

Supporting Information

Diversity-Oriented Synthesis of 1,2,4-Triazols, 1,3,4-Thiadiazols and 1,3,4-Selenadiazoles from *N*-Tosylhydrazones

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General Information.

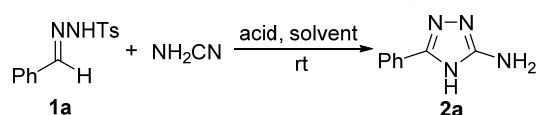
For product purification by flash column chromatography, silica gel (200-300 mesh) and light petroleum ether (bp. 60-90 °C) are used. All organic extracts were dried over anhydrous MgSO₄. ¹H and ¹³C NMR spectra were taken on a Bruker AVANCE III 400 MHz spectrometer. The HRMS data were determined on Bruker Daltonics APEXII 47e FT-ICR or Agilent UPLC-IM-QTOF (6560).

General Procedure for the Preparation of *N*-Tosylhydrazones **1**.

All *N*-tosylhydrazones **1** were known compounds and prepared from TsNHNH₂ and corresponding aldehydes by the known procedure.¹ To a rapidly stirred suspension of TsNHNH₂ (1.05 equiv) in methanol was added aldehydes (1.0 equiv) dropwise (solid reagents were added portion-wise). A mildly exothermic reaction ensued and the hydrazide dissolved. Within 5-10 min the tosylhydrazone began to precipitate. After approximately 30 min, the mixture was cooled to 0 °C and the product was collected by filtration, washed with cooled methanol. All of the obtained solids could be recrystallized from methanol or used without further purification.

Table S1

Table S1. Screening the reaction conditions of **1a** with cyanamide.^a



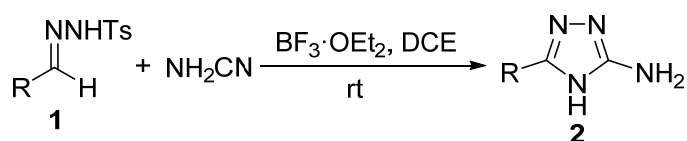
entry	acid (equiv)	solv	time (h)	yield (%) ^b
1	no	DCE	20	N.R.
2	BF ₃ ·OEt ₂ (0.5)	DCE	20	39
3	BF ₃ ·OEt ₂ (1.25)	DCE	20	75
4	BF ₃ ·OEt ₂ (1.5)	DCE	9	93
5	FeCl ₃ (1.5)	DCE	20	58
6	AlBr ₃ (1.5)	DCE	20	31
7	TiCl ₄ (1.5)	DCE	20	19
8	Sc(OTf) ₃ (1.5)	DCE	20	18
9	AlCl ₃ (1.5)	DCE	20	trace
10	ZnBr ₂ (1.5)	DCE	20	N.R.
11	H ₂ SO ₄ (1.5)	DCE	20	N.R.
12	HCl (1.5)	DCE	20	N.R.
13	BF ₃ ·OEt ₂ (1.5)	CH ₂ Cl ₂	20	68
14	BF ₃ ·OEt ₂ (1.5)	CHCl ₃	20	55
15	BF ₃ ·OEt ₂ (1.5)	CH ₃ CN	20	56
16	BF ₃ ·OEt ₂ (1.5)	CH ₃ NO ₂	20	37
17	BF ₃ ·OEt ₂ (1.5)	toluene	20	38

18	BF ₃ ·OEt ₂ (1.5)	THF	20	N.R.
19	BF ₃ ·OEt ₂ (1.5)	<i>t</i> -BuOH	20	N.R.
20 ^c	BF ₃ ·OEt ₂ (1.5)	DCE	9	68

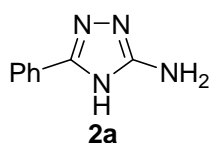
^a Unless noted otherwise, the reactions were conducted with **1a** (0.1 mmol), NH₂CN (0.2 mmol) and acid (0.15 mmol) in 2 mL solvent at room temperature under an argon atmosphere. ^b Isolated yields. ^c 0.2 mmol NCS was added.

As shown in Tabel S1. Initially, we performed the reaction in DCE without using any additive, and no reaction was detected (entry 1). Then, the reaction was conducted in the presence of 0.5 equivalent of BF₃·OEt₂, after 20 hours 1,2,4-triazol-3-amine **2a** could be isolated in 39% yield (entry 2). To our delight, increasing the amount of BF₃·OEt₂ could improve the yields apparently (entries 3, 4), and 1.5 equivalent of BF₃·OEt₂ resulted in 93% yield of **2a** within 9 hours. FeCl₃ gave moderate yield (entry 5), other Lewis acids, such as AlBr₃, TiCl₄, Sc(OTf)₃, and AlCl₃ resulted in lower yields (entries 6-9), but ZnBr₂ and some Brønsted acids could not promoted the reaction (entries 10-12). Of the solvents screened, CH₂Cl₂, CHCl₃, CH₃CN, CH₃NO₂, and toluene, could give moderate yields (entries 13-17); THF and *t*-BuOH gave disappointing results (entries 18, 19). We also tried to add NCS in the reaction, but it did not improve the yield; on the contrary, there were more by-products like **12**, resulted in lower yield (entry 20).

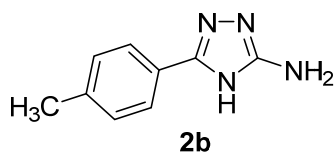
General Procedure for the Synthesis of 1,2,4-triazol-3-amines **2a-2p**.



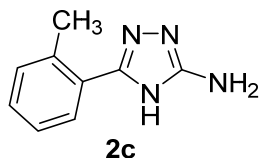
Under an argon atmosphere, a mixture of *N*-tosylhydrazones **1** (0.2 mmol), NH₂CN (0.4 mmol) and BF₃·OEt₂ (0.3 mmol) in DCE (3 mL) were stirred at room temperature for 5-24 hours. After quenching by water, the product was extracted with ethyl acetate and the organic layer was washed with saturated Na₂CO₃ solution and brine, dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded the products **2a-2p**.



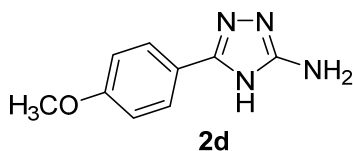
2a was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 25:1) as eluent as a white solid (14.9 mg, 93% yield). The spectral data is in agreement with the literature values.^{2d} ¹H NMR (400 MHz, DMSO-d₆) δ = 12.05 (brs, 1H), 7.91-7.88 (m, 2H), 7.42-7.34 (m, 3H), 6.07 (brs, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 158.4, 157.3, 132.3, 128.4, 128.1, 125.3 ppm.



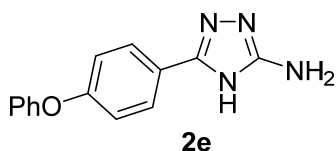
2b was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 25:1) as eluent as a white solid (30.3 mg, 87% yield). The spectral data is in agreement with the literature values.^{2c} ¹H NMR (400 MHz, DMSO-d₆) δ = 11.98 (brs, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.02 (brs, 2H), 2.32 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 158.4, 157.2, 137.4, 129.0, 128.8, 125.3, 20.9 ppm.



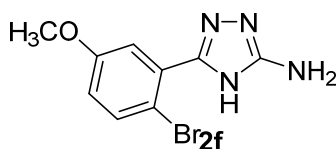
2c was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 25:1) as eluent as a white solid (30.5 mg, 87% yield). The spectral data is in agreement with the literature values.^{2e} ¹H NMR (400 MHz, DMSO-d₆) δ = 12.07 (brs, 1H), 7.82 (s, 1H), 7.23-7.19 (m, 3H), 6.01 (brs, 2H), 2.55 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 159.4, 156.6, 135.9, 131.3, 131.0, 128.7, 127.8, 125.6, 21.9 ppm.



2d was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 20:1) as eluent as a white solid (24.0 mg, 63% yield). The spectral data is in agreement with the literature values.^{2d} ¹H NMR (400 MHz, DMSO-d₆) δ = 11.91 (brs, 1H), 7.83-7.79 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.00 (brs, 2H), 3.77 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 159.3, 158.3, 157.2, 126.7, 125.1, 113.8, 55.1 ppm.

