Supporting Information

Direct Reaction of Nitroarenes and Thiols via Photo-Driven Oxygen Atom-Transfer for Access to Sulfonamides

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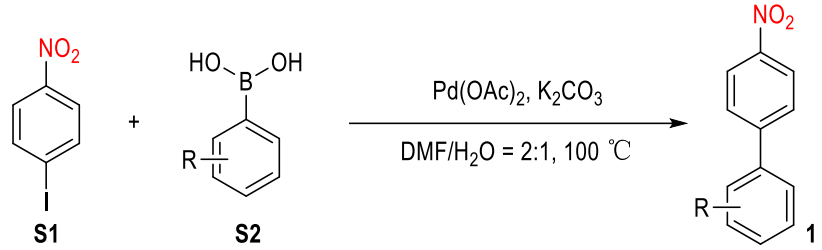
1. General information

Commercially available materials and dry solvents purchased from Energy Chemical, J&K and Leyan were used as received. Unless otherwise specified, all reactions were prepared using 10 mL quartz tube under N_2 atmosphere in glove-box from Mbraun (UNILAB SP). All reactions were performed in a WATTCAS WP-TEC-1020SL photochemical reactor (for more details please see page S5-S7). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (AVANCE III HD 400 MHz) spectrometer. The chemical shift values were corrected to 7.26 ppm (^{1}H NMR) and 77.00 ppm (^{13}C NMR) for $CHCl_3$. The chemical shift values were corrected to 2.50 ppm (^{1}H NMR) and 39.52 ppm (^{13}C NMR) for DMSO. ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (AVANCE III HD 101 MHz) spectrometer. Fluorine (^{19}F) nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker (AVANCE III HD 376 MHz) spectrometer. The melting points (m.p.) of the title compounds were determined when left untouched on an XT-4-MP apparatus from Beijing Tech. Instrument Co. (Beijing, China). High resolution mass spectrometer analysis (HRMS) was performed on Thermo Fisher Q Exactive mass spectrometer. Structure of the products was determined by X-ray crystallography (Bruker d_8 quest). Analytical thin-layer chromatography (TLC) was carried out pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp. Cyclic voltammetry studies were carried out on a Thermo Fisher SP50 electrochemical workstation.

All the thiols (**2**) used in the current work are commercially available and used directly without further purification.

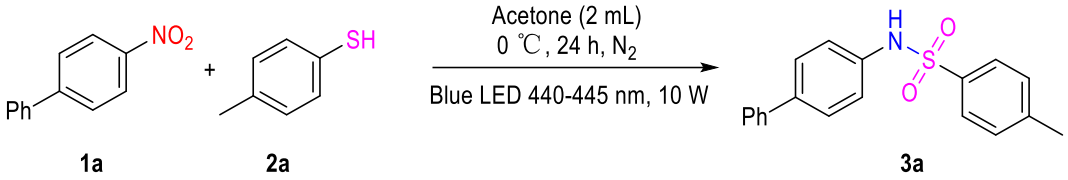
2. General procedure for nitroarenes synthesis[1-2]



Under N_2 atmosphere, to an oven-dried 250.0 mL Schlenk flask equipped with magnetic stirrer, were charged with **S1** (5.0 g, 20.0 mmol), **S2** (2.9 g, 24.0 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol), K_2CO_3 (3.3 g, 24.0 mmol). DMF (66.0 mL) and H_2O (33.0 mL) were then added via syringe. The reaction mixture was allowed to stir for 30 min at 100 ℃. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature, water (33.0 mL) was added. The resulting mixture was extracted with ethyl acetate (20.0 mL × 3). The combined organic layers were then washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by column chromatography on silica gel to provide the desired product **1**.

3. General procedure for sulfonamides synthesis

General procedure A: synthesis of sulfonamides (**3**) from nitroarenes (**1**) and thiols (**2**) under visible light irradiation.



1a **2a** **3a**

To a dry 10.0 mL quartz tube equipped with a magnetic stir bar was added **1a** (59.8 mg, 0.3 mmol) and **2a** (12.4 mg, 0.1 mmol). The reaction tube was sealed and placed under N_2 before acetone (2.0 mL) was added. The resulting mixture was stirred and irradiated (0.5 cm away from the LED) with blue LEDs (λ_{max} = 441 nm) for 24 hours at 0 ℃. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the desired product **3a**.

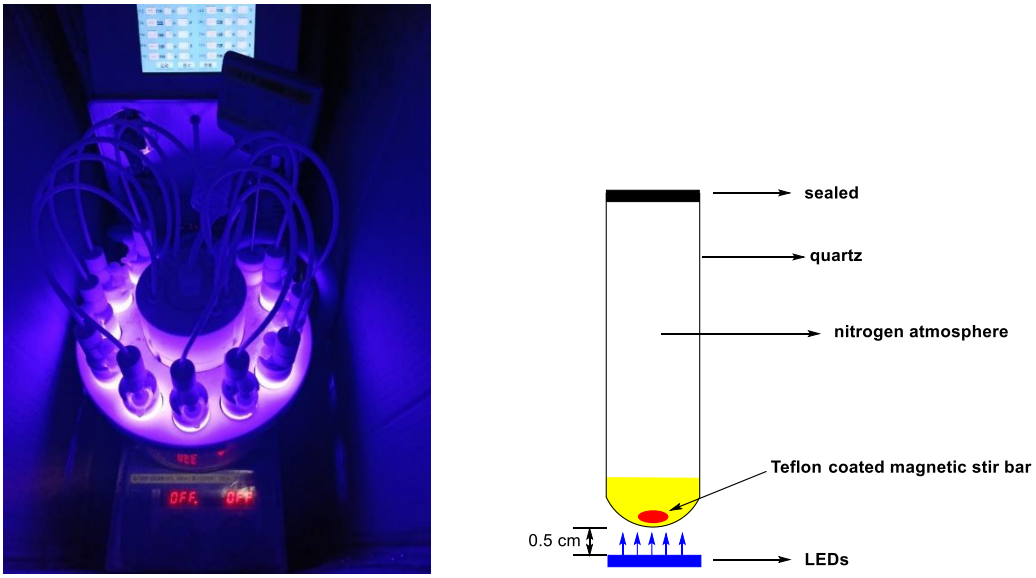


Figure S1 Photochemical reaction device

Photochemical Reaction Device Information

Manufacturer: WATTCAS, Xi'An, China

Photochemical Reaction Device Model: WP-TEC-1020SL

LEDs Test report:

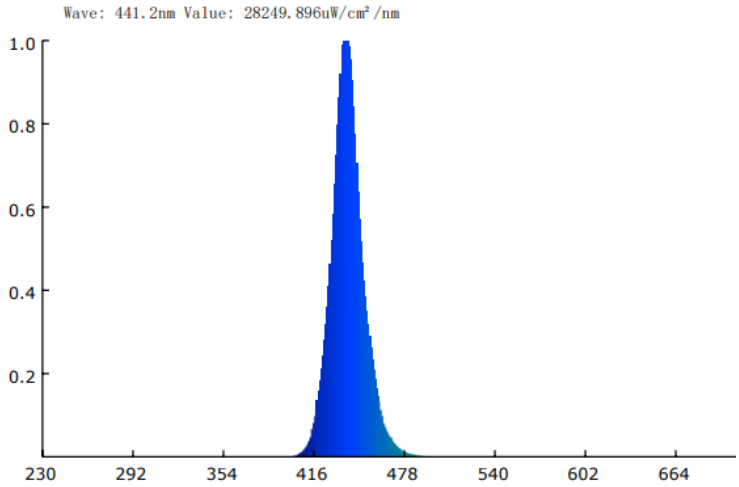
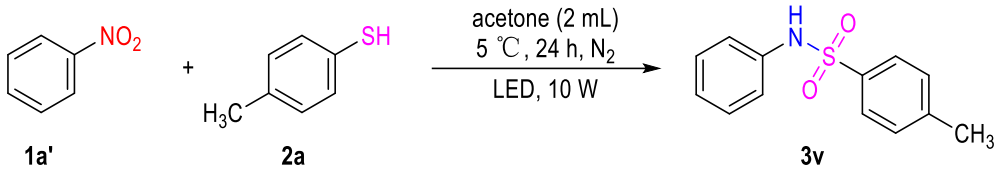


Figure S2. The emission spectrum and emission intensity of LEDs (λ_{max} = 441 nm) used in our general procedure**.** The λ_{max} is measured as 441 nm**,** and the corresponding intensity value is measured as 28249.896 uW/cm^2/nm (0.3 cm away from the LED).

Figure S3. Picture of reaction tube: 10 mL quartz tube, 0.5 cm away from the LED.

General procedure B: synthesis of sulfonamides (**3**) from simple nitrobenzenes (**1**) and thiols (**2**) under UV light irradiation.



1a' **2a** **3v**

To a 10 mL Schlenk tube equipped with a stir bar was added nitrobenzene **1a'** (36.9 mg, 0.3 mmol), and **2a** (12.4 mg, 0.1 mmol). The reaction tube was sealed and placed under N_2 before acetone (2.0 mL) was added. The resulting mixture was stirred and irradiated (0.5 cm away from the LED) with blue LEDs (λ_{max} = 366 nm) for 24 hours at 5 ℃. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 15 / 1) to afford the desired product **3v**.

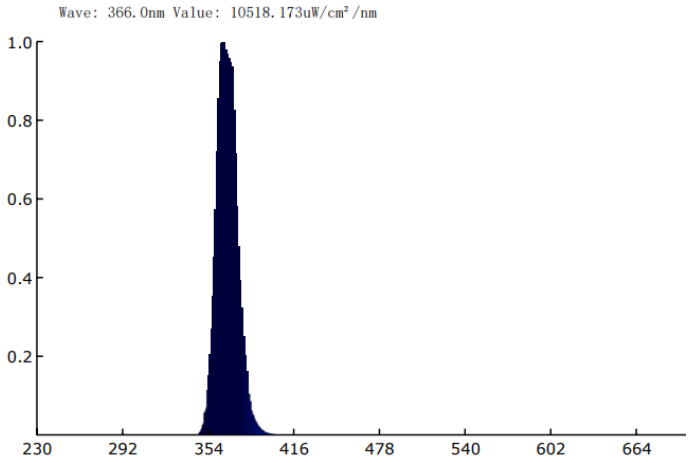
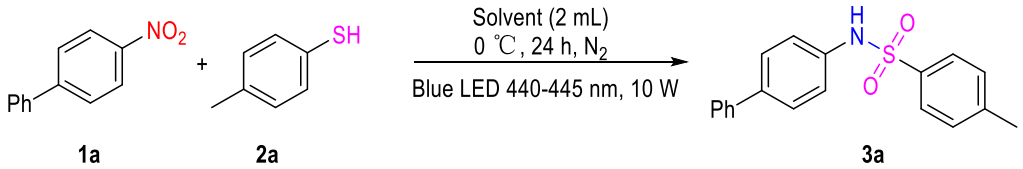


Figure S4. The emission spectrum and emission intensity of LEDs (λ_{max} = 366 nm) used in our general procedure B**.** The λ_{max} is measured as 366 nm, and the corresponding intensity value is measured as 10518.173 uW/cm^2/nm (0.3 cm away from the LED).

Figure S5. Picture of reaction tube: 10 mL Schlenk tube, 0.5 cm away from the LED.

4. Condition optimizations

Table S1 Influence of solvent[a]

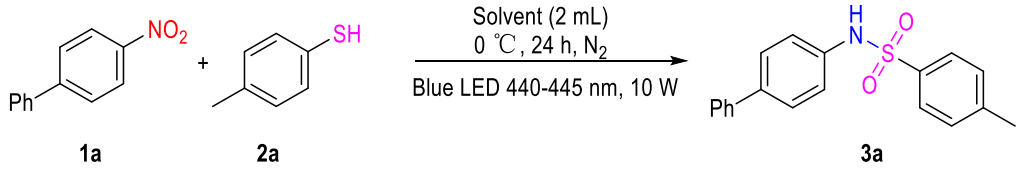


1a **2a** **3a**

Entry	Solvent	Yield (%)[b]
1	Acetone	64
2	EA	47
3	THF	40
4	Acetonitrile	51
5	Toluene	54

[a] Standard condition: **1a** (0.3 mmol), **2a** (0.1 mmol) in solvent (2.0 mL), blue LED, N_2 atmosphere, 0 ℃, 24 h. [b] Isolated yields.

Table S2 Influence of **1a**/**2a**[a]

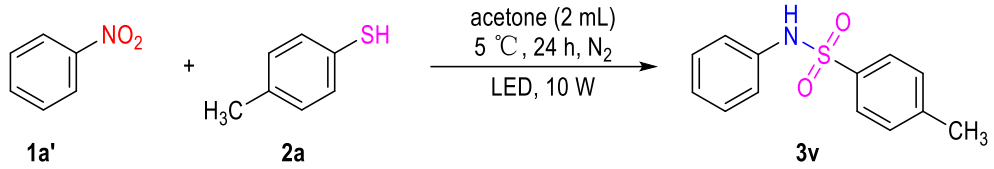


1a **2a** **3a**

Entry	**1a**/**2a**	Yield (%)[b]
1	3:1	62
2	2:1	55
3	1:1	47
4	1:2	39
5	1:3	28

[a] Standard condition: **1a** and **2a** in acetone (2.0 mL), blue LED, N_2 atmosphere, 0 ℃, 24 h.
[b] Isolated yields.

Table S3 Screening of wavelength for simple nitrobenzenes[a]



1a' 2a 3v

Entry	Wavelength	Yield (%)[b]
1	λ_{max}= 460 nm	Trace
2	λ_{max}= 440 nm	22
3	λ_{max}= 395 nm	35
4	λ_{max}= 366 nm	49

[a] Standard condition: **1a** and **2a** in acetone (2.0 mL), LED, N_2 atmosphere, 5 ℃, 24 h.

[b] Isolated yields.

5. Structure determination *via* X-ray crystallographic analysis

Good quality crystal of **3ag** (colourless needle crystal) was obtained by vaporization of a petroleum ether / dichloromethane solution of cycloaddition compound **3ag** (~60mg). A suitable crystal with dimensions 0.1 × 0.16 × 0.2 mm^3 was selected and mounted on a Bruker APEX-II CCD diffractometer. CCDC **2168659** contains the supplementary crystallographic data for this paper. The crystal was kept at a steady T = 298 K during data collection. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/.

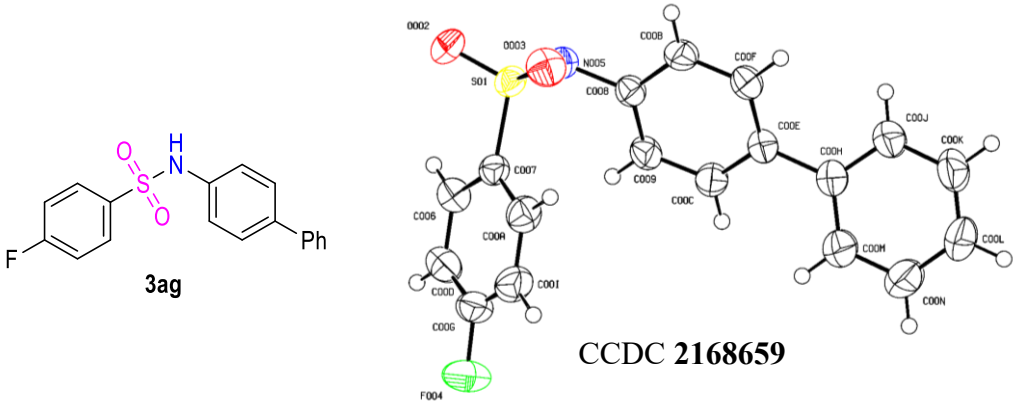


Figure S6. *X*-ray crystallography of compound 3ag. the ellipsoid contour % probability level is 50%.

Crystal Data. $C_{18}H_{14}FNO_2S$, (*M* =327.36 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 6.2663(9) Å, *b* = 8.002(2) Å, *c* = 31.195(7) Å, $\alpha = \beta = \gamma = 90^{\circ}$, *V* = 1564.3(6) $Å^3$, *Z* = 4, Z' = 1, *T* = 298 K, μ(CuKα) = 2.014 mm^{-1}, *Dcalc* = 1.390 g/cm^3, 12414 reflections measured, 3012 unique (R_{int} = 0.0350, R_{sigma} = 0.0374) which were used in all calculations. The final R_1 was 0.0309 (I > 2σ(I)) and wR_2 was 0.0897 (all data).

Table S4 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ag. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S01	6095.9(8)	6192.6(6)	4525.2(2)	39.86(19)
O002	6587(3)	6302(3)	4972.5(5)	57.3(5)
O003	7755(3)	5916(2)	4218.4(6)	54.7(4)
F004	-601(4)	1244(3)	4278.7(7)	87.0(6)
N005	4947(3)	7972(2)	4407.9(5)	39.7(4)
C006	2494(4)	4532(3)	4753.0(7)	44.0(5)
C007	4159(3)	4627(2)	4461.5(6)	38.0(4)
C008	4313(3)	8208(2)	3968.8(6)	37.1(4)
C009	2274(4)	7805(3)	3835.5(7)	44.1(5)
C00A	4246(4)	3550(3)	4112.8(7)	50.4(6)
C00B	5772(4)	8854(3)	3678.3(7)	45.5(5)
C00C	1721(4)	8004(3)	3407.7(7)	46.8(5)
C00D	893(4)	3374(3)	4694.4(8)	51.8(5)
C00E	3174(4)	8589(3)	3106.1(6)	41.5(5)
C00F	5195(4)	9045(3)	3252.1(7)	47.1(5)
C00G	1009(5)	2348(3)	4344.8(9)	55.6(6)
C00H	2583(4)	8697(3)	2642.8(7)	45.9(5)
C00I	2636(5)	2396(3)	4054.2(8)	59.9(7)
C00J	3648(5)	9744(3)	2362.4(8)	57.7(6)
C00K	3080(6)	9809(4)	1931.3(8)	66.9(8)
C00L	1465(6)	8867(5)	1778.2(8)	69.1(8)
C00M	982(6)	7702(5)	2478.2(9)	73.5(9)
C00N	410(7)	7798(6)	2048.9(10)	89.1(12

Table S5 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3ag. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S01	33.3(3)	48.5(3)	37.8(3)	0.52(19)	-3.69(18)	-2.2(2)
O002	56.0(10)	71.6(11)	44.4(8)	4.1(8)	-17.4(7)	-9.9(9)
O003	37.5(8)	63.6(11)	63.1(10)	1.7(8)	6.8(7)	4.0(8)
F004	84.9(13)	71.5(11)	104.7(14)	2.3(10)	-22.9(11)	-36.8(11)
N005	39.1(9)	43.4(9)	36.7(8)	-3.0(7)	3.5(7)	-1.9(7)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C006	44.5(12)	41.7(10)	45.8(11)	0.8(8)	3.6(9)	1.8(9)
C007	39.6(10)	35.5(9)	38.9(9)	1.0(7)	-5.4(8)	1.4(8)
C008	37.0(10)	37.7(9)	36.7(9)	0.5(7)	3.1(8)	-0.3(8)
C009	36.9(11)	52.6(11)	42.8(11)	6.9(9)	6.3(9)	-5.1(9)
C00A	58.3(14)	51.0(12)	42.0(10)	-5.7(9)	3.5(10)	1.4(11)
C00B	36.9(11)	54.2(12)	45.5(10)	0.1(9)	2.5(9)	-9.9(10)
C00C	35.6(11)	59.9(13)	44.8(11)	7.5(9)	-1.5(9)	-5.6(9)
C00D	46.8(13)	45.9(11)	62.8(13)	10.4(10)	1.9(11)	-2.5(10)
C00E	43.1(11)	42.4(10)	39.0(9)	4.4(8)	2.3(8)	0.4(9)
C00F	42.0(11)	58.3(13)	41.0(10)	5.5(9)	8.4(9)	-10.0(10)
C00G	57.9(14)	41.9(11)	67.0(14)	6.7(10)	-15.0(13)	-10.5(11)
C00H	48.8(12)	48.3(11)	40.6(10)	3.5(9)	2.9(9)	1.5(11)
C00I	80.7(19)	45.9(12)	53.1(13)	-9.0(10)	-12.4(13)	-3.2(13)
C00J	69.8(17)	58.4(14)	45.0(11)	4.9(10)	4.3(12)	-13.3(13)
C00K	93(2)	65.6(16)	42.0(12)	9.8(11)	8.3(13)	-10.4(16)
C00L	83(2)	87(2)	37.9(11)	5.8(12)	-3.9(12)	-5.7(18)
C00M	76(2)	96(2)	48.0(13)	12.9(13)	-3.2(14)	-32.8(19)
C00N	93(3)	125(3)	49.6(14)	4.9(17)	-11.7(16)	-46(2)

Table S6 Bond Lengths for 3ag.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S01	O002	1.4318(16)	C00B	C00F	1.386(3)
S01	O003	1.4303(18)	C00C	C00E	1.391(3)
S01	N005	1.6369(19)	C00D	C00G	1.367(4)
S01	C007	1.756(2)	C00E	C00F	1.394(3)
F004	C00G	1.357(3)	C00E	C00H	1.494(3)
N005	C008	1.439(3)	C00G	C00I	1.365(4)
C006	C007	1.386(3)	C00H	C00J	1.383(3)
C006	C00D	1.378(3)	C00H	C00M	1.380(4)
C007	C00A	1.389(3)	C00J	C00K	1.392(4)
C008	C009	1.382(3)	C00K	C00L	1.349(5)
C008	C00B	1.387(3)	C00L	C00N	1.372(5)
C009	C00C	1.388(3)	C00M	C00N	1.389(4)
C00A	C00I	1.380(4)			

Table S7 Bond Angles for 3ag.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O002	S01	N005	105.01(11)	C00G	C00D	C006	118.1(2)
O002	S01	C007	107.62(10)	C00C	C00E	C00F	117.5(2)
O003	S01	O002	120.35(12)	C00C	C00E	C00H	120.8(2)
O003	S01	N005	107.74(10)	C00F	C00E	C00H	121.7(2)
O003	S01	C007	108.45(11)	C00B	C00F	C00E	121.4(2)
N005	S01	C007	106.95(10)	F004	C00G	C00D	118.2(3)
C008	N005	S01	116.63(14)	F004	C00G	C00I	118.2(2)
C00D	C006	C007	119.9(2)	C00I	C00G	C00D	123.6(2)
C006	C007	S01	119.03(15)	C00J	C00H	C00E	121.8(2)
C006	C007	C00A	120.6(2)	C00M	C00H	C00E	120.4(2)
C00A	C007	S01	120.27(18)	C00M	C00H	C00J	117.7(2)
C009	C008	N005	120.77(18)	C00G	C00I	C00A	118.5(2)
C009	C008	C00B	119.98(19)	C00H	C00J	C00K	120.7(3)
C00B	C008	N005	119.25(19)	C00L	C00K	C00J	120.8(3)
C008	C009	C00C	119.6(2)	C00K	C00L	C00N	119.5(3)
C00I	C00A	C007	119.4(2)	C00H	C00M	C00N	121.0(3)
C00F	C00B	C008	119.7(2)	C00L	C00N	C00M	120.2(3)
C009	C00C	C00E	121.7(2)				

Table S8 Torsion Angles for 3ag.

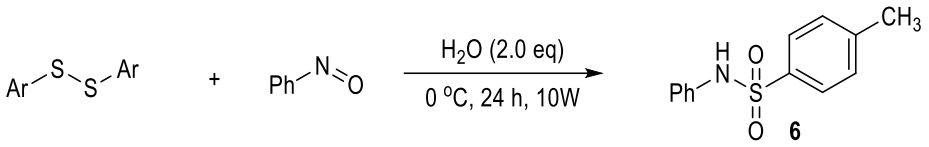
A	B	C	D	Angle/°	A	B	C	D	Angle/°
S01	N005	C008	C009	93.1(2)	C009	C008	C00B	C00F	-1.9(3)
S01	N005	C008	C00B	-87.1(2)	C009	C00C	C00E	C00F	-2.8(4)
S01	C007	C00A	C00I	-176.0(2)	C009	C00C	C00E	C00H	176.3(2)
O002	S01	N005	C008	178.96(16)	C00B	C008	C009	C00C	1.9(3)
O002	S01	C007	C006	41.8(2)	C00C	C00E	C00F	C00B	2.8(4)
O002	S01	C007	C00A	-141.09(19)	C00C	C00E	C00H	C00J	158.3(3)
O003	S01	N005	C008	49.54(18)	C00C	C00E	C00H	C00M	-23.8(4)
O003	S01	C007	C006	173.49(17)	C00D	C006	C007	S01	176.28(17)
O003	S01	C007	C00A	-9.4(2)	C00D	C006	C007	C00A	-0.8(3)
F004	C00G	C00I	C00A	178.1(2)	C00D	C00G	C00I	C00A	-0.6(4)
N005	S01	C007	C006	-70.57(18)	C00E	C00H	C00J	C00K	179.3(3)
N005	S01	C007	C00A	106.53(19)	C00E	C00H	C00M	C00N	179.6(3)
N005	C008	C009	C00C	-178.3(2)	C00F	C00E	C00H	C00J	-22.6(3)
N005	C008	C00B	C00F	178.3(2)	C00F	C00E	C00H	C00M	155.3(3)

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
C006	C007	C00A	C00I	1.0(4)	C00H	C00E	C00F	C00B	-176.3(2)
C006	C00D	C00G	F004	-177.8(2)	C00H	C00J	C00K	C00L	0.7(5)
C006	C00D	C00G	C00I	0.8(4)	C00H	C00M	C00N	C00L	1.4(7)
C007	S01	N005	C008	-66.87(17)	C00J	C00H	C00M	C00N	-2.4(5)
C007	C006	C00D	C00G	-0.1(3)	C00J	C00K	C00L	C00N	-1.8(6)
C007	C00A	C00I	C00G	-0.4(4)	C00K	C00L	C00N	C00M	0.8(7)
C008	C009	C00C	C00E	0.5(4)	C00M	C00H	C00J	C00K	1.4(4)
C008	C00B	C00F	C00E	-0.5(4)				

Table S9 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3ag.

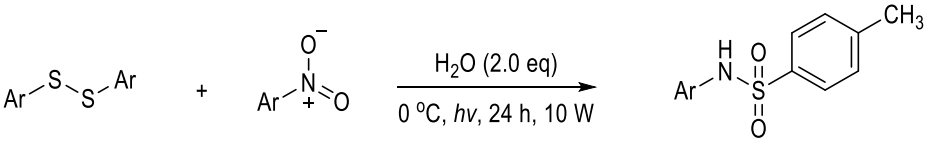
Atom	*x*	*y*	*z*	U(eq)
H005	3922.23	8197.25	4581.93	48
H006	2457.22	5248.85	4987.6	53
H009	1278.94	7403.69	4031.16	53
H00A	5378.26	3607.03	3920.66	61
H00B	7132.16	9156.64	3769.03	55
H00C	342.81	7738.29	3320.54	56
H00D	-234.82	3292.74	4887.19	62
H00F	6176.63	9486.39	3059.4	57
H00I	2659.58	1667.12	3821.94	72
H00J	4755.28	10411.38	2462.94	69
H00K	3823.56	10511.25	1746.42	80
H00L	1070.82	8941.45	1491.39	83
H00M	276.39	6955.57	2657.41	88
H00N	-693.73	7136.18	1944.46	107

6. Mechanistic studies

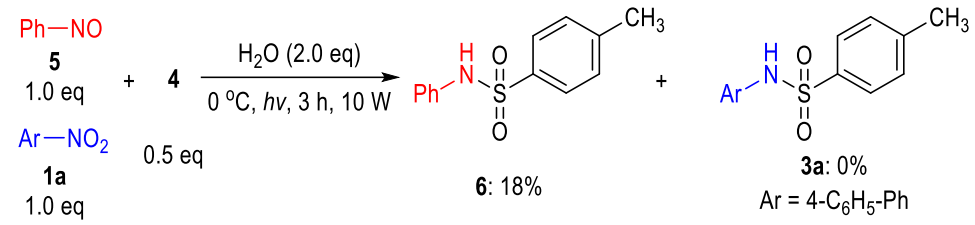


In gloves box, to a dried 10 mL quartz tube equipped with a stir bar was added **4** (12.3 mg, 0.05 mmol), **5** (16.1 mg, 0.15 mmol) and acetone (2.0 mL). The quartz tube was sealed and took out from the gloves box and H_2O (1.8 mg, 0.1 mmol) was added by microliter syringe. The resulting mixture was stirred at 0 ℃ for 24 hours in photochemical reaction device. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the desired product **6** (8.4 mg, 34% yield).

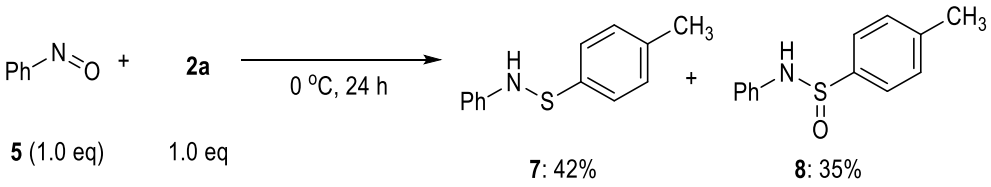
The ^{1}H NMR date of (**6**) matches the reported one.[3] **6** **<u>^{1}H NMR</u>** (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 2H), 7.26 – 7.21 (m, 4H), 7.14 – 7.08 (m, 1H), 7.08 – 7.04 (m, 2H), 6.63 (s, 1H), 2.37 (s, 3H).



In gloves box, to a dried 10 mL quartz tube equipped with a stir bar was added **4** (12.3 mg, 0.05 mmol), **5** (29.9 mg, 0.15 mmol) and acetone (2.0 mL). The quartz tube was sealed and took out from the gloves box and H_2O (1.8 mg, 0.1 mmol) was added by microliter syringe. The resulting mixture was stirred at 0 ℃ for 24 hours in photochemical reaction device. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the desired product **3a** (14.5 mg, 45% yield).



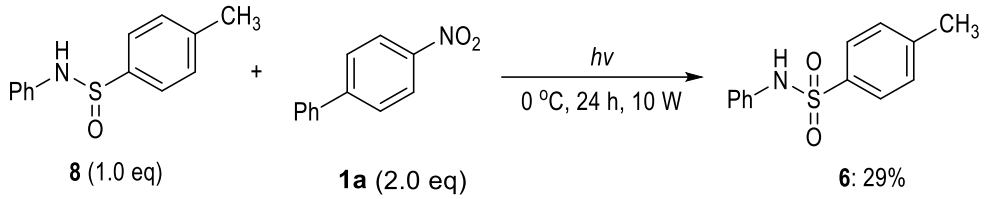
In gloves box, to a dried 10 mL quartz tube equipped with a stir bar was added **4** (12.3 mg, 0.05 mmol), **5** (29.9 mg, 0.1 mmol) or **1a** (19.9 mg, 0.1 mmol) and acetone (2.0 mL). The quartz tube was sealed and took out from the gloves box and H_2O (1.8 mg, 0.1 mmol) was added by microliter syringe. The resulting mixture was stirred at 0 °C for 3 hours in photochemical reaction device. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the desired product **6** (4.5 mg, 18% yield).



In gloves box, to a dried 10 mL quartz tube equipped with a stir bar was added **5** (10.7 mg, 0.1 mmol), **2a** (12.4 mg, 0.1 mmol) and acetone (2.0 mL). The quartz tube was sealed and took out from the gloves box. The resulting mixture was stirred at 0 °C for 24 hours. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford sulfenamide **7** (9.0 mg, 42% yield) and sulfinamide **8** (8.1 mg, 35% yield).

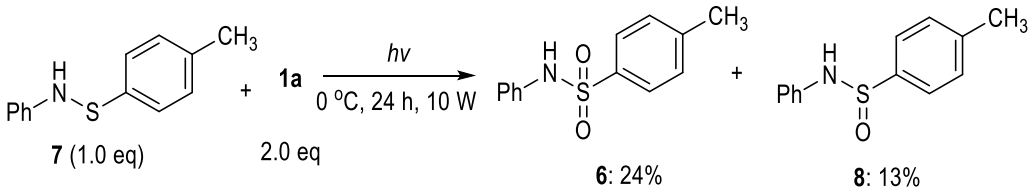
The ^{1}H NMR date of Sulfenamide (**7**) matches the reported one.[4] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (dd, J = 8.6, 7.2 Hz, 2H), 7.11 (d, J = 6.9 Hz, 4H), 7.03 (dd, J = 8.7, 1.1 Hz, 2H), 6.86 (tt, J = 7.3, 1.1 Hz, 1H), 5.17 (s, 1H), 2.29 (s, 3H).

The ^{1}H NMR date of Sulfinamide (**8**) matches the reported one.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.10 – 7.06 (m, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.59 (s, 1H), 2.41 (s, 3H).



8 (1.0 eq) **1a** (2.0 eq) **6**: 29%

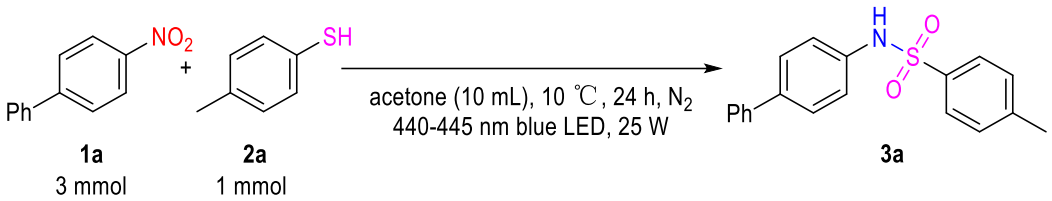
In gloves box, to a dried 10 mL quartz tube equipped with a stir bar was added **5** (10.7 mg, 0.1 mmol), 2**a** (12.4 mg, 0.1 mmol) and acetone (2.0 mL). The quartz tube was sealed and took out from the gloves box. The resulting mixture was stirred at 0 ℃ for 24 hours in photochemical reaction device. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the desired product **6** (7.2 mg, 29% yield).



7 (1.0 eq) 2.0 eq **6**: 24% **8**: 13%

In gloves box, to a dried 10 mL quartz tube equipped with a stir bar was added **5** (10.7 mg, 0.1 mmol), 2**a** (12.4 mg, 0.1 mmol) and acetone (2.0 mL). The quartz tube was sealed and took out from the gloves box. The resulting mixture was stirred at 0 ℃ for 24 hours in photochemical reaction device. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the desired product **6** (6.0 mg, 24% yield) and **8** (3.1 mg, 13% yield).

7. Large scale reaction for 3a synthesis



1a 3 mmol **2a** 1 mmol **3a**

To a dry 10.0 mL quartz tube equipped with a magnetic stir bar was added **1a** (598.0 mg, 3 mmol) and **2a** (124.0 mg, 1 mmol). The reaction tube was sealed and placed under N_2 before acetone (10.0 mL) was added. The resulting mixture was stirred and irradiated (0.5 cm away from the LED) with blue LEDs (λ_{max} = 441 nm)

for 24 hours at 10 ℃. Then the mixture was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 10 / 1) to afford the desired product **3a**.

Limited to the size of the photo reactor and the location of the LEDs (below the reaction tubes), large scale reaction encountered low yield due to the lower utilization rate of the light. For example, when the model reaction was conducted in 1.0 mmol scale, the desired sulfonamide **3a** was obtained in 35% yield (112.0 mg). Fortunately, the reaction mixture of our method is clear solution, which is a big advantage for large scale reaction via flow chemistry. We are searching for further exploration and cooperation.

8. Estimation of the excited potential of 1a

8.1 UV-Vis absorption experiments

The UV-Vis absorption spectra were measured on a SHIMADZU UV-3600 UV/Vis spectrometer.

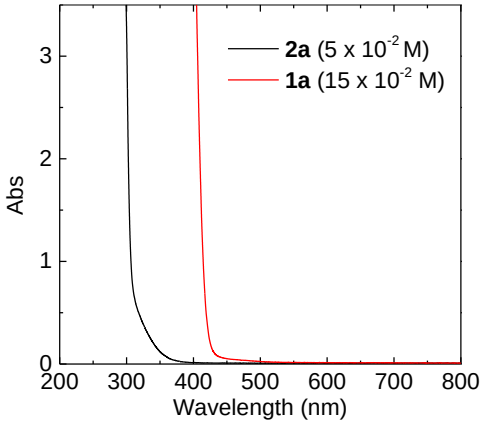


Figure S7: UV-Vis absorption spectra of 1a and 2a under reaction concentration

The absorption spectrum of nitroarene (**1a**) revealed a significant absorption of visible light, and the tail wavelength reached over 450 nm (Figure S7, red line). In contrast, **2a** (Figure S7, black line) has no absorptions at the visible light region (> 400 nm).

8.2 Cyclic Voltammetry Studies

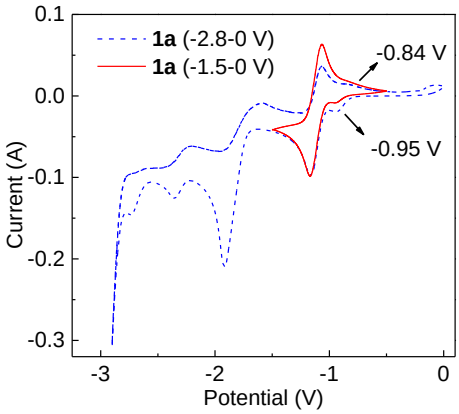


Figure S8: Cyclic voltammogram of 1a

The cyclic voltammogram of **1a** (0.01 M) was measured in [0.1 M] $TBAPF_6$ in CH_3CN under room temperature. Sweep rate: 100 mV/s. Pt electrode working electrode, calomel electrode reference electrode, Pt wire auxiliary electrode. Scan direction: from 0 V to -2.8 V, then back to 0 V. Plotting convention: IUPAC. The cyclic voltammograms of **1a** in MeCN features multi steps of sequential single electron reduction processes (Figure S8), and the first reductive potential of **1a** was measured as -0.95 V (vs SCE).

8.3 Evaluation of the Excited State Potential of 1a

Based on the data collected from the UV-vis absorption spectra (Figure S7) and cyclic voltammetry studies (Figure S8), the excited state potential of **1a** was estimated from the following equation[6].

$$E\ (\mathbf{1a}^*/\dot{\mathbf{1}}\bar{\mathbf{a}}) = E\ (\mathbf{1a}/\dot{\mathbf{1}}\bar{\mathbf{a}}) + E_{0\text{-}0}(\mathbf{1a}^*/\mathbf{1a})$$

The excited state energy of acyl azolium intermediate **1a** ($E_{0\text{-}0}$) was estimated spectroscopically from the position of the tail wavelength of absorption spectrum of **1a** (Figure S7). The tail wavelength of absorption spectrum of **1a** was estimated at 450 nm, which translates into an $E_{0\text{-}0}$ as 2.75 eV.

$$E\ (\mathbf{1a}^*/\dot{\mathbf{1}}\bar{\mathbf{a}}) = -0.95\ V + 2.75\ V = +1.80\ V\ (\textit{vs}\ SCE)$$

The estimated redox potential of excited state of **1a** is higher than thiol (**2a**, E_{ox} = +1.47 V *vs* SCE, Figure S8), indicating that thermodynamically SET oxidation of **2a** by **1a** (at its excited state) is feasible.

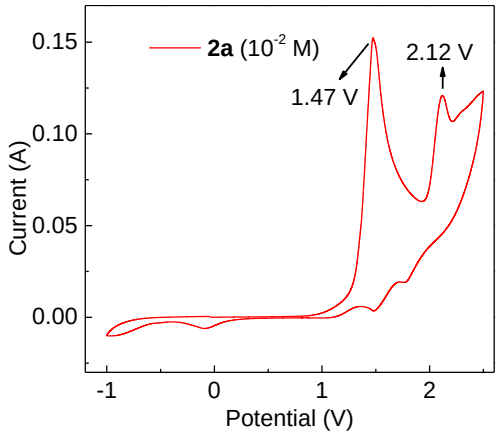


Figure S9: Cyclic voltammogram of 2a

The cyclic voltammogram of **2a** (0.01 M) was measured in [0.1 M] $TBAPF_6$ in CH_3CN under room temperature. Sweep rate: 100 mV/s. Pt electrode working electrode, calomel electrode reference electrode, Pt wire auxiliary electrode. Scan direction: from -1.0 V to +2.5 V, then back to -1.0 V. Plotting convention: IUPAC.

9. HRMS of nitrosoarene (II)

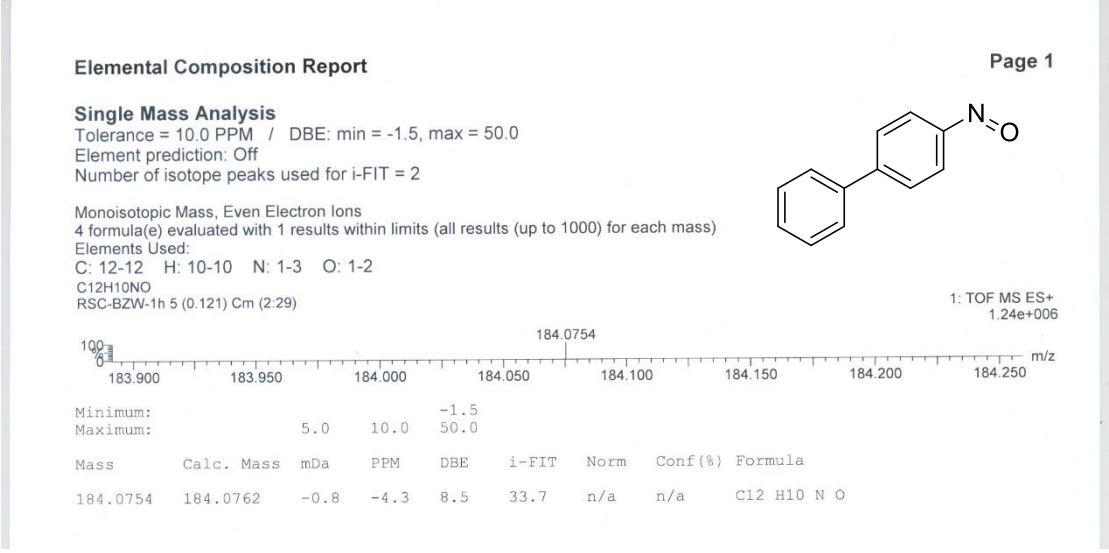


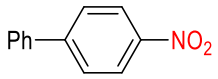
Figure S10: HRMS of nitrosoarene (II)

10. Characterization of substrates and products

All the thiols (**2**) used in this work were purchased from Energy Chemical, J&K or Leyan, and were used directly without further purification.

10.1. Characterization of substrates

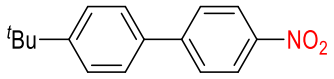
4-nitro-1,1'-biphenyl (1a)[2]



1a

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 70% yield, 2.8 g, m.p. 113-115 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.55 – 7.39 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 147.1, 138.8, 129.2, 129.0, 127.8, 127.4, 124.1.

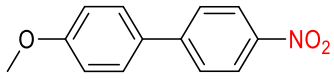
4-(*tert*-butyl)-4'-nitro-1,1'-biphenyl (1b)[7]



1b

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 92% yield, 4.7 g, m.p. 111-113 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.63 – 7.47 (m, 4H), 1.38 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.3, 147.5, 146.9, 135.8, 127.5, 127.1, 126.1, 124.1, 34.7, 31.2.

1-methoxy-4-nitrobenzene (1c)[8]

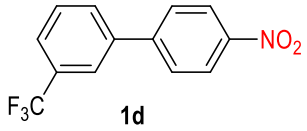


1c

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 30/1). White solid, 44% yield, 2.0 g, m.p. 104-105 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.9 Hz, 2H), 7.68 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H),

7.02 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 147.2, 146.5, 131.0, 128.5, 127.0, 124.1, 114.6, 55.4.

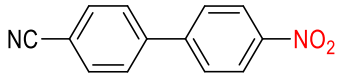
4'-nitro-3-(trifluoromethyl)-1,1'-biphenyl (1d)[9]



1d

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 52% yield, 2.8 g, m.p. 84-85 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.8 Hz, 2H), 7.86 (s, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.76 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 146.0, 139.7, 131.7 (q, J = 32.4 Hz), 130.7, 129.7, 128.0, 125.6 (q, J = 3.7 Hz), 124.3, 124.2 (q, J = 3.7 Hz), 123.9 (q, J = 272.7 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.7.

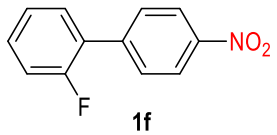
4'-nitro-[1,1'-biphenyl]-4-carbonitrile (1e)[8]



1e

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 50/1). White solid, 71% yield, 3.2 g, m.p. 201-202 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.74 (t, J = 8.9 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 145.4, 143.1, 132.9, 128.14, 128.08, 124.3, 118.3, 112.6.

2-fluoro-4'-nitro-1,1'-biphenyl (1f)[7]

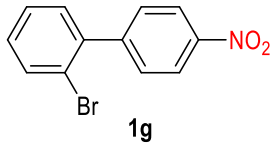


1f

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 63% yield, 2.7 g, m.p. 82-83 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.9 Hz, 2H), 7.72 (dd, J = 8.9, 1.6 Hz, 2H), 7.47 (td, J = 7.8, 1.8 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.27 (td, J = 7.5, 1.2 Hz, 1H), 7.21 (ddd, J = 10.8, 8.2, 1.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.6 (d, J = 249.3 Hz), 147.2, 142.4, 130.6

(d, J = 8.3 Hz), 130.5 (d, J = 2.9 Hz), 129.8 (d, J = 3.5 Hz), 126.8 (d, J = 12.5 Hz), 124.8 (d, J = 3.7 Hz), 123.7, 116.5 (d, J = 22.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.2.

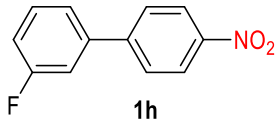
2-bromo-4'-nitro-1,1'-biphenyl (1g)[10]



1g

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 20% yield, 1.1 g, m.p. 79-81 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.42 (td, J = 7.5, 1.2 Hz, 1H), 7.35 – 7.26 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 147.2, 140.3, 133.4, 130.9, 130.5, 129.9, 127.7, 123.3, 122.0.

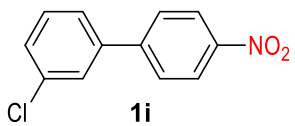
3-fluoro-4'-nitro-1,1'-biphenyl (1h)[7]



1h

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 74% yield, 3.2 g, m.p. 85-86 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.44 – 7.35 (m, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.24 (dt, J = 9.8, 2.1 Hz, 1H), 7.06 (td, J = 8.4, 1.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, J = 247.1 Hz), 147.5, 146.2 (d, J = 2.2 Hz), 141.0 (d, J = 7.4 Hz), 130.8 (d, J = 8.1 Hz), 127.9, 124.2, 123.1 (d, J = 3.0 Hz), 115.8 (d, J = 21.1 Hz), 114.4 (d, J = 22.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.0.

3-chloro-4'-nitro-1,1'-biphenyl (1i)[11]

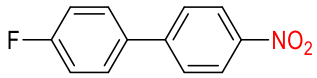


1i

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 83% yield, 3.9 g, m.p. 89-90 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.9 Hz, 2H), 7.60 (s, 1H), 7.50 (dt, J = 6.3, 2.5

Hz, 1H), 7.45 – 7.40 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4, 146.1, 140.6, 135.1, 130.4, 128.9, 127.9, 127.5, 125.5, 124.2.

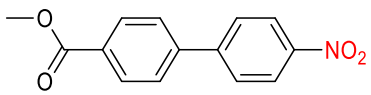
4-fluoro-4'-nitro-1,1'-biphenyl (1j)[7]



1j

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 83% yield, 3.6 g, m.p. 124-126 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.9 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.65 – 7.54 (m, 2H), 7.19 (t, J = 8.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.4 (d, J = 249.3 Hz), 147.1, 146.6, 134.9 (d, J =3.0), 129.2 (d, J =8.1), 127.7, 124.2, 116.2 (d, J =21.8). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.7.

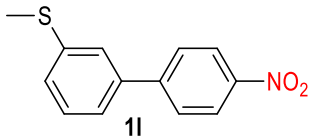
methyl 4'-nitro-[1,1'-biphenyl]-4-carboxylate (1k)[12]



1k

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 30/1). White solid, 31% yield, 1.6 g, m.p. 189-190 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.9 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.9 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 3.96 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 147.5, 146.3, 143.0, 130.4, 130.3, 128.1, 127.4, 124.2, 52.3.

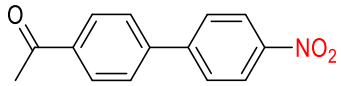
methyl(4'-nitro-[1,1'-biphenyl]-3-yl)sulfane (1l)[13]



1l

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 30/1). Yellow solid, 82% yield, 4.0 g, m.p. 89-90 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.48 (t, J = 1.8 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.37 (dt, J = 7.7, 1.5 Hz, 1H), 7.32 (dt, J = 7.5, 1.6 Hz, 1H), 2.55 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3, 147.2, 139.9, 139.5, 129.6, 127.9, 126.7, 125.4, 124.1, 15.8.

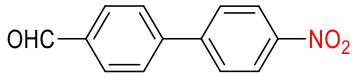
1-(4'-nitro-[1,1'-biphenyl]-4-yl)ethan-1-one (1m)[10]



1m

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 50/1). White solid, 95% yield, 4.6 g, m.p. 150-151 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 2.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.5, 147.6, 146.2, 143.1, 137.1, 129.1, 128.1, 127.6, 124.2, 26.7.

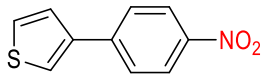
4'-nitro-[1,1'-biphenyl]-4-carbaldehyde (1n)[14]



1n

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 50/1). White solid, 96% yield, 2.6 g, m.p. 126-128 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.35 (d, J = 8.8 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.6 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.6, 147.8, 146.1, 144.5, 136.3, 130.5, 128.3, 128.1, 124.3.

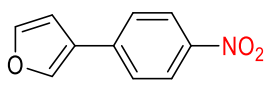
3-(4-nitrophenyl)thiophene (1o)[15]



1o

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 50/1). White solid, 22% yield, 0.9 g, m.p. 144-146 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.9 Hz, 2H), 7.63 (dd, J = 2.9, 1.5 Hz, 1H), 7.48 – 7.43 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.6, 141.9, 139.9, 127.3, 126.8, 126.0, 124.3, 123.2.

3-(4-nitrophenyl)furan (1p)[16]

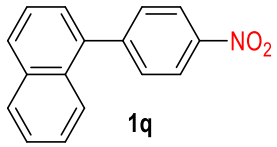


1p

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 50/1). White solid, 58% yield, 2.2 g, m.p. 119-120 ℃. **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 8.24 (d, J = 8.9 Hz, 2H), 7.88 – 7.85 (m, 1H), 7.62 (d, J = 8.9 Hz, 2H), 7.54 (t, J = 1.7 Hz, 1H), 6.76 (dd, J = 1.9, 0.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.6, 144.6, 140.3, 139.2, 126.2, 124.9, 124.4, 108.6.

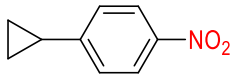
1-(4-nitrophenyl)naphthalene (1q)[15]



1q

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). White solid, 90% yield, 4.5 g, m.p. 128-130 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.8 Hz, 2H), 7.94 (dd, J = 8.2, 2.9 Hz, 2H), 7.79 (d, J = 8.5 Hz, 1H), 7.68 (d, J = 8.7 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.53 – 7.47 (m, 1H), 7.47 – 7.41 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 147.2, 137.8, 133.8, 130.9, 129.0, 128.6, 127.1, 126.7, 126.2, 125.3, 125.1, 123.6.

4'-nitro-[1,1'-biphenyl]-4-carbaldehyde (1r)[17]

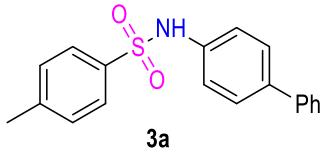


1r

Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). Light yellow solid, 82% yield, 2.7 g, m.p. 30-31 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) 8.07 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 1.97 (ddd, J = 13.3, 8.4, 5.0 Hz, 1H), 1.16 – 1.09 (m, 2H), 0.80 (dt, J = 6.8, 4.9 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) 152.7, 145.6, 125.8, 123.5, 15.7, 11.0.

10.2. Characterization of products

***N*-([1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3a)**[18]

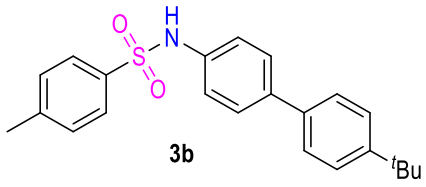


3a

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 64% yield, 20.7 mg, m.p. 154-155 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz,

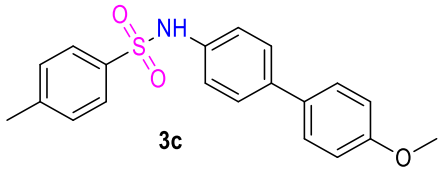
2H), 7.55 – 7.50 (m, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.36 – 7.29 (m, 1H), 7.24 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 6.88 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 140.0, 138.2, 136.1, 135.7, 129.7, 128.8, 127.9, 127.33, 127.29, 126.8, 121.8, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{16}NO_2S^-$ [M - H]$^-$ 322.0907, found: 322.0910.

***N*-(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3b)**



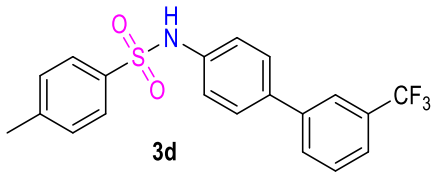
According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 54% yield, 20.5 mg, m.p. 185-187 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.47 (s, 2H), 7.46 – 7.43 (m, 4H), 7.23 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 6.80 (s, 1H), 2.38 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.4, 143.9, 138.1, 137.1, 136.1, 135.4, 129.7, 127.7, 127.3, 126.4, 125.8, 122.0, 34.5, 31.3, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{23}H_{24}NO_2S^-$ [M - H]$^-$ 378.1533; found 378.1540.

***N*-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3c)**[19]



According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). White solid, 44% yield, 15.5 mg, m.p. 190-192 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.43 (dd, J = 11.9, 8.7 Hz, 4H), 7.23 (d, J = 7.7 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.72 (s, 1H), 3.84 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.2, 143.9, 138.0, 136.1, 135.1, 132.6, 129.7, 127.8, 127.4, 127.3, 122.1, 114.2, 55.3, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{20}H_{18}NO_3S^-$ [M - H]$^-$ 352.1013; found 352.1019.

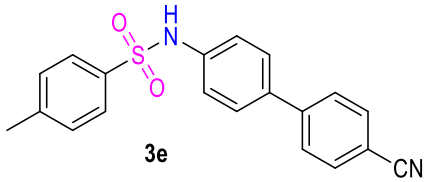
4-methyl-*N*-(3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)benzenesulfonamide(3d)



3d

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 78% yield, 30.5 mg, m.p. 113-115 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 3H), 7.68 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 7.3 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 7.09 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 140.9, 136.6, 136.5, 136.1, 131.2 (q, J = 32.2 Hz), 130.1, 129.8, 129.3, 128.0, 127.3, 124.2 (q, J = 272.7 Hz), 124.0 (q, J = 3.8 Hz), 123.6 (q, J = 4.0 Hz), 121.7, 21.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{20}H_{15}F_3NO_2S^-$ [M - H]$^-$ 390.0781; found 390.0792.

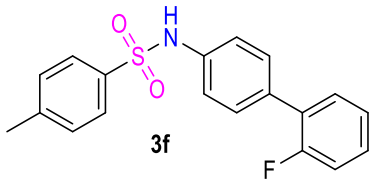
***N*-(4'-cyano-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3e)**[19]



3e

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). White solid, 52% yield, 18.1 mg, m.p. 190-191 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 7.05 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.5, 144.2, 137.2, 136.0, 135.7, 132.6, 129.8, 128.2, 127.33, 127.25, 121.4, 118.8, 110.9, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{20}H_{15}N_2O_2S^-$ [M - H]$^-$ 347.0860; found 347.0870.

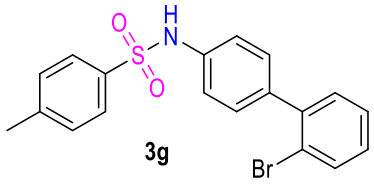
***N*-(2'-fluoro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3f)**



3f

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 67% yield, 22.9 mg, m.p. 147-148 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.46 (dd, J = 8.6, 1.7 Hz, 2H), 7.39 (td, J = 7.8, 1.9 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.24 – 7.19 (m, 1H), 7.19 – 7.13 (m, 3H), 6.90 (s, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7 (d, J = 247.8 Hz), 144.1, 136.1 (d, J = 10.0 Hz), 132.7, 130.5 (d, J = 3.6 Hz), 130.0 (d, J = 3.4 Hz), 129.8, 129.1 (d, J = 8.6 Hz), 128.1, 128.0, 127.3, 124.4 (d, J = 3.6 Hz), 121.1, 116.2 (d, J = 22.6 Hz), 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.05. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{15}FNO_2S^-$ [M - H]$^-$ 340.0813; found 340.0819.

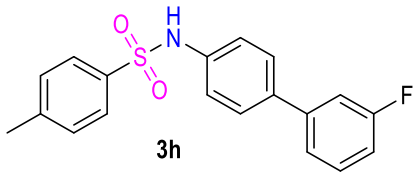
***N*-(2'-bromo-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3g)**



3g

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 57% yield, 22.9 mg, m.p. 131-133 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.5 Hz, 2H), 7.66 (dd, J = 8.0, 1.2 Hz, 1H), 7.36 (td, J = 7.4, 1.2 Hz, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 5.4 Hz, 3H), 7.21 (td, J = 7.8, 1.9 Hz, 1H), 7.14 (d, J = 8.5 Hz, 2H), 6.81 (s, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 141.5, 138.0, 136.1, 135.9, 133.2, 131.1, 130.4, 129.7, 128.8, 127.4, 127.3, 122.5, 120.8, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{15}BrNO_2S^-$ [M - H]$^-$ 400.0012; found 400.0004.

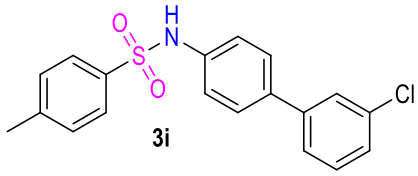
***N*-(3'-fluoro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3h)**



3h

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 69% yield, 23.5 mg, m.p. 120-121 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.39 (td, J = 7.9, 5.9 Hz, 1H), 7.31 (dt, J = 7.7, 1.3 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.25 – 7.20 (m, 1H), 7.18 (d, J = 8.6 Hz, 2H), 7.07 (s, 1H), 7.06 – 7.01 (m, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.2 (d, J = 245.6 Hz), 144.1, 142.4 (d, J = 7.4 Hz), 136.8 (d, J = 2.2 Hz), 136.4, 136.1, 130.3 (d, J = 8.6 Hz), 129.8, 128.0, 127.3, 122.4 (d, J = 2.8 Hz), 121.6, 114.1 (d, J = 21.1 Hz), 113.7 (d, J = 22.4 Hz), 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.93. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{15}FNO_2S^-$ $[M - H]^-$ 340.0813; found 340.0823.

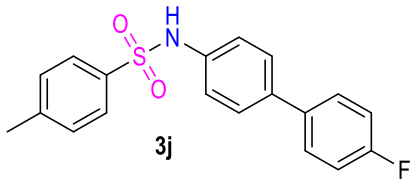
***N*-(3'-chloro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3i)**



3i

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 55% yield, 19.6 mg, m.p. 50-52 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.50 (t, J = 1.9 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.40 (dt, J = 7.5, 1.7 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.31 (dt, J = 7.7, 1.8 Hz, 1H), 7.28 (d, J = 1.8 Hz, 2H), 7.26 (s, 1H), 7.22 – 7.17 (m, 2H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 141.9, 136.6, 136.4, 136.0, 134.7, 130.1, 129.8, 128.0, 127.3, 127.0, 125.0, 121.5, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{16}ClNO_2SNa^+$ $[M + Na]^+$ 380.0482; found 380.0479.

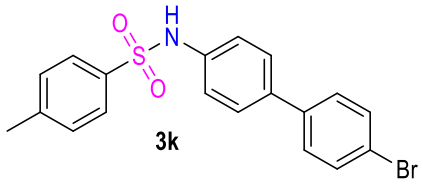
***N*-(4'-fluoro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3j)**



3j

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 61% yield, 20.8 mg, m.p. 138-140 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 7.12 (t, J = 8.7 Hz, 2H), 6.87 (s, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, J = 246.5 Hz), 144.0, 137.3, 136.2 (d, J = 3.2 Hz), 136.1, 135.8, 129.8, 128.4 (d, J = 8.0 Hz), 127.8, 127.3, 121.9, 115.7 (d, J = 21.7 Hz), 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{15}FNO_2S^-$ $[M - H]^-$ 340.0813; found 340.0823.

