Supporting Information

Desulfurdioxidative N-N Coupling of *N*-Arylhydroxylamines and *N*-Sulfinylanilines: Reaction Development and Mechanism

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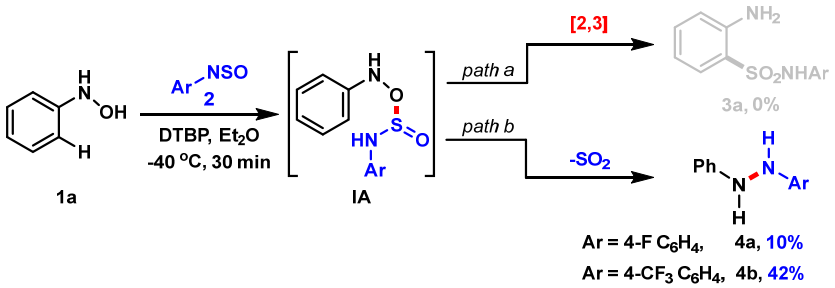
1. General remarks

Unless otherwise noted, commercially available reagents were purchased from commercial suppliers (such as Adamas, Sigma-Aldrich Co., Energy Chemical. Bidepharm etc), and used without further purification. All reactions were carried out under air atmosphere with magnetic stirring unless otherwise noted. Solvents were dried by passage through an activated alumina column under argon. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography (TLC) with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Silica gel (particle size 0.032-0.063 mm) purchased from SiliCycle was used for flash chromatography.

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker AV-500 spectrometer operating at 500 MHz for proton and 126 MHz for carbon nuclei using $CDCl_3$ or DMSO-*d*$_6$ as solvent, respectively. Fluorine magnetic resonance (^{19}F NMR) spectra were recorded at 471 MHz. Chemical shifts are reported parts per million (ppm) referenced to $CDCl_3$ (δ 7.26 ppm), tetramethylsilane (TMS, δ 0.00 ppm), or DMSO-*d*$_6$ (δ 2.50 ppm) for ^{1}H NMR; $CDCl_3$ (δ 77.16 ppm), or DMSO-*d*$_6$ (δ 39.52 ppm) for ^{13}C NMR. Proton signal data uses the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and *J* = coupling constant. High Resolution Mass Spectrometry was performed on a Bruker Apex II mass instrument under the conditions of electrospray ionization (ESI) in both positive and negative mode. ^{35}Cl was used to calculate the theoretical m/z for all chlorine containing compounds. ^{79}Br was used to calculate the theoretical m/z for all bromine containing compounds.

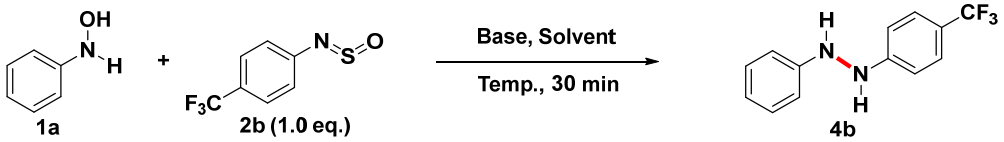
2. Initial attempt

We have previously reported that *N*-arylhydroxylamines and trifluoromethanesulfinic chloride underwent an unconventional cascade *O*-trifluoromethanesulfinylation and concerted [2,3]-sigmatropic rearrangement to afford synthetically useful *ortho*-trifluoromethanesulfonylated aniline derivatives [*Angew. Chem. Int. Ed.* **2022**, ***61***, e202115611]. Inspired by this work, we envisioned that phenylhydroxylamine **1a** might react with *N*-sulfinylaniline **2a** to generate *ortho*-sulfonylated aniline **3a** through the similar [2,3]-sigmatropic rearrangement in the presence of 2,6-di-tert-butylpyridine (path a). Interestingly, 10% yield of diarylhydrazine **4a** was obtained rather than the expected product **3a** (path b). Increasing the electrophilicity of *N*-sulfinylaniline by employing the *para*-CF_3 substituted substrate **2b** resulted in the higher yield (42%) of the corresponding *N,N′*-diarylhydrazine product **4b** (path b).



3. Table for the optimization of reaction conditions

Table S1. Condition optimization of desulfurdioxidative N-N coupling of *N*-arylhydroxylamine **1a** and *N*-sulfinylaniline **2b**

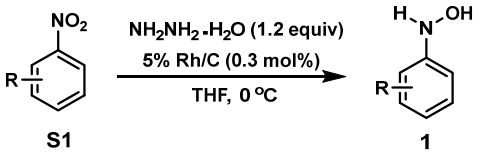


Entry[a]	1a (eq.)	Solvent	Base (eq.)	Temp	Yield (%)[b]
1	3.0	Et_2O	DTBP (6.0 eq.)	-40 °C	42%
2	3.0	Et_2O	DTBP (6.0 eq.)	-60 °C	63%
3	3.0	Et_2O	DTBP (6.0 eq.)	-78 °C	75%
4	3.0	Hexane	DTBP (6.0 eq.)	-78 °C	34%
5	3.0	DCM	DTBP (6.0 eq.)	-78 °C	39%
6	3.0	Toluene	DTBP (6.0 eq.)	-78 °C	29%
7	3.0	THF	DTBP (6.0 eq.)	-78 °C	27%
8	3.0	Et_2O	DIPEA (6.0 eq.)	-78 °C	26%
9	3.0	Et_2O	Imidazole (6.0 eq.)	-78 °C	20%
10	3.0	Et_2O	DMAP (6.0 eq.)	-78 °C	48%
11	3.0	Et_2O	Pyridine (6.0 eq.)	-78 °C	28%
12	3.0	Et_2O	Et_3N (6.0 eq.)	-78 °C	20%
13	3.0	Et_2O	KF (6.0 eq.)	-78 °C	35%
14	3.0	Et_2O	$NaNO_2$ (6.0 eq.)	-78 °C	46%
15	3.0	Et_2O	Na_2SO_3 (6.0 eq.)	-78 °C	40%
16	3.0	Et_2O	K_2CO_3 (6.0 eq.)	-78 °C	40%
18	3.0	Et_2O	K_2HPO_4 (6.0 eq.)	-78 °C	70%
19	3.0	Et_2O	Na_2CO_3 (6.0 eq.)	-78 °C	39%
20	3.0	Et_2O	no base	-78 °C	28%
21	3.0	Et_2O	$CsCO_3$ (6.0 eq.)	-78 °C	34%
22	3.0	Et_2O	KNO_3 (6.0 eq.)	-78 °C	36%
23	3.0	Et_2O	$NaNO_3$ (6.0 eq.)	-78 °C	34%
24	3.0	Et_2O	$NaHCO_3$ (6.0 eq.)	-78 °C	36%
25	3.0	Et_2O	CH_3COONa (6.0 eq.)	-78 °C	34%
26	3.0	Et_2O	KNO_2 (6.0 eq.)	-78 °C	80%
27	1.2	Et_2O	KNO_2 (2.0 eq.)	-78 °C	47%
28	2.0	Et_2O	KNO_2 (2.0 eq.)	-78 °C	55%
29	3.0	Et_2O	KNO_2 (2.0 eq.)	-78 °C	58%
30	3.0	Et_2O	KNO_2 (8.0 eq.)	-78 °C	73%
31	4.0	Et_2O	KNO_2 (8.0 eq.)	-78 °C	78%

[a]Reaction conditions: all reactions were carried out with **1a** (0.60 mmol, 3.0 equiv), **2** (0.20 mmol, 1.0 equiv), KNO_2 (1.2 mmol, 6.0 equiv), Et_2O (2.0 mL) at -78 °C under N_2 for 30 minutes. [b]Isolated yield.

4. General procedure for the synthesis of arylhydroxylamines

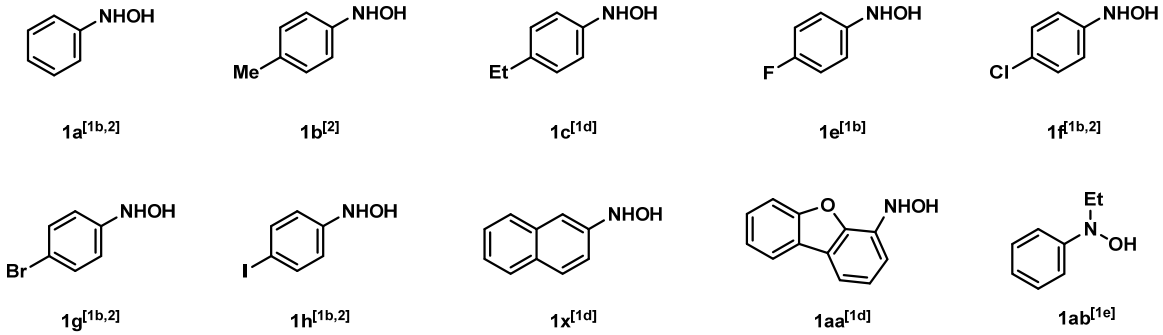
General procedure A:[1]



S1 1

Under nitrogen atmosphere, a suspension of nitroarene **S1** (1.0 equiv) and 5% Rh/C (0.3 mol% Rh) in THF (0.32 M) was cooled to 0 °C. Hydrazine monohydrate (1.2 equiv) was added dropwise. The reaction mixture was stirred at 0 °C for 1 hour and then slowly warmed up to r.t. and stirred at r.t. for 3 hours. The reaction mixture was filtered through a short pad of celite and concentrated *in vacuo*. Recrystallization from DCM/PE afforded the title compound **1**.

5. Previously reported arylhydroxylamines



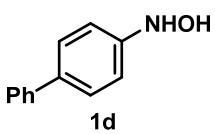
1a[1b,2] **1b**[2] **1c**[1d] **1e**[1b] **1f**[1b,2]

1g[1b,2] **1h**[1b,2] **1x**[1d] **1aa**[1d] **1ab**[1e]

1a-1c, 1e-1h, 1x, 1aa, 1ab were known compounds and were prepared according to the literature-reported procedures.[1,2]

6. Analytical data of arylhydroxylamines 1

(1) *N*-([1,1'-biphenyl]-4-yl)hydroxylamine (1d)

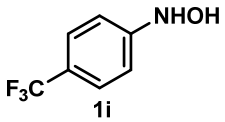


1d

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1d** (1.517 g, 82% yield), m.p. = 97-99 °C; R_f = 0.2 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.43 (s, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.50 (d, J = 8.3 Hz,

2H), 7.40 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 6.94 (d, J = 8.2 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 151.69, 140.41, 131.07, 128.84, 126.81, 126.30, 125.86, 113.38; HRMS (ESI) m/z calcd for $[C_{12}H_{12}NO]^+$ $[M+H]^+$: 186.0913, found: 186.0922.

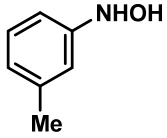
(2) *N*-(4-(trifluoromethyl)phenyl)hydroxylamine (1i)



1i

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1i** (1.152 g, 65% yield), m.p. = 100-102 ºC; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 8.4 Hz, 2H), 7.01 (t, J = 20.7 Hz, 3H), 5.70 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.7, 126.4 (q, J_{C-F} = 3.8 Hz), 124.6 (q, J_{C-F} = 270.9 Hz), 124.0 (q, J_{C-F} = 32.6 Hz), 113.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.64 (s); HRMS (ESI) m/z calcd for $[C_7H_7F_3NO]^+$ $[M+H]^+$: 178.0474, found: 178.0460.

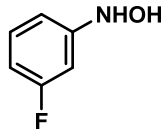
(3) *N*-(*m*-tolyl)hydroxylamine (1j)



1j

Followed General Procedure A on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid 1j (0.566 g, 42% yield), m.p. = 91-93 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.24 (d, J = 1.8 Hz, 1H), 8.16 (s, 1H), 7.04 (t, J = 7.7 Hz, 1H), 6.70–6.60 (m, 2H), 6.56 (d, J = 7.4 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 152.1, 137.5, 128.3, 120.1, 113.5, 110.3, 21.3; HRMS (ESI) m/z calcd for $[C_7H_{10}NO]^+$ $[M+H]^+$: 124.0757, found: 124.0755.

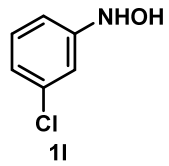
(4) *N*-(3-fluorophenyl)hydroxylamine (1k)



1k

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1k** (1.045 g, 83% yield), m.p. = 85-87 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21 (td, J = 8.1, 6.4 Hz, 1H), 6.76 (dt, J = 10.6, 2.2 Hz, 1H), 6.71-6.66 (m, 2H), 6.14 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.7 (d, J_{C-F} = 244.8 Hz), 151.5 (d, J_{C-F} = 9.7 Hz), 130.3 (d, J_{C-F} = 9.5 Hz), 109.9 (d, J_{C-F} = 2.2 Hz), 109.1 (d, J_{C-F} = 21.5 Hz), 102.2 (d, J_{C-F} = 25.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -112.07 (s); HRMS (ESI) m/z calcd for $[C_6H_7FNO]^+$ $[M+H]^+$: 128.0506, found: 128.0498.

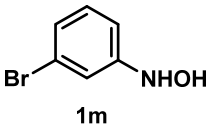
(5) *N*-(3-chlorophenyl)hydroxylamine (1l)



1l

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1l** (0.973 g, 68% yield), m.p. = 90-92 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.81 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.21 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.8, 135.0, 130.1, 122.5, 114.9, 112.7; HRMS (ESI) m/z calcd for $[C_6H_7ClNO]^+$ $[M+H]^+$: 144.0211, found: 144.0227.

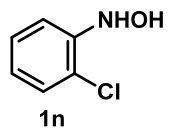
(6) *N*-(3-bromophenyl)hydroxylamine (1m)



1m

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1m** (1.010 g, 54% yield); m.p. = 94-96 °C; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ7.17 (s, 1H), 7.16–7.04 (m, 2H), 6.86 (dt, *J* = 7.0, 2.1 Hz, 1H), 6.11 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.9, 130.4, 125.4, 123.0, 117.7, 113.2; HRMS (ESI) m/z calcd for $[C_6H_7BrNO]^+$ $[M+H]^+$: 187.9706, found: 187.9718.

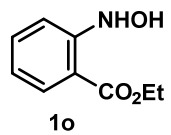
(7) *N*-(2-chlorophenyl)hydroxylamine (1n)



1n

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1n** (0.786 g, 55% yield), m.p. = 85-86 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.23 (m, 3H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.40 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.6, 129.1, 127.8, 122.7, 119.5, 116.3; HRMS (ESI) m/z calcd for $[C_6H_7ClNO]^+$ $[M+H]^+$: 144.0211, found: 144.0214.

(8) ethyl 2-(hydroxyamino)benzoate (1o)

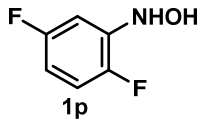


1o

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1o** (0.977 g, 54% yield), m.p. = 89-91 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 9.17 (s, 1H), 8.88 (d, *J* = 1.5 Hz, 1H), 7.80 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.54–7.43

(m, 1H), 7.27 (dd, J = 8.5, 1.2 Hz, 1H), 6.86–6.70 (m, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 166.7, 153.4, 134.3, 130.3, 117.7, 113.6, 110.7, 60.4, 14.1; HRMS (ESI) m/z calcd for $[C_9H_{12}NO_3]^+$ $[M+H]^+$: 182.0812, found: 182.0811.

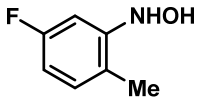
(9) *N*-(2,5-difluorophenyl)hydroxylamine (1p)



1p

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1p** (1.116 g, 77% yield), m.p. = 101-103 °C; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.66–8.64 (m, 2H), 7.07–7.01 (m, 1H), 6.94–6.76 (m, 1H), 6.53–6.48 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 159.1 (d, J_{C-F} = 237.4 Hz), 145.9 (d, J_{C-F} = 235.4 Hz), 141.5（dd, J_{C-F} = 12.6, 11.3 Hz）, 115.3（dd, J_{C-F} = 20.2, 10.1 Hz）,104.3（dd, J_{C-F} = 23.9, 6.3 Hz）, 101.5 (d, J_{C-F} = 29.2 Hz); ^{19}F NMR (471 MHz, DMSO-d_6): δ -117.77 (s), -137.11 (s); HRMS (ESI) m/z calcd for $[C_6H_6F_2NO]^+$ $[M+H]^+$: 146.0412, found: 146.0411.

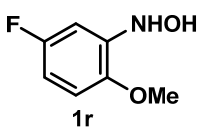
(10) *N*-(5-fluoro-2-methylphenyl)hydroxylamine (1q)



1q

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1q** (0.539 g, 38% yield), m.p. = 84-86 °C; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.42 (s, 1H), 8.17 (s, 1H), 6.95 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 11.6 Hz, 1H), 6.44 (td, J = 8.5, 2.7 Hz, 1H), 2.02 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 161.8 (d, J_{C-F} = 237.9 Hz), 151.6 (d, J_{C-F} = 9.9 Hz), 130.4 (d, J_{C-F} = 9.3 Hz), 117.4 (d, J_{C-F} = 2.6 Hz), 104.4 (d, J_{C-F} = 21.1 Hz), 98.8 (d, J_{C-F} = 26.5 Hz), 16.12; ^{19}F NMR (471 MHz, DMSO-d_6): δ -116.39 (s); HRMS (ESI) m/z calcd for $[C_7H_9FNO]^+$ $[M+H]^+$: 142.0663, found: 142.0671.

(11) *N*-(5-fluoro-2-methoxyphenyl)hydroxylamine (1r)

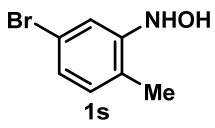


1r

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1r** (1.066 g, 68% yield), m.p. = 95-97 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR

(500 MHz, DMSO-d_6): δ 8.46 (d, J = 1.6 Hz, 1H), 7.99 (s, 1H), 6.79 (dd, J = 8.8, 5.0 Hz, 1H), 6.73 (d, J = 10.6 Hz, 1H), 6.48 (td, J = 8.6, 3.1 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 157.3 (d, $J_{C\text{-}F}$ = 233.4 Hz), 142.5 (d, $J_{C\text{-}F}$ = 10.3 Hz), 142.4 (d, $J_{C\text{-}F}$ = 1.6 Hz), 110.6 (d, $J_{C\text{-}F}$ = 9.6 Hz), 103.6 (d, $J_{C\text{-}F}$ = 22.9 Hz), 100.0 (d, $J_{C\text{-}F}$ = 28.4 Hz); ^{19}F NMR (471 MHz, DMSO-d_6): δ -122.51 (s); HRMS (ESI) m/z calcd for $[C_7H_9FNO_2]^+$ $[M+H]^+$: 158.0612, found: 158.0612.

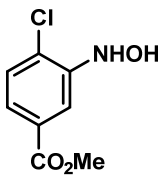
(12) *N*-(5-bromo-2-methylphenyl)hydroxylamine (1s)



1s

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1s** (1.744 g, 87% yield); m.p. = 110-112 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 1.8 Hz, 1H), 7.11–6.36 (m, 3H), 5.62 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.7, 131.5, 124.6, 121.7, 120.6, 117.0, 16.5; HRMS (ESI) m/z calcd for $[C_7H_9BrNO]^+$ $[M+H]^+$: 201.9862, found: 201.9862.

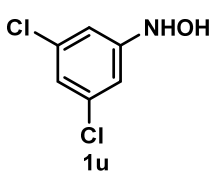
(13) methyl 4-chloro-3-(hydroxyamino)benzoate (1t)



1t

Followed **General Procedure A** on 10.0 mmol scale. Purified via column chromatography on silica gel (eluted with PE:EtOAc = 5:1) to obtain the pink solid **1t** (0.824 g, 41% yield); m.p. = 103-105 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.76 (s, 1H), 8.53 (s, 1H), 7.86–7.66 (m, 1H), 7.49–7.17 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 166.0, 148.0, 129.2, 129.1, 121.9, 120.6, 114.4, 52.3; HRMS (ESI) m/z calcd for $[C_8H_9ClNO_3]^+$ $[M+H]^+$: 202.0265, found: 202.0277.

(14) *N*-(3,5-dichlorophenyl)hydroxylamine (1u)

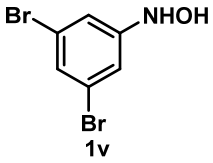


1u

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the pink solid **1u** (1.852 g, 85% yield), m.p. = 95-97 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.94 (t, J = 1.7 Hz, 1H), 6.87 (d, J = 1.7 Hz, 2H), 6.80 (s, 1H), 6.77 (d, J = 1.9 Hz, 1H), 5.45 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$):

δ 151.8, 135.5, 122.0, 112.7; HRMS (ESI) m/z calcd for $[C_6H_6Cl_2NO]^+$ $[M+H]^+$: 177.9821, found: 177.9825.

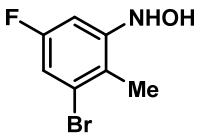
(15) *N*-(3,5-dibromophenyl)hydroxylamine (1v)



1v

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the pink solid **1v** (1.110 g, 45% yield), m.p. = 107-109 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.75 (d, *J* = 1.8 Hz, 1H), 8.69 (d, *J* = 1.8 Hz, 1H), 7.06 (t, *J* = 1.7 Hz, 1H), 6.94 (d, *J* = 1.7 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 154.8, 122.9, 122.5, 113.9; HRMS (ESI) m/z calcd for $[C_6H_6Br_2NO]^+$ $[M+H]^+$: 265.8811, found: 265.8814.

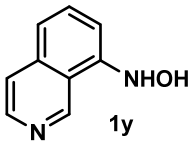
(16) *N*-(3-bromo-5-fluoro-2-methylphenyl)hydroxylamine (1w)



1w

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1w** (1.686 g, 77% yield), m.p. = 104-106 °C; R_f = 0.2 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.98 (dd, *J* = 10.4, 2.6 Hz, 1H), 6.93 (dd, *J* = 8.1, 2.6 Hz, 1H), 5.90 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6 (d, $J_{C\text{-}F}$ = 245.8 Hz), 149.8 (d, $J_{C\text{-}F}$ = 10.3 Hz), 124.8 (d, $J_{C\text{-}F}$ = 11.2 Hz), 117.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 112.5 (d, $J_{C\text{-}F}$ = 24.7 Hz), 100.9 (d, $J_{C\text{-}F}$ = 26.5 Hz), 15.6; ^{19}F NMR (471 MHz, $CDCl_3$): δ -113.96 (s); HRMS (ESI) m/z calcd for $[C_7H_8BrFNO]^+$ $[M+H]^+$: 219.9768, found: 219.9752.

(17) *N*-(isoquinolin-5-yl)hydroxylamine (1y)

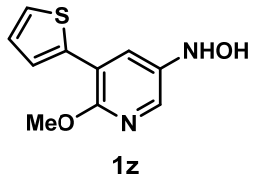


1y

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1y** (0.944 g, 59% yield), m.p. = 151-153 °C; R_f = 0.1 (PE:EtOAc = 1:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 9.20-9.19 (m, 2H), 8.64 (s, 1H), 8.42 (d, *J* = 5.9 Hz, 1H), 7.80 (d, *J* = 5.8 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 152.2, 146.1, 141.59,

128.5, 128.0, 124.3, 117.7, 114.9, 109.8; HRMS (ESI) m/z calcd for $[C_9H_9N_2O]^+$ $[M+H]^+$: 161.0907, found: 161.0917.

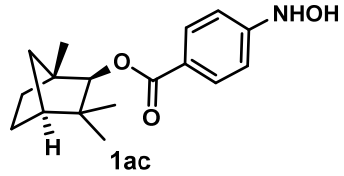
(18) *N*-(6-methoxy-5-(thiophen-2-yl)pyridin-3-yl)hydroxylamine (1z)



1z

Followed **General Procedure A** on 5.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1z** (0.745 g, 68% yield); m.p. = 133-135 ºC; R_f = 0.1 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.58 (s, 1H), 8.52 (s, 1H), 8.04 (s, 1H), 7.63 (t, *J* = 4.9 Hz, 1H), 7.25 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.22–7.14 (m, 2H), 2.48 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 183.7, 183.1, 178.47, 171.7, 166.0, 165.6, 164.8, 164.3, 158.7, 60.6; HRMS (ESI) m/z calcd for $[C_{10}H_{11}N_2O_2S]^+$ $[M+H]^+$: 223.0536, found: 223.0520.

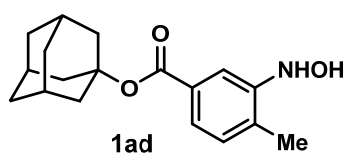
(19) (1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-(hydroxyamino)benzoate (1ac)



1ac

Followed **General Procedure A** on 10.0 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 5/1) to obtain the white solid **1ac** (2.226 g, 77% yield); m.p. = 96-98 ºC; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.95 (s, 1H), 8.65 (d, *J* = 1.6 Hz, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 4.46 (d, *J* = 1.8 Hz, 1H), 1.91-1.85 (ddt, *J* = 14.6, 8.2, 3.9 Hz, 1H), 1.76–1.67 (m, 2H), 1.64 (d, *J* = 10.2 Hz, 1H), 1.51–1.39 (m, 1H), 1.20 (d, *J* = 10.2 Hz, 1H), 1.18–1.13 (m, 1H), 1.11 (s, 3H), 1.04 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 166.1, 156.0, 130.4, 119.5, 111.3, 85.0, 48.1, 47.8, 40.8, 29.5, 26.5, 25.6, 20.1, 19.3; HRMS (ESI) m/z calcd for $[C_{17}H_{24}NO_3]^+$ $[M+H]^+$: 290.1751, found: 290.1740.

(20) (3*s*,5*s*,7*s*)-adamantan-1-yl 3-(hydroxyamino)-4-methylbenzoate (1ad)

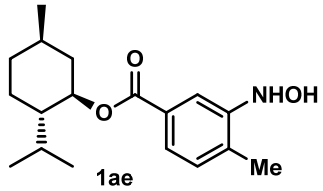


1ad

Followed **General Procedure A** on 10.0 mmol scale. Purified via column chromatography on silica gel (eluted with (PE/EtOAc = 5/1) to obtain the white solid **1ad**

(2.710 g, 90% yield); m.p. = 122-124 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.36 (s, 1H), 8.13 (s, 1H), 7.62 (s, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 2.17 (s, 9H), 2.10 (s, 3H), 1.66 (s, 6H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 165.2, 149.7, 129.6, 129.4, 127.2, 120.0, 112.2, 79.8, 41.0, 35.7, 30.3, 17.0; HRMS (ESI) m/z calcd for $[C_{18}H_{24}NO_3]^+$ $[M+H]^+$: 302.1751, found: 302.1770.

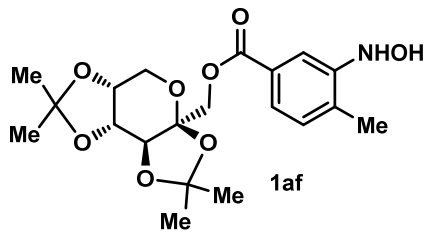
(21) (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-(hydroxyamino)-4-methylbenzoate (1ae)



1ae

Followed **General Procedure A** on 10.0 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain the white solid **1ae** (1.714 g, 56% yield); m.p. = 115-117 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.41 (s, 1H), 8.17 (s, 1H), 7.70 (s, 1H), 7.38-7.28 (m, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 4.82 (td, *J* = 10.8, 4.2 Hz, 1H), 2.12 (s, 3H), 1.98 (d, *J* = 11.9 Hz, 1H), 1.92–1.78 (m, 1H), 1.64 (d, *J* = 11.4 Hz, 2H), 1.49 (m, 2H), 1.07 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 7H), 0.74 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 165.8, 150.0, 129.5, 128.4, 127.6, 120.1, 112.3, 73.6, 46.7, 40.7, 33.8, 31.0, 26.2, 23.4, 21.9, 20.5, 17.0, 16.5; HRMS (ESI) m/z calcd for $[C_{18}H_{28}NO_3]^+$ $[M+H]^+$: 306.2064, found: 306.2066.

(22) ((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 3-(hydroxyamino)-4-methylbenzoate (1af)

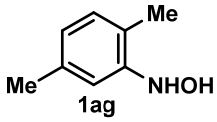


1af

Followed **General Procedure A** on 10.0 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain the white solid **1af** (3.893 g, 92% yield); m.p. = 121-123 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.43 (d, *J* = 2.0 Hz, 1H), 8.19 (s, 1H), 7.73 (s, 1H), 7.38 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 4.64 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.56 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 2.6 Hz, 1H), 4.27 (d, *J* = 7.3 Hz, 1H), 4.14 (d, *J* = 11.7 Hz, 1H), 3.80 (dd, *J* = 13.1, 1.8 Hz, 1H), 3.65 (d, *J* = 13.0 Hz, 1H), 2.13 (s, 3H), 1.46 (s,

3H), 1.37 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 165.6, 149.9, 129.7, 128.0, 127.5, 120.3, 112.4, 108.3, 108.2, 101.1, 70.1, 70.0, 69.3, 64.5, 60.7, 26.3, 25.7, 25.3, 23.9, 17.0; HRMS (ESI) m/z calcd for $[C_{20}H_{28}NO_8]^+$ $[M+H]^+$: 410.1809, found: 410.1815.

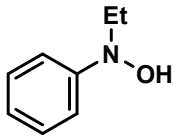
(23) *N*-(2,5-dimethylphenyl)hydroxylamine (1ag)



1ag

Followed **General Procedure A** on 10.0 mmol scale. Recrystallization from DCM/PE to obtain the white solid **1ag** (0.849 g, 62% yield); m.p. = 84-86 ºC; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.16 (d, *J* = 2.0 Hz, 1H), 7.84 (s, 1H), 6.91 (d, *J* = 1.8 Hz, 1H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.50 (d, *J* = 7.5 Hz, 1H), 2.23 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 149.4, 135.0, 129.3, 119.6, 118.9, 112.9, 21.2, 16.5; HRMS (ESI) m/z calcd for $[C_8H_{12}NO]^+$ $[M+H]^+$: 138.0913, found: 138.0925.

(24) *N*-ethyl-*N*-phenylhydroxylamine (1ah)

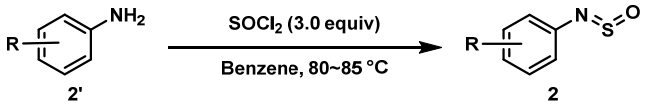


1ah

Followed Procedure: Under nitrogen atmosphere, a dry and argon flushed flask equipped with a magnetic stirring bar and a septum was charged with *N*-phenylhydroxylamine (327 mg, 3.00 mmol, 1.00 equiv) dissolved in dry methanol (10 mL). Acetaldehyde (264 mg, 6 mmol, 2.00 equiv) was added in at 0 °C. $NaBH_4$ (114 mg, 3.00 mmol, 1.00 equiv) was added into resulting mixture after stirred for 5 min at 0 °C. The mixture was stirred at 0 °C for 30min-50min and reaction was traced by TLC analysis (PE:EtOAc = 3:1). When starting material of reaction was completely comsumed, with sat. aqueous NH_4Cl solution (10 mL) reaction was terminated. The organic layer was removed and the aqueous phase was extracted from EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$ and then solvent was removed under vacuum. Purification of the crude product by flash chromatography (silica gel, isohexane/EtOAc = 9:1) afforded the title compound as a yellow oil (249 mg, 1.82 mmol, 61%); R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.69 (s, 1H), 7.26–7.18 (m, 2H), 7.08–7.02 (m, 2H), 6.84-6.81 (m, 1H), 3.31 (q, *J* = 7.0 Hz, 2H), 1.10 (td, *J* = 7.0, 1.4 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 153.2, 128.4, 120.0, 115.4, 51.4, 11.0.

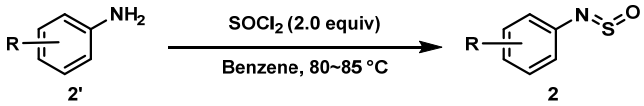
7. General procedure for the synthesis of *N*-sulfinylanilines 2

General procedure B1:[3]



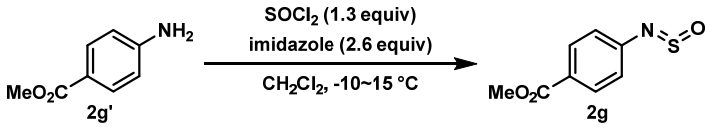
Aniline **2'** (24 mmol, 1.0 equiv) and benzene (170 mmol, 7.0 equiv) were first placed in a three-neck round-bottom flask equipped with a Liebig condenser which was sealed with a $CaCl_2$ trap. Then, thionylchloride (72 mmol, 3.0 equiv) was added drop wise to the mixture. To prevent the interaction with air humidity, the loading of the three components was carried out under nitrogen atmosphere. Since a vigorous reaction took place while thionyl chloride was added, the mixture was continuously stirred. Then, the flask was closed and the mixture was heated at 80-85 ºC for 8 h. Once the reaction was over, the dark liquid obtained was subsequently purified by reduced pressure distillation. **2b**, **2j** were prepared according to **General Procedure B1**.

General procedure B2: [4]



Aniline **2'** (24 mmol, 1.0 equiv) and benzene (120 mmol) were first placed in a three-neck round-bottom flask equipped with a Liebig condenser which was sealed with a $CaCl_2$ trap. Then, thionylchloride (48 mmol, 2.0 equiv) was added drop wise to the mixture. To prevent the interaction with air humidity, the loading of the three components was carried out under nitrogen atmosphere. Since a vigorous reaction took place while thionyl chloride was added, the mixture was continuously stirred. Then, the flask was closed and the mixture was heated at 80-85 ºC for 8 h. Once the reaction was over, the dark liquid obtained was subsequently purified by reduced pressure distillation. **2a**, **2c-2i**, **2k**, **2l** were prepared according to **General Procedure B2**.

General procedure B3: [5]



To a three-necked flask equipped with a magnetic stirrer, gas inlet adapter, addition funnel, and a temperature probe were charged imidazole (1.8 g, 26 mmol) and 25 mL

of anhydrous CH_2Cl_2. The mixture was cooled to -10 °C, and $SOCl_2$ (0.48 mL, 6.5 mmol) was added dropwise while the internal temperature was maintained at ca. -10 °C. The mixture was then warmed to 15 °C, stirred for 10 min, and filtered through an oven-dried glass funnel. The solids were washed with 3 mL of dichloromethane, and the filtrate was transferred to a flask equipped with a magnetic stirrer, gas inlet adapter, addition funnel, and a temperature probe, and cooled to ca. -10 °C. Additional $SOCl_2$ (0.48 mL, 6.5 mmol) was added dropwise to the mixture, which was warmed to 15 °C and stirred for an additional 10 min. This solution was transferred to an addition funnel and added dropwise to a solution of the aniline (10 mmol) in 13 mL of anhydrous CH_2Cl_2 and 3 mL of anhydrous THF cooled to -30 °C and contained in three-necked flask equipped with a mechanical stirrer, gas inlet adapter, and a temperature probe while the temperature was maintained between -15 and -25 °C. The mixture was then warmed to 15 °C and stirred for an hour. The solids were removed by filtration and washed with 2 × 4 mL of CH_2Cl_2. Argon was bubbled through the filtrate for about one minute. The solvent was removed under reduced pressure, and CH_2Cl_2 was distillatively replaced with heptane, which was removed under reduced pressure; the residual yellowish solid was dried to give **2g.**

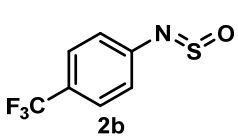
8. Analytical data of *N*-sulfinylanilines 2

(1) (phenylimino)-λ⁴-sulfanone (2a)

2a

Followed **General Procedure B2** on 5.0 mmol scale. Purified via vacuum distillation to obtain the oily liquid **2a** (0.336 g, 48% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.86 (m, 2H), 7.44–7.39 (m, 3H); Analytical data are in accordance with the literature values[6].

(2) ((4-(trifluoromethyl)phenyl)imino)-λ⁴-sulfanone (2b)

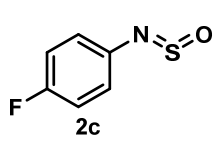


2b

Followed **General Procedure B1** on 20.0 mmol scale. Purified via vacuum distillation to obtain the oily liquid **2b** (3.312 g, 80% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.90 (s, 1H), 7.69 (s, 1H), 7.68 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.5, 131.7 (q, $J_{C\text{-}F}$ = 33.0 Hz), 127.0, 126.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $J_{C\text{-}F}$ = 272.4 Hz); ^{19}F NMR (471 MHz,

$CDCl_3$): δ -62.93 (s); HRMS (ESI) m/z calcd for $[C_7H_5F_3NOS]^+$ $[M+H]^+$: 208.0038, found: 208.0033.

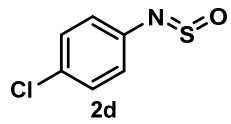
(3) ((4-fluorophenyl)imino)-λ⁴-sulfanone (2c)



2c

Followed **General Procedure B2** on 20.0 mmol scale. Purified via vacuum distillation to obtain the oily liquid **2c** (1.959 g, 62% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93-7.90 (m, 2H), 7.11-7.08 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.9 (d, $J_{C\text{-}F}$ = 254.4 Hz), 139.5 (d, $J_{C\text{-}F}$ = 3.4 Hz), 129.7 (d, $J_{C\text{-}F}$ = 8.9 Hz), 116.4 (d, $J_{C\text{-}F}$ = 23.0 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -106.25 (s); HRMS (ESI) m/z calcd for $[C_6H_5FNOS]^+$ $[M+H]^+$: 158.0070, found: 158.0074.

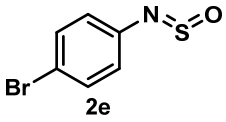
(4) ((4-chlorophenyl)imino)-λ⁴-sulfanone (2d)



2d

Followed **General Procedure B2** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.75 (d, *J* = 1.8 Hz, 1H), 8.69 (d, *J* = 1.8 Hz, 1H), 7.06 (t, *J* = 1.7 Hz, 1H), 6.94 (d, *J* = 1.7 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 154.8, 122.9, 122.5, 113.9 Analytical data are in accordance with the literature values[7].

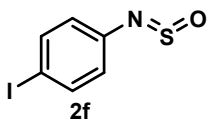
(5) ((4-bromophenyl)imino)-λ⁴-sulfanone (2e)



2e

Followed **General Procedure B2** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.73 (s, 1H), 7.55 (s, 1H), 7.53 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 103.9, 95.0, 91.0, 87.0; HRMS (ESI) m/z calcd for $[C_6H_5BrNOS]^+$ $[M+H]^+$: 217.9270, found: 217.9277.

(6) ((4-iodophenyl)imino)-λ⁴-sulfanone (2f)

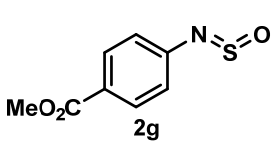


2f

Followed **General Procedure B2** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.75 (s, 1H), 7.59 (s, 1H), 7.58 (s, 1H); ^{13}C NMR (126 MHz,

$CDCl_3$): δ 142.1, 138.7, 128.6, 96.9; HRMS (ESI) m/z calcd for $[C_6H_5INOS]^+$ $[M+H]^+$: 265.9131, found: 265.9132.

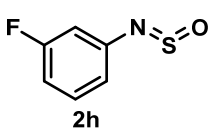
(7) methyl 4-((oxo-λ^4-sulfaneylidene)amino)benzoate (2g)



2g

Followed **General Procedure B3** on 10.0 mmol scale without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92–7.71 (m, 2H), 6.71–6.43 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.3, 151.0, 131.7, 119.7, 113.9, 51.7; HRMS (ESI) m/z calcd for $[C_8H_8NO_2S]^+$ $[M+H]^+$: 182.0270, found: 182.0277.

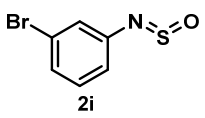
(8) ((3-fluorophenyl)imino)-λ^4-sulfanone (2h)



2h

Followed **General Procedure B2** on 20.0 mmol scale. Purified via vacuum distillation to obtain the oily liquid **2i** (1.507 g, 48% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67–7.56 (m, 2H), 7.45–7.36 (m, 1H), 7.18–7.09 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.4 (d, $J_{C\text{-}F}$ = 248.5 Hz), 143.4 (d, $J_{C\text{-}F}$ = 9.7 Hz), 130.5 (d, $J_{C\text{-}F}$ = 8.8 Hz), 123.1 (d, $J_{C\text{-}F}$ = 3.3 Hz), 117.8 (d, $J_{C\text{-}F}$ = 21.4 Hz), 114.2 (d, $J_{C\text{-}F}$ = 23.2 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -110.60 (s); HRMS (ESI) m/z calcd for $[C_6H_5FNOS]^+$ $[M+H]^+$: 158.0070, found: 158.0074.

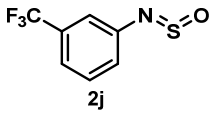
(9) ((3-bromophenyl)imino)-λ^4-sulfanone (2i)



2i

Followed **General Procedure B2** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (t, J = 1.8 Hz, 1H), 7.78 (ddd, J = 8.0, 1.7, 0.9 Hz, 1H), 7.53 (ddd, J = 8.1, 1.7, 0.9 Hz, 1H), 7.30 (t, J = 8.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.3, 133.5, 130.6, 129.9, 125.7, 122.7; HRMS (ESI) m/z calcd for $[C_6H_5BrNOS]^+$ $[M+H]^+$: 217.9270, found: 217.9274.

(10) ((3-(trifluoromethyl)phenyl)imino)-λ^4-sulfanone (2j)

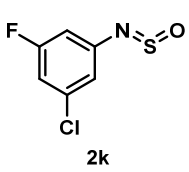


2j

Followed **General Procedure B1** on 20.0 mmol scale. Purified via vacuum distillation to obtain the oily liquid **2k** (2.417 g, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06-8.05 (m, 2H), 7.65 (d,

J = 7.9 Hz, 1H), 7.58-7.54 (m, 1H). Analytical data are in accordance with the literature values[8l].

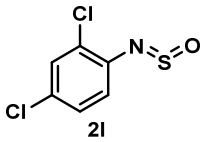
(11) ((4-chloro-2-fluorophenyl)imino)-λ⁴-sulfanone (2k)



2k

Followed **General Procedure B2** on 10.0 mmol scale. Purified via vacuum distillation to obtain the oily liquid **2l** (1.406 g, 74% yield); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 1.0 Hz, 1H), 7.53–7.45 (m, 1H), 7.14 (dt, J = 8.1, 2.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 162.3 (d, $J_{C\text{-}F}$ = 251.6 Hz), 143.2 (d, $J_{C\text{-}F}$ = 11.0 Hz), 135.6 (d, $J_{C\text{-}F}$ = 11.7 Hz), 123.1 (d, $J_{C\text{-}F}$ = 3.7 Hz), 118.2 (d, $J_{C\text{-}F}$ = 25.0 Hz), 112.6 (d, $J_{C\text{-}F}$ = 23.4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -108.72 (s); HRMS (ESI) m/z calcd for $[C_6H_4FClNOS]^+$ $[M+H]^+$:191.9681, found:191.9677.

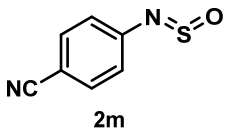
(12) ((2,4-dichlorophenyl)imino)-λ⁴-sulfanone (2l)



2l

Followed **General Procedure B2** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.15 (d, J = 8.7 Hz, 1H), 7.81 (d, J = 1.8 Hz, 1H), 7.55 (dd, J = 8.7, 2.3 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 137.6, 133.8, 129.8, 129.1, 128.3; HRMS (ESI) m/z calcd for $[C_6H_4Cl_2NOS]^+$ $[M+H]^+$: 207.9385, found: 207.9394.

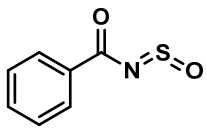
(13)4-((oxo-l4-sulfaneylidene)amino)benzonitrile (2m)



2m

Followed **General Procedure B2** on 5.0 mmol scale without further purification. Yellow solid, m.p. = 210-212 °C ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.02–7.92 (m, 2H), 7.82–7.70 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 144.55, 133.79, 125.83, 118.32, 111.02; HRMS (ESI) m/z calcd for $[C_7H_5N_2OS]^+$ $[M+H]^+$: 165.0117, found: 165.0124.

(14)*N*-(oxo-l4-sulfaneylidene)benzamide (2n)

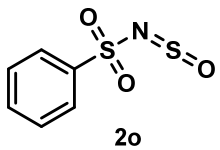


2n

Followed **General Procedure B3** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.90 (d, J = 7.5 Hz, 2H), 7.51-7.48 (m, 1H), 7.45-7.42 (m, 3H); ^{13}C NMR (126 MHz,

DMSO-d_6): δ 168.0, 134.3, 131.3, 128.2, 127.5. Analytical data are in accordance with the literature values [5b].

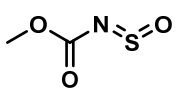
(15)*N*-(oxo-l4-sulfaneylidene)benzenesulfonamide (2o)



2o

Followed **General Procedure B3** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.39 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.9 Hz, 2H), 7.04 (t, J = 7.2 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 141.9, 129.4, 123.6, 114.8. Analytical data are in accordance with the literature values [5b].

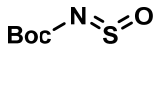
(16)methyl (oxo-l4-sulfaneylidene)carbamate (2p)



2p

Followed **General Procedure B3** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.78 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 172.2, 22.3. Analytical data are in accordance with the literature values [5b].

(17)tert-butyl (oxo-l4-sulfaneylidene)carbamate (2q)

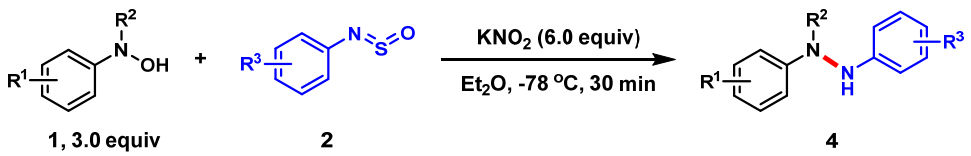


2q

Followed **General Procedure B3** on 5.0 mmol scale without further purification. ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.37 (s, 9H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 156.2, 77.0, 28.2. Analytical data are in accordance with the literature values[5b].

9. General procedure for the synthesis of *N,N'*-diarylhydrazine 4

General procedure C:



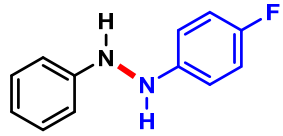
1, 3.0 equiv　　2　　4

To a Schlenk tube was added a small stir bar, the corresponding arylhydroxylamine **1** (0.6 mmol, 3.0 equiv), potassium nitrite (102.1 mg, 1.2 mmol, 6.0 equiv) unless otherwise noted. Following evacuation and the introduction of nitrogen on a Schlenk

line, diethyl ether (2.0 mL, 0.05 M) was added via syringe. The mixture is then stirred at room temperature for 2 minutes and then transferred to -78 ºC. *N*-sulfinylbenzenamine **2** (0.2 mmol, 1.0 equiv) were added into the mixture via microsyringe at -78 ºC and then stirred for 30 minutes until the complete consumption of **2**, which was monitored by TLC analysis. Afterwards, the mixture (the temperature in the rotary evaporator was maintained below 30 ºC) was concentrated *in vacuo* and the residue was purified by flash column chromatography (eluted with PE/EtOAc) to afford the title compound **4**. The same procedure was employed for the corresponding gram-scale reaction.

10. Analytical data of *N,N′*-diarylhydrazine 4

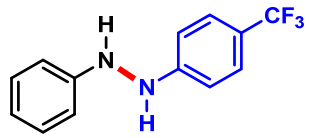
(1) 1-(4-fluorophenyl)-2-phenylhydrazine (4a)



4a

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4a**: 21 mg, 52% yield; White solid, m.p. = 78-79 ºC; R_f = 0.6 (PE:EtOAc = 3:1);^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 7.64 (s, 1H), 7.59 (s, 1H), 7.17–7.06 (m, 2H), 6.99–6.91 (m, 2H), 6.76–6.67 (m, 4H), 6.63 (tt, *J* = 7.2, 1.1 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 155.3 (d, $J_{C\text{-}F}$ = 232.2 Hz), 149.8, 146.5, 128.9, 117.7, 115.3 (d, $J_{C\text{-}F}$ = 22.0 Hz), 112.7 (d, $J_{C\text{-}F}$ = 7.4 Hz), 111.7; ^{19}F NMR (471 MHz, DMSO-*d*$_6$) δ -127.58 (s). Analytical data are in accordance with the literature values [9]

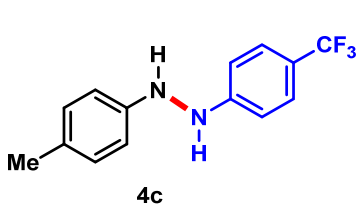
(2) 1-phenyl-2-(4-(trifluoromethyl)phenyl)hydrazine (4b)



4b

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4b**: 40 mg, 80% yield; White solid, m.p. = 78-79 ºC; R_f = 0.6 (PE:EtOAc = 3:1);^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 2H), 6.89 (dd, *J* = 17.2, 8.0 Hz, 3H), 6.82 (d, *J* = 7.7 Hz, 2H), 5.86 (s, 1H), 5.69 (s, 1H). Analytical data are in accordance with the literature values [9].

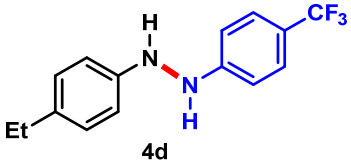
(3) 1-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4c)



4c

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4c**: 38 mg, 66% yield; White solid, m.p. = 78-80 ºC; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.75– 6.73 (m, 2H), 5.81 (s, 1H), 5.59 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.8, 145.8, 130.1, 130.0, 126.9 (q, J_{C-F} = 3.8 Hz), 124.8 (q, J_{C-F} = 270.9 Hz), 121.5 (q, J_{C-F} = 32.8 Hz), 112.6, 111.7, 20.6; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.18 (s); HRMS (ESI) m/z calcd for $[C_{14}H_{14}F_3N_2]$+ $[M+H]^+$: 267.1104, found: 267.1103.

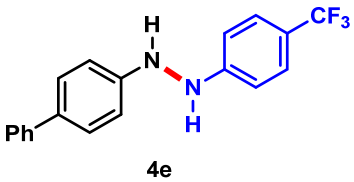
(4) 1-(4-ethylphenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4d)



4d

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4d**: 50 mg, 89% yield; White solid, m.p. = 48-49 ºC; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 5.81 (s, 1H), 5.60 (s, 1H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.9, 146.0, 136.6, 128.9, 126.9 (q, J_{C-F} = 3.7 Hz), 124.8 (q, J_{C-F} = 270.9 Hz), 121.5 (q, J_{C-F} = 32.6 Hz), 112.7, 111.7, 28.1, 16.0; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.19 (s); HRMS (ESI) m/z calcd for $[C_{15}H_{16}F_3N_2]^+$ $[M+H]^+$: 281.1260, found: 281.1274.

(5) 1-([1,1'-biphenyl]-4-yl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4e)

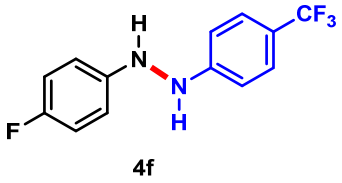


4e

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4e**: 34 mg, 53% yield; White solid, m.p. = 69-71 ºC; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, J = 8.2, 1.1 Hz, 2H), 7.51–7.45 (m, 4H), 7.42 (t, J = 7.7 Hz, 2H), 7.33-7.27 (m, 1H), 6.98–6.84 (m, 4H), 5.90 (s,

1H), 5.76 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.6, 147.5, 140.9, 133.7, 128.9, 128.3, 126.9 (q, J_{C-F} = 3.8 Hz), 126.74, 126.67, 124.8 (q, J_{C-F} = 270.9 Hz), 121.8 (q, J_{C-F} = 32.8 Hz), 112.8, 111.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.24 (s); HRMS (ESI) m/z calcd for $[C_{19}H_{16}F_3N_2]^+$ $[M+H]^+$: 329.1260, found:3293.1265.

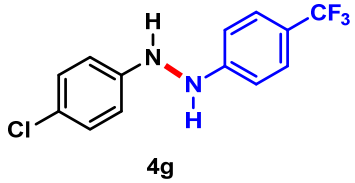
(6) 1-(4-fluorophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4f)



4f

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4f**: 30 mg, 57% yield; White solid, m.p. = 77-78 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, J = 8.5 Hz, 2H), 6.94 (t, J = 8.7 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 6.79–6.76 (m, 2H), 5.87 (s, 1H), 5.63 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.6 (d, J_{C-F} = 238.0 Hz), 151.5, 144.3 (d, J_{C-F} = 2.0 Hz), 126.9 (q, J_{C-F} = 3.8 Hz), 124.8 (q, J_{C-F} = 270.9 Hz), 121.8 (q, J_{C-F} = 32.8 Hz), 116.1 (d, J_{C-F} = 22.7 Hz), 113.6 (d, J_{C-F} = 7.6 Hz), 111.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.27 (s), -124.34 (s); HRMS (ESI) m/z calcd for $[C_{13}H_{11}F_3N_2]^+$ $[M+H]^+$: 271.0853, found: 271.0855.

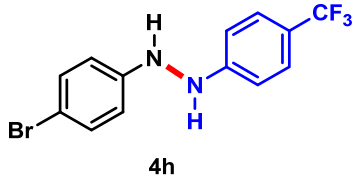
(7) 1-(4-chlorophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4g)



4g

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromato-graphy on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4g**: 27 mg, 48% yield; White solid, m.p. = 73-75 °C; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.9 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.9 Hz, 2H), 5.88 (s, 1H), 5.70 (s, 1H). Analytical data are in accordance with the literature values.[10]

(8) 1-(4-bromophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4h)

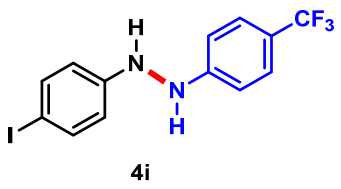


4h

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4h**: 36 mg, 54%

yield; White solid, m.p. = 156-158 ºC; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 5.87 (s, 1H), 5.70 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.2, 147.2, 132.4, 127.0 (q, J_{C-F} = 3.8 Hz), 124.7 (q, J_{C-F} = 270.9 Hz), 122.0 (q, J_{C-F} = 32.8 Hz), 114.1, 112.3, 111.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.30; HRMS (ESI) m/z calcd for $[C_{13}H_{11}BrF_3N_2]^+$ $[M+H]^+$:331.0052, found:331.0052.

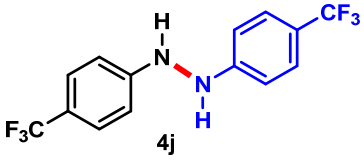
(9) 1-(4-iodophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4i)



4i

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4i**: 46 mg, 61% yield; White solid, m.p. = 201-203 ºC; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 5.86 (s, 1H), 5.70 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 147.9, 138.2, 127.0 (q, J_{C-F} = 3.8 Hz), 124.7 (q, J_{C-F} = 270.9 Hz), 122.0 (q, J_{C-F} = 32.8 Hz) , 114.6, 111.7, 81.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.29 (s); HRMS (ESI) m/z calcd for $[C_{13}H_{11}F_3IN_2]^+$ $[M+H]^+$: 378.9914, found: 378.9923.

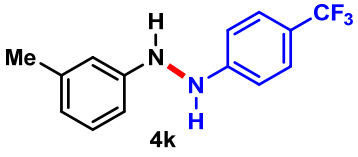
(10) 1,2-bis(4-(trifluoromethyl)phenyl)hydrazine (4j)



4j

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4j**: 37 mg, 58% yield; White solid, m.p. = 92-94 ºC; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.5 Hz, 4H), 6.88 (d, *J* = 8.5 Hz, 4H), 5.95 (s, 2H). Analytical data are in accordance with the literature values.[9]

(11) 1-(*m*-tolyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4k)

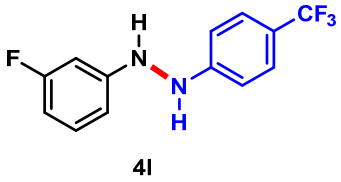


4k

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4k**: 30 mg, 56% yield;

White solid, m.p. = 76-78 °C; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 7.4 Hz, 1H), 6.66–6.63 (m, 2H), 5.81 (s, 1H), 5.62 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.7, 148.2, 139.6, 129.5, 126.9 (q, J_{C-F} = 3.8 Hz), 124.8 (q, J_{C-F} = 272.2 Hz), 121.5 (q, J_{C-F} = 32.8 Hz), 113.1, 111.7, 109.6, 21.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.15 (s); HRMS (ESI) m/z calcd for $[C_{14}H_{14}F_3N_2]^+$ $[M+H]^+$: 267.1104, found: 267.1111.

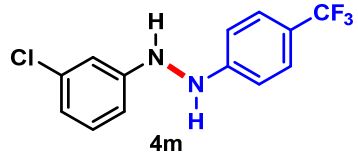
(12) 1-(3-fluorophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4l)



4l

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with (PE/EtOAc = 9/1) to obtain **4l**: 28 mg, 50% yield; White solid, m.p. = 63-65 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.20–7.15 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.60–6.54 (m, 3H), 5.88 (s, 1H), 5.77 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 164.2 (d, J_{C-F} = 244.4 Hz), 151.1, 150.2 (d, J_{C-F} = 10.0 Hz), 130.9 (d, J_{C-F} = 9.9 Hz), 127.0 (q, J_{C-F} = 3.8 Hz), 124.7 (q, J_{C-F} = 270.9 Hz), 122.0 (q, J_{C-F} = 32.8 Hz), 111.7, 108.0 (d, J_{C-F} = 2.5 Hz), 107.1 (d, J_{C-F} = 21.6 Hz), 99.7 (d, J_{C-F} = 26.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.31 (s), -111.82 (s); HRMS (ESI) m/z calcd for $[C_{13}H_{131}F_4N_2]^+$ $[M+H]^+$: 271.0853, found: 271.0855.

(13) 1-(3-chlorophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4m)

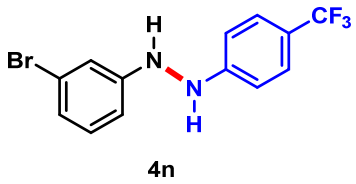


4m

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4m**: 40 mg, 70% yield; White solid, m.p. = 64-66 °C; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.16–7.13 (m, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.85–6.84 (m, 2H), 6.71–6.69 (m, 1H), 5.87 (s, 1H), 5.73 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 149.5, 135.5, 130.7, 127.0 (q, J_{C-F} = 3.8 Hz), 124.7 (q, J_{C-F} = 270.9 Hz), 122.0 (q, J_{C-F} = 32.8 Hz), 120.5, 112.4, 111.7, 110.6; ^{19}F NMR

(471 MHz, $CDCl_3$): δ -61.30; HRMS (ESI) m/z calcd for $[C_{13}H_{11}ClF_3N_2O]^+$ $[M+H]^+$: 287.0557, found: 287.0554.

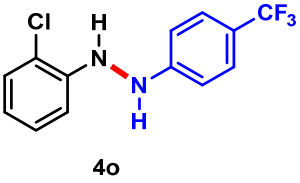
(14) 1-(3-bromophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4n)



4n

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 3/1) to obtain **4n**: 46 mg, 71% yield; White solid, m.p. = 67-69 °C; R_f = 0.5 (PE:EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.28 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.12 (ddd, *J* = 11.4, 8.8, 5.0 Hz, 1H), 6.92–6.82 (m, 2H), 6.52 (ddd, *J* = 10.3, 7.0, 3.1 Hz, 1H), 6.45 (tt, *J* = 8.5, 3.2 Hz, 1H; ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 149.6, 130.9, 127.0 (q, J_{C-F} = 3.8 Hz), 124.7 (q, J_{C-F} = 272.2 Hz), 123.6, 123.4, 122.1 (q, J_{C-F} = 32.8 Hz), 115.3, 111.7, 111.0; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.30; HRMS (ESI) m/z calcd for $[C_{13}H_{11}BrN_2O]^+$ $[M+H]^+$: 331.0052, found: 331.0554.

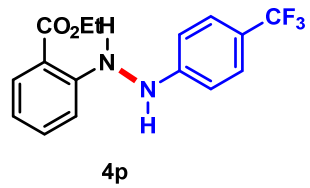
(15) 1-(2-chlorophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4o)



4o

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 3/1) to obtain **4o**: 49 mg, 89% yield; White solid, m.p. = 54-56 °C; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.32 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.16–7.12 (m, 1H), 6.94 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.81 (td, *J* = 7.9, 1.3 Hz, 1H), 6.26 (s, 1H), 5.88 (s, 1H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 151.1, 143.7, 129.7, 128.1, 127.0 (q, J_{C-F} = 3.8 Hz), 124.7 (q, J_{C-F} = 270.9 Hz), 122.1 (q, J_{C-F} = 32.8 Hz), 120.6, 118.1, 113.0, 111.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.33 (s); HRMS (ESI) m/z calcd for $[C_{13}H_{11}FNO_2]^+$ $[M+H]^+$: 287.0557, found: 287.0550.

(16) ethyl 2-(2-(4-(trifluoromethyl)phenyl)hydrazineyl)benzoate (4p)

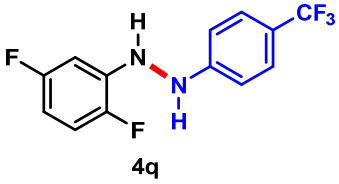


4p

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/THF = 15/1) to obtain **4p**: 36 mg, 55% yield; White solid,

m.p. = 127-129 °C; R_f = 0.6 (PE:THF = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.16 (s, 1H), 7.99 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.36 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.05 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.78 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 5.92 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.4, 151.6, 151.2, 134.8, 131.6, 126.9 (q, J_{C-F} = 3.7 Hz), 124.8 (q, J_{C-F} = 270.7 Hz), 121.8 (q, J_{C-F} = 32.6 Hz), 117.8, 112.2, 111.7, 111.2, 60.9, 14.5; ^{19}F NMR (471 MHz, $CDCl_3$):) δ -61.28 (s); HRMS (ESI) m/z calcd for $[C_{16}H_{16}F_3N_2O_2]^+$ $[M+H]^+$: 325.1158, found: 325.1169.

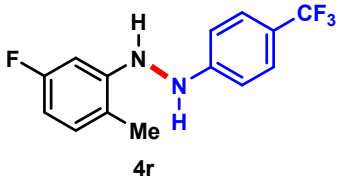
(17) 1-(2,5-difluorophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4q)



4q

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4q**: 24 mg, 42% yield; White solid, m.p. = 68-70 °C; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 6.98 (ddd, *J* = 11.0, 8.9, 4.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.68 (ddd, *J* = 9.9, 6.8, 3.0 Hz, 1H), 6.46 (tt, *J* = 8.5, 3.3 Hz, 1H), 6.00 (s, 1H), 5.84 (s, 1H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 159.2 (d, J_{C-F} = 237.6 Hz), 152.4, 146.1 (dd, J_{C-F} = 234.8, 2.1 Hz), 138.6 (dd, J_{C-F} = 12.8, 10.7 Hz), 126.5 (q, J_{C-F} = 3.8 Hz), 125.1 (q, J_{C-F} = 270.2 Hz), 118.2 (q, J_{C-F} = 31.9 Hz), 115.9 (dd, J_{C-F} = 20.1, 10.3 Hz), 111.2, 103.2 (dd, J_{C-F} = 24.5, 7.2 Hz), 99.5 (dd, J_{C-F} = 29.2, 4.0 Hz); ^{19}F NMR (471 MHz, DMSO-*d*$_6$): δ -61.42 (s), -116.89 (d, *J* = 15.8 Hz), -141.33 (d, *J* = 15.9 Hz); HRMS (ESI) m/z calcd for $[C_{13}H_{10}F_5N_2]^+$ $[M+H]^+$: 289.0759, found: 289.0747.

(18) 1-(5-fluoro-2-methylphenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4r)



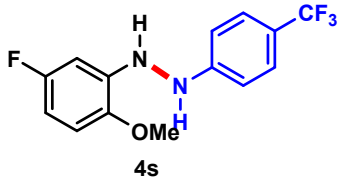
4r

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4r**: 29 mg, 52% yield; White solid, m.p. = 112-114 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.38 (s, 1H), 7.68 (s, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.05–6.94 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.42–6.38 (m, 1H), 6.37 (s, 1H), 2.17

(s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 161.9 (d, $J_{C\text{-}F}$ = 237.8 Hz), 152.6, 148.4 (d, $J_{C\text{-}F}$ = 9.9 Hz), 131.2 (d, $J_{C\text{-}F}$ = 9.5 Hz), 126.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.1 (q, $J_{C\text{-}F}$ = 270.2 Hz), 117.7 (q, $J_{C\text{-}F}$ = 31.8 Hz), 117.0 (d, $J_{C\text{-}F}$ = 2.7 Hz), 111.0, 103.5 (d, $J_{C\text{-}F}$ = 21.1 Hz), 97.2 (d, $J_{C\text{-}F}$ = 26.7 Hz), 16.7; ^{19}F NMR (471 MHz, DMSO-*d*$_6$): δ -59.22 (s), -116.39 (s); HRMS (ESI) m/z calcd for $[C_{14}H_{13}F_3N_2]^+$ $[M+H]^+$:285.1009, found: 280.1010.

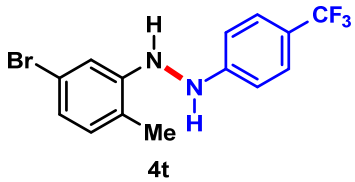
(19) 1-(5-fluoro-2-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4s)

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4s**: 24 mg, 40% yield; White solid, m.p. = 113-115 °C; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.27 (s, 1H), 7.64 (s, 1H), 7.45 (d, *J* = 9.0 Hz, 2H), 6.85 (dd, *J* = 8.7, 5.0 Hz, 1H), 6.82 (d, *J* = 8.9 Hz, 2H), 6.42 (td, *J* = 8.5, 3.1 Hz, 1H), 6.37 (dd, *J* = 10.8, 3.1 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 157.5 (d, $J_{C\text{-}F}$ = 233.5 Hz), 152.7, 142.4, 139.7 (d, $J_{C\text{-}F}$ = 10.4 Hz), 126.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 125.1 (q, $J_{C\text{-}F}$ = 270.2 Hz), 117.7 (q, $J_{C\text{-}F}$ = 31.8 Hz), 111.3 (d, $J_{C\text{-}F}$ = 9.8 Hz), 111.0, 102.5 (d, $J_{C\text{-}F}$ = 22.8 Hz), 97.8 (d, $J_{C\text{-}F}$ = 28.6 Hz), 56.0; ^{19}F NMR (471 MHz, DMSO-*d*$_6$): δ -59.22 (s), -122.42 (s); HRMS (ESI) m/z calcd for $[C_{14}H_{13}F_3N_2O]^+$ $[M+H]^+$: 301.0959, found: 301.0954.



4s

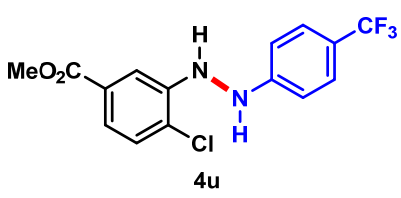
(20) 1-(5-bromo-2-methylphenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4t)



4t

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4t**: 35 mg, 51% yield; White solid, m.p. = 95-97 °C; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 1.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.82 (s, 1H), 5.60 (s, 1H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.1, 146.9, 132.0, 127.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.7 (q, $J_{C\text{-}F}$ = 270.9 Hz), 122.1 (q, $J_{C\text{-}F}$ = 32.8 Hz), 121.0, 120.1, 114.0, 111.8, 16.9; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.31 (s); HRMS (ESI) m/z calcd for $[C_{14}H_{13}BrN_2]^+$ $[M+H]^+$: 345.0209, found: 345.0215.

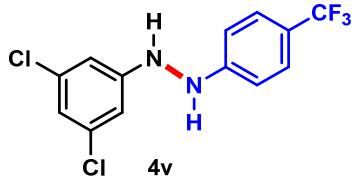
(21) methyl 4-chloro-3-(2-(4-(trifluoromethyl)phenyl)hydrazineyl)benzoate (4u)



4u

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9Z/1) to obtain **4u**: 45 mg, 66% yield; White solid, m.p. = 88-90 ºC; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 1.9 Hz, 1H), 7.50–7.45 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.31 (s, 1H), 5.99 (s, 1H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.6, 150.7, 143.9, 130.2, 129.7, 127.0 (q, J_{C-F} = 3.8 Hz), 124.7 (q, J_{C-F} = 270.8 Hz), 122.6, 122.4 (q, J_{C-F} = 32.8 Hz), 121.6, 113.8, 111.9, 52.4; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.40 (s); HRMS (ESI) m/z calcd for $[C_{15}H_{13}ClF_3N_2O_2]^+$ $[M+H]^+$: 345.0612, found: 345.0615.

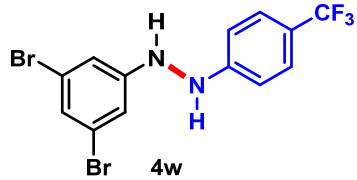
(22) 1-(3,5-dichlorophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4v)



4v

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4v**: 50 mg, 79% yield; White solid, m.p. = 79-81 ºC; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 6.96–6.80 (m, 3H), 6.73 (d, *J* = 1.3 Hz, 2H), 5.89 (s, 1H), 5.78 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.6, 150.2, 136.0, 127.0 (q, J_{C-F} = 3.7 Hz), 124.6 (q, J_{C-F} = 270.9 Hz) ,122.5 (q, J_{C-F} = 32.6 Hz), 120.3, 111.8, 110.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.36 (s); HRMS (ESI) m/z calcd for $[C_{13}H_{10}Cl_2F_3N_2]^+$ $[M+H]^+$: 321.0168, found: 321.0164.

(23) 1-(3,5-dibromophenyl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4w)

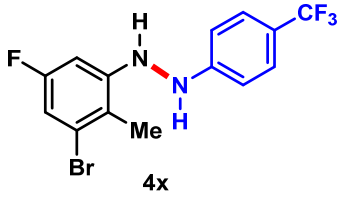


4w

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4w**: 36 mg, 44% yield; White solid, m.p. = 121-123 ºC; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.46 (s, 1H), 8.40 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.01 (s, 1H), 6.88 (t, *J* = 1.7 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 152.2, 152.2, 126.5 (q, J_{C-F} = 3.9 Hz), 125.0 (q, J_{C-F} =

270.3 Hz), 123.1, 122.2, 118.3 (q, J_{C-F} = 31.9 Hz), 113.0, 111.2; ^{19}F NMR (471 MHz, DMSO-d_6): δ -59.38 (s); HRMS (ESI) m/z calcd for $[C_{13}H_{10}Br_2F_3N_2]^+$ $[M+H]^+$: 408.9157, found: 408.9155.

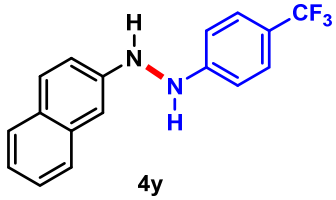
(24) 1-(3-bromo-5-fluoro-2-methylphenyl)-2-(4-(trifluoromethyl)phenyl) hydrazine (4x)



4x

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4x**: 36 mg, 50% yield; White solid, m.p. = 84-86 ºC; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.47 (s, 1H), 8.02 (s, 1H), 7.46 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.79 (dd, J = 8.2, 2.7 Hz, 1H), 6.50 (dd, J = 11.4, 2.7 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 161.3 (d, J_{C-F} = 242.1 Hz), 152.2, 149.5 (d, J_{C-F} = 10.5 Hz), 126.4 (q, J_{C-F} = 3.7 Hz), 125.1 (q, J_{C-F} = 270.3 Hz), 124.6 (d, J_{C-F} = 12.0 Hz), 118.2 (q, J_{C-F} = 31.9 Hz), 116.4 (d, J_{C-F} = 2.8 Hz), 111.2, 107.9 (d, J_{C-F} = 24.7 Hz), 96.9 (d, J_{C-F} = 26.4 Hz), 16.1; ^{19}F NMR (471 MHz, DMSO-d_6): δ - 59.42 (s), - 114.81 (s); HRMS (ESI) m/z calcd for $[C_{14}H_{12}BrF_4N_2]^+$ $[M+H]^+$: 363.0115, found: 363.0114.

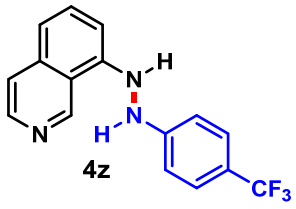
(25) 1-(naphthalen-2-yl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4y)



4y

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4y**: 42 mg, 71% yield; White solid, m.p. = 113-115 ºC; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80–7.70 (m, 2H), 7.63 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 8.6 Hz, 2H), 7.43–7.38 (m, 1H), 7.35–7.28 (m, 1H), 7.12–7.02 (m, 2H), 6.92 (d, J = 8.6 Hz, 2H), 5.87 (s, 1H), 5.79 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.4, 145.7, 134.7, 129.7, 129.2, 127.9, 126.9 (q, J_{C-F} = 3.8 Hz), 126.8, 126.6, 124.8 (q, J_{C-F} = 270.7 Hz), 123.4, 121.7 (q, J_{C-F} = 32.6 Hz), 115.4, 111.8, 106.2; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.17 (s); HRMS (ESI) m/z calcd for $[C_{17}H_{14}F_3N_2]^+$ $[M+H]^+$: 303.1104, found: 303.1105.

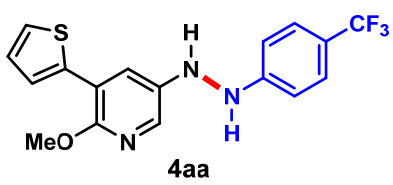
(26) 7-(2-(4-(trifluoromethyl)phenyl)hydrazineyl)isoquinoline (4z)



4z

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 1/1) to obtain **4z**: 31 mg, 51% yield; White solid, m.p. = 154-156 ºC; R_f = 0.1 (PE:EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (s, 1H), 8.51 (d, *J* = 2.7 Hz, 1H), 7.66 (d, *J* = 3.8 Hz, 1H), 7.50–7.42 (m, 4H), 7.13 (d, *J* = 6.9 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.58 (s, 1H), 6.13 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.2, 150.9, 142.6, 141.8, 129.4, 128.1, 127.0 (q, J_{C-F} = 3.8 Hz), 125.7, 125.0, 124.7 (q, J_{C-F} = 270.9 Hz), 122.2 (q, J_{C-F} = 32.6 Hz), 119.6, 113.2, 111.9, 110.0; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.34 (s); HRMS (ESI) m/z calcd for $[C_{16}H_{13}F_3N_3]^+$ $[M+H]^+$: 304.1056, found: 304.1058.

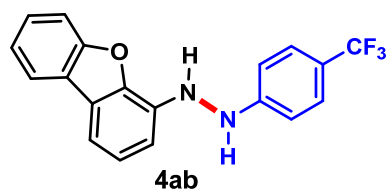
(27) 2-methoxy-3-(thiophen-3-yl)-5-(2-(4-(trifluoromethyl)phenyl)hydrazineyl) pyridine (4aa)



4aa

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4aa**: 32 mg, 44% yield; White solid, m.p. = 134-136 ºC; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 2.7 Hz, 1H), 7.53 (dd, *J* = 3.7, 0.9 Hz, 1H), 7.50–7.44 (m, 3H), 7.35 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.08 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 5.91 (s, 1H), 5.56 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.9, 151.4, 139.2, 137.7, 129.4, 127.4, 127.0 (q, J_{C-F} = 3.7 Hz), 126.6, 126.5, 124.7 (q, J_{C-F} = 270.8 Hz), 122.2, 122.1 (q, J_{C-F} = 32.8 Hz), 118.2, 111.9, 53.8; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.33 (s); HRMS (ESI) m/z calcd for $[C_{18}H_{16}F_3N_2OS]^+$ $[M+H]^+$: 365.0930, found: 365.0941.

(28) 1-(dibenzo[b,d]furan-2-yl)-2-(4-(trifluoromethyl)phenyl)hydrazine (4ab)



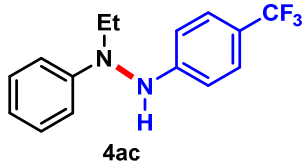
4ab

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4ab**: 37 mg, 54% yield; White solid, m.p. = 78-80 ºC; R_f = 0.6

(PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.53–7.44 (m, 4H), 7.42–7.33 (m, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.97-6.94 (m, 3H), 6.32 (s, 1H), 5.94 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.2, 151.4, 143.5, 133.6, 127.3, 126.9 (q, J_{C-F} = 3.7 Hz), 124.8, 124.8 (q, J_{C-F} = 270.7 Hz), 124.6, 123.9, 123.1, 121.9 (q, J_{C-F} = 32.6 Hz), 121.1, 112.0, 111.9, 111.8, 109.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.25 (s); HRMS (ESI) m/z calcd for $[C_{19}H_{14}F_3N_2O]^+$ $[M+H]^+$: 343.1053, found: 343.1055.

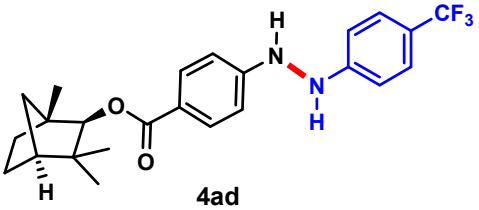
(29) 1-ethyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)hydrazine (4ac)

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 20/1) to obtain **4ac**: 40 mg, 71% yield; viscous oily liquid, R_f = 0.5 (PE:EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.26-7.23 (m, 2H), 6.89-6.83 (m, 5H), 5.78 (s, 1H), 3.57 (d, *J* = 6.5 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.0, 149.2, 129.5, 127.0 (q, J_{C-F} = 3.8 Hz), 124.9 (q, J_{C-F} = 270.4 Hz), 121.3 (q, J_{C-F} = 32.6 Hz), 119.5, 113.4, 111.5, 46.5, 11.0; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.36 (s); HRMS (ESI) m/z calcd for $[C_{15}H_{16}F_3N_2]^+$ $[M+H]^+$: 281.1260, found: 281.1266.



4ac

(30) (1*R*,2*R*,4*S*)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-(2-(4-(trifluoromethyl) phenyl)hydrazineyl)benzoate (4ad)

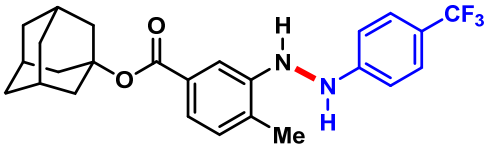


4ad

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4ad**: 45 mg, 53% yield; White solid, m.p. = 104-106 °C; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.60-8.51 (m, 2H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.46 (s, 2H), 6.95–6.47 (m, 4H), 4.44 (d, *J* = 7.8 Hz, 1H), 1.86 (s, 1H), 1.70-1.63 (m, 3H), 1.45 (s, 1H), 1.21-1.17 (m, 2H), 1.11-1.09 (m, 3H), 1.04-1.03 (m, 3H), 0.74 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 166.0, 153.5, 152.4, 131.1, 126.5, 125.1 (q, J_{C-}

$_F$ = 270.8 Hz), 119.0, 118.0 (q, J_{C-F} = 32.0 Hz), 111.1, 110.6, 85.0, 48.1, 47.8, 40.8, 29.5, 26.4, 25.5, 20.1, 19.3; ^{19}F NMR (471 MHz, DMSO-*d*$_6$): δ -59.32 (s); HRMS (ESI) m/z calcd for $[C_{24}H_{28}F_3N_2O_2]^+$ $[M+H]^+$: 433.2097, found: 433.2099.

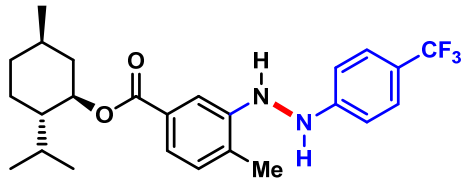
(31) (3*s*,5*s*,7*s*)-adamantan-1-yl 4-methyl-3-(2-(4-(trifluoromethyl) phenyl) hydrazineyl)benzoate (4ae)



4ae

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4ae**: 46 mg, 52% yield; White solid, m.p. = 133-135 ºC; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.39 (s, 1H), 7.60 (s, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 1.0 Hz, 1H), 7.18 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 2.25 (s, 3H), 2.12-2.08 (m, 9H), 1.61 (s, 6H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 165.0, 152.9, 146.7, 130.2, 129.8, 126.8, 126.5, 126.4, 125.2 (q, J_{C-F} = 270.6 Hz), 119.0, 117.5 (q, J_{C-F} = 31.7 Hz), 110.9, 110.7, 79.8, 40.9, 35.6, 30.2, 17.6; ^{19}F NMR (471 MHz, DMSO-*d*$_6$): δ -59.15(s); HRMS (ESI) m/z calcd for $[C_{25}H_{28}F_3N_2O_2]^+$ $[M+H]^+$: 445.2097, found: 445.2082.

(32) (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-methyl-3-(2-(4-(trifluoromethyl)phenyl)hydrazineyl)benzoate (4af)

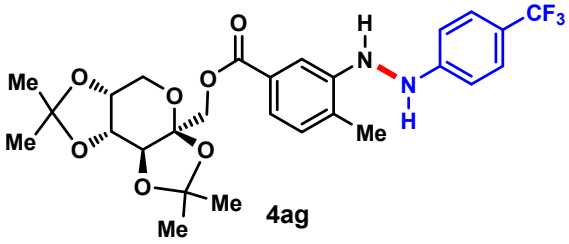


4af

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4af**: 36 mg, 40% yield; White solid, m.p. = 149-151 ºC; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57–7.40 (m, 4H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.92 (s, 1H), 5.69 (s, 1H), 4.82 (td, *J* = 10.8, 4.3 Hz, 1H), 2.29 (s, 3H), 2.06 (d, *J* = 11.9 Hz, 1H), 1.82 (dq, *J* = 11.4, 3.4 Hz, 1H), 1.74–1.64 (m, 2H), 1.56–1.40 (m, 2H), 1.06 (ddt, *J* = 31.3, 23.4, 11.1 Hz, 2H), 0.89 (d, *J* = 6.5 Hz, 4H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.70 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.4, 151.3,

145.7, 130.7, 130.2, 126.9 (q, J_{C-F} = 3.8 Hz), 126.7, 124.8 (q, J_{C-F} = 270.7 Hz), 121.8 (q, J_{C-F} = 32.6 Hz), 111.9, 111.8, 74.9, 47.3, 41.0, 34.4, 31.5, 26.7, 23.9, 22.2, 20.7, 17.5, 16.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.28 (s); HRMS (ESI) m/z calcd for $[C_{25}H_{32}F_3N_2O_2]^+$ $[M+H]^+$: 449.2410, found: 449.2411.

(33) ((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 4-methyl-3-(2-(4-(trifluoromethyl)phenyl) hydrazineyl)benzoate (4ag)

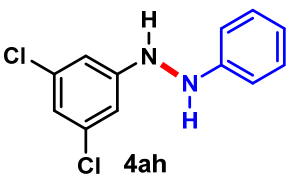


4ag

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 5/1) to obtain **4ag**: 75 mg, 67% yield; White solid, m.p. = 144-146 °C; R_f = 0.4 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.44 (s, 1H), 7.68 (s, 1H), 7.45 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 1.8 Hz, 1H), 7.34 (dd, J = 7.6, 1.8 Hz, 1H), 7.18 (d, J = 7.7 Hz, 1H), 6.88 (d, J = 8.5 Hz, 2H), 4.60 (dd, J = 7.9, 2.6 Hz, 1H), 4.51 (d, J = 11.7 Hz, 1H), 4.28 – 4.16 (m, 2H), 4.06 (d, J = 11.8 Hz, 1H), 3.77 (d, J = 11.3 Hz, 1H), 3.62 (d, J = 13.0 Hz, 1H), 2.29 (s, 3H), 1.36 (d, J = 16.4 Hz, 6H), 1.27 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.5, 152.8, 146.9, 130.5, 127.8, 127.5, 126.4 (q, J_{C-F} = 3.9 Hz), 125.2 (q, J_{C-F} = 278.5 Hz), 119.4, 117.7 (q, J_{C-F} = 31.8 Hz), 113.0, 111.0, 110.6, 108.22, 108.18, 101.0, 70.1, 69.8, 69.3, 64.1, 60.6, 26.2, 25.7, 25.0, 23.8, 17.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.28 (s); HRMS (ESI) m/z calcd for $[C_{27}H_{32}F_3N_2O_7]^+$ $[M+H]^+$: 533.2156, found:533.2167.

(34) 1-(3,5-dichlorophenyl)-2-phenylhydrazine (4ah)

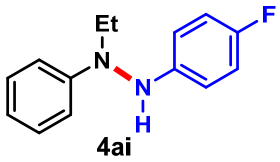
Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4ah**: 21mg, 42% yield; White solid, m.p. = 85-87 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.22 (m, 2H), 6.89 (t, J = 7.3 Hz, 1H), 6.80-6.77 (m, 5H), 5.66 (s, 1H), 5.63 (s, 1H); ^{13}C NMR (126 MHz,



4ah

$CDCl_3$): δ 151.0, 147.9, 135.9, 129.6, 120.8, 119.7, 112.5, 110.7; HRMS (ESI) m/z calcd for $[C_{12}H_{11}ClN_2]^+$ $[M+H]^+$: 253.0294, found: 253.0299.

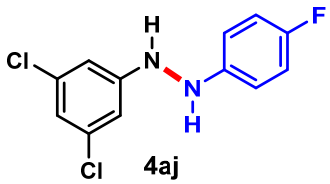
(35) 1-ethyl-2-(4-fluorophenyl)-1-phenylhydrazine (4ai)



4ai

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 20/1) to obtain **4ai**: 31 mg, 67% yield; viscous oily liquid, R_f = 0.5 (PE:EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (t, J = 8.0 Hz, 2H), 6.81 (t, J = 8.8 Hz, 4H), 6.72-6.64 (m, 3H), 5.39 (s, 1H), 3.45 (q, J = 7.0 Hz, 2H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.1 (d, $J_{C\text{-}F}$ = 236.6 Hz), 149.6, 144.3 (d, $J_{C\text{-}F}$ = 2.0 Hz), 129.4, 116.0 (d, $J_{C\text{-}F}$ = 22.6 Hz), 113.3 (d, $J_{C\text{-}F}$ = 7.5 Hz), 113.2, 46.1, 10.9; ^{19}F NMR (471 MHz, $CDCl_3$): δ -125.62 (s); HRMS (ESI) m/z calcd for $[C_{14}H_{16}FN_2]^+$ $[M+H]^+$: 231.1292, found: 231.1299.

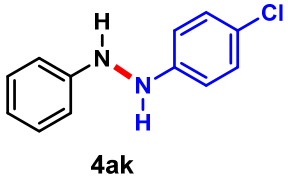
(36) 1-(3,5-dichlorophenyl)-2-(4-fluorophenyl)hydrazine (4aj)



4aj

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4aj**: 23 mg, 42% yield; White solid, m.p. = 72-74 °C; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.98–6.90 (m, 2H), 6.81 (t, J = 1.7 Hz, 1H), 6.76-6.74 (m, 4H), 5.69 (s, 1H), 5.58 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 157.6 (d, $J_{C\text{-}F}$ = 238.2 Hz), 150.8, 144.1 (d, $J_{C\text{-}F}$ = 2.1 Hz), 135.9, 119.8, 116.2 (d, $J_{C\text{-}F}$ = 22.7 Hz), 113.6 (d, $J_{C\text{-}F}$ = 7.7 Hz), 110.6; ^{19}F NMR (471 MHz, $CDCl_3$): δ -124.04 (s); HRMS (ESI) m/z calcd for $[C_{12}H_{10}Cl_2FN_2]^+$ $[M+H]^+$: 271.0200, found: 271.0211.

(37) 1-(4-chlorophenyl)-2-phenylhydrazine (4ak)

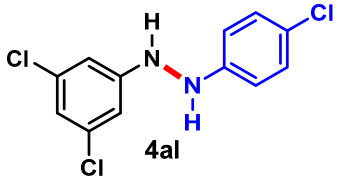


4ak

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4ak**: 27 mg, 61% yield; White solid, m.p. = 79-81 °C; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ7.23 (dd, J = 8.4, 7.5 Hz, 2H), 7.19–7.13 (m,

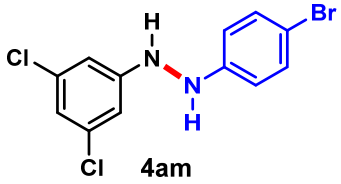
2H), 6.89– 6.77 (m, 5H), 5.62 (s, 2H); Analytical data are in accordance with the literature values [9].

(38) 1-(4-chlorophenyl)-2-(3,5-dichlorophenyl)hydrazine (4al)



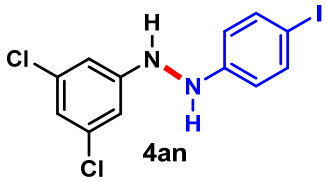
Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4al**: 32 mg, 57% yield; White solid, m.p. = 79-81 ºC; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.15 (m, 2H), 6.82 (t, *J* = 1.8 Hz, 1H), 6.76–6.70 (m, 4H), 5.69 (s, 1H), 5.64 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.5, 146.5, 135.9, 129.5, 125.3, 120.0, 113.7, 110.7; HRMS (ESI) m/z calcd for $[C_{12}H_{10}Cl_3N_2]^+$ $[M+H]^+$: 286.9904, found: 286.9901.

(39) 1-(4-bromophenyl)-2-(3,5-dichlorophenyl)hydrazine (4am)



Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4am**: 28 mg, 42% yield; White solid, m.p. = 239-241 ºC; R_f = 0.7 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.82 (s, 1H), 6.72 (d, *J* = 1.5 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 5.69 (s, 1H), 5.64 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.5, 147.0, 135.9, 132.4, 120.0, 114.1, 112.5, 110.6; HRMS (ESI) m/z calcd for $[C_{12}H_{10}Cl_2BrN_2]^+$ $[M+H]^+$: 330.9399, found: 330.9384.

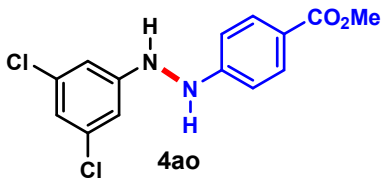
(40) 1-(3,5-dichlorophenyl)-2-(4-iodophenyl)hydrazine (4an)



Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4an**: 37 mg, 49% yield; White solid, m.p. = 134-136 ºC; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.43 (m, 2H), 6.81 (t, *J* = 1.8 Hz, 1H), 6.72 (d, *J* = 1.8 Hz, 2H), 6.62–6.55 (m, 2H), 5.69 (s, 1H), 5.65 (s, 1H); ^{13}C NMR (126 MHz,

$CDCl_3$): δ 150.4, 147.7, 138.3, 135.9, 120.0, 114.6, 110.7, 82.1; HRMS (ESI) m/z calcd for $[C_{12}H_{10}Cl_2IN_2]^+$ $[M+H]^+$: 378.9260, found: 378.9264.

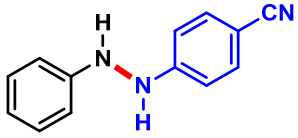
(41) methyl 4-(2-(3,5-dichlorophenyl)hydrazineyl)benzoate (4ao)



4ao

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4ao**: 34 mg, 54% yield; White solid, m.p. = 100-102 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.55 (s, 1H), 8.46 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 6.83-6.76 (m, 3H), 6.67 (d, *J* = 1.8 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 166.1, 153.2, 151.8, 134.7, 131.2, 118.9, 116.9, 110.7, 109.7, 51.4; HRMS (ESI) m/z calcd for $[C_{14}H_{13}Cl_2N_2O_2]^+$ $[M+H]^+$: 311.0349, found: 311.0358.

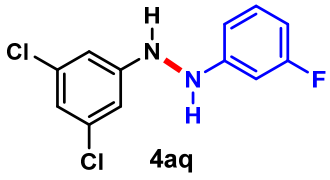
(42) 4-(2-phenylhydrazineyl)benzonitrile (4ap)



4ap

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 7/1) to obtain **4ap**: 25 mg, 59% yield; White solid, m.p. = 100-102 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 8.57 (s, 1H), 7.90 (s, 1H), 7.57–7.47 (m, 2H), 7.17 – 7.06 (m, 2H), 6.83–6.76 (m, 2H), 6.72-6.67 (m, 3H); ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 153.7, 148.9, 133.6, 129.1, 120.3, 118.5, 111.8, 111.2, 97.9; HRMS (ESI) m/z calcd for $[C_{13}H_{12}N_3]^+$ $[M+H]^+$: 210.1026, found: 210.1037.

(43) 1-(3,5-dichlorophenyl)-2-(3-fluorophenyl)hydrazine (4aq)

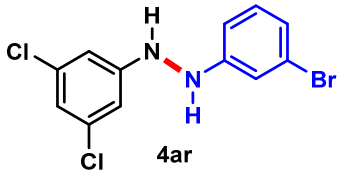


4aq

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4aq**: 22 mg, 41% yield; White solid, m.p. = 85-87 °C; R_f = 0.6 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (td, *J* = 8.1, 6.6 Hz, 1H), 6.83 (t, *J* = 1.7 Hz, 1H), 6.74 (d, *J* = 1.7 Hz, 2H), 6.59-6.51 (m, 3H), 5.70 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (126

MHz, $CDCl_3$): δ 164.1 (d, J_{C-F} = 244.6 Hz), 150.4, 149.9 (d, J_{C-F} = 9.9 Hz), 135.9, 130.9 (d, J_{C-F} = 9.8 Hz), 120.0, 110.7, 108.0 (d, J_{C-F} = 2.5 Hz), 107.2 (d, J_{C-F} = 21.5 Hz), 99.7 (d, J_{C-F} = 26.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -111.62 (s); HRMS (ESI) m/z calcd for $[C_{12}H_{10}Cl_2FN_2]^+$ $[M+H]^+$: 271.0200, found: 271.0215.

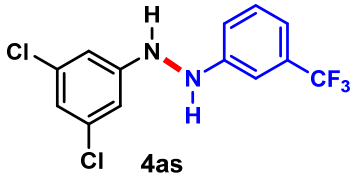
(44) 1-(3-bromophenyl)-2-(3,5-dichlorophenyl)hydrazine (4ar)



4ar

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 3/1) to obtain **4ar**: 42 mg, 64% yield; White solid, m.p. = 111-113 °C; R_f = 0.8 (PE:EtOAc = 3:1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.09 (t, *J* = 8.0 Hz, 1H), 7.02–6.95 (m, 2H), 6.82 (t, *J* = 1.7 Hz, 1H), 6.75–6.68 (m, 3H), 5.70 (s, 1H), 5.67 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.4, 149.3, 136.0, 131.0, 123.6, 120.1, 115.3, 111.1, 110.7; HRMS (ESI) m/z calcd for $[C_{12}H_{10}Cl_2BrN_2]^+$ $[M+H]^+$: 330.9399, found: 330.9402.

(45) 1-(3,5-dichlorophenyl)-2-(3-(trifluoromethyl)phenyl)hydrazine (4as)

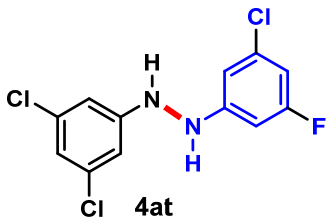


4as

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4as**: 35 mg, 54% yield; White solid, m.p. = 88-90 °C; R_f = 0.7 (PE:EtOAc = 3:1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.06 (s, 1H), 6.97 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.84 (t, *J* = 1.7 Hz, 1H), 6.75 (d, *J* = 1.7 Hz, 2H), 5.79 (s, 1H), 5.75 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 150.3, 148.3, 135.9, 132.0 (q, J_{C-F} = 32.2 Hz), 130.2, 124.2 (q, J_{C-F} = 272.5 Hz), 120.2, 117.2 (q, J_{C-F} = 3.9 Hz), 115.37, 110.7, 108.9 (q, J_{C-F} = 3.9 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.73 (s); HRMS (ESI) m/z calcd for $[C_{13}H_{10}Cl_2F_3N_2]^+$ $[M+H]^+$: 321.0168, found: 321.0166.

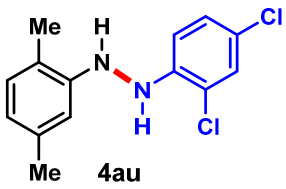
(46) 1-(4-chloro-2-fluorophenyl)-2-(3,5-dichlorophenyl)hydrazine (4at)

Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/EtOAc = 9/1) to obtain **4at**: 34 mg, 57% yield; White solid, m.p. = 99-101 °C; R_f = 0.5 (PE:EtOAc = 3:1); ^1H NMR (500 MHz,



$CDCl_3$): δ 6.84 (t, J = 1.7 Hz, 1H), 6.84 (t, J = 1.7 Hz, 1H), 6.71 (d, J = 1.7 Hz, 2H), 6.60-6.57 (m, 2H), 6.43 (dt, J = 10.4, 2.1 Hz, 1H), 5.76 (s, 1H), 5.73 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 163.9 (d, $J_{C\text{-}F}$ = 247.4 Hz), 150.3 (d, $J_{C\text{-}F}$ = 11.3 Hz), 149.9, 136.1 (d, $J_{C\text{-}F}$ = 13.0 Hz), 136.0, 120.4, 110.7, 108.2 (d, $J_{C\text{-}F}$ = 2.8 Hz), 108.0 (d, $J_{C\text{-}F}$ = 25.4 Hz), 98.1 (d, $J_{C\text{-}F}$ = 26.2 Hz); ^{19}F NMR (471 MHz, $CDCl_3$): δ -109.75 (s); HRMS (ESI) m/z calcd for $[C_{12}H_9Cl_3FN_2]^+$ $[M+H]^+$: 303.0937, found: 303.9395.

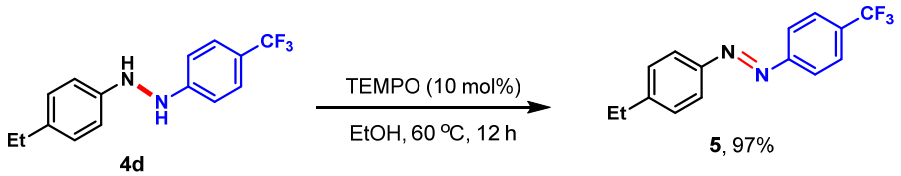
(47) 1-(2,4-dichlorophenyl)-2-(2,5-dimethylphenyl)hydrazine (4au)



Followed **General Procedure C** on 0.2 mmol scale. Purified via column chromatography on silica gel (eluted with PE/Et_2O = 20/1) to obtain **4au**: 24 mg, 42% yield; White solid, m.p. = 96-98 °C; R_f = 0.8 (PE:Et_2O = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.69 (s, 1H), 7.40 (d, J = 2.4 Hz, 1H), 7.27 (s, 1H), 7.16 (dd, J = 8.8, 2.4 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.80 (d, J = 8.8 Hz, 1H), 6.48–6.42 (m, 2H), 2.15 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 146.1, 144.5, 135.3, 130.1, 128.4, 127.8, 120.6, 118.8, 118.3, 116.6, 113.7, 110.9, 21.2, 17.0; HRMS (ESI) m/z calcd for $[C_{14}H_{15}Cl_2N_2]^+$ $[M+H]^+$: 281.0607, found: 281.0600.

