Supporting Information

A catalyst-free method for the synthesis of 1,4,2-dithiazoles from isothiocyanates and hydroxylamine triflic acid salts

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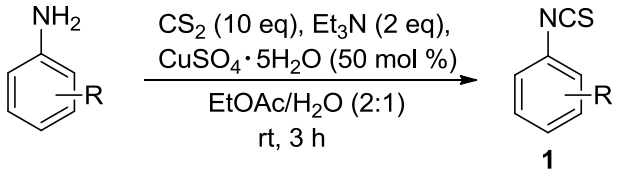
General remark

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400M and JNM-ECS 400M in $CDCl_3$. All ^{1}H NMR and ^{13}C NMR chemical shifts were given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. All reagents were purchased commercially and used as received, unless otherwise noted.

Experimental Procedures

General procedure for the synthesis of phenyl isothiocyanate 1b-1u[1]:



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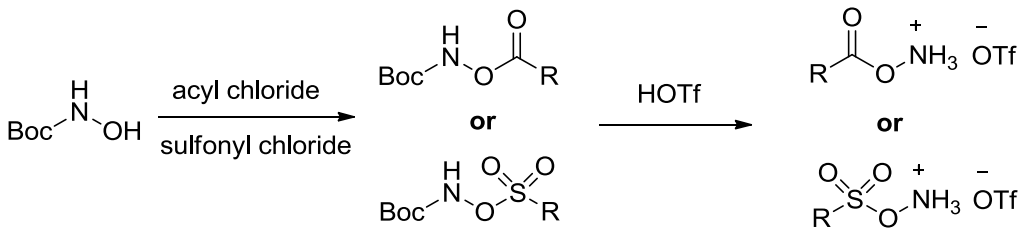
To a stirred solution of EtOAc/H_2O (2:1, 20 mL), substituted aniline (10 mmol) was added in slowly and followed by carbon disulphide (100 mmol, 7.60 g) and trimethylamine (10 mmol, 1.01 g) at room temperature. The whole reaction mixture was stirred for one hour (until get the yellow color solid) at room temperature. Thiocarbomate formation was monitored by TLC. To this, $CuSO_4{\cdot}5H_2O$ (50 mol %, 1.25 mg) was added slowly for 5 min and the reaction mixture was stirred for 1 h. During this period, black precipitate was observed and settles at bottom of round bottom flask. The progress of the reaction was investigated by TLC (5% ethylacetate in hexane). After finishing the reaction, the reaction mixture was transferred into centrifuged tubes and the mixture was centrifuged for 10 min by centrifugation machine. Black color solid was settled in the bottom of centrifuged tubes. The resulted clear solution was washed with ethyl acetate (10 mL) and water (7 mL) for 3 times. And organic layer was concentrated by rotary evaporator and the crude product was purified by silica gel (200-300 mesh) column chromatography using 2%

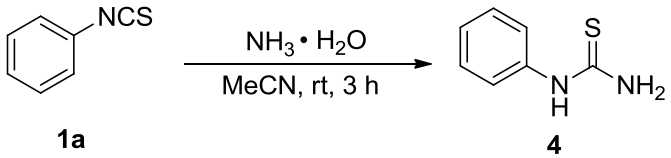
ethylacetate in hexane as eluent to obtain substituted phenyl isothiocyanate **1b-1u**.

General procedure for the synthesis of aminating reagents 2a-2e[2]:



The corresponding acyl chlorides or sulfonyl chlorides (11 mmol, 1.1 equiv) and triethylamine (11 mmol, 1.1 equiv) were added to the solution of *tert*-butyl hydroxycarbamate (1.33g, 10 mmol, 1.0 equiv) in Et_2O (80 mL) at 0 ^oC. The reaction mixture was stirred for 4-8h until the *tert*-butyl hydroxycarbamate was completely consumed. Then, the reaction mixture was filtered and washed by sat. $NaHCO_3$ three times. The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of the solvent, the crude product was recrystallized to afford the pure solid. The obtained solid was dissolved in petroleum ether, then trifluoromethanesulfonic acid (11 mmol, 1.1 equiv) was added dropwise to acidize and precipitate the product at 0 ^oC and continued to stir for 4 hours. The mixture were filtrated and washed with petroleum ether several times to obtain the desired products.

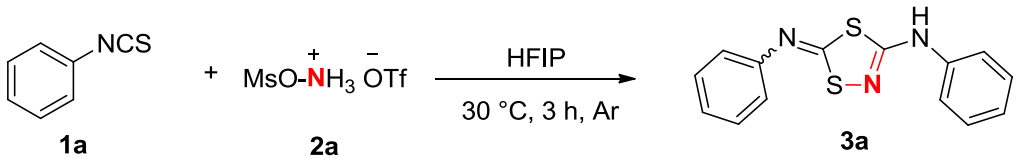
General procedure for the synthesis of 4.[3]



1a **4**

To a solution of isothiocyanatobenzene (5 mmol) in MeCN (10 mL) was added aqueous ammonia (25%, 1.5 equiv). The solution was stirred at room temperature for 3 h. The reaction mixture was then concentrated. Purification was done by precipitation from a mixture of n-hexane/ethyl acetate mixture (3 : 2). The pure product was recovered as a powder after filtration in 95% yield.

General procedure for the synthesis of 1,4,2-dithiazole derivatives



1a 2a 3a

The mixture of 1-phenylcyclobutanol **1a** (1 equiv, 0.2 mmol), **2a** (0.7 equiv, 0.14 mmol), HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) (2 mL) were stirred at ambient temperature under argon atmosphere for 3 h (TLC monitored). Upon completion of the reaction, the solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/ ethyl acetate (10:1) to afford the desired **3a**. All products **3a**-**3t** were obtained as inseparable Z/E isomer mixtures (about 1/1). The ratio of Z/E isomers was determined by the integral of ^{1}H NMR analysis.

EPR experiments

Following the general procedure for the synthesis of 1,4,2-dithiazole: the mixture of 1-phenylcyclobutanol **1a** (1 equiv, 0.2 mmol), **2a** (0.7 equiv, 0.14 mmol), HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) (1.5 mL) were added to Shlenk tube. The tube was evacuated and backfilled with nitrogen for total of three times. Then anaerobic 5,5-dimethy-1-pyrroline-*N*-oxide (DMPO) solution (0.5 mL, 0.8 M in HFIP, 2.0 equiv) was added into the tube by syringe. The mixture was stirred at ambient temperature, and the mixture was detected after 5 min. As shown in Figure S1, some radical signals were detected. These results indicated that the reactions involved radical-mediated pathways.

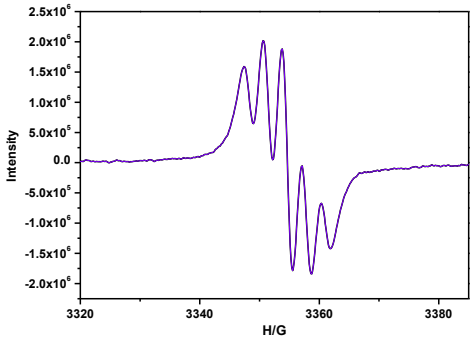


Figure S1. EPR experiment **1a** (1.0 equiv) and **2a** (0.7 equiv), in HFIP (2 mL) in the presence of DMPO (2.0 equiv).

The X-ray data of 3a (CCDC 2032219)

Crystal **3a** growth with the volatilization method: an amount of 20 mg **3a** was dissolved in acetone on the brown small reagent bottle (5 mL), which acted as good solvent, and a layer of petroleum ether was injected on the surface of acetone, and the cap is covered with a thin film, white crystals will be presented after seven days.

Single crystals of $C_{28}H_{22}N_6S_4$ (**3a**) was determinate. A suitable crystal was selected and determinate on a SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 294.51(13) K during data collection. Using Olex2,[4] the structure was solved with the ShelXS[5] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.

All hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculations. The crystal structure (excluding structure factor) has been deposited to Cambridge Crystallographic Data Centre and allocated deposition number: 2032219.

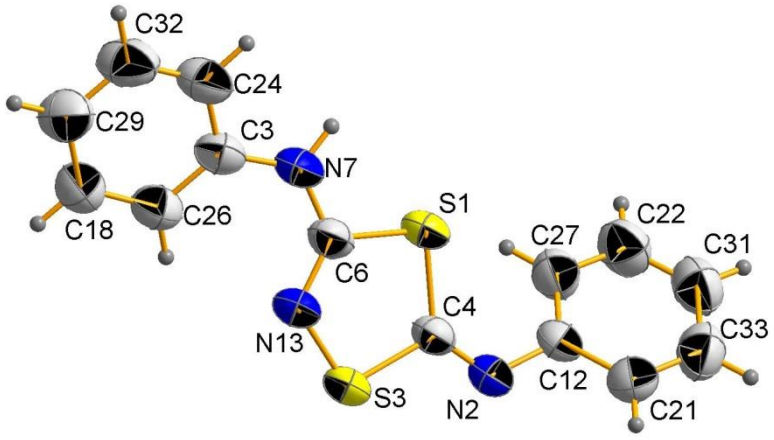


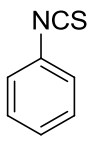
Figure S2. X-ray crystal structure of compound **3a**, thermal ellipsoids are drawn at 30% probability level

Table S1. Crystal data and structure refinement for **3a**.

Identification code	**3a**

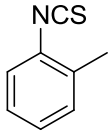
Empirical formula	$C_{28}H_{22}N_6S_4$
Formula weight	570.75
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	16.8782(3)
b/Å	17.0499(3)
c/Å	19.0329(4)
α/°	90
β/°	99.6071(19)
γ/°	90
Volume/Å^3	5400.32(18)
Z	8
ρ_{calc}g/cm^3	1.404
μ/mm^{-1}	3.474
F(000)	2368.0
Crystal size/mm^3	0.2 × 0.16 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.424 to 133.198
Index ranges	-20 ≤ h ≤ 19, -20 ≤ k ≤ 20, -22 ≤ l ≤ 22
Reflections collected	10491
Independent reflections	4766 [R_{int} = 0.0199, R_{sigma} = 0.0245]
Data/restraints/parameters	4766/0/343
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0376, wR_2 = 0.0978
Final R indexes [all data]	R_1 = 0.0459, wR_2 = 0.1059
Largest diff. peak/hole / e Å^{-3}	0.26/-0.26

The Data of Products:



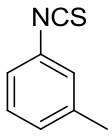
isothiocyanatobenzene (1a)

Colorless oil (1.32 g, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 2H), 7.26-7.22 (m, 1H), 7.18-7.16 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 135.3, 131.1, 129.4, 127.2, 125.6



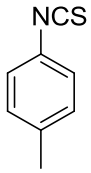
1-isothiocyanato-2-methylbenzene (1b)

Colorless oil (1.28 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.19-7.16 (m, 4 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 134.9, 130.6, 130.2, 127.3, 126.8, 125.8, 18.3.



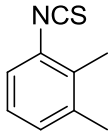
1-isothiocyanato-3-methylbenzene (1c)

Colorless oil (1.34 g, 90% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.22-7.19 (m, 1 H), 7.08-7.06 (d, *J* = 8.0 Hz, 1 H), 7.01-6.99 (d, *J* = 8.0 Hz, 2 H), 2.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 139.6, 134.8, 130.9, 129.2, 128.1, 126.2, 122.6, 21.1.



1-isothiocyanato-4-methylbenzene (1d)

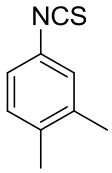
Colorless solid (1.27 g, 85% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.15-7.09 (m, 4 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 137.5, 134.4, 130.1, 128.3, 125.5, 21.2.



1-isothiocyanato-2,3-dimethylbenzene (1e)

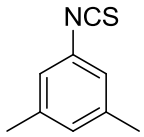
Colorless oil (1.34 g, 82% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.04 (s, 3 H),

2.26 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 138.1, 134.5, 133.0, 130.1, 128.8, 126.2, 123.9, 20.2, 14.8.



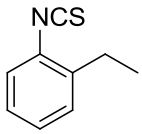
4-isothiocyanato-1,2-dimethylbenzene (1f)

Colorless oil (1.29 g, 79% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.07-7.05 (m, 1 H), 6.96 (s, 1 H), 6.93-6.91 (d, *J* = 4.0 Hz, 1 H), 2.22 (s, 3 H), 2.21 (s, 3 H) ; ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 138.0, 136.2, 133.9, 130.4, 128.3, 126.5, 122.8 , 19.5, 19.4.



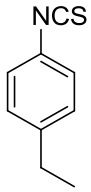
1-isothiocyanato-3,5-dimethylbenzene (1g)

Colorless oil (1.39 g, 85% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.89 (s, 1 H), 6.82 (s, 2 H), 2.28 (s, 6 H) ; ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 139.3, 134.3, 130.6, 129.1, 123.3, 21.0.



1-ethyl-2-isothiocyanatobenzene (1h)

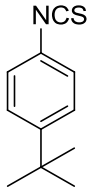
Colorless oil (1.24 g, 76% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.21-7.19 (m, 2 H), 7.17-7.13 (m, 2 H), 2.75-2.68 (m, 2 H), 1.26-1.22 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 140.5, 135.1, 129.6, 129.0, 127.5, 126.8, 126.2, 25.3, 14.2.



1-ethyl-4-isothiocyanatobenzene (1i)

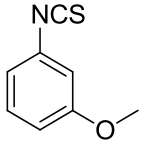
Colorless oil (1.29 g, 79% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.16-7.09 (m, 4

H), 2.65-2.59 (m, 2 H), 1.23-1.19 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 143.7, 134.3, 128.8, 128.4, 125.5, 28.4, 15.3.



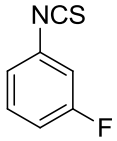
1-(*tert*-butyl)-4-isothiocyanatobenzene (1j)

Yellow solid (1.22 g, 64% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.36-7.34 (d, *J* = 8.0 Hz, 2 H), 7.16-7.14 (d, *J* = 8.0 Hz, 2 H), 1.30 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 150.7, 134.3, 128.2, 126.4, 125.3, 34.7, 31.1.



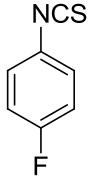
1-isothiocyanato-3-methoxybenzene (1k)

Colorless oil (1.57 g, 95% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.24-7.20 (m, 1 H), 6.82-6.80 (d, *J* = 8.0 Hz, 2 H), 6.71 (s, 1 H), 3.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 160.1, 135.1, 131.9, 130.1, 118.0, 113.5, 111.0, 55.3.



1-fluoro-3-isothiocyanatobenzene (1l)

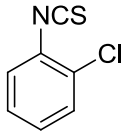
Colorless oil (0.87 g, 57% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.36-7.26 (m, 1 H), 7.04-6.90 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 162.7 (d, *J* = 330.0 Hz, 1 C), 137.0, 132.5, 130.7, (d, *J* = 10.0 Hz, 1 C), 121.7 (d, *J* = 4.0 Hz, 1 C), 114.6 (d, *J* = 30.0 Hz, 1 C), 113.1 (d, *J* = 30.0 Hz, 1 C).



1-fluoro-4-isothiocyanatobenzene (1m)

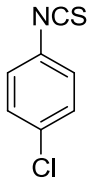
Colorless oil (0.93 g, 59% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.22-7.18 (m, 2

H), 7.06-7.02 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 162.3, 159.8, 135.8, 127. 3 (d, *J* = 10.0 Hz, 1 C), 116.6 (d, *J* = 30.0 Hz, 1 C).



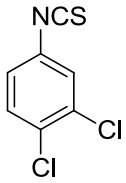
1-chloro-4-isothiocyanatobenzene (1n)

Colorless oil (0.91 g, 54% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.43-7.41(d, *J* = 8.0 Hz, 1 H), 7.24-7.20 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 138.6, 131.7, 130.1, 129.7, 127.9, 127.6, 126.6.



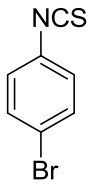
1-chloro-2-isothiocyanatobenzene (1o)

Colorless solid (1.00 g, 59% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.32-7.29 (m, 2 H), 7.16-7.13 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 136.6, 132.9, 129.9, 129.7, 126.9.



1,2-dichloro-4-isothiocyanatobenzene (1p)

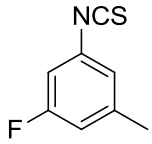
Colorless oil (0.91 g, 45% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.42-7.40 (d, *J* = 8.0 Hz, 1 H), 7.31 (m, 1 H), 7.07-7.04 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 138.5, 133.5, 131.4, 131.1, 131.0, 127.4, 124.9.



1-bromo-4-isothiocyanatobenzene (1q)

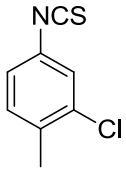
Yellow solid (1.28 g, 60% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.48-7.44 (m, 2 H), 7.10-7.06 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 136.7, 132.7, 130.4,

127.1, 120.7.



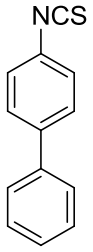
1-fluoro-4-isothiocyanato-2-methylbenzene (1r)

Yellow oil (1.19 g, 71% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 6.82-6.78 (m, 2 H), 6.72-6.70 (d, *J* = 8.0 Hz, 1 H), 2.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 162.6 (d, *J* = 247.0 Hz, 1 C), 141.6 (d, *J* = 10.0 Hz, 1 C), 136.7, 132.3 (d, *J* = 12.0 Hz, 1 C), 122.3 (d, *J* = 3.0 Hz, 1 C), 115.3 (d, *J* = 20.0 Hz, 1 C), 110.0 (d, *J* = 25.0 Hz, 1 C), 21.2 (d, *J* = 8.0 Hz, 1 C).



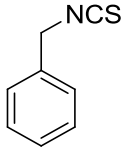
1-chloro-4-isothiocyanato-2-methylbenzene (1s)

Colorless oil (1.36 g, 74% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.19-7.16 (d, *J* = 8.0 Hz, 2 H), 7.01-6.99 (m, 1 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 136.5, 135.6, 134.9, 131.4, 129.8, 126.0, 123.8, 19.8.



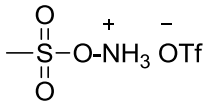
4-isothiocyanato-1,1'-biphenyl (1t)

Yellow solid (1.29 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.54-7.51 (d, *J* = 12.0 Hz, 4 H), 7.42-7.40 (m, 2 H),7.36-7.33 (m, 1 H), 7.25-7.23(d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 140.2, 139.6, 135.5, 130.2, 128.9, 128.1, 127.8, 126.9, 126.0.



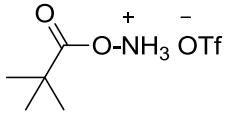
(isothiocyanatomethyl)benzene (1u)

Yellow solid (0.67 g, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.39-7.32 (m, 3 H), 7.30-7.28 (m, 2 H),4.67 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 134.1, 131.9, 128.8, 128.2, 126.7, 48.5.



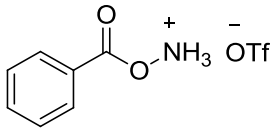
***O*-(methylsulfonyl)hydroxylamine trifluoromethanesulfonate (2a)**

White solid (2.24 g, 86% yield)). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 11.56 (s, 1 H), 9.25 (s, 2H), 2.56 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 120.9 (q, *J* = 321.0 Hz, 1C), 39.9.



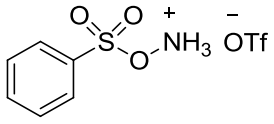
***O*-pivaloylhydroxylamine trifluoromethanesulfonate (2b)**

White solid (2.16 g, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.99 (s, 3 H), 1.24 (s, 9 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 174.9, 120.8 (q, *J* = 320.0 Hz, 1C), 38.0, 26.5.



