

Supplementary Information

Visible-light-driven photocatalyst-free deoxygenative alkylation of imines with alcohols

Wei Zhang,^{†a} Shen Ning,^{†ab} Yi Li,^a and Xuesong Wu^{*a}

^aHubei Key Laboratory of Bioinorganic Chemistry & Materia Medica, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

^bMacrocean Materials Technology Co., Ltd., Suzhou 215000, China.

[†]These authors contributed equally to this work.

*Email: xswu@hust.edu.cn

Table of Contents

1. General Information	S2
2. Detailed Optimization of Reaction Conditions	S4
2.1 Optimization of Reaction Conditions of <i>N</i> -Sulfonylimide with Alcohols.....	S4
2.2 Optimization of Reaction Conditions of Schiff Base with Alcohols	S7
3. General Procedure and Characterization Data of Products	S9
3.1 General Procedure for Deoxygenative Alkylation of Alcohols with <i>N</i> -Sulfonylimide	S9
3.2 Characterization Data of Products of <i>N</i> -Sulfonylimide with Alcohols.....	S10
3.3 General Procedure for Deoxygenative Alkylation of Alcohols with schiff base.....	S21
3.4 Characterization Data of Products of schiff base with Alcohols	S22
4. Procedure for Gram-Scale Reaction	S26
5. Mechanism Studies	S27
5.1 TEMPO Trapping Experiments	S27
5.2 EPR Experiments	S27
5.3 Exclusion of EDA Complexes	S28
5.4 Luminescence Quenching Experiments	S29
5.5 Cyclic Voltammetry	S30
5.6 Light On-Off Experiments	S30
5.7 Measurement of Quantum Yields	S31
6. Preparation and Characterization Data of Substrates.....	S33
6.1 General Procedure for Synthesis of <i>N</i> -Sulfonylimide.....	S33
6.2 Characterization Data of <i>N</i> -Sulfonylimide.....	S33
7. References.....	S38
8. NMR Spectra.....	S39

1. General Information

Commercially Reagents: Commercially reagents were purchased from Sigma Aldrich, Energy Chemical, TCI or Alfa Aesar and used without further purification. All experiments were performed in oven-dried glassware under an atmosphere of N₂. Diethyl ether, 1,4-dioxane were extra-dry solvents with molecular sieve (MS) purchased from Energy Chemical and stored within a N₂ filled glove box.

NMR Spectra: ¹H NMR spectra were recorded on a 400 or 600 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent (CDCl₃: 7.26 ppm). ¹³C NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl₃: 77.16 ppm, t). Data are reported as follows: chemical shift δ /ppm, integration (¹H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof; ¹³C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment.

Gas Chromatograph-Mass Spectrometer (GC-MS): All GC-MS were recorded on Agilent 5977B-7890B. Measured values are reported to 3 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

Gas Chromatograph (GC): All GC were recorded on Fuli GC9790II.

Chromatography: Analytical thin layer chromatography was performed using Qingdao Puke Parting Materials Co. silica gel plates (Silicagel 60 F254). Visualisation was by ultraviolet fluorescence (λ = 254 nm) and/or staining with phosphomolybdic acid or potassium permanganate (KMnO₄). Flash column chromatography was performed using 200-300 mesh silica gel.

UV/Vis: Measurements were made on Shanghai JiaPeng technology co. ZF-7 Spectro Fluorophotometer.

Photoreactor: The photoreactors used in this research were purchased from Changji Engineering Lighting on Taobao (IP66-5054-YV35C2BAXV, Figure S1: 30W and 50 W blue LEDs).

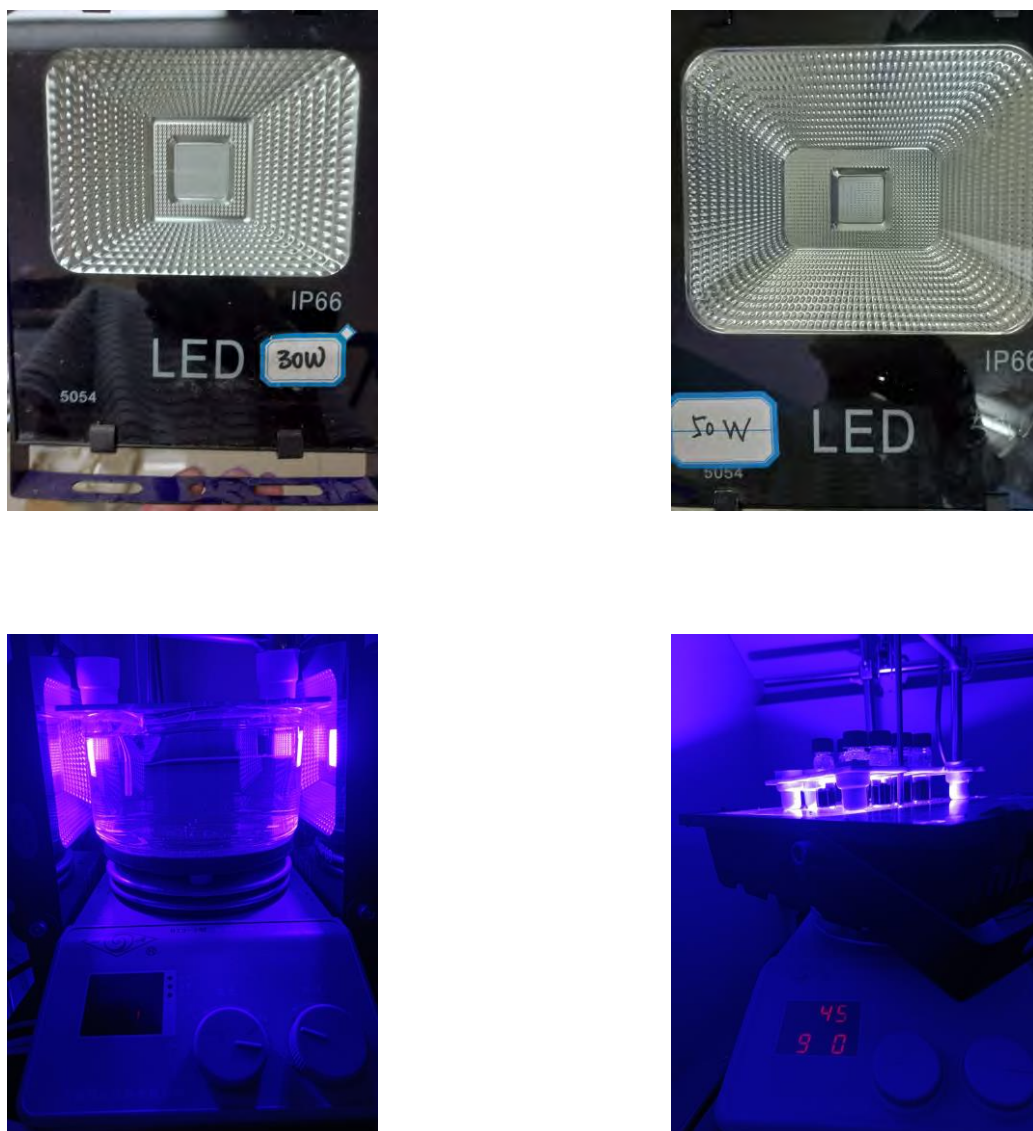


Figure S1. Photoreactor used in this research (30 W and 50 W blue LEDs)

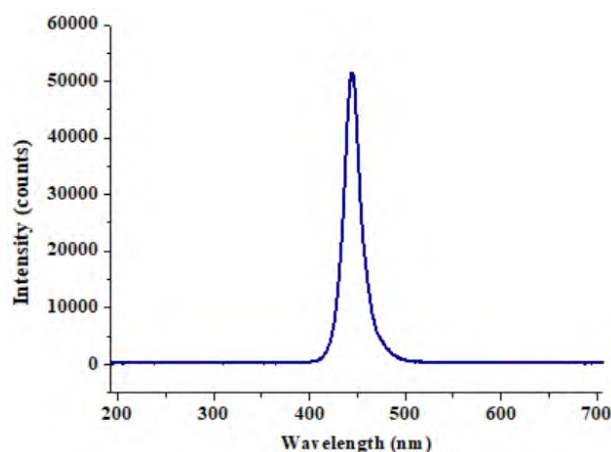


Figure S2. Emission spectra of the 30W blue LEDs, its emission wavelength range is from 401 nm to 510 nm, and its maximum emission wavelength is 444 nm. (The emission spectra was recorded on a Marine optical spectrometer USB2000+)

2. Detailed Optimization of Reaction Conditions

2.1 Optimization of Reaction Conditions of *N*-Sulfonylimide with Alcohols

Table S1. Screening of PR₃^a

Entry	PR ₃	Yield (%) ^b
1	PCy ₃	60
2	PPh ₃	55
3	P ⁿ Bu ₃	21
4	P(4-OMeC ₆ H ₄) ₃	22
5	PPh ₂ OEt	32
6	P(C ₈ H ₁₇) ₃	38
7	P(OEt) ₃	0
8	H ₃ PO ₃	0

^aStandard procedure: **1a** (0.30 mmol), KO^tBu (1.05 equiv.), Et₂O (3.0 mL), CS₂ (5.0 equiv.), 3 h. After removing solvent in vacuo, then imine (1.5 equiv.), PR₃ (1.5 equiv.), MeCN (3.0 mL), 24 h 30 W blue LEDs irradiation. ^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S2. Screening of Additives^a

Entry	Additives	Yield (%) ^b
1	3 Å MS (45 mg)	61
2	4 Å MS (45 mg)	68
3	5 Å MS (45 mg)	61
4	Na ₂ SO ₄ (45 mg)	59
5	MgSO ₄ (45 mg)	58
6	Celite (45 mg)	58
7	none	60

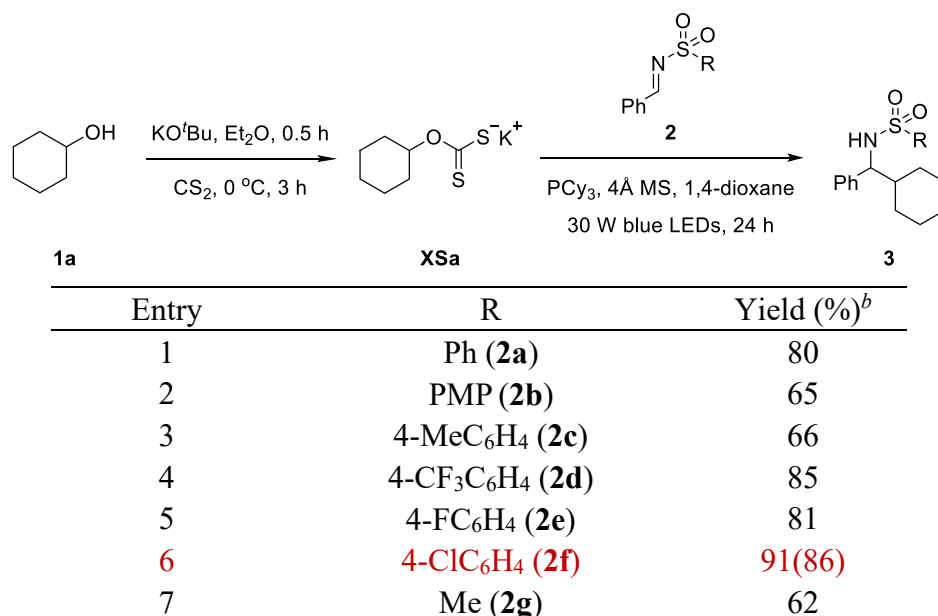
^aStandard procedure: **1a** (0.30 mmol), KO^tBu (1.05 equiv.), Et₂O (3.0 mL), CS₂ (5.0 equiv.), 3 h. After removing solvent in vacuo, then imine (1.5 equiv.), PCy₃ (1.5 equiv.), additives (45 mg), MeCN (3.0 mL), 24 h 30 W blue LEDs irradiation. ^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S3. Screening of Solvents^a

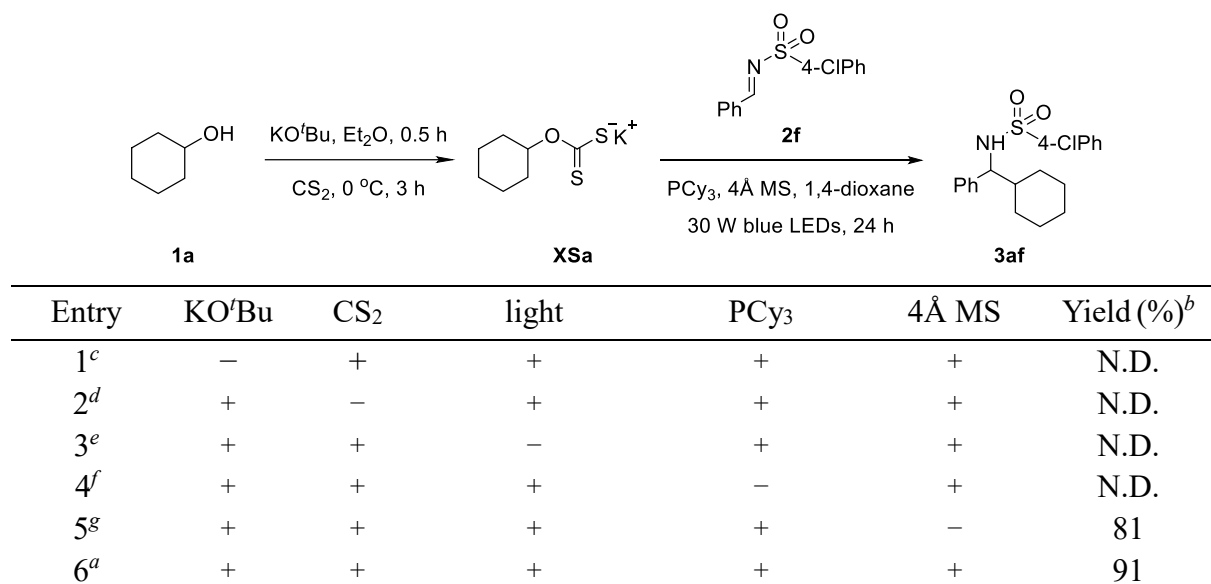
Entry	Solvent (3.0 mL)	Yield (%) ^b
1	DCM	0
2	DMF	0
3	DMSO	0
4	THF	61
5	PhCF ₃	66
6	DME	62
7	MeCN	68
8	1,4-dioxane	80

^aStandard procedure: **1a** (0.30 mmol), KO^tBu (1.05 equiv.), Et₂O (3.0 mL), CS₂ (5.0 equiv.), 3 h. After removing solvent in vacuo, then imine (1.5 equiv.), PCy₃ (1.5 equiv.), 4 Å MS (45 mg), solvent (3.0 mL), 24 h 30 W blue LEDs irradiation.

^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S4. Screening of *N*-Sulfonylimide^a

^aStandard procedure: **1a** (0.30 mmol), KO^tBu (1.05 equiv.), Et₂O (3.0 mL), CS₂ (5.0 equiv.), 3 h. After removing solvent in vacuo, then imine (1.5 equiv.), PCy₃ (1.5 equiv.), 4 Å MS (45 mg), 1,4-dioxane (3.0 mL), 24 h 30 W blue LEDs irradiation. ^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S5. Control Experiments^a

^aStandard procedure: **1a** (0.30 mmol), KO^tBu (1.05 equiv.), Et₂O (3.0 mL), CS₂ (5.0 equiv.), 3 h. After removing solvent in vacuo, then imine (**2f**) (1.5 equiv.), PCy₃ (1.5 equiv.), 4 Å MS (45 mg), 1,4-dioxane (3.0 mL), 24 h 30 W blue LEDs irradiation. ^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard. ^cWithout KO^tBu.

^dWithout CS₂. ^eWithout light. ^fWithout PCy₃. ^gWithout 4 Å MS.

2.2 Optimization of Reaction Conditions of Schiff Base with Alcohols

Table S6. Screening of PR₃^a

$\text{1a} \xrightarrow[\text{CS}_2, 0\text{ }^\circ\text{C}, 3\text{ h}]{\text{KO}^t\text{Bu}, \text{Et}_2\text{O}, 0.5\text{ h}} \text{XSa} \xrightarrow[\text{50 W blue LEDs, 24 h}]{[\text{P}], ^n\text{Bu}_4\text{NBr, DMSO}} \text{5aa}$

Entry	PR ₃	Yield (%) ^b
1	PCy ₃	51
2	P(Ada) ₂ ⁿ Bu	42
3	P ⁿ Bu ₃	6
4	P(4-OMeC ₆ H ₄) ₃	10
5	PPh ₃	8
6	PPh ₂ Cy	28
7	P(OEt) ₃	0
8	PPh ₂ OEt	0

^aStandard procedure: **1a** (30.4 mg 0.30 mmol), KO^tBu (36.5 mg, 1.05 equiv.), Et₂O (3 mL), CS₂ (114 mg, 5.0 equiv.), 3 h. After removing solvent in vacuo, then imine **4a** (111 mg 2.0 equiv.), PR₃ (2.0 equiv.), ⁿBu₄NBr (50 mg, 0.50 equiv.), DMSO:PhCF₃ = 9:1 (3.0 mL), 24 h 50 W blue LEDs irradiation. ^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S7. Screening of Additives^a

$\text{1a} \xrightarrow[\text{CS}_2, 0\text{ }^\circ\text{C}, 3\text{ h}]{\text{KO}^t\text{Bu}, \text{Et}_2\text{O}, 0.5\text{ h}} \text{XSa} \xrightarrow[\text{50 W blue LEDs, 24 h}]{\text{PCy}_3, ^n\text{Bu}_4\text{NBr, DMSO}} \text{5aa}$

Entry	Additive	Yield (%) ^b
1	3Å MS	21
2	4Å MS	24
3	5Å MS	19
4	Na ₂ SO ₄	23
5	Et ₄ NOTf	44
6	Et ₄ NPF ₆	42
7	ⁿ Bu ₄ NOTf	47
8	ⁿ Bu ₄ NBr	51
9	none	23

^aStandard procedure: **1a** (30.4 mg 0.30 mmol), KO^tBu (36.5 mg, 1.05 equiv.), Et₂O (3 mL), CS₂ (114 mg, 5.0 equiv.), 3 h. After removing solvent in vacuo, then imine **4a** (111 mg 2.0 equiv.), PCy₃ (172 mg, 2.0 equiv.), ⁿBu₄NBr (50 mg, 0.50 equiv.), DMSO:PhCF₃ = 9:1 (3.0 mL), 24 h 50 W blue LEDs irradiation. ^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S8. Screening of Solvents^a

Entry	Solvent (3.0 mL)	Yield (%) ^b
1	DCE	0
2	DMF	22
3	DMSO	51
4	THF	28
5	PhCF ₃	11
6	DME	23
7	MeCN	22
8	1,4-dioxane	0
9	DMSO : DCE (9:1)	15
10	DMSO : 1,4-dioxane (9:1)	46
11	DMSO : THF (9:1)	47
12	DMSO : DME (9:1)	54
13	DMSO : MeCN (9:1)	33
14	DMSO : DMF (9:1)	52
15	DMSO : PhCF₃ (9:1)	84(81)

^aStandard procedure: **1a** (30.4 mg 0.30 mmol), KO^tBu (36.5 mg, 1.05 equiv.), Et₂O (3.0 mL), CS₂ (114 mg, 5.0 equiv.), 3 h. After removing solvent in vacuo, then imine **4a** (111 mg, 2.0 equiv.), PCy₃ (172 mg, 2.0 equiv.), ⁿBu₄NBr (50.0 mg, 0.50 equiv.), solvent (3.0 mL), 24 h 50 W blue LEDs irradiation. ^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

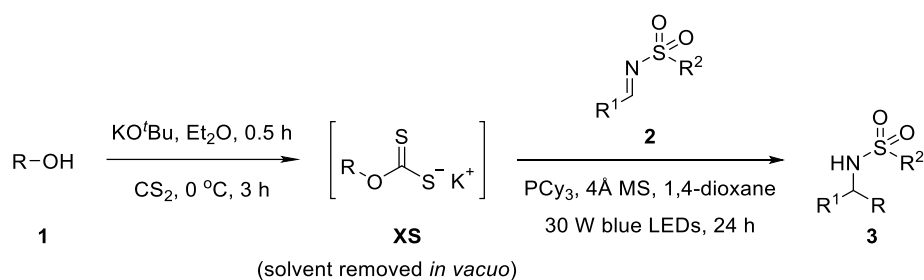
Table S9. Control Experiments^a

Entry	KO ^t Bu	CS ₂	light	PCy ₃	^t Bu ₄ NBr	Yield (%) ^b
1 ^c	—	+	+	+	+	N.D.
2 ^d	+	—	+	+	+	N.D.
3 ^e	+	+	—	+	+	N.D.
4 ^f	+	+	+	—	+	N.D.
5 ^g	+	+	+	+	—	24
6 ^a	+	+	+	+	+	84

^aStandard procedure: **1a** (30.4 mg 0.30 mmol), KO^tBu (36.5 mg, 1.05 equiv.), Et₂O (3 mL), CS₂ (114 mg, 5.0 equiv.), 3 h. After removing solvent in vacuo, then imine **4a** (111 mg 2.0 equiv.), PCy₃ (172 mg, 2.0 equiv.), ^tBu₄NBr (50 mg, 0.50 equiv.), DMSO:PhCF₃ = 9:1 (2.7:0.3 mL), 24 h 50 W blue LEDs irradiation. ^bDetermined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard. ^cWithout KO^tBu. ^dWithout CS₂. ^eWithout light. ^fWithout PCy₃. ^gWithout ^tBu₄NBr.

3. General Procedure and Characterization Data of Products

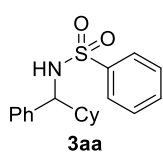
3.1 General Procedure for Deoxygenative Alkylation of Alcohols with *N*-Sulfonylimide



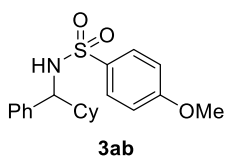
In a N₂-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with alcohol **1** (0.30 mmol), KO^tBu (35.3 mg, 0.32 mmol), and dry Et₂O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS₂ (114 mg, 90.0 μL, 1.5 mmol) via microsyringe at 0 °C and continued to be stirred for 3 hours at 0 °C before removing the solvent *in vacuo*. The system was transferred into the glovebox, then *N*-sulfonylimide **2** (0.45

mmol), PCy₃ (129 mg, 0.45 mmol), 4Å MS (45 mg), and 1,4-dioxane (3.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at ambient temperature, and stirred for 24 hours. The solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product.

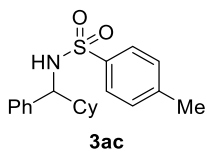
3.2 Characterization Data of Products of *N*-Sulfonylimide with Alcohols



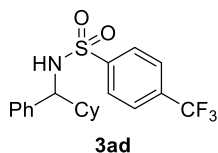
***N*-(Cyclohexyl(phenyl)methyl)benzenesulfonamide (3aa):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (79.0 mg, yield: 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.58 (m, 2H), 7.37 (m, 1H), 7.25 (m, 2H), 7.15 – 7.01 (m, 3H), 6.89 (m, 2H), 5.11 (d, *J* = 8.5 Hz, 1H), 4.14 – 4.06 (m, 1H), 2.02 – 1.89 (m, 1H), 1.80 – 1.69 (m, 1H), 1.58 (m, 3H), 1.29 (m, 1H), 1.17 – 0.79 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 140.7, 139.7, 132.0, 128.5, 128.1, 127.2, 127.1, 127.0, 63.5, 43.8, 29.8, 29.4, 26.1, 25.9 (2C). HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₉H₂₄NO₂S: 330.1522, found: 330.1523.



***N*-(Cyclohexyl(phenyl)methyl)-4-methoxybenzenesulfonamide (3ab):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (70.1 mg, yield: 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.18 – 7.00 (m, 3H), 6.95 – 6.89 (m, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 5.66 (d, *J* = 8.4 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.77 (s, 3H), 1.97 (d, *J* = 12.9 Hz, 1H), 1.79 – 1.46 (m, 4H), 1.35 – 0.75 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 162.4, 140.1, 132.5, 129.2, 128.1, 127.1, 127.0, 113.7, 63.6, 55.6, 43.8, 29.9, 29.6, 26.3, 26.0 (2C). HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₀H₂₆NO₃S: 360.1628, found: 360.1629.

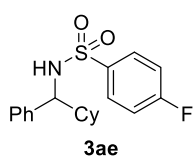


***N*-(Cyclohexyl(phenyl)methyl)-4-methylbenzenesulfonamide (3ac):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (67.9 mg, yield: 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.17 – 6.96 (m, 5H), 6.96 – 6.83 (m, 2H), 5.42 (d, *J* = 8.6 Hz, 1H), 4.06 – 3.99 (m, 1H), 2.31 (s, 3H), 1.95 (d, *J* = 13.1 Hz, 1H), 1.78 – 1.67 (m, 1H), 1.66 – 1.48 (m, 3H), 1.27 (d, *J* = 13.1 Hz, 1H), 1.21 – 0.77 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 142.8, 140.1, 137.8, 129.2, 128.1, 127.1 (2C), 127.0, 63.6, 43.9, 29.9, 29.6, 26.3, 26.0 (2C), 21.5. HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₀H₂₆NO₂S: 344.1679, found: 344.1680.



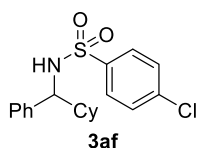
***N*-(Cyclohexyl(phenyl)methyl)-4-(trifluoromethyl)benzenesulfonamide (3ad):**

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (101.2 mg, yield: 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.05 (m, 3H), 6.83 (d, *J* = 7.0 Hz, 2H), 5.55 (d, *J* = 8.8 Hz, 1H), 4.11 – 4.04 (m, 1H), 2.02 (m, 1H), 1.81 – 1.69 (m, 1H), 1.67 – 1.50 (m, 3H), 1.27 (m, 1H), 1.21 – 0.77 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 144.3, 139.2, 133.7 (q, *J* = 33 Hz), 128.3, 127.6, 127.4, 127.1, 125.7 (q, *J* = 4 Hz), 123.3 (q, *J* = 265 Hz), 64.0, 43.7, 29.9, 29.8, 26.2, 25.9 (2C). HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₀H₂₃F₃NO₂S: 398.1396, found: 398.1396.



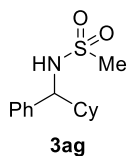
***N*-(Cyclohexyl(phenyl)methyl)-4-fluorobenzenesulfonamide (3ae):**

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (84.3 mg, yield: 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.51 (m, 2H), 7.09 (m, 3H), 6.99 – 6.75 (m, 4H), 5.24 (d, *J* = 8.6 Hz, 1H), 4.08 – 4.02 (m, 1H), 1.98 (d, *J* = 13.0 Hz, 1H), 1.81 – 1.68 (m, 1H), 1.67 – 1.51 (m, 3H), 1.25 (m, 1H), 1.18 – 0.81 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 164.7 (d, *J* = 253 Hz), 139.7, 136.9, 129.8 (d, *J* = 9 Hz), 128.3, 127.3, 127.1, 115.7 (d, *J* = 22 Hz), 63.7, 43.8, 29.9, 29.7, 26.3, 26.0 (2C). HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₉H₂₃FO₂S: 348.1428, found: 348.1429.



4-Chloro-*N*-(cyclohexyl(phenyl)methyl)benzenesulfonamide (3af):

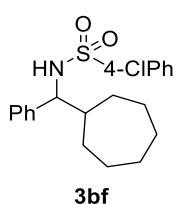
The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (93.9 mg, yield: 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.14 – 7.00 (m, 3H), 6.88 (m, 2H), 5.49 (d, *J* = 8.7 Hz, 1H), 4.08 – 4.01 (m, 1H), 2.04 – 1.92 (m, 1H), 1.78 – 1.69 (m, 1H), 1.57 (m, 3H), 1.27 (m, 1H), 1.19 – 0.77 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 139.6, 139.4, 138.5, 128.8, 128.5, 128.3, 127.3, 127.1, 63.8, 43.8, 29.9, 29.7, 26.3, 26.0 (2C). HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₉H₂₃ClNO₂S: 364.1133, found: 364.1133.



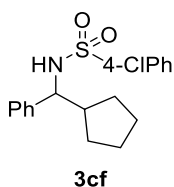
***N*-(Cyclohexyl(phenyl)methyl)methanesulfonamide (3ag):**

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (49.7 mg, yield: 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.21 (m, 5H), 5.39 (d, *J* = 8.9 Hz, 1H), 4.21 – 4.13 (m, 1H), 2.51 (s, 3H), 2.03 (m, 1H), 1.84 – 1.73 (m, 1H), 1.71 – 1.55 (m, 3H), 1.41 – 1.33 (m, 1H), 1.27 – 0.89 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 140.8, 128.8, 127.8,

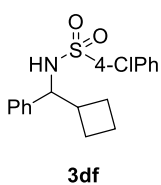
127.3, 63.6, 43.7, 41.8, 30.0, 29.7, 26.3, 26.0, 25.9. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{14}H_{22}NO_2S$: 268.1366, found: 268.1366.



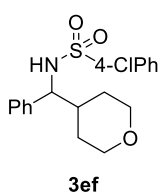
4-Chloro-*N*-(cycloheptyl(phenyl)methyl)benzenesulfonamide (3bf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (83.9 mg, yield: 74%). 1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 7.11 – 7.03 (m, 3H), 6.87 – 6.78 (m, 2H), 5.70 (d, J = 8.9 Hz, 1H), 4.15 – 4.09 (m, 1H), 1.93 – 1.85 (m, 1H), 1.82 – 1.74 (m, 1H), 1.54 (m, 1H), 1.50 – 1.12 (m, 9H), 1.12 – 1.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 139.2, 128.7, 128.4, 128.1, 127.0 (2C), 63.7, 45.2, 31.3, 30.0, 28.2, 28.0, 26.4, 26.3. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{20}H_{25}ClNO_2S$: 378.1289, found: 378.1291.



4-Chloro-*N*-(cyclopentyl(phenyl)methyl)benzenesulfonamide (3cf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (85.1 mg, yield: 81%). 1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 7.11 – 7.03 (m, 3H), 7.01 – 6.89 (m, 2H), 5.87 (d, J = 8.2 Hz, 1H), 4.08 – 4.01 (m, 1H), 2.20 – 2.08 (m, 1H), 1.95 – 1.83 (m, 1H), 1.72 – 1.37 (m, 5H), 1.31 – 1.20 (m, 1H), 1.10 – 0.97 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 139.3, 138.3, 128.6, 128.4, 128.2, 127.2, 126.9, 63.4, 46.5, 30.2, 30.0, 25.1, 25.0. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{18}H_{21}ClNO_2S$: 350.0976, found: 350.0976.

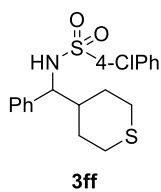


4-Chloro-*N*-(cyclobutyl(phenyl)methyl)benzenesulfonamide (3df): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (44.4 mg, yield: 44%). 1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H), 7.03 (m, 3H), 6.87 (d, J = 6.9 Hz, 2H), 5.32 (d, J = 7.6 Hz, 1H), 4.24 – 4.17 (m, 1H), 2.46 (m, 1H), 2.05 – 1.92 (m, 1H), 1.81 – 1.53 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.9, 138.5, 128.7, 128.4, 128.3, 127.4, 126.8, 63.5, 41.1, 25.8, 25.1, 17.2. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}ClNO_2S$: 336.0820, found: 336.0821.



4-Chloro-*N*-((2,3-dihydro-1H-inden-2-yl)(phenyl)methyl)benzenesulfonamide (3ef): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (60.4 mg, yield: 55%). 1H NMR (400 MHz,

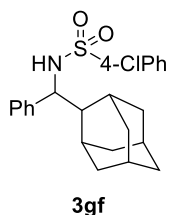
CDCl₃) δ 7.49 (d, J = 8.3 Hz, 2H), 7.23 – 7.06 (m, 5H), 6.94 – 6.80 (m, 2H), 5.74 (d, J = 9.2 Hz, 1H), 4.08 – 4.01 (m, 1H), 3.67 – 3.43 (m, 4H), 2.36 – 2.25 (m, 1H), 1.67 – 1.55 (m, 2H), 1.46 – 1.21 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 138.7, 138.5, 128.8, 128.4, 128.4, 127.5, 126.9, 63.4, 43.2, 30.9, 30.6, 28.4, 28.3. HRMS (EI): m/z [M + H]⁺ calcd for C₁₈H₂₁ClNO₃S: 366.0925, found: 366.0927.



4-Chloro-*N*-(phenyl(tetrahydro-2-*H*-thiopyran-4-yl)methyl)benzenesulfonamide

(3ff): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (71.1 mg, yield: 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 8.3 Hz, 2H), 7.23 – 7.06 (m, 5H), 6.87 (d, J = 7.0 Hz, 2H), 5.74

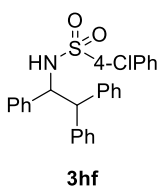
(d, J = 9.2 Hz, 1H), 4.09 – 4.02 (m, 1H), 2.67 – 2.43 (m, 4H), 2.36 – 2.25 (m, 1H), 1.67 – 1.55 (m, 2H), 1.46 – 1.21 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 138.7, 138.5, 128.8, 128.4, 128.4, 127.5, 126.9, 63.4, 43.2, 30.9, 30.6, 28.4, 28.3. HRMS (EI): m/z [M + H]⁺ calcd for C₁₈H₂₁ClNO₂S₂: 382.0697, found: 382.0698.



***N*-(((1*r*,3*r*,5*r*,7*r*)-Adamantan-2-yl)(phenyl)methyl)-4-chlorobenzenesulfonamide**

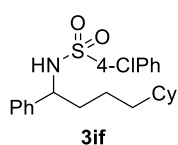
(3gf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (74.9 mg, yield: 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.34 (d, J = 8.3 Hz, 2H), 7.03 (m, 5H), 6.84 (d, J = 7.0 Hz, 2H), 5.05 (m,

1H), 4.48 (m, 1H), 2.22 (m, 1H), 1.98 – 1.84 (m, 2H), 1.81 – 1.76 (m, 2H), 1.72 – 1.68 (m, 1H), 1.64 – 1.50 (m, 5H), 1.42 (m, 1H), 1.34 – 1.25 (m, 1H), 1.19 (m, 1H), 1.05 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.9, 139.4, 138.4, 128.7, 128.5, 128.4, 127.4, 126.9, 59.3, 50.1, 38.9, 38.8, 38.1, 31.6, 31.3, 28.6, 28.5, 27.9, 27.6. HRMS (EI): m/z [M + H]⁺ calcd for C₂₃H₂₇ClNO₂S: 416.1446, found: 416.1445.

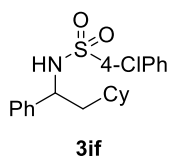


4-Chloro-*N*-(1,2-diphenylethyl)benzenesulfonamide (3hf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (56.3 mg, yield: 42%). ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.15 (m, 7H), 7.04 (d, J = 8.3 Hz, 2H), 7.01 – 6.83 (m, 8H), 6.77 (d, J = 7.5 Hz, 2H), 5.03 (dd, J = 10.3,

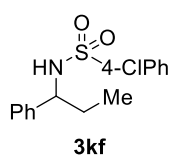
5.0 Hz, 1H), 4.94 – 4.81 (m, 1H), 4.03 (d, $J = 10.3$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.3, 139.6, 138.7, 138.5, 138.4, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.5, 127.3, 126.7, 61.3, 58.6. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{23}\text{ClNO}_2\text{S}$: 448.1133, found: 448.1135.



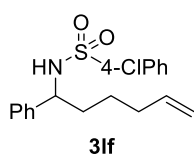
4-Chloro-*N*-(4-cyclohexyl-1-phenylbutyl)benzenesulfonamide (3if): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (65.8 mg, yield: 54%). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 7.17 – 7.09 (m, 3H), 7.01 – 6.95 (m, 2H), 5.33 (d, $J = 7.6$ Hz, 1H), 4.32 – 4.25 (m, 1H), 1.76 – 1.52 (m, 7H), 1.32 – 0.98 (m, 8H), 0.83 – 0.70 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 139.4, 138.7, 128.9, 128.6, 128.5, 127.5, 126.6, 58.7, 38.0, 37.5, 37.0, 33.4, 33.3, 26.8, 26.5 (2C), 23.3. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{29}\text{ClNO}_2\text{S}$: 406.1602, found: 406.1603.



4-Chloro-*N*-(2-cyclohexyl-1-phenylethyl)benzenesulfonamide (3jf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (51.0 mg, yield: 45%). ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 8.3$ Hz, 2H), 7.15 – 7.09 (m, 3H), 7.02 – 6.93 (m, 2H), 5.33 (d, $J = 7.7$ Hz, 1H), 4.44 – 4.36 (m, 1H), 1.57 (m, 7H), 1.11 (m, 4H), 0.93 – 0.77 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.1, 139.4, 138.6, 128.9, 128.6, 128.5, 127.5, 126.6, 56.1, 45.7, 34.0, 33.3, 32.9, 26.5, 26.2, 26.1. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{ClNO}_2\text{S}$: 378.1289, found: 378.1289.

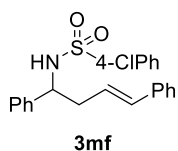


4-Chloro-*N*-(1-phenylpropyl)benzenesulfonamide (3kf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (38.9 mg, yield: 42%). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 7.16 – 7.11 (m, 3H), 7.00 – 6.95 (m, 2H), 5.33 (d, $J = 7.6$ Hz, 1H), 4.25 – 4.18 (m, 1H), 1.87 – 1.65 (m, 2H), 0.81 (t, $J = 7.4$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.3, 139.4, 138.7, 128.9, 128.6, 128.5, 127.6, 126.7, 60.2, 30.8, 10.7. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{ClNO}_2\text{S}$: 310.0663, found: 310.0665.



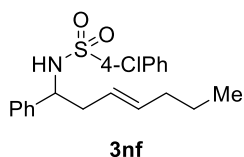
4-Chloro-*N*-(1-phenylhex-5-en-1-yl)benzenesulfonamide (3lf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (45.2 mg, yield: 43%). ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.5$ Hz, 2H), 7.18 – 7.09 (m, 3H), 7.00 – 6.94 (m, 2H), 5.76 – 5.61 (m,

1H), 5.35 – 5.20 (m, 1H), 4.97 – 4.88 (m, 2H), 4.35 – 4.26 (m, 1H), 2.04 – 1.94 (m, 2H), 1.80 – 1.62 (m, 2H), 1.44 – 1.19 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.5, 139.4, 138.7, 138.0, 129.0, 128.6, 128.5, 127.7, 126.6, 115.2, 58.6, 37.1, 33.2, 25.2. HRMS (EI): m/z [M + H]⁺ calcd for C₁₈H₂₁ClNO₂S: 350.0976, found: 350.0978.



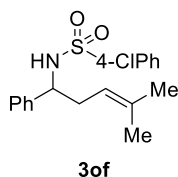
4-Chloro-N-(1,4-diphenylbut-3-en-1-yl)benzenesulfonamide (3mf):

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (86.0 mg, yield: 72%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.08 (m, 10H), 7.05 – 6.99 (m, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 5.82 – 5.72 (m, 1H), 5.26 – 5.15 (m, 1H), 4.43 – 4.36 (m, 1H), 2.59 – 2.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.1, 139.0, 138.9, 136.6, 134.2, 129.0, 128.6, 128.6, 128.5, 127.7, 127.6, 126.5, 126.2, 124.2, 57.8, 41.2. HRMS (EI): m/z [M + H]⁺ calcd for C₂₂H₂₁ClNO₂S: 398.0976, found: 398.0978.



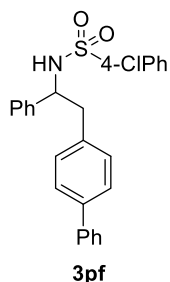
4-Chloro-N-(cyclohex-2-en-1-yl(phenyl)methyl)benzenesulfonamide (3nf):

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (55.7 mg, yield: 51%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.13 – 7.04 (m, 3H), 7.00 – 6.92 (m, 2H), 5.50 – 5.40 (m, 1H), 5.25 – 5.05 (m, 2H), 4.38 – 4.30 (m, 1H), 2.52 – 2.32 (m, 2H), 1.93 – 1.82 (m, 2H), 1.34 – 1.21 (m, 2H), 0.77 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.3, 139.3, 138.8, 135.9, 128.9, 128.6, 128.5, 127.5, 126.8, 124.4, 57.9, 40.9, 34.7, 22.5, 22.4, 13.7. HRMS (EI): m/z [M + H]⁺ calcd for C₁₉H₂₃ClNO₂S: 364.1133, found: 364.1135.

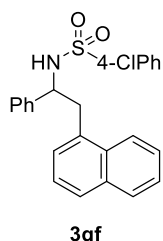


4-Chloro-N-(4-methyl-1-phenylpent-3-en-1-yl)benzenesulfonamide (3of):

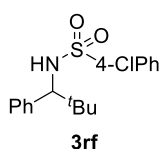
The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (50.4 mg, yield: 48%). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.13 – 7.06 (m, 3H), 7.01 – 6.95 (m, 2H), 5.13 – 5.00 (m, 1H), 4.81 (t, *J* = 7.4 Hz, 1H), 4.30 – 4.22 (m, 1H), 2.39 – 2.26 (m, 2H), 1.55 (s, 3H), 1.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.4, 139.1, 138.7, 136.4, 128.9, 128.7, 128.4, 127.4, 126.6, 118.5, 58.1, 36.3, 25.8, 17.9. HRMS (EI): m/z [M + H]⁺ calcd for C₁₈H₂₁ClNO₂S: 350.0976, found: 350.0978.



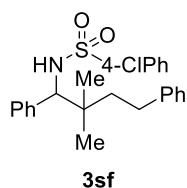
***N*-([1,1'-Biphenyl]-4-yl(phenyl)methyl)-4-chlorobenzenesulfonamide (3pf):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (80.6 mg, yield: 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.33 (m, 7H), 7.23 – 7.16 (m, 5H), 7.13 – 7.08 (m, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 5.30 – 5.20 (m, 1H), 4.62 – 4.54 (m, 1H), 3.11 – 2.93 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.5, 140.3, 139.9, 138.8, 138.7, 135.4, 129.8, 128.9 (2C), 128.6, 128.4, 127.8, 127.5, 127.3, 127.0, 126.8, 59.4, 43.7. HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₆H₂₃ClNO₂S: 448.1133, found: 448.1137.



4-Chloro-*N*-(2-(naphthalen-1-yl)-1-phenylethyl)benzenesulfonamide (3qf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (64.6 mg, yield: 51%). ¹H NMR (400 MHz, CDCl₃) δ 7.83 – 7.70 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.21 – 7.13 (m, 6H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 6.9 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.30 – 5.18 (m, 1H), 4.58 – 4.50 (m, 1H), 3.40 (dd, *J* = 14.4, 5.4 Hz, 1H), 3.16 (dd, *J* = 14.3, 9.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 138.4, 137.7, 134.0, 132.4, 131.5, 129.1, 128.7, 128.6, 128.0, 127.9, 127.8, 127.8, 126.5, 126.4, 125.9, 125.3, 123.0, 58.4, 41.9. HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₄H₂₁ClNO₂S: 422.0976, found: 422.0979.

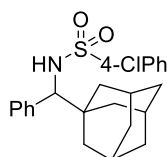


4-Chloro-*N*-(2,2-dimethyl-1-phenylpropyl)benzenesulfonamide (3rf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (62.9 mg, yield: 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.13 – 6.99 (m, 5H), 6.80 (d, *J* = 7.0 Hz, 2H), 5.79 (d, *J* = 9.9 Hz, 1H), 4.09 – 4.00 (m, 1H), 0.91 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 138.5, 137.9, 128.7, 128.6, 128.2, 127.8, 127.1, 67.3, 35.4, 31.4, 26.7 (3C). HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₇H₂₁ClNO₂S: 338.0976, found: 338.0976.



4-Chloro-*N*-(2,2-dimethyl-1,4-diphenylbutyl)benzenesulfonamide (3sf): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (59.1 mg, yield: 46%). ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.36 (m, 2H), 7.25 – 7.21 (m, 2H), 7.18 – 7.11 (m, 4H), 7.08 – 6.99 (m, 4H), 6.87 – 6.82 (m, 2H), 5.67 (d, *J* = 9.9 Hz, 1H), 4.17 (d, *J* = 9.9 Hz, 1H), 2.62 – 2.45 (m, 2H), 1.57 – 1.44 (m,

2H), 0.94 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.7, 138.9, 138.5, 137.5, 128.7, 128.5 (3C), 128.4, 127.9, 127.2, 125.9, 65.7, 41.7, 38.0, 30.2, 23.9, 23.4. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{ClNO}_2\text{S}$: 428.1446, found: 428.1445.

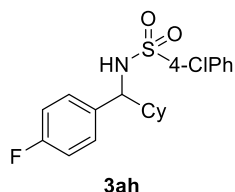


3tf

***N*-((Adamantan-1-yl)(phenyl)methyl)-4-chlorobenzenesulfonamide (3tf):** The title

compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (54.9 mg, yield: 44%). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, J = 8.3 Hz, 2H), 7.03 (m, 5H), 6.84 (d, J = 7.0 Hz, 2H), 5.05 (m, 1H), 4.48 (m, 1H),

2.22 (m, 1H), 1.98 – 1.84 (m, 2H), 1.81 – 1.76 (m, 2H), 1.72 – 1.68 (m, 1H), 1.64 – 1.50 (m, 5H), 1.42 (m, 1H), 1.34 – 1.25 (m, 1H), 1.19 (m, 1H), 1.05 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.3, 138.7, 138.0, 128.6, 128.4, 128.3, 127.3, 126.8, 59.2, 50.0, 38.8, 38.7, 38.0, 31.5, 31.2, 28.5, 28.4, 27.8, 27.5. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{27}\text{ClNO}_2\text{S}$: 416.1446, found: 416.1446.

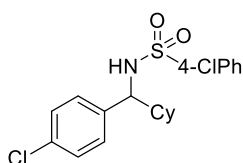


3ah

4-Chloro-*N*-(cyclohexyl(4-fluorophenyl)methyl)benzenesulfonamide (3ah):

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (97.4 mg, yield: 85%). ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 6.91 – 6.85

(m, 2H), 6.83 – 6.76 (m, 2H), 5.71 (d, J = 8.4 Hz, 1H), 4.06 – 3.99 (m, 1H), 1.98 – 1.90 (m, 1H), 1.76 – 1.67 (m, 1H), 1.66 – 1.45 (m, 3H), 1.30 – 1.20 (m, 1H), 1.20 – 0.73 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.9 (d, J = 244 Hz), 139.3, 138.8, 135.5 (d, J = 4 Hz), 128.9, 128.7 (d, J = 8 Hz), 128.5, 115.1 (d, J = 22 Hz), 63.1, 43.8, 29.8, 29.7, 26.2, 25.9 (2C). HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{ClFNO}_2\text{S}$: 382.1038, found: 382.1038.

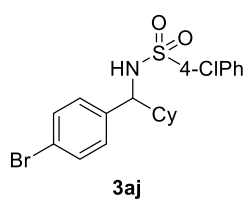


3ai

4-Chloro-*N*-((4-chlorophenyl)(cyclohexyl)methyl)benzenesulfonamide (3ai):

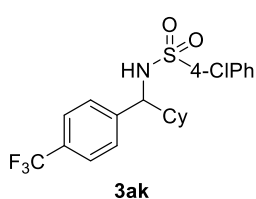
The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (99.1 mg, yield: 83%). ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.3 Hz, 2H), 7.08 (d, J =

8.0 Hz, 2H), 6.88 (d, J = 8.1 Hz, 2H), 6.12 – 5.94 (m, 1H), 4.06 – 3.99 (m, 1H), 1.99 – 1.88 (m, 1H), 1.77 – 1.67 (m, 1H), 1.66 – 1.47 (m, 3H), 1.26 (m, 1H), 1.21 – 0.76 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.1, 138.8, 138.1, 133.1, 128.8, 128.5, 128.4, 128.3, 63.1, 43.5, 29.6, 29.5, 26.1, 25.8 (2C). HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{Cl}_2\text{NO}_2\text{S}$: 398.0743, found: 398.0745.



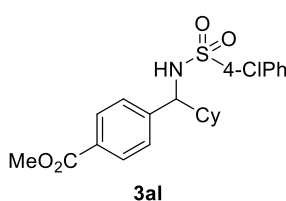
***N*-((4-Bromophenyl)(cyclohexyl)methyl)-4-chlorobenzenesulfonamide (3aj):**

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (110.3 mg, yield: 83%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.16 (m, 4H), 6.73 (d, *J* = 8.0 Hz, 2H), 5.77 (d, *J* = 8.2 Hz, 1H), 3.96 – 3.89 (m, 1H), 1.89 – 1.81 (m, 1H), 1.71 – 1.58 (m, 1H), 1.58 – 1.38 (m, 3H), 1.23 – 1.13 (m, 1H), 1.09 – 0.68 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 138.9, 138.7, 131.3, 129.0, 128.9, 128.4, 121.2, 63.1, 43.4, 29.7, 29.6, 26.1, 25.9 (2C). HRMS (EI): *m/z* [*M* + *H*]⁺ calcd for C₁₉H₂₂BrClNO₂S: 442.0238, found: 442.0240.



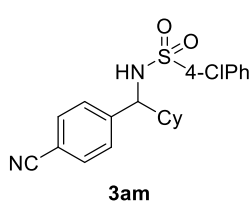
4-Chloro-*N*-(cyclohexyl(4-(trifluoromethyl)phenyl)methyl)benzenesulfonamide (3ak):

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (110.1 mg, yield: 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 5.89 – 5.60 (m, 1H), 4.15 – 4.08 (m, 1H), 1.98 – 1.89 (m, 1H), 1.77 – 1.69 (m, 1H), 1.68 – 1.50 (m, 3H), 1.28 – 1.20 (m, 1H), 1.18 – 0.77 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 143.7, 139.0, 138.9, 129.7 (q, *J* = 33 Hz), 129.0, 128.5, 127.7, 125.2 (q, *J* = 4 Hz), 124.0 (q, *J* = 271 Hz), 63.4, 43.5, 29.8, 29.5, 26.1, 25.9 (2C). HRMS (EI): *m/z* [*M* + *H*]⁺ calcd for C₂₀H₂₂ClF₃NO₂S: 432.1006, found: 432.1006.



4-Chloro-*N*-(cyclohexyl(*p*-tolyl)methyl)benzenesulfonamide compound with carbon dioxide (3al):

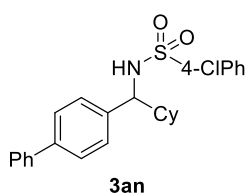
The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (107.6 mg, yield: 85%). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.49 (d, *J* = 8.3 Hz, 1H), 4.16 – 4.08 (m, 1H), 3.90 (s, 3H), 1.95 – 1.86 (m, 1H), 1.78 – 1.68 (m, 1H), 1.63 – 1.49 (m, 3H), 1.28 – 1.22 (m, 1H), 1.18 – 0.78 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 144.9, 139.1, 138.9, 129.6, 129.3, 129.0, 128.5, 127.2, 63.4, 52.3, 43.7, 29.8, 29.5, 26.1, 25.9 (2C). HRMS (EI): *m/z* [*M* + *H*]⁺ calcd for C₂₁H₂₅ClNO₄S: 422.1187, found: 422.1188.



4-Chloro-*N*-((4-cyanophenyl)(cyclohexyl)methyl)benzenesulfonamide

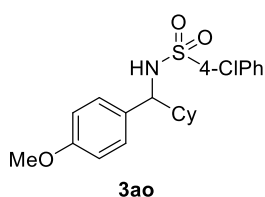
(3am): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (95.7 mg, yield: 82%). ¹H NMR

(400 MHz, CDCl₃) δ 7.56 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.98 (d, J = 8.2 Hz, 1H), 4.13 – 4.06 (m, 1H), 1.89 – 1.82 (m, 1H), 1.75 – 1.67 (m, 1H), 1.66 – 1.49 (m, 3H), 1.29 – 1.17 (m, 1H), 1.16 – 0.77 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 145.7, 139.2, 138.8, 132.0, 129.1, 128.4, 128.0, 118.5, 111.1, 63.2, 43.5, 29.7, 29.2, 26.0, 25.8 (2C). HRMS (EI): m/z [M + H]⁺ calcd for C₂₀H₂₂ClN₂O₂S: 389.1085, found: 389.1085.



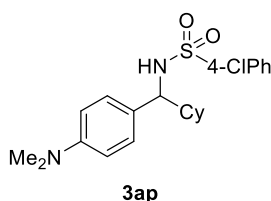
***N*-([1,1'-Biphenyl]-4-yl(cyclohexyl)methyl)-4-chlorobenzenesulfonamide**

(3an): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (100.3 mg, yield: 76%). ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.48 (m, 4H), 7.46 – 7.40 (m, 2H), 7.37 – 7.28 (m, 3H), 7.19 – 7.15 (m, 2H), 6.99 – 6.94 (m, 2H), 5.85 (d, J = 9.5 Hz, 1H), 4.16 – 4.08 (m, 1H), 2.08 – 2.00 (m, 1H), 1.80 – 1.72 (m, 1H), 1.68 – 1.56 (m, 3H), 1.39 – 1.32 (m, 1H), 1.22 – 0.84 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 140.6, 140.3, 139.3, 138.4, 138.3, 128.8, 128.7, 128.5, 127.5, 127.4, 127.1, 126.9, 63.5, 43.5, 29.8, 29.7, 26.2, 25.9 (2C). HRMS (EI): m/z [M + H]⁺ calcd for C₂₅H₂₇ClNO₂S: 440.1446, found: 440.1446.



4-Chloro-*N*-(cyclohexyl(4-methoxyphenyl)methyl)benzenesulfonamide

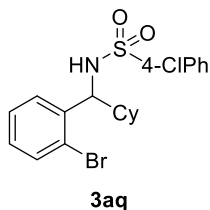
(3ao): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (75.4 mg, yield: 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H), 6.60 (d, J = 8.2 Hz, 2H), 5.53 (d, J = 8.6 Hz, 1H), 4.01 – 3.95 (m, 1H), 3.73 (s, 3H), 2.02 – 1.94 (m, 1H), 1.76 – 1.67 (m, 1H), 1.64 – 1.47 (m, 3H), 1.31 – 1.23 (m, 1H), 1.15 – 0.75 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 139.4, 131.6, 128.6, 128.4, 128.1, 113.5, 63.3, 55.3, 43.6, 29.8, 29.7, 26.2, 25.9 (2C). HRMS (EI): m/z [M + H]⁺ calcd for C₂₀H₂₅ClNO₃S: 394.1238, found: 394.1240.



4-Chloro-*N*-(cyclohexyl(4-(dimethylamino)phenyl)methyl)benzenesulfonamide

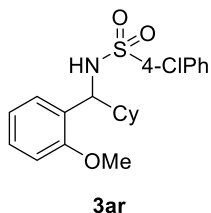
(3ap): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a yellow solid (57.4 mg, yield: 47%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 8.7 Hz, 2H), 6.40 (d, J = 8.7 Hz, 2H), 5.31 (d, J = 8.5 Hz, 1H), 3.97 – 3.91 (m, 1H), 2.87 (s, 6H), 2.05 – 1.98 (m, 1H), 1.78 – 1.69 (m, 1H), 1.64 – 1.47 (m, 3H), 1.36 – 1.27 (m, 1H),

1.20 – 0.76 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.8, 139.6, 138.0, 128.7, 128.6, 127.9, 127.2, 112.2, 63.6, 43.7, 40.7 (2C), 30.0, 29.8, 26.3, 26.0 (2C). HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{28}\text{ClN}_2\text{O}_2\text{S}$: 407.1555, found: 407.1548.



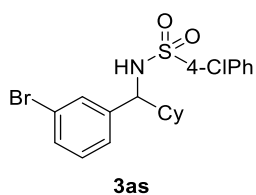
***N*-((2-Bromophenyl)(cyclohexyl)methyl)-4-chlorobenzenesulfonamide (3aq):**

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a yellow solid (115.6 mg, yield: 87%). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 7.7 Hz, 1H), 7.18 (d, J = 8.2 Hz, 2H), 7.10 – 6.93 (m, 3H), 5.96 (d, J = 9.3 Hz, 1H), 4.62 (br, 1H), 2.06 – 1.84 (m, 1H), 1.78 – 1.49 (m, 4H), 1.32 – 1.20 (m, 1H), 1.16 – 0.95 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.3, 138.7, 138.6, 132.8, 128.8, 128.6, 128.1, 127.5, 123.8, 61.4, 43.4, 29.7, 28.8, 26.2, 26.1, 26.0. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{BrClNO}_2\text{S}$: 442.0238, found: 442.0239.



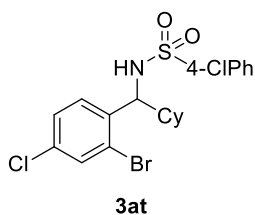
4-Chloro-*N*-(cyclohexyl(2-methoxyphenyl)methyl)benzenesulfonamide (3ar):

The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (92.2 mg, yield: 78%). ^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, J = 8.5 Hz, 2H), 7.15 – 7.02 (m, 3H), 6.77 – 6.64 (m, 2H), 6.56 (d, J = 8.2 Hz, 1H), 5.97 – 5.79 (m, 1H), 4.06 – 3.97 (m, 1H), 3.69 (s, 3H), 2.22 – 2.14 (m, 1H), 1.80 – 1.66 (m, 2H), 1.62 – 1.52 (m, 2H), 1.20 – 0.97 (m, 5H), 0.84 – 0.73 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 156.1, 139.2, 138.0, 129.9, 128.4, 128.3, 128.2, 126.7, 120.2, 110.5, 55.1, 41.6, 30.4, 30.3, 26.3, 25.9, 25.8. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{ClNO}_3\text{S}$: 394.1238, found: 394.1240.



***N*-((3-Bromophenyl)(cyclohexyl)methyl)-4-chlorobenzenesulfonamide (3as):**

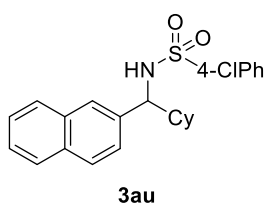
The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (90.4 mg, yield: 68%). ^1H NMR (400 MHz, CDCl_3) δ 7.53 – 7.47 (m, 2H), 7.25 – 7.19 (m, 3H), 7.01 – 6.93 (m, 2H), 6.92 – 6.87 (m, 1H), 5.83 (d, J = 8.6 Hz, 1H), 4.03 – 3.97 (m, 1H), 1.99 – 1.91 (m, 1H), 1.75 – 1.67 (m, 1H), 1.65 – 1.48 (m, 3H), 1.29 – 1.21 (m, 1H), 1.19 – 0.77 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.8, 139.0, 138.8, 130.3, 130.2, 129.8, 128.8, 128.3, 125.8, 122.4, 63.2, 43.3, 29.7, 29.5, 26.1, 25.8 (2C). HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{BrClNO}_2\text{S}$: 442.0238, found: 442.0240.



N-((2-Bromo-4-chlorophenyl)(cyclohexyl)methyl)-4-chlorobenzenesulfonamide

mide (3at): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (110.2 mg, yield: 77%). ¹H

NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.35 (s, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.08 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.05 (d, *J* = 8.5 Hz, 1H), 4.56 (br, 1H), 2.00 – 1.83 (m, 1H), 1.78 – 1.48 (m, 4H), 1.28 – 1.18 (m, 1H), 1.16 – 0.91 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 138.5, 138.0, 133.7, 132.2, 129.2, 128.9, 128.6, 127.8, 123.8, 61.0, 43.4, 29.5, 28.8, 26.1, 26.0, 25.9. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₉H₂₁BrCl₂NO₂S: 475.9848, found: 475.9847.

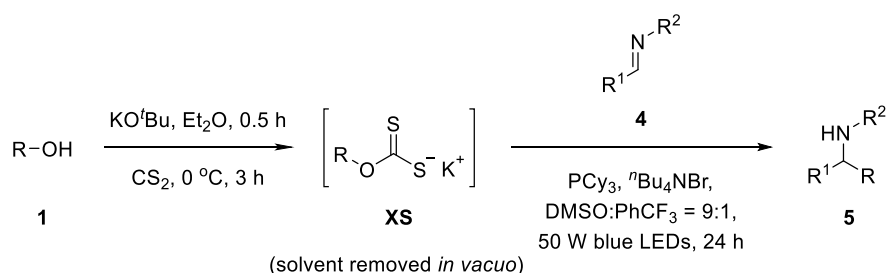


4-Chloro-N-(cyclohexyl(naphthalen-1-yl)methyl)benzenesulfonamide

(3au): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 25:1) as a white solid (63.7 mg, yield: 56%). ¹H NMR

(400 MHz, CDCl₃) δ 7.89 – 7.77 (m, 1H), 7.73 – 7.62 (m, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.20 – 7.10 (m, 3H), 7.08 – 7.02 (m, 1H), 6.72 (d, *J* = 8.1 Hz, 2H), 5.62 (d, *J* = 9.1 Hz, 1H), 4.87 (br, 1H), 2.12 – 1.96 (m, 1H), 1.82 – 1.64 (m, 2H), 1.56 – 1.47 (m, 2H), 1.26 – 0.88 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 144.7, 138.5, 138.0, 133.5, 131.0, 128.9, 128.1, 128.0, 127.7, 126.2, 125.5, 125.0, 124.9, 122.6, 60.4, 43.7, 30.2, 29.5, 26.2, 26.0, 25.9. HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₃H₂₅ClNO₂S: 414.1289, found: 414.1288.

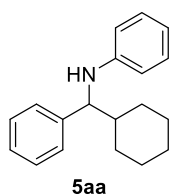
3.3 General Procedure for Deoxygenative Alkylation of Alcohols with schiff base



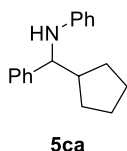
In a N₂-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with alcohol **1** (0.30 mmol), KO^tBu (35.3 mg, 0.32 mmol), and dry Et₂O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS₂ (114 mg, 90.0 μL, 1.5 mmol) via microsyringe at 0 °C and continued to be stirred for 3 hours at 0 °C before removing

the solvent *in vacuo*. The system was transferred into the glovebox, then schiff base **4** (0.60 mmol), PCy₃ (172 mg, 0.60 mmol), ⁿBu₄NBr (50 mg, 0.15mmol), and the mixed solvents of DMSO/PhCF₃ (2.7 mL/0.3 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 50 W blue LEDs lamp, and stirred for 24 hours. The solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product.

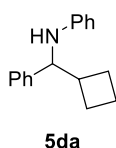
3.4 Characterization Data of Products of schiff base with Alcohols



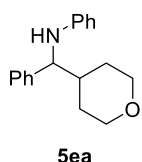
N-Phenyl-(1-phenyl-1-cyclohexyl-methyl)amine (5aa): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (62.0 mg, yield: 78%). ¹H NMR (400 MHz, CDCl₃): δ 7.28 – 7.27 (m, 4H), 7.21 – 7.18 (m, 1H), 7.06 – 7.02 (m, 2H), 6.64 – 6.55 (m, 1H), 6.48 (d, *J* = 7.72 Hz, 2H), 4.12 (br, 1H), 4.10 (d, *J* = 6.32 Hz, 1H), 1.89 – 1.86 (m, 1H), 1.76 – 1.60 (m, 4H), 1.54 – 1.47 (m, 1H), 1.26 – 1.00 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 147.8, 142.7, 129.0, 128.2, 127.2, 126.7, 116.9, 113.1, 63.4, 44.9, 30.2, 29.4, 26.4, 26.3, 26.2. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₉H₂₄N: 266.1903, found: 266.1903.



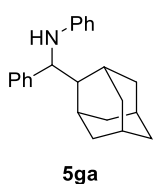
N-(Cyclopentyl(phenyl)methyl)aniline (5ca): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (59.8 mg, yield: 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.16 (m, 4H), 7.15 – 7.09 (m, 1H), 7.01 – 6.94 (m, 2H), 6.55 – 6.49 (m, 1H), 6.42 (d, *J* = 7.9 Hz, 2H), 4.10 (br, 1H), 4.00 (d, *J* = 8.4 Hz, 1H), 2.14 – 2.02 (m, 1H), 1.86 – 1.76 (m, 1H), 1.65 – 1.29 (m, 6H), 1.25 – 1.16 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 147.8, 144.1, 129.2, 128.4, 127.1, 126.9, 117.1, 113.4, 63.2, 47.9, 30.3, 30.1, 25.4, 25.3. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₈H₂₂N: 252.1746, found: 252.1747.



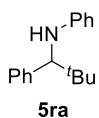
N-(Cyclobutyl(phenyl)methyl)aniline (5da): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (39.1 mg, yield: 54%). ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.17 (m, 4H), 7.17 – 7.09 (m, 1H), 7.03 – 6.94 (m, 2H), 6.56 – 6.51 (m, 1H), 6.41 (d, *J* = 7.9 Hz, 2H), 4.08 (d, *J* = 9.1 Hz, 1H), 3.95 (br, 1H), 2.48 – 2.42 (m, 1H), 2.06 – 2.03 (m, 1H), 1.83 – 1.68 (m, 4H), 1.27 – 1.18 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 147.8, 142.6, 129.2, 128.5, 127.0, 126.7, 117.3, 113.5, 63.9, 42.7, 26.2, 25.6, 17.7. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₇H₂₀N: 238.1590, found: 238.1590.



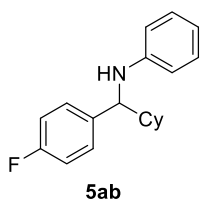
N-(Phenyl(tetrahydro-2H-pyran-4-yl)methyl)aniline (5ea): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (59.0 mg, yield: 73%). ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.25 (m, 4H), 7.23 – 7.18 (m, 1H), 7.10 – 7.01 (m, 2H), 6.65 – 6.57 (m, 1H), 6.51 (d, J = 7.9 Hz, 2H), 4.12 (d, J = 7.5 Hz, 2H), 4.05 – 3.86 (m, 2H), 3.40 – 3.20 (m, 2H), 1.90 – 1.74 (m, 2H), 1.52 – 1.39 (m, 2H), 1.35 – 1.21 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.5, 141.9, 129.2, 128.5, 127.2 (2C), 117.4, 113.4, 68.1, 68.0, 63.0, 42.3, 30.3, 29.9. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{NO}$: 268.1698, found: 268.1694.



N-((Adamantan-2-yl)(phenyl)methyl)aniline (5ga): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (69.1 mg, yield: 73%). ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.24 (m, 4H), 7.21 – 7.14 (m, 1H), 7.09 – 6.98 (m, 2H), 6.61 – 6.50 (m, 3H), 4.54 (d, J = 10.7 Hz, 1H), 4.16 – 3.91 (br, 1H), 2.32 – 2.26 (m, 1H), 2.07 – 1.92 (m, 3H), 1.90 – 1.67 (m, 7H), 1.61 – 1.45 (m, 3H), 1.31 – 1.26 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.9, 143.7, 129.2, 128.5, 127.2, 126.9, 116.9, 113.2, 58.3, 51.7, 39.2, 39.1, 38.2, 32.2, 32.0, 29.2, 28.8, 28.1, 27.9. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{28}\text{N}$: 318.2216, found: 318.2216.

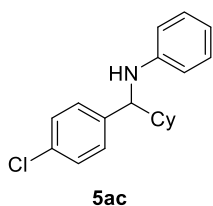


N-(2,2-Dimethyl-1-phenylpropyl)aniline (5ra): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (45.1 mg, yield: 64%). ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.23 (m, 5H), 7.10 – 6.98 (m, 2H), 6.61 – 6.55 (m, 1H), 6.48 (d, J = 8.0 Hz, 2H), 4.25 (br, 1H), 4.04 (s, 1H), 0.99 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.8, 141.2, 129.0, 128.5, 127.7, 126.8, 116.9, 113.2, 67.2, 34.9, 27.1 (3 C). HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{22}\text{N}$: 240.1747, found: 240.1746.

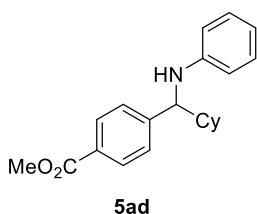


N-(Cyclohexyl(4-fluorophenyl)methyl)aniline (5ab): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (69.2 mg, yield: 82%). ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.20 (m, 2H), 7.08 – 7.02 (m, 2H), 6.99 – 6.93 (m, Hz, 2H), 6.63 – 6.57 (m, 1H), 6.46 (d, J = 7.9 Hz, 2H), 4.14 – 4.07 (m, 2H), 1.93 – 1.80 (m, 1H), 1.79 – 1.45 (m, 5H), 1.27 – 0.94 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 161.8 (d, J = 243 Hz), 147.7, 138.3 (d, J = 3 Hz), 129.2, 128.7 (d, J =

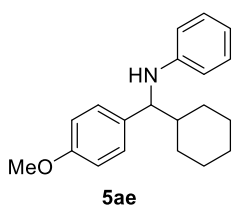
8 Hz), 117.2, 115.1 (d, $J = 21$ Hz), 113.3, 62.9, 45.0, 30.2, 29.5, 26.5, 26.4, 26.4. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{23}FN$: 284.1809, found: 284.1808.



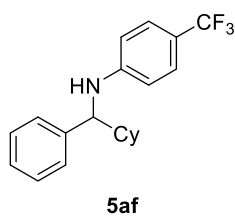
***N*-((4-Chlorophenyl)(cyclohexyl)methyl)aniline (5ac):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (66.3 mg, yield: 74%). 1H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 4H), 7.09 – 7.03 (m, 2H), 6.64 – 6.58 (m, 2H), 6.60 (t, $J = 7.3$ Hz, 1H), 6.46 (d, $J = 7.9$ Hz, 2H), 4.14 – 4.06 (m, 2H), 1.90 – 1.80 (m, 2H), 1.79 – 1.69 (m, 2H), 1.68 – 1.49 (m, 4H), 1.24 – 0.96 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 141.3, 132.4, 129.2, 128.7, 128.5, 117.3, 113.3, 63.0, 45.0, 30.2, 29.5, 26.5, 26.4, 26.4. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{19}H_{23}ClN$: 300.1514, found: 300.1513.



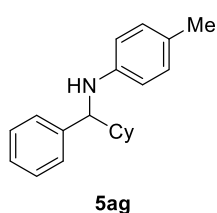
Methyl 4-(cyclohexyl(phenylamino)methyl)benzoate (5ad): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (80.7 mg, yield: 78%). 1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.09 – 7.01 (m, 2H), 6.65 – 6.59 (m, 1H), 6.46 (d, $J = 7.9$ Hz, 2H), 4.17 (d, $J = 6.1$ Hz, 2H), 3.88 (s, 3H), 1.90 – 1.82 (m, 1H), 1.80 – 1.61 (m, 4H), 1.57 – 1.49 (m, 1H), 1.27 – 1.00 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 148.5, 147.5, 129.7, 129.2, 128.9, 127.4, 117.4, 113.3, 63.4, 52.1, 44.9, 30.3, 29.4, 26.5 (2C), 26.4. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{21}H_{26}NO_2$: 324.1958, found: 324.1958.



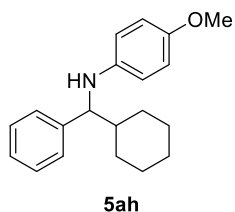
***N*-(Cyclohexyl(4-(trifluoromethyl)phenyl)methyl)aniline (5ae):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (71.2 mg, yield: 80%). 1H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, $J = 8.3$ Hz, 2H), 7.12 – 7.05 (m, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.65 – 6.59 (m, 1H), 6.52 (d, $J = 7.9$ Hz, 2H), 4.09 (d, $J = 6.2$ Hz, 1H), 3.79 (s, 3H), 1.95 – 1.87 (m, 1H), 1.84 – 1.52 (m, 5H), 1.31 – 1.00 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 147.9, 134.7, 129.1, 128.3, 117.0, 113.7, 113.3, 62.9, 55.3, 45.1, 30.2, 29.7, 26.6, 26.5, 26.4. HRMS (EI): m/z $[M + H]^+$ calcd for $C_{20}H_{26}NO$: 296.2009, found: 296.2006.



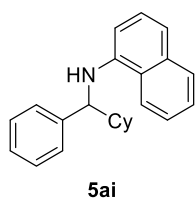
***N*-(Cyclohexyl(phenyl)methyl)-4-(trifluoromethyl)aniline (5af):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (74.9 mg, yield: 75%). ¹H NMR (400 MHz, CDCl₃): δ 7.25 – 7.14 (m, 7H), 6.43 (d, *J* = 8.79 Hz, 2H), 4.46 (br, 1H), 4.04 (d, *J* = 6.16 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.74 – 1.54 (m, 4H), 1.50 – 1.41 (m, 1H), 1.20 – 0.94 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 150.2, 141.8, 128.5, 127.2, 126.5 (q, *J* = 4 Hz), 125.1 (q, *J* = 214 Hz), 118.6 (q, *J* = 27 Hz), 112.4, 63.2, 44.8, 30.3, 29.6, 26.5, 26.4, 26.3. HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₀H₂₃F₃N: 334.1777, found: 334.1776.



***N*-(Cyclohexyl(phenyl)methyl)-4-methylaniline (5ag):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (66.1 mg, yield: 78%). ¹H NMR (400 MHz, CDCl₃): δ 7.25 – 7.07 (m, 5H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 8.3 Hz, 2H), 4.00 (d, *J* = 6.2 Hz, 1H), 2.08 (s, 3H), 1.85 – 1.75 (m, 1H), 1.71 – 1.50 (m, 4H), 1.48 – 1.44 (m, 1H), 1.18 – 0.91 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 145.7, 143.0, 129.7, 128.3, 127.4, 126.8, 126.1, 113.4, 63.8, 45.1, 30.4, 29.6, 26.6, 26.5, 26.5, 20.4. HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₀H₂₆N: 280.2060, found: 280.2060.



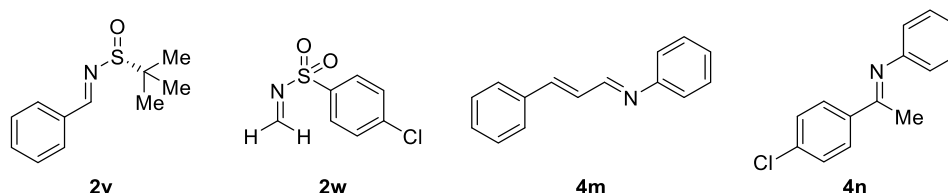
***N*-(Cyclohexyl(phenyl)methyl)-4-methoxyaniline (5ah):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (72.6 mg, yield: 82%). ¹H NMR (400 MHz, CDCl₃): δ 7.26 – 7.07 (m, 5H), 6.58 (d, *J* = 9.0 Hz, 2H), 6.37 (d, *J* = 8.9 Hz, 2H), 3.96 (d, *J* = 6.1 Hz, 1H), 3.59 (s, 3H), 1.86 – 1.77 (m, 1H), 1.71 – 1.50 (m, 4H), 1.48 – 1.44 (m, 1H), 1.19 – 0.89 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 151.8, 143.0, 142.2, 128.3, 127.4, 126.8, 114.9, 114.5, 64.4, 55.9, 45.1, 30.3, 29.6, 26.6, 26.5, 26.5. HRMS (EI): *m/z* [M + H]⁺ calcd for C₂₀H₂₆NO: 296.2009, found: 296.2007.



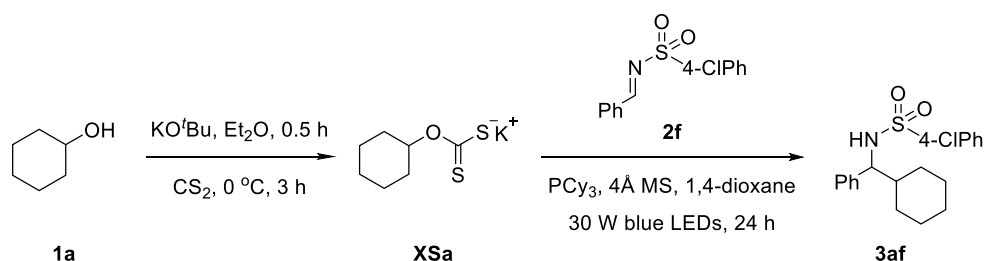
***N*-(Cyclohexyl(phenyl)methyl)naphthalen-1-amine (5ai):** The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 200:1) as a light yellow oil (48.1 mg, yield: 51%). ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.92 (m, 1H), 7.80 – 7.75 (m, 1H), 7.52 – 7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.17 – 7.11 (m, 2H), 6.35 – 6.30 (m, 1H), 4.92 (br, 1H), 4.32 (d, *J* =

6.0 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.85 – 1.63 (m, 5H), 1.26 – 1.06 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.6, 142.4, 134.4, 128.9, 128.3, 127.3, 127.0, 126.8, 125.7, 124.7, 123.5, 119.7, 116.9, 105.7, 63.5, 45.2, 30.6, 29.6, 26.6 (2C), 26.6. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{26}\text{N}$: 316.2060, found: 316.2059.

Table S10. Unsuccessful substrates.



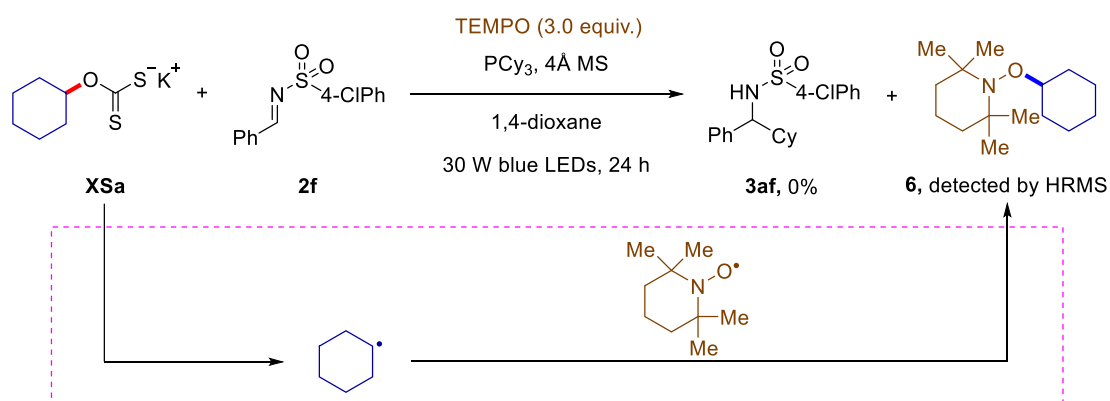
4. Procedure for Gram-Scale Reaction



An oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with alcohol **1a** (0.507 g, 5.0 mmol), KO^tBu (0.608 g, 5.25 mmol). The reaction vessel was evacuated and backfilled with nitrogen (three cycles) and dry 1,4-dioxane (30 mL) was added under nitrogen atmosphere, a balloon was attached. Then the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (1.89 g, 1.5 mL, 25 mmol) via syringe at $0\text{ }^\circ\text{C}$ and stirred for 3 hours at $0\text{ }^\circ\text{C}$ before removing the solvent *in vacuo*. Then *N*-sulfonylimide **2f** (2.10 g, 7.5 mmol), PCy_3 (2.15 g, 7.5 mmol), 4 Å MS (0.50 g), were added. The Schlenk tube was sealed with a rubber plug, evacuated and backfilled with nitrogen (three cycles), and a nitrogen balloon was attached, followed by the addition of 1,4-dioxane (30 mL) via syringe. The reaction mixture was irradiated with a 30 W blue LEDs lamp, and stirred for 72 hours. The solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the product **3af** as a white solid (1.32 g, 73% yield).

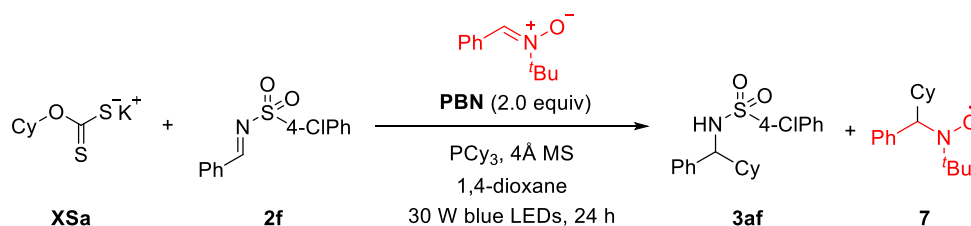
5. Mechanism Studies

5.1 TEMPO Trapping Experiments



In a N₂-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with **XSa** (64.7 mg, 0.30 mmol), **2f** (132 mg, 0.45 mmol), PCy₃ (129 mg, 0.45 mmol), 4 Å MS (45 mg) and TEMPO (141 mg, 0.9 mmol) in the solvent of 1,4-dioxane (3.0 mL). The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at ambient temperature, and stirred for 24 hours. The solvent was removed *in vacuo* and the residue was purified by column chromatography to afford **6**.

5.2 EPR Experiments



In a N₂-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with **XSa** (64.7 mg, 0.30 mmol), **2f** (132 mg, 0.45 mmol), PCy₃ (129 mg, 0.45 mmol), and 4 Å MS (45 mg) in the solvent of 1,4-dioxane (3.0 mL). The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at ambient temperature, and stirred for 1 hour. Then *tert*-butyl- α -phenylnitron (PBN) (106mg, 0.60 mmol) was added. The electron paramagnetic

resonance (EPR) spectroscopy was recorded on a Bruker EMXmicro-6/1. With the addition of PBN as a free radical spin trap, we detected signals that are clearly identified as EPR signals of the CyPBN adduct according to the literature data.³ EPR spectra obtained in MeCN at 298 K in the presence of PBN. Line I: A solution of PBN (106 mg, 0.6 mmol) in 1,4-dioxane (3.0 mL). Line II: A solution of **XSa** (64.7 mg, 0.30 mmol), **2f** (132 mg, 0.45 mmol), PCy₃ (129 mg, 0.45 mmol), 4 Å MS (45 mg) and PBN (106 mg, 0.6 mmol) in the solvent of 1,4-dioxane (3.0 mL).

