Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Electrochemical oxidative synthesis of 1,3,4-thiadiazoles from isothiocyanates and hydrazones

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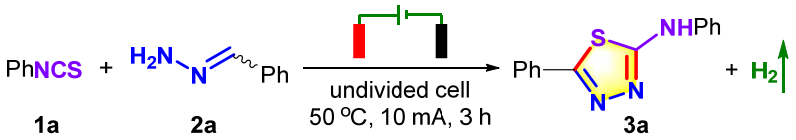
I. General considerations

Unless otherwise stated, commercially available chemicals were used without treatment. Solvents were degassed by bubbling Ar for 30 minutes before use. Reactions were monitored by Thin Layer Chromatography (TLC) using silica gel F254 plates. Products were purified by column chromatography over 300-400 mesh silica gel under a positive pressure of air. ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and DEPT NMR spectra were recorded at 25 °C on a Bruker Ascend^{TM} 400 spectrometer using TMS as internal standard. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II Focus spectrometer (ESI). UV-Vis measurements were carried out on a UV-2450 UV-Visible spectrophotometer (Shimadzu, Japan) or a UV-3600 Plus UV-VIS-NIR spectrophotometer (Shimadzu, Japan). Cyclic voltammetry studies were carried out on a CHI600E electrochemical workstation (Shanghai CH Instruments Co., China). Electrolysis was performed using a DJS-292B dual display potentiostat (Shanghai Xinrui Instruments Co., China, Figure S1).

Figure S1 Electrochemical setup

II. Optimization of reaction conditions

Table S1 Optimization of reaction conditions[a]



entry	anode	cathode	electrolyte	mediator	solvent	yield (%)
1	C cloth	Pt	nBu$_4$NBF$_4$	none	CH$_3$CN/H$_2$O[b]	trace
2	C cloth	Pt	nBu$_4$NBF$_4$	TEMPO	CH$_3$CN/H$_2$O[b]	trace
3	C cloth	Pt	nBu$_4$NBF$_4$	NHPI	CH$_3$CN/H$_2$O[b]	trace
4	C cloth	Pt	nBu$_4$NBF$_4$	Cp$_2$Fe	CH$_3$CN/H$_2$O[b]	31
5	C cloth	Pt	nBu$_4$NBF$_4$	TBAI	CH$_3$CN/H$_2$O[b]	0
6	C cloth	Pt	nBu$_4$NBF$_4$	TBAB	CH$_3$CN/H$_2$O[b]	21
7	C cloth	Pt	**nBu$_4$NBF$_4$**	**DDQ**	**CH$_3$CN/H$_2$O[b]**	56
8	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/HFIP[b]	43
9	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/TFE[b]	31
10	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/MeOH[b]	41
11	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/HOAc[b]	31
12	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/TFA[b]	23
13	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN	30
14	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	HFIP	16
15	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	TFE	31
16	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	MeOH	14
17	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	DCE/H$_2$O[b]	trace
18	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	PhCF$_3$/H$_2$O[b]	0
19	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	acetone/H$_2$O[b]	trace
20	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$NO$_2$/H$_2$O[b]	0
21	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	THF/H$_2$O[b]	19
22	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	DMF/H$_2$O[b]	52
23	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	DMA/H$_2$O[b]	35
24	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	DMSO/H$_2$O[b]	27
25	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	HFIP/H$_2$O[b]	12
26	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	TFE/H$_2$O[b]	30
27	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	MeOH/H$_2$O[b]	38
28	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[c]	34
29	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[d]	50
30	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[e]	47
31	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[f]	38
32	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[g]	38
33	C cloth	Pt	nBu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[h]	30

34	C cloth	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[i]	trace
35	C cloth	Pt	*n*Bu$_4$NBF$_4$	DDQ	MeOH/H$_2$O[d]	34
36	C cloth	Pt	*n*Bu$_4$NBF$_4$	DDQ	MeOH/H$_2$O[e]	34
37	C cloth	Pt	LiClO$_4$	DDQ	CH$_3$CN/H$_2$O[b]	51
38	C cloth	Pt	Et$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	50
39	C cloth	Pt	*n*Bu$_4$NPF$_6$	DDQ	CH$_3$CN/H$_2$O[b]	52
40	C cloth	Pt	*n*Bu$_4$NOAc	DDQ	CH$_3$CN/H$_2$O[b]	0
41	C cloth	Pt	*n*Bu$_4$NClO$_4$	DDQ	CH$_3$CN/H$_2$O[b]	44
42[j]	C cloth	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	20
43[k]	C cloth	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	0
44[l]	C cloth	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	0
45	Pt	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	29
46	graphite felt	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	47
47	**graphite rod**	**Pt**	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	59
48	graphite rod	stainless steel	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	46
49	graphite rod	Ni	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	44
50	graphite rod	Ni foam	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	50
51	graphite rod	Cu foam	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	37
52	graphite rod	C cloth	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	22
53	graphite rod	graphite felt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	44
54	graphite rod	graphite rod	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	56
55	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	50
56	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	45
57	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	54
58	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	13
59	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b,m]	58
60[n]	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	48
61[o]	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	40
62[p]	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	51
63	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ[q]	CH$_3$CN/H$_2$O[b]	49
64	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ[r]	CH$_3$CN/H$_2$O[b]	36
65	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ[s]	CH$_3$CN/H$_2$O[b]	35
66	graphite rod	Pt	none	DDQ	CH$_3$CN/H$_2$O[b]	36
67	graphite rod	Pt	*n*Bu$_4$NBF$_4$[t]	DDQ	CH$_3$CN/H$_2$O[b]	38
68	graphite rod	Pt	*n*Bu$_4$NBF$_4$[u]	DDQ	CH$_3$CN/H$_2$O[b]	58
69[v]	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	43
70[w]	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	61
71[x]	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	60
72[y]	**graphite rod**	**Pt**	***n*Bu$_4$NBF$_4$**	**DDQ**	**CH$_3$CN/H$_2$O[b]**	**62**
73[z]	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	56
74[aa]	graphite rod	Pt	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	54
75[ab]	-	-	*n*Bu$_4$NBF$_4$	DDQ	CH$_3$CN/H$_2$O[b]	0

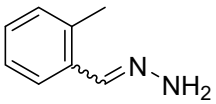
[a] Reaction conditions: Undivided cell, electrodes (15 mm × 15 mm), constant current electrolysis at 10 mA, **1a** (0.5 mmol), **2a** (0.75 mmol), mediator (0.1 mmol),

supporting electrolyte (0.5 mmol), solvents (12.0 mL), Ar, 50 °C, 3 h. [b] 9:1, v/v. [c] 15:1, v/v. [d] 12:1, v/v. [e] 7:1, v/v. [f] 4:1, v/v. [g] 2:1, v/v. [h] 1:1, v/v. [i] 1:2, v/v. [j] Trifluoroacetic acid (1.0 equiv) was added as an additive. [k] KOAc (1.0 equiv) was added as an additive. [l] K_2CO_3 (1.0 equiv) was added as an additive. [m] 6.0 mL. [n] 2.0 equiv of **2a** were used. [o] 1.2 equiv of **2a** were used. [p] The reaction was run with 0.5 mmol of **2a** and 0.75 mmol of **1a**. [q] 10 mol%. [r] 30 mol%. [s] 40 mol%. [t] 0.5 equiv. [u] 1.5 equiv. [v] The reaction was run at room temperature. [w] **The reaction was run at 35 °C**. [x] The reaction was run at 65 °C. [y] **The reaction time was 2.7 h**. [z] The reaction time was 3.5 h. [aa] The reaction was run under air atmosphere. [ab] No electricity.

III. Experimental details

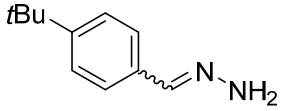
1. General procedure for the synthesis of hydrazone substrates 2[1]

A conical flask, equipped with a dropping funnel and a magnetic stirring bar, was charged with hydrazine hydrate (12.0 mmol, 1.2 equiv), then a solution of aldehyde (10.0 mmol) in methanol (25.0 mL) was added dropwise for 30 min. The mixture was stirred at room temperature for 1 h. After the aldehyde was consumed as indicated by TLC, methanol and the extra hydrazine were removed under reduced pressure at 25 °C. Water (30.0 mL) was added and the mixture was extracted with dichloromethane (3 × 20 mL). The combined extracts were washed with brine and dried with anhydrous sodium sulfate. Solvent was removed by rotary evaporation at 25 °C to provide the desired hydrazones **2**, which were used directly without further purification.

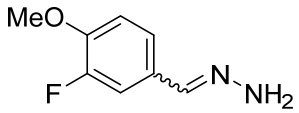


2p, (2-methylbenzylidene)hydrazine, yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (s, 1H), 7.98 (d, J = 7.4 Hz, 1H), 7.41 (ddd, J = 7.3, 7.3, 1.5 Hz, 1H), 7.31 (ddd, J = 7.6, 3.7, 3.7 Hz, 2H), 2.54 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 160.4, 139.0, 132.2, 131.6, 131.5, 127.7, 126.7, 19.8. HRMS (ESI-TOF) Calcd for $C_8H_{11}N_2^+$ ([M+H]$^+$) 135.0917. Found 135.0925.

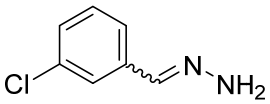
[1] D. Cao, P. Pan, H. Zeng and C.-J. Li, *Chem. Commun.*, 2019, **55**, 9323−9326.



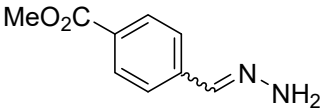
2q, (4-(*tert*-butyl)benzylidene)hydrazine, yellow solid: mp 199–200 °C. ^{1}H NMR (400 MHz, Pyridine-d_5) δ 8.92 (s, 1H), 8.00 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 1.24 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, Pyridine-d_5) δ 161.6, 154.6, 132.1, 128.6, 126.0, 34.8, 30.9. HRMS (ESI-TOF) Calcd for $C_{11}H_{17}N_2^+$ ([M+H]$^+$) 177.1386. Found 177.1389.



2r, (3-fluoro-4-methoxybenzylidene)hydrazine, yellow solid: mp 204–205 °C. ^{1}H NMR (400 MHz, Pyridine-d_5) δ 8.80 (d, J = 1.4 Hz, 1H), 7.94 (dd, J = 12.1, 2.0 Hz, 1H), 7.63 (ddd, J = 8.5, 1.5, 1.5 Hz, 1H), 7.06 (dd, J = 8.5, 8.5 Hz, 1H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, Pyridine-d_5) δ 160.5 (d, J = 2.7 Hz), 152.5 (d, J = 246.2 Hz), 150.4 (d, J = 10.9 Hz), 127.8 (d, J = 6.6 Hz), 126.5 (d, J = 3.1 Hz), 114.7 (d, J = 19.0 Hz), 113.5 (d, J = 2.0 Hz), 55.9. ^{19}F NMR (376 MHz, Pyridine-d_5) δ -134.27 – -134.32 (m, 1F). HRMS (ESI-TOF) Calcd for $C_8H_{10}FN_2O^+$ ([M+H]$^+$) 169.0772. Found 169.0770.



2v, (3-chlorobenzylidene)hydrazine, yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (s, 1H), 7.94 (dd, J = 1.8, 1.8 Hz, 1H), 7.86 (ddd, J = 7.6, 1.4, 1.4 Hz, 1H), 7.61 (ddd, J = 8.0, 2.2, 1.3 Hz, 1H), 7.56 (dd, J = 7.8, 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 161.2, 136.2, 134.2, 131.7, 131.4, 128.3, 127.4. HRMS (ESI-TOF) Calcd for $C_7H_8ClN_2^+$ ([M+H]$^+$) 155.0371. Found 155.0359.



2ab, methyl 4-(hydrazonomethyl)benzoate, yellow solid: mp 191–192 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.23 (s, 2H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.5, 141.7, 136.4, 130.0, 128.1, 125.4, 52.5. HRMS (ESI-TOF) Calcd for $C_9H_{11}N_2O_2^+$ ([M+H]$^+$) 179.0815.

Found 179.0814.

2. General procedure for the electrosynthesis of 2-amino-1,3,4-thiadiazoles 3

A custom-made undivided cell, equipped with a magnetic stirring bar, a graphite rod anode (Ø 6 mm) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged under argon sequentially with hydrazone **2** (1.5 equiv, 0.75 mmol), electrolyte *n*Bu_4NBF_4 (1.0 equiv, 0.5 mmol), aryl isothiocyanate **1** (0.5 mmol), degassed CH_3CN (8.8 mL), and water (1.2 mL), followed by the addition of a solution of DDQ (20 mol%, 0.1 mmol) in CH_3CN (2.0 mL). The mixture was electrolyzed with stirring using a constant current of 10.0 mA at 35 °C (oil bath) for 2.7 h (2 F/mol); then it was quenched with water (60.0 mL) and extracted with CH_2Cl_2 (50.0 mL) four times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate–dichloromethane–triethylamine = 60:5:12:1) to afford 2-amino-1,3,4-thiadiazoles **3**.

3. Procedure for the gram-scale synthesis

A 100-mL two-necked flask, equipped with a magnetic stirring bar, a graphite rod anode (Ø 6 mm) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, carefully polished until shining), was charged under argon sequentially with benzaldehyde hydrazone **2a** (1.5 equiv, 12.0 mmol, 1.44 g), electrolyte *n*Bu_4NBF_4 (1.0 equiv, 8.0 mmol, 2.63 g), phenyl isothiocyanate **1a** (8.0 mmol, 0.96 mL), degassed CH_3CN (62.0 mL), and water (8.0 mL), followed by the addition of a solution of DDQ (20 mol%, 1.6 mmol, 0.36 g) in CH_3CN (10.0 mL). The mixture was electrolyzed with stirring using a constant current of 10.0 mA at 35 °C (oil bath) for 44 h (2 F/mol, Figure S2); then it was quenched with water (200.0 mL) and extracted with CH_2Cl_2 (150.0 mL) four times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate–dichloromethane–triethylamine = 60:5:12:1) to afford the 2-amino-1,3,4-thiadiazole **3a**.

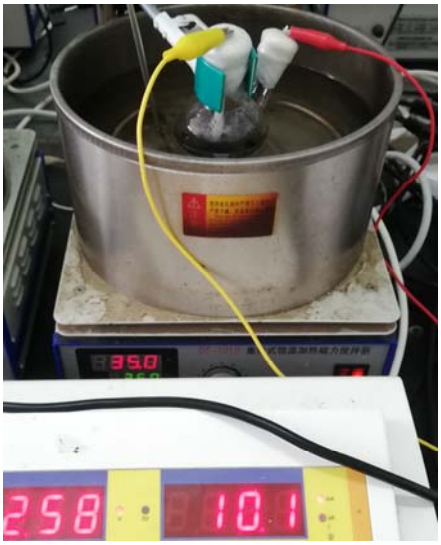
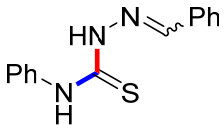


Figure S2 Setup for the gram-scale synthesis

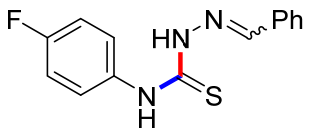
4. General procedure for the synthesis of thiosemicarbazides 4a,j

A custom-made undivided cell, equipped with a magnetic stirring bar, was charged sequentially with hydrazone **2** (1.5 equiv, 0.75 mmol), degassed CH_3CN (10.8 mL), and water (1.2 mL), followed by the addition of aryl isothiocyanate **1** (0.5 mmol). The mixture was stirred at 35 °C (oil bath) for 2.0 h; then it was quenched with water (60.0 mL) and extracted with CH_2Cl_2 (50.0 mL) four times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate–dichloromethane–triethylamine = 60:5:12:1) to afford the thiosemicarbazides **4a** and **4j**.



4a, 2-benzylidene-*N*-phenylhydrazine-1-carbothioamide, [2] white solid: mp 190–191 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.75 (brs, 1H), 10.11 (s, 1H), 8.14 (s, 1H), 7.89 – 7.86 (m, 2H), 7.52 (d, J = 7.1 Hz, 2H), 7.42 (p, J = 3.5 Hz, 3H), 7.37 (t, J = 7.8 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 176.4, 143.7, 139.3, 134.2, 130.7, 129.2, 128.6, 128.0, 126.4, 126.0. HRMS (ESI-TOF) Calcd for $C_{14}H_{14}N_3S^+$ ([M+H]$^+$) 256.0903. Found 256.0905.

[2] M. Bonizzoni, L. Fabbrizzi, A. Taglietti and F. Tiengo, *Eur. J. Org. Chem.*, 2006, 3567–3574.



4j, 2-benzylidene-*N*-(4-fluorophenyl)hydrazine-1-carbothioamide, white solid: mp 190–191 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.89 (s, 1H), 10.14 (s, 1H), 8.20 (s, 1H), 7.92 (dd, J = 6.6, 2.9 Hz, 2H), 7.58 (dd, J = 8.8, 5.1 Hz, 2H), 7.45 – 7.42 (m, 3H), 7.21 (dd, J = 8.8, 8.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 176.9, 160.15 (d, J = 242.1 Hz), 143.5, 135.89 (d, J = 2.9 Hz), 134.5, 130.5, 129.1, 128.64 (d, J = 8.3 Hz), 128.1, 115.17 (d, J = 22.4 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -116.98 – -117.05 (m, 1F). HRMS (ESI-TOF) Calcd for $C_{14}H_{13}FN_3S^+$ ([M+H]$^+$) 274.0809. Found 274.0816.

5. Procedures for stoichiometric DDQ-mediated syntheses

From **1a** and **2a**: A custom-made undivided cell, equipped with a magnetic stirring bar, was charged under argon sequentially with hydrazone **2a** (1.5 equiv, 0.75 mmol, 90 mg), isothiocyanate **1a** (0.5 mmol, 68 mg), degassed CH_3CN (8.8 mL), and water (1.2 mL), followed by the addition of a solution of DDQ (1.2 equiv, 136 mg) in CH_3CN (2.0 mL). The mixture was stirred at 35 °C (oil bath) for 2.7 h; then it was quenched with saturated aqueous $Na_2S_2O_3$ (2.0 mL) and saturated aqueous $NaHCO_3$ (60.0 mL), and extracted with CH_2Cl_2 (50.0 mL) four times. No 1,3,4-thiadiazole product **3a** was detected by TLC.

From **4a**: A custom-made undivided cell, equipped with a magnetic stirring bar, was charged under argon sequentially with thiosemicarbazide **4a** (0.5 mmol, 128 mg) and DDQ (1.2 equiv, 136 mg), followed by the addition of degassed CH_3CN (10.8 mL) and water (1.2 mL). The mixture was stirred at 35 °C (oil bath) for 2.7 h; then it was quenched with saturated aqueous $Na_2S_2O_3$ (2.0 mL) and saturated aqueous $NaHCO_3$ (60.0 mL), and extracted with CH_2Cl_2 (50.0 mL) four times. The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel (petroleum ether–ethyl acetate–dichloromethane–triethylamine = 60:5:12:1) to afford the 2-amino-1,3,4-thiadiazole **3a**.

6. General procedure for quenching experiments

A custom-made undivided cell, equipped with a magnetic stirring bar, a graphite rod anode (Ø 6 mm) and a platinum plate cathode (15 mm × 15 mm × 0.3 mm, carefully

polished until shining), was charged under argon sequentially with 2-benzylidene-*N*-(4-fluorophenyl)hydrazine-1-carbothioamide **4j** (0.5 mmol, 137 mg), electrolyte *n*Bu$_4$NBF$_4$ (1.0 equiv, 0.5 mmol), a quencher (2.0 equiv, 1.0 mmol), degassed CH$_3$CN (8.8 mL), and water (1.2 mL), followed by the addition of a solution of DDQ (20 mol%, 0.1 mmol) in CH$_3$CN (2.0 mL). The mixture was electrolyzed with stirring using a constant current of 10.0 mA at 35 °C (oil bath) for 2.7 h (2 F/mol), and the yield of product **3j** formed was determined by ^{19}F NMR analysis based on a 4,4'-difluoro-1,1'-biphenyl internal standard.

IV. Spectroscopic investigations and DFT caclulations

1. Cyclic voltammetry studies

General procedure: Cyclic voltammetries were performed in a three-electrode cell at room temperature. The working electrode was a platinum disk electrode, and the counter electrode was a platinum wire. The reference was an Ag/AgCl electrode submerged in a saturated aqueous KCl solution, and separated from reactions by a salt bridge. 10 mL of CH$_3$CN/H$_2$O (9:1, v/v) or CH$_3$CN solution containing 1.0 mmol *n*Bu$_4$NBF$_4$ was poured into the electrochemical cell. The scan rate was 0.05 V/s, ranging from 0 V to 1.8 V.

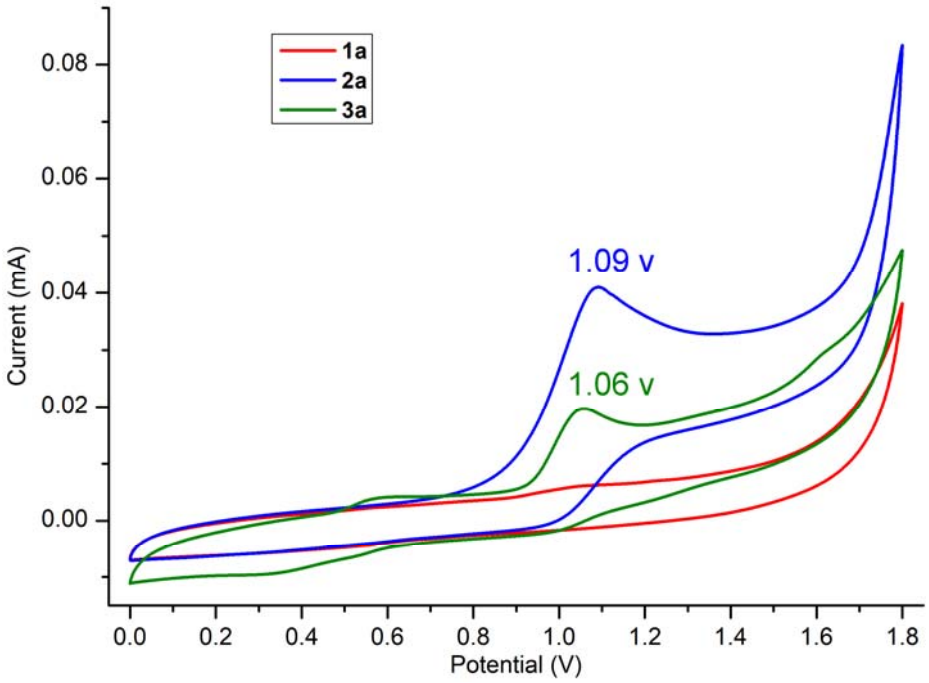


Figure S3 Cyclic voltammograms of **1a**, **2a** and **3a** (10^{-3} M in CH$_3$CN/H$_2$O (9:1, v/v))

No obvious oxidation wave was observed in the cyclic voltammogram of intermediate **4a** in aqueous CH_3CN in the region of 0.0–1.8 V vs. Ag/AgCl (Figure S4).

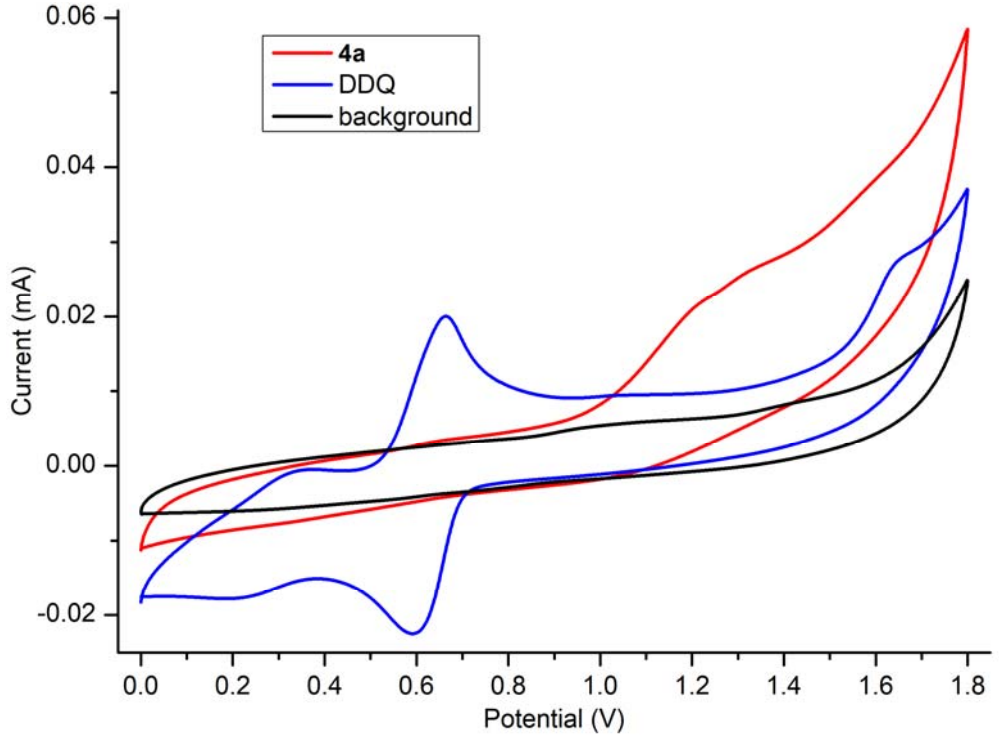


Figure S4 Cyclic voltammograms of **4a** and DDQ (10^{-3} M in CH_3CN/H_2O (9:1, v/v))

Upon mixed with DDQ, the peak current diminished and the potential increased. Furthermore, the oxidation wave of DDQ disappeared (Figure S5).

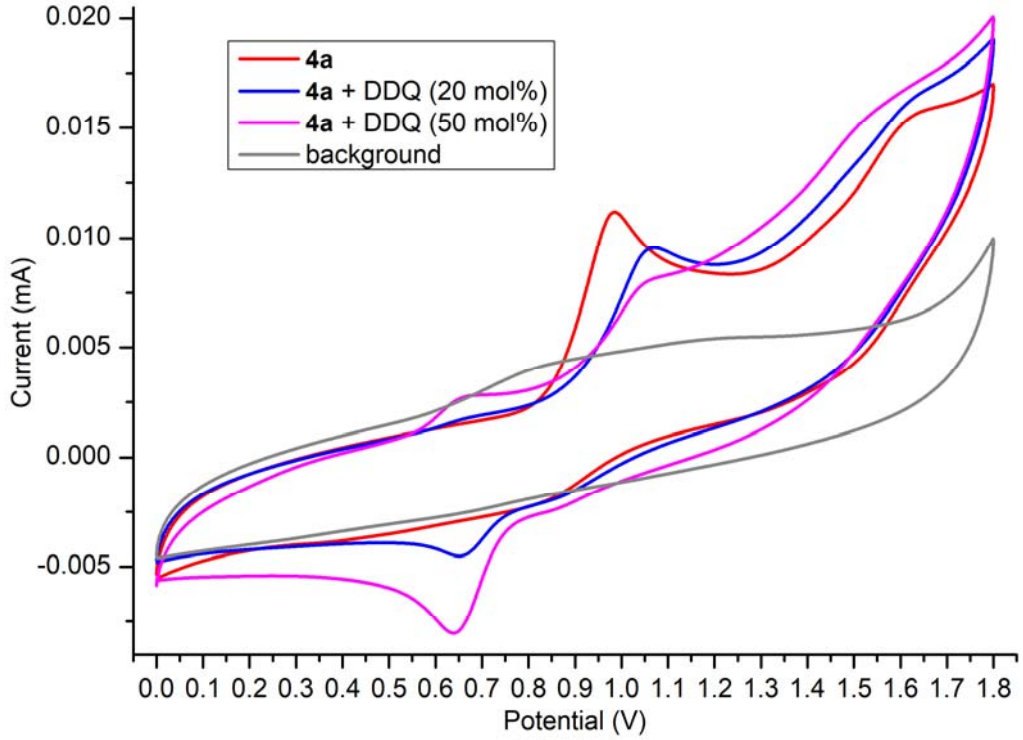


Figure S5 Cyclic voltammograms of **4a** (10^{-3} M **in CH_3CN**) and mixtures of **4a** (10^{-3} M **in CH_3CN**) and DDQ

2. UV-Vis spectroscopic measurements

The following UV-Vis absorption spectra were collected on a UV-2450 UV-Visible spectrophotometer (Shimadzu, Japan). A significant bathochromic shift was observed.

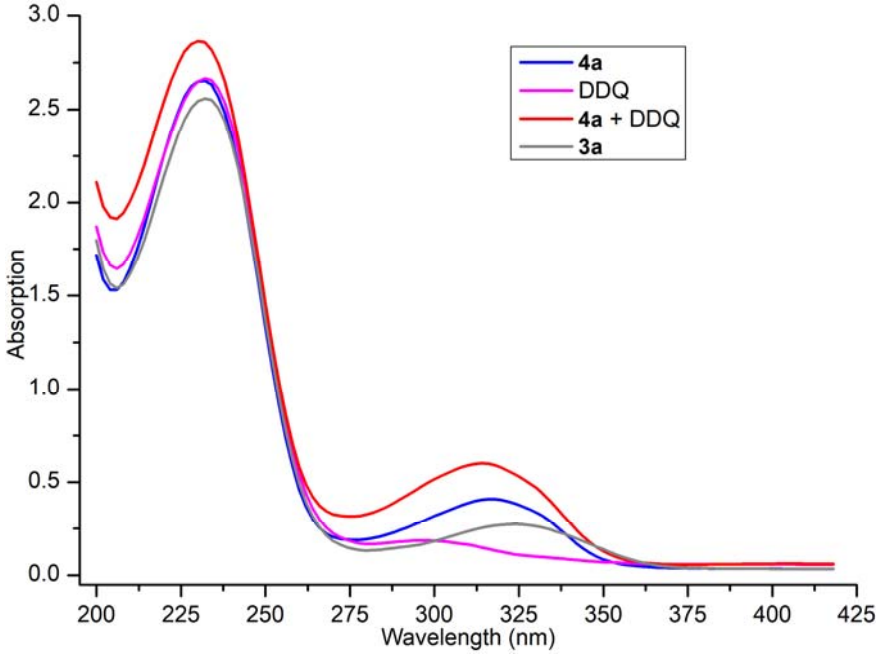


Figure S6 UV−vis spectra of **4a**, DDQ, **3a** and an equimolar mixture of **4a** and DDQ (**10^{-5} M** in CH_3CN/H_2O (9:1, v/v))

The following UV-Vis absorption spectra were collected on a UV-3600 Plus UV-VIS-NIR spectrophotometer (Shimadzu, Japan). A significant bathochromic shift was observed.

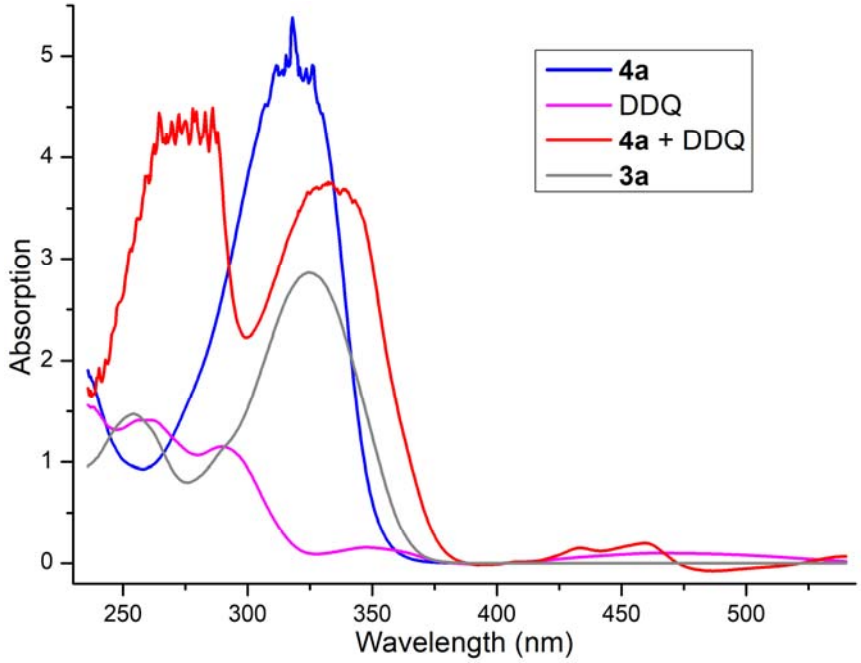
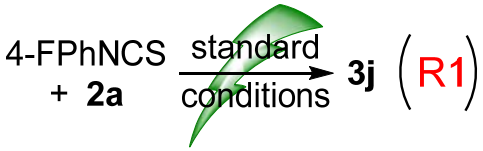


Figure S7 UV−vis spectra of **4a**, DDQ, **3a** and an equimolar mixture of **4a** and DDQ (**10^{-4} M** in CH_3CN/H_2O (9:1, v/v))

3. Reaction kinetic profiles

4,4'-Difluoro-1,1'-biphenyl (1 equiv) was added as an internal standard to the reaction mixture before electrolysis. 0.1 mL of the crude reaction solution was taken out each time via a syringe and was subjected to ^{19}F NMR analysis.

Table S2 Kinetic profiles of reaction R1



time (h)	yield of **3j** (%)	yield of **4j** (%)	yield of 4-FPhNCS (%)
0	0 (not determined)	0 (not determined)	100 (not determined)
0.5	13.4	75.9	10
1	27.7	60.7	-
1.5	47.3	47.3	-
2	68.8	25.9	-
2.5	91.3	8.9	-
2.7	95.5	0	-
3	83.0	-	-
3.5	63.4	-	-
4	36.6	-	-

Table S3 Kinetic profiles of reaction R2

time (h)	yield of **3j** (%)	yield of **4j** (%)
0	0 (not determined)	100 (not determined)
0.5	32.7	67.2
1	48.2	50.0
1.5	64.3	33.0
2	80.5	19.5
2.5	94.1	5.9
2.7	96.8	3.2
3	93.7	0
3.5	89.7	-
4	82.5	-

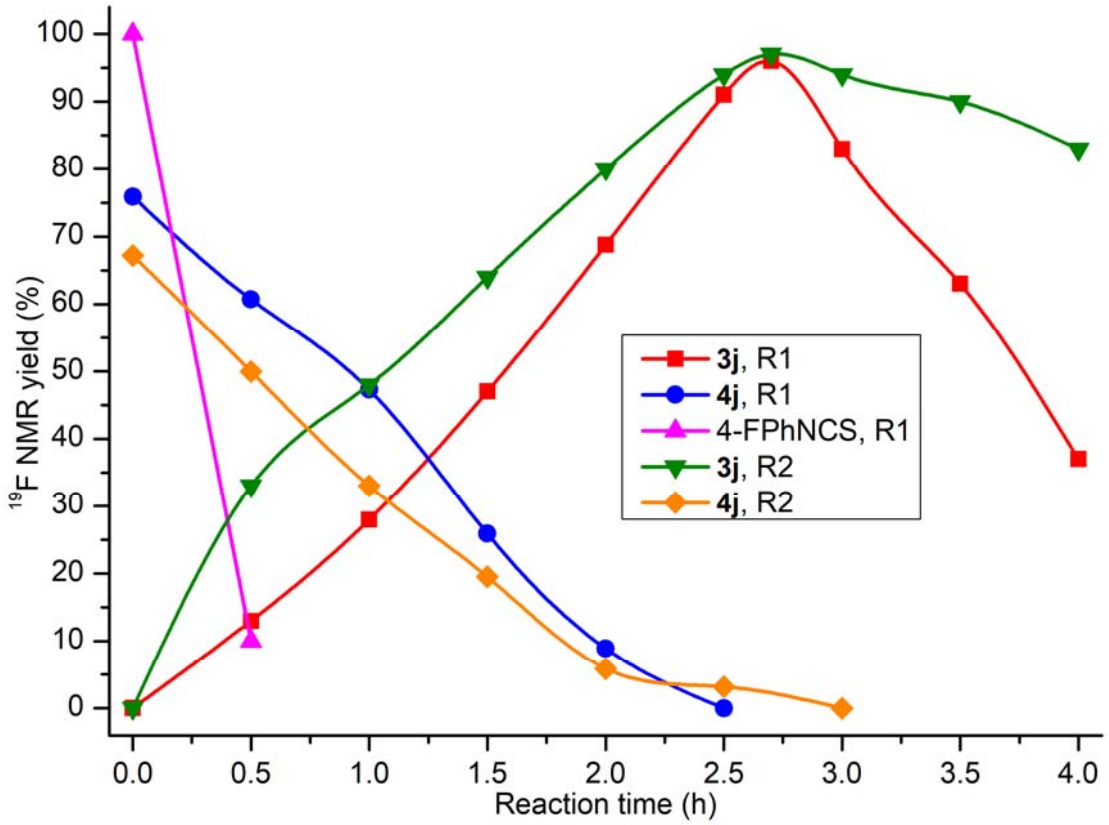


Figure S8 Reaction kinetic profiles

4. Hydrogen detection tests

The hydrogen detection tests were conducted with a H_2 detector (XLA-BX-H2, Figure S9), which was connected with a model reaction under standard conditions by a syringe with pumping off. The detector readings were recorded (Table S4), which reached 910 ppm within 7 min.

Table S4 Readings of the H_2 detector

time (min)	1	2	3	4	5	6	7
concentration (ppm)	610	675	710	765	813	854	910

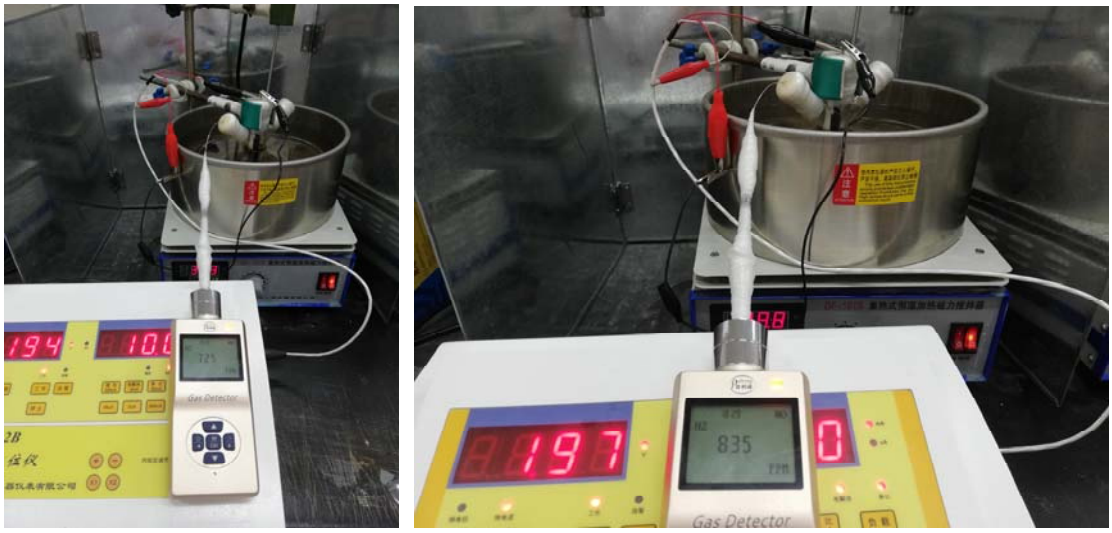


Figure S9 Setup for hydrogen detection tests

5. Electricity on-off experiments

4,4'-Difluoro-1,1'-biphenyl (1 equiv) was added as an internal standard to the reaction mixture before electrolysis. 0.1 mL of the crude reaction solution was taken out each time via a syringe and was subjected to ^{19}F NMR analysis.

Table S5 Electricity on-off experiments using **4j** as the starting material

time (min)	40	80	120	160	200	240
yield (%)	37.5	36.6	58.9	58.9	83.1	83.0

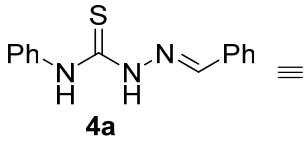
6. DFT caclulations

All calculations were performed using the Gaussian 16 package.[3] Geometries were optimised and harmonic frequencies were performed at the M062X/6-31g(d) level.[4] The solvation effects on the structures and molecular properties were accounted using

[3] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[4] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

the integral-equation-formalism polarizable continuum model (IEF-PCM),[5] and the dielectric constant for 90% acetonitrile/water solvent, ε = 39.95473, were used for all calculations. Harmonic vibration frequencies and the intrinsic reaction coordinates (IRC)[6,7] were computed at the same level (IEF-PCM/M062X/6-31g(d)) to characterize the stationary points and the reaction path, respectively.



4a

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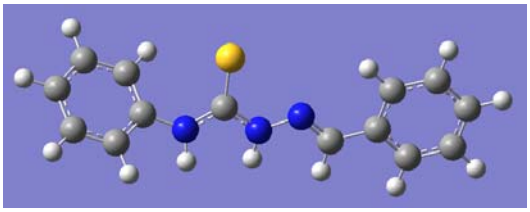

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C	5.29396100	0.87231200	0.86760500
H	3.26525500	1.06947200	1.57784000

[5] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.
[6] C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523–5527.
[7] C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154–2161.

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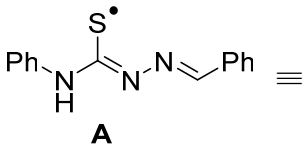
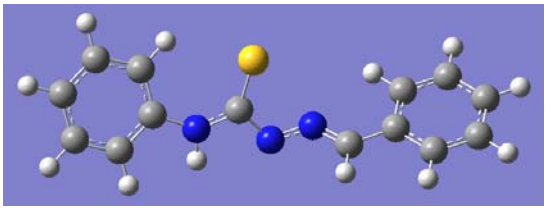


A ≡ 

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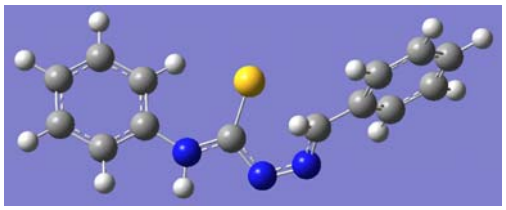
TS1 ≡ 

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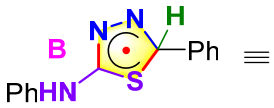

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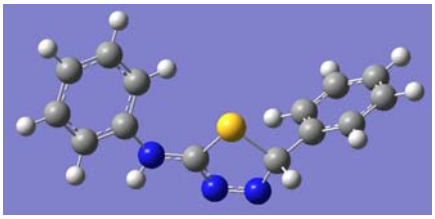

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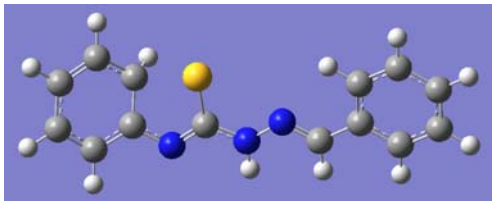
TS2 ≡ 

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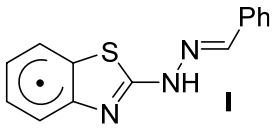
C	5.50629900	-0.31176400	-0.78326700
C	5.42676700	1.05138600	-0.40152700
H	4.49246200	-2.22231100	-0.82507800
H	6.36848400	-0.66258000	-1.33994300
H	6.24325300	1.72040000	-0.65457400
N	2.18592800	-1.47029600	0.28573000
S	1.29754400	1.05919200	0.07091800
C	1.14070400	-0.69221300	0.23604300
H	-0.15167100	-2.26454200	0.29968700
C	-2.33441800	-1.11033200	0.11229000
H	-2.38852500	-2.20247600	0.17581100
C	-3.60027500	-0.37991200	-0.01019500
C	-3.63926200	1.01936000	-0.09091800

C	-4.79678000	-1.10315000	-0.04862100
C	-4.85678300	1.67608900	-0.20813400
H	-2.70918900	1.57801600	-0.06036700
C	-6.01632000	-0.44138500	-0.16598300
H	-4.76915700	-2.18790700	0.01321200
C	-6.04877200	0.94850800	-0.24604200
H	-4.88050200	2.75951600	-0.27027000
H	-6.93920200	-1.01170900	-0.19504300
H	-6.99835300	1.46622900	-0.33766700
N	-0.09749100	-1.24727400	0.26068400
N	-1.21314500	-0.49417700	0.14254400
H	2.96979500	0.72064300	1.74257700
C	4.36586100	1.52168100	0.32549000
H	4.34811600	2.54606000	0.68260600



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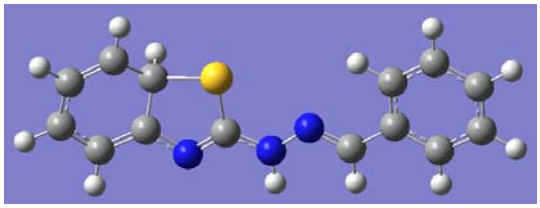

0 2

C	3.09860900	0.69911600	0.56180800
C	3.34243500	-0.73829900	0.17223800
C	4.59977700	-1.15463100	-0.21897100
C	5.59441900	-0.20886700	-0.48744900
C	5.28700600	1.18675700	-0.45727100
H	4.77055900	-2.21215400	-0.39590800
H	6.57531500	-0.53325500	-0.81537100
H	6.03707800	1.89273700	-0.80198100
N	2.22355300	-1.53465000	0.19278900
S	1.29921900	0.95872300	0.18420600
C	1.14653500	-0.80964100	0.19324200
H	-0.15943100	-2.37580700	0.09048300
C	-2.32443600	-1.15716100	0.00664100
H	-2.40382200	-2.24835700	-0.03895100
C	-3.57137300	-0.38814900	-0.04554800

C	-3.57858200	1.01277700	0.01498800
C	-4.78387200	-1.07640500	-0.15947100
C	-4.78056900	1.70536600	-0.03858100
H	-2.63676900	1.54494900	0.10422900
C	-5.98754800	-0.37866400	-0.21274900
H	-4.78093900	-2.16223700	-0.20673600
C	-5.98843000	1.01263700	-0.15252200
H	-4.77977000	2.78979500	0.00873000
H	-6.92288600	-0.92193400	-0.30134400
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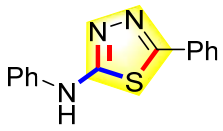
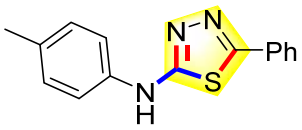
N	-0.08947000	-1.36089100	0.14821400
N	-1.18792100	-0.57537100	0.10169800
H	3.13543900	0.77809400	1.66299000
C	4.08239400	1.65076900	-0.03412500
H	3.86205000	2.71285500	-0.01172400

V. Spectral data of products

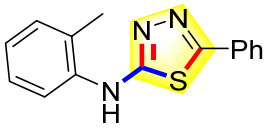


3a, *N*,5-diphenyl-1,3,4-thiadiazol-2-amine,[8] white solid: mp 206–207 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.57 (s, 1H), 7.88 – 7.86 (m, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.52 (h, J = 3.6 Hz, 3H), 7.38 (t, J = 7.8 Hz, 2H), 7.03 (t, J = 7.3 Hz, 1H). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (brs, 1H), 7.88 (dd, J = 7.5, 1.9 Hz, 2H), 7.49 – 7.40 (m, 7H), 7.14 (t, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.5, 158.0, 140.9, 130.74, 130.72, 129.7, 129.6, 127.2, 122.6, 118.0. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1 (br), 157.9 (br), 140.3, 130.7, 130.1, 129.7, 129.0, 127.0, 123.7, 118.4. HRMS (ESI-TOF) Calcd for $C_{14}H_{12}N_3S^+$ ($[M+H]^+$) 254.0746. Found 254.0759.

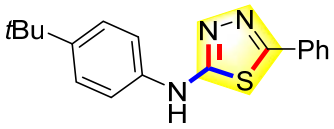
[8] S. J. Singh, S. Rajamanickam, A. Gogoi and B. K. Patel, *Tetrahedron Lett.*, 2016, **57**, 1044−1047



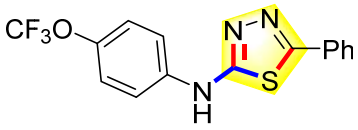
3b, 5-phenyl-*N*-(*p*-tolyl)-1,3,4-thiadiazol-2-amine, [9] pale yellow solid: mp 179–180 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.46 (s, 1H), 7.87 – 7.83 (m, 2H), 7.56 – 7.47 (m, 5H), 7.18 (d, *J* = 8.2 Hz, 2H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 164.7, 157.7, 138.6, 131.6, 130.8, 130.6, 130.0, 129.7, 127.2, 118.1, 20.8. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}N_3S^+$ ([M+H]$^+$) 268.0903. Found 268.0901.



3c, 5-phenyl-*N*-(*o*-tolyl)-1,3,4-thiadiazol-2-amine,[8] pale yellow solid: mp 140–141 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.66 (s, 1H), 7.86 – 7.81 (m, 3H), 7.52 – 7.46 (m, 3H), 7.25 (dd, *J* = 9.6, 7.4 Hz, 2H), 7.08 (dd, *J* = 7.3, 7.3 Hz, 1H), 2.51 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 167.0 (br), 157.9 (br), 139.6 (br), 131.2, 131.0, 130.5, 130.0, 129.7, 127.2, 127.1, 124.8, 122.2, 18.4. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}N_3S^+$ ([M+H]$^+$) 268.0903. Found 268.0888.



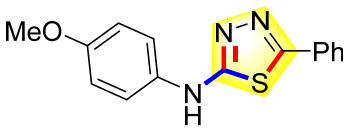
3d, *N*-(4-(*tert*-butyl)phenyl)-5-phenyl-1,3,4-thiadiazol-2-amine, white solid: mp 224–225 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.46 (s, 1H), 7.86 – 7.84 (m, 2H), 7.57 – 7.47 (m, 5H), 7.39 (d, *J* = 8.7 Hz, 2H), 1.28 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 164.8, 157.7, 145.1, 138.5, 130.8, 130.6, 129.7, 127.2, 126.2, 117.9, 34.4, 31.7. HRMS (ESI-TOF) Calcd for $C_{18}H_{20}N_3S^+$ ([M+H]$^+$) 310.1372. Found 310.1375.



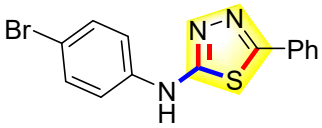
3e, 5-phenyl-*N*-(4-(trifluoromethoxy)phenyl)-1,3,4-thiadiazol-2-amine, yellowish

[9] U. Salar, M. Taha, N. H. Ismail, K. M. Khan, S. Imran, S. Perveen, A. Wadood, M. Riaz, *Bioorg. Med. Chem.*, 2016, **24**, 1909–1918.

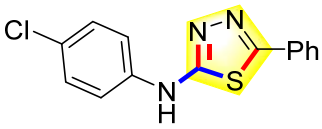
solid: mp 220–221 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H), 7.88 – 7.86 (m, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.55 – 7.49 (m, 3H), 7.38 (d, J = 8.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.3, 158.6, 143.0 (q, J = 1.7 Hz), 140.1, 130.8, 130.6, 129.8, 127.3, 122.5, 120.7 (q, J = 255.3 Hz), 119.2. ^{19}F NMR (376 MHz, DMSO-d_6) δ -57.11 – -57.12 (m, 3F). HRMS (ESI-TOF) Calcd for $C_{15}H_{11}F_3N_3OS^+$ ([M+H]$^+$) 338.0569. Found 338.0580.



3f, *N*-(4-methoxyphenyl)-5-phenyl-1,3,4-thiadiazol-2-amine,[10] pale yellow solid: mp 175–176 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.33 (s, 1H), 7.85 – 7.82 (m, 2H), 7.56 (d, J = 9.0 Hz, 2H), 7.54 – 7.47 (m, 3H), 6.96 (d, J = 9.0 Hz, 2H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.2, 157.3, 155.2, 134.5, 130.9, 130.5, 129.7, 127.1, 119.9, 114.8, 55.7. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}N_3OS^+$ ([M+H]$^+$) 284.0852. Found 284.0856.



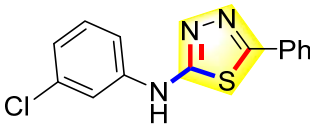
3g, *N*-(4-bromophenyl)-5-phenyl-1,3,4-thiadiazol-2-amine,[11] yellowish solid: mp 223–224 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.72 (s, 1H), 7.88 – 7.85 (m, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.55 – 7.51 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.1, 158.5, 140.2, 132.3, 130.9, 130.6, 129.8, 127.3, 119.9, 113.8. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}BrN_3S^+$ ([M+H]$^+$) 331.9852. Found 331.9854.



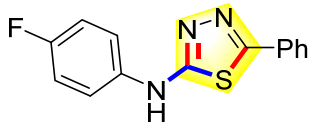
3h, *N*-(4-chlorophenyl)-5-phenyl-1,3,4-thiadiazol-2-amine, yellowish solid: mp 222–223 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.71 (s, 1H), 7.88 – 7.85 (m, 2H), 7.71 (d, J = 8.9 Hz, 2H), 7.55 – 7.48 (m, 3H), 7.42 (d, J = 8.9 Hz, 2H). ^{13}C{^{1}H} NMR

[10] S.-J. Yang, S.-H. Lee, H.-J. Kwak and Y.-D. Gong, *J. Org. Chem.*, 2013, **78**, 438−444.
[11] E. E. Oruç, S. Rollas, F. Kandemirli, N. Shvets and A. S. Dimoglo, *J. Med. Chem.*, 2004, **47**, 6760−6767.

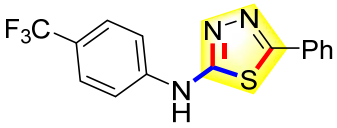
(100 MHz, DMSO-d_6) δ 164.2, 158.5, 139.8, 130.8, 130.6, 129.8, 129.4, 127.3, 125.9, 119.5. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}ClN_3S^+$ ([M+H]$^+$) 288.0357. Found 288.0359.



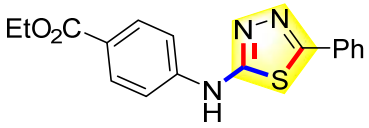
3i, *N*-(3-chlorophenyl)-5-phenyl-1,3,4-thiadiazol-2-amine, white solid: mp 198–199 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.76 (s, 1H), 7.96 (dd, J = 2.1, 2.1 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.56 – 7.51 (m, 3H), 7.47 (dd, J = 7.8, 1.5 Hz, 1H), 7.39 (dd, J = 8.0, 8.0 Hz, 1H), 7.08 (dd, J = 7.8, 1.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.1, 158.8, 142.2, 134.0, 131.2, 130.9, 130.6, 129.8, 127.3, 122.0, 117.4, 116.4. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}ClN_3S^+$ ([M+H]$^+$) 288.0357. Found 288.0353.



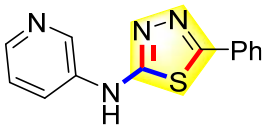
3j, *N*-(4-fluorophenyl)-5-phenyl-1,3,4-thiadiazol-2-amine,[10] yellowish solid: mp 204–205 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.87 – 7.84 (m, 2H), 7.72 – 7.66 (m, 2H), 7.55 – 7.47 (m, 3H), 7.25 – 7.19 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.6, 158.1, 157.8 (d, J = 238.6 Hz), 137.4 (d, J = 2.2 Hz), 130.74, 130.68, 129.7, 127.2, 119.7 (d, J = 7.8 Hz), 116.2 (d, J = 22.4 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -120.96 – -121.03 (m, 1F). HRMS (ESI-TOF) Calcd for $C_{14}H_{11}FN_3S^+$ ([M+H]$^+$) 272.0652. Found 272.0653.



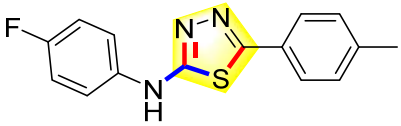
3k, 5-phenyl-*N*-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-amine, yellowish solid: mp 250–251 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.99 (brs, 1H), 7.89 – 7.86 (m, 4H), 7.72 (d, J = 8.4 Hz, 2H), 7.55 – 7.51 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 163.9, 159.3, 144.1, 131.0, 130.5, 129.8, 127.4, 126.9 (q, J = 3.9 Hz), 125.0 (q, J = 271.1 Hz), 122.2 (q, J = 32.0 Hz), 117.7. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.00 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{15}H_{11}F_3N_3S^+$ ([M+H]$^+$) 322.0620. Found 322.0633.



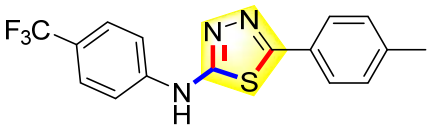
3l, ethyl 4-((5-phenyl-1,3,4-thiadiazol-2-yl)amino)benzoate, white solid: mp 208–209 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.97 (d, J = 8.9 Hz, 2H), 7.90 – 7.88 (m, 2H), 7.79 (d, J = 8.9 Hz, 2H), 7.56 – 7.49 (m, 3H), 4.29 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.8, 163.8, 159.3, 144.9, 131.1, 131.0, 130.5, 129.8, 127.4, 123.2, 117.3, 60.8, 14.7. HRMS (ESI-TOF) Calcd for $C_{17}H_{16}N_3O_2S^+$ ([M+H]$^+$) 326.0958. Found 326.0956.



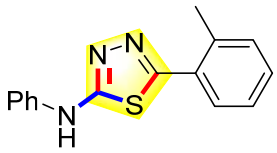
3m, 5-phenyl-*N*-(pyridin-3-yl)-1,3,4-thiadiazol-2-amine, yellow solid: mp 226–227 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H), 8.80 (d, J = 2.7 Hz, 1H), 8.25 – 8.21 (m, 2H), 7.89 – 7.87 (m, 2H), 7.56 – 7.49 (m, 3H), 7.42 (dd, J = 8.3, 4.7 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.2, 159.0, 143.3, 139.7, 137.7, 130.9, 130.6, 129.8, 127.3, 124.6, 124.4. HRMS (ESI-TOF) Calcd for $C_{13}H_{11}N_4S^+$ ([M+H]$^+$) 255.0699. Found 255.0687.