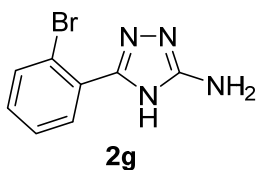


2e was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:2) as eluent as a white solid (40.9 mg, 81% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 12.03 (brs, 1H), 7.92-7.88 (m, 2H), 7.43-7.39 (m, 2H), 7.18-7.15 (m, 1H), 7.07-7.02 (m, 4H), 5.99 (brs, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 156.9, 156.3, 130.06, 130.05, 127.1, 123.6, 118.9, 118.3 ppm; HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₁₄H₁₃N₄O 253.1084; Found 253.1092.

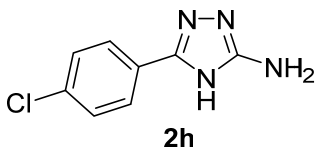


2f was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:2) as eluent as a white solid (40.2 mg, 75% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 12.21 (brs, 1H), 7.55 (d, *J* = 8.8

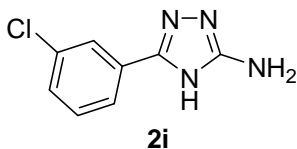
Hz, 1H), 7.28 (d, $J = 3.2$ Hz, 1H), 6.88 (dd, $J = 8.8, 3.2$ Hz, 1H), 6.06 (brs, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) $\delta = 158.3, 157.7, 156.8, 134.5, 133.8, 116.1, 110.9, 55.4$ ppm; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_9\text{H}_{10}\text{N}_4\text{OBr}$ 269.0033; Found 269.0029.



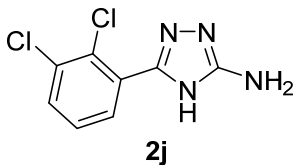
2g was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 25:1) as eluent as a white solid (38.3 mg, 80% yield). The spectral data is in agreement with the literature values.^{2d} ^1H NMR (400MHz, DMSO- d_6) $\delta = 12.18$ (brs, 1H), 7.74-7.67 (m, 2H), 7.44-7.40 (dd, $J = 14.8, 7.6$ Hz, 1H), 7.29 (d, $J = 7.6$ Hz, 1H), 6.09 (brs, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) $\delta = 158.0, 156.7, 133.6, 133.3, 131.3, 129.7, 127.3, 120.6$ ppm.



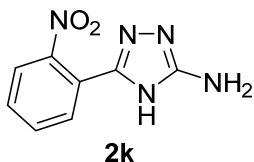
2h was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 25:1) as eluent as a white solid (35.0 mg, 90% yield). The spectral data is in agreement with the literature values.^{2d} ^1H NMR (400 MHz, DMSO- d_6) $\delta = 12.14$ (brs, 1H), 7.92-7.89 (m, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 6.12 (brs, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) $\delta = 158.03, 157.98, 133.2, 131.7, 129.0, 127.5$ ppm.



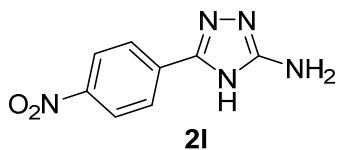
2i was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 25:1) as eluent as a white solid (33.4 mg, 86% yield). The spectral data is in agreement with the literature values.^{2d} ^1H NMR (400 MHz, DMSO- d_6) $\delta = 12.19$ (brs, 1H), 7.87-7.83 (m, 2H), 7.46-7.39 (m, 2H), 6.14 (brs, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) $\delta = 157.5, 157.2, 134.4, 133.2, 130.4, 127.9, 124.9, 123.8$ ppm.



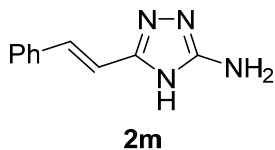
2j was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:2) as eluent as a white solid (31.1 mg, 68% yield). ^1H NMR (400 MHz, DMSO- d_6) $\delta = 12.28$ (brs, 1H), 7.74 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.63 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.39 (dd, $J = 8.0, 8.0$ Hz, 1H), 6.11 (brs, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) $\delta = 156.8, 133.5, 132.8, 130.2, 129.6, 129.4, 127.8$ ppm; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_8\text{H}_7\text{N}_4\text{Cl}_2$ 229.0042; Found 229.0041.



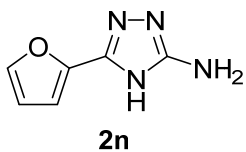
2k was prepared according to the general procedure at reflux temperature. The reaction mixture was heated in an oil bath and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 20:1) as eluent as a yellow solid (14.0 mg, 34% yield). The spectral data is in agreement with the literature values.^{2d} ¹H NMR (400 MHz, DMSO-d₆) δ = 12.28 (brs, 1H), 7.91 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.74 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.69-7.65 (m, 1H), 7.58-7.54 (m, 1H), 6.18 (brs, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 157.3, 154.7, 148.8, 131.6, 129.4, 129.3, 124.6, 123.1 ppm.



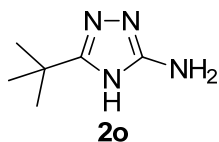
2l was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 20:1) as eluent as a yellow solid (11.9 mg, 29% yield). The spectral data is in agreement with the literature values.^{2e} ¹H NMR (400 MHz, DMSO-d₆) δ = 12.39 (brs, 1H), 8.26 (d, *J* = 9.2 Hz, 2H), 8.13-8.10 (m, 2H), 6.23 (brs, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 157.8, 156.8, 147.0, 138.4, 126.1, 123.9 ppm.



2m was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 25:1) as eluent as a white solid (14.9 mg, 40% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 12.02 (brs, 1H), 7.57-7.55 (m, 2H), 7.38-7.23 (m, 4H), 6.92 (d, *J* = 16.4, 1H), 6.00 (brs, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 158.4, 157.0, 136.5, 131.0, 128.6, 127.8, 126.5, 119.4 ppm; HRMS (ESI) *m/z* : [M + H]⁺ Calcd for C₁₀H₁₁N₄ 187.0978; Found 187.0977.



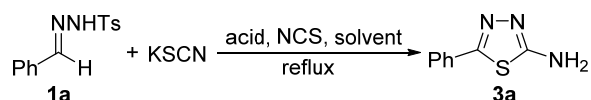
2n was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 20:1) as eluent as a white solid (13.2 mg, 44% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 7.69 (d, *J* = 1.6 Hz, 1H), 6.70 (d, *J* = 3.2 Hz, 1H), 6.54 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.11 (brs, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 157.3, 151.6, 147.3, 142.9, 111.4, 107.9 ppm; HRMS (ESI) *m/z* : [M + H]⁺ Calcd for C₆H₇N₄O 151.0614; Found 151.0614.



2o was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 30:1) as eluent as a white solid (10.1 mg, 36% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 11.88 (brs, 1H), 6.00 (brs, 2H), 1.20 (s, 9H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 164.8, 158.1, 32.0, 29.3 ppm; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₆H₁₃N₄ 141.1135; Found 141.1137.