11. Synthetic applications of the *N,N′*-diarylhydrazines

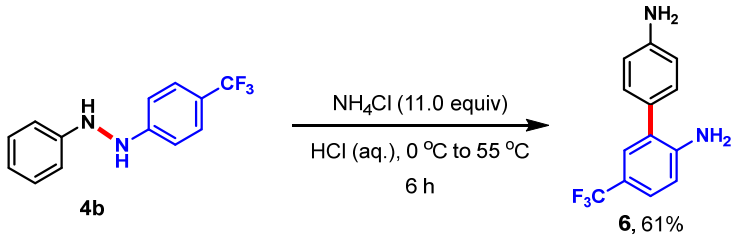
(i) General procedure for the synthesis of 5 [11]



To a solution of *N,N′*-diarylhydrazine **4d** (0.2 mmol) in EtOH (2 mL) was added TEMPO (10 mol%). The reaction mixture was open to air and stirred at 60 °C for 18 h. After completion of the reaction (indicated by TLC), the solution was concentrated in vacuum. The residue was purified by column chromatography using a mixture of

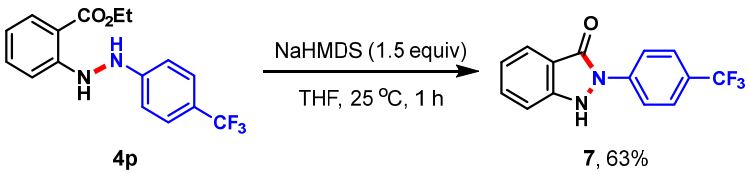
petroleum ether and ethyl acetate as eluent to give the desired product **5** (53 mg, 97% yield).

(ii) General procedure for the synthesis of 6 [12]



To a Schlenk flask equipped with a stir bar was added the *N,N′*-diarylhydrazine **4b** (0.22 mmol, 1.0 equiv, 56 mg) and ammonium chloride (2.45 mmol, 11.0 equiv, 130 mg) in sequence. Followed by evacuation and the introduction of nitrogen on a Schlenk line, 2 mL of water was added via syringe. The mixture was then stirred at room temperature for 2 minutes and then transferred into the ice-water bath at around 0 °C. Subsequently, 2 mL of concentrated hydrochloric acid were added via microsyringe at 0 °C and the reaction mixture was stirred for 30 minutes. Afterwards, the mixture was transferred to 55 °C oil bath, which was monitored by TLC analysis. The reaction mixture was neutralized to pH = 7 using 1M NaOH solution, and the resulting mixture was extracted by EtOAc (3x10 mL). The combined organic layer was washed with brine (20 mL) and dried over Na_2SO_4. Finally, the mixture was concentrated *in vacuo* and the residue was purified by flash column chromatography (eluted with PE/EtOAc) to afford the title compound **6** (34 mg, 61% yield) .

(iii) General procedure for the synthesis of 7 [10].

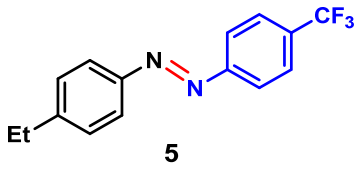


Under air atmosphere, a solution of sodium bis(trimethylsilyl)amide (5 M, 1.5 equiv, 122 μL) was added slowly to the solution of *N,N′*-diarylhydrazine **4p** (0.2 mmol, 1.0 equiv, 64.8 mg) in 1mL of THF at room temperature and stirred it for 1 h. The reaction mixture was then poured into 10 mL of saturated ammonium chloride solution, and the resulting mixture was extracted by EtOAc (3x10 mL). The combined organic layer was

washed with brine (20 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the crude product was purified by column chromatography with petroleum ether/EtOAc (4/1) on silica gel (35 mg, 63% yield).

12. Analytical data of synthetic application products

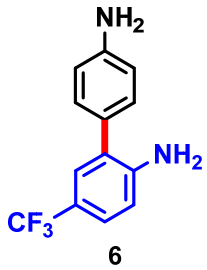
(1) (*E*)-1-(4-ethylphenyl)-2-(4-(trifluoromethyl)phenyl)diazene (5)



5

5: 53 mg, 97% yield. Yellow solid, m.p. = 75-77 °C; R_f = 0.7 (PE:EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.7, 150.9, 149.0, 132.0 (q, J_{C-F} = 32.4 Hz), 128.8, 126.4 (q, J_{C-F} = 3.8 Hz), 124.1 (q, J_{C-F} = 272.2 Hz); 123.4, 123.0, 29.1, 15.5; ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.47 (s); HRMS (ESI) m/z calcd for $[C_{15}H_{14}F_3N_2]^+$ $[M+H]^+$: 279.1104, found: 279.1117.

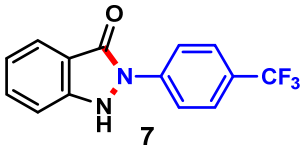
(2) 5-ethyl-5'-(trifluoromethyl)-[1,1'-biphenyl]-2,2'-diamine (6)



6

Purified via column chromatography on silica gel (eluted with PE/EtOAc = 3/1) to obtain **6**: 34 mg, 61% yield. White solid; m.p. = 91-93 °C; R_f = 0.2 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, *J* = 6.9 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.76 (t, *J* = 9.5 Hz, 3H), 3.97 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.9, 146.2, 130.0, 128.1, 127.7 (q, J_{C-F} = 3.8 Hz), 127.3, 125.1 (q, J_{C-F} = 3.8 Hz), 125.0 (q, J_{C-F} = 270.7 Hz), 120.3 (q, J_{C-F} = 32.5 Hz), 115.6, 114.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -61.04 (s); HRMS (ESI) m/z calcd for $[C_{13}H_{12}F_3N_2]^+$ $[M+H]^+$: 253.0947, found: 253.0944.

(3) 2-(4-(trifluoromethyl)phenyl)-1,2-dihydro-3*H*-indazol-3-one (7)

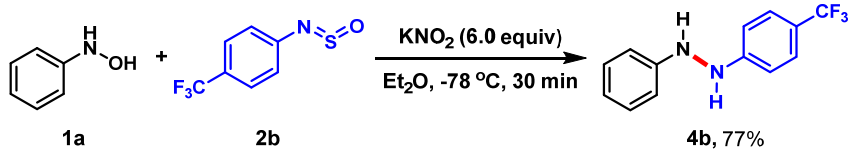


7

Purified via column chromatography on silica gel (eluted with PE/EtOAc = 5/1) to obtain **7**: 35 mg, 63% yield. White solid, m.p. = 106-108 °C; R_f = 0.3 (PE:EtOAc = 3:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.77 (s, 1H), 8.16 (d, *J* =

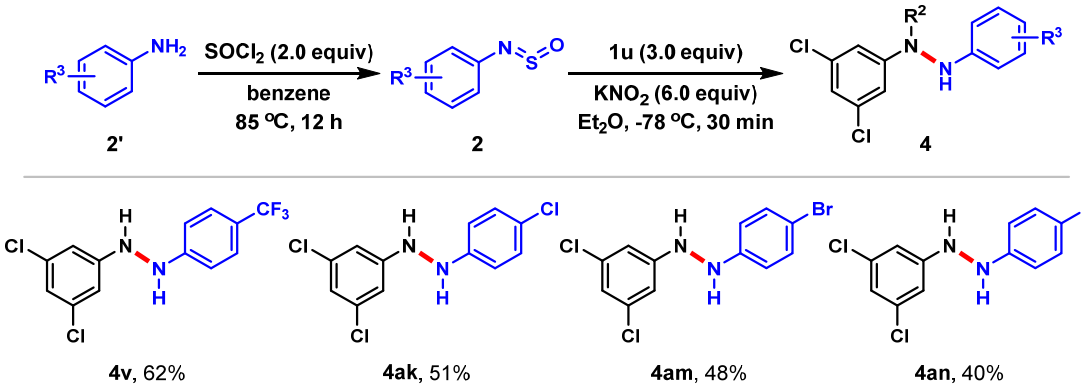
8.6 Hz, 2H), 7.88 (d, J = 8.7 Hz, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.68–7.60 (m, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H). Analytical data are in accordance with the literature values [10]

13. Experimental procedure for the gram scale reaction



To a Schlenk flask equipped with a stir bar was added the corresponding arylhydroxylamine **1a** (15 mmol, 3.0 equiv, 1.635 g) and potassium nitrite (30 mmol, 6.0 equiv, 2.553 g). Followed by evacuation and the introduction of nitrogen on a Schlenk line, diethyl ether (50.0 mL, 0.05 M) was added via syringe. The mixture was then stirred at room temperature for 2 minutes and then transferred to -78 °C bath. Then, *N*-sulfinylaniline **2b** (5 mmol, 1.0 equiv, 1.035 g) was added via microsyringe at -78 °C and stirred for 30 minutes until the complete consumption of **2b**, which was monitored by TLC analysis. Afterwards, the mixture (the temperature in the rotary evaporator was maintained below 30 °C) was concentrated *in vacuo* and the residue was purified by flash column chromatography (eluted with PE/EtOAc) to afford the title compound **4b** (970 mg, 77% yield) .

14. General procedure for one-pot, two-step synthesis of hydrazine 4



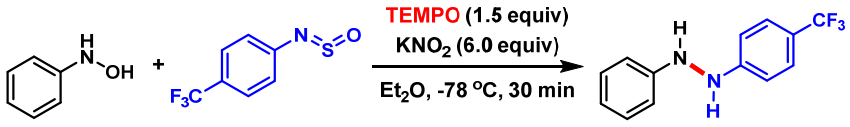
Step one: Aniline **2'** (0.2 mmol, 1.0 equiv) and benzene (2.0 mL) were first placed in a Schlenk tube.Then, thionylchloride (0.4 mmol, 2.0 equiv) was added drop wise to the mixture. To prevent the interaction with air humidity, the loading of the three

components was carried out under nitrogen atmosphere. Since a vigorous reaction took place while thionyl chloride was added, the mixture was continuously stirred. Then the mixture was heated for 12 h at 85 °C. Afterwards, the mixture was concentrated *in vacuo* without further purification.

Step two: To a Schlenk flask equipped with a stir bar was added the corresponding arylhydroxylamines **1** (0.6 mmol, 3.0 equiv, if solid), potassium nitrite (102.1 mg, 1.2 mmol, 6.0 equiv) unless otherwise noted. Following evacuation and the introduction of nitrogen on a Schlenk line, diethyl ether (2.0 mL, 0.05 M) was added via syringe. The mixture is then stirred at room temperature for 2 minutes and then transferred to -78 °C. Lastly, *N*-Sulfinylbenzenamine **2** from step one were added via microsyringe at -78 °C then stirred for 30 minutes until the complete consumption of **2**, which was monitored by TLC analysis. Afterwards, the mixture (the temperature in the rotary evaporator was maintained below 30 °C) was concentrated *in vacuo* and the residue was purified by flash column chromatography (eluted with PE/EtOAc) to afford the title compound **4** .

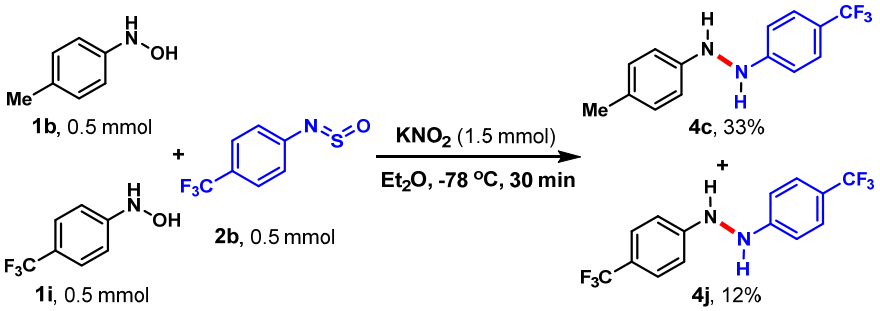
15. Experimental procedure for control experiments

15.1 General procedure for free radical capture experiment

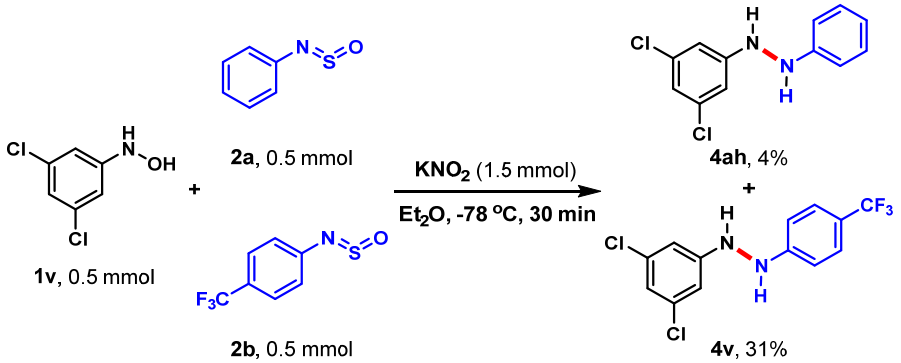


To a Schlenk Flask was added a small stir bar, the corresponding arylhydroxylamines **1a** (0.6 mmol, 3.0 equiv, 65.4 mg), potassium nitrite (1.2 mmol, 6.0 equiv, 102.0 mg) and 2,2,6,6-tetramethylpiperidinooxy (0.3 mmol, 1.5 equiv, 46.9 mg). Following evacuation and the introduction of nitrogen on a Schlenk line, diethyl ether (2.0 mL, 0.05 M) was added via syringe. The mixture is then stirred at room temperature for 2 minutes and then transferred to -78 °C. Lastly, **2b** (0.2 mmol, 1.0 equiv, 41.4 mg) were added via microsyringe at -78 °C then stirred for 30 minutes until the complete consumption of **2b**, which was monitored by TLC analysis. Afterwards, the mixture (the temperature in the rotary evaporator was maintained below 30 °C) was concentrated *in vacuo* and the residue was purified by flash column chromatography (eluted with PE/EtOAc) to afford the title compound **4b** (36 mg,71%) .

15.2 General procedure for competition experiment



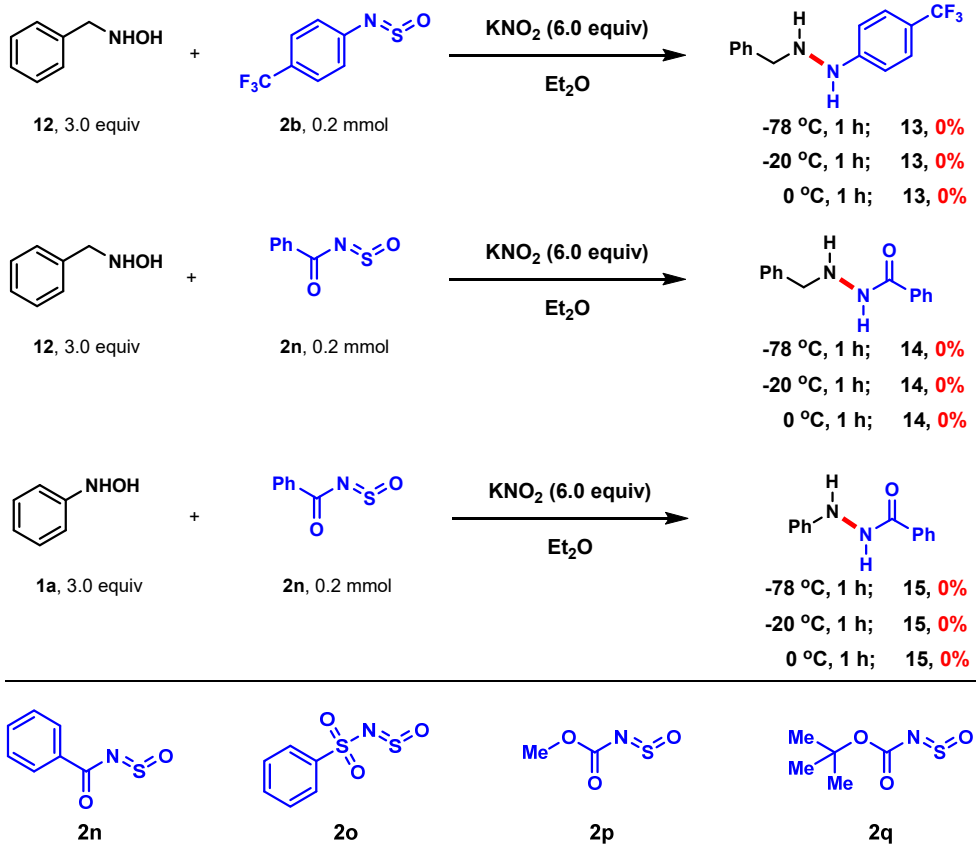
To a Schlenk Flask was added a small stir bar, the corresponding arylhydroxylamines **1b** (0.5 mmol, 1.0 equiv, 61.5 mg), **1i** (0.5 mmol, 1.0 equiv, 88.5 mg) and potassium nitrite (1.5 mmol, 3.0 equiv, 127.7 g) unless otherwise noted. Following evacuation and the introduction of nitrogen on a Schlenk line, diethyl ether (4.0 mL) was added via syringe. The mixture is then stirred at room temperature for 2 minutes and then transferred to -78 °C. Lastly, **2b** (0.5 mmol, 1.0 equiv, 103.5 mg) were added via microsyringe at -78 °C then stirred for 30 minutes, diluted in DCM and evaporated under reduced pressure (the temperature in the rotary evaporator was maintained below 30 °C) and the residue was purified by flash column chromatography (eluted with PE/EtOAc) to afford the title compound **4c** (41 mg, 33%) and **4j** (19 mg, 12%) .



To a Schlenk Flask was added a small stir bar, the corresponding arylhydroxylamines **1v** (0.5 mmol, 1.0 equiv, 89.0 mg) and potassium nitrite (1.5 mmol, 3.0 equiv, 127.7 g). Following evacuation and the introduction of nitrogen on a Schlenk line, diethyl ether (4.0 mL) was added via syringe. The mixture is then stirred at room temperature for 2 minutes and then transferred to -78 °C. Lastly, the mixture of **2a** (0.5 mmol, 1.0 equiv, 69.5 mg) and **2b** (0.5 mmol, 1.0 equiv, 103.5 mg) were added via microsyringe at -78 °C then stirred for 30 minutes, diluted in DCM and evaporated under reduced pressure (the temperature in the rotary evaporator was maintained below 30 °C) and the residue

was purified by flash column chromatography (eluted with PE/EtOAc) to afford the title compound **4ah** (5 mg, 4%) and **4v** (49 mg, 31%)) .

15.3 Evaluation of other type of substrates

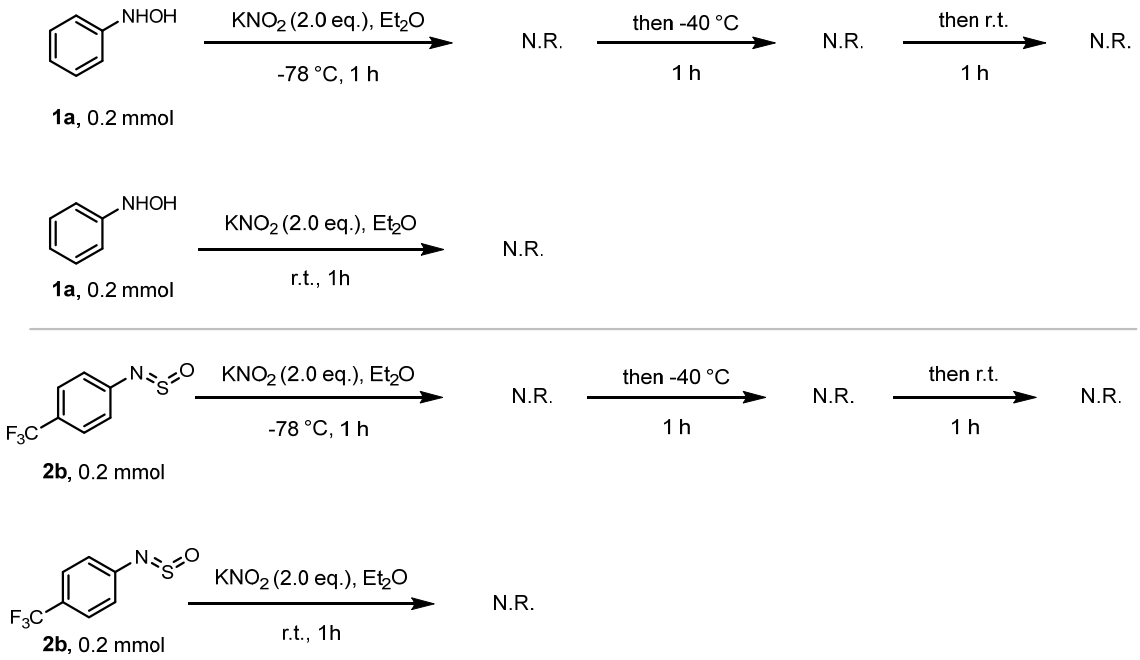


It was found that *N*-alkylhydroxylamine **12** did not react with *N*-arylsulfinylaniline **2b** or *N*-sulfinylbenzamide **2n**, and the simple phenylhydroxylamine **1a** did not react with *N*-sulfinylamines **2n** or **2o**-**2q** as well under similar conditions (even at higher temperatures), which means that both aromatic substrates are really required.

15.4 Evaluation of the role of KNO_2

In order to investigate the role of KNO_2 in this novel transformation, we tried to set up several control experiments. Those experimental results were shown in the following equations and schemes:

Based on these experimental results, we do not have any evidence to support that KNO_2 is an oxidant in our reaction system. In addition, phenylhydroxylamine **1a** or *N*-sulfinylamine **2b** did not react with KNO_2 under standard conditions or even high temperature at r.t., and we did not find any isolatable intermediates in both reactions.



With regards to the solubility of KNO_2 in Et_2O, we also carried out the corresponding test under -78 ºC and 25 ºC, respectively. The results revealed that around 6.5 mg of KNO_2 could be dissolved in 100 mL of Et_2O at -78 ºC and 10.5 mg of KNO_2 could be dissolved in 100 mL of Et_2O at 25 ºC in the absence of *N*-arylhydroxylamine **1a** and *N*-arylsulfinylaniline **2b**. Interestingly, 8.8 mg of KNO_2 could be dissolved in 100 mL of Et_2O at -78 ºC in the presence of 30 mmol *N*-arylhydroxylamine **1a** and 10 mmol *N*-arylsulfinylaniline **2b**. These results were consistent with our proposed mechanism and indicated that the hydrogen bonding between KNO_2 and substrates or products might be helpful to increase the solubility of KNO_2 in Et_2O.

As we mentioned in the newly revised main text, it was a serendipitous finding for using KNO_2 and there was no specific reason for using KNO_2.We proposed that the hydrogen bonding interactions exist between NO_2 anion and the hydrogen bond donors, since such complex has been widely used in supramolecular chemistry, see 10.1016/j.chempr.2016.08.004 (*Chem* **2016**, *1*, 351-422.), 10.1021/ol402819m (*Org. Lett.* **2014**, *16*, 334-337.), the NO_2 anion could form a complex through hydrogen-bonding even with C-H bonds of hosts.

16. References

[1] a) Guo, L.; Liu, F.; Wang, L.; Yuan, H.; Feng, L.; Kurti, L.; Gao, H., Cascade Approach to Highly Functionalized Biaryls by a Nucleophilic Aromatic Substitution with Arylhydroxylamines. *Org. Lett.* **2019,** *21*, 2894-2898; b) Hojczyk, K. N.; Feng, P.; Zhan, C.; Ngai, M., Trifluoromethoxylation of Arenes: Synthesis of *ortho*-Trifluoromethoxylated Aniline Derivatives by OCF_3 Migration. *Angew. Chem. Int. Ed.* **2014,** *53*, 14559-14563; c) Yuan, H.; Guo, L.; Liu, F.; Miao, Z.; Feng, L.; Gao, H., Copper-Catalyzed Tandem *O*-Vinylation of Arylhydroxylamines/3,3-Rearrangement /Cyclization: Synthesis of Highly Substituted Indoles and Benzoindoles. *ACS Catal.* **2019,** *9*, 3906-3912; d) Liu, Y.; Bai, S.; Du, Y.; Qi, X.; Gao, H.*, Expeditious and Efficient ortho-Selective Trifluoromethane-sulfonylation of Arylhydroxylamines. Angew. Chem. Int. Ed.* **2022,** *61,* e202115611; e) Chen, Y.; Grassl, S.; Knochel, P., Cobalt-Catalyzed Electrophilic Amination of Aryl- and Heteroarylzinc Pivalates with N-Hydroxylamine Benzoates. *Angew. Chem. Int. Ed.* **2018,** *57,* 1108-1111.

[2] Kallitsakis, M. G.; Ioannou, D. I.; Terzidis, M. A.; Kostakis, G. E.; Lykakis, I. N., Selective Photoinduced Reduction of Nitroarenes to *N*-Arylhydroxylamines. *Org. Lett.* **2020,** *22*, 4339-4343.

[3] Chemes, D. M.; Cutin, E. H.; Alvarez, R. M. S.; Robles, N. L.; Oberhammer, H., On the search of the influence of substituents in the structural and vibrational properties of *p*-substituted sulfinylanilines: Study of *p*-trifluoromethylsulfinylaniline. *J. Fluor. Chem.* **2018,** *210*, 94-101.

[4] Jerez, A. L. P.; Antognini, A. F.; Cutin, E. H.; Robles, N. L., Synthesis, characterization and vibrational properties of p-fluorosulfinylaniline. *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **2015,** *137*, 300-305.

[5] a) Chidambaram, R.; Kant, J.; Zhu, J.; Lajeunesse, J.; Sirard, P.; Ermann, P.; Schierling, P.; Lee, P.; Kronenthal, D., A practical synthesis of the RAR gamma agonist, BMS-270394. *Org. Process Res. Dev.* **2002,** *6*, 632-636; b) Yong, H. K.; Jai M. S. *Tetrahedron Lett.* **1985**, *26*, 3821-3824.

[6] Sahoo, M. K.; Sivakumar, G.; Jadhav, S.; Shaikh, S.; Balaraman, E., Convenient semihydrogenation of azoarenes to hydrazoarenes using H-2. *Org. Biomol. Chem.* **2021,** *19*, 5289-5293.

[7] Chemes, D. M.; de Armino, D. J. A.; Cutin, E. H.; Oberhammer, H.; Robles, N. L., Synthesis, characterization and vibrational studies of p-chlorosulfinylaniline. *J. Mol. Struct.* **2017,** *1127*, 191-198.

[8] Chemes, D. M.; Lezama, J. O. G.; Cutin, E. H.; Robles, N. L., Assessment of the molecular structure and spectroscopic properties of CF3-substituted sulfinylaniline derivatives. *J. Mol. Struct.* **2021,** *1230*, 10.

[9] Wang, X. Y.; Wang, X. J.; Xia, C. G.; Wu, L. P., Visible-light-promoted oxidative dehydrogenation of hydrazobenzenes and transfer hydrogenation of azobenzenes. *Green Chem.* **2019,** *21*, 4189-4193.

[10] Li, G.; Miller, S. P.; Radosevich, A. T., P-III/P-V=O-Catalyzed Intermolecular N-N Bond Formation: Cross-Selective Reductive Coupling of Nitroarenes and Anilines. *J. Am. Chem. Soc.* **2021,** *143*, 14464-14469.

[11] Lv, H..; Laishram, R. D.; Yang, Y.; Li, J; Xu, D.; Zhan, Y.; Luo, Y.; Su, Z; More, S.; Fan, B., TEMPO catalyzed oxidative dehydrogenation of hydrazobenzenes to azobenzenes. *Org. Biomol. Chem.* **2020,** *18*, 3471-3474.

[12] Bouillon, M. E.; Meyer, H. H., The 4.4 '-benzidine rearrangement of 4-alkyl substituted hydrazobenzenes. *Tetrahedron* **2016,** *72*, 3151-3161.

17. X-ray crystal structures and data

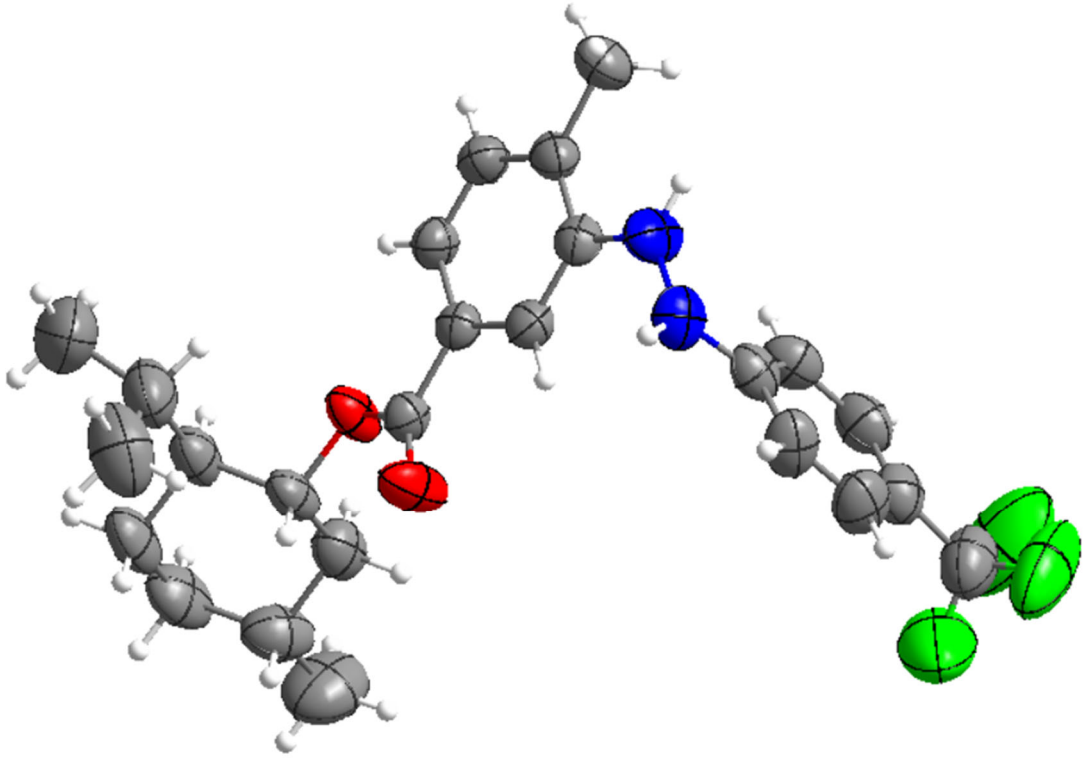
Suitable crystals of compound **4af** was obtained by slowly evaporating a mixture of diethyl ether and hexane solution at ambient temperature. Single crystal was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) to prevent decomposition. Intensity data and cell parameters of **4af** was recorded at 293 K on an Agilent Supernova X-Ray diffractometer equipped with a large area CCD detector, employing a Cu K_α radiation (λ = 1.54184 Å). The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[1] The structure was solved using the charge-flipping algorithm, as implemented in the program *SUPERFLIP*[2] and refined by full-matrix least-squares techniques against F_o^2 using the SHELXL program[3] through the OLEX2 interface.[4] Hydrogen atoms at carbon were placed in calculated positions and refined isotropically by using a riding model. Appropriate restraints or constraints were applied to the geometry and the atomic displacement parameters of the atoms in the cluster. All structures were examined using the Addsym subroutine of PLATON[5] to ensure that no additional symmetry could be

applied to the models. **CCDC 2236222** (**4af**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

References

1. *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA, 2015.
2. L. Palatinus, G. Chapuis, *J. Appl. Crystallogr*., **2007**, *40*, 786.
3. G. M. Sheldrick, *Acta. Crystallogr*. *Sect. C.*, **2015**, *71*, 3.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl*. *Crystallogr*., **2009**, *42*, 339.
5. A. L. Spek, *Acta. Crystallogr. Sect*. D. **2009**, *65*, 148.

Crystal data and structure refinement for 4af (Thermal ellipsoids at the 30% probability level)



CCDC: 2236222

Table S4 Crystal data and structure refinement for 4af	
Identification code	**4af**
Empirical formula	$C_{25}H_{31}F_3N_2O_2$
Formula weight	448.52
Temperature/K	293
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.30380(10)
b/Å	14.6308(2)
c/Å	22.9973(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2457.50(6)
Z	4
ρ_{calc}mg/mm^3	1.212
μ/mm^{-1}	0.768
F(000)	952.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection	7.162 to 133.176
Index ranges	$-8 \le h \le 8$, $-17 \le k \le 17$, $-27 \le l \le 27$
Reflections collected	36468
Independent reflections	4357 [R_{int} = 0.0402, R_{sigma} = 0.0181]
Data/restraints/parameters	4357/10/293
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0525, wR_2 = 0.1462
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1502
Largest diff. peak/hole / e Å^{-3}	0.35/-0.32
Flack parameter	-0.14(8)

18. Computational part

18.1 General information

DFT calculations were performed with the Gaussian 09 software package, E.01 version unless otherwise specified.[1] Geometric optimizations of intermediates and transition states were calculated in gas phase at the (U)B3LYP-D3(BJ)[2,3]/6-311+G(d,p)[4] (5d was used) level. Diradical species were located using the key words: guess=(mix, always). The wave function stability of the stationary points was carried out with the key words stable=opt to confirm that the wavefunctions were stable. Frequency calculations at the same level were performed to validate each structure as either a minimum or a transition state. IRC calculations were carried out to confirm that the transition state structures connect corresponding reactants and products. Solvation effect was evaluated by calculating the single-point energy in solution ($\Delta G_{sol}=E_{sol}-E_{gas}$) at SMD[5]($Et_2O$)/(U)B3LYP-D3(BJ)/6-311+G(d,p) (5d). For the formation of **A**, high level single-point energies were calculated at the ωB97M-V[6]/ma-def2-QZVP[7] level, ωB97M-V was used because it is a good functional for close-shell main group chemistry according to several benchmark studies.[8] For the retro-[2π+2σ] reaction, high level single-point energies were calculated at (U)B3LYP-D3(BJ)/ma-def2-QZVP. DLPNO-CCSD(T)/cc-PVTZ (with cc-PVTZ/C auxiliary basis set and tight thresholds)[9] and ωB97M-V/ma-def2-QZVP (with RIJCOSX/autoaux) were performed with Orca 4.2.1.[10] DMRG-PDFT: tPBE[11] using cc-PVTZ basis set with a large active space DMRG(22e, 19o) including σ(N-O), σ(O-S), σ(N-S) orbitals and n(N), n(O), π(aromatic rings) orbitals, was performed with *OpenMolcas 23.10* software package and *QCMaquis* software suite therein.[12] 3D structures were prepared with CYLview.[13] IBO analysis was prepared with IboView.[14] All discussed energy differences were based on Gibbs energies at 298 K (standard states are the hypothetical states at 1 mol/L).

18.2 Benchmark study

Different methods and functionals for the key step (N-O homolysis of **A** via **TS2**, and the close-shell concerted transition state **TS2'**) with large basis sets were tested. B3LYP-D3(BJ), which performs well for weak interactions[15] and broken-symmetry (U)DFT[16], with 6-311+G(d,p) basis set were used for optimization. Then (U)DFT of different functionals including pure functional BP86[17], PBE[18], TPSS[19], and hybrid functionals, B3LYP[2], PBE0[20], BMK[21], ωB97X-D[22] and ωB97M-V[6], M06-2X[23], M06[23] with or without D3 correction[3] were used to calculated the single-point energies based on the optimized structures. DLPNO-UCCSD(T)[9] were also tested, but note that DLPNO-UCCSD(T) could lead to unphysical behavior when preceding symmetry-broken self-consistent field (SCF) calculations[24] and is not a good method for open shell radicals.[16b,25] Therefore, the multi-reference approach DMRG-PDFT[11] with a large active space DMRG(22e, 19o) were also used to study this key step. MC-PDFT combined with DMRG wave functions[11], called DMRG-PDFT, gives good results in previous studies compared to other multi-reference method such as CASPT2 at a significantly lower computational cost.[26]

The results are shown in Table S5. For the open-shell singlet transition state **TS2**, the GGA functionals PBE, BP86, and meta-GGA functionals TPSS, TPSS-D3(BJ) give very low activation free energies (-4.8-2.3 kcal/mol), while hybrid functionals B3LYP-D3(BJ), BMK, PBE0, PBE0-D3(BJ), ωB97X-D, ωB97M-V, M06-2X, M06 give higher activation free energies around 7.9-21.6 kcal/mol. It's not surprised that (U)DFT gives quite different results, because the single-reference method (U)DFT has shortcomings on the open-shell singlet diradicals.[14] Among these functionals, the hybrid functional B3LYP, which considers more about static electron correlation effects, has been shown to perform better than pure DFT functionals for open shell singlet species.[16] In this case, B3LYP with D3(BJ) dispersion correction gives a 7.9 kcal/mol of activation free energy, which is consistent with the reaction temperature (-78°C). DLPNO-UCCSD(T) based on UHF gives a high activation free energy of 23.1 kcal/mol, this is overestimated probably due to the limitations of the single-reference method such as the large spin contaminant ($<S^2>$=2.13 for **TS2** using UHF-DLPNO-CCSD(T))[25] or the unphysical behavior of DLPNO-CCSD(T) when proceeding symmetry-broken SCF calculations.[24] Finally, the multi-reference approach DMRG-PDFT, using a large active space (22e, 19o), suggests an activation free energy of 14.3 kcal/mol, which is consistent well with the experiments ($t_{1/2}$=0.18 hour at -78 °C with 14 kcal/mol of activation free energy).

While for the close-shell concerted transition state **TS2'**, the state-of-art methods DMRG-PDFT and DLPNO-CCSD(T) give similar results (27.9 kcal/mol and 29.6 kcal/mol), indicating a high activation free energy of this concerted pathway. For the DFT calculations, ωB97M-V, M06-2X are also good functionals for the close-shell main group chemistry, as shown in many benchmark studies.[8] On the other hand,

B3LYP-D3(BJ) underestimates the activation free energy of this concerted pathway via **TS2'** by more than 14 kcal/mol (6 kcal/mol for **TS2**).[27] But among all methods and functionals, **TS2'** is less favored over **TS2** by 5.2-15.4 kcal/mol. Thus, the retro-[2π+2σ] reaction could happen through a stepwise diradical mechanism at -78 °C.

Table S5. Benchmark study of the retro-[2π+2σ] reaction.

Method[a]	DMRG-PDFT[b]	DLPNO-(U)CCSD(T)[b]	BP86	PBE	TPSS	TPSS-D3(BJ)	B3LYP-D3(BJ)	PBE0	PBE0-D3(BJ)	BMK	ωB97X-D	ωB97M-V	M06-2X	M06
$\Delta G^{\ddagger}$ (**TS2**)	**14.3**	23.1	-4.7	-2.6	-4.8	2.3	**7.9**	6.7	12.1	11.3	16.5	20.9	21.6	10.2
$\Delta G^{\ddagger}$ (**TS2'**)	**27.9**	29.6	9.7	10.3	9.6	7.5	**13.5**	22.1	20.6	23.4	25.5	28.4	28.7	17.5
$\Delta\Delta G^{\ddagger}$	**13.6**	6.5	14.4	12.9	14.4	5.2	**5.6**	15.4	8.5	12.1	9.0	7.5	7.1	7.3

[a]The single point energies are calculated with ma-def2-QZVP basis set based on the optimized structures at (U)B3LYP-D3(BJ)/6-311+G(d,p) (5d) unless otherwise specified. The DFT functionals are unrestricted for symmetry-broken wavefunctions. [b]with cc-PVTZ basis set.

18.3 IBO analysis along IRC for the pseudo-pericyclic transition state TS2'

For the concerted pathway via **TS2'**, IBO analysis along IRC was carried out, showing the electron flow from σ(N-O) orbital (red) to π(S=0) orbital, σ(N-S) orbital (blue) to n(N) orbital, and n(N) orbital (green) to σ(N-N) orbital. Thus, **TS2'** could be regarded as a $6e^-$ pseudo-pericyclic reaction.

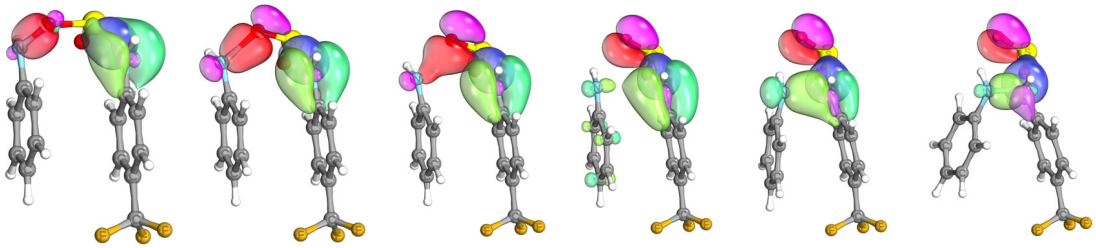


Figure S2. IBO analysis along IRC of **TS2'**, computed at PBE/def2-TZVP using IboView.

18.4 The retro-[2π+2σ] reaction for other substrates.

Other substrates were also studied by DFT calculations. Our calculations found that the N-N coupling proceed through a stepwise diradical mechanism, which firstly undergoes σ bond homolysis via **TS2** to obtain the diradical species. Thus, the aromatic rings are required to stabilize the nitrogen radical through conjugation effect. For the N-alkyl substrates **A-Bn**, the alkyl nitrogen radical is not stable enough and the activation free energy of σ bond homolysis via **TS2-Bn** (<S^2>=0.68) is 21.5 kcal/mol, which is much higher than N-phenylhydroxylamine **2b** and very slow at -78 °C (note that (U)B3LYP-D3(BJ) may underestimate the activation free energy of this step by 6 kcal/mol, see benchmark study and ref. 27). The concerted transition state could not be located probably due to the lack of π-π stacking, which makes the N···N distance longer.

DFT calculations were carried out to study the effects of SO_3 and CO_2 (Figure S3). For the SO_3 intermediate **A-SO$_3$**, the N-O homolysis via **TS2-SO$_3$** is easy, requiring an activation free energy of 6.3 kcal/mol, while the concerted pathway via **TS2'-SO$_3$** requires an activation free energy of 8.3 kcal/mol, though **A-SO$_3$** could not be synthesized experimentally. For the CO_2 intermediate **A-CO$_2$** (if it can be obtained), the N-O homolysis via **TS2-CO$_2$** requires a higher activation free energy of 17.6 kcal/mol. This could be understood because the nitrogen atom (blue) in **A-CO$_2$** is conjugated well with carbonyl group (C-N bond in **A-CO$_2$** is as short as 1.37 Å while S-N bond in **A** is 1.71 Å), making it more difficult to simultaneously break the N-O bond, C-N bond, and release CO_2 than extrusions of SO_2 and SO_3.

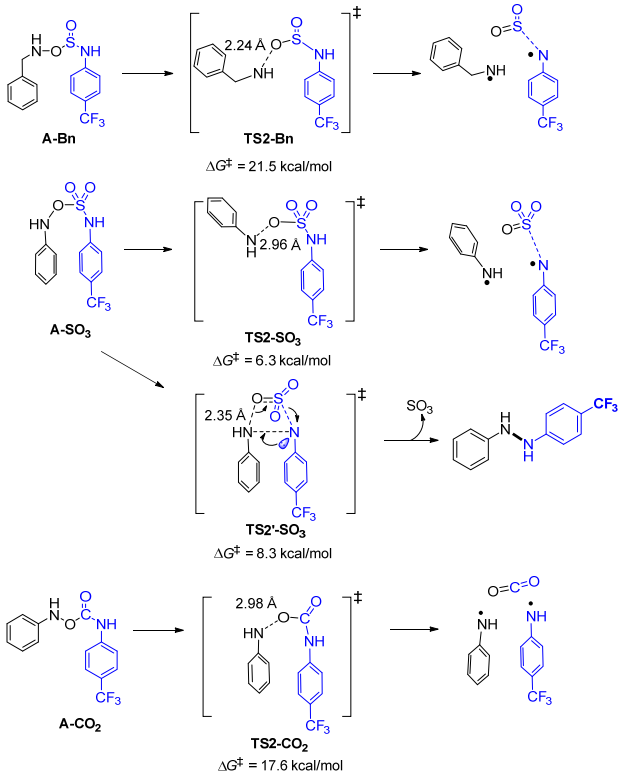


Figure S3 The retro-[2π+2σ] reaction for other substrates.

18.5 Computed energies of the stationary points

Table S6. Thermal Corrections to Gibbs Energies (TCGs) and Single-Point Energies (SPEs)

Stationary point	Imaginary Frequency (cm^{-1})	SPE[a] (hartree)	SPE'[b] (hartree)	TCG[a] (hartree)	SPE[c] (hartree)
1a	none	-362.89804	-362.90984	0.089947	-362.7935029
2b	none	-1097.059966	-1097.073832	0.063558	-1096.964582
HNO_2	none	-205.772146	-205.774962	-0.003918	-205.7533002
$NO2^-$	none	-205.226518	-205.299117	-0.015846	-205.2051854
Int1	none	-1459.985584	-1460.006796	0.176106	-1459.775916
Int2	none	-1665.264011	-1665.324035	0.176917	-1665.033528
Int3	none	-1665.260239	-1665.317709	0.175853	-1665.032221
Int4	none	-1459.456099	-1459.517271	0.161856	-1459.251992
TS1	-275.48	-1665.25901	-1665.316122	0.174174	-1665.028938
A	none	-1459.982062	-1460.004098	0.177965	-1459.787082

[a]Computed at the B3LYP-D3(BJ) /6-311+G(d,p) level.

[b] Computed at the SMD(Et_2O)/B3LYP-D3(BJ) /6-311+G(d,p) level.

[c]Computed at the ωB97M-V/ma-def2-QZVP//B3LYP-D3(BJ)/6-311+G(d,p) level.

Table S6. Thermal Corrections to Gibbs Energies (TCGs) and Single-Point Energies (SPEs)

Stationary point	Imaginary Frequency (cm^{-1})	SPE[a] (hartree)	SPE'[b] (hartree)	TCG[a] (hartree)	SPE[c] (hartree)	SPE[d] (hartree)
A	none	-1459.982062	-1460.004098	0.177965	-1459.787082	-1458.39294839
SO_2	none	-548.667407	-548.675019	-0.017507	-548.749867	
Int5	none	-1459.968785	-1459.989666	0.169214	-1460.210561	
4b	none	-911.338574	-911.357028	0.174167	-911.503585	
TS2	-137.55	-1459.948972	-1459.974209	0.168696	-1460.195833	-1458.35770189
TS2'	-128.60	-1459.952085	-1459.976474	0.17573	-1460.19486	-1458.34397612
TS3	-34.20	-1459.96276	-1459.984852	0.167753	-1460.205773	
A-Bn	none	-1499.309354	-1499.33378	0.204663	-1499.555751	
A-SO_3	none	-1535.211921	-1535.235164	0.183528	-1535.492382	
A-CO_2	none	-1099.951491	-1099.97267	0.182822	-1100.150755	
TS2-Bn	-226.99	-1499.259632	-1499.283729	0.196536	-1499.51363	
TS2-SO_3	-13.90	-1535.180087	-1535.2112	0.174689	-1535.465648	
TS2'-SO_3	-49.94	-1535.188652	-1535.21941	0.181721	-1535.469863	
TS2-CO_2	-60.43	-1099.915093	-1099.943503	0.177528	-1100.110249	

[a]Computed at the (U)B3LYP-D3(BJ) /6-311+G(d,p) level.

[b]Computed at the SMD(Et_2O)/(U)B3LYP-D3(BJ) /6-311+G(d,p) level.

[c]Computed at the (U)B3LYP-D3(BJ)/ma-def2-QZVP//(U)B3LYP-D3(BJ)/6-311+G(d,p) level.

[d]Computed at the DMRG-PDFT:tPBE/cc-PVTZ with the (22e,19o) active space.

18.6 DMRG-PDFT calculations

Sample Inputs of A:

&GATEWAY

Coord

32

Angstrom

C	1.31856300	-1.73565600	-0.58823000
C	-0.03615800	-1.89440500	-0.34326100
C	-0.63700200	-1.21039700	0.71909800
C	0.14362700	-0.40654700	1.55235800
C	1.50266400	-0.26216600	1.31306200
C	2.09298300	-0.91672800	0.23551300
H	1.77862800	-2.25914800	-1.41668300
H	-0.62796700	-2.53902500	-0.97953900
H	-0.32000400	0.13498200	2.36726600
H	2.09542300	0.37787400	1.95227300
C	3.53469400	-0.68460400	-0.09347000
F	3.68827200	0.28754100	-1.03756400
F	4.13432200	-1.78987900	-0.59369300
F	4.25469700	-0.28810300	0.97908500
N	-2.01873400	-1.33316200	0.97372700
S	-3.21568200	-1.36379100	-0.24341600
O	-4.47317000	-1.51911700	0.50127200
N	-2.07036700	0.59109900	-1.41493100
O	-3.27961500	0.33424000	-0.72247800
H	-2.36148300	-0.85941800	1.80495500
H	-2.33371400	0.88651400	-2.34955000
C	-1.23352300	1.53578700	-0.75125100
C	-1.62453000	2.20491800	0.40729700
C	0.04997200	1.71951400	-1.27116500
C	-0.72325000	3.05873400	1.04108500
H	-2.62013000	2.05288800	0.80018200
C	0.93541400	2.58195100	-0.63722000
H	0.35908500	1.15827300	-2.14509100
C	0.55556500	3.25219800	0.52589500
H	-1.02928900	3.57839000	1.94201400
H	1.93431800	2.70672000	-1.03727800
H	1.25229500	3.91442900	1.02546000

Basis=cc-pVTZ

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&SEWARD

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Fiedler= ON

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EndDMRGSettings

OOptimizationSettings
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   Spin= 1
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   nActEl= 22
   RAS2= 19
   CIRoot= 1 1; 1
EndOOptimizationSettings

&MCPDFT
KSDFT=T:PBE
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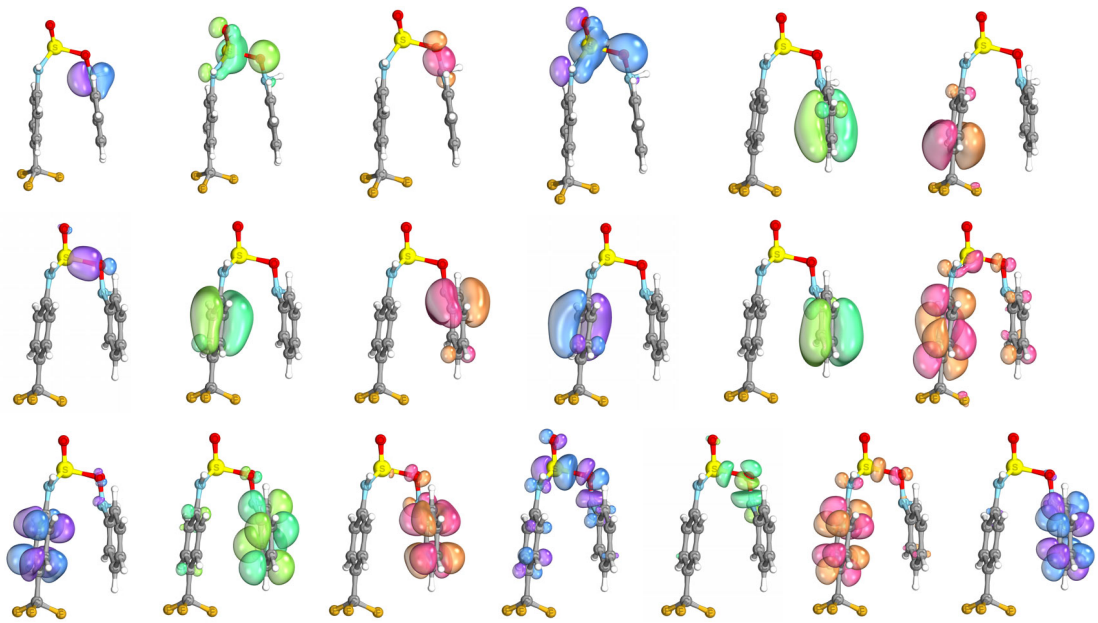
Sample Active Space: (22e, 19o) of A



18.7 Cartesian coordinates of the stationary points

1a

C	1.338598	1.347348	0.013149
C	-0.025093	1.067239	0.068631
C	-0.457883	-0.259912	0.067556
C	0.482613	-1.296045	0.004815
C	1.839722	-1.002498	-0.045354
C	2.278667	0.321722	-0.040739
H	1.664921	2.381191	0.008910
H	-0.753691	1.865098	0.095053
H	0.147931	-2.328431	0.003873
H	2.557438	-1.813409	-0.093287
H	3.337002	0.547960	-0.083777
N	-1.822822	-0.605448	0.208702
H	-2.049244	-1.433085	-0.333520
O	-2.706053	0.416521	-0.249502
H	-3.235931	0.619524	0.529504

2b

C	0.691310	-1.079100	0.178998
C	-0.683822	-0.930240	0.292368
C	-1.261575	0.348164	0.224327
C	-0.435041	1.471896	0.076011
C	0.936466	1.316721	-0.048909
C	1.501707	0.040617	-0.001697
H	1.134614	-2.064671	0.235296
H	-1.306352	-1.798010	0.472484
H	-0.891559	2.452599	0.048682
H	1.569846	2.184602	-0.179456
C	2.994276	-0.117390	-0.065059
F	3.571713	0.820271	-0.848309
F	3.359098	-1.325303	-0.548305
F	3.563350	-0.001700	1.161602
N	-2.638741	0.583513	0.350168
S	-3.656646	-0.384925	-0.311291
O	-5.054550	-0.055466	0.016417

4b

C	1.652118	0.037431	-1.070425
C	0.390683	-0.531217	-0.958539
C	0.019940	-1.181473	0.223642

C	0.931211	-1.245233	1.288731
C	2.187321	-0.673684	1.169721
C	2.556403	-0.025388	-0.010971
H	1.929482	0.545398	-1.985143
H	-0.318755	-0.469538	-1.771727
H	0.649841	-1.745496	2.209161
H	2.881023	-0.722222	1.999542
C	3.931713	0.545679	-0.148703
F	4.392502	1.062885	1.016931
F	3.992271	1.532601	-1.072432
F	4.844637	-0.389925	-0.530603
N	-1.225968	-1.800384	0.364434
H	-1.536681	-1.906985	1.325598
N	-2.236407	-1.464851	-0.530144
H	-2.676544	-2.285080	-0.922327
C	-3.119363	-0.416088	-0.210771
C	-4.378813	-0.377037	-0.824162
C	-2.751693	0.608038	0.668490
C	-5.252115	0.670312	-0.560699
H	-4.667772	-1.169210	-1.507412
C	-3.639381	1.650732	0.926426
H	-1.774838	0.602773	1.133478
C	-4.890397	1.692272	0.317854
H	-6.223722	0.685384	-1.040938
H	-3.341397	2.439293	1.607789
H	-5.574466	2.506210	0.523321

A-Bn

C	1.077703	-1.849907	-0.947328
C	-0.296810	-1.934486	-0.810220
C	-0.895198	-1.686456	0.434054
C	-0.087092	-1.373602	1.531068
C	1.294548	-1.303281	1.391462
C	1.881534	-1.531500	0.151586
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H	-0.908840	-2.194702	-1.663437
H	-0.540432	-1.183707	2.497254
H	1.909426	-1.053957	2.245614
C	3.362481	-1.419904	-0.041351
F	3.683455	-0.420273	-0.908785
F	3.896400	-2.551186	-0.564412
F	4.020742	-1.164834	1.107982
N	-2.285147	-1.795023	0.598362

S	-3.427470	-1.255991	-0.560737
O	-4.712919	-1.778568	-0.076201
N	-2.305577	1.047821	-0.531416
O	-3.545977	0.425346	-0.146957
H	-2.642117	-1.709898	1.545630
H	-2.576456	1.725381	-1.241204
C	-1.775602	1.760276	0.639189
H	-2.519900	2.441172	1.067306
H	-1.541429	1.004690	1.392702
C	-0.528353	2.512569	0.246303
C	0.544935	1.835534	-0.341854
C	-0.419148	3.884046	0.481869
C	1.711833	2.515659	-0.673846
H	0.459127	0.776360	-0.539930
C	0.749848	4.568130	0.150264
H	-1.248764	4.418517	0.932606
C	1.817262	3.884619	-0.426275
H	2.539169	1.975060	-1.117594
H	0.824569	5.632238	0.342099
H	2.727393	4.414529	-0.682224

A-CO_2

C	2.229579	-0.300327	0.866876
C	1.040487	0.411797	0.762929
C	0.868598	1.323996	-0.284340
C	1.908701	1.511843	-1.206114
C	3.093527	0.803407	-1.091013
C	3.257263	-0.114687	-0.054123
H	2.352789	-1.006878	1.677565
H	0.259595	0.262356	1.490356
H	1.781552	2.213068	-2.023549
H	3.884037	0.954707	-1.814511
C	4.556193	-0.846255	0.103187
F	5.447828	-0.143345	0.850358
F	5.157489	-1.081375	-1.086136
F	4.401247	-2.041217	0.716362
N	-0.287266	2.106417	-0.473596
O	-2.481747	2.696209	-0.380091
N	-3.059126	0.758616	1.311235
O	-1.701416	1.014137	0.932688
H	-0.216654	2.834212	-1.170378
H	-3.553946	1.637784	1.165670
C	-3.628675	-0.275432	0.516481

C	-2.856423	-1.324151	0.015613
C	-5.012935	-0.270888	0.324529
C	-3.475051	-2.359759	-0.680385
H	-1.785554	-1.326020	0.166986
C	-5.619302	-1.317413	-0.360888
H	-5.609230	0.549989	0.707978
C	-4.854750	-2.366669	-0.869440
H	-2.869901	-3.168836	-1.072669
H	-6.692905	-1.305005	-0.507996
H	-5.329231	-3.176678	-1.409618
C	-1.572143	1.988996	-0.013205

A-SO_3

C	1.332201	-1.790704	-0.476101
C	-0.026915	-1.867026	-0.209758
C	-0.565627	-1.094917	0.820914
C	0.263633	-0.291026	1.603398
C	1.625692	-0.232999	1.344217
C	2.160817	-0.973409	0.294391
H	1.751695	-2.377795	-1.283099
H	-0.671586	-2.494423	-0.807432
H	-0.159800	0.317088	2.393333
H	2.261033	0.406140	1.941864
C	3.608158	-0.832577	-0.066134
F	3.791798	0.086373	-1.056239
F	4.141461	-1.988478	-0.521806
F	4.364713	-0.424271	0.976223
N	-1.955706	-1.113962	1.123879
S	-3.190907	-0.991363	0.005526
O	-4.415753	-0.904156	0.761722
N	-1.817622	0.675522	-1.339439
O	-3.050411	0.558231	-0.641122
H	-2.211421	-0.599693	1.959284
H	-2.063891	0.852075	-2.307603
C	-0.952600	1.649897	-0.767667
C	-1.302494	2.417065	0.341729
C	0.328764	1.744807	-1.316675
C	-0.359608	3.279753	0.899321
H	-2.297112	2.339175	0.758310
C	1.254635	2.616110	-0.758365
H	0.604289	1.108556	-2.149356
C	0.917818	3.384011	0.357013
H	-0.633031	3.876260	1.762169

H	2.251142	2.672546	-1.179230
H	1.646375	4.053335	0.798036
O	-2.958647	-1.946439	-1.051485

A

C	1.318563	-1.735656	-0.588230
C	-0.036158	-1.894405	-0.343261
C	-0.637002	-1.210397	0.719098
C	0.143627	-0.406547	1.552358
C	1.502664	-0.262166	1.313062
C	2.092983	-0.916728	0.235513
H	1.778628	-2.259148	-1.416683
H	-0.627967	-2.539025	-0.979539
H	-0.320004	0.134982	2.367266
H	2.095423	0.377874	1.952273
C	3.534694	-0.684604	-0.093470
F	3.688272	0.287541	-1.037564
F	4.134322	-1.789879	-0.593693
F	4.254697	-0.288103	0.979085
N	-2.018734	-1.333162	0.973727
S	-3.215682	-1.363791	-0.243416
O	-4.473170	-1.519117	0.501272
N	-2.070367	0.591099	-1.414931
O	-3.279615	0.334240	-0.722478
H	-2.361483	-0.859418	1.804955
H	-2.333714	0.886514	-2.349550
C	-1.233523	1.535787	-0.751251
C	-1.624530	2.204918	0.407297
C	0.049972	1.719514	-1.271165
C	-0.723250	3.058734	1.041085
H	-2.620130	2.052888	0.800182
C	0.935414	2.581951	-0.637220
H	0.359085	1.158273	-2.145091
C	0.555565	3.252198	0.525895
H	-1.029289	3.578390	1.942014
H	1.934318	2.706720	-1.037278
H	1.252295	3.914429	1.025460

HNO_2

O	1.057932	0.258733	0.000030
O	-1.089460	0.066460	0.000070
N	0.171824	-0.519745	-0.000106

H	-0.950541	1.036673	-0.000055

Int1

C	1.815937	-1.207694	-0.868881
C	0.479815	-1.493339	-0.653765
C	-0.139050	-1.133620	0.560002
C	0.628043	-0.502280	1.547842
C	1.968443	-0.214515	1.329502
C	2.563630	-0.560536	0.119897
H	2.284334	-1.484347	-1.804866
H	-0.085380	-1.989321	-1.433198
H	0.142400	-0.230174	2.474829
H	2.547878	0.282653	2.096320
C	3.984315	-0.172367	-0.160628
F	4.057069	1.023497	-0.807887
F	4.616649	-1.070084	-0.950228
F	4.717371	-0.042054	0.966282
N	-1.488775	-1.325986	0.876082
S	-2.521917	-1.905767	-0.130501
O	-3.888332	-1.920168	0.480117
N	-3.267820	0.485420	-1.049170
O	-4.489882	0.566823	-0.375378
H	-3.440466	0.599778	-2.042586
C	-2.237780	1.308045	-0.547658
C	-2.229623	1.724322	0.783335
C	-1.142006	1.575339	-1.376821
C	-1.126002	2.417222	1.273638
H	-3.079774	1.507788	1.413500
C	-0.041868	2.251926	-0.870762
H	-1.145918	1.231650	-2.406218
C	-0.027209	2.674994	0.459789
H	-1.124145	2.744460	2.306820
H	0.810570	2.443532	-1.511143
H	0.835065	3.199292	0.852665
H	-4.571704	-0.309547	0.069142

Int2

C	-1.759221	0.525758	-1.162434
C	-0.557684	1.211265	-1.079786
C	-0.274972	2.027078	0.029203
C	-1.248309	2.151110	1.035701
C	-2.448201	1.465138	0.952349

C	-2.707756	0.645990	-0.147684
H	-1.948489	-0.125829	-2.004384
H	0.179664	1.088895	-1.861834
H	-1.023742	2.783528	1.884968
H	-3.180711	1.554949	1.745184
C	-4.028081	-0.045813	-0.247286
F	-4.424813	-0.588018	0.933079
F	-4.043721	-1.036906	-1.164080
F	-5.032131	0.814193	-0.606041
N	0.896207	2.767407	0.214305
S	2.256522	2.366616	-0.434416
O	3.286391	3.378967	-0.105093
N	2.008624	-0.702038	-0.296085
O	2.616138	0.058742	0.728053
H	2.751080	-1.257884	-0.753453
C	0.877682	-1.406142	0.096862
C	0.188238	-1.125295	1.284843
C	0.344602	-2.357752	-0.792053
C	-1.010820	-1.773687	1.561120
H	0.601245	-0.393676	1.964018
C	-0.849784	-3.000002	-0.497155
H	0.877760	-2.578050	-1.710687
C	-1.545203	-2.710999	0.679414
H	-1.541350	-1.532688	2.476239
H	-1.246353	-3.730159	-1.195075
H	-2.486989	-3.199797	0.897612
H	3.537898	-0.368599	0.828530
O	4.412773	-1.994075	-1.047873
O	4.918696	-1.159136	0.852121
N	5.256124	-1.883347	-0.130124

Int3

C	2.133439	-0.067393	-0.880428
C	0.915407	-0.664794	-0.590361
C	0.826660	-1.714132	0.350136
C	2.020623	-2.120371	0.989558
C	3.232034	-1.522211	0.699524
C	3.300719	-0.486744	-0.242516
H	2.169318	0.747634	-1.591800
H	0.016956	-0.297367	-1.067740
H	1.955329	-2.917338	1.719926
H	4.131961	-1.852404	1.206029
C	4.613046	0.157569	-0.517611

F	5.146420	0.771182	0.581484
F	4.554705	1.102949	-1.485736
F	5.567263	-0.738048	-0.915902
N	-0.333885	-2.357846	0.744814
S	-1.607104	-2.372290	-0.194193
O	-2.648143	-3.223504	0.432444
N	-2.165167	0.538951	-0.578081
O	-2.595963	-0.515589	0.214047
H	-2.917836	0.857402	-1.181261
C	-1.470389	1.556703	0.076491
C	-0.838036	1.329479	1.305808
C	-1.310443	2.798648	-0.559597
C	-0.055806	2.328756	1.874506
H	-0.963067	0.368334	1.784204
C	-0.526369	3.786640	0.022606
H	-1.798033	2.977341	-1.512976
C	0.111735	3.561197	1.244267
H	0.438210	2.134406	2.820498
H	-0.412538	4.740487	-0.482001
H	0.730473	4.330291	1.691615
H	-4.106428	-0.488932	0.284782
O	-6.408690	0.722297	-1.103600
O	-5.127864	-0.322192	0.231210
N	-5.274749	0.416589	-0.882436

Int4

C	2.371256	-0.896948	-0.685488
C	1.079125	-1.334527	-0.441985
C	0.348295	-0.887356	0.697795
C	1.011522	0.036806	1.552752
C	2.296151	0.469258	1.300311
C	3.001943	0.002394	0.178989
H	2.898626	-1.258137	-1.560607
H	0.613202	-2.019090	-1.139883
H	0.463496	0.394079	2.415718
H	2.768716	1.173594	1.975459
C	4.356422	0.523175	-0.118488
F	4.349437	1.736037	-0.765672
F	5.084657	-0.301848	-0.918270
F	5.104779	0.733279	1.002639
N	-0.927610	-1.235163	1.040739
S	-1.677608	-2.397309	0.210444
O	-3.031588	-2.591577	0.806010

N	-1.693819	-0.058410	-1.457278
O	-1.987002	-1.386528	-1.510605
H	-0.699402	0.122946	-1.370119
C	-2.514622	0.818857	-0.761201
C	-3.808497	0.462628	-0.354766
C	-2.054534	2.125280	-0.517423
C	-4.616978	1.403637	0.270088
H	-4.136781	-0.557586	-0.491834
C	-2.876396	3.052638	0.108412
H	-1.046160	2.397905	-0.812313
C	-4.169498	2.705257	0.505586
H	-5.609438	1.107977	0.594759
H	-2.499869	4.053084	0.296640
H	-4.806947	3.428199	1.001858

Int5

C	1.192358	-1.656153	-0.398084
C	-0.139176	-1.713953	-0.023442
C	-0.605344	-0.982646	1.116842
C	0.347605	-0.203344	1.856529
C	1.654806	-0.146491	1.460984
C	2.084923	-0.870693	0.325181
H	1.529666	-2.194345	-1.272665
H	-0.850581	-2.298755	-0.588776
H	0.004270	0.362397	2.714489
H	2.365710	0.459333	2.008494
C	3.519411	-0.744047	-0.099771
F	3.866616	-1.644392	-1.038078
F	4.365761	-0.903441	0.946040
F	3.779900	0.486658	-0.615119
N	-1.896515	-1.017181	1.424705
S	-3.876241	-1.386800	0.002339
O	-4.475224	-0.088053	0.330980
N	-0.688240	0.273375	-2.011449
O	-3.162625	-1.452825	-1.282484
H	-2.122904	-0.438452	2.234245
H	-1.640646	-0.103262	-1.982184
C	-0.577449	1.323696	-1.196232
C	0.703812	1.954793	-1.089005
C	-1.644801	1.828622	-0.381409
C	0.907450	2.992061	-0.203052
H	1.502068	1.579084	-1.715661
C	-1.419195	2.866777	0.499017

H	-2.627722	1.380269	-0.460784
C	-0.145650	3.447086	0.602798
H	1.885041	3.453362	-0.124711
H	-2.231956	3.237621	1.113203
H	0.019985	4.261557	1.298436

NO_2^-

O	-1.070969	-0.200762	-0.000003
O	1.070965	-0.200764	-0.000004
N	0.000004	0.458887	0.000008

SO_2

S	0.000000	-0.000000	0.371733
O	0.000000	-1.254619	-0.371733
O	0.000000	1.254619	-0.371733

TS1

C	-2.050577	0.106546	-0.843803
C	-0.824313	0.694187	-0.573314
C	-0.725397	1.776239	0.326890
C	-1.909858	2.227136	0.947460
C	-3.132180	1.639021	0.674856
C	-3.213432	0.573601	-0.229134
H	-2.098730	-0.733057	-1.525672
H	0.070341	0.297174	-1.034323
H	-1.833269	3.050895	1.646177
H	-4.028812	2.004751	1.160772
C	-4.521532	-0.097775	-0.466531
F	-4.827349	-1.029423	0.486134
F	-4.573249	-0.754134	-1.652698
F	-5.566993	0.776130	-0.461537
N	0.447932	2.419470	0.696835
S	1.719842	2.384169	-0.231512
O	2.785063	3.215464	0.375123
N	2.187951	-0.628600	-0.580663
O	2.660733	0.400021	0.226246
H	2.942311	-0.959115	-1.181440
C	1.455374	-1.621469	0.066957
C	0.845235	-1.389721	1.307154
C	1.227107	-2.841390	-0.592158
C	0.018716	-2.360196	1.863665

H	1.024224	-0.447201	1.805008
C	0.399920	-3.800351	-0.022005
H	1.698215	-3.023953	-1.552705
C	-0.216145	-3.569132	1.210263
H	-0.455941	-2.161502	2.818726
H	0.234860	-4.737198	-0.544122
H	-0.868561	-4.315627	1.647940
H	3.962232	0.292099	0.289584
O	4.971685	-0.810610	-1.486650
O	5.093941	0.181262	0.406438
N	5.697703	-0.398929	-0.596728

TS2'-SO_3

C	1.526933	-0.812262	1.085518
C	0.184255	-1.126037	0.978667
C	-0.372941	-1.424663	-0.277344
C	0.469207	-1.421782	-1.404688
C	1.822249	-1.134061	-1.285978
C	2.357696	-0.813032	-0.041729
H	1.945809	-0.593336	2.060248
H	-0.444646	-1.140282	1.854886
H	0.054035	-1.658936	-2.377948
H	2.454876	-1.147063	-2.164248
C	3.786135	-0.398185	0.094181
F	3.913513	0.970694	0.116295
F	4.558129	-0.825697	-0.925700
F	4.349558	-0.834222	1.241840
N	-1.702230	-1.801645	-0.420874
S	-3.058295	-0.979776	0.298171
O	-2.452102	-0.092814	1.317220
N	-2.609012	1.798619	-1.477971
O	-3.644144	-0.222339	-0.854826
H	-1.958531	-2.086653	-1.358087
C	-1.558749	1.950291	-0.713581
C	-0.264087	1.828177	-1.342993
C	-1.619672	2.237039	0.702432
C	0.876208	2.047654	-0.621742
H	-0.249286	1.590257	-2.398317
C	-0.454596	2.442748	1.408276
H	-2.588290	2.324878	1.172231
C	0.777539	2.339502	0.753954
H	1.852484	1.975442	-1.078778
H	-0.488563	2.662185	2.467370

H	1.691556	2.492729	1.316278
H	-3.484042	1.918275	-0.966051
O	-3.934485	-2.025996	0.799087

TS2'

C	-1.287423	-0.613537	-1.091945
C	0.056225	-0.895609	-0.933598
C	0.539528	-1.359692	0.310592
C	-0.397029	-1.569796	1.358162
C	-1.733905	-1.272174	1.186302
C	-2.189665	-0.773746	-0.038153
H	-1.641668	-0.251770	-2.048759
H	0.748946	-0.759628	-1.748850
H	-0.047517	-1.957225	2.308734
H	-2.428749	-1.425003	2.002697
C	-3.620572	-0.369776	-0.187254
F	-3.845363	0.891206	0.298727
F	-4.462625	-1.181125	0.492191
F	-4.028421	-0.351136	-1.474358
N	1.862509	-1.550727	0.572818
S	3.355221	-1.383955	-0.455209
O	2.862898	-0.764540	-1.715590
N	2.994408	1.426936	1.038839
O	4.109123	-0.417709	0.442786
H	2.108739	-1.866788	1.502240
C	1.772921	1.630013	0.547038
C	0.672975	1.505901	1.455790
C	1.502968	2.096469	-0.781430
C	-0.583933	1.947585	1.099422
H	0.883726	1.118348	2.443965
C	0.245451	2.539880	-1.116298
H	2.308813	2.084985	-1.505445
C	-0.799298	2.472440	-0.177411
H	-1.408848	1.874979	1.795646
H	0.048631	2.916825	-2.112440
H	-1.791244	2.809450	-0.452970
H	3.719275	1.665388	0.362999

TS2-Bn

C	-3.511588	0.489090	0.807344
C	-2.249164	1.045052	0.676401
C	-1.363317	0.541869	-0.291041

C	-1.763087	-0.528803	-1.107133
C	-3.017655	-1.096177	-0.948983
C	-3.899218	-0.585962	0.004524
H	-4.191960	0.876595	1.554523
H	-1.933627	1.850499	1.325800
H	-1.081871	-0.912267	-1.857721
H	-3.315186	-1.930230	-1.571206
C	-5.281981	-1.154583	0.123973
F	-5.787625	-1.015809	1.369591
F	-5.320374	-2.472384	-0.179912
F	-6.155378	-0.541249	-0.717226
N	-0.075312	1.045971	-0.420917
S	0.369883	2.718205	-0.244750
O	0.254132	3.052326	1.189668
N	2.676265	0.609003	-0.842413
O	1.741824	2.642214	-0.872287
H	0.586953	0.589782	-1.052963
C	3.262909	0.495219	0.481944
H	3.350256	1.083941	-1.448062
H	3.666929	1.449052	0.834047
H	2.494362	0.161748	1.181793
C	4.372712	-0.533647	0.366811
C	4.063586	-1.897685	0.355986
C	5.703380	-0.134534	0.210898
C	5.070717	-2.847314	0.212897
H	3.031493	-2.210469	0.468031
C	6.711680	-1.083874	0.068172
H	5.949870	0.921996	0.216051
C	6.396761	-2.441941	0.068401
H	4.822585	-3.902274	0.215518
H	7.741986	-0.765057	-0.038176
H	7.181750	-3.181019	-0.040609

TS2-CO_2

C	1.759067	-1.126022	0.651862
C	0.419647	-1.394197	0.441074
C	-0.247421	-0.829671	-0.684381
C	0.494697	0.015837	-1.560798
C	1.830821	0.262306	-1.338620
C	2.471364	-0.305604	-0.228243
H	2.264151	-1.565503	1.502260
H	-0.148027	-2.042992	1.091864
H	-0.009636	0.459844	-2.410764

H	2.387227	0.894795	-2.018255
C	3.904909	0.039898	0.053173
F	3.999816	1.199869	0.759049
F	4.617208	0.220855	-1.079793
F	4.530093	-0.907710	0.779295
N	-1.548342	-1.061948	-0.928993
O	-2.199651	-2.518133	0.829982
N	-4.362317	1.138891	-0.522309
O	-3.716524	-1.765934	-0.699405
H	-1.948216	-0.642786	-1.762142
C	-3.192510	1.320077	0.057671
C	-2.275207	2.248915	-0.551304
C	-2.752301	0.630103	1.245191
C	-1.017033	2.432643	-0.035180
H	-2.617306	2.774552	-1.434409
C	-1.498497	0.853334	1.765922
H	-3.423976	-0.081768	1.709015
C	-0.613951	1.722195	1.113389
H	-0.321961	3.113865	-0.510522
H	-1.175870	0.316756	2.648844
H	0.388854	1.857626	1.500395
H	-4.878241	0.386306	-0.059145
C	-2.639760	-1.928794	-0.141357

TS2-SO_3

C	2.818349	0.865219	-0.193955
C	1.599316	0.221997	-0.134247
C	1.553287	-1.172116	0.114342
C	2.766811	-1.881130	0.296818
C	3.977060	-1.222405	0.232430
C	4.011825	0.154512	-0.016473
H	2.850845	1.929614	-0.387566
H	0.680198	0.769900	-0.274931
H	2.735313	-2.947934	0.485070
H	4.900070	-1.770436	0.367270
C	5.321932	0.885517	-0.035999
F	5.606469	1.440225	1.170332
F	5.326017	1.895759	-0.933878
F	6.356860	0.071893	-0.341187
N	0.376968	-1.847718	0.175524
S	-1.261741	-1.194757	0.060015
O	-2.042147	-2.423971	0.182427
N	-2.874207	1.857177	-0.299117

O	-1.334129	-0.231759	1.168781
H	0.387958	-2.838089	0.386165
H	-2.233532	1.234689	-0.807708
C	-4.063974	1.309196	-0.205225
C	-4.420579	0.040156	-0.800301
C	-5.068912	2.015480	0.552347
C	-5.682198	-0.474010	-0.620781
H	-3.671408	-0.484099	-1.379767
C	-6.320726	1.477107	0.720426
H	-4.782088	2.963311	0.989930
C	-6.629327	0.234094	0.137887
H	-5.947379	-1.429150	-1.056627
H	-7.071866	1.999312	1.300084
H	-7.619106	-0.185636	0.277012
O	-1.291446	-0.542293	-1.268088

TS2

C	3.385194	-0.924830	-0.400750
C	2.009472	-1.020366	-0.274062
C	1.270129	0.090440	0.169230
C	1.938593	1.288220	0.467171
C	3.313881	1.381901	0.314120
C	4.043485	0.274779	-0.116597
H	3.951344	-1.781051	-0.745039
H	1.494071	-1.937110	-0.526486
H	1.372528	2.145899	0.812598
H	3.819997	2.312648	0.533900
C	5.536835	0.344312	-0.226052
F	6.151585	-0.168272	0.872813
F	5.985486	1.612802	-0.359974
F	6.004257	-0.358819	-1.284157
N	-0.119348	0.034261	0.253988
S	-0.984489	-1.355127	0.949537
O	-2.345075	-0.717992	1.085837
N	-2.986014	0.563235	-0.704002
O	-0.845324	-2.441008	-0.048206
H	-0.581969	0.885330	0.559503
H	-2.685404	-0.249931	-1.245738
C	-4.312694	0.523331	-0.514784
C	-4.922288	1.619191	0.161749
C	-5.144919	-0.544454	-0.965512
C	-6.289513	1.654481	0.348098
H	-4.277973	2.415126	0.513308

C	-6.510578	-0.493211	-0.777346
H	-4.680350	-1.396569	-1.449178
C	-7.088231	0.603305	-0.121164
H	-6.748175	2.492950	0.858203
H	-7.138737	-1.303977	-1.126336
H	-8.160941	0.634244	0.028972

TS3

C	2.955836	1.061567	0.186200
C	1.649275	1.318000	-0.173601
C	0.875860	0.332399	-0.853735
C	1.483298	-0.929920	-1.125989
C	2.789279	-1.174697	-0.761560
C	3.533347	-0.180036	-0.109788
H	3.539683	1.817756	0.694334
H	1.191170	2.270964	0.054737
H	0.891811	-1.697573	-1.609095
H	3.244671	-2.133190	-0.975054
C	4.936302	-0.479462	0.336008
F	5.572229	-1.315330	-0.514898
F	4.954788	-1.078215	1.553840
F	5.689218	0.636660	0.440785
N	-0.384569	0.623231	-1.199816
S	-1.841433	2.429510	-0.337021
O	-3.078908	1.939732	-0.948474
O	-1.647957	2.109926	1.086973
H	-0.856333	-0.147147	-1.670289
N	-1.599911	-1.069424	0.389954
H	-1.291141	-0.408988	1.108118
C	-2.935813	-1.136099	0.393007
C	-3.570849	-2.003631	-0.550136
C	-3.770302	-0.389960	1.285026
C	-4.944092	-2.115960	-0.591035
H	-2.935827	-2.569086	-1.221563
C	-5.142128	-0.520142	1.235049
H	-3.298124	0.298020	1.975297
C	-5.737735	-1.377804	0.299969
H	-5.414731	-2.775729	-1.310401
H	-5.764866	0.053431	1.911373
H	-6.816883	-1.468083	0.261905

References for computational part

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision E.01; Gaussian, Inc.: Wallingford, CT, **2013**.

2. a) Becke. A. D.; *J. Chem. Phys.* **1993**, *98*, 5648-5652. b) Lee, C.; Yang, W.; Parr, R. G. *Phys.Rev. B.* **1988**, *37*, 785-789.

3. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**,*132*, 154104.

4. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, **1986**.

5. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B.* **2009**, *113*, 6378-6396.

6 Mardirossian, N.; Head-Gordon, M. *J. Chem. Phys.* **2016**, *144*, 214110.

7. (a) Weigend F.; Ahlrichs R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305. (b) Papajak, E.; Zheng, J.; Xu, X.; Leverentz, H. R.; Truhlar, D. G. *J. Chem. Theory Comput.* **2011**, *7*, 3027-3034.

8. (a) Chan, B.; Gill, P. M. W.; Kimura, M. *J. Chem. Theory Comput.* **2019**, *15*, 3610-3622. (b) Prasad, V. K.; Pei, Z.; Edelmann, S.; Otero-de-la-Roza, A.; DiLabio, G. A. *J. Chem. Theory Comput.* **2022**, *18*, 151-166. (c) Mardirossian, N.; Head-Gordon, M. *Mol. Phys.* **2017**, *115*, 2315-2372.

9. (a) Riplinger, C.; Neese, F. *J. Chem. Phys.* **2013**, *138*, 034106. (b) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. *J. Chem. Phys.* **2013**, *139*, 134101. (c) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

10. (a) Neese, F. The ORCA Program System. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73−78. (b) Neese, F. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2017**, *8*, e1327.

11. (a) Li Manni, G.; Carlson, R. K.; Luo, S.; Ma, D.; Olsen, J.; Truhlar, D. G.; Gagliardi, L. *Journal of Chemical Theory and Computation* **2014**, *10*, 3669-3680. (b) Sharma, P.; Bernales, V.; Knecht, S.; Truhlar, D. G.; Gagliardi, L. *Chem. Sci.* **2019**, *10*, 1716-1723.

12 (a) Li Manni, G.; Fdez. Galván, I.; Alavi, A.; Aleotti, F.; Aquilante, F.; Autschbach, J.; Avagliano, D.; Baiardi, A.; Bao, J. J.; Battaglia, S.; Birnoschi, L.; Blanco-González, A.; Bokarev, S. I.; Broer, R.; Cacciari, R.; Calio, P. B.; Carlson, R. K.; Carvalho Couto, R.; Cerdán, L.; Chibotaru, L. F.; Chilton, N. F.; Church, J. R.; Conti, I.; Coriani, S.; Cuéllar-Zuquin, J.; Daoud, R. E.; Dattani, N.; Decleva, P.; de Graaf, C.; Delcey, M. G.; De Vico, L.; Dobrautz, W.; Dong, S. S.; Feng, R.; Ferré, N.; Filatov, M.; Gagliardi, L.; Garavelli, M.; González, L.; Guan, Y.; Guo, M.; Hennefarth, M. R.; Hermes, M. R.; Hoyer, C. E.; Huix-Rotllant, M.; Jaiswal, V. K.; Kaiser, A.; Kaliakin, D. S.; Khamesian, M.; King, D. S.; Kochetov, V.; Krośnicki, M.; Kumaar, A. A.; Larsson, E. D.; Lehtola, S.; Lepetit, M.-B.; Lischka, H.; López Ríos, P.; Lundberg, M.; Ma, D.; Mai, S.; Marquetand, P.; Merritt, I. C. D.; Montorsi, F.; Mörchen, M.; Nenov, A.; Nguyen, V. H. A.; Nishimoto, Y.; Oakley, M. S.; Olivucci, M.; Oppel, M.; Padula, D.; Pandharkar, R.; Phung, Q. M.; Plasser, F.; Raggi, G.; Rebolini, E.; Reiher, M.; Rivalta, I.; Roca-Sanjuán, D.; Romig, T.; Safari, A. A.; Sánchez-Mansilla, A.; Sand, A. M.; Schapiro, I.; Scott, T. R.; Segarra-Martí, J.; Segatta, F.; Sergentu, D.-C.; Sharma, P.; Shepard, R.; Shu, Y.; Staab, J. K.; Straatsma, T. P.; Sørensen, L. K.; Tenorio, B. N. C.; Truhlar, D. G.; Ungur, L.; Vacher, M.; Veryazov, V.; Voß, T. A.; Weser, O.; Wu, D.; Yang, X.; Yarkony, D.; Zhou, C.; Zobel, J. P.; Lindh, R., The OpenMolcas Web: A Community-Driven Approach to Advancing Computational Chemistry. *J. Chem. Theory Comput.* **2023**, *19*, 6933-6991. (b) Keller, S.; Dolfi, M.; Troyer, M.; Reiher, M. *J. Chem. Phys.* **2015**, *143*, 244118.

13. CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org)

14. Knizia, G. IboView. http://www.iboview.org.

15. (a) Witte, J.; Goldey, M.; Neaton, J. B.; Head-Gordon, M. *Journal of Chemical Theory and Computation* **2015**, *11*, 1481-1492. (b) Řezáč, J. *J. Chem. Theory Comput.* **2020**, *16*, 6305-6316.

16. (a) Gräfenstein, J.; Kraka, E.; Filatov, M.; Cremer, D. Can Unrestricted Density-Functional Theory Describe Open Shell Singlet Biradicals? *Int. J. Mol. Sci.* **2002**, *3*, 360-394. (b) Tentscher, P. R.; Arey, J. S. *J. Chem. Theory Comput.* **2012**, *8*, 2165-2179. (c) Svatunek, D.; Pemberton, R. P.; Mackey, J. L.; Liu, P.; Houk, K. N. *J. Org. Chem.* **2020**, *85*, 3858-3864.

17. (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.

18. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868.

19. Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

20. Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158−6170.

21. Boese, A. D.; Martin, J. M. L. *J. Chem. Phys.* **2004**, *121*, 3405−3416.

22. Chai, J.-D.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.

23. Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215−241.

24. (a) Piecuch, P.; Kowalski, K.; Pimienta, I. S. O.; McGuire, M. J. *Int. Rev. Phys. Chem.* **2002**, *21*, 527−655. (b) ORCA 4.2.1 Manual. https://www.kofo.mpg.de/412442/orca_manual-opt.pdf.

25. (a) Byrd, E. F. C.; Sherrill, C. D.; Head-Gordon, M. *J. Phys. Chem. A* **2001**, *105*, 9736-9747. (b) Beran, G. J. O.; Gwaltney, S. R.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2488-2493. (c)

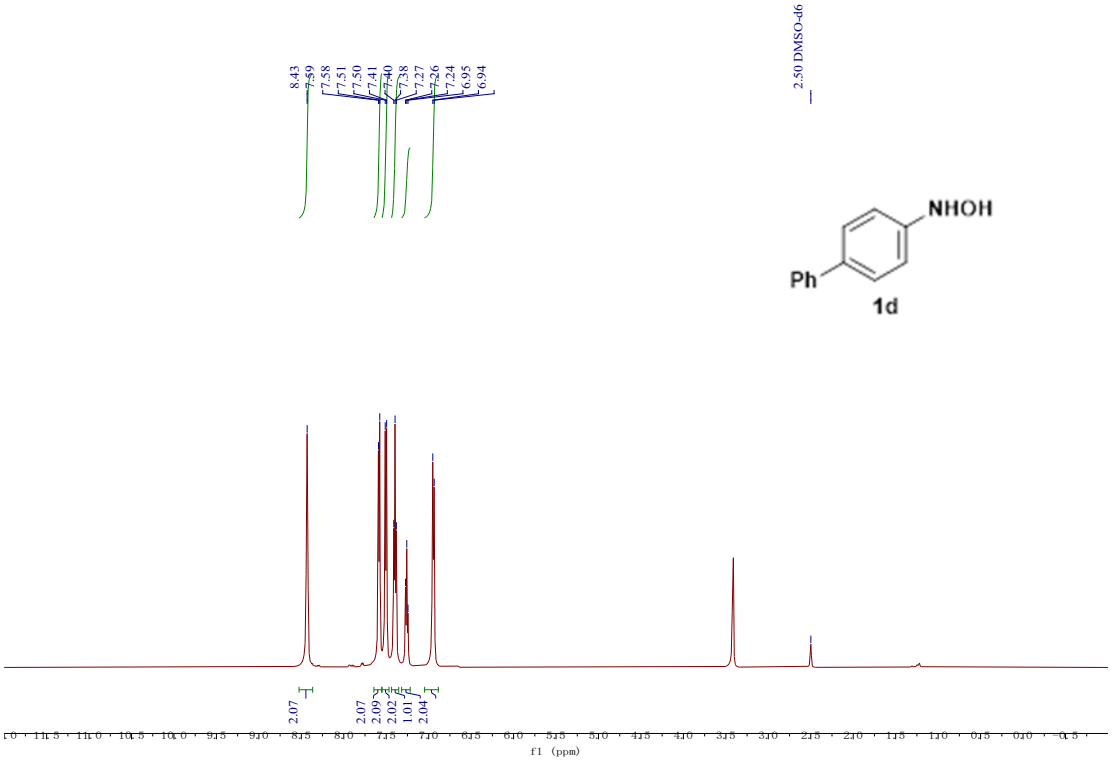
26. (a) Sharma, P.; Truhlar, D. G.; Gagliardi, L. *J. Am. Chem. Soc.* **2020**, *142*, 16644-16650. (b) Zhou, C.; Gagliardi, L.; Truhlar, D. G. *J. Phys. Chem. A* **2019**, *123*, 3389-3394.

27. (a) Zhao, Y.; González-García, N.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 2012-2018. (b) Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 5656-5667.