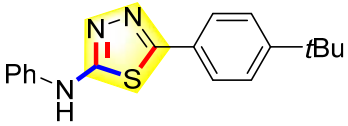
3n, *N*-(4-fluorophenyl)-5-(*p*-tolyl)-1,3,4-thiadiazol-2-amine, yellowish solid: mp 210–211 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.52 (s, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.70 – 7.66 (m, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.21 (dd, J = 8.9, 8.9 Hz, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.3, 158.1, 157.8 (d, J = 238.6 Hz), 140.6, 137.5 (d, J = 2.1 Hz), 130.3, 128.0, 127.2, 119.6 (d, J = 7.8 Hz), 116.1 (d, J = 22.4 Hz), 21.4. ^{19}F NMR (376 MHz, DMSO-d_6) δ -121.10 – -121.15 (m, 1F). HRMS (ESI-TOF) Calcd for $C_{15}H_{13}FN_3S^+$ ([M+H]$^+$) 286.0809. Found 286.0812.



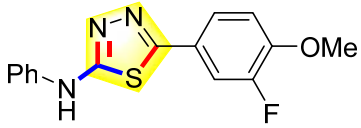
3o, 5-(*p*-tolyl)-*N*-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-amine, yellowish solid: mp 215–216 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.94 (s, 1H), 7.87 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 163.5, 159.3, 144.2, 140.9, 130.3, 127.8, 127.3, 126.9 (q, J = 3.7 Hz), 125.0 (q, J = 271.1 Hz), 122.1 (q, J = 31.8 Hz), 117.7, 21.4. ^{19}F NMR (376 MHz, DMSO-d_6) δ -59.98 (s, 3F). HRMS (ESI-TOF) Calcd for $C_{16}H_{13}F_3N_3S^+$ ([M+H]$^+$) 336.0777. Found 336.0792.



3p, *N*-phenyl-5-(*o*-tolyl)-1,3,4-thiadiazol-2-amine, pale yellow solid: mp 168–169 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.67 (d, J = 7.4 Hz, 2H), 7.62 (d, J = 7.1 Hz, 1H), 7.42 – 7.31 (m, 5H), 7.03 (dd, J = 7.4, 7.4 Hz, 1H), 2.53 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.9, 157.3, 141.0, 136.7, 131.9, 130.6, 130.1, 129.8, 129.6, 126.9, 122.5, 118.0, 21.7. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}N_3S^+$ ([M+H]$^+$) 268.0903. Found 268.0907.

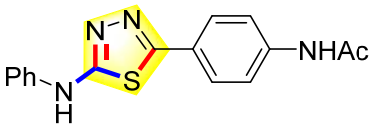


3q, 5-(4-(*tert*-butyl)phenyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine,[8] white solid: mp 178–179 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.51 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.37 (dd, J = 8.5, 7.3 Hz, 2H), 7.03 (dd, J = 7.3, 7.3 Hz, 1H), 1.31 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.3, 158.0, 153.5, 141.0, 129.6, 128.1, 127.0, 126.5, 122.5, 117.9, 35.1, 31.4. HRMS (ESI-TOF) Calcd for $C_{18}H_{20}N_3S^+$ ([M+H]$^+$) 310.1372. Found 310.1372.

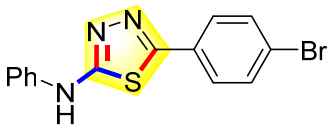


3r, 5-(3-fluoro-4-methoxyphenyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine, white solid: mp

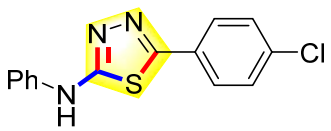
250–251 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.52 (s, 1H), 7.73 (dd, J = 12.2, 2.2 Hz, 1H), 7.66 – 7.62 (m, 3H), 7.39 – 7.35 (m, 2H), 7.30 (dd, J = 8.7, 8.7 Hz, 1H), 7.03 (dd, J = 7.4, 7.4 Hz, 1H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.4, 156.8 (d, J = 2.8 Hz), 151.9 (d, J = 245.2 Hz), 149.2 (d, J = 10.5 Hz), 141.0, 129.6, 124.3 (d, J = 3.2 Hz), 123.6 (d, J = 7.1 Hz), 122.5, 118.0, 114.8 (d, J = 2.2 Hz), 114.2 (d, J = 20.1 Hz), 56.7. ^{19}F NMR (376 MHz, DMSO-d_6) δ -134.26 – -134.32 (m, 1F). HRMS (ESI-TOF) Calcd for $C_{15}H_{13}FN_3OS^+$ ([M+H]$^+$) 302.0758. Found 302.0760.



3s, *N*-(4-(5-(phenylamino)-1,3,4-thiadiazol-2-yl)phenyl)acetamide, white solid: mp 227–228 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.51 (s, 1H), 10.23 (s, 1H), 7.80 (d, J = 8.7 Hz, 2H), 7.73 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 7.3 Hz, 2H), 7.37 (dd, J = 8.6, 7.3 Hz, 2H), 7.02 (dddd, J = 7.4, 7.4, 1.1, 1.1 Hz, 1H), 2.09 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 169.1, 164.0, 157.9, 141.5, 141.1, 129.6, 127.9, 125.3, 122.4, 119.6, 117.9, 24.6. HRMS (ESI-TOF) Calcd for $C_{16}H_{15}N_4OS^+$ ([M+H]$^+$) 311.0961. Found 311.0957.

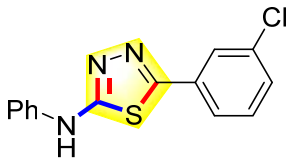


3t, 5-(4-bromophenyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine,[9] yellowish solid: mp 210–211 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.61 (s, 1H), 7.82 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 7.8 Hz, 2H), 7.38 (dd, J = 8.6, 7.3 Hz, 2H), 7.04 (dd, J = 7.4, 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.8, 156.9, 140.8, 132.7, 129.9, 129.6, 129.0, 123.9, 122.7, 118.0. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}BrN_3S^+$ ([M+H]$^+$) 331.9852. Found 331.9853.

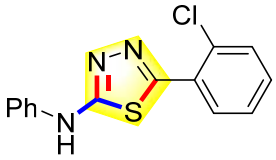


3u, 5-(4-chlorophenyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine,[8] yellowish solid: mp 228–229 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 7.88 (d, J = 8.6 Hz, 2H),

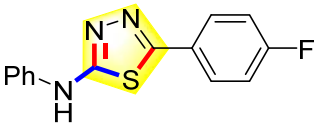
7.66 (d, J = 7.4 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.37 (dd, J = 8.5, 7.2 Hz, 2H), 7.04 (dd, J = 7.3, 7.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 164.9, 156.8, 140.9, 135.1, 129.8, 129.64, 129.62, 128.8, 122.7, 118.0. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}ClN_3S^+$ ($[M+H]^+$) 288.0357. Found 288.0358.



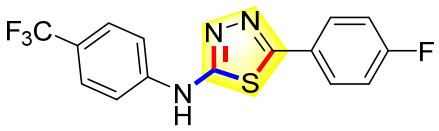
3v, 5-(3-chlorophenyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine, pale yellow solid: mp 182–183 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.63 (s, 1H), 7.92 – 7.90 (m, 1H), 7.85 – 7.79 (m, 1H), 7.66 (d, J = 7.5 Hz, 2H), 7.59 – 7.52 (m, 2H), 7.38 (dd, J = 8.6, 7.3 Hz, 2H), 7.04 (dd, J = 7.4, 7.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.1, 156.5, 140.8, 134.4, 132.7, 131.7, 130.4, 129.7, 126.4, 126.0, 122.7, 118.1. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}ClN_3S^+$ ($[M+H]^+$) 288.0357. Found 288.0365.



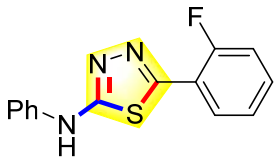
3w, 5-(2-chlorophenyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine, pale yellow solid: mp 218–219 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.58 (s, 1H), 8.11 – 8.07 (m, 1H), 7.68 – 7.66 (m, 3H), 7.57 – 7.50 (m, 2H), 7.38 (dd, J = 8.6, 7.3 Hz, 2H), 7.04 (dddd, J = 7.3, 7.3, 1.1, 1.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 166.2, 153.3, 140.9, 132.0, 131.3, 131.0, 129.7, 129.4, 128.3, 122.7, 118.1. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}ClN_3S^+$ ($[M+H]^+$) 288.0357. Found 288.0355.



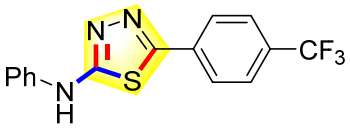
3x, 5-(4-fluorophenyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine,[11] white solid: mp 214–215 °C. ^1H NMR (400 MHz, DMSO-d_6) δ 10.55 (s, 1H), 7.95 – 7.90 (m, 2H), 7.66 (d, J = 7.3 Hz, 2H), 7.40 – 7.34 (m, 4H), 7.03 (dddd, J = 7.4, 7.4, 1.1, 1.1 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 164.6, 163.5 (d, J = 248.1 Hz), 156.9, 140.9, 129.6, 129.5 (d, J = 8.8 Hz), 127.4 (d, J = 3.1 Hz), 122.6, 118.0, 116.8 (d, J = 22.1 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -110.43 – -110.51 (m, 1F). HRMS (ESI-TOF) Calcd for $C_{14}H_{11}FN_3S^+$ ($[M+H]^+$) 272.0652. Found 272.0651.



3y, 5-(4-fluorophenyl)-*N*-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-amine, white solid: mp 268–269 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.95 (s, 1H), 7.93 (dd, *J* = 8.5, 5.3 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.36 (dd, *J* = 8.6, 8.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 164.0, 163.7 (d, *J* = 248.4 Hz), 158.1, 144.1, 129.6 (d, *J* = 8.7 Hz), 127.1 (d, *J* = 3.2 Hz), 126.9 (q, *J* = 3.9 Hz), 125.0 (q, *J* = 271.1 Hz), 122.3 (q, *J* = 32.1 Hz), 117.7, 116.8 (d, *J* = 22.1 Hz). ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -60.04 (s, 3F), -110.02 – -110.08 (m, 1F). HRMS (ESI-TOF) Calcd for $C_{15}H_{10}F_4N_3S^+$ ([M+H]$^+$) 340.0526. Found 340.0529.

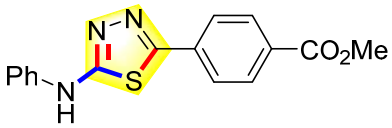


3z, 5-(2-fluorophenyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine,[8] white solid: mp 206–207 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.58 (s, 1H), 8.18 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.58 (dddd, *J* = 8.6, 7.2, 5.5, 1.8 Hz, 1H), 7.47 – 7.37 (m, 4H), 7.04 (dddd, *J* = 7.3, 7.3, 1.1, 1.1 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 166.0 (d, *J* = 4.7 Hz), 158.6 (d, *J* = 249.0 Hz), 150.2 (d, *J* = 7.8 Hz), 140.9, 132.6 (d, *J* = 8.6 Hz), 129.6, 128.4 (d, *J* = 2.4 Hz), 125.8 (d, *J* = 3.2 Hz), 122.7, 118.6 (d, *J* = 12.0 Hz), 118.1, 116.9 (d, *J* = 21.7 Hz). ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -113.09 – -113.16 (m, 1F). HRMS (ESI-TOF) Calcd for $C_{14}H_{11}FN_3S^+$ ([M+H]$^+$) 272.0652. Found 272.0652.

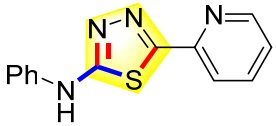


3aa, *N*-phenyl-5-(4-(trifluoromethyl)phenyl)-1,3,4-thiadiazol-2-amine, white solid: mp 232–233 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.68 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.39 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.05 (dd, *J* = 7.4, 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$) δ 165.4, 156.4, 140.8, 134.5 (d, *J* = 1.0 Hz), 130.3 (q, *J* = 32.1 Hz), 129.7, 127.8, 126.7 (q, *J* = 3.8 Hz), 124.4 (d, *J* = 272.3 Hz), 122.9, 118.2. ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -61.29

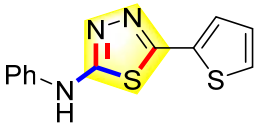
(s, 3F). HRMS (ESI-TOF) Calcd for $C_{15}H_{11}F_3N_3S^+$ ([M+H]$^+$) 322.0620. Found 322.0627.



3ab, methyl 4-(5-(phenylamino)-1,3,4-thiadiazol-2-yl)benzoate, yellow solid: mp 214–215 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.68 (s, 1H), 8.08 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 7.3 Hz, 2H), 7.39 (dd, J = 8.6, 7.3 Hz, 2H), 7.05 (dddd, J = 7.3, 7.3, 1.1, 1.1 Hz, 1H), 3.89 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.1, 165.3, 156.8, 140.8, 134.9, 131.0, 130.5, 129.7, 127.4, 122.8, 118.2, 52.8. HRMS (ESI-TOF) Calcd for $C_{16}H_{14}N_3O_2S^+$ ([M+H]$^+$) 312.0801. Found 312.0800.



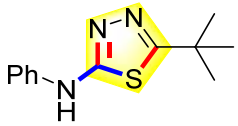
3ac, *N*-phenyl-5-(pyridin-2-yl)-1,3,4-thiadiazol-2-amine,[12] pale yellow solid: mp 219–220 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.64 (s, 1H), 8.64 (ddd, J = 4.9, 1.4, 1.4 Hz, 1H), 8.15 (ddd, J = 8.0, 1.1, 1.1 Hz, 1H), 7.98 (ddd, J = 7.7, 7.7, 1.7 Hz, 1H), 7.67 (d, J = 7.4 Hz, 2H), 7.49 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 7.38 (dd, J = 8.5, 7.3 Hz, 2H), 7.04 (dd, J = 7.4, 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.0, 160.1, 150.3, 149.5, 140.8, 138.1, 129.6, 125.4, 122.7, 119.9, 118.1. HRMS (ESI-TOF) Calcd for $C_{13}H_{11}N_4S^+$ ([M+H]$^+$) 255.0699. Found 255.0692.



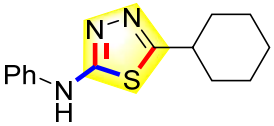
3ad, *N*-phenyl-5-(thiophen-2-yl)-1,3,4-thiadiazol-2-amine,[13] pale yellow solid: mp 175–176 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.53 (s, 1H), 7.67 (dd, J = 5.1, 1.2 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.53 (dd, J = 3.7, 1.2 Hz, 1H), 7.36 (dd, J = 8.6, 7.3 Hz, 2H), 7.17 (dd, J = 5.1, 3.7 Hz, 1H), 7.03 (ddd, J = 7.4, 7.4, 1.2, 1.2 Hz, 1H). ^{13}C{^{1}H}

[12] A. Bharti, P. Bharati, N. K. Singh and M. K. Bharty, *J. Coord. Chem.*, 2016, **69**, 1258−1271.
[13] H. Muğlu, H. Yakan, H. A. Shouaib, *J. Mol. Struct.*, 2020, **1203**, 127470.

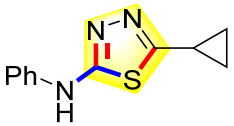
NMR (100 MHz, DMSO-d_6) δ 164.2, 152.5, 140.7, 132.6, 129.7, 129.3, 129.1, 128.8, 122.9, 118.1. HRMS (ESI-TOF) Calcd for $C_{12}H_{10}N_3S_2^+$ ([M+H]$^+$) 260.0311. Found 260.0313.



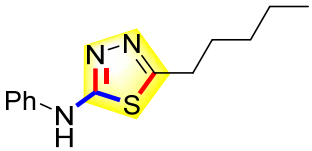
3ae, 5-(*tert*-butyl)-*N*-phenyl-1,3,4-thiadiazol-2-amine, pale yellow solid: mp 194–195 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.23 (s, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.31 (dd, J = 8.6, 7.3 Hz, 2H), 6.97 (dd, J = 8.1, 6.8 Hz, 1H), 1.34 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 170.1, 164.6, 141.2, 129.5, 122.3, 117.8, 36.0, 30.9. HRMS (ESI-TOF) Calcd for $C_{12}H_{16}N_3S^+$ ([M+H]$^+$) 234.1059. Found 234.1055.



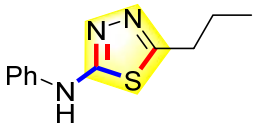
3af, 5-cyclohexyl-*N*-phenyl-1,3,4-thiadiazol-2-amine, white solid: mp 188–189 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 7.55 (d, J = 7.4 Hz, 2H), 7.31 (dd, J = 8.5, 7.3 Hz, 2H), 6.97 (dd, J = 7.3, 7.3 Hz, 1H), 2.94 (tt, J = 11.1, 3.6 Hz, 1H), 1.97 (dd, J = 10.5, 4.8 Hz, 2H), 1.73 (dt, J = 12.5, 3.3 Hz, 2H), 1.66 – 1.61 (m, 1H), 1.48 – 1.29 (m, 4H), 1.22 (ddt, J = 15.5, 12.1, 6.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.9, 164.1, 141.1, 129.6, 122.3, 117.7, 39.3, 33.4, 25.71, 25.66. HRMS (ESI-TOF) Calcd for $C_{14}H_{18}N_3S^+$ ([M+H]$^+$) 260.1216. Found 260.1214.



3ag, 5-cyclopropyl-*N*-phenyl-1,3,4-thiadiazol-2-amine, white solid: mp 153–154 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.18 (s, 1H), 7.52 (d, J = 7.5 Hz, 2H), 7.31 (dd, J = 8.5, 7.2 Hz, 2H), 6.97 (dd, J = 7.3, 7.3 Hz, 1H), 2.27 (tt, J = 8.3, 4.9 Hz, 1H), 1.15 – 1.03 (m, 2H), 0.94 – 0.83 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 163.5, 163.3, 141.1, 129.6, 122.3, 117.6, 11.3, 10.2. HRMS (ESI-TOF) Calcd for $C_{11}H_{12}N_3S^+$ ([M+H]$^+$) 218.0746. Found 218.0747.



3ah, 5-pentyl-*N*-phenyl-1,3,4-thiadiazol-2-amine,[14] white solid: mp 157–158 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.23 (s, 1H), 7.57 – 7.53 (m, 2H), 7.32 (ddd, J = 8.6, 7.3, 2.0 Hz, 2H), 6.98 (ddd, J = 7.3, 7.3, 1.2 Hz, 1H), 2.87 (t, J = 7.5 Hz, 2H), 1.64 (p, J = 7.3 Hz, 2H), 1.28 (h, J = 3.7 Hz, 4H), 0.86 – 0.82 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.6, 160.8, 141.1, 129.6, 122.3, 117.7, 30.9, 29.6, 29.2, 22.1, 14.2. HRMS (ESI-TOF) Calcd for $C_{13}H_{18}N_3S^+$ ([M+H]$^+$) 248.1216. Found 248.1222.

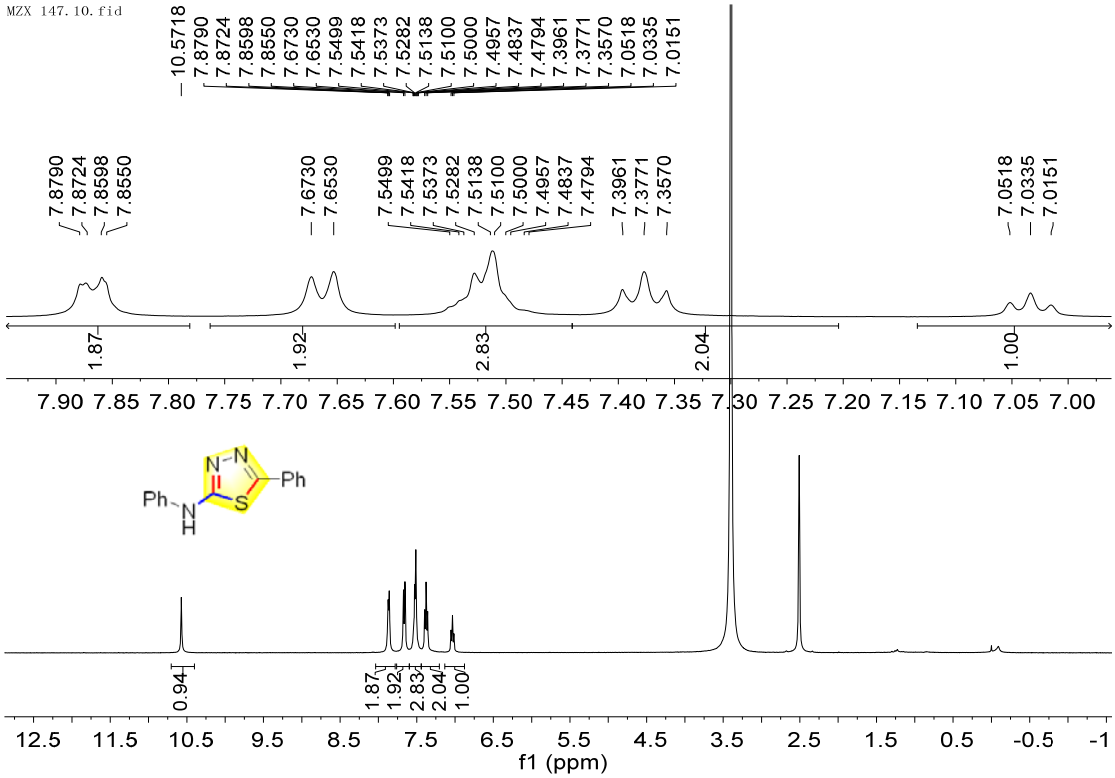


3ai, *N*-phenyl-5-propyl-1,3,4-thiadiazol-2-amine, white solid: mp 186–187 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.23 (s, 1H), 7.59 (d, J = 7.4 Hz, 2H), 7.33 (dd, J = 8.6, 7.3 Hz, 2H), 6.98 (dddd, J = 7.3, 7.3, 1.2, 1.2 Hz, 1H), 2.88 (t, J = 7.4 Hz, 2H), 1.69 (h, J = 7.4 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.4, 160.1, 141.3, 129.5, 122.0, 117.6, 31.6, 23.0, 13.8. HRMS (ESI-TOF) Calcd for $C_{11}H_{14}N_3S^+$ ([M+H]$^+$) 220.0903. Found 220.0906.

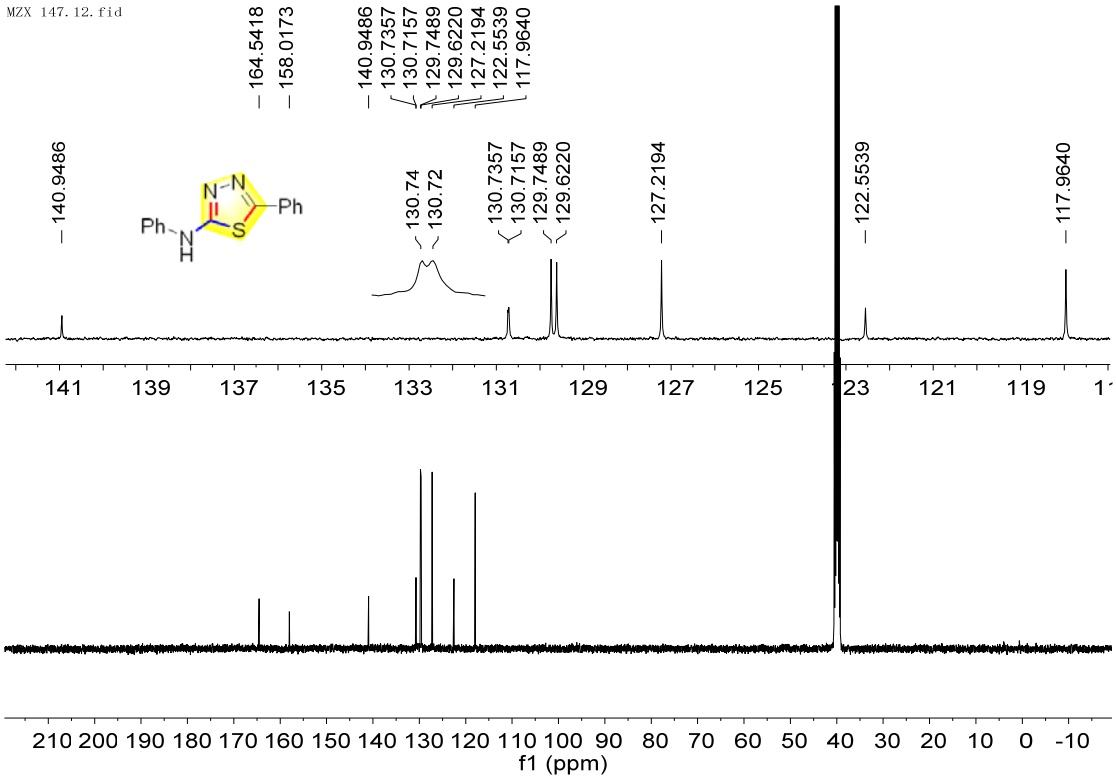
[14] E. N. W. Howe, N. Busschaert, X. Wu, S. N. Berry, J. Ho, M. E. Light, D. D. Czech, H. A. Klein, J. A. Kitchen and P. A. Gale, *J. Am. Chem. Soc.*, 2016, **138**, 8301–8308.

VI. Copies of ^{1}H, ^{19}F, ^{13}C and DEPT NMR spectra

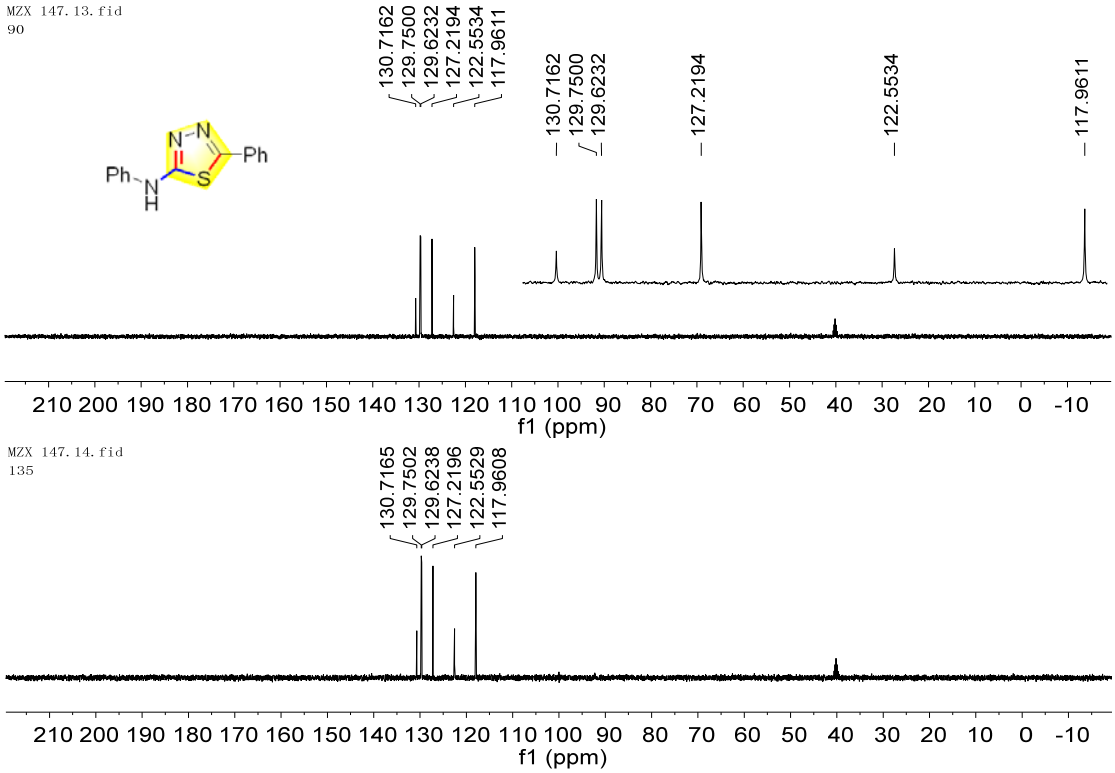
3a, ^{1}H NMR (in DMSO-d_6)



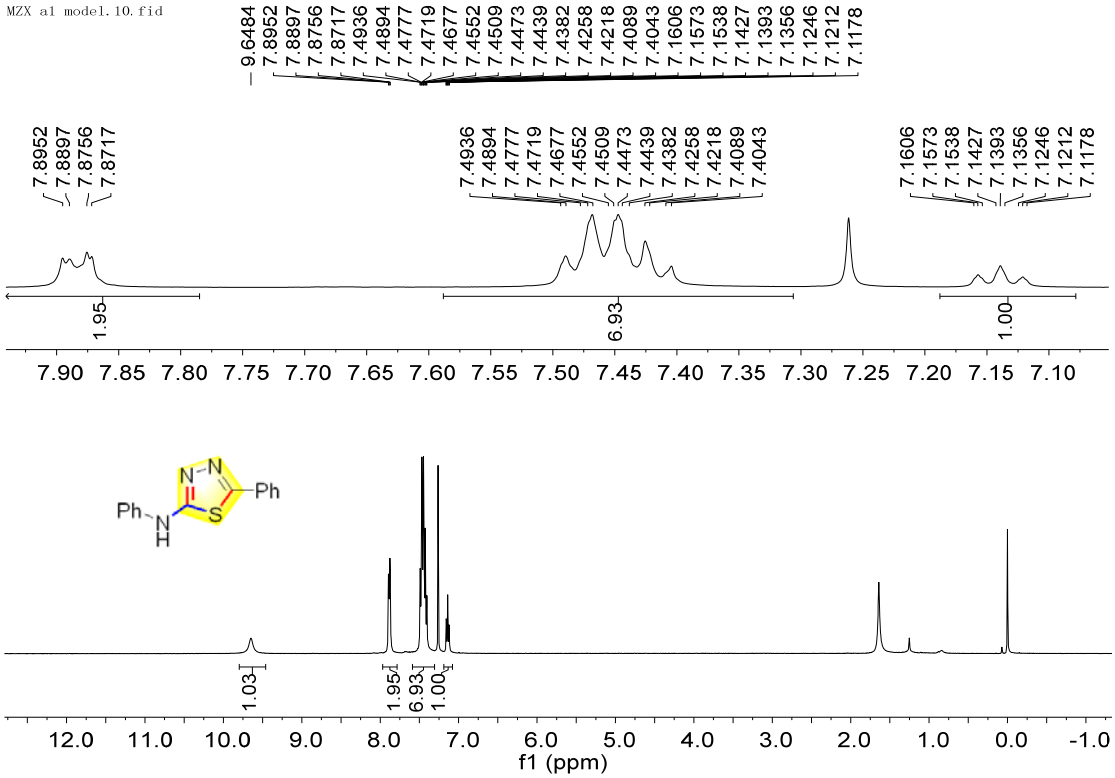
^{13}C NMR (in DMSO-d_6)



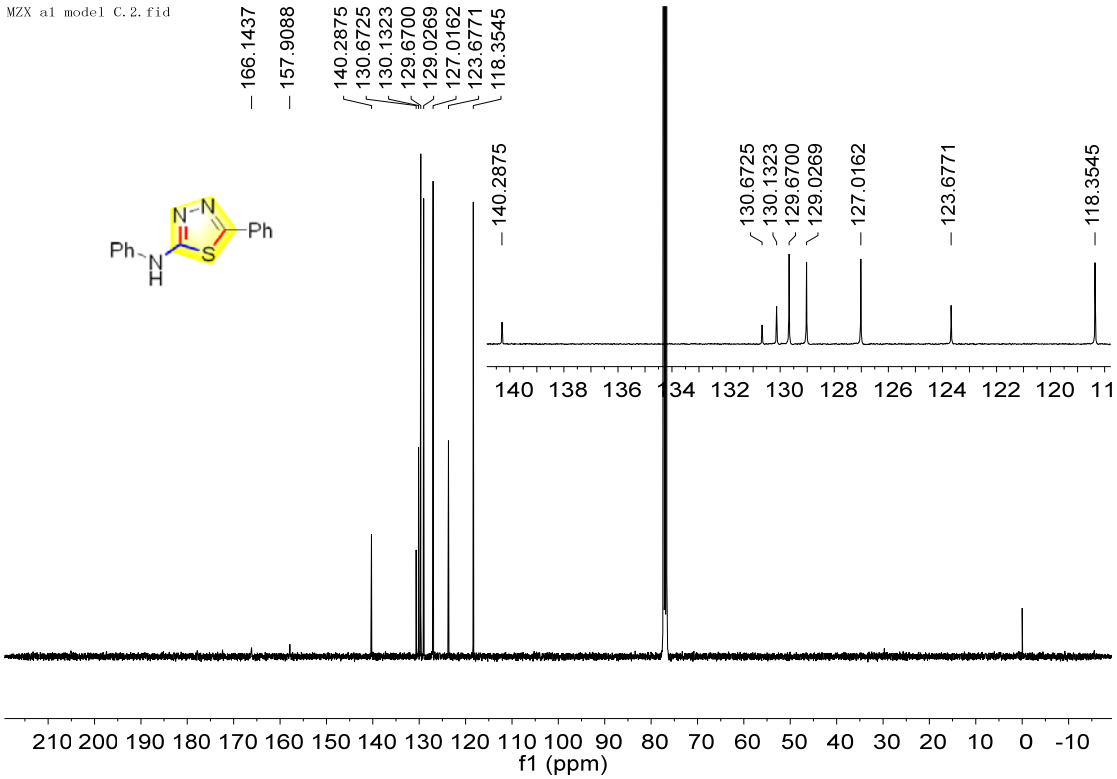
DEPT 90 and DEPT 135 (in DMSO-d_6)



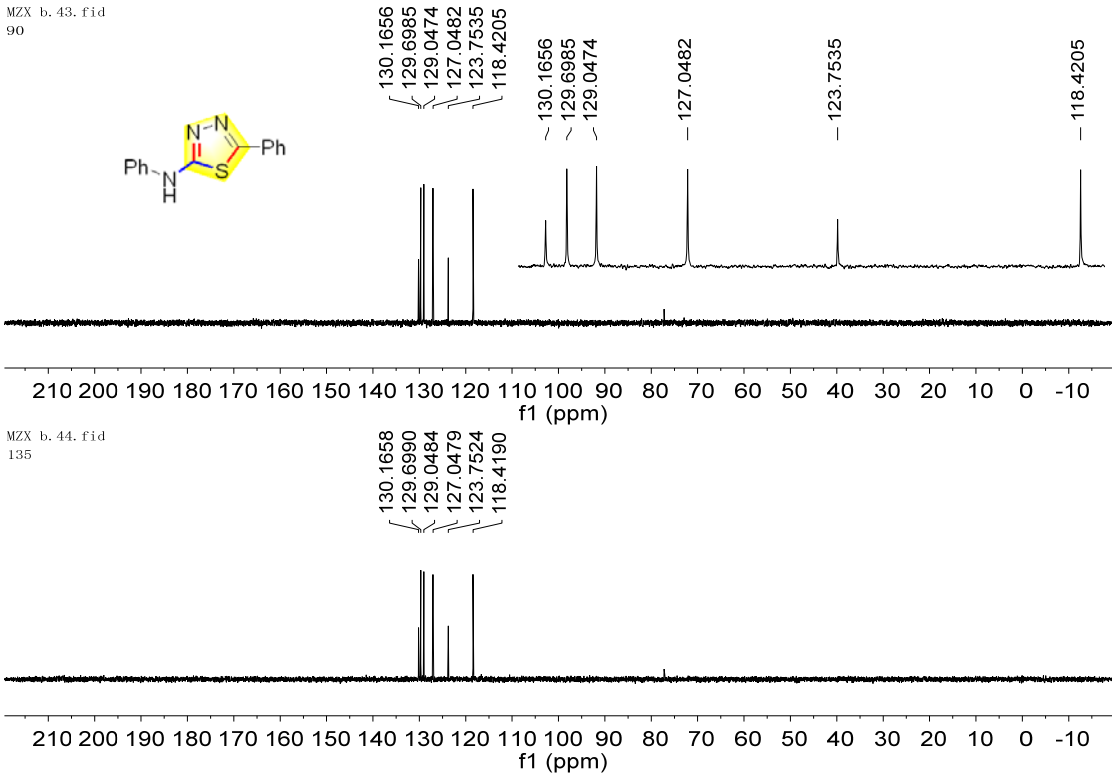
^{1}H NMR (in $CDCl_3$)



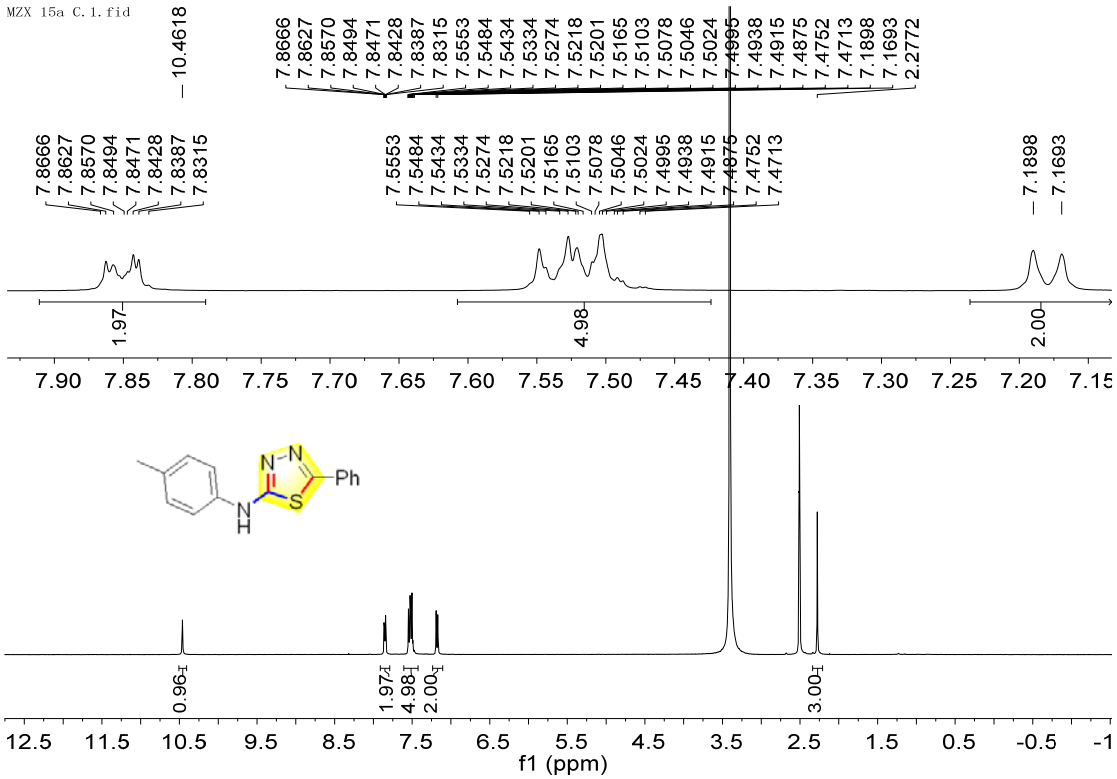
^{13}C NMR (in $CDCl_3$)



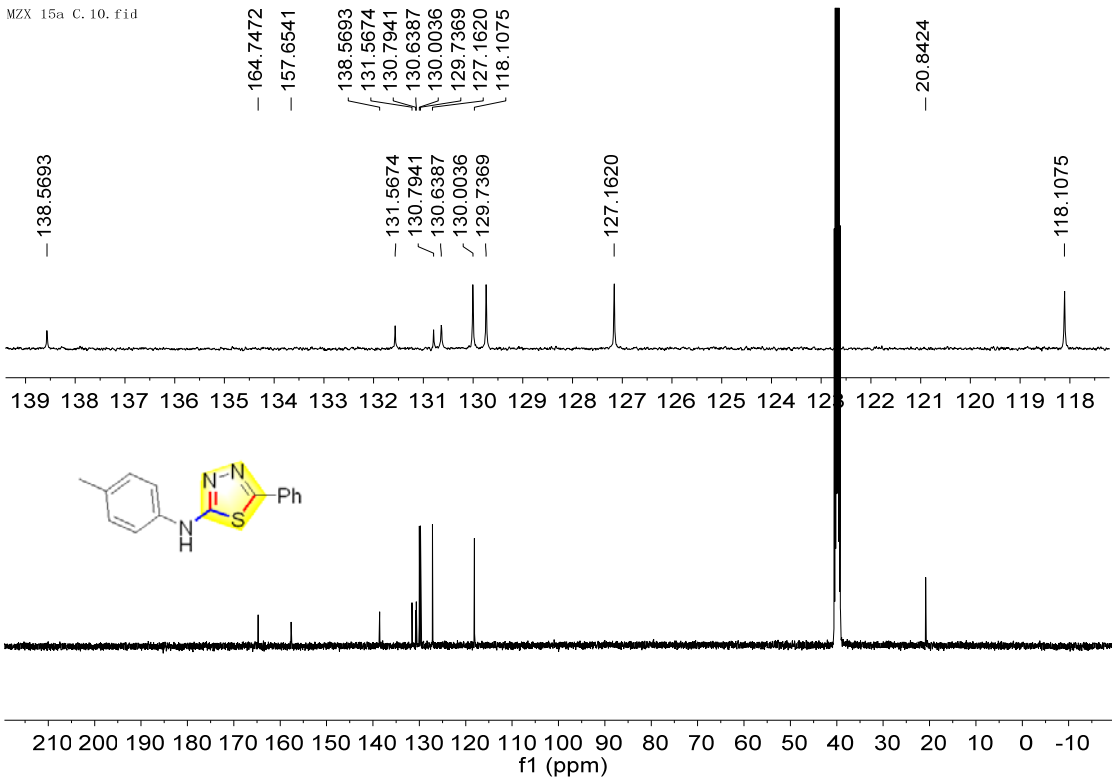
DEPT 90 and DEPT 135 (in $CDCl_3$)



