Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Synthesis of Multisubstituted Carbazol-4-amines from Tetrahydrocarbazol-4-one-oximes

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Contents

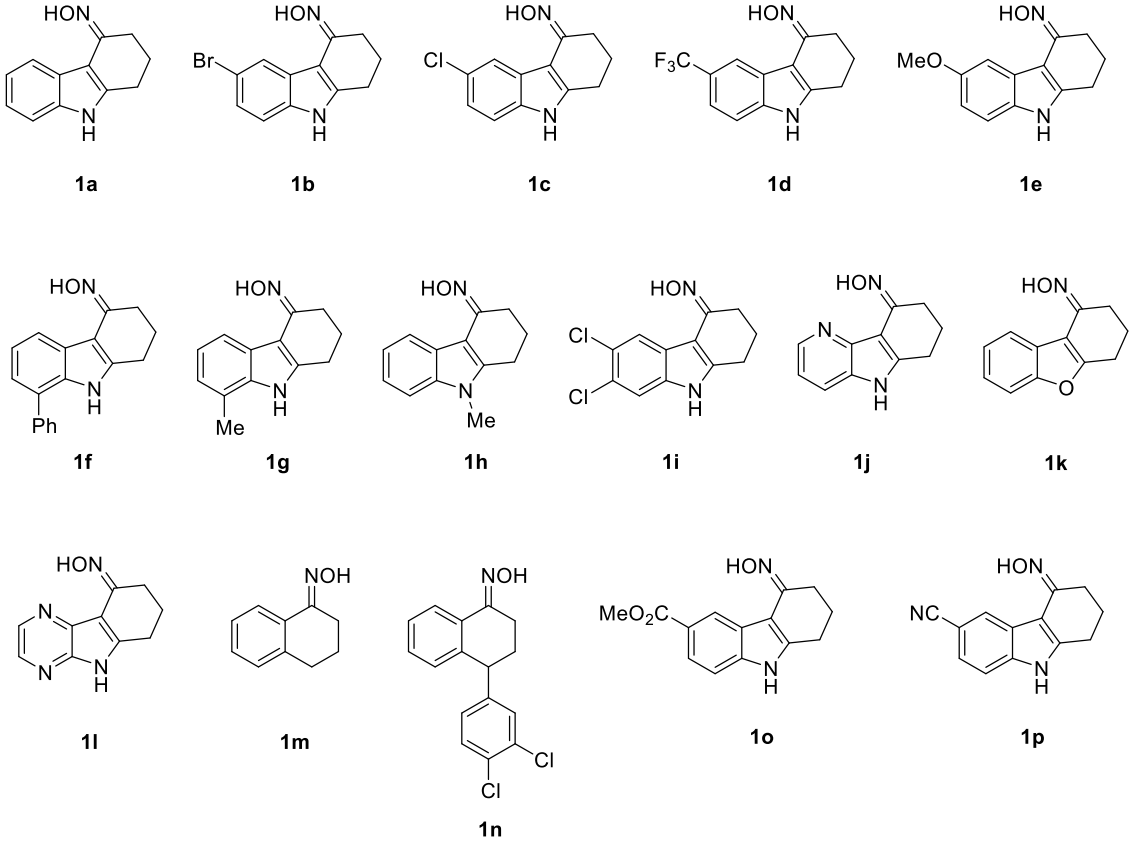
1. General experimental information

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AV-400 spectrometer with TMS as internal reference in $CDCl_3$ or DMSO-d_6. All coupling constants (J values) were reported in hertz (Hz), and chemical shifts (δ) are expressed in ppm. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra (HRMS) were measured by using a Bruker micro TOF II focus spectrometer (ESI). Melting points were measured with a SGWX-4 Microscopic Melting Point Tester. The single crystal was measured with an XtaLAB PRO MM007HF diffractometer (Rigaku, Japan, Cu). All reactions were monitored by thin-layer chromatography (TLC) with GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. All chemicals were purchased from Leyan.com, Energy chemical company and meryer.com. Solvents were purchased from Sinopharm chemical reagent company without further purification unless otherwise stated.

2. The list of starting materials

2.1 The list of oxime compounds

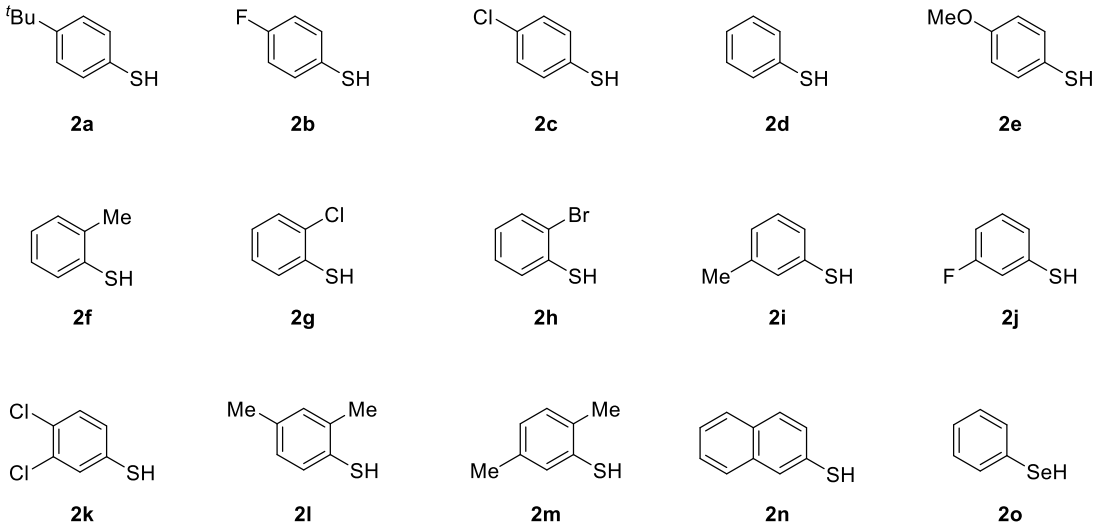
1a[1], **1b**[2], **1c**[2], **1h**[1], **1m**[3], **1n**[3] were prepared according to the literatures.



Scheme S1 The list of oxime compounds

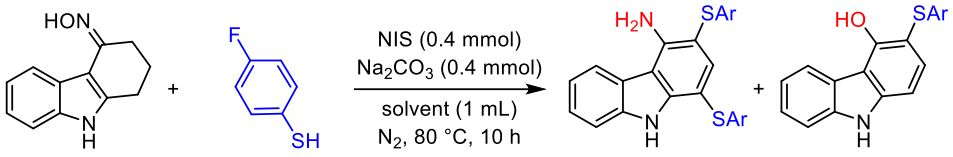
2.2 The list of thiols or selenols

All the thiols or selenols are purchased from commercial source and used without further purification.



Scheme S2 The list of thiols or selenols

3. Condition optimization

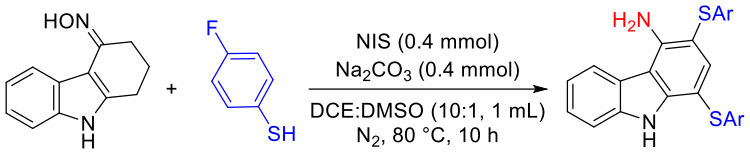


1a **2a** 0.4 mmol **3aa** **4aa** Ar = 4-F-Ph

entry	molar ratio (**1a**:**2a**)	solvent	yield of **3aa** [%][a]	yield of **4aa** [%][a]
1	1:1	ethyl acetate	25	22
2	1:1	acetonitrile	10	<5
3	1:1	tetrahydrofuran	<5	10
4	1:1	1,4-dioxane	21	17
5	1:1	diethyl carbonate	28	25
6	1:1	DCE	40	18
7	1:1	DCE:DMSO = 1:1	75	n.d.
8	1:1	DCE:DMSO = 10:1	85	n.d.
9	1.2:1	DCE:DMSO = 10:1	95	n.d.

[a] isolated yield based on the amount of compound **2a**

Table S1 Condition optimization



1a 0.48 mmol | **2a** 0.4 mmol | **3aa** 95%

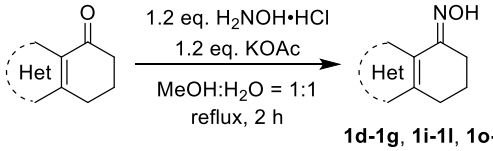
variation from "stanrdard condition"	yield of **3aa** [%][a]
60 °C	55
100 °C	85
K_2CO_3	55
Cs_2CO_3	20
KOAc	33
DMSO	15
1,4-dioxane	30
1,4-dioxane/DMSO (10:1)	65
NCS instead of NIS	n.d.
NBS instead of NIS	n.d.

[a] Isolated yield based on the amount of compound **2a**

Table S2 Evaluation of other reaction parameters

4. Preparation and characterization data of oximes

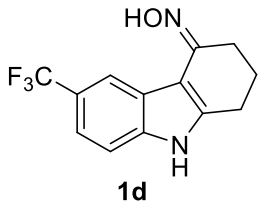
The procedure for the synthesis of oximes 1d–1g, 1i–1l, 1o–p



1d-1g, **1i-1l**, **1o-1p**

In a 25 mL round flask, potassium acetate (236 mg, 2.4 mmol) and hydroxylamine hydrochloride (167 mg, 2.4 mmol) were added to a solution of corresponding ketones (2.0 mmol) in 10 mL of MeOH/water (v/v = 1:1). The mixture was refluxed for 2 h with a condenser by oil bath. After cooling to room temperature, 15 mL water was added to the mixture to give a suspension. Then the suspension was filtrated and dried, giving the corresponding oximes (**1d–1g**, **1i–1l**, **1o-1p**).

Characterization data of oximes 1d-1g, 1i-1l, 1o-1p



1d

6-(Trifluoromethyl)-1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime (**1d**), following the procedure for the synthesis of oximes, **1d** was isolated as a grey solid (456 mg, 1.7 mmol, 85 % yield).

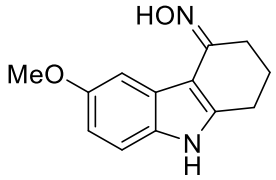
m.p. 219–220 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H), 10.51 (s, 1H), 8.24 (s, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.38 (d, J = 8.5 Hz, 1H), 2.84 (t, J = 6.2 Hz, 2H), 2.70 (t, J = 6.5 Hz, 2H), 1.93 (p, J = 6.3 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.5, 144.2, 138.1, 126.1 (q, J = 271.4 Hz), 123.9, 121.0 (q, J = 30.8 Hz). 118.6 (q, J = 4.3 Hz), 118.3 (q, J = 3.9 Hz). 112.1, 107.7, 22.9, 22.7, 22.2.

^{19}F NMR (376 MHz, DMSO-d_6) δ -58.5 (m, 3F).

HRMS (ESI) calcd (m/z) for $C_{13}H_{12}F_3N_2O^+$ ([M+H]$^+$): 269.0896, found: 269.0901.



1e

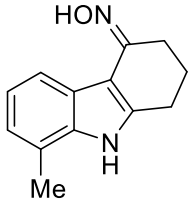
6-Methoxy-1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime (**1e**), following the general procedure for the synthesis of oximes, **1e** was isolated as a greyish white solid (386 mg, 1.68 mmol, 84 % yield).

m.p. 208–209 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.08 (s, 1H), 10.27 (m, 1H), 7.40 (d, J = 2.2 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 6.71 (dd, J = 8.8, 2.2 Hz, 1H), 3.72 (s, 3H), 2.77 (t, J = 6.1 Hz, 2H), 2.67 (t, J = 6.3 Hz, 2H), 1.89 (p, J = 6.3 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 154.0, 152.9, 142.1, 130.9, 124.6, 111.6, 110.8, 106.4, 103.4, 55.3, 22.8, 22.6, 22.0.

HRMS (ESI) calcd (m/z) for $C_{13}H_{15}N_2O_2^+$ ([M+H]$^+$): 231.1128, found: 231.1132.



1f

8-Methyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime (**1f**), following the procedure for the synthesis of oxime, **1f** was isolated as a greyish white solid (342 mg, 1.6 mmol, 80% yield).

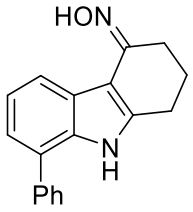
m.p. 202–203 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.12 (s, 1H), 10.23 (s, 1H), 7.72 (d, J = 7.6 Hz, 1H), 6.93 (t, J

= 7.5 Hz, 1H), 6.87 (d, *J* = 7.0 Hz, 1H), 2.82 (t, *J* = 6.2 Hz, 2H), 2.68 (t, *J* = 6.5 Hz, 2H), 2.44 (s, 3H), 1.91 (p, *J* = 6.4 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.0, 141.7, 135.8, 124.2, 122.4, 120.4, 120.3, 119.2, 107.3, 23.1, 22.9, 22.4, 17.2.

HRMS (ESI) calcd (m/z) for $C_{13}H_{15}N_2O^+$ ([M+H]$^+$): 215.1179, found: 215.1183.



1g

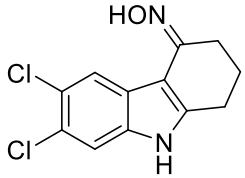
8-Phenyl-1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime (**1g**), following the procedure for the synthesis of oximes, **1g** was isolated as a white solid (469 mg, 1.7 mmol, 85% yield).

m.p. 210–211 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.04 (s, 1H), 10.30 (s, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.18 – 7.06 (m, 2H), 2.82 (t, *J* = 6.2 Hz, 2H), 2.70 (t, *J* = 6.5 Hz, 2H), 1.91 (p, *J* = 6.4 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 153.0, 143.0, 139.2, 133.7, 129.4, 128.9, 127.7, 125.5, 125.4, 122.1, 120.9, 120.8, 107.4, 23.1, 22.9, 22.4.

HRMS (ESI) calcd (m/z) for $C_{18}H_{17}N_2O^+$ ([M+H]$^+$): 277.1335, found: 277.1340.



1i

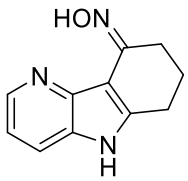
6,7-Dichloro-1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime 1i, following the procedure for the synthesis of oximes, **1i** was isolated as a white solid (343 mg, 1.28 mmol, 64% yield).

m.p. 171–172 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.57 (s, 1H), 10.46 (s, 1H), 8.01 (s, 1H), 7.57 (s, 1H), 2.81 (t, *J* = 6.2 Hz, 2H), 2.67 (t, *J* = 6.4 Hz, 2H), 1.92 (p, *J* = 6.4 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.3, 144.6, 135.5, 124.4, 123.8, 122.6, 122.0, 113.1, 106.8, 22.9, 22.6, 22.1.

HRMS (ESI) calcd (m/z) for $C_{12}H_{11}Cl_2N_2O^+$ ([M+H]$^+$): 269.0243, found: 269.0247.

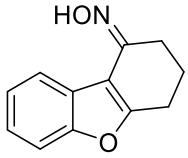


1j

5,6,7,8-Tetrahydro-9*H*-pyrido[3,2-*b*]indol-9-one oxime 1j, following the procedure for the synthesis of oximes, **1j** was isolated as a yellow solid (362 mg, 1.8 mmol, 90% yield).

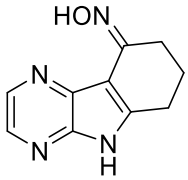
m.p. 226–227 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.42 (s, 1H), 10.78 (s, 1H), 8.55 (dd, J = 8.2, 1.2 Hz, 1H), 8.49 (dd, J = 6.0, 1.2 Hz, 1H), 7.65 (dd, J = 8.2, 6.0 Hz, 1H), 3.03 (t, J = 6.2 Hz, 2H), 2.79 – 2.73 (m, 2H), 1.99 (p, J = 6.5 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.5, 150.6, 135.3, 132.9, 132.1, 127.8, 117.4, 103.3, 23.5, 22.4, 21.5.
HRMS (ESI) calcd (m/z) for $C_{11}H_{12}N_3O^+$ ([M+H]$^+$): 202.0975, found: 202.0974.



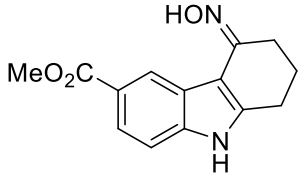
1k

3,4-Dihydrodibenzo[*b,d*]furan-1(2*H*)-one oxime 1k, following the procedure for the synthesis of oximes, **1k** was isolated as a white solid (320 mg, 1.6 mmol, 80% yield).
m.p. 110–111 ℃.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.92 – 7.84 (m, 1H), 7.49 – 7.41 (m, 1H), 7.34 – 7.26 (m, 2H), 2.89 (t, J = 6.4 Hz, 4H), 2.09 (p, J = 6.4 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 160.9, 154.8, 153.7, 124.5, 124.4, 123.7, 121.9, 111.3, 111.1, 23.5, 22.3, 21.6.
HRMS (ESI) calcd (m/z) for $C_{12}H_{12}NO_2^+$ ([M+H]$^+$): 202.0863, found: 203.0866.
NMR data are in agreement with literature reported chemical shifts and signal pattern.[4]



1l

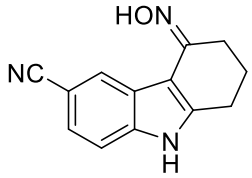
5,6,7,8-Tetrahydro-9*H*-pyrazino[2,3-*b*]indol-9-one oxime 1l, following the procedure for the synthesis of oximes, **1l** was isolated as a white solid (364 mg, 1.8 mmol, 90% yield).
m.p. > 250 ℃.
^{1}H NMR (400 MHz, DMSO-d_6) δ 12.14 (s, 1H), 10.63 (s, 1H), 8.35 (s, 1H), 8.15 (s, 1H), 2.88 (t, J = 5.4 Hz, 2H), 2.71 (t, J = 5.8 Hz, 2H), 2.04 – 1.83 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 150.2, 147.1, 142.2, 138.7, 136.5, 106.1, , 23.4, 22.7, 21.7.
HRMS (ESI) calcd (m/z) for $C_{10}H_{11}N_4O^+$ ([M+H]$^+$): 203.0927, found: 203.0926.



1o

Methyl-4-(hydroxyimino)-2,3,4,9-tetrahydro-1*H*-carbazole-6-carboxylate 1o, following the procedure for the synthesis of oximes, **1o** was isolated as a white solid (474 mg, 1.84 mmol, 92% yield).
m.p. 204–205 ℃.

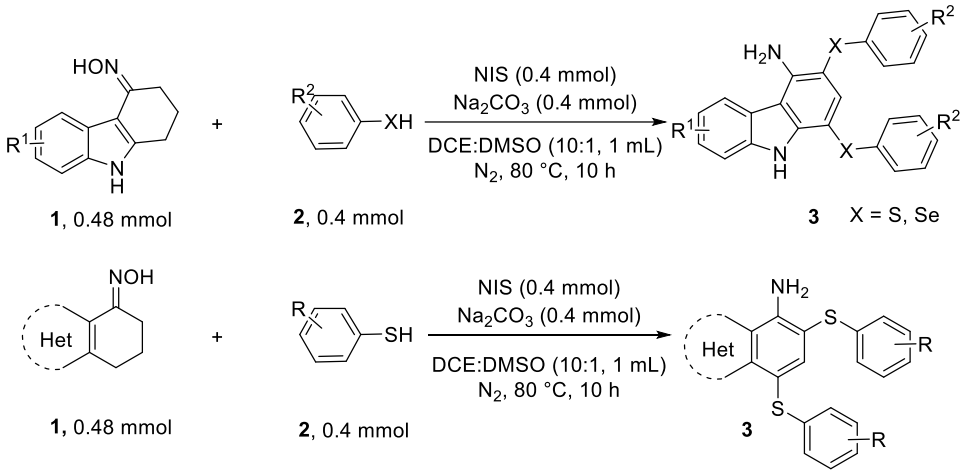
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.65 (s, 1H), 10.54 (s, 1H), 8.64 (d, J = 1.8 Hz, 1H), 7.74 (dd, J = 8.5, 1.8 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 3.84 (s, 3H), 2.82 (t, J = 6.2 Hz, 2H), 2.70 (t, J = 6.5 Hz, 2H), 1.93 (p, J = 6.4 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 167.8, 152.5, 143.7, 139.2, 124.1, 123.9, 123.0, 121.6, 111.4, 108.1, 52.1, 22.9, 22.7, 22.2.
HRMS (ESI) calcd (m/z) for $C_{14}H_{15}N_2O_3^+$ ([M+H]$^+$): 259.1077, found: 259.1082.



1p

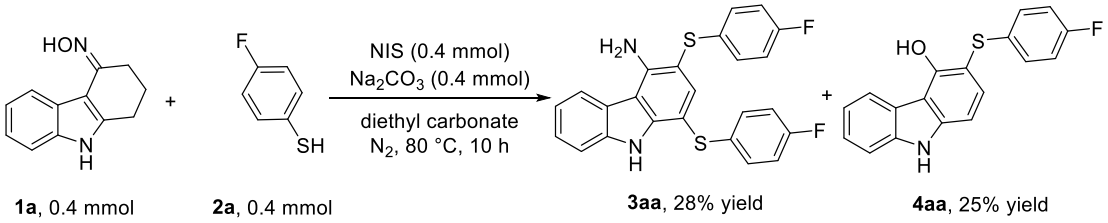
4-(Hydroxyimino)-2,3,4,9-tetrahydro-1H-carbazole-6-carbonitrile 1p, following the procedure for the synthesis of oximes, **1p** was isolated as a white solid (112 mg, 1.0 mmol, 50% yield).
m.p. 226–227 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.82 (s, 1H), 10.53 (s, 1H), 8.22 (s, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 2.88 – 2.77 (m, 2H), 2.73 – 2.63 (m, 2H), 1.99 – 1.84 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 152.0, 144.1, 138.0, 125.8, 124.4, 123.9, 120.8, 112.4, 107.3, 101.8, 22.5, 22.3, 21.7.
HRMS (ESI) calcd (m/z) for $C_{13}H_{12}N_3O^+$ ([M+H]$^+$): 226.0975, found: 226.0977.

5. General procedure for the synthesis of the compounds 3



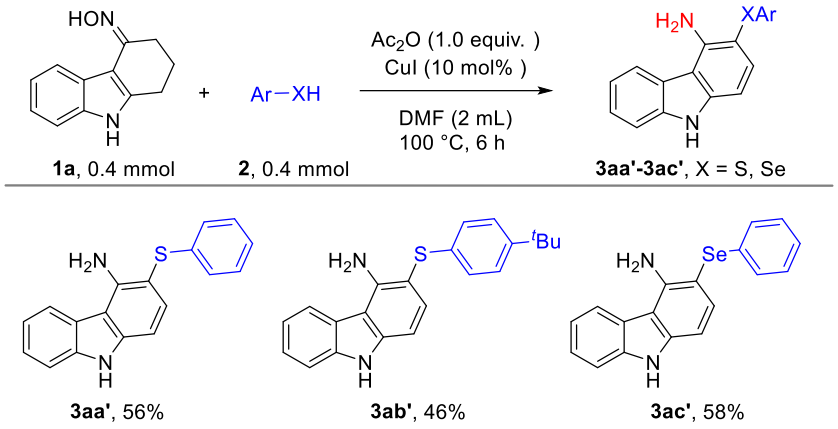
To an oven-dried screw-capped reaction tube with a magnetic stir bar, the corresponding oxime **1** (0.48 mmol), *N*-iodosuccinimide (90.0 mg, 0.4 mmol), sodium carbonate (42.4 mg, 0.4 mmol) were added. Then a solution of aryl thiol or selenol **2** (0.4 mmol) in mix solvent (DCE/DMSO = 10:1, 1.0 mL) were added under nitrogen atmosphere. The cap was screwed on, and the reaction mixture was stirred at 80 °C for 10 h in the heating mantle. After cooling down to room temperature, the reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the desired compound **3**.

Isolation for the compound 4aa



To an oven-dried screw-capped reaction tube with a magnetic stir bar, 1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime **1a** (80.4 mg, 0.4 mmol, 2.0 equiv.), *N*-iodosuccinimide (90.0 mg, 0.4 mmol, 2.0 equiv.), sodium carbonate (42.4 mg, 0.4 mmol) were added, then a solution of 4-fluorothiophenol **2a** (51.2 mg, 0.4 mmol, 2.0 equiv.) in diethyl carbonate (1 mL) were added under nitrogen atmosphere. The cap was screwed on, and the reaction mixture was stirred at 80 °C for 10 h in the heating mantle. After cooling down to room temperature, the reaction mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give **3aa** (white solid, 24.3 mg, 0.056 mmol, 28% yield) and **4aa** (grey solid, 30.9 mg, 0.1 mmol, 25% yield).

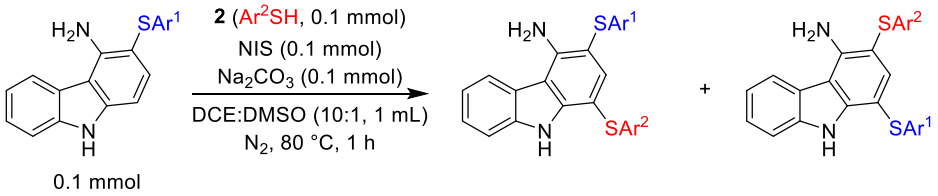
6. General procedure for the compounds 3aa'–3ac'



To an oven-dried screw-capped reaction tube with a magnetic stir bar, a solution of oxime **1** (80.0 mg, 0.4 mmol), CuI (7.6 mg, 0.04 mmol), acetic anhydride (37.5 μL, 0.4 mmol) in DMF (2 mL), substituted thiophenol (0.4 mmol) or selenophenol (62.8 mg, 0.4 mmol) was then added under nitrogen atmosphere. The reaction was stirred at 100 °C for 6 h in the heating mantle. After cooling down to room temperature, brine (10 mL) was added into the reaction mixture. Then resulting mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layer was dried with Na_2SO_4 and concentrated under vacuum. The residue was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the compounds **3aa'–3ac'**.

7. The synthesis of compounds 5 and C–S bond metathesis

The synthesis for compound 5

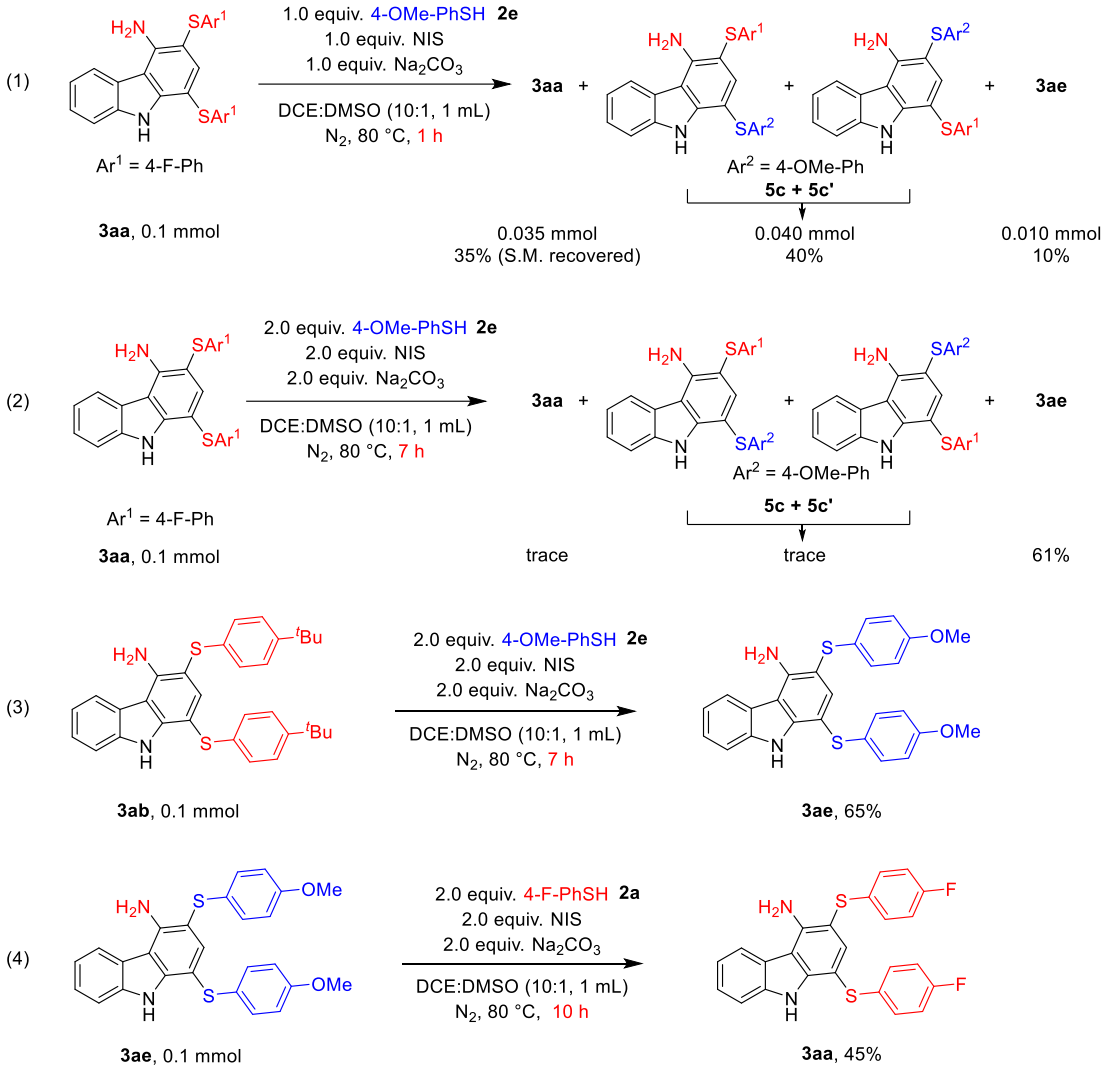


3aa', Ar^1 = Ph
3ab', Ar^1 = 4-^{t}Bu-Ph

5a+5a', Ar^1 = Ph, Ar^2 = 4-^{t}Bu-Ph, 47%, (ca. 1:1)
5b+5b', Ar^1 = 4-^{t}Bu-Ph, Ar^2 = 4-OMe-Ph, 54%, (ca. 1:1)

To an oven-dried screw-capped reaction tube with a magnetic stir bar, a solution of compound **3aa'** or **3ab'** (0.1 mmol, 1.0 equiv.), substituted thiophenol (0.1 mmol, 1.0 equiv.) in mix solvent (DCE/DMSO = 10:1, 1 mL), *N*-iodosuccinimide (22.5 mg, 0.1 mmol, 1.0 equiv.) and sodium carbonate (10.6 mg, 0.1 mmol, 1.0 equiv.) were then added to the solution under nitrogen atmosphere. The reaction was stirred at 80 °C for 1 h in the heating mantle. After cooling to room temperature, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give the compounds **5** with two isomers.

The C–S bond metathesis reactions



Scheme S3 The C–S bond metathesis of 1,3-dithiolated carbazol-4-amines

(1)

To an oven-dried screw-capped reaction tube with a magnetic stir bar, a solution of compound **3aa** (43.4 mg, 0.1 mmol, 1.0 equiv.), 4-methoxybenzenethiol **2e** (14.0 mg, 0.1 mmol, 1.0 equiv.) in solvent (DCE/DMSO = 10:1, 1 mL), *N*-iodosuccinimide (22.5 mg, 0.1 mmol, 1.0 equiv.) and sodium carbonate (10.6 mg, 0.1 mmol, 1.0 equiv.) were then added to the solution under nitrogen atmosphere. The reaction was stirred at 80 °C for 1 h in the heating mantle. After cooling to room temperature, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give the compound **5c** + **5c'** (with two isomers) in 40% yield and **3ae** in 10% yield (the starting material **3aa** was recovered in 35% yield).

(2)

To an oven-dried screw-capped reaction tube with a magnetic stir bar, a solution of compound **3aa** (43.4 mg, 0.1 mmol, 1.0 equiv.), 4-methoxybenzenethiol **2e** (28.0 mg, 0.2 mmol, 2.0 equiv.) in solvent (DCE/DMSO = 10:1, 1 mL), *N*-iodosuccinimide (45 mg, 0.2 mmol, 2.0 equiv.) and sodium carbonate (21.2 mg, 0.2 mmol, 2.0 equiv.) were then added to the solution under nitrogen atmosphere. The reaction was stirred at 80 °C for 7 h in the heating mantle. After cooling to room temperature, the residue was purified by silica gel column chromatography (petroleum ether/ethyl

acetate = 10:1) to give the compound **3ae** in 61% yield (only trace amount of the starting material **3aa** and **5c** + **5c'** were detected).

(3)

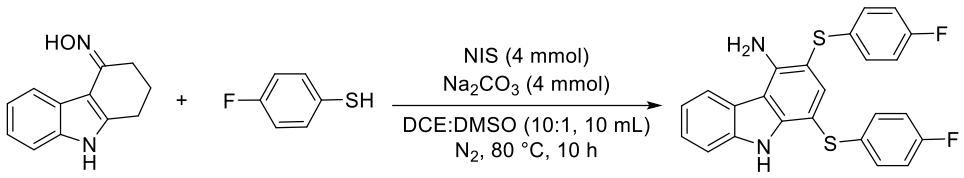
To an oven-dried screw-capped reaction tube with a magnetic stir bar, a solution of compound **3ab** (51.0 mg, 0.1 mmol, 1.0 equiv.), 4-methoxybenzenethiol **2e** (28.0 mg, 0.2 mmol, 2.0 equiv.) in solvent (DCE/DMSO = 10:1, 1 mL), *N*-iodosuccinimide (45.0 mg, 0.2 mmol, 2.0 equiv.) and sodium carbonate (21.2 mg, 0.2 mmol, 2.0 equiv.) were then added to the solution under nitrogen atmosphere. The reaction was stirred at 80 °C for 7 h in the heating mantle. After cooling to room temperature, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give the compound **3ae** in 65% yield.

(4)

To an oven-dried screw-capped reaction tube with a magnetic stir bar, a solution of compound **3ae** (45.8 mg, 0.1 mmol, 1.0 equiv.), 4-fluorobenzenethiol **2a** (25.6 mg, 0.2 mmol, 2.0 equiv.) in solvent (DCE/DMSO = 10:1, 1 mL), *N*-iodosuccinimide (45.0 mg, 0.2 mmol, 2.0 equiv.) and sodium carbonate (21.2 mg, 0.2 mmol, 2.0 equiv.) were then added to the solution under nitrogen atmosphere. The reaction was stirred at 80 °C for 10 h in the heating mantle. After cooling to room temperature, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give the compound **3aa** in 45% yield.

8. Scale up reaction and transformations

Scale up reaction



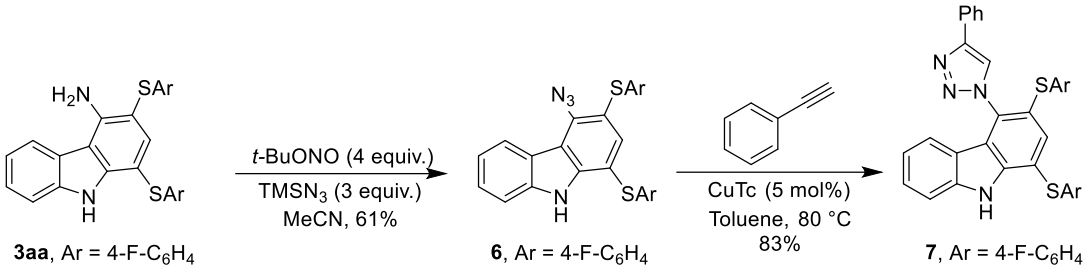
1a
4.8 mmol

2a
4 mmol

3aa, 720 mg
1.66 mmol, 83%

To an oven-dried screw-capped reaction tube with a magnetic stir bar, 1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime **1a** (965 mg, 4.8 mmol), *N*-iodosuccinimide (900 mg, 4.0 mmol), sodium carbonate (424 mg, 4.0 mmol) were added, then 4-fluorothiophenol **2a** (512 mg, 4.0 mmol) dissolved in mix solvent (DCE/DMSO = 10:1, 10 mL) were added sequentially under nitrogen atmosphere. The cap was screwed on, and the reaction mixture was stirred at 80 °C for 10 h in the heating mantle. After cooling down to room temperature, the reaction mixture was mixed with silica gel and concentrated under vacuum. The solid mixture was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give the compound **3aa** as white solid (720 mg, 1.66 mmol, 83% yield).

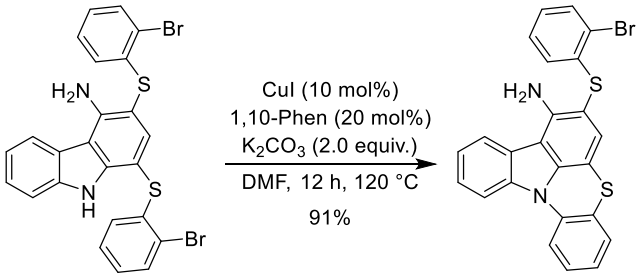
Transformations from compound 3



3aa, Ar = 4-F-C_6H_4 **6**, Ar = 4-F-C_6H_4 **7**, Ar = 4-F-C_6H_4

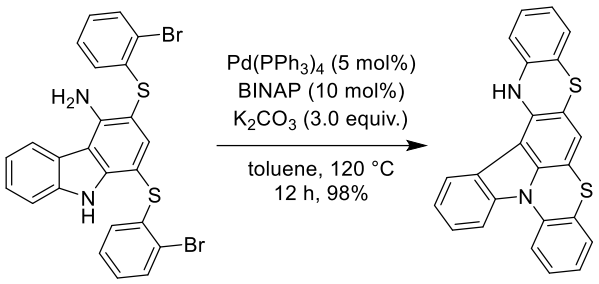
In an oven-dried screw-capped reaction tube with a magnetic stir bar, compound **3aa** (44.0 mg, 0.1 mmol, 1 equiv.) was dissolved in MeCN (1 mL) before being cooled to 0 °C with stirring. The solution of *tert*-butylnitrite (48 μL, 0.4 mmol, 4 equiv.) was then added dropwise to the solution. After the addition, the mixture was allowed to warm up to room temperature, and then stirred for further 1 h. Then a solution of azidotrimethylsilane (40 μL, 0.3 mmol, 3 equiv.) in MeCN (0.5 mL) was added dropwise to the reaction mixture. The resulting solution was stirred at room temperature for 1.5 h. The reaction mixture was concentrated under vacuum and the residue was purified by silica gel column chromatography (hexane) to give the azides **6** as a yellow oil (28.1 mg, 0.061 mmol, 61% yield).[5]

In a Schlenk tube, to a stirred solution of phenylacetylene (10 μL, 0.05 mmol, 1.0 equiv.), a solution of azide **6** (23.0 mg, 0.05 mmol, 1.0 equiv.) in toluene (1 mL) was added copper(I) thiophene-2-carboxylate (CuTc, 1.0 mg, 5 mol%). The reaction mixture was stirred at 80 ℃ for 2 h in the heating mantle, and then concentrated in vacuo. The resulting residue was further purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 4:1) to afford compound **7** as a yellow solid (23.3 mg, 0.041 mmol, 83% yield).



3ah **8**

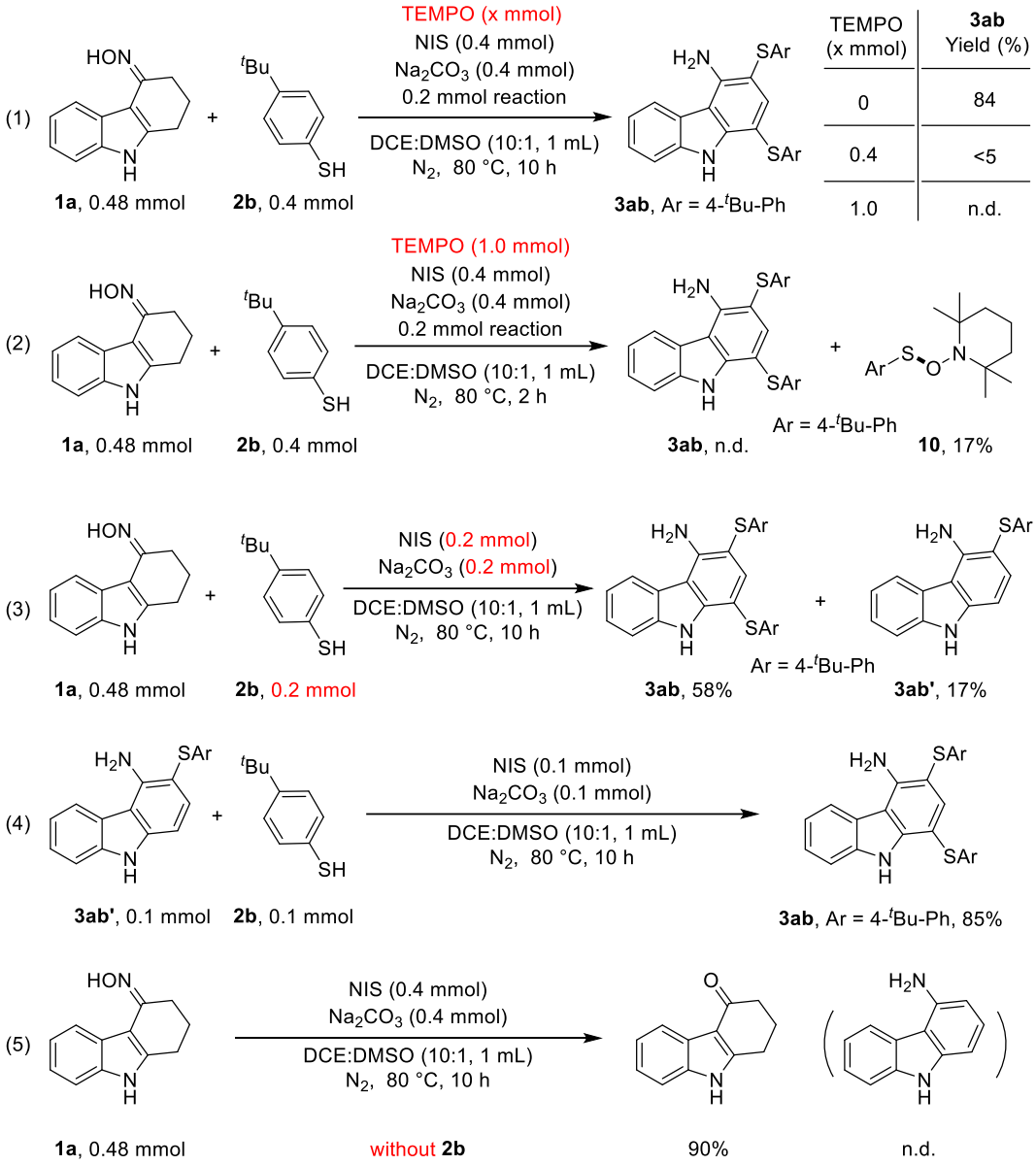
In a Schlenk tube, a mixture of **3ah** (36.0 mg, 0.065 mmol), CuI (1.2 mg, 0.0065 mmol), 1,10-phenanthroline (2.3 mg, 0.013 mmol), and potassium carbonate (18.0 mg, 0.13 mmol, 2.0 equiv.) in DMF (1 mL) was stirred at 120 °C under nitrogen atmosphere for 12 h in the heating mantle. After cooling down to room temperature, brine (5 mL) was poured into the reaction mixture. Then resulting mixture was extracted with ethyl acetate (2 × 5 mL). The combined organic layer was dried with Na_2SO_4 and concentrated under vacuum. The residue was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the compound **8** as a yellow solid (28.0 mg, 0.059 mmol, 91% yield).



3ah **9**

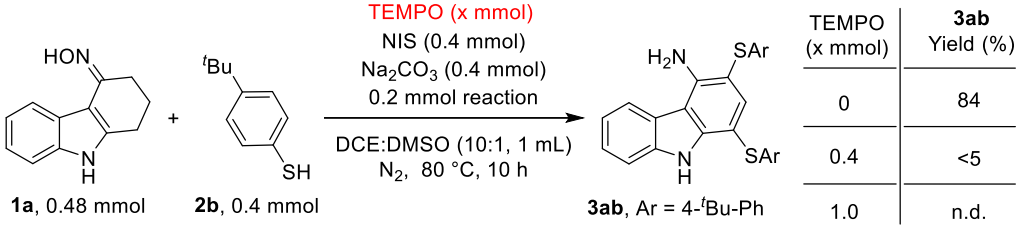
In a Schlenk tube, a mixture of **3ah** (28.0 mg, 0.05 mmol, 1 equiv.), $Pd(PPh_3)_4$ (2.9 mg, 0.0025 mmol, 5 mol%), BINAP (3.1 mg, 0.005 mmol, 10 mol%), and potassium carbonate (20.7 mg, 0.15 mmol, 3.0 equiv.) in toluene (1 mL) was stirred at 120 °C under nitrogen atmosphere for 12 h in the heating mantle. After cooling down to room temperature, brine (5 mL) was poured into the reaction mixture. Then resulting mixture was extracted with ethyl acetate (2 × 5 mL). The combined organic layer was dried with Na_2SO_4 and concentrated under vacuum. The residue was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the compound **9** as a yellow solid (19.3 mg, 0.049 mmol, 98% yield).

9. Control experiments



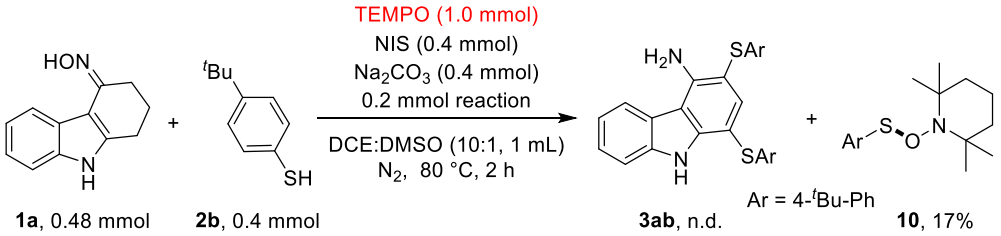
Scheme S4 Control experiments

Radical trapping experiments



To three oven-dried screw-capped reaction tubes with magnetic stir bars, 1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime **1a** (96.5 mg, 0.48 mmol), *N*-iodosuccinimide (90.0 mg, 0.4 mmol), sodium carbonate (42.4 mg, 0.4 mmol) were added. To each tube [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl]

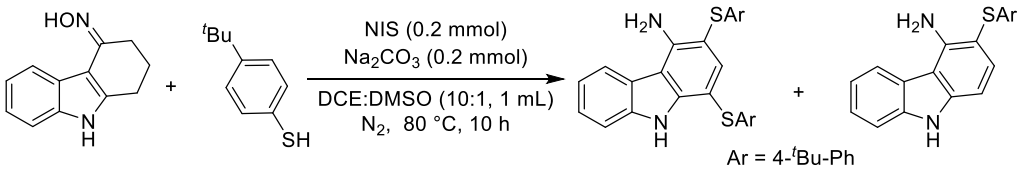
(0, 0.4 mmol, 1.0 mmol TEMPO) was added respectively. Then 4-(*tert*-butyl)benzenethiol **2b** (66.5 mg, 0.4 mmol) dissolved in mix solvent (DCE/DMSO = 10:1, 1 mL) were added sequentially under nitrogen atmosphere. The cap was screwed on, and the reaction mixture was stirred at 80 °C for 10 h in the heating mantle. Without tempo, the compound **3ab** could be obtained in 84% yield, while 0.4 mmol and 1.0 mmol tempo inhibited the formation of **3ab**.



1a, 0.48 mmol **2b**, 0.4 mmol **3ab**, n.d. **10**, 17%

To an oven-dried screw-capped reaction tube with a magnetic stir bar, 1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime **1a** (96.5 mg, 0.48 mmol), *N*-iodosuccinimide (90.0 mg, 0.4 mmol), sodium carbonate (42.4 mg, 0.4 mmol), [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] (156 mg, 1.0 mmol TEMPO) were added. Then 4-(*tert*-butyl)benzenethiol **2b** (66.5 mg, 0.4 mmol) dissolved in solvent (DCE/DMSO = 10:1, 1 mL) were added sequentially under nitrogen atmosphere. The cap was screwed on, and the reaction mixture was stirred at 80 °C for 2 h in the heating mantle. After colling to room temperature, the reaction mixture was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give the tempo trapping product **10** as colorless oil (21.8 mg, 0.068 mmol, 17% yield).

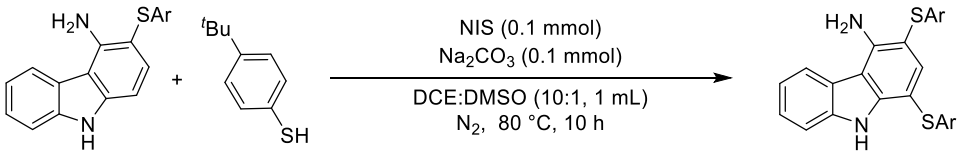
The reaction between **1a** and **2b** with reduced amount of **2b**



1a, 0.48 mmol **2b**, 0.2 mmol **3ab**, 58% **3ab'**, 17%

To an oven-dried screw-capped reaction tube with a magnetic stir bar, 1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime **1a** (95.5 mg, 0.48 mmol), *N*-iodosuccinimide (45.0 mg, 0.2 mmol), sodium carbonate (42.4 mg, 0.4 mmol) were added. Then a solution of 4-(*tert*-butyl)benzenethiol **2b** (33.2 mg, 0.2 mmol) in solvent (DCE/DMSO = 10:1, 1 mL) was added under nitrogen atmosphere. The sealed reaction mixture was stirred at 80 °C for 10 h in the heating mantle. After colling to room temperature, the reaction mixture was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product **3ab** (29.6 mg, 0.058 mmol, 58% yield) and **3ab'** (11.5 mg, 0.033 mmol, 17% yield).

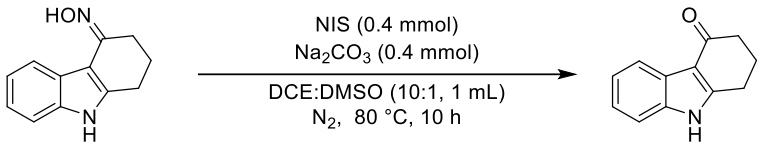
Transformation of **3ab'** to **3ab**



3ab', 0.1 mmol **2b**, 0.1 mmol **3ab**, Ar = 4-tBu-Ph, 85%

The reaction was carried at the conditions (0.1 mmol **3ab'**, 0.1 mmol **2b**, 0.1 mmol NIS, 0.1 mmol

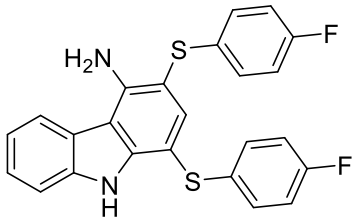
Na_2CO_3) in solvent (DCE/DMSO = 10:1, 1 mL), heating at 80 ℃ with heating mantle under nitrogen atmosphere for 10 h. After cooling down to room temperature, the reaction mixture was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford compound **3ab** as a grey solid (43.2 mg, 0.085 mmol, 85% yield).



1a, 0.48 mmol 90%

To an oven-dried screw-capped reaction tube with a magnetic stir bar, 1,2,3,9-tetrahydro-4*H*-carbazol-4-one oxime **1a** (95.5 mg, 0.48 mmol), *N*-iodosuccinimide (90.0 mg, 0.4 mmol), sodium carbonate (42.4 mg, 0.4 mmol) were added. Under nitrogen atmosphere, the mixture was dissolved in solvent (DCE/DMSO = 10:1, 1 mL) and was stirred at 80 °C for 1 h in the heating mantle. After cooling down to room temperature, 1,2,3,9-tetrahydro-4*H*-carbazol-4-one was obtained in 90% yield.

10. Characterization data of the compounds 3–10



3aa

1,3-Bis((4-fluorophenyl)thio)-9*H*-carbazol-4-amine 3aa, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (82.5 mg, 0.19 mmol, 95% yield) as a white solid.

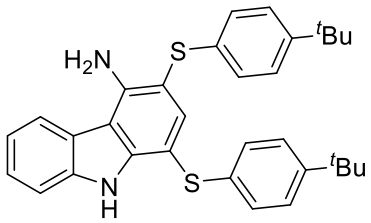
m.p. 157–158 °C.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.55 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.85 (s, 1H), 7.50 – 7.39 (m, 2H), 7.34 – 7.28 (m, 1H), 7.13 – 7.00 (m, 4H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.33 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 161.1 (d, *J* = 245.4 Hz, 2C), 147.0, 144.1, 143.0, 138.4, 132.8 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 2.9 Hz), 127.9 (d, *J* = 5.6 Hz), 127.8 (d, *J* = 5.6 Hz) 125.3, 123.2, 120.6 (d, *J* = 2.6 Hz), 116.3 (d, *J* = 8.2 Hz), 116.0 (d, *J* = 8.7 Hz) 111.1, 110.1, 105.1, 101.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.2 (m, 1F), -117.4 (m, 1F).

HRMS (ESI) calcd (m/z) for $C_{24}H_{17}F_2N_2S_2^+$ ([M+H]$^+$): 435.0796, found: 435.0794.



3ab

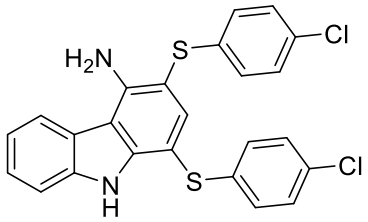
1,3-Bis((4-(tert-butyl)phenyl)thio)-9*H*-carbazol-4-amine 3ab, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (85.5 mg, 0.168 mmol, 84% yield) as a white solid.

m.p. 112–113 °C.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.57 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.86 (s, 1H), 7.46 – 7.39 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.19 (m, 4H), 7.02 (d, *J* = 8.4 Hz, 4H), 5.32 (s, 2H), 1.26 (s, 9H), 1.24 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 148.5, 148.4, 147.0, 144.3, 143.4, 138.4, 134.5, 134.4, 126.1, 126.0, 125.7, 125.7, 125.1, 123.3, 120.6, 120.3, 111.0, 110.0, 105.0, 101.1, 34.3, 31.3.

HRMS (ESI) calcd (m/z) for $C_{32}H_{35}N_2S_2^+$ ([M+H]$^+$): 511.2236, found: 511.2233.



3ac

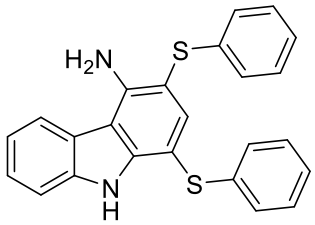
1,3-Bis((4-chlorophenyl)thio)-9*H*-carbazol-4-amine 3ac, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (71.6 mg, 0.154 mmol, 77% yield) as a white solid.

m.p. 176–177 °C.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.53 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.82 (s, 1H), 7.50 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 7.21 – 7.10 (m, 4H), 7.05 – 6.91 (m, 4H), 5.33 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 147.2, 144.2, 143.2, 138.4, 136.5, 136.3, 131.2, 131.2, 129.2, 129.1, 127.1, 125.4, 123.1, 120.7, 120.6, 111.1, 110.1, 104.2, 100.5.