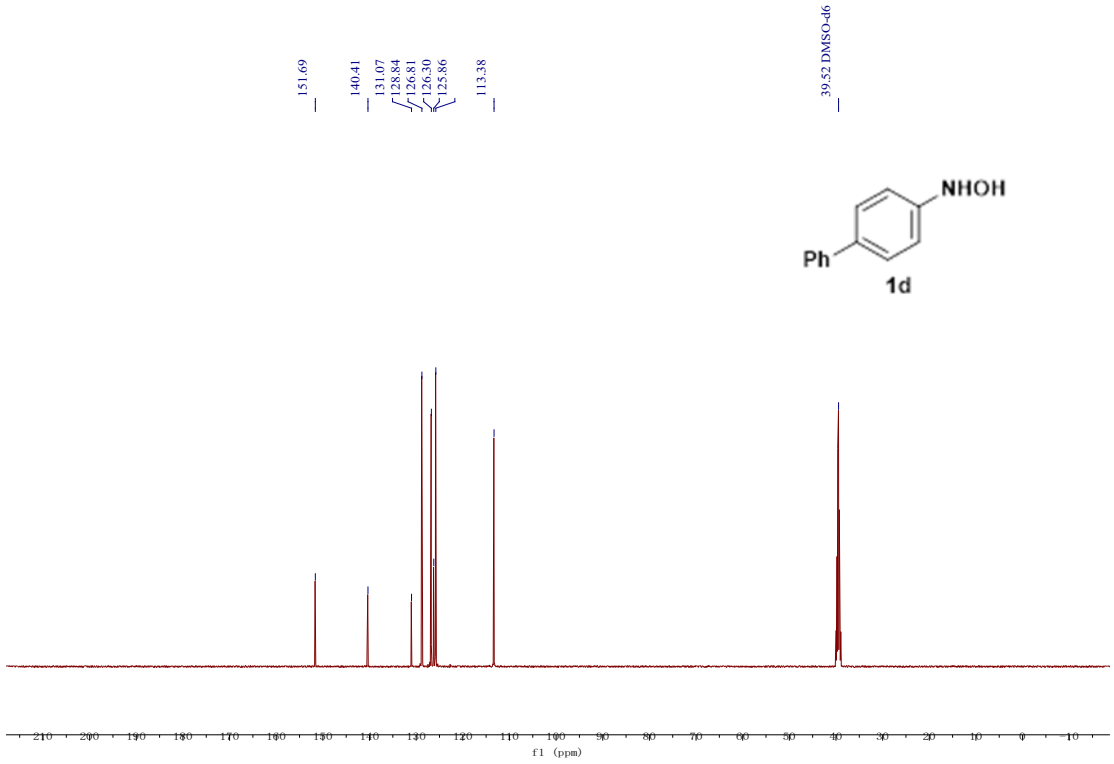
19. NMR spectra

NMR spectra for the starting materials

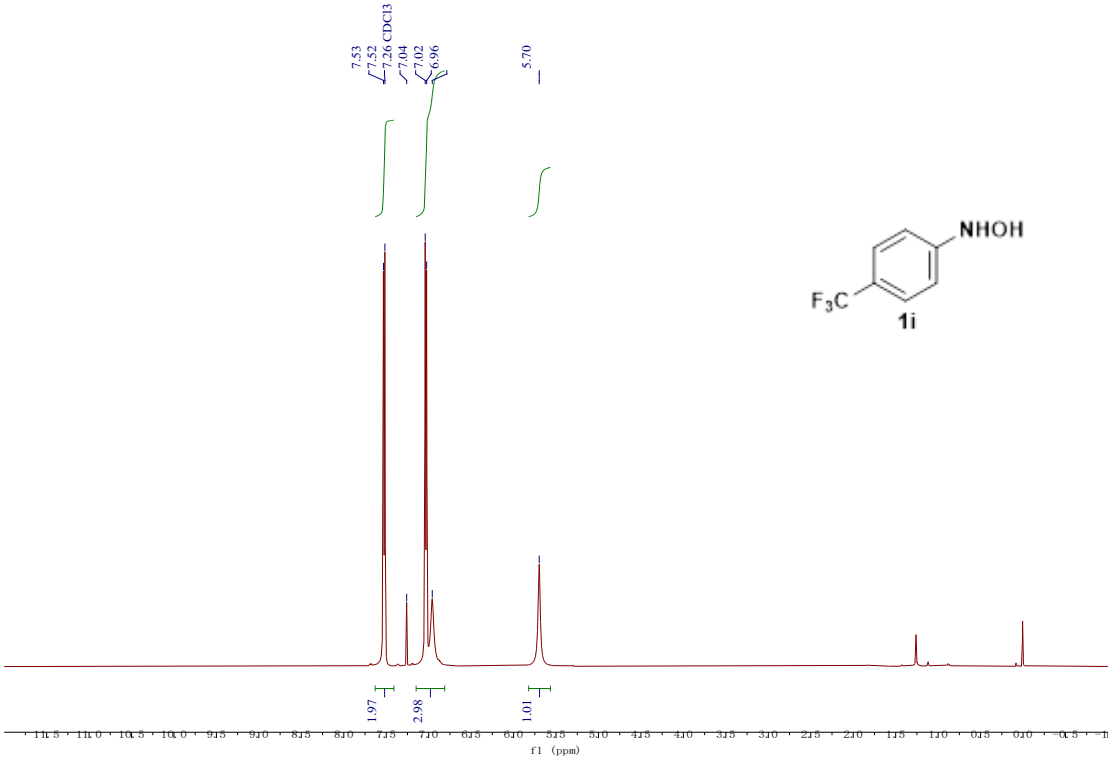
^{1}H NMR of Compound 1d (500 MHz, DMSO-d_6)



^{13}C NMR of Compound 1d (126 MHz, DMSO-d_6)



^{1}H NMR of Compound 1i (500 MHz, $CDCl_3$)



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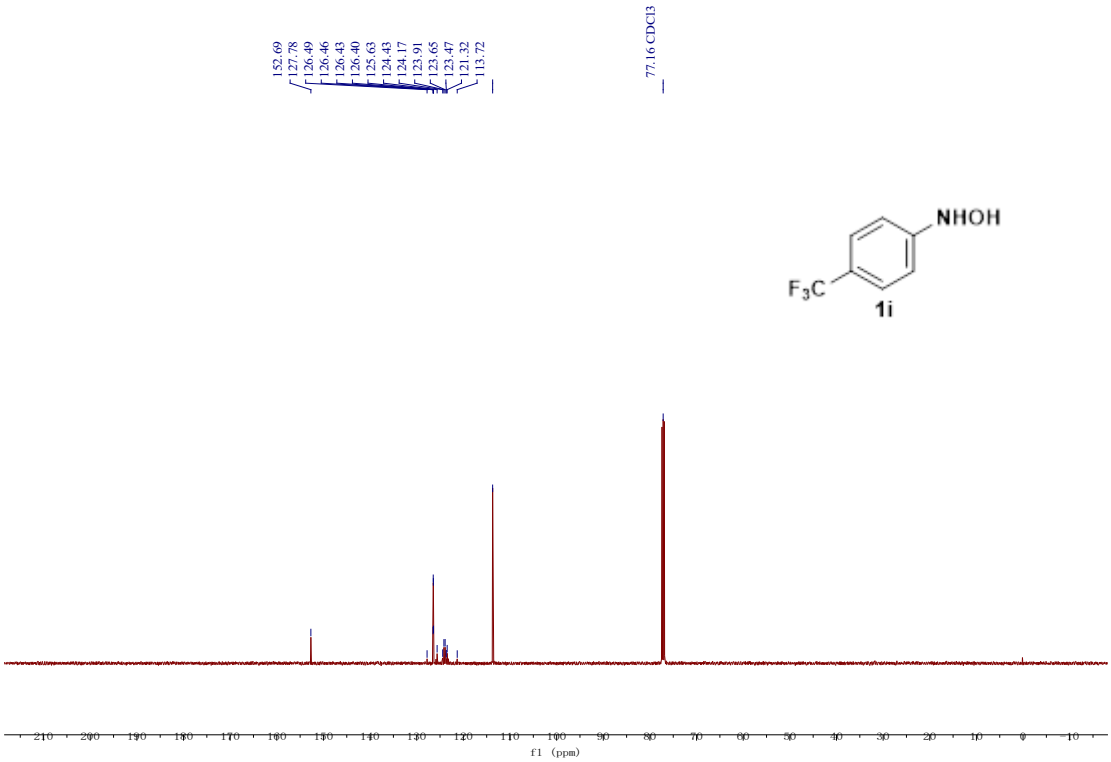
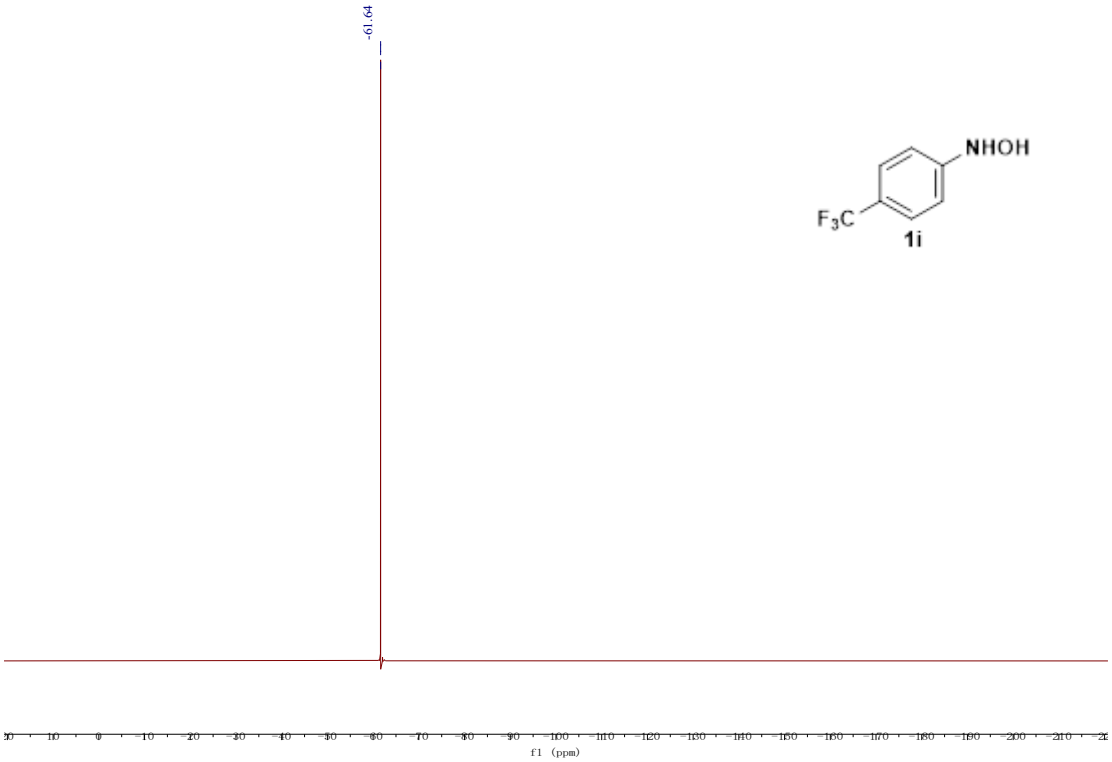


^{19}F NMR of Compound 1i (471 MHz, $CDCl_3$)



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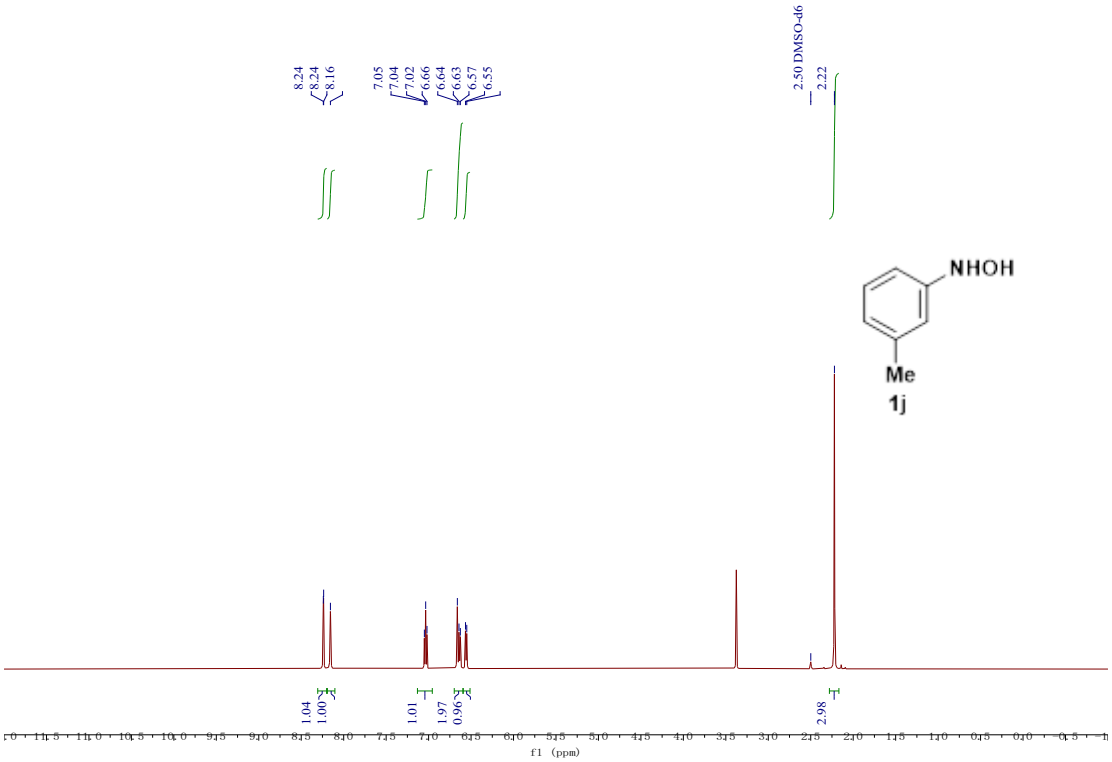

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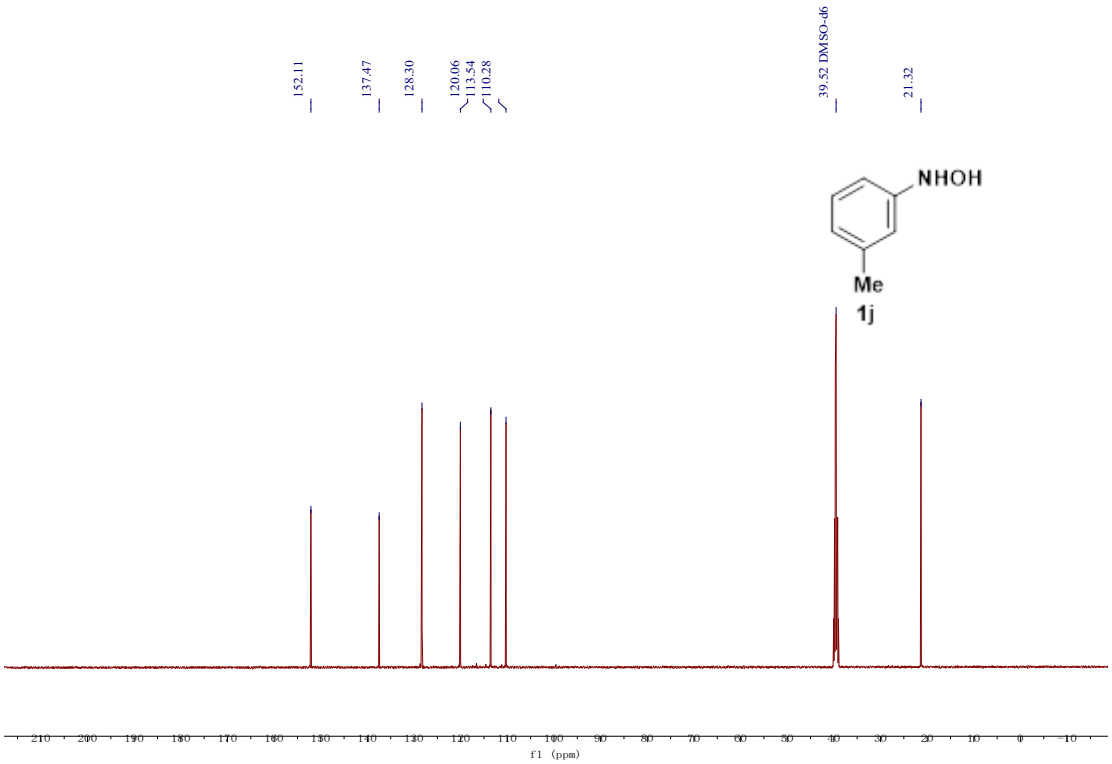
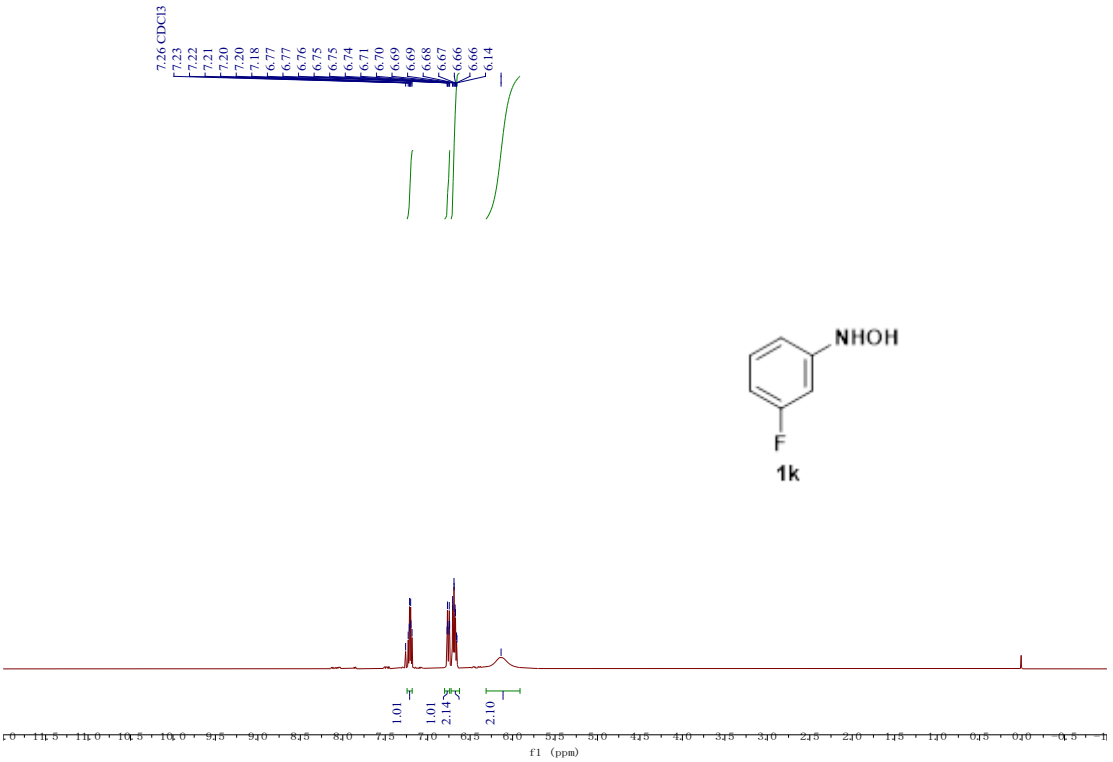


^{1}H NMR of Compound 1k (500 MHz, $CDCl_3$



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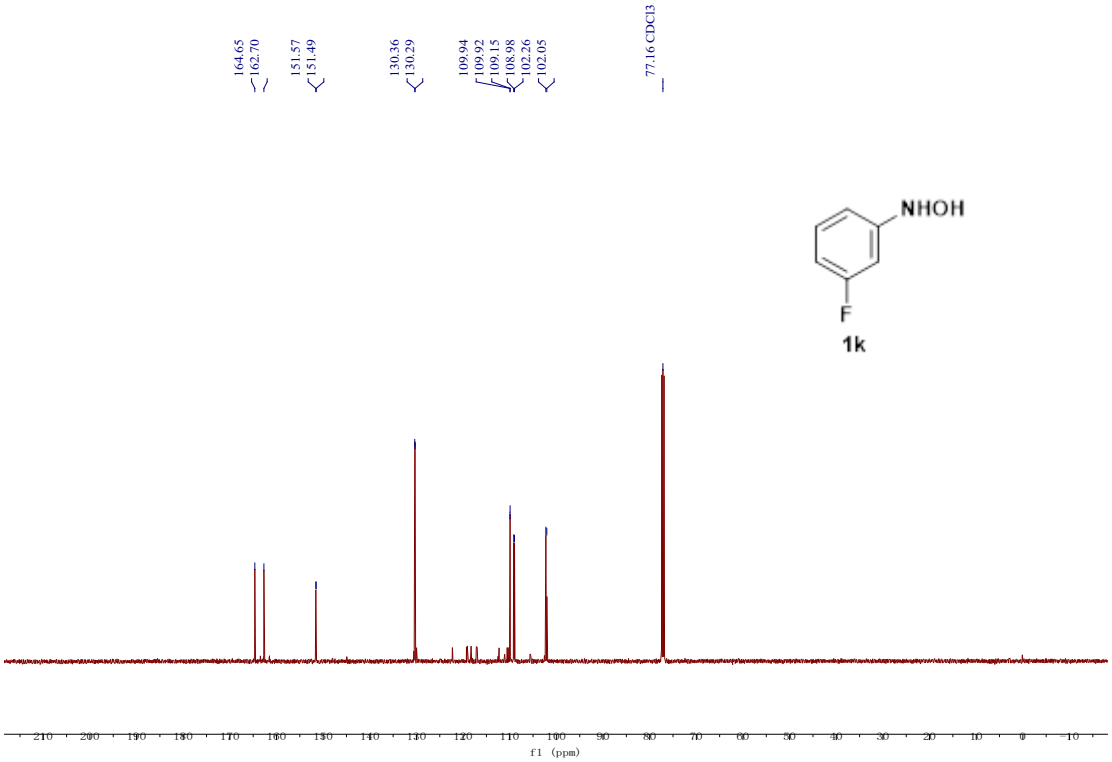

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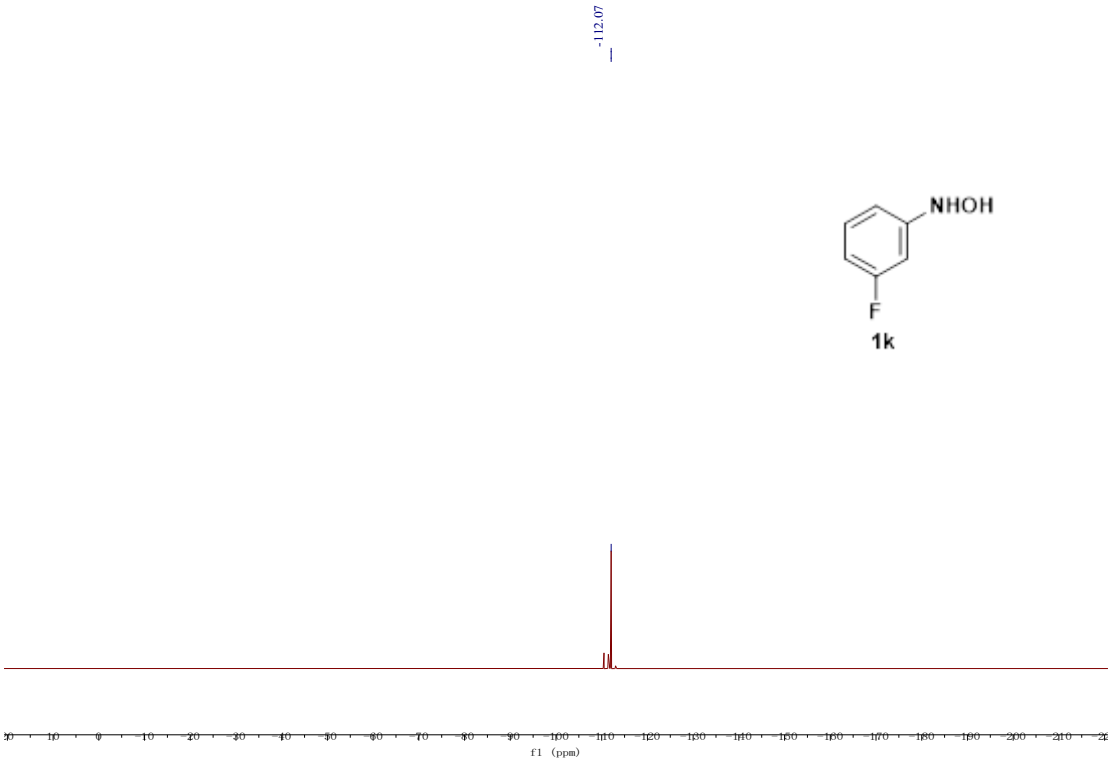

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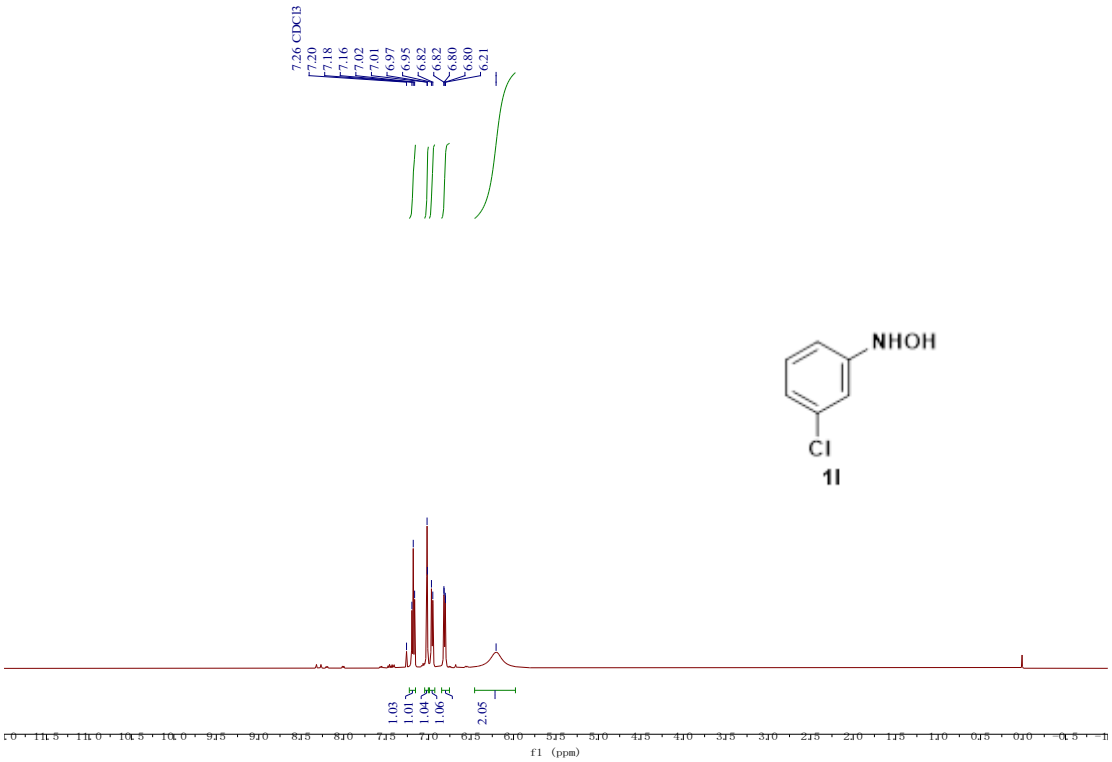

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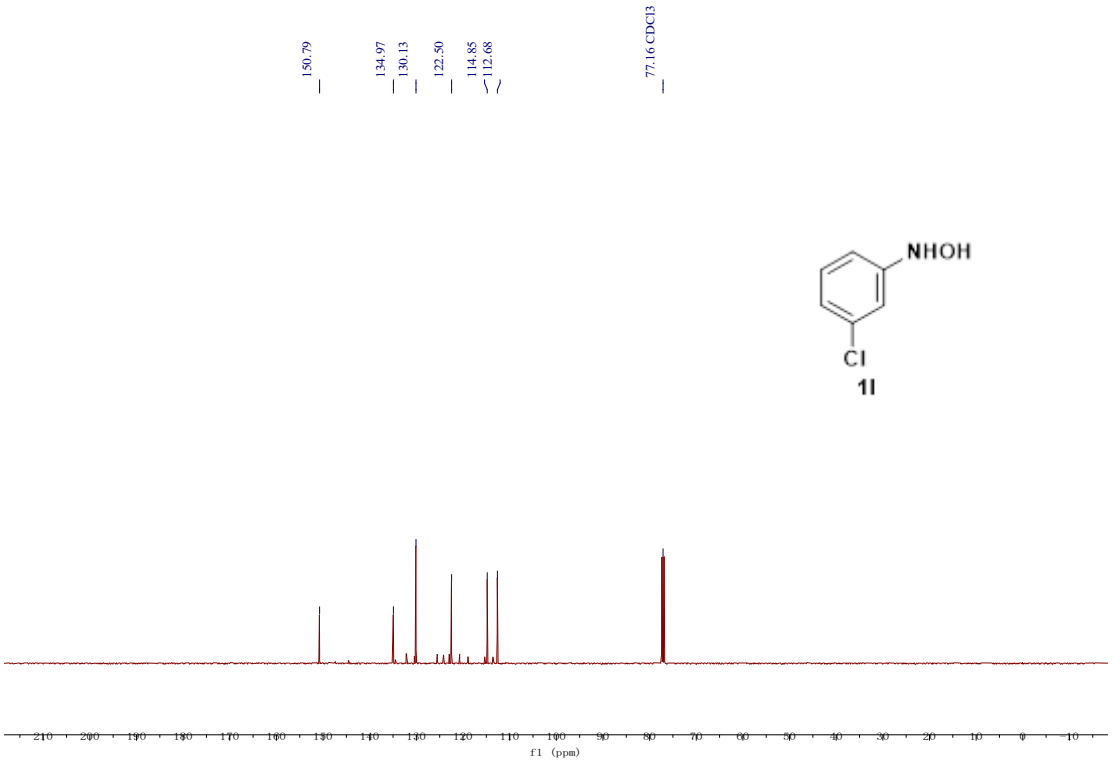
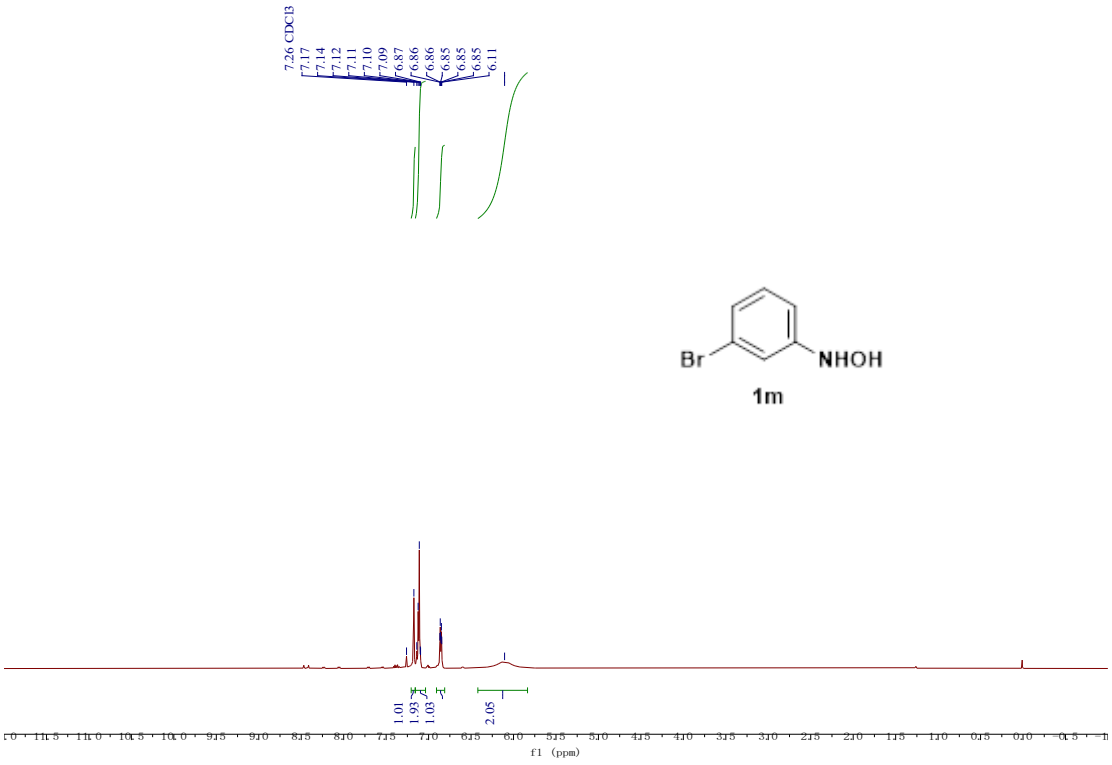
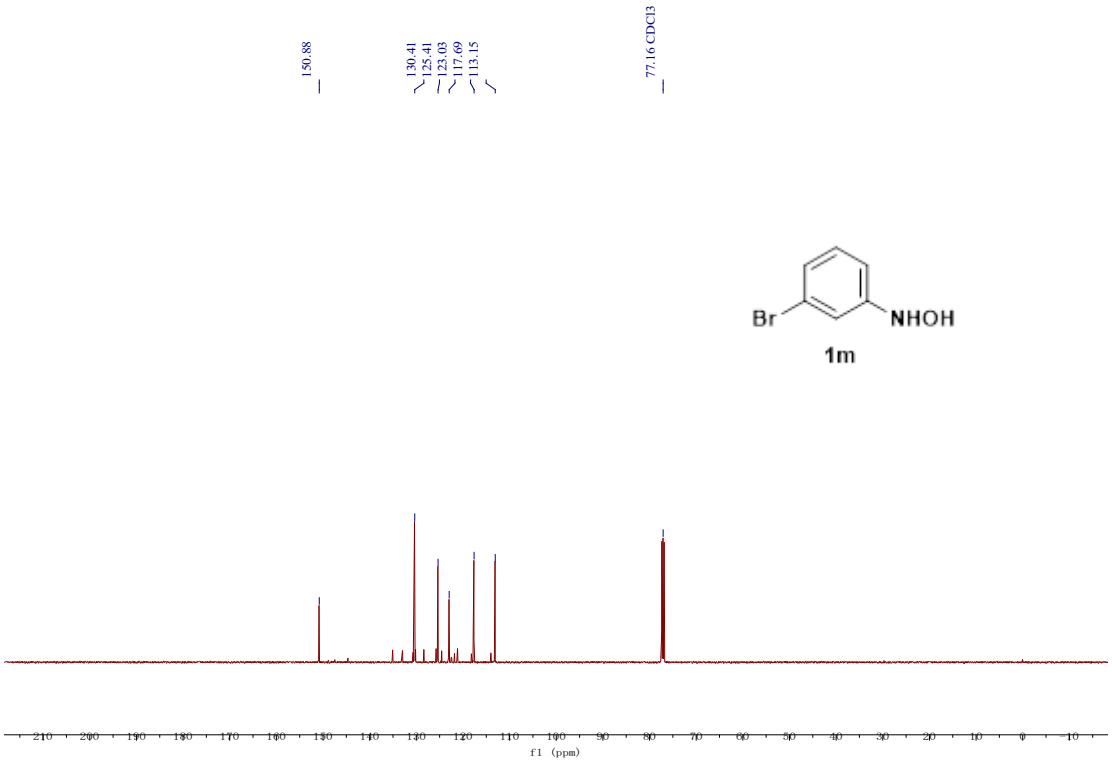


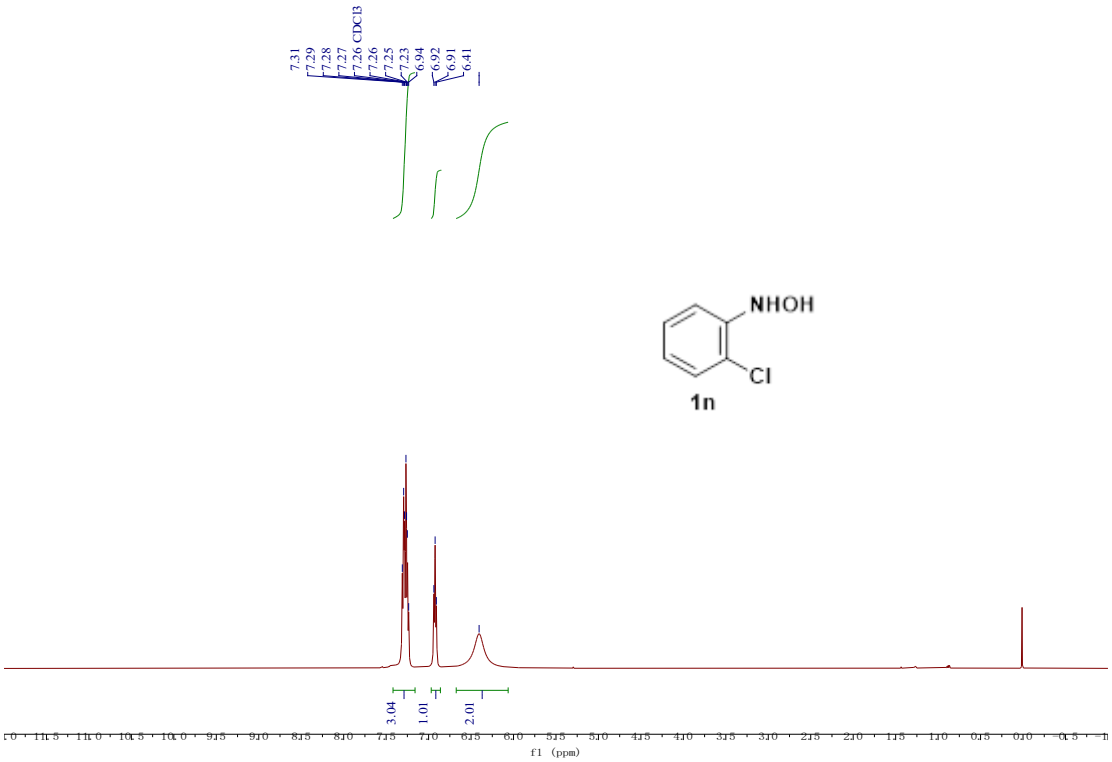
^{1}H NMR of Compound 1m (500 MHz, $CDCl_3$)



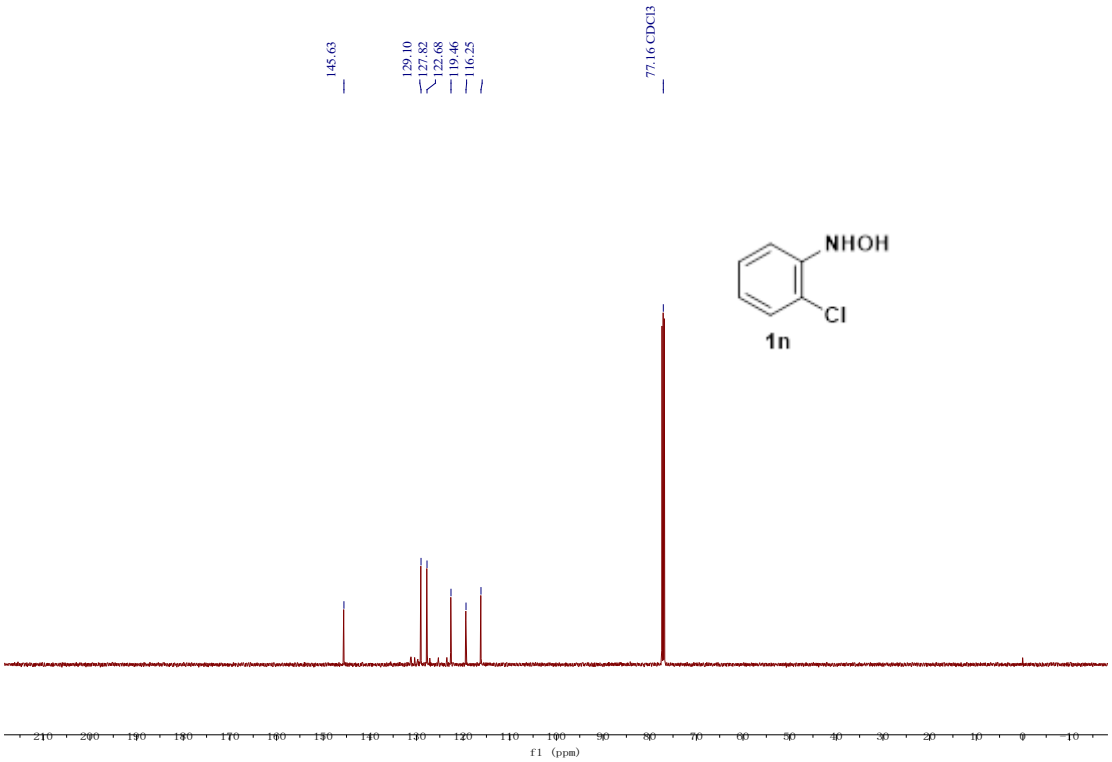
^{13}C NMR of Compound 1m (126 MHz, $CDCl_3$)



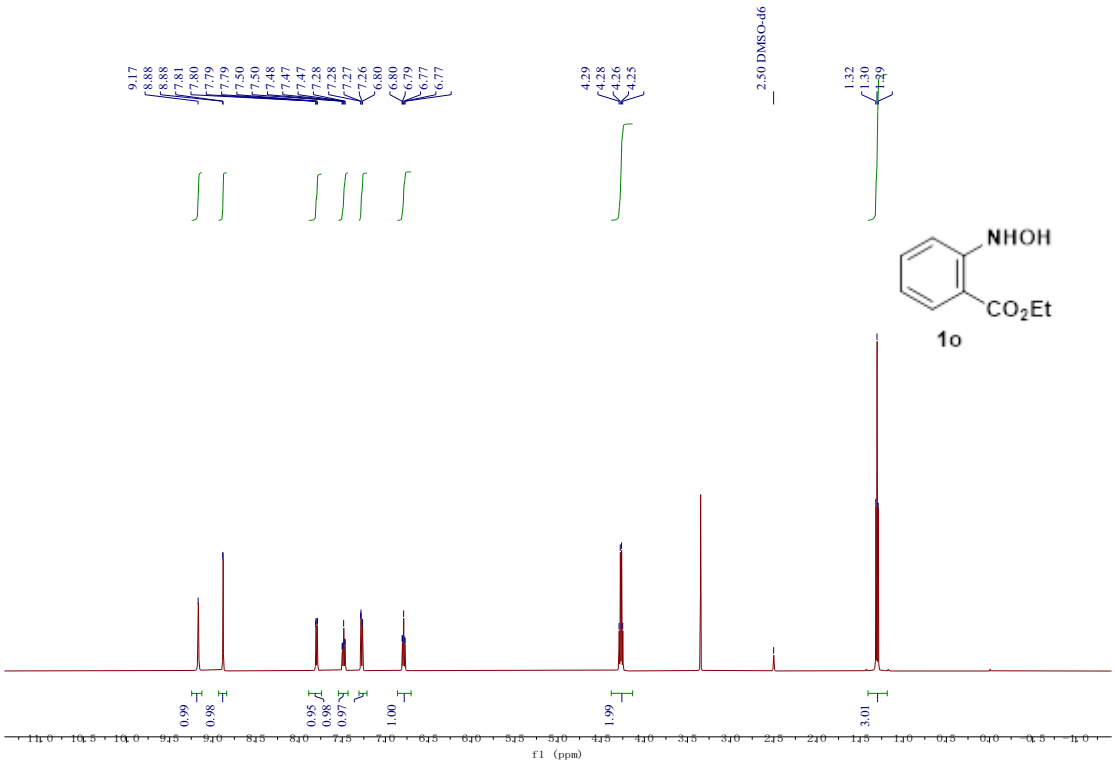
^{1}H NMR of Compound 1n (500 MHz, $CDCl_3$)



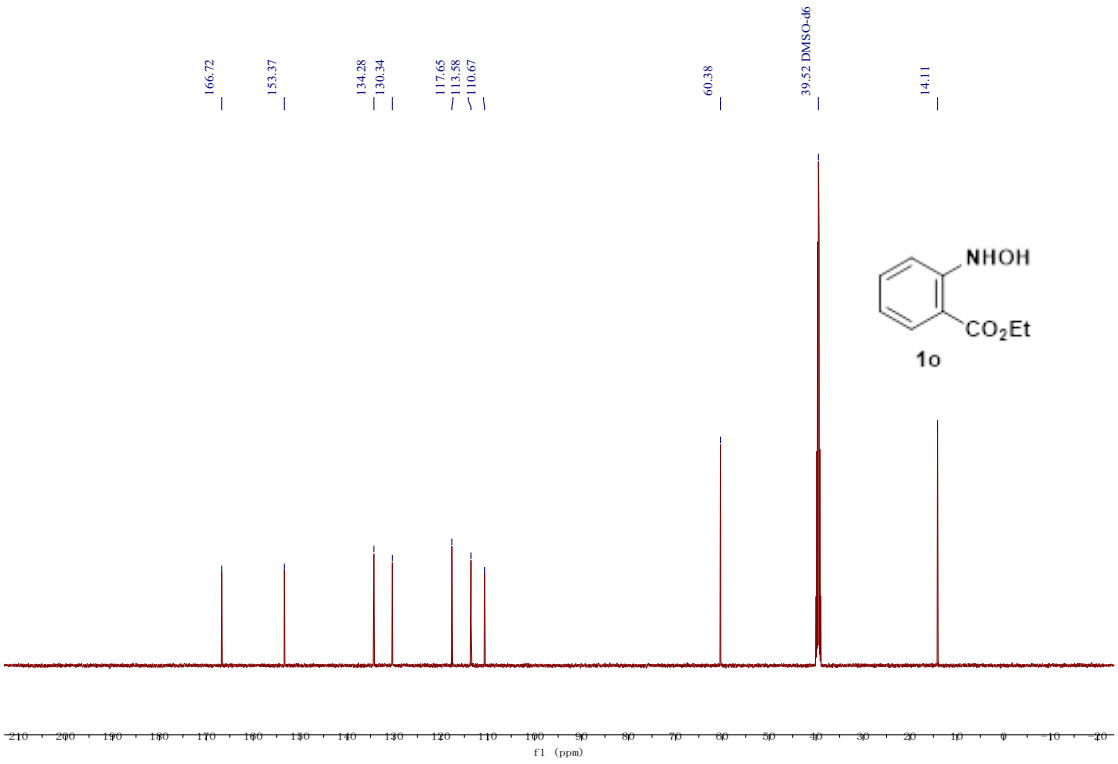
^{13}C NMR of Compound 1n (126 MHz, $CDCl_3$)



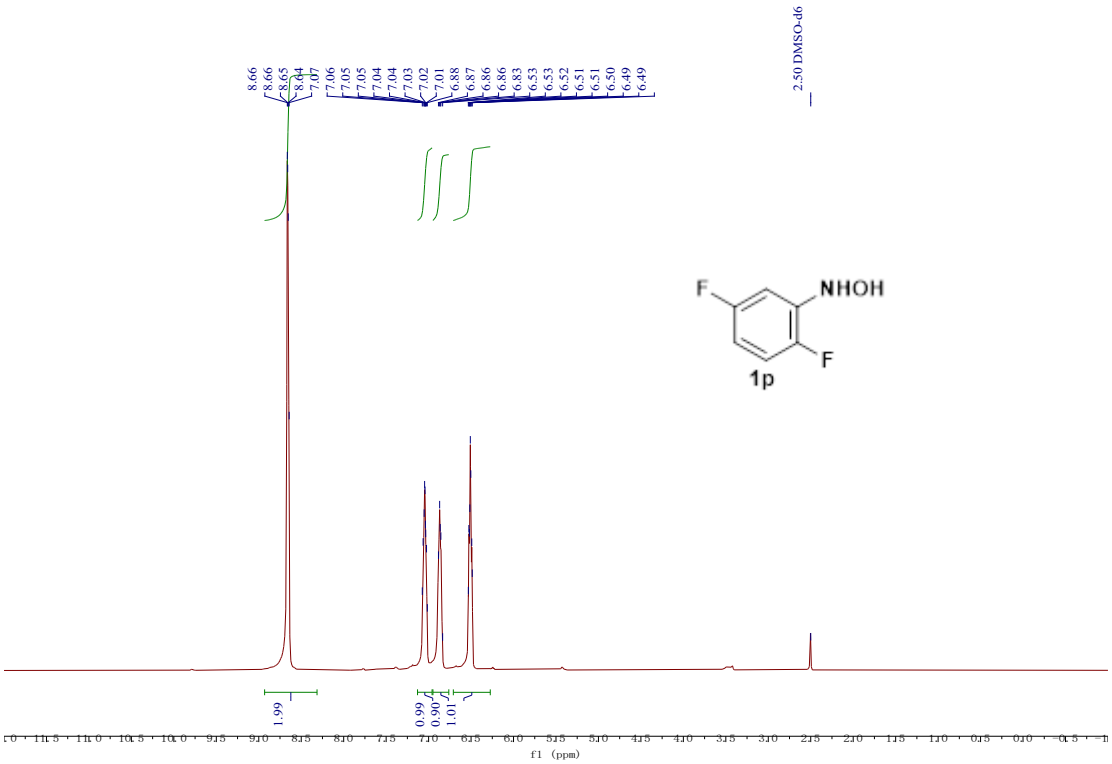
^{1}H NMR of Compound 1o (500 MHz, DMSO-d_6)



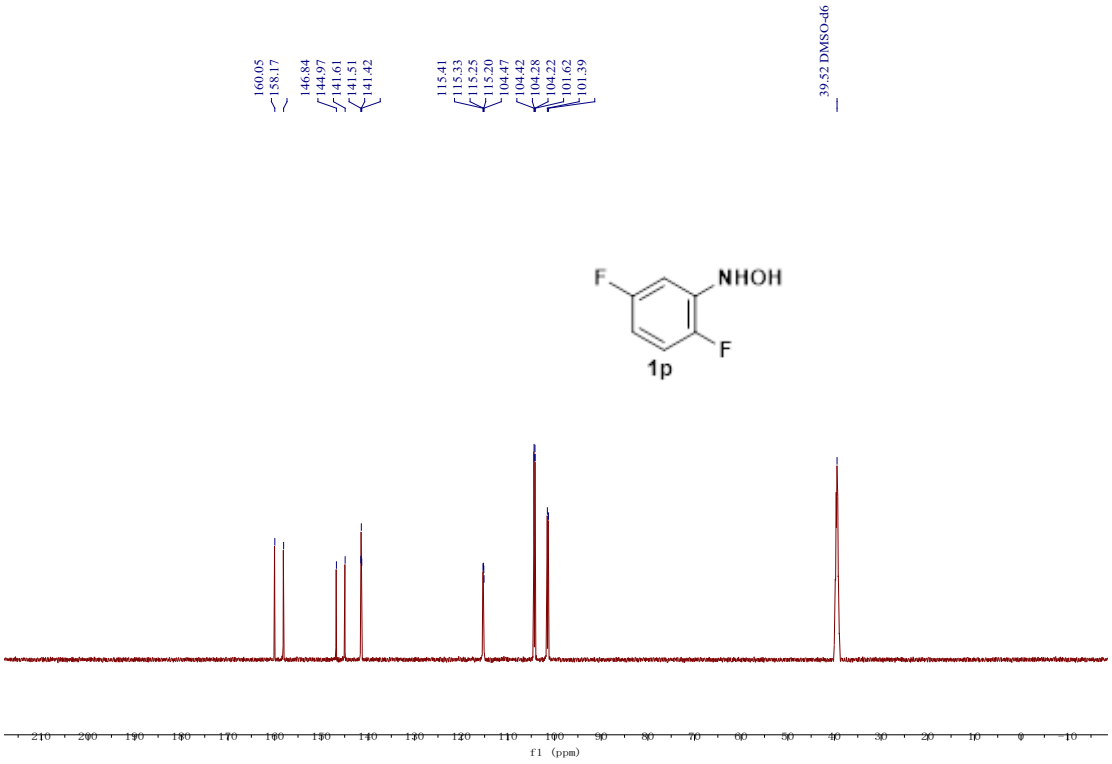
^{13}C NMR of Compound 1o (126 MHz, DMSO-d_6)



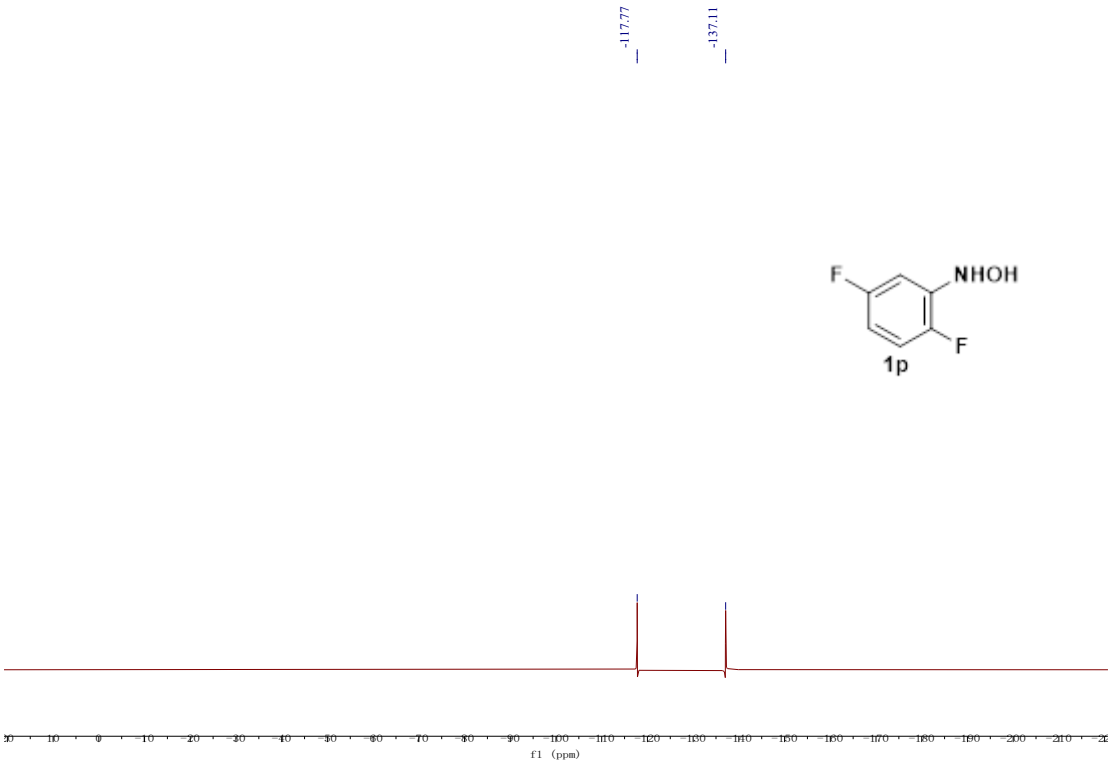
^{1}H NMR of Compound 1p (500 MHz, DMSO-d_6)



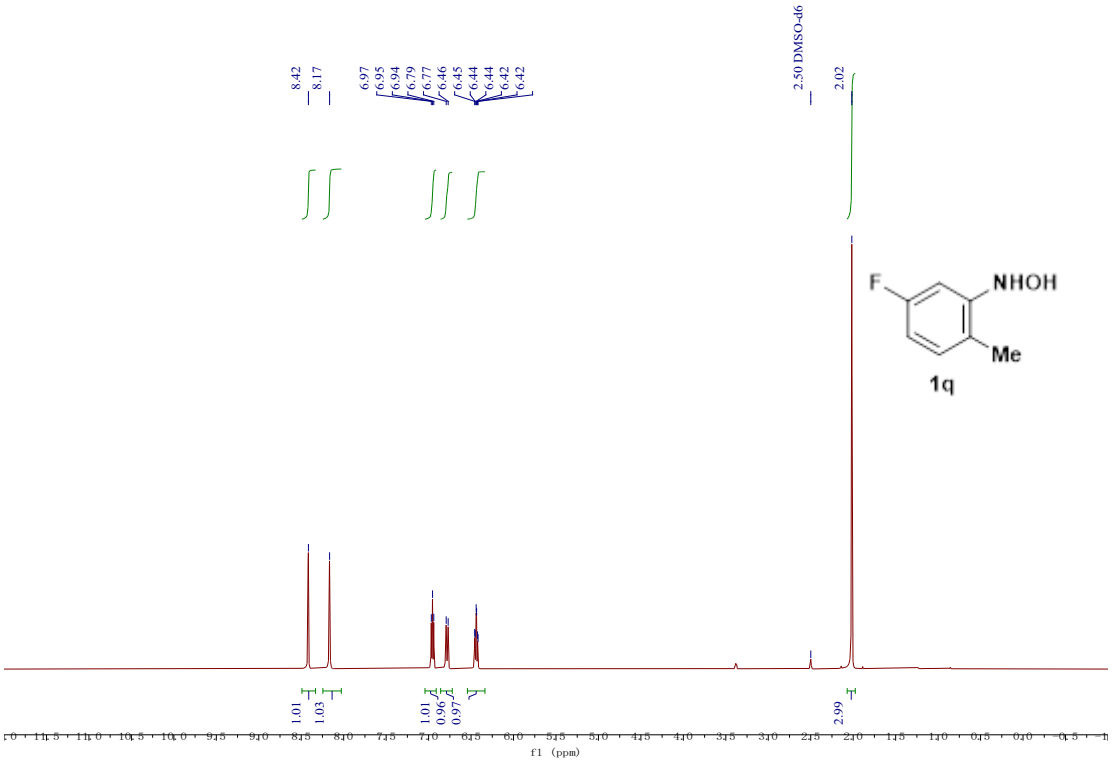
^{13}C NMR of Compound 1p (126 MHz, DMSO-d_6)



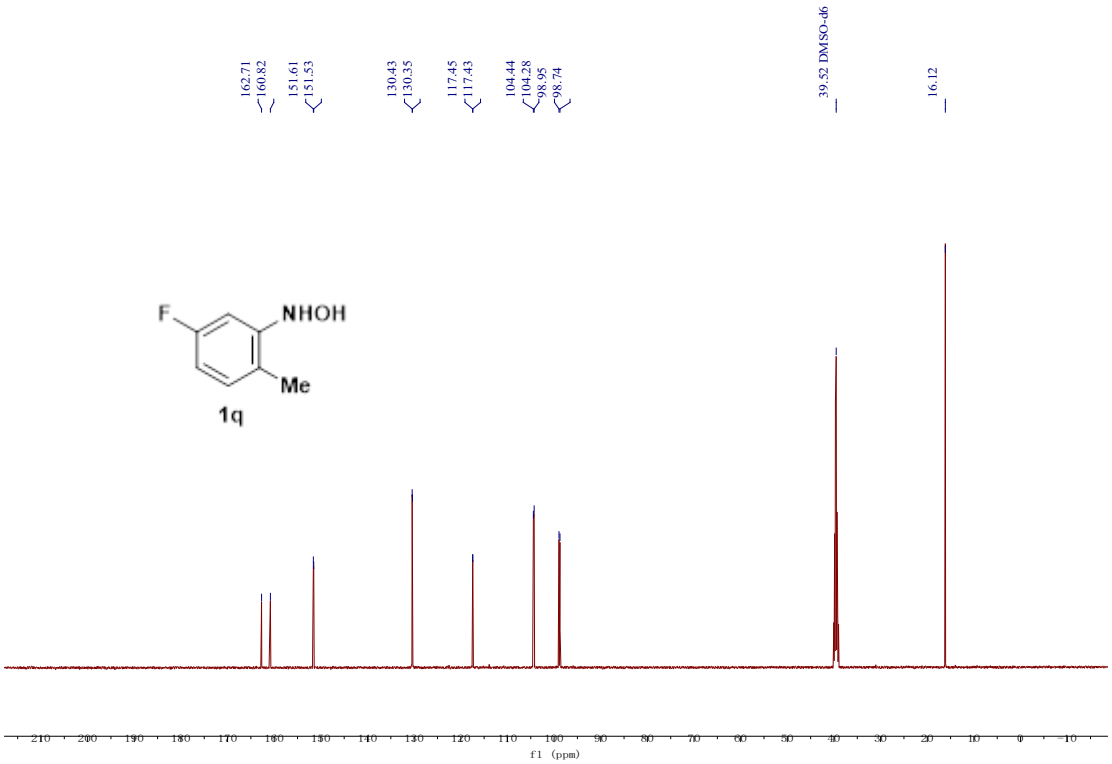
^{19}F NMR of Compound 1p (471 MHz, DMSO-d_6)



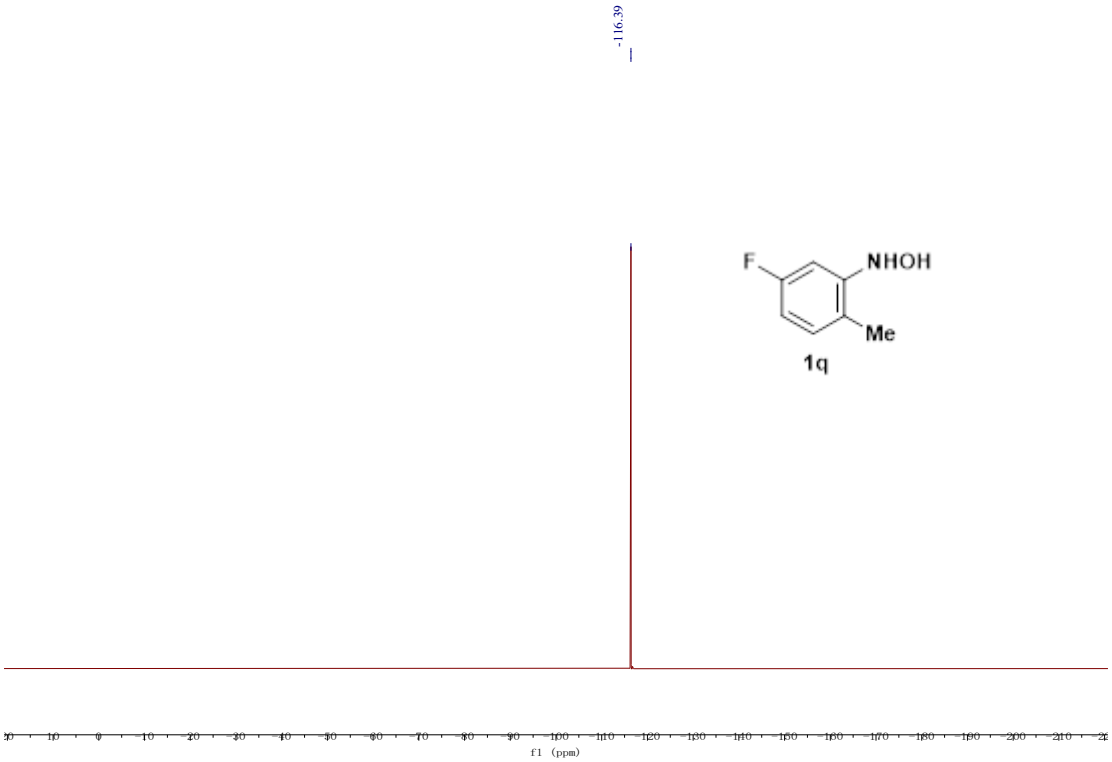
^{1}H NMR of Compound 1q (500 MHz, DMSO-d_6)



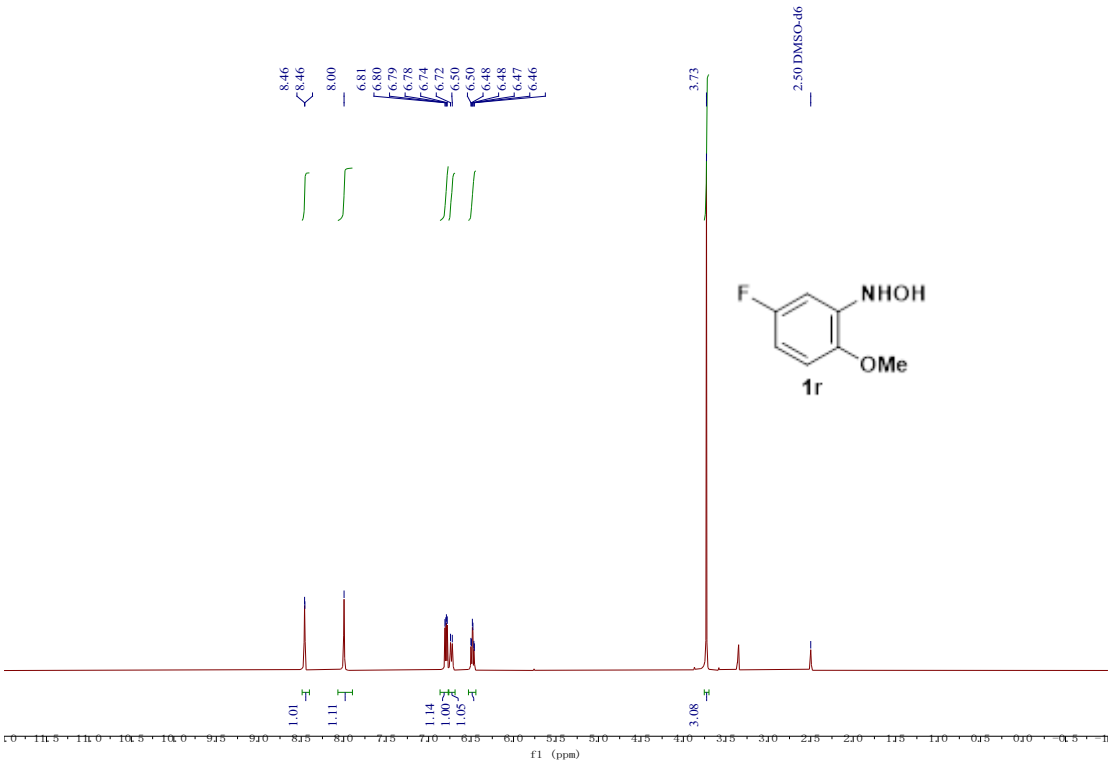
^{13}C NMR of Compound 1q (126 MHz, DMSO-d_6)



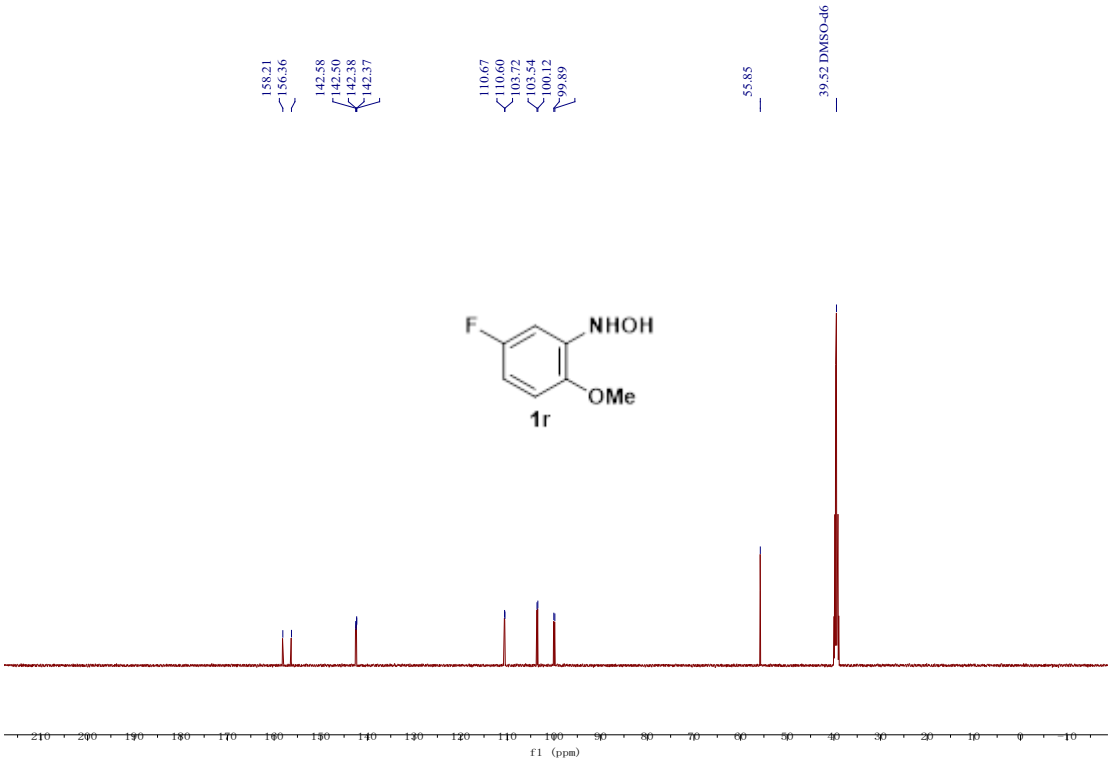
^{19}F NMR of Compound 1q (471 MHz, DMSO-d_6)



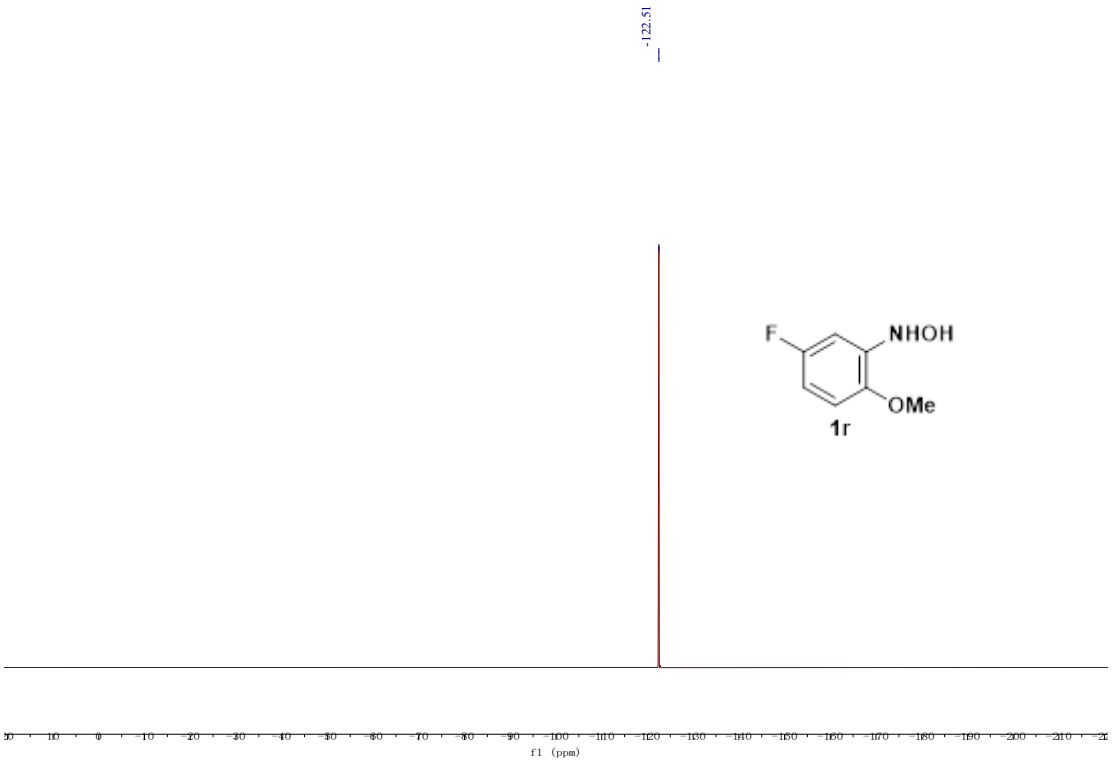
^{1}H NMR of Compound 1r (500 MHz, DMSO-d_6)



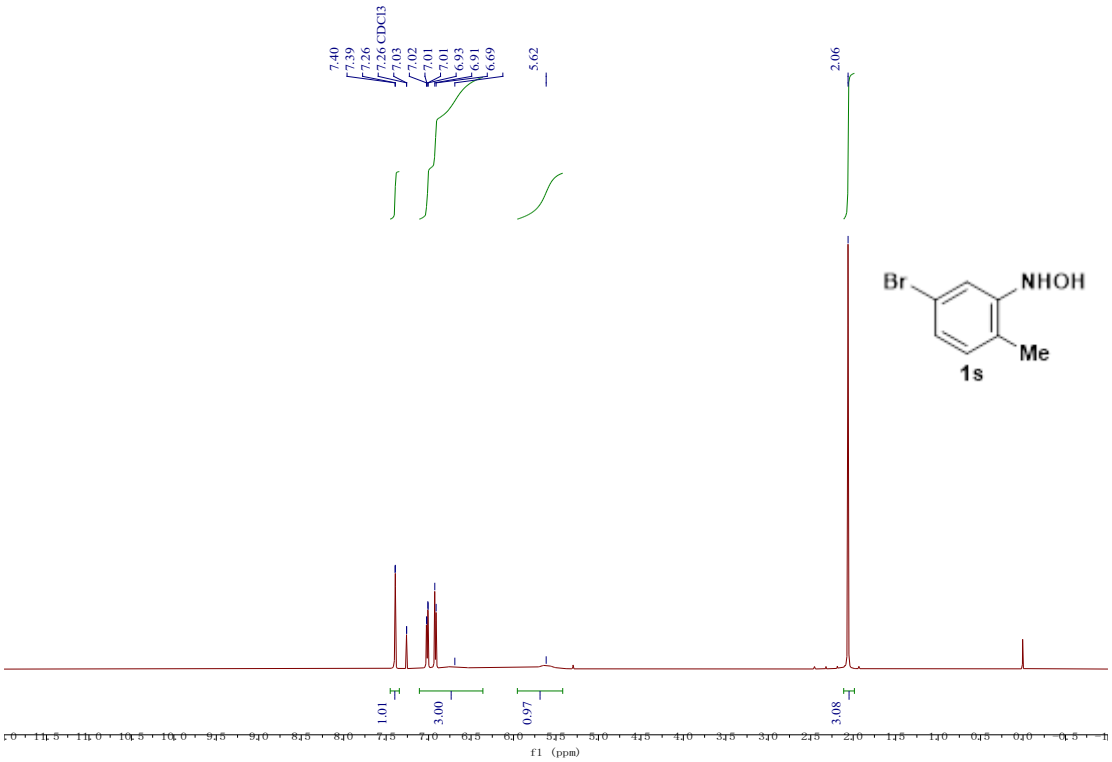
^{13}C NMR of Compound 1r (126 MHz, DMSO-d_6)



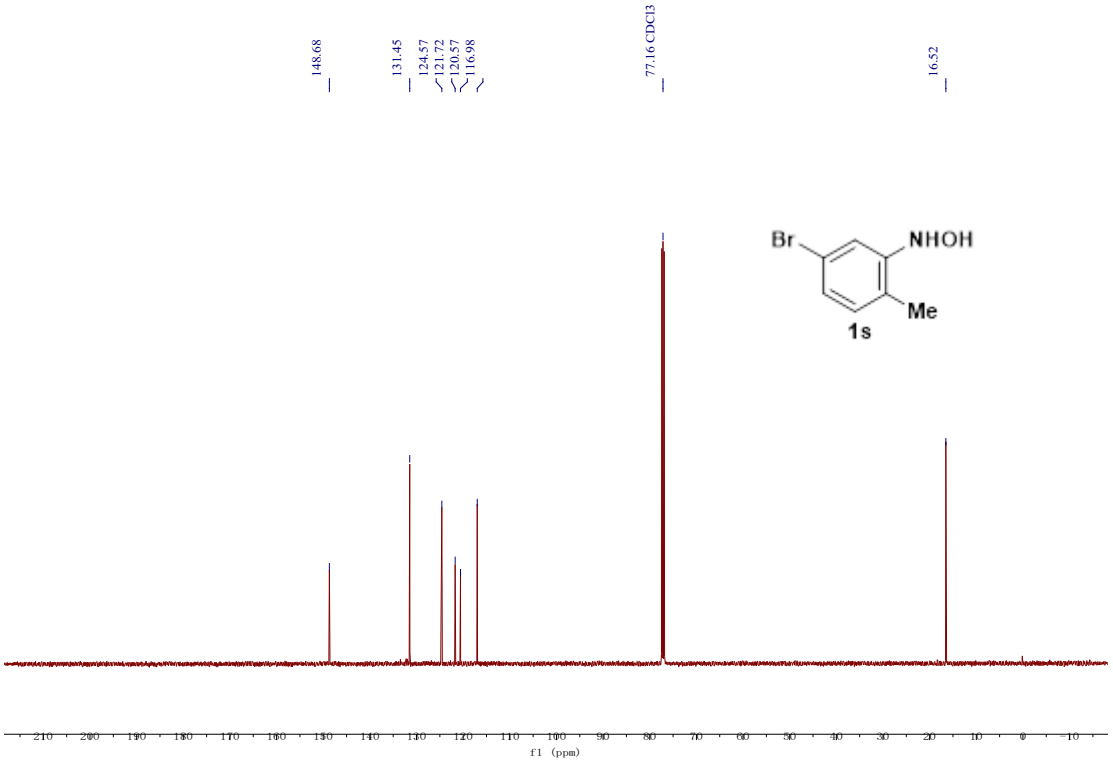
^{19}F NMR of Compound 1r (471 MHz, DMSO-d_6)



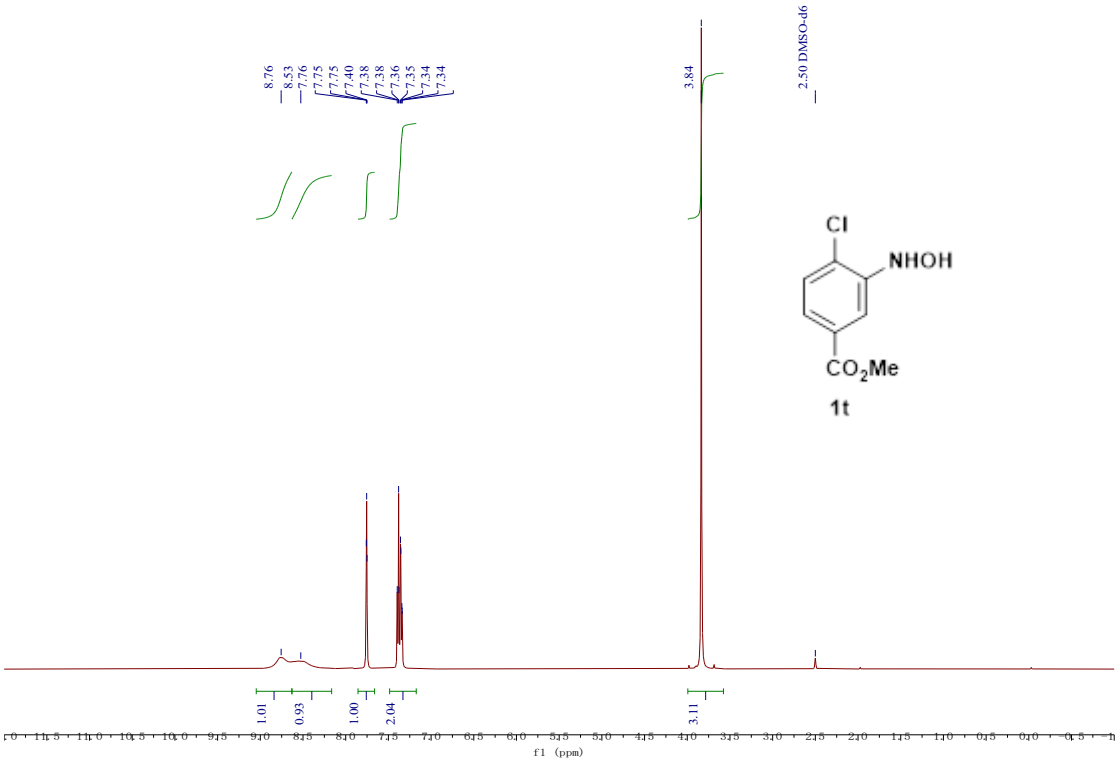
^{1}H NMR of Compound 1s (500 MHz, $CDCl_3$)



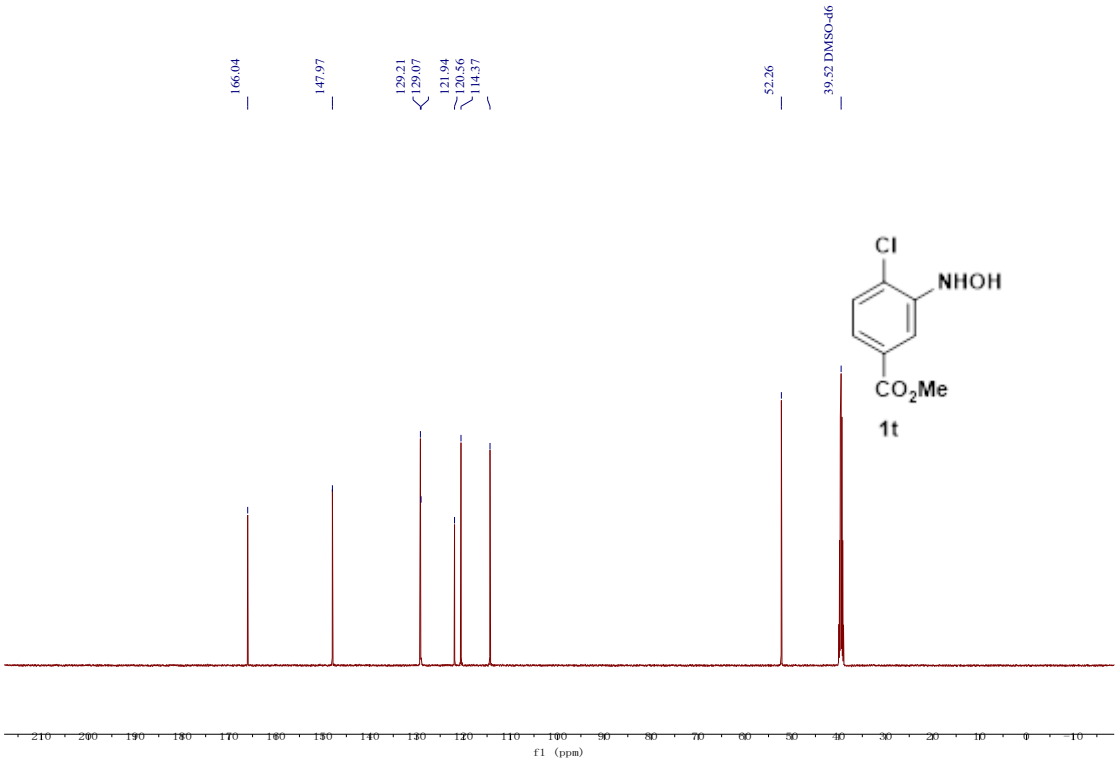
^{13}C NMR of Compound 1s (126 MHz, $CDCl_3$)



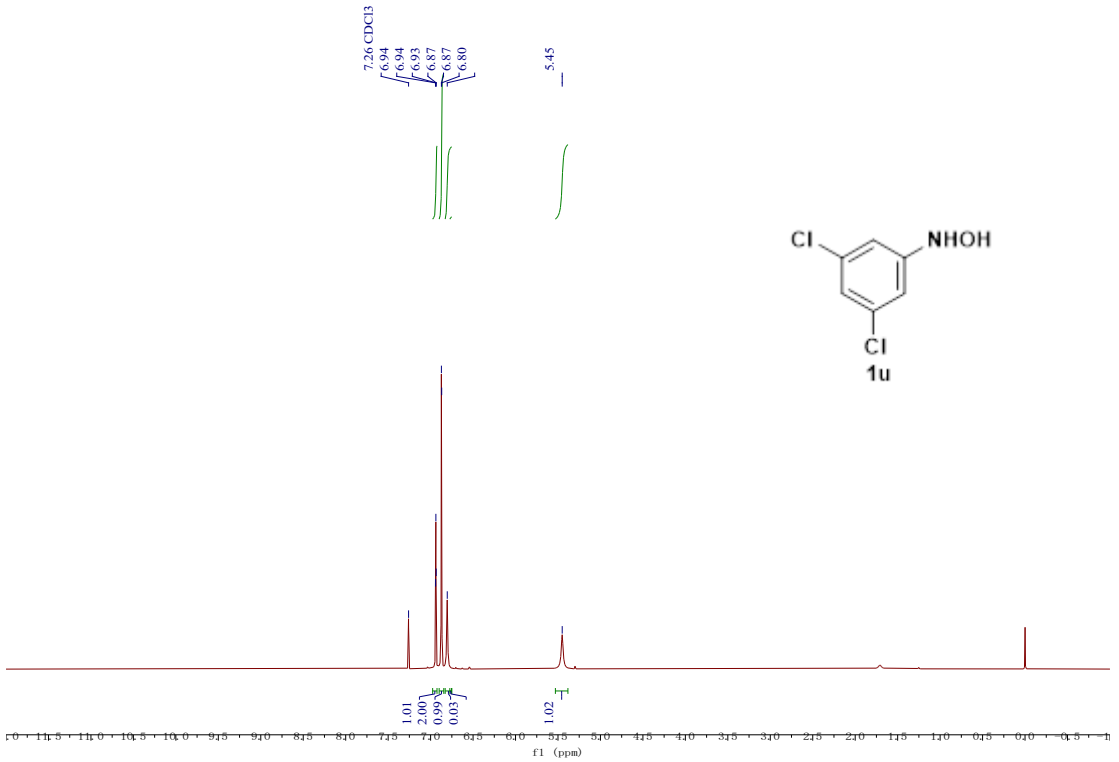
^{1}H NMR of Compound 1t (500 MHz, DMSO-d_6)



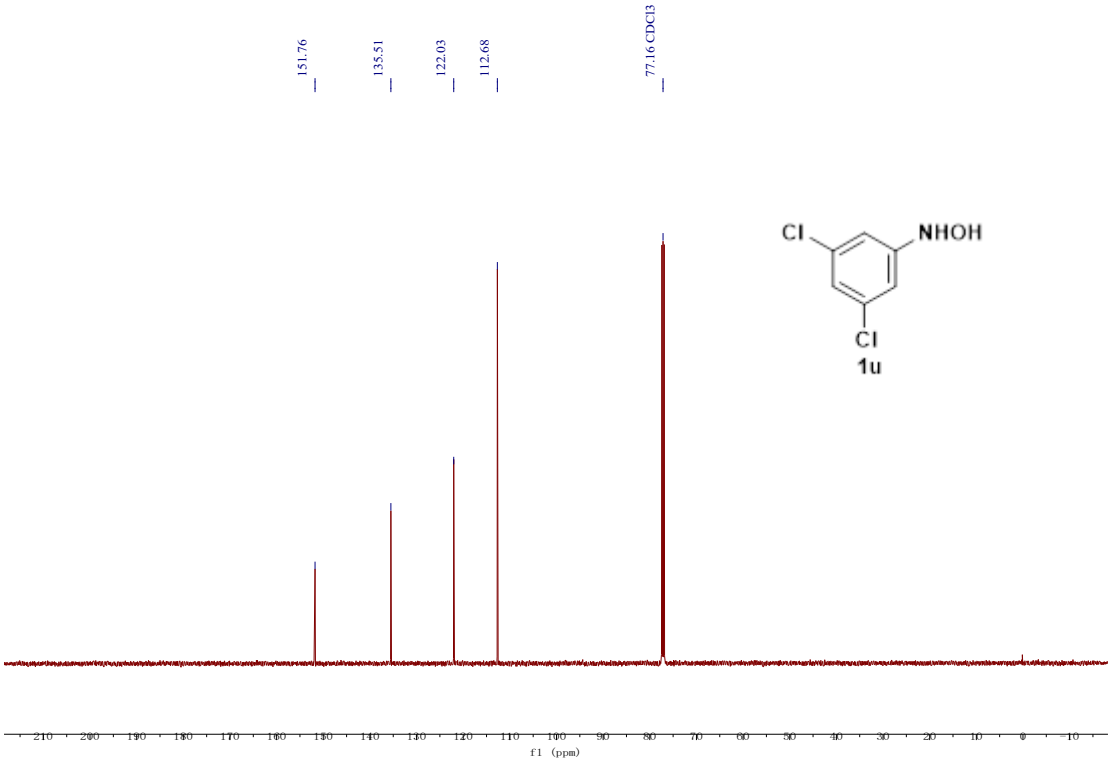
^{13}C NMR of Compound 1t (126 MHz, DMSO-*d*$_6$)



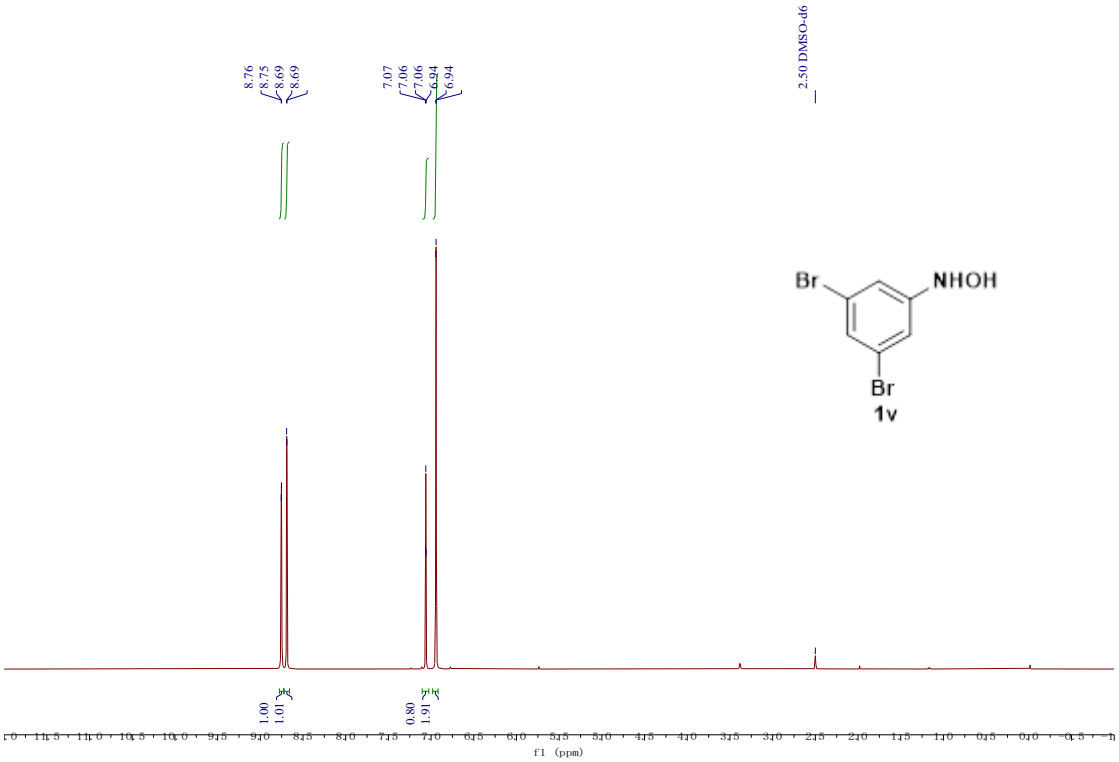
^{1}H NMR of Compound 1u (500 MHz, $CDCl_3$)



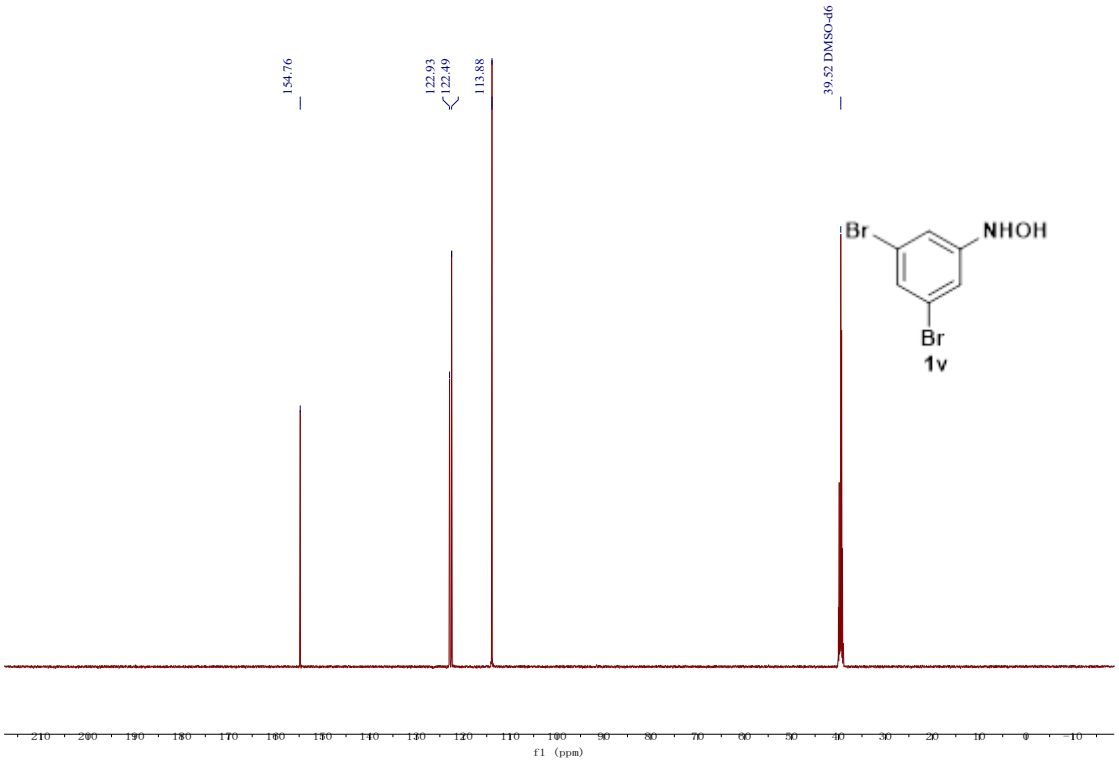
^{13}C NMR of Compound 1u (126 MHz, $CDCl_3$)



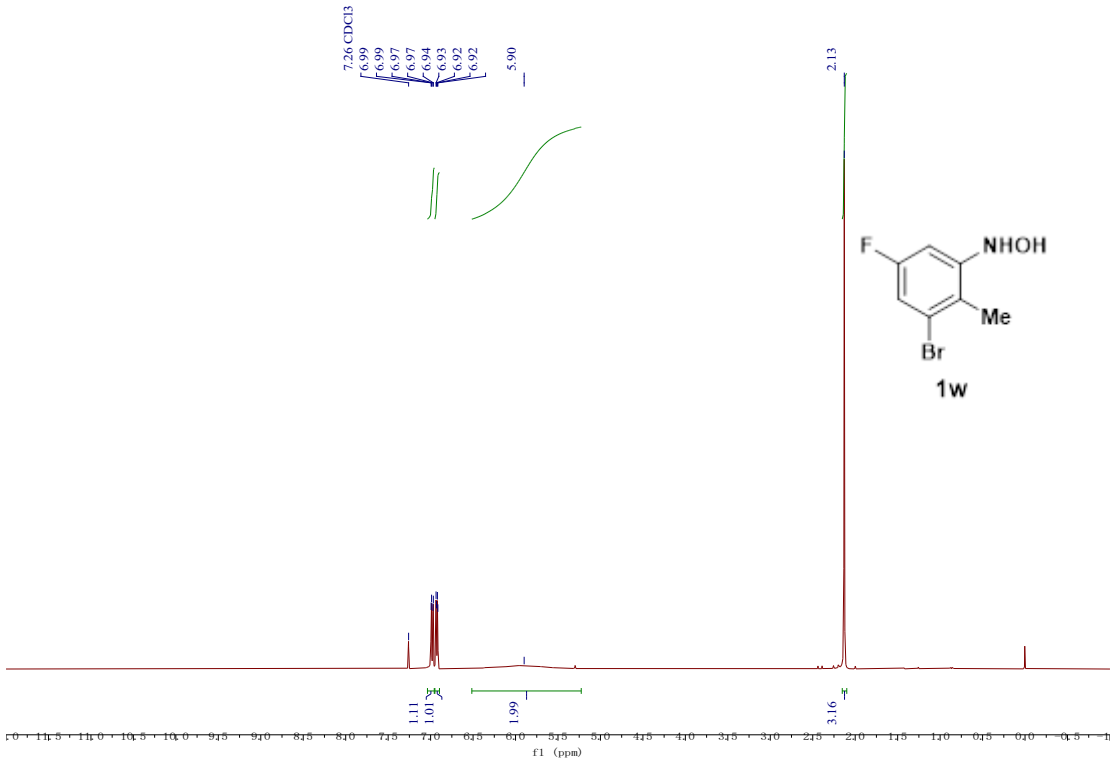
^{1}H NMR of Compound 1v (500 MHz, DMSO-d_6)



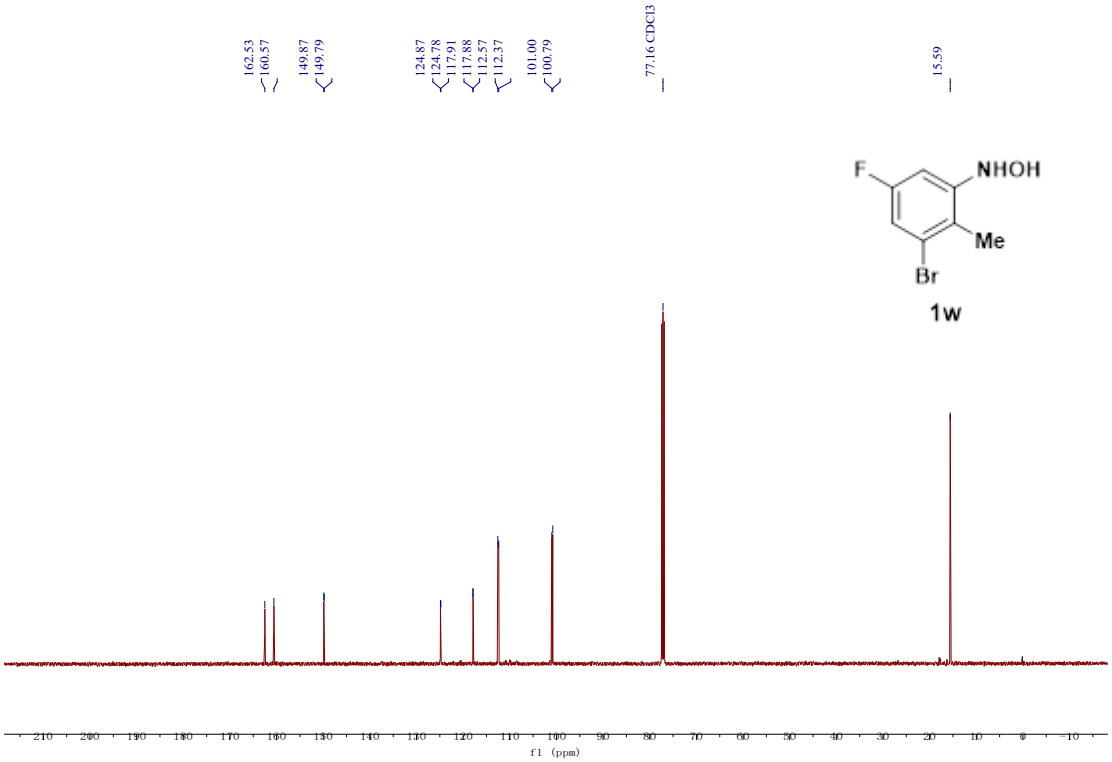
^{13}C NMR of Compound 1v (126 MHz, DMSO-*d*$_6$)



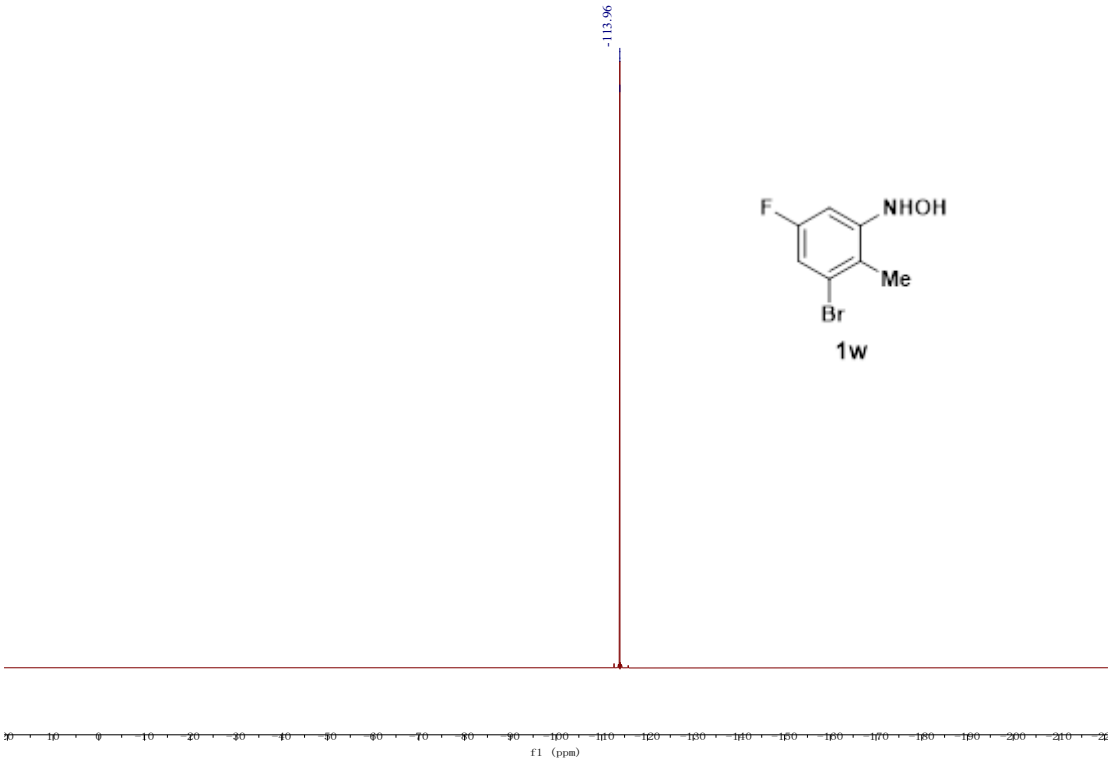
^{1}H NMR of Compound 1w (500 MHz, $CDCl_3$)



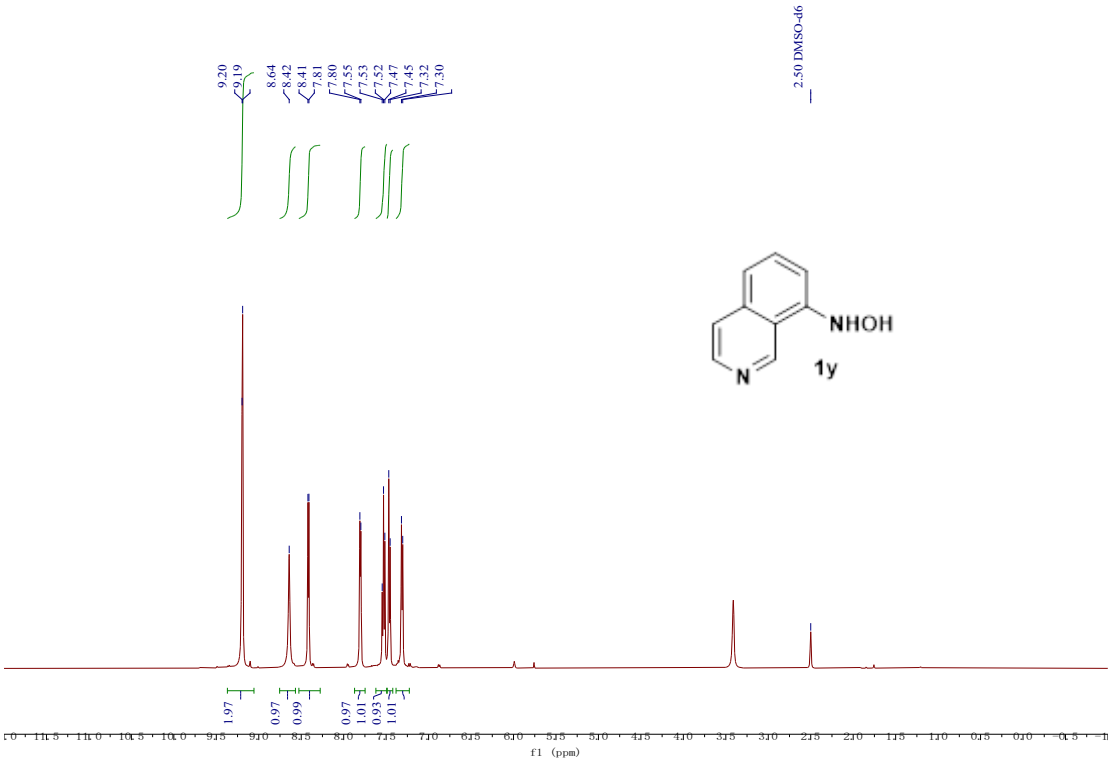
^{13}C NMR of Compound 1w (126 MHz, $CDCl_3$)



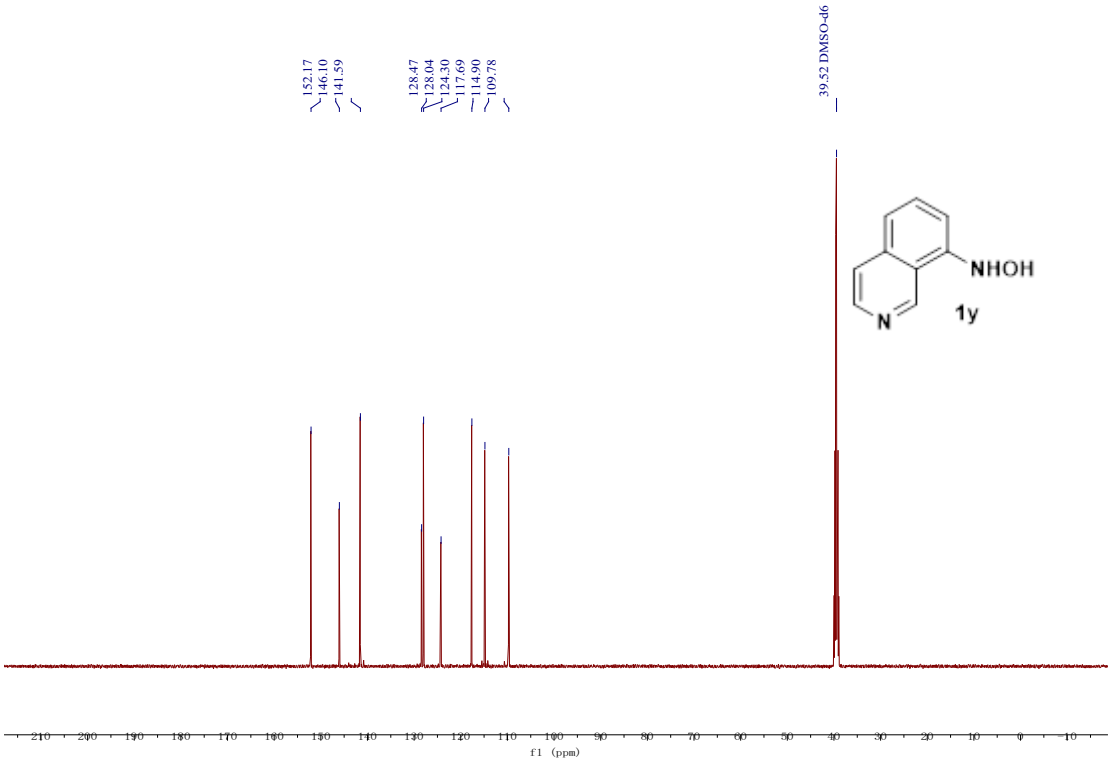
^{19}F NMR of Compound 1w (471 MHz, $CDCl_3$)



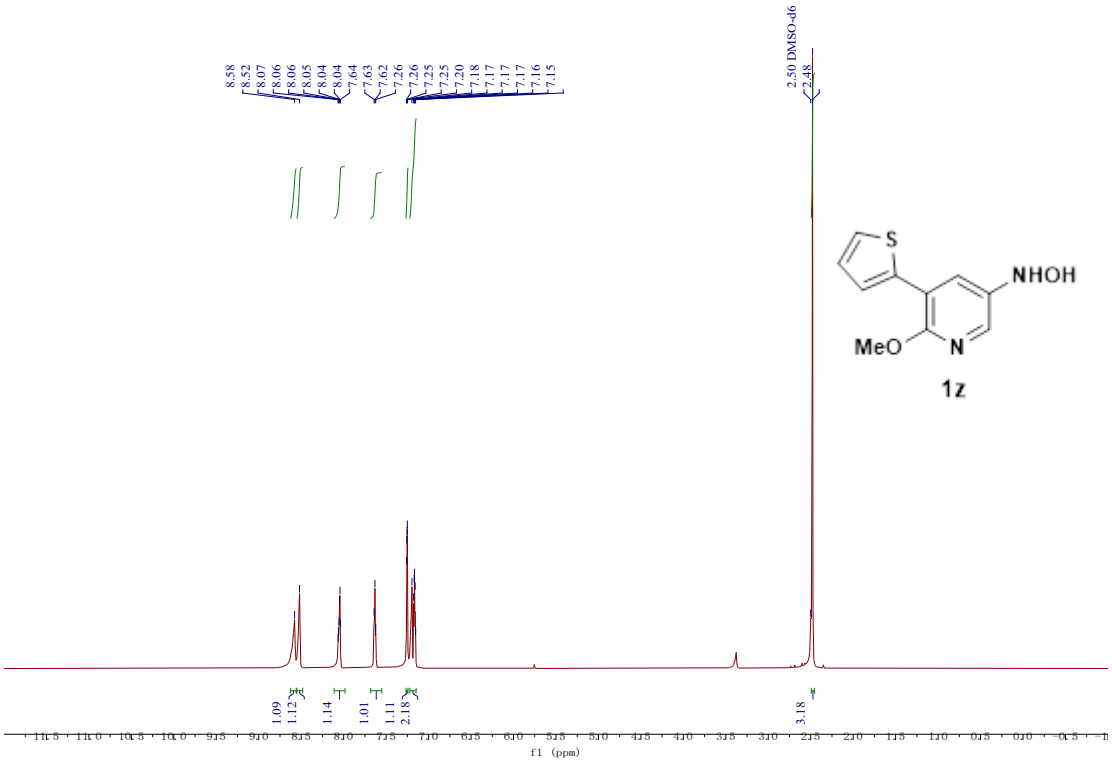
^{1}H NMR of Compound 1y (500 MHz, DMSO-d_6)