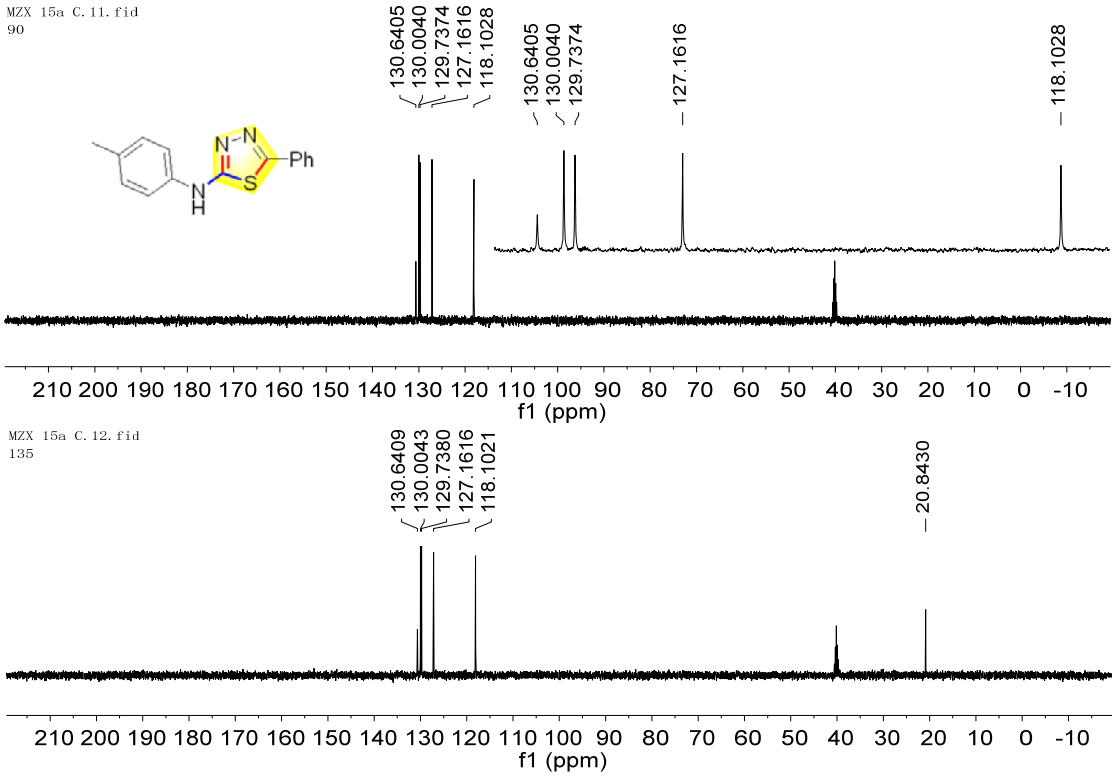
3b, ^{1}H NMR



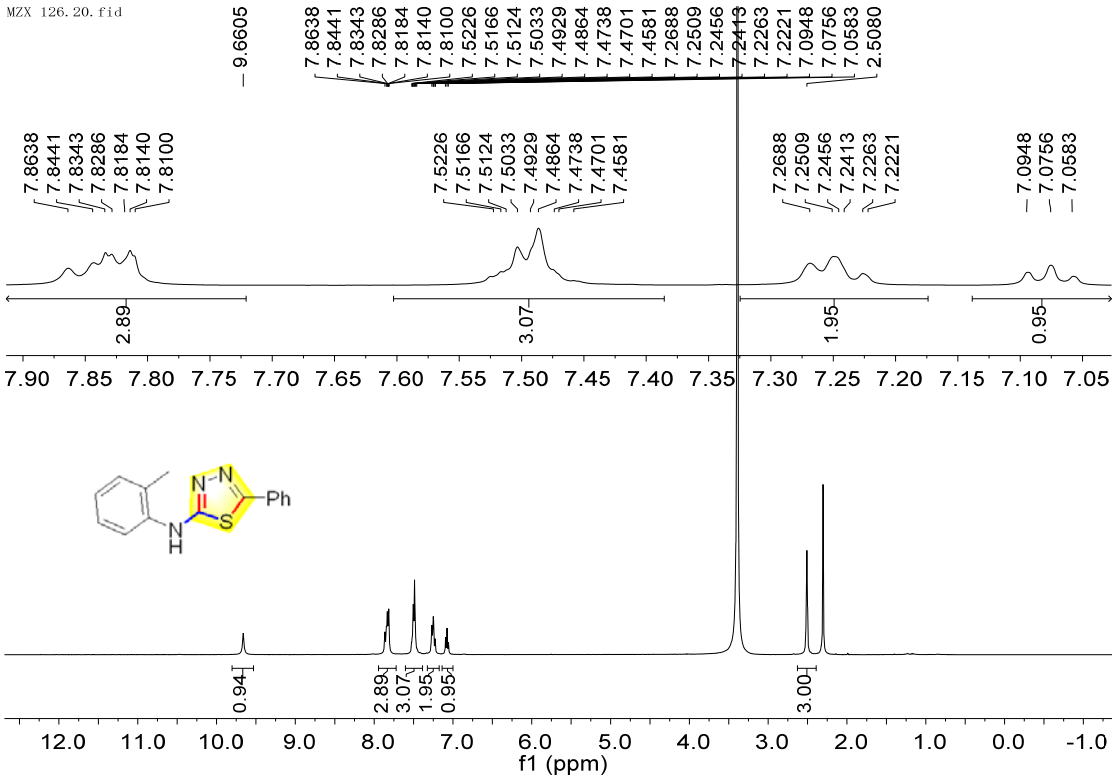
^{13}C NMR



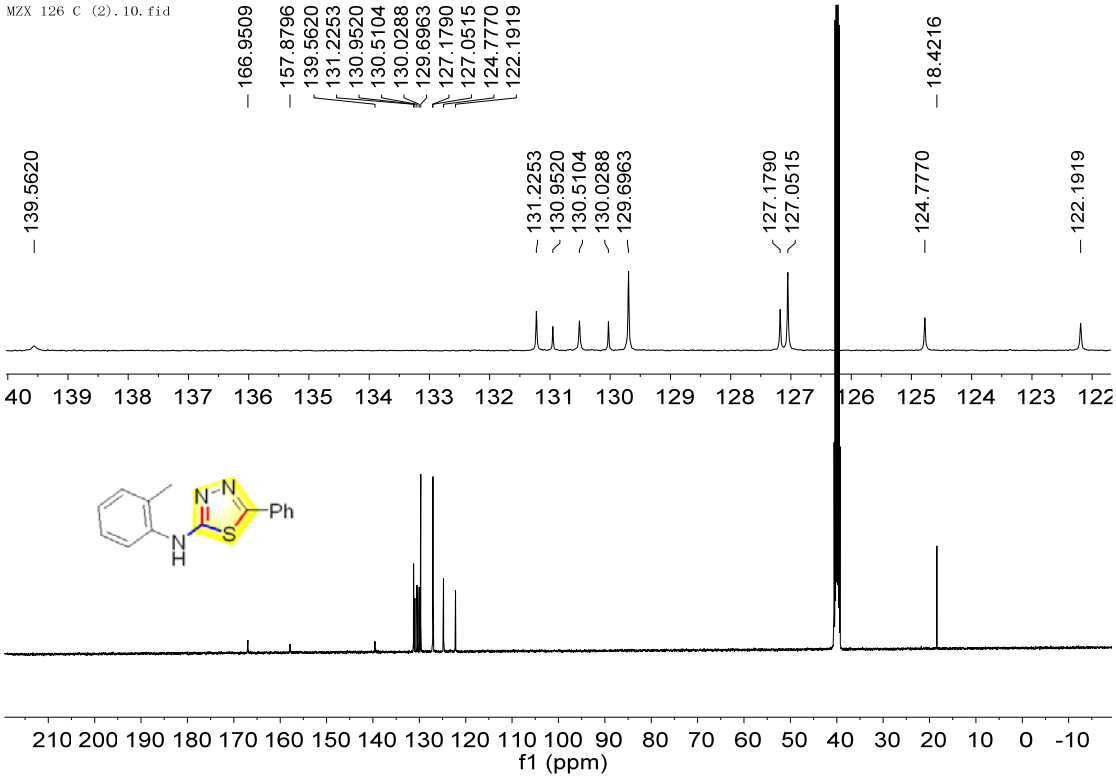
DEPT 90 and DEPT 135



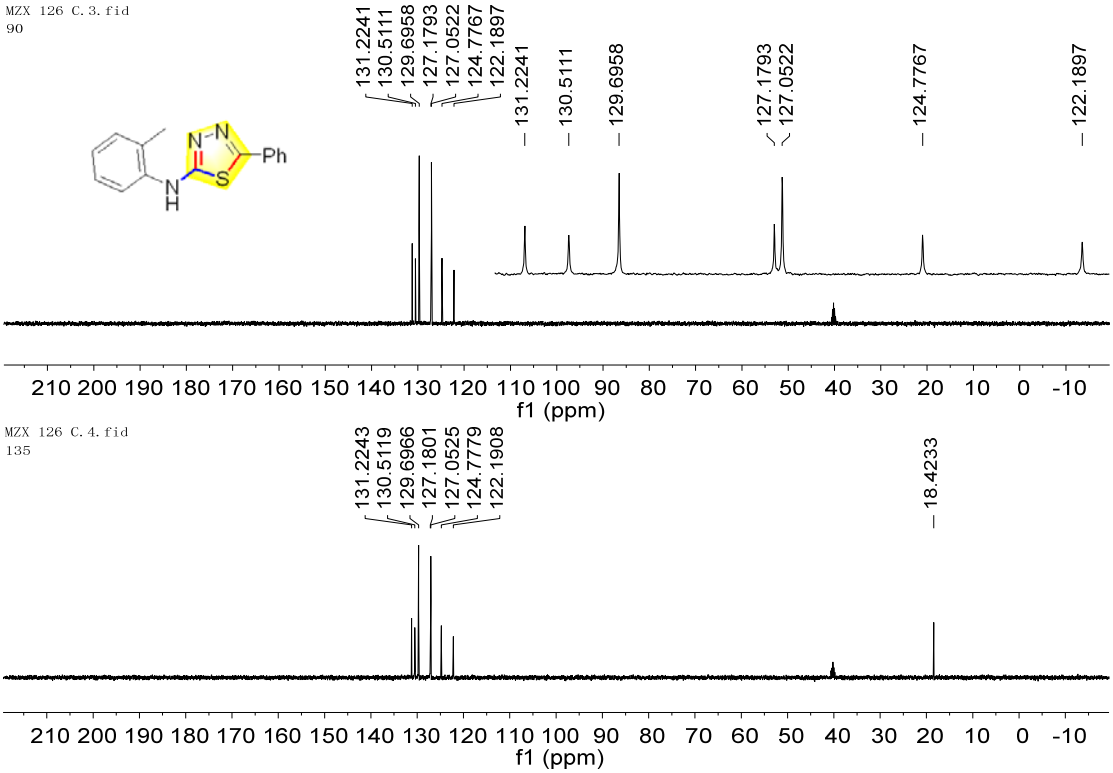
3c, ^{1}H NMR



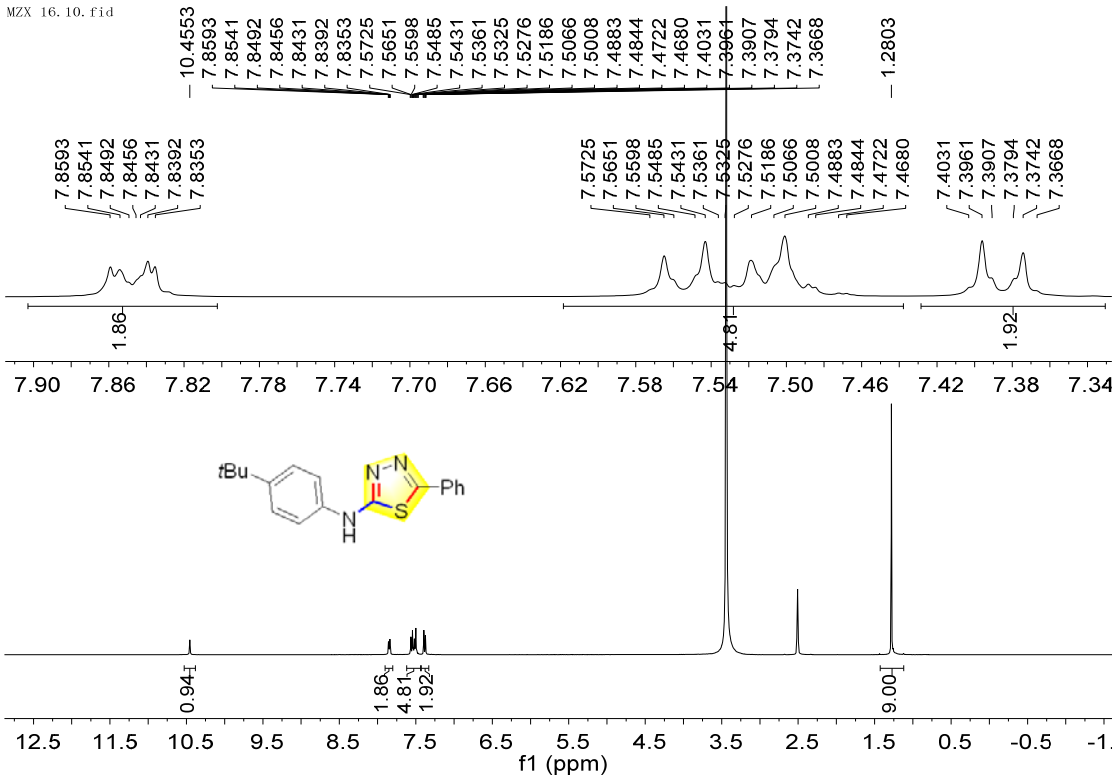
^{13}C NMR



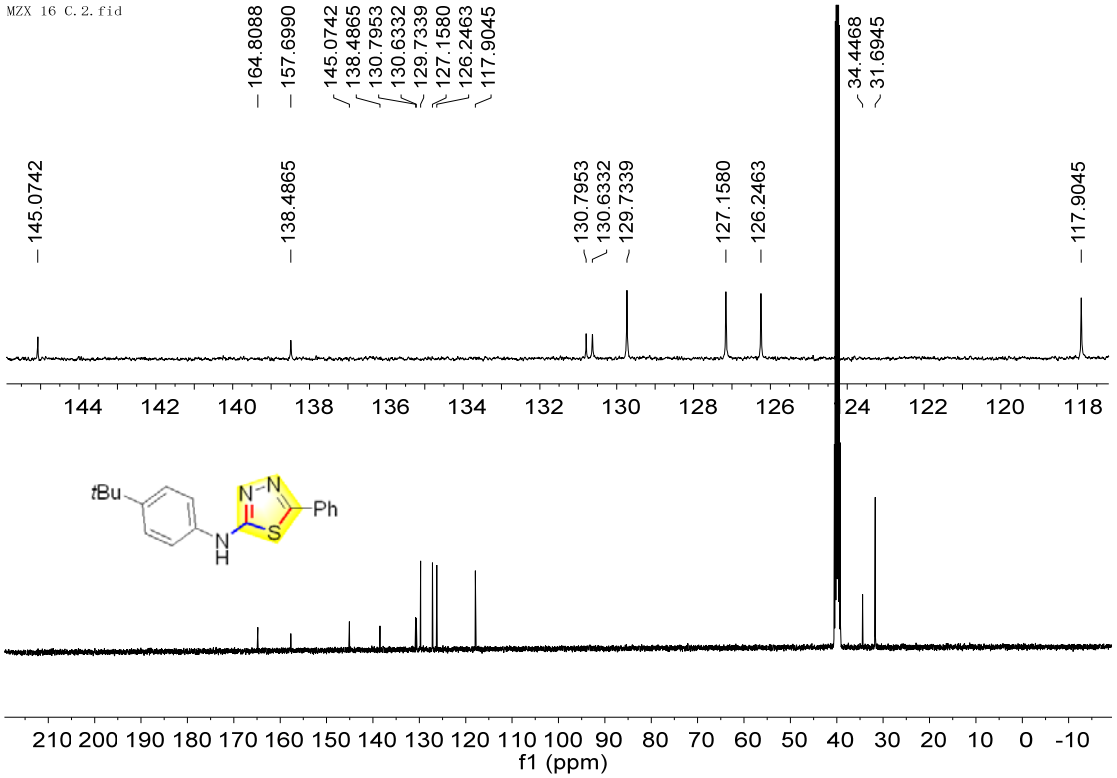
DEPT 90 and DEPT 135



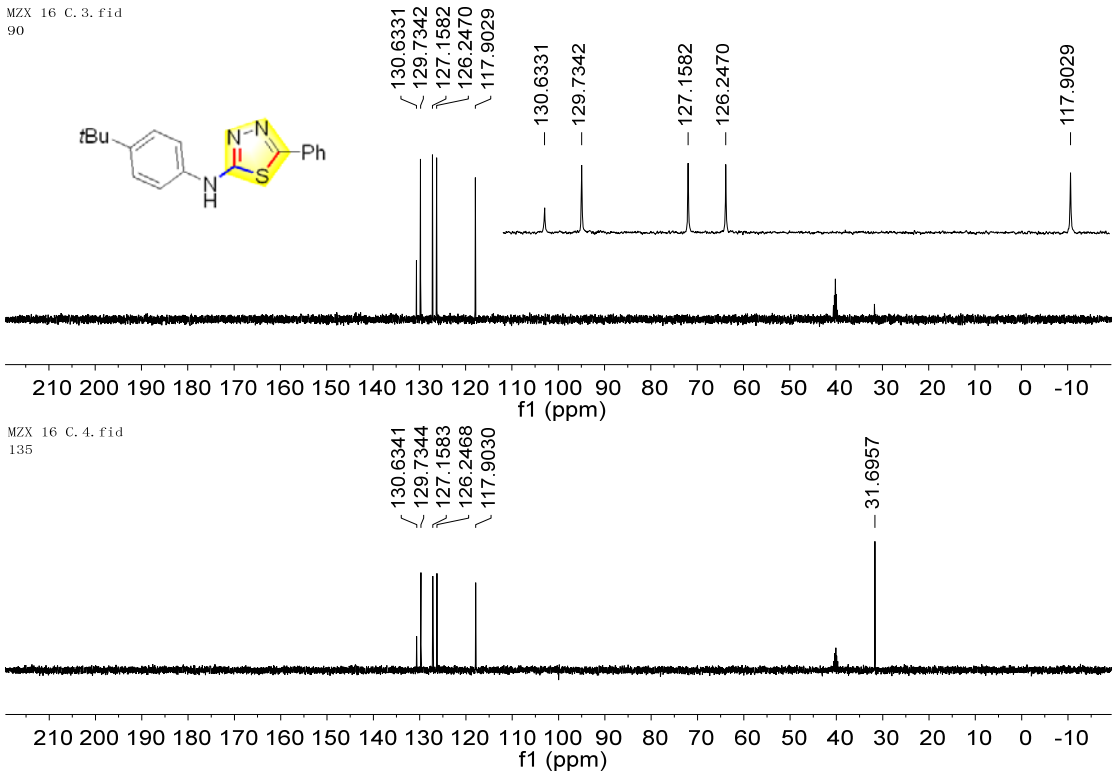
3d, ^{1}H NMR



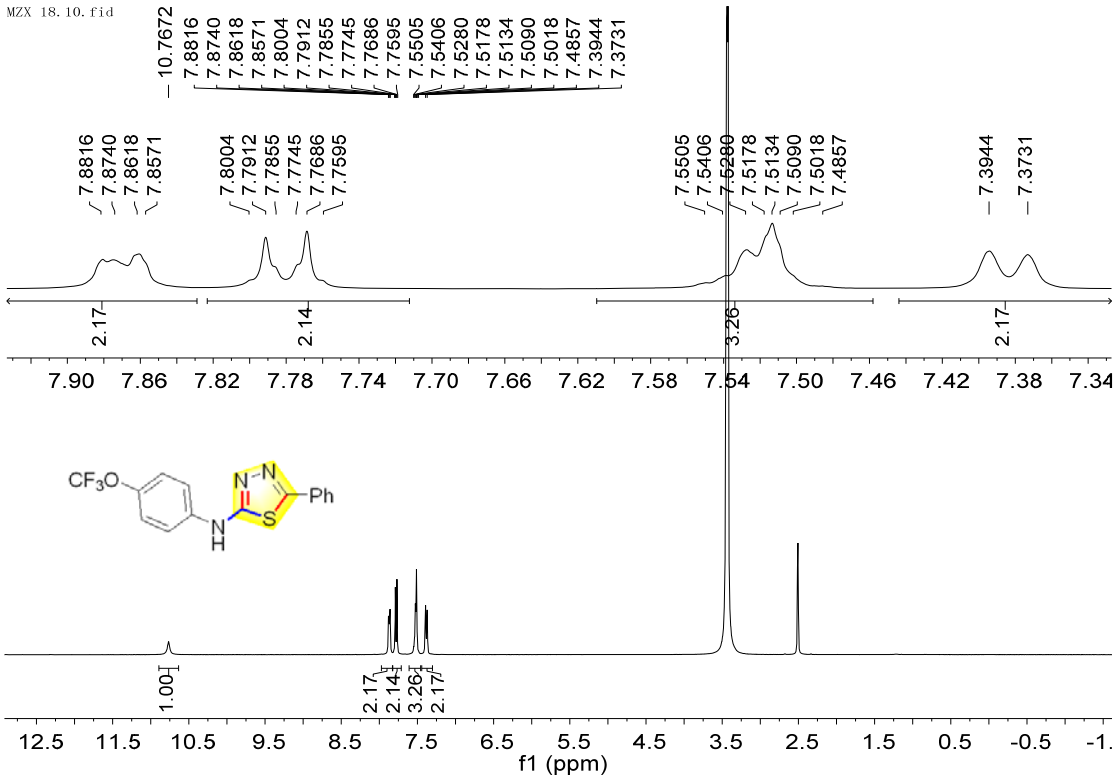
^{13}C NMR



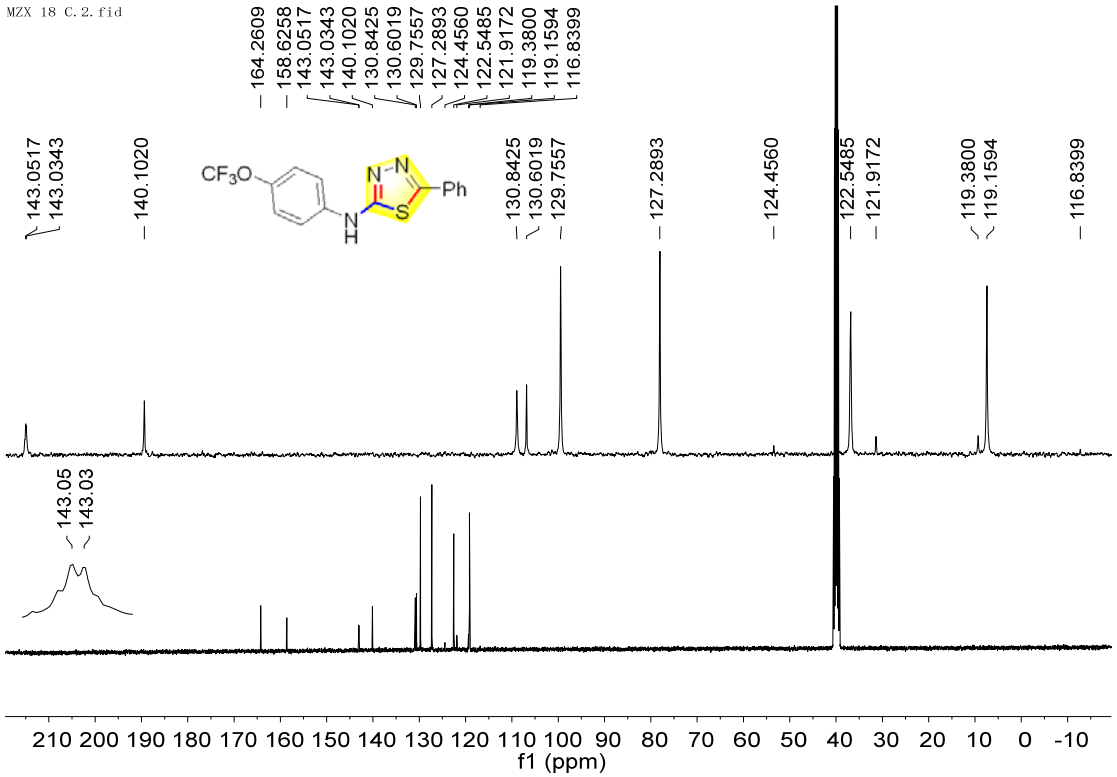
DEPT 90 and DEPT 135



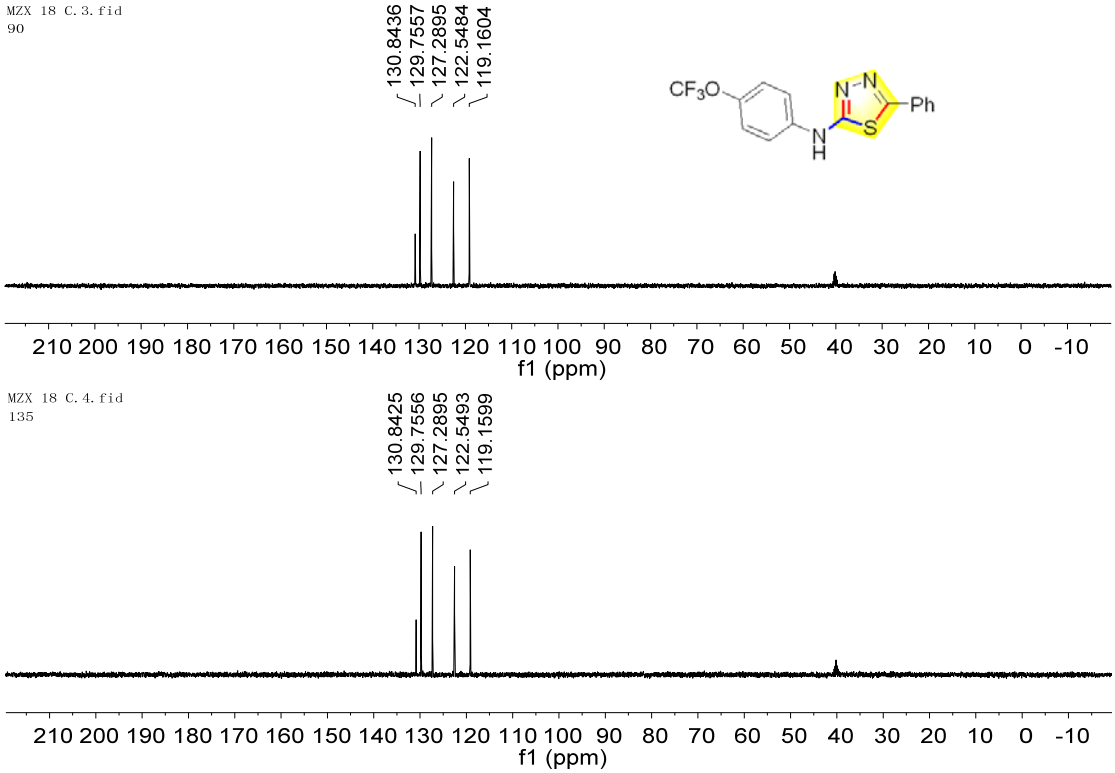
3e, ^{1}H NMR



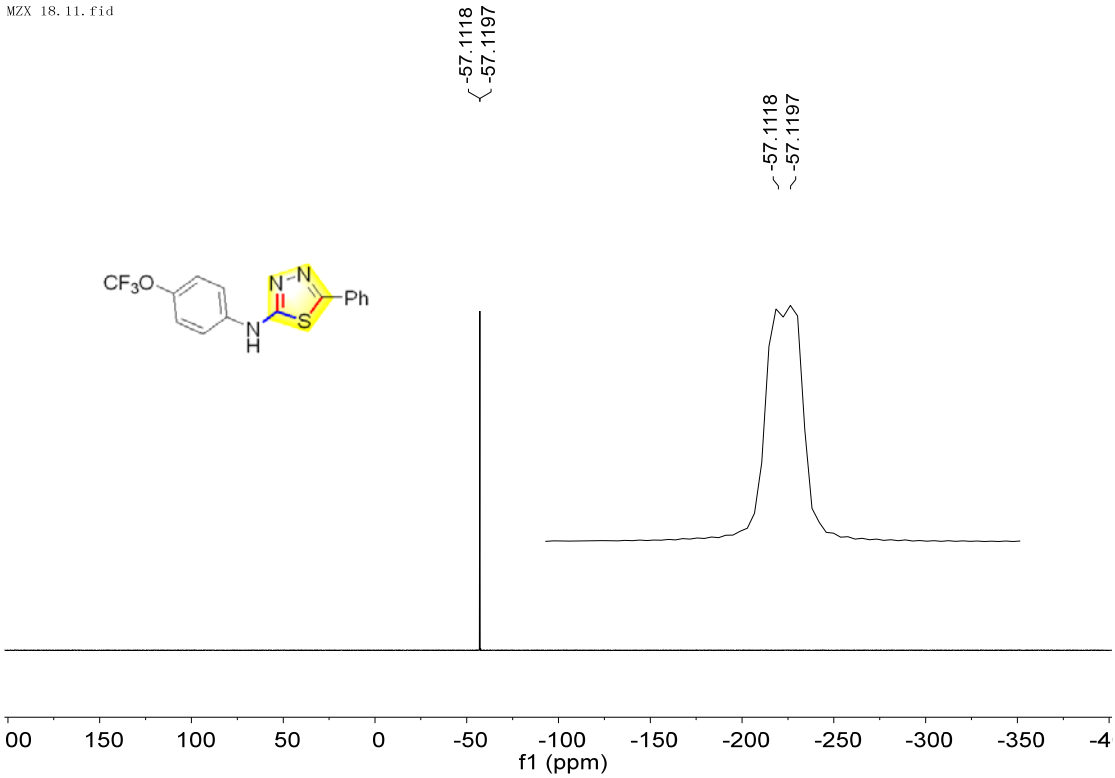
^{13}C NMR



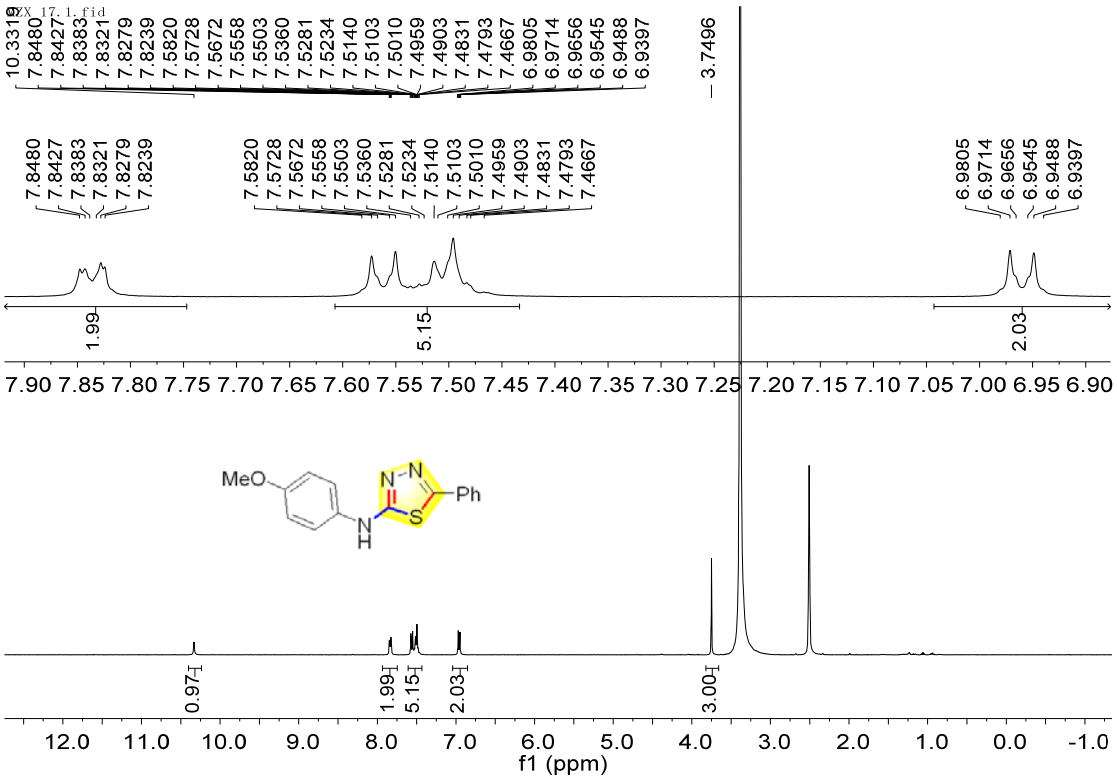
DEPT 90 and DEPT 135



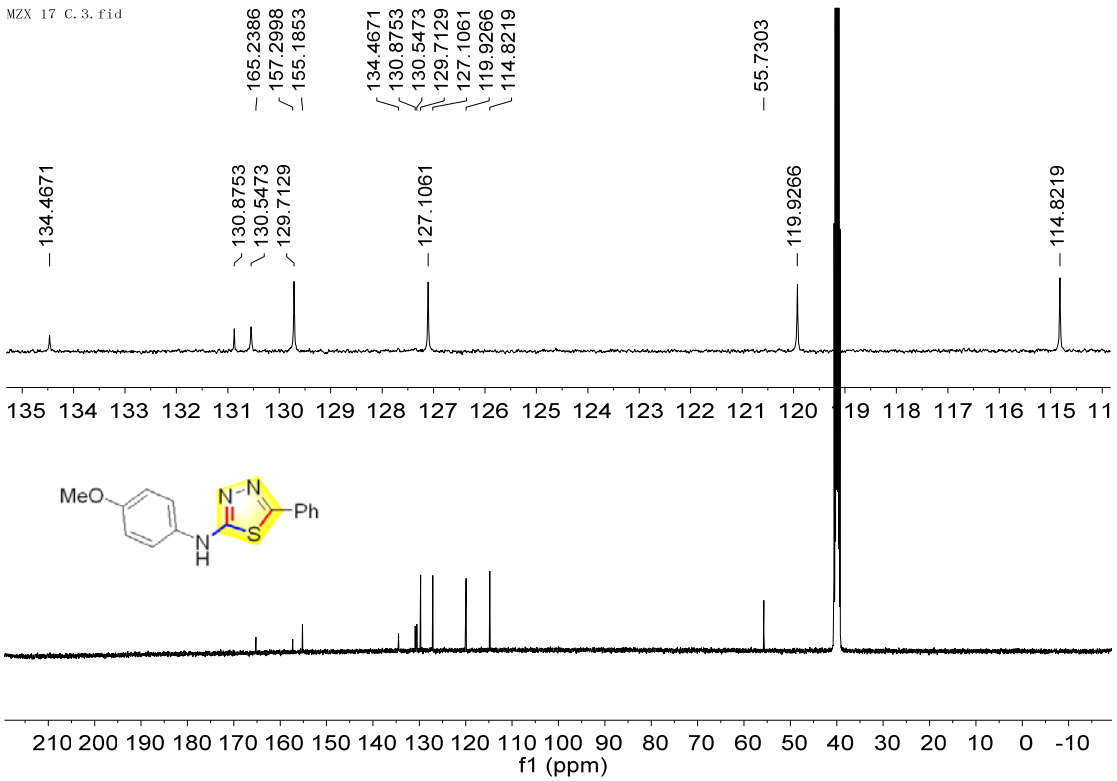
^{19}F NMR



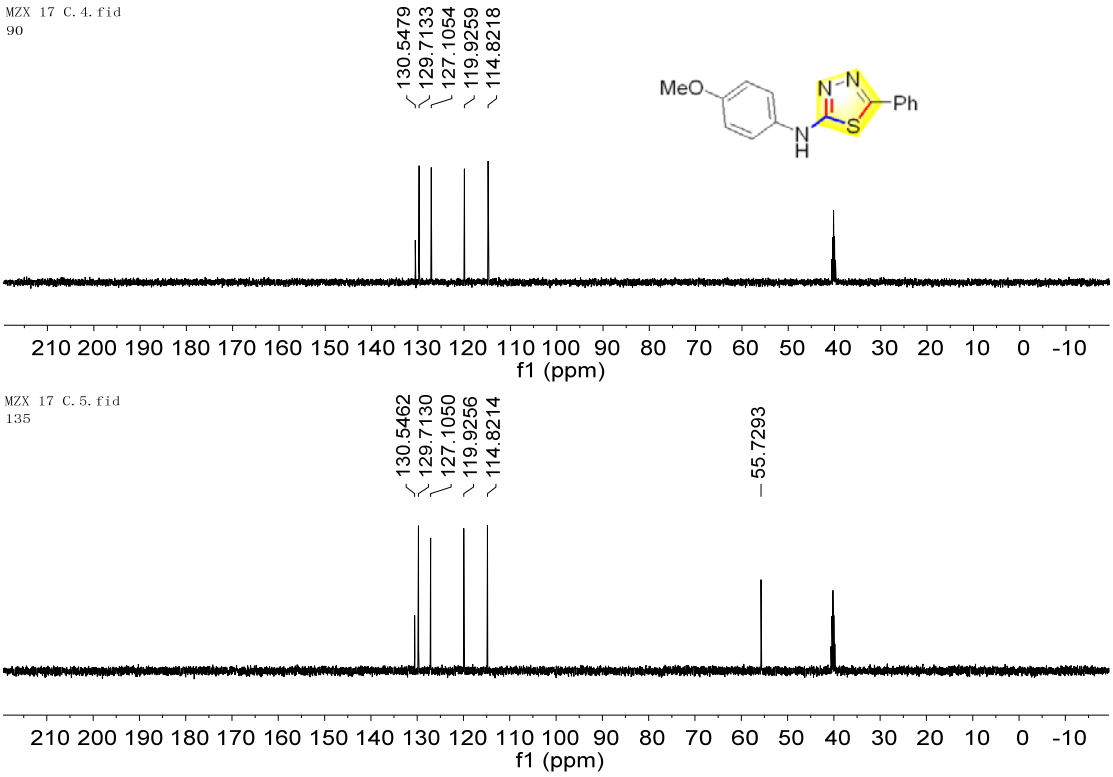
3f, ^{1}H NMR



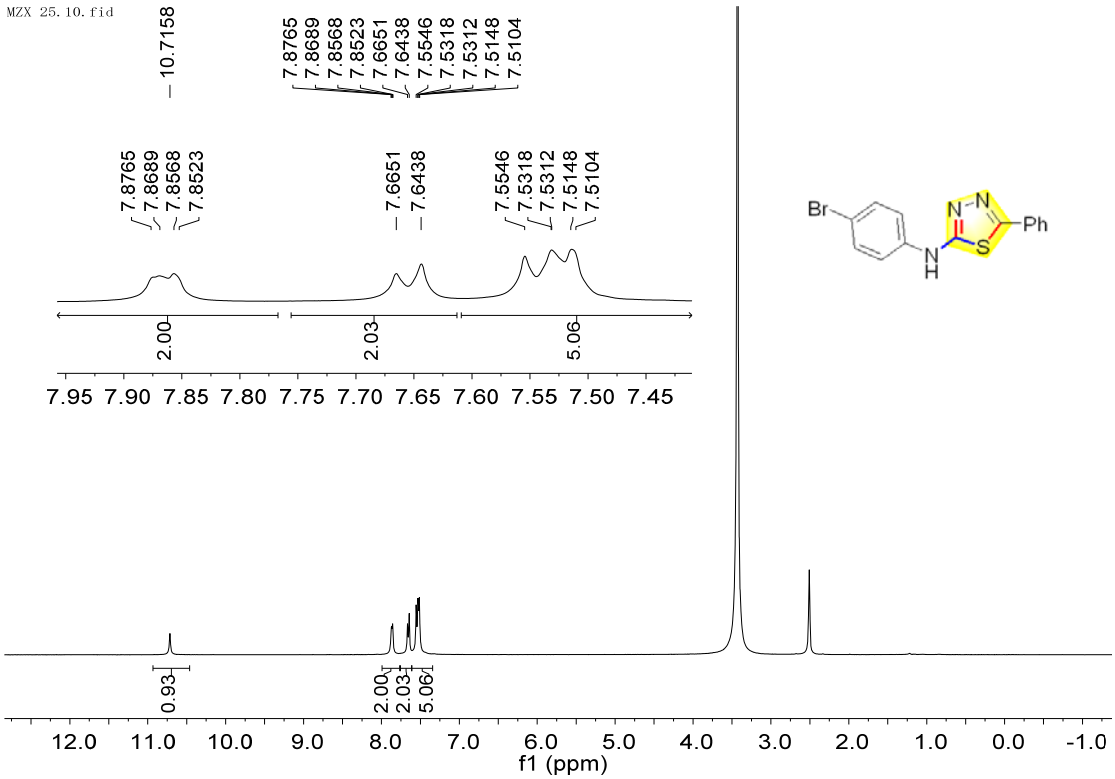
^{13}C NMR



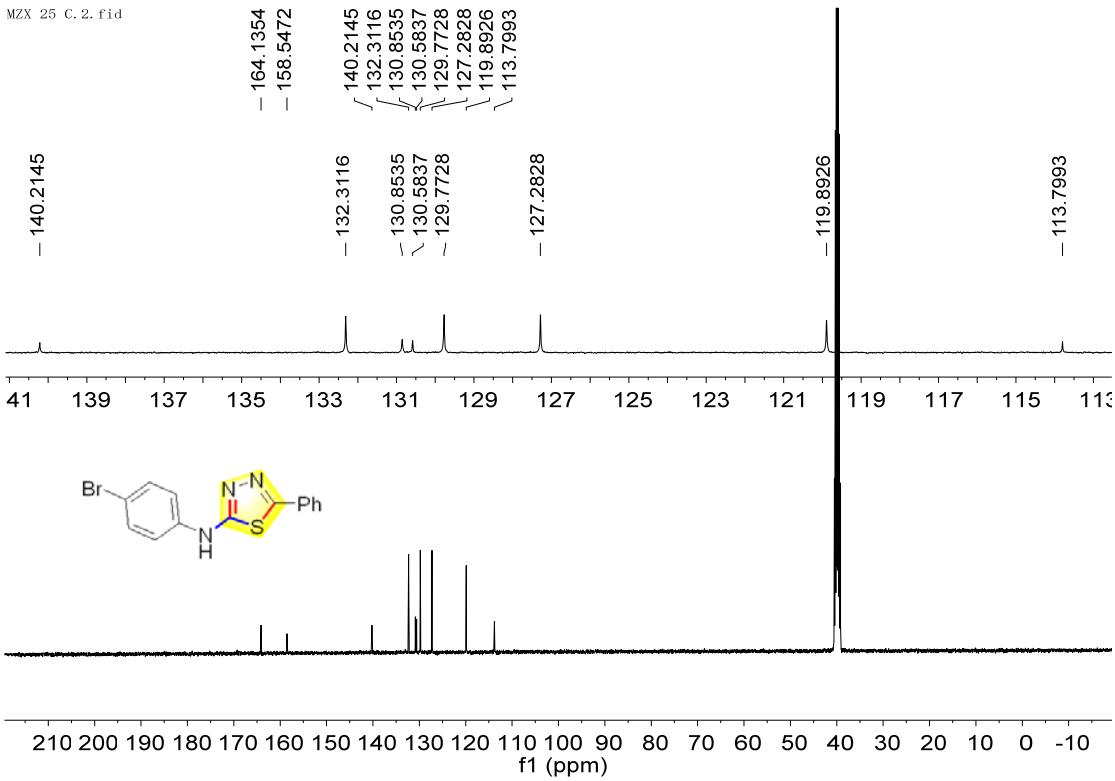
DEPT 90 and DEPT 135



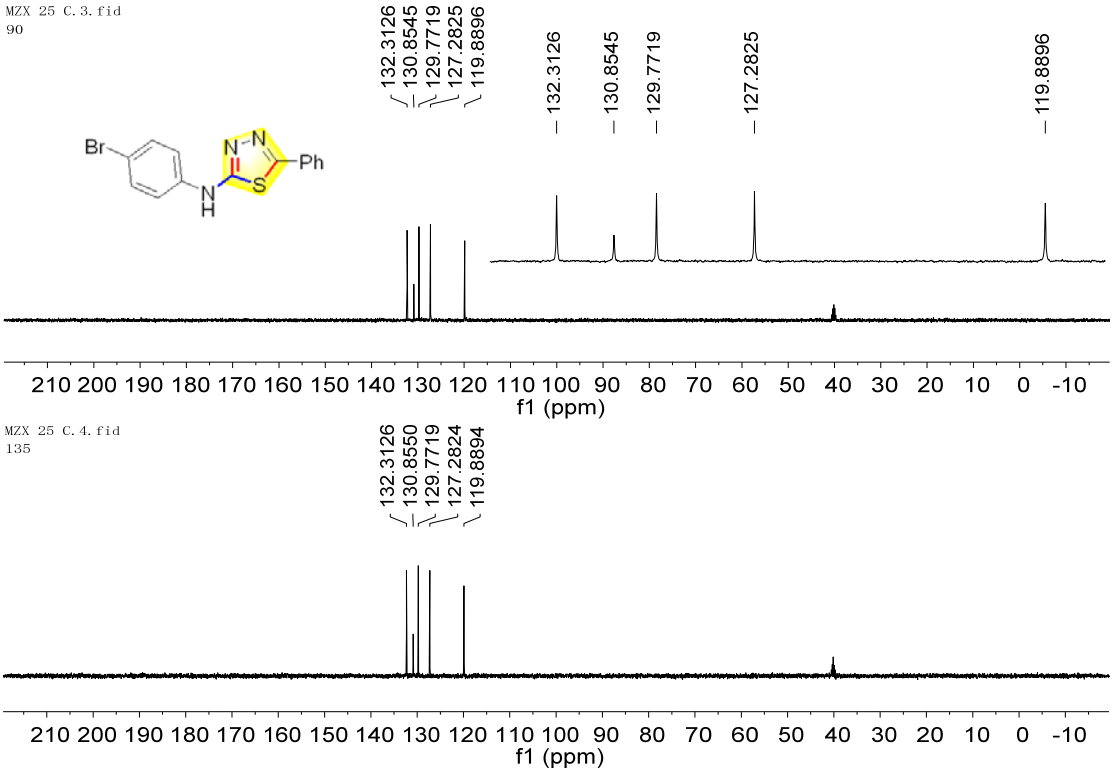
3g, ^{1}H NMR



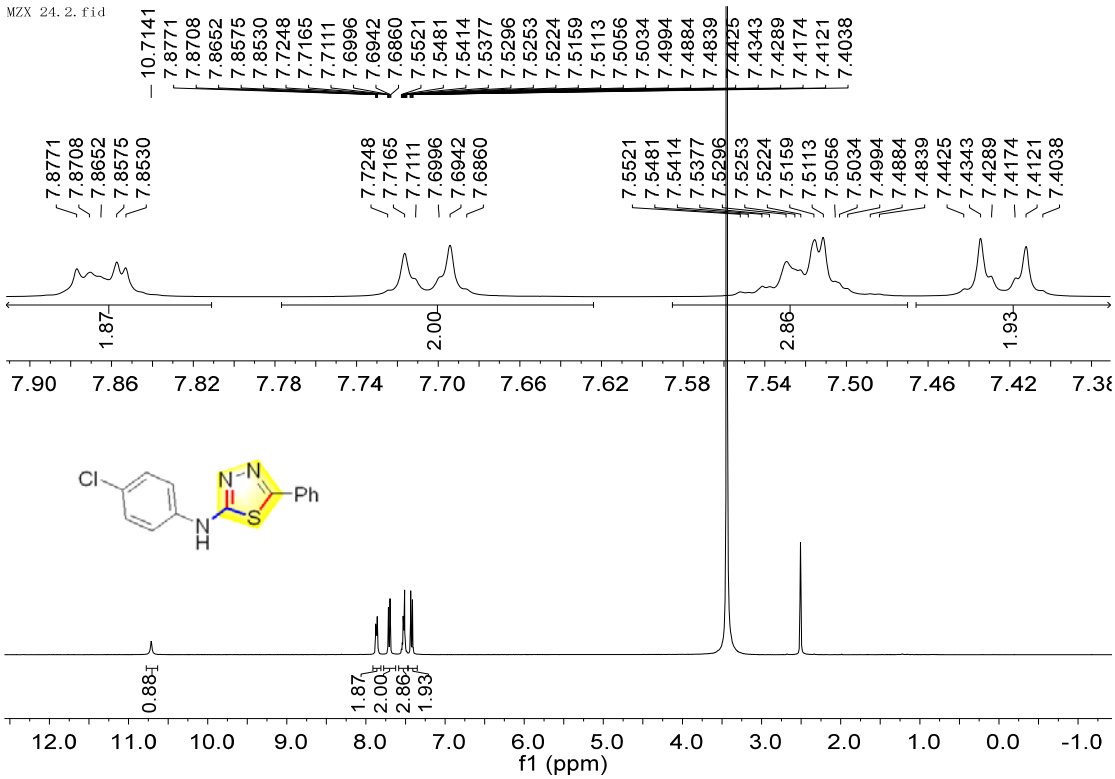
^{13}C NMR



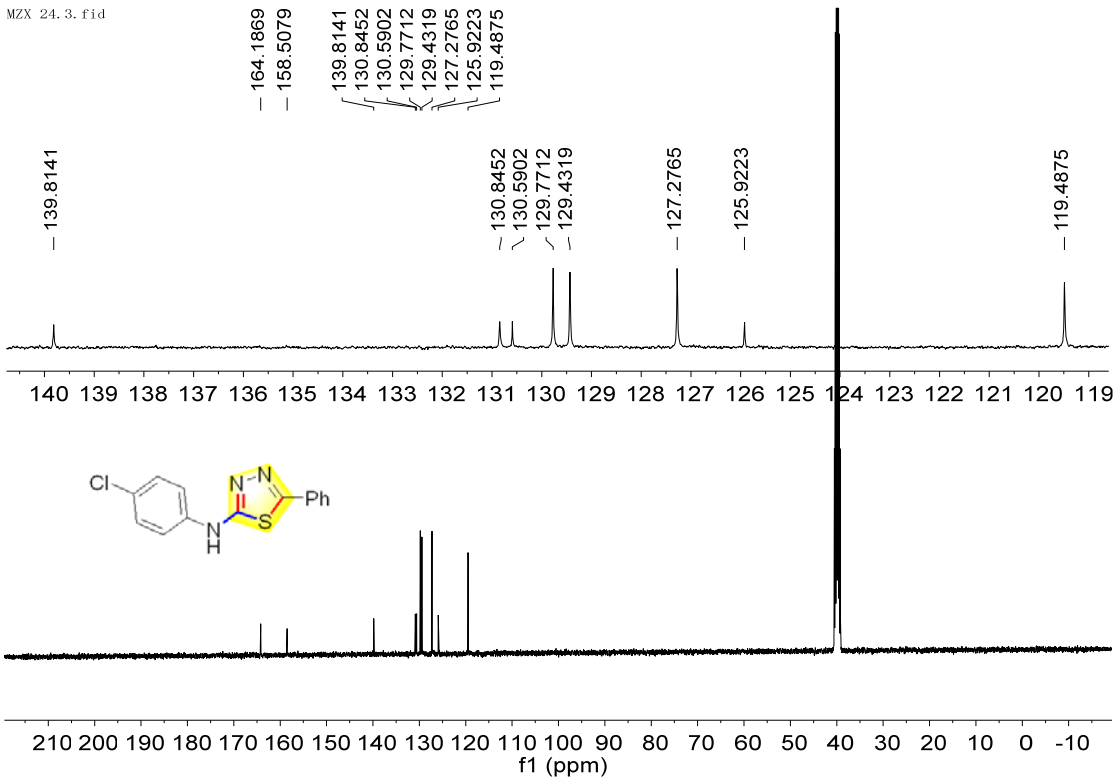
DEPT 90 and DEPT 135



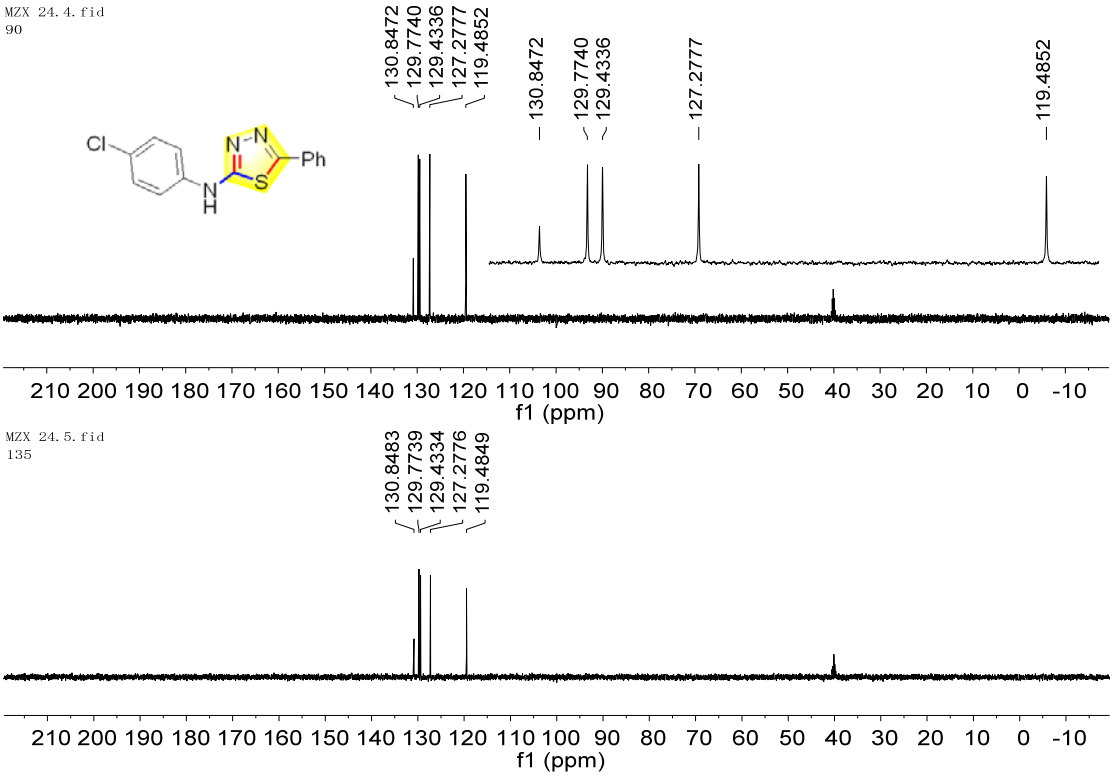
3h, ^{1}H NMR



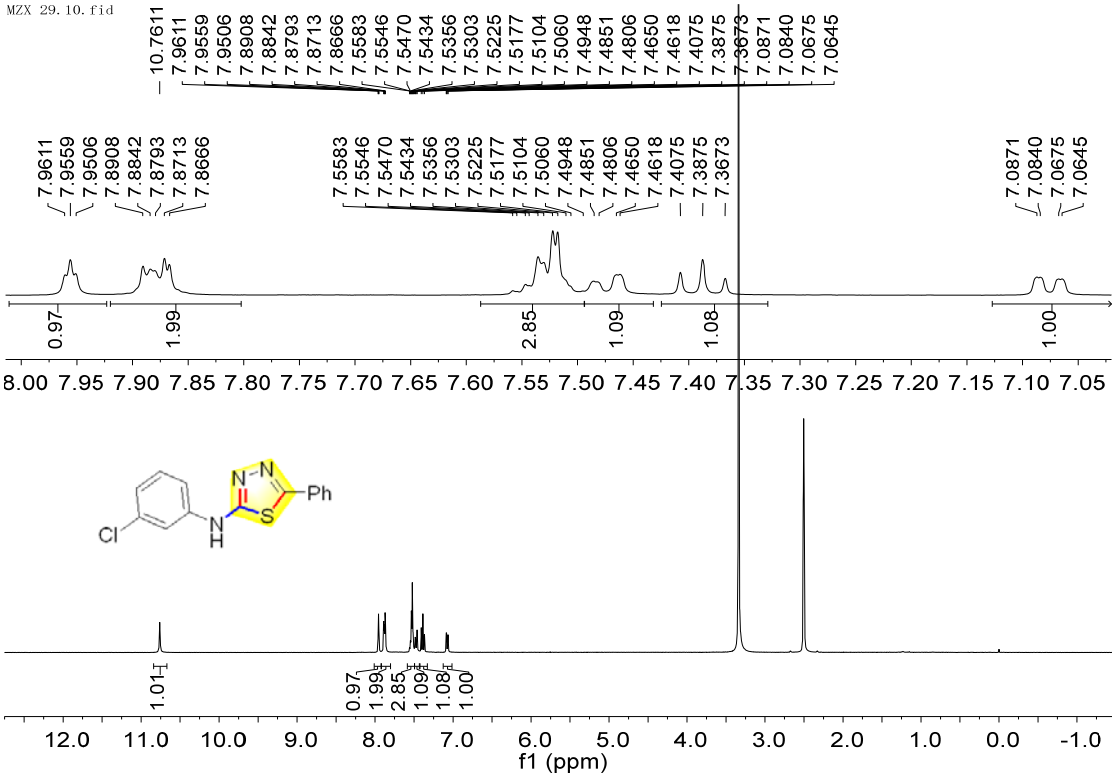
^{13}C NMR



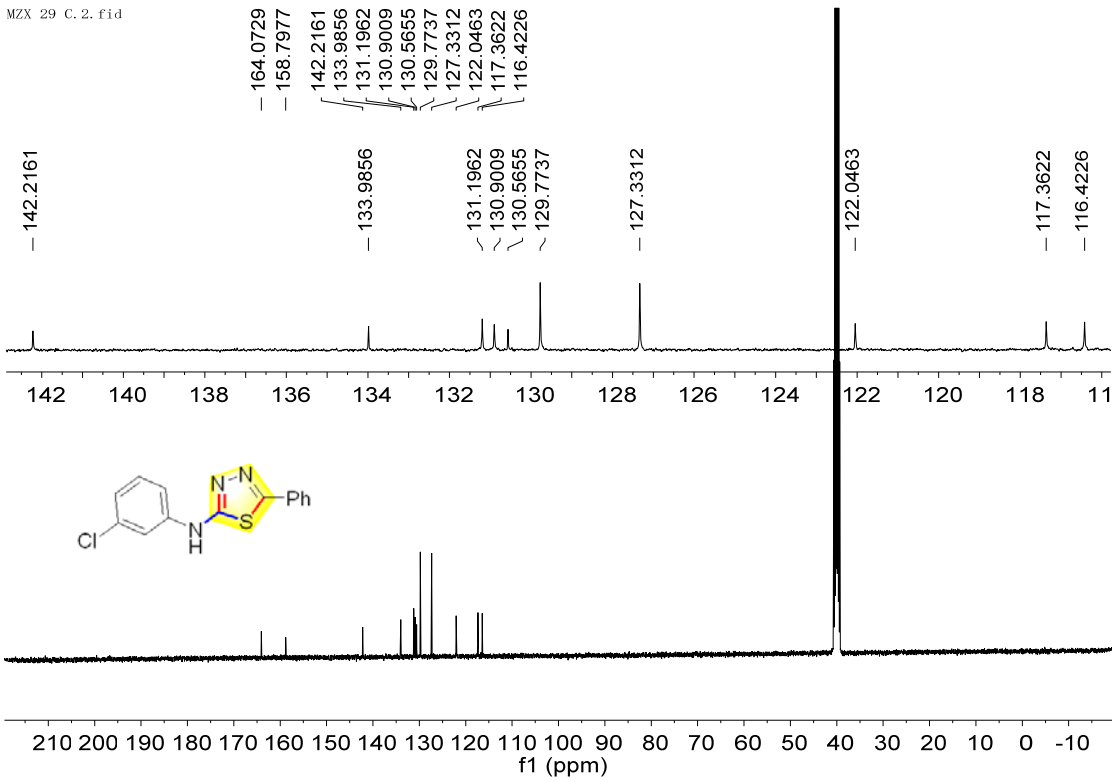
DEPT 90 and DEPT 135



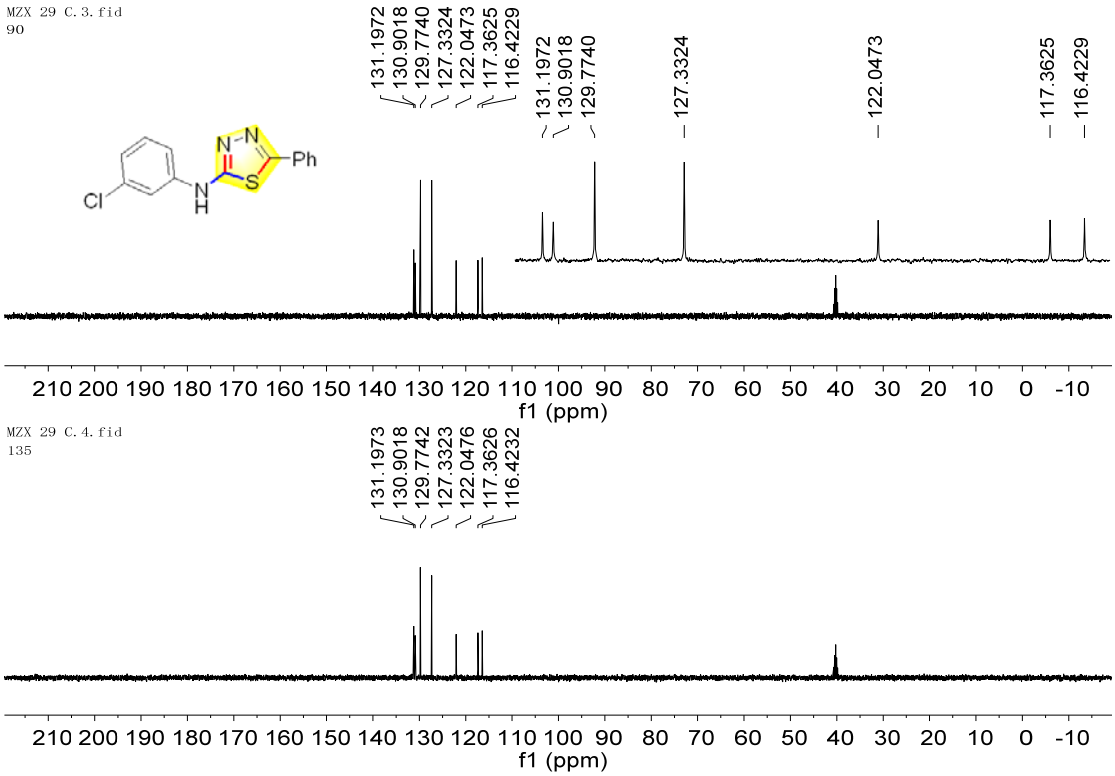
3i, ^{1}H NMR



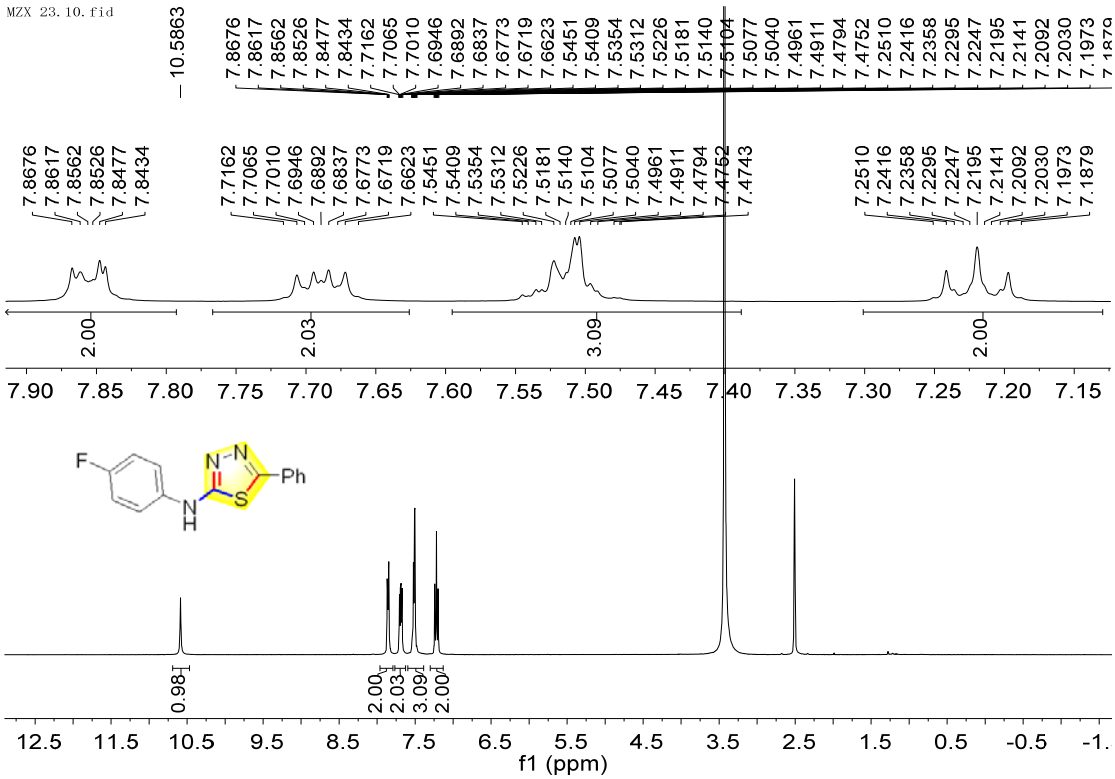
^{13}C NMR



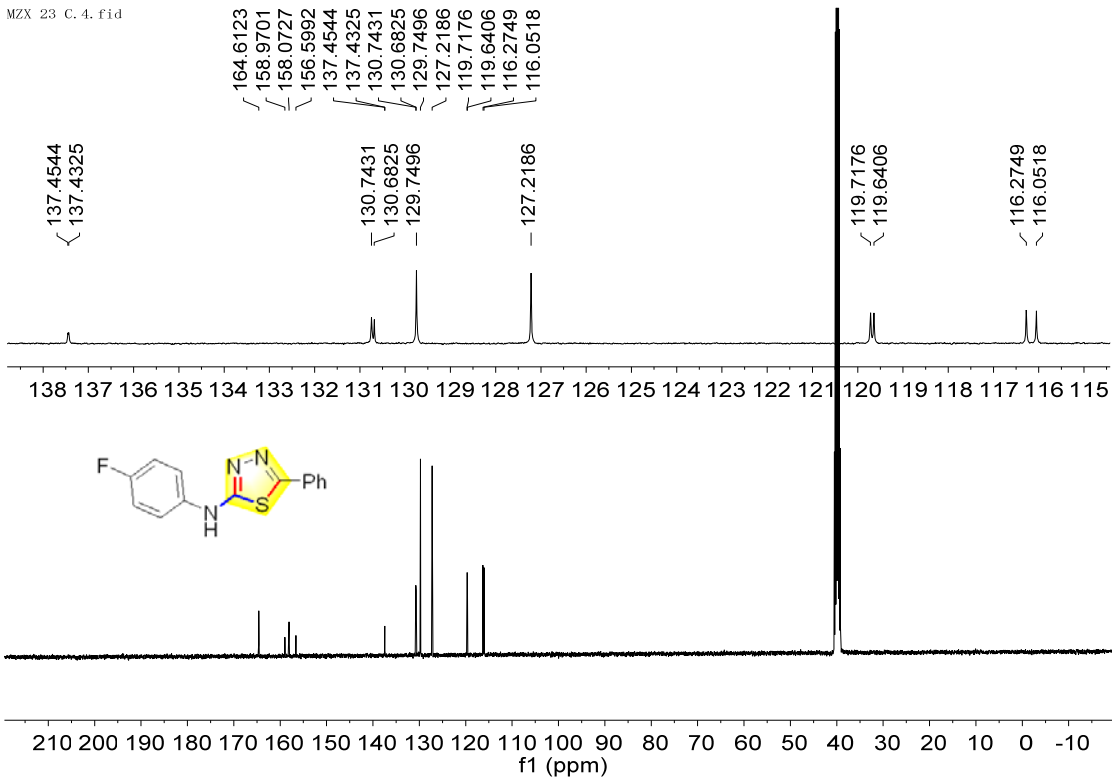
DEPT 90 and DEPT 135