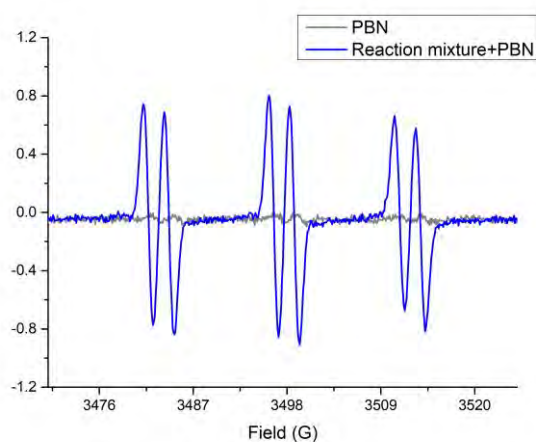
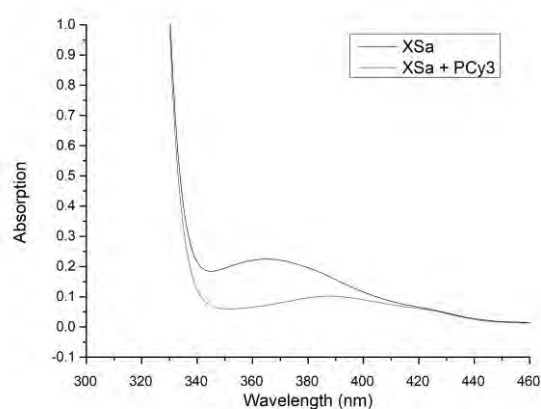
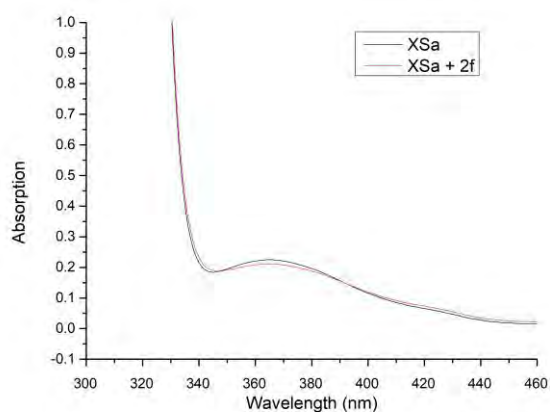


Figure S3. EPR spectra. AN $\approx$ 14.5 G, AH $\approx$ 2.2 G.

5.3 Exclusion of EDA Complexes



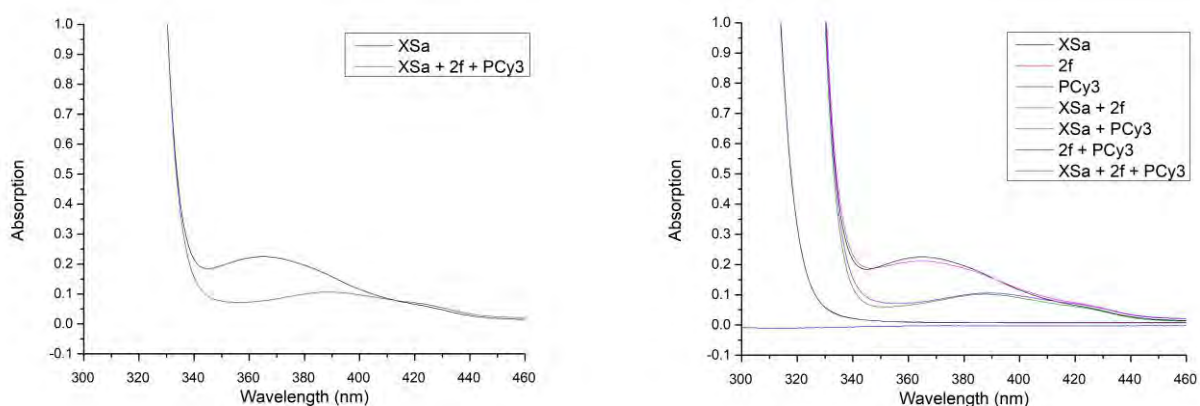


Figure S4. UV/Vis absorption spectrum of the combined reaction components

The UV-Vis Absorption Spectra of all solution was introduced to a 1 cm path length quartz cuvette and analyzed using a Shimadzu UV/Vis spectrophotometer UV-2600. **XSa**: 1.0×10^{-3} M in 1,4-dioxane. **2f**: 1.5×10^{-3} M in 1,4-dioxane. **PCy₃**: 1.5×10^{-3} M in 1,4-dioxane.

5.4 Luminescence Quenching Experiments

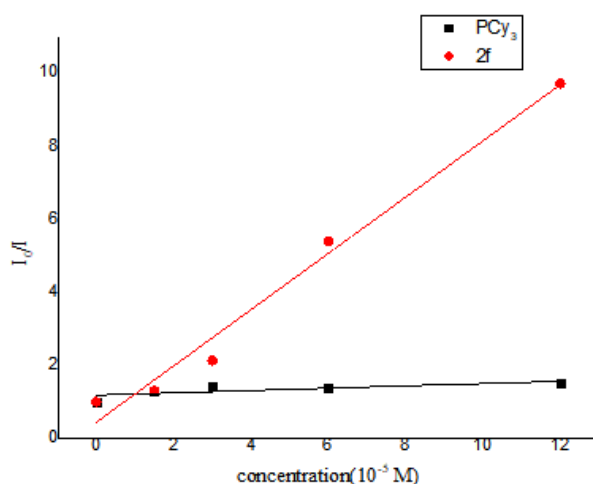


Figure S5. XSa emission quenching by **2f** and **PCy₃**.

Fluorescence spectra was collected on Shimadzu Fluorescence Spectrophotometer RF-5301PC for all experiments. All **XSa** solutions were excited at 390 nm and the emission intensity was collected at 447 nm^[1]. In a typical experiment, the emission spectrum of a 10×10^{-3} M solution of **XSa** in 1,4-dioxane was collected. The significant decrease of **XSa** luminescence could be observed in the presence of substrate **2f**.

5.5 Cyclic Voltammetry

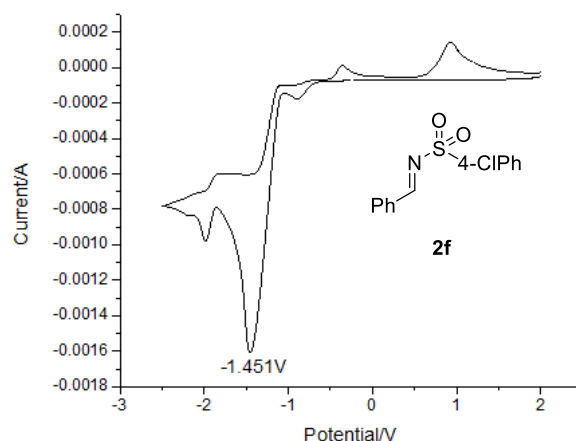
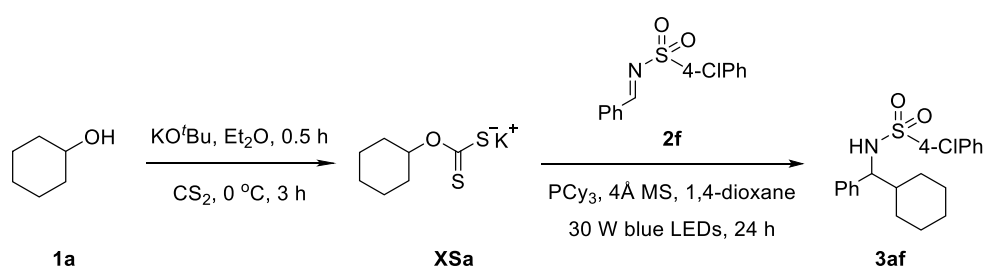


Figure S6. Cyclic voltammetry of **2f** in MeCN (5×10^{-3} M).

Cyclic voltammetry (CV) was taken using a CHI830C potentiostation. CV measurement was performed in a three-electrode cell (volume 30 mL), MeCN as solvent, $n\text{Bu}_4\text{PF}_6$ (0.1 M) as the supporting electrolyte, 5×10^{-3} M concentration of **2f** with glassy carbon as working electrode, Pt wire as the auxiliary electrode, and saturated calomel electrode as the reference electrode. Samples were examined at a scan rate of 0.1 V/s.

5.6 Light On-Off Experiments



In a N_2 -filled glove box, add **1a** (0.3 mmol, 30.4 mg), KO^tBu (0.32 mmol, 37.1 mg) and Et_2O (3.0 mL) to an oven-dried 12 mL glass vial equipped with a magnetic stir bar in sequence, seal the lid, take it out and stir at room temperature. After half an hour, the reaction flask was then placed in a cold trap at $0\text{ }^\circ\text{C}$, and CS_2 (1.5 mmol, 114 mg) was added dropwise to the system under stirring, and the reaction was continued for 3 hours. After 3 hours, the reaction flask was taken out, and the solvent was removed under vacuum with a rotary evaporator to obtain **XSa**. Then **2f** (132 mg, 0.45

mmol), PCy₃ (129 mg, 0.45 mmol), 4 Å MS (45 mg) and 1,4-dioxane (3.0 mL) were added in glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp, and stirred for 2 hours. The vial was wrapped in tin foil and a 50 µL sample of the reaction mixture was taken with a syringe and measured by GC. After being stirred for 2 hours, a 50 µL sample of the reaction mixture was taken with a syringe and measured by GC. The reaction mixture was then irradiated with a 30 W blue LEDs lamp, and stirred for 2 hours. Repeating this process three times.

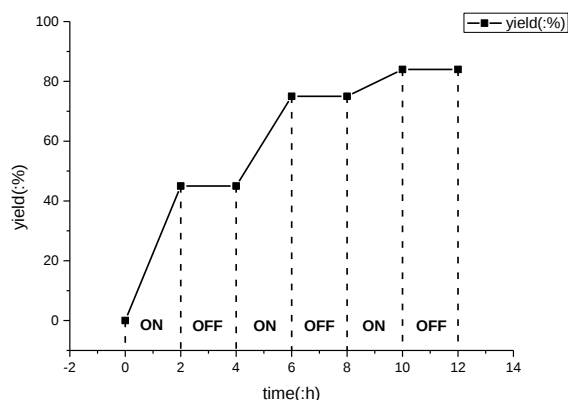


Figure S7. Light on-off experiments.

5.7 Measurement of Quantum Yields

The photon flux of blue LED was determined by standard ferrioxalate actinometry.

0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328 mg, 0.750 mmol) in 5.0 mL of 0.20 M aqueous sulfuric acid.

0.15 M buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg, 0.300 mmol) and sodium acetate (1.23 g, 15.0 mmol) in 20 mL of 0.20 M aqueous sulfuric acid.

The actinometry measurements were done as follows:

To a 4-mL borosilicate vial equipped with a stir bar was added 0.50 mL of the ferrioxalate solution. The vial was sealed and placed 2 cm away from a 25 W blue LEDs. After irradiation for 10 seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution was added to the vial. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50 µL of the resulting solution was taken as an aliquot and

diluted with 3.0 mL of 0.20 M aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette ($l = 1.0$ cm) at 510 nm was measured by UV-Vis spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

The amount of ferrous ion formed was calculated as follows:

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \epsilon}$$

where V is the total volume (0.24 L) of the solution that was analyzed, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.00 cm), and ϵ is the molar absorptivity at 510 nm (11,100 L/mol•cm).

The photon flux was calculated as follows:

$$\text{photo flux} = \frac{\text{mol Fe}^{2+}}{\Phi \times t \times f}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 M solution at $\lambda = 457.9$ nm), t is the irradiation time, and f is the fraction of light absorbed at 450 nm (0.9870).

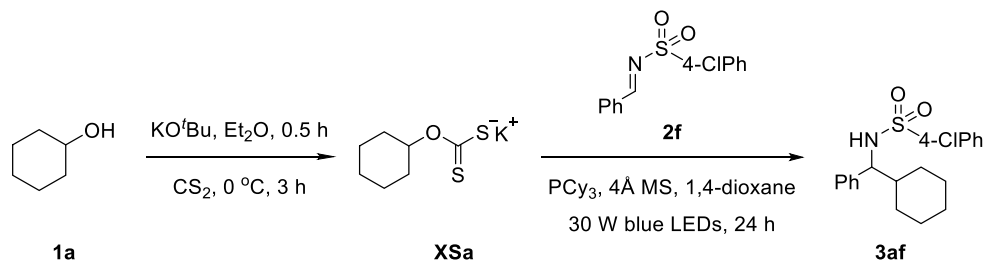
The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-A}$$

where A is the measured absorbance (1.887) of the 0.15 M solution of potassium ferrioxalate at 450 nm.

The photo flux is 5.62×10^{-7} Einstein/s.

Determination of quantum yield:



In a N_2 -filled glove box, add **1a** (0.3 mmol, 30.4 mg), KO^tBu (0.32 mmol, 37.1 mg) and Et_2O (3 mL) to an oven-dried 12 mL glass vial equipped with a magnetic stir bar in sequence, seal the lid,

take it out and stir at room temperature. After half an hour, the reaction flask was then placed in a cold trap at 0 °C, and CS₂ (1.5 mmol, 114 mg) was added dropwise to the system under stirring, and the reaction was continued for 3 hours. After 3 hours, the reaction flask was taken out, and the solvent was removed under vacuum with a rotary evaporator to obtain **XSa**. Then **2f** (132 mg, 0.45 mmol), PCy₃ (129 mg, 0.45 mmol), 4 Å MS (45 mg) and the solvent of 1,4-dioxane were added in glovebox. The vial was sealed with a septum cap and transferred out of the glovebox, and placed 2 cm away from 25 W blue LEDs. After irradiation for 1 hours. The moles of product **3af** formed for the model reaction were determined by GC measurement using 1,2,4,5-tetramethylbenzene as internal standard, and revealed 11% yield of **3af** (0.033 mmol).

The quantum yield was calculated as follows:

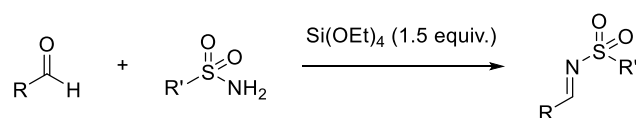
$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f}$$

where flux is the photon flux determined by ferrioxalate actinometry (5.62×10^{-7} Einstein/s), t is the time (3600 s), and f is the fraction of light absorbed by the irradiated reaction system at 450 nm, and the absorbance of the irradiated reaction system at 450 nm was 0.565. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-0.028} = 0.728$.

The quantum yield was calculated: $\Phi = 0.022$

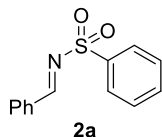
6. Preparation and Characterization Data of Substrates

6.1 General Procedure for Synthesis of *N*-Sulfonylimide

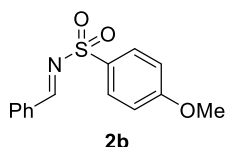


A mixture of aldehyde (5.0 mmol), sulfonamide (3.0 mmol), and tetraethoxysilane (4.37 g, 5.0 mL, 21.0 mmol) was heated at 120 °C for 5 h, and then cooled to room temperature. The mixture was crystallized with ethyl acetate and petroleum ether (10:1 to 1:1), and the resulting solid was collected by filtration and then dried in vacuum to afford the desired product.^[2]

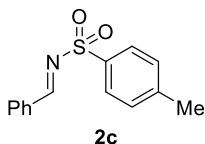
6.2 Characterization Data of *N*-Sulfonylimide



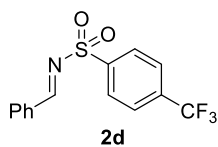
N-Benzylidenebenzenesulfonamide (2a): White solid, 574 mg, yield: 78%. ^1H NMR (400 MHz, CDCl_3) δ 9.06 (s, 1H), 8.02 (d, $J = 7.7$ Hz, 2H), 7.94 (d, $J = 7.7$ Hz, 2H), 7.67 – 7.59 (m, 2H), 7.59 – 7.53 (m, 2H), 7.52 – 7.46 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.8, 138.3, 135.2, 133.7, 132.4, 131.5, 129.3(2C), 128.2. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{12}\text{NO}_2\text{S}$: 246.0583, found: 246.0583.



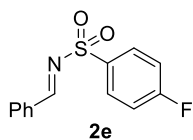
N-Benzylidene-4-methoxybenzenesulfonamide (2b): Pale yellow solid, 583 mg, yield: 71%. ^1H NMR (400 MHz, CDCl_3) δ 9.01 (s, 1H), 7.96 – 7.90 (m, 4H), 7.64 – 7.58 (m, 1H), 7.50 – 7.46 (m, 2H), 7.07 – 6.95 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 163.8, 135.0, 132.6, 131.4, 130.4, 129.7, 129.3, 114.6, 55.8. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{NO}_3\text{S}$: 276.0689, found: 276.0689.



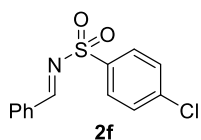
N-Benzylidene-4-methylbenzenesulfonamide (2c): White solid, 609 mg, yield: 78%. ^1H NMR (400 MHz, CDCl_3) δ 9.03 (s, 1H), 7.95 – 7.87 (m, 4H), 7.63 – 7.60 (m, 1H), 7.51 – 7.47 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.1, 144.6, 135.2, 134.9, 132.4, 131.3, 129.8, 129.2, 128.1, 21.7. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$: 260.0740, found: 260.0739.



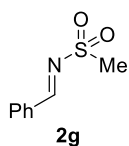
N-Benzylidene-4-(trifluoromethyl)benzenesulfonamide (2d): White solid, 563 mg, yield: 60%. ^1H NMR (400 MHz, CDCl_3) δ 9.11 (s, 1H), 8.16 (d, $J = 8.1$ Hz, 2H), 7.95 (d, $J = 7.7$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H), 7.68 – 7.62 (m, 1H), 7.54 – 7.48 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.9, 142.1, 135.8, 135.3 (q, $J = 33$ Hz), 132.2, 131.7, 129.4, 128.7, 126.4 (q, $J = 4$ Hz), 123.3 (q, $J = 271$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -63.20. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NO}_2\text{S}$: 314.0457, found: 314.0457.



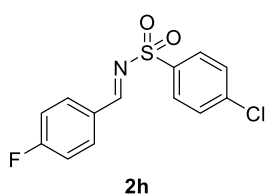
N-Benzylidene-4-fluorobenzenesulfonamide (2e): White solid, 574 mg, yield: 73%. ^1H NMR (400 MHz, CDCl_3) δ 9.06 (s, 1H), 8.07 – 8.01 (m, 2H), 7.94 (d, $J = 7.6$ Hz, 2H), 7.67 – 7.61 (m, 1H), 7.54 – 7.48 (m, 2H), 7.27 – 7.20 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.8, 167.1, 135.4, 132.3, 131.6, 131.1, 131.0, 129.4, 116.6. ^{19}F NMR (376 MHz, CDCl_3) δ -103.59. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{11}\text{FNO}_2\text{S}$: 264.0489, found: 264.0488.



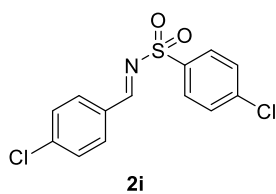
N-Benzylidene-4-chlorobenzenesulfonamide (2f): White solid, 704 mg, yield: 84%. ^1H NMR (400 MHz, CDCl_3) δ 9.06 (s, 1H), 7.97 – 7.91 (m, 4H), 7.67 – 7.61 (m, 1H), 7.55 – 7.47 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 140.4, 136.9, 135.4, 132.3, 131.6, 129.6, 129.4, 128.1. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{11}\text{ClNO}_2\text{S}$: 280.0194, found: 280.0193.



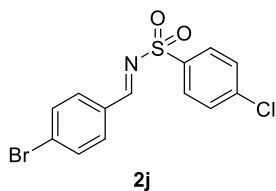
N-Benzylidenemethanesulfonamide (2g): White solid, 428 mg, yield: 78%. ^1H NMR (400 MHz, CDCl_3) δ 9.04 (s, 1H), 7.96 (d, $J = 7.6$ Hz, 2H), 7.69 – 7.61 (m, 1H), 7.57 – 7.51 (m, 2H), 3.14 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.8, 135.3, 132.6, 131.5, 129.4, 40.4. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_8\text{H}_{10}\text{NO}_2\text{S}$: 184.0427, found: 184.0426.



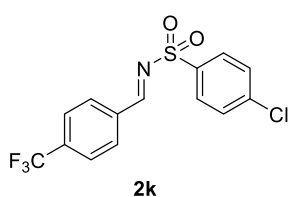
4-Chloro-N-(4-fluorobenzylidene)benzenesulfonamide (2h): White solid, 635 mg, yield: 71%. ^1H NMR (400 MHz, CDCl_3) δ 9.02 (s, 1H), 8.00 – 7.92 (m, 4H), 7.53 (d, $J = 8.7$ Hz, 2H), 7.23 – 7.16 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.3, 167.2 (d, $J = 258$ Hz), 140.4, 136.7, 134.1 (d, $J = 9$ Hz), 129.6, 129.5, 128.6, 116.7 (d, $J = 22$ Hz). HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{ClFNO}_2\text{S}$: 298.0099, found: 298.0100.



4-Chloro-N-(4-chlorobenzylidene)benzenesulfonamide (2i): White solid, 724 mg, yield: 77%. ^1H NMR (400 MHz, CDCl_3) δ 9.02 (s, 1H), 7.99 – 7.91 (m, 2H), 7.91 – 7.83 (m, 2H), 7.57 – 7.44 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.6, 142.0, 140.6, 136.6, 132.6, 130.7, 129.8, 129.7, 129.7. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{NO}_2\text{S}$: 313.9804, found: 313.9803.

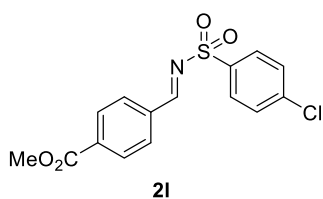


N-(4-Bromobenzylidene)-4-chlorobenzenesulfonamide (2j): White solid, 886 mg, yield: 82%. ^1H NMR (400 MHz, CDCl_3) δ 9.01 (s, 1H), 7.98 – 7.88 (m, 2H), 7.83 – 7.74 (m, 2H), 7.69 – 7.60 (m, 2H), 7.57 – 7.48 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.8, 140.6, 136.6, 132.8, 132.6, 131.1, 130.8, 129.7, 129.6. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{10}\text{BrClNO}_2\text{S}$: 357.9299, found: 357.9300.



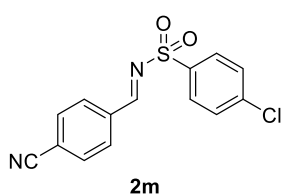
4-Chloro-N-(4-(trifluoromethyl)benzylidene)benzenesulfonamide (2k): White solid, 692 mg, yield: 66%. ^1H NMR (400 MHz, CDCl_3) δ 9.11 (s, 1H), 8.06 (d, $J = 8.1$ Hz, 2H), 8.00 – 7.92 (m, 2H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.59

– 7.51 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 140.9, 136.4, 136.3, 136.1, 135.3, 131.6, 129.8, 126.3 (q, $J = 4$ Hz), 123.4 (q, $J = 271$ Hz). HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{10}\text{ClF}_3\text{NO}_2\text{S}$: 348.0067, found: 348.0067.



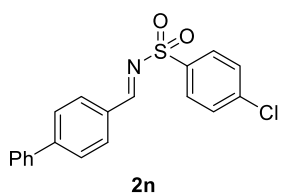
Methyl 4-((((4-chlorophenyl)sulfonyl)imino)methyl)benzoate (2l):

White solid, 729 mg, yield: 72%. ^1H NMR (400 MHz, CDCl_3) δ 9.10 (s, 1H), 8.18 – 8.11 (m, 2H), 8.05 – 7.91 (m, 4H), 7.58 – 7.50 (m, 2H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 165.8, 140.6, 136.2, 135.6, 131.2, 130.2, 129.7, 129.6, 100.0, 52.7. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{ClNO}_4\text{S}$: 338.0248, found: 338.0248.



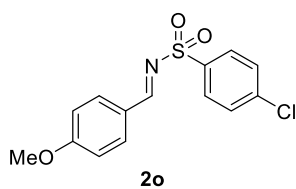
4-Chloro-N-(4-cyanobenzylidene)benzenesulfonamide (2m):

White solid, 748 mg, yield: 82%. ^1H NMR (400 MHz, CDCl_3) δ 9.09 (s, 1H), 8.04 (d, $J = 8.1$ Hz, 2H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.80 (d, $J = 8.1$ Hz, 2H), 7.55 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 141.0, 136.0, 135.8, 133.0, 131.5, 129.9, 129.8, 118.1, 117.7. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_9\text{ClN}_2\text{O}_2\text{S}$: 305.0146, found: 305.0146.



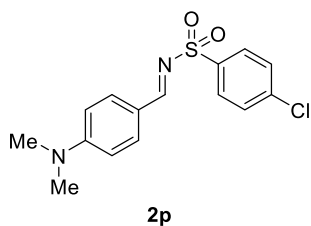
N-([1,1'-Biphenyl]-4-ylmethylene)-4-chlorobenzenesulfonamide (2n):

White solid, 815 mg, yield: 76%. ^1H NMR (400 MHz, CDCl_3) δ 9.12 (s, 1H), 8.01 (m, 4H), 7.76 (m, 2H), 7.70 – 7.62 (m, 2H), 7.51 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.5, 148.1, 140.2, 139.3, 136.9, 132.0, 131.0, 129.5, 129.5, 129.1, 128.8, 127.8, 127.3. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{ClNO}_2\text{S}$: 356.0507, found: 356.0506.



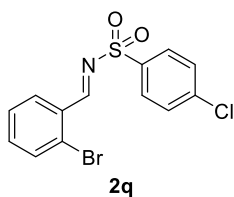
4-Chloro-N-(4-methoxybenzylidene)benzenesulfonamide (2o):

White solid, 744 mg, yield: 80%. ^1H NMR (400 MHz, CDCl_3) δ 8.96 (s, 1H), 8.00 – 7.80 (m, 4H), 7.59 – 7.41 (m, 2H), 7.05 – 6.89 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.0, 165.6, 139.9, 137.4, 134.0, 129.4, 129.3, 125.0, 114.8, 55.7. HRMS (EI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{ClNO}_3\text{S}$: 310.0299, found: 310.0300.



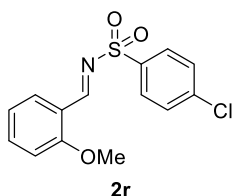
4-Chloro-*N*-(4-(dimethylamino)benzylidene)benzenesulfonamide (2p):

Yellow solid, 620 mg, yield: 64%. ¹H NMR (400 MHz, CDCl₃) δ 8.82 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 3.11 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 169.5, 155.1, 139.2, 138.5, 129.2, 129.0 (2C), 119.6, 111.4, 40.1. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₅H₁₆ClN₂O₂S: 323.0616, found: 323.0616.



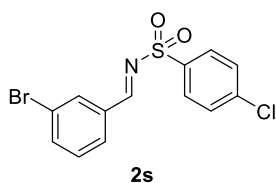
***N*-(2-Bromobenzylidene)-4-chlorobenzenesulfonamide (2q):**

White solid, 811 mg, yield: 75%. ¹H NMR (400 MHz, CDCl₃) δ 9.40 (s, 1H), 8.07 (m, 1H), 7.89 (m, 2H), 7.68 – 7.57 (m, 1H), 7.47 (m, 2H), 7.43 – 7.28 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 170.0, 140.5, 136.3, 136.0, 133.9, 131.0, 130.7, 129.7, 129.6, 129.1, 128.0. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₃H₁₀BrClNO₂S: 357.9299, found: 357.9300.



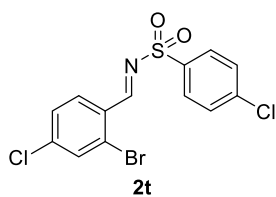
4-Chloro-*N*-(2-methoxybenzylidene)benzenesulfonamide (2r):

White solid, 717 mg, yield: 77%. ¹H NMR (600 MHz, CDCl₃) δ 9.56 (s, 1H), 8.05 – 8.03 (m, 1H), 7.96 – 7.91 (m, 2H), 7.58 (m, 1H), 7.52 – 7.48 (m, 2H), 7.01 – 6.94 (m, 2H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 161.9, 139.9, 137.3 (2C), 129.4, 129.4, 121.0, 120.7, 111.5, 55.8. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₄H₁₃ClNO₃S: 310.0299, found: 310.0300.



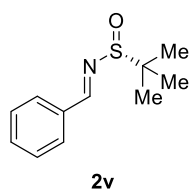
***N*-(3-Bromobenzylidene)-4-chlorobenzenesulfonamide (2s):**

White solid, 674 mg, yield: 63%. ¹H NMR (400 MHz, CDCl₃) δ 8.93 (s, 1H), 8.03 (t, *J* = 1.9 Hz, 1H), 7.92 – 7.82 (m, 2H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.29 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 169.3, 140.6, 137.9, 134.0, 133.4, 130.7, 130.4, 129.6 (2C), 123.5, 100.0. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₃H₁₀BrClNO₂S: 357.9299, found: 357.9300.



***N*-(2-Bromo-4-chlorobenzylidene)-4-chlorobenzenesulfonamide (2t):**

White solid, 726 mg, yield: 68%. ¹H NMR (400 MHz, CDCl₃) δ 9.40 (s, 1H), 8.14 – 8.04 (m, 1H), 8.01 – 7.90 (m, 2H), 7.71 (s, 1H), 7.55 (d, *J* = 6.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 168.7, 142.1, 140.7, 136.1, 133.6, 131.4, 129.7, 129.6, 129.5, 129.3, 128.6. HRMS (EI): *m/z* [M + H]⁺ calcd for C₁₃H₉BrCl₂NO₂S: 391.8909, found: 391.8909.

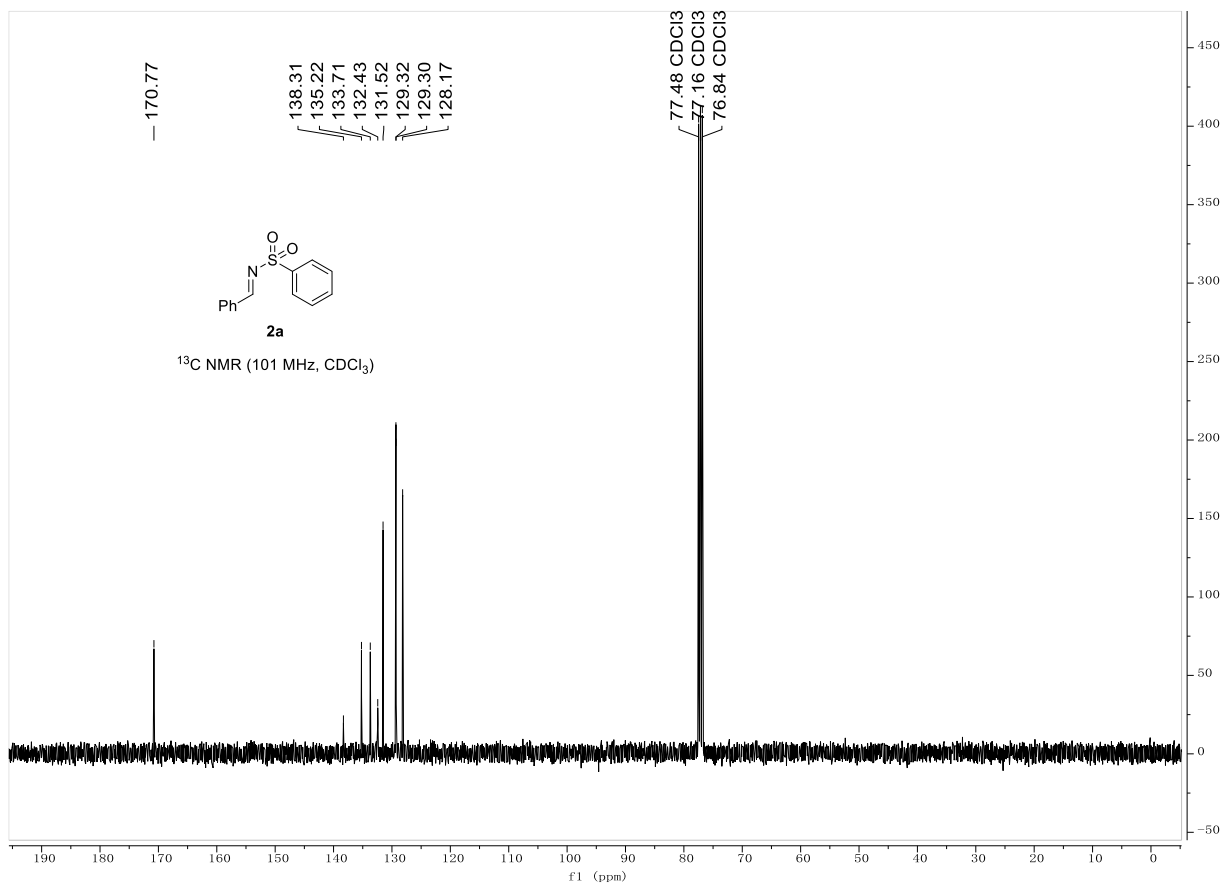
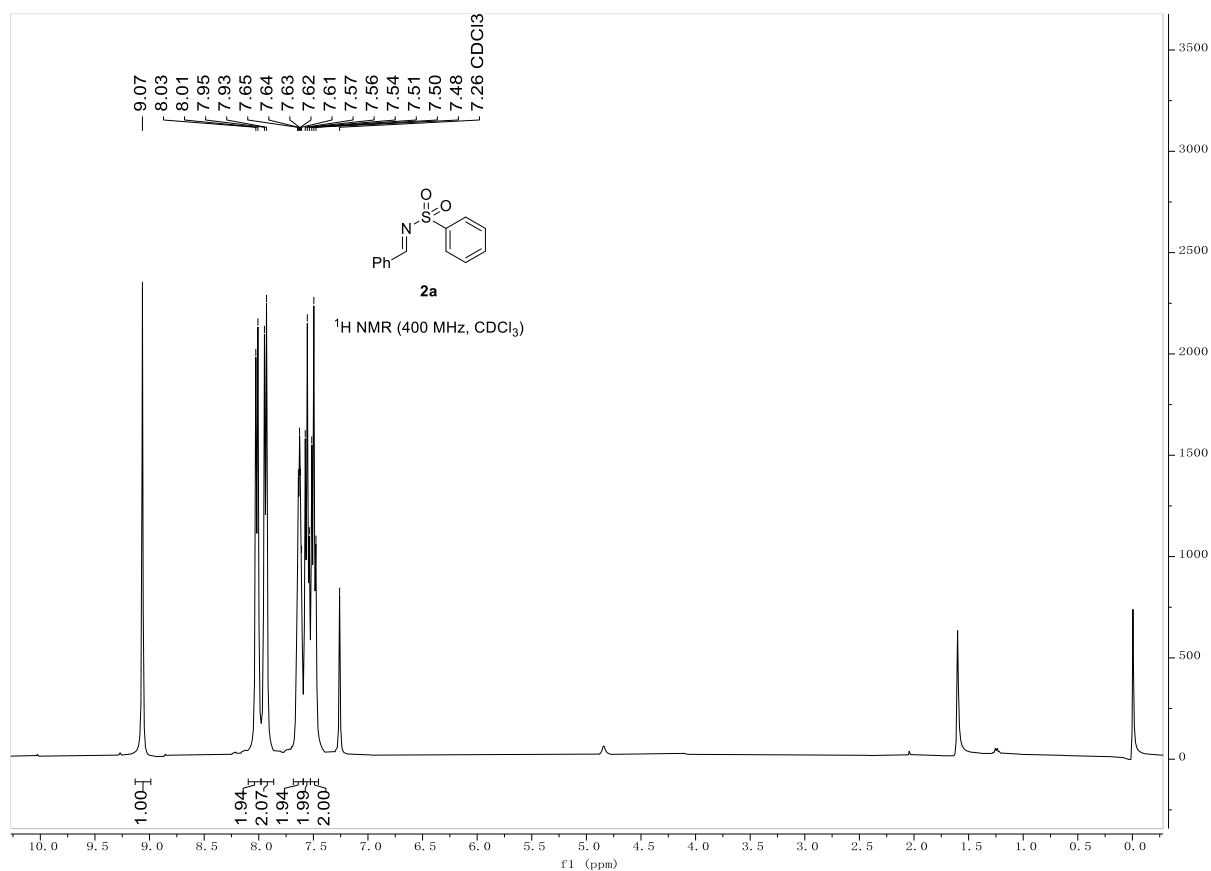


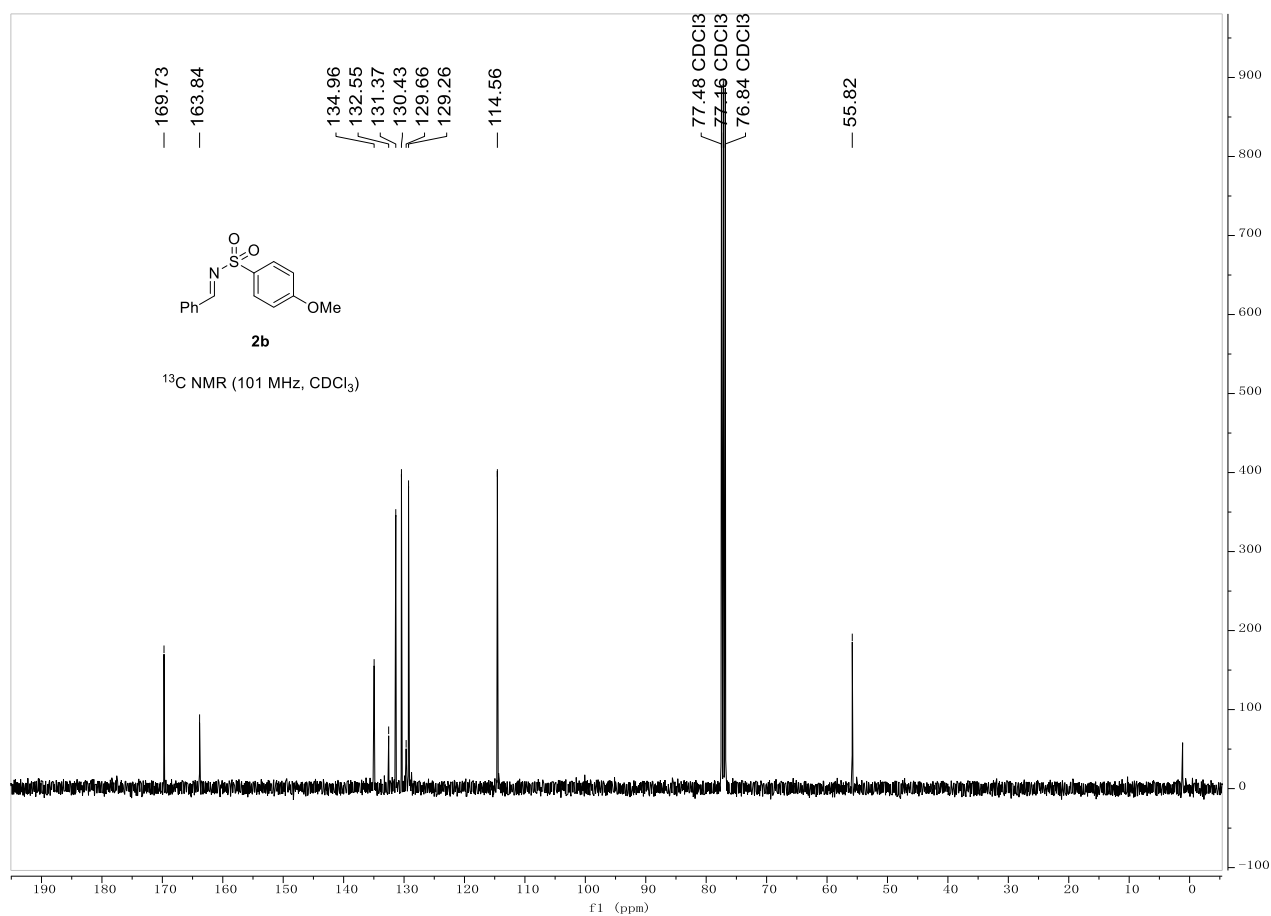
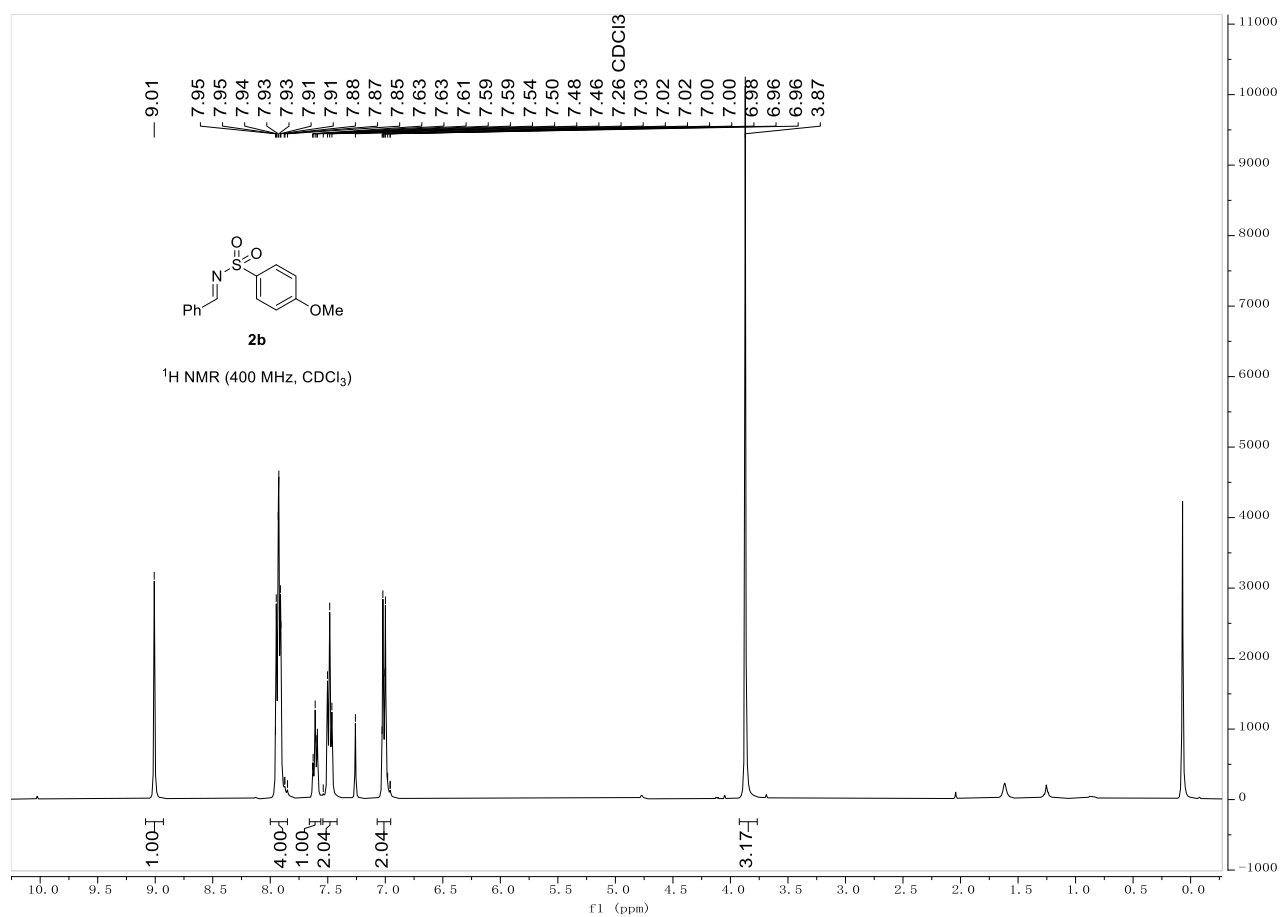
(R)-N-benzylidene-2-methylpropane-2-sulfinamide (2v): White solid, 439 mg, yield: 70%. ¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 1H), 7.84 (d, *J* = 7.0 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.47 – 7.43 (m, 2H), 1.25 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 162.8, 134.2, 132.5, 129.4, 129.0, 57.8, 22.7.⁴

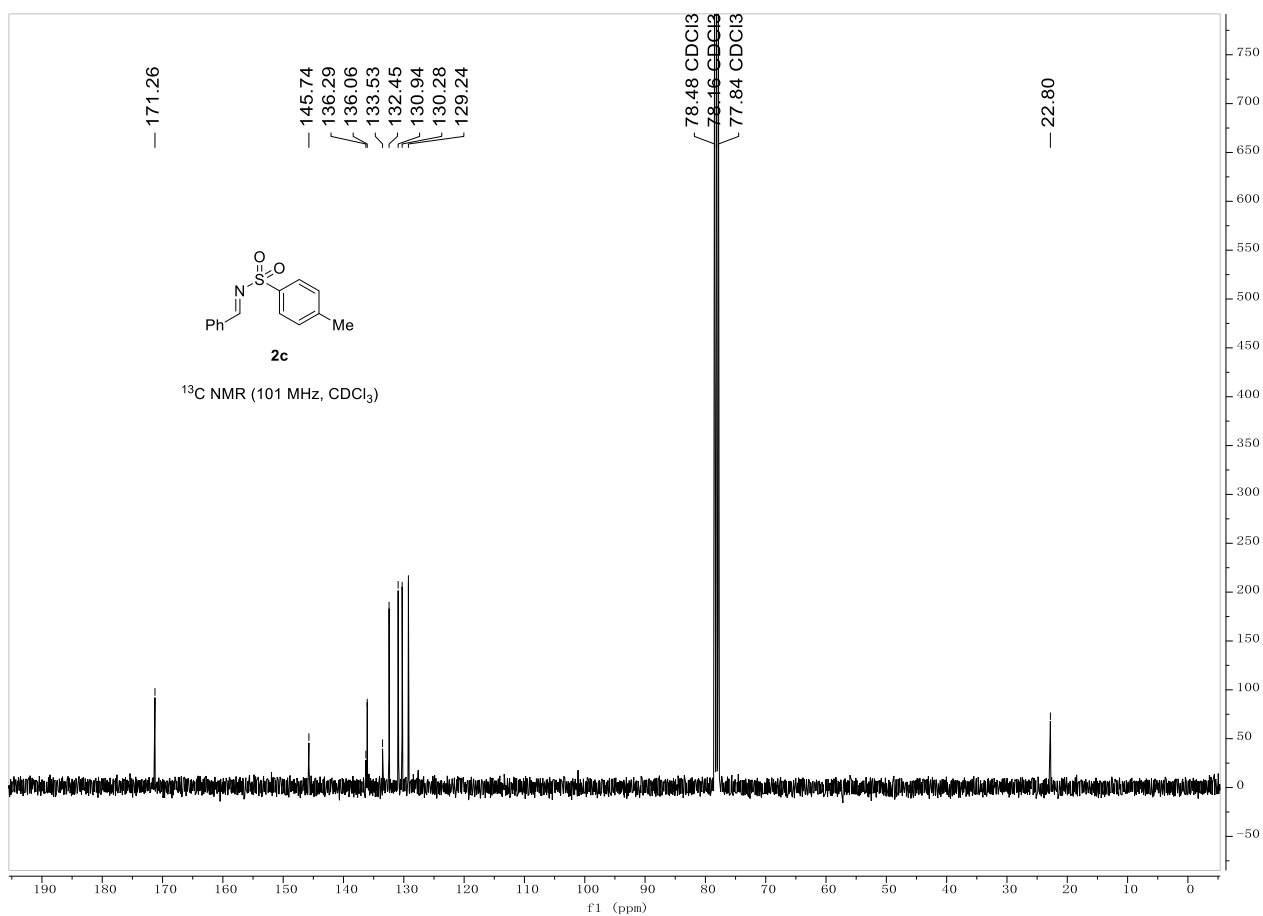
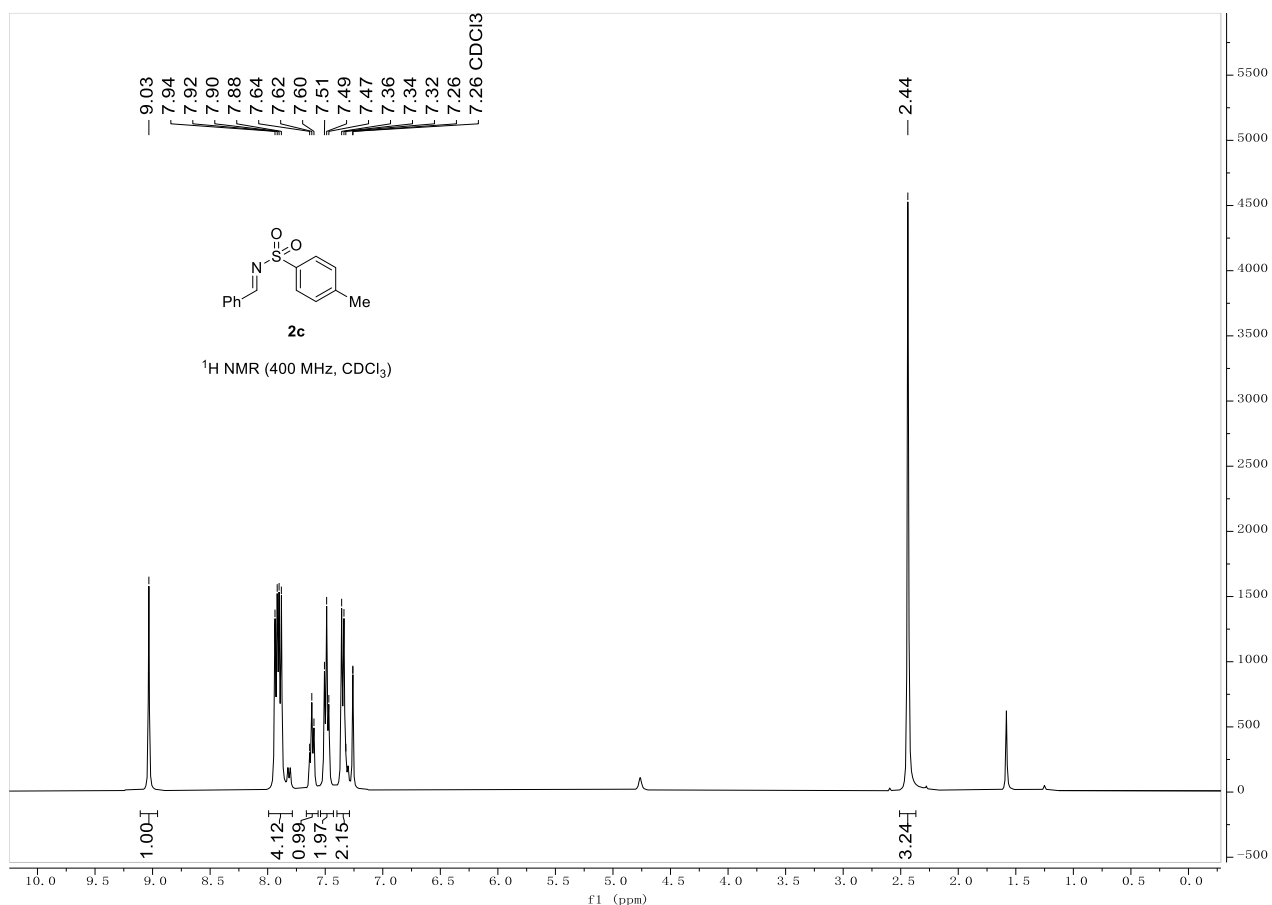
7. References

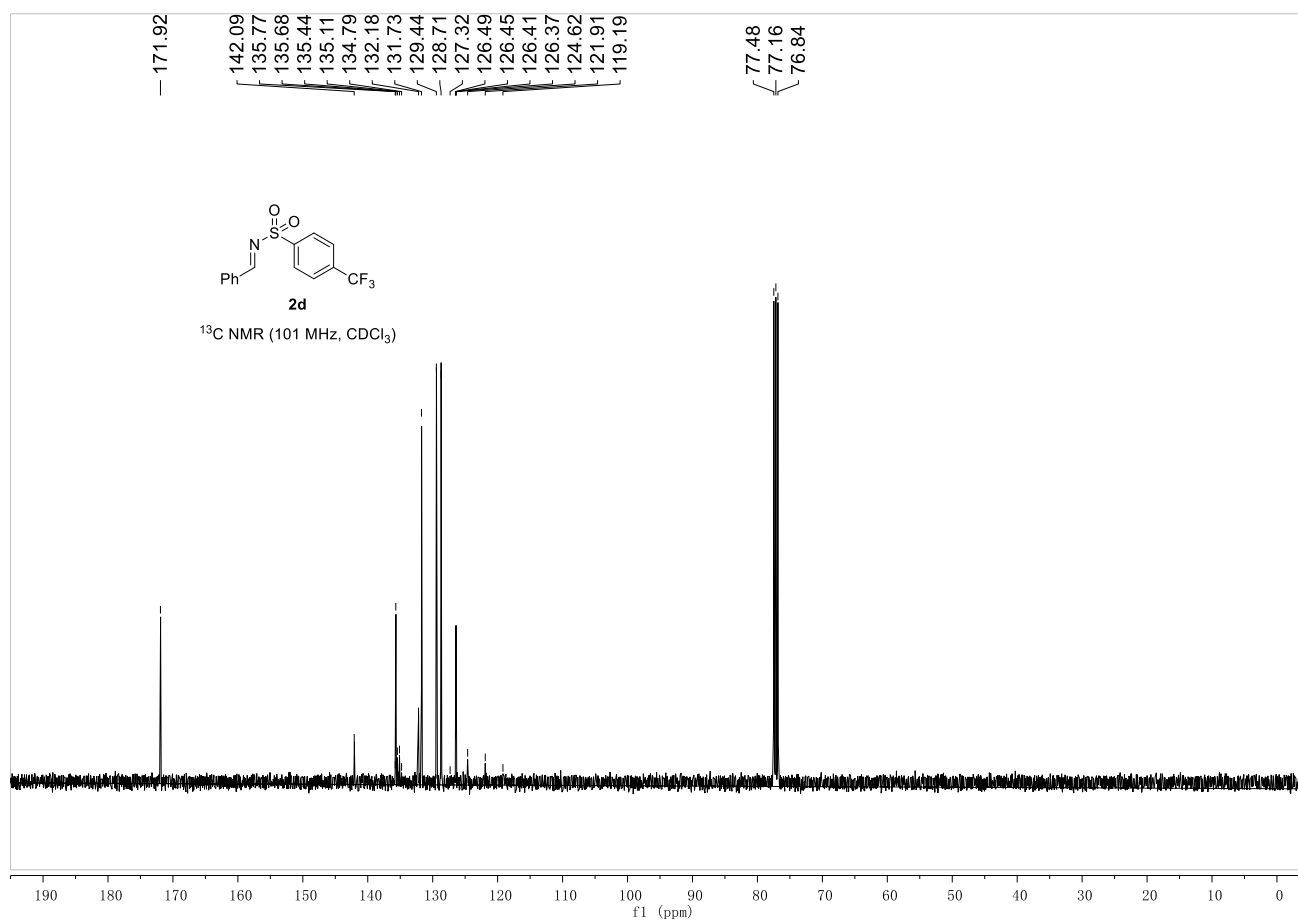
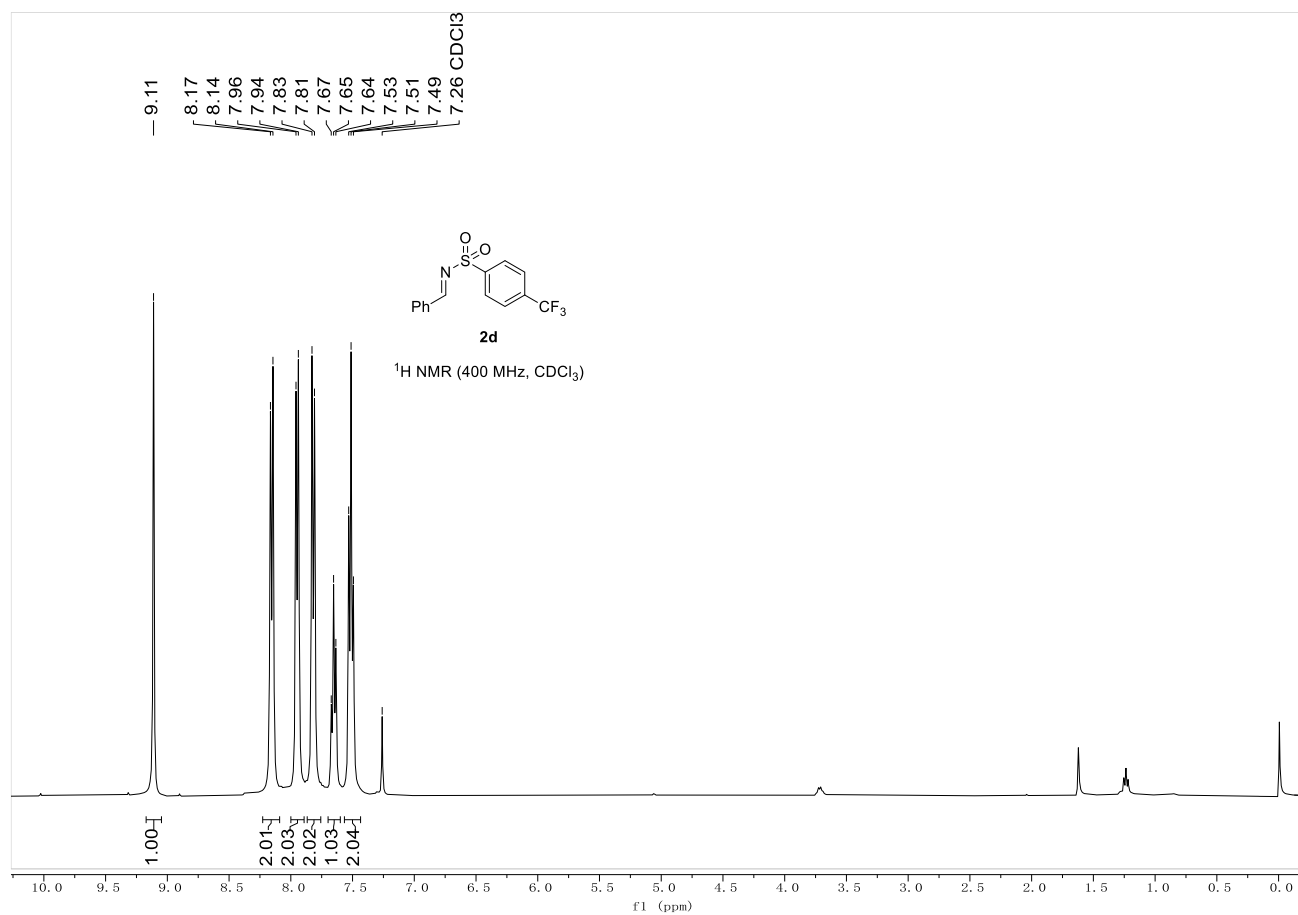
- (1) H.-M. Guo, X. Wu, Selective deoxygenative alkylation of alcohols via photocatalytic domino radical fragmentations. *Nat. Commun.*, 2021, **12**, 5365.
- (2) D.-J. Cheng, Y. Tian, S.-K. Tian, Catalytic asymmetric synthesis of dihydroquinazolinones from imines and 2-aminobenzamides. *Adv. Syn. Catal.*, 2012, **354**, 995-999.
- (3) L. I. Panferova, M. O. Zubkov, V. A. Kokorekin, V. V. Levin, A. D. Dilman, Application of chiral *N*-tert-butylsulfinyl vinyl aziridines in Rh(I) catalyzed 1,4-addition of aryl boronic acids to cyclic enones. *Angew. Chem., Int. Ed.* 2021, **60**, 2849–2854.
- (4) Q. Chen, C. Chen, F. Guo, W. Xia, Using the thiyl radical for aliphatic hydrogen-atom transfer: thiolation of unactivated C–H bonds. *Chem. Commun.*. 2013, **49**, 6433-6435.

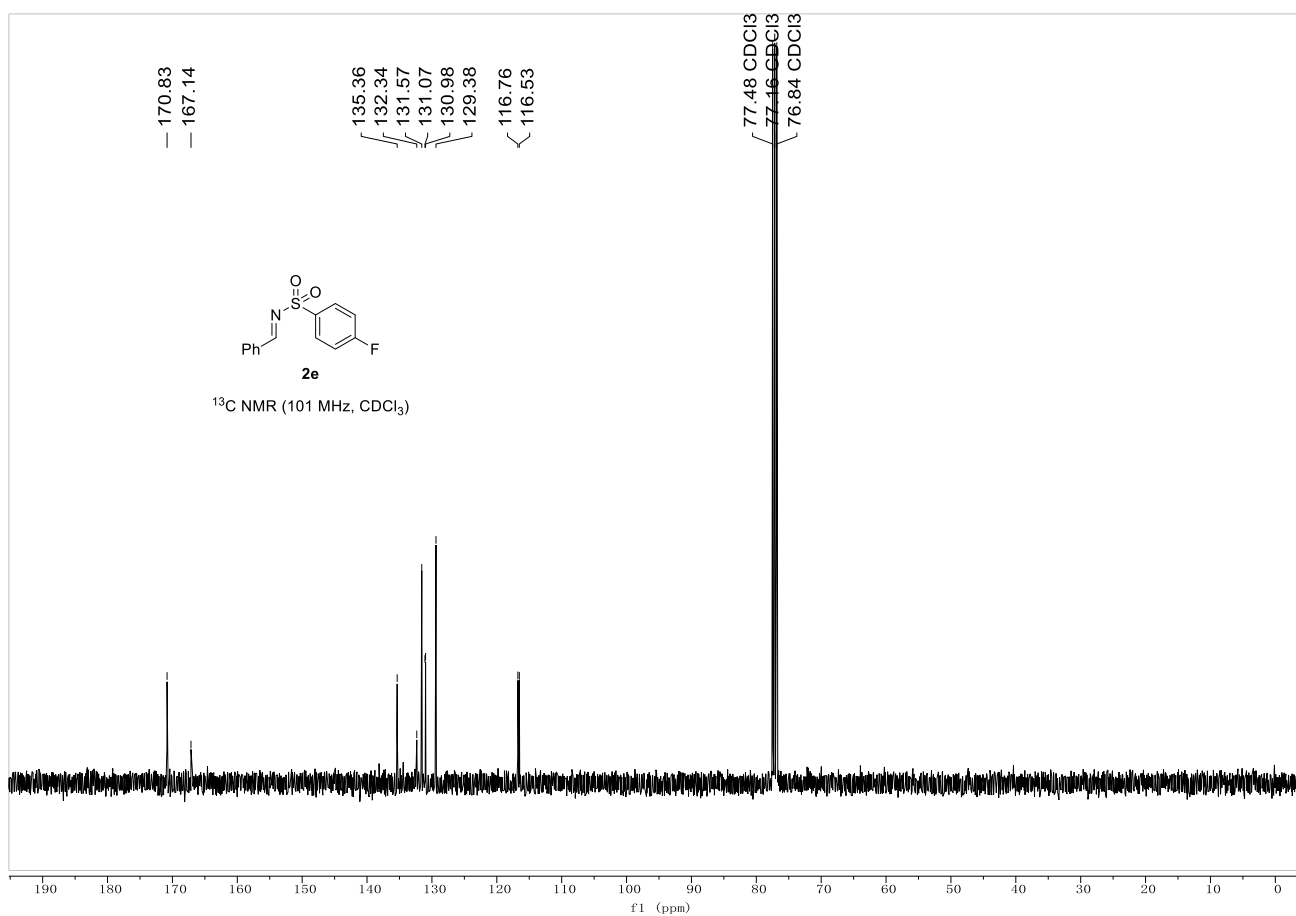
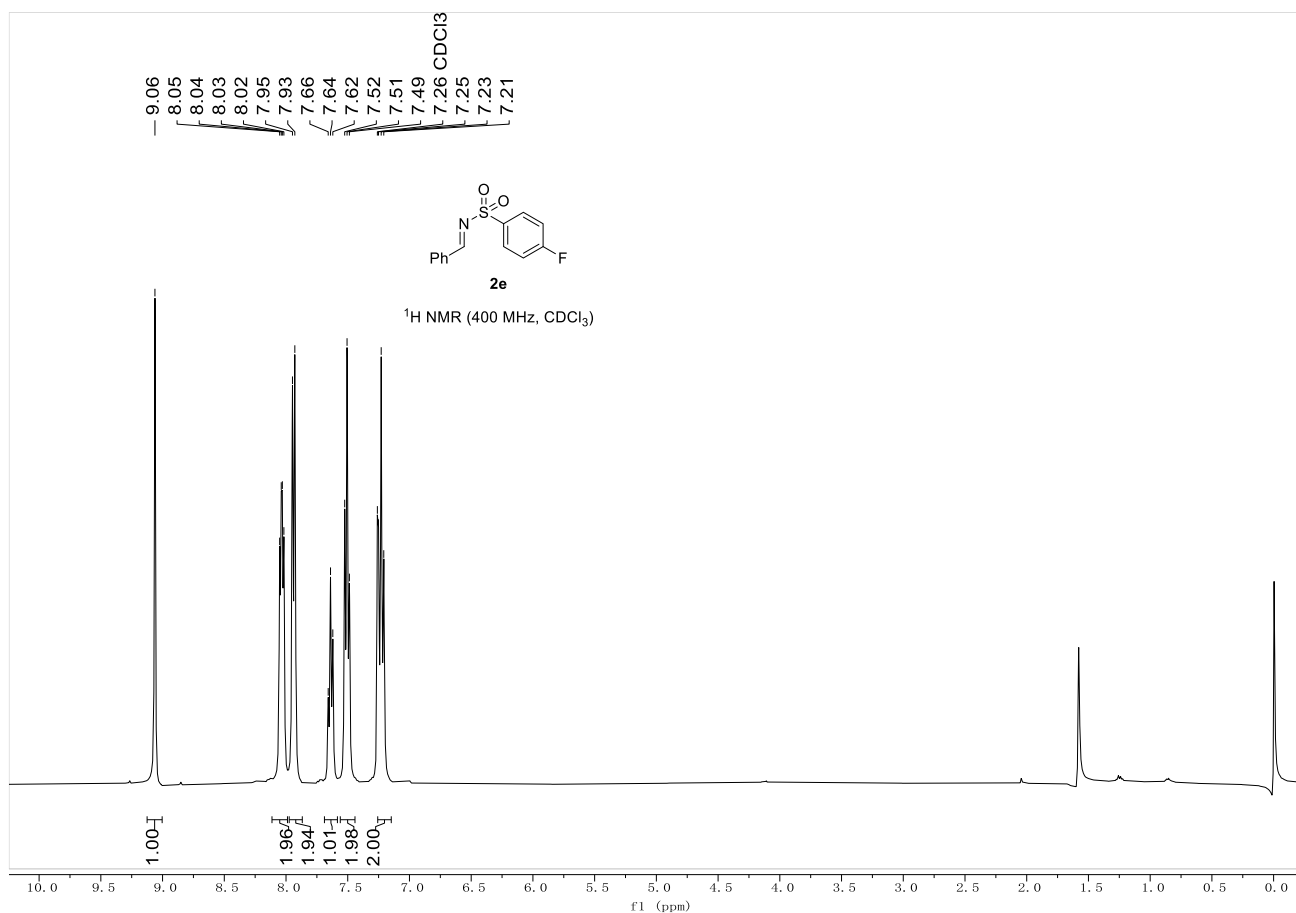
8. NMR Spectra

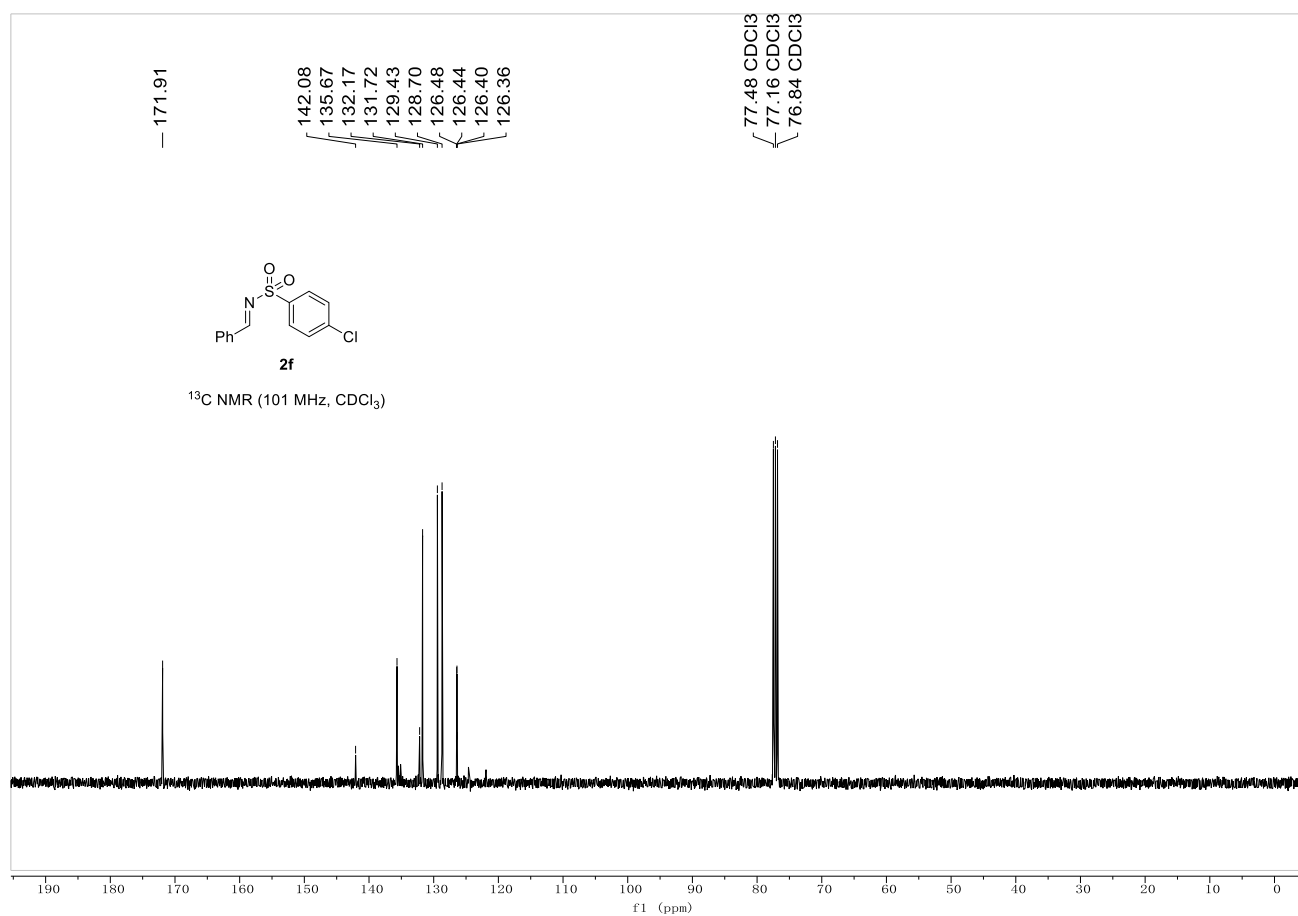
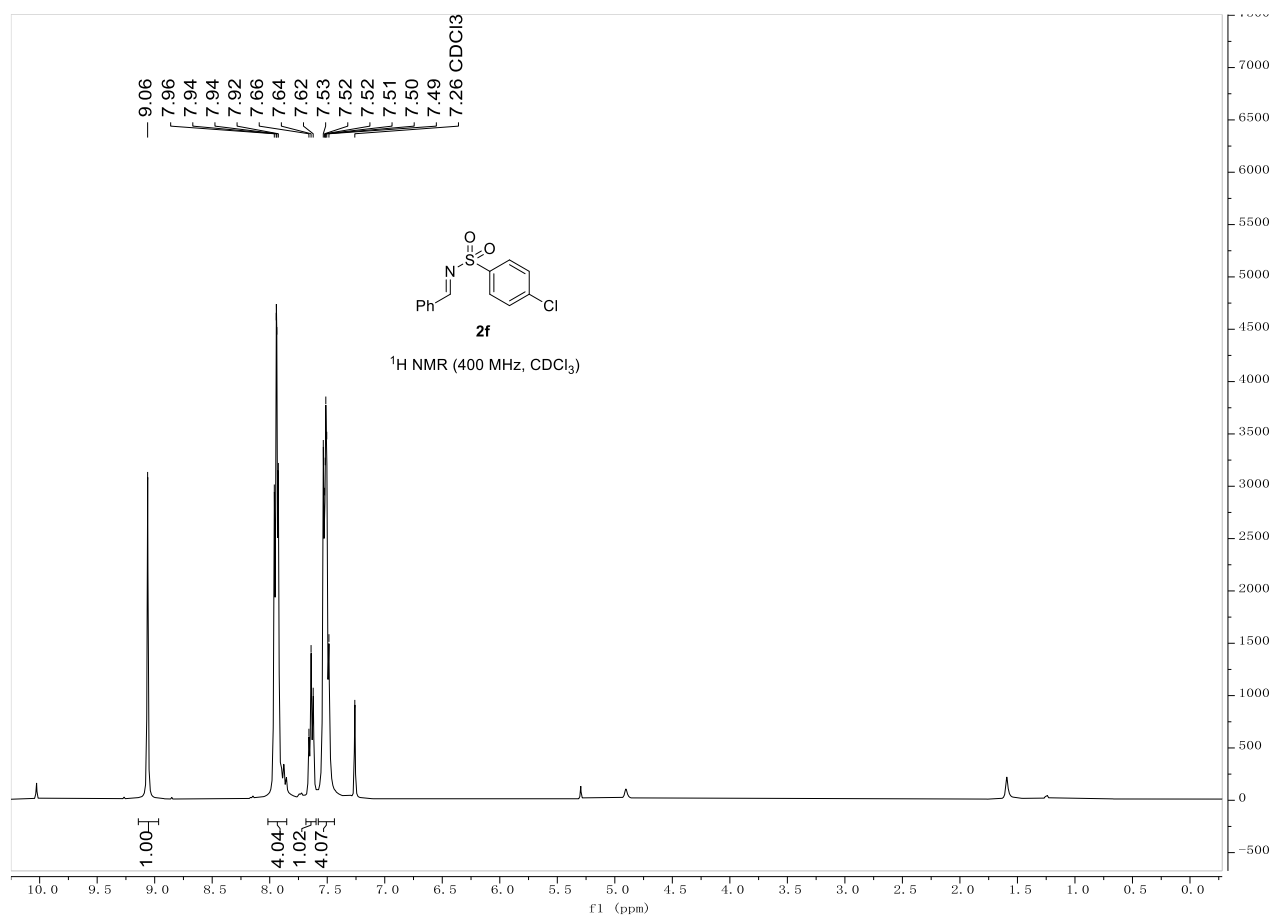


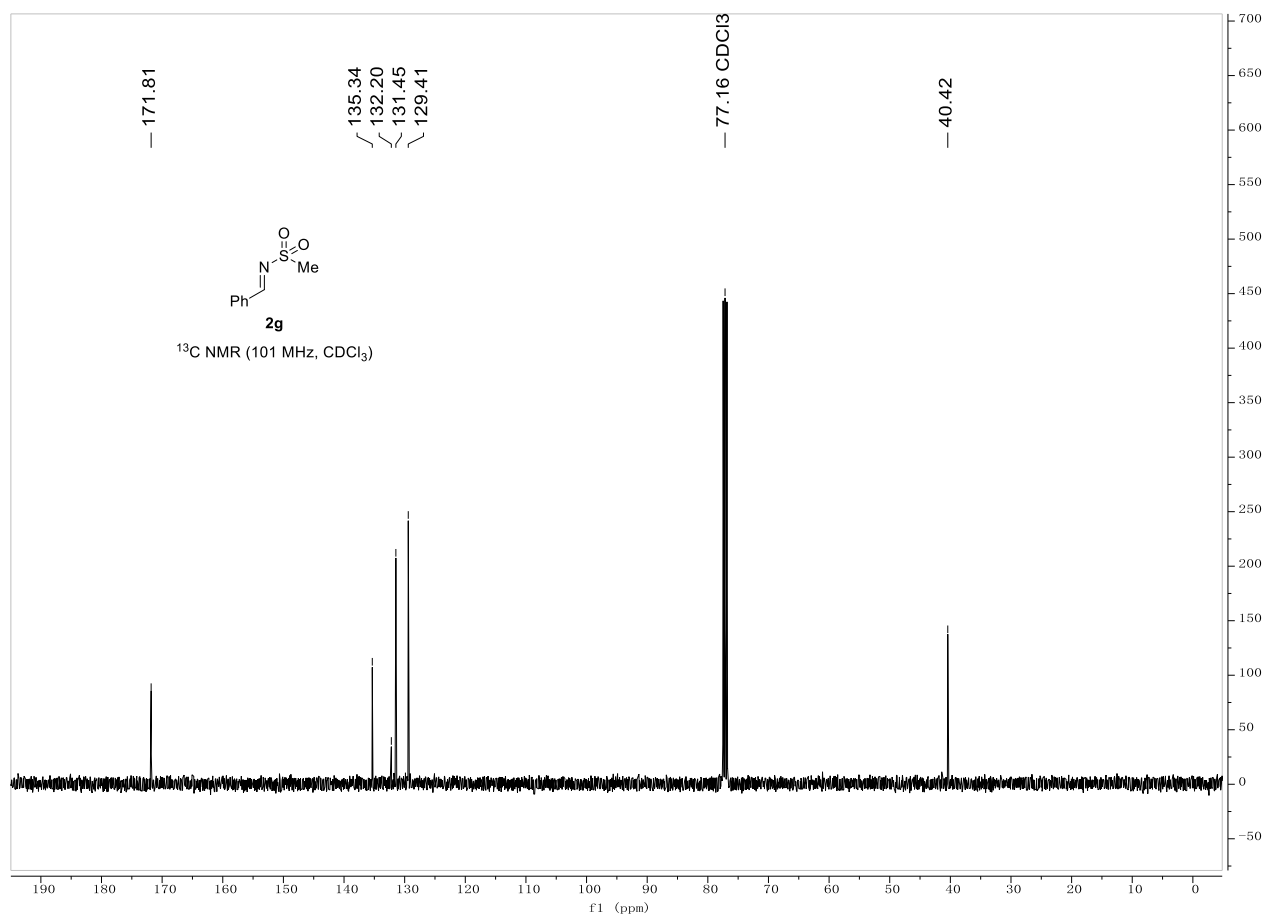
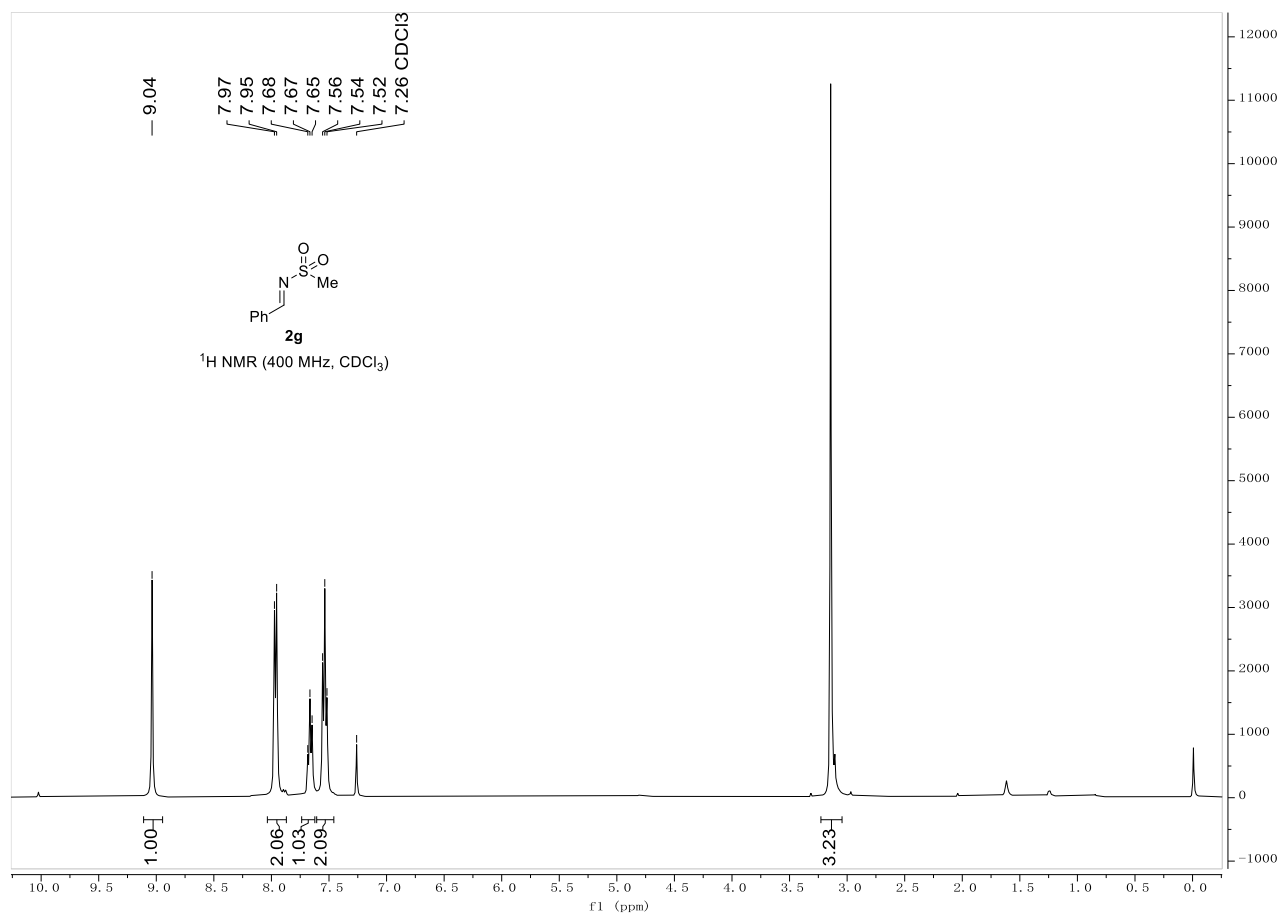