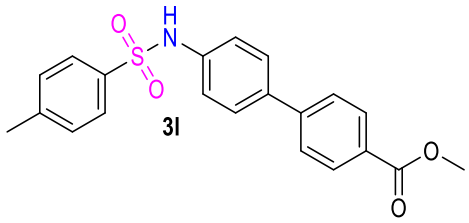
***N*-(4'-bromo-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3k)**



3k

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 70% yield, 28.1 mg, m.p. 170-172 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.92 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 139.0, 136.9, 136.1, 136.0, 131.9, 129.7, 128.4, 127.8, 127.3, 121.7, 121.6, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{16}BrNO_2SNa$ $[M + Na]^+$ 423.9977; found 423.9969.

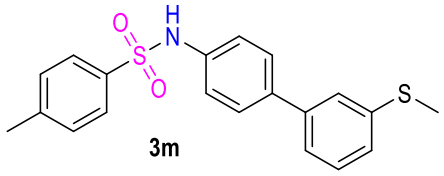
methyl 4'-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-4-carboxylate (3l)



3l

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). White solid, 54% yield, 20.6 mg, m.p. 160-162 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 2.7 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.05 (s, 1H), 3.96 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 144.5, 144.1, 136.8, 136.7, 136.1, 130.2, 129.8, 128.9, 128.2, 127.3, 126.7, 121.6, 52.2, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{21}H_{18}NO_4S^-$ [M - H]$^-$ 380.0962; found 380.0969.

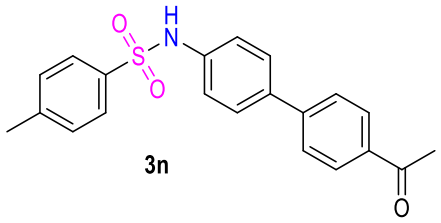
4-methyl-*N*-(3'-(methylthio)-[1,1'-biphenyl]-4-yl)benzenesulfonamide (3m)



3m

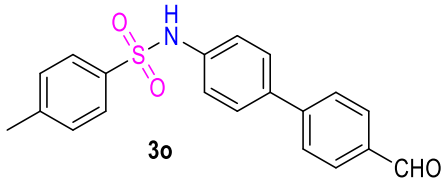
According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). Yellow solid, 37% yield, 13.7 mg, m.p. 112-115 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.38 (t, J = 1.8 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.28 (t, J = 1.5 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.21 (dt, J = 7.7, 1.6 Hz, 1H), 7.13 (d, J = 8.5 Hz, 2H), 6.76 (s, 1H), 2.51 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 140.8, 139.1, 137.8, 136.1, 136.0, 129.8, 129.3, 128.0, 127.3, 125.4, 125.0, 123.7, 121.8, 21.6, 15.9. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{20}H_{18}NO_2S_2^-$ [M - H]$^-$ 368.0784; found 368.0794.

***N*-(4'-acetyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3n)**



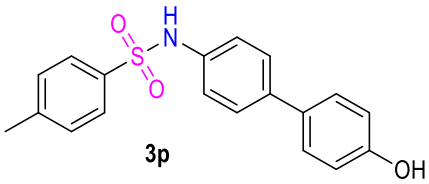
According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 45% yield, 16.4 mg, m.p. 206-207 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.93 (s, 1H), 2.65 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.8, 144.6, 144.1, 136.8, 136.6, 136.1, 135.9, 129.8, 129.0, 128.2, 127.3, 126.9, 121.5, 26.7, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{21}H_{18}NO_3S^-$ [M - H]$^-$ 364.1013; found 364.1026.

***N*-(4'-formyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3o)**



According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). Yellow solid, 47% yield, 16.5 mg, m.p. 131-133 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 6.96 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 191.9, 146.0, 144.1, 137.0, 136.3, 136.1, 135.2, 130.3, 129.8, 128.3, 127.28, 127.26, 121.4, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{20}H_{16}NO_3S^-$ [M - H]$^-$ 350.0856; found 350.0867.

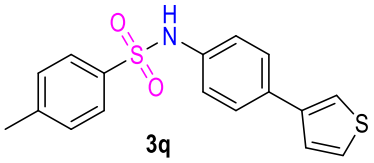
***N*-(4'-hydroxy-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3p)**



3p

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 1/1). White solid, 43% yield, 14.6 mg, m.p. 259-260 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 3.3 Hz, 2H), 7.39 (d, J = 3.4 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.63 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 143.9, 138.0, 136.1, 135.0, 132.7, 129.7, 128.1, 127.4, 127.3, 122.2, 115.7, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{16}NO_3S^-$ [M - H]$^-$ 338.0856; found 338.0864.

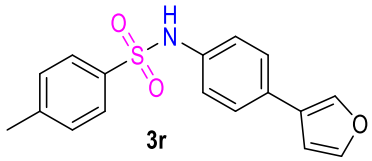
4-methyl-*N*-(4-(thiophen-2-yl)phenyl)benzenesulfonamide (3q)



3q

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). White solid, 44% yield, 14.5 mg, m.p. 159-161 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.31 (dd, J = 4.8, 1.6 Hz, 1H), 7.23 (d, J = 7.7 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 6.72 (s, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 141.3, 136.1, 135.4, 133.1, 129.7, 127.31, 127.25, 126.5, 126.0, 122.1, 120.2, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{17}H_{14}NO_2S_2^-$ [M - H]$^-$ 328.0471; found 328.0478.

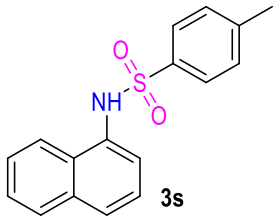
_N_-(4-(furan-2-yl)phenyl)-4-methylbenzenesulfonamide (3r)



3r

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). White solid, 17% yield, 5.3 mg, m.p. 100-101 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 1.7 Hz, 1H), 7.35 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H), 6.63 (dd, J = 1.9, 0.9 Hz, 1H), 6.50 (s, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 143.8, 138.4, 136.1, 135.1, 129.8, 129.7, 127.3, 126.7, 125.6, 122.4, 108.6, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{17}H_{14}NO_3S^-$ [M - H]$^-$ 312.0700; found 312.0702.

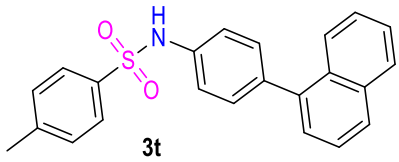
4-methyl-_N_-(naphthalen-1-yl)benzenesulfonamide (3s)



3s

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 30% yield, 8.9 mg, m.p. 153-154 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (t, J = 9.8 Hz, 2H), 7.71 (dd, J = 6.5, 2.9 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.49 – 7.39 (m, 2H), 7.37 (q, J = 4.2, 3.7 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.95 (s, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.8, 136.4, 134.3, 131.5, 129.6, 128.9, 128.4, 127.4, 127.2, 126.7, 126.3, 125.5, 122.7, 121.5, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{17}H_{14}NO_2S^-$ [M - H]$^-$ 320.0716; found 320.0718.

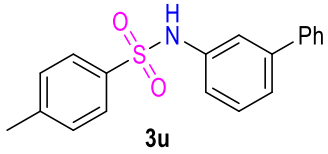
4-methyl-*N*-(4-(naphthalen-1-yl)phenyl)benzenesulfonamide (3t)



3t

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). Light yellow solid, 51% yield, 19.0 mg, m.p. 142-143 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.79 (d, J = 8.5 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.44 – 7.40 (m, 1H), 7.40 – 7.33 (m, 3H), 7.29 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.5 Hz, 2H), 6.84 (s, 1H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 139.2, 137.8, 136.3, 135.7, 133.8, 131.5, 131.0, 129.8, 128.4, 127.8, 127.4, 126.9, 126.1, 125.9, 125.7, 125.4, 121.4, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{23}H_{18}NO_2S^-$ [M - H]$^-$ 372.1064; found 372.1079.

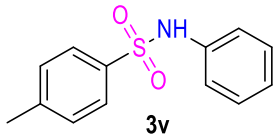
***N*-([1,1'-biphenyl]-3-yl)-4-methylbenzenesulfonamide (3u)**



3u

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 58% yield, 18.8 mg, m.p. 114-116 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.31 (d, J = 7.6 Hz, 1H), 7.28 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 7.06 (ddd, J = 7.6, 2.2, 1.4 Hz, 1H), 6.77 (s, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 142.4, 140.1, 137.0, 136.1, 129.68, 129.67, 128.8, 127.7, 127.3, 127.1, 124.1, 120.3, 120.2, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{16}NO_2S^-$ [M - H]$^-$ 346.0872; found 346.0870.

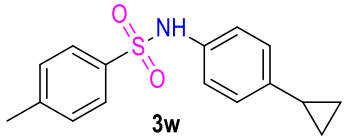
4-methyl-*N*-phenylbenzenesulfonamide (3v)



3v

According to general procedure B, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 49% yield, 12.0 mg, m.p. 100-101 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 2.8 Hz, 2H), 7.21 (d, *J* = 2.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.61 (s, 1H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.9, 136.5, 136.1, 129.6, 129.3, 127.3, 125.4, 121.7, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{13}H_{13}NO_2SNa^+$ $[M + Na]^+$ 270.0565, found: 270.0562.

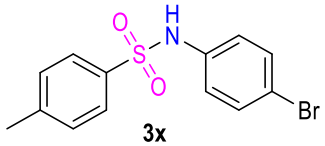
***N*-(4-cyclopropylphenyl)-4-methylbenzenesulfonamide (3w)**



3w

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 46% yield, 12.2 mg, m.p. 114-115 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.61 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.93 (s, 4H), 6.47 (s, 1H), 2.38 (s, 3H), 1.81 (tt, *J* = 8.4, 5.1 Hz, 1H), 0.97 – 0.88 (m, 2H), 0.61 (dt, *J* = 6.6, 4.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 143.7, 141.6, 136.1, 133.6, 129.6, 127.3, 126.4, 122.5, 21.5, 14.9, 9.2. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{16}H_{16}NO_2S^-$ $[M - H]^-$ 286.0907; found 286.0916.

***N*-(4-bromophenyl)-4-methylbenzenesulfonamide (3x)**

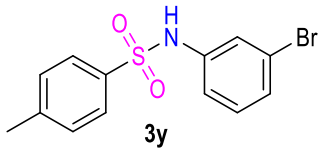


3x

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). Light yellow solid, 47% yield, 14.6 mg, m.p. 154-157 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.65 (d, *J*

= 8.3 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.90 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.2, 135.6, 132.4, 129.8, 127.2, 123.1, 122.2, 118.6, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{13}H_{12}BrNO_2SNa^+$ $[M + Na]^+$ 347.9664; found 347.9655.

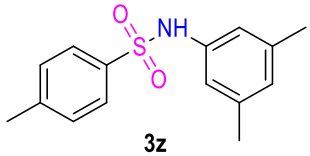
***N*-(3-bromophenyl)-4-methylbenzenesulfonamide (3y)**



3y

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). Light yellow solid, 52% yield, 16.7 mg, m.p. 122-124 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.27 (s, 1H), 7.25 – 7.23 (m, 2H), 7.21 (dd, *J* = 1.9, 1.1 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 7.01 (ddd, *J* = 8.1, 2.2, 1.1 Hz, 1H), 6.78 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.3, 137.9, 135.8 130.6, 129.8, 128.3, 127.2, 124.0, 122.8, 119.6, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{13}H_{11}BrNO_2S^-$ $[M - H]^-$ 323.9699; found 323.9688.

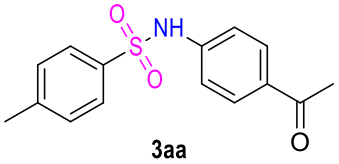
***N*-(3,5-dimethylphenyl)-4-methylbenzenesulfonamide (3z)**



3z

According to general procedure B, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 41% yield, 11.2 mg, m.p. 92-93 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 6.94 (s, 1H), 6.74 (s, 1H), 6.72 (s, 2H), 2.40 (s, 3H), 2.23 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 139.0, 136.4, 136.3, 129.6, 127.3, 126.9, 118.9, 21.5, 21.2. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{15}H_{17}NO_2SNa^+$ $[M + Na]^+$ 298.0878, found: 298.0875.

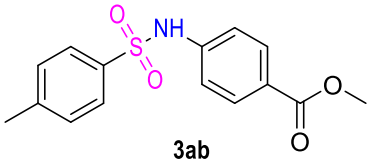
***N*-(4-acetylphenyl)-4-methylbenzenesulfonamide (3aa)**



3aa

According to general procedure B, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 66% yield, 19.0 mg, m.p. 188-189 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 1H), 7.24 (s, 1H), 7.18 (s, 1H), 7.15 (d, *J* = 8.7 Hz, 2H), 2.53 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 144.5, 141.1, 135.9, 133.3, 130.0, 129.9, 127.3, 119.0, 26.4, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{15}H_{15}NO_3SNa^+$ $[M + Na]^+$ 312.0671, found: 312.0669.

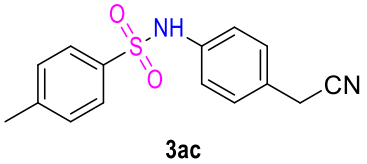
Methyl-4-((4-methylphenyl)sulfonamido)benzoate (3ab)



3ab

According to general procedure B, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 46% yield, 14.0 mg, m.p. 186-187 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.27 (s, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.4, 144.4, 141.0, 135.8, 131.1, 129.9, 127.3, 126.2, 119.0, 52.1, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{15}H_{15}NO_4SNa^+$ $[M + Na]^+$ 328.0620, found: 328.0620.

***N*-(4-(cyanomethyl)phenyl)-4-methylbenzenesulfonamide (3ac)**

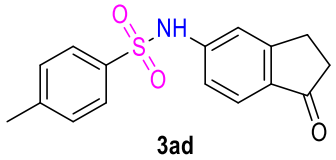


3ac

According to general procedure B, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 49%

yield, 14.0 mg, m.p. 193-194 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.01 (s, 1H), 3.67 (s, 2H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 136.5, 135.8, 129.8, 128.9, 127.2, 126.6, 121.8, 117.6, 23.0, 21.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{15}H_{15}N_2O_2S^+$ $[M + H]^+$ 287.0849, found: 287.0850.

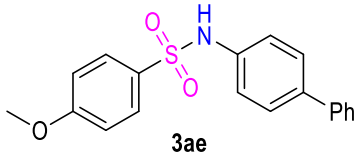
4-methyl-*N*-(1-oxo-2,3-dihydro-1H-inden-5-yl)benzenesulfonamide (3ad)



3ad

According to general procedure B, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 37% yield, 11.4 mg, m.p. 189-190 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.52 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 2.2 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.01 (s, 1H), 3.12 – 3.06 (m, 2H), 2.72 – 2.67 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) 206.3, 152.1, 144.2, 138.0, 136.3, 135.8, 129.8, 128.7, 127.6, 127.2, 116.0, 36.7, 25.4, 21.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{16}H_{16}NO_3S^+$ $[M + H]^+$ 302.0851, found: 302.0851.

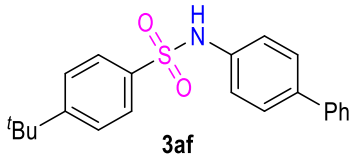
***N*-([1,1'-biphenyl]-4-yl)-4-methoxybenzenesulfonamide (3ae)**



3ae

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). White solid, 65% yield, 22.1 mg, m.p. 153-155 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.78 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 7.0 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.18 (s, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 163.1, 140.0, 138.0, 135.8, 130.5, 129.4, 128.8, 127.9, 127.3, 126.8, 121.7, 114.2, 55.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{17}NO_3SNa^+$ $[M + Na]^+$ 362.0821; found 362.0814.

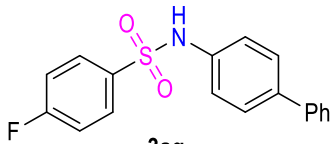
***N*-([1,1'-biphenyl]-4-yl)-4-(*tert*-butyl)benzenesulfonamide (3af)**



3af

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 42% yield, 15.4 mg, m.p. 117-119 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 7.0 Hz, 2H), 7.50 – 7.44 (m, 4H), 7.41 (t, J = 7.7 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.18 (d, J = 8.6 Hz, 2H), 7.11 (s, 1H), 1.30 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.9, 140.0, 138.0, 136.1, 135.8, 128.8, 127.9, 127.3, 127.1, 126.8, 126.1, 121.5, 35.1, 31.0. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{22}H_{22}NO_2S^-$ [M - H]$^-$ 364.1377; found 364.1387.

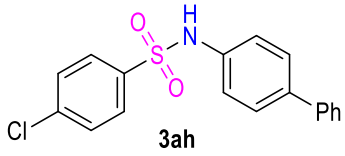
***N*-([1,1'-biphenyl]-4-yl)-4-fluorobenzenesulfonamide (3ag)**



3ag

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 65% yield, 21.3 mg, m.p. 175-178 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 8.9, 5.0 Hz, 2H), 7.55 (d, J = 7.0 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.15 (t, J = 8.6 Hz, 4H), 6.81 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3 (d, J = 255.3 Hz), 139.9, 138.8, 135.2, 135.0 (d, J = 3.4 Hz), 130.1 (d, J = 9.5 Hz), 128.9, 128.1, 127.5, 126.9, 122.3, 116.4 (d, J = 22.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.2. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{18}H_{14}FNO_2SNa^+$ [M + Na]$^+$ 350.0621; found 350.0621.

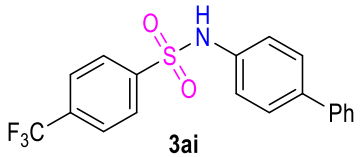
***N*-([1,1'-biphenyl]-4-yl)-4-chlorobenzenesulfonamide (3ah)**



3ah

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 60% yield, 20.6 mg, m.p. 180-182 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 7.0 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.45 – 7.39 (m, 4H), 7.38 – 7.31 (m, 1H), 7.15 (d, J = 8.6 Hz, 2H), 6.97 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 139.7, 138.8, 137.4, 135.1, 129.4, 128.8, 128.7, 128.1, 127.5, 126.8, 122.3. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{18}H_{13}ClNO_2S^-$ [M - H]$^-$ 342.0361; found 342.0373.

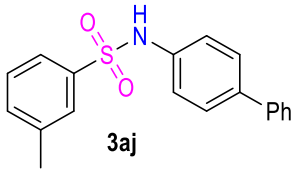
***N*-([1,1'-biphenyl]-4-yl)-4-(trifluoromethyl)benzenesulfonamide (3ai)**



3ai

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 40% yield, 15.1 mg, m.p. 177-178 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.55 – 7.48 (m, 4H), 7.46 – 7.39 (m, 2H), 7.37 – 7.31 (m, 1H), 7.16 (d, J = 8.6 Hz, 2H), 6.98 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.7, 139.8, 139.1, 134.9, 134.8 (q, J = 33.2 Hz), 128.9, 128.2, 127.8, 127.6, 126.9, 126.3 (q, J = 3.7 Hz), 123.2 (q, J = 272.7 Hz), 122.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.2. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{13}F_3NO_2S^-$ [M - H]$^-$ 376.0624; found 376.0626.

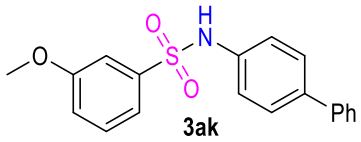
***N*-([1,1'-biphenyl]-4-yl)-3-methylbenzenesulfonamide (3aj)**



3aj

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 70% yield, 22.6 mg, m.p. 118-119 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.65 – 7.61 (m, 1H), 7.54 – 7.50 (m, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.35 (d, J = 1.2 Hz, 2H), 7.32 (dd, J = 7.5, 1.5 Hz, 1H), 7.16 (d, J = 8.5 Hz, 2H), 7.06 (s, 1H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 139.3, 138.8, 138.2, 135.7, 133.9, 128.9, 128.8, 127.9, 127.6, 127.3, 126.8, 124.4, 121.8, 21.3. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{17}NO_2SNa^+$ $[M + Na]^+$ 346.0872; found 346.0870.

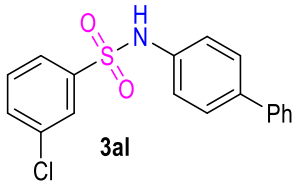
***N*-([1,1'-biphenyl]-4-yl)-3-methoxybenzenesulfonamide (3ak)**



3ak

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). White solid, 48% yield, 16.3 mg, m.p. 148-149 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.42 (dd, J = 7.7, 6.8 Hz, 3H), 7.38 – 7.32 (m, 2H), 7.30 (dd, J = 2.6, 1.7 Hz, 1H), 7.17 (d, J = 8.6 Hz, 2H), 7.06 (ddd, J = 8.1, 2.6, 1.1 Hz, 1H), 7.01 (s, 1H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 140.0, 138.4, 135.6, 130.1, 128.8, 127.9, 127.4, 126.8, 122.1, 119.7, 119.4, 111.6, 55.5. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{17}NO_3SNa^+$ $[M + Na]^+$ 362.0821; found 362.0817.

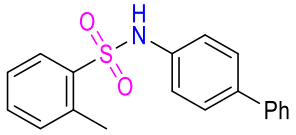
***N*-([1,1'-biphenyl]-4-yl)-3-chlorobenzenesulfonamide (3al)**



3al

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 56% yield, 19.3 mg, m.p. 111-112 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (t, J = 1.9 Hz, 1H), 7.68 (dt, J = 7.9, 1.4 Hz, 1H), 7.52 (dd, J = 9.8, 1.8 Hz, 4H), 7.49 (d, J = 2.0 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.37 – 7.31 (m, 1H), 7.16 (d, J = 8.5 Hz, 2H), 7.01 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.6, 139.9, 138.8, 135.3, 135.0, 133.3, 130.4, 128.8, 128.1, 127.5, 127.3, 126.9, 125.3, 122.3. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{18}H_{13}ClNO_2S^-$ $[M - H]^-$ 342.0361; found 342.0371.

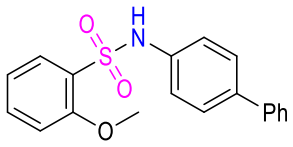
***N*-([1,1'-biphenyl]-4-yl)-2-methylbenzenesulfonamide (3am)**



3am

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 65% yield, 20.0 mg, m.p. 134-135 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.2, 1.4 Hz, 1H), 7.50 (d, J = 1.6 Hz, 1H), 7.48 (s, 1H), 7.44 (d, J = 8.5 Hz, 3H), 7.40 (dd, J = 8.4, 6.8 Hz, 2H), 7.32 (ddd, J = 7.9, 3.1, 1.6 Hz, 2H), 7.29 (s, 1H), 7.22 (s, 1H), 7.11 (d, J = 8.6 Hz, 2H), 2.70 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 137.8, 137.3, 137.2, 135.6, 133.2, 132.7, 130.0, 128.8, 128.0, 127.3, 126.8, 126.3, 120.7, 20.4. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{17}NO_2SNa^+$ $[M + Na]^+$ 346.0872; found 346.0868.

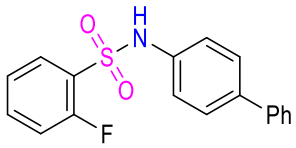
***N*-([1,1'-biphenyl]-4-yl)-2-methoxybenzenesulfonamide (3an)**



3an

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 8/1). White solid, 52% yield, 17.6 mg, m.p. 177-179 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.7, 1.7 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.43 – 7.36 (m, 4H), 7.35 – 7.27 (m, 2H), 7.16 (d, J = 8.5 Hz, 2H), 7.03 – 6.97 (m, 2H), 4.06 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.2, 140.1, 138.0, 136.0, 135.0, 131.0, 128.7, 127.8, 127.2, 126.7, 126.2, 121.4, 120.7, 112.0, 56.4. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{19}H_{17}NO_3SNa^+$ $[M + Na]^+$ 362.0821; found 362.0816.

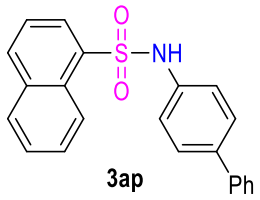
***N*-([1,1'-biphenyl]-4-yl)-2-fluorobenzenesulfonamide (3ao)**



3ao

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 60% yield, 19.6 mg, m.p. 146-148 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (td, J = 7.5, 1.8 Hz, 1H), 7.60 – 7.54 (m, 1H), 7.51 (dd, J = 8.4, 1.4 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.26 – 7.19 (m, 4H), 7.06 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.8 (d, J = 254.3 Hz), 140.0, 138.6, 135.6 (d, J = 8.7 Hz), 135.0, 131.1, 128.9, 128.1, 127.5, 126.9, 126.8 (d, J = 13.7 Hz), 124.7 (d, J = 3.8 Hz), 121.7, 117.0 (d, J = 21.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.51. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{18}H_{14}FNO_2SNa^+$ $[M + Na]^+$ 350.0621; found 350.0617.

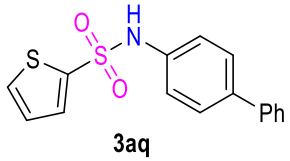
***N*-([1,1'-biphenyl]-4-yl)naphthalene-1-sulfonamide (3ap)**



3ap

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 36% yield, 12.9 mg, m.p. 174-175 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, J = 8.6 Hz, 1H), 8.24 (dd, J = 7.4, 1.3 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.69 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.48 (d, J = 7.7 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 7.01 (s, 2H), 6.99 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.0, 138.3, 135.4, 134.7, 134.2, 134.0, 130.4, 129.3, 128.7, 128.6, 128.1, 127.8, 127.3, 126.9, 126.8, 124.13, 124.11, 122.0. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{22}H_{16}NO_2S^-$ [M - H]$^-$ 358.0907; found 358.0914.

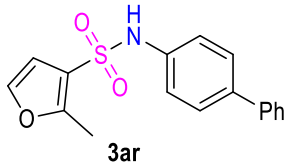
***N*-([1,1'-biphenyl]-4-yl)thiophene-2-sulfonamide (3aq)**



3aq

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 40% yield, 12.6 mg, m.p. 130-133 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 3H), 7.53 (s, 2H), 7.51 (s, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.21 (d, J = 8.6 Hz, 2H), 7.02 (dd, J = 5.0, 3.8 Hz, 1H), 6.88 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9, 139.3, 138.7, 135.2, 133.0, 132.5, 128.8, 128.0, 127.44, 127.36, 126.8, 122.2. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{16}H_{12}NO_2S_2^-$ [M - H]$^-$ 314.0315; found 314.0325.

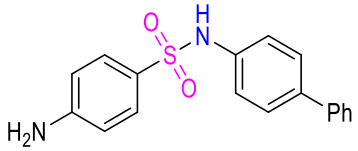
***N*-([1,1'-biphenyl]-4-yl)-2-methylfuran-3-sulfonamide (3ar)**



3ar

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). Light yellow solid, 39% yield,12.2 mg, m.p. 85-87 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (t, J = 8.6 Hz, 4H), 7.43 (t, J = 7.5 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.24 (d, J = 2.1 Hz, 1H), 7.19 (d, J = 8.6 Hz, 2H), 6.94 (s, 1H), 6.56 (d, J = 2.1 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 141.1, 140.0, 138.7, 135.4, 128.8, 127.9, 127.4, 126.8, 122.5, 119.9, 109.6, 12.8. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{17}H_{14}NO_3S^-$ [M - H]$^-$ 312.0700; found 312.0710.

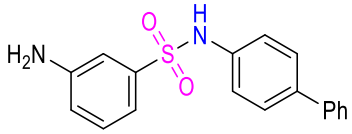
***N*-([1,1'-biphenyl]-4-yl)-4-aminobenzenesulfonamide (3as)**



3as

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 3/1). Yellow solid, 35% yield, 11.4 mg, m.p. 230-233 ℃. **^{1}H NMR** (400 MHz, DMSO) δ (s, 1H), 7.57 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.44 (s, 1H), 7.42 – 7.37 (m, 3H), 7.31 (d, J = 7.4 Hz, 1H), 7.15 (d, J = 8.6 Hz, 2H), 6.54 (d, J = 8.7 Hz, 2H), 5.99 (s, 2H). **^{13}C NMR** (101 MHz, DMSO) δ 152.9, 139.5, 138.0, 135.0, 128.9, 128.8, 127.3, 127.1, 126.3, 124.4, 119.6, 112.6. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{18}H_{15}N_2O_2S^-$ [M - H]$^-$ 323.0860; found 323.0866.

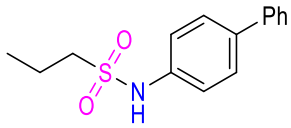
***N*-([1,1'-biphenyl]-4-yl)-3-aminobenzenesulfonamide (3at)**



3at

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 3/1). Yellow solid, 43% yield, 13.9 mg, m.p. 101-103 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.0 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.20 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 8.6 Hz, 3H), 7.10 (t, J = 2.0 Hz, 1H), 6.83 (s, 1H), 6.80 (ddd, J = 7.8, 2.4, 1.2 Hz, 1H), 3.87 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.1, 140.1, 139.9, 138.3, 135.7, 130.0, 128.8, 127.9, 127.3, 126.8, 122.0, 119.3, 116.9, 112.9. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{18}H_{15}N_2O_2S^-$ [M - H]$^-$ 323.0860; found 323.0870.

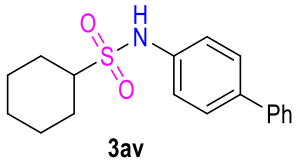
***N*-([1,1'-biphenyl]-4-yl)propane-1-sulfonamide (3au)**



3au

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 60% yield, 16.5 mg, m.p. 138-139 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.38 – 7.32 (m, 1H), 7.29 (d, J = 8.6 Hz, 2H), 6.74 (s, 1H), 3.17 – 3.08 (m, 2H), 1.94 – 1.85 (m, 2H), 1.04 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 138.1, 136.0, 128.9, 128.3, 127.4, 126.9, 120.7, 53.4, 17.3, 12.9. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{15}H_{16}NO_2S^-$ [M - H]$^-$ 274.0907; found 274.0914.

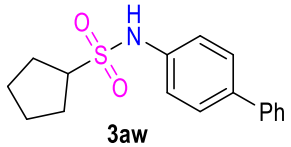
***N*-([1,1'-biphenyl]-4-yl)cyclohexanesulfonamide (3av)**



3av

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 49% yield, 18.0 mg, m.p. 159-160 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 2.8 Hz, 2H), 7.55 (d, J = 2.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 7.30 (d, J = 8.6 Hz, 2H), 6.82 (s, 1H), 3.06 (tt, J = 12.1, 3.5 Hz, 1H), 2.20 (ddd, J = 15.0, 4.8, 2.7 Hz, 2H), 1.88 (dq, J = 10.2, 3.5 Hz, 2H), 1.71 – 1.65 (m, 1H), 1.58 (dd, J = 12.4, 3.6 Hz, 1H), 1.24 (q, J = 12.1, 11.6 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 137.6, 136.5, 128.8, 128.2, 127.3, 126.8, 120.3, 60.4, 26.3, 25.0, 24.9. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{18}H_{20}NO_2S^-$ [M - H]$^-$ 314.1220; found 314.1229.

***N*-([1,1'-biphenyl]-4-yl)cyclopentanesulfonamide (3aw)**



3aw

According to general procedure A, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). White solid, 42% yield, 12.7 mg, m.p. 118-120 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 1.6 Hz, 2H), 7.55 (d, J = 2.1 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.37 – 7.34 (m, 1H), 7.31 (d, J = 8.6 Hz, 2H), 6.80 (s, 1H), 3.60 (ddd, J = 16.0, 8.8, 7.1 Hz, 1H), 2.09 (dt, J = 15.4, 7.6 Hz, 2H), 2.05 – 1.95 (m, 2H), 1.87 – 1.77 (m, 2H), 1.63 – 1.55 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 138.1, 136.2, 128.9, 128.2, 127.4, 126.9, 121.1, 60.6, 28.0, 25.9. **HRMS** (ESI-TOF, m/z): Mass calcd. for $C_{17}H_{18}NO_2S$ [M - H]$^-$ 300.1064; found 300.1074.

11. References

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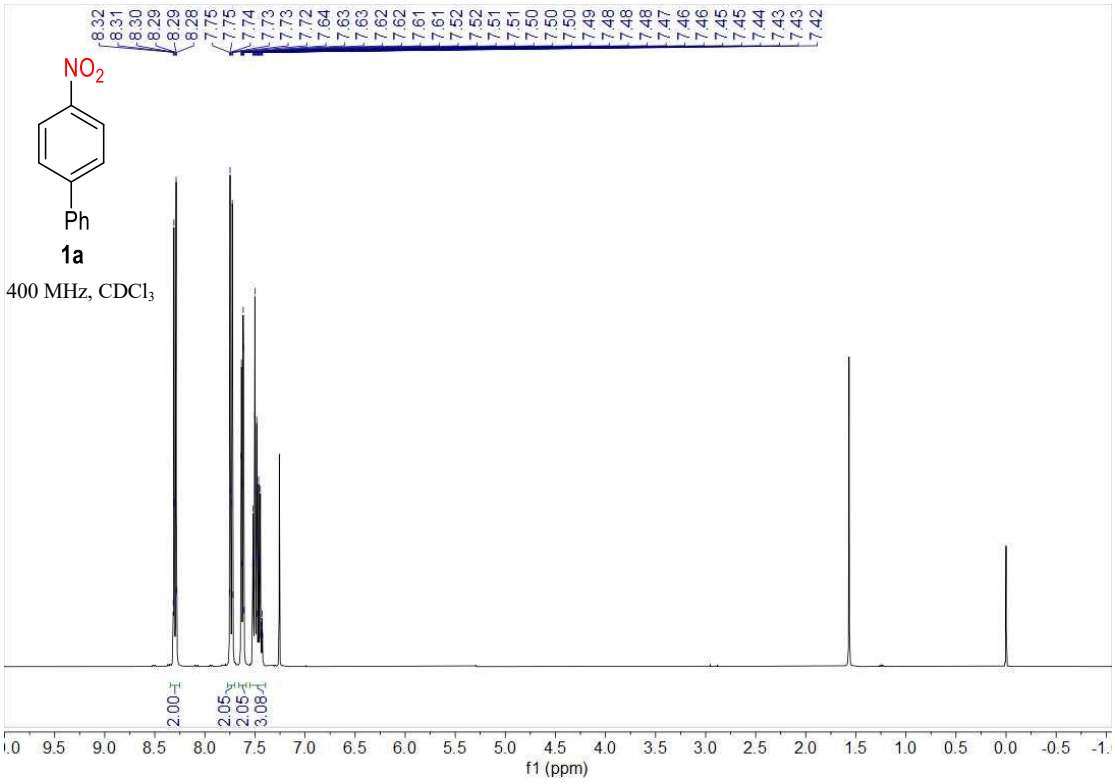
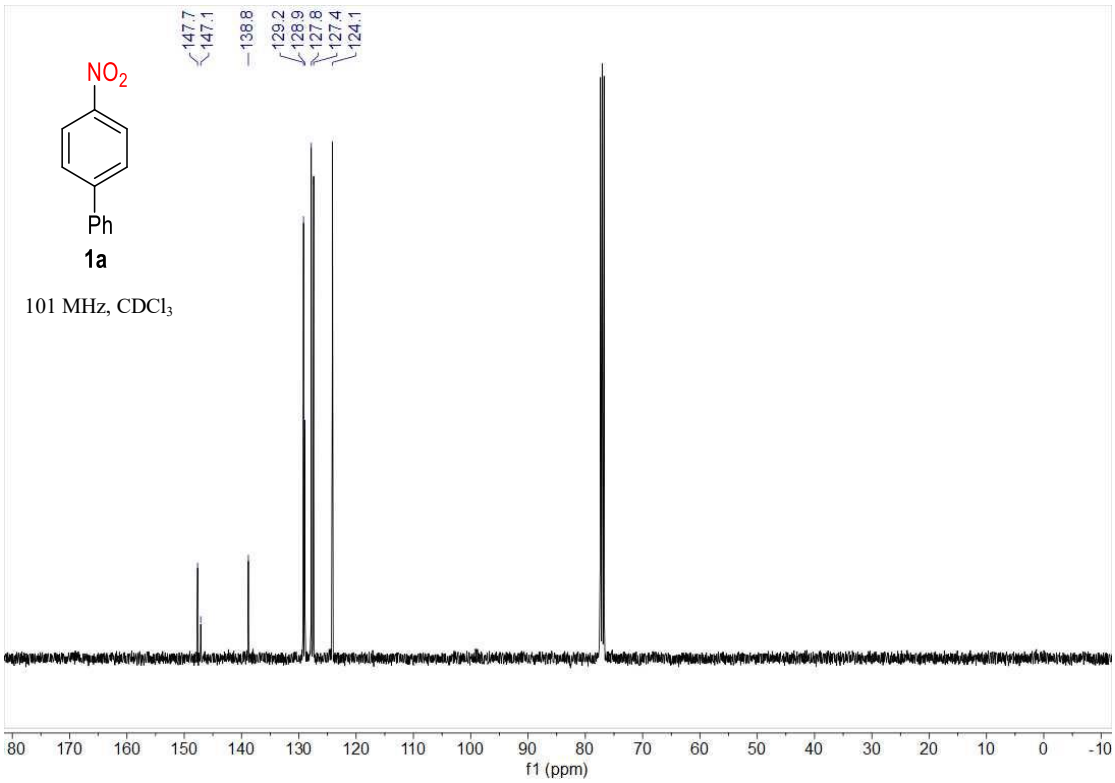
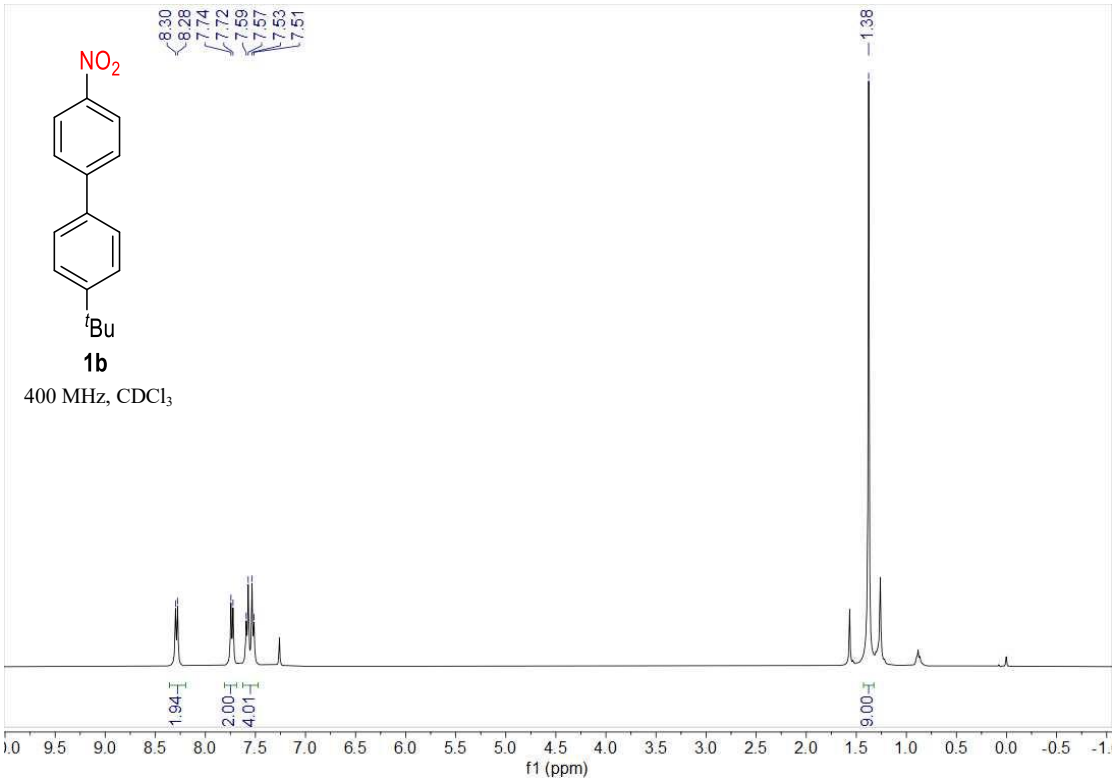
Appendix: ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra for new compounds

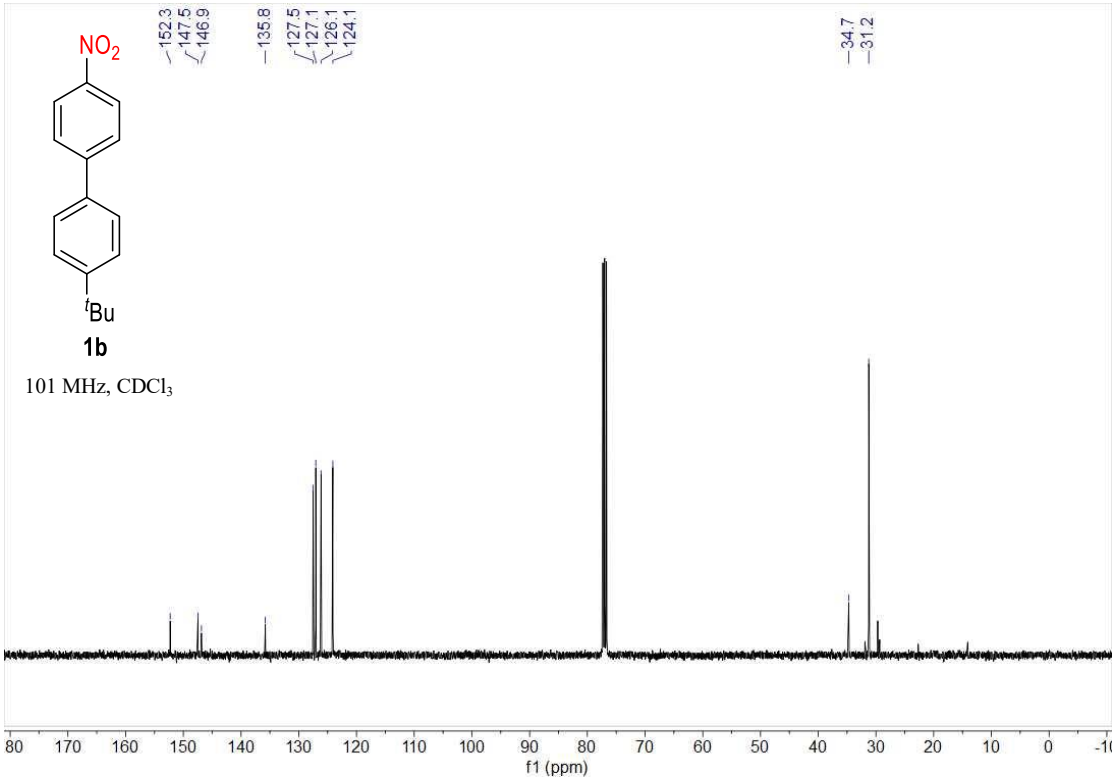
4-nitro-1,1'-biphenyl (1a)



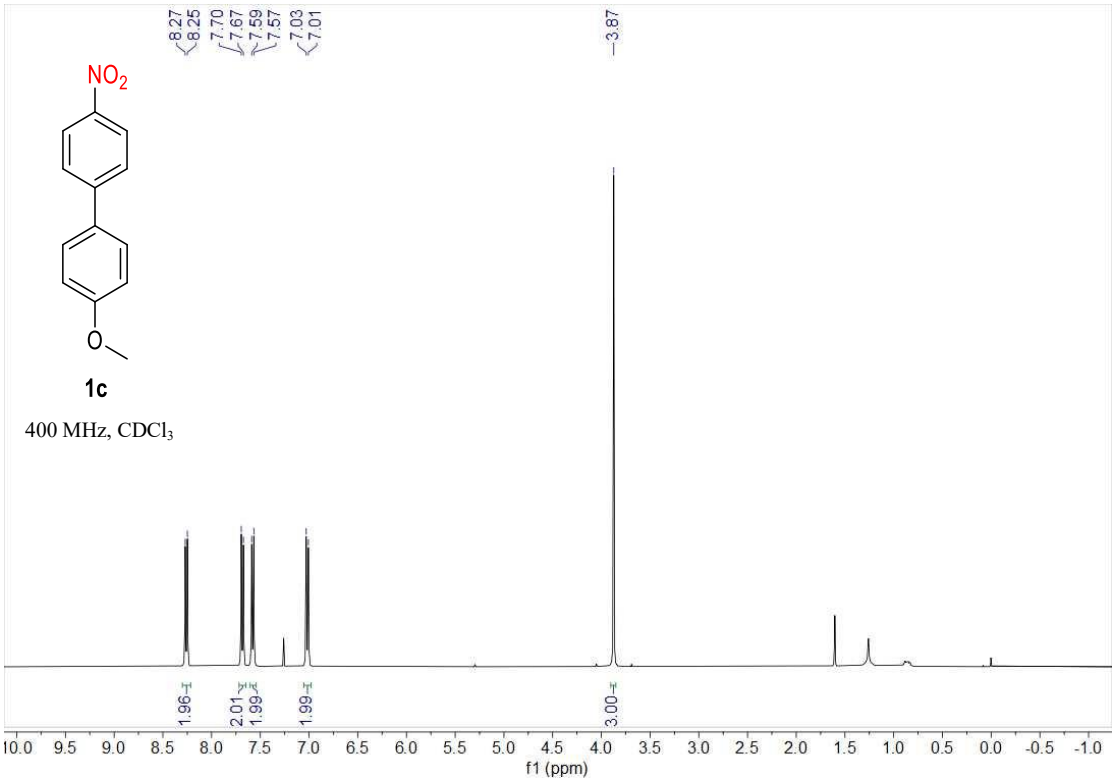


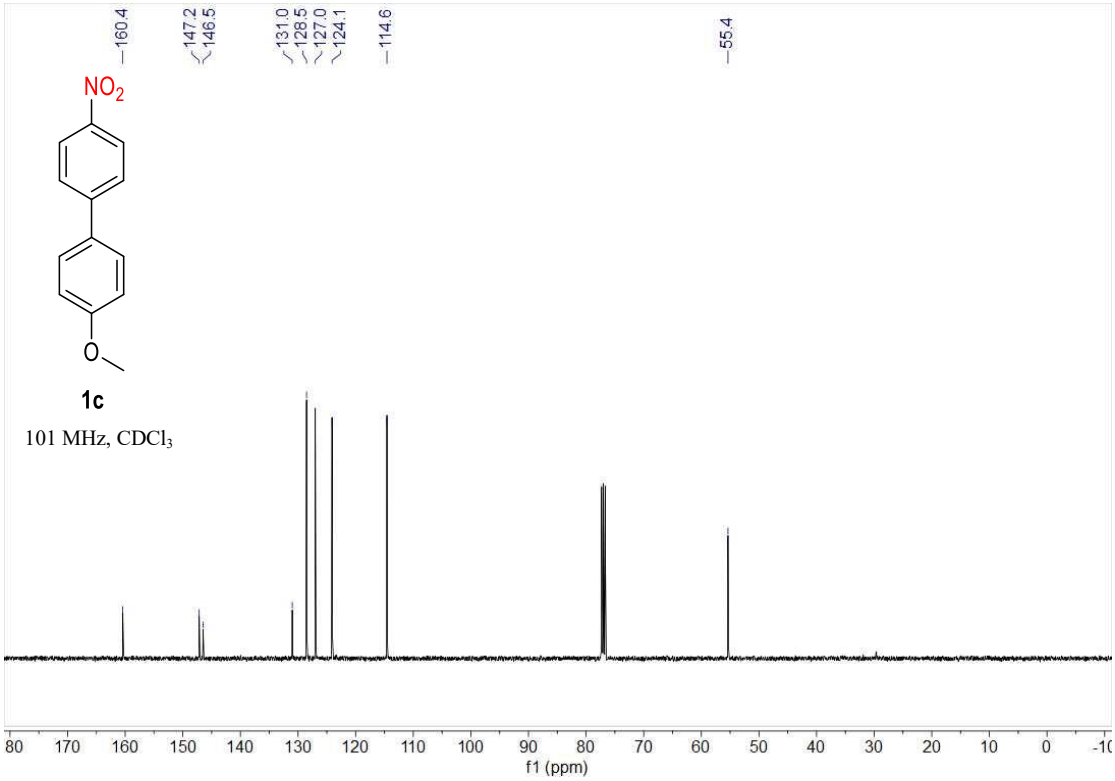
4-(*tert*-butyl)-4'-nitro-1,1'-biphenyl (1b)



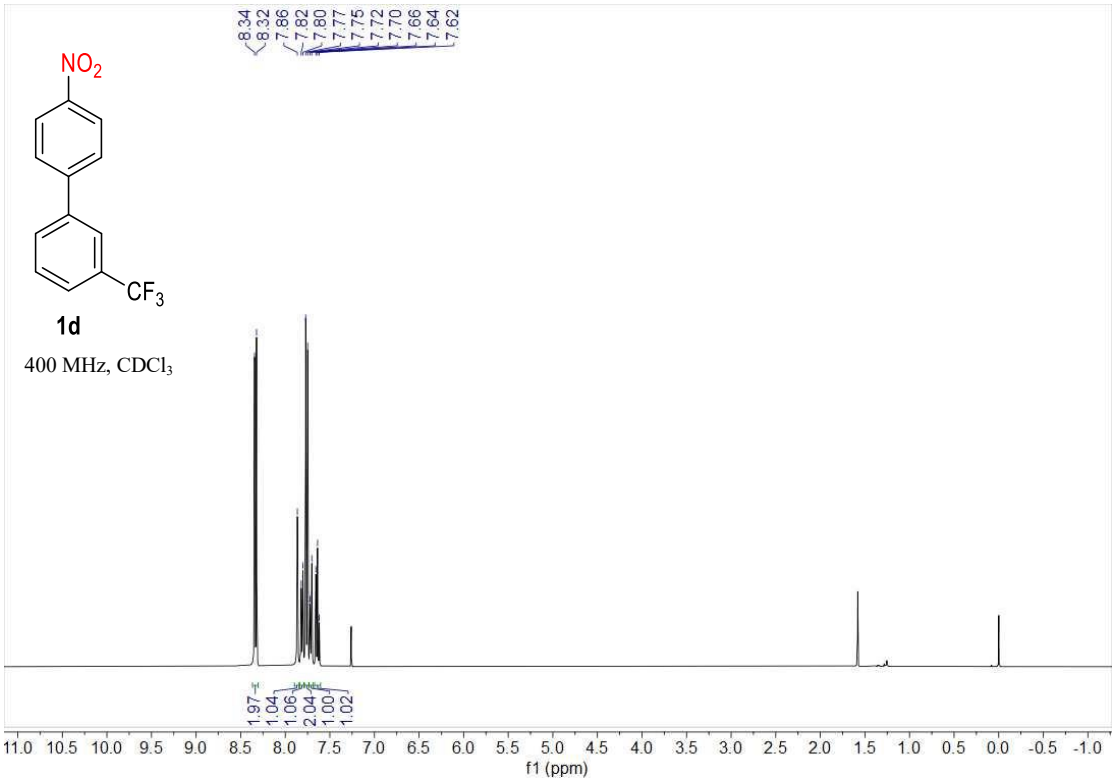


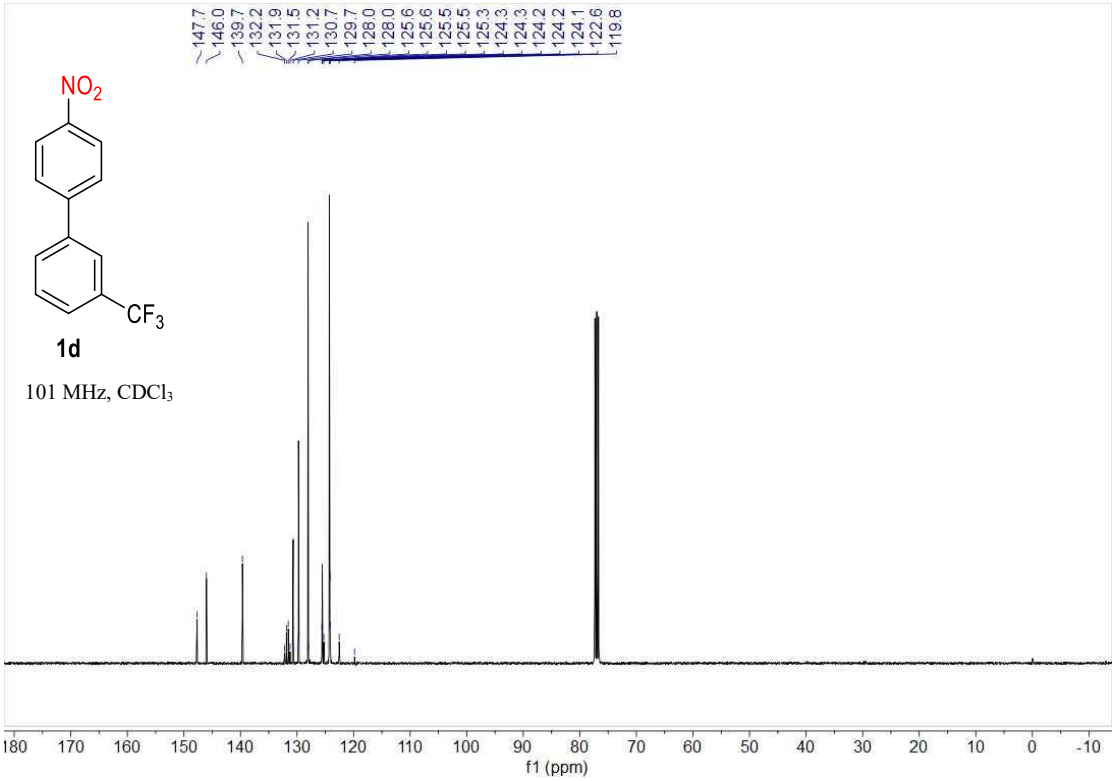
1-methoxy-4-nitrobenzene (1c)

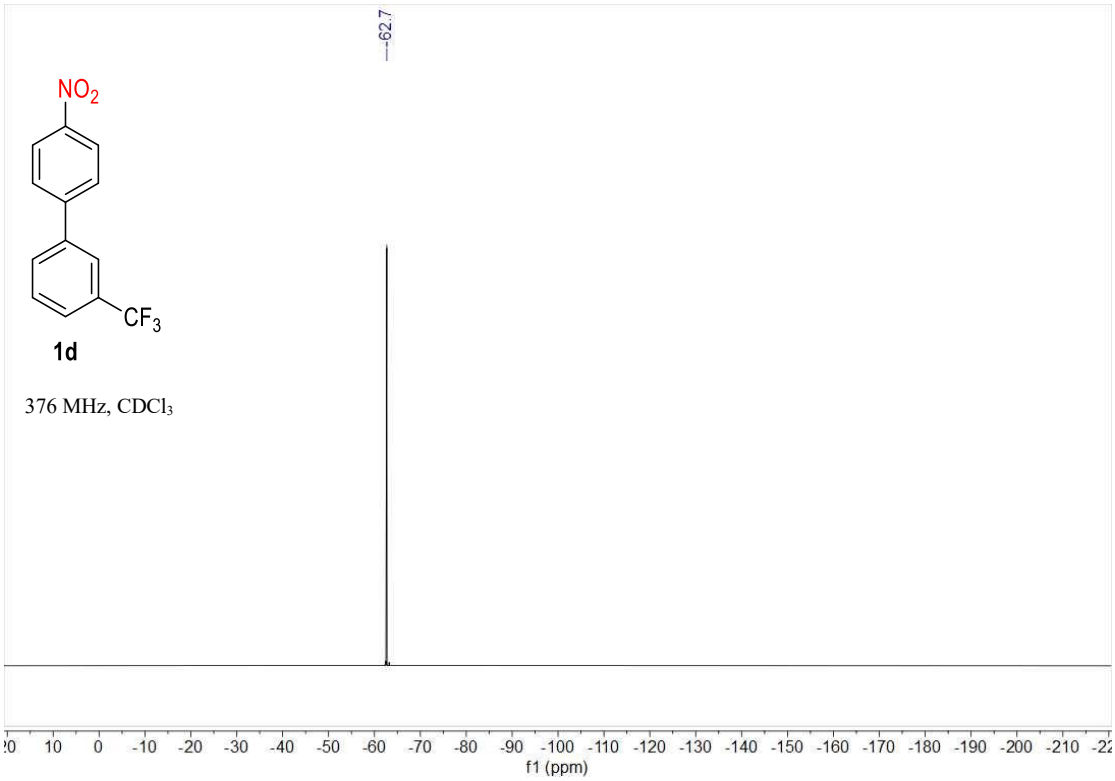




4'-nitro-3-(trifluoromethyl)-1,1'-biphenyl (1d)



