

Supporting Information

Visible Light-Induced Iron Catalyzed Synthesis of N-Aryl Amides from Nitroarenes and Chloroalkanes

Qun-Liang Zhang, Wenxin Liu, Yirong Zhou*[§] and Fang-Lin Zhang*^{†,‡}

[†]School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, China

[‡]Shenzhen Research Institute, Wuhan University of Technology, Shenzhen, Guangdong, 518057, China

[§]Hubei Key Laboratory of Natural Medicinal Chemistry and Resource Evaluation, School of Pharmacy, Tongji Medical College, Huazhong University of Science and Technology, No. 13 Hangkong Road, Wuhan, 430030, China

Table of Contents

1. General Information	S2
2. Experimental Section of Amides Construction	S2
2.1 Materials	S2
2.2 Optimization of Conditions	S2
2.3 General Procedures and Characterization	S5
3. Experimental Section of Aryl amides Construction	S9
3.1 Optimization of Conditions	S9
3.2 General Procedures and Characterization	S10
4. Synthetic Application	S14
4.1 Synthesis and Characterization of 5	S14
4.2 Synthetic application	S15
5. Control experiments	S15
5.1 Possible active intermediate	S15
5.2 The reaction of possible nitrogencontaining intermediates	S16
5.3 Radical Trapping Experiments	S16
5.4 Light On-Off switching experiments	S17
6. Reference	S19
7. NMR Spectra of Products	S21

1. General Information

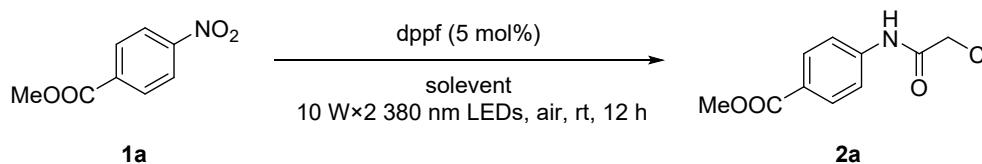
General Methods. ^1H NMR spectra were recorded on 500 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. All NMR spectra were recorded on a Bruker spectrometer at 500 MHz (^1H NMR), 125 MHz (^{13}C NMR) and 500 MHz (^{19}F NMR). HRMS was recorded on Bruker micrOTOF II ESI-TOF. Optical rotations were measured with a polarimeter. All air- and moisture-sensitive reactions were performed under an atmosphere of Nitrogen in fire dried glassware. The manipulations for cyclization and formylation reactions were carried out with standard Schlenk techniques. Flash column chromatography was performed using 200-300 mesh silica gel.

2. Experimental Section of Amides construction

2.1 Materials All the solvents were treated according to standard methods and all chemicals were used without purification. The substrates were purchased commercially unless noted otherwise.

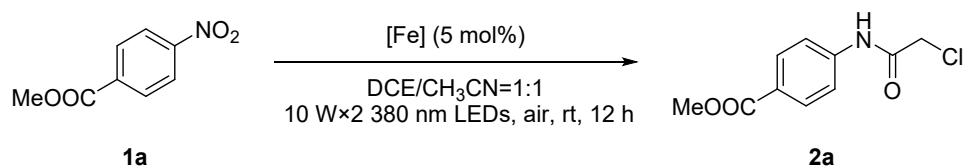
2.2. Optimization of Conditions

Table S1 The Effect of solvents.^[a]



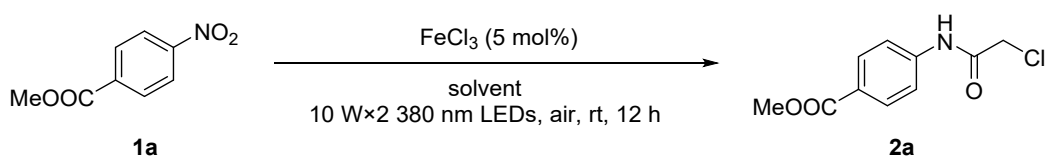
Entry	Solvent	Yield of 2a (%) ^[b]
1	DCE	50
2	DCE:CH ₃ CN=5:1	39
3	DCE:CH ₃ CN=2:1	61
4	DCE:CH ₃ CN=1:1	65
5	DCE:CH ₃ CN=1:2	58

^[a]Unless noted otherwise, reactions were performed with **1a** (0.2 mmol, 1.0 equiv.), dppf(5 mol%), in Solvents (2.0 mL) under irradiation of 10 W x 2 purple LEDs (380-400 nm) at rt. ^[b]Isolated yield.

Table S2 The Effect of Iron source.^[a]

Entry	[Fe]	Yield of 2a (%) ^[b]
1	DPPF	65
2	FeCl ₂ ·4H ₂ O	71
3	FeCl ₃	72
4	FeCl ₃ ·6H ₂ O	72
5	Fe ₂ (SO ₄) ₃	70
6	Fe(acac) ₃	68
7	Fe(acac) ₂	31
8	Fe(NO ₃) ₃ ·9H ₂ O	72
9	FeSO ₄	63
10	Fe(OAc) ₂ ·4H ₂ O	70
11	FeBr ₃	72
12	2 mol% of FeCl ₃	70
13	10 mol% of FeCl ₃	69

^[a]Unless noted otherwise, reactions were performed with **1a** (0.2 mmol, 1.0 equiv.), [Fe] (5 mol%), in 1:1 mixture of DCE and MeCN (2 mL) under irradiation of 10 W x 2 purple LEDs (380-400 nm) at rt. ^[b]Isolated yield.

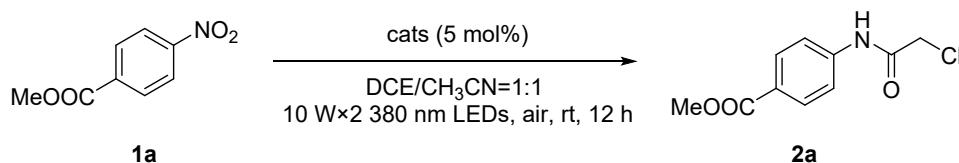
Table S3 The Effect of solvents.^[a]

Entry	Solvent	Yield of 2a (%) ^[b]
1	DCE	69
2	DCE:DCM=1:1	40
3	DCE:CHCl ₃ =1:1	65
4	DCE:PhCl=1:1	38
5	DCE:Acetone=1:1	39
6	DCE:DMF=1:1	Trace

7	DCE:DMSO=1:1	31
8	DCE:MeOH=1:1	Trace
9	DCE:THF=1:1	Trace
10	DCE:CH ₃ CN=1:1	72

^[a]Unless noted otherwise, reactions were performed with **1a** (0.2 mmol, 1.0 equiv.), dppf(5 mol%), in Solvents (2 mL) under irradiation of 10 W×2 purple LEDs (380-400 nm) at rt. ^[b]Isolated yield.

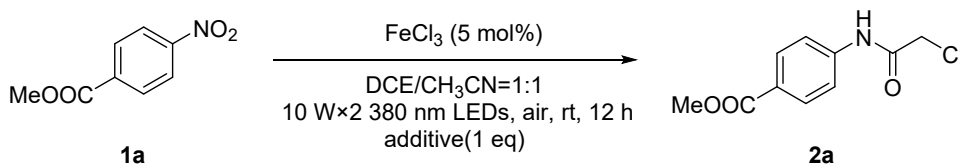
Table S4 The Effect of catalyst.^[a]



Entry	cats	Yield of 2a (%) ^[b]
1	MnCl ₂	trace
2	ZnCl ₂	NR
3	CoCl ₂	NR
4	CeCl ₃	NR
5	CuCl ₂	NR
6	FeCl ₃	72

^[a]Unless noted otherwise, reactions were performed with **1a** (0.2 mmol, 1.0 equiv.), [Fe] (5 mol%), in 1:1 mixture of DCE and MeCN (2 mL) under irradiation of 10 W×2 purple LEDs (380-400 nm) at rt. ^[b]Isolated yield.

Table S5 The Effect of additive.^[a]



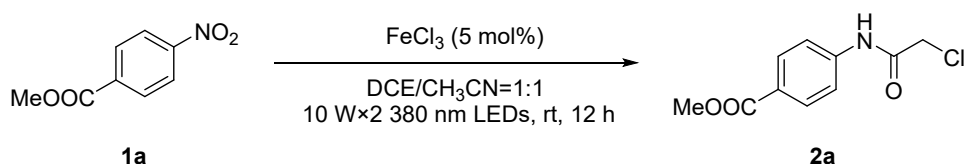
Entry	additive	Yield of 2a (%) ^[b]
1	\	72
2	NH ₄ Cl	71
3	CH ₃ COOH	72
4	TFE	69
5	HCl	68

6	Glycine	64
7	H ₂ O	70
8	4Å MS	68
9	TBACl	67
10	TBABr	41

^[a]Unless noted otherwise, reactions were performed with **1a** (0.2 mmol, 1.0 equiv.), FeCl₃ (5 mol%), additive (1.0 equiv.), in 1:1 mixture of DCE and MeCN (2 mL) under irradiation of 10 W × 2 purple LEDs (380-400 nm) at rt.

^[b]Isolated yield.

Table S6 The control experiment.^[a]

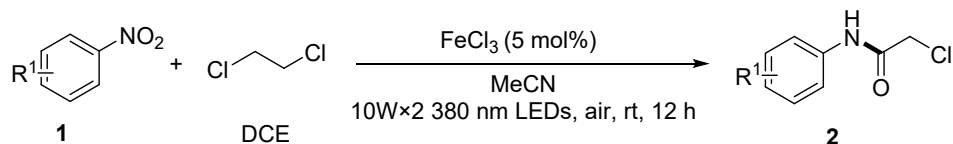


Entry	Another parameters	Yield of 2a (%) ^[b]
1	air	72
2	O ₂	72
3	N ₂	72
4	Dark	NR

^[a]Unless noted otherwise, reactions were performed with **1a** (0.2 mmol, 1.0 equiv.), FeCl₃ (5 mol%), in 1:1 mixture of DCE and MeCN (2 mL) under irradiation of 10 W × 2 purple LEDs (380-400 nm) at rt. ^[b]Isolated yield.

2.3. General Procedures and Characterization

2.3.1. Conditions of Amides Construction

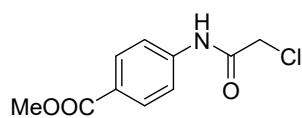


In a flask dried tube, substituted nitrobenzene **1** (0.2 mmol, 1.0 eq) and FeCl₃ (5 mol%) were dissolved into the mixed solution of MeCN (1 mL) and DCE (1 mL). The resulting solution was stirred at room temperature under the irradiation of 10 W × 2 purple LEDs (380-400 nm). The mixture was

stirred until complete conversion of the substituted nitrobenzene (monitored by TLC). The product was purified on silica gel (petroleum ether, gradient from 10:1 to 5:1).

2.3.2 Characterization of Products

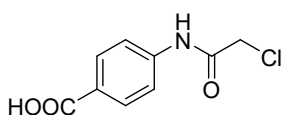
4-Chloroacetylaminobenzoic acid methylester(2a)^[1]



White solid, 72% yield, ¹H NMR (500 MHz, CDCl₃) δ 8.36 (s, 1H), 8.05 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 4.21 (s, 2H), 3.91 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 166.4, 164.0, 140.7, 130.9, 126.7, 119.2, 52.1,

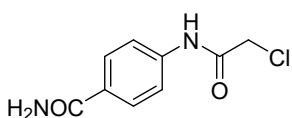
42.9.

4-(2-Chloroethanoylamino)benzoic acid(2b)^[2]



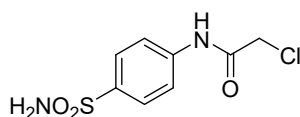
White solid, 84% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 12.69 (s, 1H), 10.66 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 4.31 (s, 2H). ¹³C{¹H} NMR (126 MHz, DMSO-*d*₆) δ 167.3, 165.6, 143.0, 130.9, 126.2, 119.1, 44.0.

4-[(2-Chloroacetyl)amino]benzamide(2c)^[2]



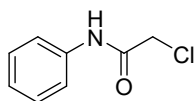
White solid, 74% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.50 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 3H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.25 (s, 1H), 4.30 (s, 2H). ¹³C{¹H} NMR (126 MHz, DMSO) δ 167.7, 165.4, 141.5, 129.9, 128.9, 118.9, 44.1.

N-[4-(Aminosulfonyl)phenyl]-2-chloroacetamide(2d)^[3]



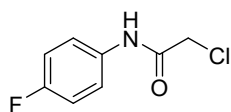
White solid, 55% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.85 (s, 1H), 7.80 (s, 4H), 7.29 (s, 2H), 4.35 (s, 2H). ¹³C{¹H} NMR (126 MHz, DMSO) δ 165.7, 141.9, 139.4, 127.2, 119.4, 44.0.

2-Chloro-N-phenylacetamide(2e)^[4]



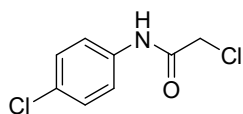
White solid, 70% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.29 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.26 (s, 2H). ¹³C{¹H} NMR (126 MHz, DMSO-*d*₆) δ 165.1, 138.9, 129.3, 124.3, 119.8, 44.0.

N-(Chloroacetyl)-4-fluoroaniline(2f)^[5]



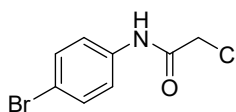
White solid, 95% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.36 (s, 1H), 7.64 – 7.59 (m, 2H), 7.18 (t, $J = 8.9$ Hz, 2H), 4.25 (s, 2H). $^{19}\text{F NMR}$ (471 MHz, $\text{DMSO-}d_6$) δ -118.89. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 165.0, 158.8 (d, $J = 240.8$ Hz), 135.3(d, $J = 2.7$ Hz), 121.7(d, $J = 52.7$ Hz), 115.9 (d, $J = 22.4$ Hz), 43.9.

N-(4-Chlorophenyl)-2-chloroacetamide(2g)^[4]



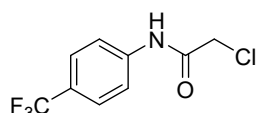
White solid, 61% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.44 (s, 1H), 7.67 – 7.60 (m, 2H), 7.43 – 7.37 (m, 2H), 4.27 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 165.3, 137.9, 129.2, 127.9, 121.4, 44.0.

N-(4-Bromophenyl)-2-chloroacetamide(2h)^[4]



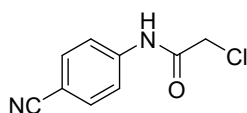
White solid, 63% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.44 (s, 1H), 7.67 – 7.58 (m, 2H), 7.43 – 7.35 (m, 2H), 4.27 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 165.3, 137.9, 129.2, 127.9, 121.4, 44.0.

N-(Chloroacetyl)-4-(trifluoromethyl)aniline(2i)^[4]



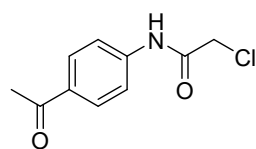
White solid, 88% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.66 (s, 1H), 7.82 (d, $J = 8.5$ Hz, 2H), 7.70 (d, $J = 8.6$ Hz, 2H), 4.31 (s, 2H). $^{19}\text{F NMR}$ (471 MHz, DMSO) δ -60.49. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 165.8, 142.5, 126.7 (q, $J = 3.9$ Hz), 124.8 (q, $J = 3.9$ Hz), 124.3 (q, $J = 32.1$ Hz), 119.8. 44.0.

2-Chloro-N-(4-cyano-phenyl)-acetamide(2j)^[6]



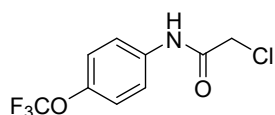
White solid, 67% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.74 (s, 1H), 7.80 (q, $J = 8.5$ Hz, 4H), 4.32 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 165.9, 143.1, 133.8, 119.9, 119.4, 106.1, 44.0.

N-(4-Acetylphenyl)-2-chloroacetamide(2k)^[2]



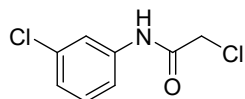
White solid, 60% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.64 (s, 1H), 7.96 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 4.31 (s, 2H), 2.54 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 197.0, 165.7, 143.2, 132.7, 130.0, 119.1, 44.1, 26.9.

N-Chloroacetyl-4-(trifluoromethoxy)aniline(2l)^[7]



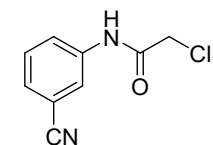
White solid, 64% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.51 (s, 1H), 7.70 (d, *J* = 9.1 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 4.27 (s, 2H). ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -57.09. ¹³C{¹H} NMR (126 MHz, DMSO-*d*₆) δ 165.3, 144.4, 138.1, 122.2, 121.6 ((q, *J* = 181.4 Hz), 121.3, 43.9.

2-Chloro-N-(3-chlorophenyl)acetamide(2m)^[8]



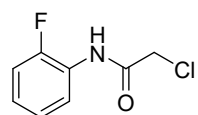
White solid, 83% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.48 (s, 1H), 7.80 (s, 1H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.37 (t, *J* = 8.1 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.27 (s, 2H). ¹³C{¹H} NMR (126 MHz, DMSO-*d*₆) δ 165.5, 140.4, 133.6, 131.0, 124.1, 119.3, 118.3, 44.0.

N-(3-Cyanophenyl)-2-chloroacetamide(2n)^[6]



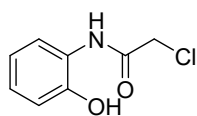
White solid, 80% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.65 (s, 1H), 8.12 – 8.06 (m, 1H), 7.82 (td, *J* = 4.7, 2.2 Hz, 1H), 7.60 – 7.54 (m, 2H), 4.31 (s, 2H). ¹³C{¹H} NMR (126 MHz, DMSO-*d*₆) δ 165.8, 139.7, 130.8, 127.9, 124.4, 122.5, 119.0, 112.2, 43.9.

2-Chloro-N-(2-fluorophenyl)acetamide(2o)^[5]



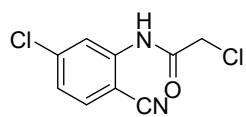
White solid, 70% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.10 (s, 1H), 7.91 – 7.83 (m, 1H), 7.32 – 7.25 (m, 1H), 7.20 (dt, *J* = 6.7, 3.5 Hz, 2H), 4.36 (s, 2H). ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -124.59. ¹³C{¹H} NMR (126 MHz, DMSO-*d*₆) δ 165.6, 154.2 (d, *J* = 245.7 Hz), 126.4 (d, *J* = 7.7 Hz), 125.9 (d, *J* = 11.5 Hz), 124.9 (d, *J* = 3.7 Hz), 124.7, 116.1 (d, *J* = 19.4 Hz), 43.5.

2-Hydroxyl-N-(3-chlorophenyl)acetamide(2p)^[9]



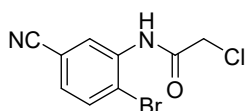
White solid, 54% yield, ¹H NMR (500 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 7.73 (s, 1H), 7.29 (d, *J* = 9.3 Hz, 1H), 7.15 (t, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 9.3 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 4.26 (s, 2H). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 160.8, 143.5, 122.8, 119.8, 117.4, 116.2, 114.6, 37.8.

2-Chloro-N-(5-chloro-2-cyanophenyl)acetamide(2q)^[10]



White solid, 45% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.63 (s, 1H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.80 (s, 1H), 7.49 (dd, $J = 8.4, 2.1$ Hz, 1H), 4.40 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 166.2, 141.3, 138.9, 135.4, 126.7, 125.4, 116.3, 105.9, 43.4.

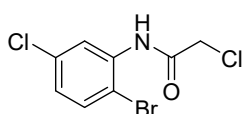
2-Chloro-N-(2-bromo-5-cyanophenyl)acetamide(2r)



White solid, 62% yield, $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.03 (s, 1H), 8.79 (s, 1H), 7.53 (d, $J = 8.3$ Hz, 1H), 7.39 (d, $J = 6.4$ Hz, 1H), 4.26 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 164.2, 134.7, 130.2, 128.5, 127.9, 124.1, 117.6, 112.1, 43.0.

HRMS (ESI) for: $\text{C}_9\text{H}_6\text{Br}^{81}\text{ClNO}$ $[\text{M-H}]^-$: calcd 272.9258, found 272.9292.

2-Chloro-N-(2-bromo-5-chlorophenyl)acetamide(2s)



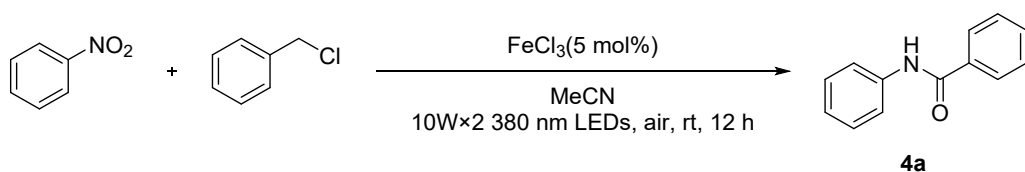
White solid, 63% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.96 (s, 1H), 7.90 (d, $J = 2.5$ Hz, 1H), 7.56 (d, $J = 8.6$ Hz, 1H), 7.31 (dd, $J = 8.6, 2.5$ Hz, 1H), 4.41 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 166.0, 136.0, 132.1, 131.4, 126.8, 125.3, 125.2, 43.5.

HRMS (ESI) for: $\text{C}_8\text{H}_6\text{Br}^{81}\text{ClNO}$ $[\text{M-H}]^-$: calcd 281.8916, found 281.8918.

3. Experimental Section of Aryl amides Construction

3.1. Optimization of Conditions

Table S7 The Effect of equivalent of benzyl chloride.^[a]

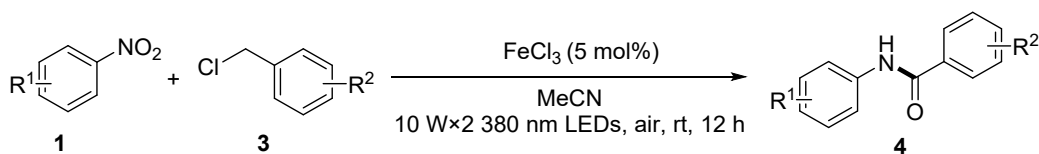


Entry	equivalent of benzyl chloride	Yield of 4a (%) ^[b]
1	10	69
2	5	69
3	2	49
4	1	29

^[a]Unless noted otherwise, reactions were performed with nitrobenzene (0.2 mmol, 1.0 equiv.), benzyl chloride, FeCl_3 (5 mol%), in MeCN (2 mL) under irradiation of 10 W \times 2 purple LEDs (380-400 nm) at rt. ^[b]Isolated yield.

3.2. General Procedures and Characterization

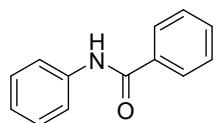
3.2.1. Conditions of Aryl amides Construction



In a flask dried tube, substituted nitrobenzene **1** (0.2 mmol, 1.0 eq), substituted benzyl chloride **3** (1 mmol, 5.0 eq) and FeCl₃ (5 mol%) were dissolved into MeCN (2 mL) (commercially, no need for further purification). The resulting solution was stirred at room temperature under the irradiation of 10 W x 2 purple LEDs (380-400 nm). The mixture was stirred until complete conversion of substituted nitrobenzene (monitored by TLC). The product **4** was purified on silica gel (petroleum ether/ethyl acetate, gradient from 20:1 to 10:1).

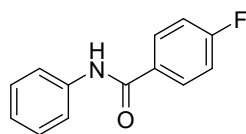
3.2.2 Characterization of Products

N-Phenylbenzamide (4a)



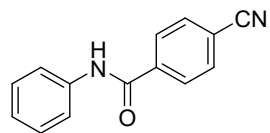
White solid, 69% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.25 (s, 1H), 7.97 (d, *J* = 7.1 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H). ¹³C{¹H} NMR (126 MHz, DMSO-*d*₆) δ 166.0, 139.6, 135.5, 132.0, 129.1, 128.8, 128.1, 124.1, 120.8. HRMS (ESI) for: C₁₃H₁₁NO [M+Na]⁺: calcd 220.0733, found 220.0740.

4-Fluoro-N-phenylbenzamide(4b)



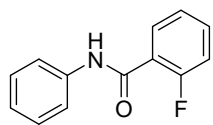
White solid, 72% yield, ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.30 (s, 1H), 8.11 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.37 (q, *J* = 8.7 Hz, 4H), 7.13 (t, *J* = 7.4 Hz, 1H). ¹⁹F NMR (471 MHz, DMSO-*d*₆) δ -108.75. ¹³C{¹H} NMR (126 MHz, DMSO-*d*₆) δ 164.9, 164.5 (d, *J* = 249.5 Hz), 139.5, 131.9 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 9.1 Hz), 129.1, 124.2, 120.9, 115.8 (d, *J* = 21.8 Hz). HRMS (ESI) for: C₁₃H₁₁NO [M+Na]⁺: calcd 238.0639, found 238.0649.

4-Cyano-N-phenylbenzamide(4c)



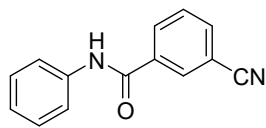
White solid, 76% yield, $^1\text{H NMR}$ (500 MHz, DMSO- d_6) δ 10.48 (s, 1H), 8.15 (d, $J = 8.3$ Hz, 2H), 7.99 (d, $J = 8.2$ Hz, 2H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.39 (t, $J = 7.9$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 164.6, 139.4, 139.3, 132.8, 129.1, 129.0, 124.6, 121.1, 118.8, 114.4. HRMS (ESI) for: $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}$ $[\text{M}+\text{Na}]^+$: calcd 245.0685, found 245.0696.

2-Fluoro-N-phenylbenzamide(4d)



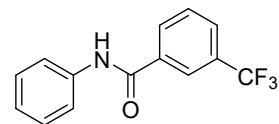
White solid, 45% yield, $^1\text{H NMR}$ (500 MHz, DMSO- d_6) δ 8.59 (d, $J = 13.1$ Hz, 1H), 8.07 (t, $J = 7.8$ Hz, 1H), 7.69 (d, $J = 7.9$ Hz, 2H), 7.47 (d, $J = 7.9$ Hz, 1H), 7.37 (t, $J = 7.9$ Hz, 2H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.20 – 7.09 (m, 2H). $^{19}\text{F NMR}$ (471 MHz, DMSO- d_6) δ -117.85. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 156.9, 155.5 (d, $J = 247.5$ Hz), 133.1, 128.8 (d, $J = 9.3$ Hz), 127.2, 124.3, 120.2 (d, $J = 3.2$ Hz), 117.0 (d, $J = 11.7$ Hz), 115.9, 111.4 (d, $J = 24.7$ Hz). HRMS (ESI) for: $\text{C}_{13}\text{H}_{10}\text{FNO}$ $[\text{M}+\text{Na}]^+$: calcd 238.0639, found 238.0640.

3-Cyano-N-phenylbenzamide(4e)



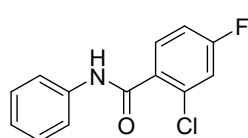
White solid, 70% yield, $^1\text{H NMR}$ (500 MHz, DMSO- d_6) δ 10.42 (s, 1H), 8.43 (s, 1H), 8.28 (d, $J = 8.0$ Hz, 1H), 8.07 (d, $J = 7.7$ Hz, 1H), 7.80 (d, $J = 7.7$ Hz, 2H), 7.77 (t, $J = 7.8$ Hz, 1H), 7.40 (t, $J = 7.9$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 164.1, 139.3, 136.4, 135.4, 133.0, 131.8, 130.3, 129.2, 124.5, 120.9, 118.8, 112.0. HRMS (ESI) for: $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}$ $[\text{M}+\text{Na}]^+$: calcd 245.0685, found 245.0686.

N-phenyl-3-(trifluoromethyl)-Benzamide(4f)



White solid, 47% yield, $^1\text{H NMR}$ (500 MHz, DMSO- d_6) δ 10.50 (s, 1H), 8.35 (s, 1H), 8.31 (d, $J = 7.8$ Hz, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 7.8$ Hz, 2H), 7.78 (t, $J = 7.8$ Hz, 1H), 7.40 (t, $J = 7.9$ Hz, 2H), 7.15 (t, $J = 7.4$ Hz, 1H). $^{19}\text{F NMR}$ (471 MHz, DMSO- d_6) δ -61.25. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 164.5, 139.4, 136.4, 132.2, 130.1, 129.8 (q, $J = 32.2$ Hz), 129.1, 128.5 (q, $J = 3.7$ Hz), 124.8 (q, $J = 3.8$ Hz), 124.5 (q, $J = 273.0$ Hz), 124.4, 121.1. HRMS (ESI) for: $\text{C}_{14}\text{H}_{10}\text{F}_3\text{NO}$ $[\text{M}+\text{Na}]^+$: calcd 288.0607, found 288.0622.

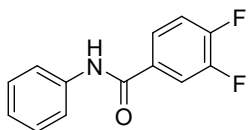
2-Chloro-4-fluoro-N-phenylbenzamide(4g)^[11]



White solid, 46% yield, $^1\text{H NMR}$ (500 MHz, DMSO- d_6) δ 10.54 (s, 1H), 7.79 (d, $J = 8.0$ Hz, 2H), 7.72 (dd, $J = 8.4, 6.2$ Hz, 1H), 7.59 (dd, $J = 9.0, 2.3$ Hz, 1H),

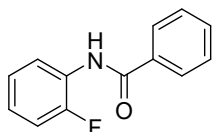
7.43 – 7.34 (m, 3H), 7.16 (t, $J = 7.4$ Hz, 1H). ^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) δ -109.08. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 164.7, 162.7 (d, $J = 250.5$ Hz), 139.4, 134.2 (d, $J = 3.5$ Hz), 132.0 (d, $J = 10.8$ Hz), 131.3 (d, $J = 9.3$ Hz), 129.3, 124.4, 120.2, 117.5 (d, $J = 25.3$ Hz), 115.0 (d, $J = 21.4$ Hz).

3, 4-Difluoro-N-phenylbenzamide(4h)^[12]



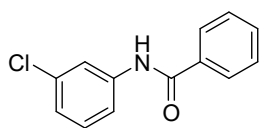
White solid, 56% yield, ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.31 (s, 1H), 8.09 – 8.03 (m, 1H), 7.91 (s, 1H), 7.81 (d, $J = 7.8$ Hz, 2H), 7.61 – 7.54 (m, 1H), 7.38 (t, $J = 7.9$ Hz, 2H), 7.13 (t, $J = 7.4$ Hz, 1H). ^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) δ -134.08, -134.09, -134.10, -134.13, -134.15, -134.17, -134.18, -137.80, -137.82, -137.84, -137.86, -137.89. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 163.6, 152.0 (dd, $J = 12.7, 12.7$ Hz), 149.7 (dd, $J = 13.0, 13.0$ Hz), 139.3, 132.7 (dd, $J = 3.6, 3.6$ Hz), 129.0, 125.7 (dd, $J = 3.5, 3.5$ Hz), 124.4, 121.0, 117.9 (d, $J = 17.6$ Hz), 117.6 (d, $J = 18.5$ Hz).

N-(2-Fluorophenyl)benzamide(4i)^[13]



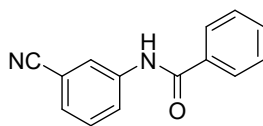
White solid, 74% yield, ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.13 (s, 1H), 8.01 (d, $J = 7.1$ Hz, 2H), 7.66 – 7.60 (m, 2H), 7.55 (t, $J = 7.5$ Hz, 2H), 7.33 – 7.27 (m, 2H), 7.24 (t, $J = 7.5$ Hz, 1H). ^{19}F NMR (471 MHz, $\text{DMSO-}d_6$) δ -121.09. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 165.9, 156.3 (d, $J = 247.0$ Hz), 134.4, 132.3, 128.9, 128.3, 127.7 (d, $J = 1.6$ Hz), 127.4 (d, $J = 7.7$ Hz), 126.2 (d, $J = 12.2$ Hz), 124.8 (d, $J = 3.6$ Hz), 116.3 (d, $J = 19.9$ Hz).

N-(3-Chlorophenyl)benzamide(4j)



White solid, 61% yield, ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.41 (s, 1H), 8.00 – 7.95 (m, 3H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.55 (t, $J = 7.4$ Hz, 2H), 7.39 (t, $J = 8.1$ Hz, 1H), 7.16 (d, $J = 6.7$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 166.3, 141.1, 135.1, 133.4, 132.3, 130.8, 128.9, 128.2, 123.8, 120.2, 119.1. HRMS (ESI) for: $\text{C}_{13}\text{H}_{10}\text{ClNO}$ [$\text{M}+\text{Na}$] $^+$: calcd 254.0343, found 254.0344.

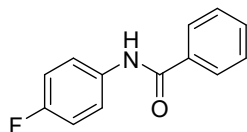
N-(3-Cyanophenyl)benzamide(4k)^[14]



White solid, 80% yield, ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.57 (s, 1H), 8.31 (s, 1H), 8.09 (dt, $J = 7.4, 2.1$ Hz, 1H), 8.00 (d, $J = 7.0$ Hz, 2H), 7.63 (t, $J = 7.3$ Hz,

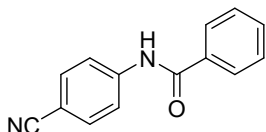
1H), 7.57 (td, $J = 7.6, 1.7$ Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 166.5, 140.5, 134.8, 132.4, 130.5, 128.9, 128.2, 127.5, 125.3, 123.5, 119.2, 112.0.

N-(4-Fluorophenyl)benzamide(4l)^[15]



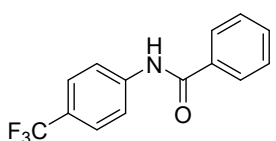
White solid, 68 % yield, ^1H NMR (500 MHz, DMSO- d_6) δ 10.34 (s, 1H), 8.00 (d, $J = 7.2$ Hz, 2H), 7.86 (dd, $J = 9.0, 5.1$ Hz, 2H), 7.60 (t, $J = 7.3$ Hz, 1H), 7.54 (t, $J = 7.4$ Hz, 2H), 7.21 (t, $J = 8.9$ Hz, 2H). ^{19}F NMR (471 MHz, DMSO- d_6) δ -118.83. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 166.0, 158.8 (d, $J = 240.8$ Hz), 136.1, 135.3, 132.0, 128.8, 128.1, 122.7 (d, $J = 7.9$ Hz), 115.6 (d, $J = 22.2$ Hz).

N-(4-Cyanophenyl)benzamide(4m)^[15]



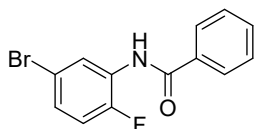
White solid, 70% yield, ^1H NMR (500 MHz, DMSO- d_6) δ 10.65 (s, 1H), 8.03 (d, $J = 8.8$ Hz, 2H), 7.99 (d, $J = 7.2$ Hz, 2H), 7.82 (d, $J = 8.7$ Hz, 2H), 7.63 (t, $J = 7.3$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 166.7, 144.0, 134.9, 133.5, 132.5, 128.9, 128.3, 120.7, 119.6, 105.9.

N-(4-(Trifluoromethyl)phenyl)benzamide(4n)^[12]



White solid, 87% yield, ^1H NMR (500 MHz, DMSO- d_6) δ 10.60 (s, 1H), 8.04 (d, $J = 8.5$ Hz, 2H), 7.99 (d, $J = 7.1$ Hz, 2H), 7.74 (d, $J = 8.6$ Hz, 2H), 7.63 (t, $J = 7.3$ Hz, 1H), 7.56 (t, $J = 7.4$ Hz, 2H). ^{19}F NMR (471 MHz, DMSO- d_6) δ -60.36. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 166.5, 143.3, 135.0, 132.4, 128.9, 128.3, 126.4 (q, $J = 3.8$ Hz), 124.9 (q, $J = 271.9$ Hz), 124.1 (d, $J = 32.0$ Hz), 120.6.

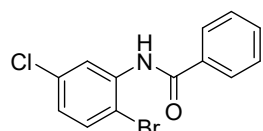
N-(2-Fluoro-5-bromophenyl)-benzamide(4o)



White solid, 51% yield, ^1H NMR (500 MHz, DMSO- d_6) δ 10.24 (s, 1H), 8.02 (d, $J = 8.5$ Hz, 2H), 7.95 (dd, $J = 6.8, 2.5$ Hz, 1H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 2H), 7.45 (dd, $J = 7.0, 4.4$ Hz, 1H), 7.34 – 7.29 (m, 1H). ^{19}F NMR (471 MHz, DMSO- d_6) δ -122.58. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 166.1, 155.2 (d, $J = 248.3$ Hz), 134.1, 132.5, 129.6 (d, $J = 7.8$ Hz), 129.4 (d, $J = 1.8$ Hz), 128.9, 128.4, 128.1 (d, $J = 13.5$ Hz),

118.3 (d, $J = 21.6$ Hz), 115.9 (d, $J = 3.4$ Hz). **HRMS** (ESI) for: $C_{13}H_{10}BrFNO$ $[M+H]^+$: calcd 293.9924, found 293.9916.

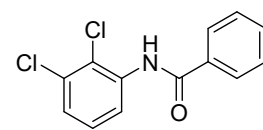
N-(2-Bromo-5-chlorophenyl)-benzamide(4p)^[16]



White solid, 61% yield, **1H NMR** (500 MHz, $DMSO-d_6$) δ 10.13 (s, 1H), 8.00 (d, $J = 7.1$ Hz, 2H), 7.78 (s, 1H), 7.65 – 7.54 (m, 4H), 7.38 (d, $J = 8.6$ Hz, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $DMSO-d_6$) δ 166.0, 136.9, 134.1, 132.5, 131.9, 131.4, 129.0, 128.3, 128.2, 128.0, 127.5.

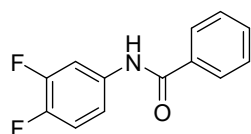
N-(2, 3-Dichlorophenyl)-benzamide(4q)^[17]



White solid, 78% yield, **1H NMR** (500 MHz, $DMSO-d_6$) δ 10.23 (s, 1H), 8.02 (s, 1H), 8.01 (s, 1H), 7.61 (d, $J = 9.6$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 3H), 7.42 (t, $J = 8.1$ Hz, 1H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $DMSO-d_6$) δ 165.9, 137.7, 134.2, 132.5,

132.5, 129.0, 128.7, 128.5, 128.4, 128.2, 127.5.