HRMS (ESI) calcd (m/z) for $C_{24}H_{17}Cl_2N_2S_2^+$ ([M+H]$^+$): 467.0205, found: 467.0201.



3ad

1,3-Bis(phenylthio)-9*H*-carbazol-4-amine 3ad

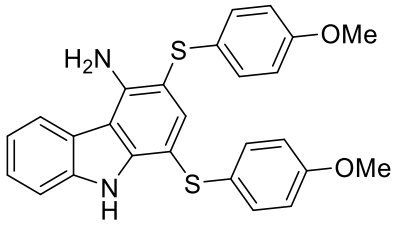
Following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (67.7 mg, 0.17 mmol, 62% yield) as a white solid.

m.p. 133–134 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.88 (s, 1H), 7.46 – 7.37 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.24 – 7.16 (m, 4H), 7.14 – 7.03 (m, 6H), 5.33 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 147.1, 144.3, 143.5, 138.4, 138.0, 137.9, 129.1, 129.0, 125.8, 125.8, 125.3, 125.2, 125.2, 123.2, 120.6, 120.5, 111.1, 110.0, 104.6, 100.7.

HRMS (ESI) calcd (m/z) for $C_{24}H_{19}N_2S_2^+$ ([M+H]$^+$): 399.0984, found: 399.0982.



3ae

1,3-Bis((4-methoxyphenyl)thio)-9*H*-carbazol-4-amine 3ae

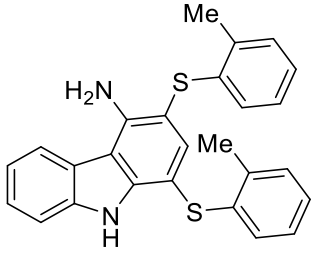
Following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (10% ethyl acetate/petroleum ether) yielded the title compound as a grey

solid, m.p. 142–144 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.85 (s, 1H), 7.42 – 7.35 (m, 2H), 7.28 – 7.25 (m, 1H), 7.08 (d, *J* = 8.8 Hz, 4H), 6.79 – 6.71 (m, 4H), 5.27 (s, 2H), 3.73 (s, 3H), 3.72 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 158.1, 158.0, 146.5, 143.8, 142.5, 138.4, 128.44, 128.38, 128.33, 128.28, 125.1, 123.2, 120.6, 120.3, 114.84, 114.77, 111.0, 110.1, 106.3, 102.5, 55.4.

HRMS (ESI$^+$) calcd (m/z) for $C_{26}H_{23}N_2O_2S_2^+$ $[M+H]^+$: 459.1195, found: 459.1198.



3af

1,3-Bis(o-tolylthio)-9*H*-carbazol-4-amine 3af

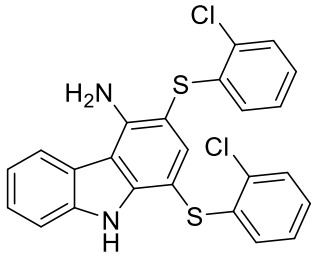
Following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (60.6 mg, 0.142 mmol, 71% yield) as a white solid.

m.p. 141–142 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.53 (s, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.81 (s, 1H), 7.46 – 7.39 (m, 2H), 7.34 – 7.28 (m, 1H), 7.20 – 7.14 (m, 2H), 7.04 – 6.96 (m, 3H), 6.92 (t, *J* = 7.0 Hz, 1H), 6.68 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.63 (d, *J* = 7.0 Hz, 1H), 5.29 (s, 2H), 2.49 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 147.3, 144.5, 143.7, 138.5, 137.2, 136.9, 134.8, 134.7, 130.31, 130.25, 126.74, 126.66, 125.3, 125.1, 125.0, 124.9, 124.7, 123.4, 120.7, 120.6, 111.2, 110.2, 104.3, 100.4, 20.1.

HRMS (ESI) calcd (m/z) for $C_{26}H_{23}N_2S_2^+$ ($[M+H]^+$): 427.1297, found: 427.1295.



3ag

1,3-Bis((2-chlorophenyl)thio)-9*H*-carbazol-4-amine 3ag

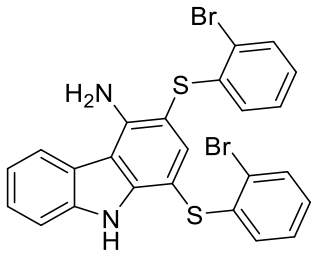
Following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (57.4 mg, 0.124 mmol, 62% yield) as a white solid. m.p. 166–167 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.64 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.84 (s, 1H), 7.49 – 7.41 (m, 2H), 7.40 – 7.29 (m, 3H), 7.08 – 6.99 (m, 3H), 6.96 (td, *J* = 7.7, 1.4 Hz, 1H), 6.66 (dd, *J* = 7.3, 2.3 Hz, 1H), 6.60 (dd, *J* = 8.0, 1.7 Hz, 1H), 5.36 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 147.8, 144.7, 144.0, 138.5, 137.3, 136.9, 131.0, 130.7, 129.73, 129.71, 127.4, 127.3, 126.3, 126.20, 126.17, 125.5, 123.2, 120.8, 120.7, 111.3, 110.2, 103.3,

99.6.

HRMS (ESI) calcd (m/z) for $C_{24}H_{17}Cl_2N_2S_2^+$ ([M+H]$^+$): 467.0205, found: 467.0201.



3ah

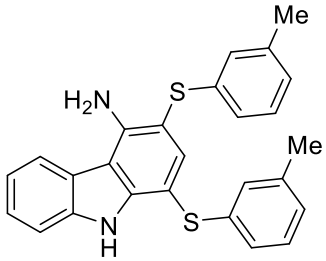
1,3-Bis((2-bromophenyl)thio)-9*H*-carbazol-4-amine 3ah

Following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (82.1 mg, 0.148 mmol, 74% yield) as a white solid. m.p. 165–167 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.64 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.84 (s, 1H), 7.58 – 7.50 (m, 2H), 7.44 (d, *J* = 6.7 Hz, 2H), 7.35 – 7.28 (m, 1H), 7.11 – 7.04 (m, 1H), 7.03 – 6.90 (m, 3H), 6.64 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.57 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.36 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 147.7, 144.6, 143.9, 139.2, 138.9, 138.5, 133.00, 132.97, 128.0, 127.9, 126.42, 126.40, 126.3, 126.2, 125.5, 123.2, 120.8, 120.6, 120.3, 111.3, 110.2, 104.0, 100.3.

HRMS (ESI) calcd (m/z) for $C_{24}H_{17}Br_2N_2S_2^+$ ([M+H]$^+$): 556.9174, found: 556.9178.



3ai

1,3-Bis(m-tolylthio)-9*H*-carbazol-4-amine 3ai

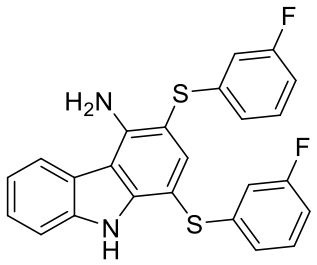
Following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (79.0 mg, 0.186 mmol, 93% yield) as a white solid.

m.p. 107–108 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.61 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.90 (s, 1H), 7.46 – 7.40 (m, 2H), 7.33 – 7.28 (m, 1H), 7.15 – 7.06 (m, 2H), 6.97 – 6.87 (m, 6H), 5.33 (s, 2H), 2.27 (s, 3H), 2.25 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 147.1, 144.4, 143.6, 138.9, 138.8, 138.4, 137.9, 137.8, 128.94, 128.88, 126.5, 126.4, 126.3, 126.2, 125.1, 123.3, 123.0, 122.9, 120.6, 120.4, 111.1, 110.1, 104.7, 100.8, 21.55, 21.52.

HRMS (ESI) calcd (m/z) for $C_{26}H_{23}N_2S_2^+$ ([M+H]$^+$): 427.1297, found: 427.1294.



3aj

1,3-Bis((3-fluorophenyl)thio)-9*H*-carbazol-4-amine 3aj

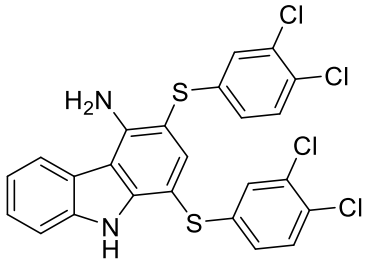
Following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (65.1 mg, 0.15 mmol, 75% yield) as a white solid. m.p. 89–90 °C.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.58 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.84 (s, 1H), 7.49 – 7.41 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.21 – 7.13 (m, 2H), 6.88 (dd, *J* = 7.8, 2.0 Hz, 1H), 6.85 (dd, *J* = 7.8, 2.0 Hz, 1H), 6.83 – 6.71 (m, 4H), 5.36 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 163.3 (d, *J* = 248.0 Hz, 2C), 147.4, 144.4, 143.6, 140.7 (d, *J* = 7.4 Hz), 140.5 (d, *J* = 7.4 Hz), 138.4, 130.3, 130.31 (d, *J* = 16.5 Hz), 125.4, 123.2, 121.24 (d, *J* = 2.8 Hz), 121.2 (d, *J* = 2.6 Hz), 120.6 (d, *J* = 10.4 Hz), 112.6 (d, *J* = 24.3 Hz), 112.4 (d, *J* = 4.3 Hz), 112.2 (d, *J* = 4.3 Hz), 111.2, 110.1, 103.7, 99.9.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -111.8 (m, 1F), -112.0 (m, 1F).

HRMS (ESI) calcd (m/z) for $C_{24}H_{17}F_2N_2S_2^+$ ([M+H]$^+$): 435.0796, found: 435.0794.



3ak

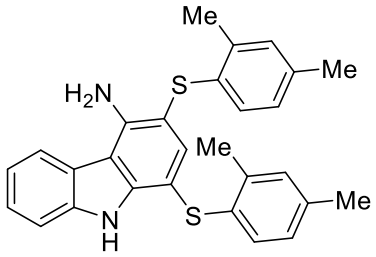
1,3-Bis((3,4-dichlorophenyl)thio)-9*H*-carbazol-4-amine 3ak, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (105 mg, 0.196 mmol, 98% yield) as a white solid.

m.p. 162–163 °C.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.48 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.44 – 7.34 (m, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 2H), 6.81 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.76 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.28 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 147.5, 144.3, 143.4, 138.4, 138.33, 138.30, 133.3, 133.2, 130.73, 130.68, 129.4, 129.3, 127.1, 125.6, 125.0, 124.9, 123.1, 120.9, 120.6, 111.2, 110.2, 103.4, 99.7.

HRMS (ESI) calcd (m/z) for $C_{24}H_{15}Cl_4N_2S_2^+$ ([M+H]$^+$): 536.9396, found: 536.9398.



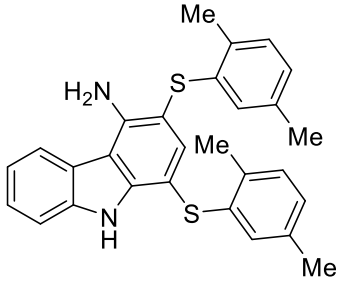
3al

1,3-Bis((2,4-dimethylphenyl)thio)-9*H*-carbazol-4-amine 3al, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (51.8 mg, 0.114 mmol, 57% yield) as colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.53 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.81 (s, 1H), 7.46 – 7.40 (m, 2H), 7.35 – 7.28 (m, 1H), 7.02 (d, *J* = 2.0 Hz, 2H), 6.82 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.76 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 5.28 (s, 2H), 2.48 (s, 6H), 2.27 (s, 3H), 2.26 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 146.9, 144.3, 143.3, 138.5, 135.0, 134.9, 134.8, 133.4, 133.3, 131.3, 131.2, 127.45, 127.38, 125.5, 125.21, 125.17, 123.3, 120.7, 120.4, 111.1, 110.2, 104.8, 101.0, 20.9, 20.8, 20.08, 20.06.

HRMS (ESI) calcd (m/z) for $C_{28}H_{27}N_2S_2^+$ ([M+H]$^+$): 455.1610, found: 455.1607.



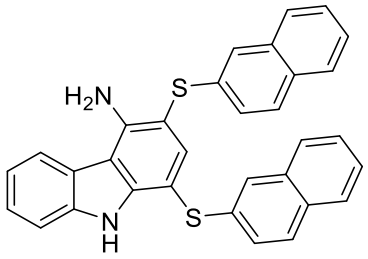
3am

1,3-Bis((2,5-dimethylphenyl)thio)-9H-carbazol-4-amine 3am, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (60.4 mg, 0.133 mmol, 67% yield) as a white solid. m.p. 151–152 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.57 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.80 (s, 1H), 7.46 – 7.40 (m, 2H), 7.36 – 7.26 (m, 1H), 7.02 (d, *J* = 2.0 Hz, 2H), 6.82 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.76 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 5.29 (s, 2H), 2.46 (s, 6H), 2.12 (s, 3H), 2.06 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 146.0, 143.4, 142.6, 137.4, 135.6, 135.4, 135.2, 135.1, 130.7, 130.5, 129.05, 129.00, 124.82, 124.76, 124.3, 124.1, 124.0, 122.3, 119.6, 119.3, 110.0, 109.1, 103.2, 99.3, 20.1, 18.5.

HRMS (ESI) calcd (m/z) for $C_{28}H_{27}N_2S_2^+$ ([M+H]$^+$): 455.1610, found: 455.1607.



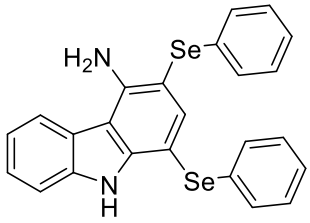
3an

1,3-Bis(naphthalen-2-ylthio)-9*H*-carbazol-4-amine 3an, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (74.7 mg, 0.15 mmol, 75% yield) as a white solid. m.p. 121–123 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*); δ 8.52 (s, 1H), 7.90 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.61 – 7.54 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.49 – 7.45 (m, 1H), 7.37 (d, *J* = 2.0 Hz, 2H), 7.33 – 7.25 (m, 6H), 7.23 – 7.15 (m, 3H), 5.27 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 147.3, 144.5, 143.6, 138.5, 135.6, 135.5, 133.94, 133.88, 131.7, 131.6, 128.84, 128.76, 127.8, 127.1, 126.73, 126.66, 125.54, 125.45, 125.3, 124.8, 124.7, 123.7, 123.4, 120.7, 120.6, 111.2, 110.3, 104.7, 101.0.

HRMS (ESI) calcd (m/z) for $C_{32}H_{23}N_2S_2^+$ ([M+H]$^+$): 499.1297, found: 499.1294.



3ao

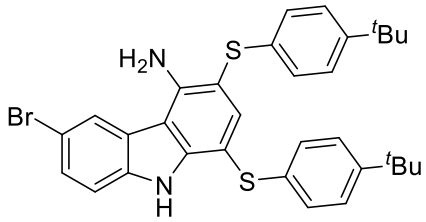
1,3-bis(phenylselanyl)-9*H*-carbazol-4-amine 3ao

Following the general procedure, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound as a white solid, m.p. 130–132 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.08 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.08 (m, 10H), 5.30 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 145.4, 144.7, 138.3, 133.0, 132.9, 129.44, 129.37, 128.8, 128.7, 126.2, 126.1, 125.2, 123.6, 120.8, 120.4, 111.1, 109.7, 103.3, 97.3.

HRMS (ESI$^+$) calcd (m/z) for $C_{24}H_{19}N_2Se_2^+$ ([M+H]$^+$): 494.9873, found: 494.9880.



3bb

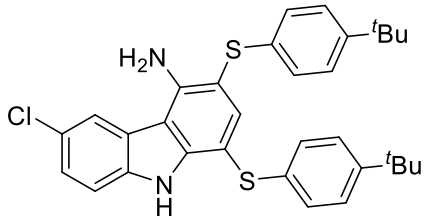
6-Bromo-1,3-bis((4-(*tert*-butyl)phenyl)thio)-9*H*-carbazol-4-amine 3bb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (82.6 mg, 0.14 mmol, 70% yield) as

a white solid. m.p. 156–158 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.57 (s, 1H), 8.03 (d, *J* = 1.8 Hz, 1H), 7.88 (s, 1H), 7.48 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 4H), 7.05 – 6.98 (m, 4H), 5.27 (s, 2H), 1.26 (s, 9H), 1.24 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 148.7, 148.6, 147.0, 144.6, 144.0, 137.0, 134.3, 134.1, 127.7, 126.2, 126.1, 126.0, 125.8, 125.0, 123.3, 113.1, 112.2, 109.2, 105.7, 101.3, 34.4, 31.3.

HRMS (ESI) calcd (m/z) for $C_{32}H_{34}BrN_2S_2^+$ ([M+H]$^+$): 589.1341, found: 589.1338.



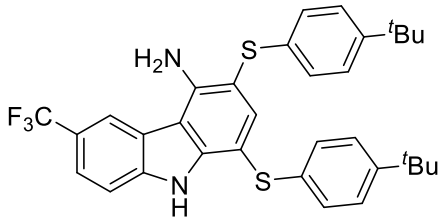
3cb

1,3-Bis((4-(*tert*-butyl)phenyl)thio)-6-chloro-9*H*-carbazol-4-amine 3cb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (99.3 mg, 0.182 mmol, 91% yield) as a white solid. m.p. 146–147 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.56 (s, 1H), 7.88 (s, 1H), 7.87 (s, 1H)., 7.35 – 7.31 (m, 2H), 7.23 (d, *J* = 8.9 Hz, 4H), 7.03 (d, *J* = 8.5 Hz, 4H), 5.26 (s, 2H), 1.27 (s, 9H), 1.25 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*): δ 148.7, 148.6, 147.0, 144.8, 144.0, 136.7, 134.3, 134.1, 126.2, 126.1, 125.9, 125.8, 125.7, 125.1, 124.4, 120.3, 111.8, 109.4, 105.7, 101.4, 34.50, 34.49, 31.41, 31.39.

HRMS (ESI) calcd (m/z) for $C_{32}H_{34}ClN_2S_2^+$ ([M+H]$^+$): 545.1846, found: 545.1841.



3db

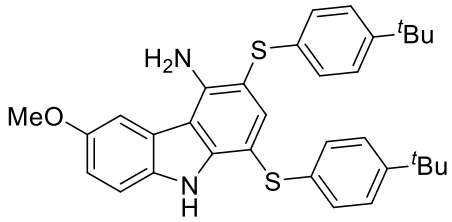
1,3-Bis((4-(*tert*-butyl)phenyl)thio)-6-(trifluoromethyl)-9*H*-carbazol-4-amine 3db, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (82.0 mg, 0.142 mmol, 71% yield) as a white solid. m.p. 132–133 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (s, 1H), 8.19 (s, 1H), 7.97 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 4H), 7.08 (d, *J* = 8.4 Hz, 4H), 5.38 (s, 2H), 1.31 (s, 9H), 1.29 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.8, 148.7, 147.0, 144.9, 144.2, 140.0, 134.1, 133.9, 126.2, 126.1, 126.0, 125.8, 123.0, 122.6 (q, *J* = 32.4 Hz), 122.0 (q, *J* = 3.4 Hz), 117.9 (q, *J* = 4.0 Hz), 111.0, 109.7, 106.5, 101.6, 34.4, 31.3.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.2 (m, 3F).

HRMS (ESI) calcd (m/z) for $C_{33}H_{34}F_3N_2S_2^+$ ([M+H]$^+$): 579.2110, found: 579.2105.



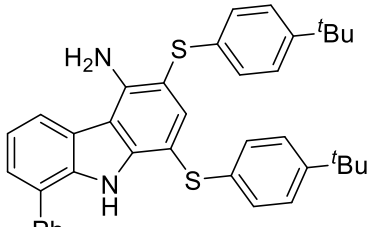
3eb

1,3-Bis((4-(*tert*-butyl)phenyl)thio)-6-methoxy-9*H*-carbazol-4-amine 3eb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (10% ethyl acetate/petroleum ether) yielded the title compound (61.5 mg, 0.114 mmol, 57% yield) as a grey solid. m.p. 176–177 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.83 (s, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.06 – 6.98 (m, 5H), 5.26 (s, 2H), 3.89 (s, 3H), 1.25 (s, 18H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 154.5, 148.6, 148.5, 147.2, 145.1, 143.5, 134.59, 134.56, 133.4, 126.23, 126.17, 125.84, 125.82, 123.9, 113.4, 111.5, 110.3, 105.0, 104.7, 101.3, 56.4, 34.48, 34.47, 31.42, 31.40.

HRMS (ESI) calcd (m/z) for $C_{33}H_{37}N_2OS_2^+$ ([M+H]$^+$): 541.2342, found: 541.2339.



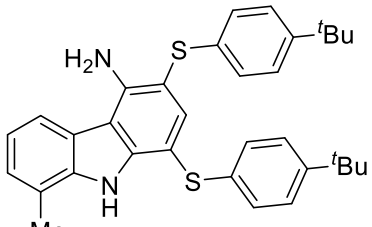
3fb

1,3-Bis((4-(*tert*-butyl)phenyl)thio)-8-phenyl-9*H*-carbazol-4-amine 3fb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (71.5 mg, 0.122 mmol, 61% yield) as a white solid. m.p. 138–139 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.86 (s, 1H), 7.49 – 7.40 (m, 6H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.25 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.31 (s, 2H), 1.26 (s, 18H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 149.2, 148.5, 146.9, 143.6, 142.4, 138.6, 136.2, 134.6, 133.9, 129.5, 128.2, 127.8, 127.3, 126.3, 126.2, 125.8, 125.3, 125.1, 123.7, 121.0, 119.8, 110.4, 105.1, 102.9, 34.55, 34.49, 31.43, 31.42.

HRMS (ESI) calcd (m/z) for $C_{38}H_{39}N_2S_2^+$ ([M+H]$^+$): 587.2549, found: 587.2552.



3gb

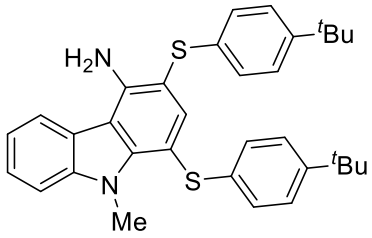
1,3-Bis((4-(tert-butyl)phenyl)thio)-8-methyl-9*H*-carbazol-4-amine 3gb, following the general

procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (61.5 mg, 0.117 mmol, 59% yield) as a brown white solid. m.p. 137–139 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.40 (s, 1H), 7.84 (s, 1H), 7.76 – 7.79 (m, 1H), 7.25 – 7.19 (m, 6H), 7.08 – 6.99 (m, 4H), 5.30 (s, 2H), 2.51 (s, 3H), 1.26 (s, 9H), 1.25 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.7, 148.5, 147.1, 144.2, 143.2, 137.8, 134.7, 134.6, 126.2 (2C), 126.1, 125.9, 125.8, 122.9, 120.6, 120.3, 118.3, 110.6, 105.1, 101.7, 34.49, 34.47, 31.42, 31.39, 17.0.

HRMS (ESI) calcd (m/z) for $C_{33}H_{37}N_2S_2^+$ ([M+H]$^+$): 525.2393, found: 525.2395.



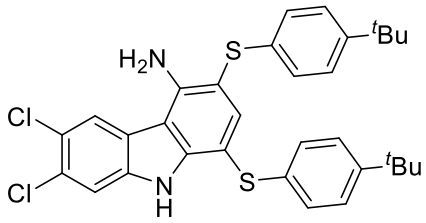
3hb

1,3-Bis((4-(*tert*-butyl)phenyl)thio)-9-methyl-9*H*-carbazol-4-amine 3hb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (73.4 mg, 0.14 mmol, 70% yield) as a white solid. m.p. 129–130 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.89 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.32 (s, 2H), 4.21 (s, 3H), 1.26 (s, 9H), 1.24 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.5, 148.1, 147.3, 147.0, 143.6, 141.3, 137.5, 134.5, 126.19, 126.15, 125.9, 125.3, 125.0, 122.2, 120.4, 120.2, 111.2, 109.1, 105.1, 101.3, 34.5, 34.4, 31.7, 31.42, 31.41.

HRMS (ESI) calcd (m/z) for $C_{33}H_{37}N_2S_2^+$ ([M+H]$^+$): 525.2393, found: 525.2390.



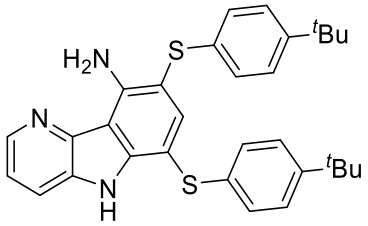
3ib

1,3-Bis((4-(tert-butyl)phenyl)thio)-6,7-dichloro-9*H*-carbazol-4-amine 3ib, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (62.4 mg, 0.108 mmol, 54% yield) as a white solid. m.p. 166–167 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 7.93 (s, 1H), 7.89 (s, 1H), 7.47 (s, 1H), 7.26 – 7.20 (m, 4H), 7.04 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 5.23 (s, 2H), 1.26 (s, 9H) 1.25 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.8, 148.7, 146.7, 145.0, 144.2, 137.3, 133.9, 133.8, 128.7, 126.2, 126.1, 126.0, 125.9, 124.0, 123.1, 121.6, 112.3, 109.0, 106.4, 101.7, 34.4, 31.3.

HRMS (ESI) calcd (m/z) for $C_{32}H_{33}Cl_2N_2S_2^+$ ([M+H]$^+$): 579.1457, found: 579.1460.



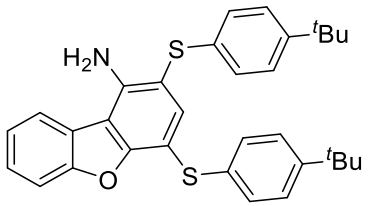
3jb

6,8-Bis((4-(*tert*-butyl)phenyl)thio)-5*H*-pyrido[3,2-*b*]indol-9-amine 3jb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (72.5 mg, 0.142 mmol, 71% yield) as a yellow solid. m.p. 194–195 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (dd, *J* = 4.8, 1.4 Hz, 1H), 8.45 (s, 1H), 7.87 (s, 1H), 7.61 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.27 – 7.18 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.40 (s, 2H), 1.25 (s, 9H), 1.24 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.6, 148.5, 148.2, 145.7, 144.7, 143.9, 142.3, 134.8, 134.3, 131.7, 126.25, 126.15, 126.0, 125.7, 119.0, 117.2, 108.2, 104.0, 99.6, 34.48, 31.42, 31.40.

HRMS (ESI) calcd (m/z) for $C_{31}H_{34}N_3S_2^+$ ([M+H]$^+$): 512.2189, found: 525.2185.



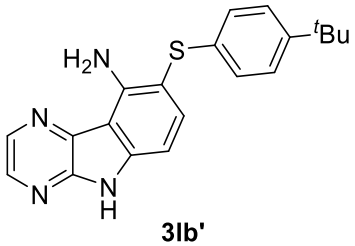
3kb

2,4-Bis((4-(*tert*-butyl)phenyl)thio)dibenzo[*b,d*]furan-1-amine 3kb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (39.9 mg, 0.078 mmol, 39% yield) as a yellow solid. m.p. 80–81 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.60 (t, *J* = 8.4 Hz, 2H), 7.51 – 7.27 (m, 5H), 7.25 – 7.20 (m, 2H), 7.06 – 6.98 (m, 3H), 5.03 (s, 2H), 1.37 – 1.19 (m, 18H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 158.4, 157.6, 155.7, 155.0, 148.5, 145.1, 136.9, 136.3, 133.9, 127.5, 126.5, 126.12, 126.07, 125.9, 125.7, 123.7, 123.0, 120.5, 111.5, 111.1, 107.9, 102.5, 34.4, 31.3, 31.2, 31.1.

HRMS (ESI) calcd (m/z) for $C_{32}H_{34}NOS_2^+$ ([M+H]$^+$): 512.2076, found: 512.2081.



3lb'

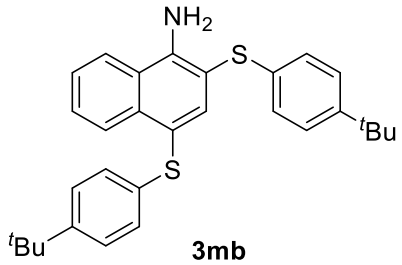
8-((4-(*tert*-Butyl)phenyl)thio)-5*H*-pyrazino[2,3-*b*]indol-9-amine 3ib', following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (33.4 mg, 0.192 mmol, 24% yield)

as a yellow solid. m.p. 252–253 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.61 (s, 1H), 8.44 (s, 1H), 8.30 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 2H), 1.25 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.4, 147.1, 142.0, 139.4, 137.2, 136.6, 134.2, 126.0, 125.8, 105.9, 104.1, 100.8, 34.3, 31.3.

HRMS (ESI) calcd (m/z) for $C_{20}H_{21}N_4S^+$ ([M+H]$^+$): 349.1481, found: 349.1481.



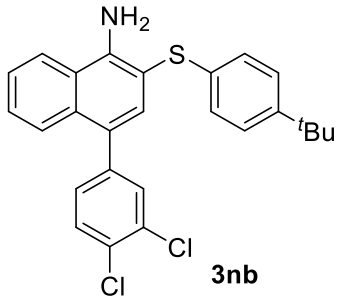
3mb

2,4-Bis((4-(*tert*-butyl)phenyl)thio)naphthalen-1-amine 3mb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (59.3 mg, 0.126 mmol, 63% yield) as a red solid. m.p. 147–148 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 8.4 Hz, 1H), 7.98 (s, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 5.25 (s, 2H), 1.27 (s, 9H), 1.25 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.9, 148.2, 147.5, 143.2, 136.1, 135.6, 133.0, 128.1, 127.2, 126.5, 126.4, 126.2, 125.9, 125.8, 123.8, 121.9, 117.7, 108.7, 34.4, 31.3.

HRMS (ESI) calcd (m/z) for $C_{30}H_{34}NS_2^+$ ([M+H]$^+$): 472.2127, found: 472.2128.



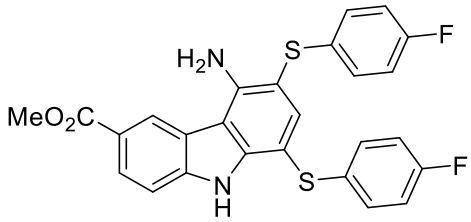
3nb

2-((4-(*tert*-Butyl)phenyl)thio)-4-(3,4-dichlorophenyl)naphthalen-1-amine 3nb, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound (81.1 mg, 0.18 mmol, 45% yield) as a white solid. m.p. 128–129 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 1H), 7.88 – 7.82 (m, 1H), 7.57 (d, *J* = 2.1 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.48 (s, 1H), 7.31 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.13 (s, 2H), 1.27 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.9, 146.0, 140.5, 134.7, 133.2, 132.8, 132.4, 132.1, 131.1, 130.3, 129.8, 128.4, 127.5, 126.5, 126.29, 126.25, 125.7, 123.3, 122.1, 108.4, 34.5, 31.4.

HRMS (ESI) calcd (m/z) for $C_{26}H_{24}Cl_2NS^+$ ([M+H]$^+$): 452.1001, found: 452.0998.



3oa

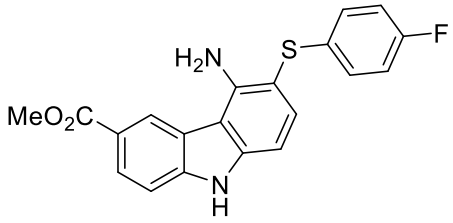
Methyl 5-amino-6,8-bis((4-fluorophenyl)thio)-9*H*-carbazole-3-carboxylate 3oa, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (20% ethyl acetate/petroleum ether) yielded the title compound (72.8 mg, 0.148 mmol, 74% yield) as a white solid. m.p. 177–178 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 8.63 (s, 1H), 8.12 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.87 (s, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.15 – 7.01 (m, 4H), 6.96 – 6.84 (m, 4H), 5.42 (s, 2H), 3.96 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 167.5, 161.2 (d, *J* = 244.1 Hz), 146.9, 144.7, 143.6, 141.3, 132.6 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 3.0 Hz), 128.1 (d, *J* = 7.8 Hz), 128.0 (d, *J* = 7.8 Hz), 126.9, 123.0, 122.8, 122.4, 116.3 (d, *J* = 22.1 Hz), 116.2 (d, *J* = 22.1 Hz), 110.5, 110.0, 106.4, 101.7, 52.2.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.8 (m, 1F), -117.0 (m, 1F).

HRMS (ESI) calcd (m/z) for $C_{26}H_{19}F_2N_2O_2S_2^+$ ([M+H]$^+$): 493.0850, found: 493.0848.



3oa'

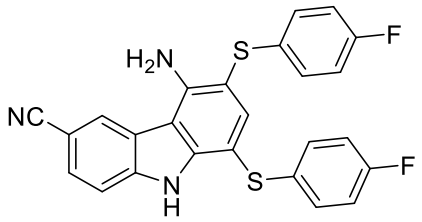
Methyl 5-amino-6-((4-fluorophenyl)thio)-9*H*-carbazole-3-carboxylate 3oa', following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (50% ethyl acetate/petroleum ether) yielded the title compound (14.6 mg, 0.04 mmol, 10% yield) as a yellow solid. m.p. 231–232 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.87 (s, 1H), 8.84 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.17 – 7.04 (m, 4H), 6.93 (d, *J* = 8.3 Hz, 1H), 5.89 (s, 2H), 3.89 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 167.2, 162.9(d, *J* = 246.4 Hz), 146.2, 143.2, 142.2, 135.8, 133.7 (d, *J* = 3.0 Hz), 127.9 (d, *J* = 7.8 Hz), 125.8, 123.4, 122.0, 120.3, 116.1 (d, *J* = 22.1 Hz), 110.4, 109.5, 102.8, 101.8, 51.9.

^{19}F NMR (376 MHz, DMSO-d_6) δ -117.9 (m, 1F).

HRMS (ESI) calcd (m/z) for $C_{20}H_{16}FN_2O_2S^+$ ([M+H]$^+$): 367.0911, found: 367.0909.



3pa

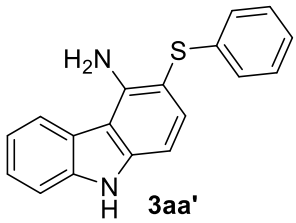
5-Amino-6,8-bis((4-fluorophenyl)thio)-9H-carbazole-3-carbonitrile 3pa, following the general procedure for the synthesis of the compounds **3**, purification through flash column chromatography (25% ethyl acetate/petroleum ether) yielded the title compound (67.1 mg, 0.146 mmol, 73% yield) as a colorless oil.

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.12 (s, 1H), 8.97 (s, 1H), 7.83 (s, 1H), 7.81 (dd, J = 8.5, 1.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.24 – 7.12 (m, 8H), 6.55 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 160.5 (d, J = 243.0 Hz, 2C), 147.6, 145.3, 144.3, 141.2, 133.6 (d, J = 3.2 Hz), 133.0 (d, J = 2.8 Hz), 128.2 (d, J = 7.8 Hz), 128.1 (d, J = 7.8 Hz), 128.0, 126.0, 122.6, 120.5, 116.4 (d, J = 6.0 Hz), 116.1 (d, J = 6.0 Hz), 112.2, 108.3, 104.3, 101.5, 99.5.

^{19}F NMR (376 MHz, DMSO-d_6) 117.4 (m, 2F).

HRMS (ESI) calcd (m/z) for $C_{25}H_{16}F_2N_3S_2^+$ ([M+H]$^+$): 460.0748, found: 460.0755.



3aa'

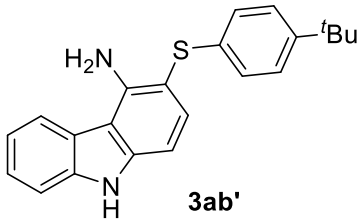
3-(phenylthio)-9*H*-carbazol-4-amine 3aa'

Following the general procedure for the synthesis of the mono-functionated compounds **3**, purification through flash column chromatography (10% ethyl acetate/petroleum ether) yielded the title compound as a white solid (64.8 mg, 0.22 mmol, 56% yield), m.p. 153–155 ℃.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.16 (s, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.19 (dd, J = 8.7, 6.6 Hz, 2H), 7.11 – 7.01 (m, 3H), 6.91 (d, J = 8.3 Hz, 1H), 5.10 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.8, 142.1, 139.1, 138.6, 135.8, 129.0, 125.8, 125.1, 125.0, 123.0, 120.8, 110.6, 110.5, 103.5, 101.9.

HRMS (ESI$^+$) calcd (m/z) for $C_{18}H_{15}N_2S_2^+$ ([M+H]$^+$): 291.0950, found: 291.0951.

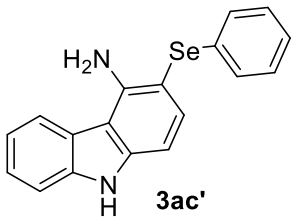


3ab'

3-((4-(*tert*-Butyl)phenyl)thio)-9*H*-carbazol-4-amine 3ab'

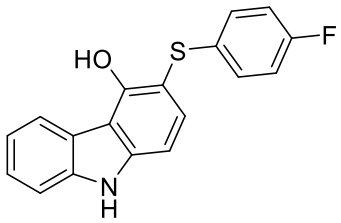
Purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound **3ab'** as red solid (63.0 mg, 0.18 mmol, 46% yield). m.p. 72–73 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.30 – 7.25 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 5.11 (s, 2H), 1.24 (s, 9H).
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 148.2, 145.8, 142.0, 139.1, 135.8, 135.1, 126.1, 125.6, 124.9, 123.0, 120.8, 120.1, 110.6, 110.5, 104.0, 101.9, 34.4, 31.4.
HRMS (ESI) calcd (m/z) for $C_{22}H_{23}N_2S^+$ ([M+H]$^+$): 347.1576, found: 347.1567.



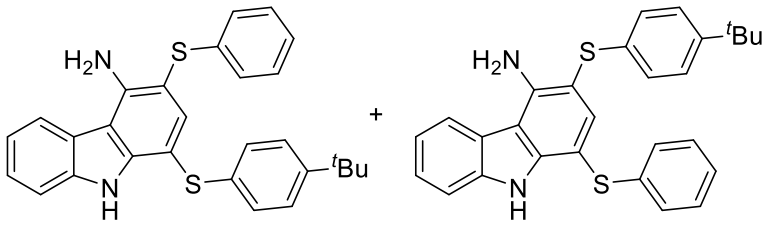
3ac'

3-(phenylselanyl)-9*H*-carbazol-4-amine 3ac'
Following the general procedure for the synthesis of the mono-functionated compounds **3**, purification through flash column chromatography (10% ethyl acetate/petroleum ether) yielded the title compound as a white solid (78.0 mg, 0.23 mmol, 58% yield), m.p. 132–134 ℃.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.27 (t, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 2H), 7.17 – 7.06 (m, 3H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.08 (s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.4, 142.1, 139.0, 136.9, 133.2, 129.3, 128.6, 125.9, 124.9, 123.0, 120.9, 120.1, 110.6, 110.3, 102.3, 102.0.
HRMS (ESI$^+$) calcd (m/z) for $C_{18}H_{15}N_2Se^+$ ([M+H]$^+$): 339.0395, found: 339.0395.



4aa

3-((4-Fluorophenyl)thio)-9*H*-carbazol-4-ol 4aa
Following the modified general procedure for the modified conditions in diethyl carbonate, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound as a grey solid, m.p. 201–202 ℃.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 7.8 Hz, 1H), 8.20 (s, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.44 (d, *J* = 3.3 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.23 (s, 1H), 7.09 – 7.01 (m, 3H), 6.95 – 6.91 (m, 1H), 6.91 – 6.88 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 161.5 (d, *J* = 245.4 Hz), 153.9, 142.9, 139.1, 134.1, 132.6 (d, *J* = 3.2 Hz), 128.3 (d, *J* = 8.0 Hz), 125.8, 123.3, 122.5, 120.6, 116.3 (d, *J* = 22.2 Hz), 111.5, 110.4, 104.9, 104.3.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.9 (m, 1F).
HRMS (ESI) calcd (m/z) for $C_{18}H_{13}FNOS^+$ ([M+H]$^+$): 310.0696, found: 310.0710.



5a + 5a'

1-((4-(*tert*-butyl)phenyl)thio)-3-(phenylthio)-9*H*-carbazol-4-amine

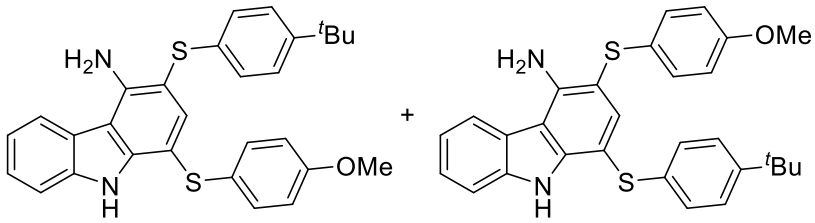
3-((4-(*tert*-butyl)phenyl)thio)-1-(phenylthio)-9*H*-carbazol-4-amine

Following the procedure of the synthesis for compound **5**, purification through flash column chromatography (5% ethyl acetate/petroleum ether) yielded the title compound as a colorless oil (21.3 mg, 0.047 mmol, 47% yield, two isomers ratio ca. 1:1, the ratio was determined by the ^{1}H NMR and based on the signal integration at 5.33 and 5.30 ppm).

^{1}H NMR (400 MHz, Chloroform-*d*) δ **5a** + **5a'**: 8.57 (s, 1H), 8.53 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.87 (d, *J* = 2.3 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 4H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.25 – 7.15 (m, 8H), 7.12 – 6.99 (m, 10H), 5.33 (s 2H), 5.30 (s, 2H), 1.26 (s, 9H), 1.24 (s, 9H). [two isomers]

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ **5a** + **5a'**: 148.7, 148.6, 147.3, 147.1, 144.5, 144.4, 143.6, 143.5, 138.5, 138.2, 138.0, 134.5, 134.6, 129.2, 129.1, 126.3, 126.2, 126.0, 125.92, 125.88, 125.86, 125.4, 125.34, 125.25, 123.4, 120.7, 120.5, 111.2, 110.2, 110.1, 105.3, 104.6, 101.4, 100.7, 34.5, 31.4. [two isomers]

HRMS (ESI$^+$) calcd (m/z) for $C_{28}H_{27}N_2S_2^+$ ([M+H]$^+$): 455.1610, found: 455.1613.



5b + 5b'

3-((4-(*tert*-butyl)phenyl)thio)-1-((4-methoxyphenyl)thio)-9*H*-carbazol-4-amine

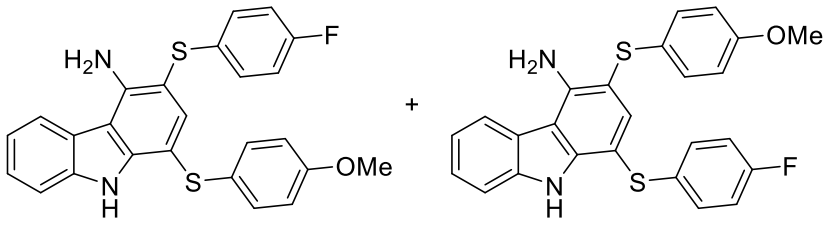
1-((4-(*tert*-butyl)phenyl)thio)-3-((4-methoxyphenyl)thio)-9*H*-carbazol-4-amine

Following the procedure of the synthesis for compound **5**, purification through flash column chromatography (10% ethyl acetate/petroleum ether) yielded the title compound as a red solid (26.1 mg, 0.054 mmol, 54% yield, two isomers ratio ca. 1:1, the ratio was determined by the ^{1}H NMR and based on the signal integration at 5.31 and 5.29 ppm), m.p. 145–147 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ **5b + 5b'**: 8.54 (s, 1H), 8.53 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.86 (s, 1H), 7.85 (s, 1H), 7.48 – 7.36 (m, 4H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 4H), 7.03 (t, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.31 (s, 2H), 5.29 (s, 2H), 3.74 (s, 3H), 3.73 (s, 3H), 1.26 (s, 9H), 1.24 (s, 9H). [two isomers]

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ **5b + 5b'**: 158.3, 158.2, 148.6, 148.5, 146.9, 146.8, 144.3, 144.1, 143.2, 142.9, 138.5, 134.6, 134.5, 128.6, 128.5, 128.4, 126.3, 126.2, 125.84, 125.81, 125.2, 123.42, 123.40, 120.7, 120.48, 120.46, 115.0, 114.9, 111.1, 110.19, 110.18, 106.5, 105.1, 102.8, 101.1, 55.5, 34.5, 31.43, 31.40. [two isomers]

HRMS (ESI$^+$) calcd (m/z) for $C_{29}H_{29}N_2OS_2^+$ ([M+H]$^+$): 485.1716, found: 485.1722.



5c + 5c'

3-((4-fluorophenyl)thio)-1-((4-methoxyphenyl)thio)-9*H*-carbazol-4-amine

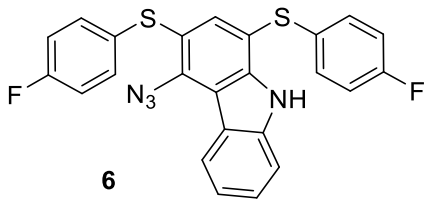
Following the procedure of the synthesis for compound **5**, purification through flash column chromatography (10% ethyl acetate/petroleum ether) yielded the title compound as a white solid (17.8 mg, 0.04 mmol, 40% yield, two isomers ratio ca. 1:1, the ratio was determined by the ^{1}H NMR and based on the signal integration at 5.33 and 5.27 ppm), m.p. 101–103 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ **5c** + **5c'**: 8.55 (s, 1H), 8.50 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.85 (s, 1H), 7.83 (s, 1H), 7.48 – 7.38 (m, 4H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.16 – 6.99 (m, 8H), 6.95 – 6.85 (m, 4H), 6.81 – 6.71 (m, 4H), 5.33 (s, 2H), 5.27 (s, 2H), 3.74 (s, 3H) 3.73 (s, 3H). [two isomers]

^{13}C NMR (101 MHz, Chloroform-*d*) δ **5c** + **5c'**: 161.2 (d, *J* = 244.7 Hz), 158.3, 158.2, 146.9, 146.8, 144.12, 144.06, 143.1, 142.7, 138.55, 138.52, 133.1 (d, *J* = 3.0 Hz), 133.0 (d, *J* = 3.0 Hz), 128.7, 128.5, 128.4, 128.2, 127.9 (d, *J* = 7.8 Hz), 125.3, 123.4, 123.3, 120.7, 120.6, 116.3 (d, *J* = 22.2 Hz), 116.2 (d, *J* = 22.1 Hz), 115.0, 114.9, 111.2, 111.1, 110.3, 110.2, 106.7, 105.1, 103.1, 101.1, 55.5.

^{19}F NMR (376 MHz, Chloroform-*d*) δ **5c** + **5c'**: -117.6 (m, 1F), -117.3 (m, 1F). [two isomers]

HRMS (ESI$^+$) calcd (m/z) for $C_{25}H_{20}FN_2OS_2^+$ $[M+H]^+$: 447.0996, found: 447.0994.



6

4-Azido-1,3-bis((4-fluorophenyl)thio)-9*H*-carbazole 6

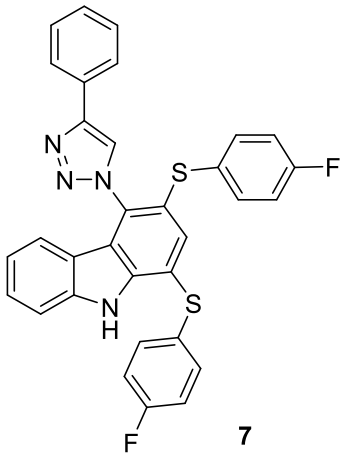
Purification through flash column chromatography (hexane) yielded the title compound (28.1 mg, 0.061 mmol, 61% yield) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.51 – 7.41 (m, 2H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.18 – 7.08 (m, 4H), 7.01 – 6.90 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 161.8 (d, *J* = 246.7 Hz), 161.6 (d, *J* = 245.8 Hz), 142.8, 141.6, 139.1, 138.6, 133.4 (d, *J* = 3.3 Hz), 130.9 (d, *J* = 3.3 Hz), 129.6 (d, *J* = 7.8 Hz), 129.2 (d, *J* = 7.8 Hz), 127.1, 123.7, 122.5, 121.0, 117.7, 117.5, 116.6 (d, *J* = 22.1 Hz), 116.5 (d, *J* = 22.1 Hz), 111.2, 111.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.4 (m, 1F), -116.1 (m, 1F).

HRMS (ESI) calcd (m/z) for $C_{24}H_{15}F_2N_4S_2^+$ ($[M+H]^+$): 461.0701, found: 461.0703.



7

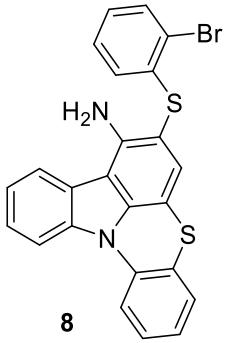
1,3-Bis((4-fluorophenyl)thio)-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-9*H*-carbazole 7

Purification through flash column chromatography (25% ethyl acetate/petroleum ether) yielded the title compound (23.3 mg, 0.041 mmol, 83% yield) as a yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (s, 1H), 8.02 (s, 1H), 7.97 (d, *J* = 7.0 Hz, 2H), 7.59 (s, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.45 – 7.36 (m, 3H), 7.25 – 7.20 (m, 2H), 7.19 – 7.12 (m, 2H), 7.05 – 6.94 (m, 3H), 6.89 (t, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 7.9 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 162.2 (d, *J* = 248.1 Hz, 2C), 147.9, 140.7, 139.8, 135.3, 132.9 (d, *J* = 8.2 Hz), 132.1, 131.7 (d, *J* = 8.2 Hz), 130.9 (d, *J* = 3.2 Hz), 130.3, 129.0 (d, *J* = 3.2 Hz), 128.9, 128.5, 127.9, 125.9, 124.3, 122.2, 122.1, 121.6, 121.3, 120.5, 118.7, 116.8 (d, *J* = 22.2 Hz), 116.4 (d, *J* = 22.1 Hz), 111.4.

HRMS (ESI) calcd (m/z) for $C_{32}H_{21}F_2N_4S_2^+$ ([M+H]$^+$): 563.1170, found: 563.1174 .



8

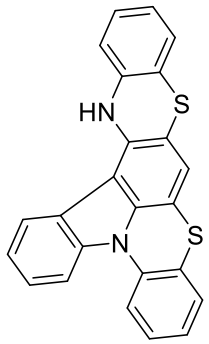
7-((2-Bromophenyl)thio)indolo[3,2,1-*kl*]phenothiazin-8-amine 8

Purification through flash column chromatography (2% – 5% ethyl acetate/petroleum ether) yielded the title compound (28.0 mg, 0.059 mmol, 91% yield) as a yellow solid (sensitive to light).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.17 (s, 1H), 7.09 – 7.02 (m, 2H), 6.95 (td, *J* = 7.6, 1.6 Hz, 1H), 6.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.92 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-*d*) δ 143.7, 141.8, 138.7, 138.1, 136.5, 132.9, 129.6, 128.5, 128.0, 127.5, 126.35, 126.32, 125.7, 125.6, 125.1, 122.9, 122.2, 121.6, 120.5, 116.0, 114.6, 110.8, 107.1, 106.2.

HRMS (ESI) calcd (m/z) for $C_{24}H_{16}BrN_2S_2^+$ ([M+H]$^+$): 474.9933, found: 474.9930.



9

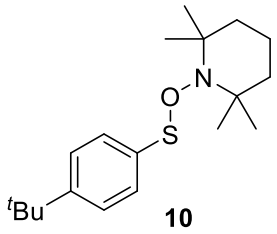
17*H*-Benzo[5,6][1,4]thiazino[3,2-*b*]indolo[1,2,3-*mn*]phenothiazine 9

Purification through flash column chromatography (2% – 5% ethyl acetate/petroleum ether) yielded the title compound **8** as yellow solid (19.3 mg, 0.049 mmol, 98% yield). m.p. 182–184 ℃.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (d, J = 7.9 Hz, 1H), 8.18 (s, 1H), 8.12 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.99 (d, J = 7.5 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 6.79 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 141.6, 138.5, 137.4, 135.6, 134.9, 128.2, 128.1, 127.4, 126.4, 126.3, 125.2, 123.6, 123.0, 122.8, 121.8, 121.1, 119.2, 118.4, 116.8, 115.8, 114.3, 111.6, 110.3, 108.2.

HRMS (ESI) calcd (m/z) for $C_{24}H_{14}N_2S_2^+$ $[M]^+$: 394.0593, found: 394.0594.



10

1-(((4-(*tert*-Butyl)phenyl)thio)oxy)-2,2,6,6-tetramethylpiperidine 10

Purification through flash column chromatography (10% ethyl acetate/petroleum ether) yielded the title compound **10** as colorless oil (21.8 mg, 0.068 mmol, 17% yield).

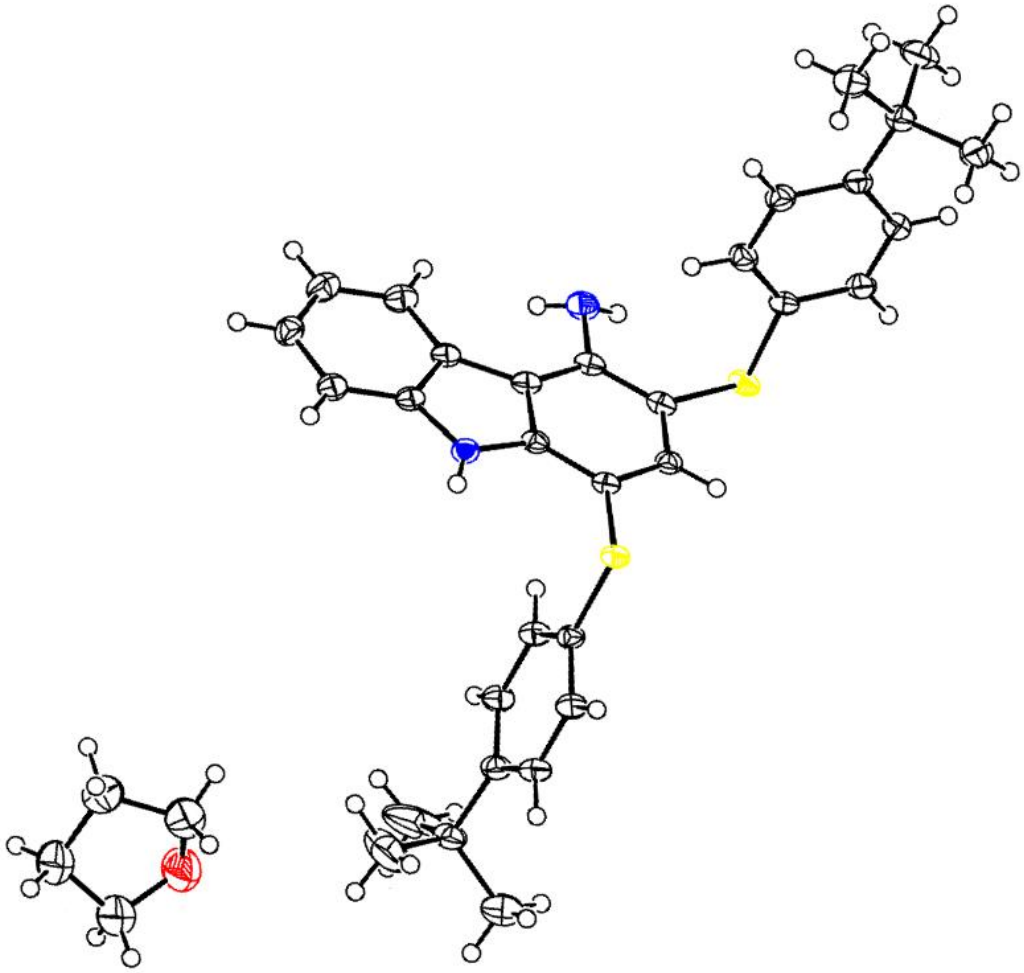
^{1}H NMR (400 MHz, Chloroform-d) δ 7.59 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 1.98 – 1.38 (m, 15H), 1.34 (s, 9H), 0.93 (s, 3H).