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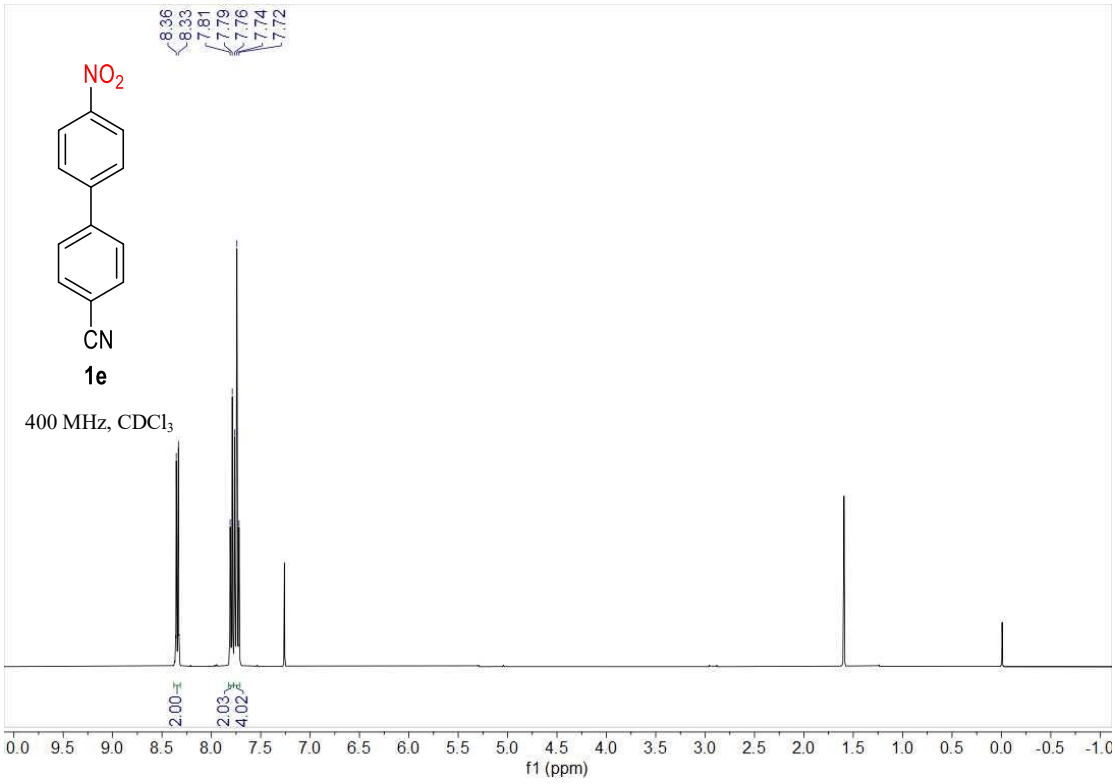
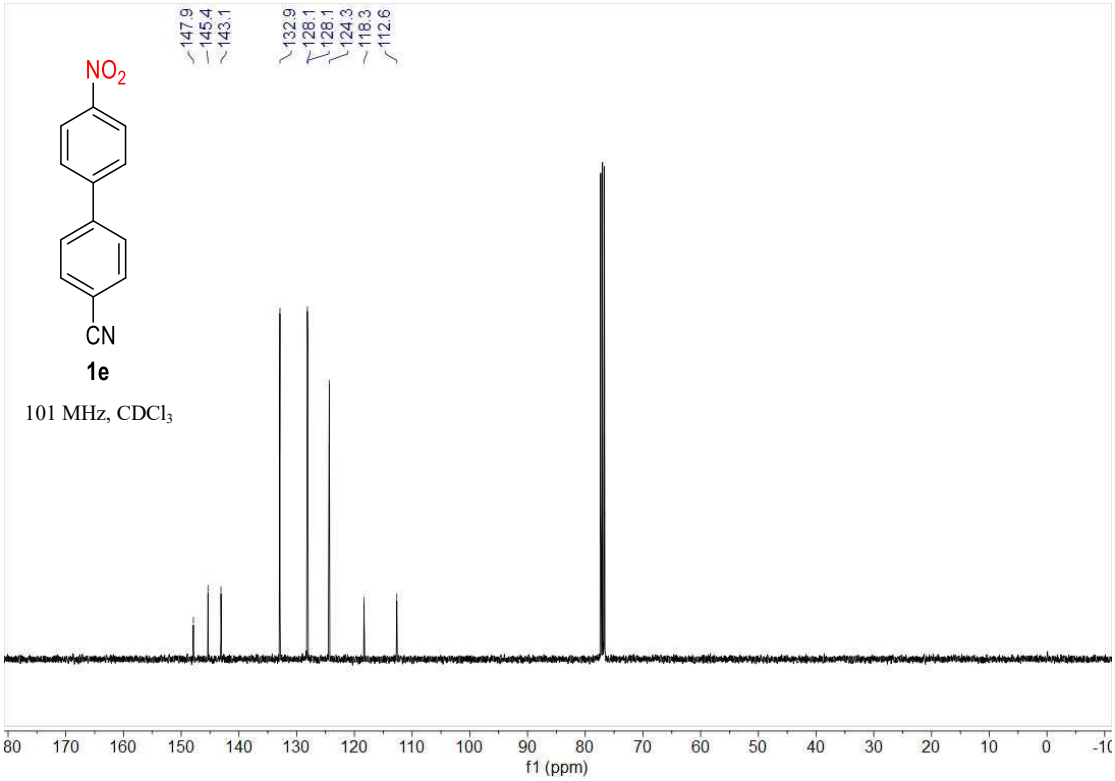
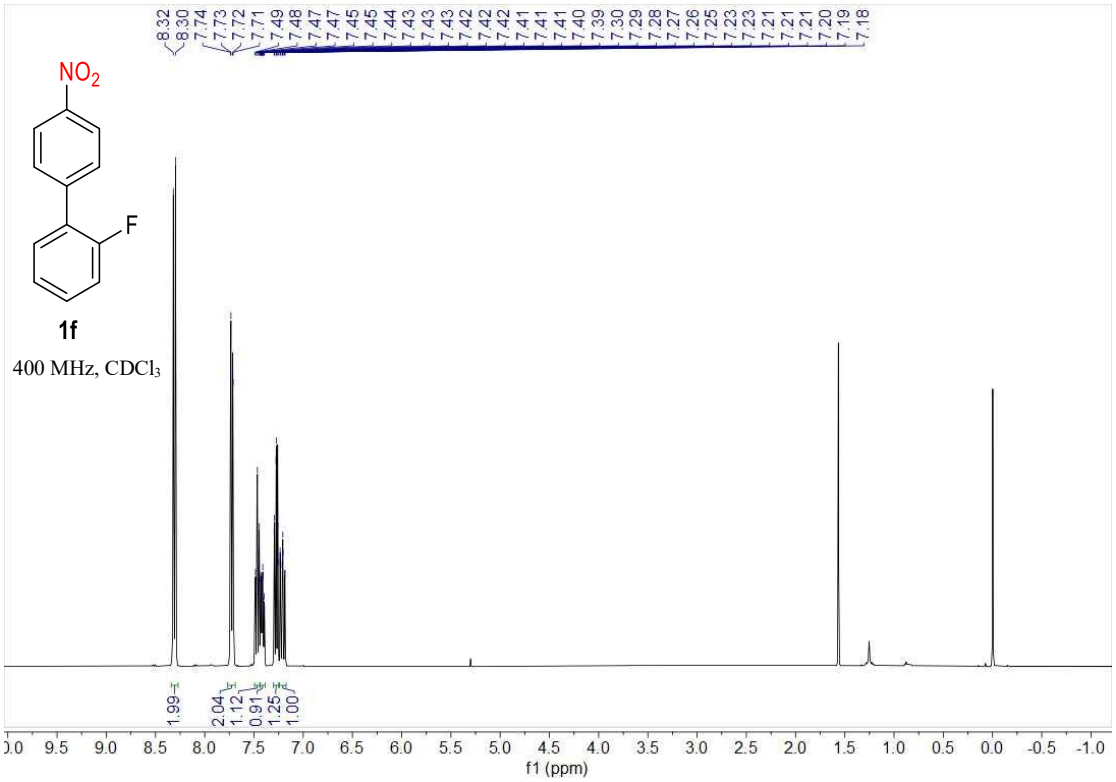
NO2
CF3
1d
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

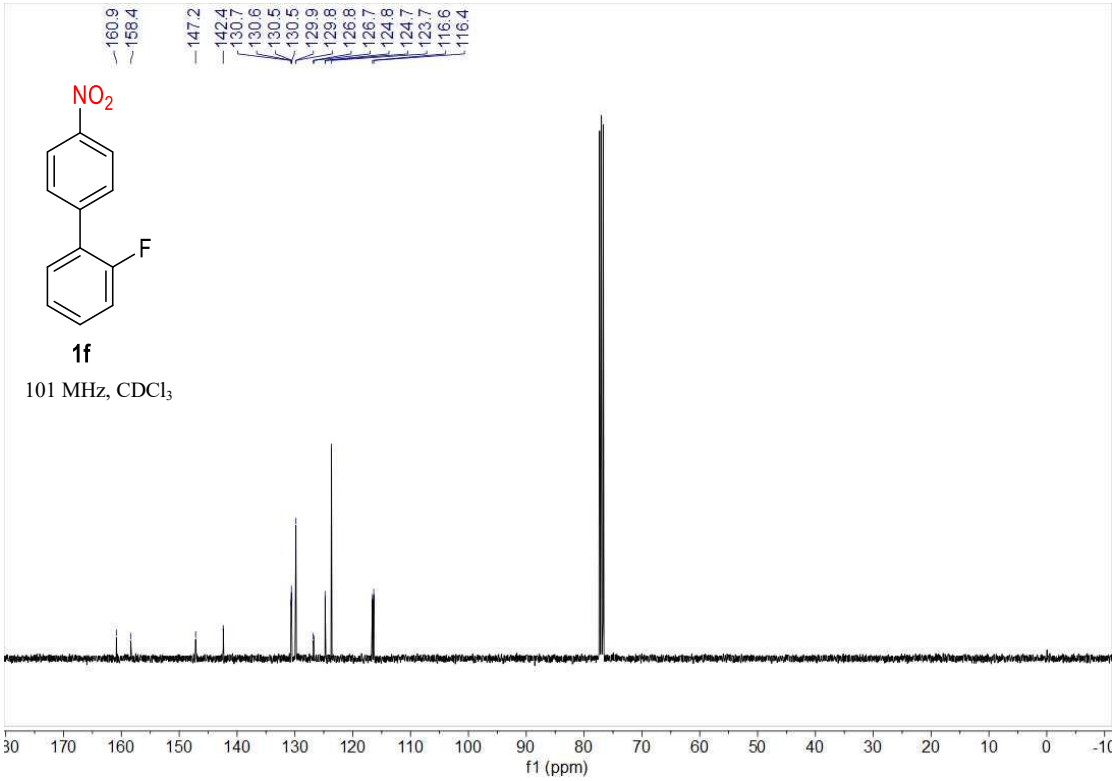
4'-nitro-[1,1'-biphenyl]-4-carbonitrile (1e)

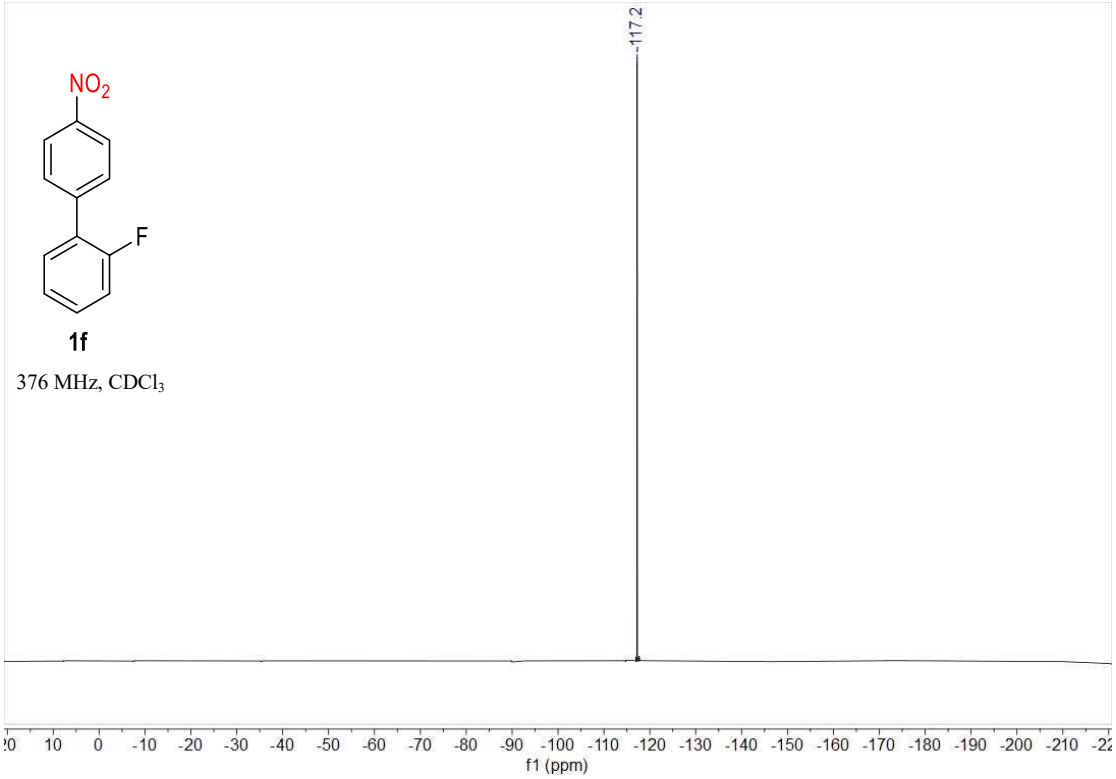




2-fluoro-4'-nitro-1,1'-biphenyl (1f)



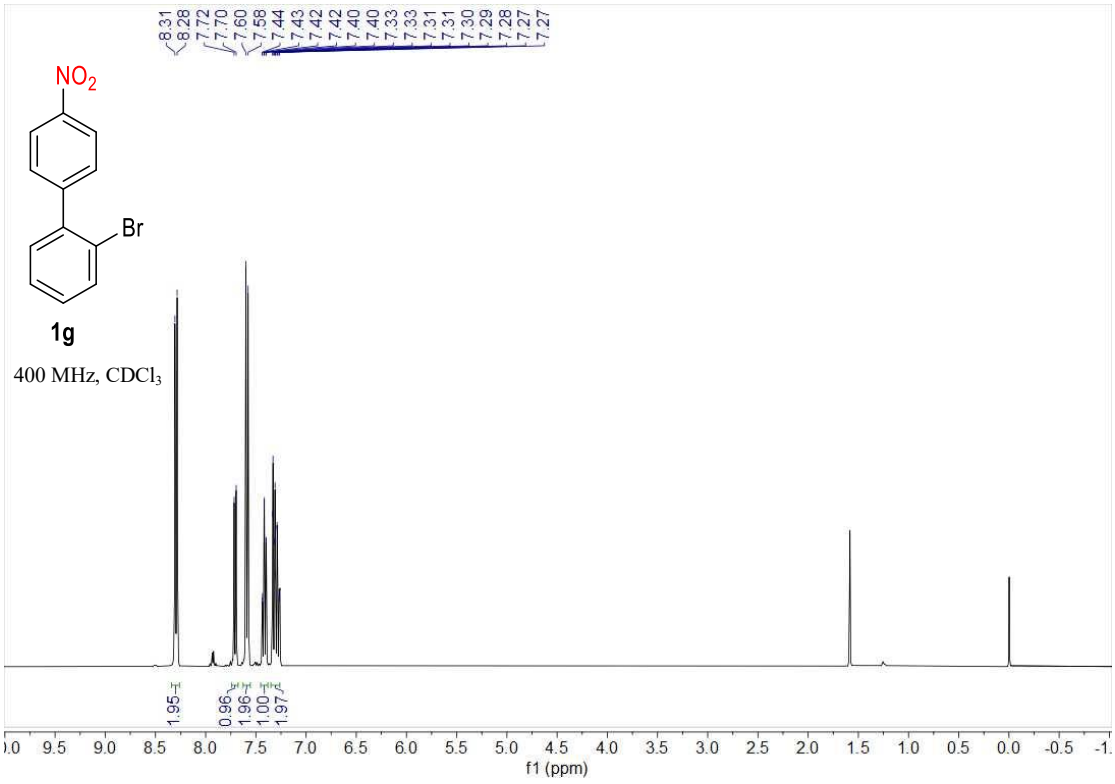


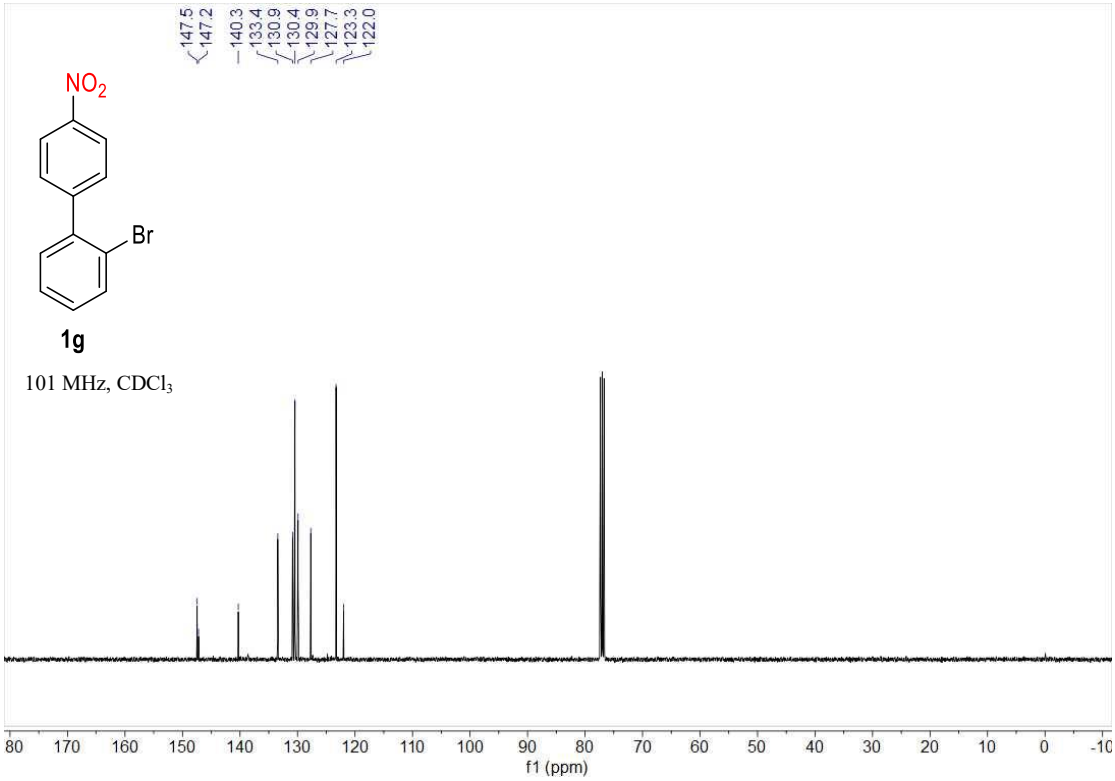


1f

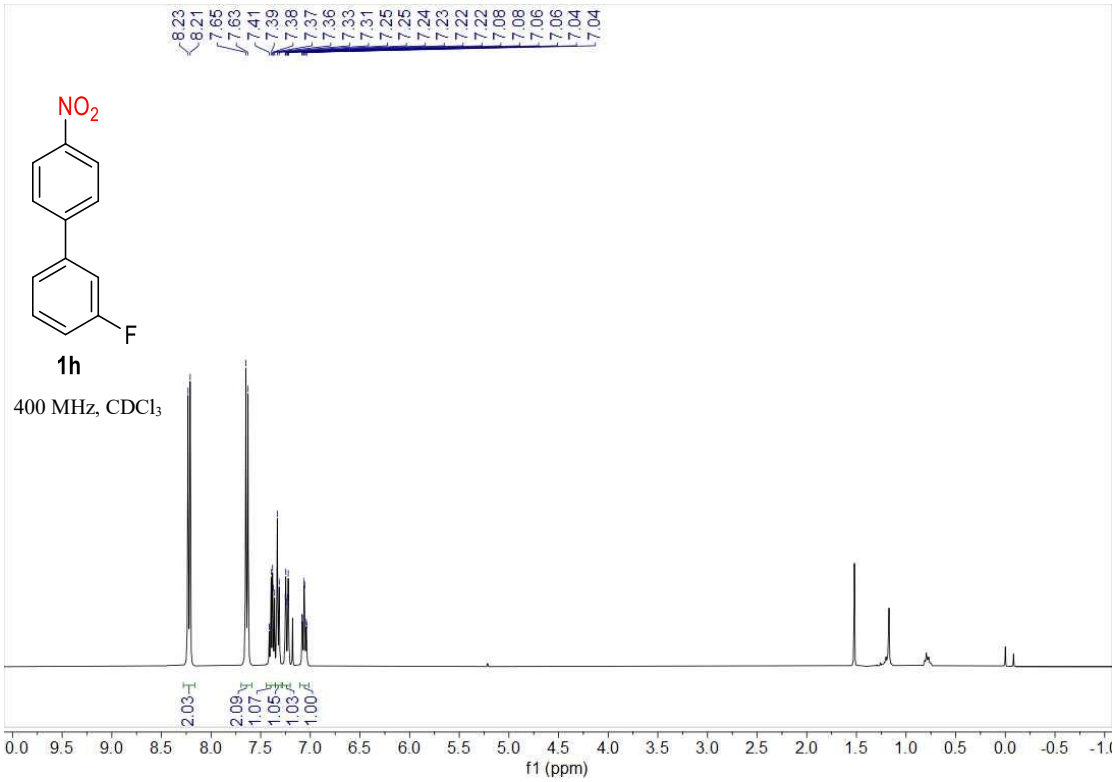
376 MHz, $CDCl_3$

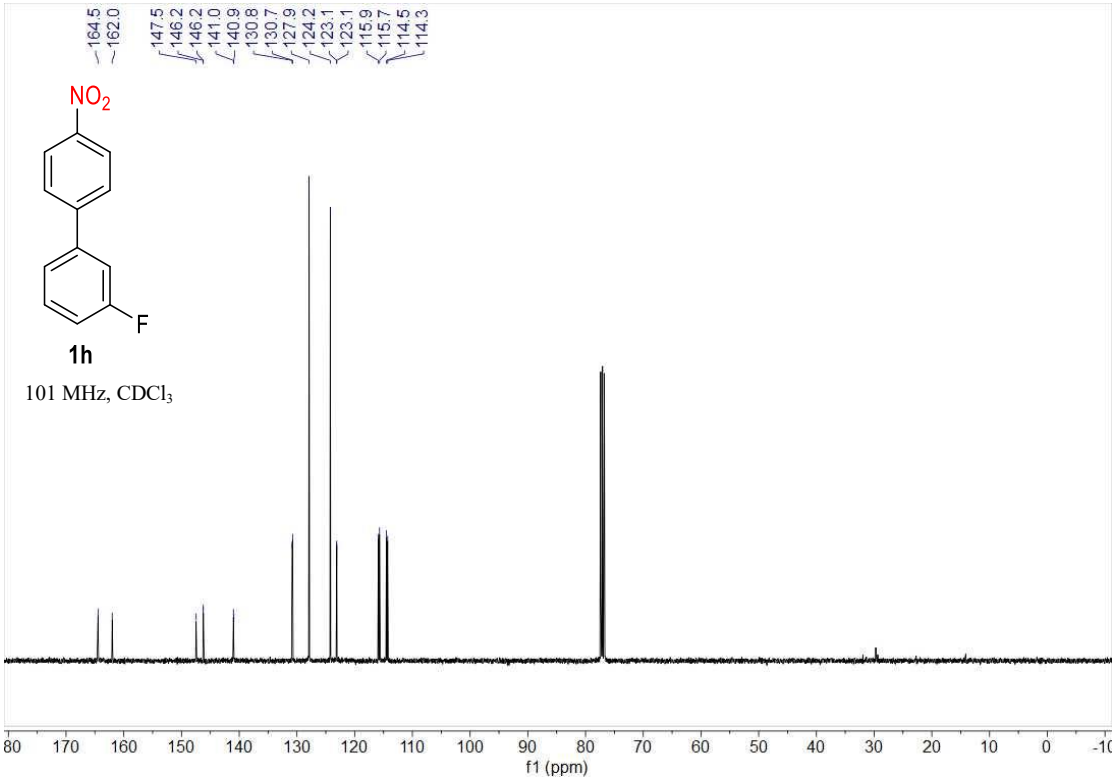
2-bromo-4'-nitro-1,1'-biphenyl (1g)

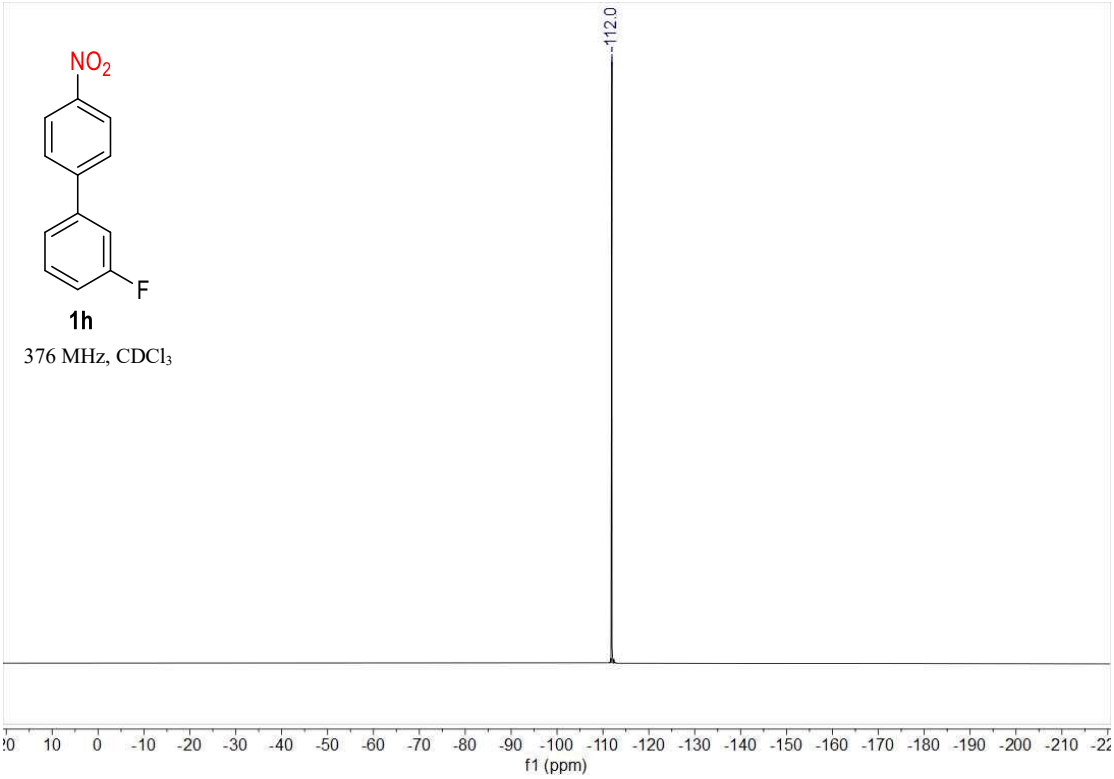




3-fluoro-4'-nitro-1,1'-biphenyl (1h)



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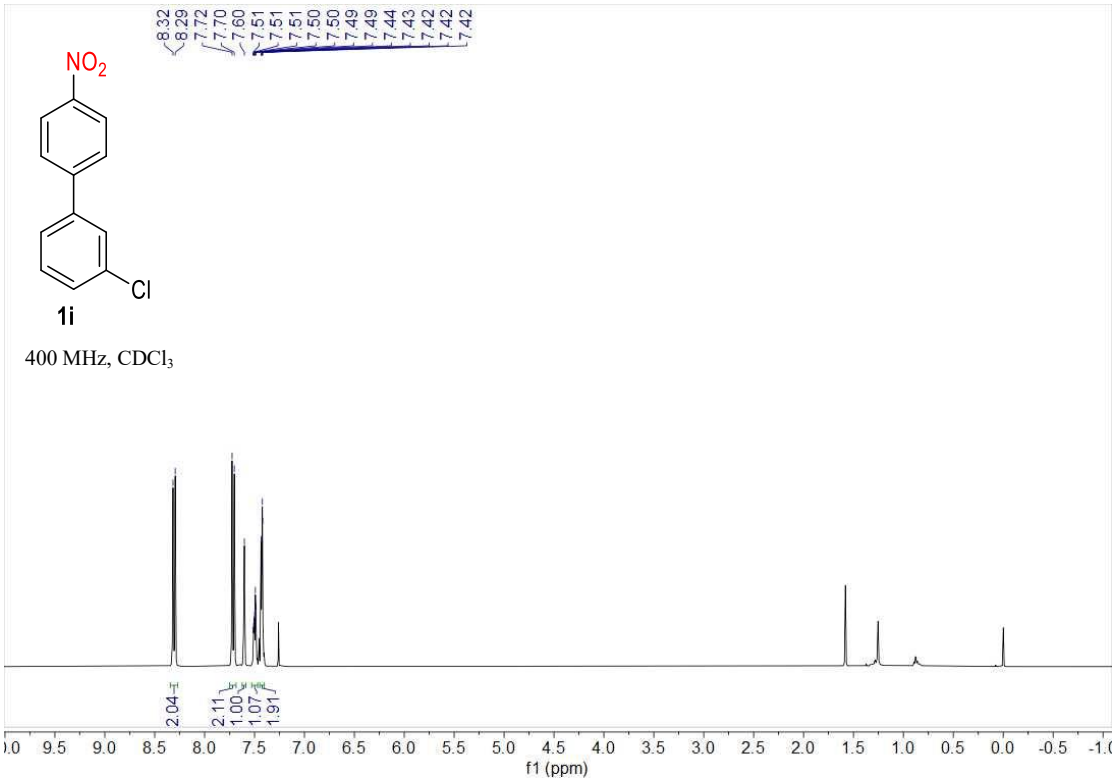
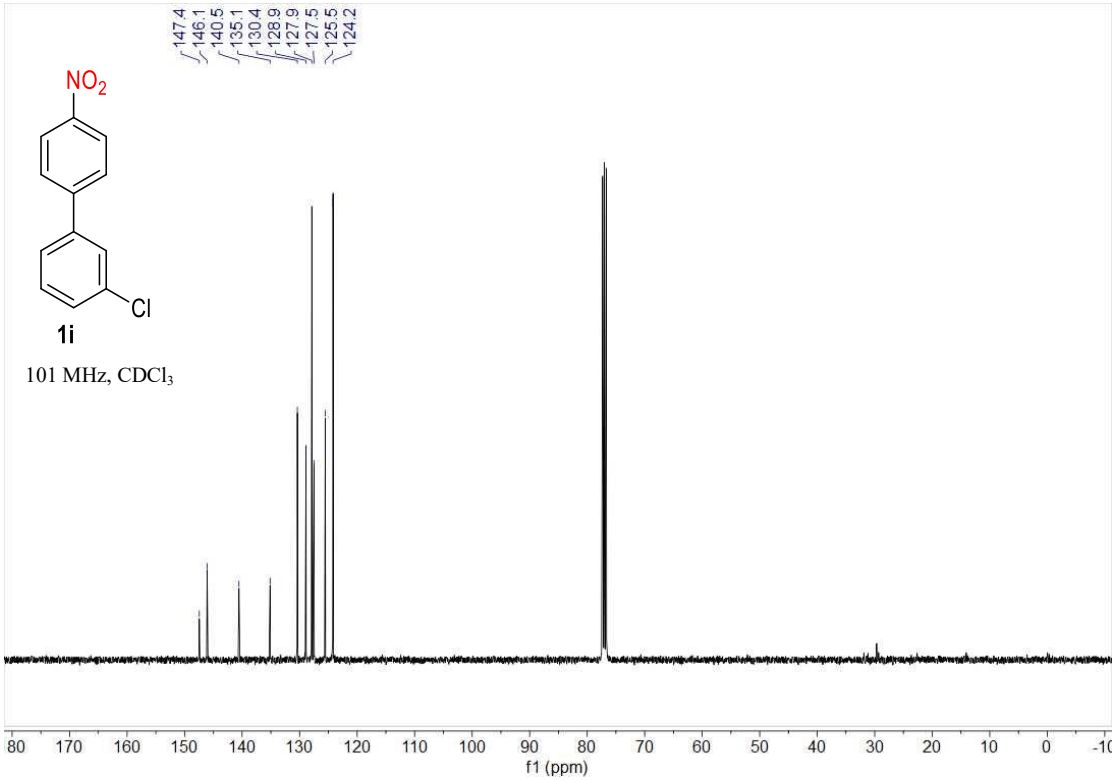
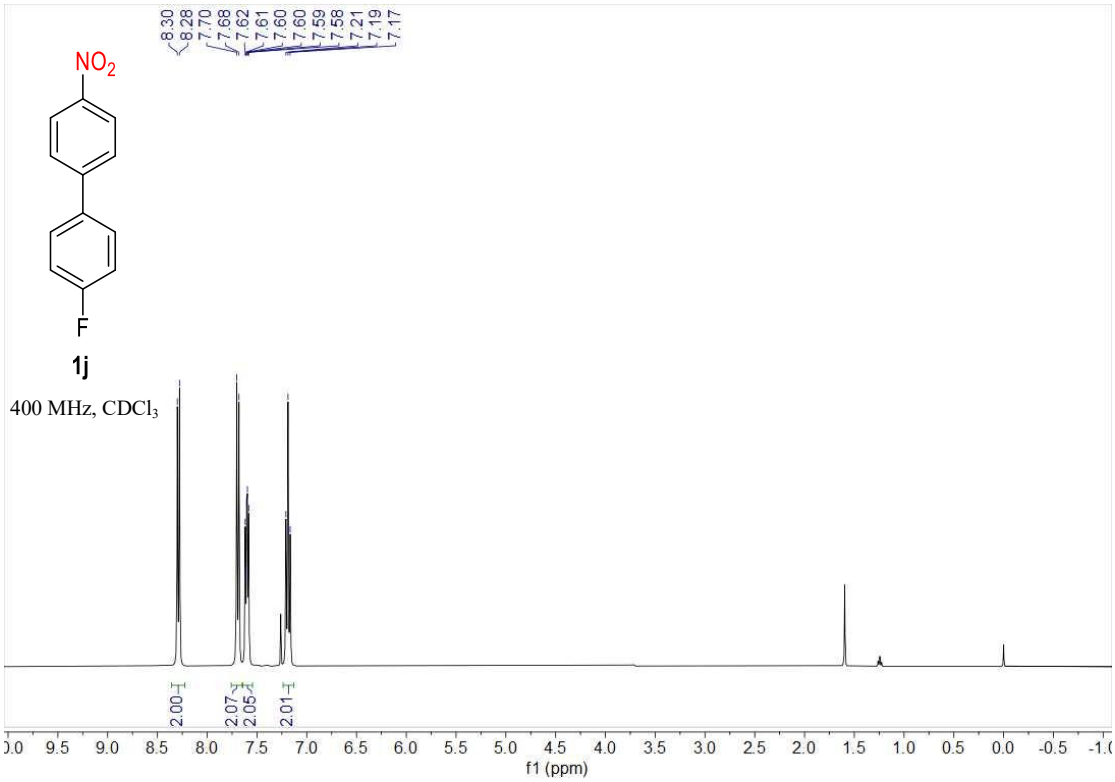
376 MHz, CDCl3
-112.0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

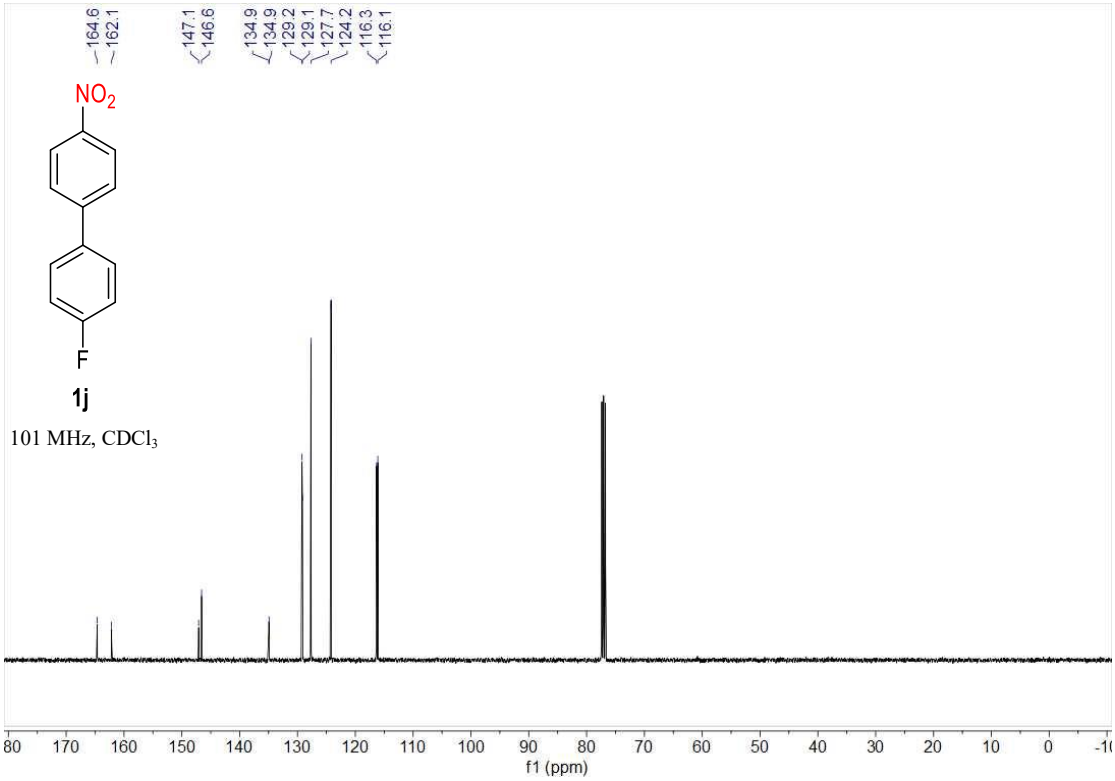
3-chloro-4'-nitro-1,1'-biphenyl (1i)

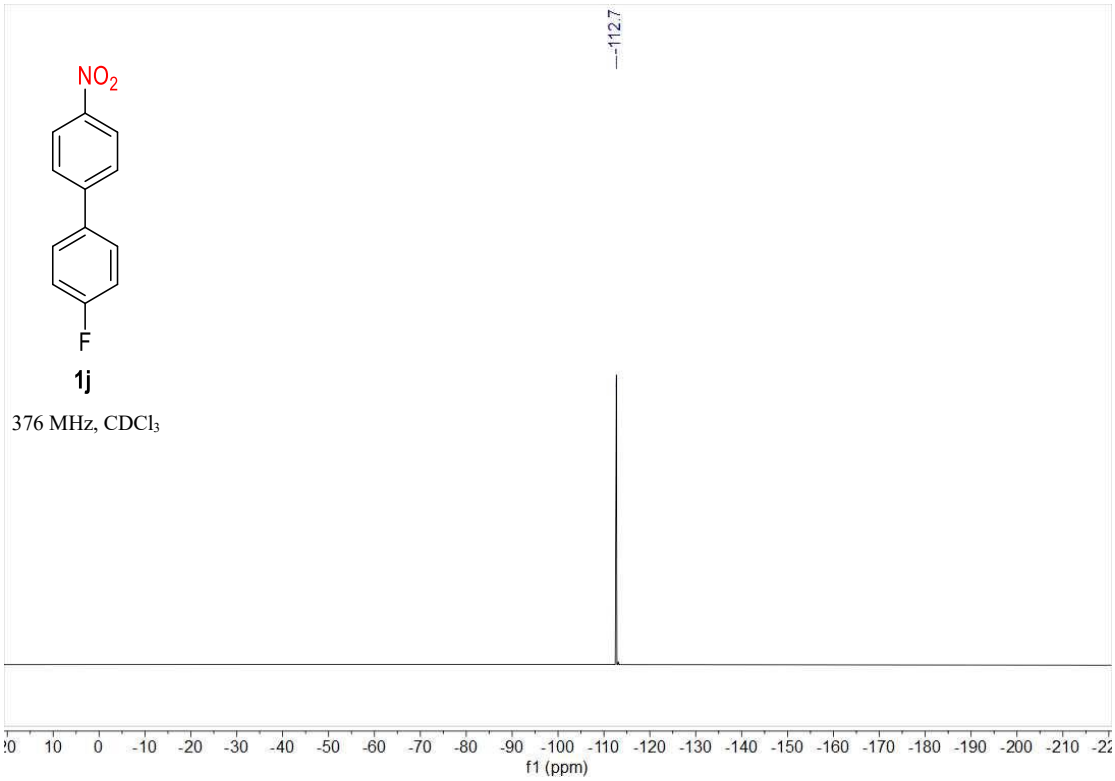




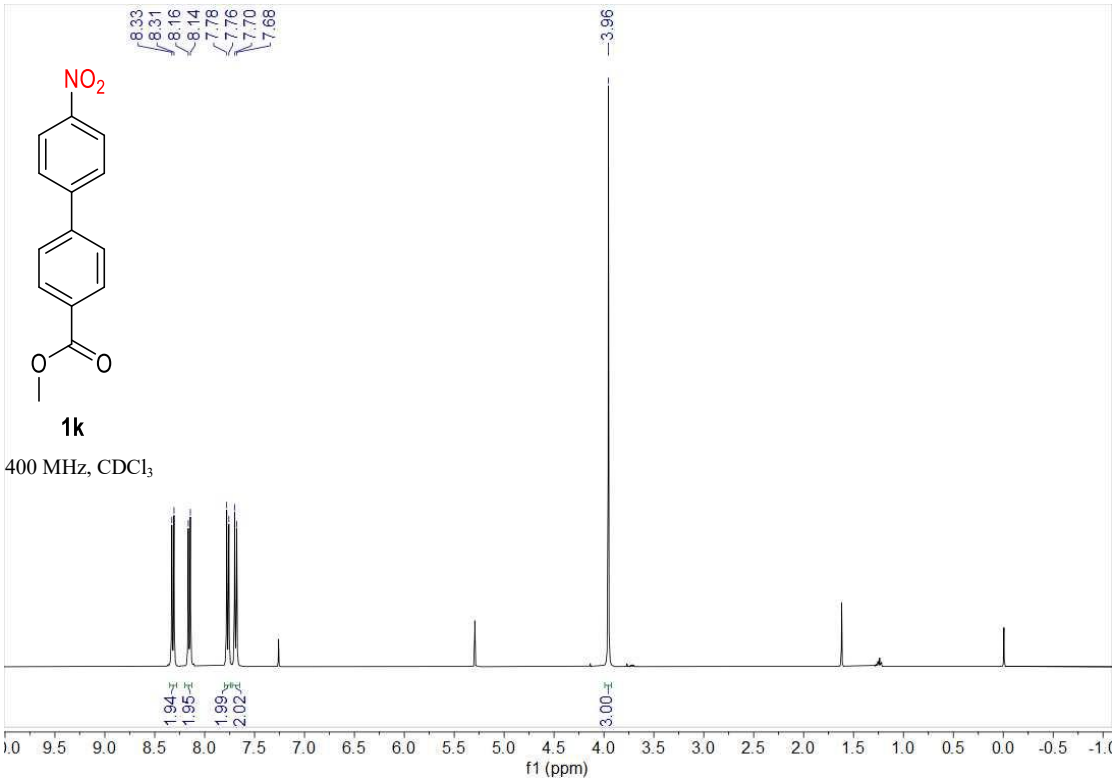
4-fluoro-4'-nitro-1,1'-biphenyl (1j)

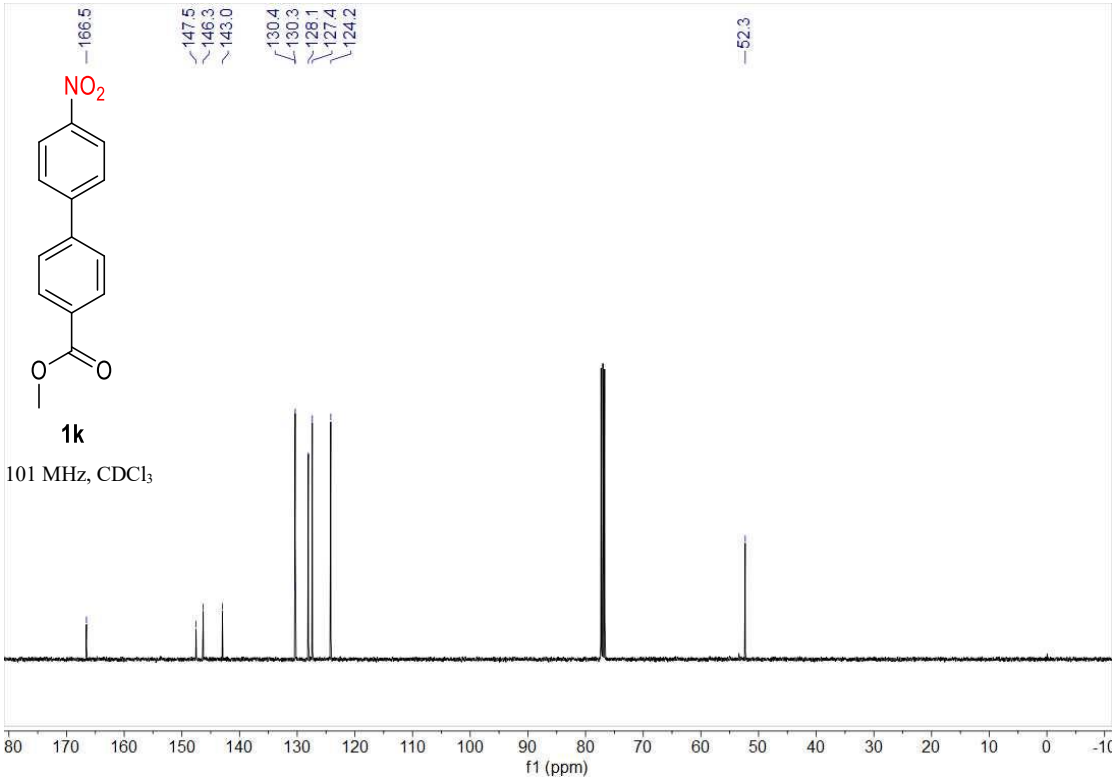




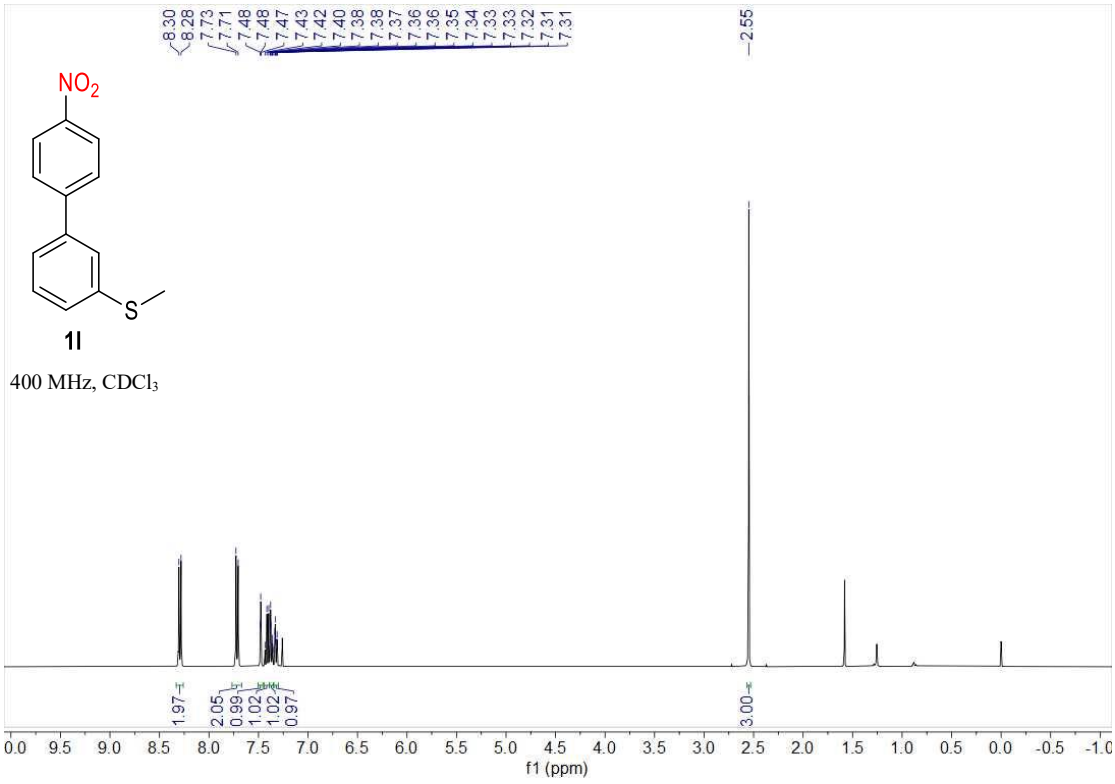

NO2
F
-112.7
1j
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

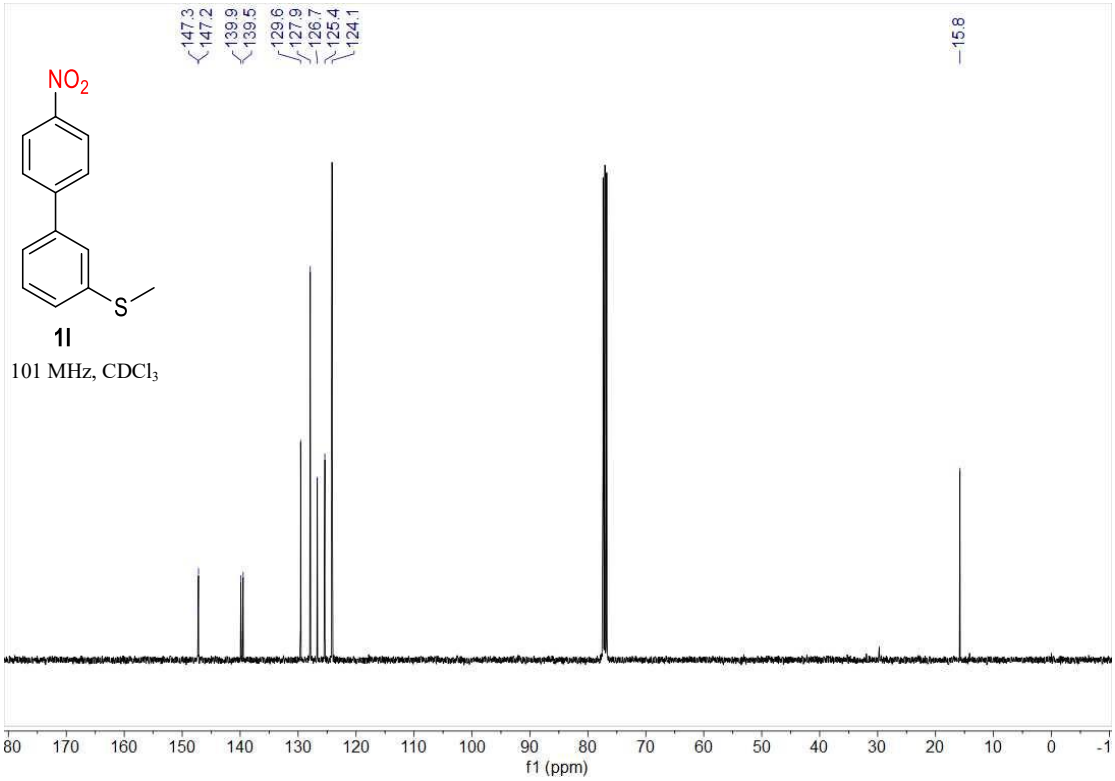
methyl 4'-nitro-[1,1'-biphenyl]-4-carboxylate (1k)



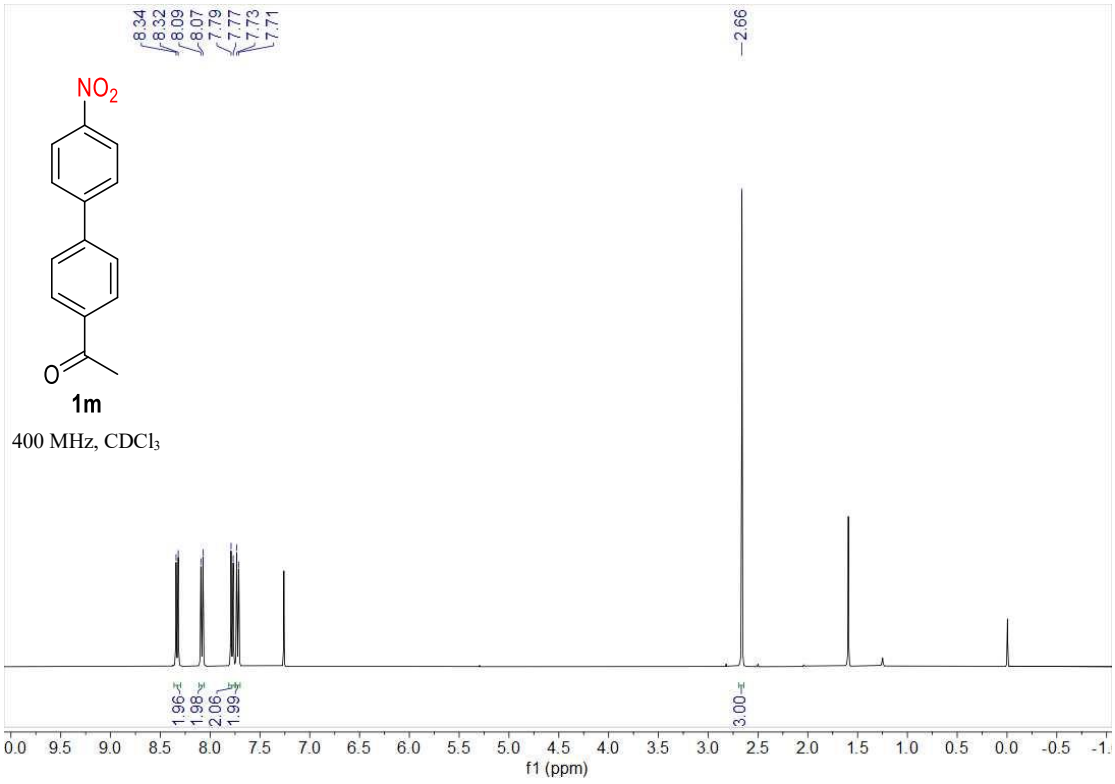


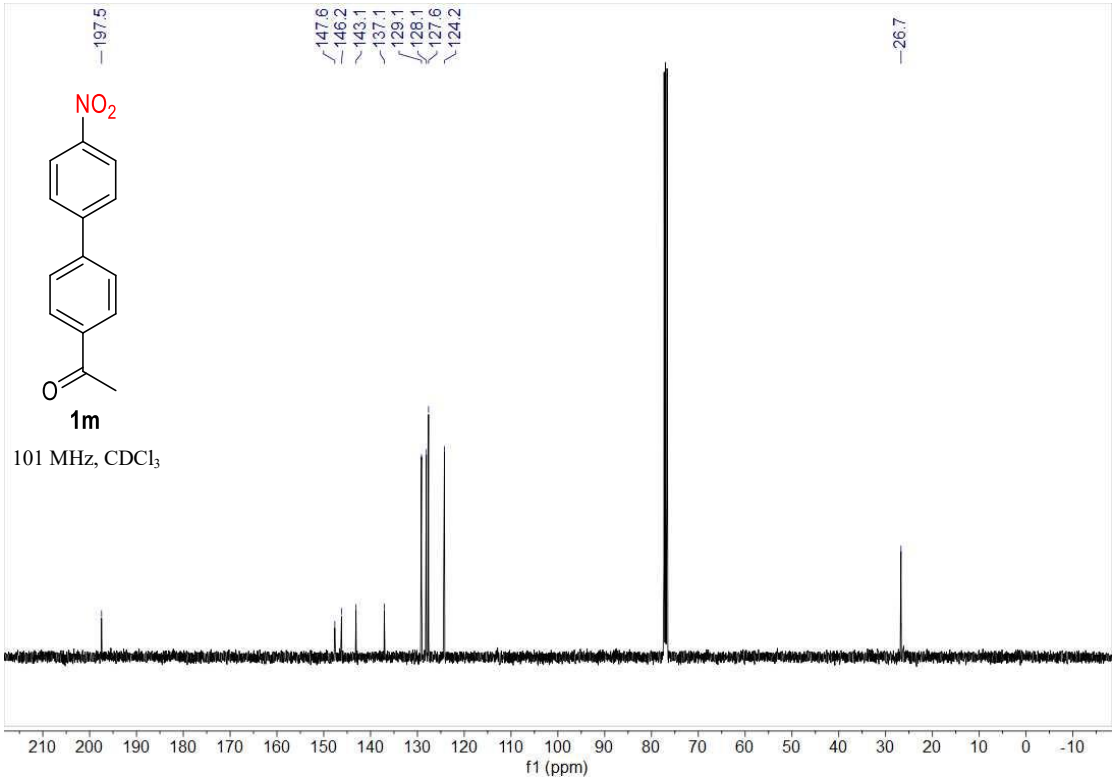
methyl(4'-nitro-[1,1'-biphenyl]-3-yl)sulfane (1l)



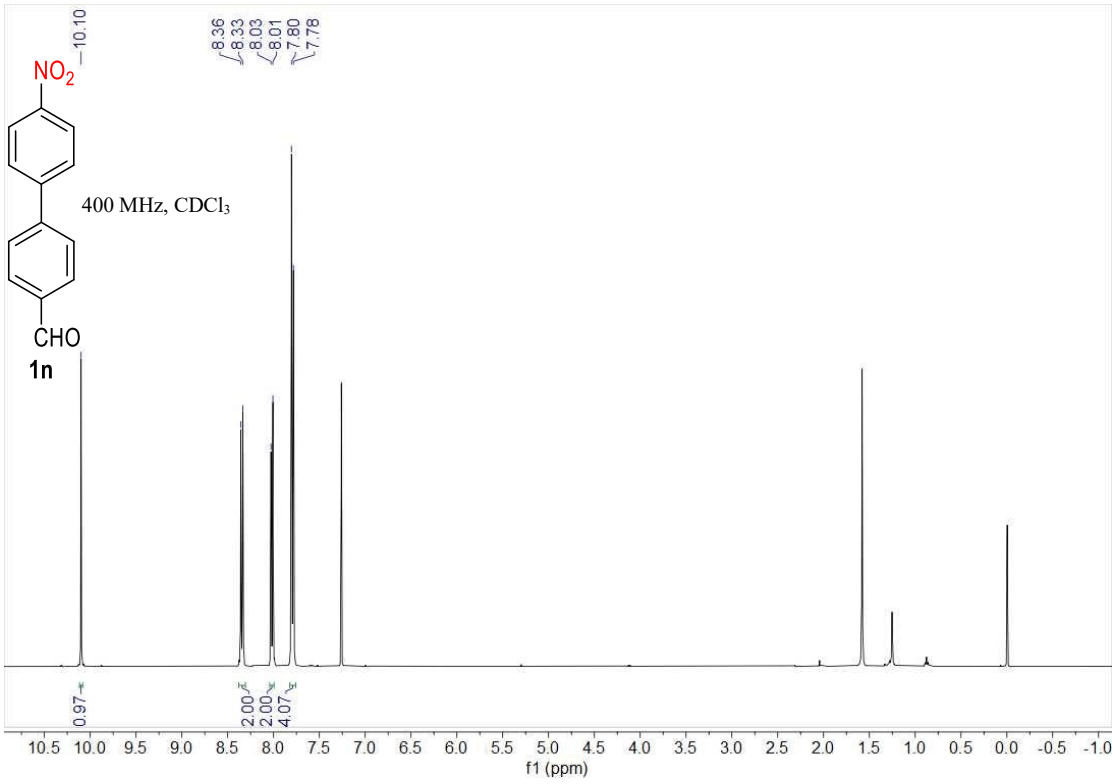


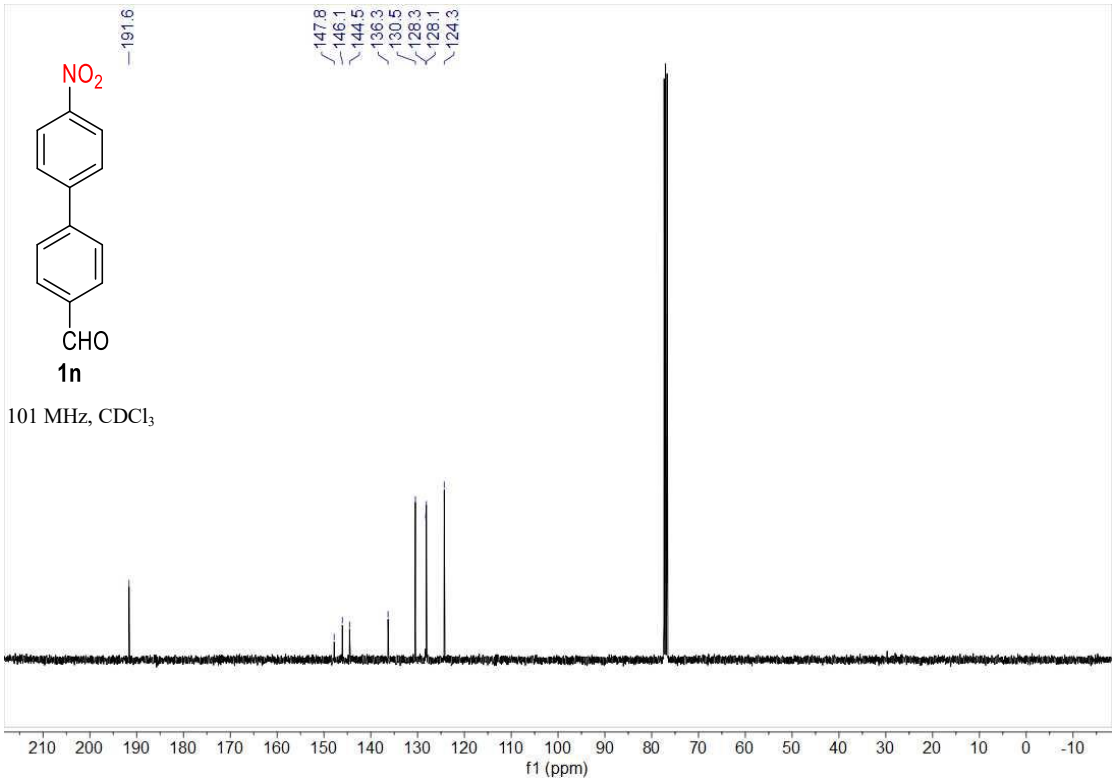
1-(4'-nitro-[1,1'-biphenyl]-4-yl)ethan-1-one (1m)