N-(3,4-Difluorophenyl)benzamide(4r)^[12]

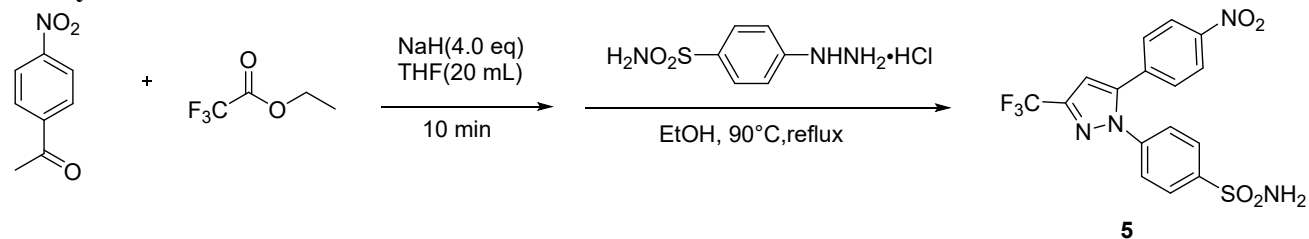


White solid, 38% yield, **1H NMR** (500 MHz, $DMSO-d_6$) δ 10.44 (s, 1H), 7.97 (d, $J = 7.2$ Hz, 3H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.57 (q, $J = 6.9$ Hz, 3H), 7.47 – 7.40 (m, 1H). **^{19}F NMR** (471 MHz, $DMSO-d_6$) δ -137.38, -137.40, -137.43, -137.45, -

137.47, -144.40, -144.41, -144.44, -144.46, -144.48. **$^{13}C\{^1H\}$ NMR** (126 MHz, $DMSO-d_6$) δ 166.2, 149.3 (dd, $J = 13.2, 13.2$ Hz), 146.0 (dd, $J = 12.7, 12.7$ Hz), 136.7 (dd, $J = 3.0, 2.9$ Hz), 135.0, 132.3, 128.9, 128.1, 117.8 (d, $J = 17.7$ Hz), 117.1 (dd, $J = 3.4, 3.4$ Hz), 109.7 (d, $J = 21.6$ Hz).

4. Synthetic application

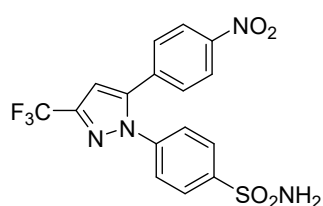
4.1 Synthesis and Characterization of 5



In a 50 mL round bottom flask, *p*-nitroacetophenone(5 mmol) was dissolved into the solution of THF(25 mL).Then,cooled the solution to $-5^{\circ}C$ and added NaH(4.0 eq). After 30 minutes of mixture, ethyl trifluoroacetate(25 mmol) was added into the solution. The mixture was stirred until complete

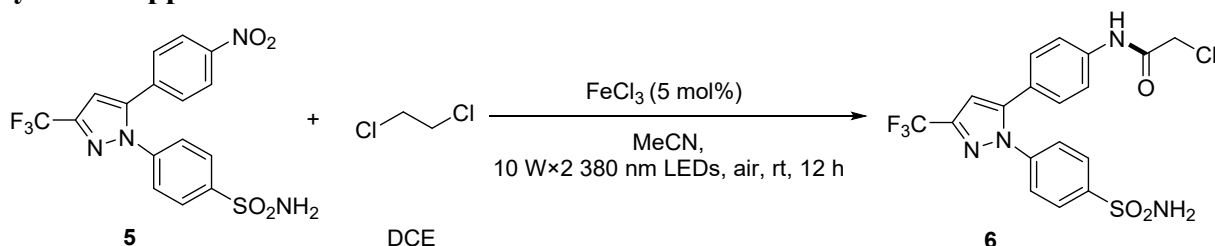
conversion (about 10 minutes) of the p-nitroacetophenone (monitored by TLC). The product was purified on silica gel (petroleum ether/ethyl acetate, gradient from 5:1 to 2:1). 4,4,4-Trifluoro-1-(4-nitrophenyl)-1,3-butanedione (1.0 eq) and 4-hydrazinebenzenesulfonamide hydrochloride (1.1 eq) were added in a 100 mL round bottom flask which was filled with EtOH (50 mL). The mixture was stirred 2 h. Then, the reaction was accomplished. The product was purified on silica gel (petroleum ether/ethyl acetate, gradient from 5:1 to 2:1).

4-(5-(4-nitrophenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (5)



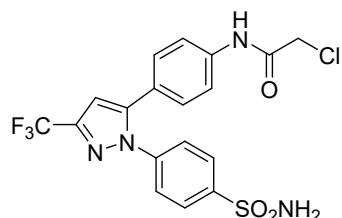
White solid, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 8.27 (d, $J = 8.8$ Hz, 2H), 7.91 (d, $J = 8.6$ Hz, 2H), 7.61 (dd, $J = 13.7, 8.7$ Hz, 4H), 7.54 (s, 2H), 7.45 (s, 1H). $^{19}\text{F NMR}$ (471 MHz, $\text{DMSO-}d_6$) δ -60.90. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO-}d_6$) δ 148.1, 144.8, 143.6, 142.9 (q, $J = 38.1$ Hz), 141.1, 135.0, 130.8, 127.5, 126.6, 124.4, 123.7 (q, $J = 263.9$ Hz), 108.2. HRMS (ESI) for: $\text{C}_{16}\text{H}_{11}\text{F}_3\text{N}_4\text{O}_4\text{S}$ $[\text{M}+\text{Na}]^+$: calcd 435.0345, found 435.0350.

4.2 Synthetic application



In a 5 mL tube, **5** (1.0 equiv., 0.2 mmol) and FeCl_3 (5 mol%) were dissolved into the mixed solution of MeCN (1 mL) and DCE (1 mL). The resulting solution was stirred at room temperature under the irradiation of 10 W \times 2 purple LEDs (380-400 nm) for 12 h. The mixture was stirred until complete conversion of the **5** (monitored by TLC). The product was purified on silica gel (petroleum ether/ethyl acetate, gradient from 2:1 to 1:1).

N-(4-(1-(4-(aminosulfinyl)phenyl)-3-(trifluoromethyl)-1H-pyrazol-5-yl)phenyl)-2-chloroacetamide (6)

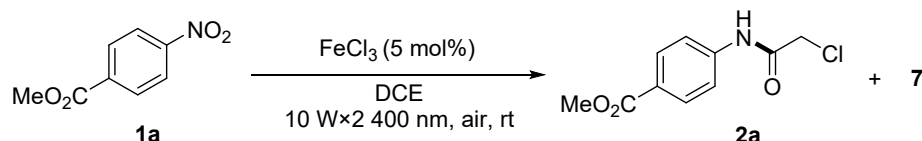


White solid, 36% yield, $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.49 (s, 1H), 7.91 (d, $J = 8.7$ Hz, 2H), 7.64 (d, $J = 8.7$ Hz, 2H), 7.57 (d, $J = 8.7$ Hz, 2H), 7.51 (s, 2H), 7.31 (d, $J = 8.7$ Hz, 2H), 7.21 (s, 1H), 4.28 (s, 2H). $^{19}\text{F NMR}$

(471 MHz, DMSO-*d*₆) δ -60.87. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO-*d*₆) δ 165.5, 145.4, 144.5, 142.7 (q, J = 36.5 Hz), 141.5, 139.9, 130.1, 127.3, 126.5, 123.9, 121.8 (d, J = 268.4 Hz), 119.7, 106.6, 44.0. HRMS (ESI) for: C₁₈H₁₄ClF₃N₄O₃S [M+Na]⁺: calcd 481.0319, found 481.0318.

5. Control experiments

5.1 Possible active intermediate



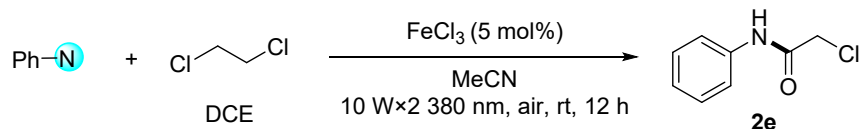
In a flask dried tube, substituted nitrogencontaining intermediates (0.2 mmol, 1.0 eq) and FeCl₃(5 mol%) were dissolved into the mixed solution of DCE(2 mL). The resulting solution was stirred at room temperature under the irradiation of 10 W×2 blue LEDs (380-400 nm).

(Z)-2-chloro-N-(4-(methoxycarbonyl)phenyl)ethan-1-imine oxide(7)

White solid, ^1H NMR (500 MHz, DMSO-*d*₆) δ 11.17 (s, 1H), 8.00 (d, J = 8.9 Hz, 2H), 7.86 (d, J = 8.9 Hz, 2H), 4.71 (s, 2H), 3.85 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO-*d*₆) δ 166.5, 166.1, 145.4, 130.4, 125.9, 119.0, 52.5, 44.3.

HRMS (ESI) for: C₁₀H₁₀ClN₄O₃ [M+K]⁺: calcd 265.9981, found 265.9918.

5.2 The reaction of possible nitrogencontaining intermediates



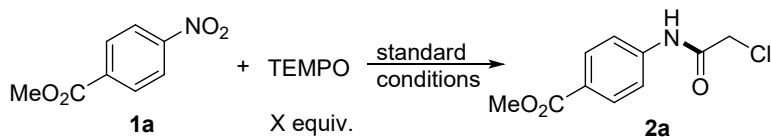
In a flask dried tube, substituted nitrogencontaining intermediates (0.2 mmol, 1.0 eq) and FeCl₃(5 mol%) were dissolved into the mixed solution of MeCN(1 mL) and DCE(1 mL). The resulting solution was stirred at room temperature under the irradiation of 10 W×2 purple LEDs. The mixture was stirred until complete conversion of the substituted nitrobenzene (monitored by TLC). The product was purified on silica gel (petroleum ether, gradient from 20:1 to 10:1).

Entry	nitrogencontaining intermediates	Yield of 2e (%) ^[a]
1	PhNO ₂	70
2	PhNO	34
3	PhNNPh	42

4	PhNONPh	0
5	PhNHOH	68
6	PhNH ₂	40

[^a] Isolated yield.

5.3 Radical Trapping Experiments

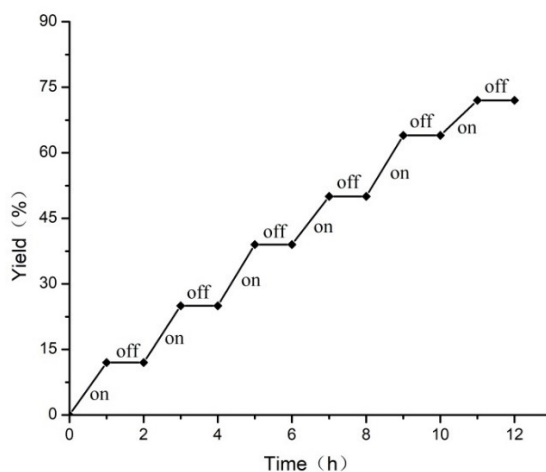
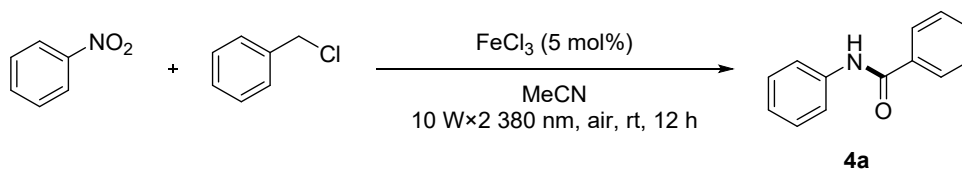


In a flask dried tube, Methyl 4-nitrobenzoate **1a** (0.2 mmol, 1.0 eq), TEMPO(X=1, 2, 3) and FeCl₃(5 mol%) were dissolved into the mixed solution of MeCN(1 mL) and DCE (1 mL). The resulting solution was stirred at room temperature under the irradiation of 10 W × 2 purple LEDs (380-400 nm). The mixture was stirred until complete conversion of the substituted nitrobenzene (monitored by TLC).

Entry	equivalent of TEMPO	Yield of 2a (%) ^[a]
1	1	0
2	2	0
3	3	0

[^a] Isolated yield.

5.4 Light On-Off switching experiments



6. Reference

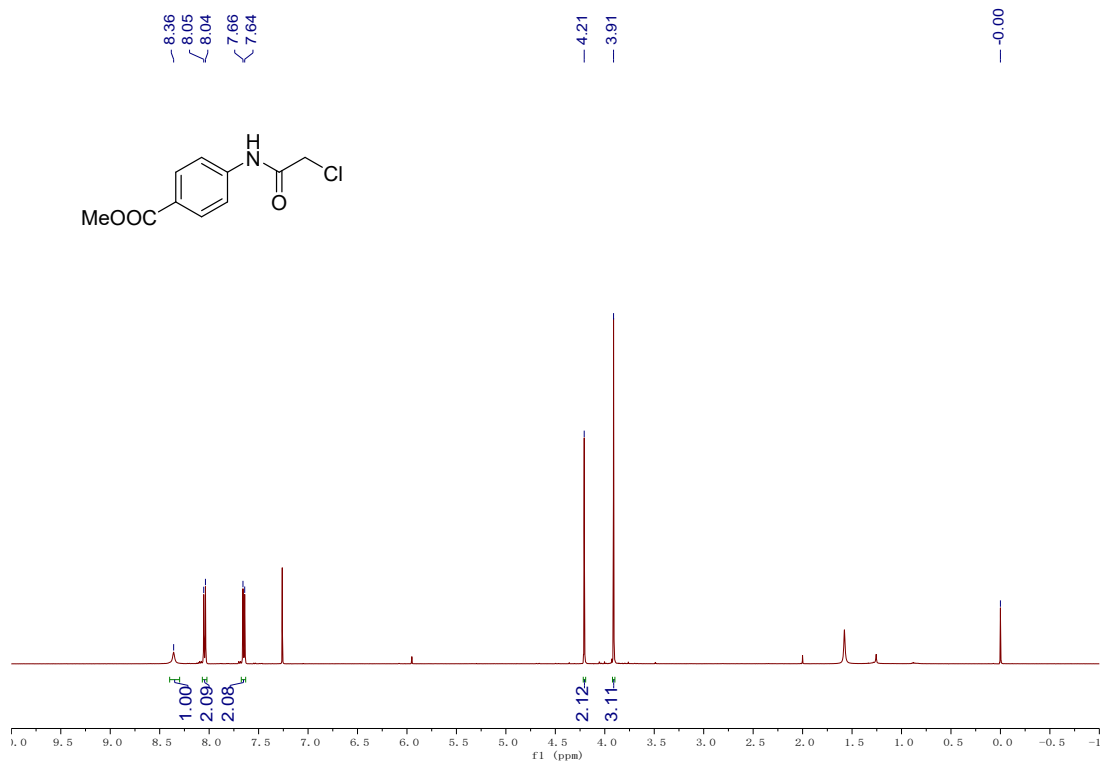
Some spectral datas match those previously reported.

- [1] Mao, R.; Shao, J.; Zhu, K.; Zhang, Y. Potent, Selective, and Cell Active Protein Arginine Methyltransferase 5 (PRMT5) Inhibitor Developed by Structure-Based Virtual Screening and Hit Optimization. *J. Med.Chem.* **2017**, *60*, 6289-6304.
- [2] Andrew, J. H.; Thorfinnur, G. Synthesis of α -chloroamides in water. *Tetrahedron Lett.* **2006**, *47*, 6321-6324.
- [3] Chandra, B. M.; Shikha, K. Discovery of Benzenesulfonamides with Potent Human Carbonic Anhydrase Inhibitory and Effective Anticonvulsant Action: Design, Synthesis, and Pharmacological Assessment. *J. Med. Chem.* **2017**, *60*, 2456–2469.
- [4] Tummala, R. K. R.; Li, C. Design, synthesis and SAR exploration of tri-substituted 1,2,4-triazoles as inhibitors of the annexin A2–S100A10 protein Interaction. *Bioorg.* **2014**, *22*, 5378-5391.
- [5] Nadjat, R.; Fawzia, F. A. Synthesis, Characterization, DNA Binding, Anticancer, and Molecular Docking Studies of Novel Imidazolium-Based Ionic Liquids with Fluorinated Phenylacetamide Tethers. *ACS Omega* **2020**, *5*, 4807-4815.
- [6] Hrast, M.; Jukič, M.; Patin, D. In silico identification, synthesis and biological evaluation of novel tetrazole inhibitors of MurB. *Chem. Biol. Drug Des.* **2018**, *91*, 1101-1112.
- [7] Guo, X.; Yang, Q.; Xu, J.; Zhang, L. Design and bio-evaluation of indole derivatives as potent Kv1.5 inhibitors. *Bioorg. Med. Chem.* **2013**, *21*, 6466-6476.
- [8] Rahul, P. M.; Sivakumar, P. K. Design, Synthesis, Biological Evaluation, and Molecular Modeling of Coumarin–Piperazine Derivatives as Acetylcholinesterase Inhibitors. *Arch. Pharm. Chem. Life Sci.* **2013**, *346*, 793–804.
- [9] Zidar, N.; Kikelj, D. A convenient synthesis of 3,4-dihydro-1,4-benzoxazin-2-ones. *Tetrahedron* **2008**, *64*, 5756-5761.
- [10] Kabri, Y.; Verhaeghe, P.; Gellis, A. Regioselective Suzuki-Miyaura Reaction: Application to the Microwave-promoted Synthesis of 4,7-Diarylquinazolines. *Molecules* **2010**, *15*, 2949-2961.
- [11] Tan, Z.; Yi, B.; Shen, F. 2-Chloro-4-fluoro-N-phenyl-benzamide. *Acta Cryst.* **2009**, *E65*, o1757.
- [12] Li, G.; Szostak, M. Highly selective transition-metal-free transamidation of amides and amidation of esters at room temperature. *Nat. Commun.* **2018**, *9*, 4165-4173.
- [13] Tan, B. Y. -H.; Teo, Y. -C. Efficient cobalt-catalyzed C–N crosscoupling reaction between benzamide and aryl iodide in water. *Org. Biomol. Chem.* **2014**, *12*, 7478-7481.

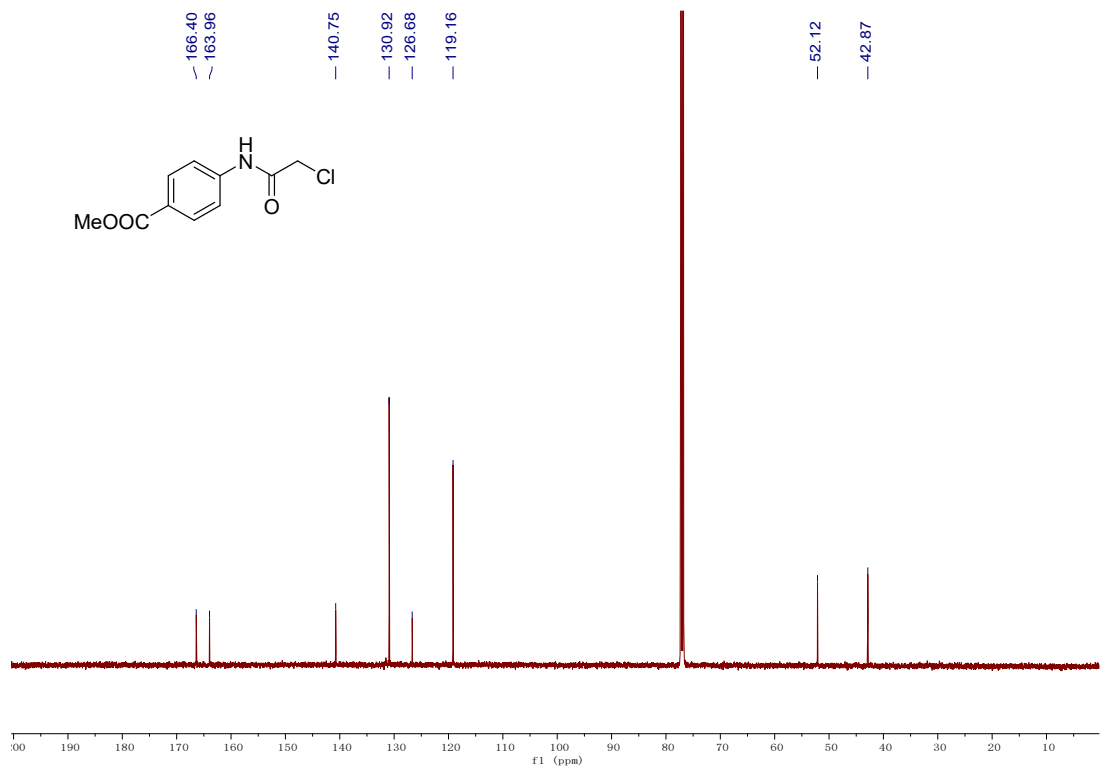
- [14] Li, H.; Heumann, H.; Beller, M.; Wu, X. Aryl Formate as Bifunctional Reagent: Applications in Palladium-Catalyzed Carbonylative Coupling Reactions Using In Situ Generated CO. *Angew. Chem. Int. Ed.* **2014**, *53*, 3035-3279.
- [15] Fan, W.; Yang, Y.; Lei, J.; Jiang, Q.; Zhou, W. Copper-Catalyzed N-Benzoylation of Amines via Aerobic C–C Bond Cleavage. *J. Org. Chem.* **2015**, *80*, 8782-8789.
- [16] Wang, J. -M.; Jiang, X.; Zhang, Y.; Zhu, Y. -M.; Shen, J. -K. Palladium-catalyzed synthesis of 4H-benzo[d][1,3]oxazin-4-ones and N-(2-cyanophenyl)benzamides via tert-butyl isocyanide insertion. *Tetrahedron Lett.* **2015**, *56*, 2349-2354.
- [17] Liu, C. -K.; Chen, M. -Y.; Lin, X. -X.; Fang, Z. Catalyst- and oxidant-free electrochemical para-selective hydroxylation of N-arylamides in batch and continuous-flow. *Green Chem.* **2020**, *22*, 6437-6443.

7. NMR Spectra of Products

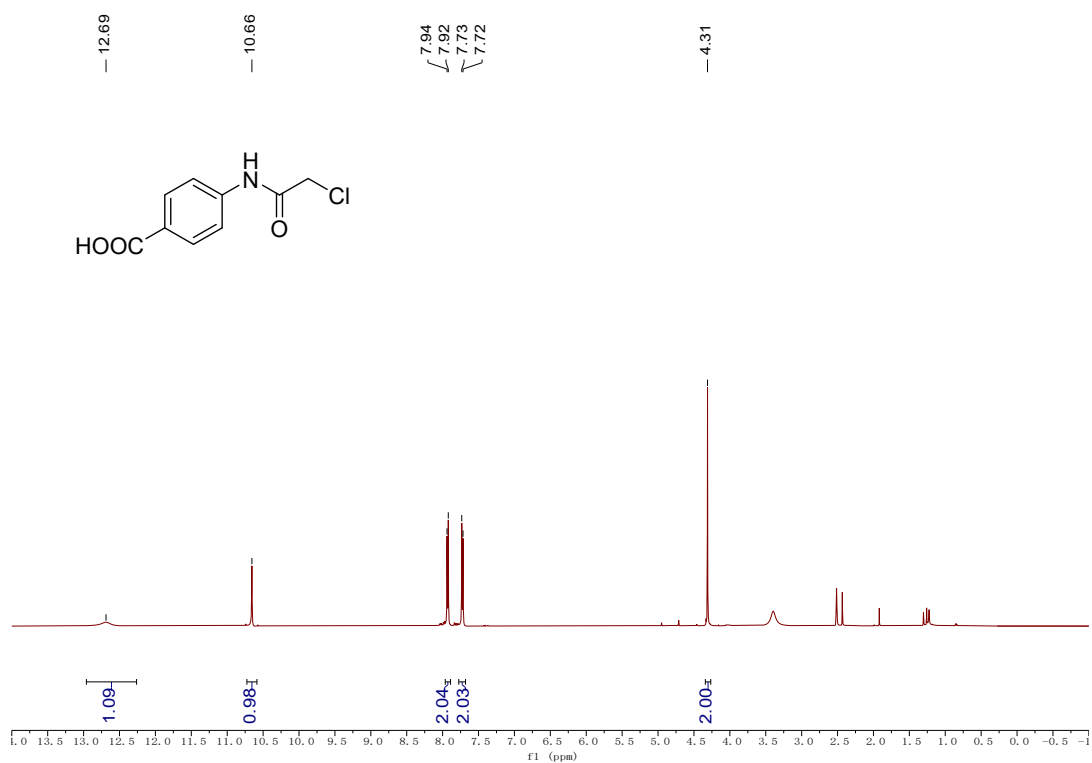
^1H NMR Spectrum of **2a** (CDCl_3)



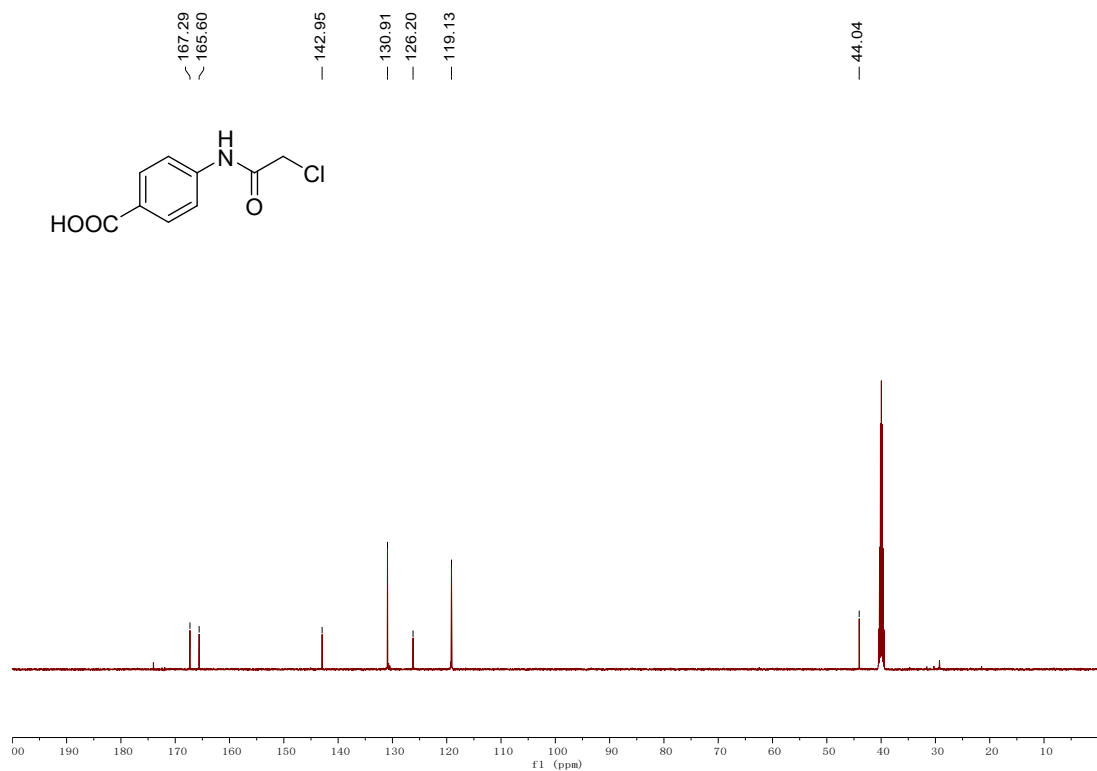
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2a** (CDCl_3)



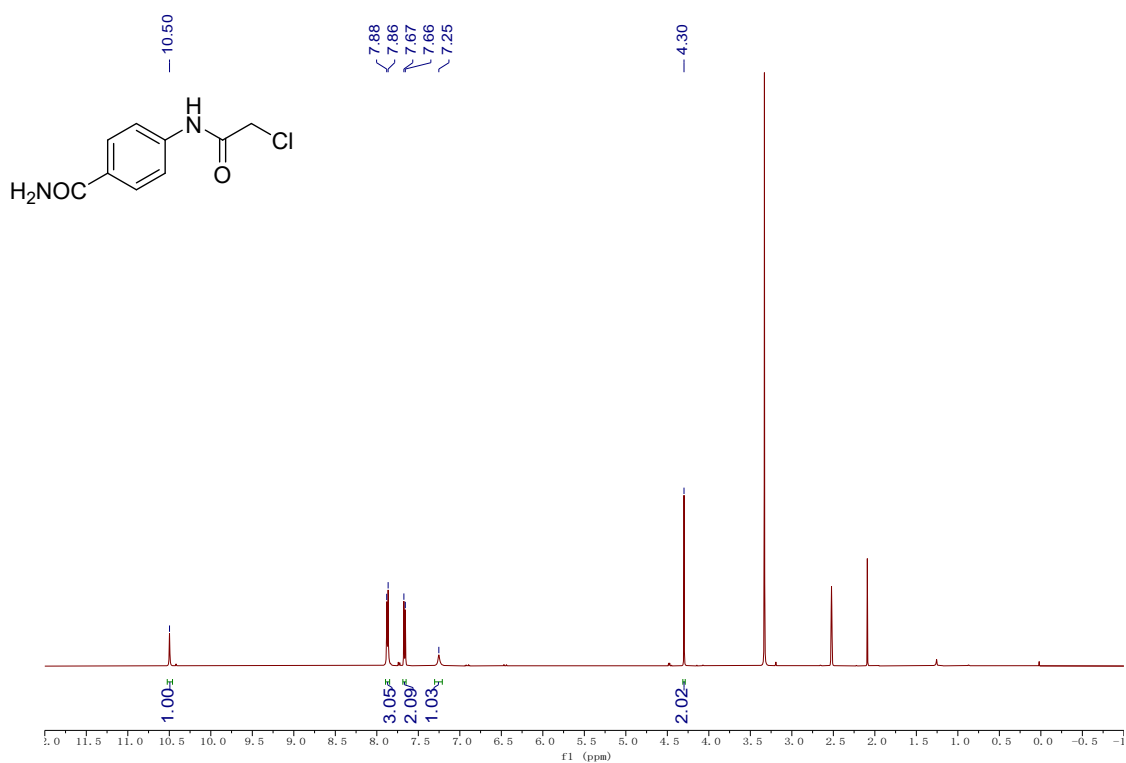
^1H NMR Spectrum of **2b** (DMSO- d_6)



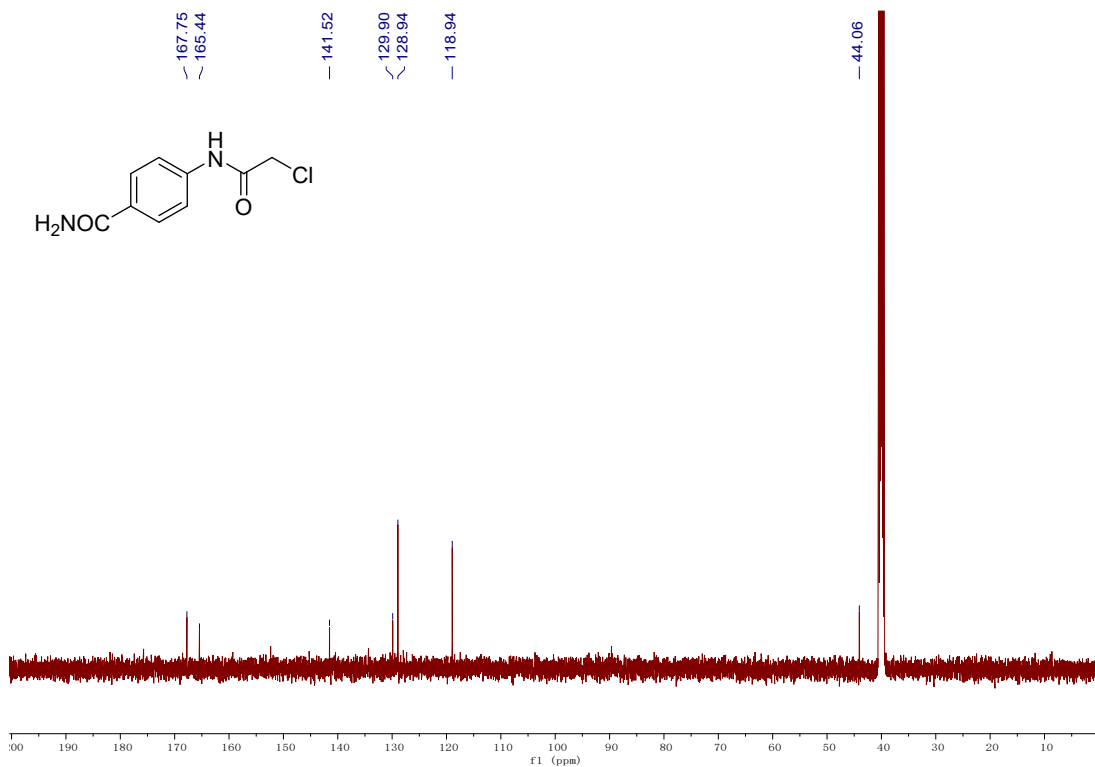
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2b** (DMSO- d_6)



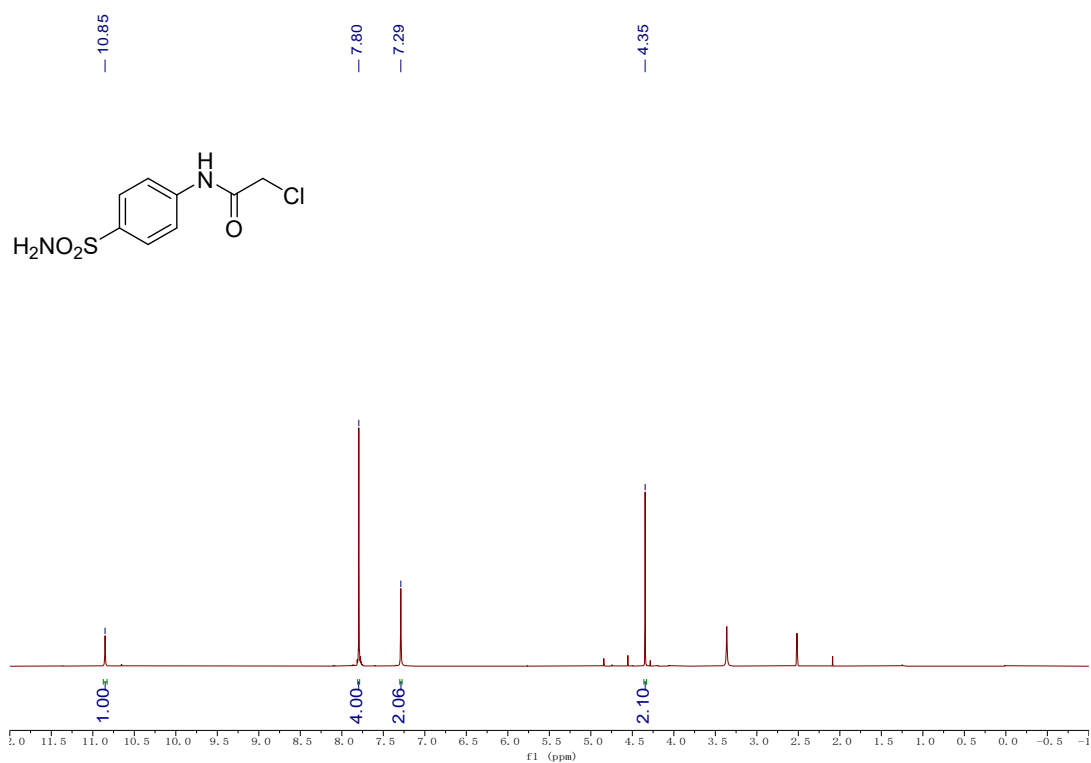
^1H NMR Spectrum of **2c** (DMSO- d_6)



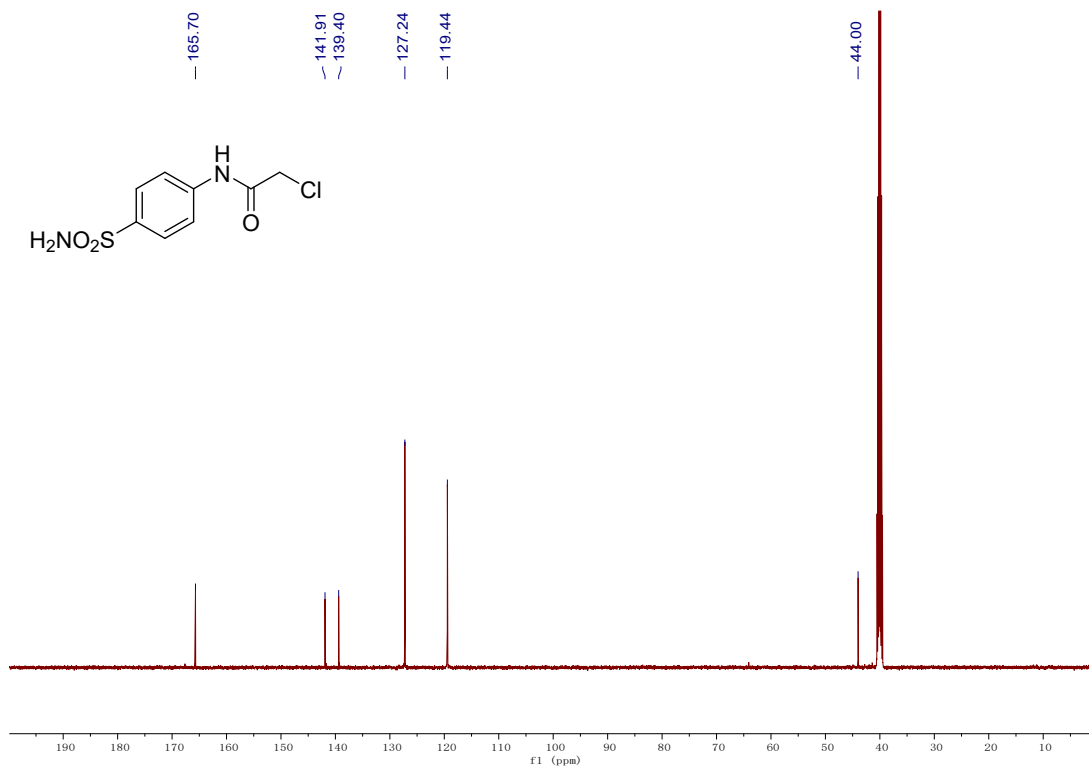
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2c** (DMSO- d_6)