NMR data are in agreement with literature reported chemical shifts and signal pattern.[6]

11. X-Ray crystallography Data of compound 3ab

Crystals suitable for X-ray analysis were obtained by the slow diffusion of hexane to a solution of compound **3ab** in tetrahydrofuran at room temperature.

Clear colourless plank, 0.3*0.2*0.1; XtaLAB PRO MM007HF Cu; Rigaku, Japan.



The X-ray crystal structure of compound **3ab** with one THF molecule (Thermal ellipsoids are at the 50% probability level; CCDC 2302367)

Crystal Data of 3ab

Empirical formula	$C_{36}H_{42}N_2OS_2$
Formula weight	582.880
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.77746(8)
b/Å	34.14872(18)
c/Å	7.20907(5)
α/°	90
β/°	100.1518(6)
γ/°	90
Volume/Å^3	3096.31(3)
Z	4
ρ_{calc}g/cm^3	1.250
μ/mm^{-1}	1.790
F(000)	1254.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.18 to 147.7
Index ranges	-15 ≤ h ≤ 15, -42 ≤ k ≤ 41, -8 ≤ l ≤ 8
Reflections collected	73789
Independent reflections	6218 [R_{int} = 0.0318, R_{sigma} = 0.0127]
Data/restraints/parameters	6218/0/377
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0507, wR_2 = 0.1405
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.1409
Largest diff. peak/hole / e Å^{-3}	1.10/-0.51

12. Reference

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[4] Q.-J. Jiang, Y.-T. Min, Y.-P. Liu, H. Li, J.-A. Peng, C.-J. Liu, *New J. Chem.* **2023**, *47*, 9421–9426.

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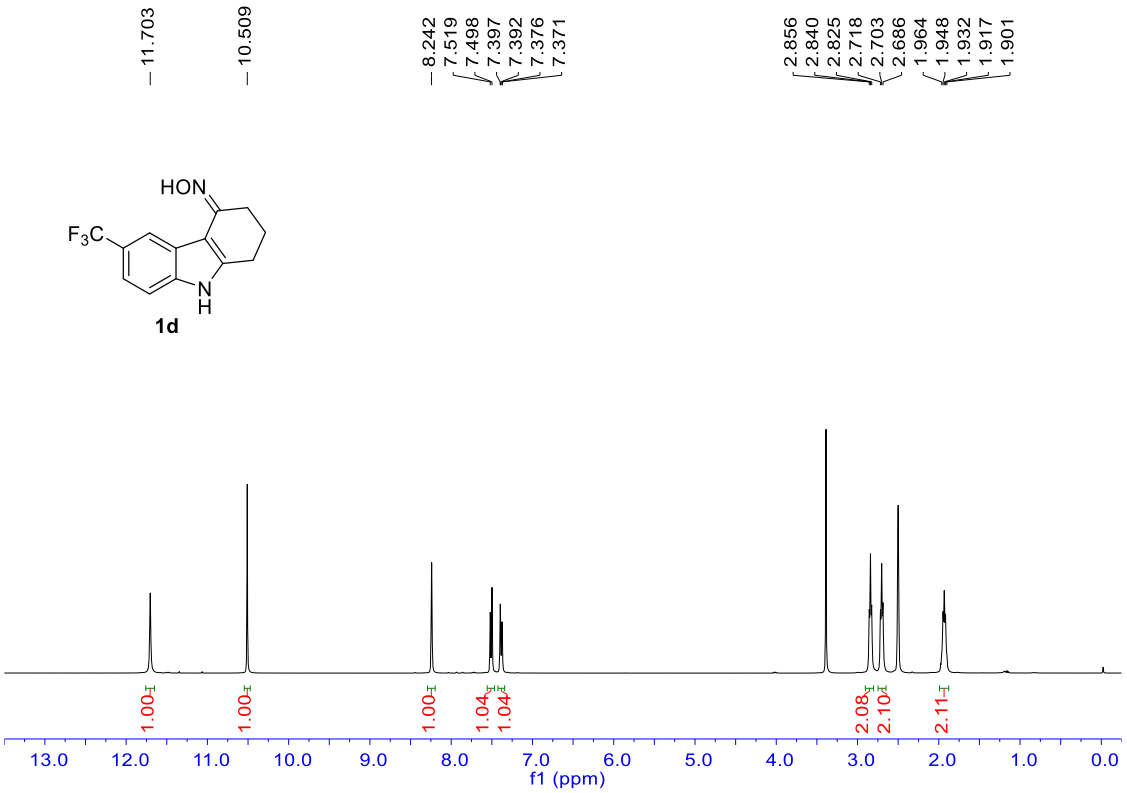
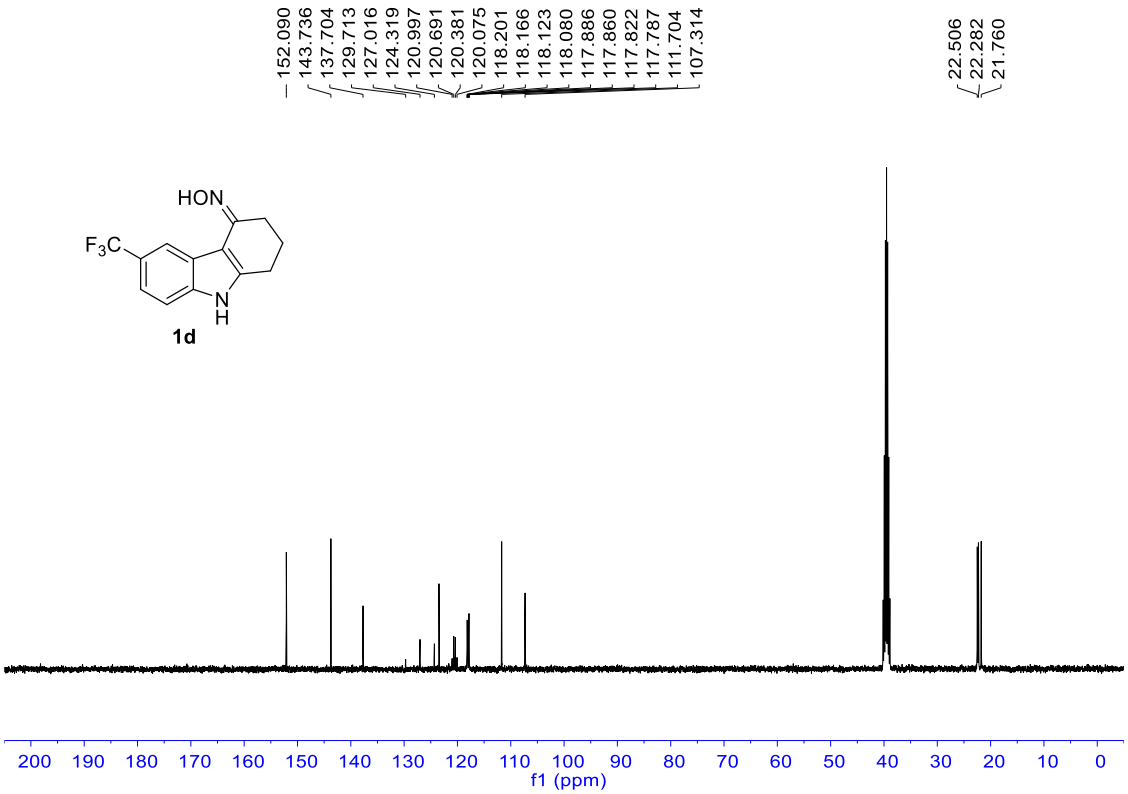
[6] J. Huang, Y.-X. Luo, L. Wang, X.-Y. Tang, *Org. Lett.* **2023**, *25*, 5613-5618.

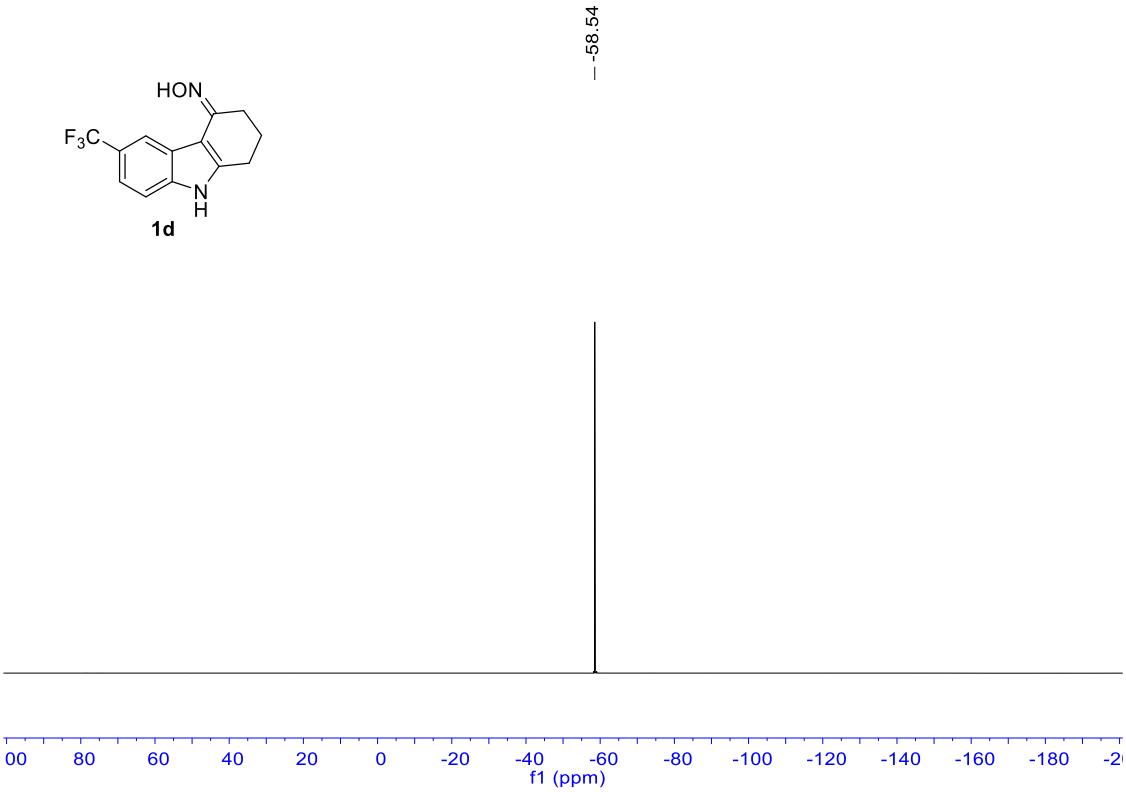
13. NMR Spectra



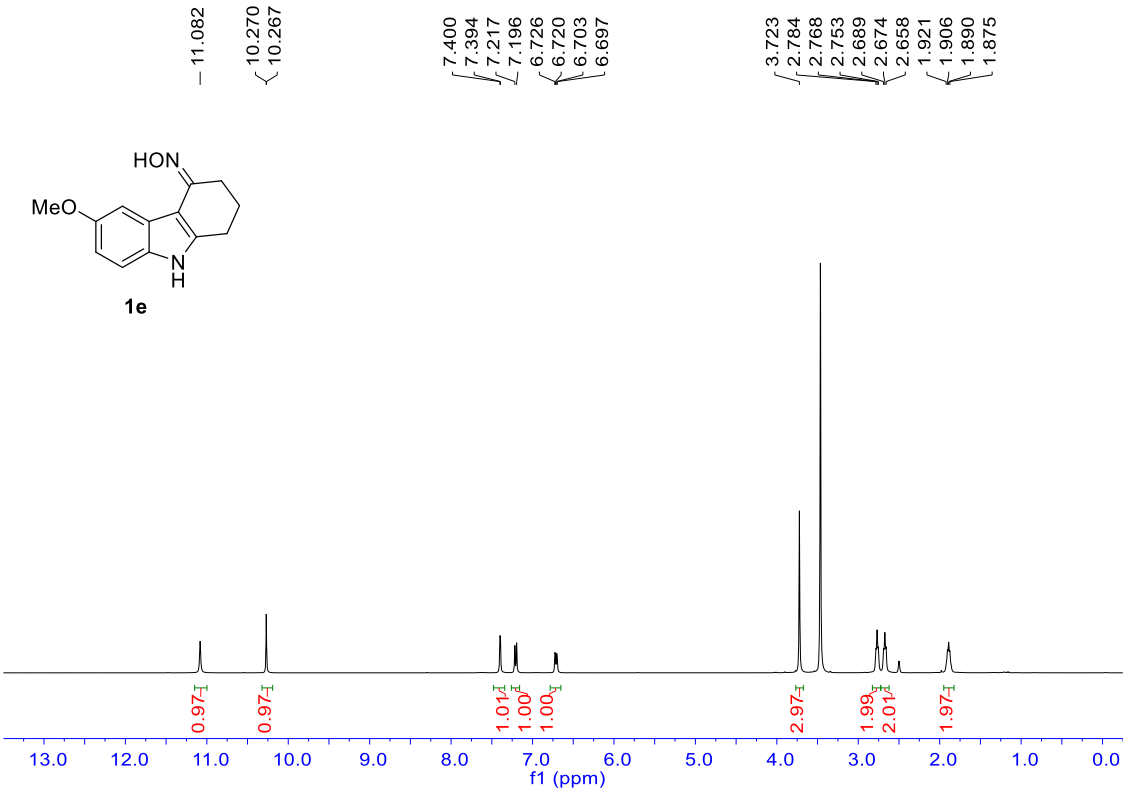
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1d**



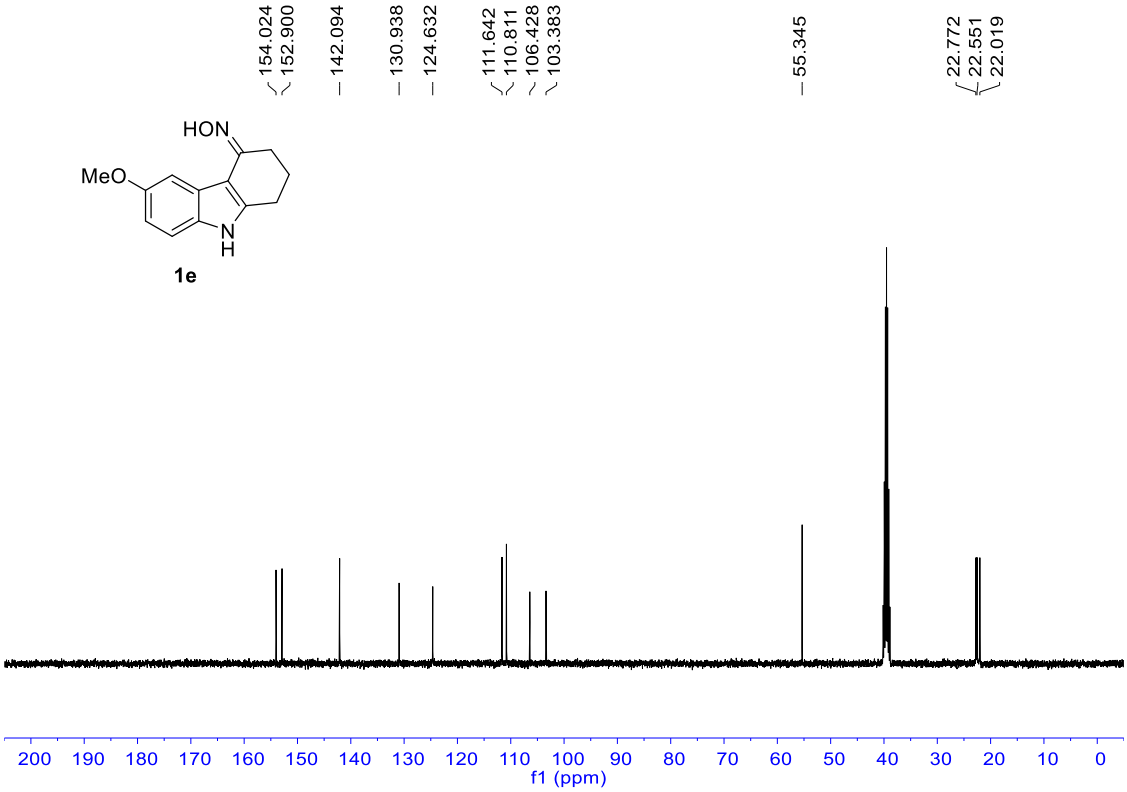
^{13}C{^{1}H} NMR spectrum (101 MHz, DMSO-d_6) of compound **1d**



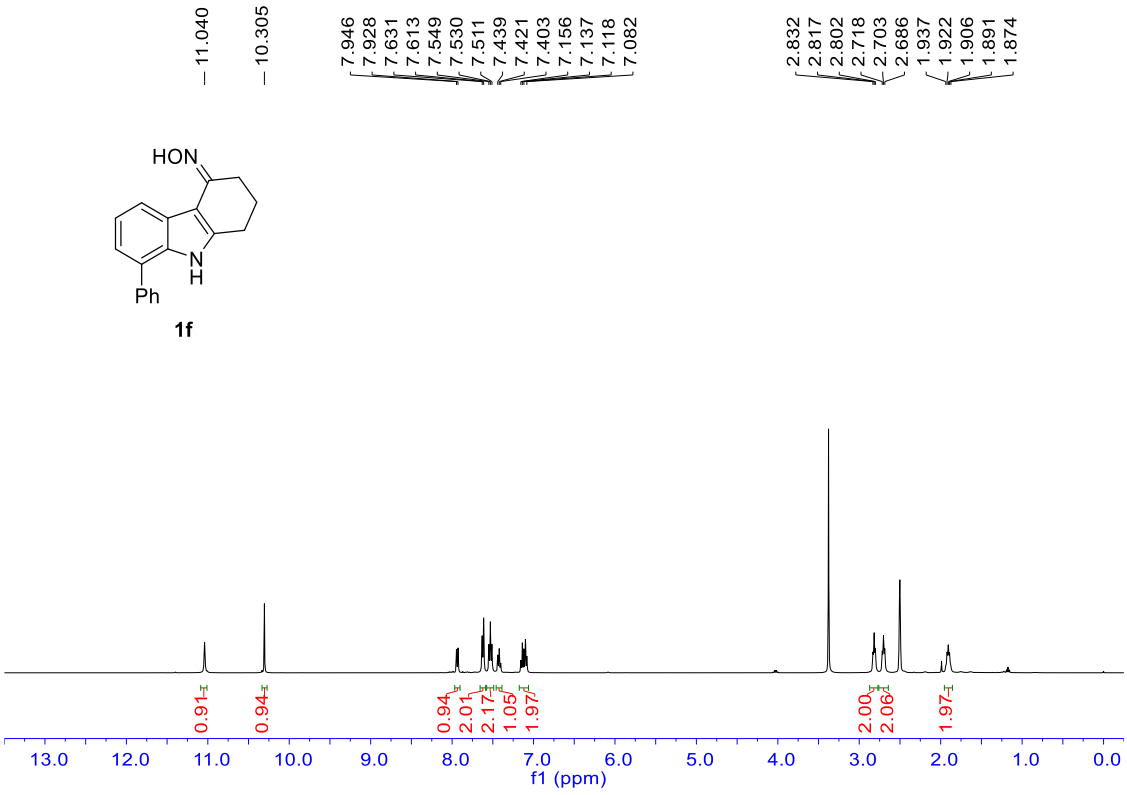
^{19}F NMR spectrum (376 MHz, DMSO-d_6) of compound **1d**



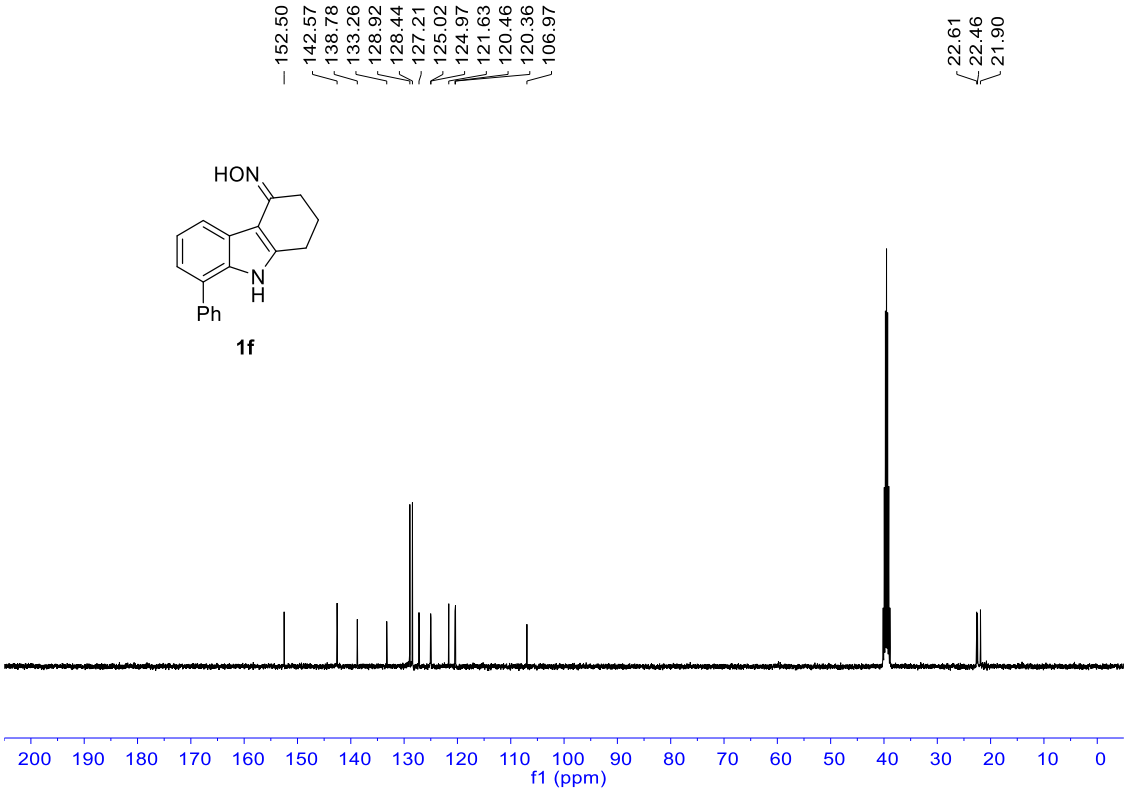
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1e**



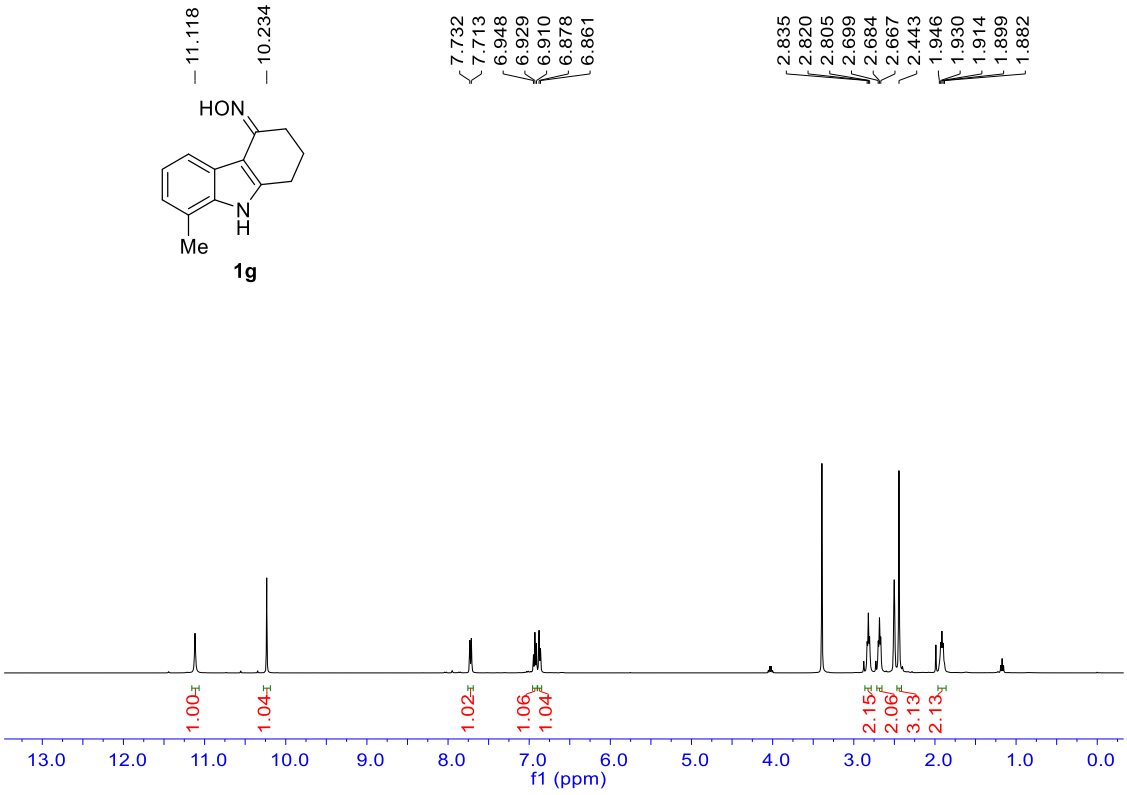
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **1e**



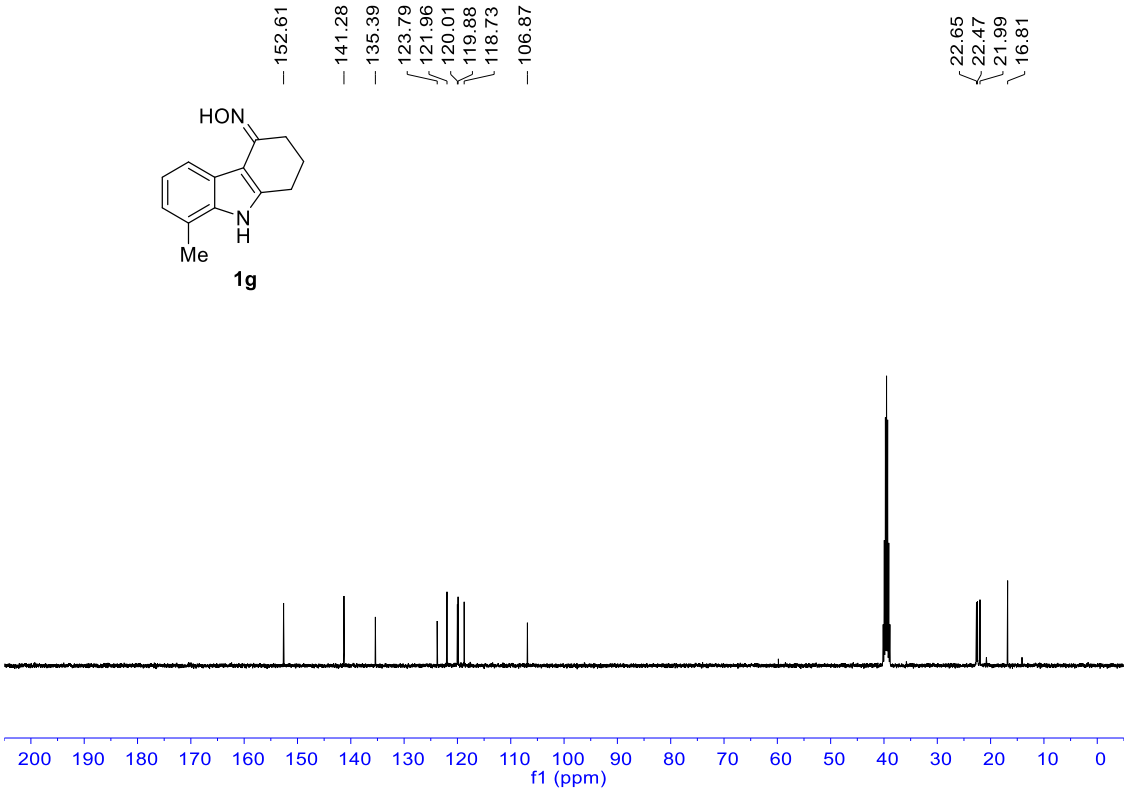
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1f**



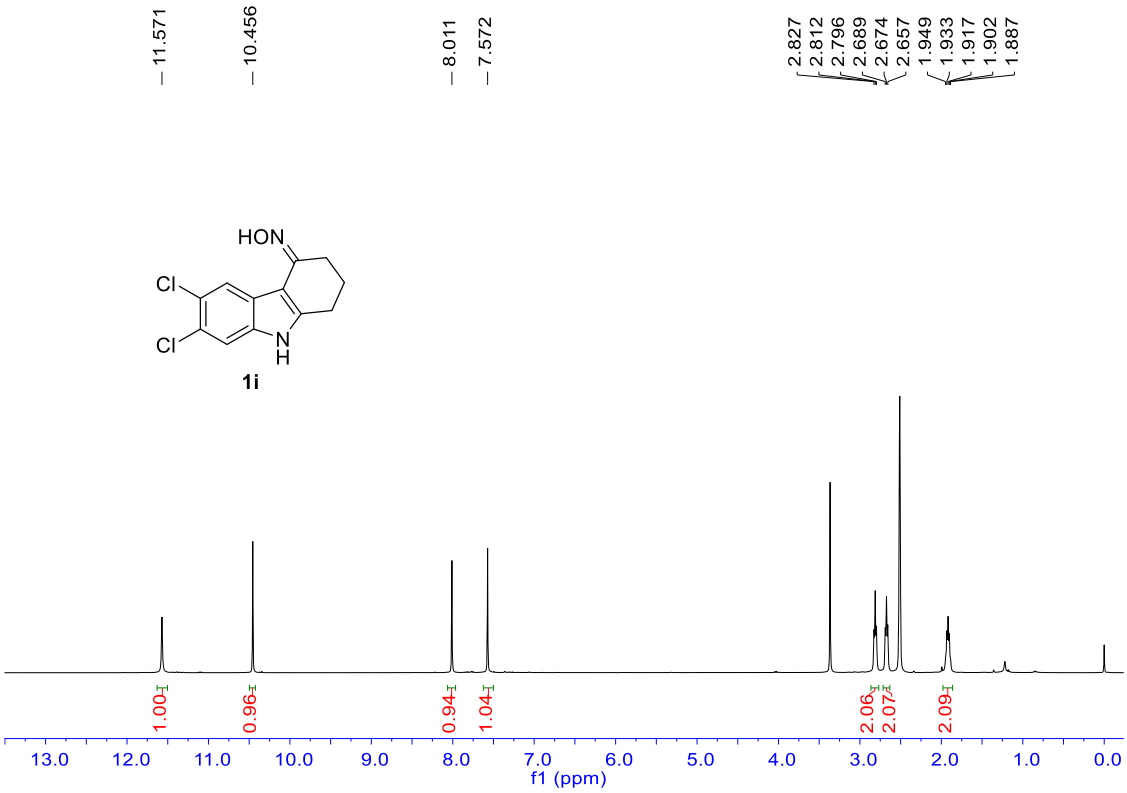
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **1f**



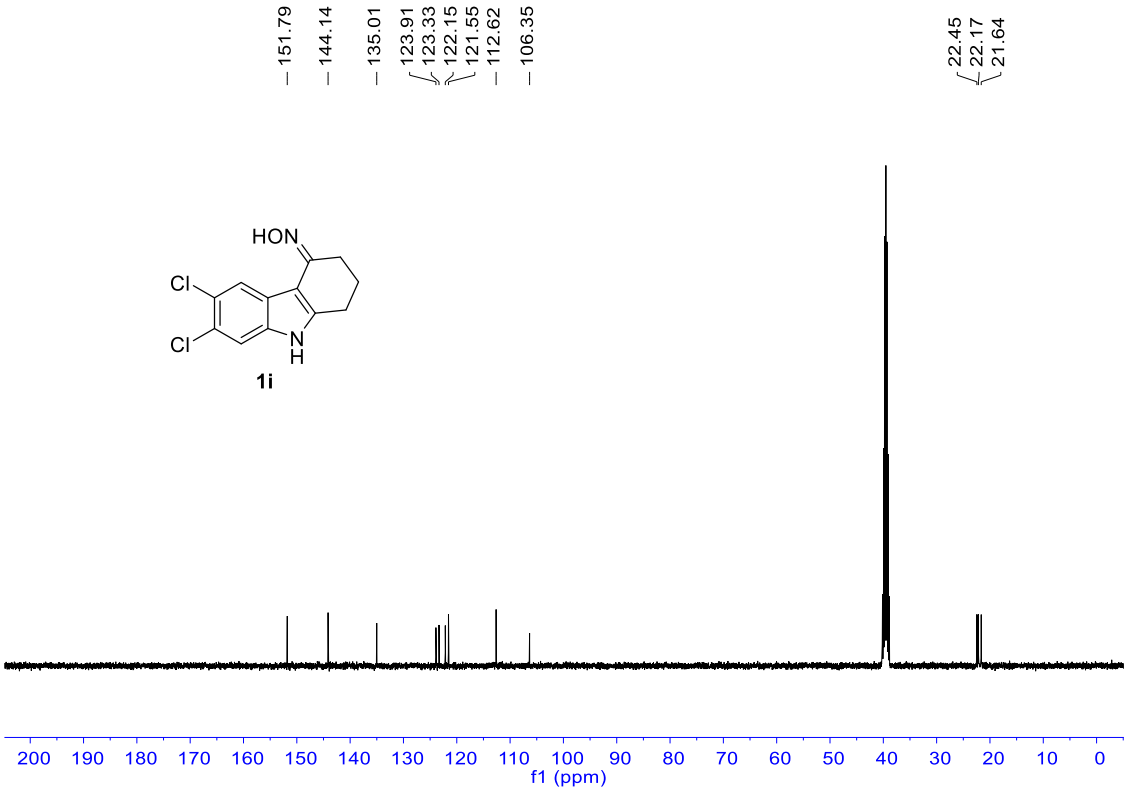
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1g**



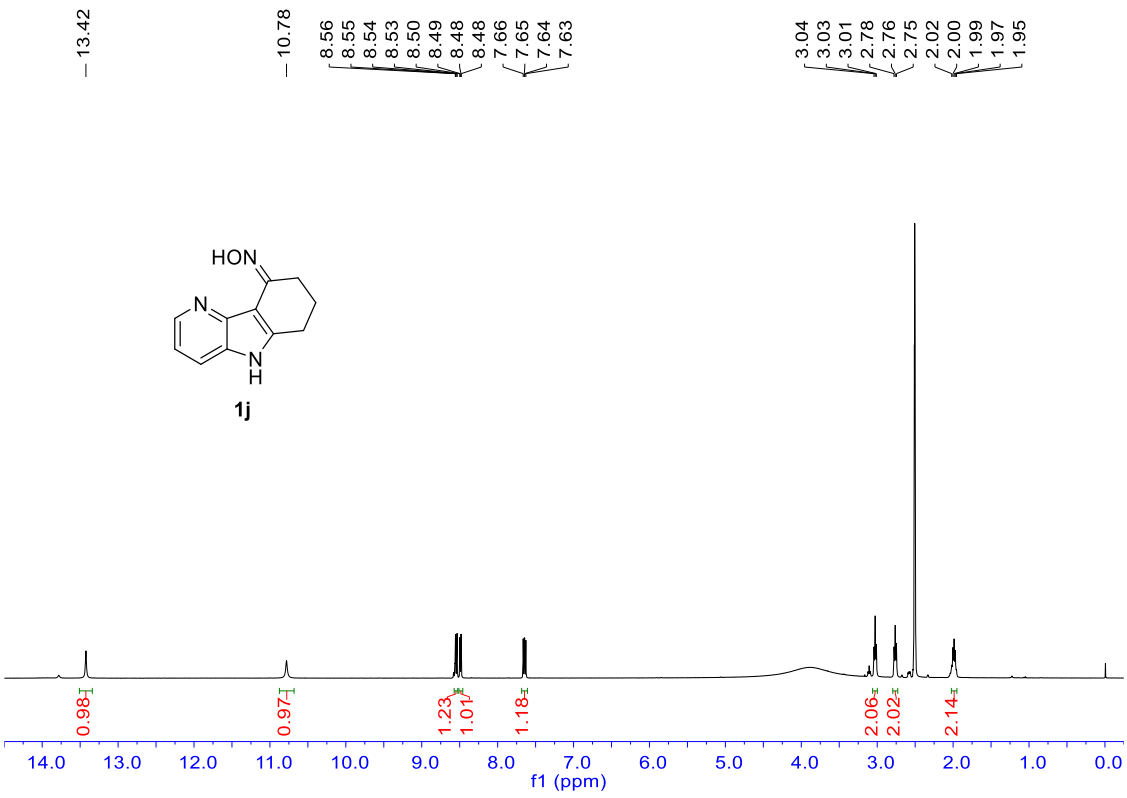
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **1g**



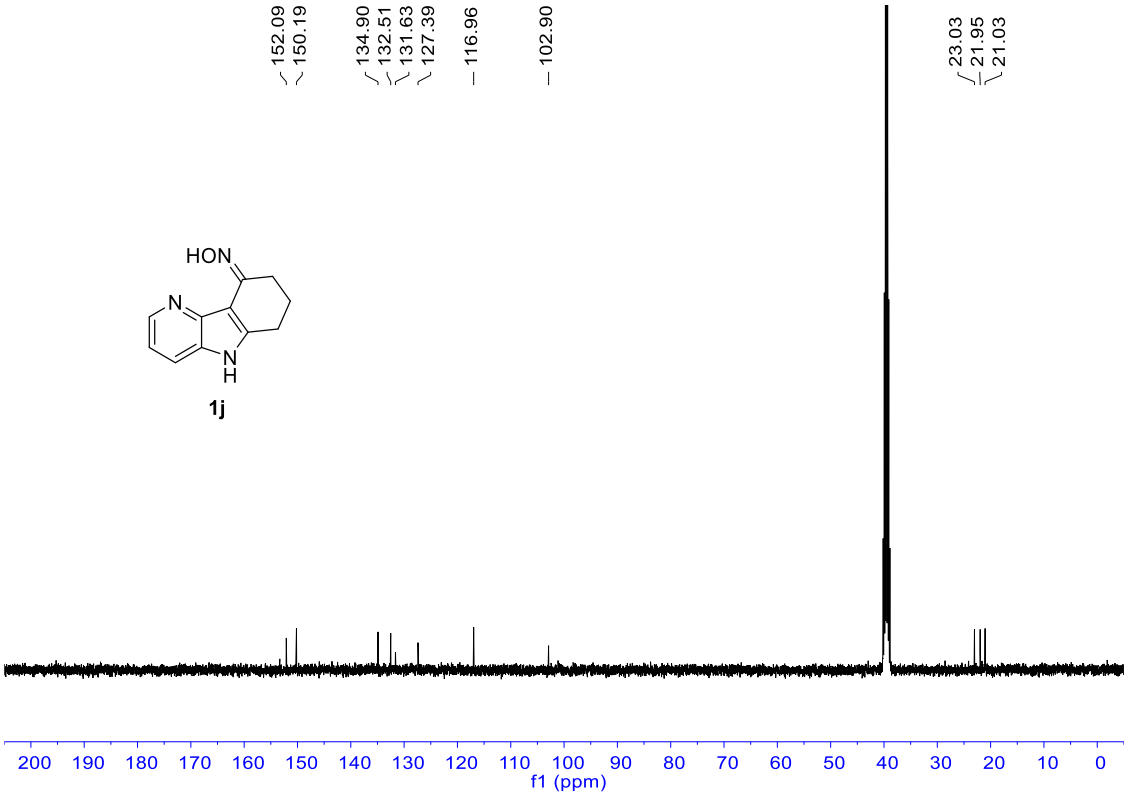
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1i**



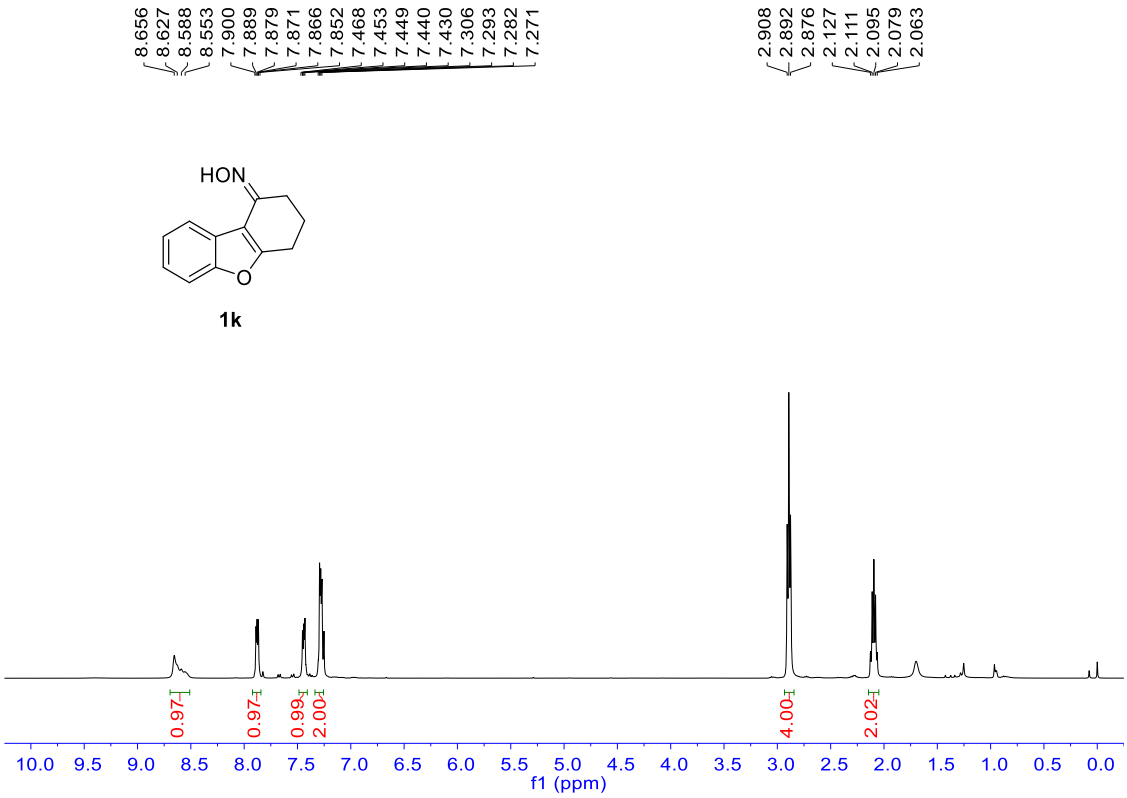
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **1i**



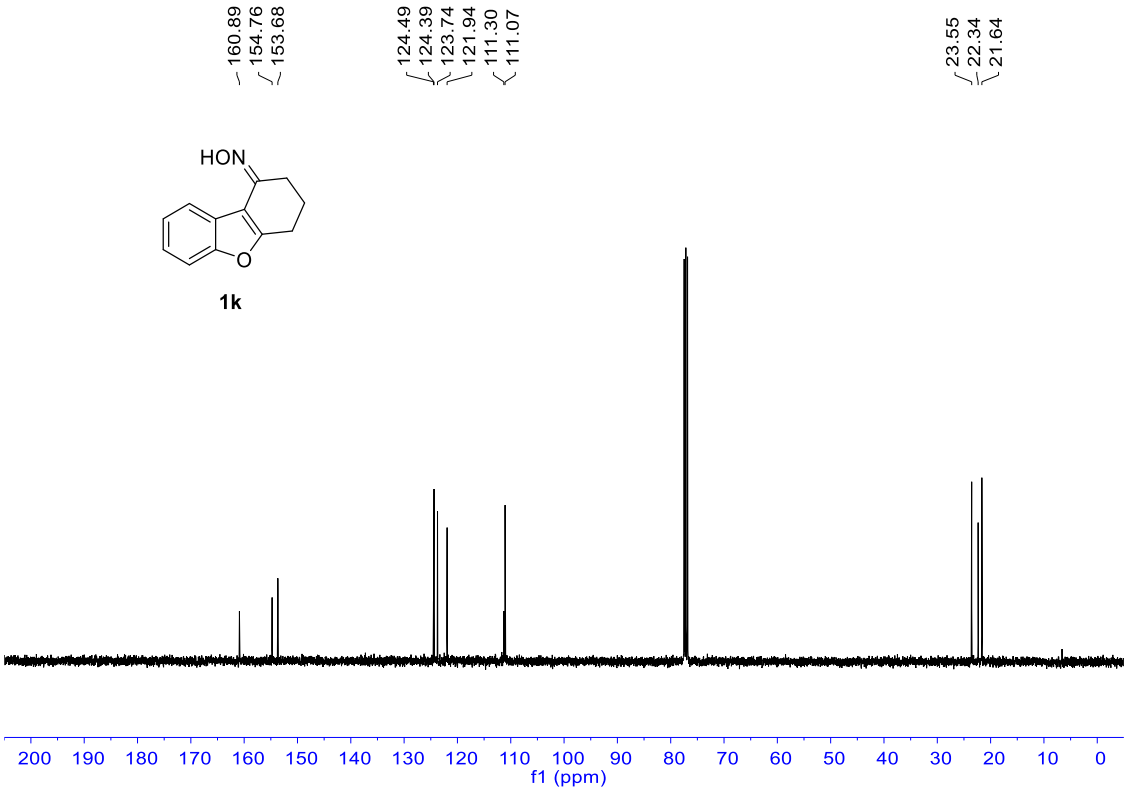
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1j**



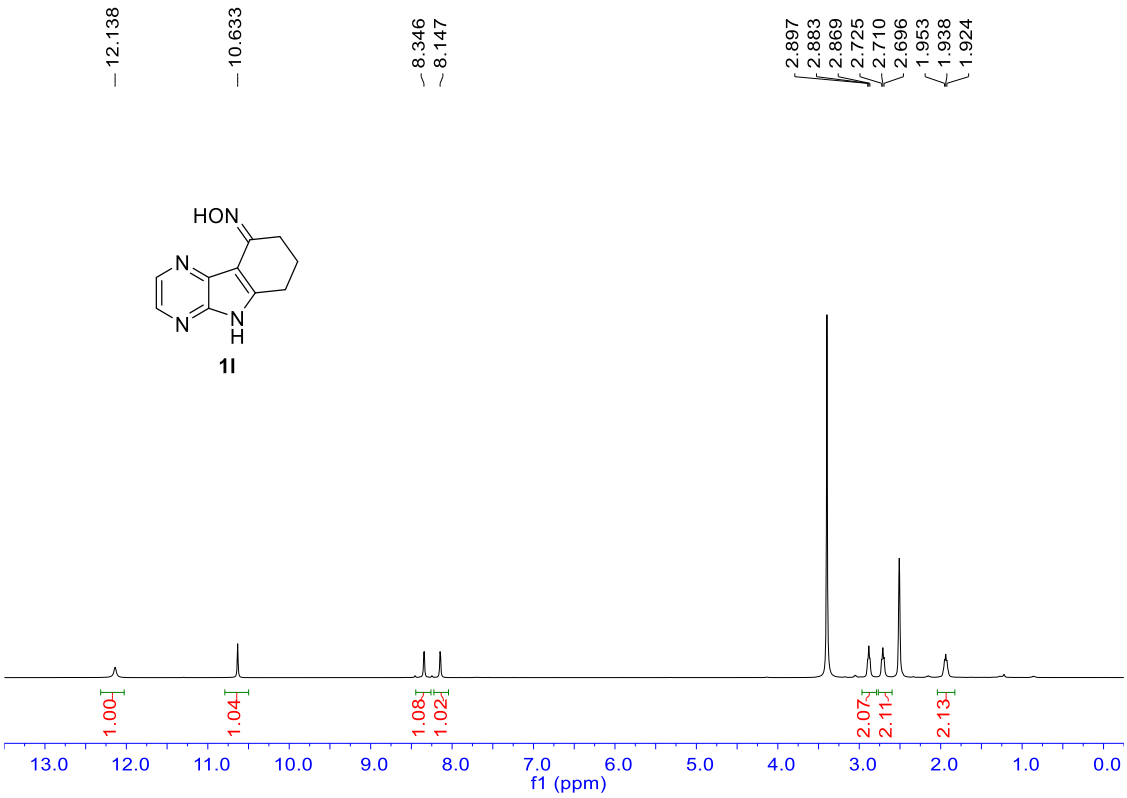
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **1j**



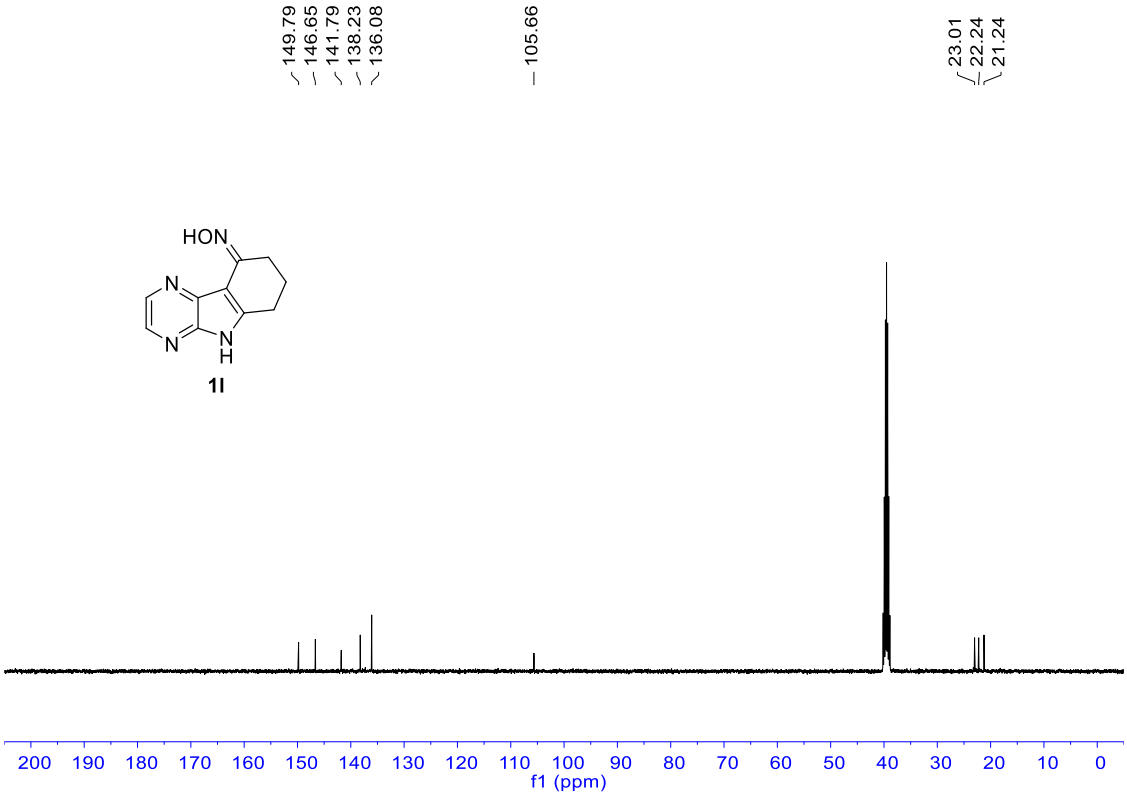
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1k**



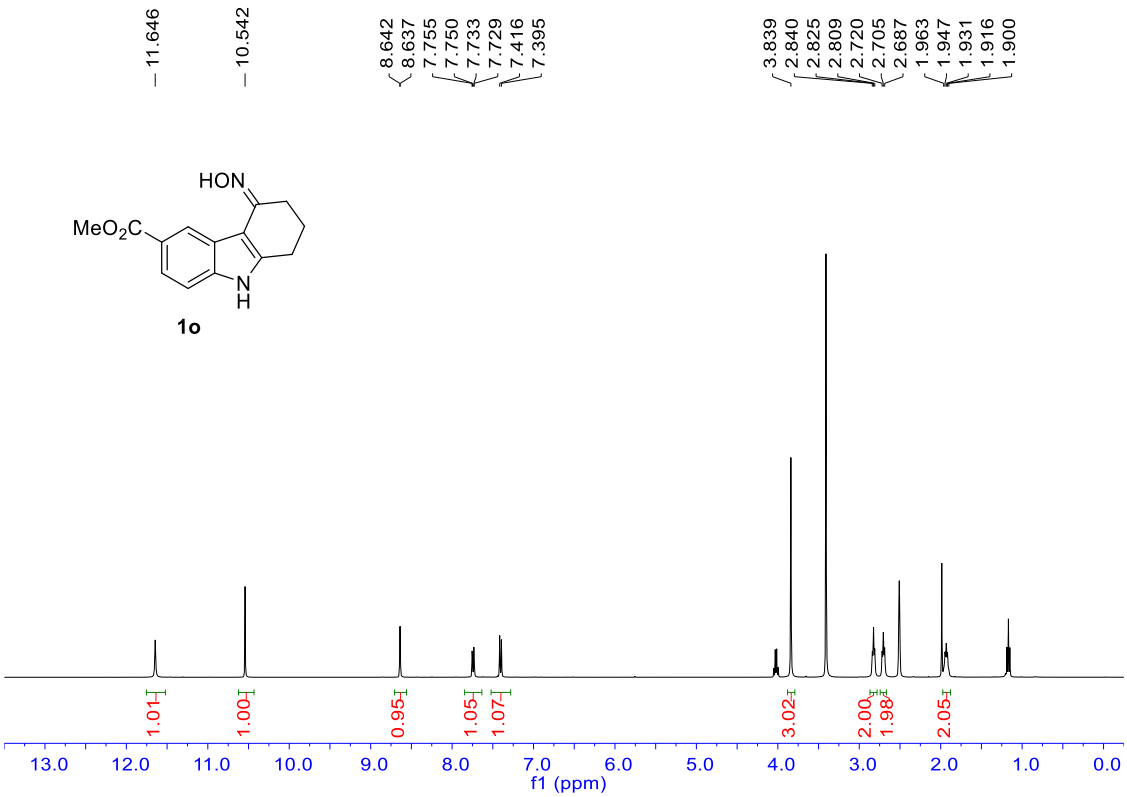
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **1k**