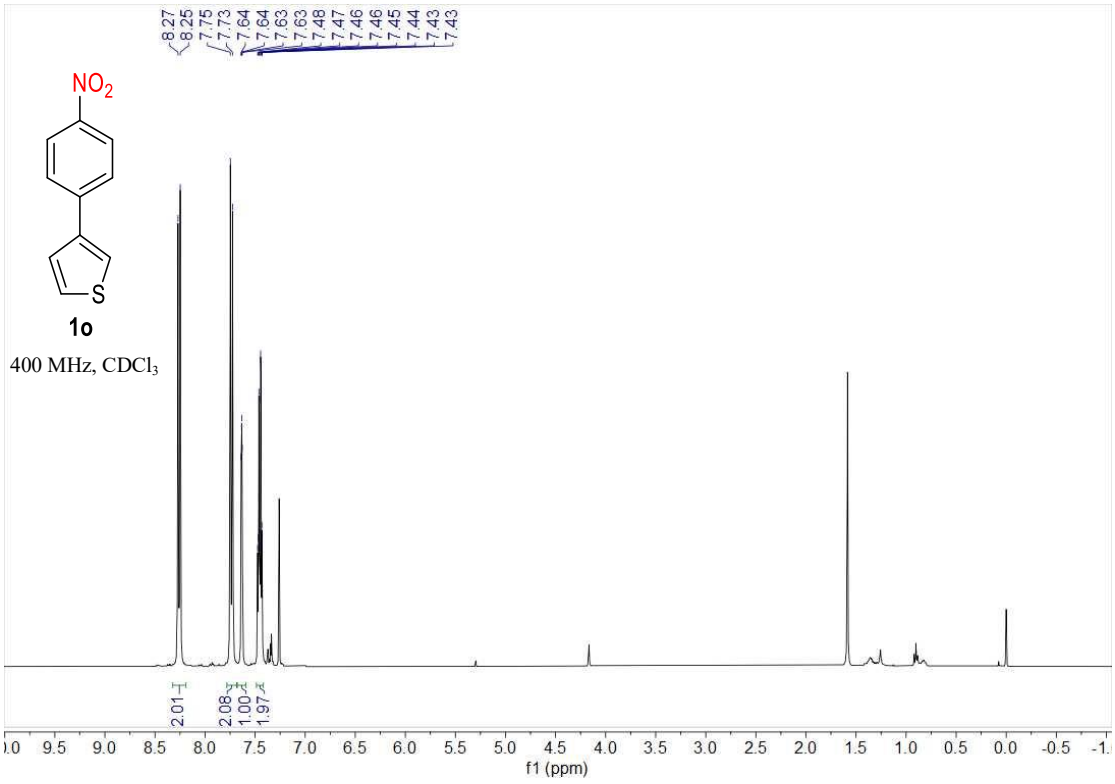


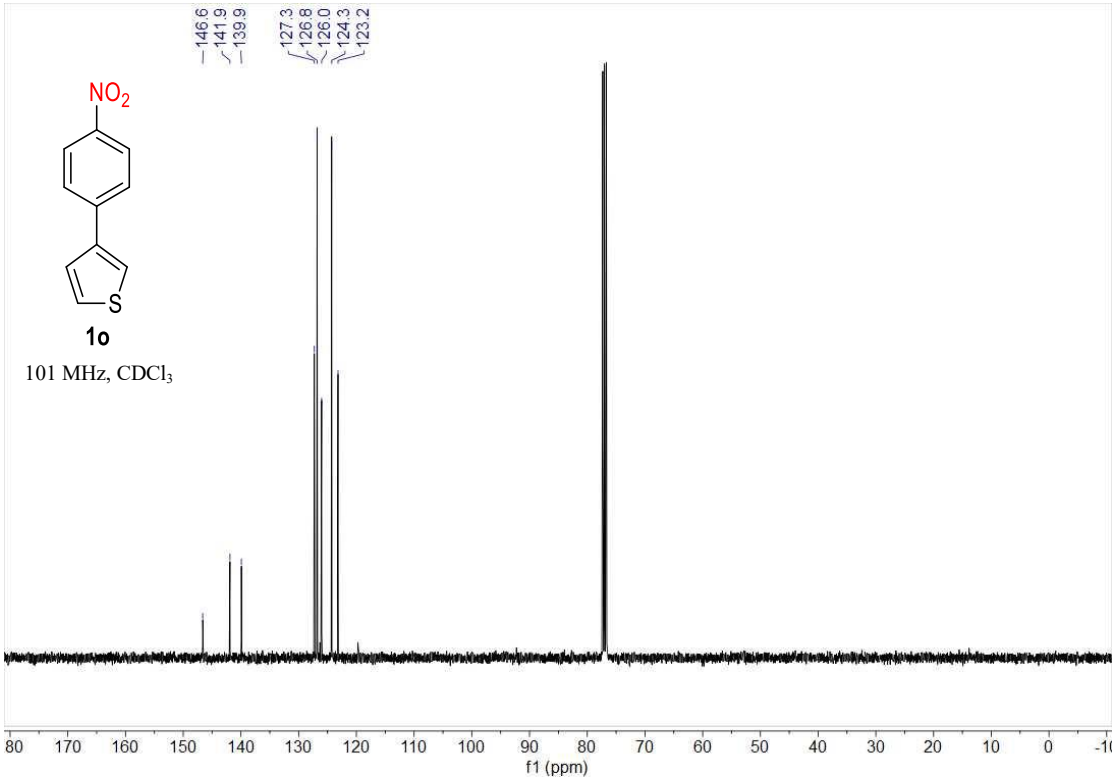
4'-nitro-[1,1'-biphenyl]-4-carbaldehyde (1n)



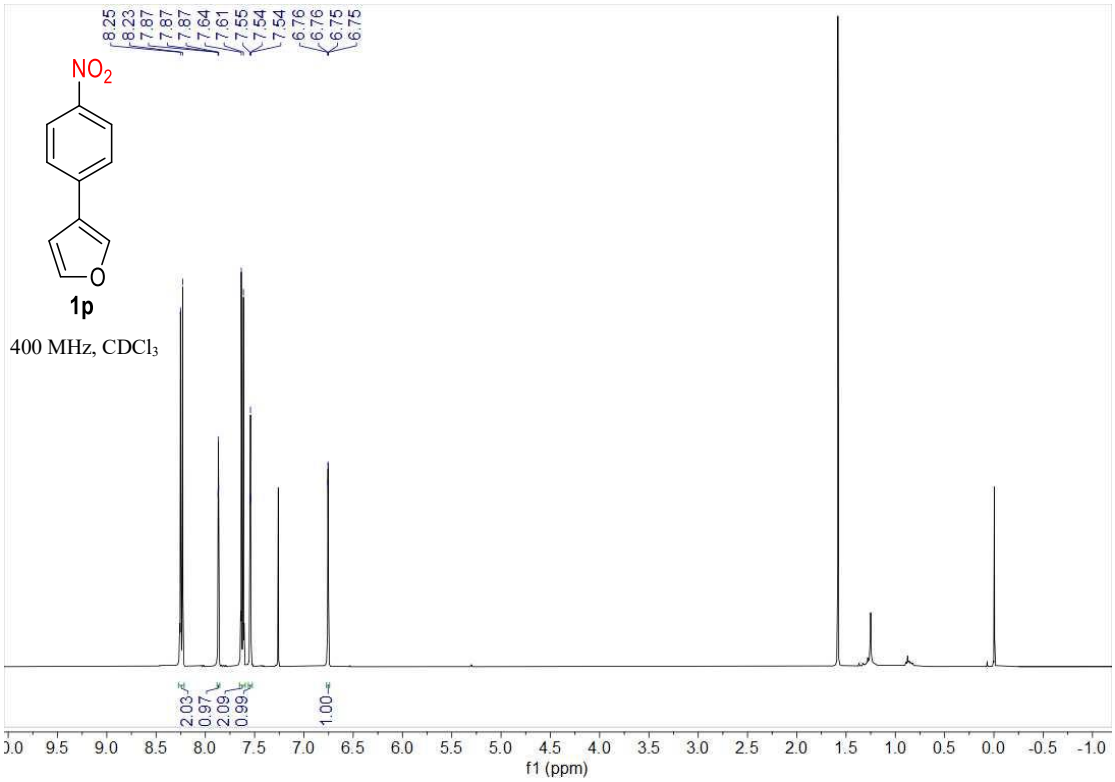


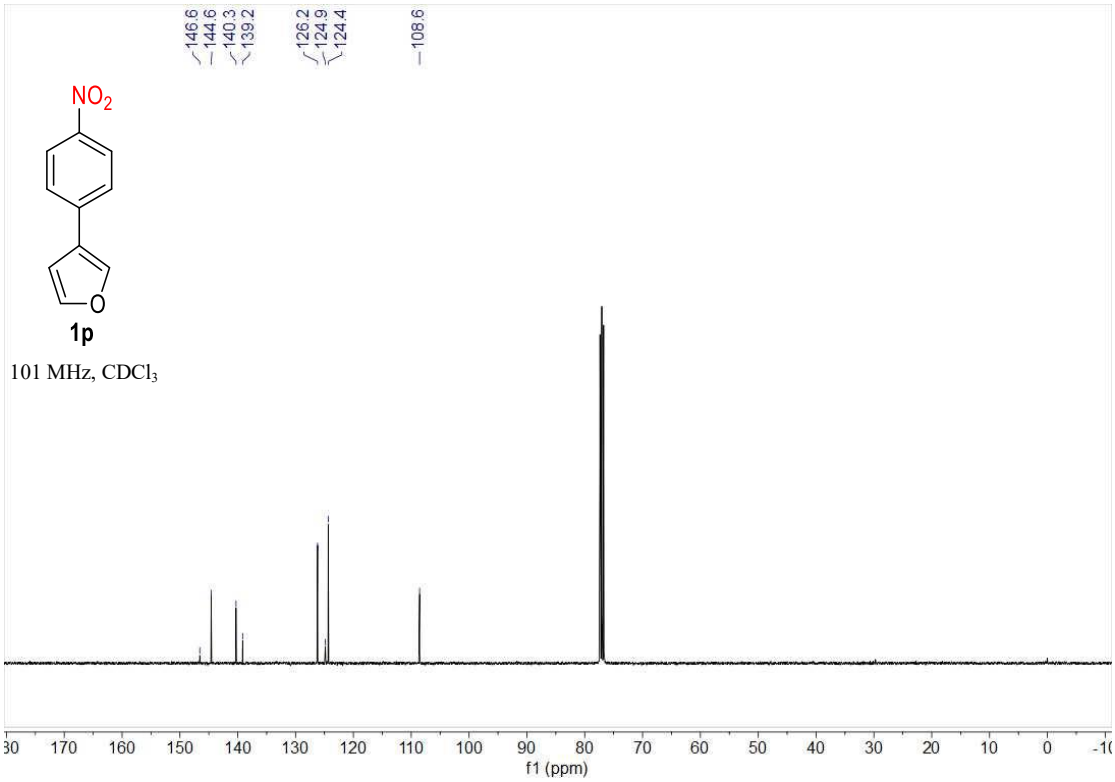
3-(4-nitrophenyl)thiophene (1o)



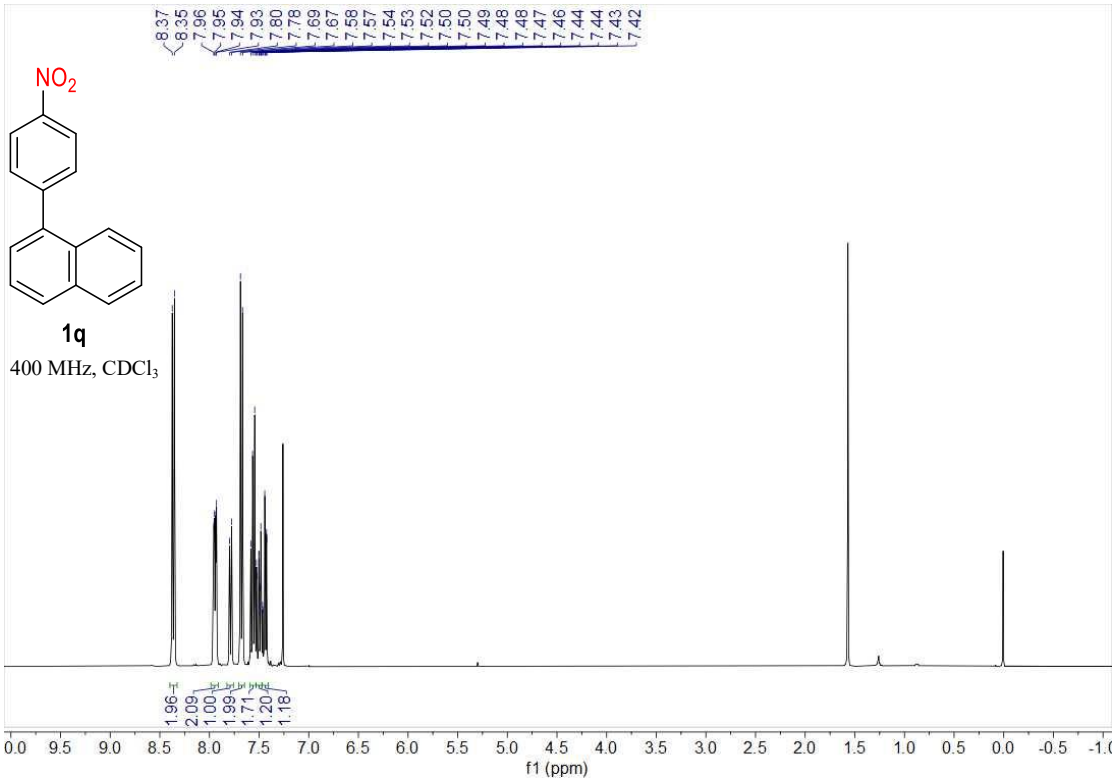


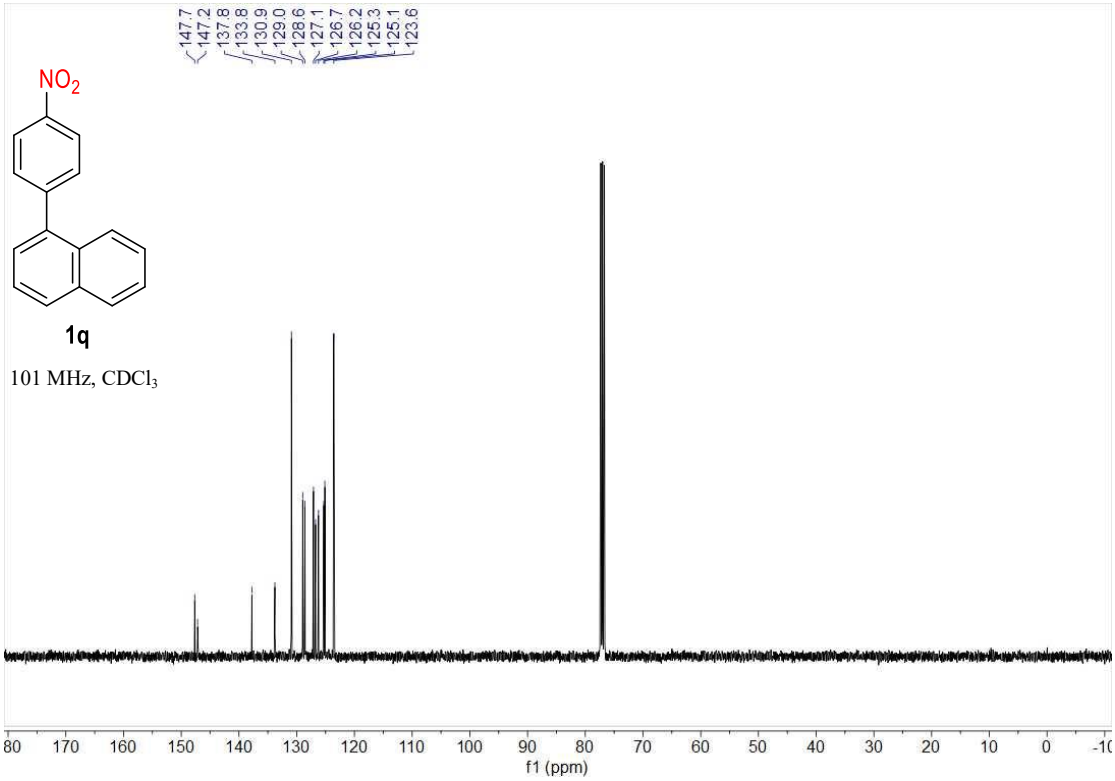
3-(4-nitrophenyl)furan (1p)



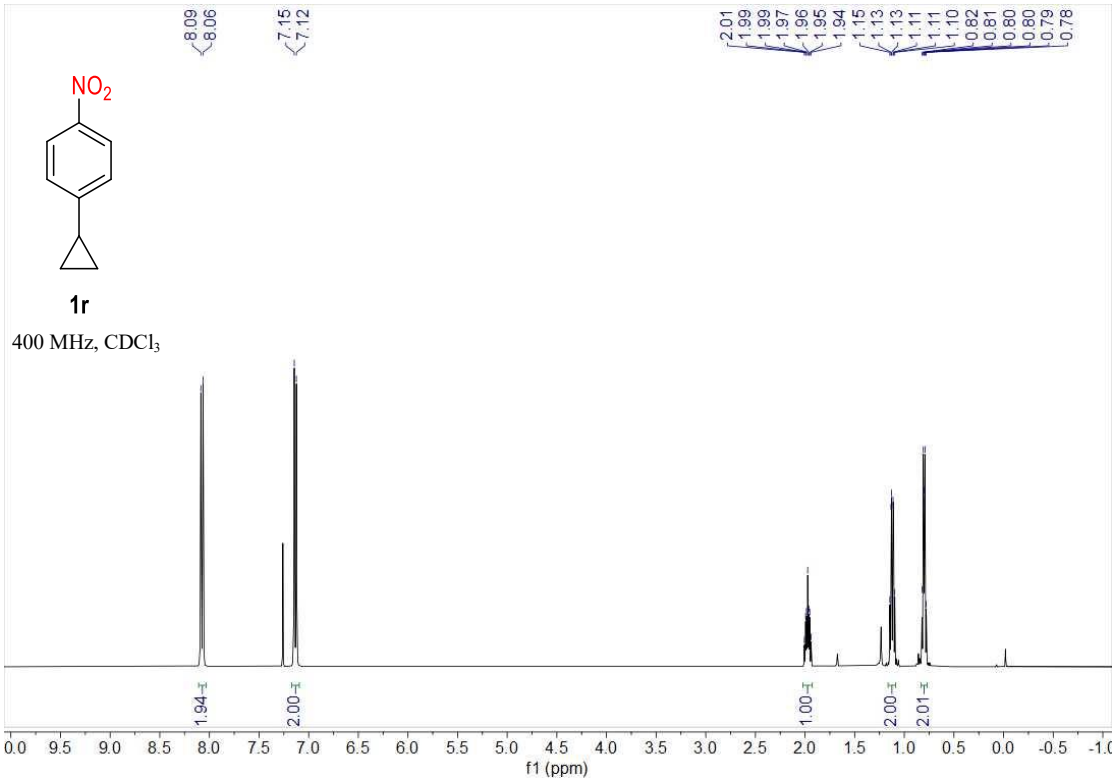


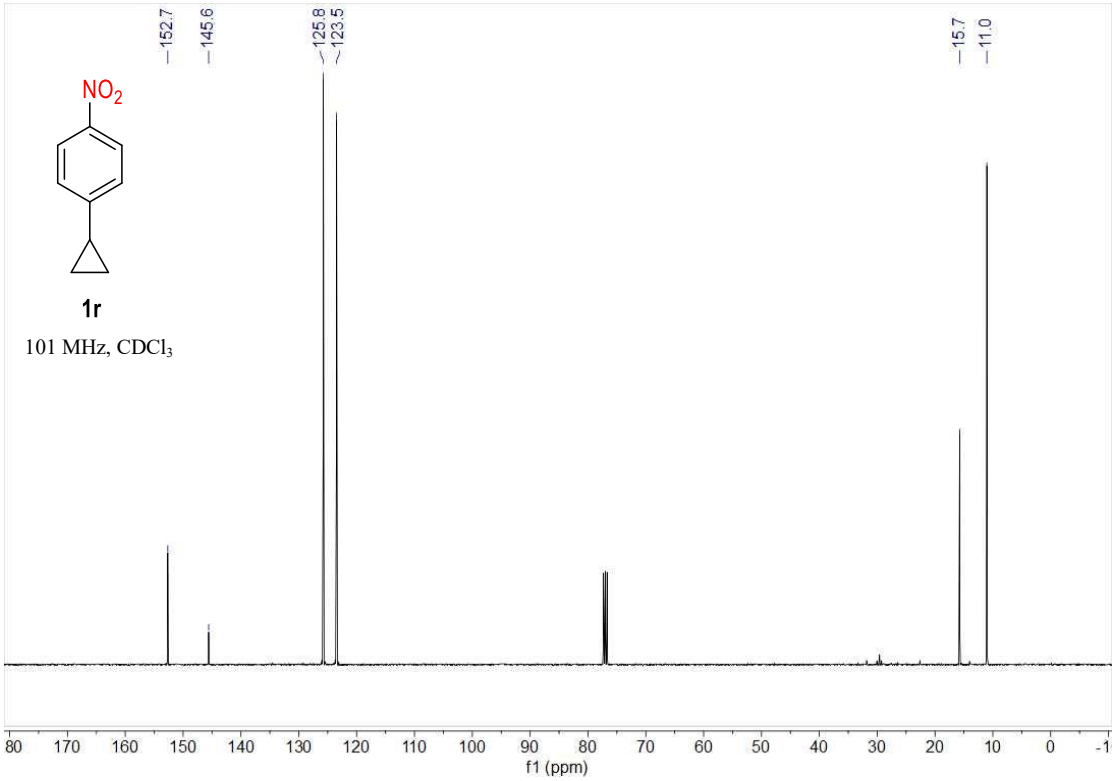
1-(4-nitrophenyl)naphthalene (1q)



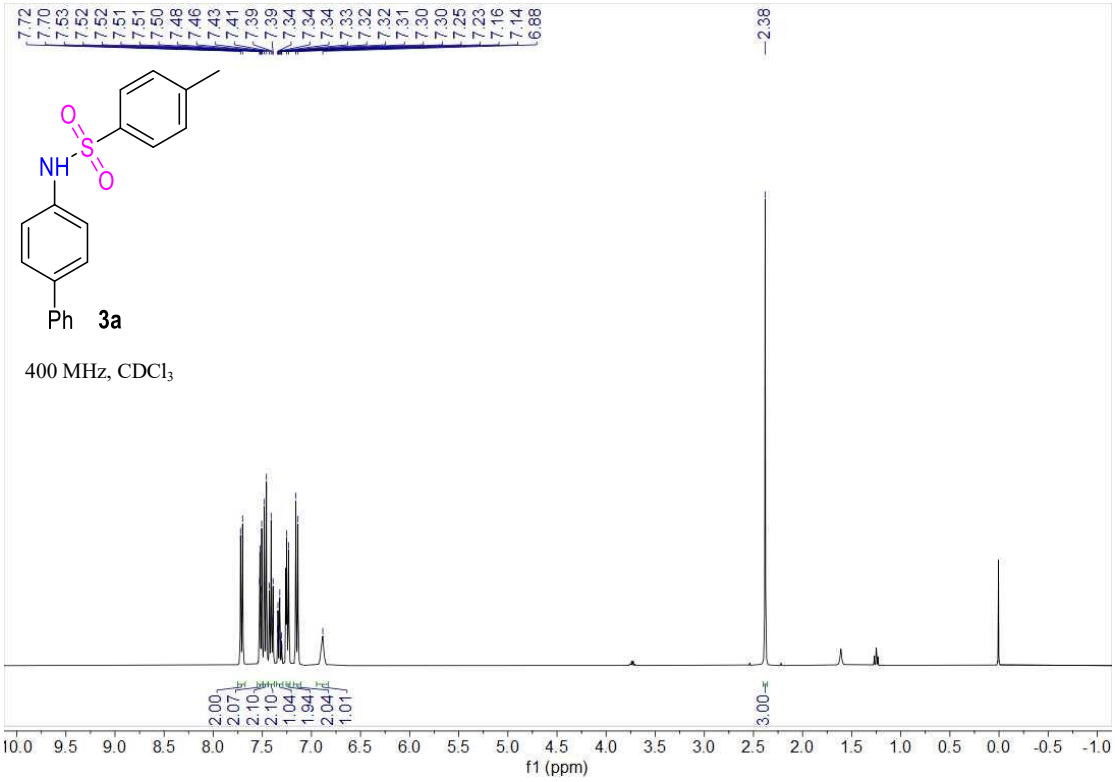


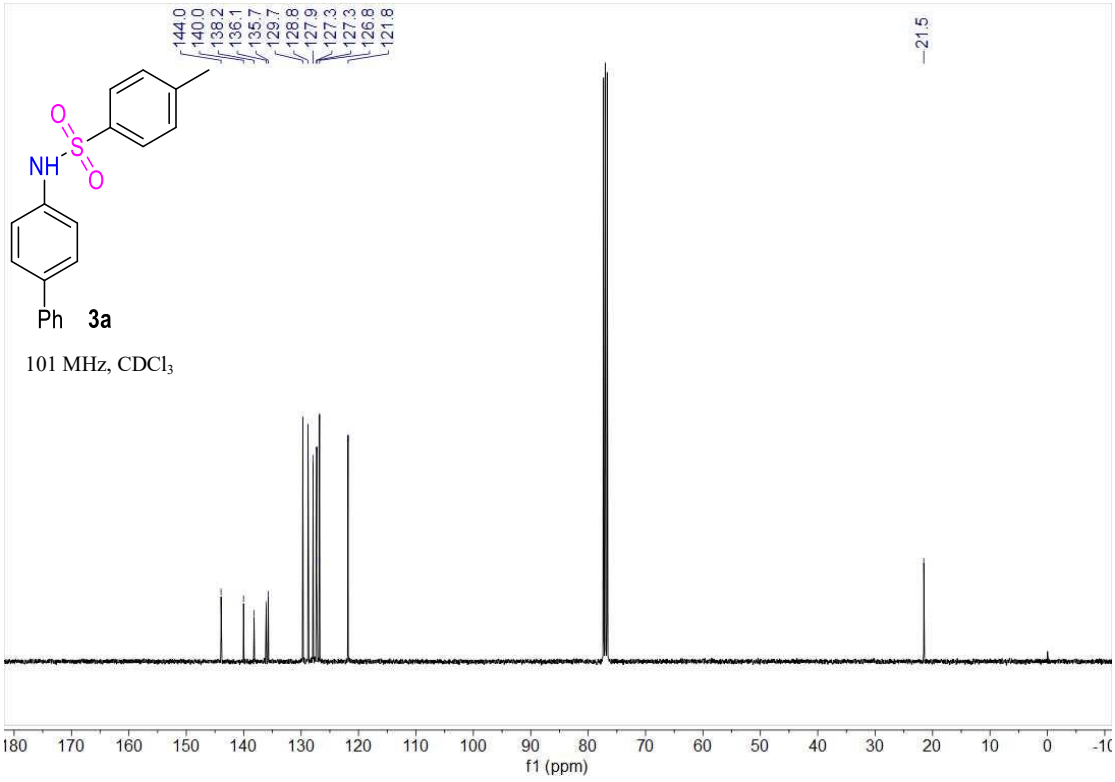
4'-nitro-[1,1'-biphenyl]-4-carbaldehyde (1r)



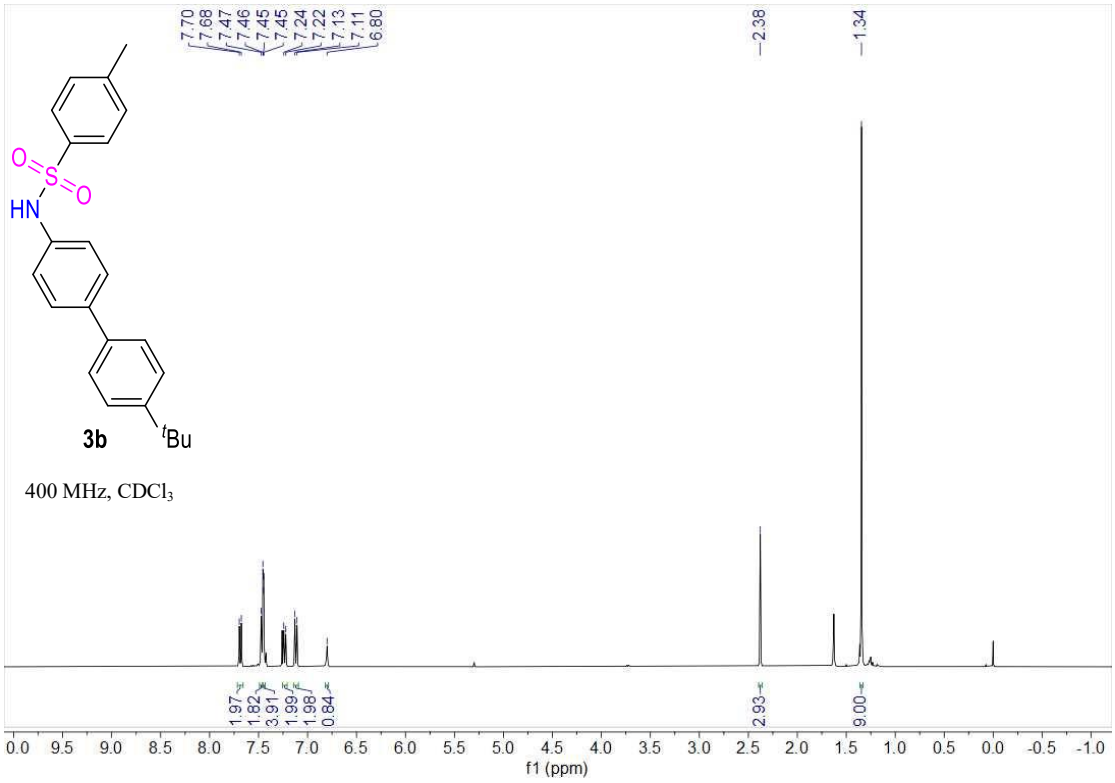


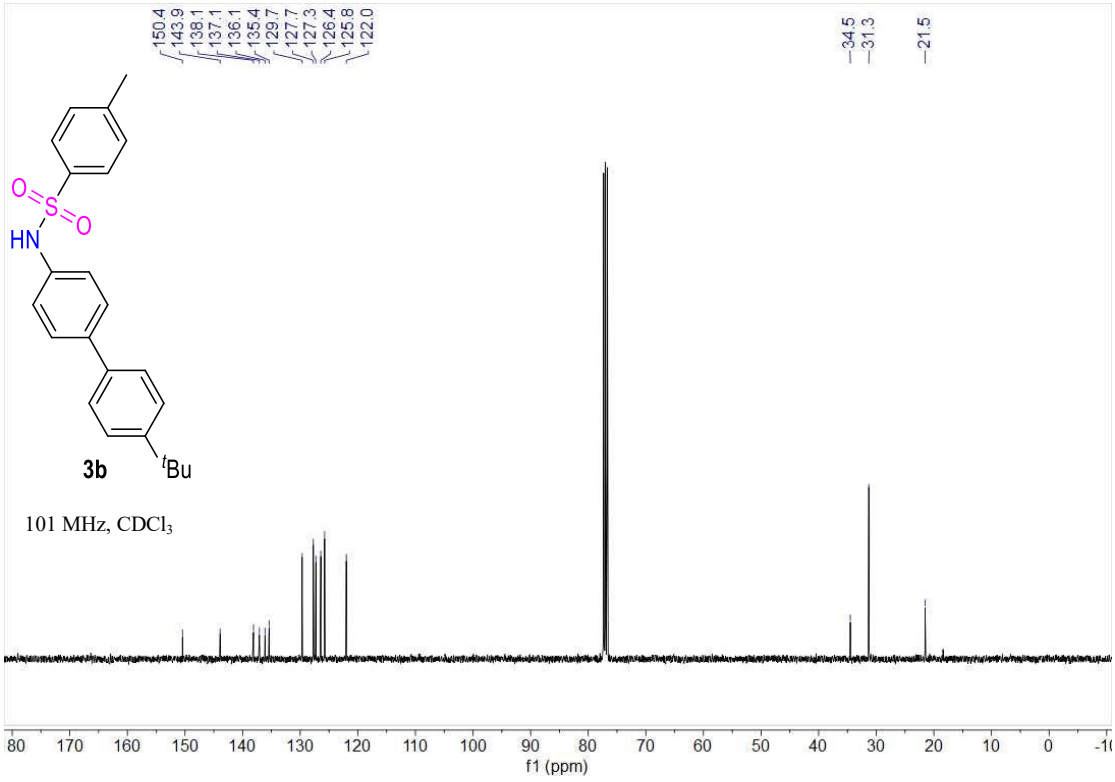
N-([1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3a)



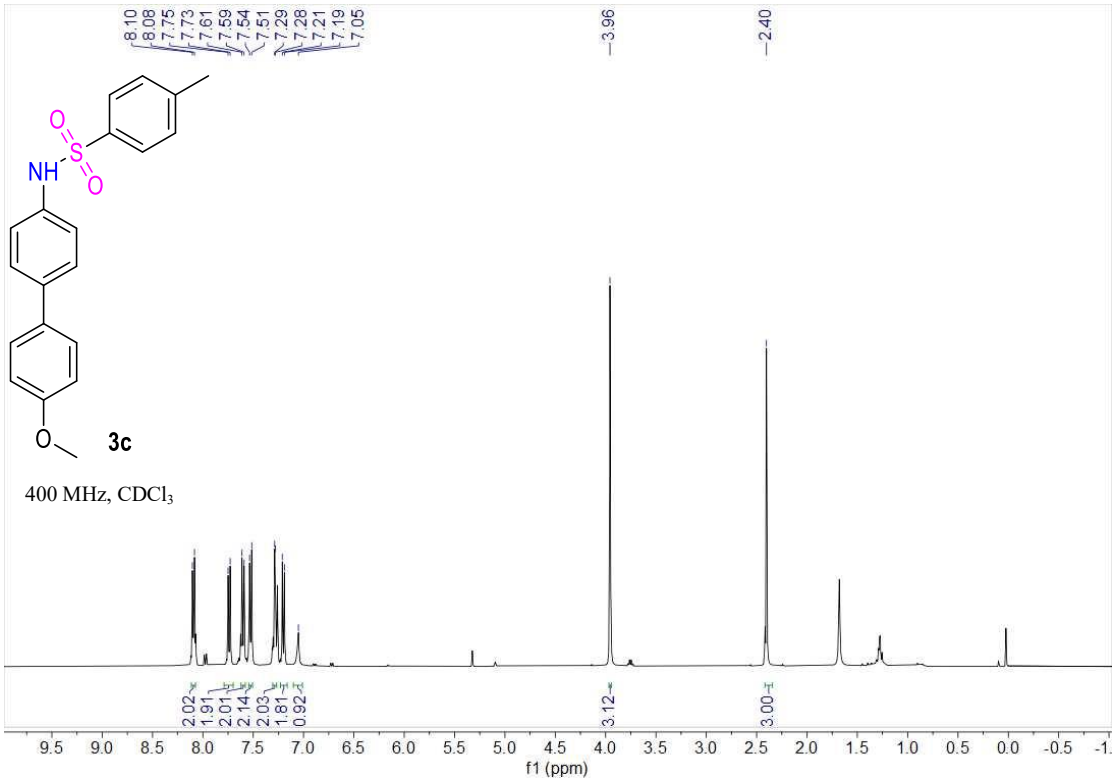


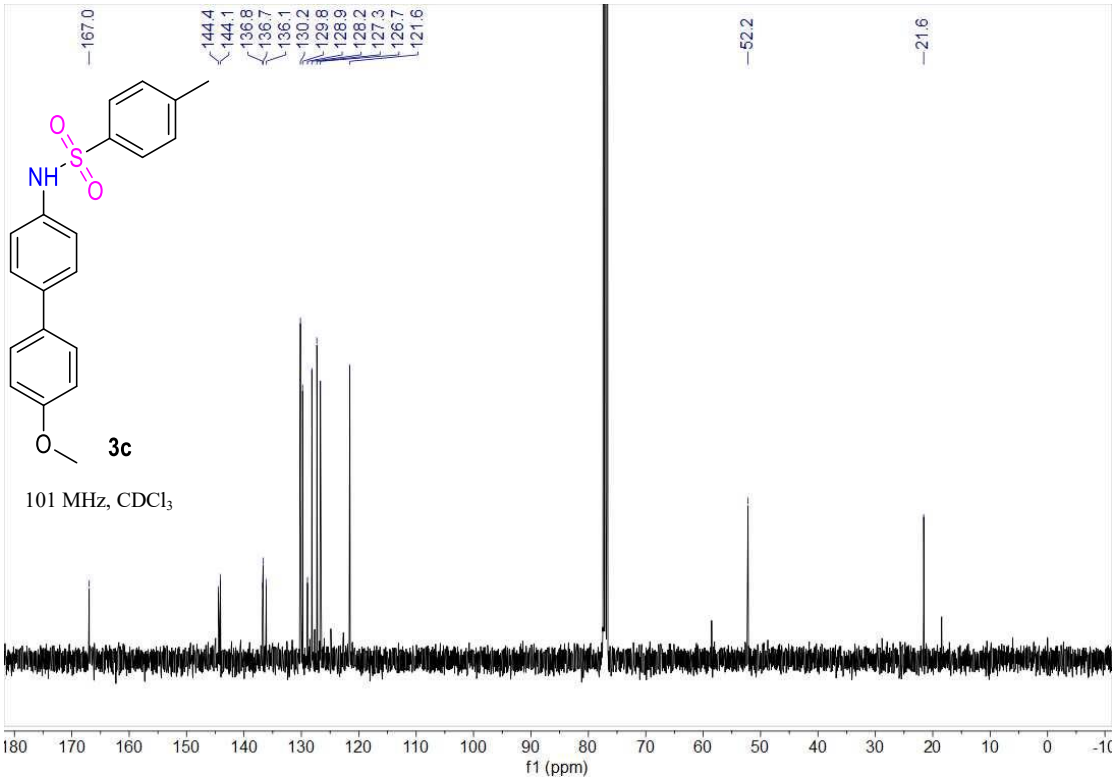
***N*-(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3b)**



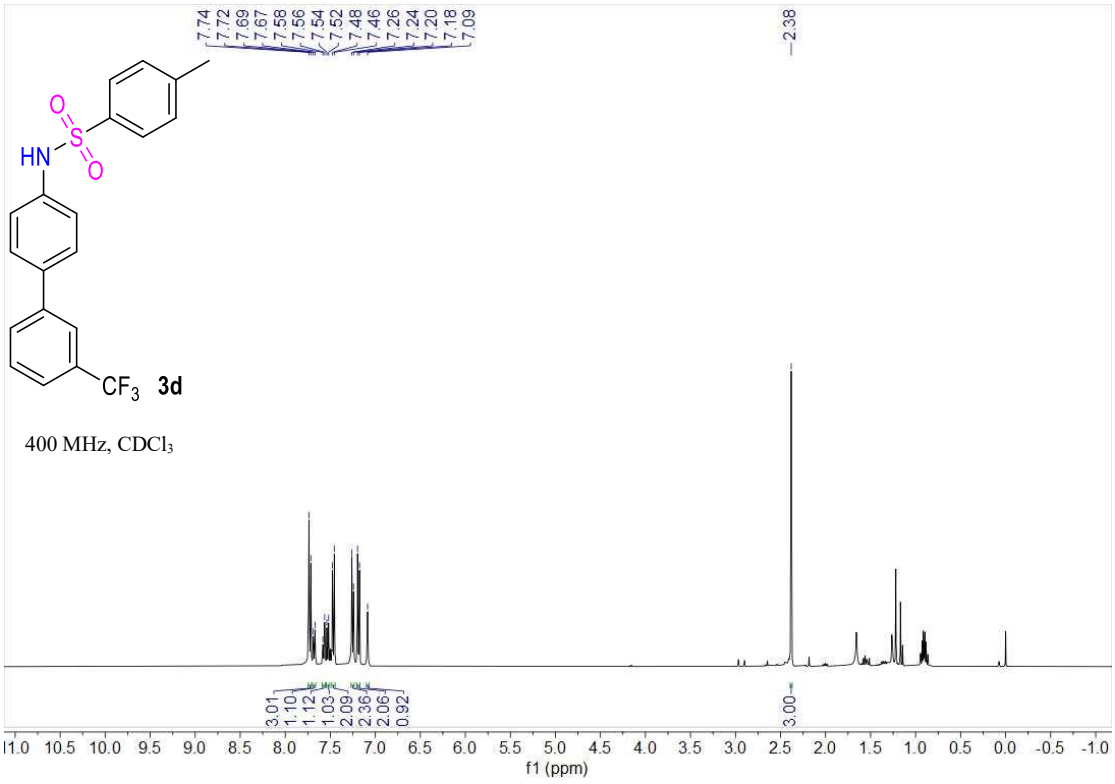


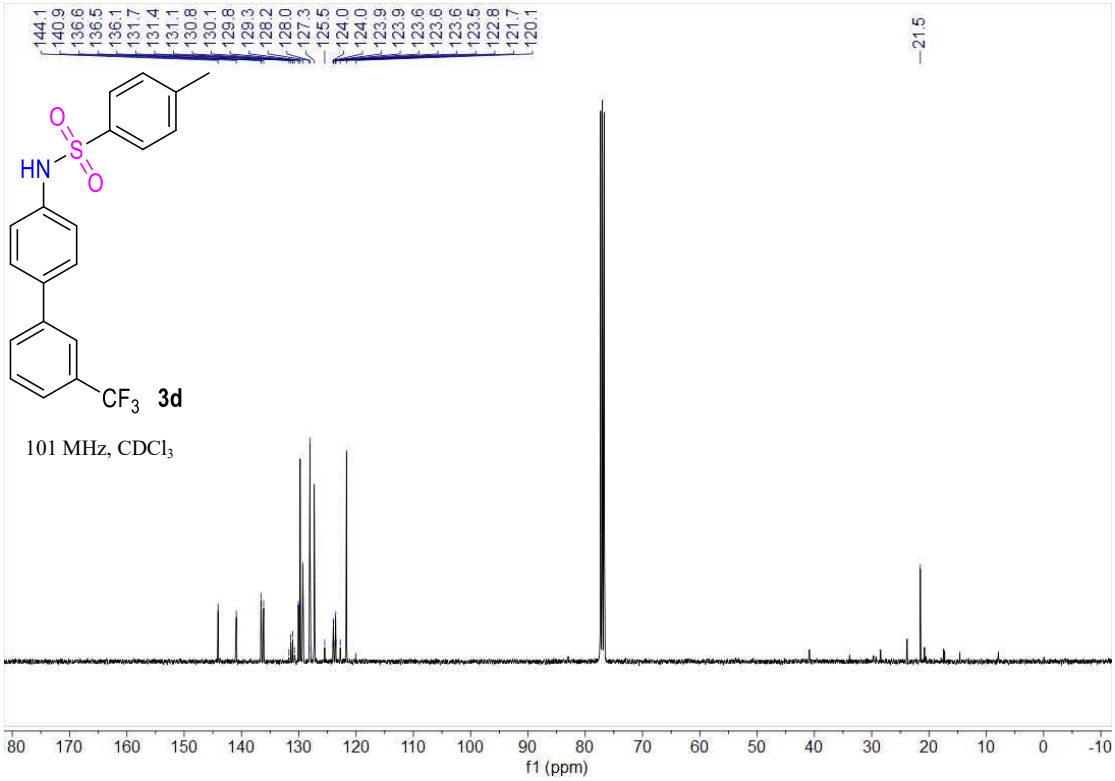
_N_-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3c)

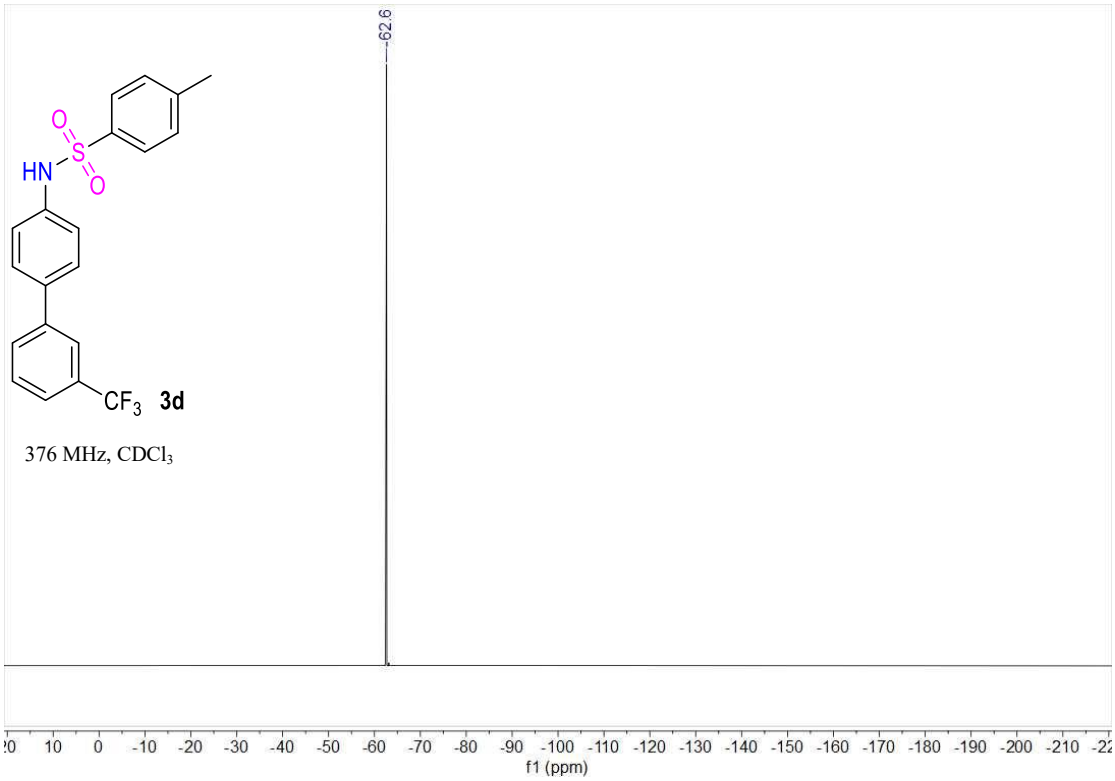




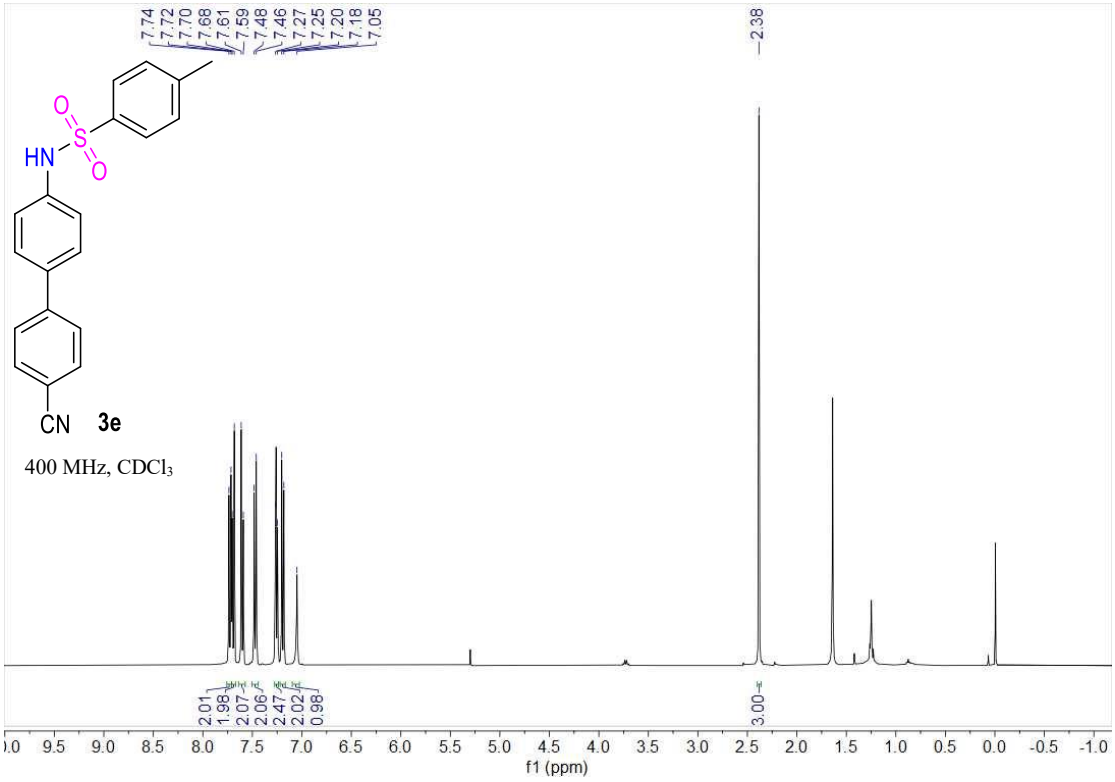
4-methyl-*N*-(3'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)benzenesulfonamide(3d)

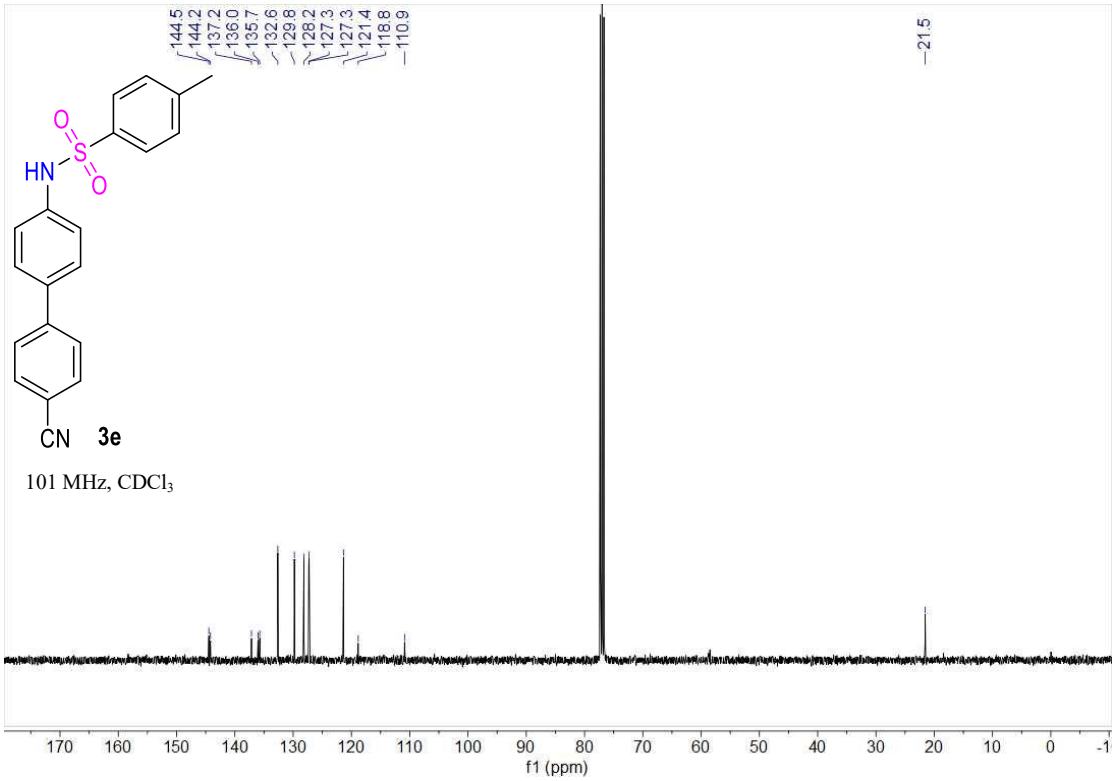




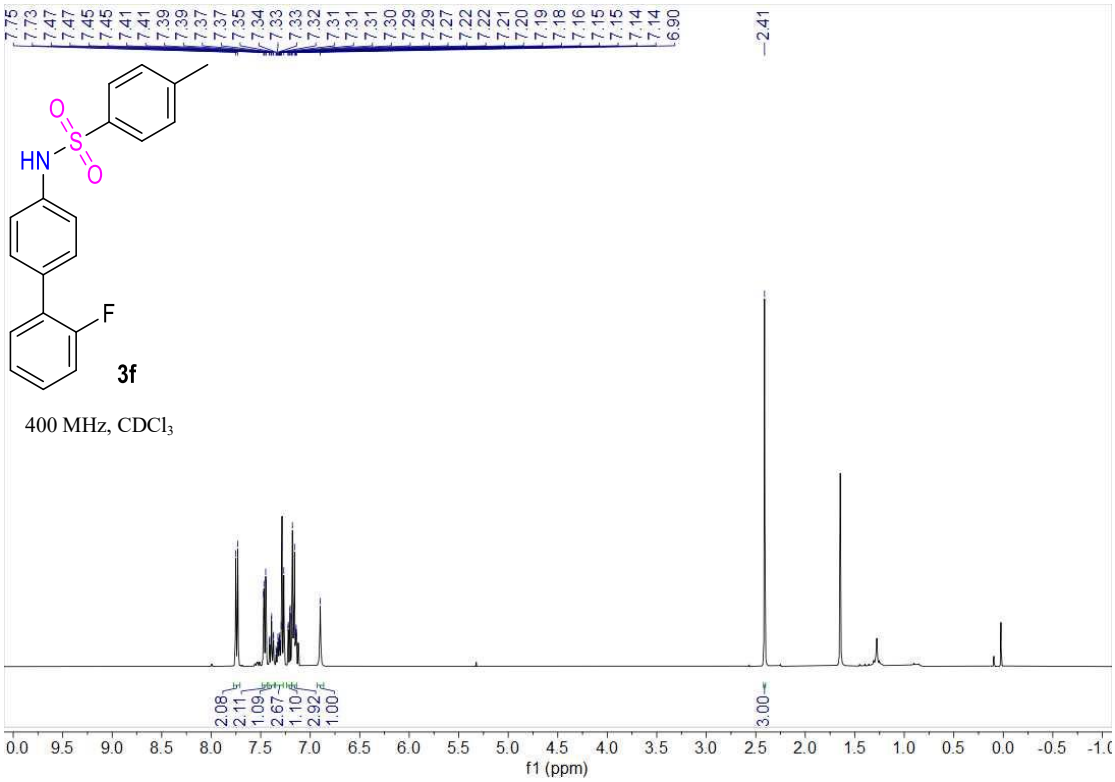

-62.6
HN
O
S
O
CF3
3d
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

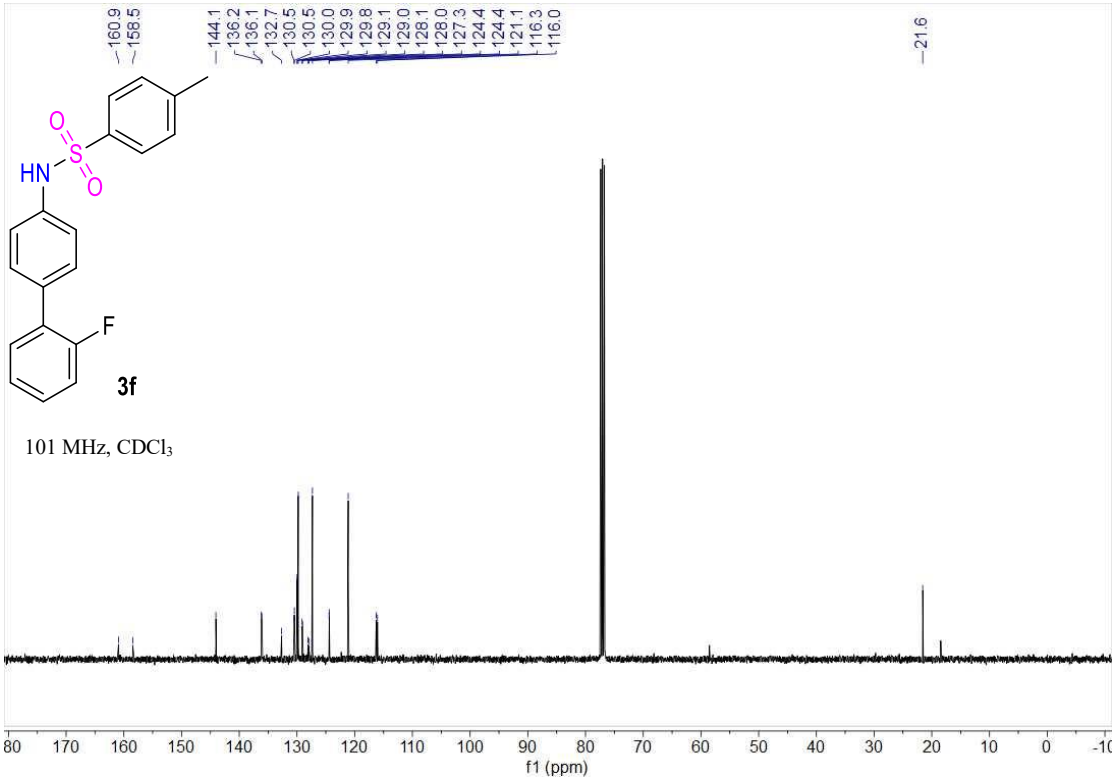
***N*-(4'-cyano-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3e)**

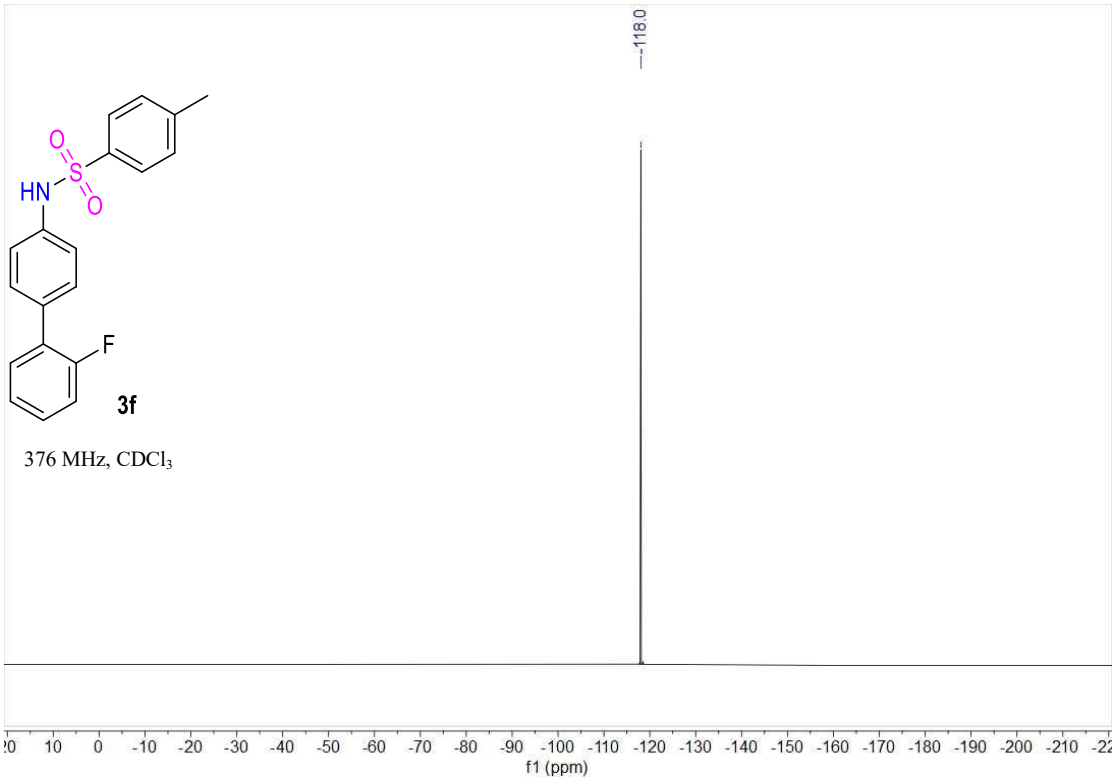




N-(2'-fluoro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3f)