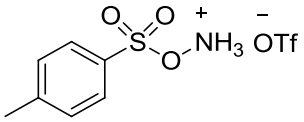
***O*-benzoylhydroxylamine triflic acid (2c)**

White solid (2.29 g, 80% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.34 (s, 3 H), 8.04-8.02 (m, 2 H), 7.83-7.79 (m, 1 H), 7.66-7.62 (m, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 163.9, 135.1, 129.6, 129.5, 125.7, 120.9 (q, *J* = 312.0 Hz, 1C).



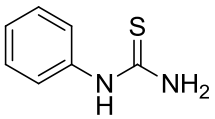
***O*-(phenylsulfonyl)hydroxylamine triflic acid (2d)**

White solid (2.53 g, 78% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.47 (s, 3 H), 7.66-7.64 (m, 2 H), 7.37-7.36 (m, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 147.4, 129.2, 128.1, 125.6, 120.8 (q, *J* = 321.0 Hz, 1C).



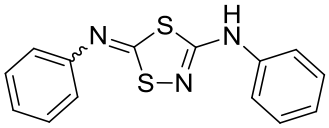
***O*-tosylhydroxylamine triflic acid (2e)**

Yellow solid (2.35 g, 70% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.93 (s, 3 H), 7.56-7.54 (d, J = 8.0 Hz, 2 H), 7.19-7.17 (d, J = 8.0 Hz, 2 H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 144.3, 139.0, 128.7, 125.8, 120.9 (q, J = 320.0 Hz, 1C), 21.1.



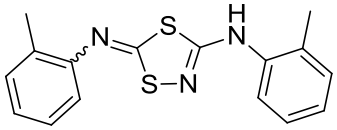
1-phenylthiourea (4)

White solid (0.72 g, 95% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.69 (s, 1 H), 7.41-7.30 (m, 5 H), 7.13-7.10 (m, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 181.1, 139.1, 128.8, 124.5, 123.1.



***N*-phenyl-5-(phenylimino)-1,4,2-dithiazol-3-amine (3a)**

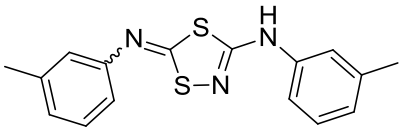
White soild (47.3 mg, 83% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.42 (s, 1 H), 10.24 (s, 1 H),7.55-7.52 (m, 4 H), 7.45-7.39 (m, 4 H), 7.33-7.30 (m, 4 H), 7.21-7.15 (m, 2 H), 7.08-6.98 (m, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 171.6, 168.9, 152.4, 151.1, 150.8, 150.2, 139.5, 129.7, 129.0, 125.2, 125.1, 122.9, 119.8, 119.5, 118.2, 118.1; HRMS calcd for $C_{14}H_{12}N_3S_2$ $[M+H]^+$ 286.0467; found: 286.0475.



***N*-(*o*-tolyl)-5-(*o*-tolylimino)-1,4,2-dithiazol-3-amine (3b)**

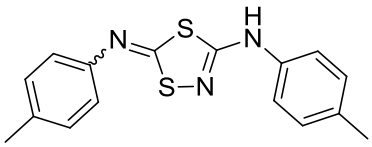
Yellow soild (43.8 mg, 70% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.62 (s, 1 H), 9.44 (s, 1 H), 7.56-7.53 (m, 2 H), 7.26-7.16 (m, 8 H), 7.08-7.07 (d, J = 4.0 Hz, 4 H), 6.93-6.91 (d, J = 8.0 Hz, 1 H), 6.84 (s, 1 H), 2.27-2.23 (m, 6 H), 2.16 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.4, 169.8, 153.4, 153.3, 152.2, 149.7, 137.3, 131.4,

130.8, 130.7, 130.6, 128.6, 127.2, 127.0, 126.4, 125.3, 125.0, 124.2, 124.1, 117.6, 117.4, 17.8, 17.2; HRMS calcd for $C_{16}H_{16}N_3S_2$ $[M+H]^+$ 314.0780; found: 314.0785.



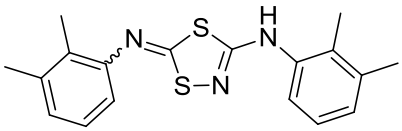
***N*-(*m*-tolyl)-5-(*m*-tolylimino)-1,4,2-dithiazol-3-amine (3c)**

White solid (50.1 mg, 80% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.31 (s, 1 H), 10.13 (s, 1 H), 7.37-7.24 (m, 6 H), 7.20-7.16 (m, 2 H), 7.00-6.96 (m, 2 H), 6.88-6.77 (m, 6 H), 2.31-2.30 (m, 6 H), 2.27 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 171.4, 168.5, 152.4, 151.0, 150.8, 150.2, 139.5, 139.1, 138.2, 129.4, 129.3, 128.7, 125.8, 125.7, 123.5, 120.5, 119.9, 118.6, 116.6, 116.5, 115.4, 21.2, 21.0; HRMS calcd for $C_{16}H_{16}N_3S_2$ $[M+H]^+$ 314.0780; found: 314.0786.



***N*-(*p*-tolyl)-5-(*p*-tolylimino)-1,4,2-dithiazol-3-amine (3d)**

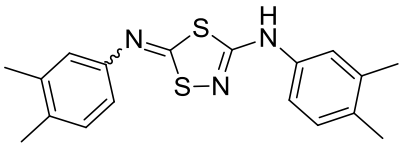
White soild (53.8 mg, 86% yield) . ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.27 (s, 1 H), 10.11 (s, 1 H), 7.42-7.39 (m, 4 H), 7.22-7.18 (m, 4 H), 7.12-7.10 (d, *J* = 8.0 Hz, 4 H), 6.96-6.94 (d, *J* = 12.0 Hz, 2 H), 6.88-6.86 (d, *J* = 8.0 Hz, 2 H), 2.29-2.28 (s, 6 H), 2.24 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 170.9, 168.0, 151.1, 151.0, 149.8, 147.6, 137.1, 134.4, 134.3, 131.9, 131.8, 130.1, 130.0, 129.4, 129.3, 119.8, 119.4, 119.3, 118.4, 118.3, 118.3, 118.2, 20.5, 20.4; HRMS calcd for $C_{16}H_{16}N_3S_2$ $[M+H]^+$ 314.0780; found: 314.0789.



***N*-(2,3-dimethylphenyl)-5-((2,3-dimethylphenyl)imino)-1,4,2-dithiazol-3-amine (3e)**

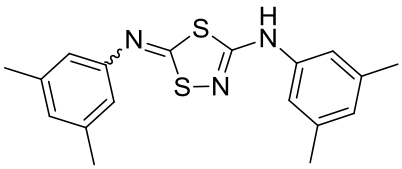
White oil (44.3 mg, 65% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.65 (s, 1 H), 9.50 (s, 1 H), 7.26 (s, 2 H), 7.10-6.95 (m, 8 H), 6.75-6.74 (d, *J* = 4.0 Hz, 1 H), 6.68-6.67

(d, *J* = 4.0 Hz, 1 H), 2.24 (s, 12 H), 2.15-2.11 (m, 6 H), 2.06 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.2, 169.5, 154.1, 154.0, 152.1, 149.6, 137.8, 137.6, 137.4, 137.2, 131.2, 127.4, 127.1, 126.5, 126.4, 126.3, 125.6, 123.1, 115.2, 115.1, 20.1, 19.8, 13.9, 13.4; HRMS calcd for $C_{18}H_{20}N_3S_2$ $[M+H]^+$ 342.1093; found: 342.1100.



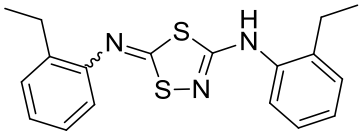
_N_-(3,4-dimethylphenyl)-5-((3,4-dimethylphenyl)imino)-1,4,2-dithiazol-3-amine (3f)

White oil (53.9 mg, 79% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.19 (s, 1 H), 10.03 (s, 1 H), 7.27-7.25 (m, 4 H), 7.17-7.12 (m, 2 H), 7.06-7.04 (d, *J* = 8.0 Hz, 2 H), 6.86 (s, 1 H), 6.79-6.77 (m, 2 H), 6.70-6.68 (d, *J* = 8.0 Hz, 1 H), 2.22-2.17 (m, 18 H), 2.15 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 170.7, 167.7, 151.0, 150.2, 148.0, 137.6, 137.4, 136.7, 133.2, 133.1, 130.7, 130.4, 129.8, 121.1, 120.5, 119.5, 116.8, 116.7, 115.9, 115.8, 19.6, 19.5, 18.9, 18.7; HRMS calcd for $C_{18}H_{20}N_3S_2$ $[M+H]^+$ 342.1093; found: 342.1101.



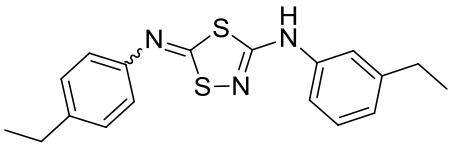
_N_-(2,4-dimethylphenyl)-5-((2,4-dimethylphenyl)imino)-1,4,2-dithiazol-3-amine (3g)

White oil (50.5 mg, 74% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.22 (s, 1 H), 10.04 (s, 1 H), 7.17 (s, 4 H), 6.80-6.77 (d, *J* = 12.8 Hz, 2 H), 6.66-6.64 (m, 4 H), 6.58 (s, 2 H), 2.26-2.24 (m, 12 H), 2.22 (s, 12 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 171.2, 168.2, 152.5, 151.0, 150.8, 150.3, 139.6, 138.8, 138.0, 126.6, 124.4, 117.4, 117.1, 115.9, 115.8, 21.1, 21.0; HRMS calcd for $C_{18}H_{20}N_3S_2$ $[M+H]^+$ 342.1093; found: 342.1103.



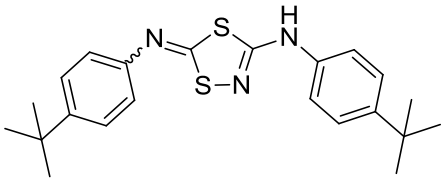
***N*-(2-ethylphenyl)-5-((2-ethylphenyl)imino)-1,4,2-dithiazol-3-amine (3h)**

White oil (53.9 mg, 79% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 9.57 (s, 1 H), 9.41 (s, 1 H), 7.45-7.43 (d, *J* = 8.0 Hz, 2 H), 7.22-7.06 (m, 12 H), 6.88-6.86 (d, *J* = 8.0 Hz, 1 H), 6.80-6.79 (d, *J* = 4.0 Hz, 1 H), 2.61-2.55 (m, 4 H), 2.48-2.46 (m, 4 H), 1.13-1.04 (m, 12 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.5, 169.8, 154.0, 153.9, 151.6, 149.2, 141.9, 139.4, 137.9, 136.6, 135.6, 134.9, 132.4, 130.8, 129.9, 129.3, 129.2, 129.1, 128.9, 128.6, 127.9, 127.3, 127.0, 126.8, 126.5, 126.4, 126.3, 126.0, 125.4, 125.3, 125.2, 117.5, 24.1, 23.7, 23.6, 23.4, 14.8, 14.3, 14.1, 13.8; HRMS calcd for $C_{18}H_{20}N_3S_2$ $[M+H]^+$ 342.1093; found: 342.1102.



***N*-(3-ethylphenyl)-5-((4-ethylphenyl)imino)-1,4,2-dithiazol-3-amine (3i)**

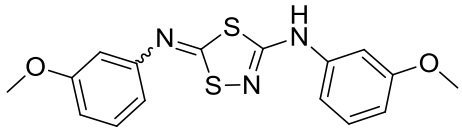
Yellow solid (58.7 mg, 86% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.26 (s, 1 H), 10.08 (s, 1 H), 7.42-7.39 (m, 4 H), 7.20-7.15 (m, 4 H), 7.10-7.08 (d, *J* = 8.4 Hz, 4 H), 6.94-6.92 (d, *J* = 8.0 Hz, 2 H), 6.87-6.85 (d, *J* = 8.4 Hz, 2 H), 2.57-2.46 (m, 8 H), 1.15-1.08 (m, 12 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ =170.9, 168.1, 151.1, 151.0, 150.1, 147.8, 140.7, 140.6, 138.3, 137.4, 137.3, 137.3, 129.1, 129.0, 128.7, 128.3, 128.0, 120.0, 119.8, 119.6, 119.3, 118.5, 118.4, 118.3, 118.2, 27.7, 27.6, 27.5, 15.7, 15.6, 15.5, 15.4; HRMS calcd for $C_{18}H_{20}N_3S_2$ $[M+H]^+$ 342.1093; found: 342.1093.



***N*-(4-(*tert*-butyl)phenyl)-5-((4-(*tert*-butyl)phenyl)imino)-1,4,2-dithiazol-3-amine (3j)**

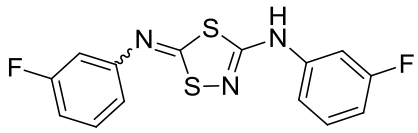
White solid; (68.3 mg, 86% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.30 (s, 1 H), 10.11 (s, 1 H), 7.46-7.30 (m, 12 H), 6.99-6.91 (m, 4 H), 1.28-1.25 (m, 36 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 170.7, 168.2, 151.0, 150.9, 149.8, 147.5, 147.4,

147.3, 145.1, 137.0, 126.2, 126.1, 125.5, 119.6, 119.1, 118.0, 34.1, 33.9, 31.1; HRMS calcd for $C_{22}H_{28}N_3S_2$ $[M+H]^+$ 398.1719; found: 398.1725.



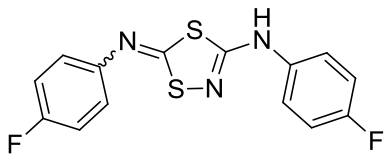
***N*-(3-methoxyphenyl)-5-((3-methoxyphenyl)imino)-1,4,2-dithiazol-3-amine (3k)**

White solid (51.8 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.50 (s, 1 H), 7.28-7.25 (m, 3 H), 7.20-7.16 (m, 2 H), 7.08-7.07 (m, 2 H), 6.91-6.85 (m, 2 H), 6.72-6.70 (m, 2 H), 6.63-6.57 (m, 6 H), 3.78 (s, 6 H), 3.77 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 173.7, 169.7, 160.5, 160.4, 160.2, 153.7, 151.7, 151.2, 151.1, 139.9, 139.8, 130.4, 130.0, 129.9, 112.1, 111.8, 111.6, 111.4, 111.2, 109.5, 109.4, 105.8, 105.6, 105.5, 105.4, 55.3; HRMS calcd for $C_{16}H_{16}N_3O_2S_2$ $[M+H]^+$ 346.0679; found: 346.0685.



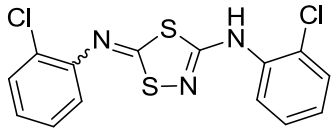
***N*-(3-fluorophenyl)-5-((3-fluorophenyl)imino)-1,4,2-dithiazol-3-amine (3l)**

Yellow solid (39.8 mg, 62% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.66 (s, 1 H), 10.50 (s, 1 H), 7.51-7.40 (m, 4 H), 7.36-7.30 (m, 2 H), 7.25-7.21 (m, 2 H), 7.04-6.99 (m, 2 H), 6.94-6.90 (m, 2 H), 6.86-6.82 (m, 4 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 173.1, 170.4, 164.0-161.6 (d, J = 244 Hz, 1 C), 163.5-161.1 (d, J = 240 Hz, 1 C), 153.9, 153.8, 151.8, 151.1, 150.6, 141.1, 141.0, 131.5-131.4 (d, J = 10 Hz, 1 C), 130.6-130.5 (d, J = 9 Hz, 1 C), 115.7, 115.6, 114.0, 112.0-111.8 (d, J = 21 Hz, 1 C), 109.3-109.1 (d, J = 21 Hz, 1 C), 107.4-107.2 (d, J = 23 Hz, 1 C), 107.1-106.8 (d, J = 22 Hz, 1 C), 105.0-104.8 (d, J = 27 Hz, 1 C); HRMS calcd for $C_{14}H_{10}F_2N_3S_2$ $[M+H]^+$ 322.0279; found: 322.0284.



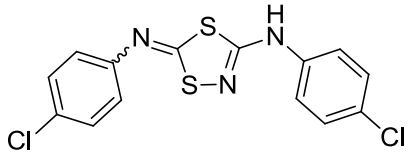
***N*-(4-fluorophenyl)-5-((4-fluorophenyl)imino)-1,4,2-dithiazol-3-amine (3m)**

White solid (50.7 mg, 79% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.45 (s, 1 H), 10.29 (s, 1 H), 7.56-7.52 (m, 4 H), 7.27-7.20 (m, 4 H), 7.17-7.08 (m, 6 H), 7.03-7.00 (m, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.1, 169.4, 160.6-158.2 (d, J = 240 Hz, 1 C), 158.9, 156.5, 151.3, 150.8, 148.8, 146.5, 135.9, 121.8-121.7 (d, J = 8 Hz, 1 C), 121.4-121.3 (d, J = 9 Hz, 1 C), 120.0-119.9 (d, J = 3 Hz, 1 C), 119.9-119.8 (d, J = 3 Hz, 1 C), 116.5-116.2 (d, J = 22 Hz, 1 C), 115.7-115.5 (d, J = 22 Hz, 1 C); HRMS calcd for $C_{14}H_{10}F_2N_3S_2$ $[M+H]^+$ 322.0279; found: 322.0285.



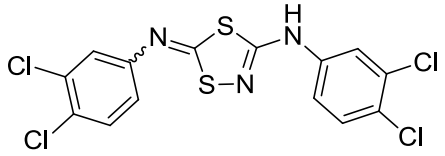
***N*-(2-chlorophenyl)-5-((2-chlorophenyl)imino)-1,4,2-dithiazol-3-amine (3n)**

White solid (40.8 mg, 58% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.04 (s, 1 H), 9.84 (s, 1 H), 7.84-7.82 (m, 2 H), 7.51-7.49 (m, 4 H), 7.35-7.31 (m, 4 H), 7.20-7.16 (m, 5 H), 7.07 (s, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 175.5, 173.2, 153.1, 152.5, 149.7, 147.4, 135.5, 130.2, 129.8, 128.6, 127.7, 126.3, 126.2, 125.2, 124.5, 120.0; HRMS calcd for $C_{14}H_{10}Cl_2N_3S_2$ $[M+H]^+$ 353.9688; found: 353.9698.



***N*-(4-chlorophenyl)-5-((4-chlorophenyl)imino)-1,4,2-dithiazol-3-amine (3o)**

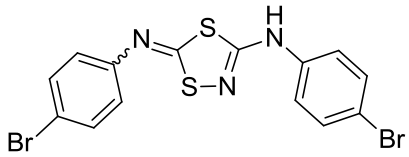
White solid (57.0 mg, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.58 (s, 1 H), 10.41 (s, 1 H), 7.55-7.53 (d, J = 12.0 Hz, 4 H), 7.47-7.42 (m, 4 H), 7.36-7.34 (d, J = 8.0 Hz, 4 H), 7.10-7.08 (d, J = 8.0 Hz, 2 H), 7.01-6.99 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.5, 169.7, 151.1, 150.8, 150.6, 148.7, 138.4, 129.6, 129.2, 128.8, 126.4, 121.7, 121.4, 119.6; HRMS calcd for $C_{14}H_{10}Cl_2N_3S_2$ $[M+H]^+$ 353.9688; found: 353.9697.