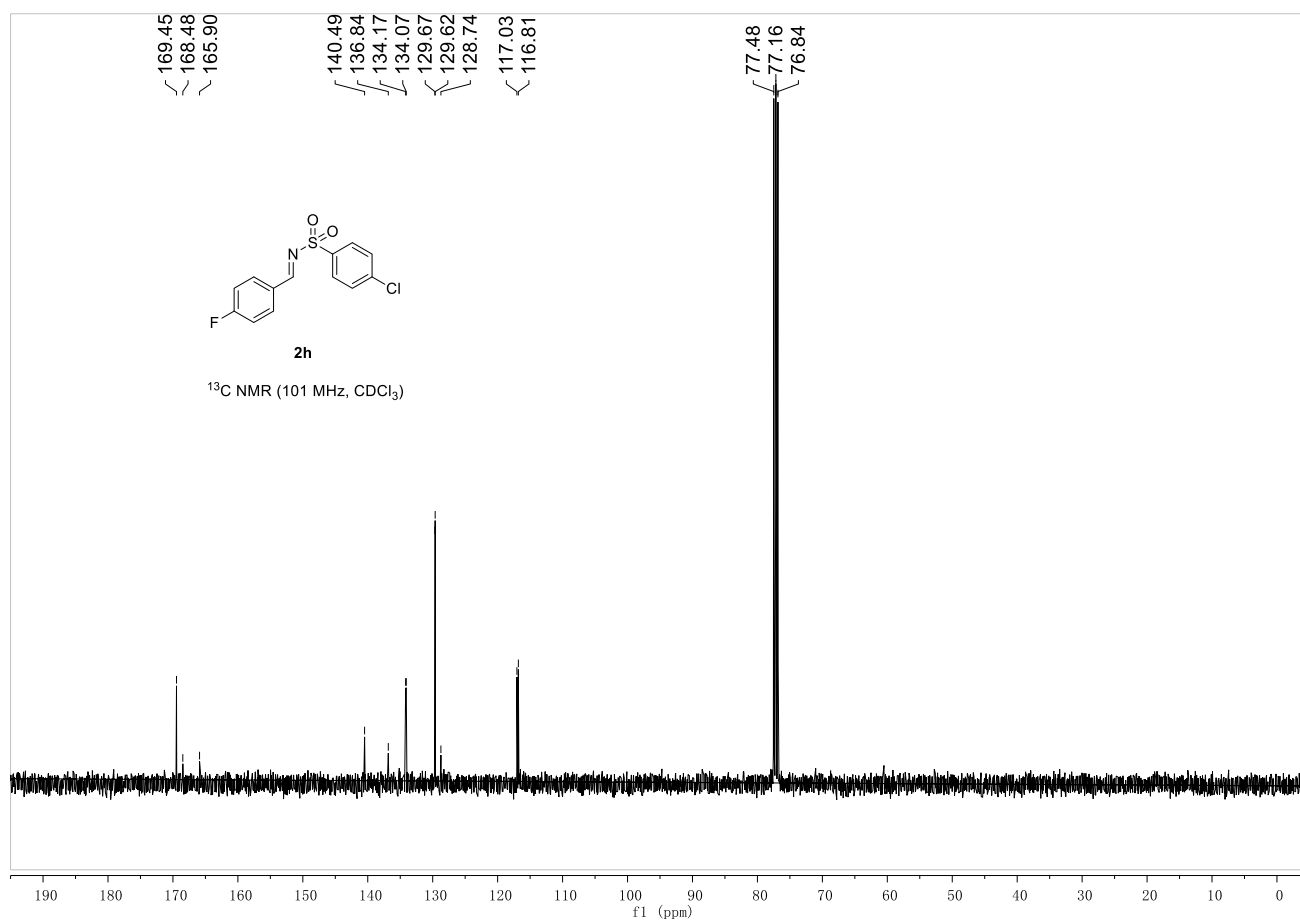
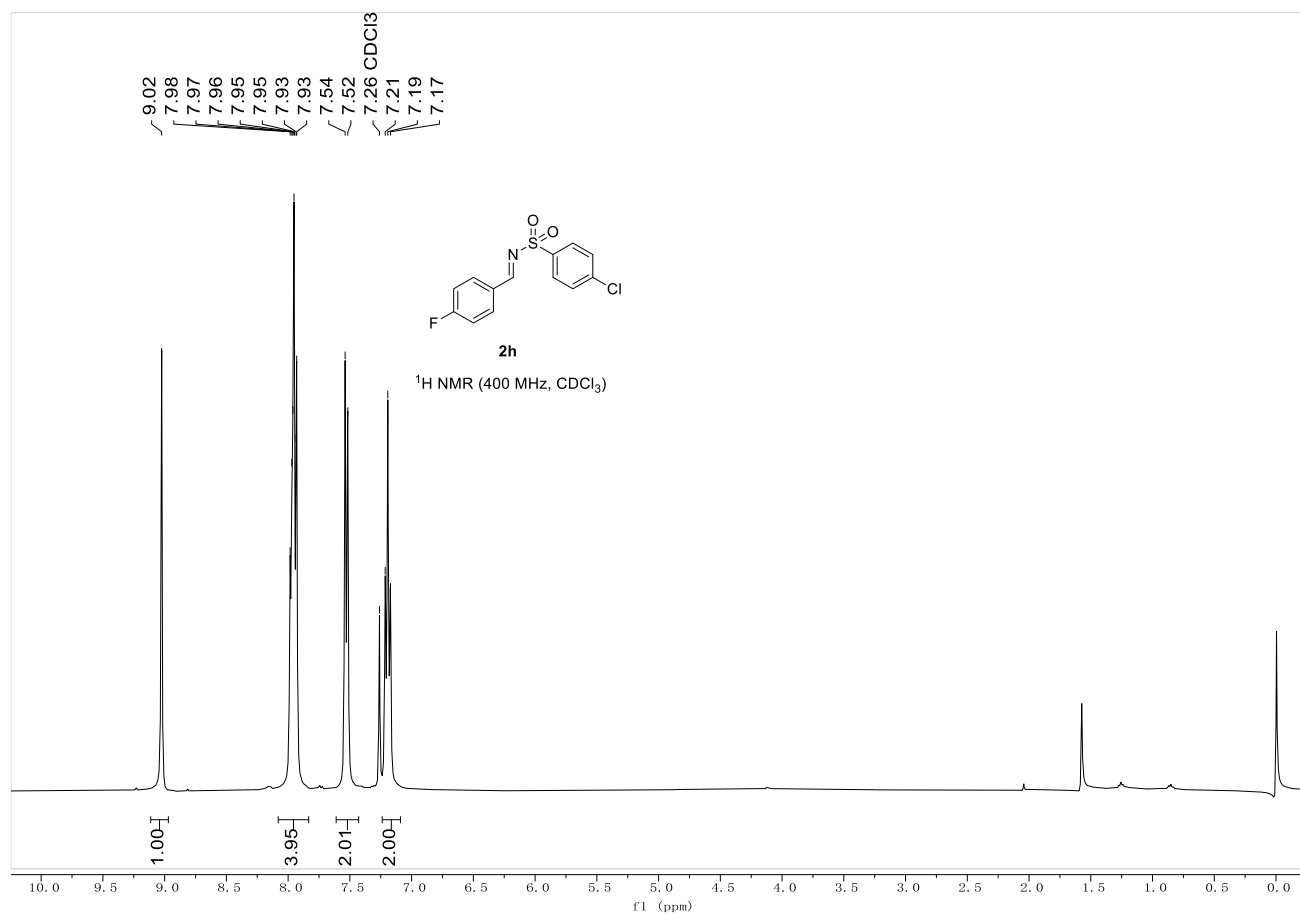


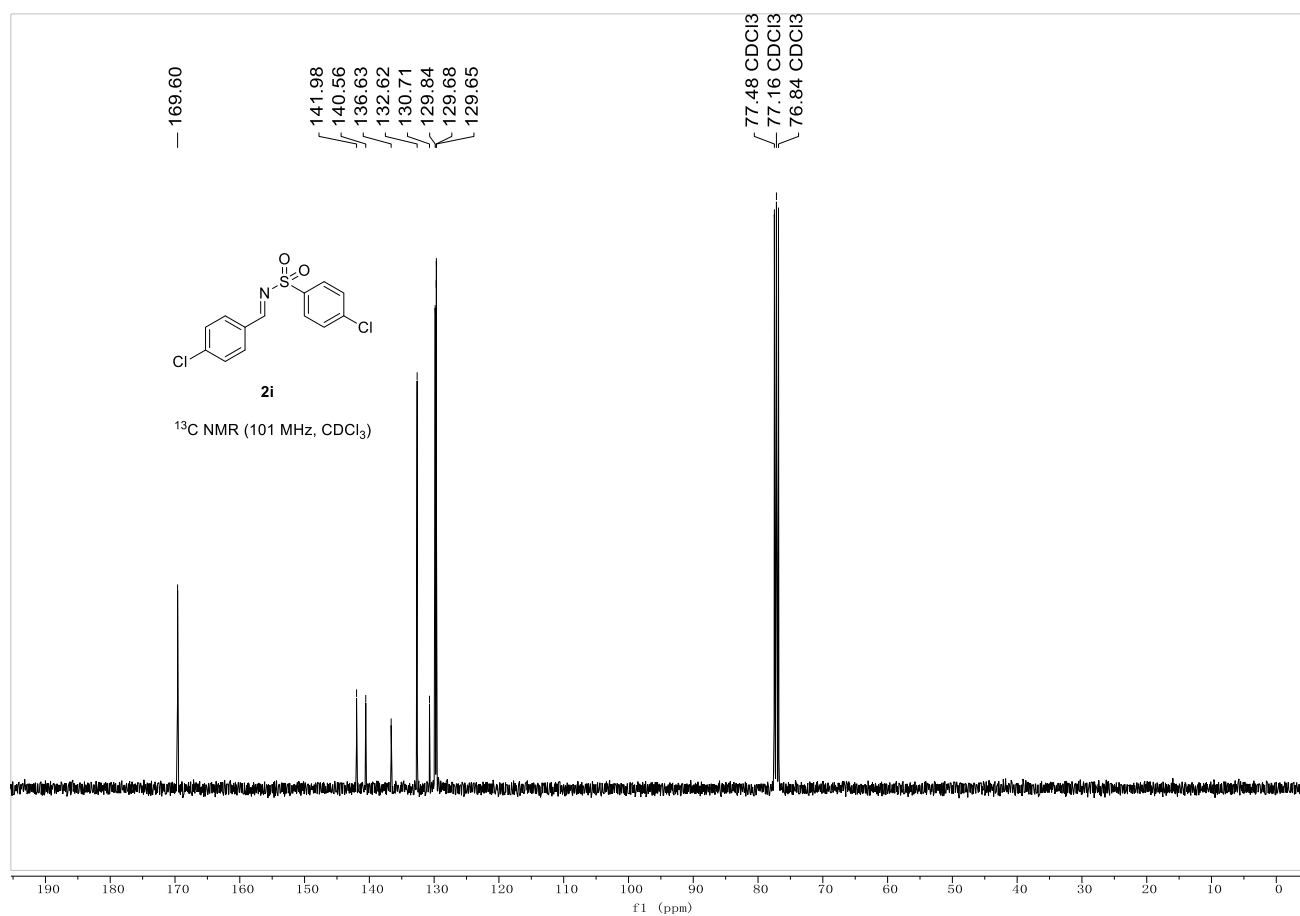
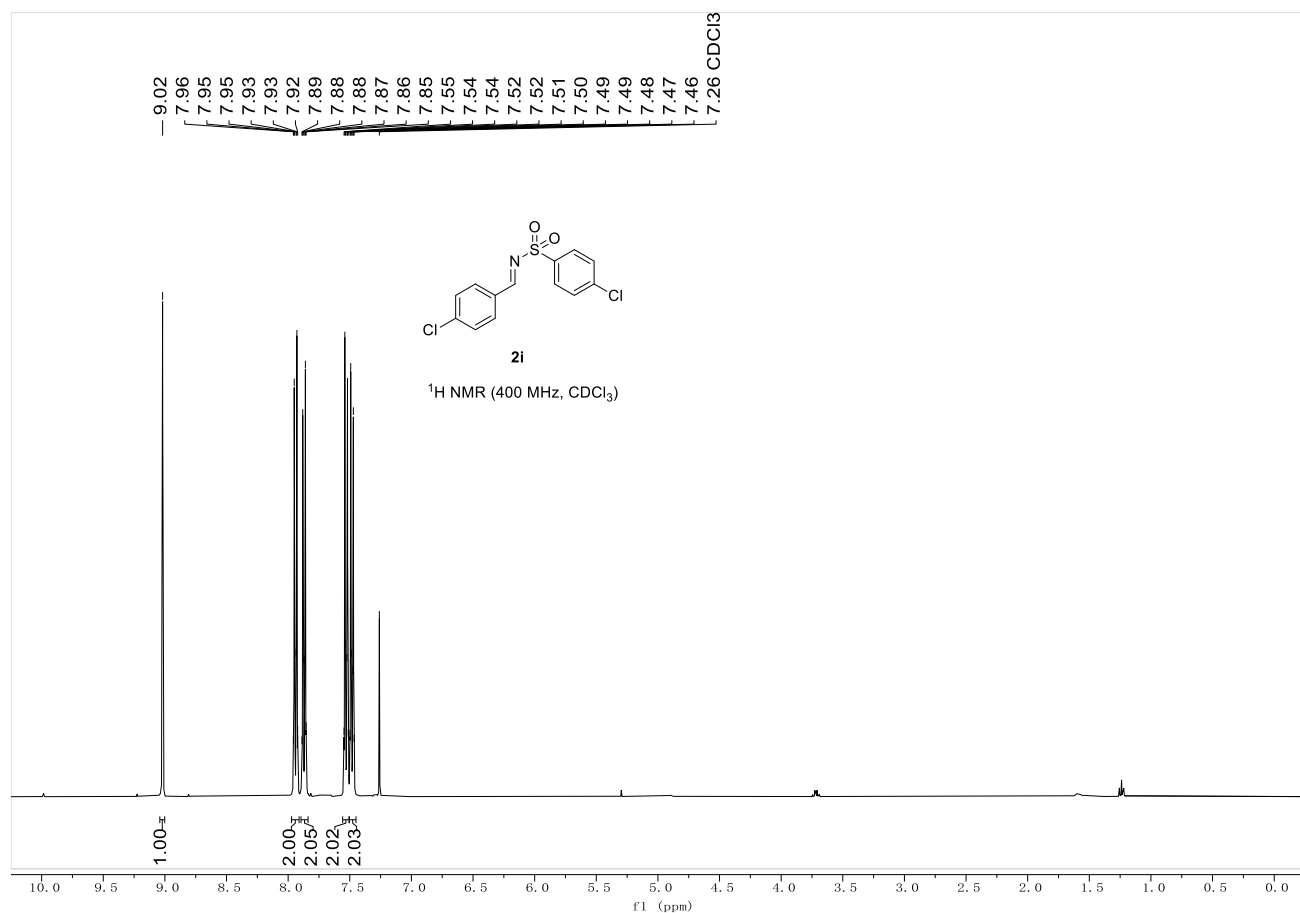


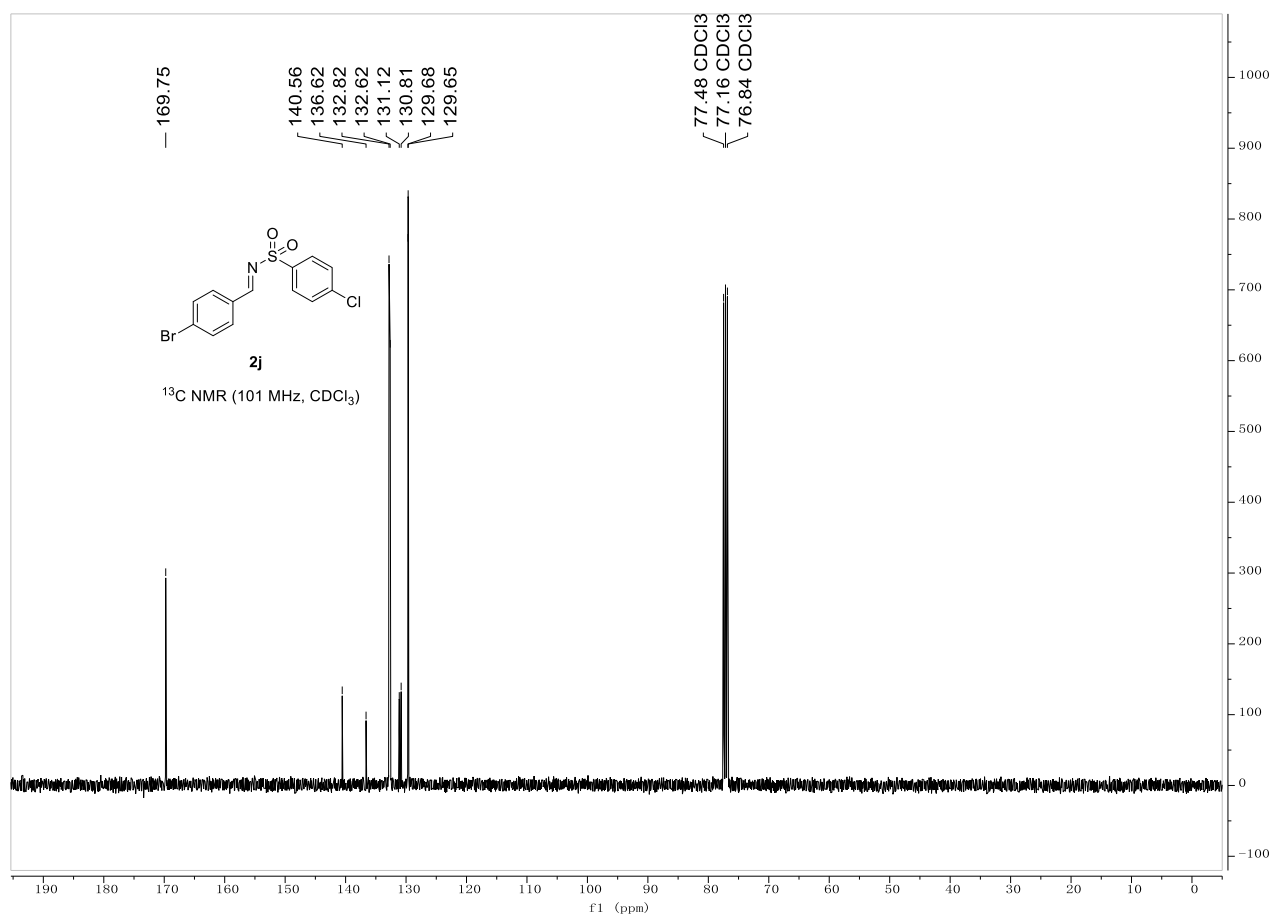
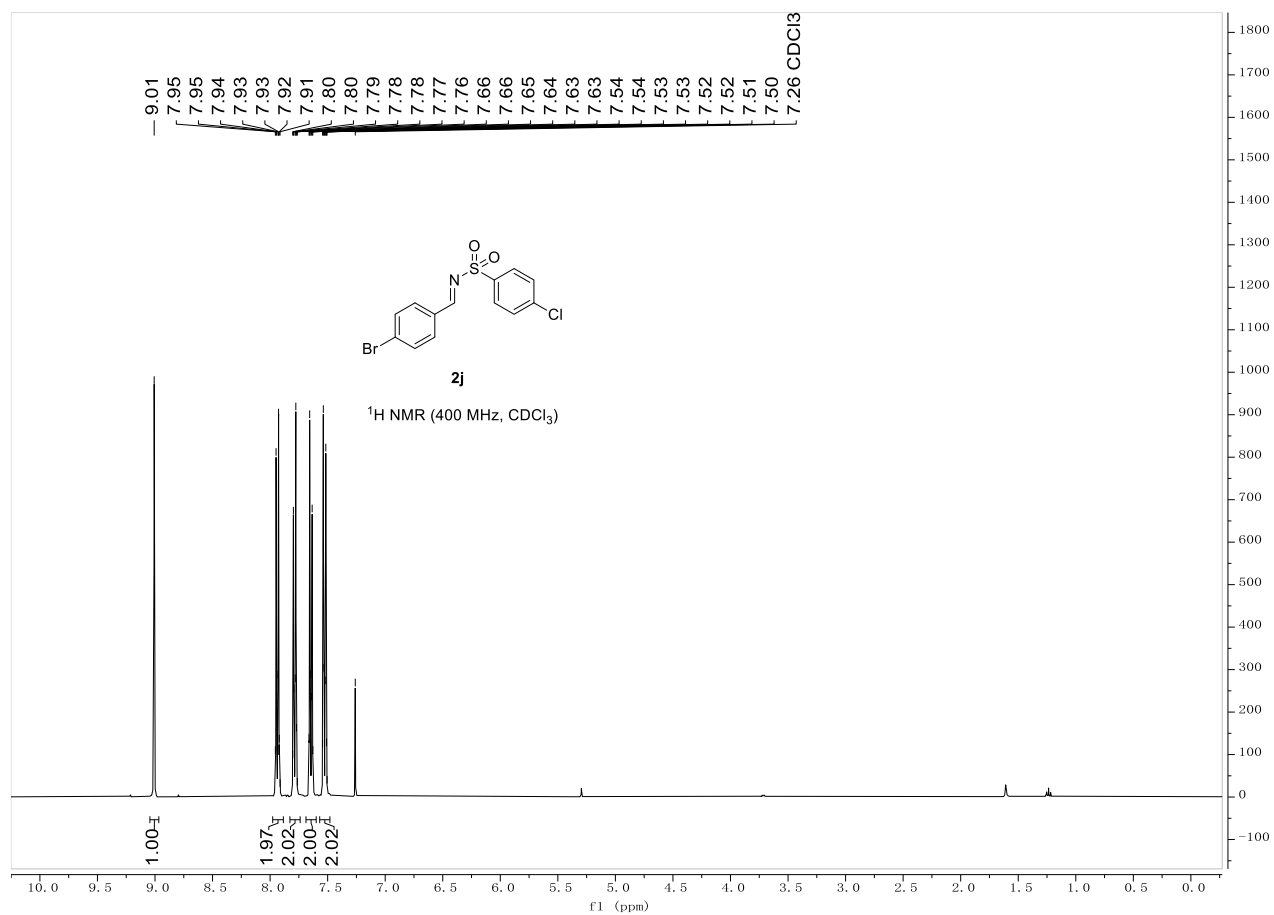


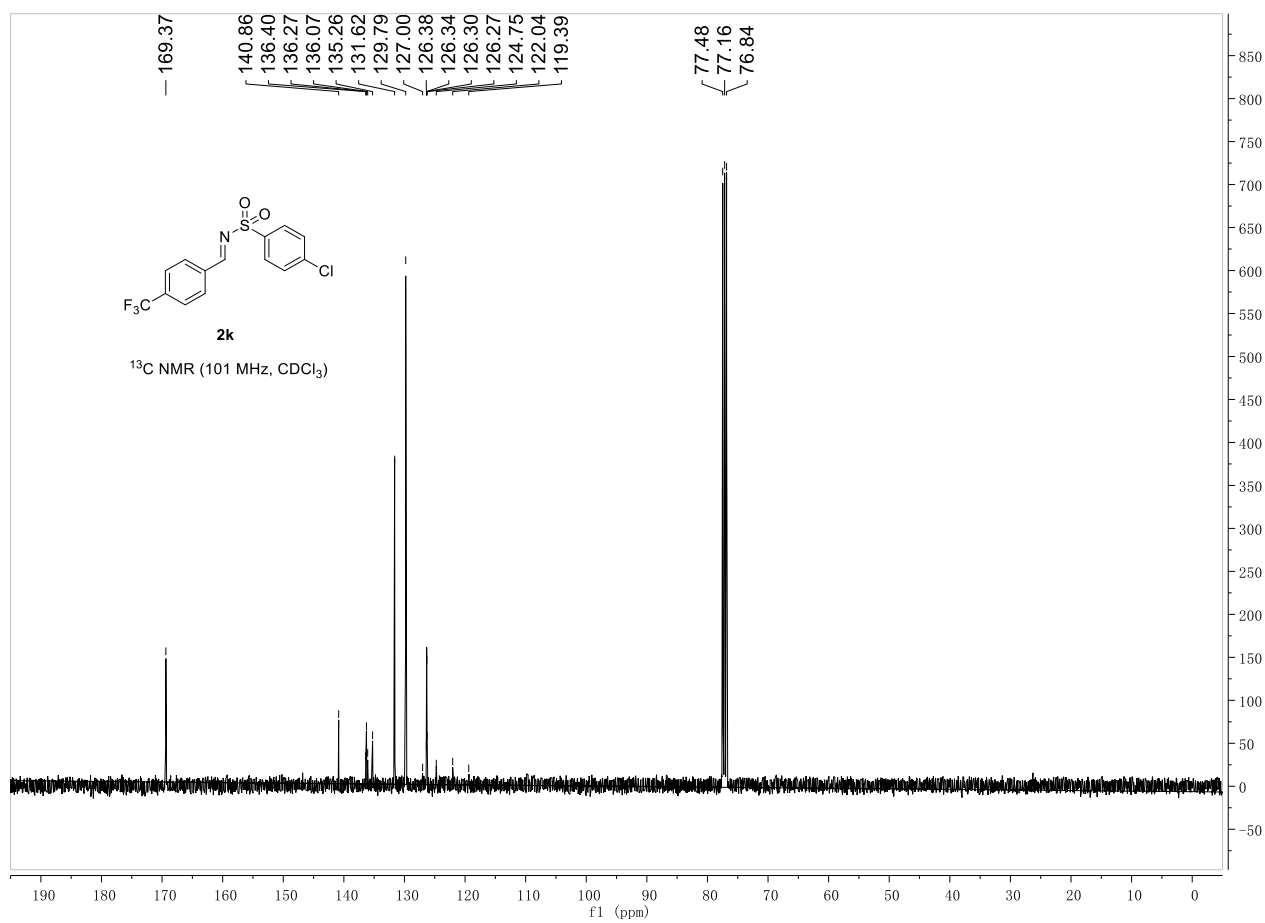
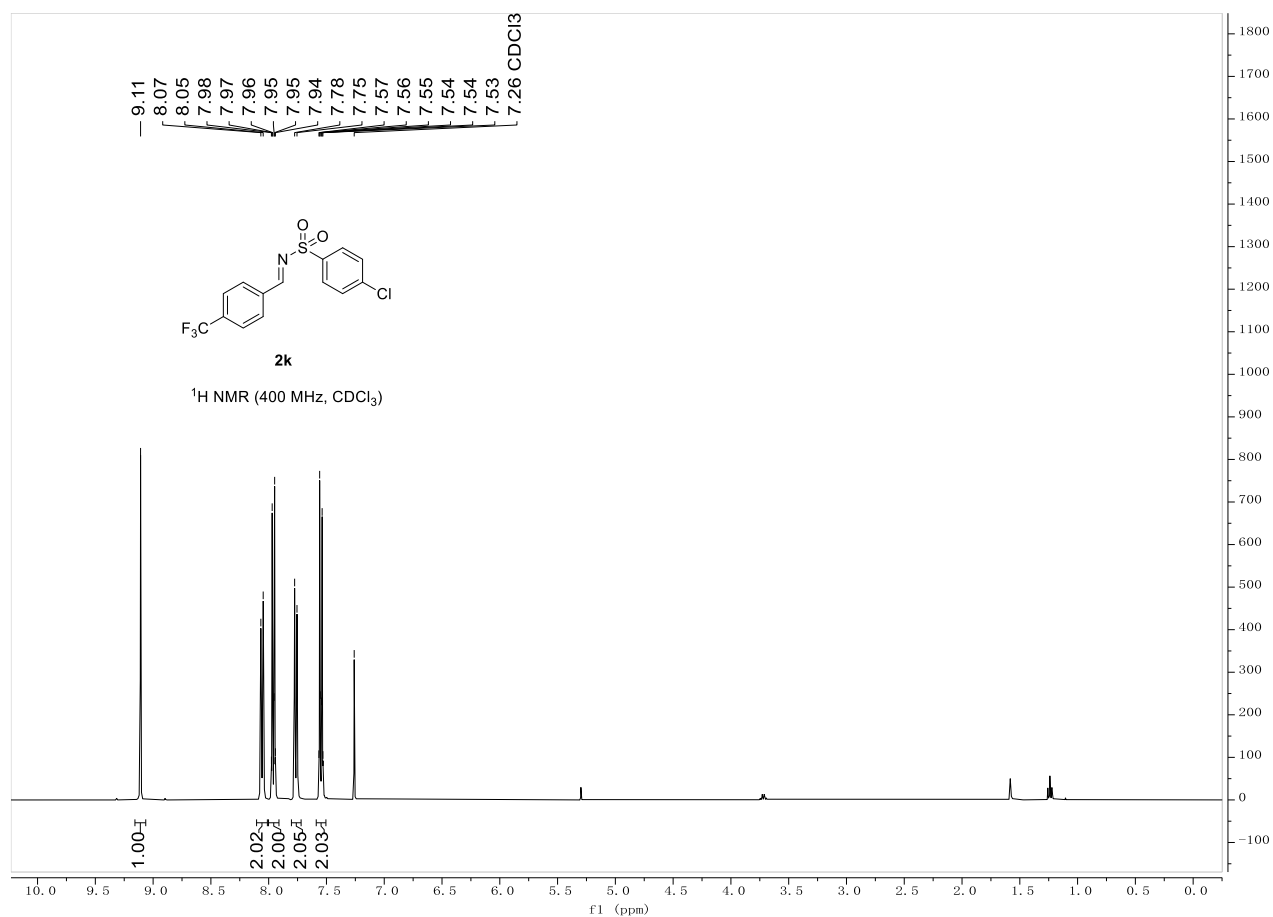


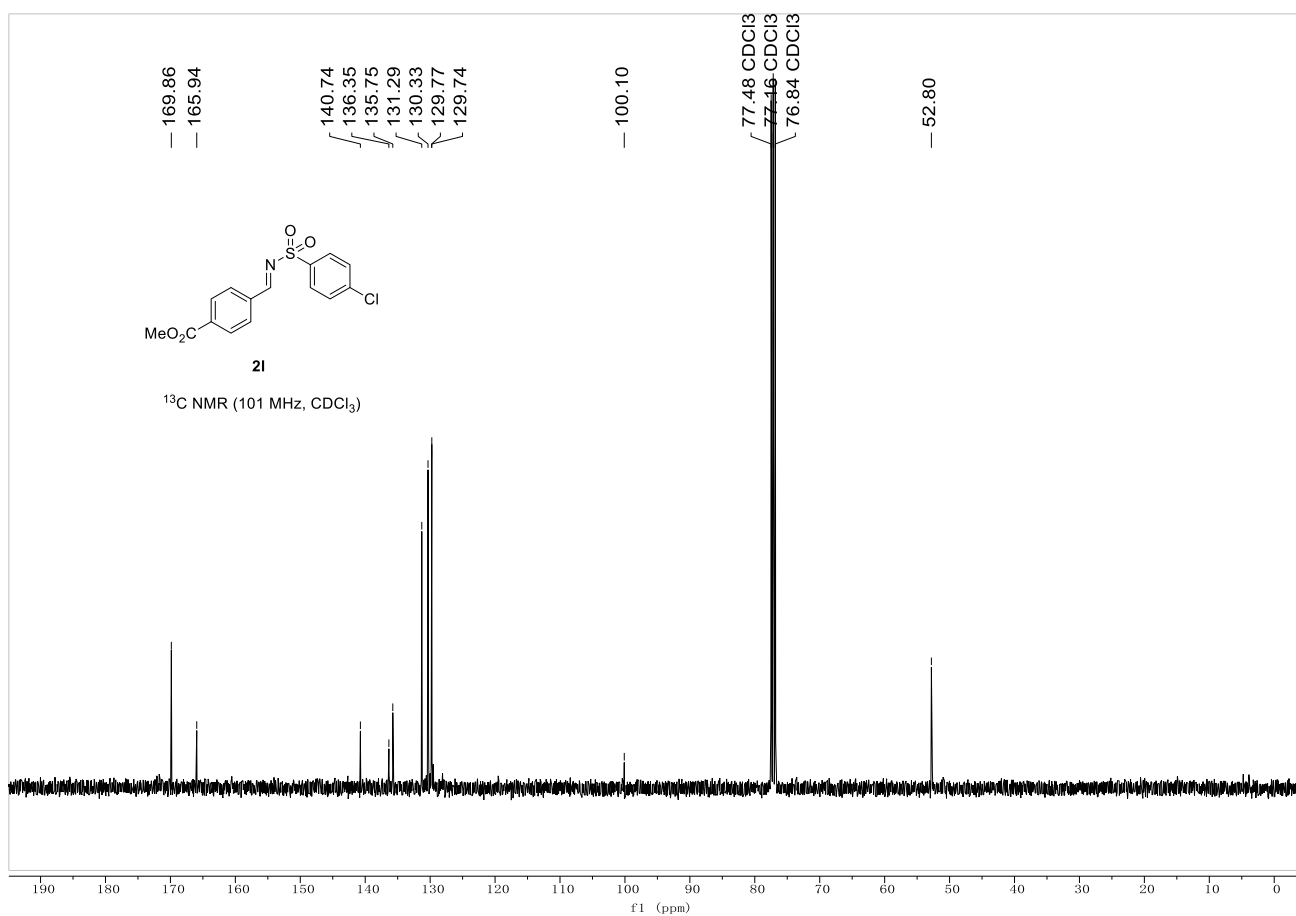
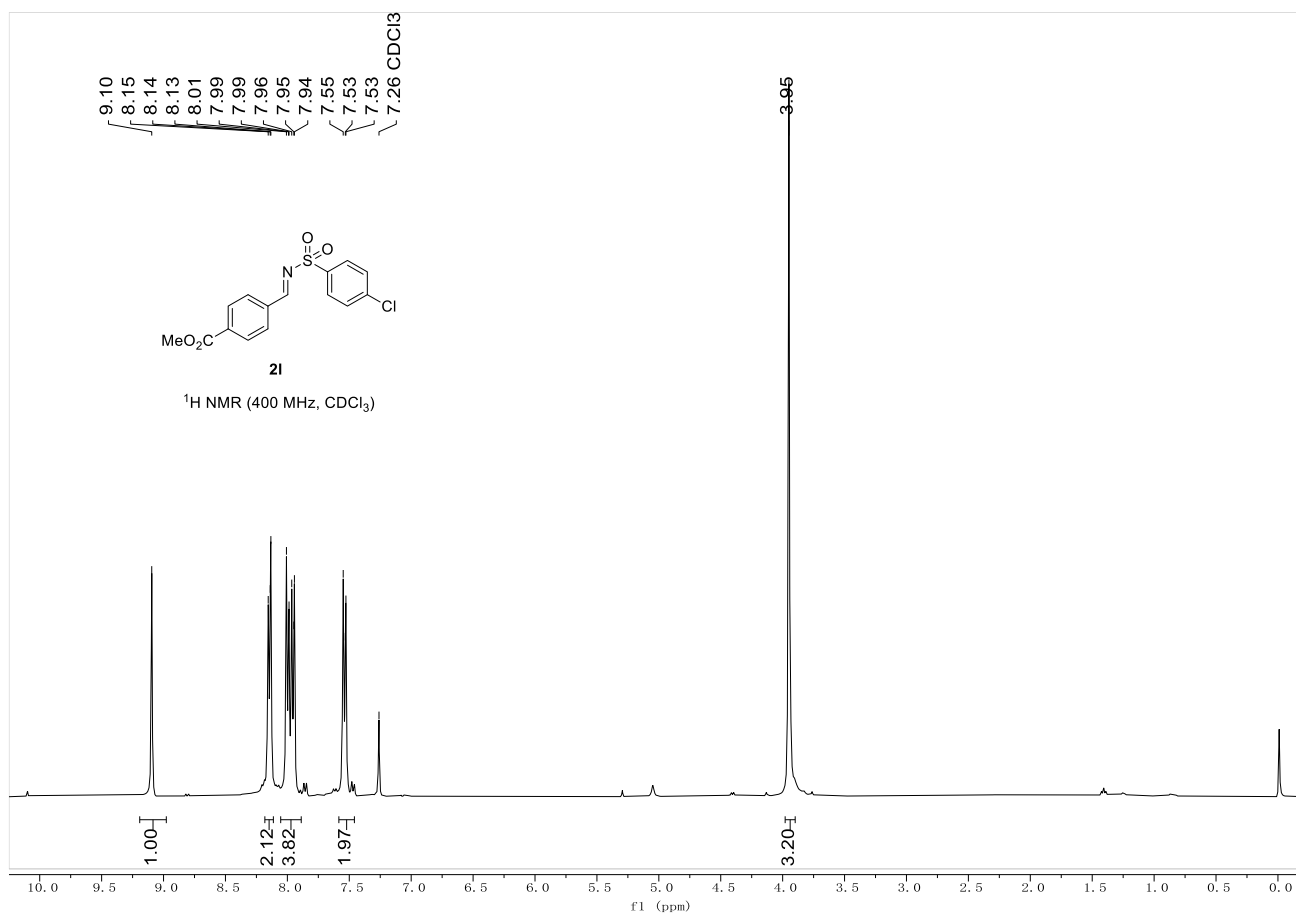


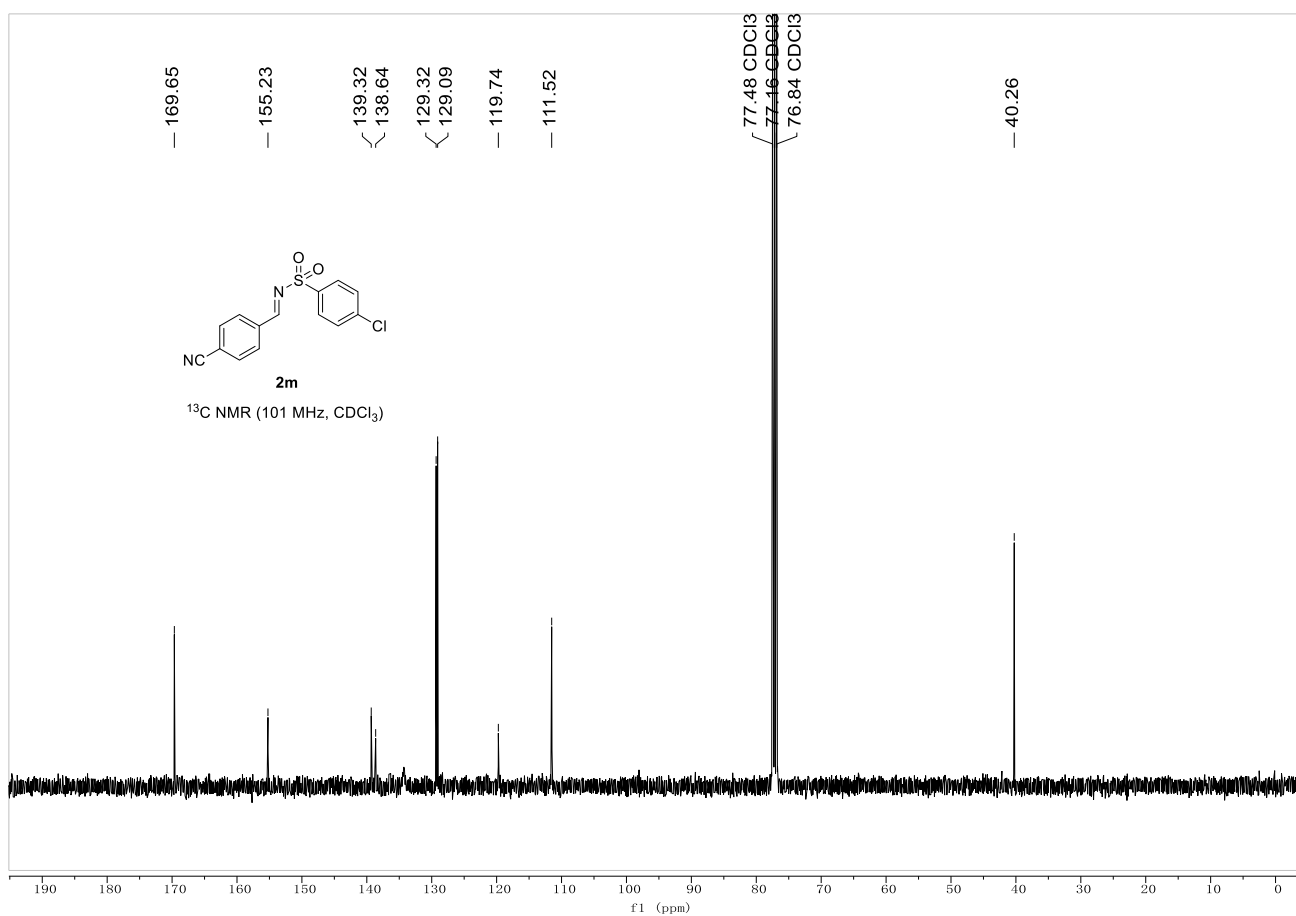
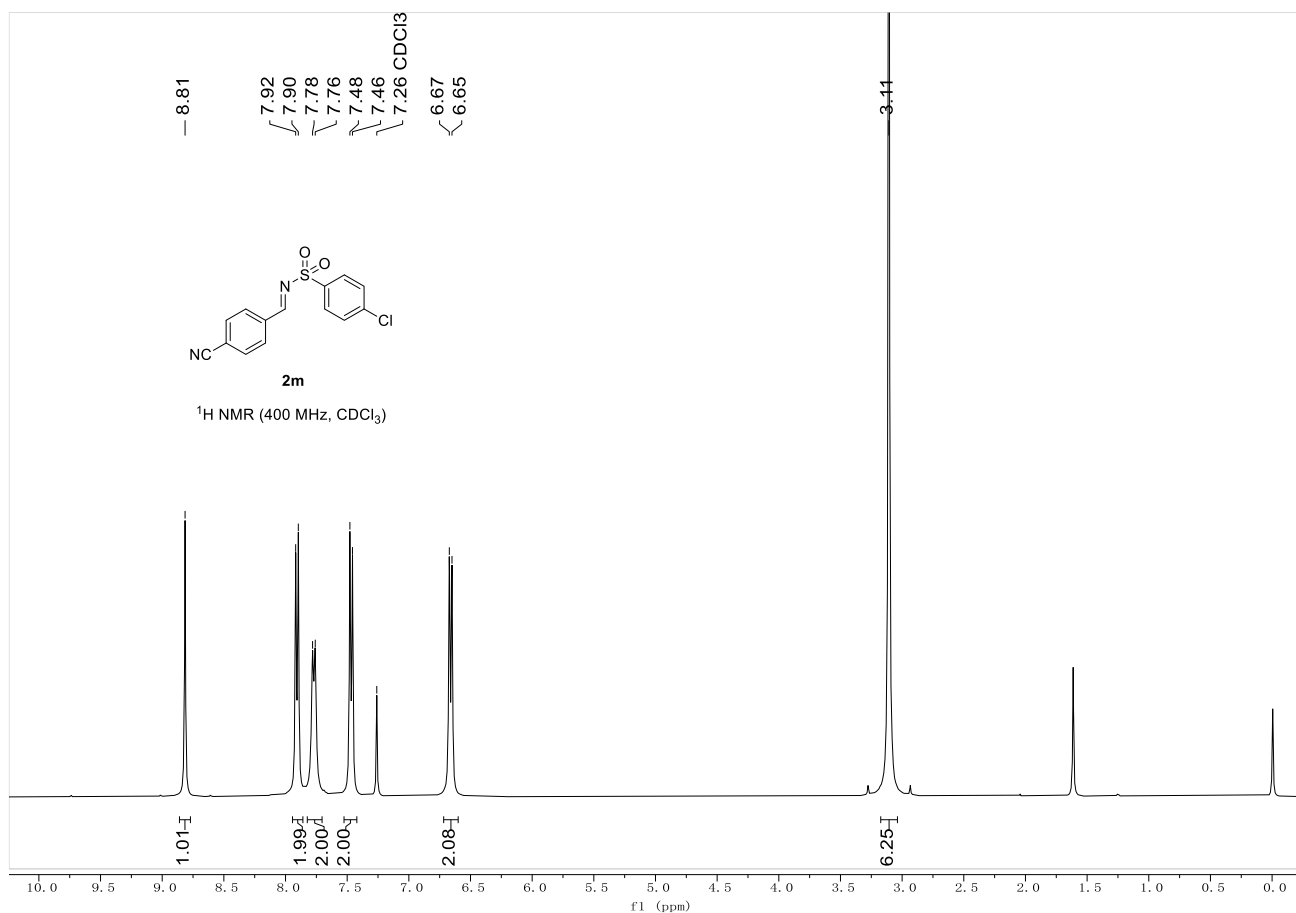


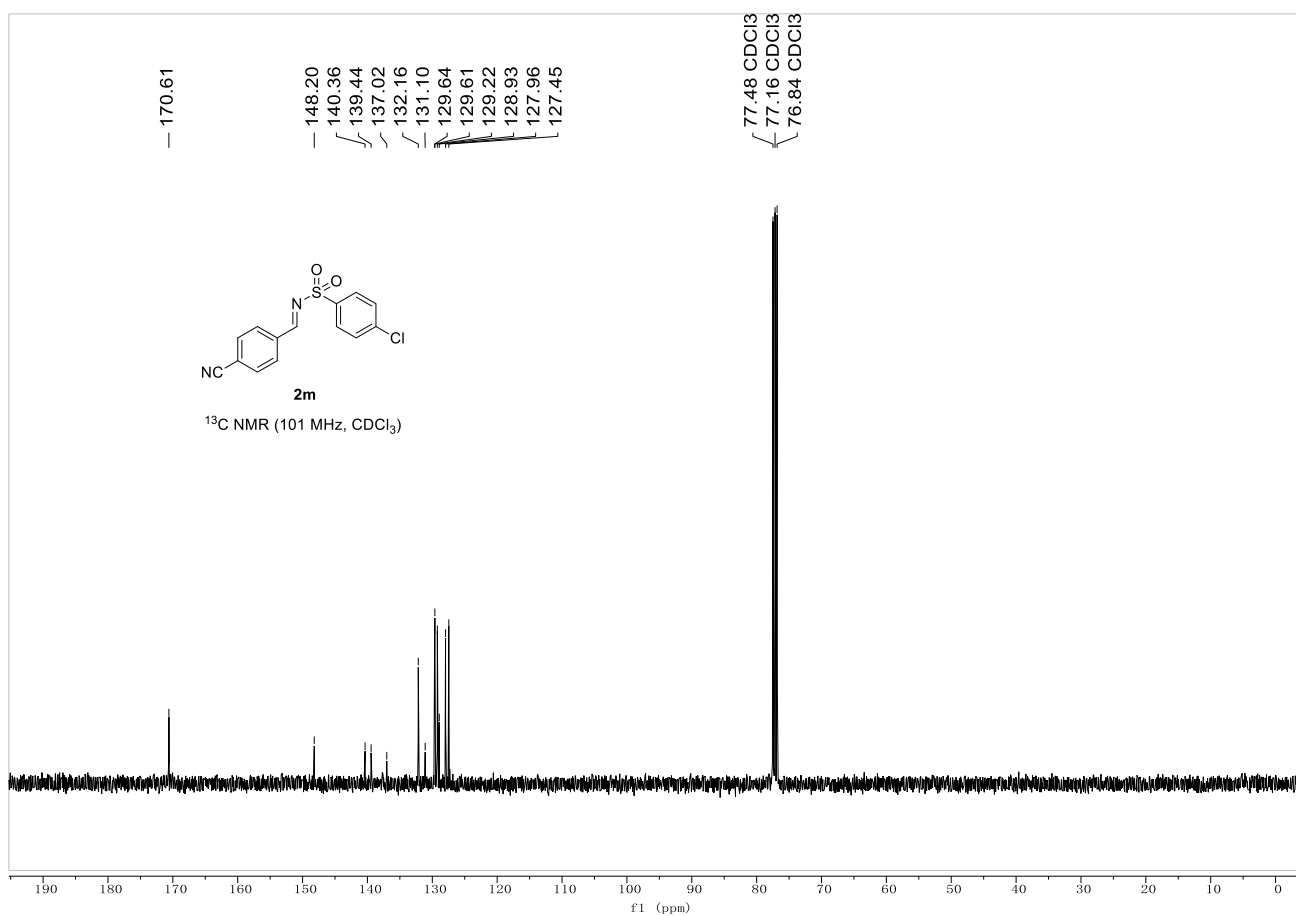
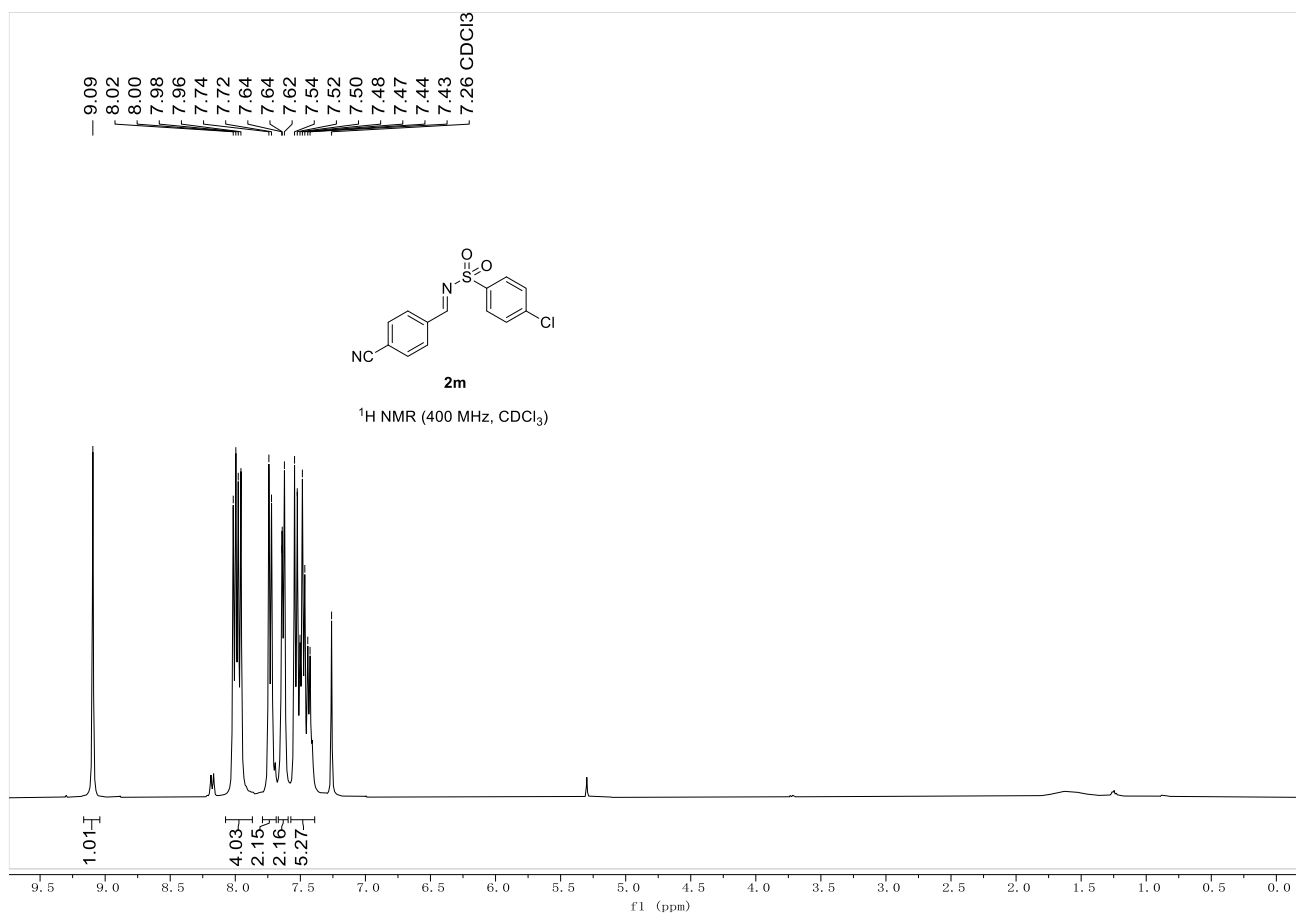


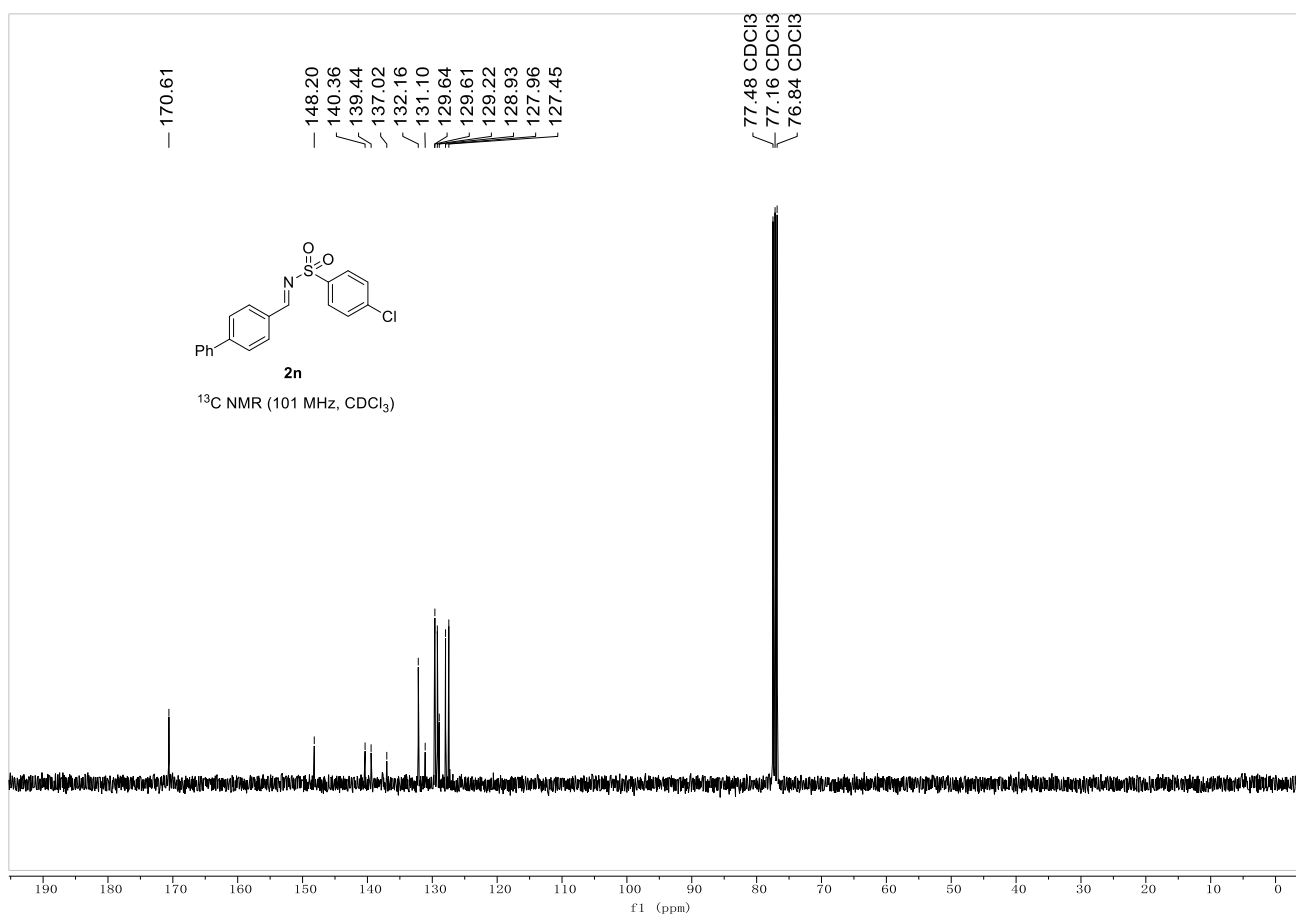
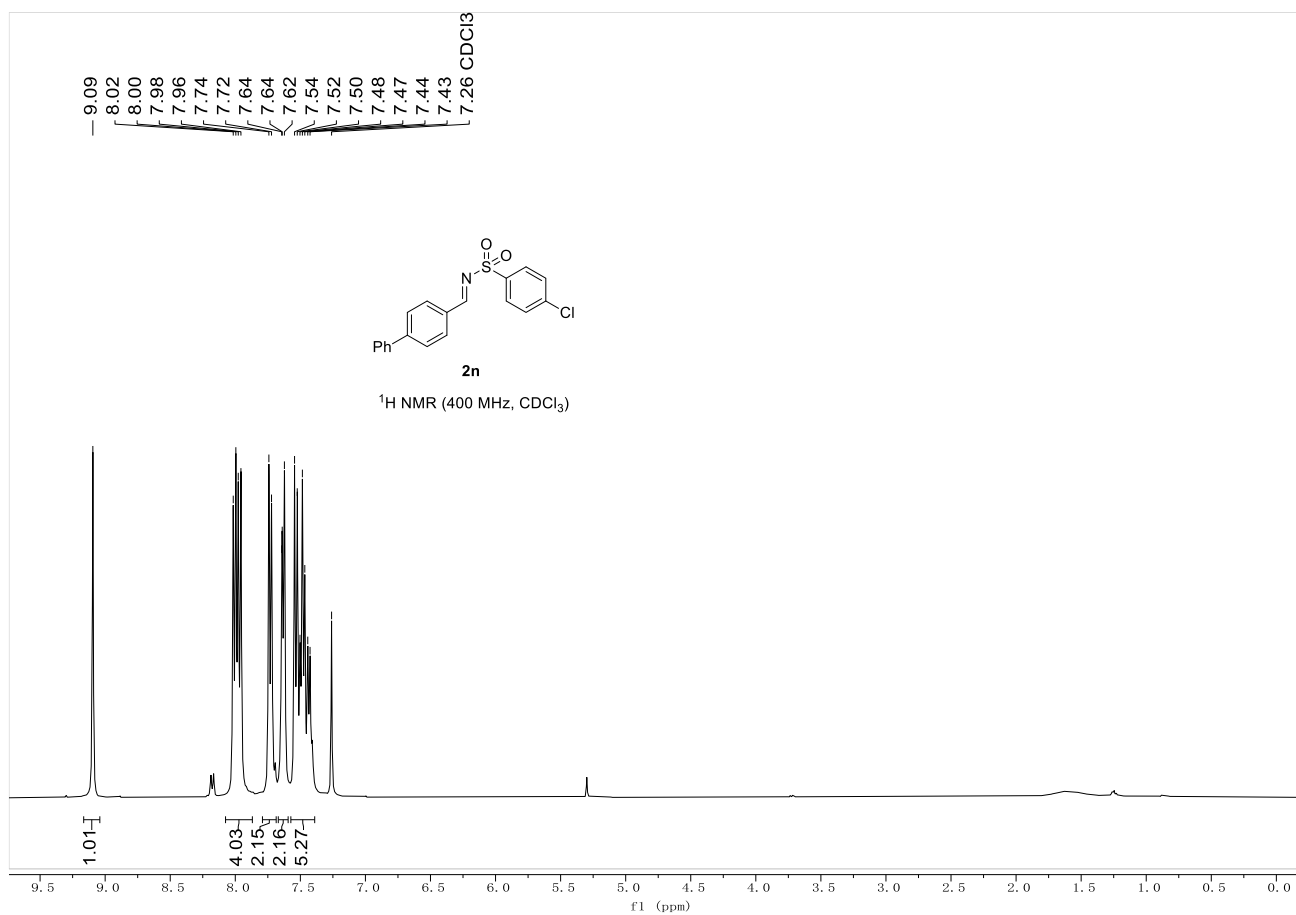


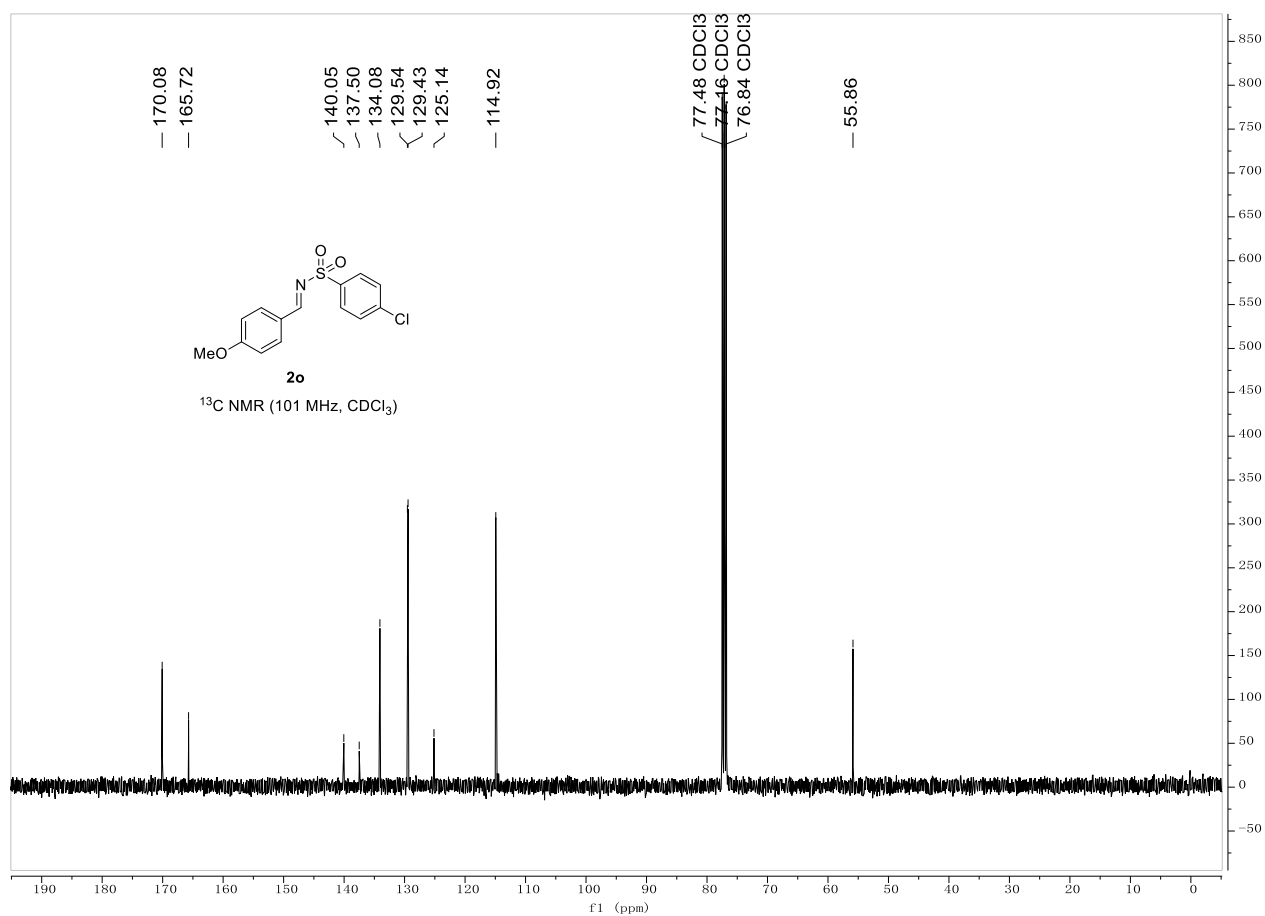
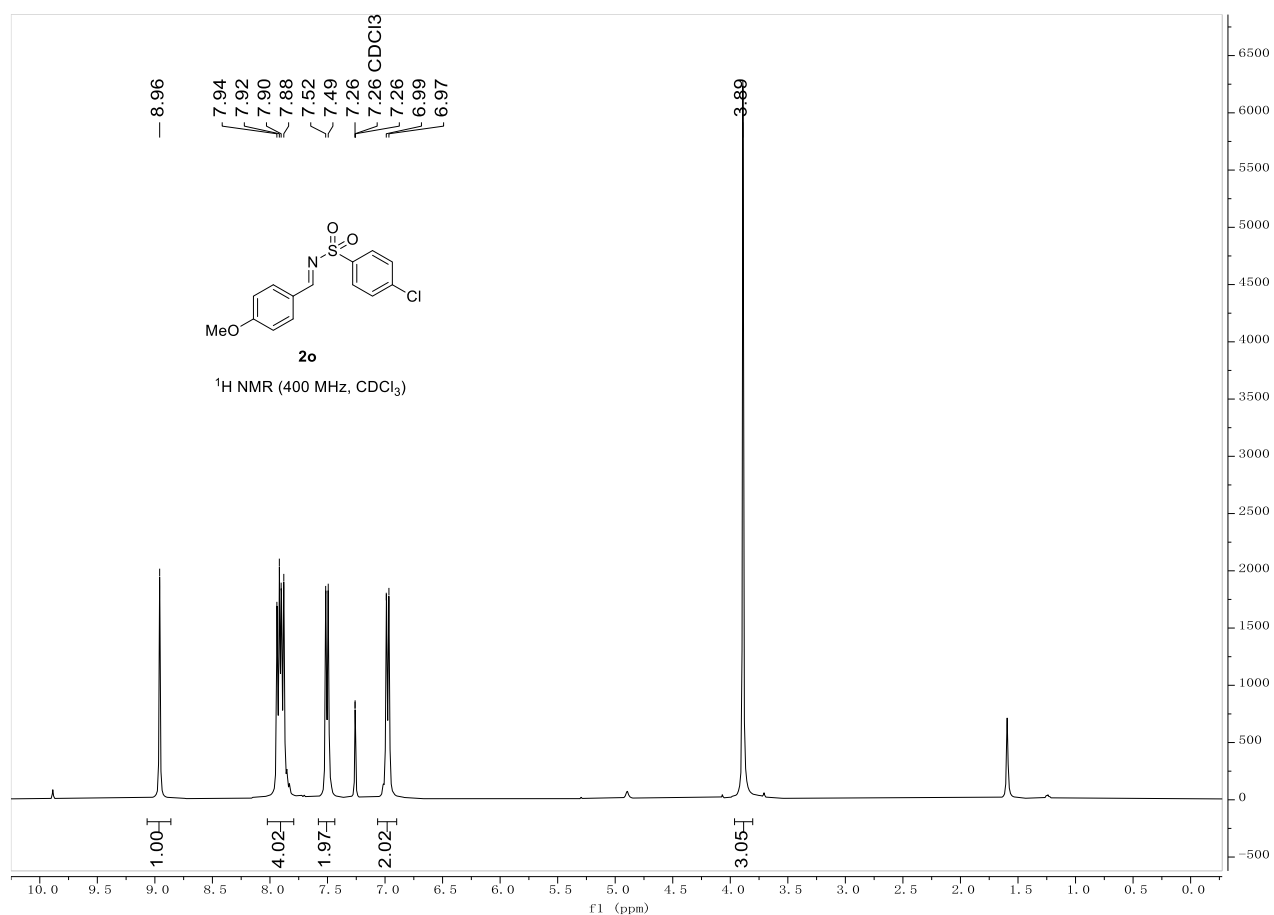


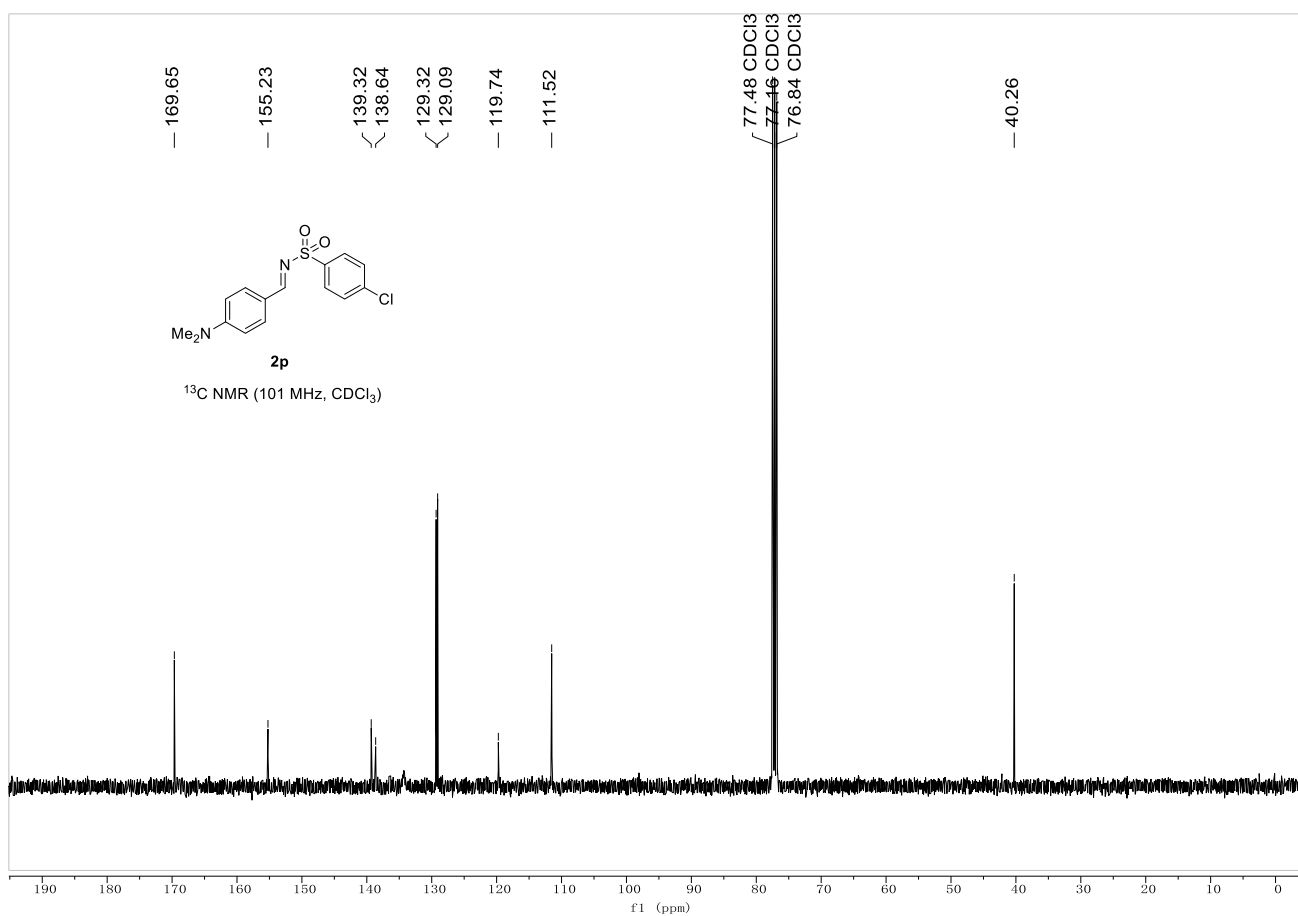
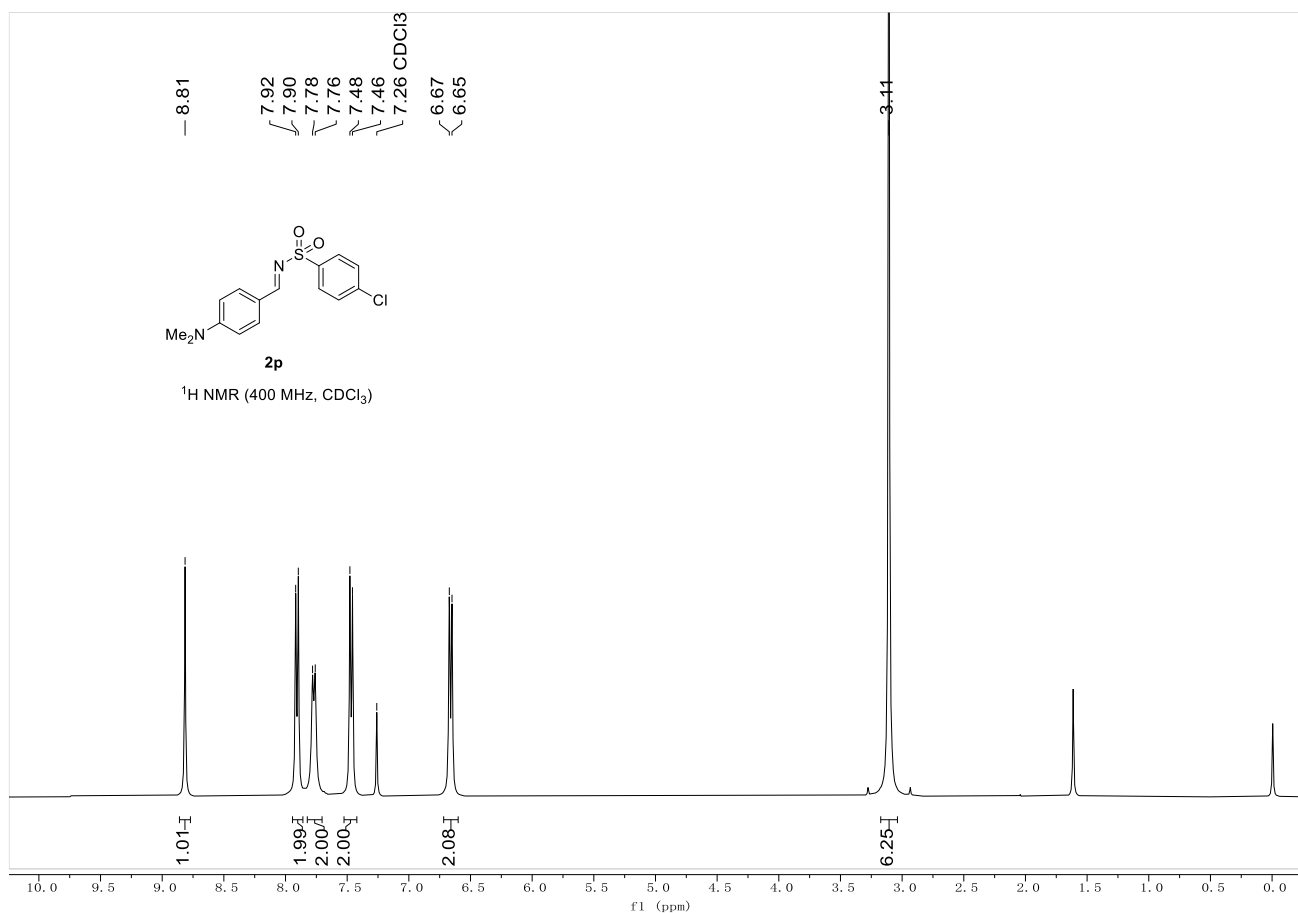


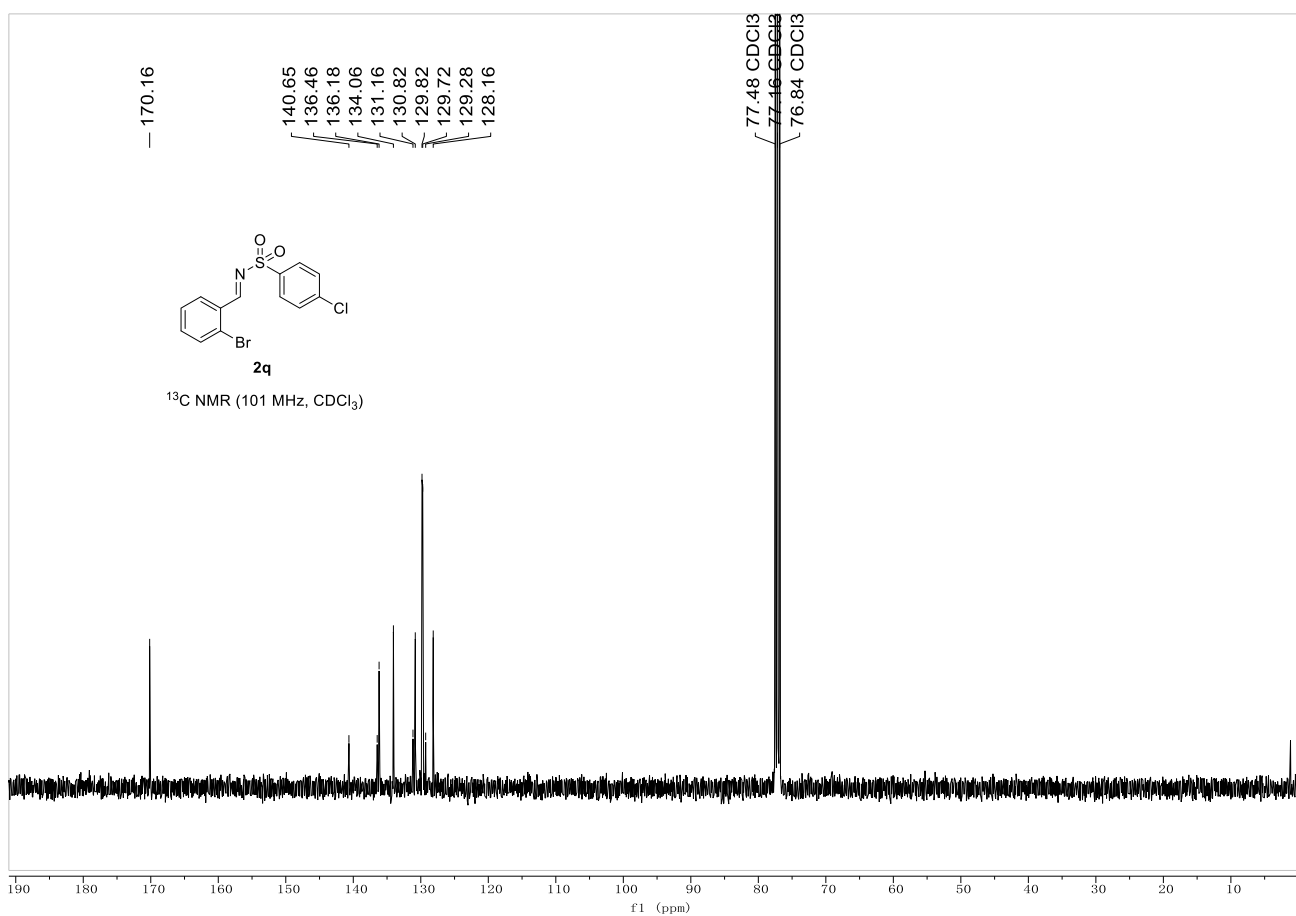
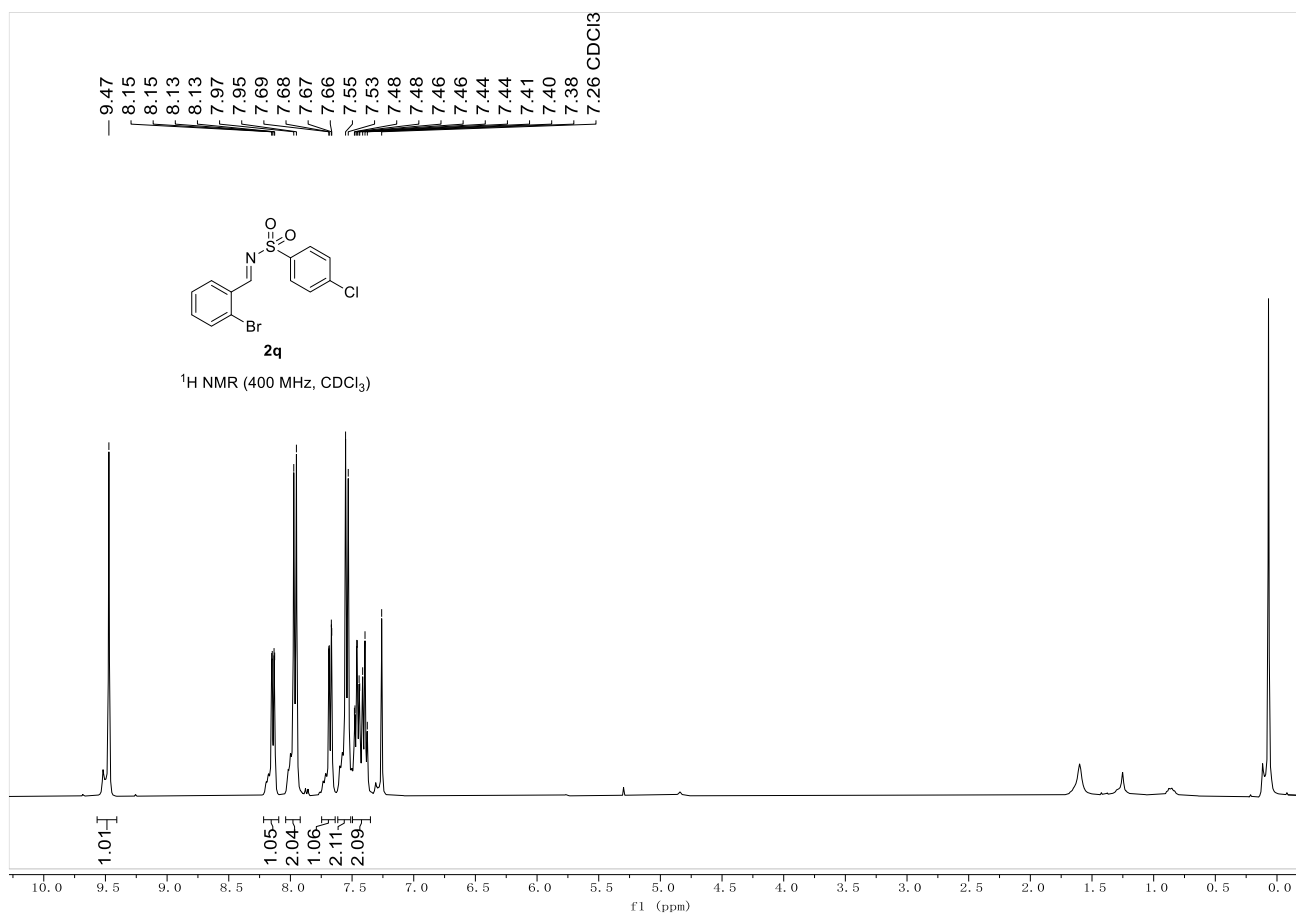