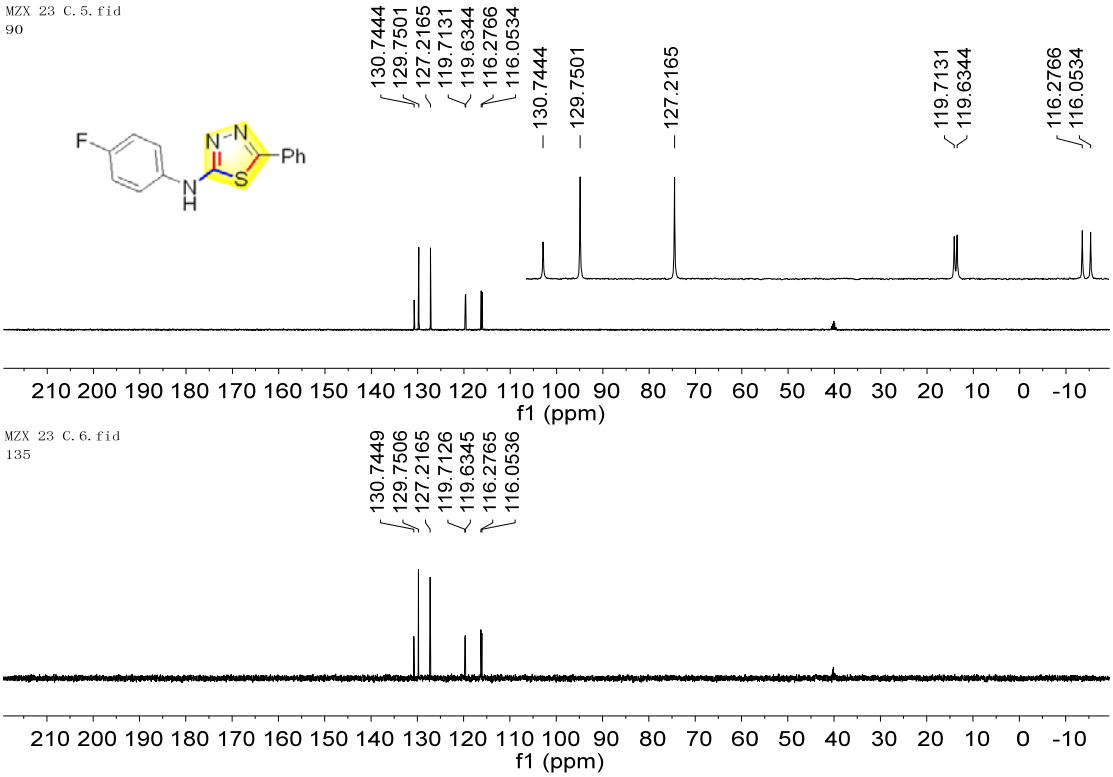
3j, ^{1}H NMR



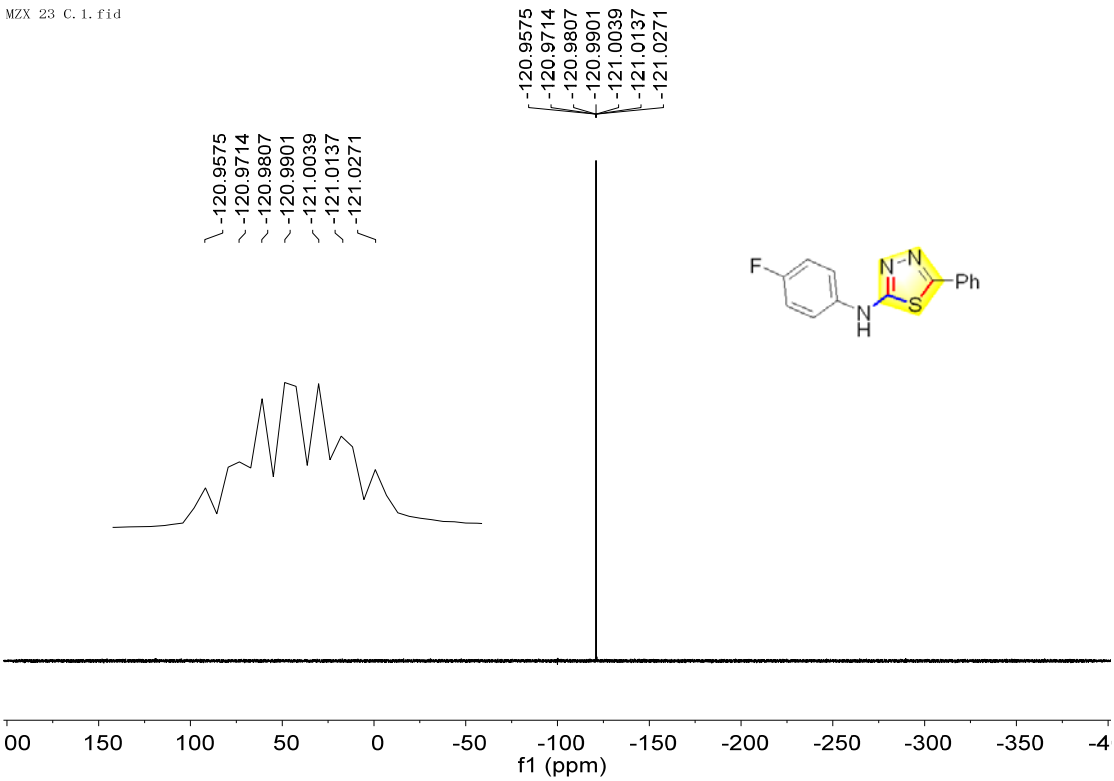
^{13}C NMR



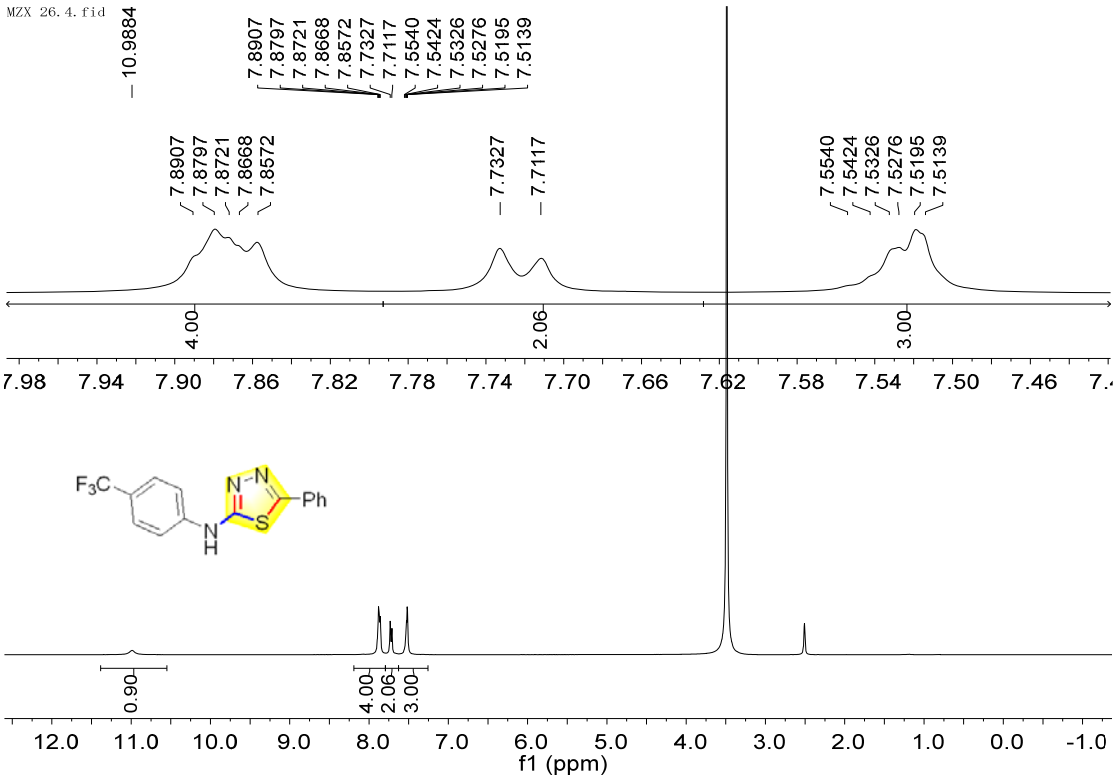
DEPT 90 and DEPT 135



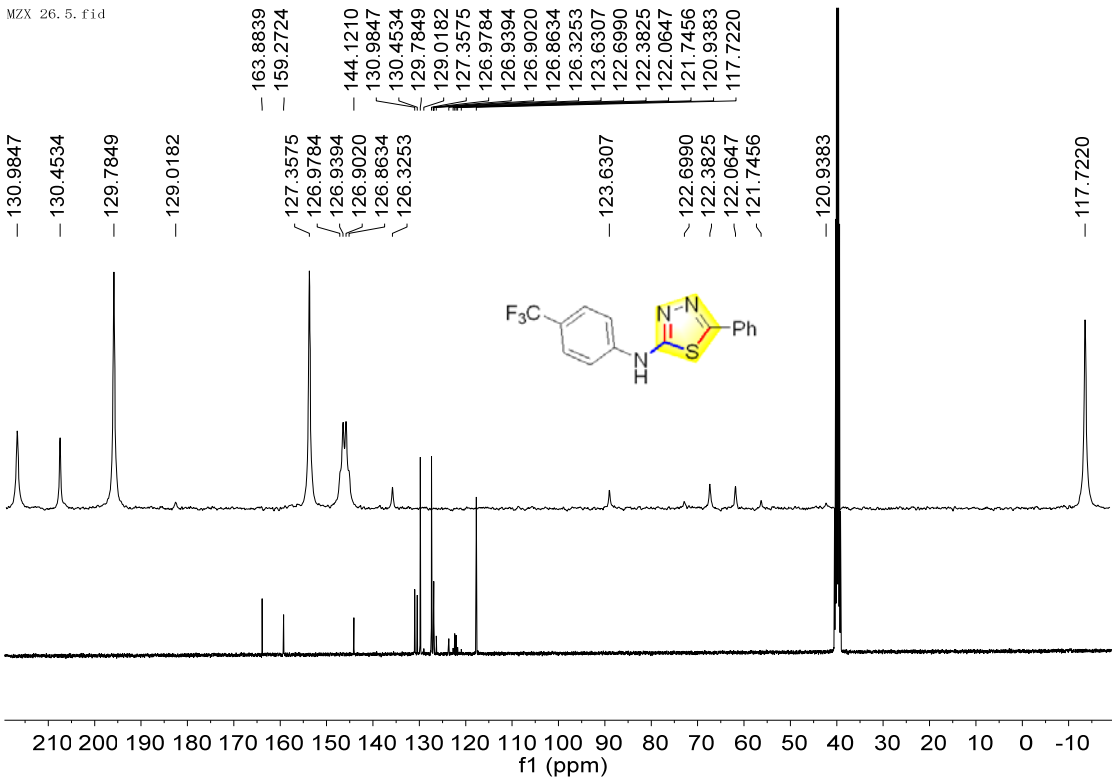
^{19}F NMR



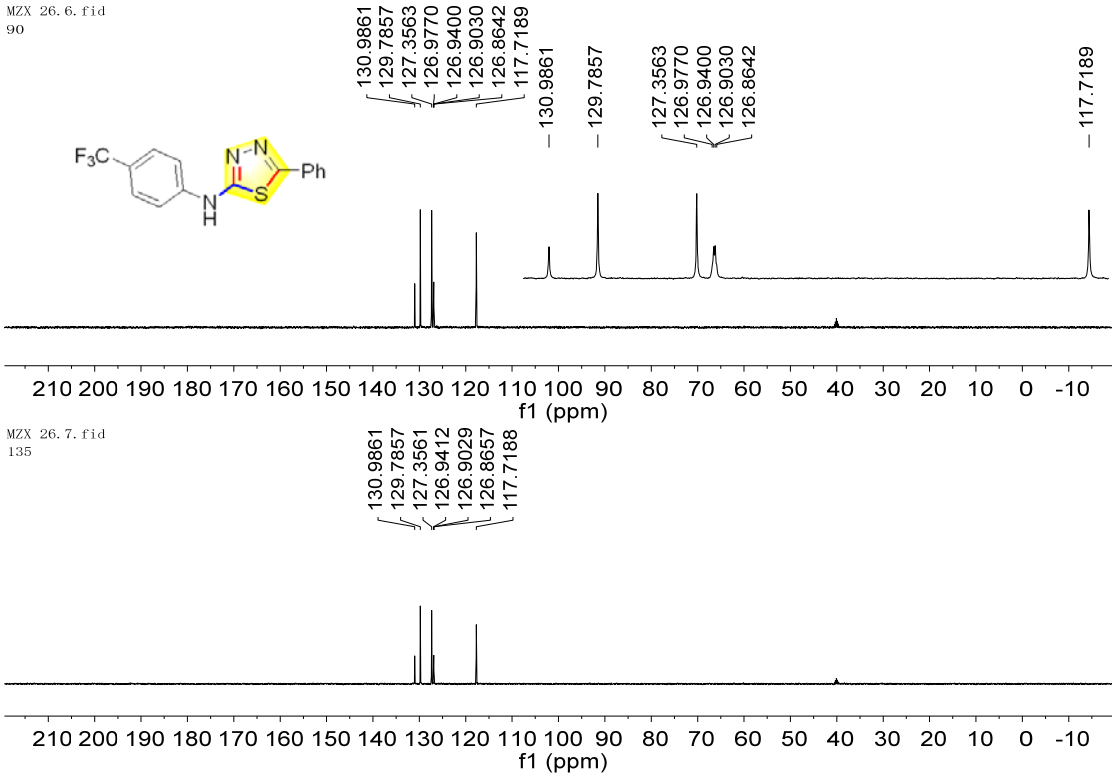
3k, ^{1}H NMR



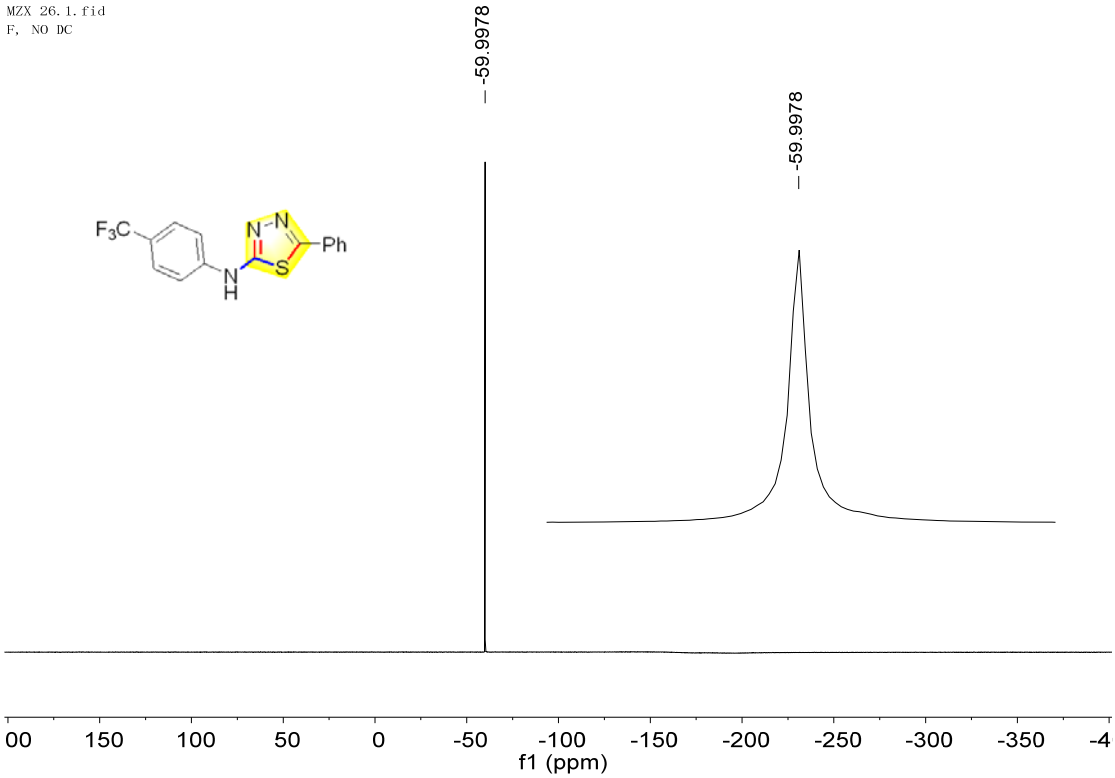
^{13}C NMR



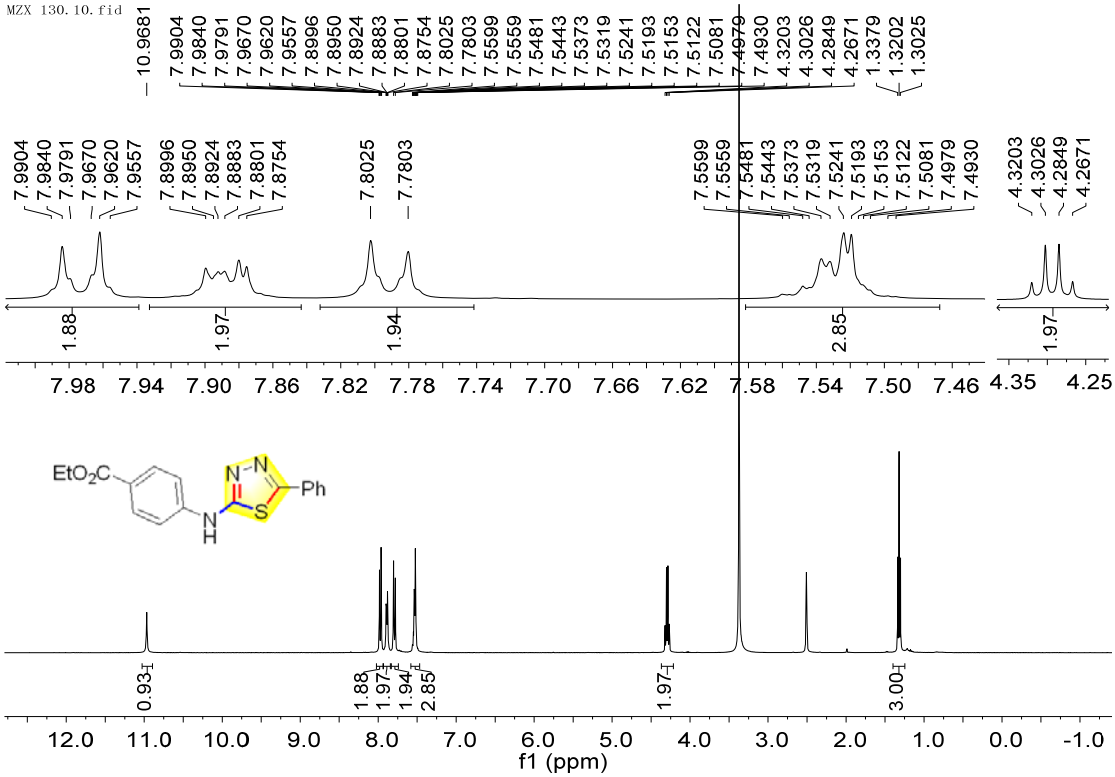
DEPT 90 and DEPT 135



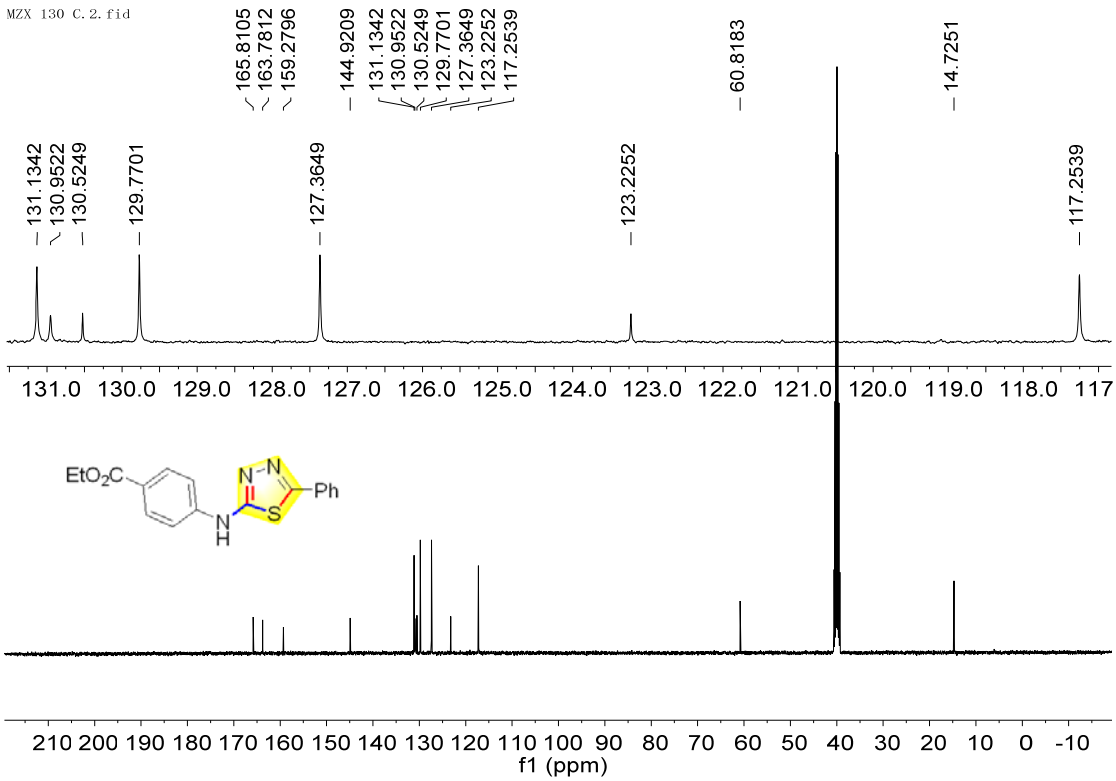
^{19}F NMR



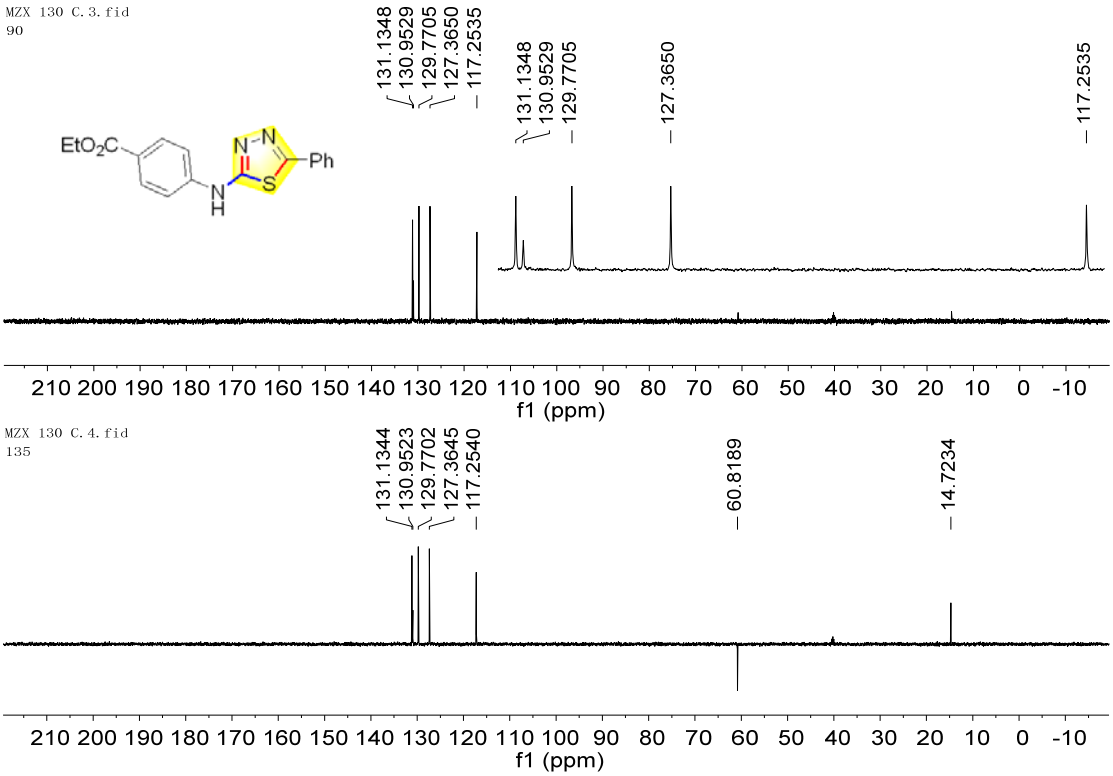
3l, ^{1}H NMR



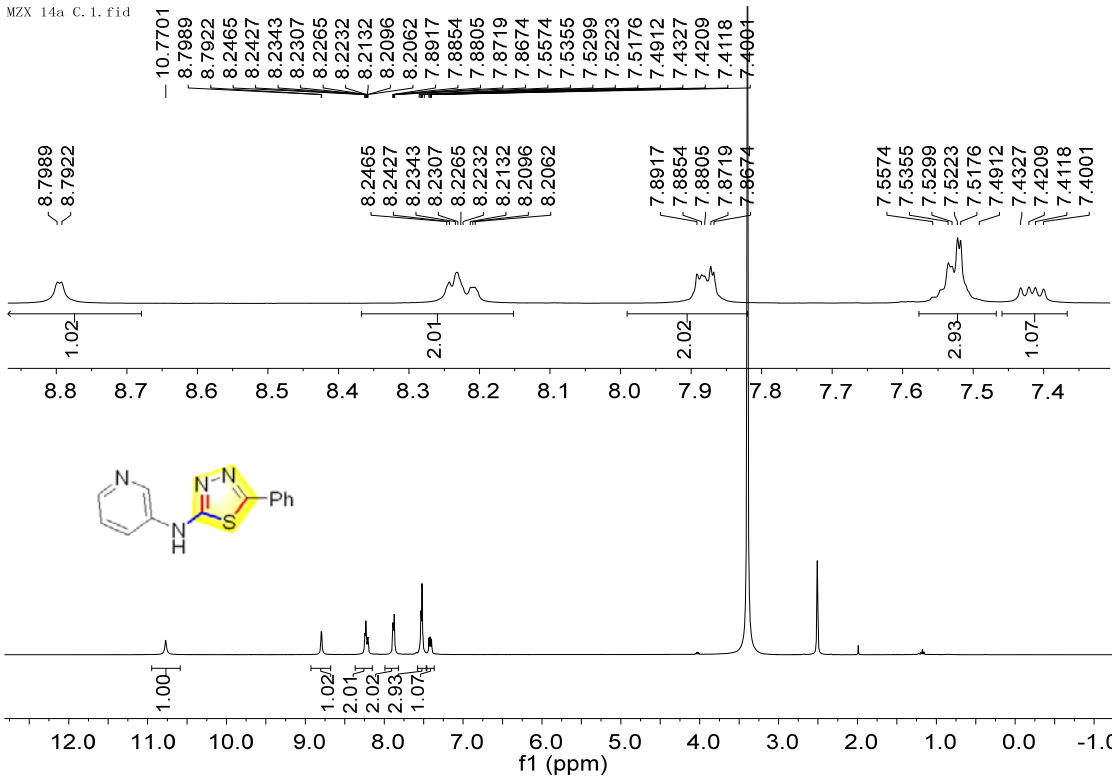
^{13}C NMR



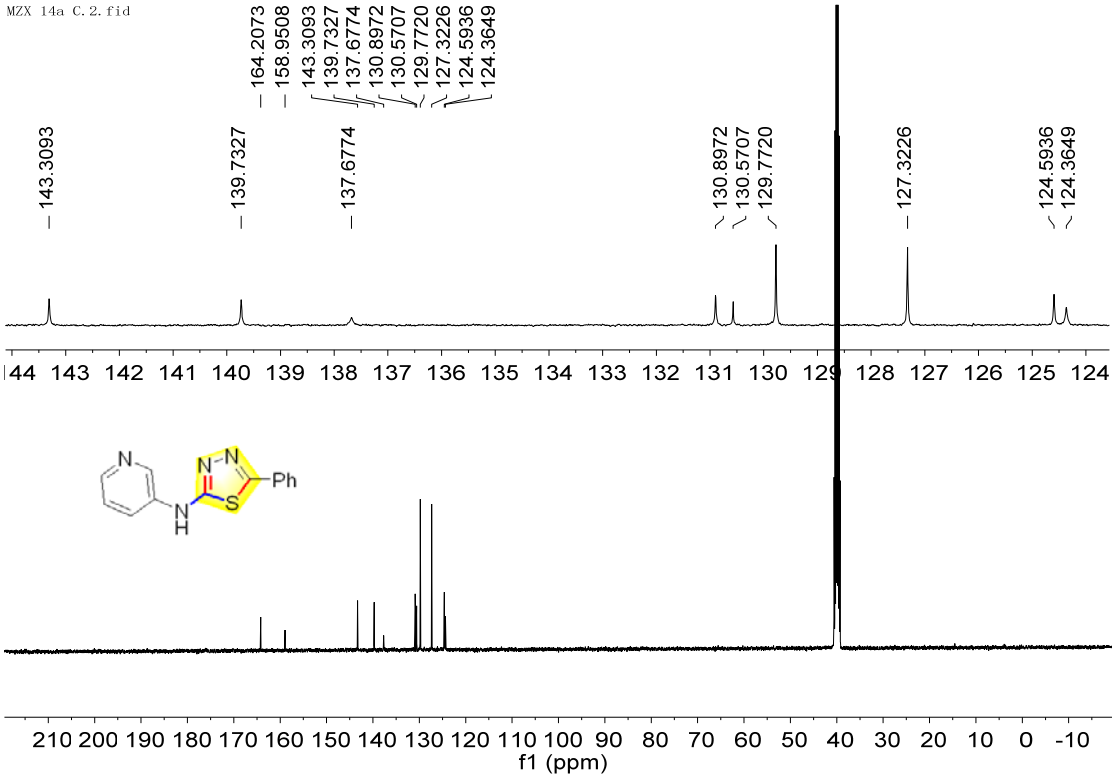
DEPT 90 and DEPT 135



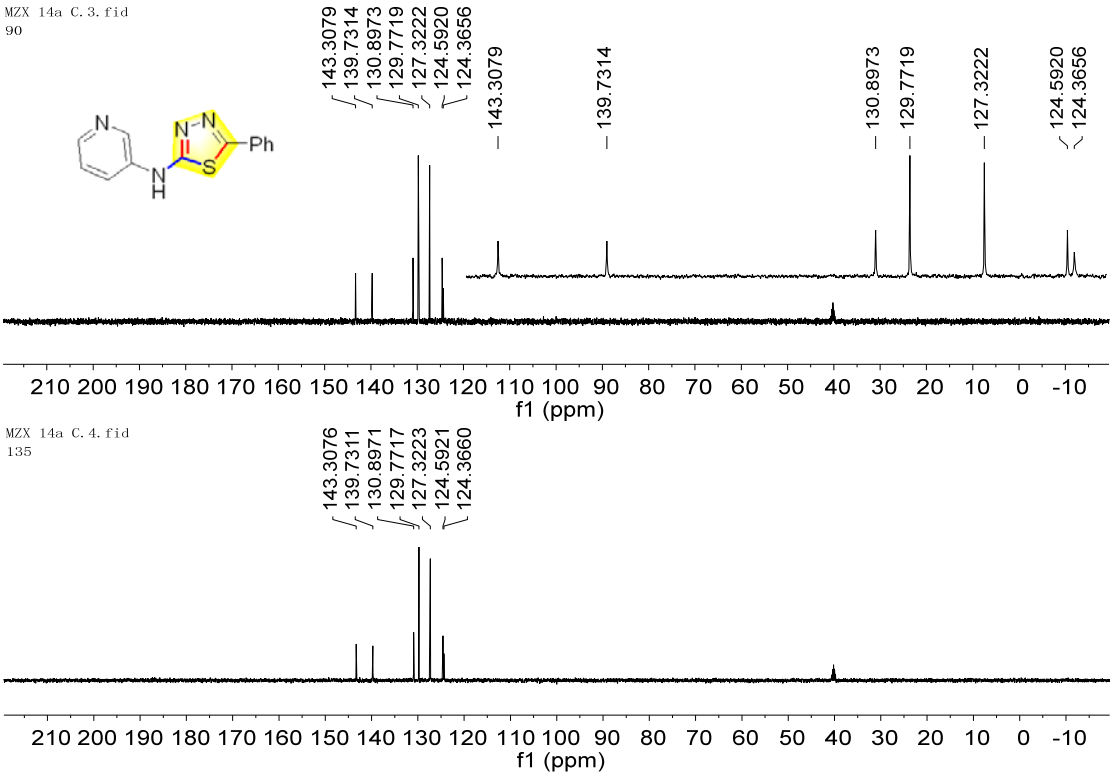
3m, ^{1}H NMR



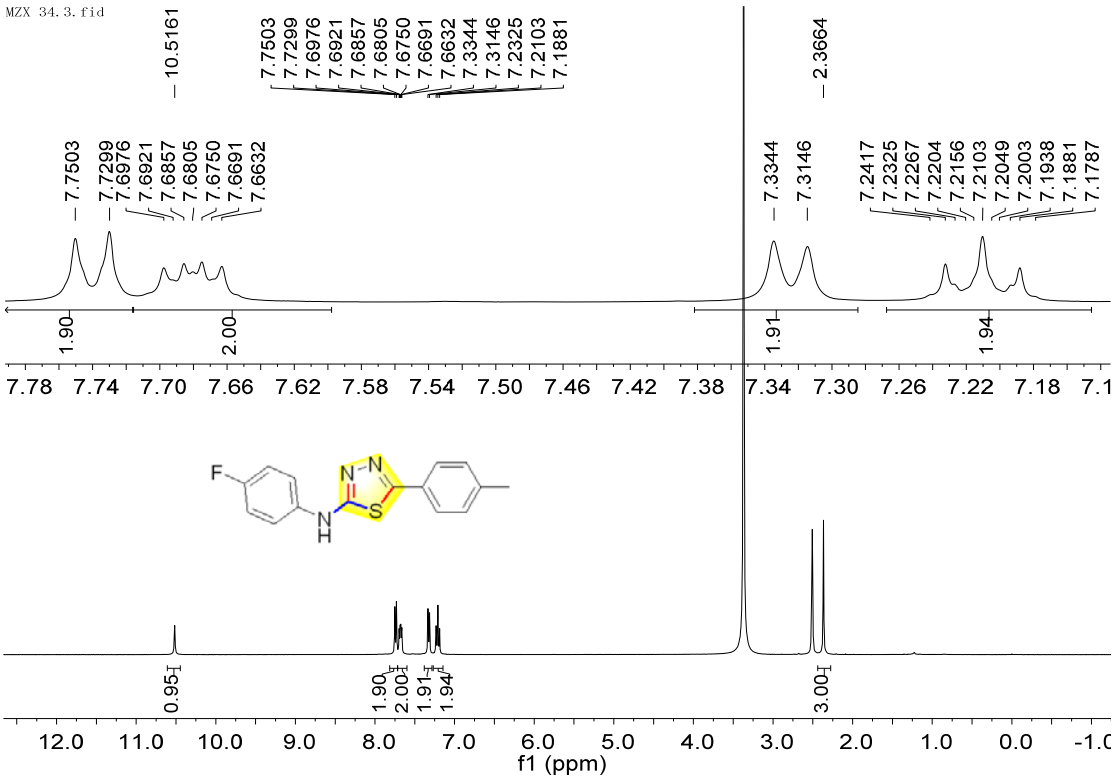
^{13}C NMR



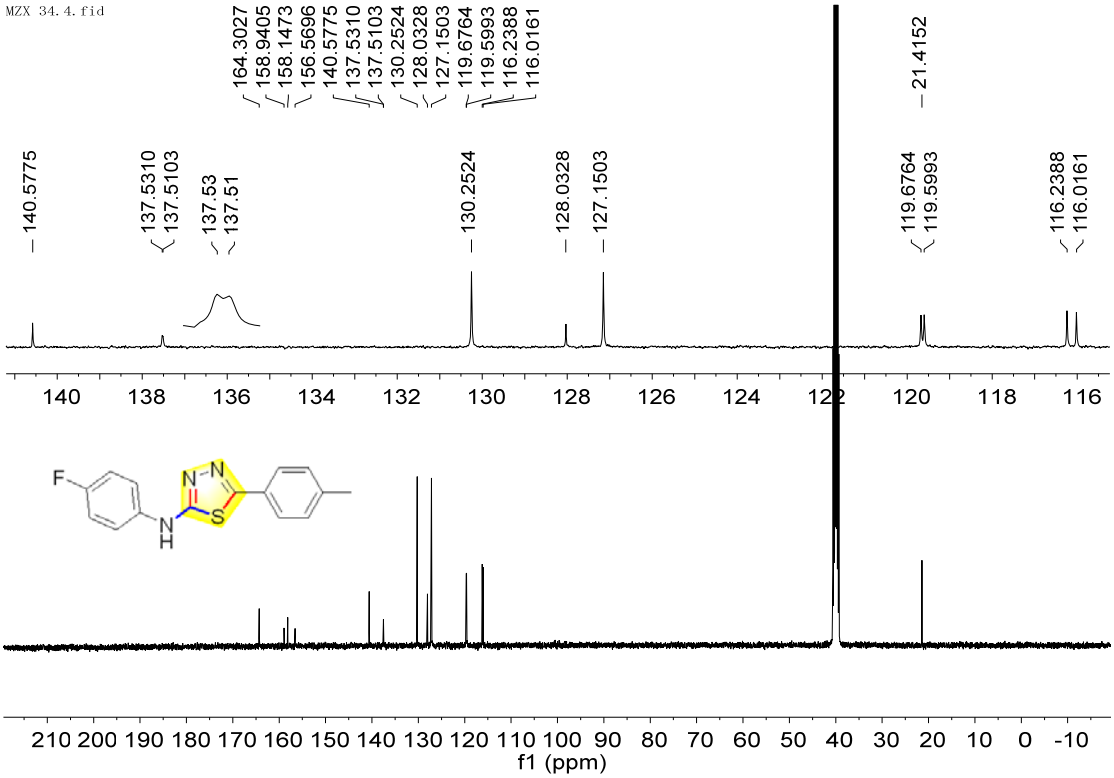
DEPT 90 and DEPT 135



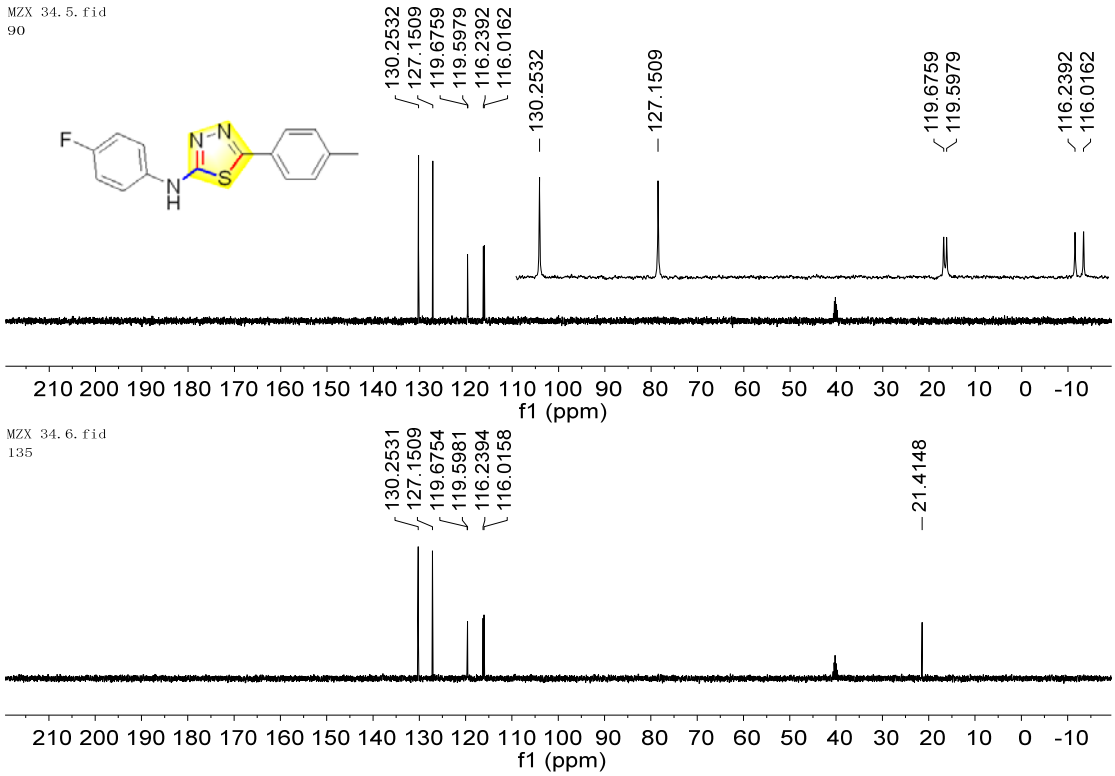
3n, ^{1}H NMR



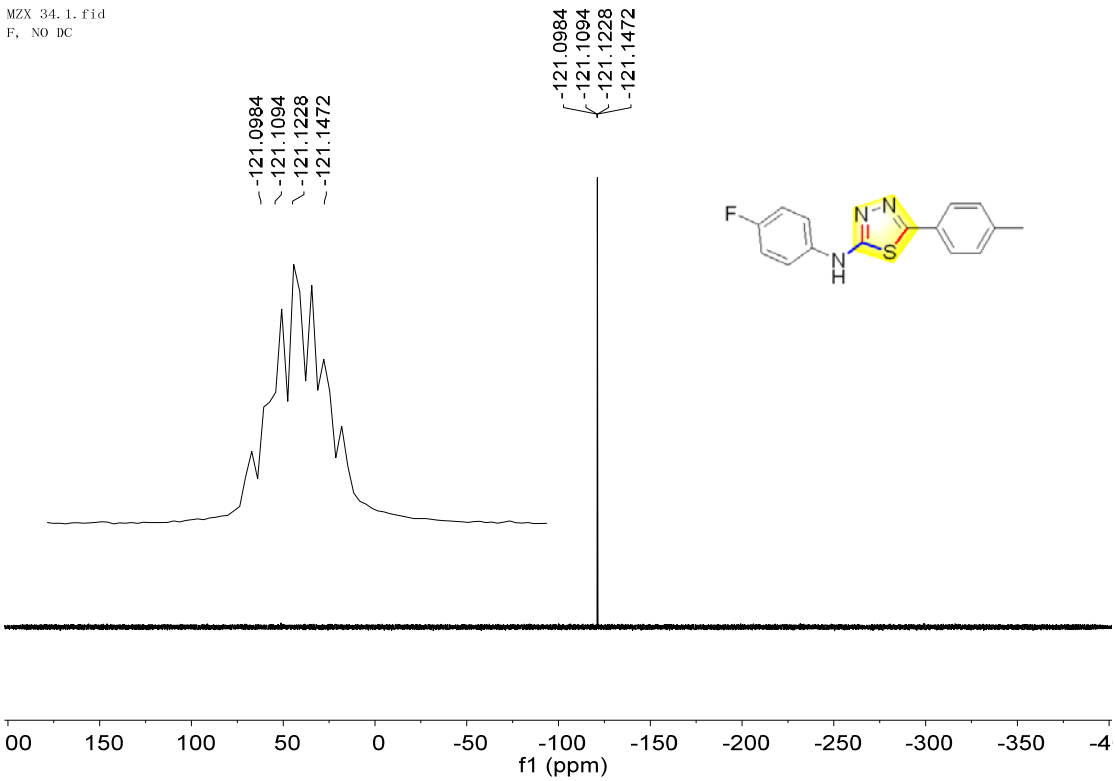
^{13}C NMR



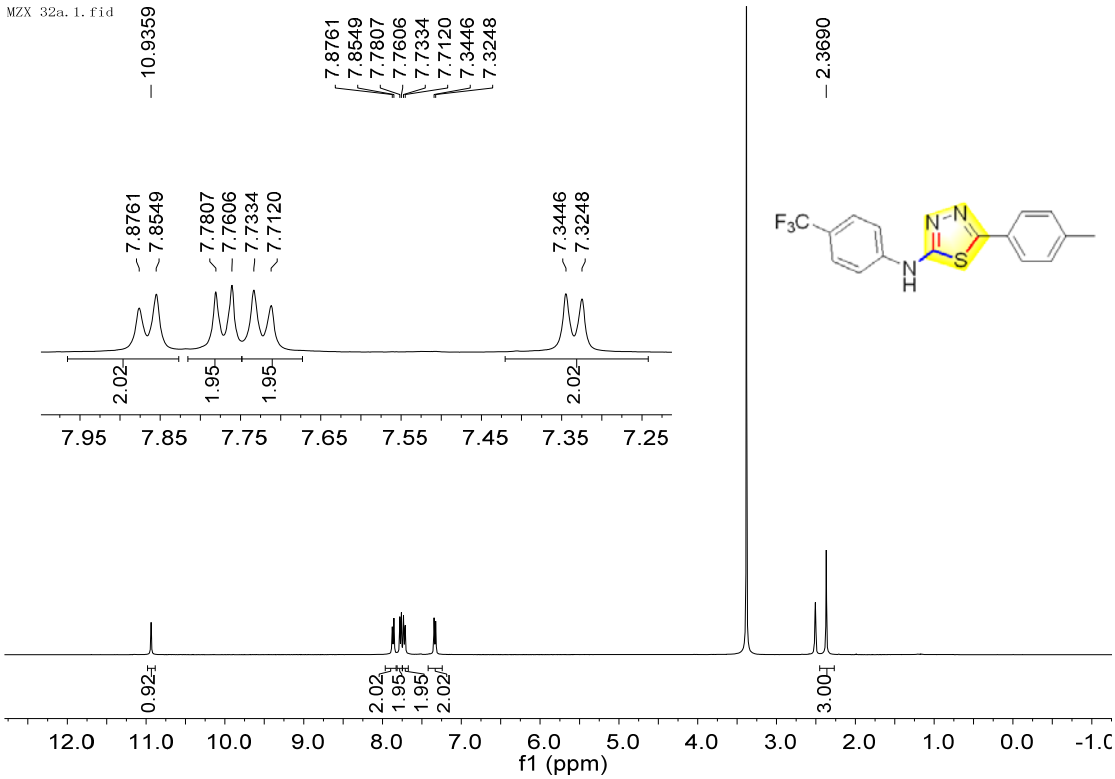
DEPT 90 and DEPT 135



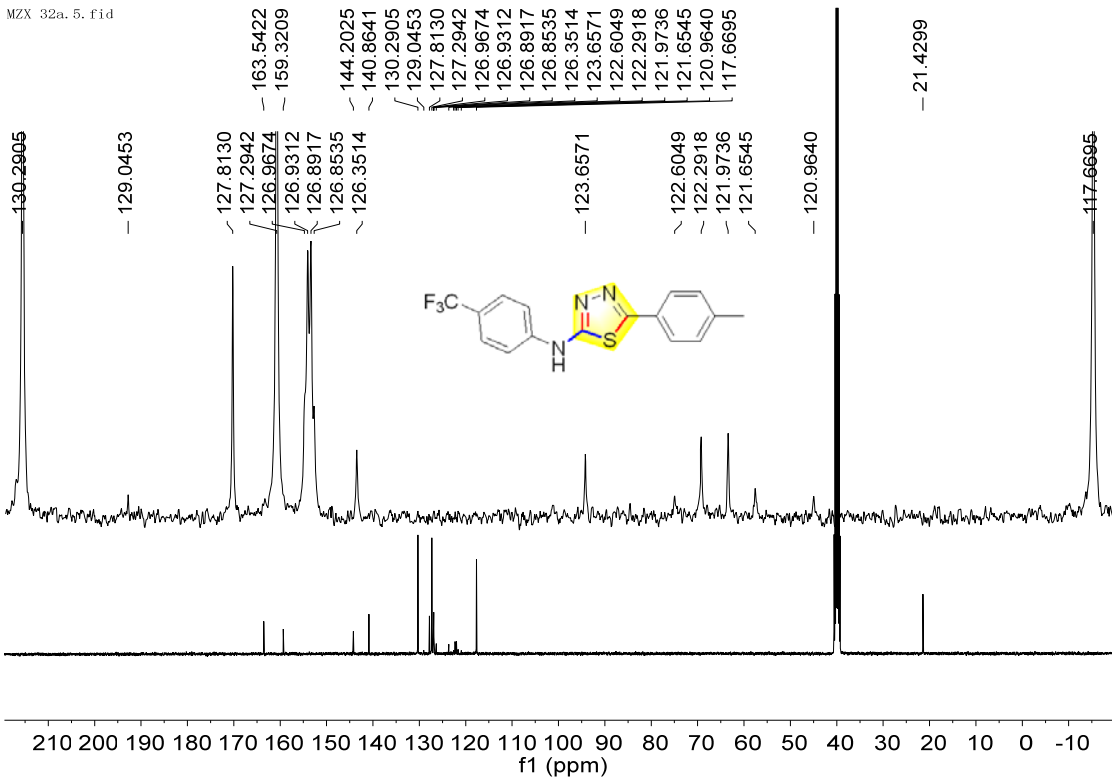
^{19}F NMR



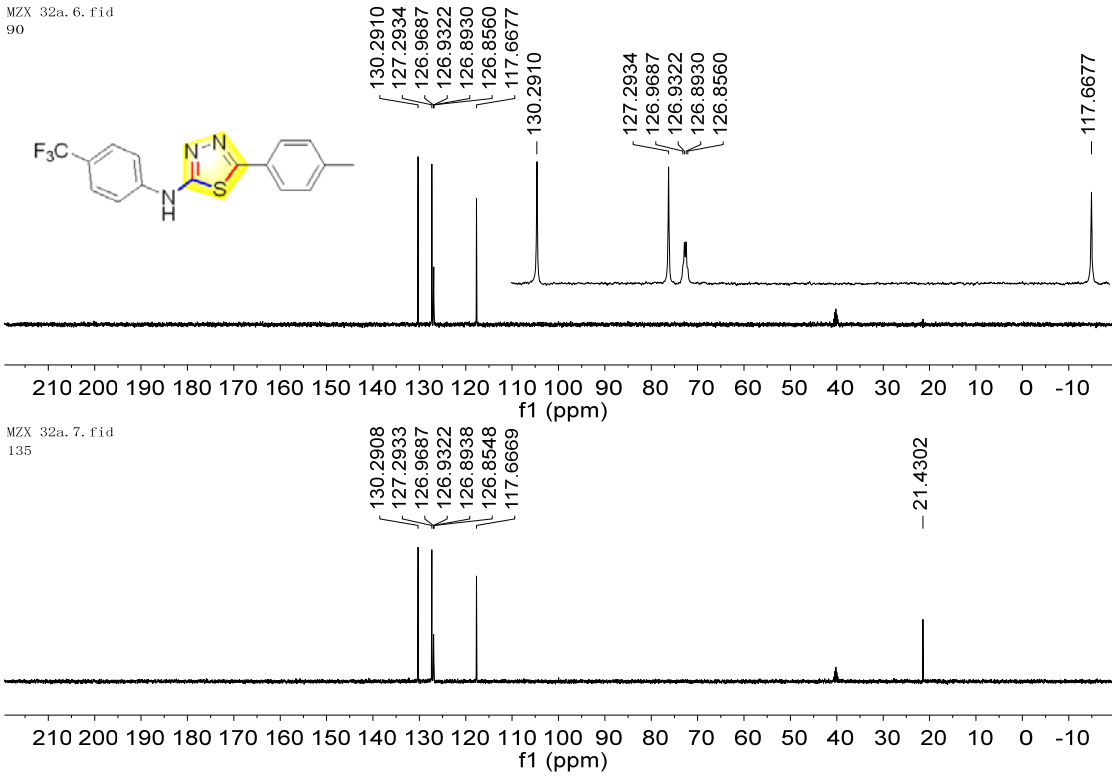
3o, ^{1}H NMR



^{13}C NMR



DEPT 90 and DEPT 135



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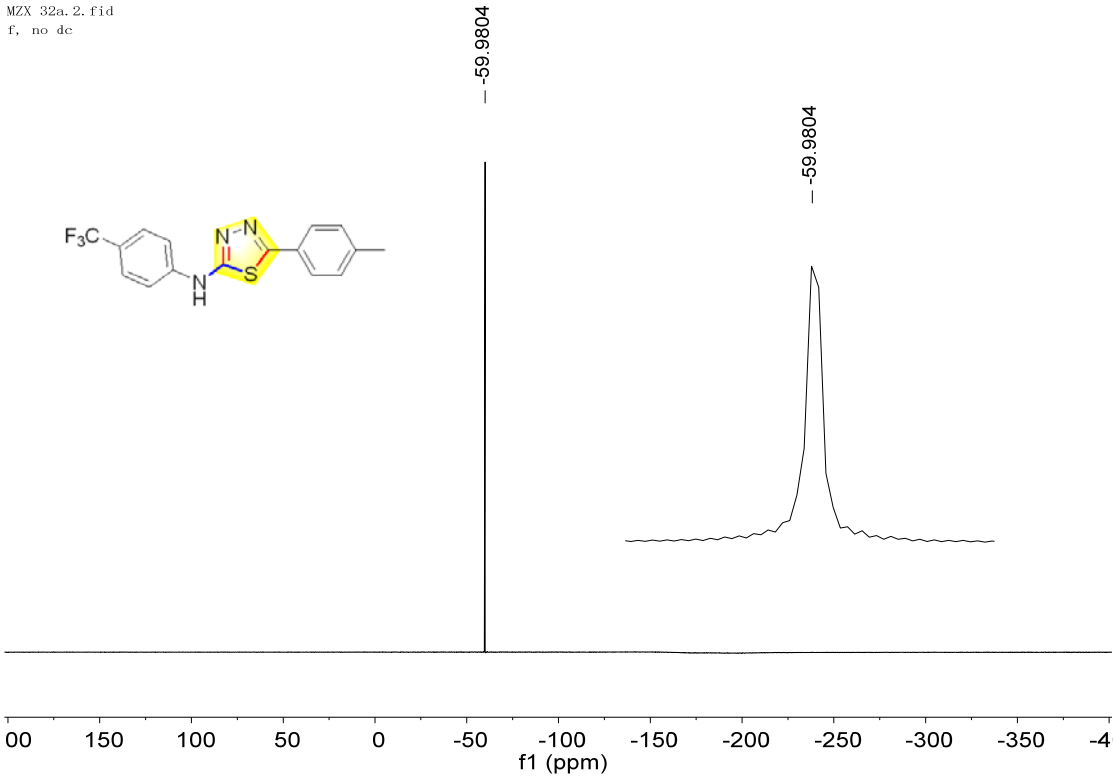
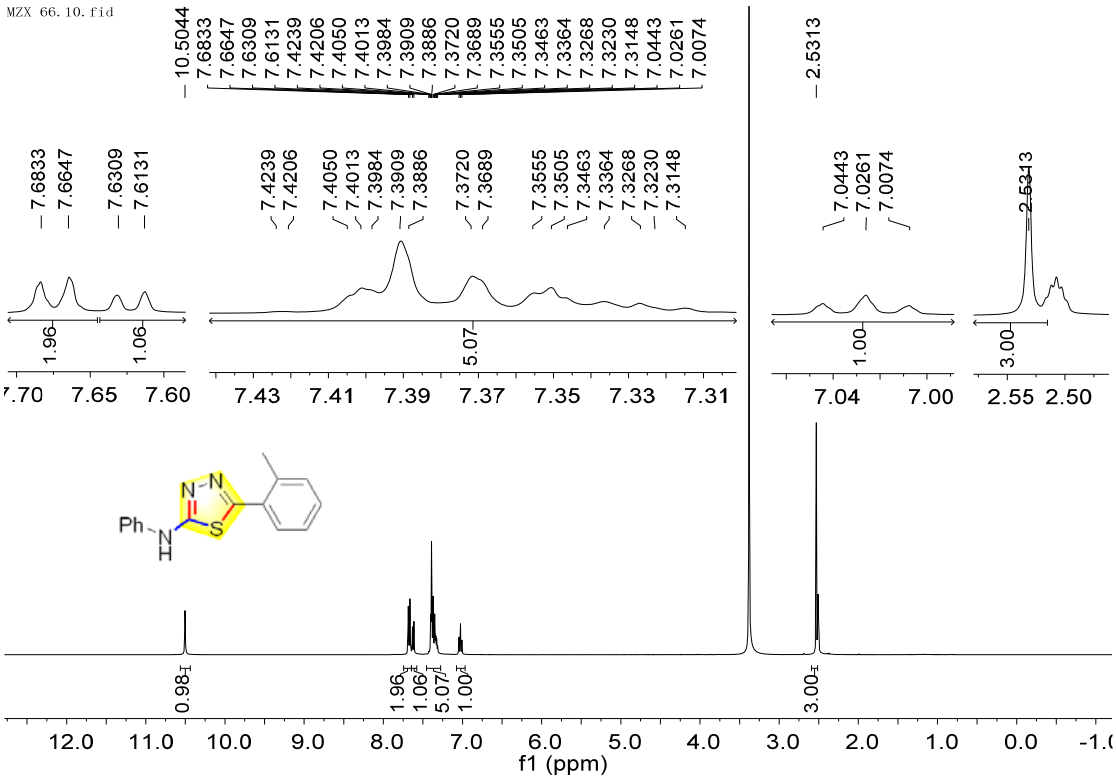


3p, ^{1}H NMR



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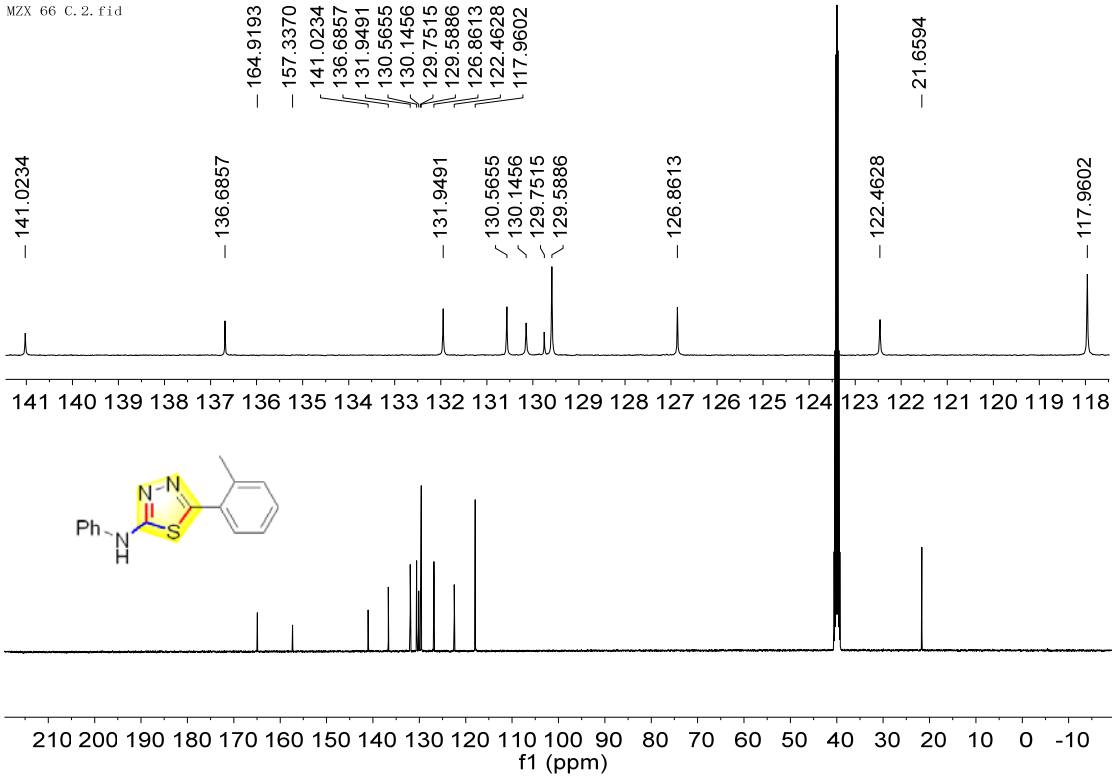
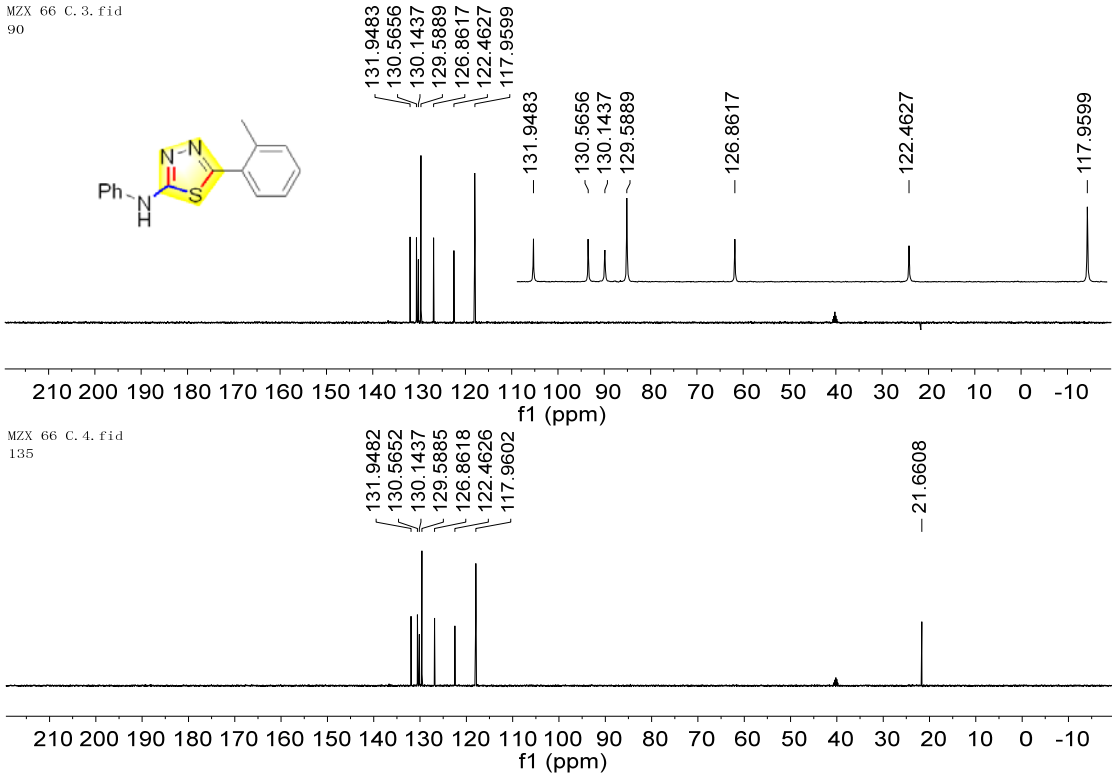
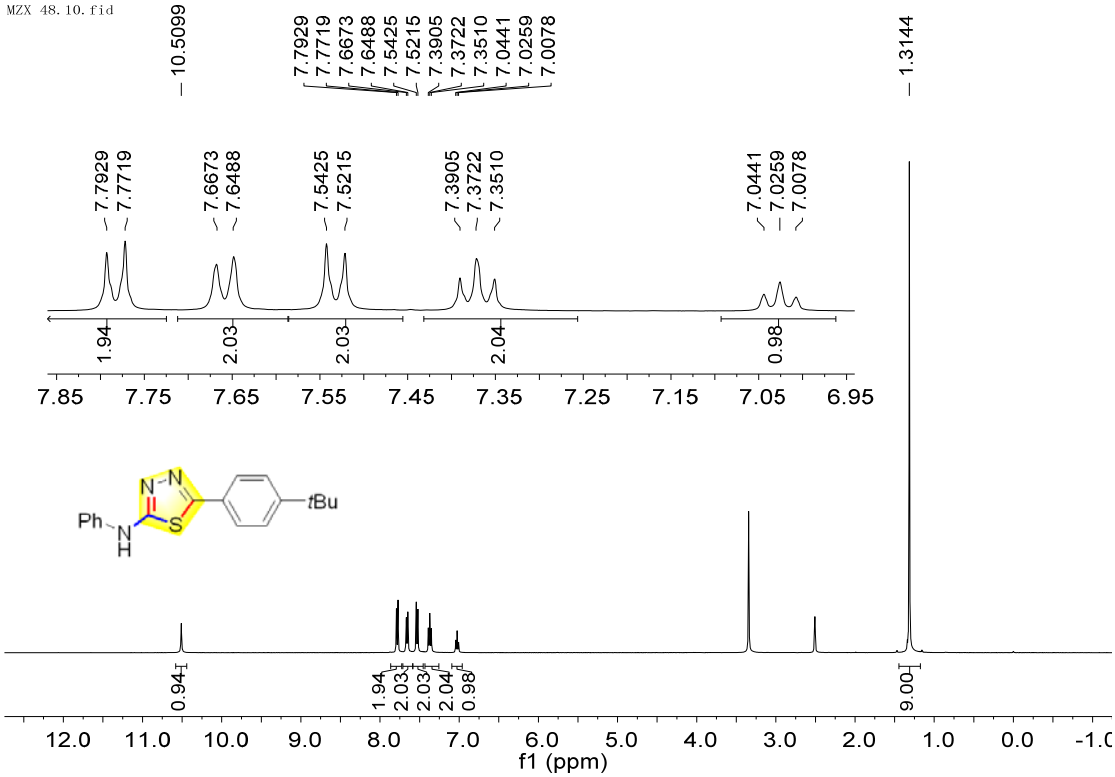