-118.0
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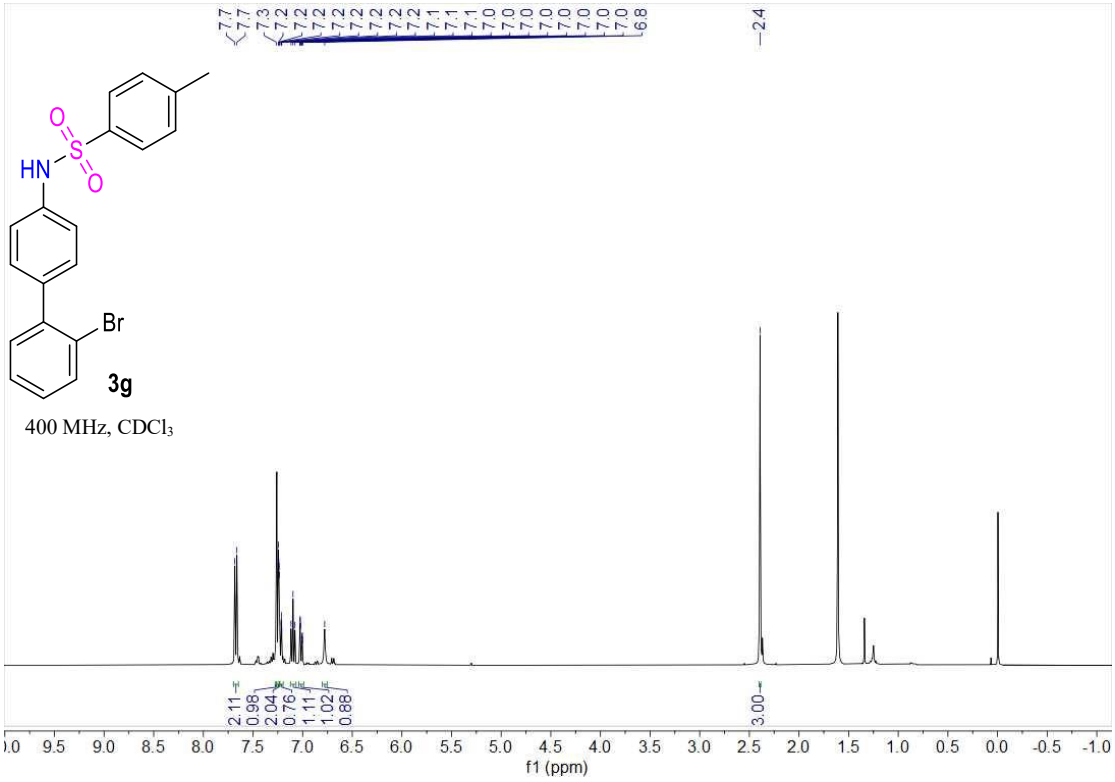
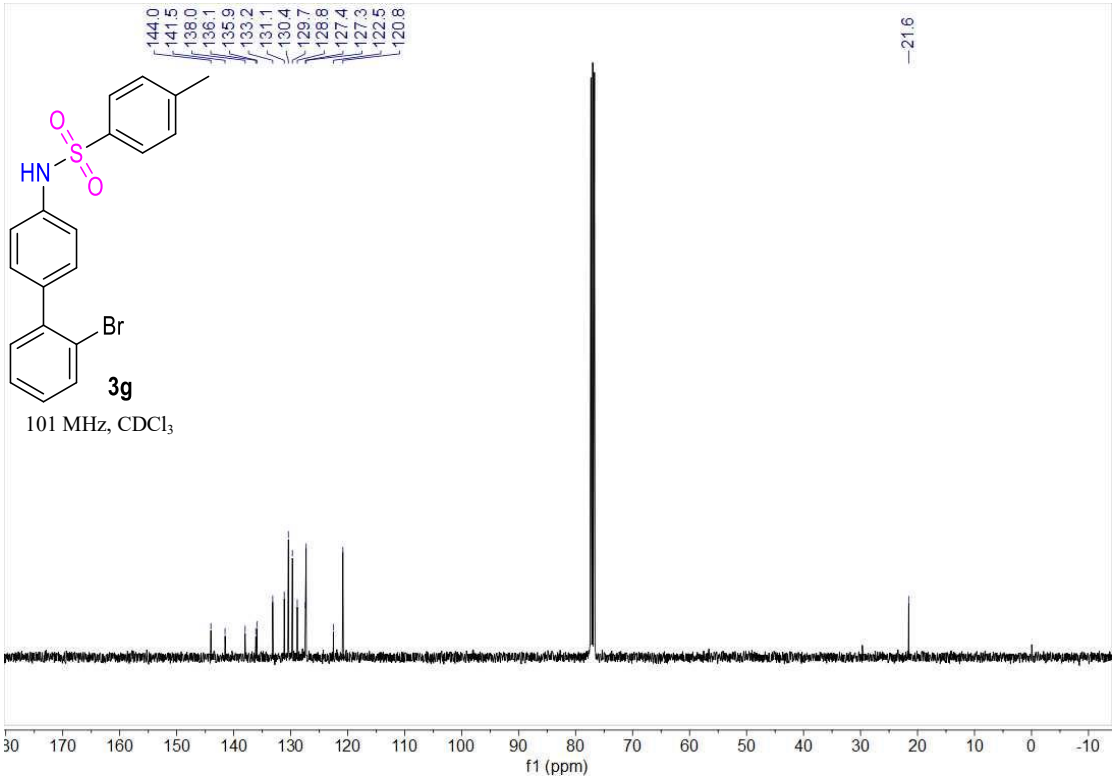
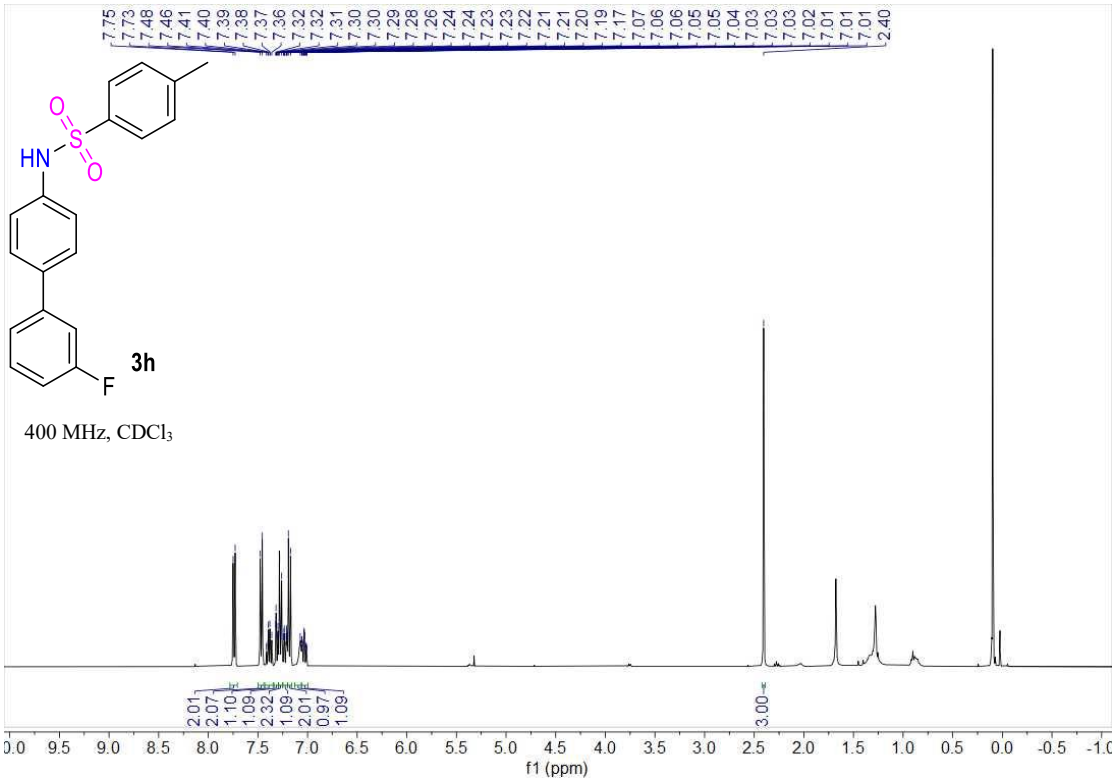
O
S
O
F
3f
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

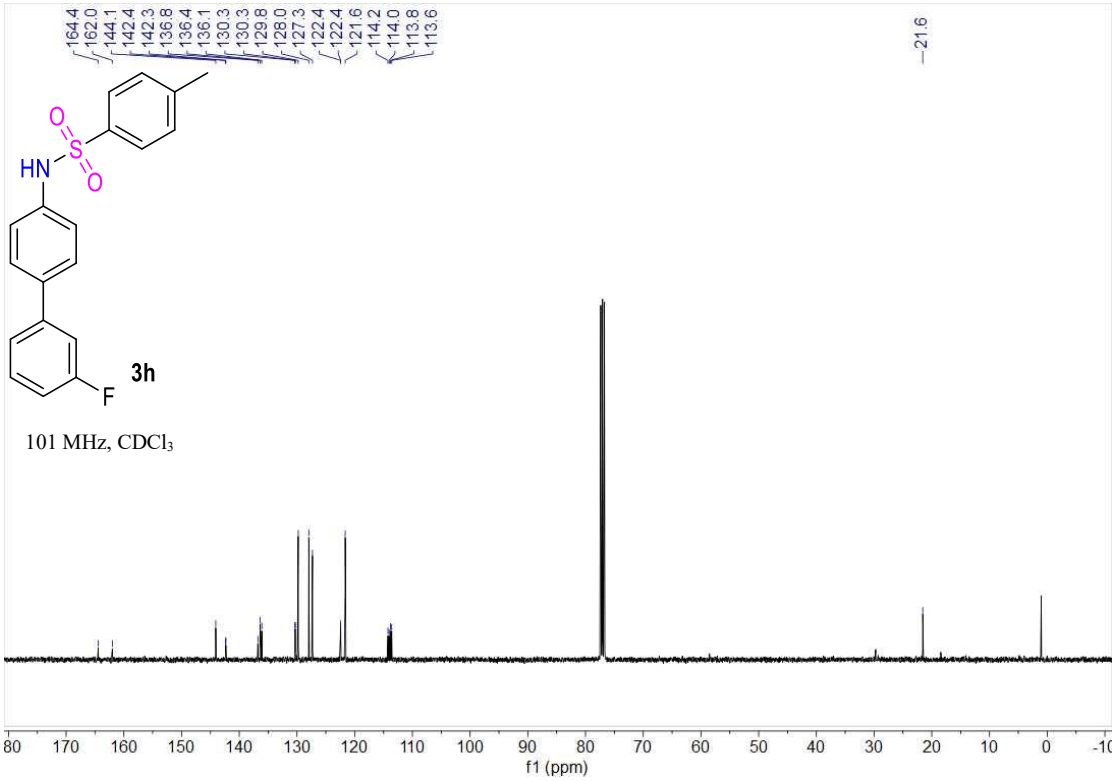
***N*-(2'-bromo-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3g)**

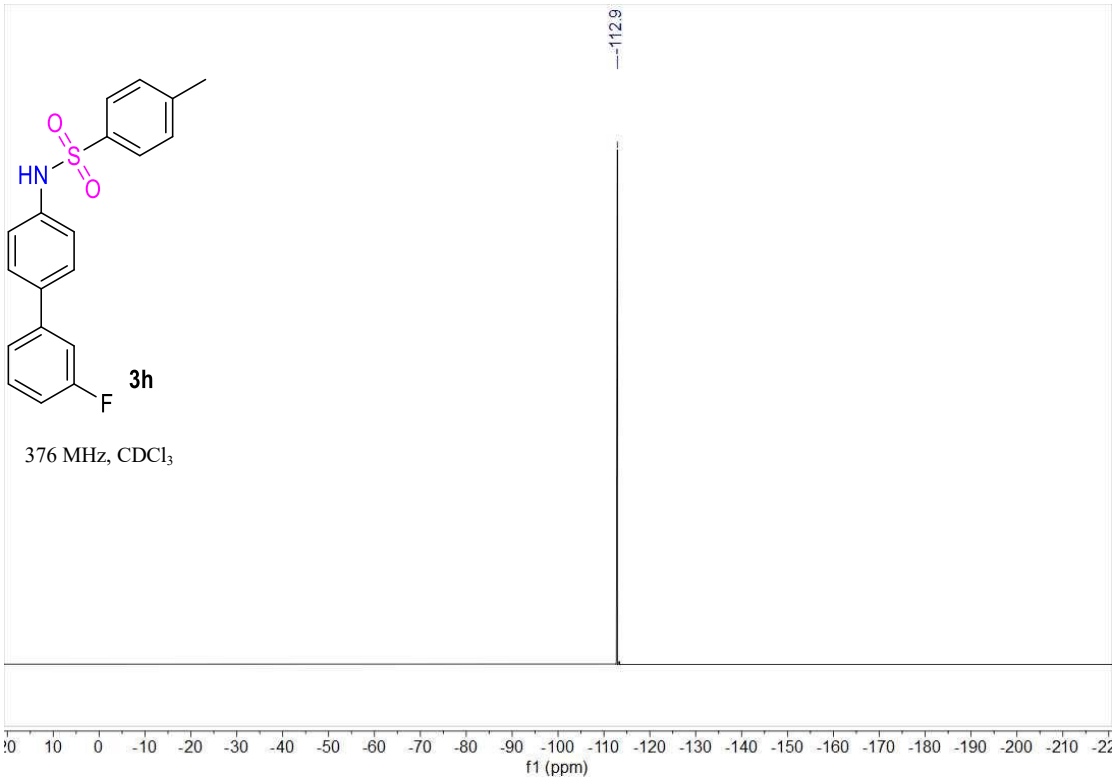




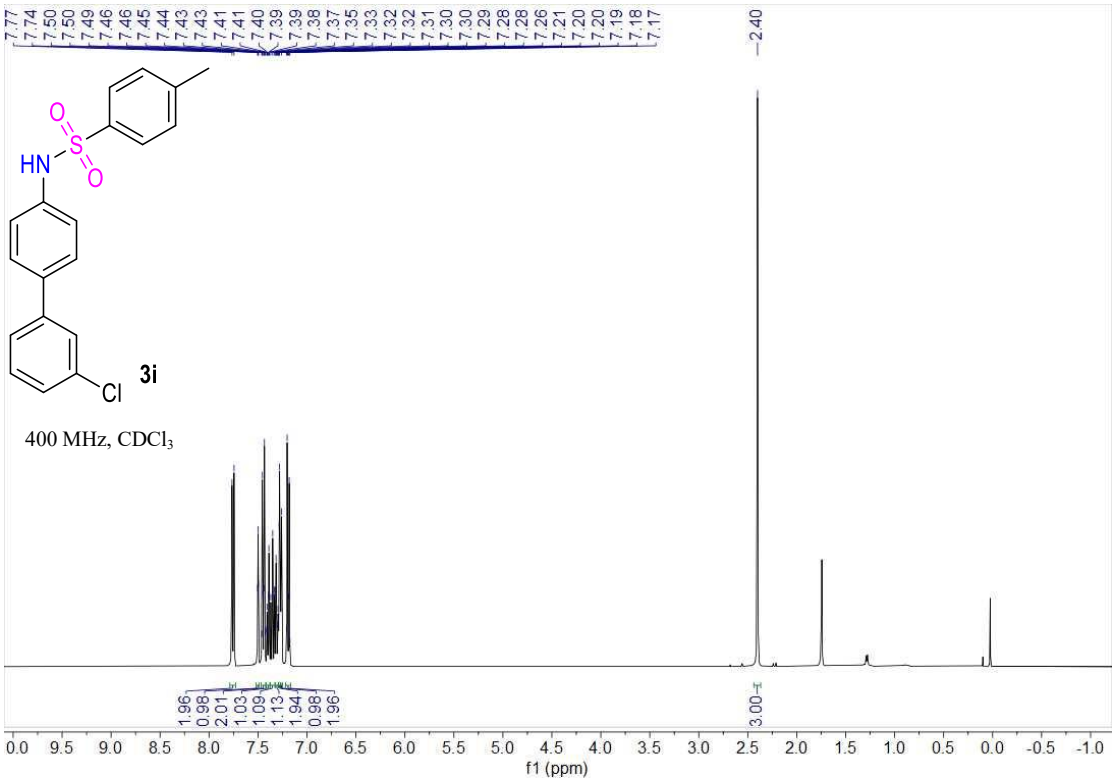
***N*-(3'-fluoro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3h)**

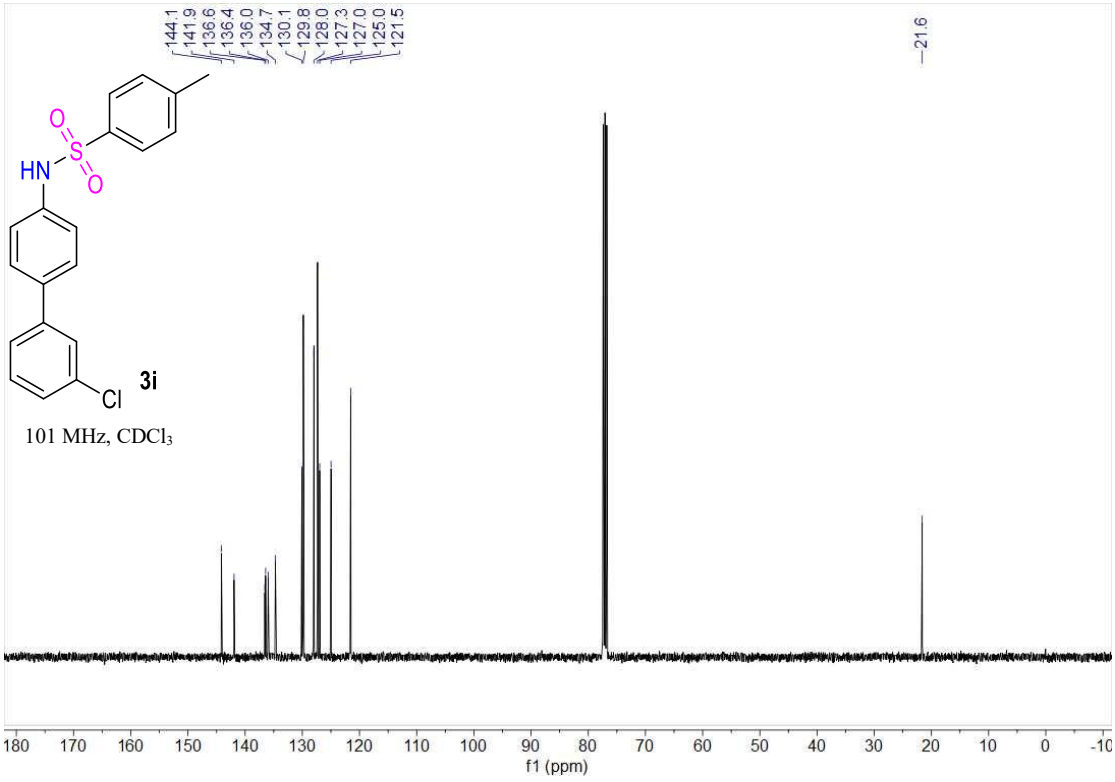




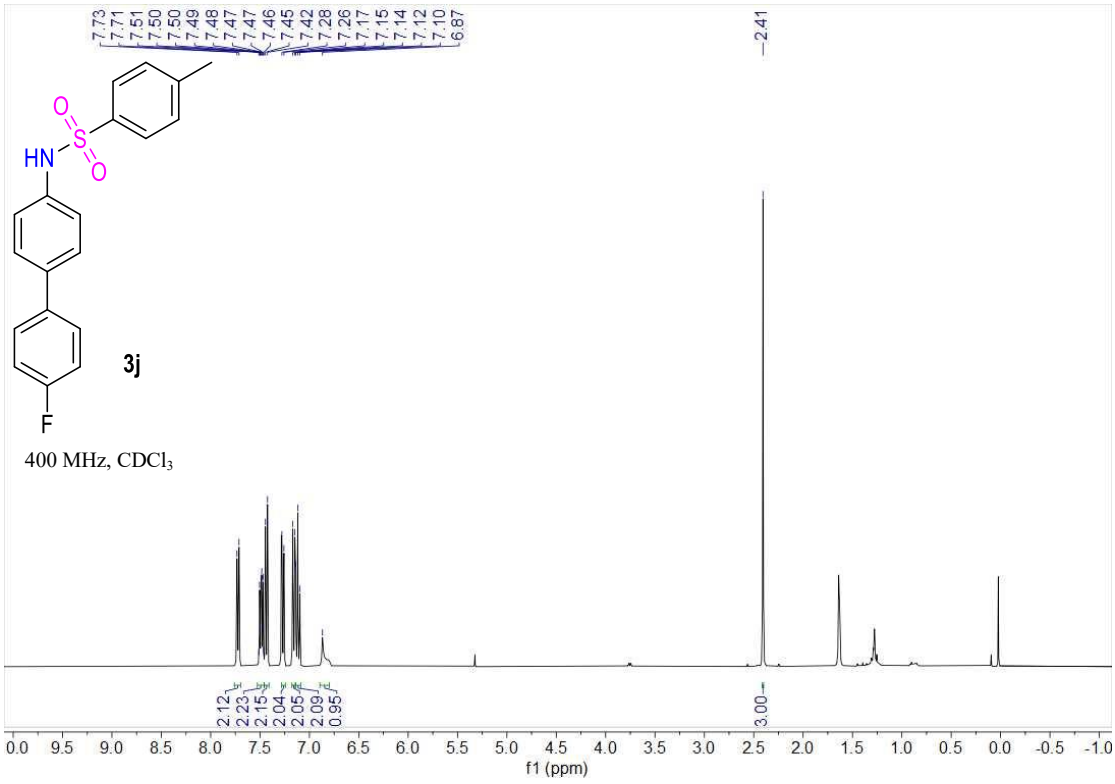

-112.9
HN
O
S
O
F
3h
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

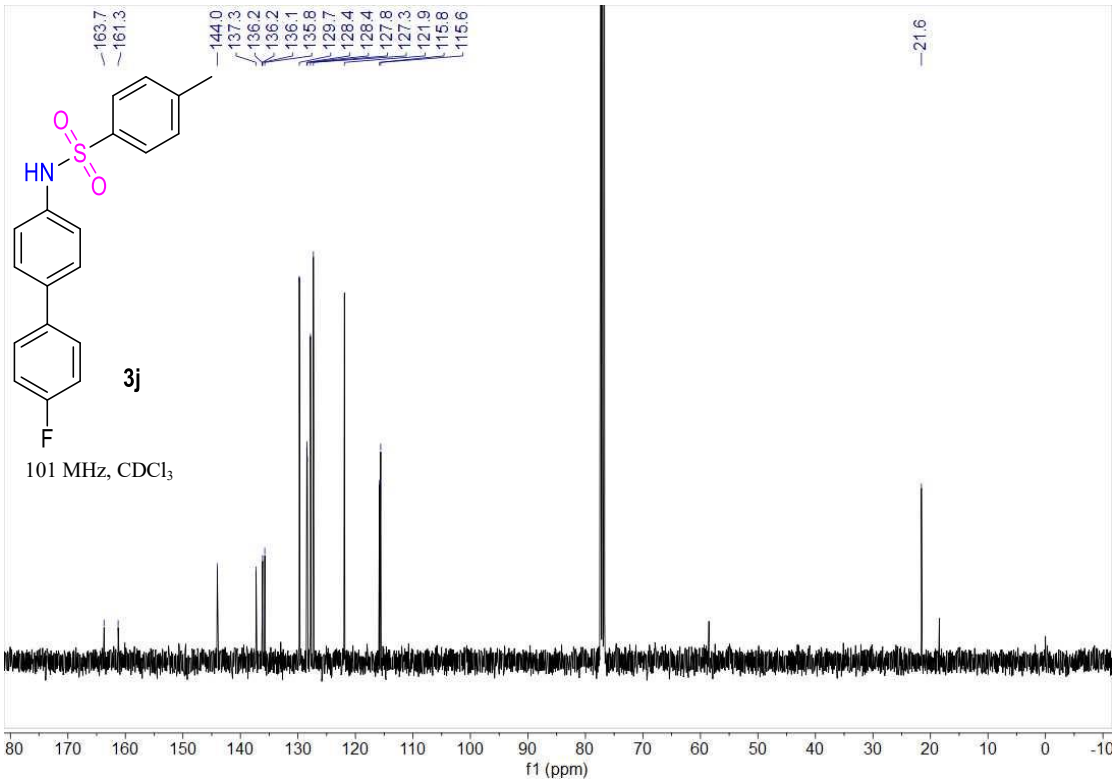
***N*-(3'-chloro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3i)**

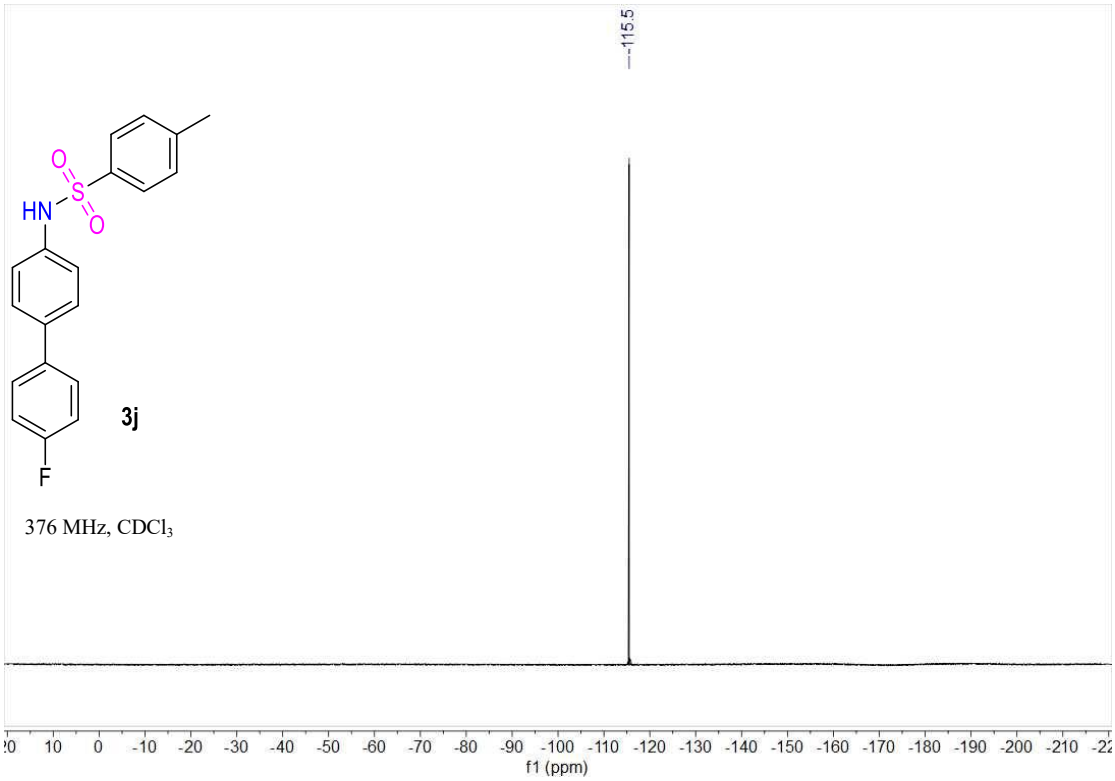




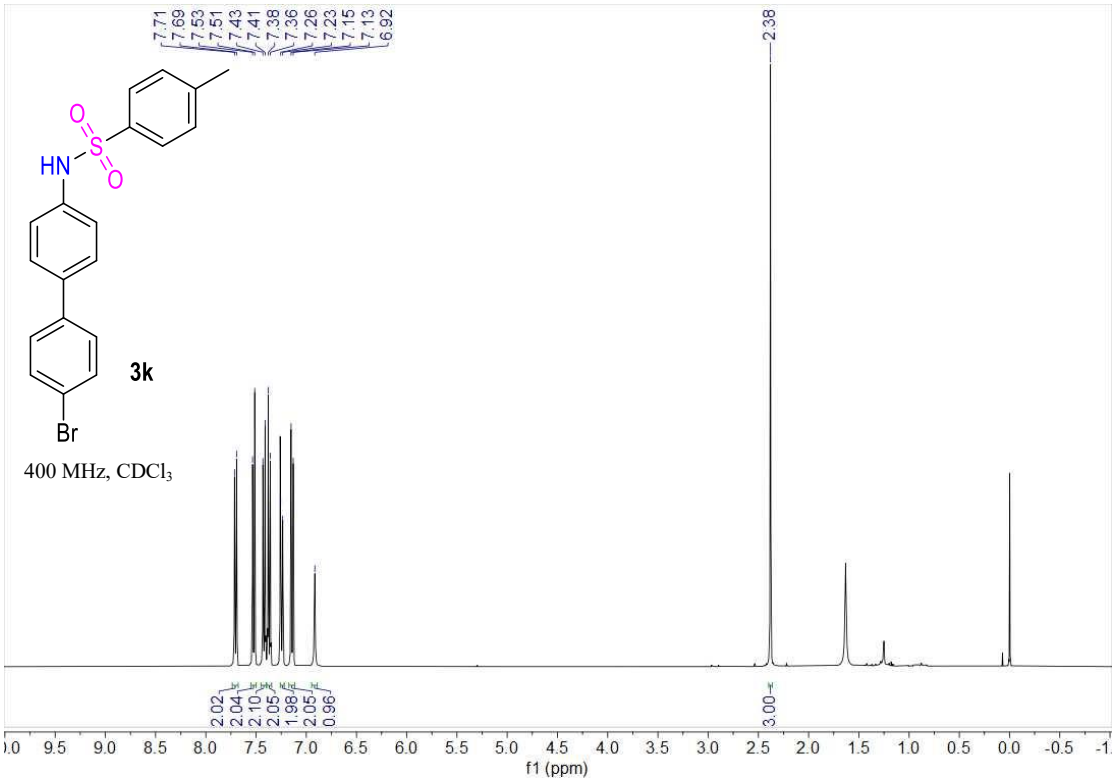
***N*-(4'-fluoro-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3j)**

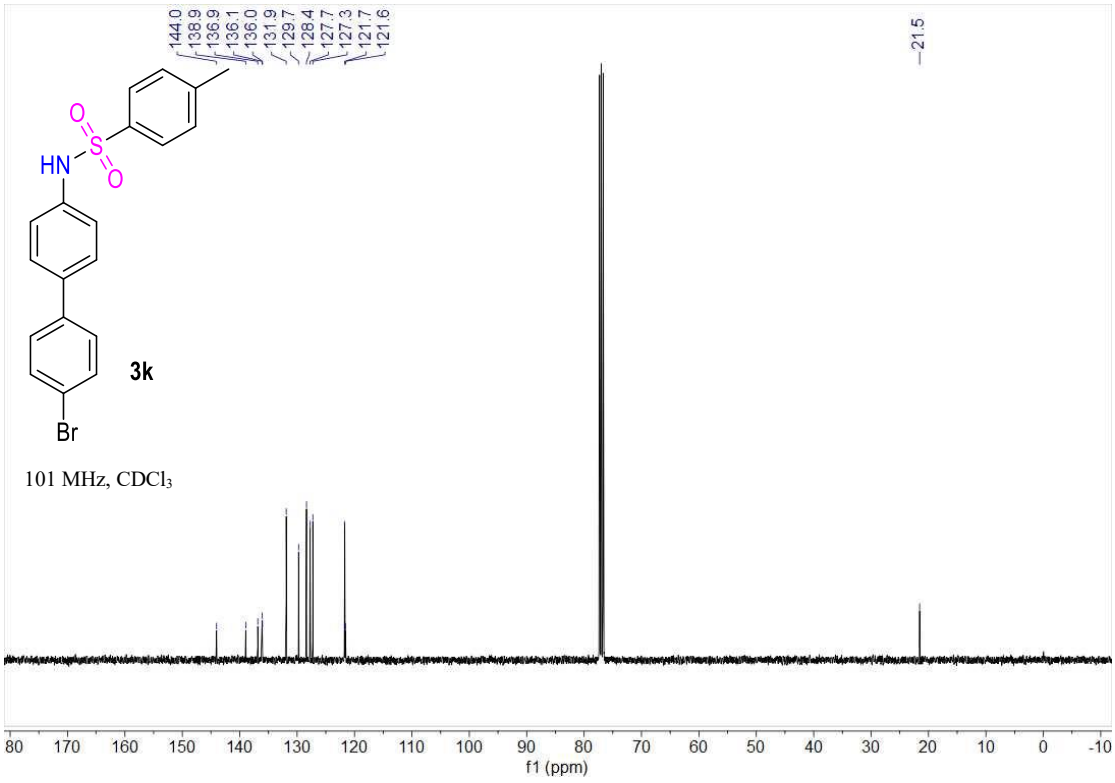




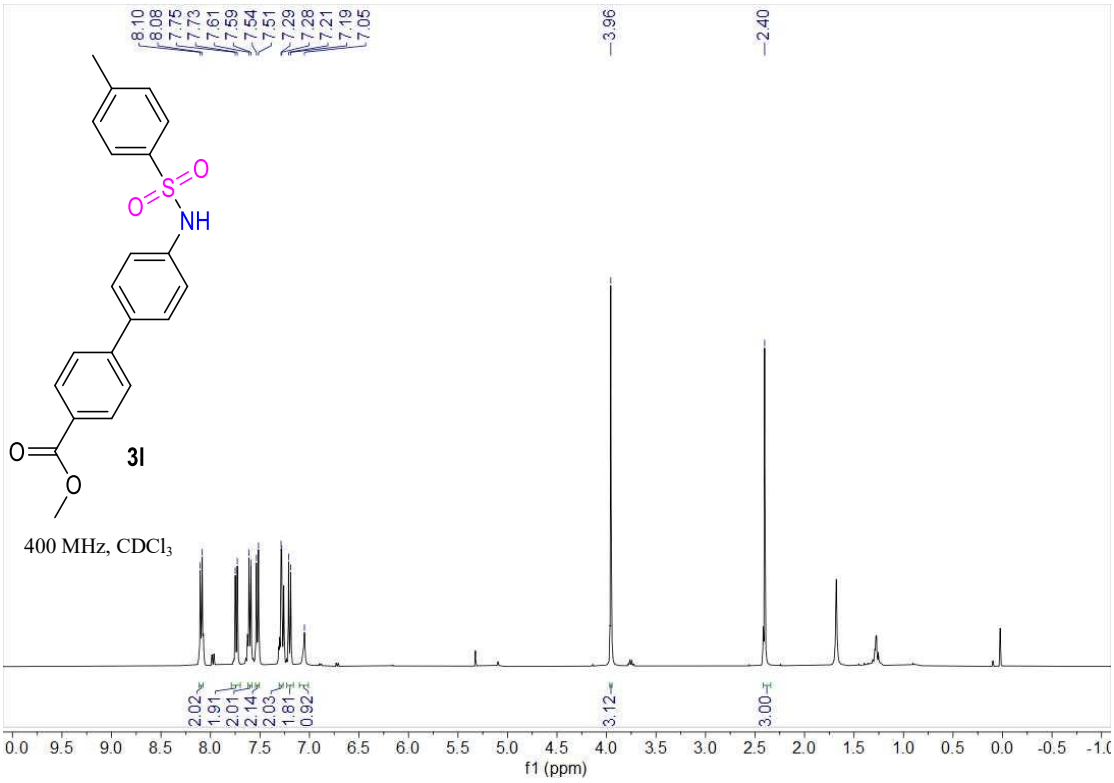

-115.5
HN
O
S
O
F
3j
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

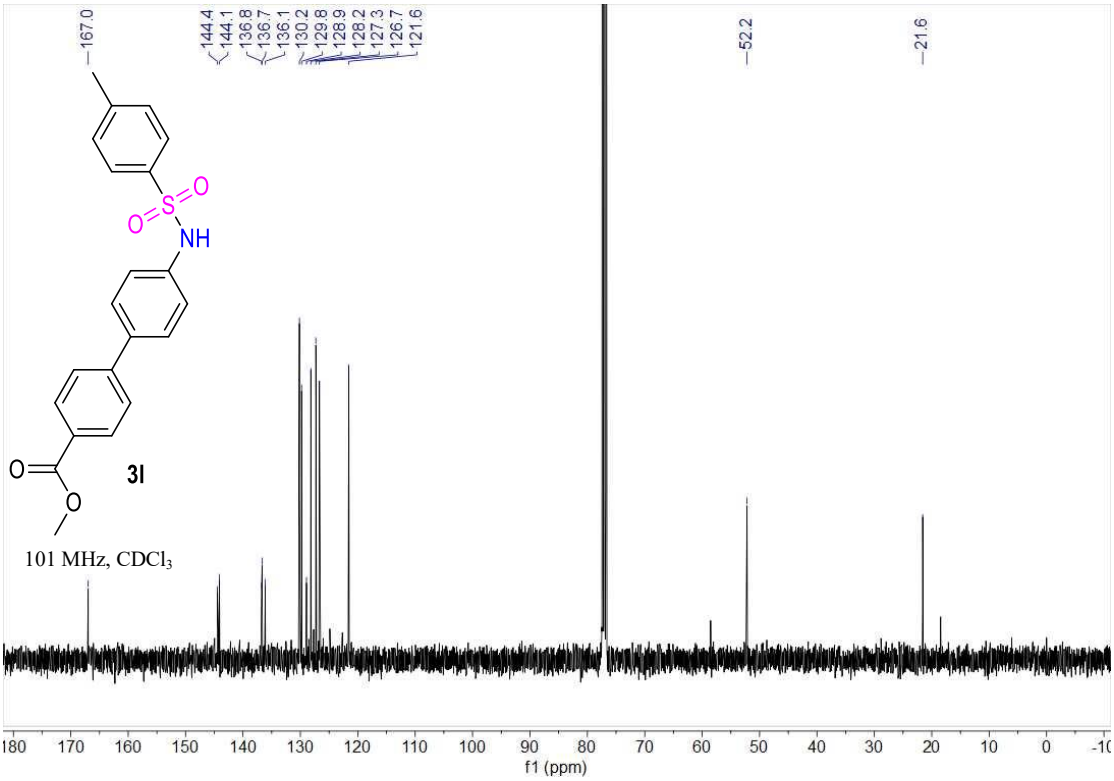
***N*-(4'-bromo-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3k)**



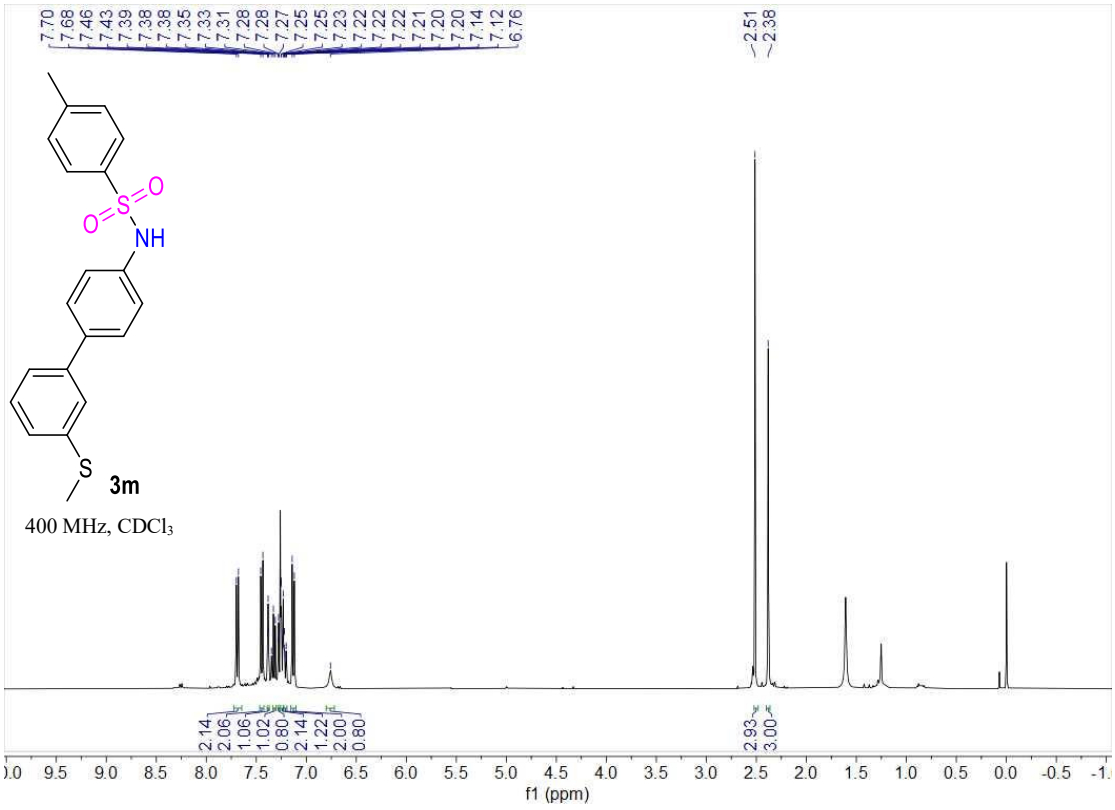


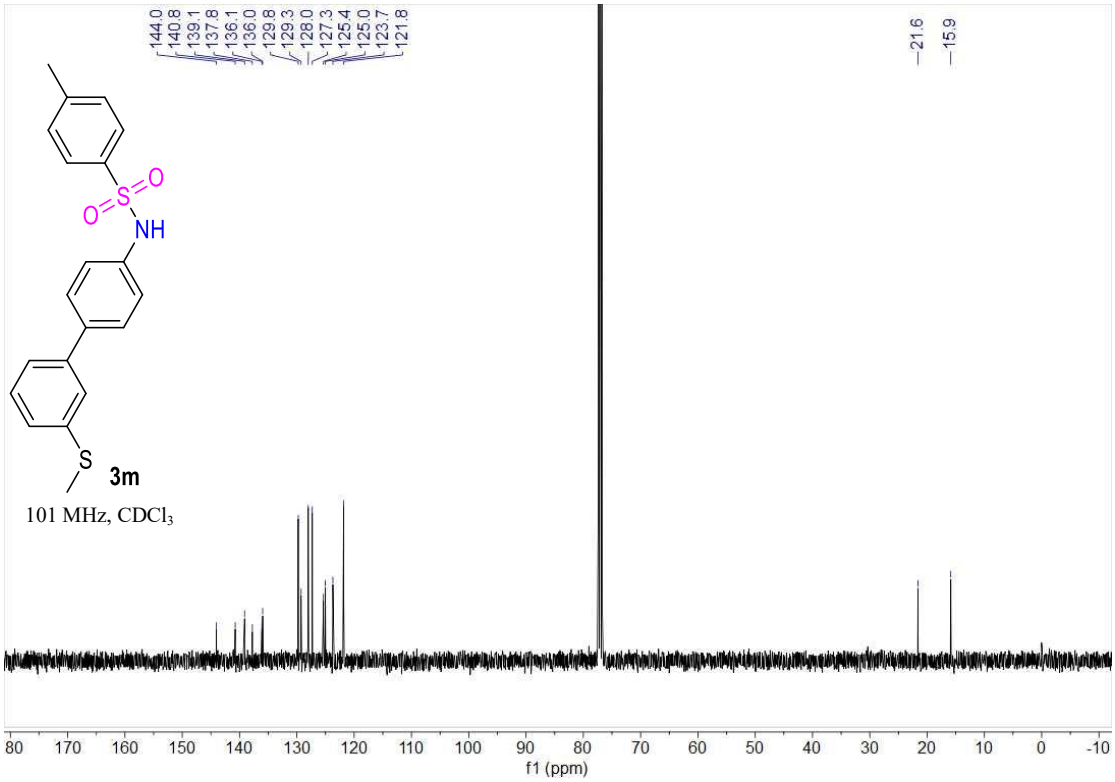
methyl 4'-((4-methylphenyl)sulfonamido)-[1,1'-biphenyl]-4-carboxylate (3l)



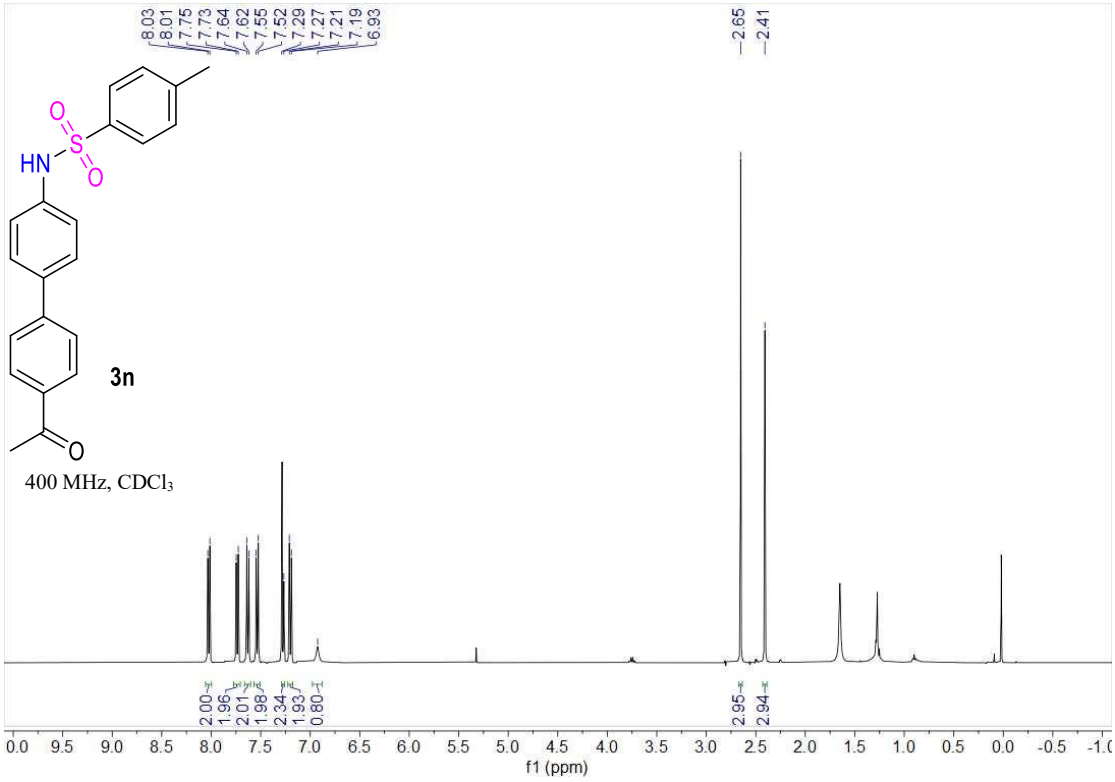


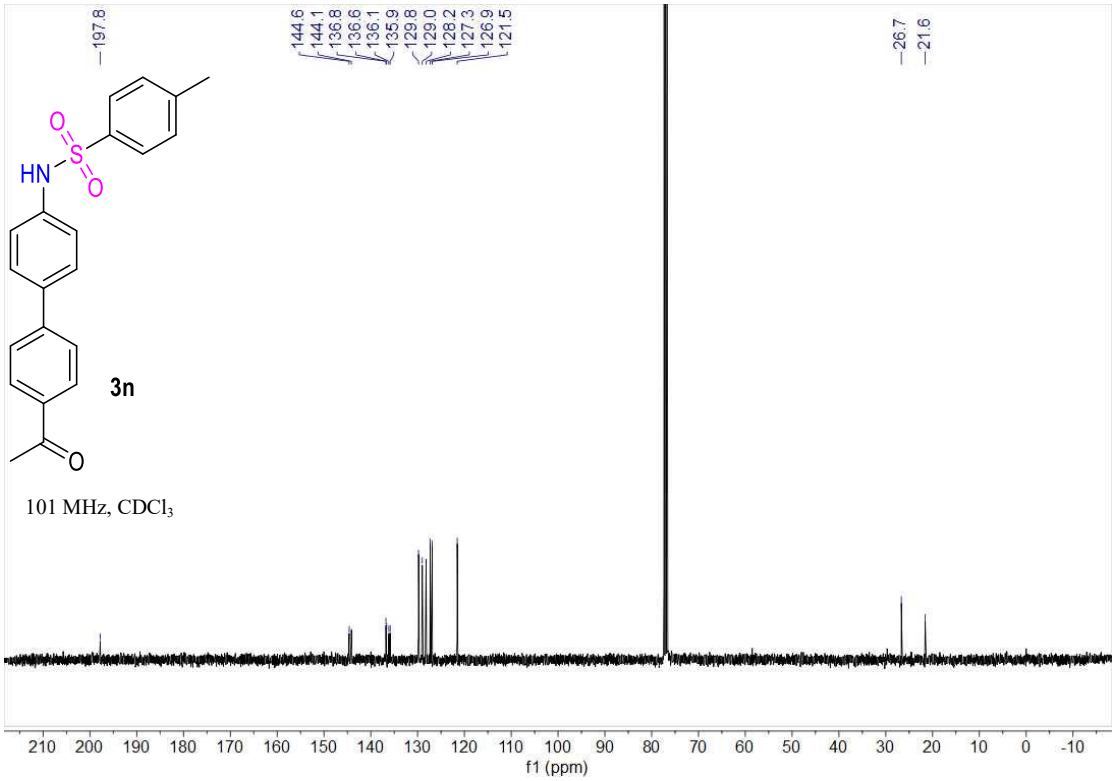
4-methyl-*N*-(3'-(methylthio)-[1,1'-biphenyl]-4-yl)benzenesulfonamide (3m)



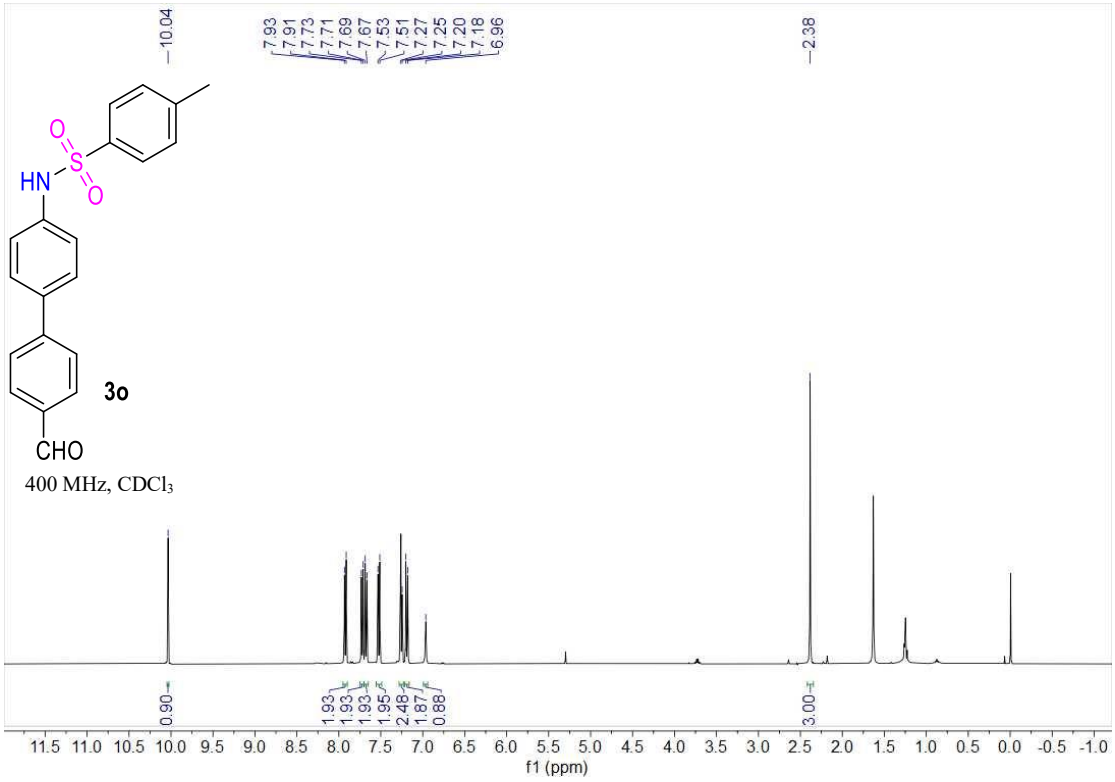


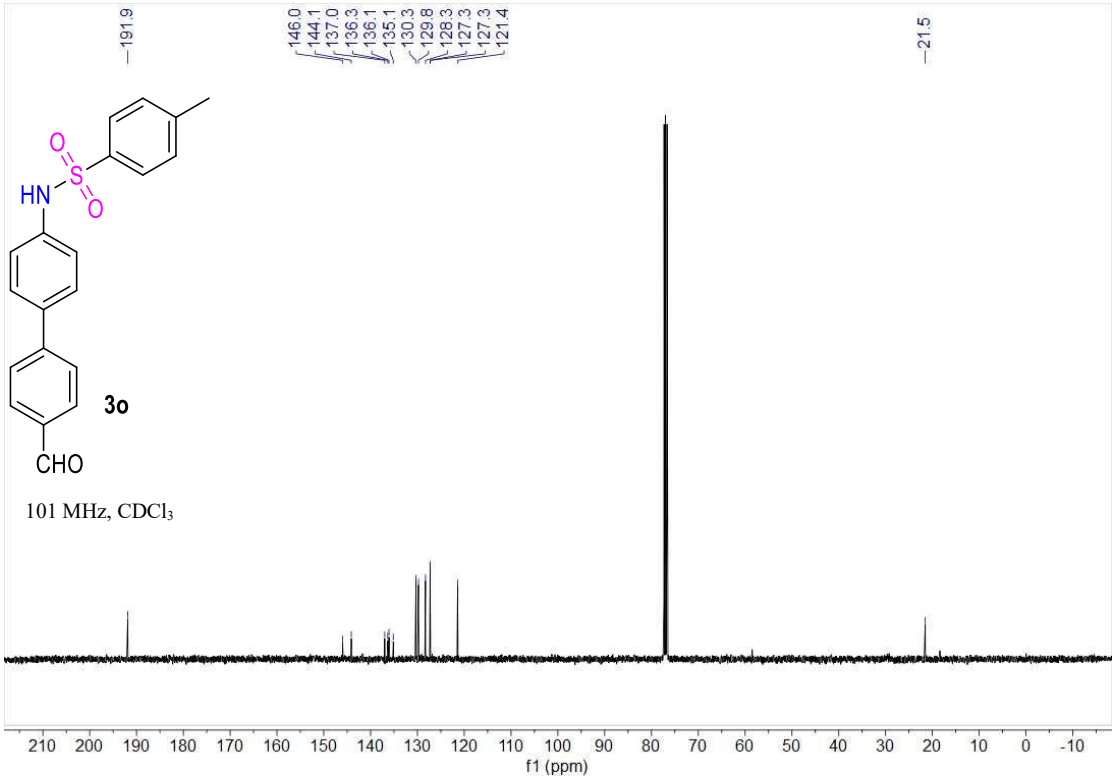
***N*-(4'-acetyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3n)**



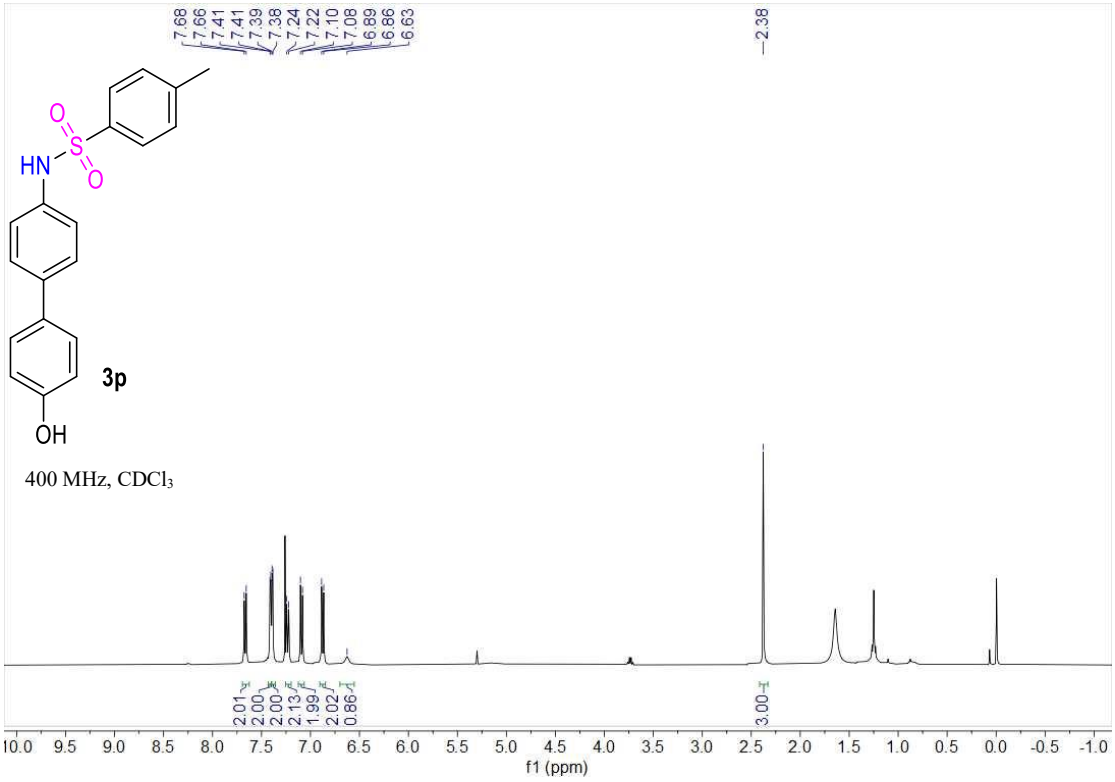


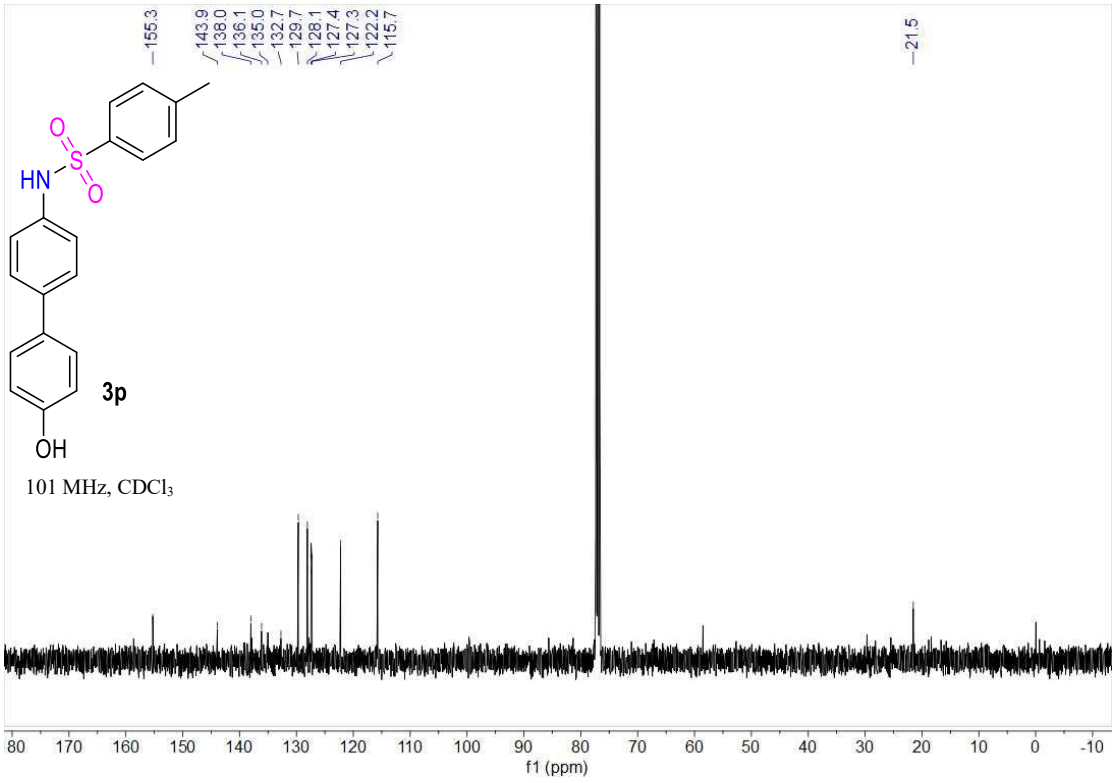
***N*-(4'-formyl-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3o)**



