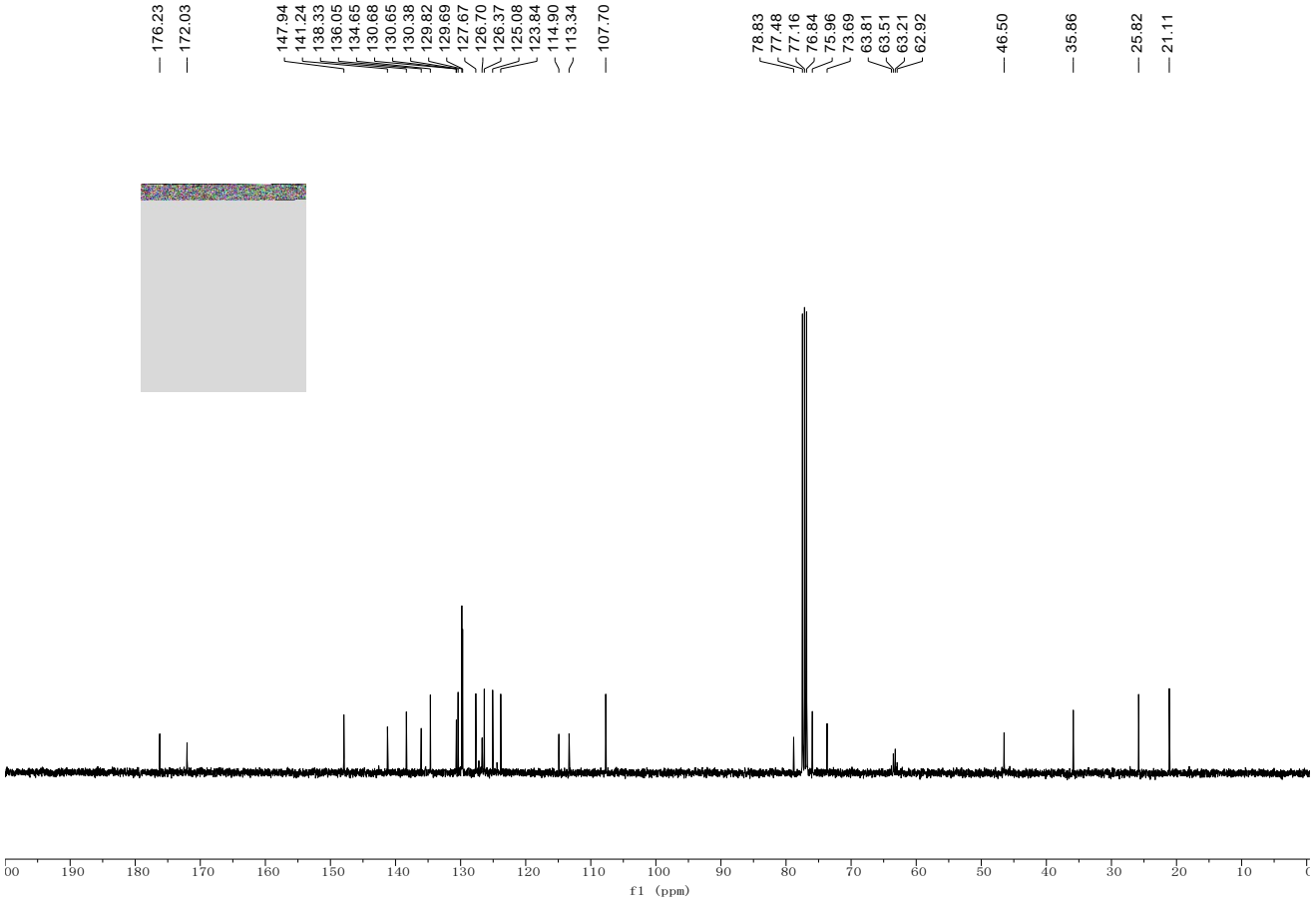
^{19}F NMR spectra for compound **5am** (376 Hz, $CDCl_3$)



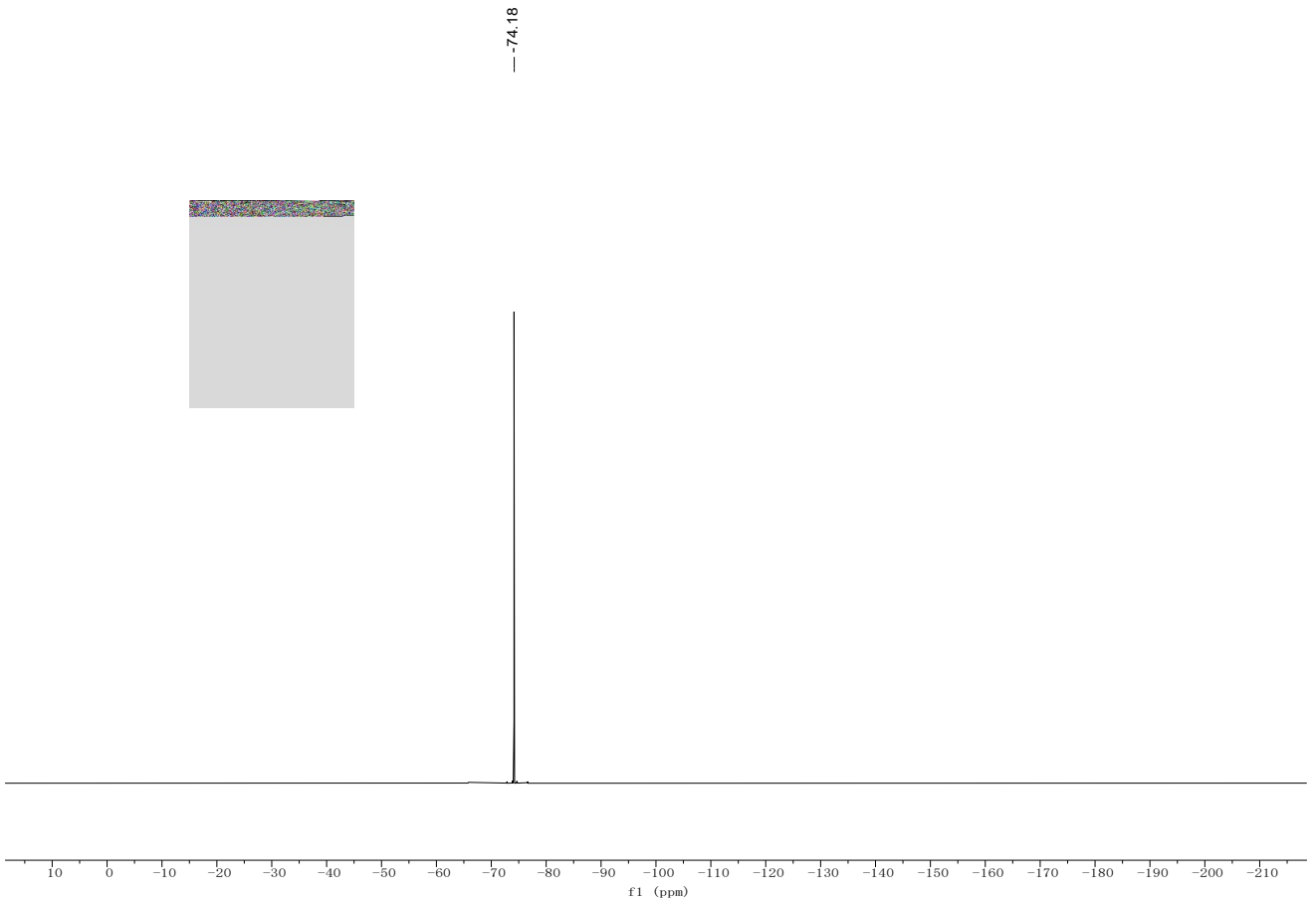
^{1}H NMR spectra for compound **5an** (400 Hz, $CDCl_3$)



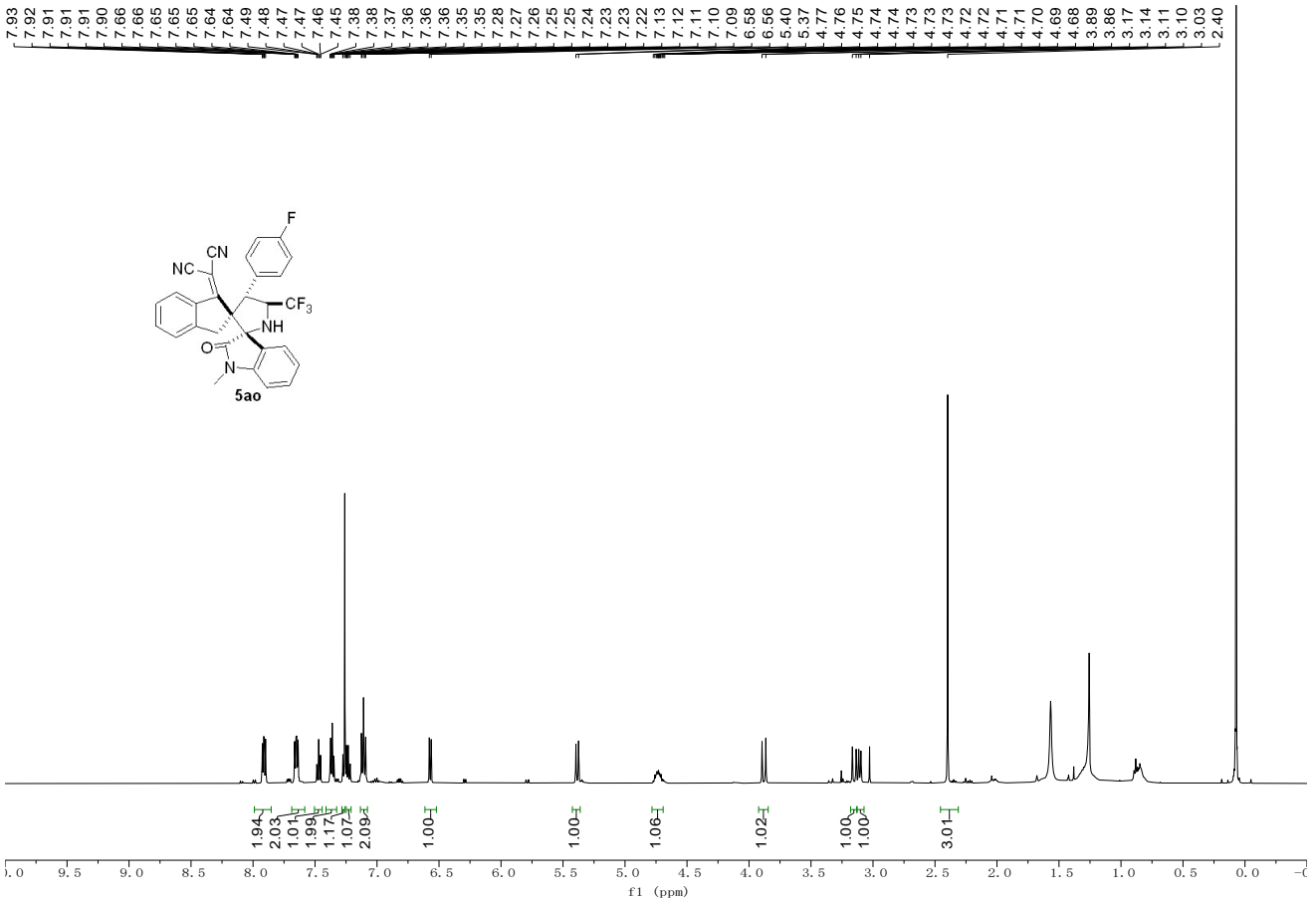
^{13}C NMR spectra for compound **5an** (100 Hz, $CDCl_3$)



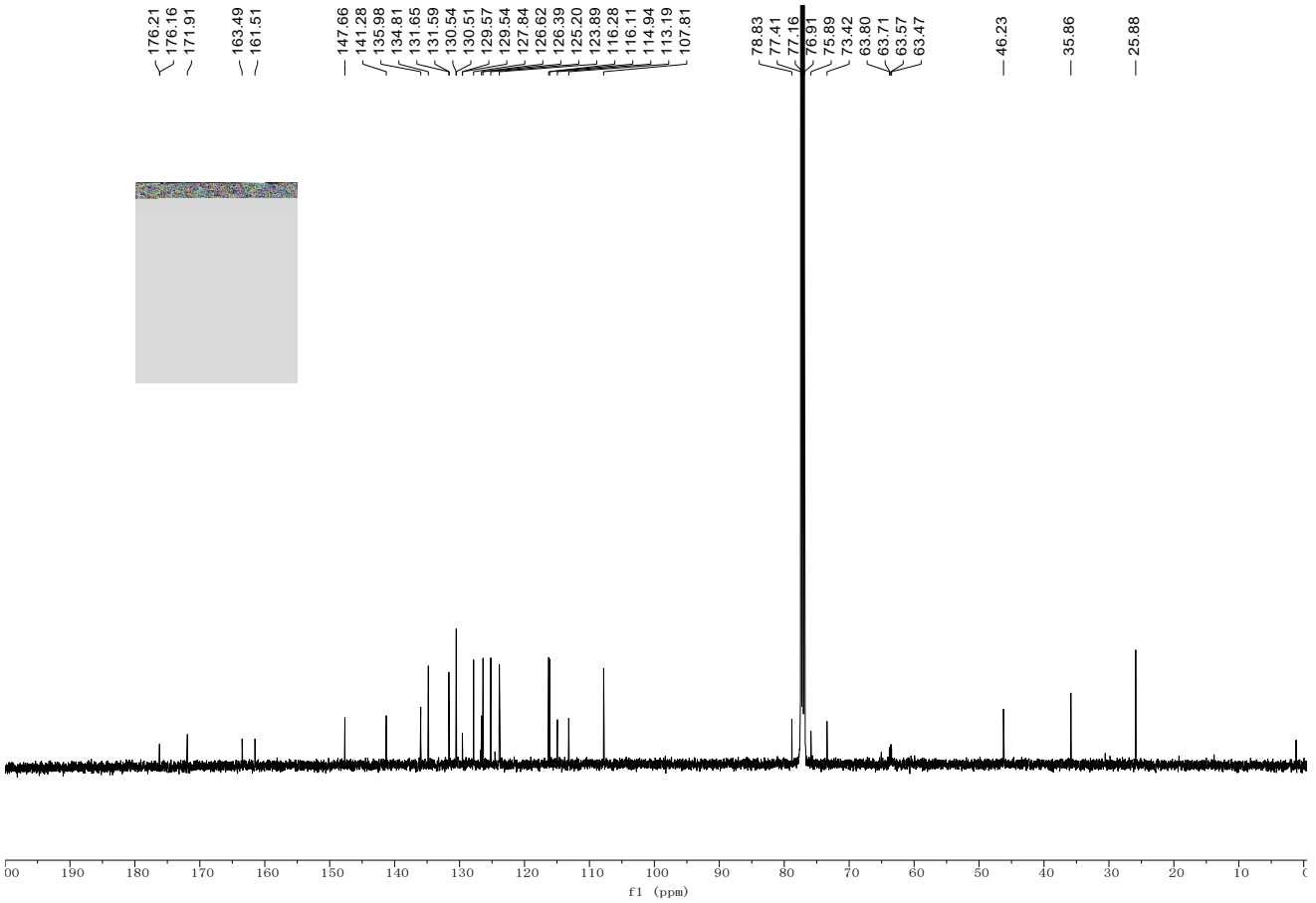
^{19}F NMR spectra for compound **5an** (376 Hz, $CDCl_3$)



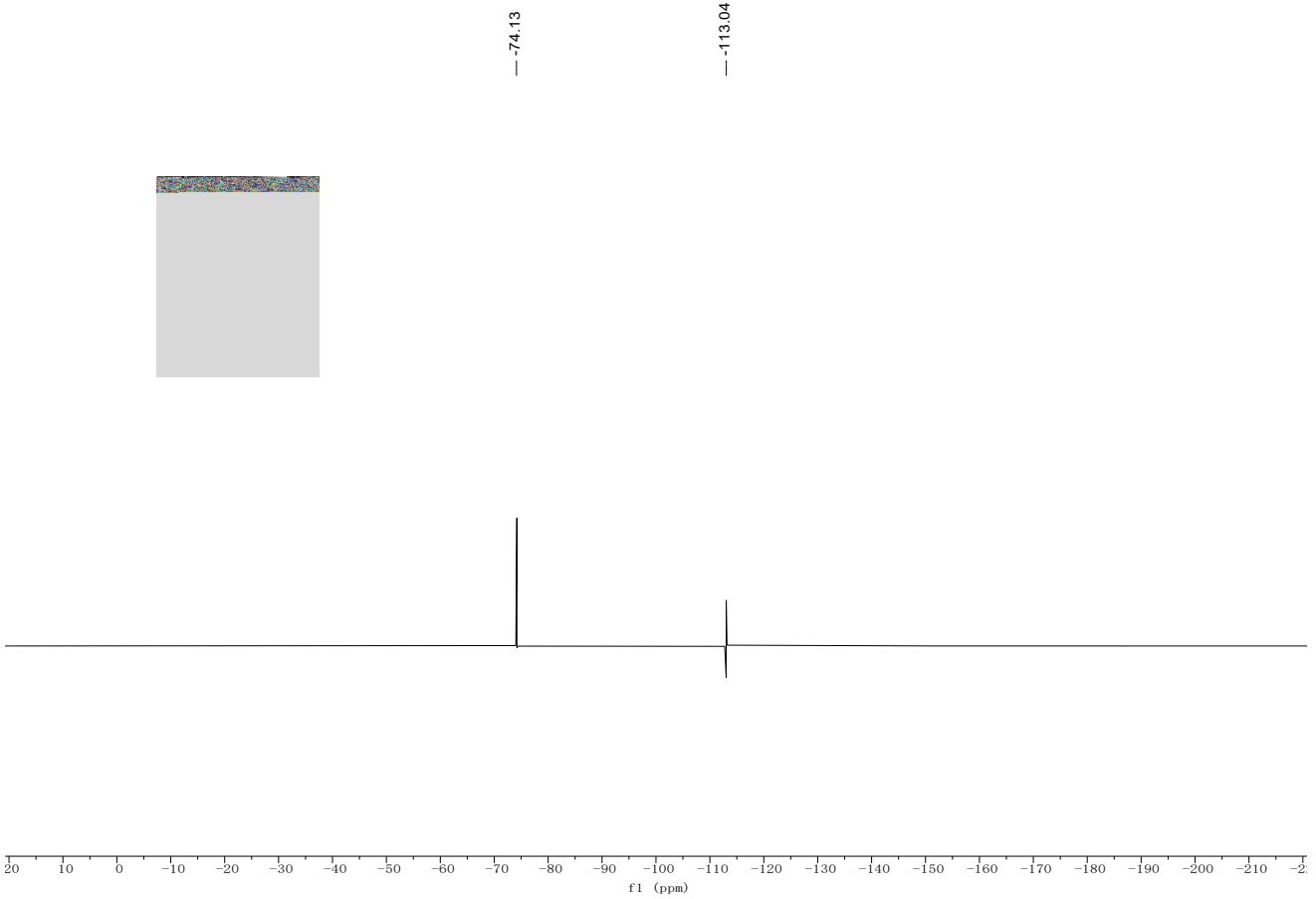
^{1}H NMR spectra for compound **5ao** (500 Hz, $CDCl_3$)