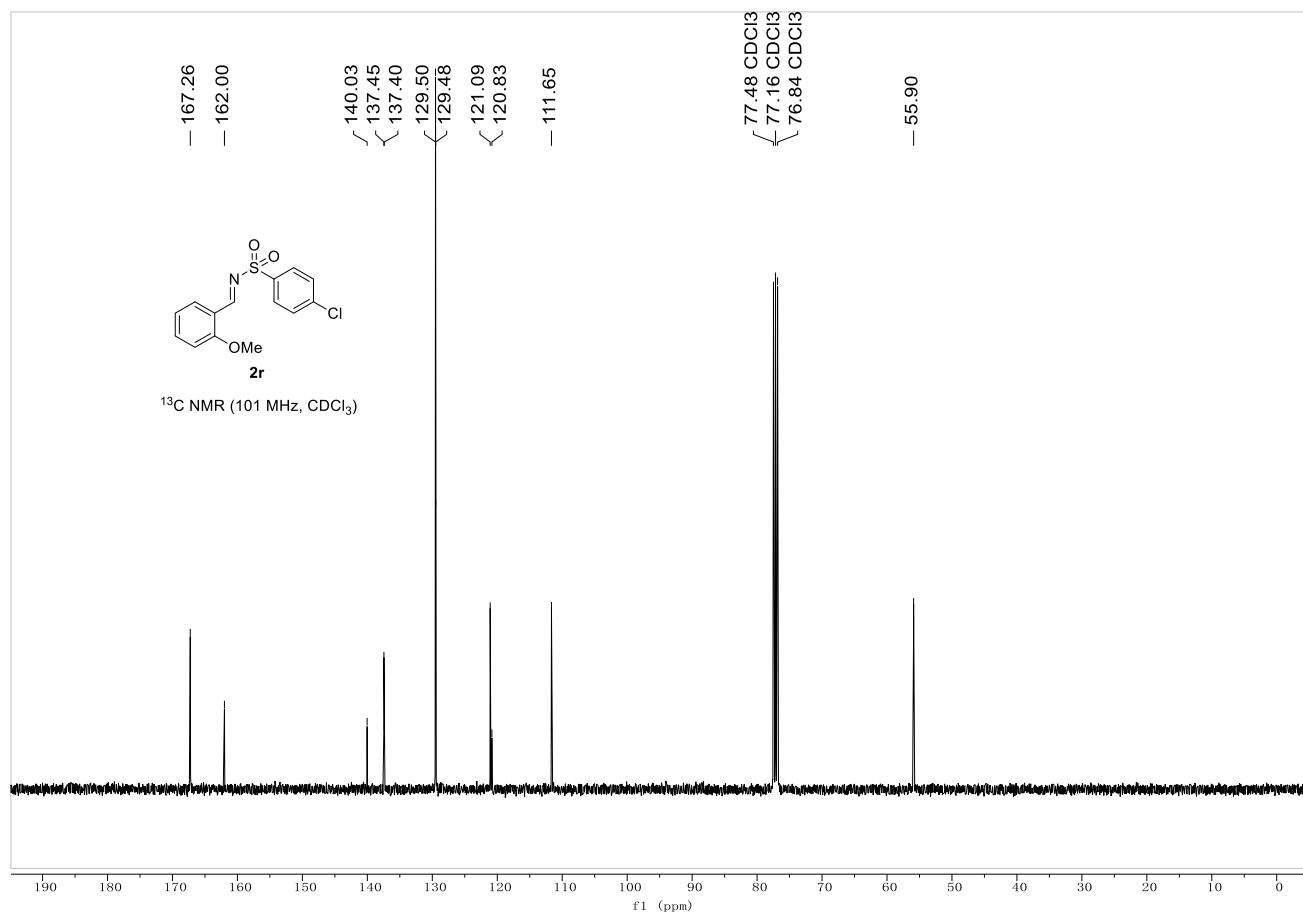
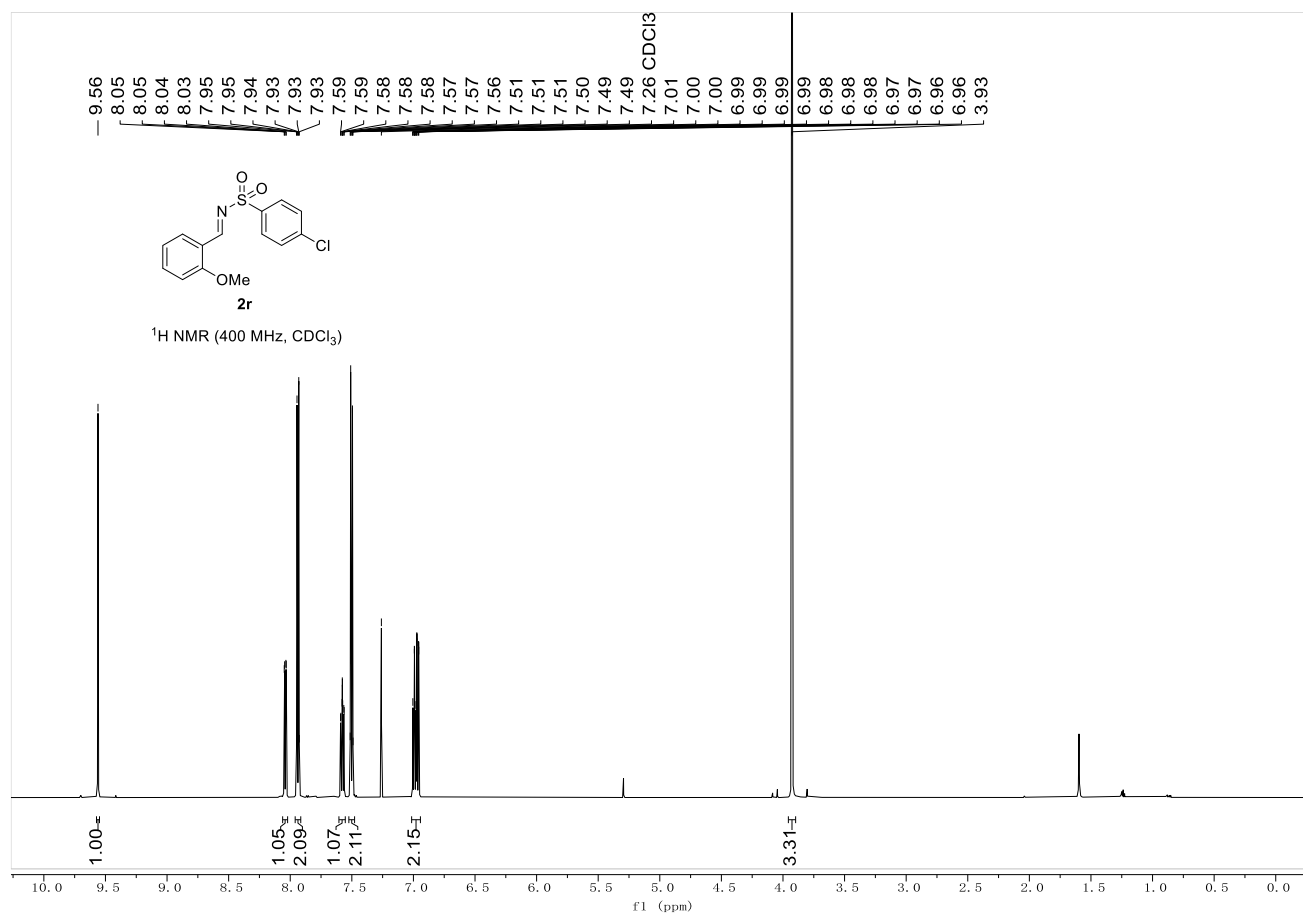


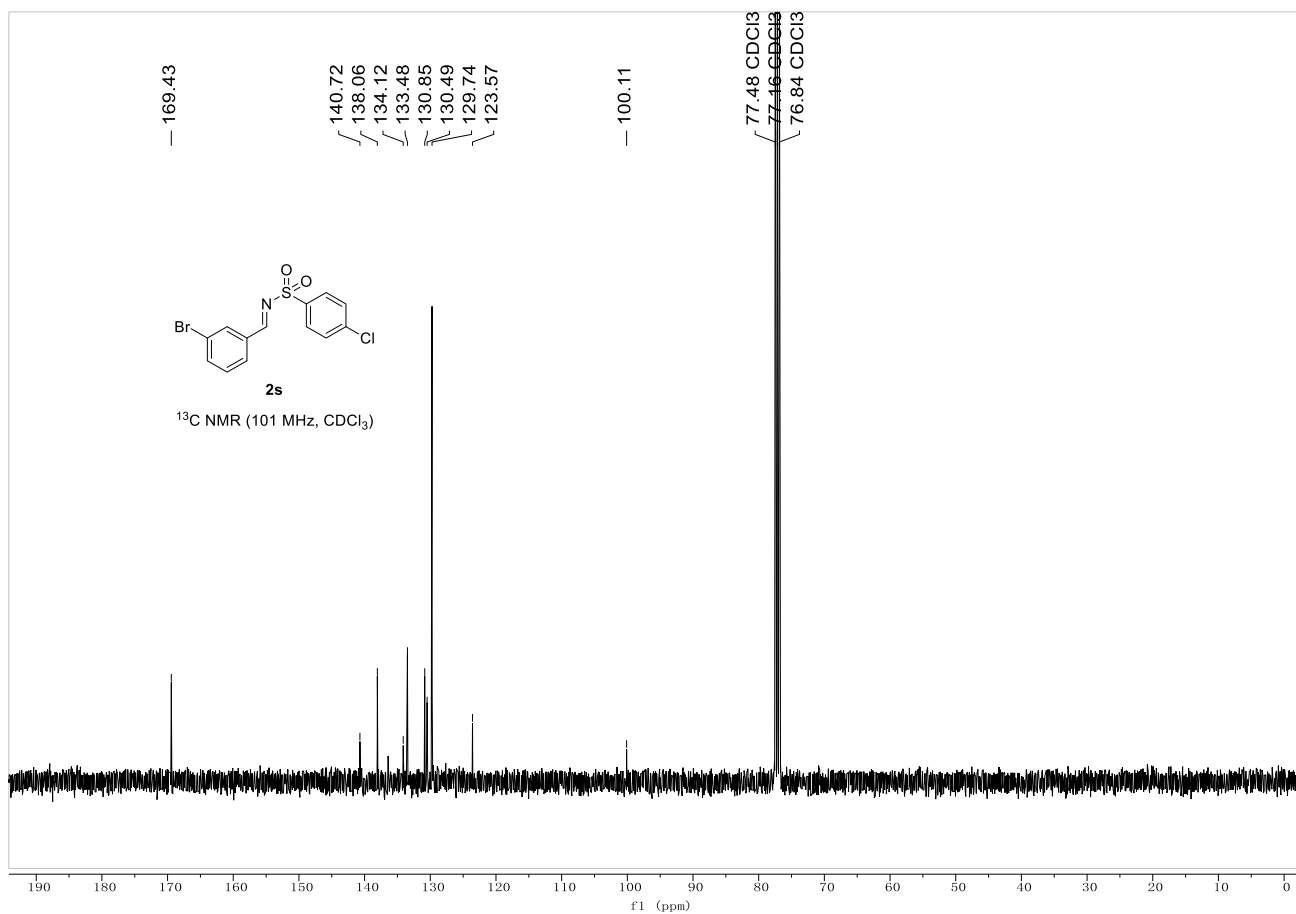
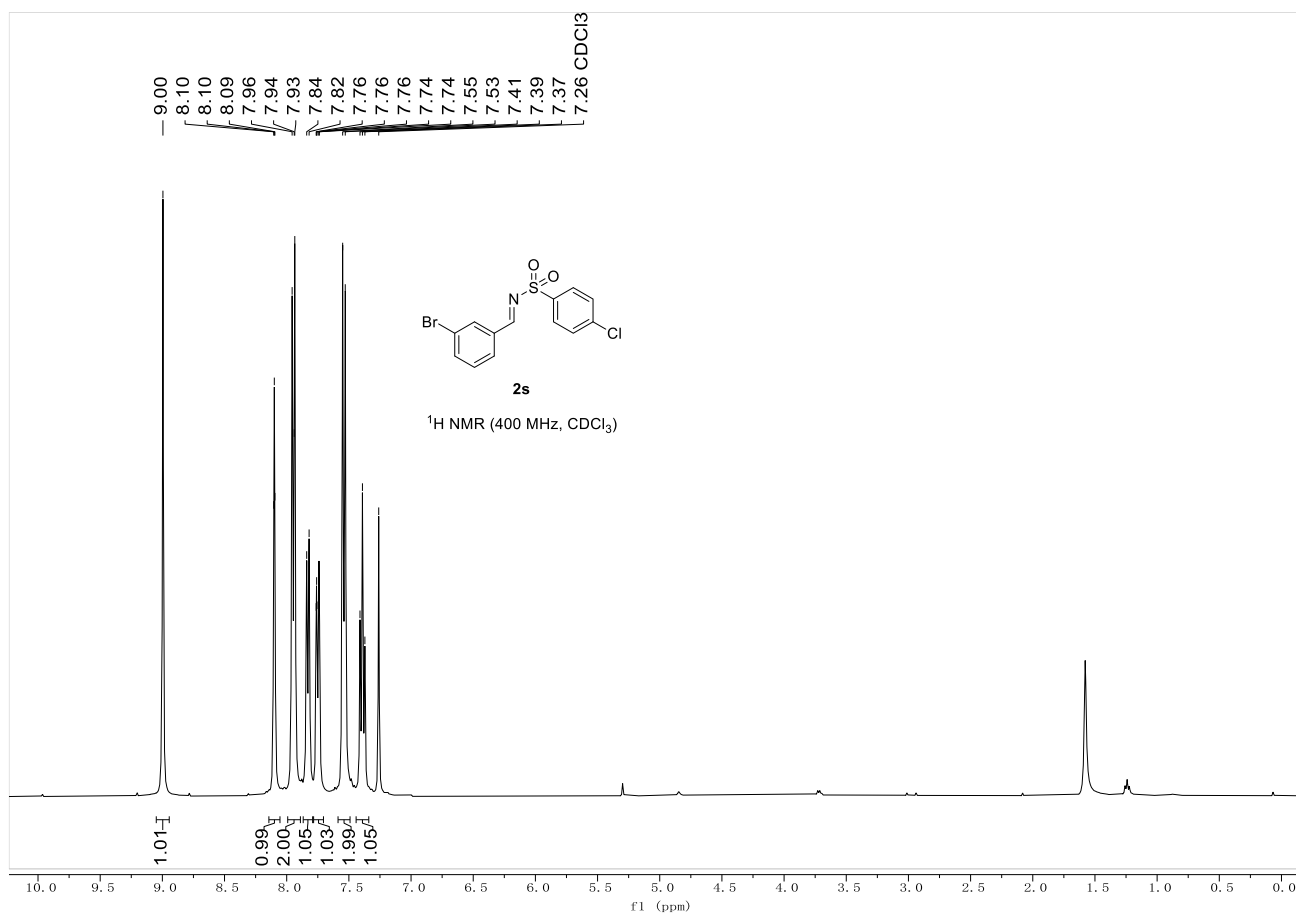


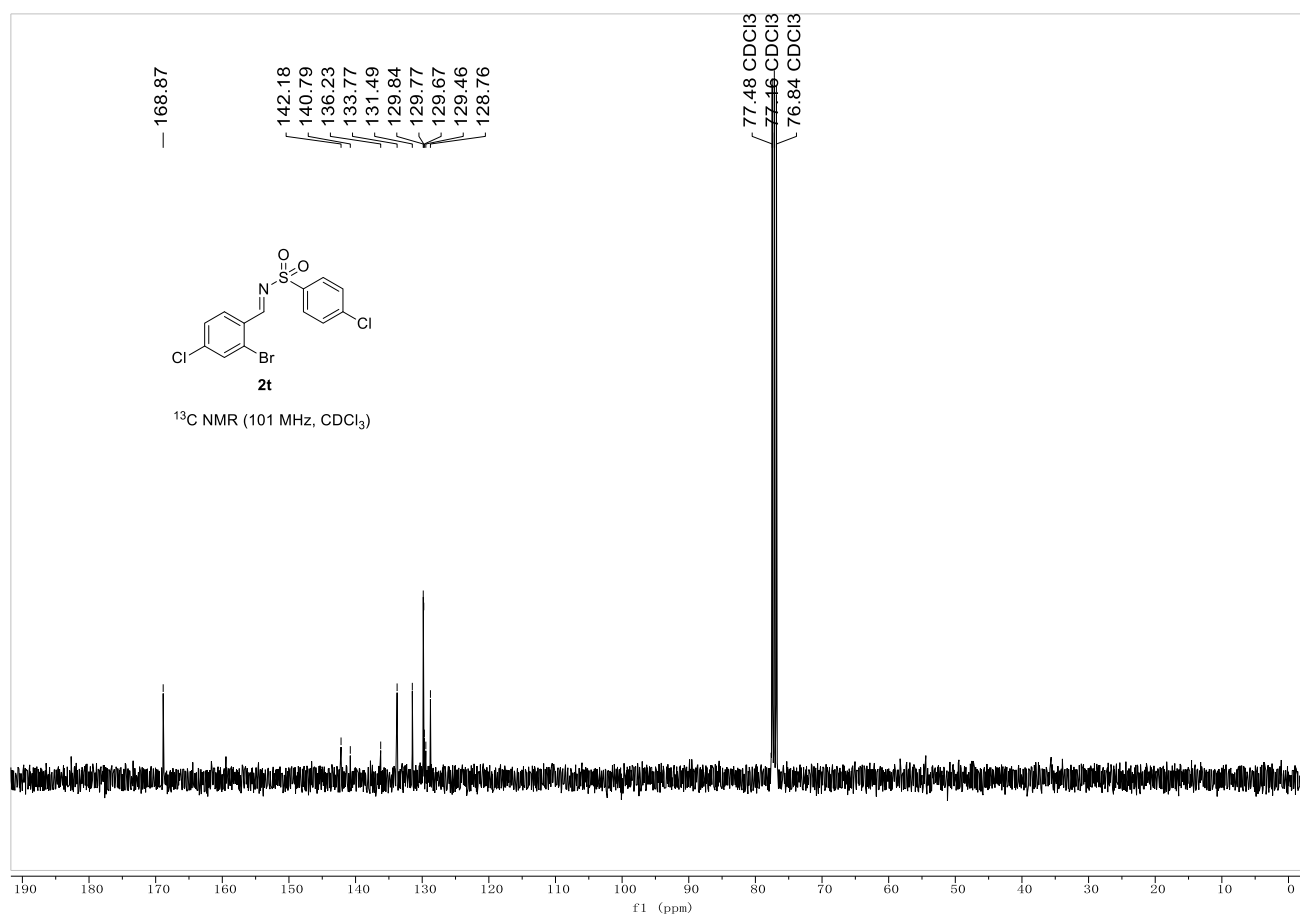
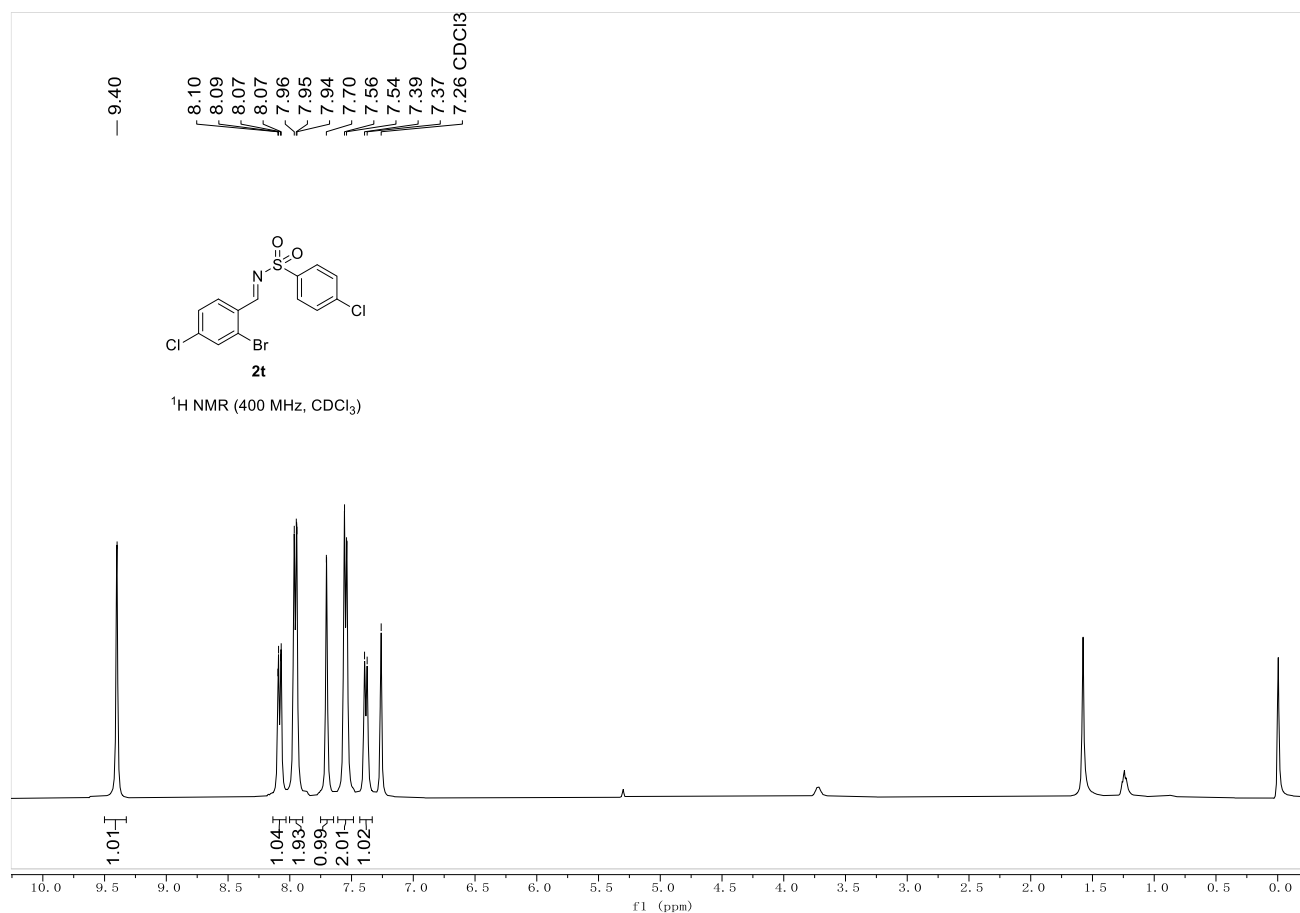


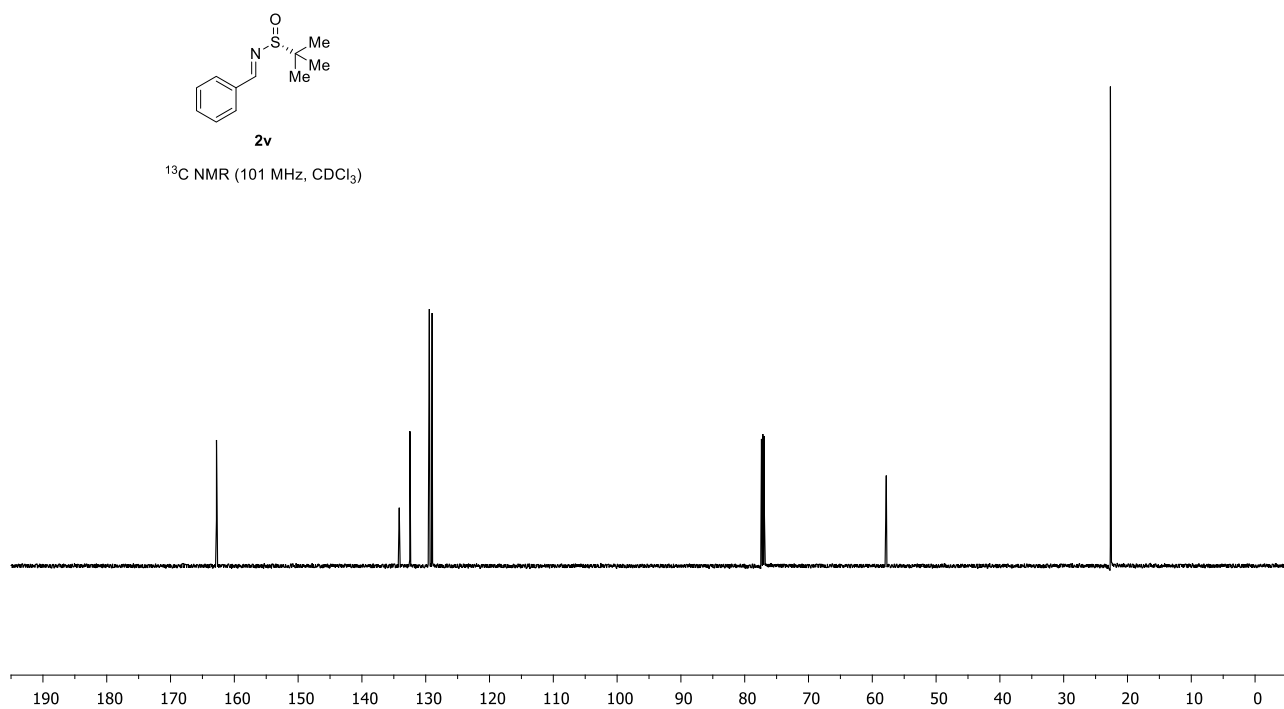
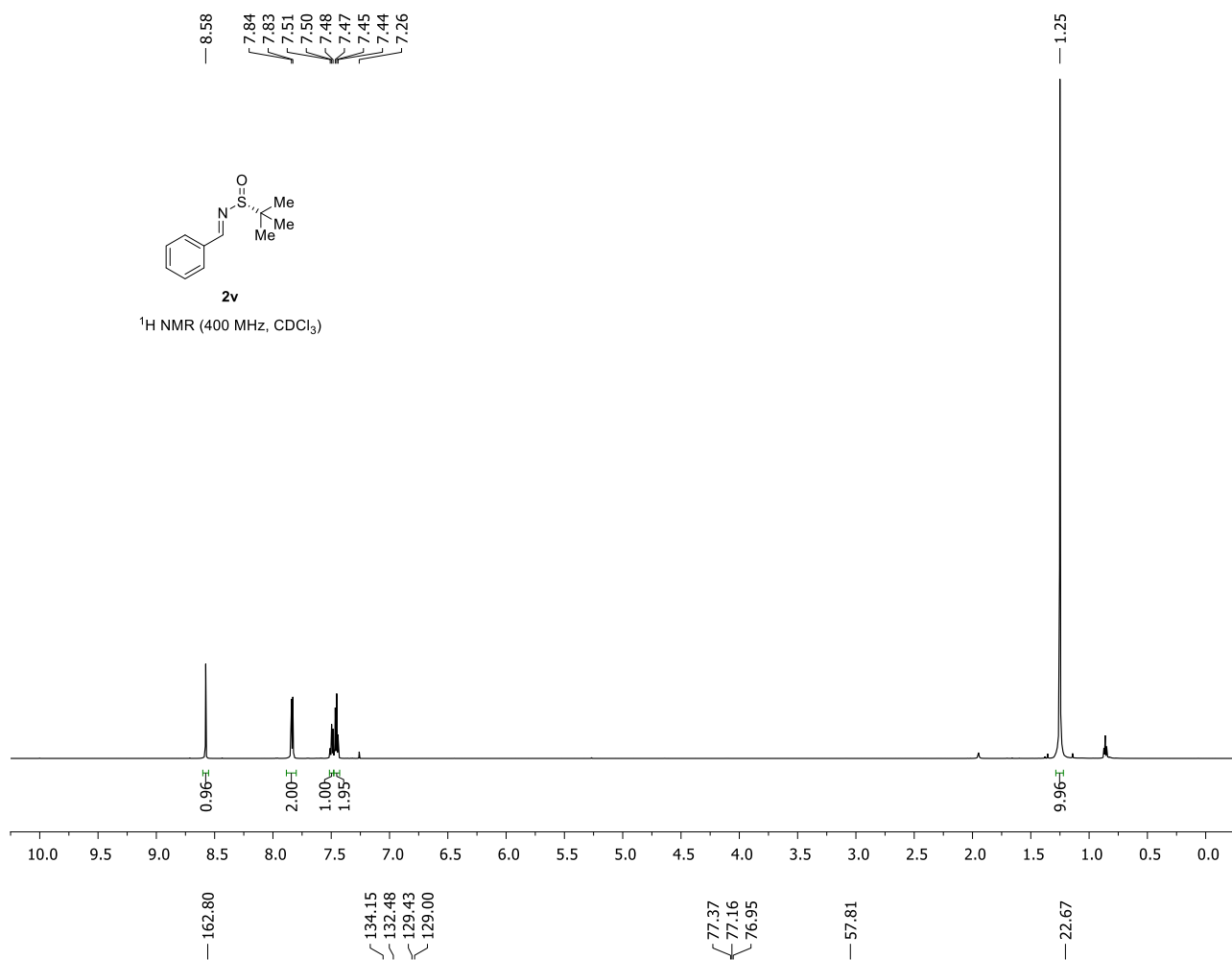


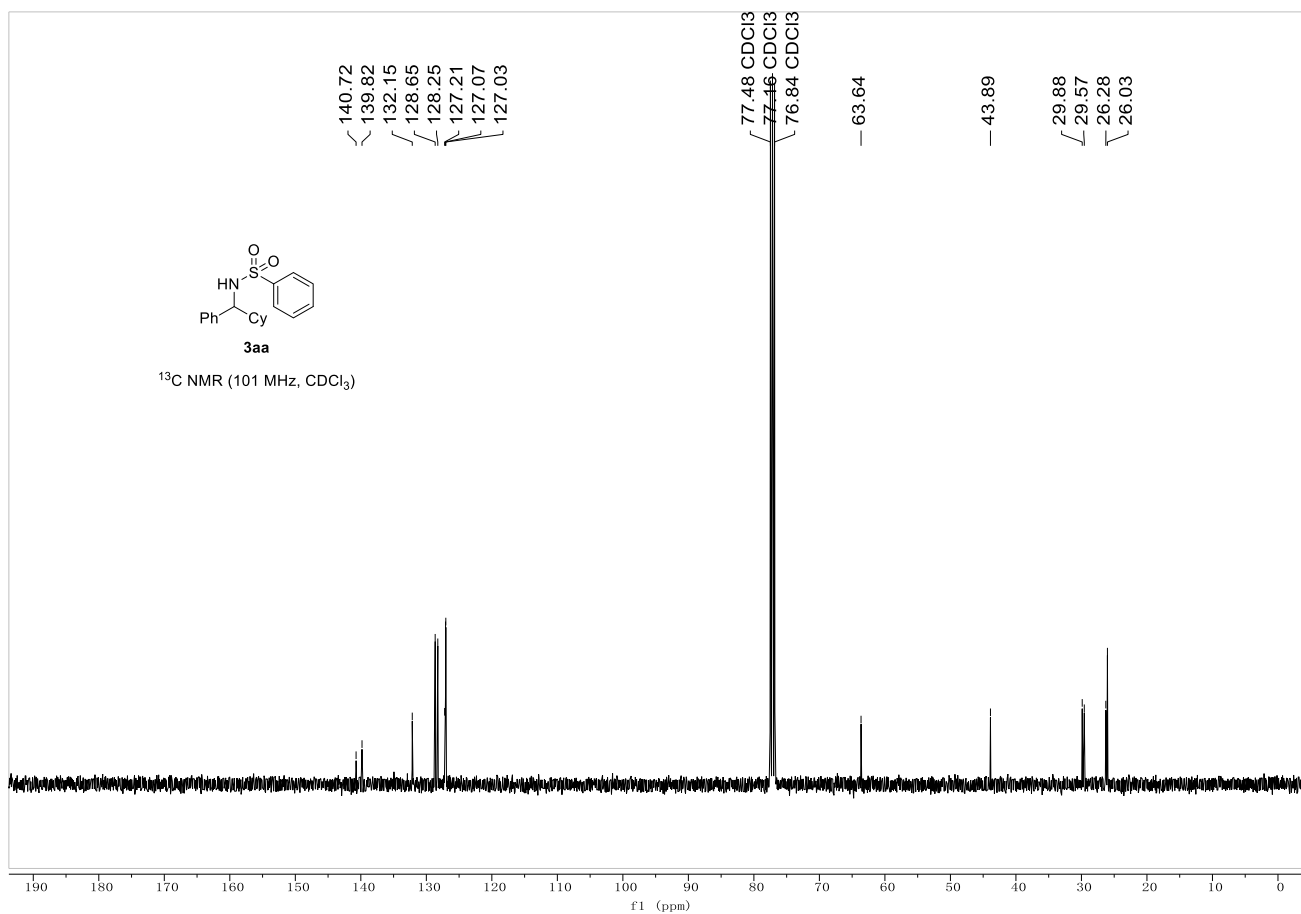
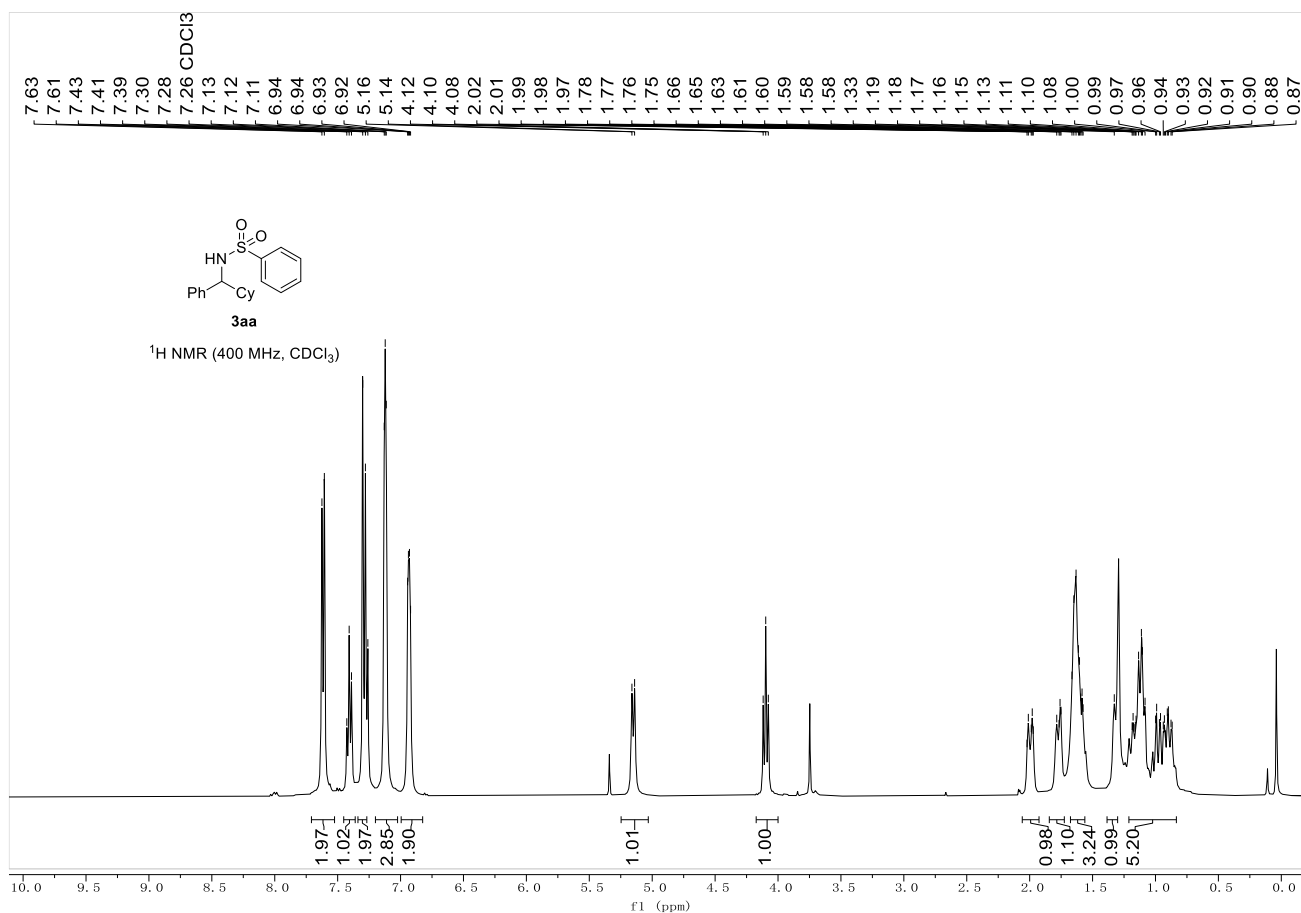


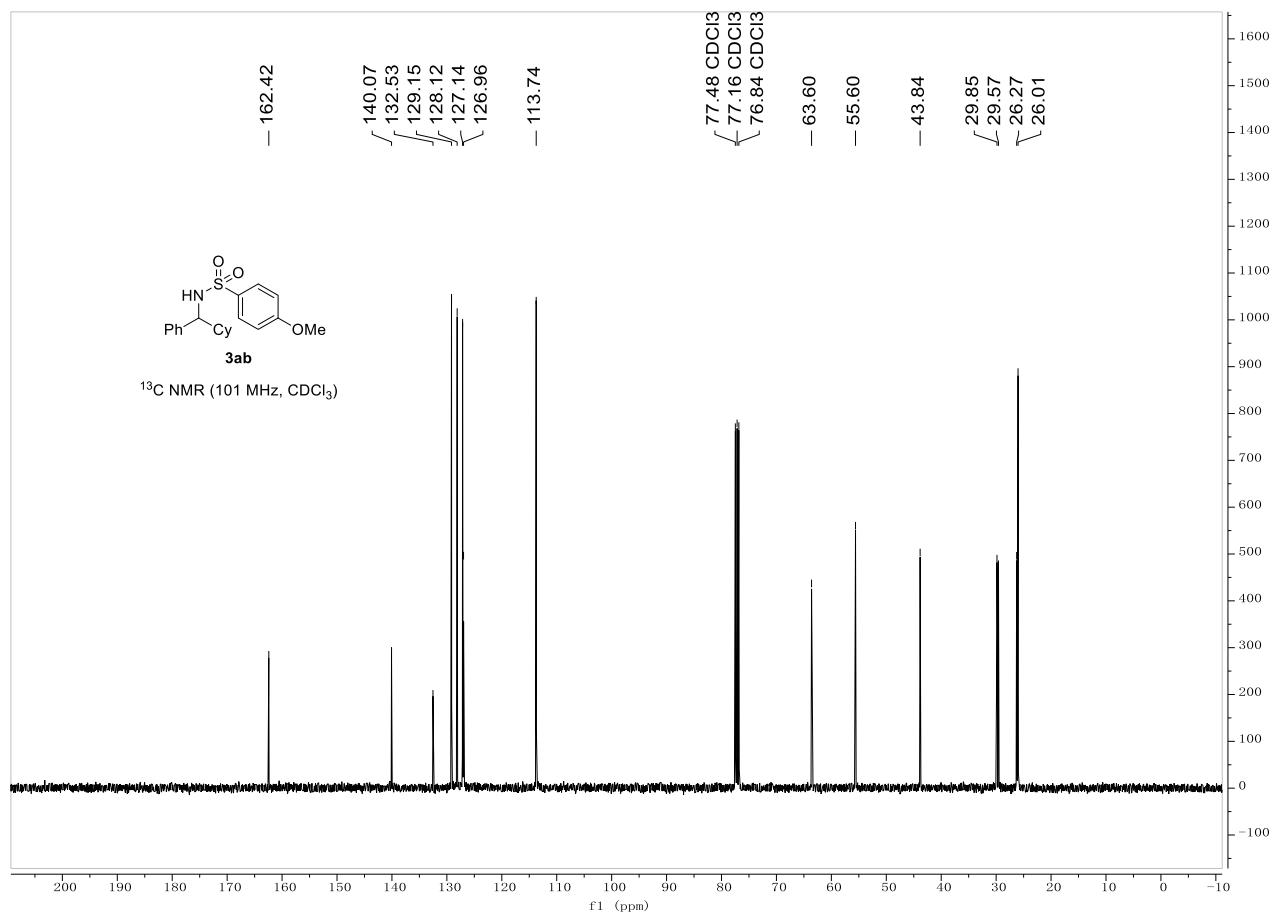
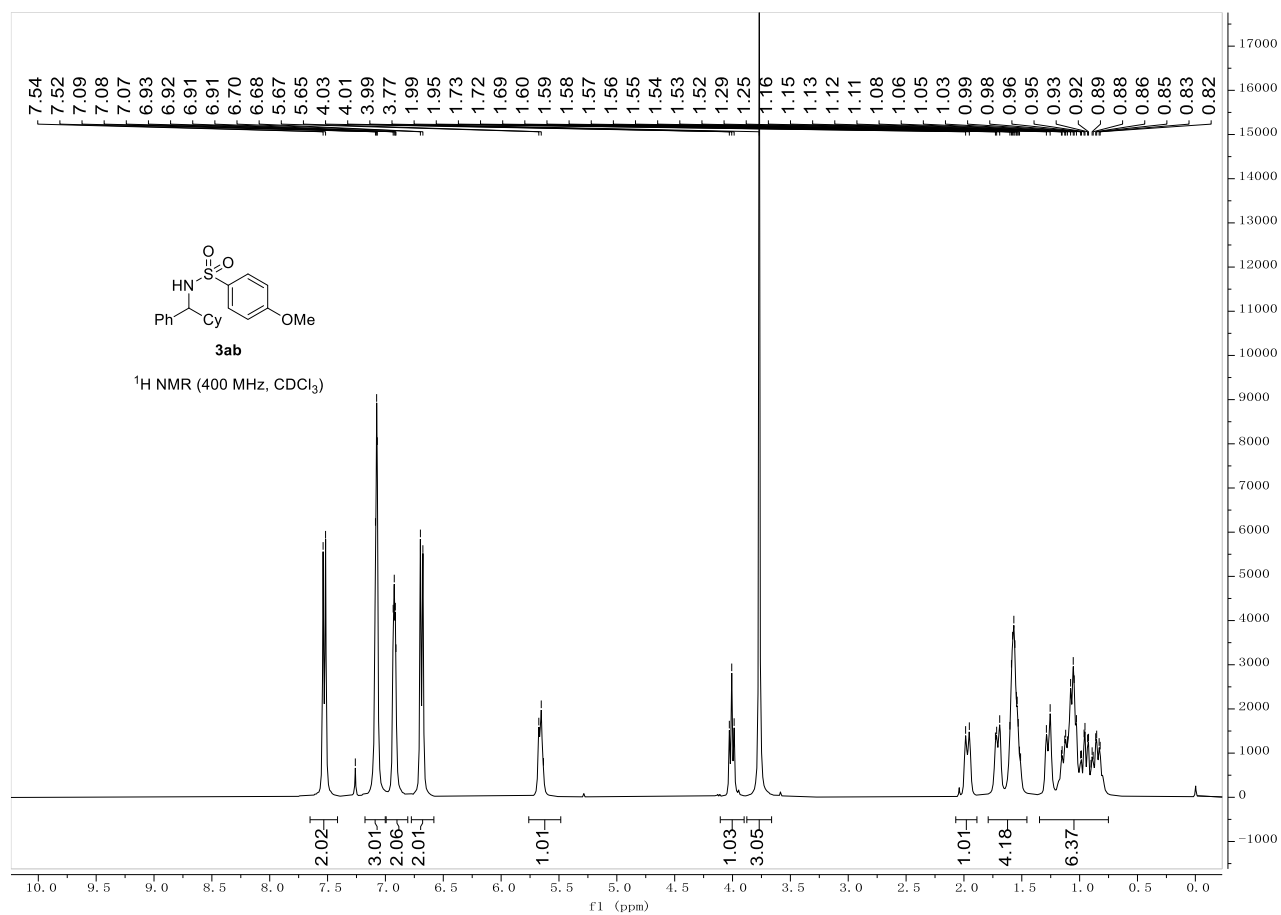


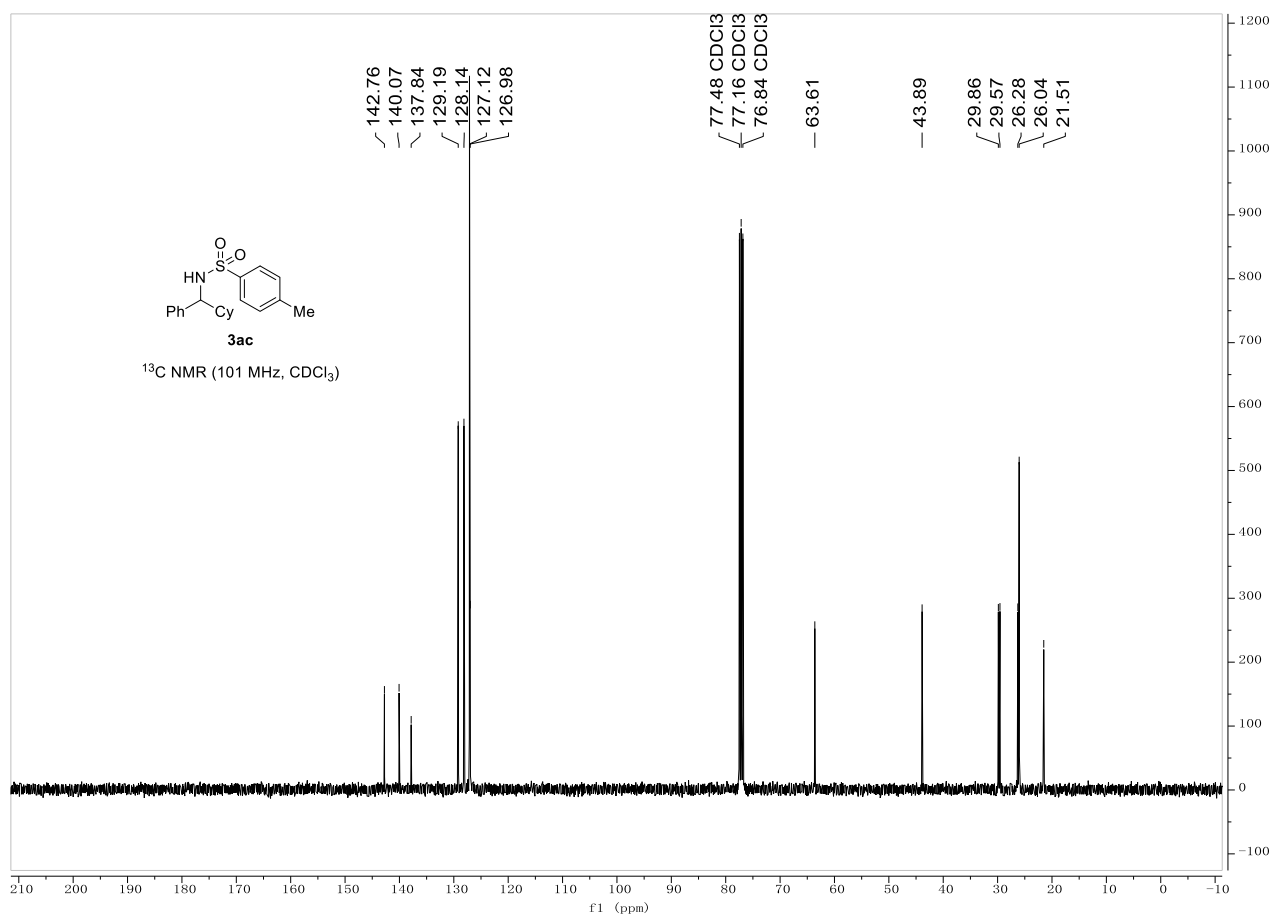
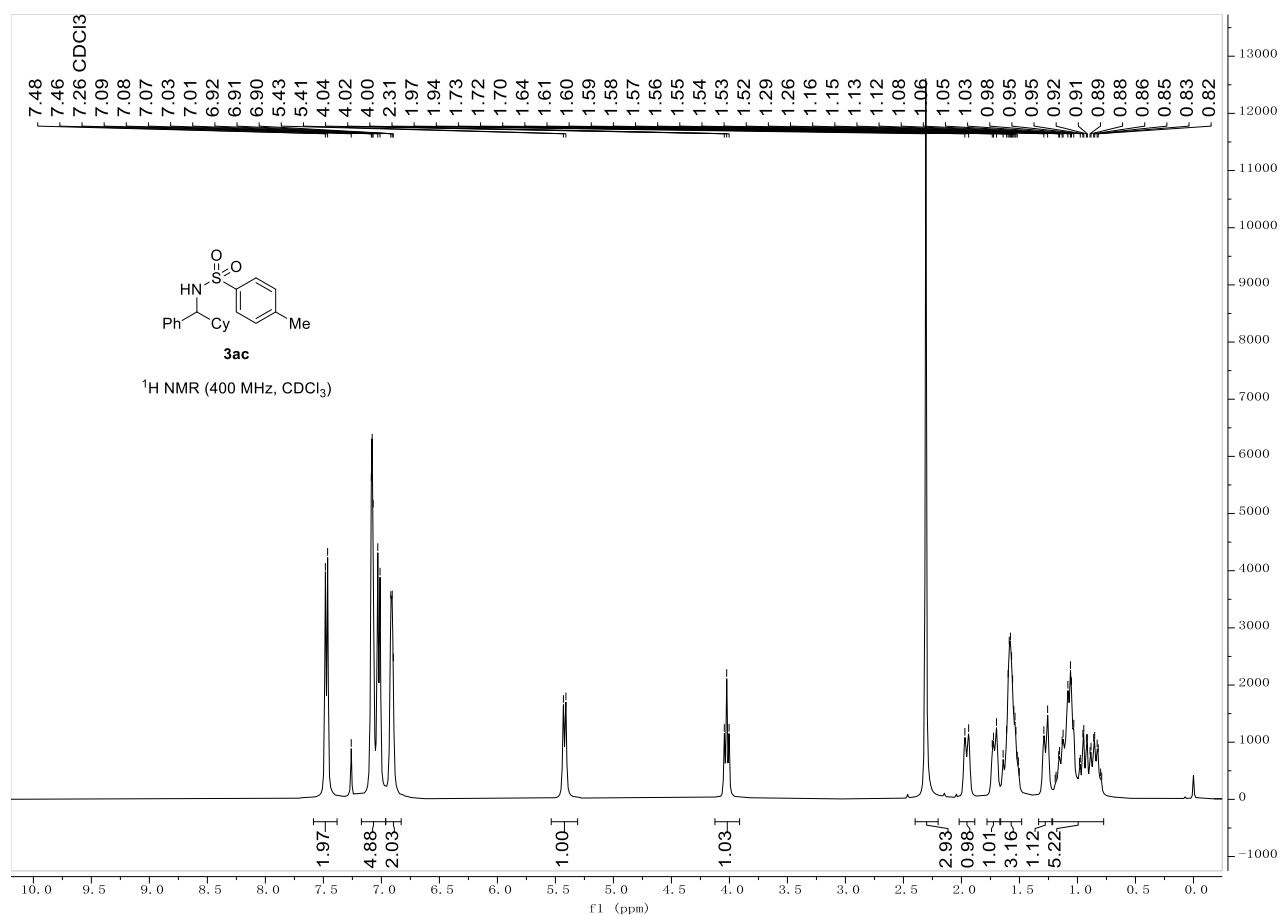


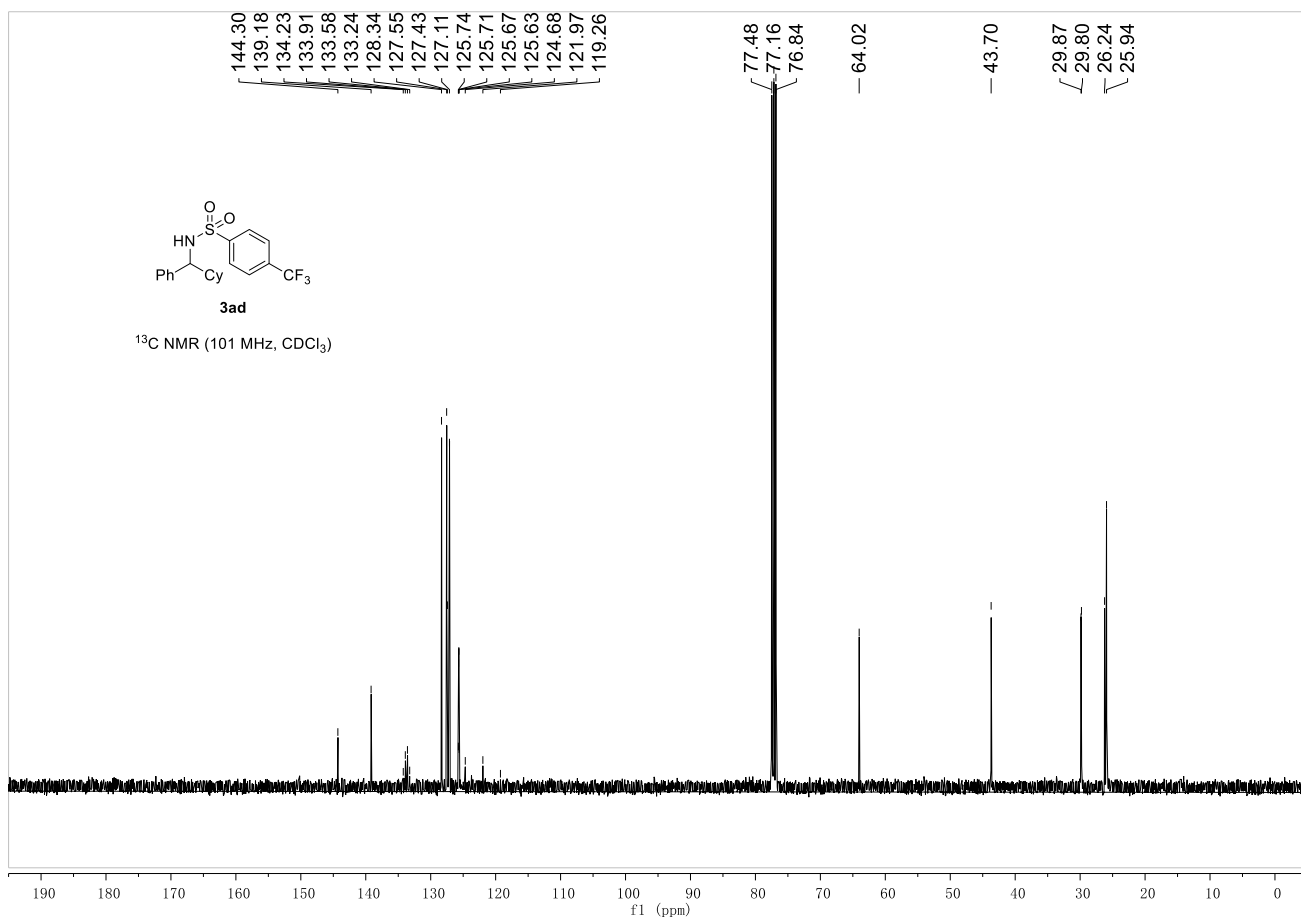
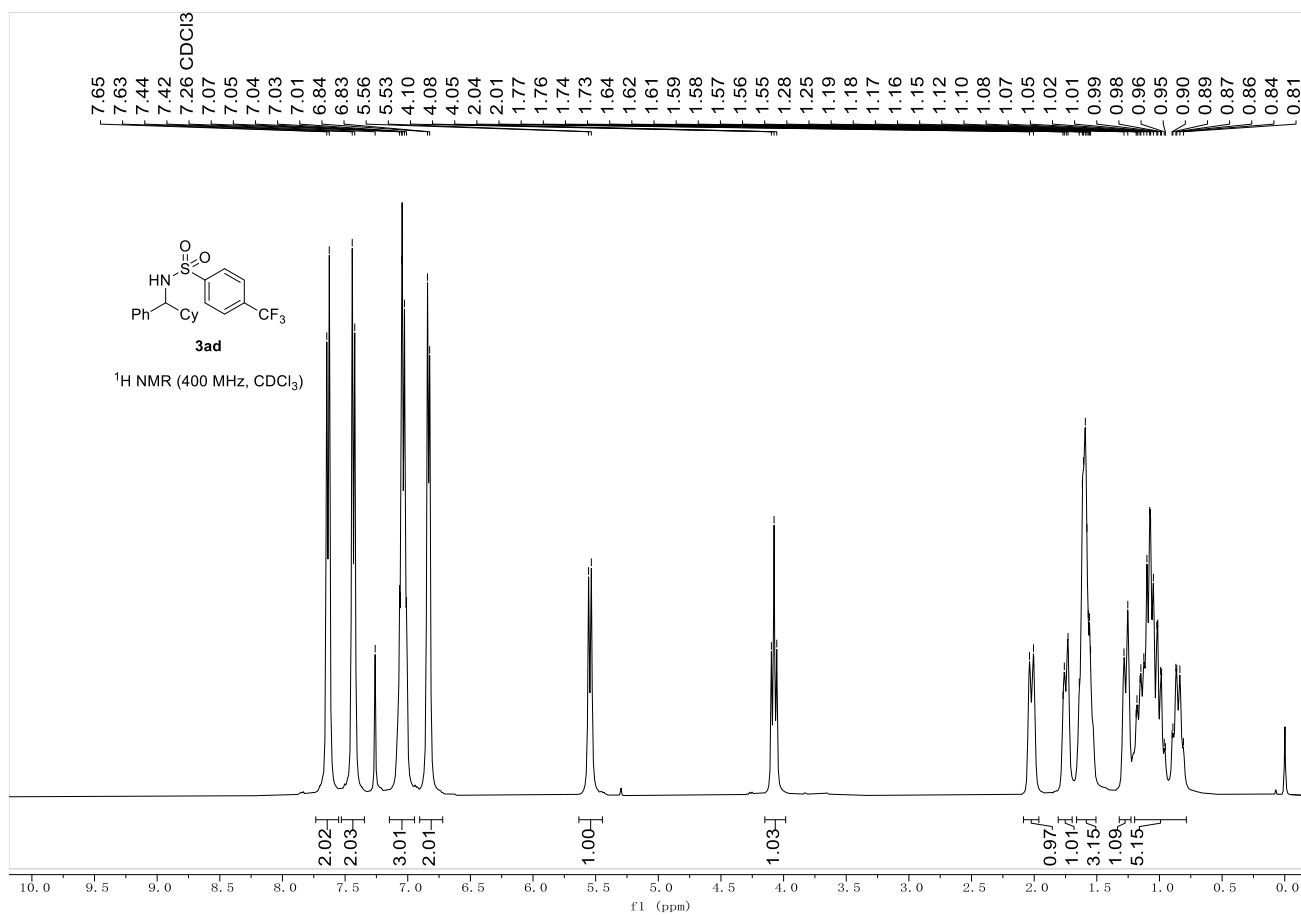


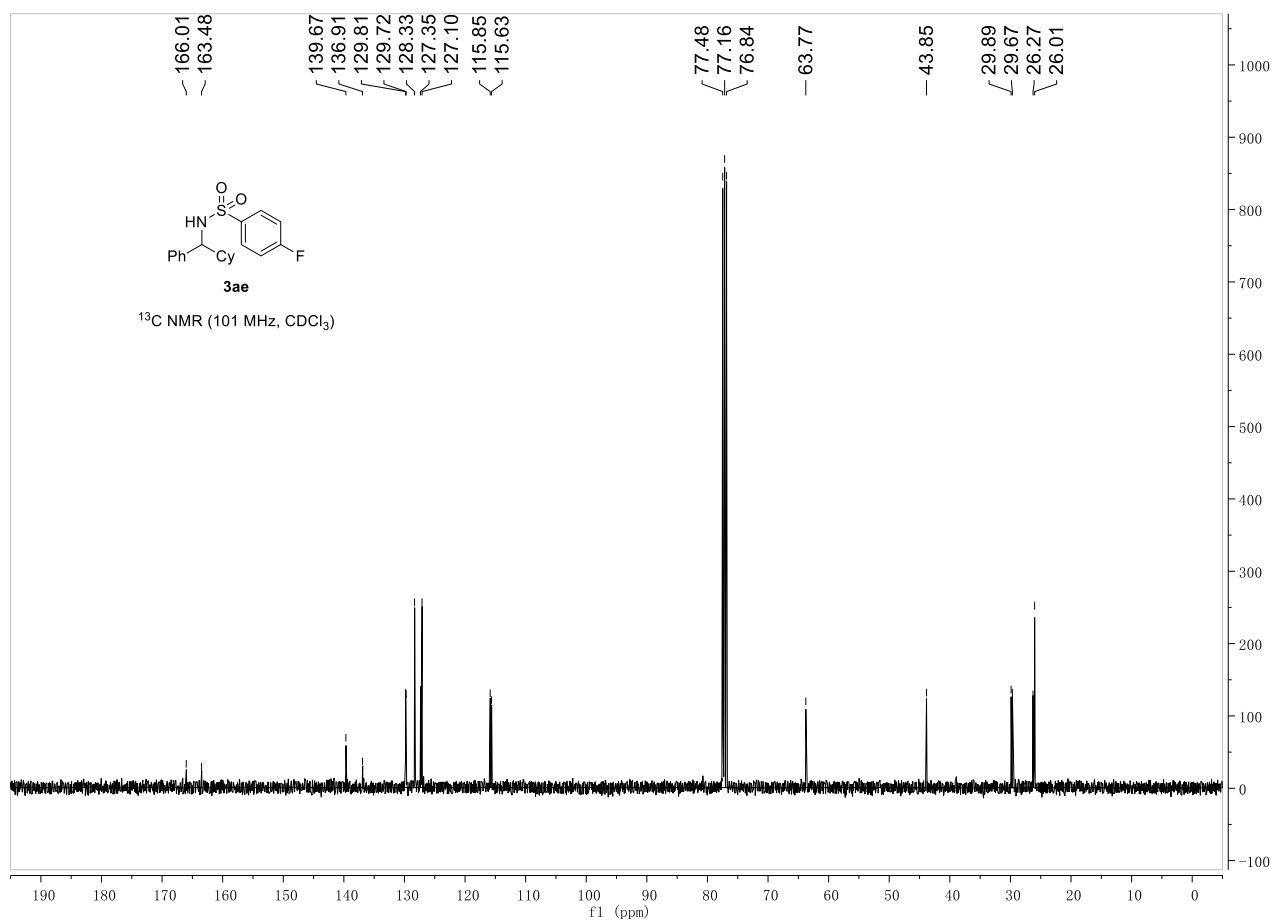
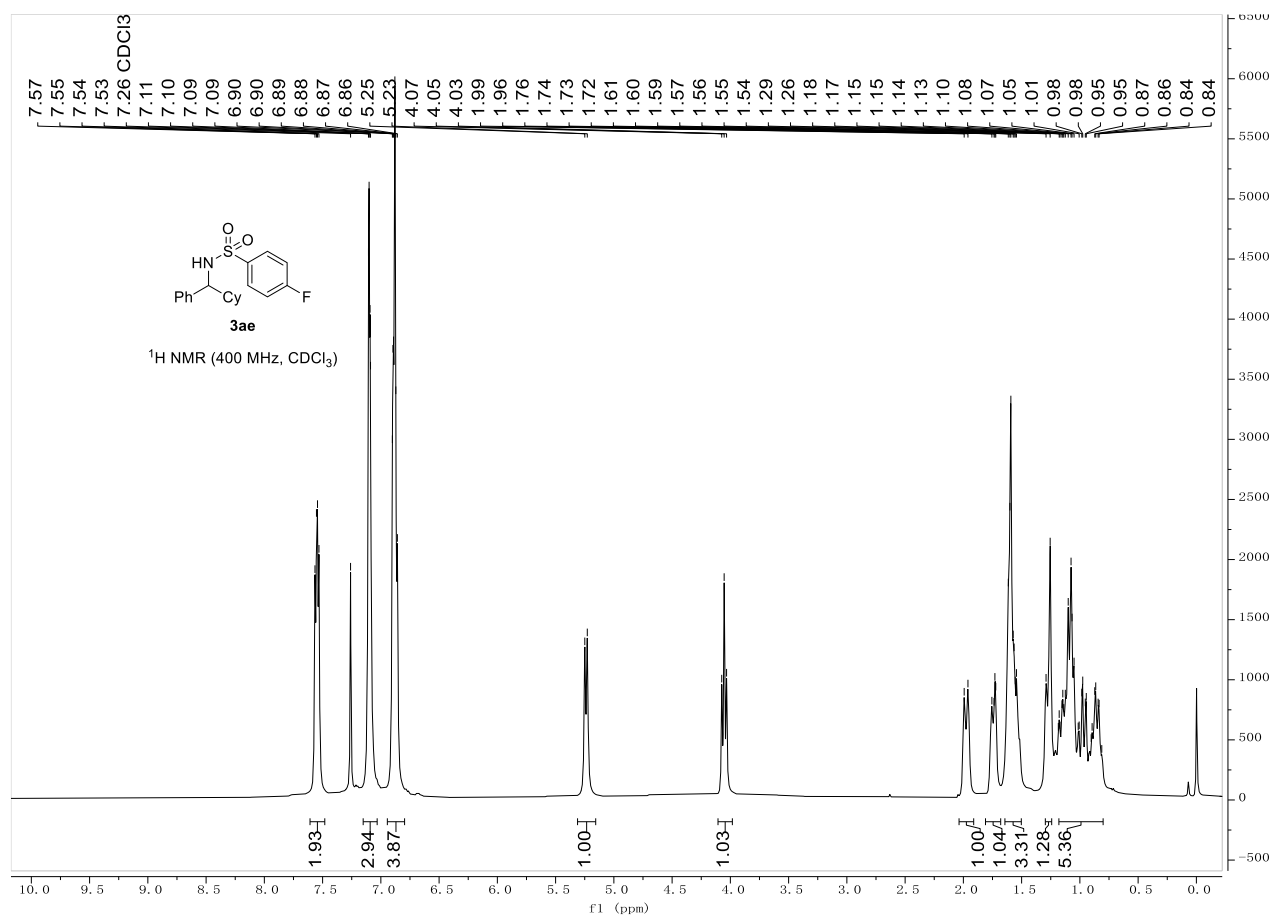


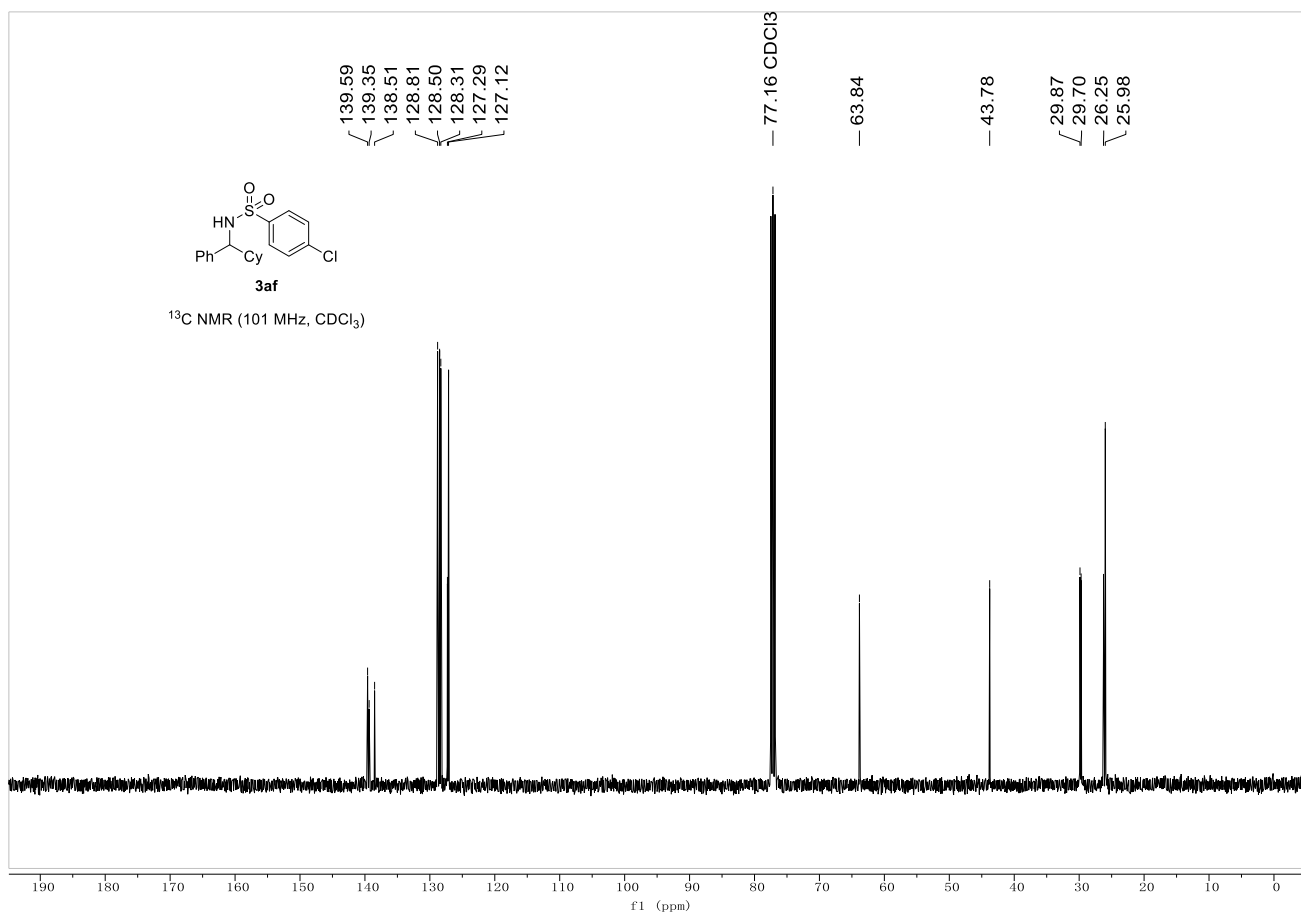
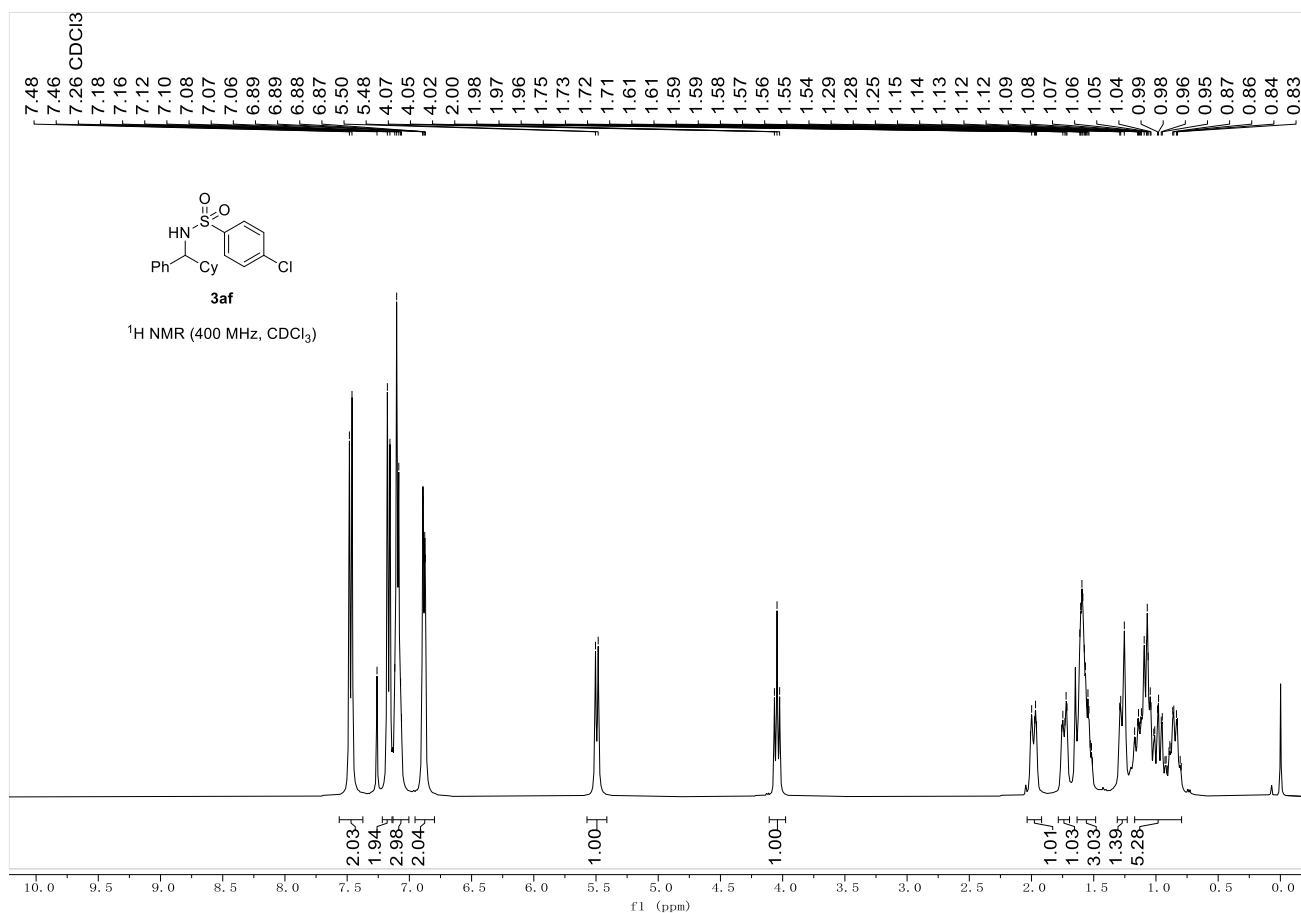


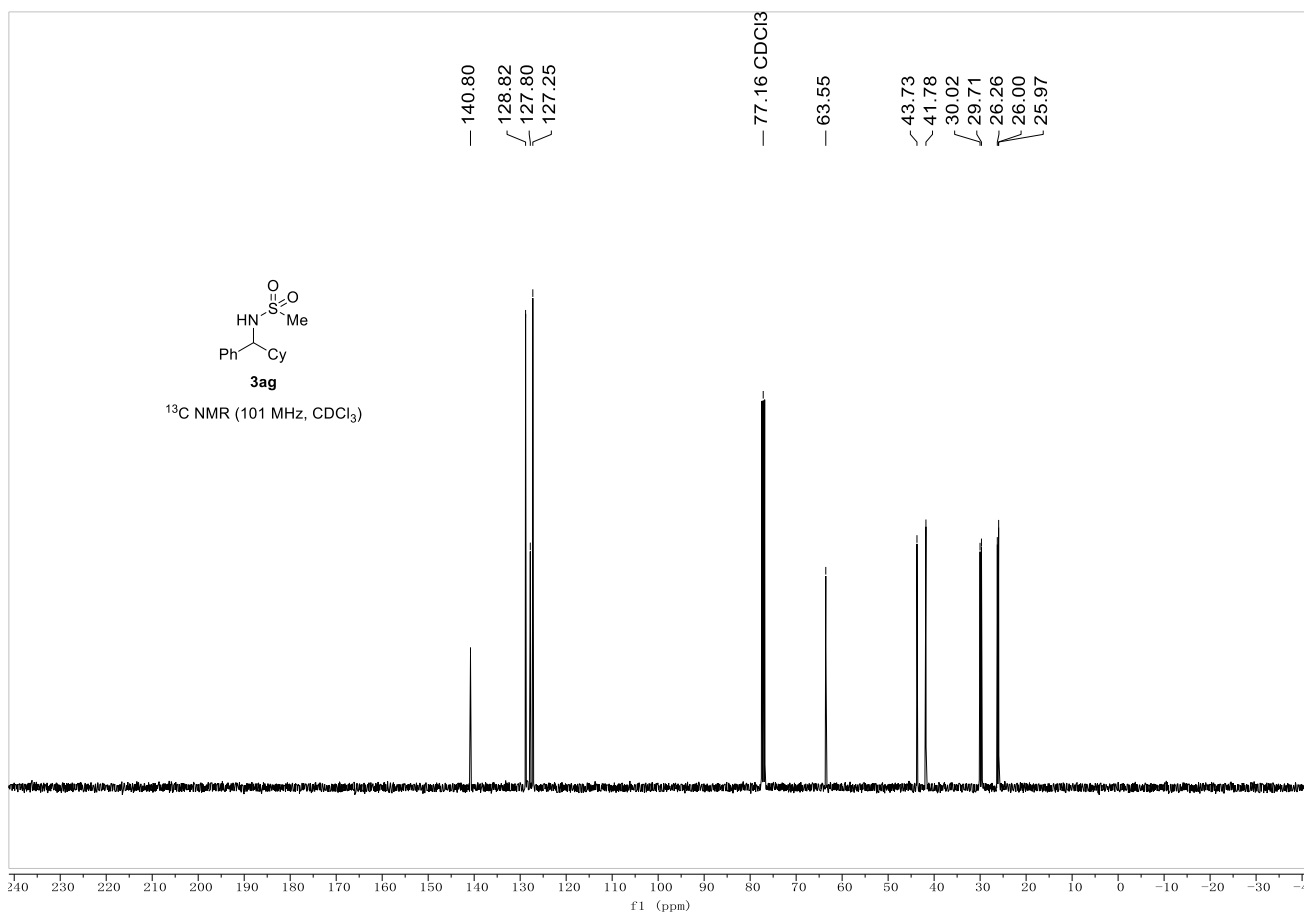
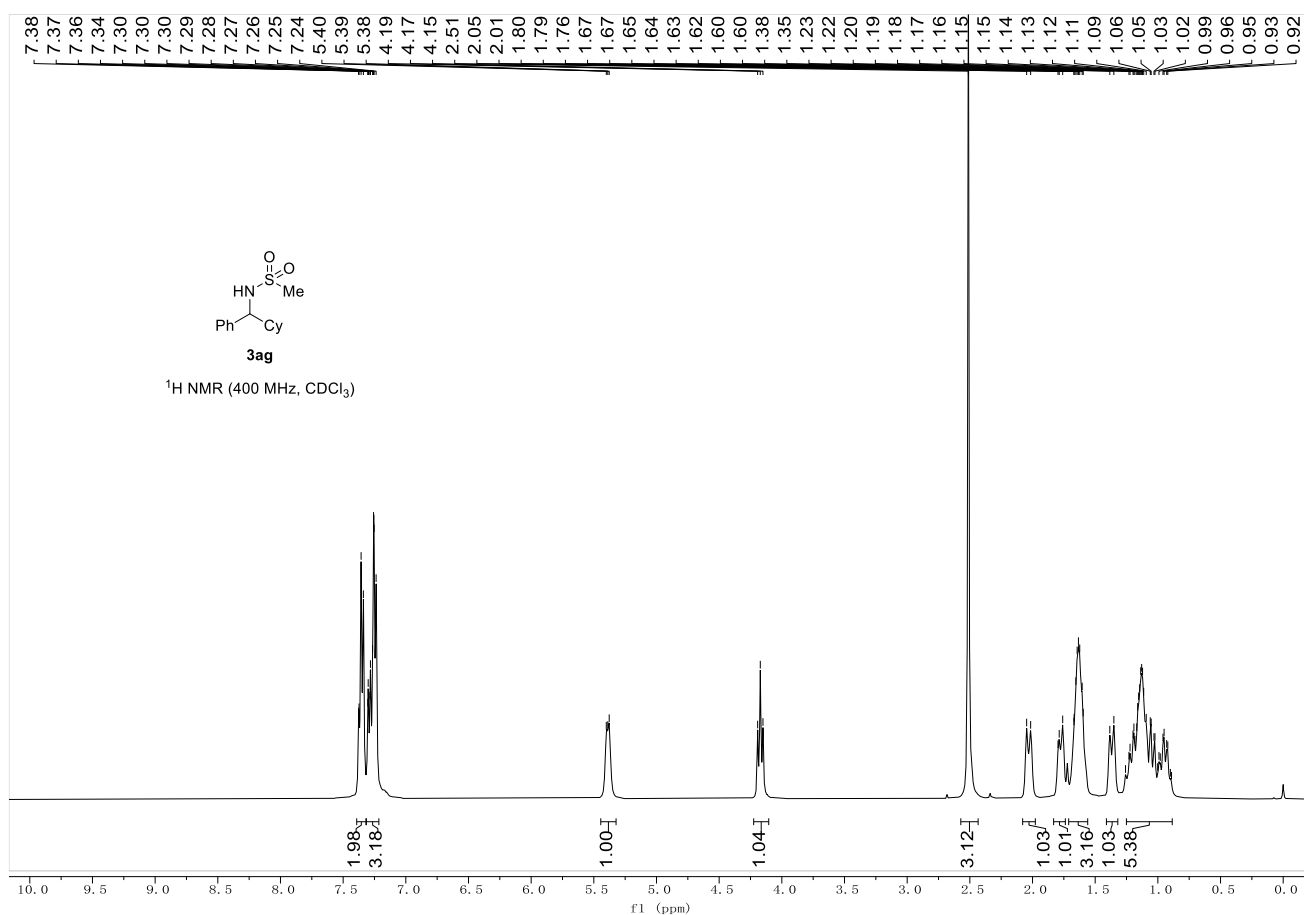