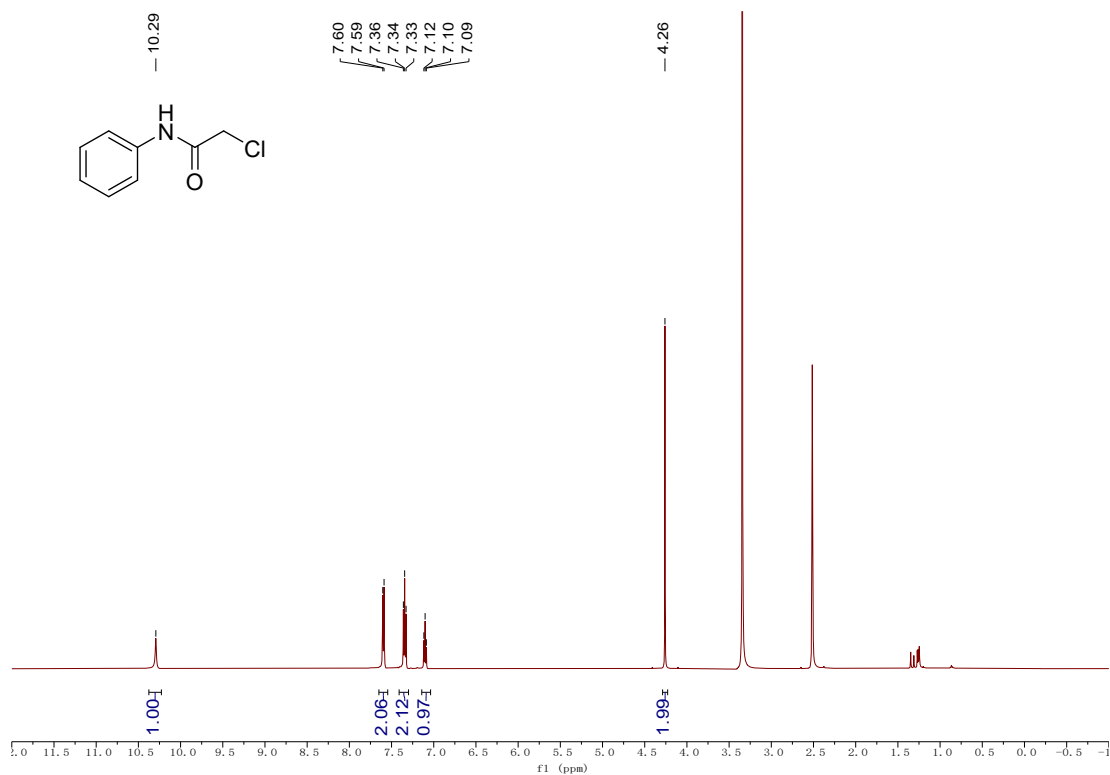
^1H NMR Spectrum of **2d** (DMSO-*d*₆)



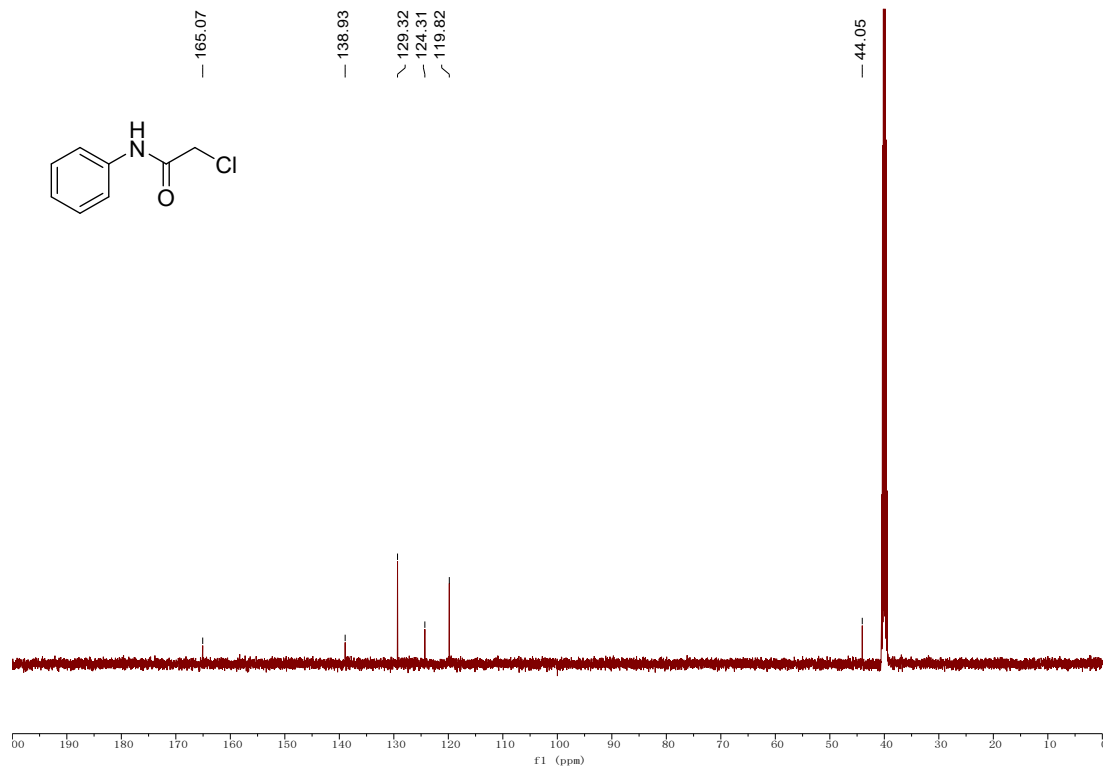
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2d** (DMSO-*d*₆)



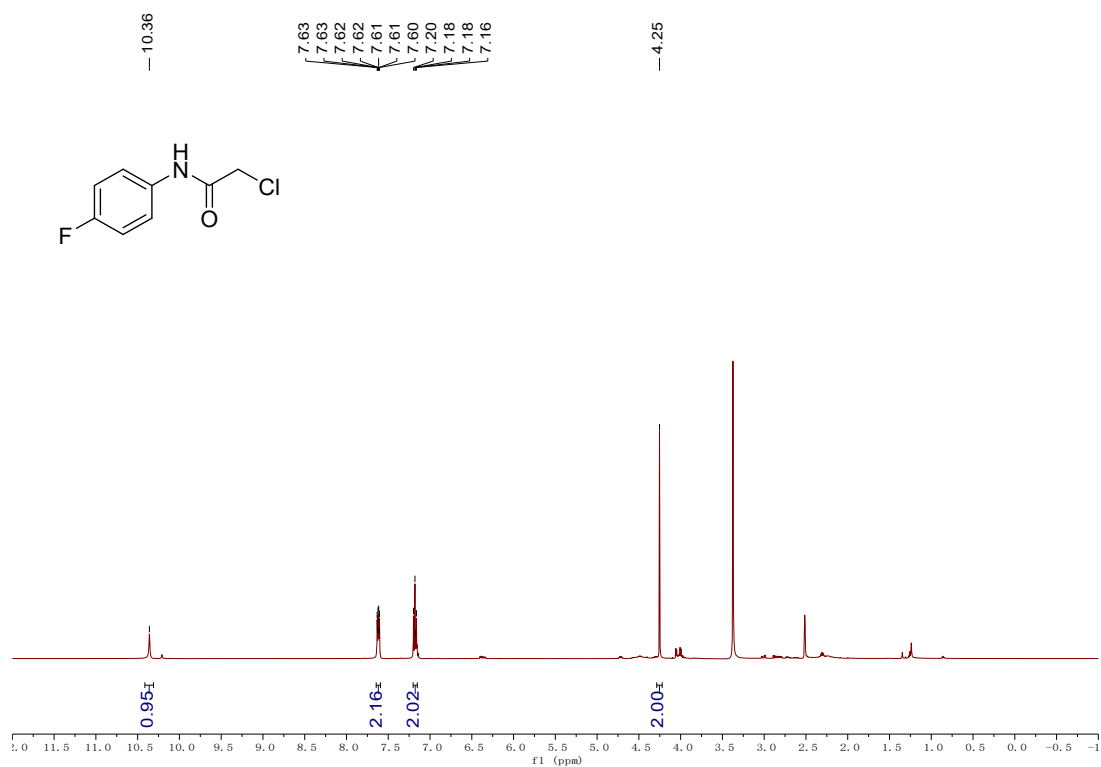
^1H NMR Spectrum of **2e** (DMSO- d_6)



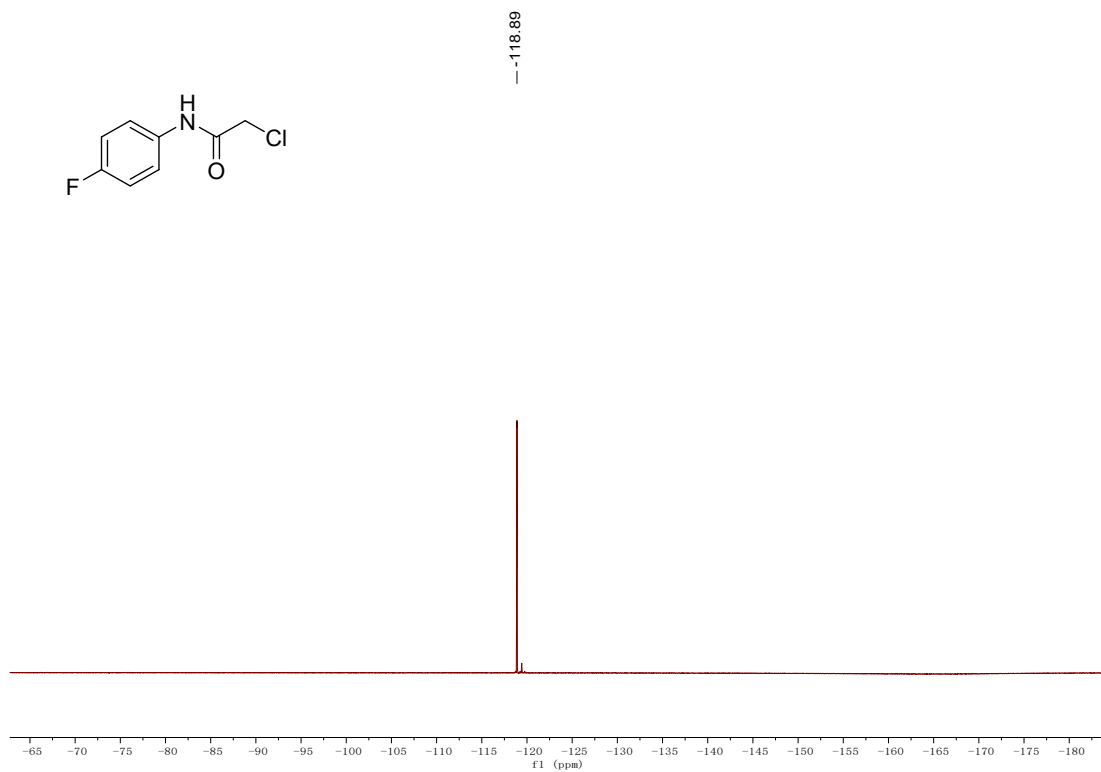
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2e** (DMSO- d_6)



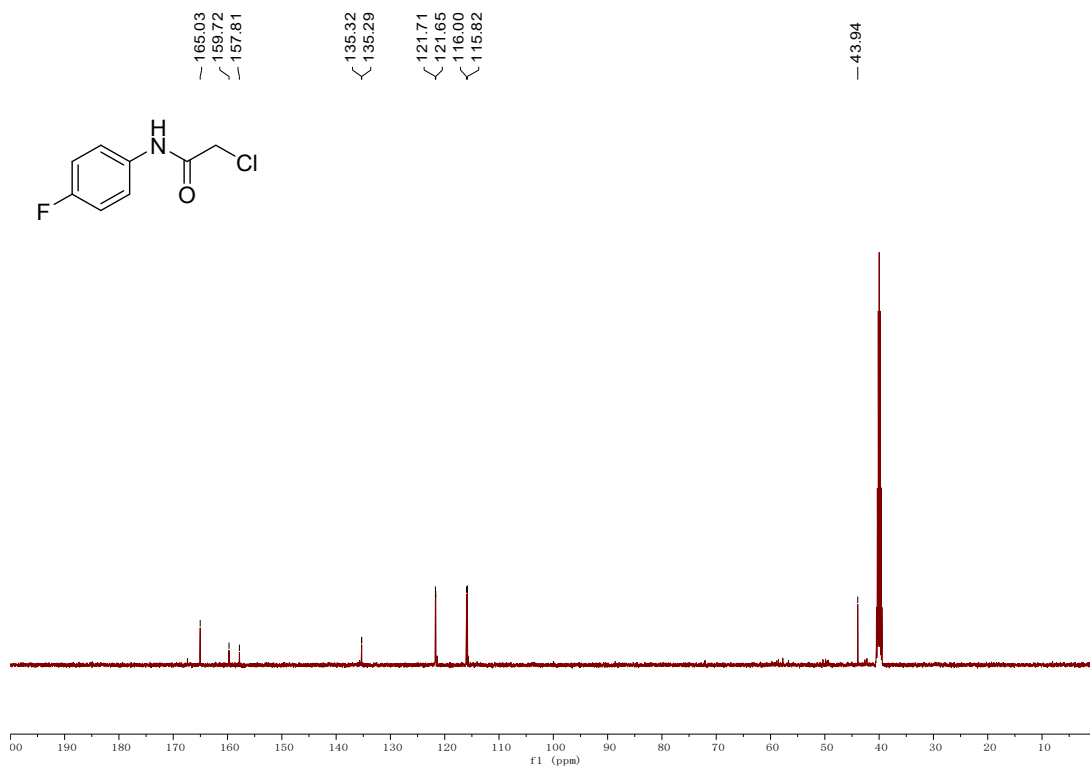
¹H NMR Spectrum of **2f** (DMSO-*d*₆)



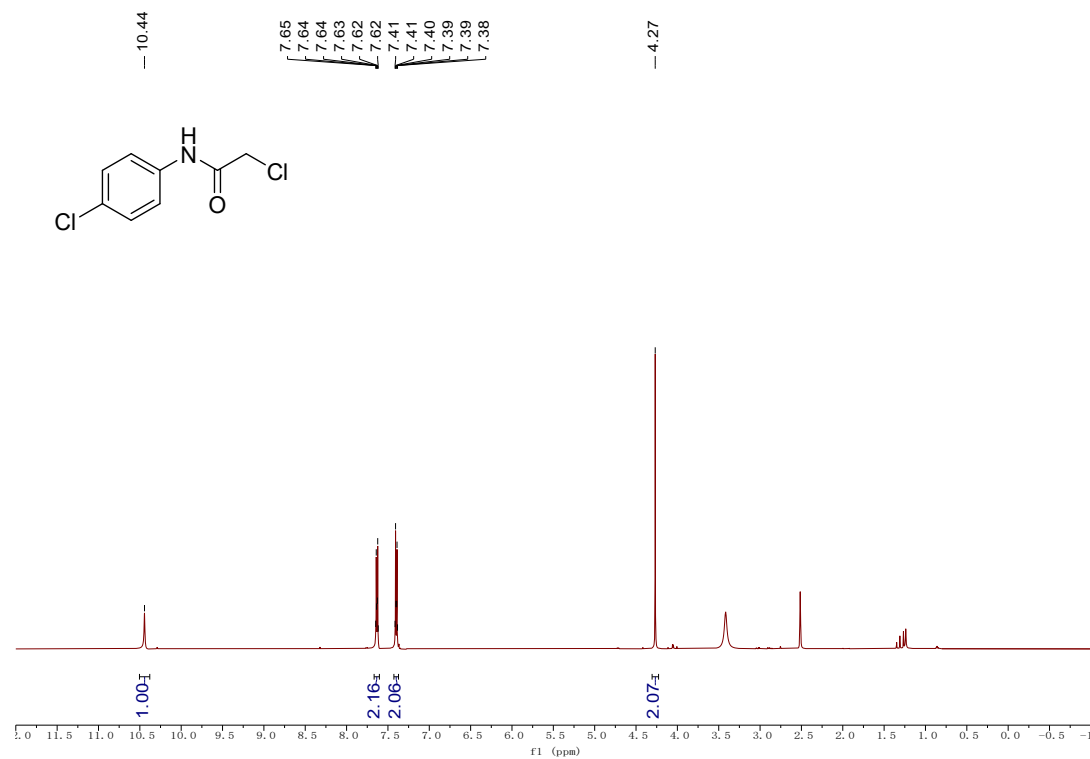
¹⁹F NMR Spectrum of **2f** (DMSO-*d*₆)



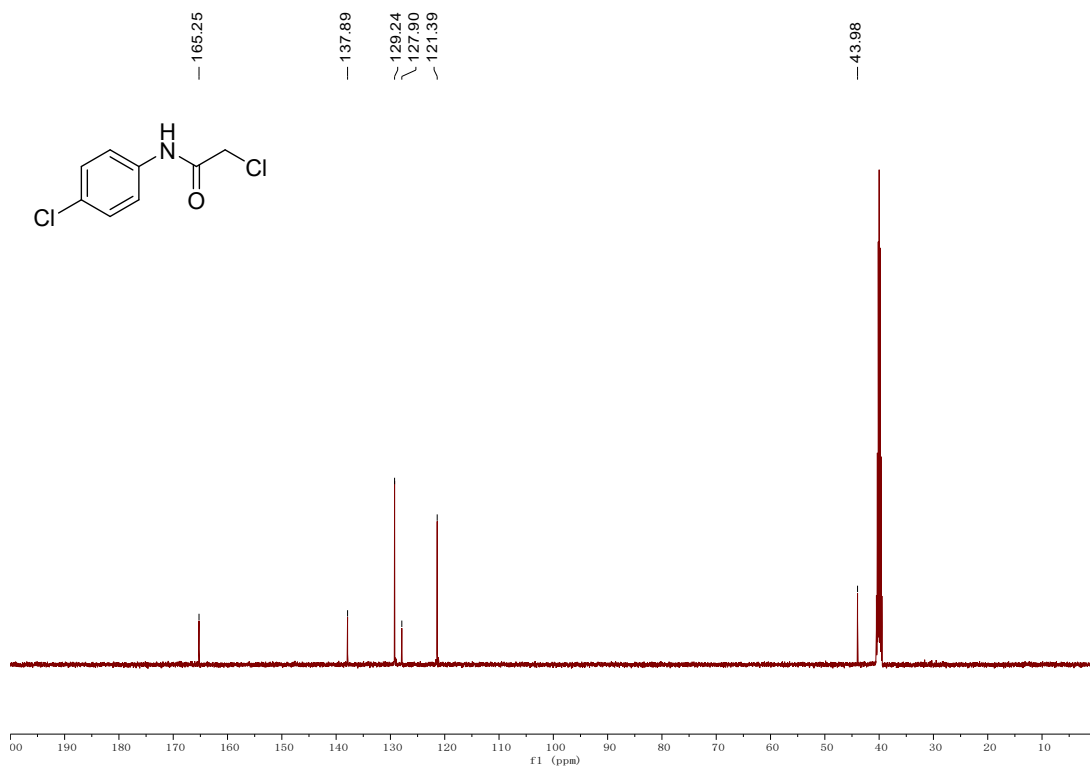
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2f** (DMSO-*d*₆)



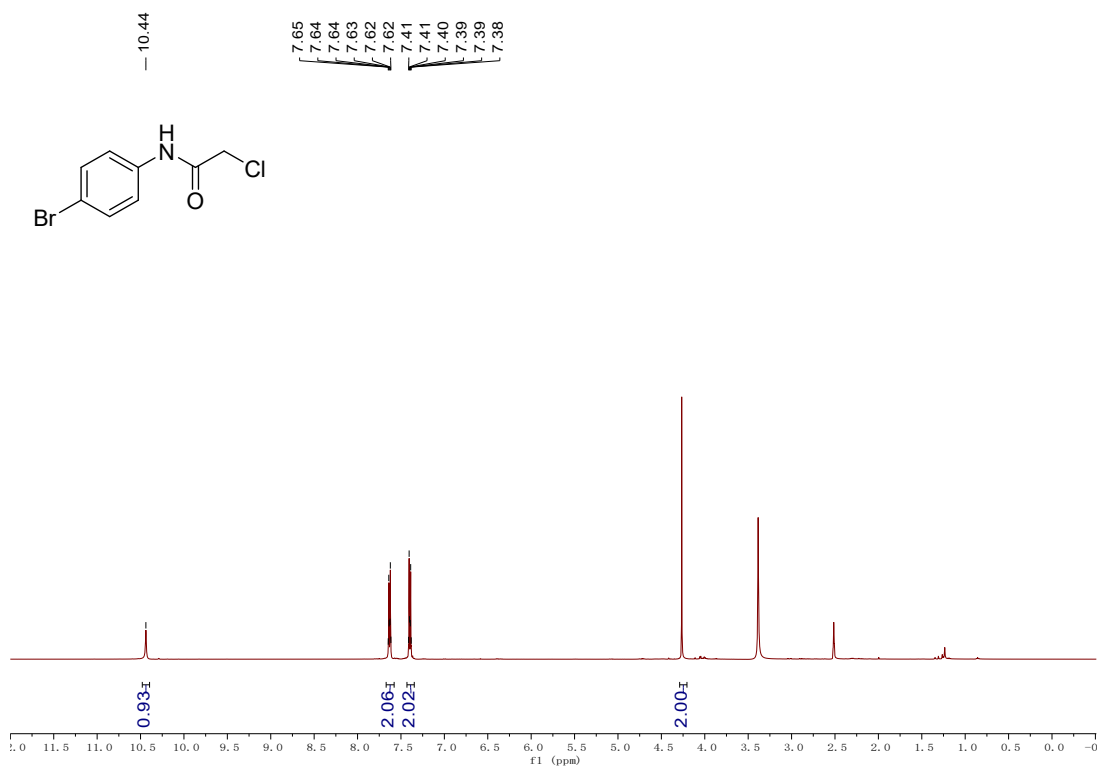
^1H NMR Spectrum of **2g** (DMSO-*d*₆)



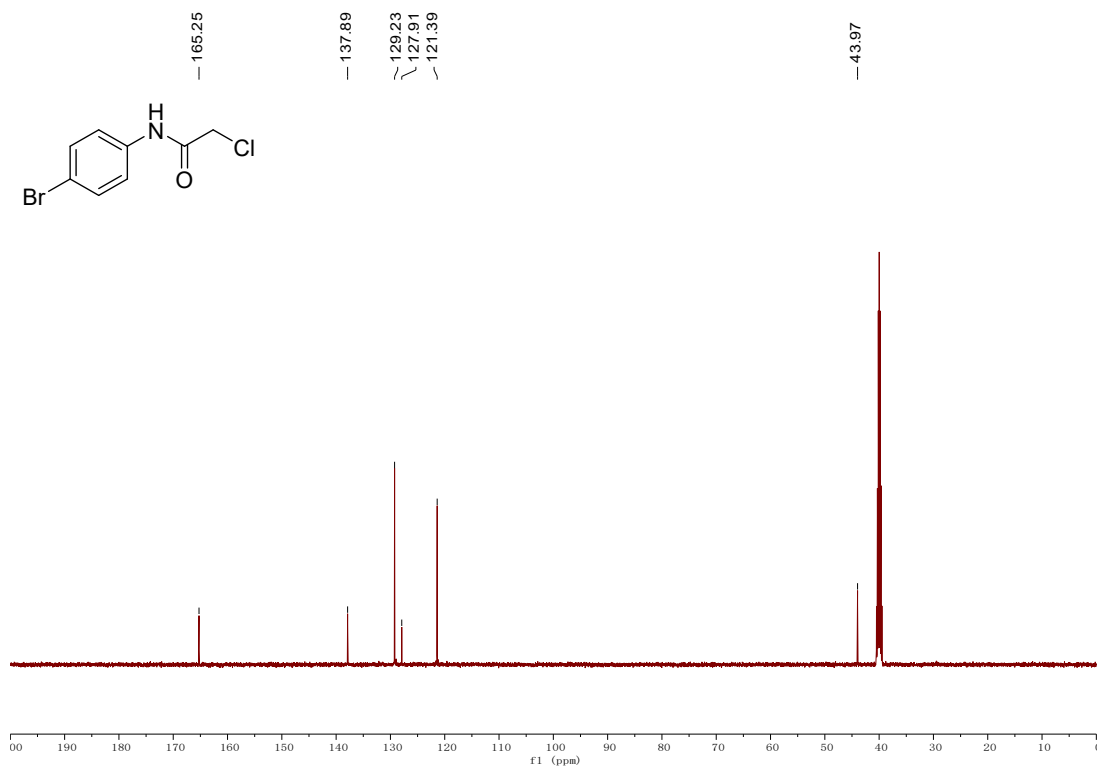
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2g** (DMSO-*d*₆)



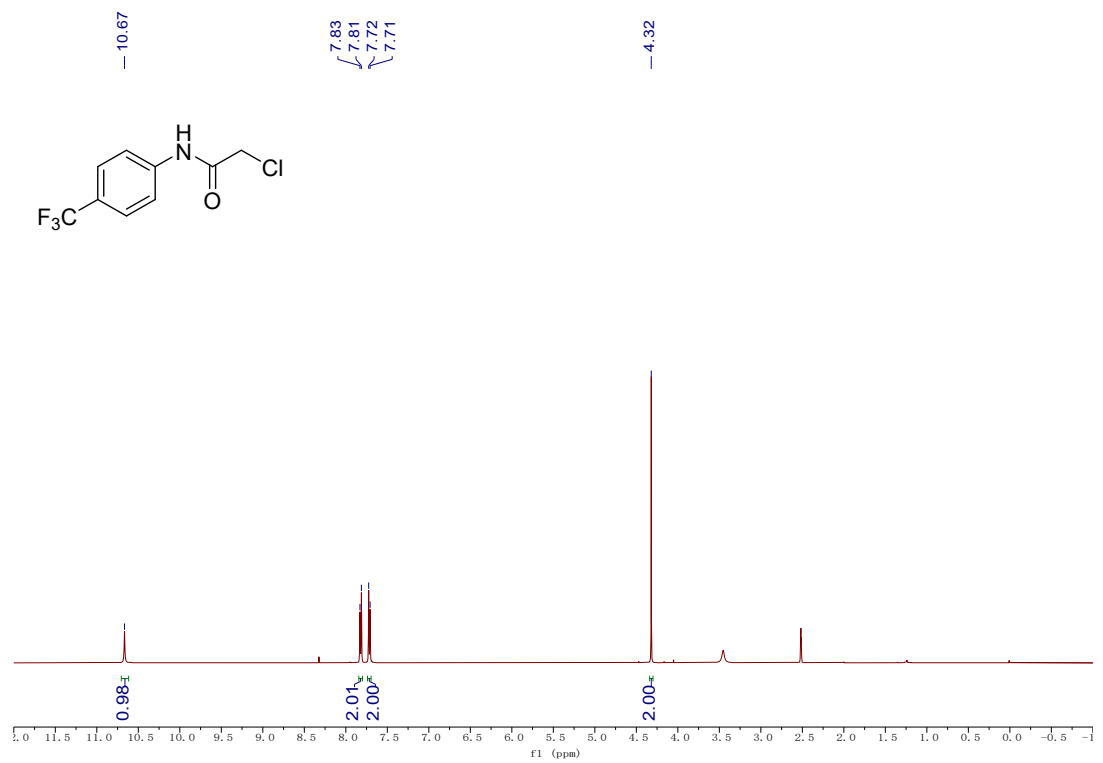
^1H NMR Spectrum of **2h** (DMSO-*d*₆)



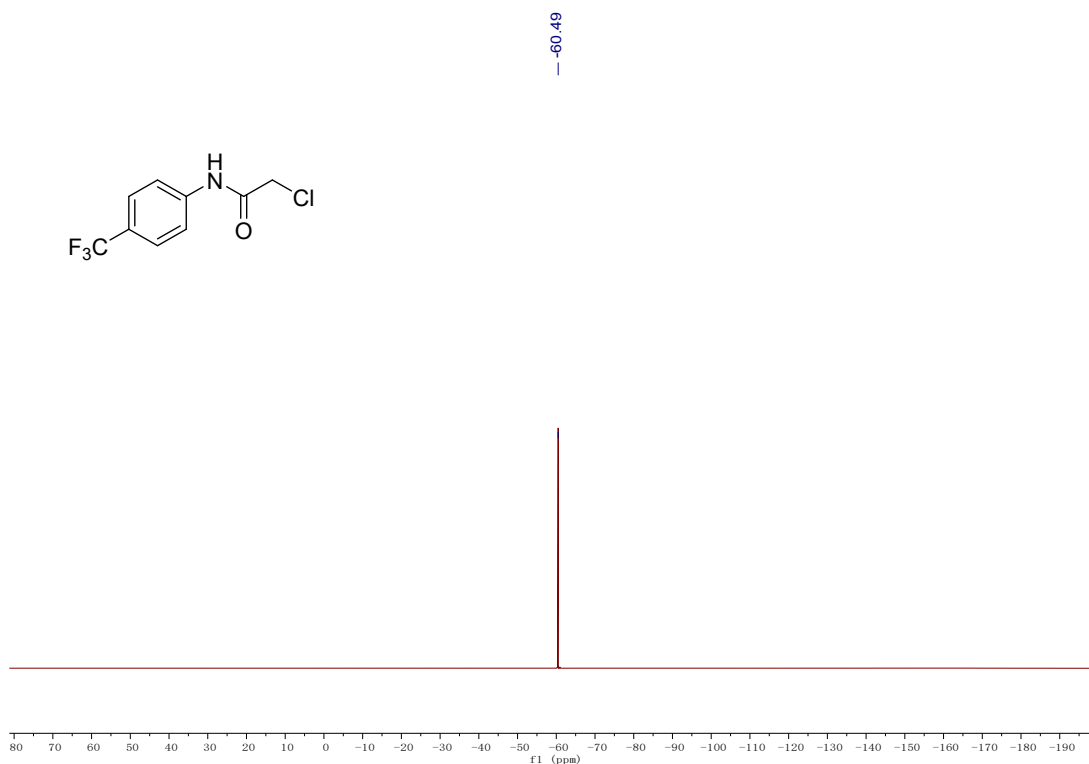
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2h** (DMSO-*d*₆)



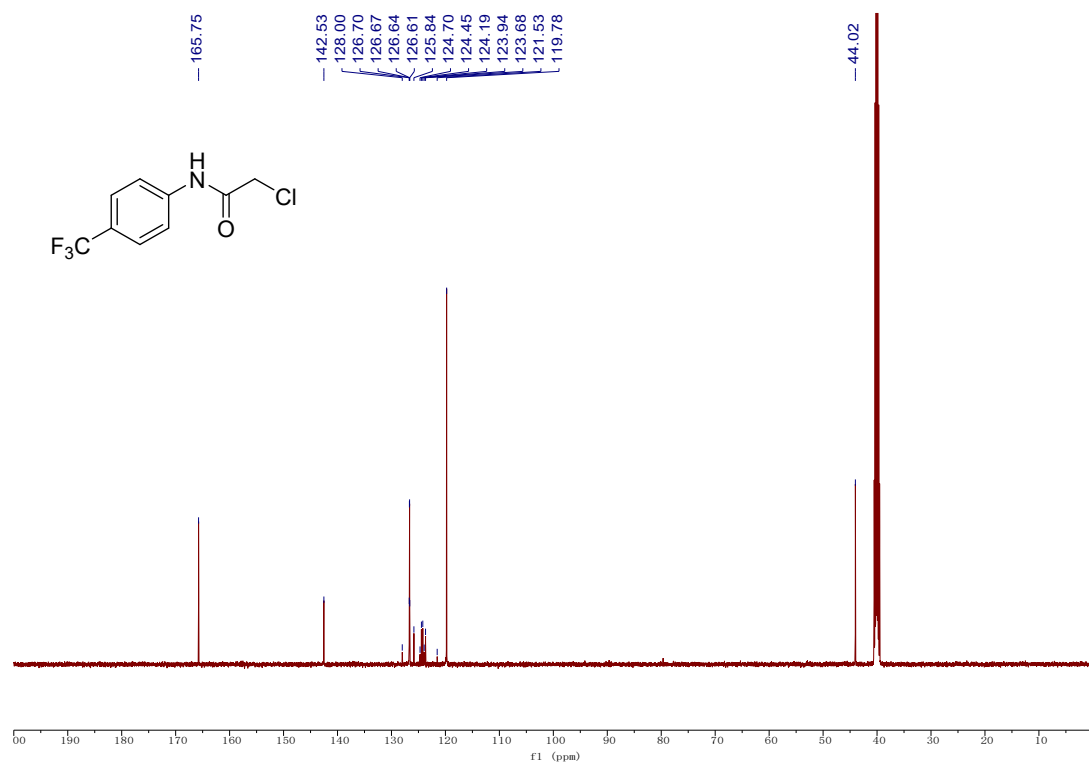
^1H NMR Spectrum of **2i** (DMSO-*d*₆)



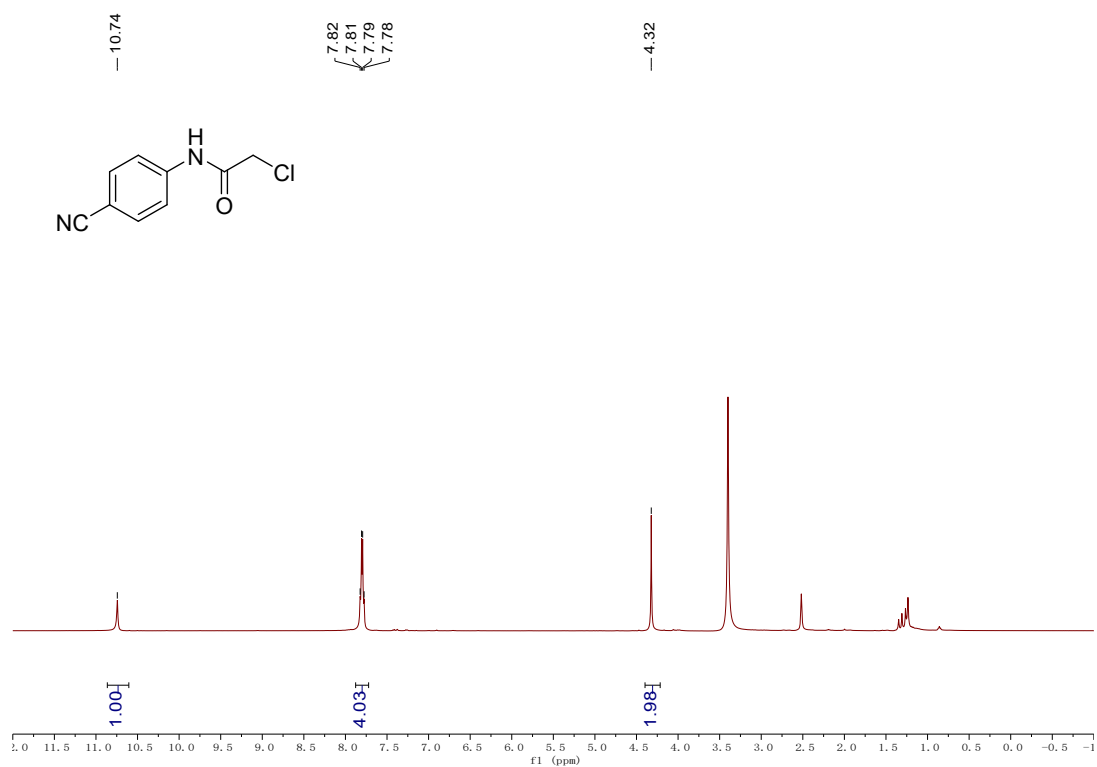
^{19}F NMR Spectrum of **2i** (DMSO-*d*₆)



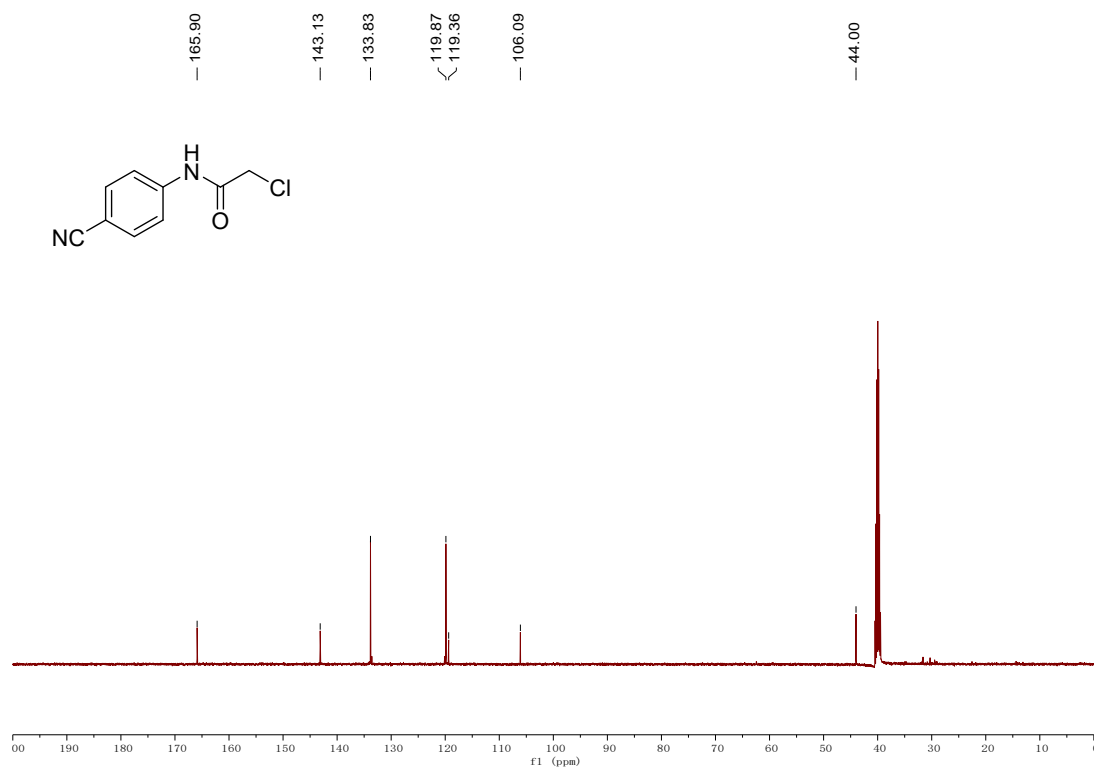
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2i** (DMSO-*d*₆)