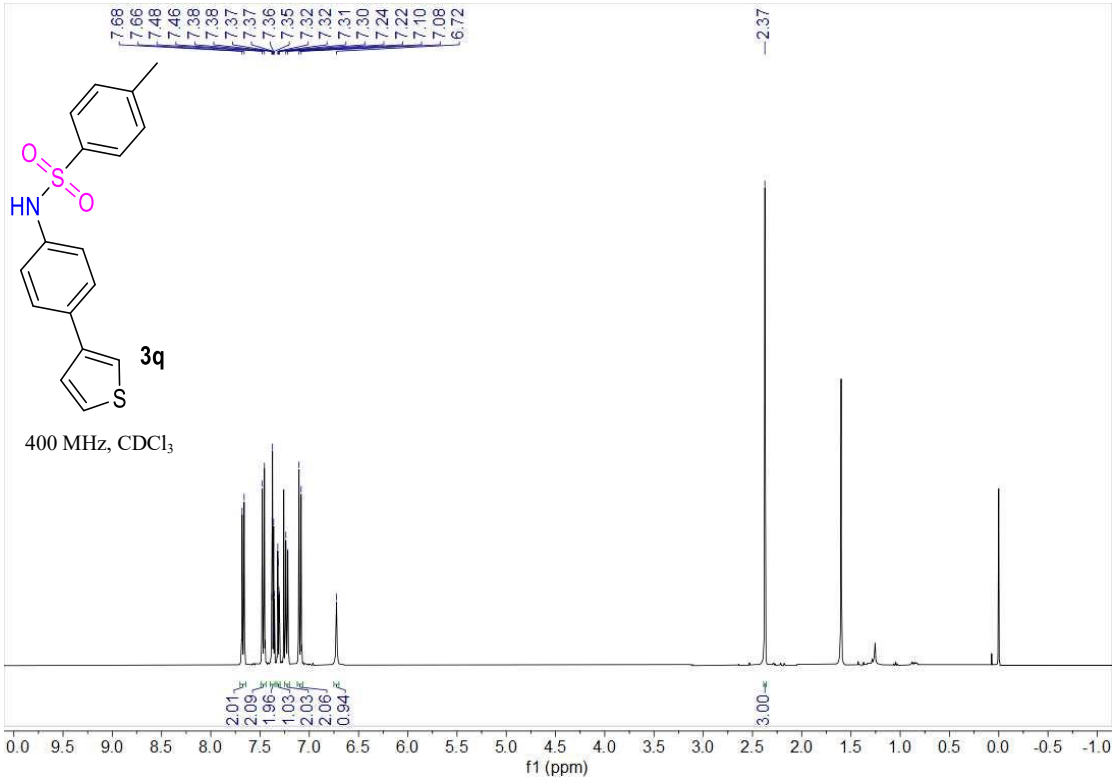


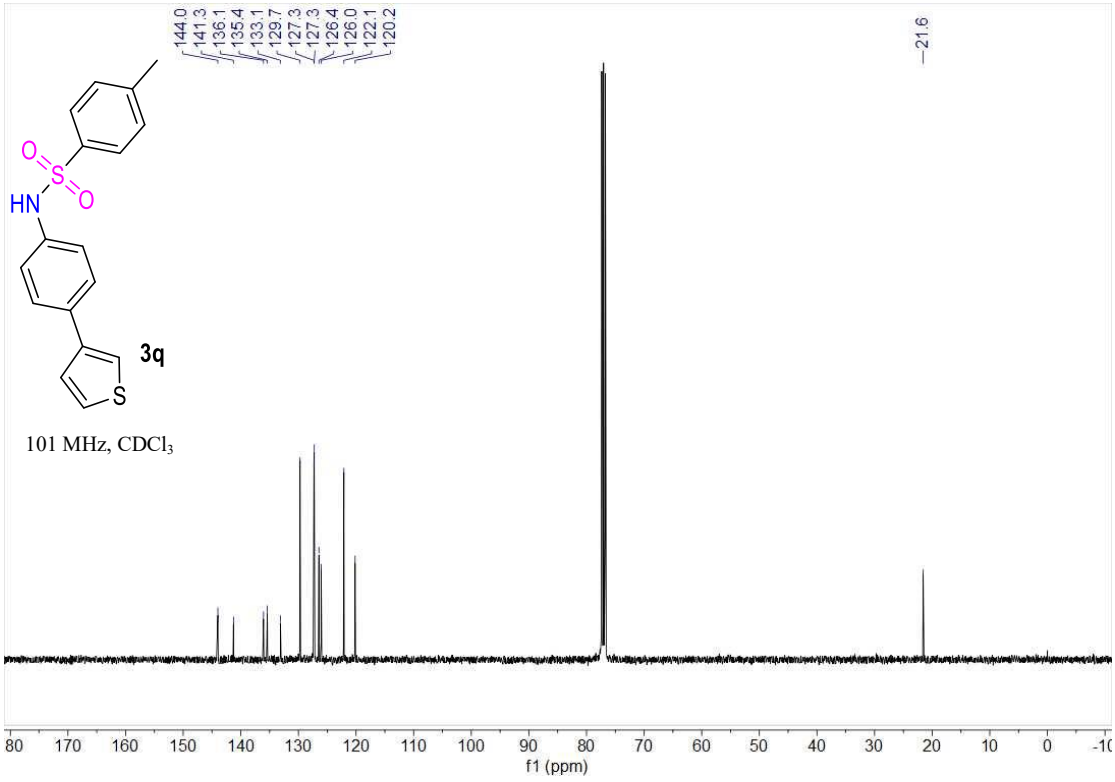
***N*-(4'-hydroxy-[1,1'-biphenyl]-4-yl)-4-methylbenzenesulfonamide (3p)**



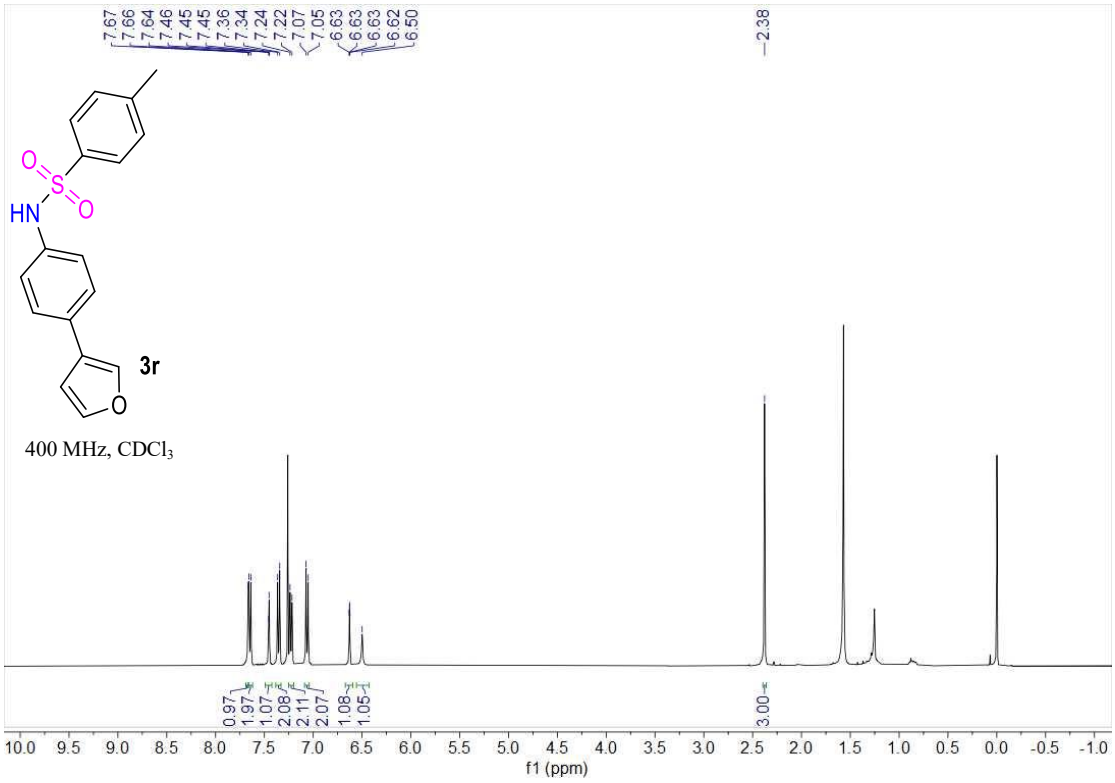


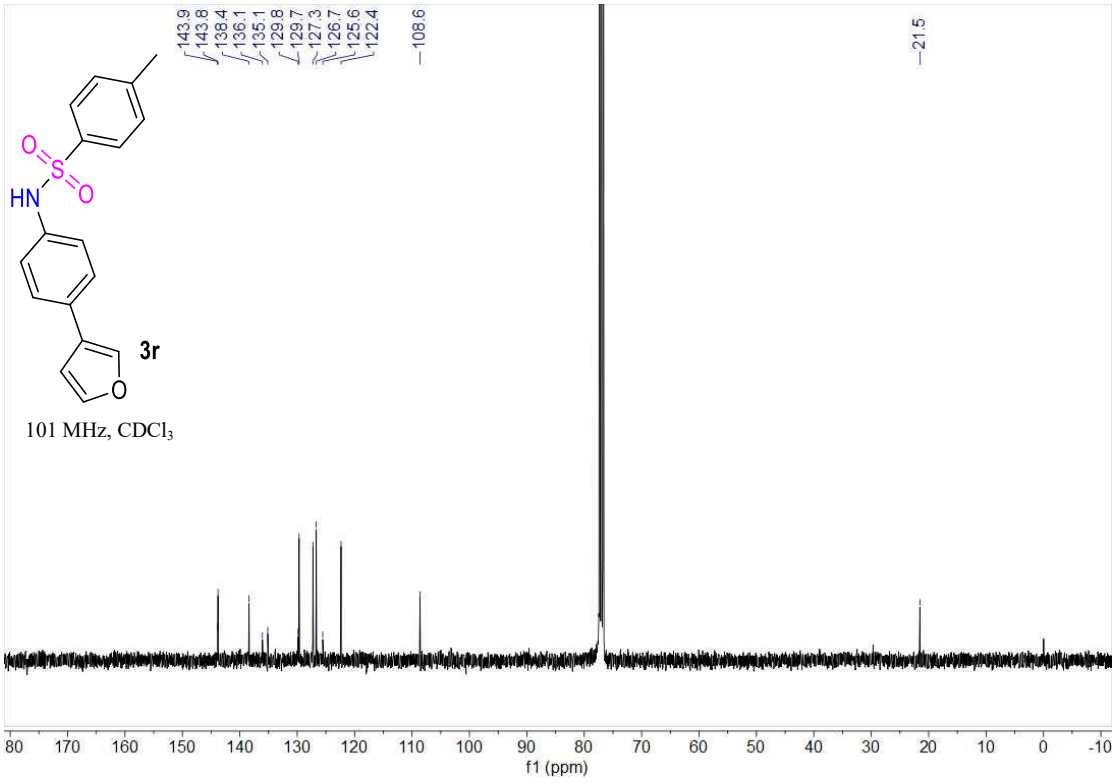
4-methyl-*N*-(4-(thiophen-2-yl)phenyl)benzenesulfonamide (3q)



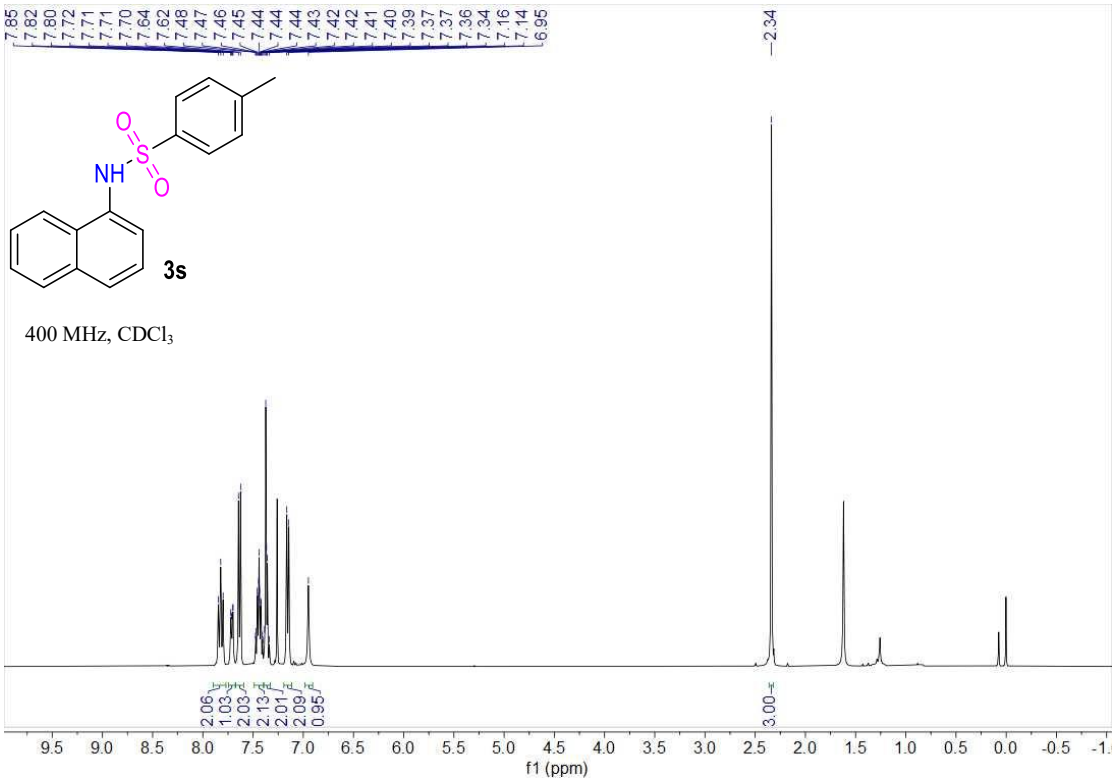


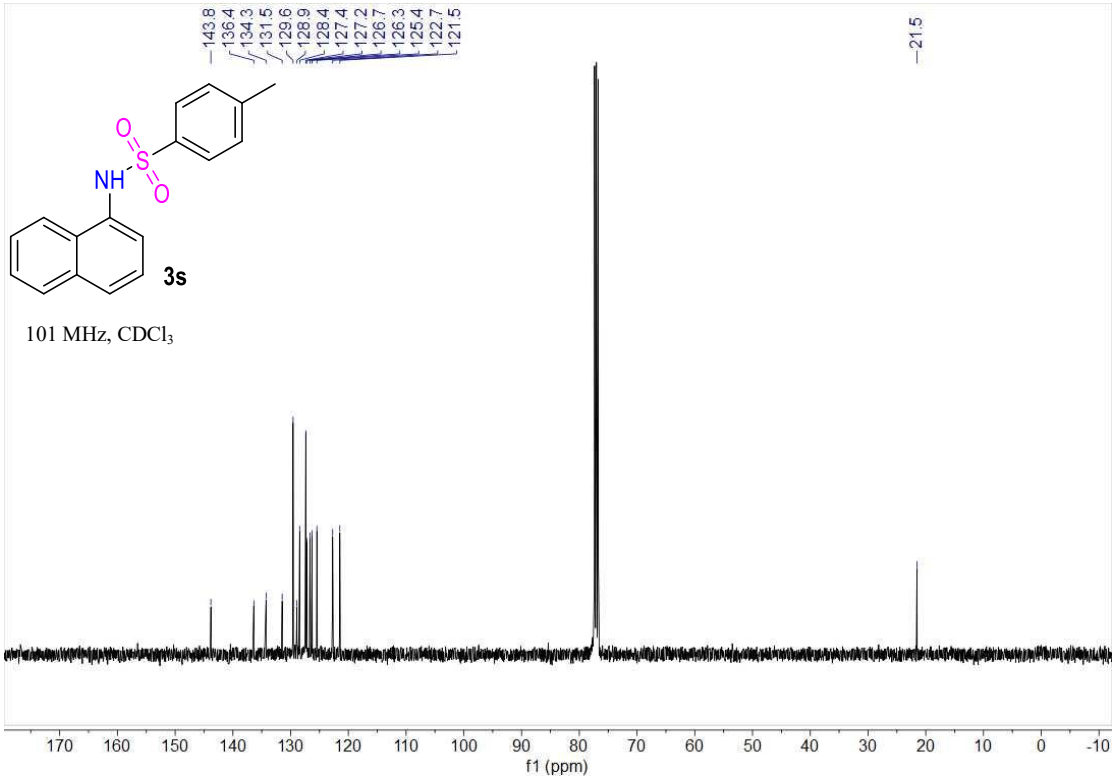
_N_-(4-(furan-2-yl)phenyl)-4-methylbenzenesulfonamide (3r)



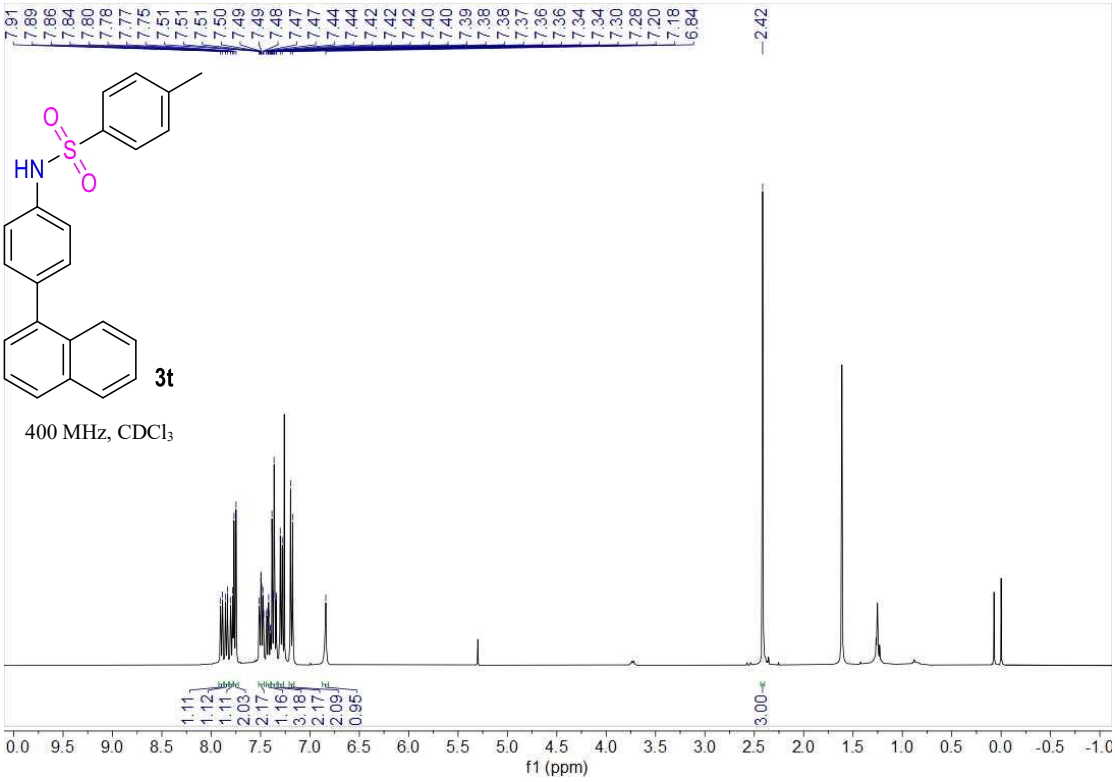


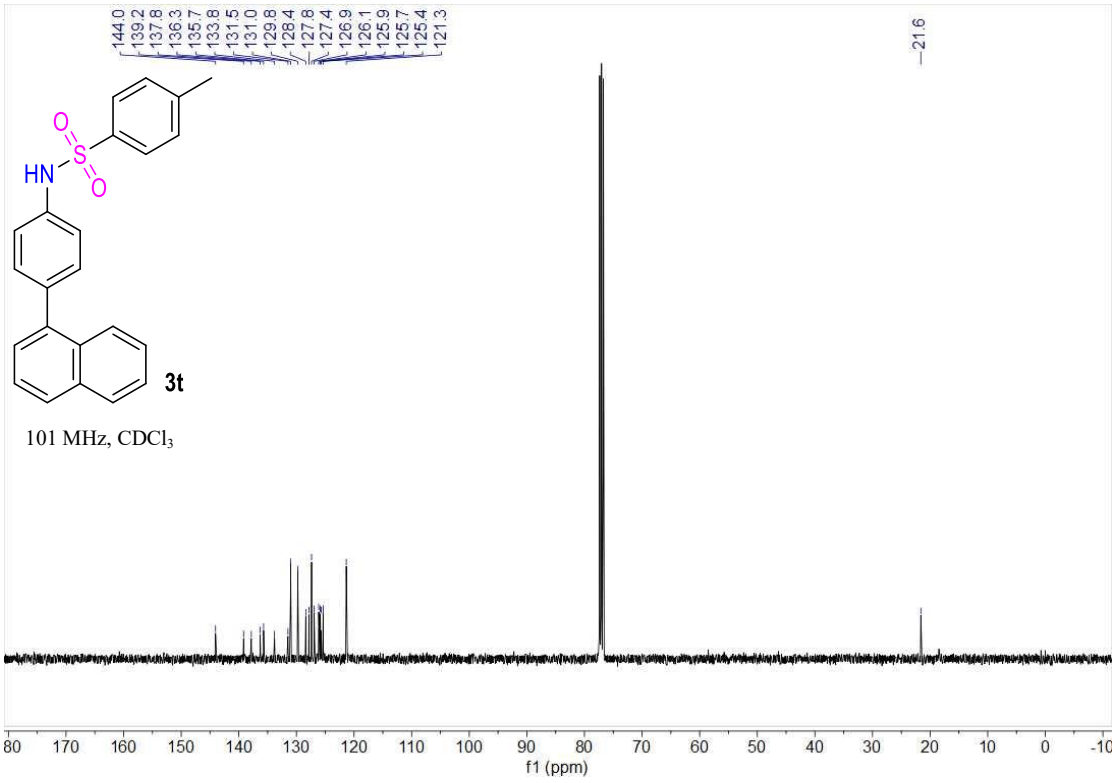
4-methyl-*N*-(naphthalen-1-yl)benzenesulfonamide (3s)



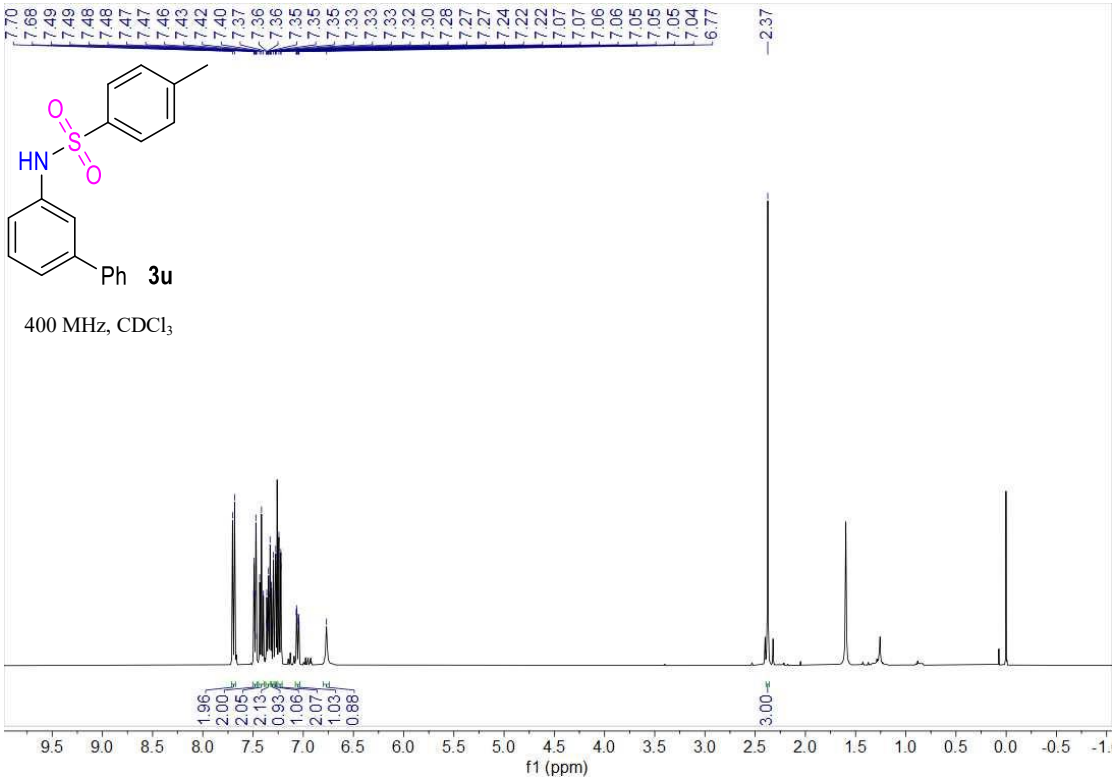


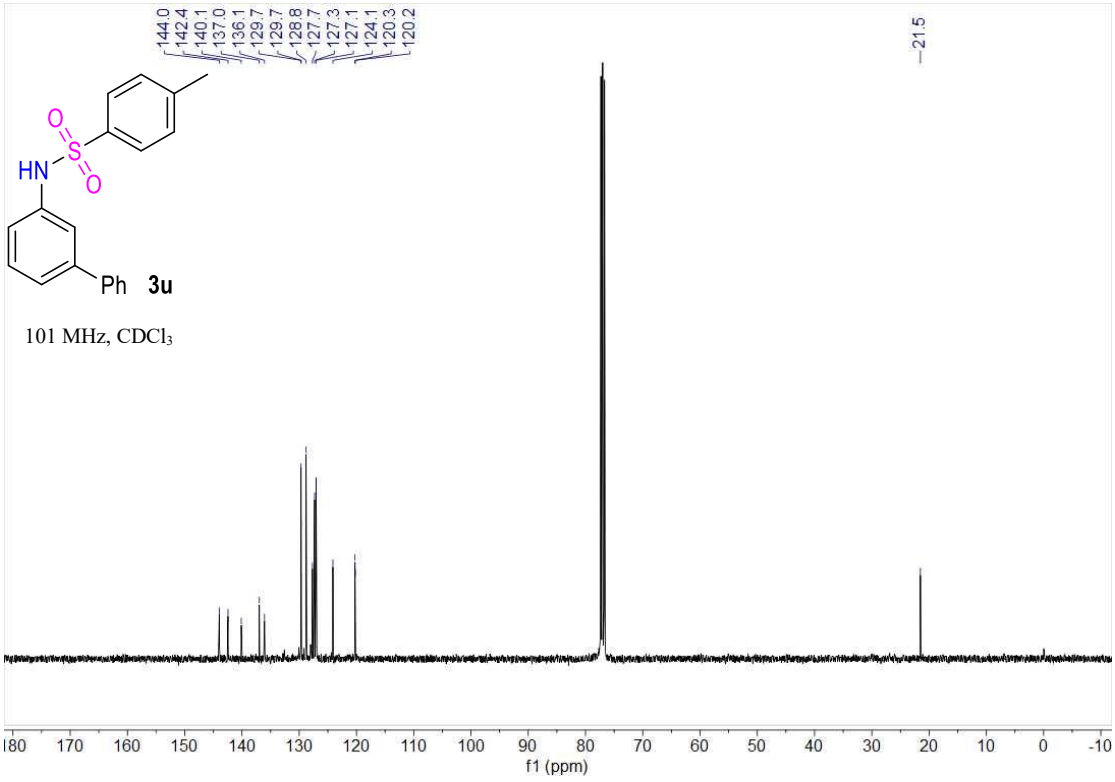
4-methyl-*N*-(4-(naphthalen-1-yl)phenyl)benzenesulfonamide (3t)



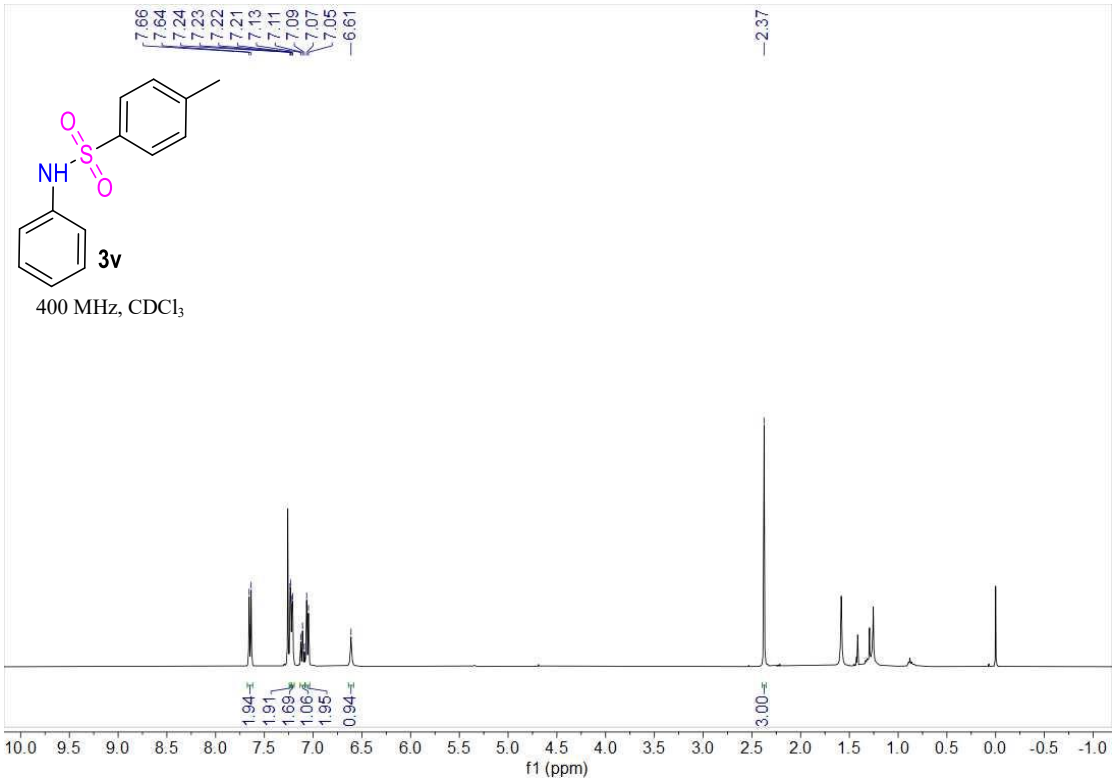


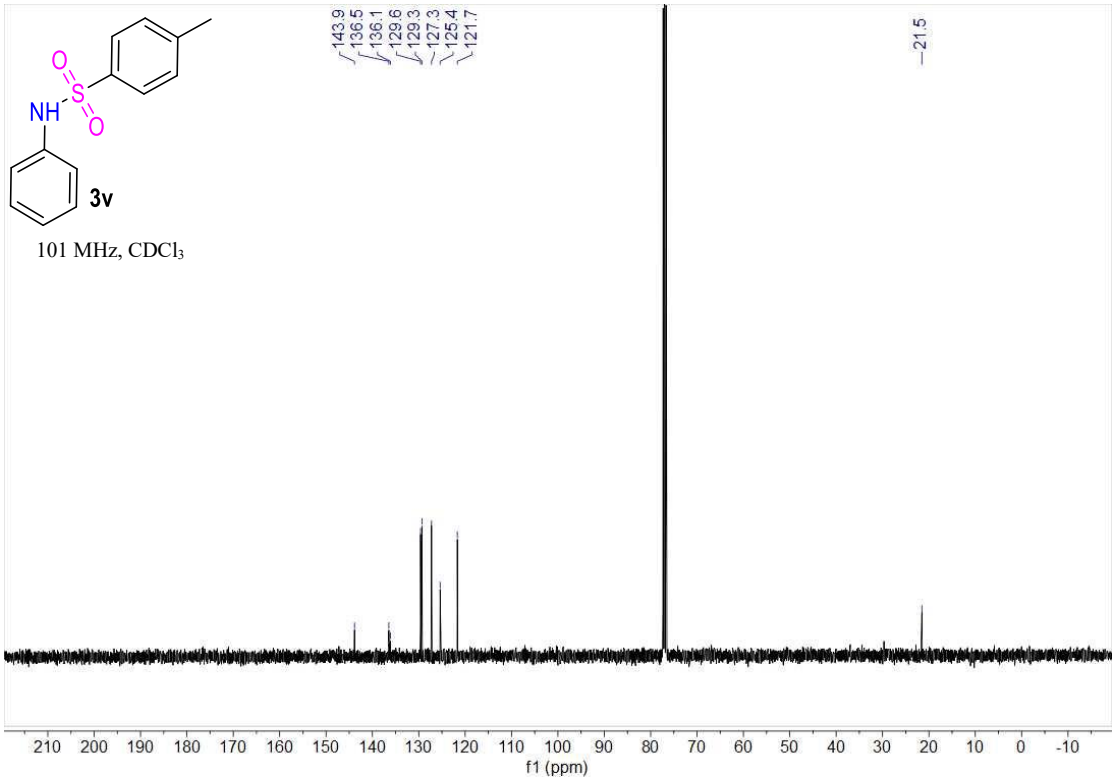
N-([1,1'-biphenyl]-3-yl)-4-methylbenzenesulfonamide (3u)



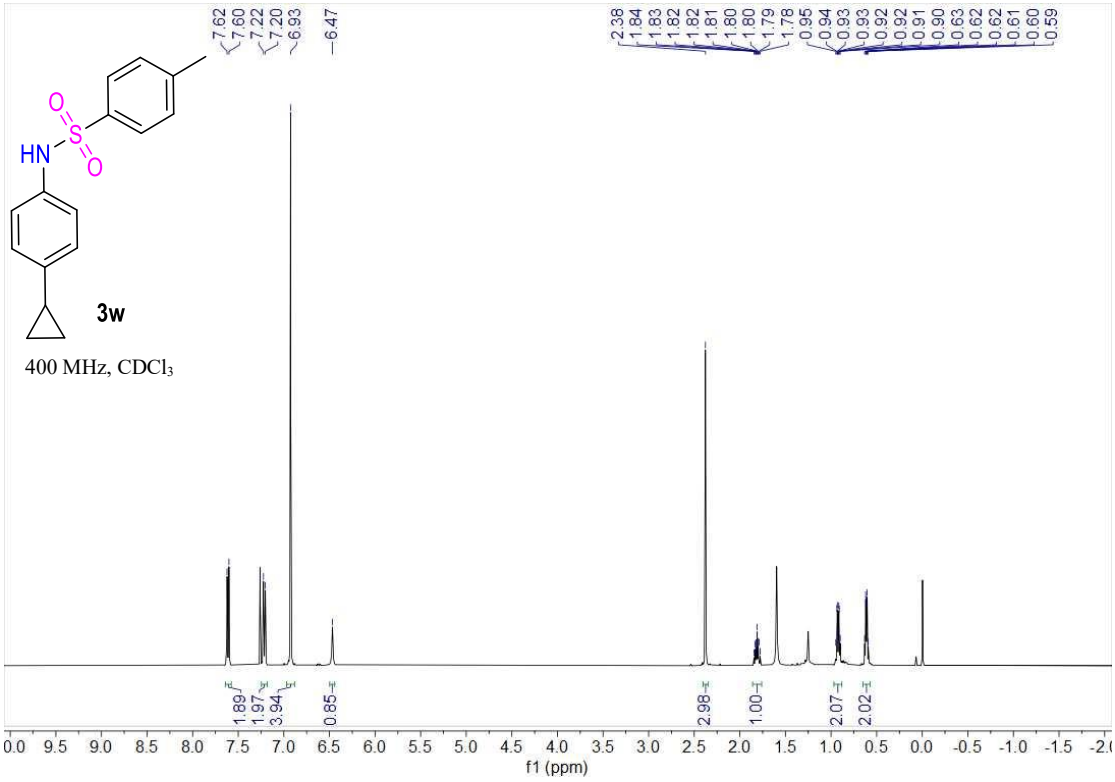


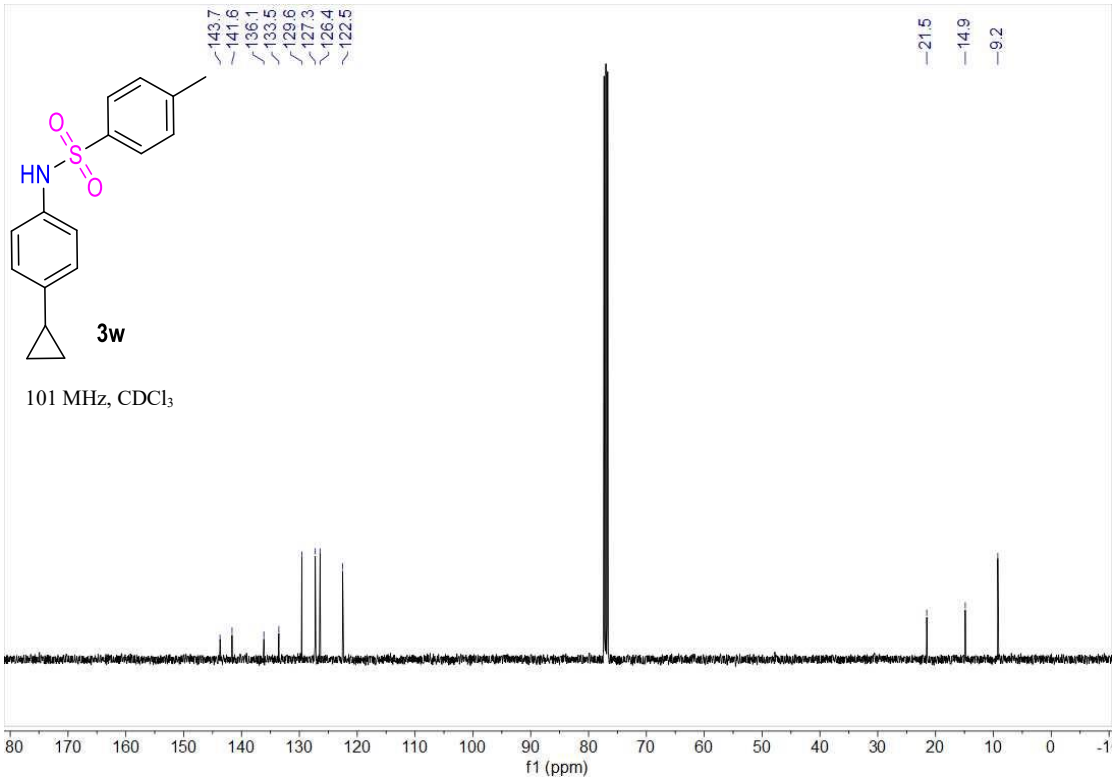
4-methyl-*N*-phenylbenzenesulfonamide (3v)



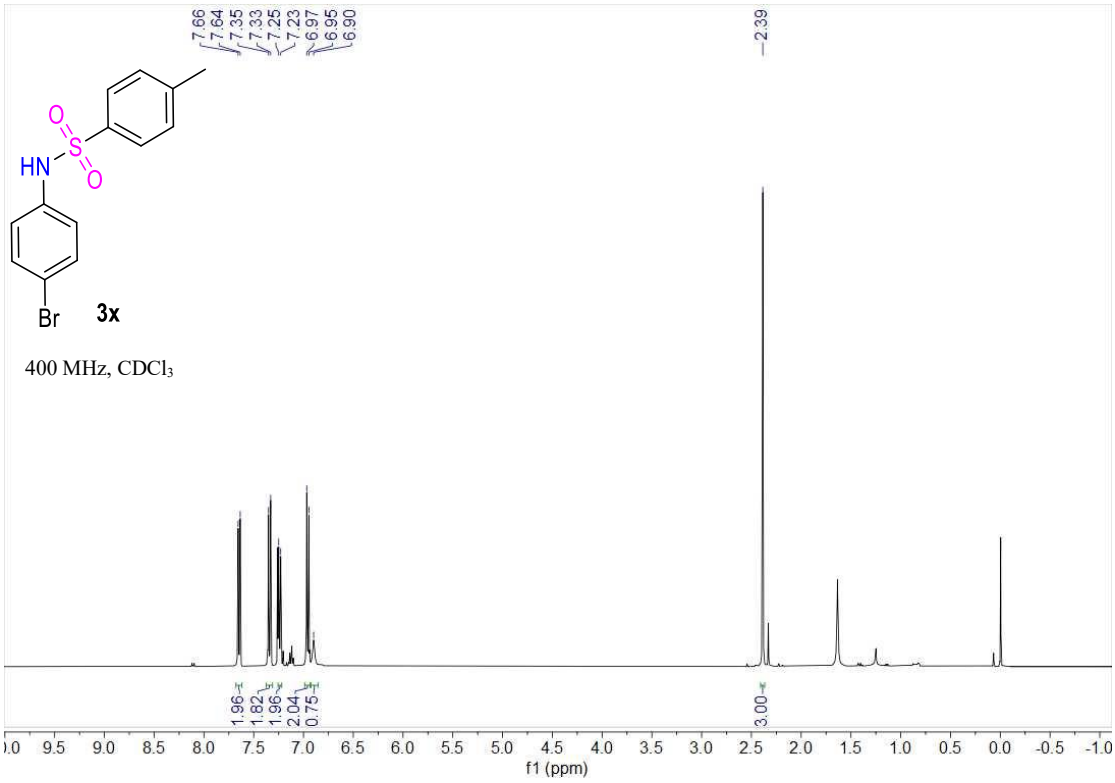


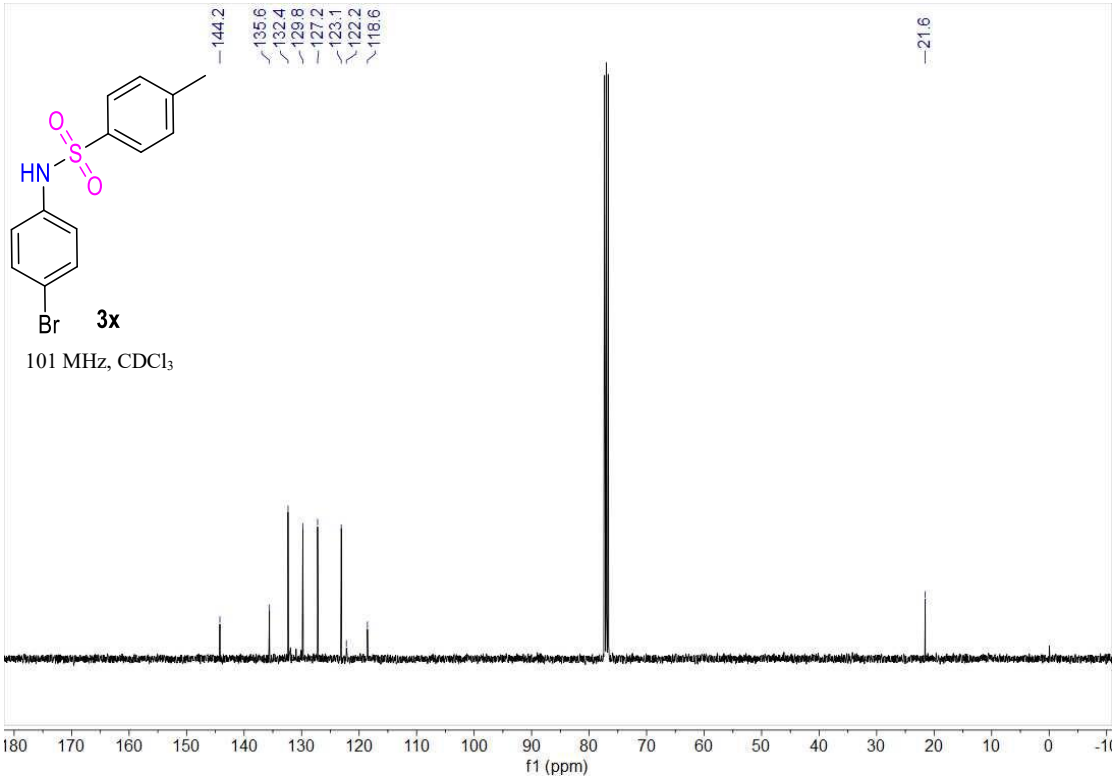
***N*-(4-cyclopropylphenyl)-4-methylbenzenesulfonamide (3w)**



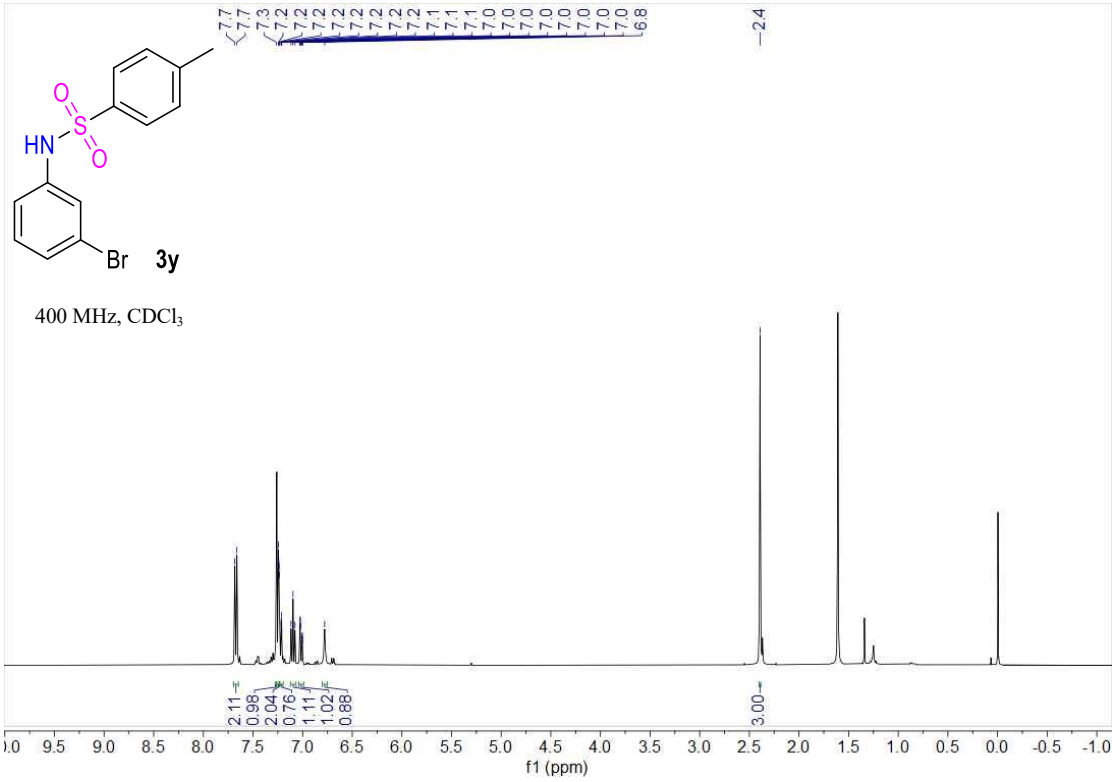


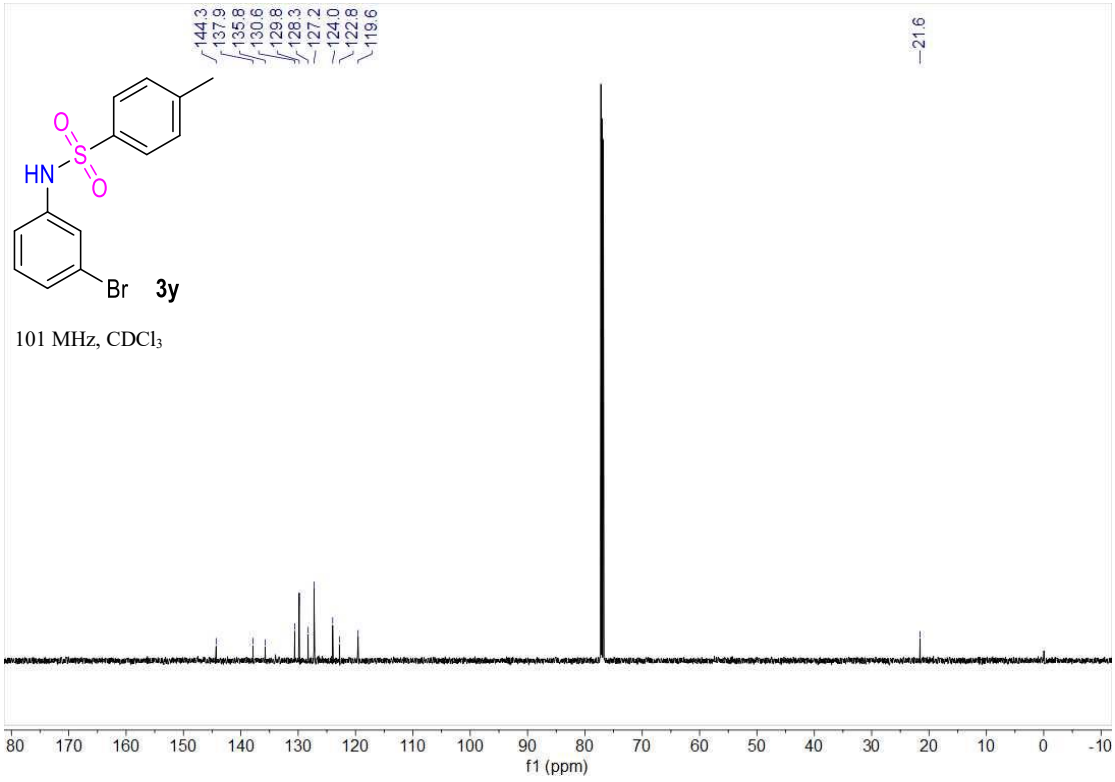
N-(4-bromophenyl)-4-methylbenzenesulfonamide (3x)



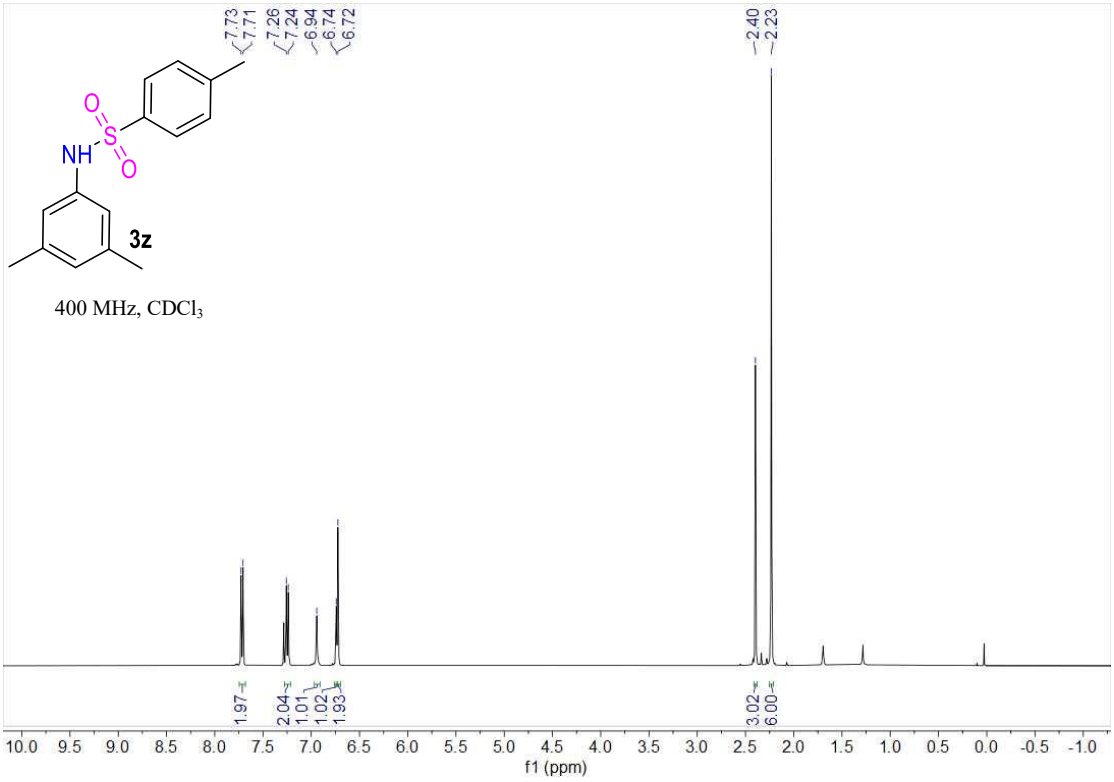


N-(3-bromophenyl)-4-methylbenzenesulfonamide (3y)

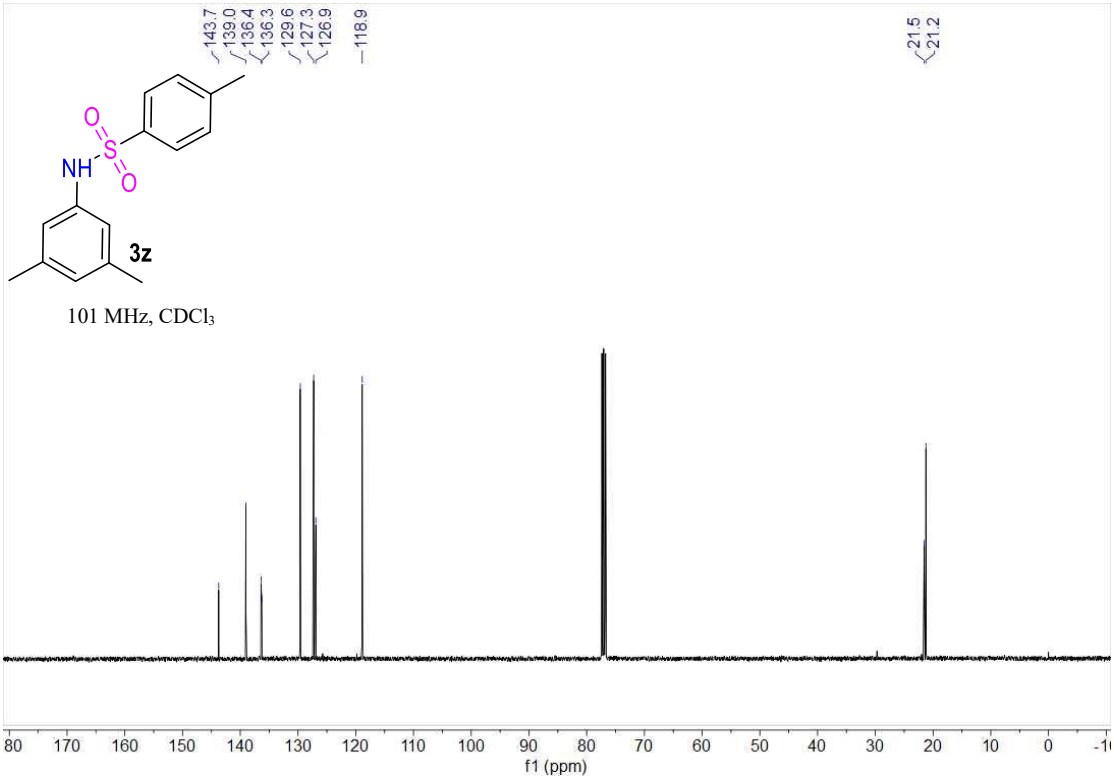




N-(3,5-dimethylphenyl)-4-methylbenzenesulfonamide (3z)

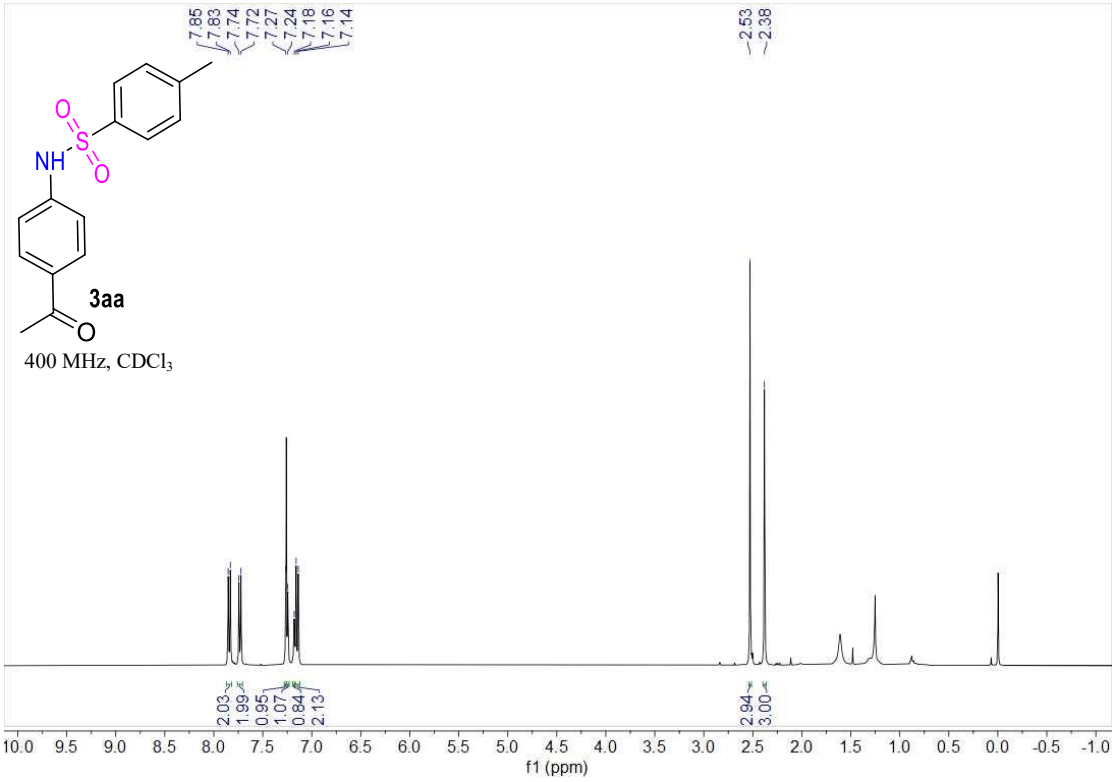


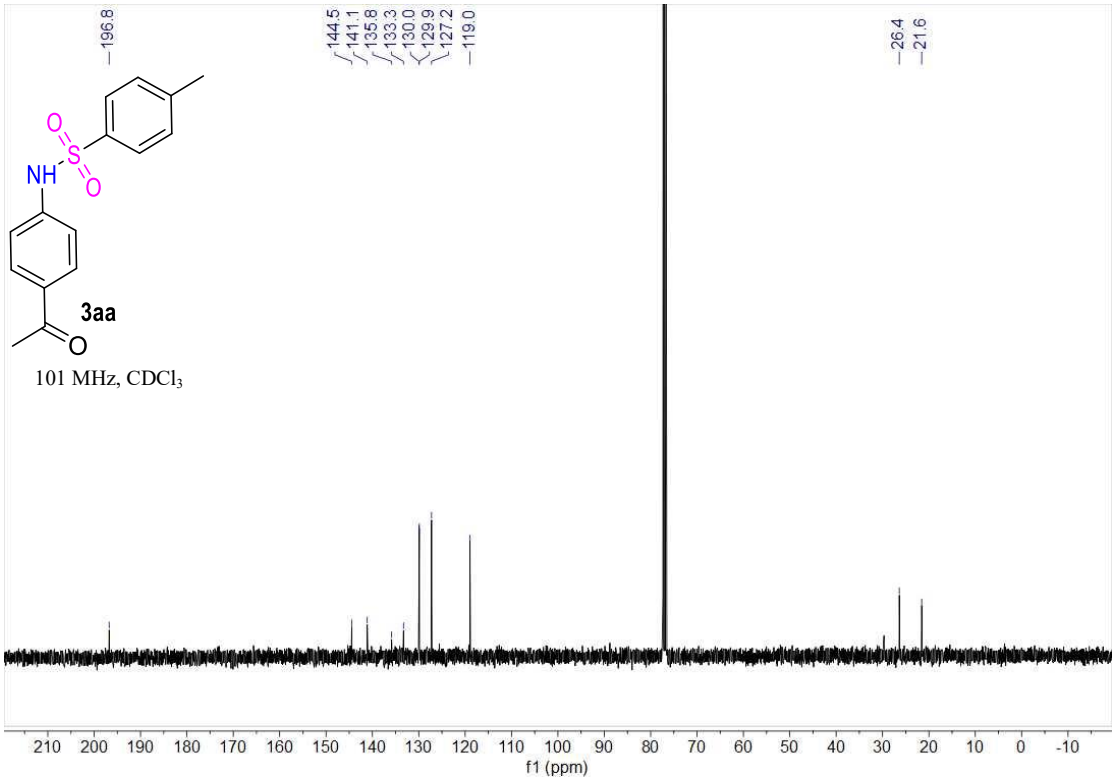
400 MHz, $CDCl_3$



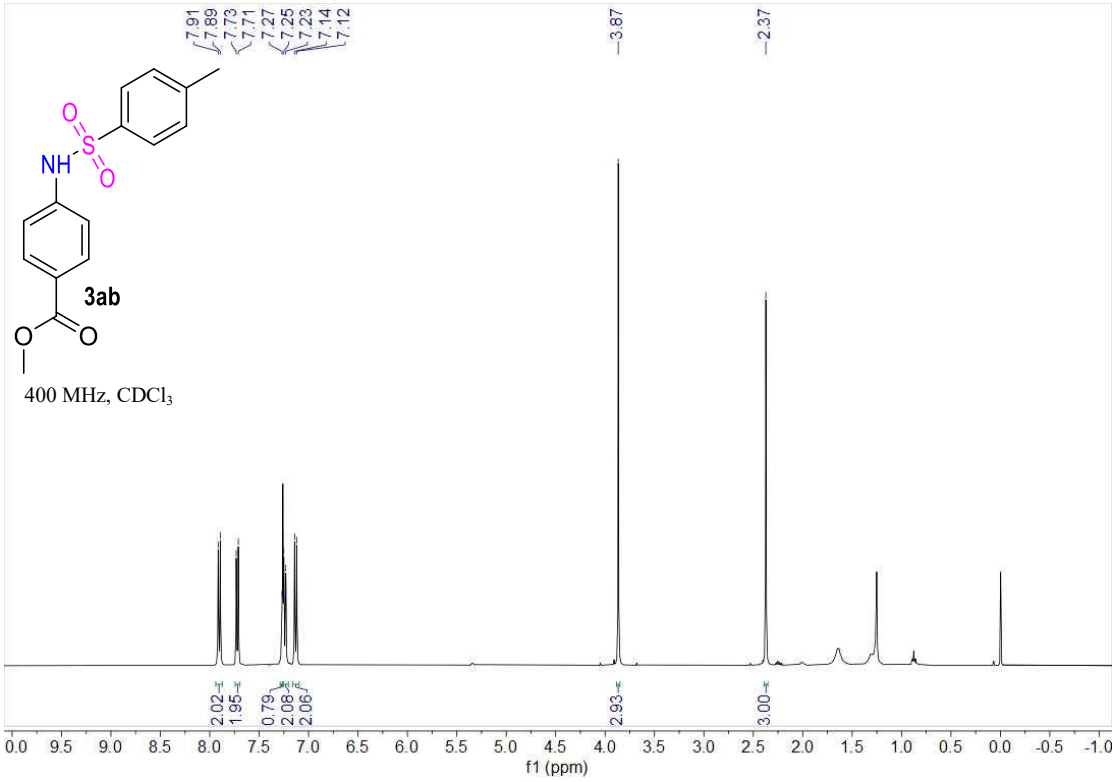
101 MHz, $CDCl_3$

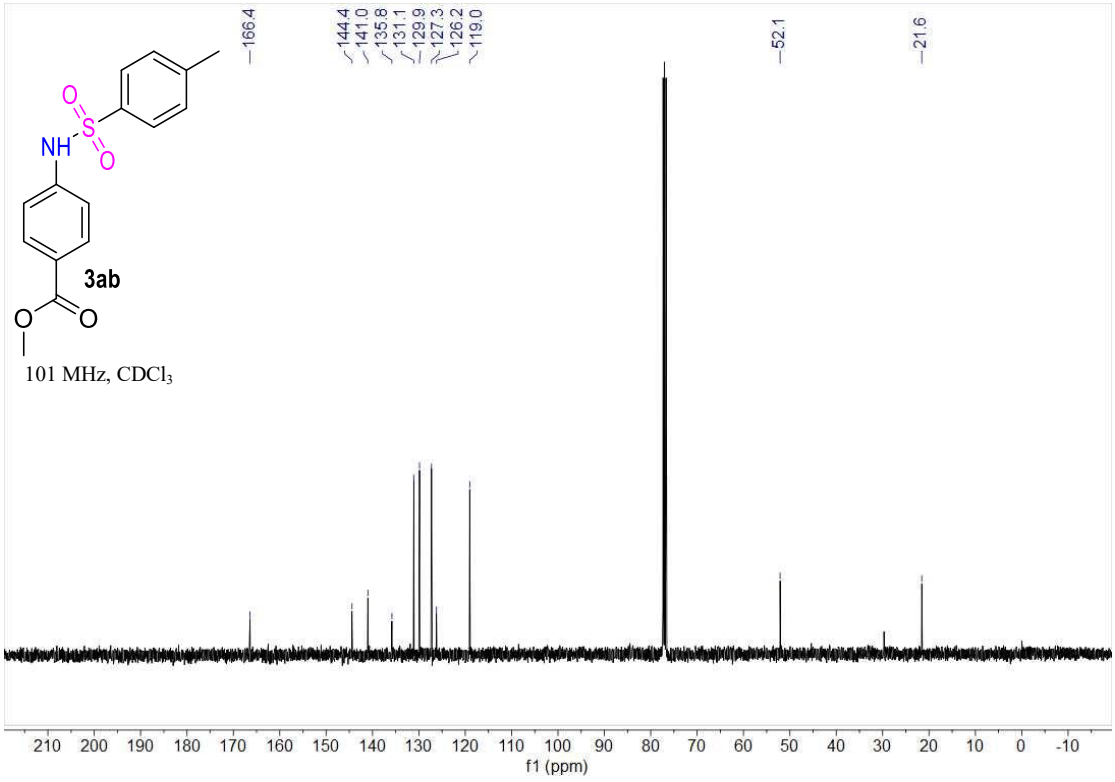
***N*-(4-acetylphenyl)-4-methylbenzenesulfonamide (3aa)**