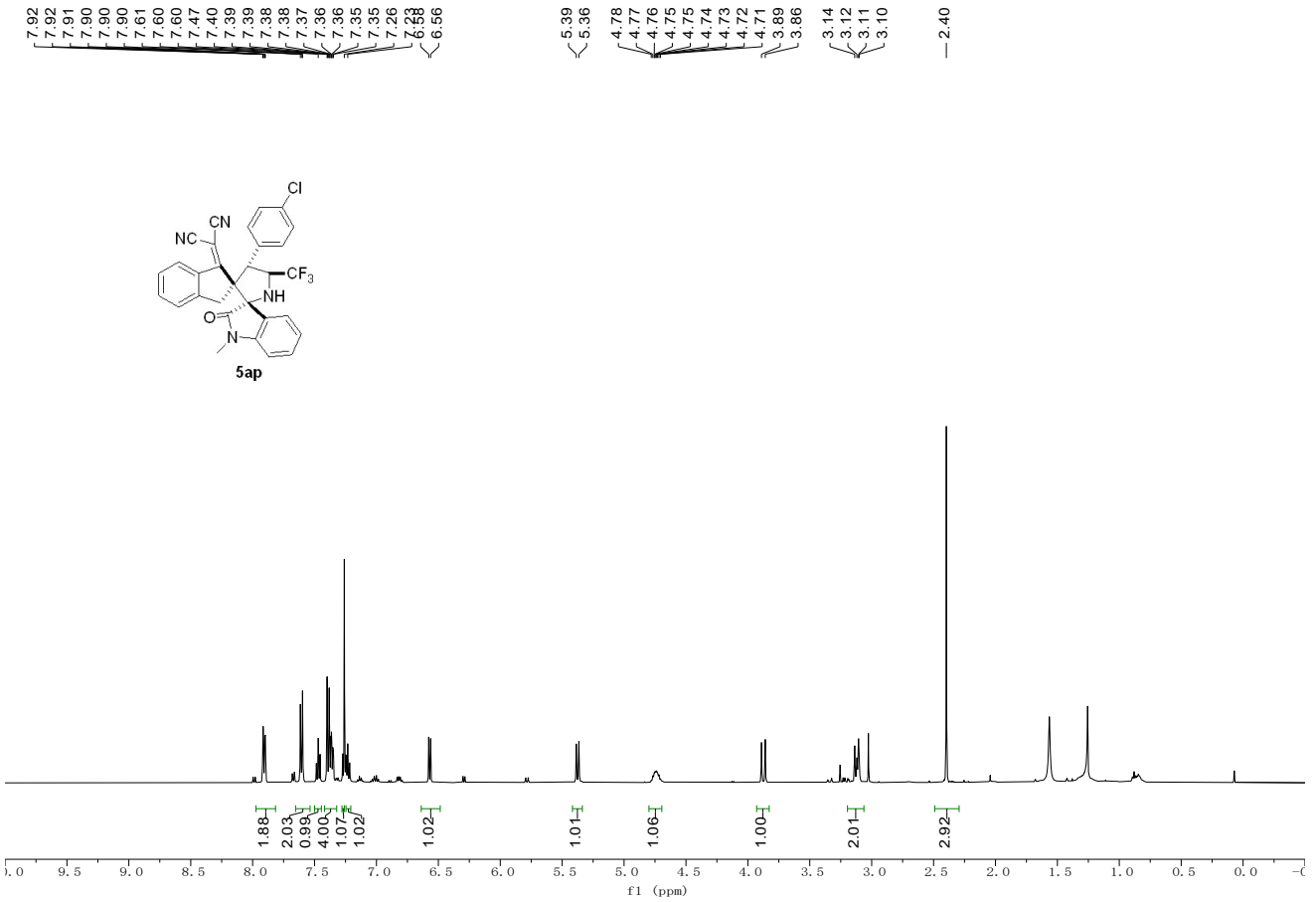
^{13}C NMR spectra for compound **5ao** (125 Hz, $CDCl_3$)



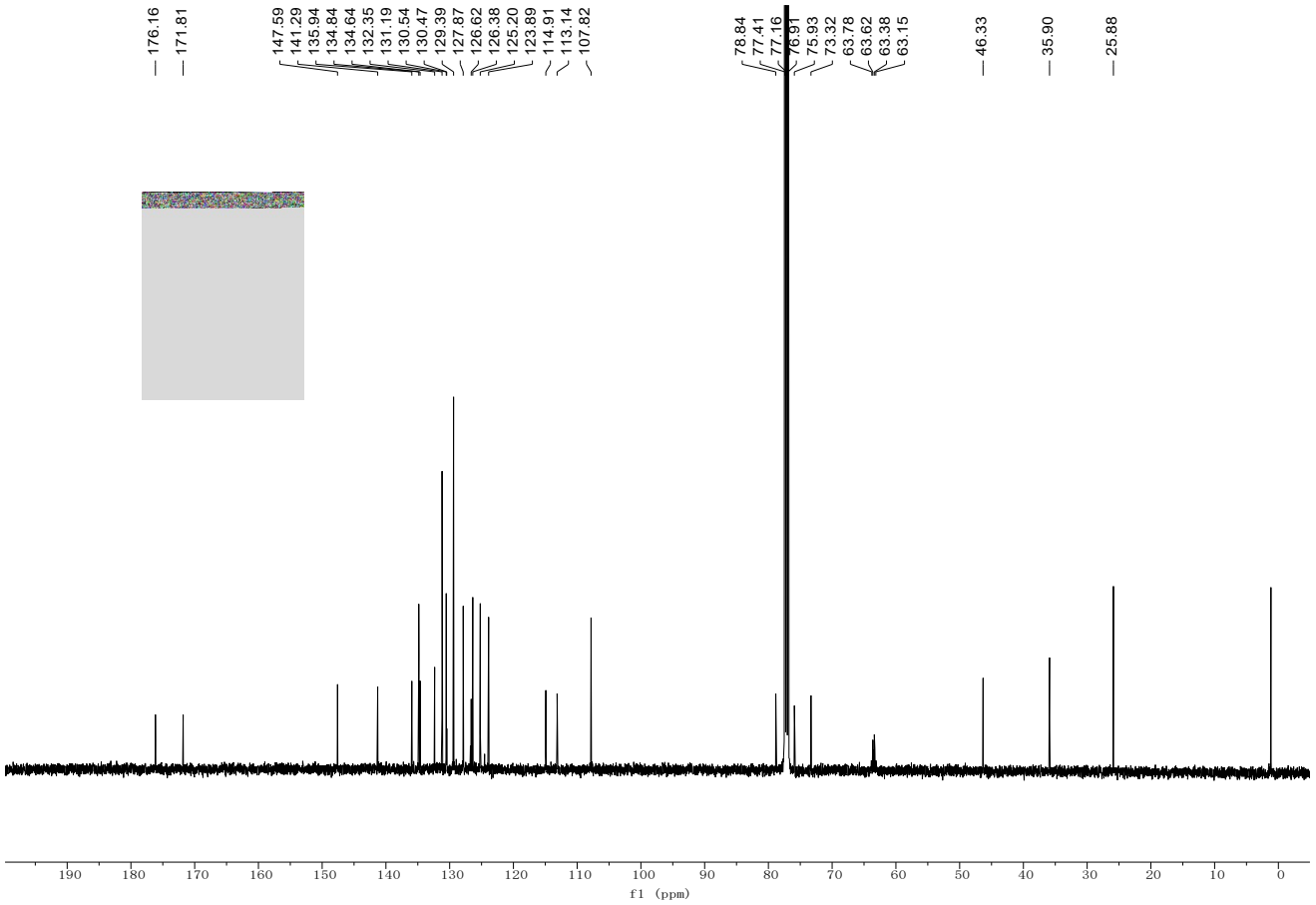
^{19}F NMR spectra for compound **5ao** (471 Hz, $CDCl_3$)



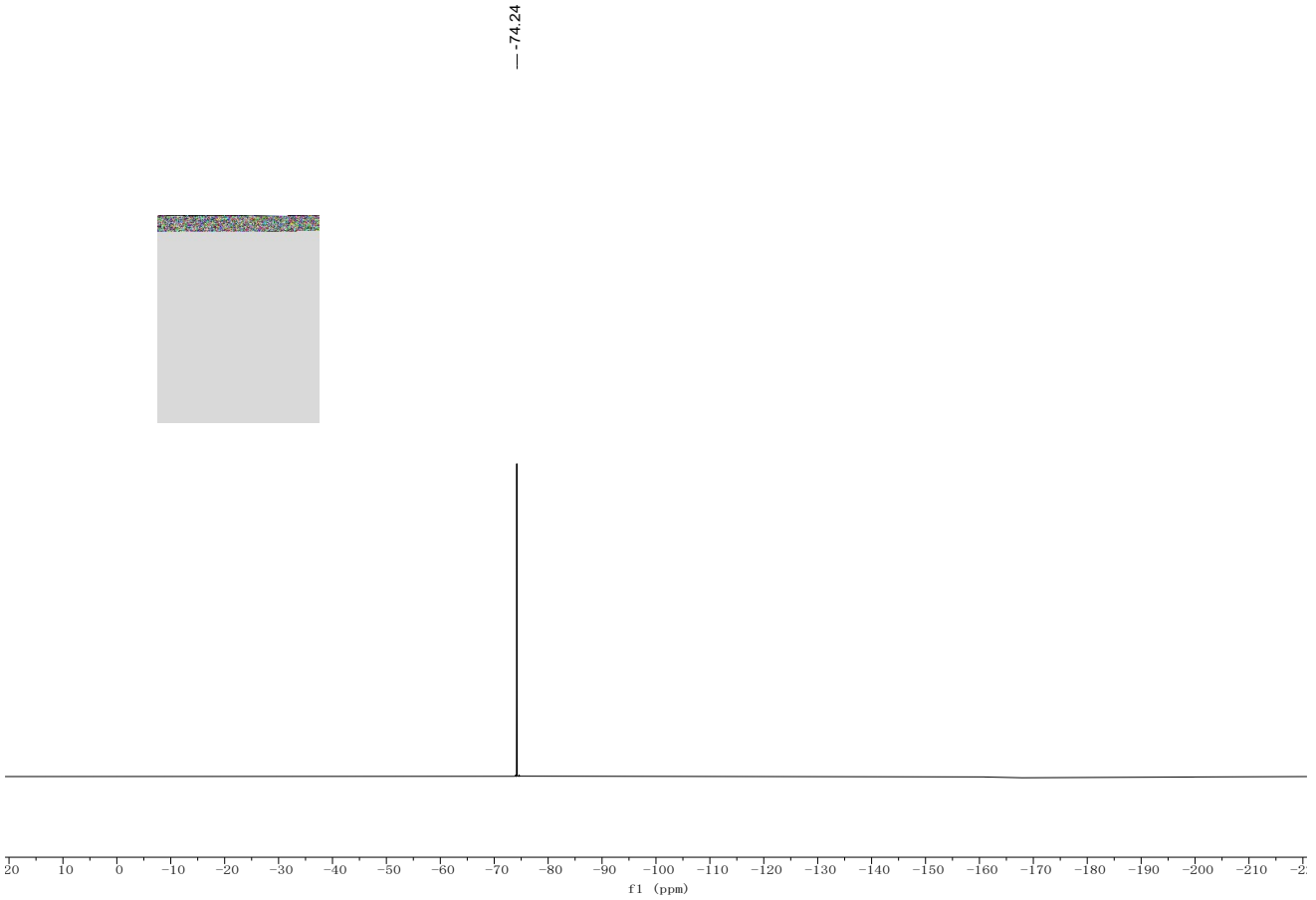
^{1}H NMR spectra for compound **5ap** (500 Hz, $CDCl_3$)



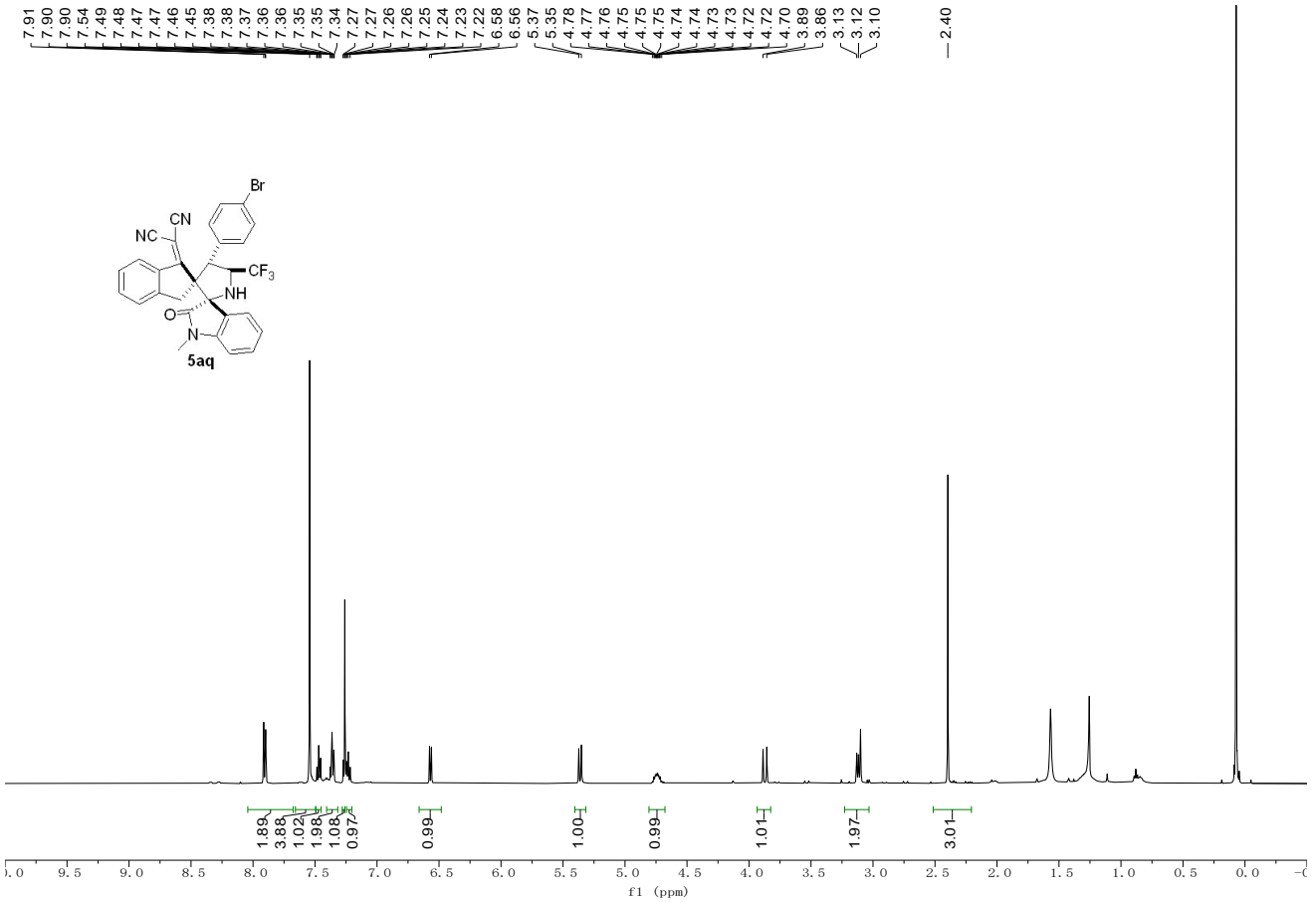
^{13}C NMR spectra for compound **5ap** (125 Hz, $CDCl_3$)