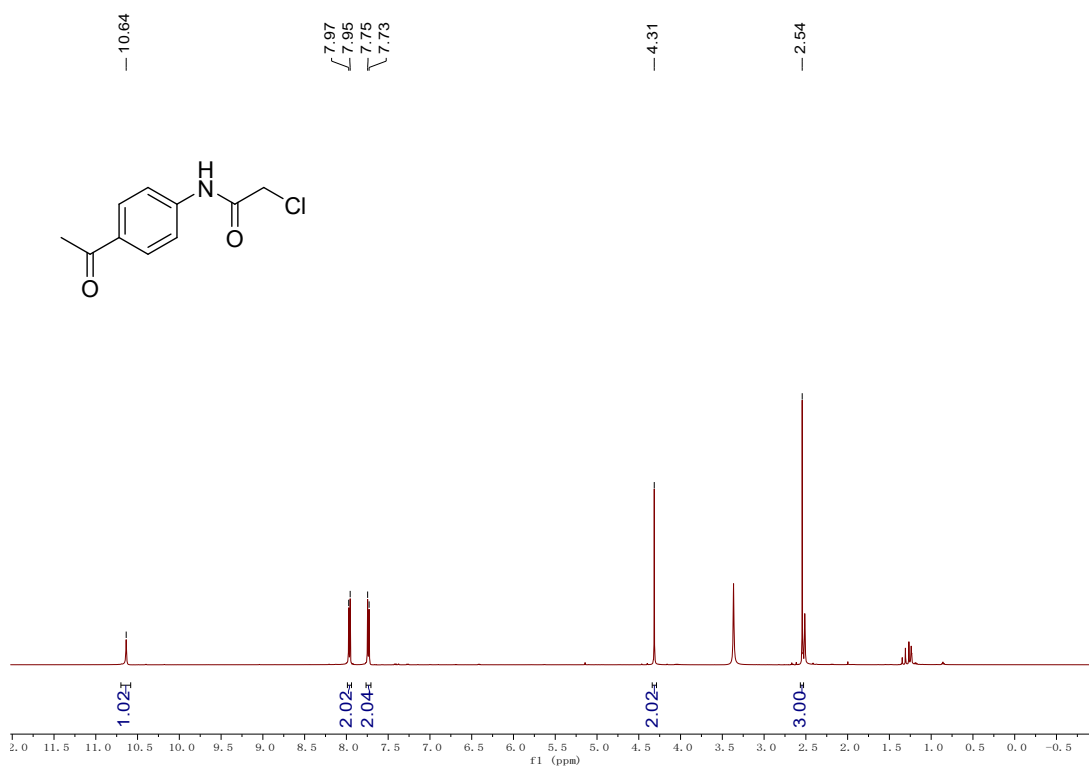
^1H NMR Spectrum of **2j** (DMSO- d_6)



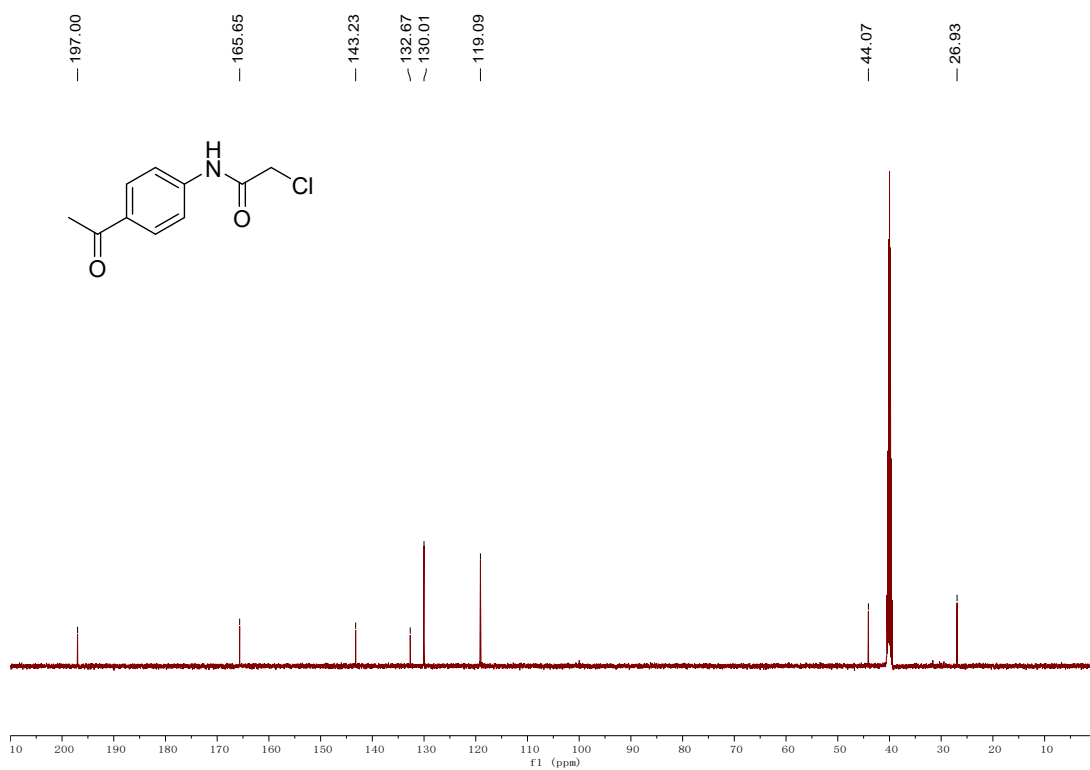
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2j** (DMSO- d_6)



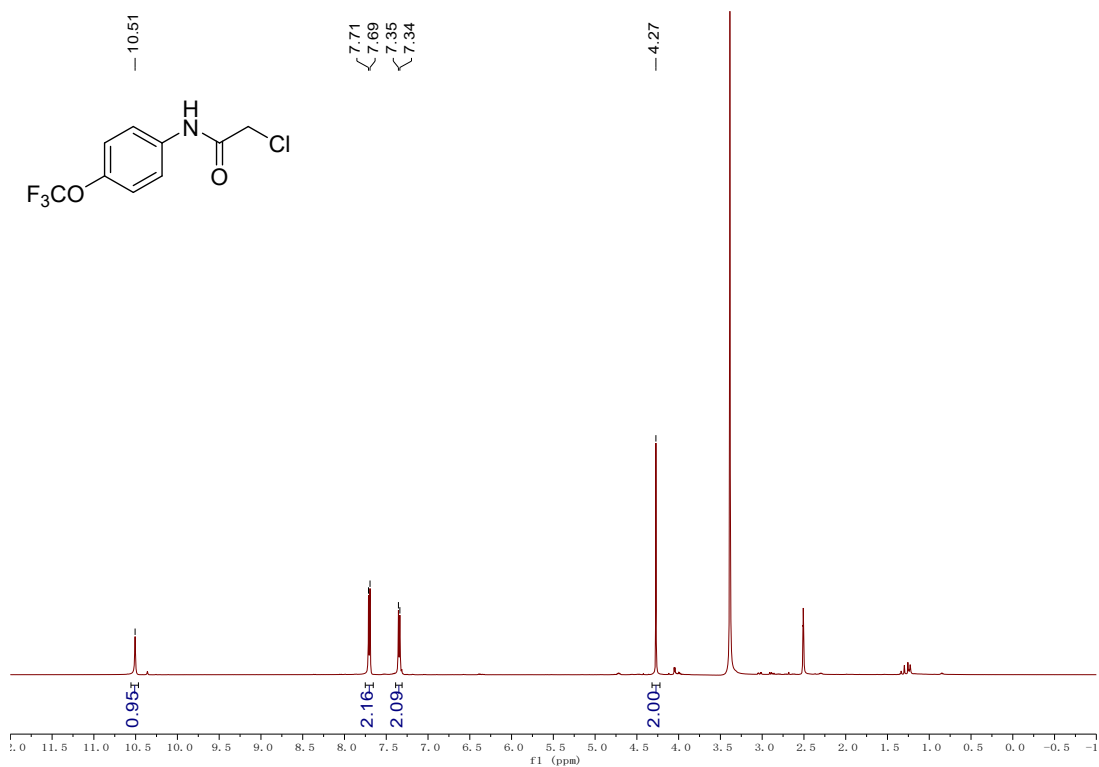
^1H NMR Spectrum of **2k** (DMSO- d_6)



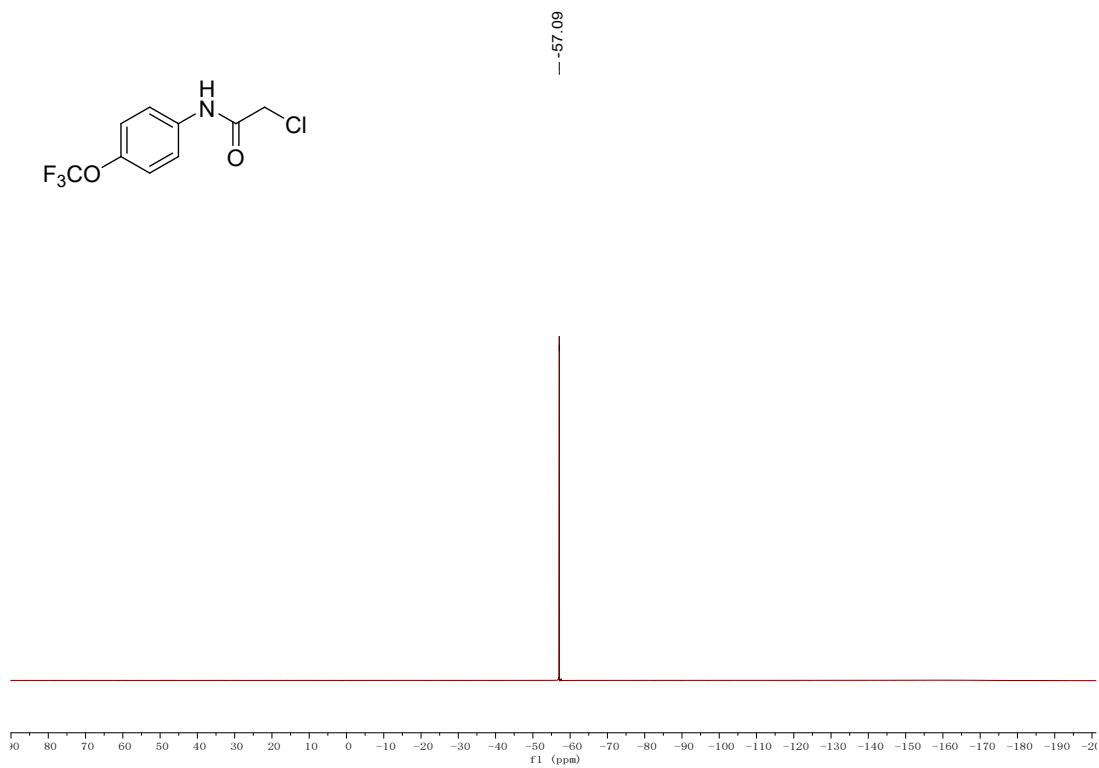
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2k** (DMSO- d_6)



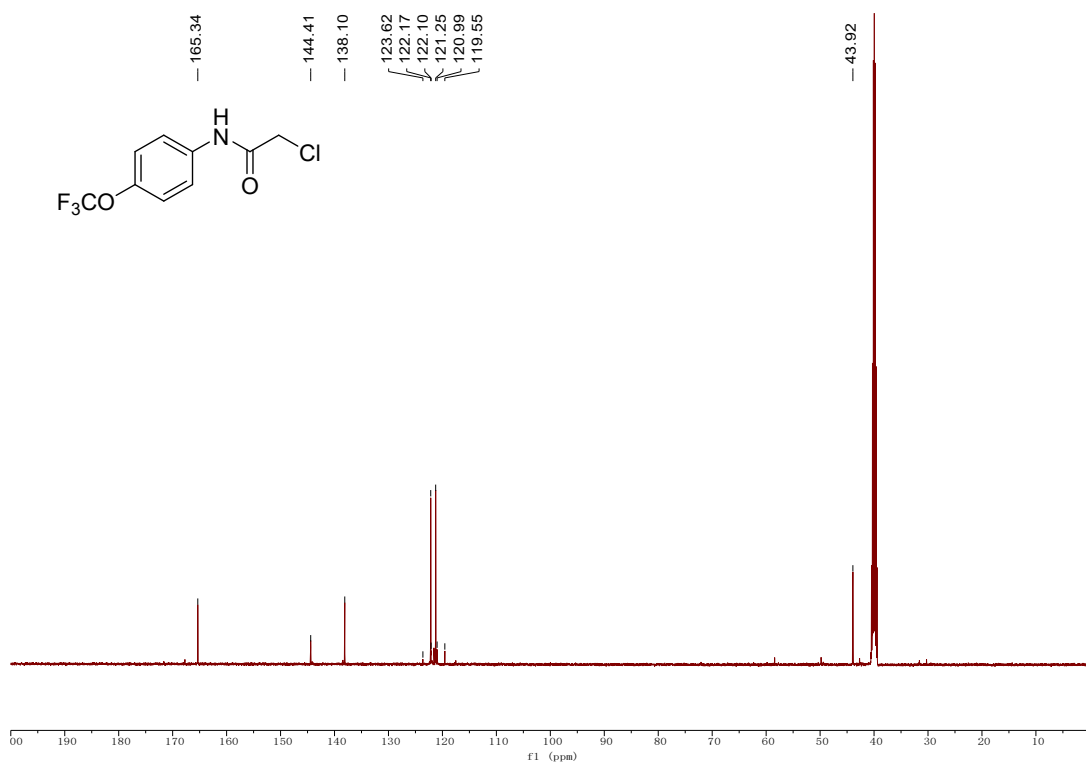
¹H NMR Spectrum of **21** (DMSO-*d*₆)



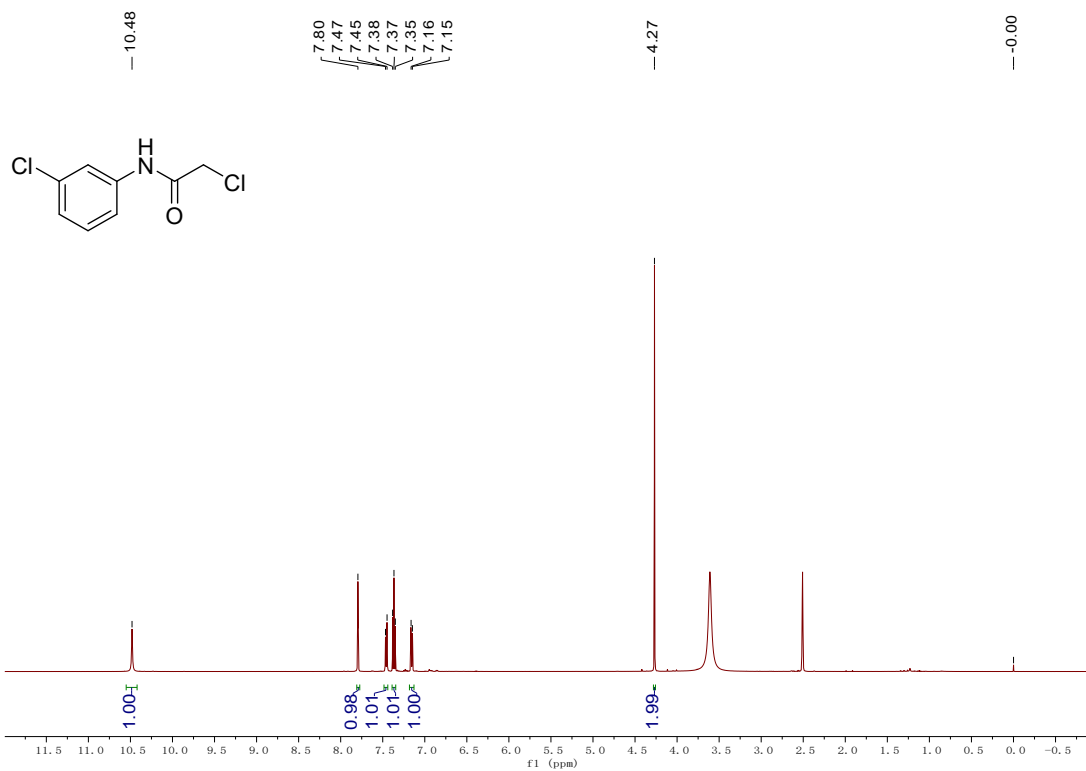
¹⁹F NMR Spectrum of **21** (DMSO-*d*₆)



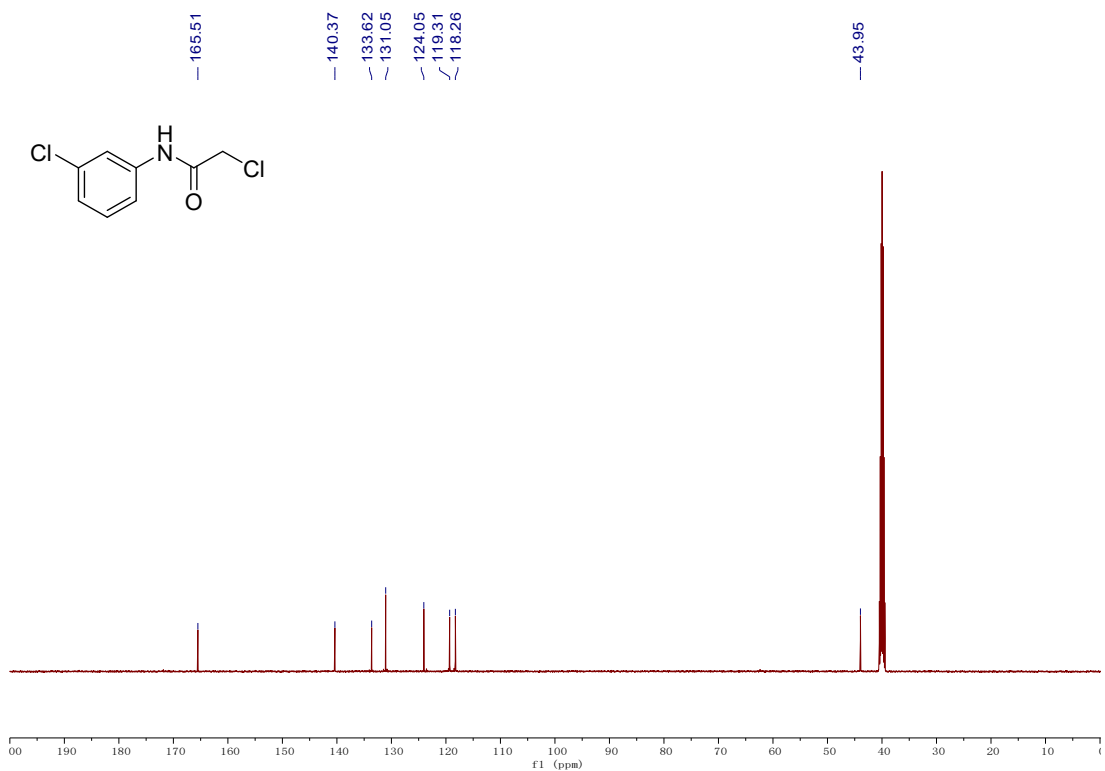
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2l** (DMSO-*d*₆)



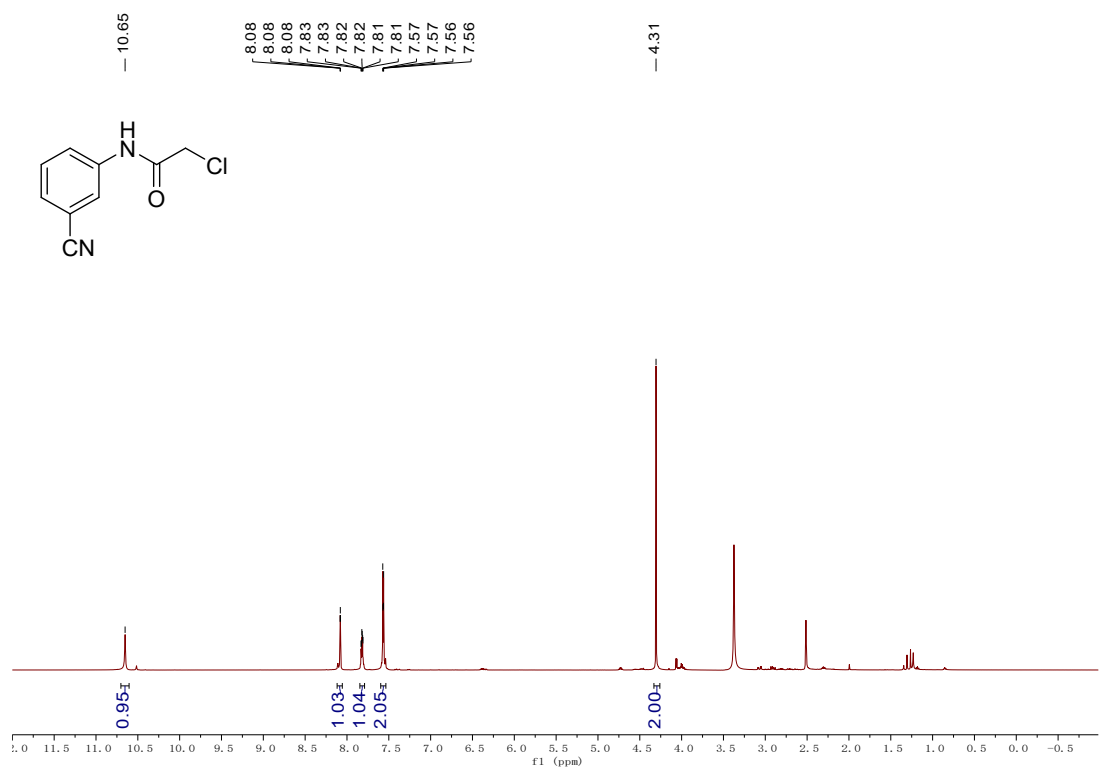
^1H NMR Spectrum of **2m** (DMSO-*d*₆)



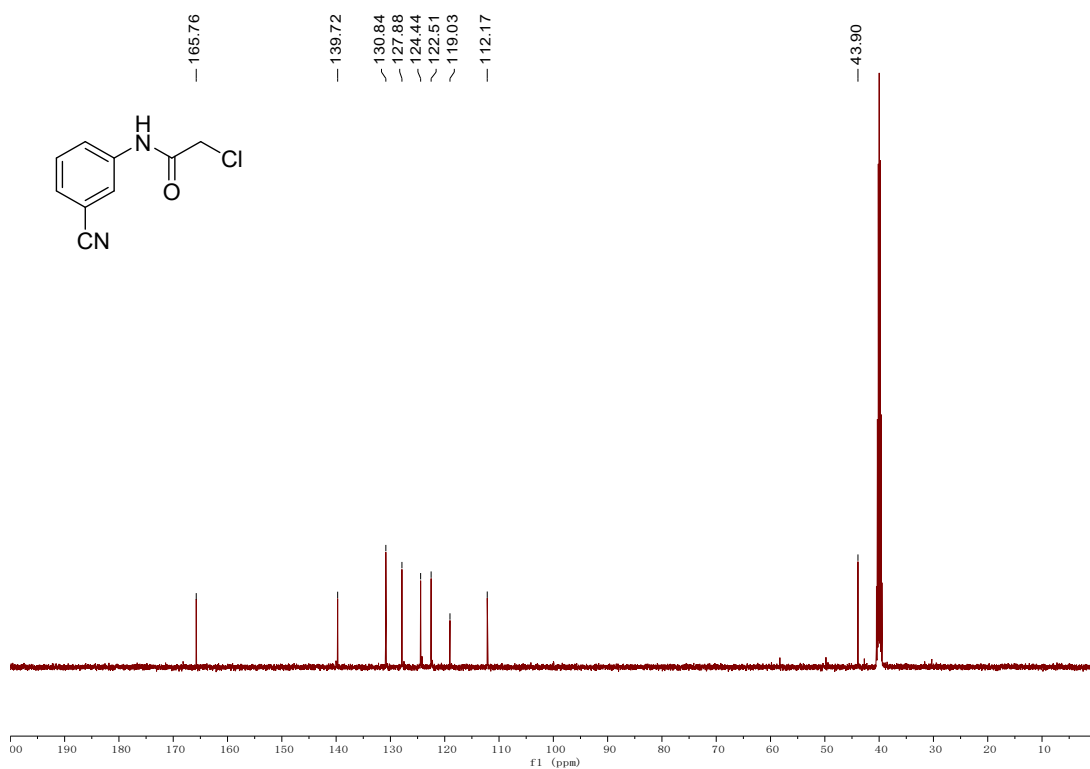
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2m** (DMSO-*d*₆)



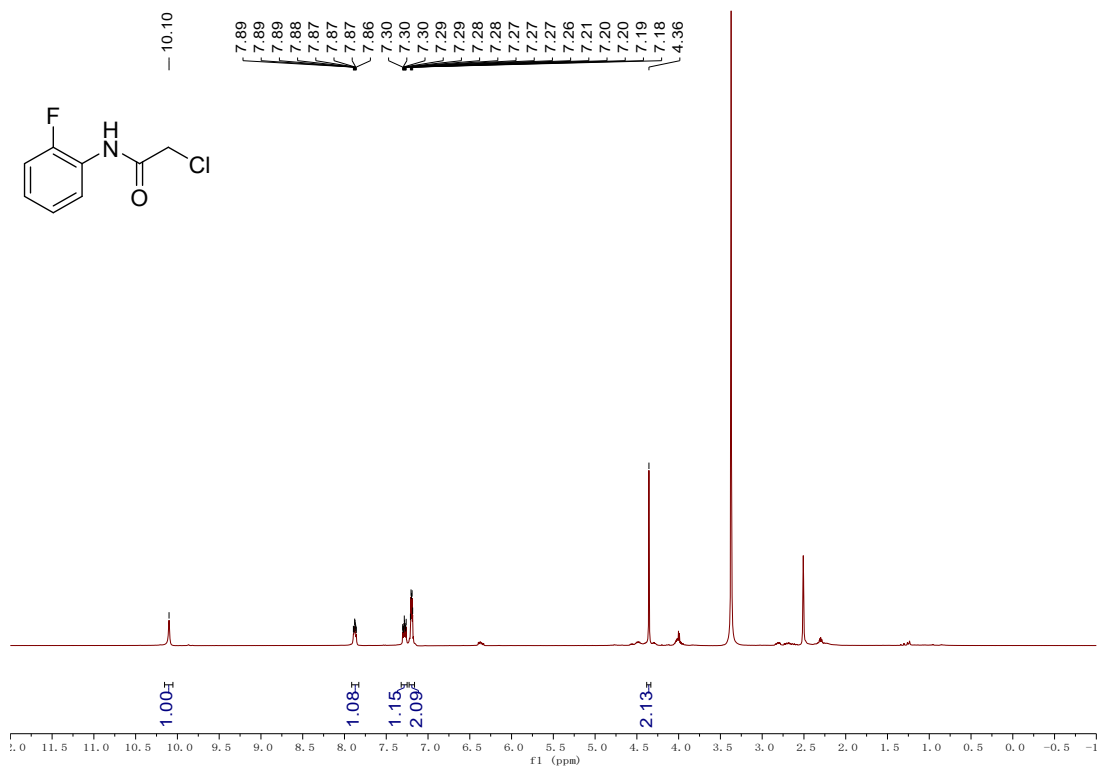
^1H NMR Spectrum of **2n** (DMSO-*d*₆)



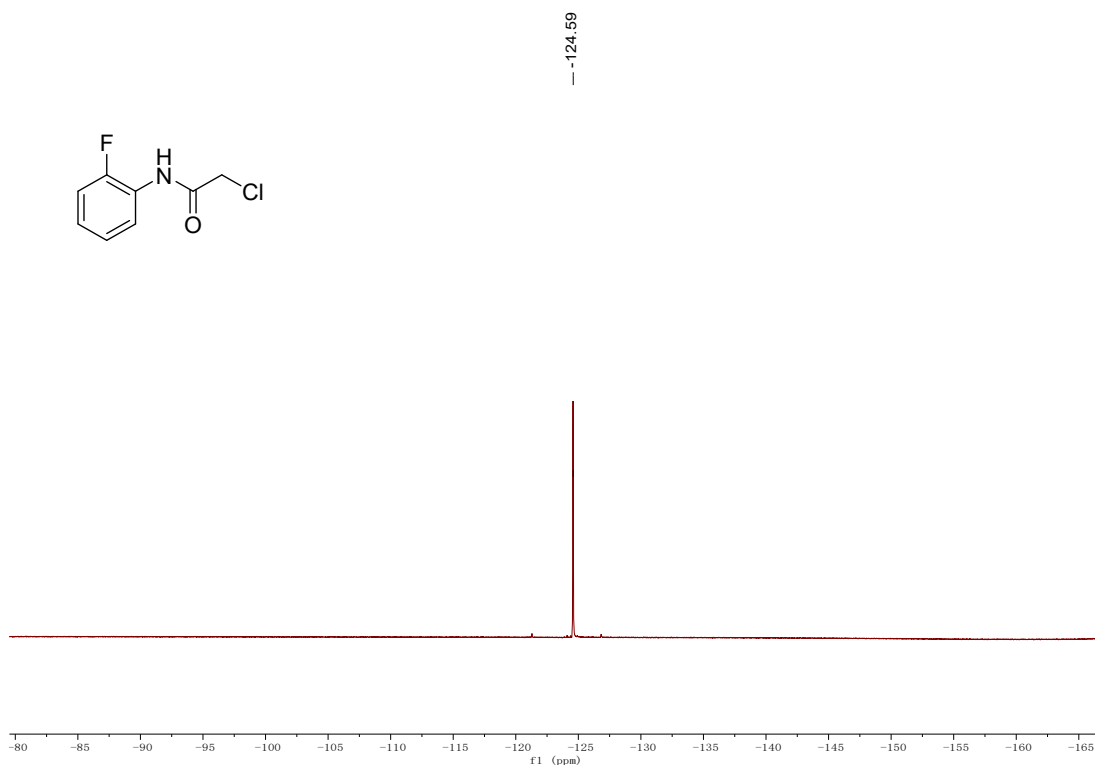
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2n** (DMSO- d_6)



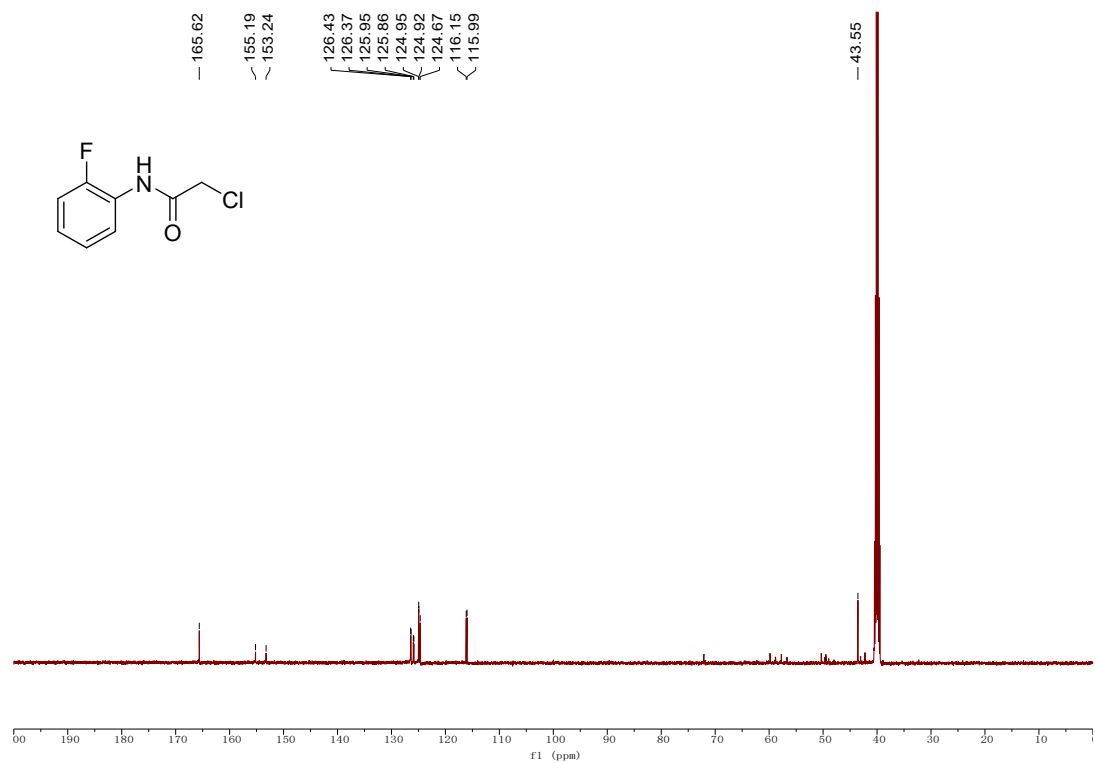
^1H NMR Spectrum of **2o** (DMSO- d_6)



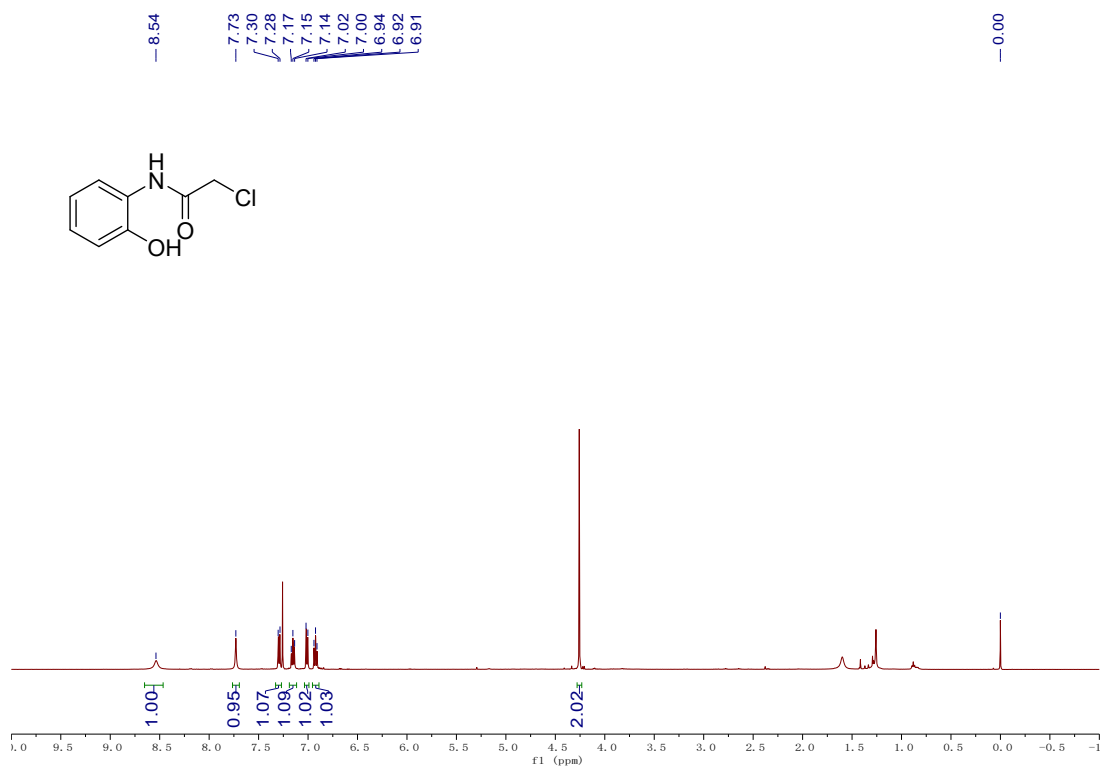
^{19}F NMR Spectrum of **2o** (DMSO-*d*₆)



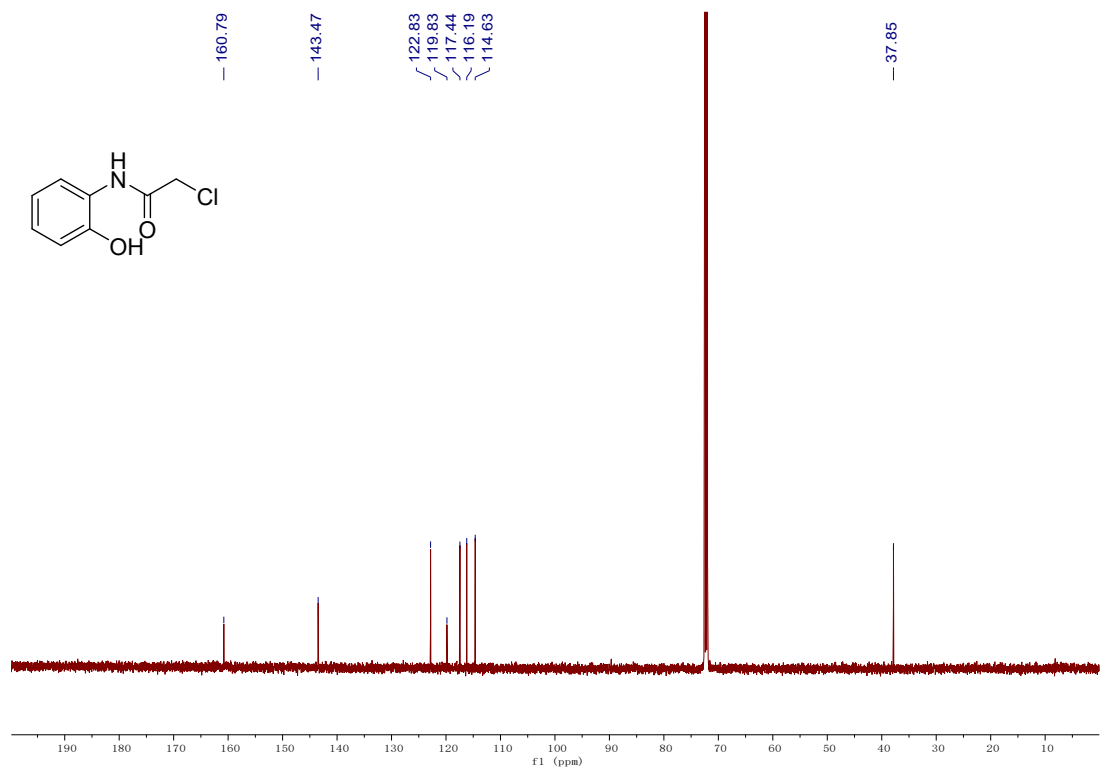
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2o** (DMSO-*d*₆)