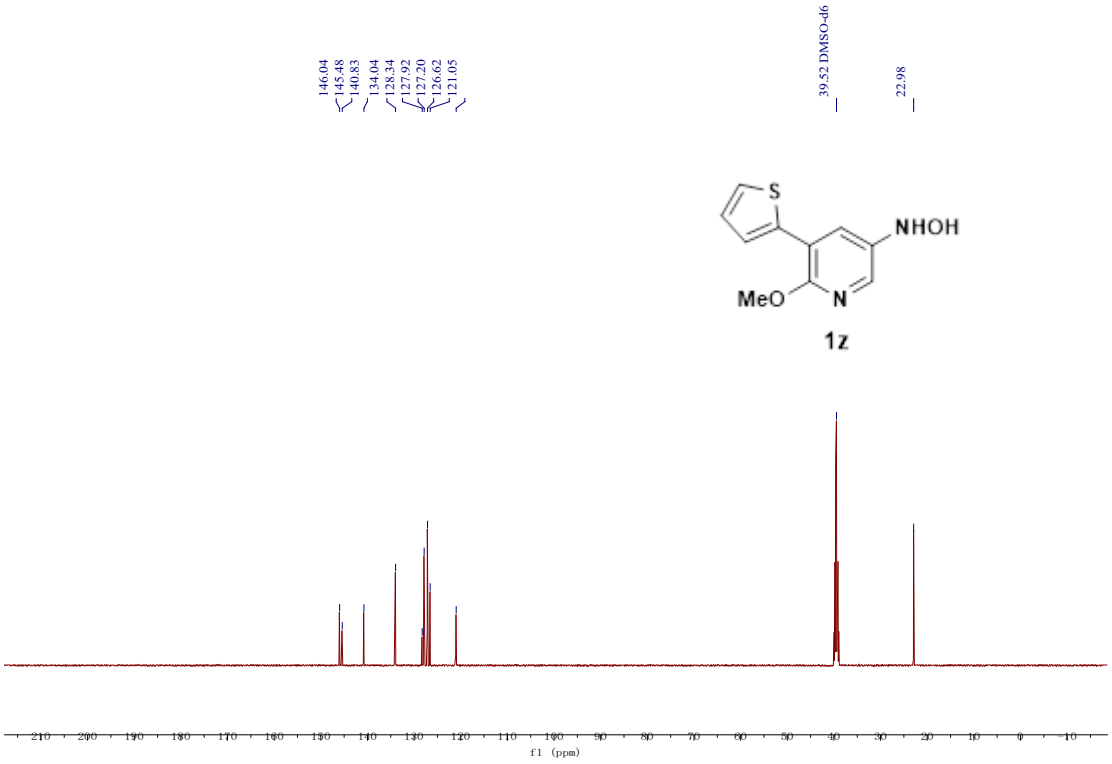
^{13}C NMR of Compound 1y (126 MHz, DMSO-d_6)



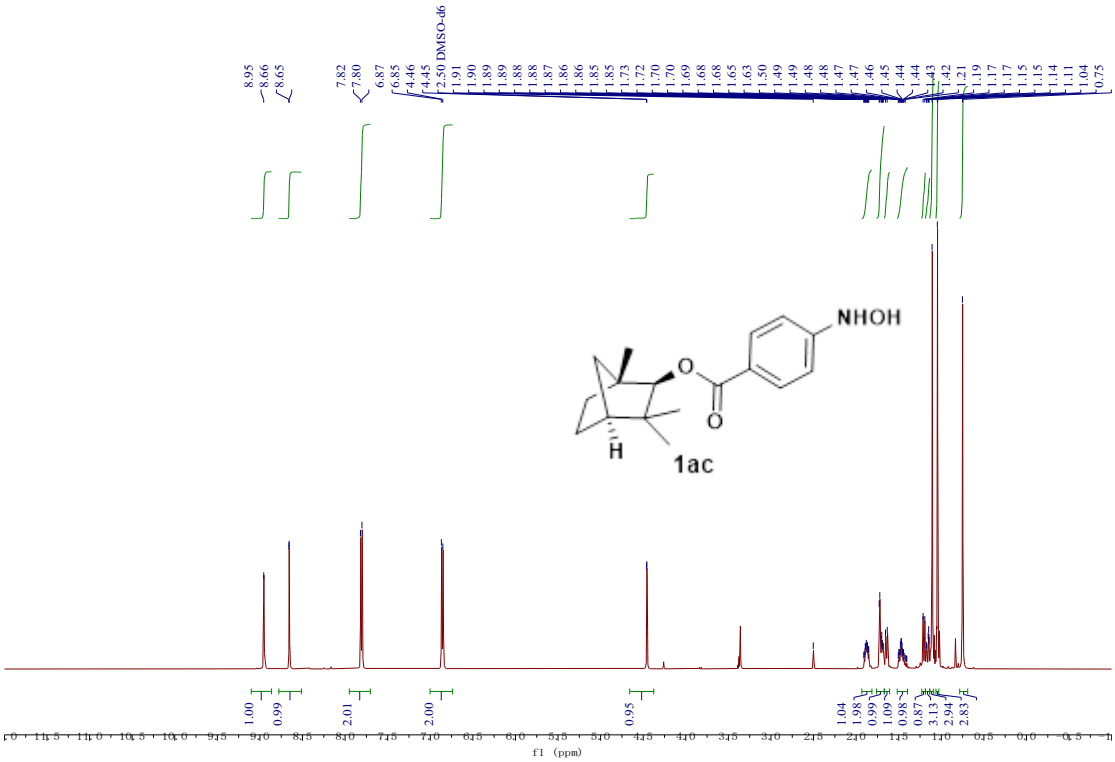
^{1}H NMR of Compound 1z (500 MHz, DMSO-d_6)



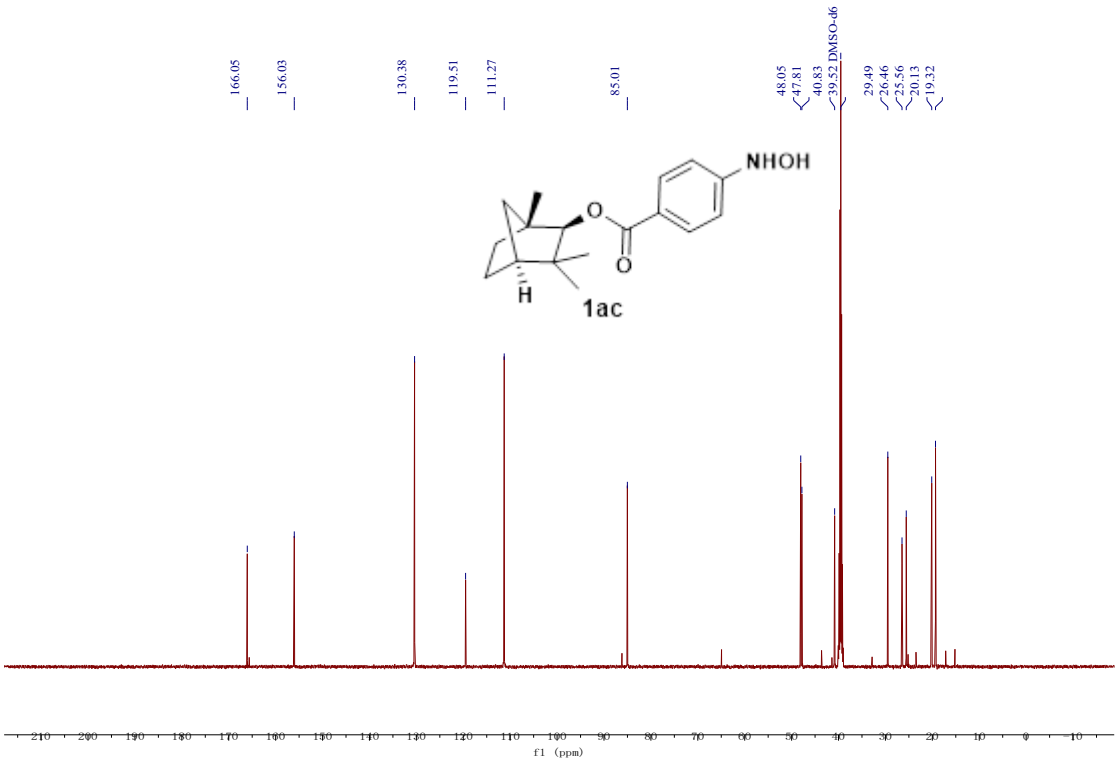
^{13}C NMR of Compound 1z (126 MHz, DMSO-d_6)



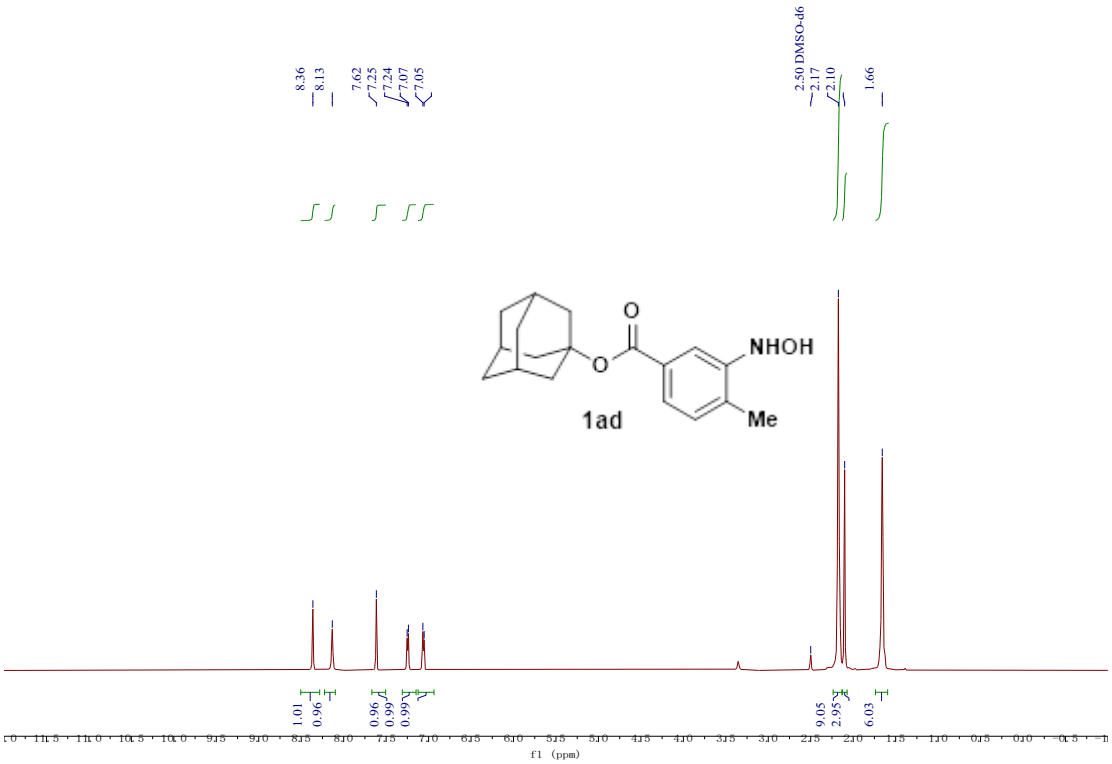
^{1}H NMR of Compound 1ac (500 MHz, DMSO-d_6)



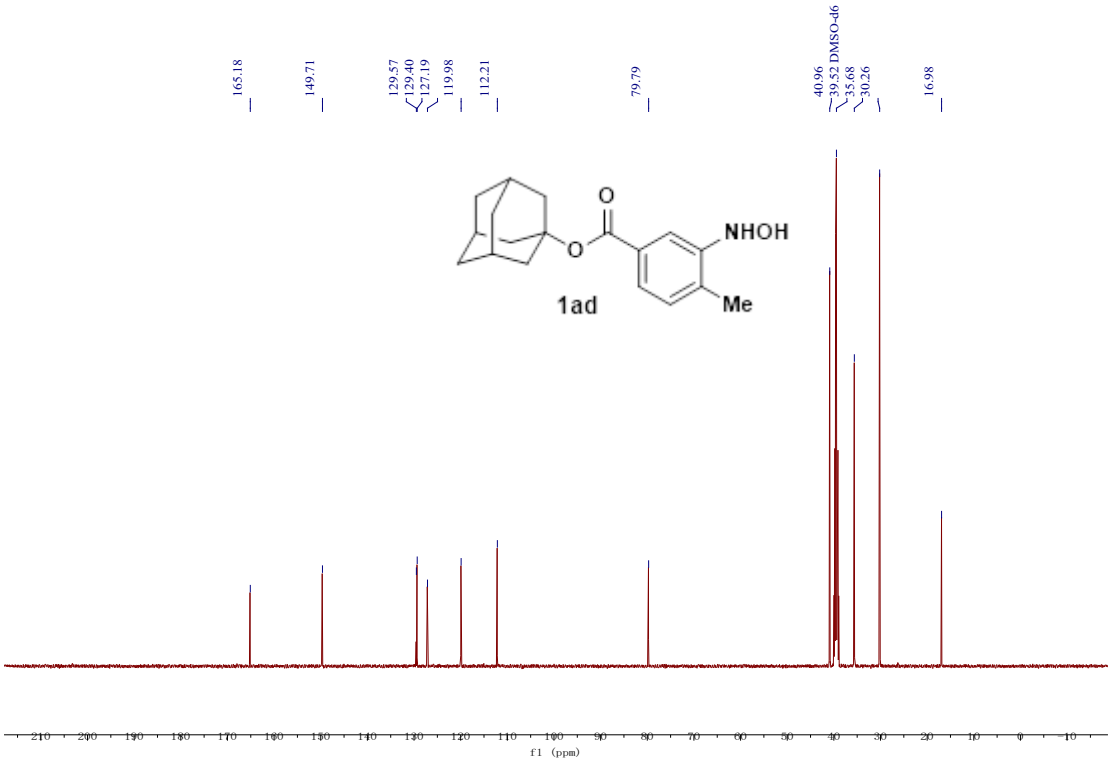
^{13}C NMR of Compound 1ac (126 MHz, DMSO-d_6)



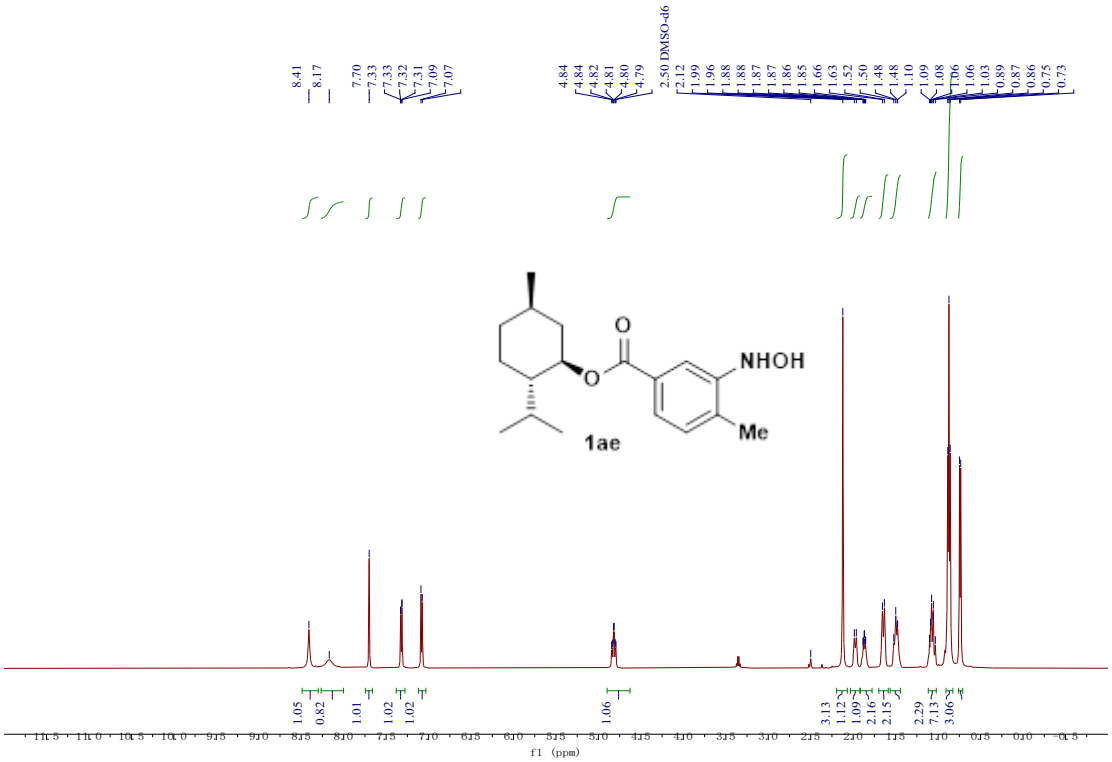
^{1}H NMR of Compound 1ad (500 MHz, DMSO-d_6)



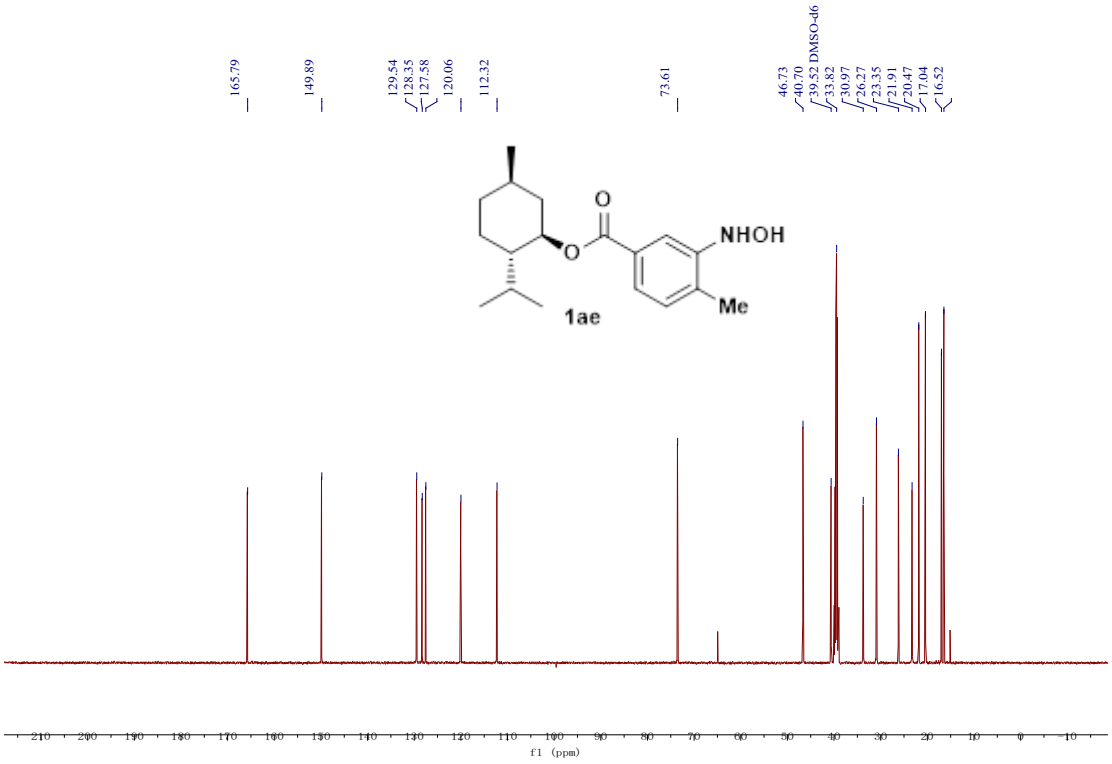
^{13}C NMR of Compound 1ad (126 MHz, DMSO-d_6)



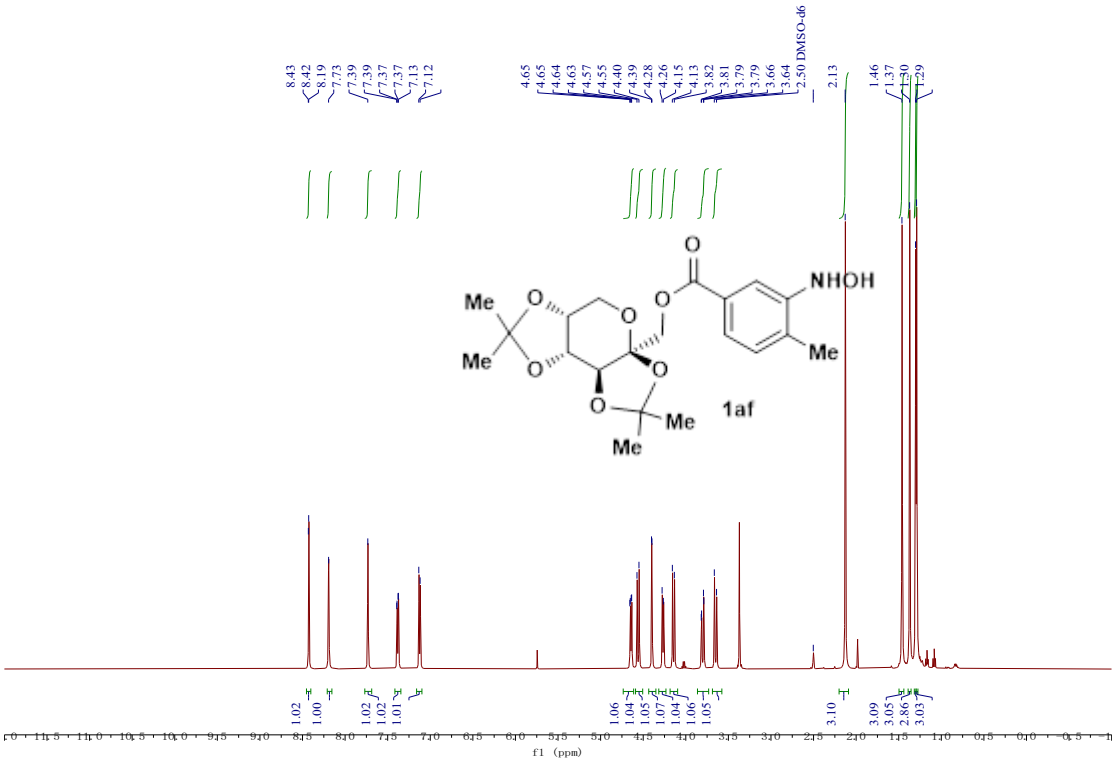
^{1}H NMR of Compound 1ae (500 MHz, DMSO-d_6)



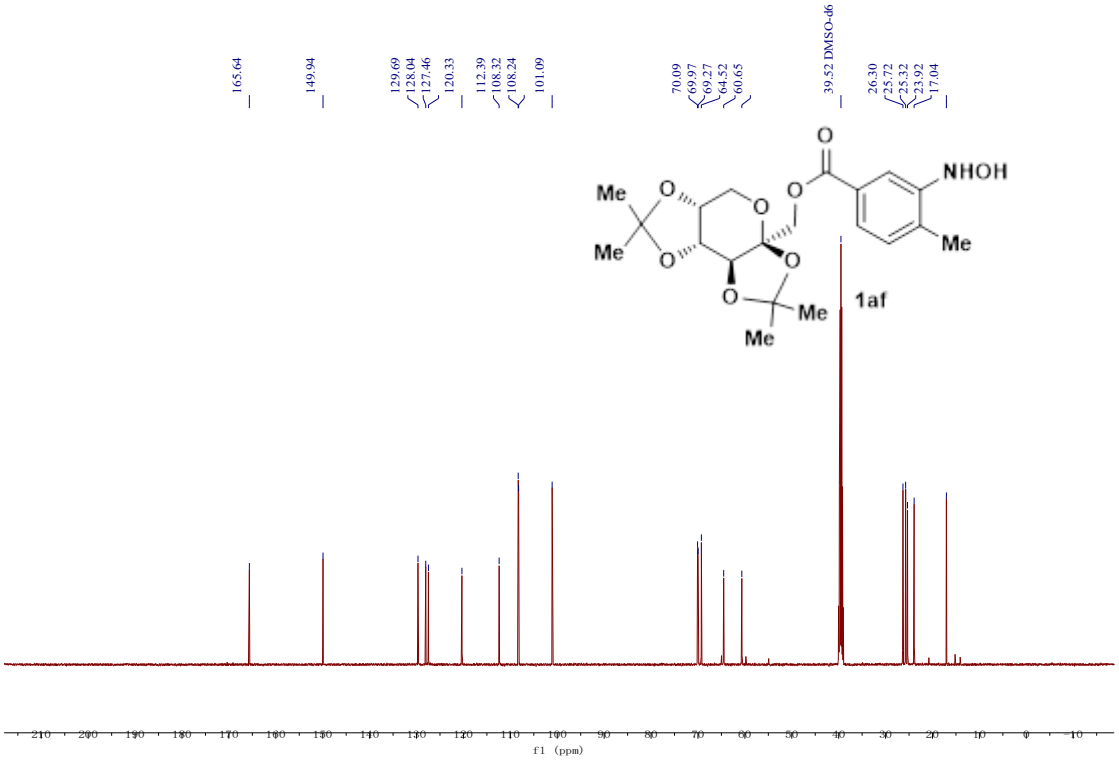
^{13}C NMR of Compound 1ae (126 MHz, DMSO-d_6)



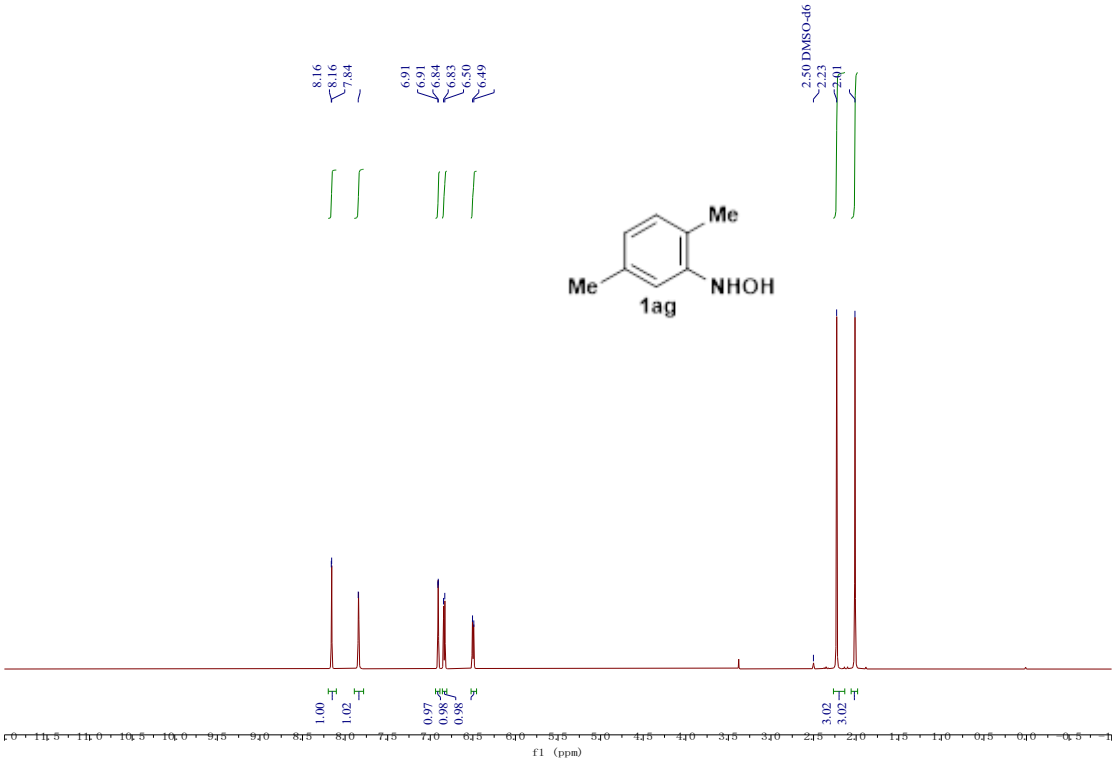
^{1}H NMR of Compound 1af (500 MHz, DMSO-d_6)



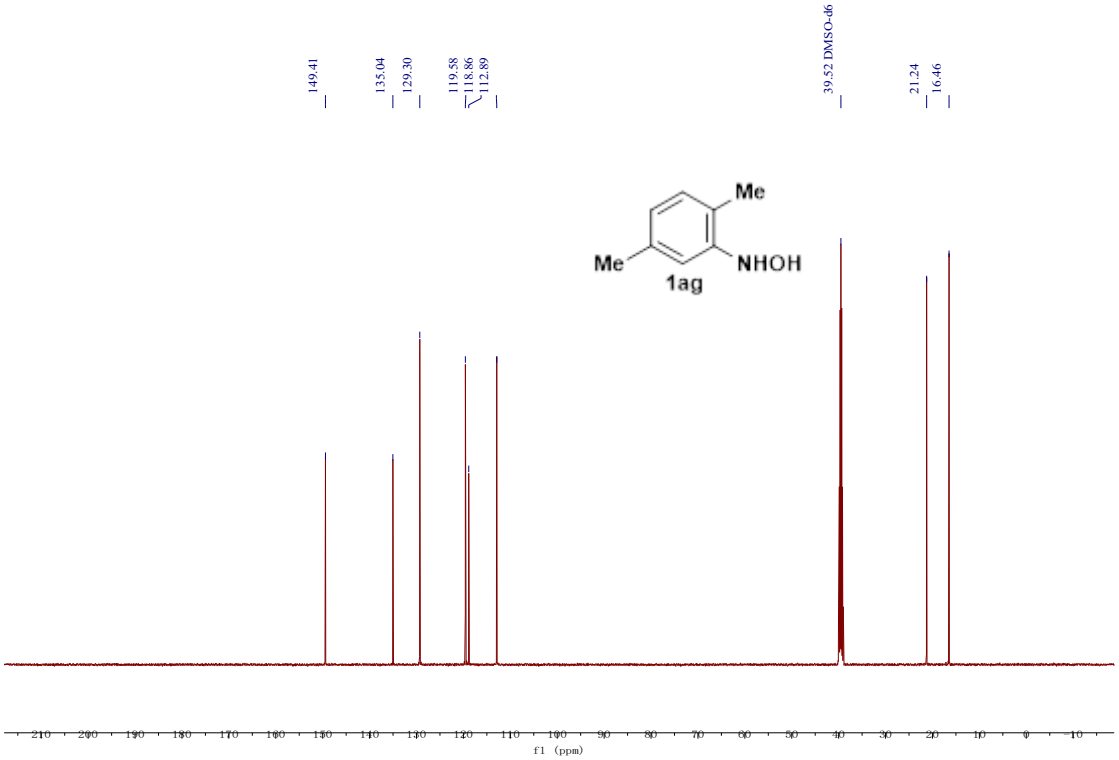
^{13}C NMR of Compound 1af (126 MHz, DMSO-d_6)



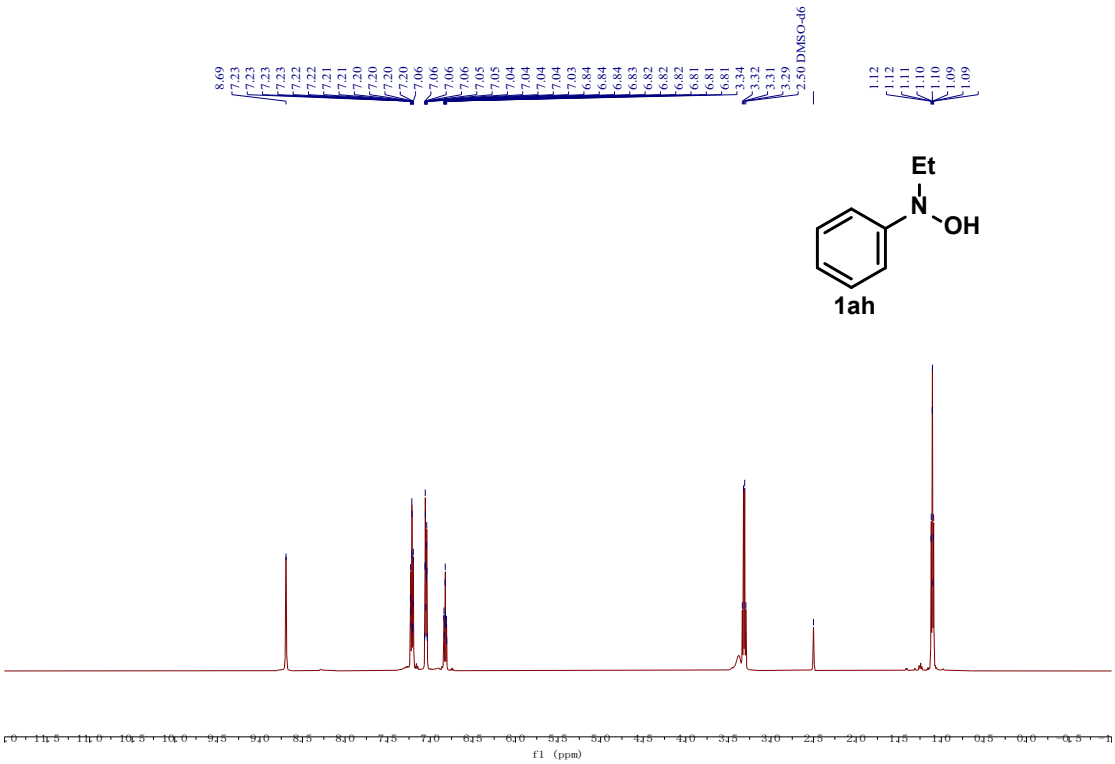
^{1}H NMR of Compound 1ag (500 MHz, DMSO-d_6)



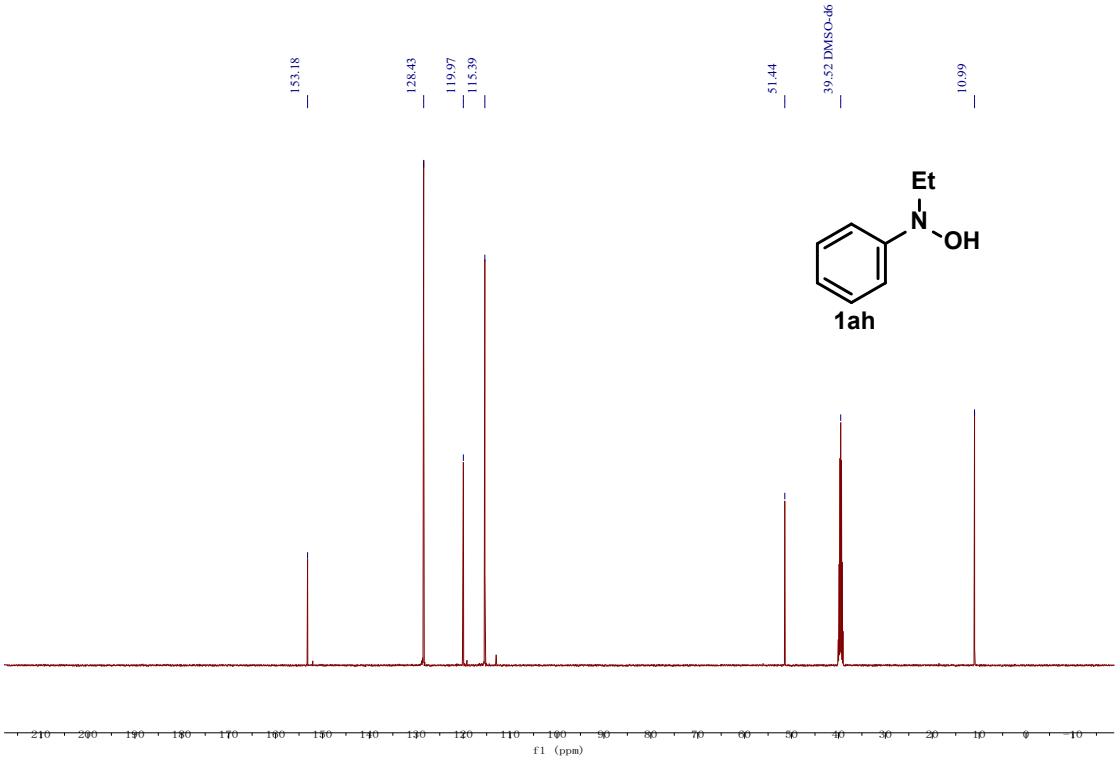
^{13}C NMR of Compound 1ag (126 MHz, DMSO-d_6)



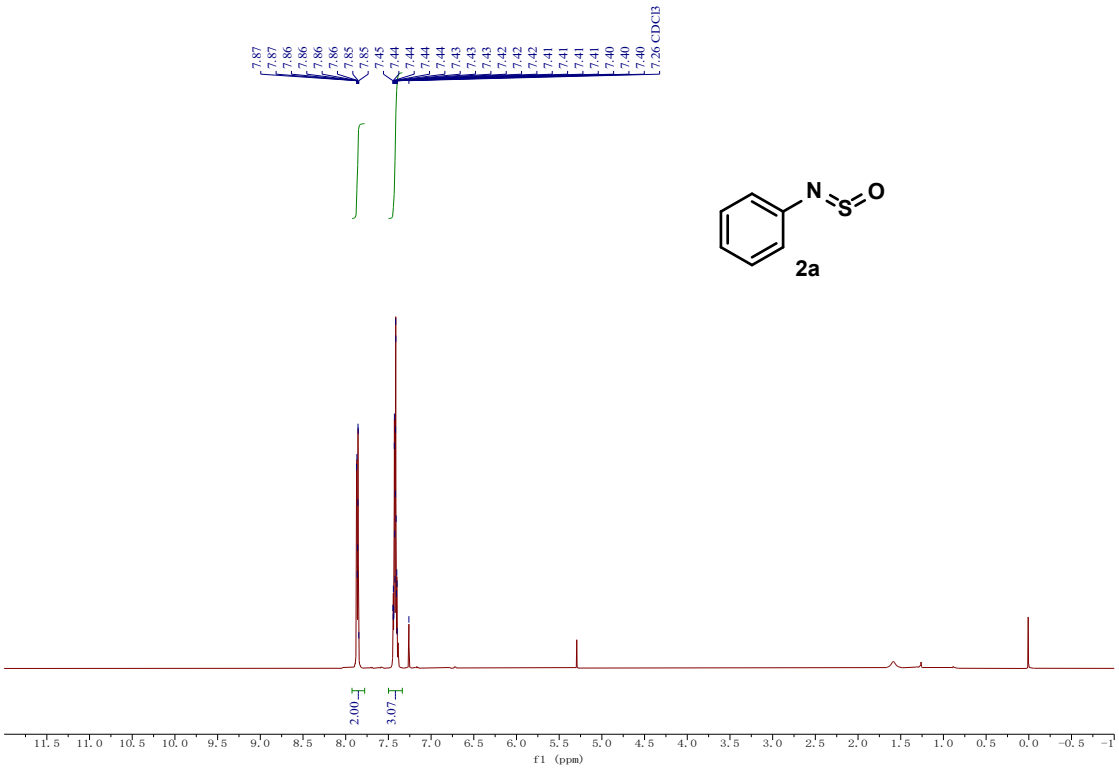
^{1}H NMR of Compound 1ah (500 MHz, DMSO-d_6)



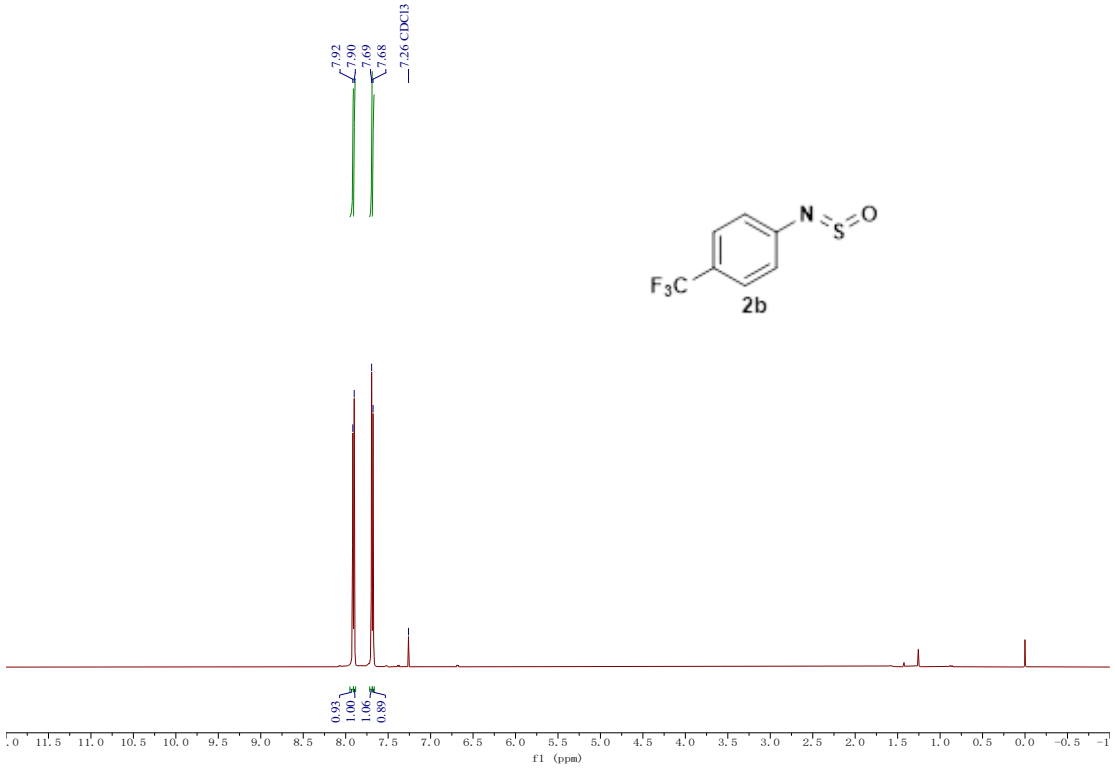
^{13}C NMR of Compound 1ag (126 MHz, DMSO-d_6)



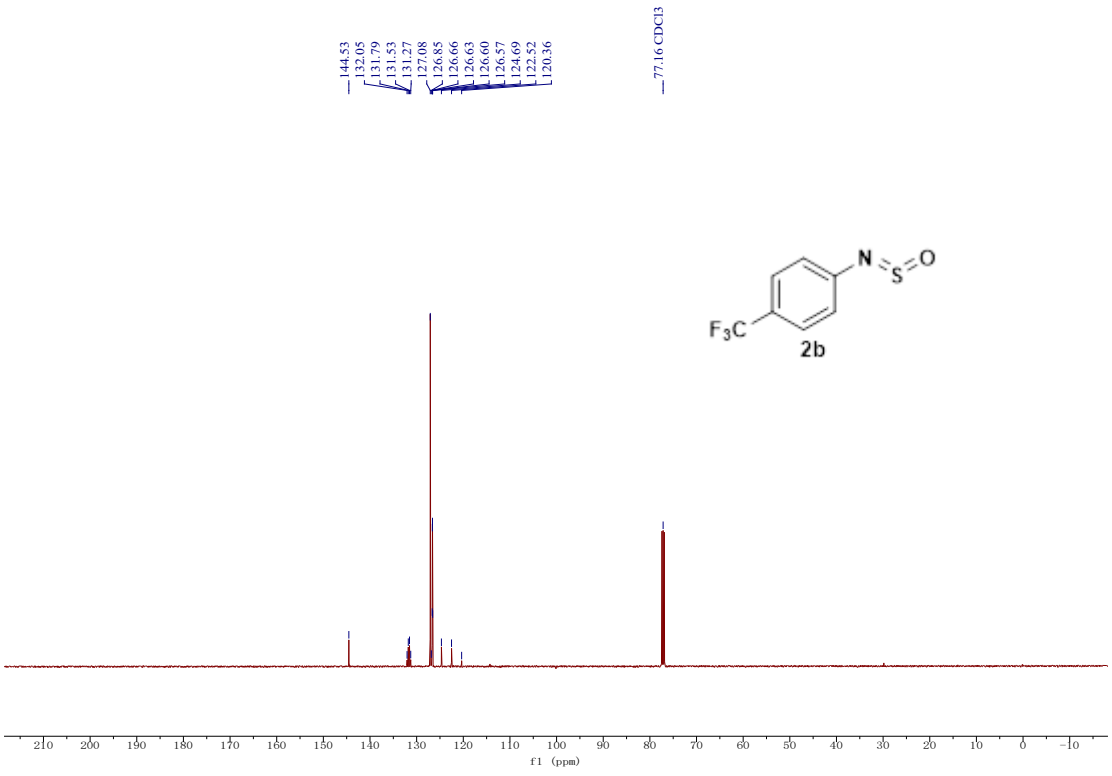
^{1}H NMR of Compound 2a (500 MHz, $CDCl_3$)



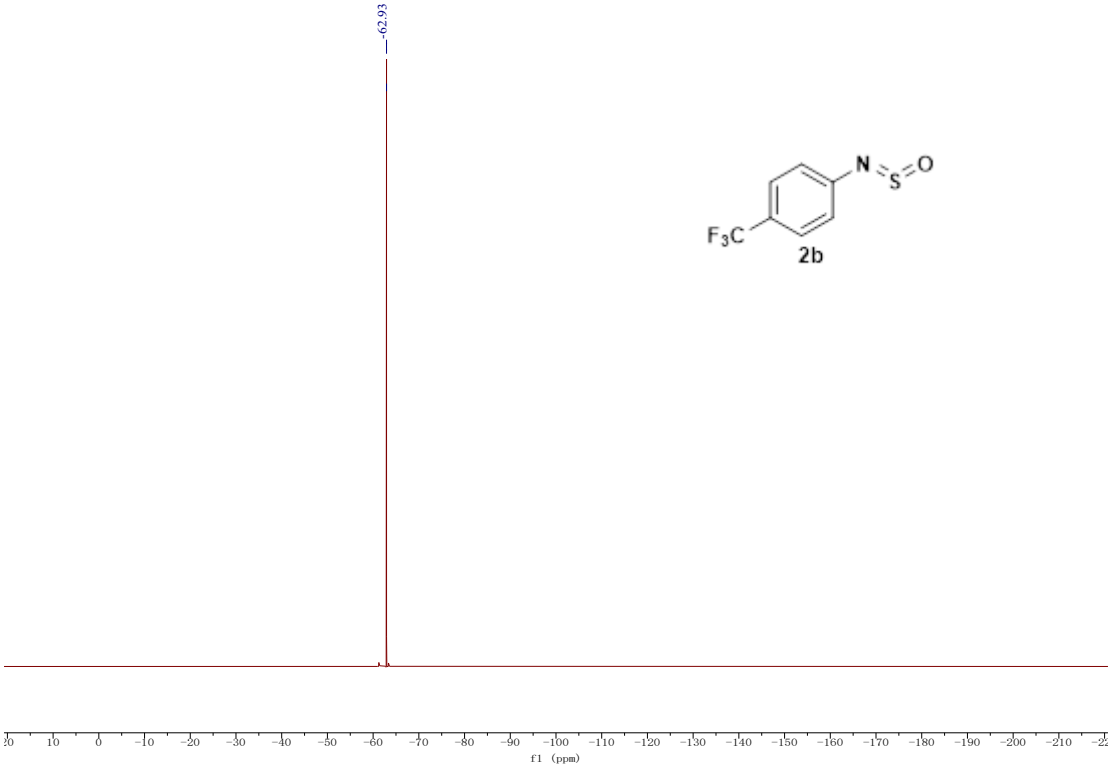
^{1}H NMR of Compound 2b (500 MHz, $CDCl_3$)



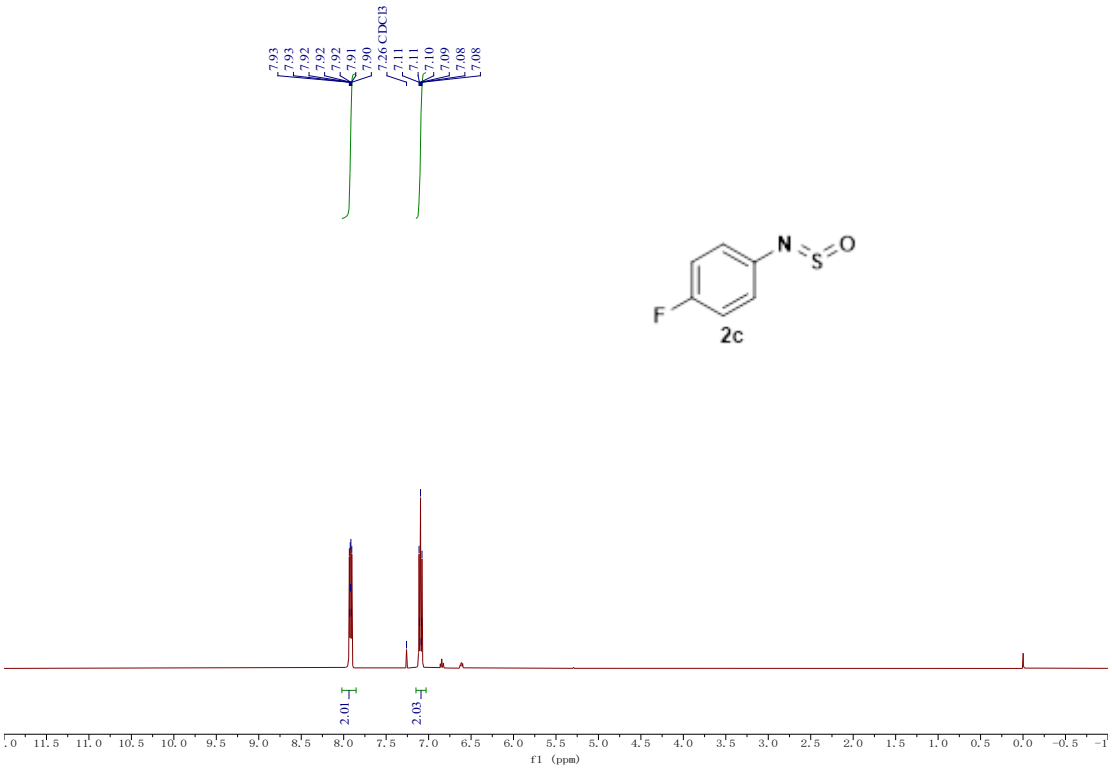
^{13}C NMR of Compound 2b (126 MHz, $CDCl_3$)



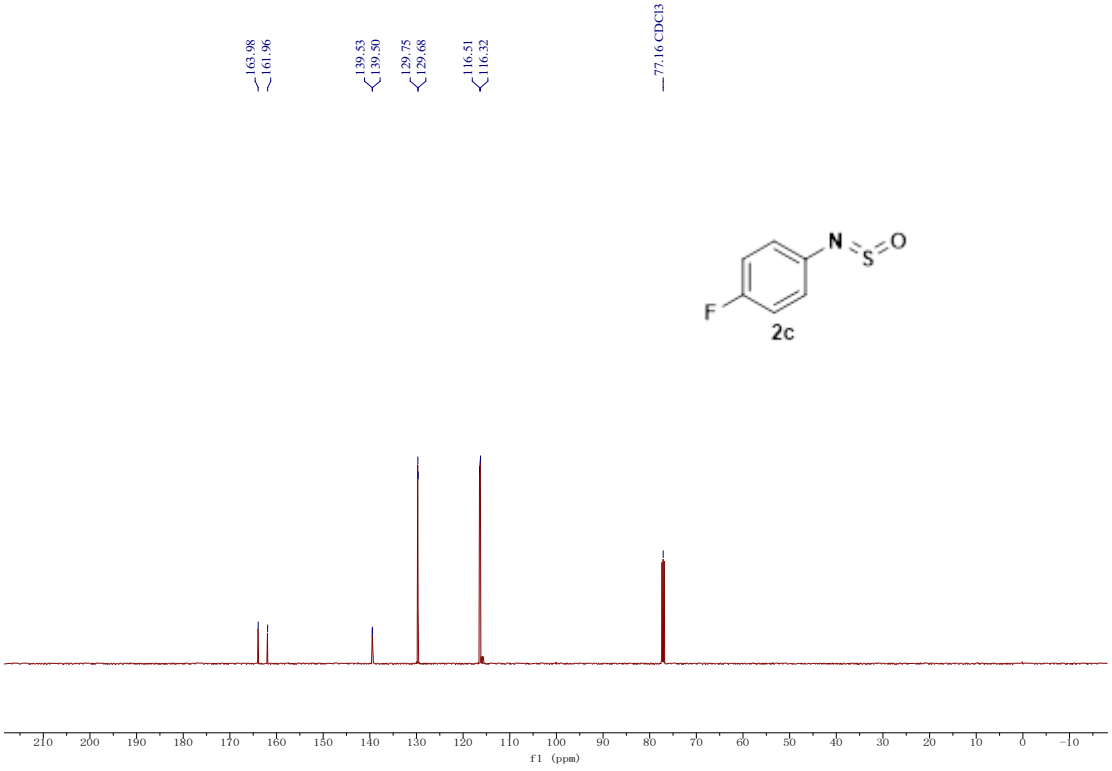
^{19}F NMR of Compound 2b (471 MHz, $CDCl_3$)



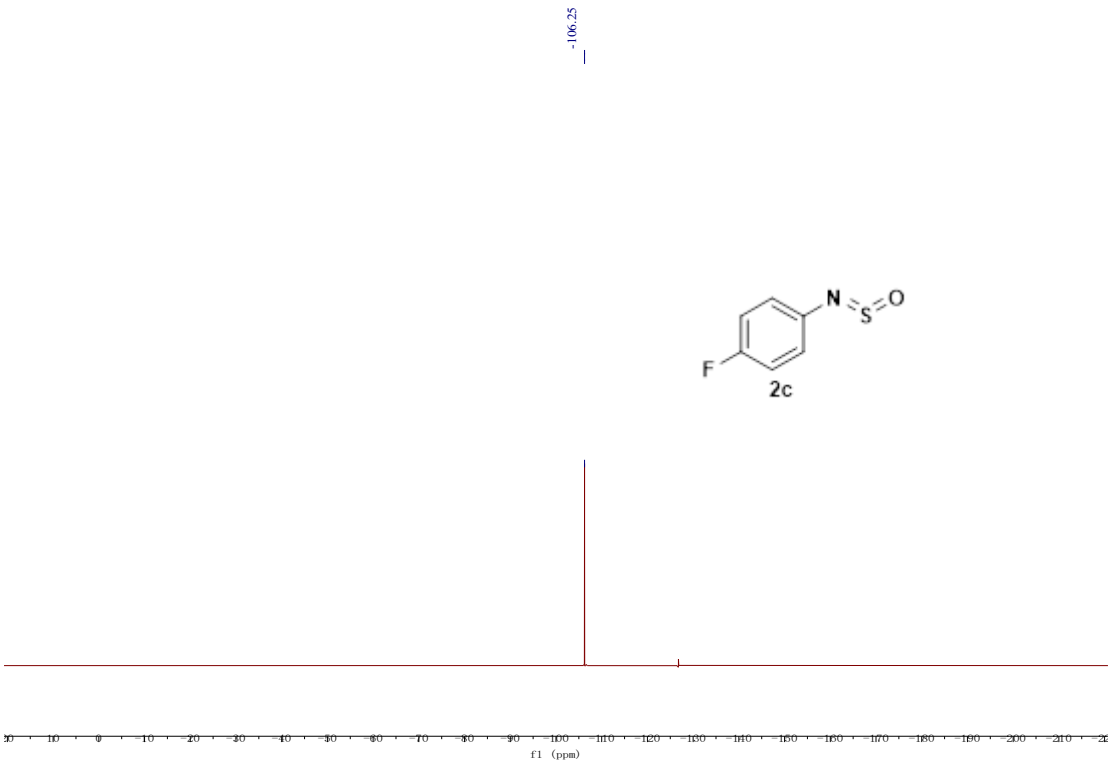
^{1}H NMR of Compound 2c (500 MHz, $CDCl_3$)



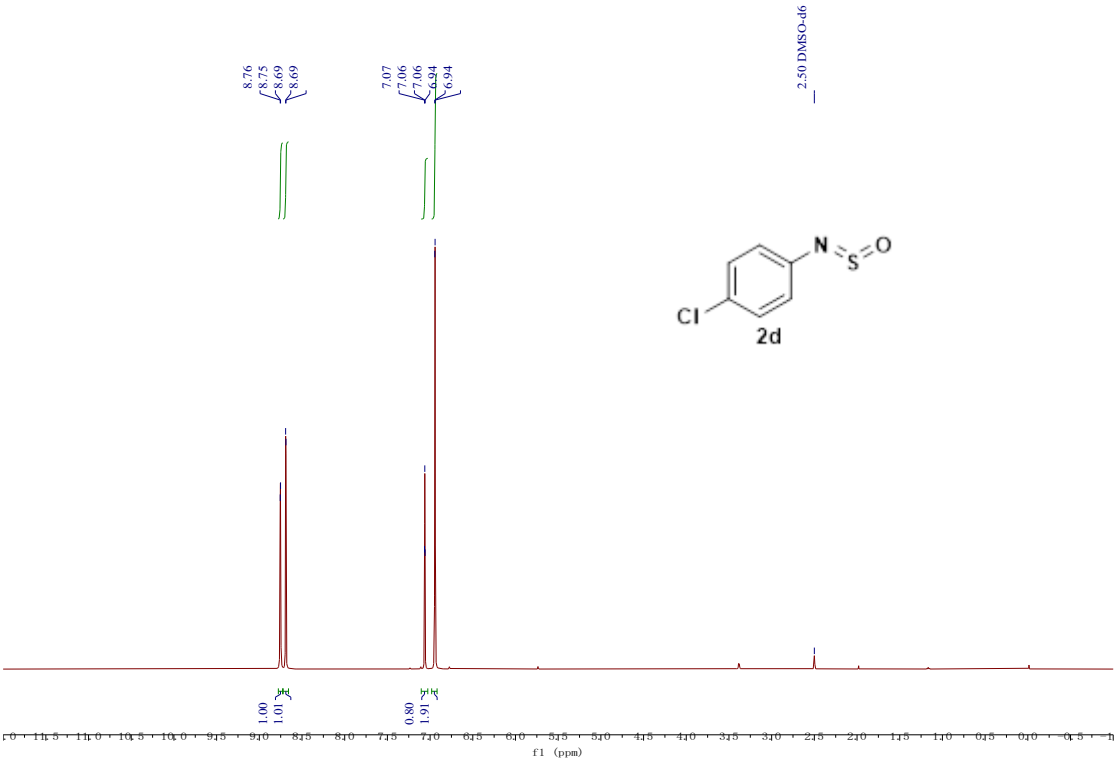
^{13}C NMR of Compound 2c (126 MHz, $CDCl_3$)



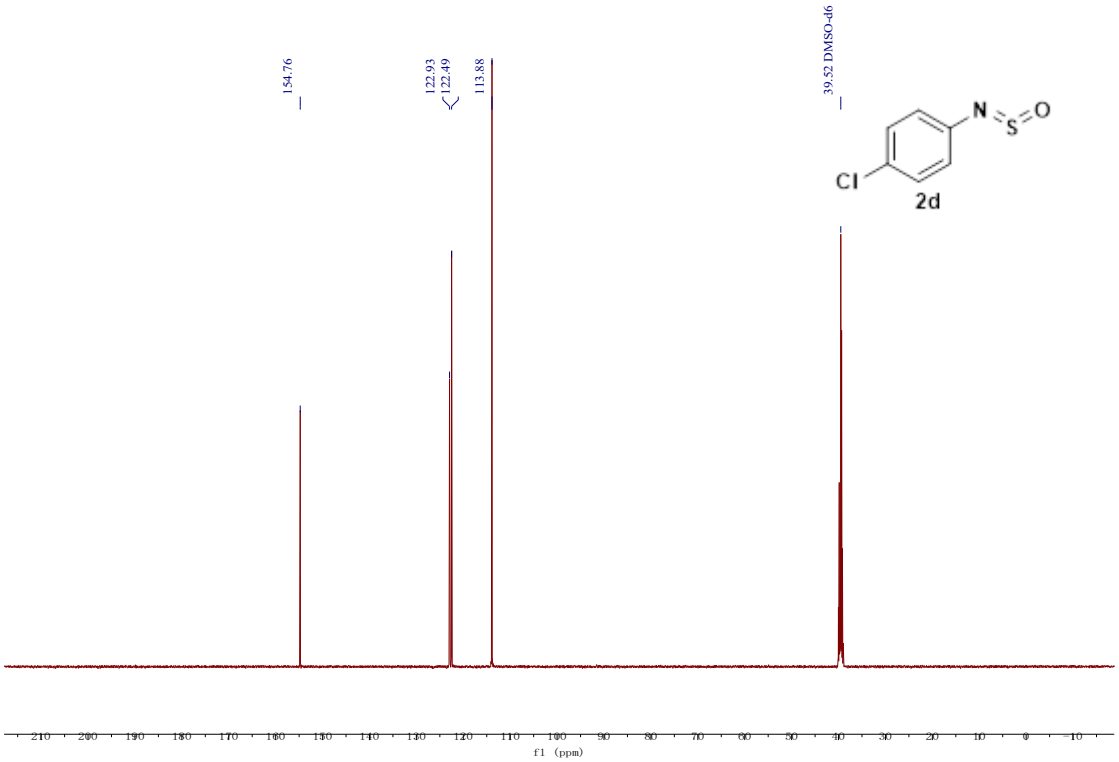
^{19}F NMR of Compound 2c (471 MHz, $CDCl_3$)



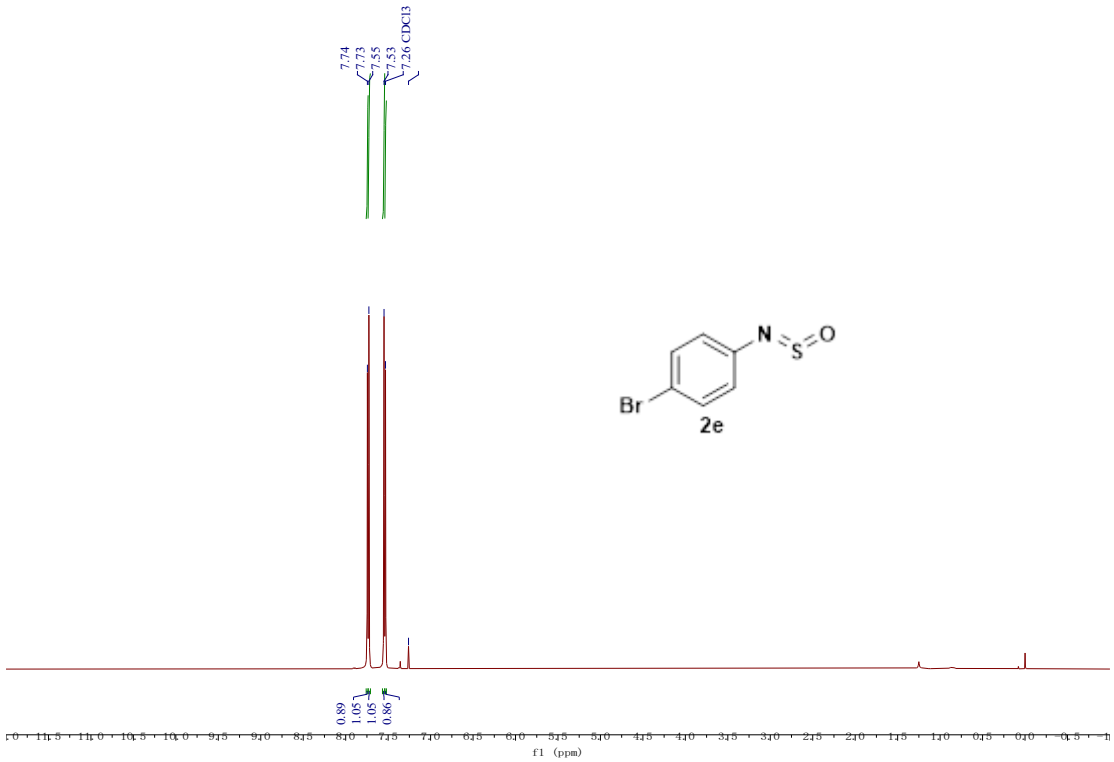
^{1}H NMR of Compound 2d (500 MHz, DMSO-d_6)



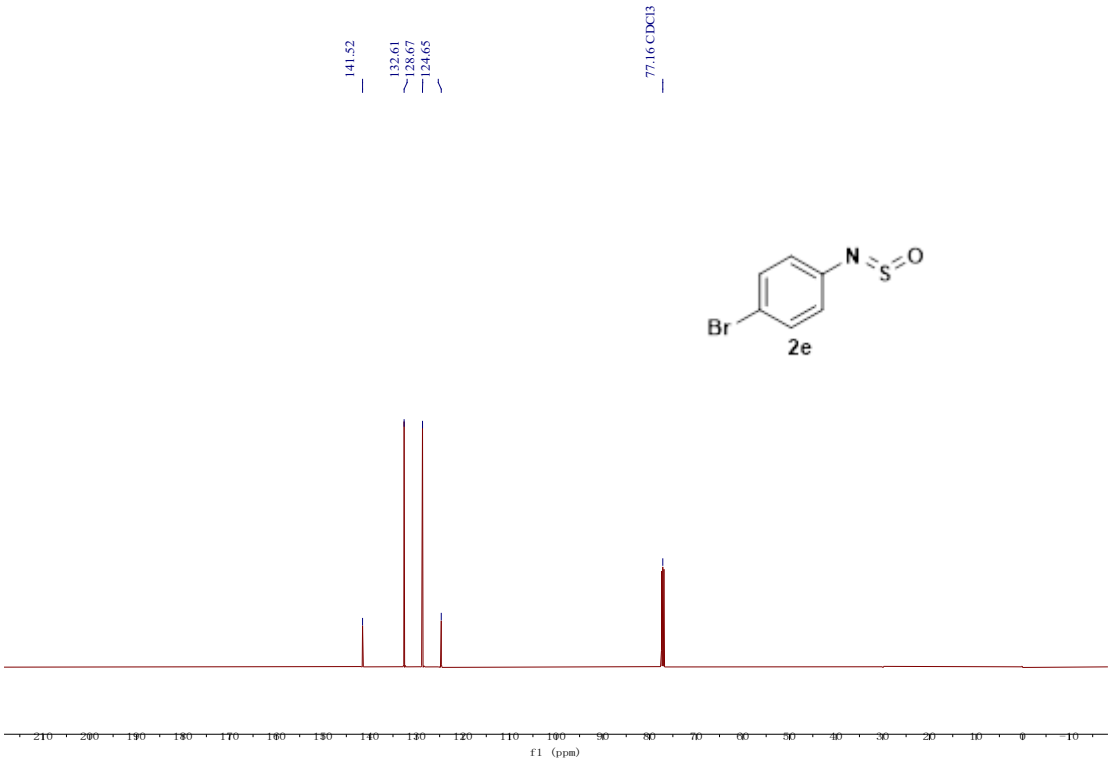
^{13}C NMR of Compound 2d (126 MHz, DMSO-*d*$_6$)



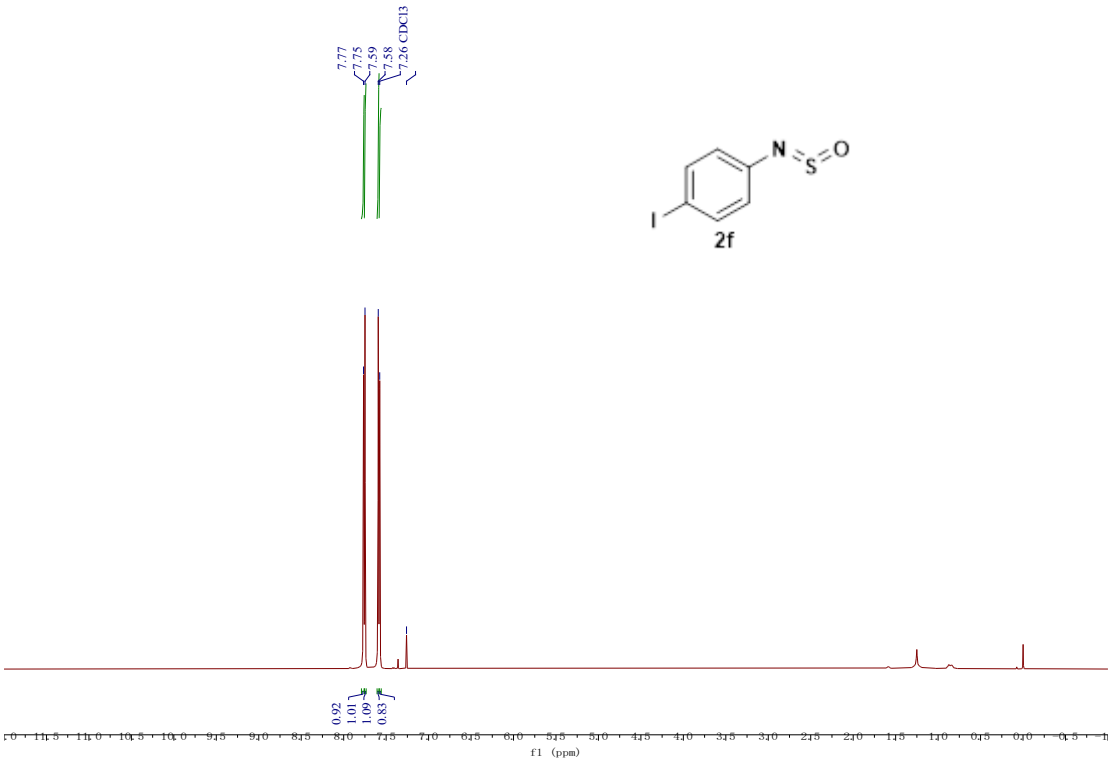
^{1}H NMR of Compound 2e (500 MHz, CDCl$_3$)



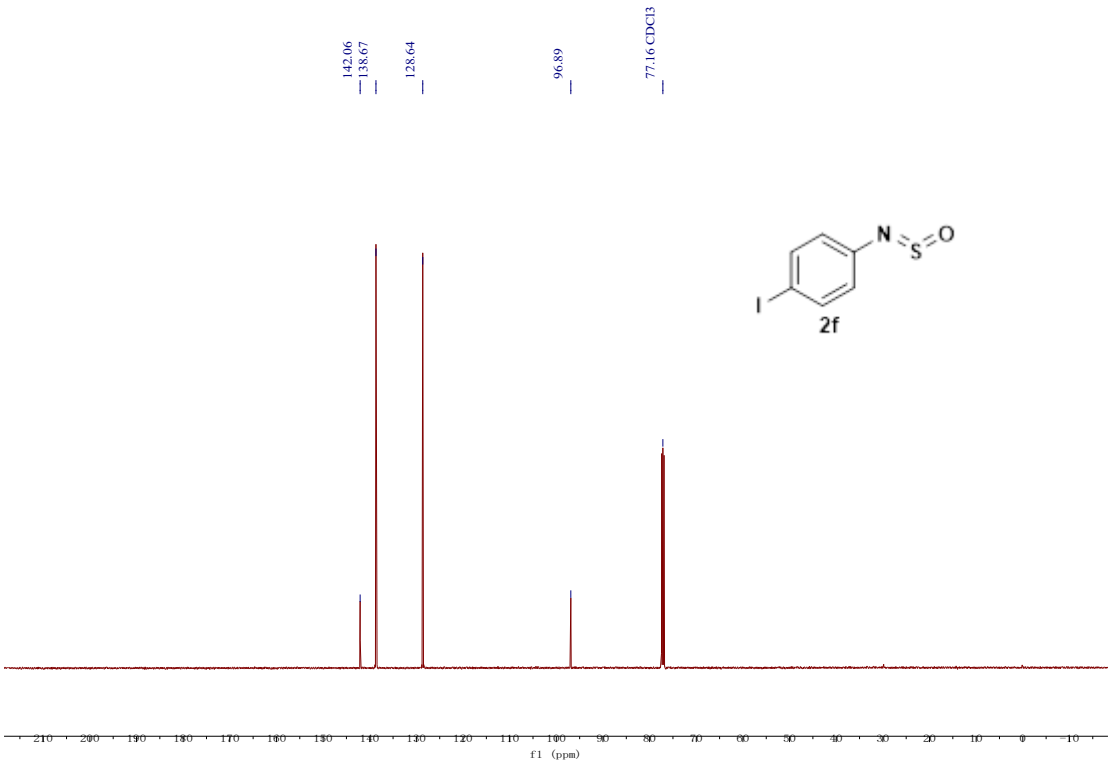
^{13}C NMR of Compound 2e (126 MHz, $CDCl_3$)



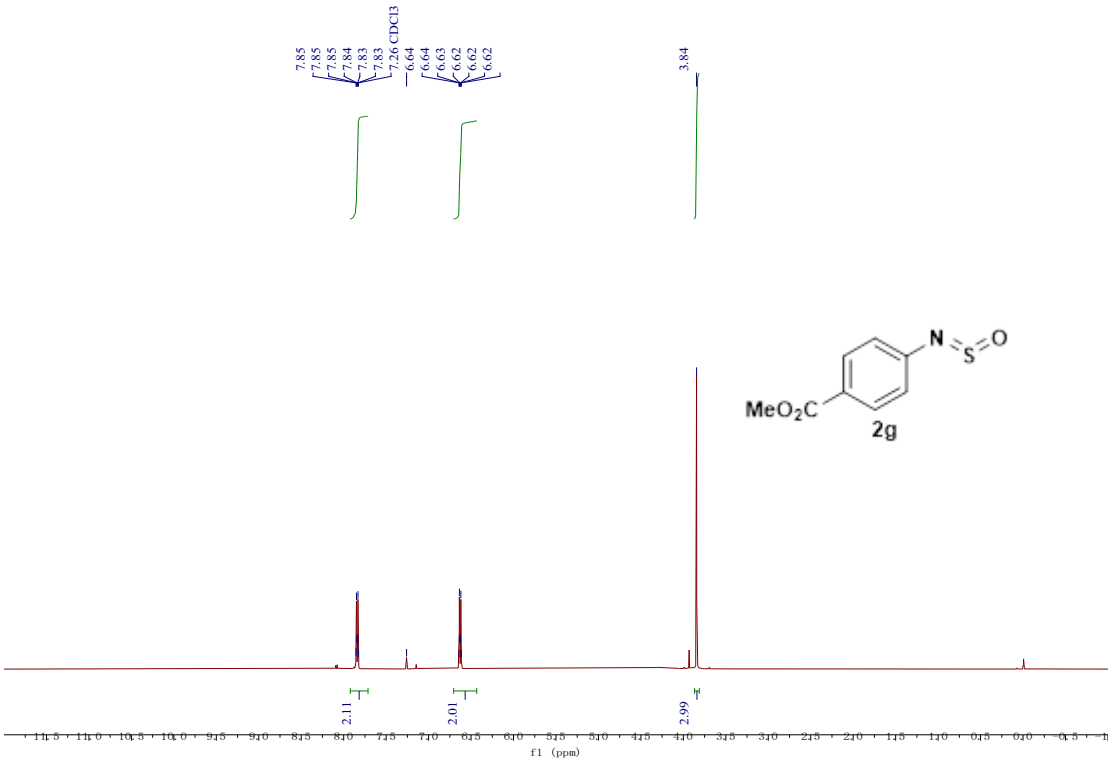
^{1}H NMR of Compound 2f (500 MHz, $CDCl_3$)



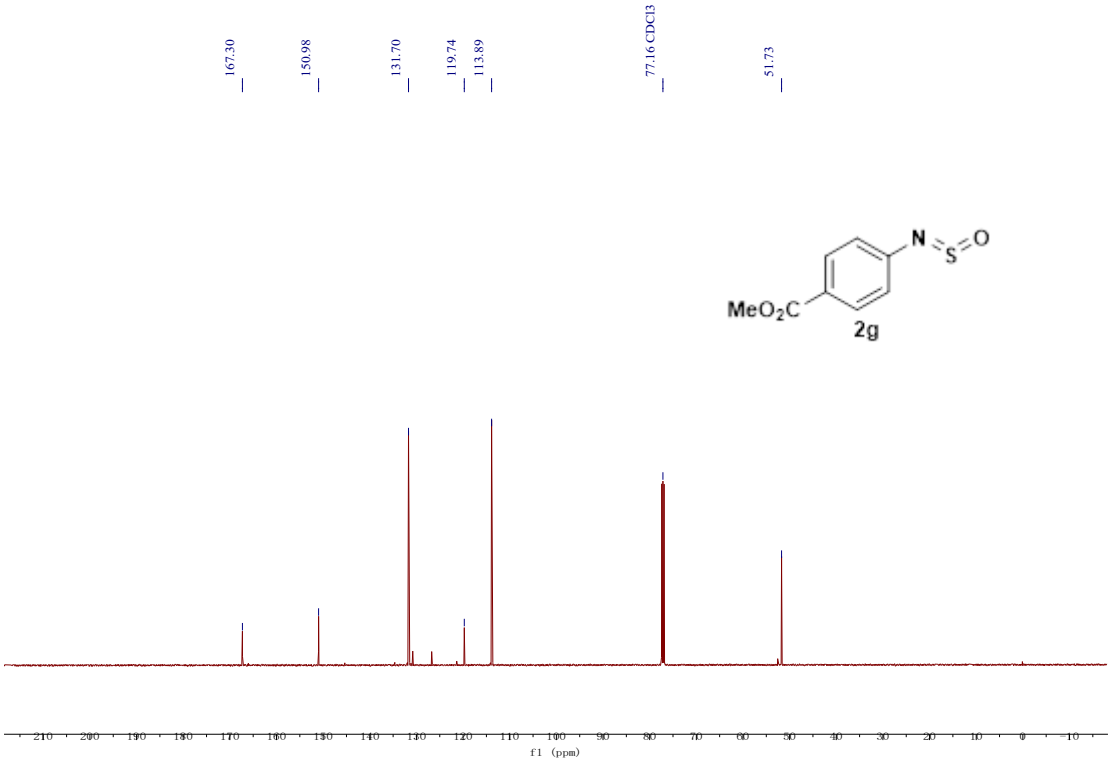
^{13}C NMR of Compound 2f (126 MHz, $CDCl_3$)



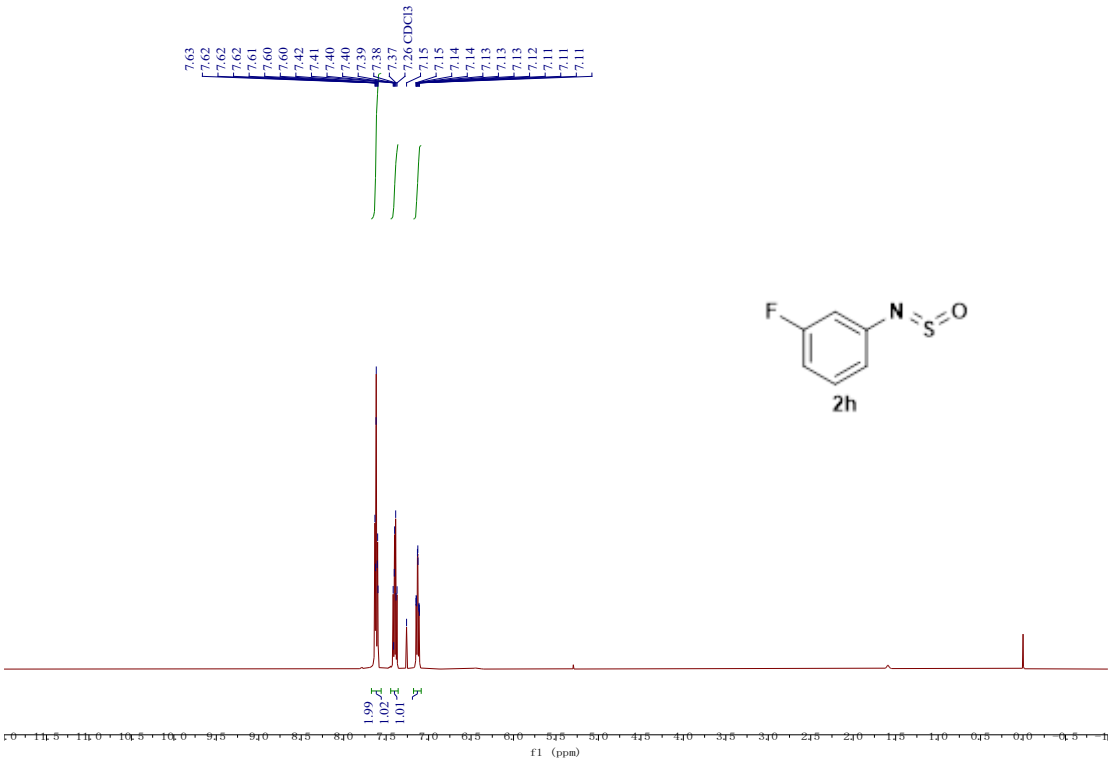
^{1}H NMR of Compound 2g (500 MHz, $CDCl_3$)



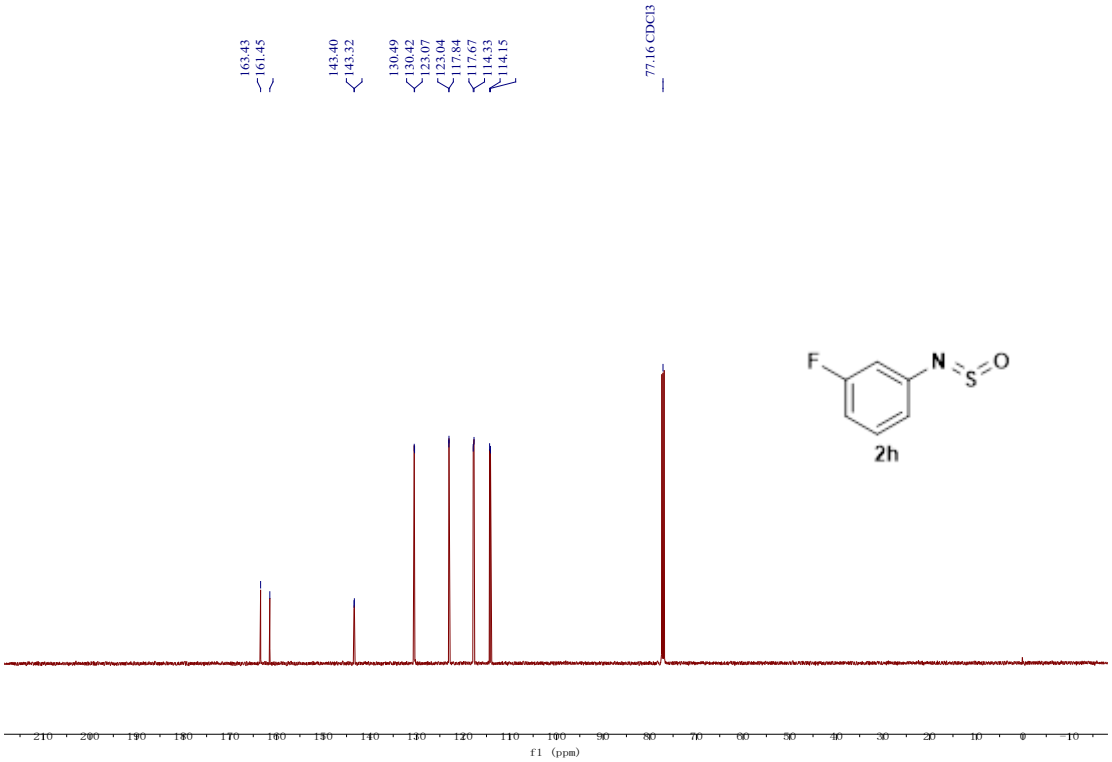
^{13}C NMR of Compound 2g (126 MHz, $CDCl_3$)



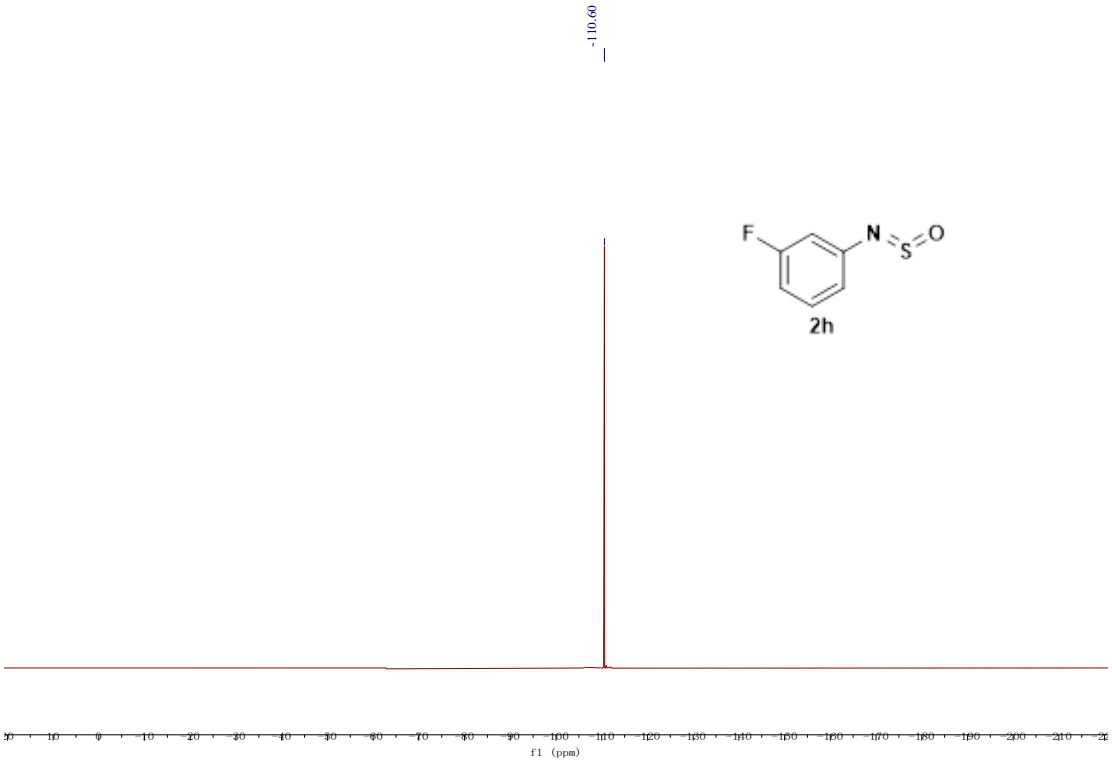
^{1}H NMR of Compound 2h (500 MHz, $CDCl_3$)



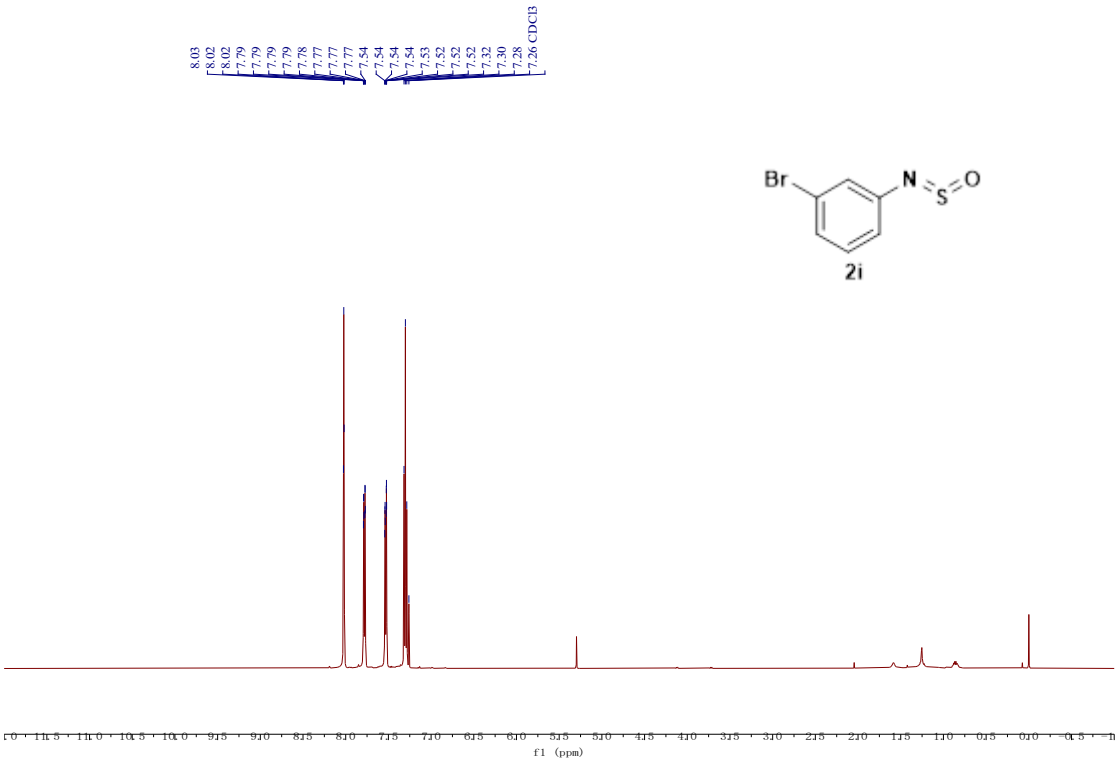
^{13}C NMR of Compound 2h (126 MHz, $CDCl_3$)



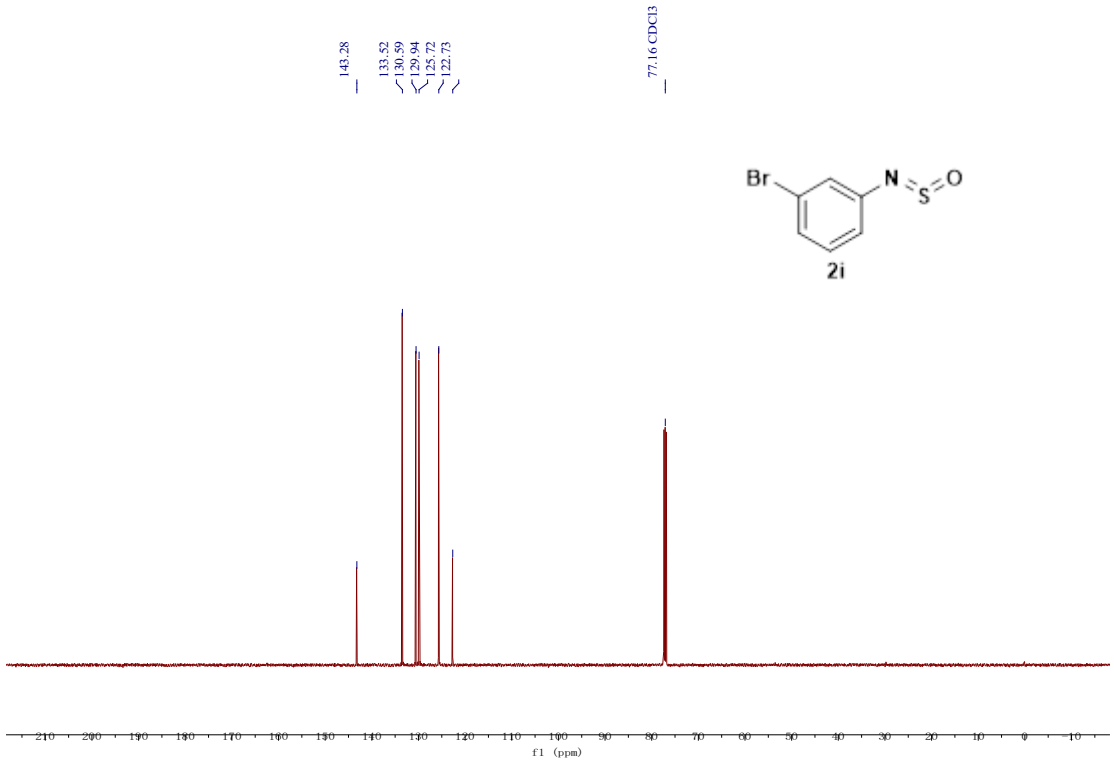
^{19}F NMR of Compound 2h (471 MHz, $CDCl_3$)



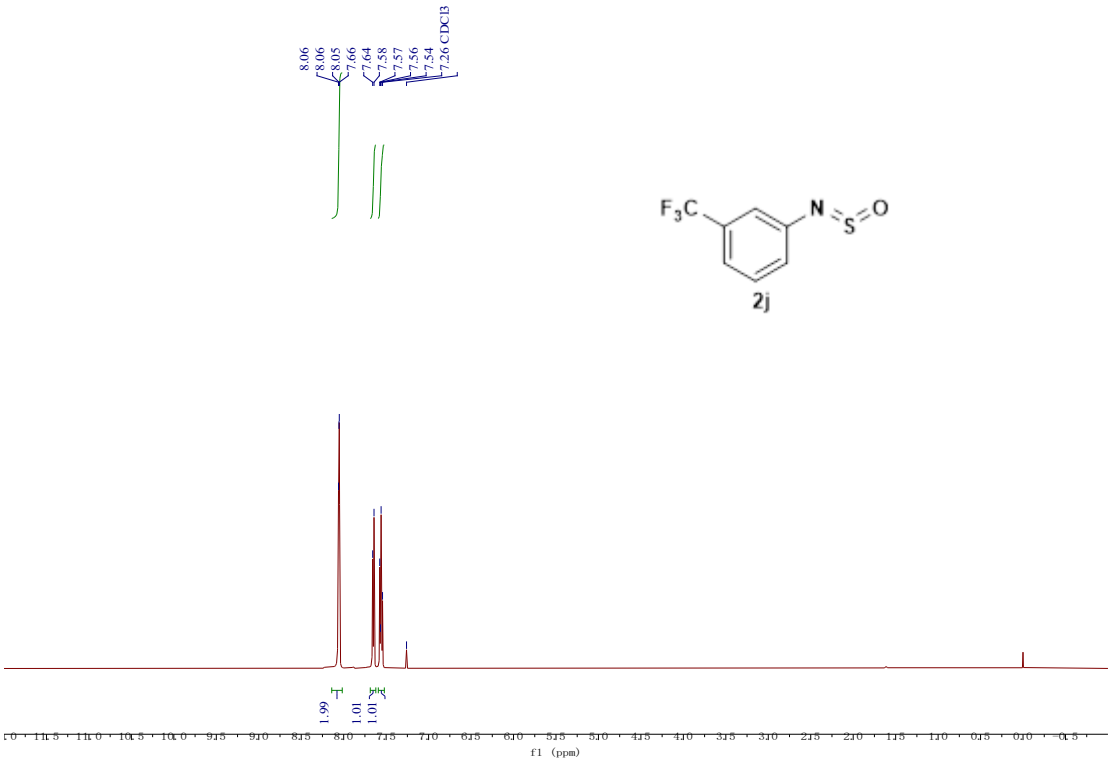
^{1}H NMR of Compound 2i (500 MHz, $CDCl_3$)



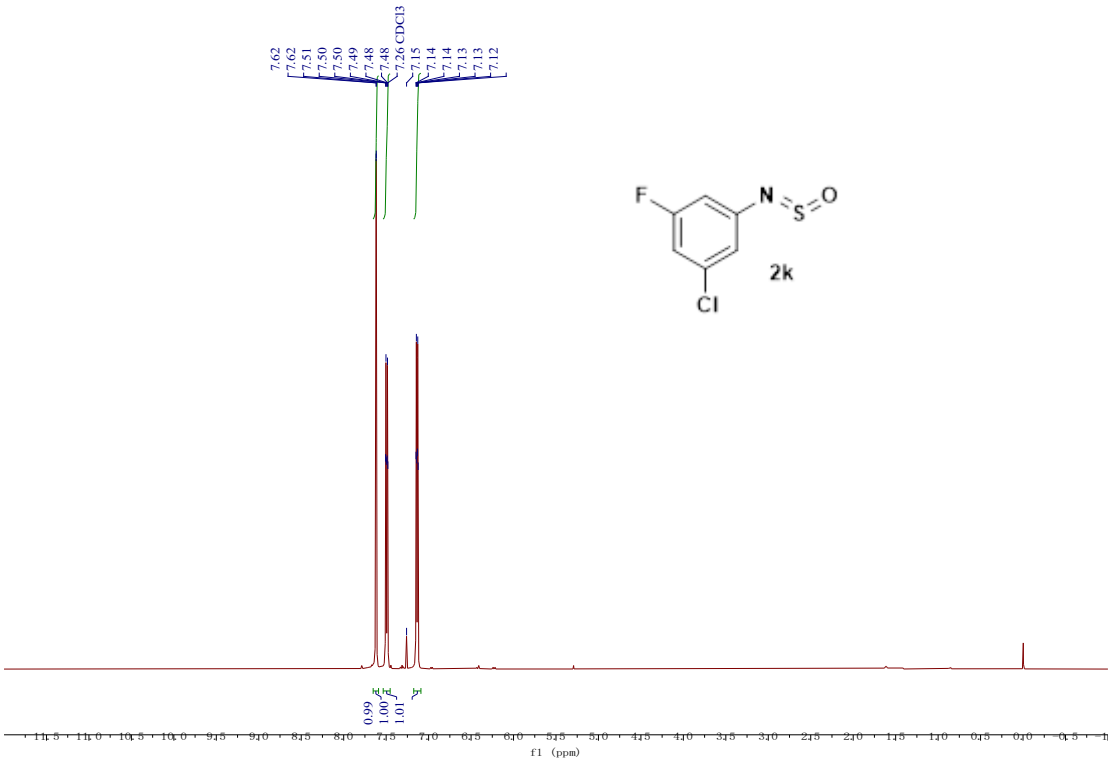
^{13}C NMR of Compound 2i (126 MHz, $CDCl_3$)



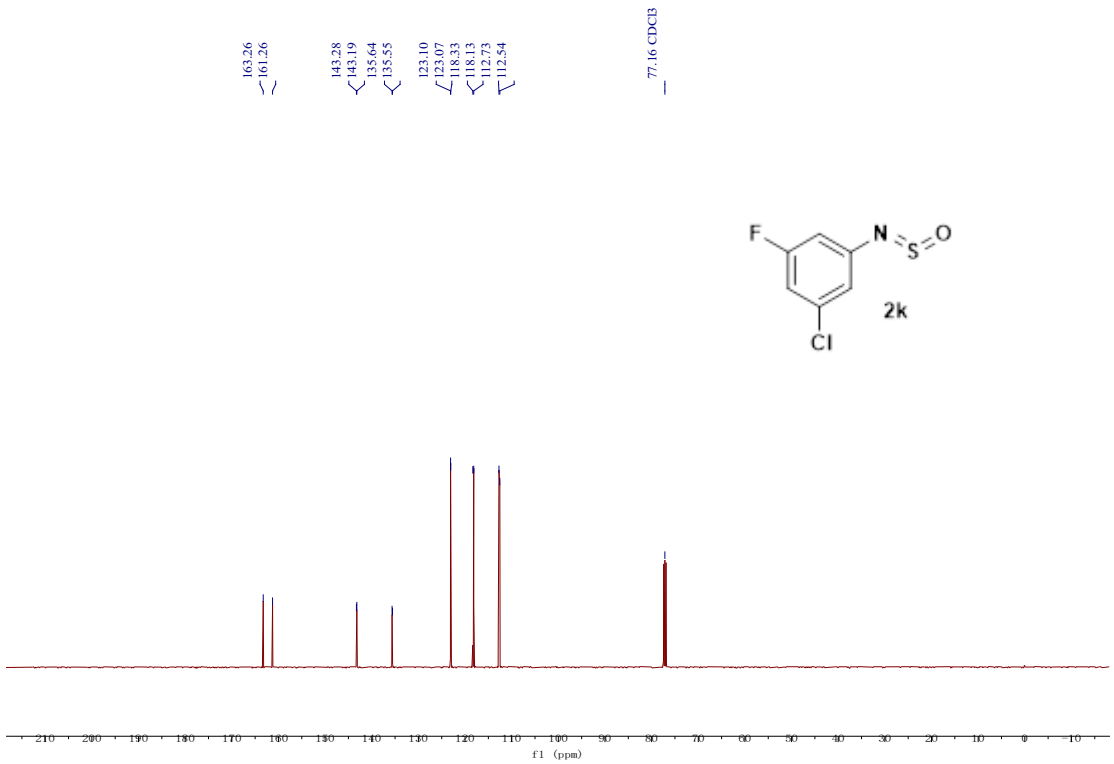
^{1}H NMR of Compound 2j (500 MHz, $CDCl_3$)