Table S2

Table S2. Screening the reaction conditions of **1a** with KSCN.^a



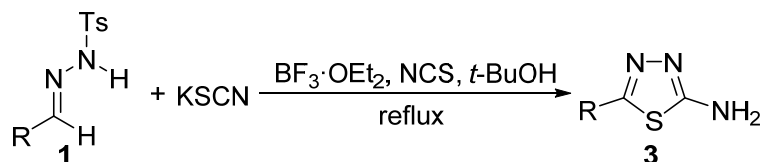
entry	acid (eq)	NCS (eq)	solv	time/h	yield (%) ^b
1	BF ₃ ·OEt ₂ (1.5)	no	DCE	5	N. R.
2	BF ₃ ·OEt ₂ (1.5)	no	CH ₃ CN	5	N. R.
3	BF ₃ ·OEt ₂ (1.5)	no	<i>t</i> -BuOH	5	N. R.
4	BF ₃ ·OEt ₂ (1.5)	1.1	DCE	5	trace
5	BF ₃ ·OEt ₂ (1.5)	1.1	<i>t</i> -BuOH	9	20
6	BF ₃ ·OEt ₂ (1.5)	2	<i>t</i> -BuOH	9	29
7	BF ₃ ·OEt ₂ (1.25)	2	<i>t</i> -BuOH	6	54
8	BF ₃ ·OEt ₂ (0.5)	2	<i>t</i> -BuOH	0.5	87
9	BF ₃ ·OEt ₂ (0.25)	2	<i>t</i> -BuOH	1	64
10	no	2	<i>t</i> -BuOH	12	33
11 ^c	BF ₃ ·OEt ₂ (0.5)	2	<i>t</i> -BuOH	30	83
12	AlCl ₃ (0.5)	2	<i>t</i> -BuOH	0.5	59
13	TiCl ₄ (0.5)	2	<i>t</i> -BuOH	0.5	73
14	Al(<i>i</i> -PrO) ₃ (0.5)	2	<i>t</i> -BuOH	3	38
15	Sc(OTf) ₃ (0.5)	2	<i>t</i> -BuOH	3	N. R.
16	ZnBr ₂ (0.5)	2	<i>t</i> -BuOH	3	trace
17	H ₂ SO ₄ (0.5)	2	<i>t</i> -BuOH	3	59
18	HCl (0.5)	2	<i>t</i> -BuOH	0.5	62
19	BF ₃ ·OEt ₂ (0.5)	2	<i>i</i> -AmOH	3	39
20	BF ₃ ·OEt ₂ (0.5)	2	<i>t</i> -AmOH	3	37
21	BF ₃ ·OEt ₂ (0.5)	2	EtOH	3	trace
22	BF ₃ ·OEt ₂ (0.5)	2	THF	3	N. R.

23	BF ₃ ·OEt ₂ (0.5)	2	toluene	3	N. R.
24	BF ₃ ·OEt ₂ (0.5)	2 ^d	<i>t</i> -BuOH	0.5	52
25	BF ₃ ·OEt ₂ (0.5)	2 ^e	<i>t</i> -BuOH	2	30

^a Unless noted otherwise, the reactions were conducted with **1a** (0.1 mmol), KSCN (0.2 mmol), NCS and acid in 2 mL solvent at reflux temperature under an argon atmosphere. ^b Isolated yields. ^c The reaction was conducted at room temperature. ^d 0.2 mmol NBS was used instead of NCS. ^e 0.2 mmol NIS was used instead of NCS.

As shown in Table S2. First, different solvents were screened even at higher temperature, but without any reactions could be detected by TLC (entries 1-3). We added 1.1 equivalent of NCS to the reaction (entries 4, 5), product **3a** could be isolated in 20% yield in *t*-BuOH after 9 hours, even though the *N*-tosylhydrazone **1a** could not be fully consumed (entry 5). Increasing the amount of NCS could not improve the transformation (entry 6). Fortunately, we found that decreasing the amount of BF₃·OEt₂ resulted in better yields (entries 7-10), and 0.5 equivalent of BF₃·OEt₂ gave 87% yield within 0.5 hour. Furthermore, the reaction could be performed at room temperature (entry 11). Then some acids were screened (entries 12-18), AlCl₃, TiCl₄, and Al(*i*-PrO)₃ gave moderate yields (entries 12-14); meanwhile, H₂SO₄ and concentrated HCl could promote the reaction (entries 17-18). Next, a variety of different solvents were also evaluated, *i*-AmOH and *t*-AmOH led to lower yields and other solvents gave disappointing results (entries 19-23). NBS and NIS could also promote the reaction, but the yields were lower (entries 24, 25).

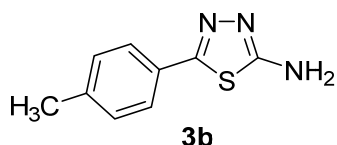
General Procedure for the Synthesis of 1,3,4-thiadiazol-2-amines **3a-3o** and furidiazine.



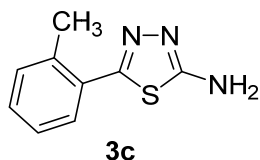
Under an argon atmosphere, a mixture of *N*-tosylhydrazones **1** (0.2 mmol), KSCN (0.4 mmol), NCS (0.4 mmol) and BF₃·OEt₂ (0.1 mmol) in *t*-BuOH (3 mL). The reaction mixture was heated in an oil bath and stirred at reflux temperature for 0.5-4 hours. After quenching by water, the product was extracted with ethyl acetate and the organic layer was washed with saturated Na₂CO₃ solution and brine, dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded the products **3**.



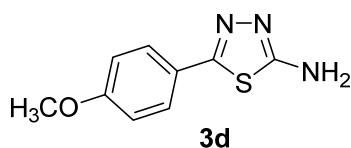
3a was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (15.5 mg, 87% yield). The spectral data is in agreement with the literature values.^{2a} ¹H NMR (400 MHz, DMSO-*d*₆) δ = 7.72-7.70 (m, 2H), 7.45-7.37 (m, 5H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ = 168.5, 156.4, 131.0, 129.6, 129.1, 126.3 ppm.



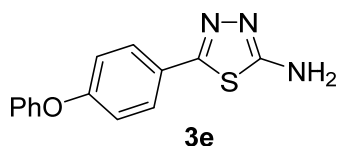
3b was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (31.0 mg, 81% yield). The spectral data is in agreement with the literature values.^{2a} ¹H NMR (400 MHz, DMSO-d₆) δ = 7.66-7.63 (m, 2H), 7.40 (brs, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 168.2, 156.5, 139.3, 129.7, 128.3, 126.3, 20.9 ppm.



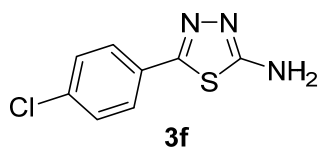
3c was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (23.4 mg, 61% yield). The spectral data is in agreement with the literature values.^{2b} ¹H NMR (400 MHz, DMSO-d₆) δ = 7.53 (d, *J* = 7.2 Hz, 1H), 7.40-7.27 (m, 5H), 2.48 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 168.8, 155.7, 135.9, 131.4, 130.0, 129.8, 129.1, 126.3, 21.2 ppm.



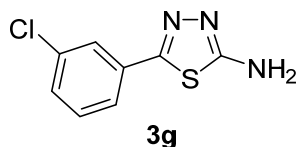
3d was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (20.3 mg, 49% yield). The spectral data is in agreement with the literature values.^{2b} ¹H NMR (400 MHz, DMSO-d₆) δ = 7.69 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.32 (brs, 2H), 7.03 (dd, *J* = 6.8, 2.0 Hz, 2H), 3.81 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 167.9, 160.3, 156.3, 127.8, 123.6, 114.5, 55.3 ppm.



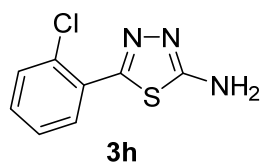
3e was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (32.9 mg, 61% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 7.79-7.76 (m, 2H), 7.47-7.41 (m, 4H), 7.21 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.11-7.05 (m, 4H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 168.3, 158.0, 155.8, 130.2, 128.2, 126.1, 124.1, 119.3, 118.6 ppm; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₄H₁₁N₃OSNa 292.0515; Found 292.0509.



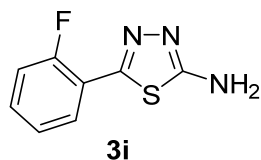
3f was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (29.6 mg, 70% yield). The spectral data is in agreement with the literature values.^{2b} ¹H NMR (400MHz, DMSO-d₆) δ = 7.80-7.77 (m, 2H), 7.55-7.51 (m, 4H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 168.9, 155.1, 134.0, 129.8, 129.2, 127.9 ppm.



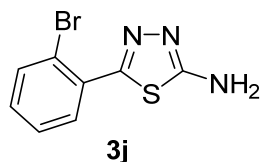
3g was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (27.1 mg, 64% yield). The spectral data is in agreement with the literature values.^{2b} ¹H NMR (400MHz, DMSO-d₆) δ = 7.81 (dd, *J* = 2.0, 1.2 Hz 1H), 7.73-7.69 (m, 1H), 7.56 (brs, 2H), 7.53-7.48 (m, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 169.1, 154.7, 133.8, 132.9, 131.1, 129.3, 125.4, 125.1 ppm.