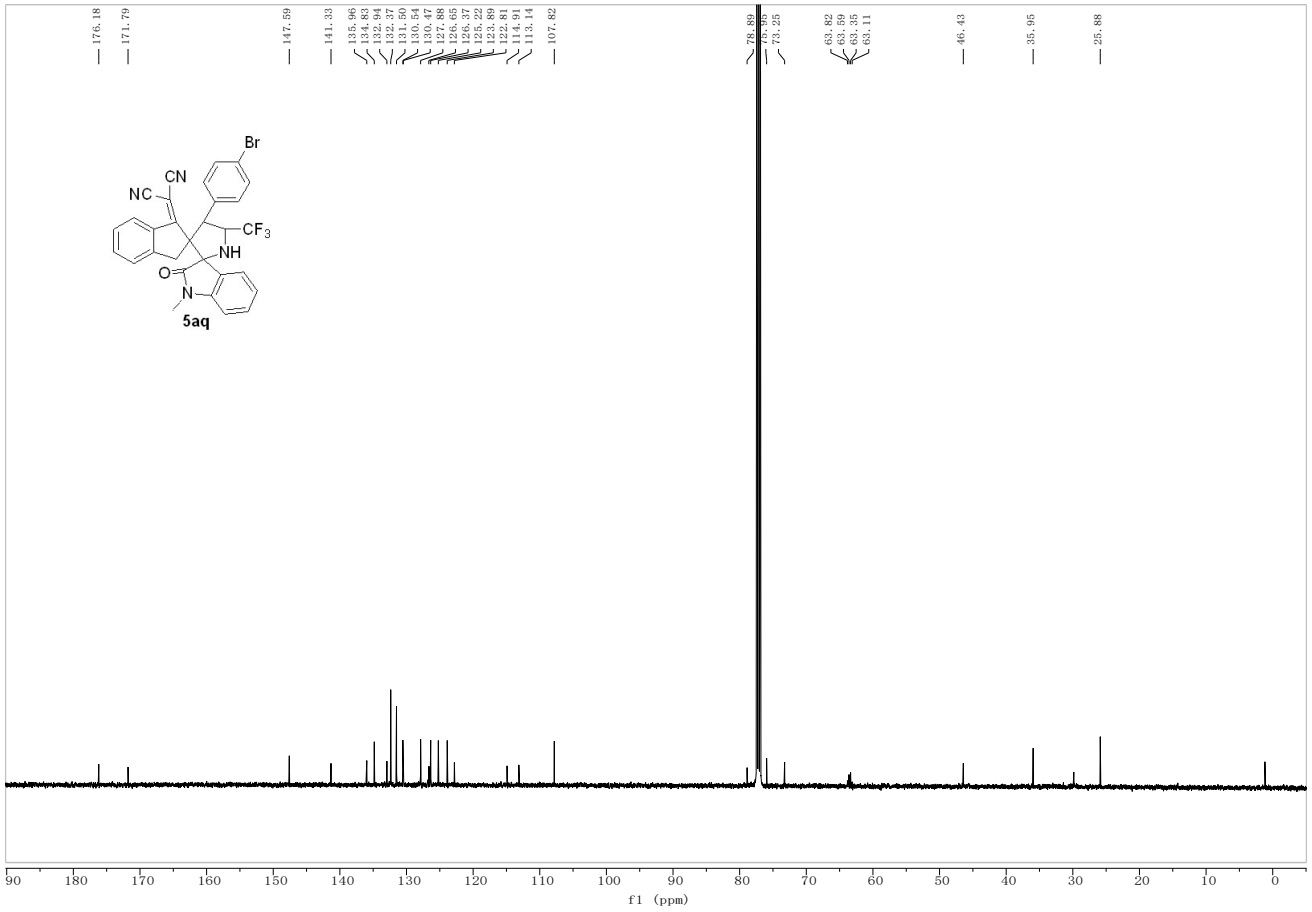
^{19}F NMR spectra for compound **5ap** (471 Hz, $CDCl_3$)



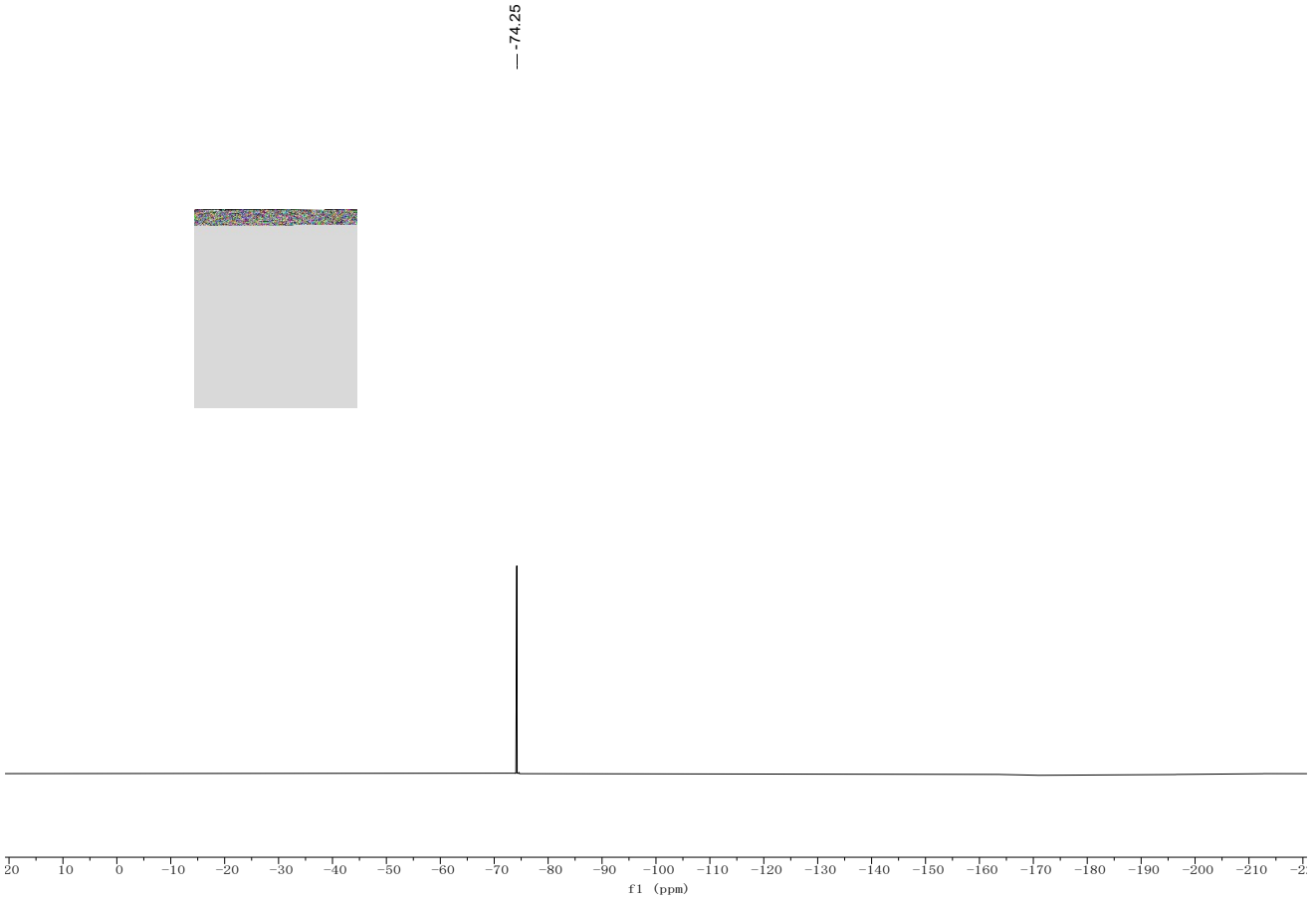
^{1}H NMR spectra for compound **5aq** (500 Hz, $CDCl_3$)



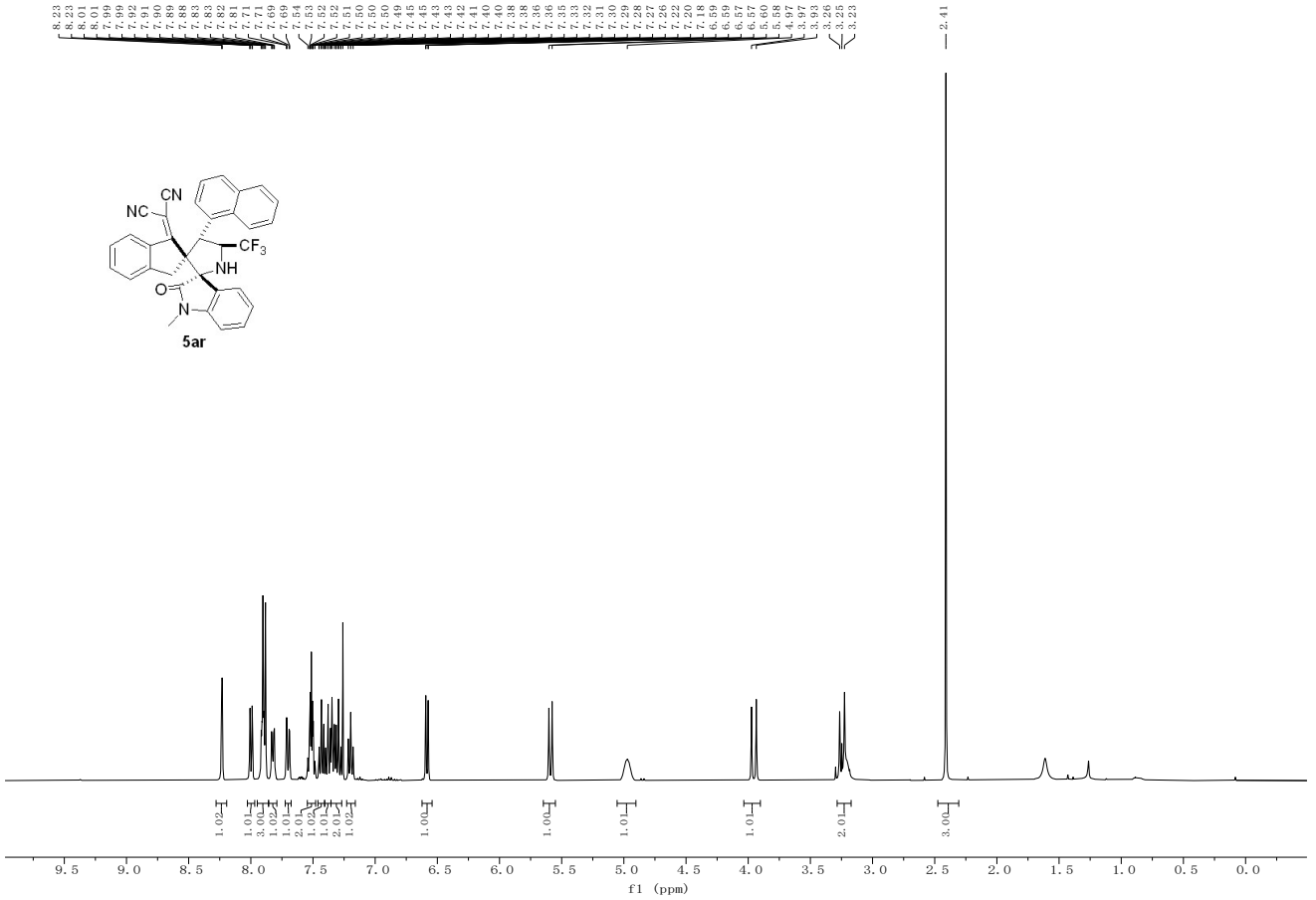
^{13}C NMR spectra for compound **5aq** (125 Hz, $CDCl_3$)



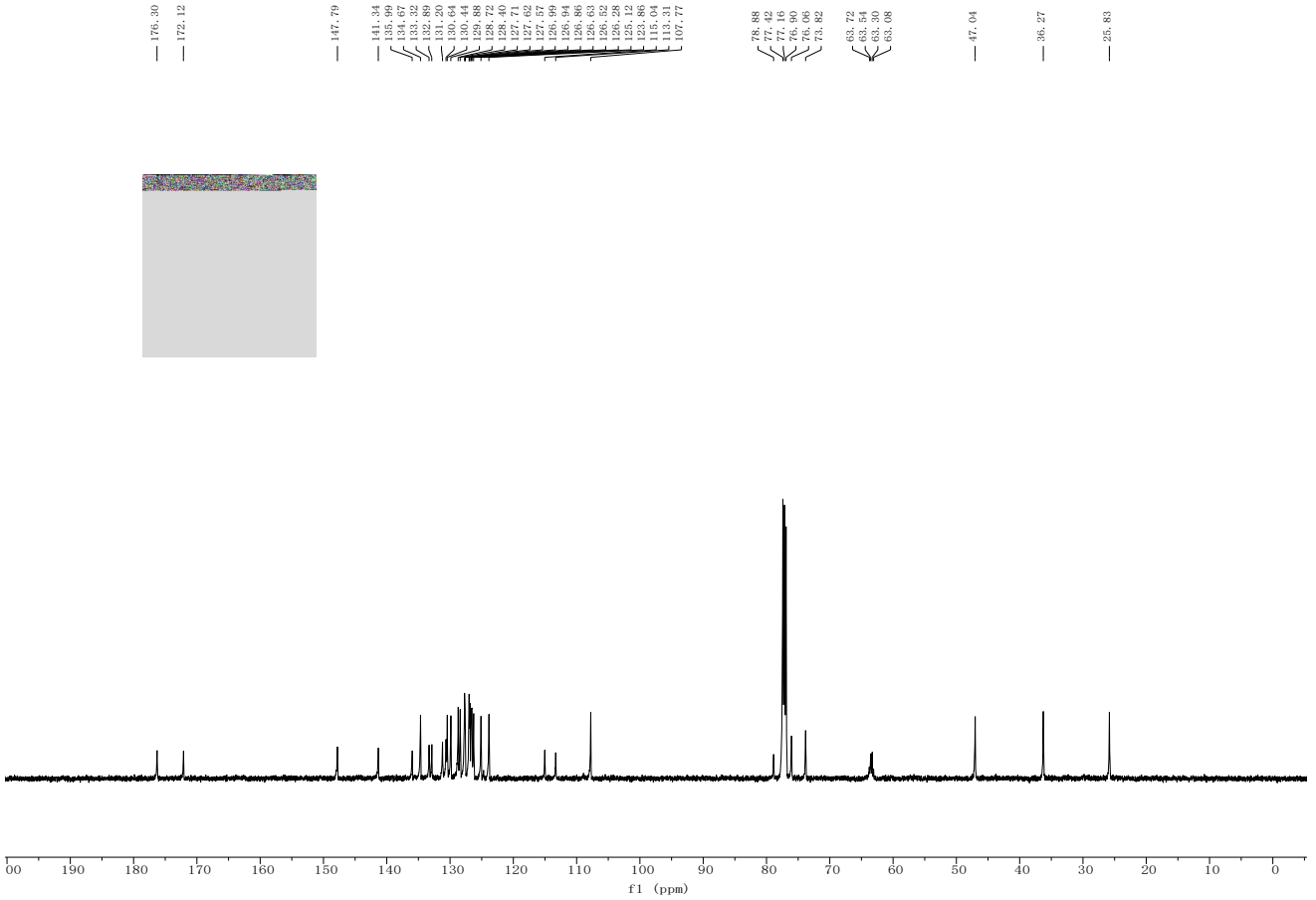
^{19}F NMR spectra for compound **5aq** (471 Hz, $CDCl_3$)



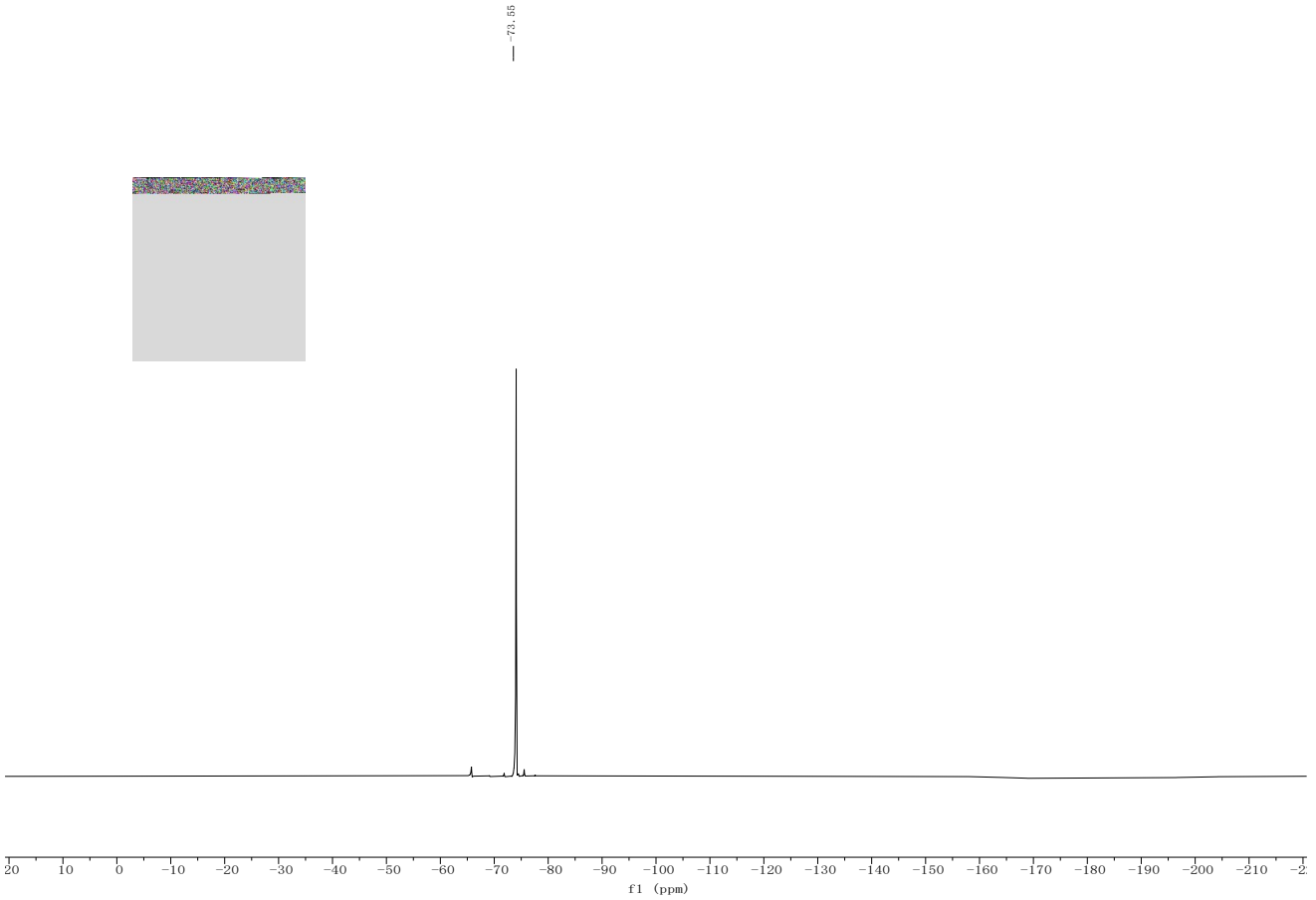
^{1}H NMR spectra for compound **5ar** (400 Hz, $CDCl_3$)