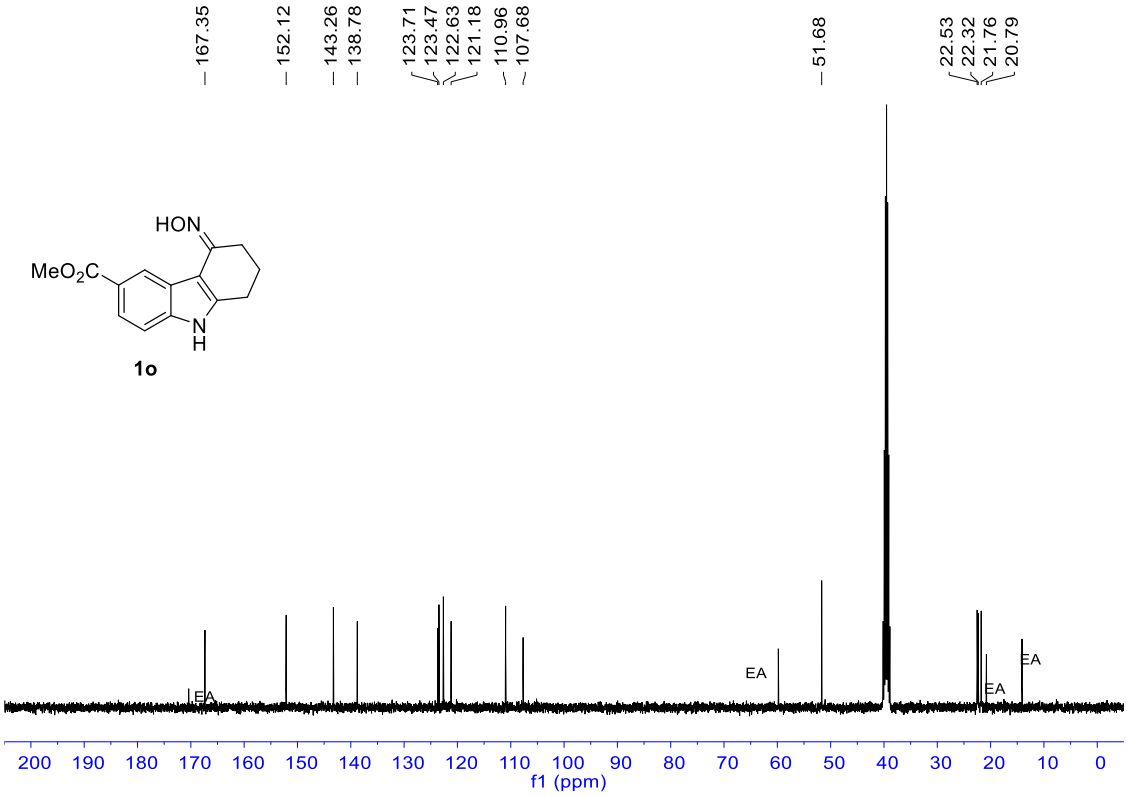
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1l**



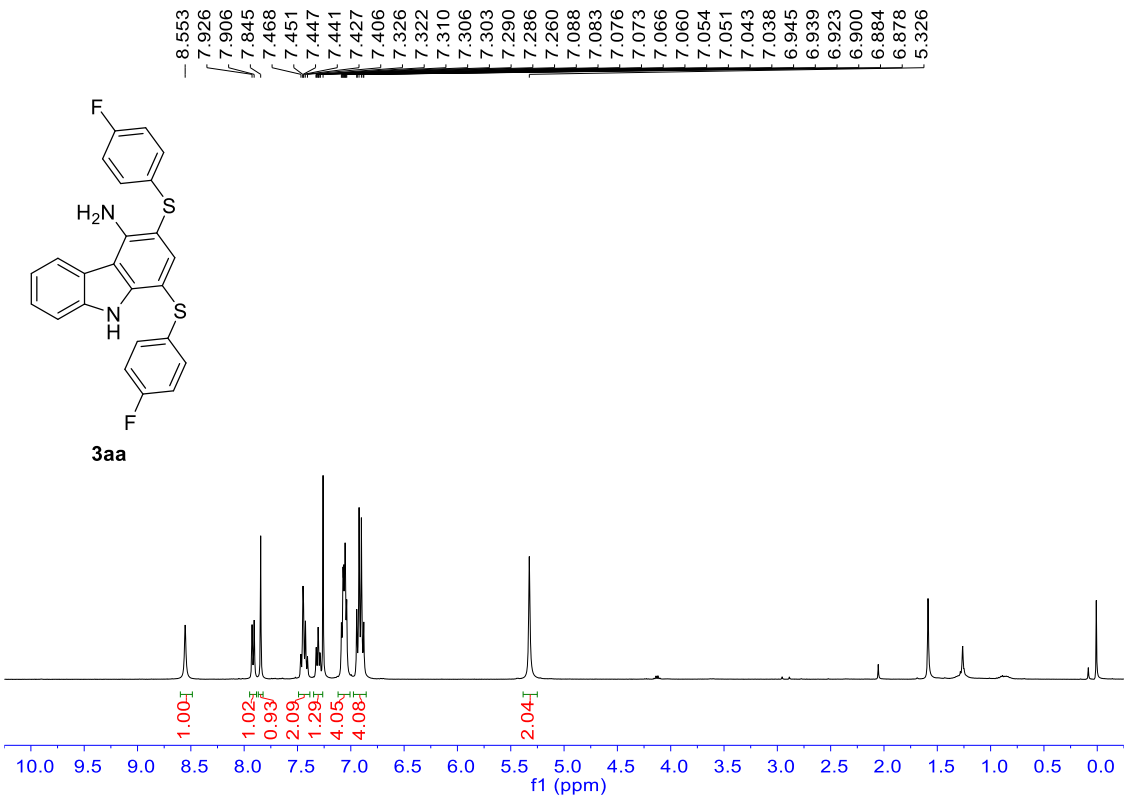
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **1l**



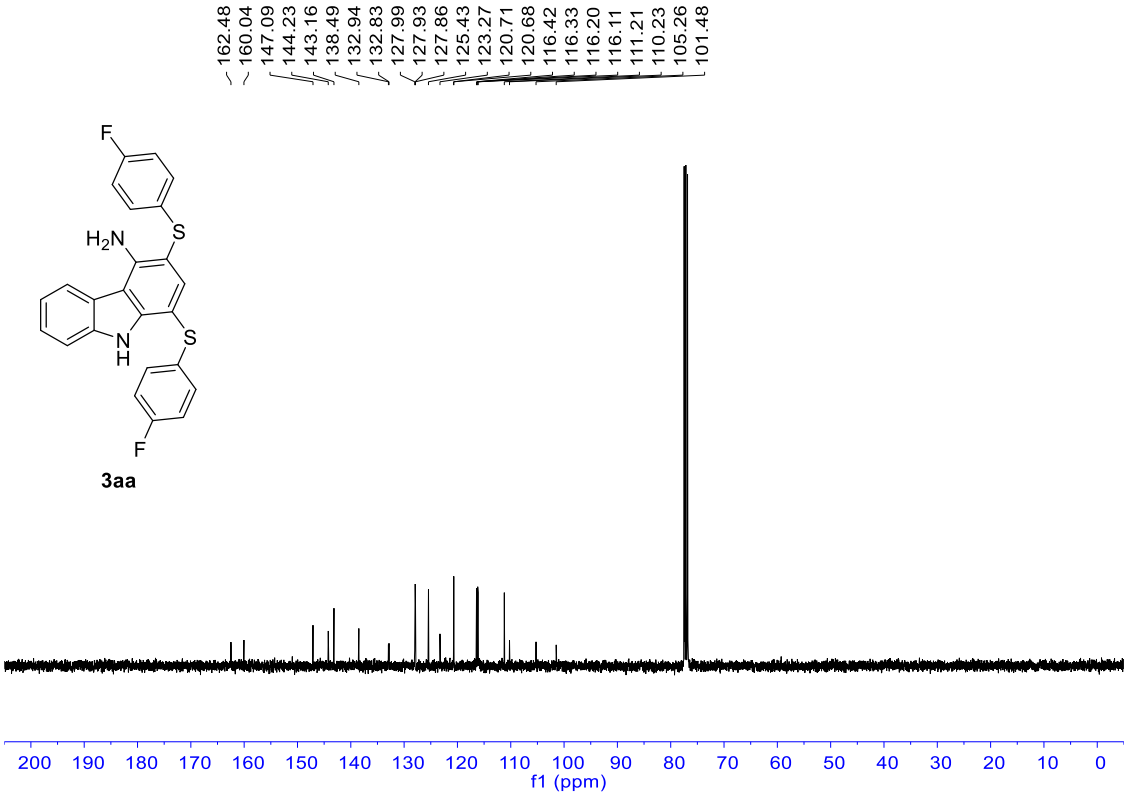
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **1o**



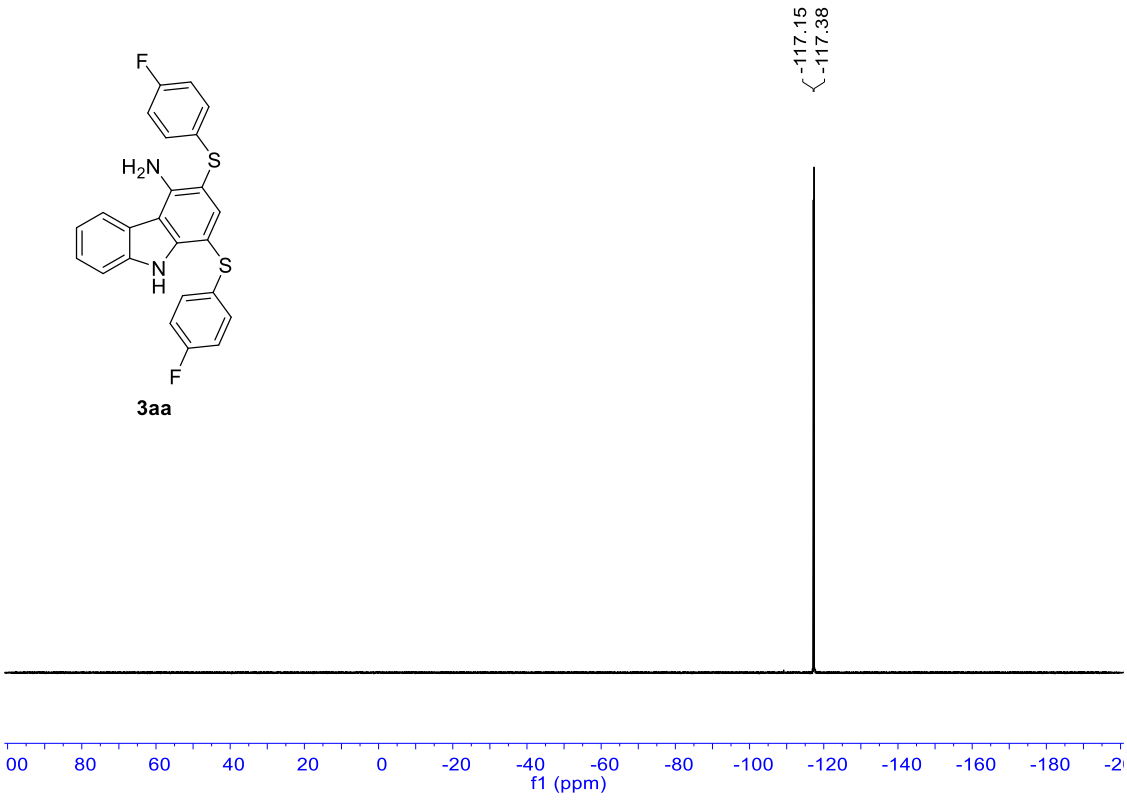
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **1o**



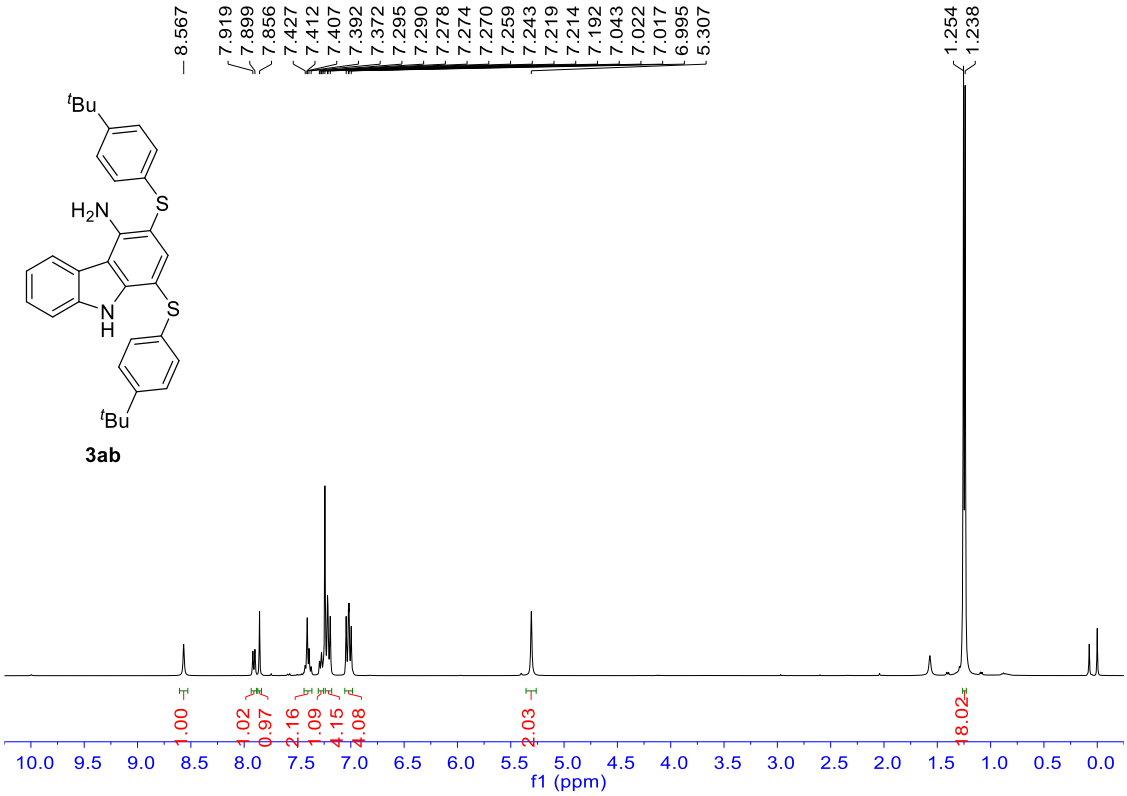
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3aa**



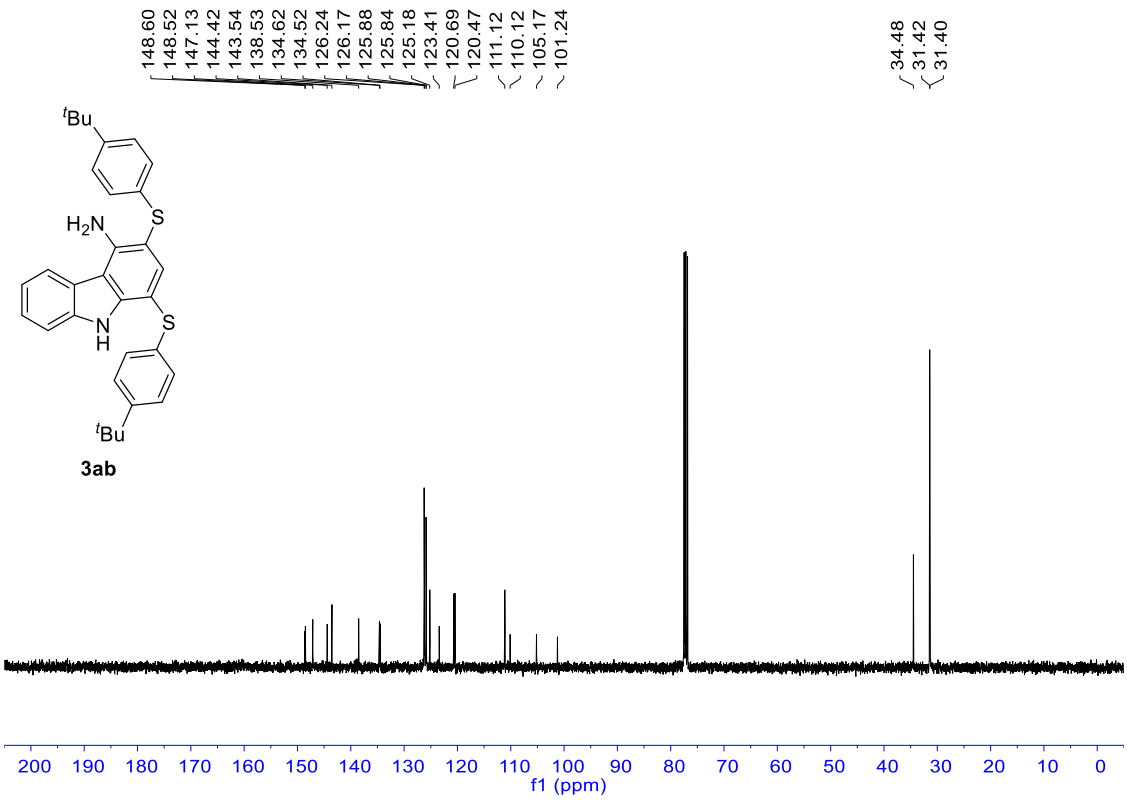
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3aa**



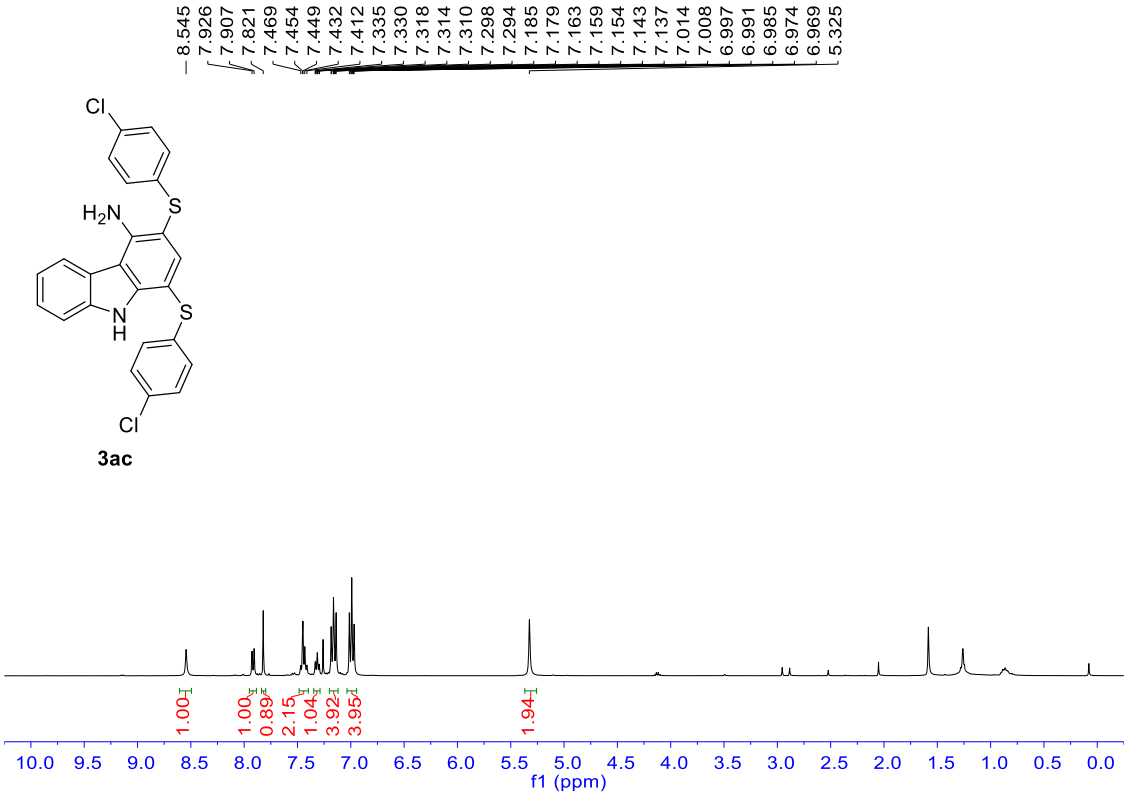
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3aa**



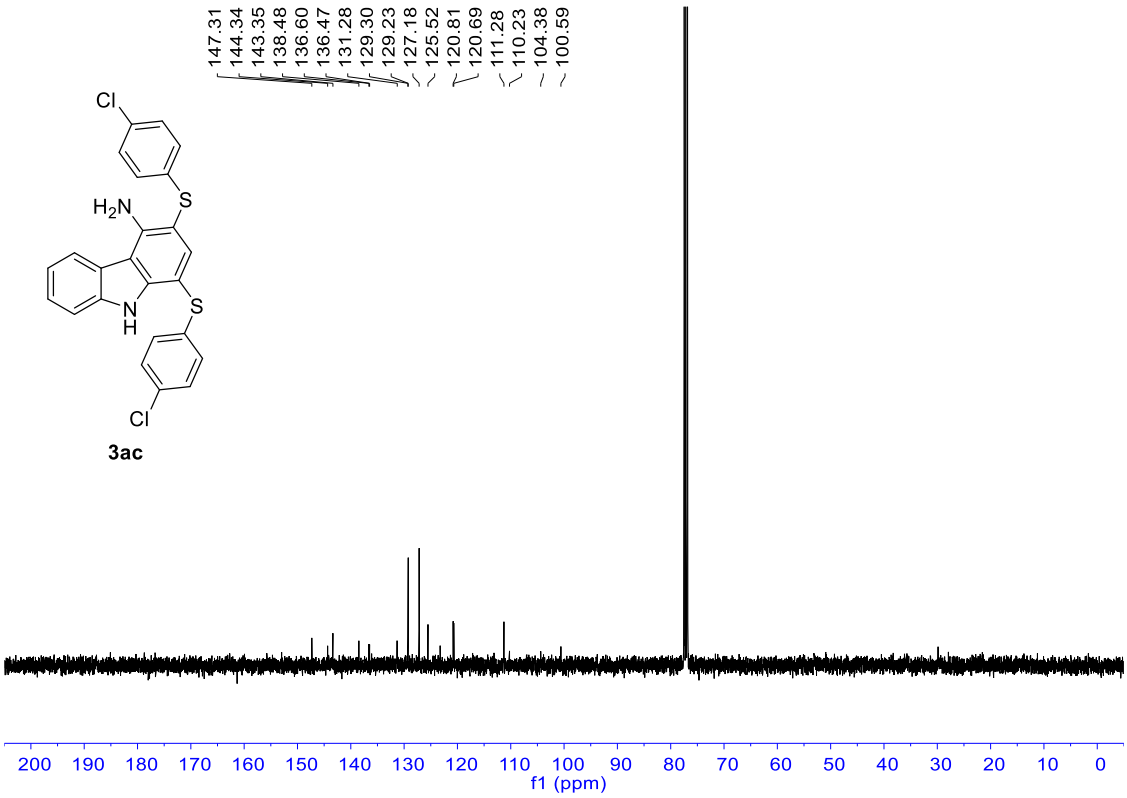
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ab**



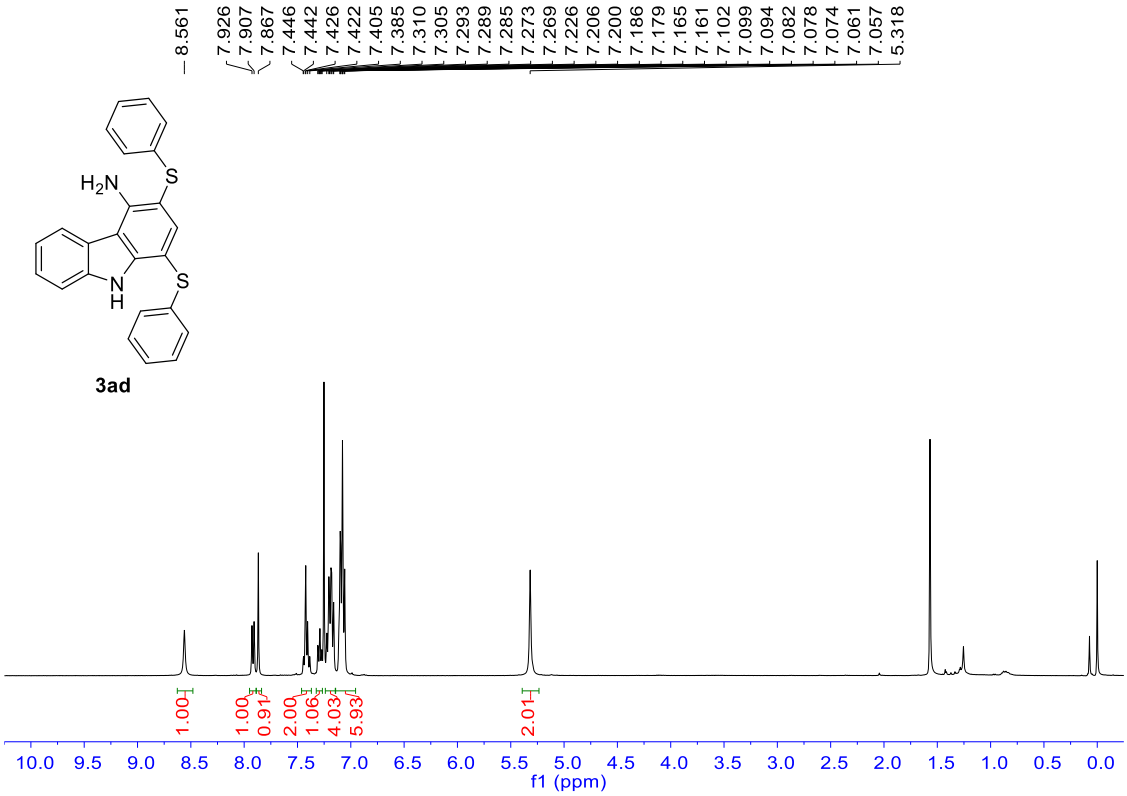
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3ab**



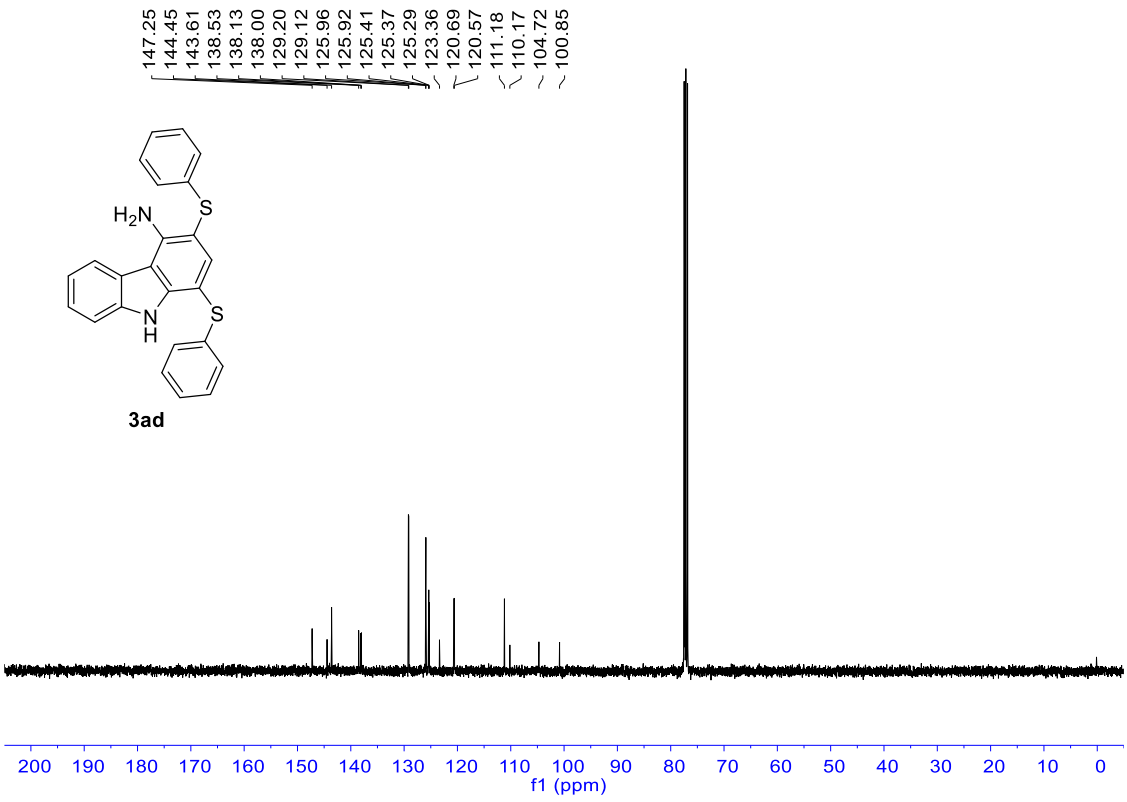
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ac**



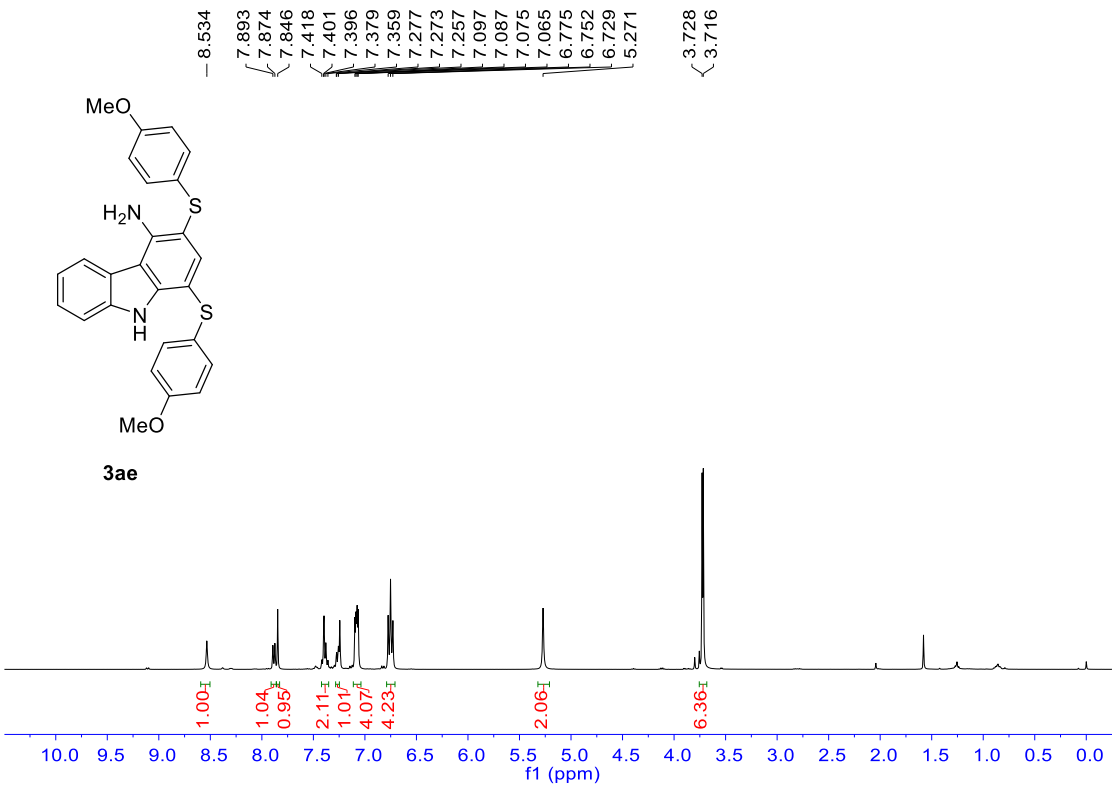
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3ac**



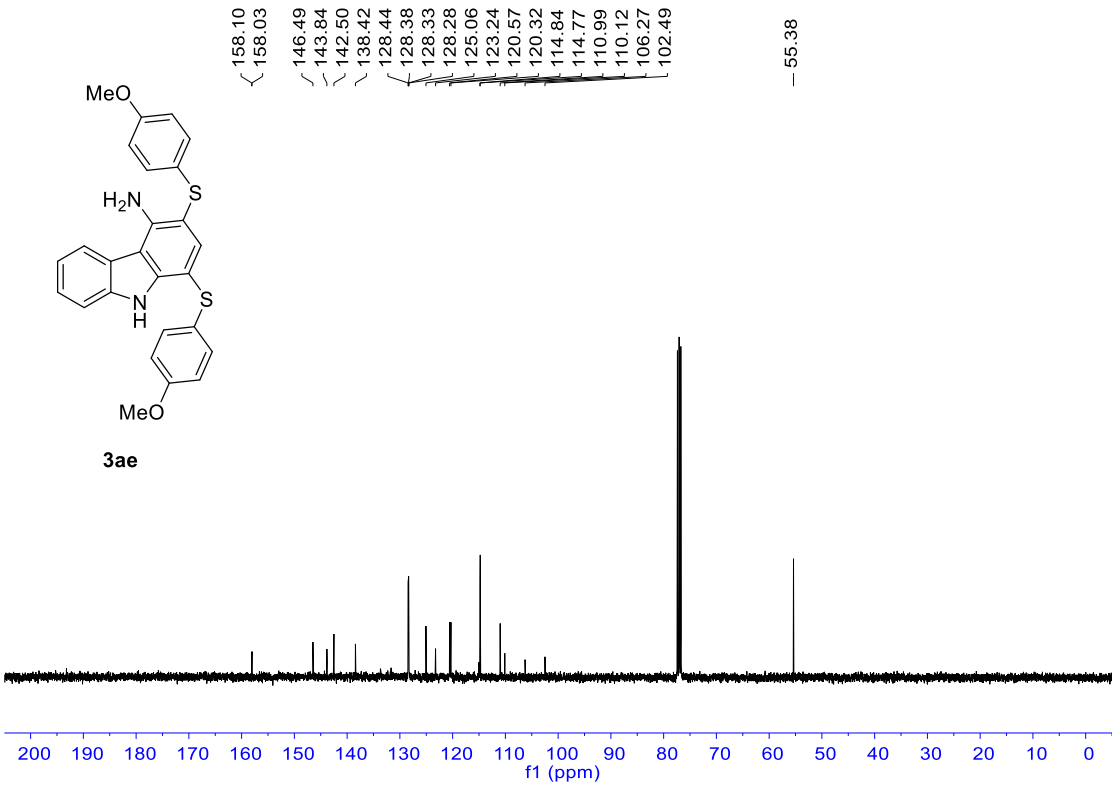
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ad**



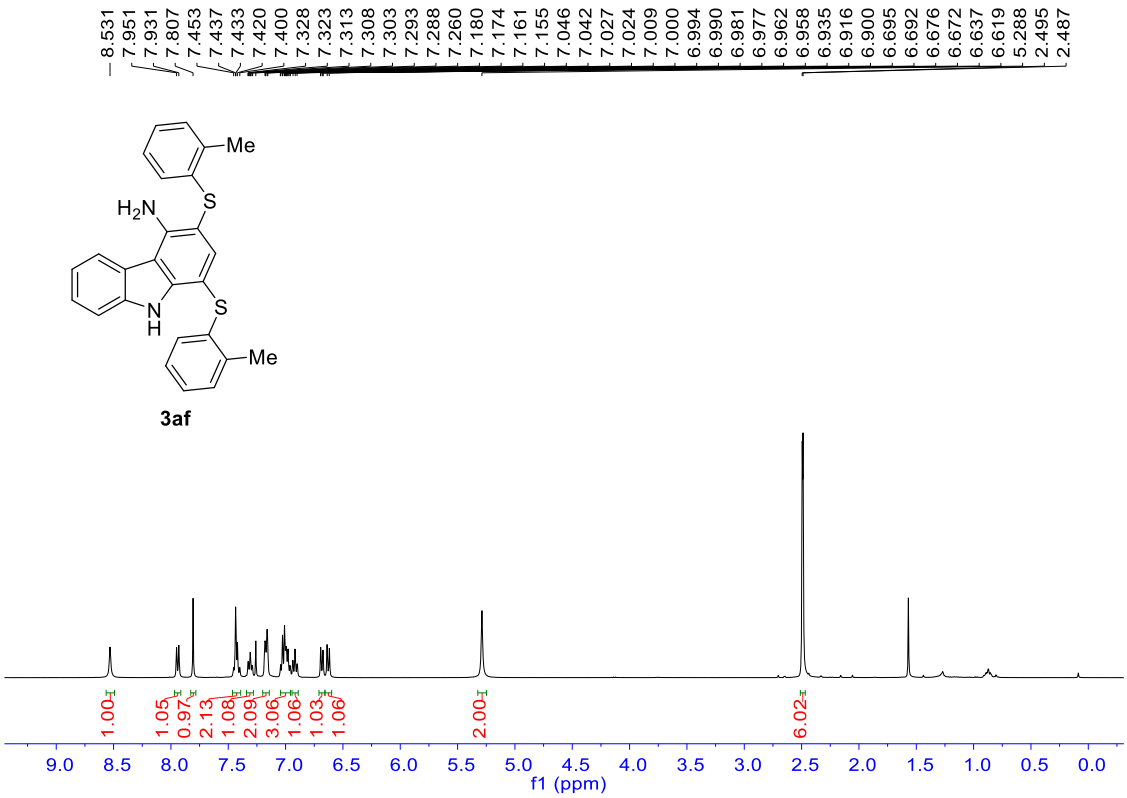
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3ad**



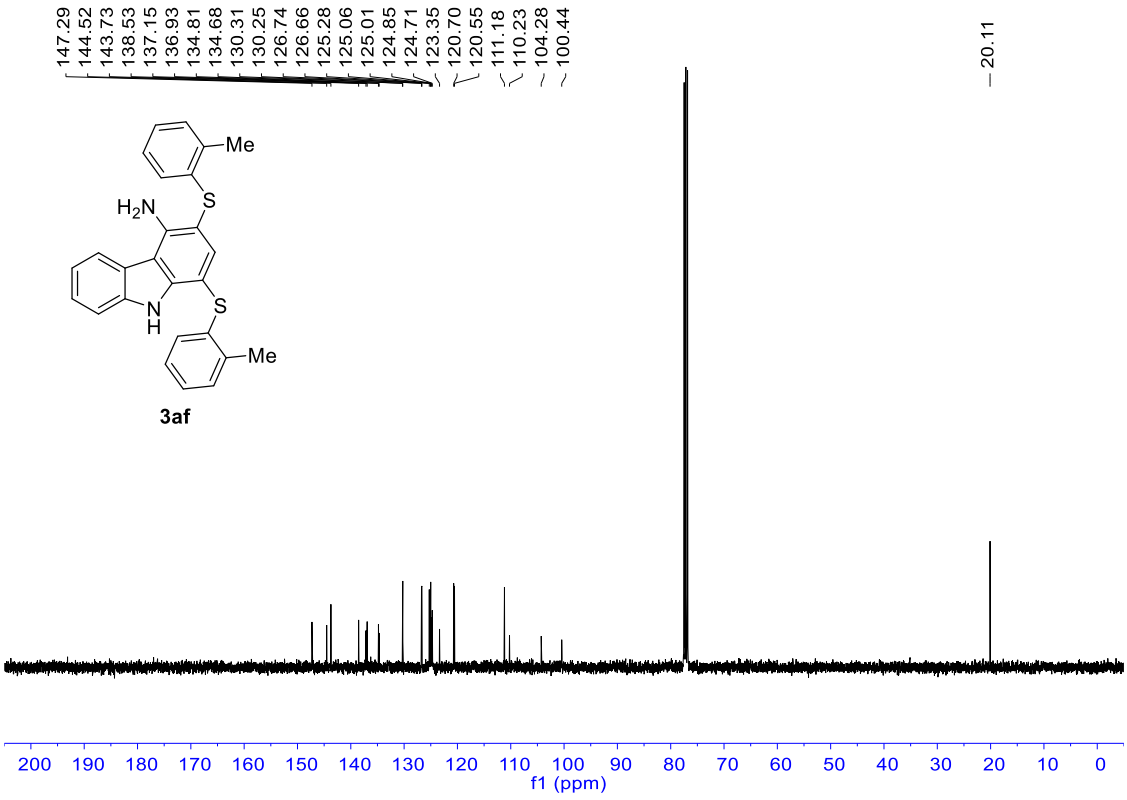
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ae**



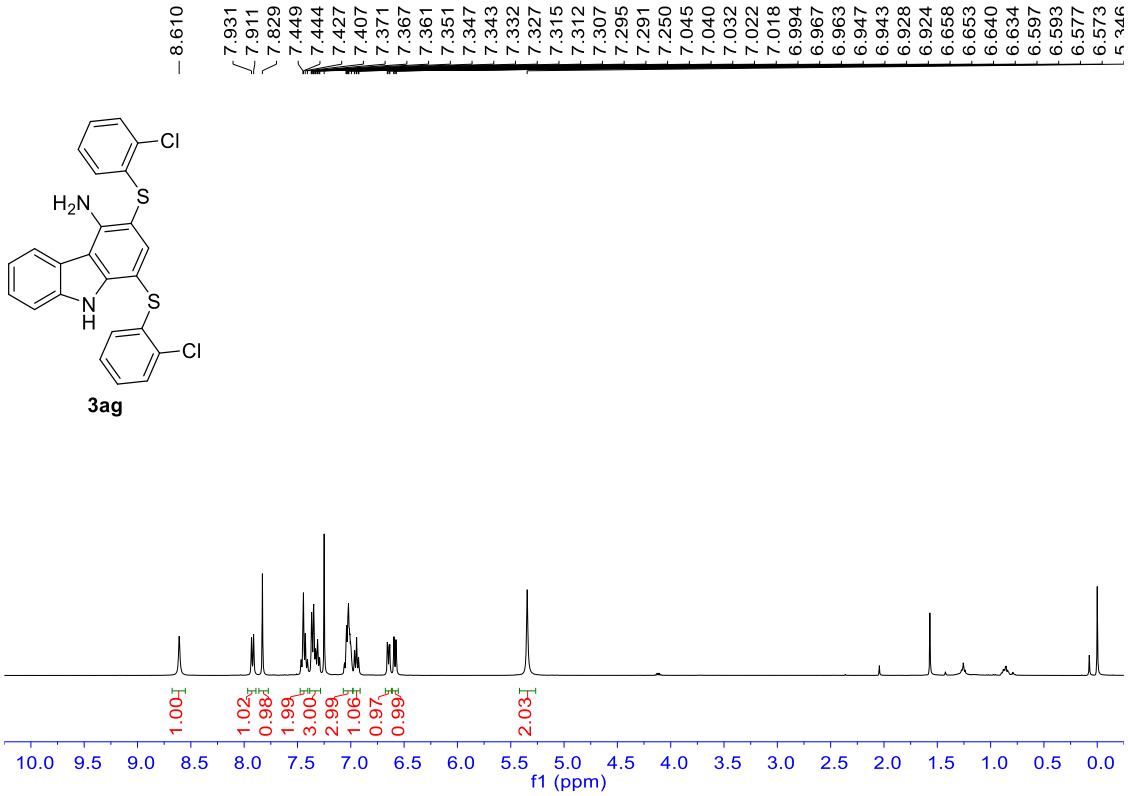
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3ae**



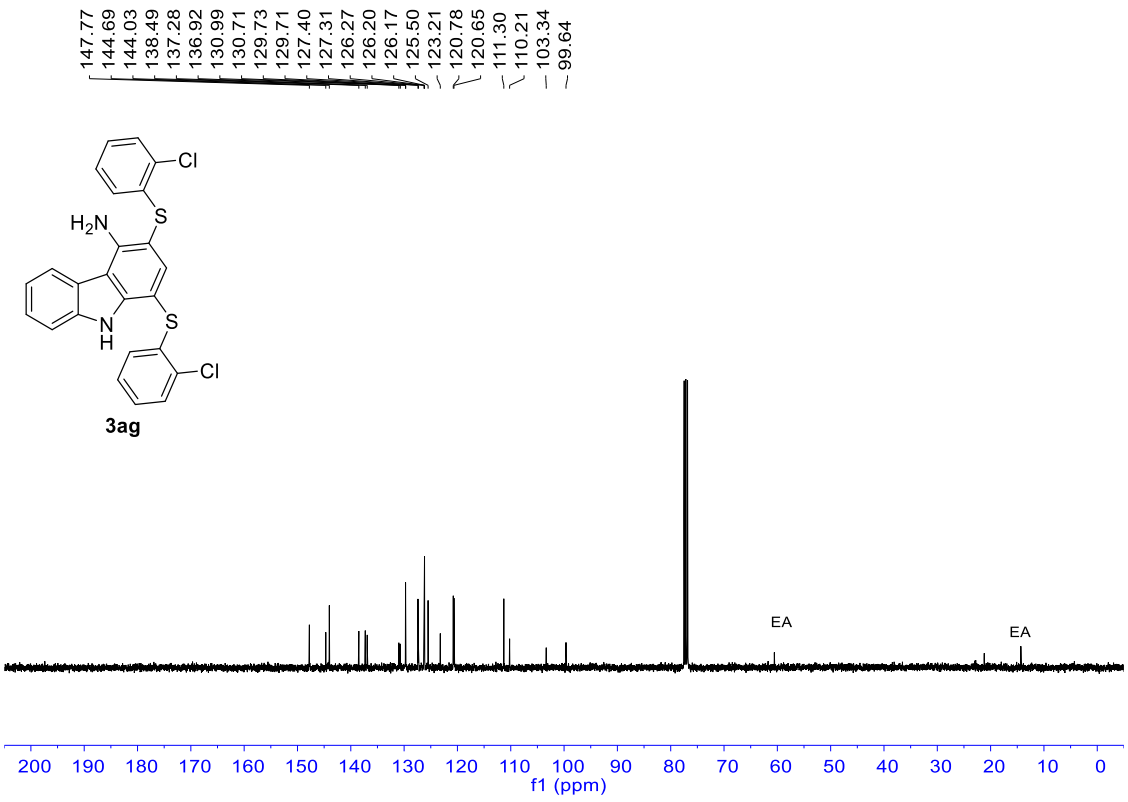
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3af**



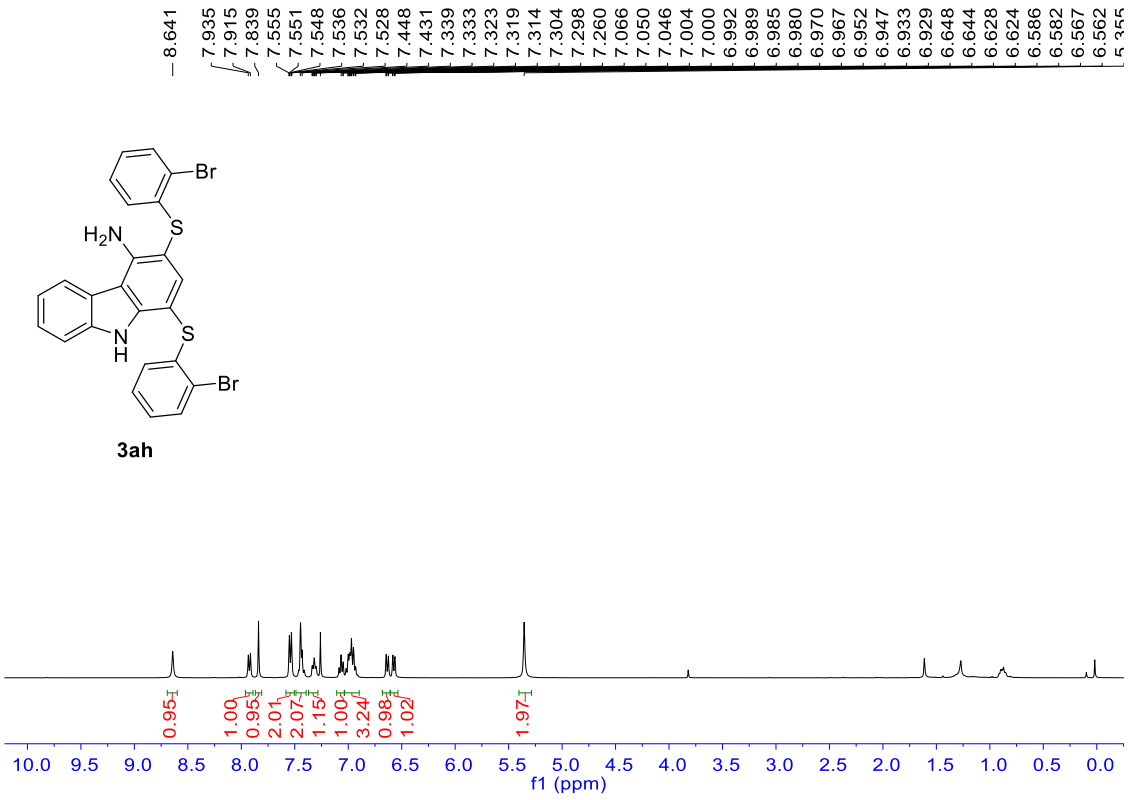
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3af**



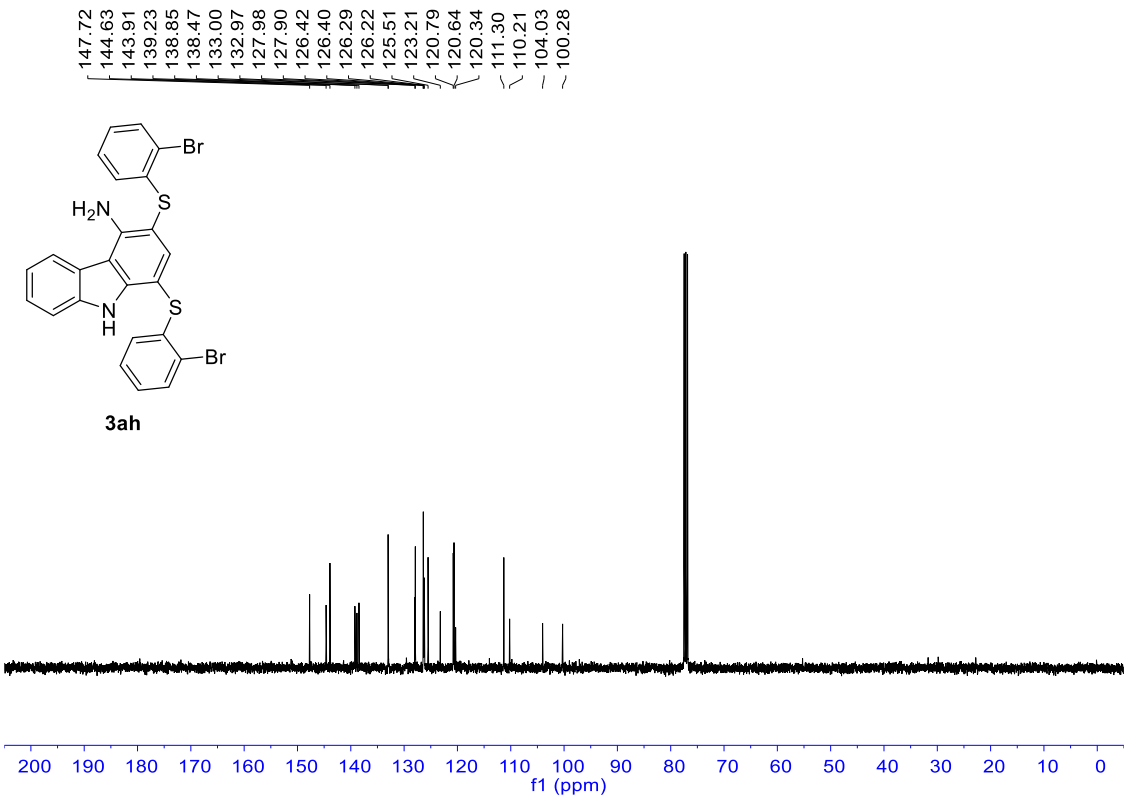
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ag**



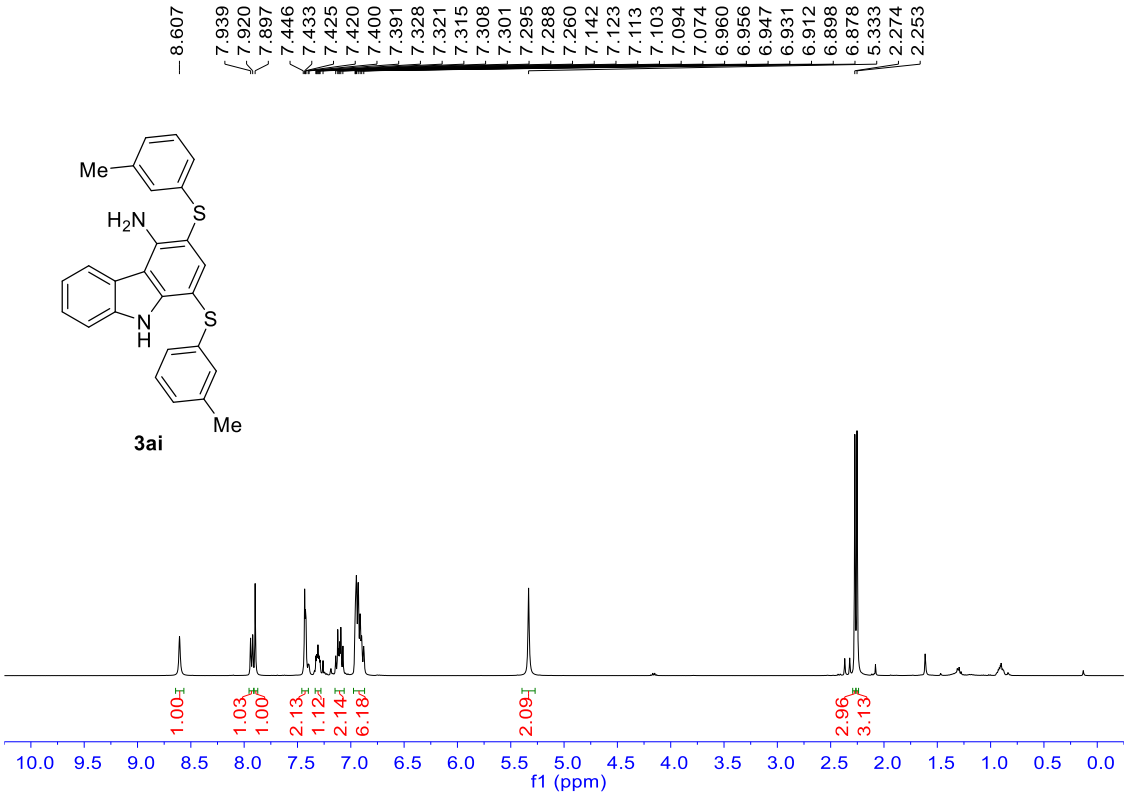
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3ag**