3h was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (35.1 mg, 83% yield). The spectral data is in agreement with the literature values.^{2b} ¹H NMR (400MHz, DMSO-d₆) δ = 8.02-7.99 (m, 1H), 7.63-7.60 (m, 1H), 7.50-7.46 (m, 4H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 170.1, 151.6, 131.0, 130.5, 130.4, 130.3, 129.6, 127.7 ppm.

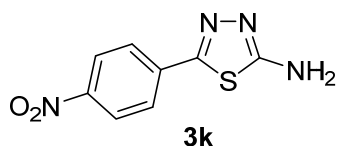


3i was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (19.9 mg, 51% yield). The spectral data is in agreement with the literature values.^{2b} ¹H NMR (400 MHz, DMSO-d₆) δ = 8.12-8.08 (m, 1H), 7.54-7.49 (m, 3H), 7.42-7.32 (m, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 170.0, 159.1, 156.6, 148.5, 131.4, 131.3, 127.7, 125.19, 125.16, 118.8, 118.6, 116.5, 116.2 ppm.

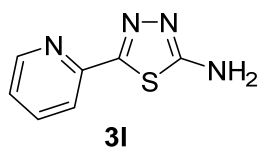


3j was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (29.2 mg, 57% yield). The spectral data is in agreement with the literature values.^{2b} ¹H NMR

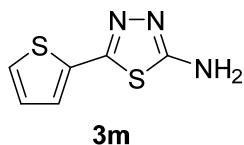
(400 MHz, DMSO- d_6) δ = 7.88 (dd, J = 8.0, 1.2 Hz, 1H), 7.78 (dd, J = 8.0, 1.2 Hz, 1H), 7.53-7.38 (m, 4H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 170.0, 153.1, 133.8, 131.6, 131.2, 128.1, 120.9 ppm.



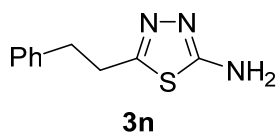
3k was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:2) as eluent as a yellow solid (30.2 mg, 68% yield). The spectral data is in agreement with the literature values.^{2b} ^1H NMR (400 MHz, DMSO- d_6) δ = 8.28 (d, J = 8.8 Hz, 2H), 8.01 (d, J = 9.2 Hz, 2H), 7.75 (brs, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 170.0, 154.1, 147.4, 136.8, 127.1, 124.4 ppm.



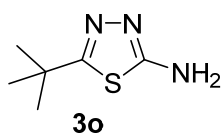
3l was prepared according to the general procedure using 0.2 mmol $\text{BF}_3 \cdot \text{OEt}_2$ and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (22.1 mg, 62% yield). The spectral data is in agreement with the literature values.^{2a} ^1H NMR (400 MHz, DMSO- d_6) δ = 8.61-8.59 (m, 1H), 8.08-8.05 (m, 1H), 7.929-7.925 (m, 1H), 7.57 (brs, 2H), 7.45-7.42 (m, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 170.1, 158.5, 149.6, 137.4, 124.3, 119.0 ppm.



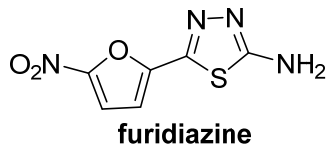
3m was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 2:1) as eluent as a white solid (19.4 mg, 53% yield). The spectral data is in agreement with the literature values.^{2a} ^1H NMR (400 MHz, DMSO- d_6) δ = 7.64 (dd, J = 4.8, 0.8 Hz, 1H), 7.45 (brs, 2H) 7.42 (dd, J = 3.6, 0.8 Hz, 1H) 7.13 (dd, J = 5.2, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 168.1, 150.6, 133.3, 128.0, 127.6 ppm.



3n was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (19.3 mg, 47% yield). The spectral data is in agreement with the literature values.^{2f} ^1H NMR (400 MHz, DMSO- d_6) δ = 7.31-7.18 (m, 5H), 7.02 (brs, 2H), 3.12 (d, J = 7.6 Hz, 2H), 2.94 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 168.3, 157.4, 140.3, 128.5, 128.3, 126.2, 34.6, 31.1 ppm.



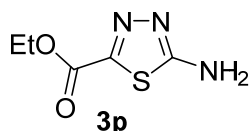
3o was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:1) as eluent as a white solid (23.3mg, 74% yield). The spectral data is in agreement with the literature values.^{2g} ¹H NMR (400 MHz, DMSO-d₆) δ = 7.01 (brs, 2H), 1.30 (s, 9H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 168.2, 167.9, 35.5, 30.5 ppm.



furidiazine was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 20:1) as eluent as a white solid (26.8 mg, 63% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 7.91 (brs, 2H), 7.84 (d, *J* = 4.0 Hz, 1H), 7.32 (d, *J* = 4.4 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 170.1, 151.3, 147.9, 144.5, 115.2, 111.7 ppm; HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₆H₅N₄O₃S 213.0077; Found 213.0084.

One-pot Procedure for the Synthesis of 1,3,4-thiadiazol-2-amines 3p.

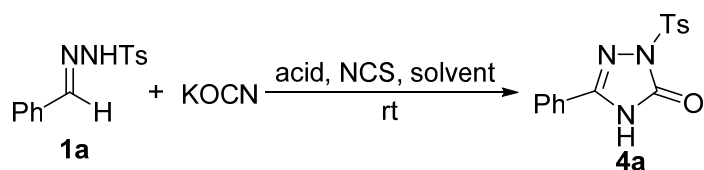
To a rapidly stirred suspension of TsNHNH₂ (0.22 mmol) in methanol (3 mL) was added ethyl 2-oxoacetate (0.2 mmol). The mixture was stirred at room temperature for 4 hours. The solvent was removed *in vacuo*. Then *t*-BuOH (3 mL), KSCN (0.4 mmol), NCS (0.4 mmol) and BF₃·OEt₂ (0.1 mmol) were subsequently added under an argon atmosphere and the reaction mixture was heated in an oil bath and stirred at reflux temperature for 2 hours. After quenching by water, the product was extracted with ethyl acetate and the organic layer was washed with saturated Na₂CO₃ solution and brine, dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 1:2) as eluent afforded the product **3p** as a white solid (18.4 mg, 53% yield).



The spectral data is in agreement with the literature values.^{2h} ¹H NMR (400 MHz, DMSO-d₆) δ = 8.01 (brs, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 172.4, 158.9, 147.6, 61.8, 14.0 ppm.

Procedure for Synthesize of 3a in Large-scale.

Under an argon atmosphere, a mixture of *N*-tosylhydrazones **1a** (100 mmol), KSCN (200 mmol), NCS (200 mmol) and BF₃·OEt₂ (50 mmol) in *t*-BuOH (250 mL). The reaction mixture was heated in an oil bath and stirred at reflux temperature for 3 hours. After quenching by water, the product was extracted with ethyl acetate and the organic layer was washed with saturated Na₂CO₃ solution and brine, dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. Purification by recrystallization from *n*-hexane and EtOAc afforded the product **3a** (10.8 g) in 61% yield.

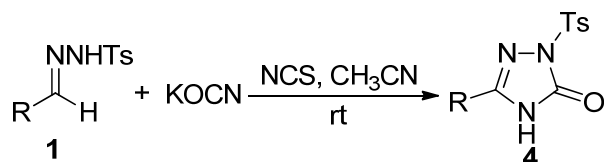
Table S3**Table S3.** Screening the reaction conditions of **1a** with KOCN.^a

entry	acid (eq)	NCS (equiv)	solv	time (h)	yield (%) ^b
1	BF ₃ ·OEt ₂ (0.5)	2	<i>t</i> -BuOH	7	29
2	no	2	<i>t</i> -BuOH	7	30
3	no	1.1	<i>t</i> -BuOH	17	31
4	no	1.1	CH ₃ CN	5	69
5	no	1.1	<i>t</i> -AmOH	24	44
6	no	1.1	<i>i</i> -PrOH	5	41
7	no	1.1	CH ₃ NO ₂	4	46
8 ^c	no	1.1	CH ₃ CN	1	71
9	BF ₃ ·OEt ₂ (0.5)	1.1	CH ₃ CN	3	64
10	Sc(OTf) ₃ (0.5)	1.1	CH ₃ CN	3	60
11	AlCl ₃ (0.5)	1.1	CH ₃ CN	3	66

^a Unless noted otherwise, the reactions were conducted with **1a** (0.1 mmol), KOCN (0.2 mmol), NCS and acid in 2 mL solvent at room temperature under an argon atmosphere. ^b Isolated yields. ^c The reaction was conducted at reflux temperature.