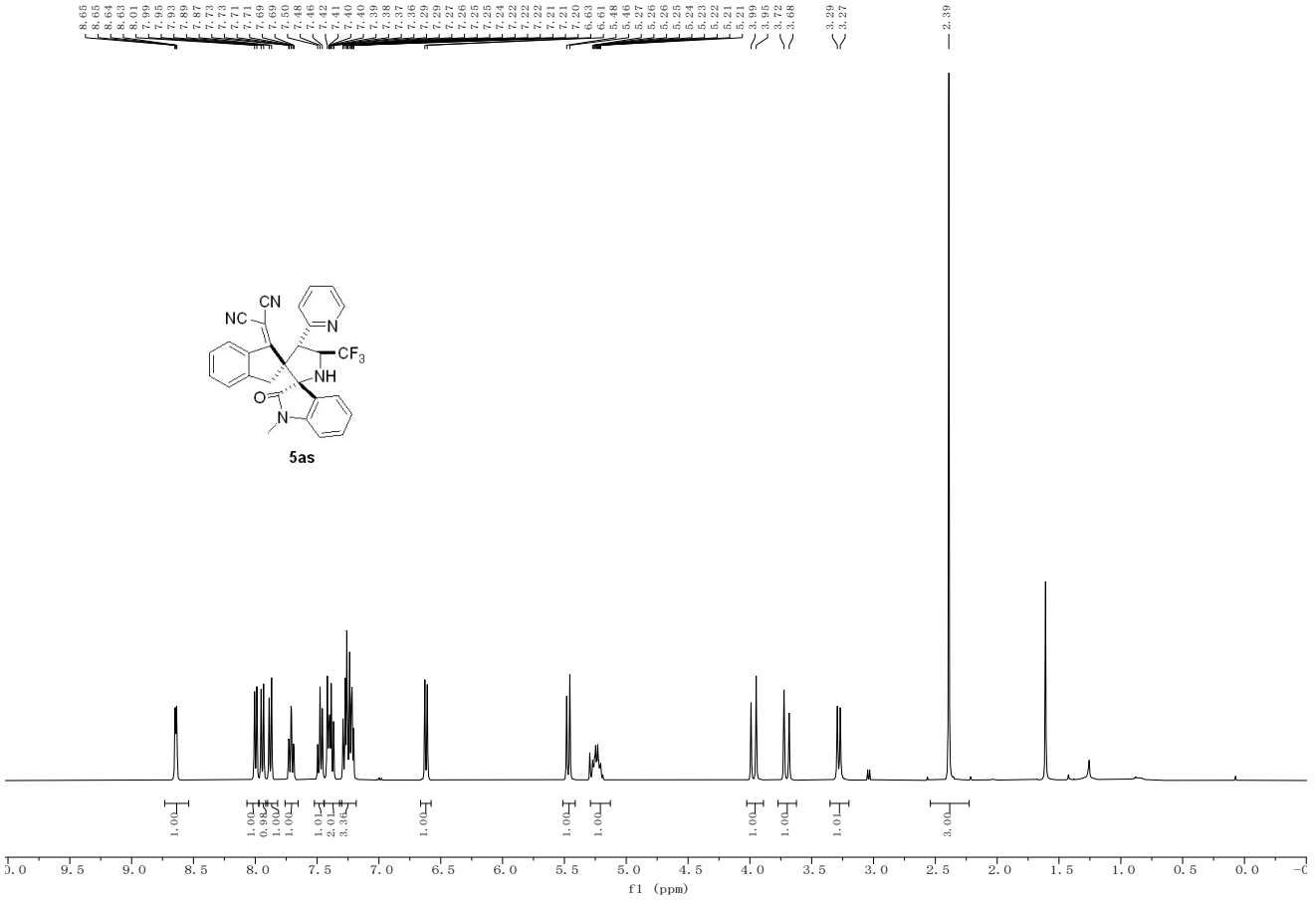
^{13}C NMR spectra for compound **5ar** (125 Hz, $CDCl_3$)



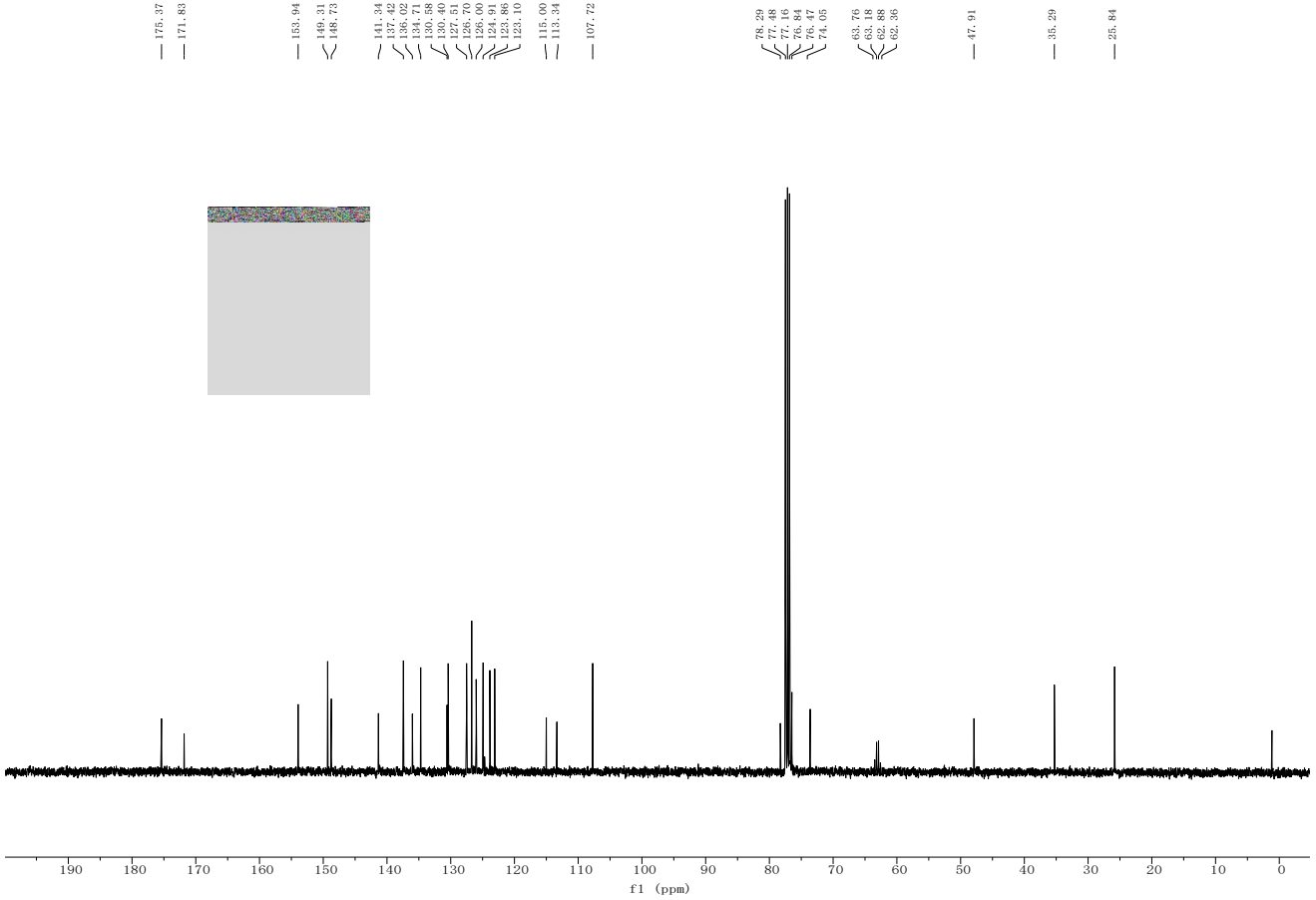
^{19}F NMR spectra for compound **5ar** (471 Hz, $CDCl_3$)



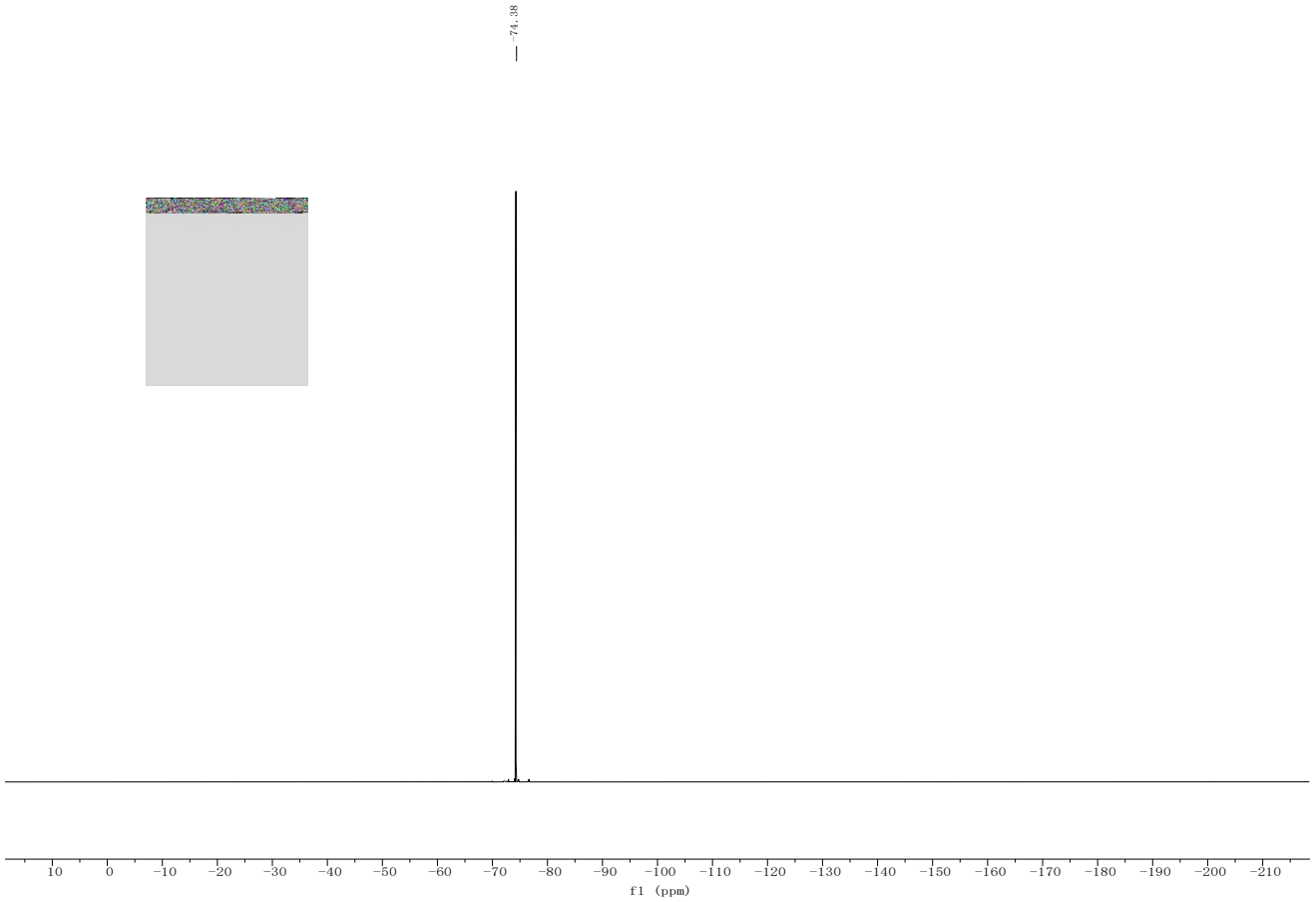
^{1}H NMR spectra for compound **5as** (400 Hz, $CDCl_3$)



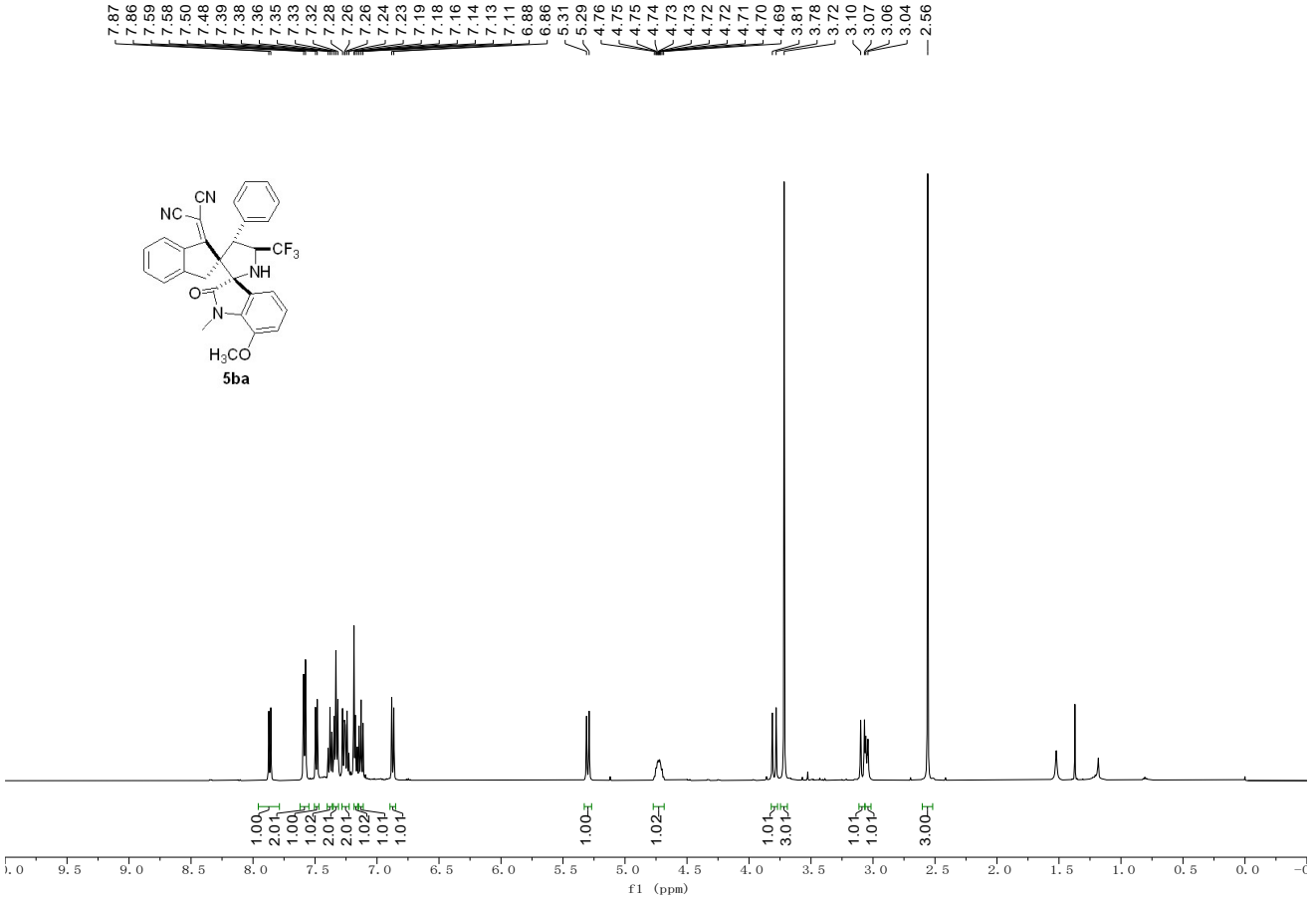
^{13}C NMR spectra for compound **5as** (100 Hz, $CDCl_3$)



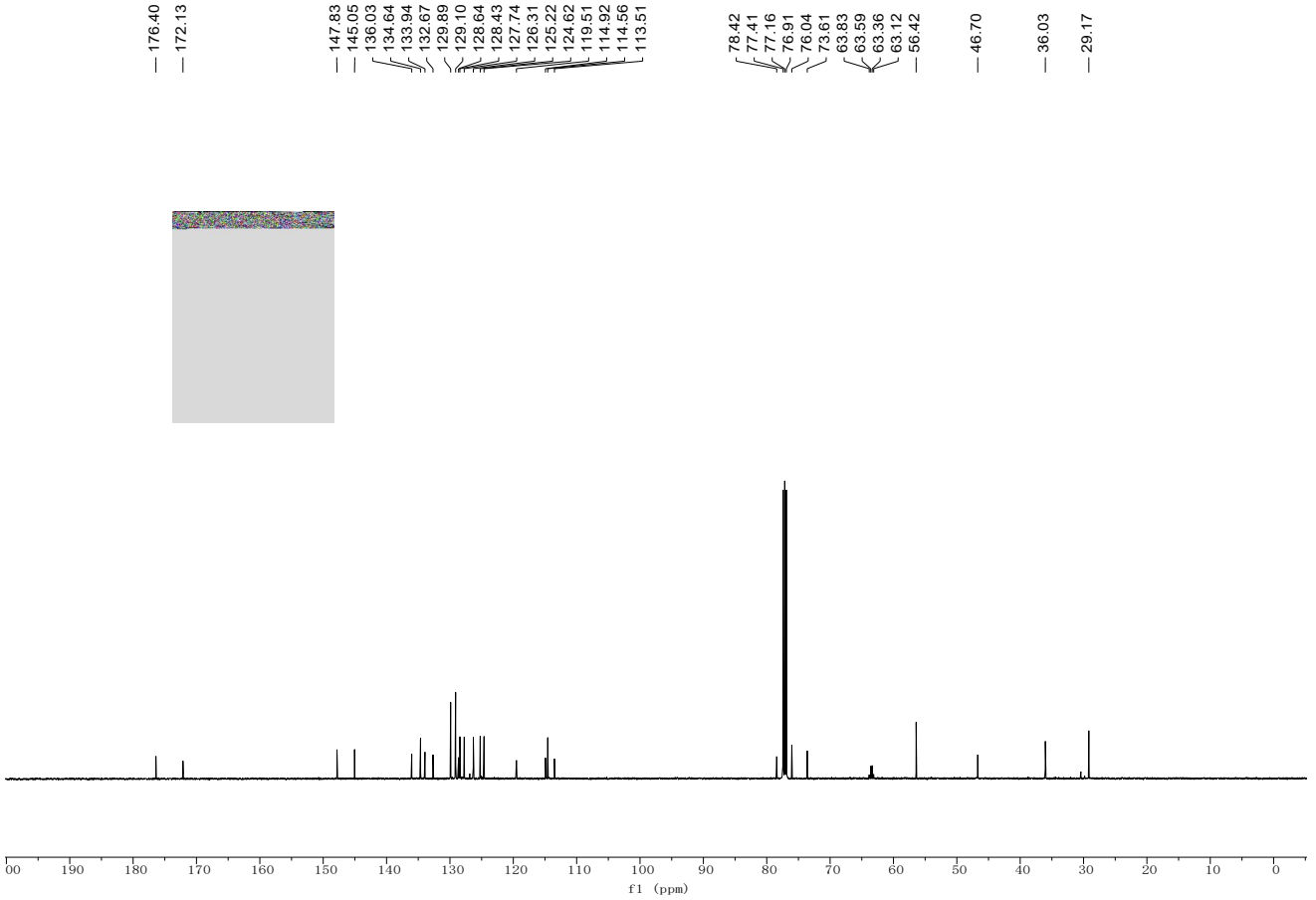
^{19}F NMR spectra for compound **5as** (376 Hz, $CDCl_3$)