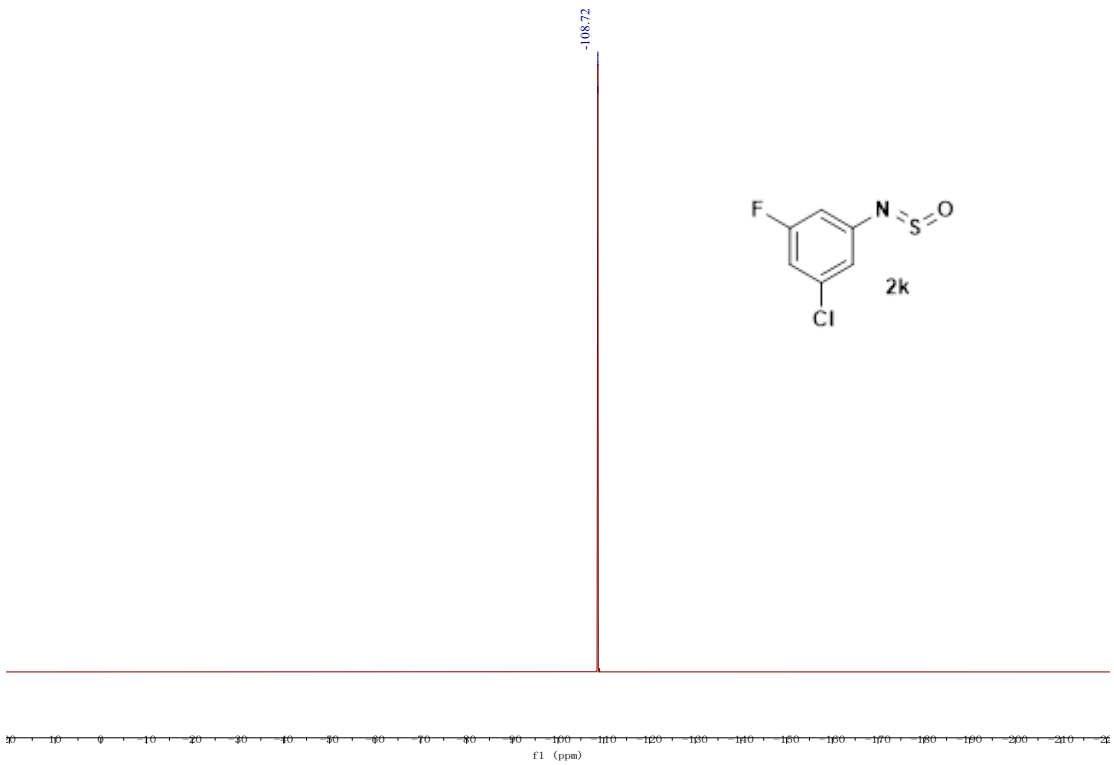
^{1}H NMR of Compound 2k (500 MHz, $CDCl_3$)



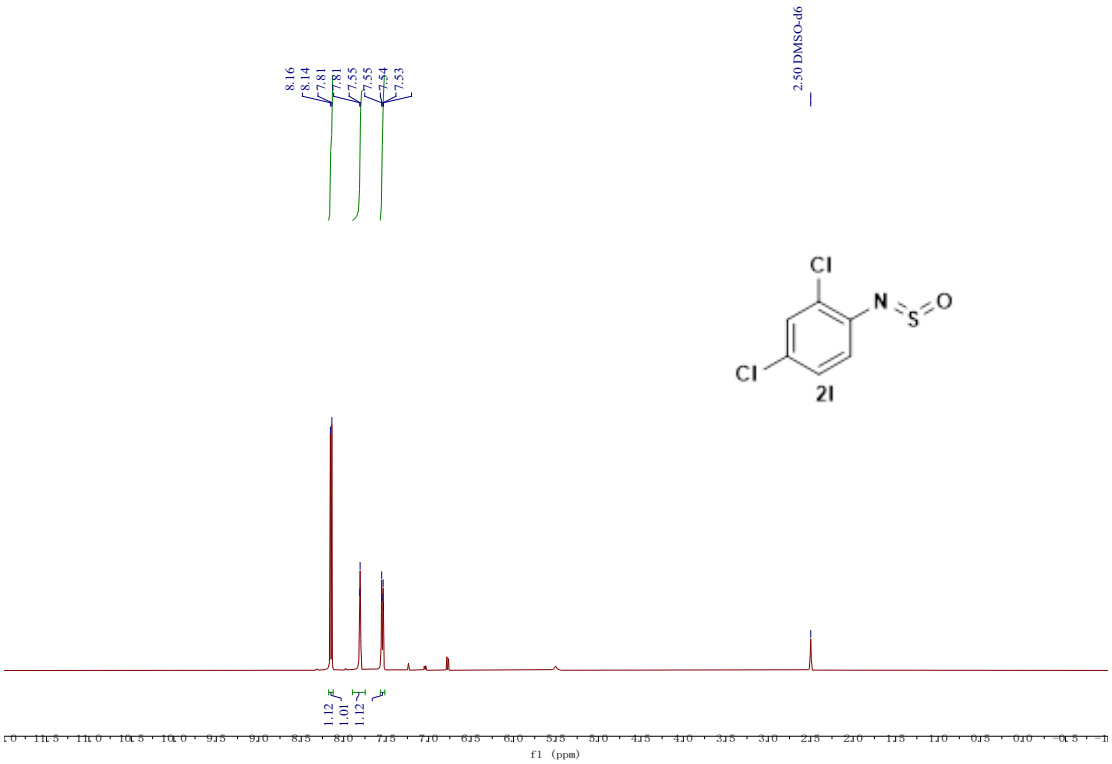
^{13}C NMR of Compound 2k (126 MHz, $CDCl_3$)



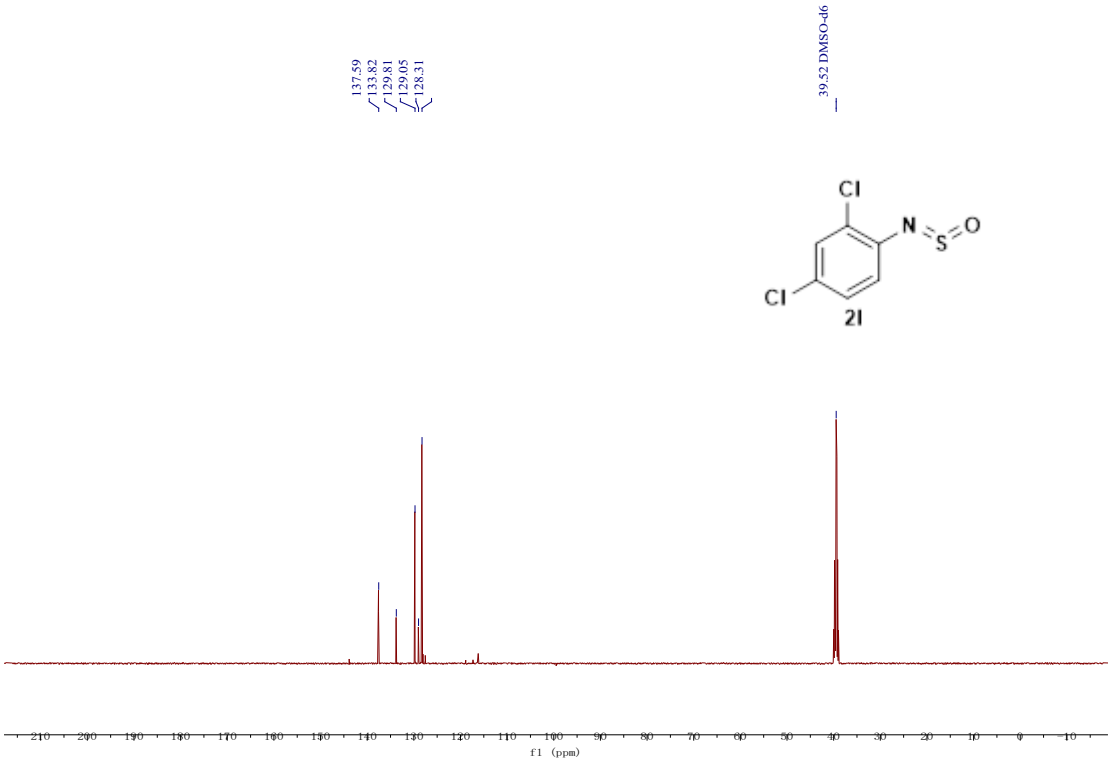
^{19}F NMR of Compound 2k (471 MHz, $CDCl_3$)



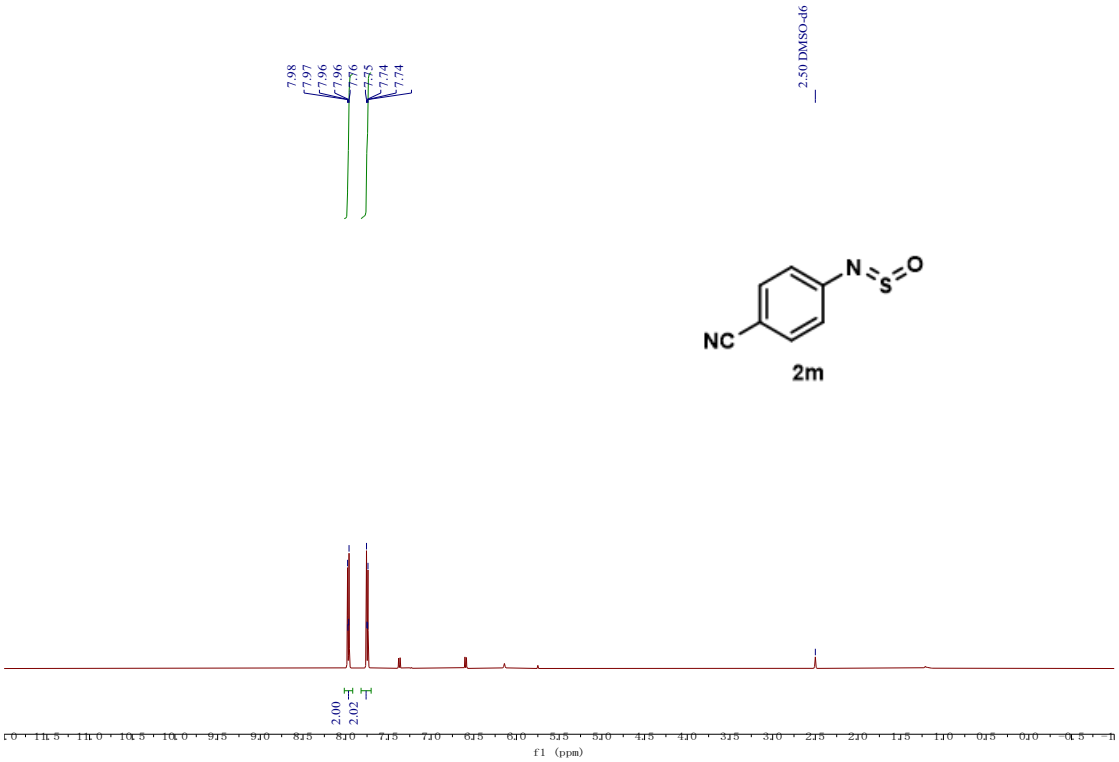
^{1}H NMR of Compound 2l (500 MHz, DMSO-d_6)



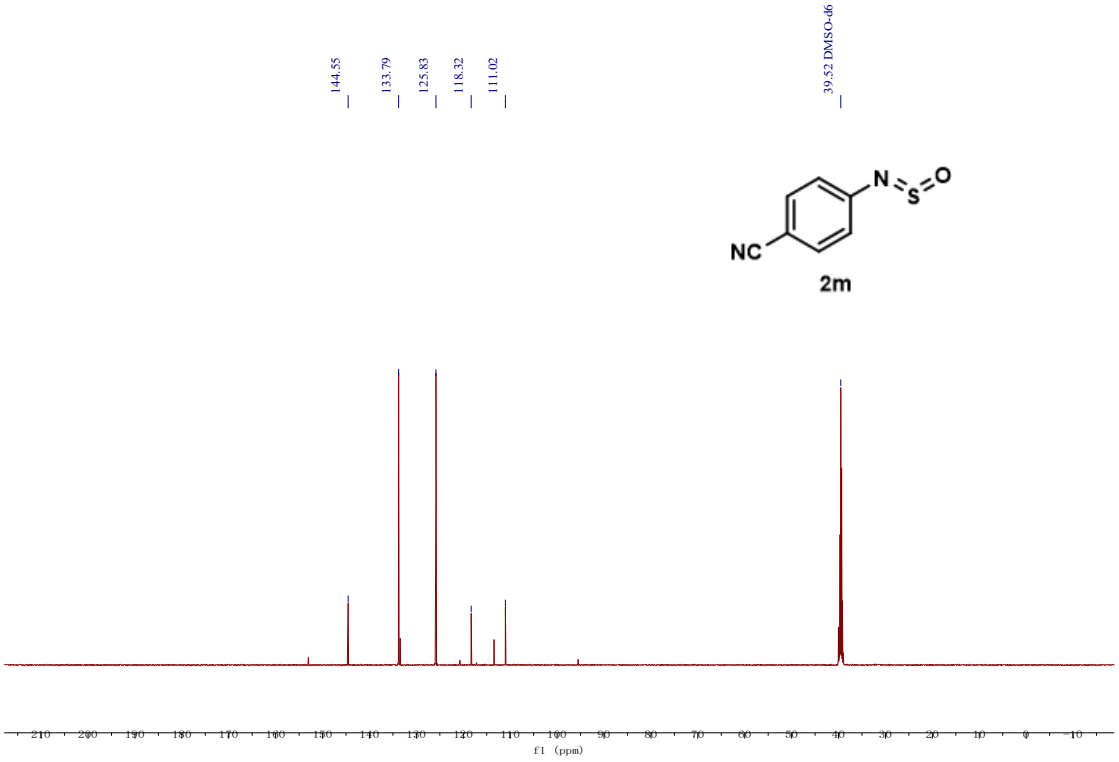
^{13}C NMR of Compound 2l (126 MHz, DMSO-d_6)



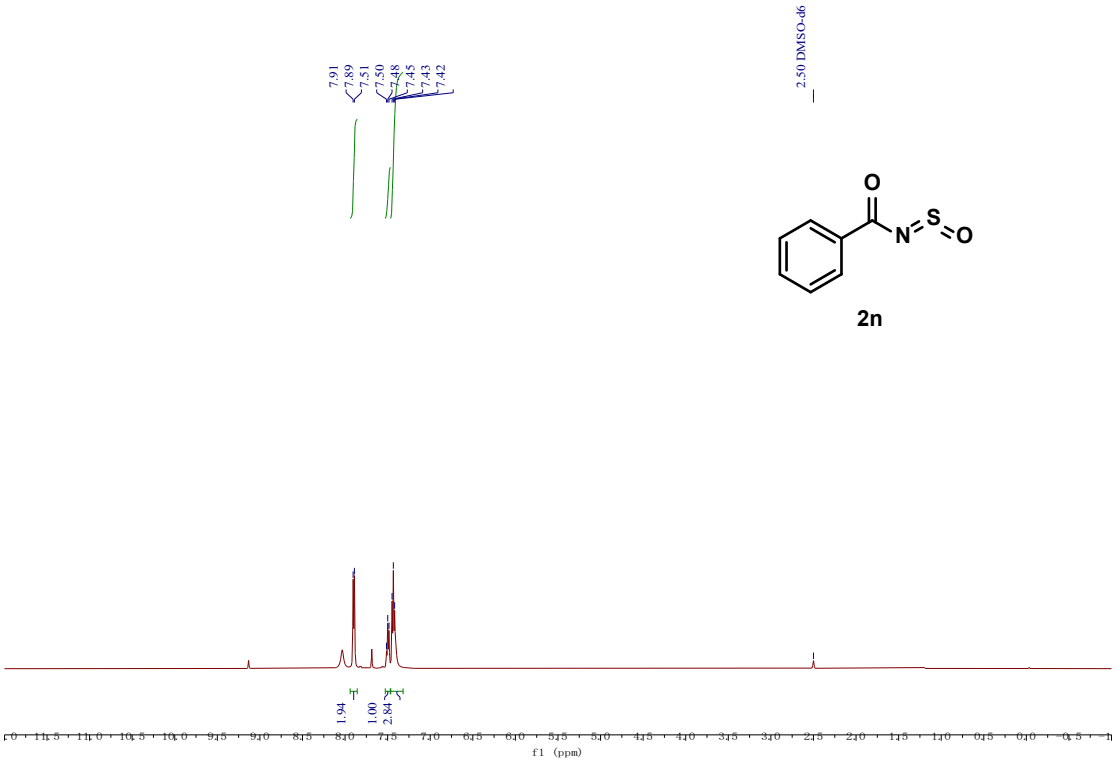
^{1}H NMR of Compound 2m (500 MHz, DMSO-d_6)



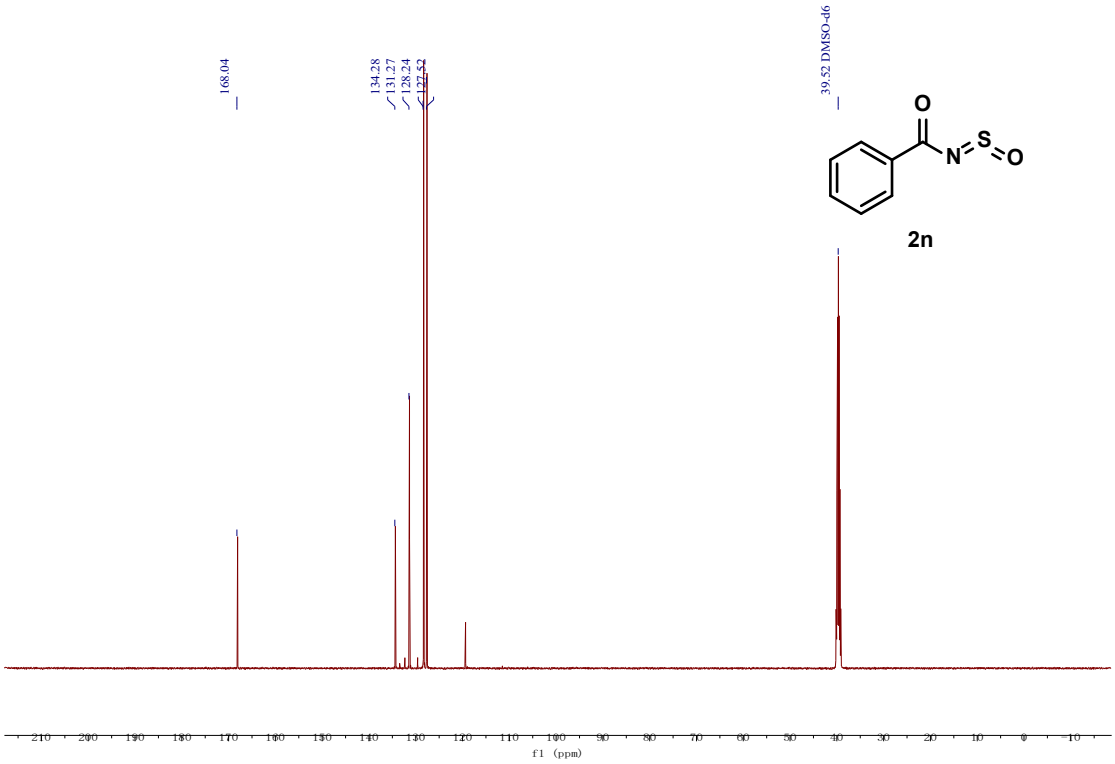
^{13}C NMR of Compound 2m (126 MHz, DMSO-d_6)



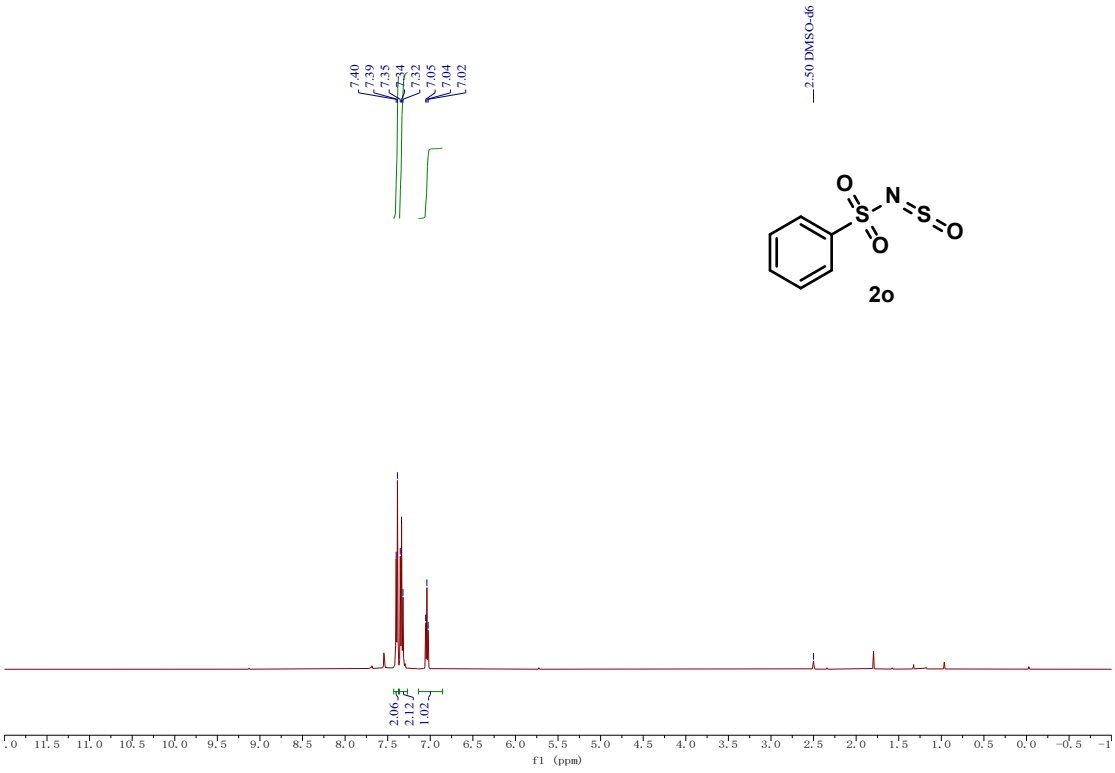
^{1}H NMR of Compound 2n (500 MHz, DMSO-d_6)



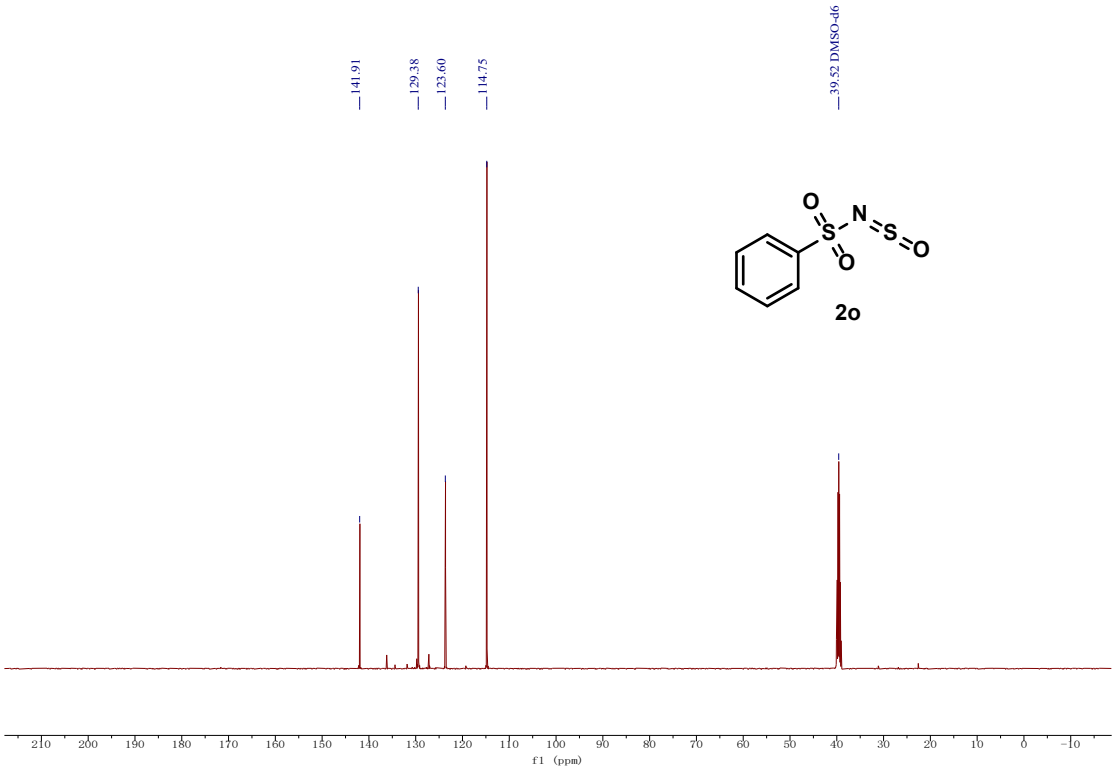
^{13}C NMR of Compound 2n (126 MHz, DMSO-d_6)



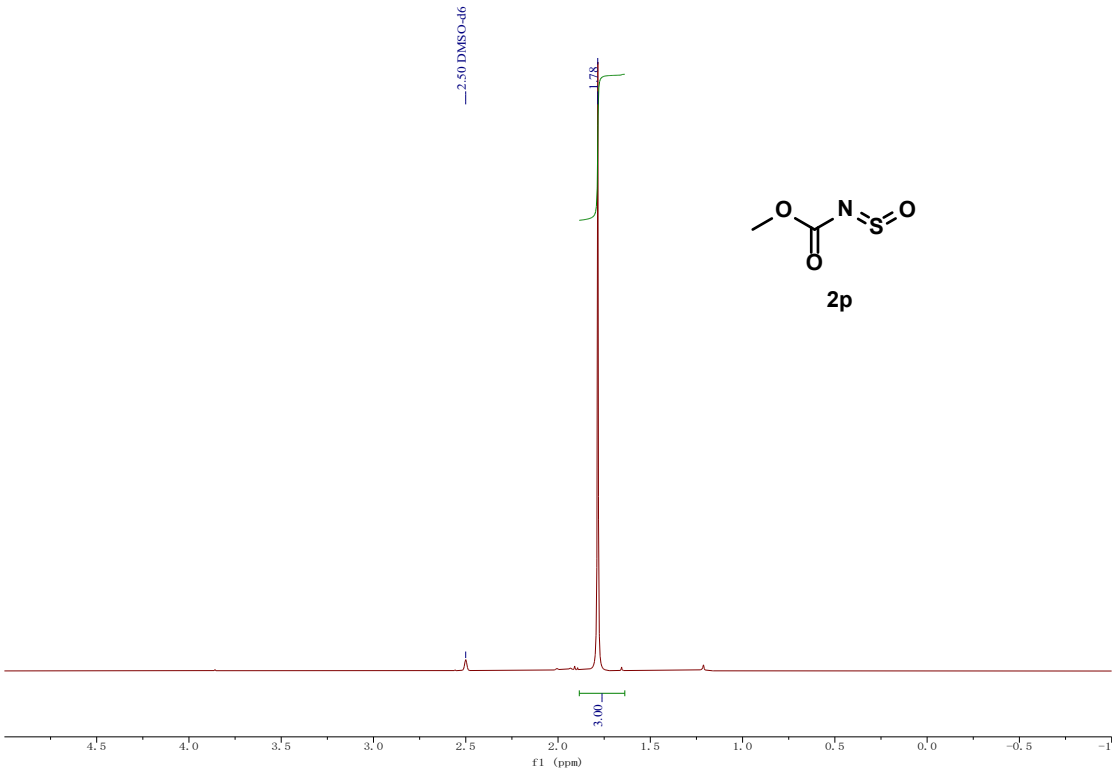
^{1}H NMR of Compound 2o (500 MHz, DMSO-d_6)



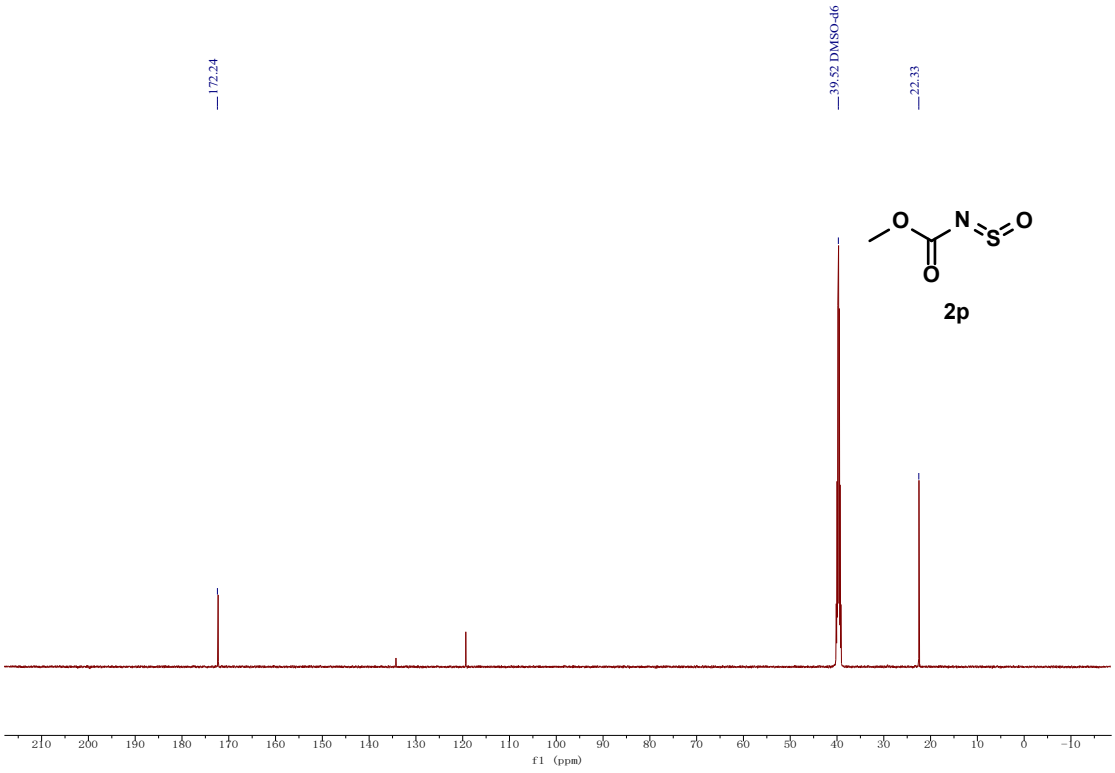
^{13}C NMR of Compound 2o (126 MHz, DMSO-d_6)



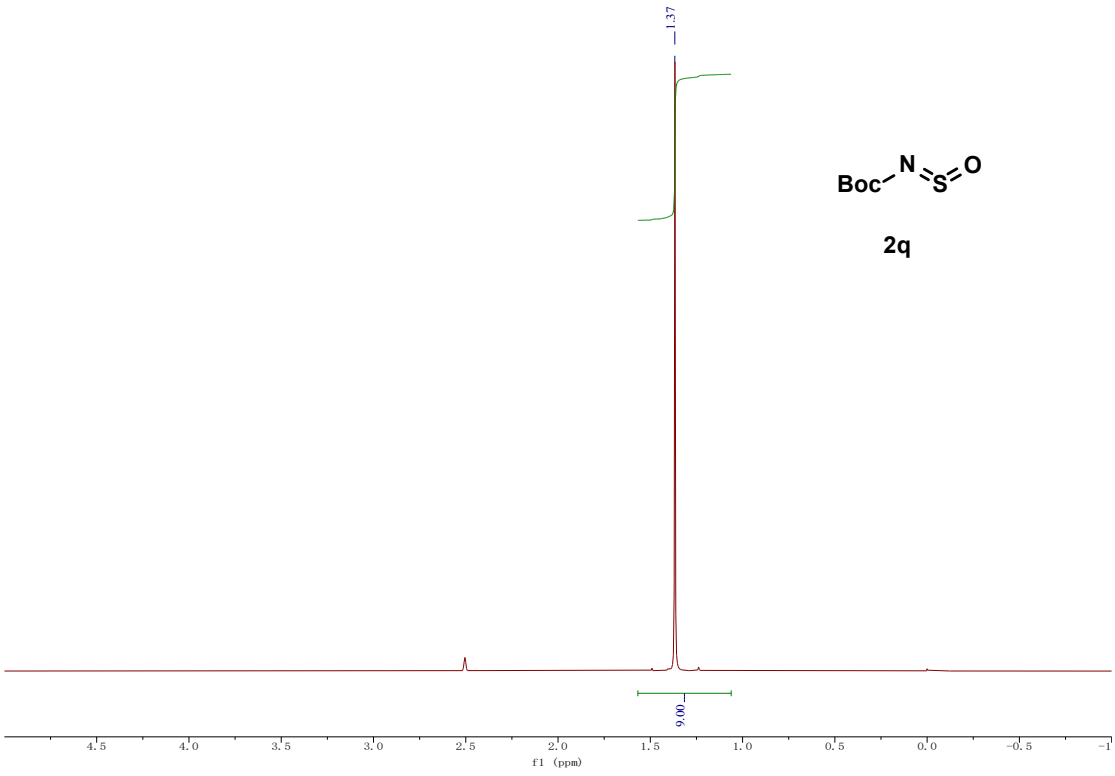
^{1}H NMR of Compound 2p (500 MHz, DMSO-d_6)



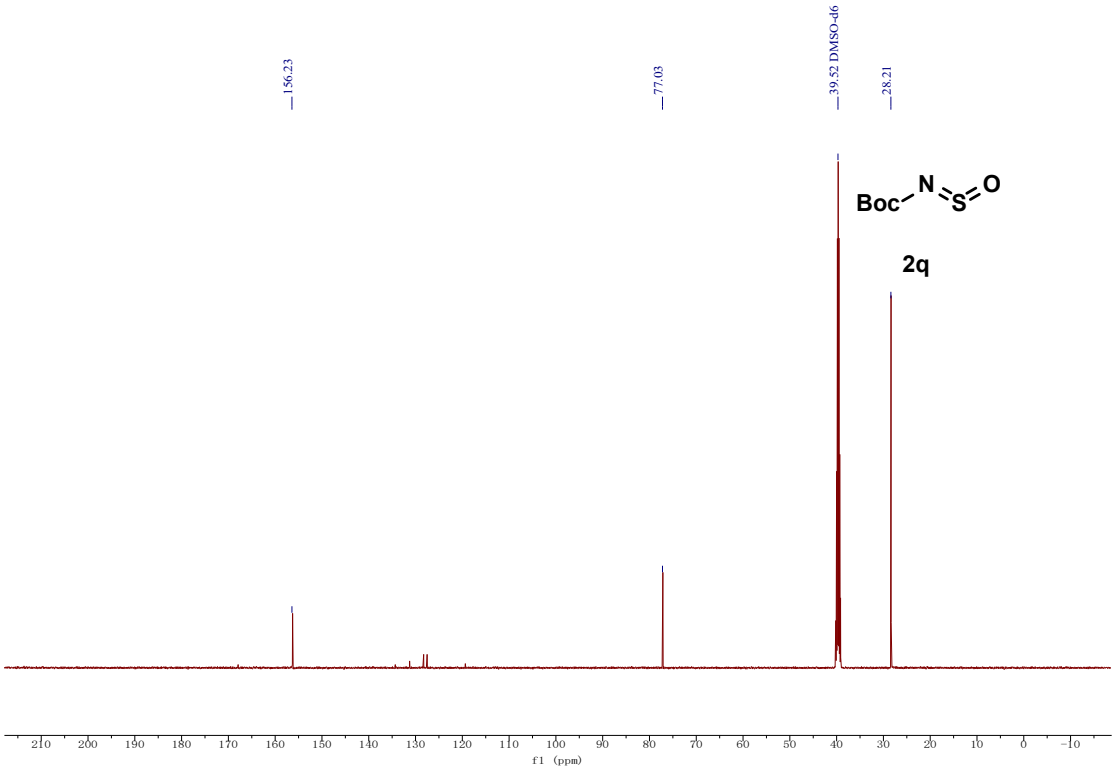
^{13}C NMR of Compound 2p (126 MHz, DMSO-d_6)



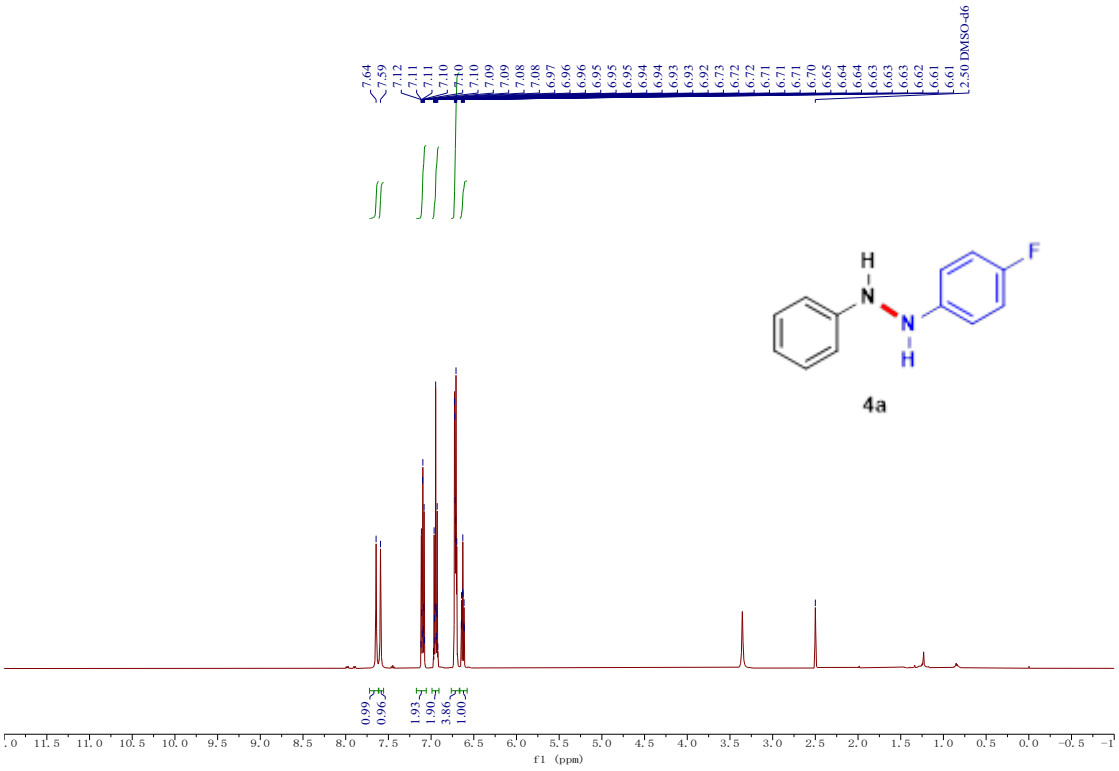
^{1}H NMR of Compound 2q (500 MHz, DMSO-d_6)



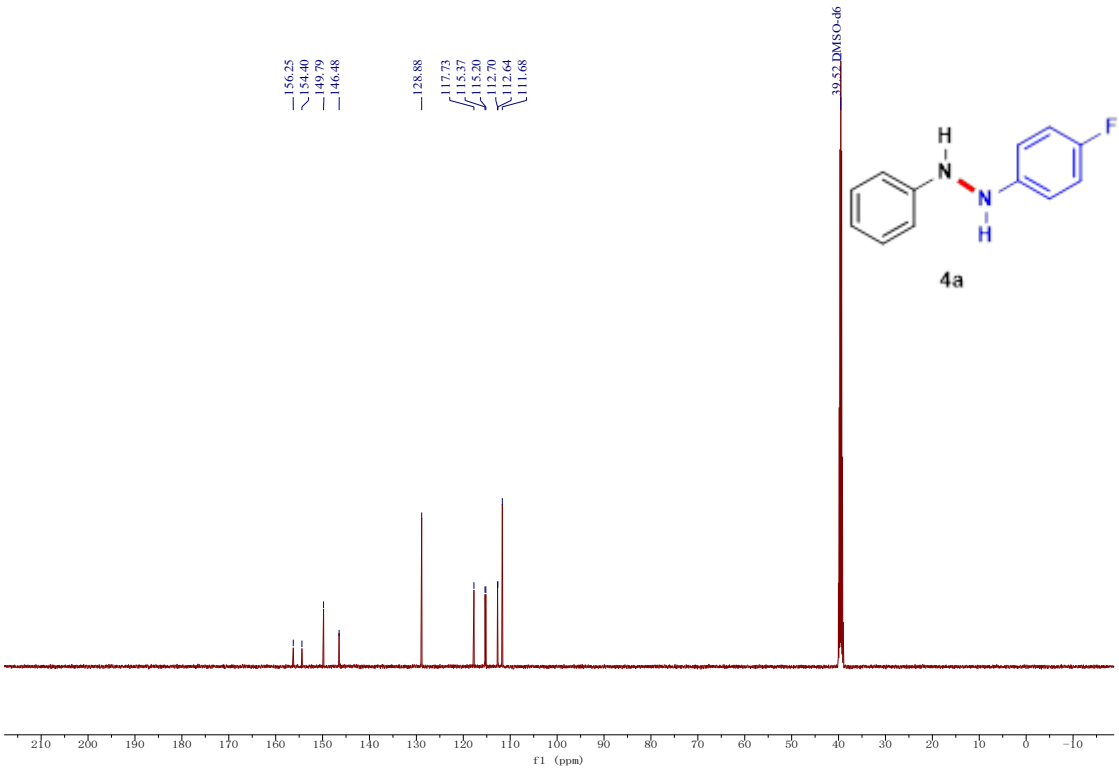
^{13}C NMR of Compound 2q (126 MHz, DMSO-d_6)



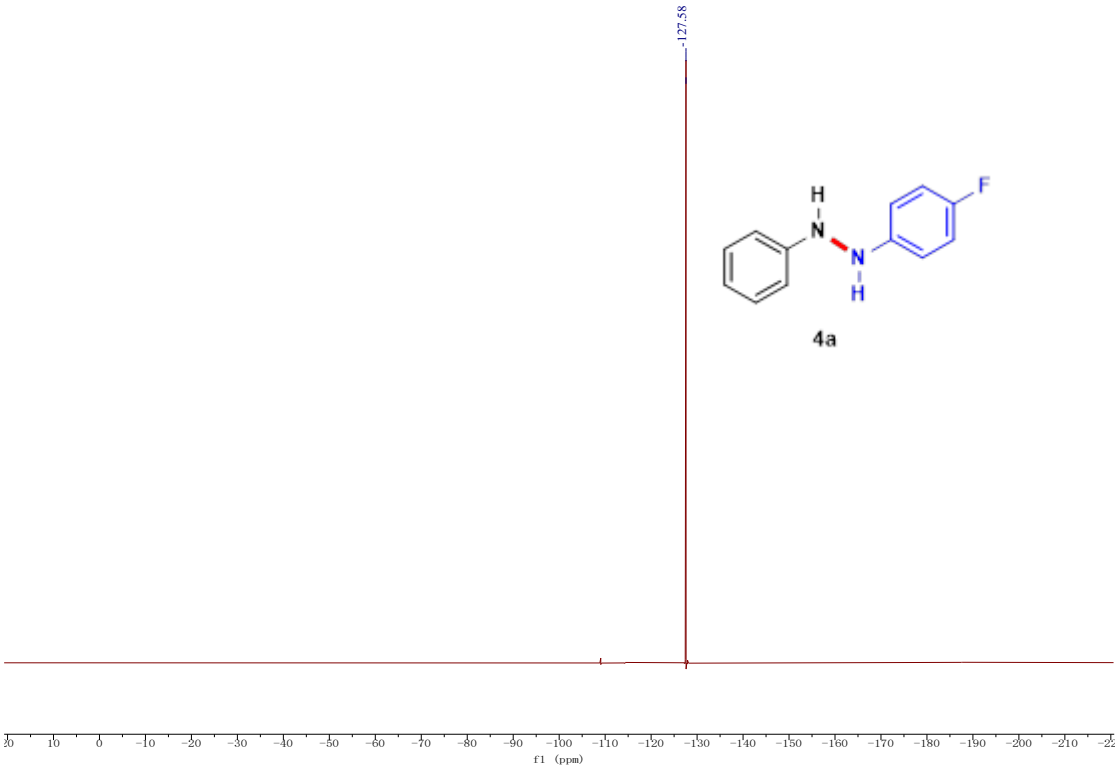
^{1}H NMR of Compound 4a (500 MHz, DMSO-d_6))



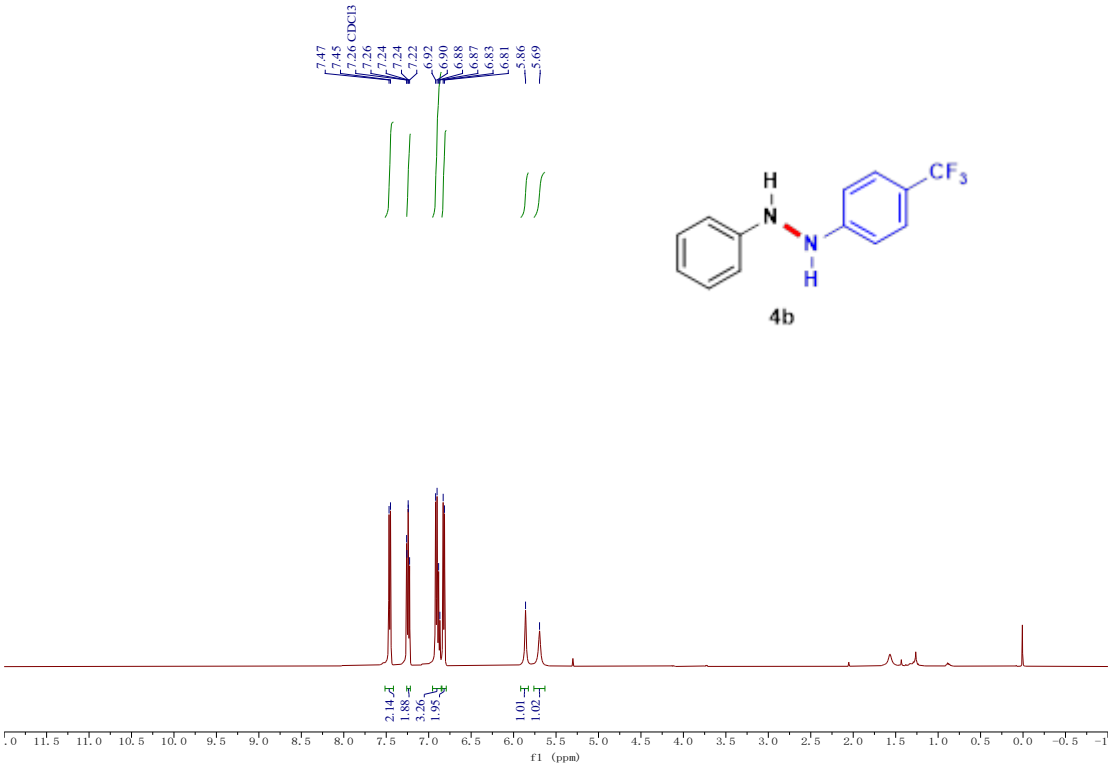
^{13}C NMR of Compound 4c (126 MHz, DMSO-d_6))



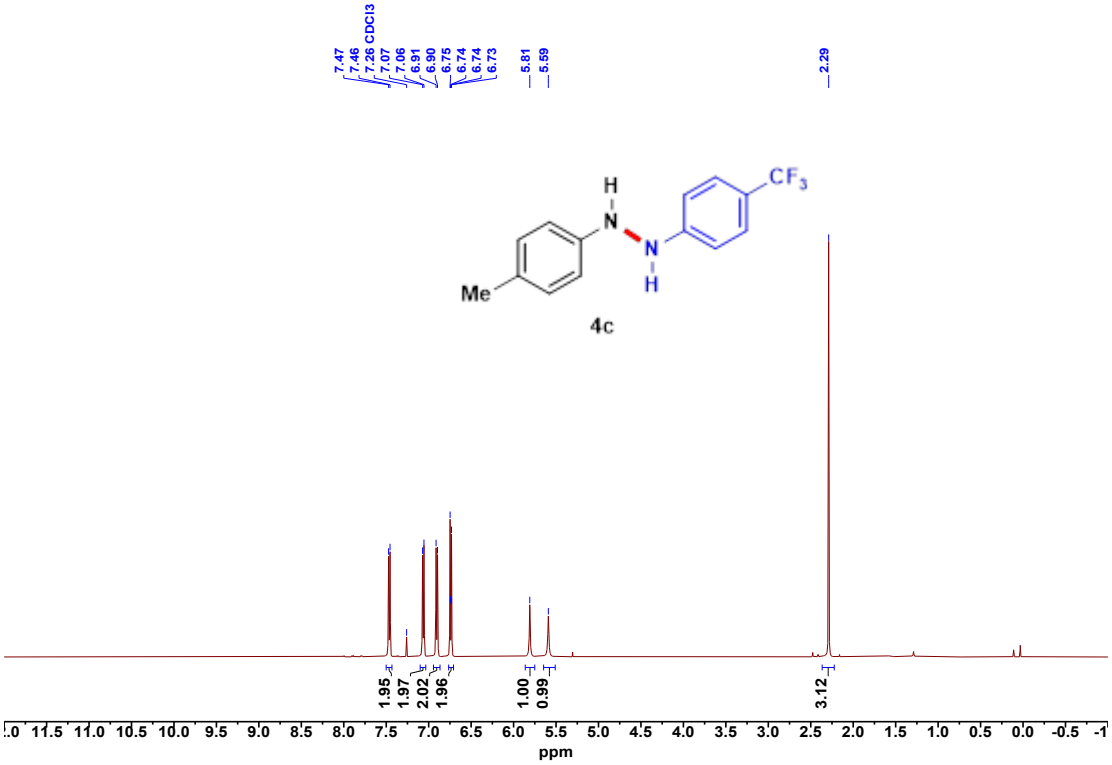
^{19}F NMR of Compound 4c (471 MHz, DMSO-d_6))



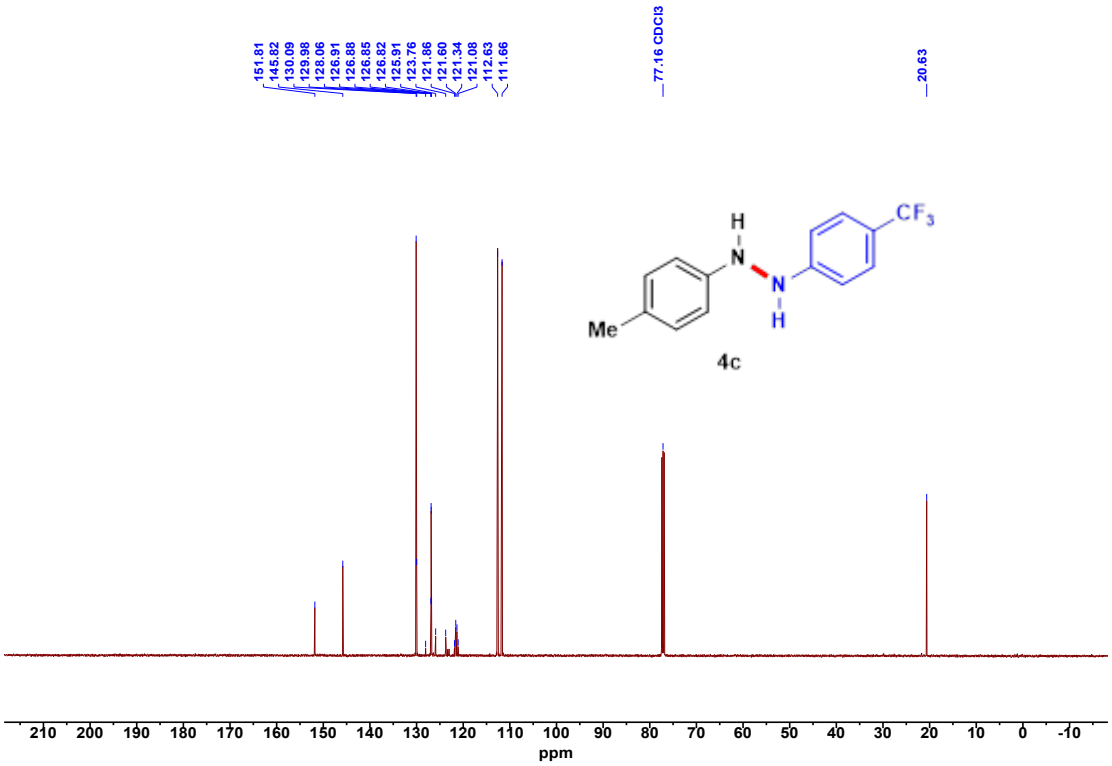
^{1}H NMR of Compound 4b (500 MHz, $CDCl_3$)



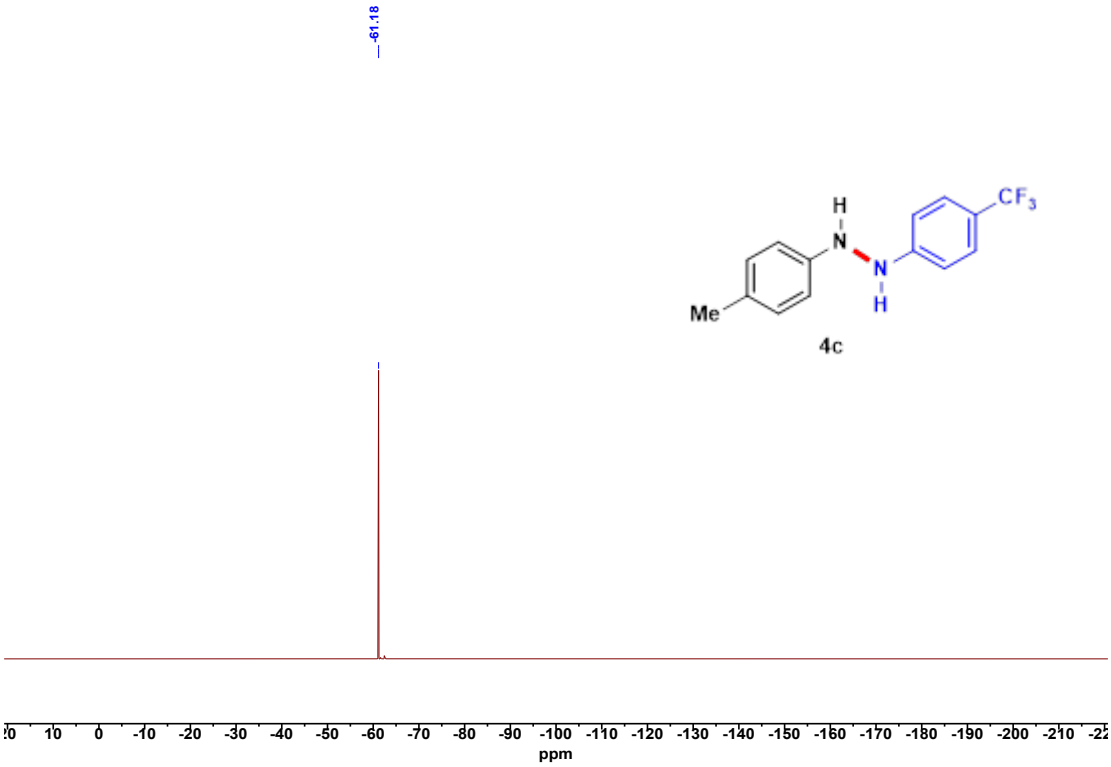
^{1}H NMR of Compound 4c (500 MHz, $CDCl_3$)



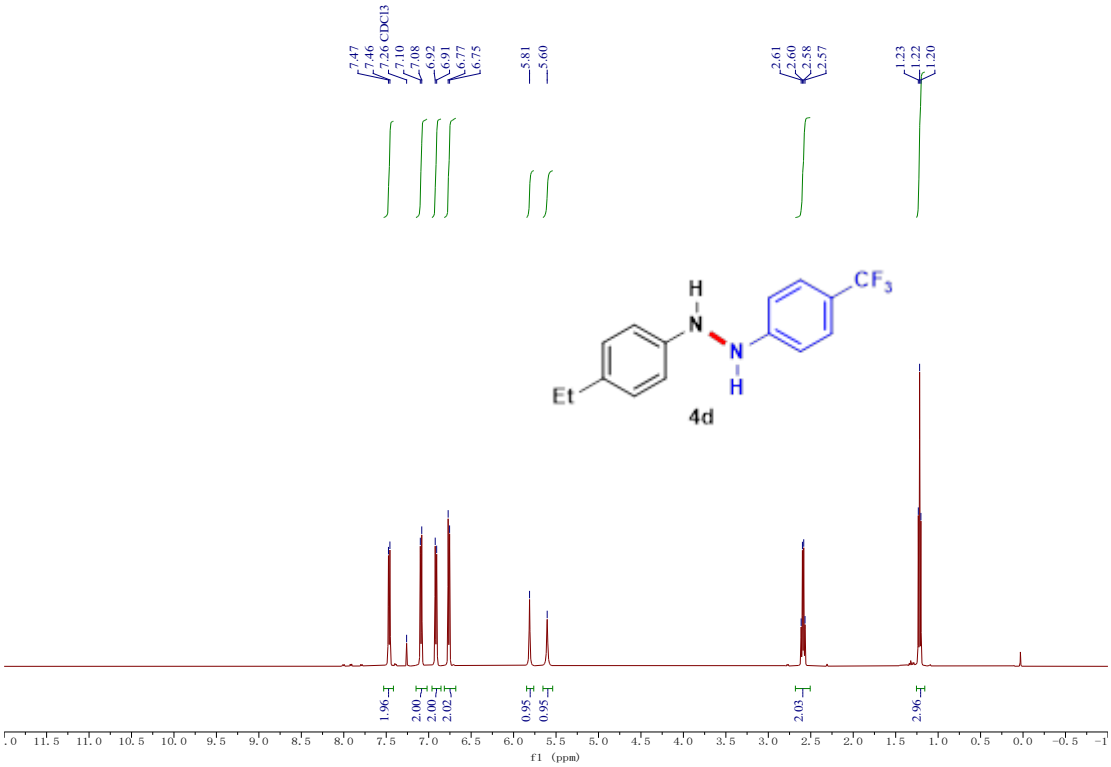
^{13}C NMR of Compound 4c (126 MHz, $CDCl_3$)



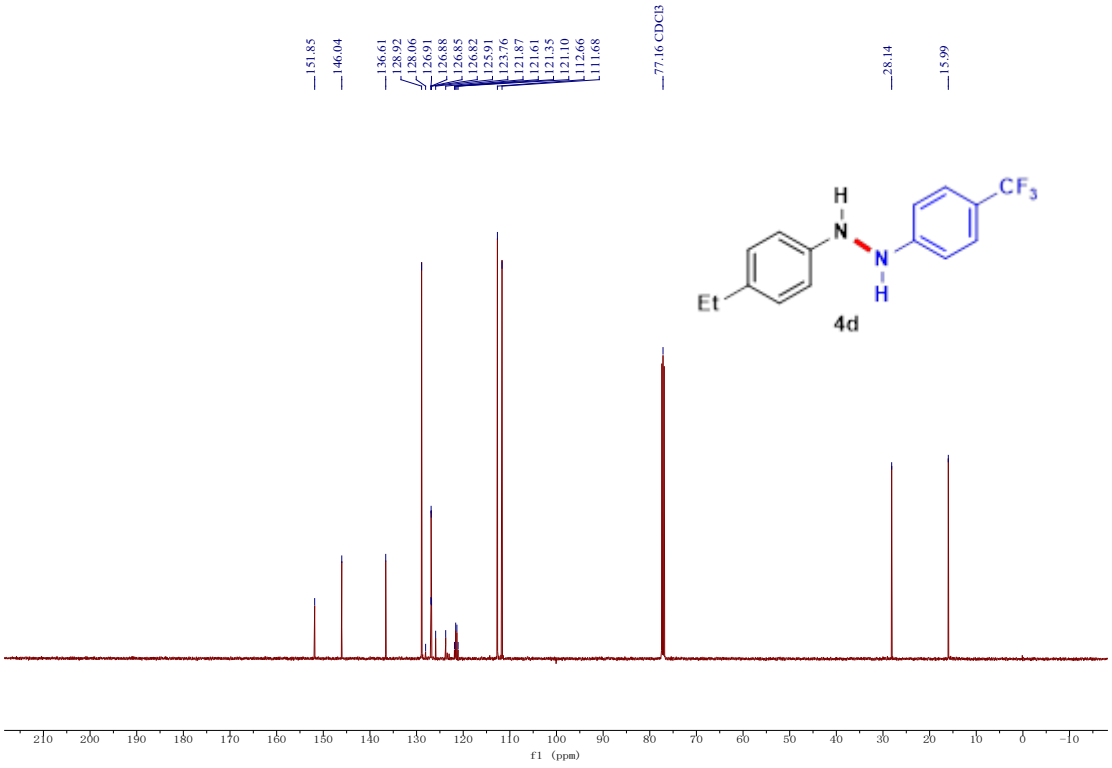
^{19}F NMR of Compound 4c (471 MHz, $CDCl_3$)



^{1}H NMR of Compound 4d (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 4d (126 MHz, $CDCl_3$)



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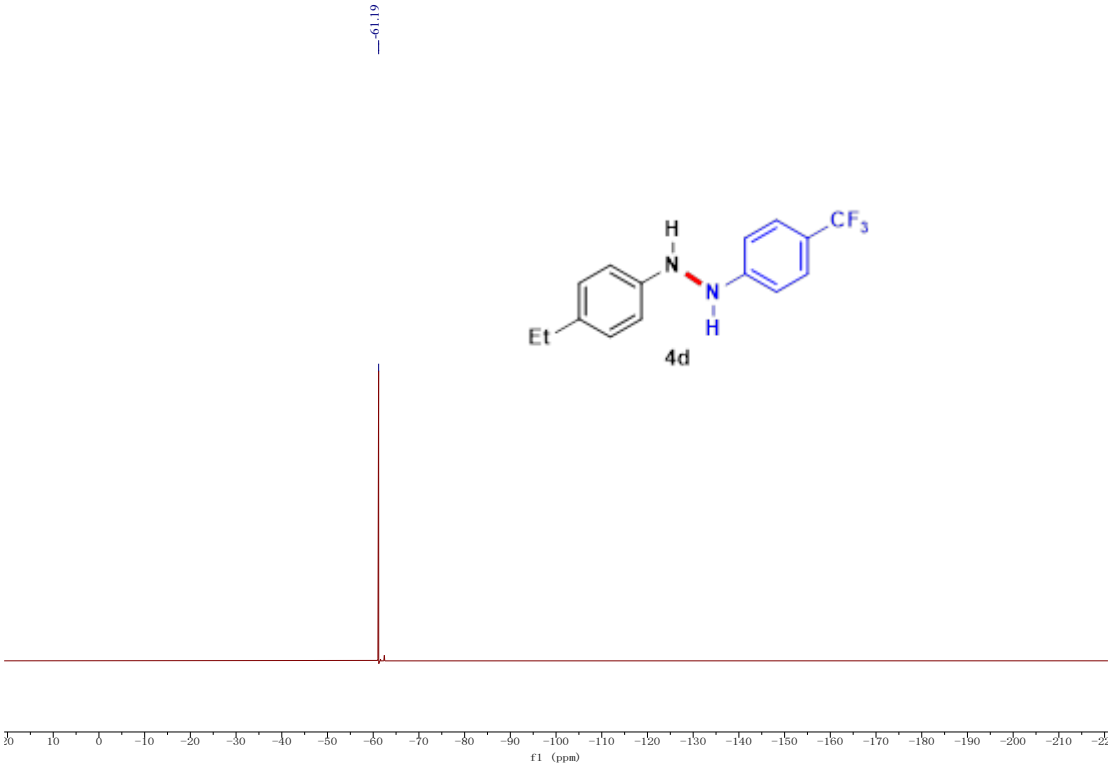
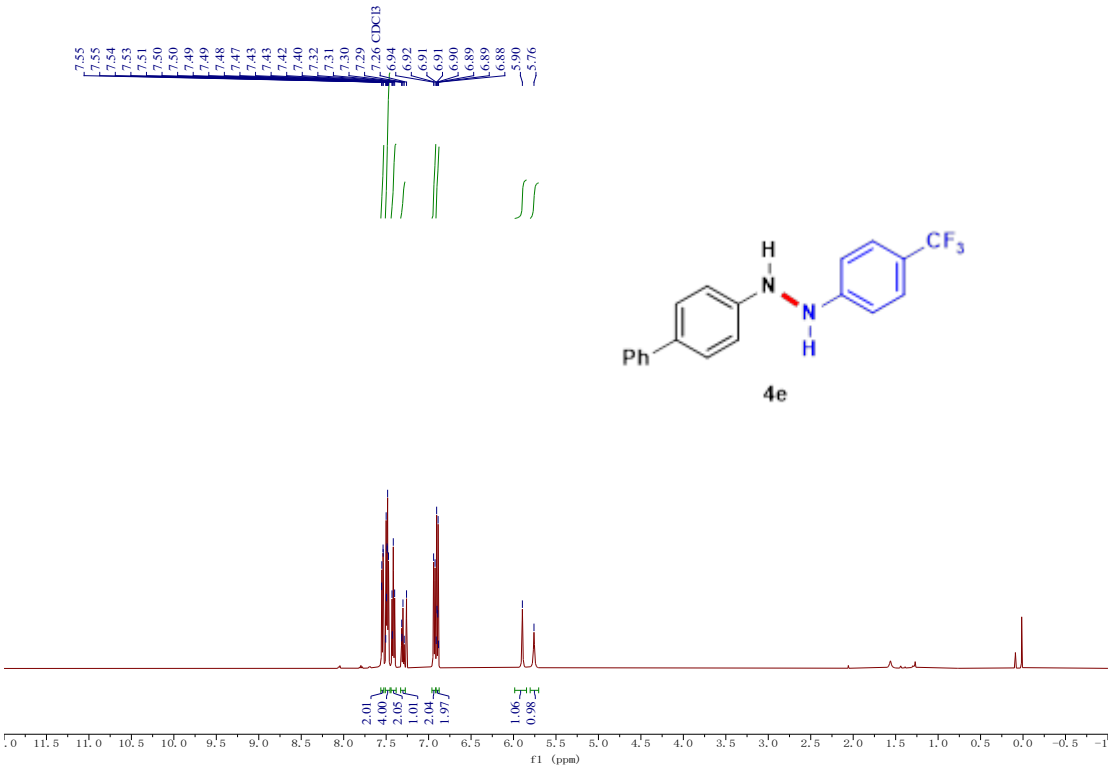
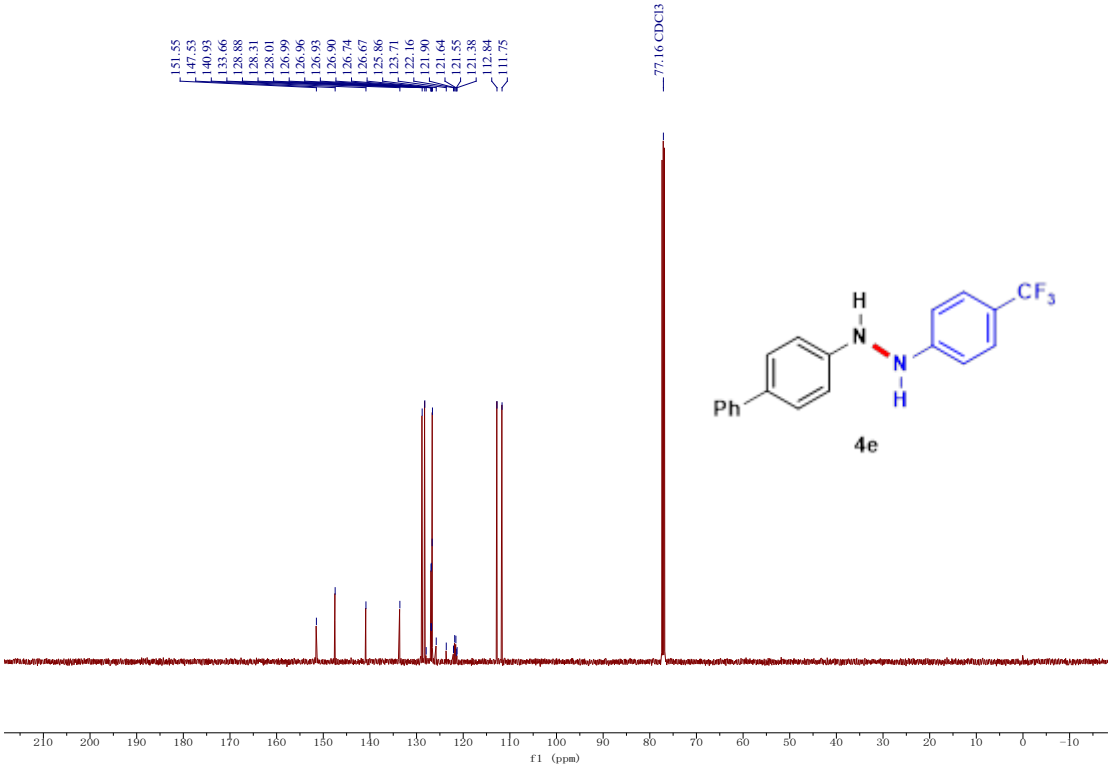


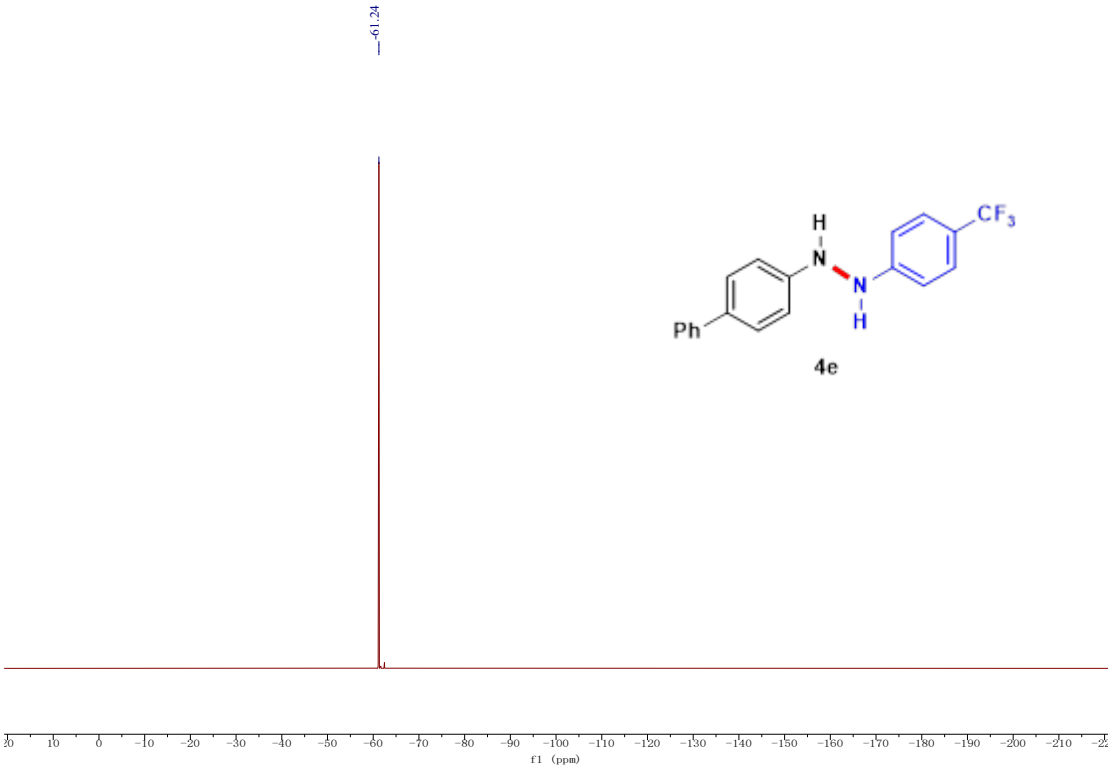
^{1}H NMR of Compound 4e (500 MHz, $CDCl_3$)



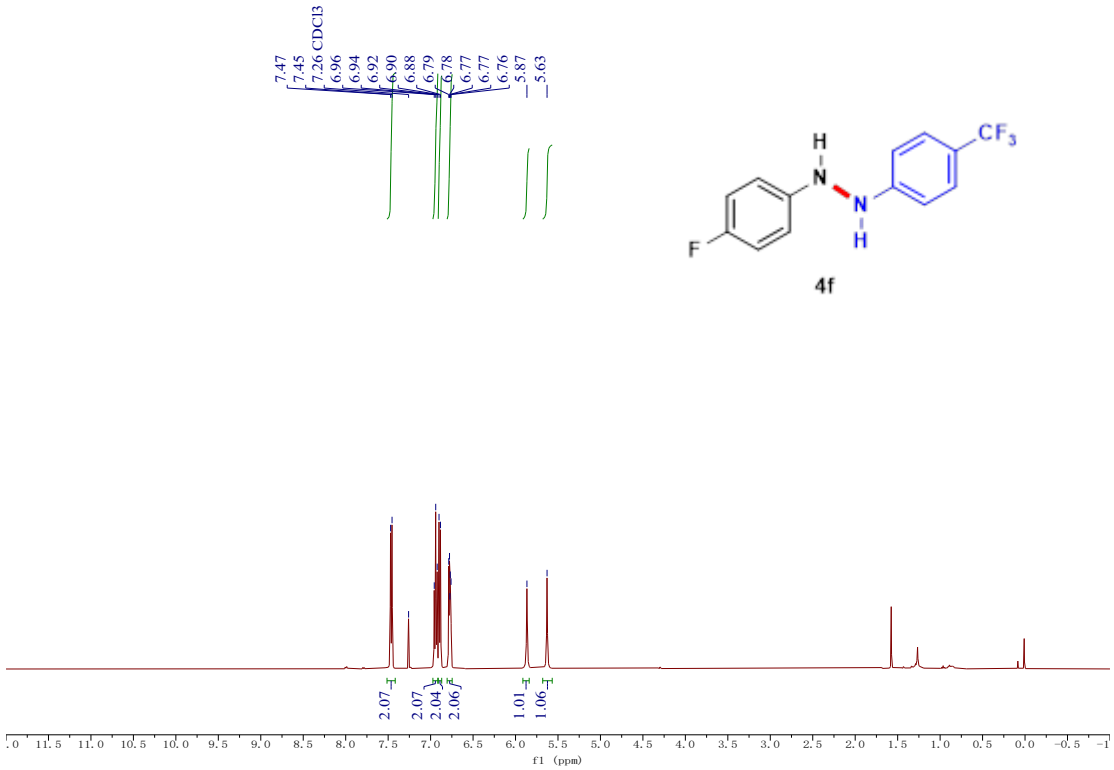
^{13}C NMR of Compound 4e (126 MHz, $CDCl_3$)



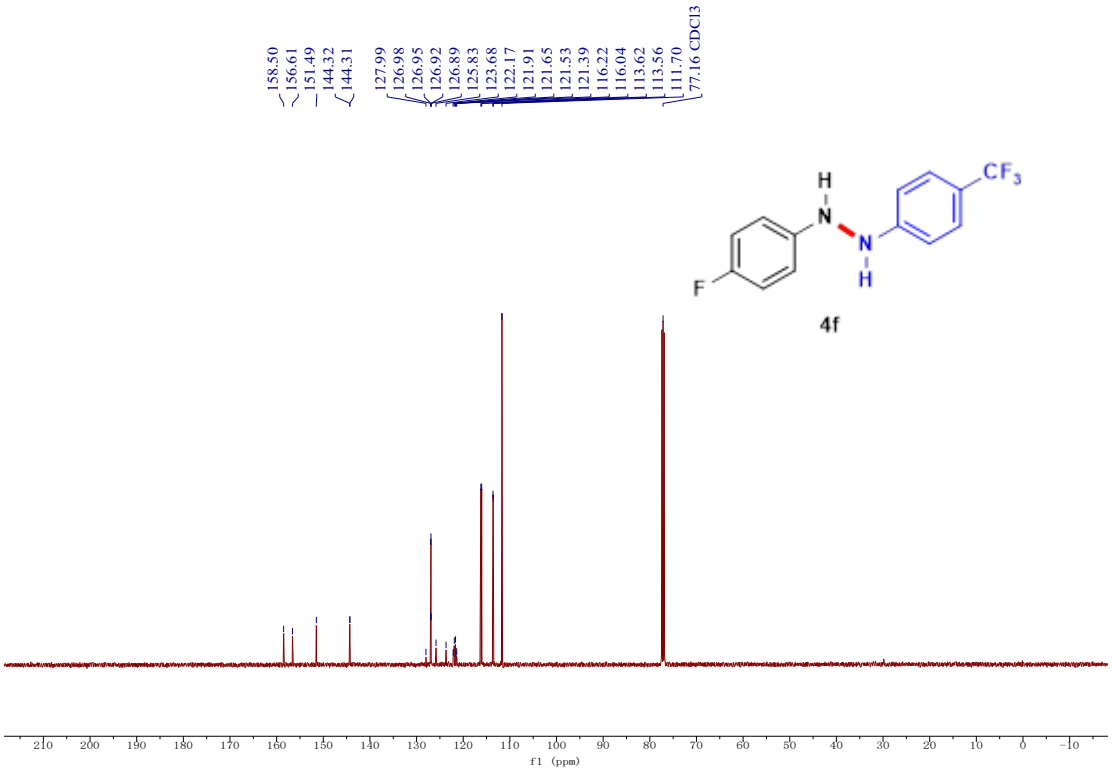
^{19}F NMR of Compound 4e (471 MHz, $CDCl_3$)



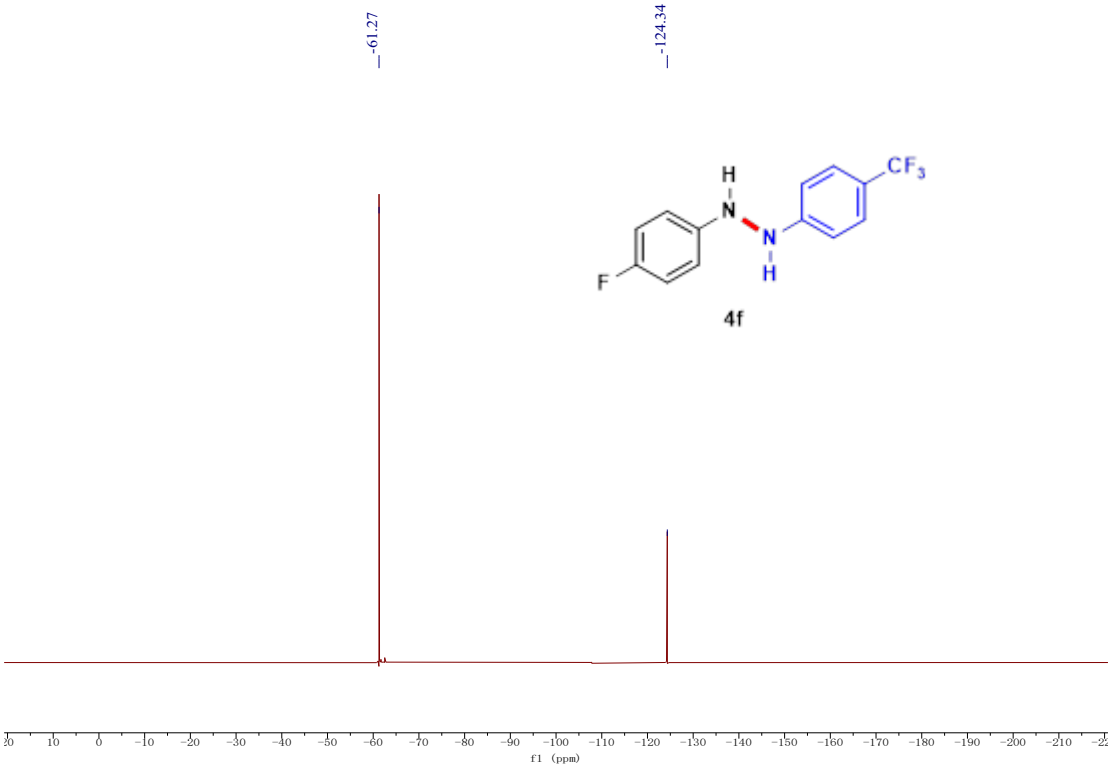
^{1}H NMR of Compound 4f (500 MHz, $CDCl_3$)



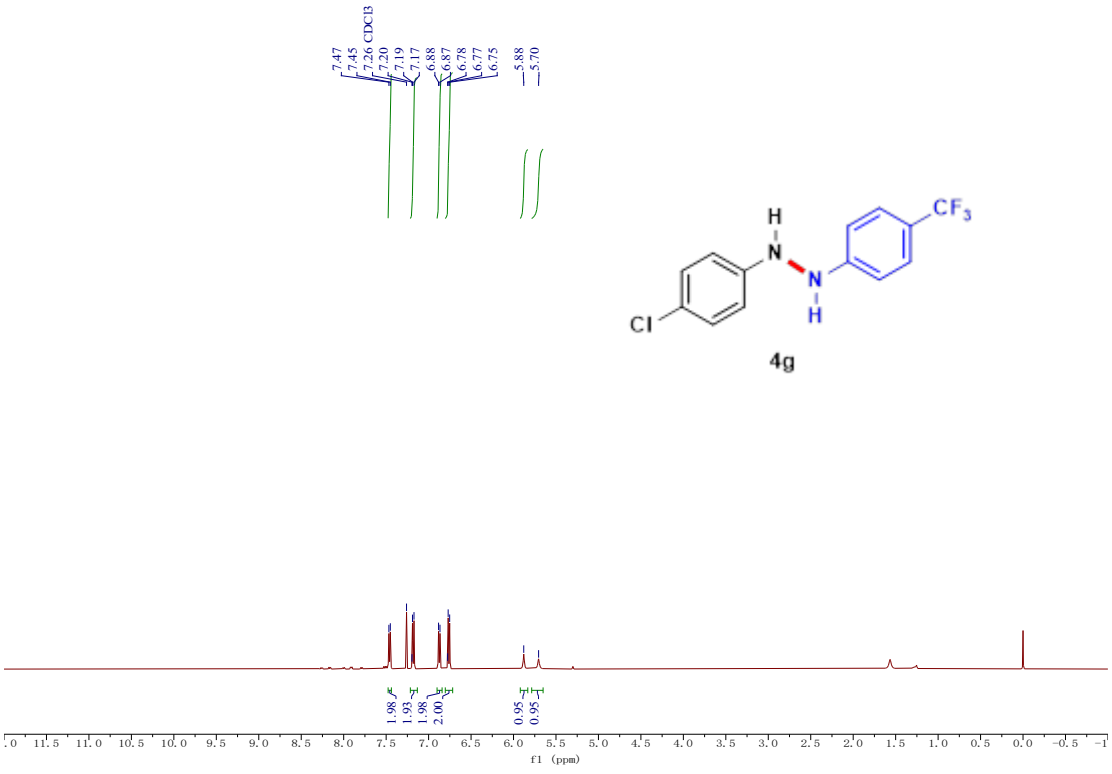
^{13}C NMR of Compound 4f (126 MHz, $CDCl_3$)



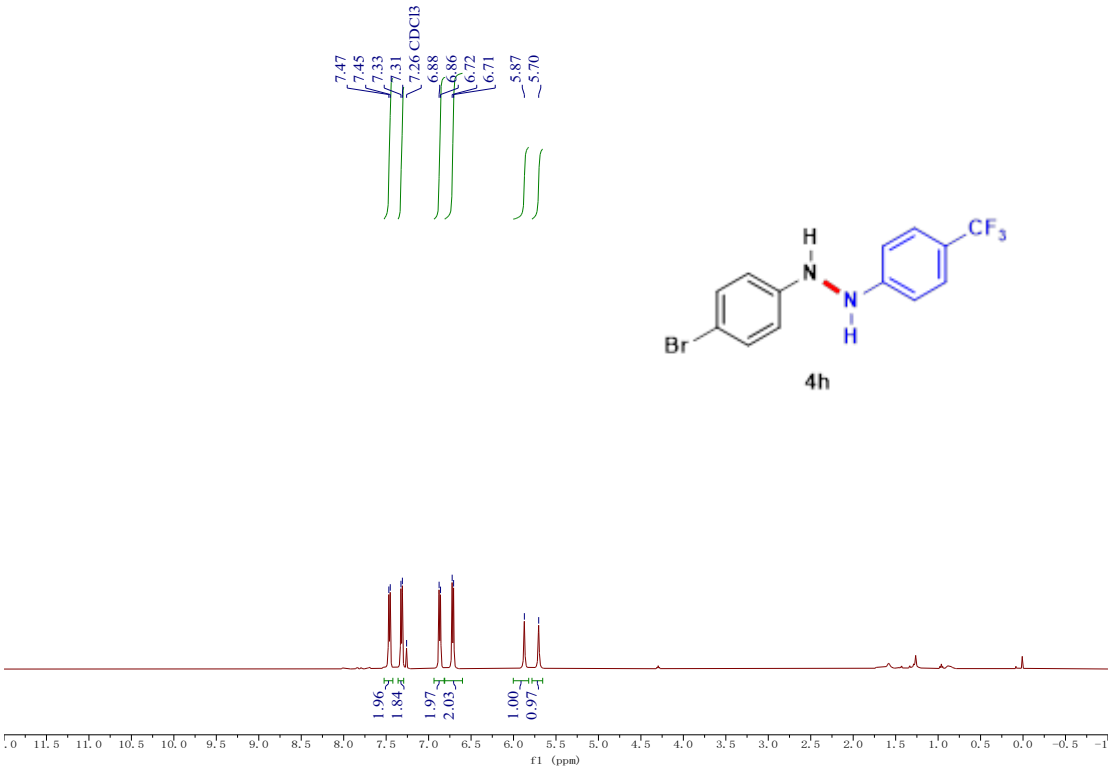
^{19}F NMR of Compound 4f (471 MHz, $CDCl_3$)



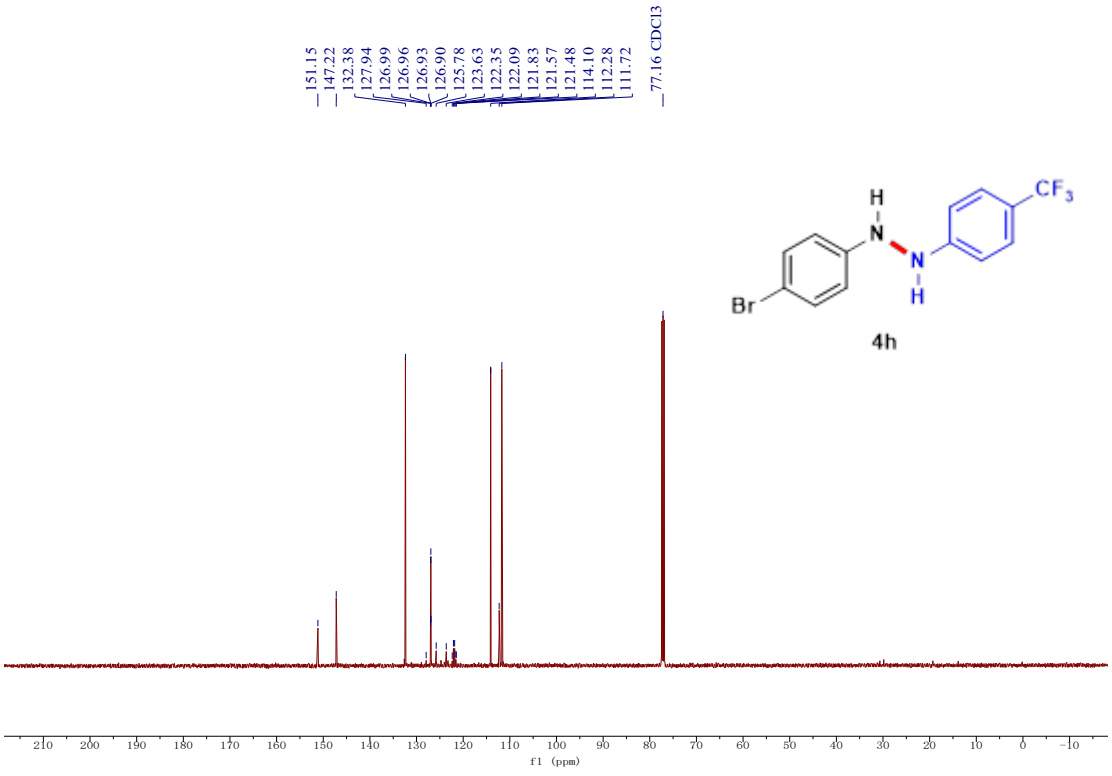
^{1}H NMR of Compound 4g (500 MHz, $CDCl_3$)



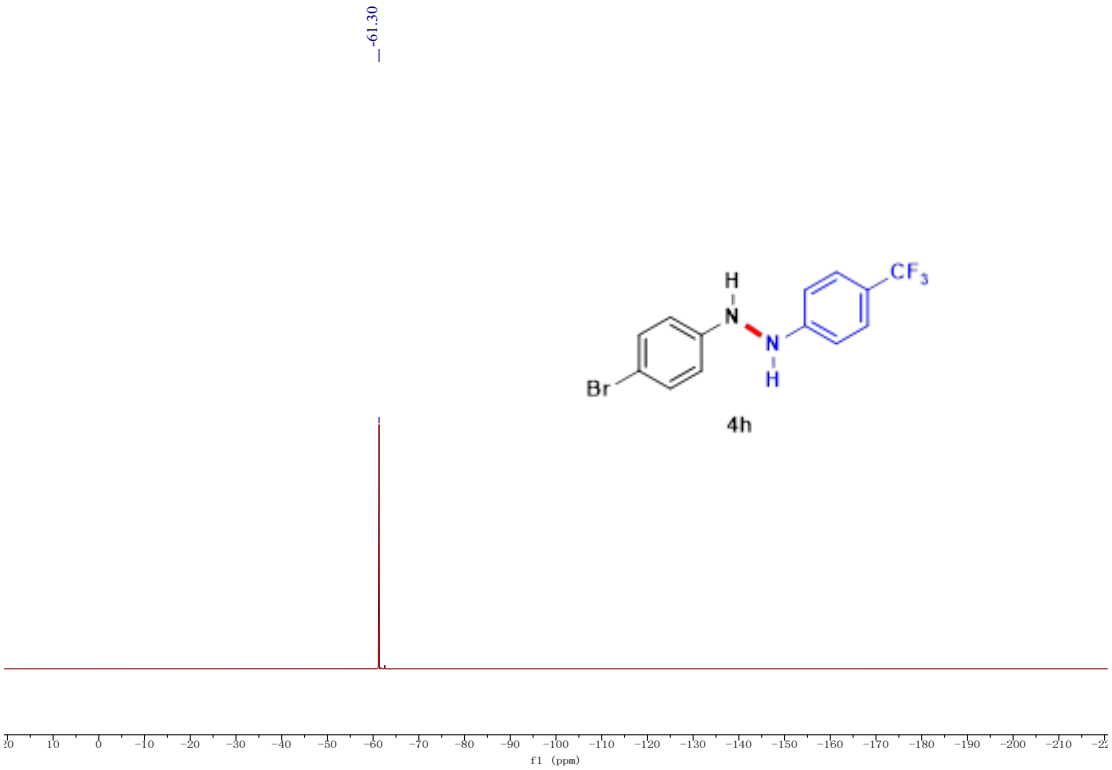
^{1}H NMR of Compound 4h (500 MHz, $CDCl_3$)



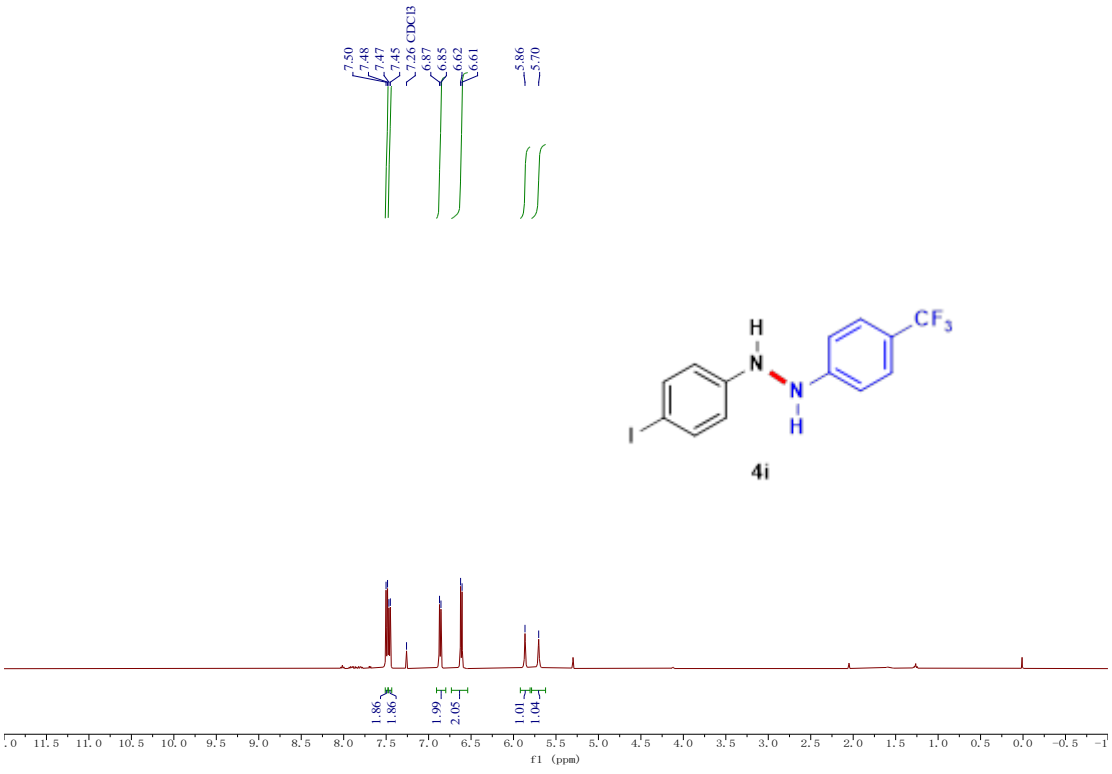
^{13}C NMR of Compound 4h (126 MHz, $CDCl_3$)



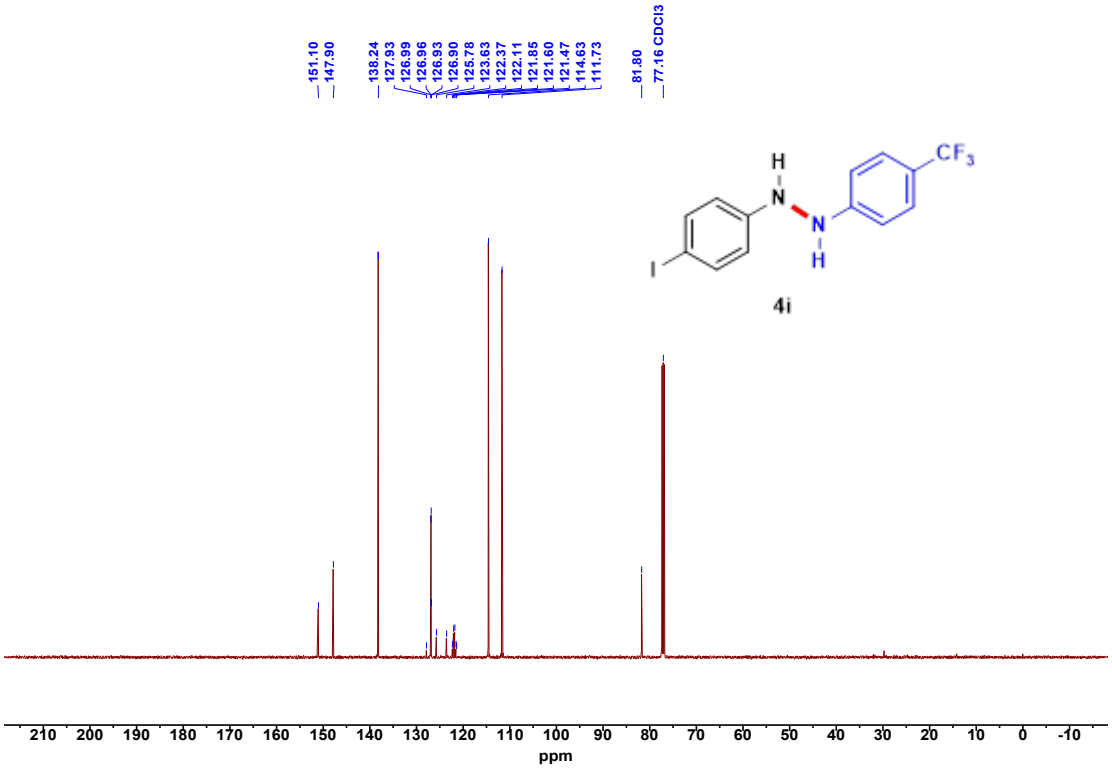
^{19}F NMR of Compound 4h (471 MHz, $CDCl_3$)