***N*-(3,4-dichlorophenyl)-5-((3,4-dichlorophenyl)imino)-1,4,2-dithiazol-3-amine**

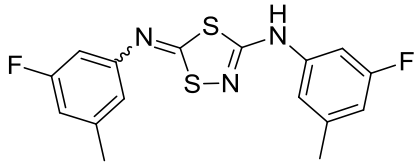
(3p)

White solid (52.9 mg, 63% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.78 (s, 1 H), 10.63 (s, 1 H), 7.86-7.85 (d, *J* = 4.0 Hz, 2 H), 7.68-7.64 (m, 2 H), 7.56-7.54 (d, *J* = 8.0 Hz, 2 H), 7.40-7.38 (m, 3 H), 7.27 (s, 1 H), 7.10-7.08 (d, *J* = 8.0 Hz, 1 H), 7.01-6.99 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 174.0, 171.2, 151.7, 151.2, 150.3, 149.7, 139.3, 132.0, 131.6, 131.2, 130.8, 127.2, 124.2, 122.0, 121.5, 120.3, 120.2, 119.0, 118.2; HRMS calcd for $C_{14}H_8Cl_4N_3S_2$ $[M+H]^+$ 421.8908; found: 421.8903.



***N*-(4-bromophenyl)-5-((4-bromophenyl)imino)-1,4,2-dithiazol-3-amine (3q)**

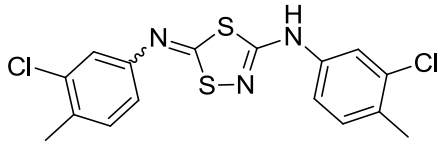
White solid (73.0 mg, 83% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.56 (s, 1 H), 10.39 (s, 1 H), 7.58-7.53 (m, 4 H), 7.50-7.44 (m, 8 H), 7.02-7.00 (d, *J* = 8.0 Hz, 2 H), 6.93-6.91 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.5, 169.7, 151.1, 151.0, 150.5, 149.1, 138.8, 132.5, 131.7, 122.1, 121.8, 119.9, 117.4, 114.3; HRMS calcd for $C_{14}H_{10}Br_2N_3S_2$ $[M+H]^+$ 441.8678; found: 441.8678.



***N*-(3-fluoro-5-methylphenyl)-5-((3-fluoro-5-methylphenyl)imino)-1,4,2-dithiazol-3-amine (3r)**

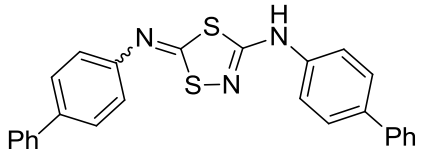
White solid (46.8 mg, 67% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.54 (s, 1 H), 10.37-10.36 (d, *J* = 4.0 Hz, 1 H), 7.30-7.27 (d, *J* = 12.0 Hz, 2 H), 7.03 (s, 2 H), 6.86-6.78 (m, 2 H), 6.72-6.63 (m, 6 H), 2.30 (s, 6 H), 2.26-2.25 (m, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.8, 170.0, 163.9-161.5 (d, *J* = 243 Hz, 1 C), 163.4-161.0 (d, *J* = 240 Hz, 1 C), 153.6-153.5 (d, *J* = 10 Hz, 1 C), 151.5-151.4 (d, *J* = 8 Hz, 1 C), 151.0, 150.5, 141.7, 141.6, 141.5, 140.8, 140.6, 140.5, 116.3, 116.0, 114.3, 112.4-112.2 (d, *J* = 21 Hz, 1 C), 110.0-109.9 (d, *J* = 7 Hz, 1 C), 109.8-109.7 (d, *J* = 7 Hz, 1 C),

104.2-104.0 (d, *J* = 23 Hz, 1 C), 104.1-103.9 (d, *J* = 22 Hz, 1 C), 102.2-102.0 (d, *J* = 26 Hz, 1 C), 21.1, 20.9; HRMS calcd for $C_{16}H_{14}F_2N_3S_2$ $[M+H]^+$ 350.0592; found: 350.0601.



***N*-(3-chloro-4-methylphenyl)-5-((3-chloro-4-methylphenyl)imino)-1,4,2-dithiazol-3-amine (3s)**

White solid (52.6 mg, 69% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.58 (s, 1 H), 10.41 (s, 1 H), 7.78-7.75 (m, 2 H), 7.44-7.40 (m, 2 H), 7.35-7.30 (m, 4 H), 7.19 (s, 1 H), 7.09 (s, 1 H), 7.02-7.00 (d, *J* = 8.0 Hz, 1 H), 6.93-6.91 (d, *J* = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.6, 169.7, 151.0, 150.9, 150.5, 149.0, 138.5, 133.9, 133.2, 132.0, 131.3, 129.4, 120.3, 119.7, 118.6, 118.4, 117.9, 116.8, 19.0, 18.8; HRMS calcd for $C_{16}H_{14}Cl_2N_3S_2$ $[M+H]^+$ 382.0001; found: 382.0010.



***N*-([1,1'-biphenyl]-4-yl)-5-([1,1'-biphenyl]-4-ylimino)-1,4,2-dithiazol-3-amine (3t)**

White solid (48.9 mg, 56% yield). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 10.69 (s, 1 H), 10.50 (s, 1 H), 8.32-8.28 (d, *J* = 16.0 Hz, 2 H), 7.99-7.79 (m, 16 H), 7.59-7.37 (m, 15 H), 7.32-7.25 (m, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 172.1, 169.2, 151.1, 150.8, 150.1, 148.0, 137.1, 133.7, 133.6, 133.5, 130.8, 130.7, 129.6, 129.5, 129.4, 128.7, 127.7, 127.6, 127.5, 127.4, 127.2, 126.7, 126.6, 125.5, 124.5, 120.9, 120.7, 119.2, 115.6, 115.2, 113.6; HRMS calcd for $C_{26}H_{20}N_3S_2$ $[M+H]^+$ 438.1093; found: 438.1087.

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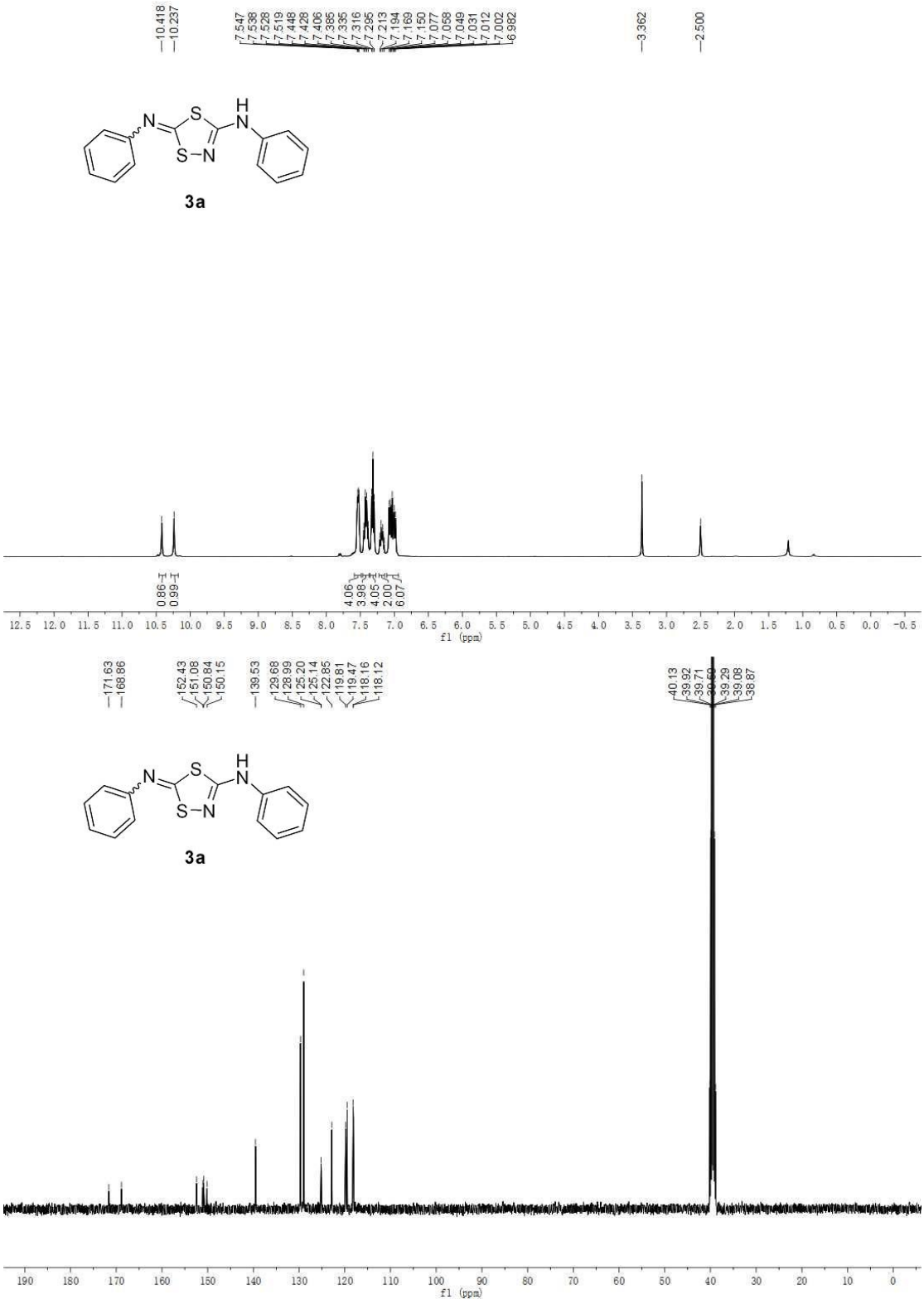
[4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *Appl. Cryst.* **2009**, *42*, 339-341;

[5] G. M. Sheldrick, *Acta Cryst. A.* **2008**, *64*, 112-122.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7.213
7.194
7.169
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7.058
7.049
7.031
7.012
7.002
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3a
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0.99
4.06
3.98
4.05
2.00
6.07
f1 (ppm)
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168.86
152.43
151.08
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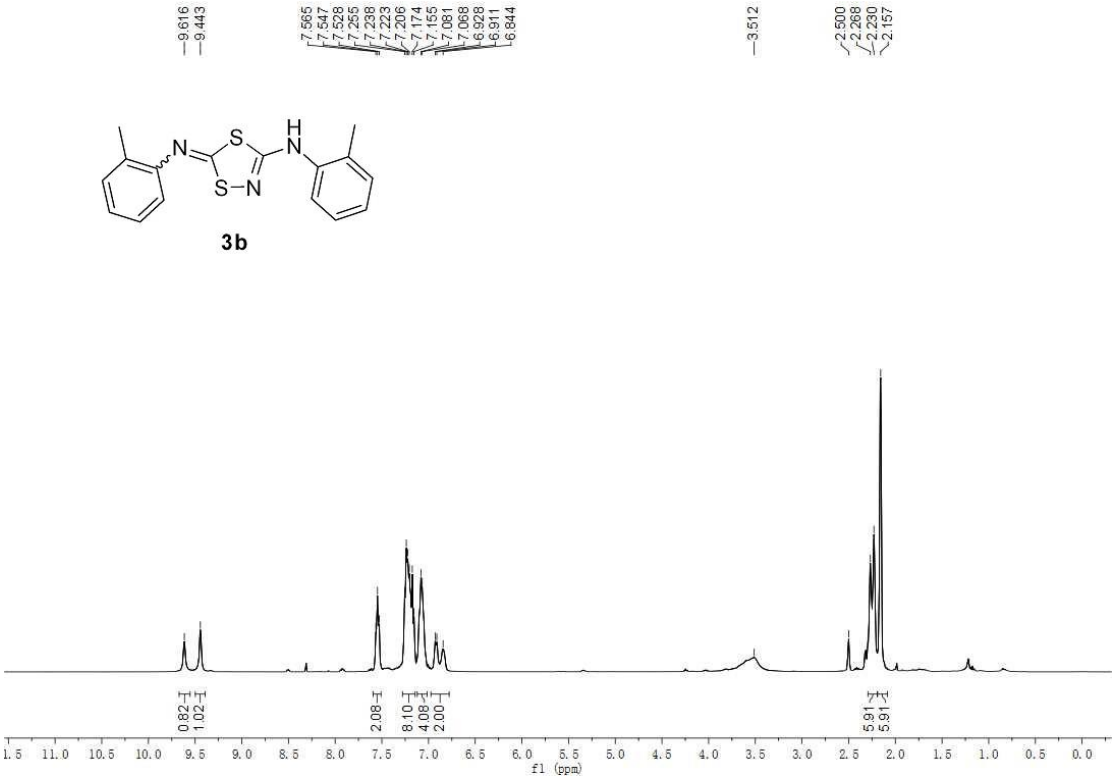
3a
f1 (ppm)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6.844
3.512
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2.268
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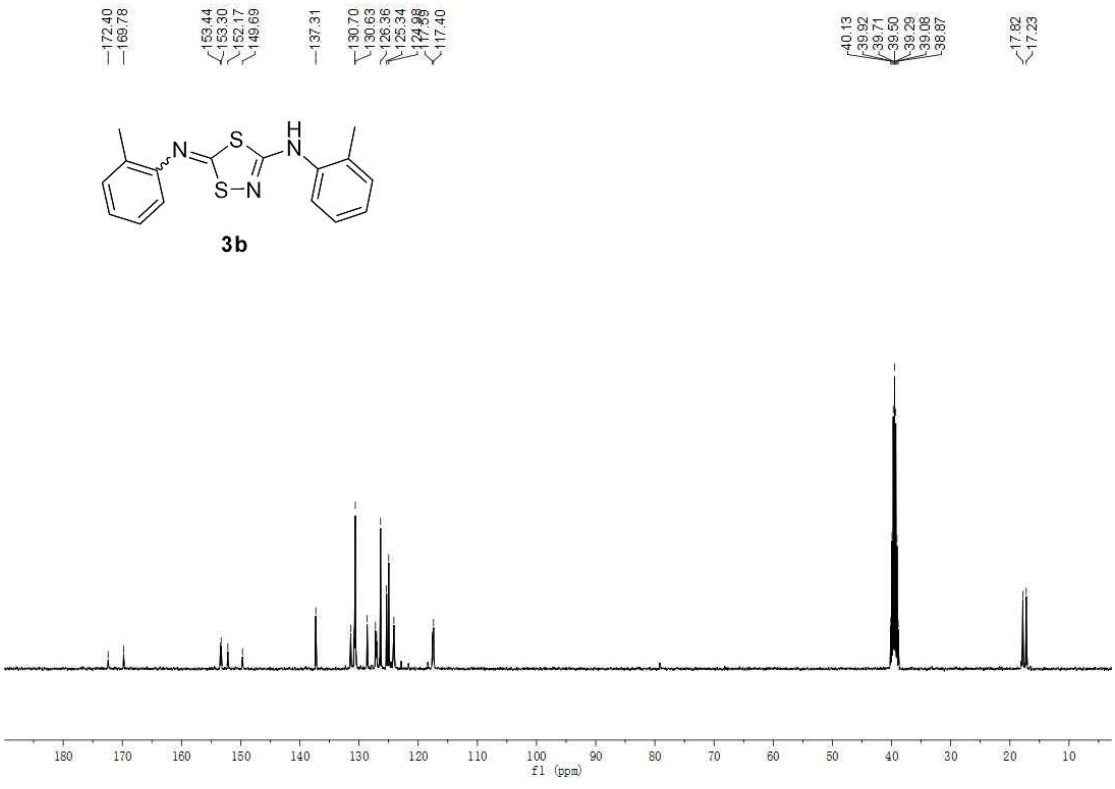
5.91
f1 (ppm)

3b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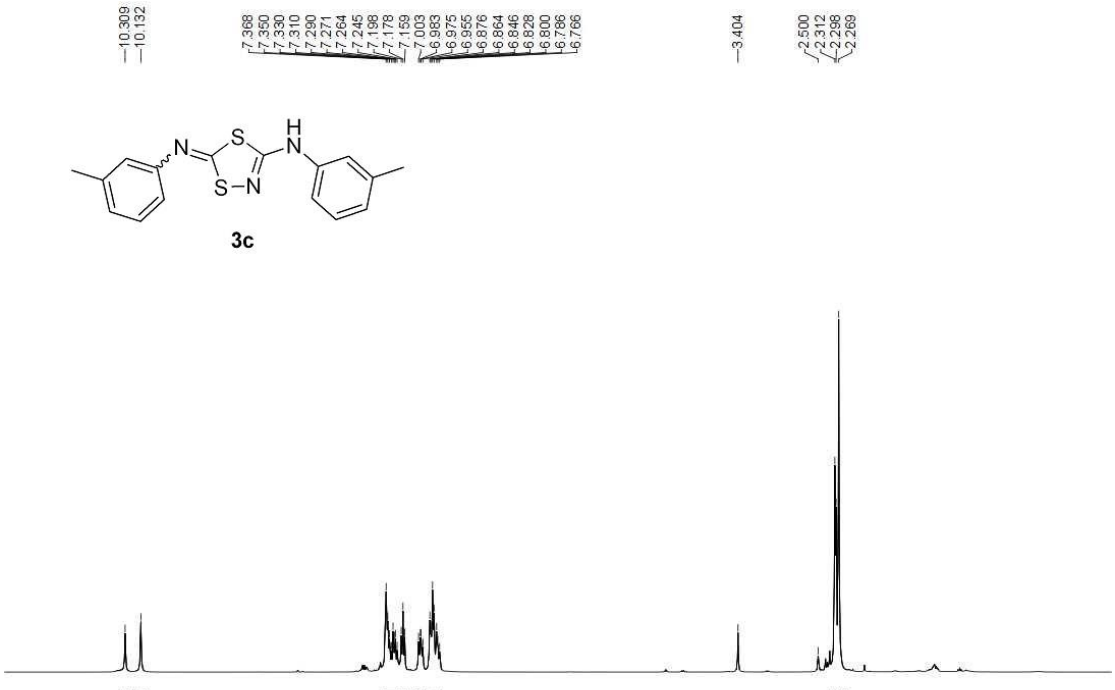
f1 (ppm)