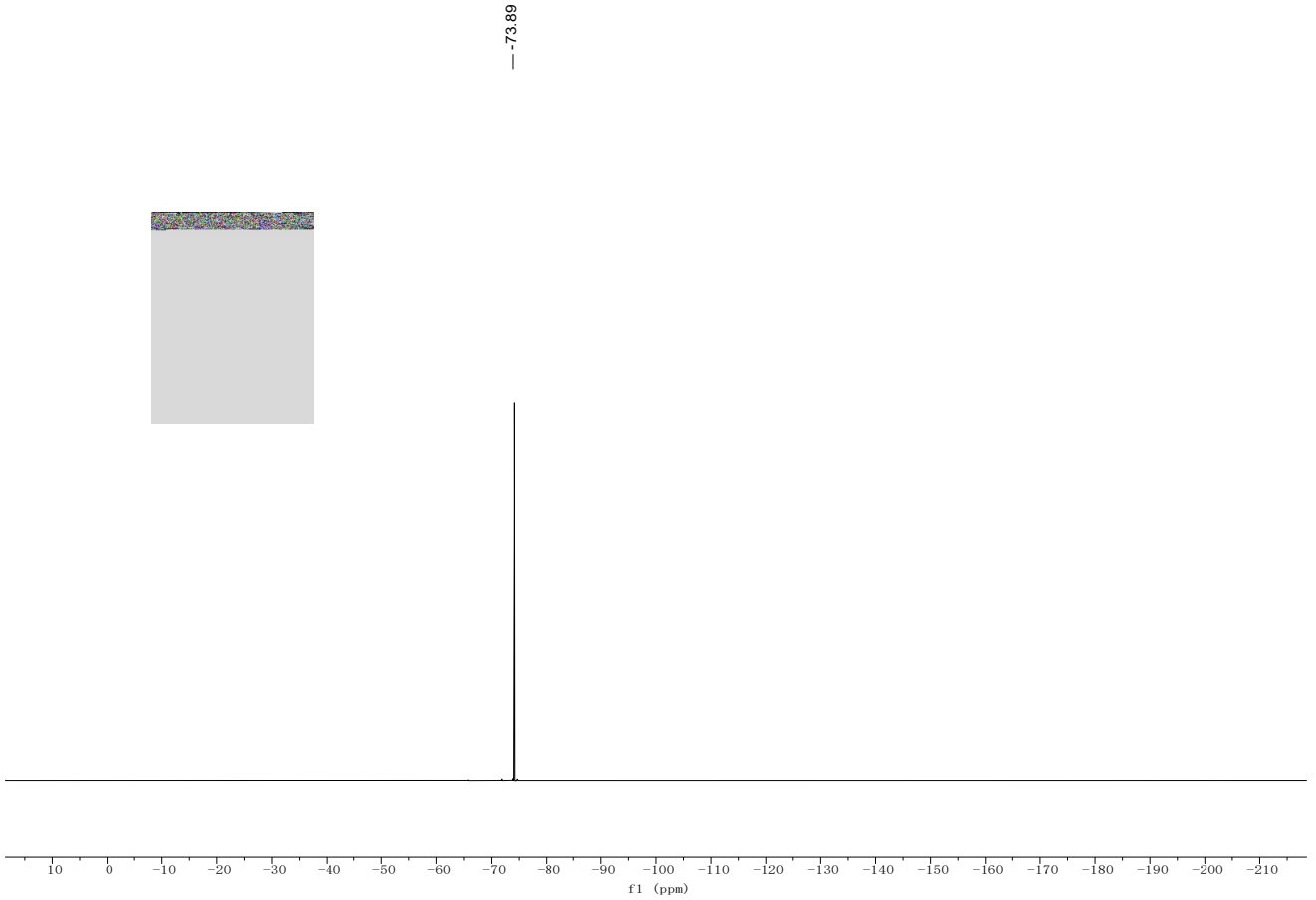
^{1}H NMR spectra for compound **5ba** (500 Hz, $CDCl_3$)



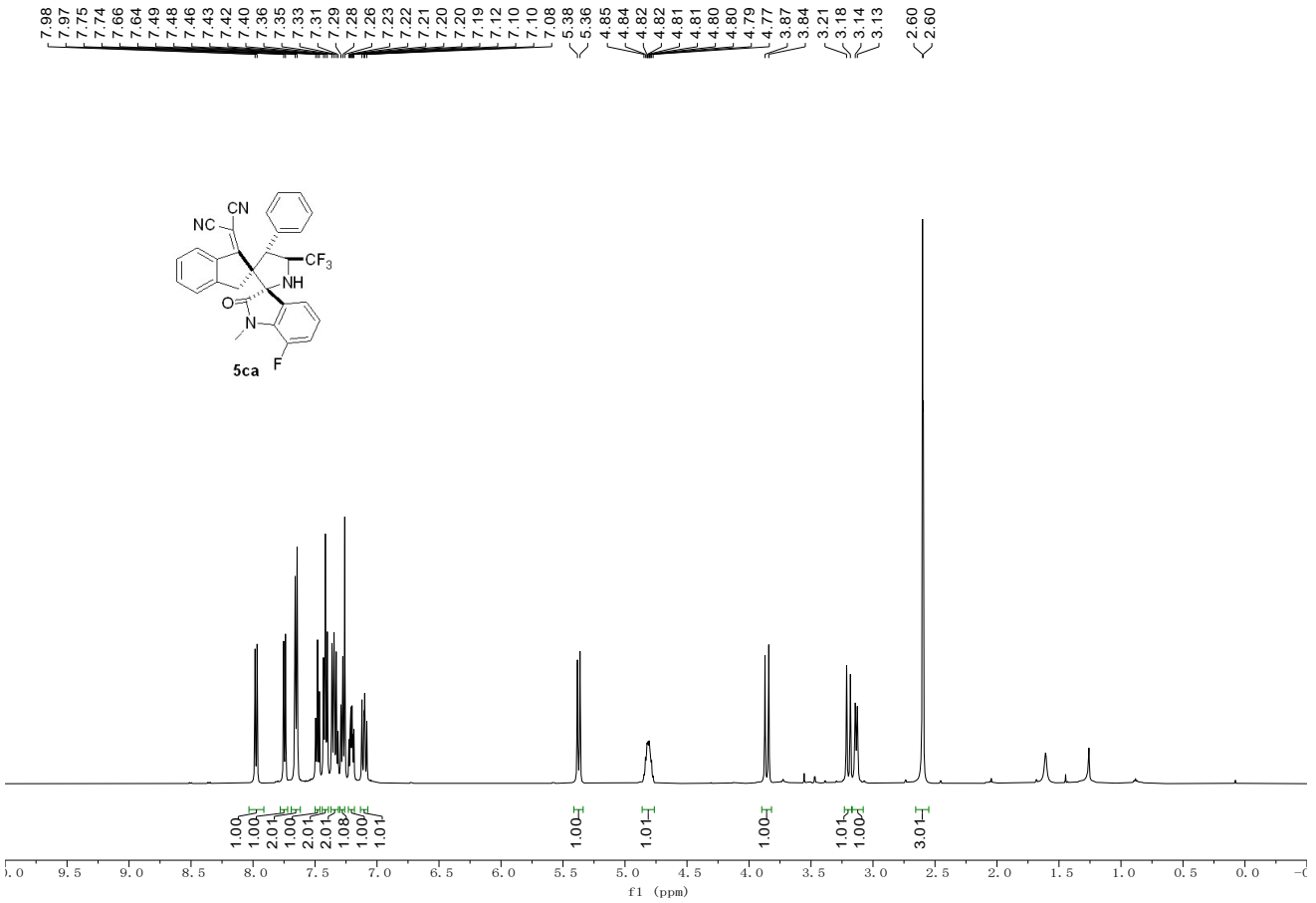
^{13}C NMR spectra for compound **5ba** (125 Hz, $CDCl_3$)



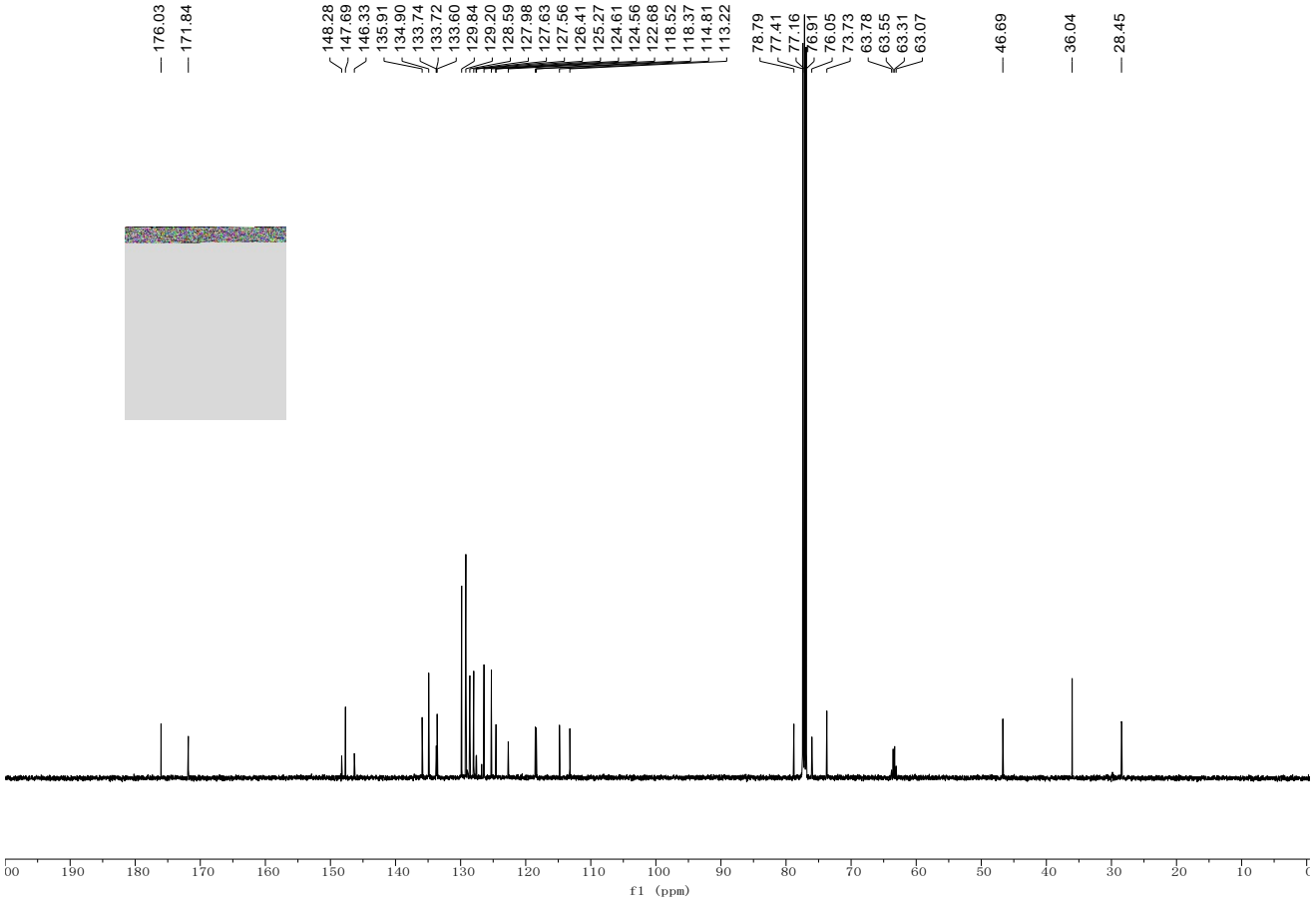
^{19}F NMR spectra for compound **5ar** (376 Hz, $CDCl_3$)



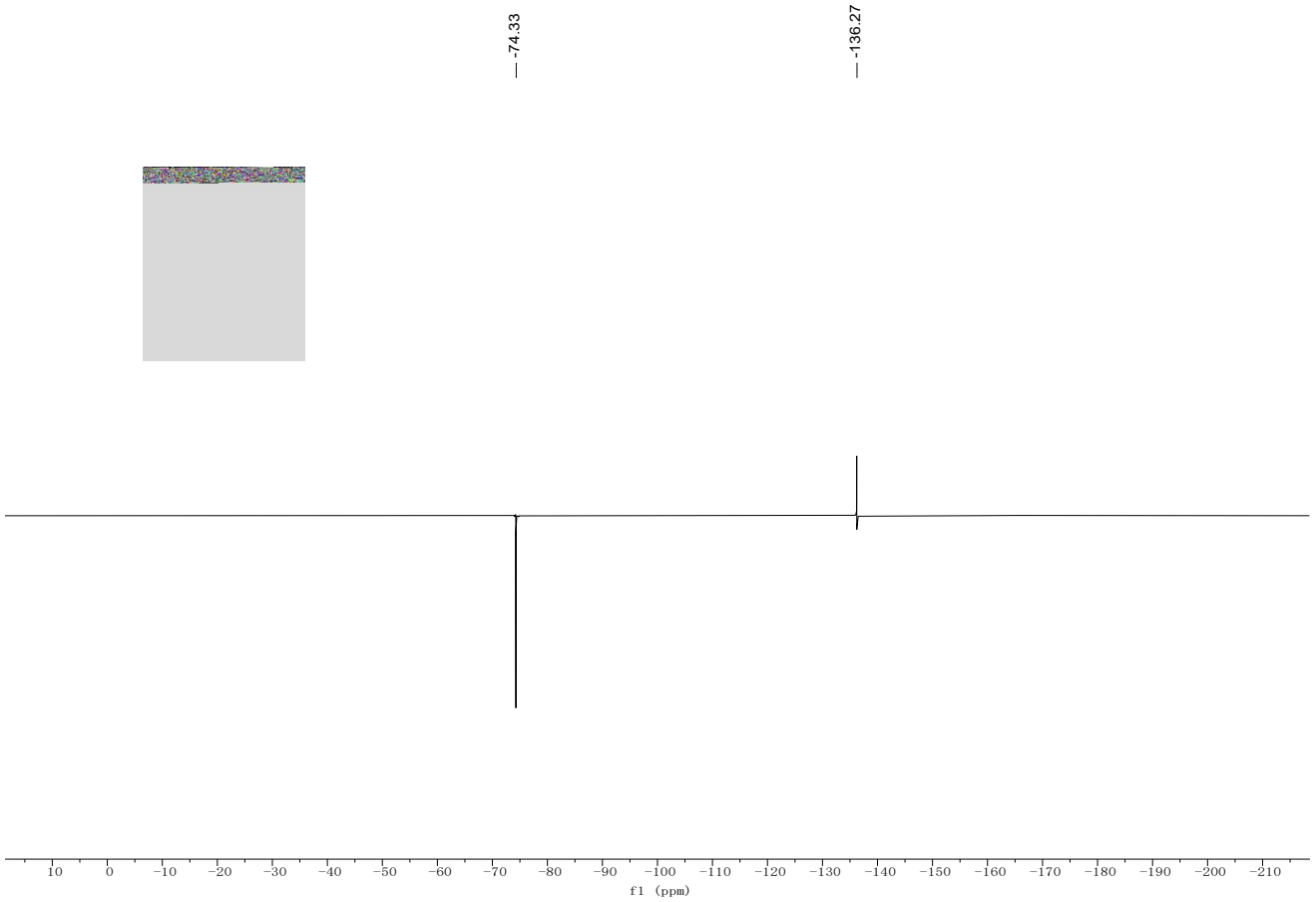
^{1}H NMR spectra for compound **5ca** (500 Hz, $CDCl_3$)



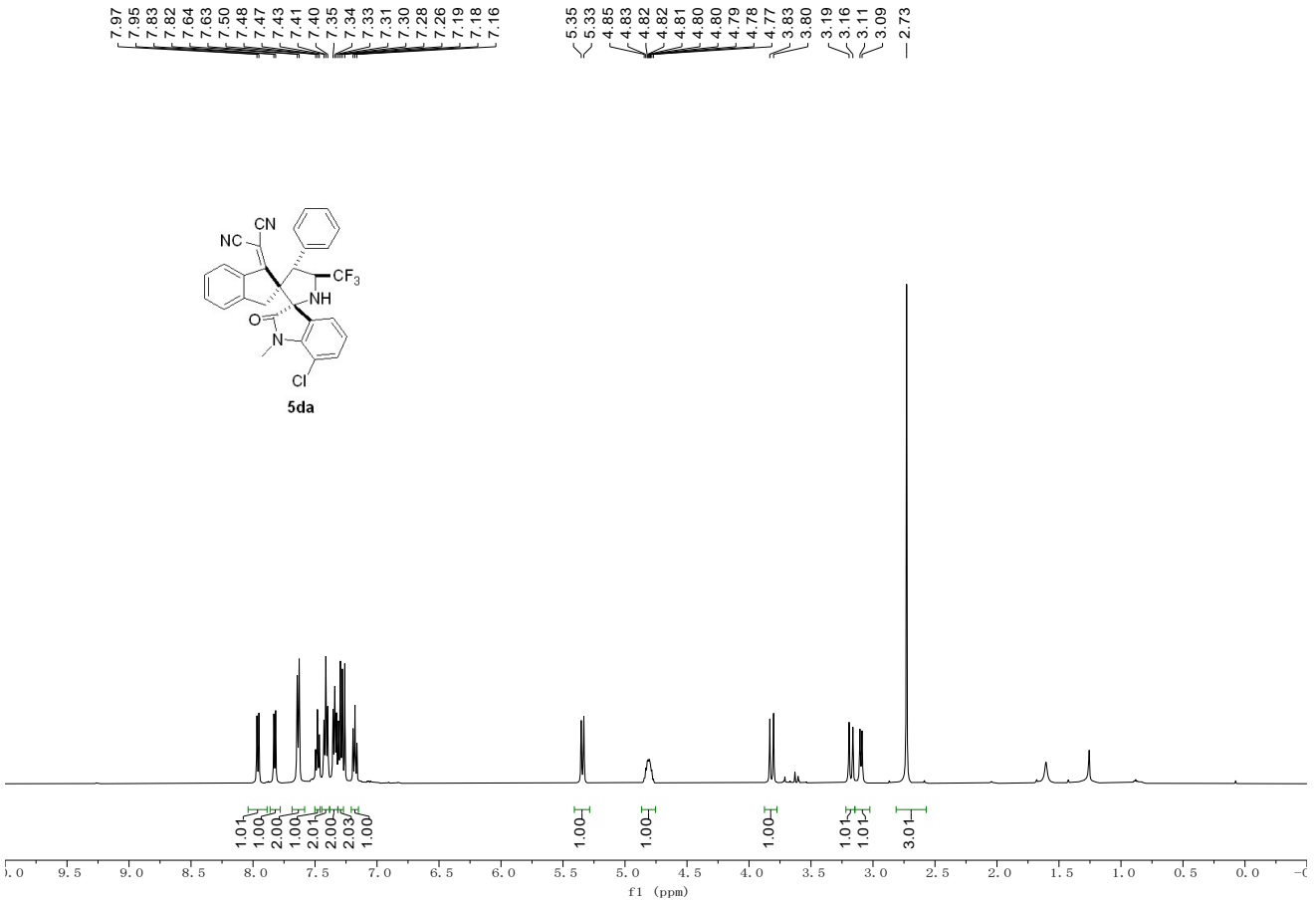
^{13}C NMR spectra for compound **5ca** (125 Hz, $CDCl_3$)