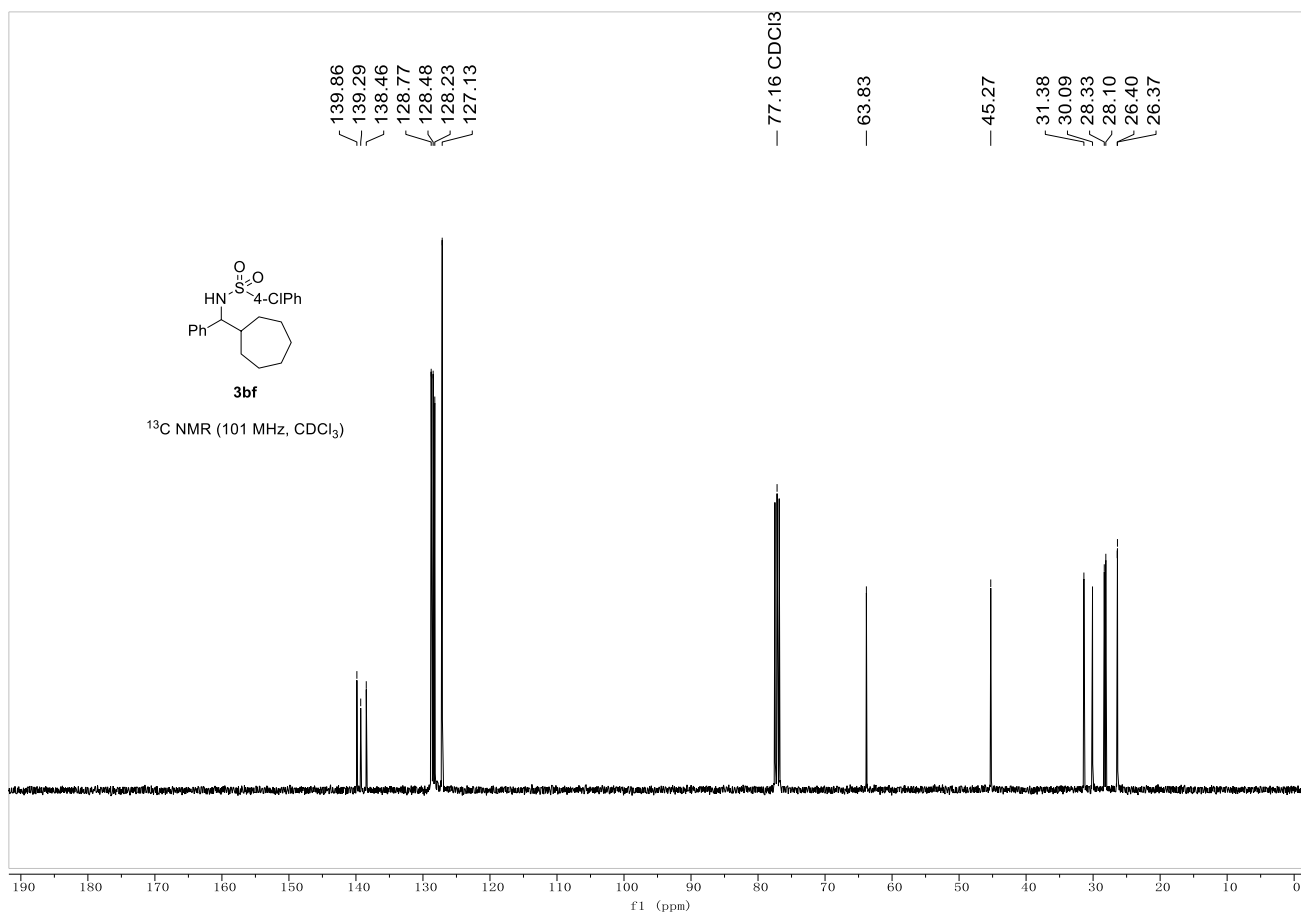
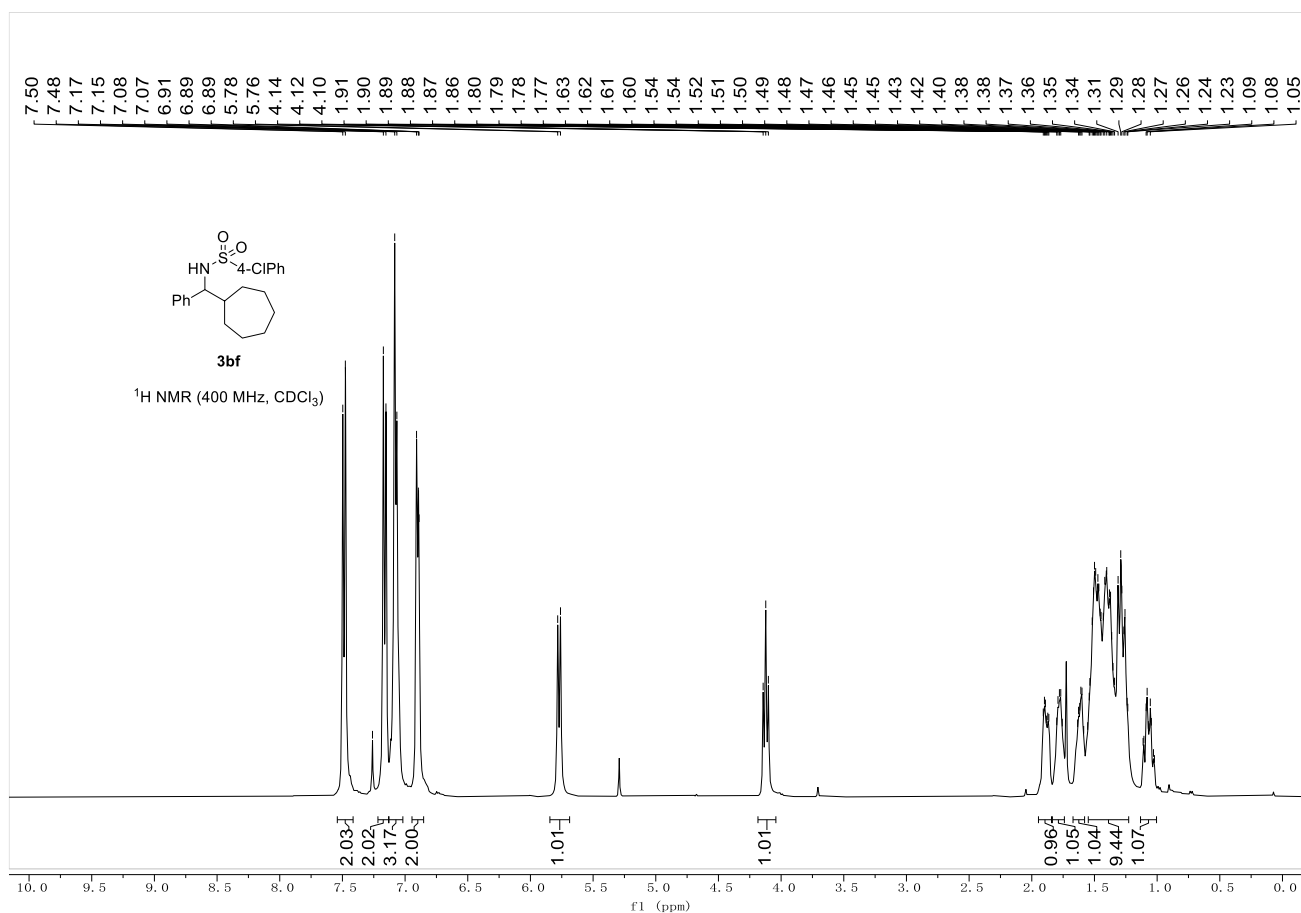


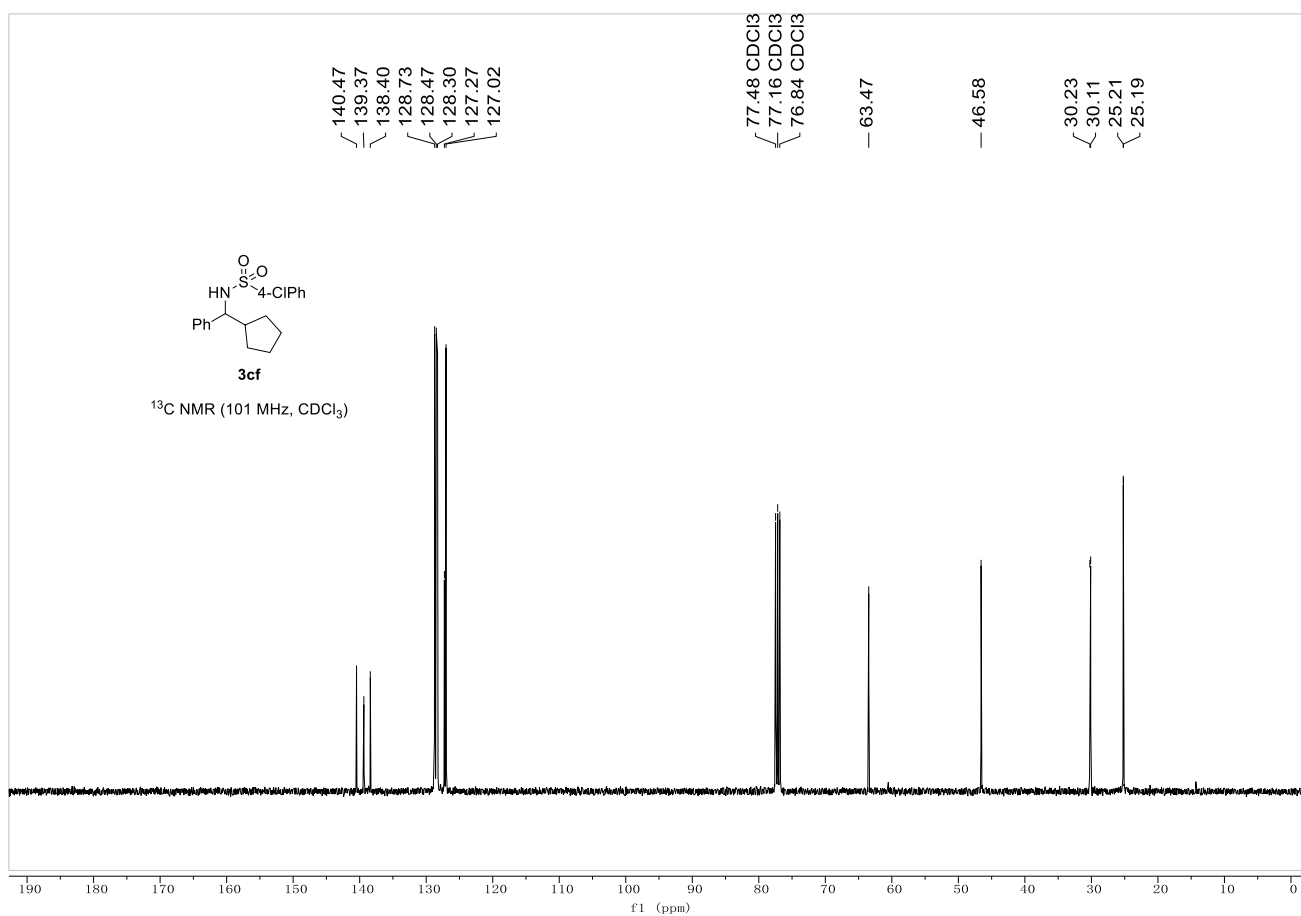
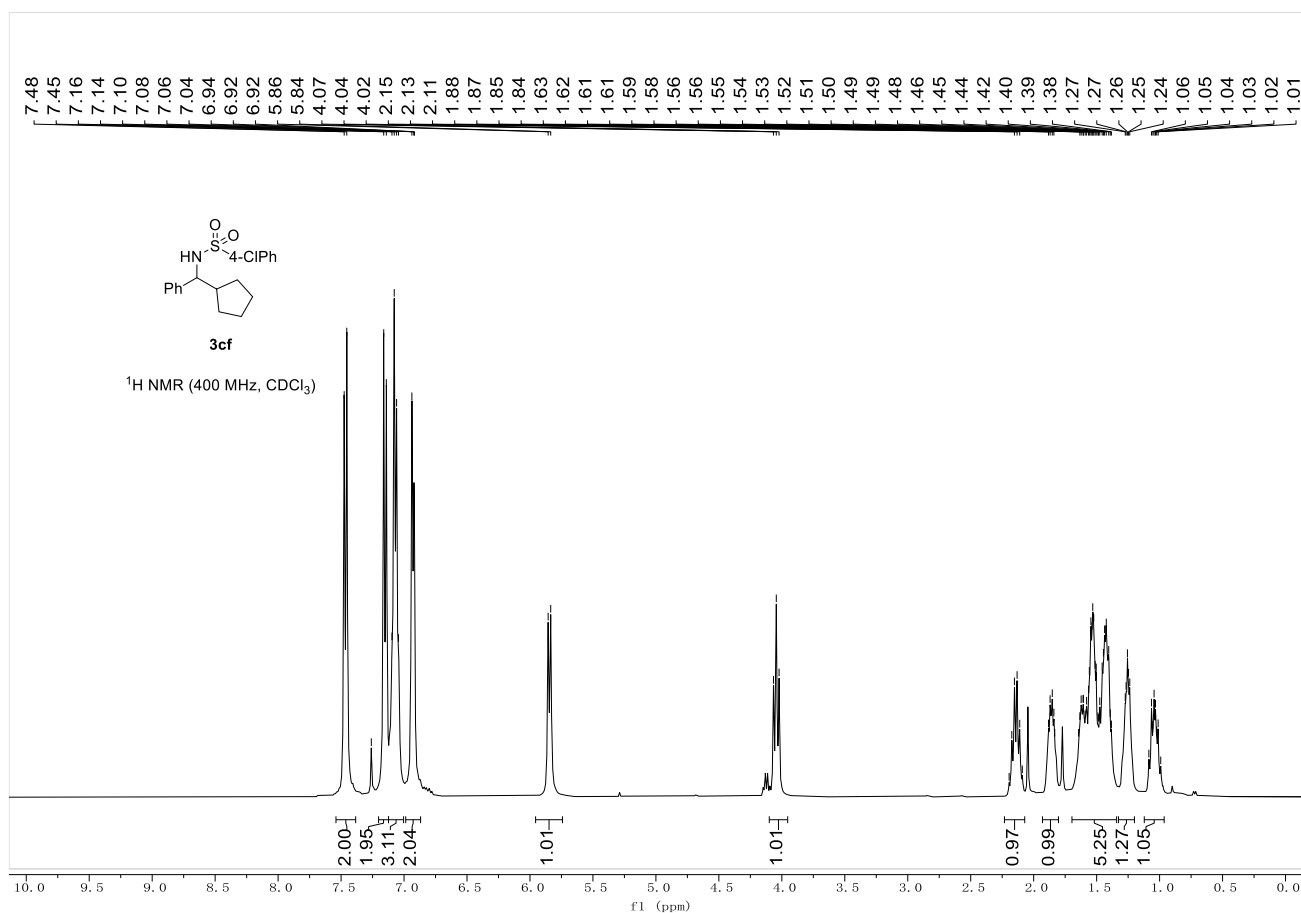


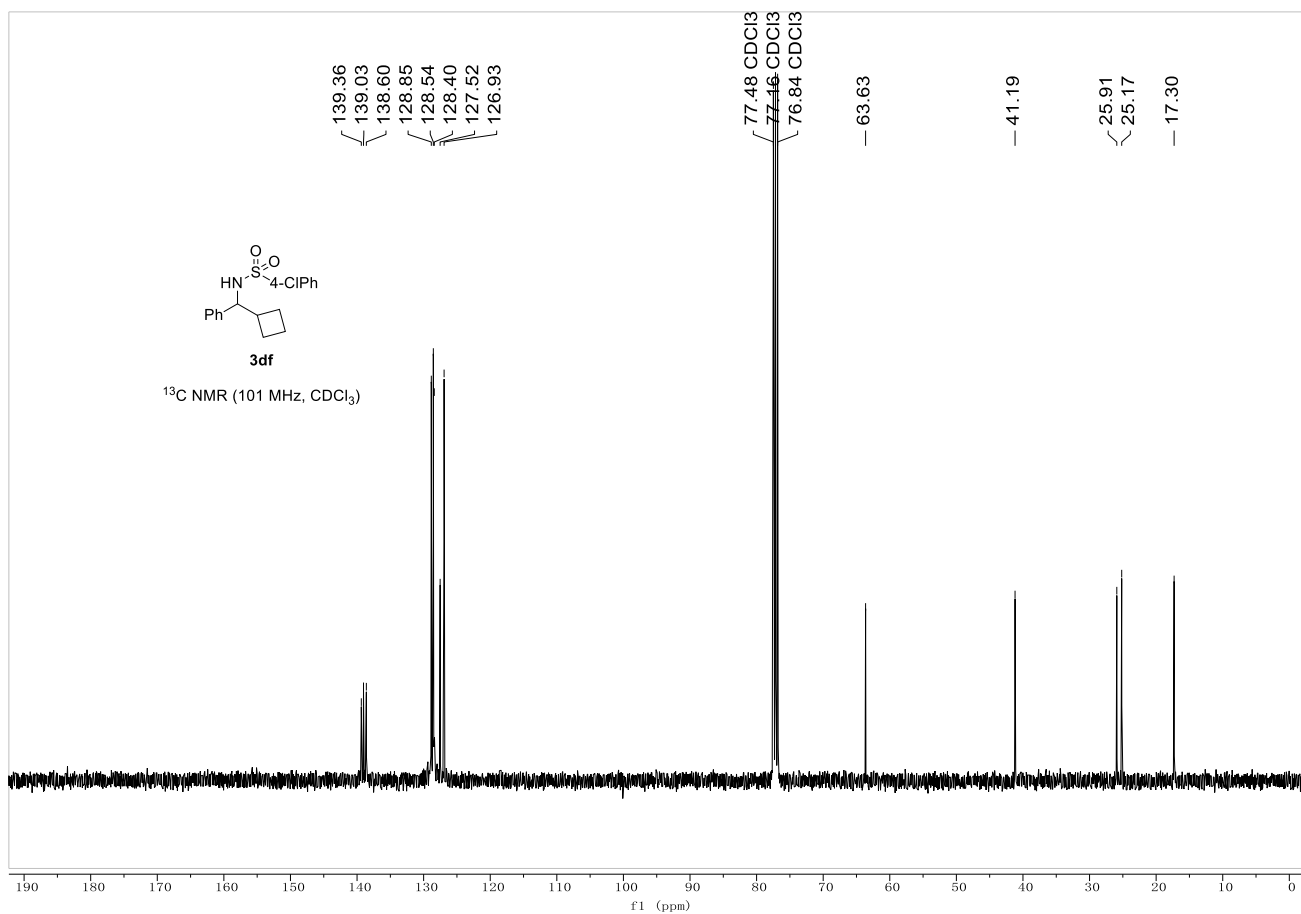
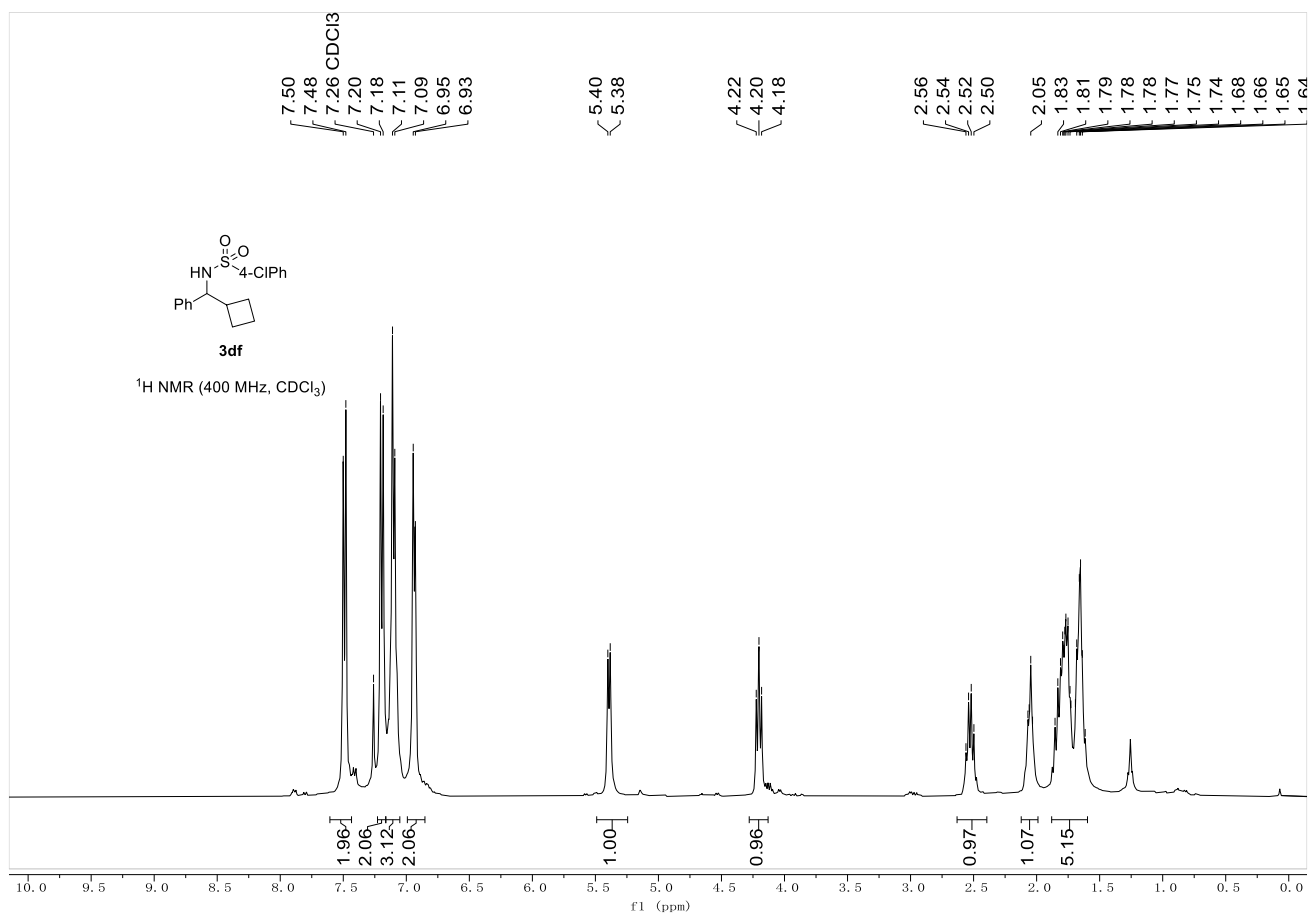


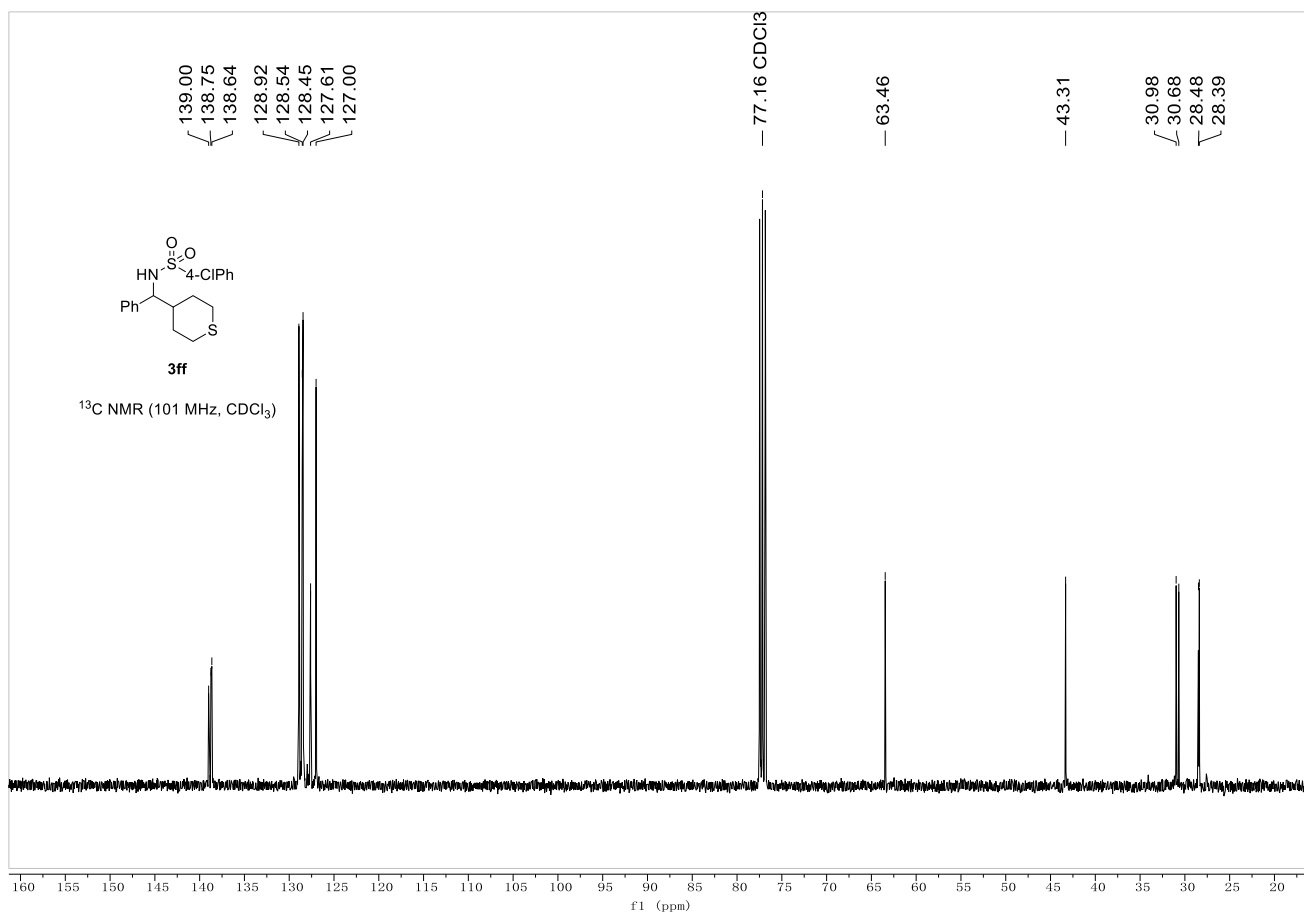
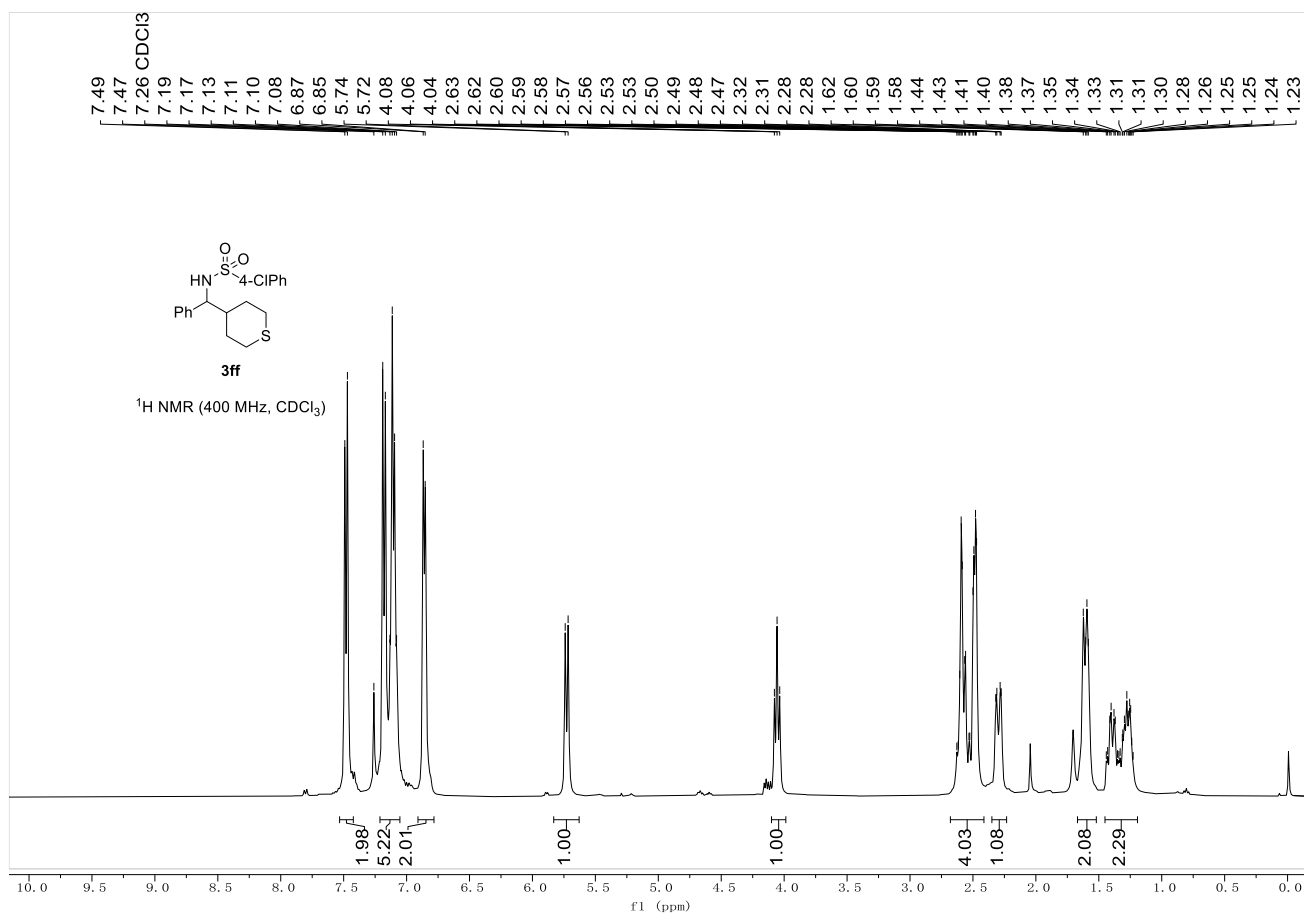


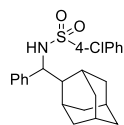






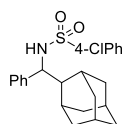
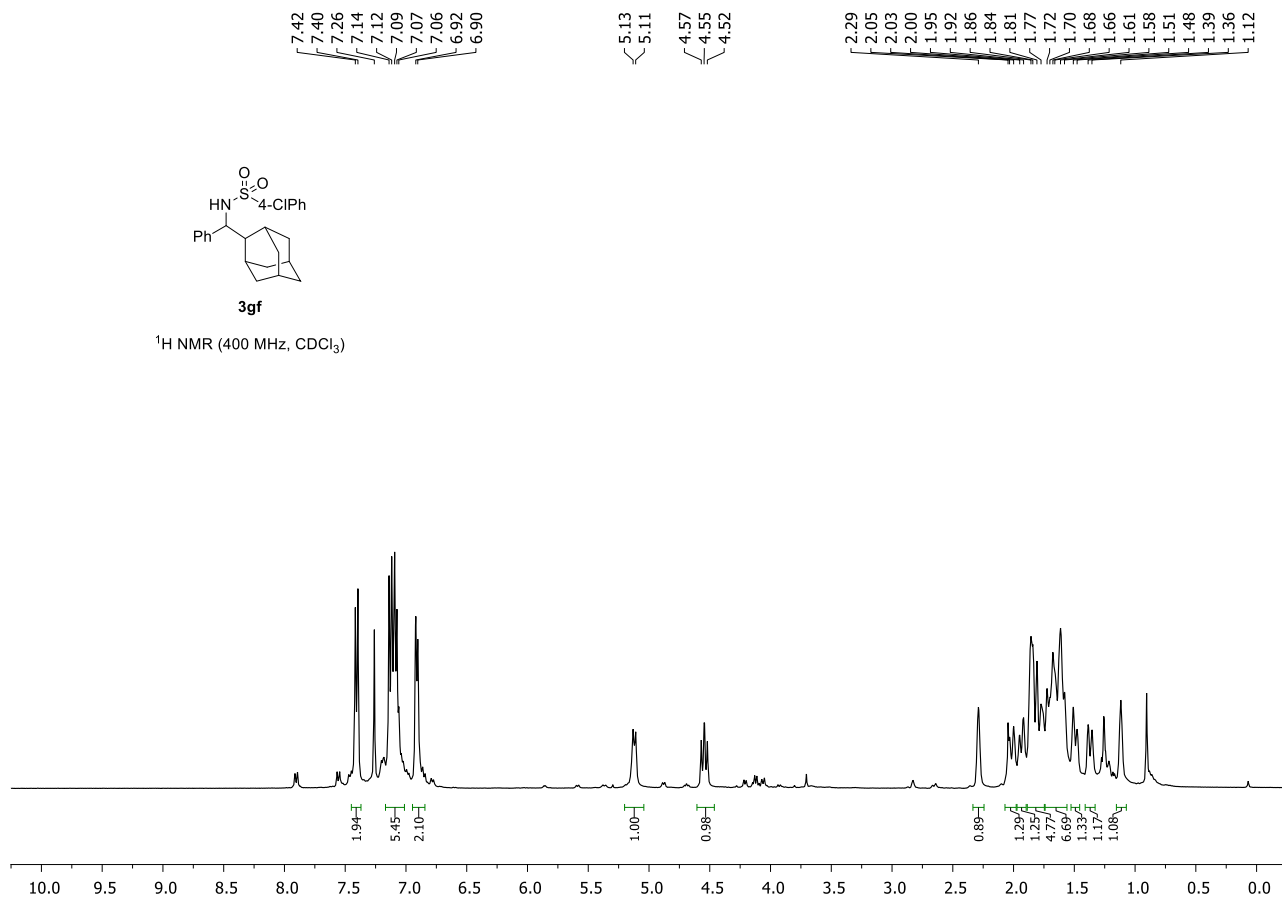






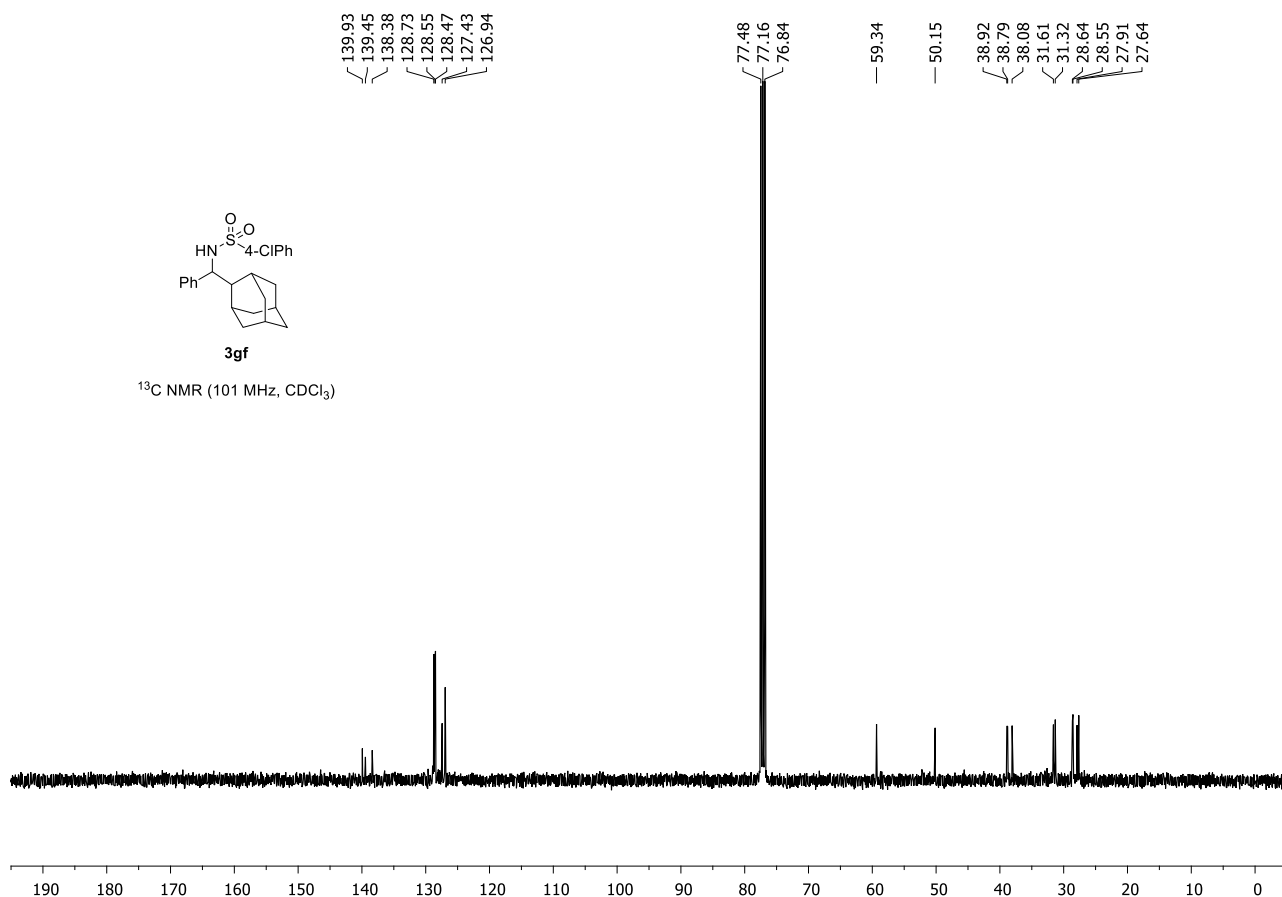
3gf

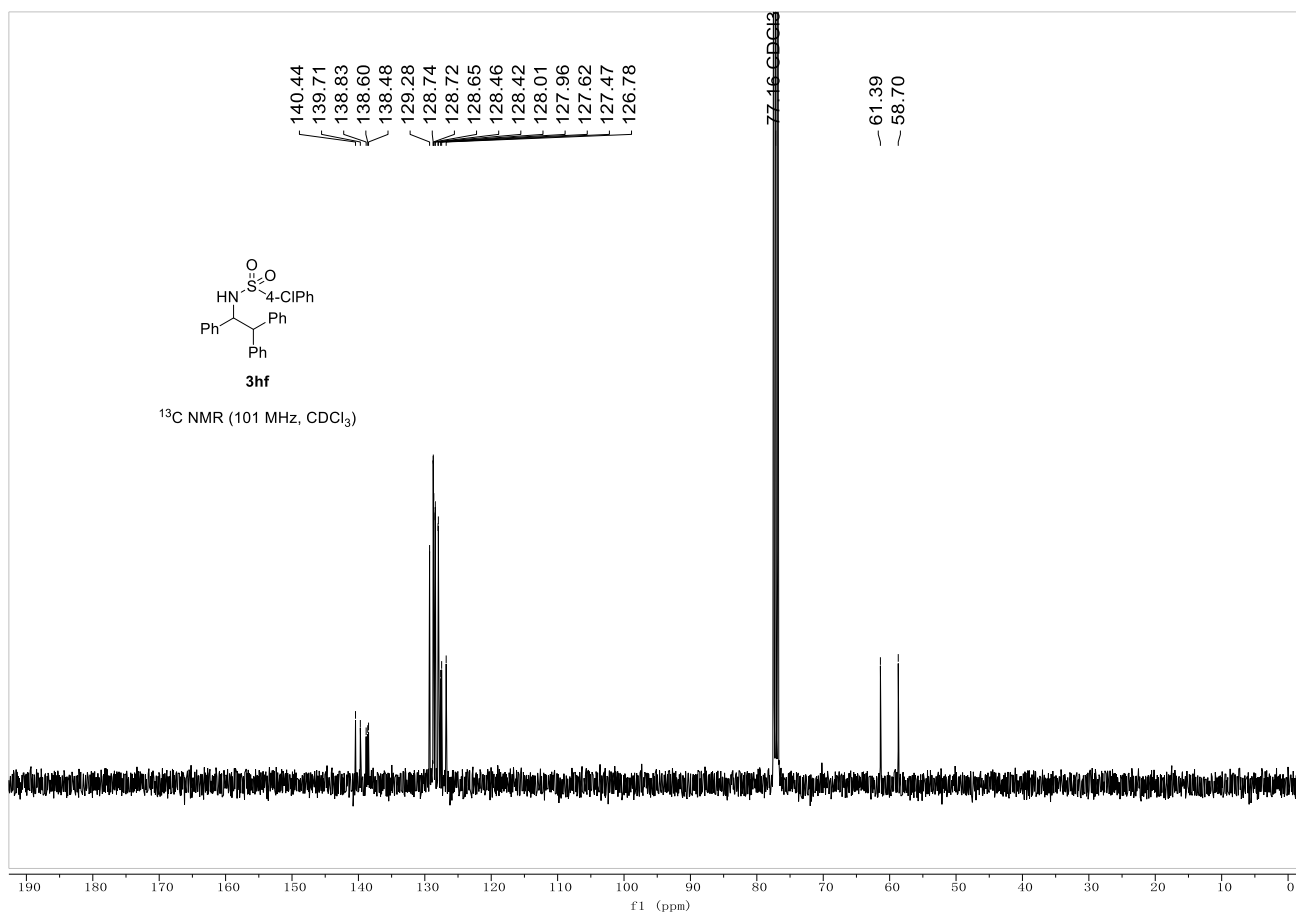
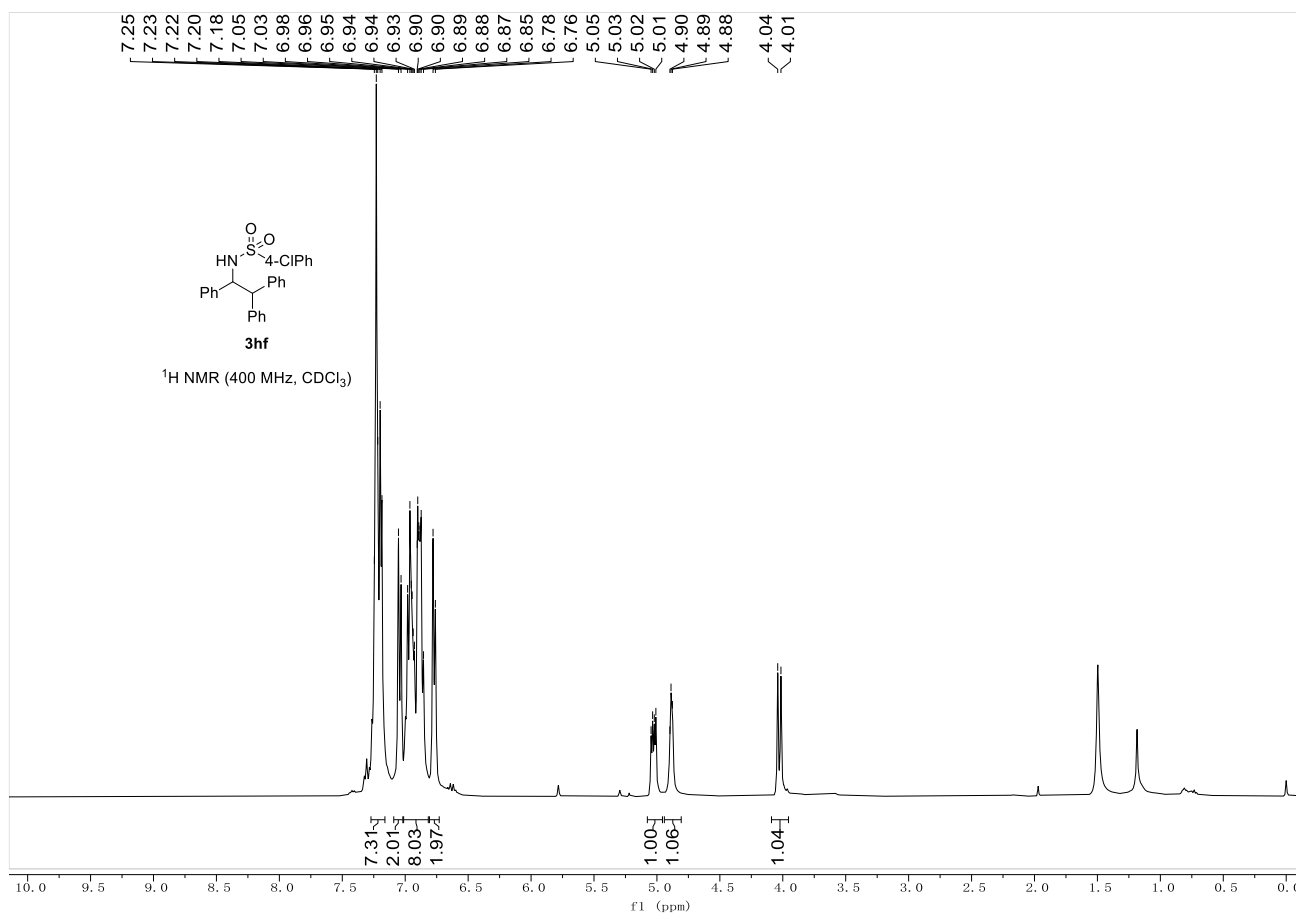
¹H NMR (400 MHz, CDCl₃)

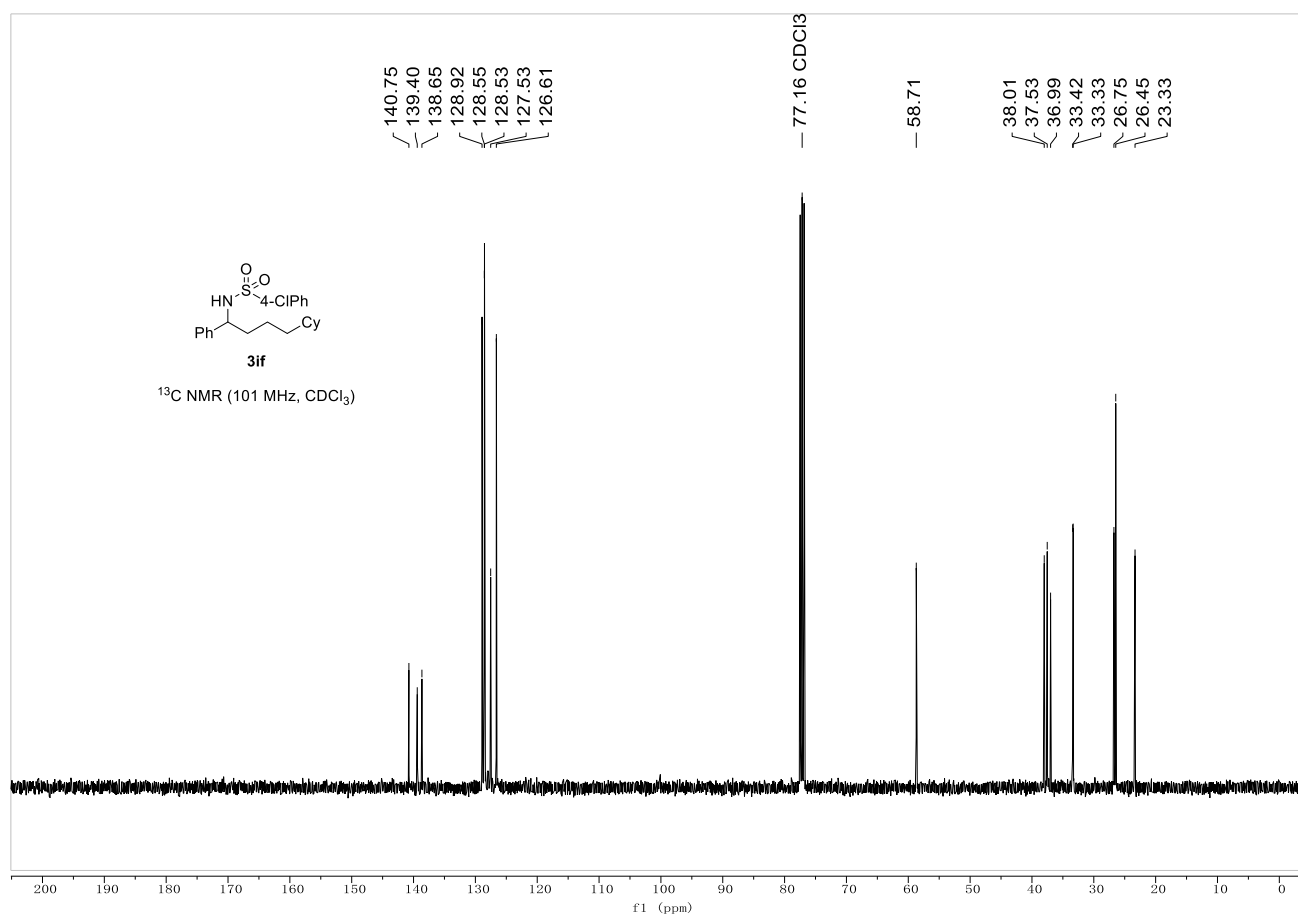
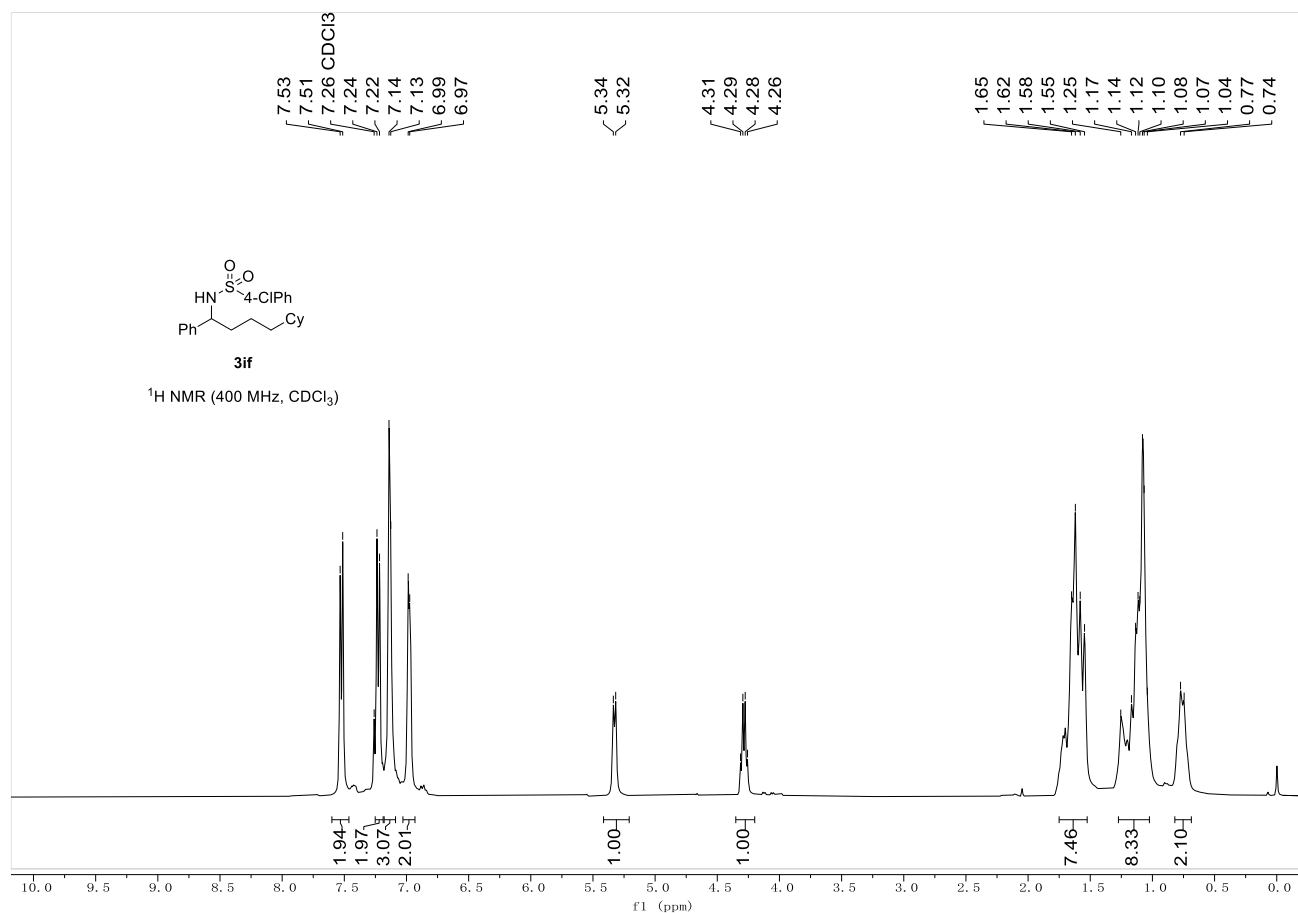


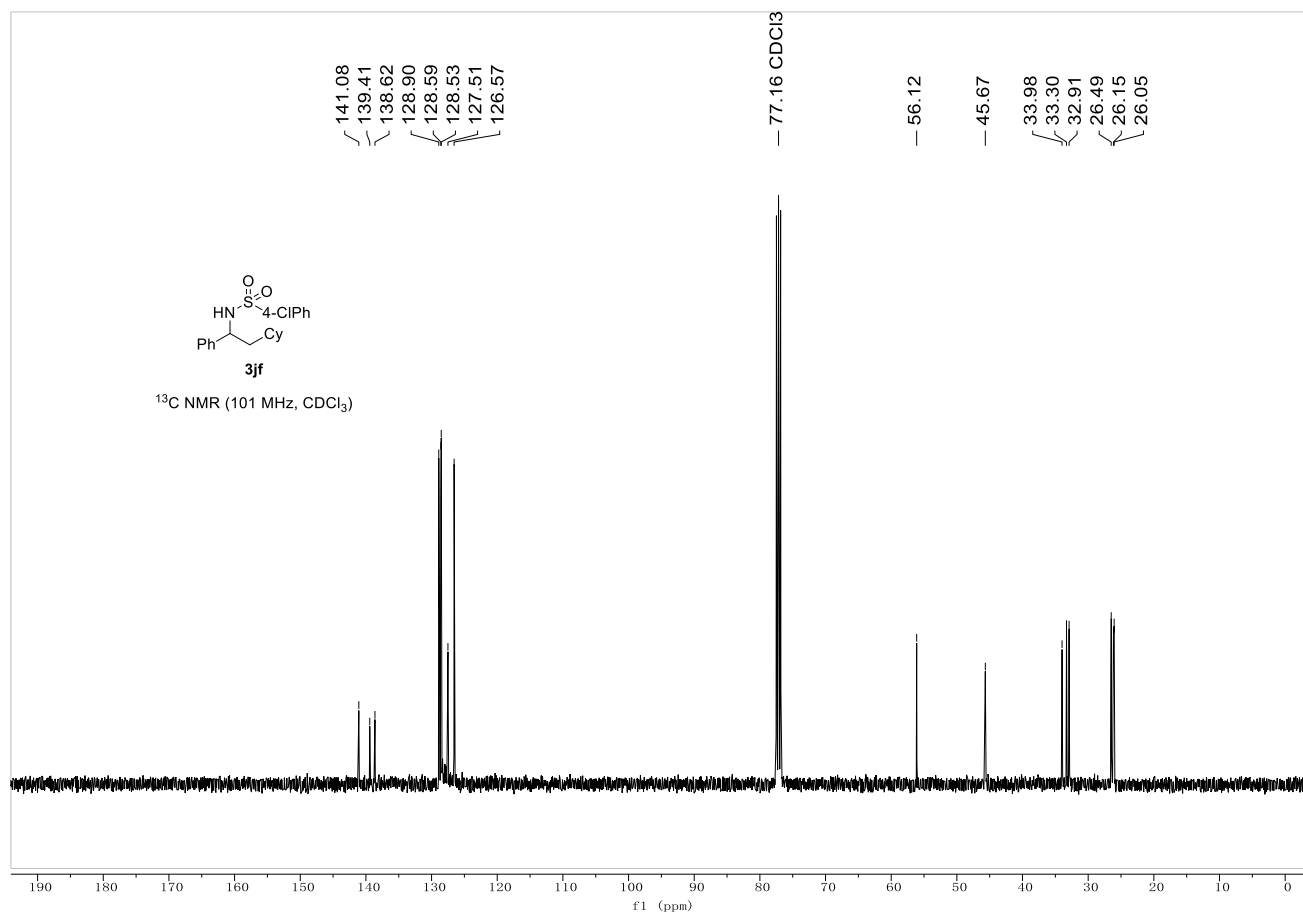
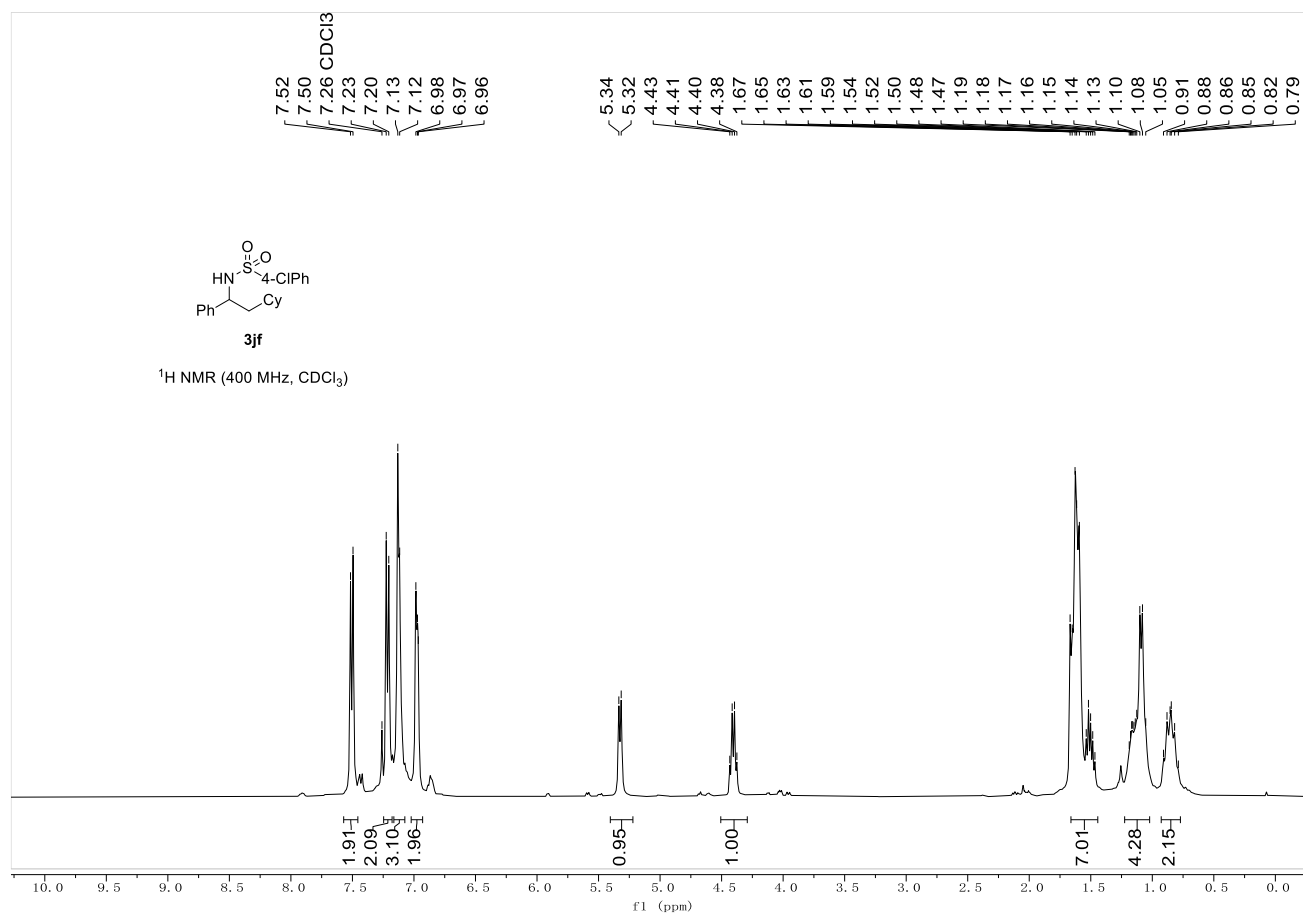
3gf

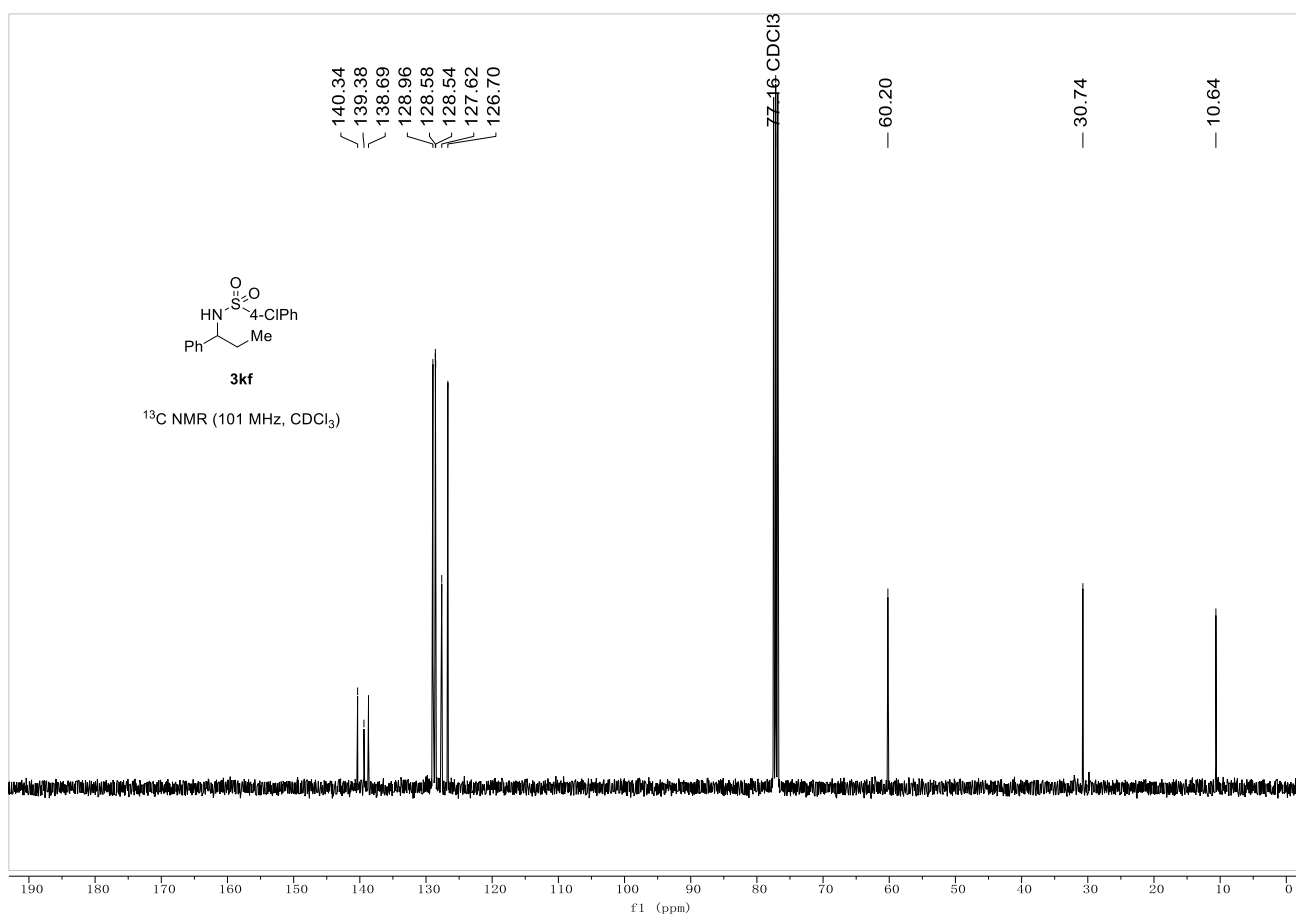
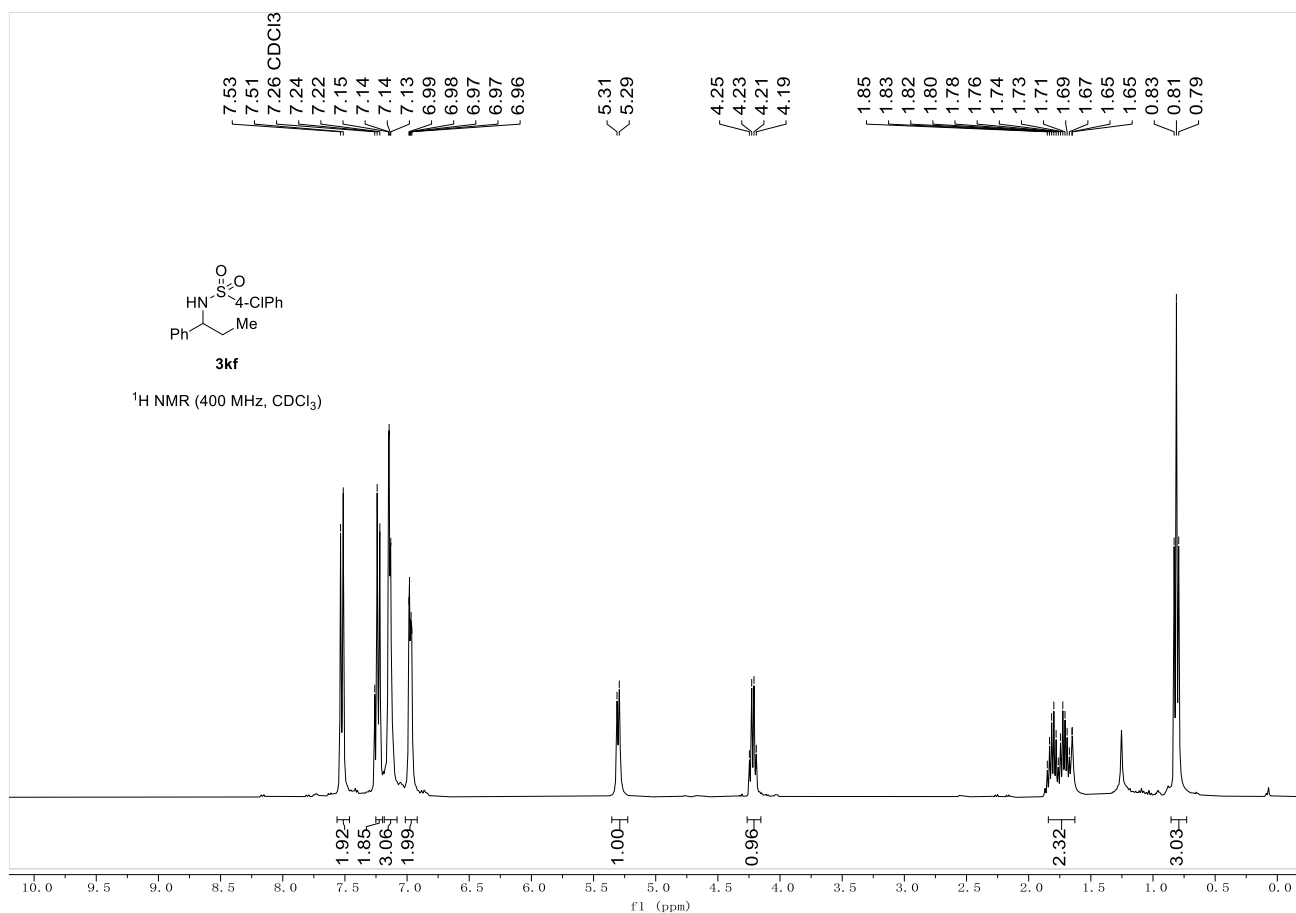
¹³C NMR (101 MHz, CDCl₃)

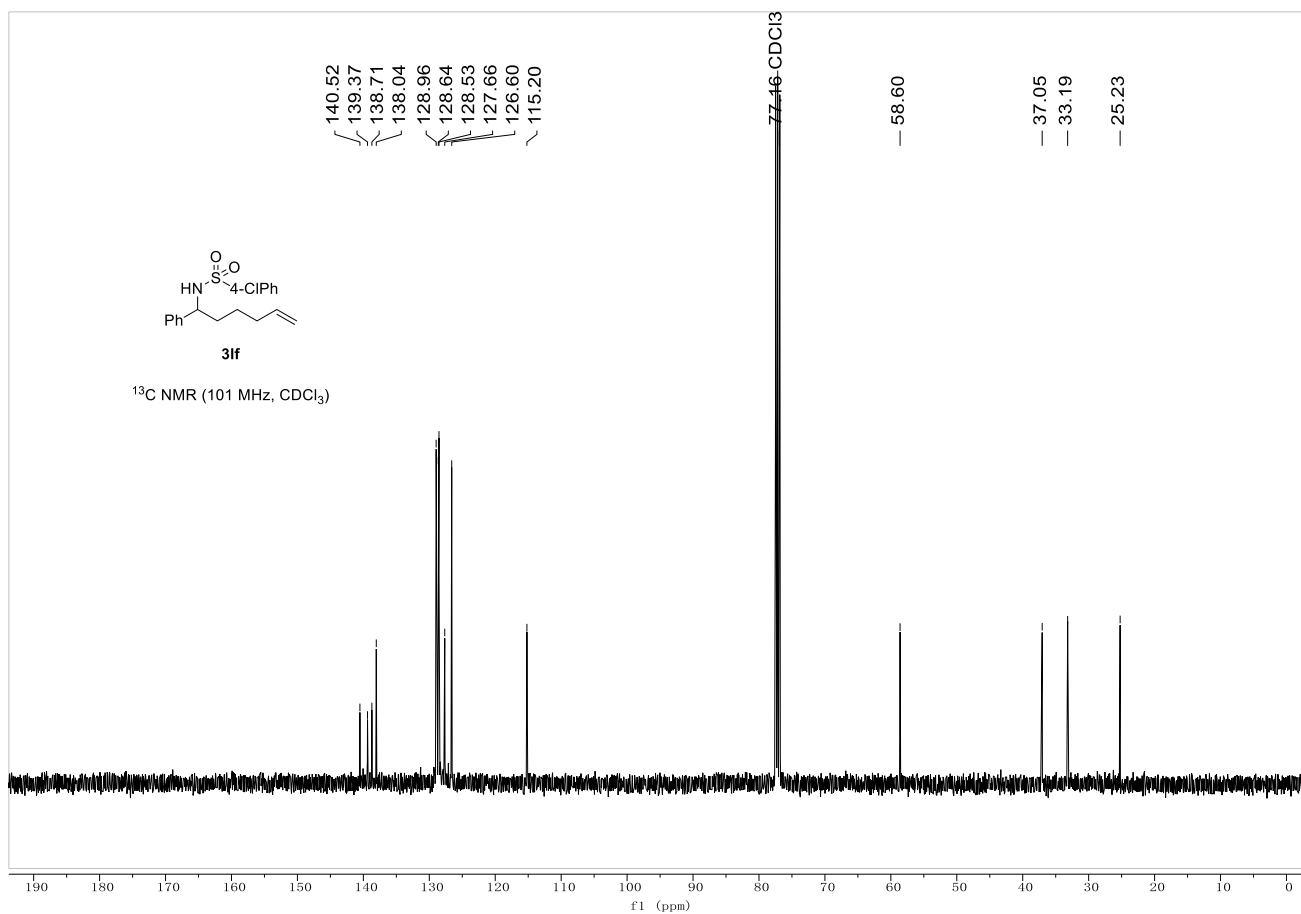
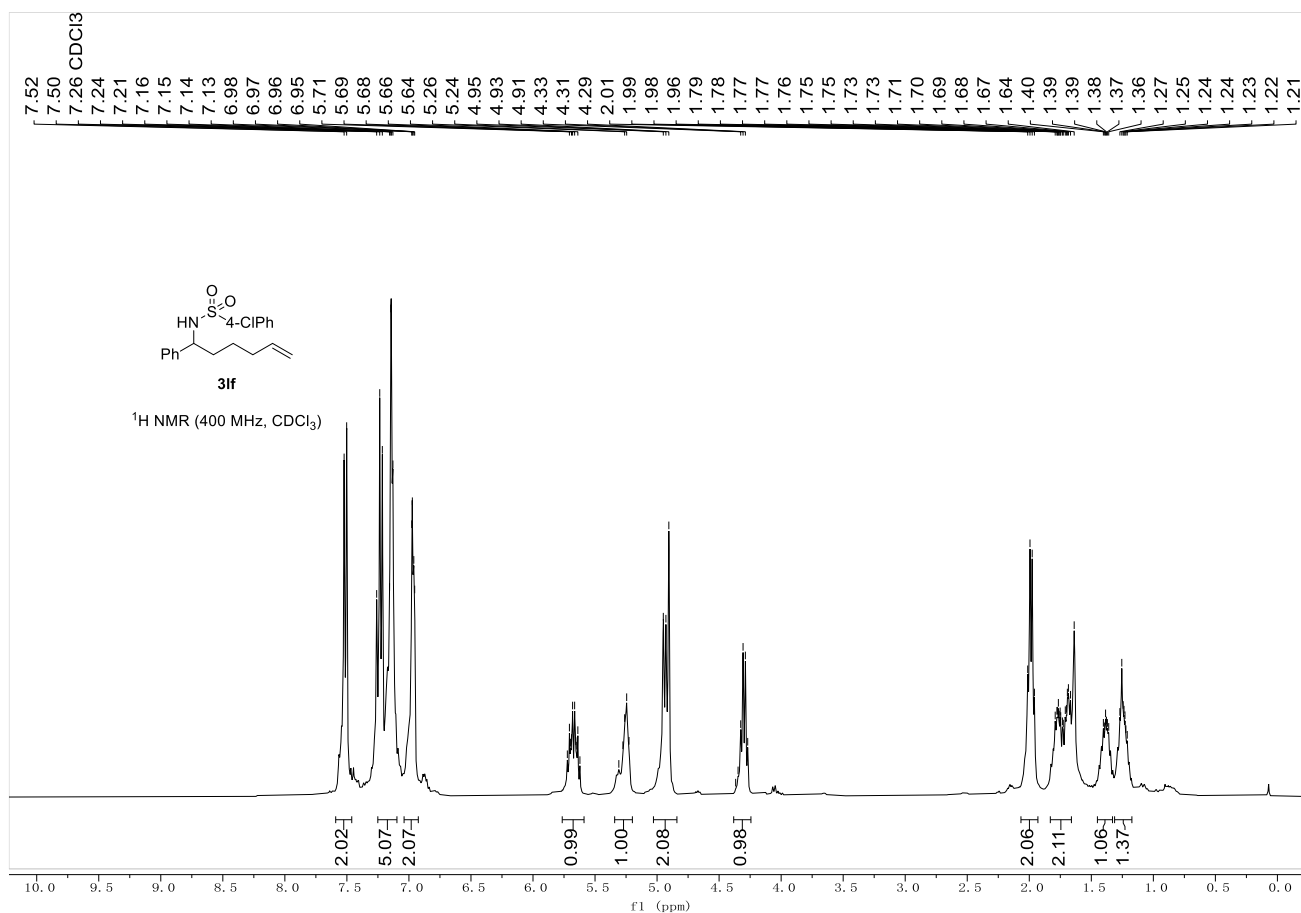


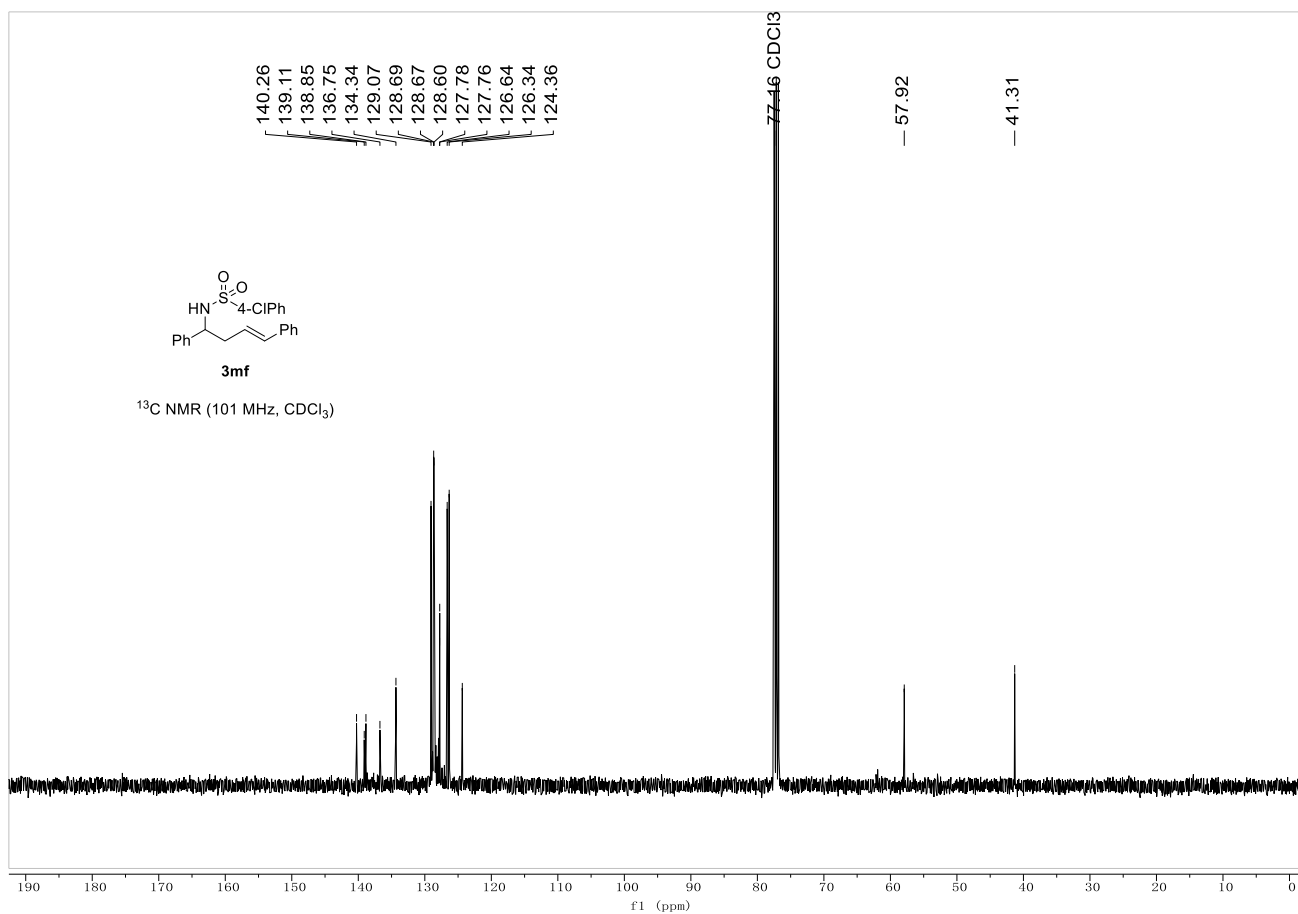
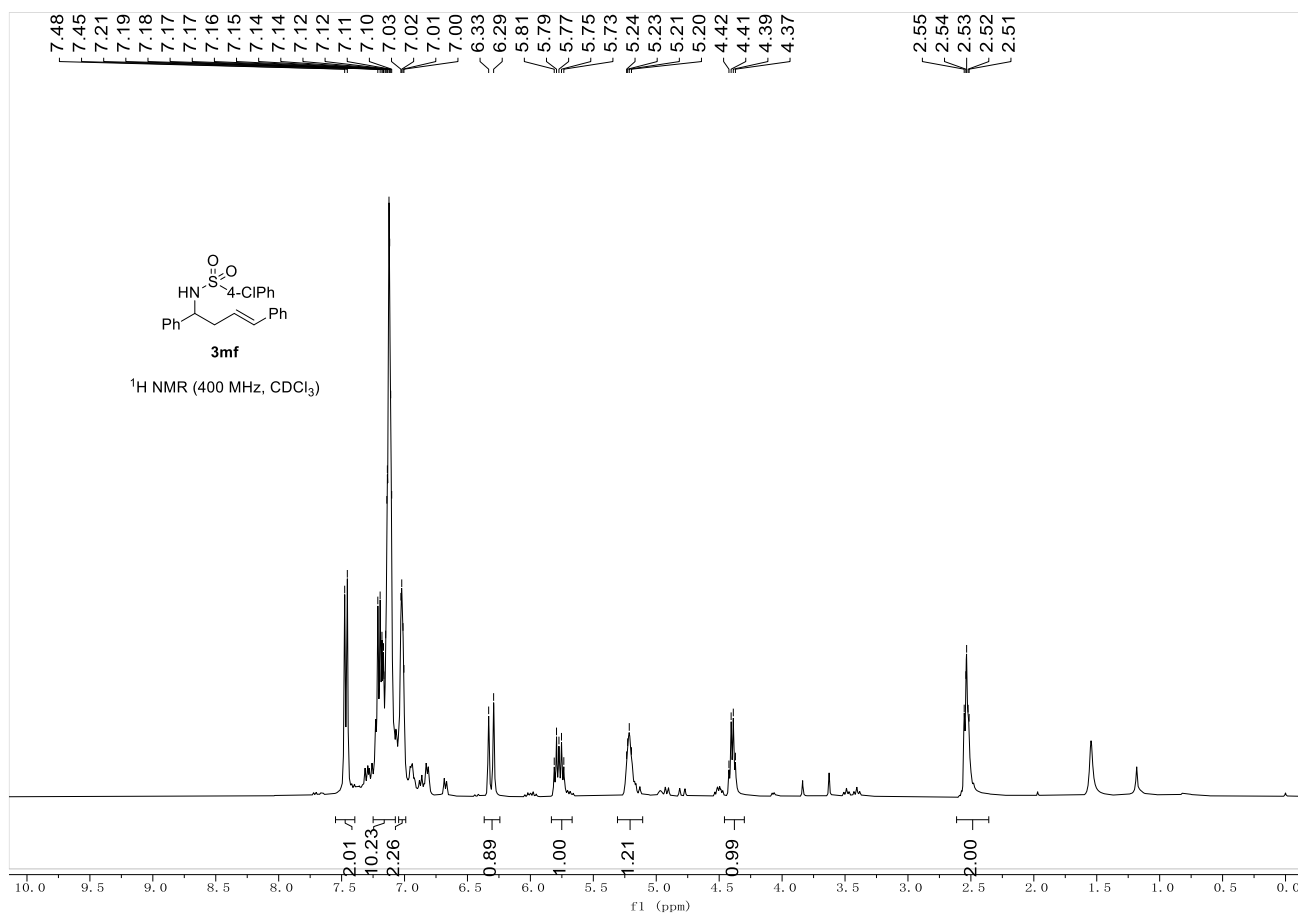