3b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6.876
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S
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H
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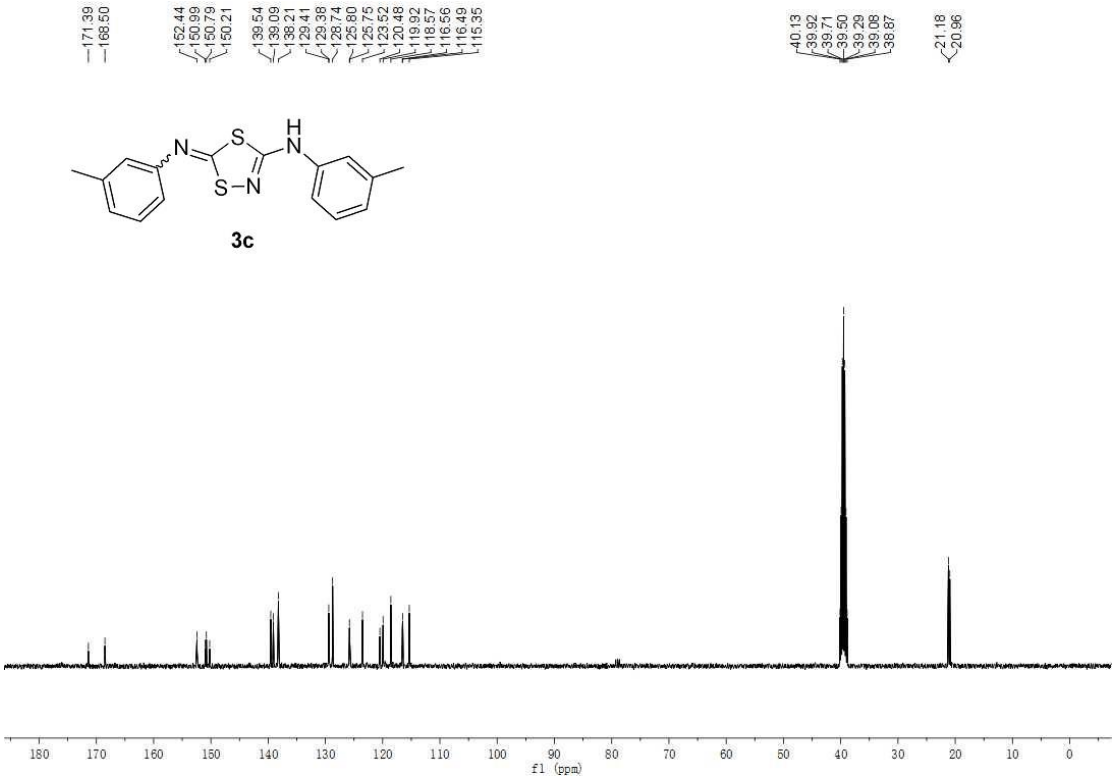
f1 (ppm)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S
S–N
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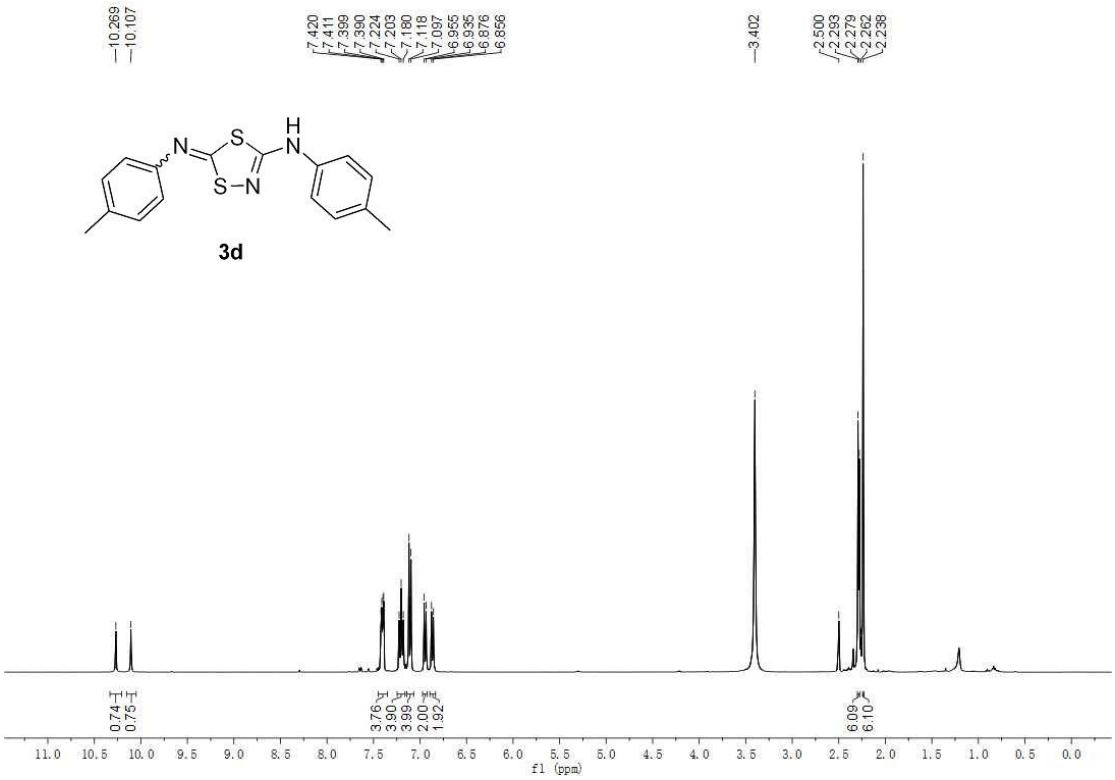
N
3c
f1 (ppm)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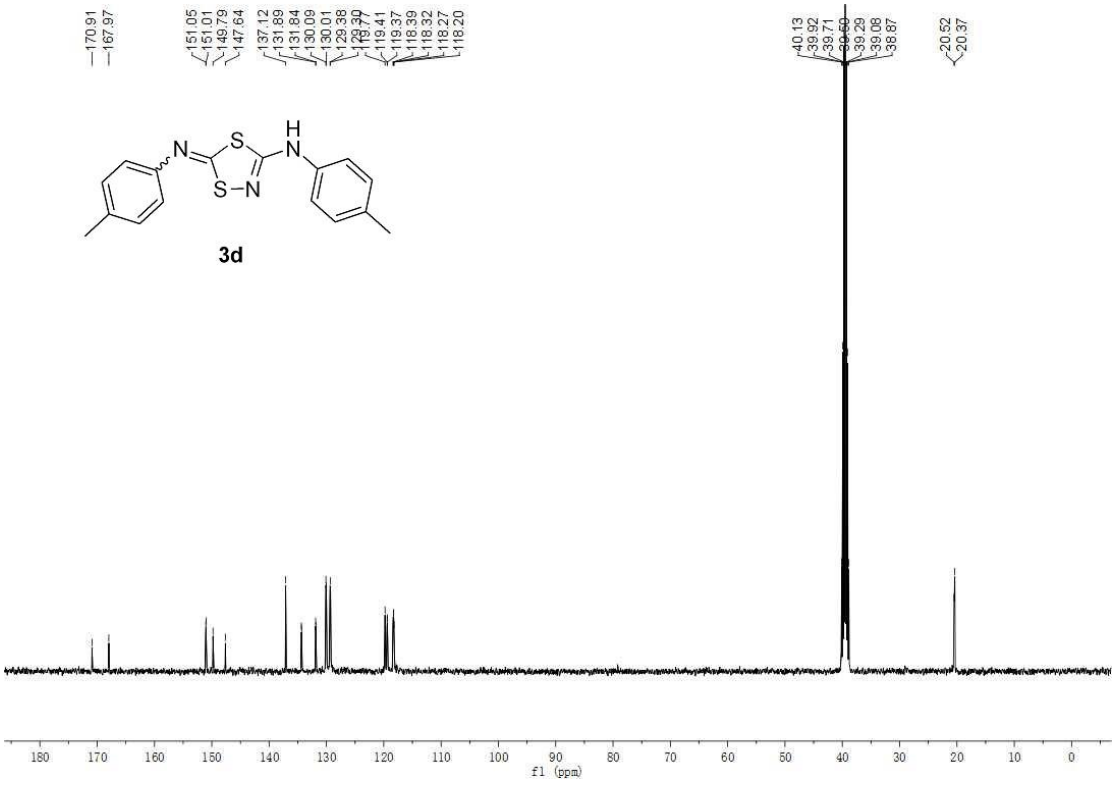
f1 (ppm)

3d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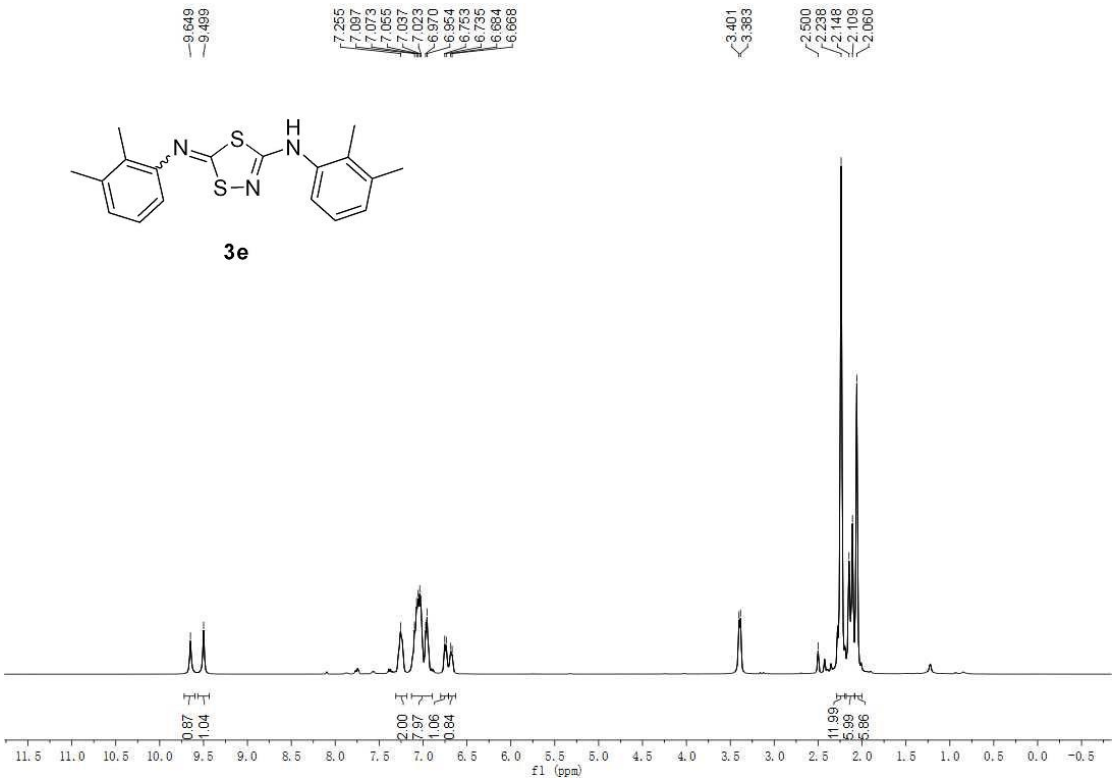
20.37
f1 (ppm)

3d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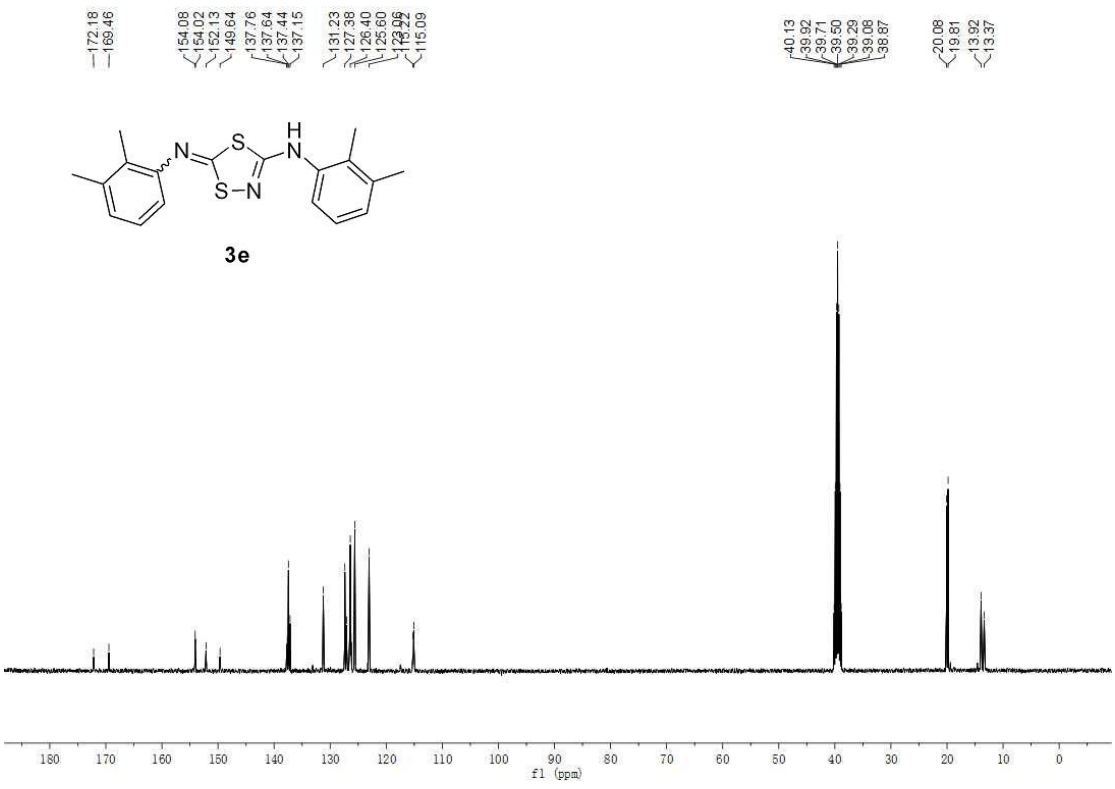
f1 (ppm)

3e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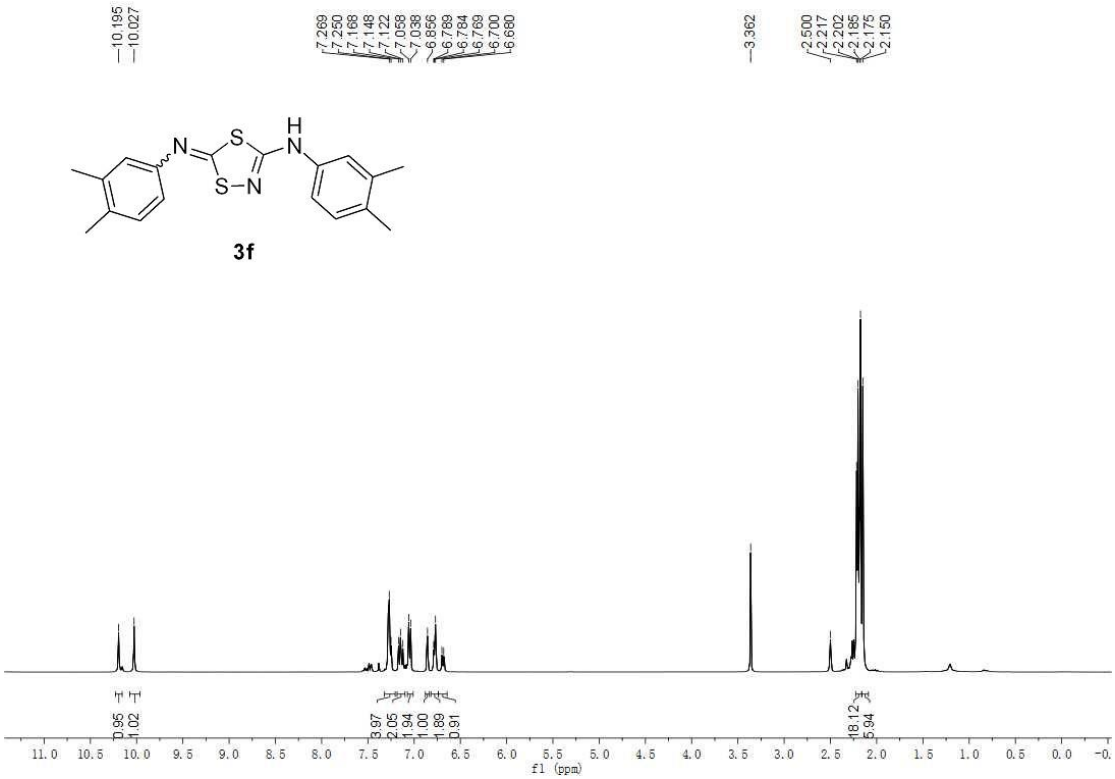
f1 (ppm)