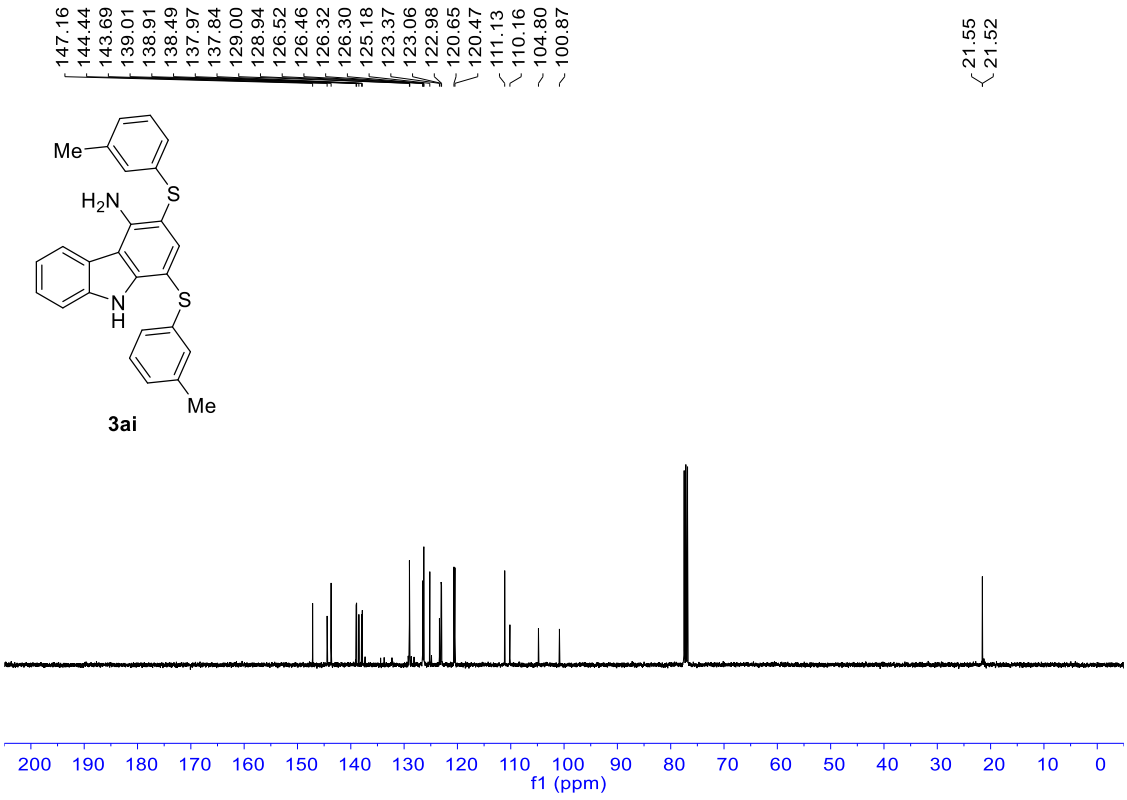
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ah**



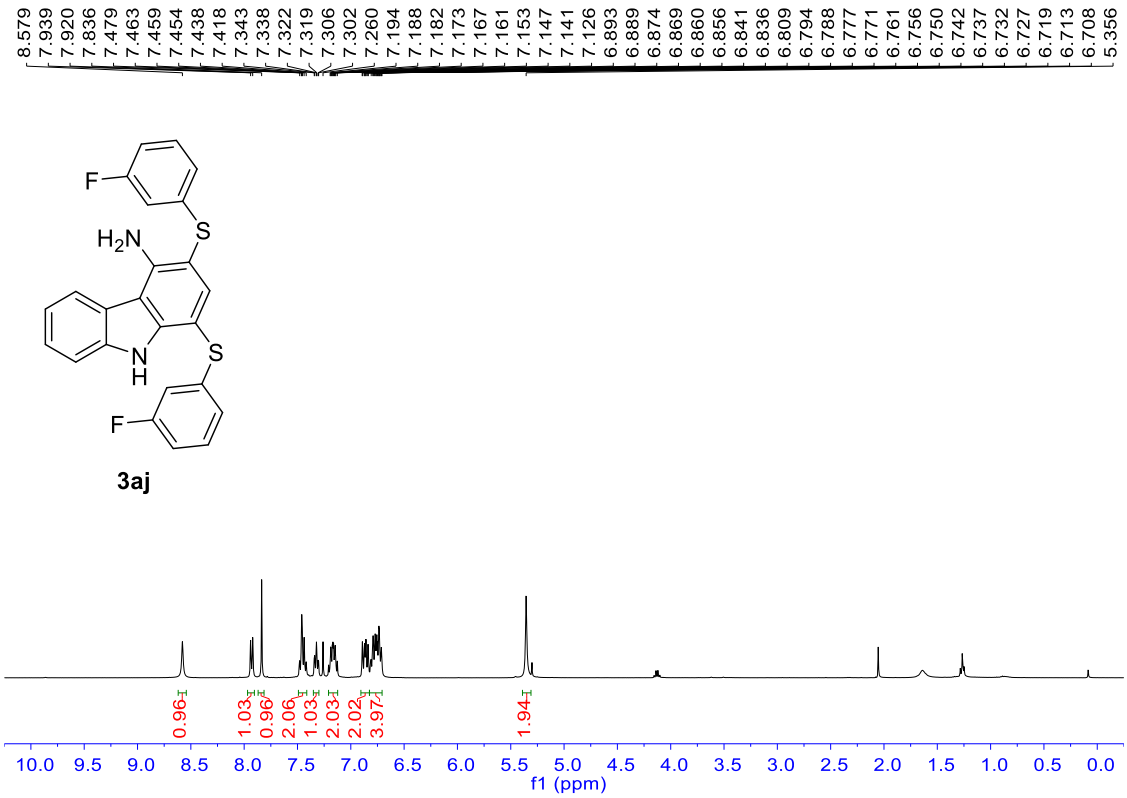
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3ah**



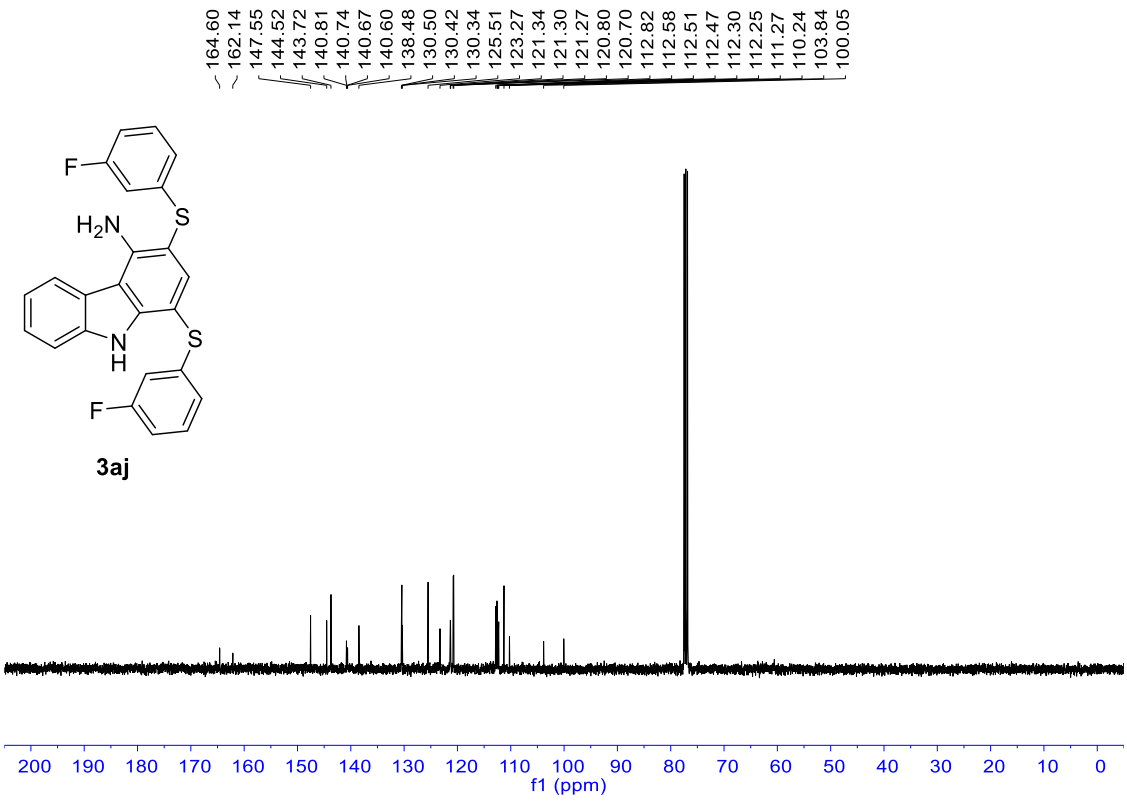
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ai**



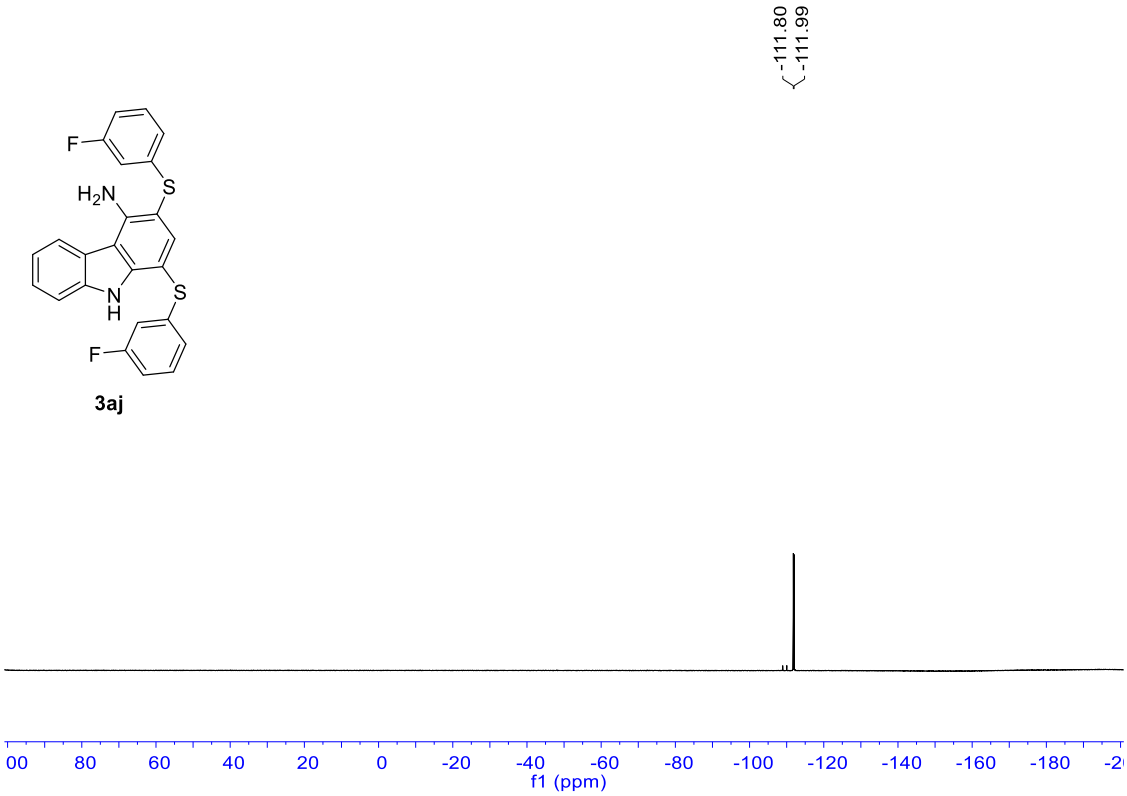
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3ai**



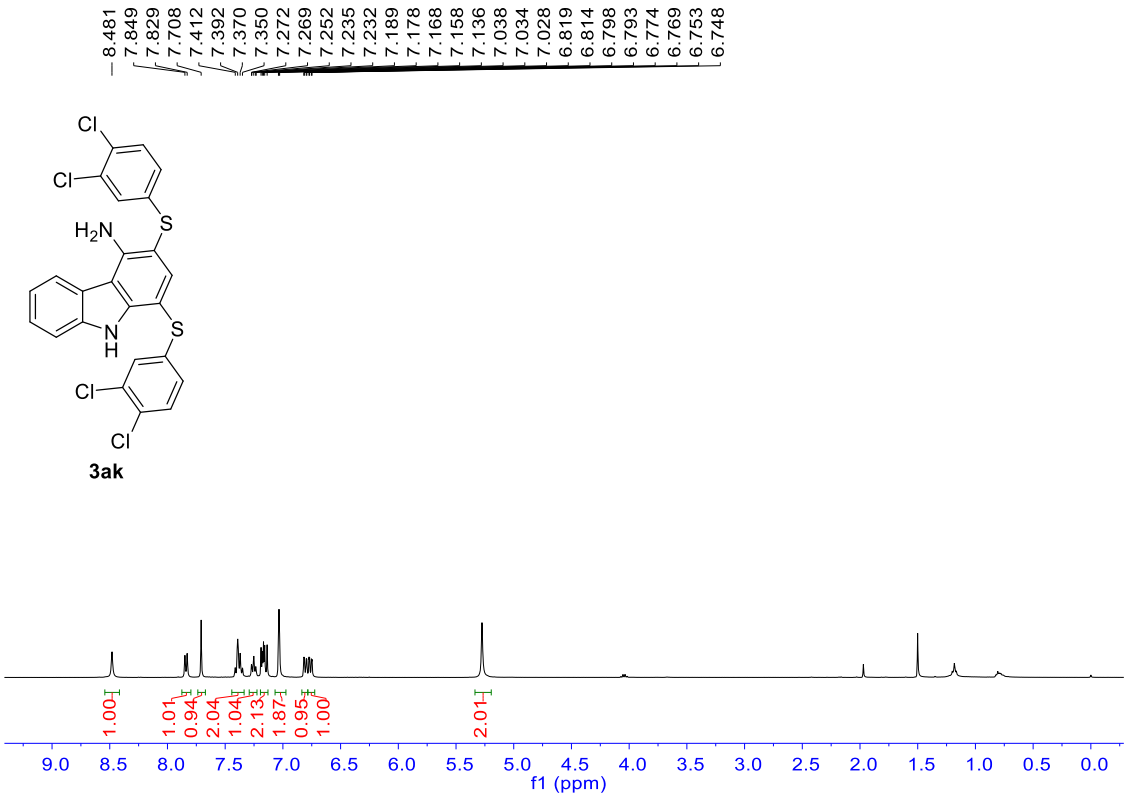
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3aj**



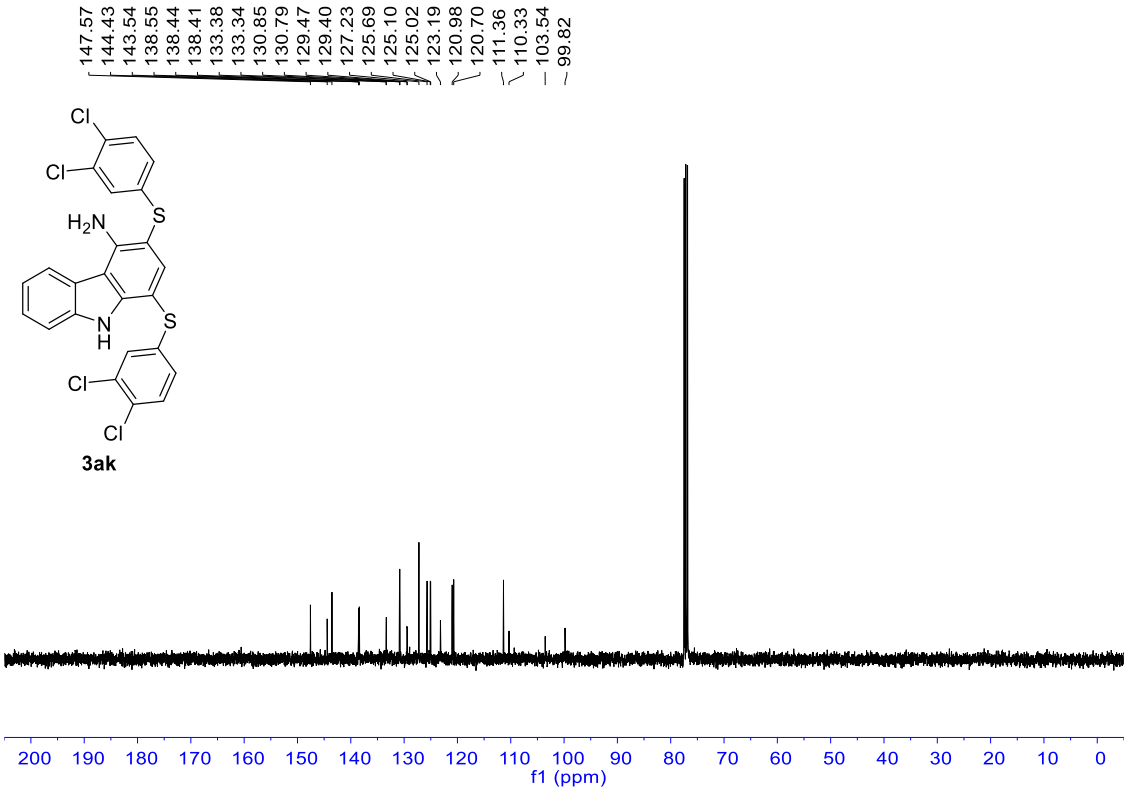
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3aj**



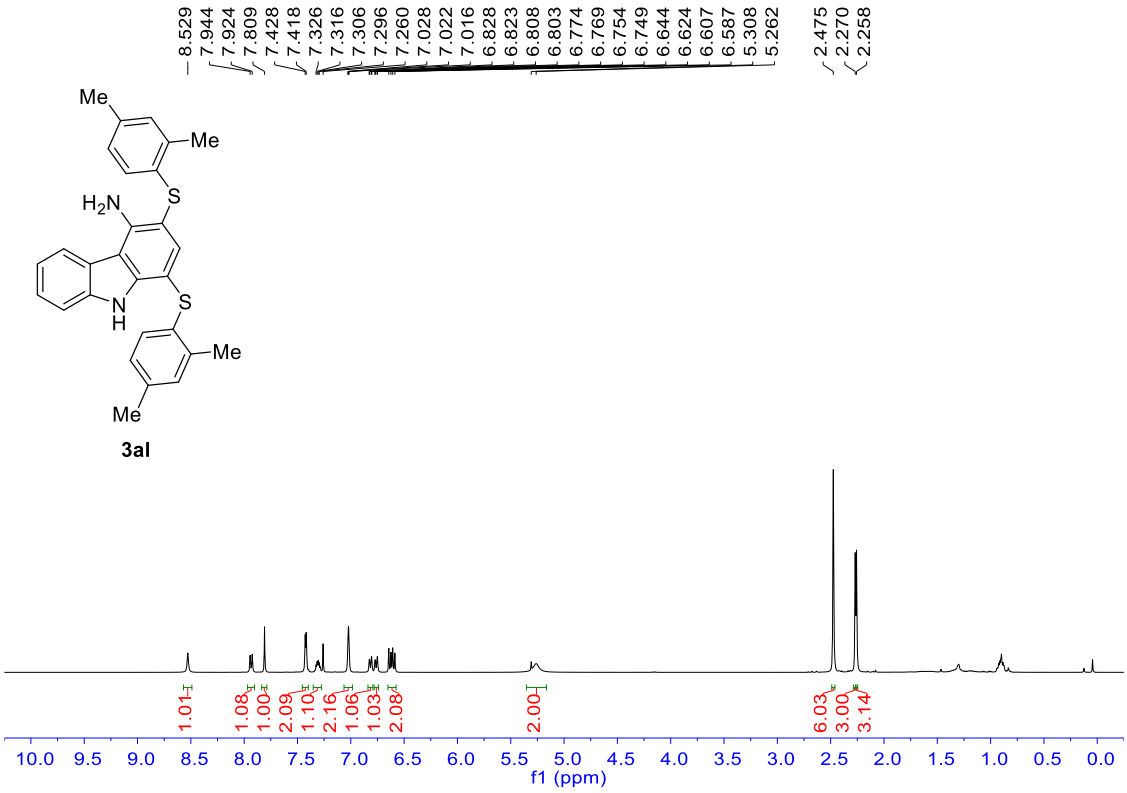
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3aj**



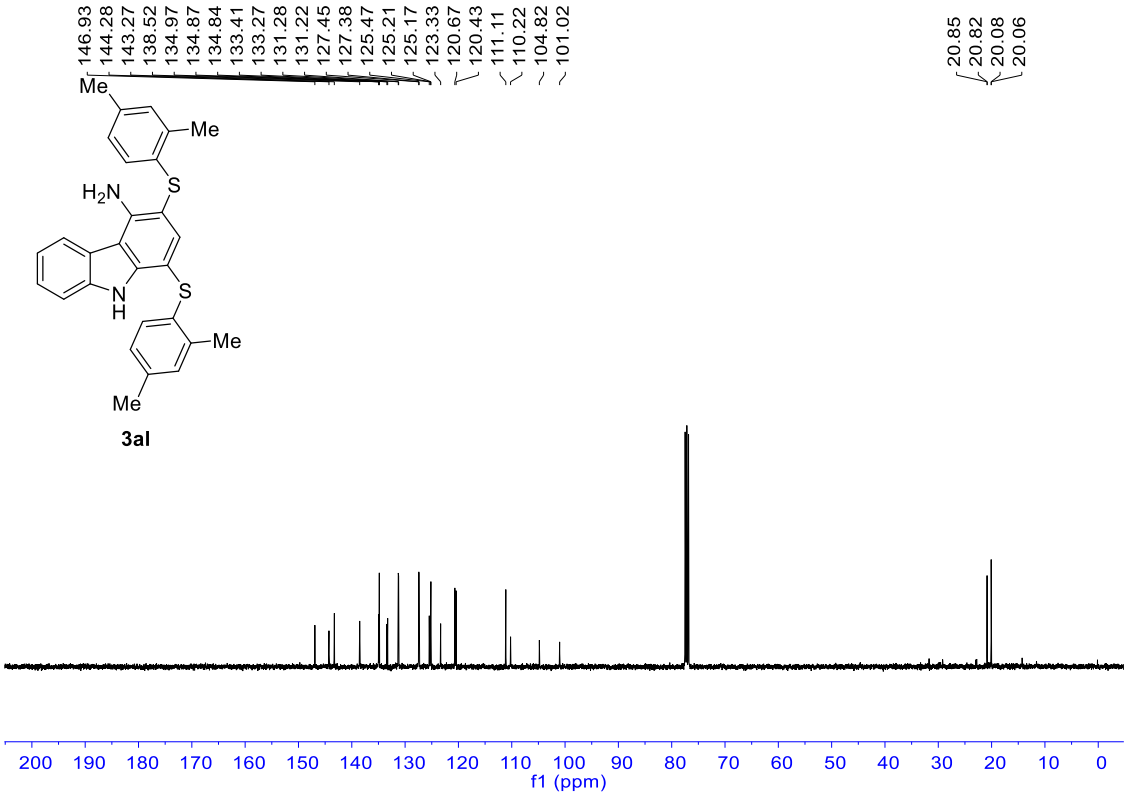
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ak**



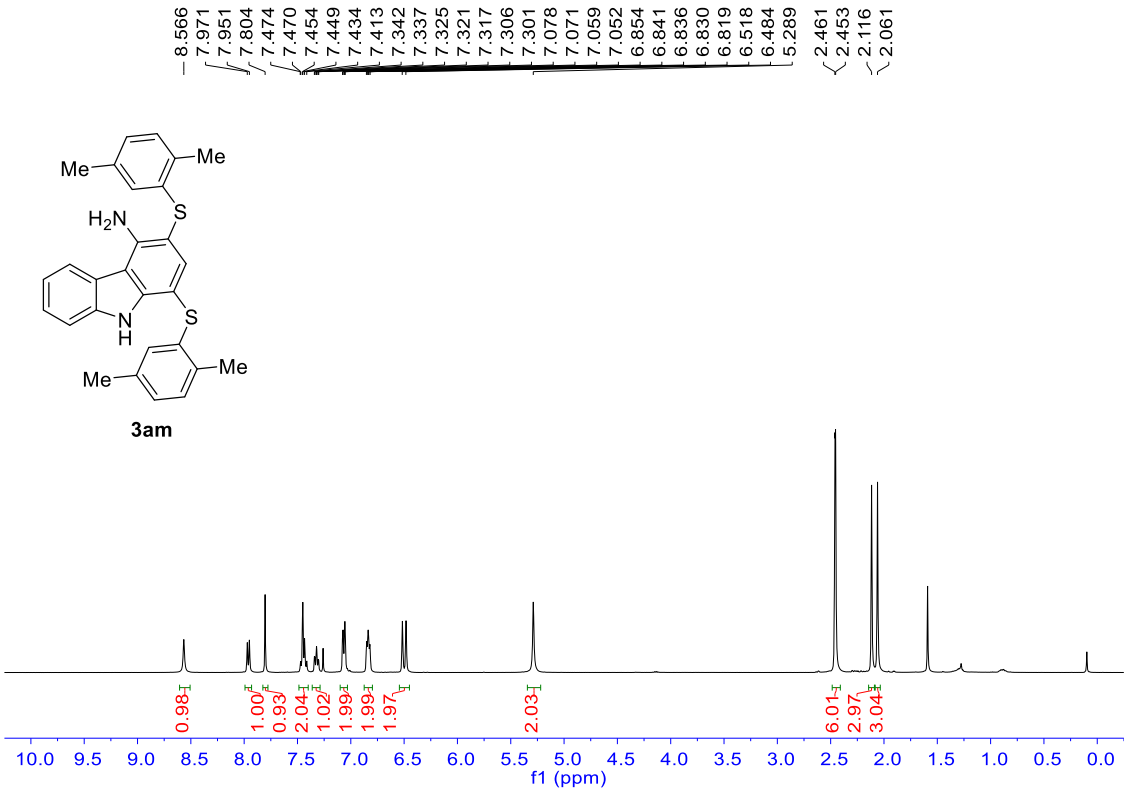
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3ak**



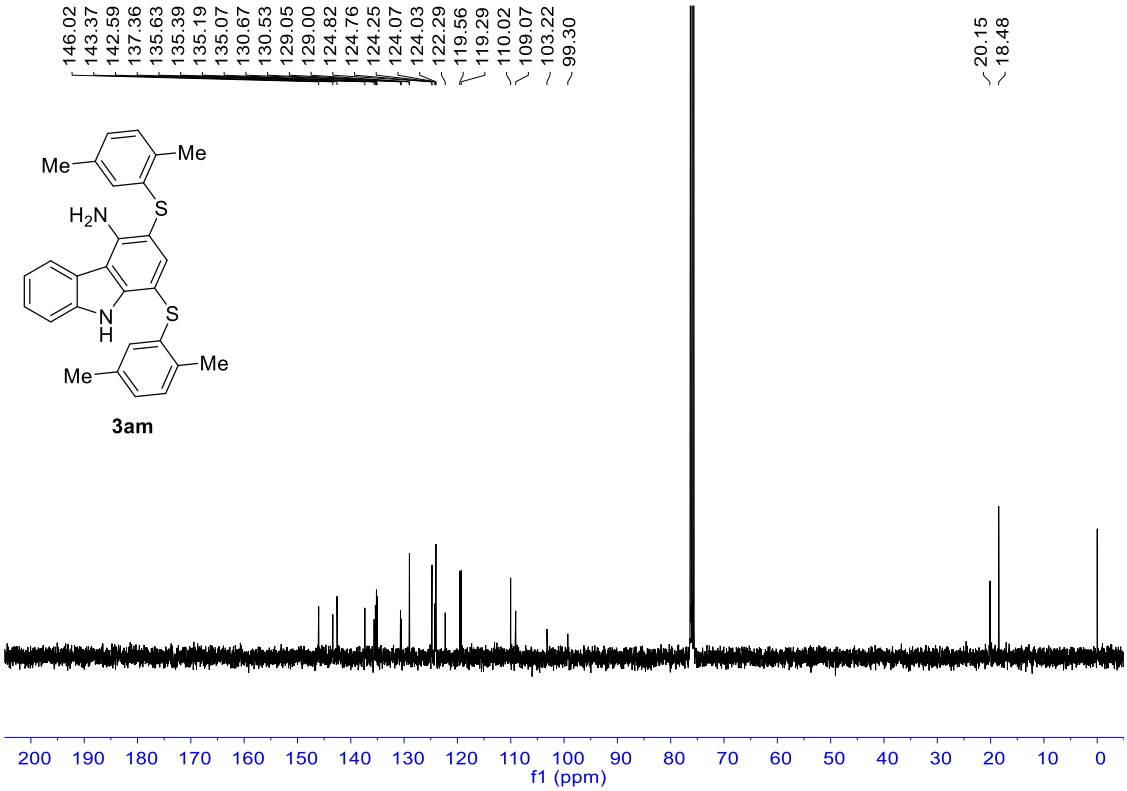
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3al**



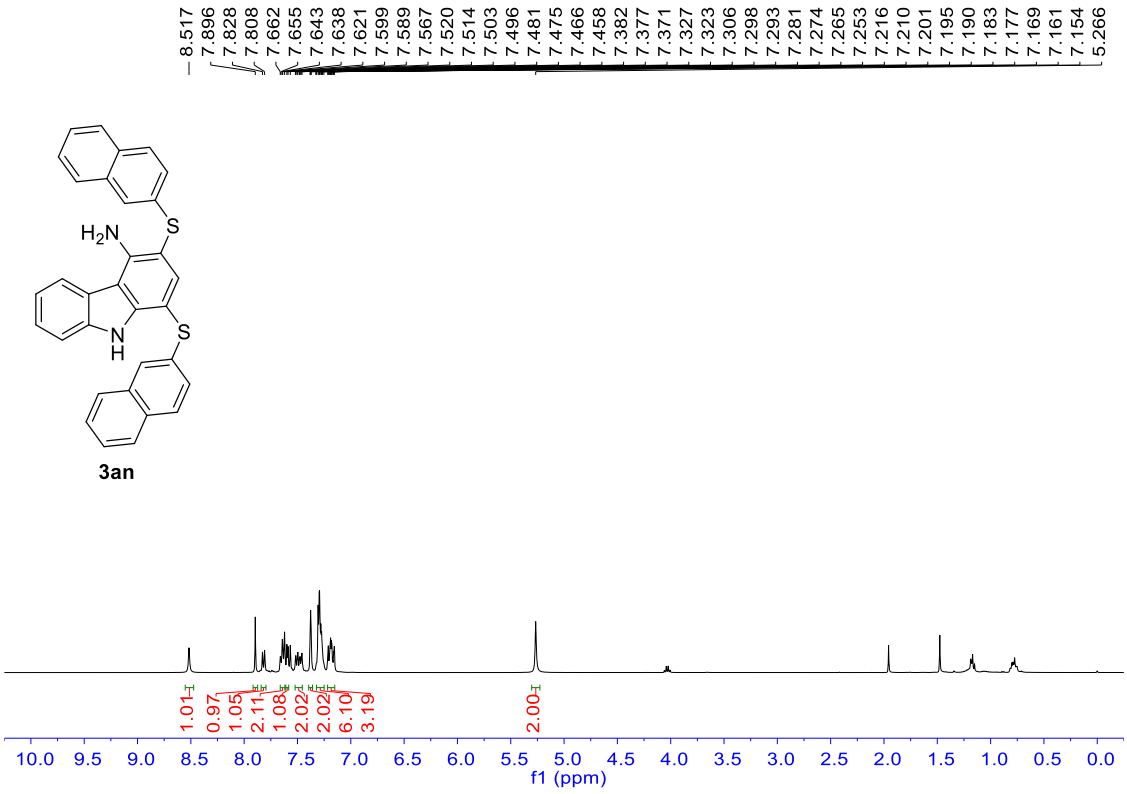
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3al**



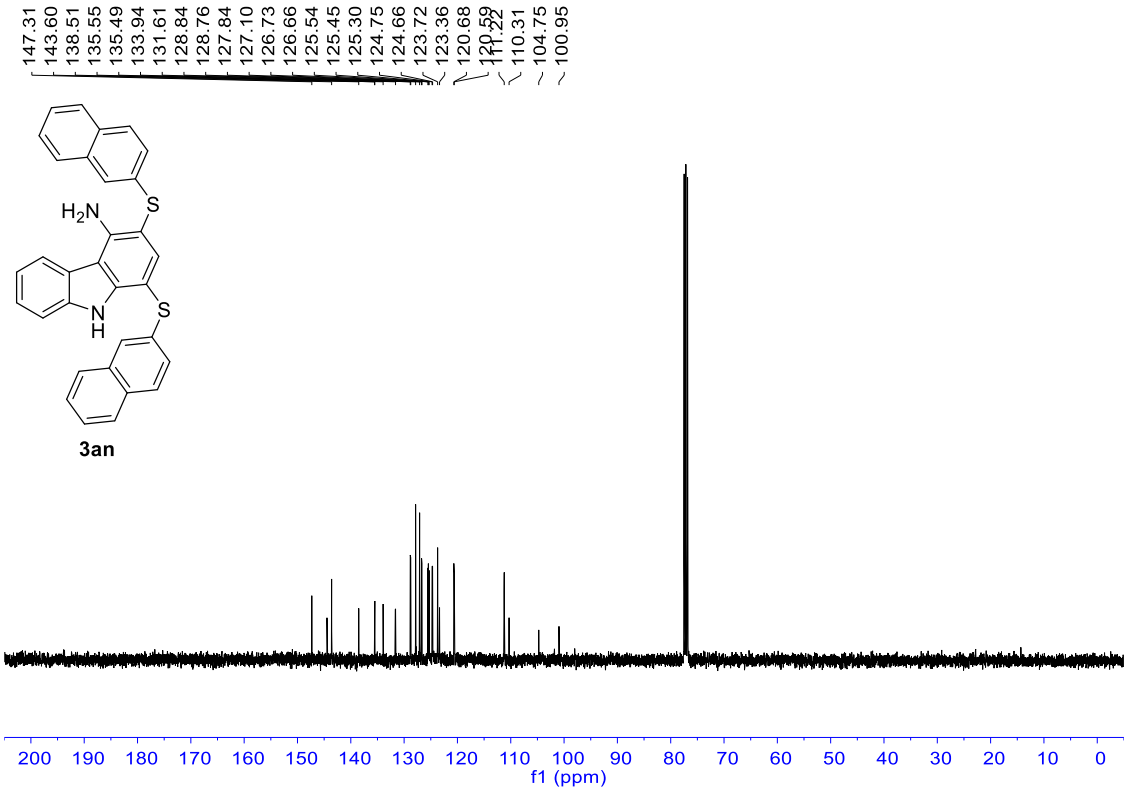
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3am**



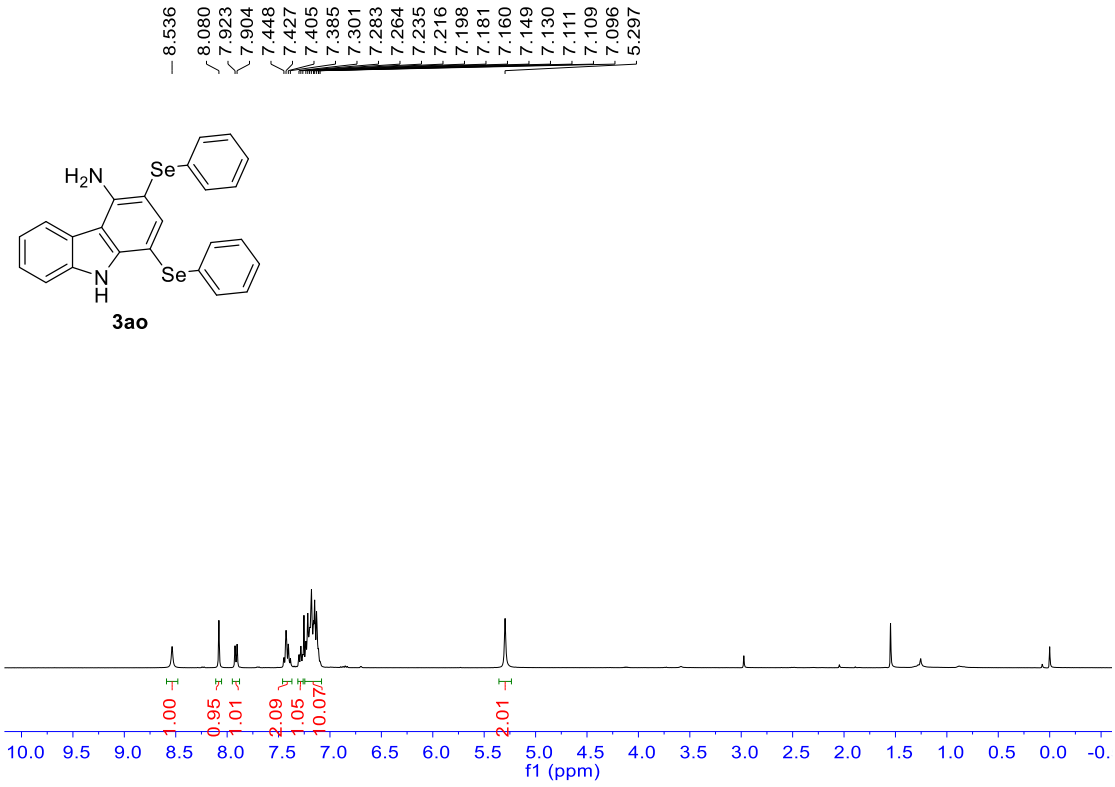
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3am**



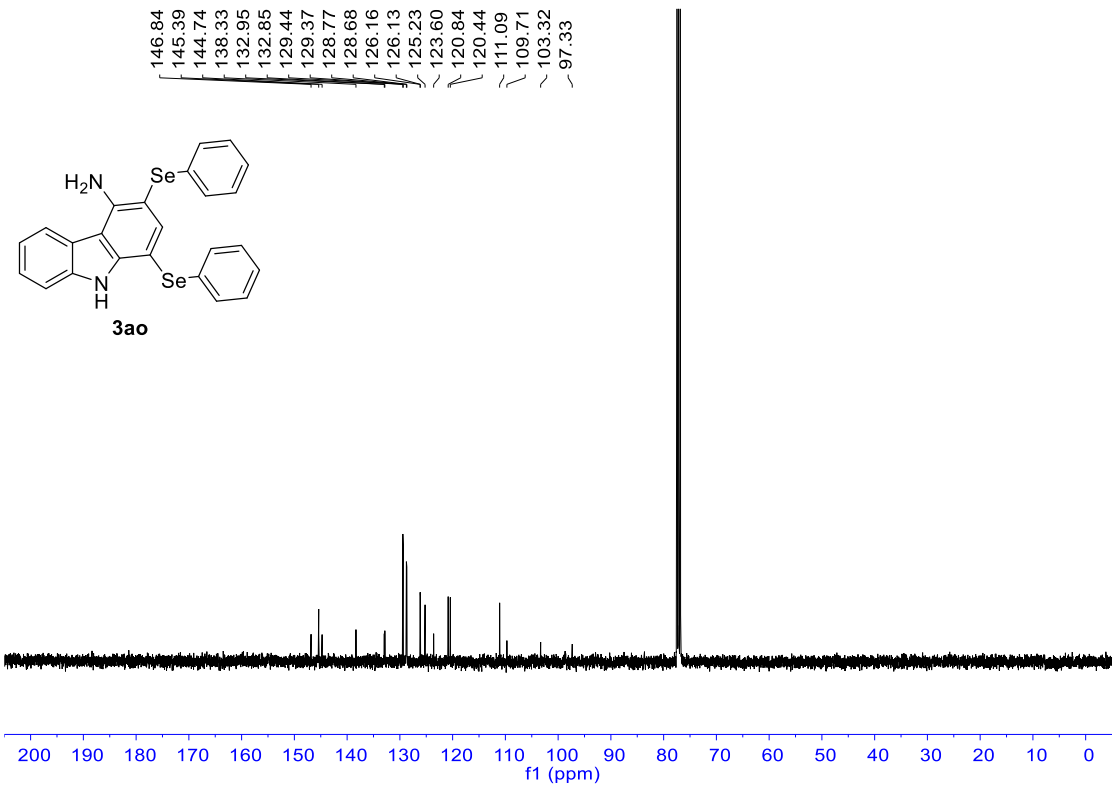
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3an**



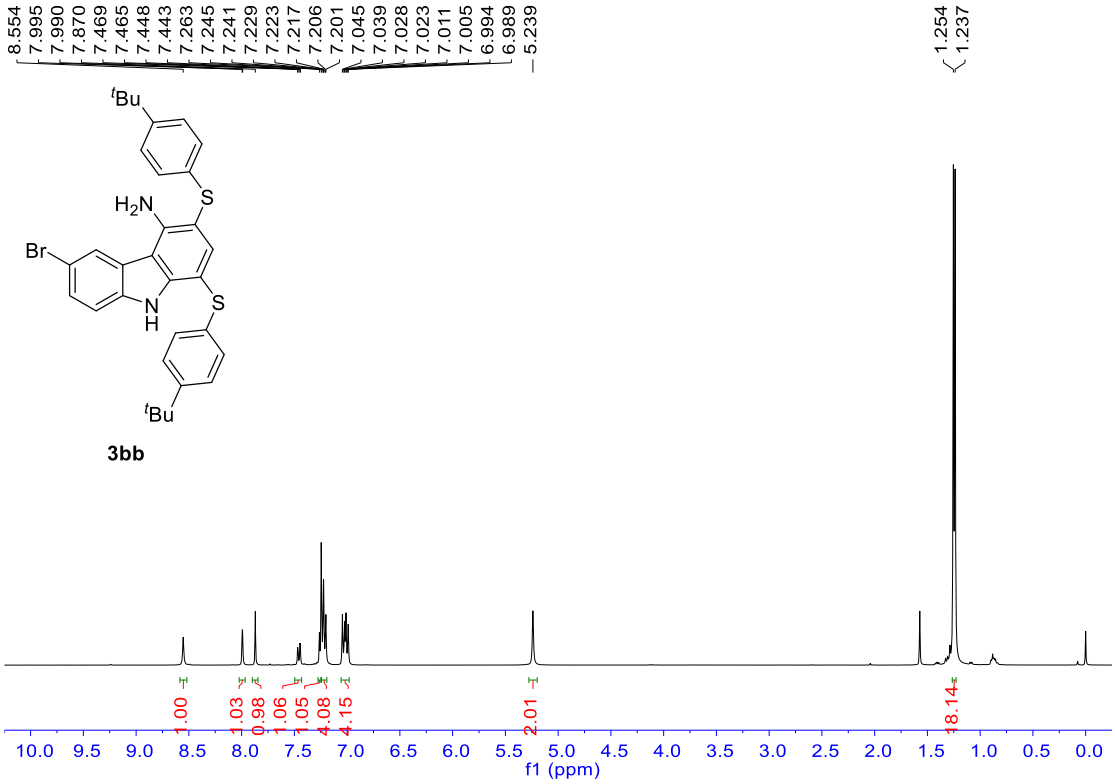
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3an**



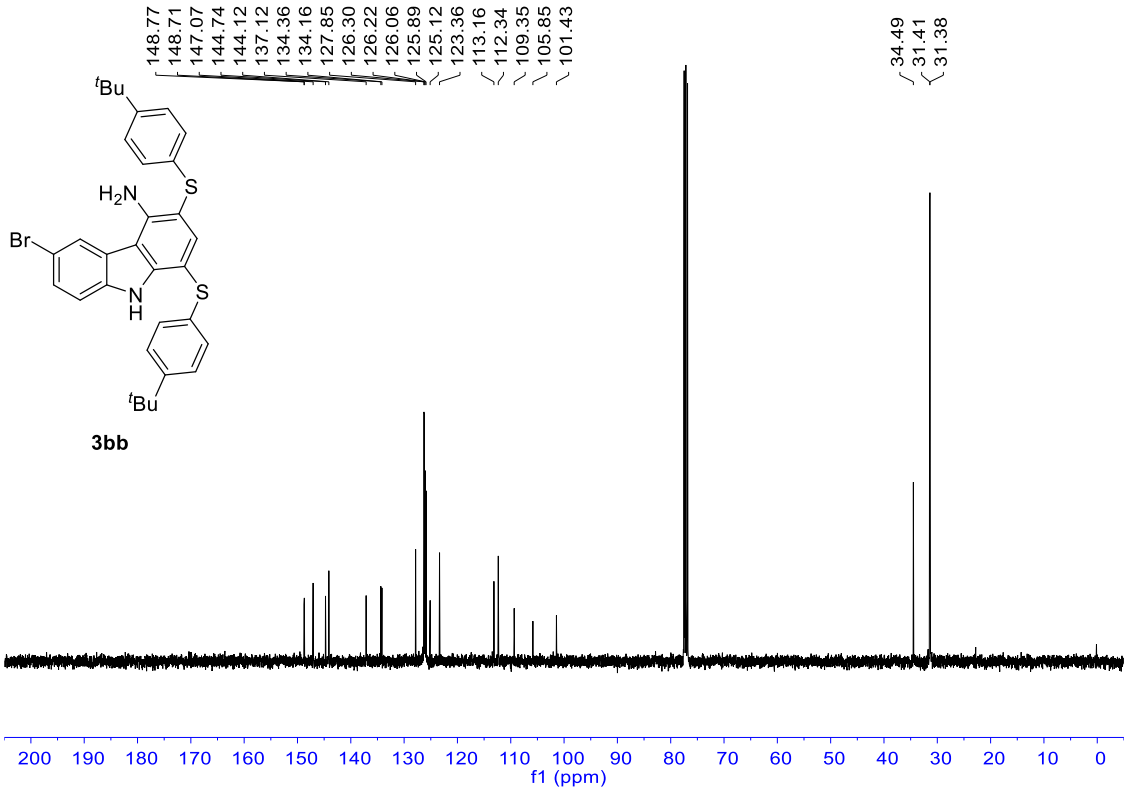
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ao**



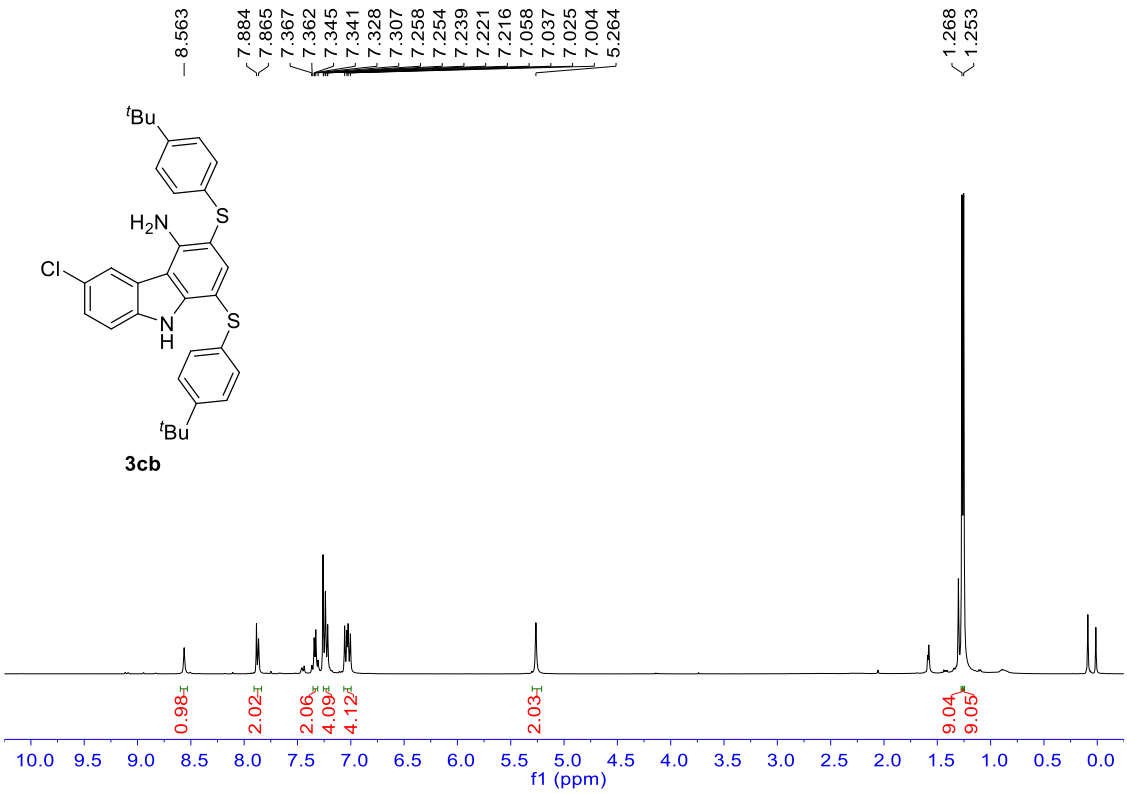
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3ao**



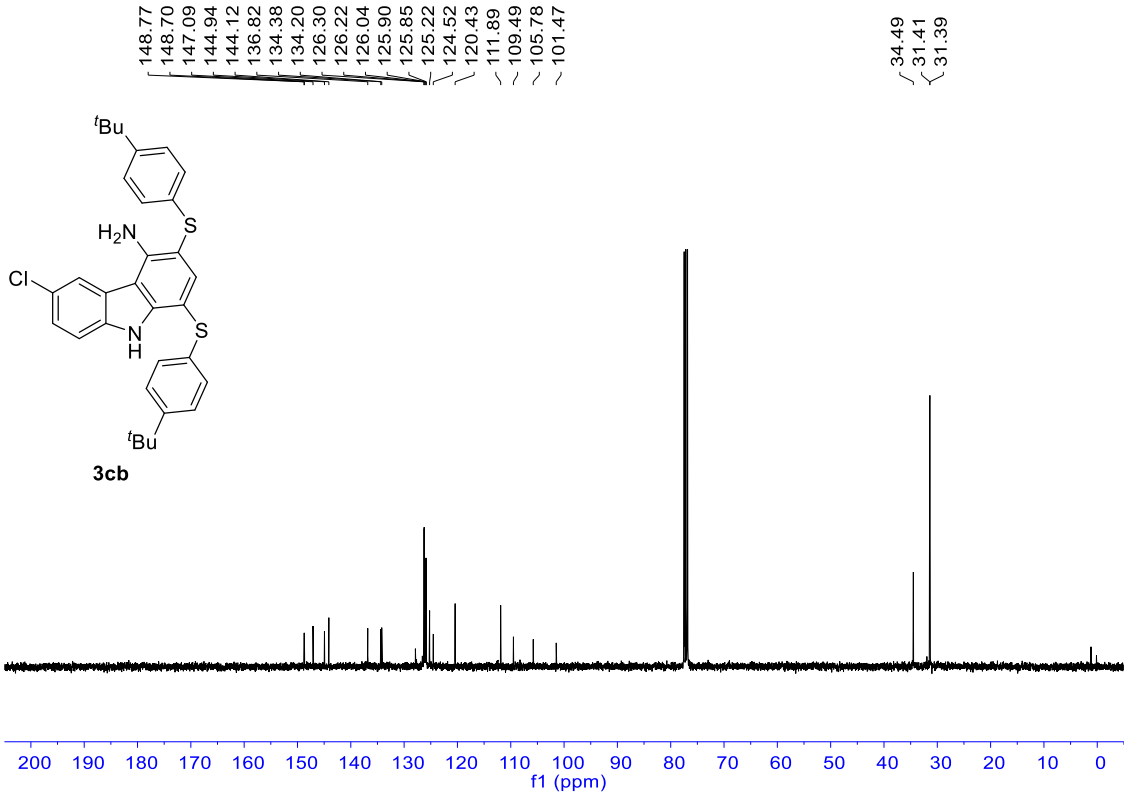
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3bb**



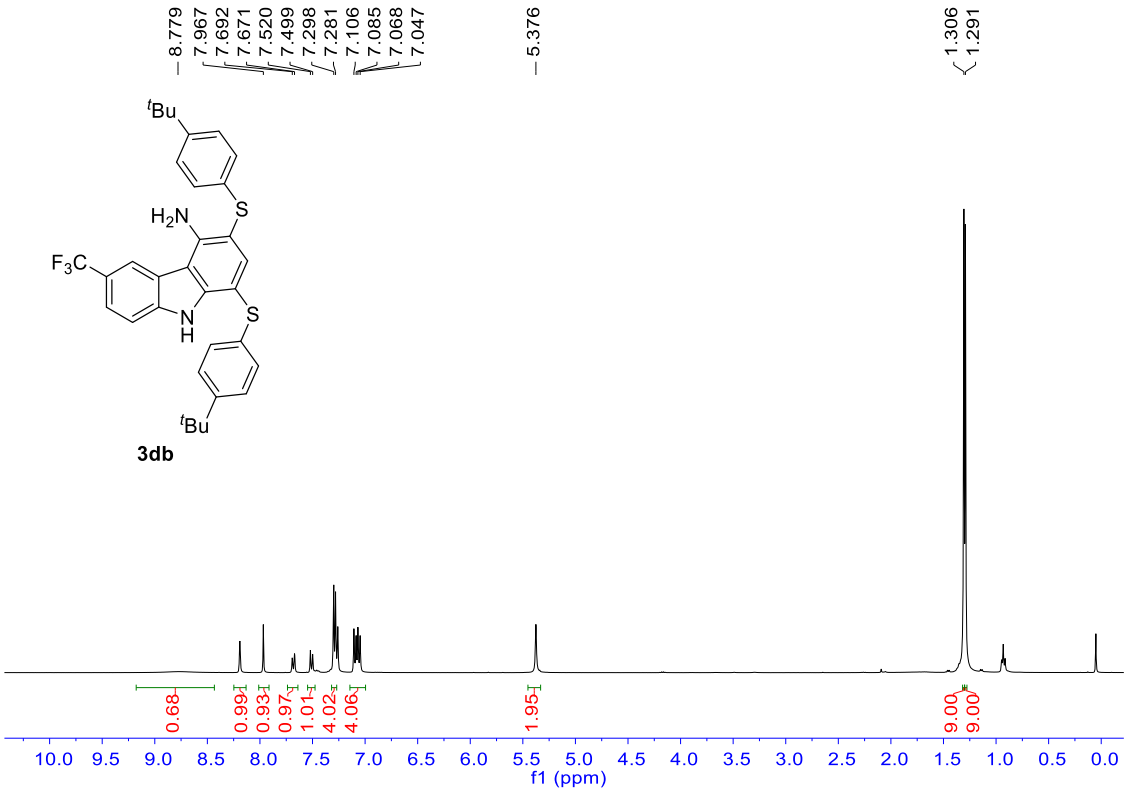
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3bb**