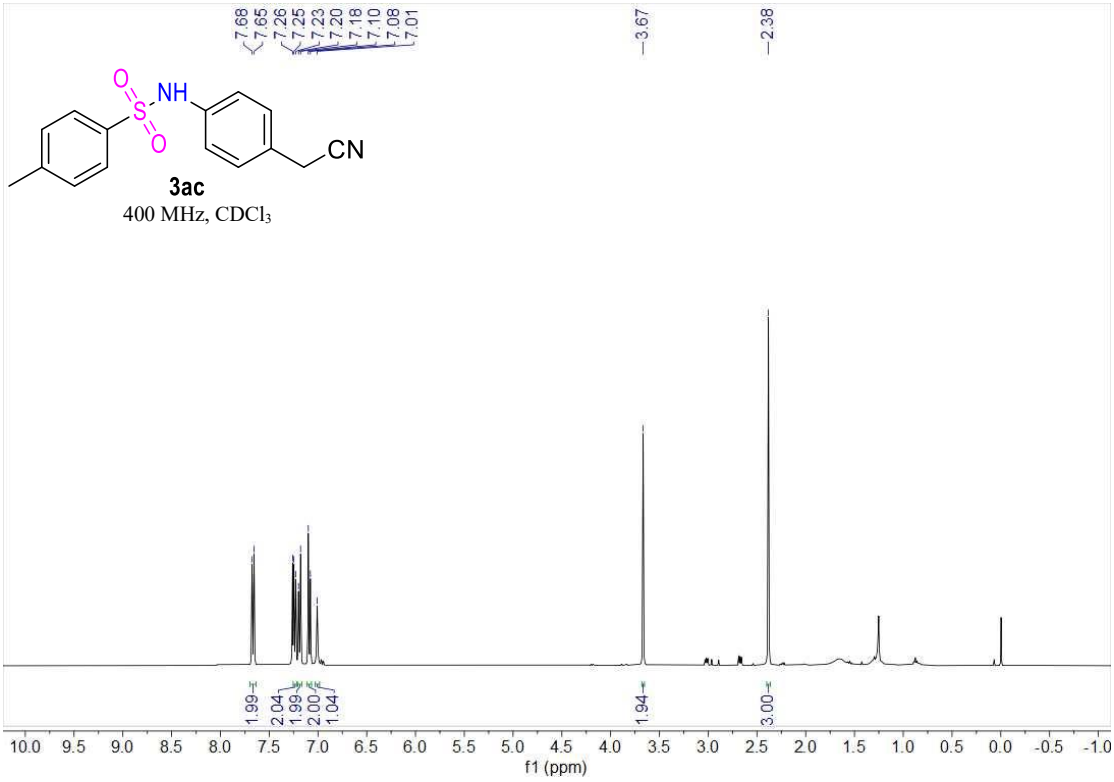


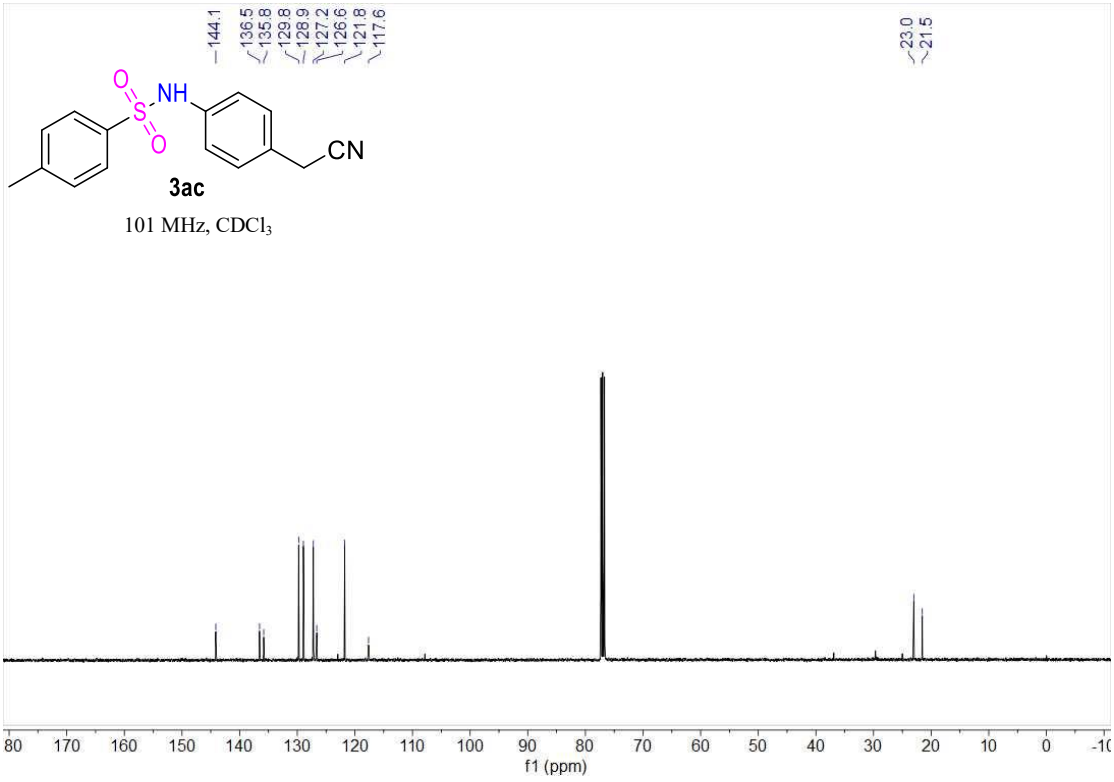
Methyl-4-((4-methylphenyl)sulfonamido)benzoate (3ab)



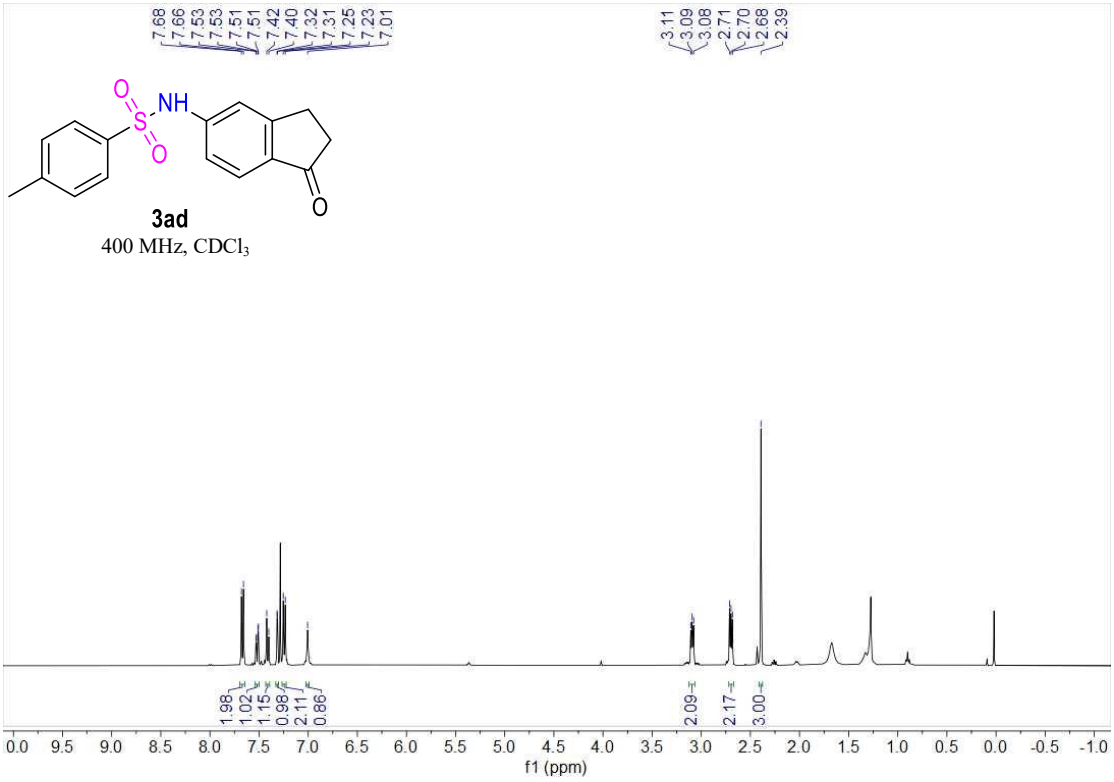


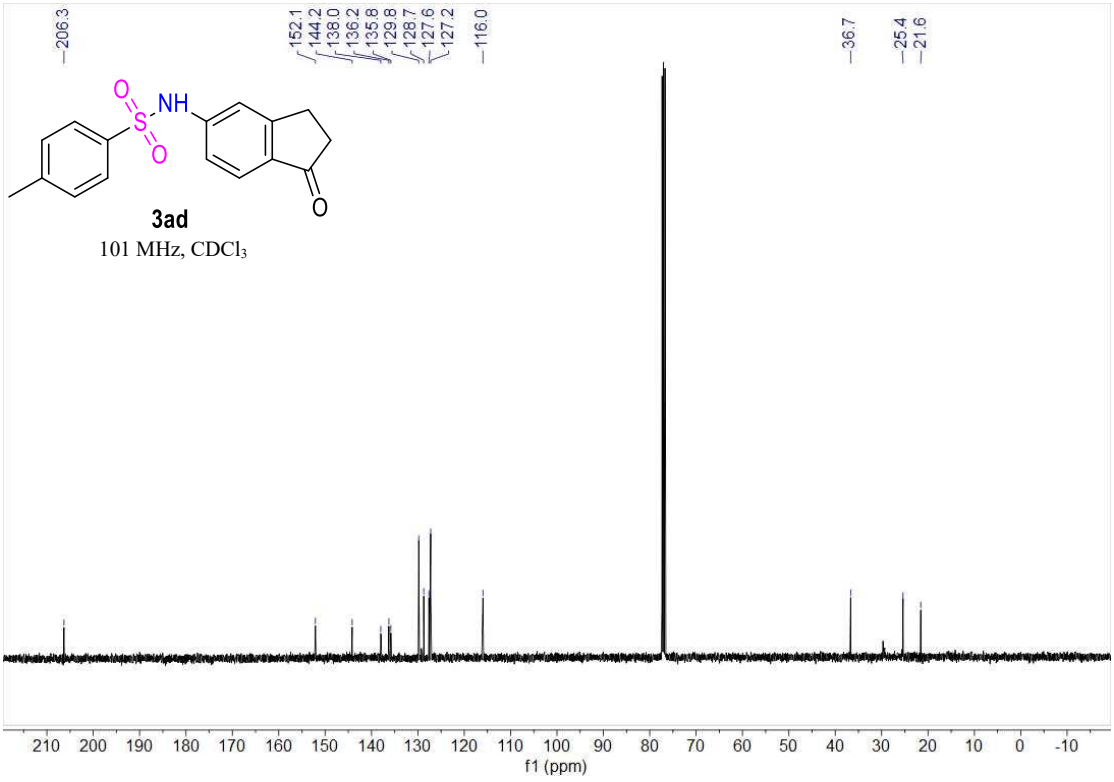
***N*-(4-(cyanomethyl)phenyl)-4-methylbenzenesulfonamide (3ac)**



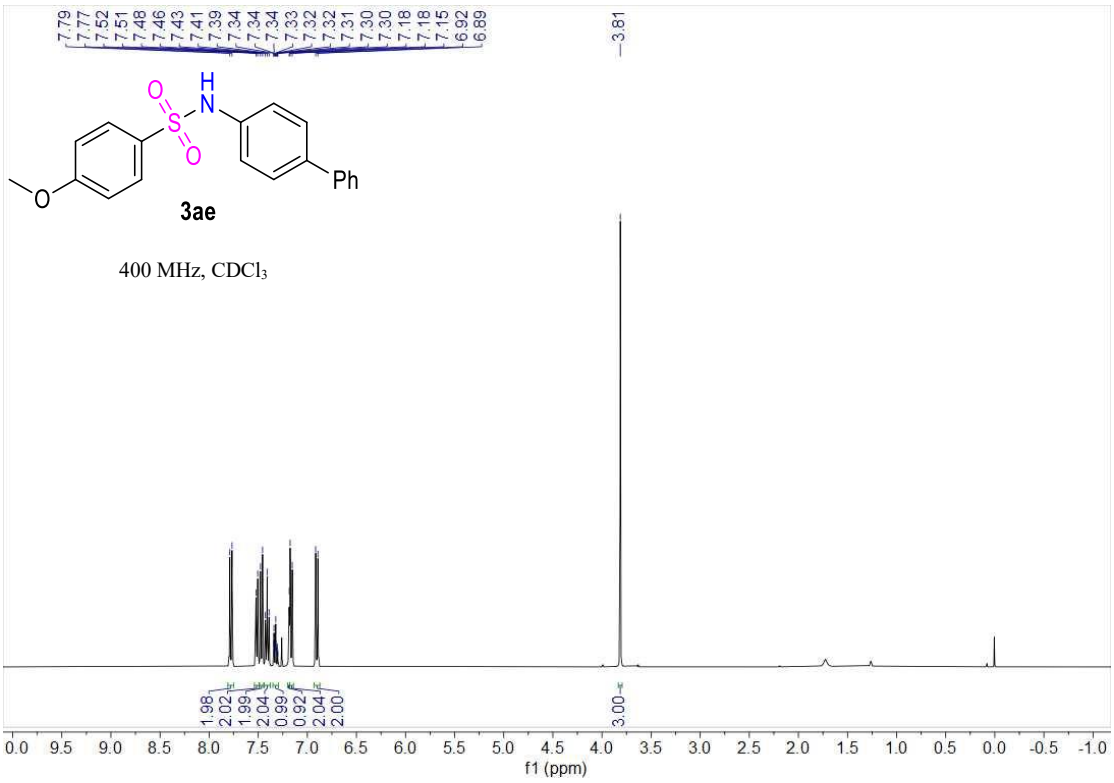


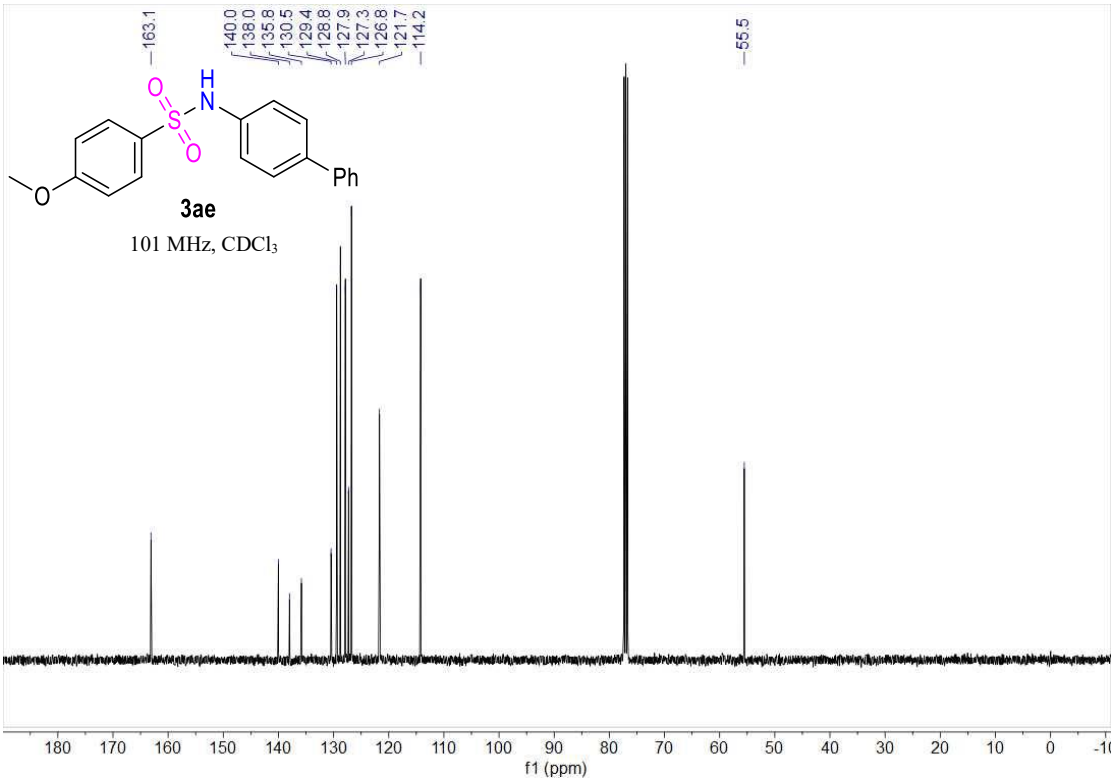
4-methyl-*N*-(1-oxo-2,3-dihydro-1H-inden-5-yl)benzenesulfonamide (3ad)



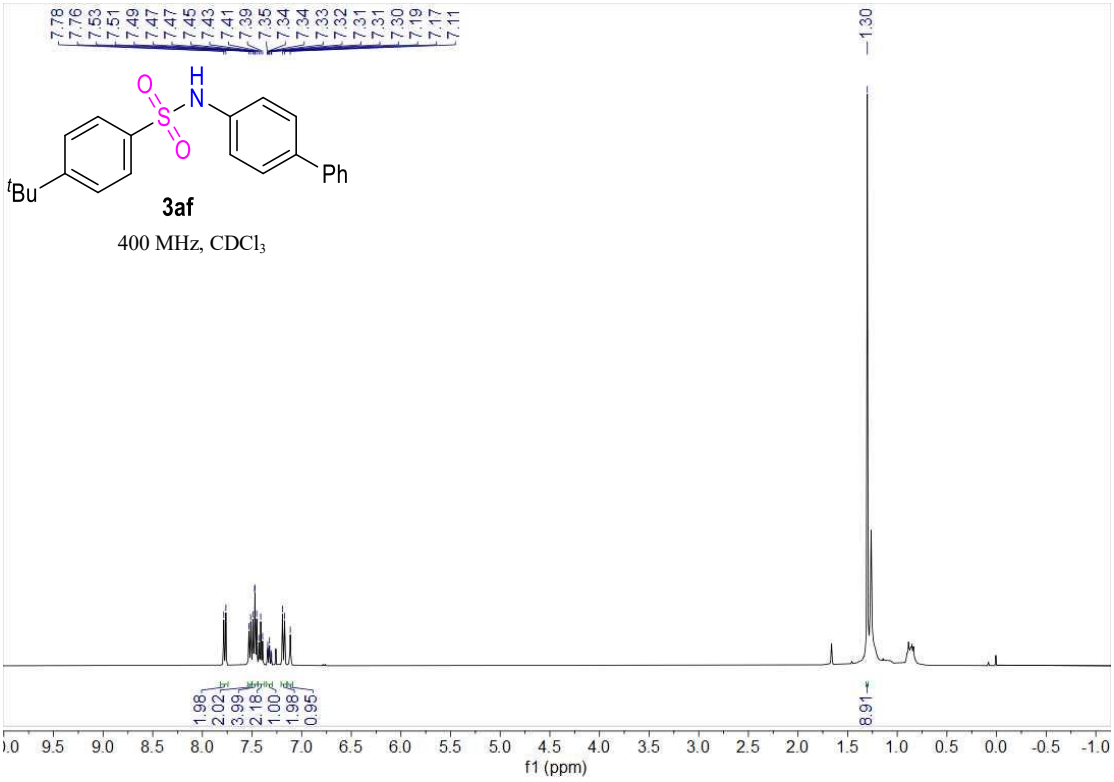


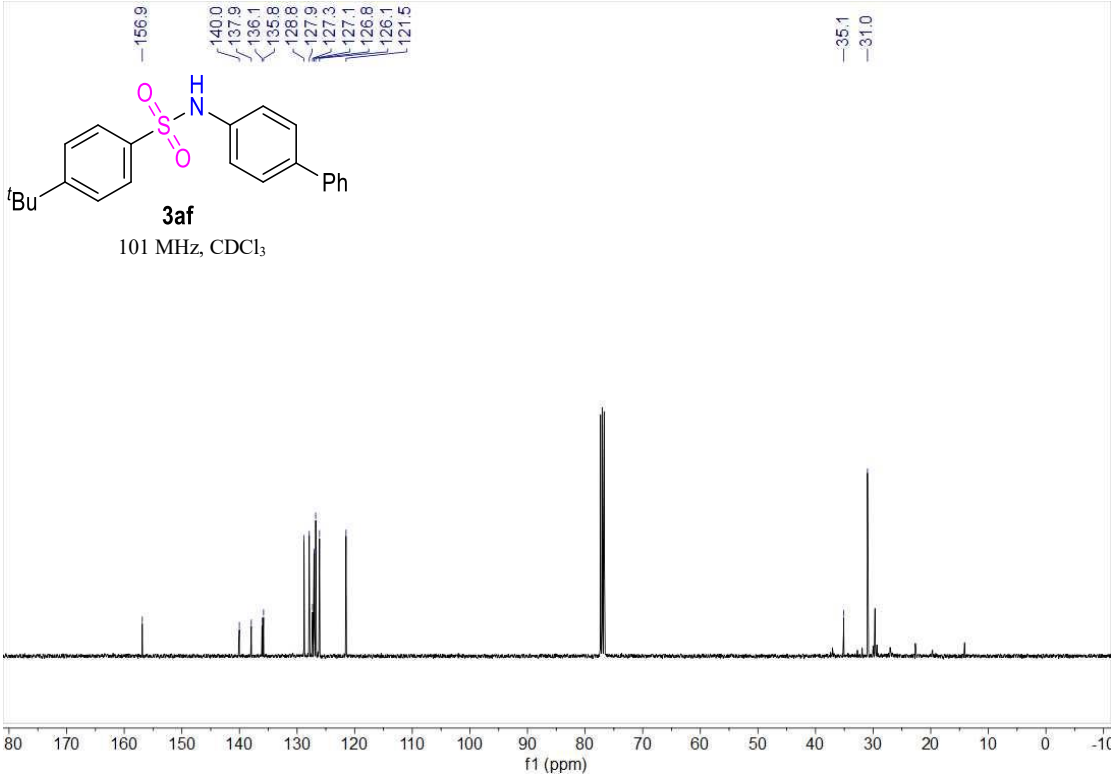
***N*-([1,1'-biphenyl]-4-yl)-4-methoxybenzenesulfonamide (3ae)**



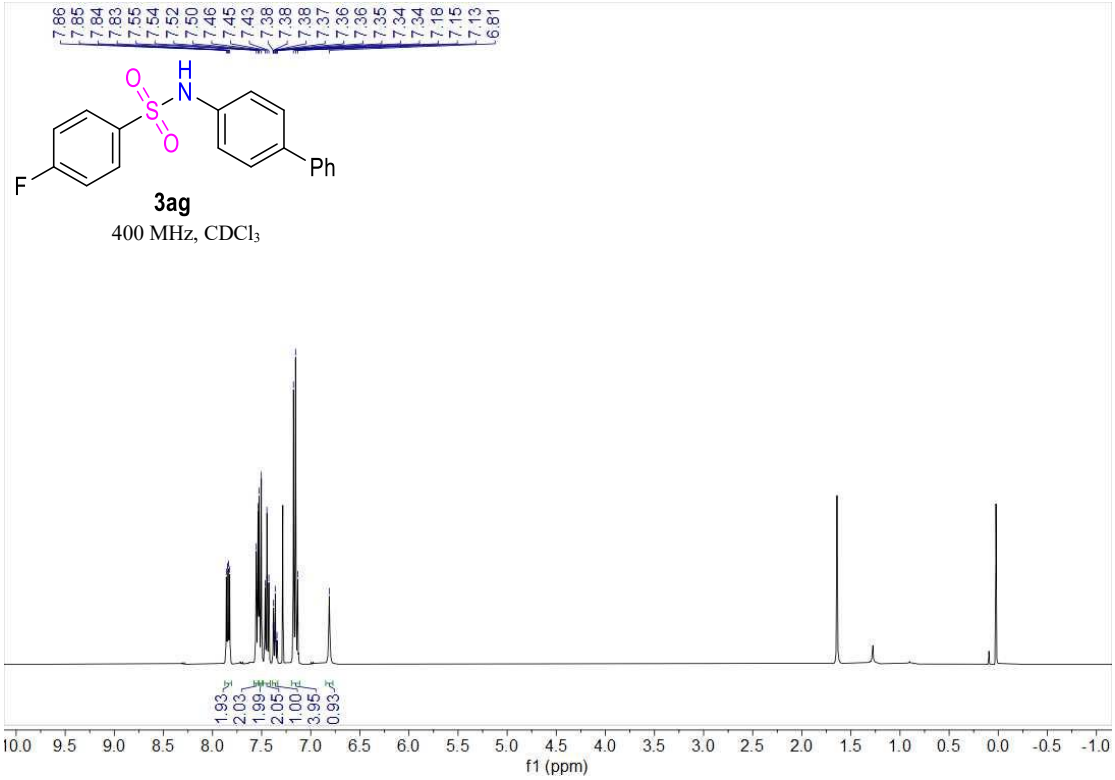


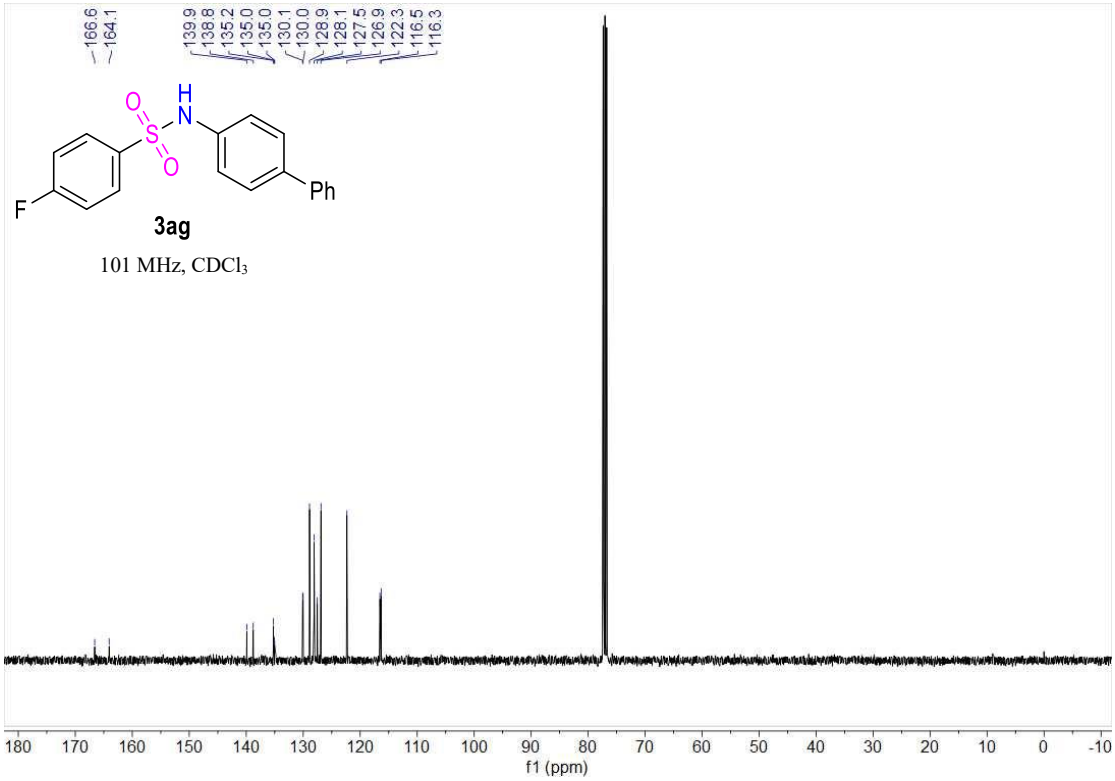
N-([1,1'-biphenyl]-4-yl)-4-(*tert*-butyl)benzenesulfonamide (3af)

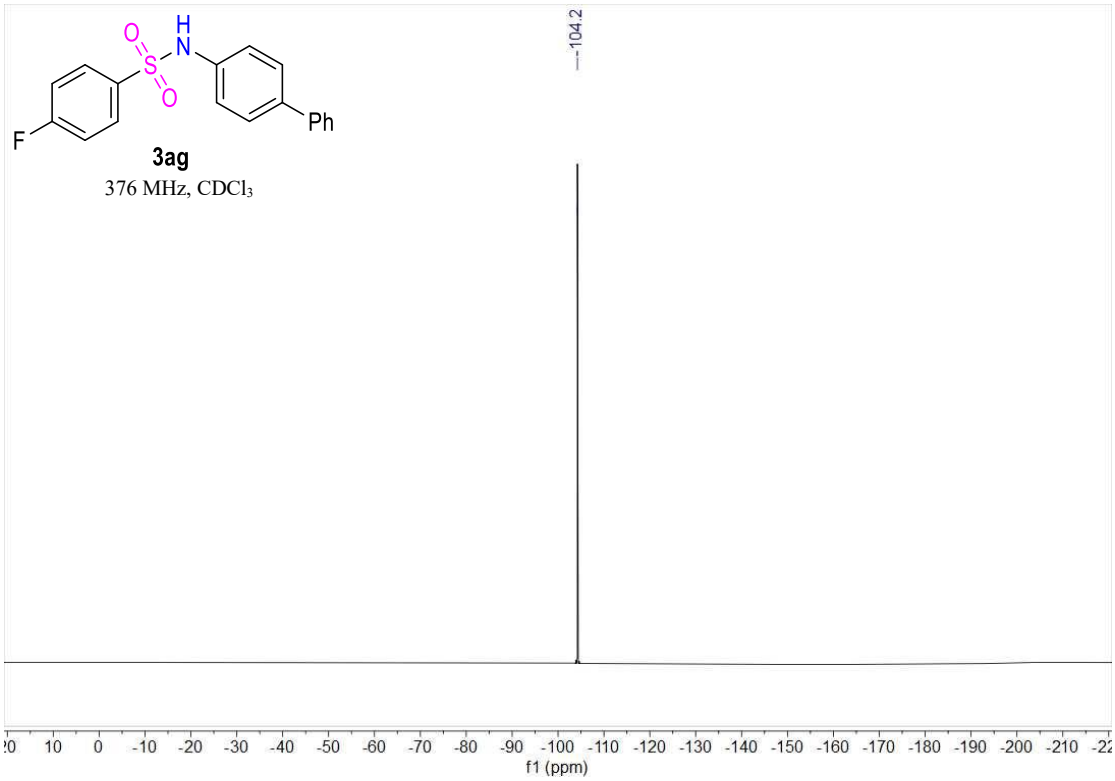




N-([1,1'-biphenyl]-4-yl)-4-fluorobenzenesulfonamide (3ag)



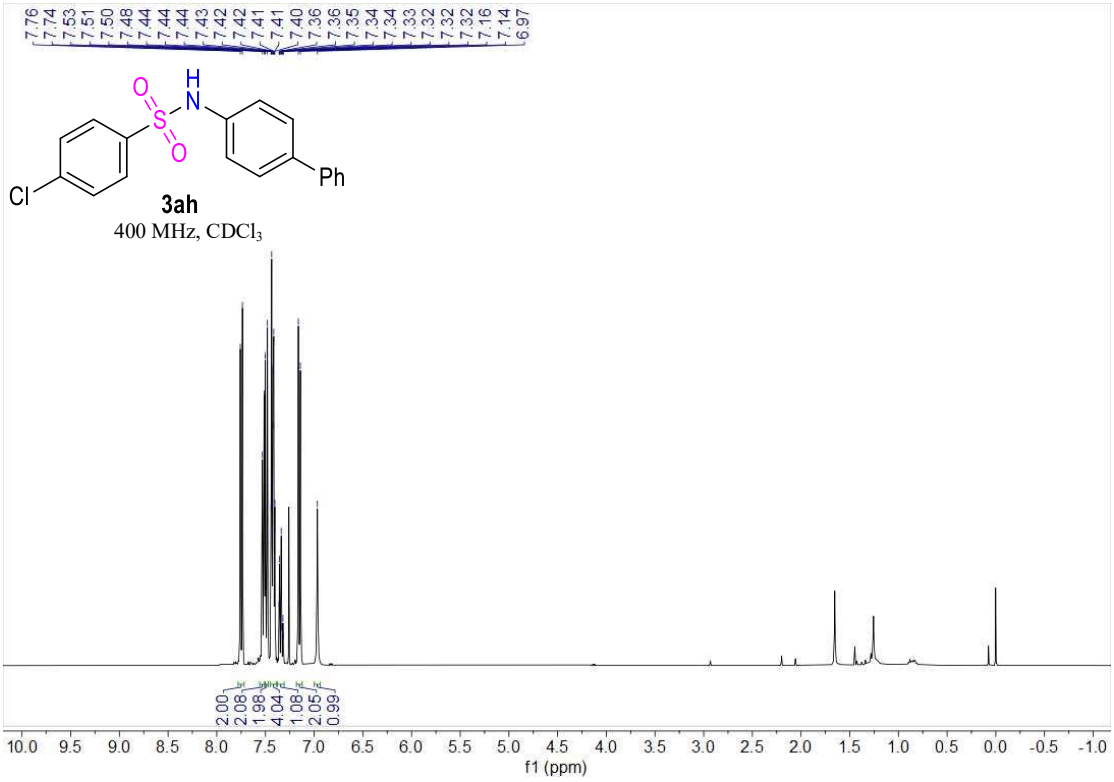


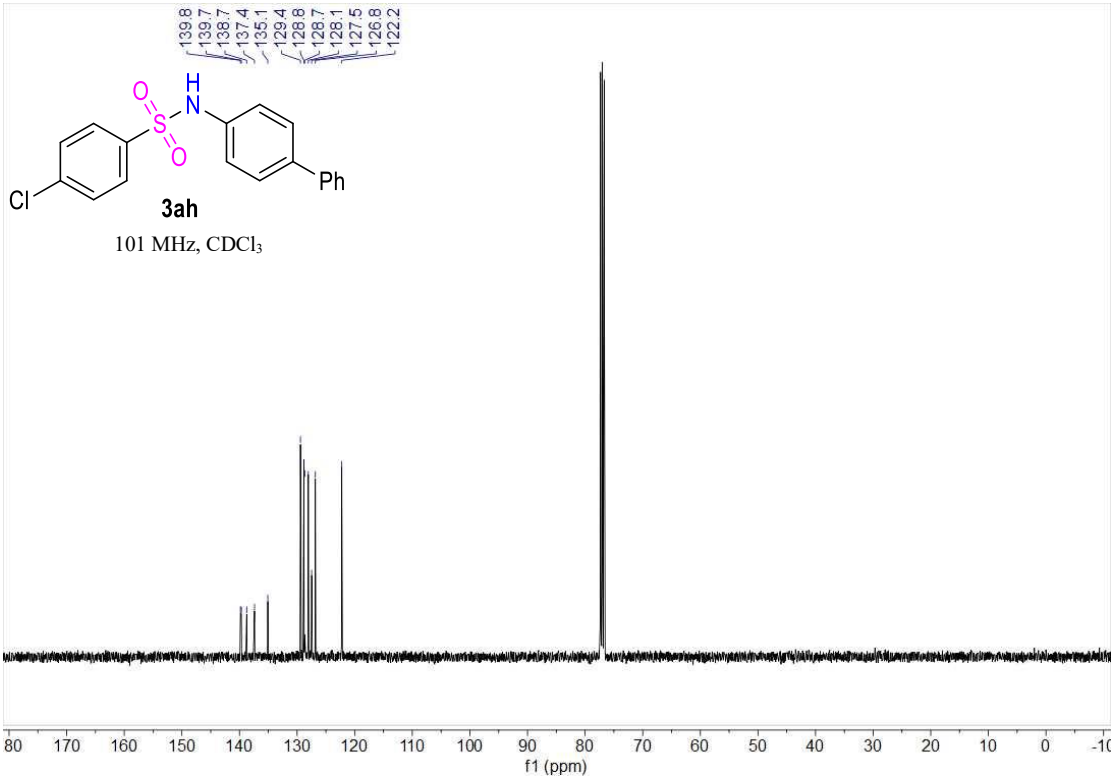


3ag

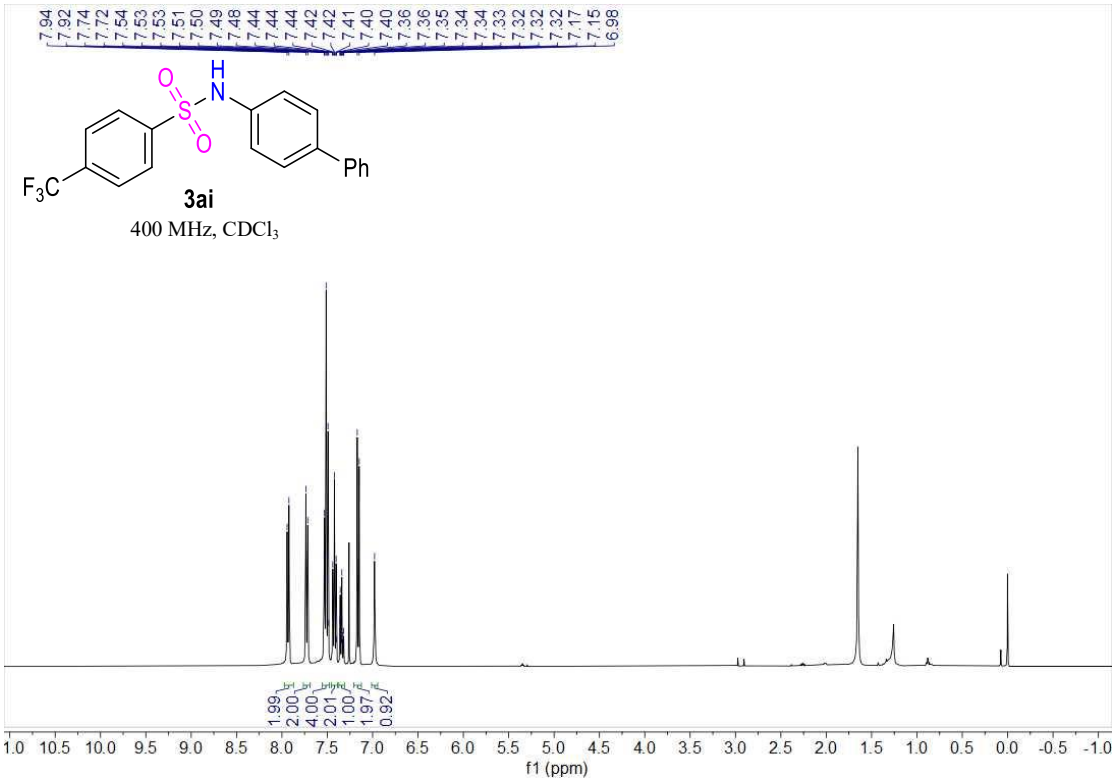
376 MHz, $CDCl_3$

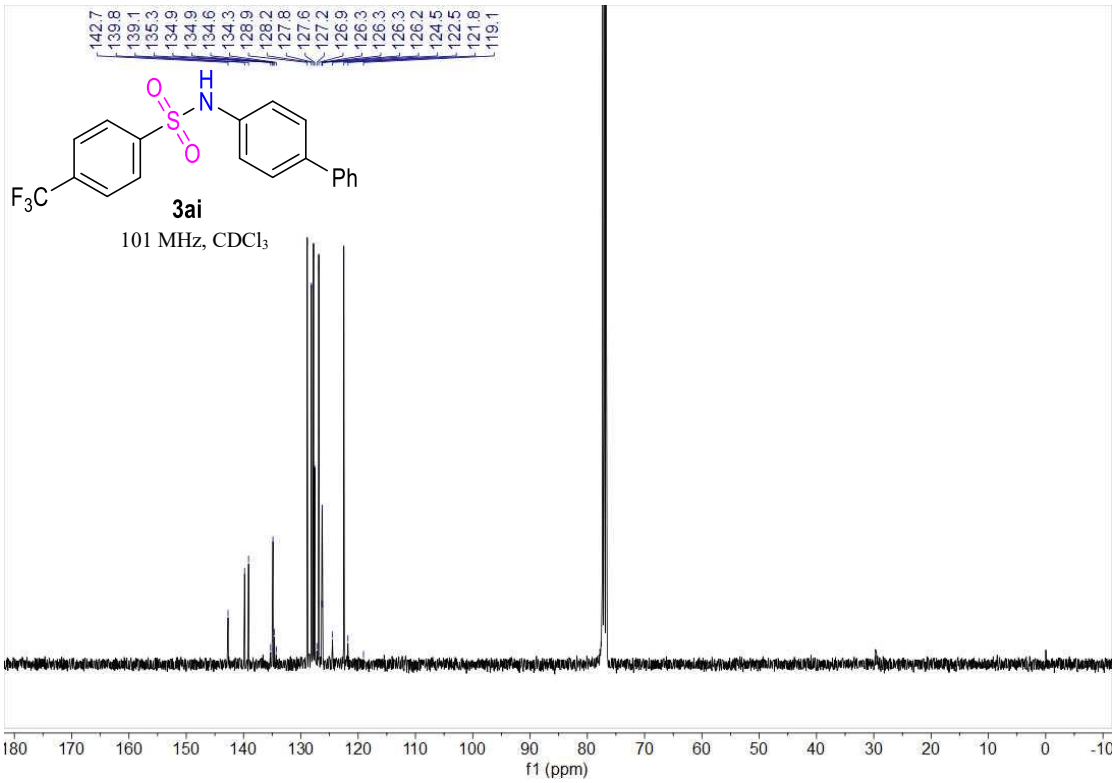
N-([1,1'-biphenyl]-4-yl)-4-chlorobenzenesulfonamide (3ah)

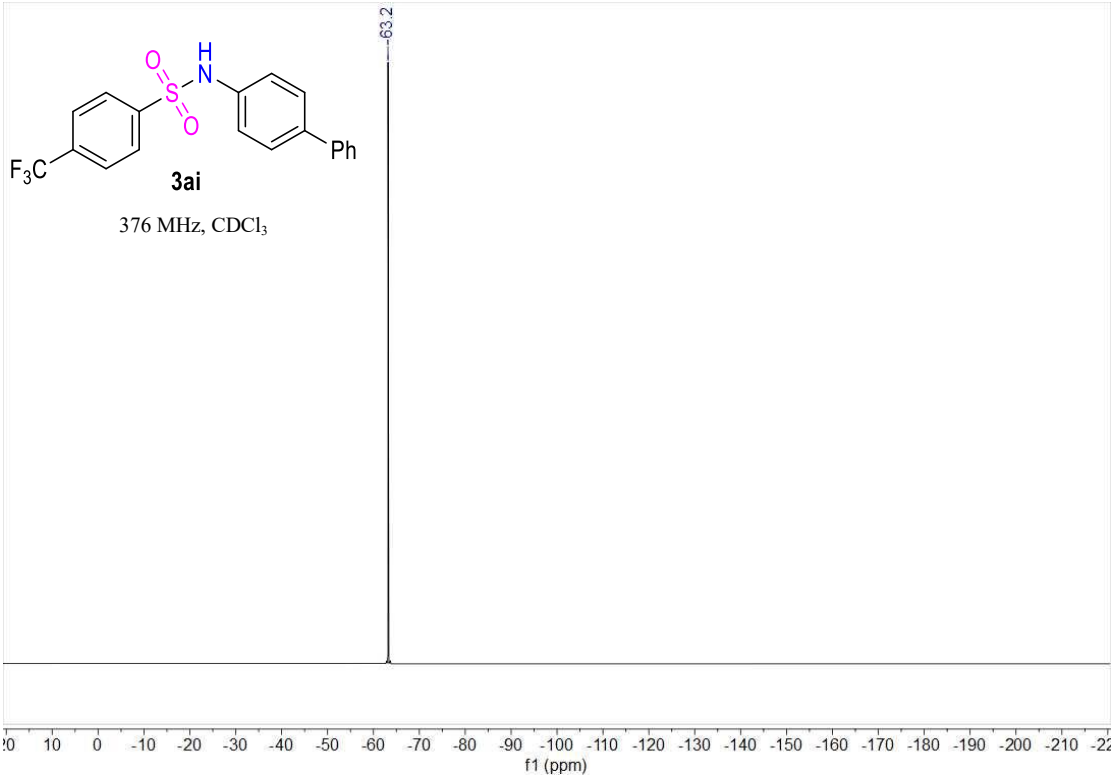




***N*-([1,1'-biphenyl]-4-yl)-4-(trifluoromethyl)benzenesulfonamide (3ai)**



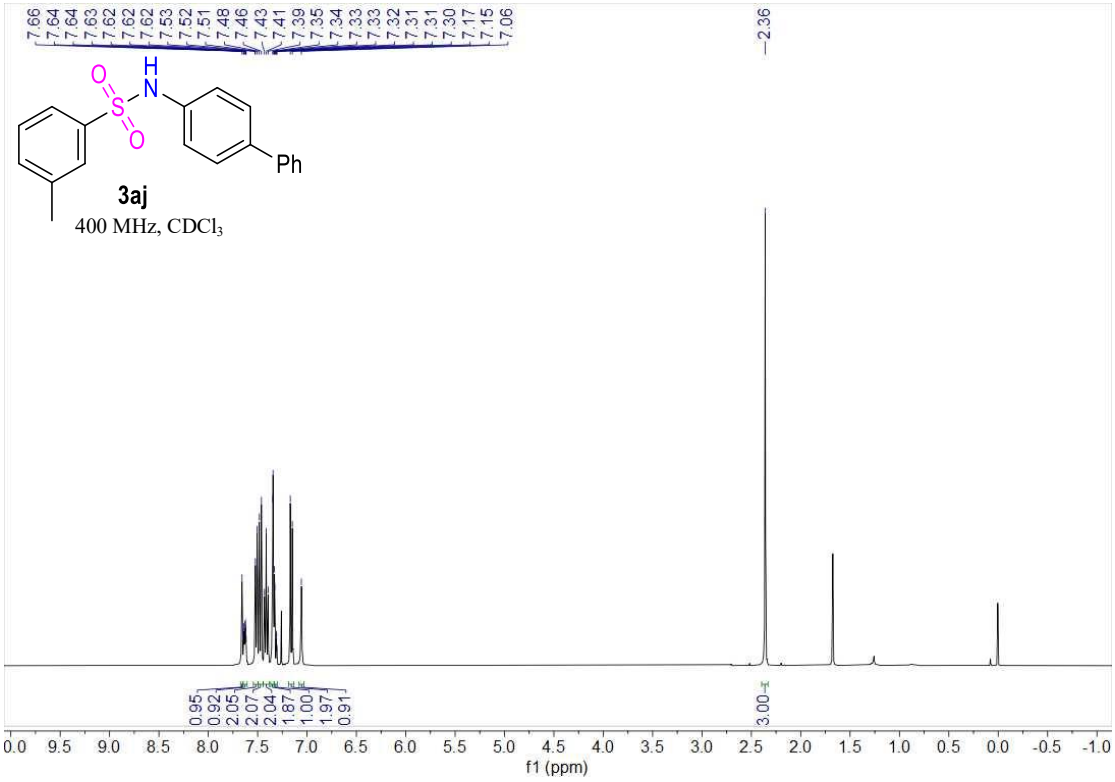


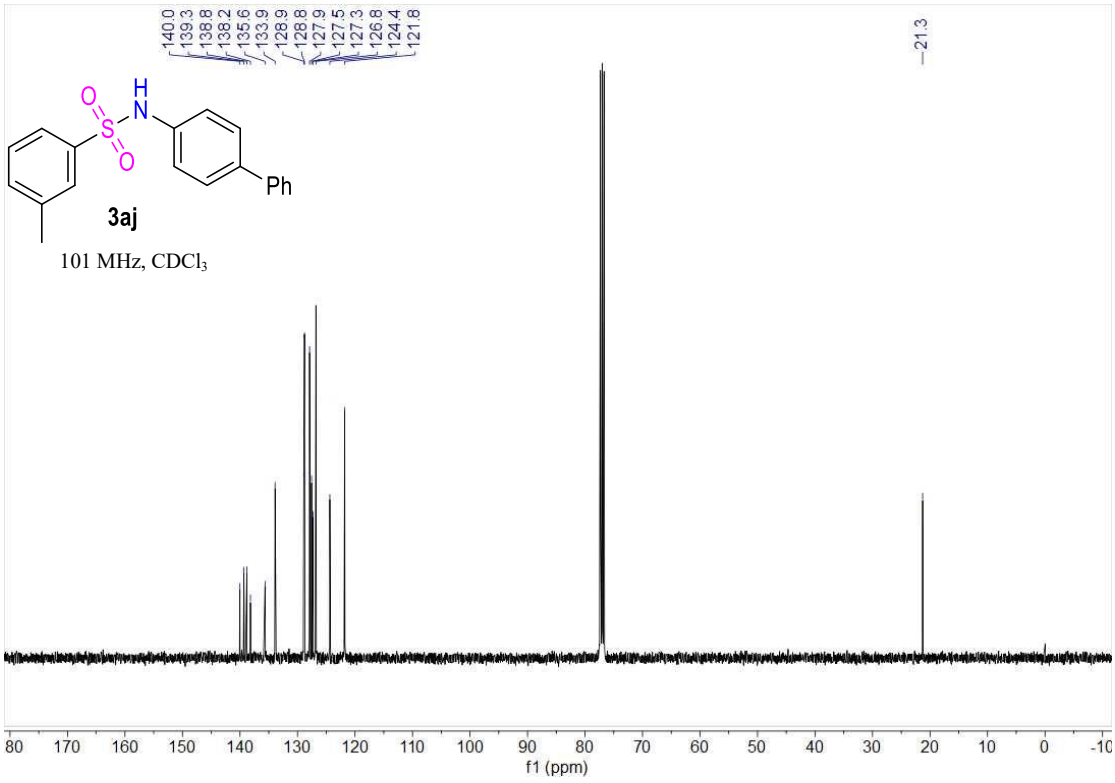


3ai

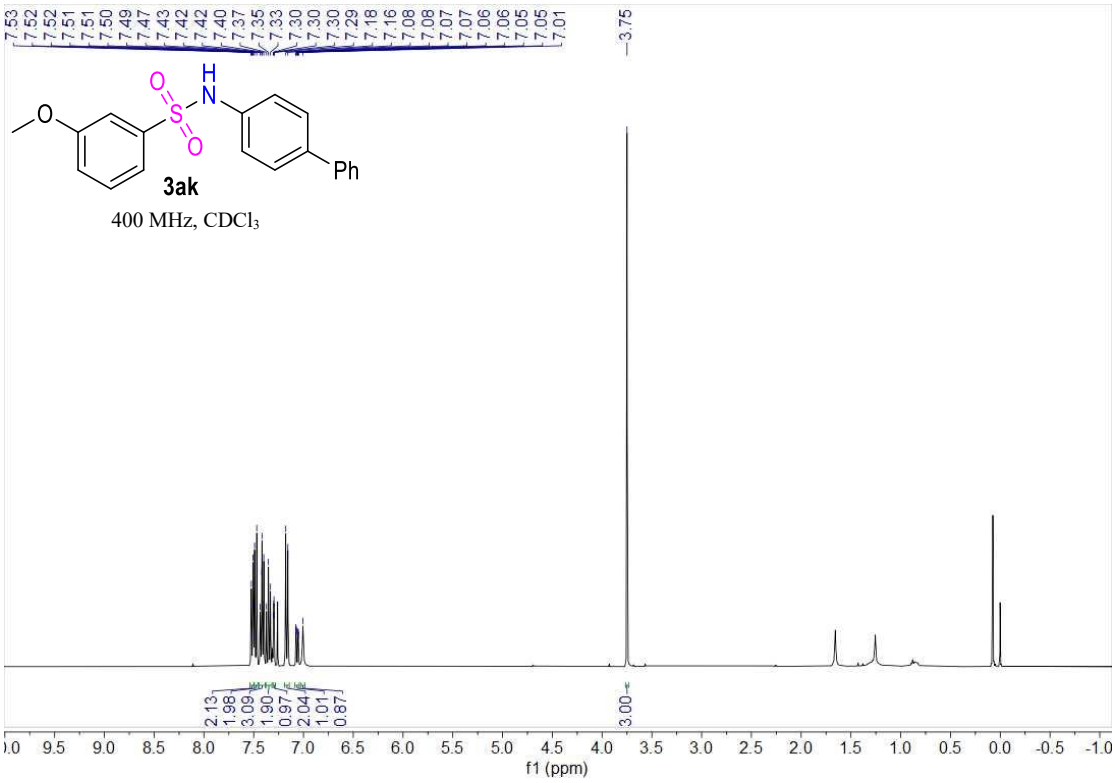
376 MHz, $CDCl_3$

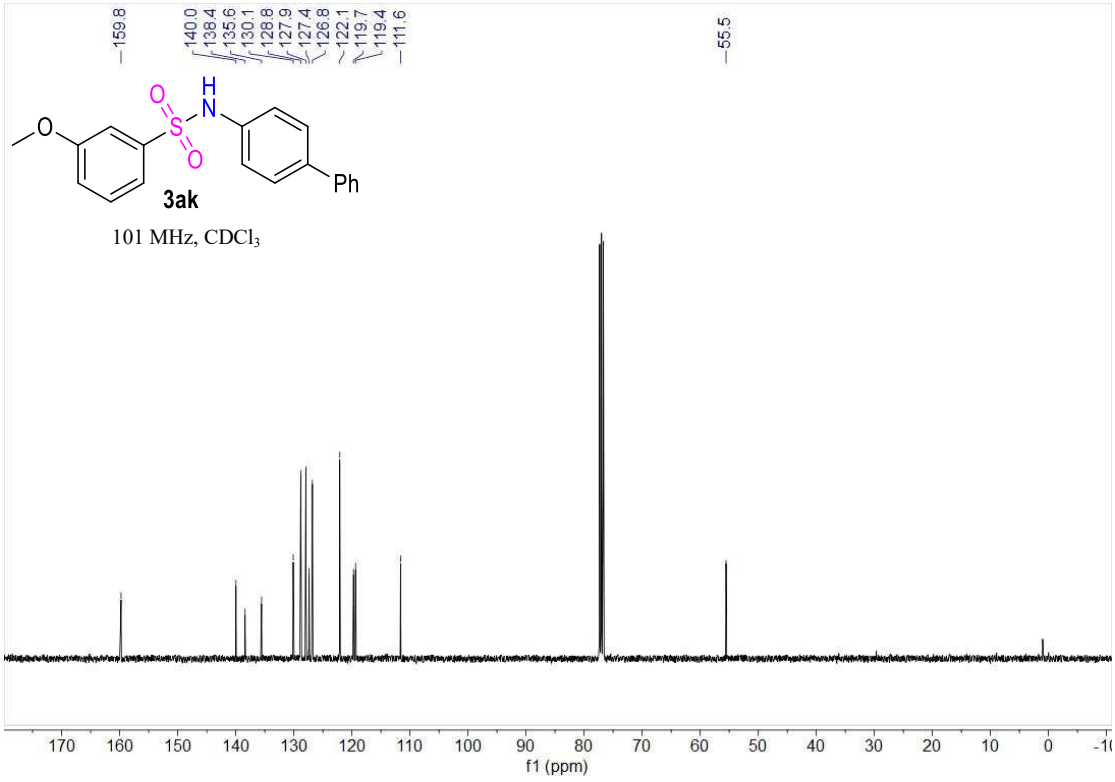
N-([1,1'-biphenyl]-4-yl)-3-methylbenzenesulfonamide (3aj)



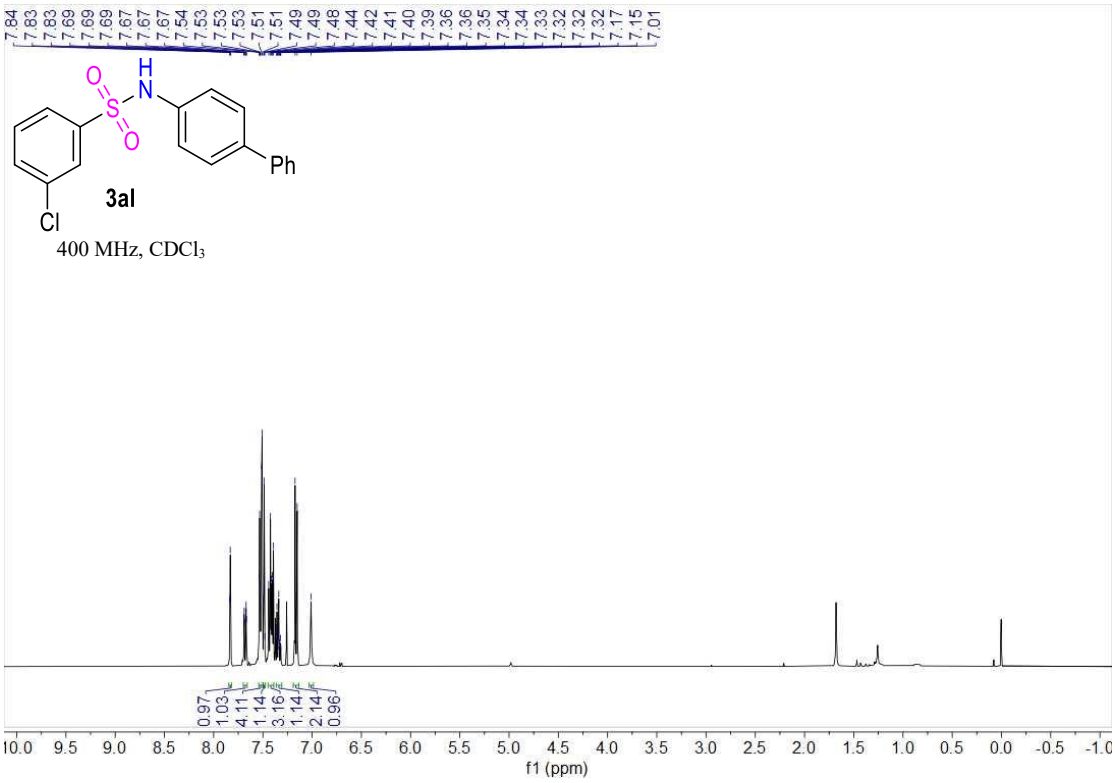


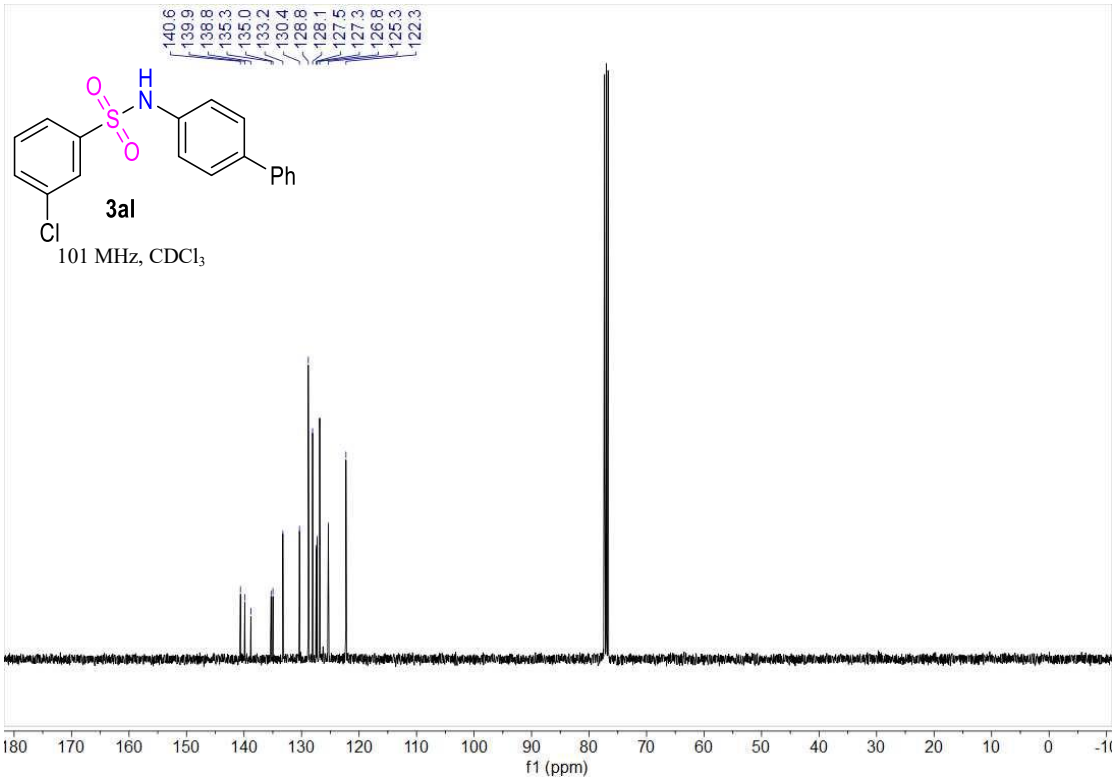
N-([1,1'-biphenyl]-4-yl)-3-methoxybenzenesulfonamide (3ak)