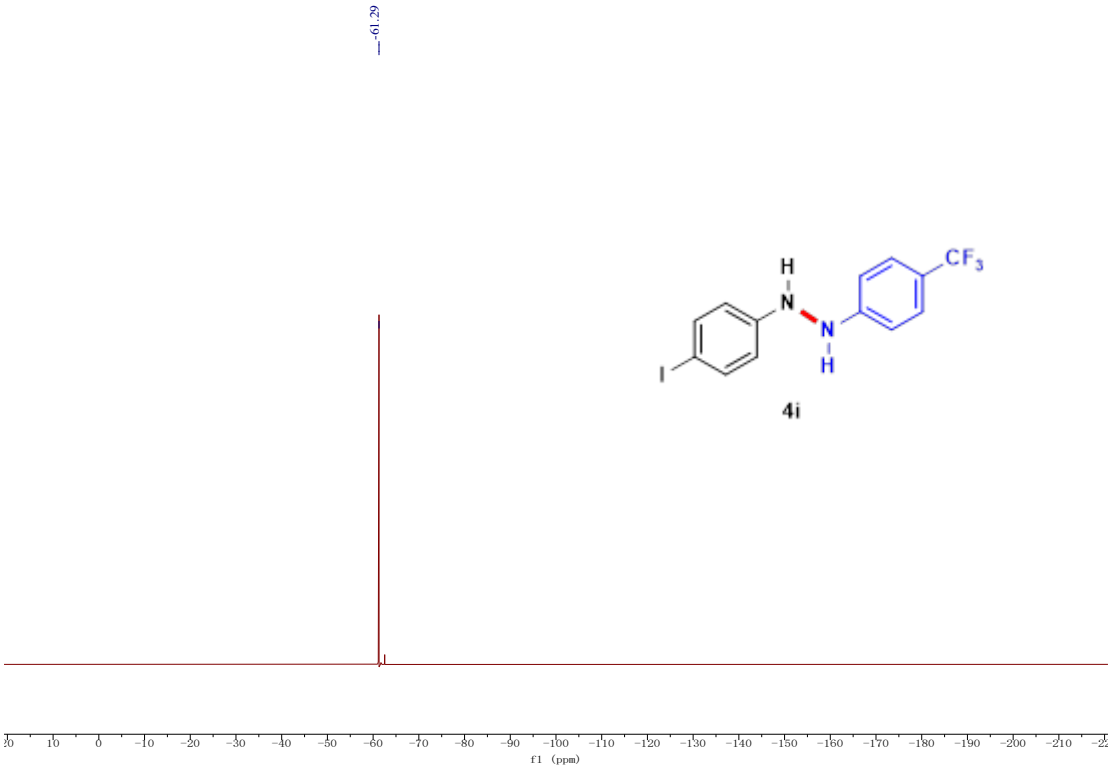
^{1}H NMR of Compound 4i (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 4i (126 MHz, $CDCl_3$)



^{19}F NMR of Compound 4i (471 MHz, $CDCl_3$)



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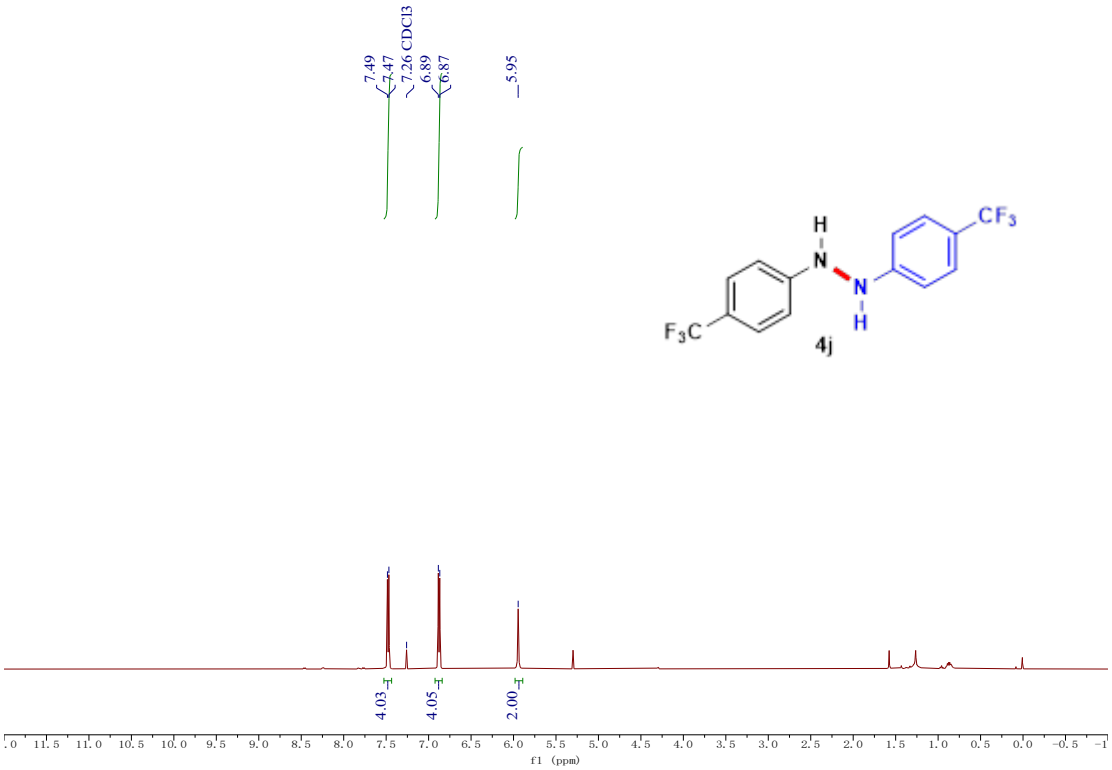
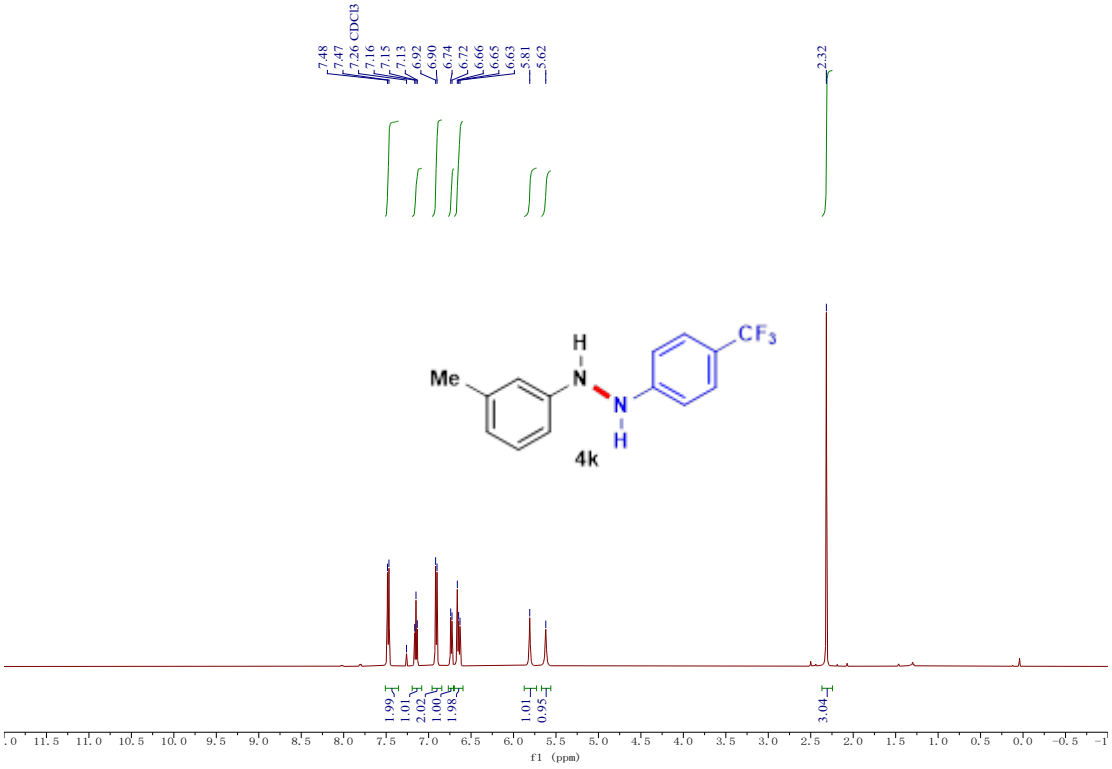
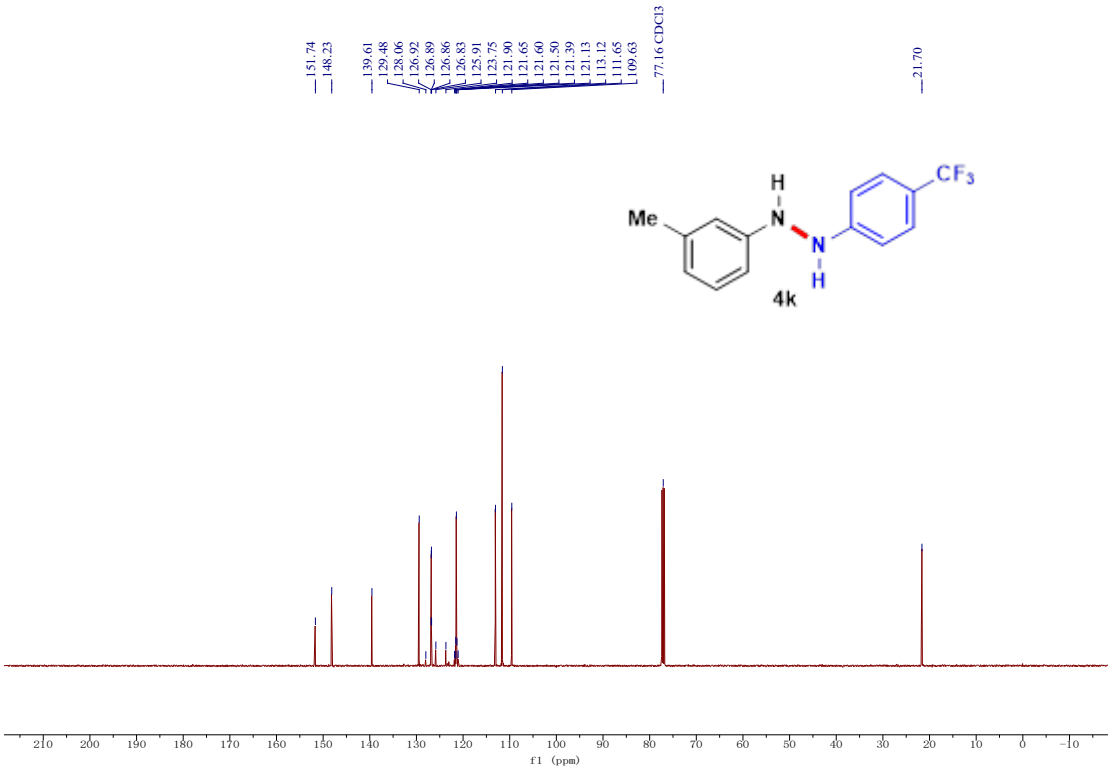


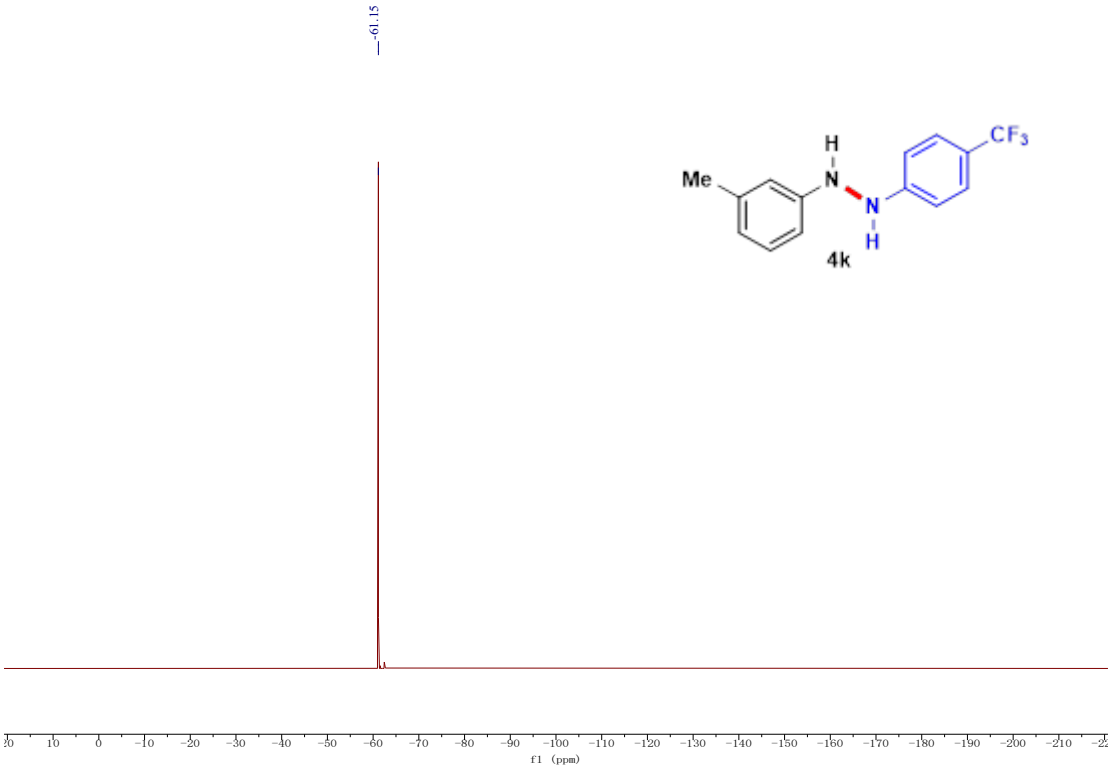
^{1}H NMR of Compound 4k (500 MHz, $CDCl_3$)



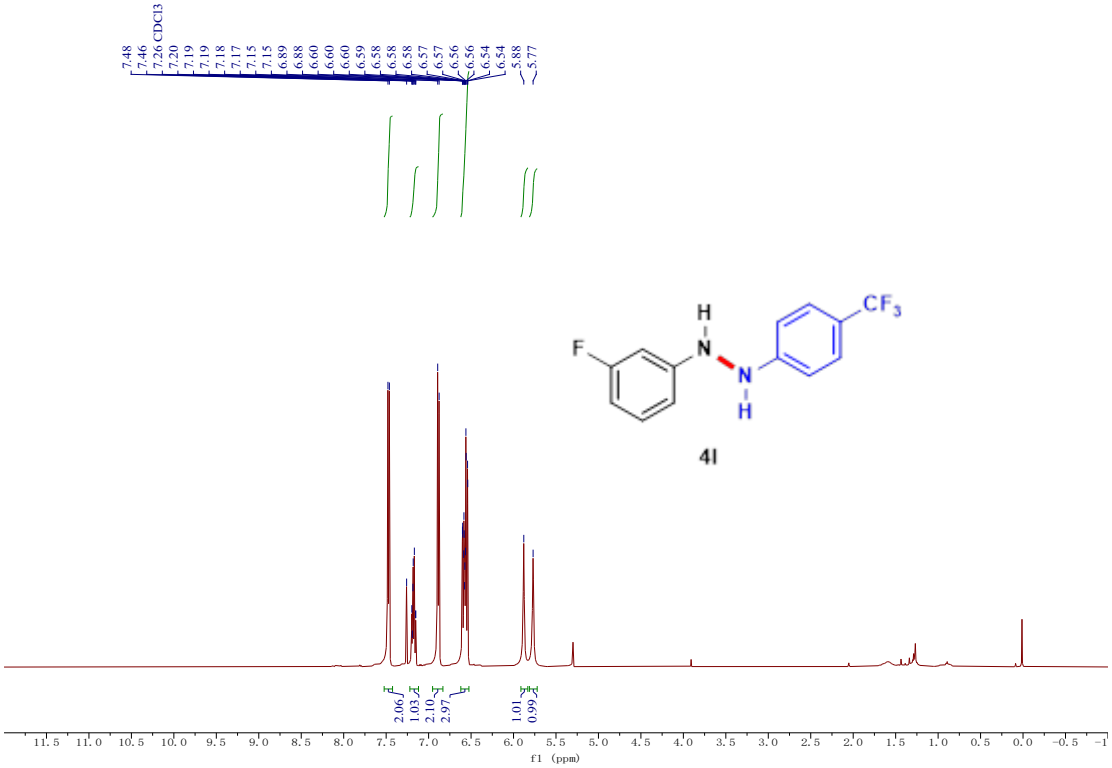
^{13}C NMR of Compound 4k (126 MHz, $CDCl_3$)



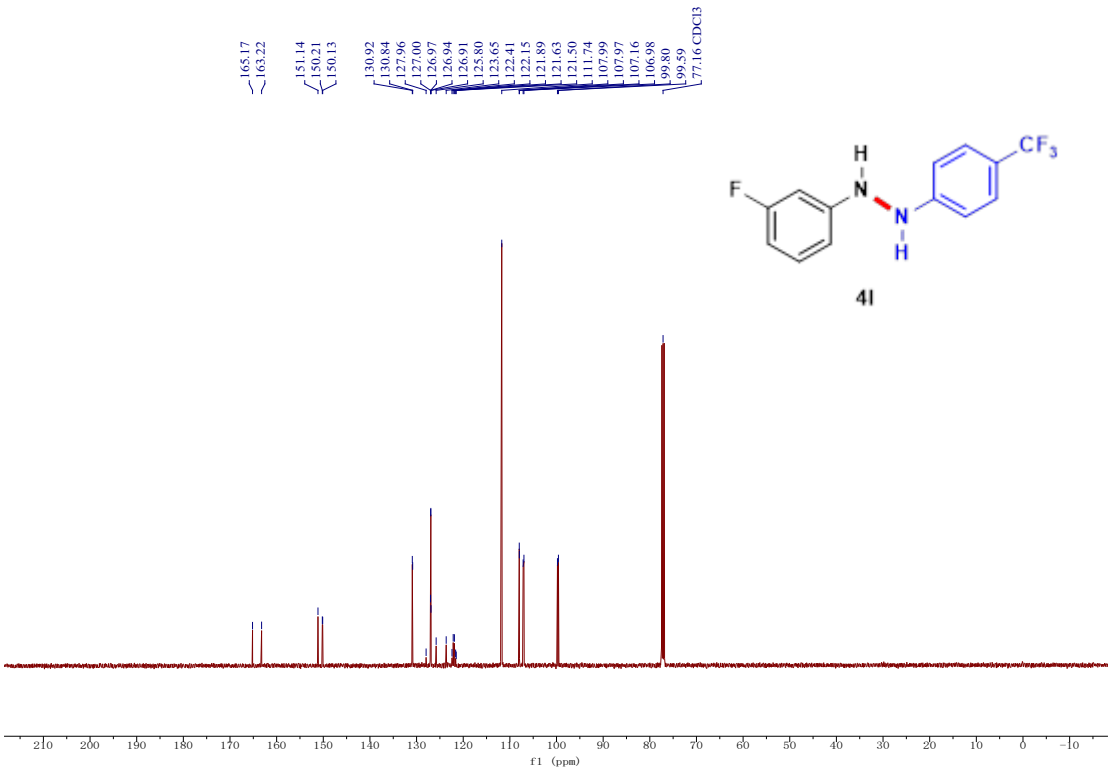
^{19}F NMR of Compound 4k (471 MHz, $CDCl_3$)



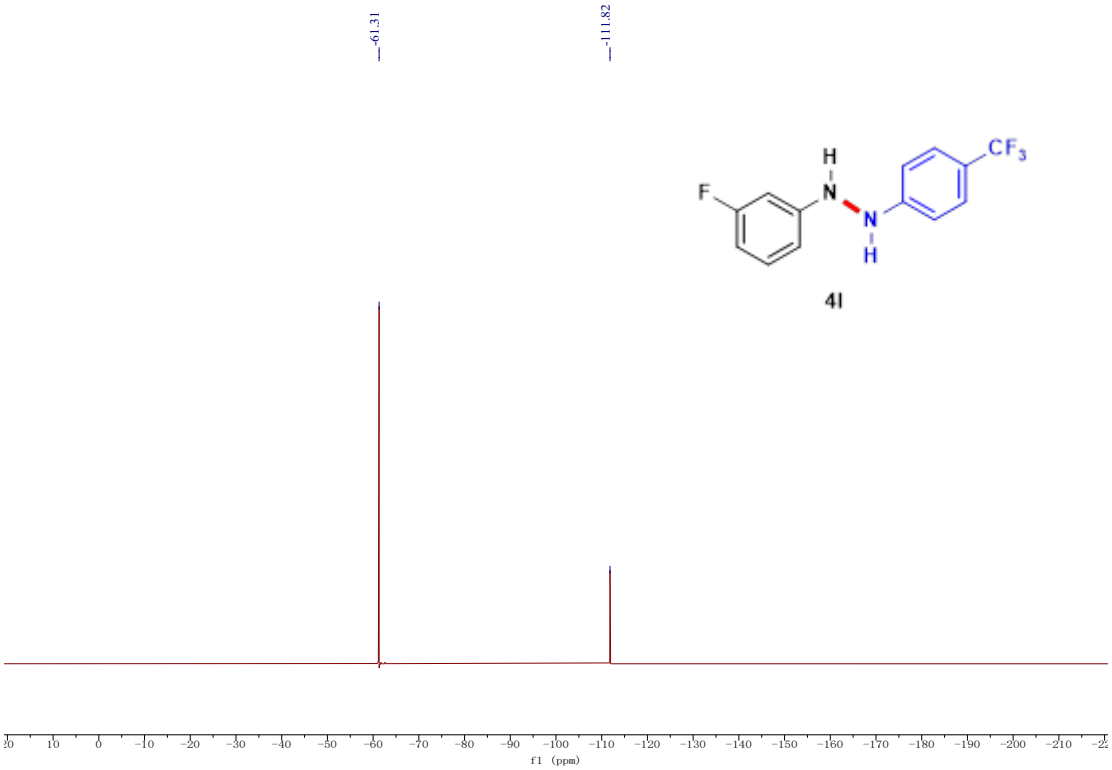
^{1}H NMR of Compound 4l (500 MHz, $CDCl_3$)



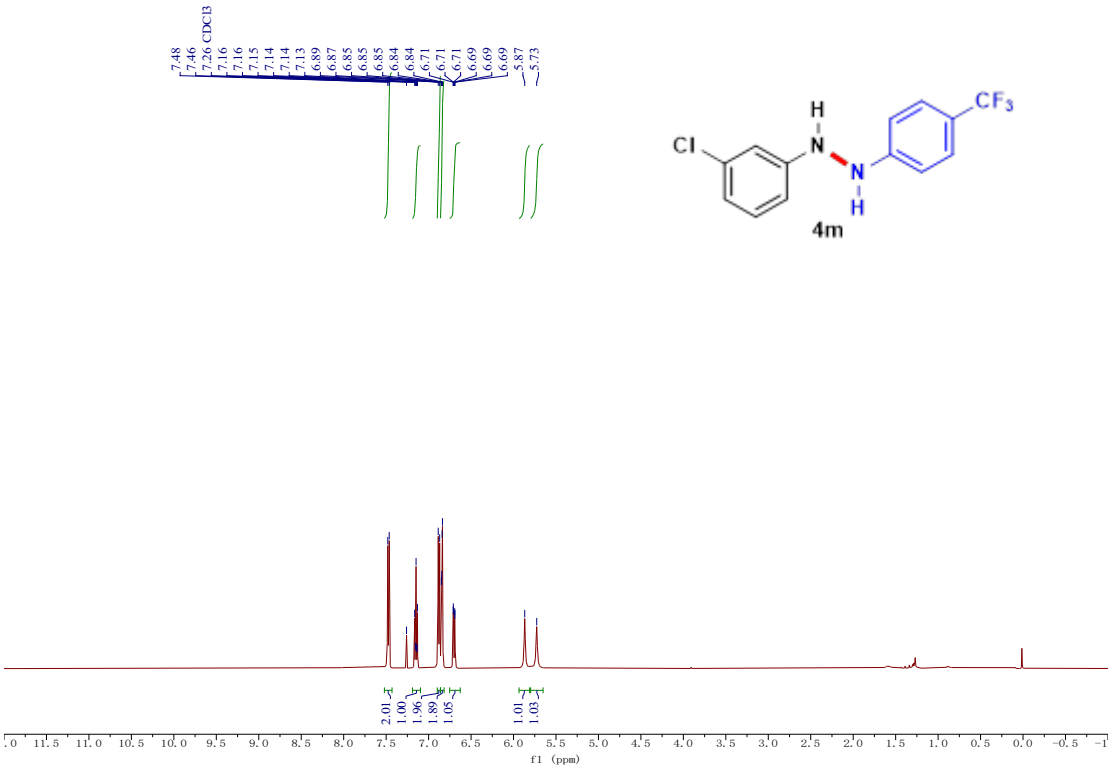
^{13}C NMR of Compound 4l (126 MHz, $CDCl_3$)



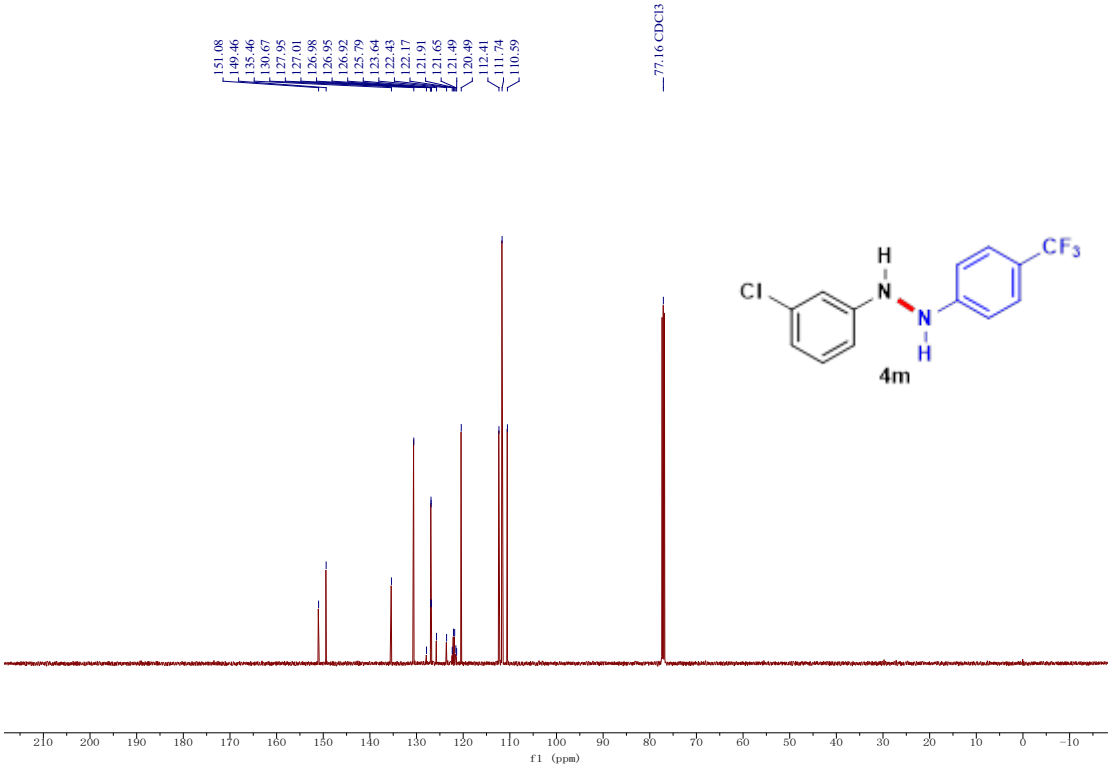
^{19}F NMR of Compound 4l (471 MHz, $CDCl_3$)



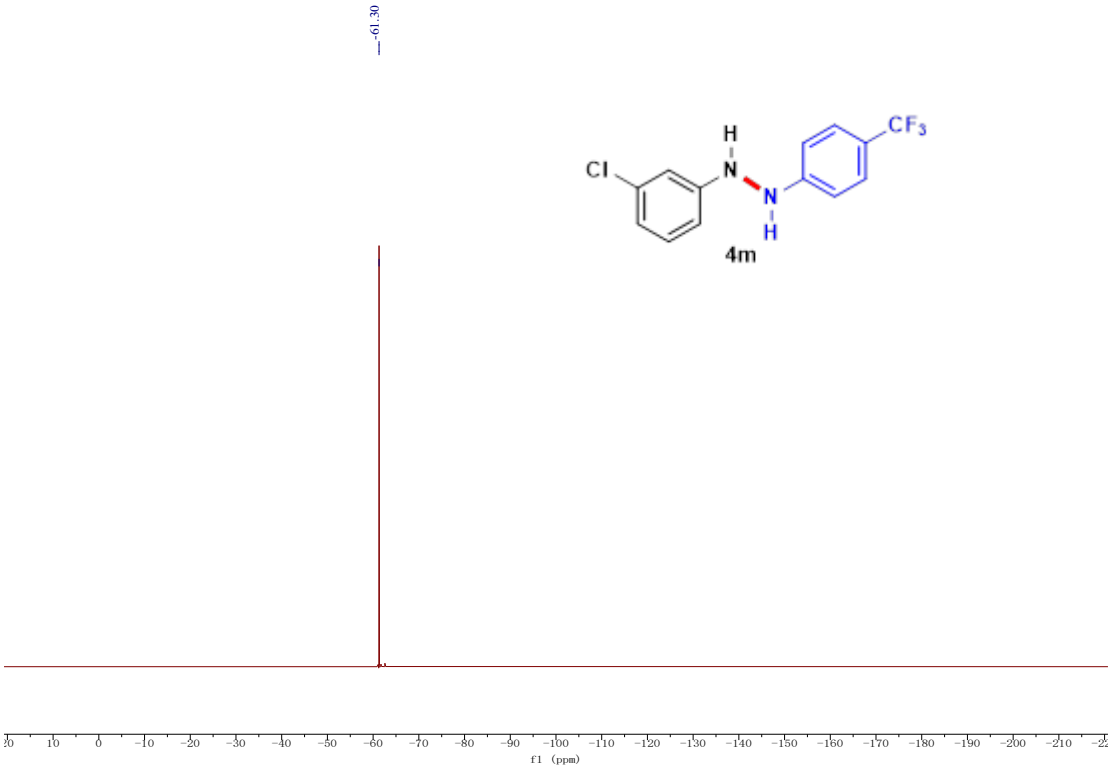
^{1}H NMR of Compound 4m (500 MHz, $CDCl_3$)



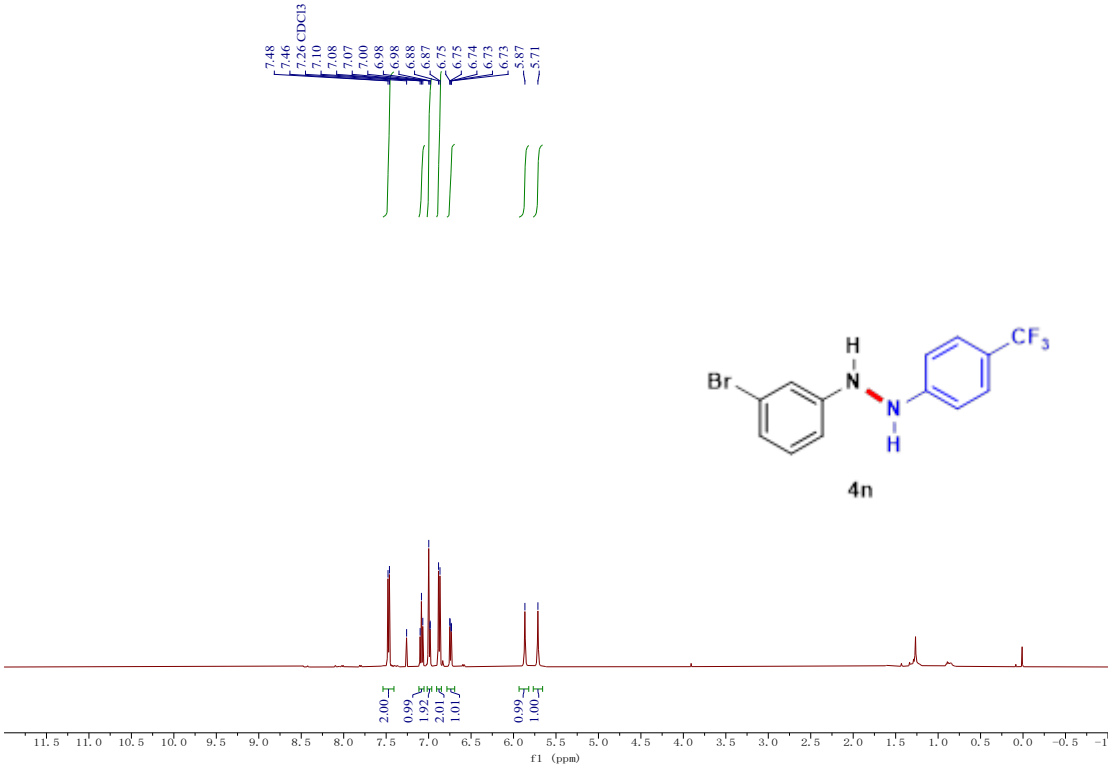
^{13}C NMR of Compound 4m (126 MHz, $CDCl_3$)



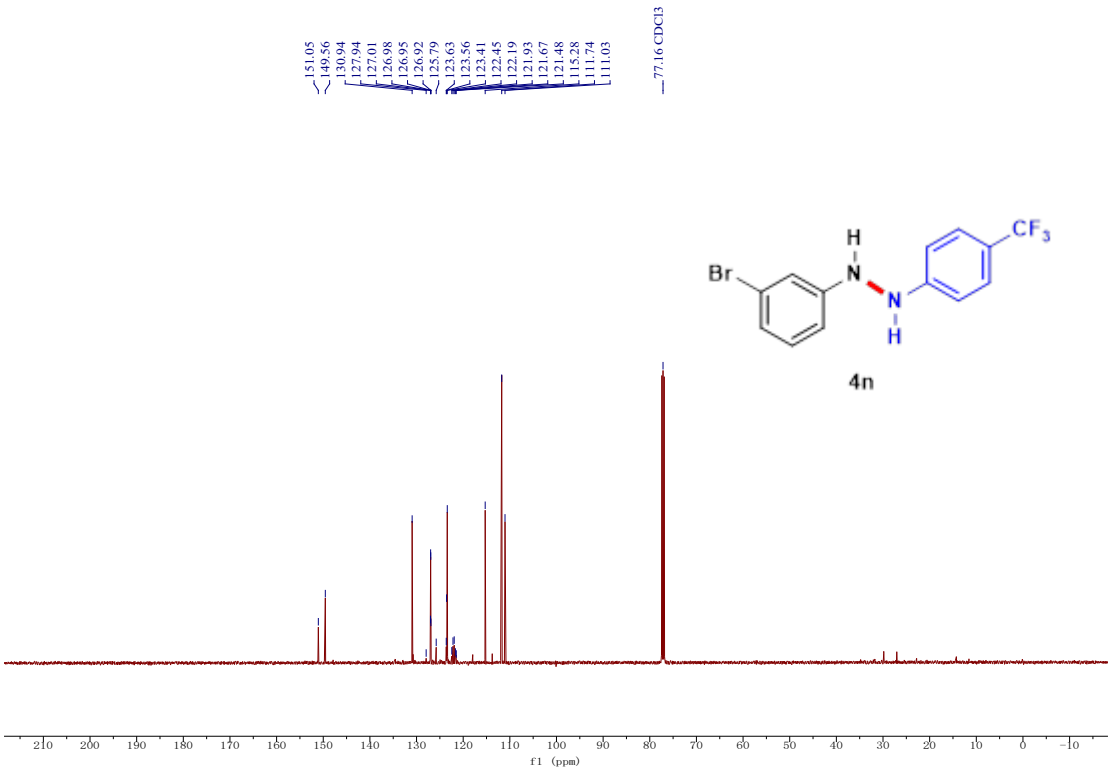
^{19}F NMR of Compound 4m (471 MHz, $CDCl_3$)



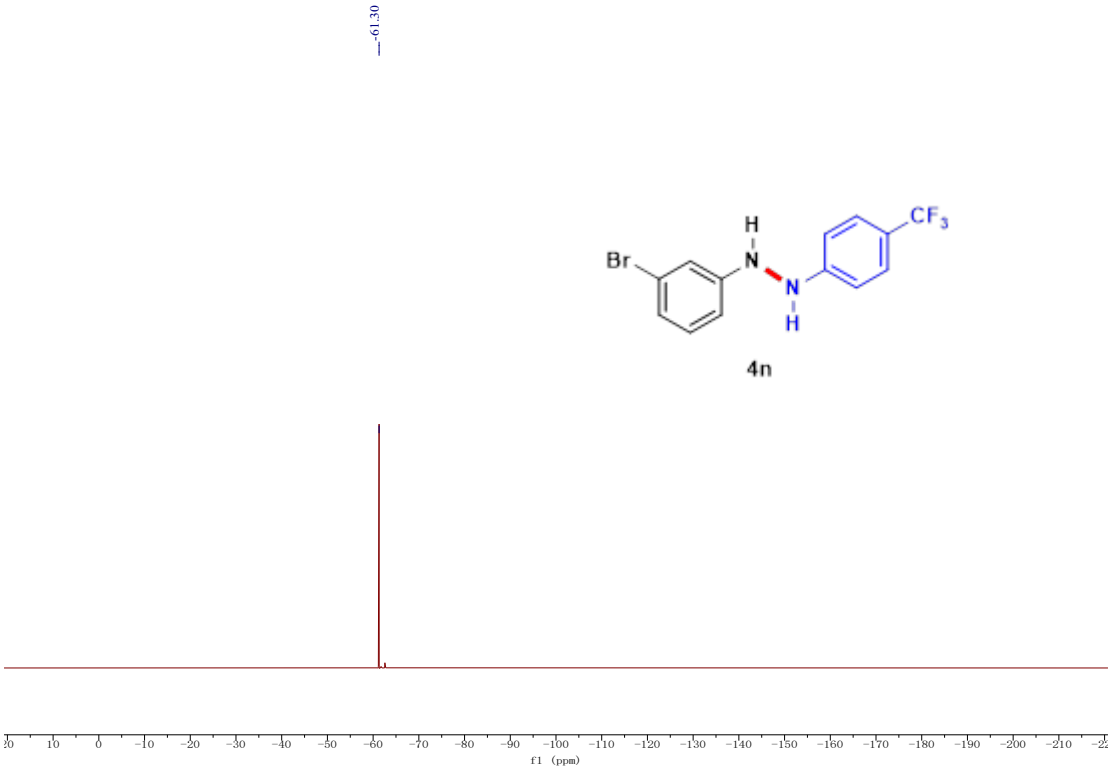
^{1}H NMR of Compound 4n (500 MHz, $CDCl_3$)



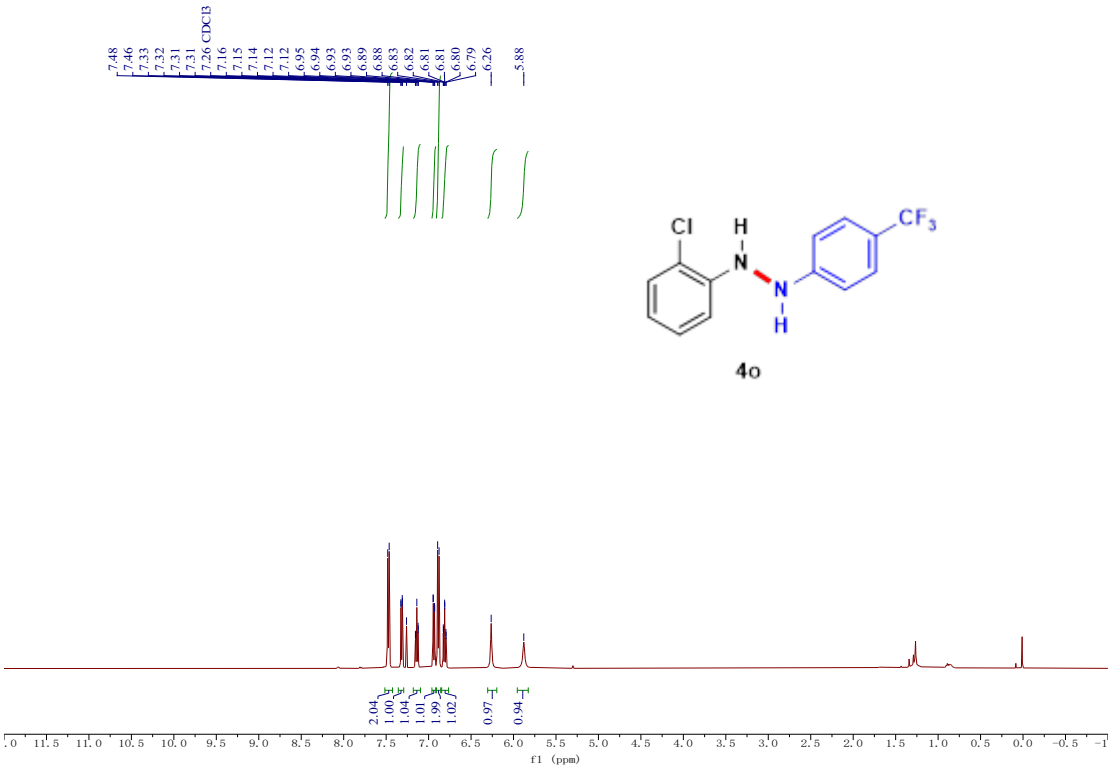
^{13}C NMR of Compound 4n (126 MHz, $CDCl_3$)



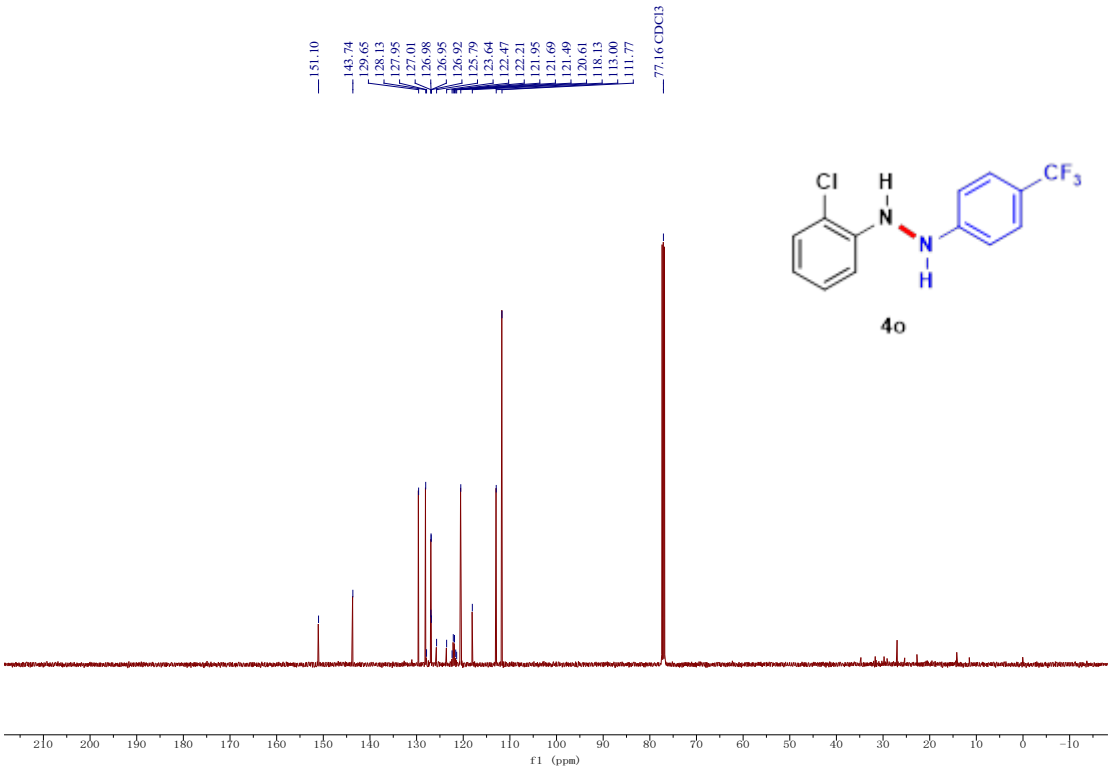
^{19}F NMR of Compound 4n (471 MHz, $CDCl_3$)



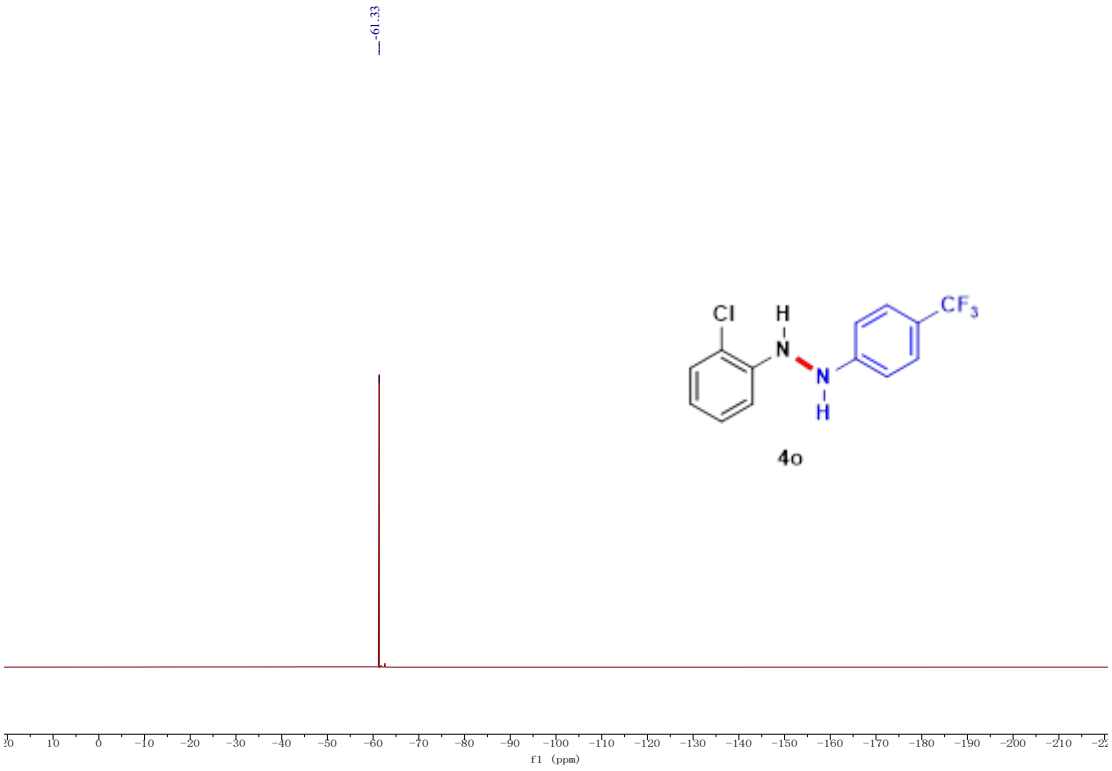
^{1}H NMR of Compound 4o (500 MHz, $CDCl_3$)



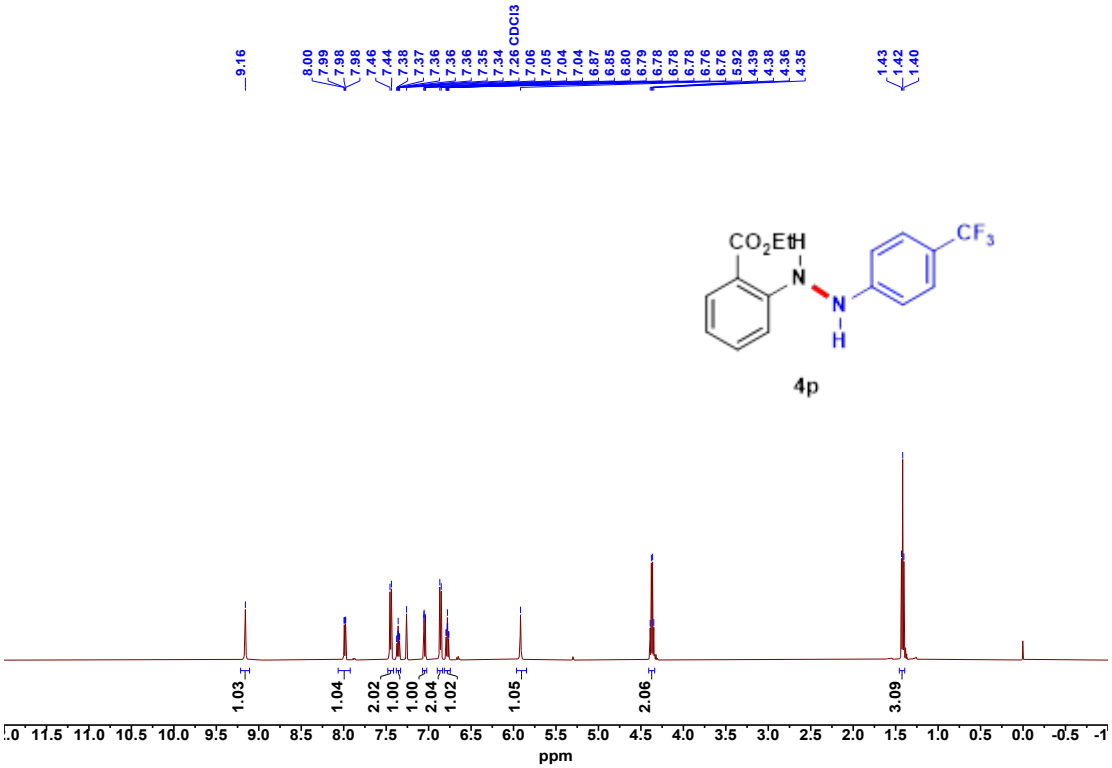
^{13}C NMR of Compound 4o (126 MHz, $CDCl_3$)



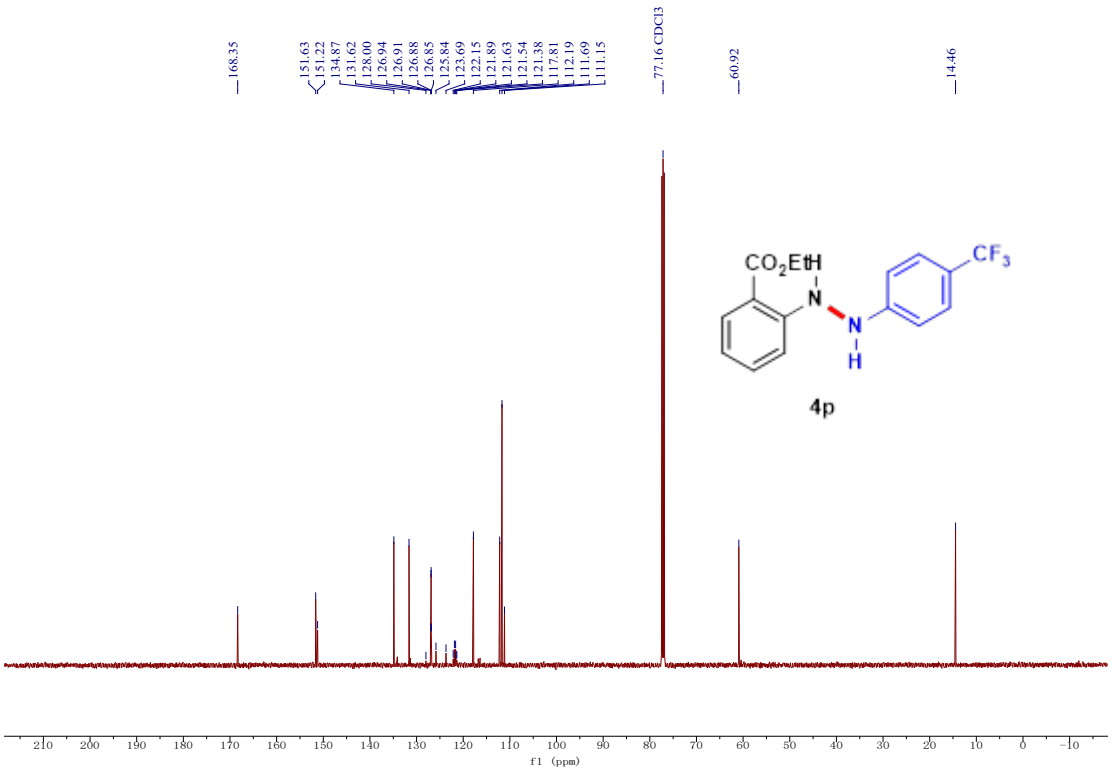
^{19}F NMR of Compound 4o (471 MHz, $CDCl_3$)



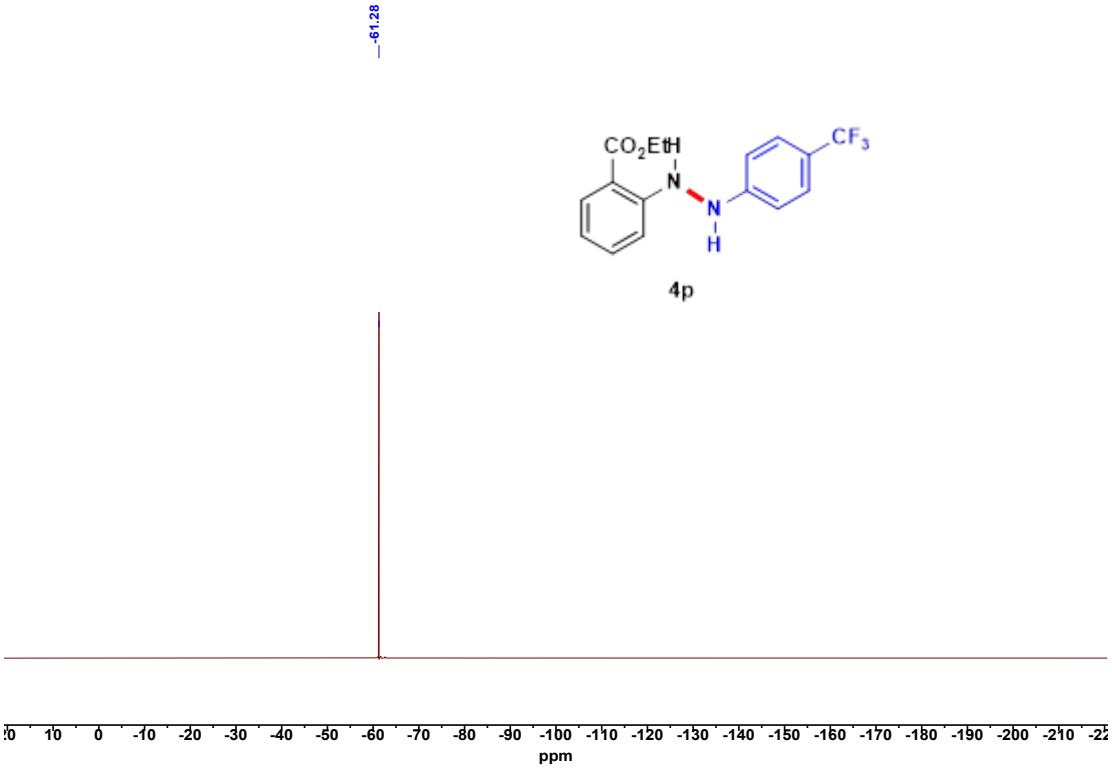
^{1}H NMR of Compound 4p (500 MHz, $CDCl_3$)



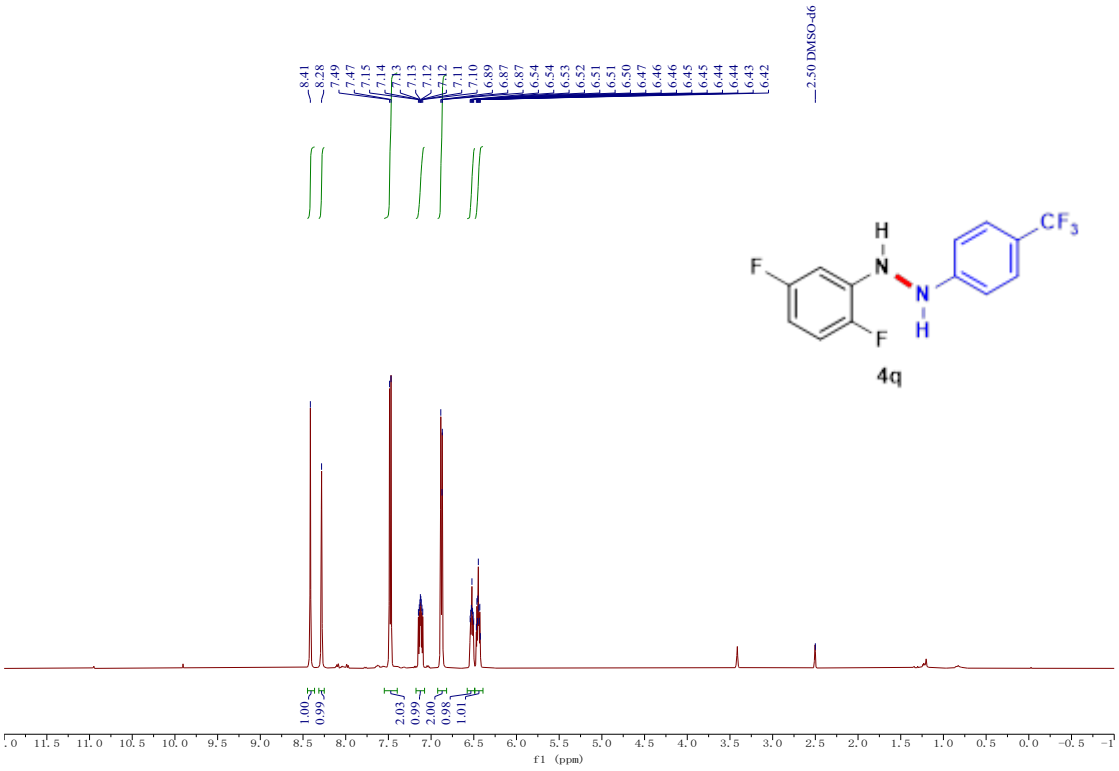
^{13}C NMR of Compound 4p (126 MHz, $CDCl_3$)



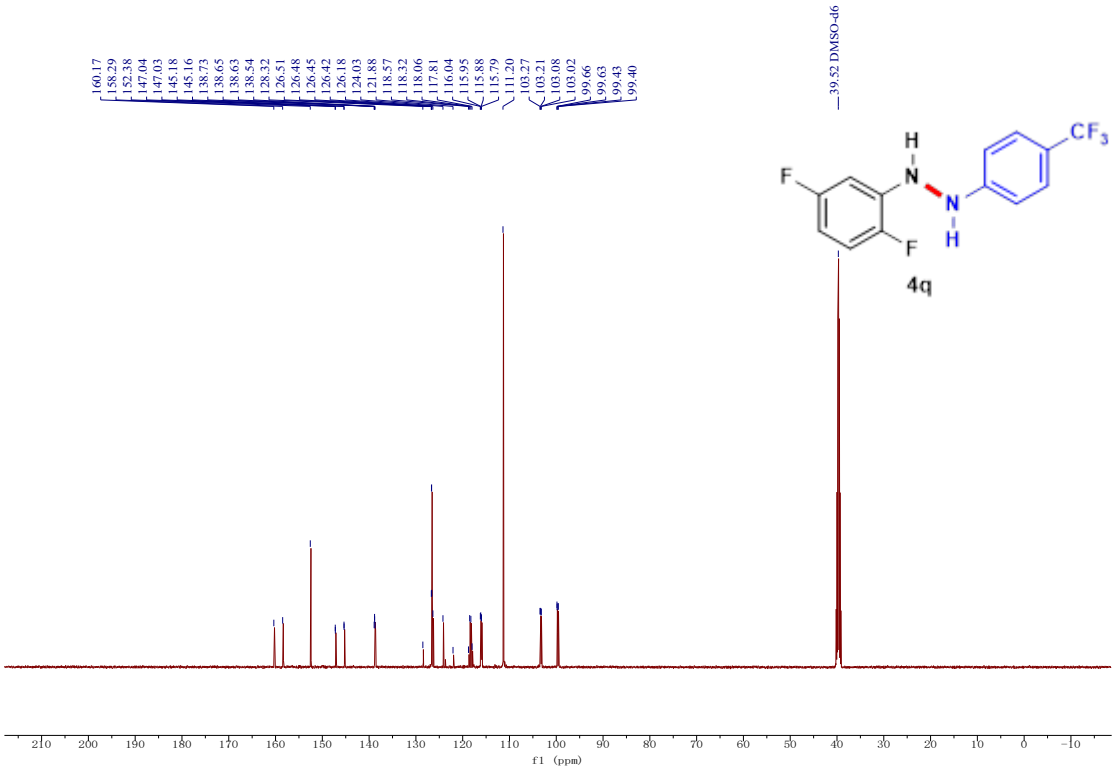
^{19}F NMR of Compound 4p (471 MHz, $CDCl_3$)



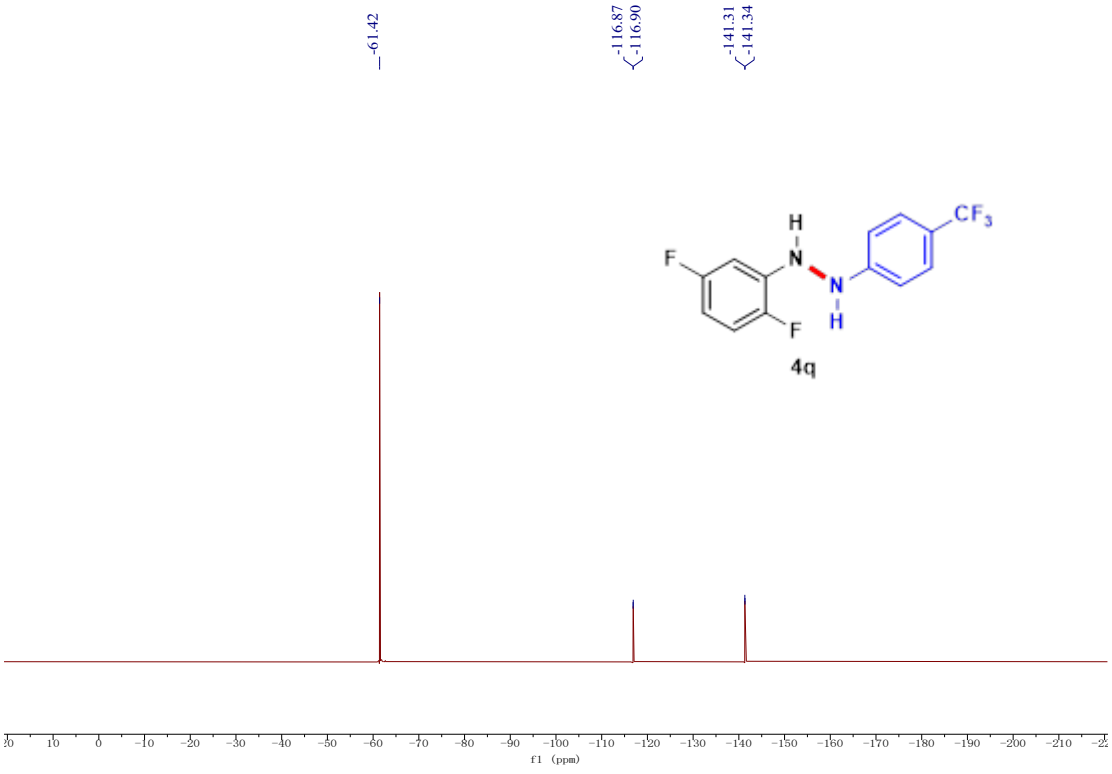
^{1}H NMR of Compound 4q (500 MHz, DMSO-d_6)



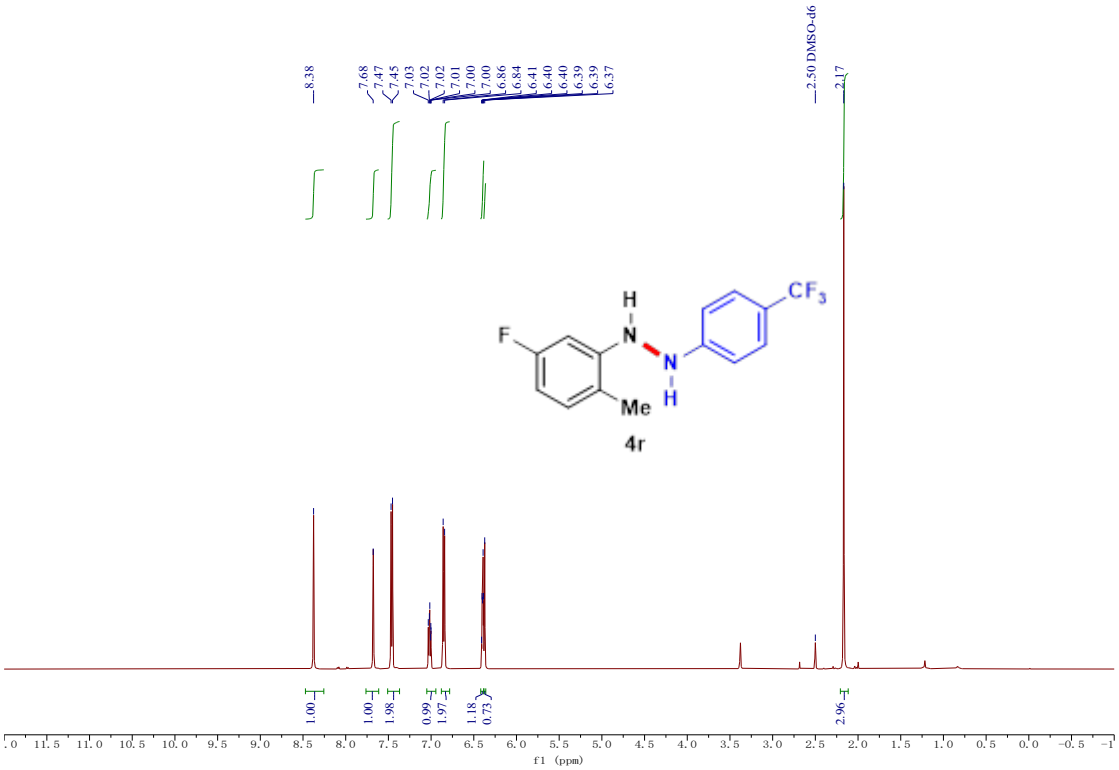
^{13}C NMR of Compound 4q (126 MHz, DMSO-d_6)



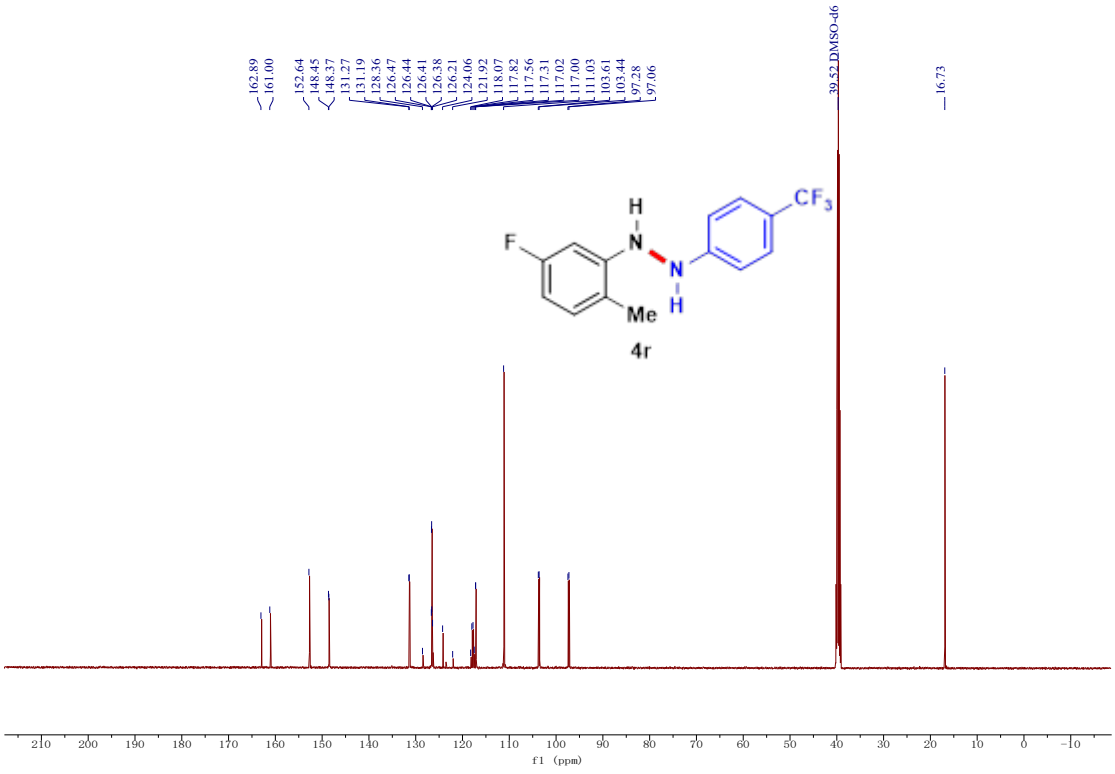
^{19}F NMR of Compound 4q (471 MHz, $CDCl_3$)



^{1}H NMR of Compound 4r (500 MHz, DMSO-d_6)

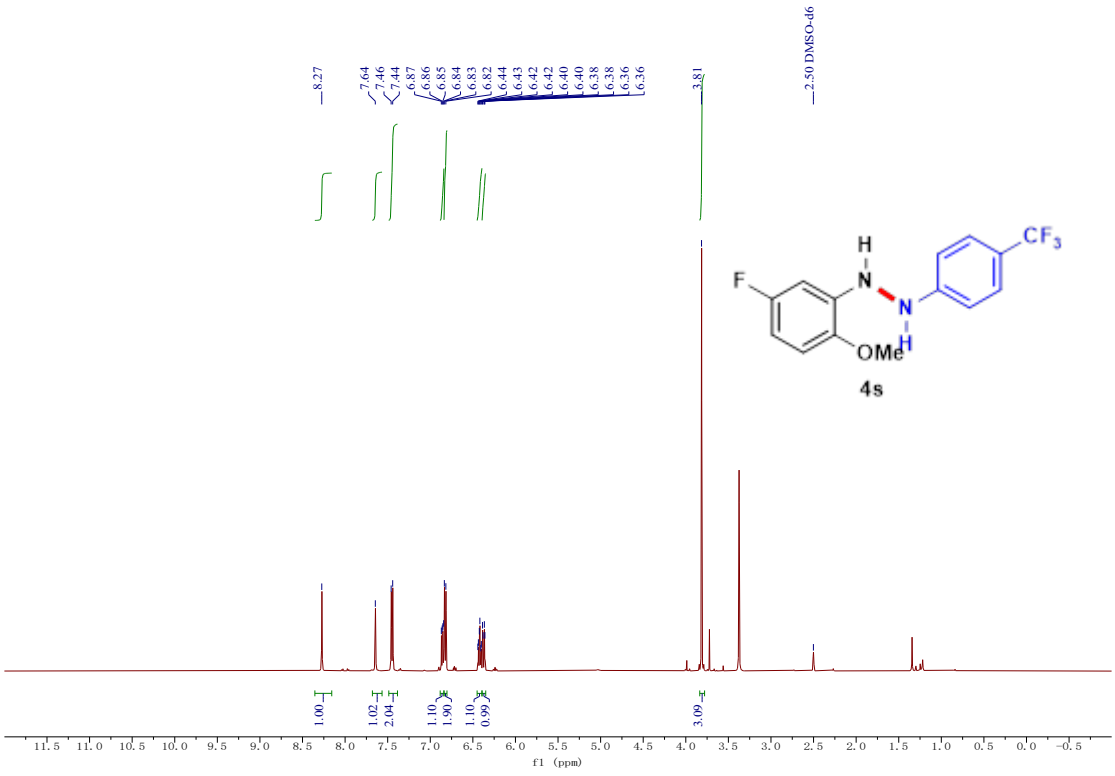


^{13}C NMR of Compound 4r (126 MHz, DMSO-d_6)

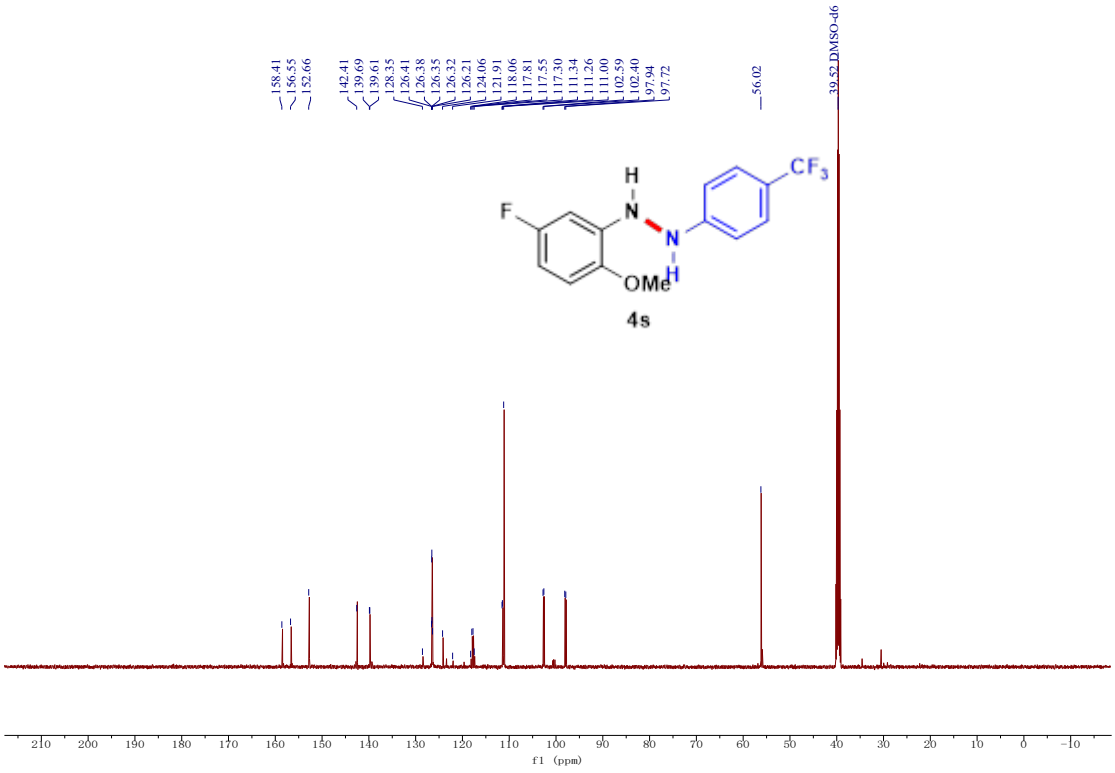


^{19}F NMR of Compound 4r (471 MHz, DMSO-d_6)

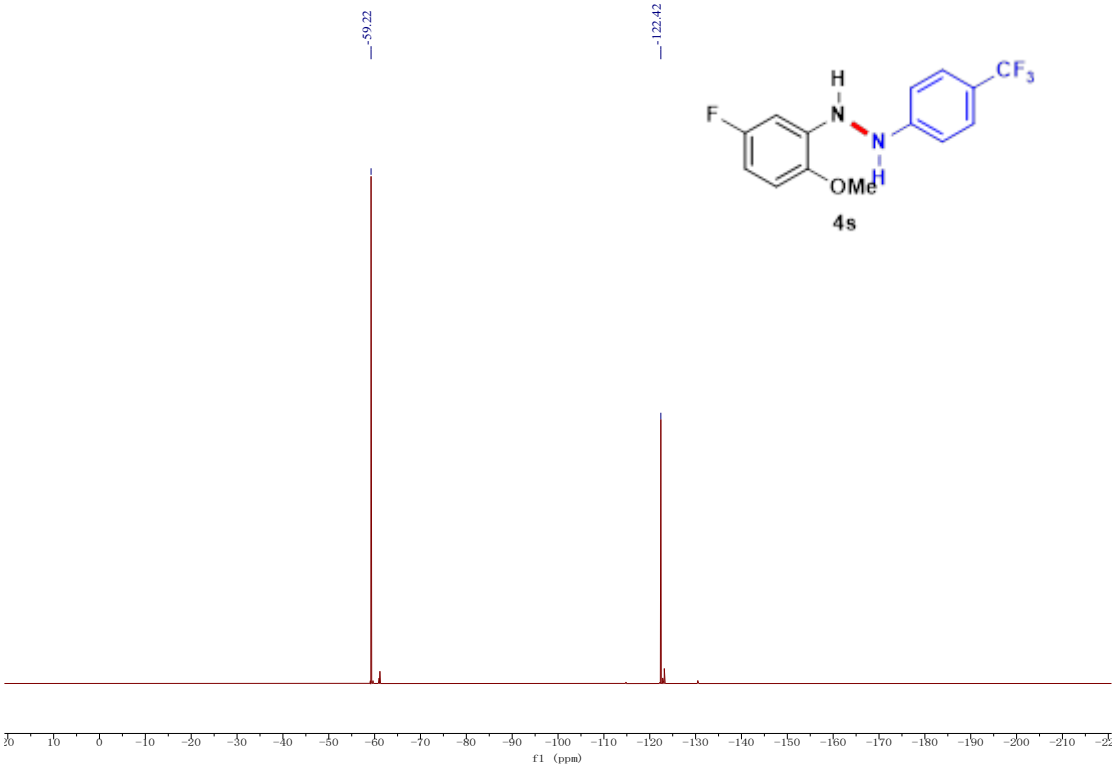
^{1}H NMR of Compound 4s (500 MHz, DMSO-d_6)



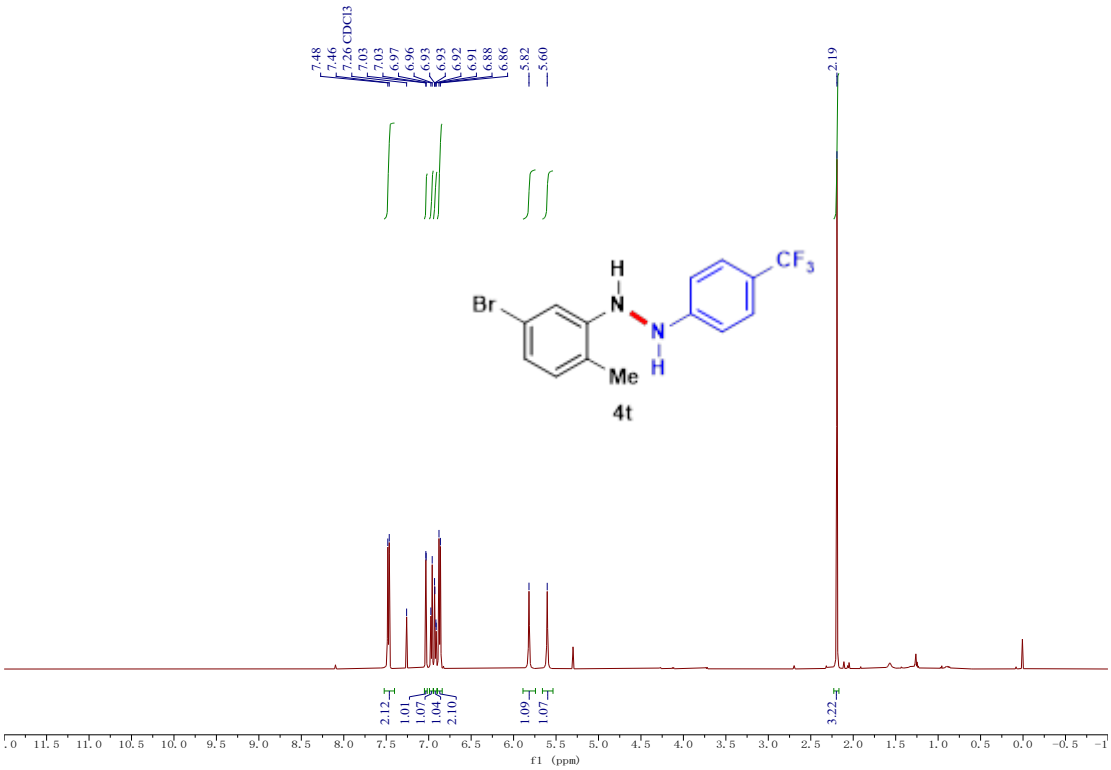
^{13}C NMR of Compound 4s (126 MHz, DMSO-d_6)



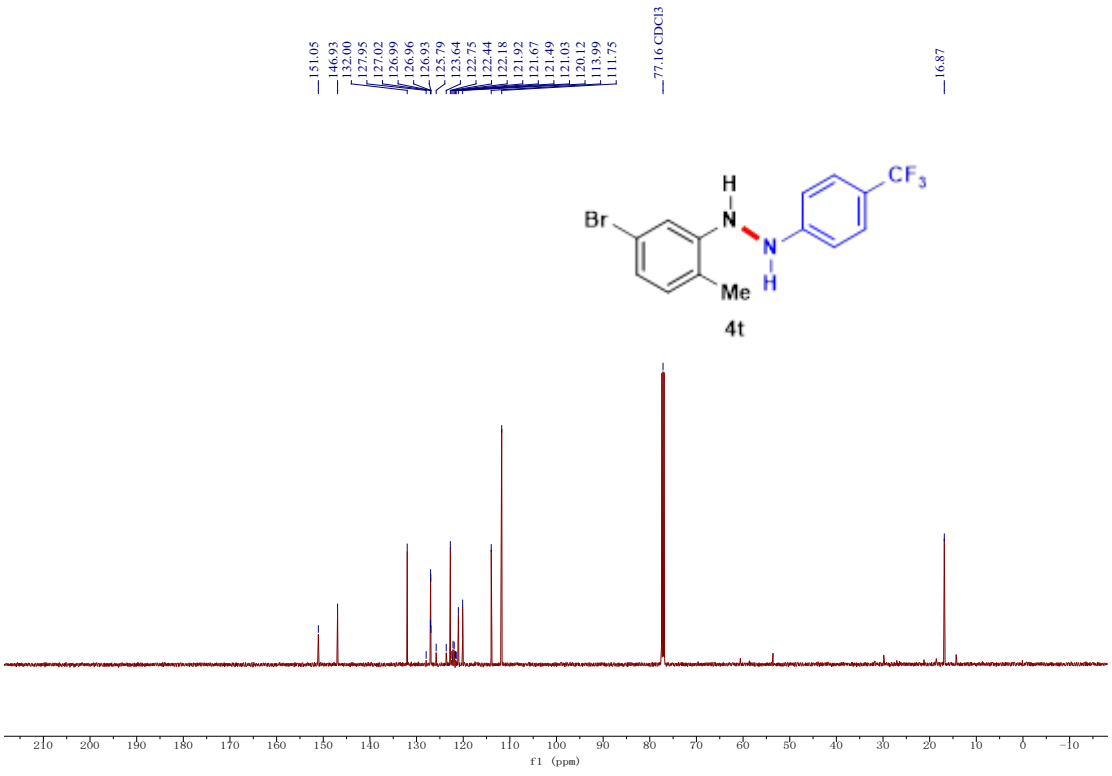
^{19}F NMR of Compound 4s (471 MHz, DMSO-d_6)



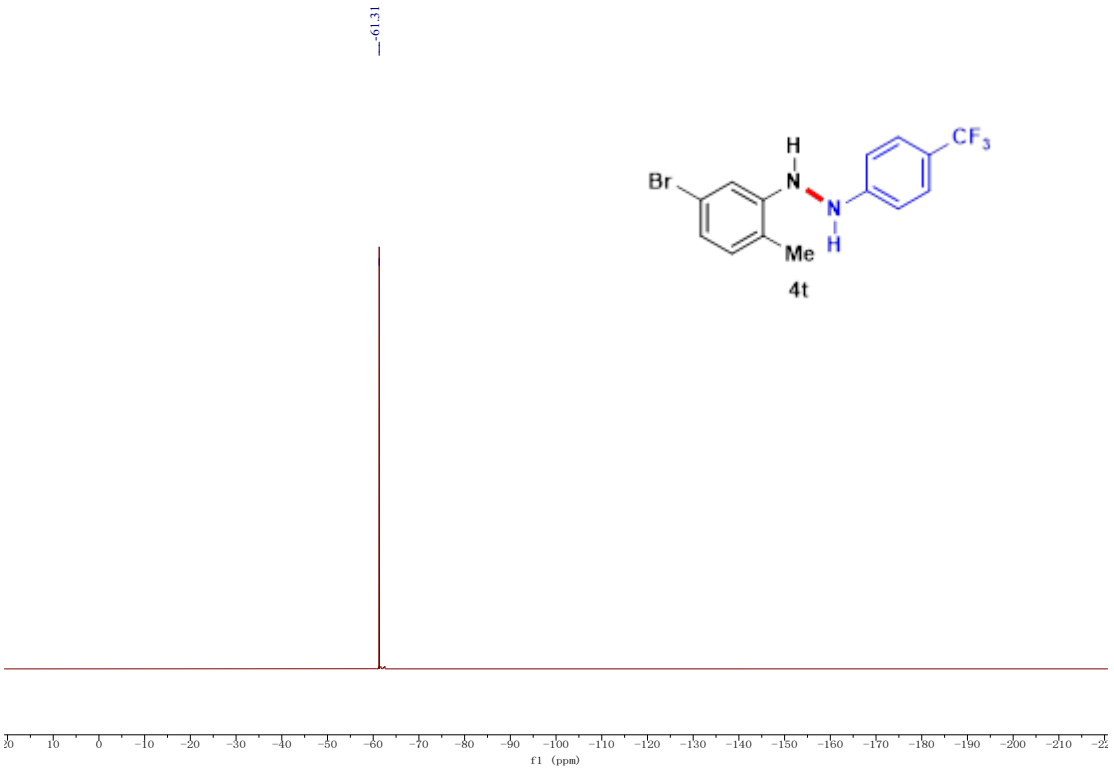
^{1}H NMR of Compound 4t (500 MHz, $CDCl_3$)



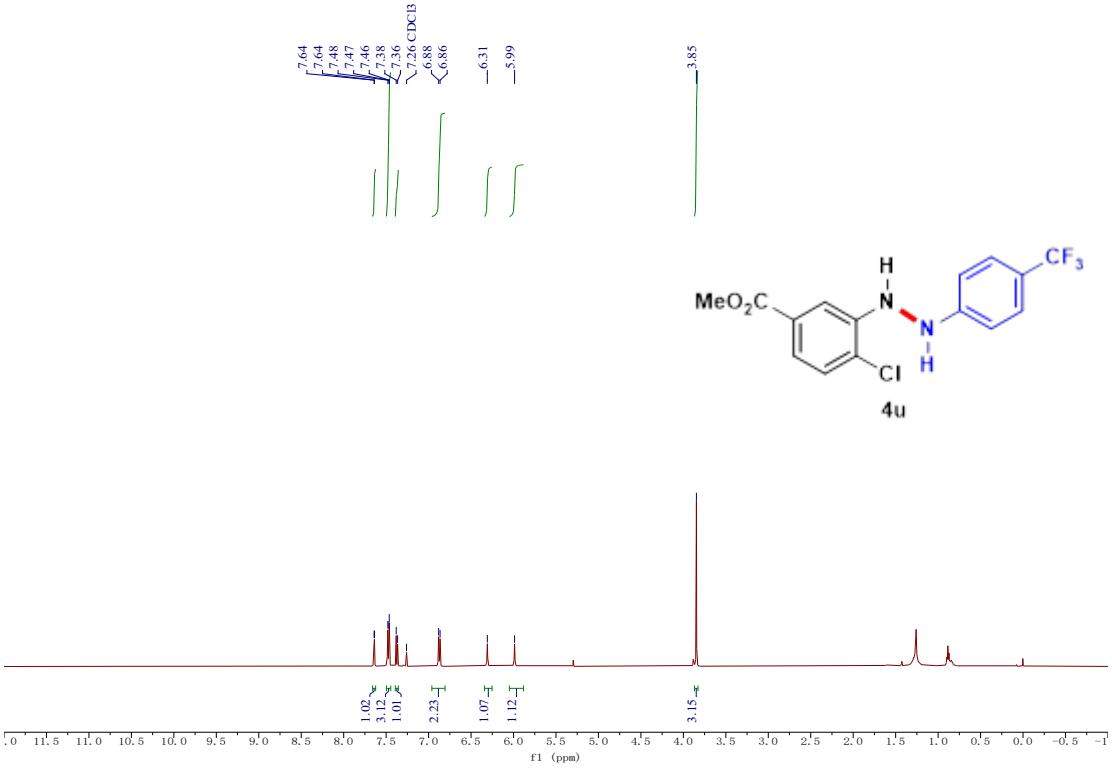
^{13}C NMR of Compound 4t (126 MHz, $CDCl_3$)



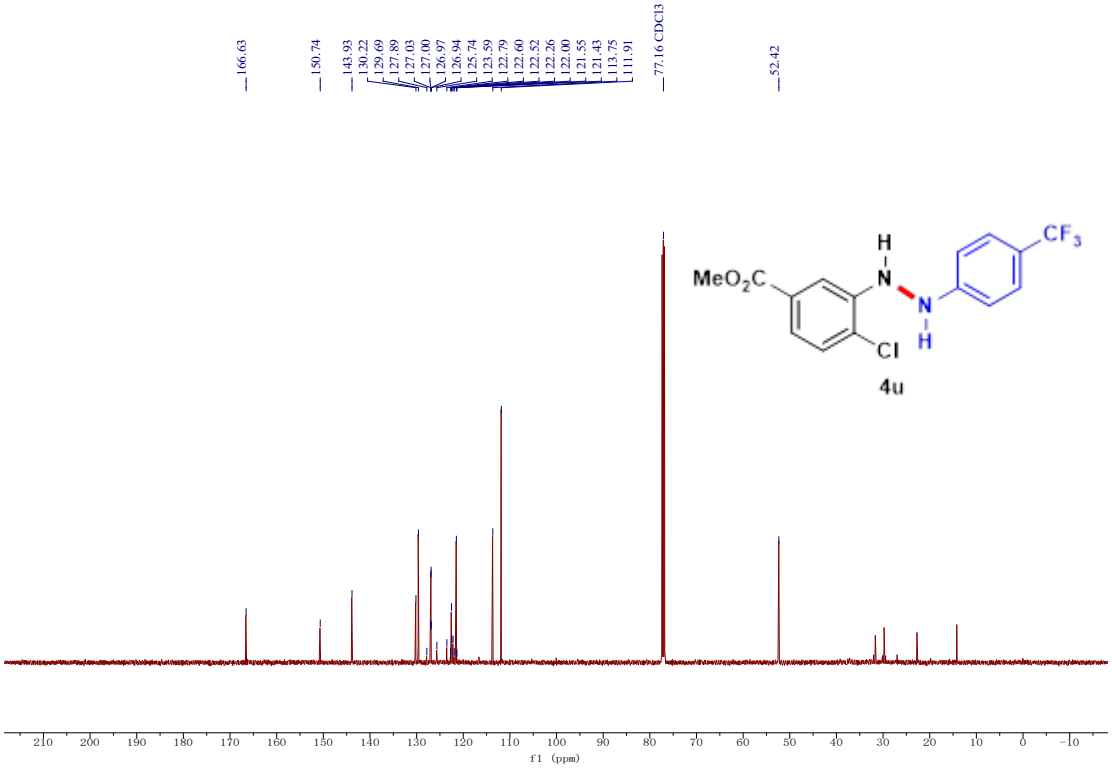
^{19}F NMR of Compound 4t (471 MHz, $CDCl_3$)



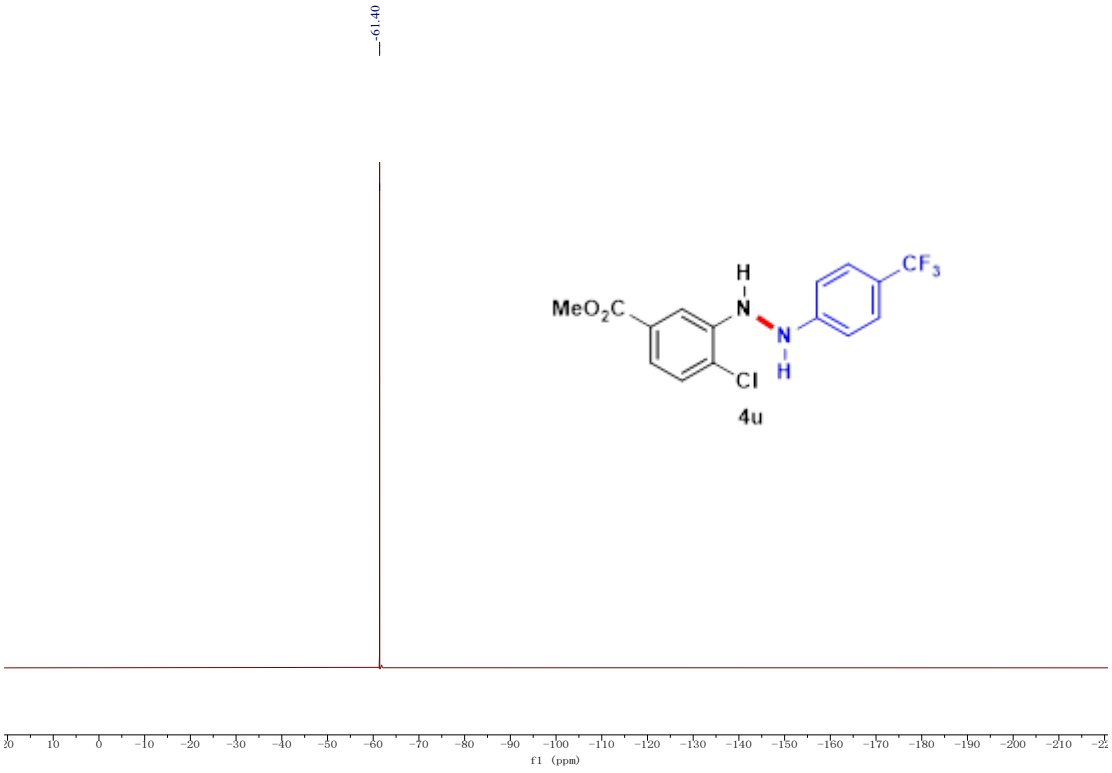
^{1}H NMR of Compound 4u (500 MHz, $CDCl_3$)



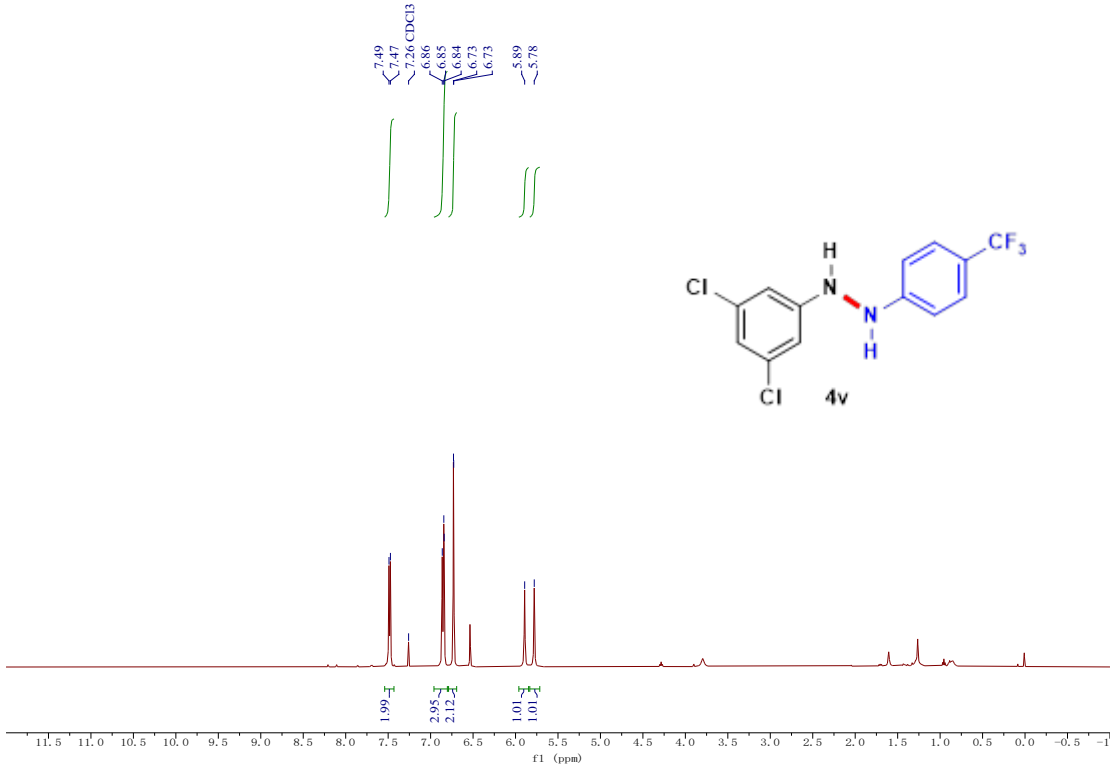
^{13}C NMR of Compound 4u (126 MHz, $CDCl_3$)



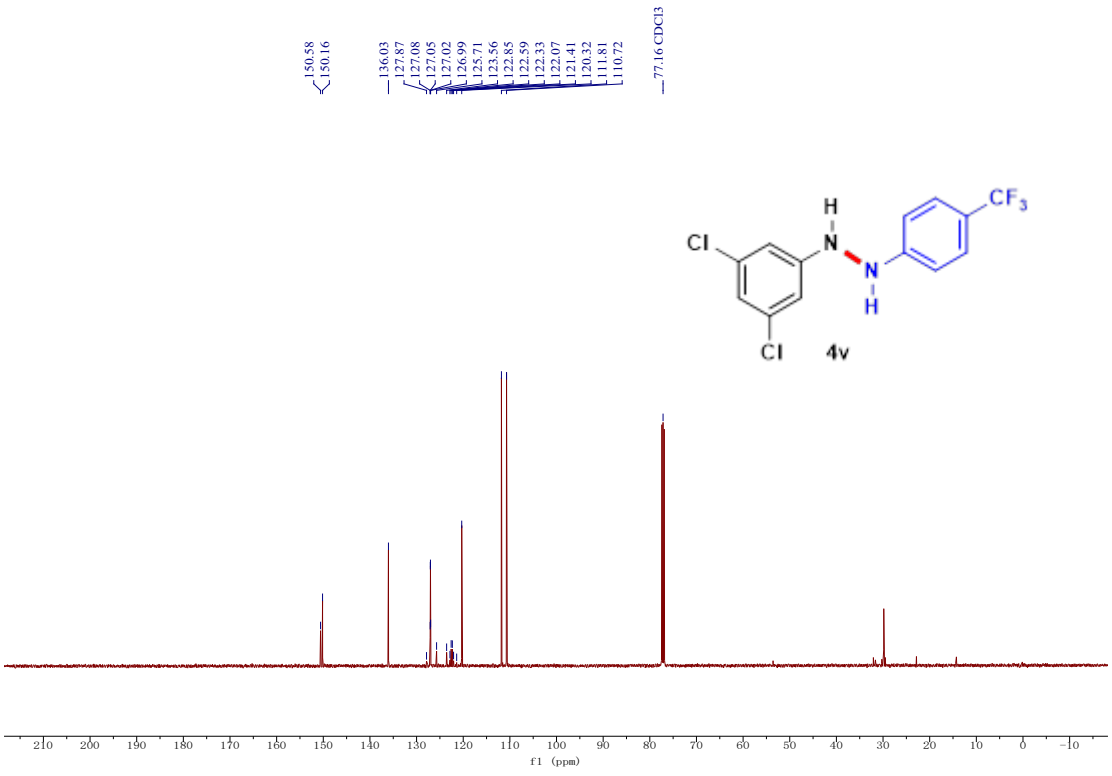
^{19}F NMR of Compound 4u (471 MHz, $CDCl_3$)