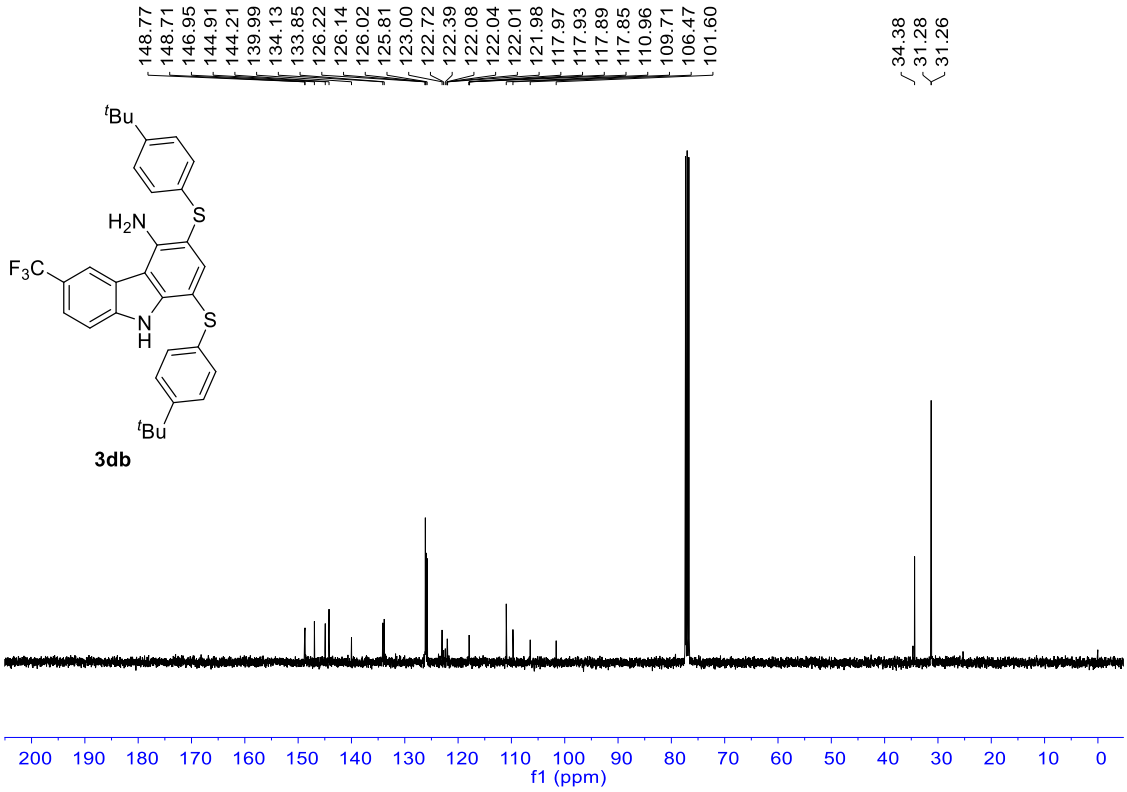
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3cb**



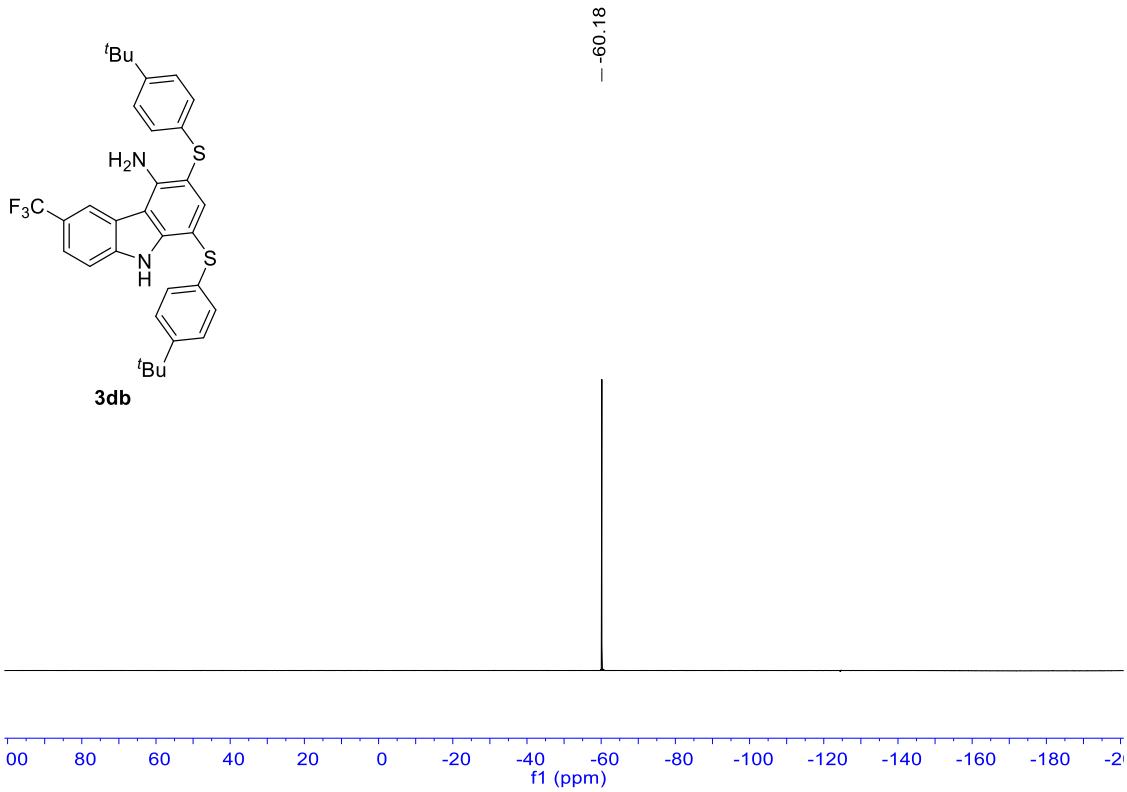
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3cb**



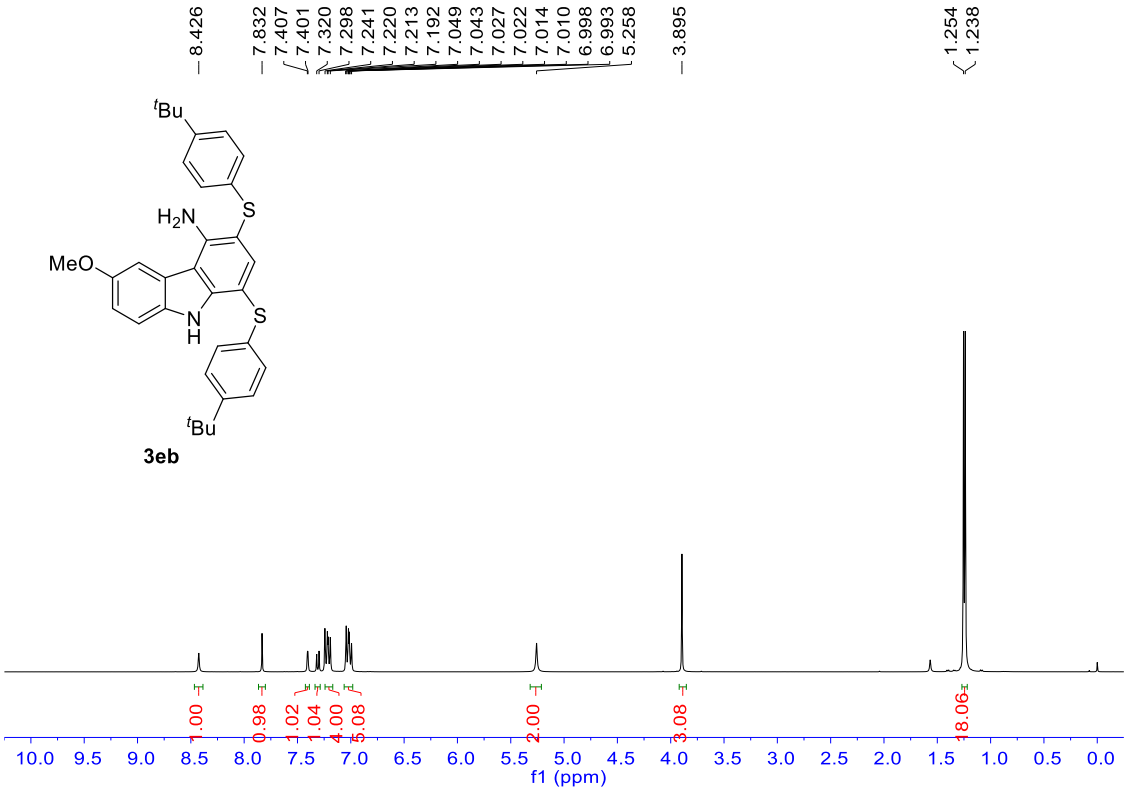
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3db**



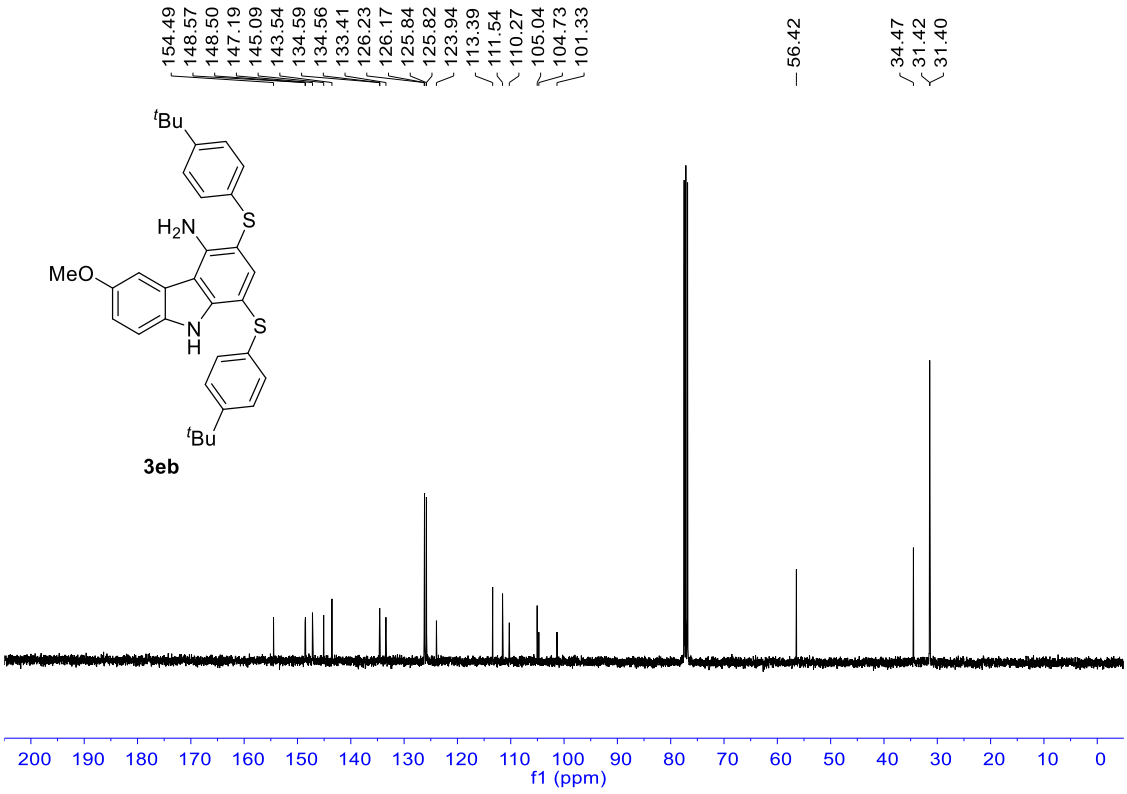
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3db**



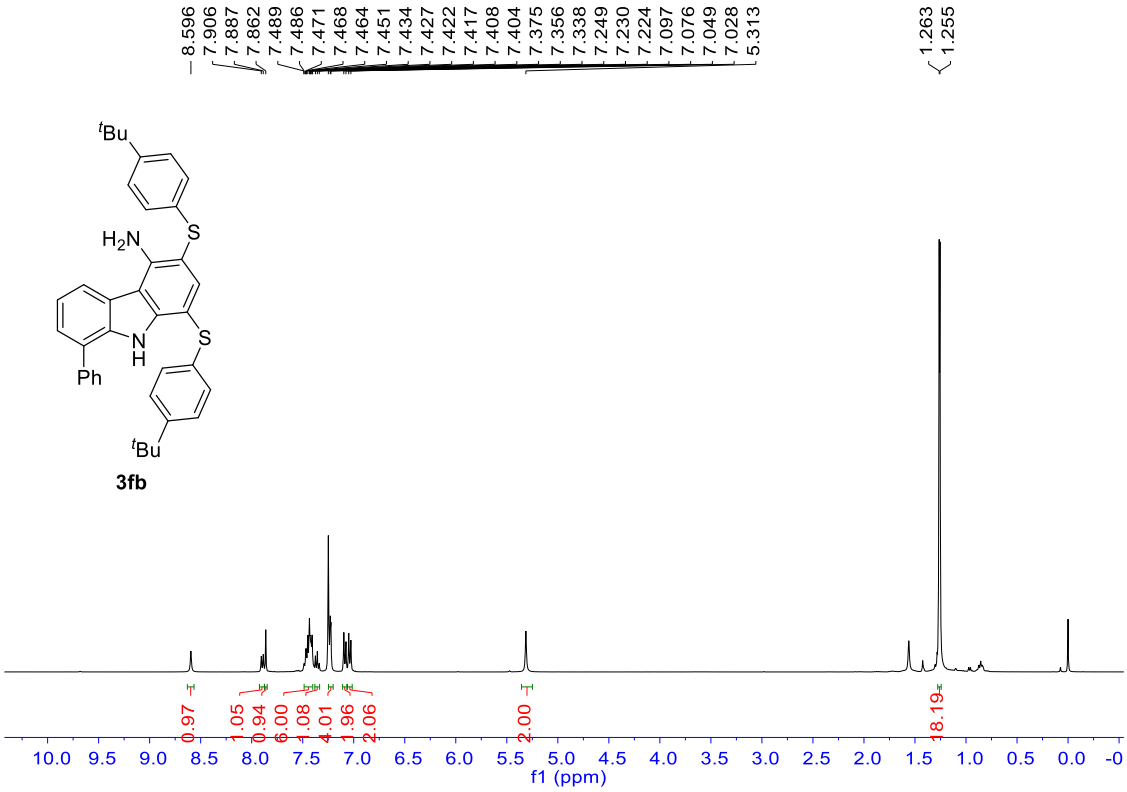
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3db**



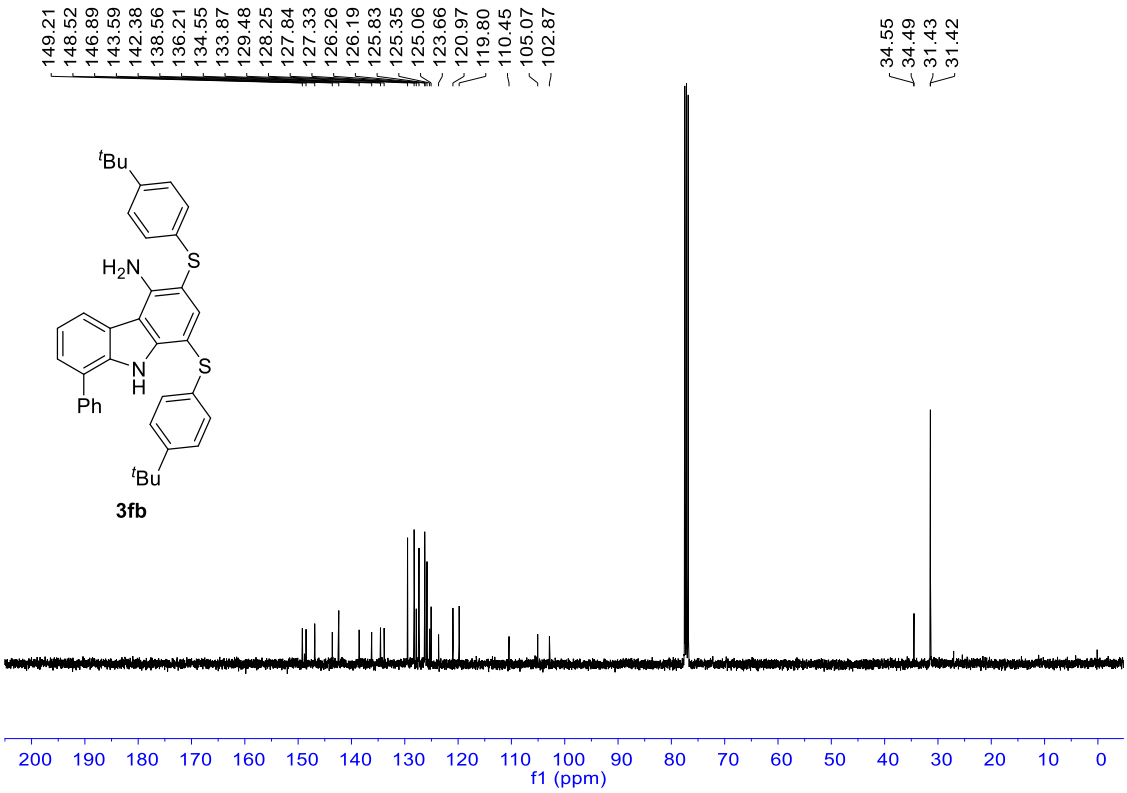
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3eb**



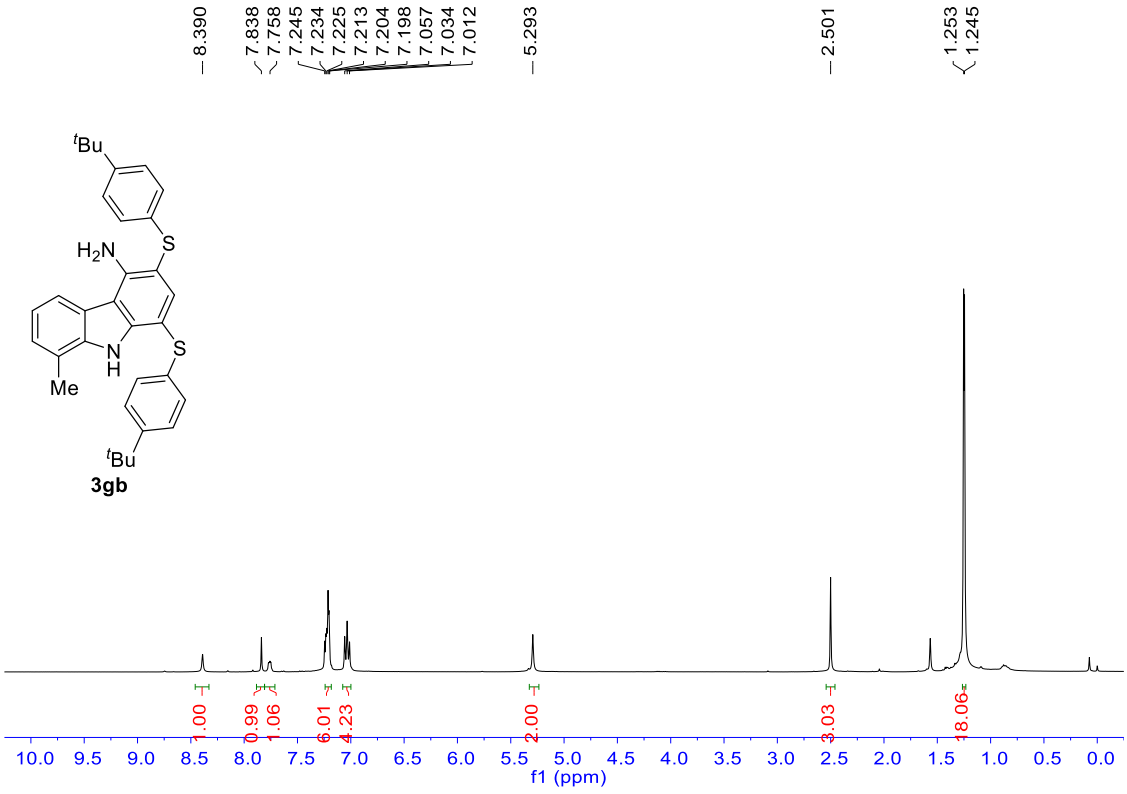
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3eb**



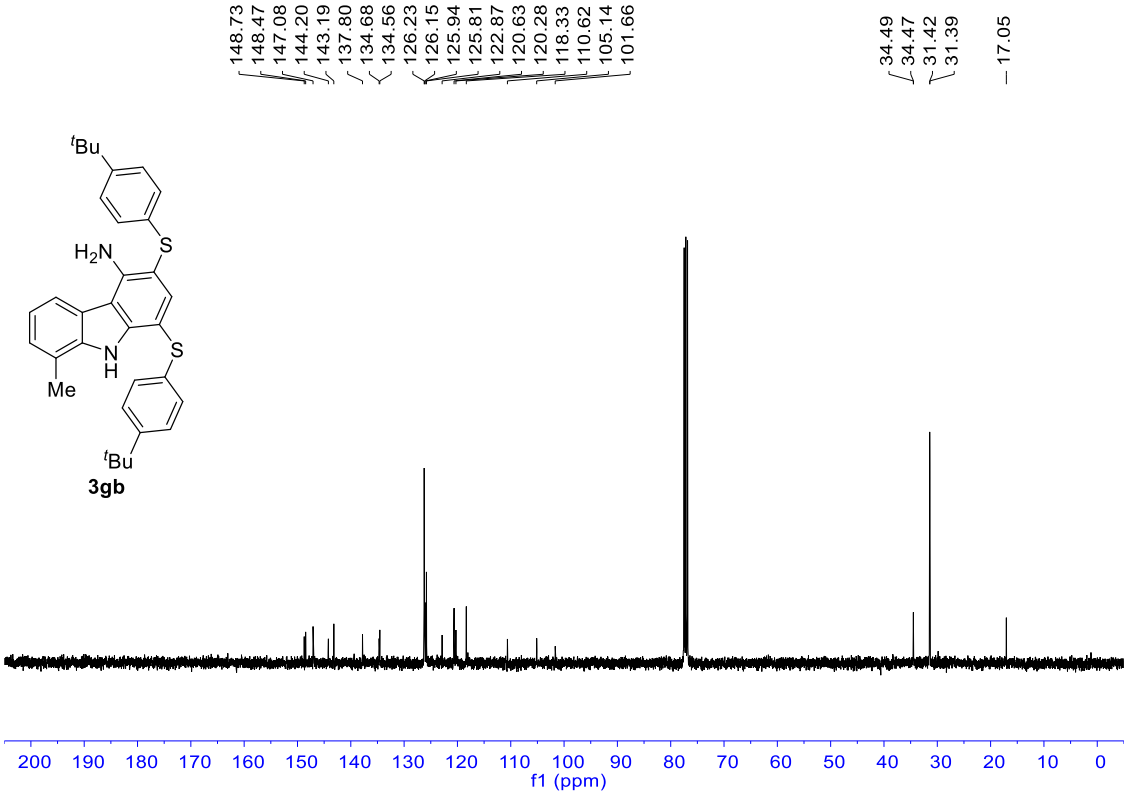
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3fb**



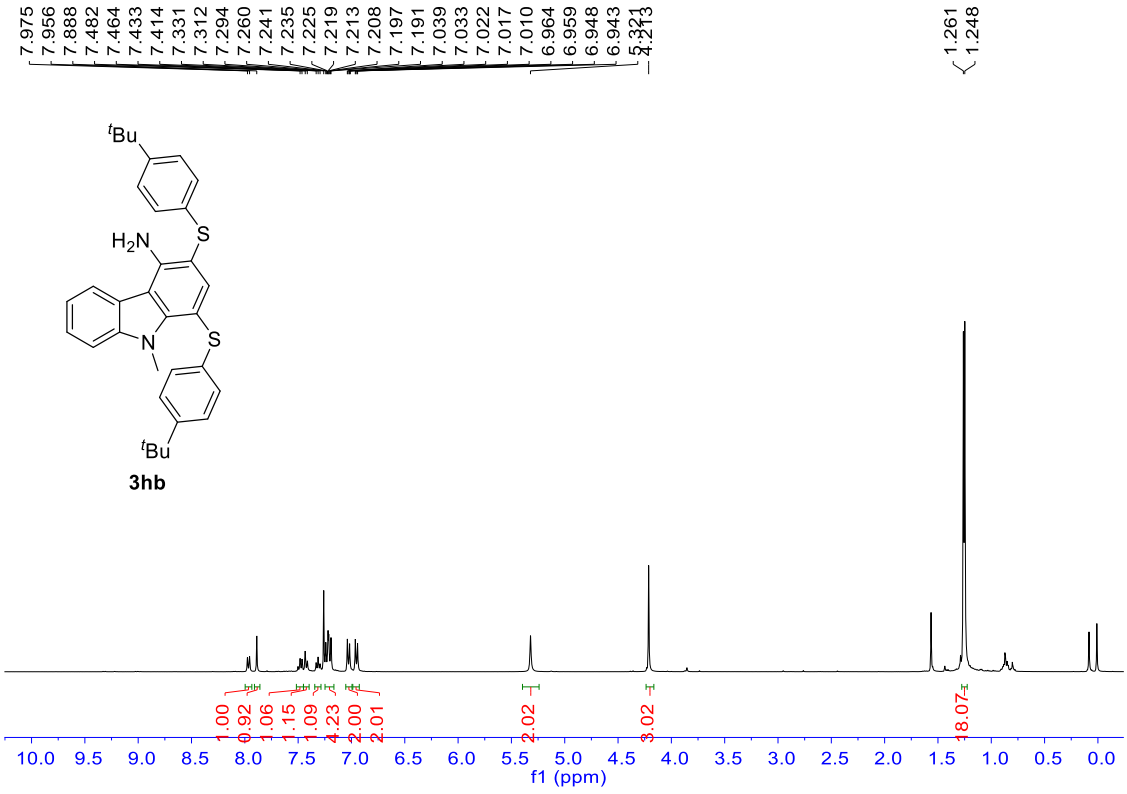
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3fb**



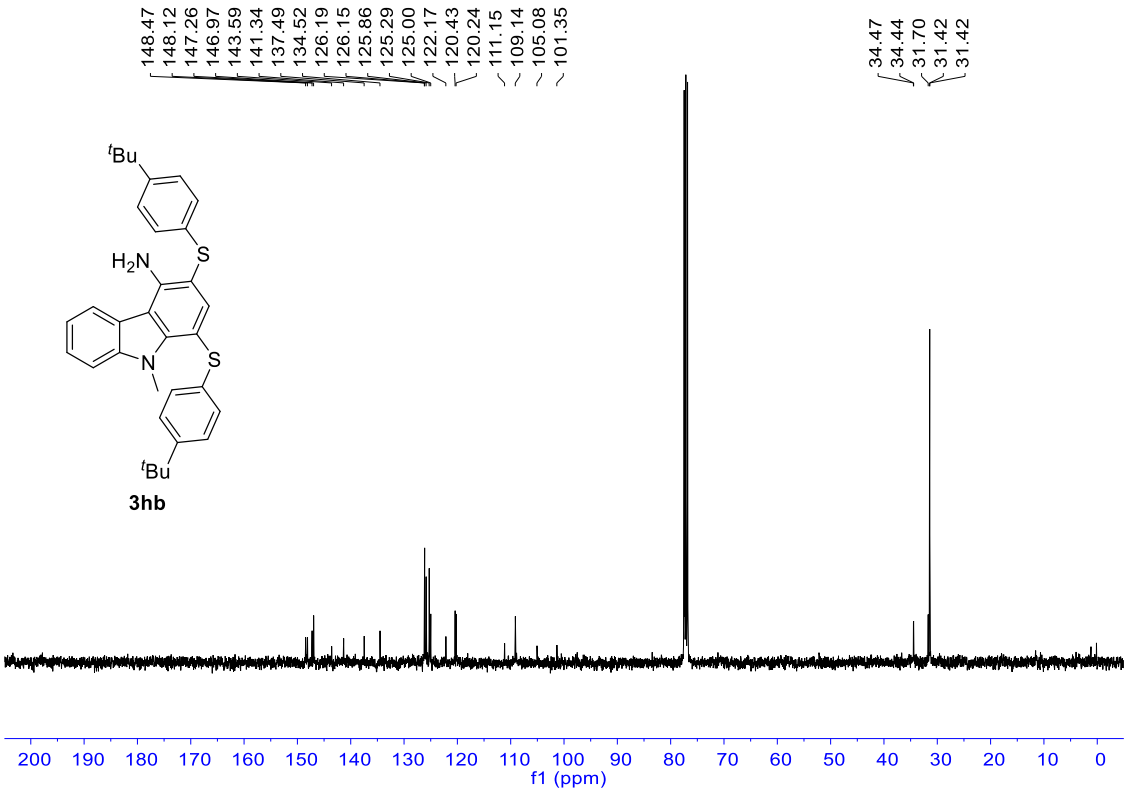
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3gb**



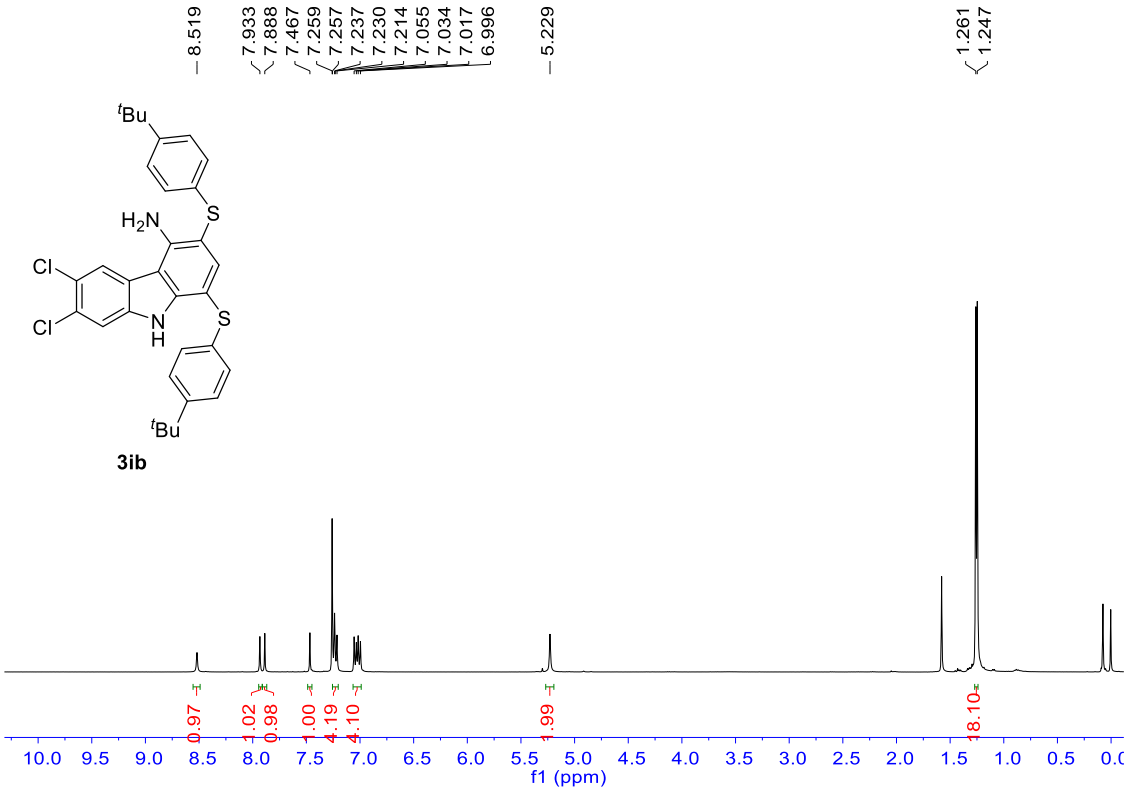
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3gb**



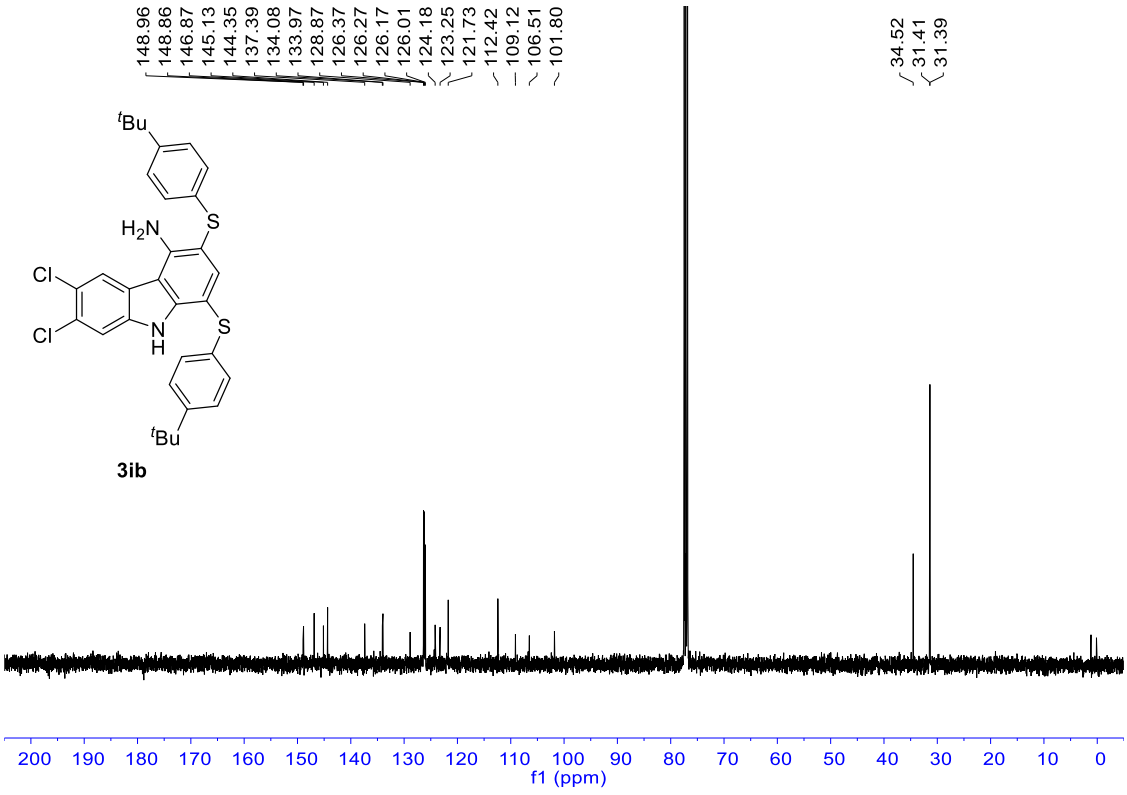
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3hb**



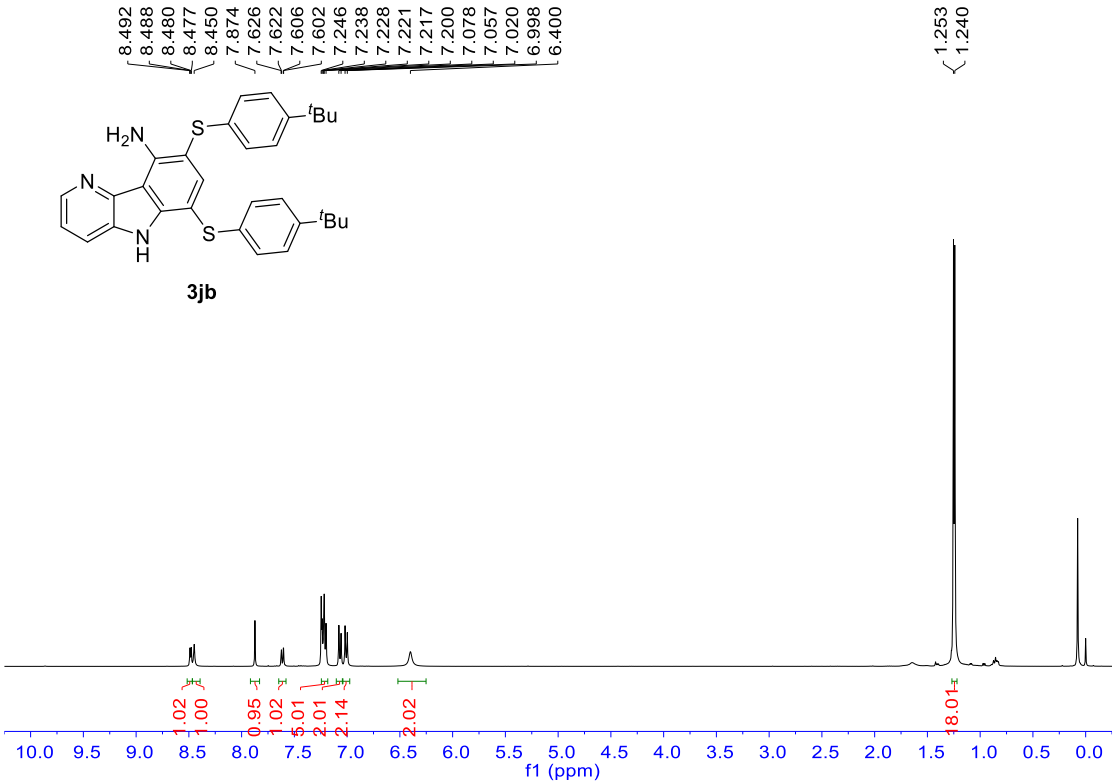
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3hb**



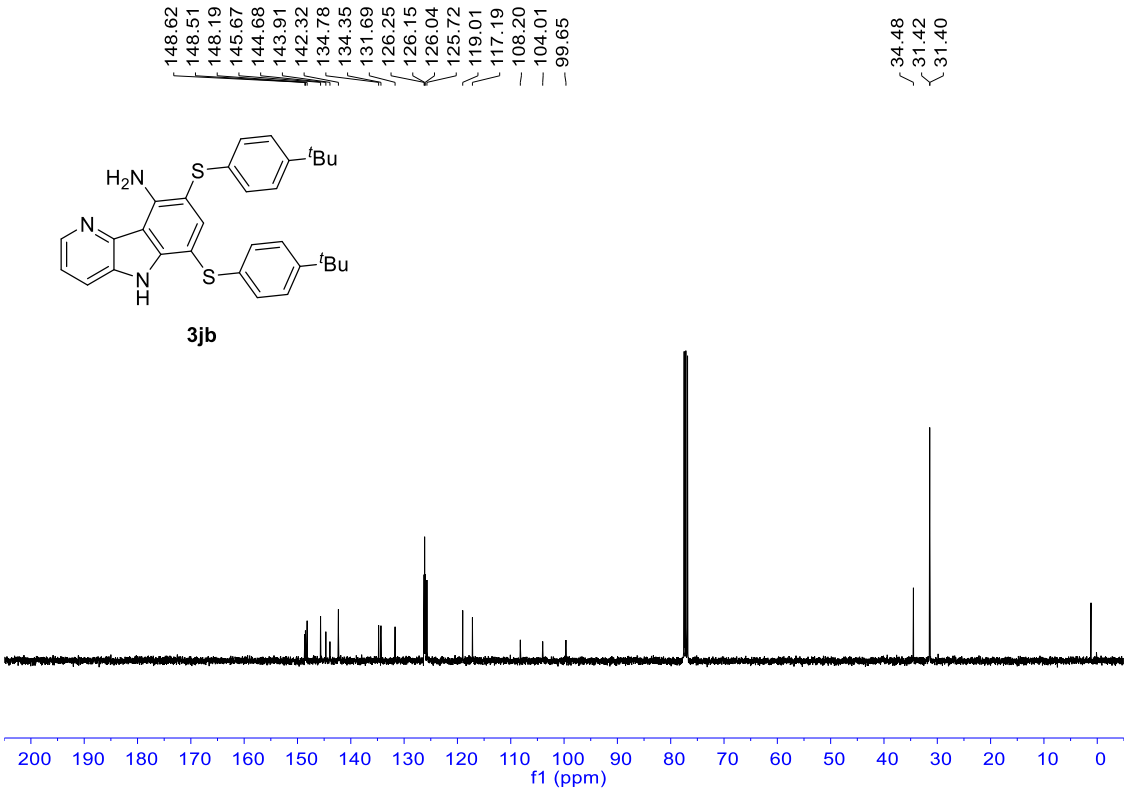
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ib**



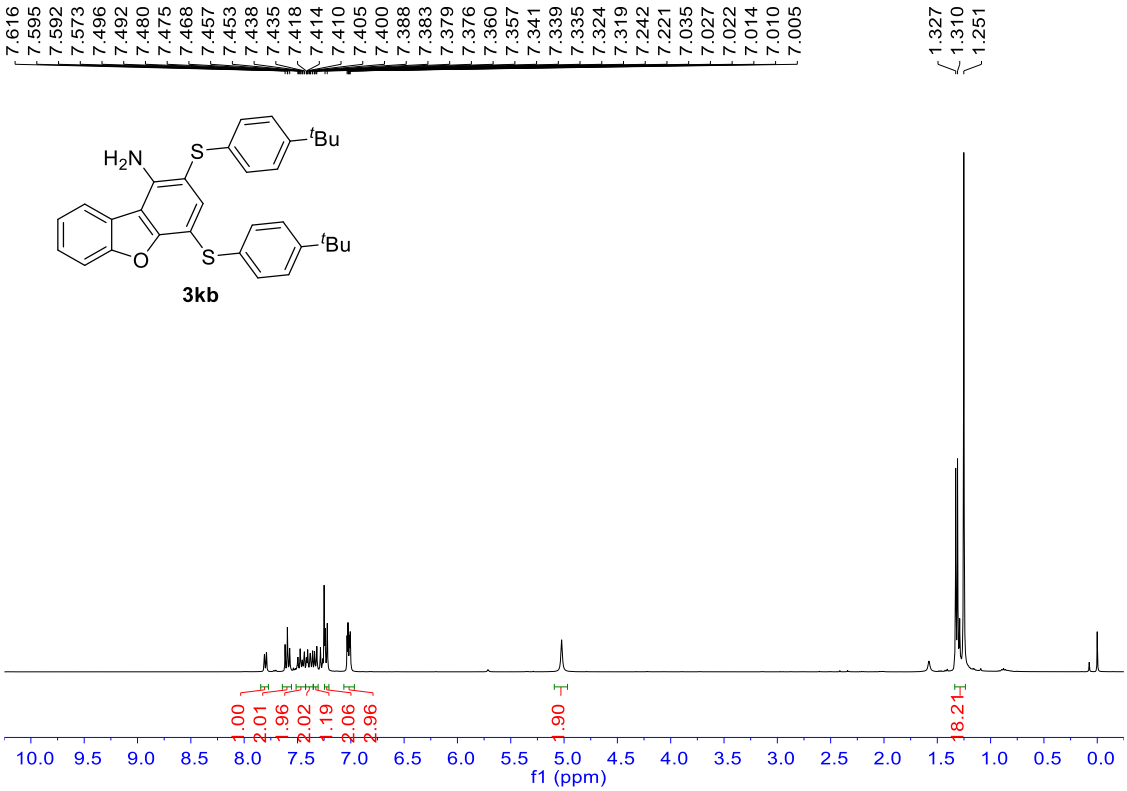
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3ib**



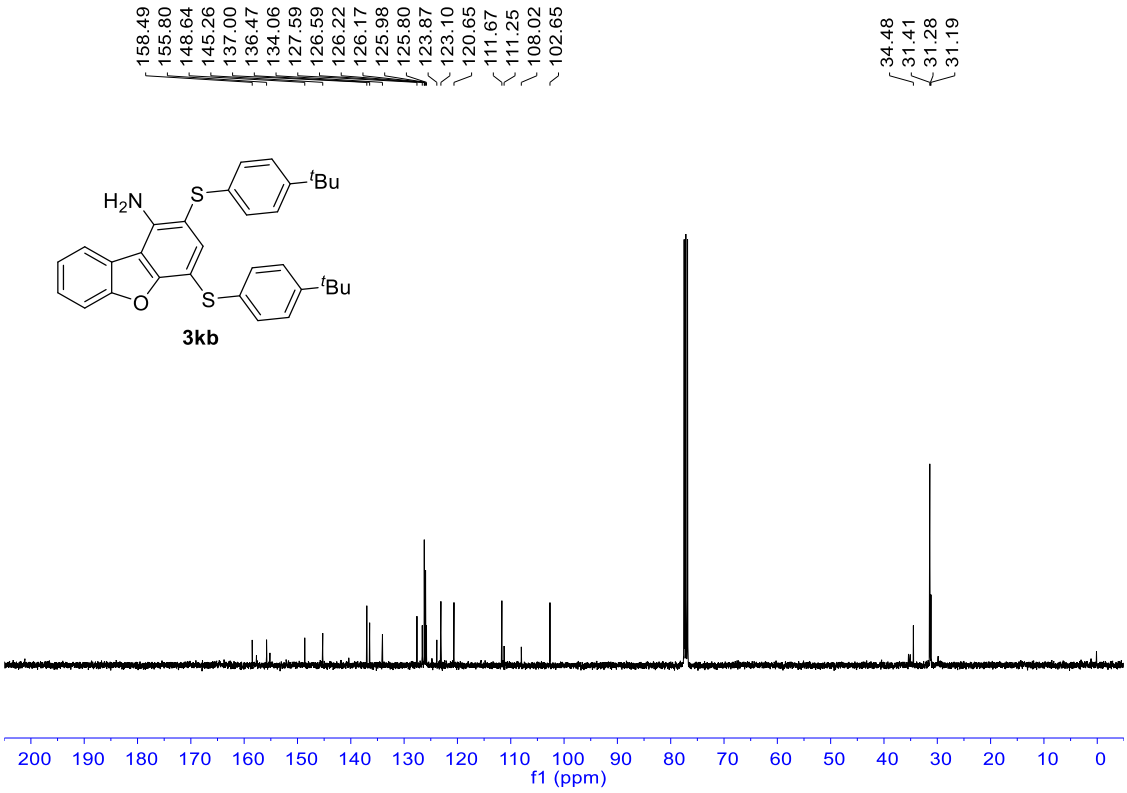
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3jb**



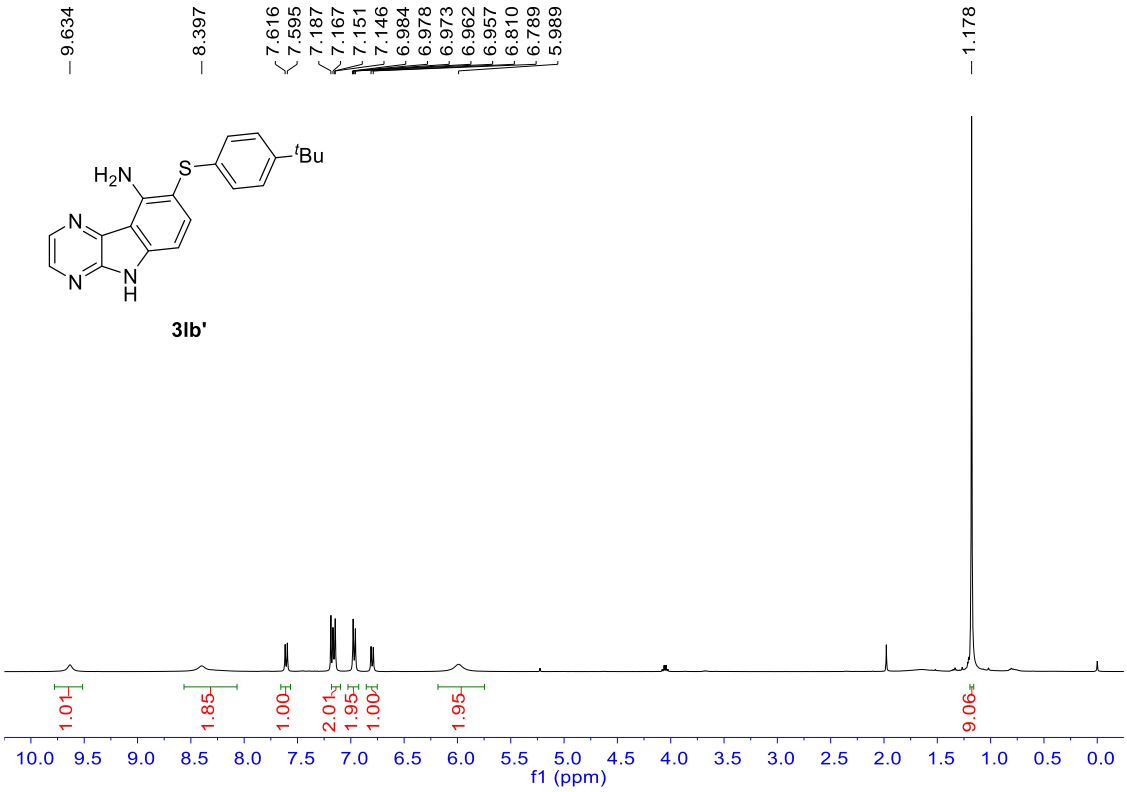
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3jb**



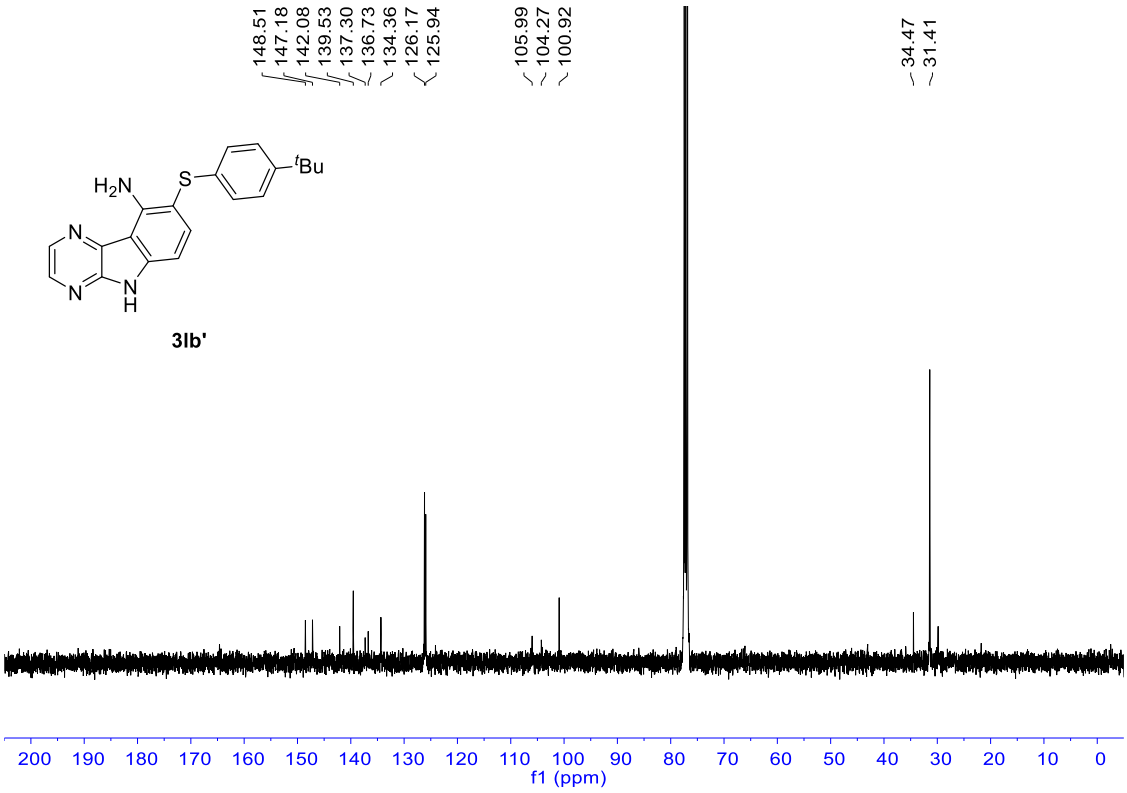
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3kb**



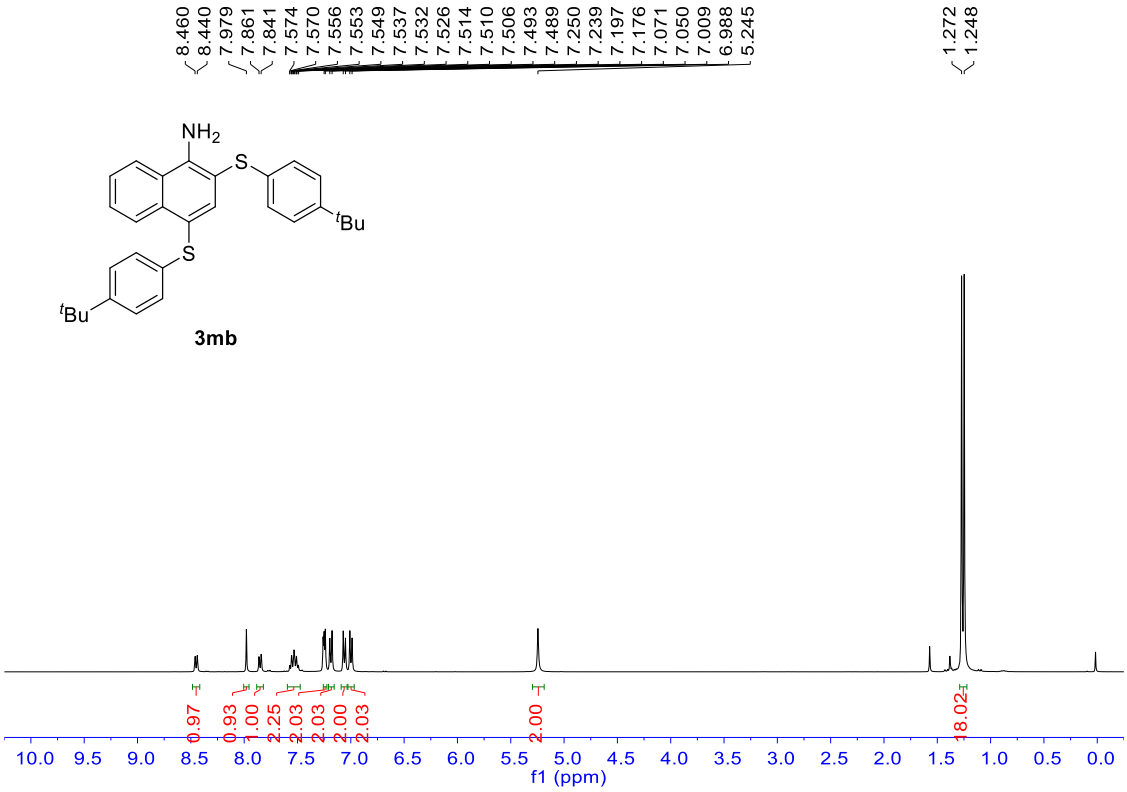
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3kb**