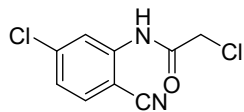
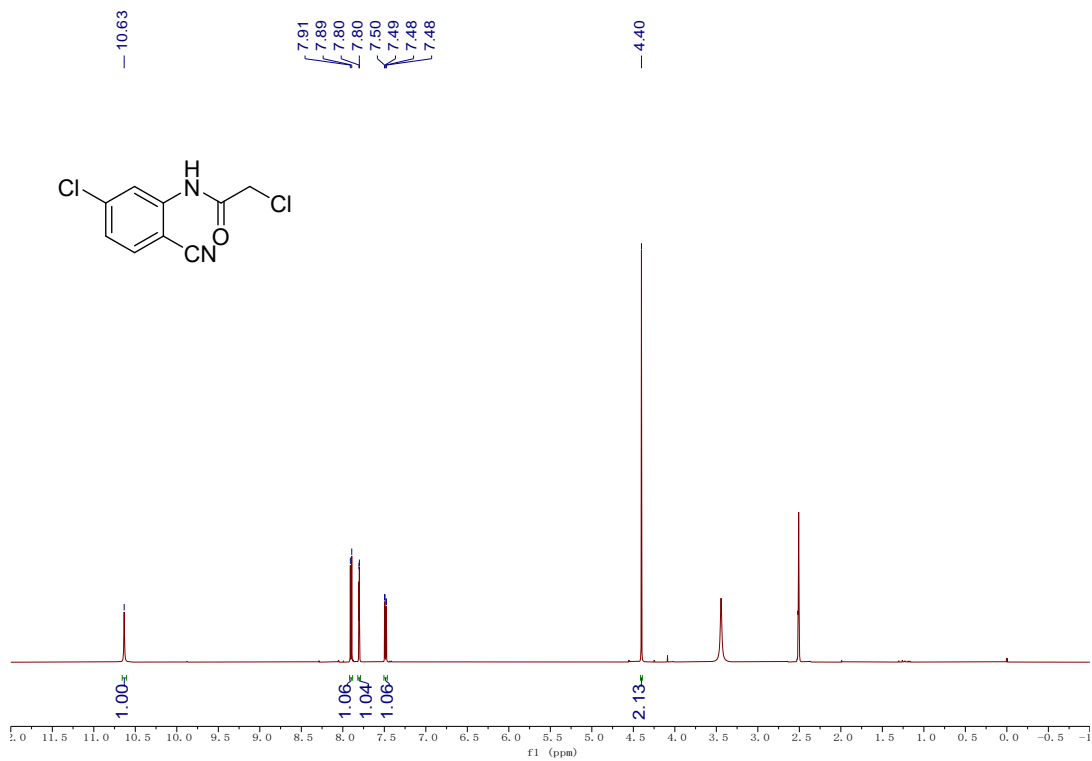
^1H NMR Spectrum of **2p** (DMSO- d_6)



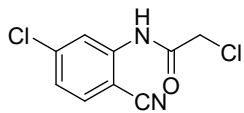
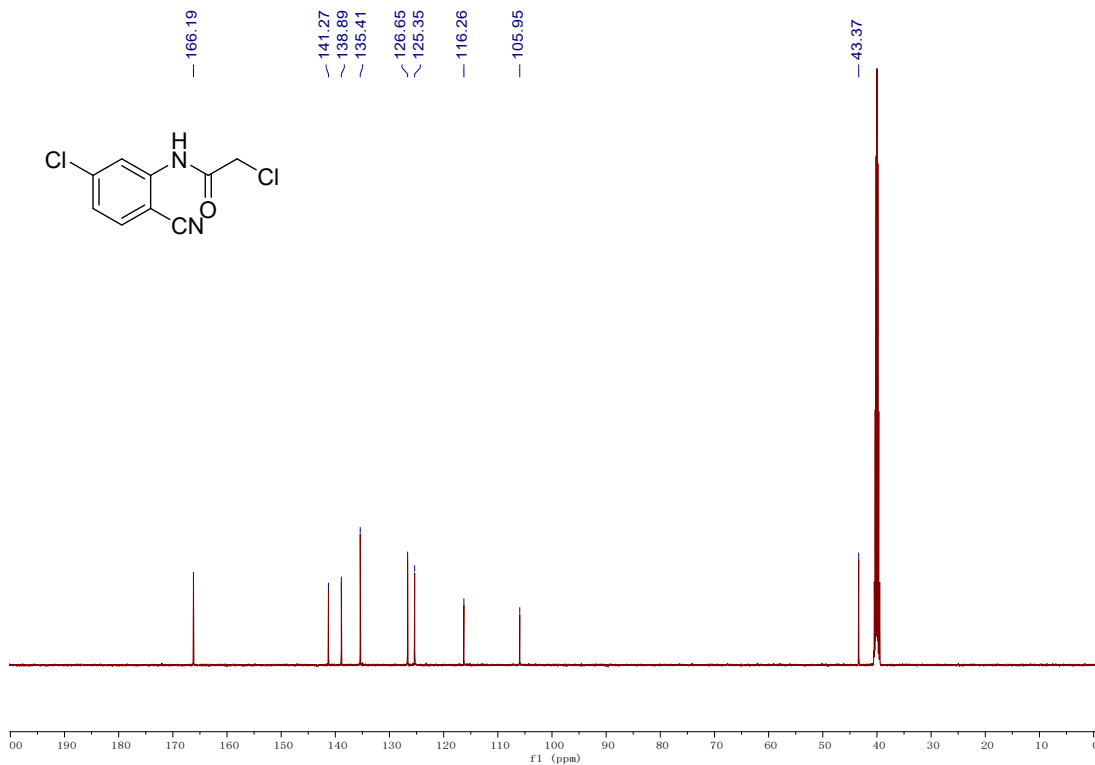
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2p** (DMSO- d_6)



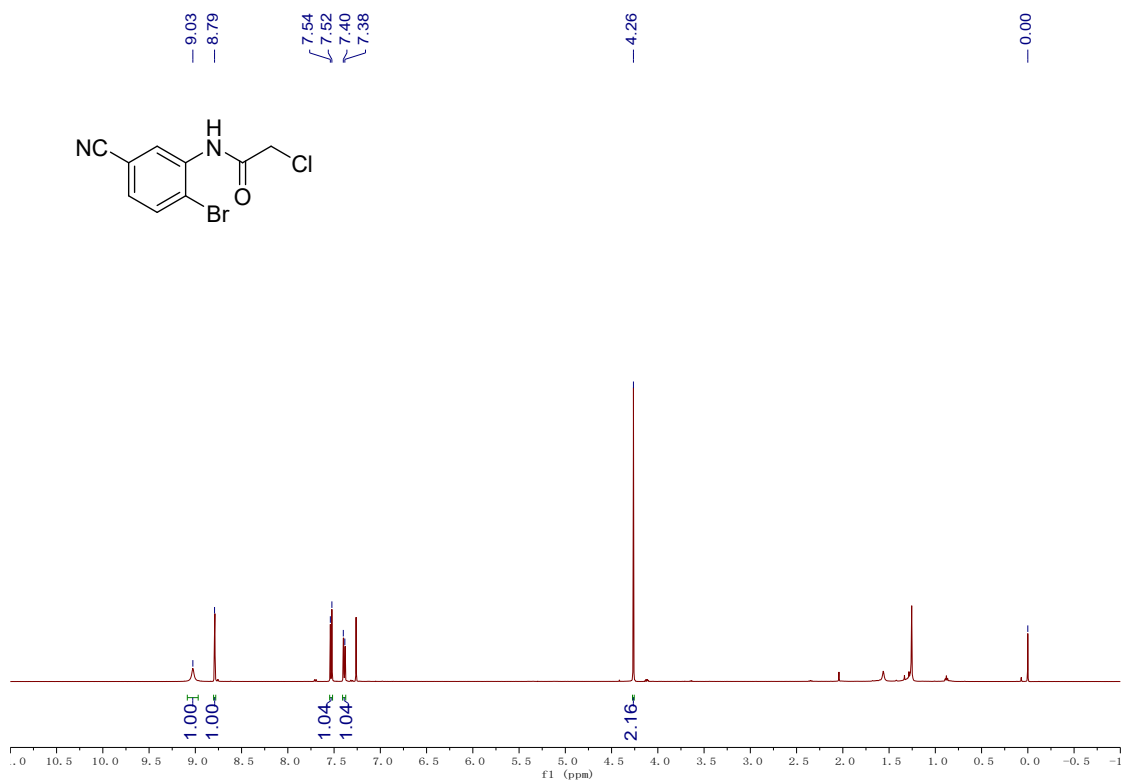
^1H NMR Spectrum of **2q** (DMSO- d_6)



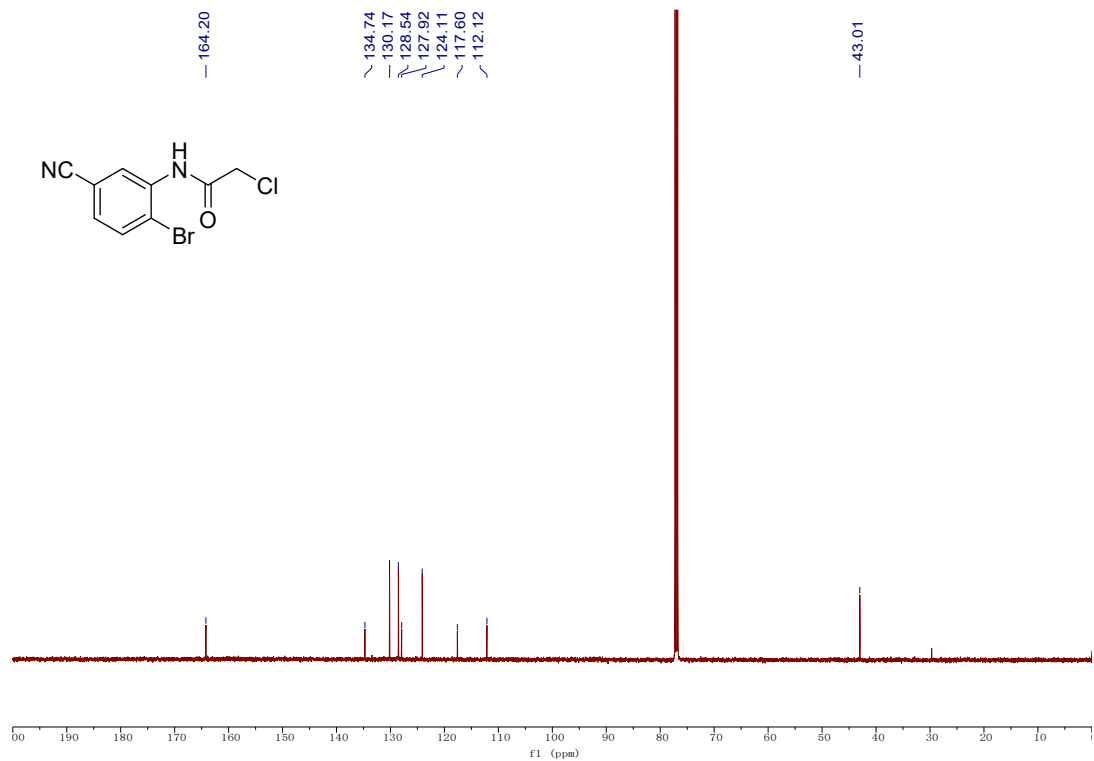
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2q** (DMSO- d_6)



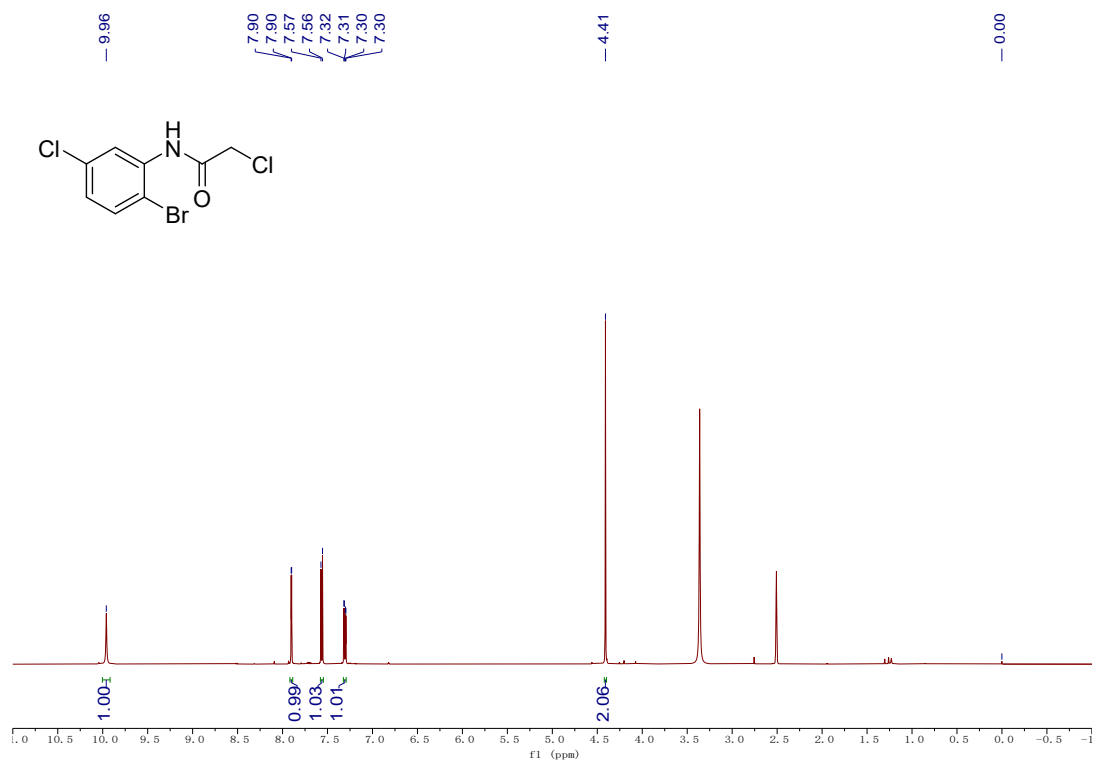
¹H NMR Spectrum of **2r** (CDCl₃)



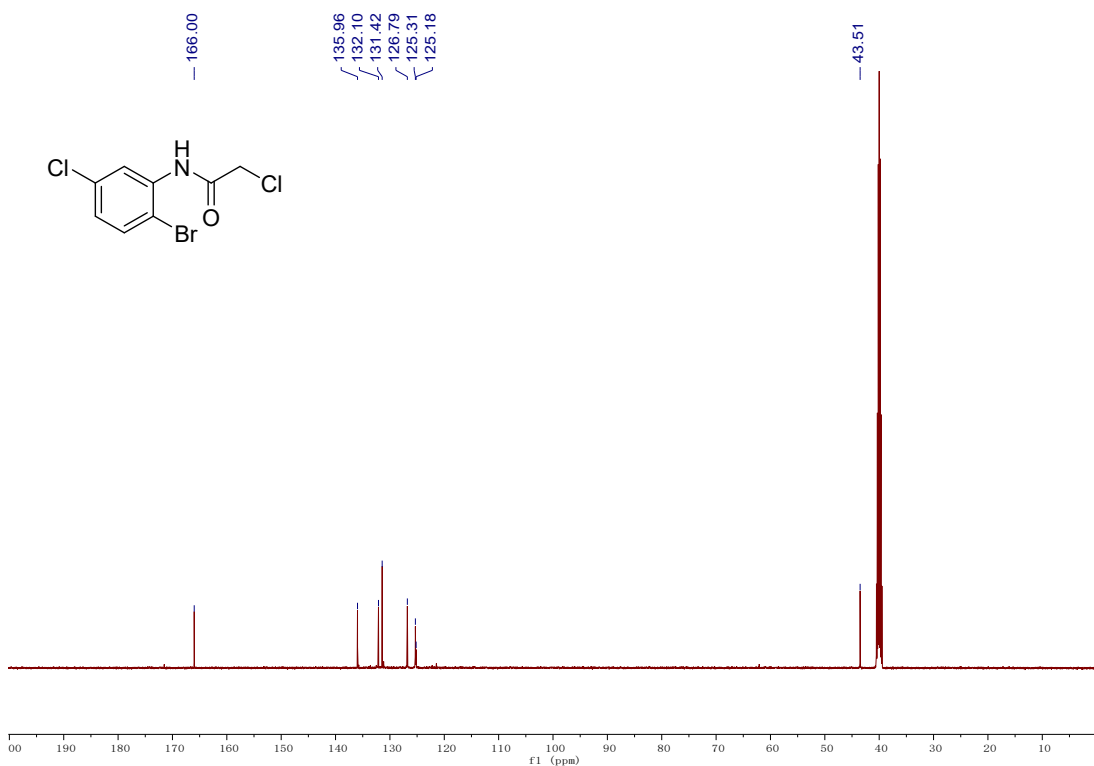
¹³C{¹H} NMR Spectrum of **2r** (CDCl₃)



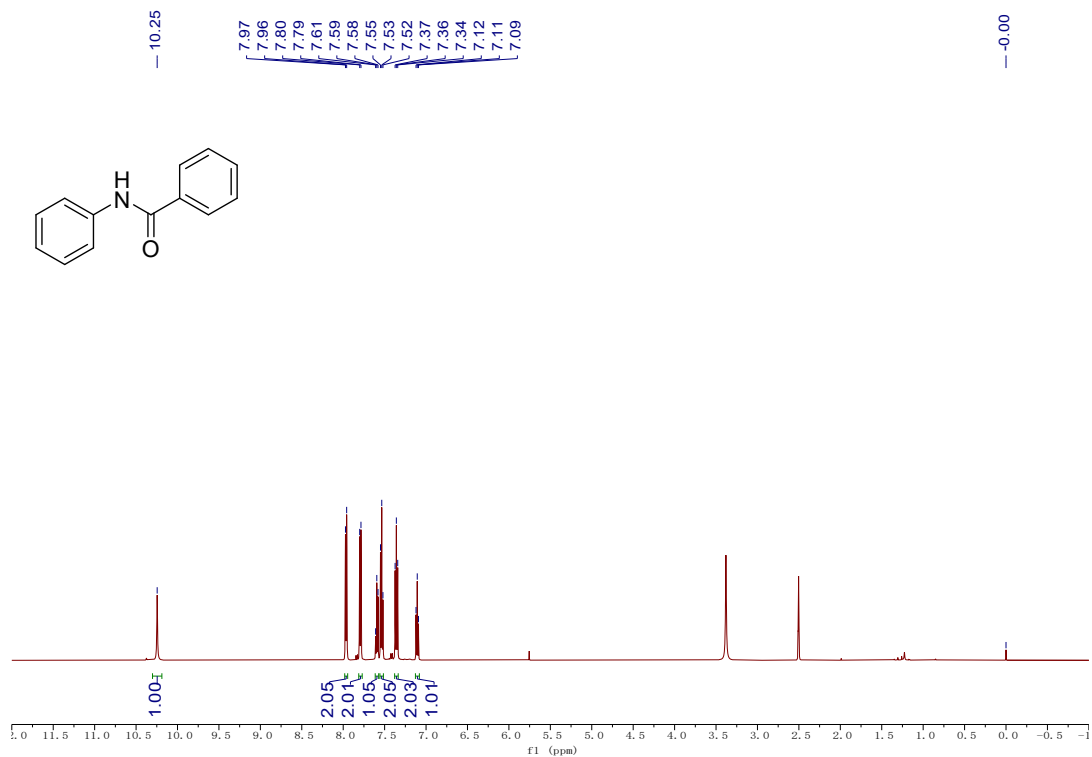
^1H NMR Spectrum of **2s** (DMSO- d_6)



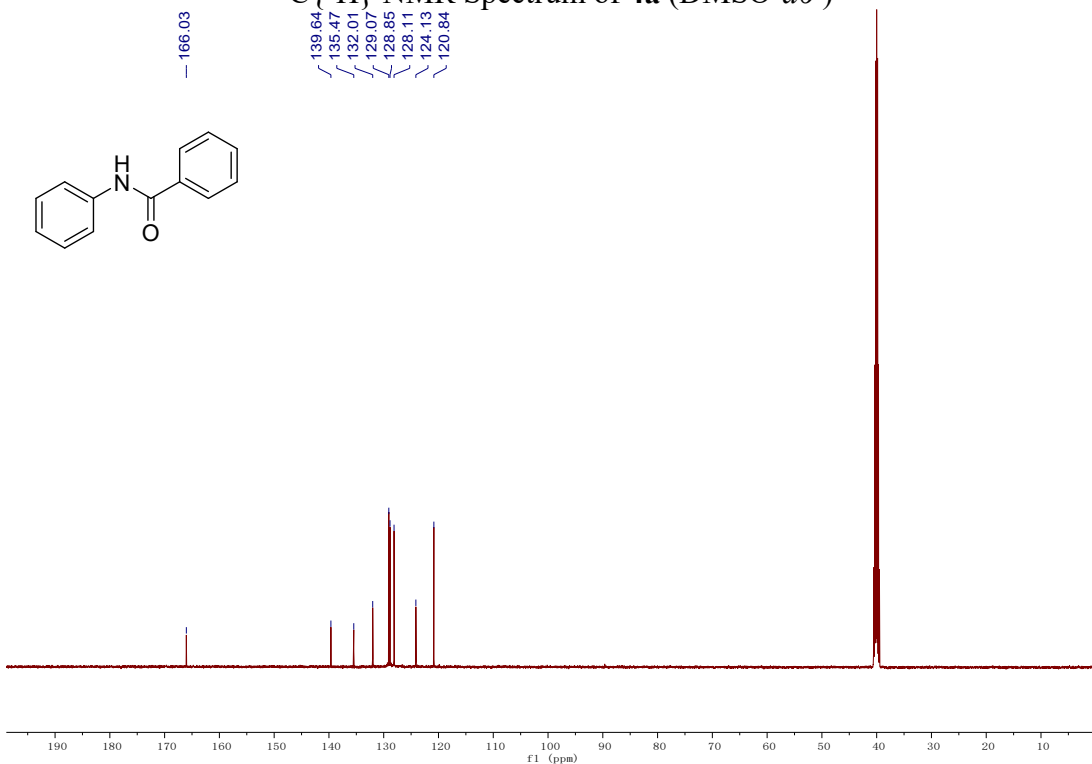
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **2s** (DMSO- d_6)



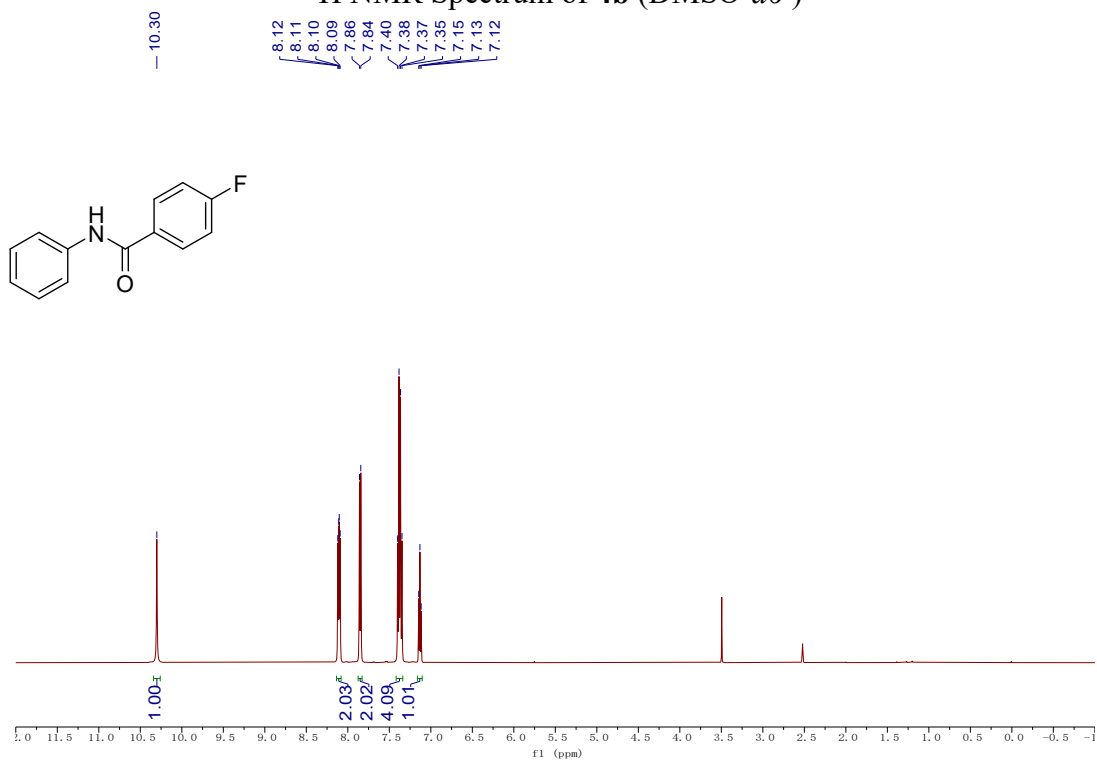
¹H NMR Spectrum of 4a (DMSO-d₆)



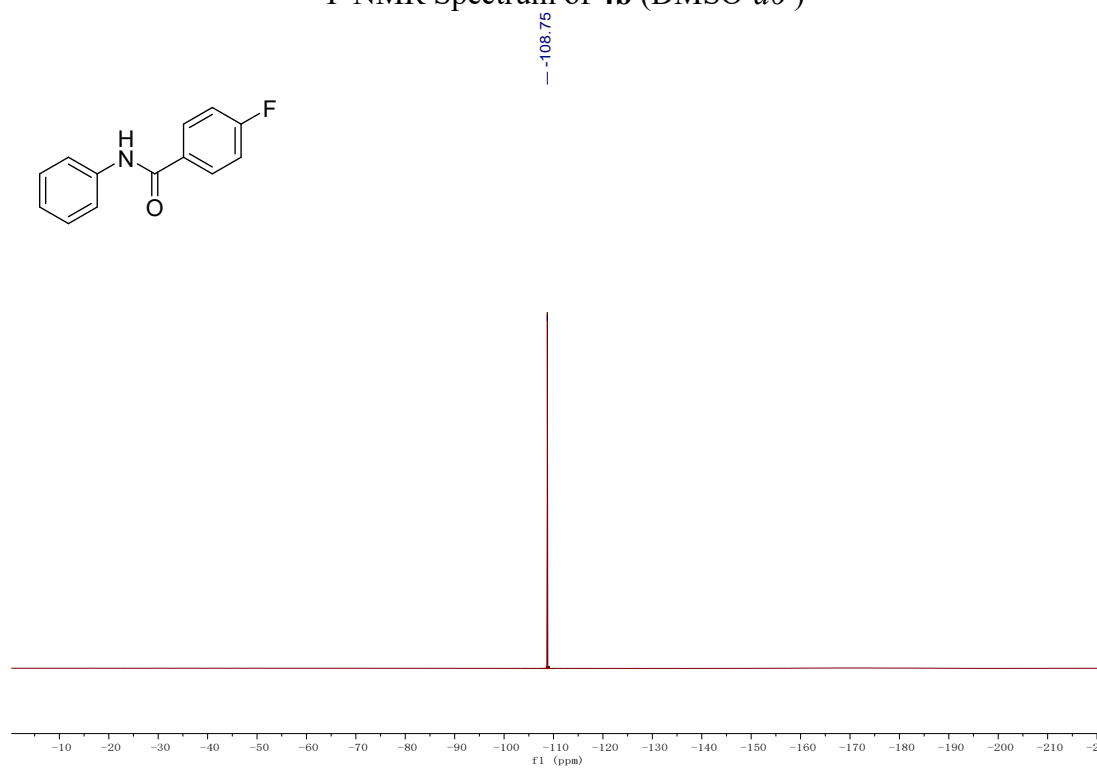
¹³C {¹H} NMR Spectrum of 4a (DMSO-d₆)



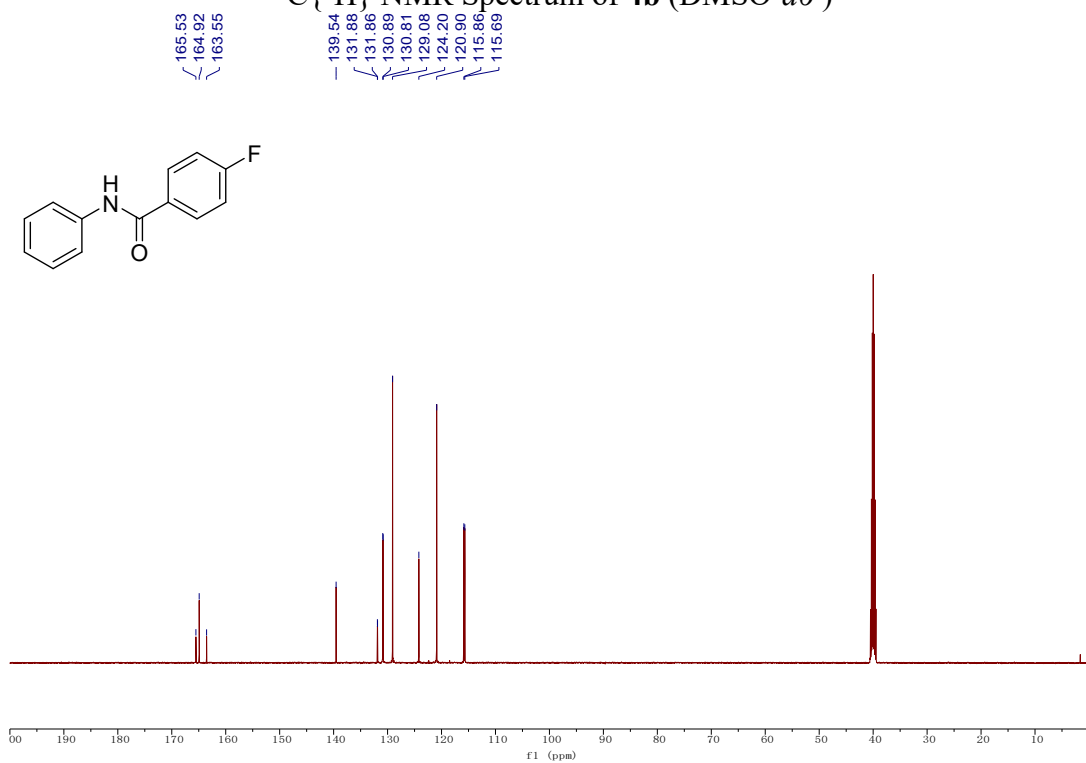
¹H NMR Spectrum of **4b** (DMSO-*d*₆)



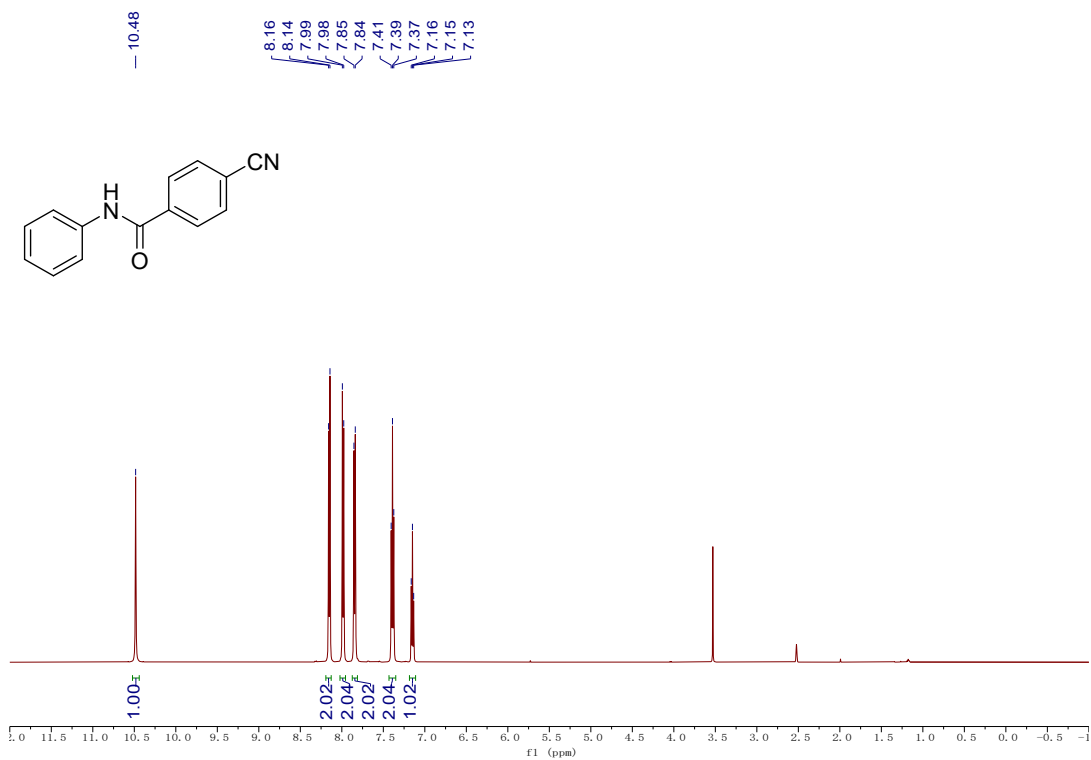
¹⁹F NMR Spectrum of **4b** (DMSO-*d*₆)



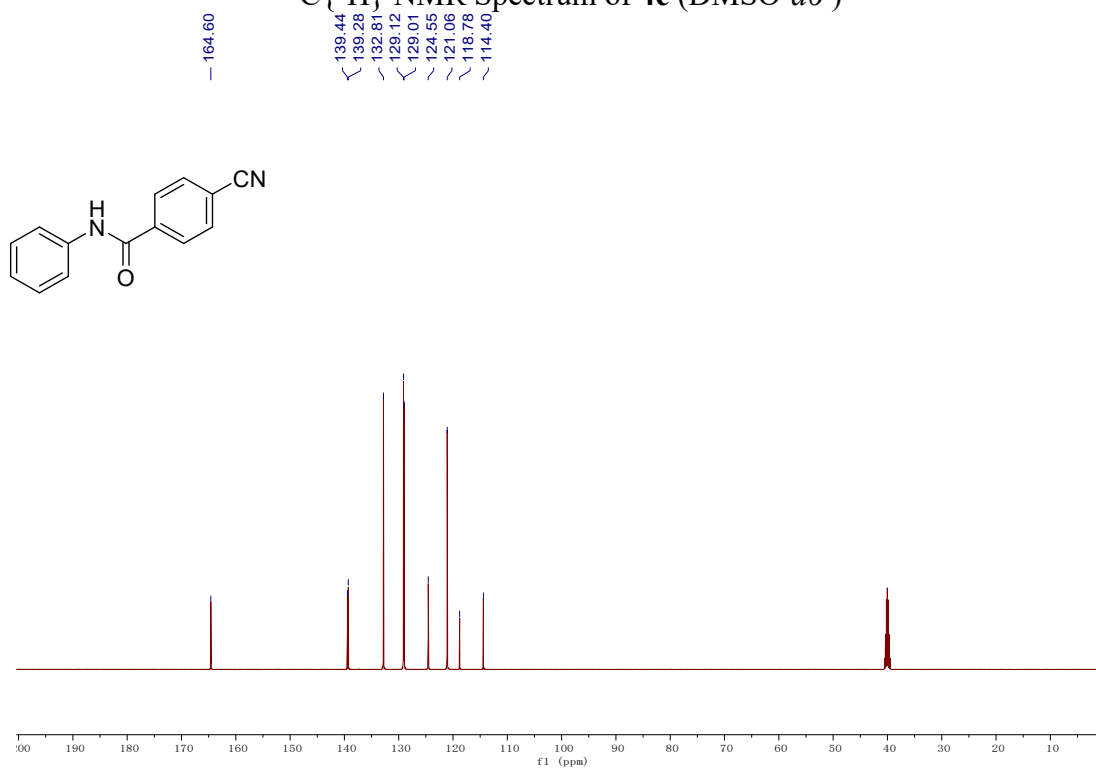
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4b** (DMSO-*d*₆)



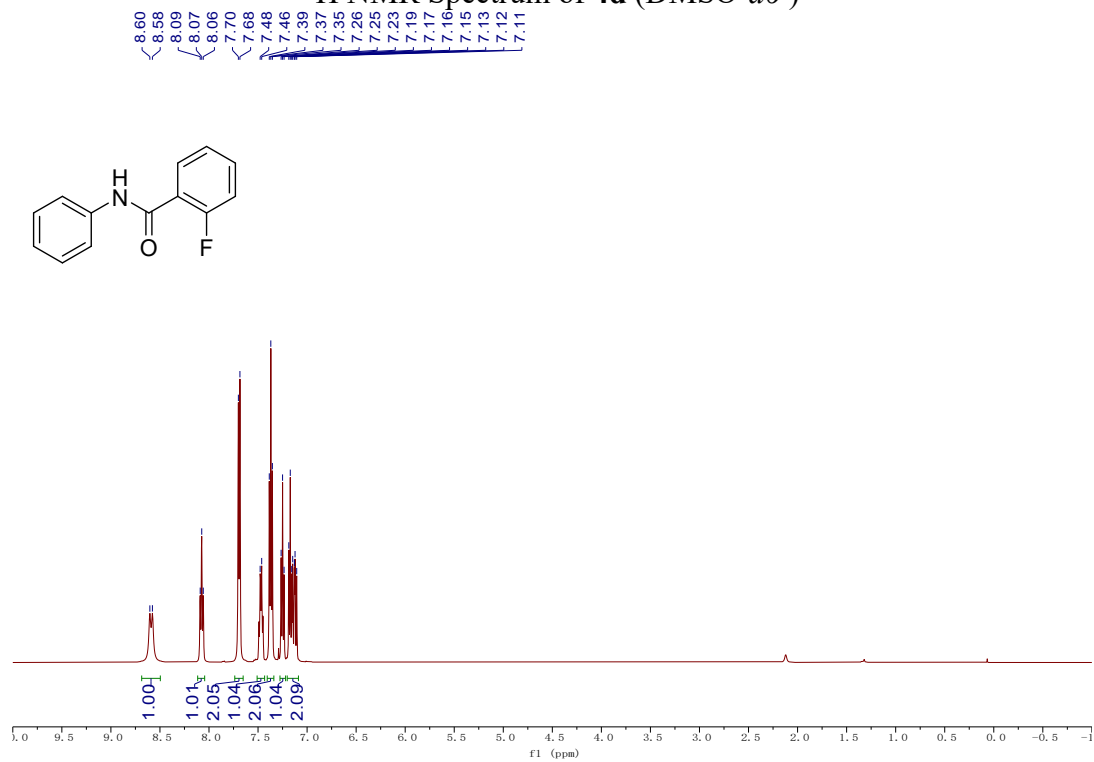
^1H NMR Spectrum of **4c** (DMSO-*d*₆)