3e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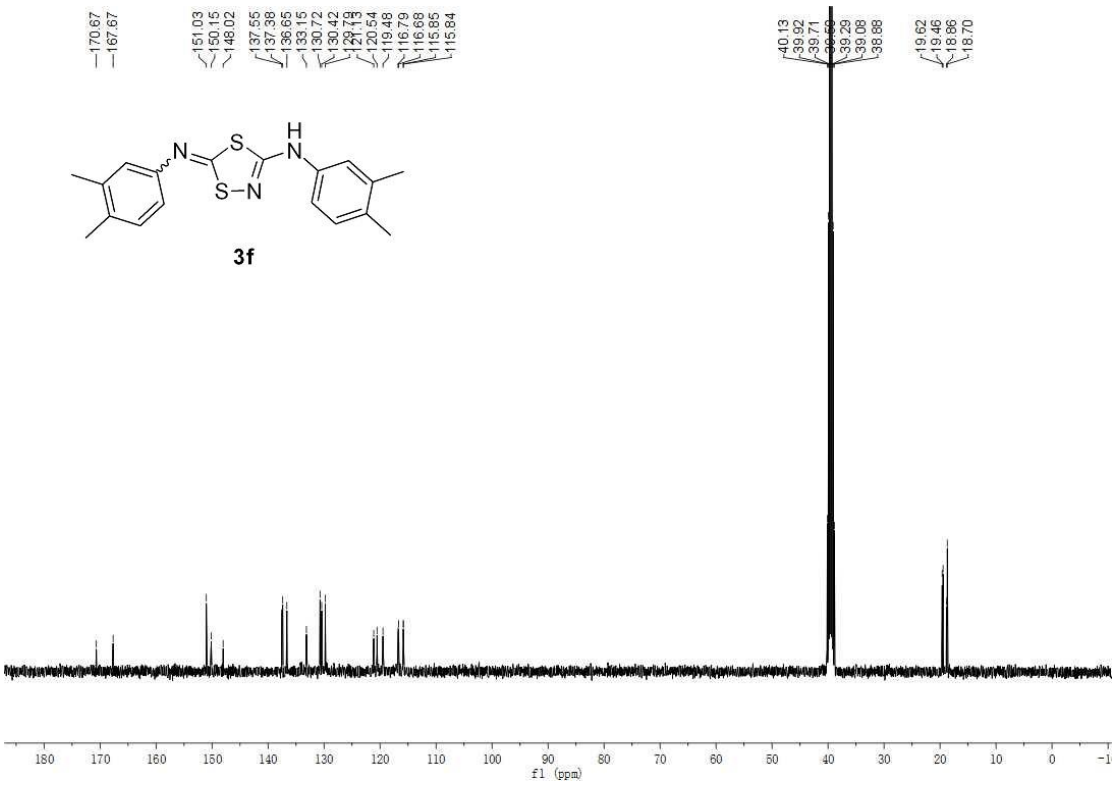
f1 (ppm)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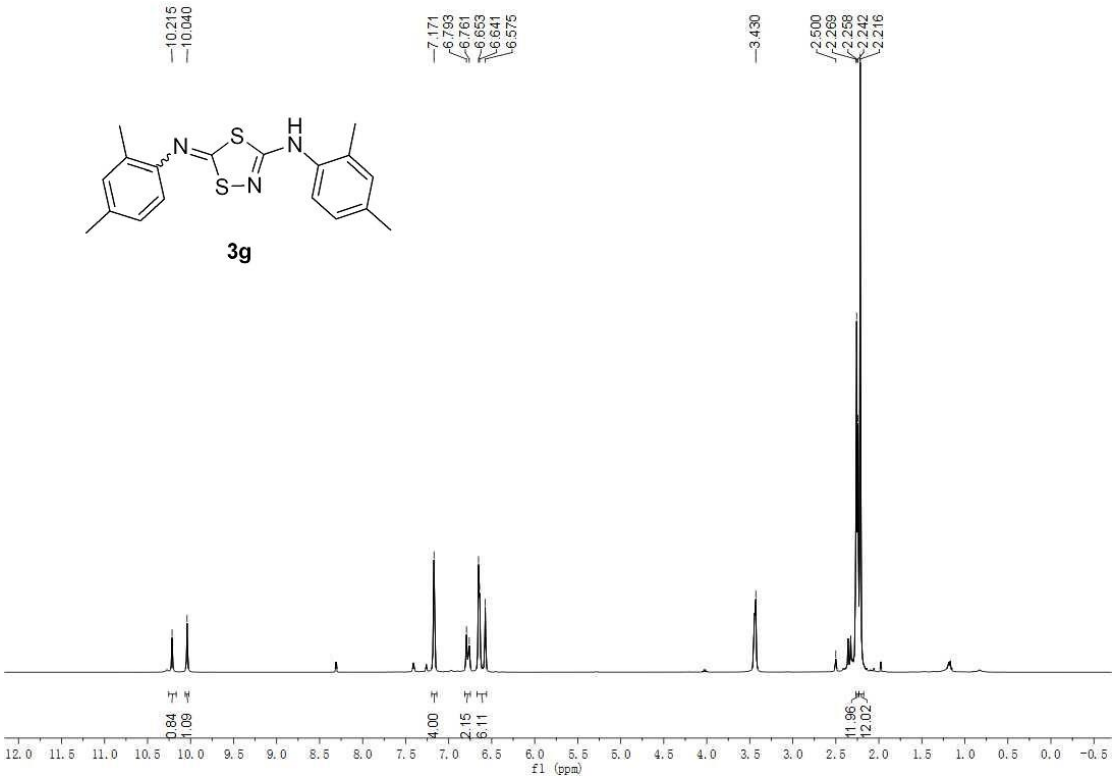
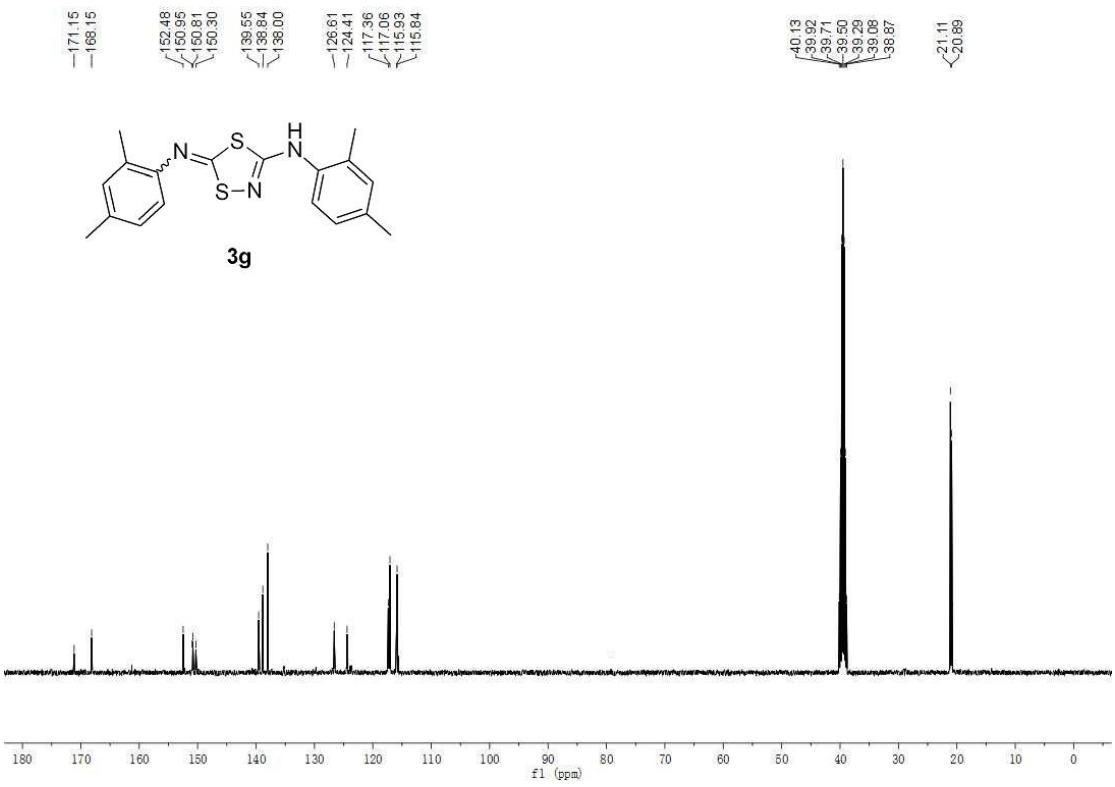
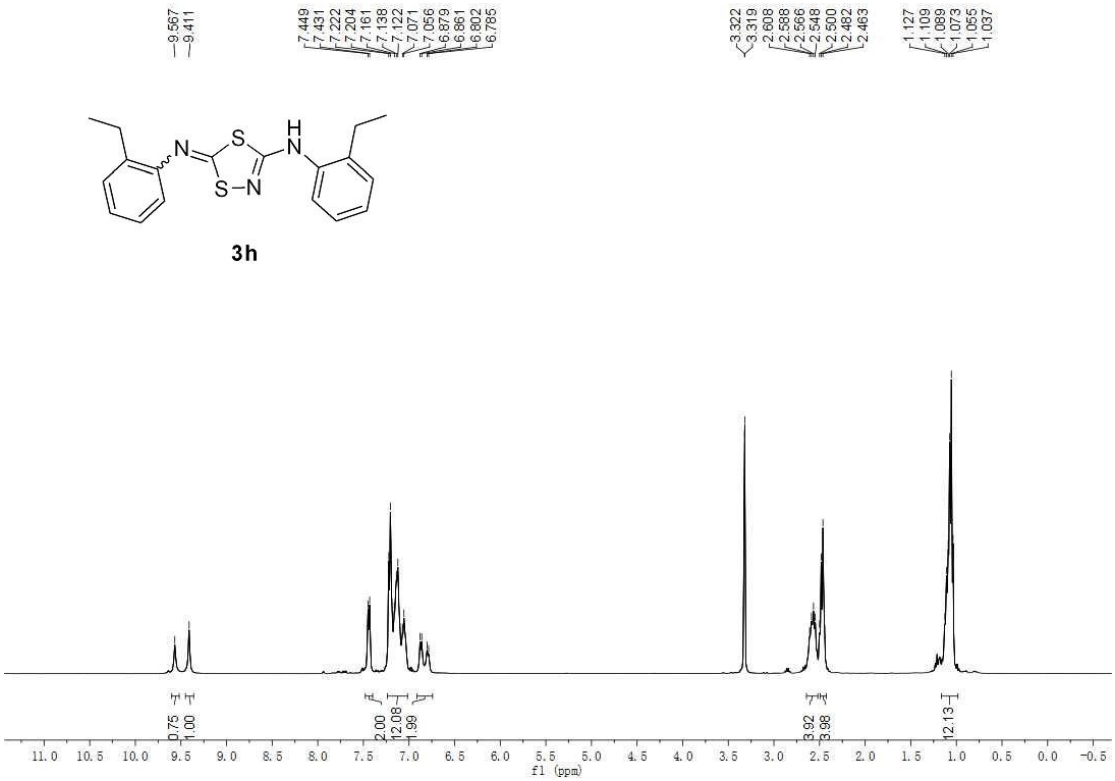
3f
f1 (ppm)


10.215
10.040
7.171
6.793
6.761
6.653
6.641
6.575
3.430
2.500
2.269
2.258
2.242
2.216
0.84
1.09
4.00
2.15
6.11
11.96
12.02
f1 (ppm)

3g


171.15
168.15
152.48
150.95
150.81
150.30
139.55
138.84
138.00
126.61
124.41
117.36
117.06
115.93
115.84
40.13
39.92
39.71
39.50
39.29
39.08
38.87
21.11
20.89
f1 (ppm)

3g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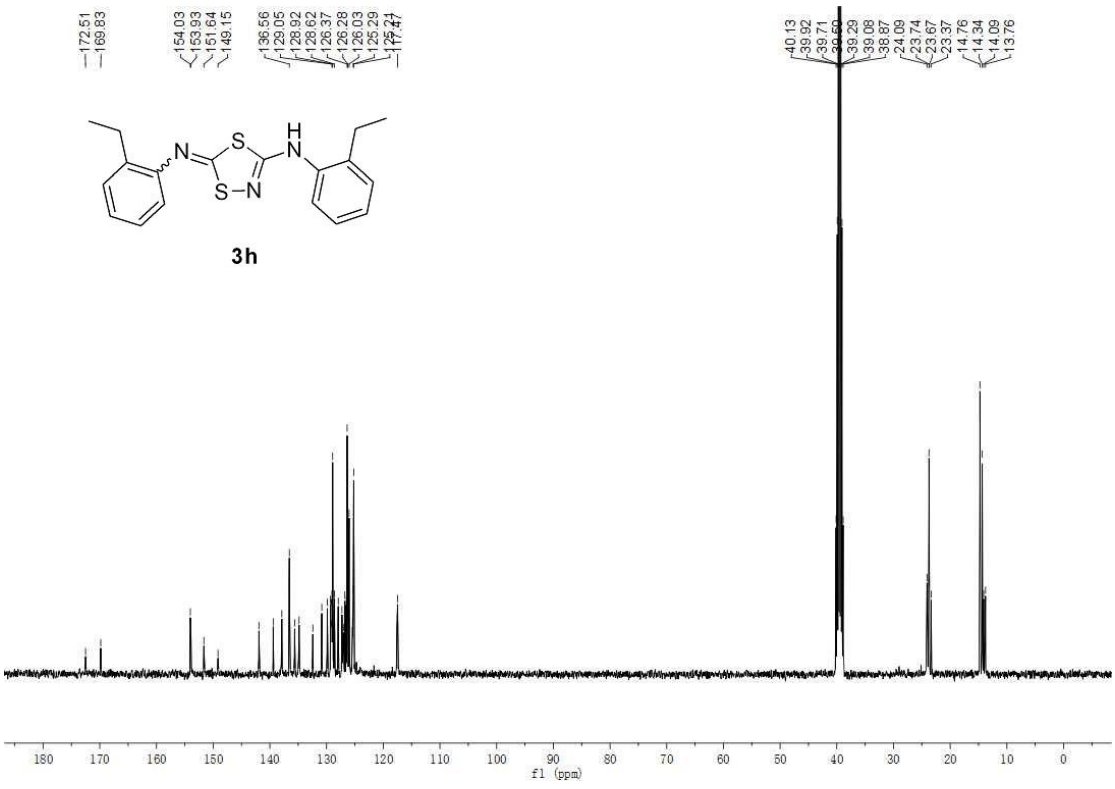
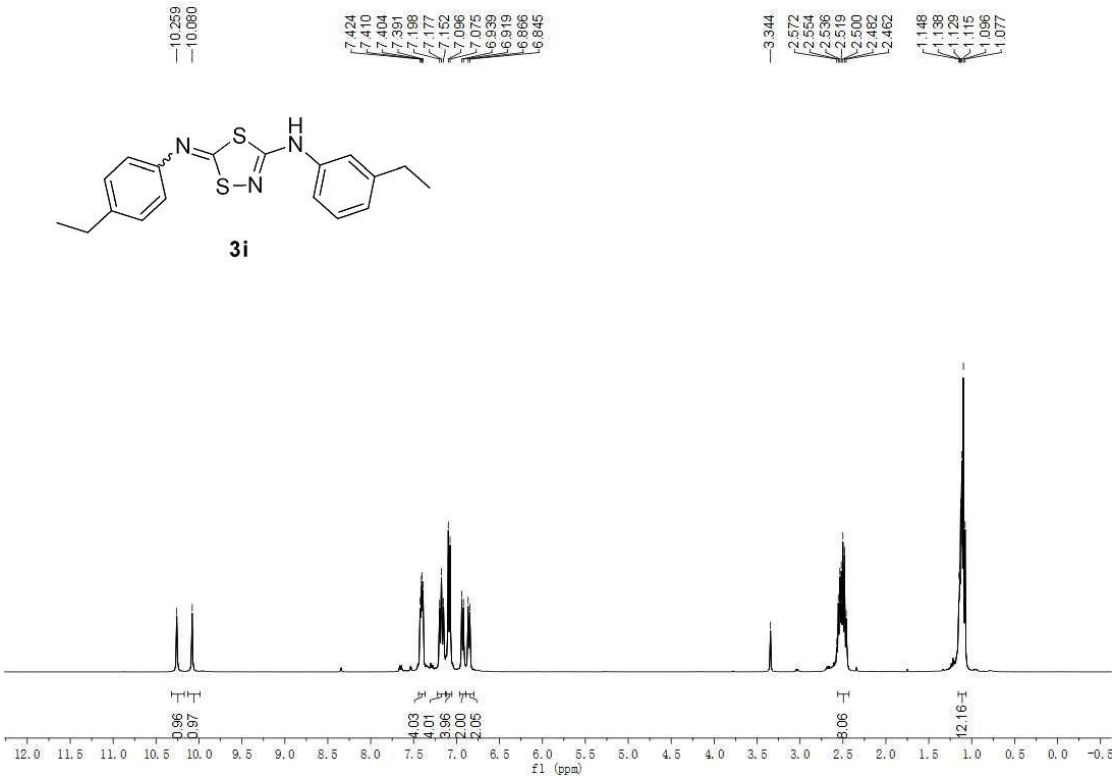
9.411
7.449
7.431
7.222
7.204
7.161
7.138
7.122
7.071
7.056
6.879
6.861
6.802
6.785
3.322
3.319
2.608
2.588
2.566
2.548
2.500
2.482
2.463
1.127
1.109
1.089
1.073
1.055
1.037
N
S
S–N
H
N
3h
0.75
1.00
2.00
2.08
1.99
3.92
3.98
12.13
f1 (ppm)