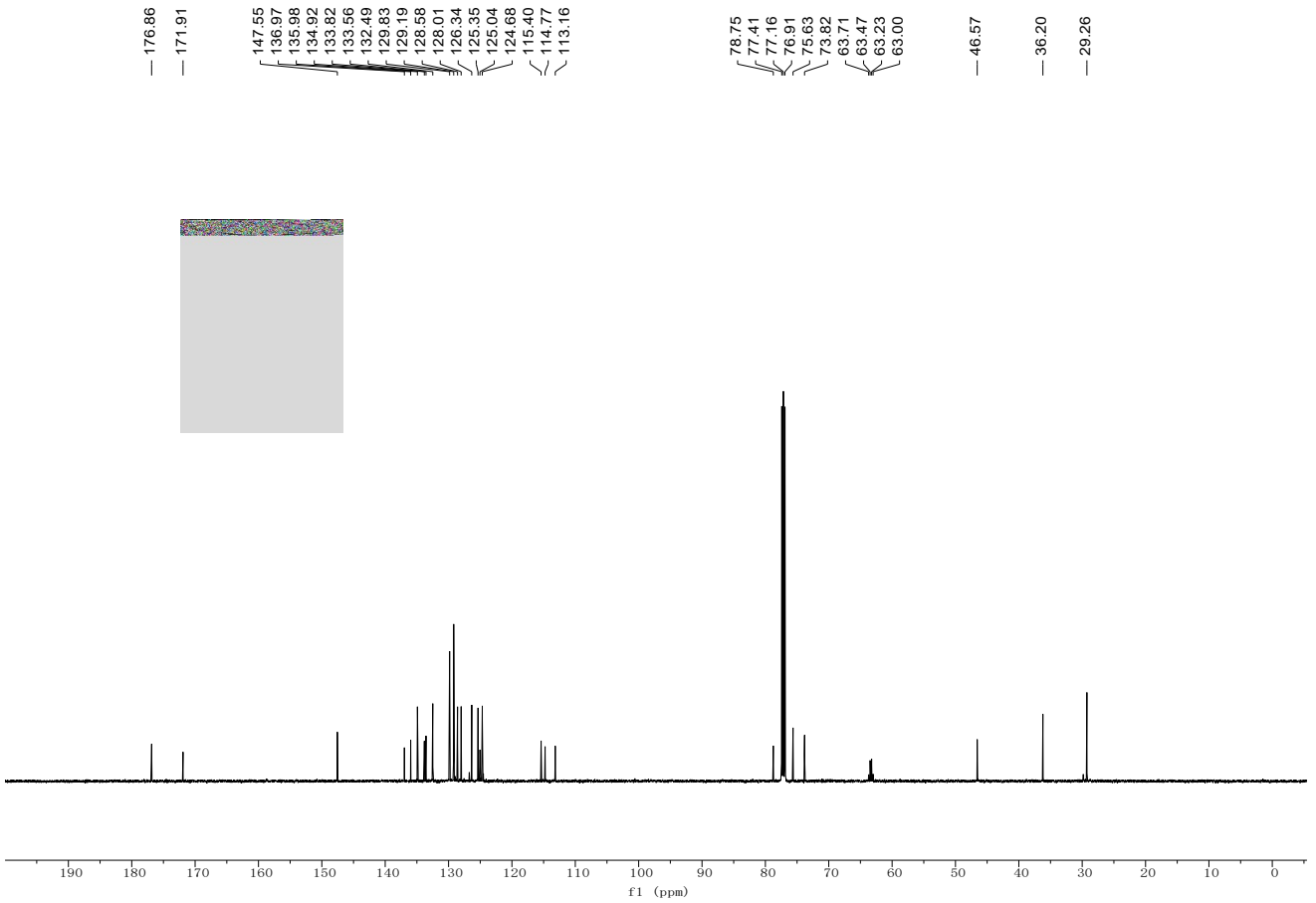
^{19}F NMR spectra for compound **5ca** (376 Hz, $CDCl_3$)



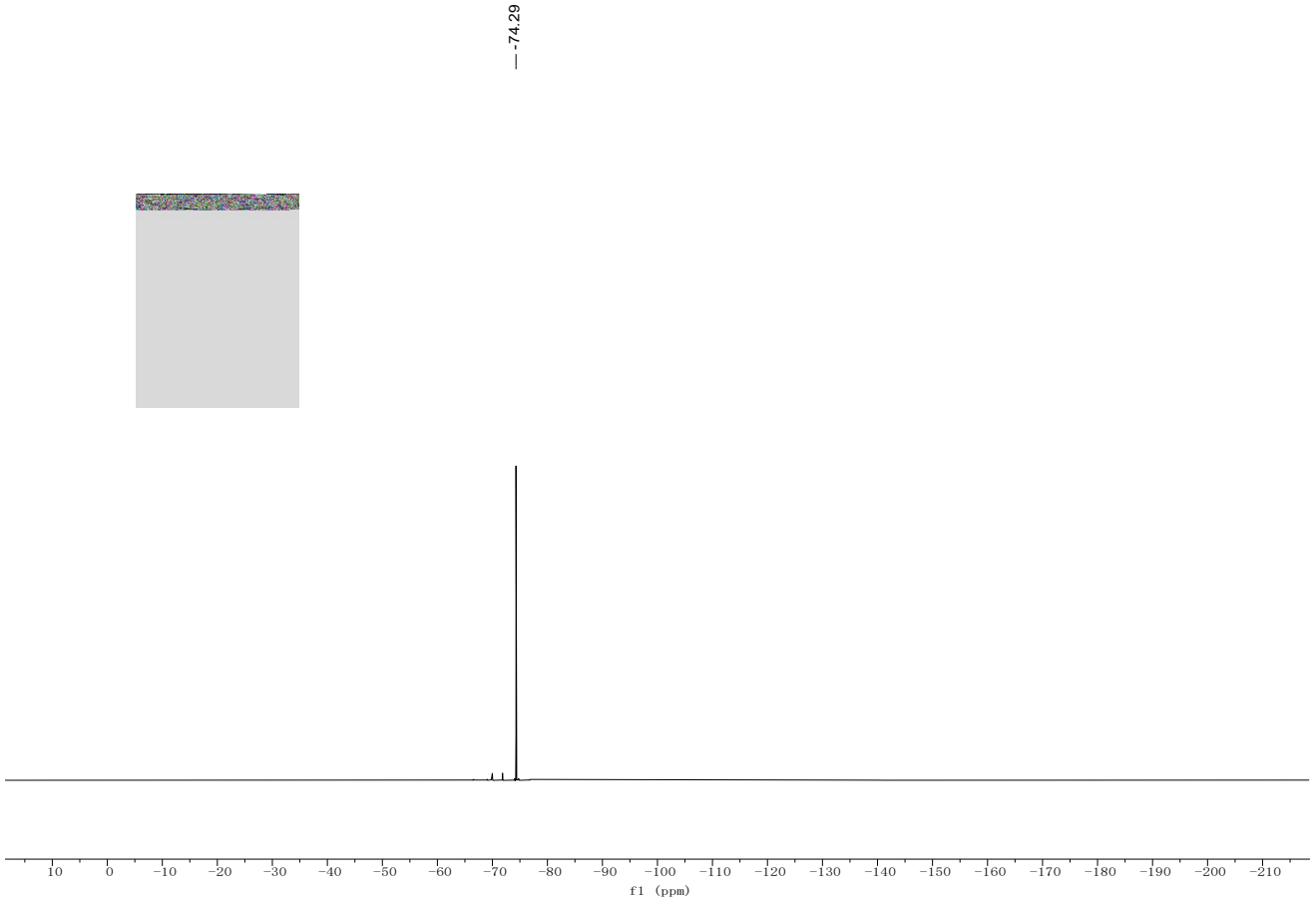
^{1}H NMR spectra for compound **5da** (500 Hz, $CDCl_3$)



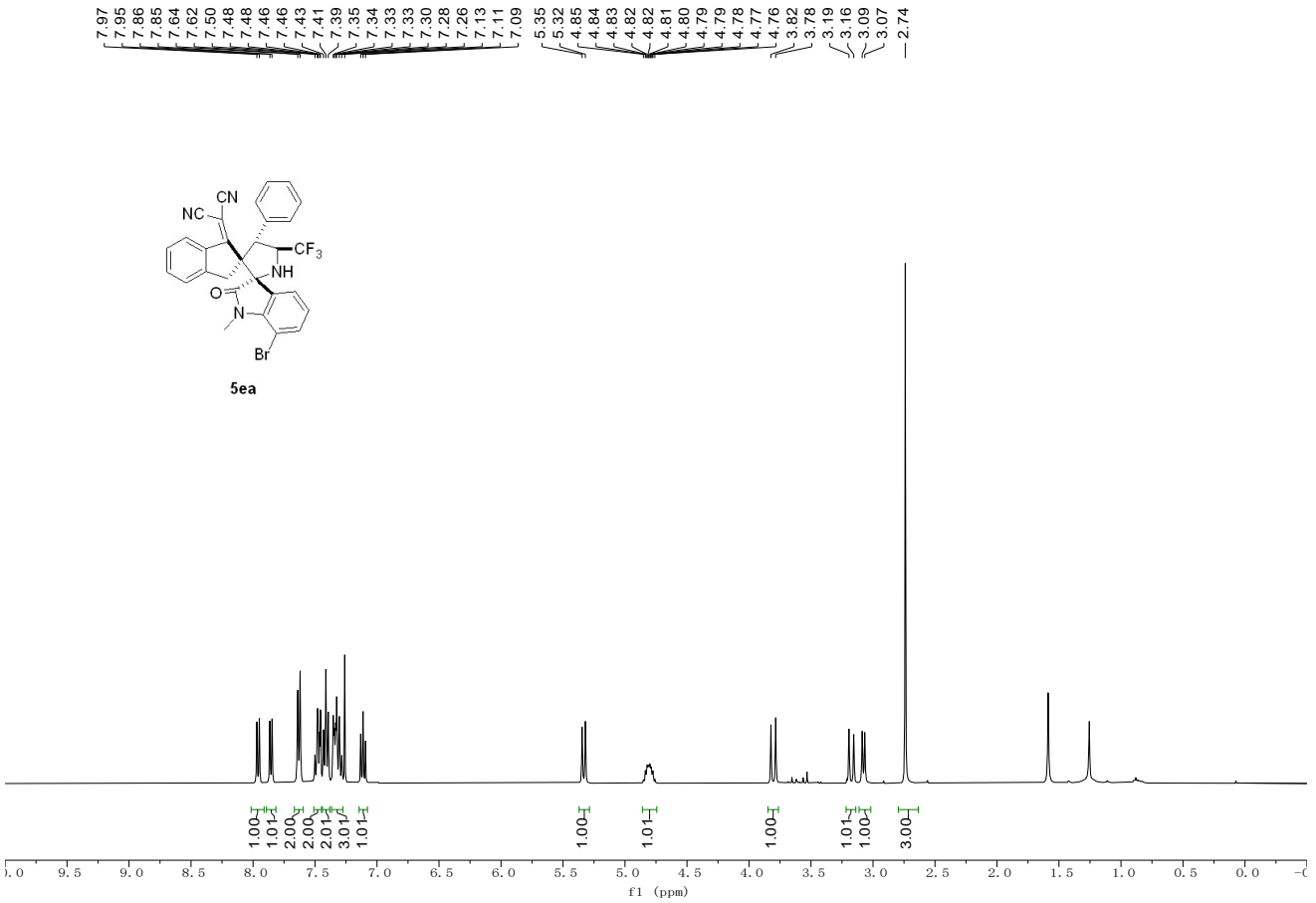
^{13}C NMR spectra for compound **5da** (125 Hz, $CDCl_3$)



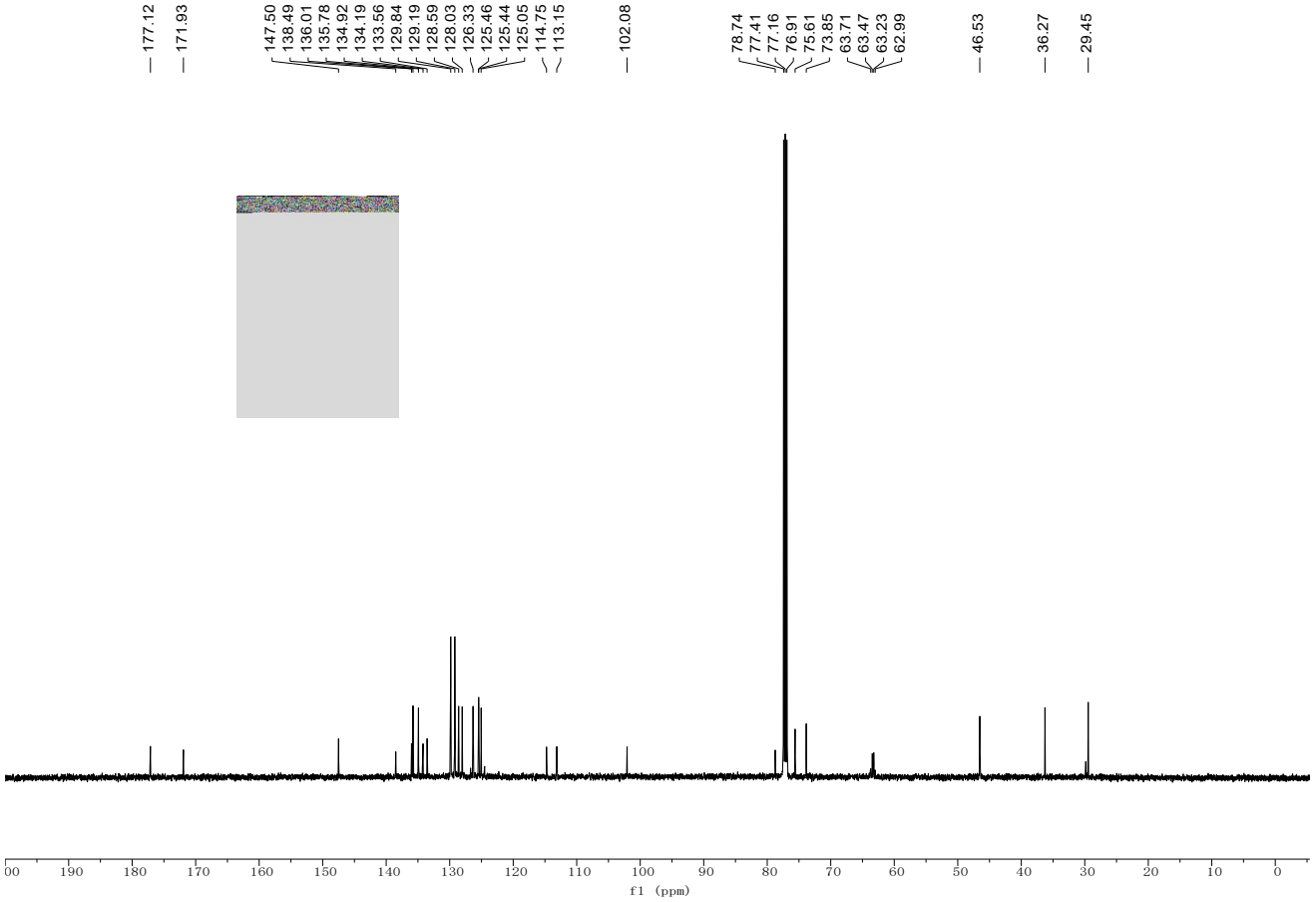
^{19}F NMR spectra for compound **5da** (376 Hz, $CDCl_3$)