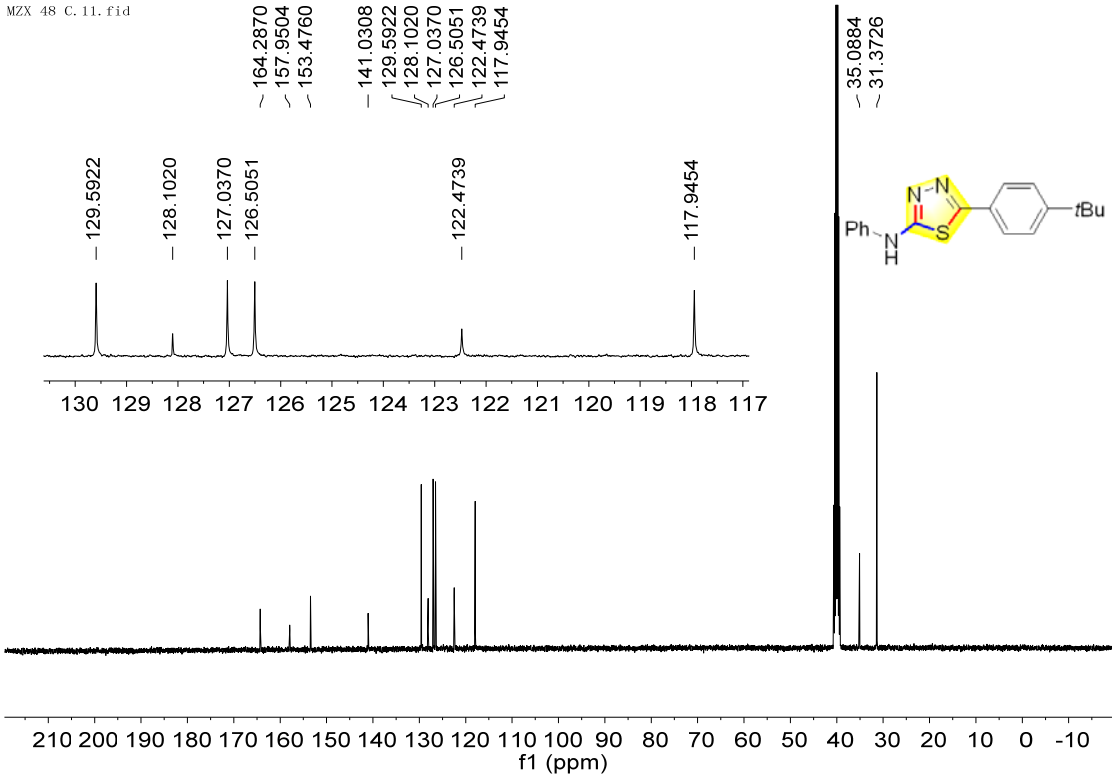
DEPT 90 and DEPT 135



3q, ^{1}H NMR



^{13}C NMR



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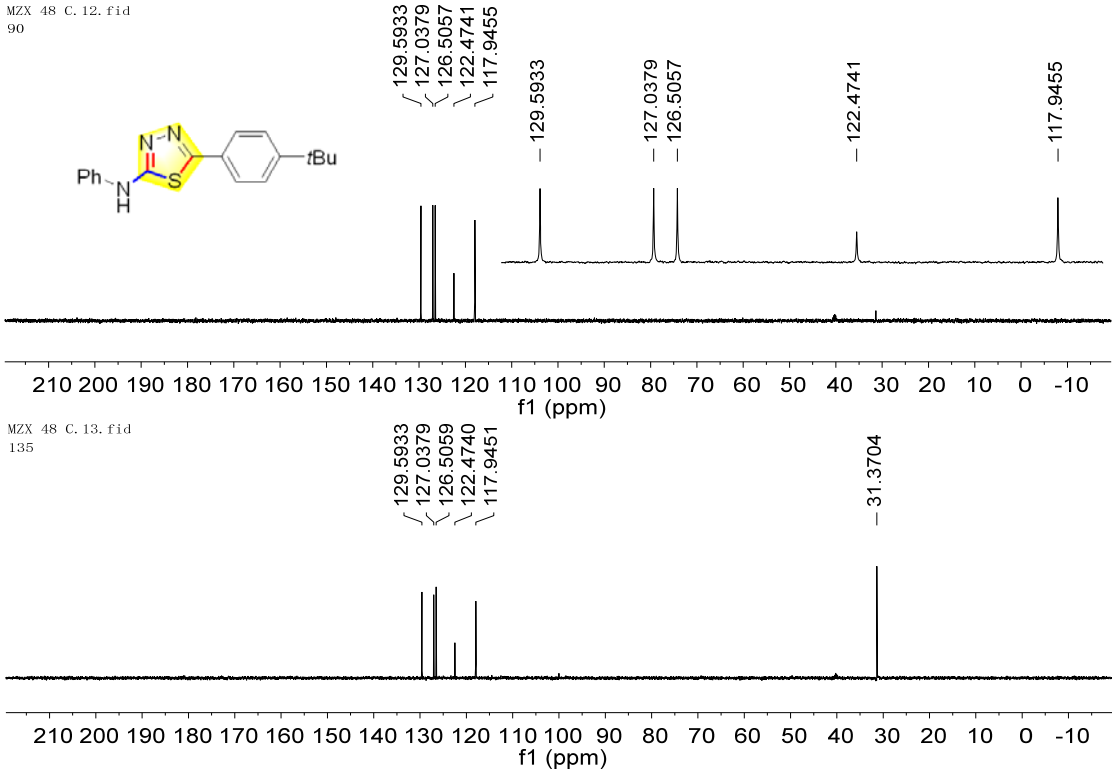

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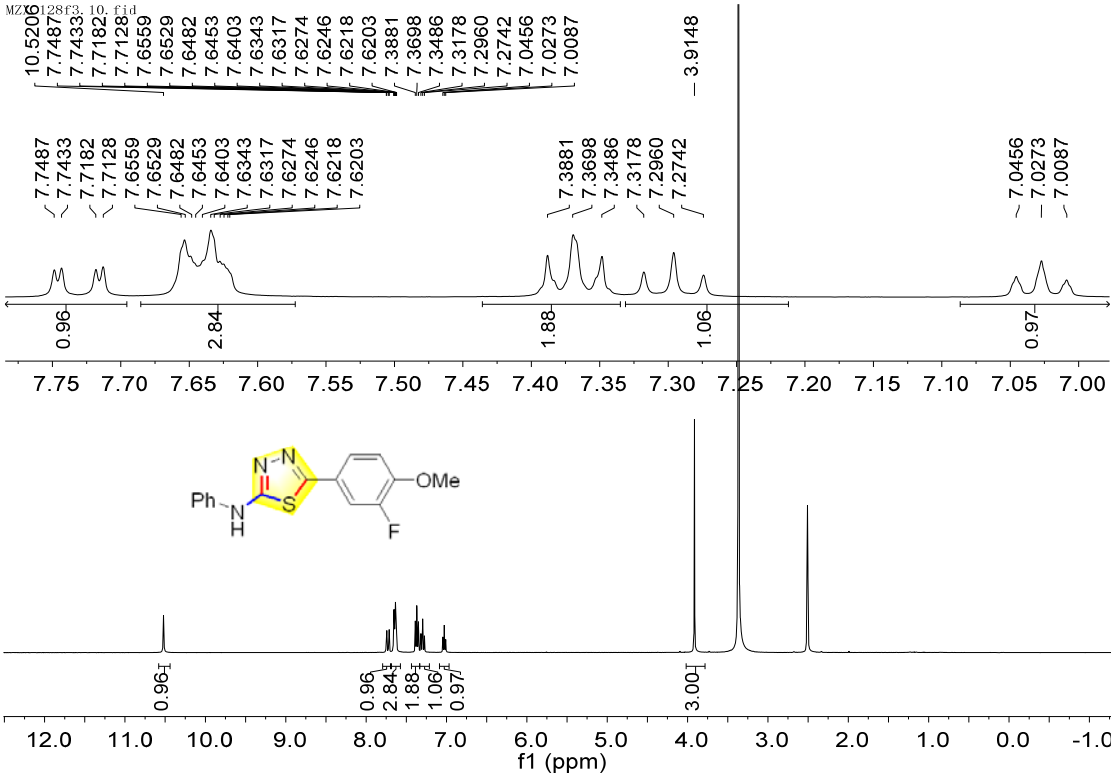
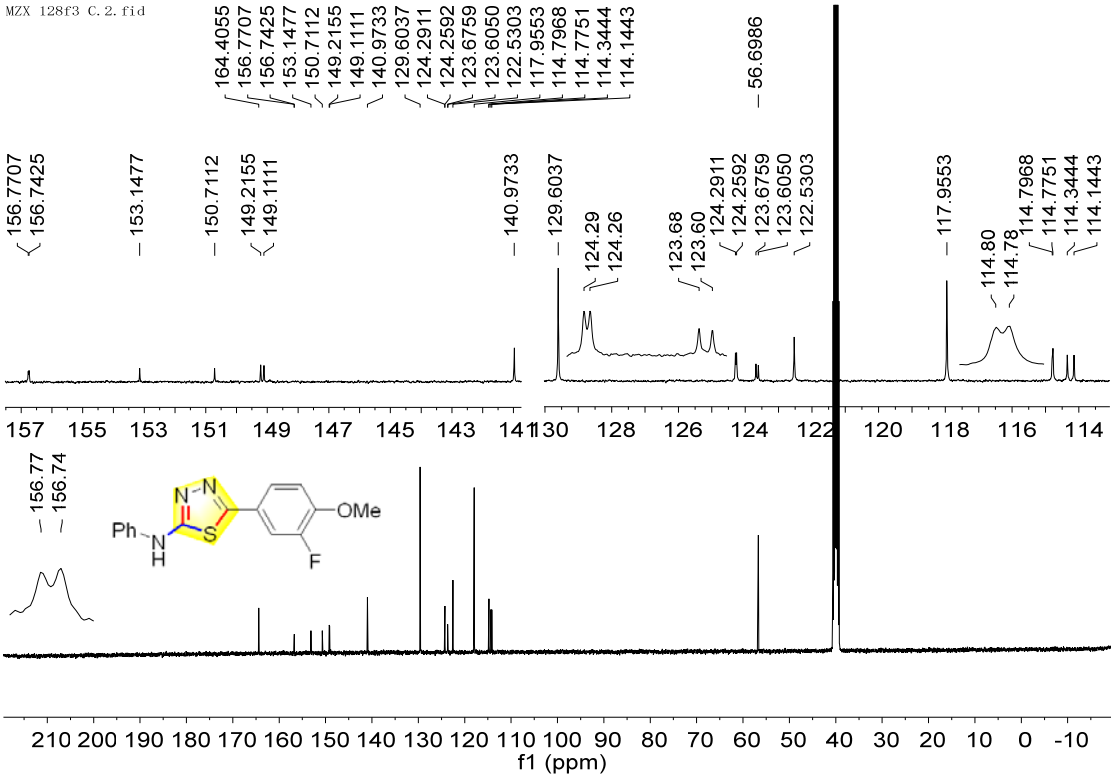


^{13}C NMR



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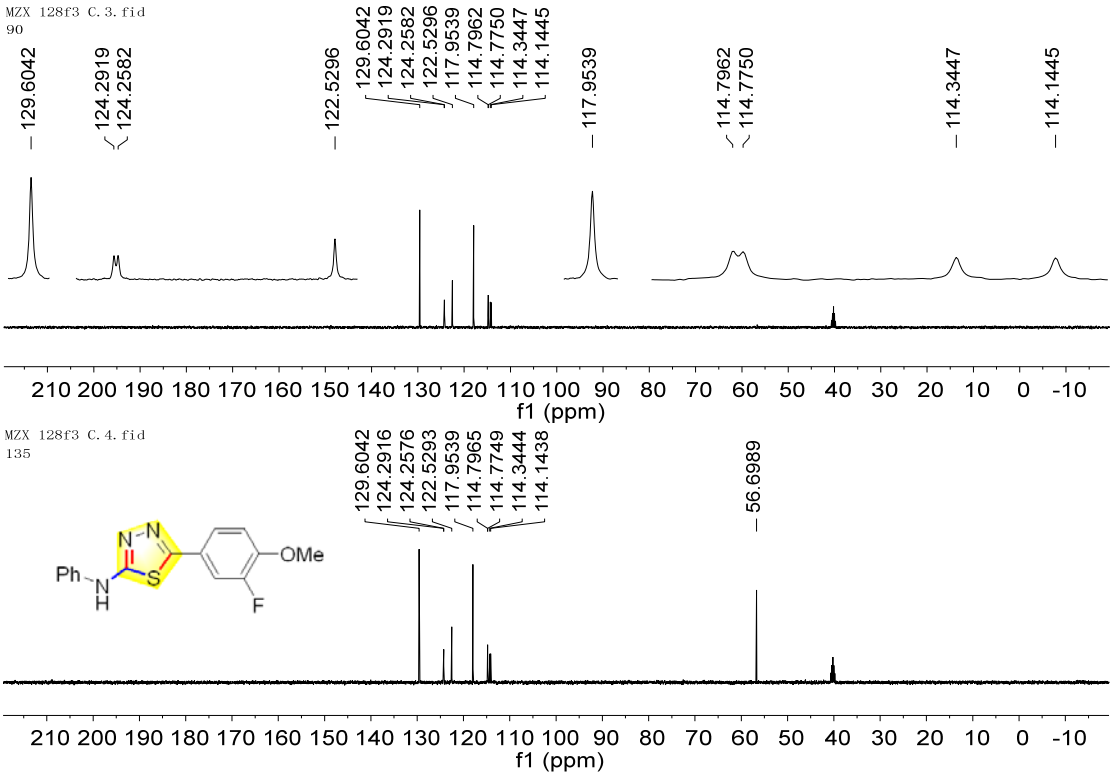
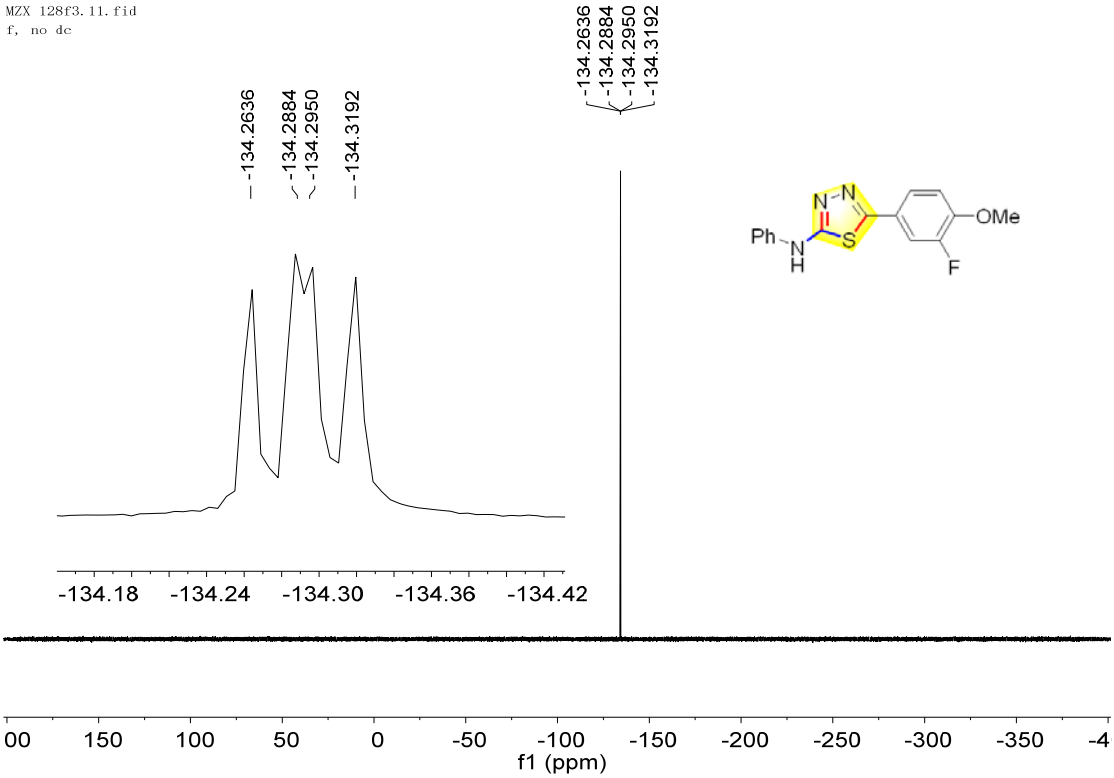
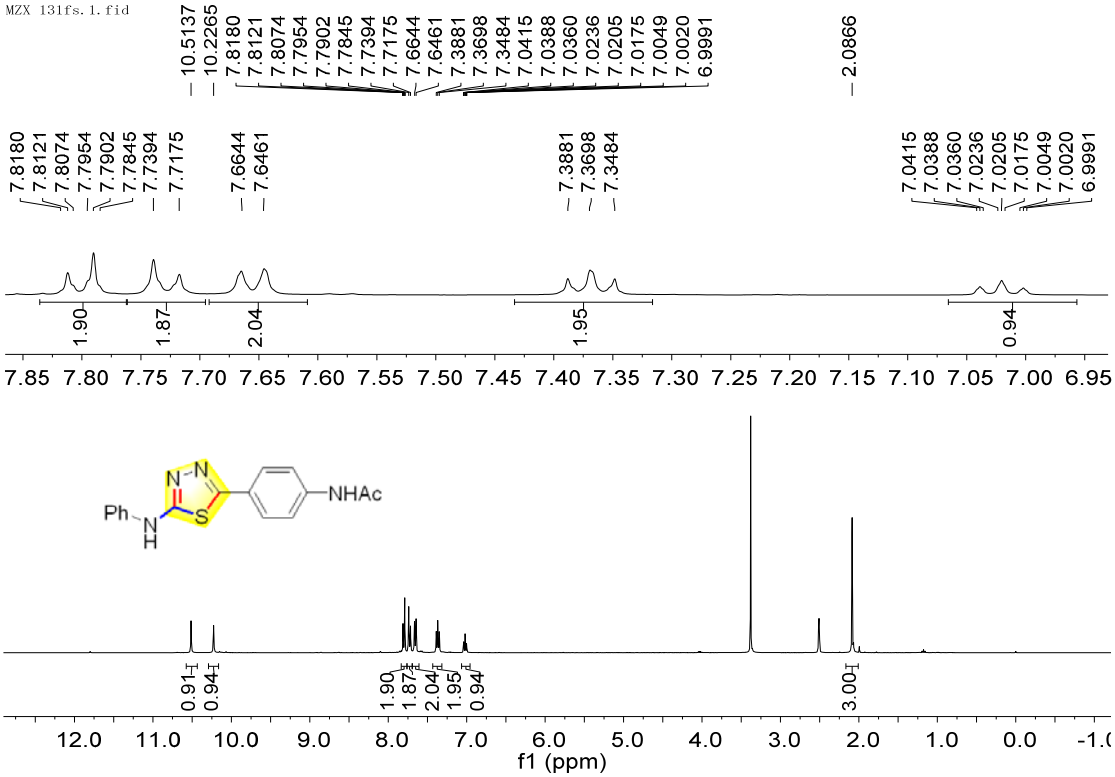


^{19}F NMR



3s, ^{1}H NMR



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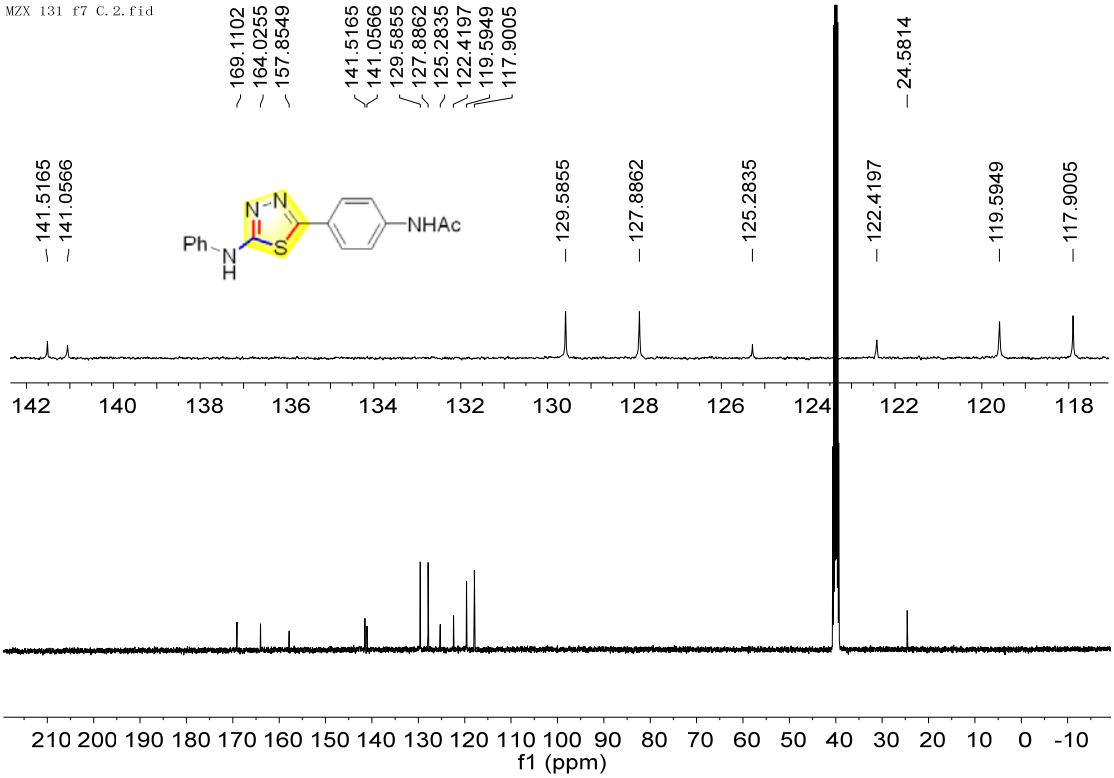

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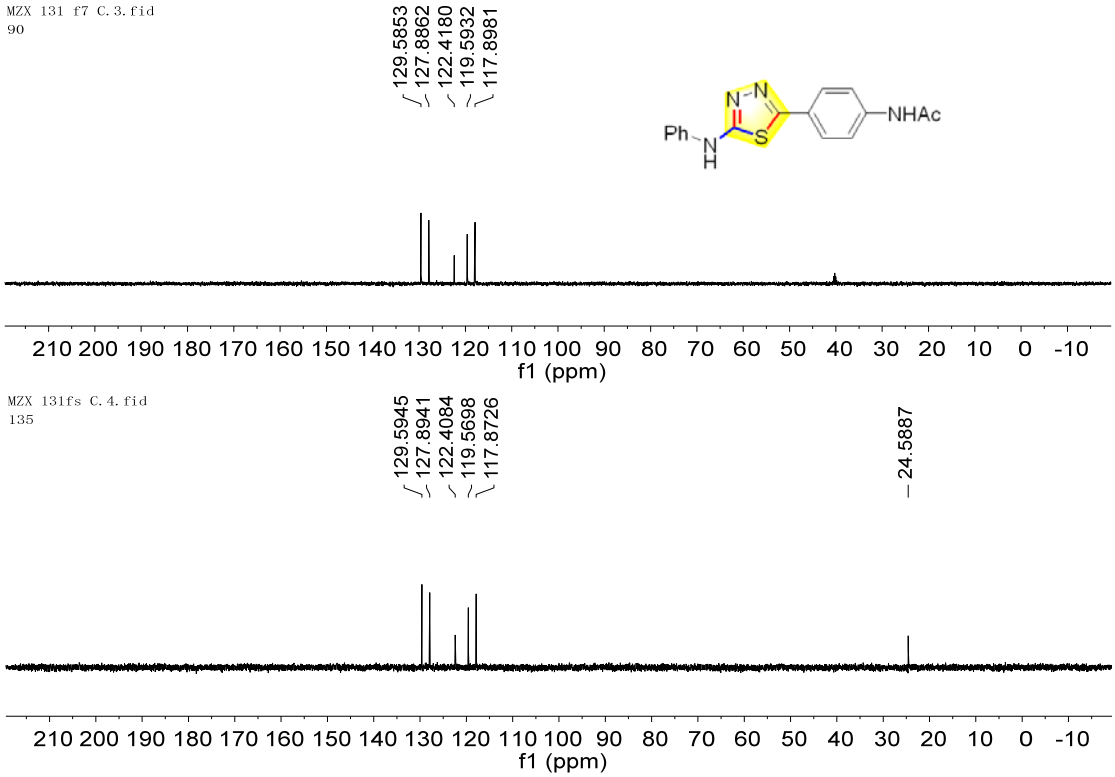
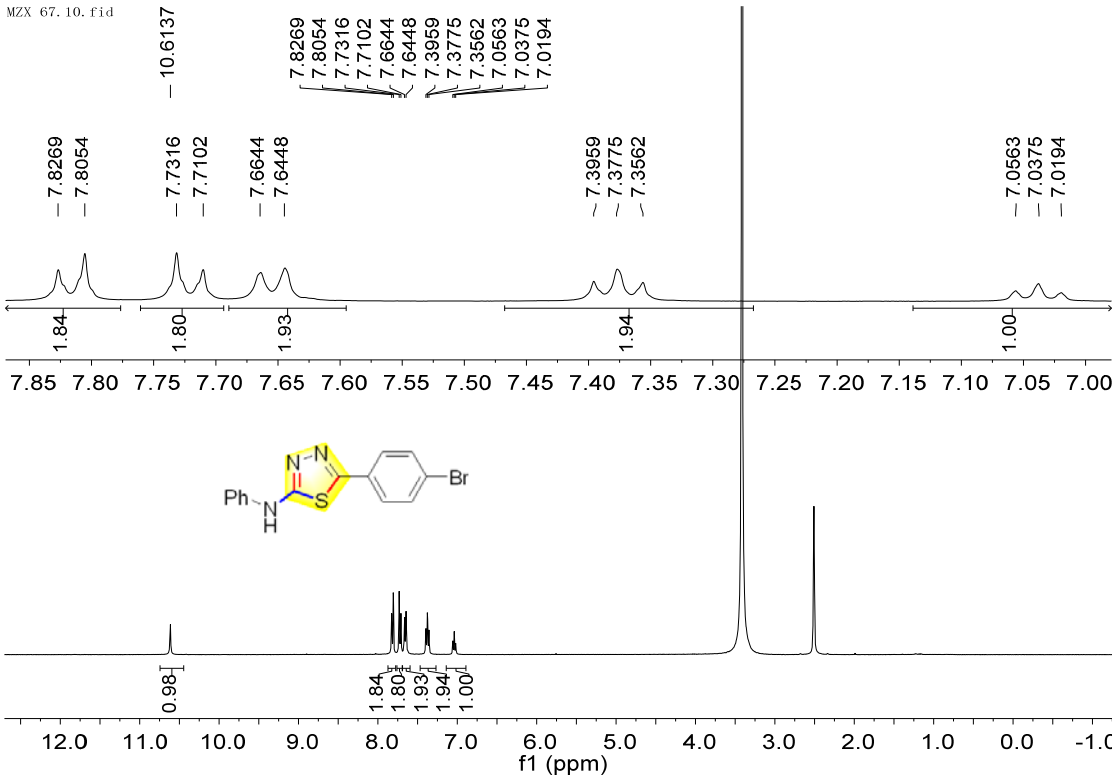


3t, ^{1}H NMR



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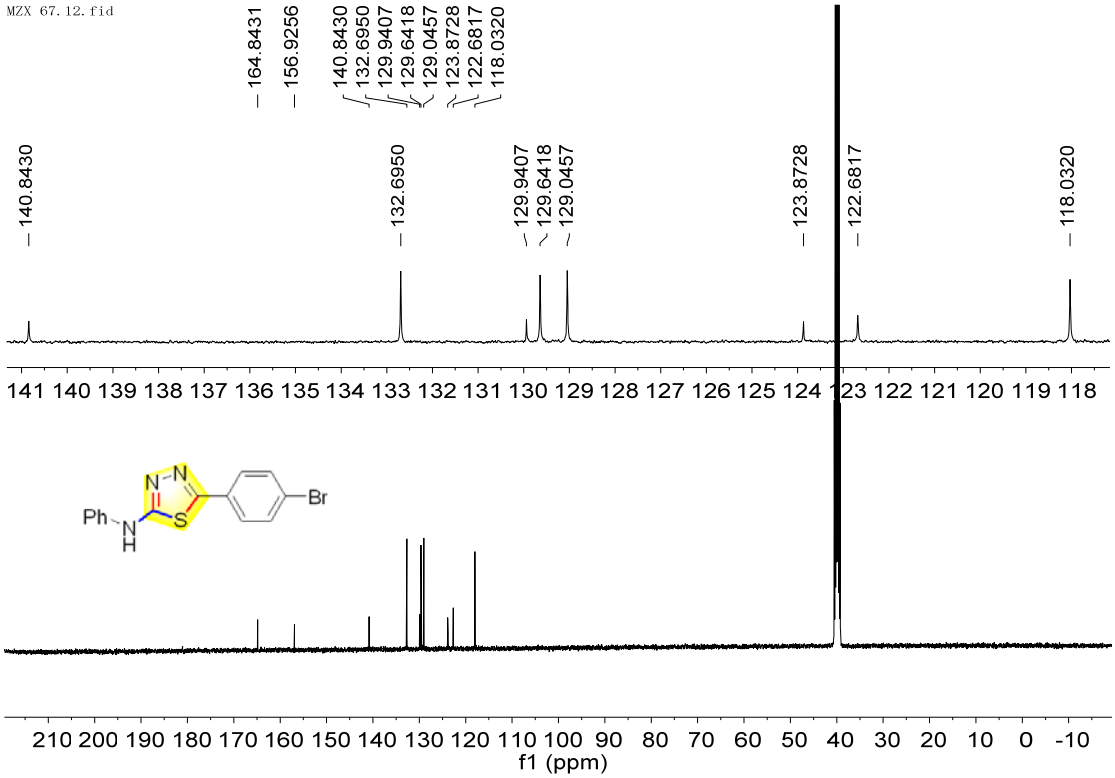
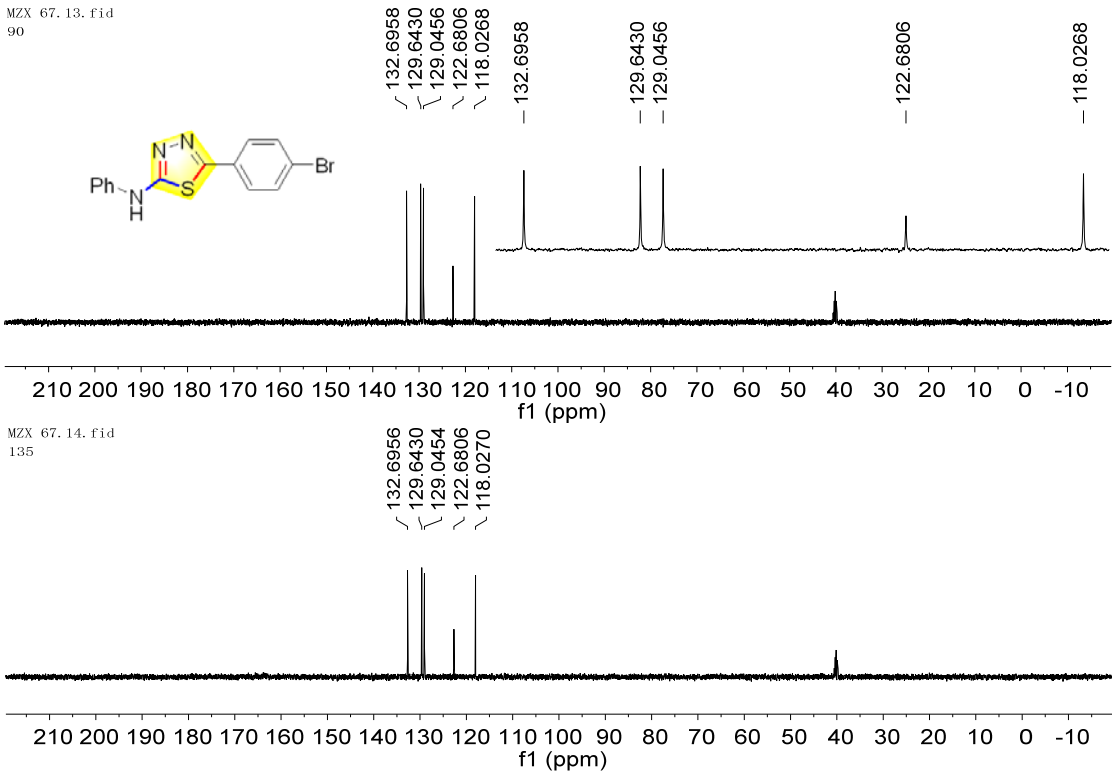
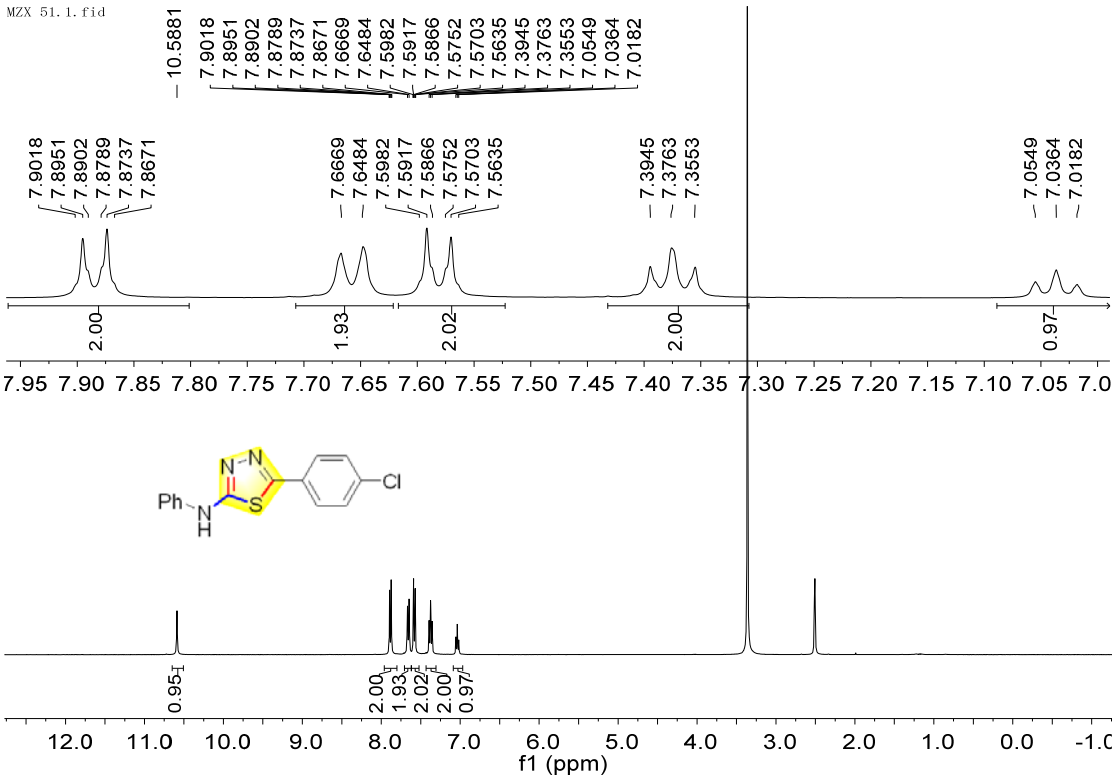


DEPT 90 and DEPT 135



3u, ^{1}H NMR



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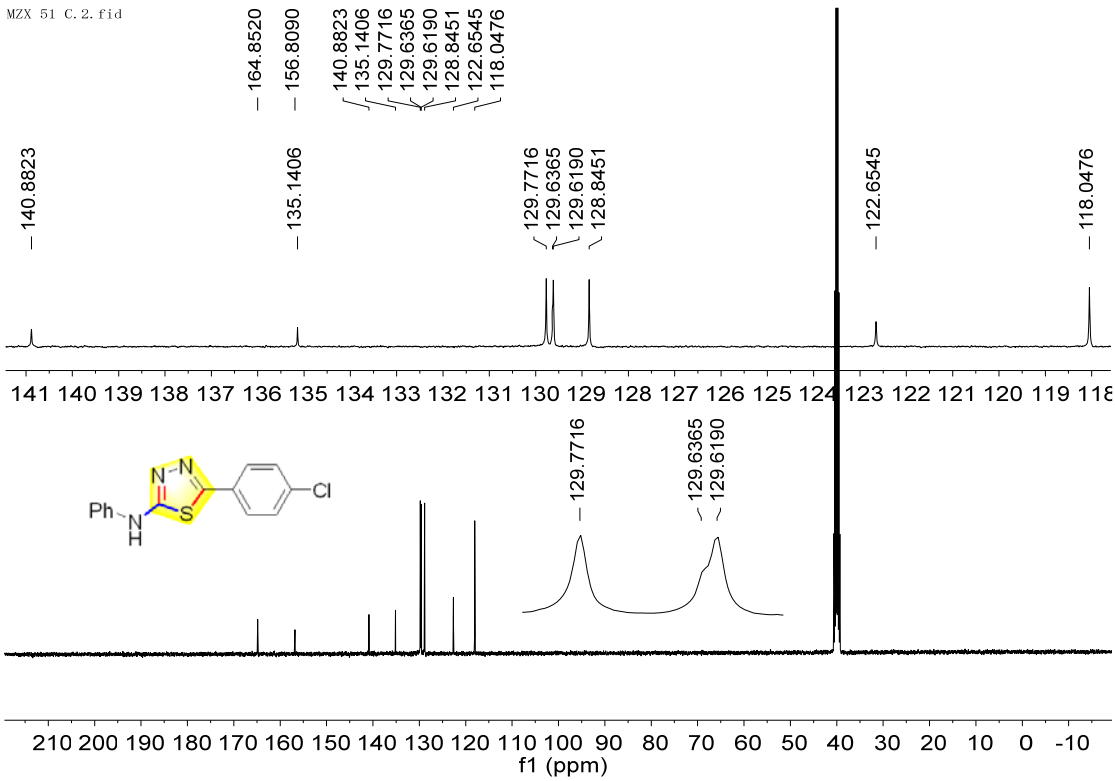
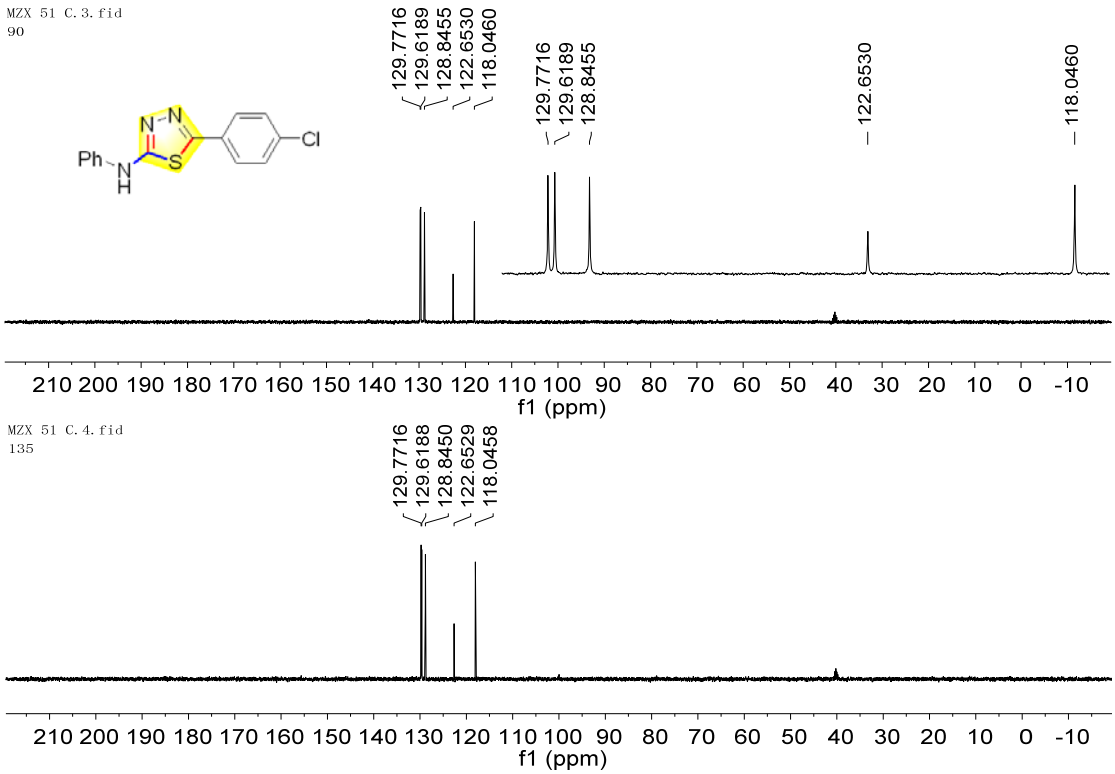
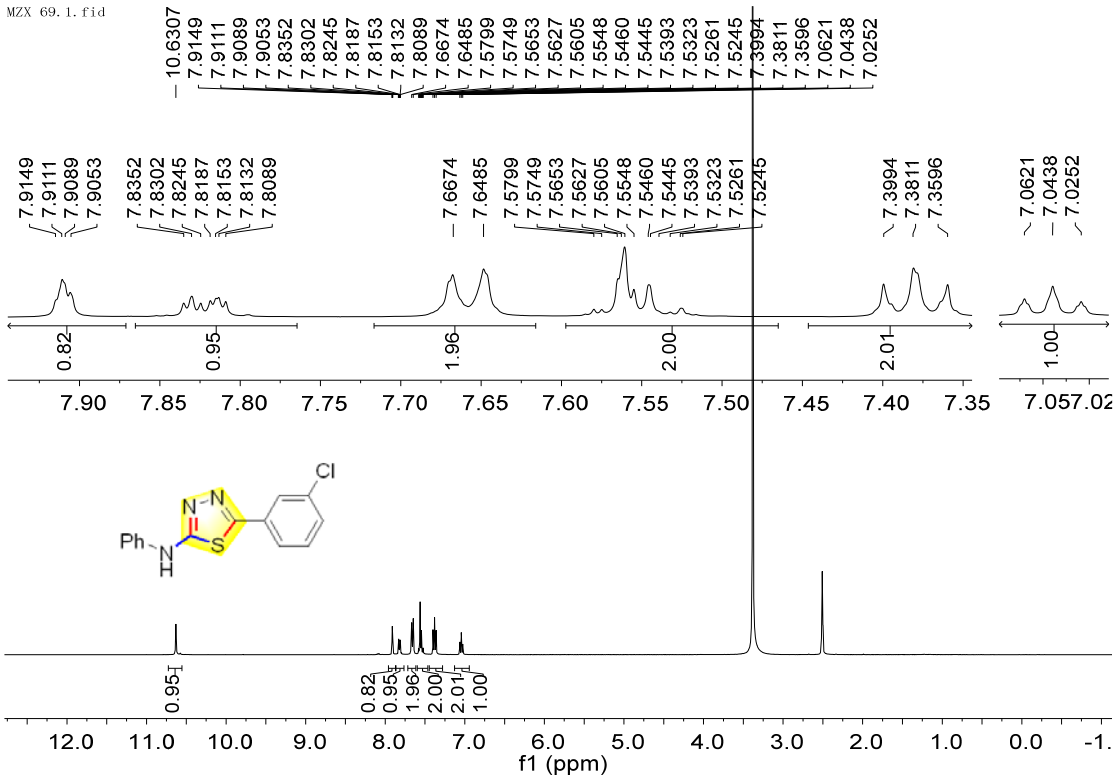