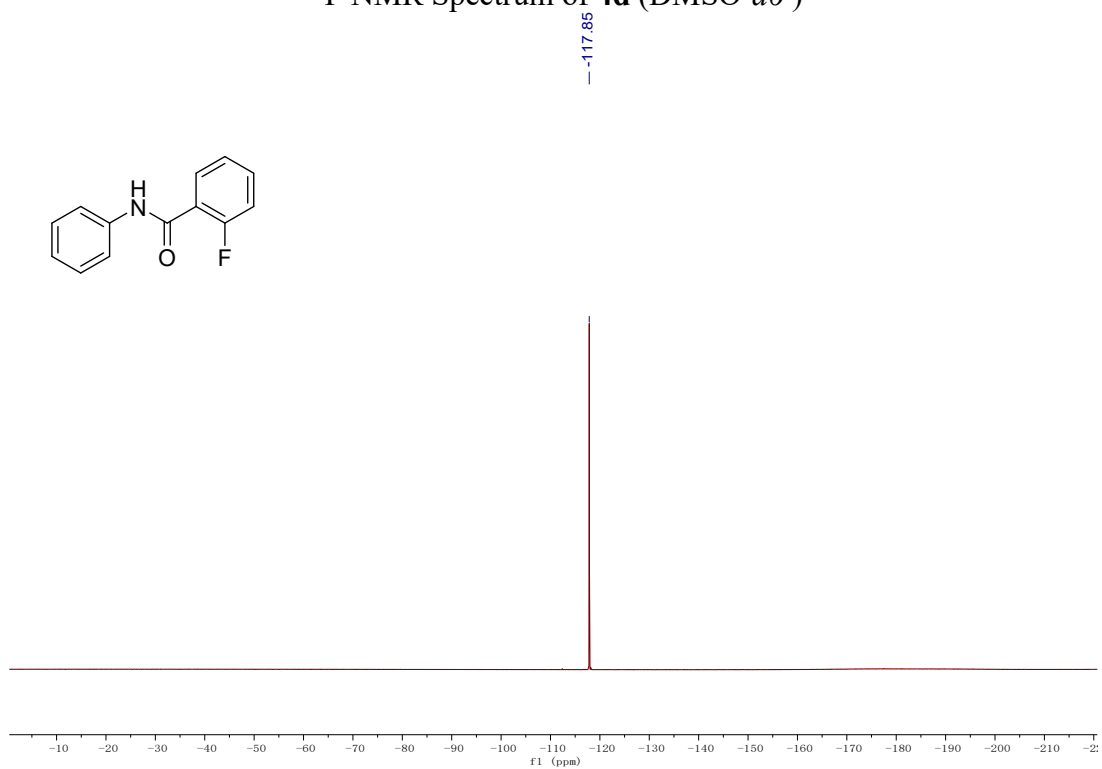
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4c** (DMSO-*d*₆)



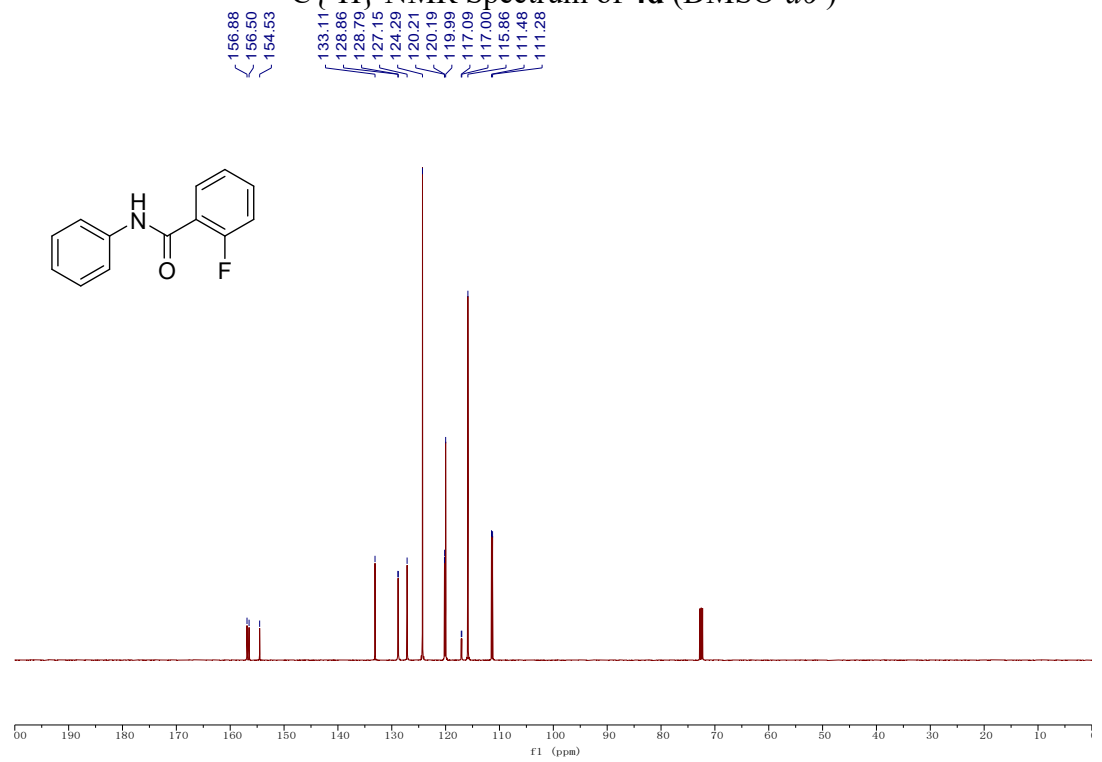
^1H NMR Spectrum of **4d** (DMSO-*d*₆)



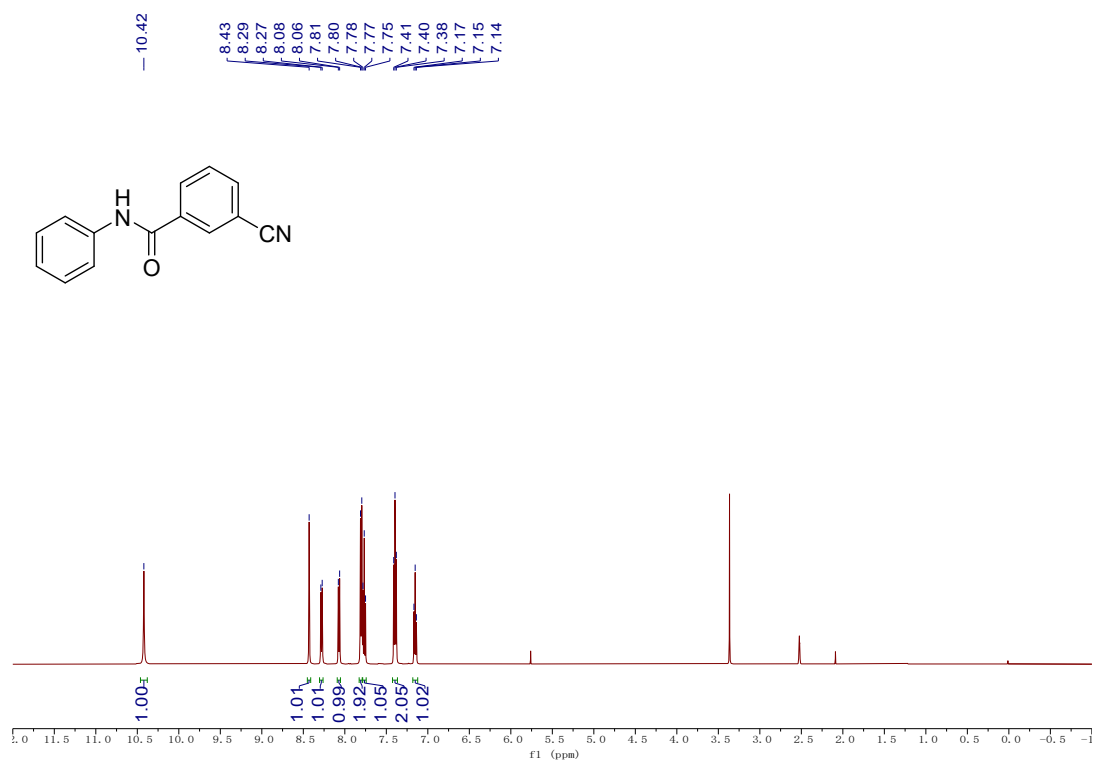
¹⁹F NMR Spectrum of **4d** (DMSO-*d*₆)



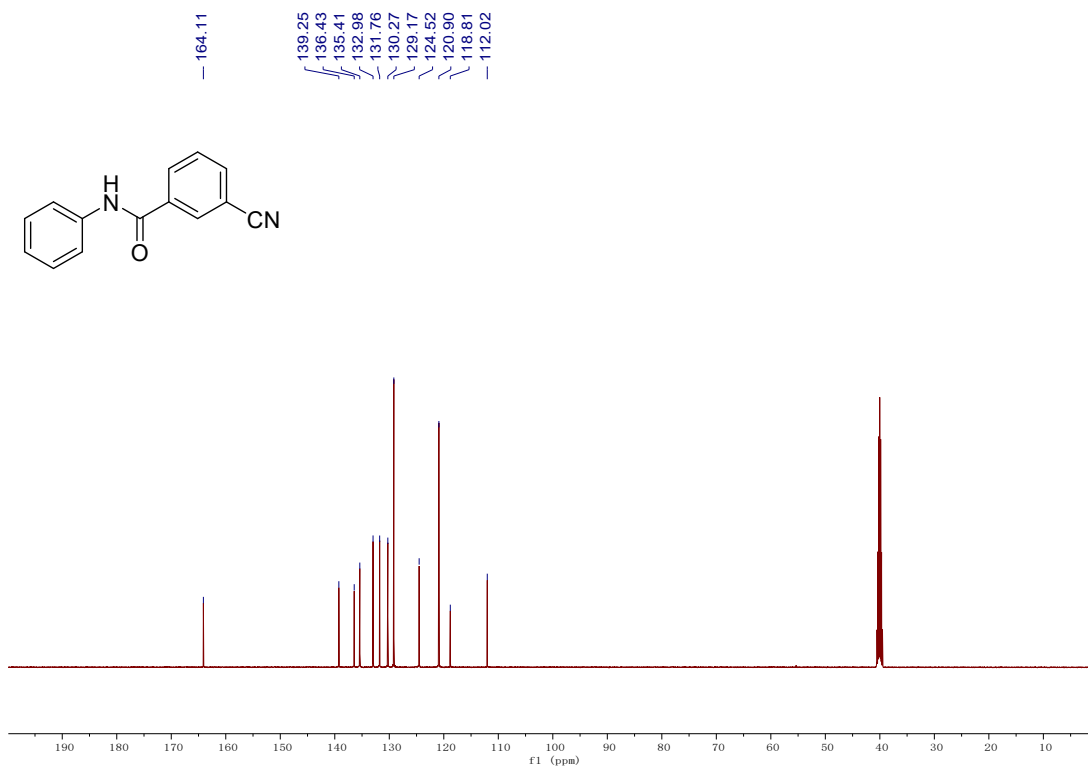
¹³C{¹H} NMR Spectrum of **4d** (DMSO-*d*₆)



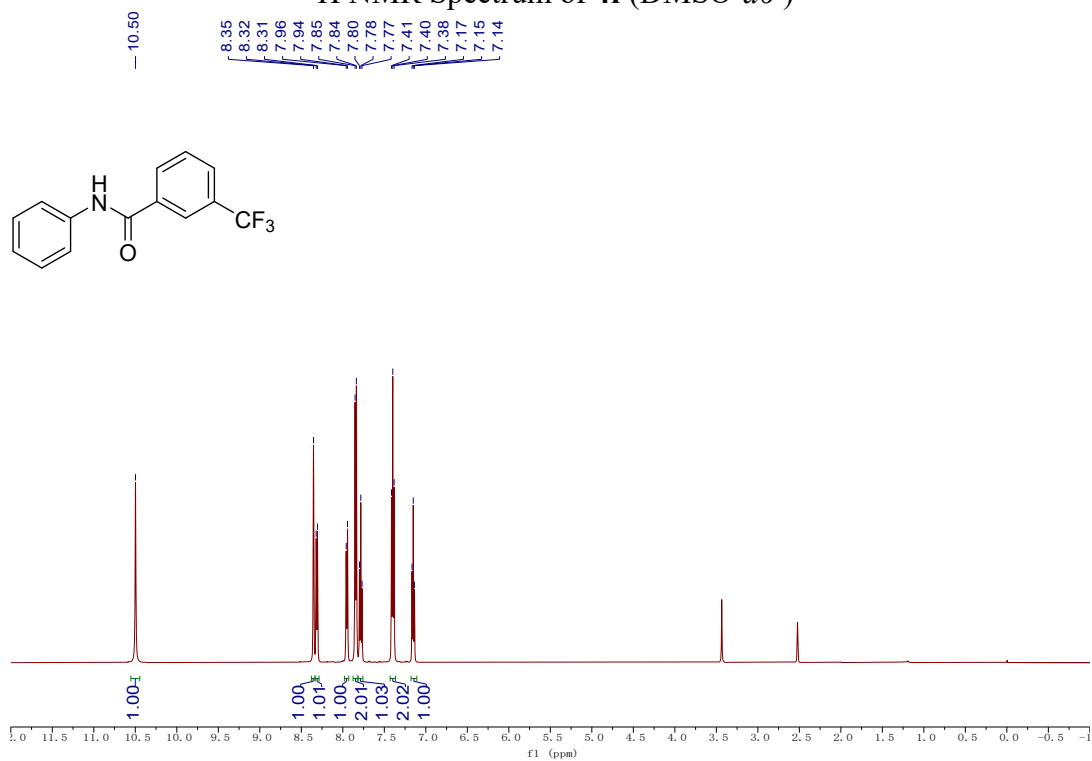
^1H NMR Spectrum of 4e (DMSO-*d*₆)



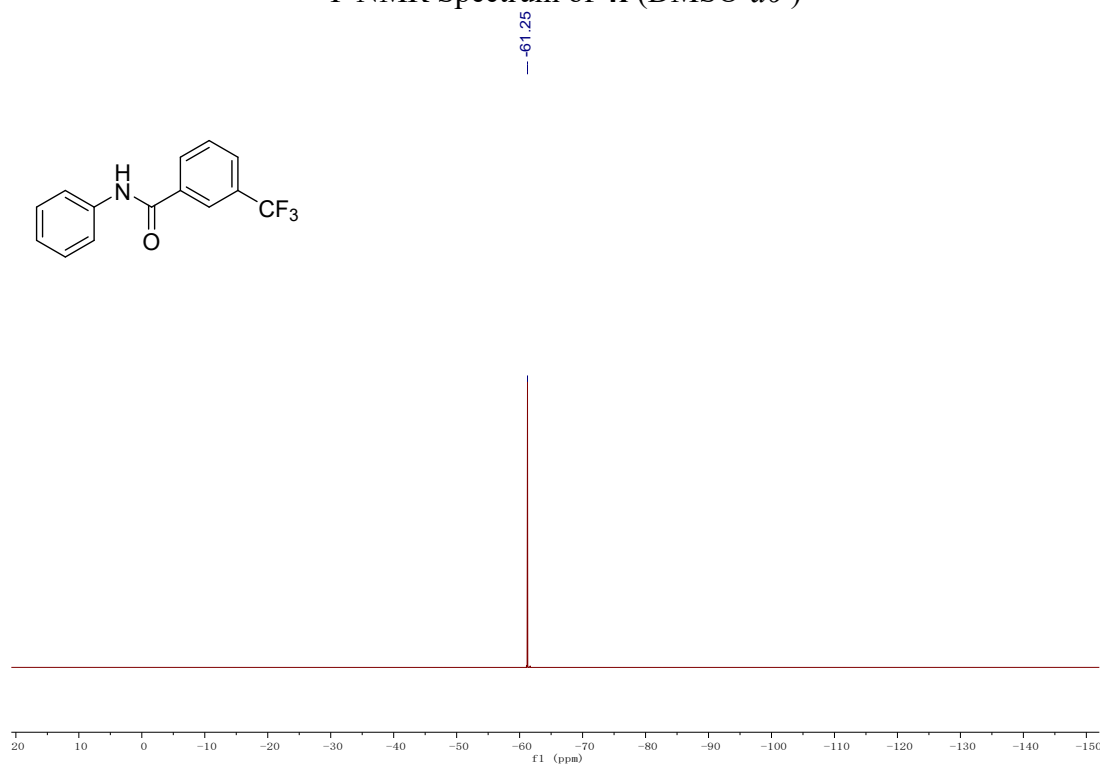
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 4e (DMSO-*d*₆)



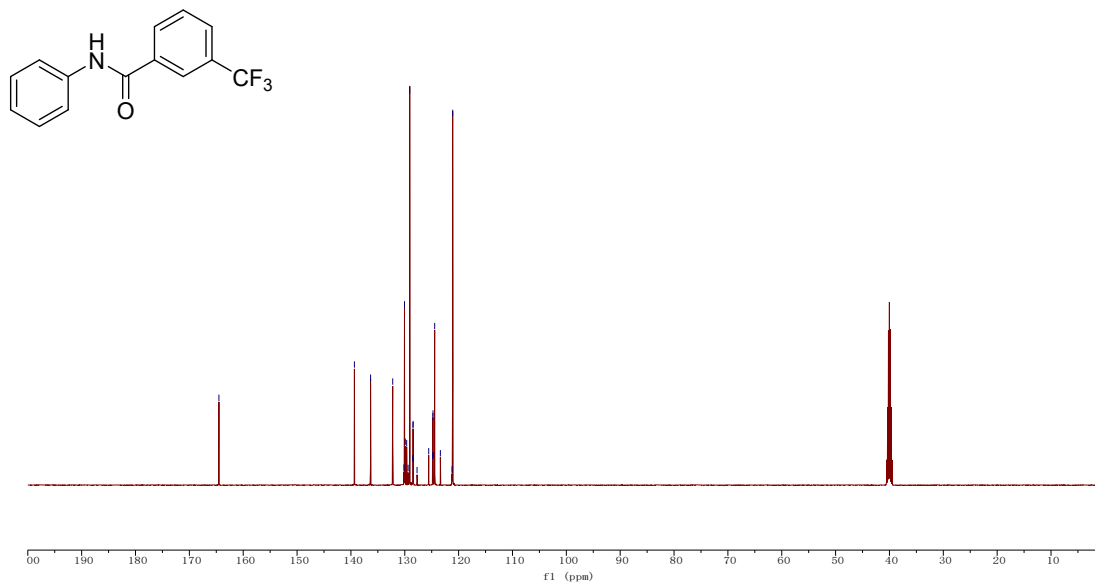
¹H NMR Spectrum of **4f** (DMSO-*d*₆)



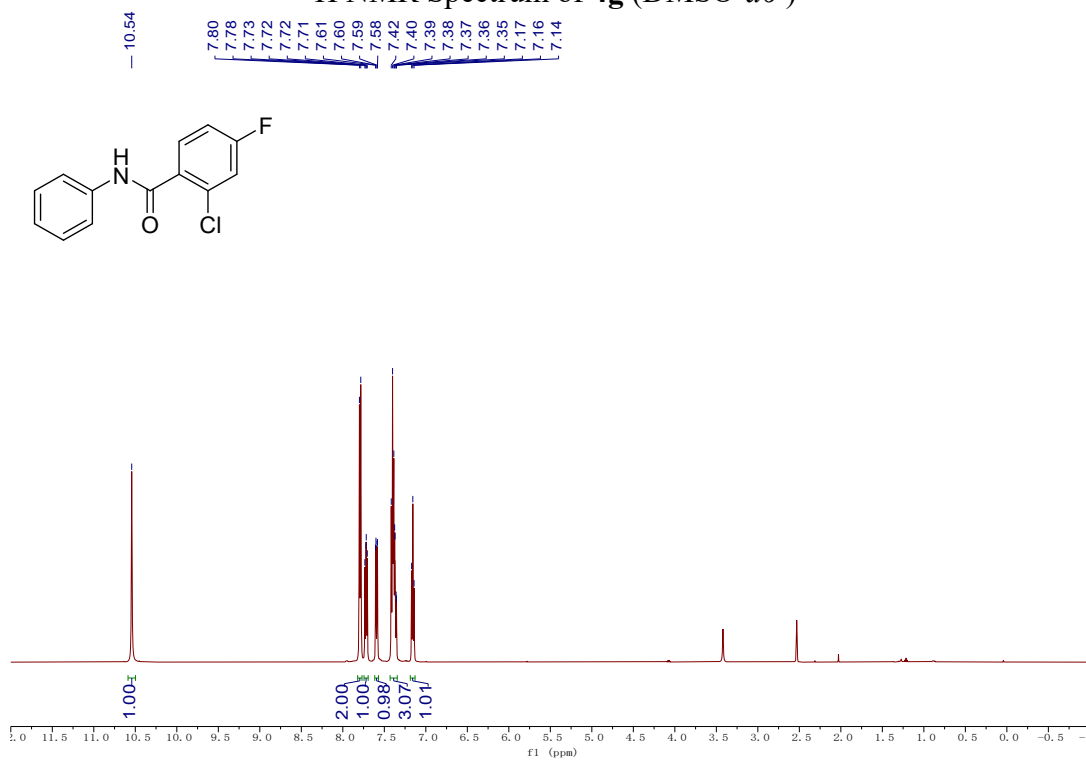
¹⁹F NMR Spectrum of **4f** (DMSO-*d*₆)



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4f** (DMSO-*d*₆)



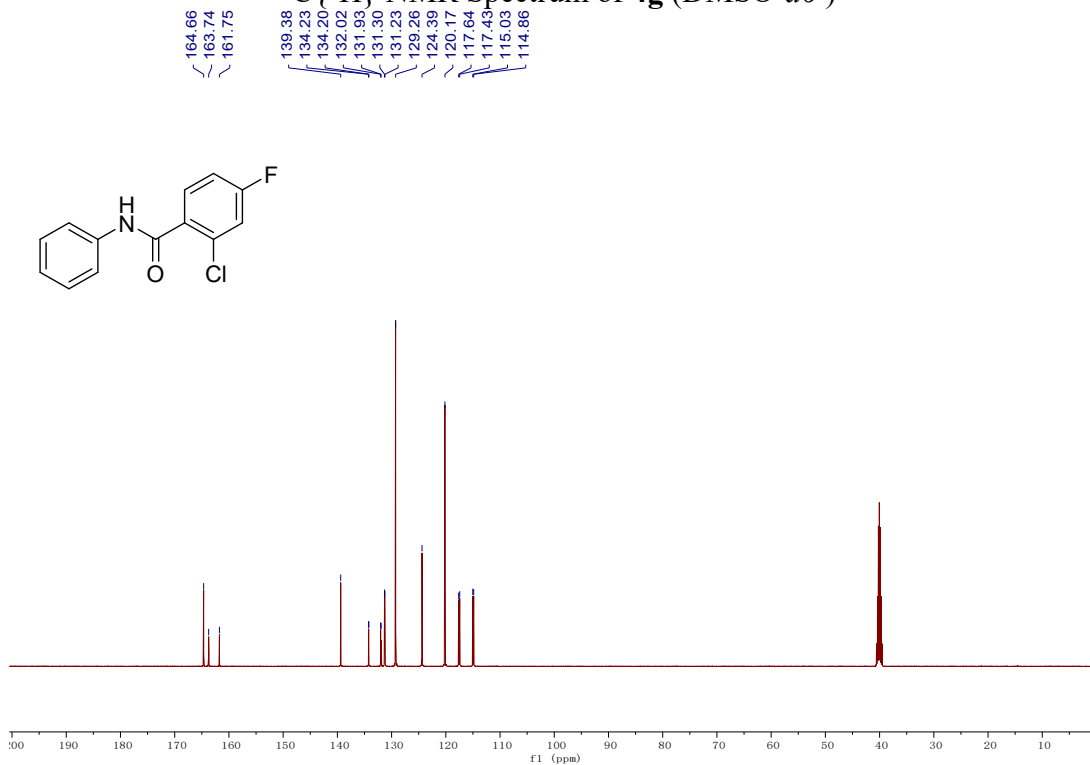
^1H NMR Spectrum of **4g** (DMSO-*d*₆)



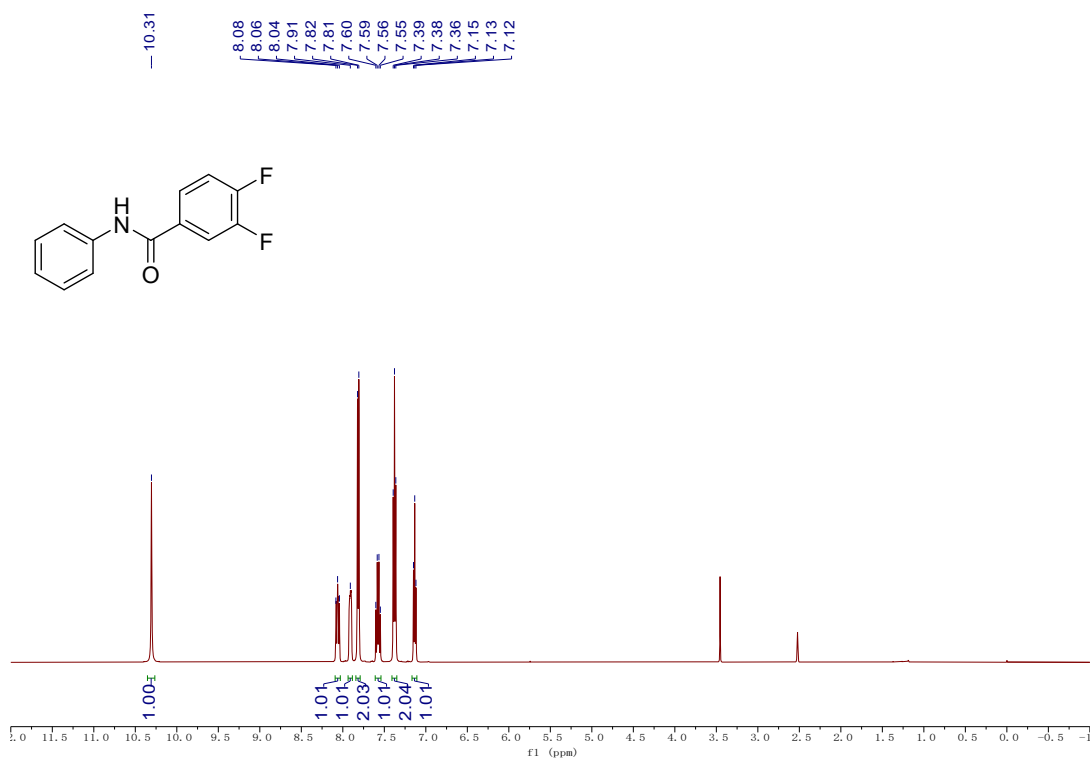
¹⁹F NMR Spectrum of **4g** (DMSO-*d*₆)



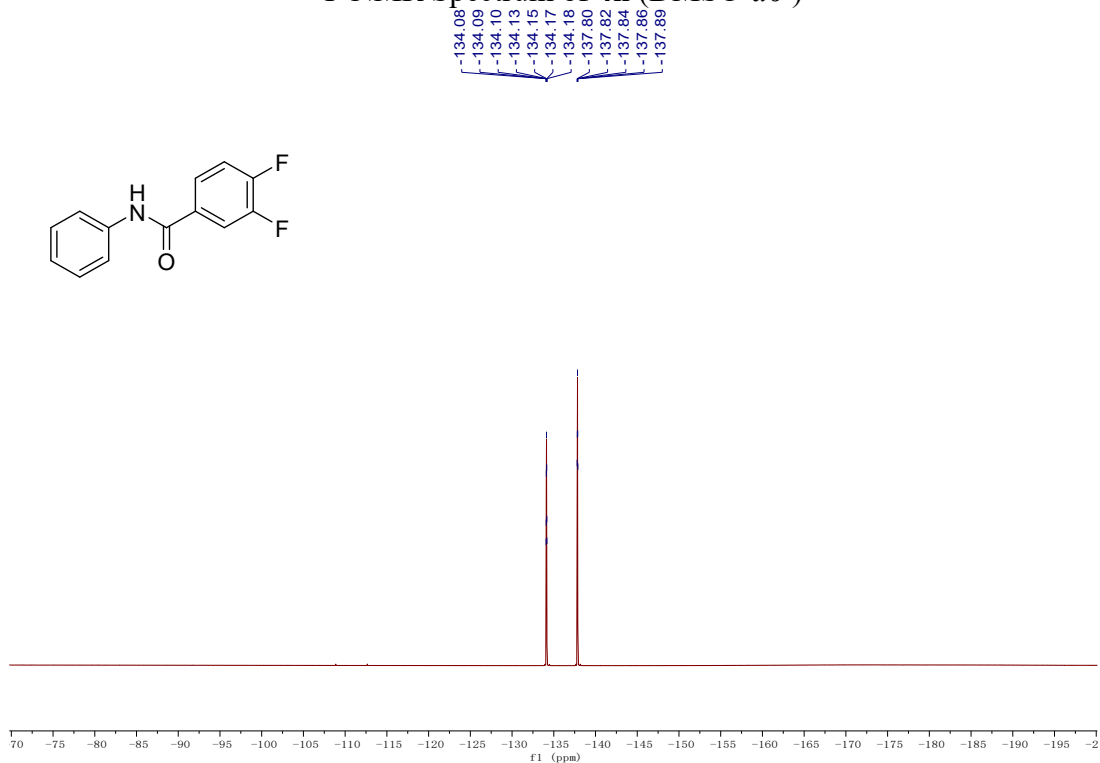
¹³C {¹H} NMR Spectrum of **4g** (DMSO-*d*₆)



^1H NMR Spectrum of **4h** (DMSO- d_6)

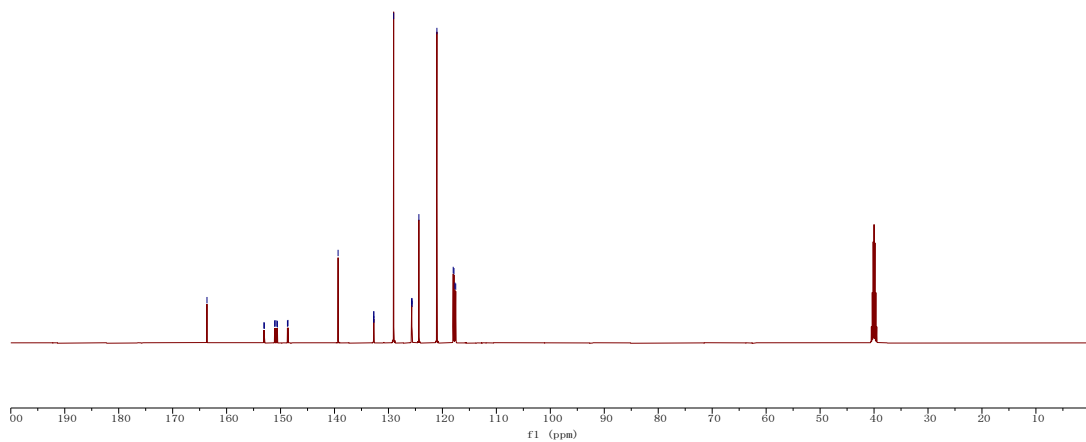
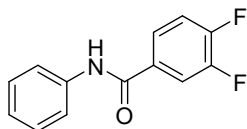


^{19}F NMR Spectrum of **4h** (DMSO- d_6)



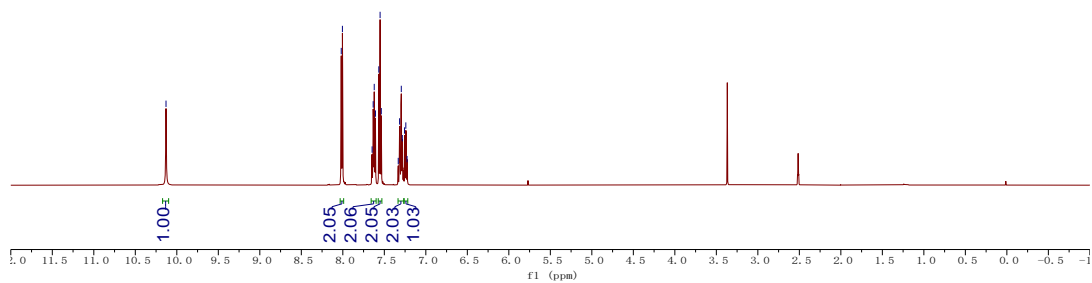
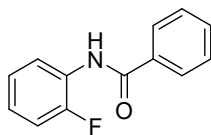
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4h** (DMSO-*d*₆)

163.64
153.10
153.00
151.10
151.00
150.69
150.59
148.73
148.62
139.34
132.76
132.73
132.72
132.69
129.04
125.71
125.68
125.65
125.62
124.36
121.02
118.00
117.86
117.68
117.53

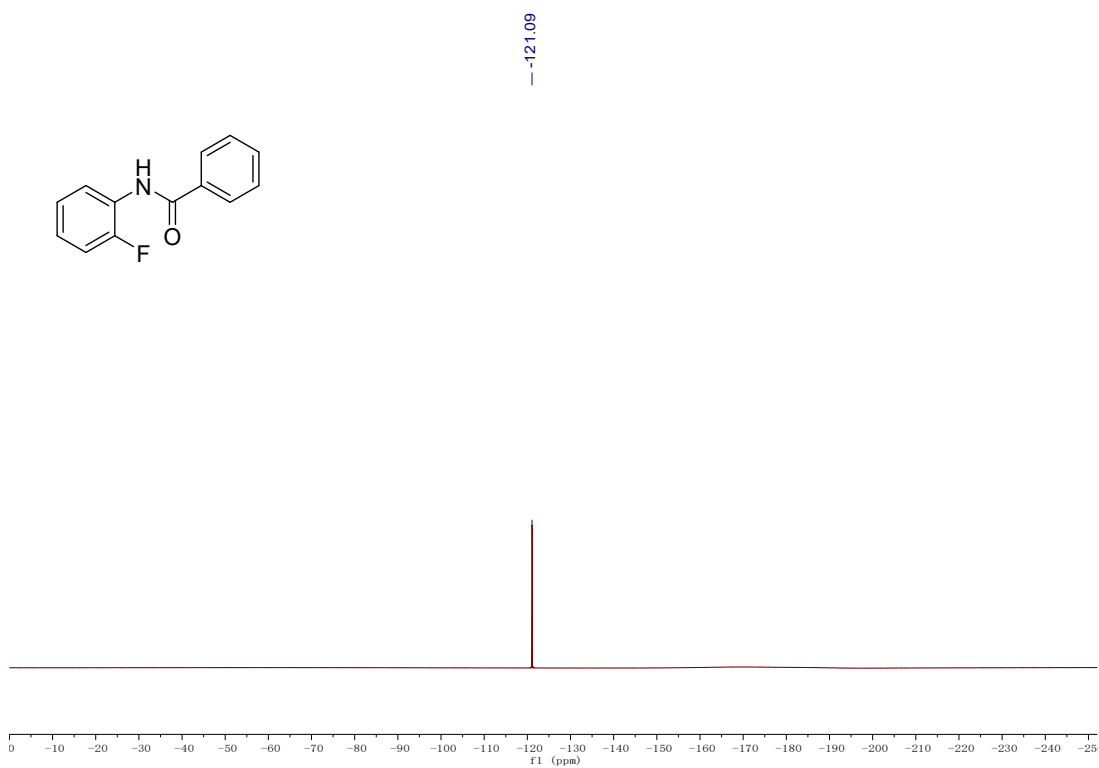


^1H NMR Spectrum of **4i** (DMSO-*d*₆)