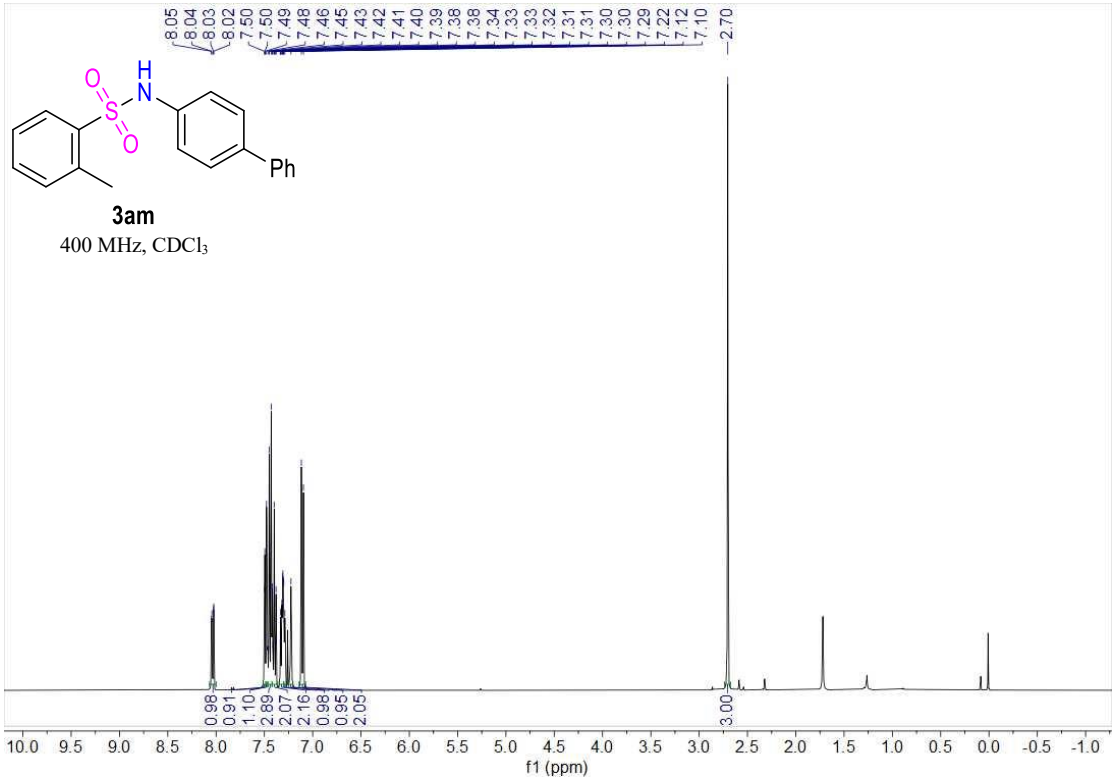


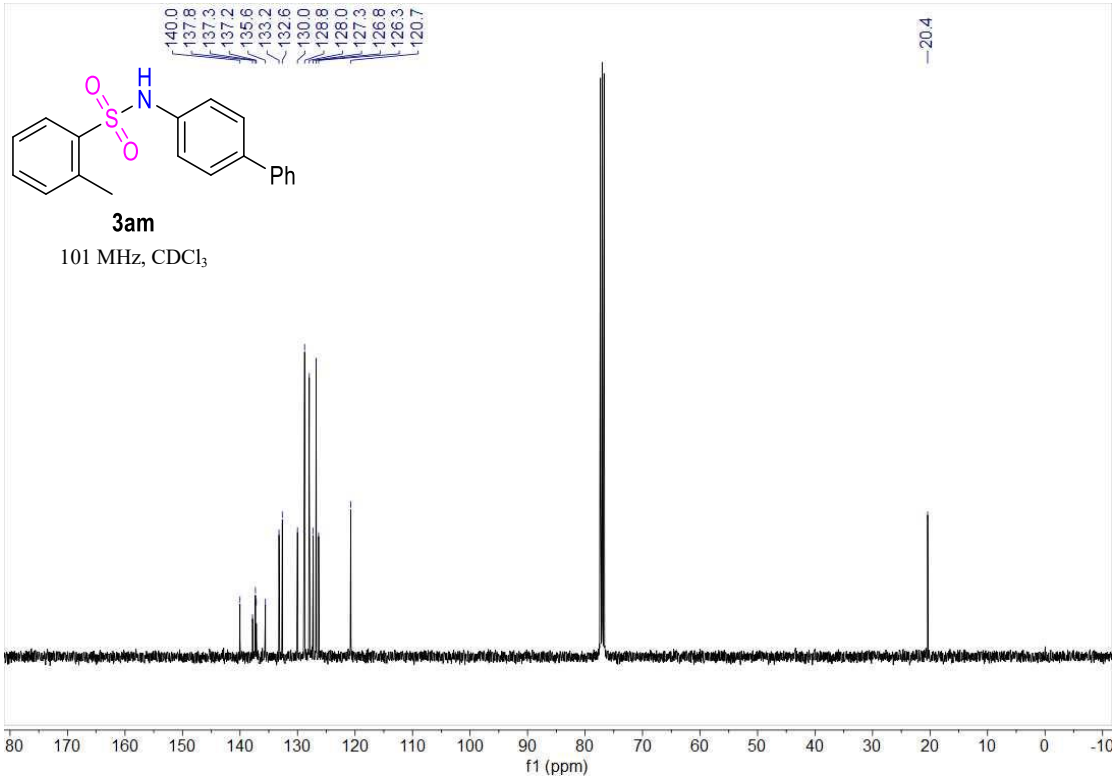
N-([1,1'-biphenyl]-4-yl)-3-chlorobenzenesulfonamide (3al)



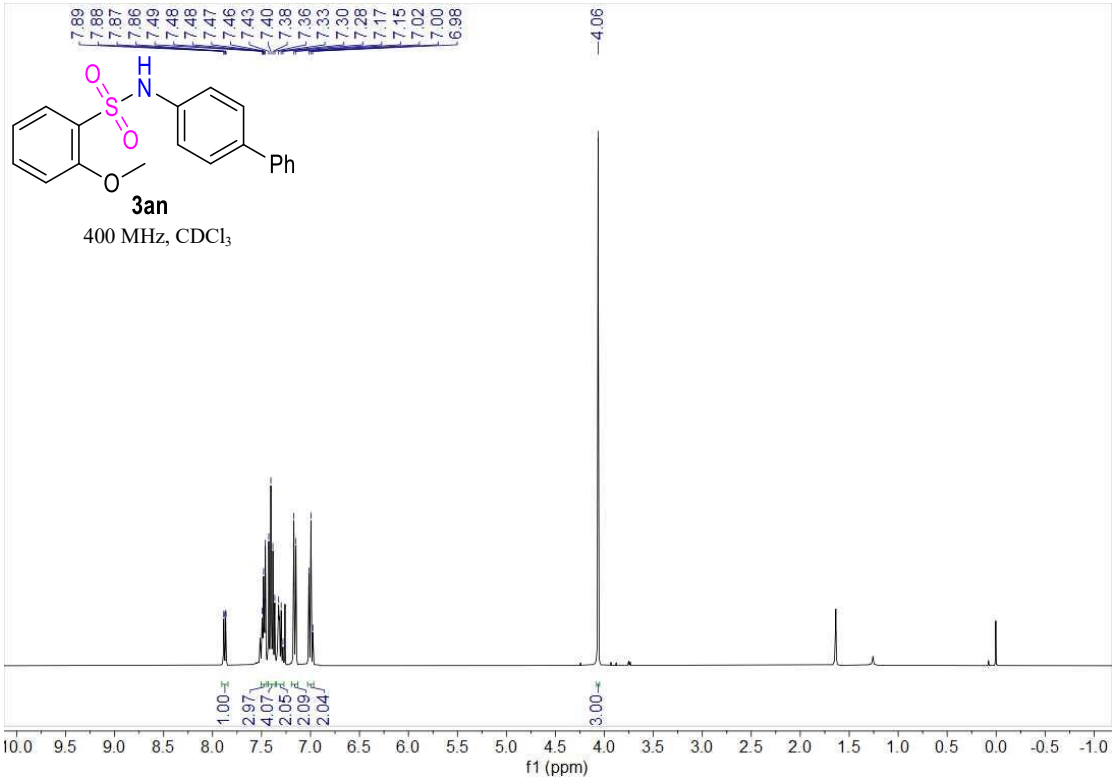


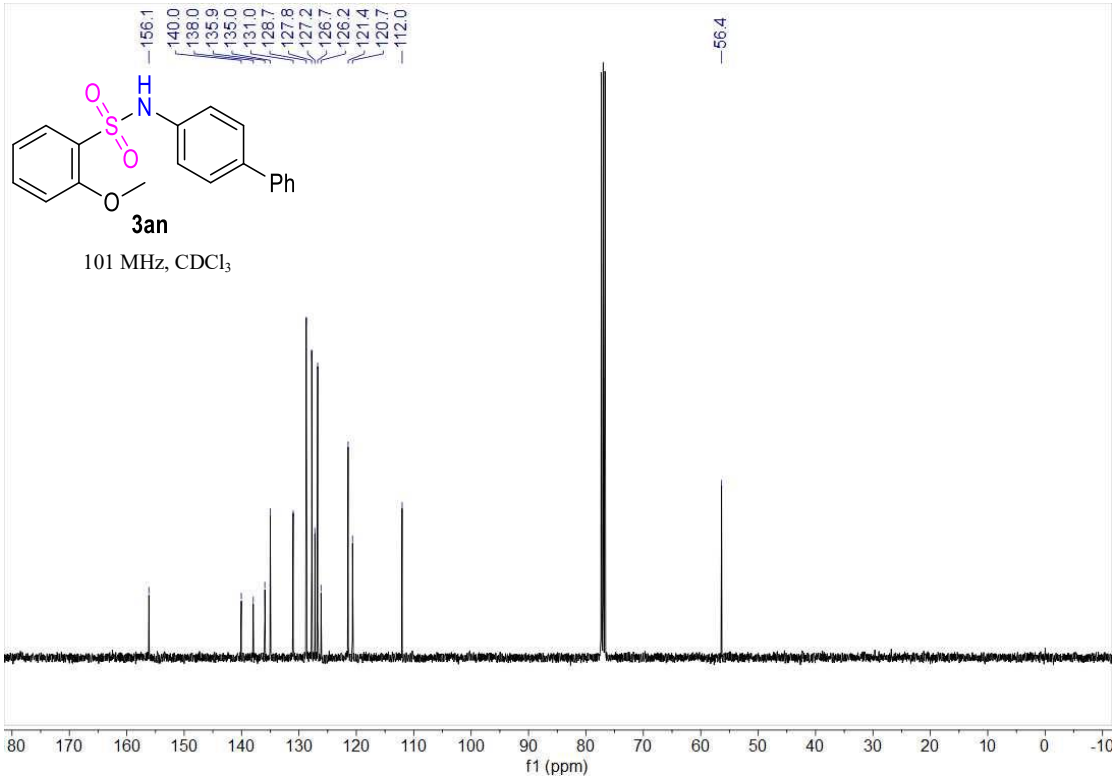
N-([1,1'-biphenyl]-4-yl)-2-methylbenzenesulfonamide (3am)



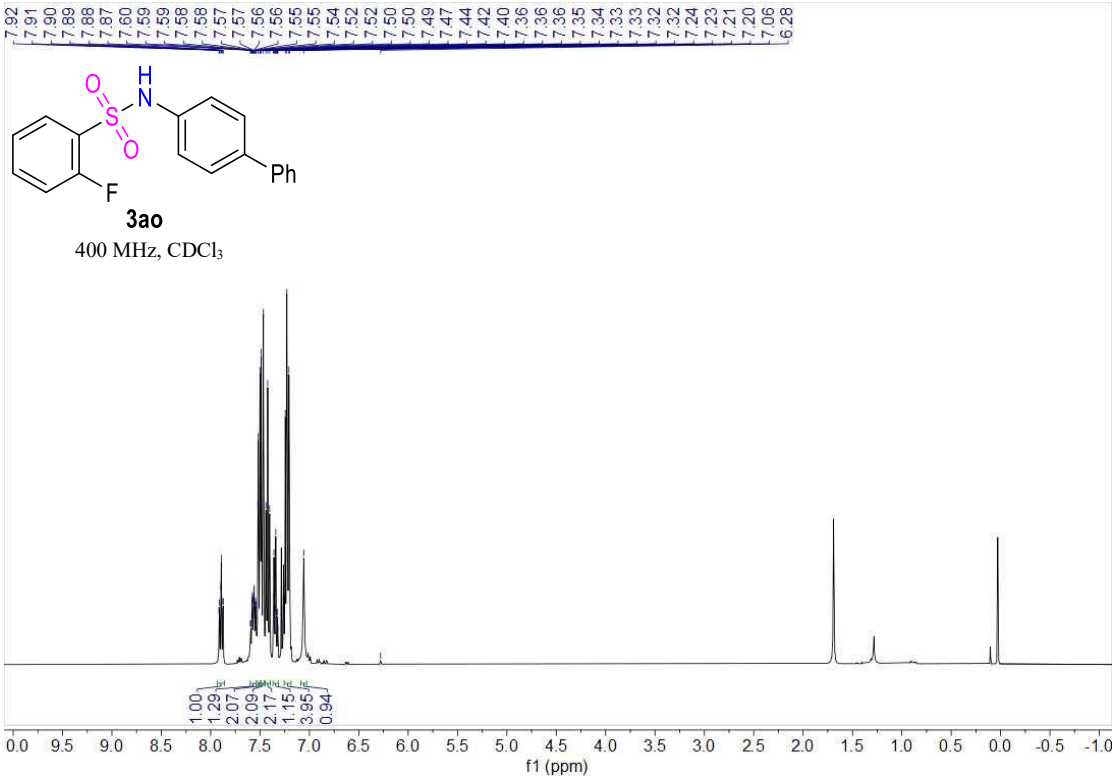


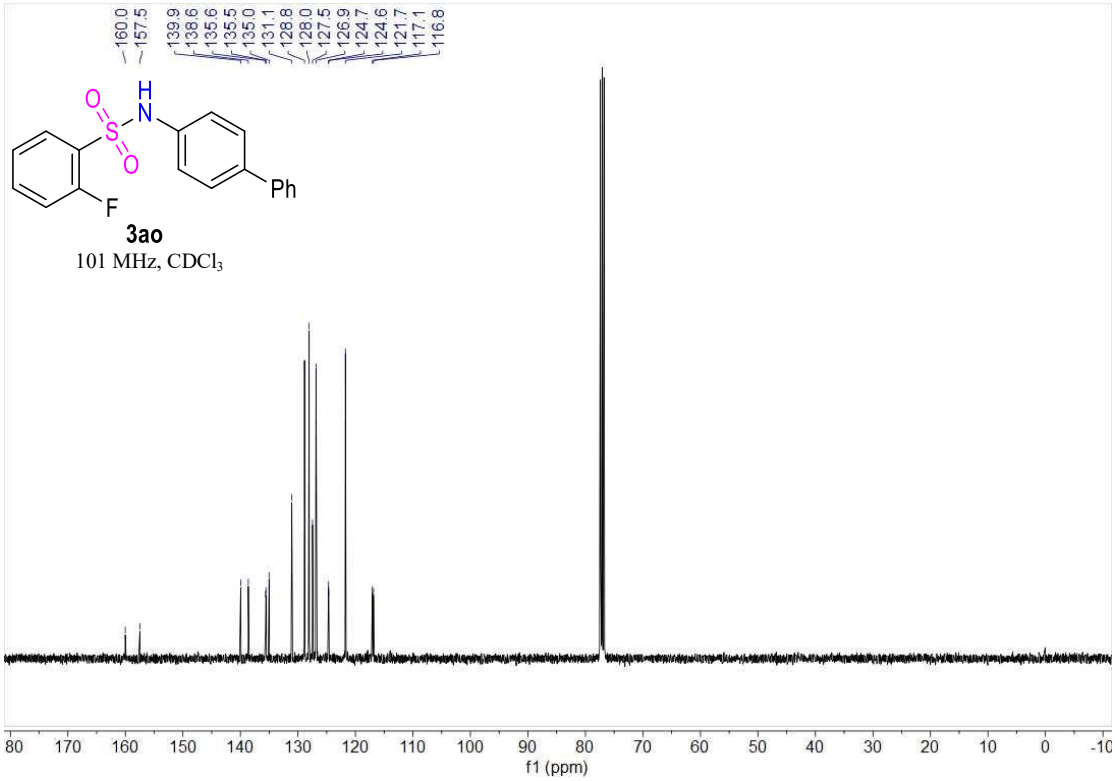
N-([1,1'-biphenyl]-4-yl)-2-methoxybenzenesulfonamide (3an)

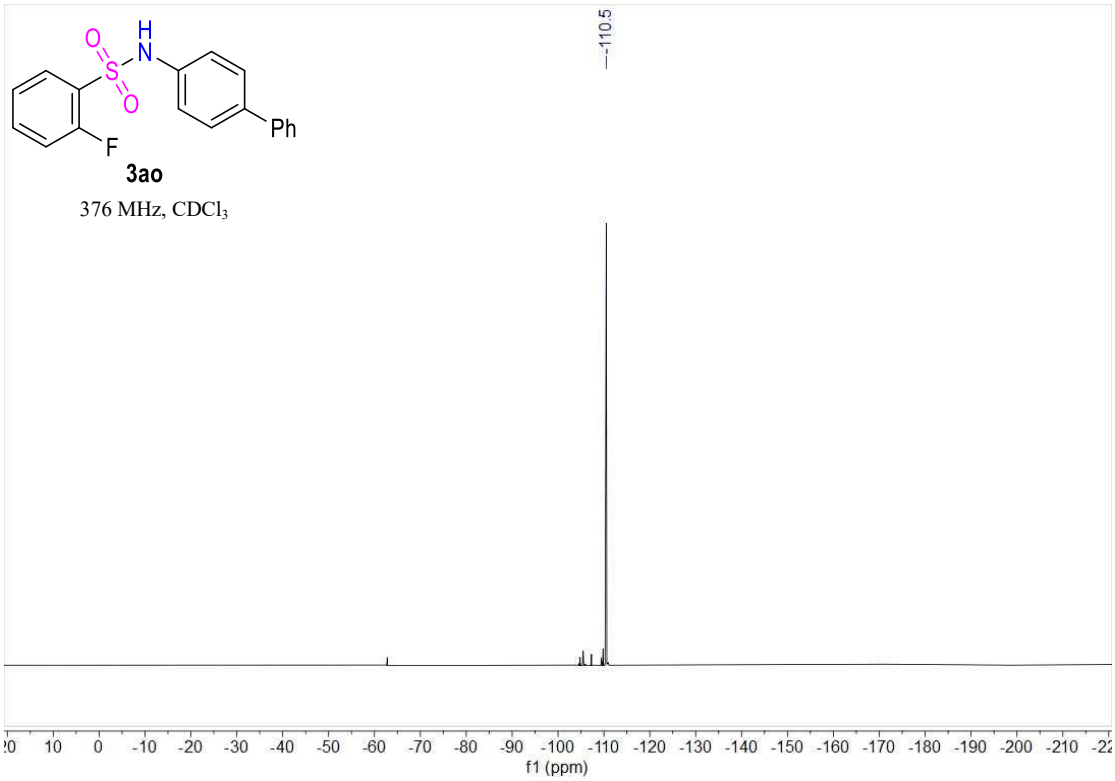




N-([1,1'-biphenyl]-4-yl)-2-fluorobenzenesulfonamide (3ao)



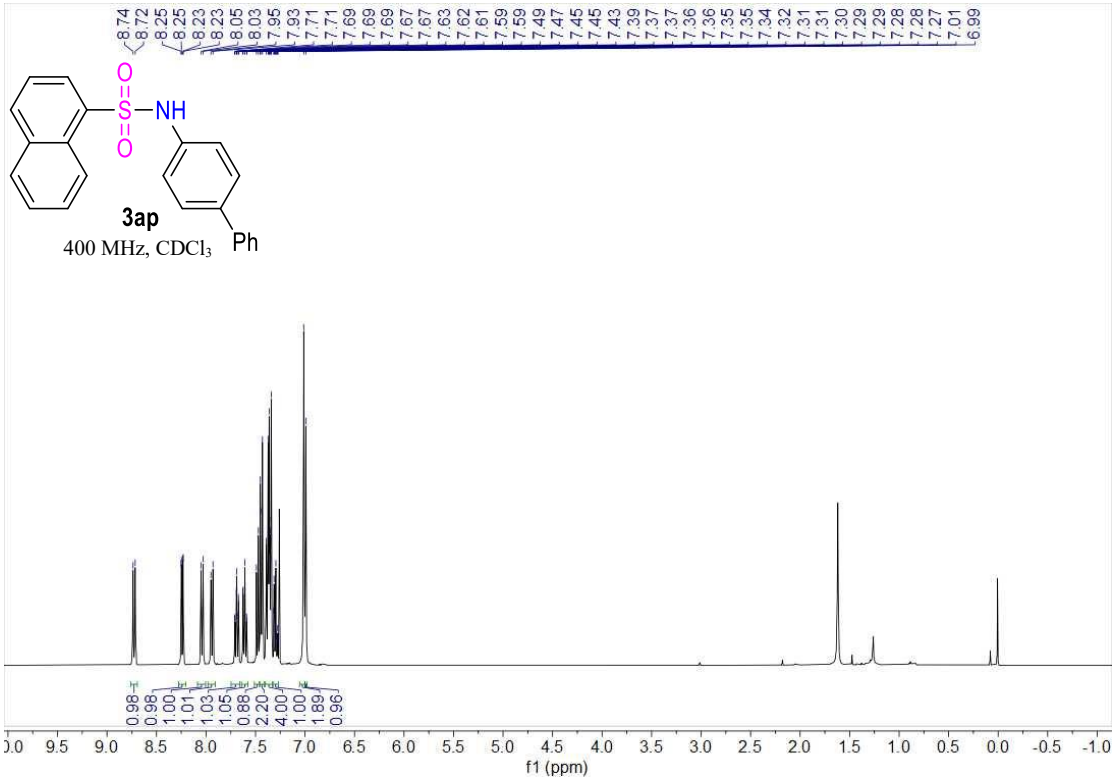


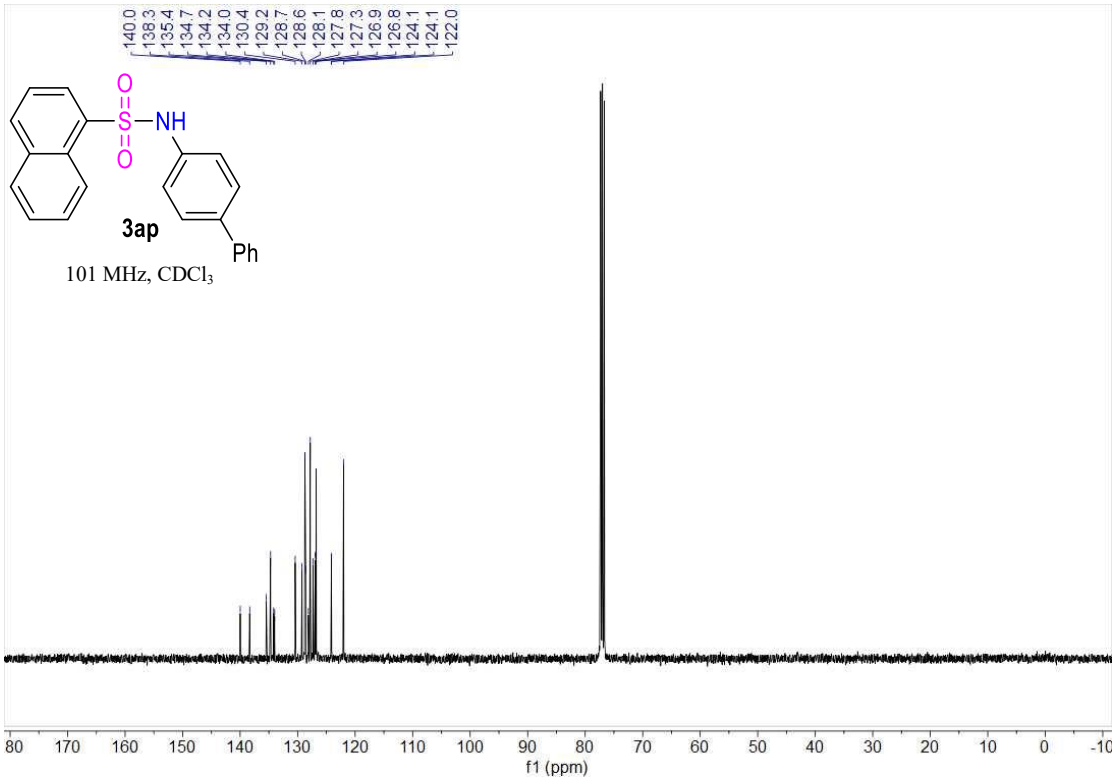


3ao

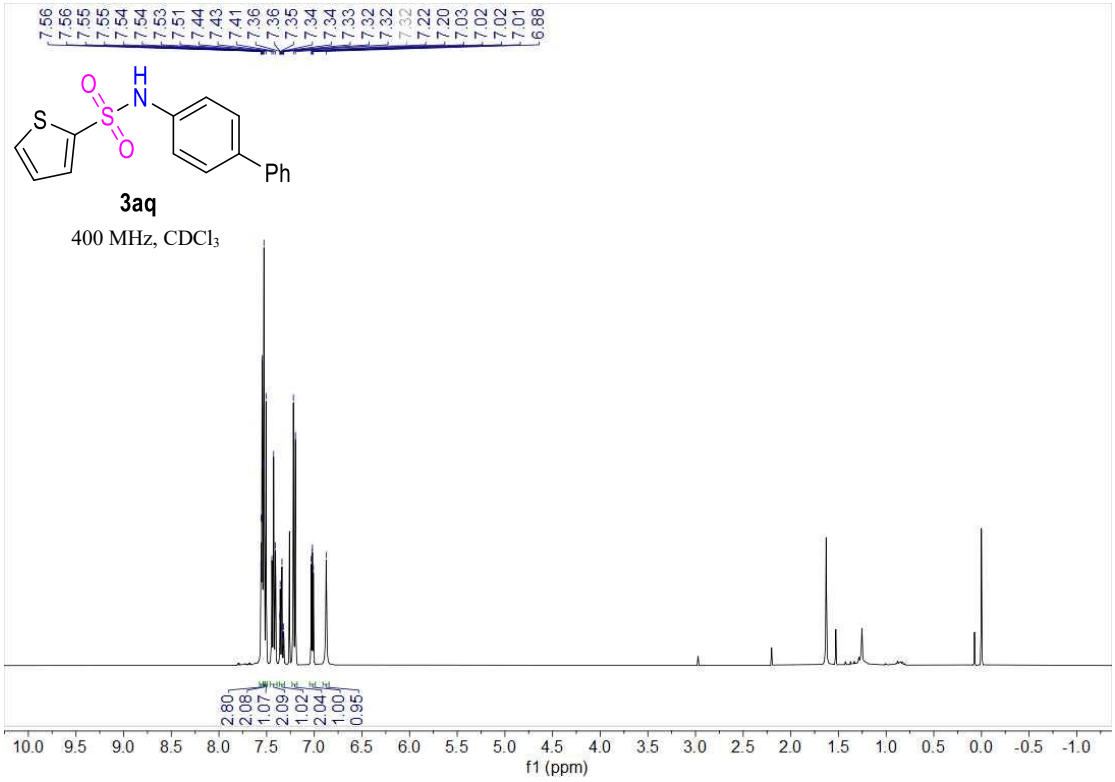
376 MHz, $CDCl_3$

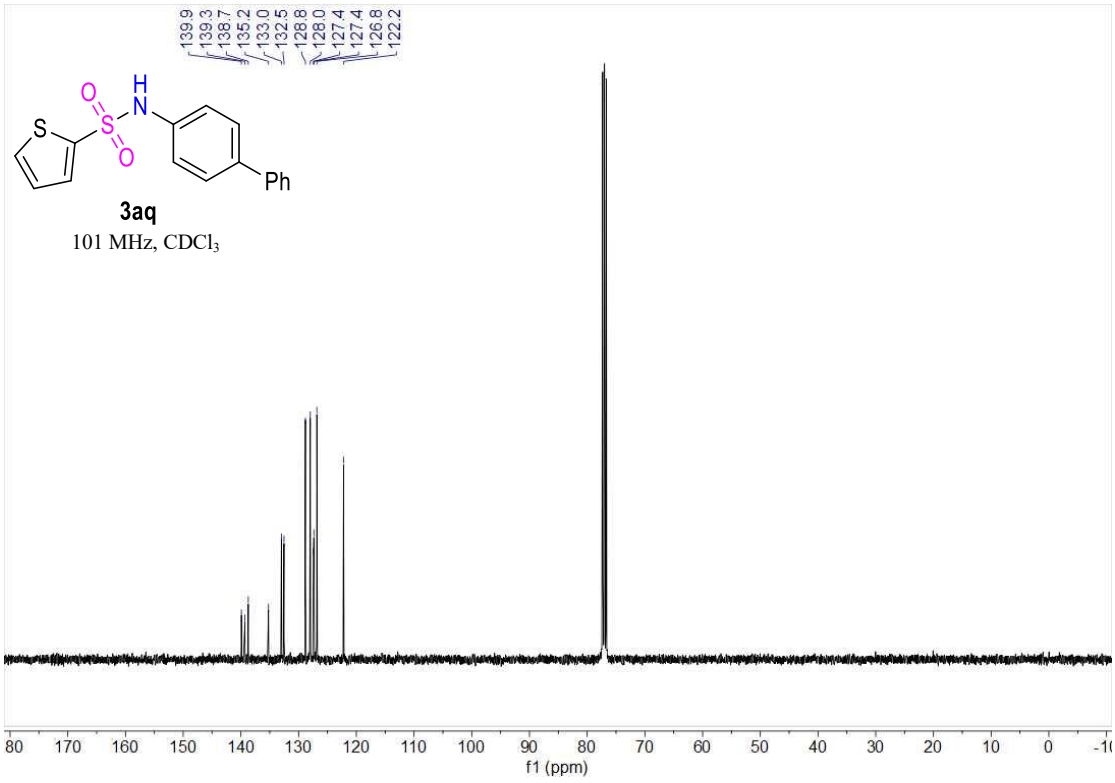
***N*-([1,1'-biphenyl]-4-yl)naphthalene-1-sulfonamide (3ap)**



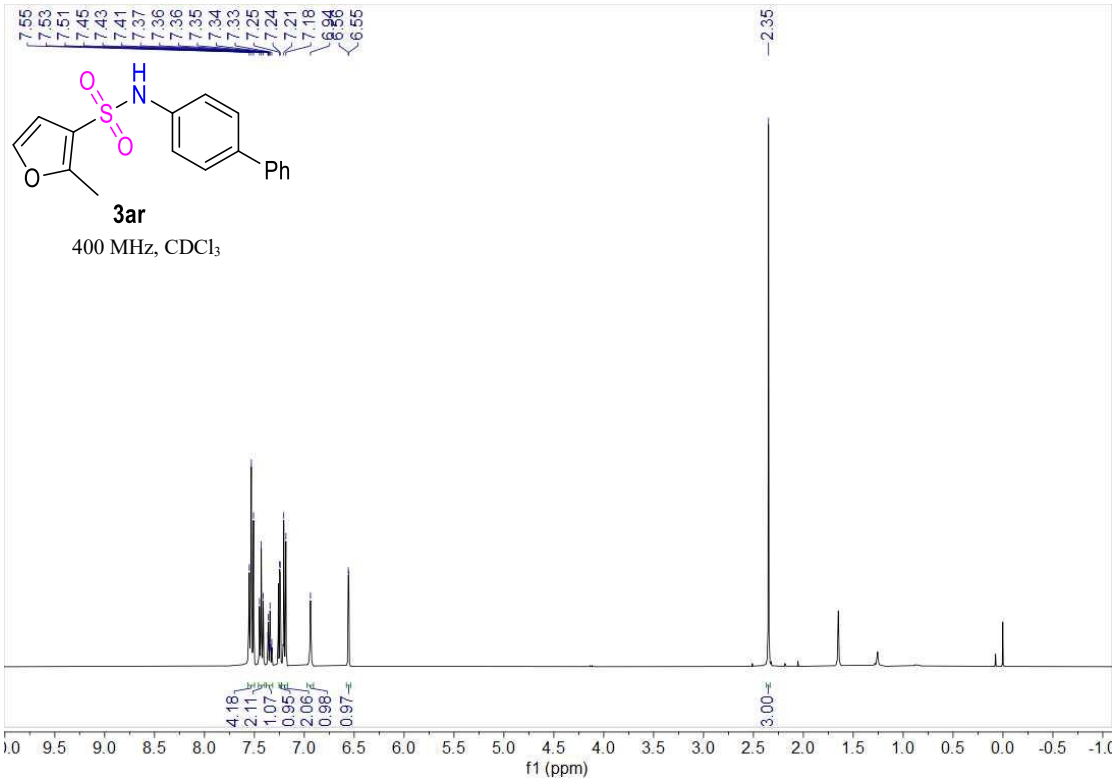


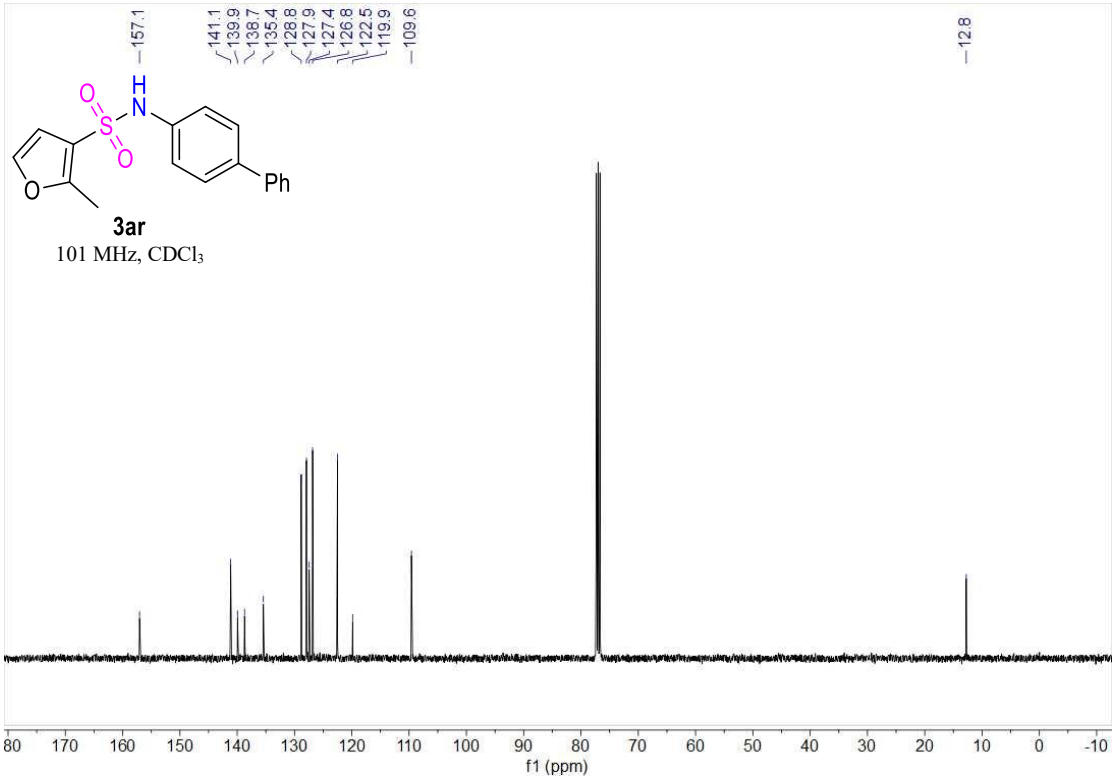
N-([1,1'-biphenyl]-4-yl)thiophene-2-sulfonamide (3aq)



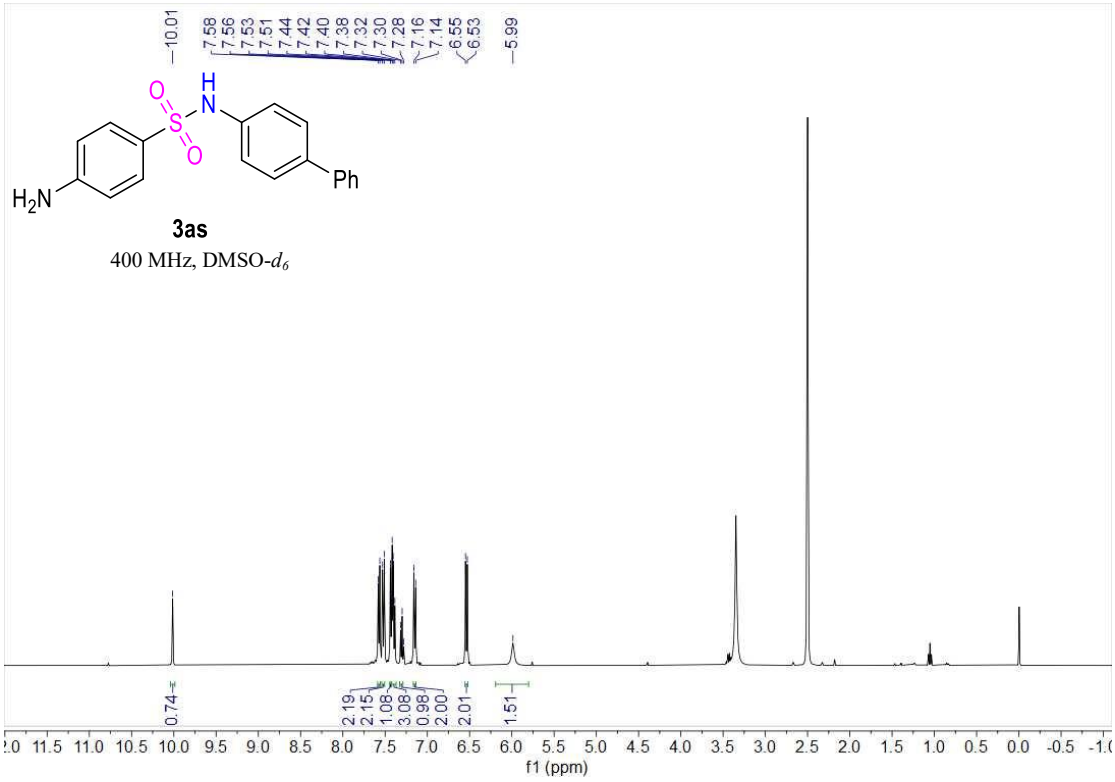


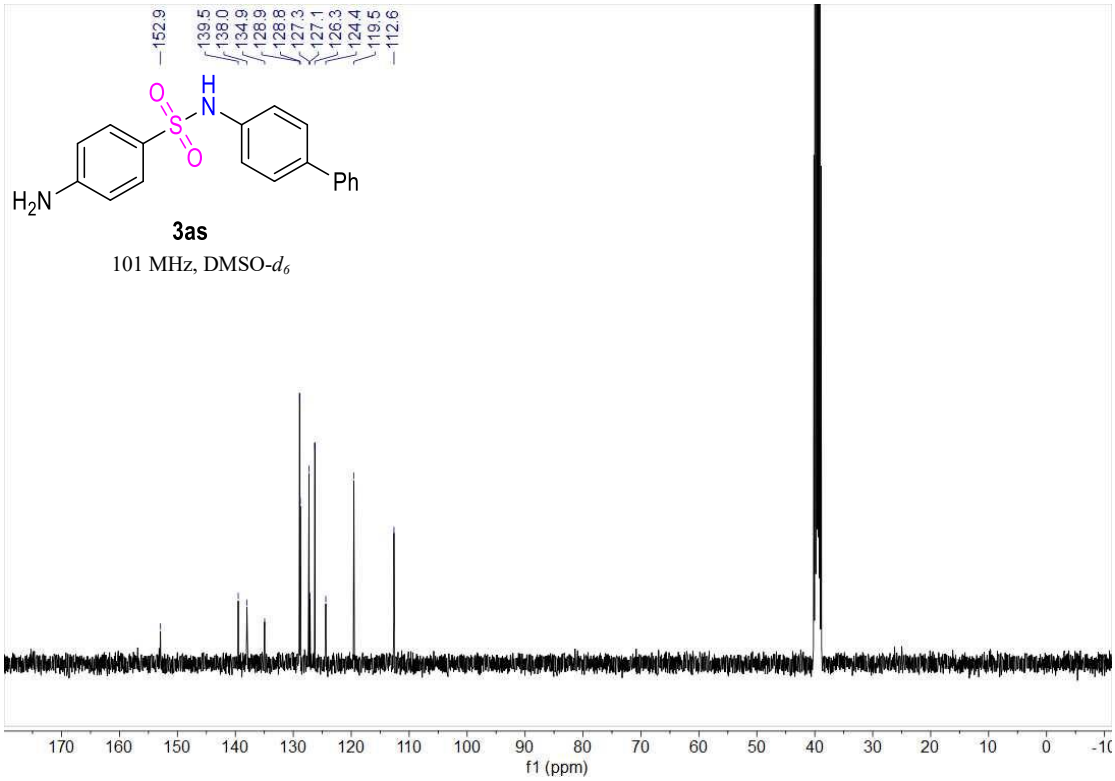
N-([1,1'-biphenyl]-4-yl)-2-methylfuran-3-sulfonamide (3ar)



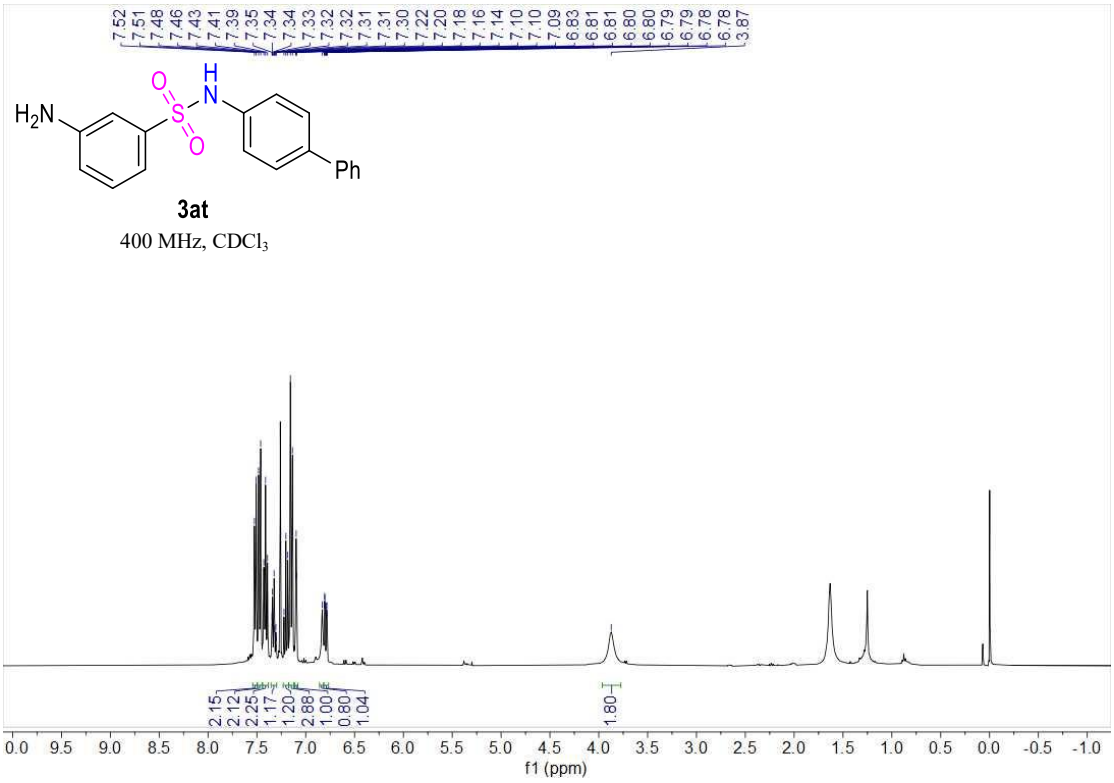


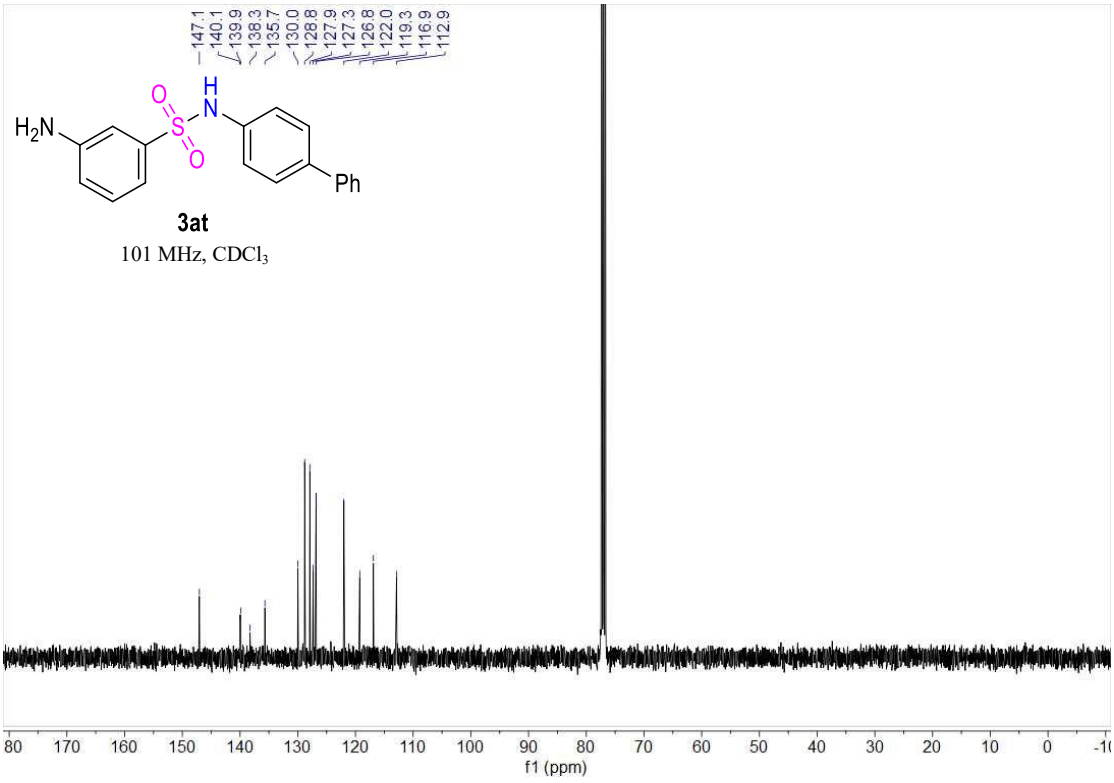
N-([1,1'-biphenyl]-4-yl)-4-aminobenzenesulfonamide (3as)



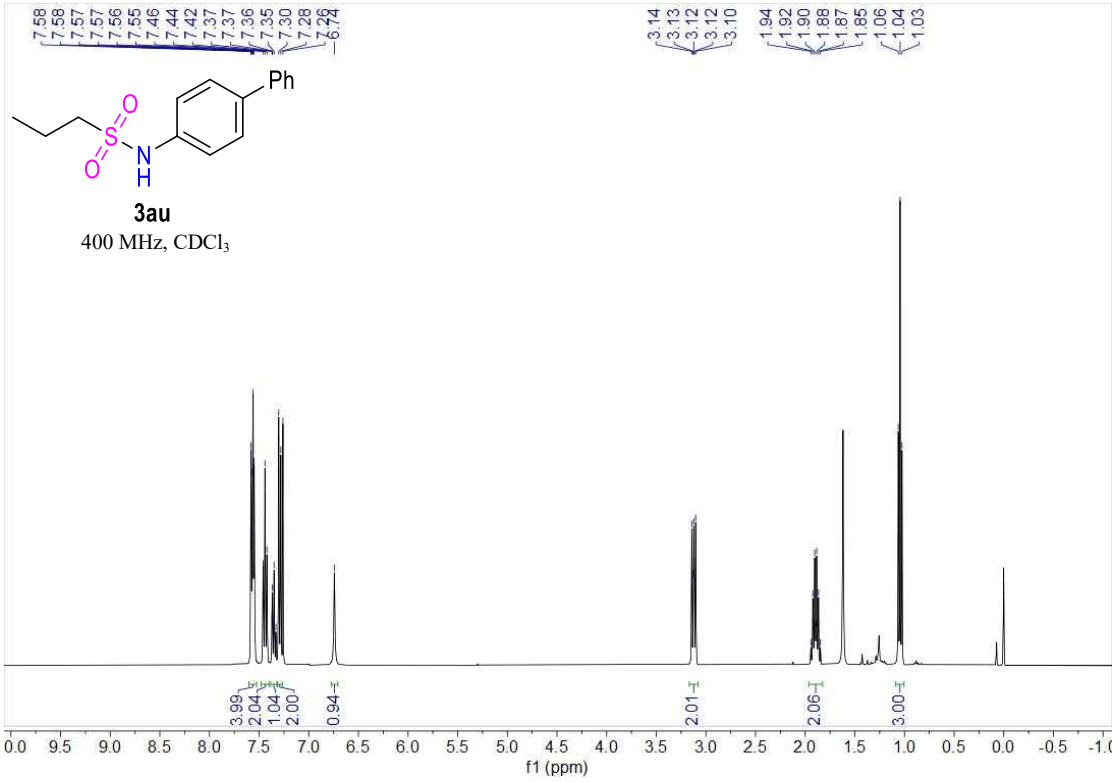


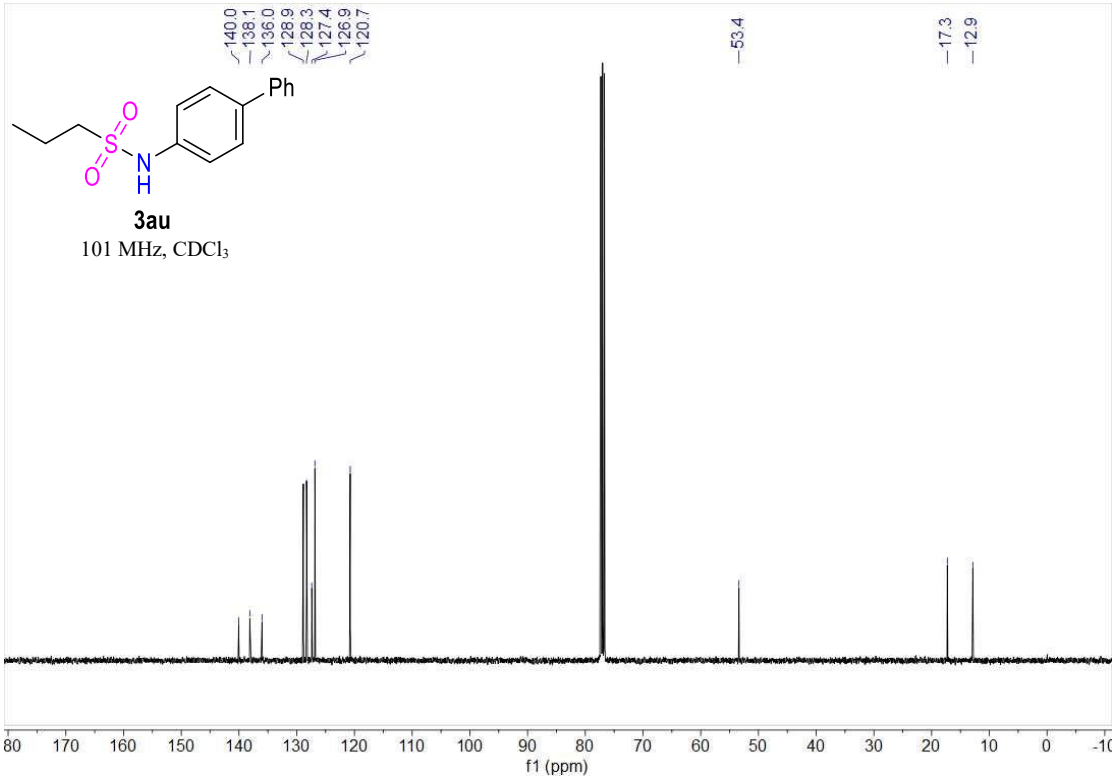
N-([1,1'-biphenyl]-4-yl)-3-aminobenzenesulfonamide (3at)



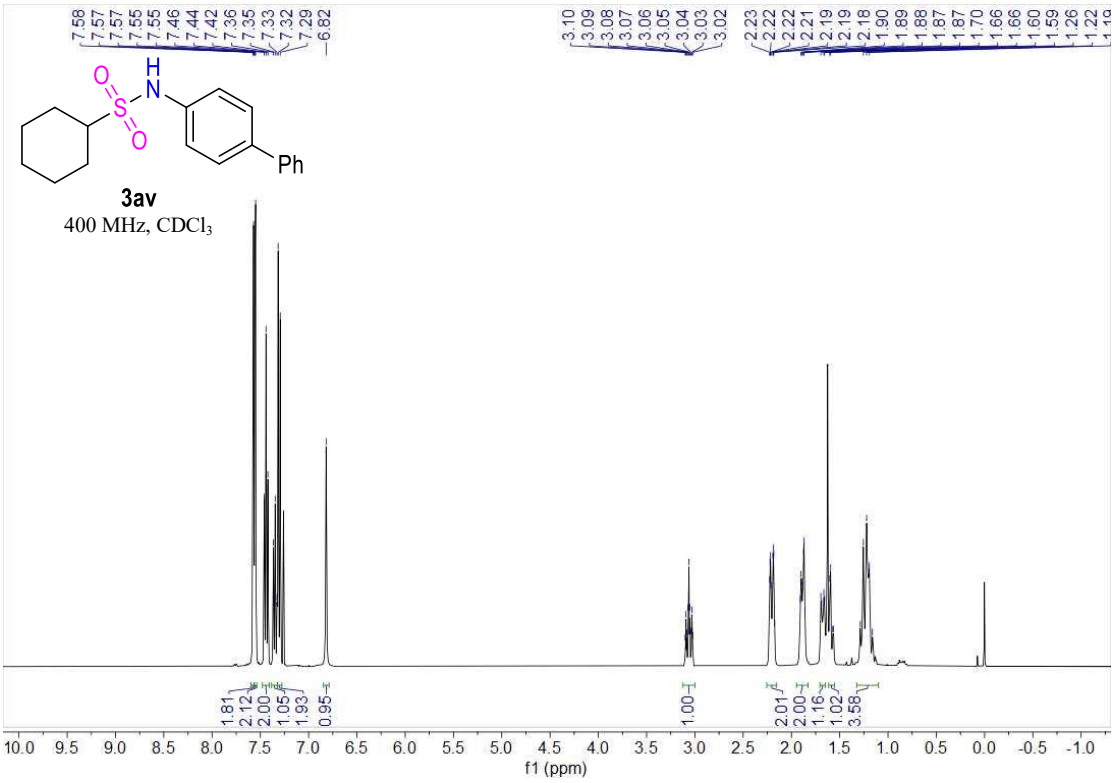


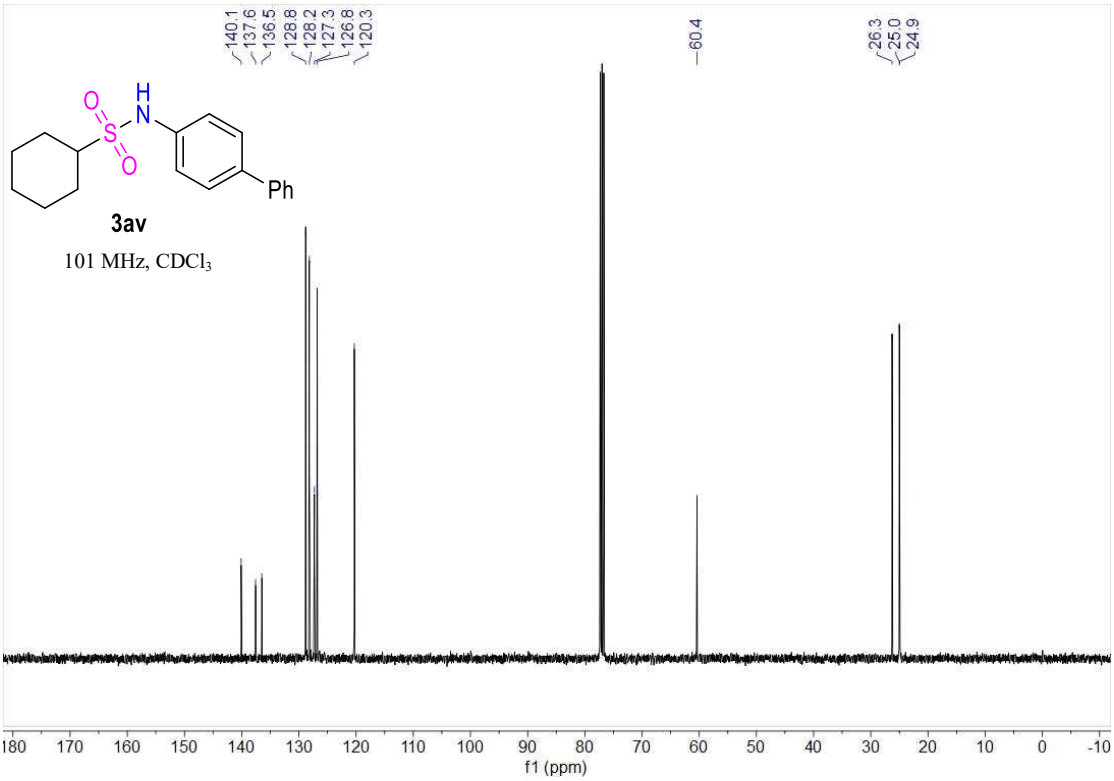
N-([1,1'-biphenyl]-4-yl)propane-1-sulfonamide (3au)





N-([1,1'-biphenyl]-4-yl)cyclohexanesulfonamide (3av)





N-([1,1'-biphenyl]-4-yl)cyclopentanesulfonamide (3aw)