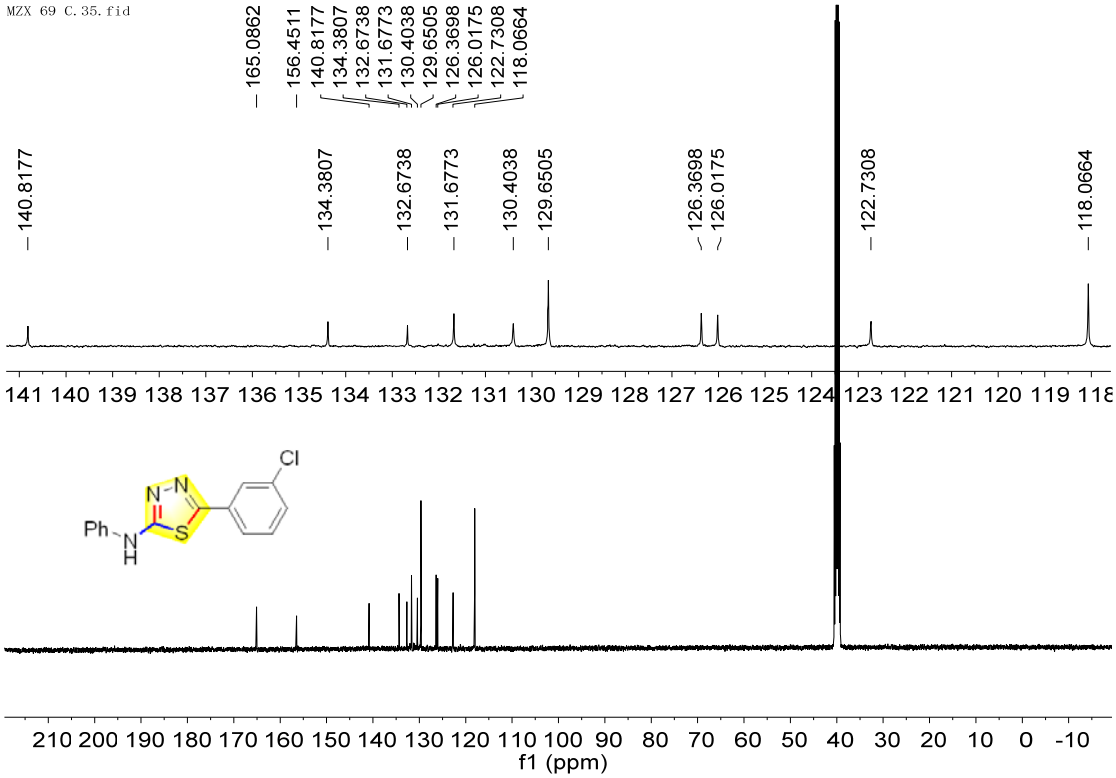
DEPT 90 and DEPT 135



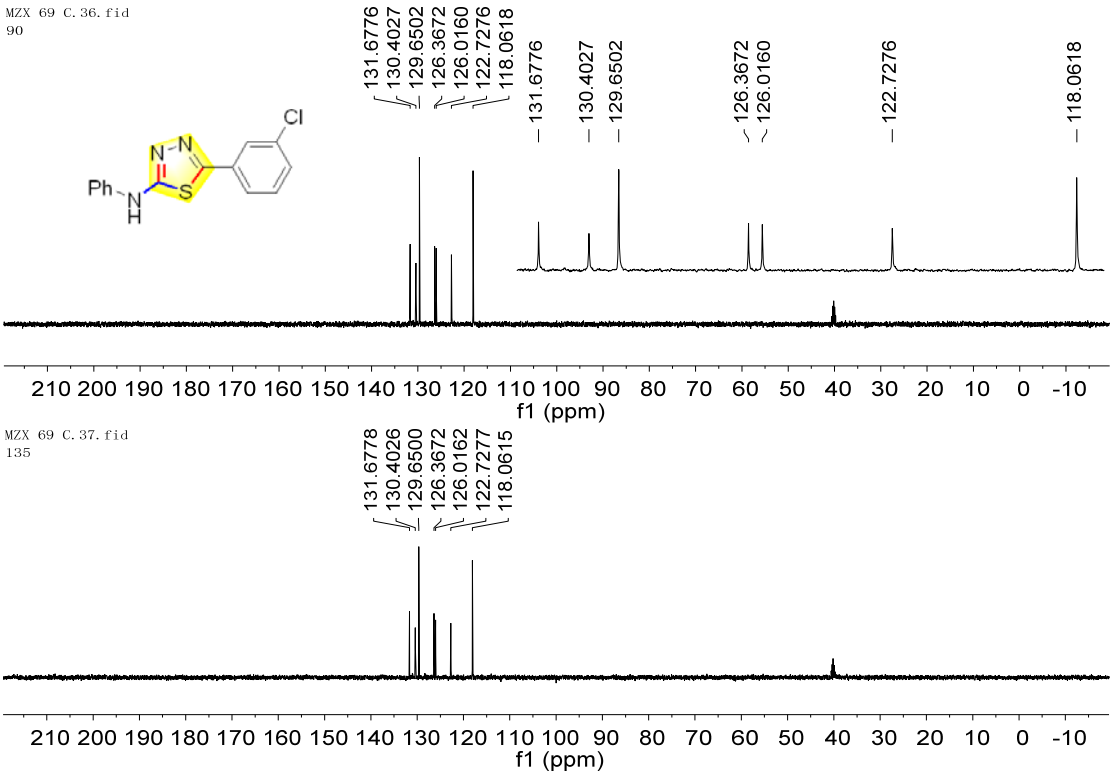
3v, ^{1}H NMR



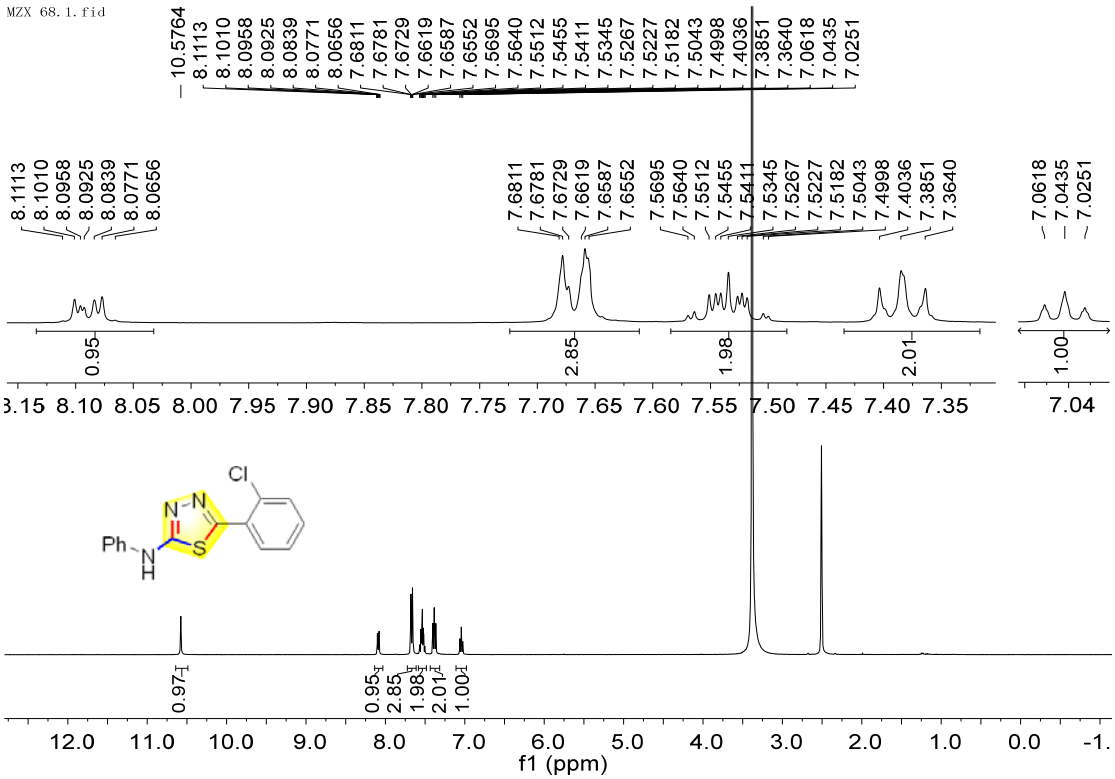
^{13}C NMR



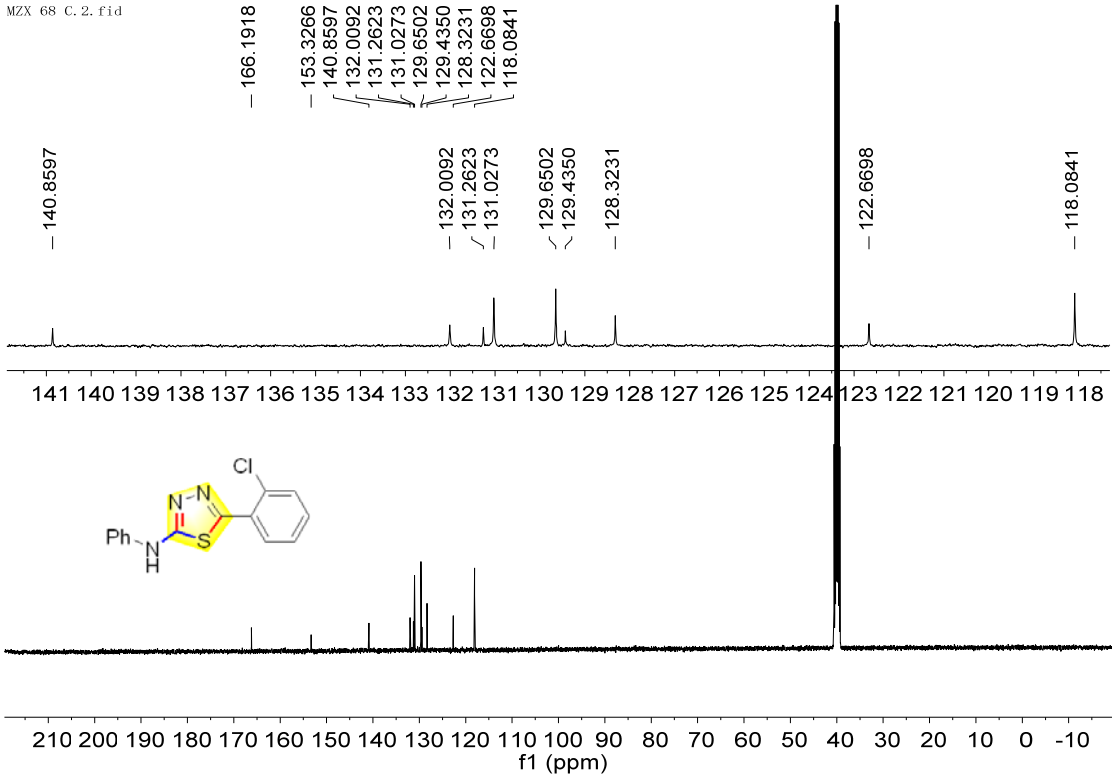
DEPT 90 and DEPT 135



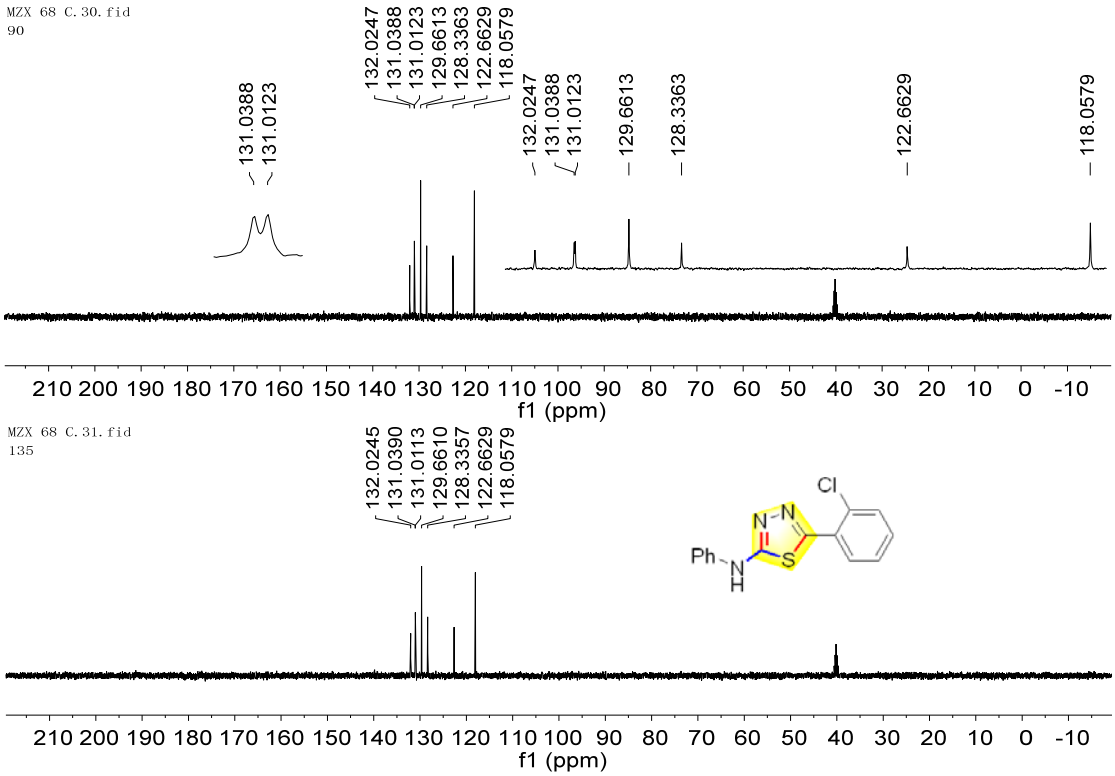
3w, ^{1}H NMR



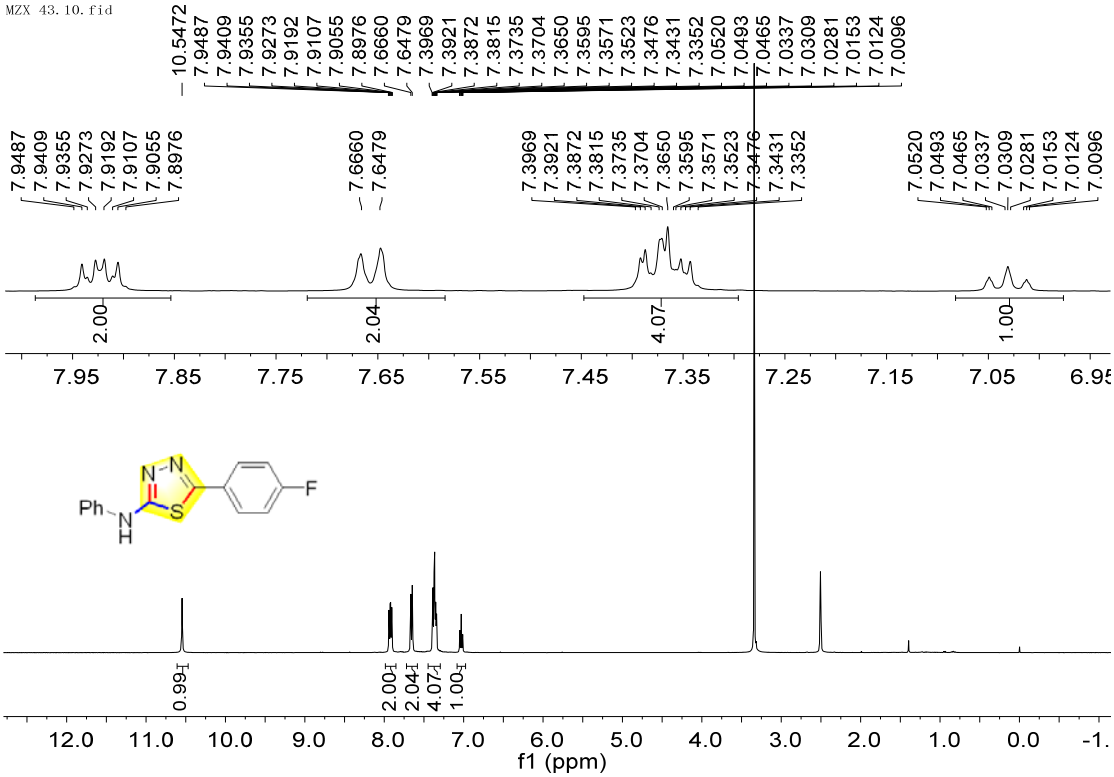
^{13}C NMR



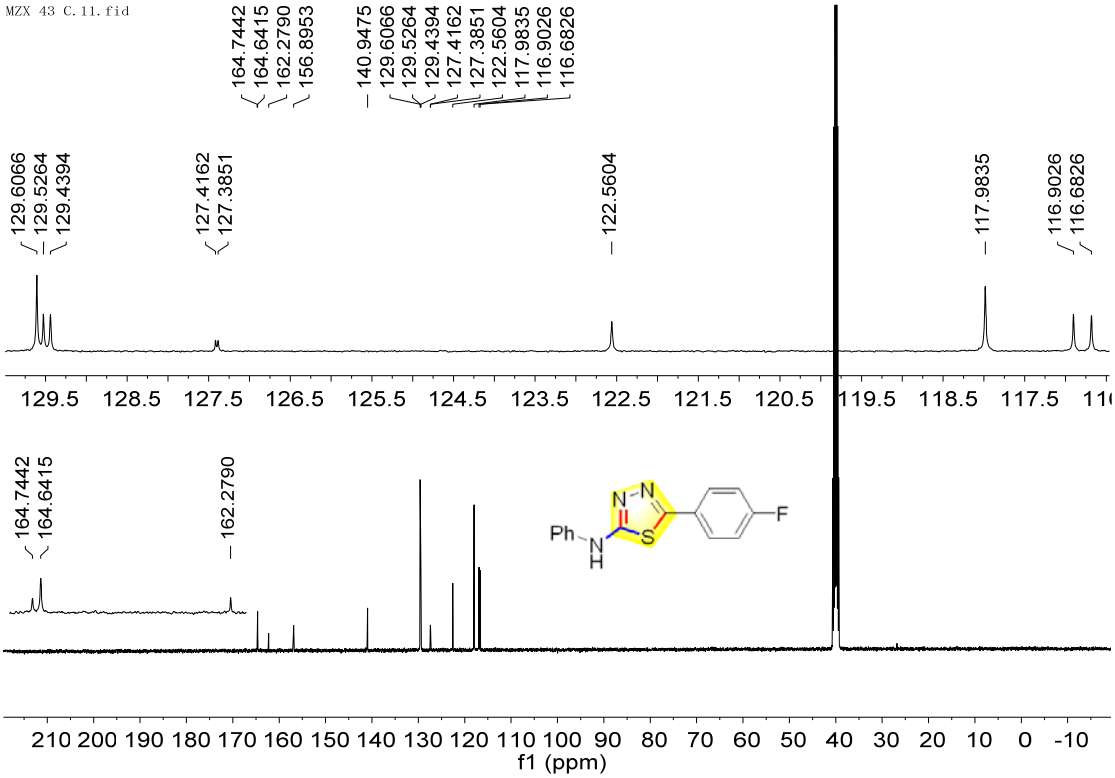
DEPT 90 and DEPT 135



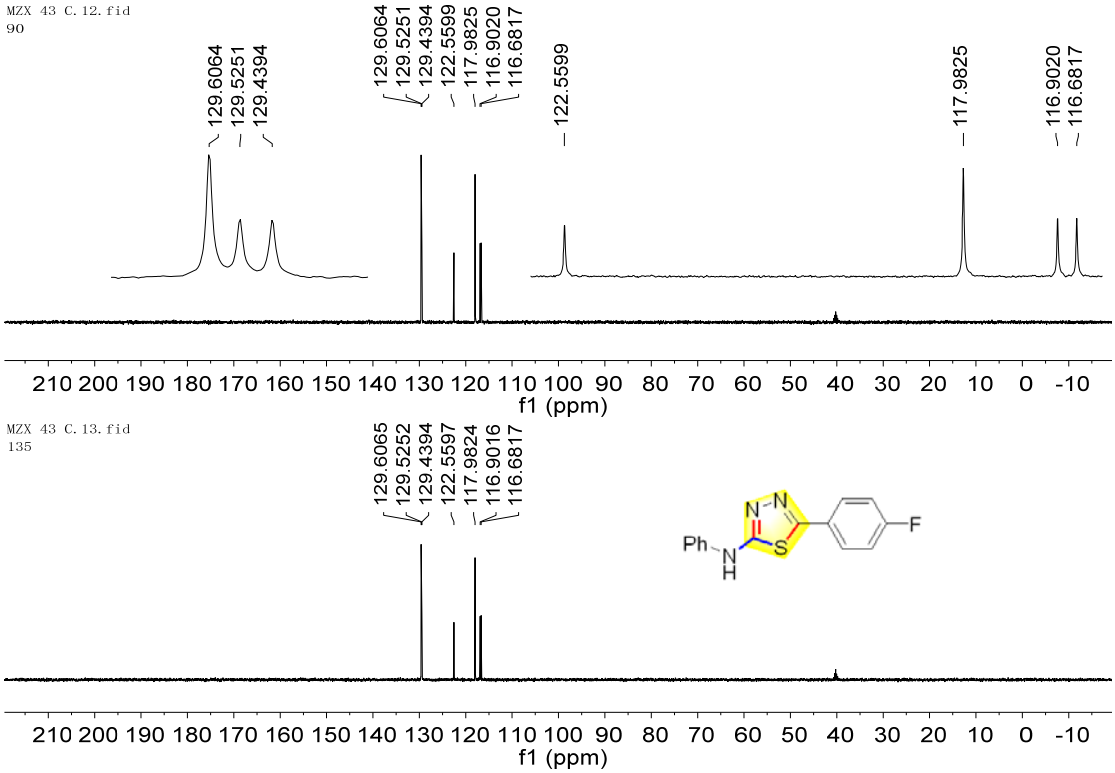
3x, ^{1}H NMR



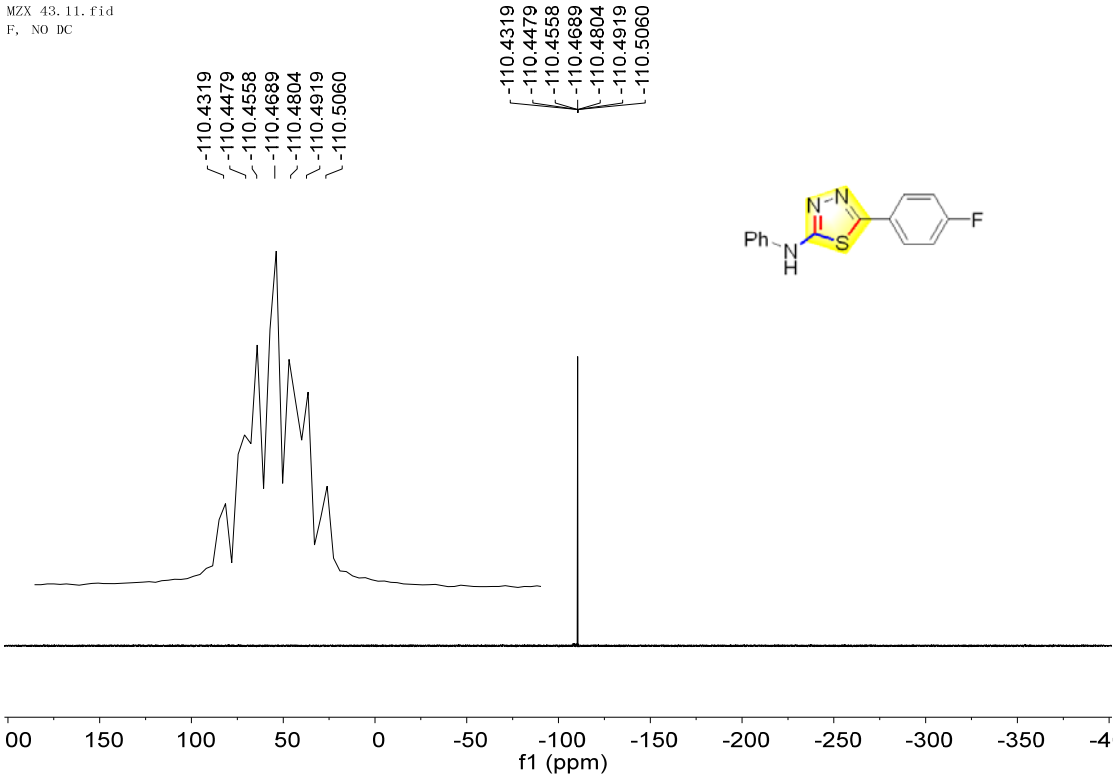
^{13}C NMR



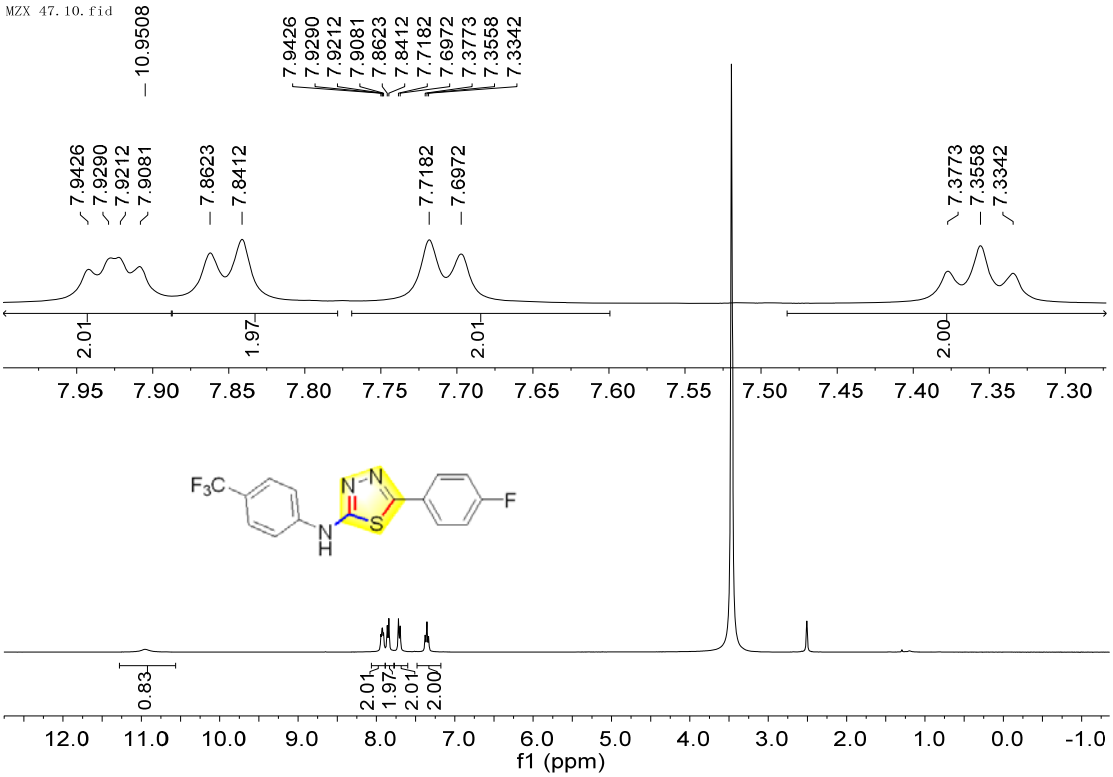
DEPT 90 and DEPT 135



^{19}F NMR



3y, ^{1}H NMR



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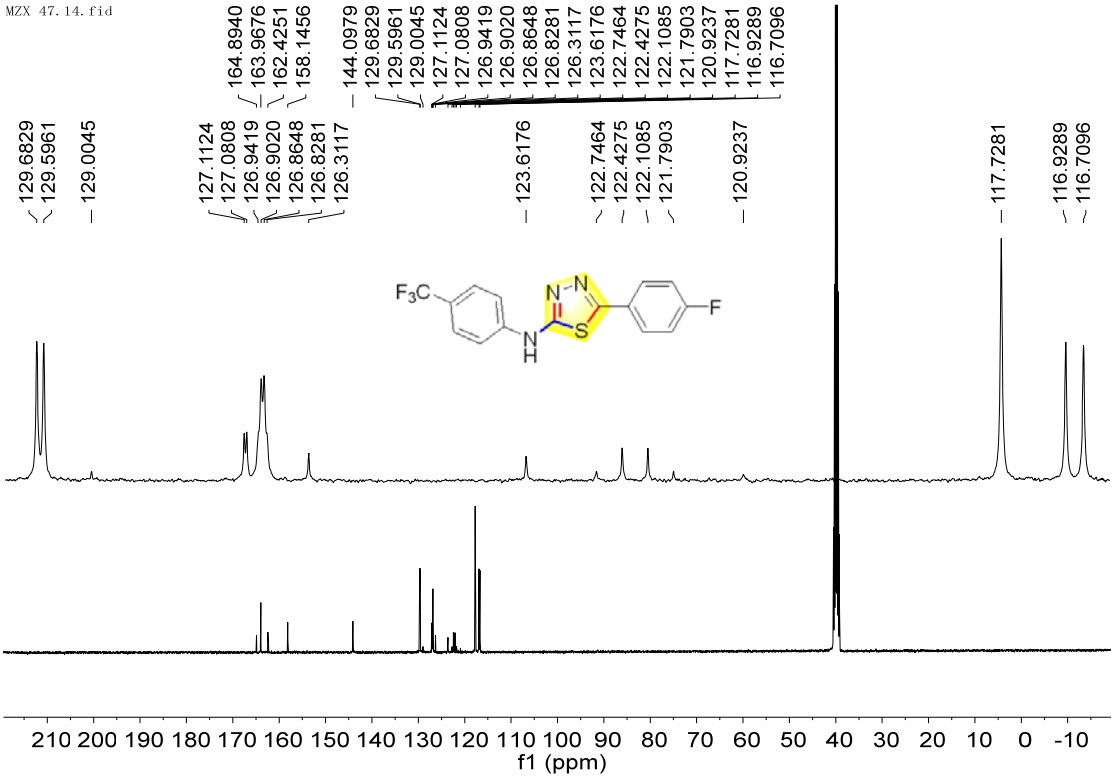
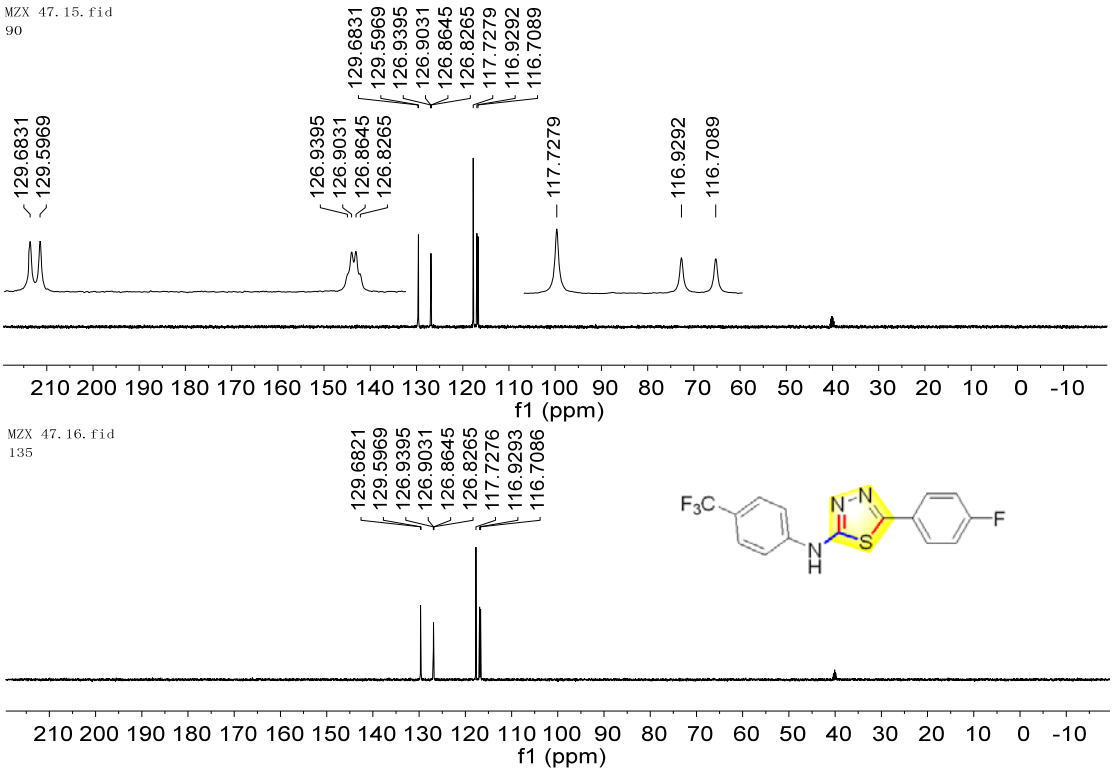


DEPT 90 and DEPT 135



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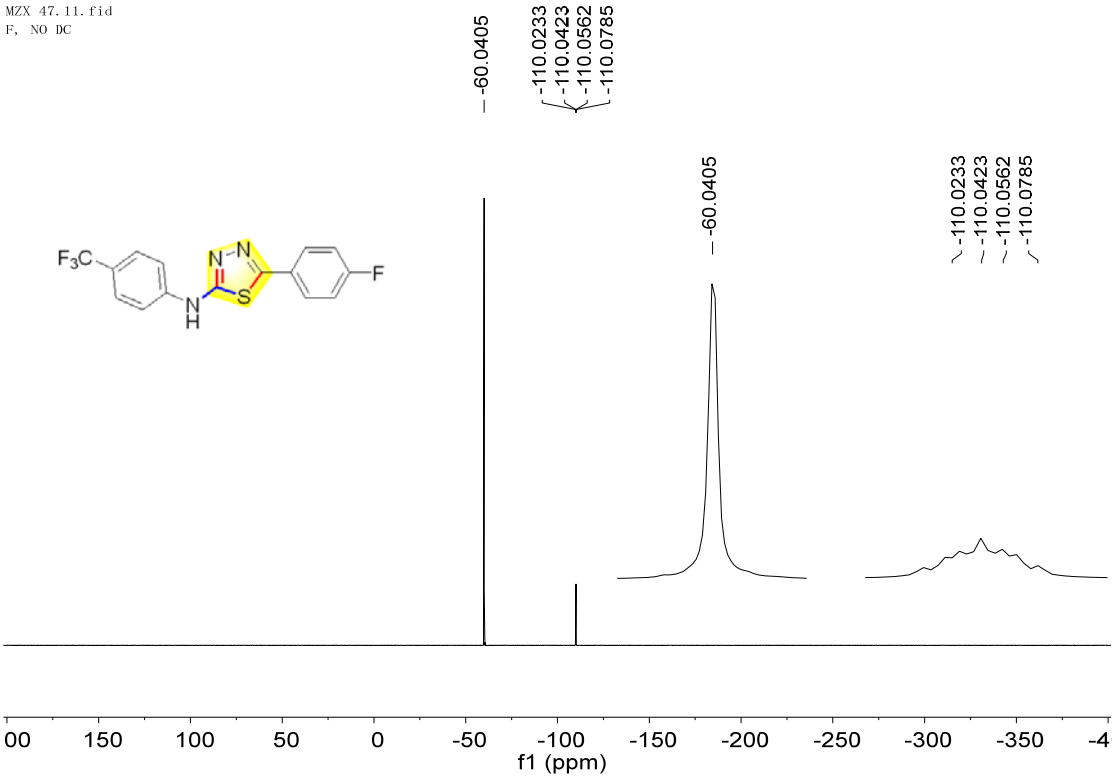
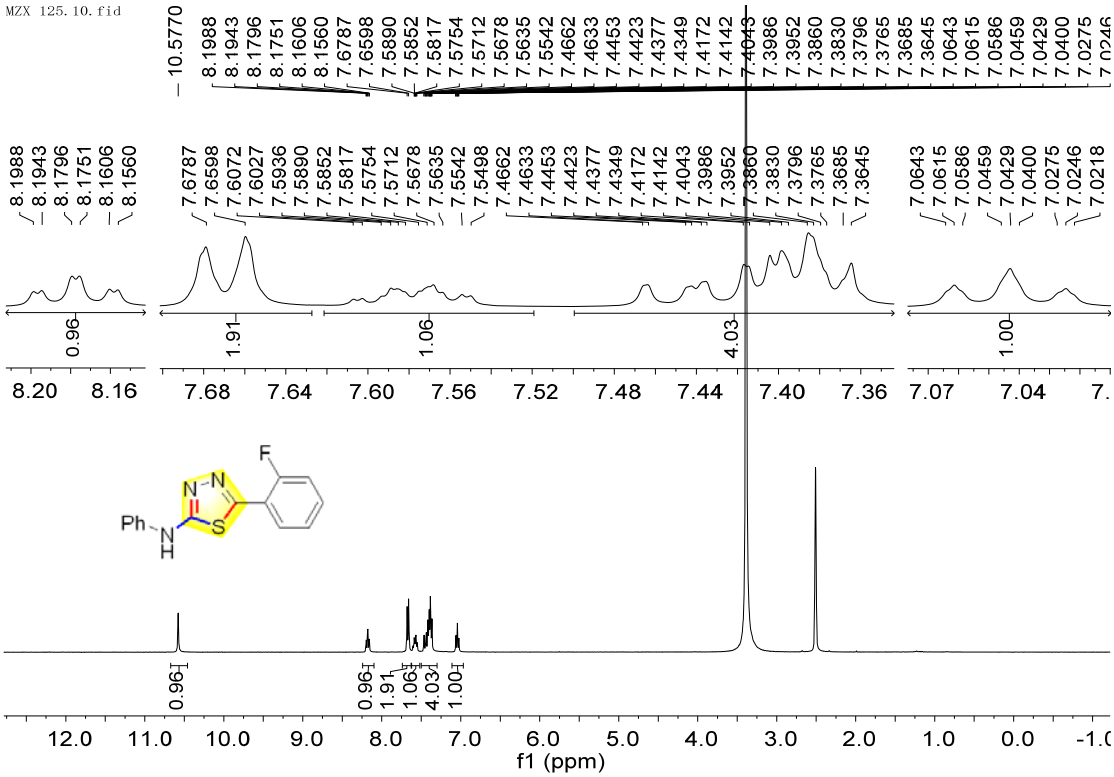
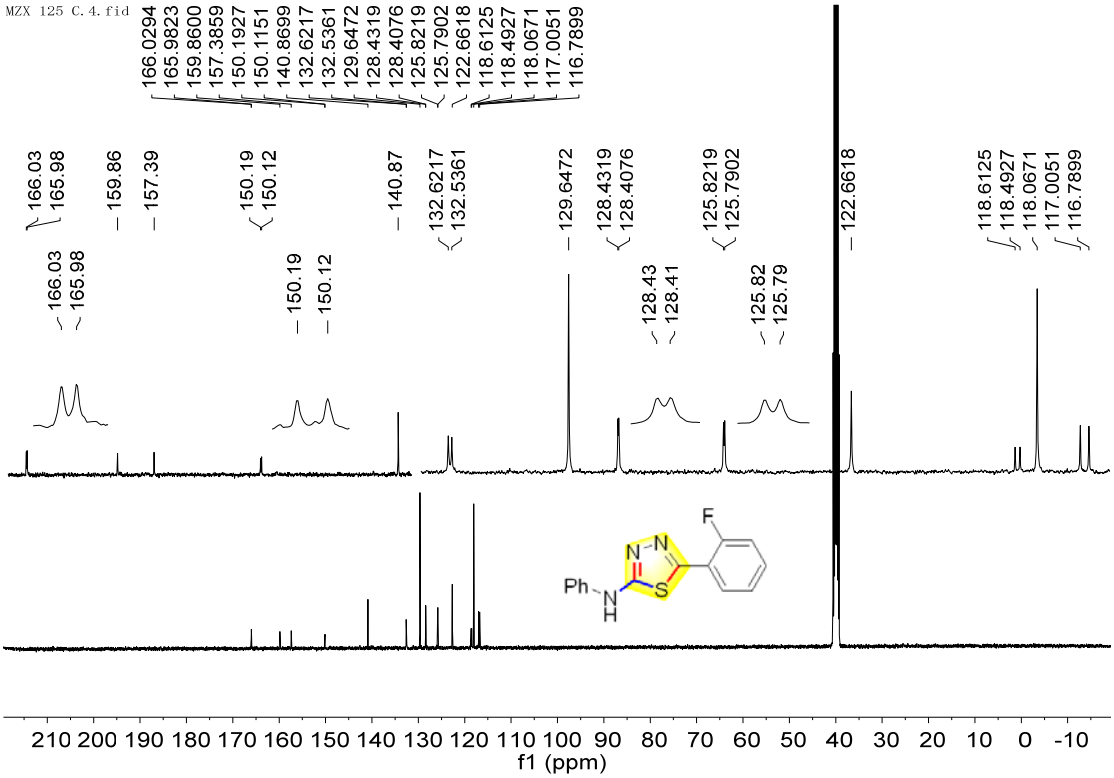