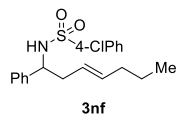




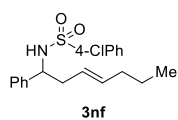
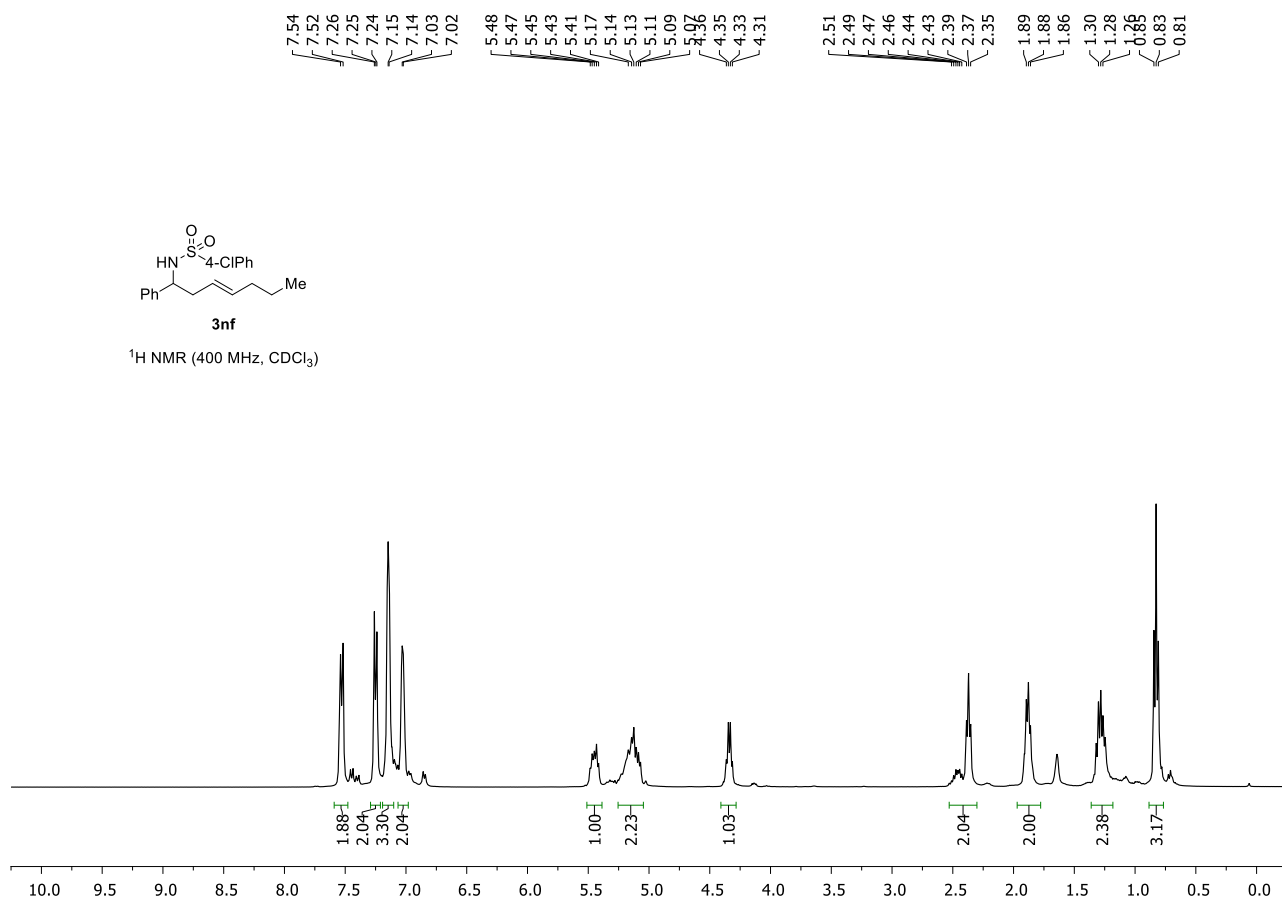




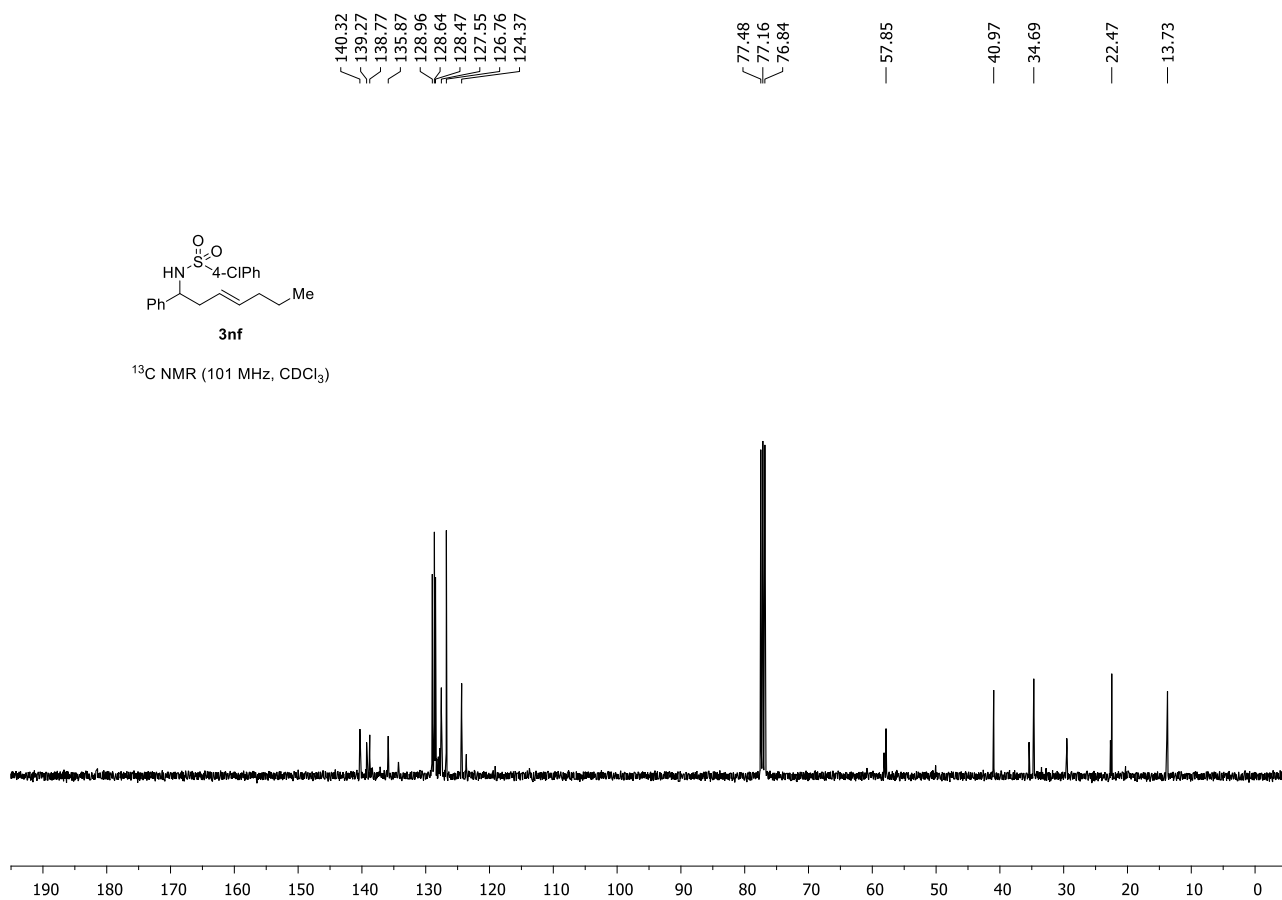


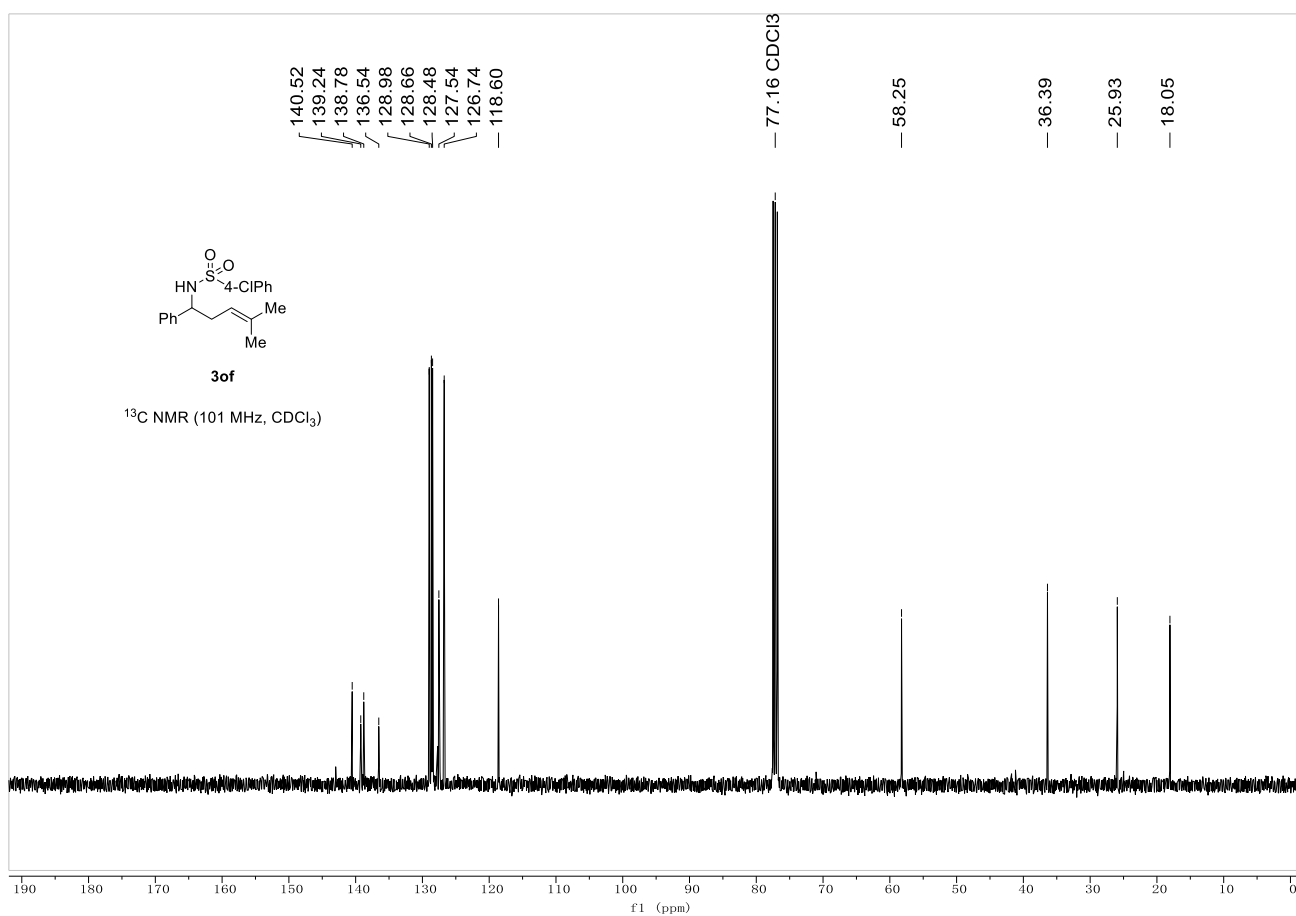
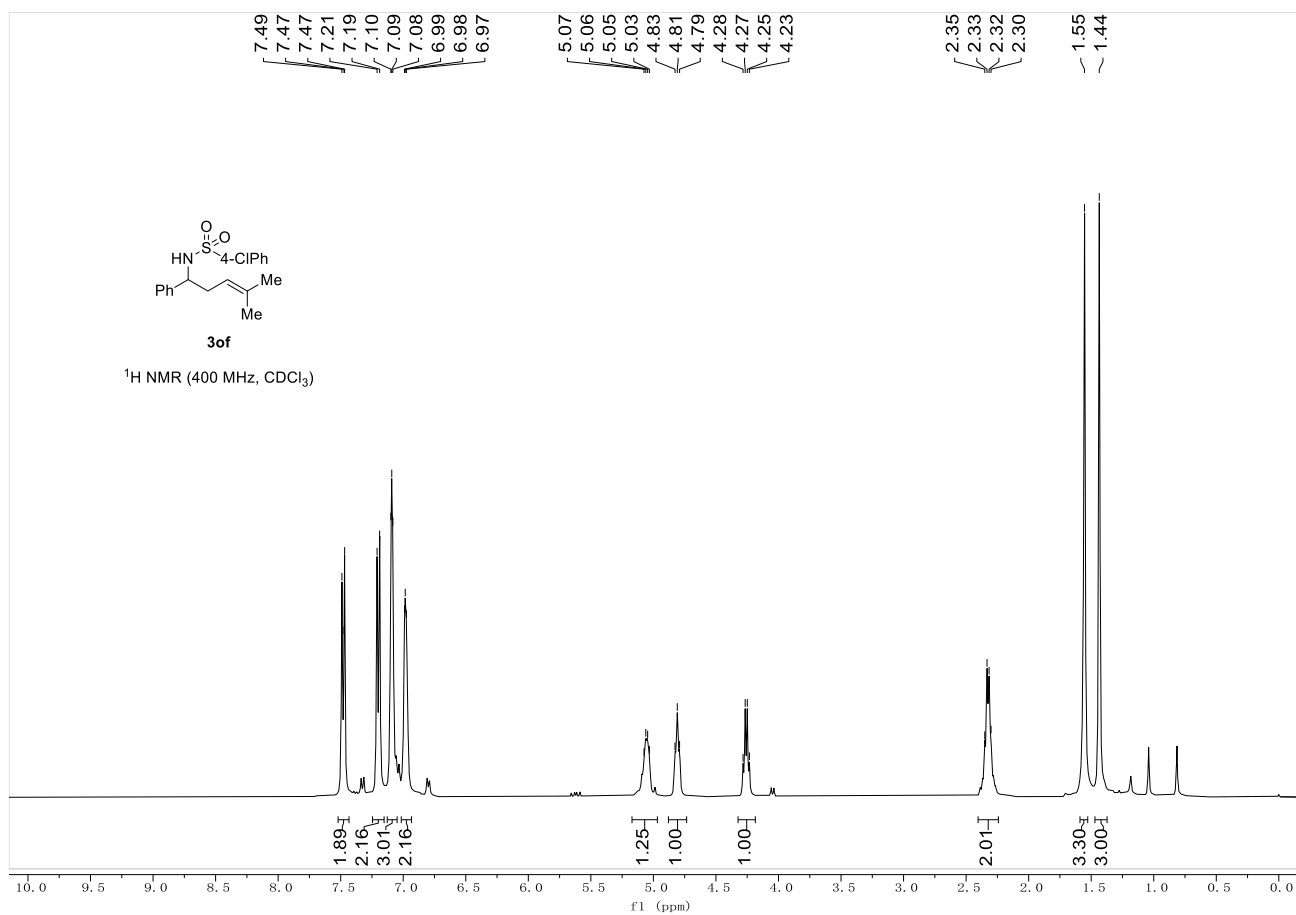


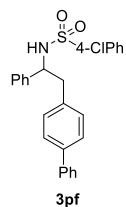
¹H NMR (400 MHz, CDCl₃)



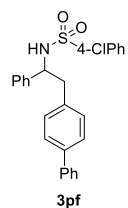
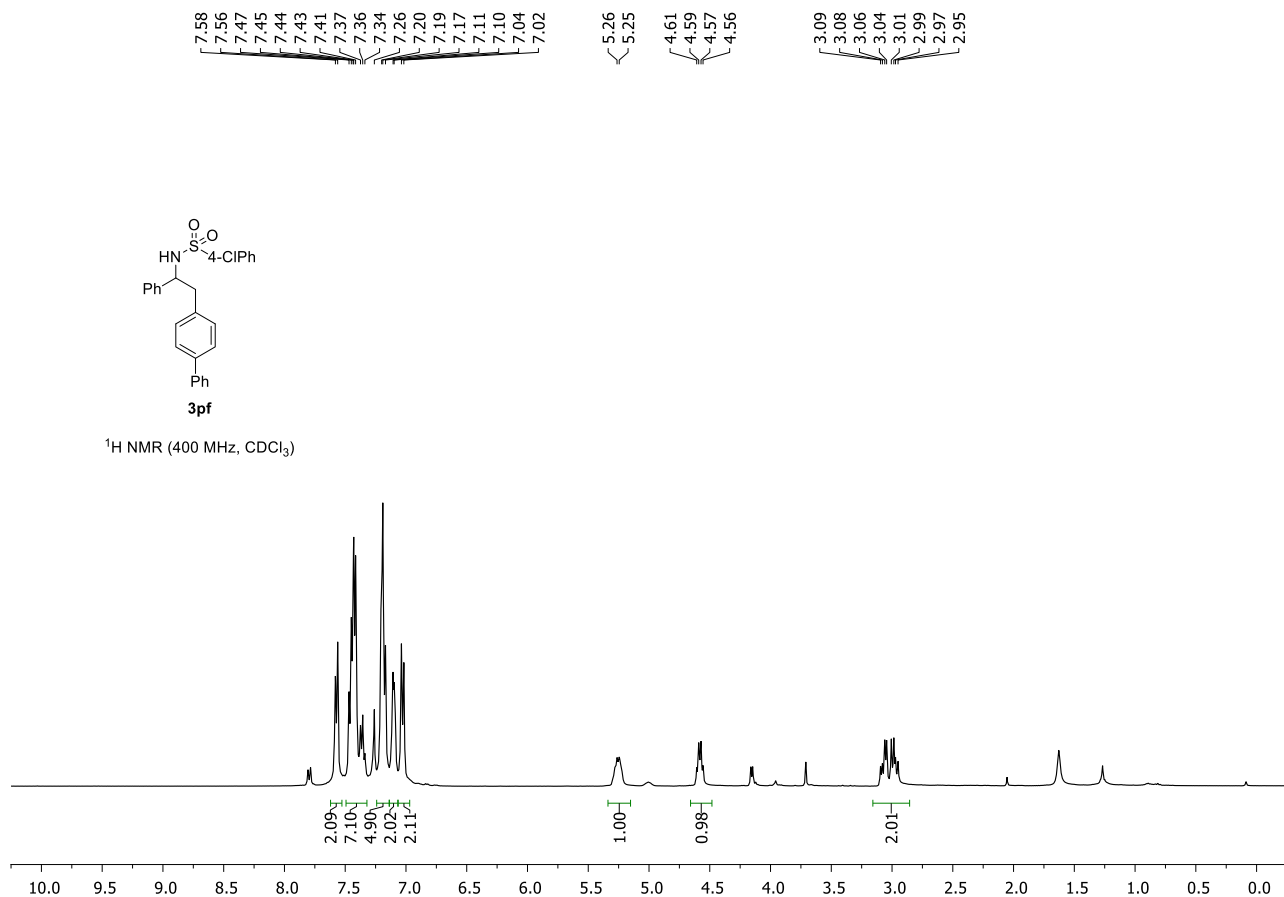
¹³C NMR (101 MHz, CDCl₃)



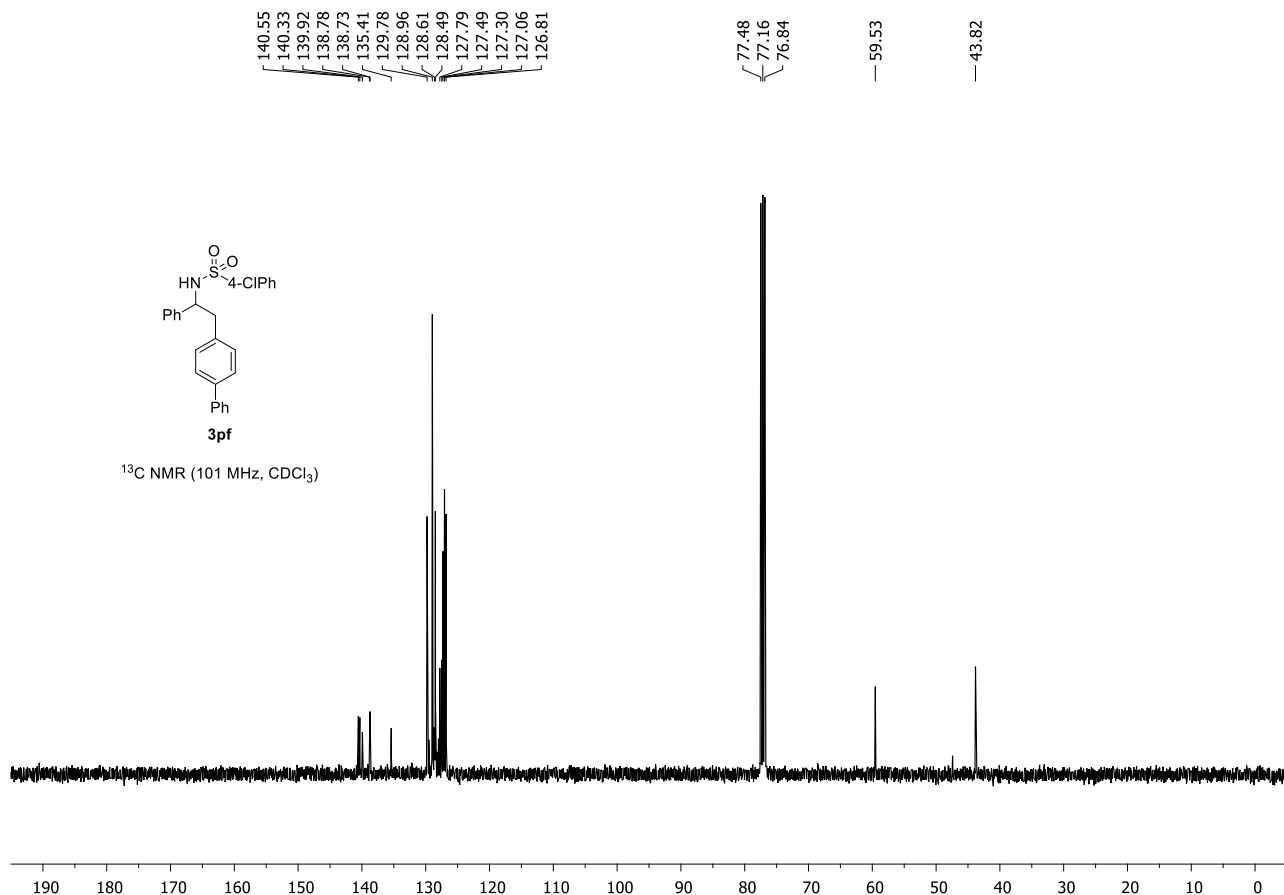


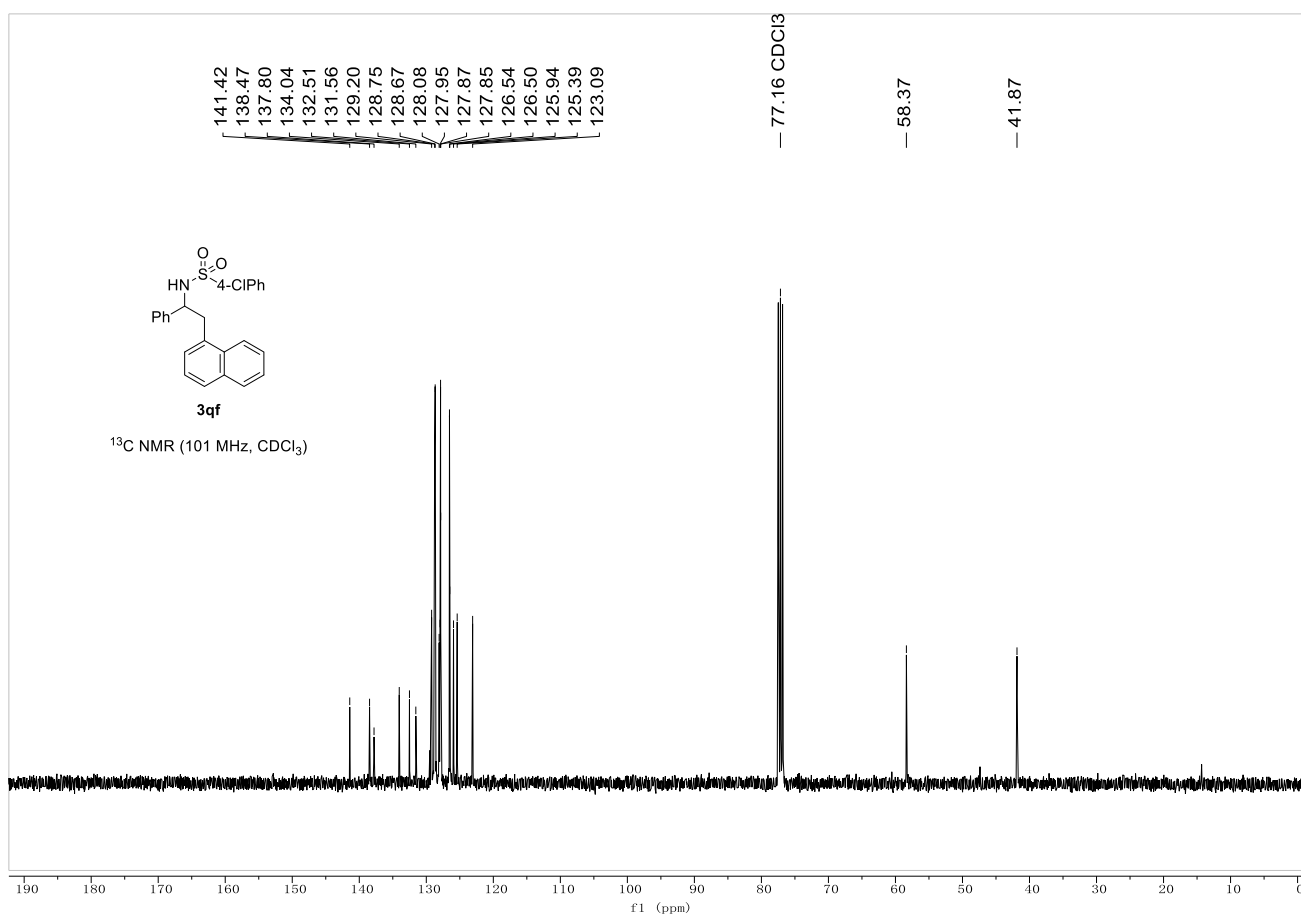
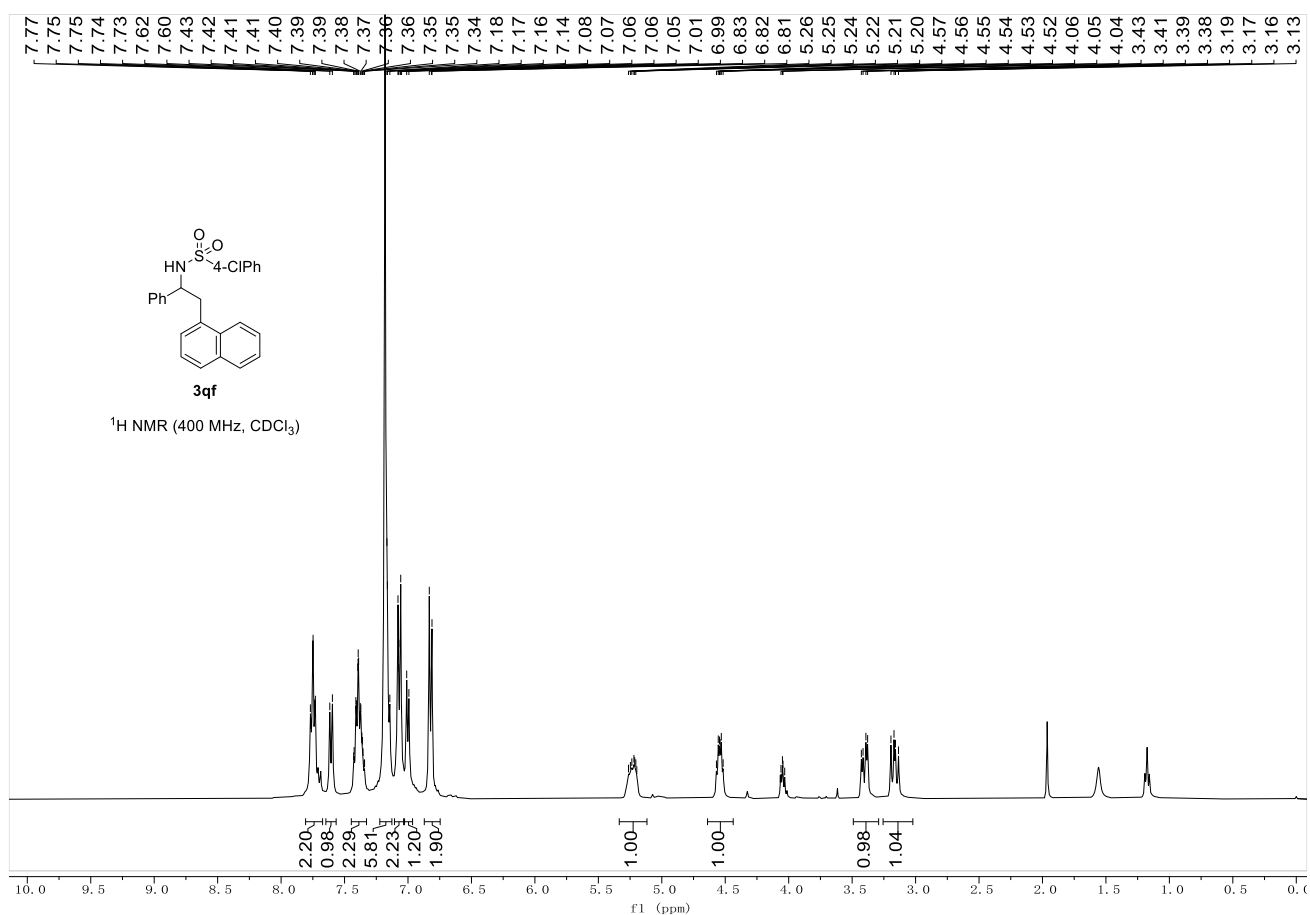


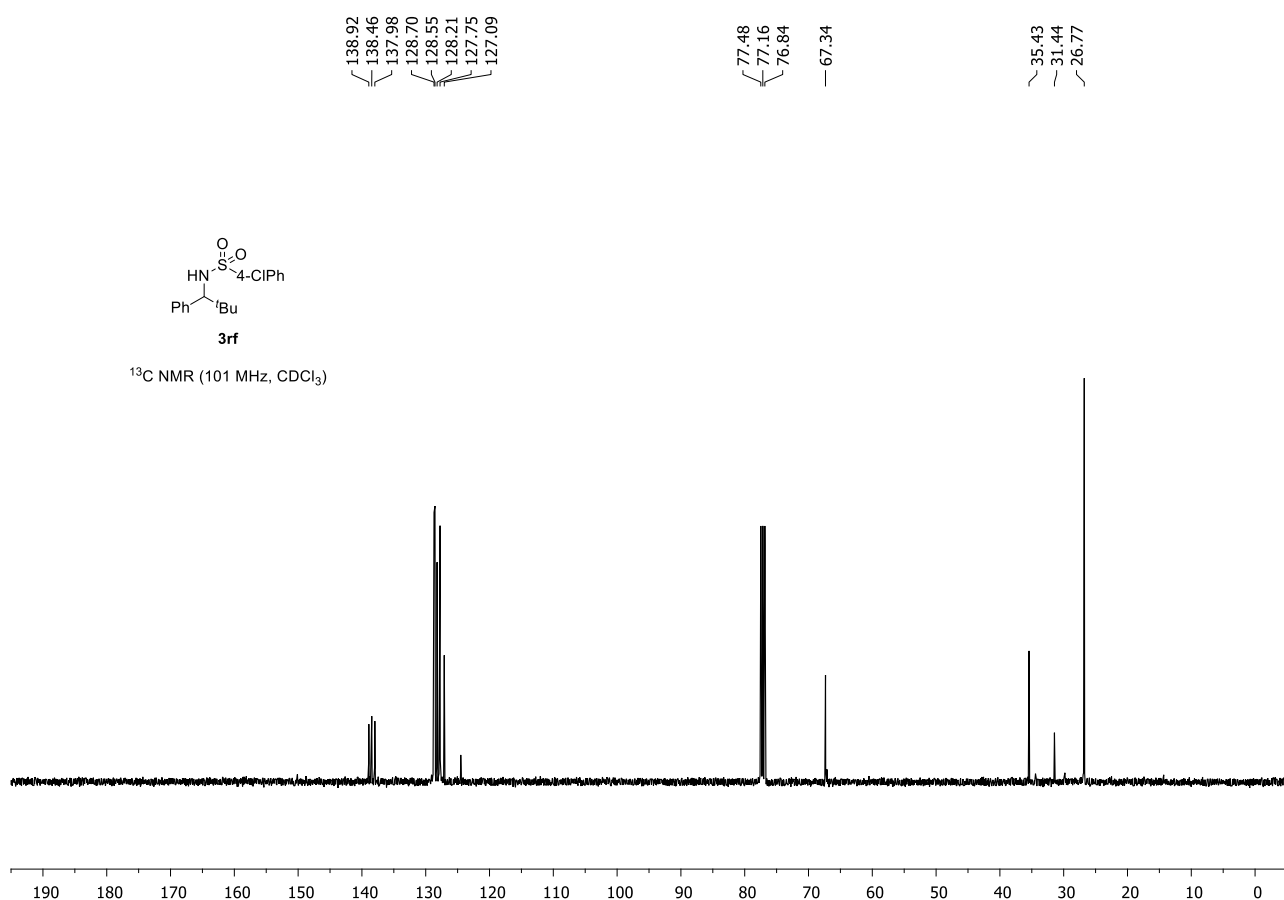
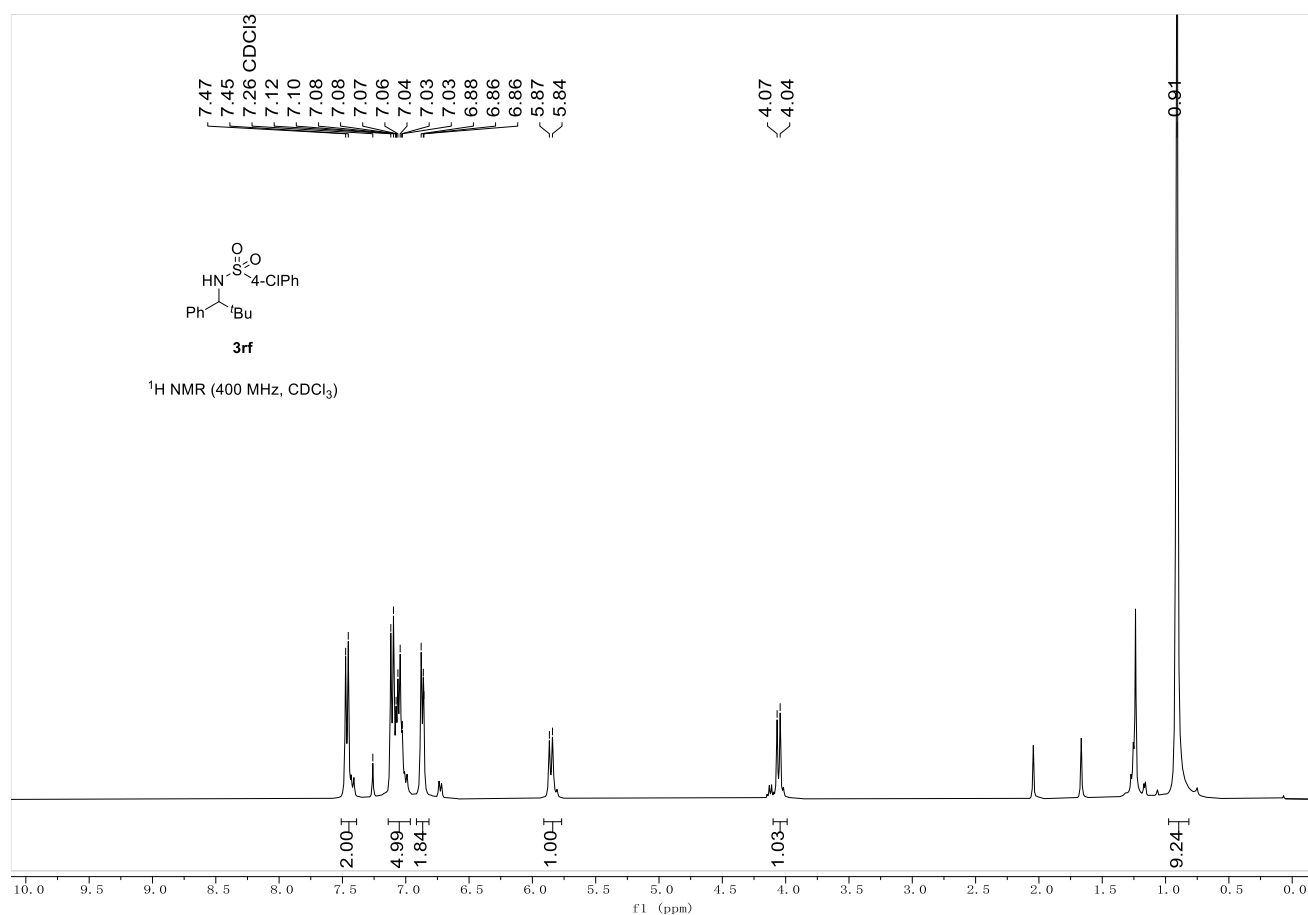
¹H NMR (400 MHz, CDCl₃)

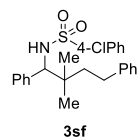


¹³C NMR (101 MHz, CDCl₃)

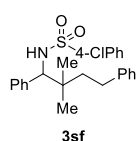
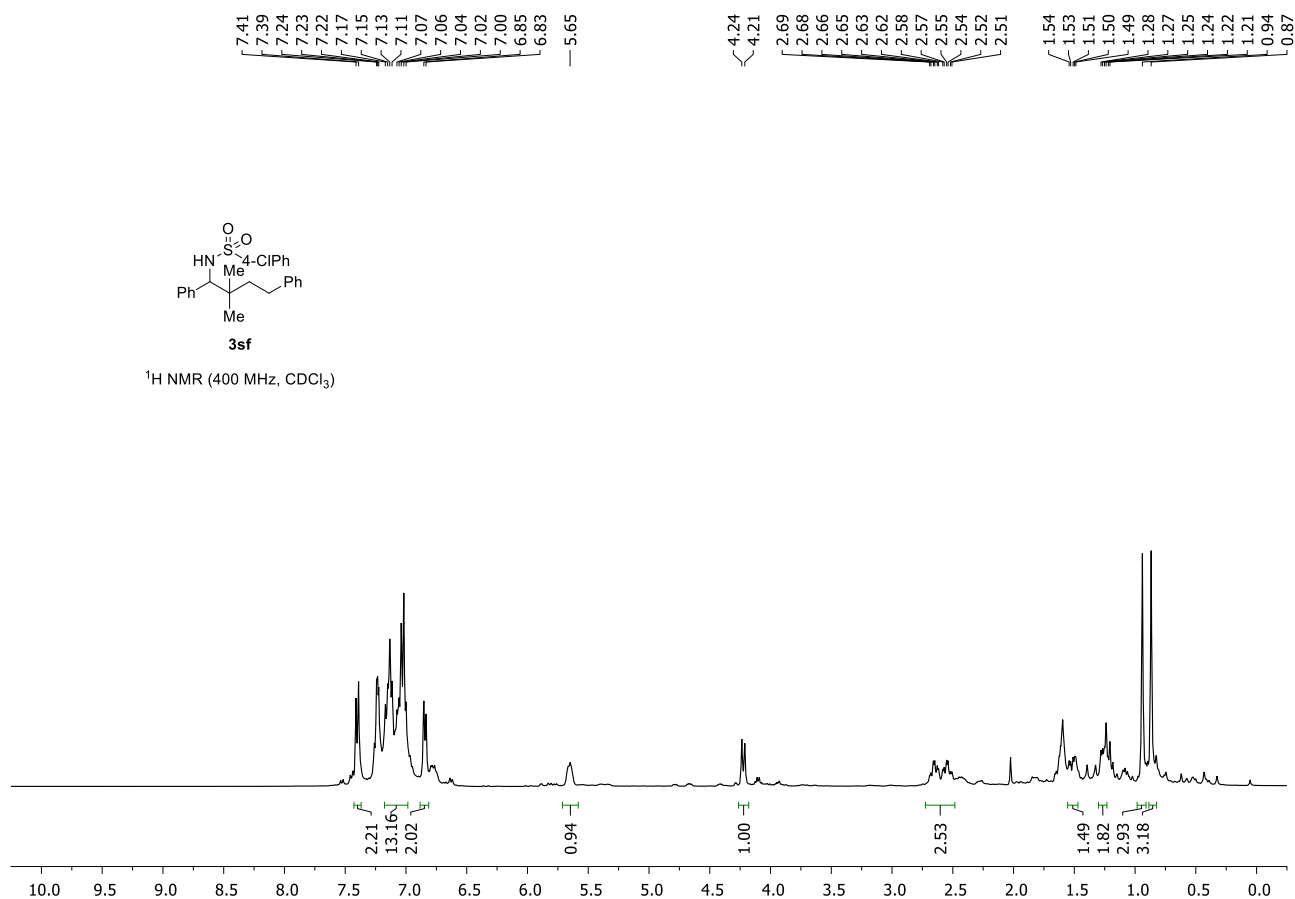




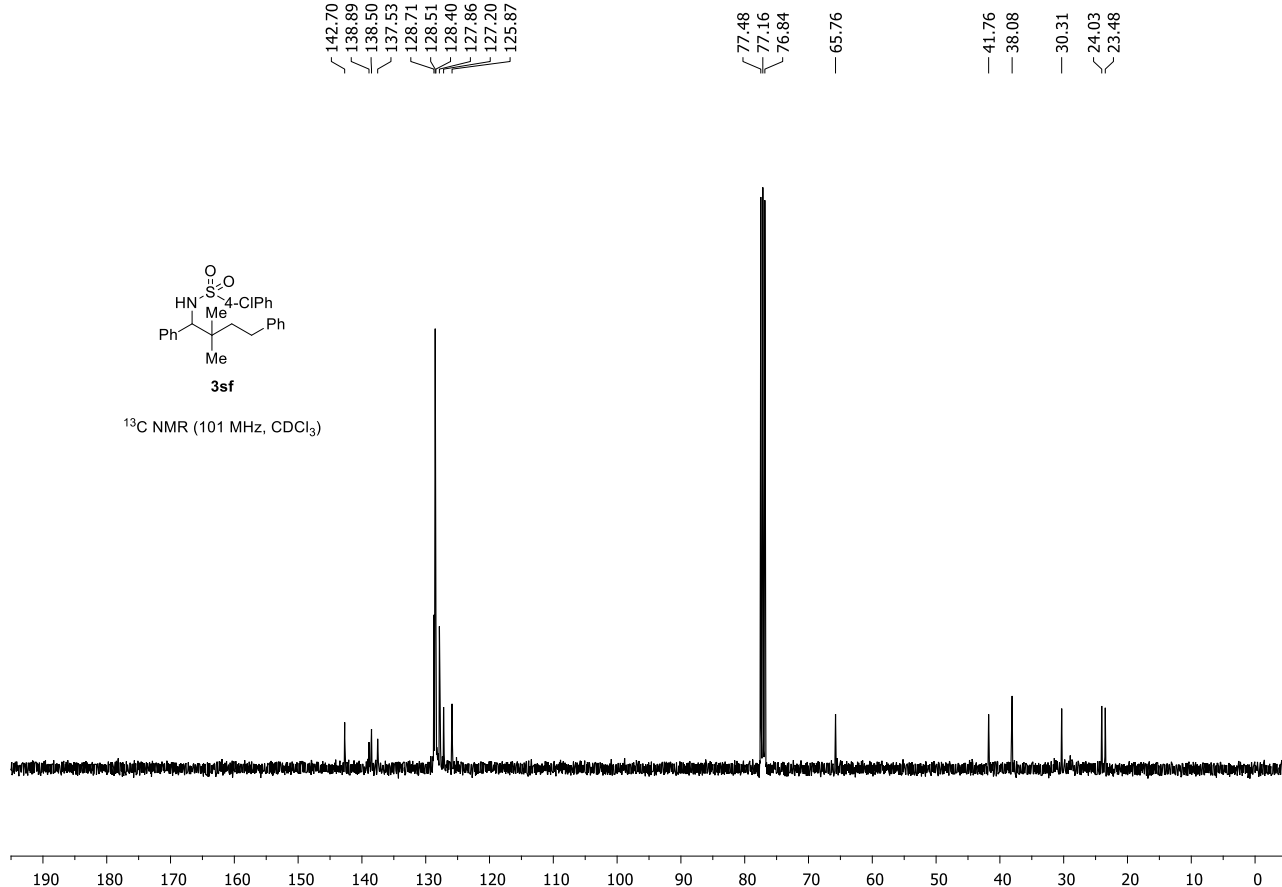


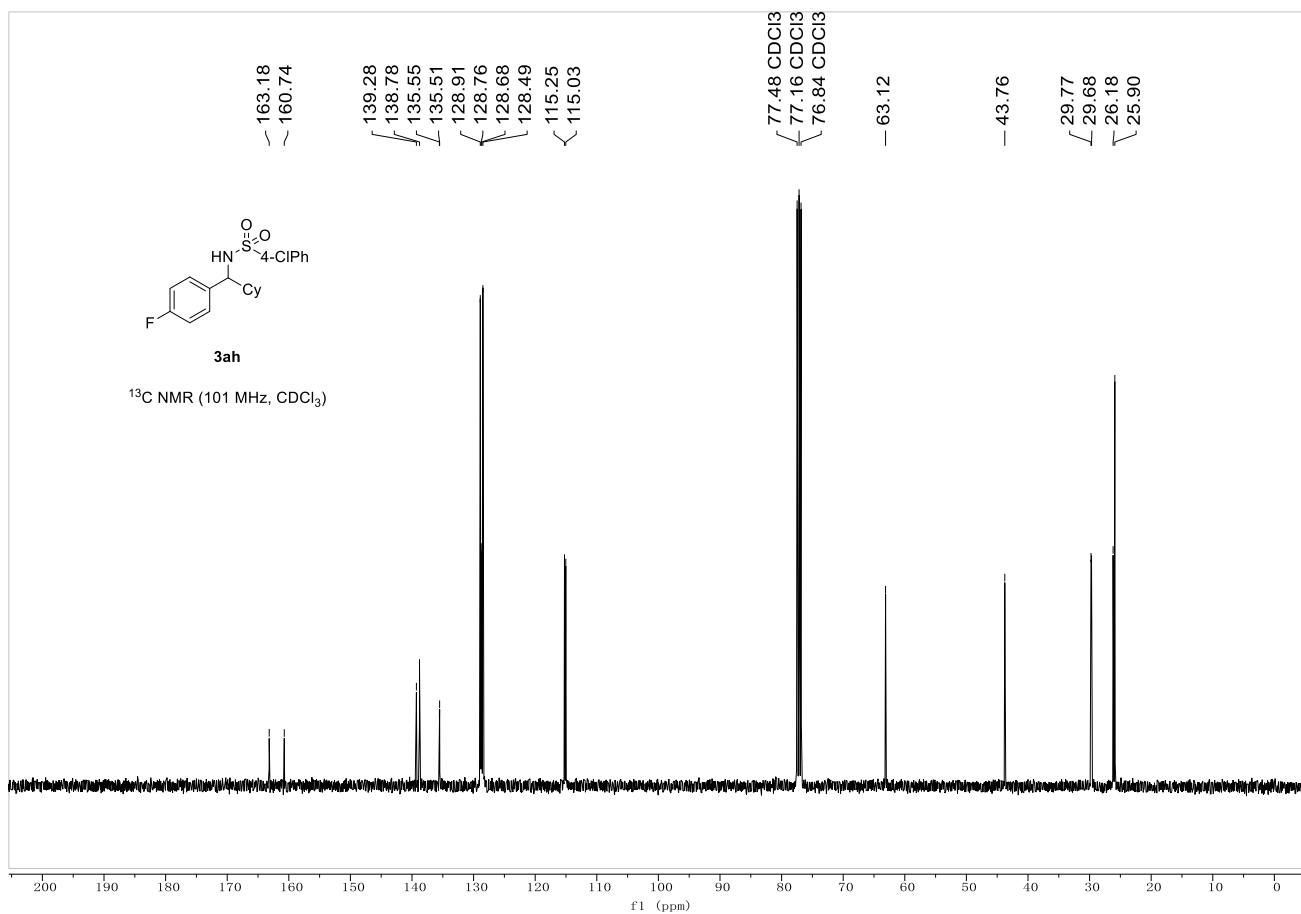
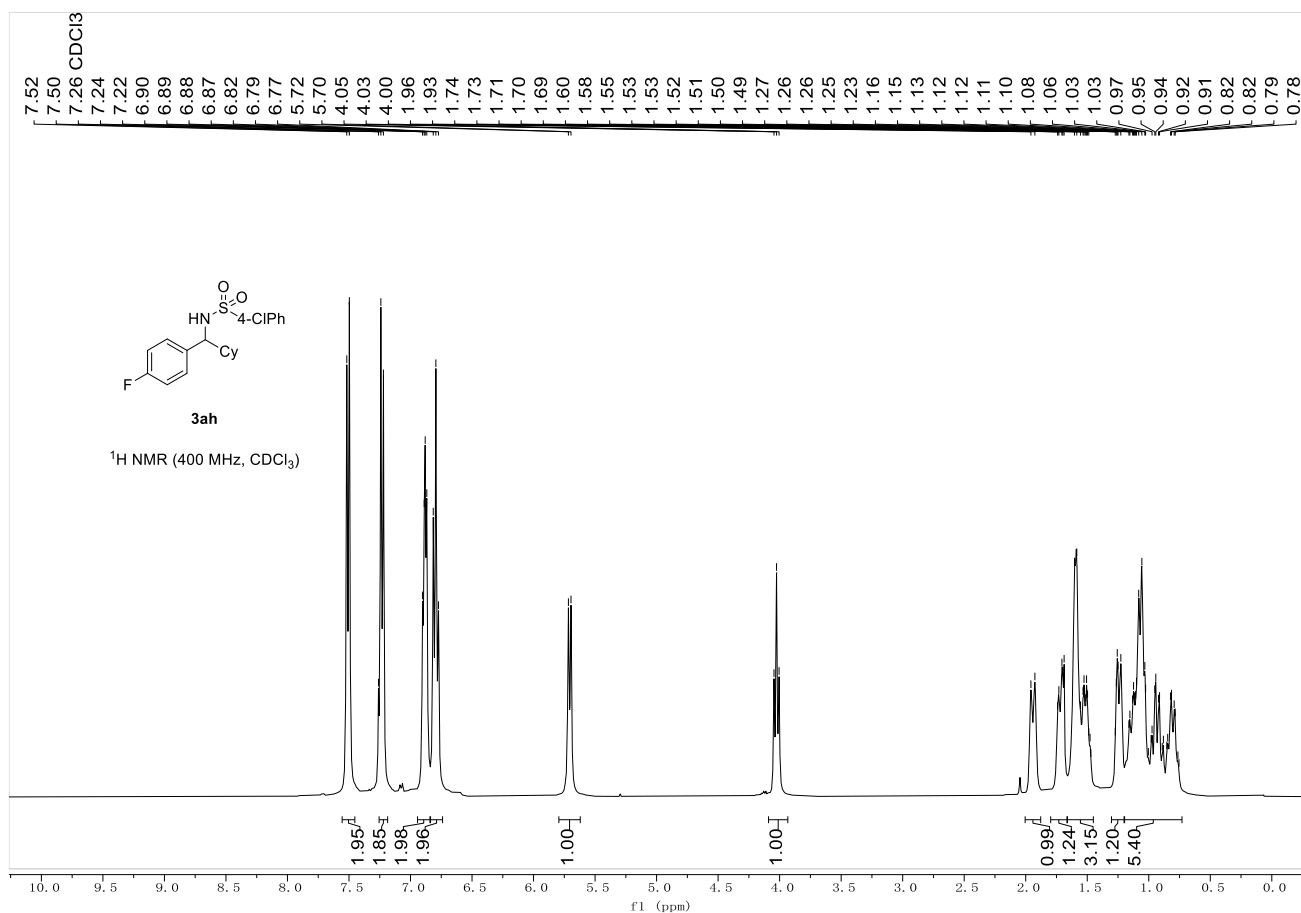


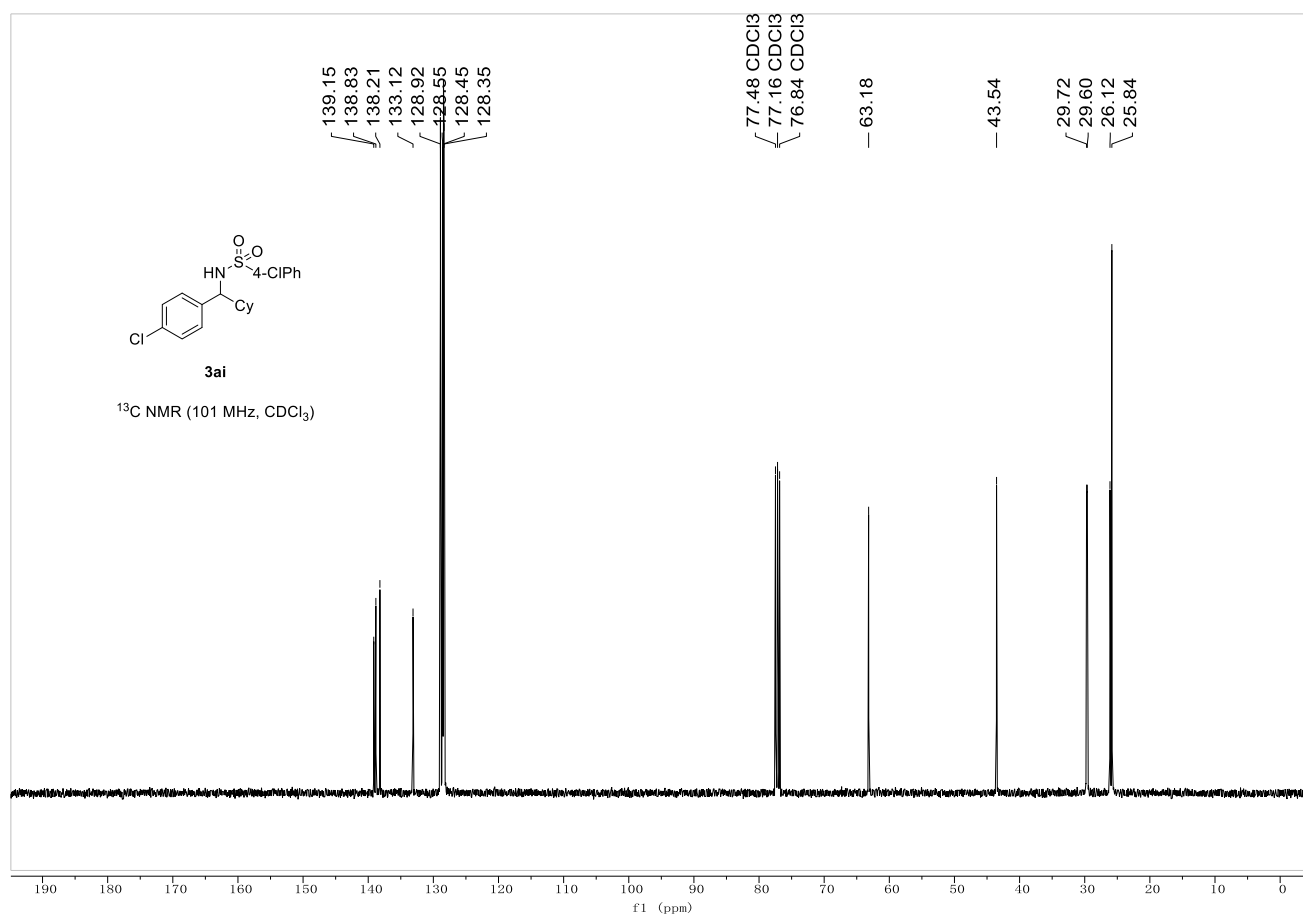
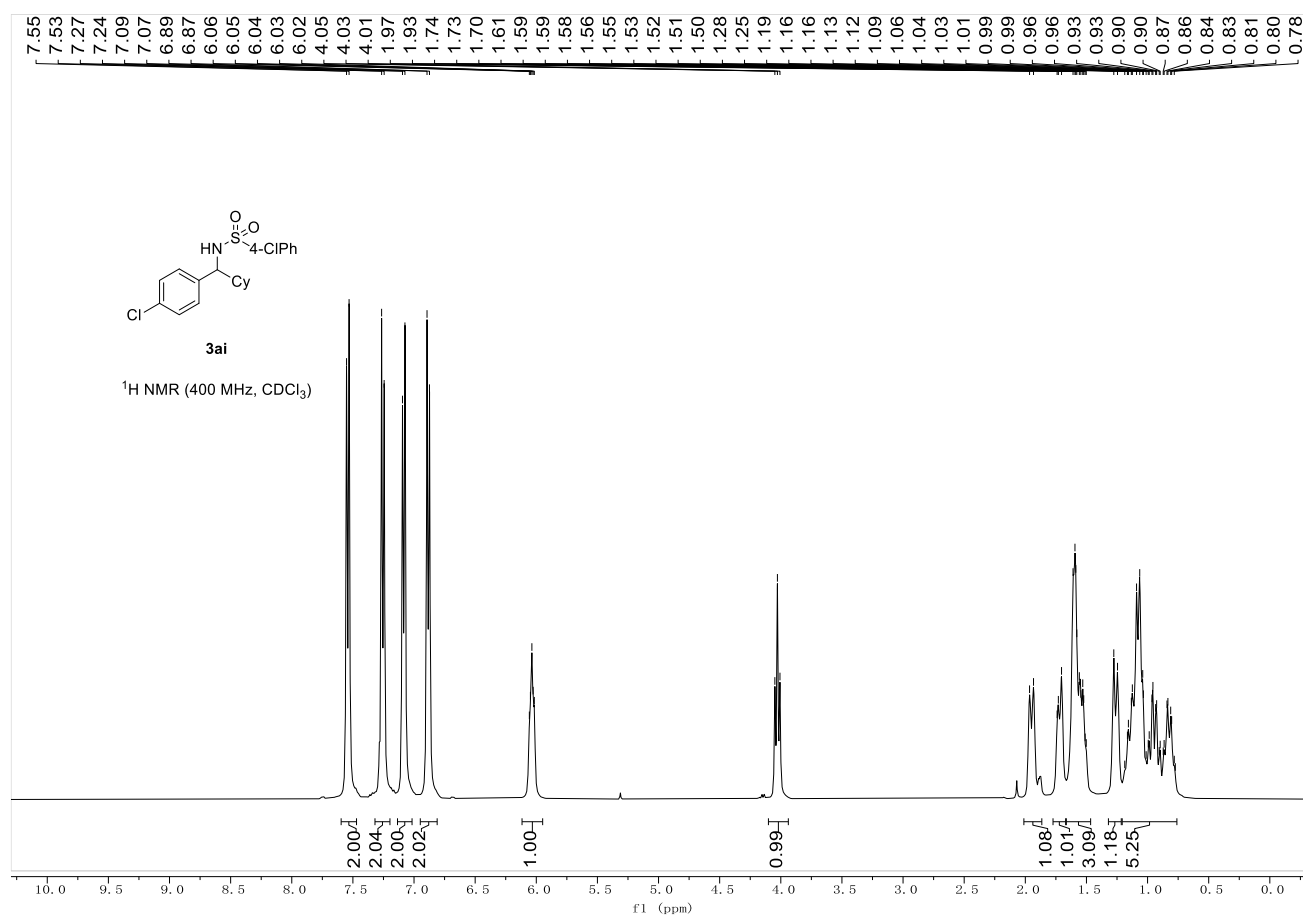
¹H NMR (400 MHz, CDCl₃)

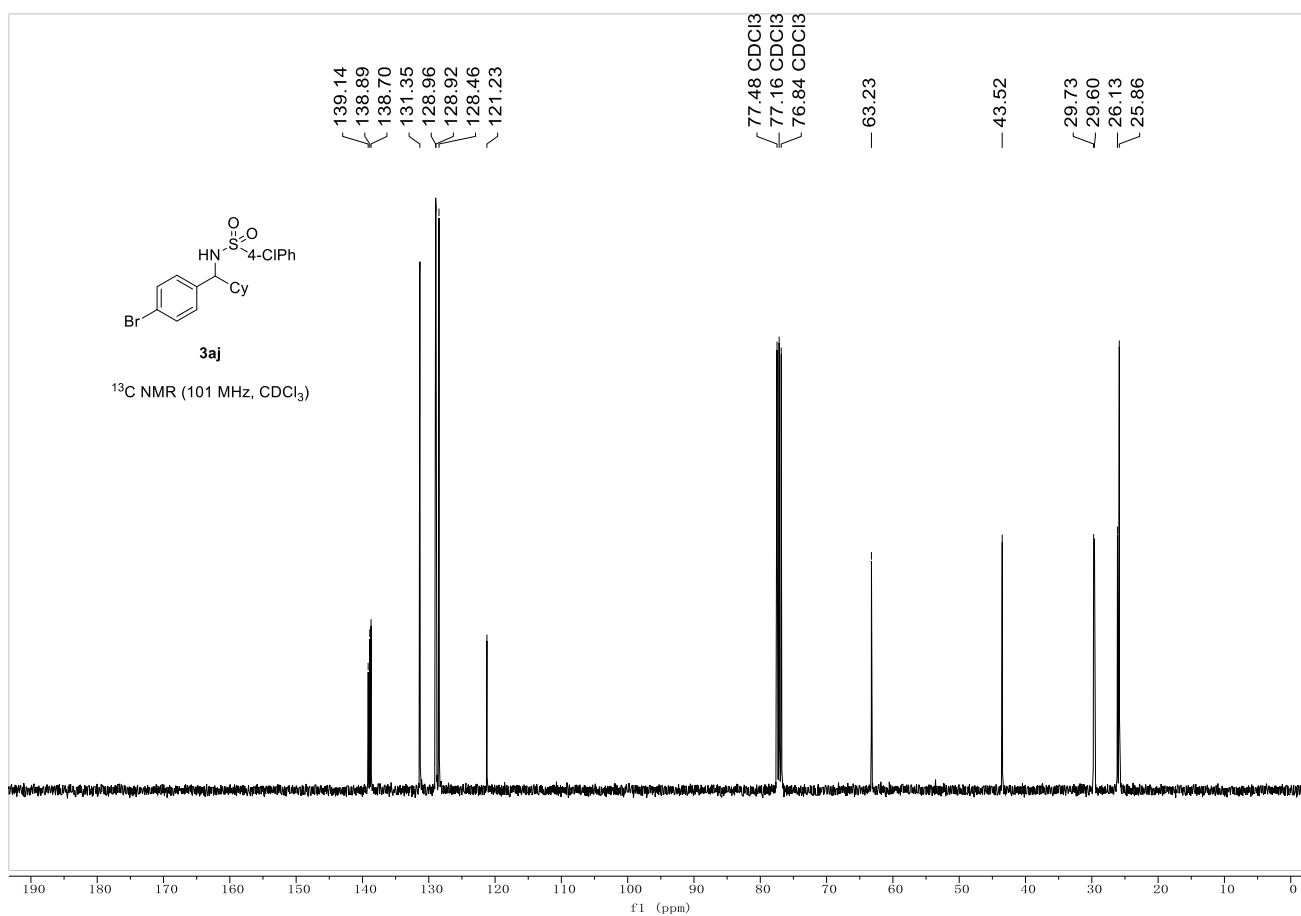
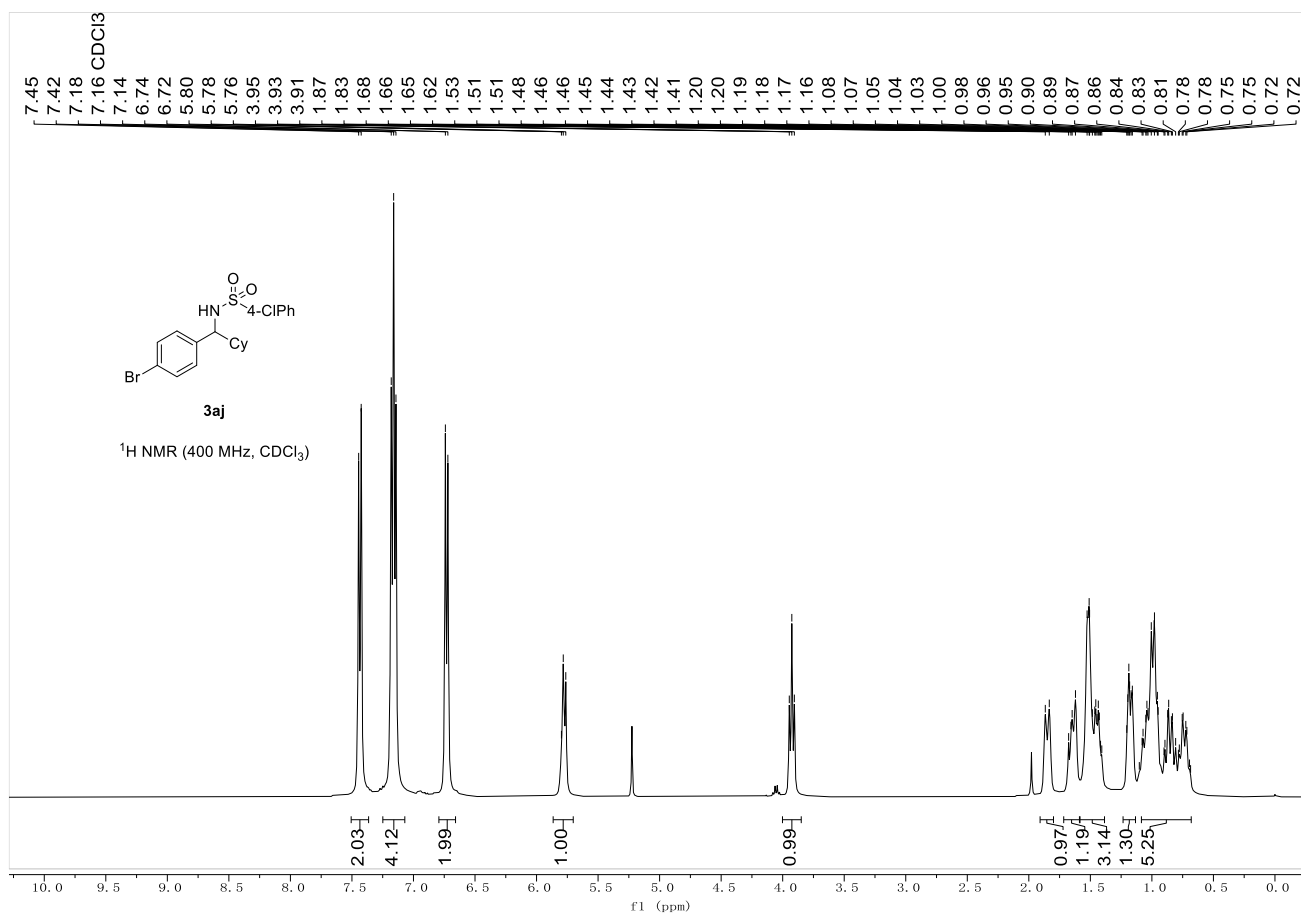


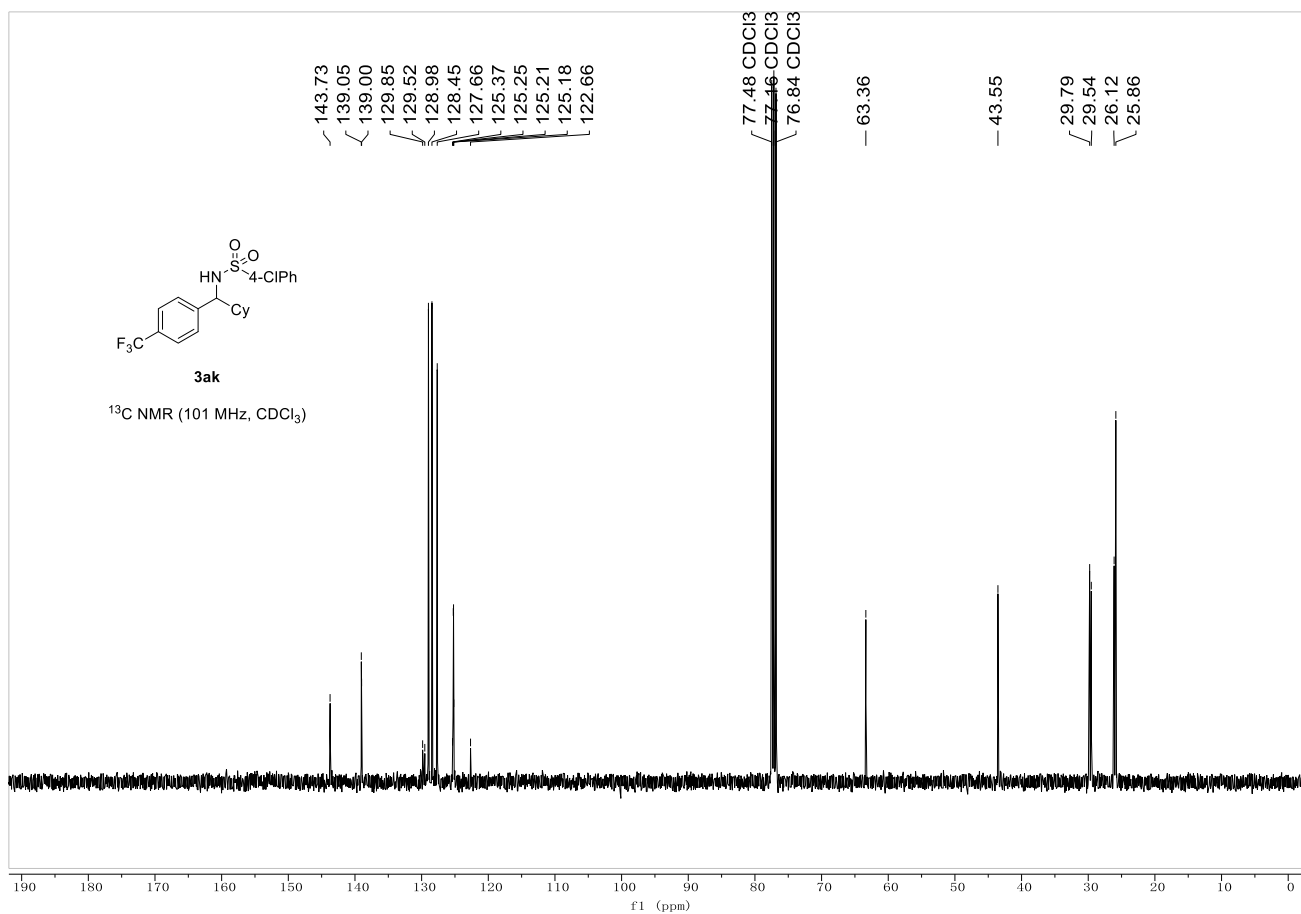
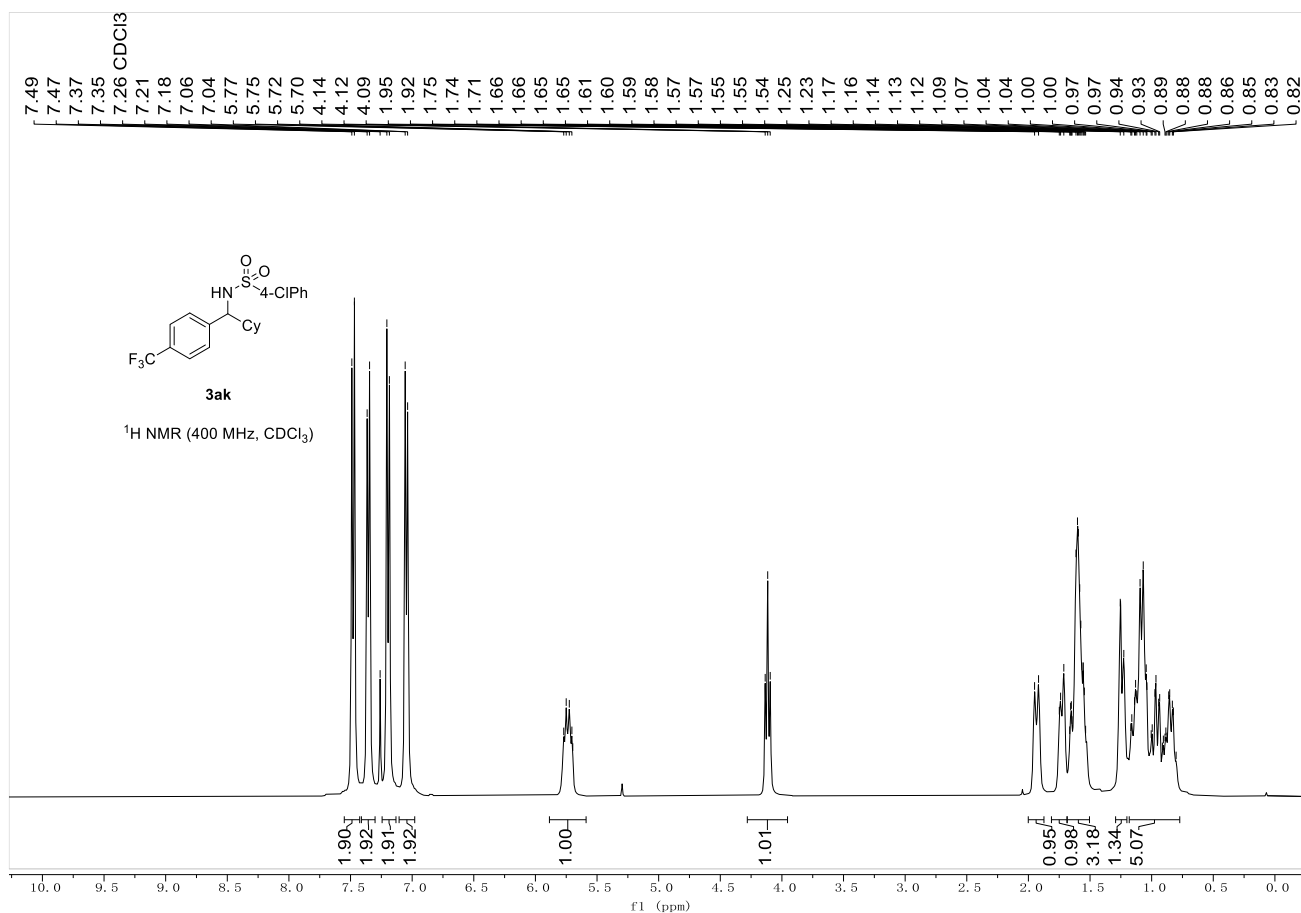
¹³C NMR (101 MHz, CDCl₃)

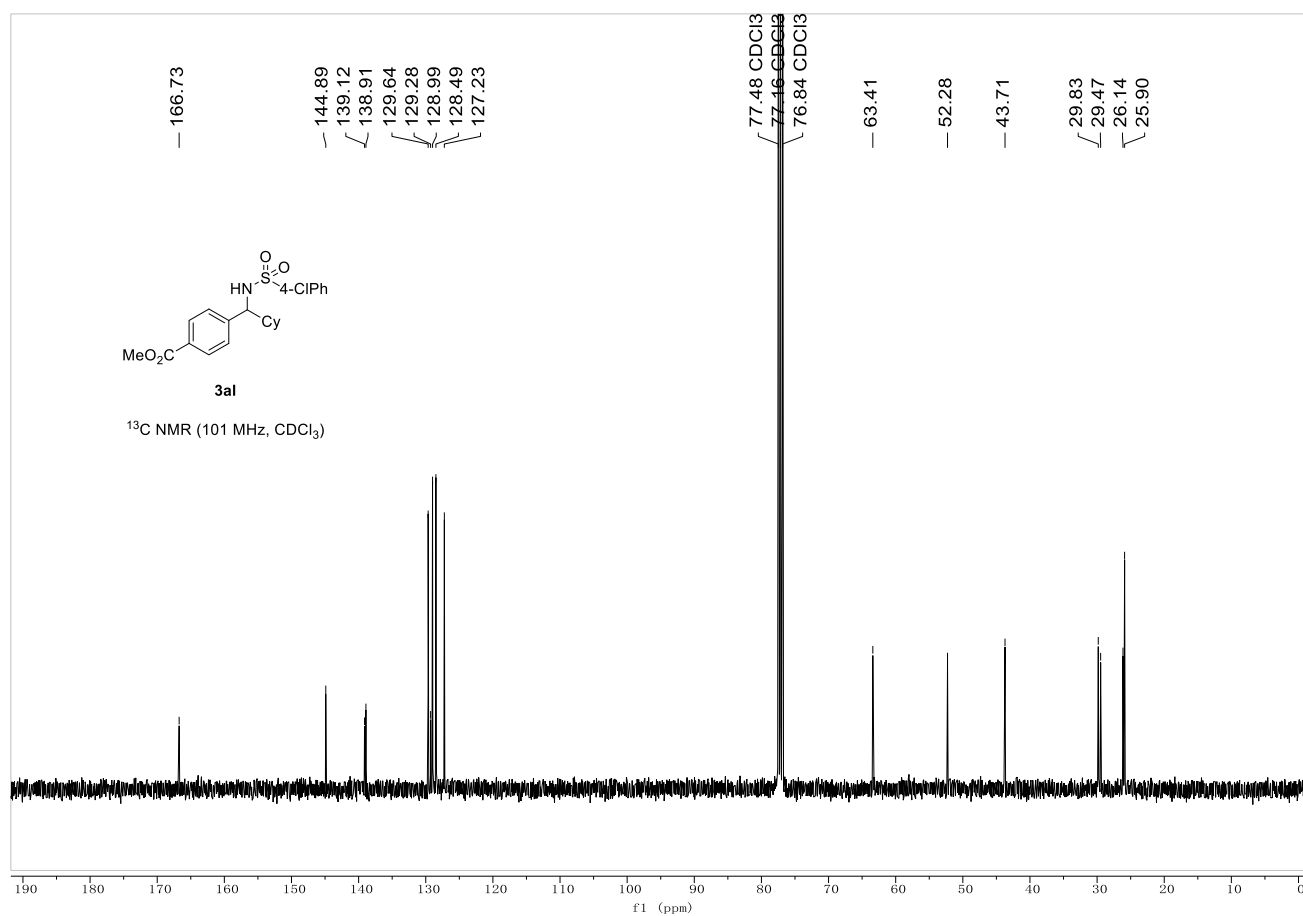
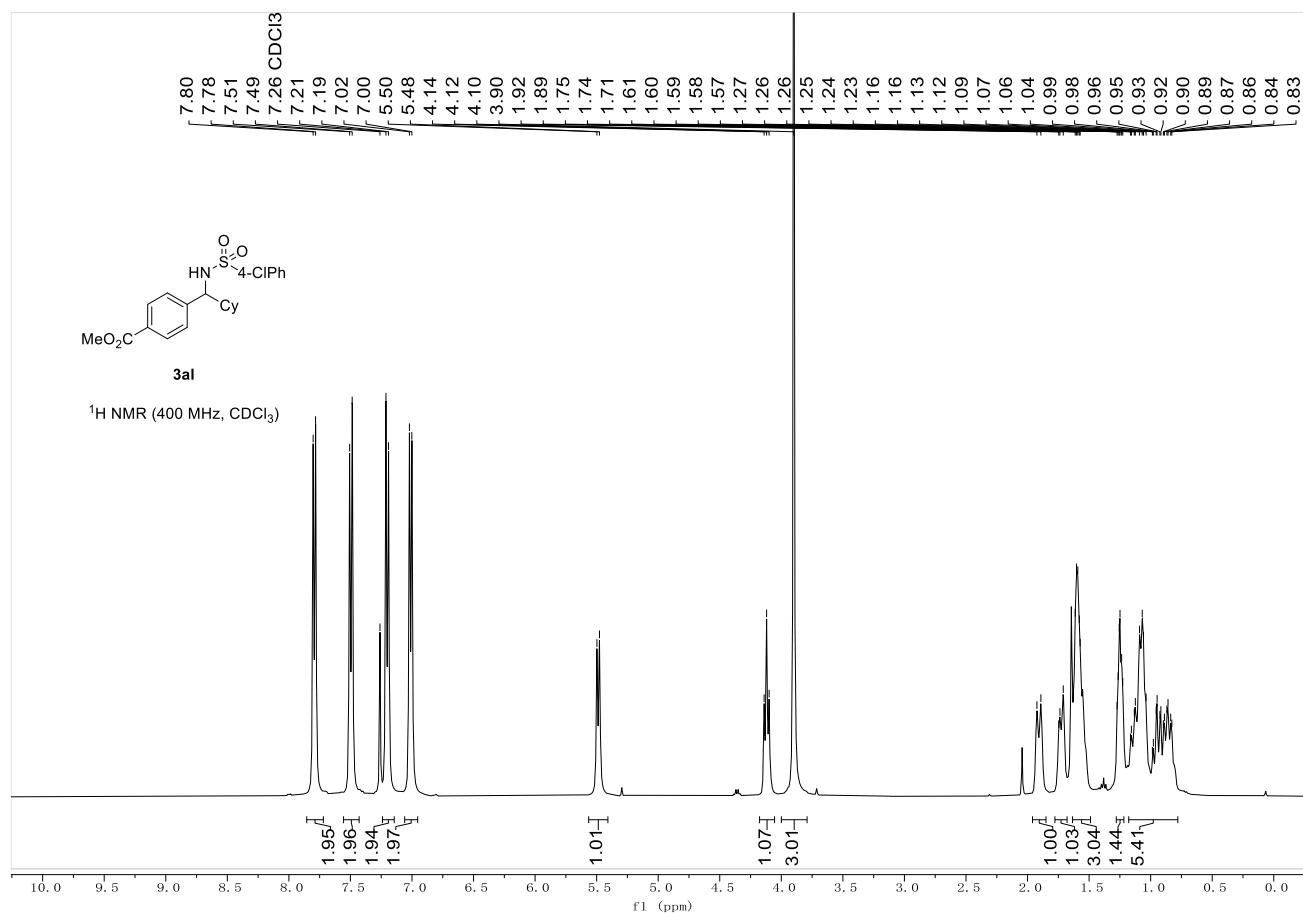