172.51
169.83
154.03
153.93
151.64
149.15
136.56
129.05
128.92
128.62
126.37
126.28
126.03
125.29
125.21
117.47
40.13
39.92
39.71
39.50
39.29
39.08
38.87
24.09
23.74
23.67
23.37
14.76
14.34
14.09
13.76
N
S
S–N
H
N
3h
f1 (ppm)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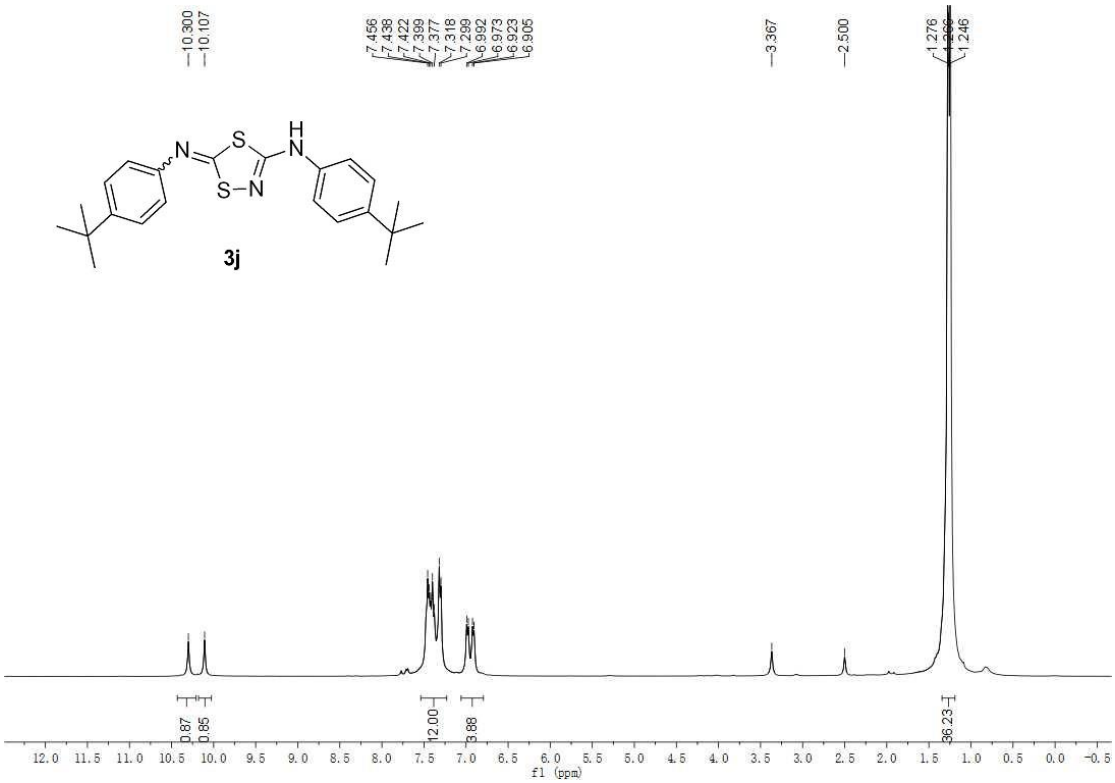
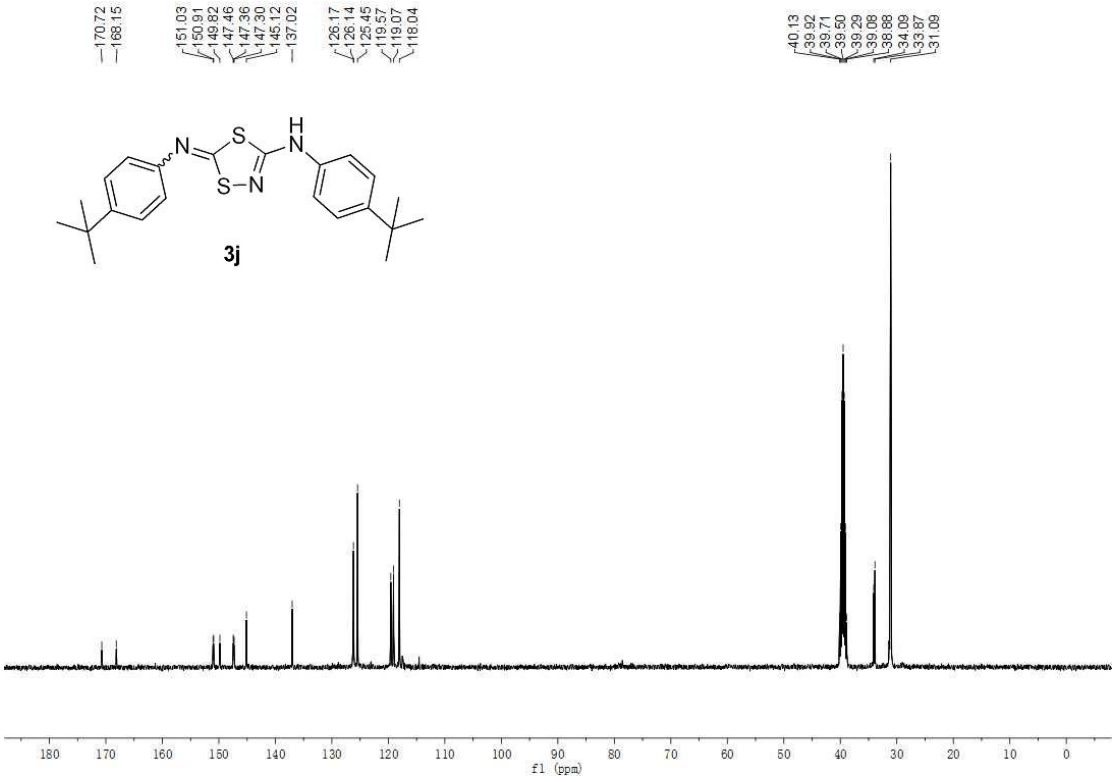
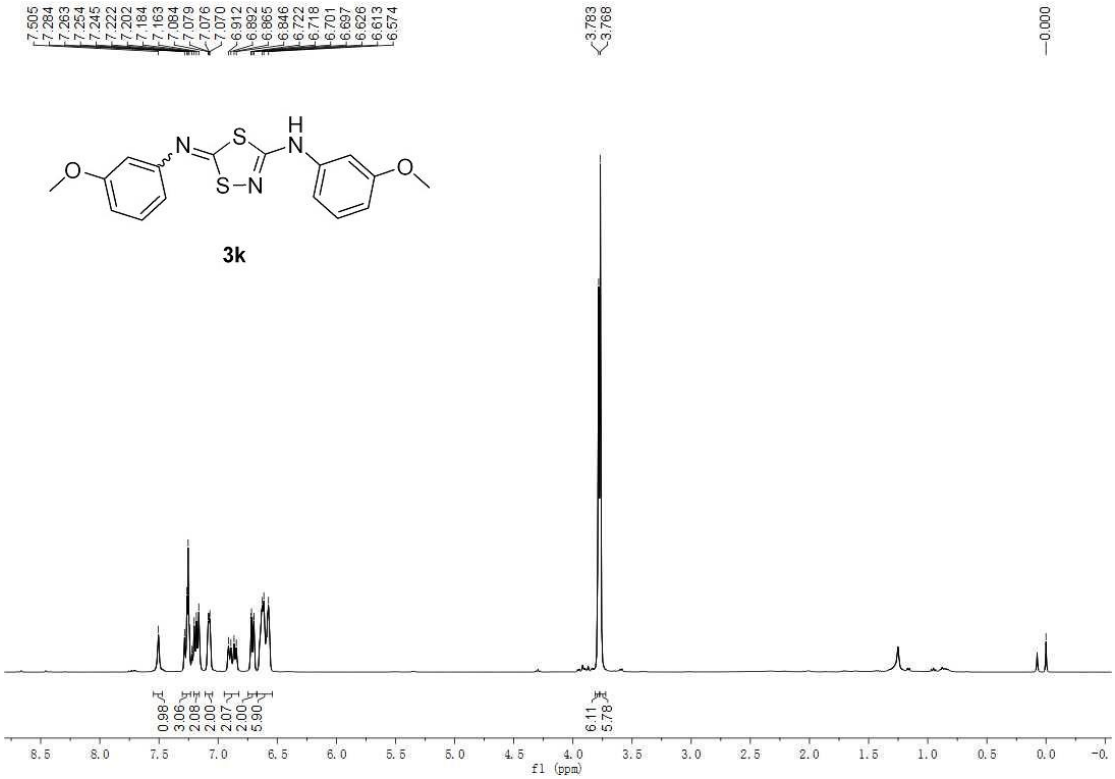
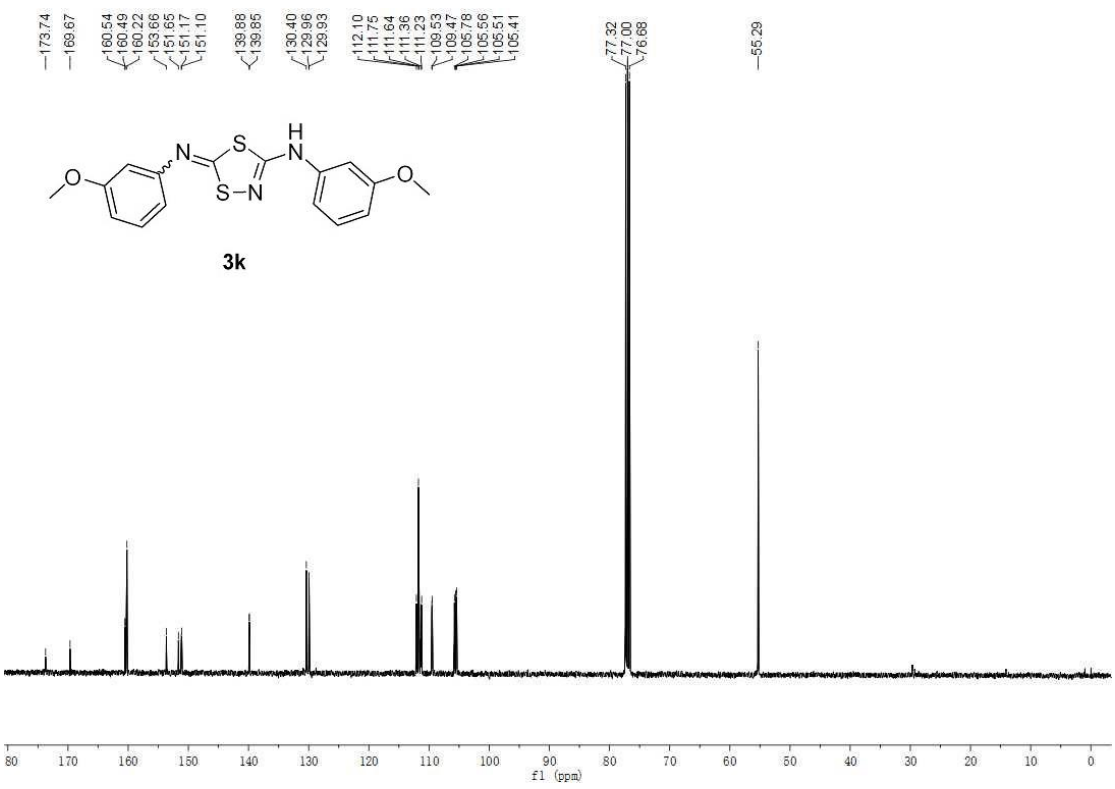
10.080
7.424
7.410
7.404
7.391
7.198
7.177
7.152
7.096
7.075
6.939
6.919
6.866
6.845
3.344
2.572
2.554
2.536
2.519
2.500
2.482
2.462
1.148
1.138
1.129
1.115
1.096
1.077
N
S
H
S
N
3i
0.96
0.97
4.03
4.01
3.96
2.00
2.05
8.06
12.16
f1 (ppm)
170.85
168.06
151.05
150.97
150.06
147.76
138.29
137.36
137.34
128.95
128.26
122.87
122.69
119.75
119.57
119.30
118.49
118.41
118.26
118.19
40.13
39.92
39.71
39.50
39.29
39.08
38.87
27.69
27.66
27.56
15.68
15.59
15.49
15.39
N
S
H
S
N
3i
f1 (ppm)


10.300
10.107
7.456
7.438
7.422
7.399
7.377
7.318
7.299
6.992
6.973
6.923
6.905
3.367
2.500
1.276
1.246
3j
0.87
0.85
12.00
3.88
36.23
f1 (ppm)

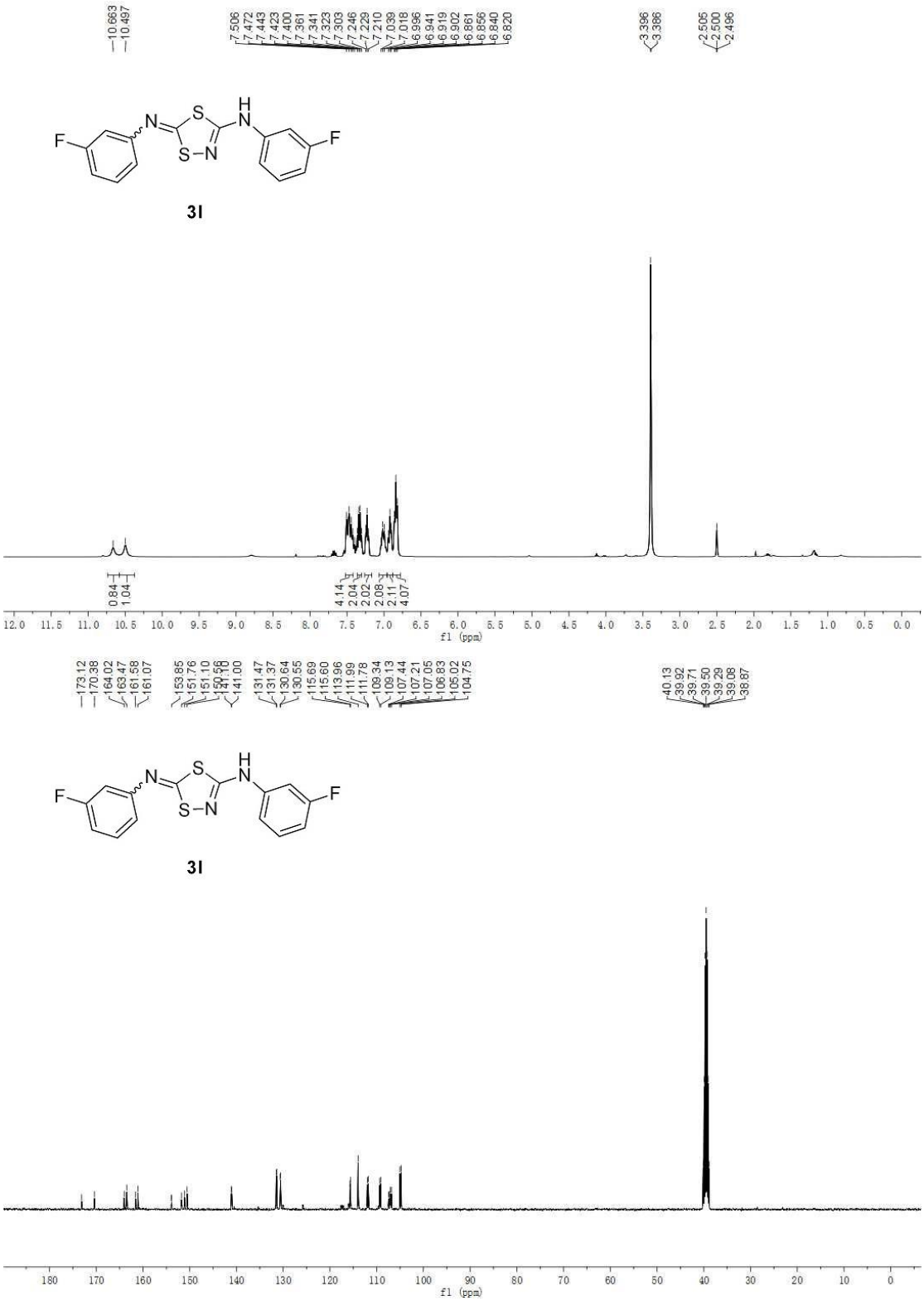

170.72
168.15
151.03
150.91
149.82
147.46
147.36
147.30
145.12
137.02
126.17
126.14
125.45
119.57
119.07
118.04
40.13
39.92
39.71
39.50
39.29
39.08
38.88
34.09
33.87
31.09
3j
f1 (ppm)

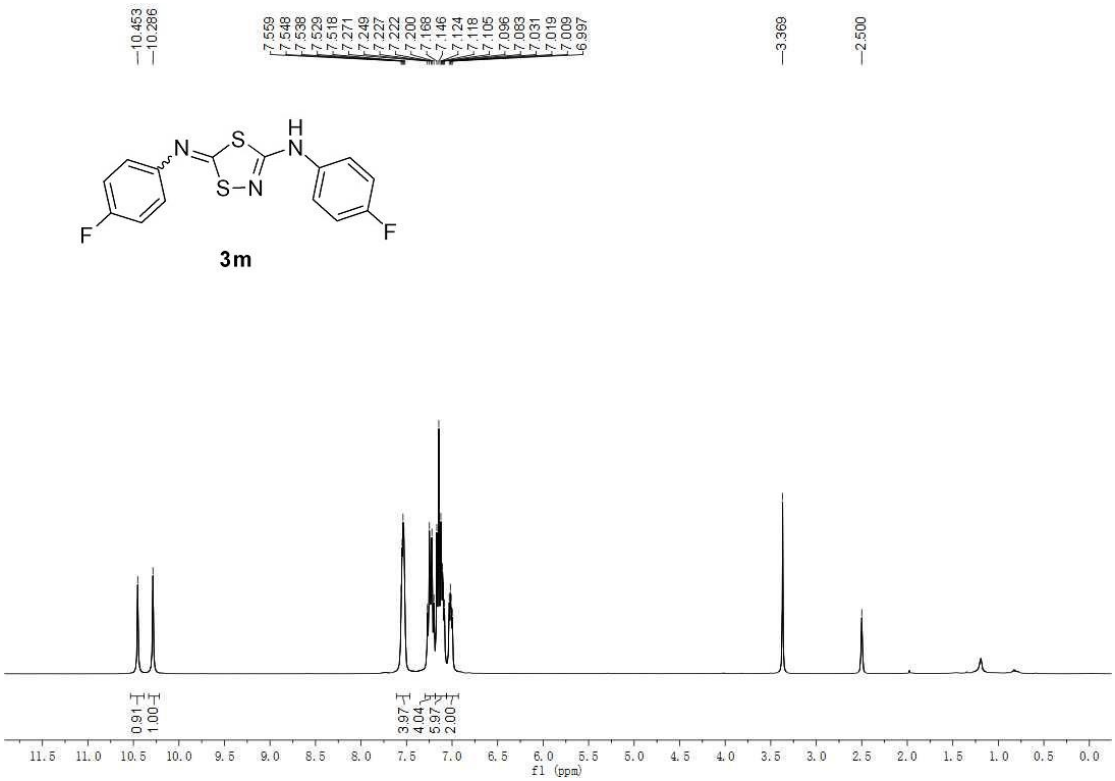

7.505
7.284
7.263
7.254
7.245
7.222
7.202
7.184
7.163
7.084
7.079
7.076
7.070
6.912
6.892
6.865
6.846
6.722
6.718
6.701
6.697
6.626
6.613
6.574
3.783
3.768
0.000
0.98
3.06
2.08
2.00
2.07
2.00
5.90
6.11
5.78
f1 (ppm)

3k

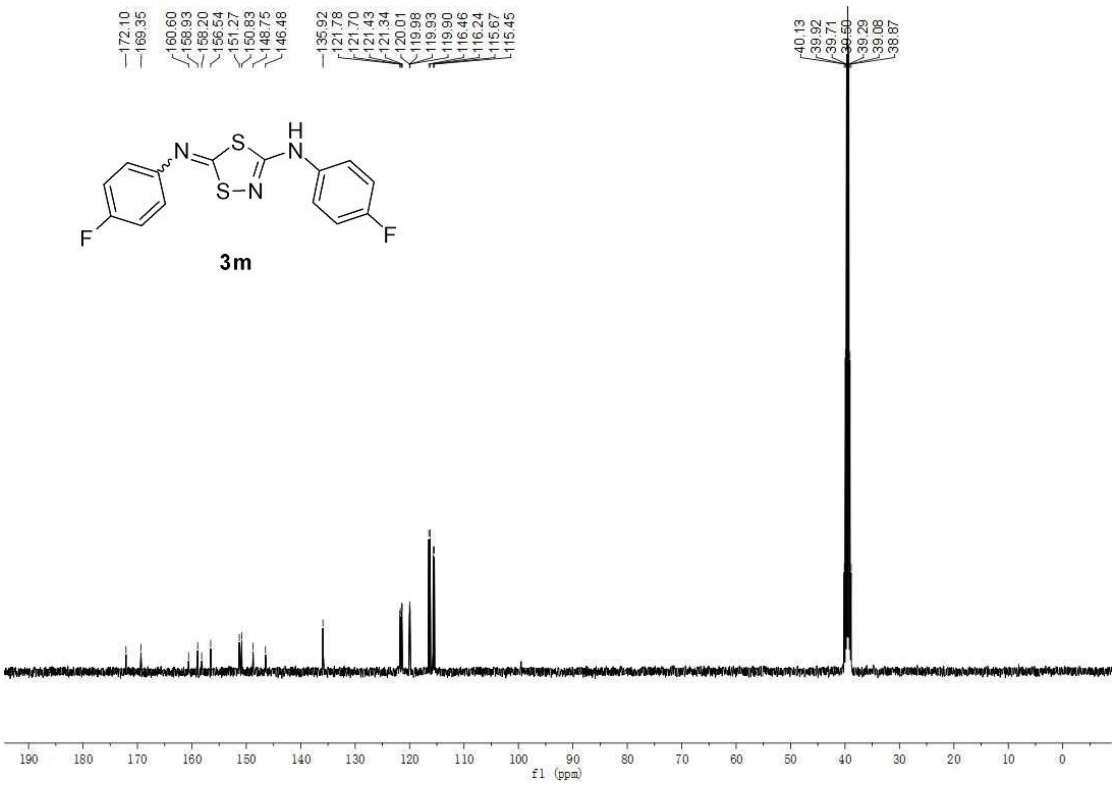

173.74
169.67
160.54
160.49
160.22
153.66
151.65
151.17
151.10
139.88
139.85
130.40
129.96
129.93
112.10
111.75
111.64
111.36
111.23
109.53
109.47
105.78
105.56
105.51
105.41
77.32
77.00
76.68
55.29
f1 (ppm)

3k

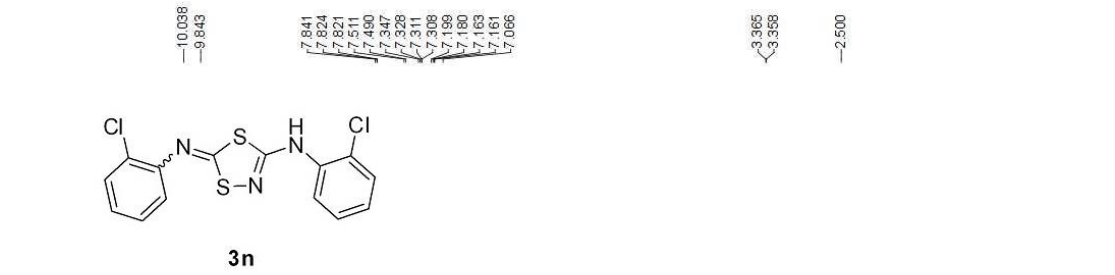

10.663
10.497
7.506
7.472
7.443
7.423
7.400
7.361
7.341
7.323
7.303
7.246
7.229
7.210
7.039
7.018
6.996
6.941
6.919
6.902
6.861
6.856
6.840
6.820
3.396
3.386
2.505
2.500
2.496
F
N
S
S
N
H
N
F
3l
0.84
1.04
4.14
2.04
2.02
2.08
2.11
4.07
f1 (ppm)
173.12
170.38
164.02
163.47
161.58
161.07
153.85
151.76
151.10
150.56
141.16
141.00
131.47
131.37
130.64
130.55
115.69
115.60
113.96
111.99
111.78
109.34
109.13
107.44
107.21
107.05
106.83
105.02
104.75
40.13
39.92
39.71
39.50
39.29
39.08
38.87
F
N
S
S
N
H
N
F
3l
f1 (ppm)


10.453
10.286
7.559
7.548
7.538
7.529
7.518
7.271
7.249
7.227
7.222
7.200
7.168
7.146
7.124
7.118
7.105
7.096
7.083
7.031
7.019
7.009
6.997
3.369
2.500
0.91
1.00
3.97
4.04
5.97
2.00
f1 (ppm)