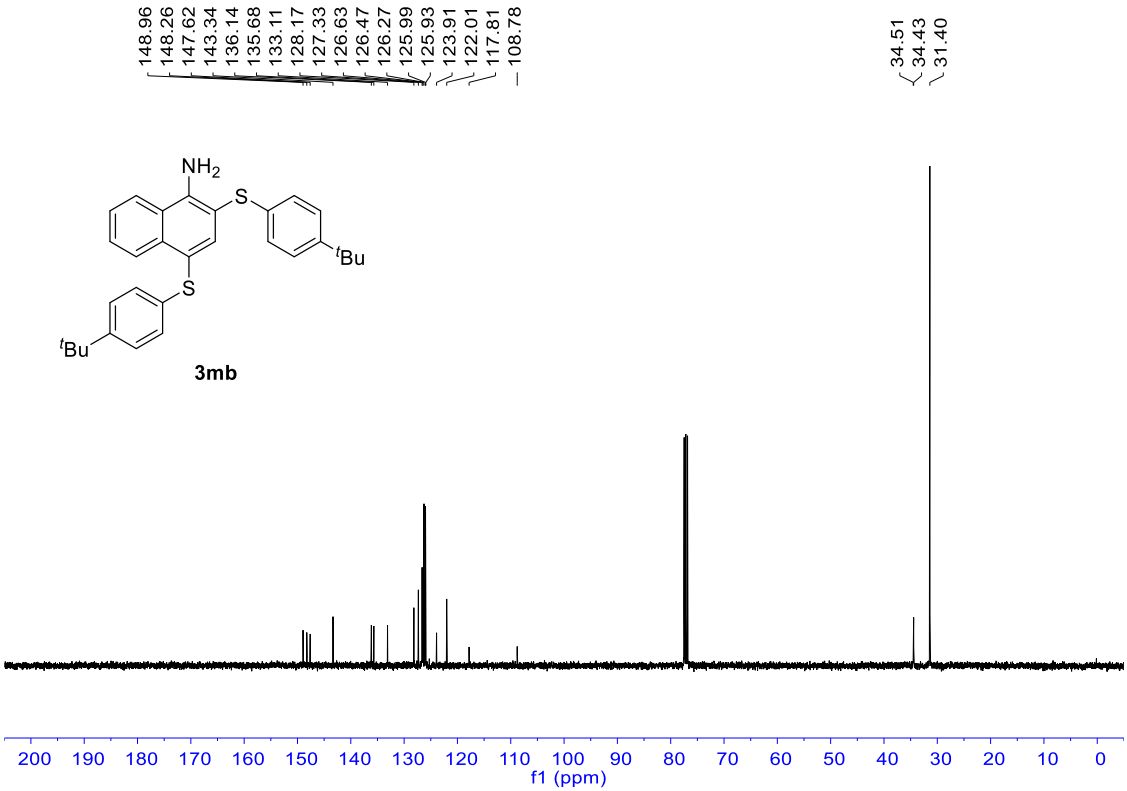
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3lb'**



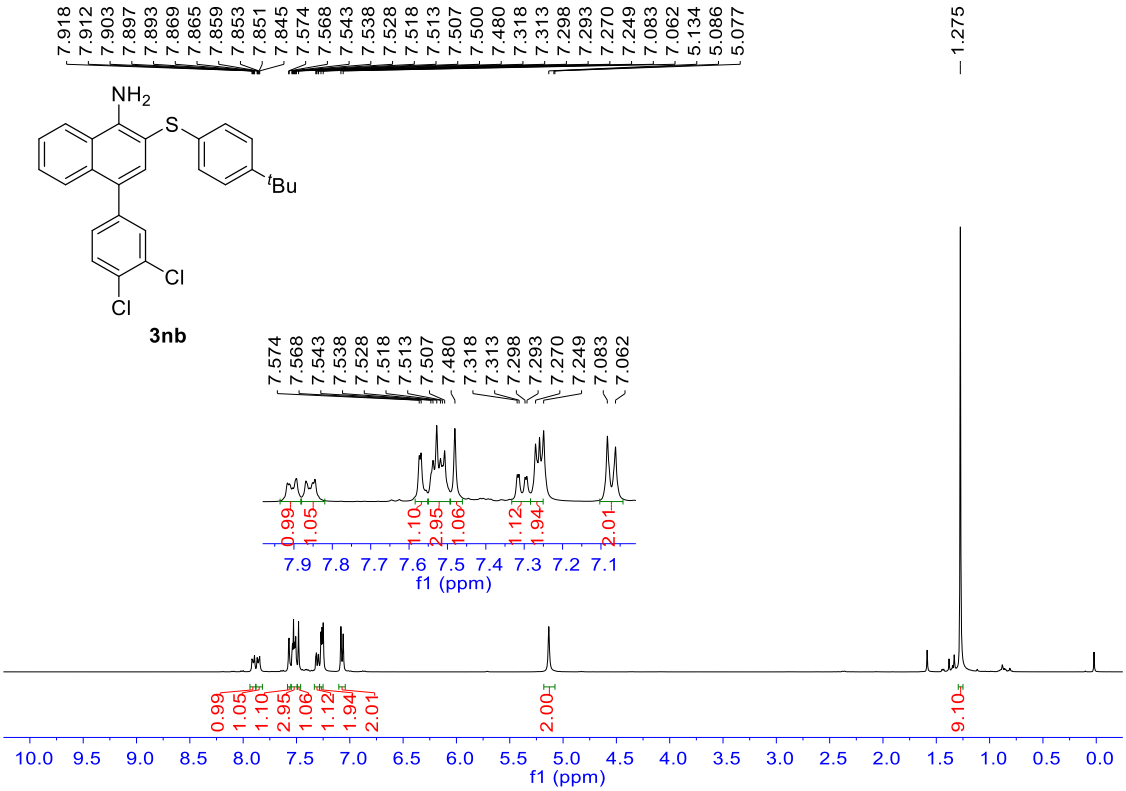
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3lb'**



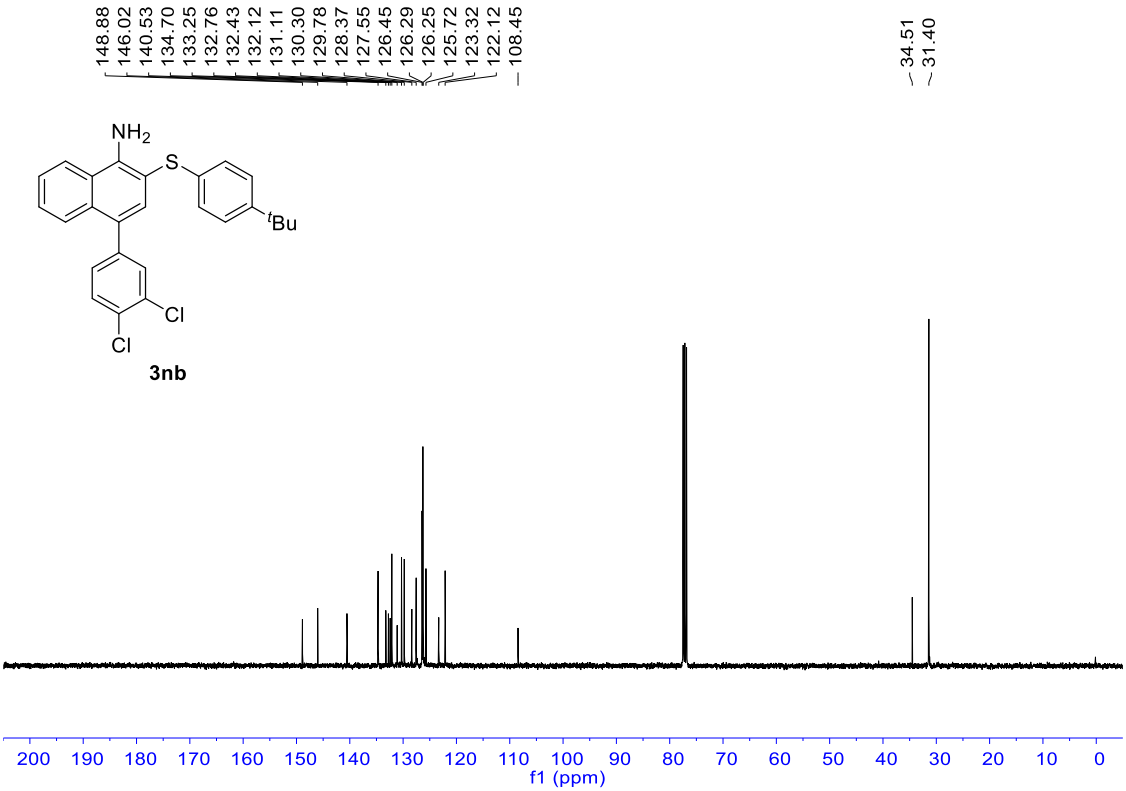
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3mb**



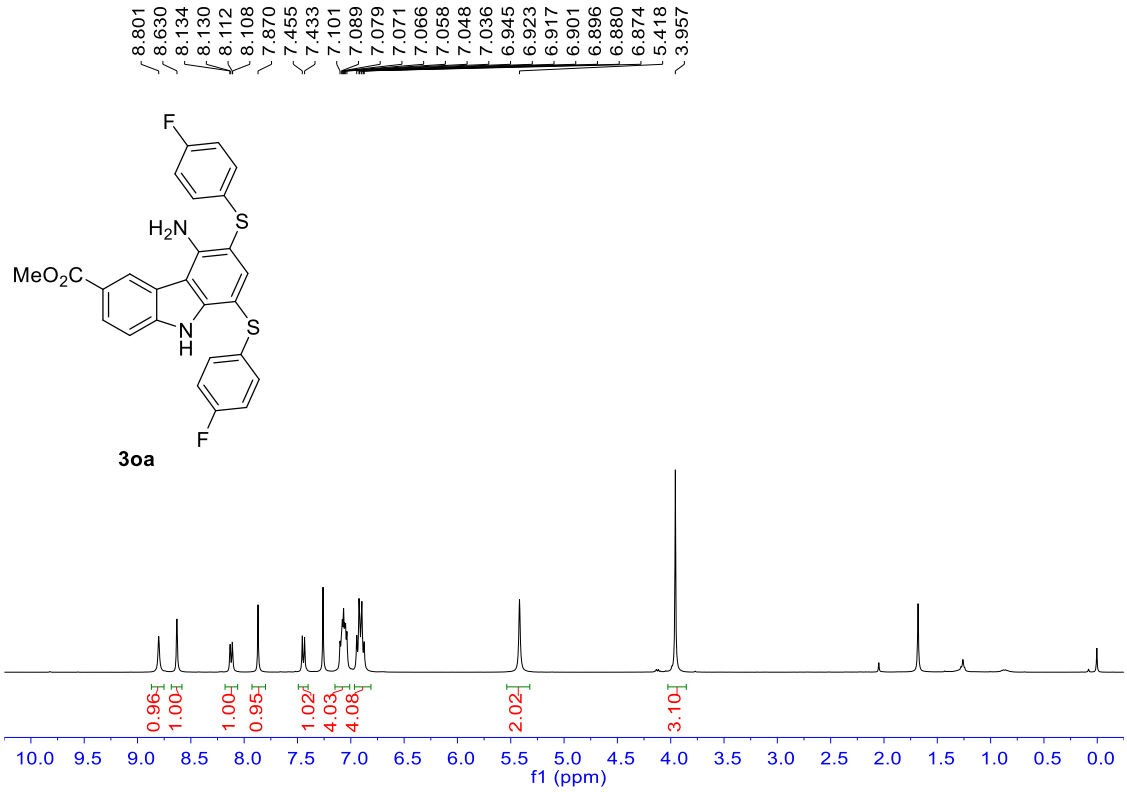
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3mb**



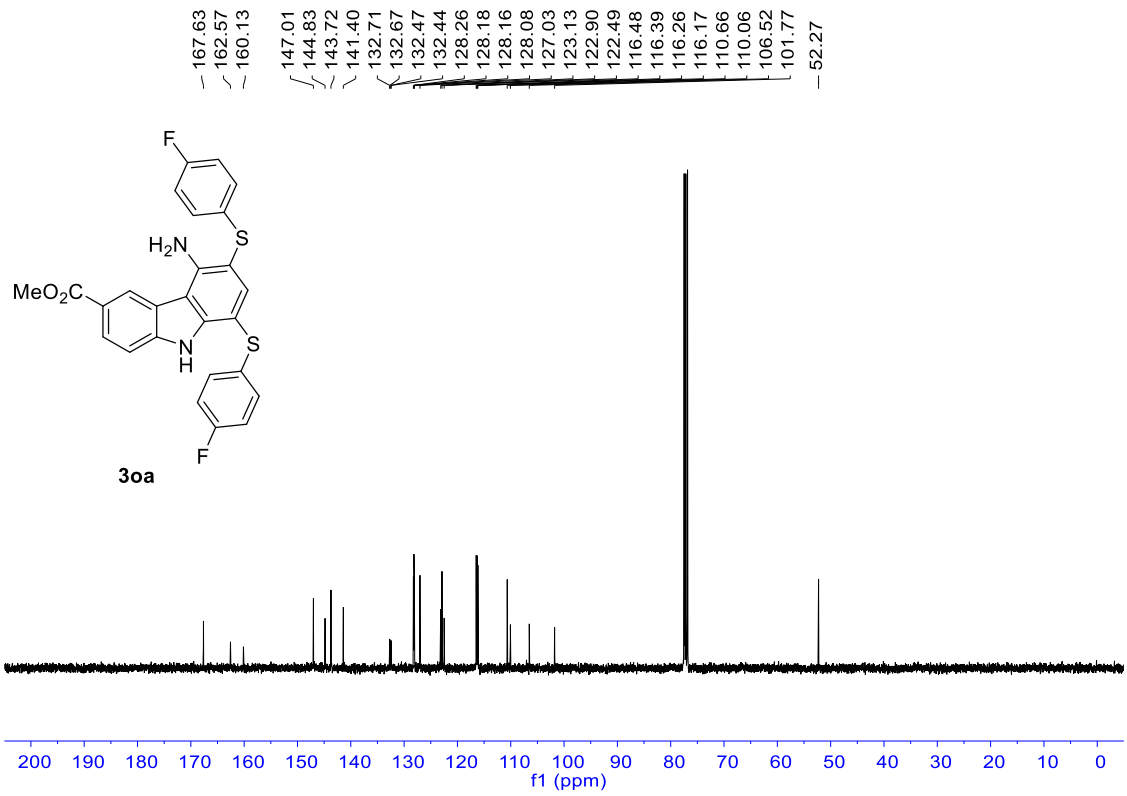
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3nb**



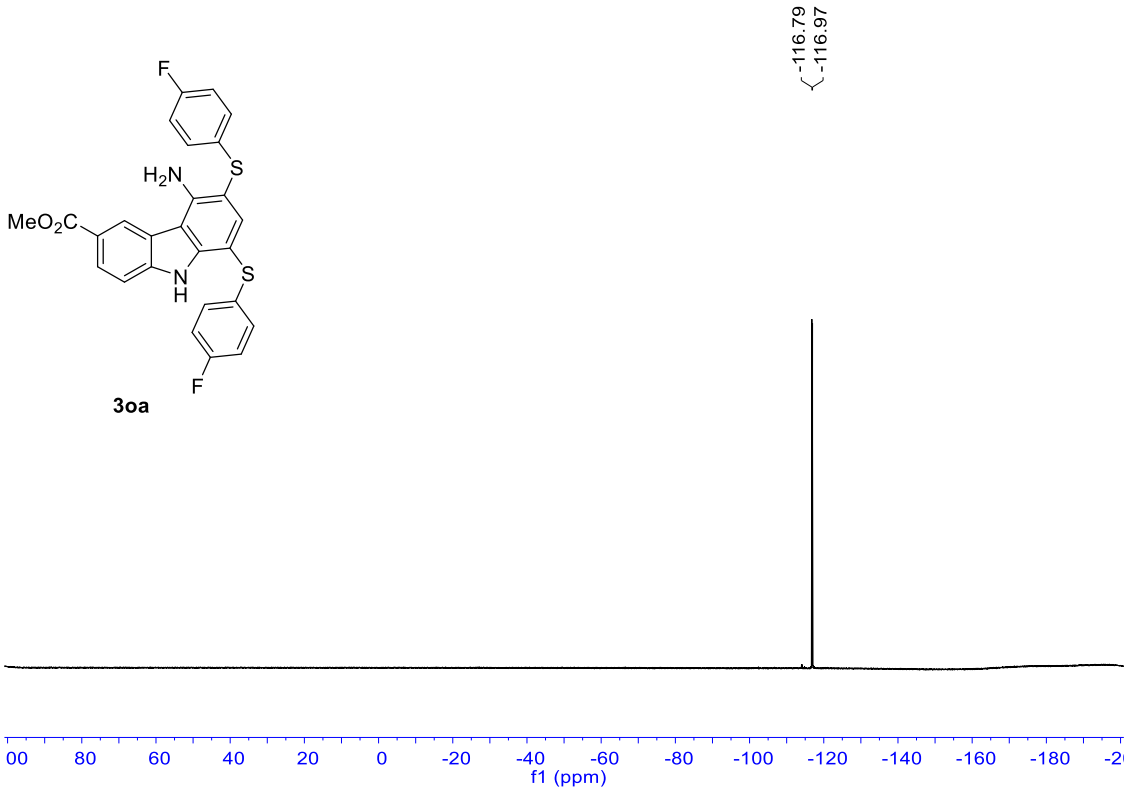
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3nb**



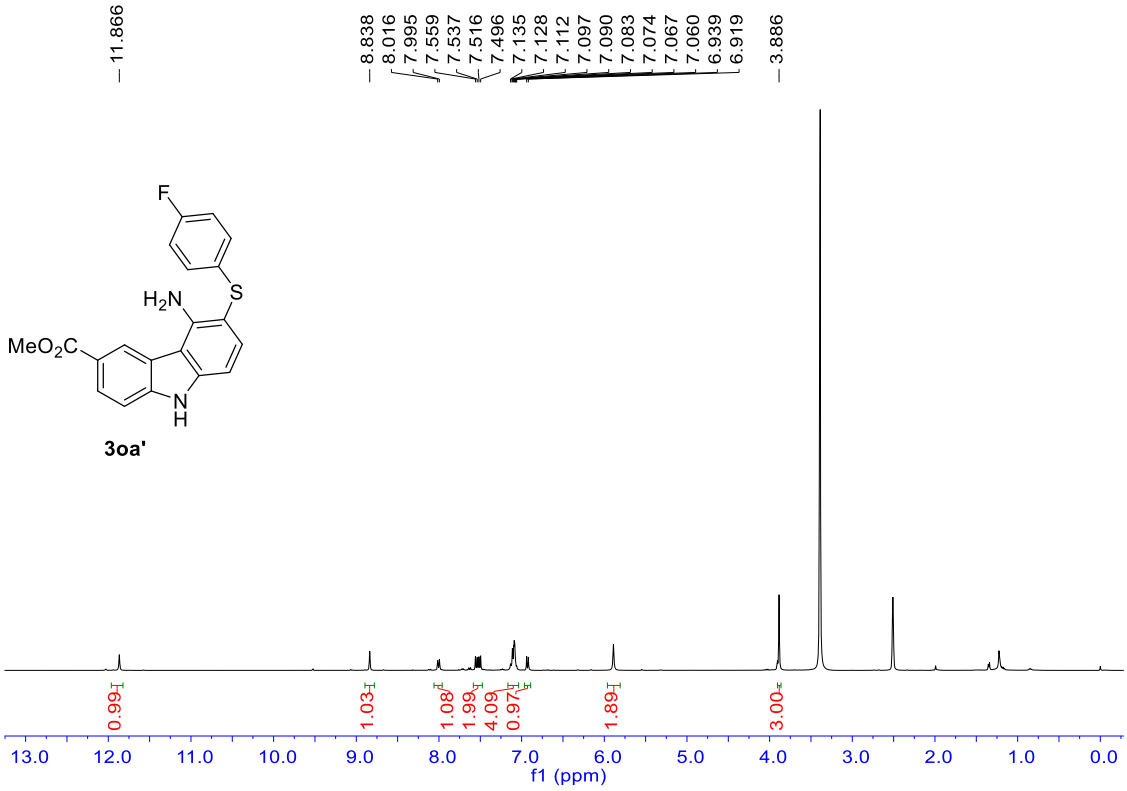
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3oa**



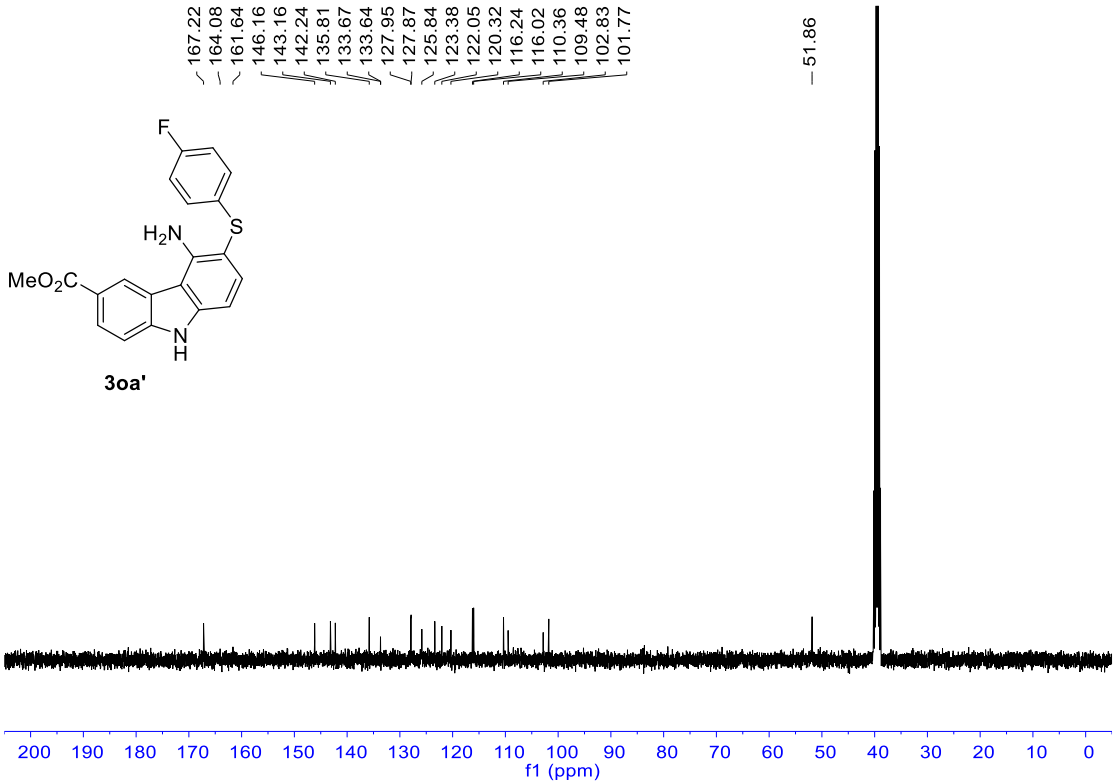
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **3oa**



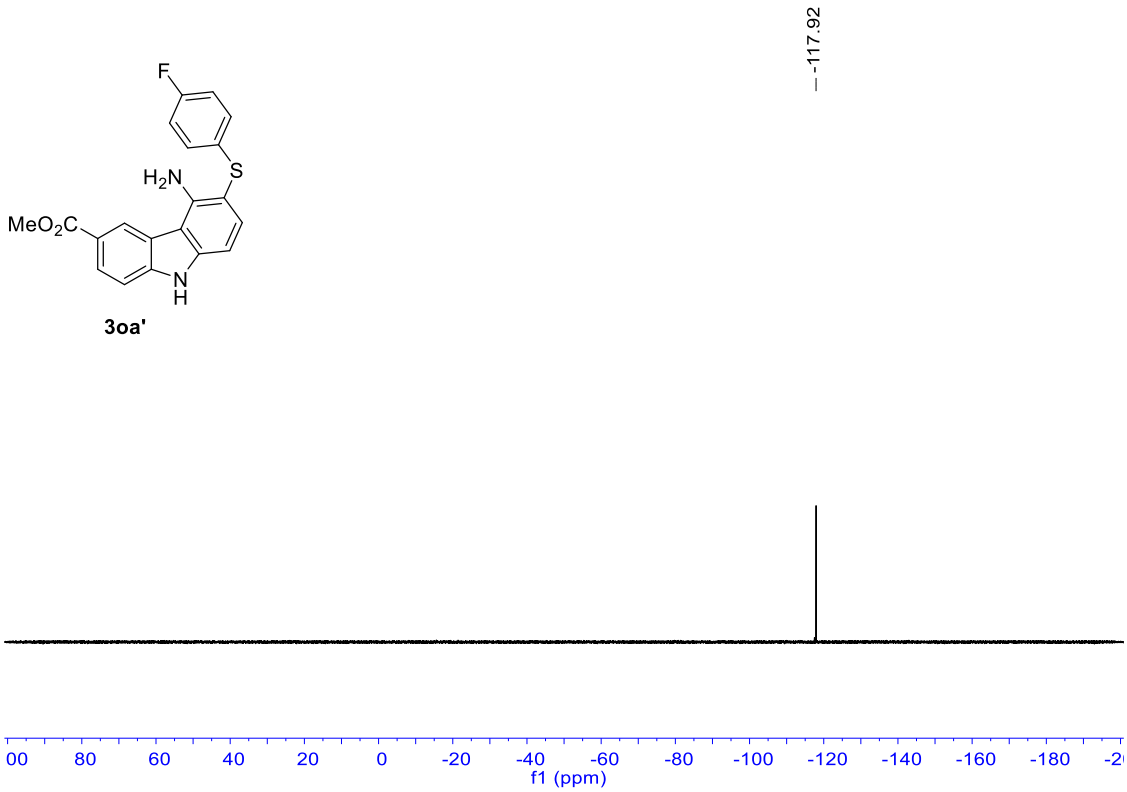
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **3oa**



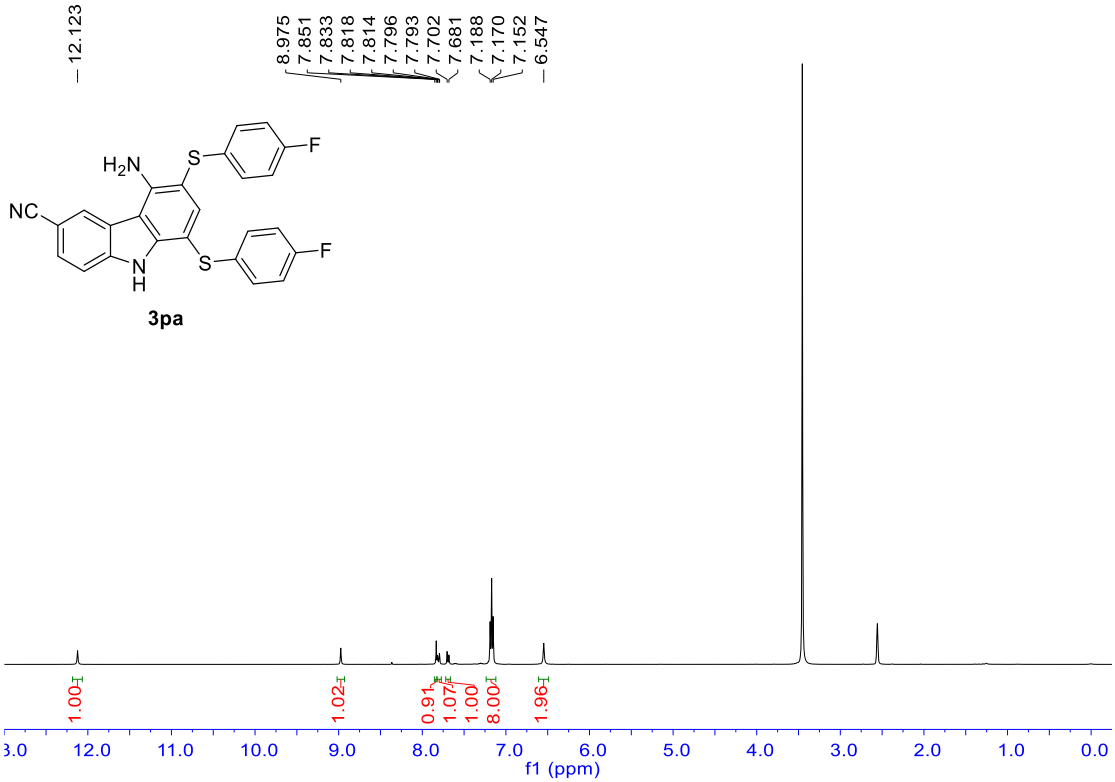
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3oa'**



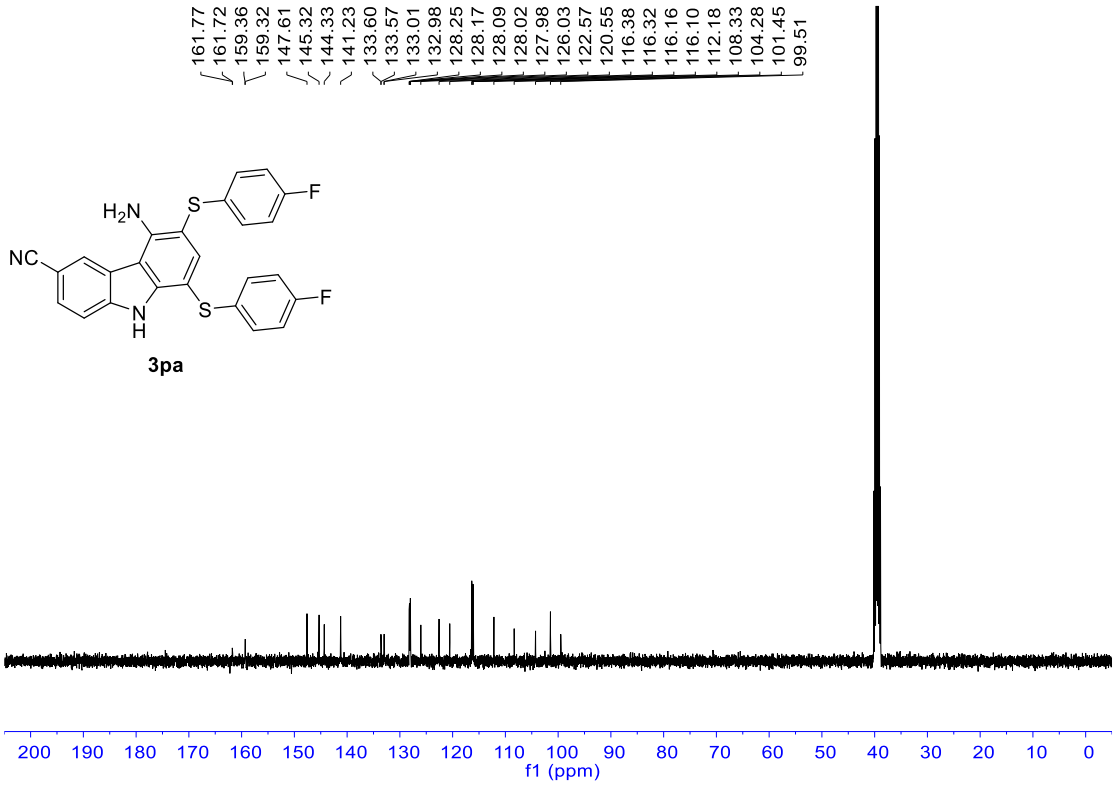
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **3oa'**



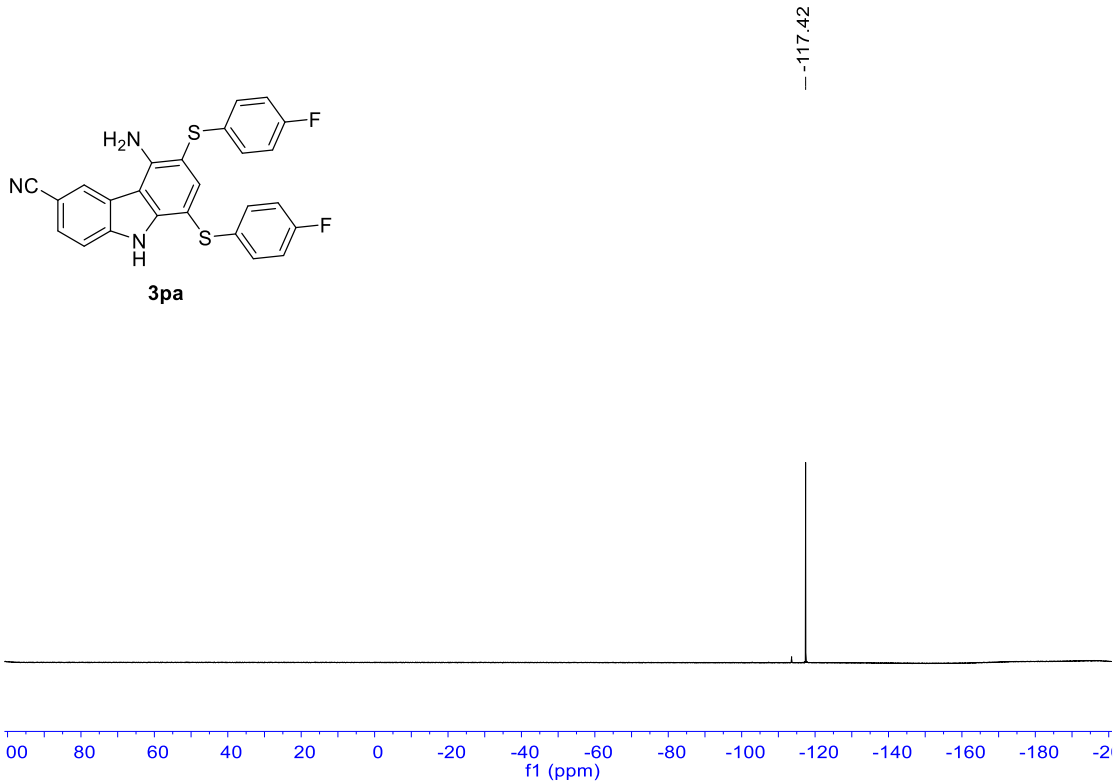
^{19}F NMR spectrum (376 MHz, DMSO-d_6) of compound **3oa'**



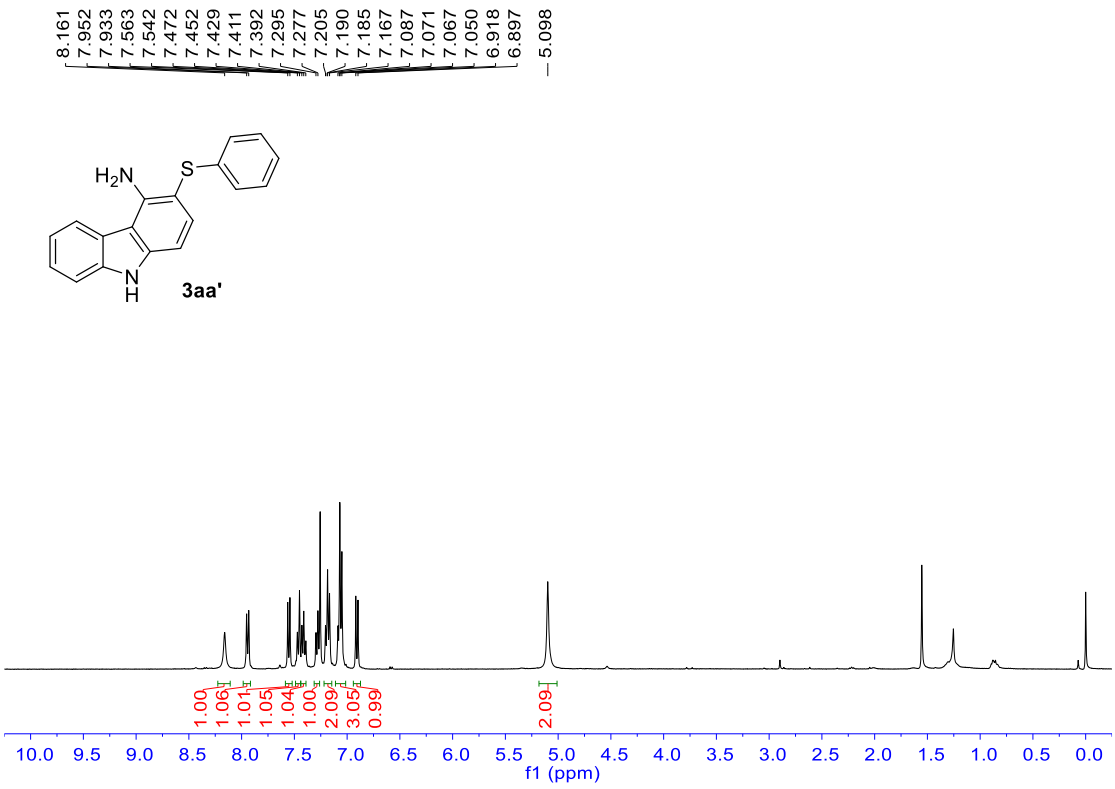
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3pa**



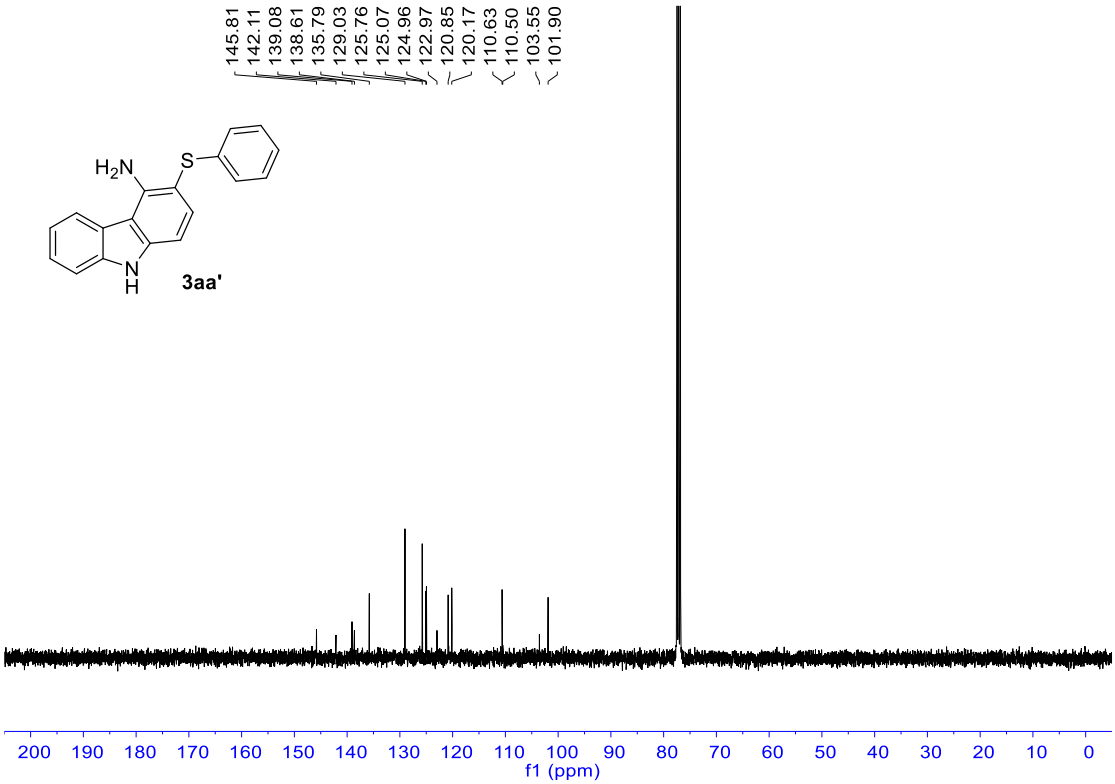
^{13}C{^{1}H} NMR spectrum (101 MHz, DMSO-d_6) of compound **3pa**



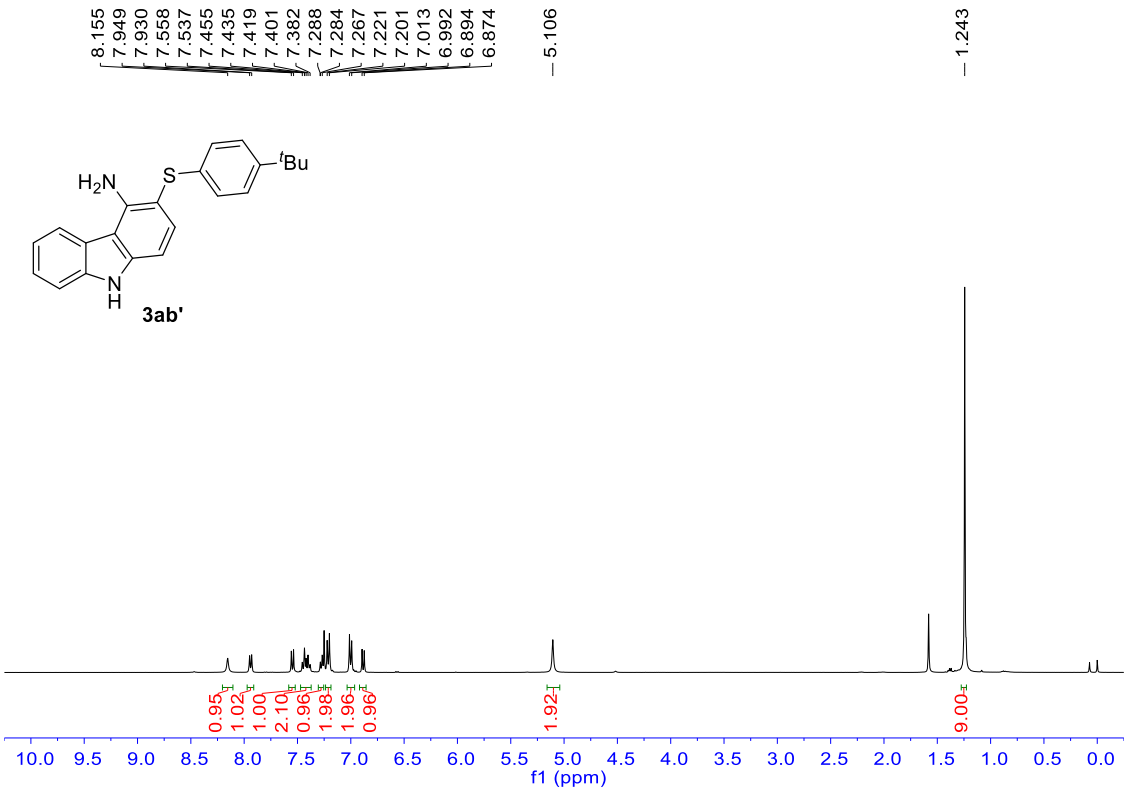
^{19}F NMR spectrum (376 MHz, DMSO-d_6) of compound **3pa**



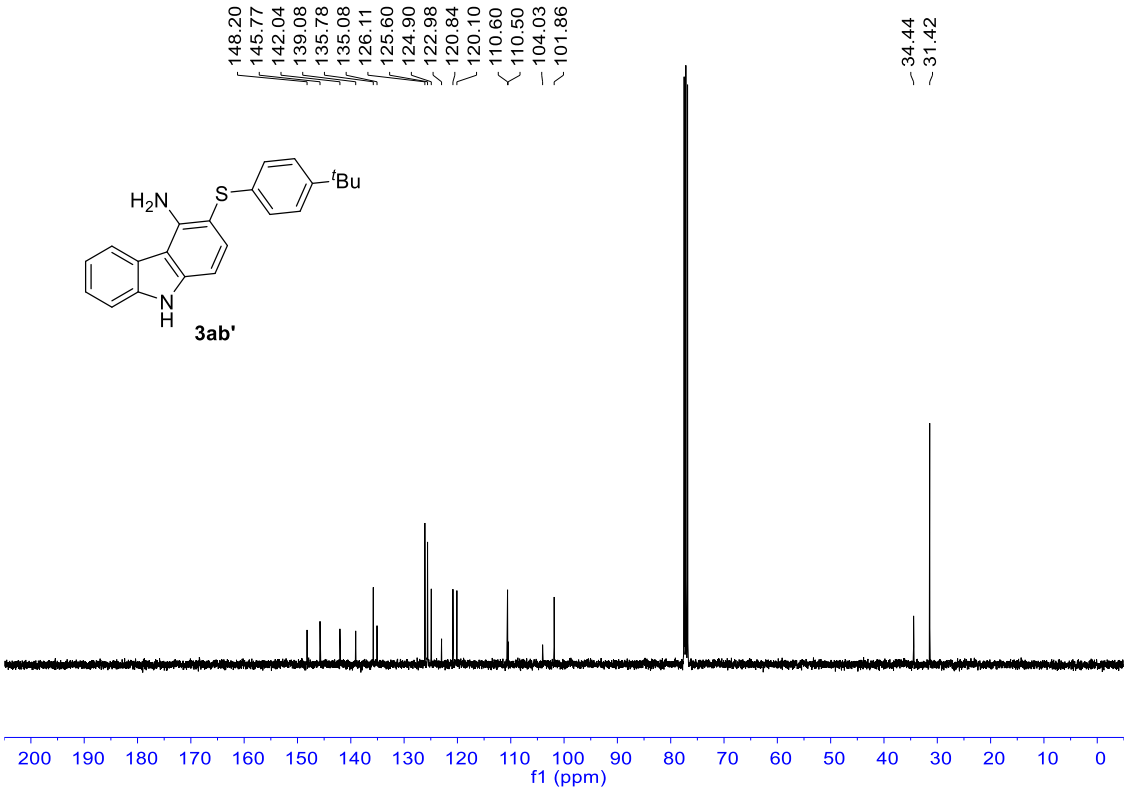
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3aa'**



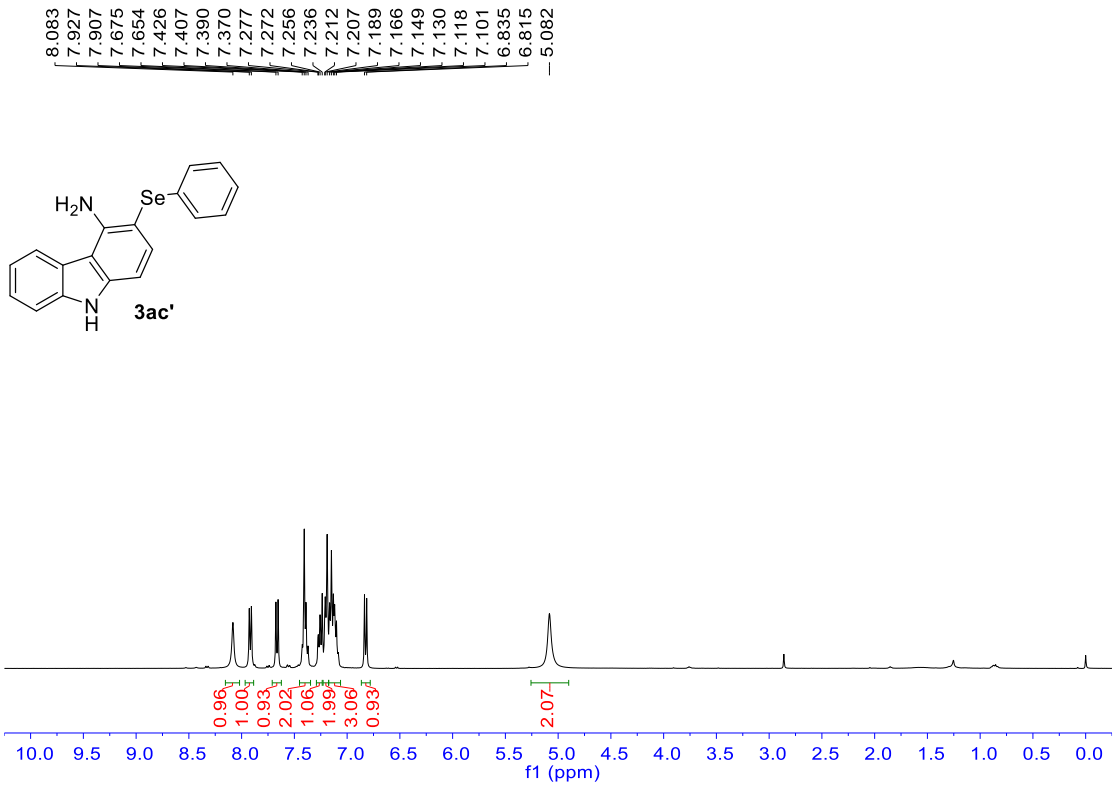
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **3aa'**



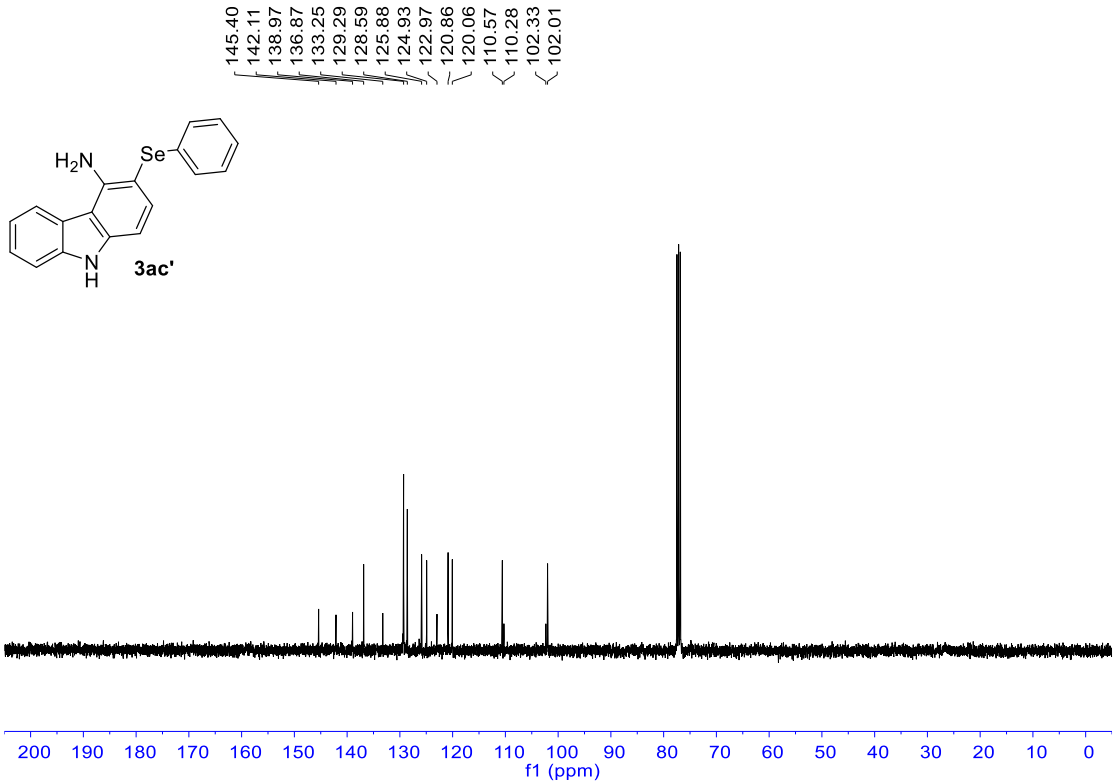
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3ab'**



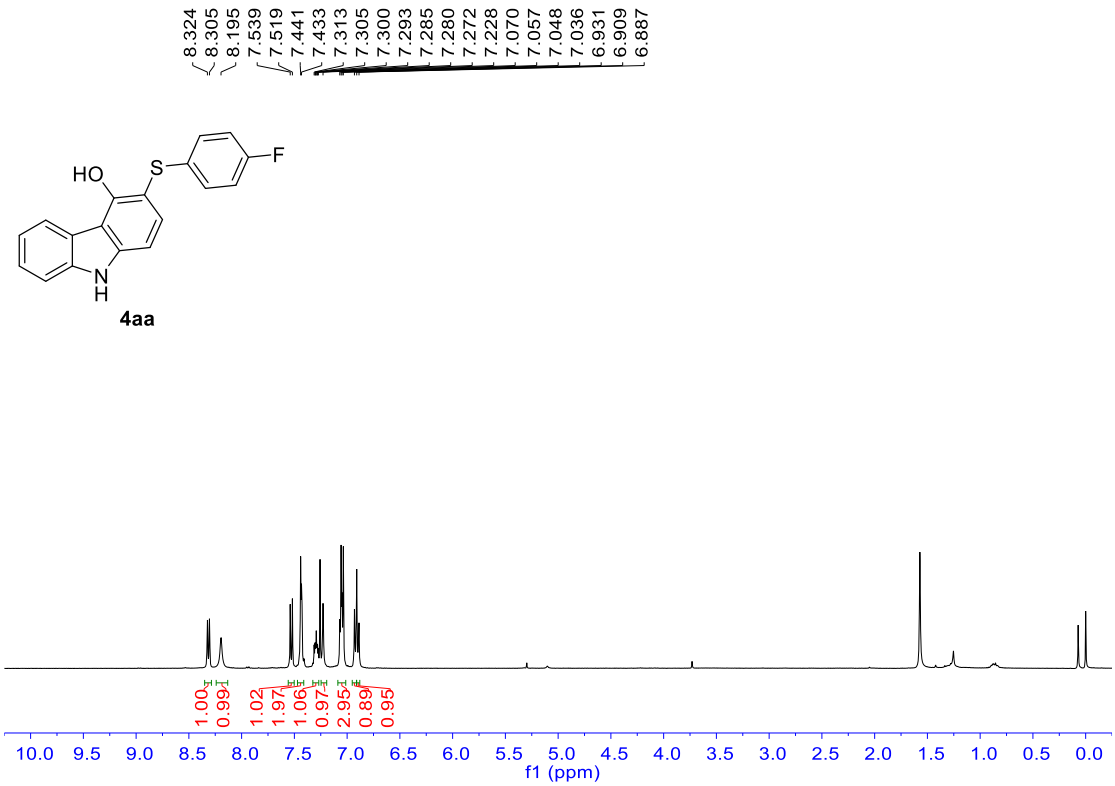
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **3ab'**



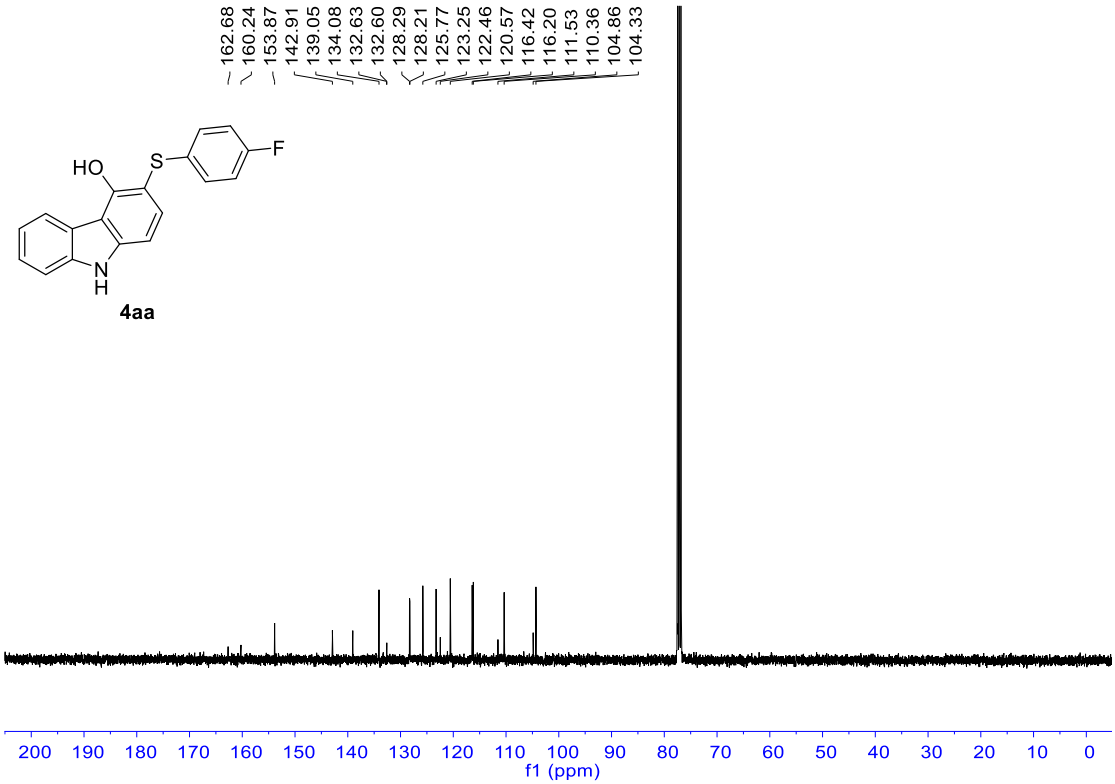
^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **3ac'**