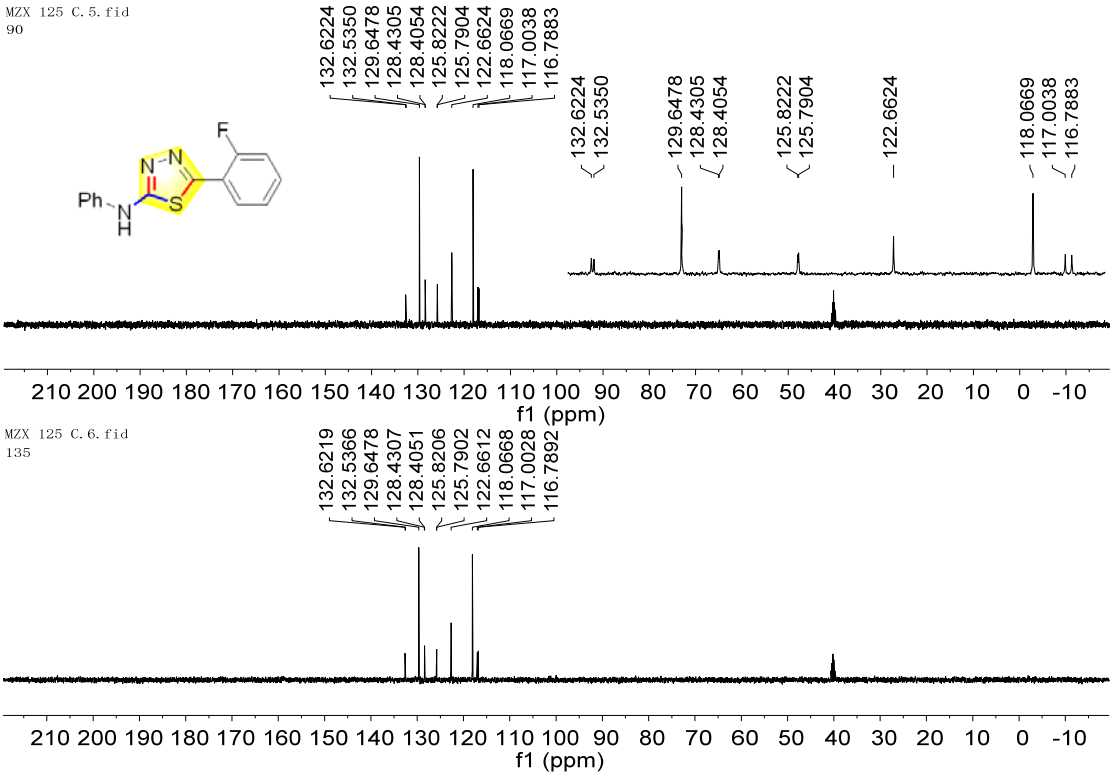
3z, ^{1}H NMR



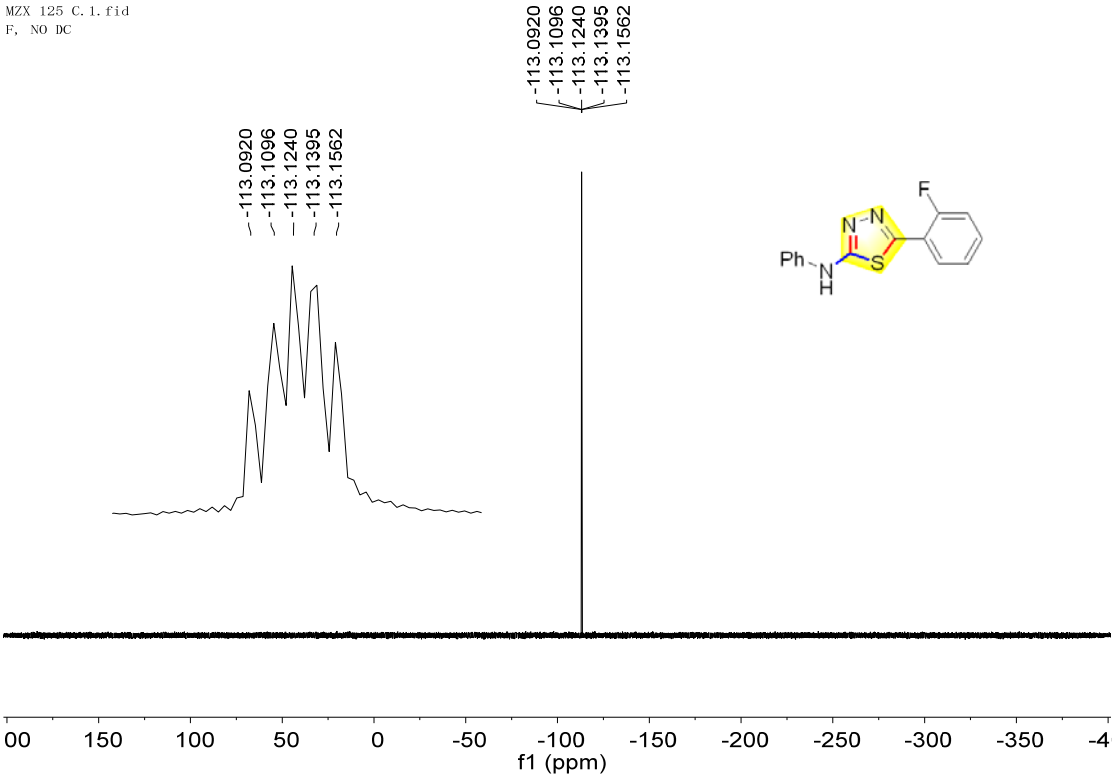
^{13}C NMR



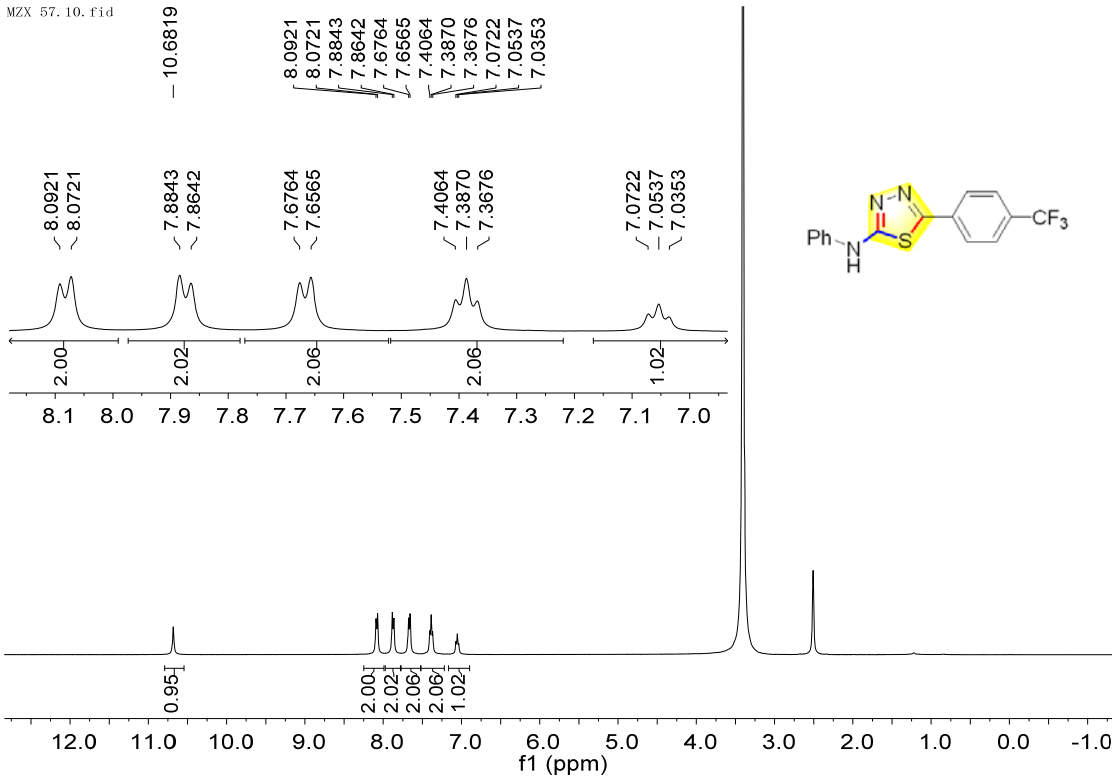
DEPT 90 and DEPT 135



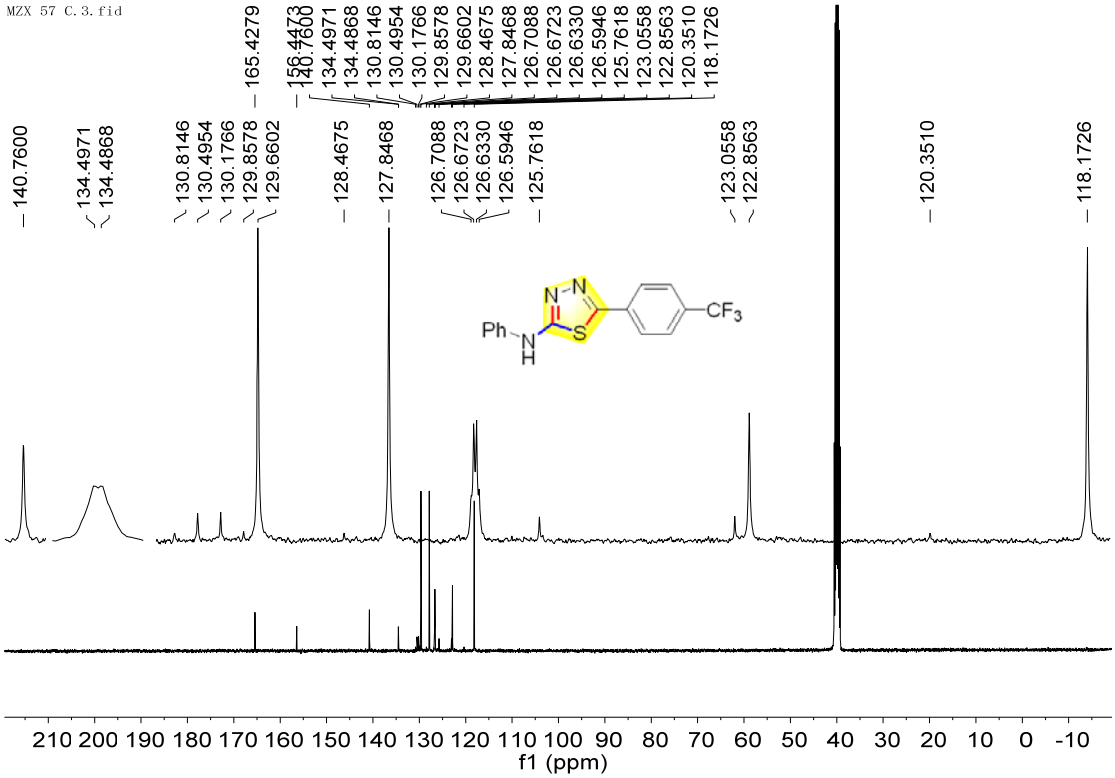
^{19}F NMR



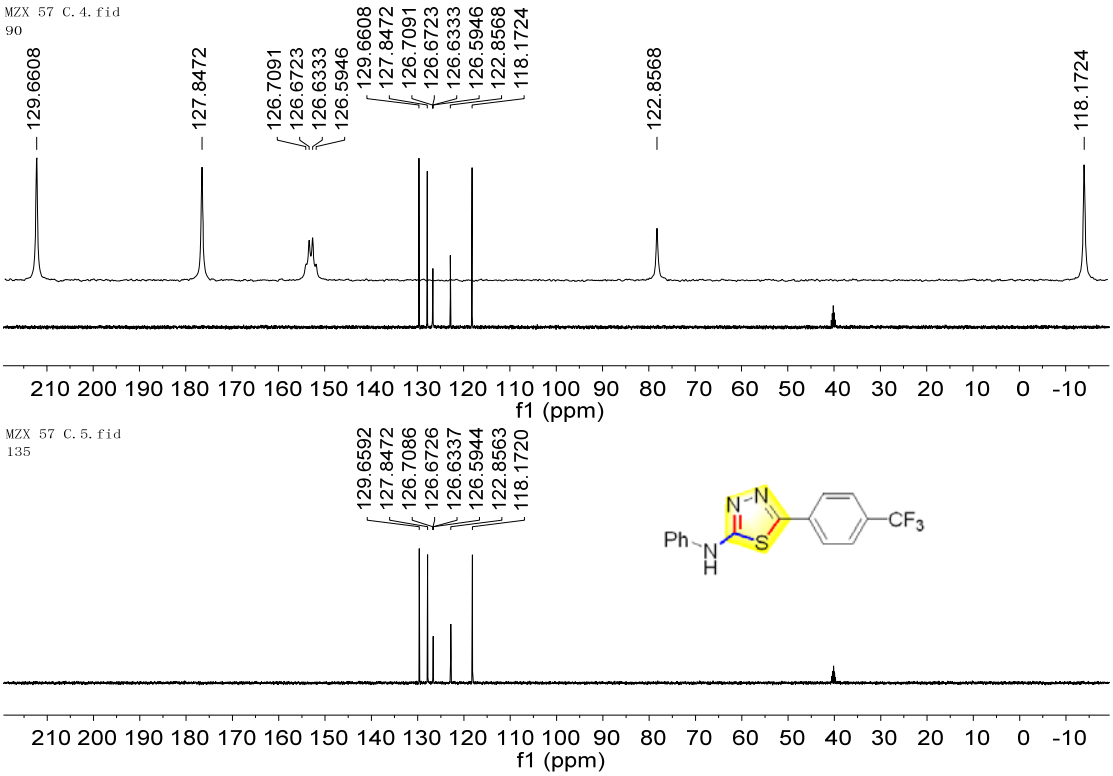
3aa, ^{1}H NMR



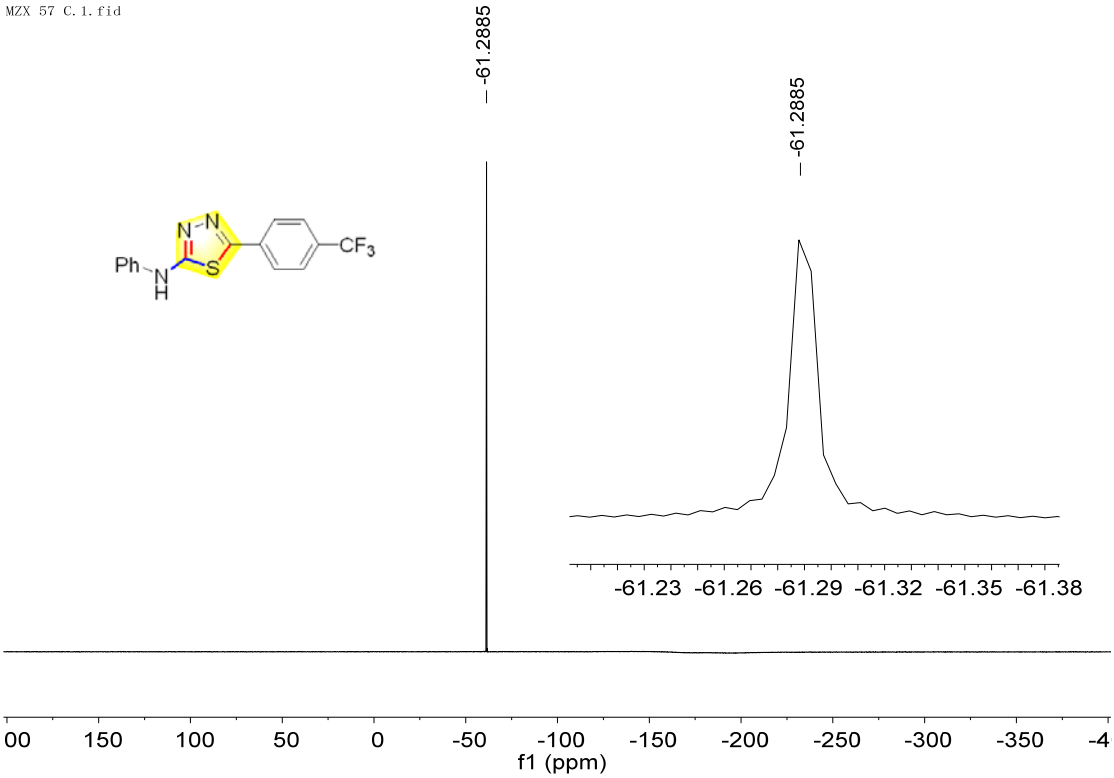
^{13}C NMR



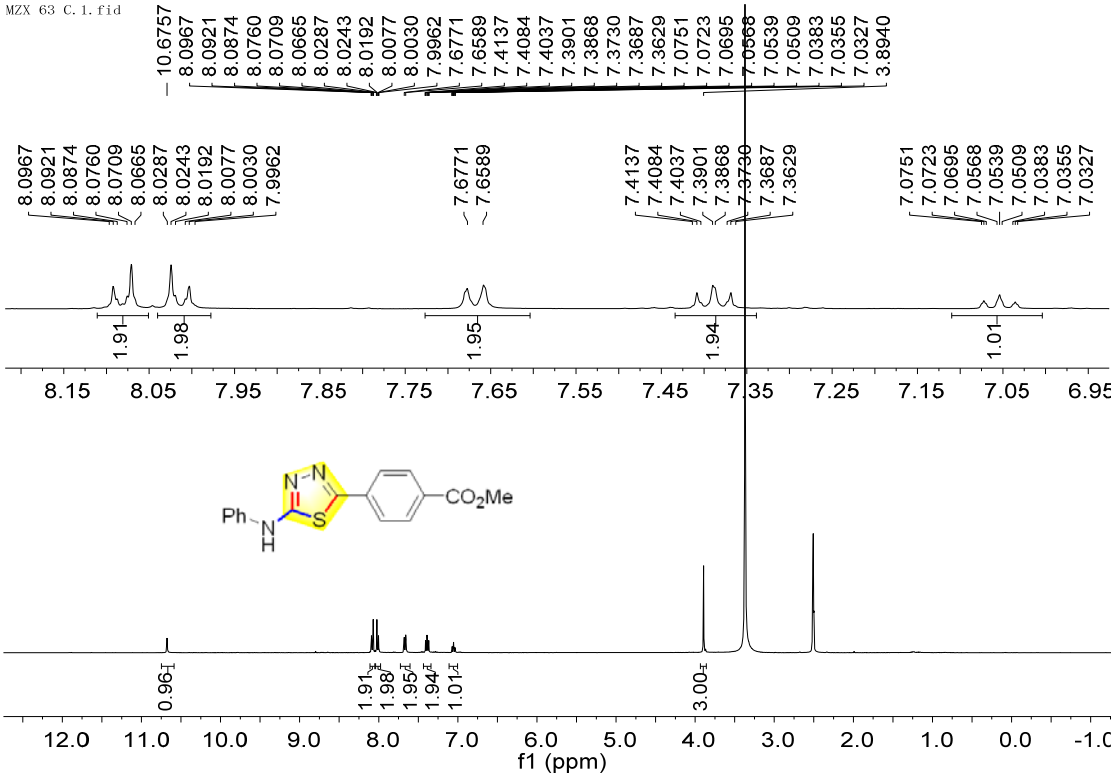
DEPT 90 and DEPT 135



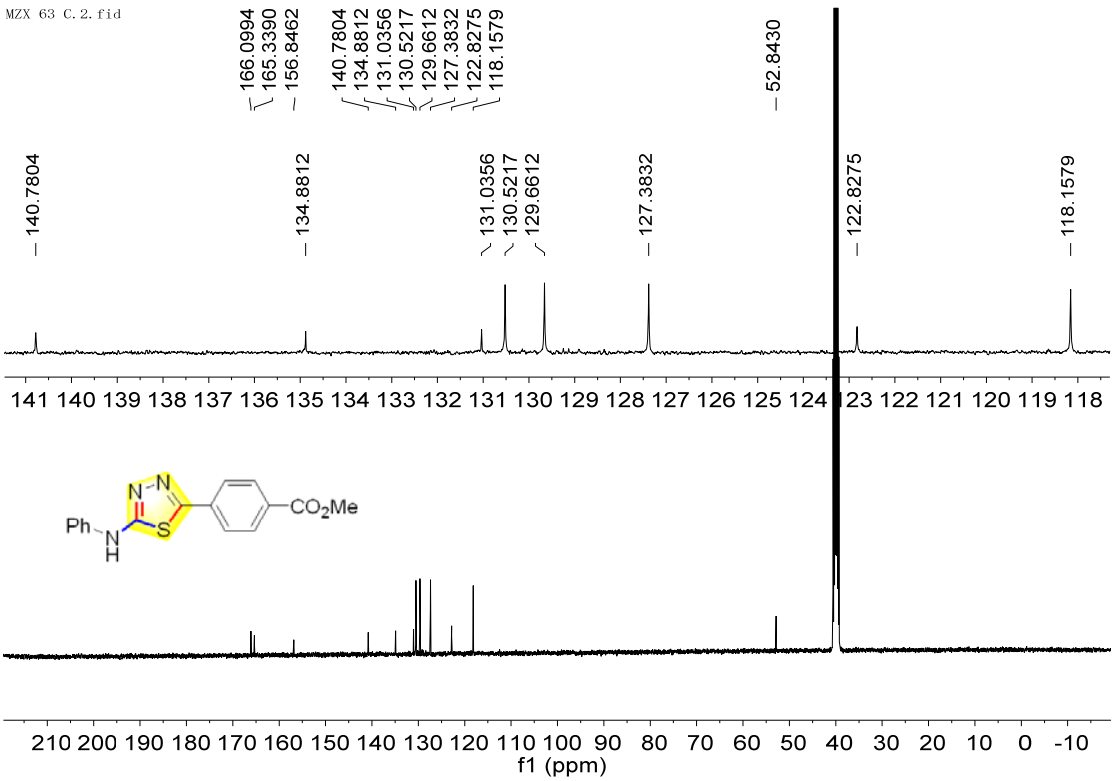
^{19}F NMR



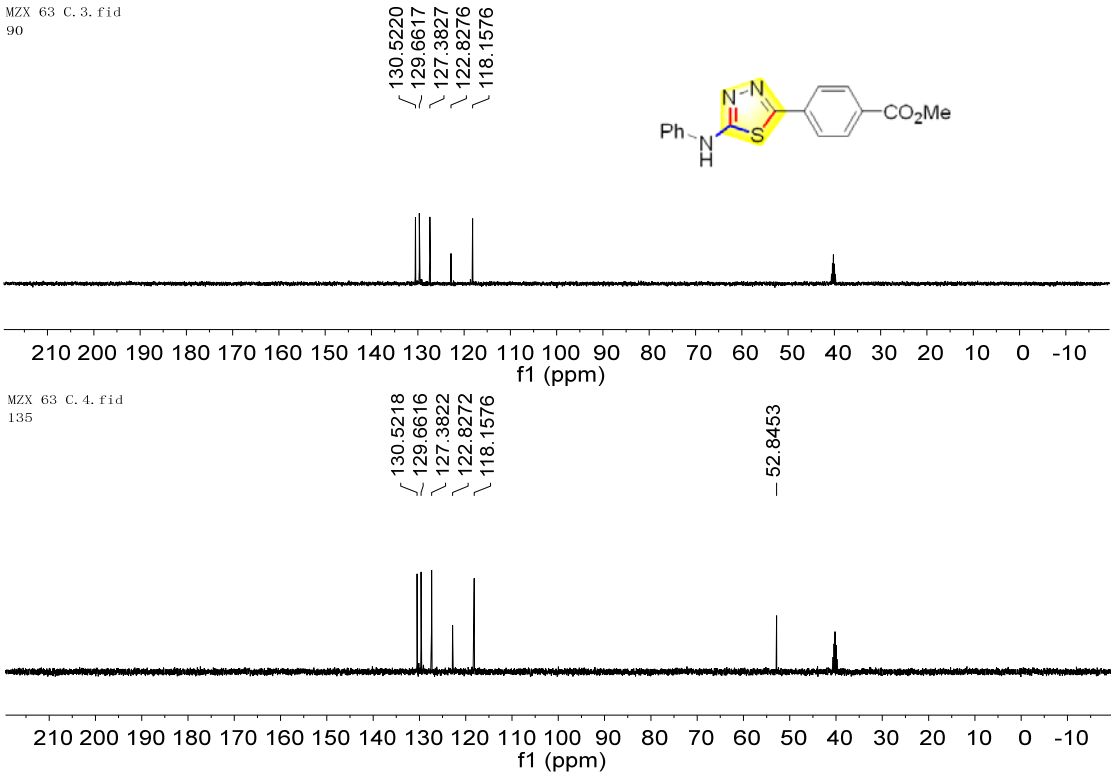
3ab, ^{1}H NMR



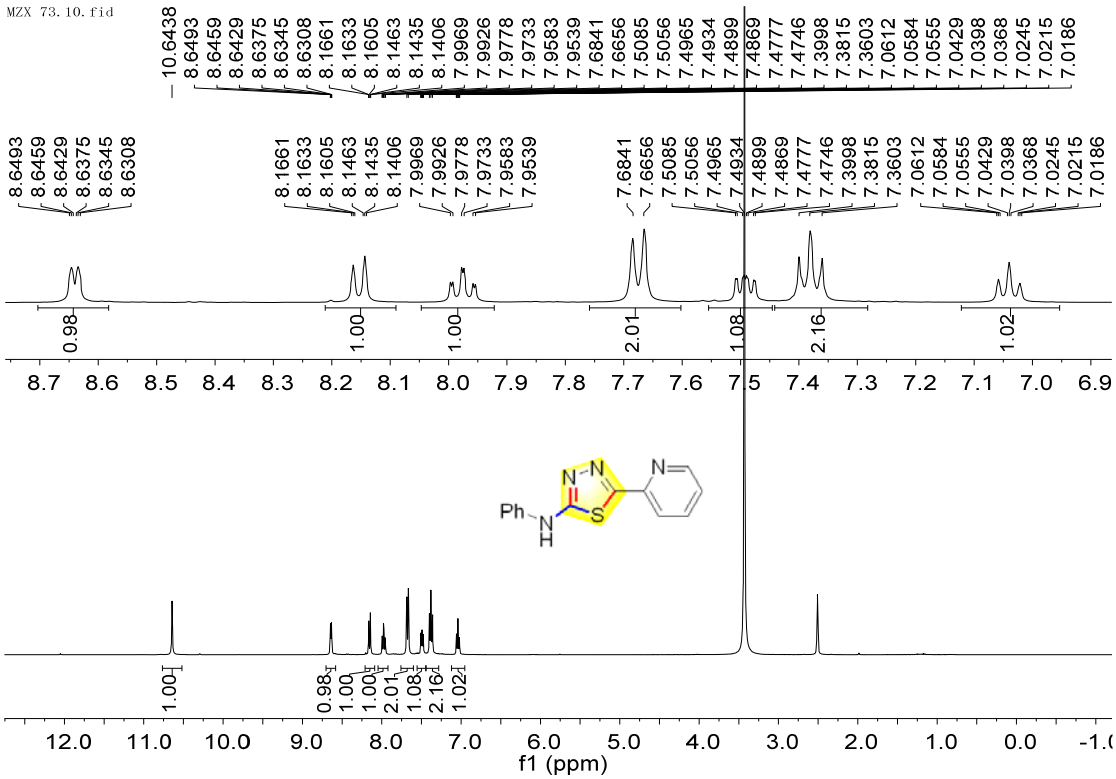
^{13}C NMR



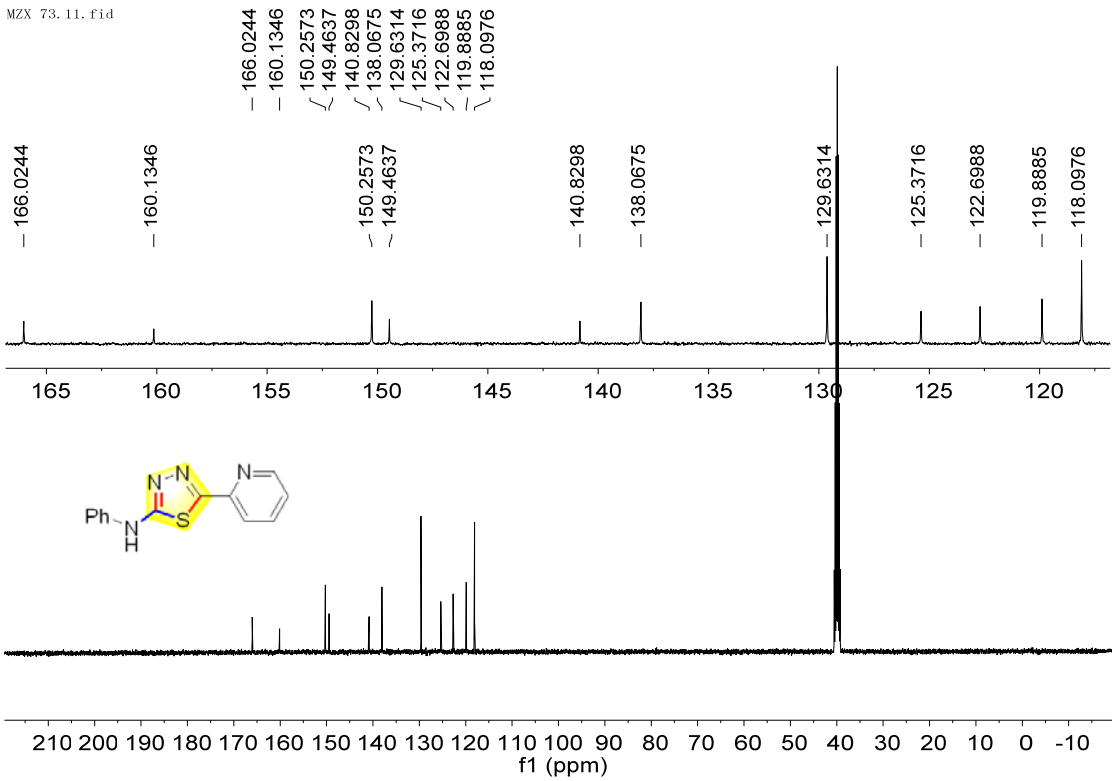
DEPT 90 and DEPT 135



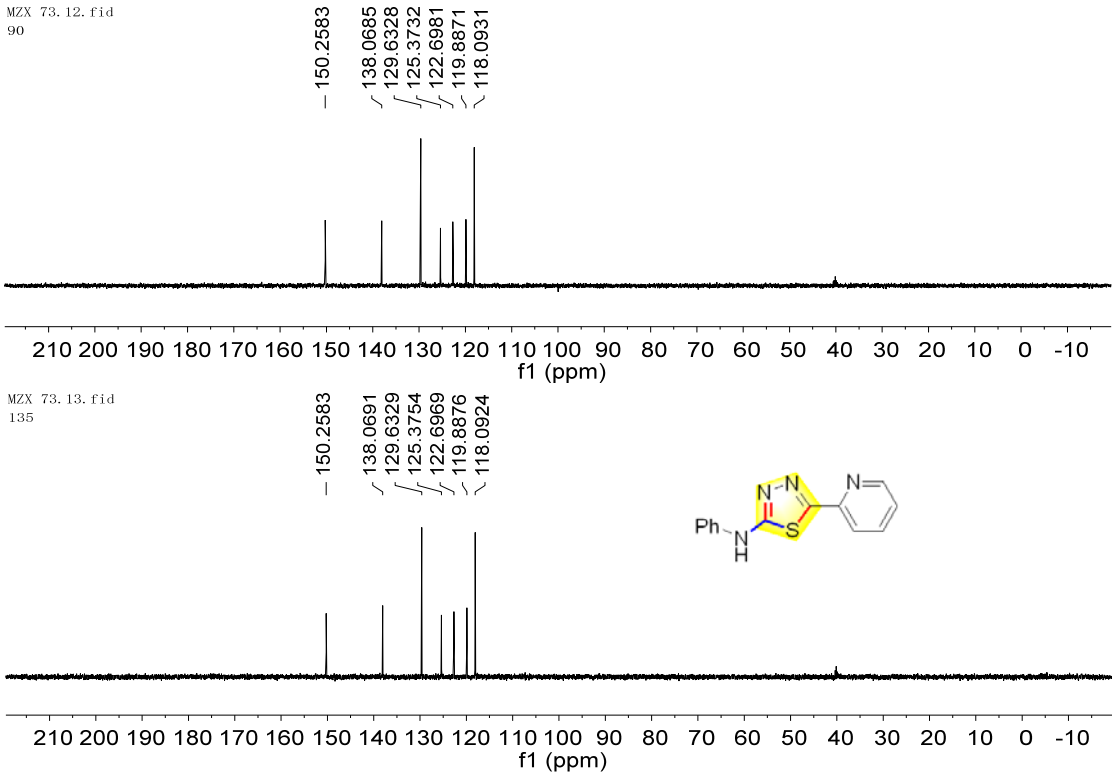
3ac, ^{1}H NMR



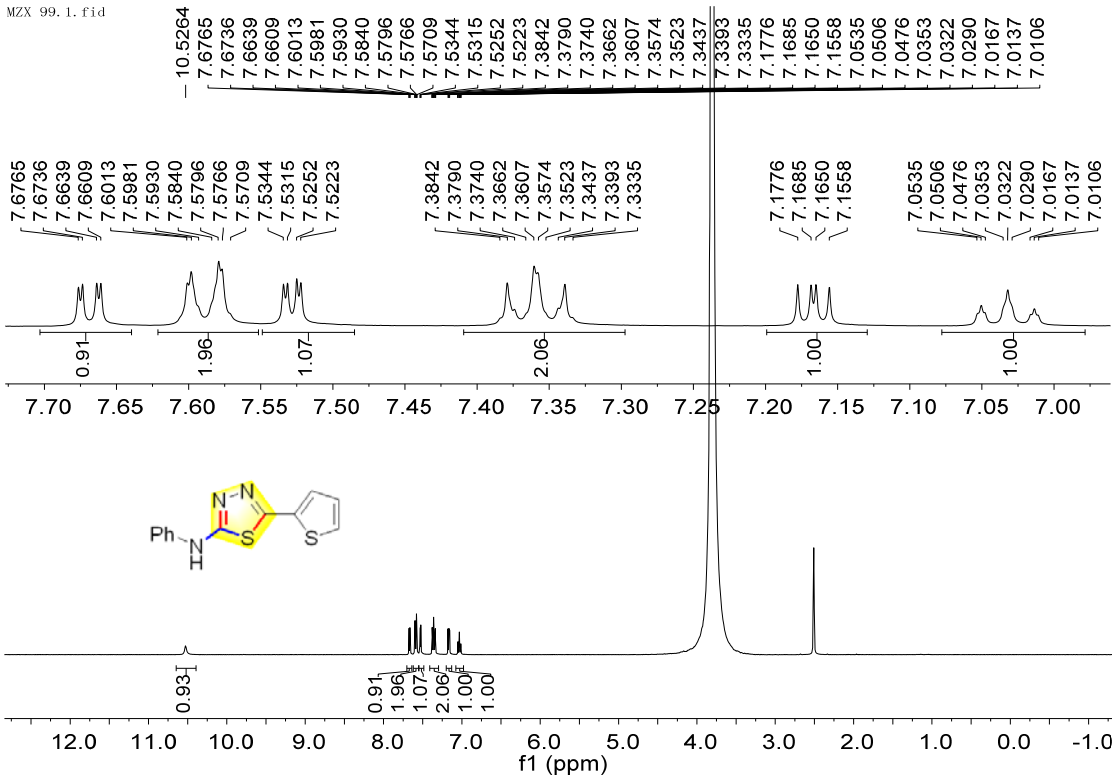
^{13}C NMR



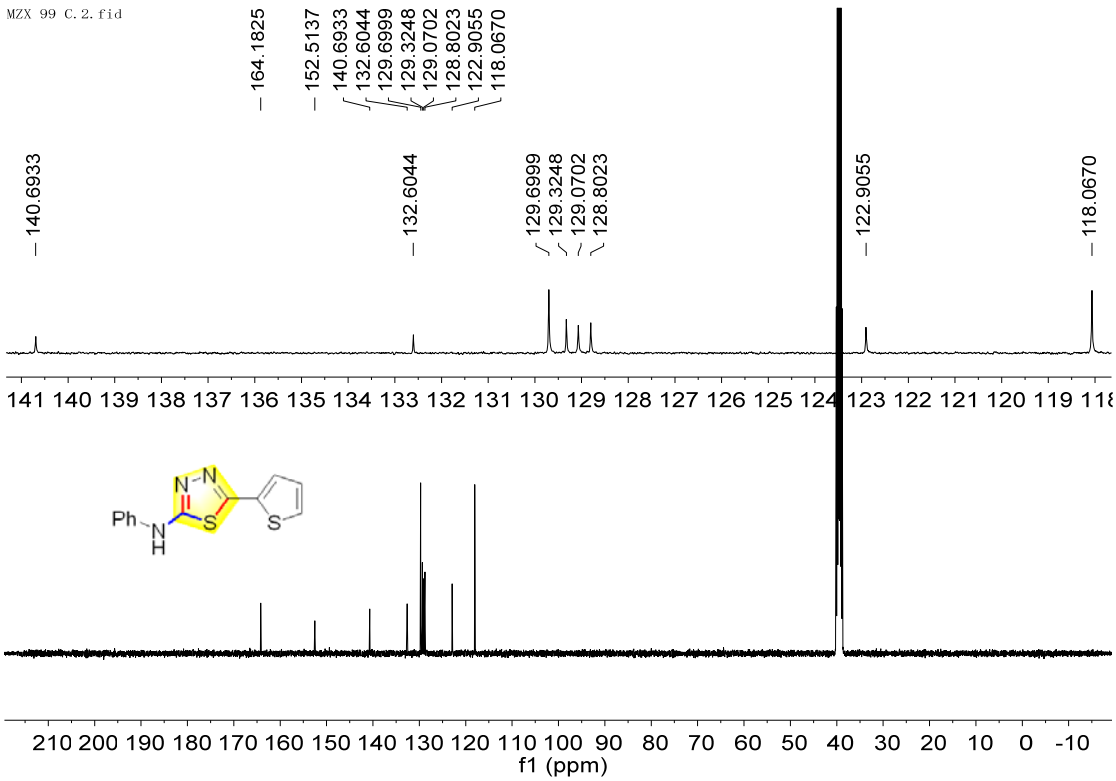
DEPT 90 and DEPT 135



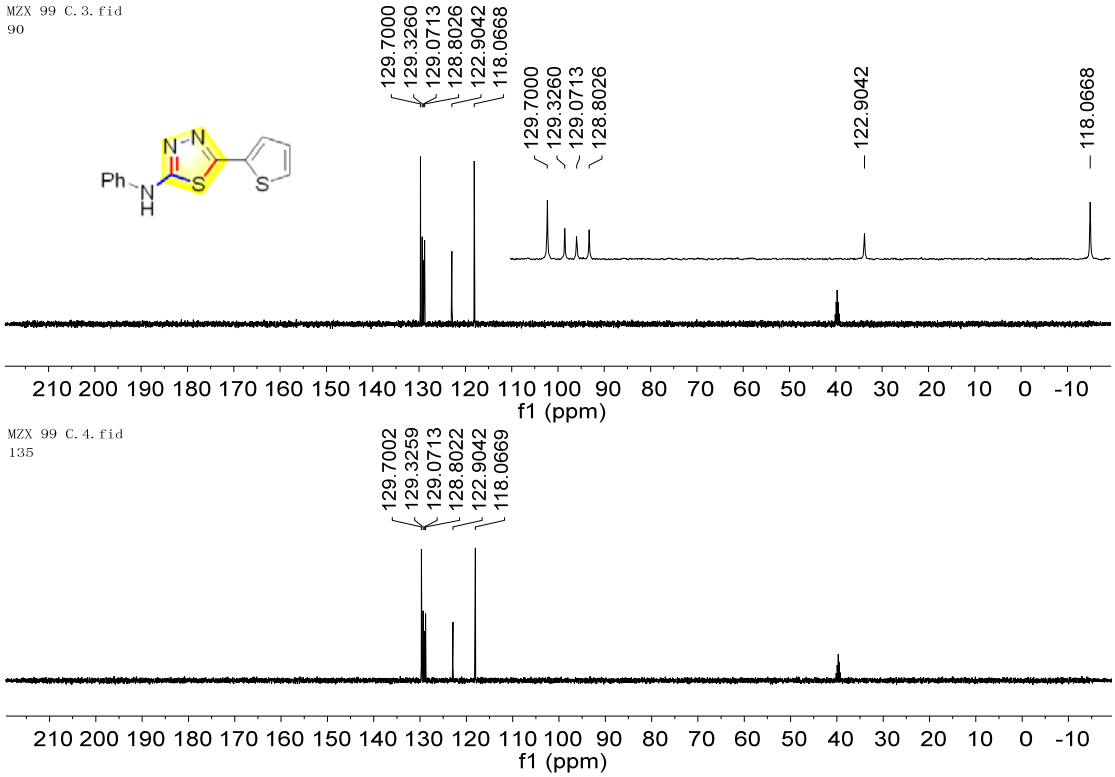
3ad, ^{1}H NMR



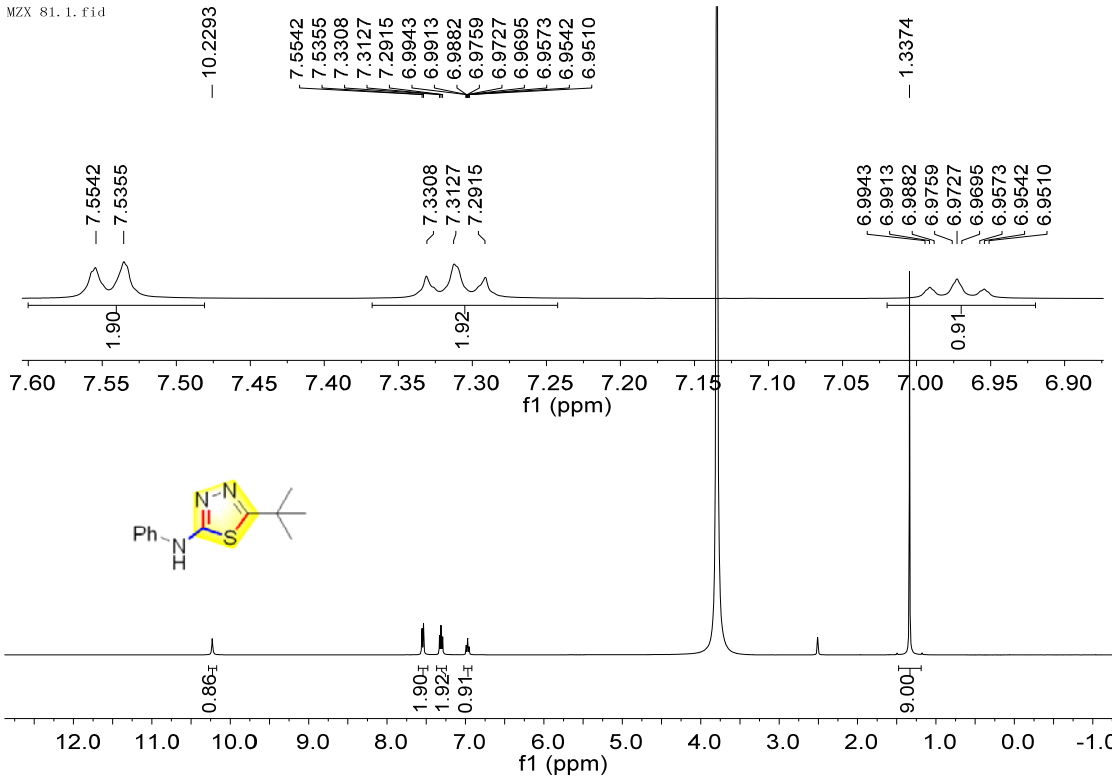
^{13}C NMR



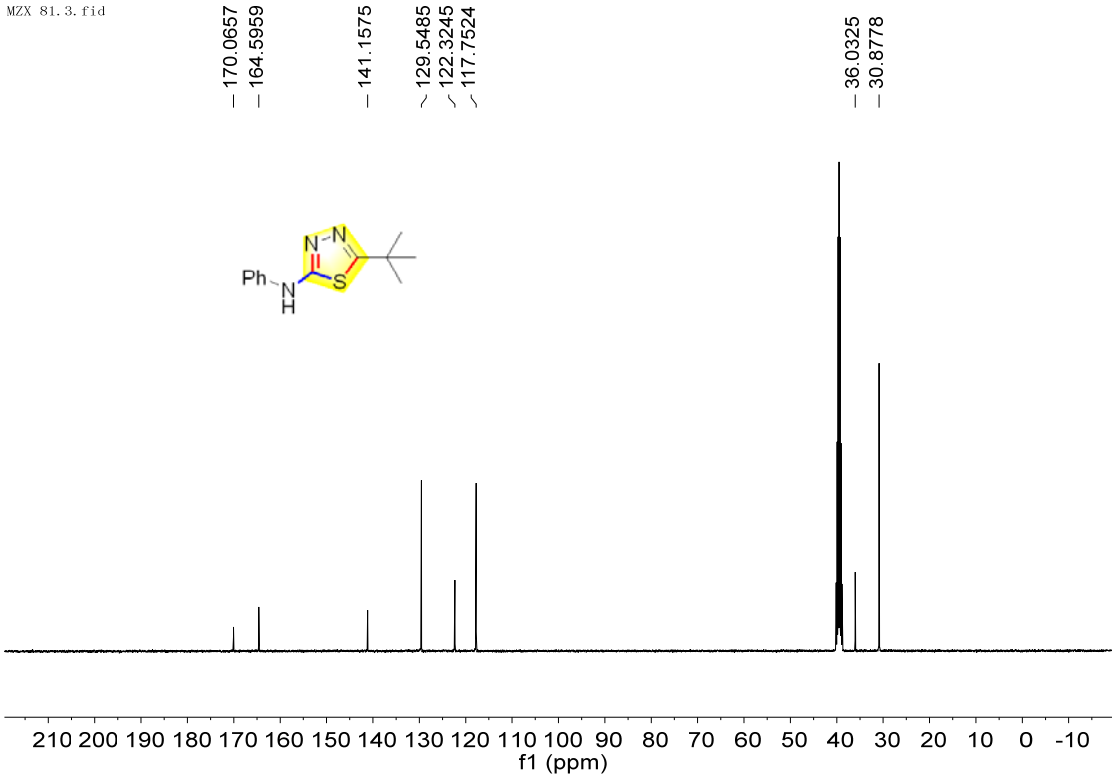
DEPT 90 and DEPT 135



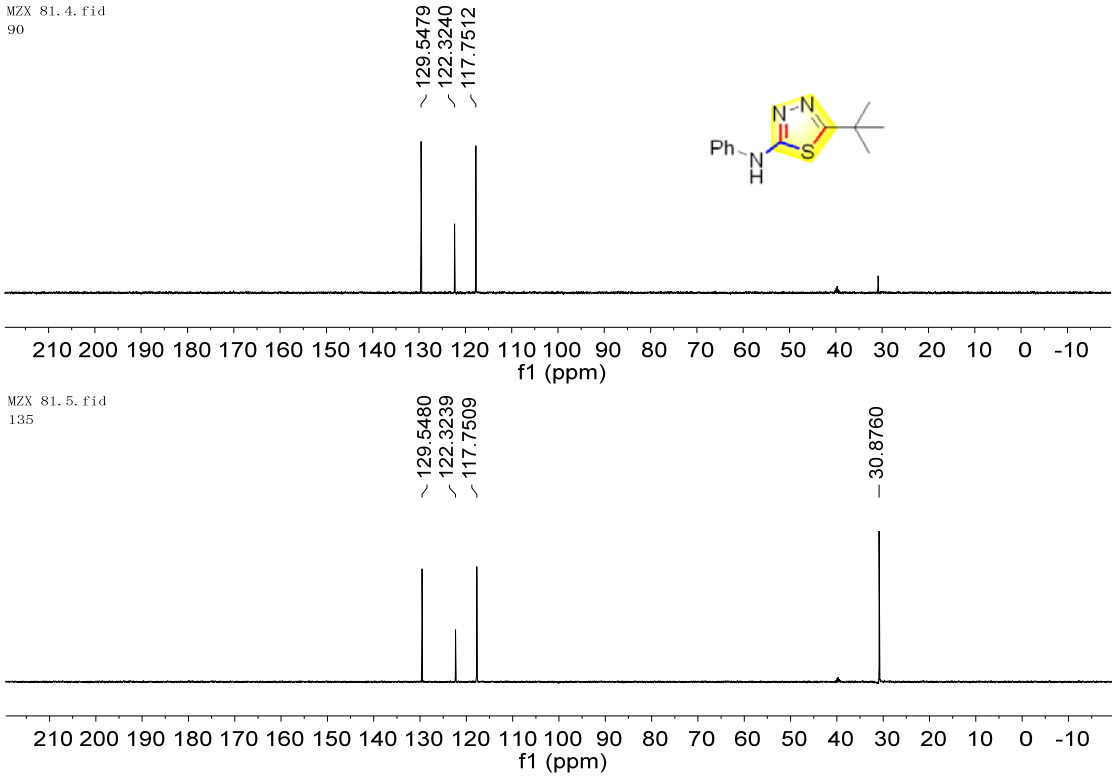
3ae, ^{1}H NMR



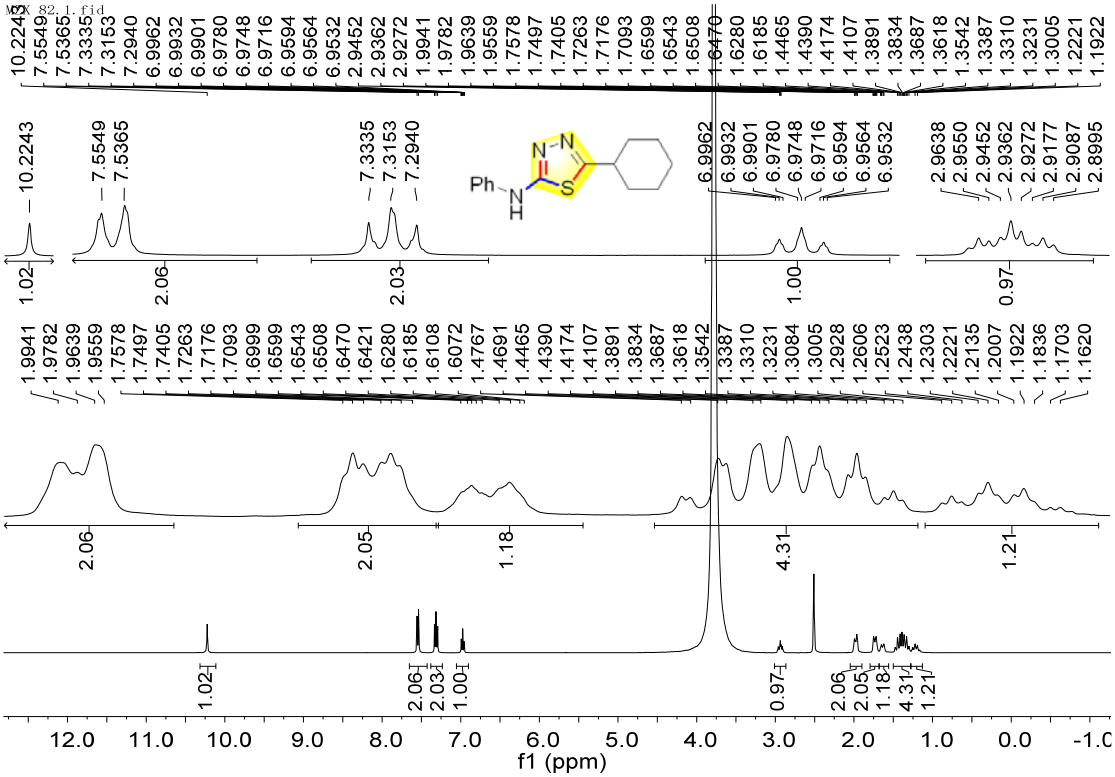
^{13}C NMR



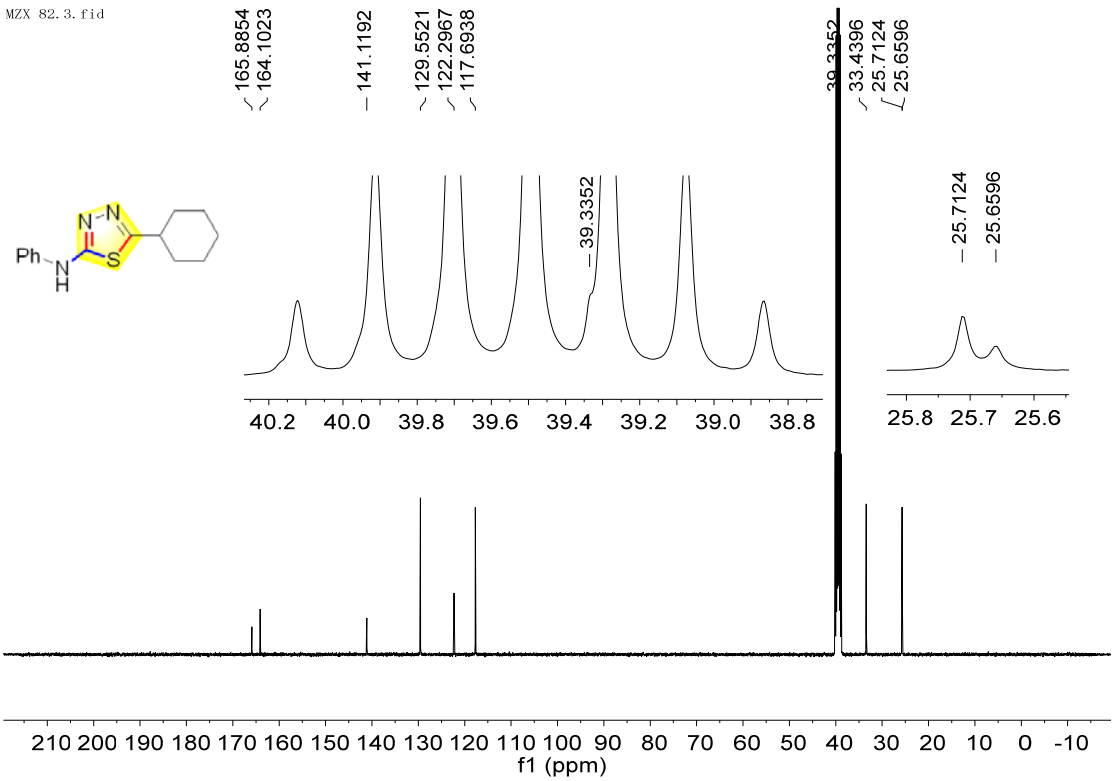
DEPT 90 and DEPT 135



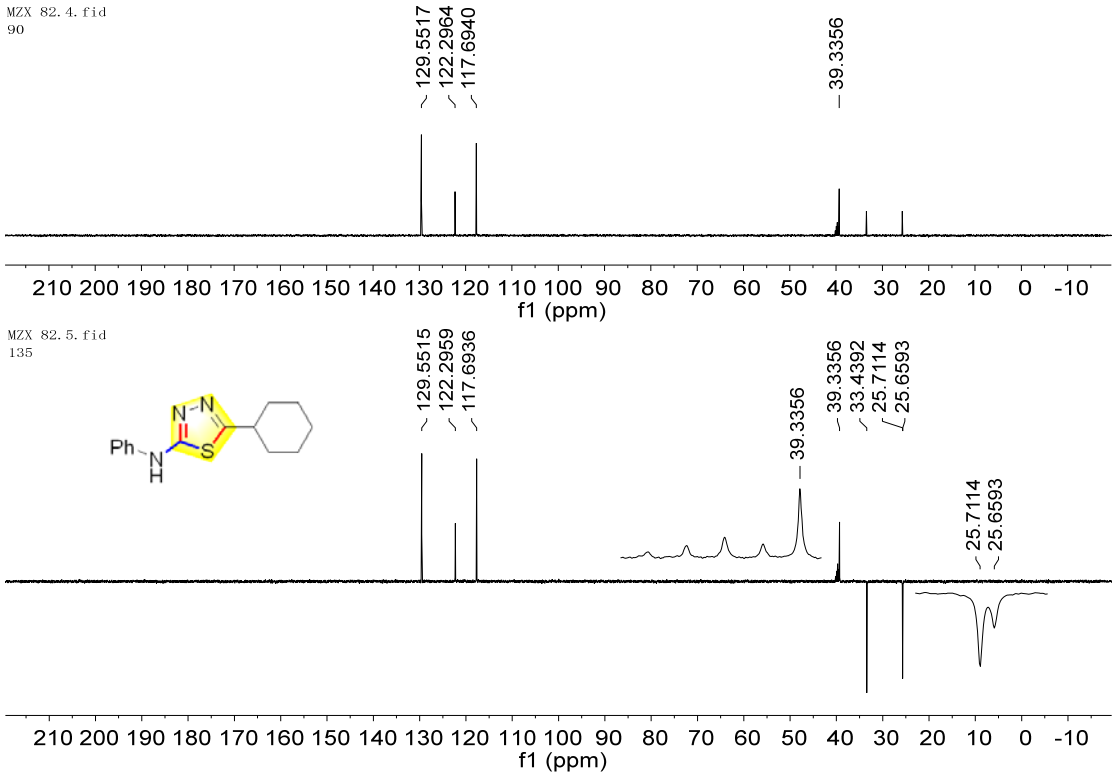
3af, ^{1}H NMR



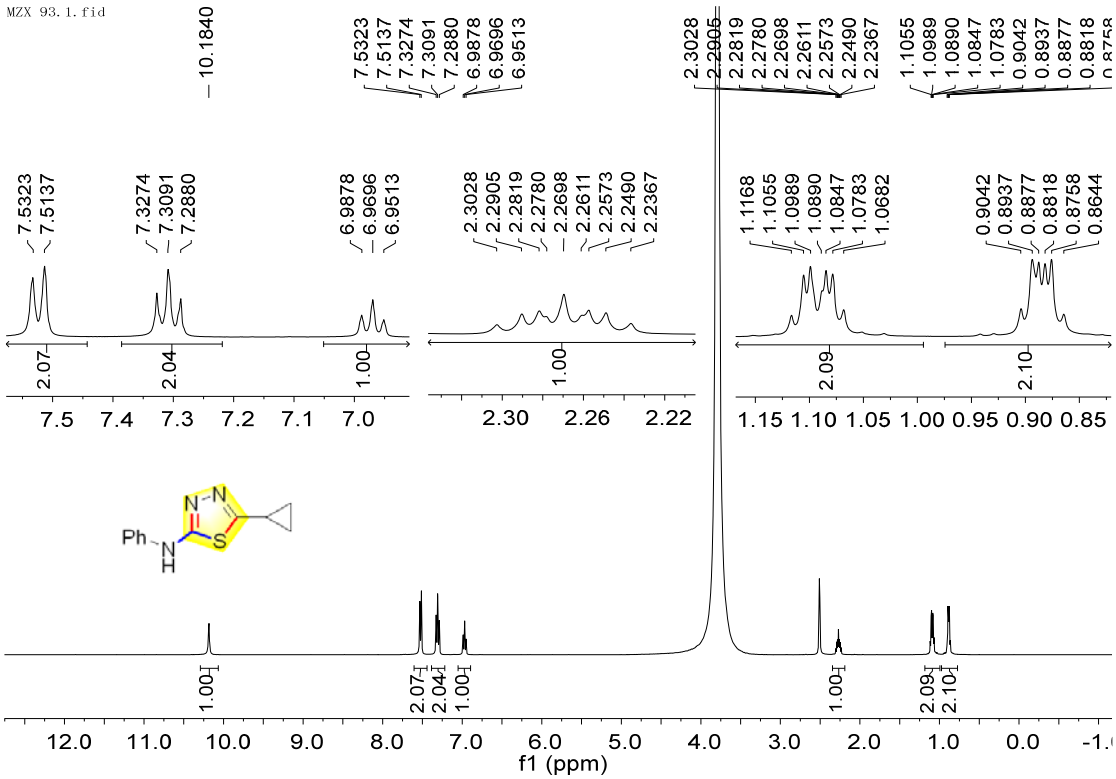
^{13}C NMR



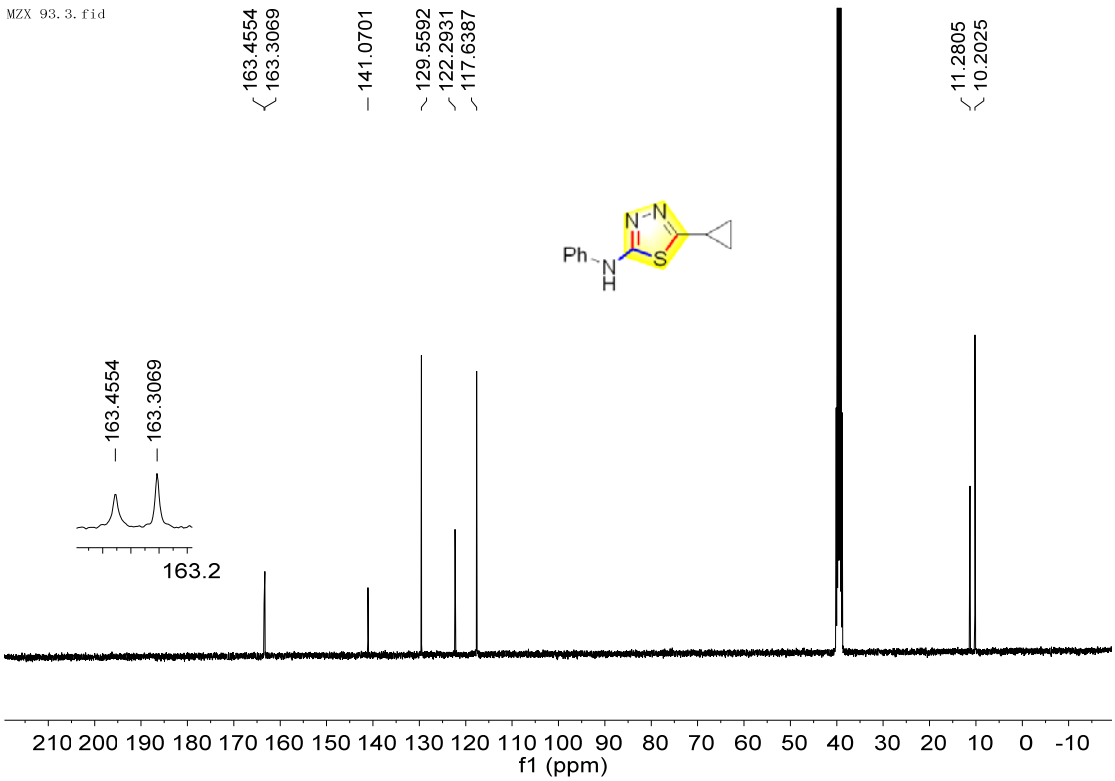
DEPT 90 and DEPT 135



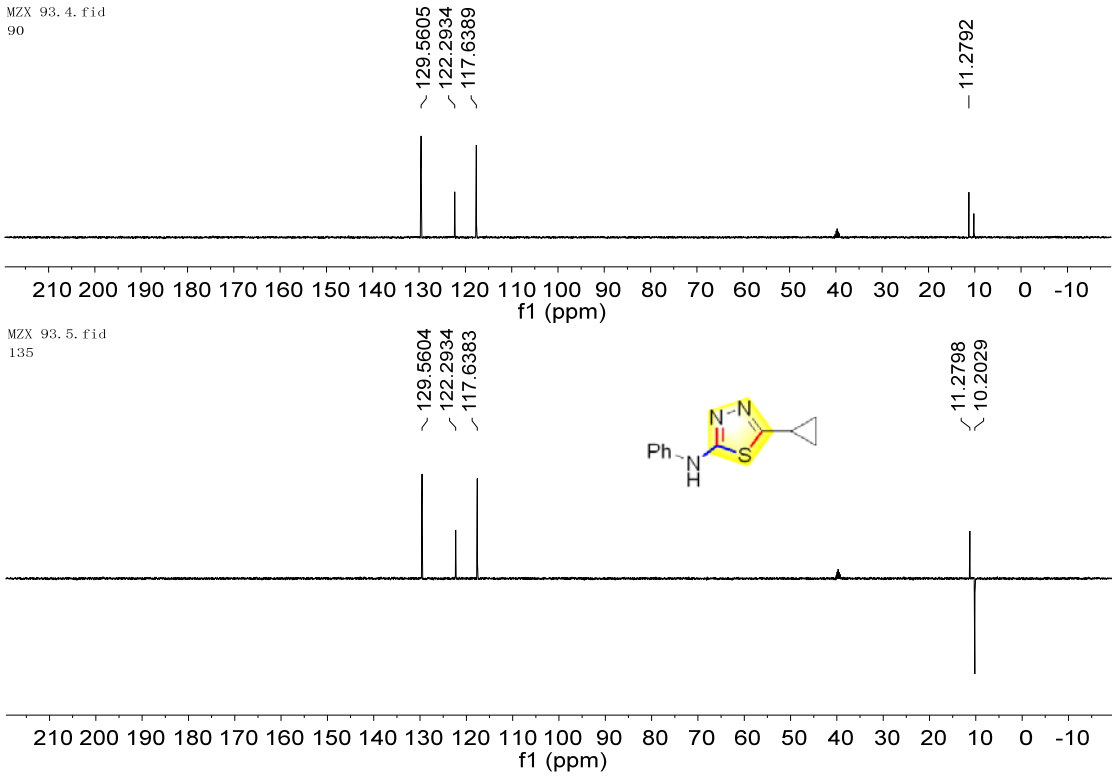
3ag, ^{1}H NMR



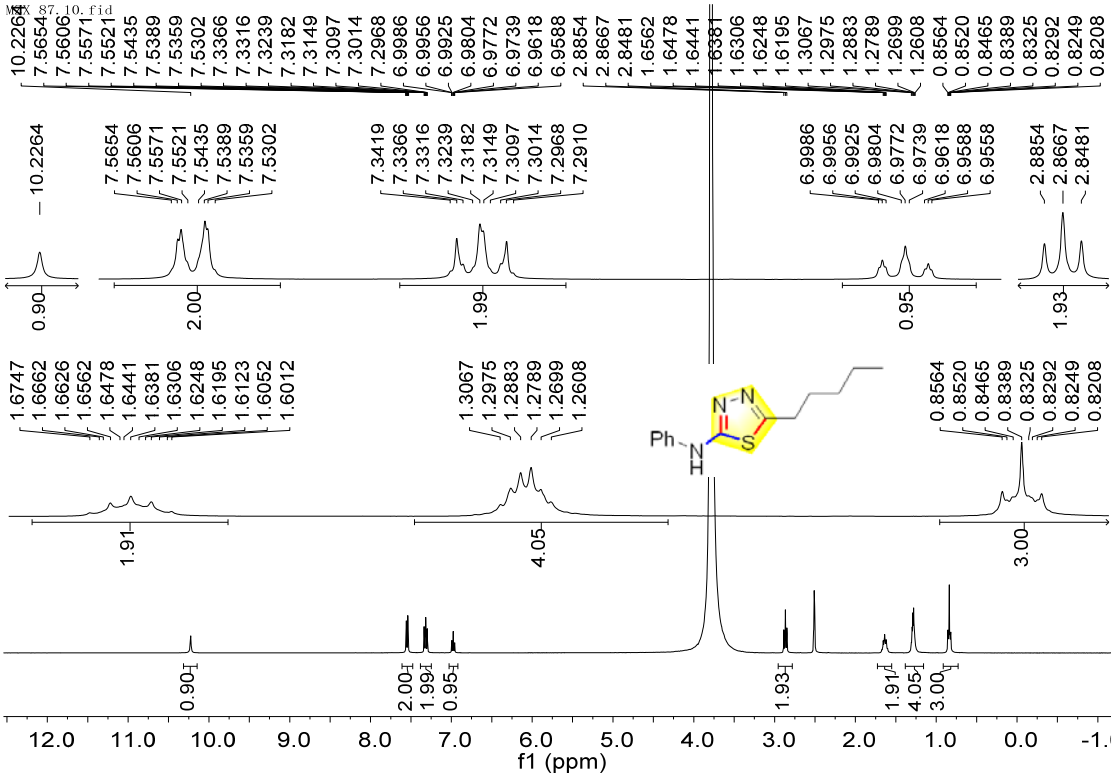
^{13}C NMR



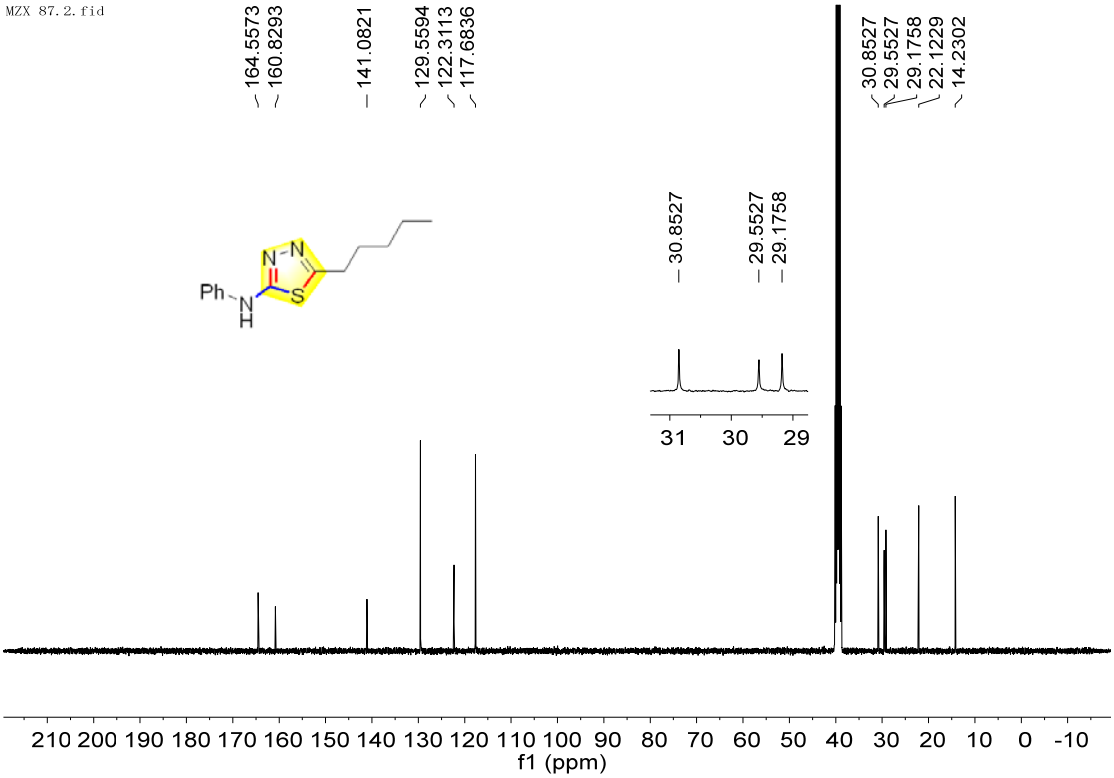
DEPT 90 and DEPT 135



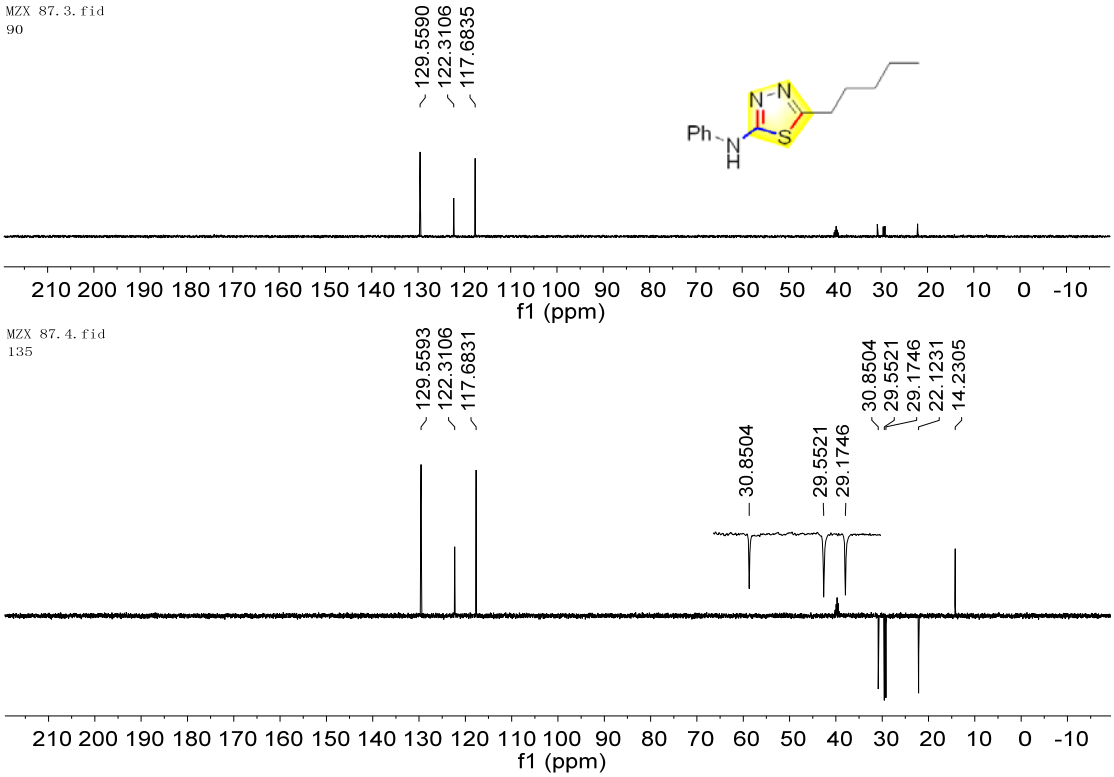
3ah, ^{1}H NMR



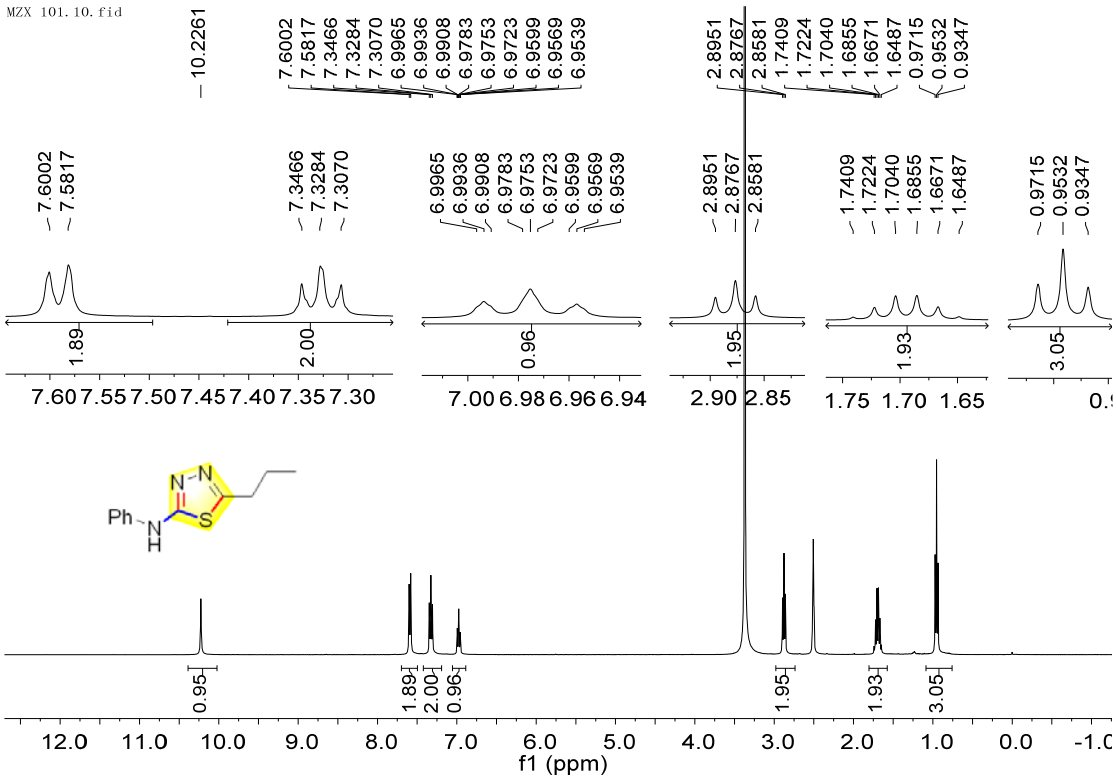