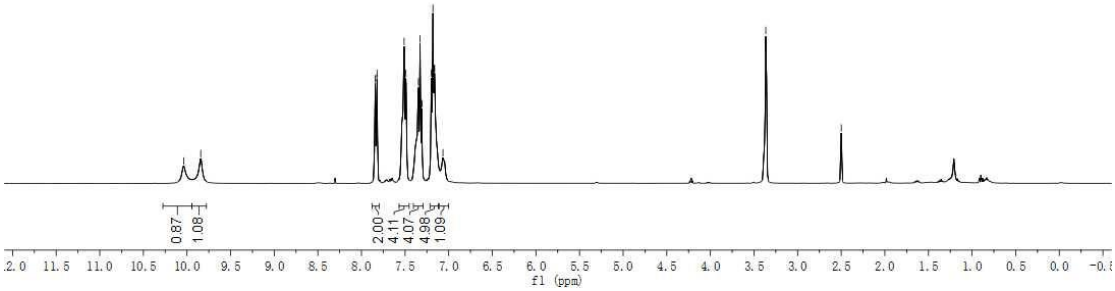
3m

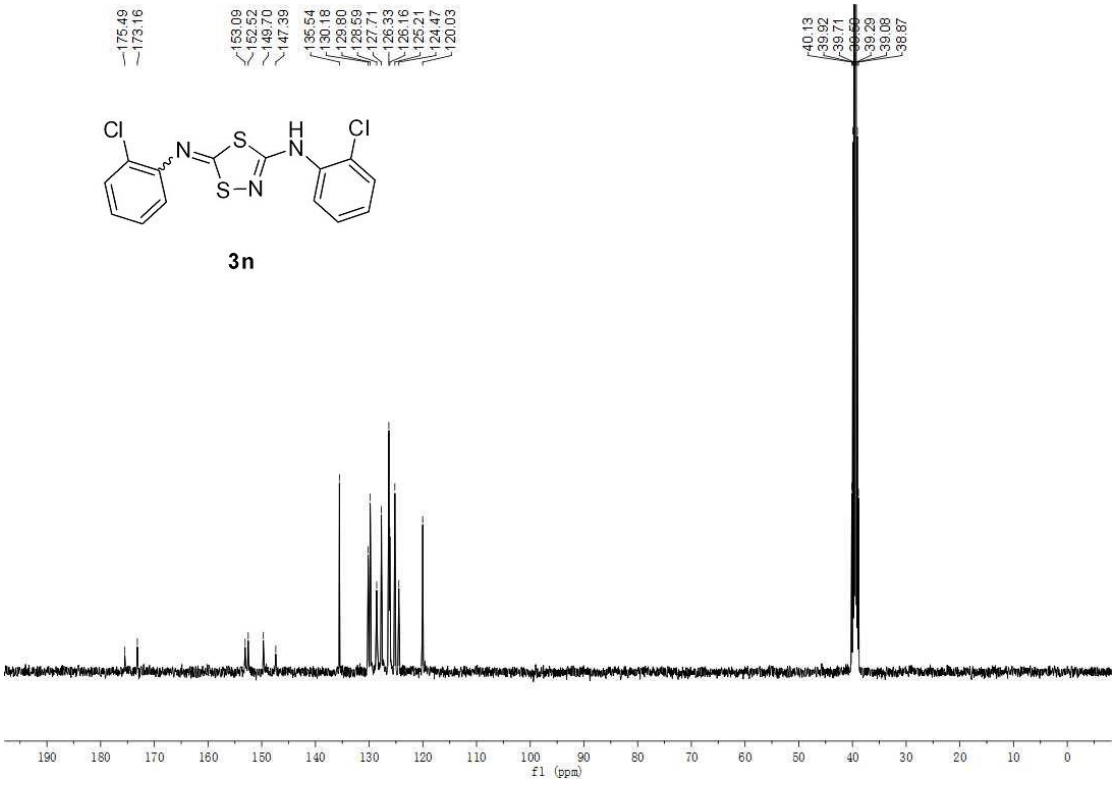

172.10
169.35
160.60
158.93
158.20
156.54
151.27
150.83
148.75
146.48
135.92
121.78
121.70
121.43
121.34
120.01
119.98
119.93
119.90
116.46
116.24
115.67
115.45
40.13
39.92
39.71
39.50
39.29
39.08
38.87
f1 (ppm)

3m

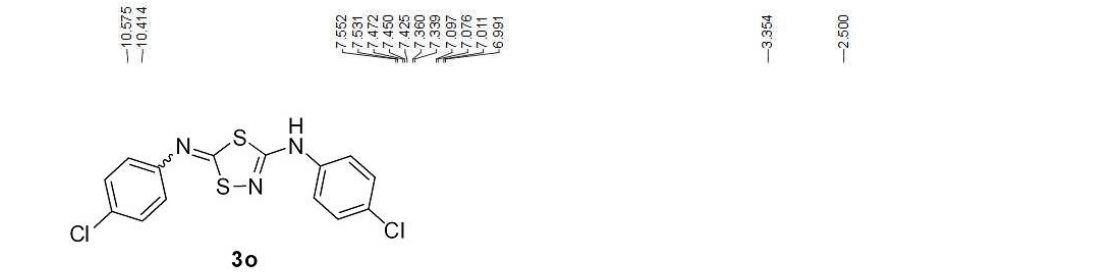

10.038
9.843
7.841
7.824
7.821
7.511
7.490
7.347
7.328
7.311
7.308
7.199
7.180
7.163
7.161
7.066
3.365
3.358
2.500
Cl
N
S
S–N
H
N
Cl

3n

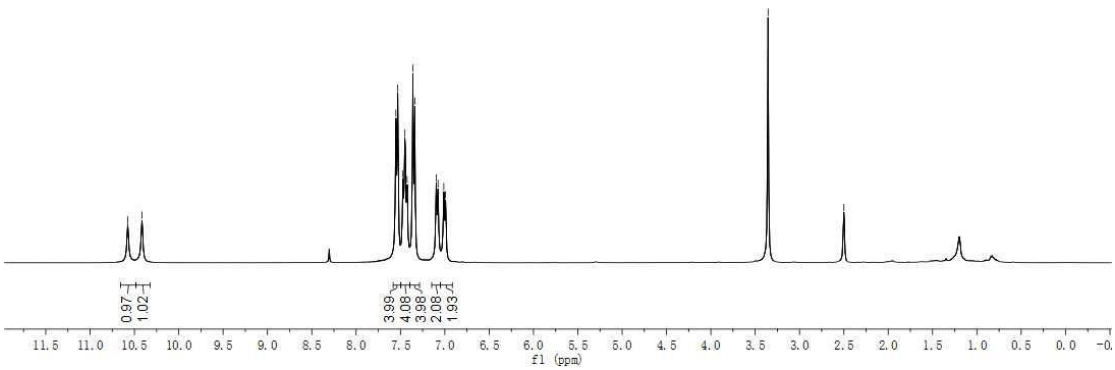

0.87
1.08
2.00
4.11
4.07
4.98
1.09
f1 (ppm)

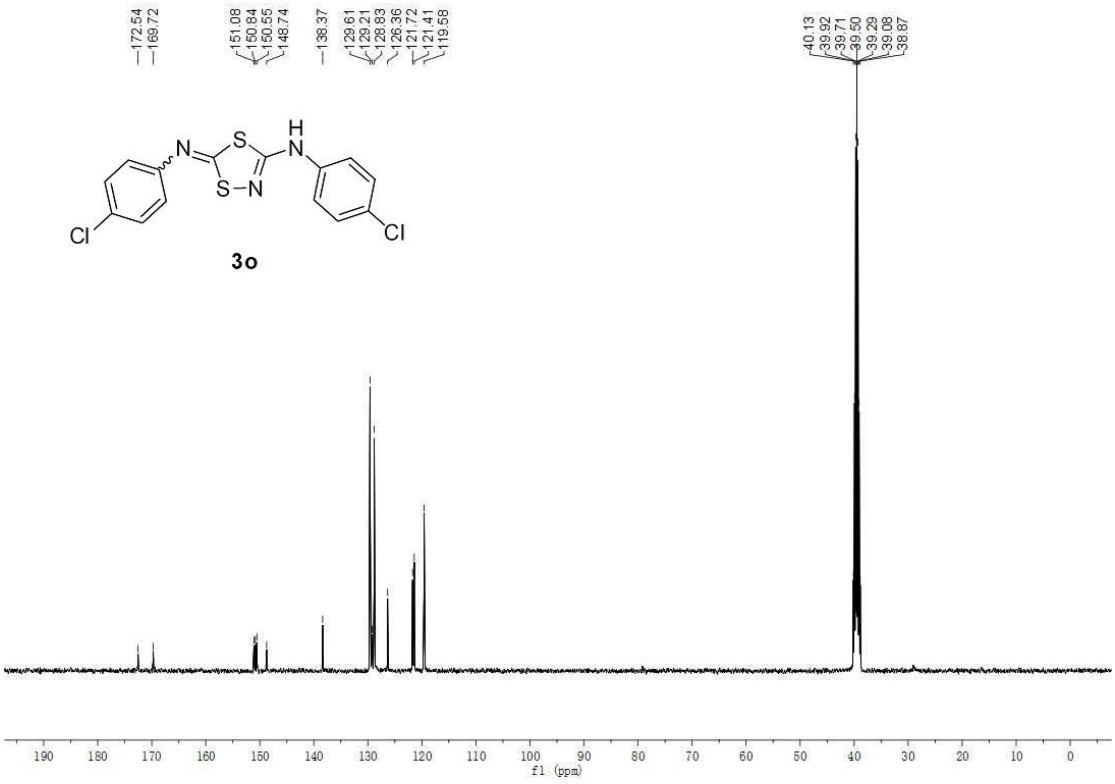

175.49
173.16
153.09
152.52
149.70
147.39
135.54
130.18
129.80
128.59
127.71
126.33
126.16
125.21
124.47
120.03
40.13
39.92
39.71
39.50
39.29
39.08
38.87
Cl
N
S
S–N
H
N
Cl
f1 (ppm)

3n

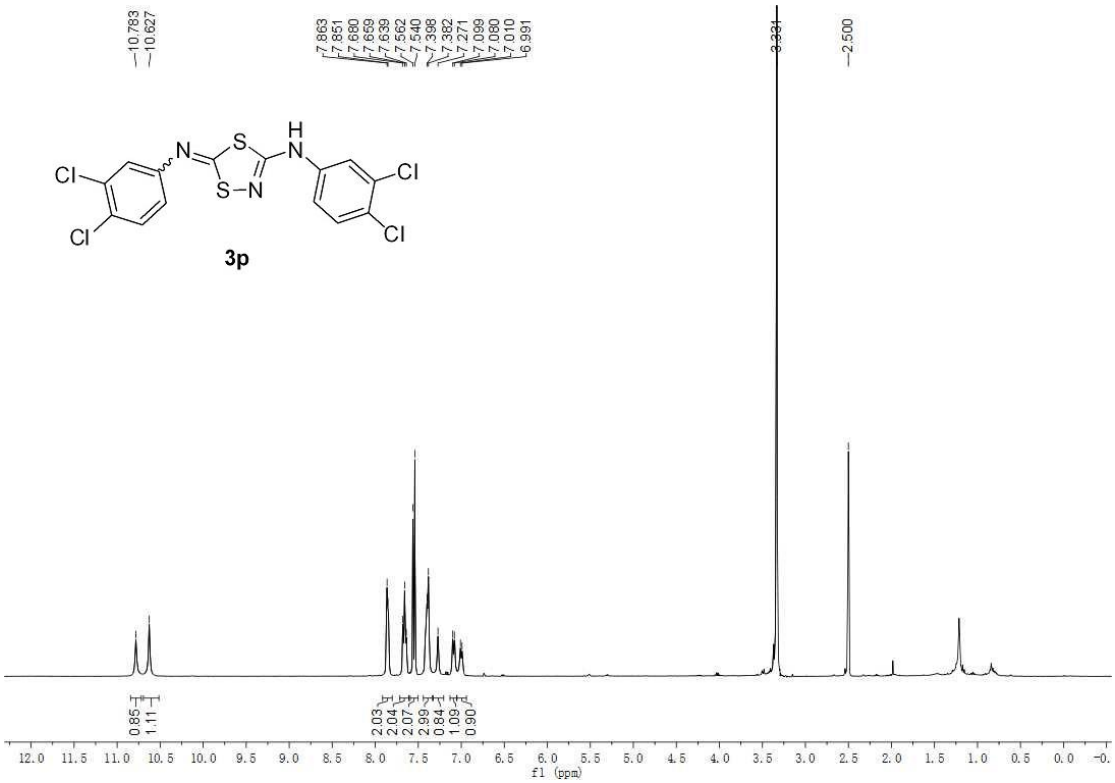

10.575
10.414
7.552
7.531
7.472
7.450
7.425
7.360
7.339
7.097
7.076
7.011
6.991
3.354
2.500
N
S
H
N
S
N
Cl
Cl

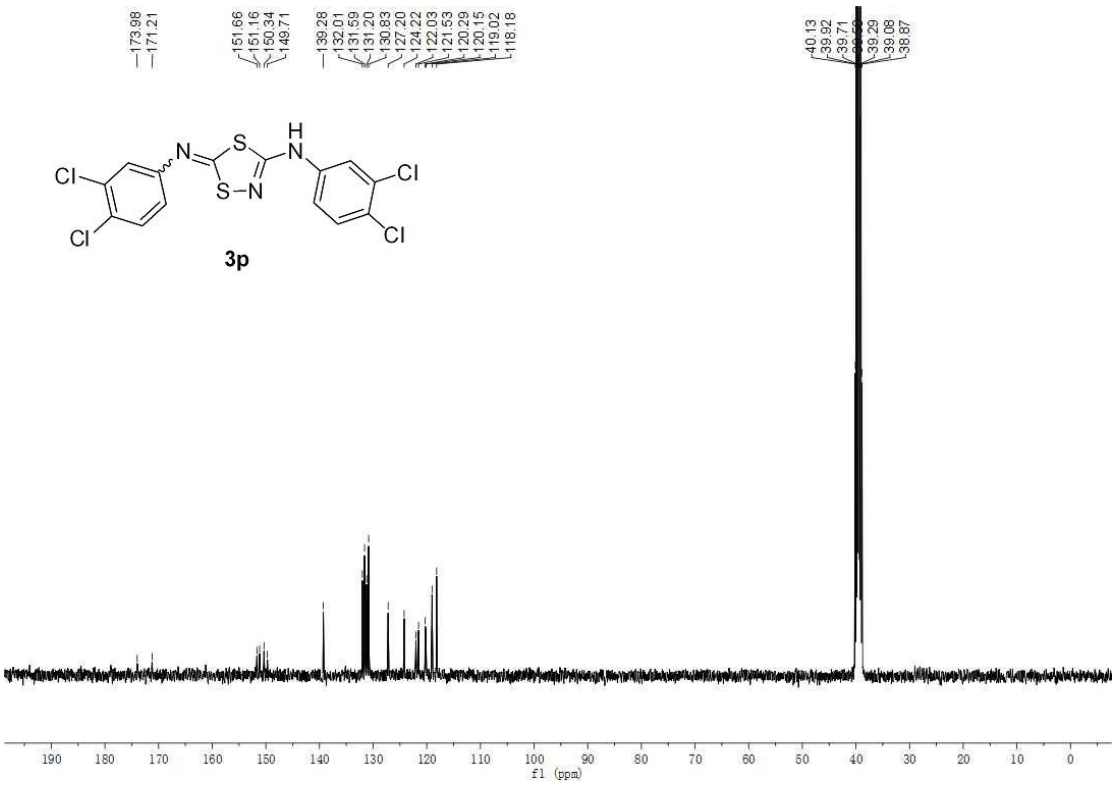
3o

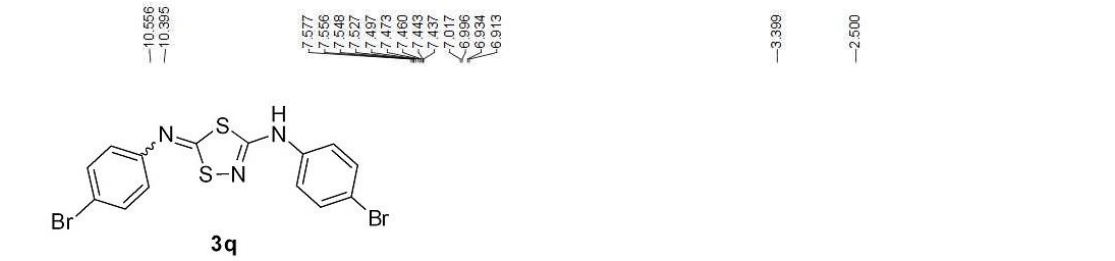

0.97
1.02
3.99
4.08
3.98
2.08
1.93
f1 (ppm)


172.54
169.72
151.08
150.84
150.55
148.74
138.37
129.61
129.21
128.83
126.36
121.72
121.41
119.58
40.13
39.92
39.71
39.50
39.29
39.08
38.87
N
S
H
N
S
N
Cl
Cl
f1 (ppm)

3o


10.783
10.627
7.863
7.851
7.680
7.659
7.639
7.562
7.540
7.398
7.382
7.271
7.099
7.080
7.010
6.991
3.331
2.500
0.85
1.11
2.03
2.04
2.07
2.99
0.84
1.09
0.90
f1 (ppm)
3p


173.98
171.21
151.66
151.16
150.34
149.71
139.28
132.01
131.59
131.20
130.83
127.20
124.22
122.03
121.53
120.29
120.15
119.02
118.18
40.13
39.92
39.71
39.50
39.29
39.08
38.87
f1 (ppm)
3p


10.556
10.395
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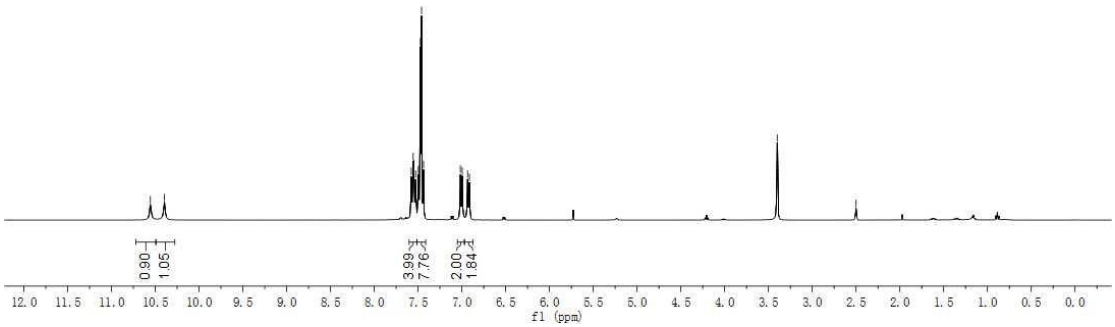
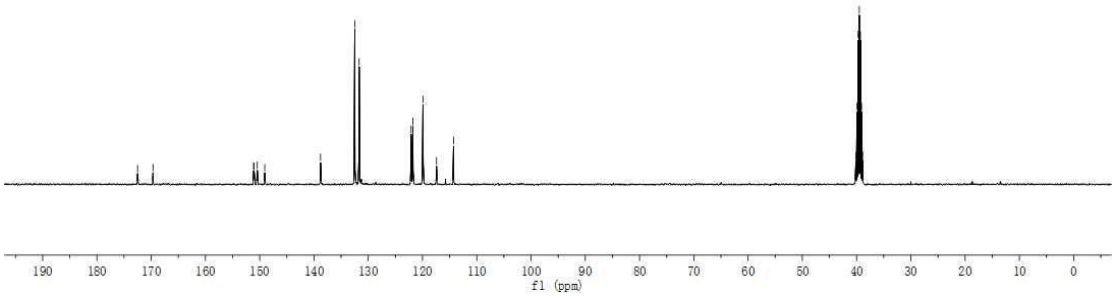
7.556
7.548
7.527
7.497
7.473
7.460
7.443
7.437
7.017
6.996
6.934
6.913
3.399
2.500
N
S
H
N
S–N
Br
Br