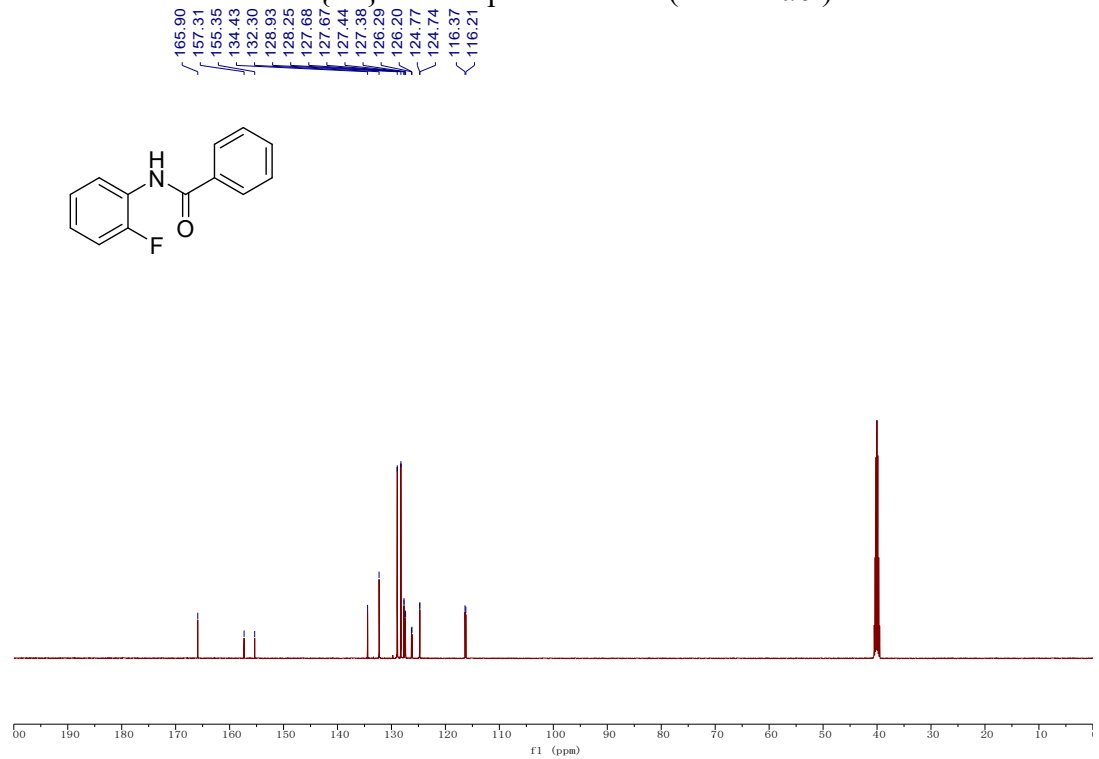
10.13
8.02
7.65
7.63
7.62
7.61
7.57
7.55
7.54
7.33
7.32
7.30
7.28
7.26
7.24
7.23



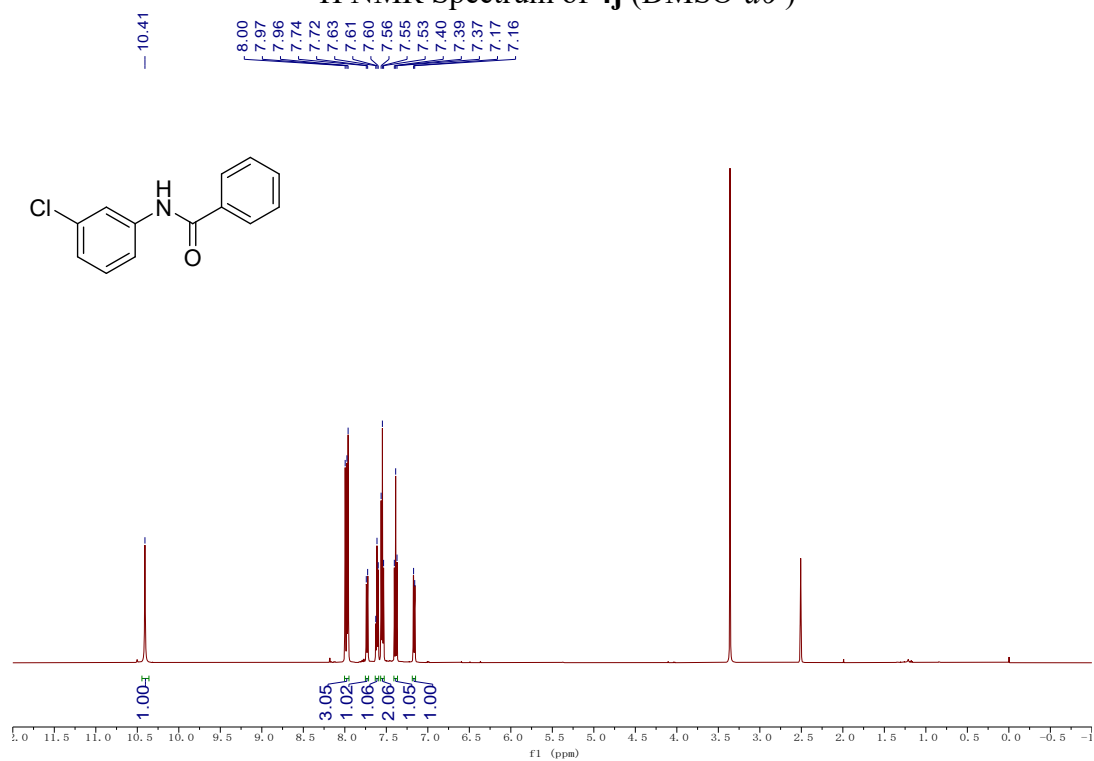
^{19}F NMR Spectrum of **4i** (DMSO- d_6)



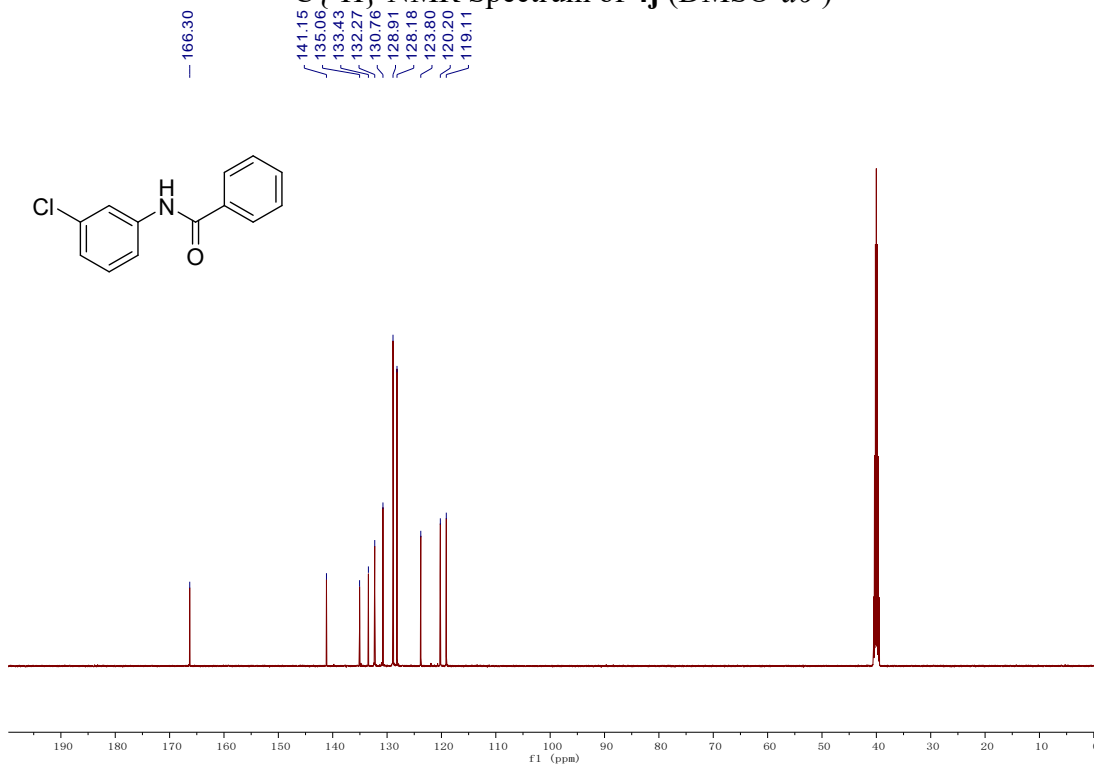
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4i** (DMSO- d_6)



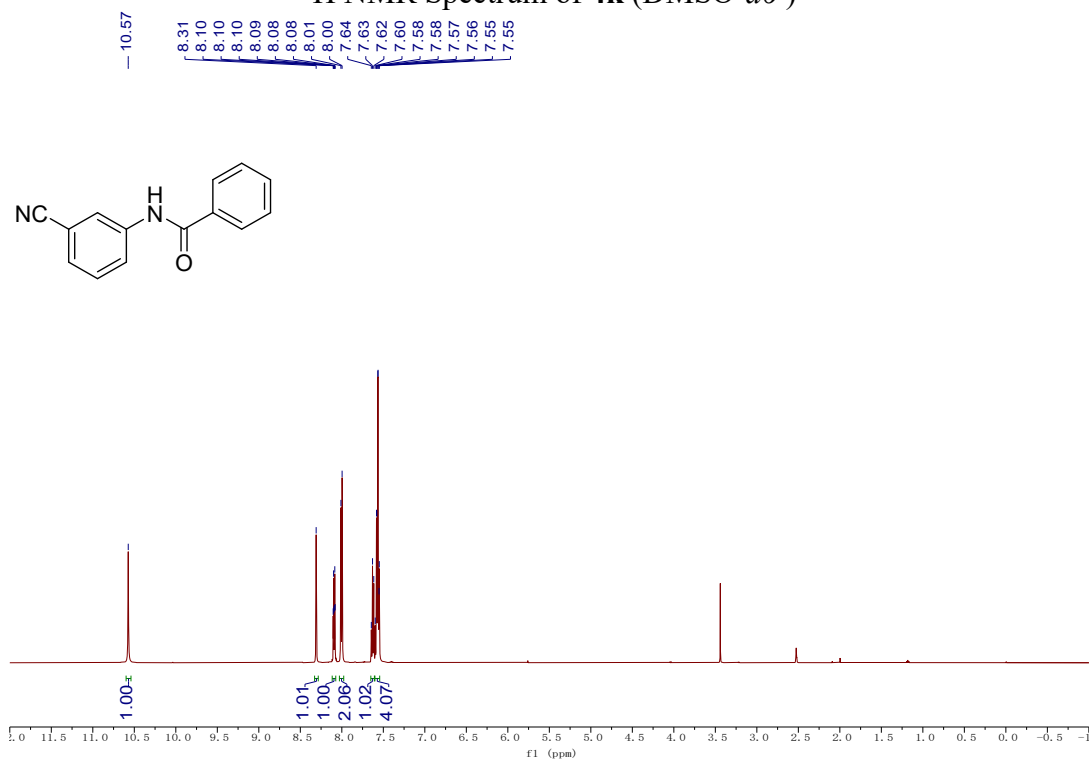
¹H NMR Spectrum of **4j** (DMSO-*d*₆)



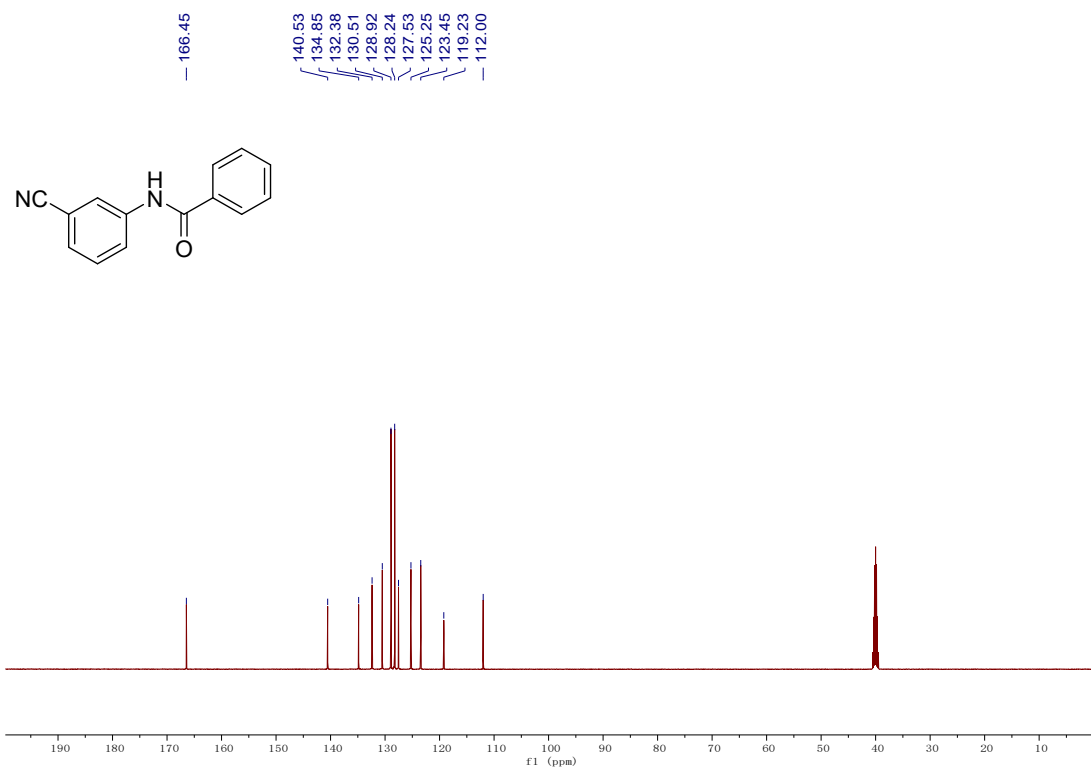
¹³C {¹H} NMR Spectrum of **4j** (DMSO-*d*₆)



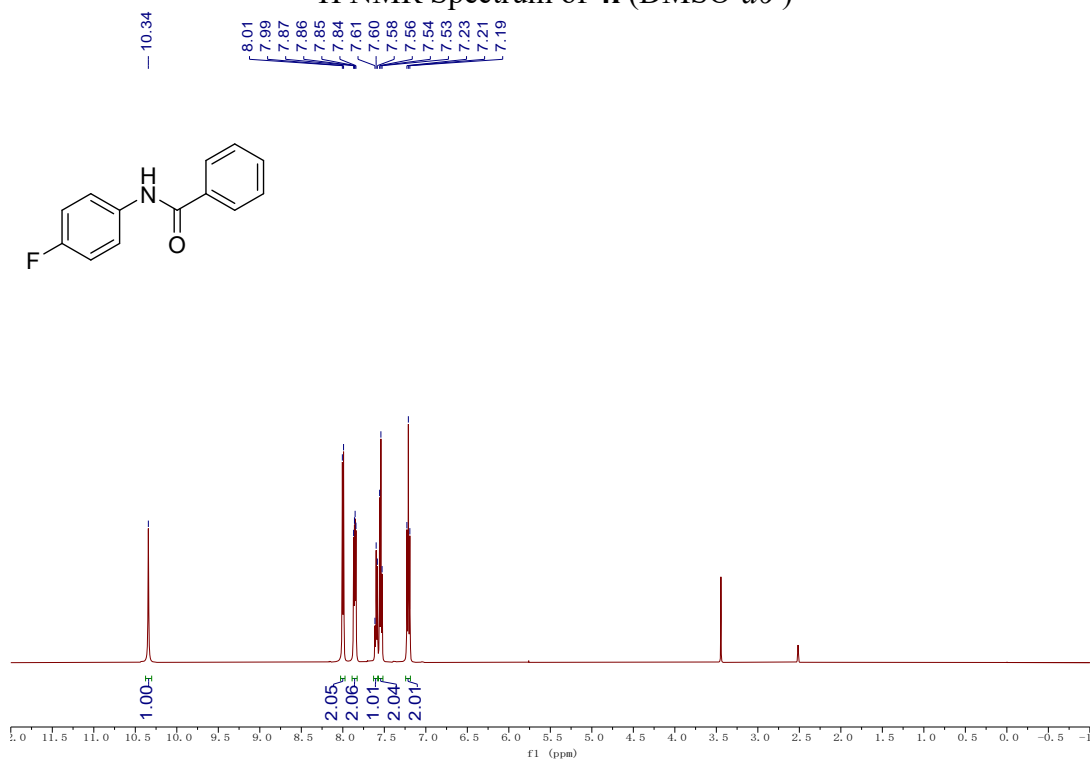
^1H NMR Spectrum of **4k** (DMSO- d_6)



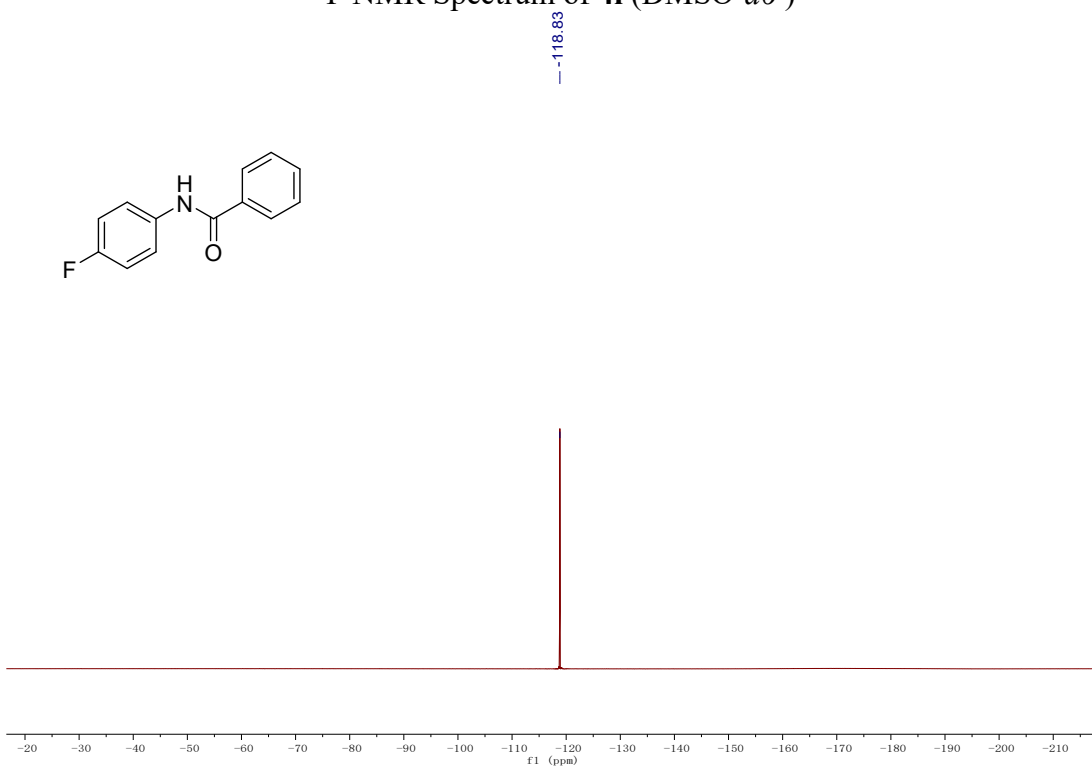
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4k** (DMSO- d_6)



¹H NMR Spectrum of **4I** (DMSO-*d*₆)

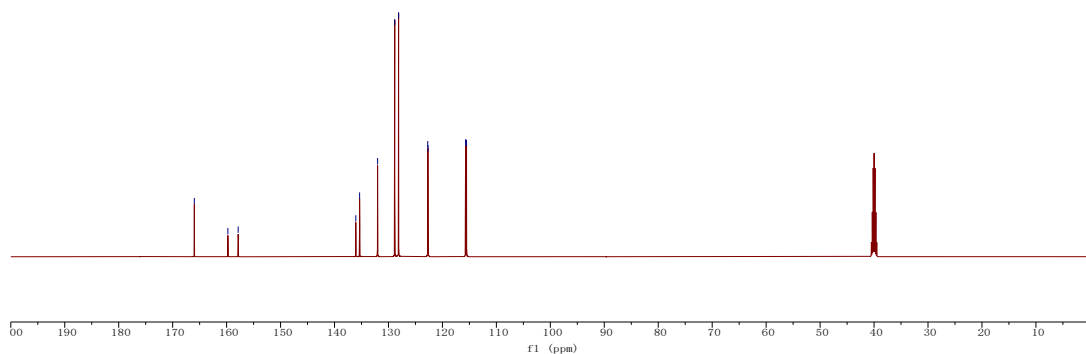
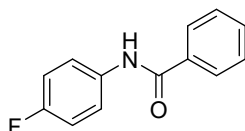


¹⁹F NMR Spectrum of **4I** (DMSO-*d*₆)



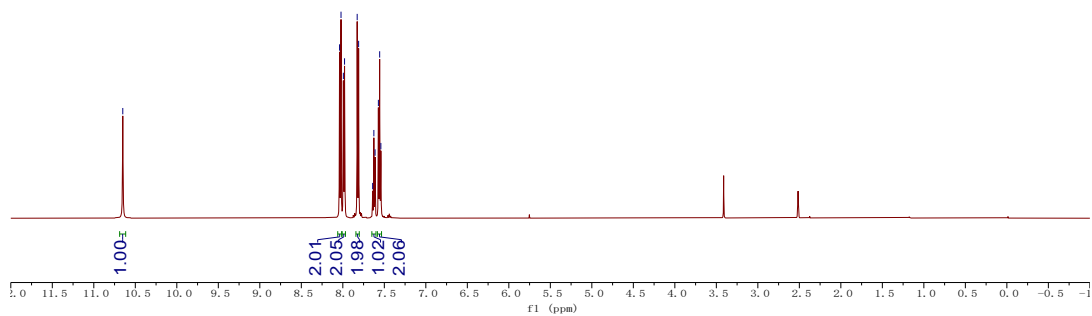
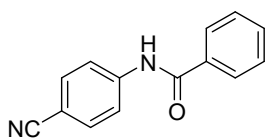
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4l** (DMSO- d_6)

165.98
159.77
157.86
136.05
135.35
132.02
128.84
128.12
122.72
122.66
115.71
115.53

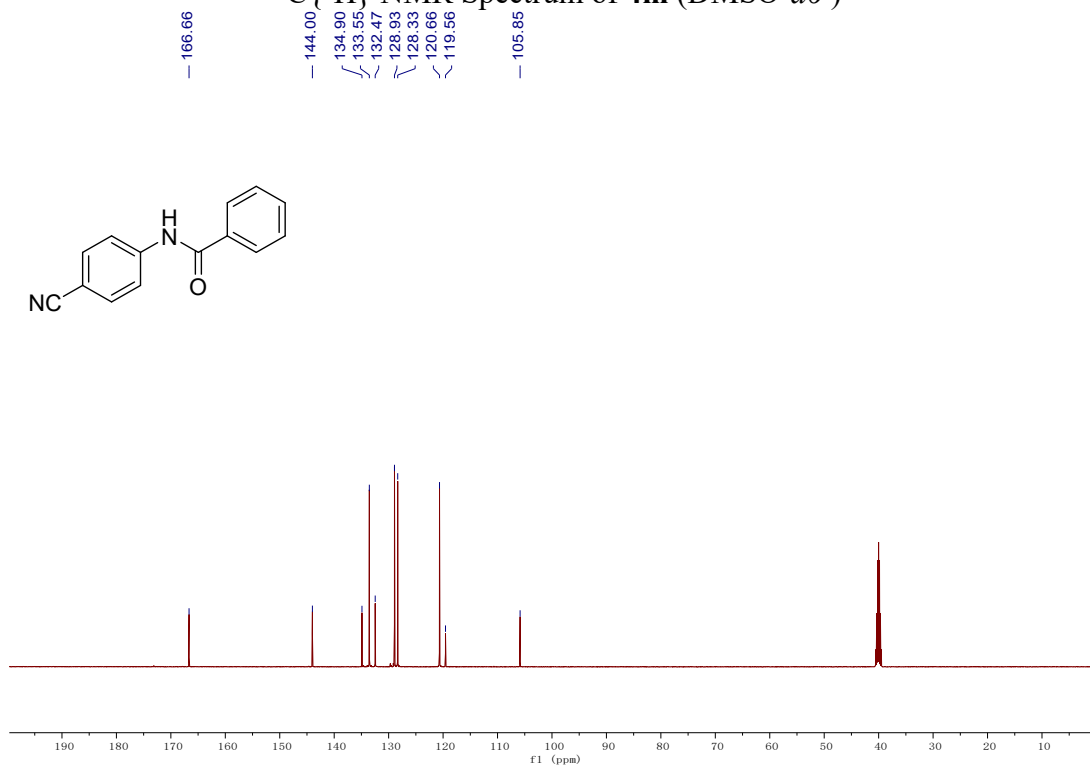


^1H NMR Spectrum of **4m** (DMSO- d_6)

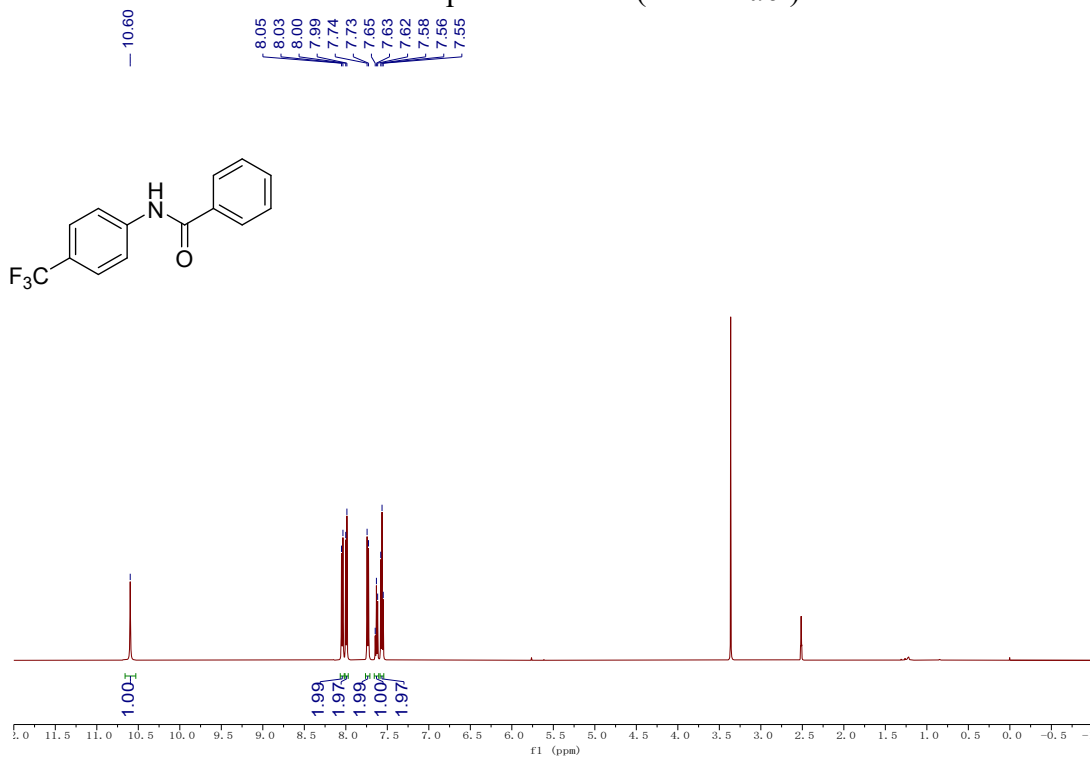
10.65
8.04
8.02
7.99
7.98
7.83
7.81
7.64
7.63
7.61
7.57
7.56
7.54



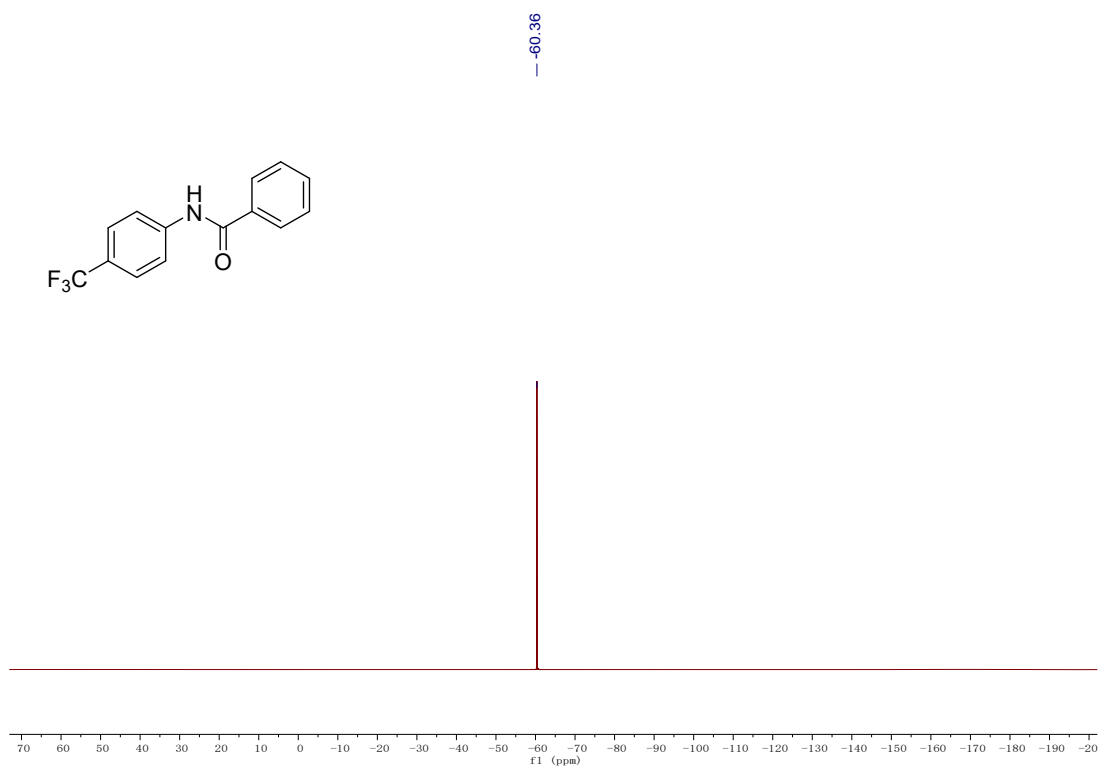
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4m** (DMSO-*d*₆)



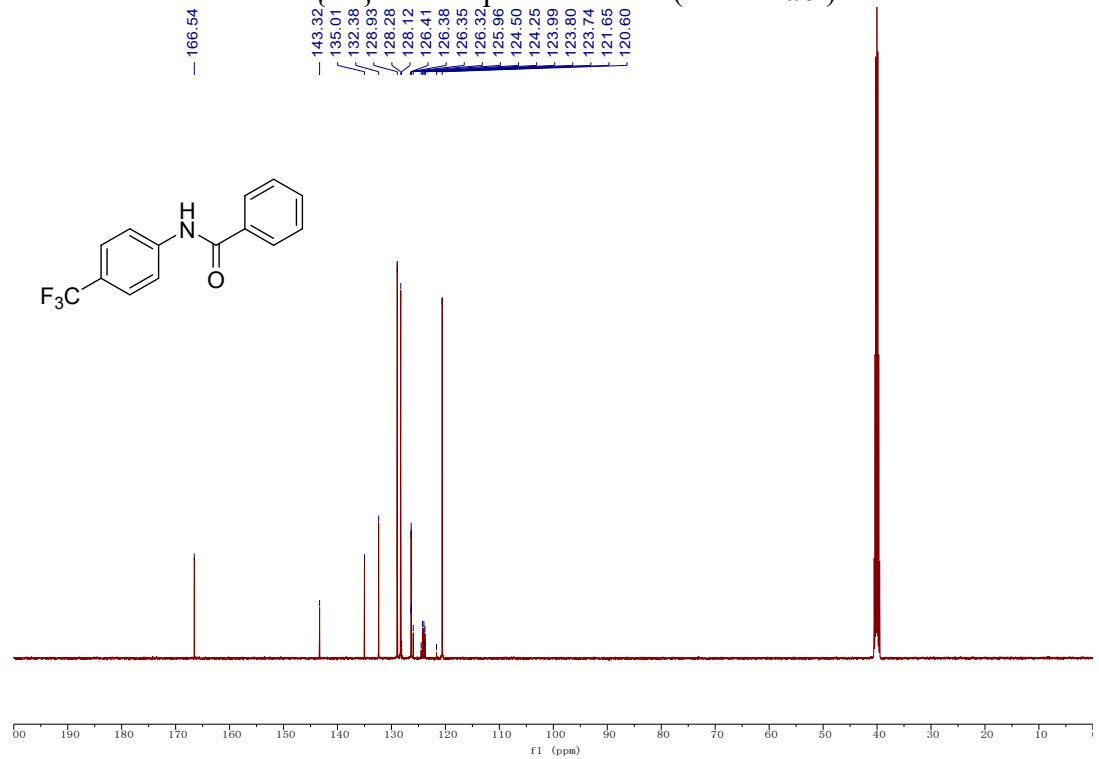
^1H NMR Spectrum of **4n** (DMSO-*d*₆)



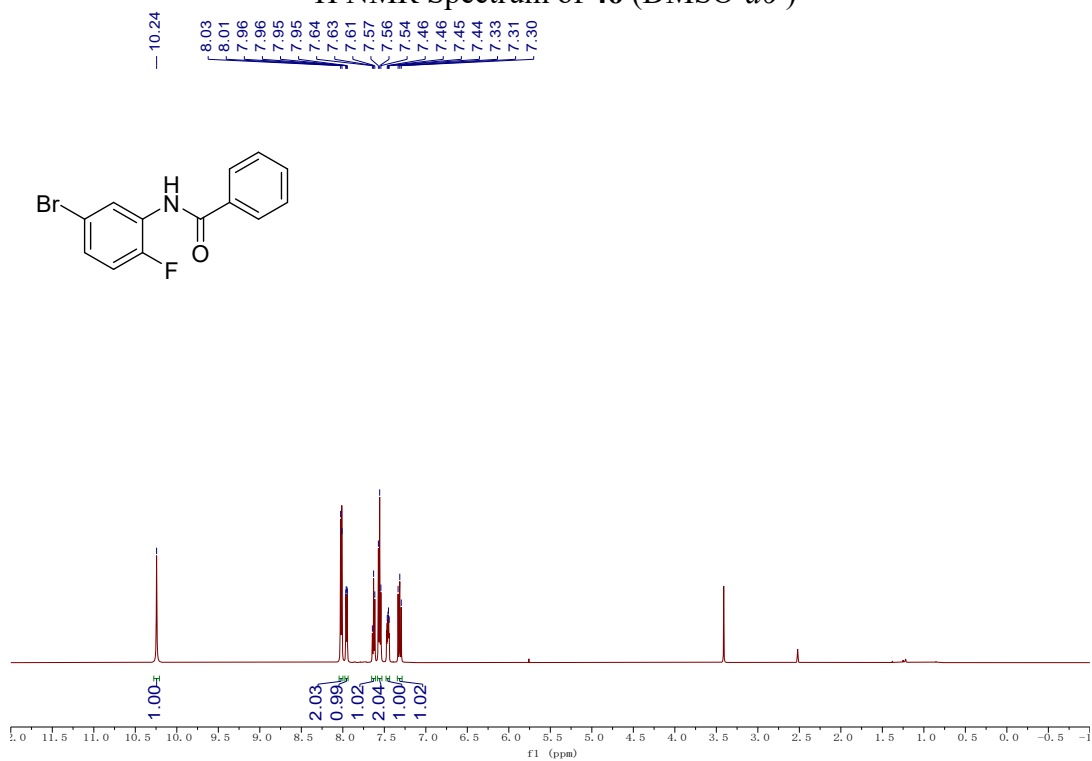
¹⁹F NMR Spectrum of **4n** (DMSO-*d*₆)



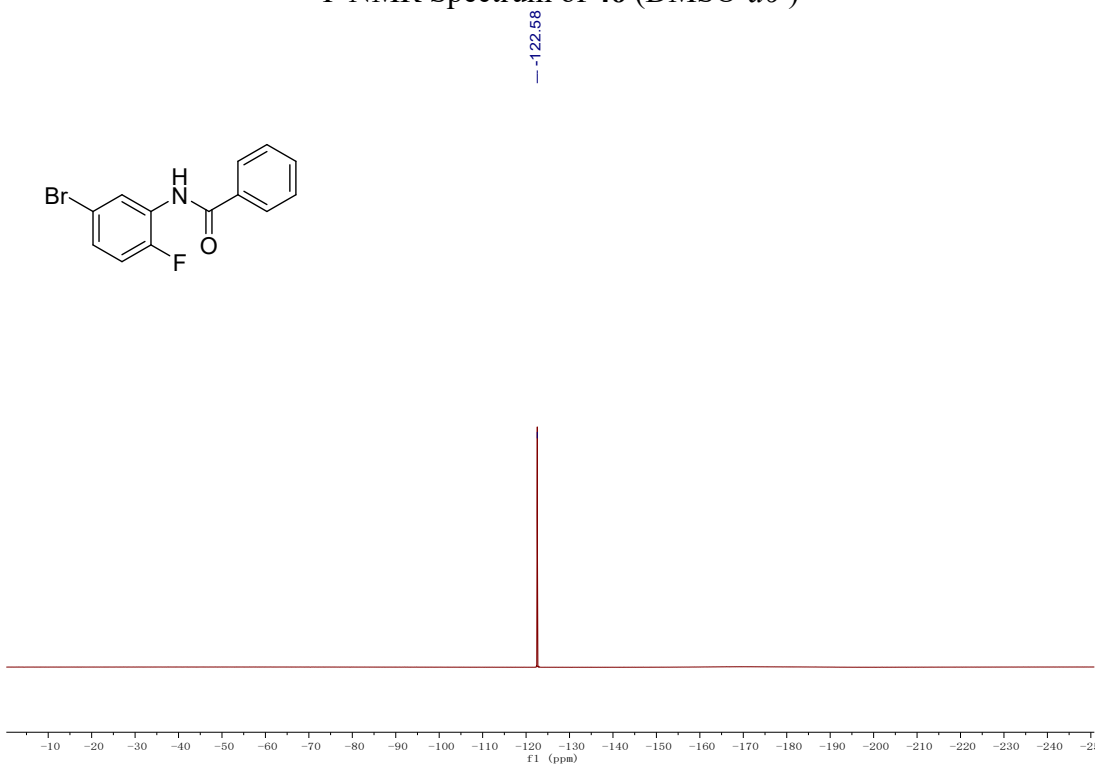
¹³C {¹H} NMR Spectrum of **4n** (DMSO-*d*₆)



^1H NMR Spectrum of **4o** (DMSO- d_6)