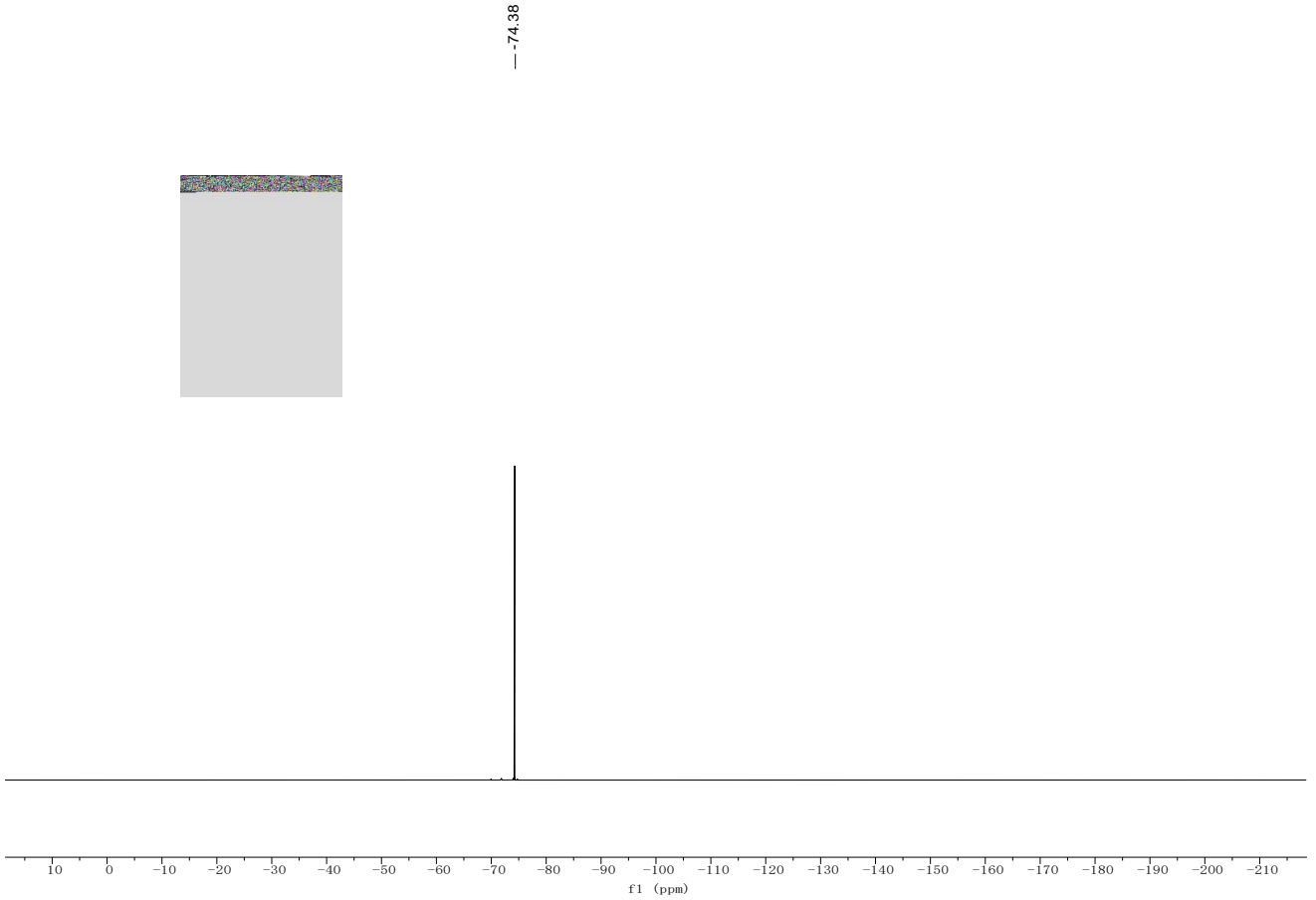
^{1}H NMR spectra for compound **5ea** (400 Hz, $CDCl_3$)



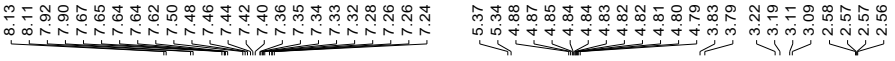
^{13}C NMR spectra for compound **5ea** (125 Hz, $CDCl_3$)

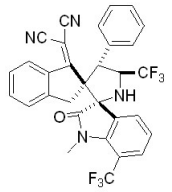


^{19}F NMR spectra for compound **5ea** (376 Hz, $CDCl_3$)

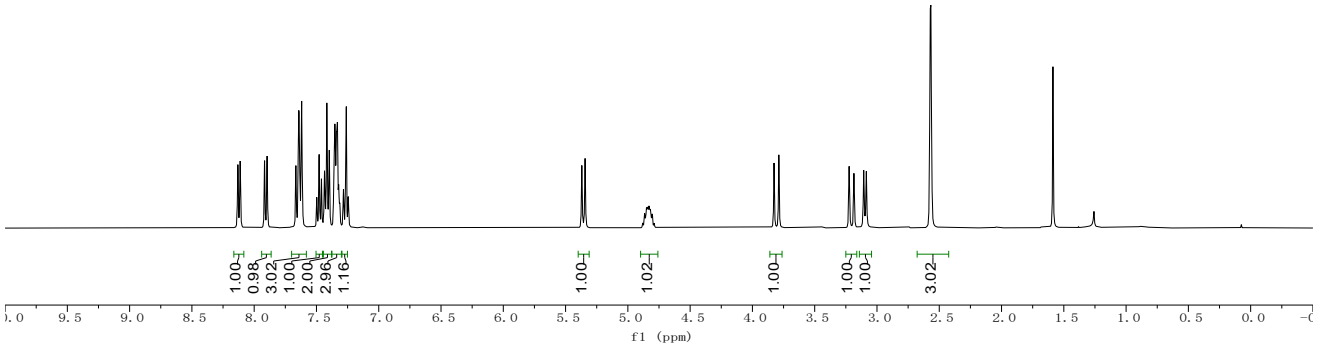


^{1}H NMR spectra for compound **5fa** (400 Hz, $CDCl_3$)

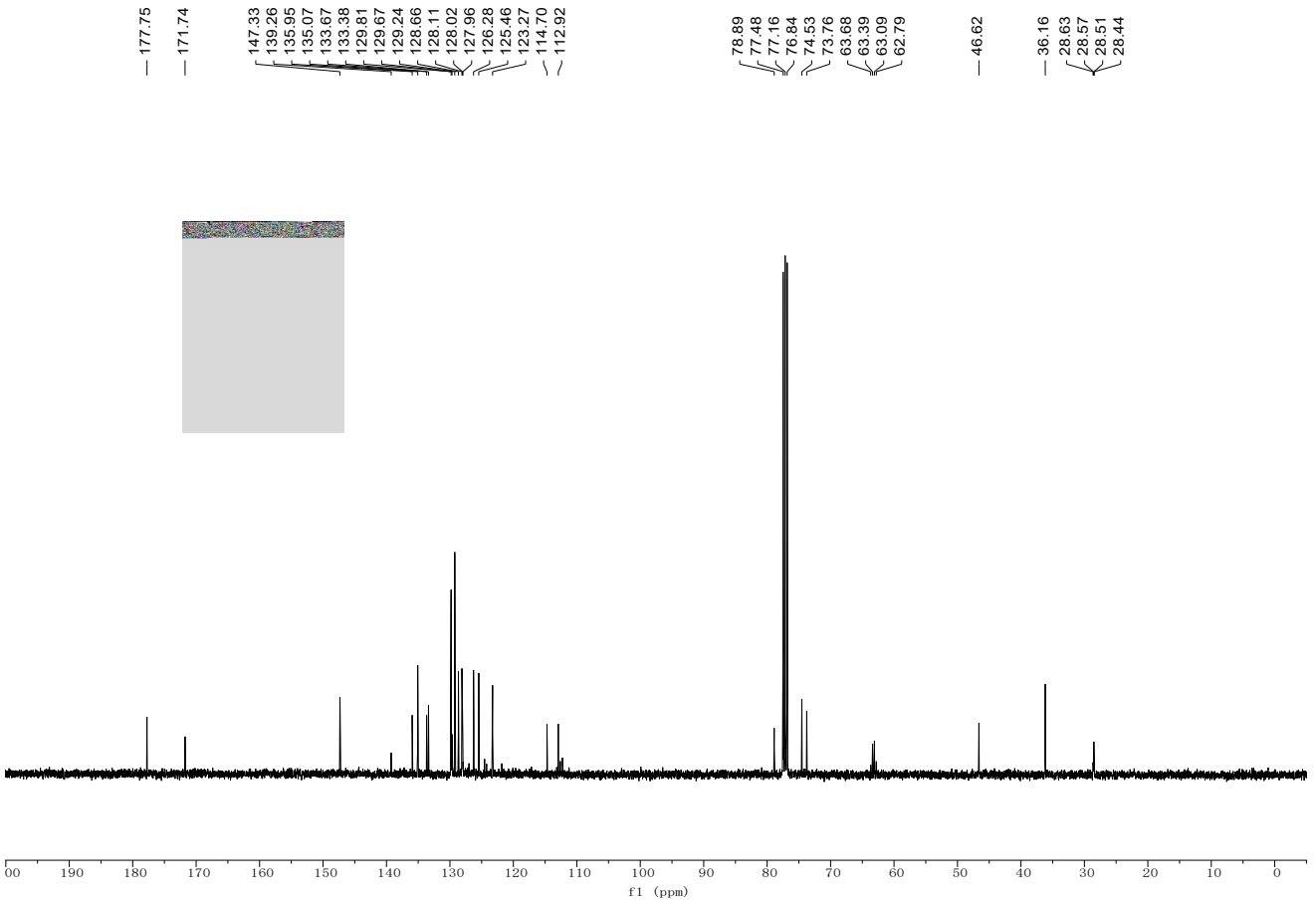




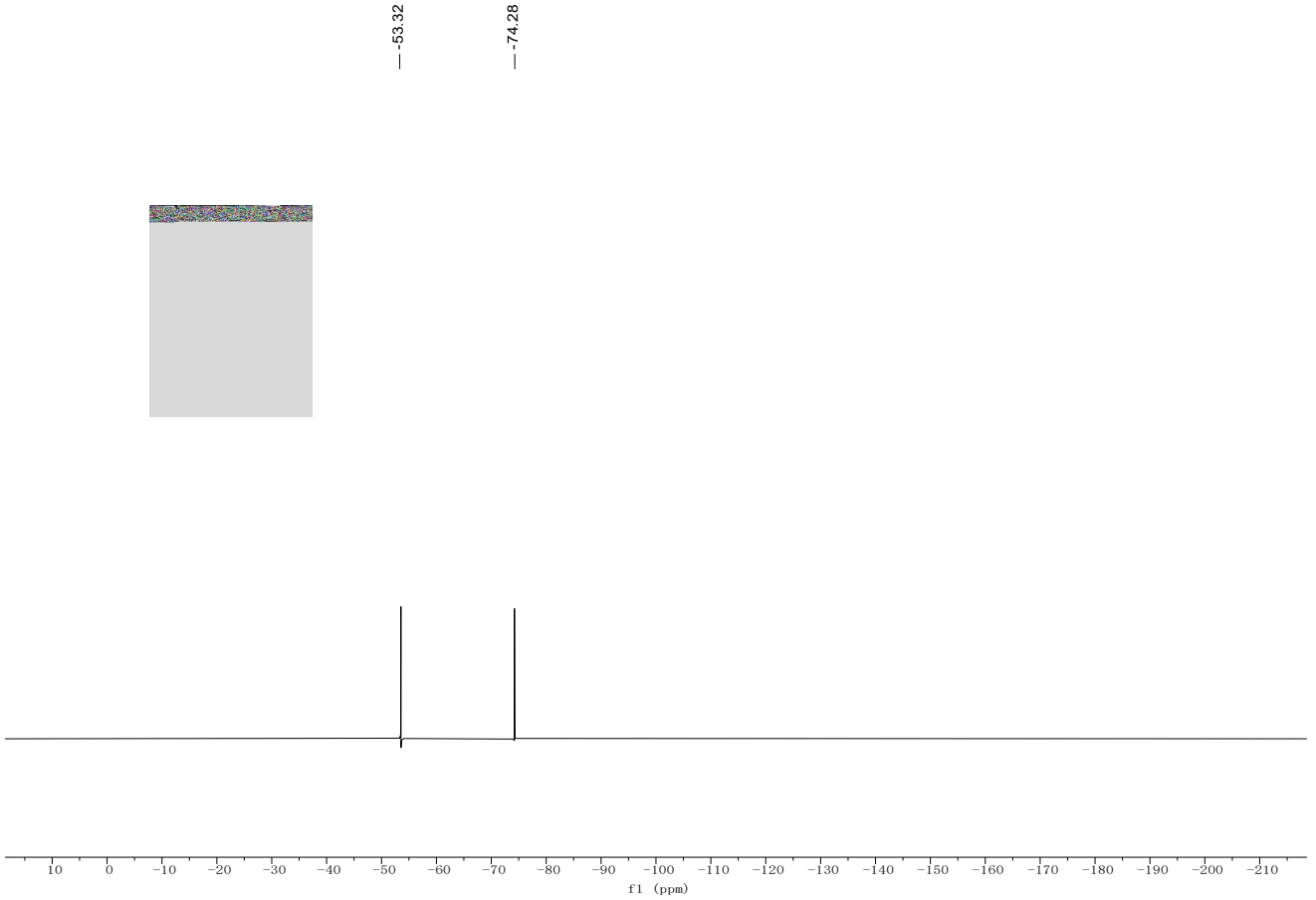
5fa



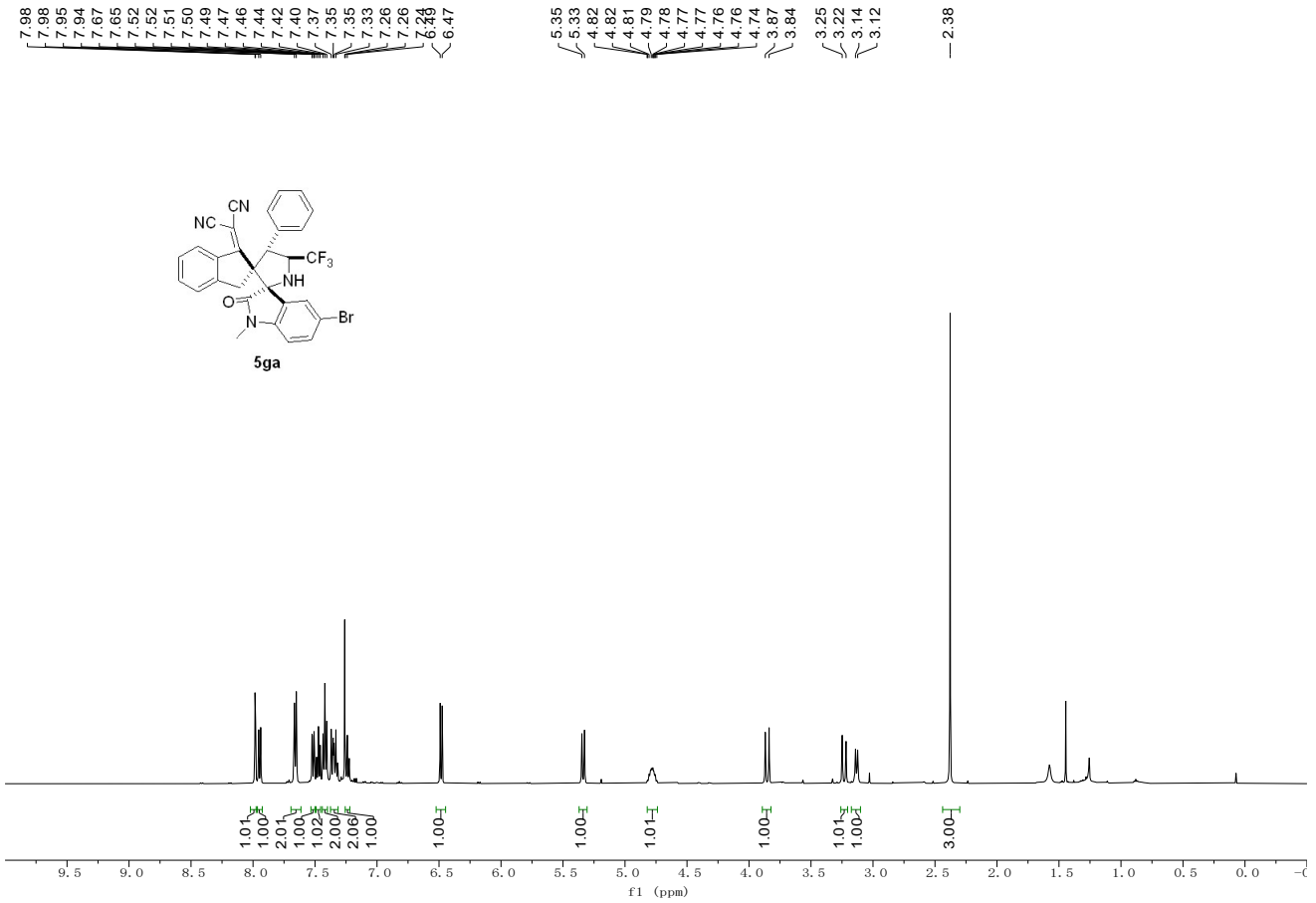
^{13}C NMR spectra for compound **5fa** (100 Hz, $CDCl_3$)