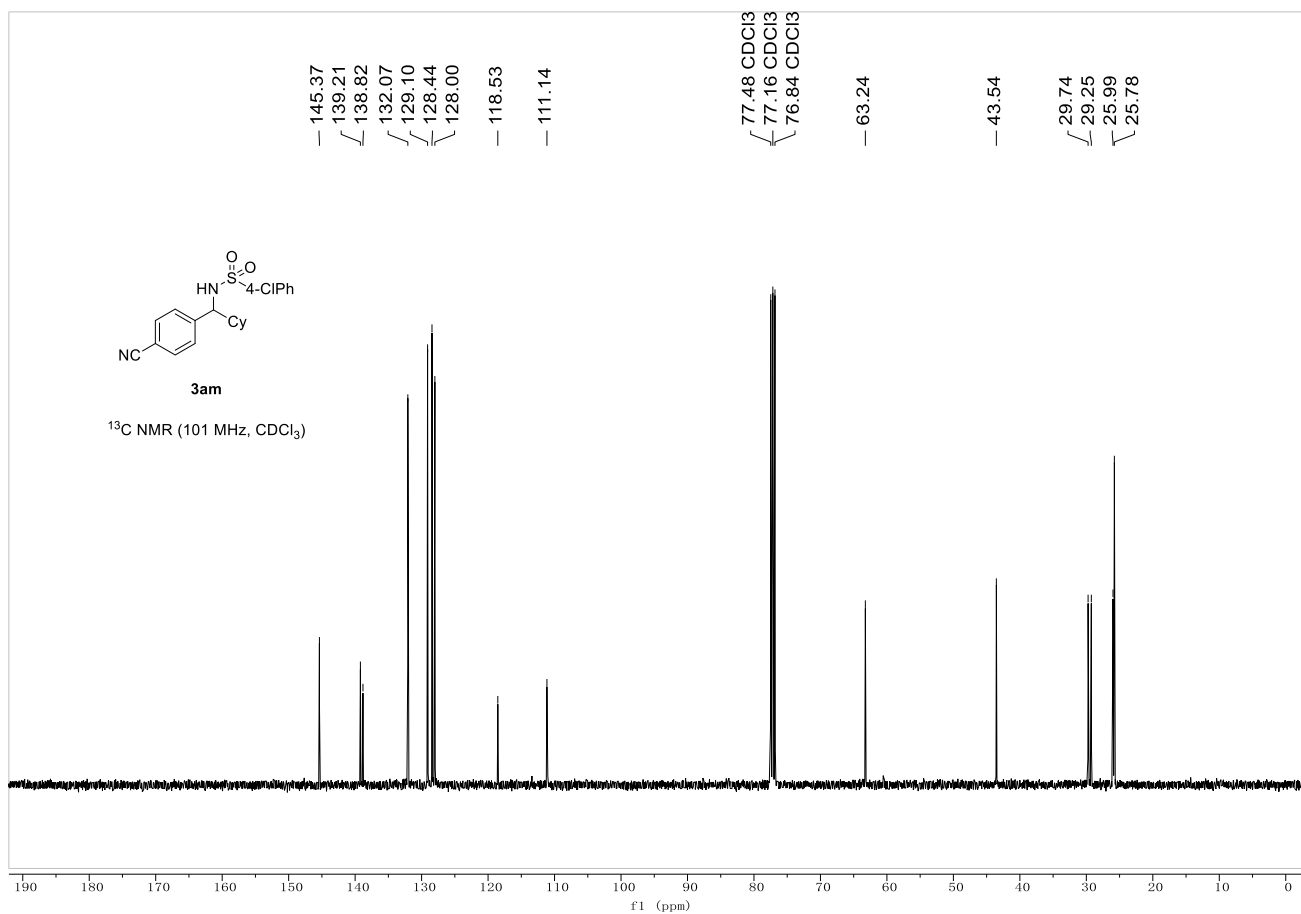
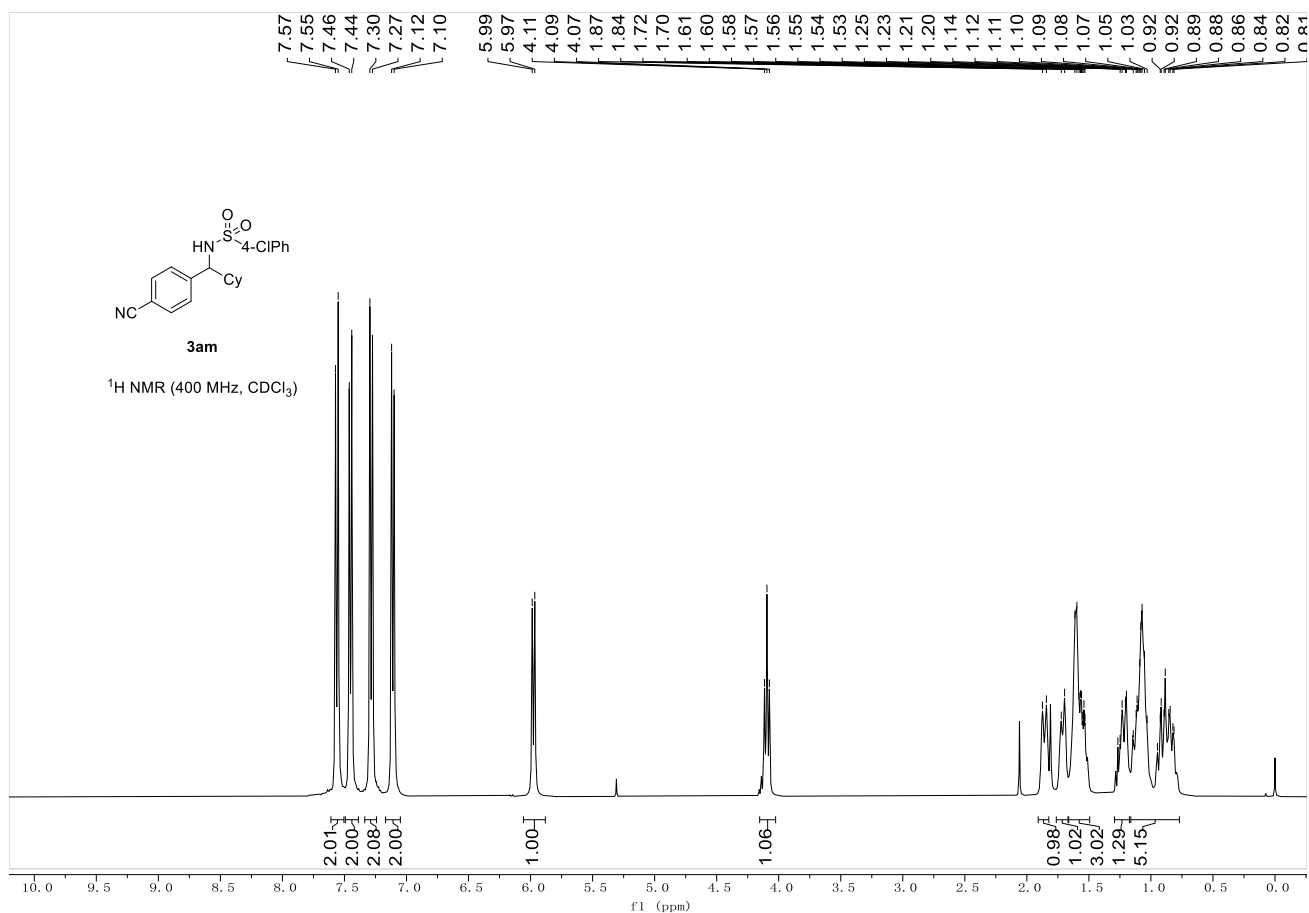


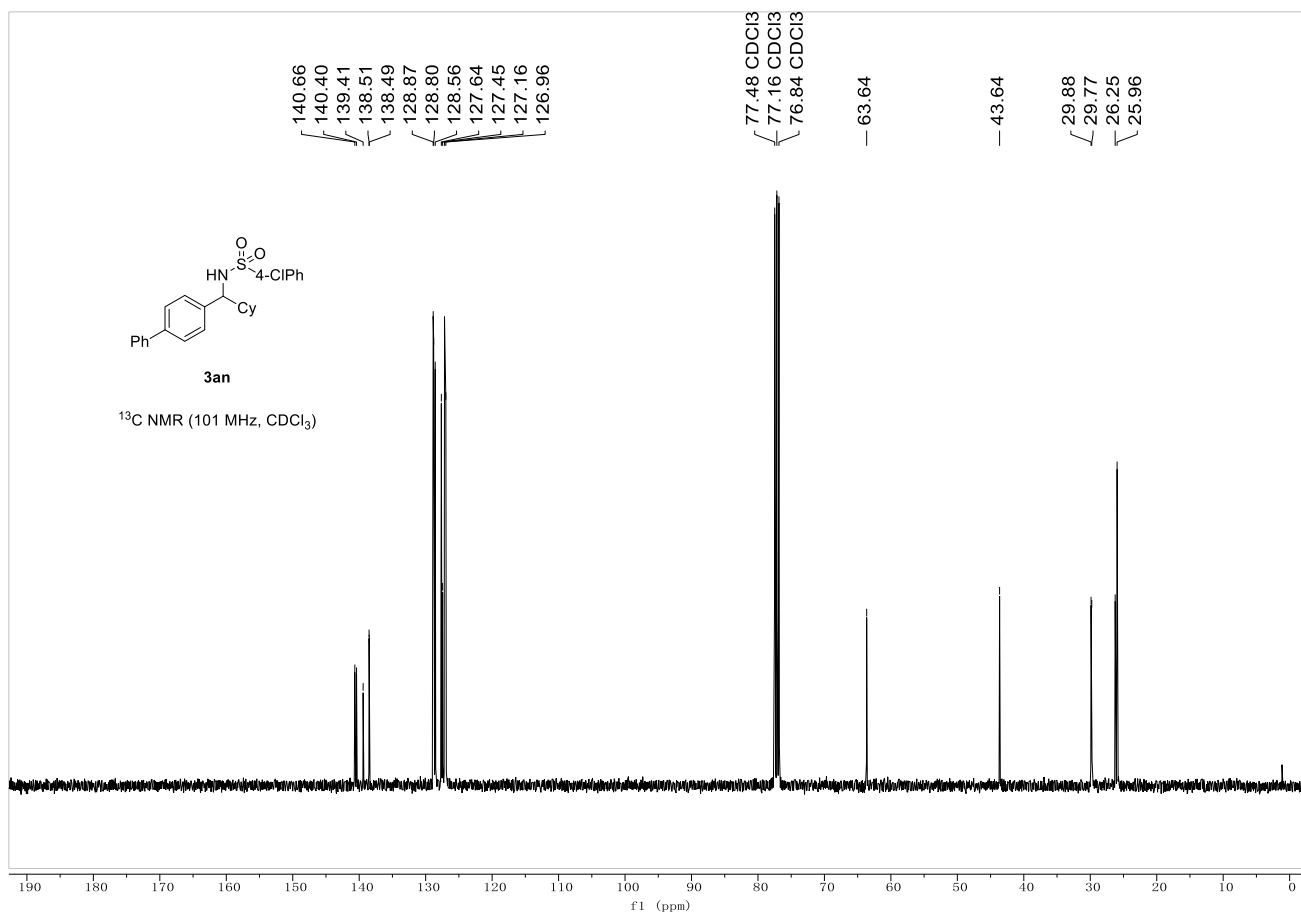
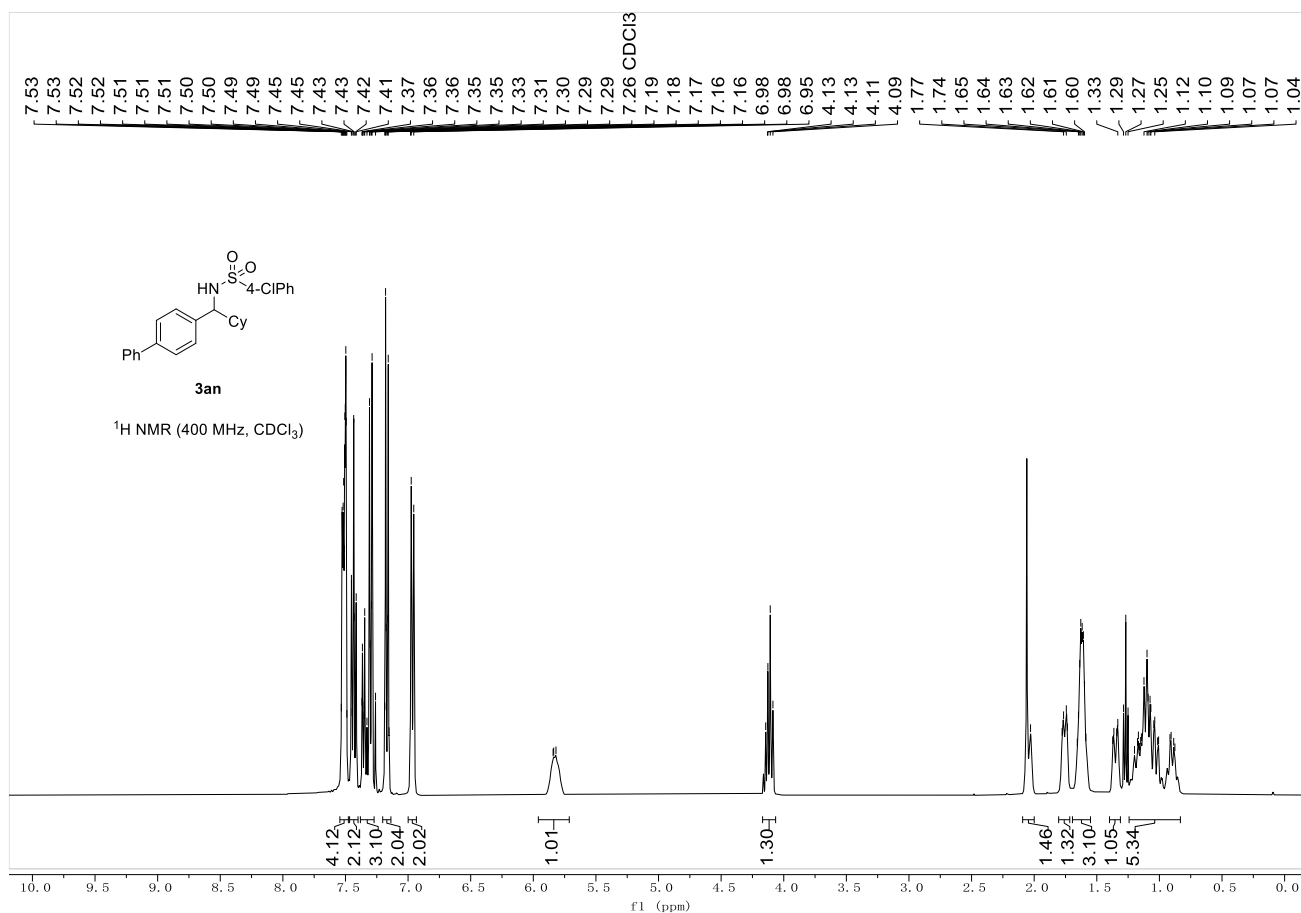


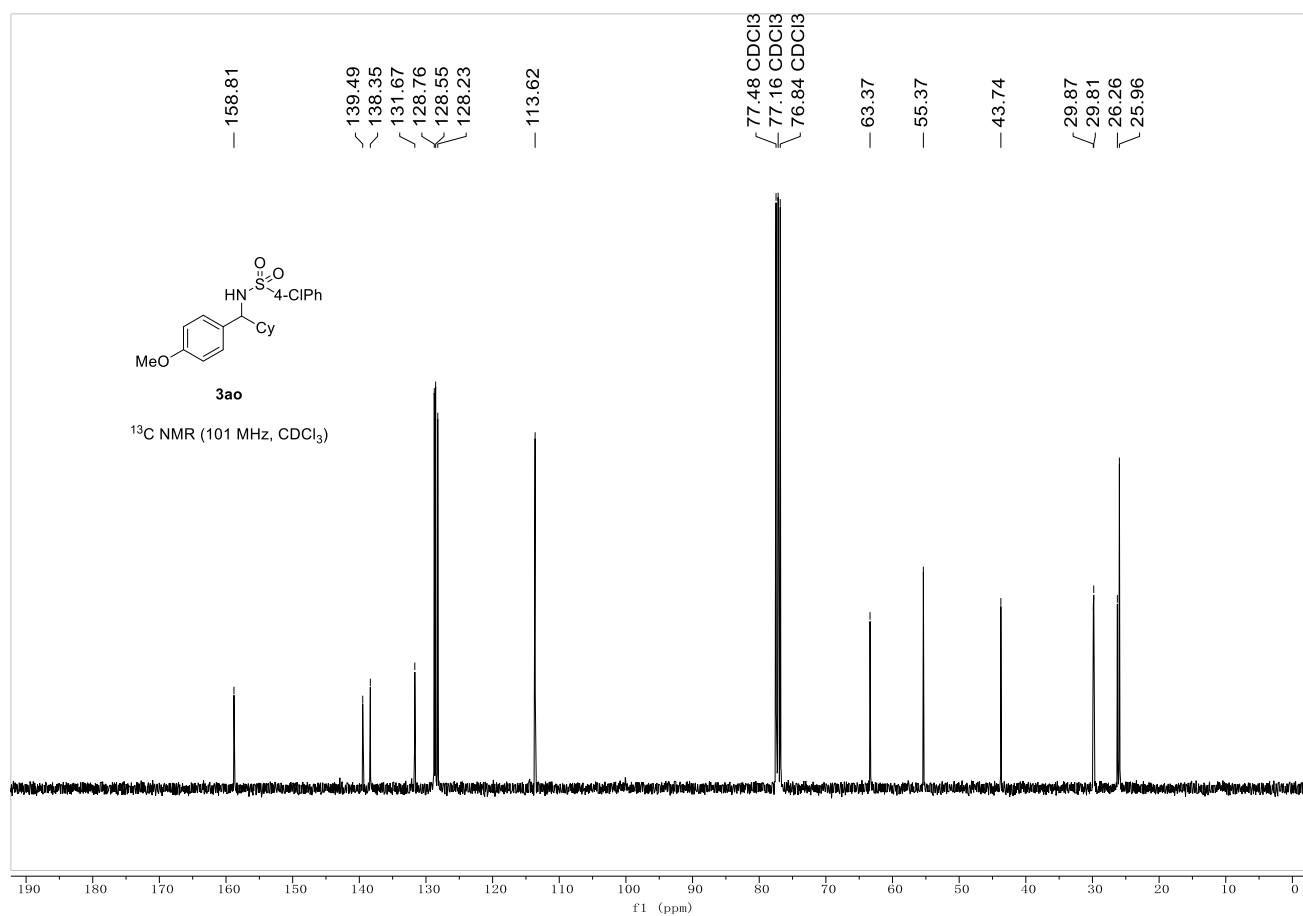
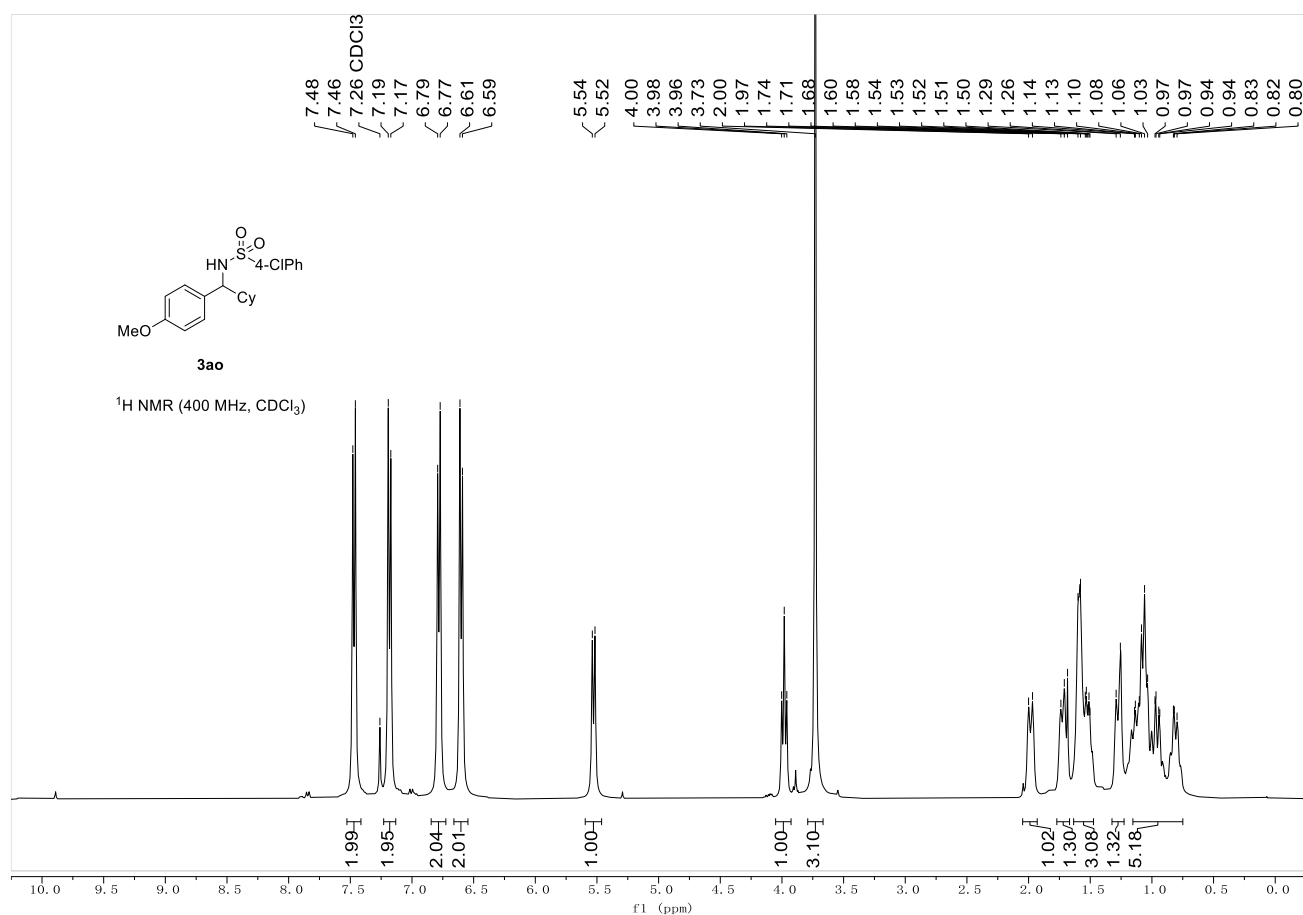


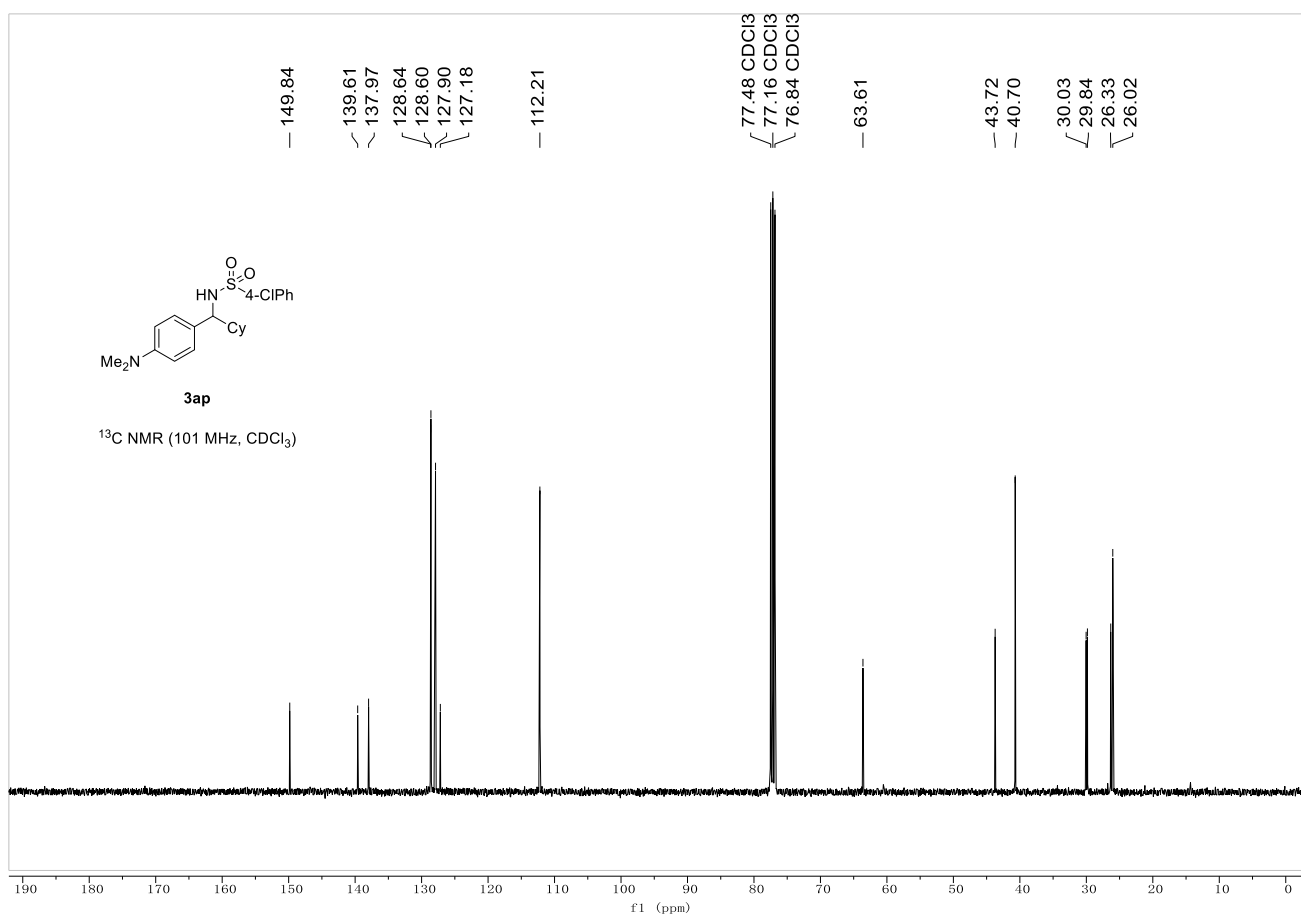
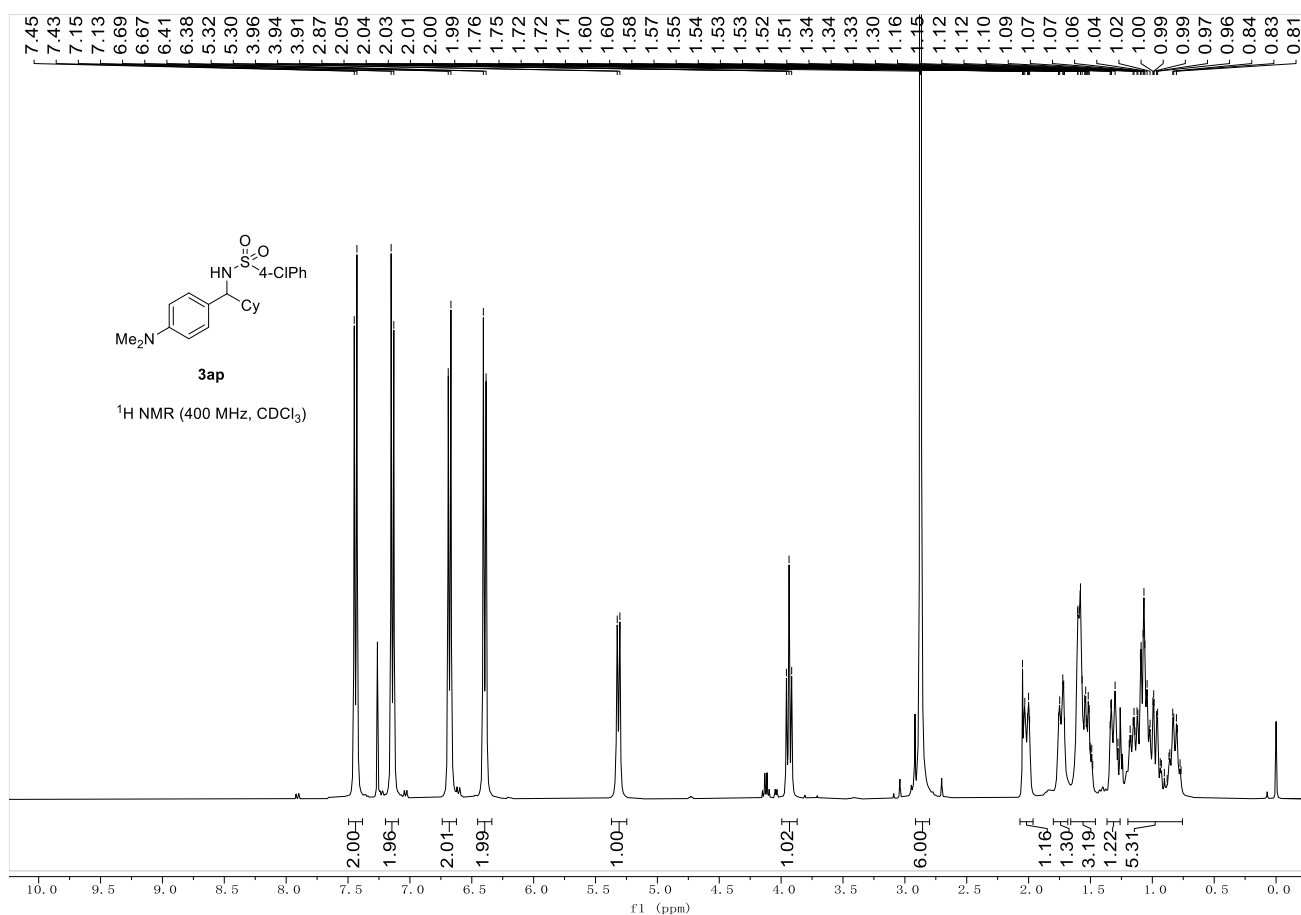


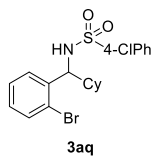




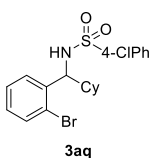
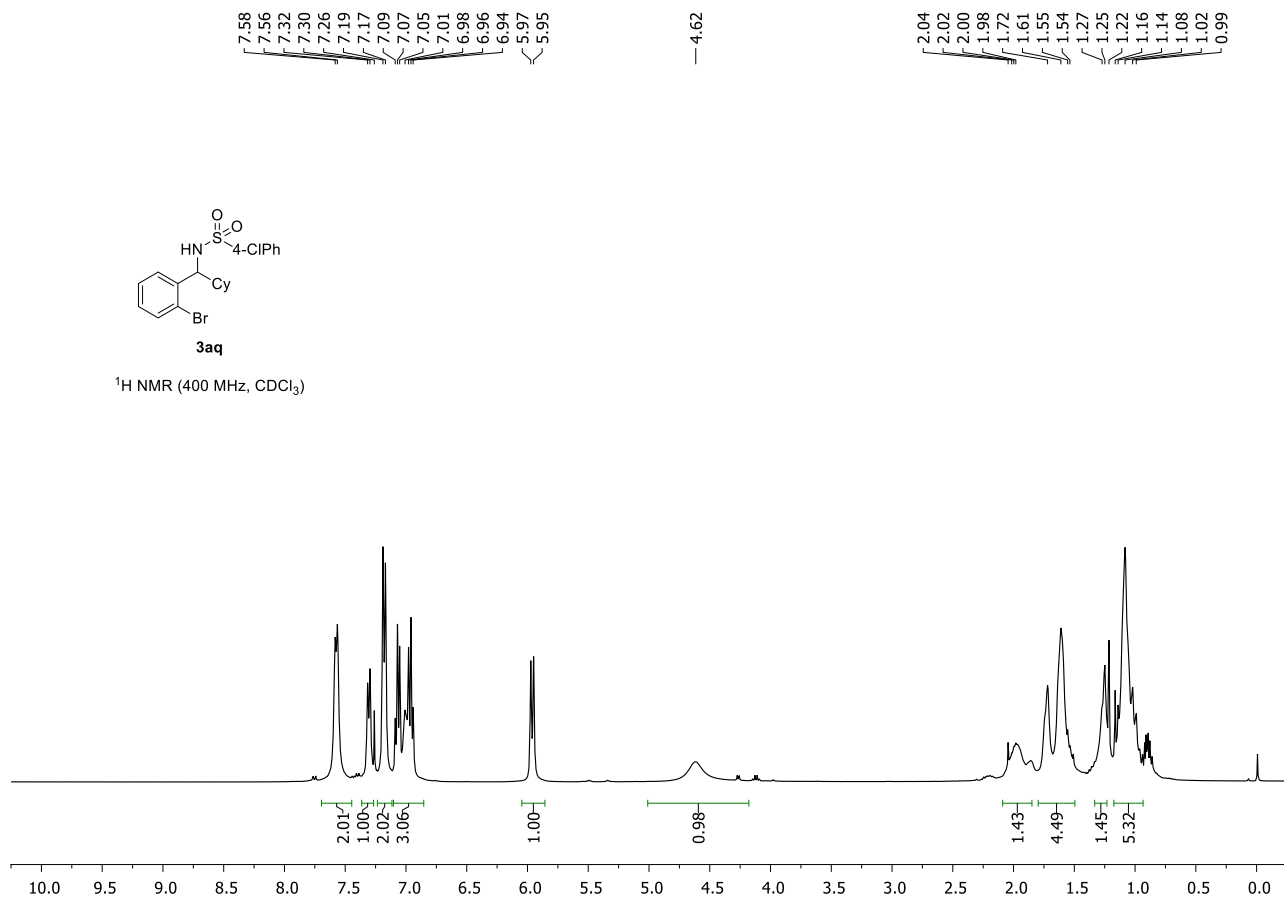




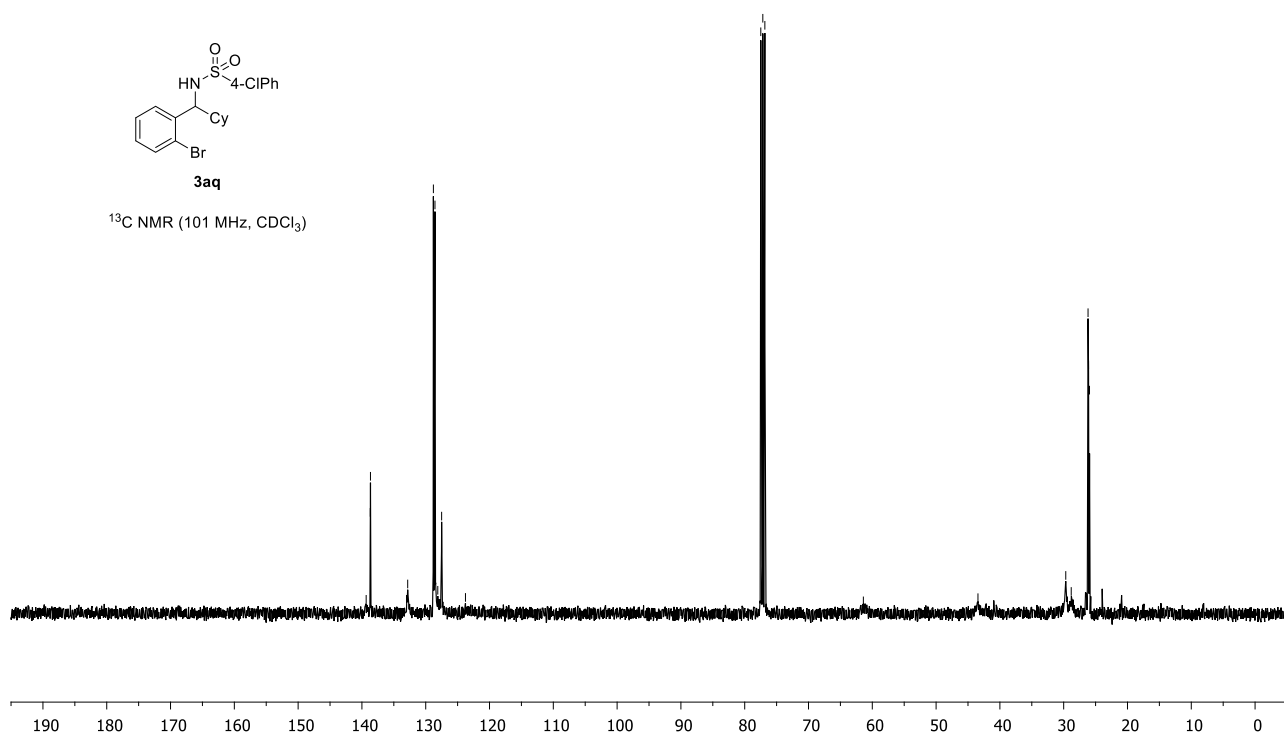


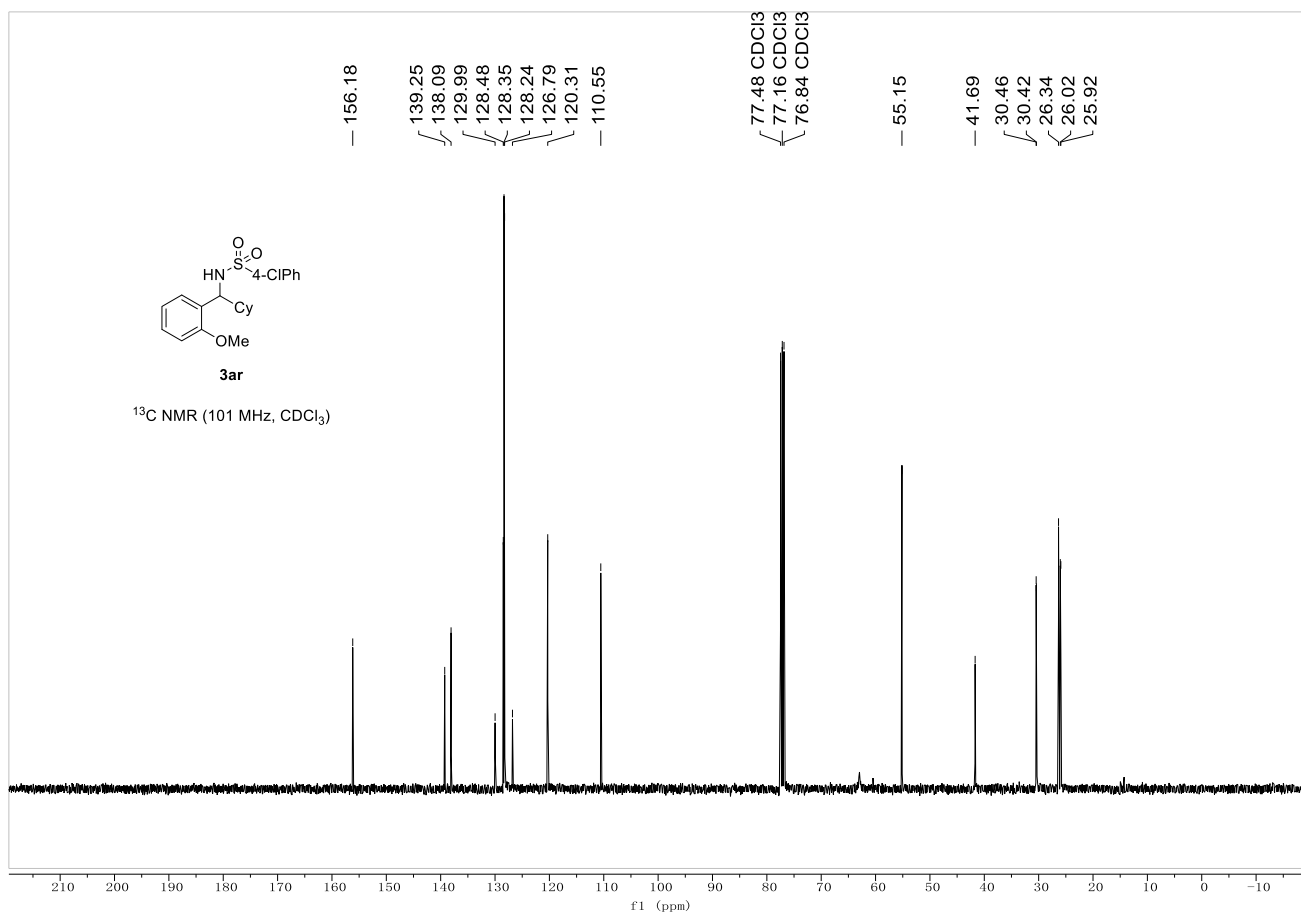
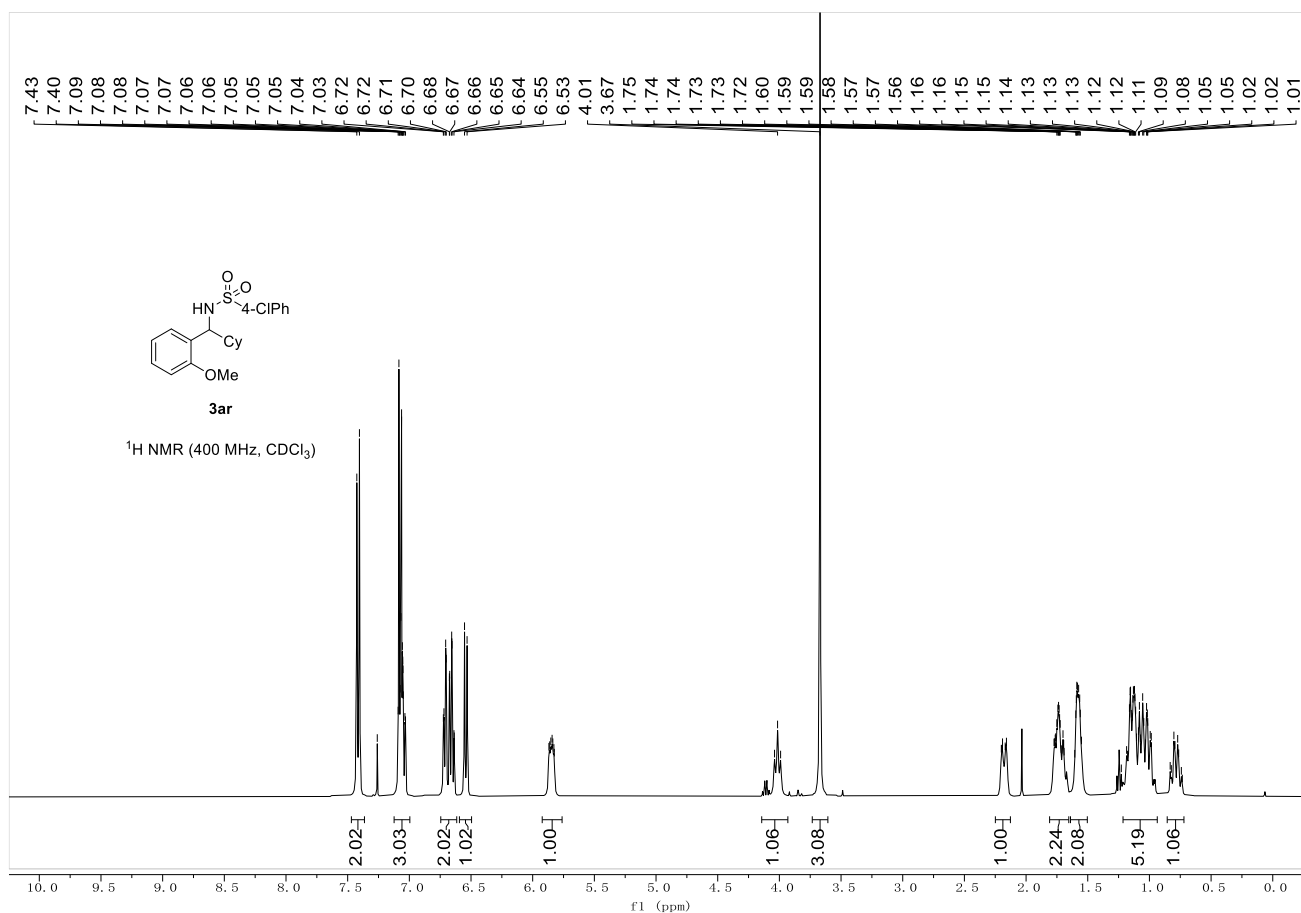


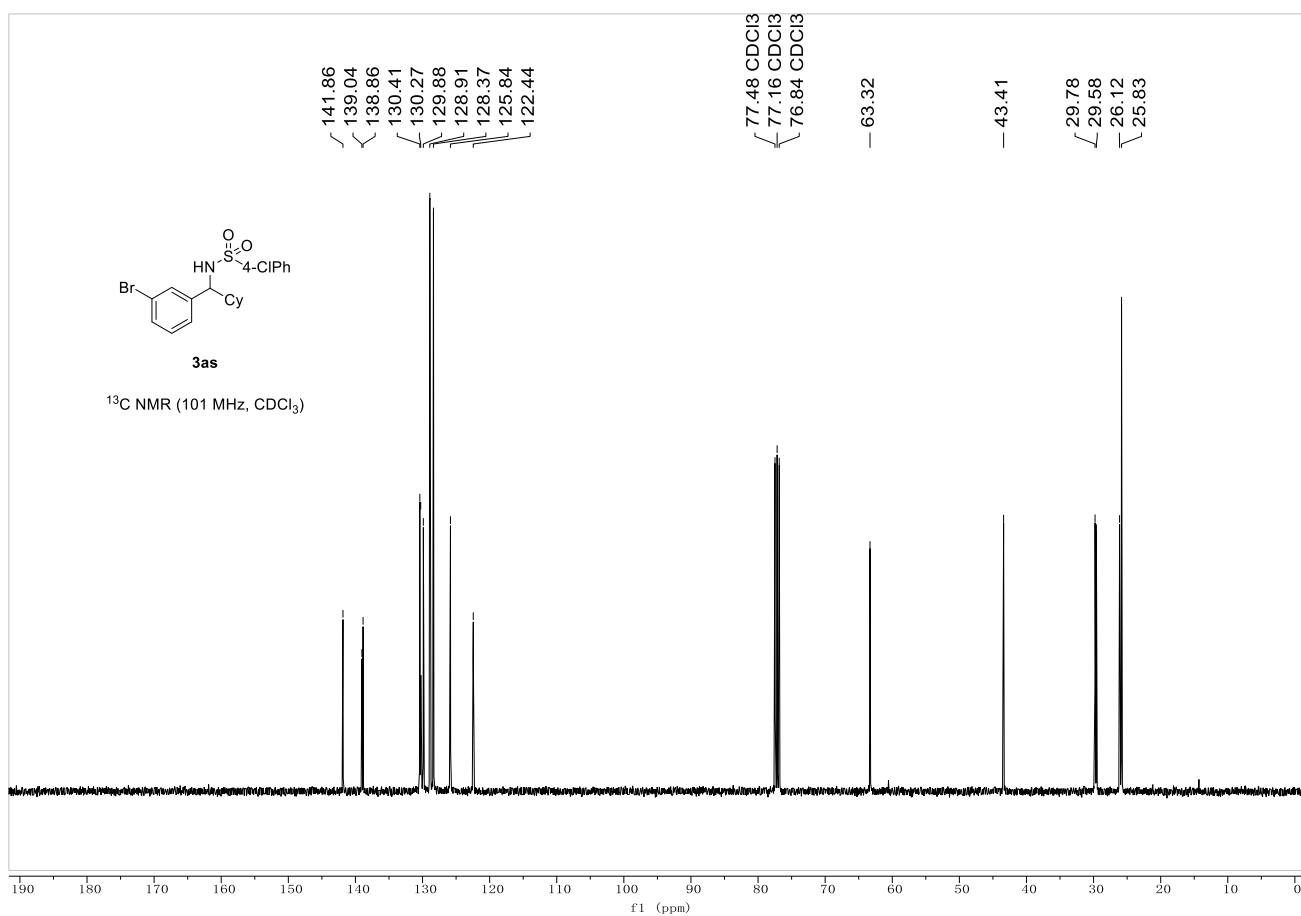
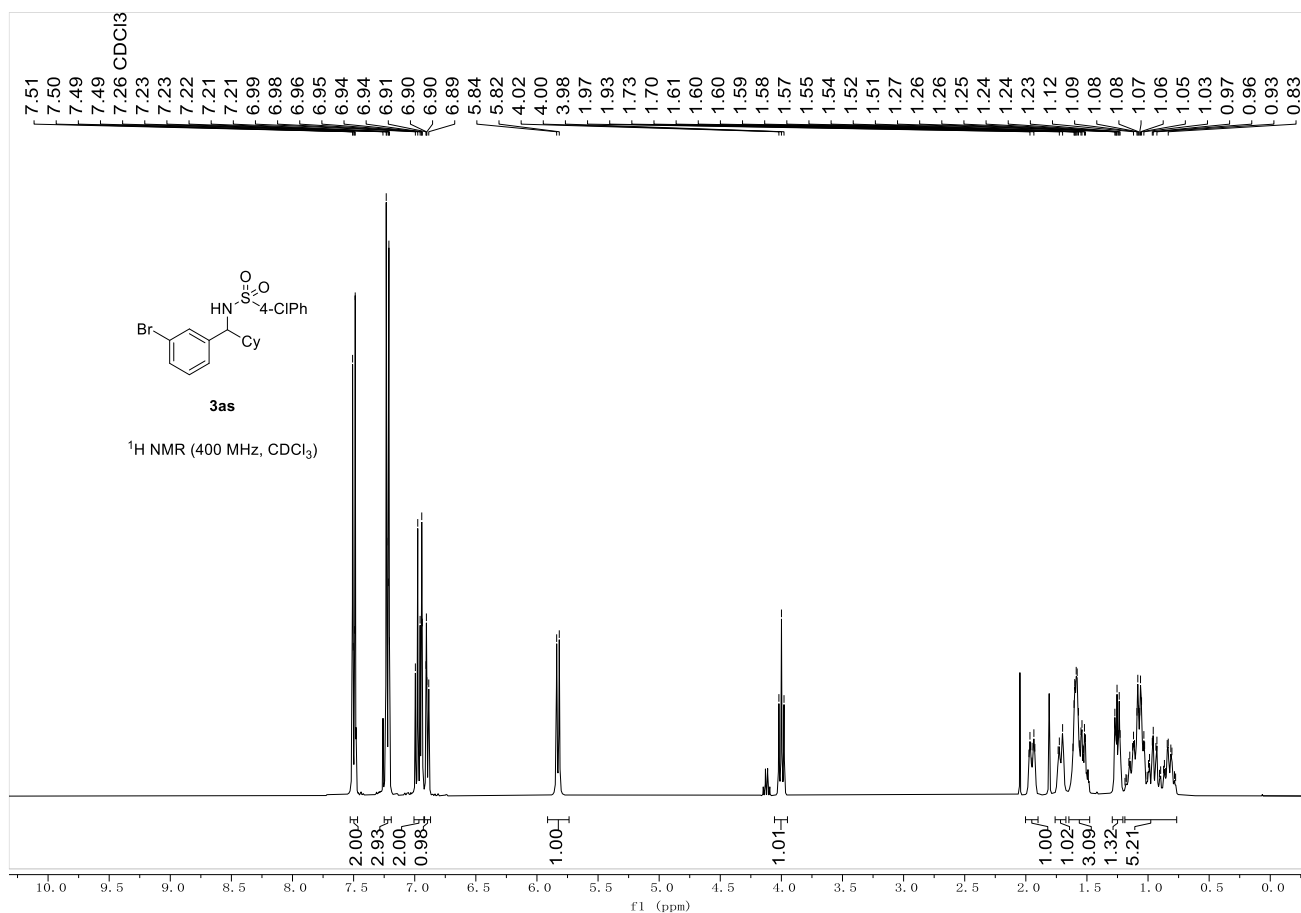
^1H NMR (400 MHz, CDCl_3)

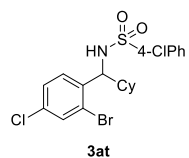


^{13}C NMR (101 MHz, CDCl_3)

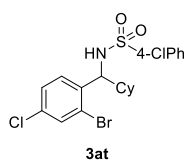
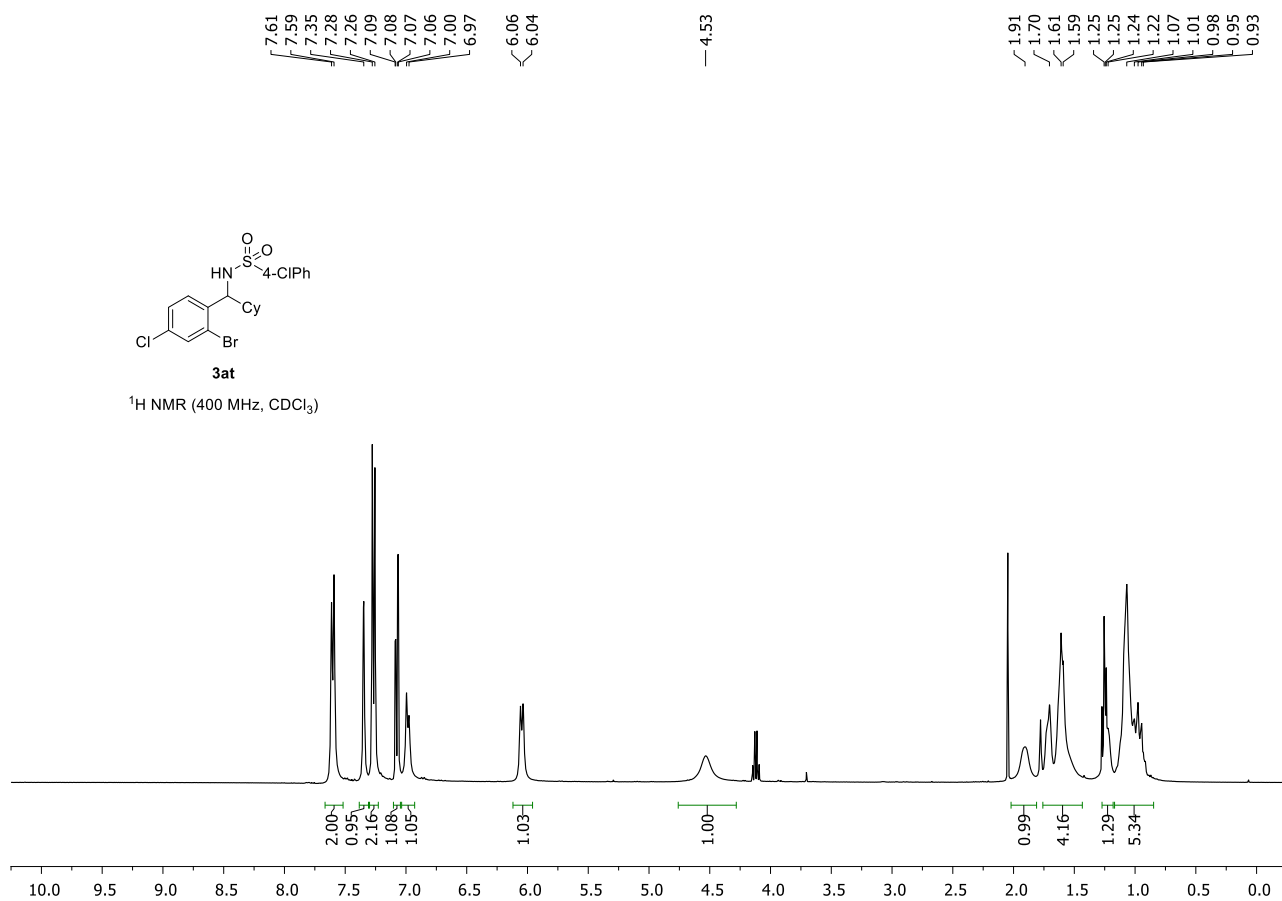




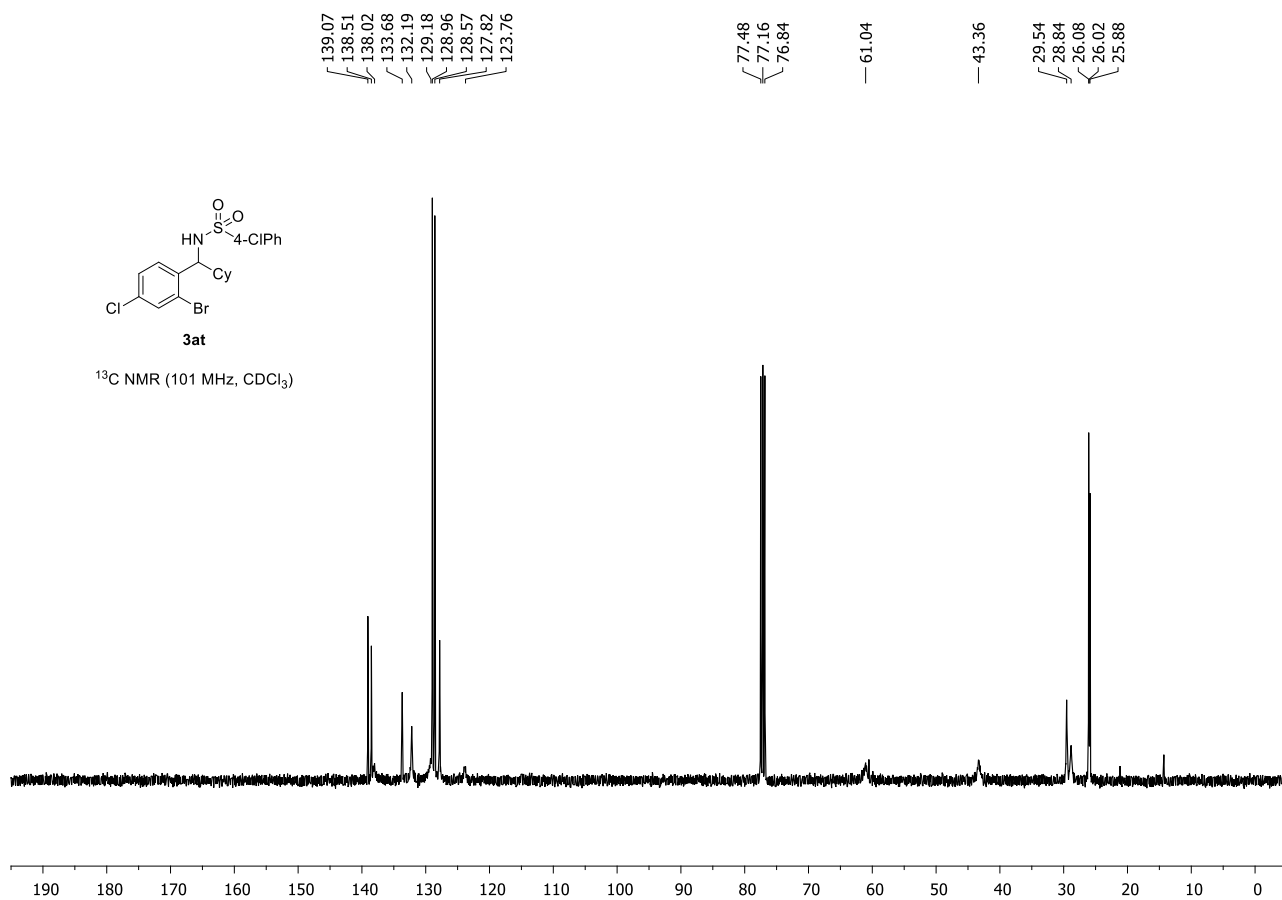


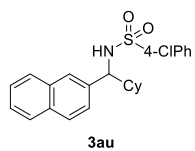


¹H NMR (400 MHz, CDCl₃)

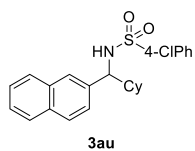
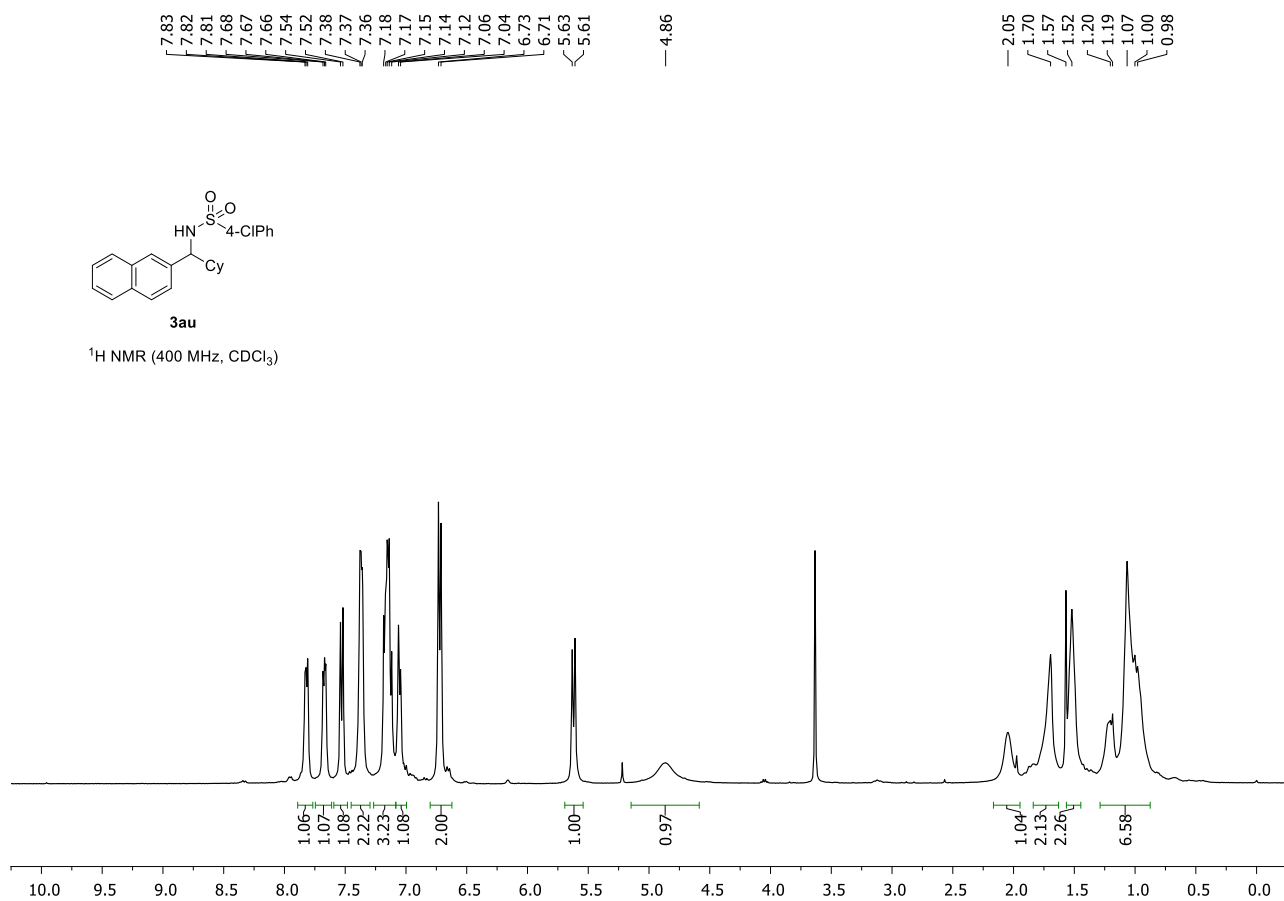


¹³C NMR (101 MHz, CDCl₃)

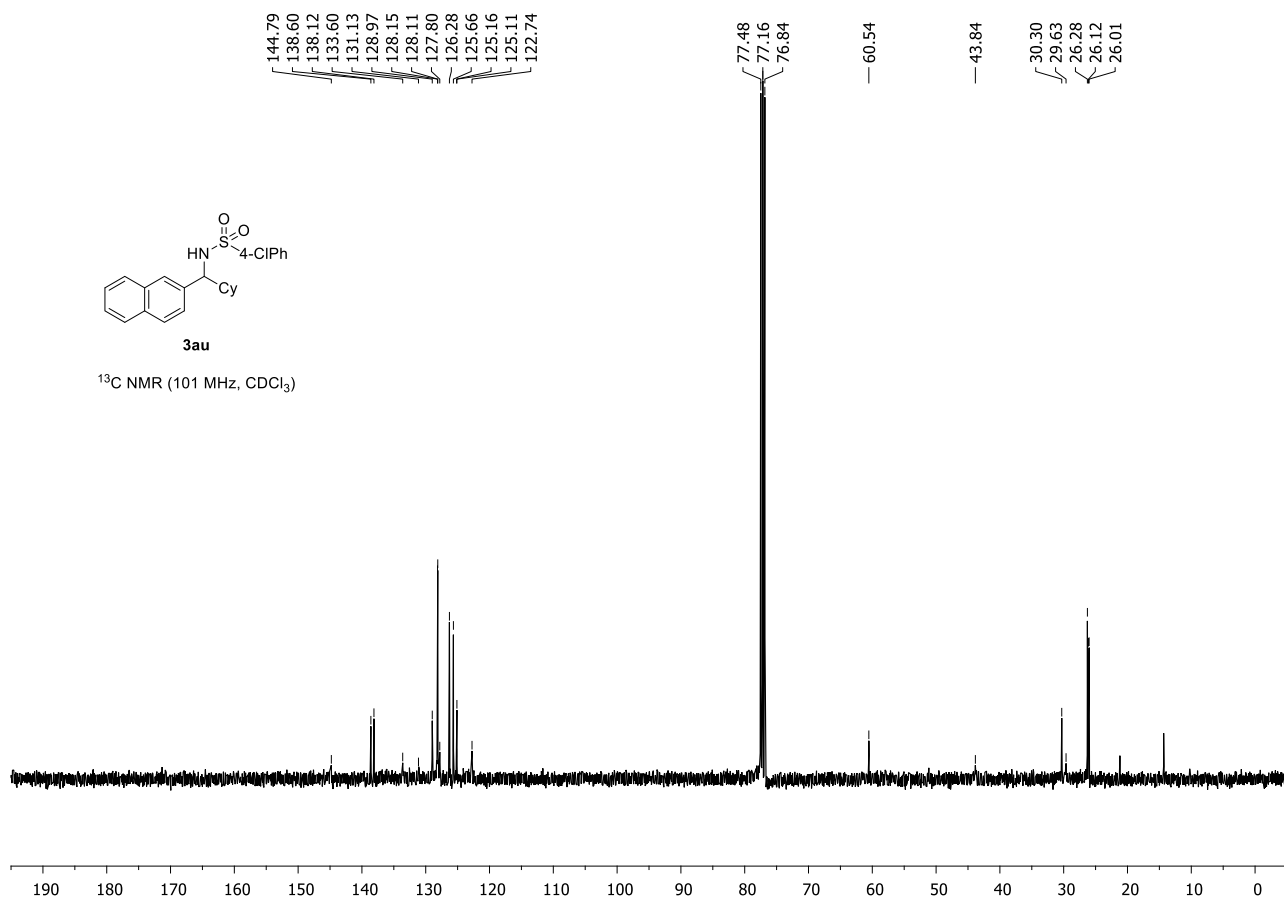


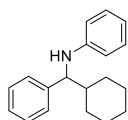


¹H NMR (400 MHz, CDCl₃)



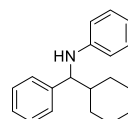
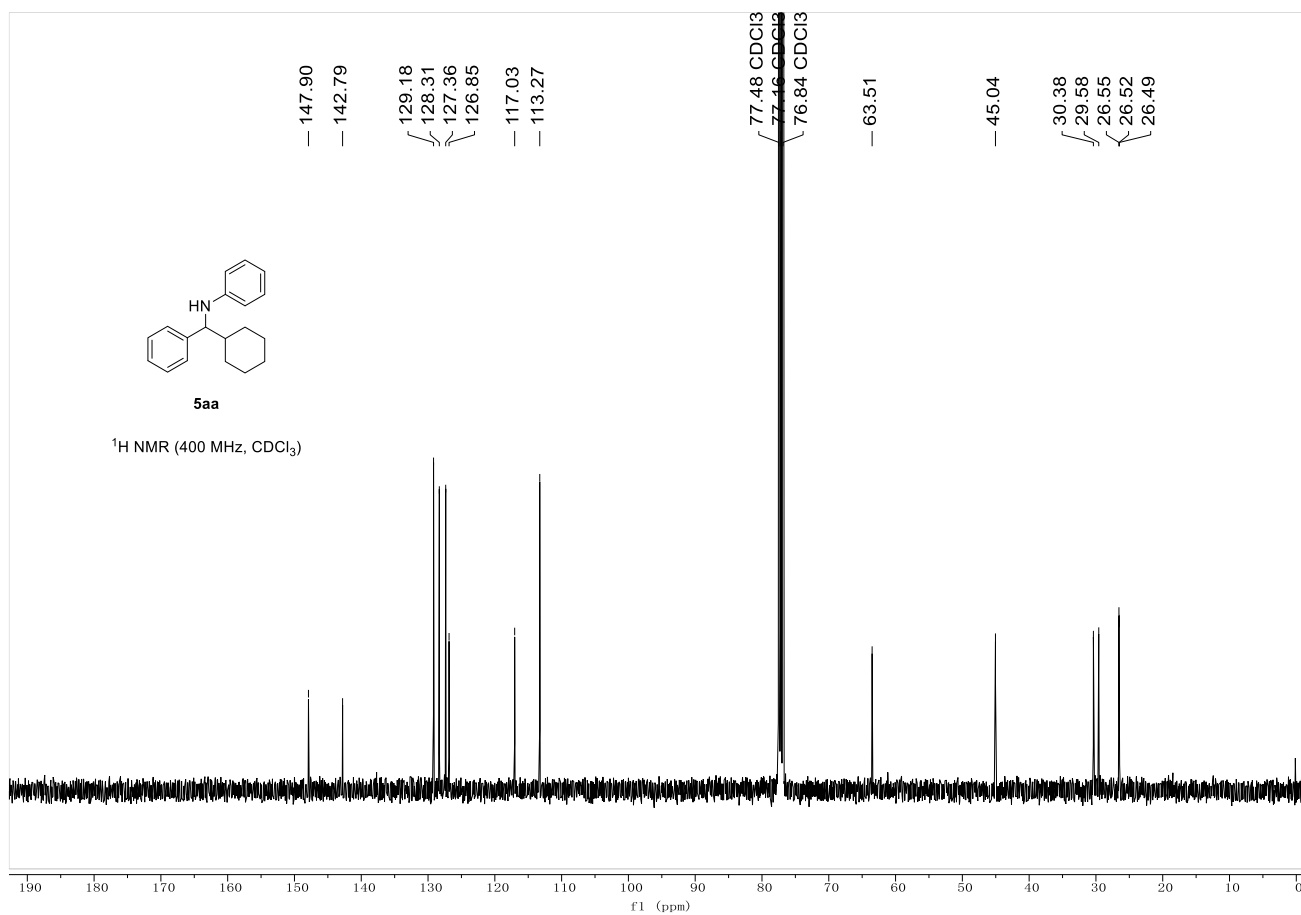
¹³C NMR (101 MHz, CDCl₃)





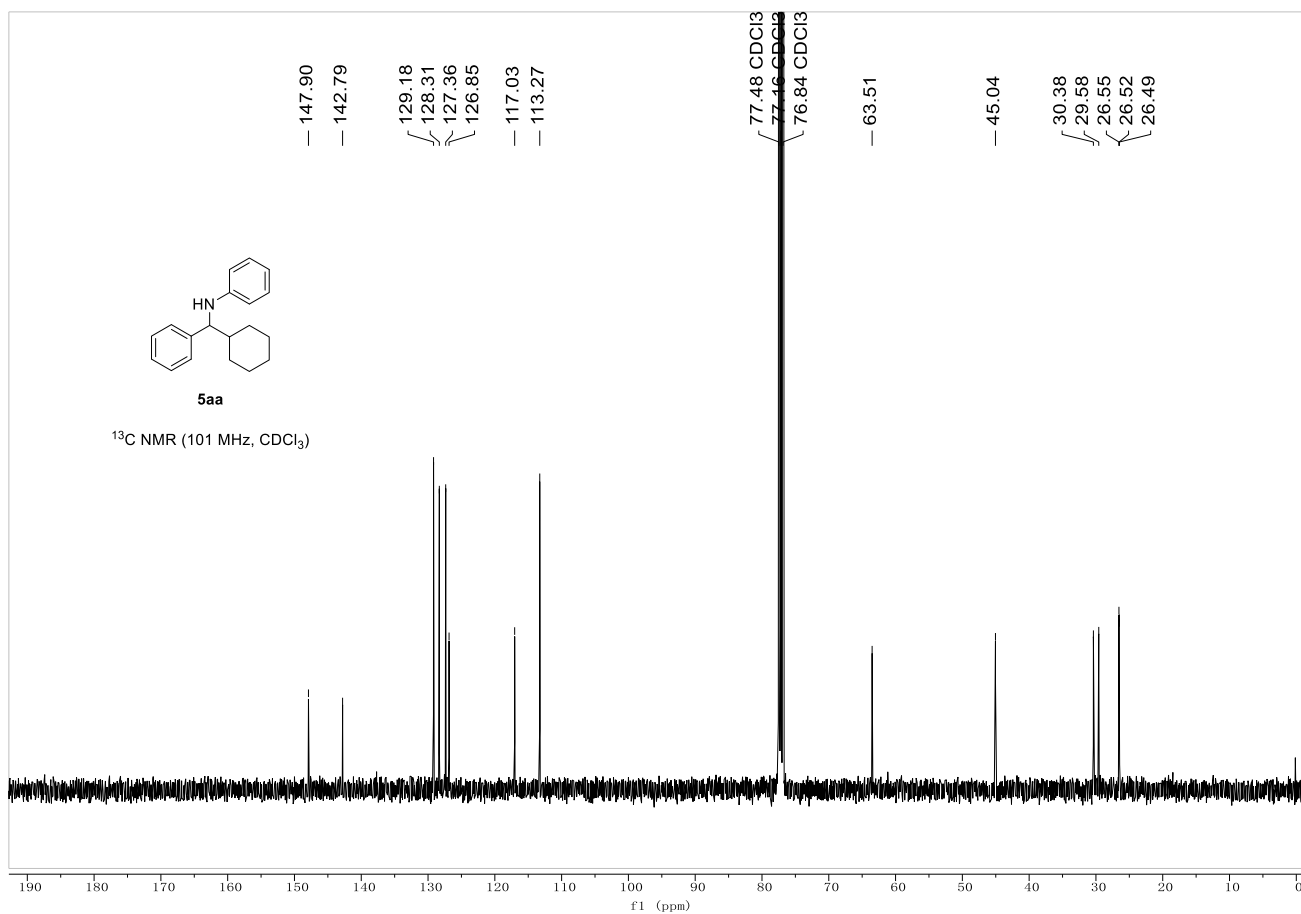
5aa

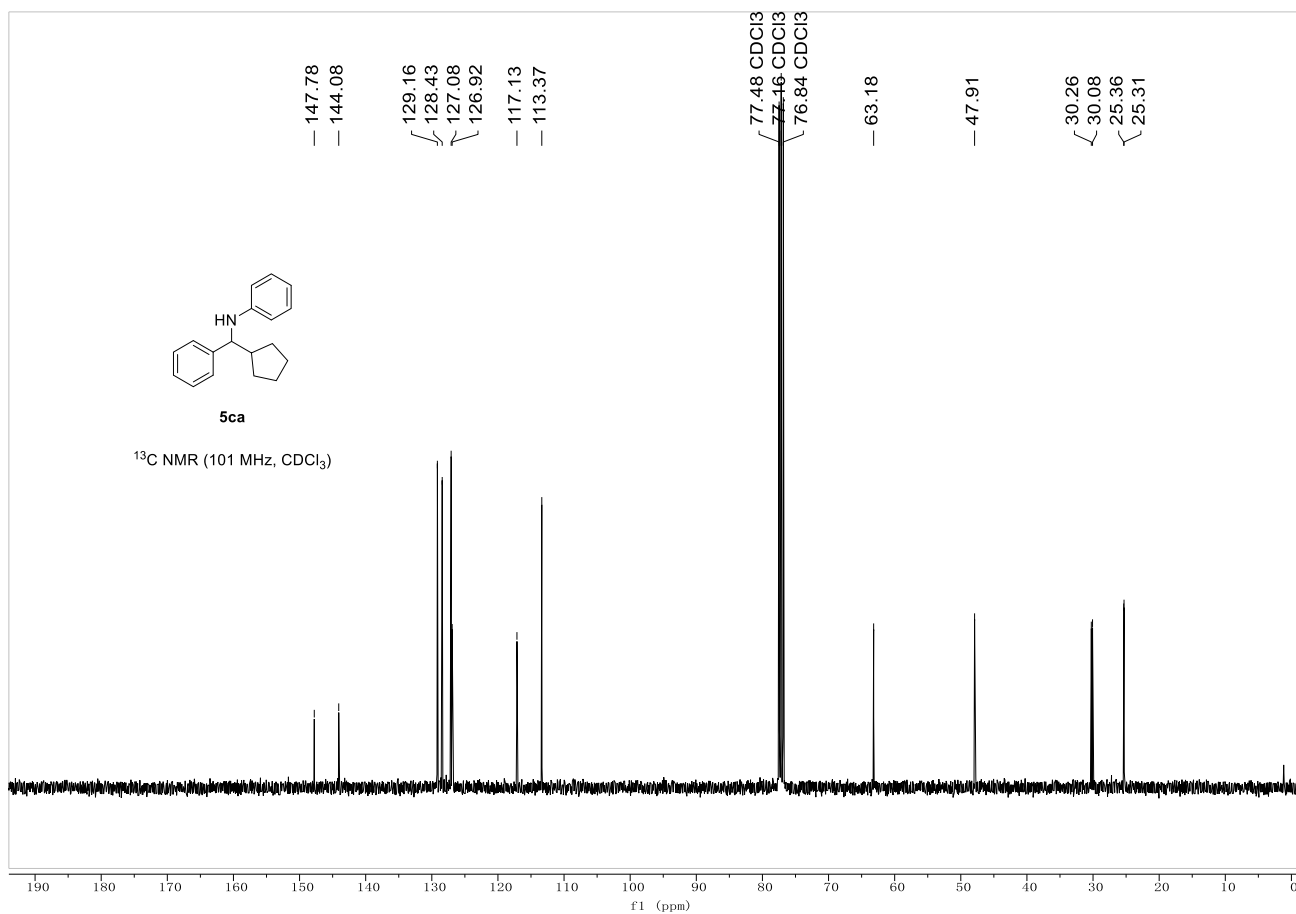
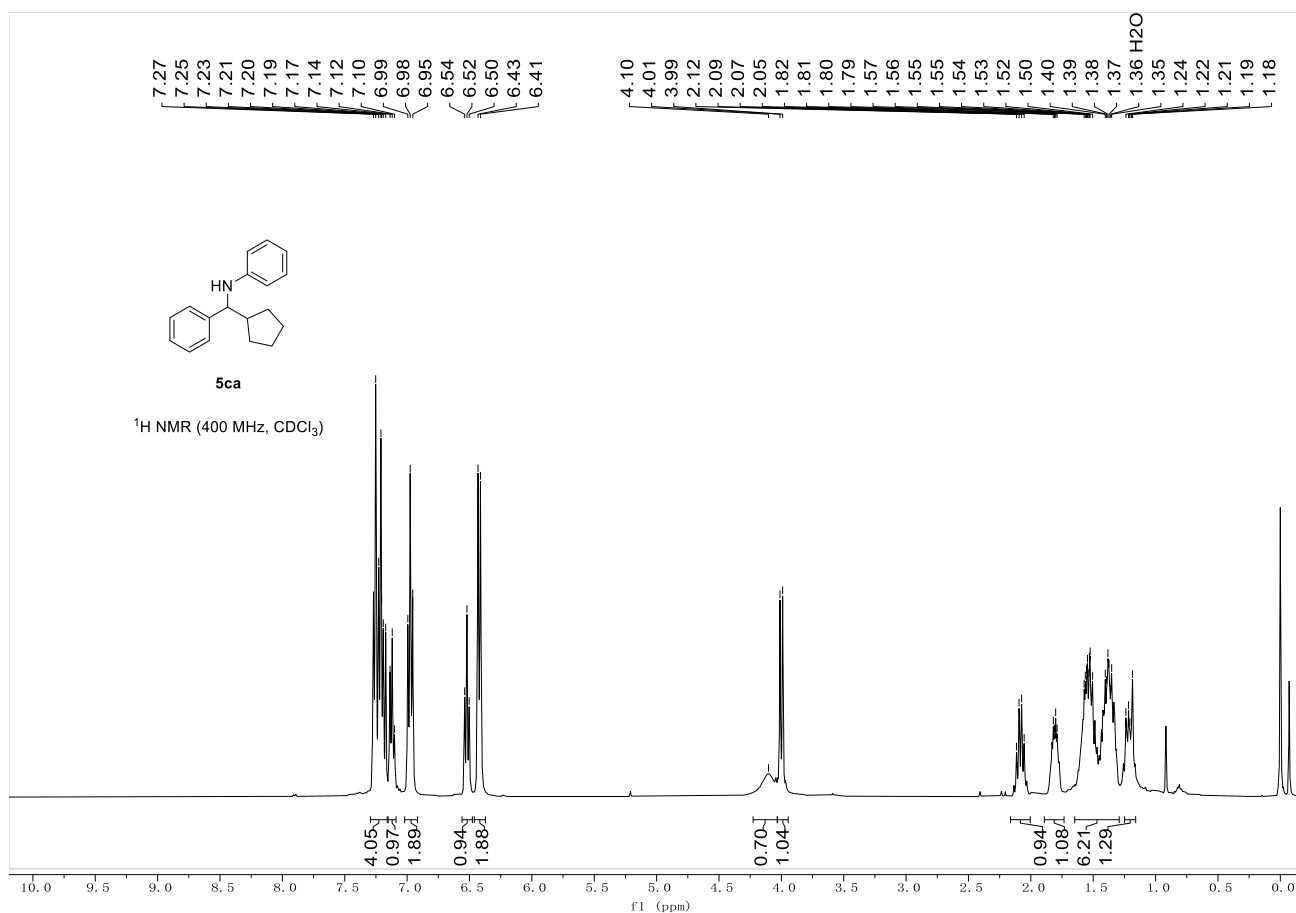
^1H NMR (400 MHz, CDCl_3)