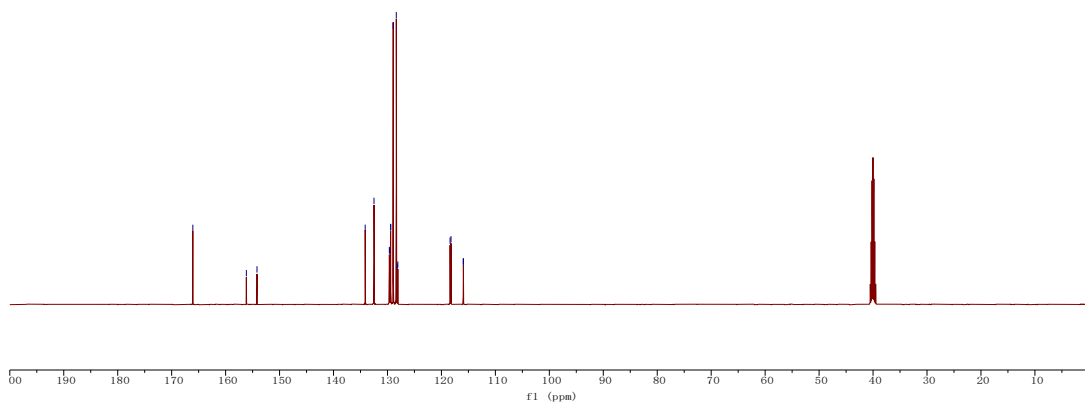
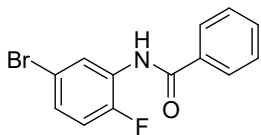


^{19}F NMR Spectrum of **4o** (DMSO- d_6)



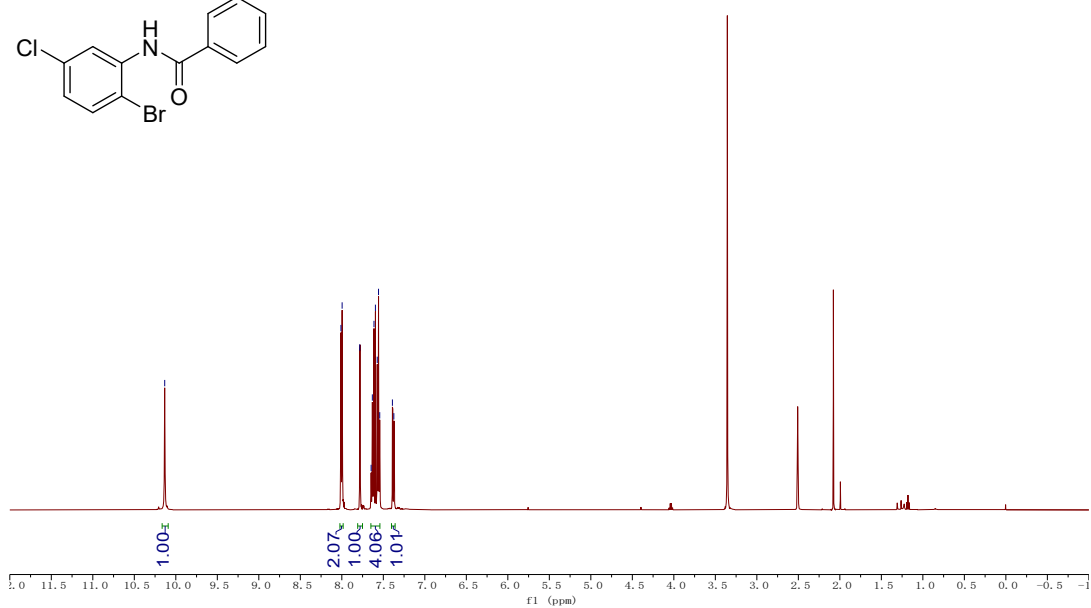
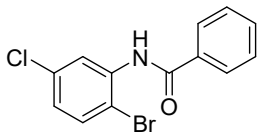
¹³C{¹H} NMR Spectrum of **4o** (DMSO-*d*₆)

166.07
156.15
154.18
134.13
132.50
129.65
129.59
129.41
129.40
128.94
128.36
128.18
128.08
118.40
118.23
115.96
115.93

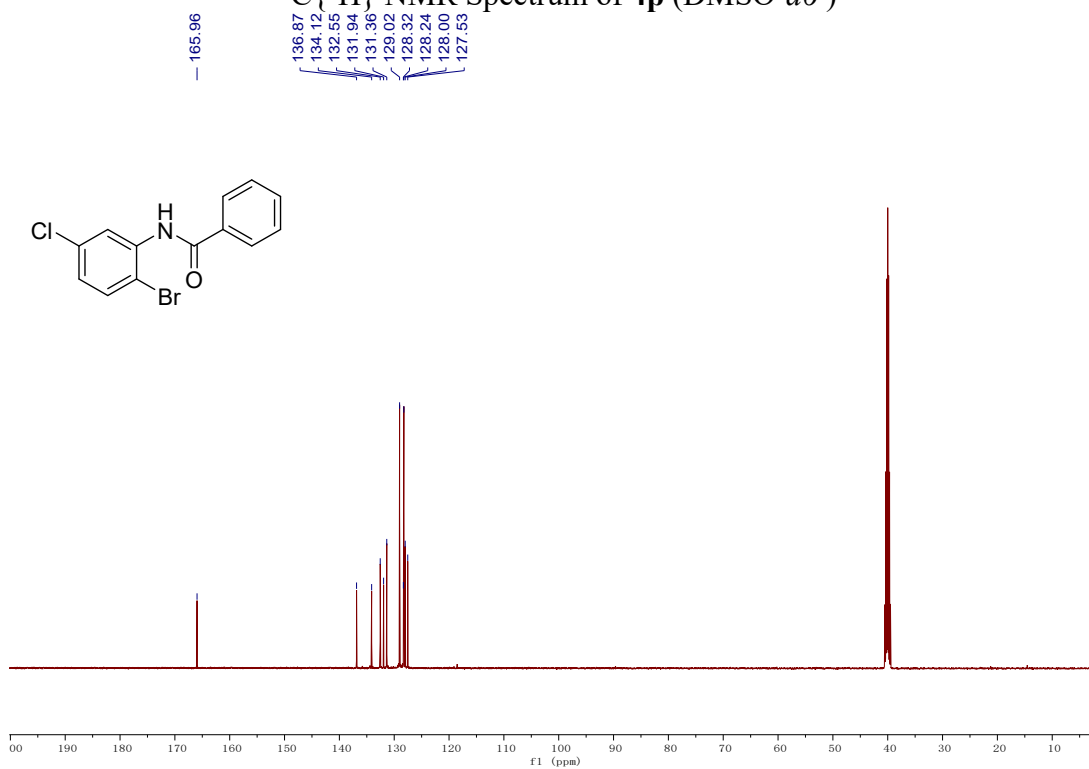


¹H NMR Spectrum of **4p** (DMSO-*d*₆)

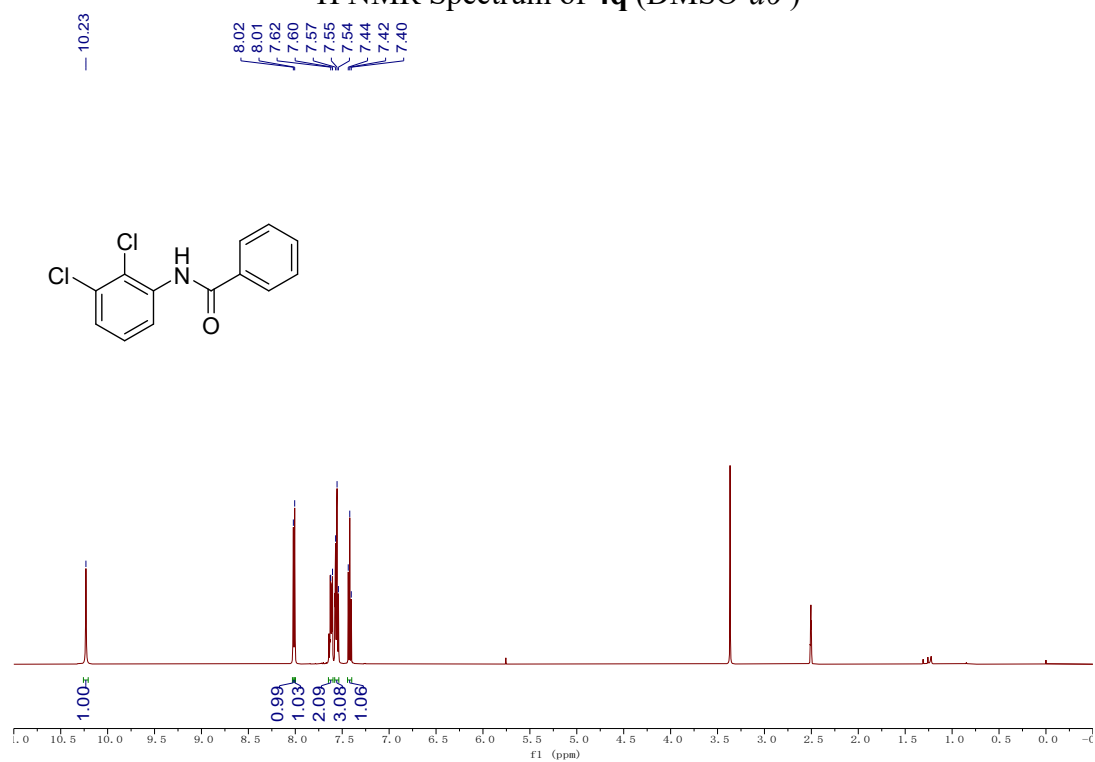
10.13
8.01
7.78
7.65
7.63
7.61
7.60
7.57
7.56
7.54
7.39
7.37



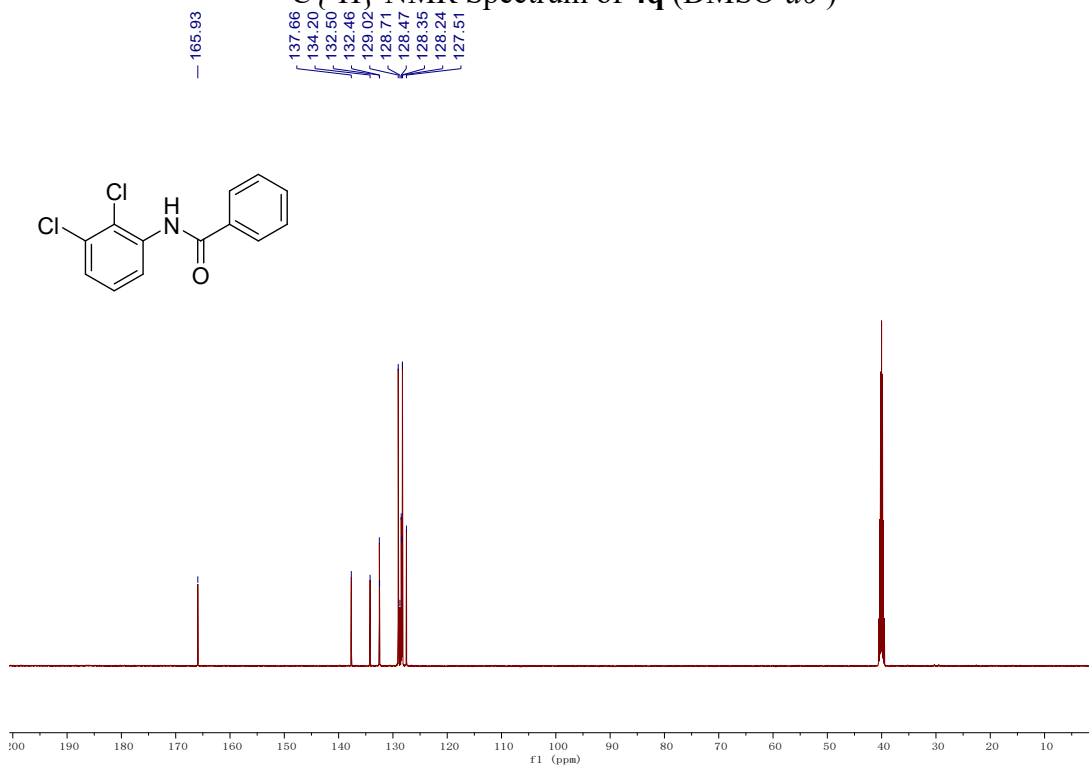
$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4p** (DMSO- d_6)



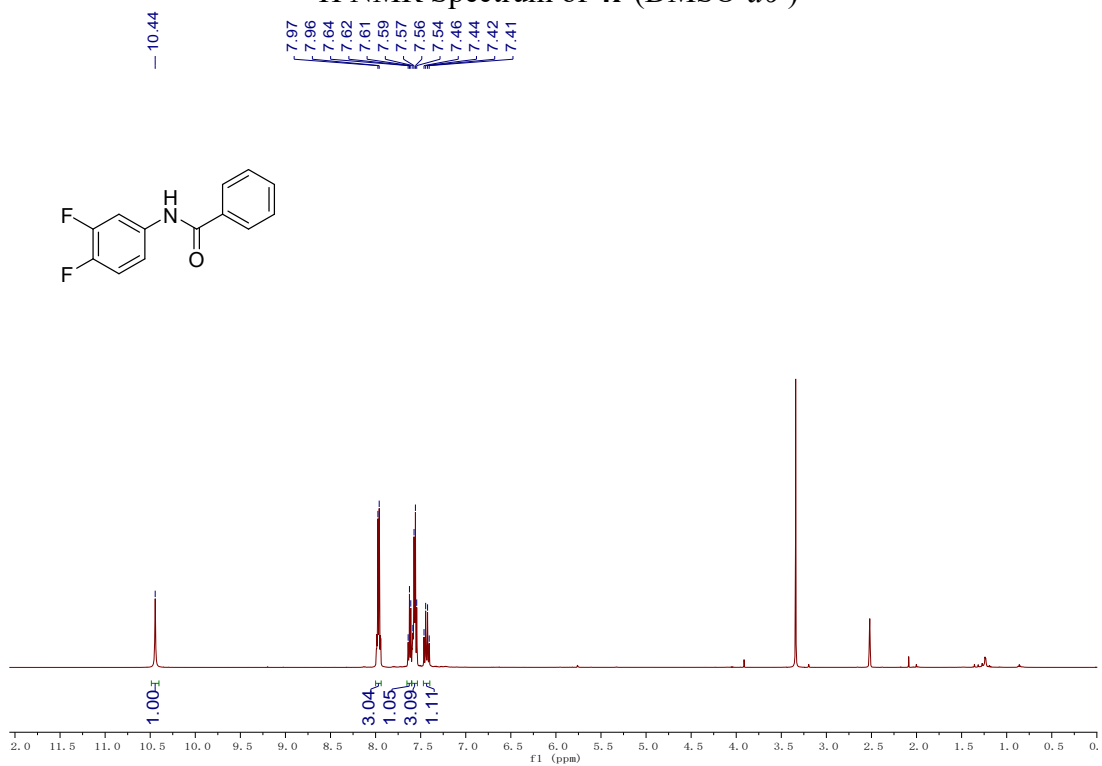
^1H NMR Spectrum of **4q** (DMSO- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of **4q** (DMSO-*d*₆)

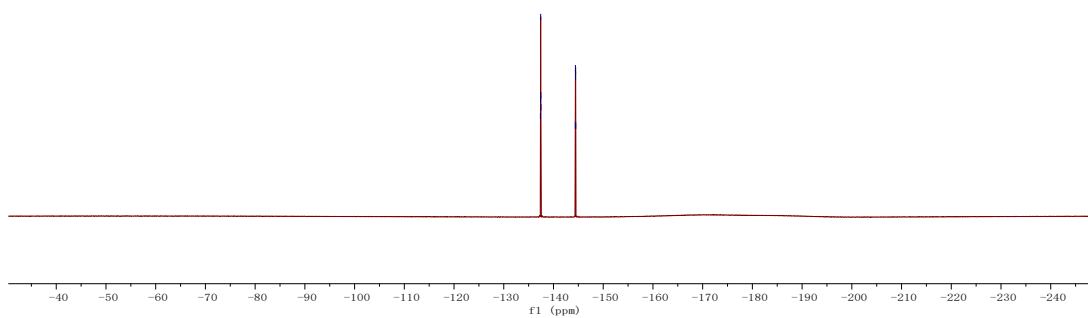
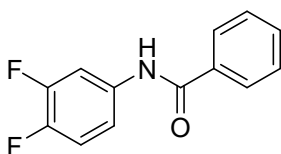


^1H NMR Spectrum of **4r** (DMSO-*d*₆)



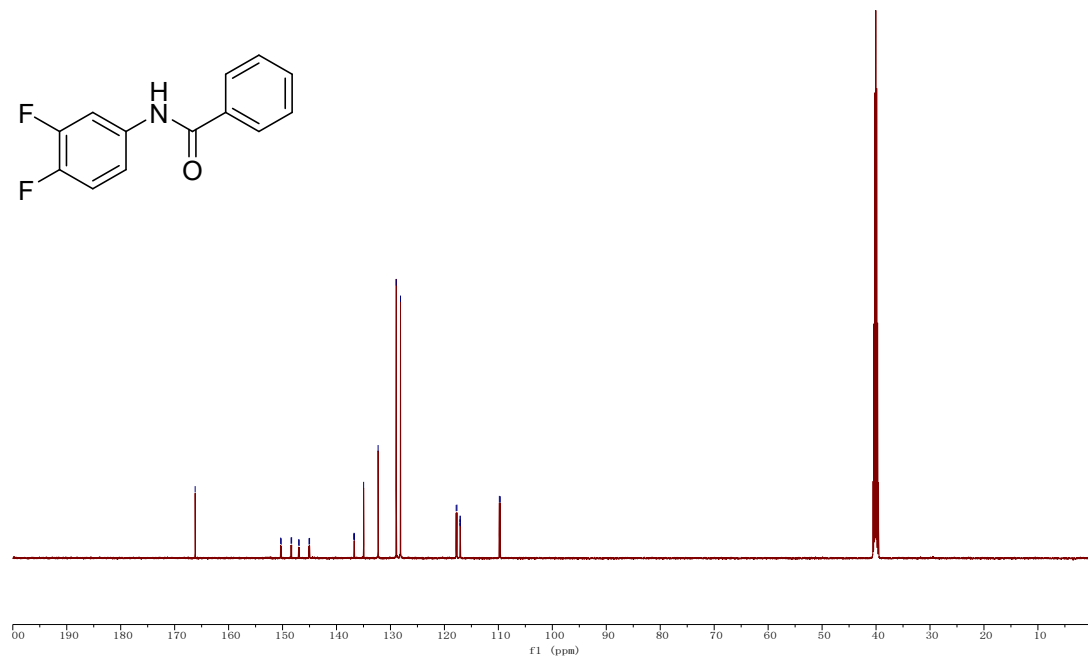
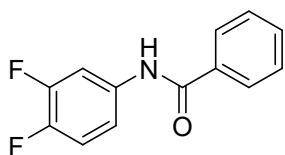
¹⁹F NMR Spectrum of **4r** (DMSO-*d*₆)

-137.38
-137.40
-137.43
-137.45
-137.47
-144.40
-144.41
-144.44
-144.46
-144.48

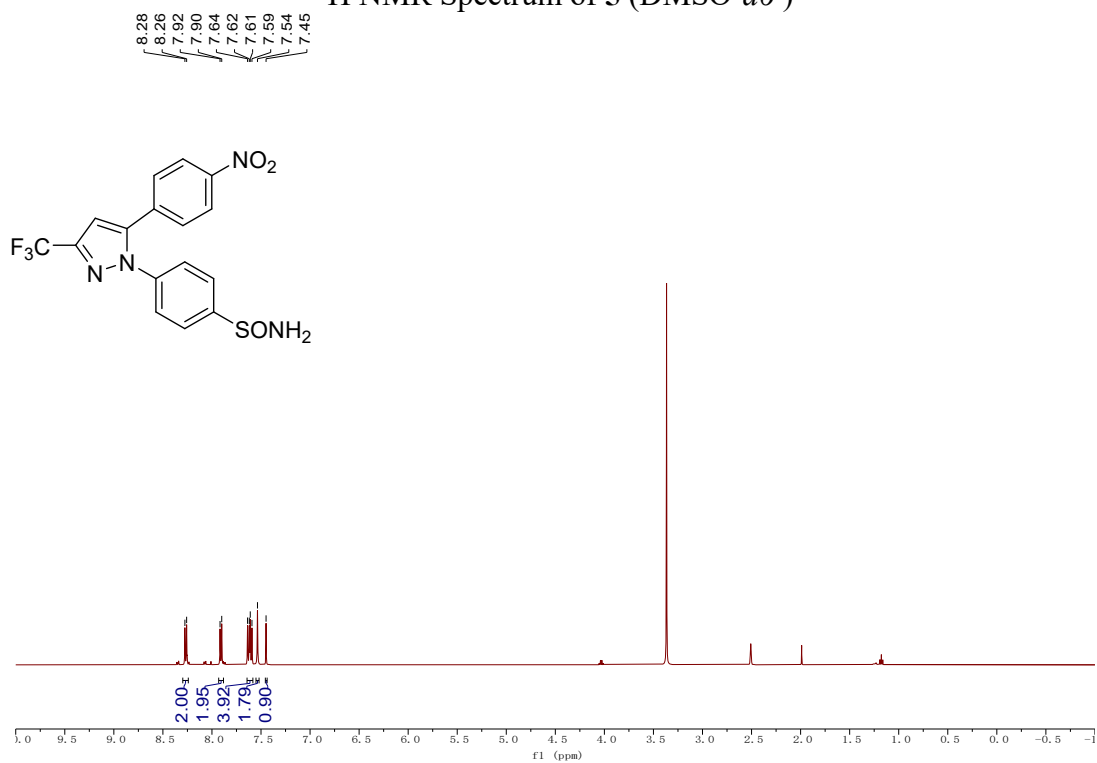


¹³C {¹H} NMR Spectrum of **4r** (DMSO-*d*₆)

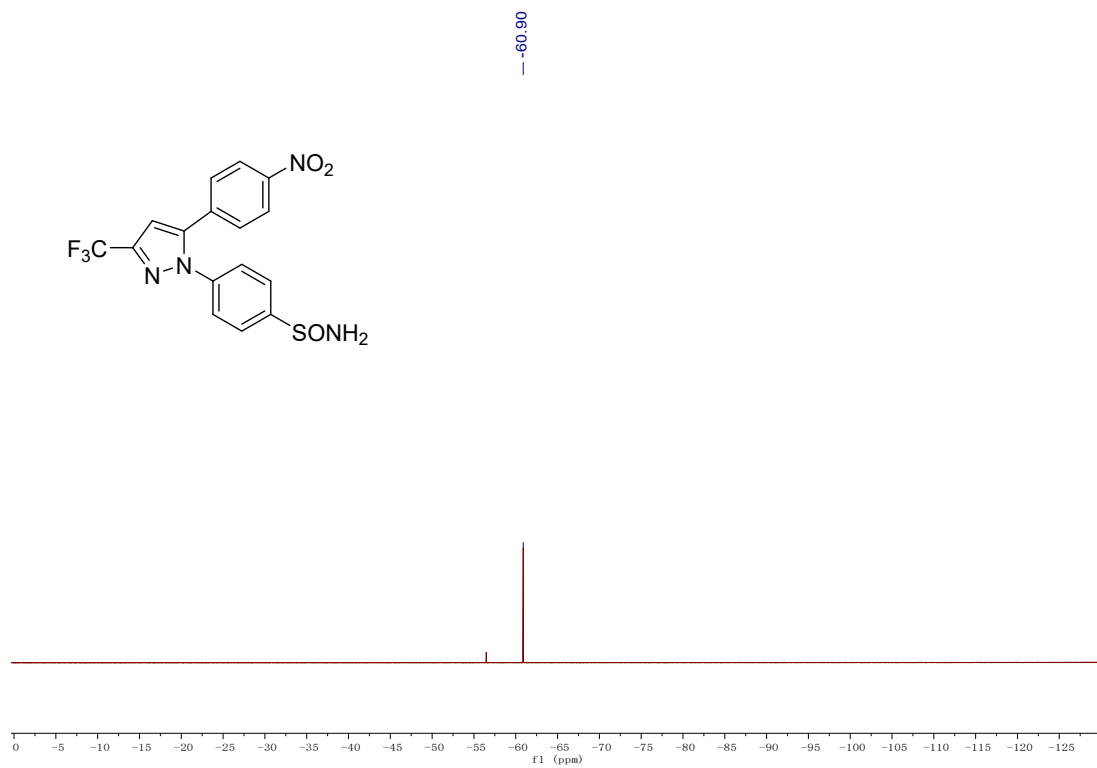
166.20
150.36
150.25
148.42
148.32
147.02
146.82
145.10
144.99
136.78
136.75
136.70
136.68
134.98
132.29
128.83
128.14
117.82
117.68
117.11
117.09
117.07
117.04
109.82
109.65



¹H NMR Spectrum of **5** (DMSO-*d*₆)

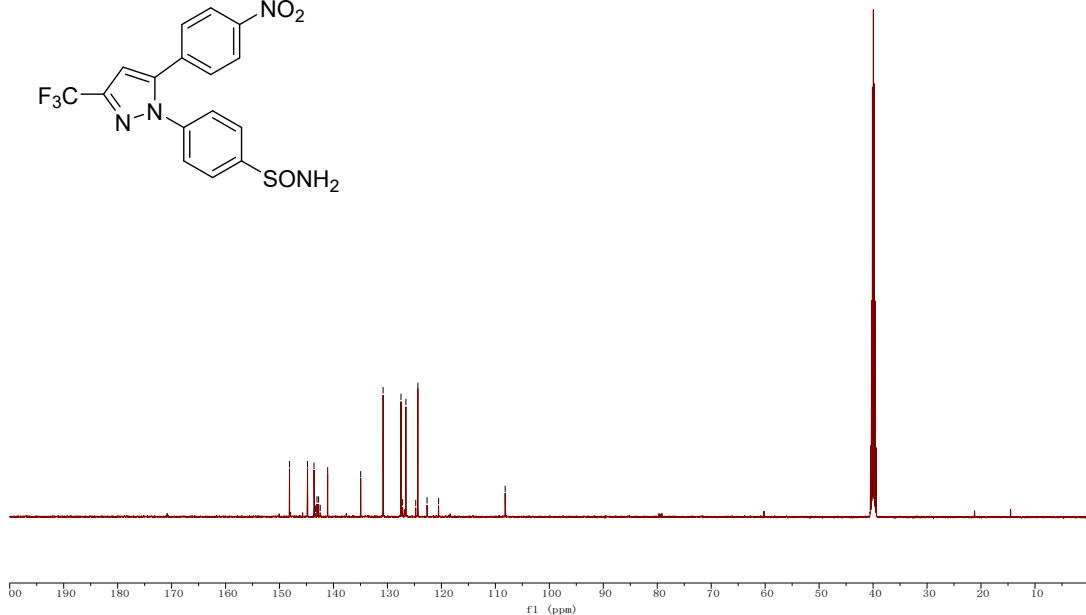
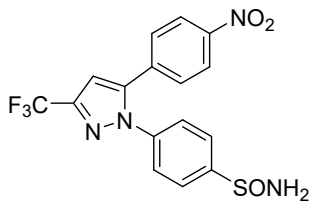


¹⁹F NMR Spectrum of **5** (DMSO-*d*₆)



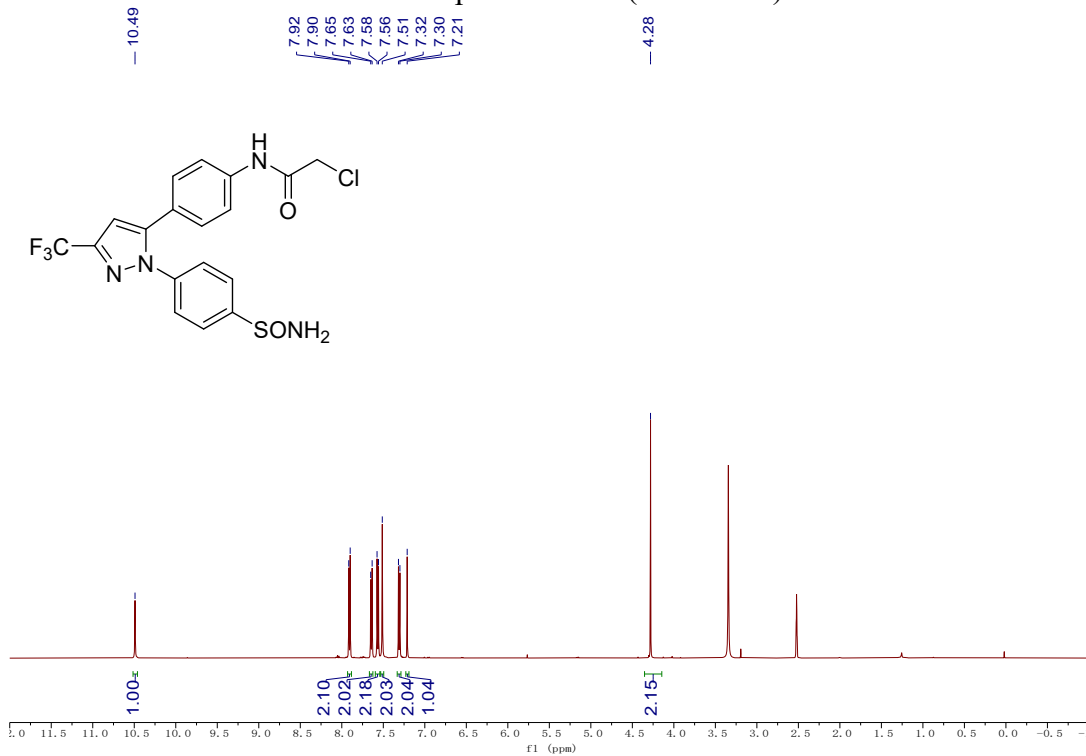
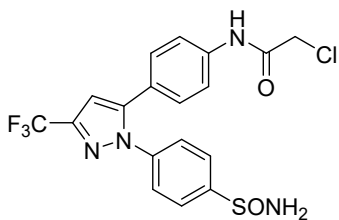
¹³C{¹H} NMR Spectrum of **5** (DMSO-*d*₆)

148.15
144.81
143.61
143.36
143.06
142.75
142.45
141.08
134.96
130.81
127.49
127.18
126.58
124.76
124.36
122.66
120.52
-108.18

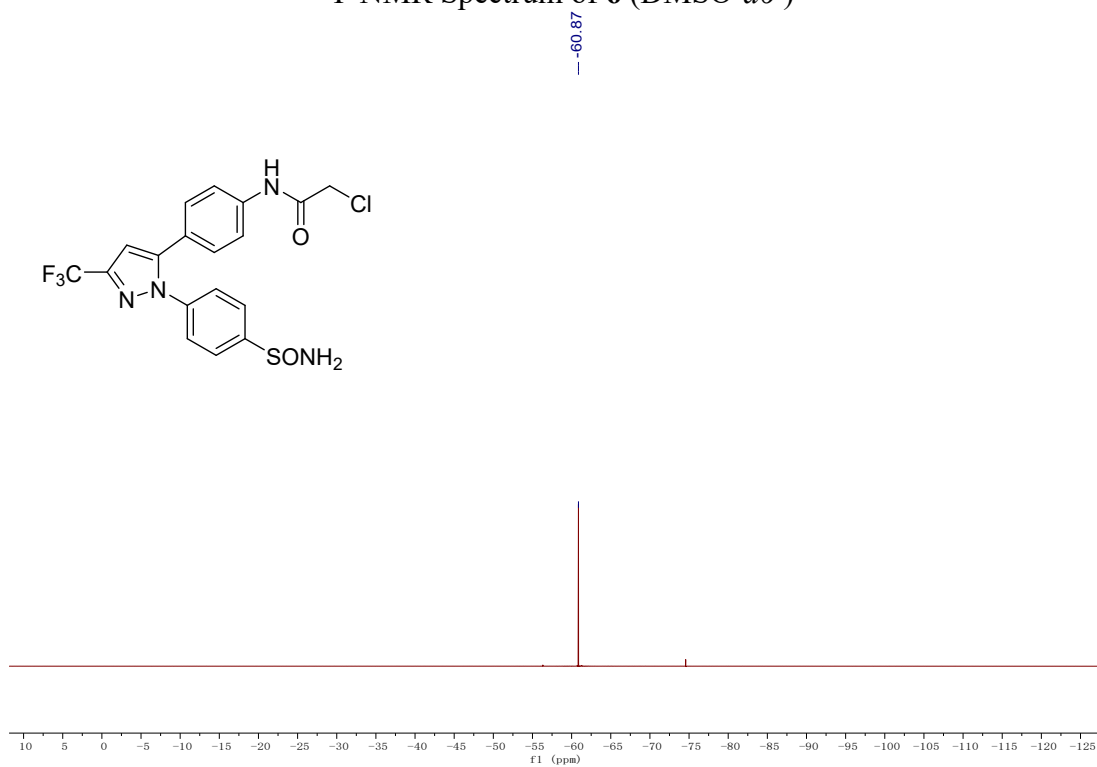


¹H NMR Spectrum of **6** (DMSO-*d*₆)

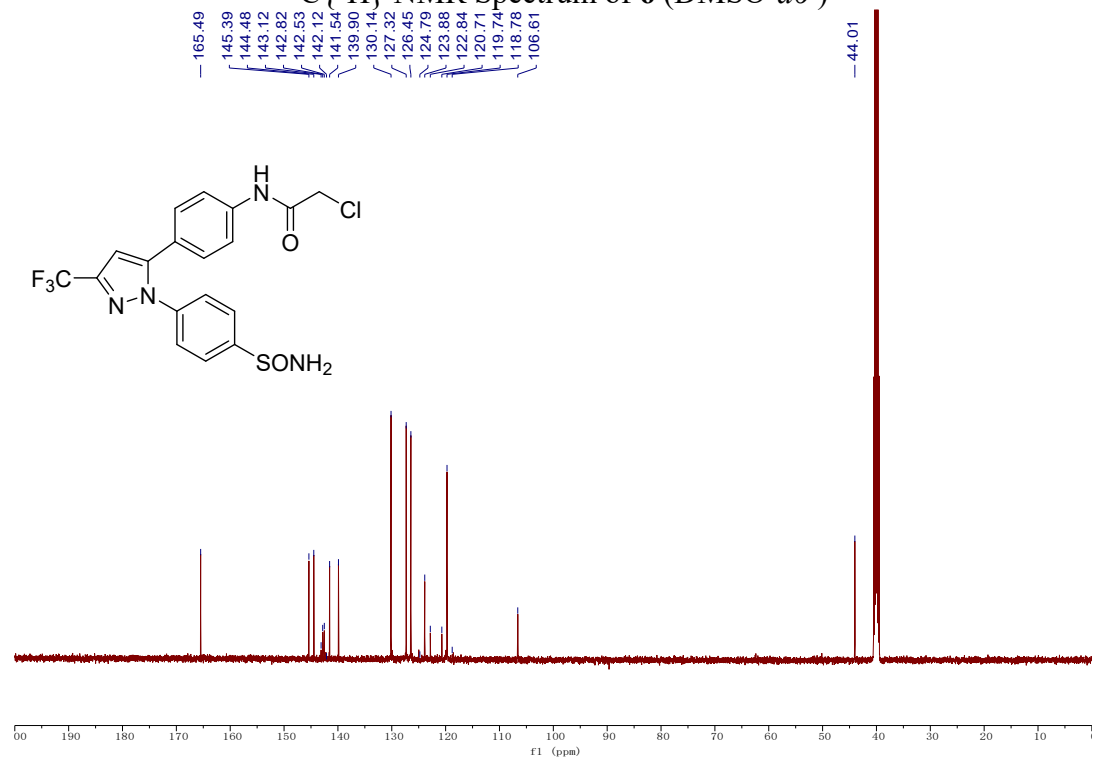
10.49
7.92
7.90
7.65
7.63
7.58
7.56
7.51
7.32
7.30
7.21
4.28



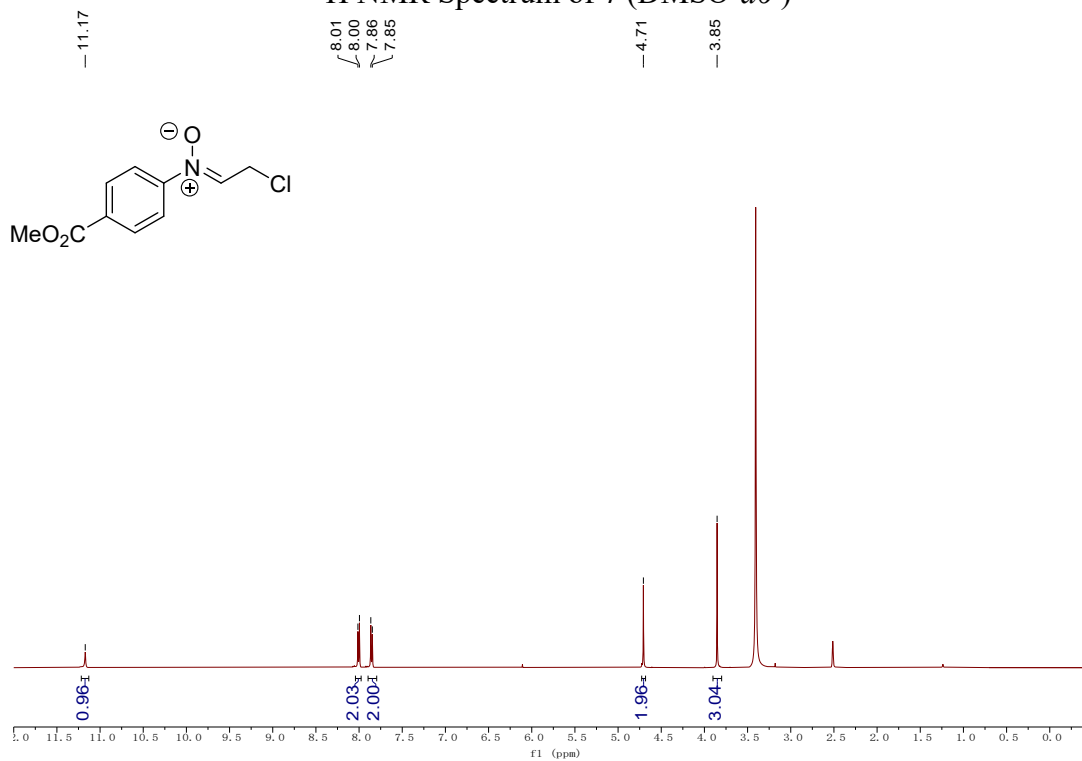
¹⁹F NMR Spectrum of **6** (DMSO-*d*₆)



¹³C {¹H} NMR Spectrum of **6** (DMSO-*d*₆)



^1H NMR Spectrum of 7 (DMSO- d_6)



$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of 7 (DMSO- d_6)