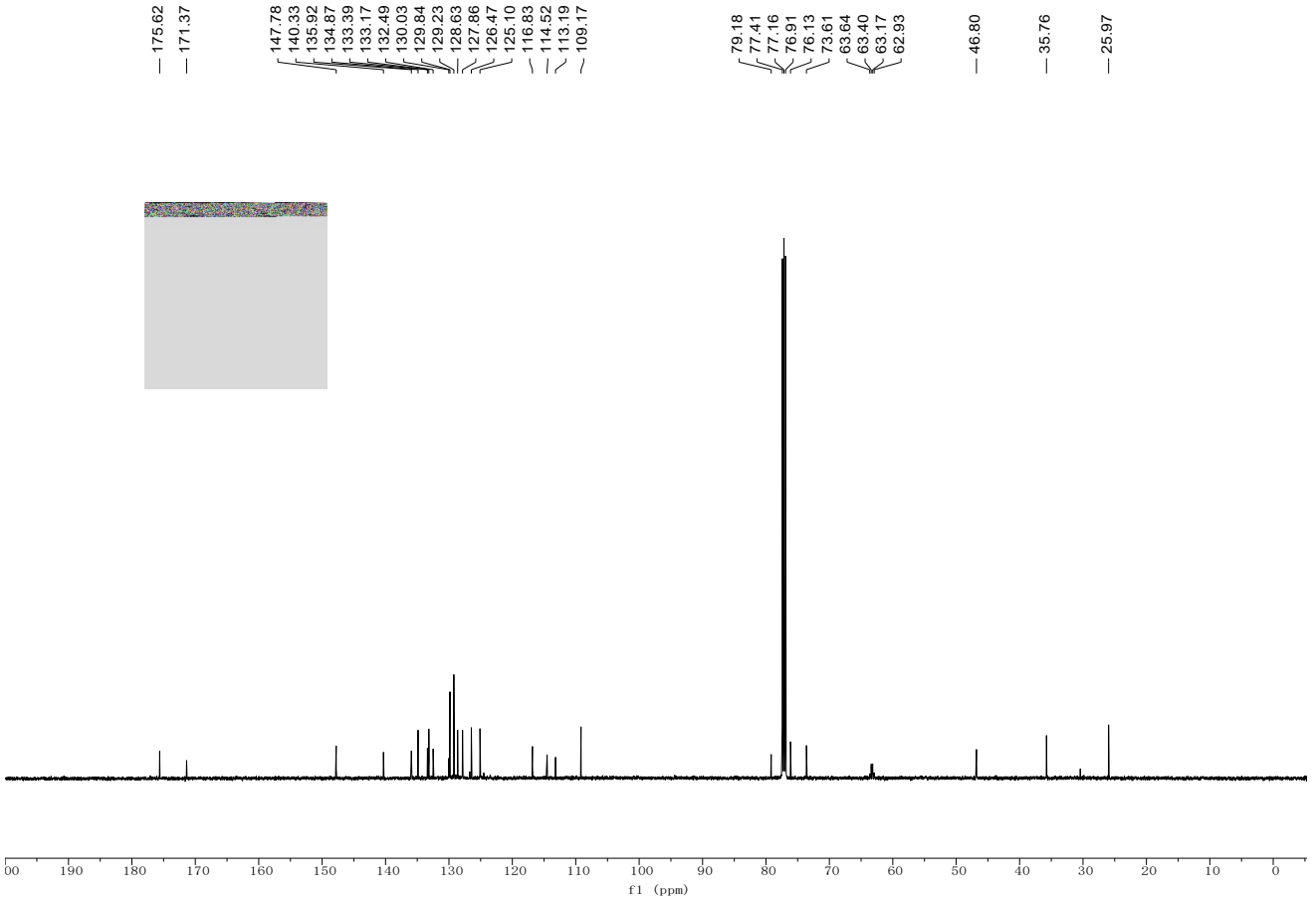
^{19}F NMR spectra for compound **5fa** (376 Hz, $CDCl_3$)



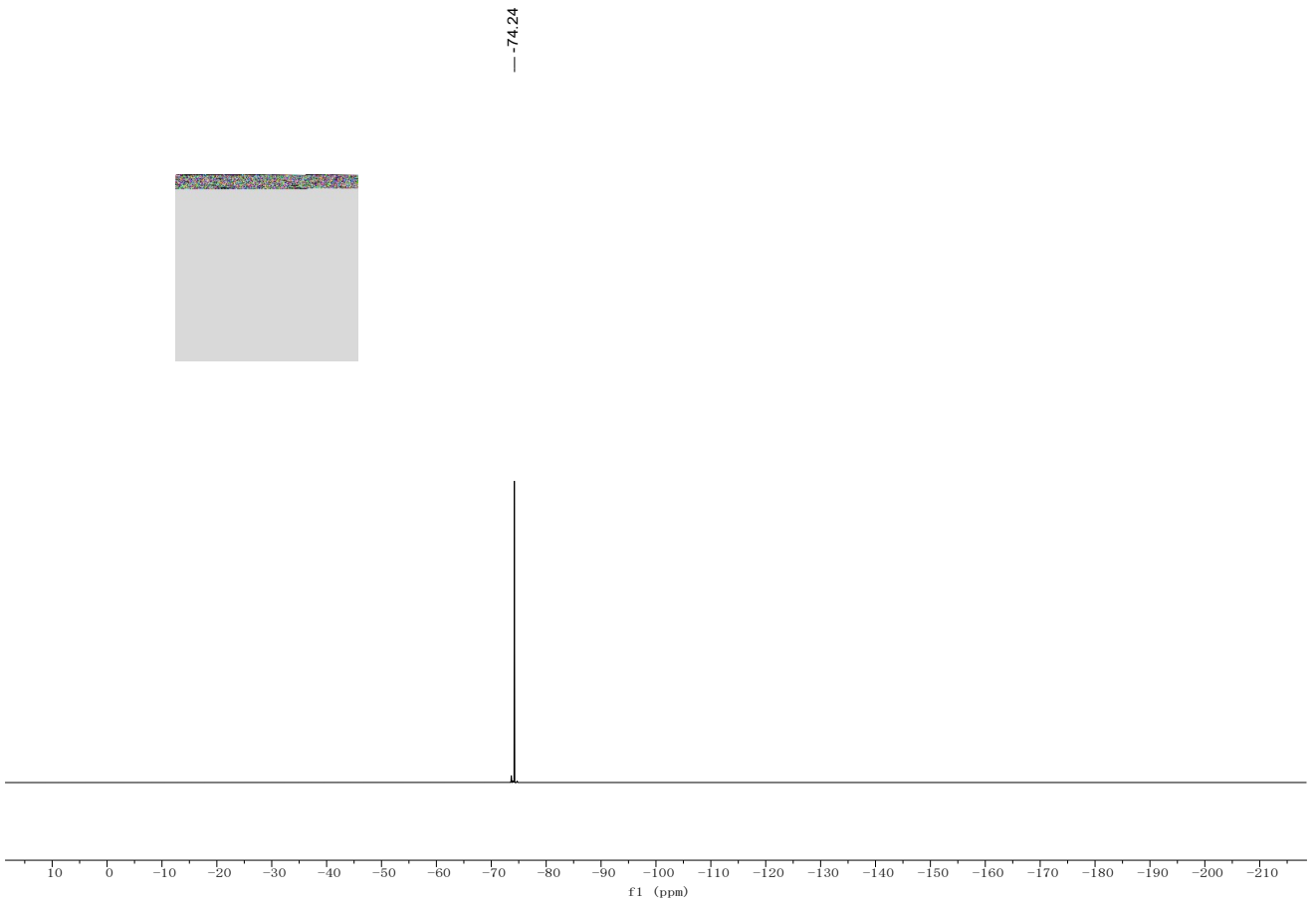
^{1}H NMR spectra for compound **5ga** (500 Hz, $CDCl_3$)



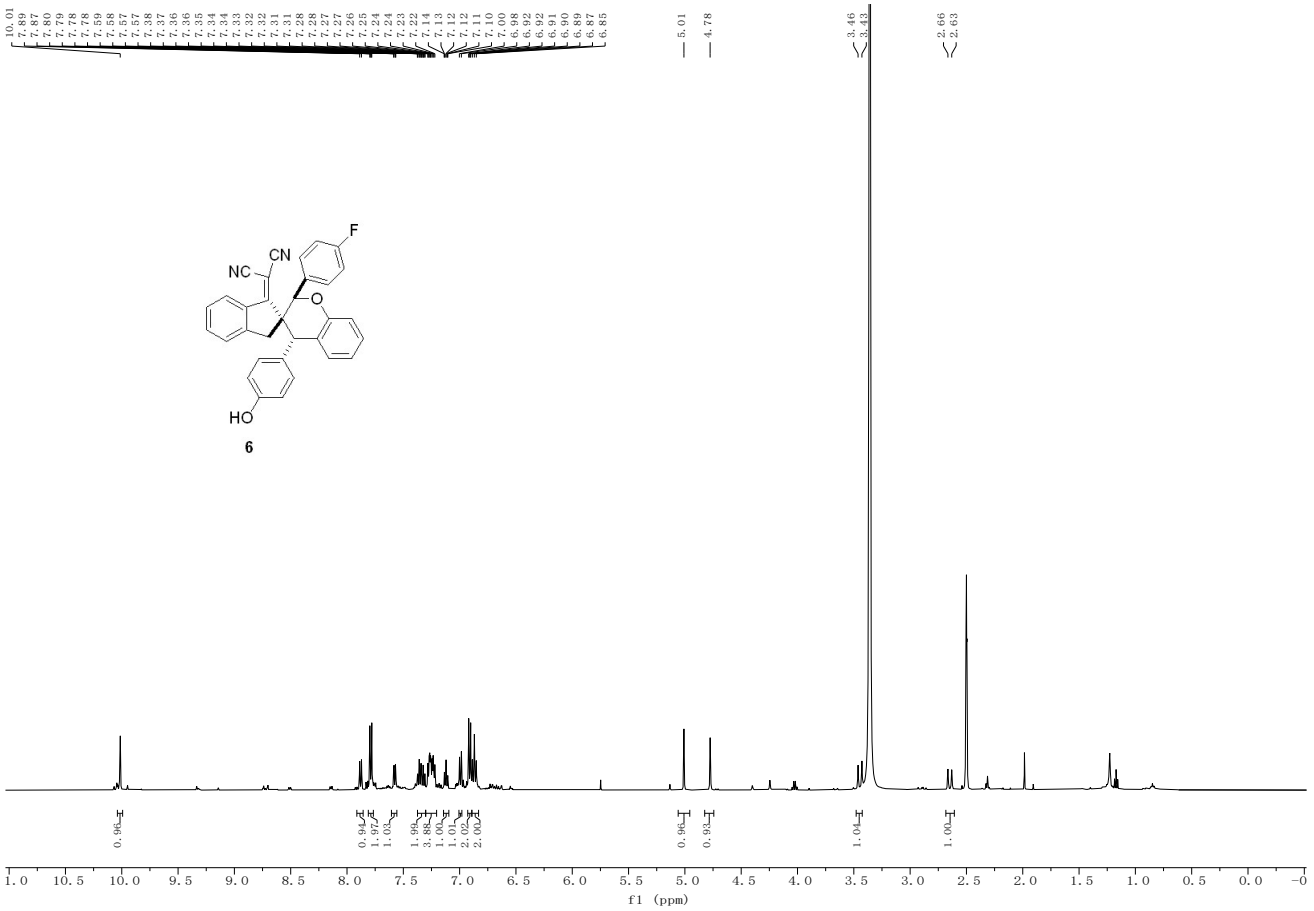
^{13}C NMR spectra for compound **5ga** (125 Hz, $CDCl_3$)



^{19}F NMR spectra for compound **5ga** (376 Hz, $CDCl_3$)



^{1}H NMR spectra for compound **6** (500 Hz, DMSO-d_6)


10.01
7.89
7.87
7.80
7.79
7.78
7.78
7.59
7.58
7.57
7.57
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.28
7.28
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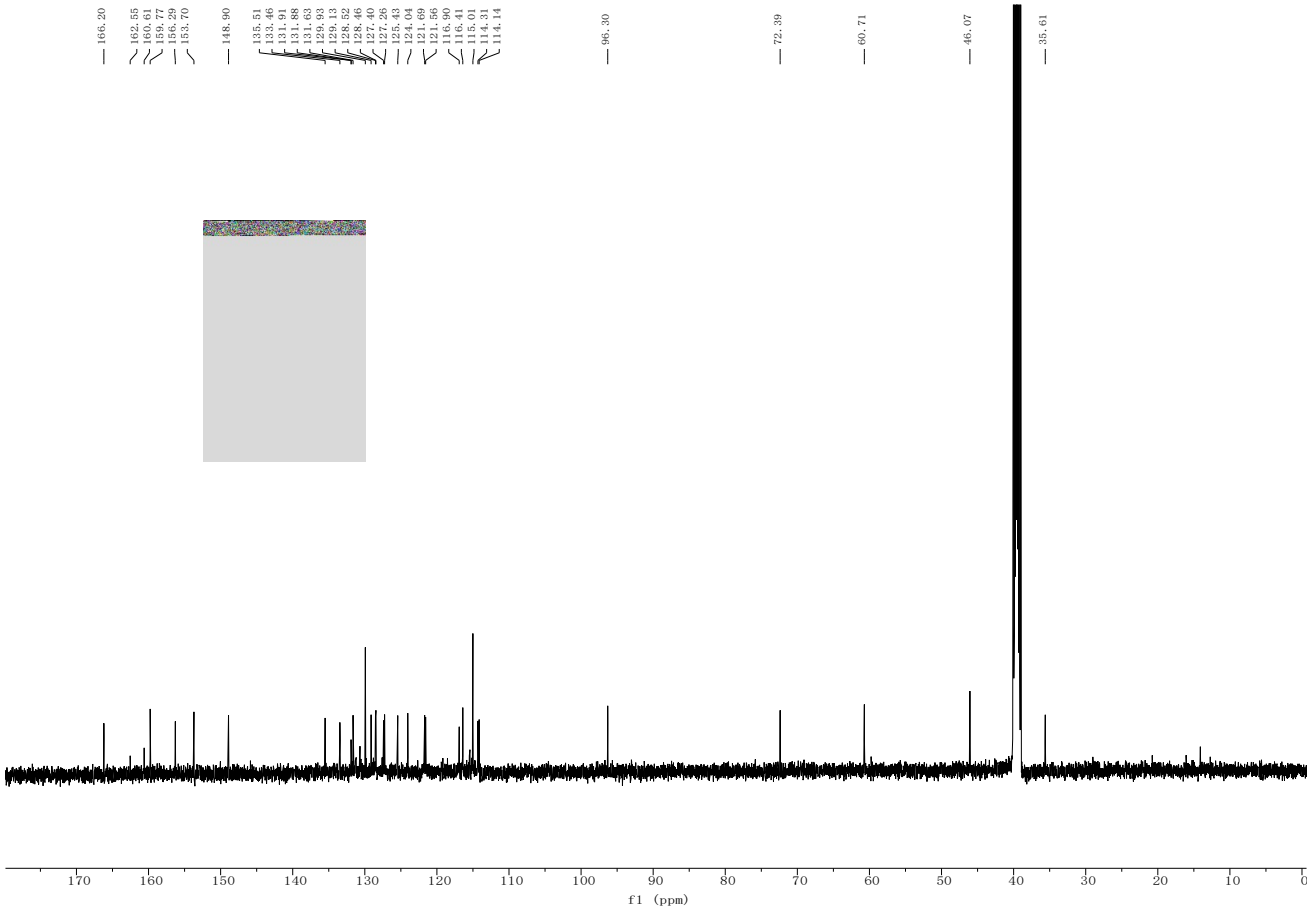
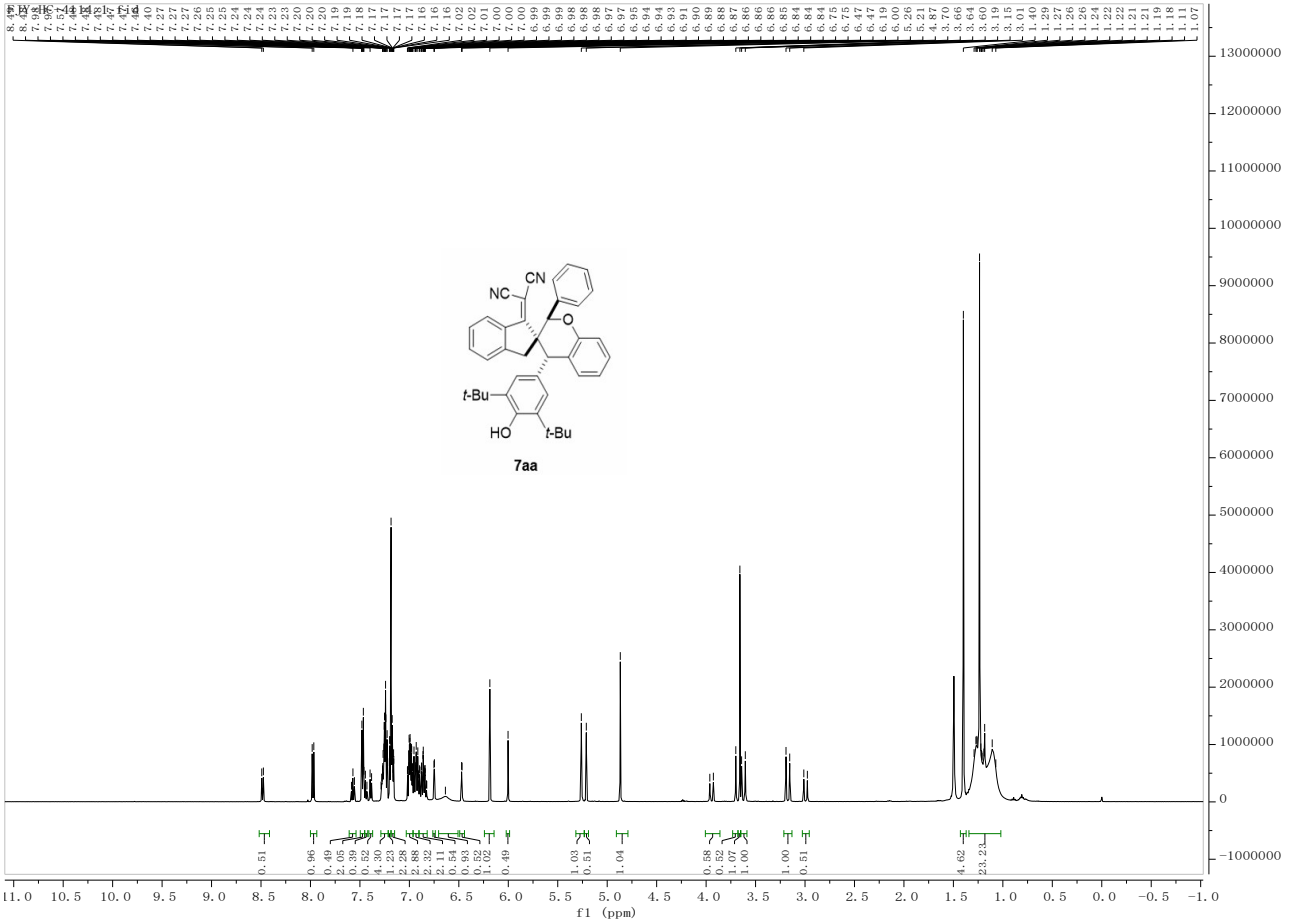
7.27
7.26
7.25
7.24
7.24
7.23
7.22
7.14
7.13
7.12
7.12
7.11
7.10
7.00
6.98
6.92
6.92
6.91
6.90
6.89
6.87
6.85
5.01
4.78
3.46
3.43
2.66
2.63
F
CN
NC
O
HO
6
0.96
0.94
1.97
1.03
1.96
3.88
1.00
1.01
2.02
2.00
0.96
0.93
1.04
1.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

^{13}C NMR spectra for compound **6** (125 Hz, DMSO-d_6)



^{1}H NMR spectra for compound **7aa** (500 Hz, $CDCl_3$)



^{13}C NMR spectra for compound **7aa** (125 Hz, $CDCl_3$)