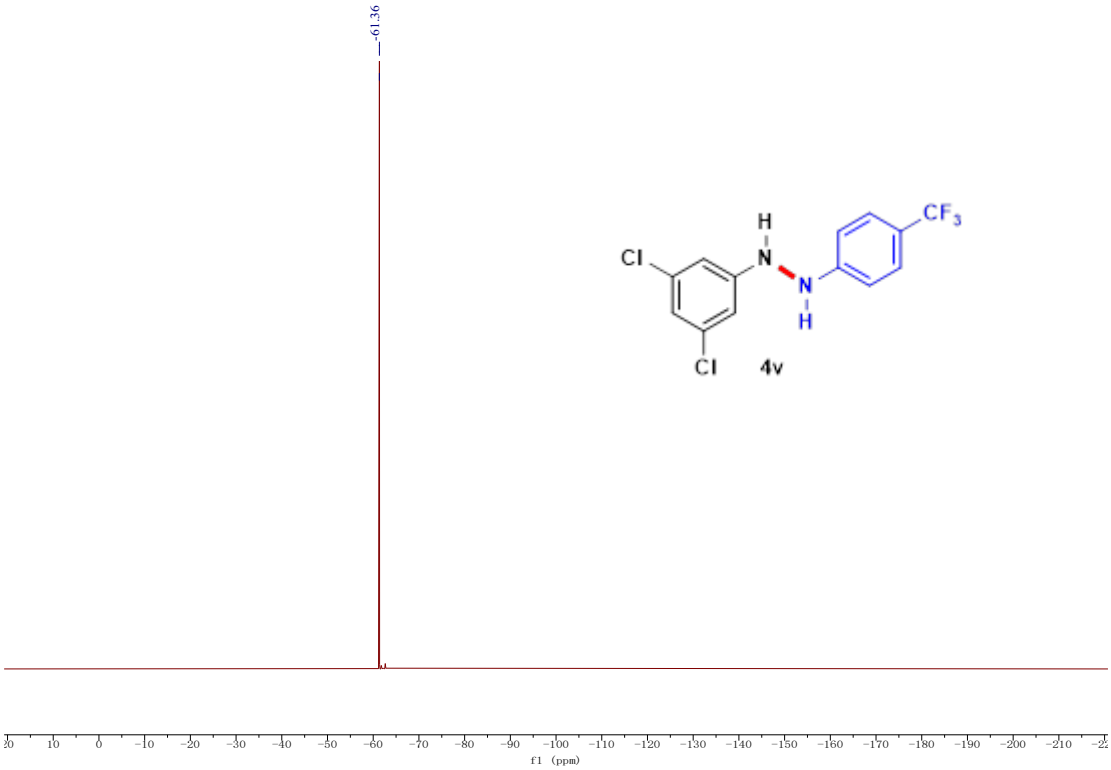
^{1}H NMR of Compound 4v (500 MHz, $CDCl_3$)



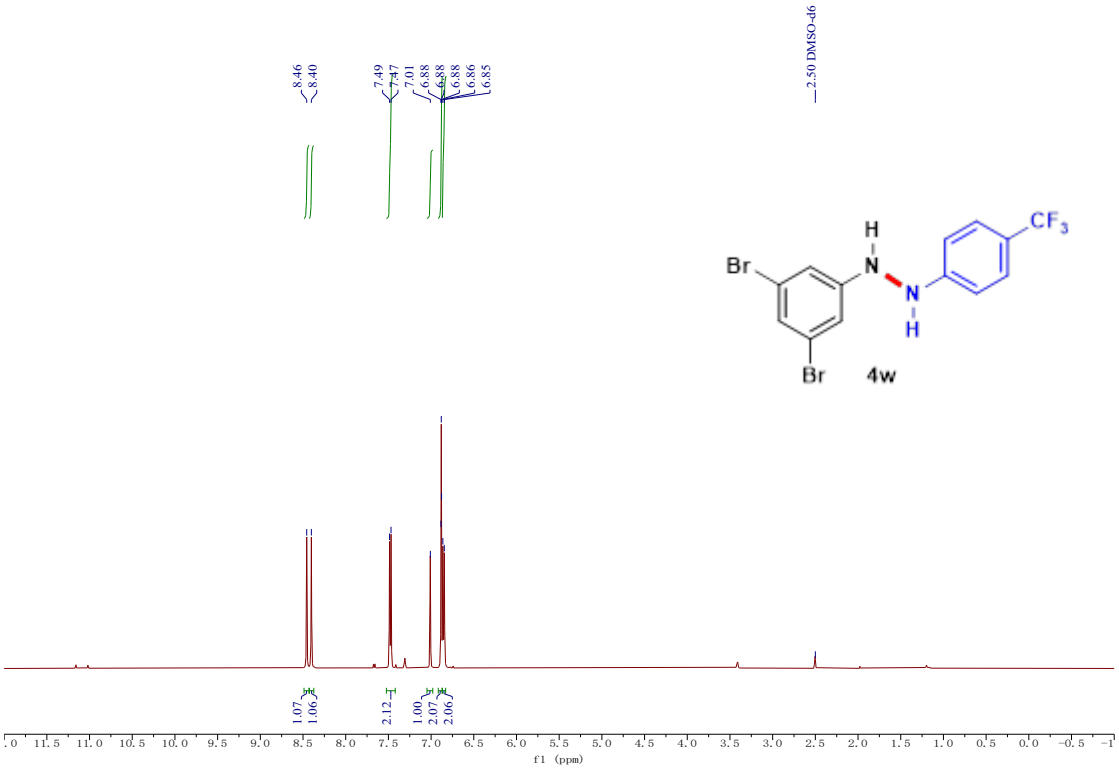
^{13}C NMR of Compound 4v (126 MHz, $CDCl_3$)



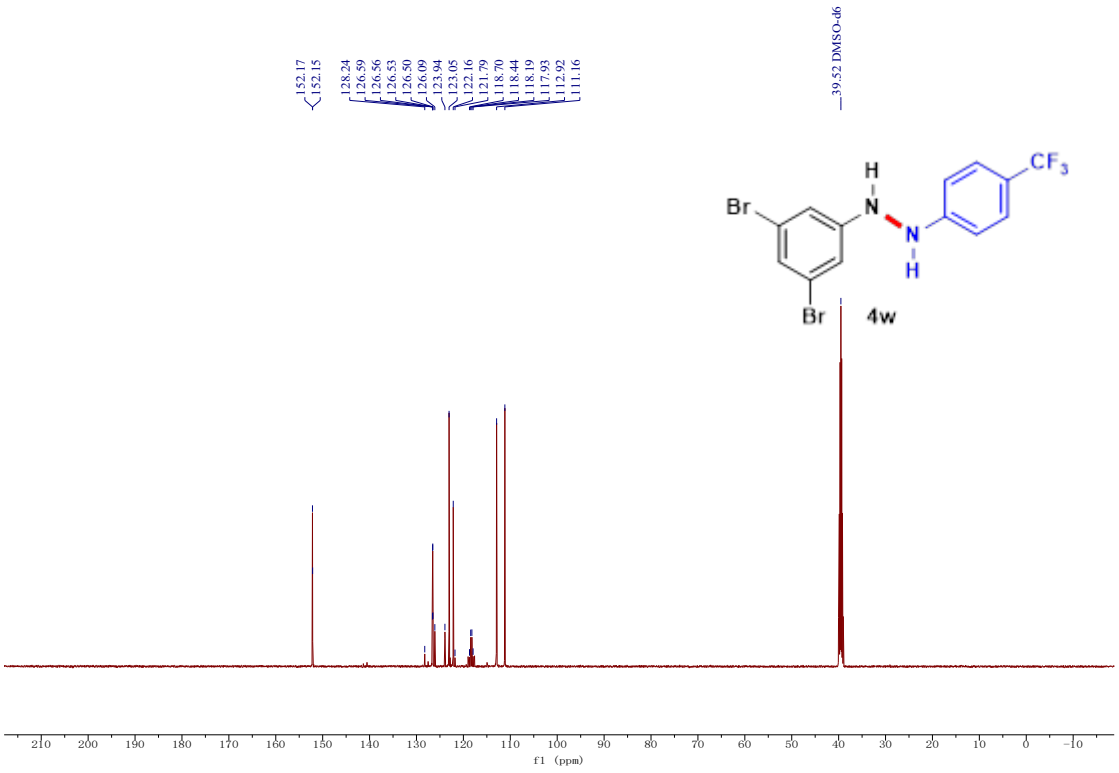
^{19}F NMR of Compound 4v (471 MHz, $CDCl_3$)



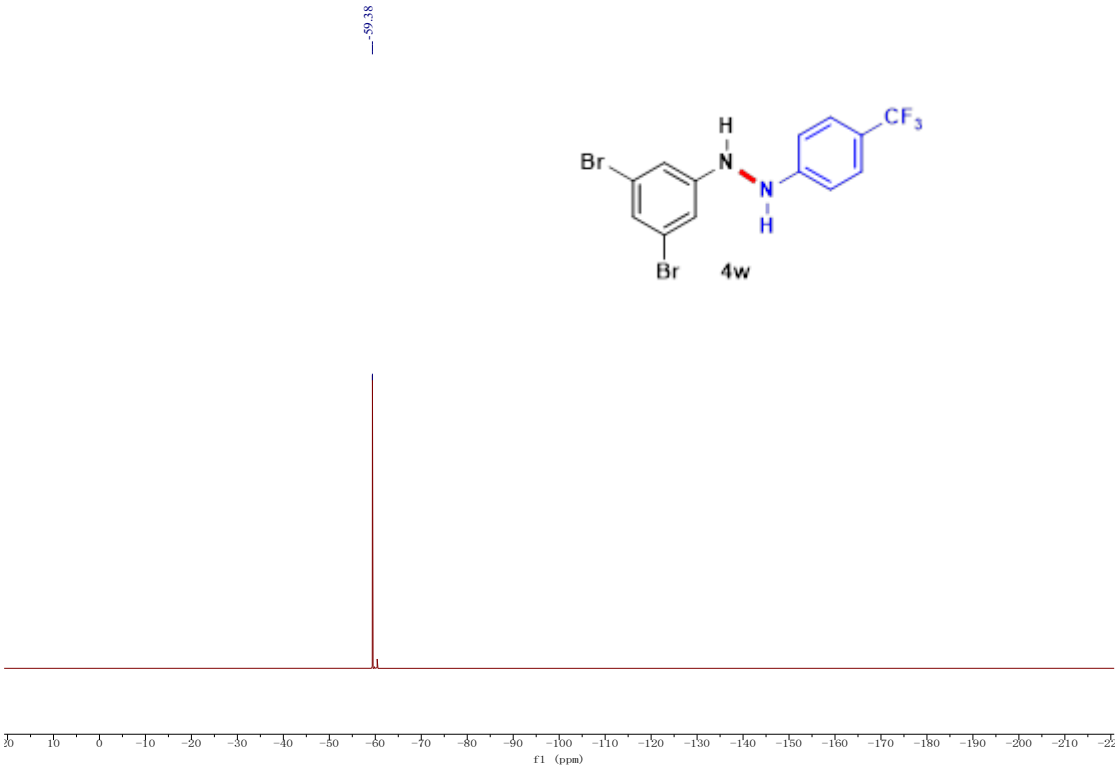
^{1}H NMR of Compound 4w (500 MHz, DMSO-d_6)



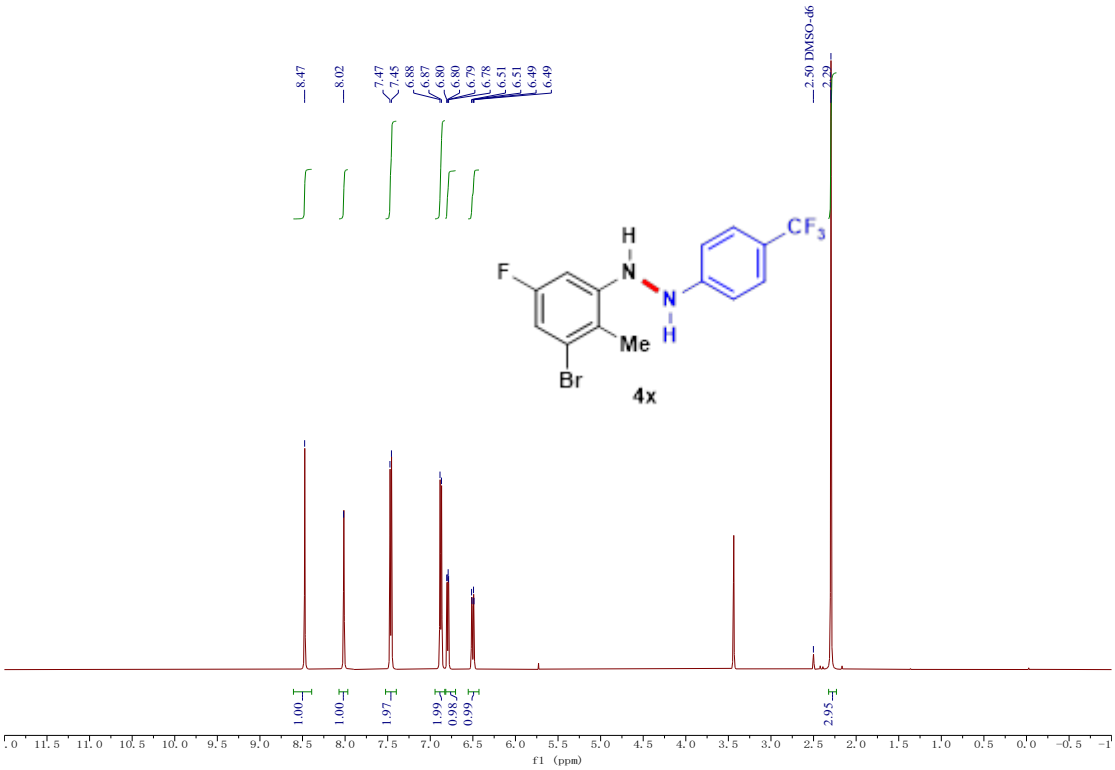
^{13}C NMR of Compound 4w (126 MHz, DMSO-d_6)



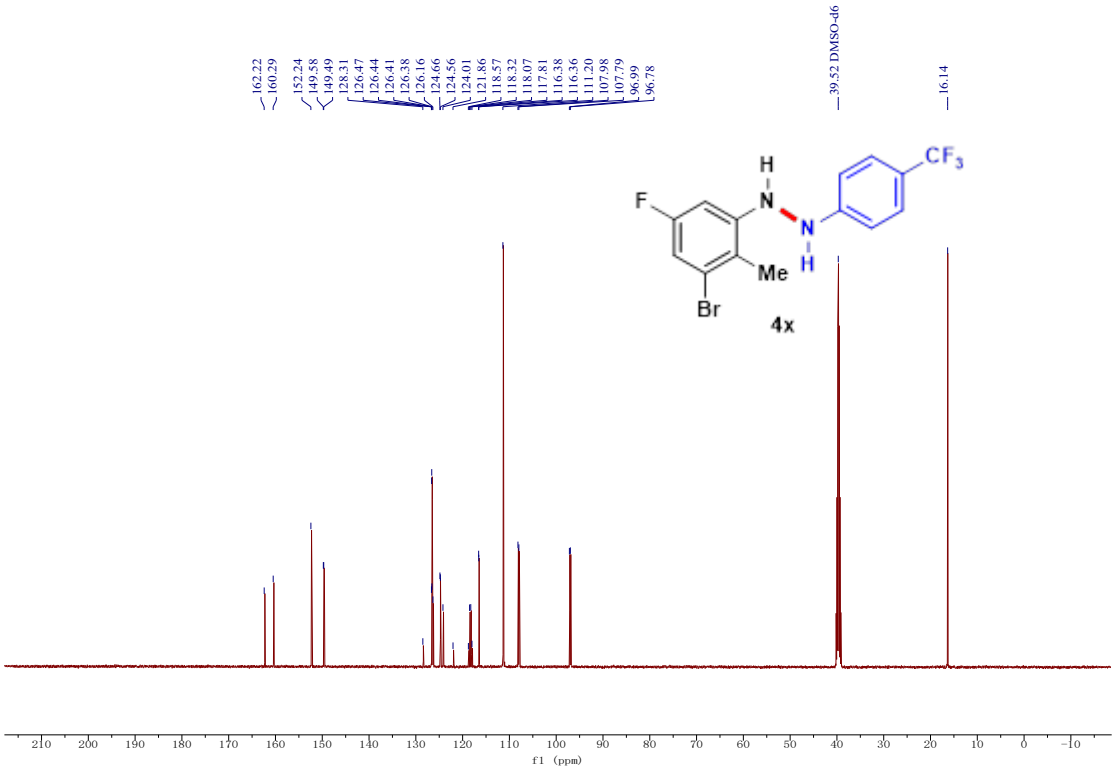
^{19}F NMR of Compound 4w (471 MHz, DMSO-d_6)



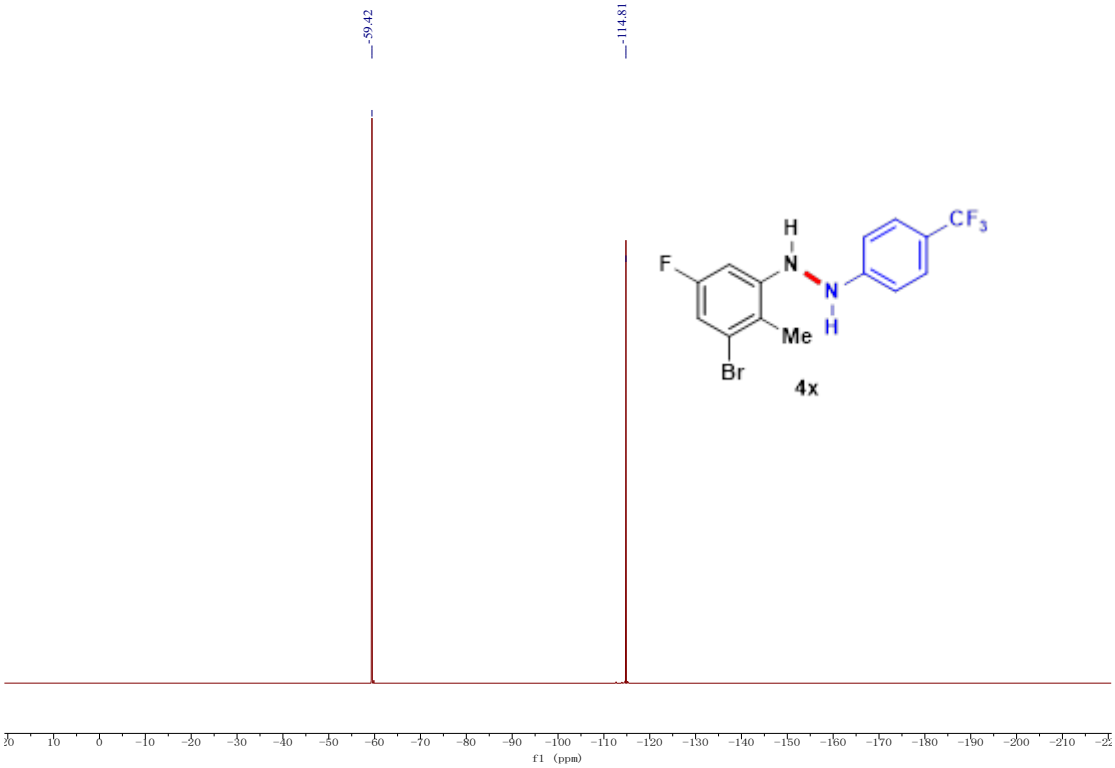
^{1}H NMR of Compound 4x (500 MHz, DMSO-d_6)



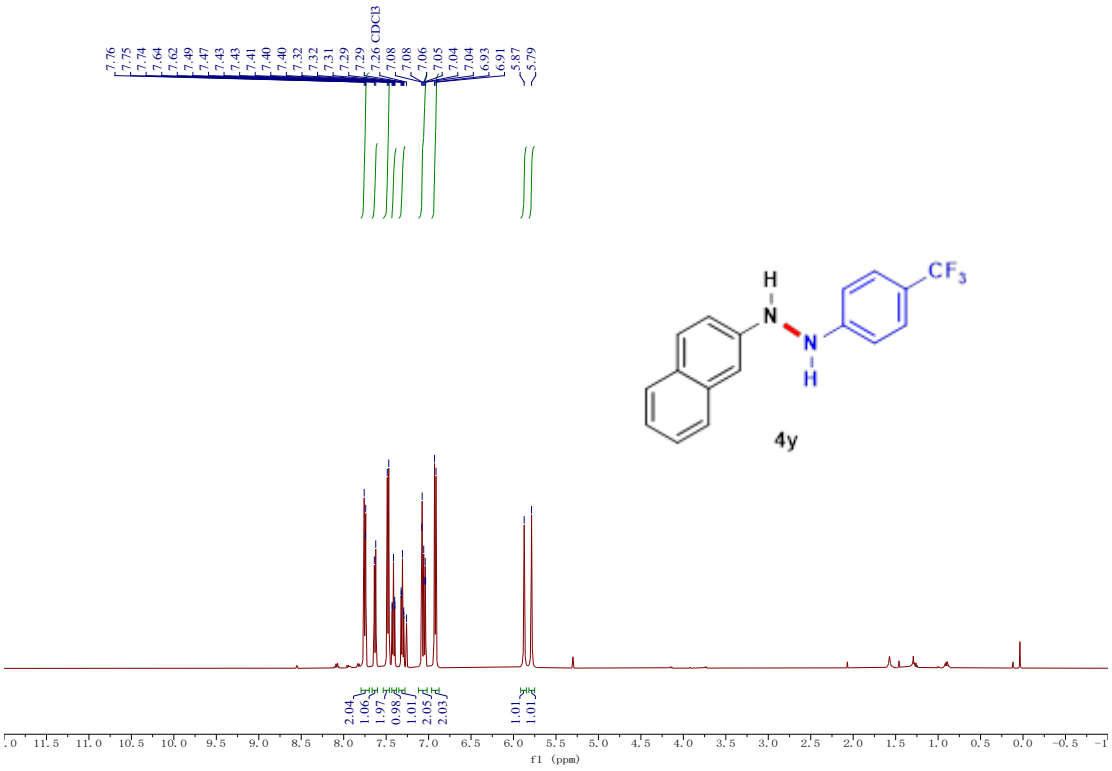
^{13}C NMR of Compound 4x (126 MHz, DMSO-*d*$_6$)



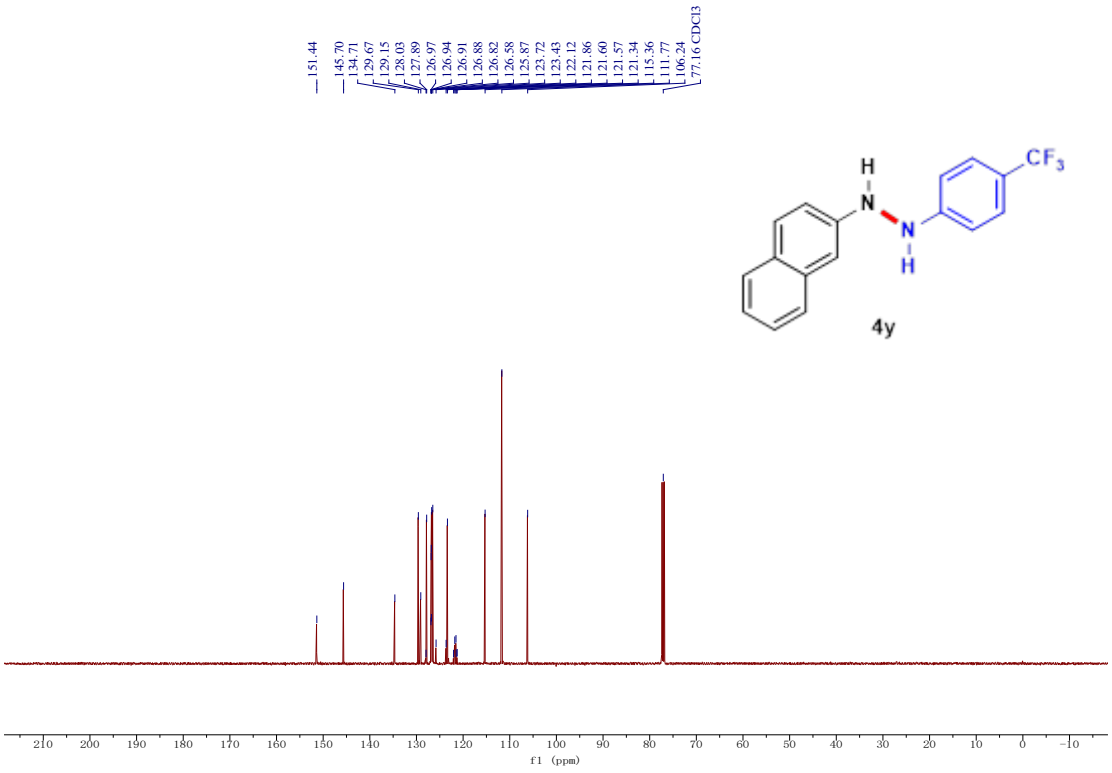
^{19}F NMR of Compound 4x (471 MHz, DMSO-*d*$_6$)



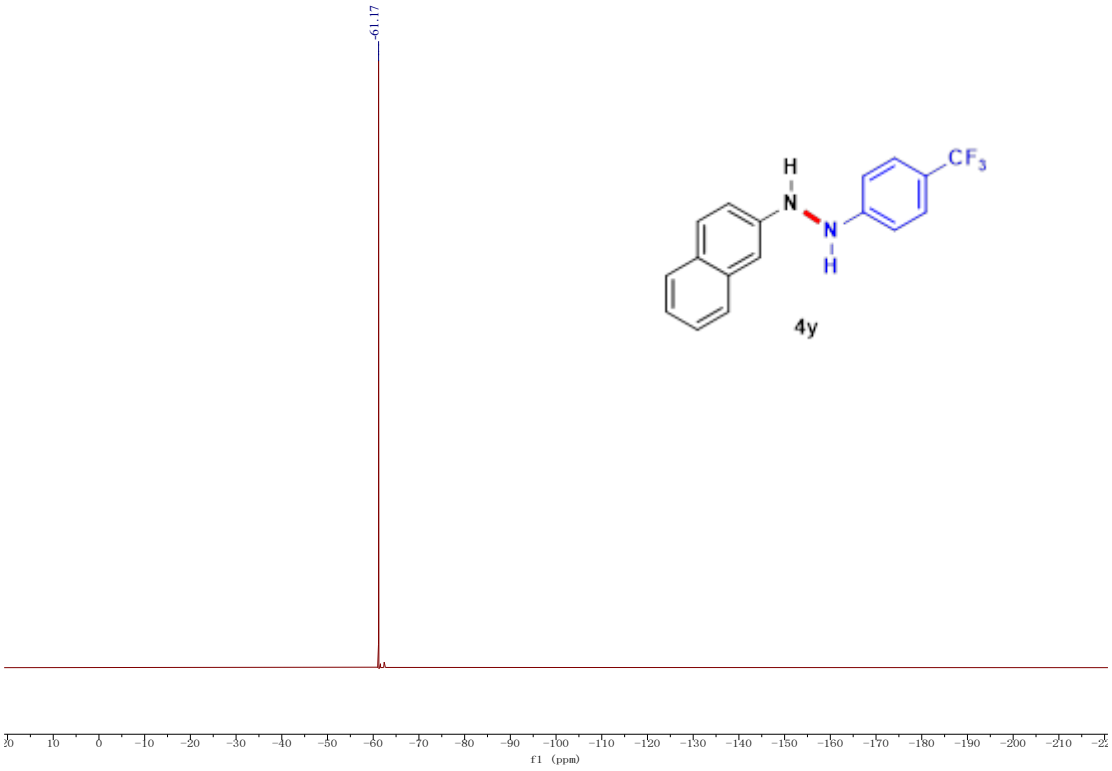
^{1}H NMR of Compound 4y (500 MHz, $CDCl_3$)



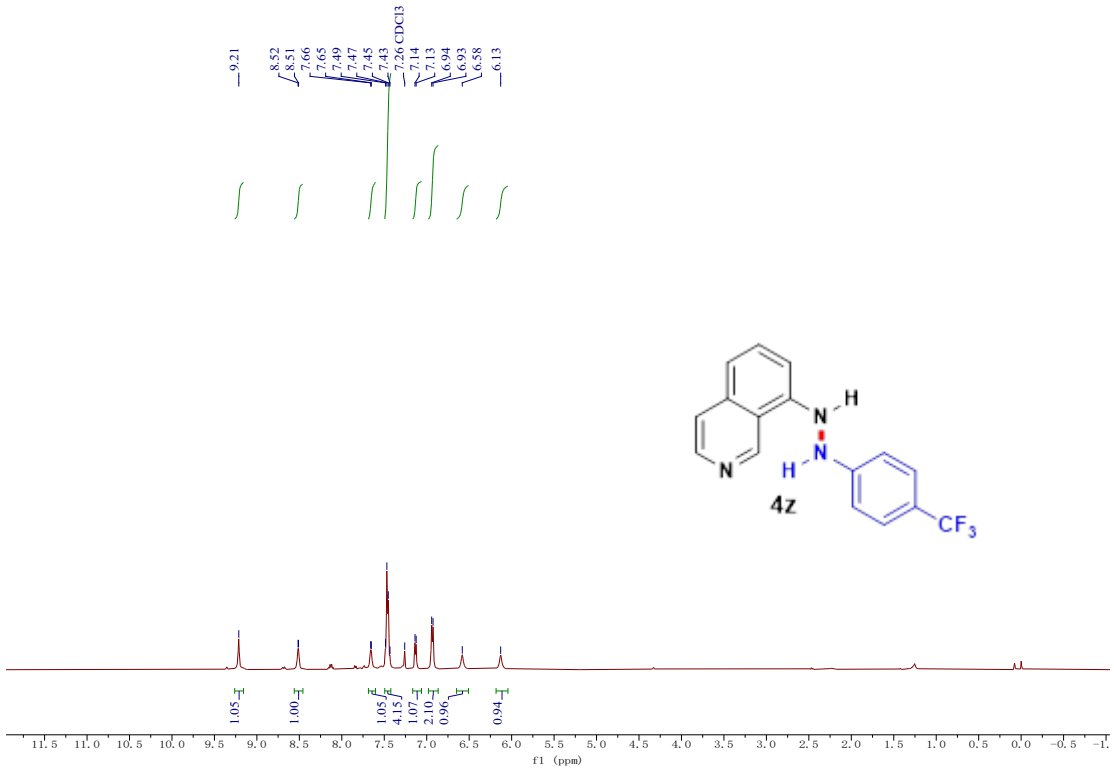
^{13}C NMR of Compound 4y (126 MHz, $CDCl_3$)



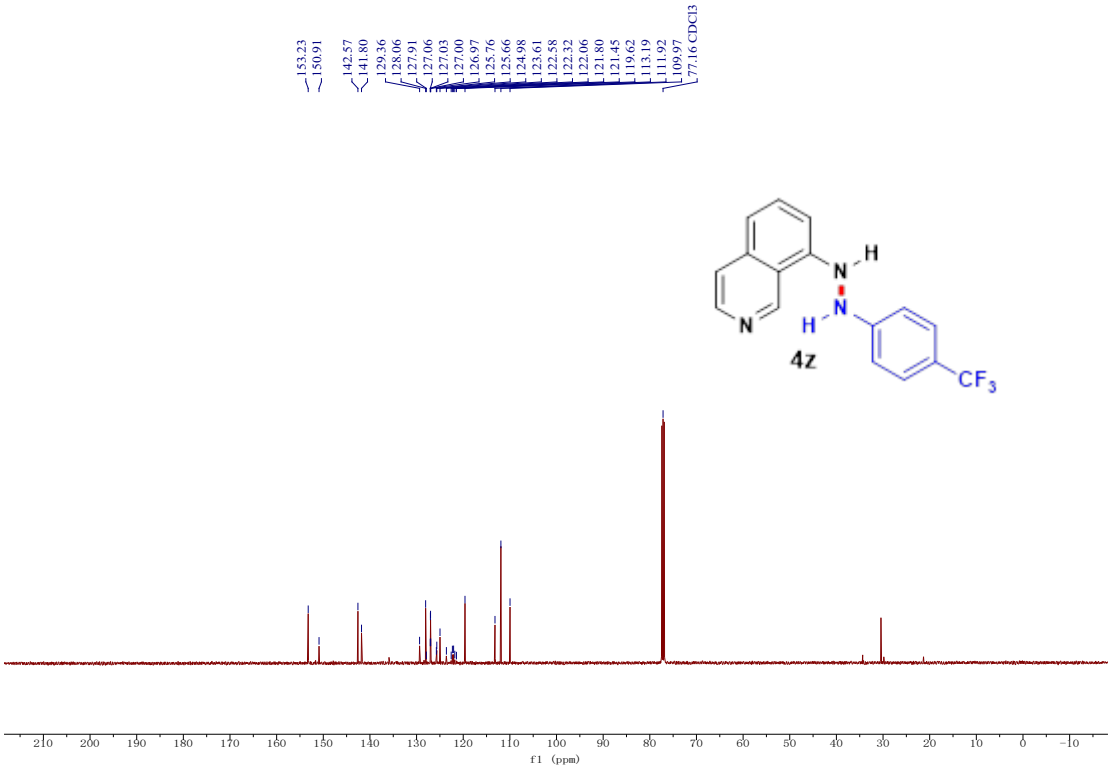
^{19}F NMR of Compound 4y (471 MHz, $CDCl_3$)



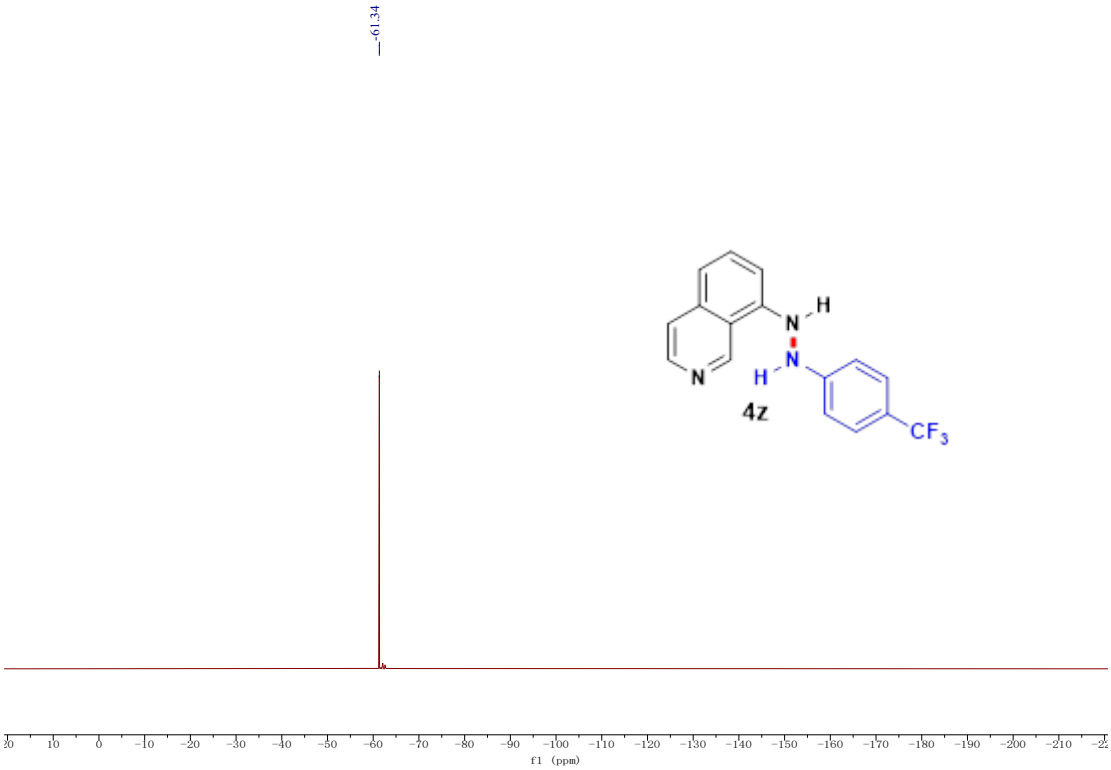
^{1}H NMR of Compound 4z (500 MHz, $CDCl_3$)



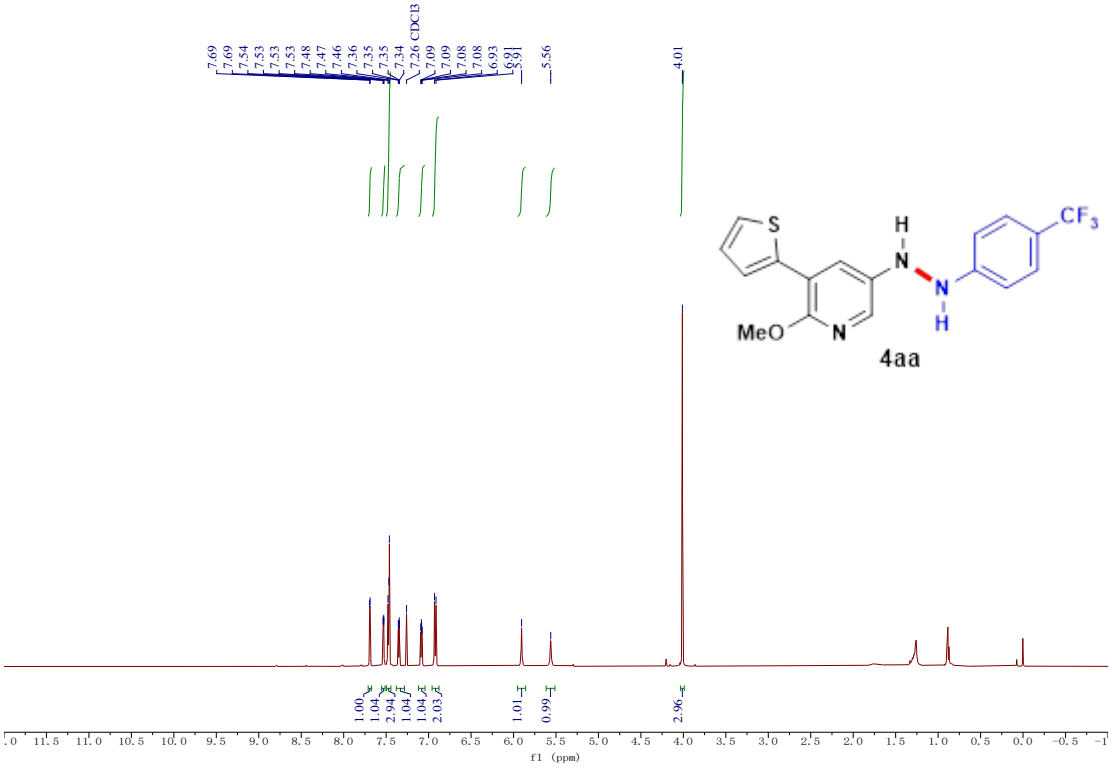
^{13}C NMR of Compound 4z (126 MHz, $CDCl_3$)



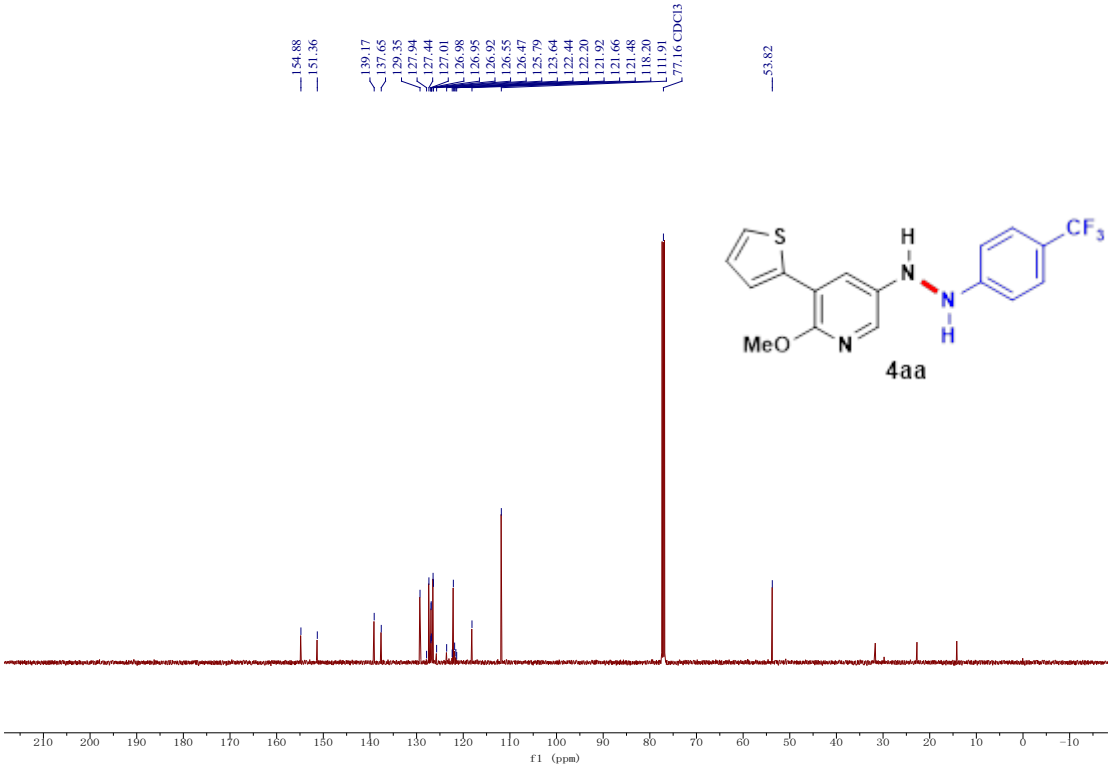
^{19}F NMR of Compound 4z (471 MHz, $CDCl_3$)



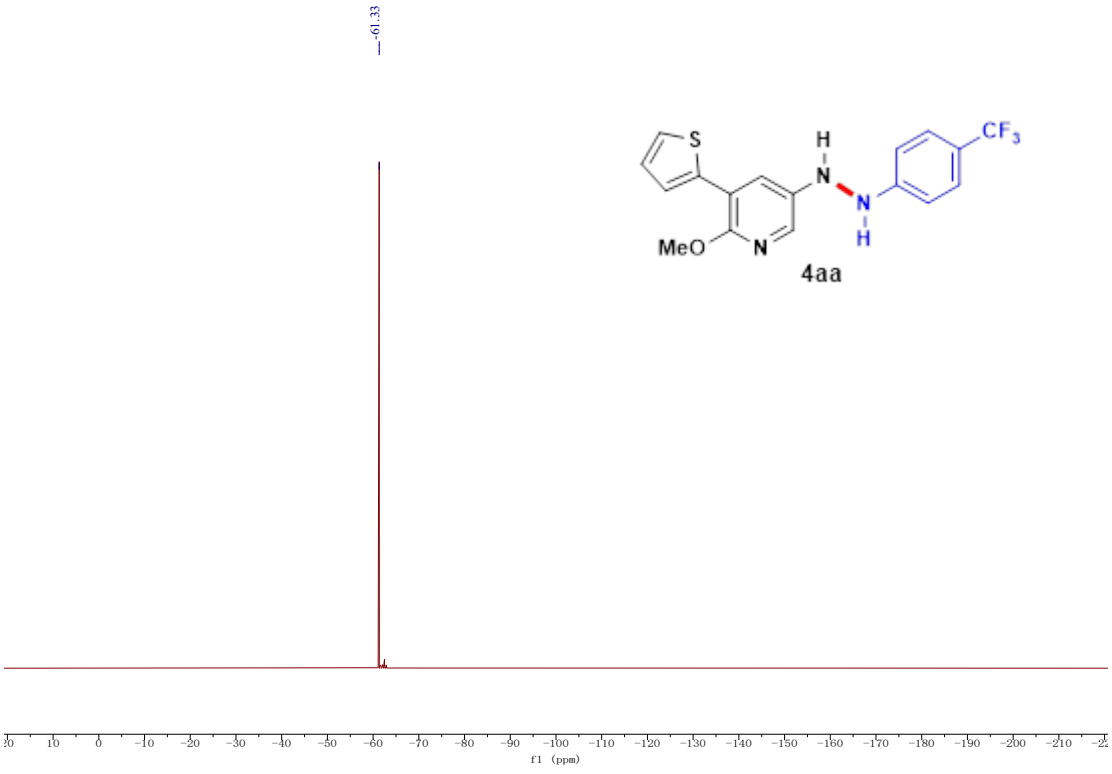
^{1}H NMR of Compound 4aa (500 MHz, $CDCl_3$)



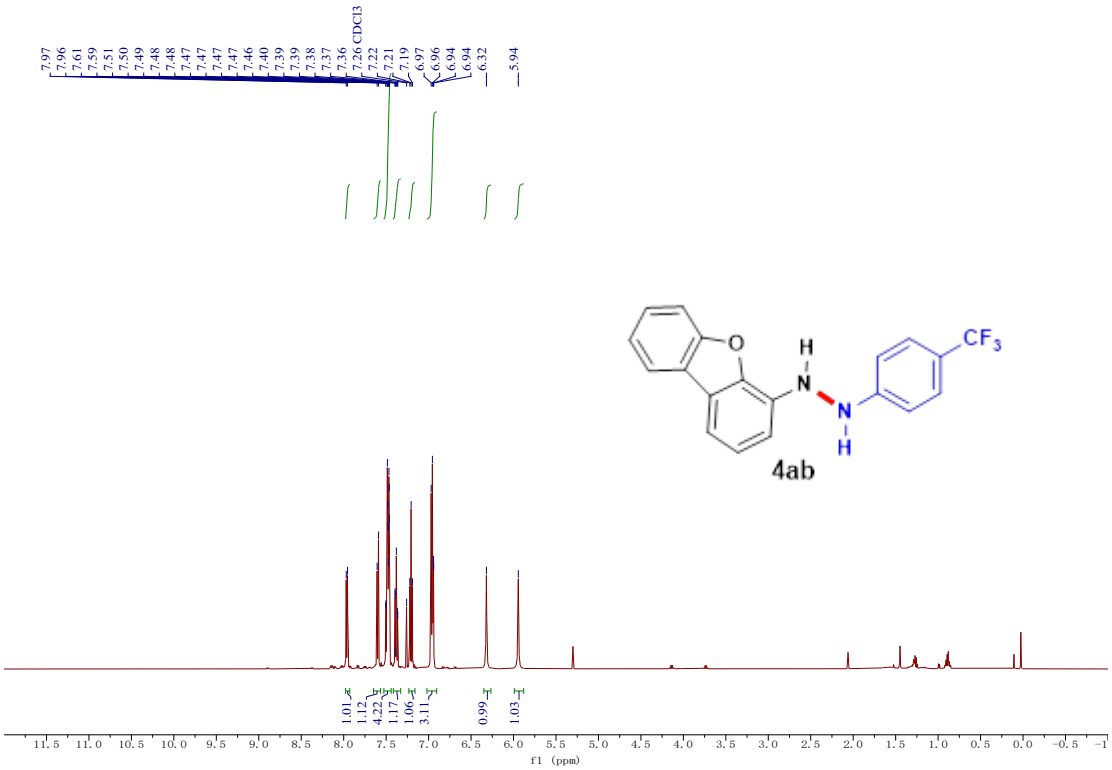
^{13}C NMR of Compound 4aa (126 MHz, $CDCl_3$)



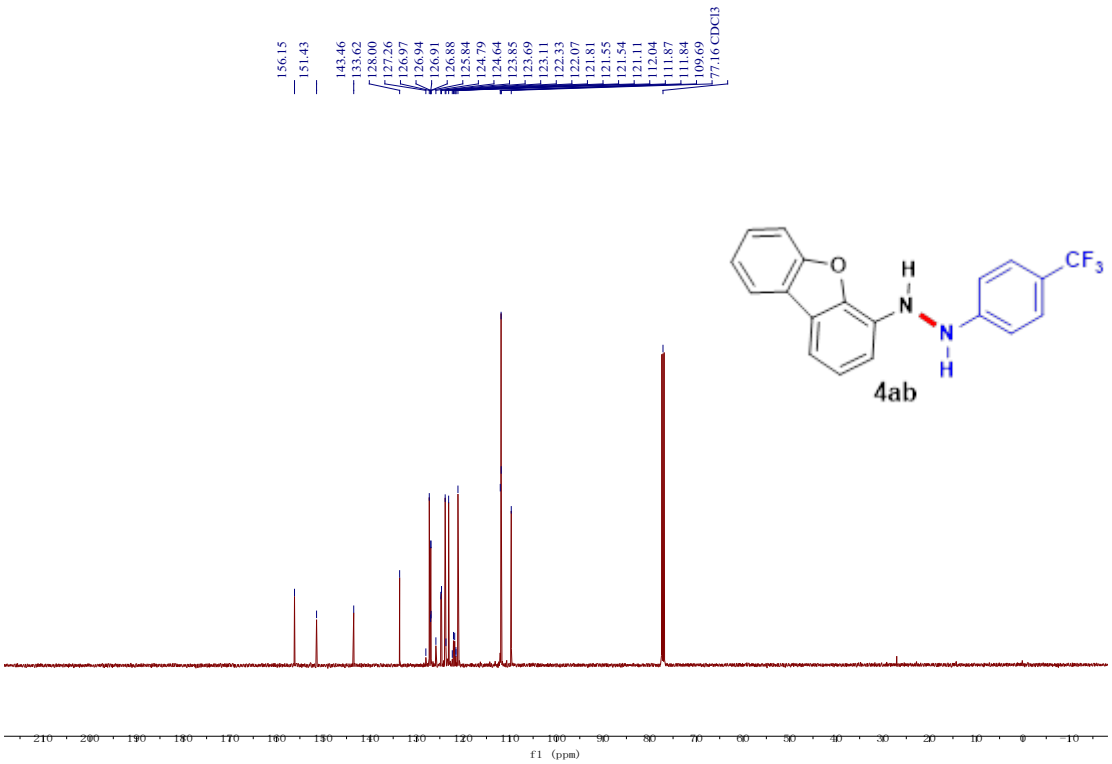
^{19}F NMR of Compound 4aa (471 MHz, $CDCl_3$)



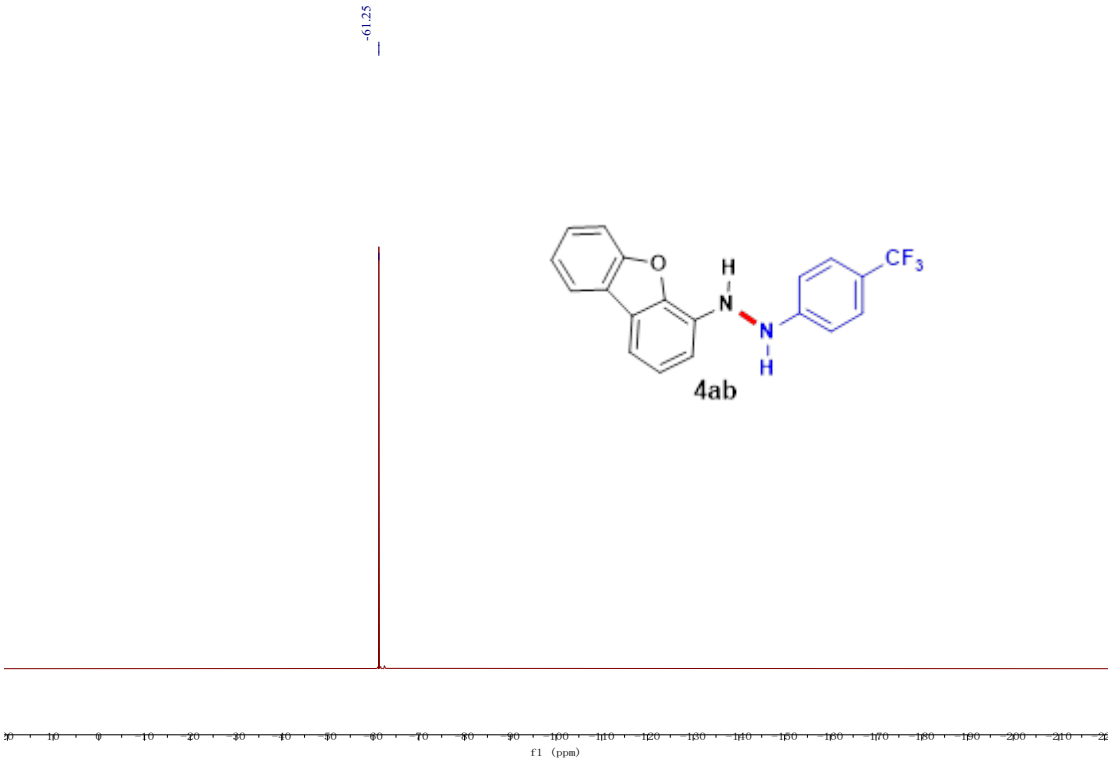
^{1}H NMR of Compound 4ab (500 MHz, $CDCl_3$)



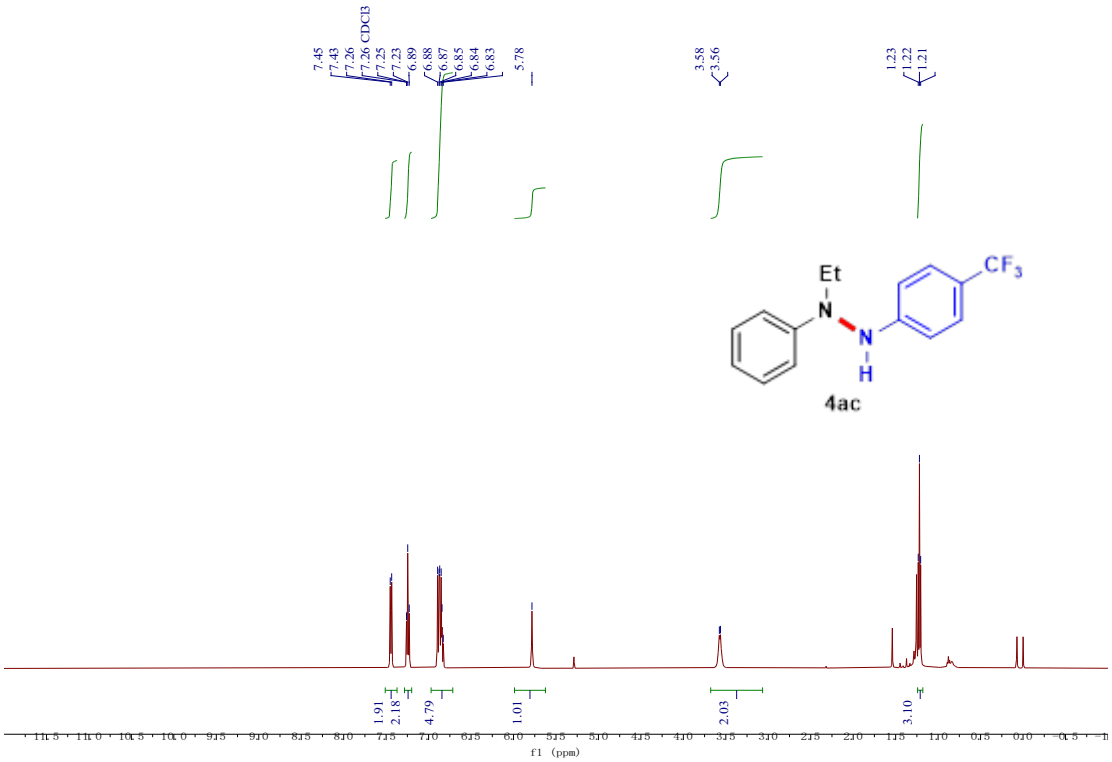
^{13}C NMR of Compound 4ab (126 MHz, $CDCl_3$)



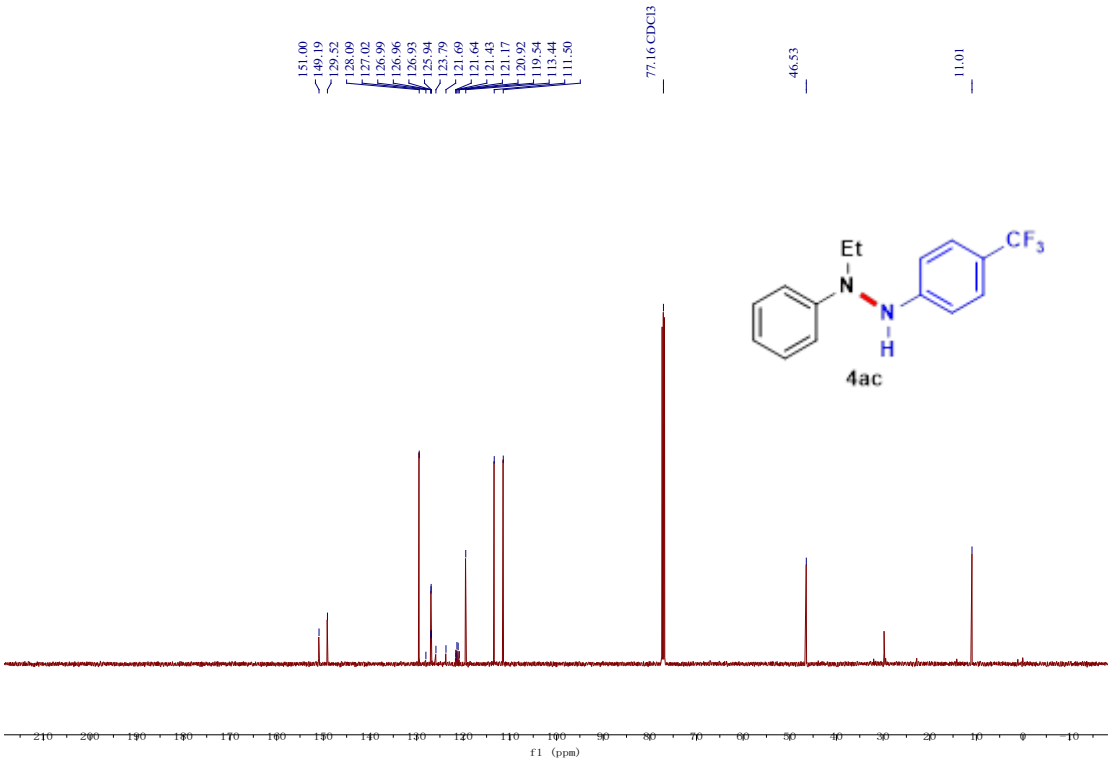
^{19}F NMR of Compound 4ab (471 MHz, $CDCl_3$)



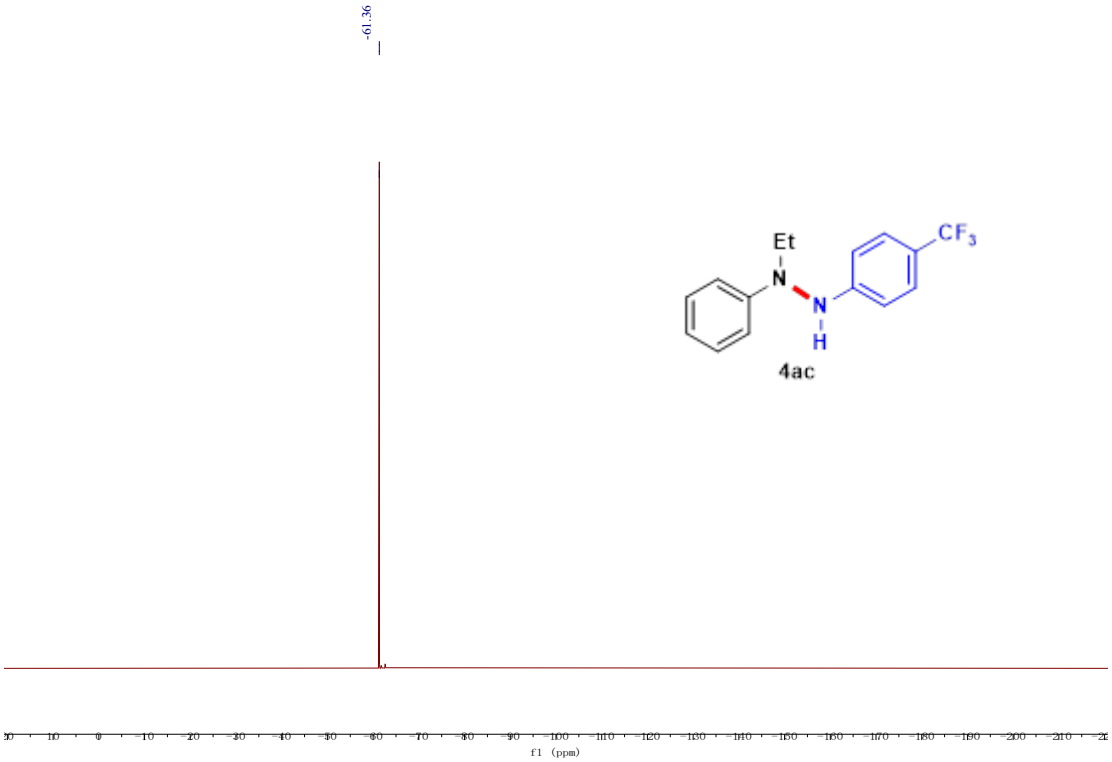
^{1}H NMR of Compound 4ac (500 MHz, $CDCl_3$)



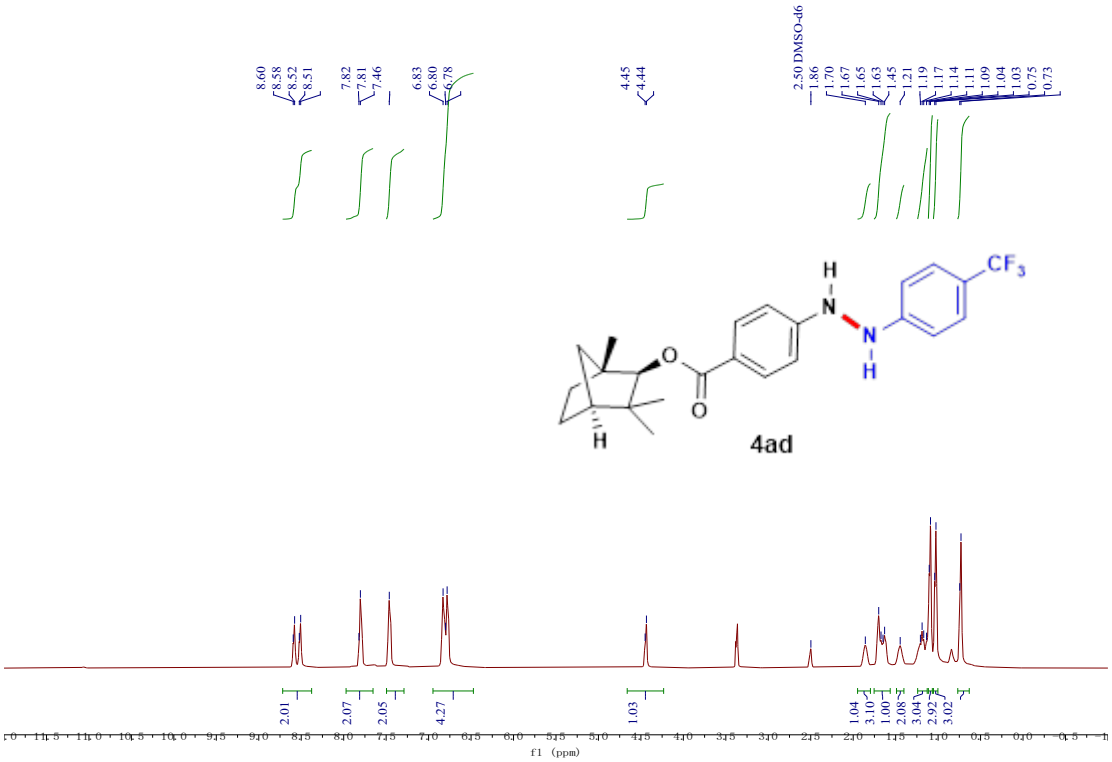
^{13}C NMR of Compound 4ac (126 MHz, $CDCl_3$)



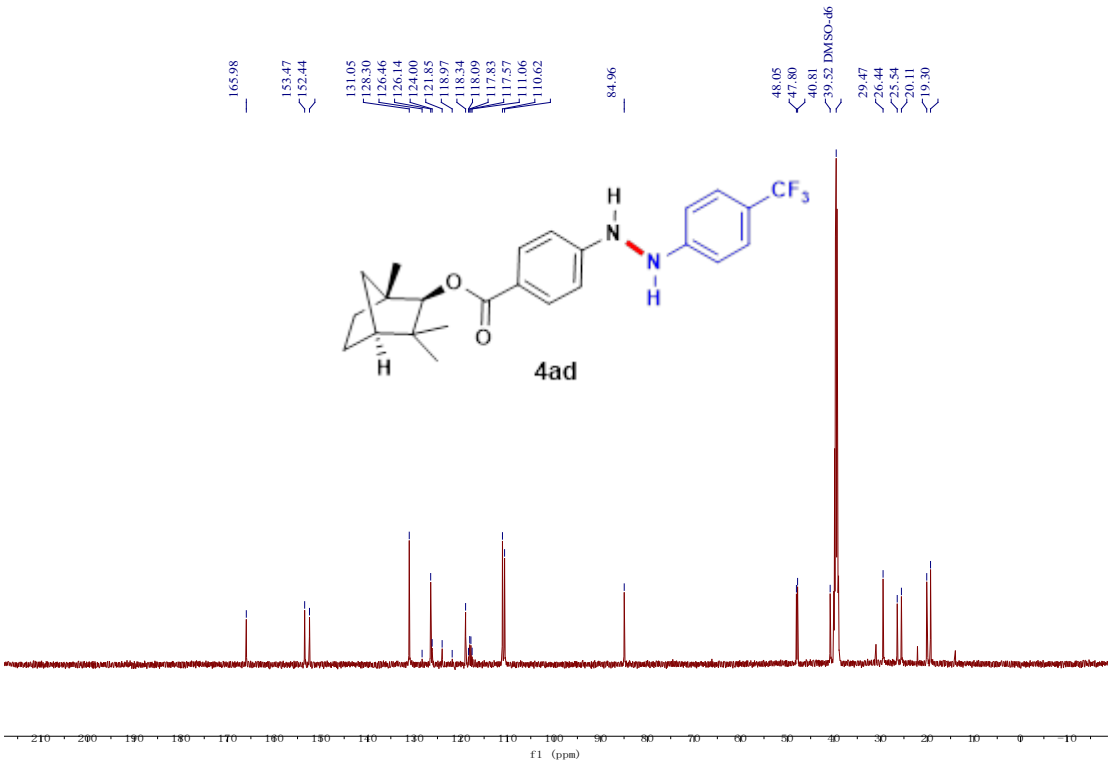
^{19}F NMR of Compound 4ac (471 MHz, $CDCl_3$)



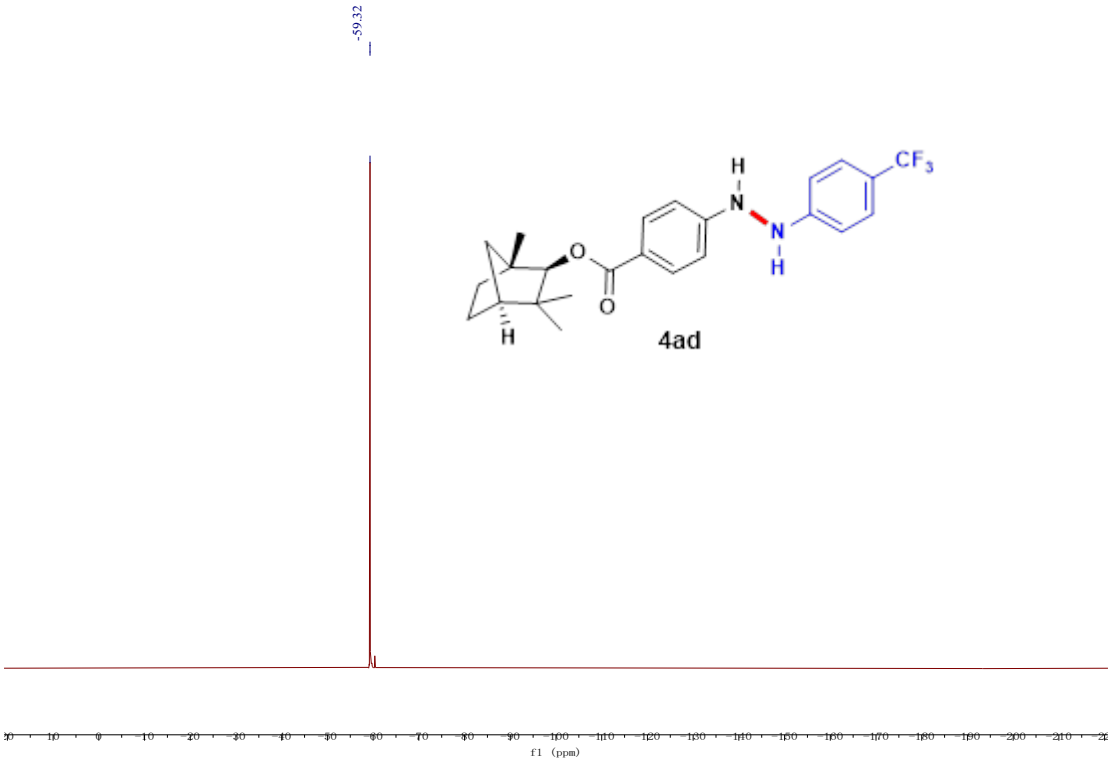
^{1}H NMR of Compound 4ad (500 MHz, DMSO-d_6)



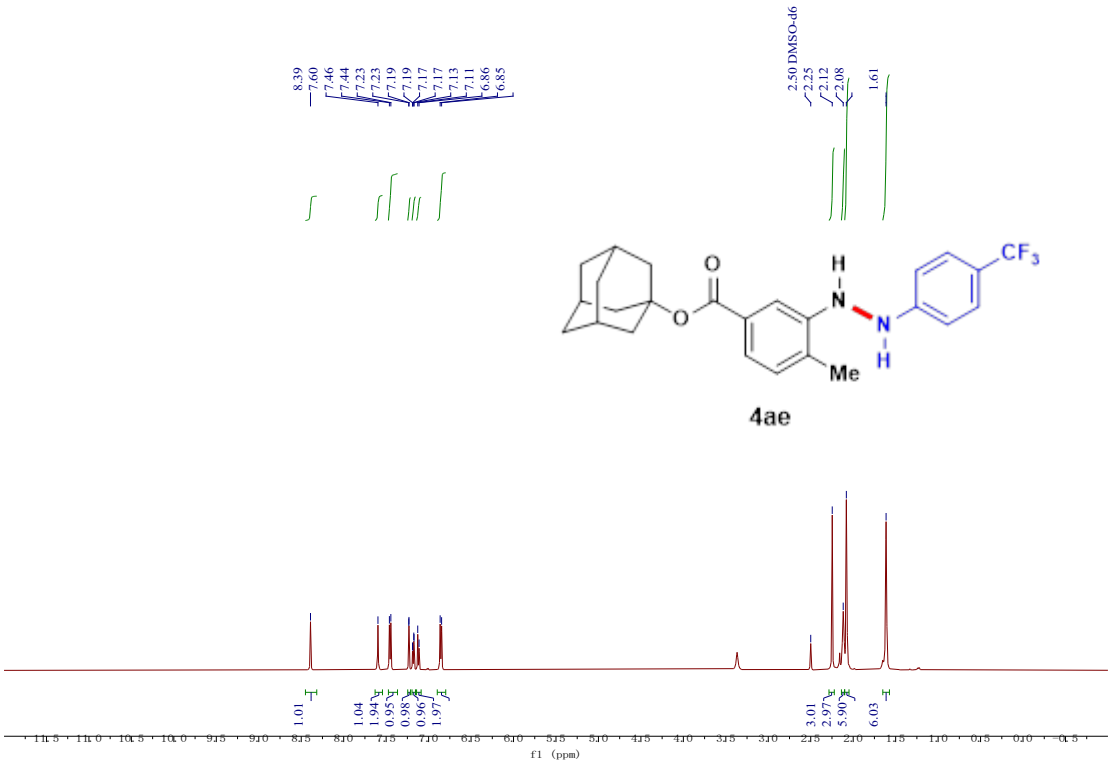
^{13}C NMR of Compound 4ad (126 MHz, DMSO-d_6)



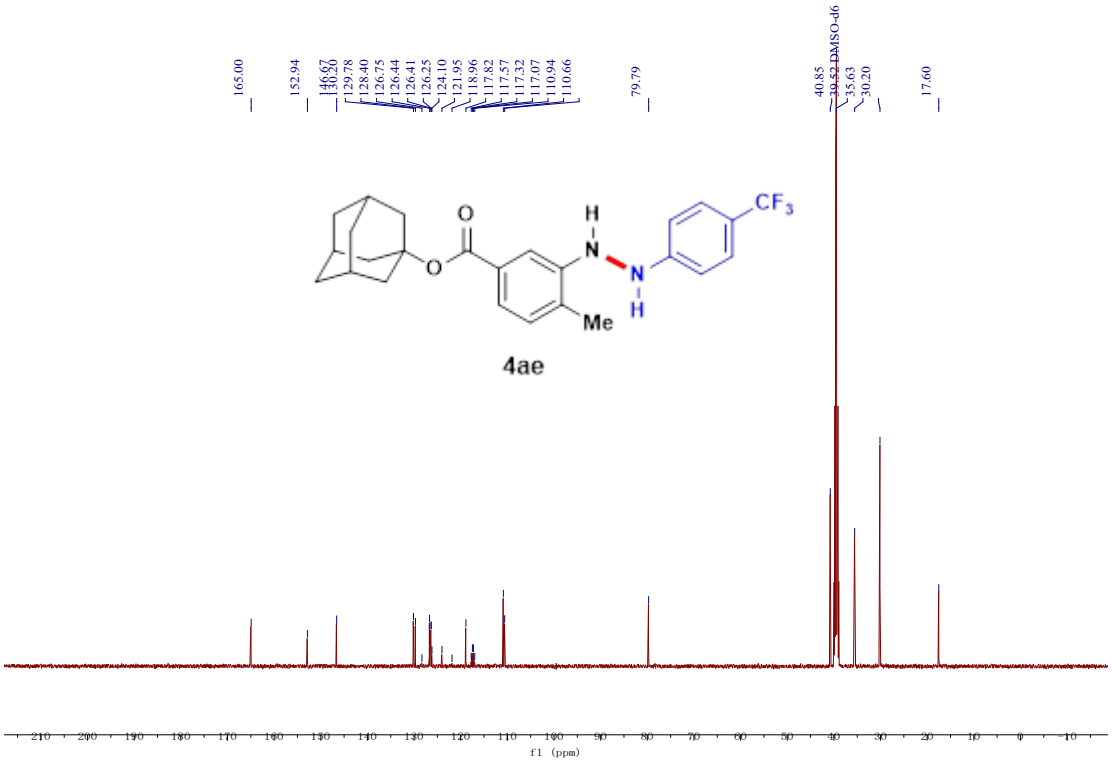
^{19}F NMR of Compound 4ad (471 MHz, DMSO-d_6)



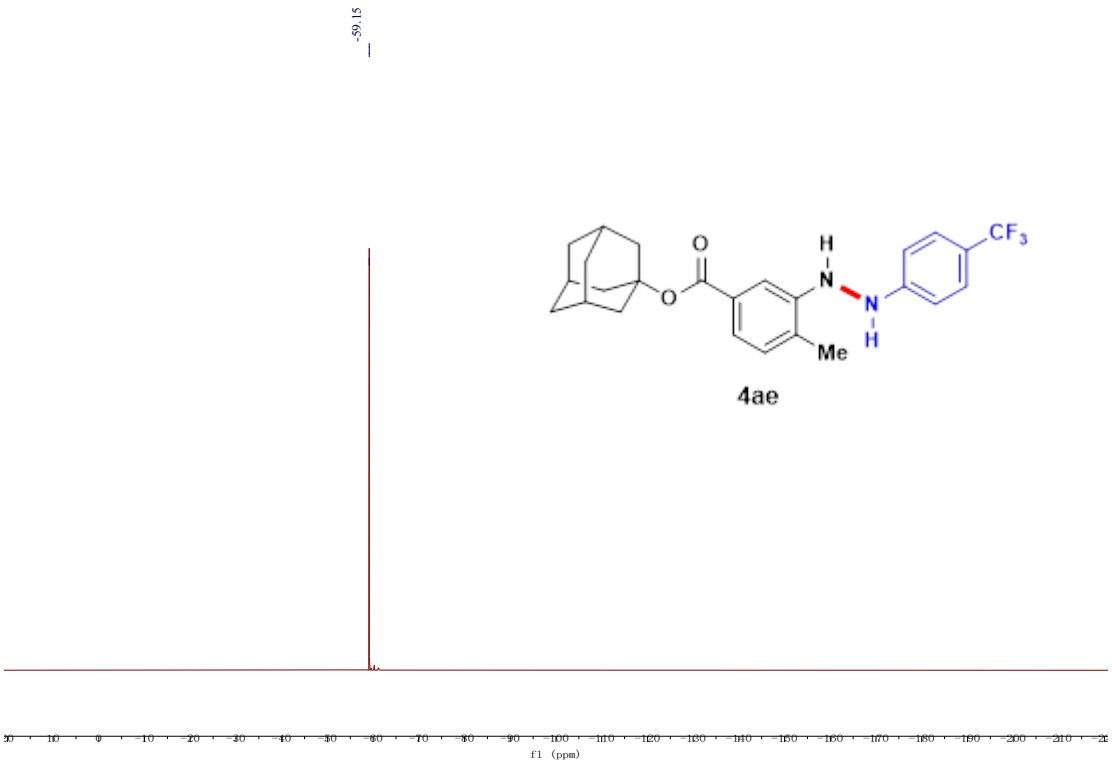
^{1}H NMR of Compound 4ae (500 MHz, DMSO-d_6)



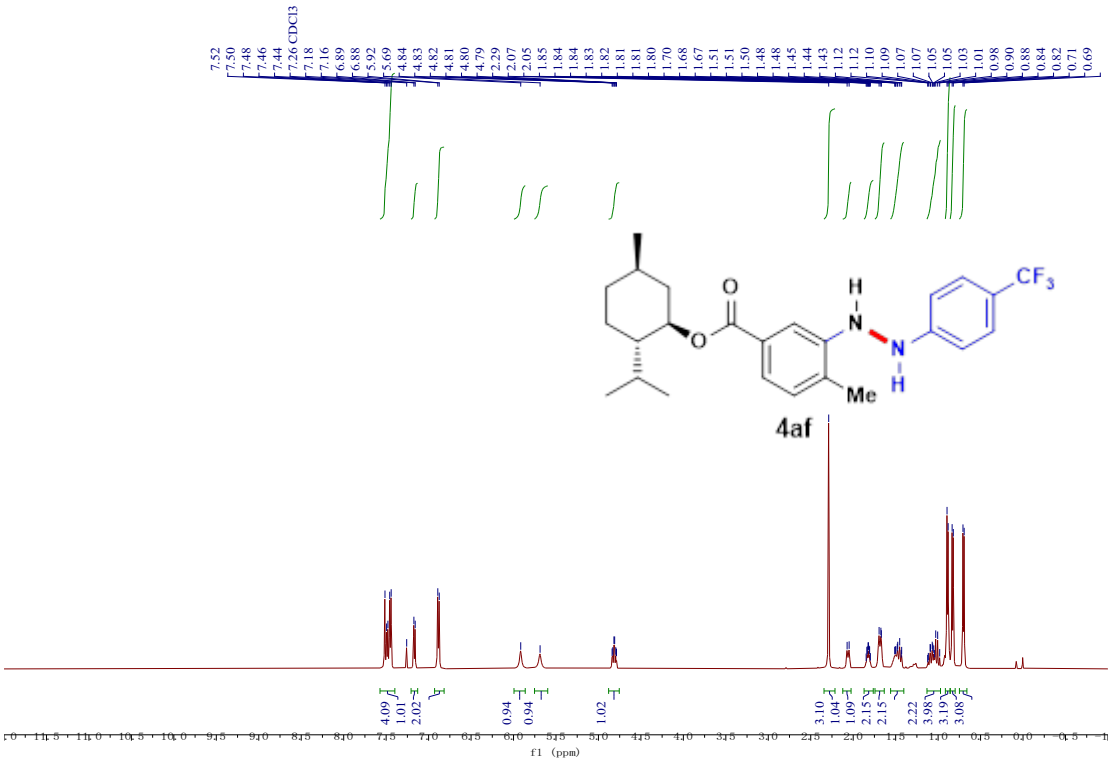
^{13}C NMR of Compound 4ae (126 MHz, DMSO-d_6)



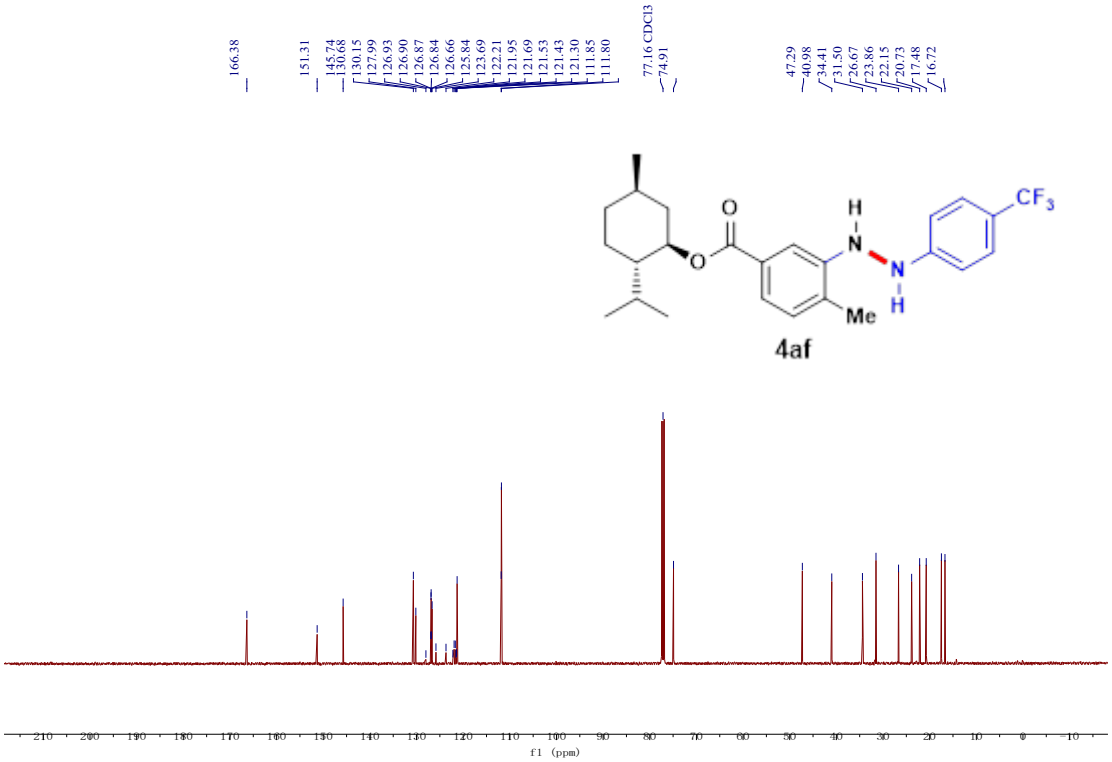
^{19}F NMR of Compound 4ae (471 MHz, DMSO-d_6)



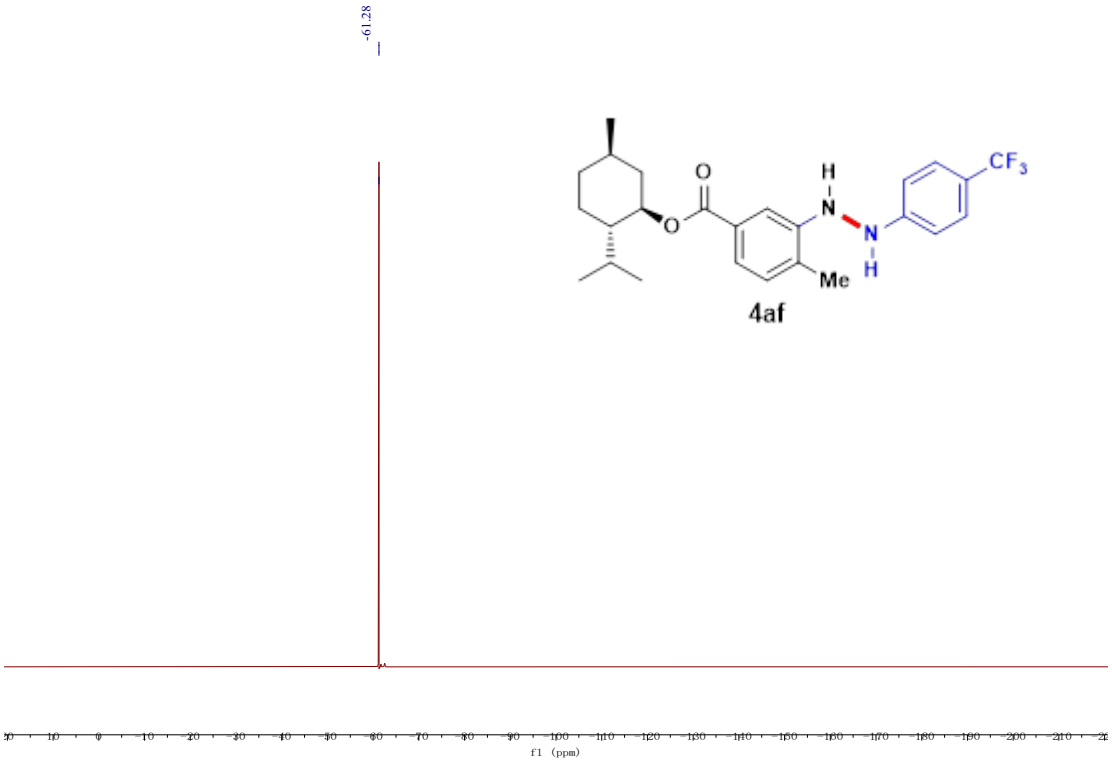
^{1}H NMR of Compound 4af (500 MHz, $CDCl_3$)



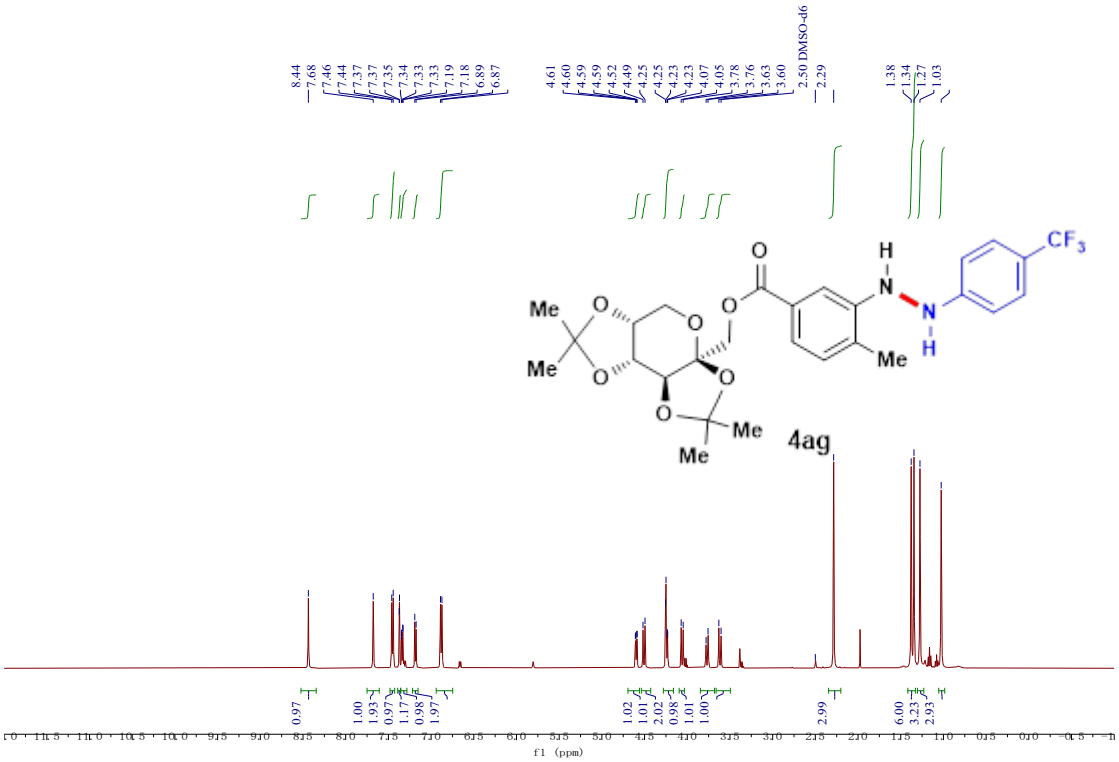
^{13}C NMR of Compound 4af (126 MHz, $CDCl_3$)



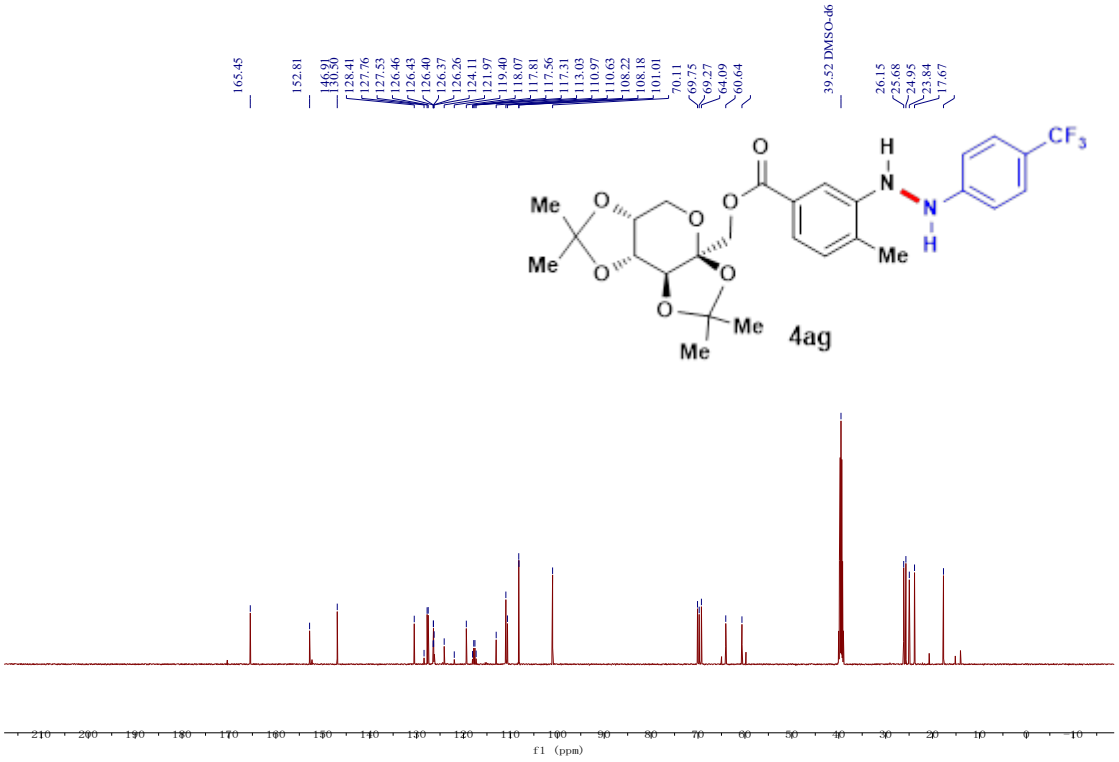
^{19}F NMR of Compound 4af (471 MHz, $CDCl_3$)



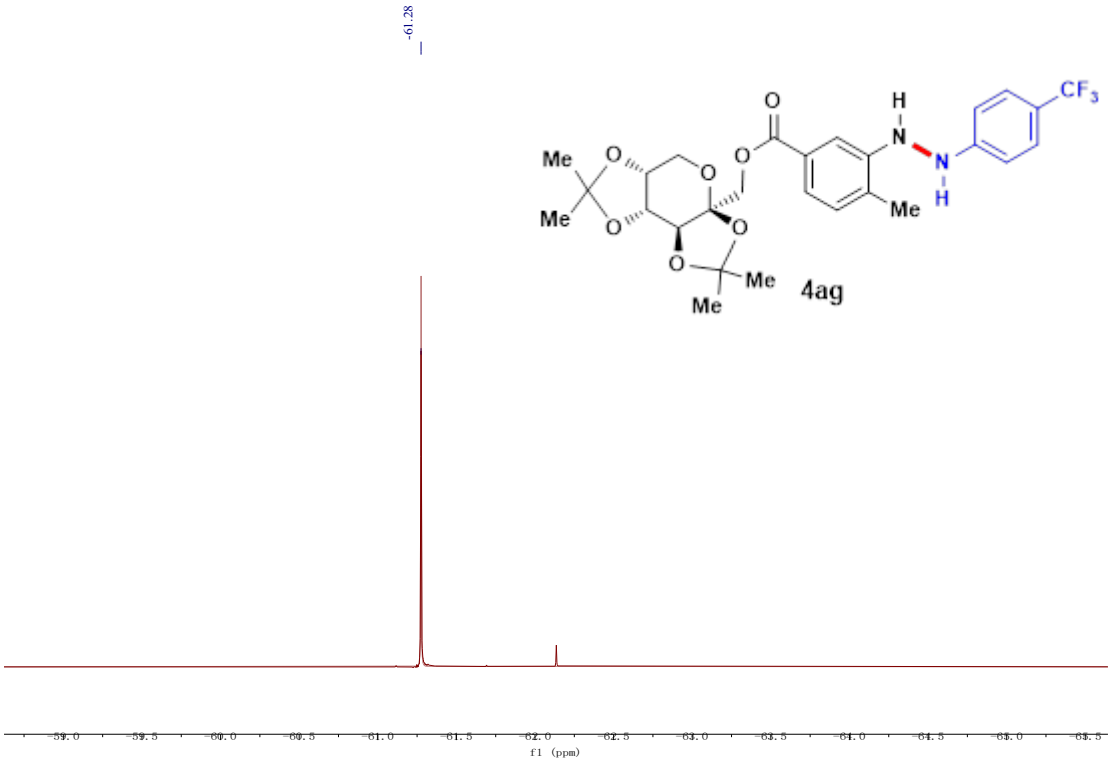
^{1}H NMR of Compound 4ag (500 MHz, DMSO-d_6)



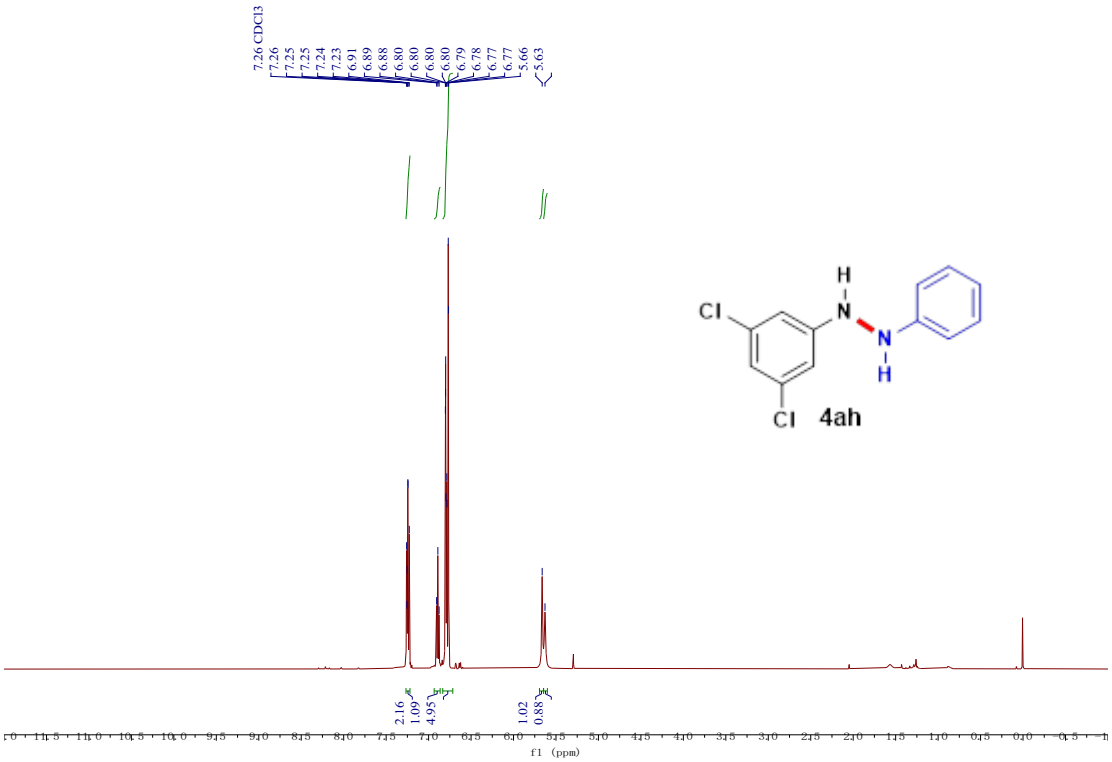
^{13}C NMR of Compound 4ag (126 MHz, DMSO-d_6)



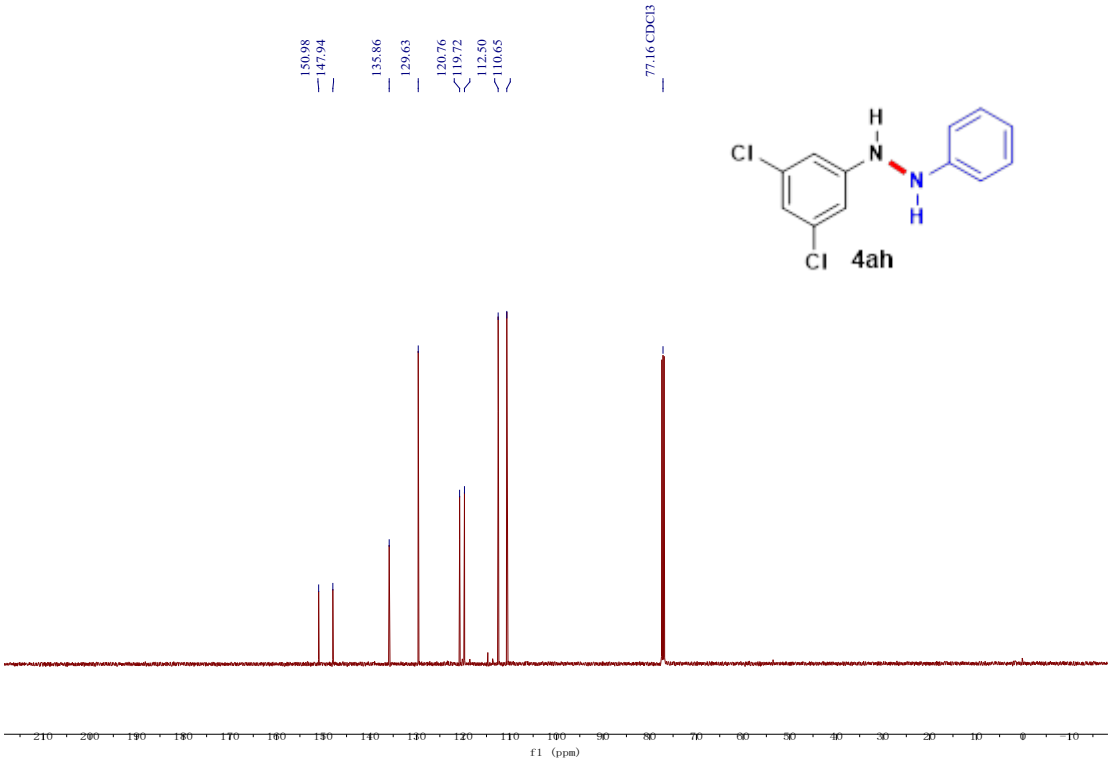
^{19}F NMR of Compound 4ag (471 MHz, $CDCl_3$)