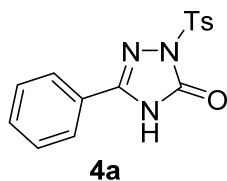
As shown in Tabela S3. We performed the reaction in the presence of 0.5 equivalent of BF₃·OEt₂ and 2 equivalent of NCS in *t*-BuOH at room temperature, after 7 hours 2-tosyl-1,2,4-triazol-3-one **4a** could be isolated in 29% yield (entry 1). Meanwhile, we found that similar yield could be obtained without BF₃·OEt₂, and 1.1 equivalent of NCS was enough for the reaction (entries 2, 3). Next, a variety of different solvents were evaluated. To our delight, **4a** could be isolated in 69% yield in CH₃CN within 5 hours (entry 4); *t*-AmOH, *i*-PrOH and CH₃NO₂ could give moderate yields (entries 5-7); Furthermore, the reaction could be performed at reflux temperature (entry 8). Acid was not essential, but it could accelerate the reaction (entries 9-11).

General Procedure for the Synthesis of 2-tosyl-1,2,4-triazol-3-ones **4a-4j**.

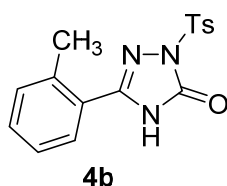


Under an argon atmosphere, a mixture of *N*-tosylhydrazones **1** (0.2 mmol), KOCN (0.4 mmol) and NCS (0.22 mmol) in CH₃CN (3 mL) were stirred at room temperature for 5-18 hours. After quenching by water, the product was extracted with ethyl acetate and the organic layer was

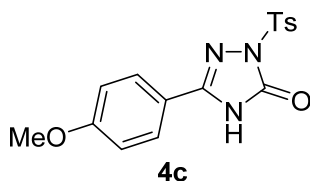
washed with saturated Na_2CO_3 solution and brine, dried over anhydrous MgSO_4 , filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded the products **4**.



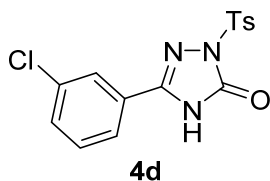
4a was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (43.5 mg, 69% yield). ^1H NMR (400 MHz, DMSO-d_6) δ = 12.85 (brs, 1H), 7.93-7.81 (m, 4H), 7.57-7.49 (m, 5H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 152.3, 147.8, 145.9, 133.9, 131.6, 130.3, 129.1, 127.5, 125.8, 125.1, 21.1 ppm; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3\text{O}_3\text{S}$ 316.0750; Found 316.0753.



4b was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (35.7 mg, 54% yield). ^1H NMR (400 MHz, DMSO-d_6) δ = 12.53 (brs, 1H), 7.90-7.87 (m, 2H), 7.52-7.48 (m, 3H), 7.45-7.40 (m, 1H), 7.35-7.29 (m, 2H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 152.1, 148.6, 145.9, 137.1, 133.9, 131.4, 130.9, 130.3, 128.9, 127.5, 126.2, 124.6, 21.2, 20.6 ppm; HRMS (ESI) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}_3\text{S}$ 328.0761; Found 328.0774.

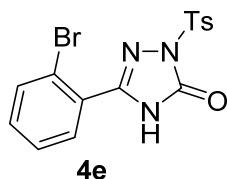


4c was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 2:1) as eluent as a white solid (42.1mg, 61% yield). ^1H NMR (400 MHz, DMSO-d_6) δ = 12.68 (brs, 1H), 7.88 (dd, J = 6.8, 2.0 Hz, 2H), 7.76-7.72 (m, 2H), 7.49-7.46 (m, 2H), 7.08-7.05 (m, 2H), 3.80 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 161.7, 152.4, 147.7, 145.8, 134.0, 130.2, 127.6, 127.5, 117.3, 114.5, 55.4, 21.1 ppm; HRMS (ESI) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}_4\text{S}$ 344.0711; Found 344.0719.

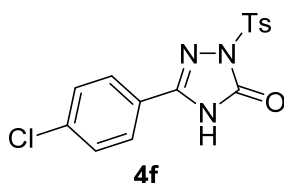


4d was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (31.5 mg, 45% yield). ^1H NMR (400 MHz, DMSO-d_6) δ = 12.90 (brs, 1H), 7.91-7.88 (m,

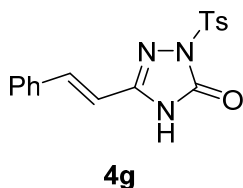
2H), 7.83-7.82 (m, 1H), 7.78-7.75 (m, 1H), 7.64-7.61 (m, 1H), 7.57-7.47 (m, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 152.0, 146.6, 146.0, 133.82, 133.78, 131.3, 131.1, 130.3, 127.6, 127.2, 125.5, 124.5, 21.2 ppm; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_3\text{O}_3\text{SClNa}$ 372.0180; Found 372.0175.



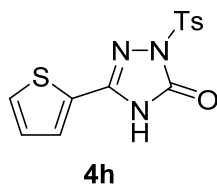
4e was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (41.7 mg, 53% yield). ^1H NMR (400 MHz, DMSO- d_6) δ = 12.66 (brs, 1H), 7.90-7.87 (m, 2H), 7.80-7.78 (m, 1H), 7.61-7.48 (m, 5H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 151.8, 147.9, 146.0, 133.8, 133.4, 133.0, 131.7, 130.3, 128.1, 127.6, 127.1, 121.5, 21.2 ppm; HRMS (ESI) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{15}\text{H}_{11}\text{BrN}_3\text{O}_3\text{S}$ 391.9710; Found 391.9719.



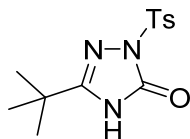
4f was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (30.1 mg, 43% yield). ^1H NMR (400 MHz, DMSO- d_6) δ = 12.90 (brs, 1H), 7.89 (dd, J = 6.4, 2.0 Hz, 2H), 7.81 (dd, J = 6.4, 2.0 Hz, 2H), 7.60 (dd, J = 6.4, 2.0 Hz, 2H), 7.49 (dd, J = 6.4, 2.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 152.1, 147.0, 146.0, 136.3, 133.8, 130.3, 129.3, 127.63, 127.55, 124.1, 21.2 ppm; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_3\text{O}_3\text{SClNa}$ 372.0180; Found 372.0177.



4g was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (44.4 mg, 65% yield). ^1H NMR (400 MHz, DMSO- d_6) δ = 12.57 (brs, 1H), 7.87-7.85 (m, 2H), 7.60-7.57 (m, 2H), 7.50-7.404 (m, 2H), 7.399-7.29 (m, 4H), 6.88 (d, J = 16.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 151.8, 147.9, 145.9, 137.6, 134.6, 133.9, 130.3, 129.7, 129.0, 127.5, 127.4, 113.0, 21.1 ppm; HRMS (ESI) m/z : $[\text{M} - \text{H}]^-$ Calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}_3\text{S}$ 340.0761; Found 340.0771.

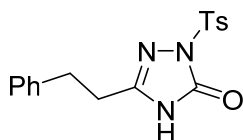


4h was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (36.6 mg, 57% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 12.95 (brs, 1H), 7.90-7.84 (m, 3H), 7.65-7.63 (m, 1H), 7.52-7.49 (m, 2H), 7.23-7.20 (m, 1H), 2.41 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 151.8, 146.0, 144.2, 133.8, 130.7, 130.3, 129.8, 128.2, 127.5, 127.0, 21.2 ppm; HRMS (ESI) m/z: [M - H]⁻ Calcd for C₁₃H₁₀N₃O₃S₂ 320.0169; Found 320.0169.