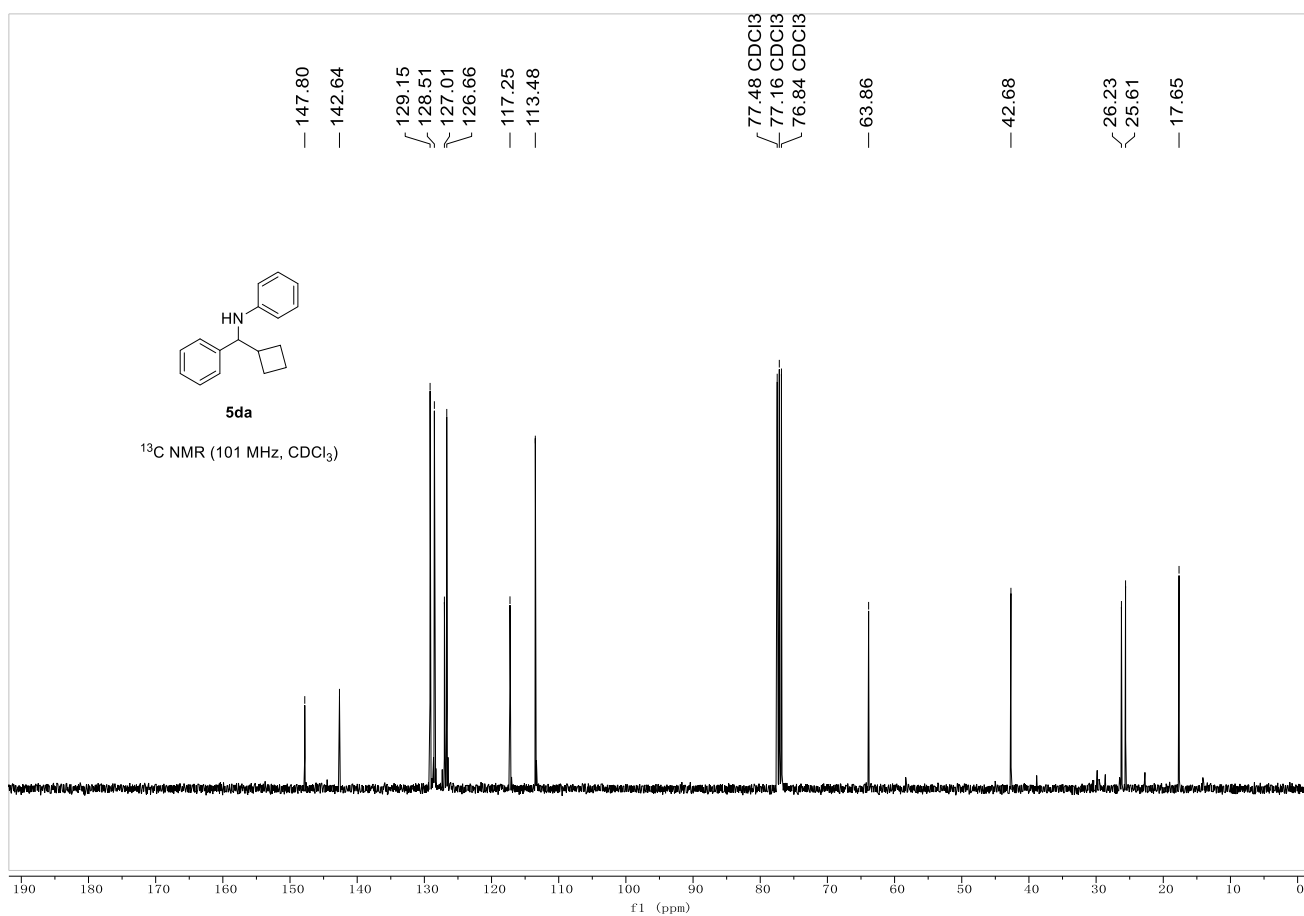
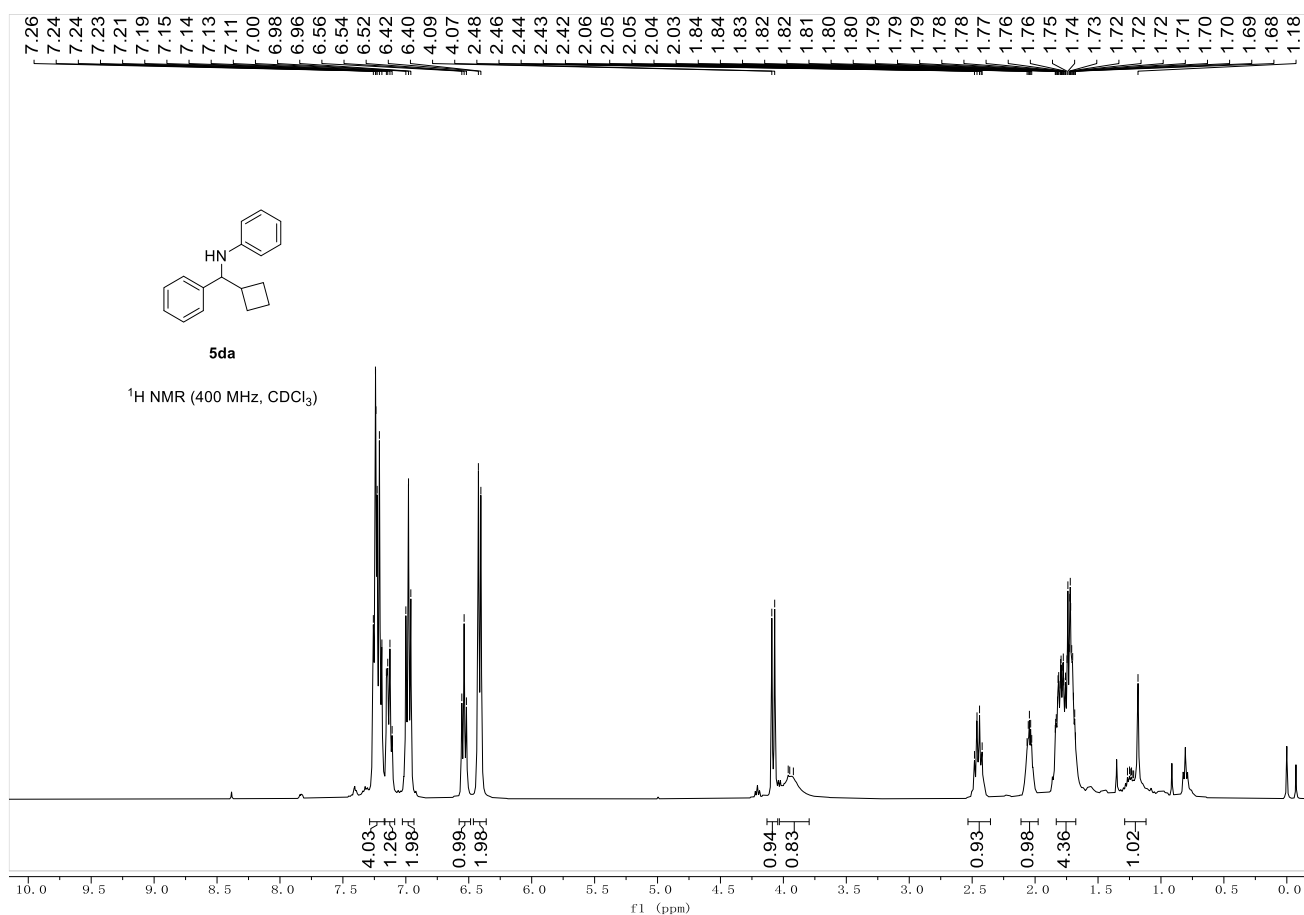


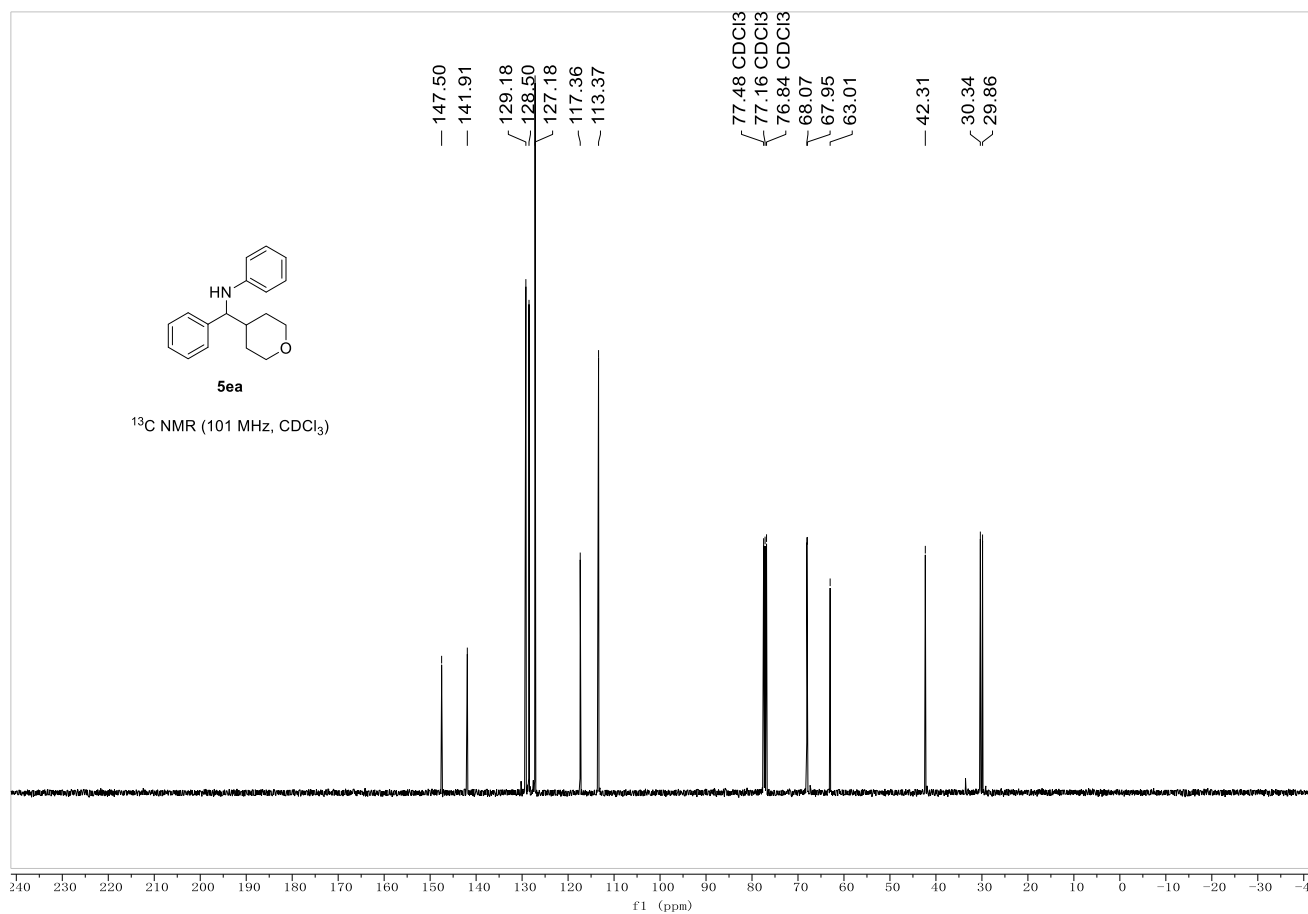
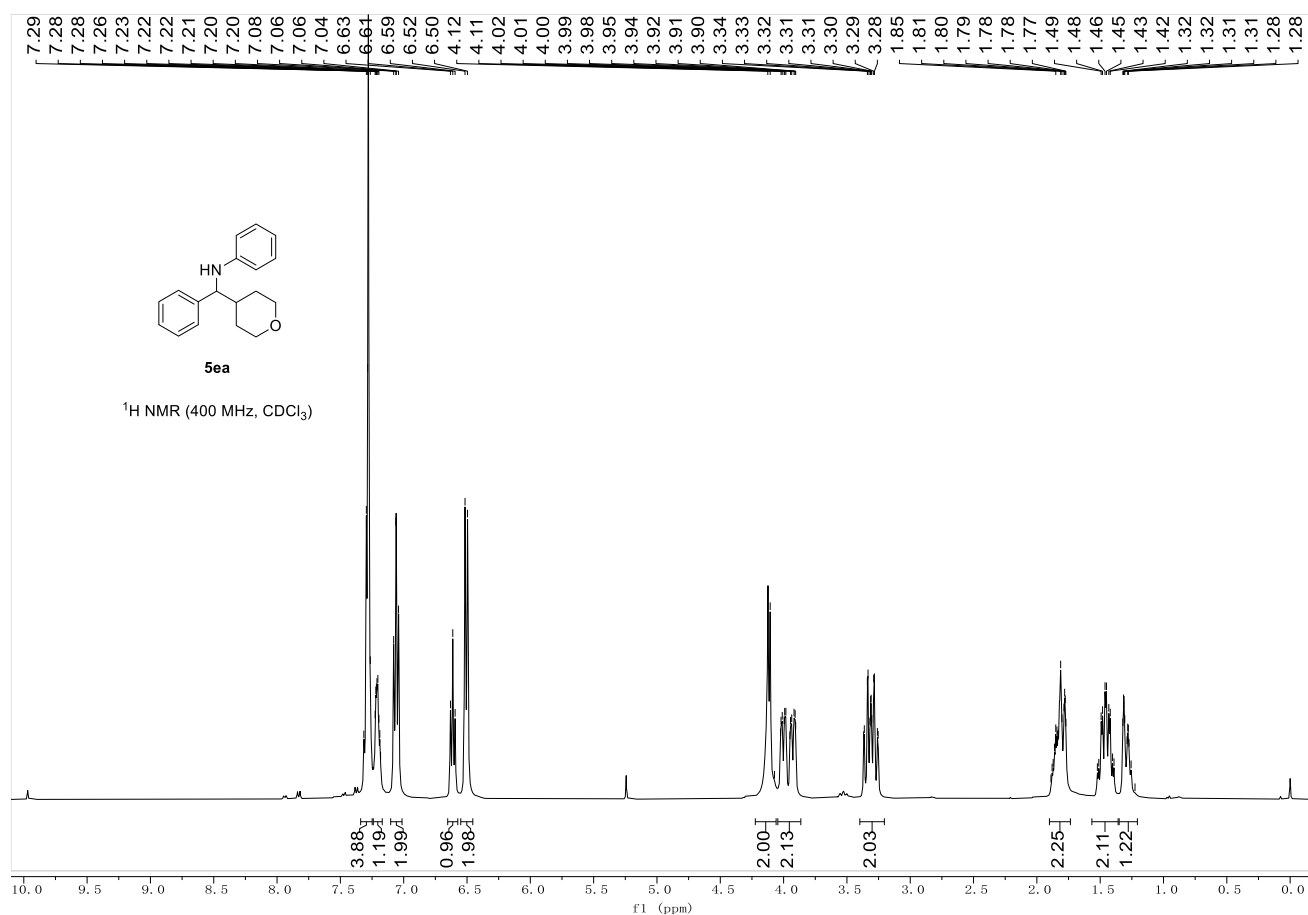
5aa

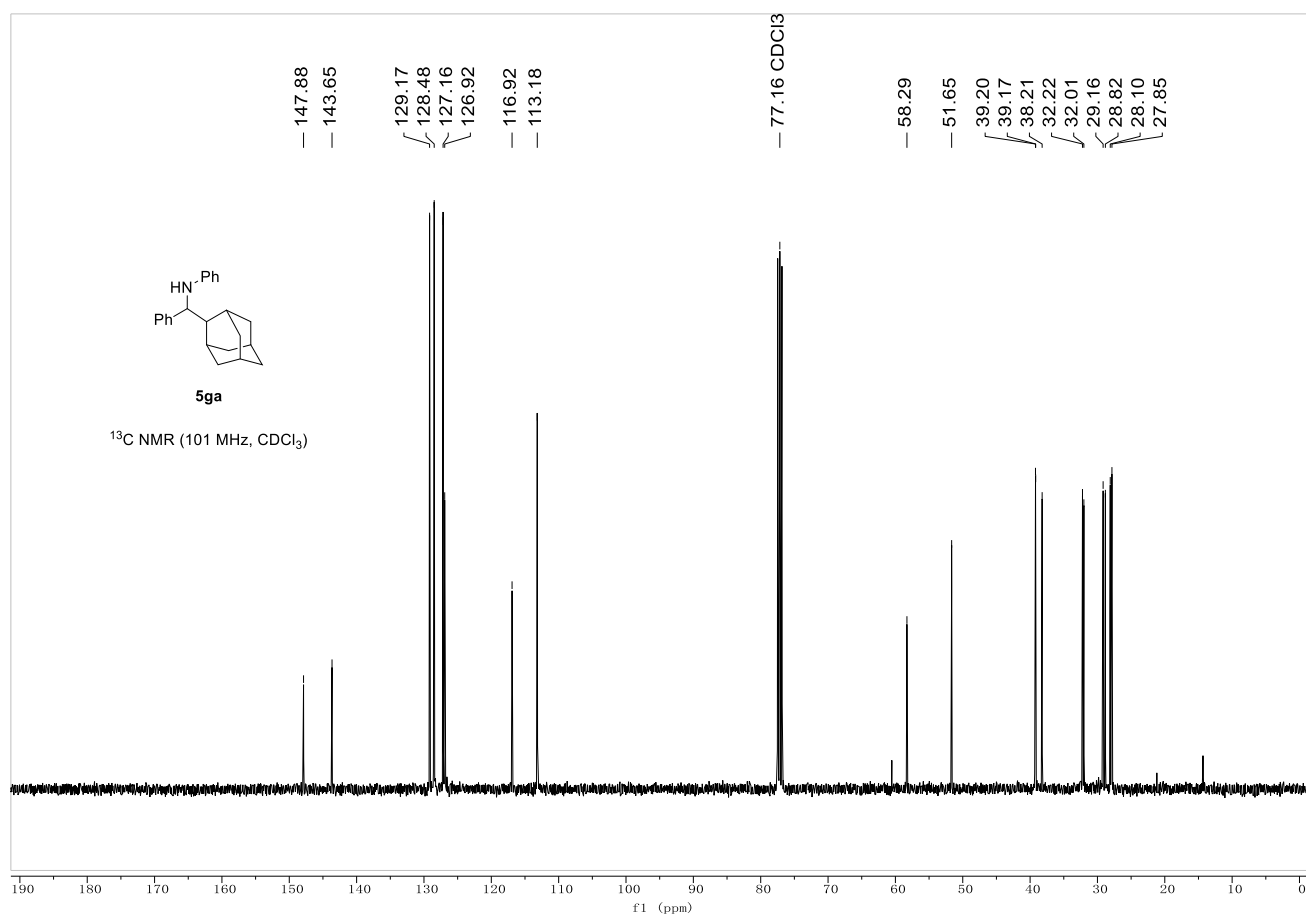
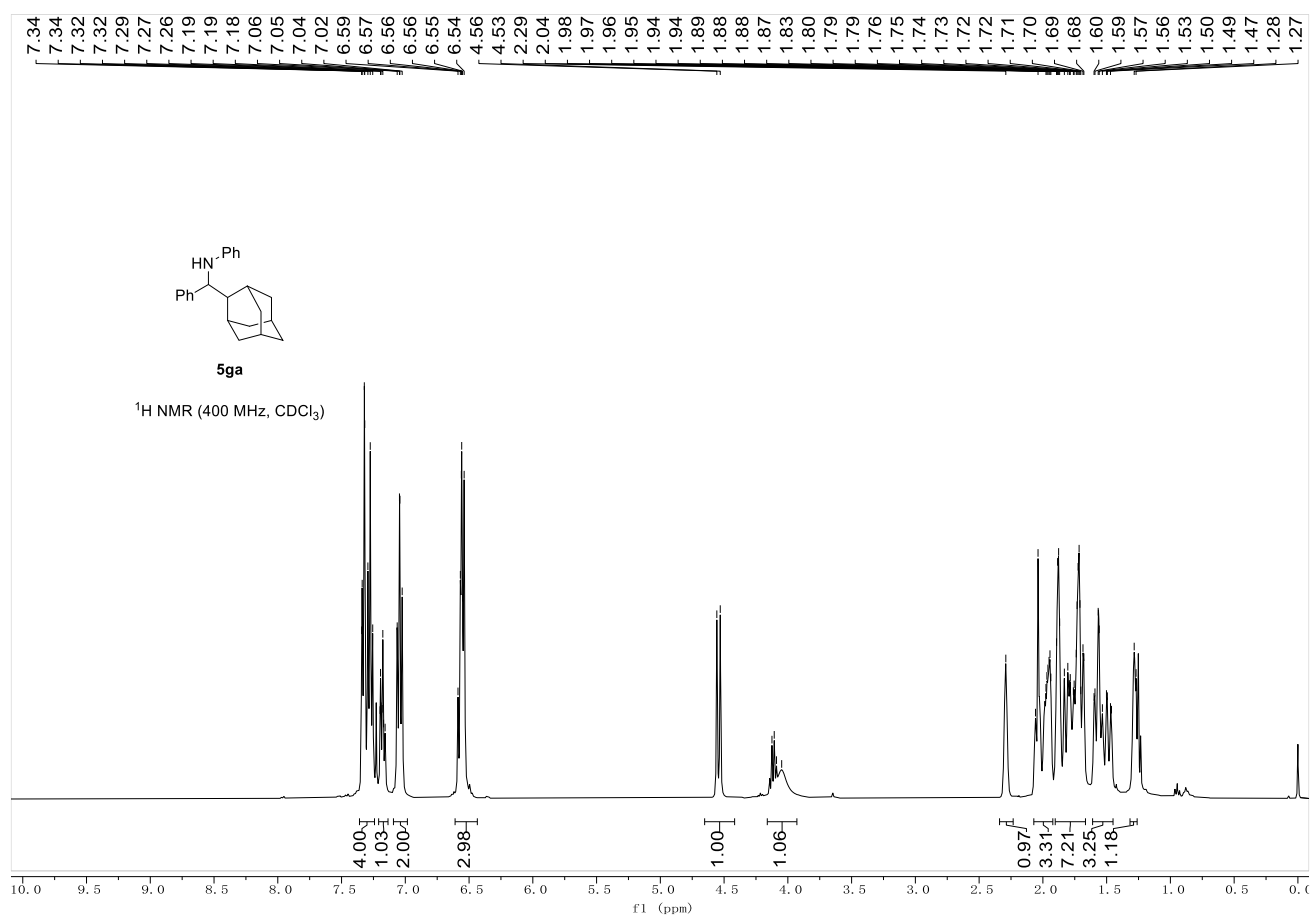
^{13}C NMR (101 MHz, CDCl_3)

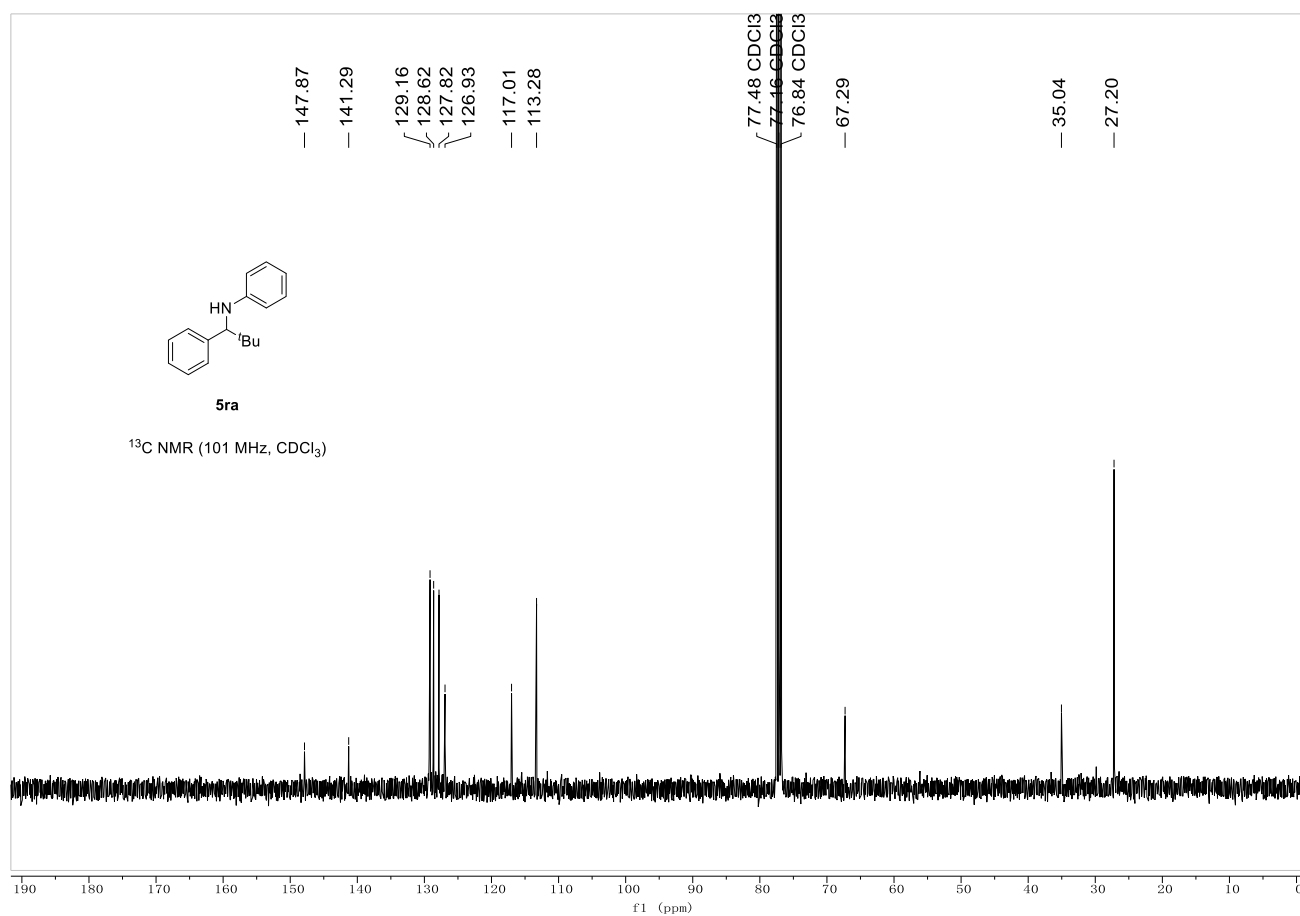
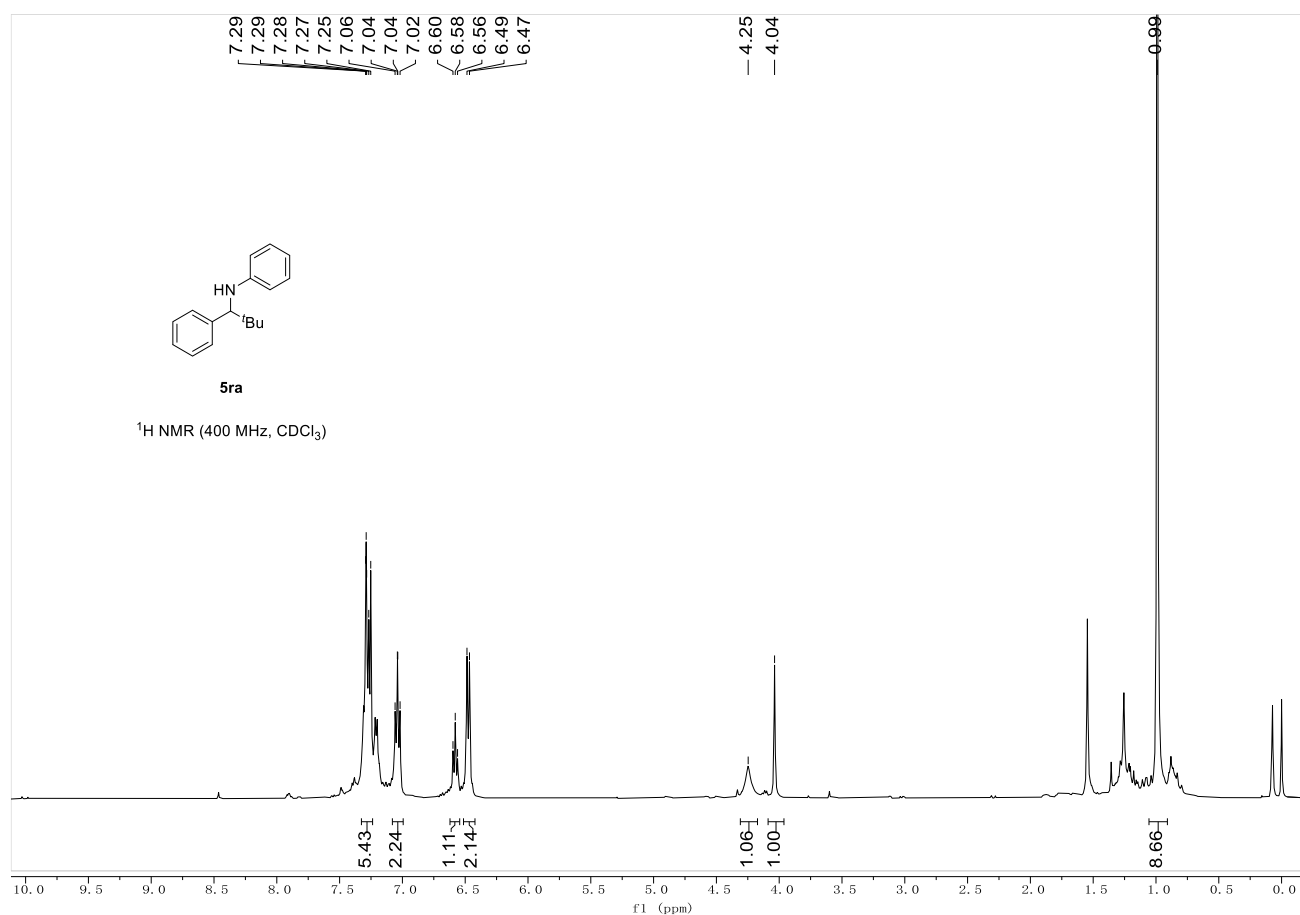


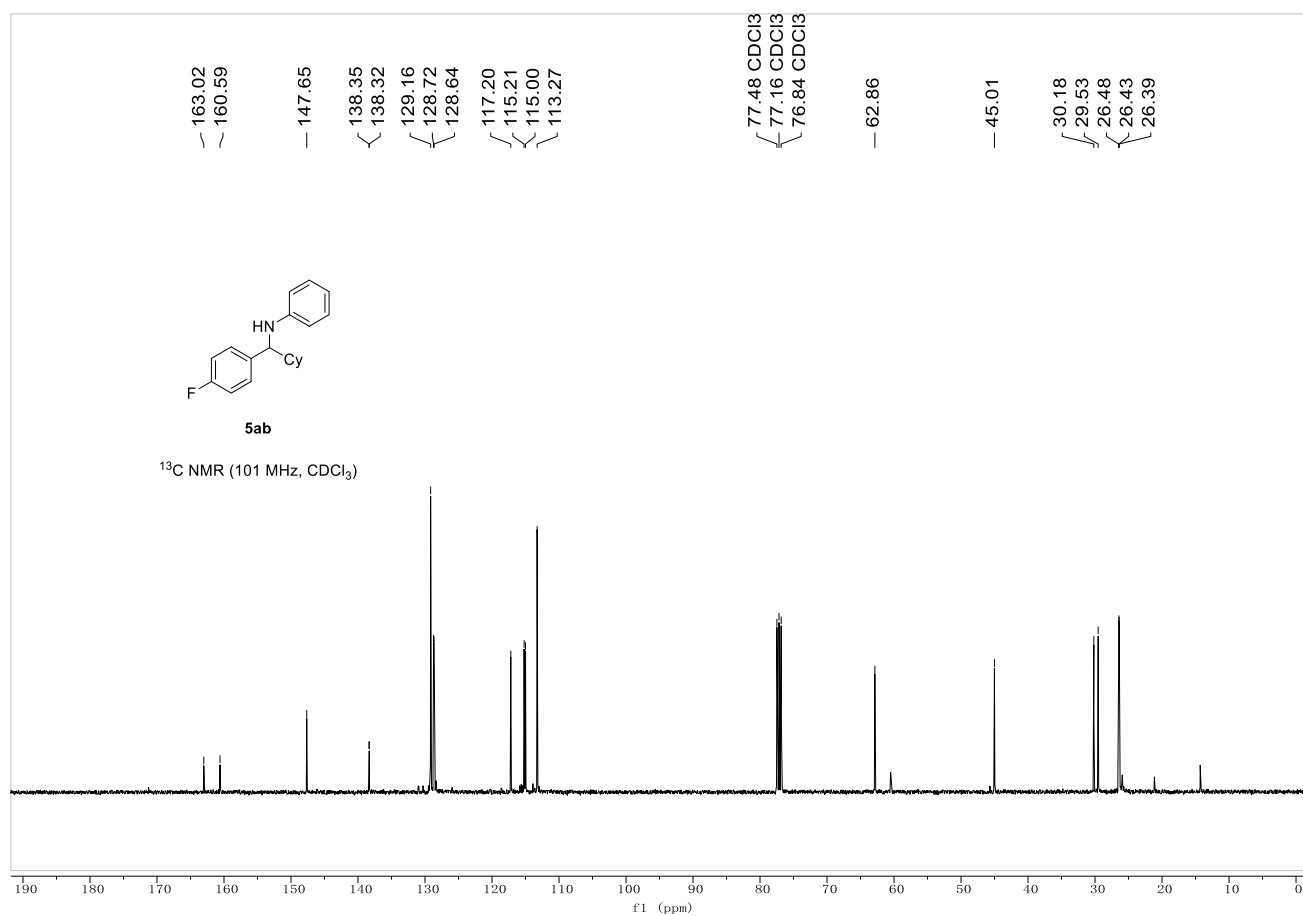
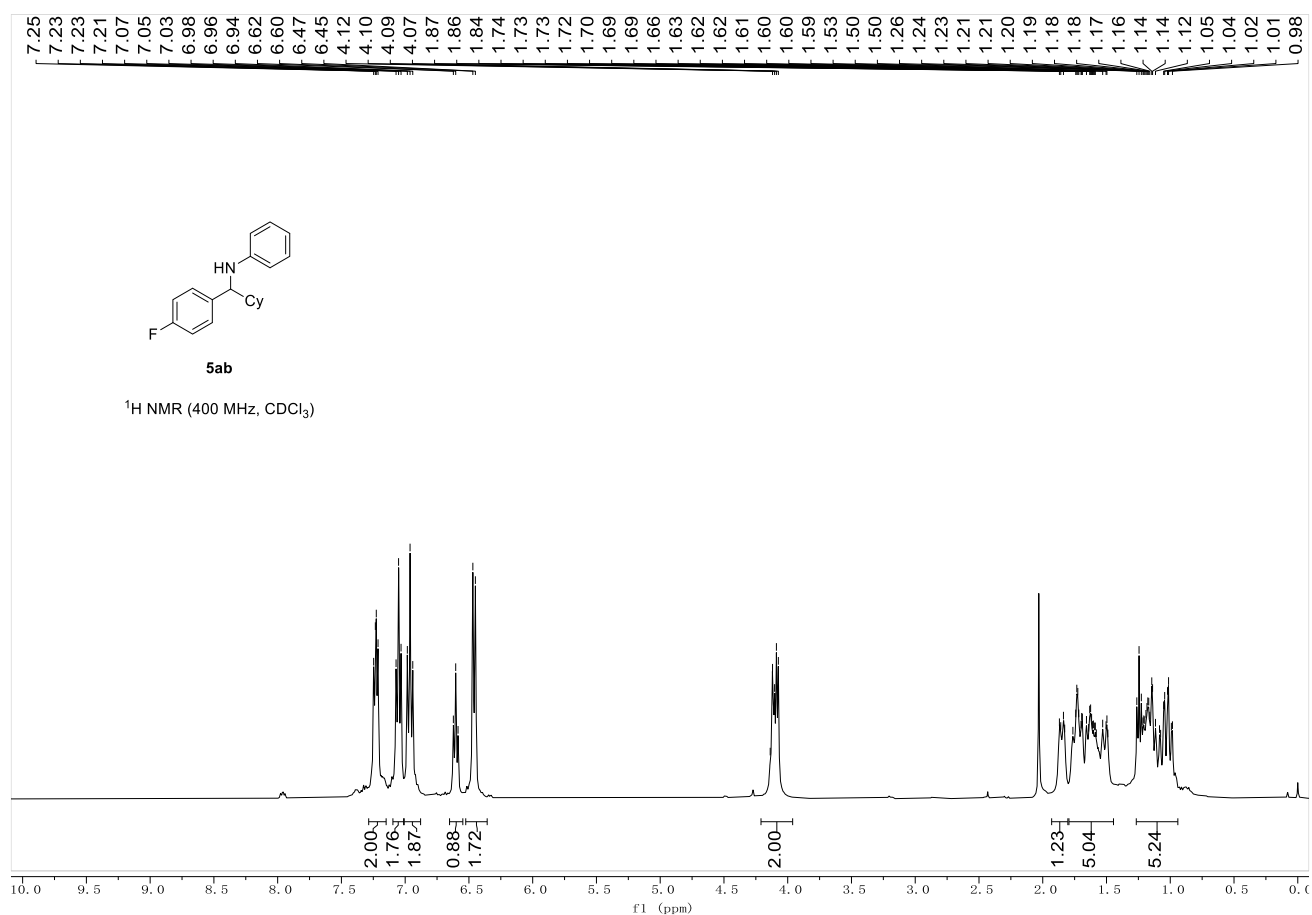


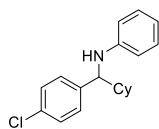






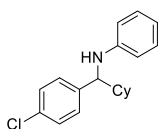
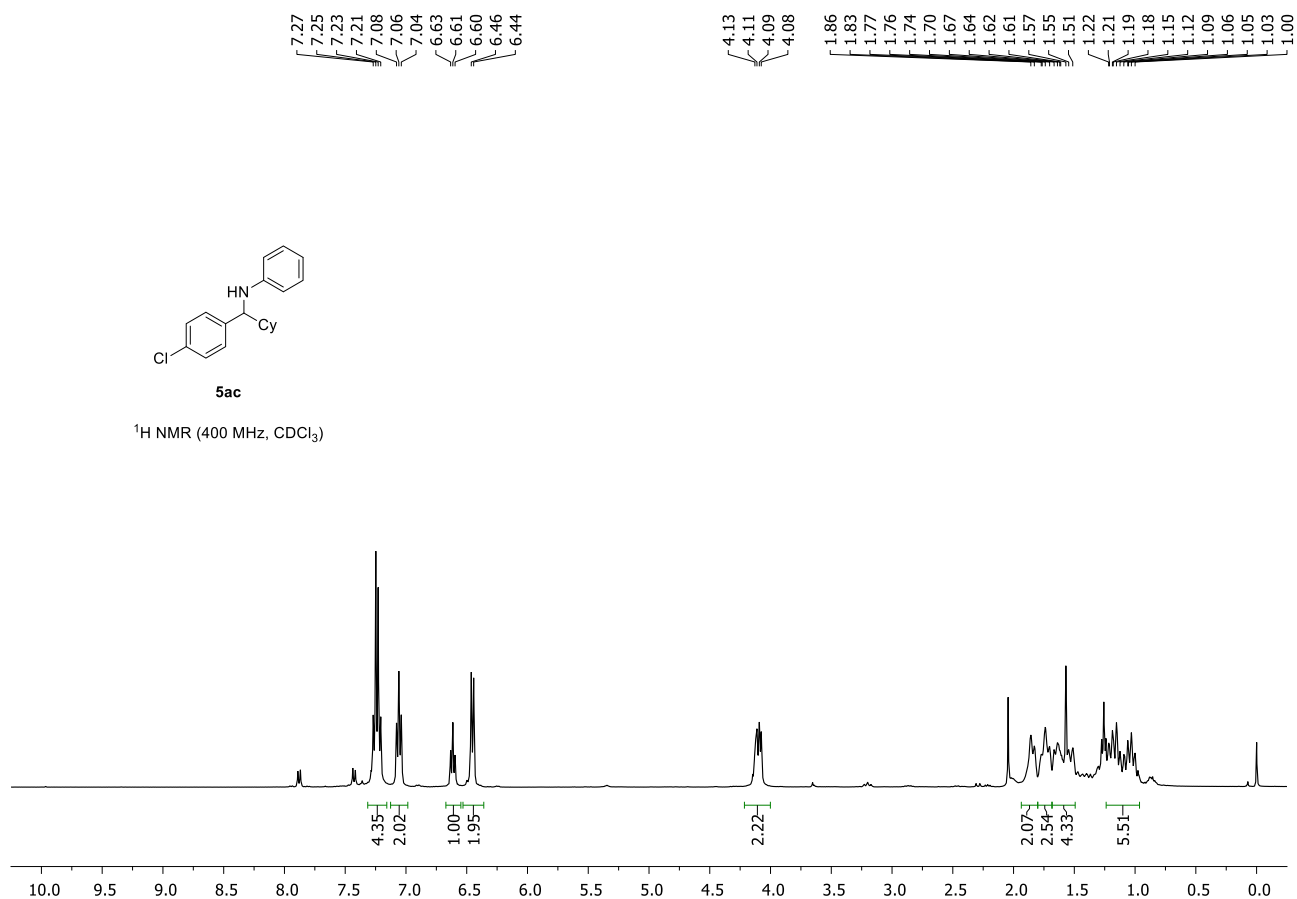






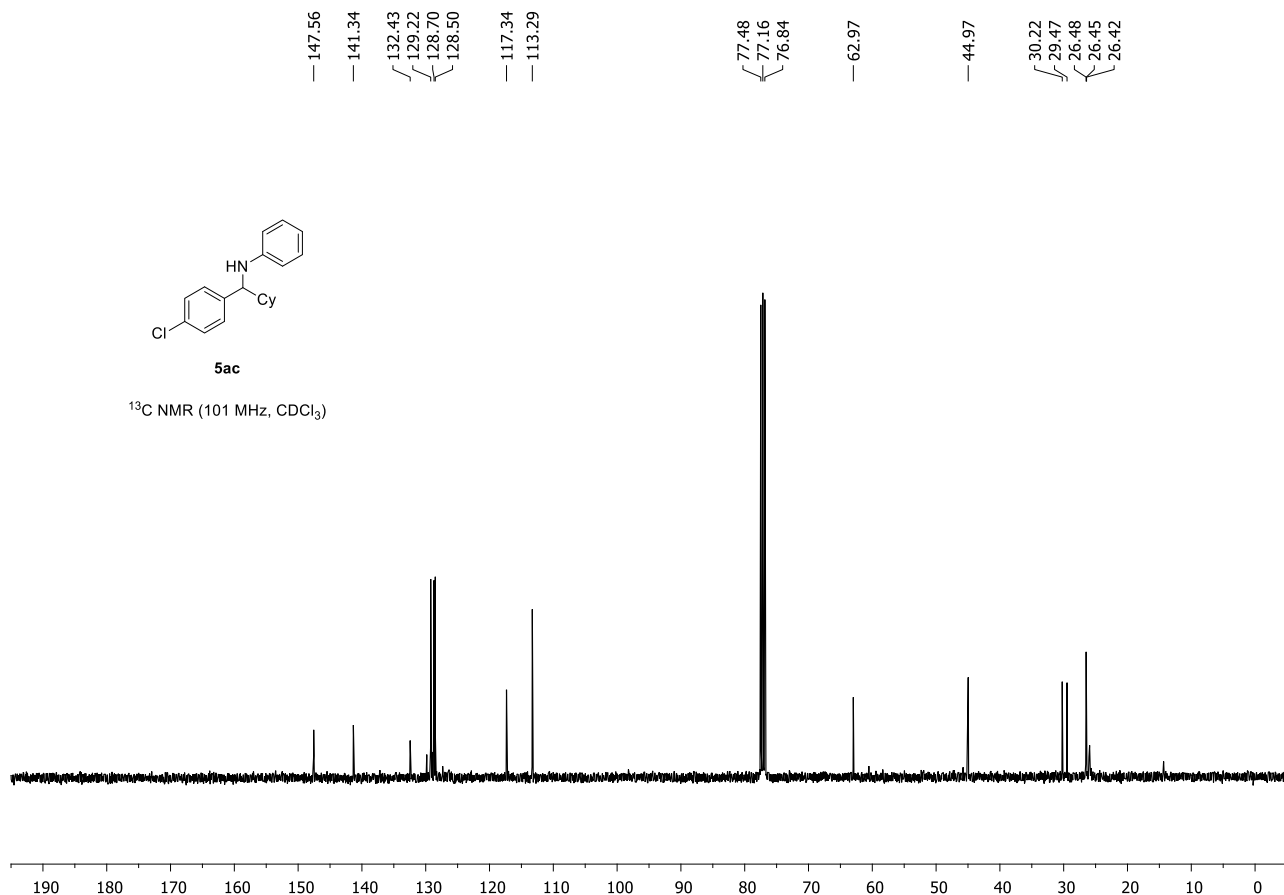
5ac

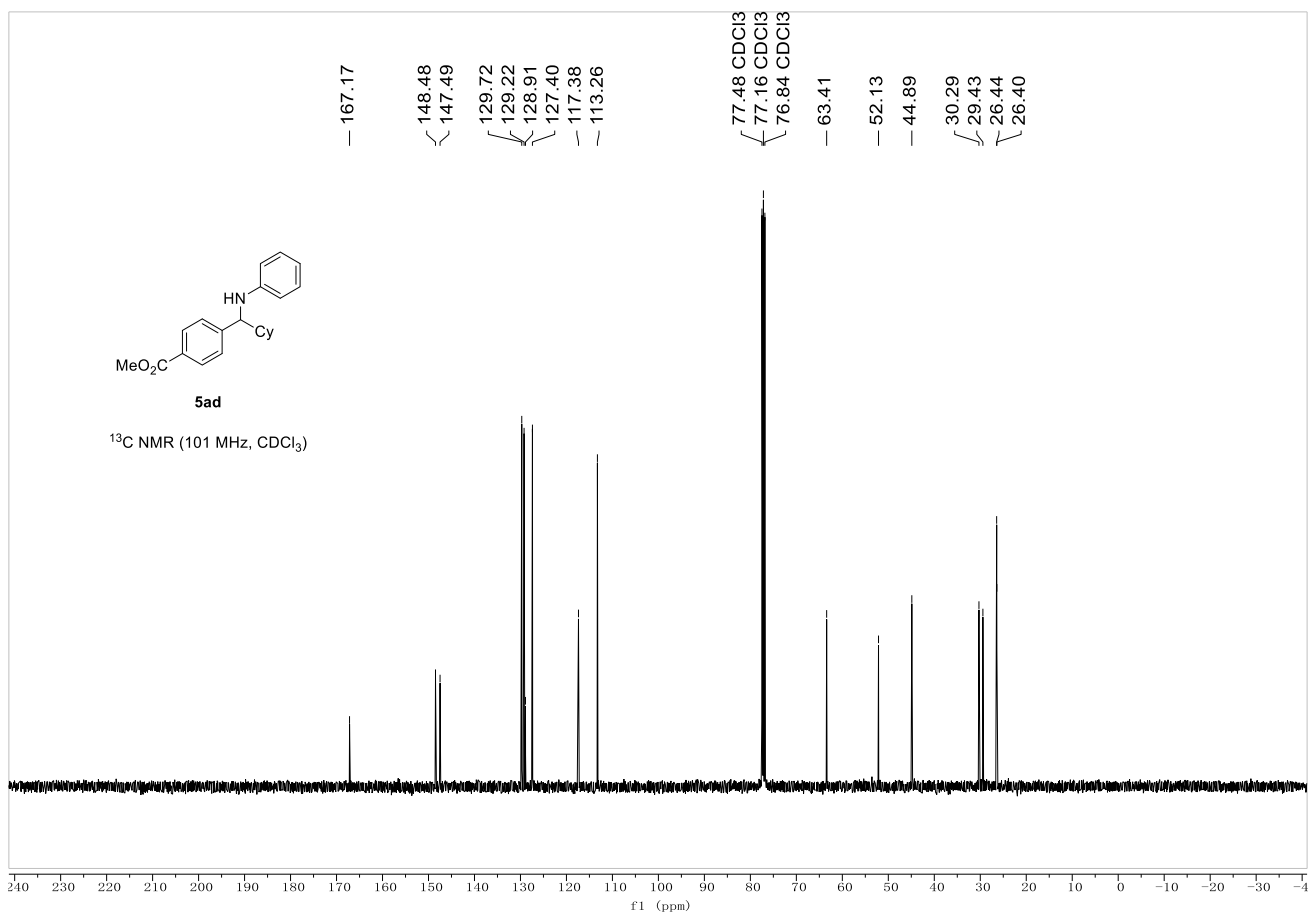
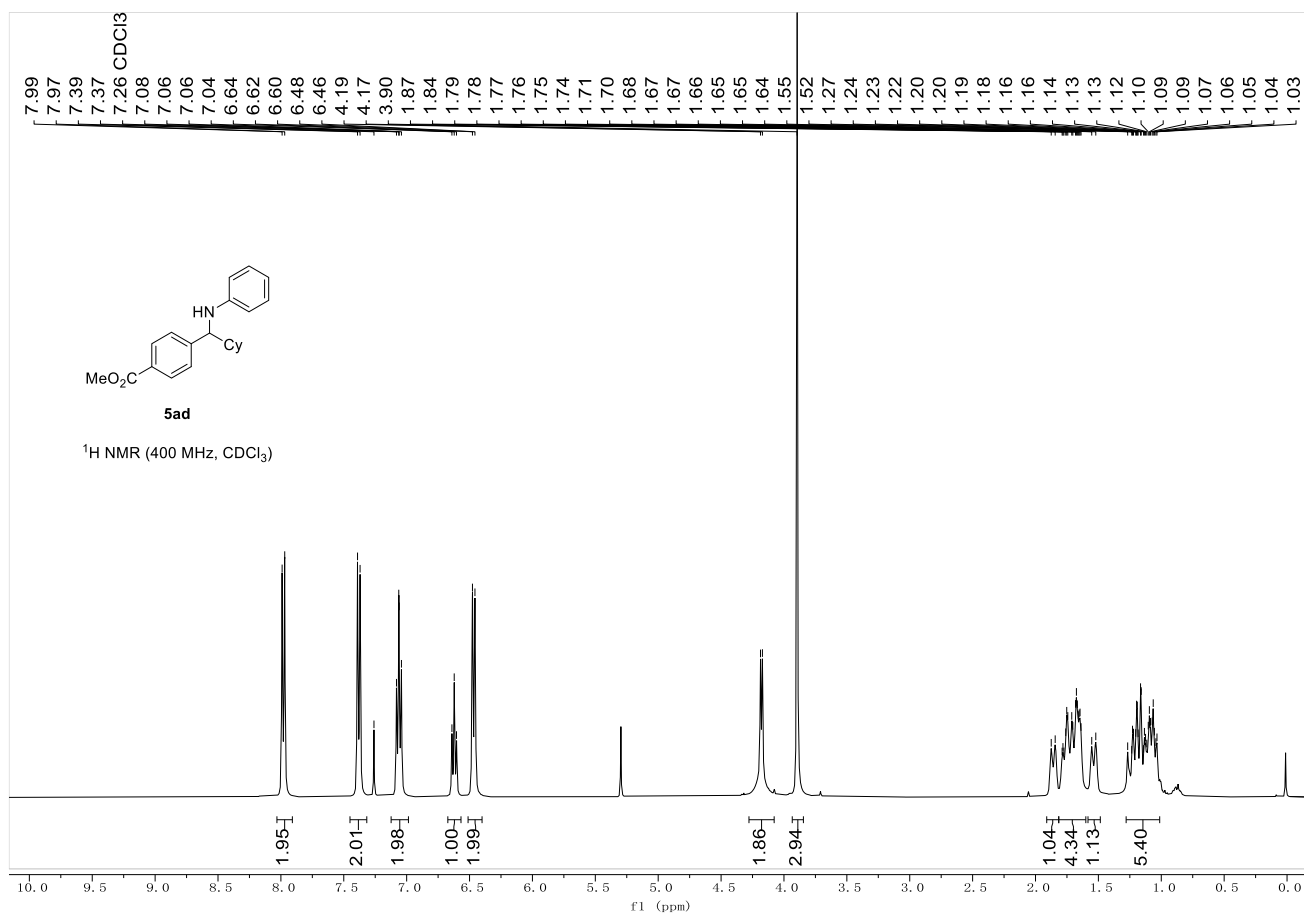
^1H NMR (400 MHz, CDCl_3)

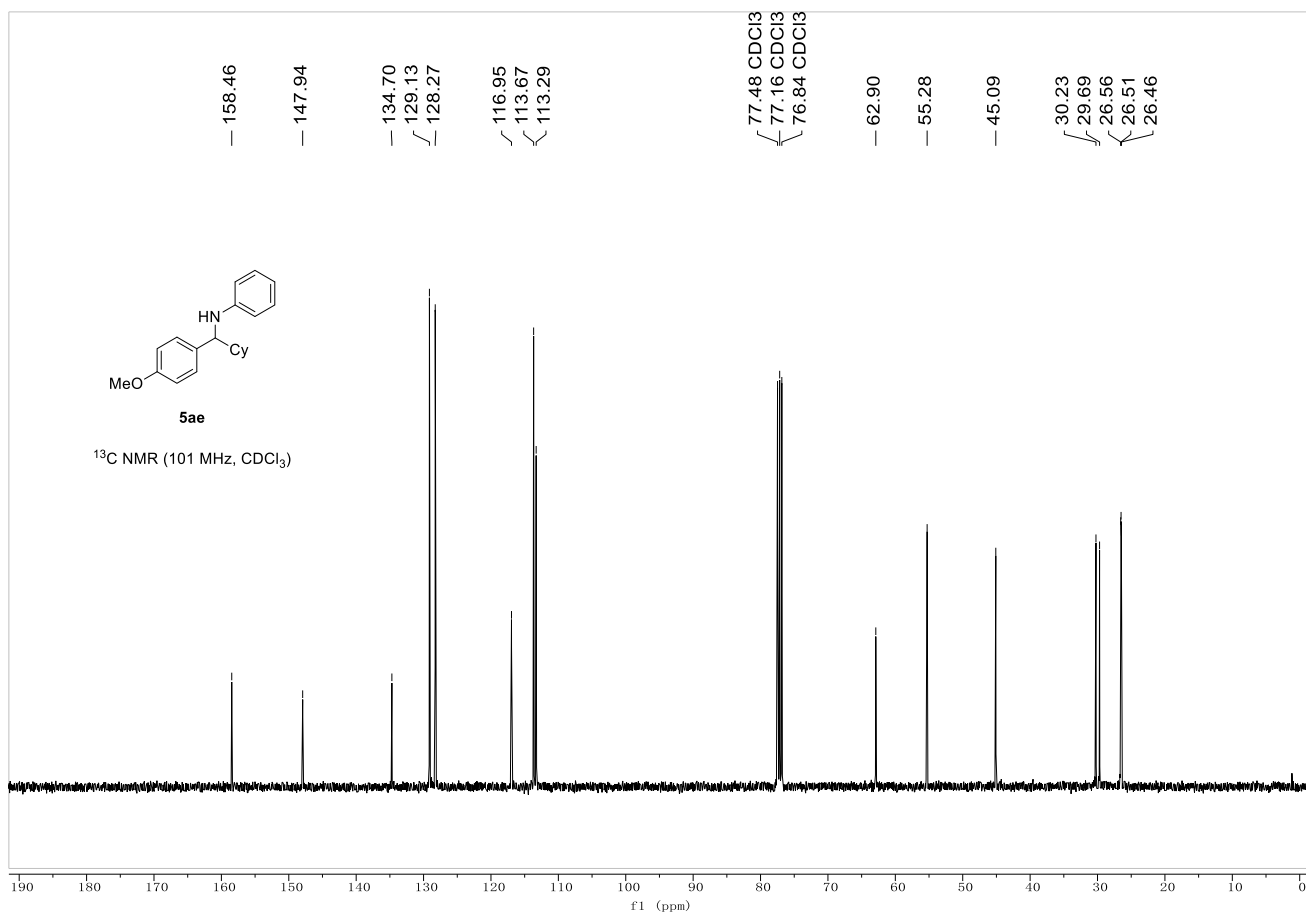
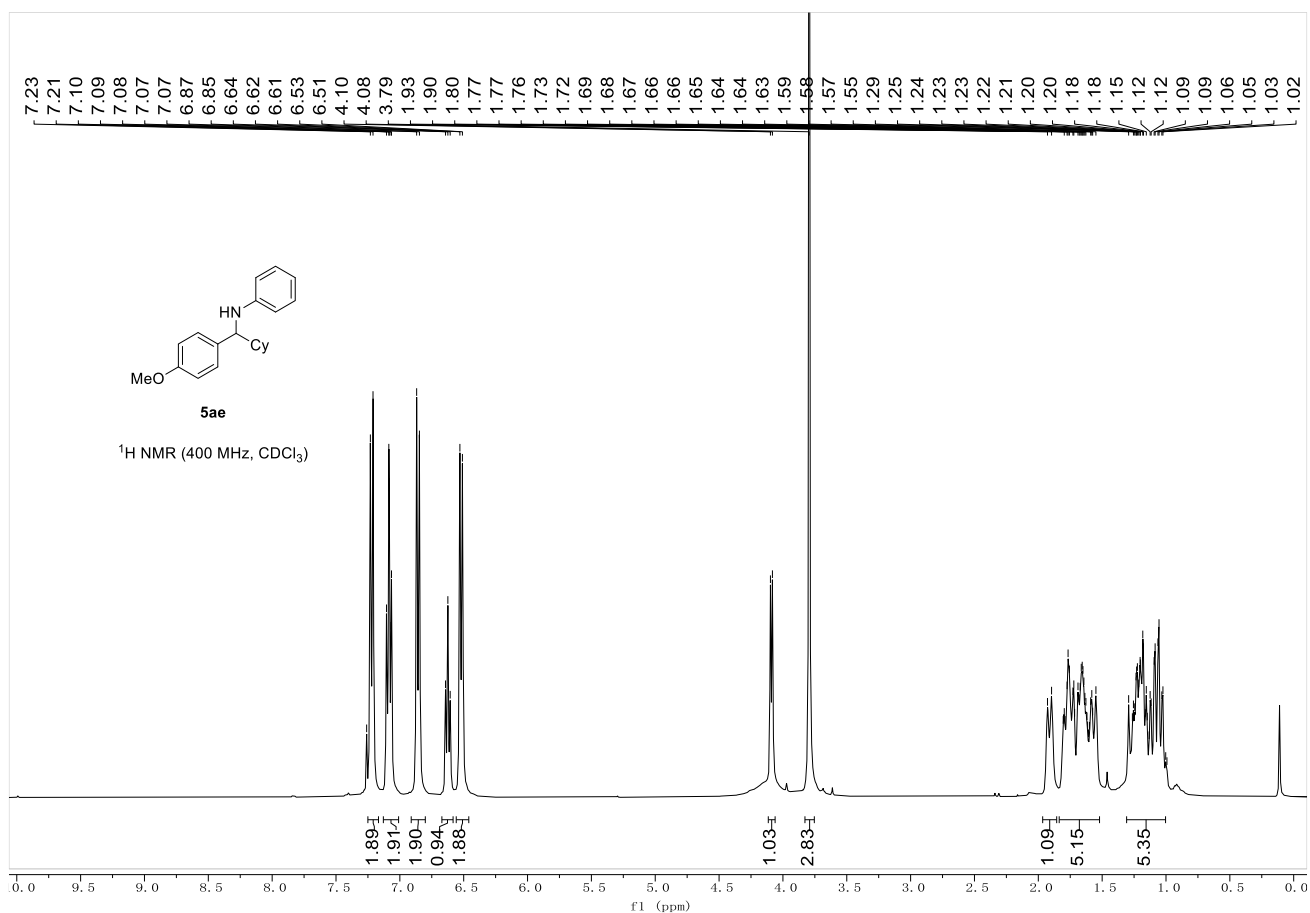


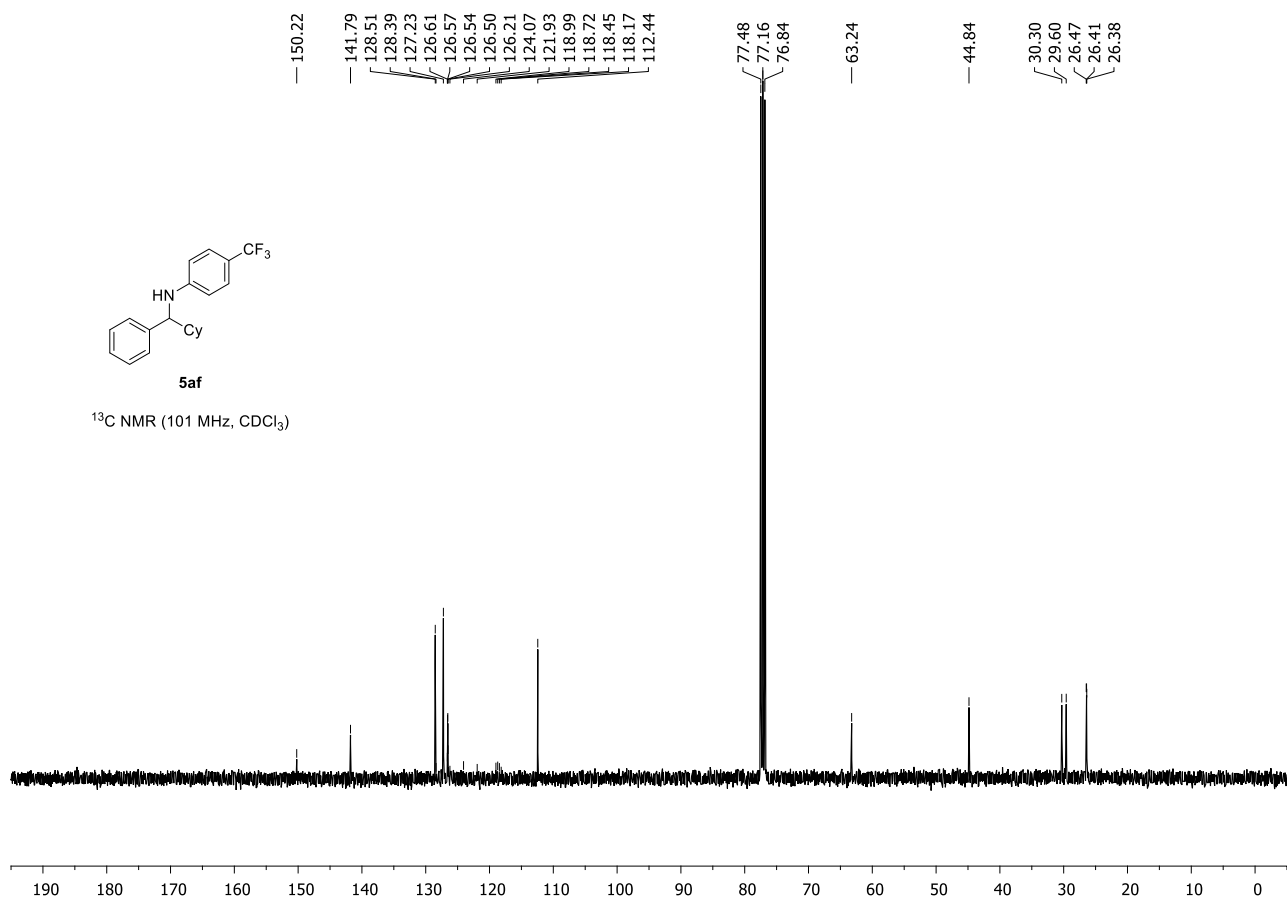
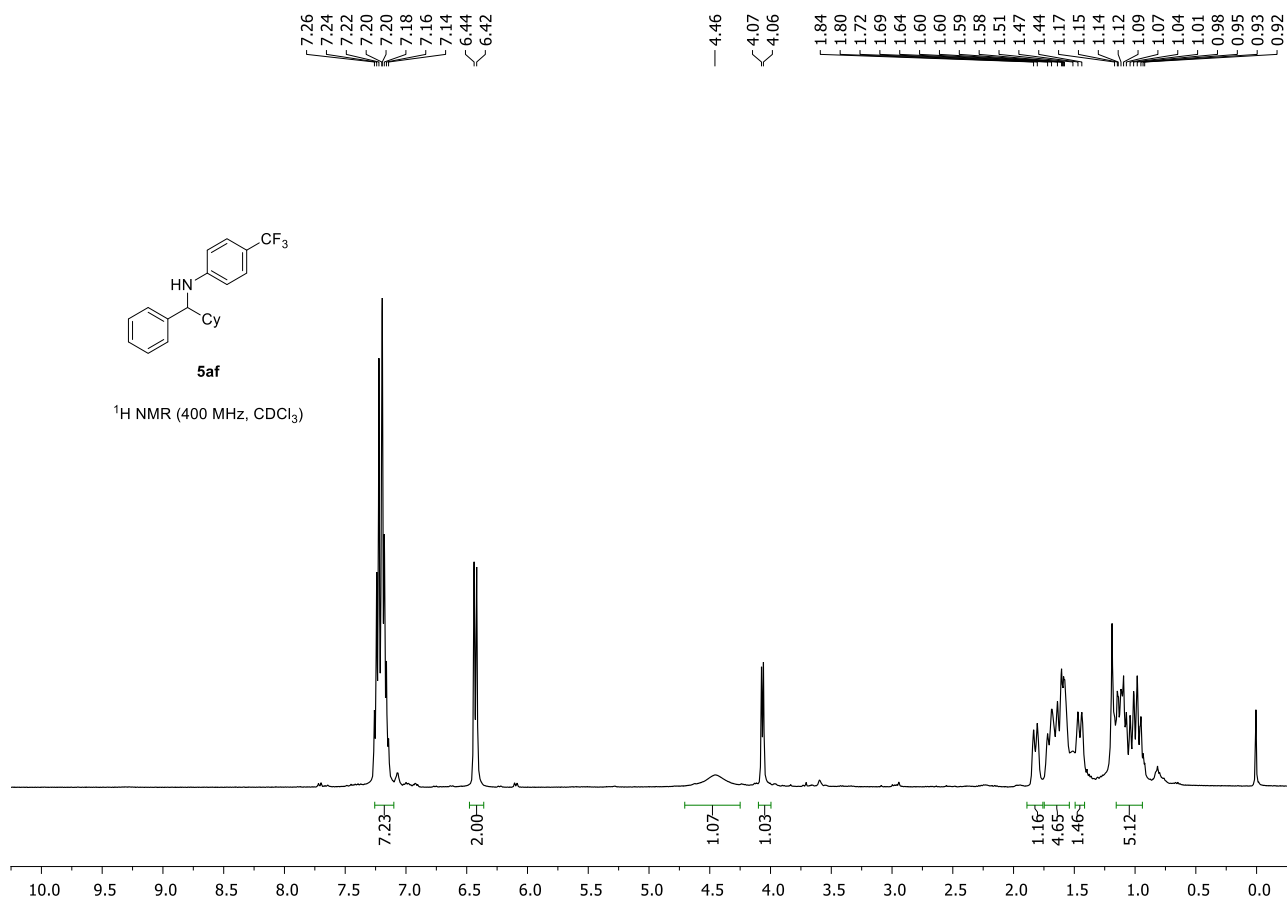
5ac

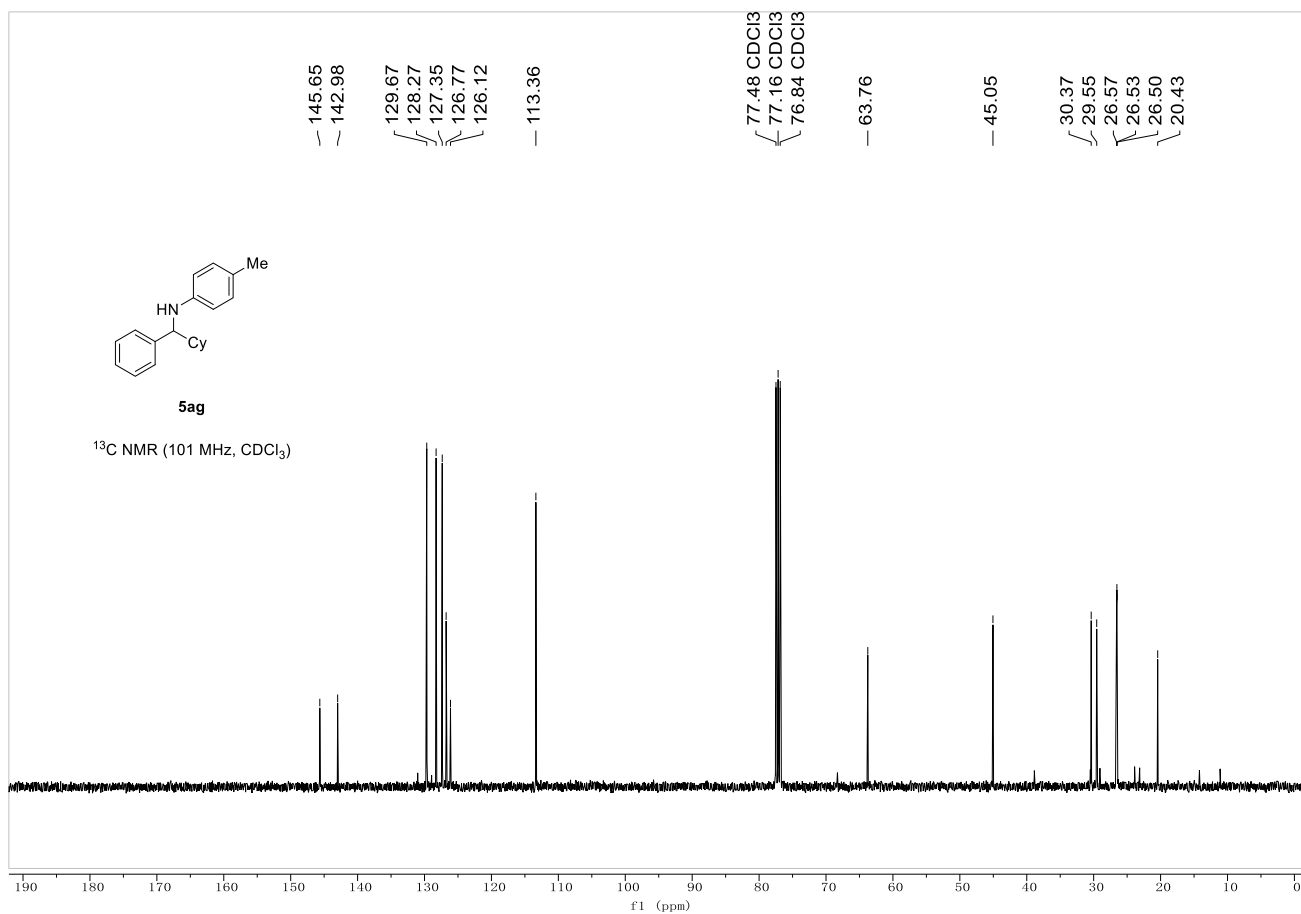
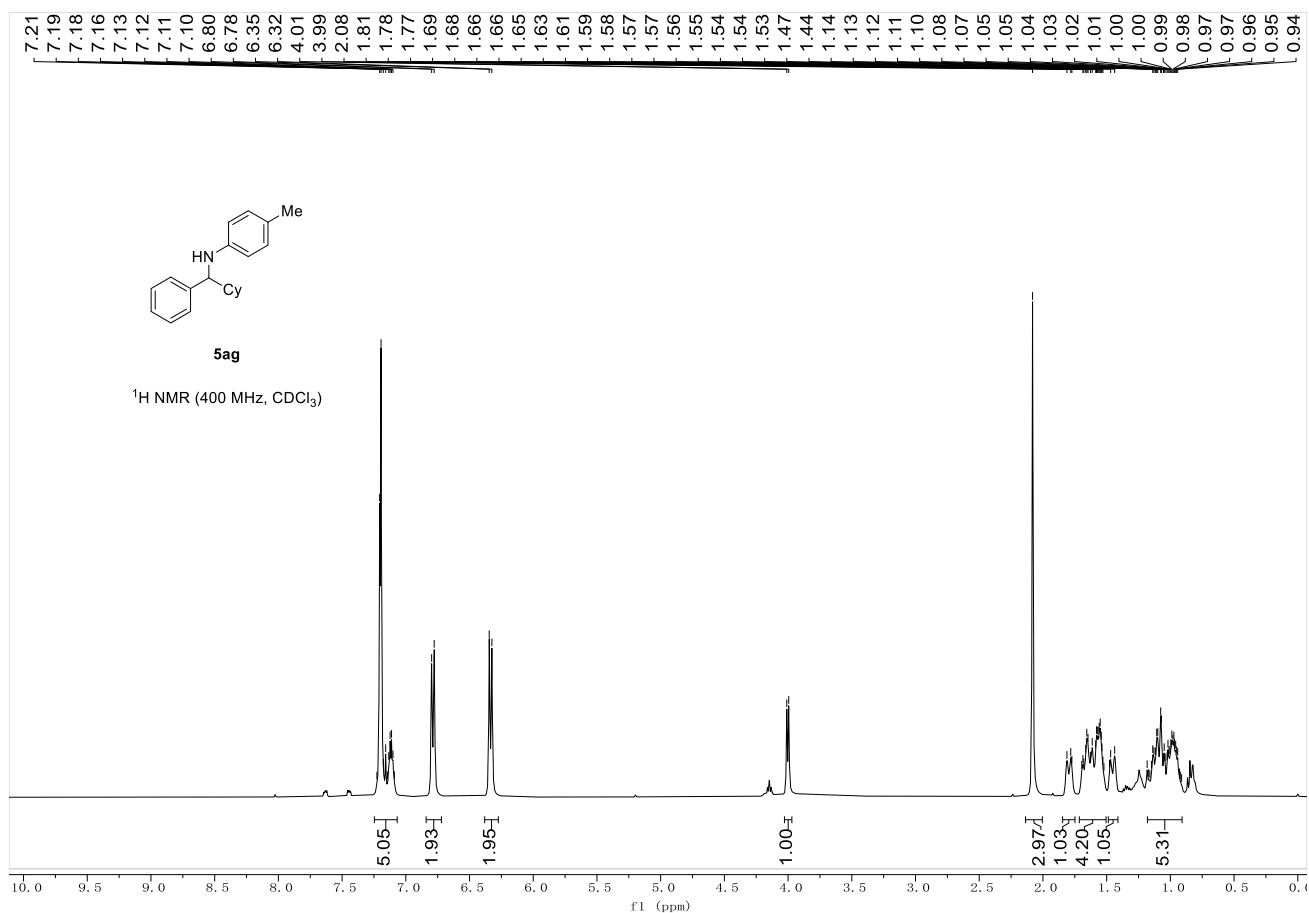
^{13}C NMR (101 MHz, CDCl_3)

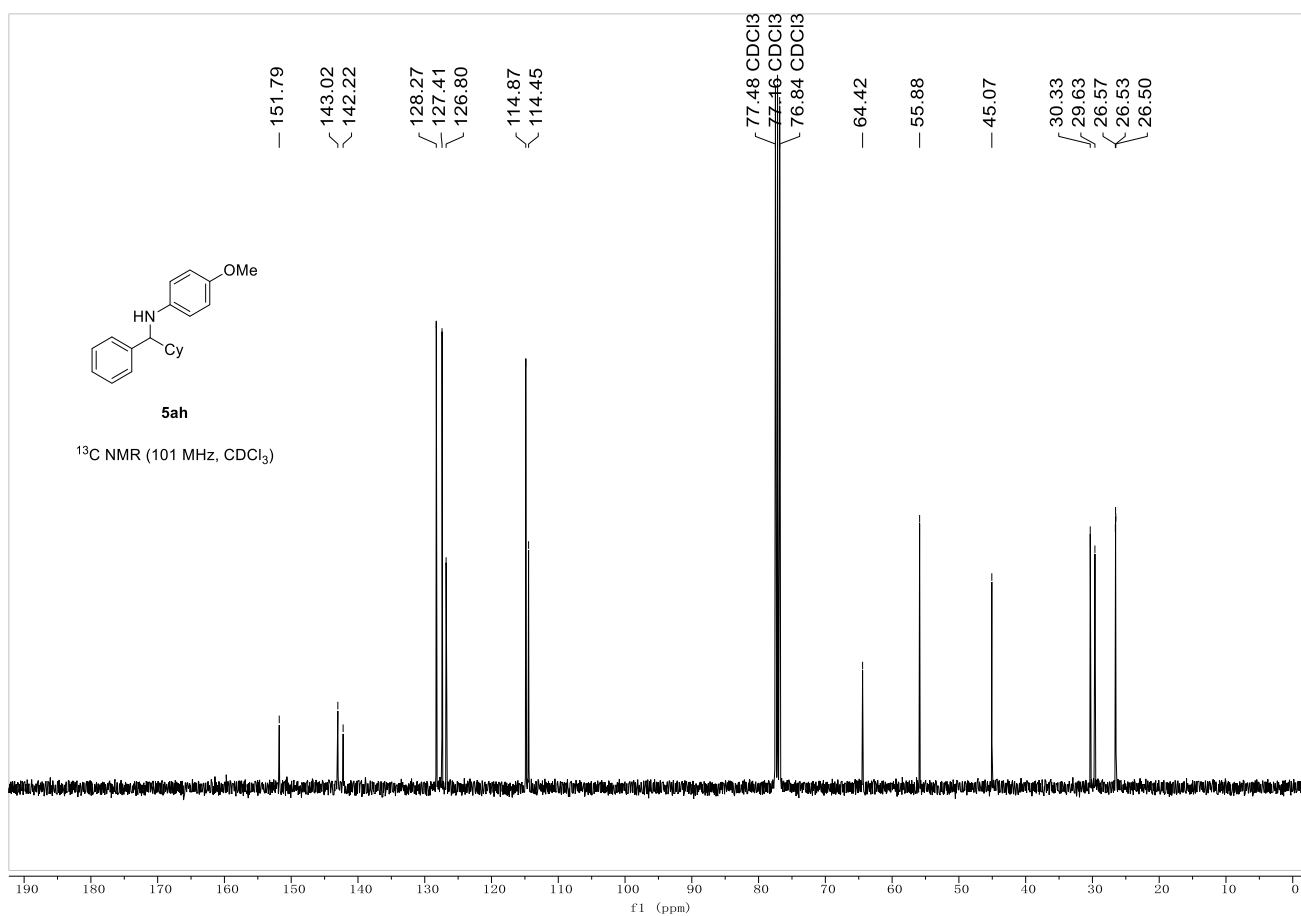
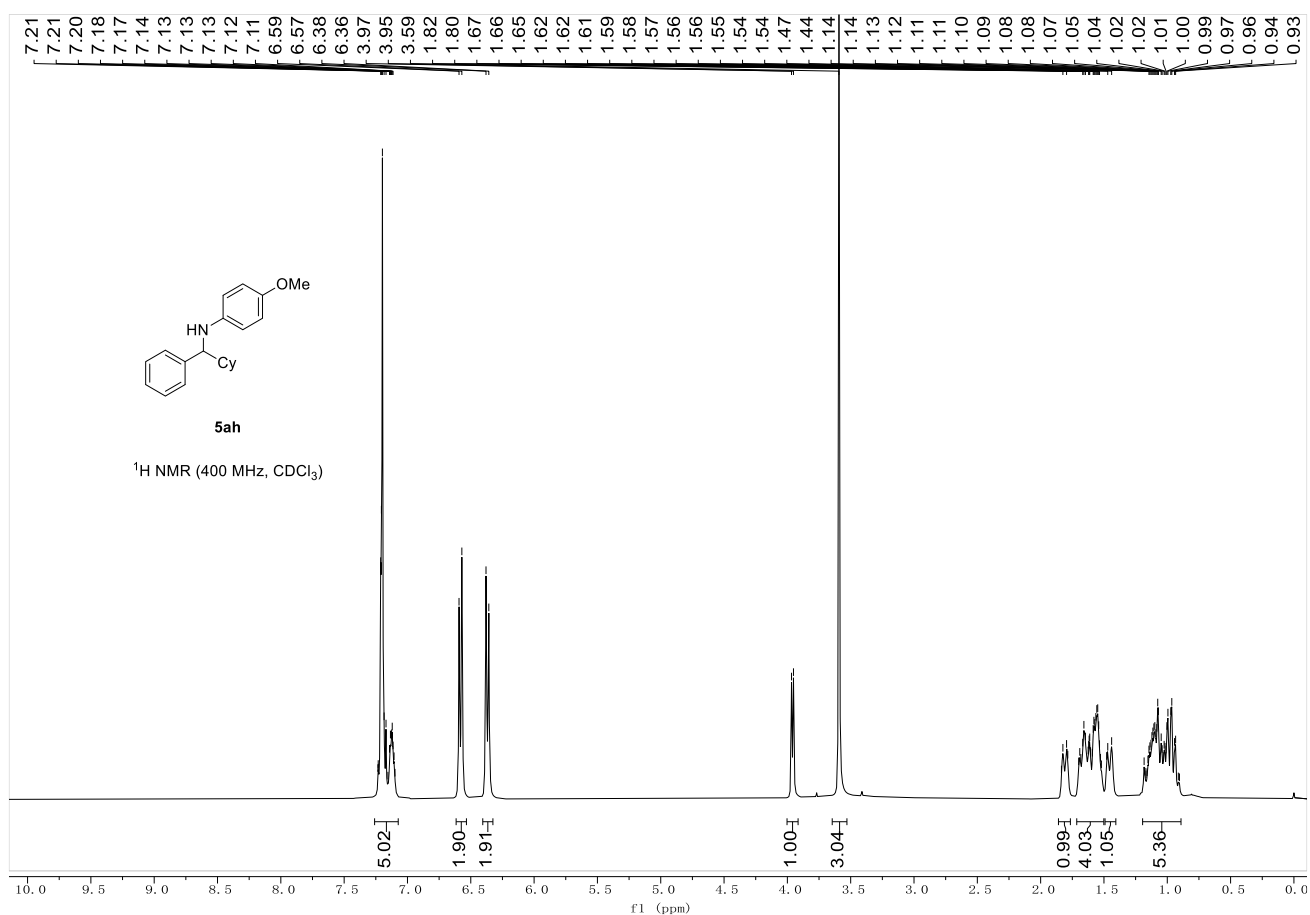






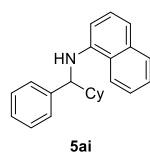
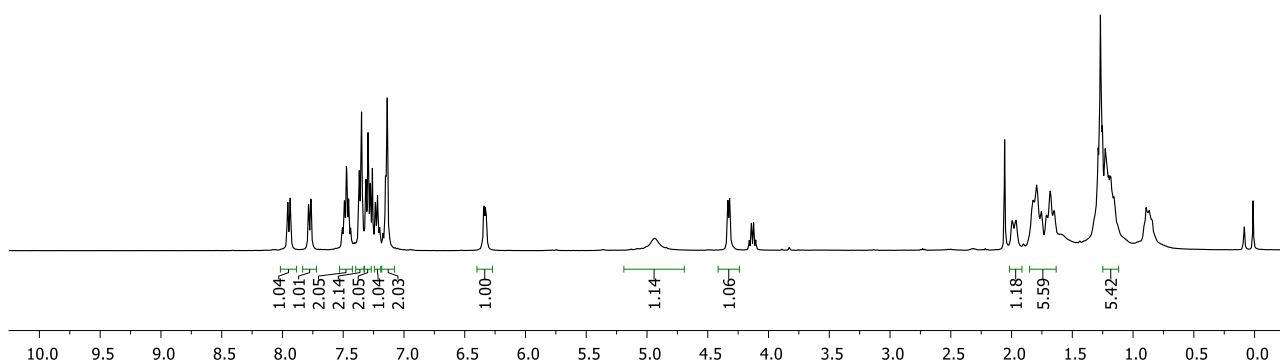








5ai
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