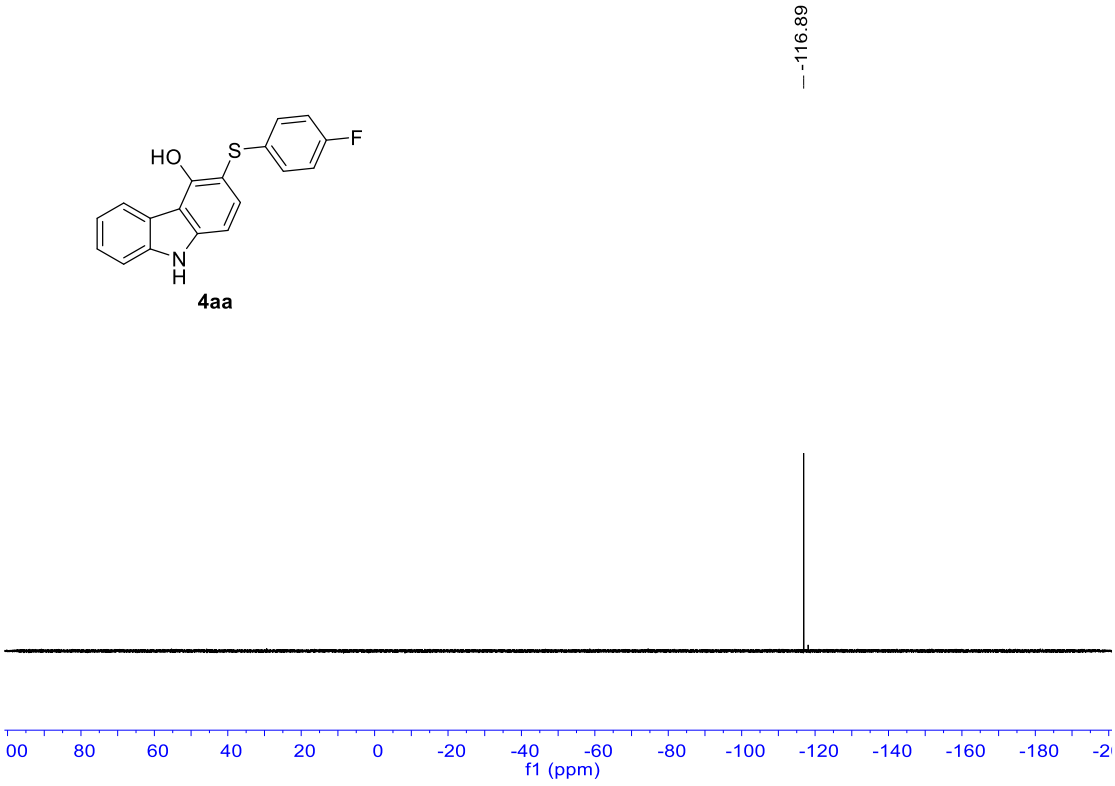
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **3ac'**



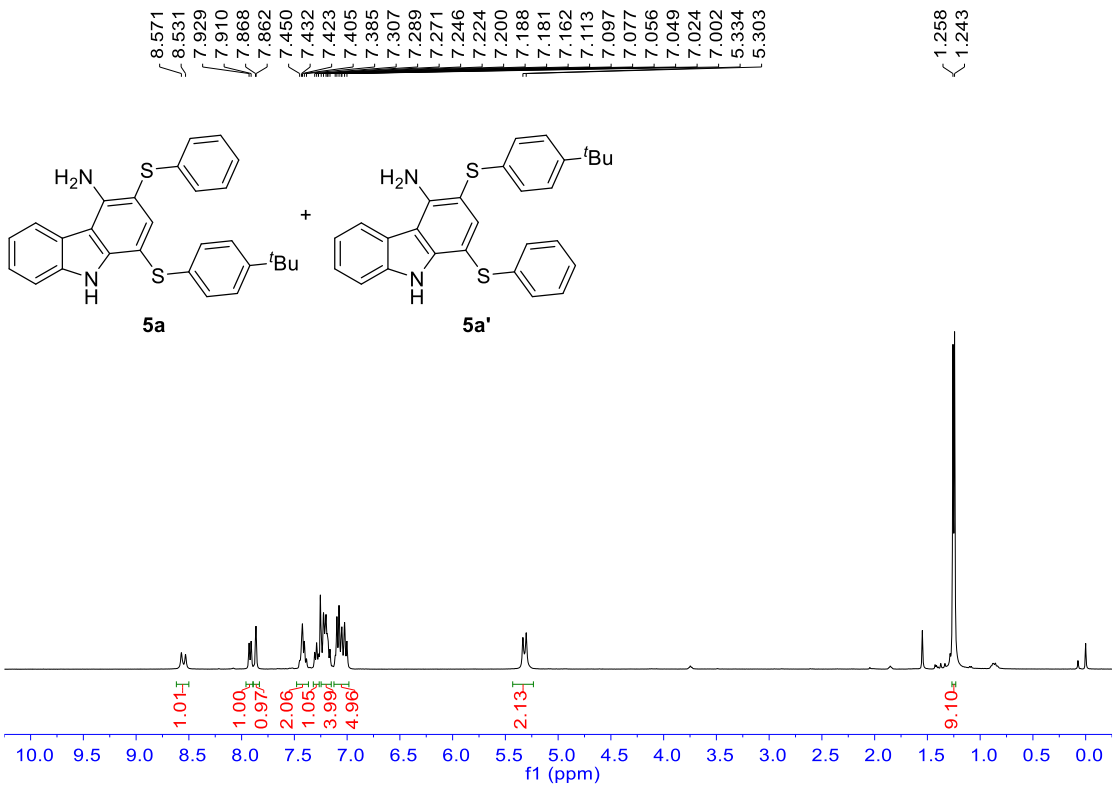
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4aa**



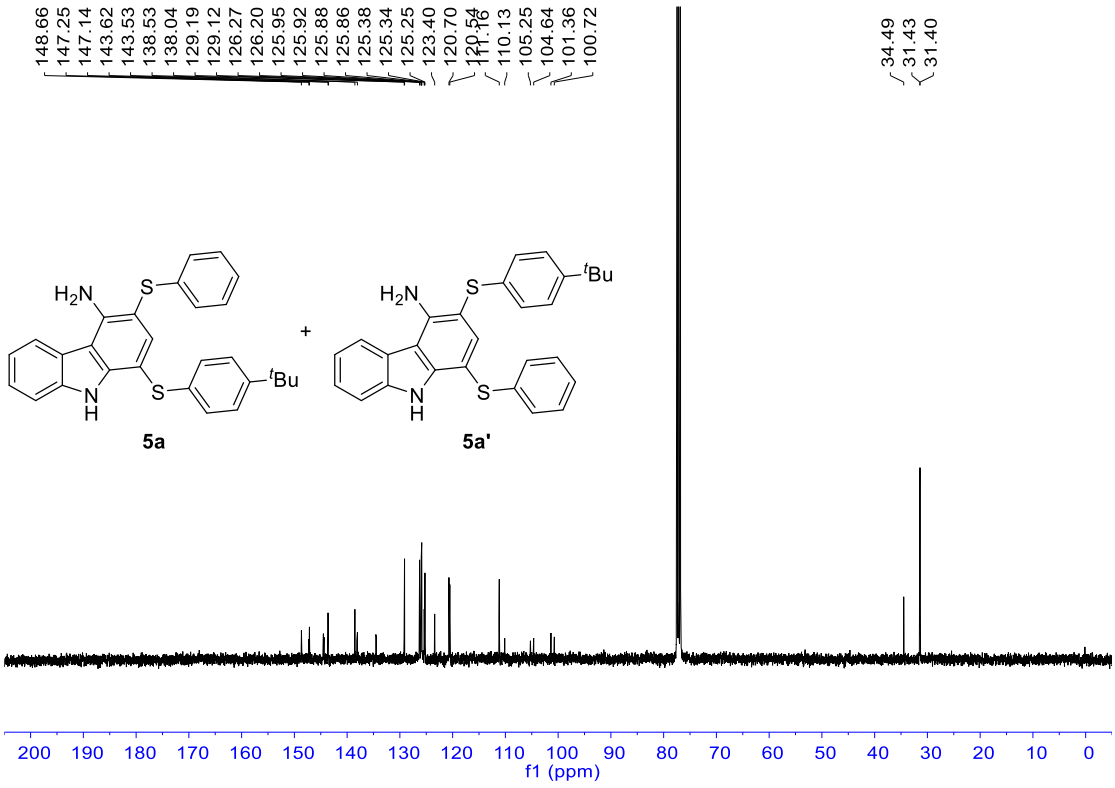
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **4aa**



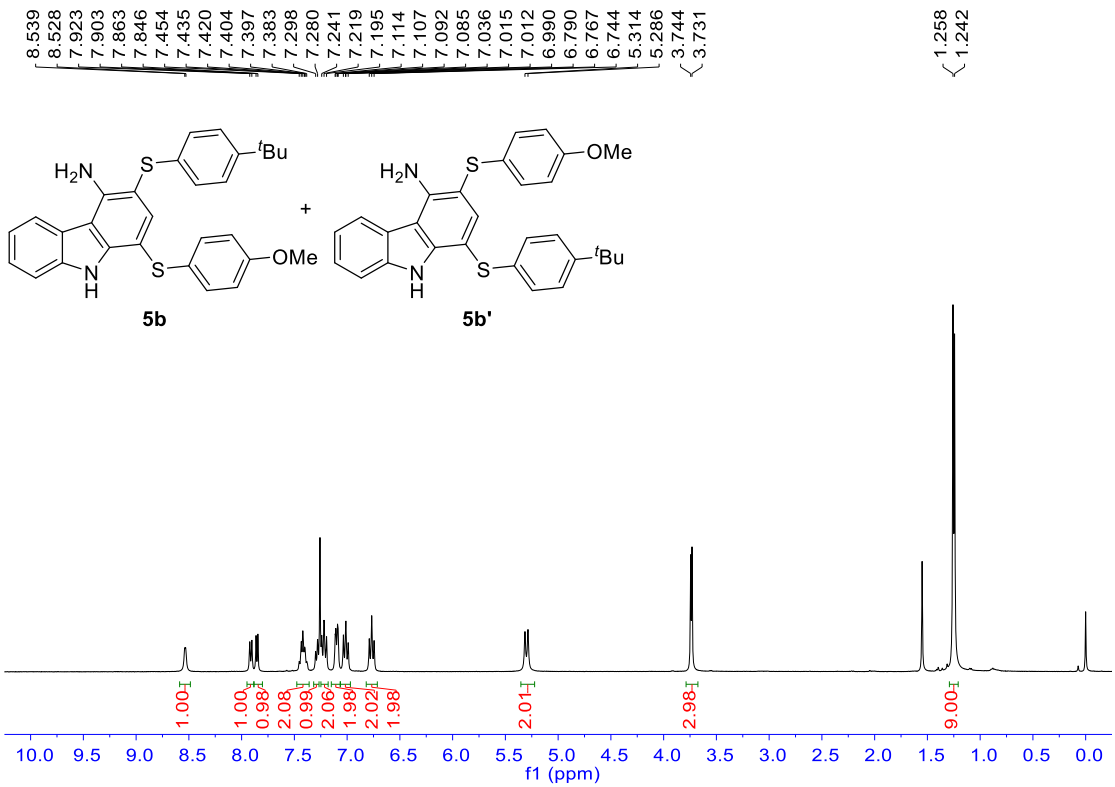
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **4aa**



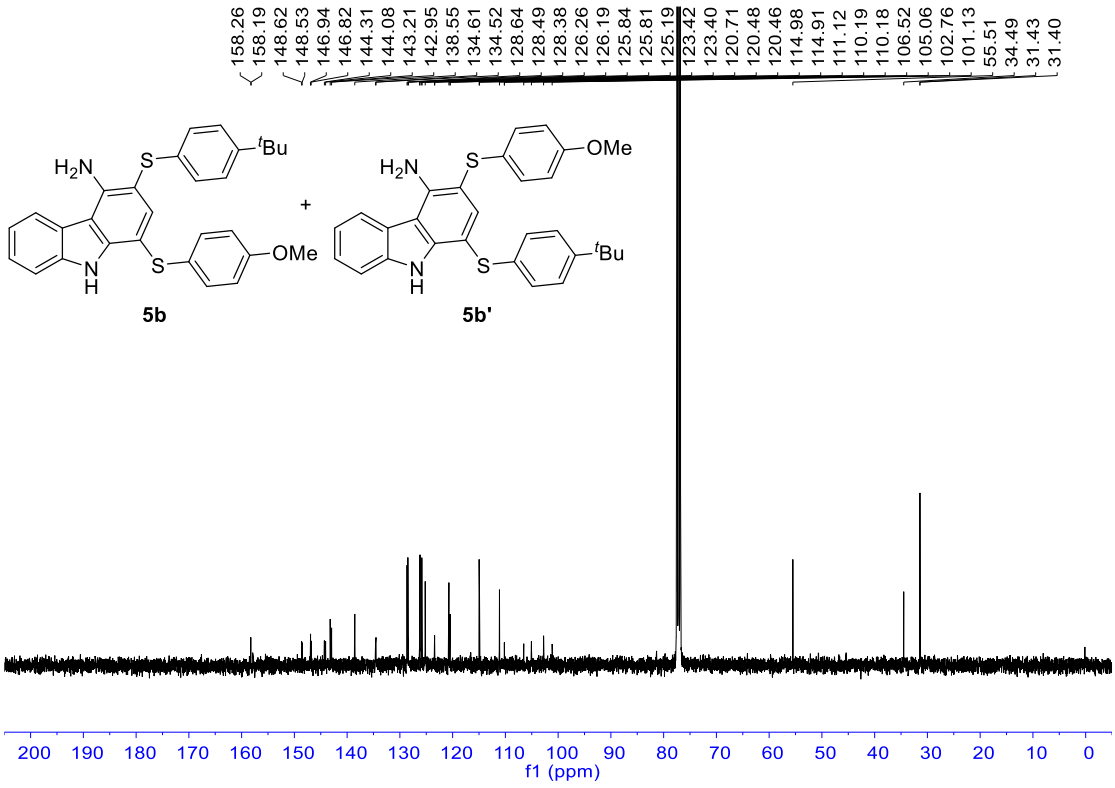
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5a** + **5a'**



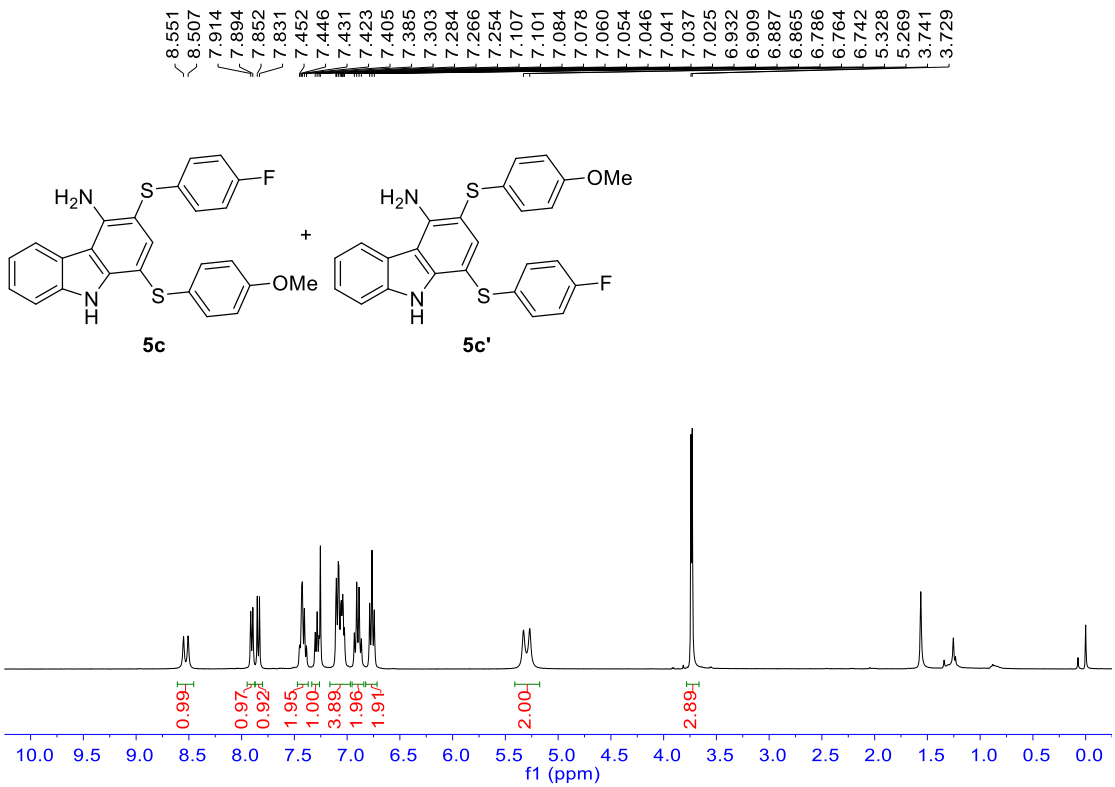
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **5a** + **5a'**



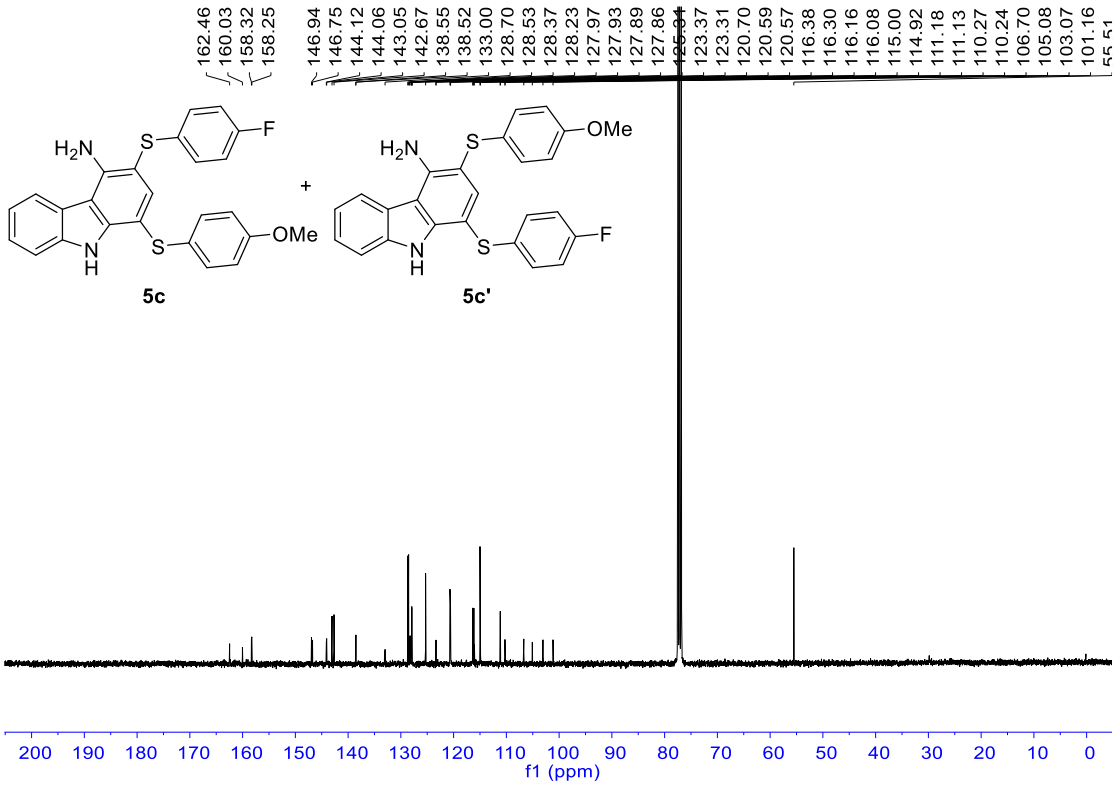
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5b** + **5b'**



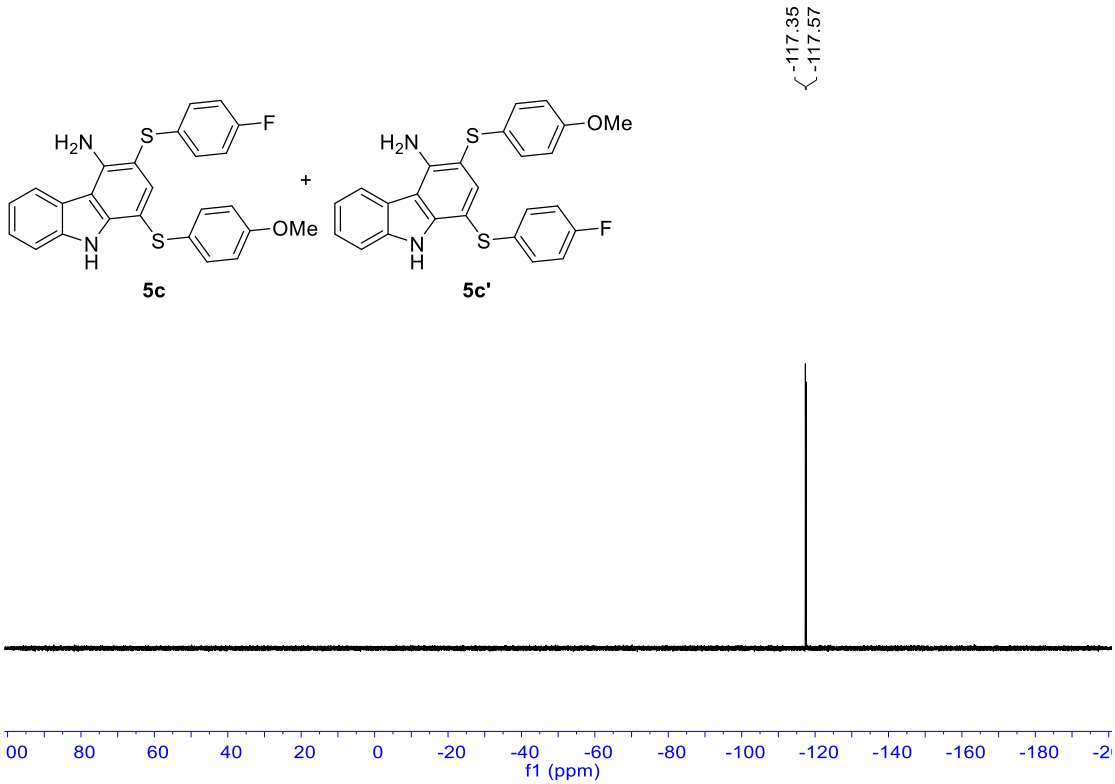
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **5b** +**5b'**



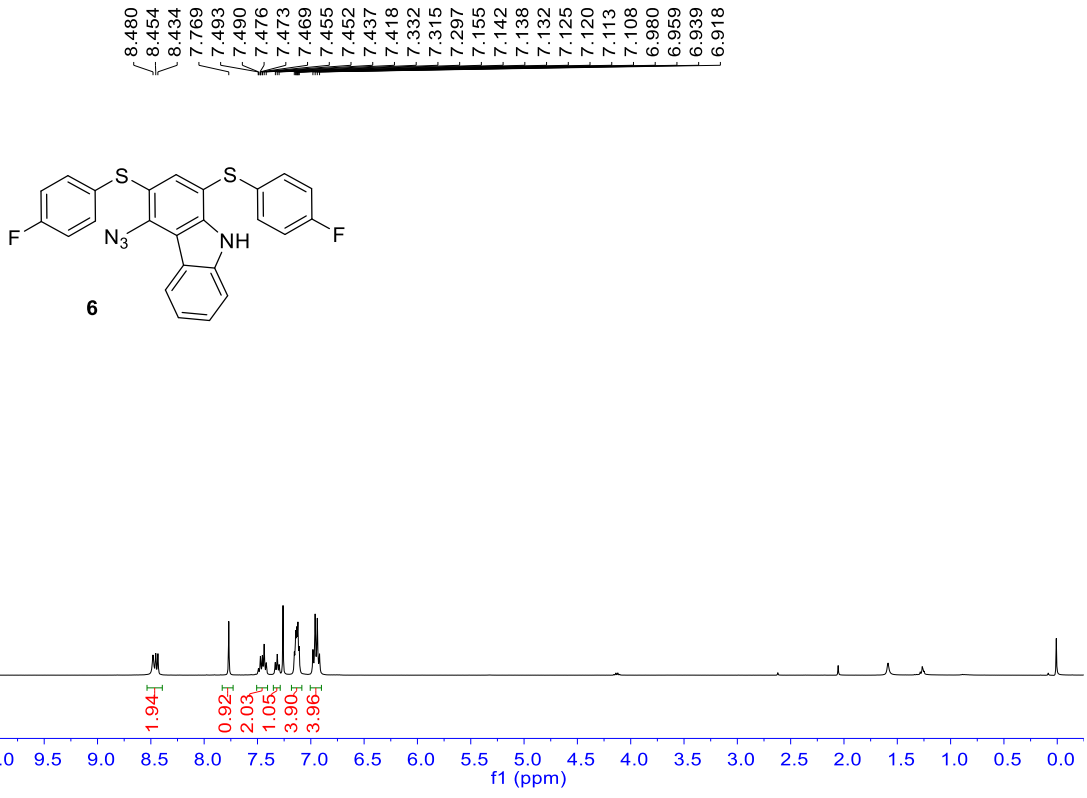
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5c** + **5c'**



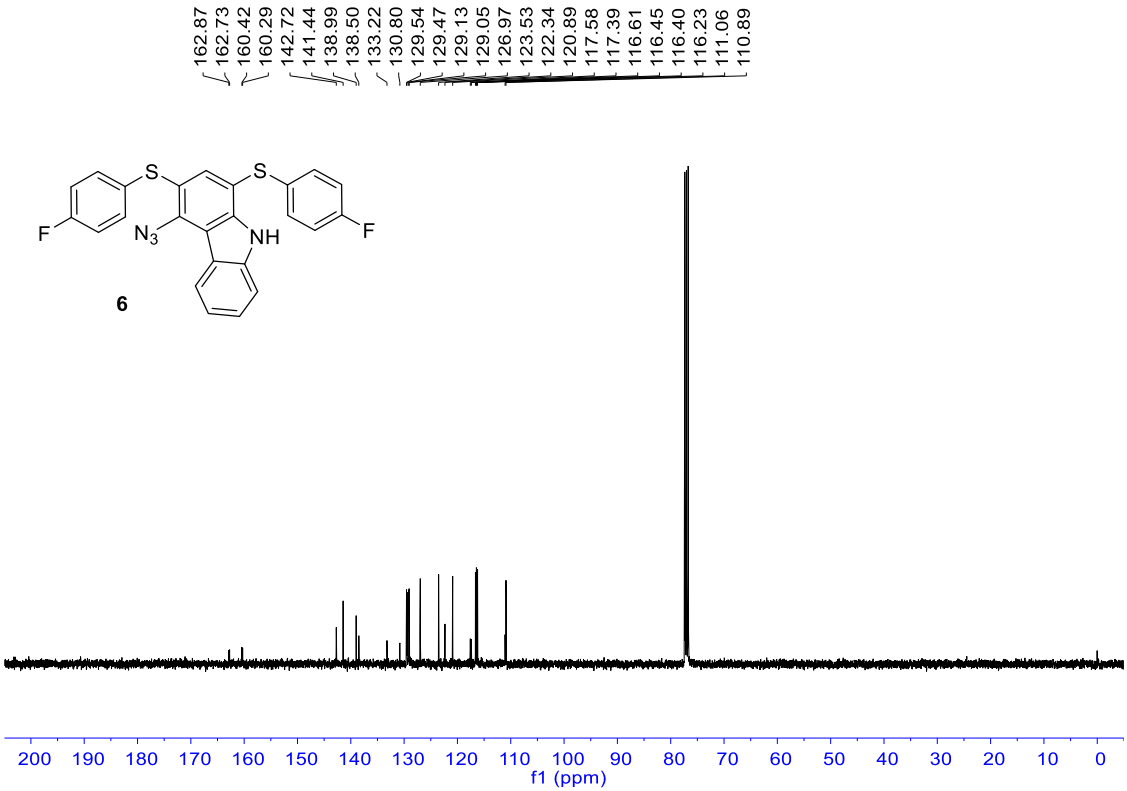
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **5c** + **5c'**



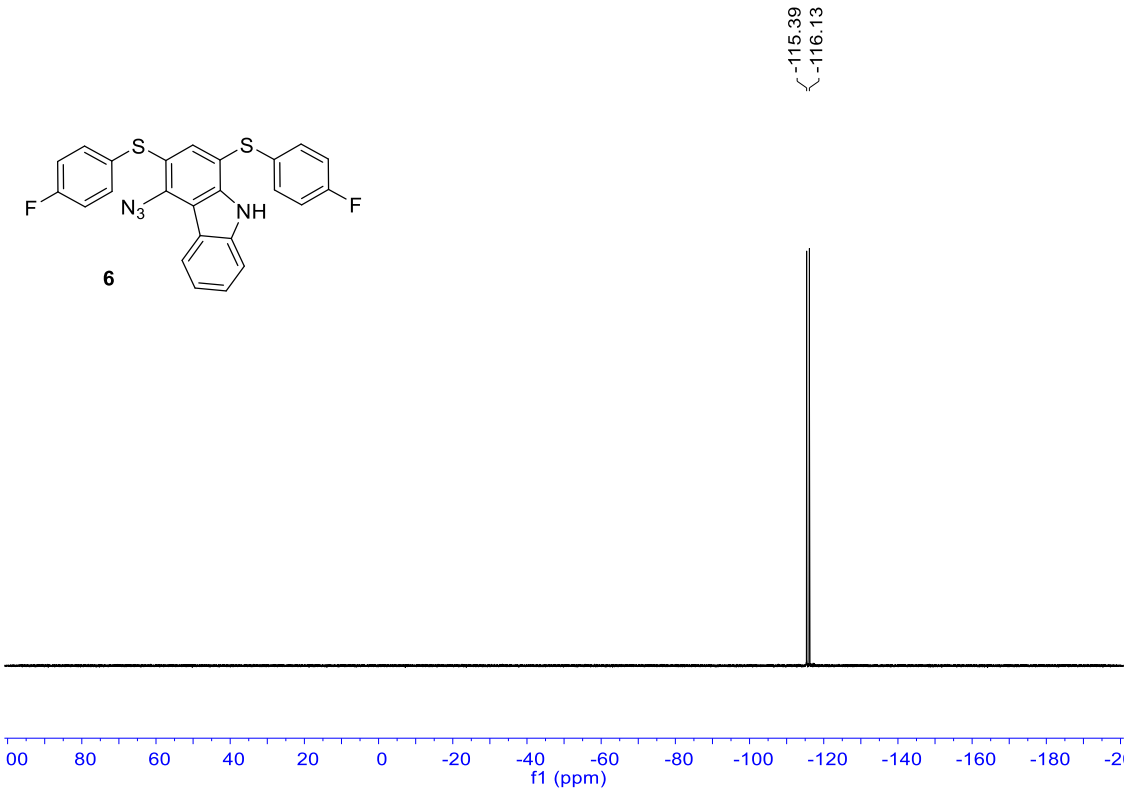
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **5c** + **5c'**



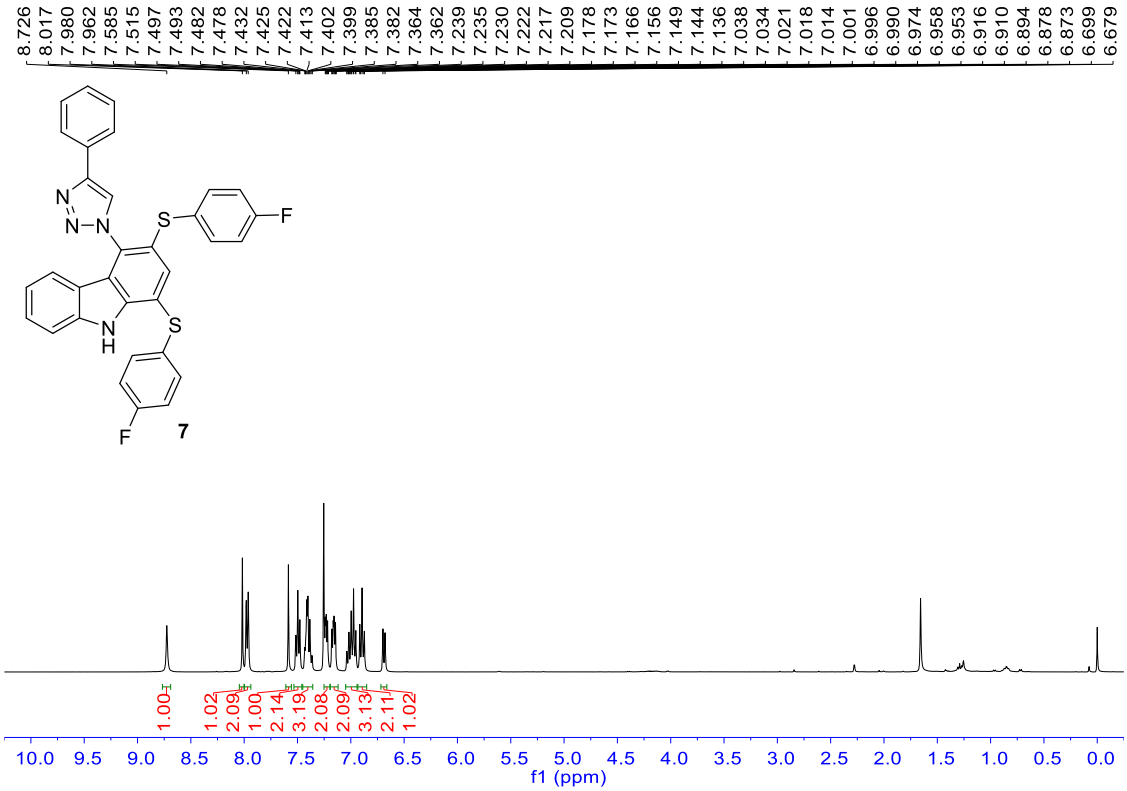
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6**



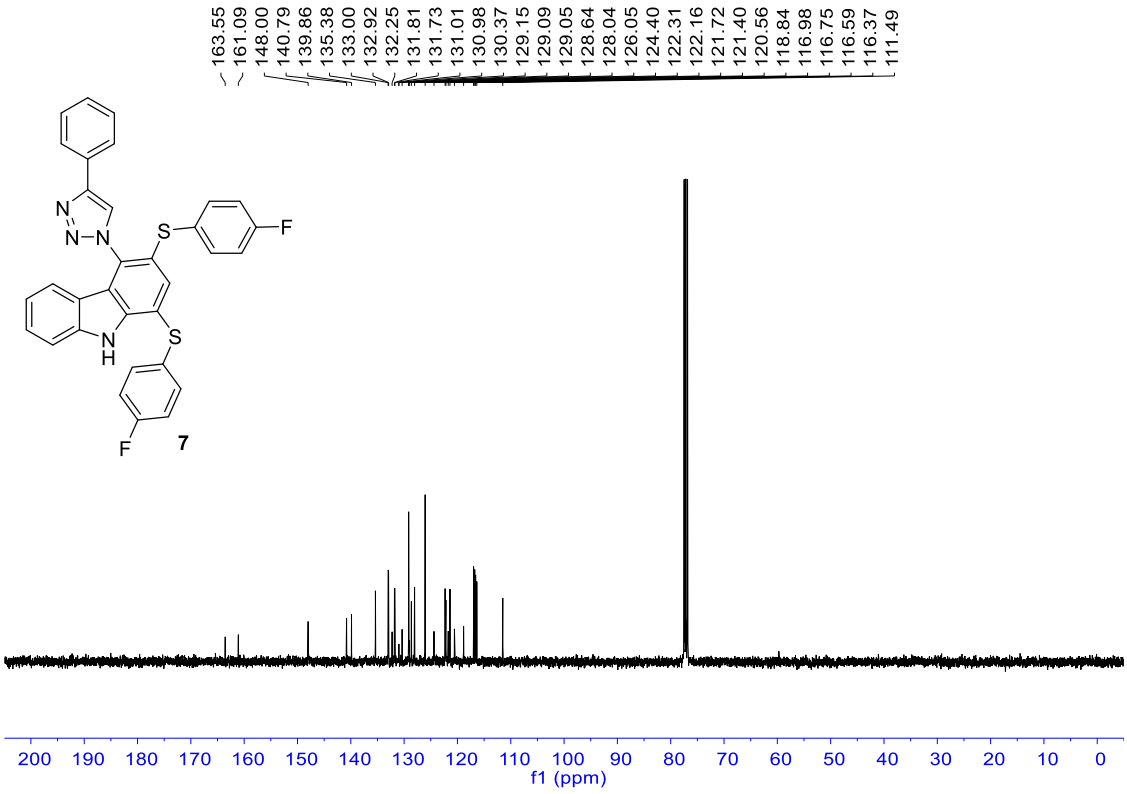
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **6**



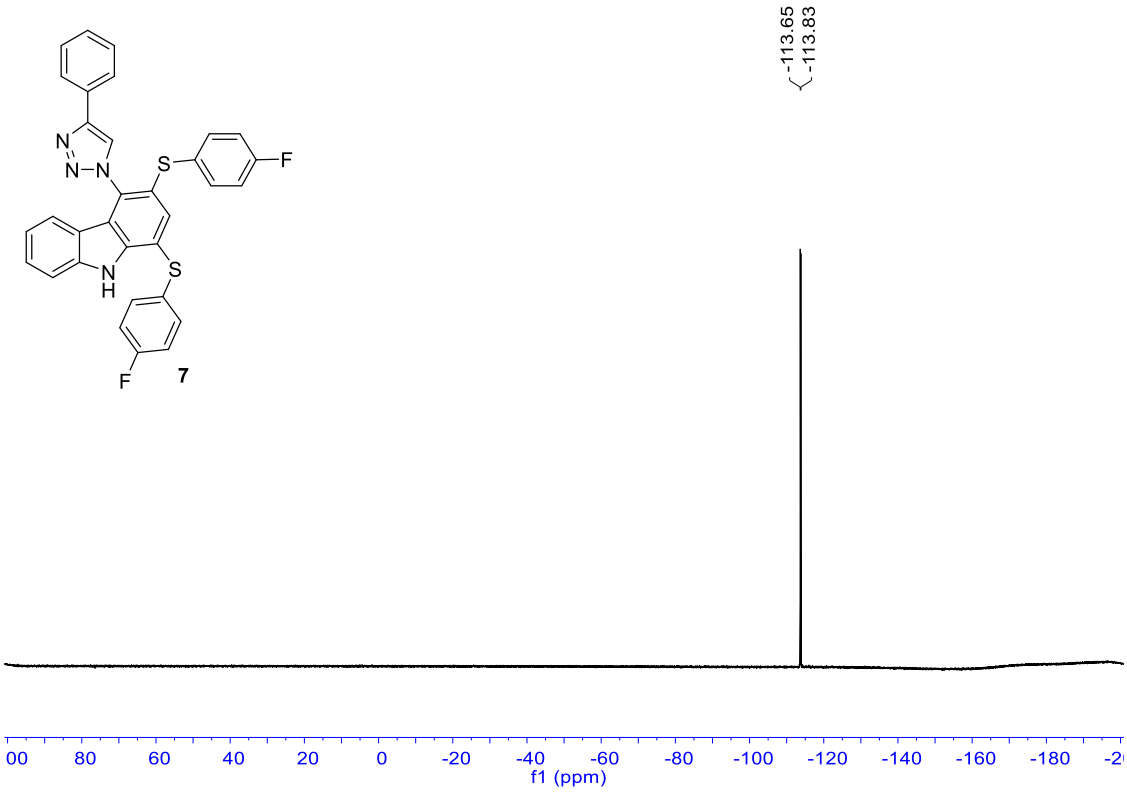
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **6**



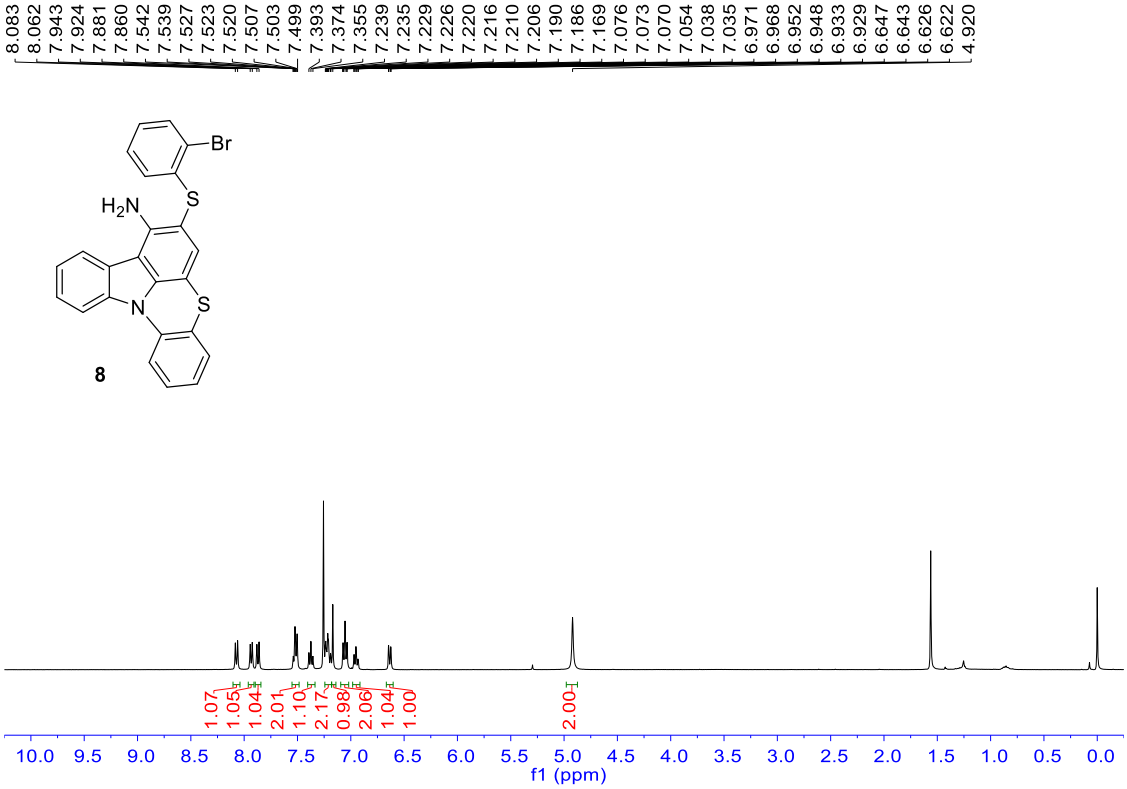
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**



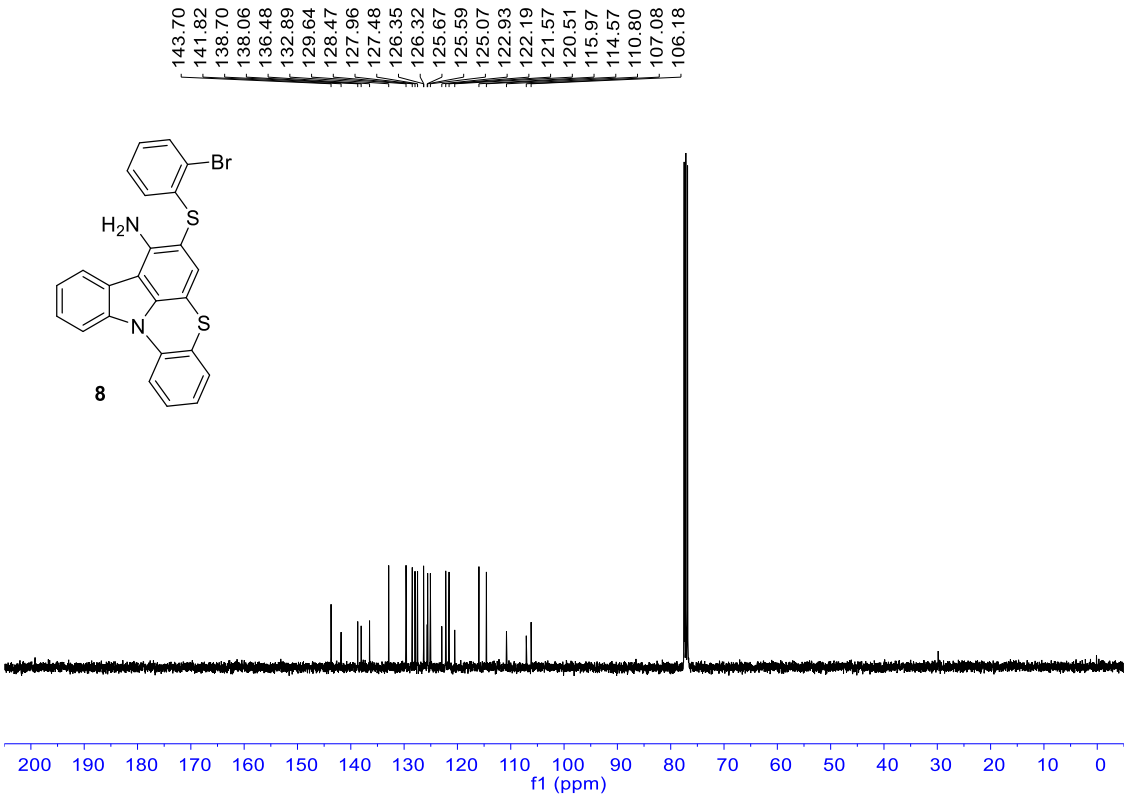
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of compound **7**



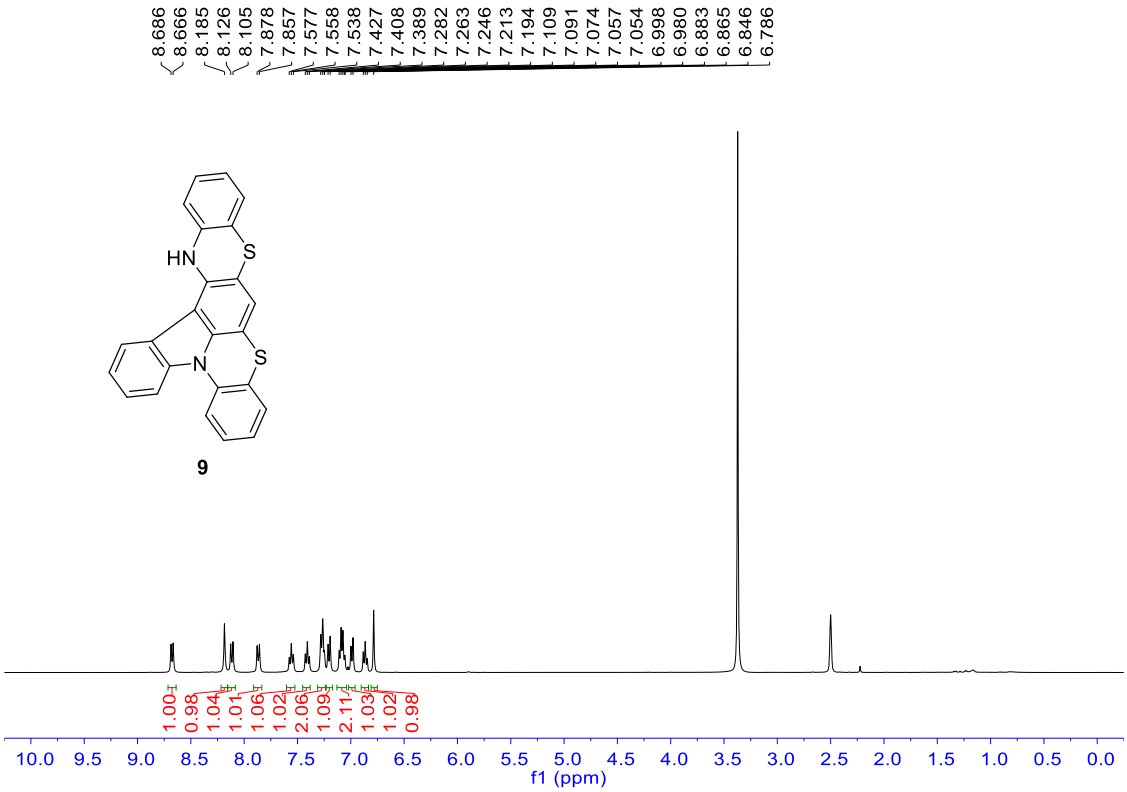
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of compound **7**



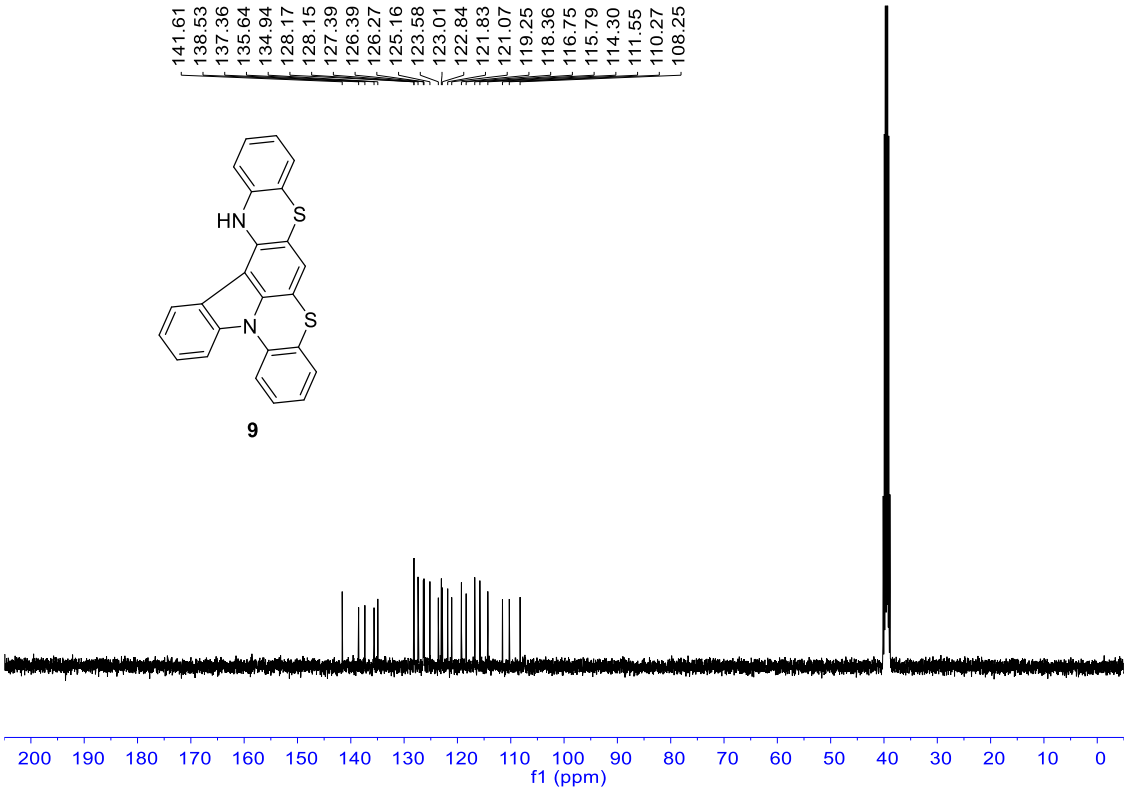
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8**



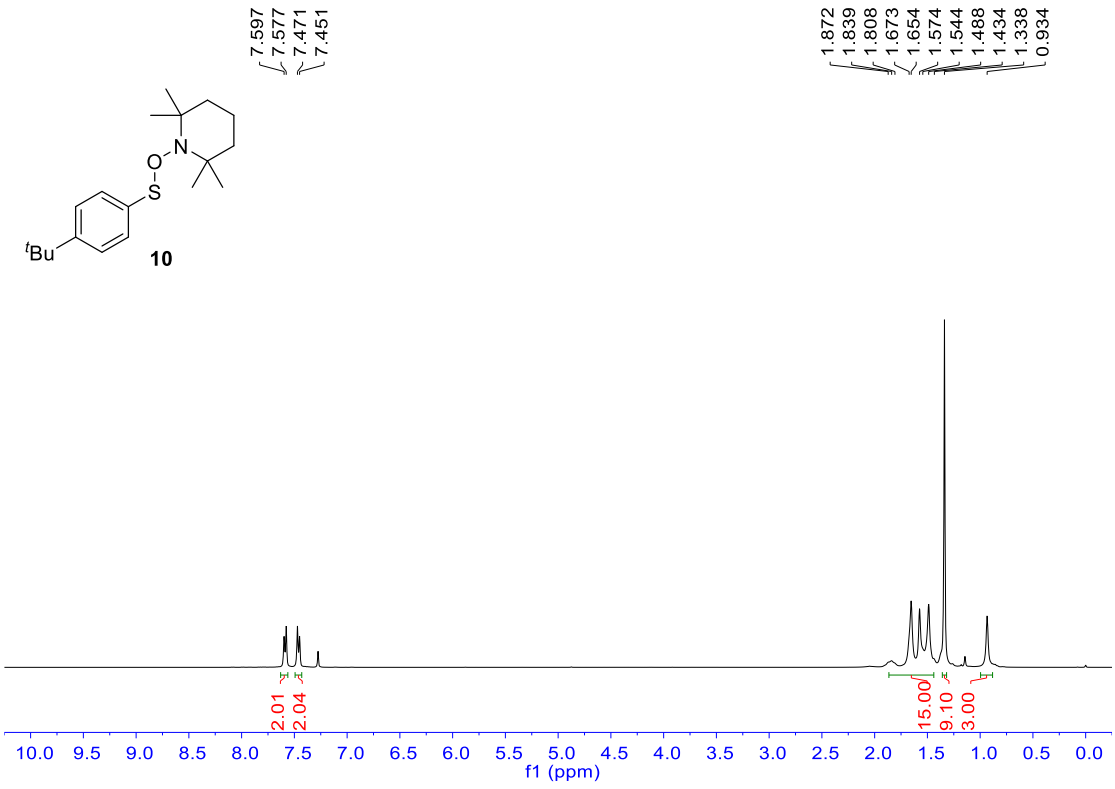
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of compound **8**



^{1}H NMR spectrum (400 MHz, DMSO-d_6) of compound **9**



$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, DMSO-d_6) of compound **9**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**