4i

4i was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (49.6 mg, 84% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 12.13 (brs, 1H), 7.82 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.48-7.46 (m, 2H), 2.40 (s, 3H), 1.15 (s, 9H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 157.5, 152.6, 145.7, 134.1, 130.0, 127.4, 32.2, 26.9, 21.2 ppm; HRMS (ESI) m/z: [M - H]⁻ Calcd for C₁₃H₁₆N₃O₃S 294.0918; Found 294.0924.

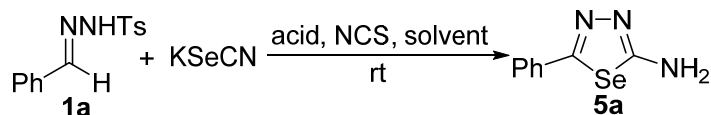


4j

4j was prepared according to the general procedure and purified by chromatography on silica gel using petroleum ether/ethyl acetate (petroleum ether/ethyl acetate = 3:1) as eluent as a white solid (43.3 mg, 63% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 12.12 (brs, 1H), 7.75-7.73 (m, 2H), 7.46-7.44 (m, 2H), 7.25-7.12 (m, 5H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 152.1, 150.4, 145.6, 139.7, 134.1, 130.2, 130.1, 128.3, 127.3, 126.2, 31.0, 27.8, 21.1 ppm; HRMS (ESI) m/z: [M - H]⁻ Calcd for C₁₇H₁₆N₃O₃S 342.0918; Found 342.0927.

Table S4

Table S4. Screening the reaction conditions of **1a** with KSeCN.^a



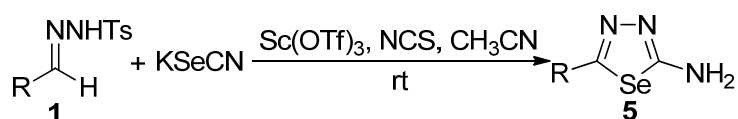
entry	acid	solv	time (h)	yield (%) ^b
1	no	CH ₃ CN	24	3 ^c
2	Sc(OTf) ₃	CH ₃ CN	2	5 ^c
3	BF ₃ ·OEt ₂	CH ₃ CN	4	3 ^c
4	AlCl ₃	CH ₃ CN	24	4 ^c
5	Al(<i>i</i> -PrO) ₃	CH ₃ CN	9	4 ^c

6	FeCl ₃	CH ₃ CN	9	44
7	ZnBr ₂	CH ₃ CN	12	49
8	H ₂ SO ₄	CH ₃ CN	7	34
9	HCl	CH ₃ CN	7	45
10	Sc(OTf) ₃	<i>t</i> -BuOH	24	18
11	Sc(OTf) ₃	MeOH	24	45
12	Sc(OTf) ₃	EtOH	24	36
13	Sc(OTf) ₃	THF	12	31

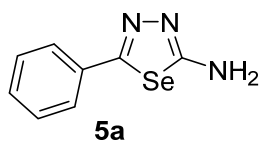
^a Unless noted otherwise, the reactions were conducted with **1a** (0.1 mmol), KSeCN (0.2 mmol), NCS (0.11 mmol) and acid (0.05 mmol) in 2 mL solvent at room temperature under an argon atmosphere. ^b Isolated yields.

As shown in Table S4. First, we performed the reaction without using any additive in CH₃CN at room temperature, 1,3,4-selenadiazol-2-amine **5a** could be isolated in 31% yield (entry 1). Then, the reactions were conducted in the presence of different acids. Fortunately, 0.5 equivalent of Sc(OTf)₃ resulted in 58% yield (entry 2). AlCl₃, Al(*i*-PrO)₃, FeCl₃ and ZnBr₂ gave moderate yields (entries 3-7); meanwhile, H₂SO₄ and concentrated HCl could promote the reaction, but the yields were lower (entries 8, 9). Next, a variety of different solvents were also evaluated, *t*-BuOH, MeOH, EtOH and THF led to lower yields (entries 10-13).

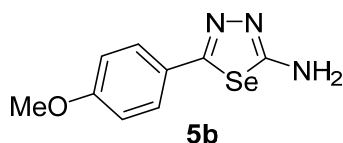
General Procedure for the Synthesis of 1,3,4-selenadiazol-2-amine **5a-5l**.



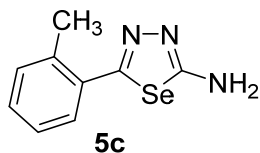
Under an argon atmosphere, a mixture of *N*-tosylhydrazones **1** (0.2 mmol), KSeCN (0.4 mmol), NCS (0.22 mmol) and Sc(OTf)₃ (0.1 mmol) in CH₃CN (3 mL) were stirred at room temperature for 2-24 hours. After quenching by water, the product was extracted with ethyl acetate and the organic layer was washed with saturated Na₂CO₃ solution and brine, dried over anhydrous MgSO₄, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded the products **5**.



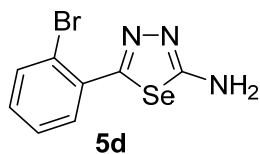
5a was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 50:1) as eluent as a white solid (26.1 mg, 58% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ = 7.73-7.70 (m, 2H), 7.55 (brs, 2H), 7.45-7.40 (m, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ = 172.2, 161.6, 133.9, 129.4, 129.1, 127.1 ppm; HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₈H₈N₃Se 225.9878; Found 225.9871.



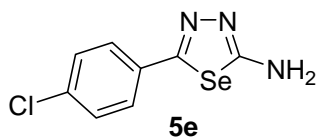
5b was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 40:1) as eluent as a white solid (34.2 mg, 67% yield). ^1H NMR (400 MHz, DMSO- d_6) δ = 7.64 (dd, J = 6.8, 2.0 Hz, 2H), 7.43 (brs, 2H), 6.98 (dd, J = 6.8, 2.0 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 171.4, 161.4, 160.2, 128.5, 126.6, 114.4, 55.3 ppm; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_9\text{H}_{10}\text{N}_3\text{OSe}$ 255.9984; Found 255.9982.



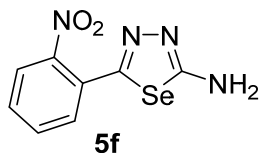
5c was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 50:1) as eluent as a white solid (29.2 mg, 61% yield). ^1H NMR (400MHz, DMSO- d_6) δ = 7.51 (brs, 2H), 7.47 (d, J = 7.2 Hz, 1H), 7.33-7.31 (m, 2H), 7.29-7.24 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 172.9, 160.6, 135.5, 132.7, 131.3, 130.6, 128.9, 126.2, 21.3 ppm; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_9\text{H}_{10}\text{N}_3\text{Se}$ 240.0034; Found 240.0029.



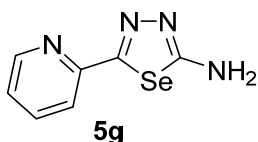
5d was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 50:1) as eluent as a white solid (26.1 mg, 43% yield). ^1H NMR (400 MHz, DMSO- d_6) δ = 7.89 (dd, J = 8.0, 2.0 Hz, 1H), 7.76 (dd, J = 8.0, 1.2 Hz, 1H), 7.58 (brs, 2H), 7.49-7.45 (m, 1H), 7.39-7.34 (m, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 174.3, 157.1, 134.2, 133.7, 130.81, 130.78, 128.0, 121.1 ppm; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_8\text{H}_6\text{N}_3\text{BrSeNa}$ 325.8803; Found 325.8797.



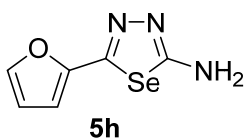
5e was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 50:1) as eluent as a white solid (29.1 mg, 56% yield). ^1H NMR (400 MHz, DMSO- d_6) δ = 7.75-7.72 (m, 2H), 7.61 (brs, 2H), 7.50-7.47 (m, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 172.6, 160.2, 133.8, 132.8, 129.1, 128.6 ppm; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_8\text{H}_7\text{N}_3\text{ClSe}$ 259.9488; Found 259.9479.