^{13}C NMR



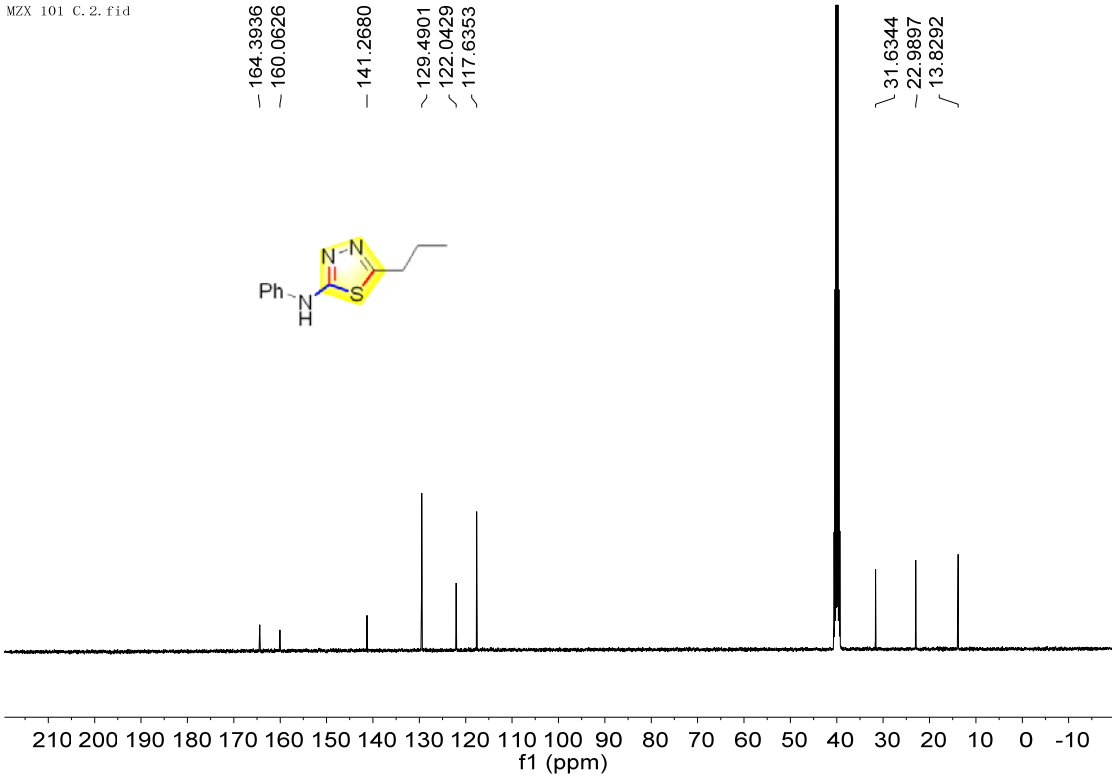
DEPT 90 and DEPT 135



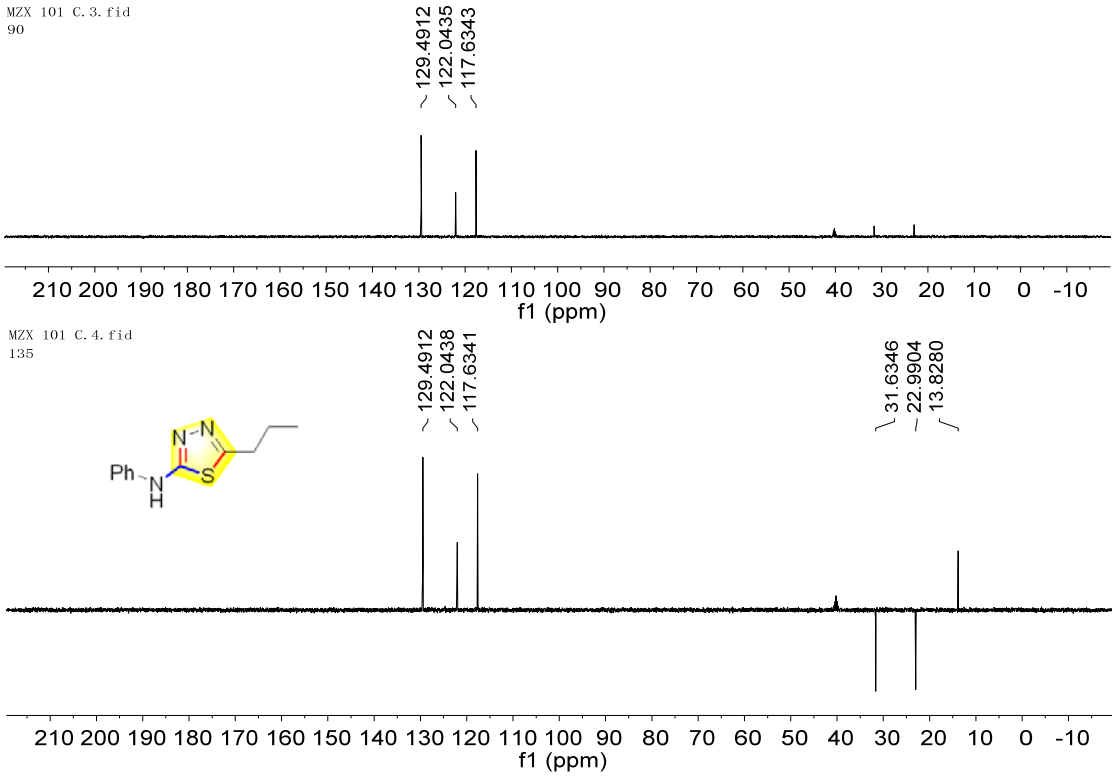
3ai, ^{1}H NMR



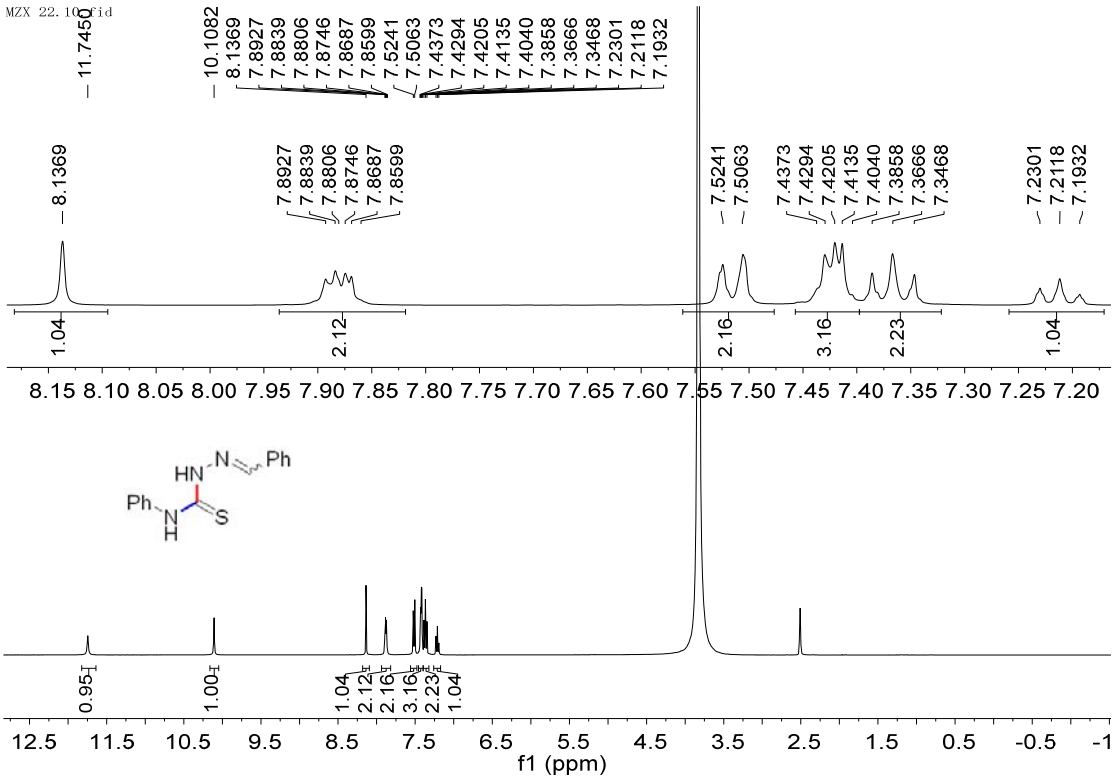
^{13}C NMR



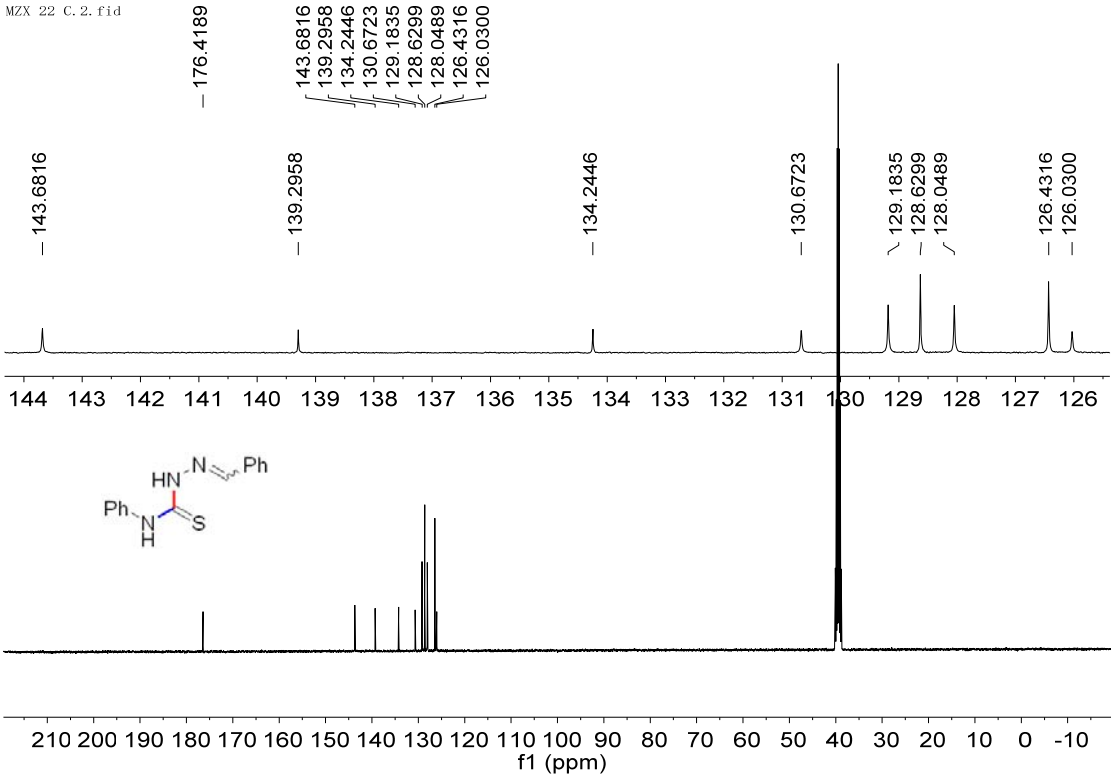
DEPT 90 and DEPT 135



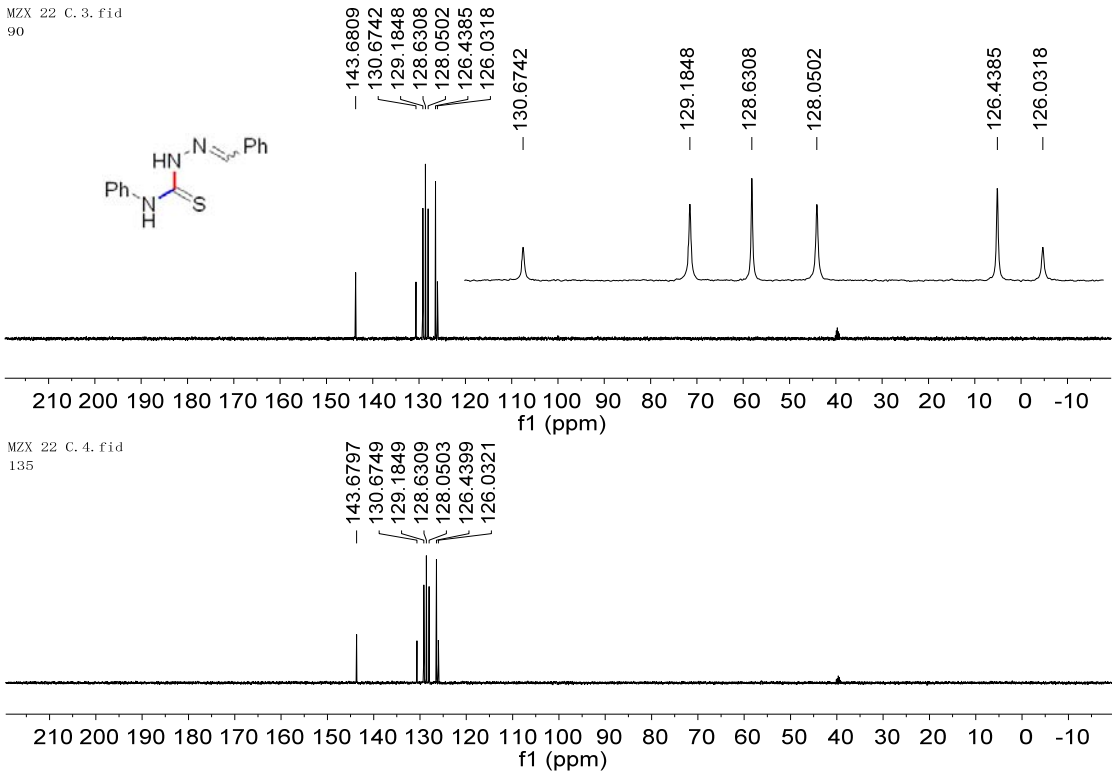
4a, ^{1}H NMR



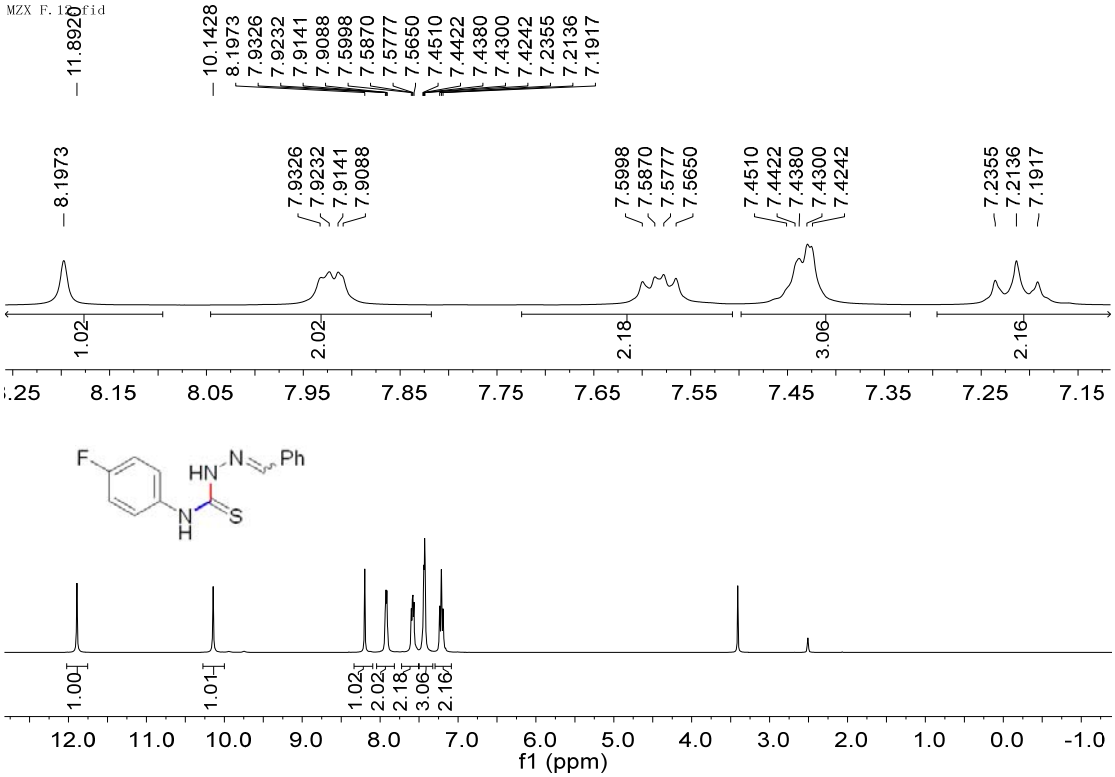
^{13}C NMR



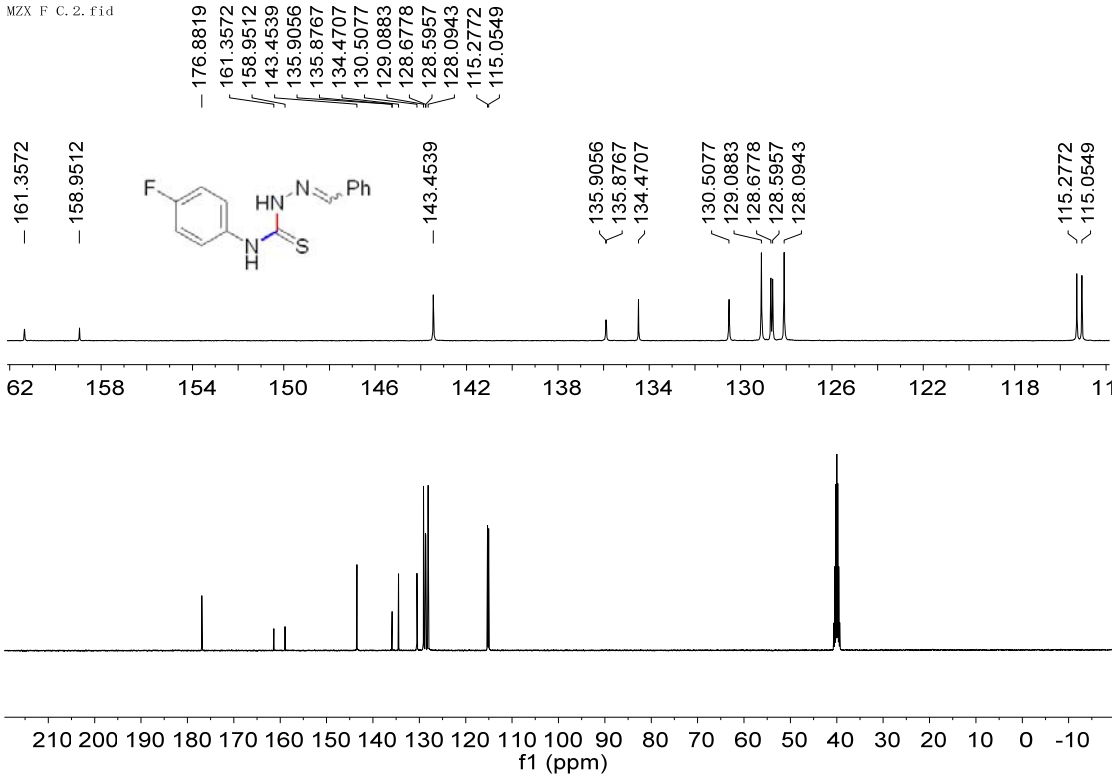
DEPT 90 and DEPT 135



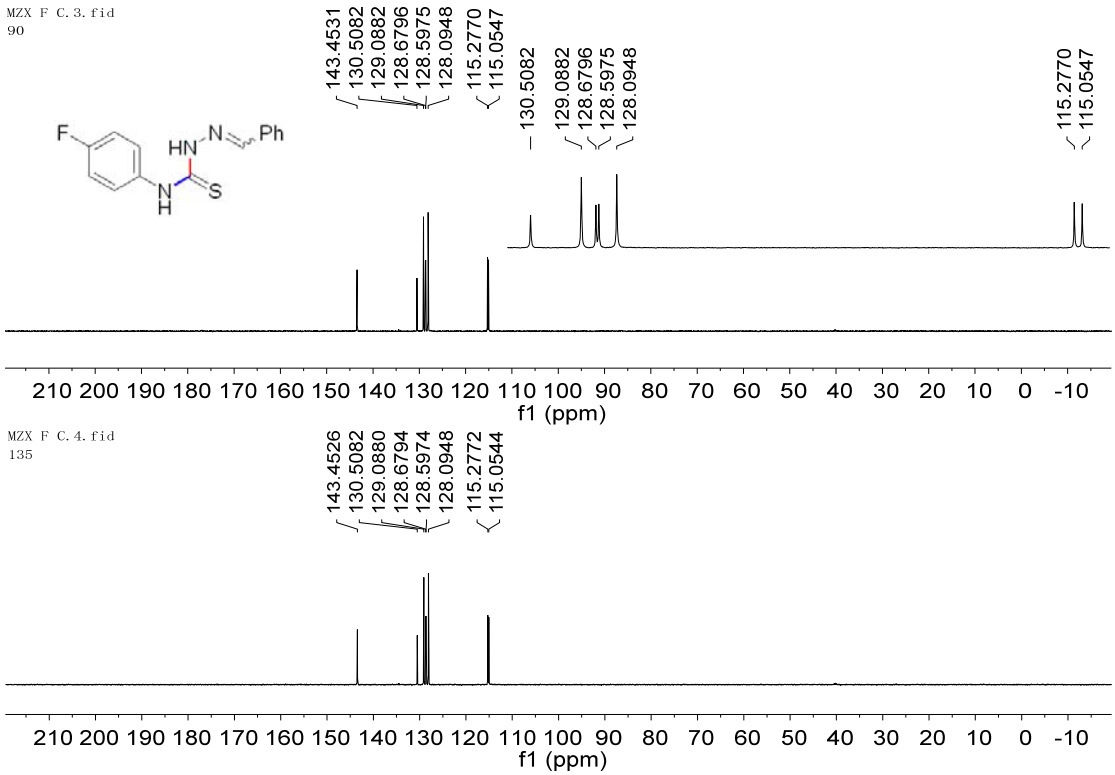
4j, ^{1}H NMR



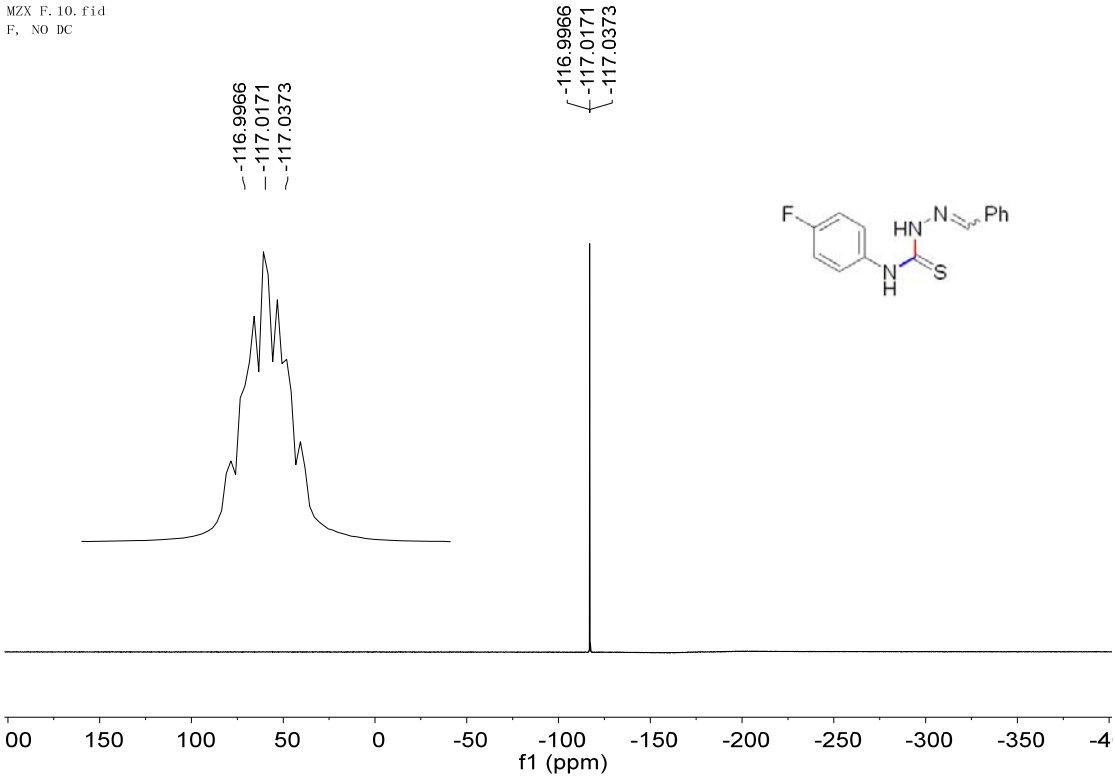
^{13}C NMR



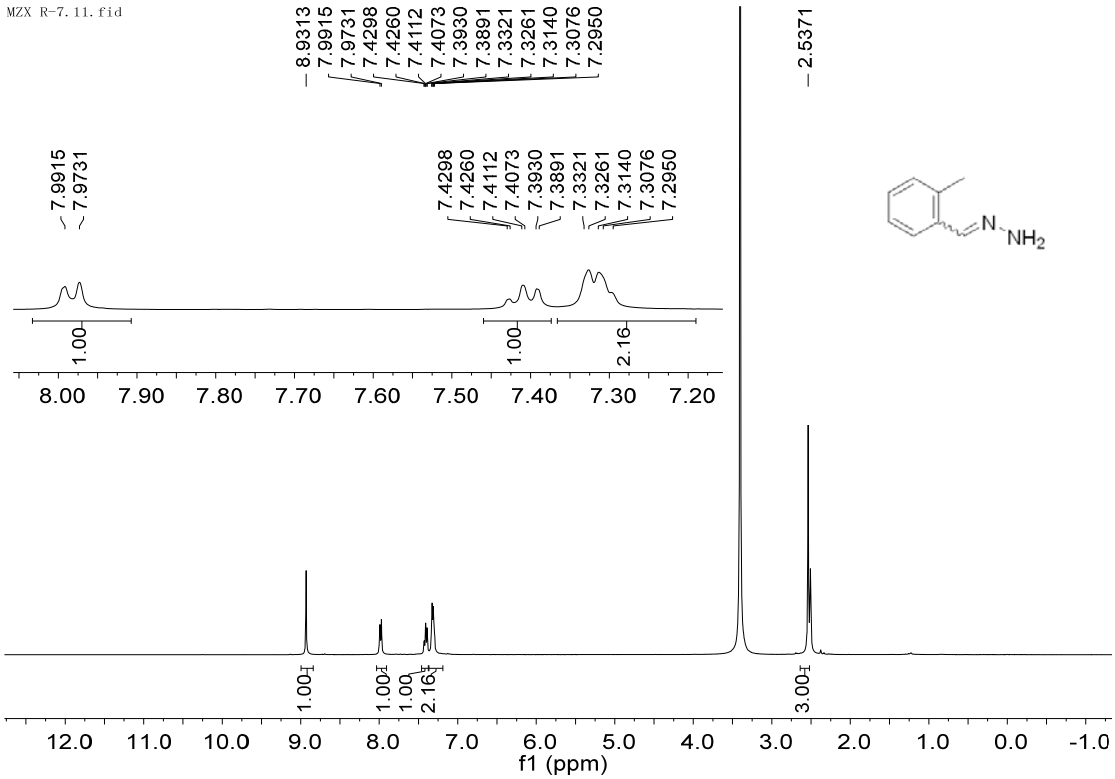
DEPT 90 and DEPT 135



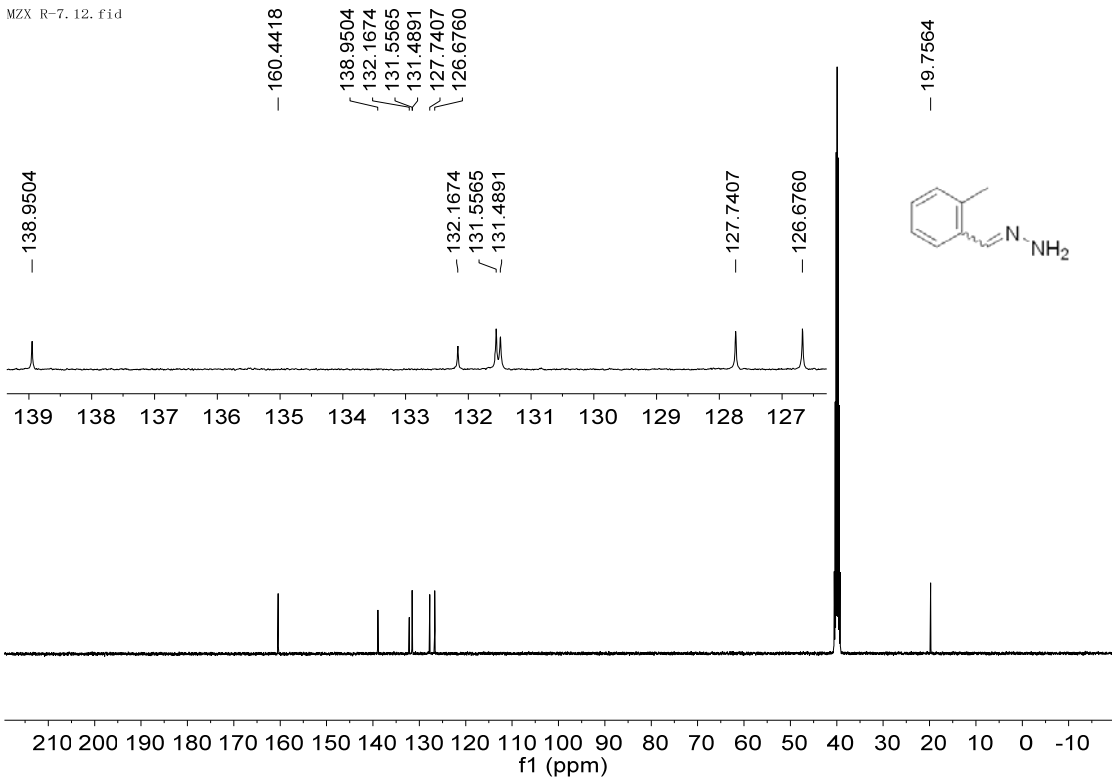
^{19}F NMR



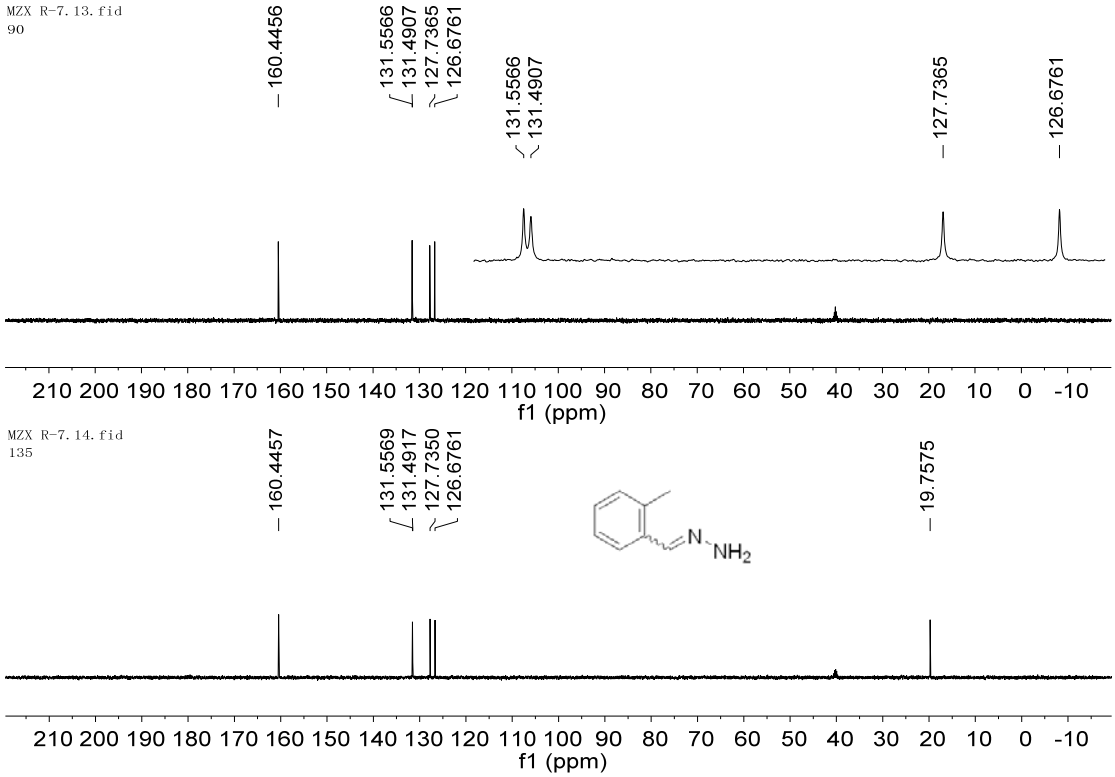
2p, ^{1}H NMR



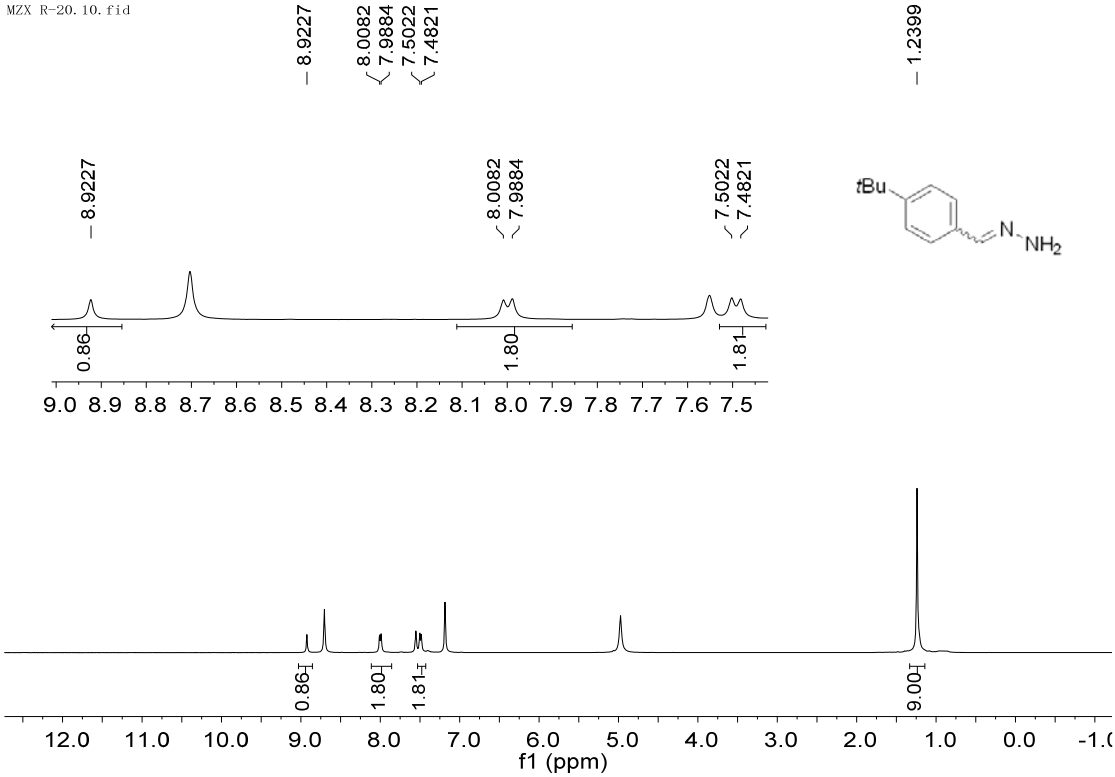
^{13}C NMR



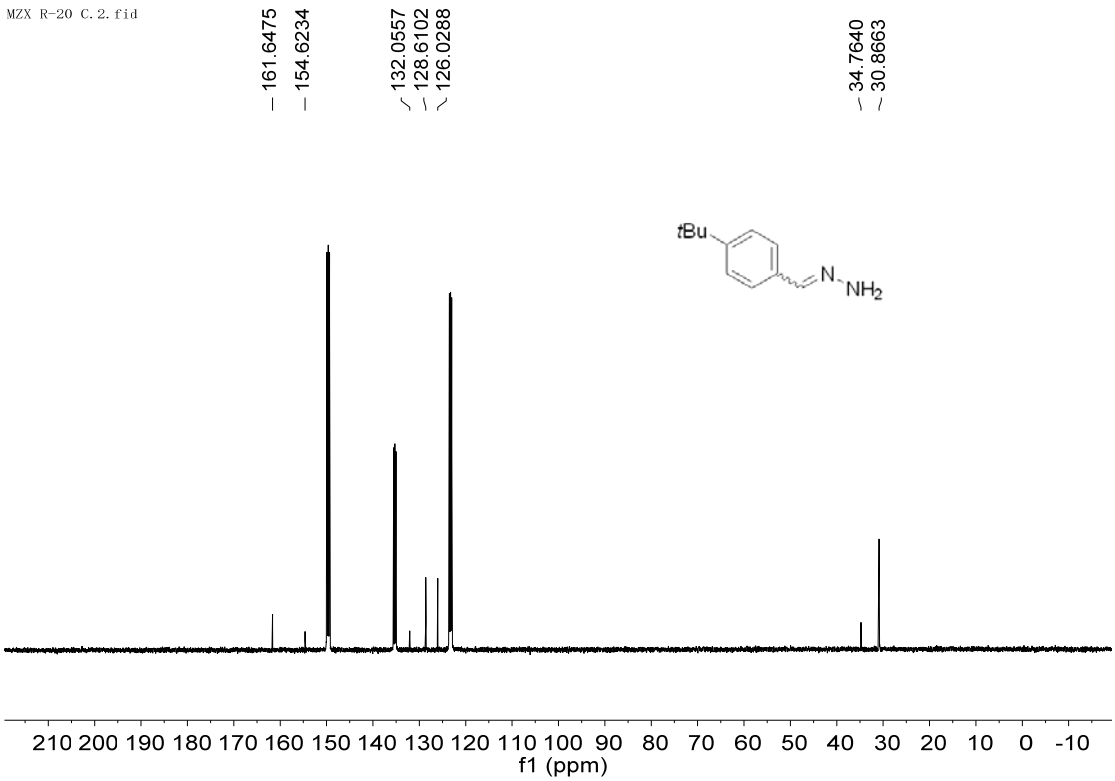
DEPT 90 and DEPT 135



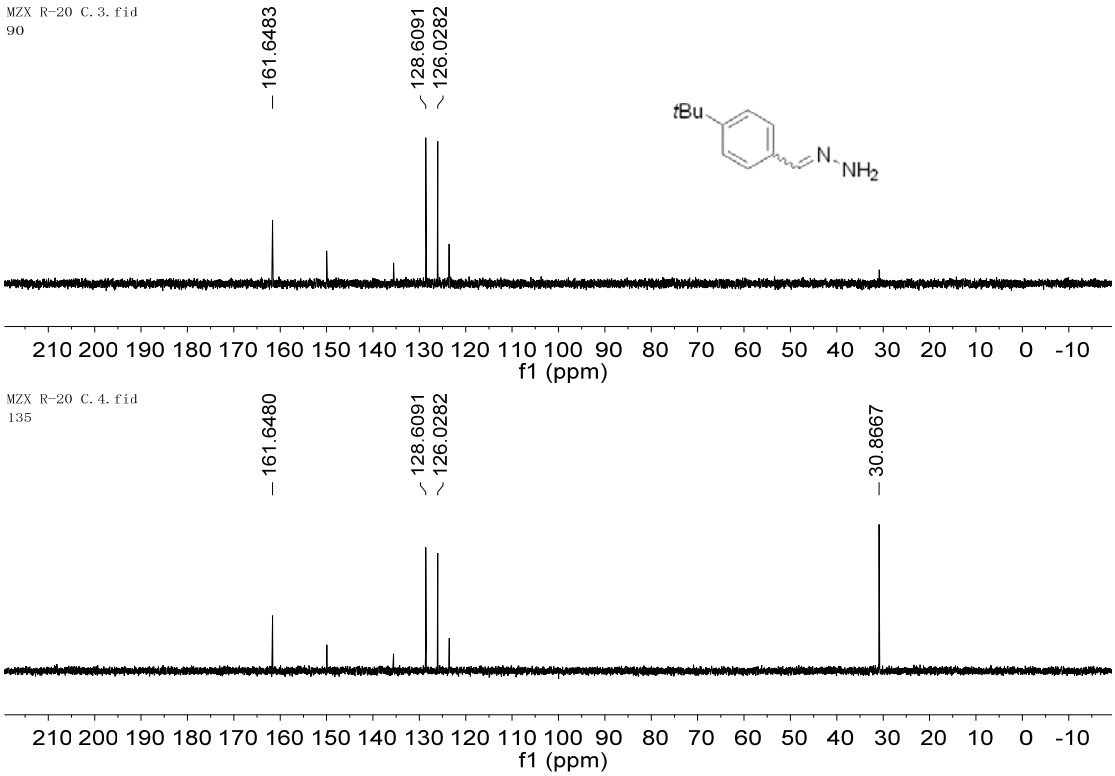
2q, ^{1}H NMR (in Pyridine-d_5)



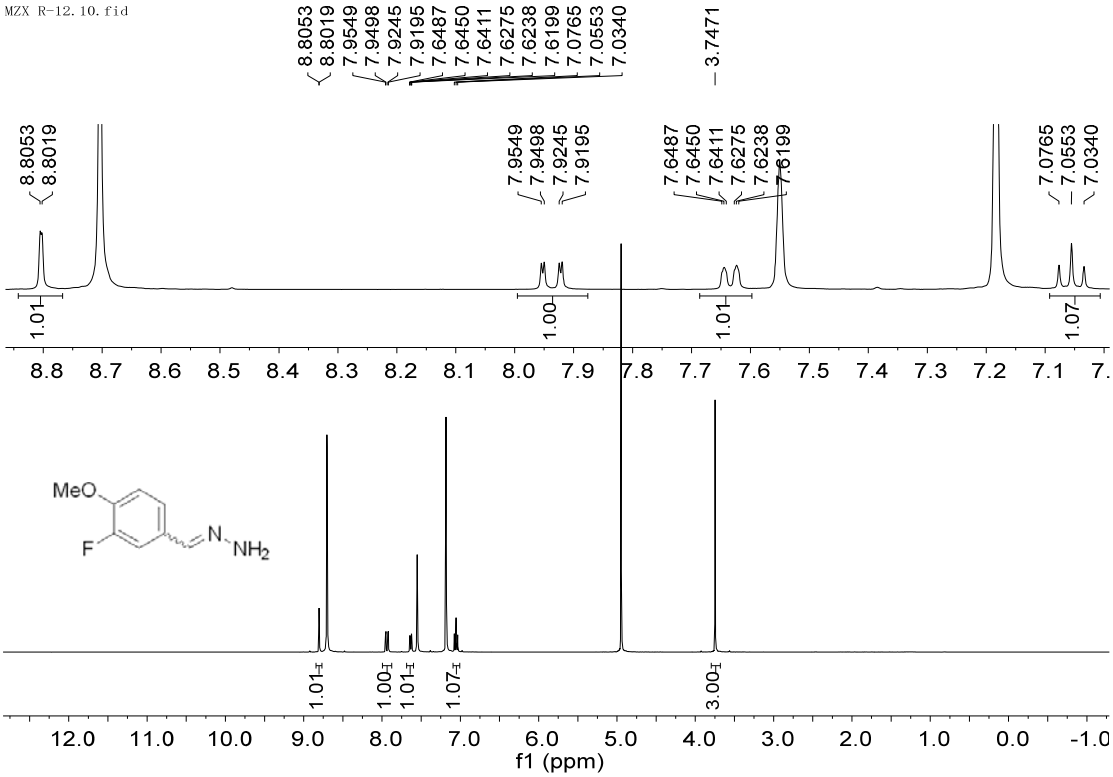
^{13}C NMR (in Pyridine-d_5)



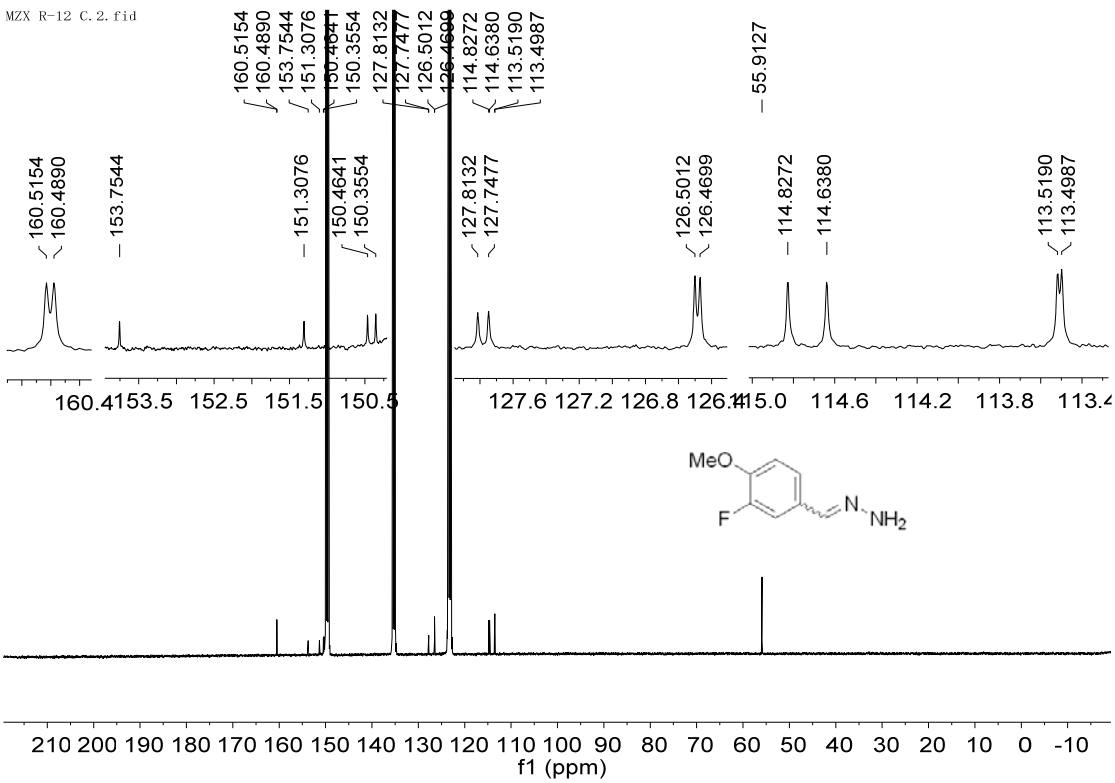
DEPT 90 and DEPT 135 (in Pyridine-d_5)



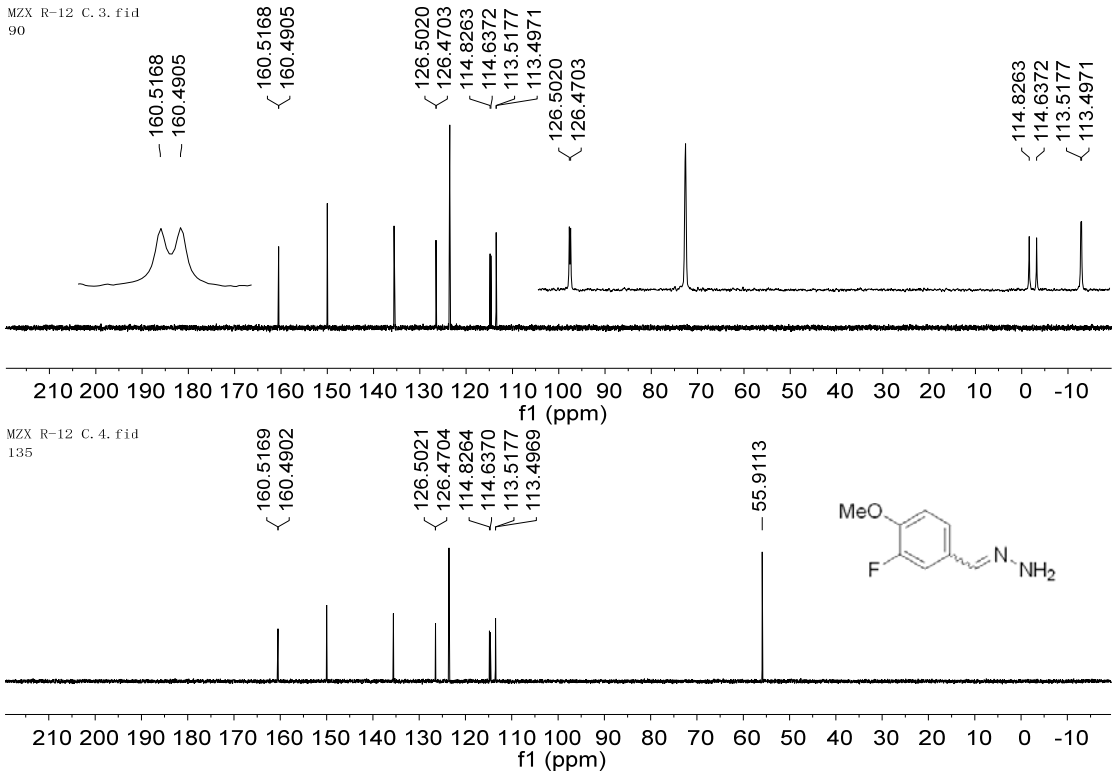
2r, ^{1}H NMR (in Pyridine-d_5)



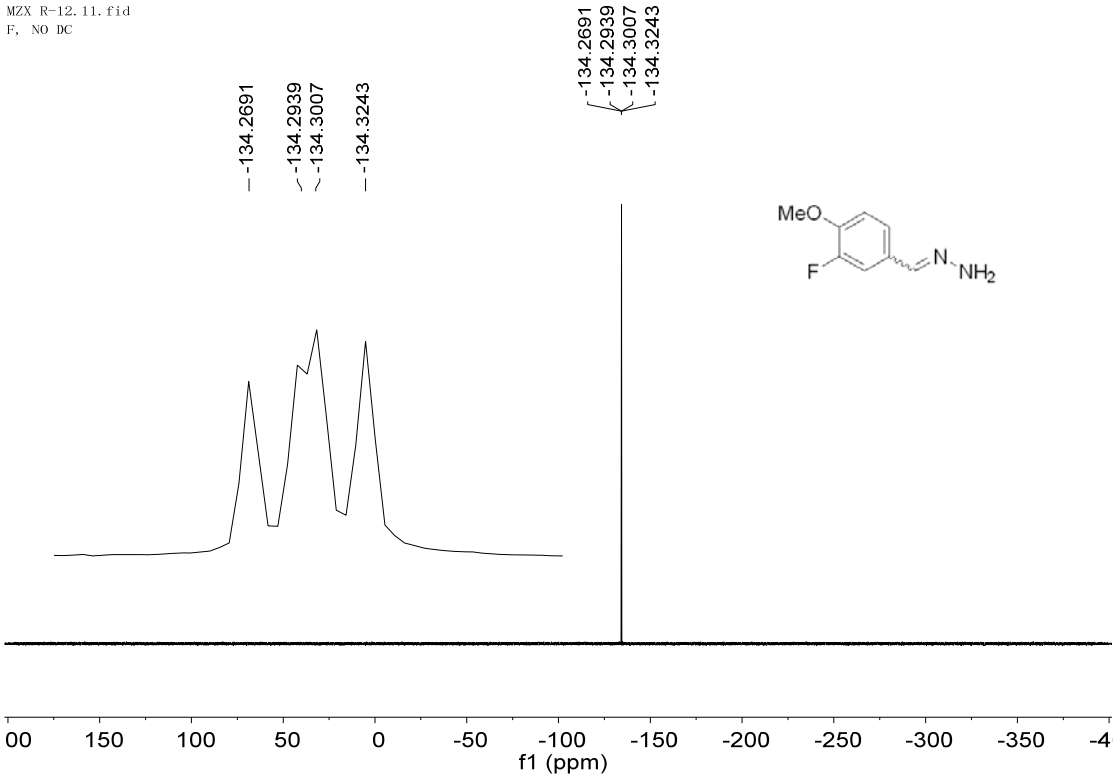
^{13}C NMR (in Pyridine-d_5)



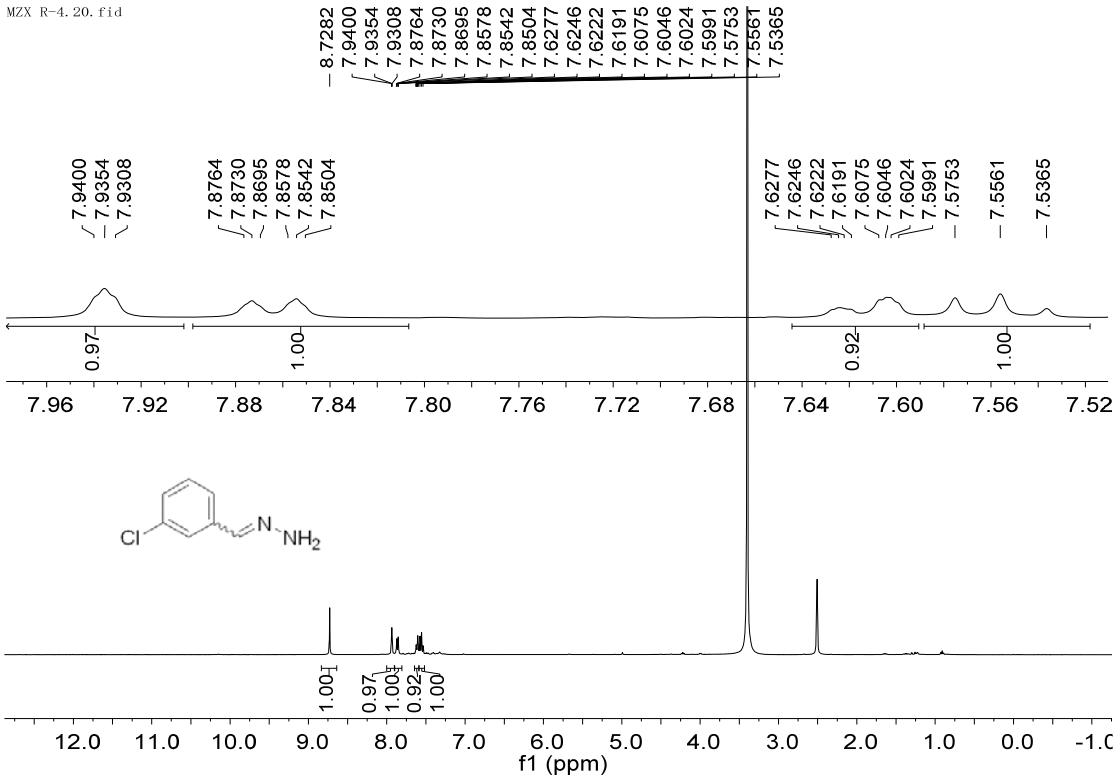
DEPT 90 and DEPT 135 (in Pyridine-d_5)



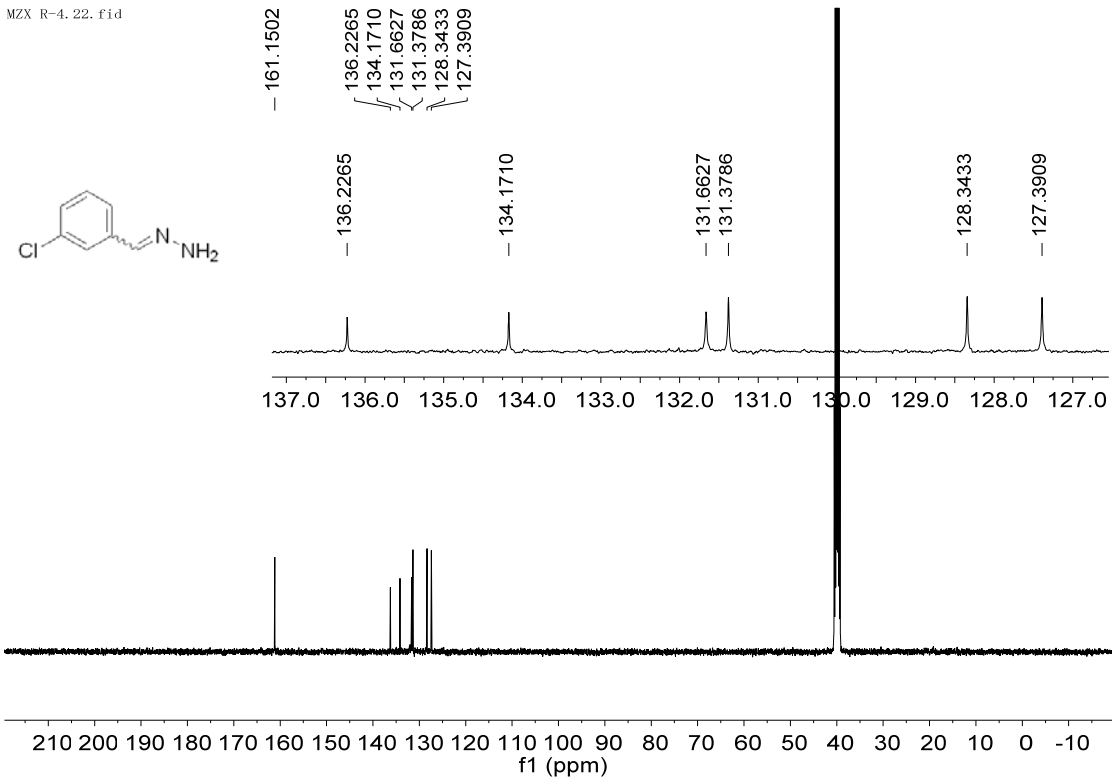
^{19}F NMR (in Pyridine-d_5)



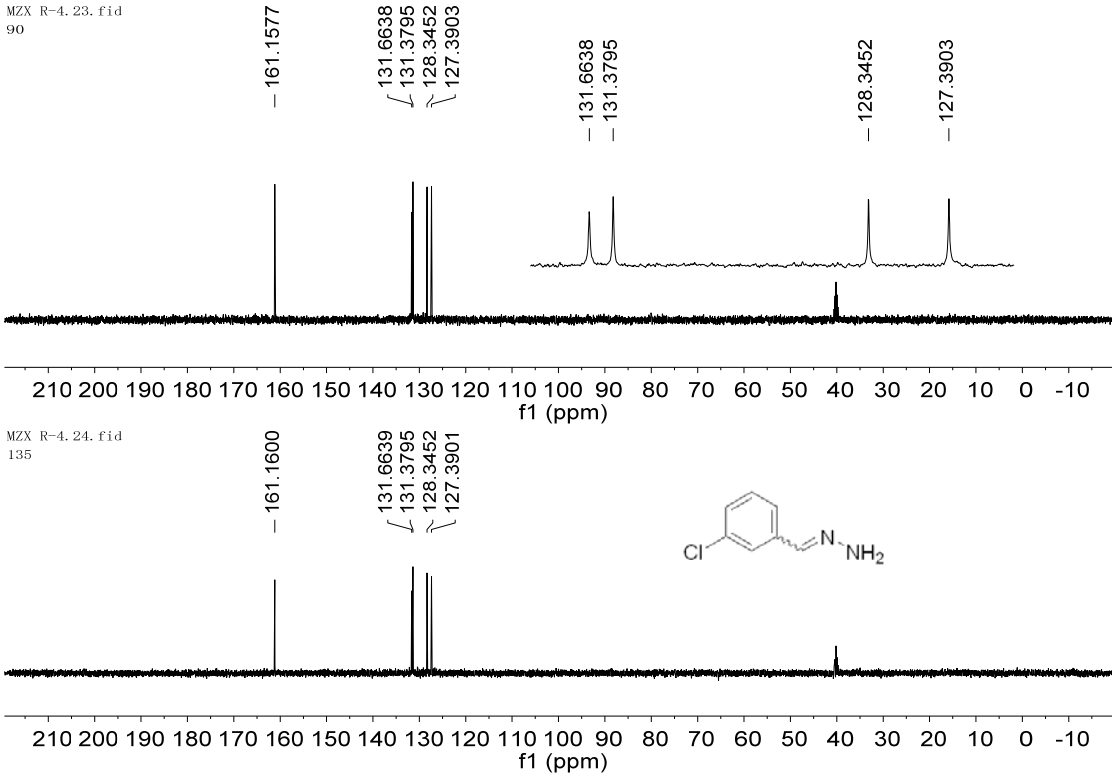
2v, ^{1}H NMR



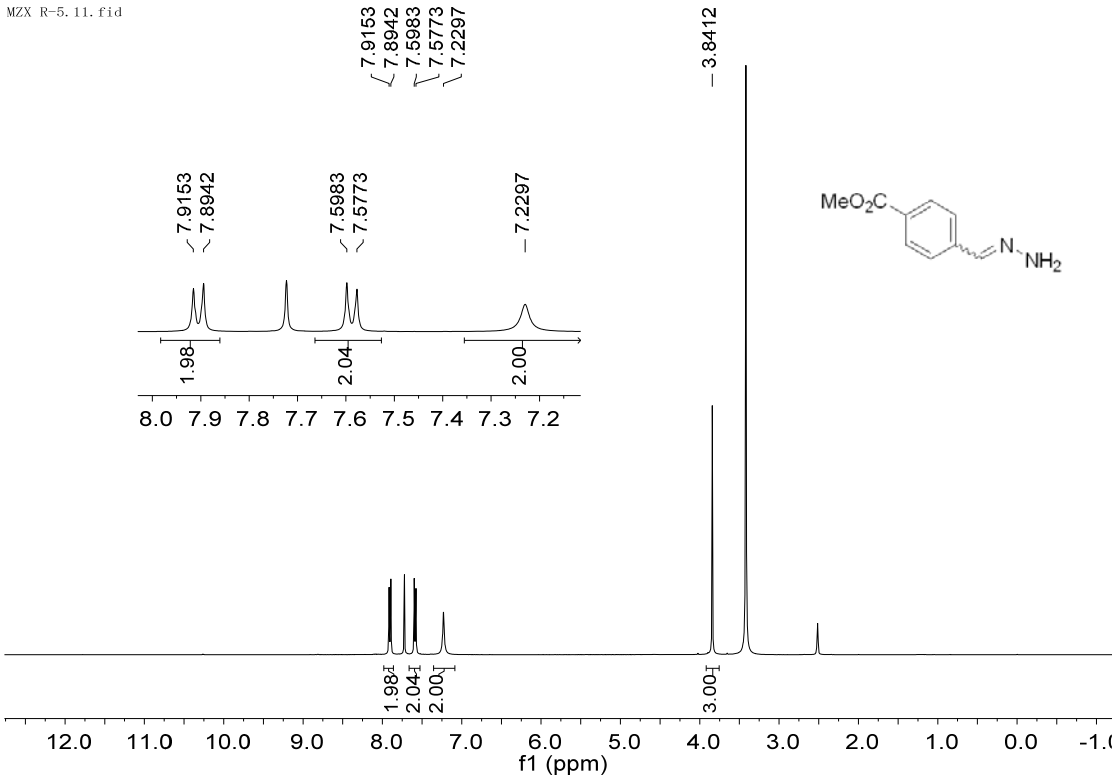
^{13}C NMR



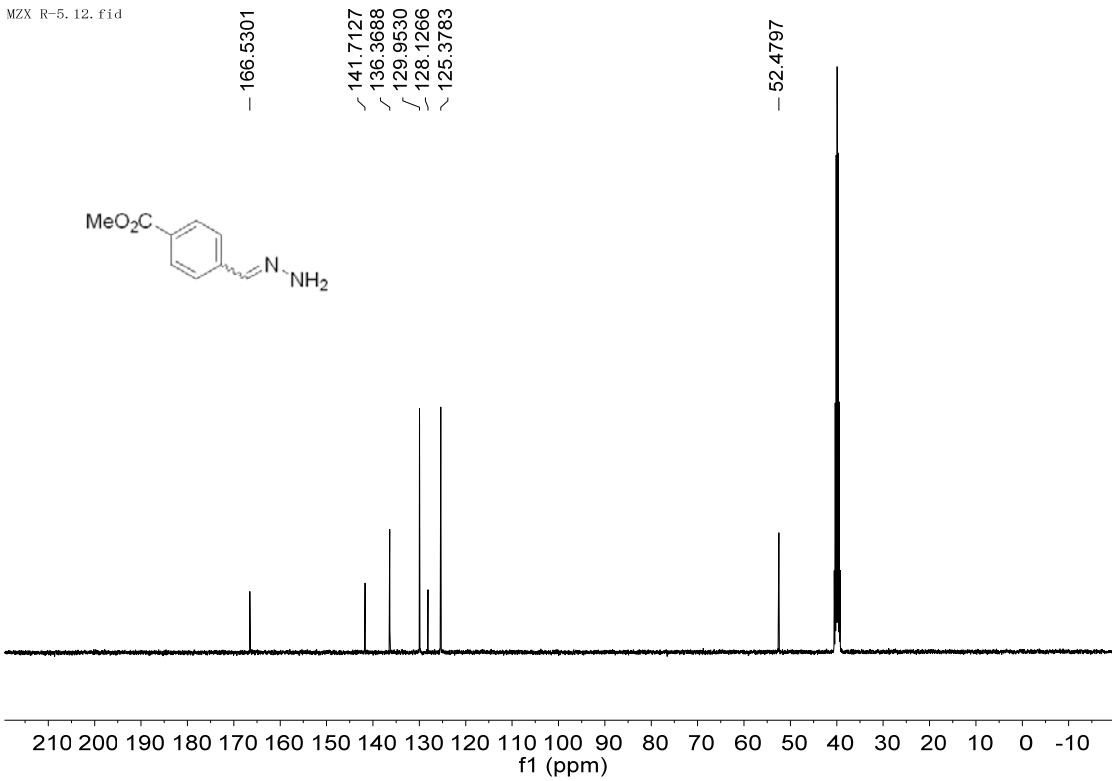
DEPT 90 and DEPT 135



2ab, ^{1}H NMR



^{13}C NMR



DEPT 90 and DEPT 135