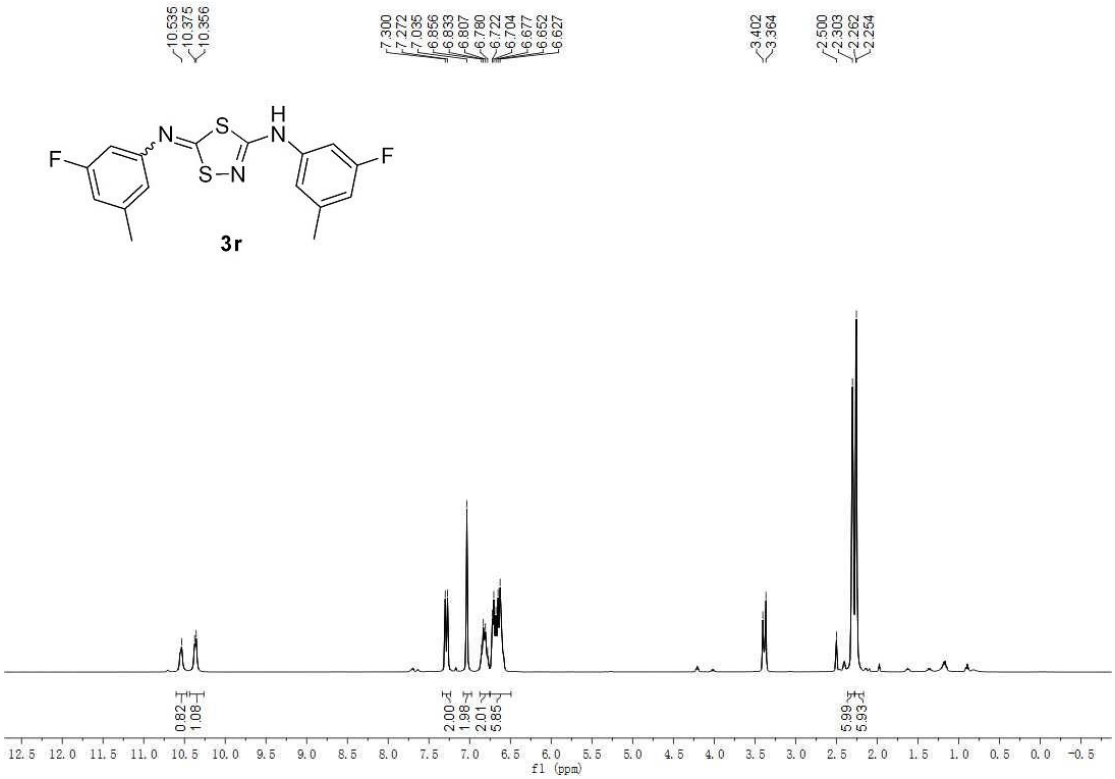
3q

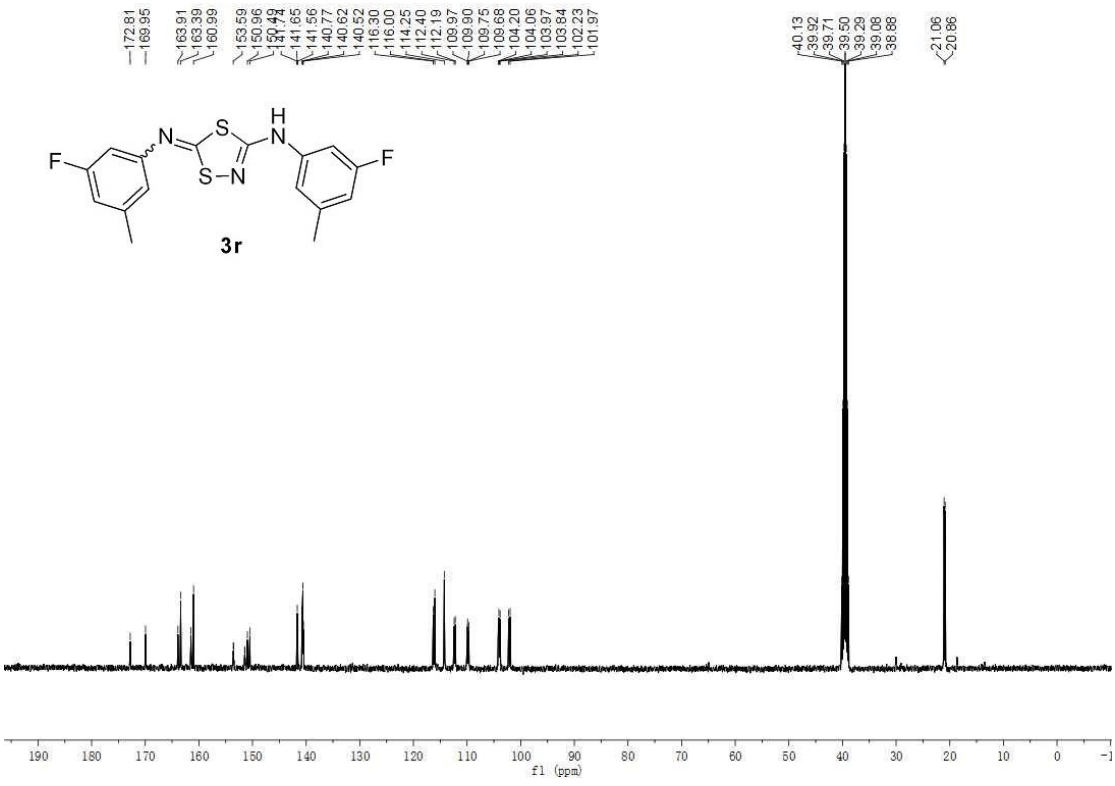

0.90
1.05
3.99
7.76
2.00
1.84
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


172.50
169.66
151.14
151.01
150.45
149.07
138.79
132.48
131.67
122.10
121.77
119.91
117.41
114.28
40.13
39.92
39.71
39.50
39.29
39.08
38.87
N
S
H
N
S–N
Br
Br

3q


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.535
10.375
10.356
7.300
7.272
7.035
6.856
6.833
6.807
6.780
6.722
6.704
6.677
6.652
6.627
3.402
3.364
2.500
2.303
2.262
2.254
F
N
S
S–N
H
N
F
3r
0.82
1.08
2.00
1.98
2.01
5.85
5.99
5.93
f1 (ppm)


172.81
169.95
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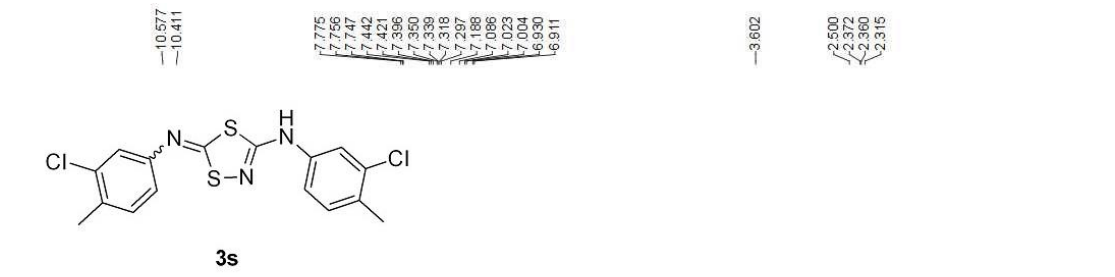
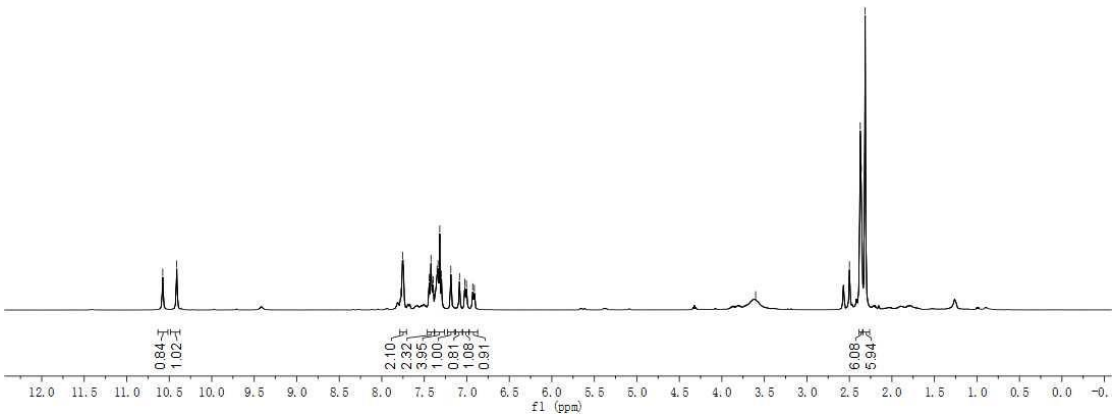
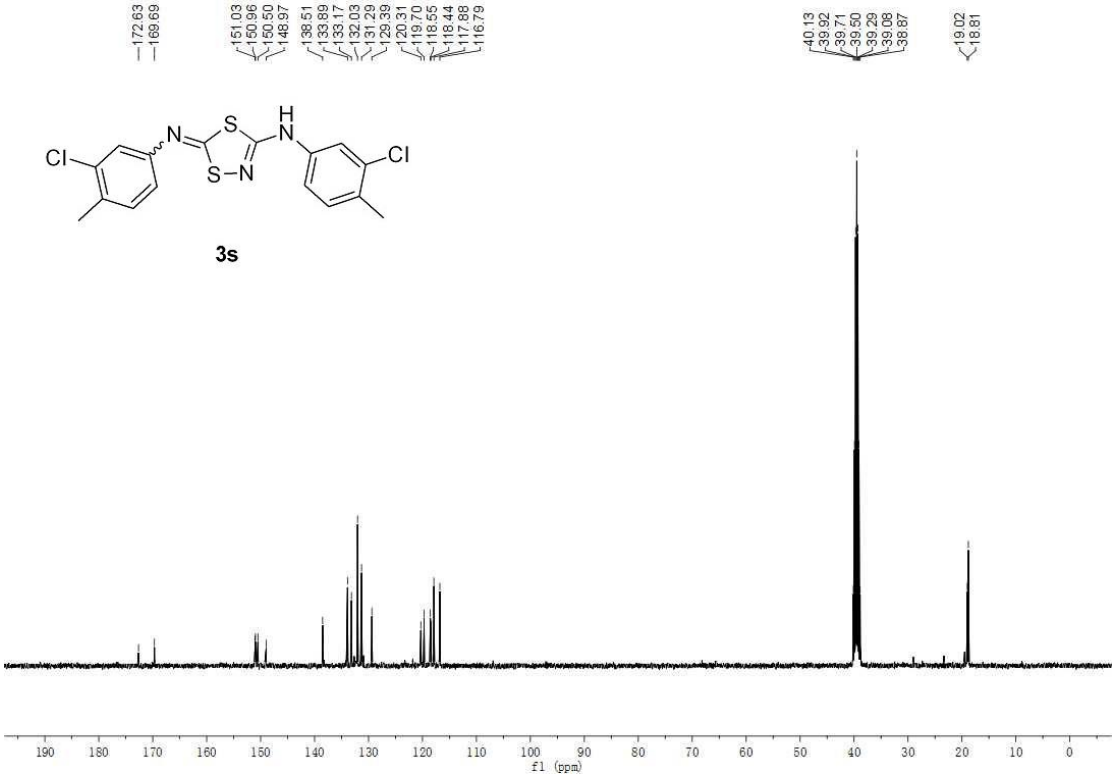
163.39
160.99
153.59
150.96
141.65
141.56
140.77
140.62
140.52
116.30
116.00
114.25
112.40
112.19
109.97
109.90
109.75
109.68
104.20
104.06
103.97
103.84
102.23
101.97
40.13
39.92
39.71
39.50
39.29
39.08
38.88
21.06
20.86
F
N
S
S–N
H
N
F
3r
f1 (ppm)

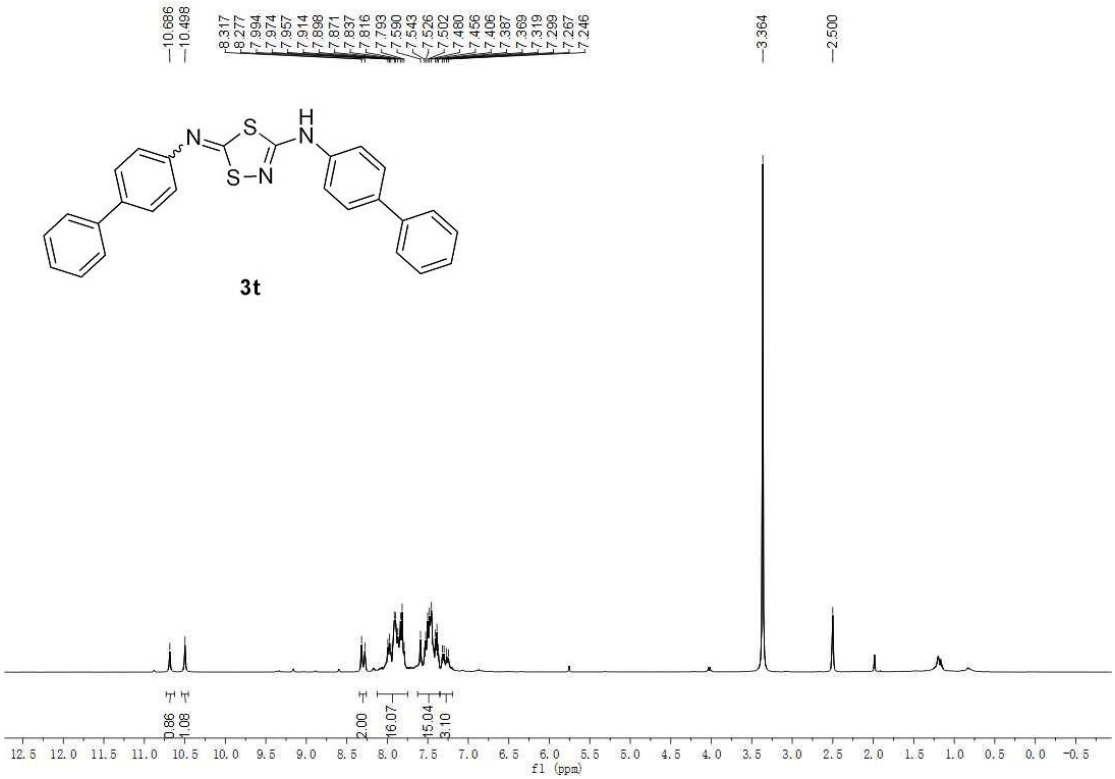

10.577
10.411
7.775
7.756
7.747
7.442
7.421
7.396
7.350
7.339
7.318
7.297
7.188
7.086
7.023
7.004
6.930
6.911
3.602
2.500
2.372
2.360
2.315
Cl
N
S
S
N
H
N
Cl

3s

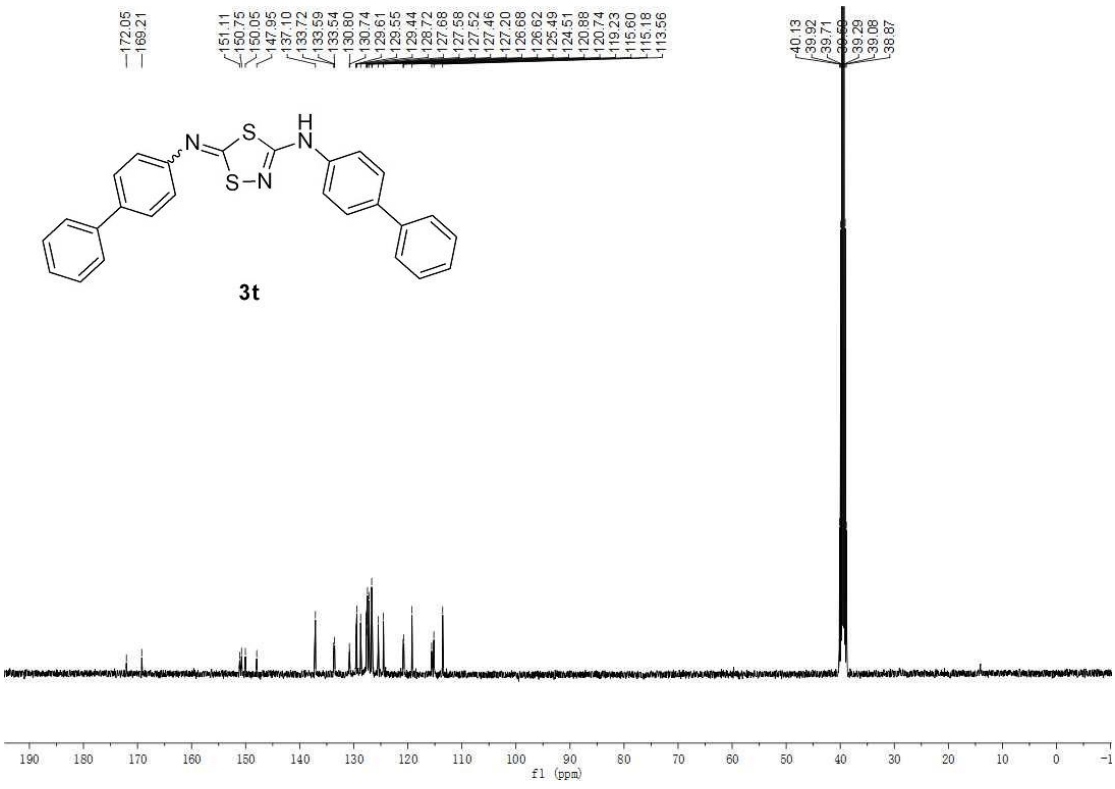

0.84
1.02
2.10
2.32
3.95
1.00
0.81
1.08
0.91
6.08
5.94
f1 (ppm)


172.63
169.69
151.03
150.96
150.50
148.97
138.51
133.89
133.17
132.03
131.29
129.39
120.31
119.70
118.55
118.44
117.88
116.79
40.13
39.92
39.71
39.50
39.29
39.08
38.87
19.02
18.81
Cl
N
S
S
N
H
N
Cl
f1 (ppm)

3s


10.686
10.498
8.317
8.277
7.994
7.974
7.957
7.914
7.898
7.871
7.837
7.816
7.793
7.590
7.543
7.526
7.502
7.480
7.456
7.406
7.387
7.369
7.319
7.299
7.267
7.246
3.364
2.500
0.86
1.08
2.00
16.07
15.04
3.10
f1 (ppm)

3t


172.05
169.21
151.11
150.75
150.05
147.95
137.10
133.72
133.59
133.54
130.80
130.74
129.61
129.55
129.44
128.72
127.68
127.58
127.52
127.46
127.20
126.68
126.62
125.49
124.51
120.88
120.74
119.23
115.60
115.18
113.56
40.13
39.92
39.71
39.50
39.29
39.08
38.87
f1 (ppm)

3t