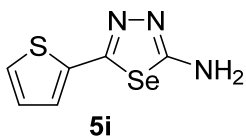
5f was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 30:1) as eluent as a brown solid (26.6 mg, 49% yield). ^1H NMR (400 MHz, DMSO- d_6) δ = 7.92-7.90 (m, 1H), 7.74-7.63 (m, 5H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 174.1, 155.2, 147.9, 132.5, 132.0, 130.3, 126.3, 124.1 ppm; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_8\text{H}_6\text{N}_4\text{O}_2\text{SeNa}$ 292.9548; Found 292.9547.



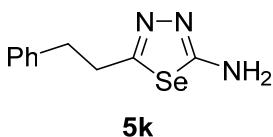
5g was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 40:1) as eluent as a white solid (29.0 mg, 64% yield). ¹H NMR (400MHz, DMSO-d₆) δ = 8.56-8.54 (m, 1H), 8.01-7.98 (m, 1H), 7.90-7.86 (m, 1H), 7.67 (brs, 2H), 7.41-7.38 (m, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 173.4, 164.1, 151.8, 149.7, 137.3, 124.2, 118.5 ppm; HRMS (ESI) m/z: [M + Na]⁺ Calcd for C₇H₆N₄SeNa 248.9650; Found 248.9646.



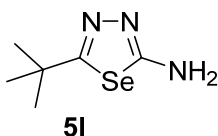
5h was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 40:1) as eluent as a white solid (23.3 mg, 54% yield). ¹H NMR (400MHz, DMSO-d₆) δ = 7.81 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.56 (brs, 2H), 6.92-6.91 (m, 1H), 6.64-6.63 (m, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 171.6, 151.0, 148.3, 144.2, 112.4, 108.6 ppm; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₆H₆N₃OSe 215.9671; Found 215.9665.



5i was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 50:1) as eluent as a white solid (21.8 mg, 47% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 7.59 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.54 (brs, 2H), 7.41 (dd, *J* = 4.0, 1.2 Hz, 1H), 7.10 (dd, *J* = 5.2, 3.6 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 171.7, 154.8, 136.5, 128.7, 127.8, 127.4 ppm; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₆H₆N₃SSe 231.9442; Found 231.9438.



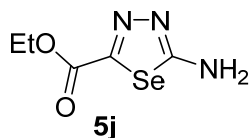
5k was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 50:1) as eluent as a white solid (19.8 mg, 39% yield). ¹H NMR (400 MHz, DMSO-d₆) δ = 7.31-7.24 (m, 4H), 7.22-7.17 (m, 1H), 7.12 (brs, 2H), 3.13-3.10 (m, 2H), 2.93 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ = 172.0, 162.9, 140.4, 128.5, 128.3, 126.1, 35.1, 34.3 ppm; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₀H₁₂N₃Se 254.0191; Found 254.0188.



5i was prepared according to the general procedure and purified by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 50:1) as eluent as a white solid (19.3 mg, 47% yield). ^1H NMR (400 MHz, DMSO- d_6) δ = 7.17 (brs, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 174.1, 171.9, 38.0, 31.0 ppm; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_6\text{H}_{12}\text{N}_3\text{Se}$ 206.0191; Found 206.0186.

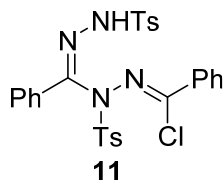
One-pot Procedure for the Synthesis of 1,3,4-selenadiazol-2-amine **5j**.

To a rapidly stirred suspension of TsNHNH_2 (0.22 mmol) in methanol (3 mL) was added ethyl 2-oxoacetate (0.2 mmol). The mixture was stirred at room temperature for 4 hours. The solvent was removed *in vacuo*. Then CH_3CN (3 mL), KSeCN (0.4 mmol), NCS (0.22 mmol) and $\text{Sc}(\text{OTf})_3$ (0.1 mmol) were subsequently added under an argon atmosphere and the mixture stirred at room temperature for 24 hours. After quenching by water, the product was extracted with ethyl acetate and the organic layer was washed with saturated Na_2CO_3 solution and brine, dried over anhydrous MgSO_4 , filtered and concentrated *in vacuo*. Purification by chromatography on silica gel using dichloromethane/methanol (dichloromethane/methanol = 40:1) as eluent afforded the product **5j** as a white solid (19.5 mg, 44% yield).

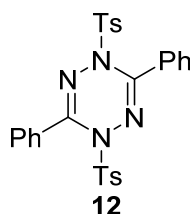


^1H NMR (400 MHz, DMSO- d_6) δ = 8.15 (brs, 2H), 4.29 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO- d_6) δ = 176.7, 160.8, 152.3, 61.8, 14.1 ppm; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_5\text{H}_7\text{N}_3\text{O}_2\text{SeNa}$ 243.9596; Found 243.9595.

Characterization Data for **11** and **12**.



^1H NMR (400MHz, CDCl_3) δ = 8.47 (d, J = 1.2 Hz, 1H), 7.84-7.80 (m, 4H), 7.76-7.73 (m, 2H), 7.49-7.47 (m, 3H), 7.41-7.34 (m, 4H), 7.27-7.25 (m, 3H), 7.20-7.16 (m, 2H), 2.47 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ = 146.2, 144.4, 144.2, 138.1, 135.5, 133.3, 132.9, 132.2, 131.3, 130.12, 130.05, 129.5, 129.1, 128.6, 128.5, 128.2, 128.04, 128.02, 21.8, 21.6 ppm; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{25}\text{N}_4\text{O}_4\text{S}_2\text{ClNa}$ 603.0898; Found 603.0898.

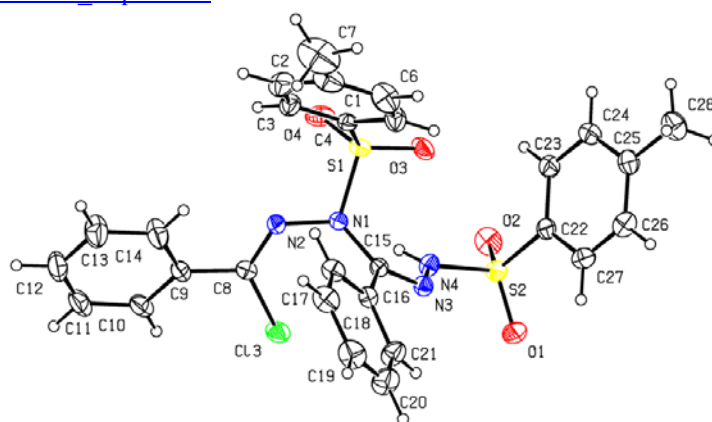


^1H NMR (400 MHz, CDCl_3) δ = 7.75 (d, J = 8.4 Hz, 4H), 7.51-7.49 (m, 6H), 7.41-7.26 (m, 8H), 2.47 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ = 154.6, 145.6, 134.4, 131.6, 129.72, 129.70,

128.9, 128.6, 128.3, 21.8 ppm; HRMS (ESI) m/z : $[M + H]^+$ Calcd for $C_{28}H_{25}N_4O_4S_2$ 545.1312; Found 545.1314.

Crystal Data and Structure Refinement for **11**.

Procedure for the recrystallization of **11**: To a 10 mL tube containing **11** (20 mg) was added a 2:1 mixture of *n*-hexane and CH_2Cl_2 (about 2 mL). The mixture was stirred until a clear solution was formed, which was kept aside for about a week at room temperature to obtain crystals. A suitable crystal was selected and tested on a **SuperNova, Dual, Cu at zero, Eos** diffractometer. The crystal was kept at 292.04(12) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. CCDC 2055756 (**11**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



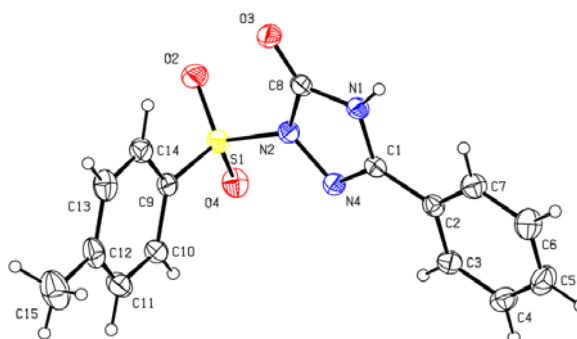
11 CCDC 2055756 (30% thermal ellipsoids).