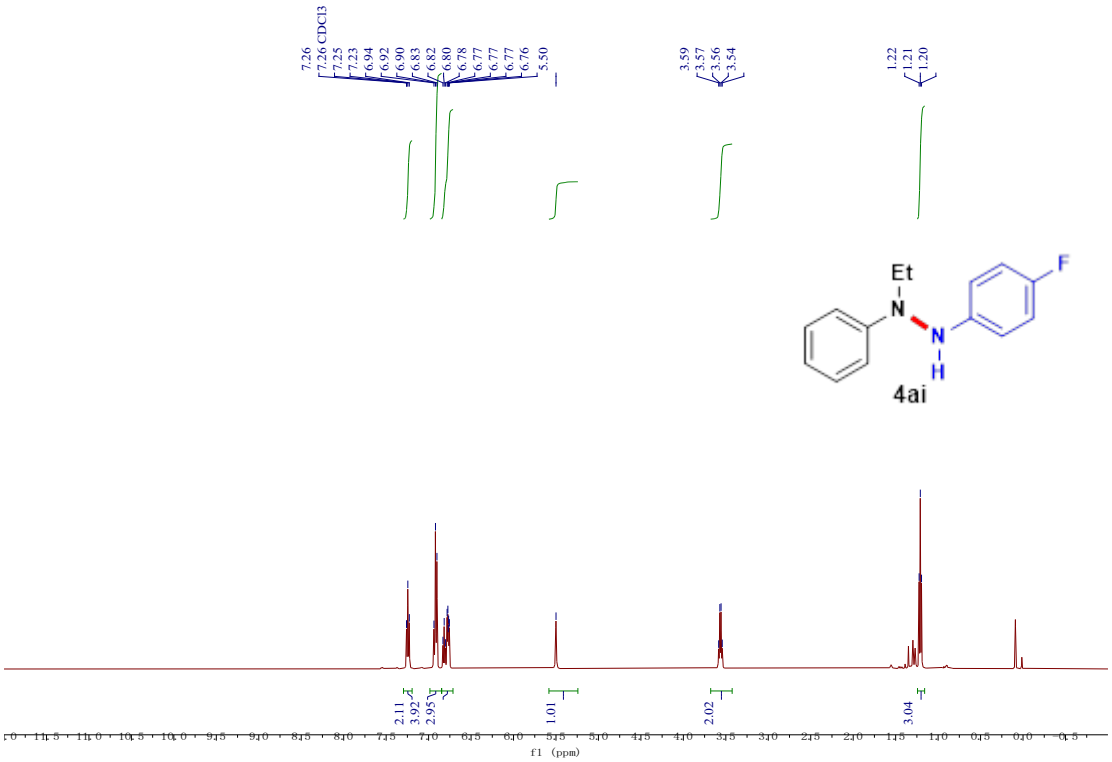
^{1}H NMR of Compound 4ah (500 MHz, $CDCl_3$)



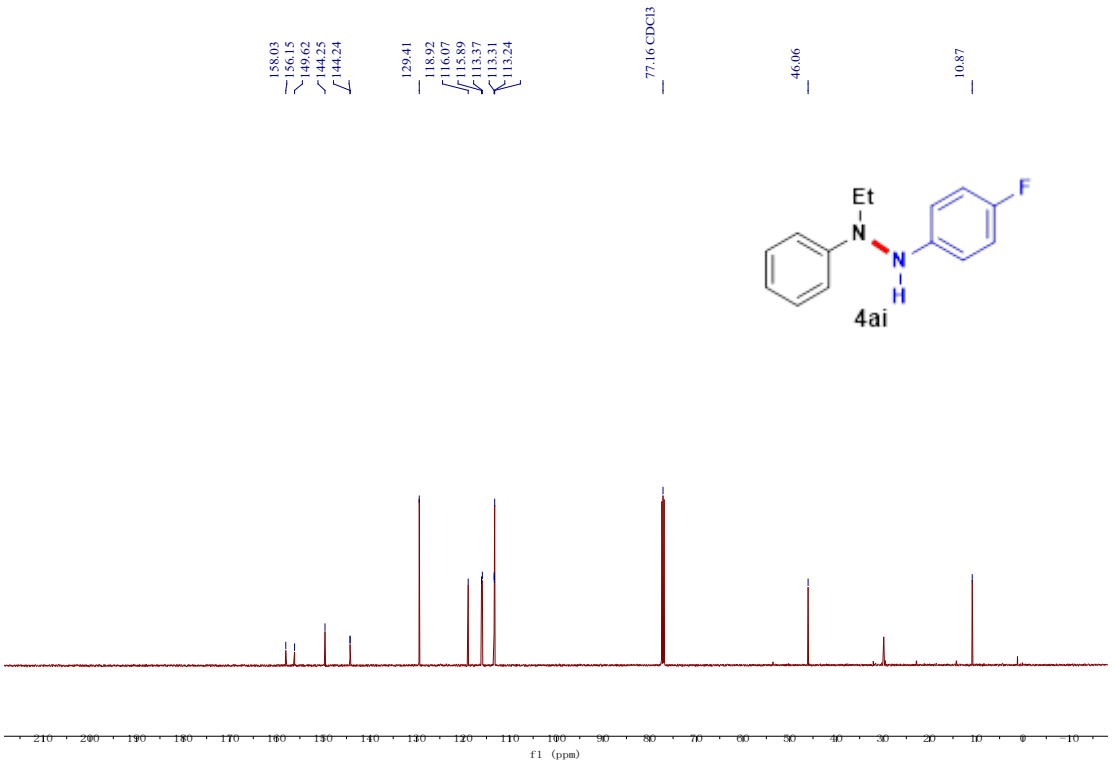
^{13}C NMR of Compound 4ah (126 MHz, $CDCl_3$)



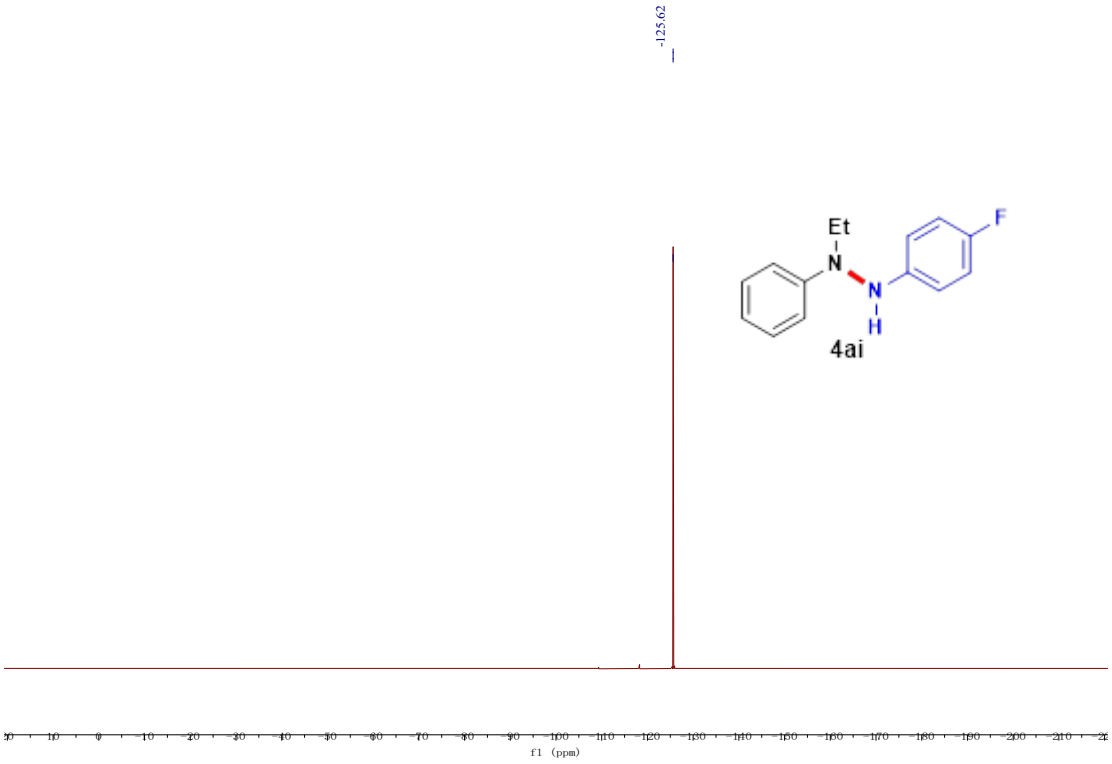
^{1}H NMR of Compound 4ai (500 MHz, $CDCl_3$)



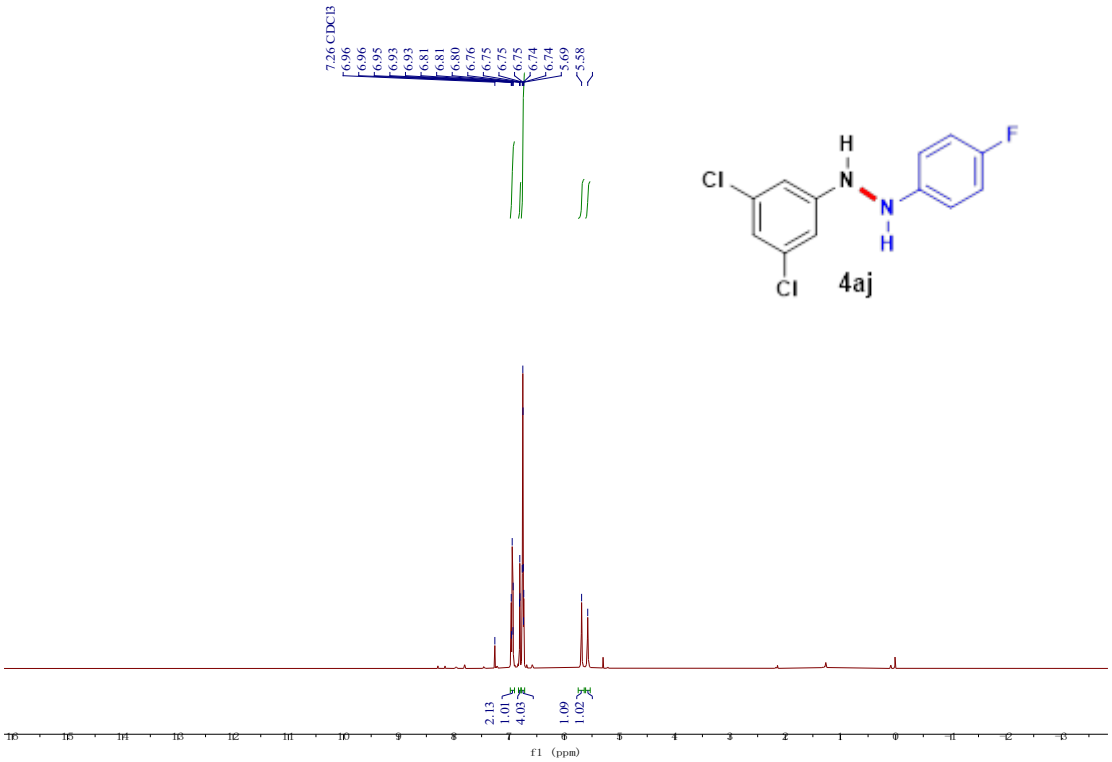
^{13}C NMR of Compound 4ai (126 MHz, $CDCl_3$)



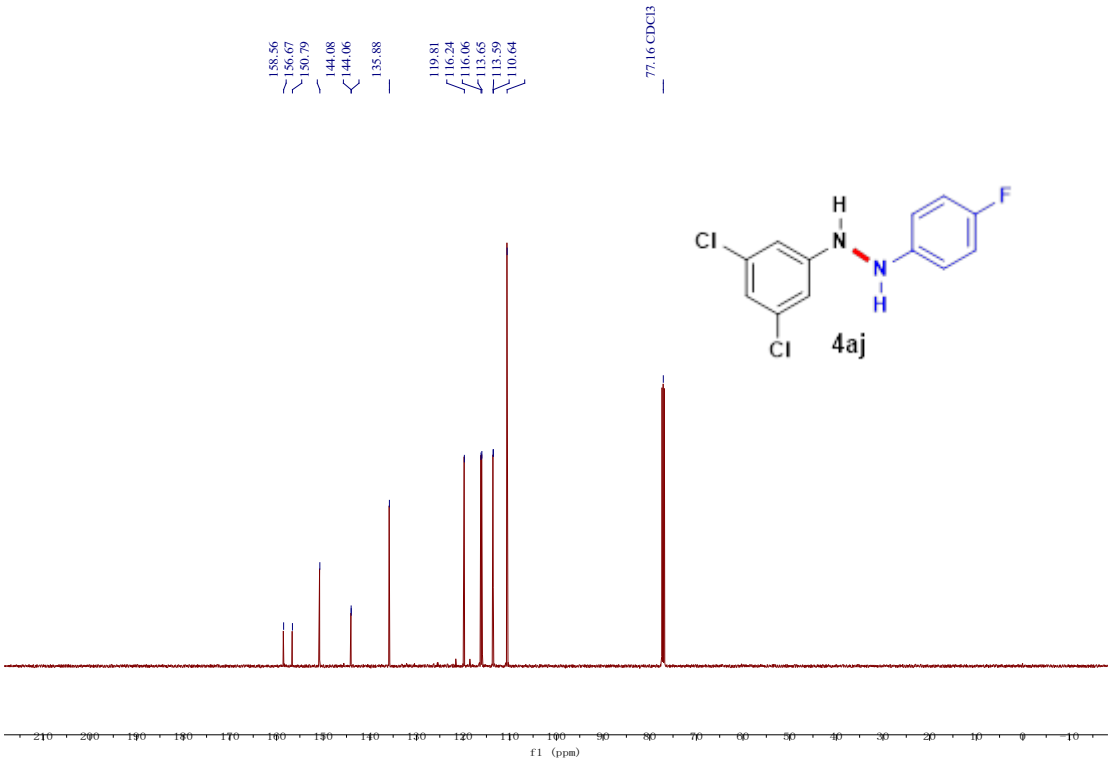
^{19}F NMR of Compound 4ai (471 MHz, $CDCl_3$)



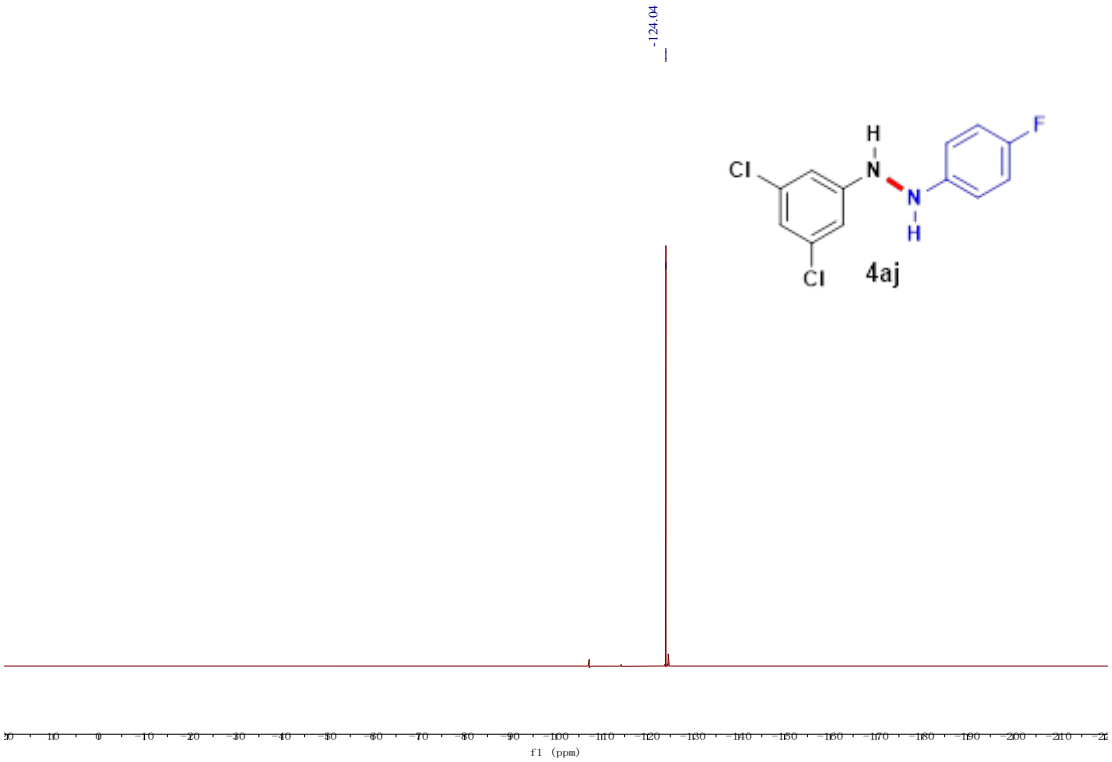
^{1}H NMR of Compound 4aj (500 MHz, $CDCl_3$)



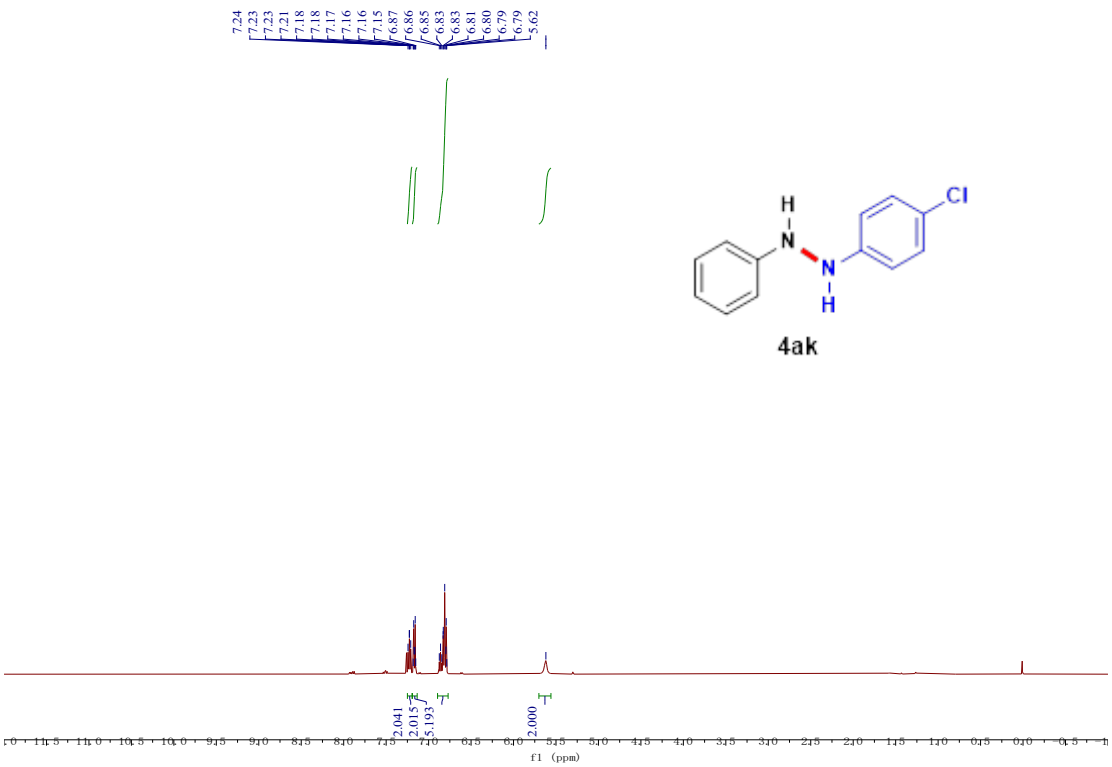
^{13}C NMR of Compound 4aj (126 MHz, $CDCl_3$)



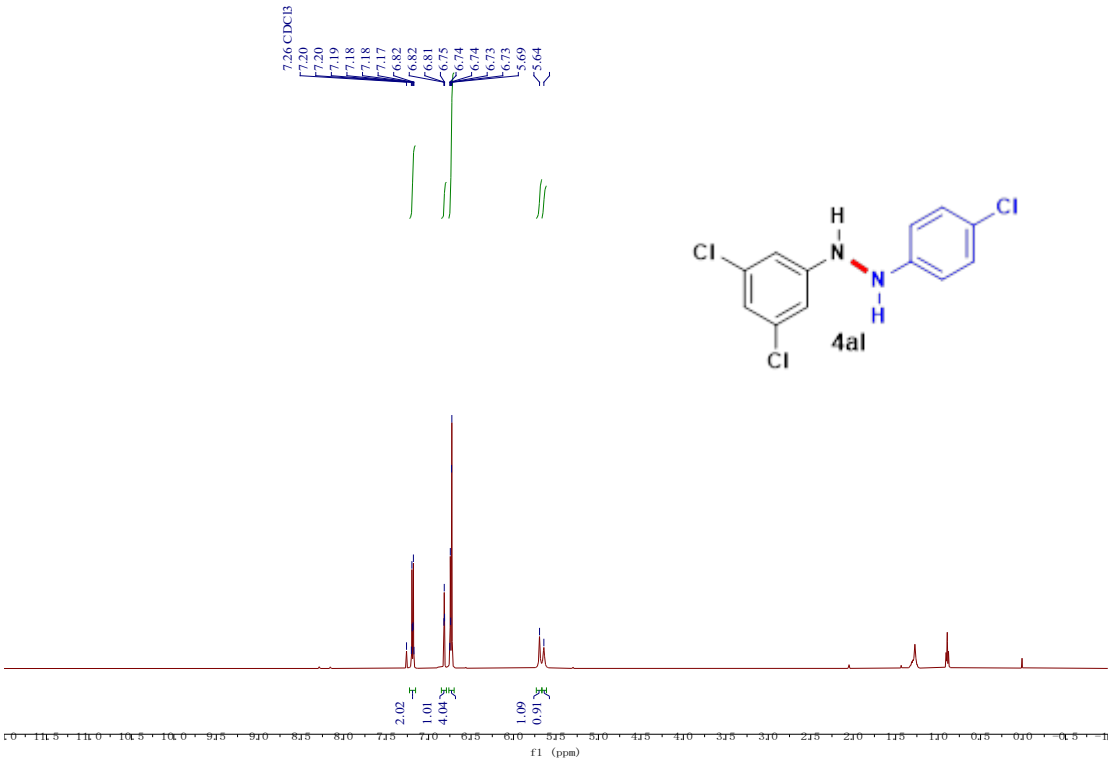
^{19}F NMR of Compound 4aj (471 MHz, $CDCl_3$)



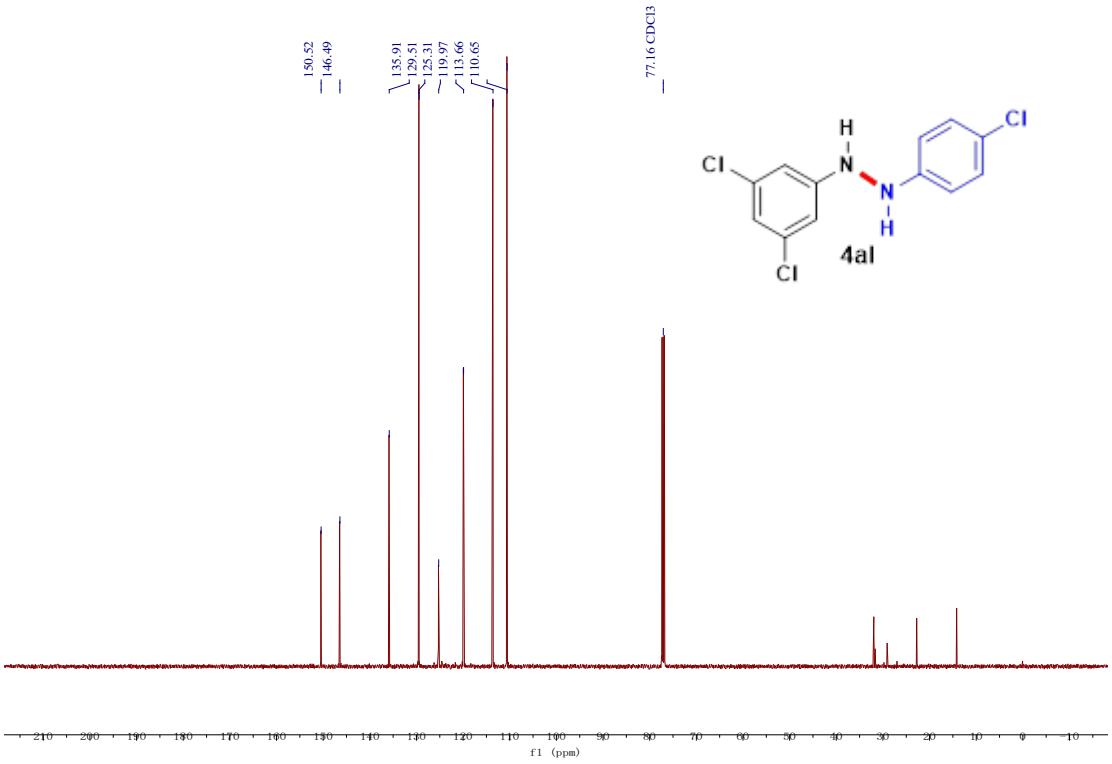
^{1}H NMR of Compound 4ak (500 MHz, $CDCl_3$)



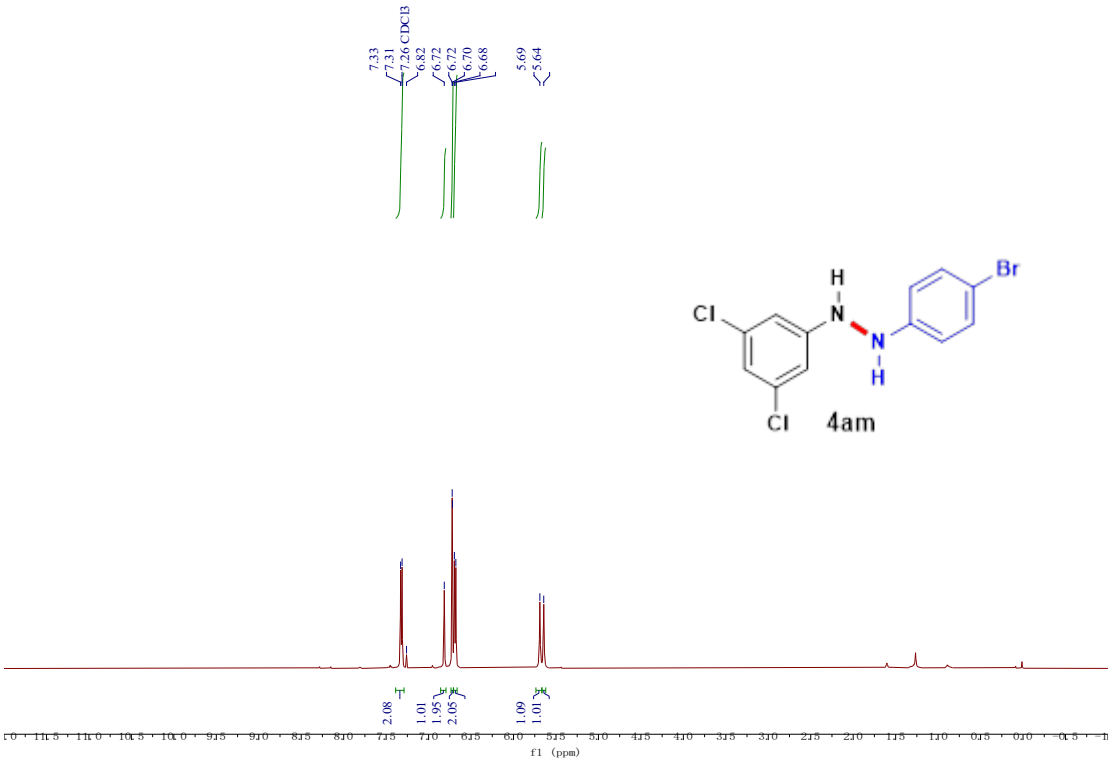
^{1}H NMR of Compound 4al (500 MHz, $CDCl_3$)



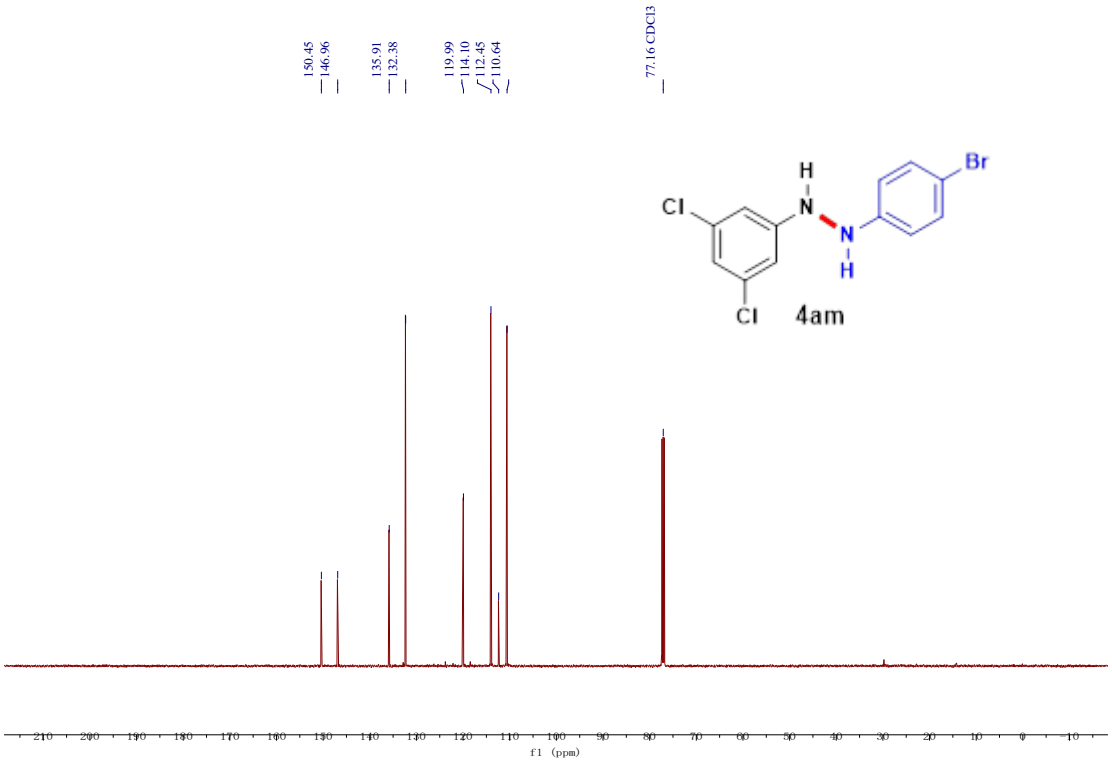
^{13}C NMR of Compound 4al (126 MHz, $CDCl_3$)



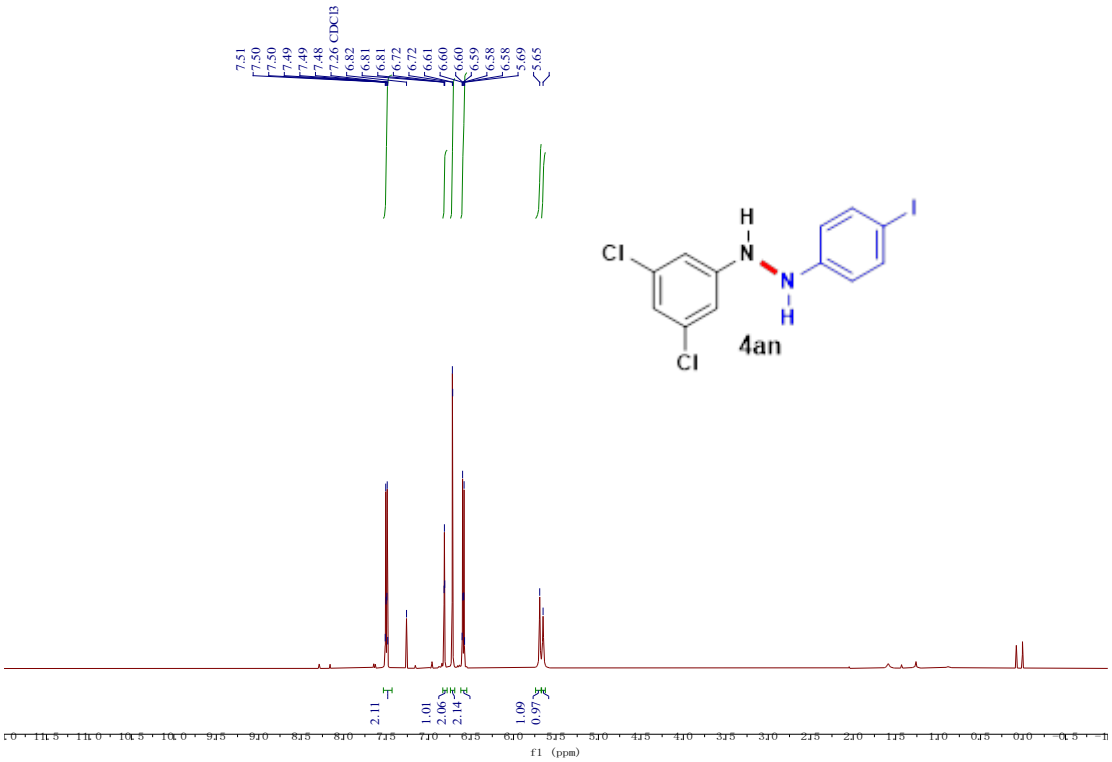
^{1}H NMR of Compound 4am (500 MHz, $CDCl_3$)



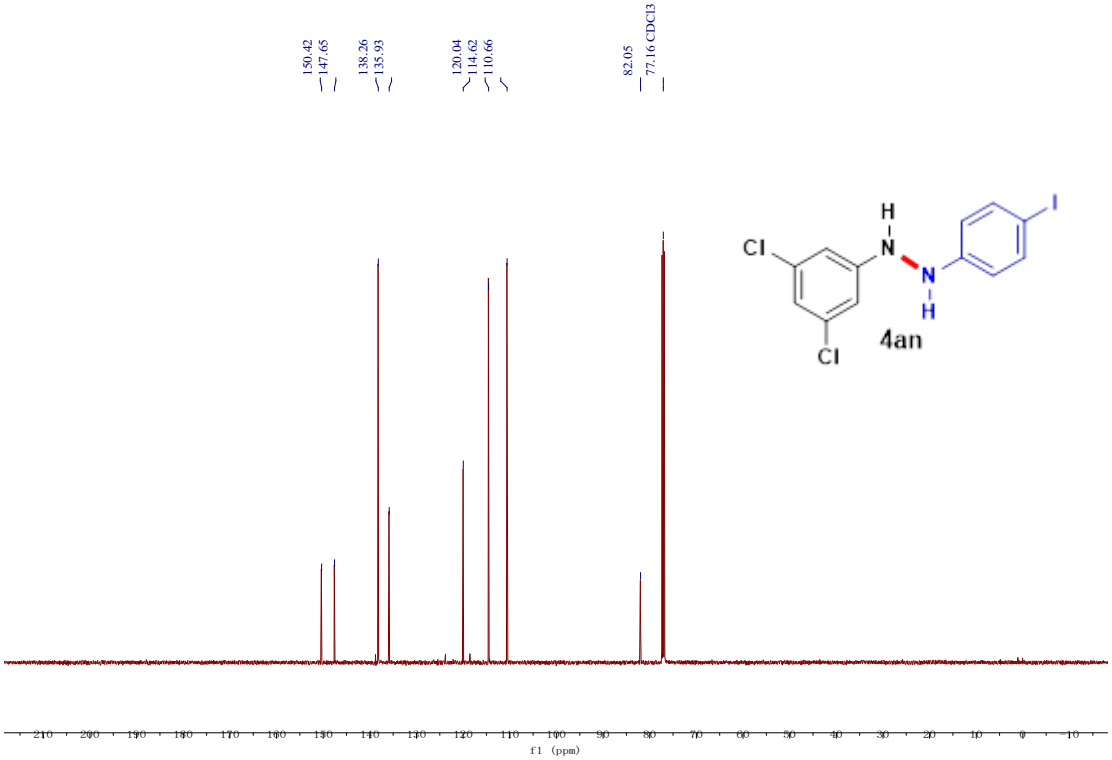
^{13}C NMR of Compound 4am (126 MHz, $CDCl_3$)



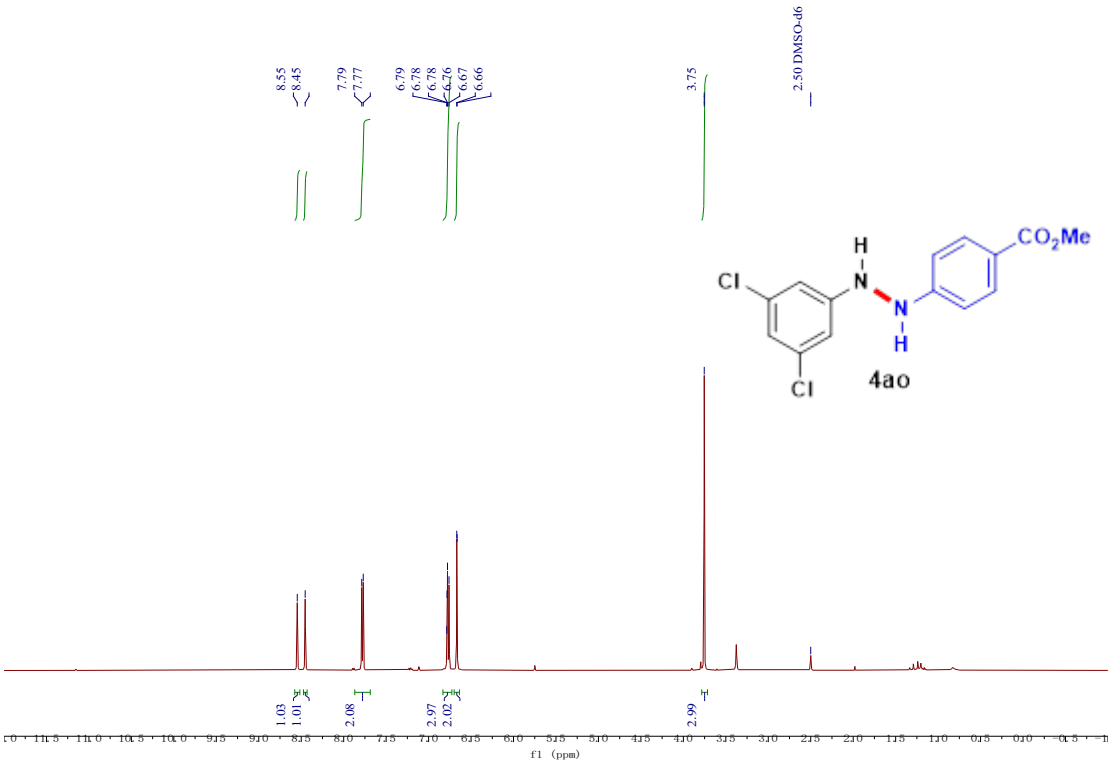
^{1}H NMR of Compound 4an (500 MHz, $CDCl_3$)



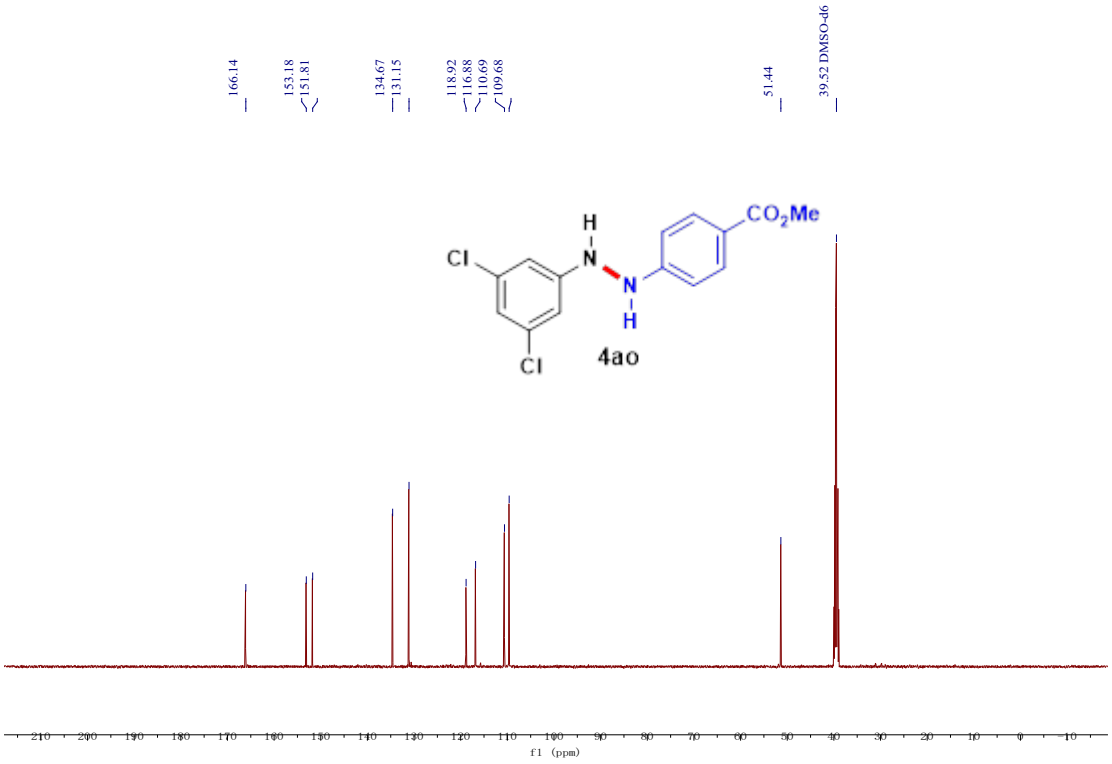
^{13}C NMR of Compound 4an (126 MHz, $CDCl_3$)



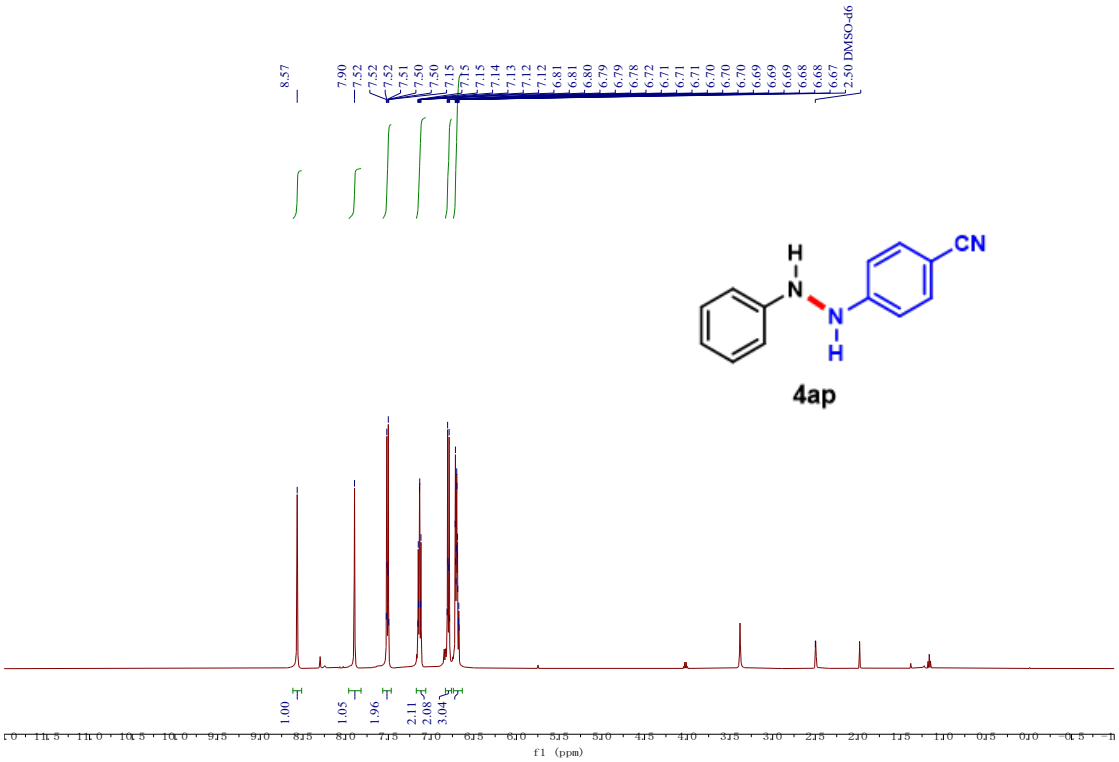
^{1}H NMR of Compound 4ao (500 MHz, $CDCl_3$)



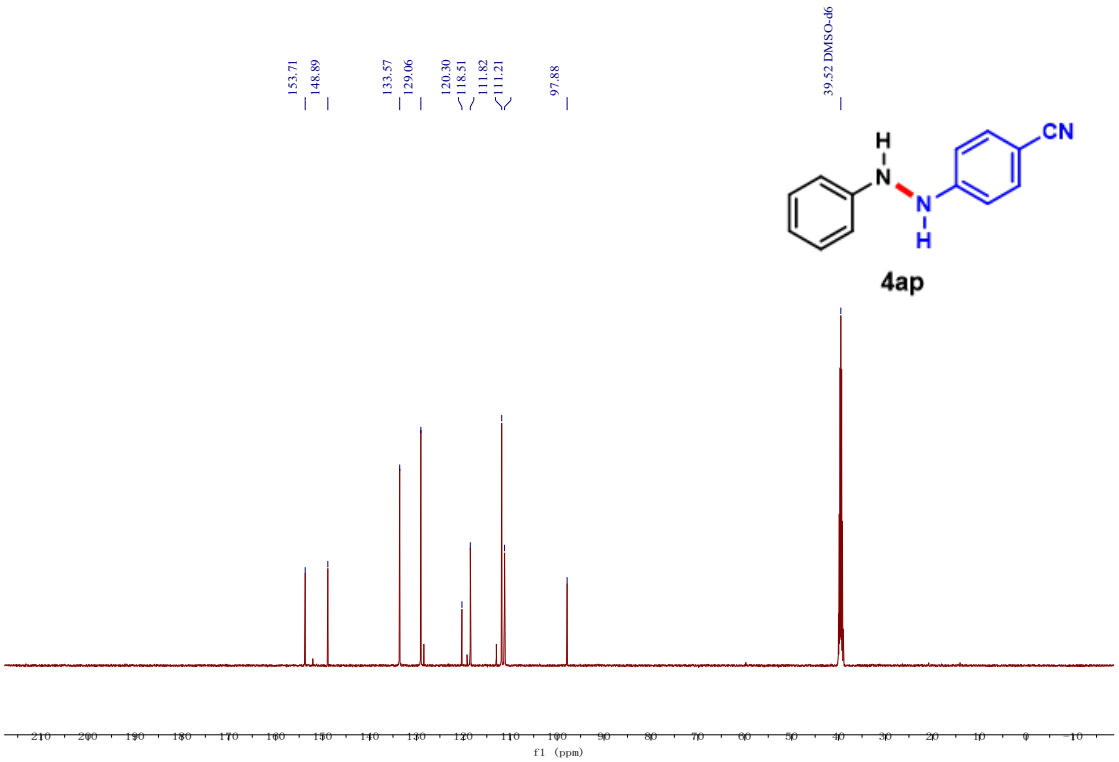
^{13}C NMR of Compound 4ao (126 MHz, $CDCl_3$)



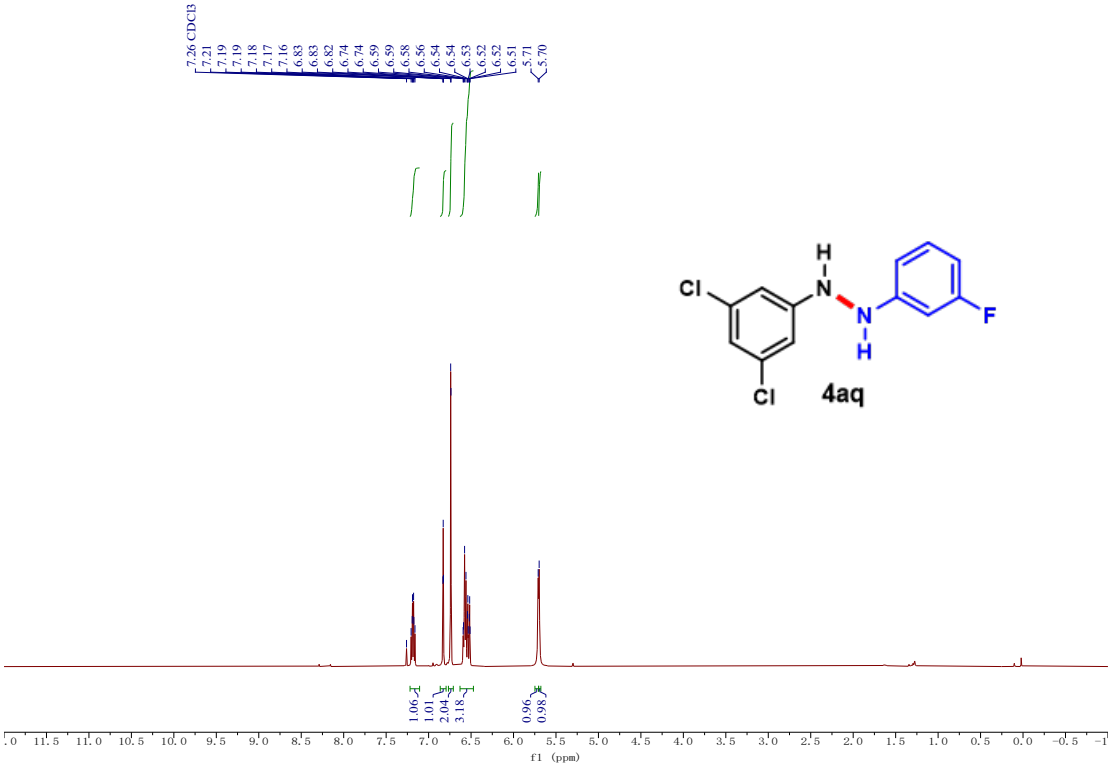
^{1}H NMR of Compound 4ap (500 MHz, DMSO-d_6)



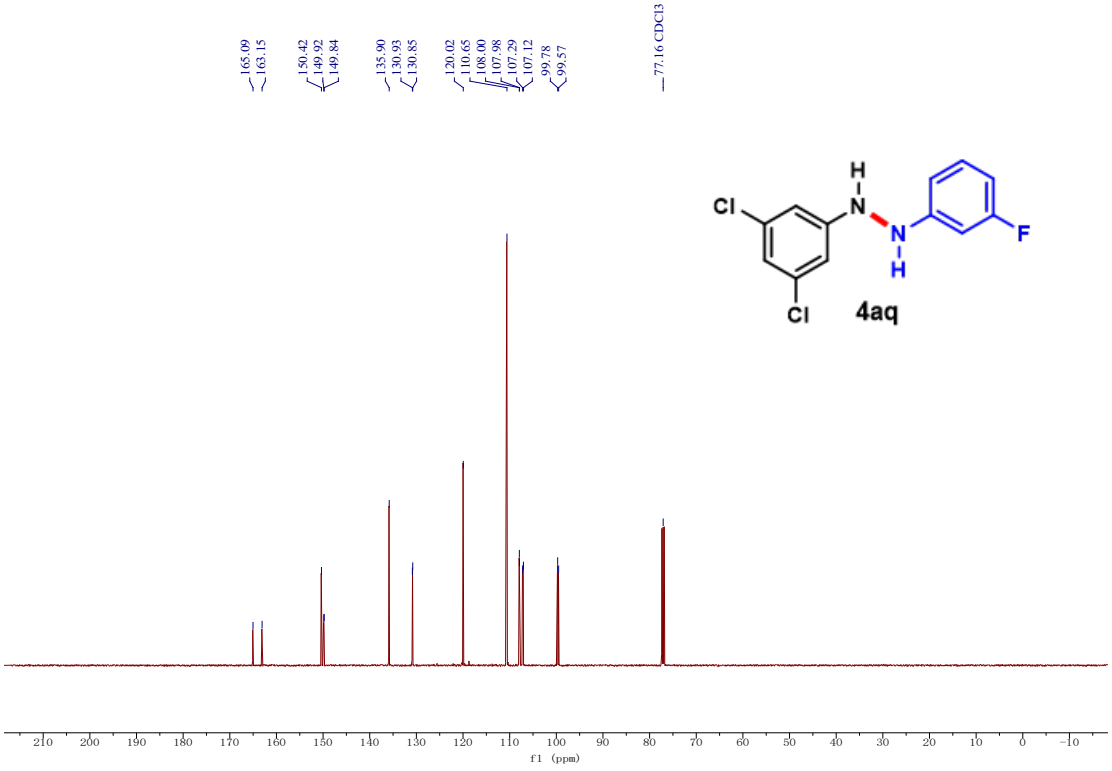
^{13}C NMR of Compound 4ap (126 MHz, DMSO-d_6)



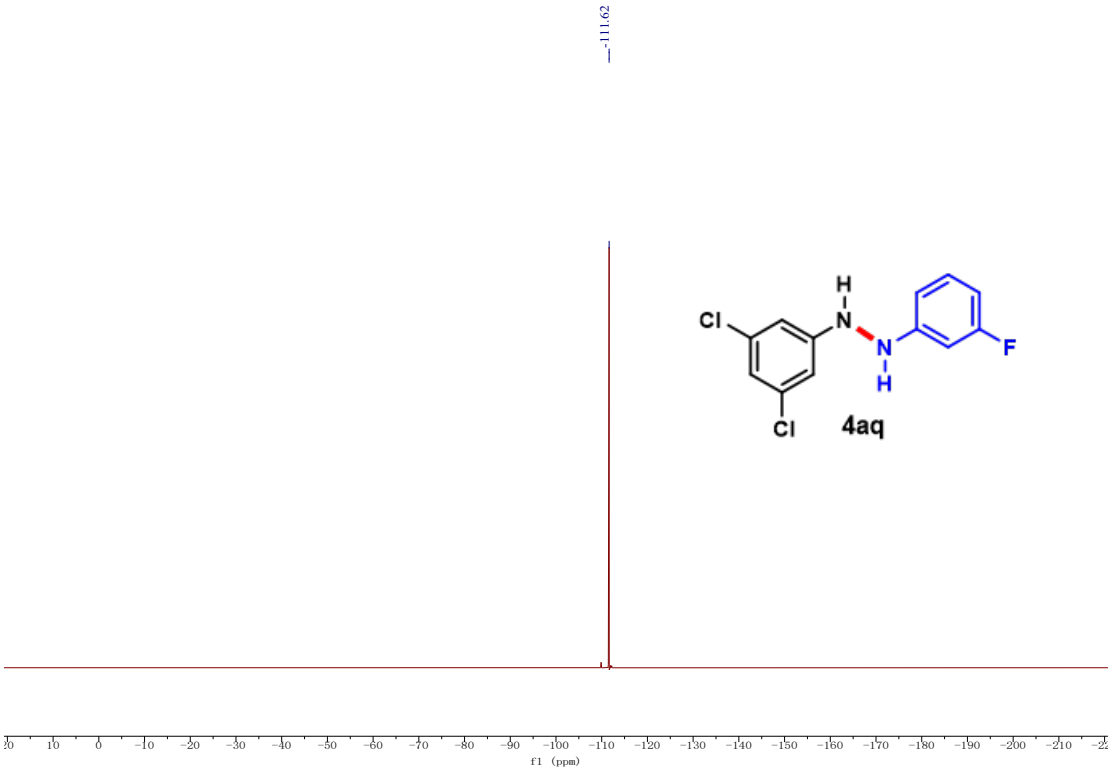
^{1}H NMR of Compound 4aq (500 MHz, $CDCl_3$)



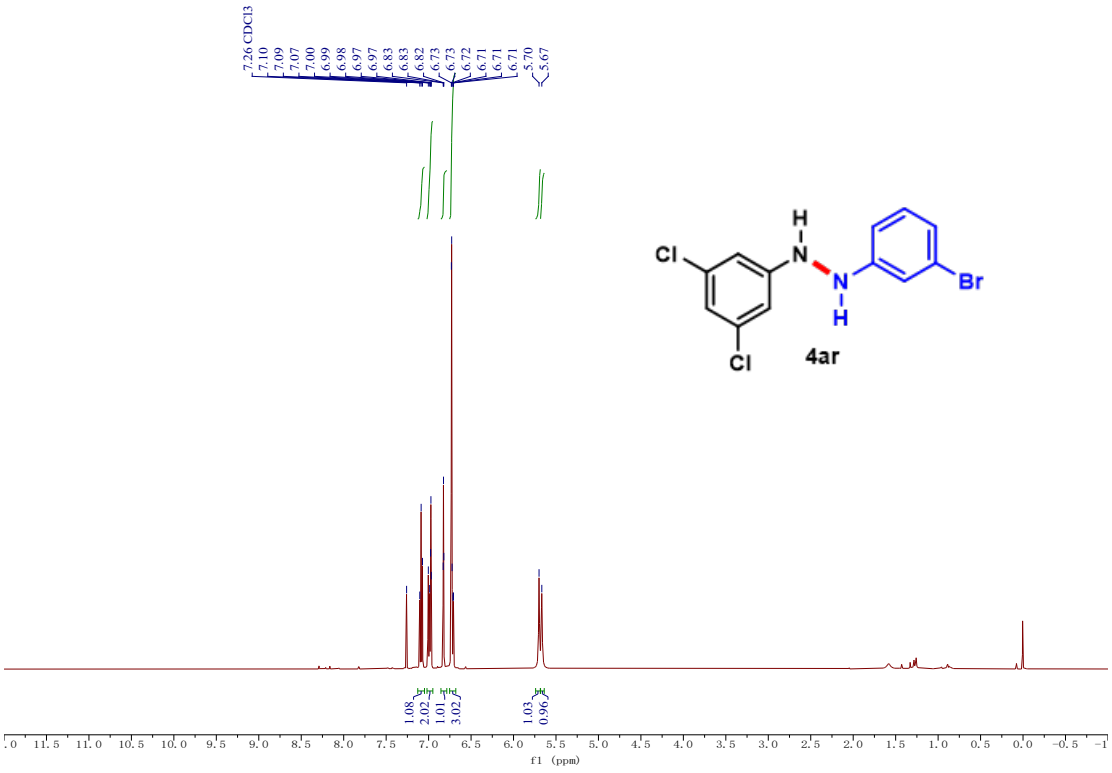
^{13}C NMR of Compound 4aq (126 MHz, $CDCl_3$)



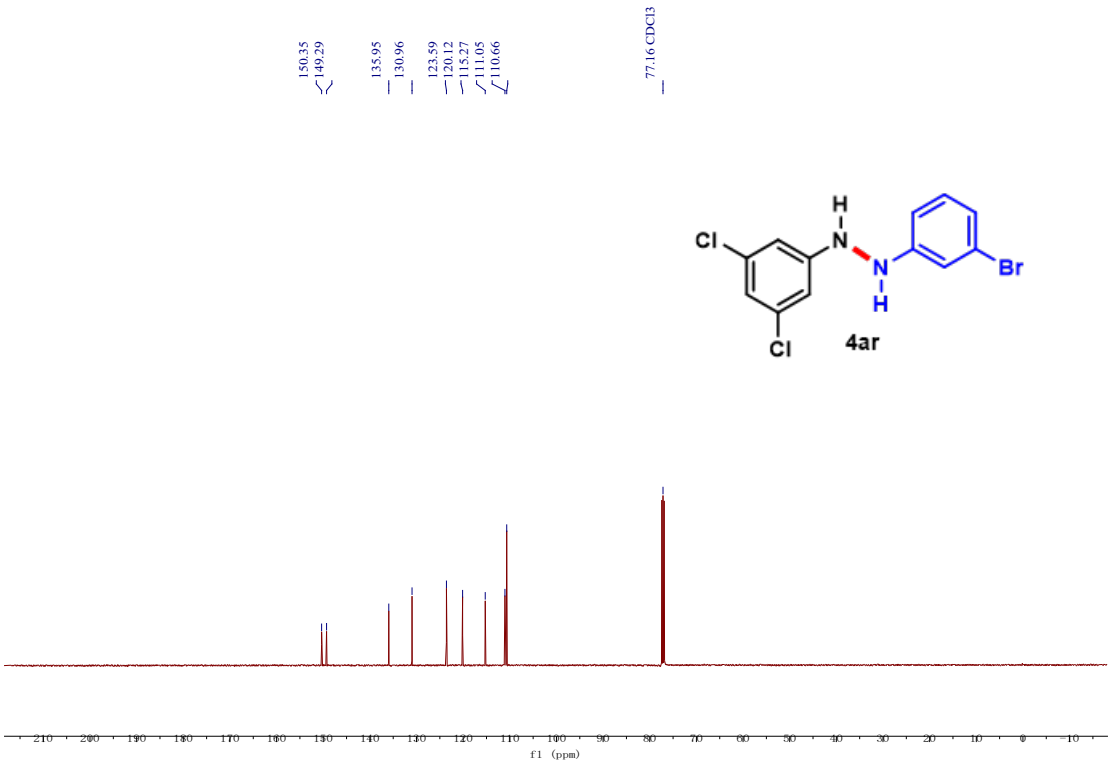
^{19}F NMR of Compound 4aq (471 MHz, $CDCl_3$)



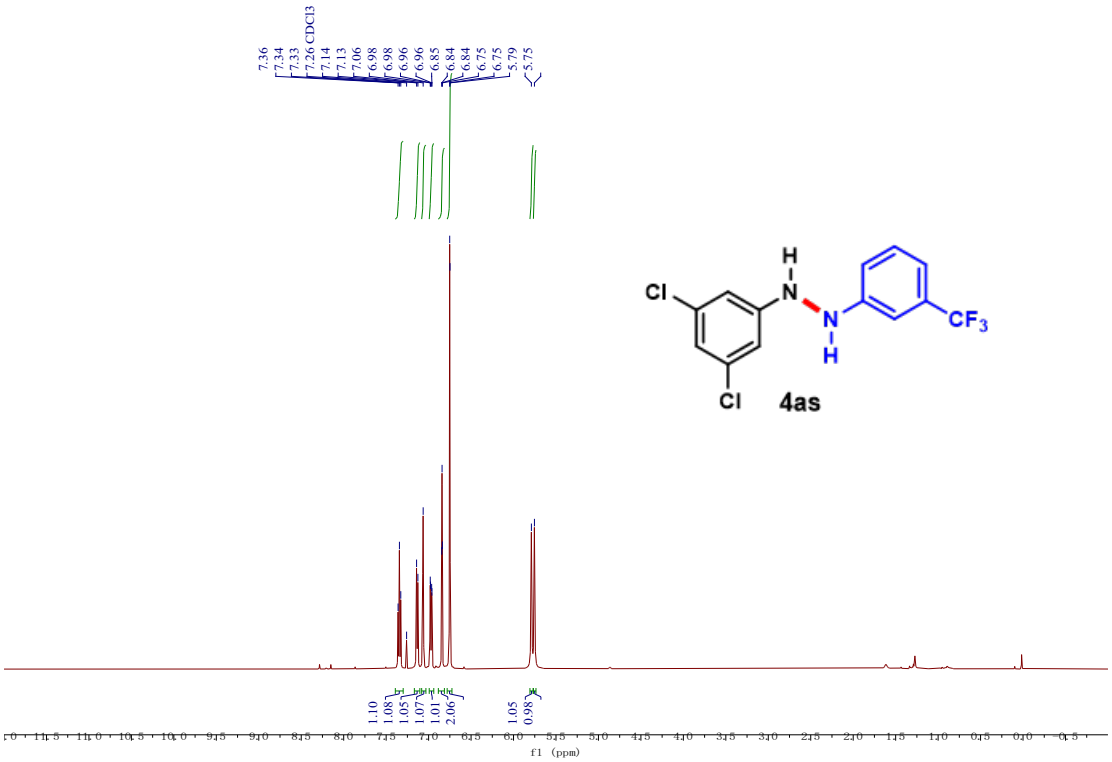
^{1}H NMR of Compound 4ar (500 MHz, $CDCl_3$)



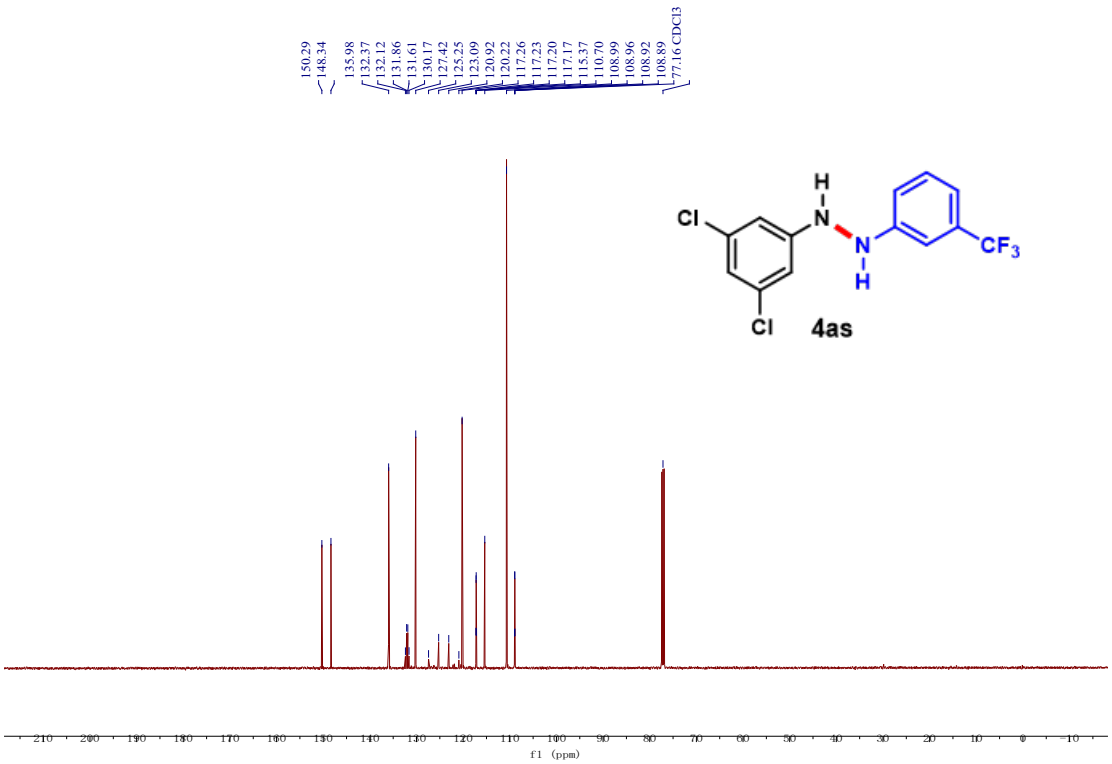
^{13}C NMR of Compound 4ar (126 MHz, $CDCl_3$)



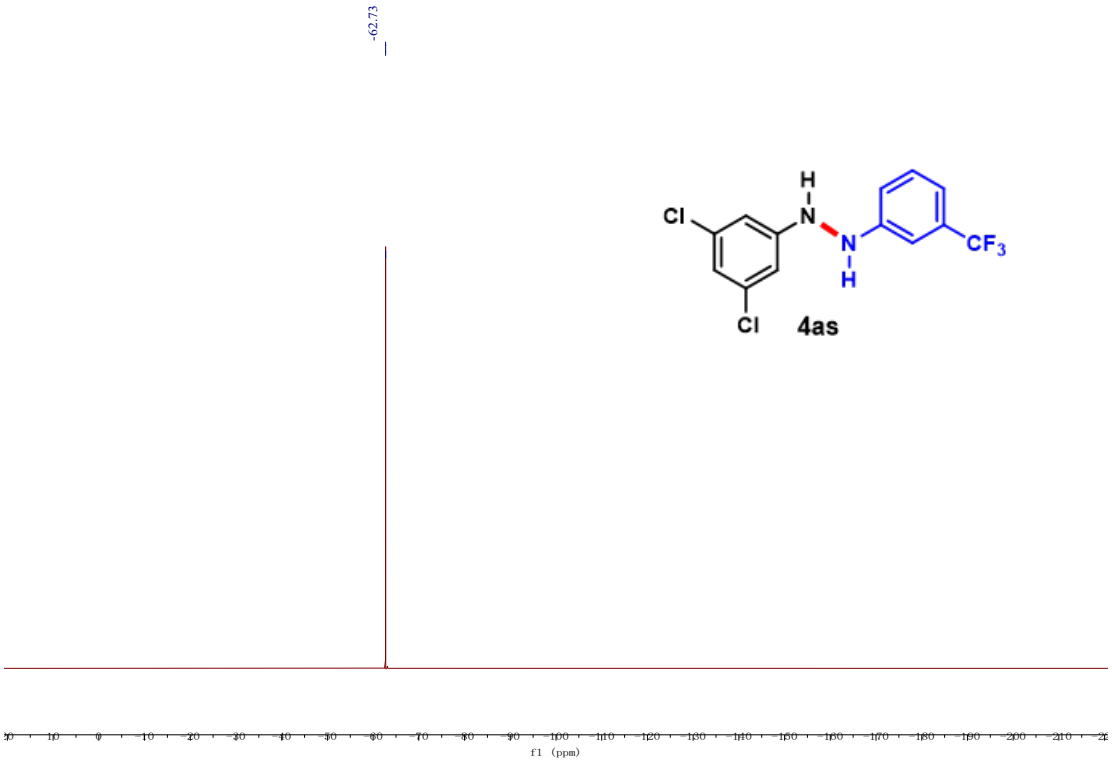
^{1}H NMR of Compound 4as (500 MHz, $CDCl_3$)



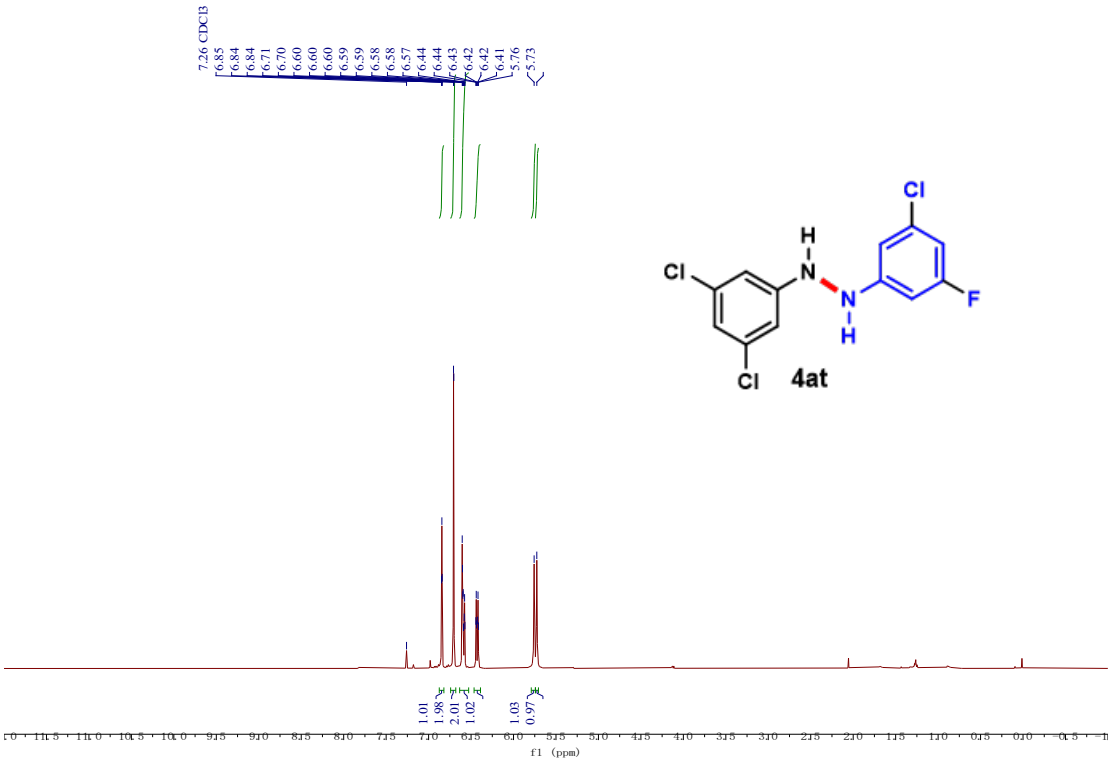
^{13}C NMR of Compound 4as (126 MHz, $CDCl_3$)



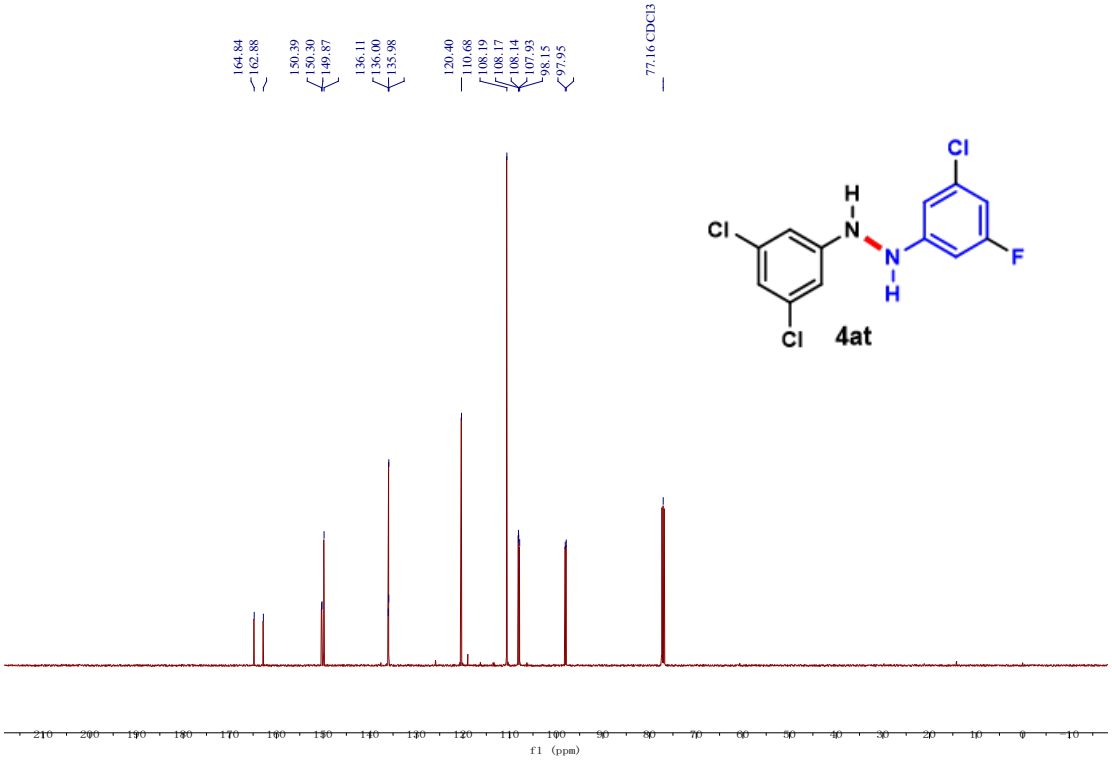
^{19}F NMR of Compound 4as (471 MHz, $CDCl_3$)



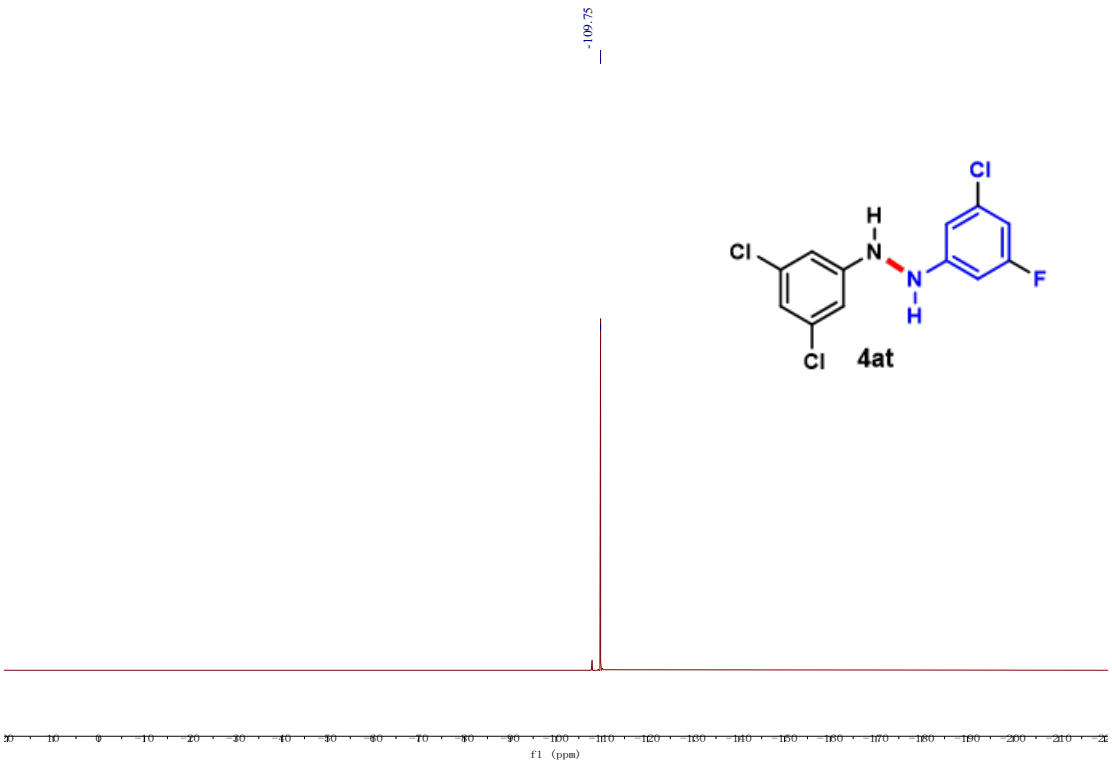
^{1}H NMR of Compound 4at (500 MHz, $CDCl_3$)



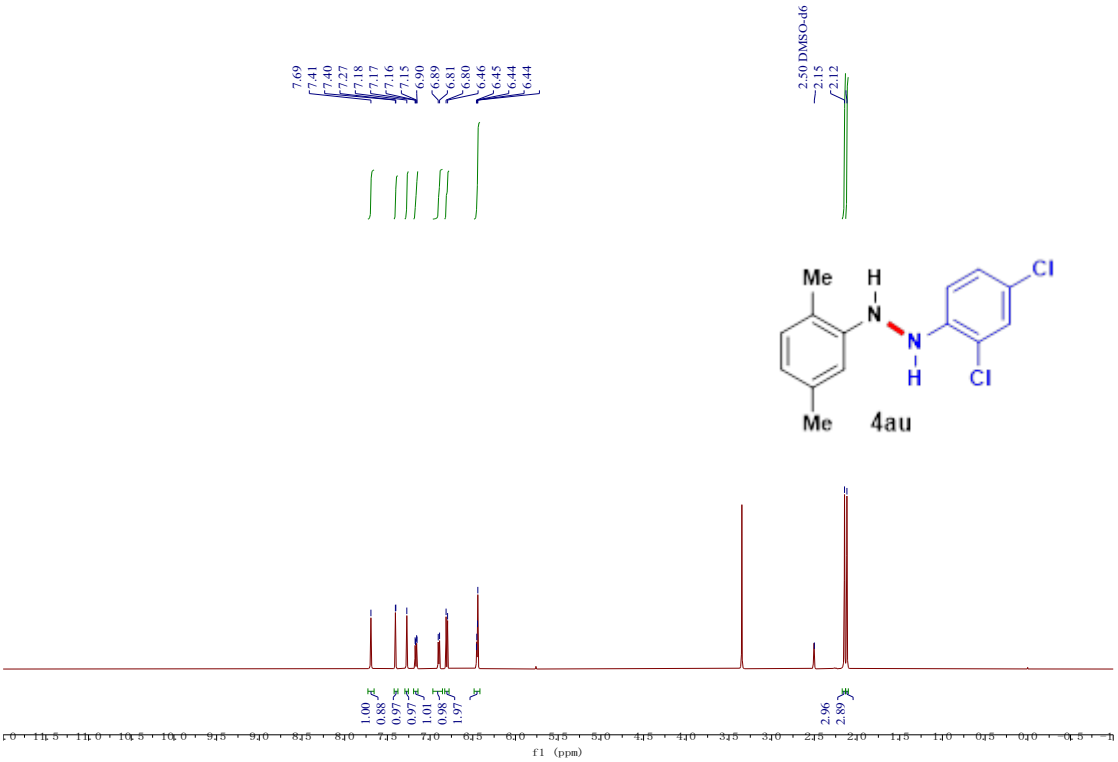
^{13}C NMR of Compound 4at (126 MHz, $CDCl_3$)



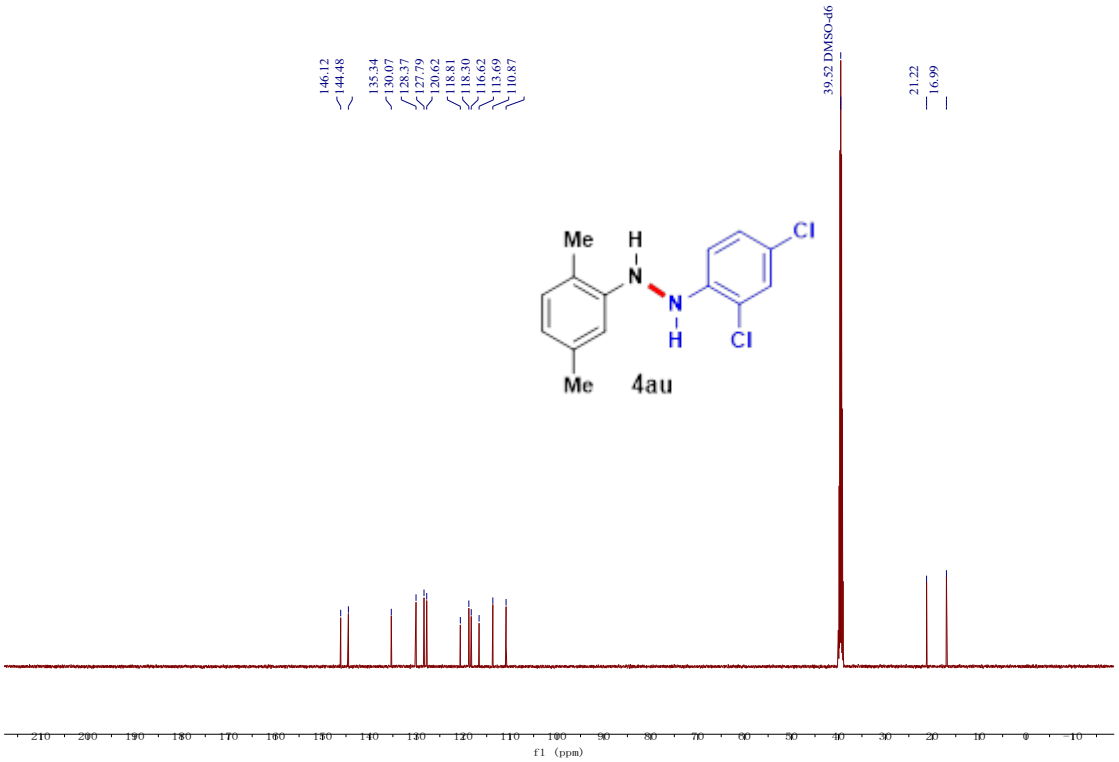
^{19}F NMR of Compound 4at (471 MHz, $CDCl_3$)



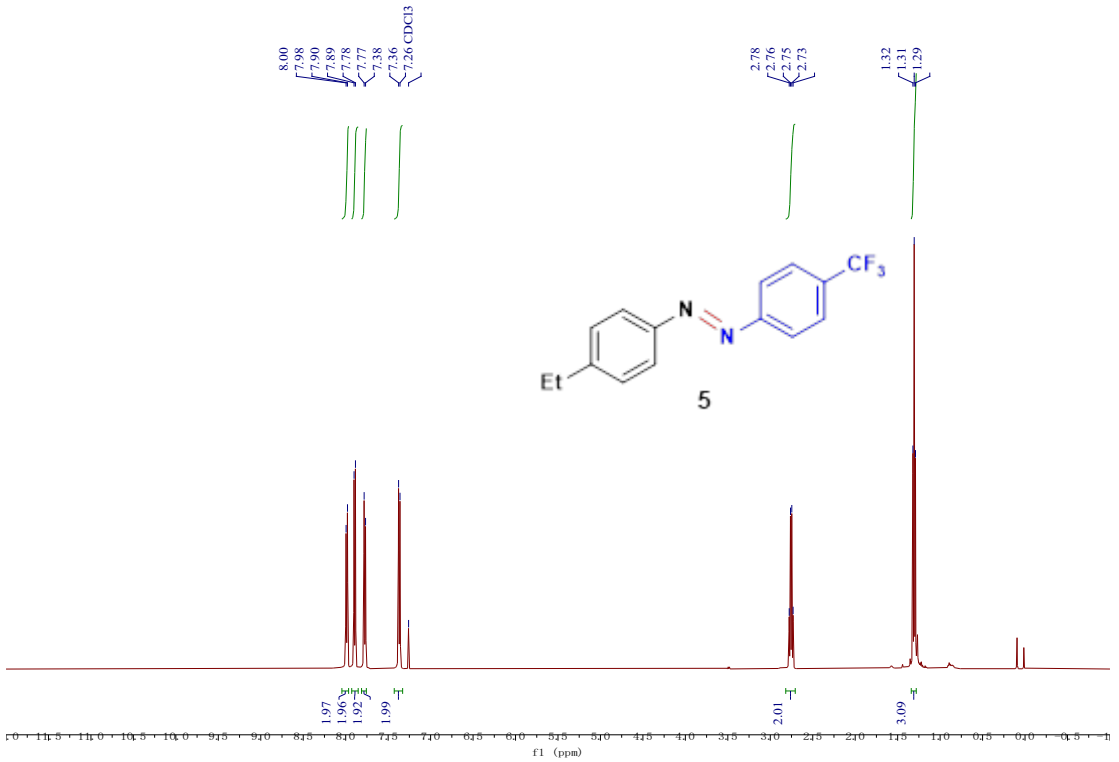
^{1}H NMR of Compound 4au (500 MHz, DMSO-d_6)



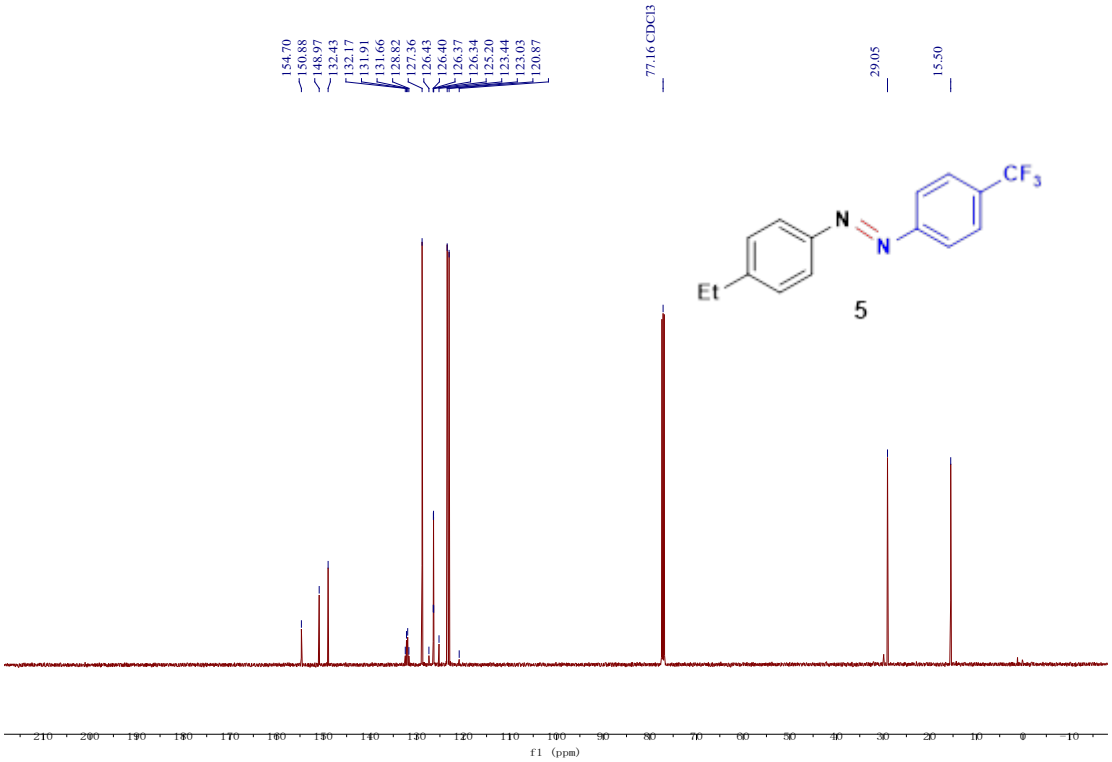
^{13}C NMR of Compound 4au (126 MHz, DMSO-*d*$_6$)



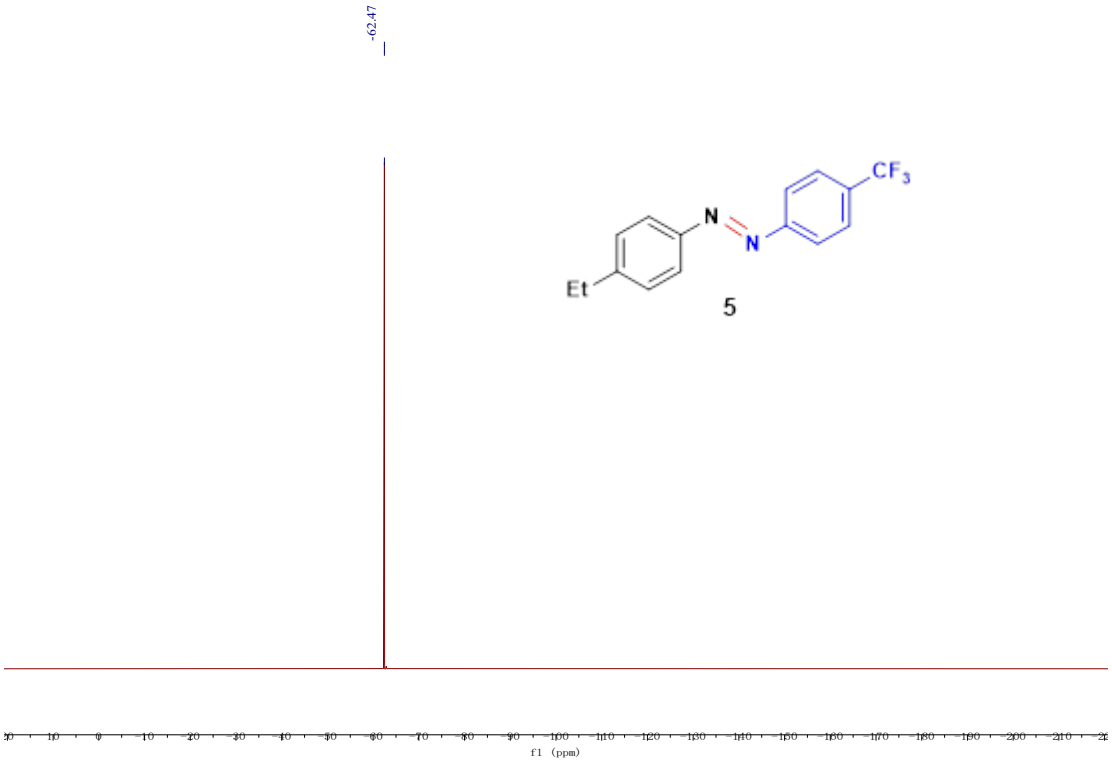
^{1}H NMR of Compound 5 (500 MHz, $CDCl_3$)



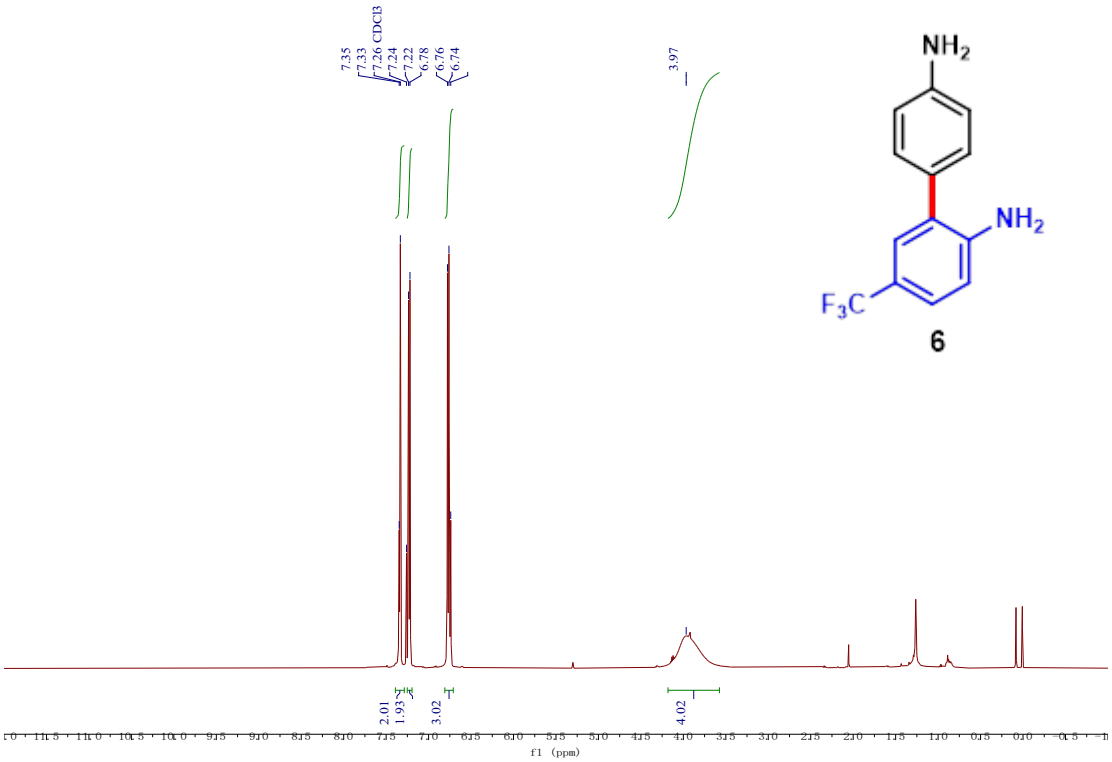
^{13}C NMR of Compound 5 (126 MHz, $CDCl_3$)



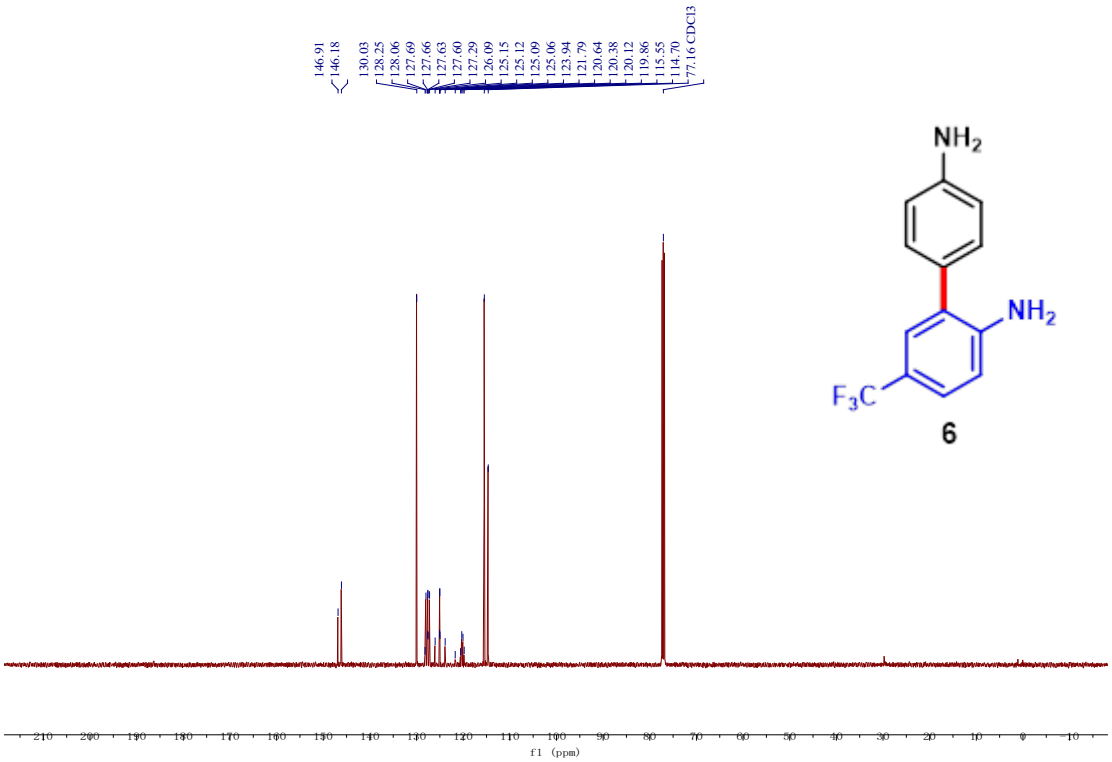
^{19}F NMR of Compound 5 (471 MHz, $CDCl_3$)



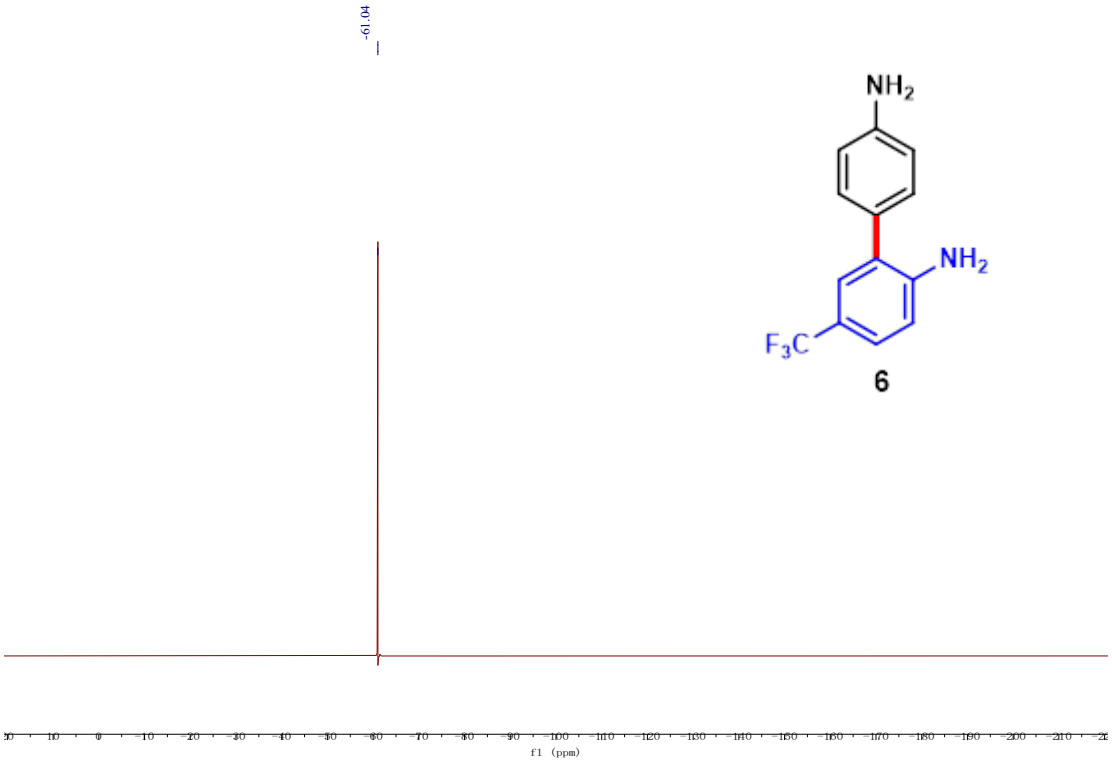
^{1}H NMR of Compound 6 (500 MHz, $CDCl_3$)



^{13}C NMR of Compound 6 (126 MHz, $CDCl_3$)



^{19}F NMR of Compound 6 (471 MHz, $CDCl_3$)



^{1}H NMR of Compound 7 (500 MHz, DMSO-d_6)