Identification code	11
Empirical formula	$C_{28}H_{25}ClN_4O_4S_2$
Formula weight	581.09
Temperature/K	292.04(12)
Crystal system	monoclinic
Space group	$C2/c$
$a/\text{\AA}$	26.6860(6)
$b/\text{\AA}$	8.33761(13)
$c/\text{\AA}$	27.8769(7)
$\alpha /^\circ$	90
$\beta /^\circ$	115.598(3)
$\gamma /^\circ$	90
Volume/ \AA^3	5593.7(2)
Z	8
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.380
μ/mm^{-1}	2.949
F(000)	2416.0
Crystal size/ mm^3	0.15 × 0.12 × 0.09
Radiation	Cu K α ($\lambda = 1.54184$)
2θ range for data collection/ $^\circ$	7.032 to 133.196
Index ranges	$-31 \leq h \leq 15, -9 \leq k \leq 9, -25 \leq l \leq 33$
Reflections collected	9862
Independent reflections	4930 [$R_{\text{int}} = 0.0207, R_{\text{sigma}} = 0.0268$]
Data/restraints/parameters	4930/0/354
Goodness-of-fit on F^2	1.078

Final R indexes [$I \geq 2 \sigma(I)$] $R_1 = 0.0448$, $wR_2 = 0.1175$
 Final R indexes [all data] $R_1 = 0.0489$, $wR_2 = 0.1216$
 Largest diff. peak/hole / $e \text{ \AA}^{-3}$ 0.29/-0.63

Crystal Data and Structure Refinement for 4a.

Procedure for the recrystallization of **4a**: To a 10 mL tube containing **4a** (20 mg) was added a 2:1 mixture of *n*-hexane and EtOAc (about 2 mL). The mixture was stirred until a clear solution was formed, which was kept aside for about a week at room temperature to obtain crystals. A suitable crystal was selected and tested on a **SuperNova, Dual, Cu at zero, Eos** diffractometer. The crystal was kept at 294.41(10) K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. CCDC 2055757 (**4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

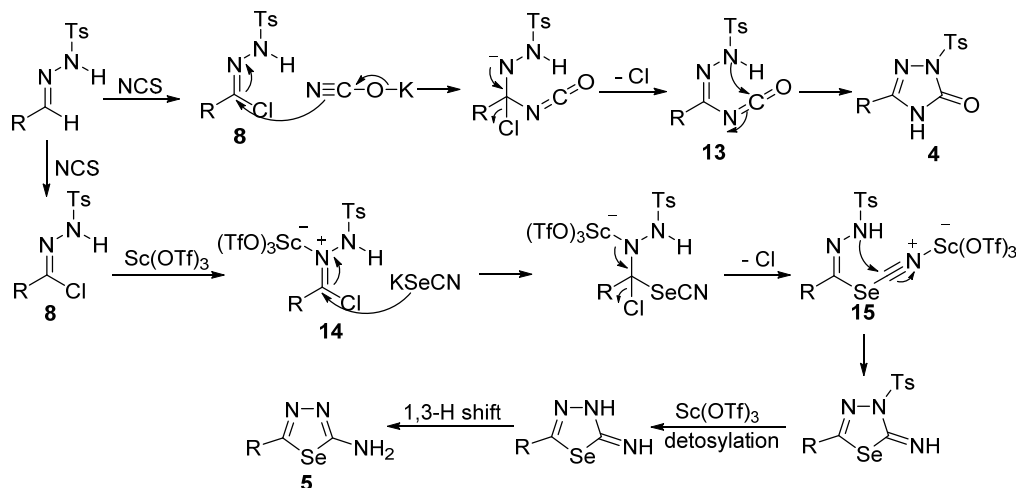


4a CCDC 2055757 (30% thermal ellipsoids).

Identification code	4a
Empirical formula	$C_{15}H_{13}N_3O_3S$
Formula weight	315.34
Temperature/K	294.41(10)
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	13.8991(4)
$b/\text{\AA}$	6.41548(14)
$c/\text{\AA}$	17.1951(4)
$\alpha /^\circ$	90
$\beta /^\circ$	108.383(3)
$\gamma /^\circ$	90
Volume/ \AA^3	1455.03(6)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.440
μ / mm^{-1}	2.133
F(000)	656.0
Crystal size/ mm^3	0.12 \times 0.09 \times 0.07
Radiation	Cu K α ($\lambda = 1.54184$)
2θ range for data collection/ $^\circ$	10.802 to 133.202
Index ranges	$-16 \leq h \leq 16$, $-5 \leq k \leq 7$, $-20 \leq l \leq 15$
Reflections collected	4619
Independent reflections	2514 [$R_{\text{int}} = 0.0177$, $R_{\text{sigma}} = 0.0259$]
Data/restraints/parameters	2514/0/201
Goodness-of-fit on F^2	1.043
Final R indexes [$I \geq 2 \sigma(I)$]	$R_1 = 0.0353$, $wR_2 = 0.0928$

Final R indexes [all data] $R_1 = 0.0413$, $wR_2 = 0.0983$
 Largest diff. peak/hole / $e \text{ \AA}^{-3}$ 0.21/-0.26

Scheme S1. Proposed pathway for 2-Tosyl-1,2,4-triazol-3-ones **4 and 1,3,4-selenadiazol-2-amine **5** formation.**



2-Tosyl-1,2,4-triazol-3-ones **4** and 1,3,4-selenadiazol-2-amine **5** were formed by the similar process from *N*-tosylhydrazone **8**. Addition-elimination reaction of KOCN and *N*-tosylhydrazone **8** producing intermediate **13**, followed by intramolecular cyclization led to 2-tosyl-1,2,4-triazol-3-ones **4**. Addition-elimination reaction of KSeCN and *N*-tosylhydrazone iminium salt **14** producing intermediate **15**, followed by intramolecular cyclization, detosylation and 1,3-H shift resulted in 1,3,4-selenadiazol-2-amine **5**.

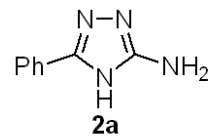
References

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Copies of ¹H and ¹³C Spectra

wzy-20200626



12.050

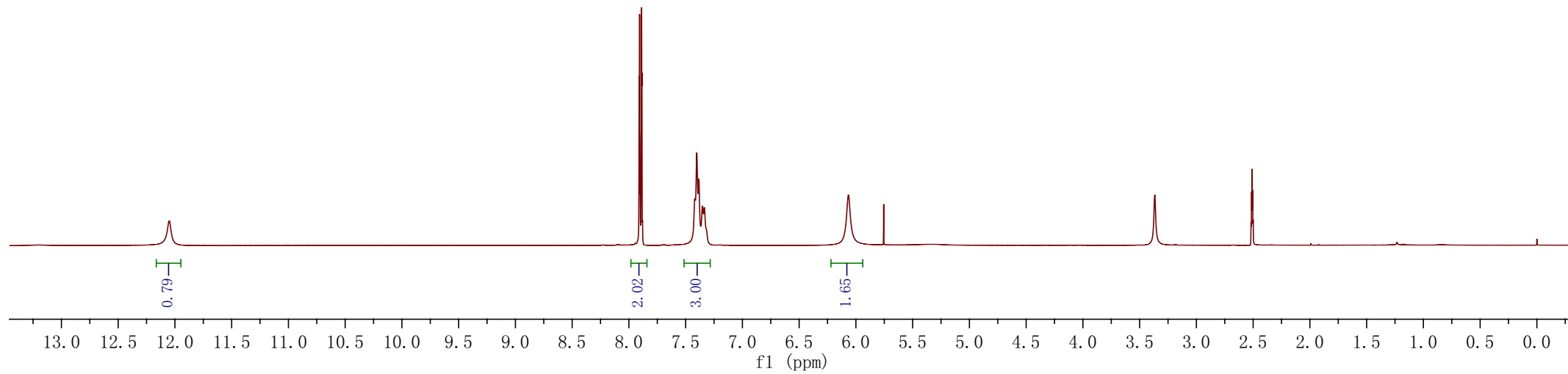
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7.402
7.384
7.352
7.335

6.066

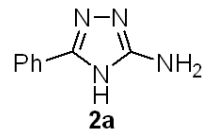
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2.513
2.509
2.504

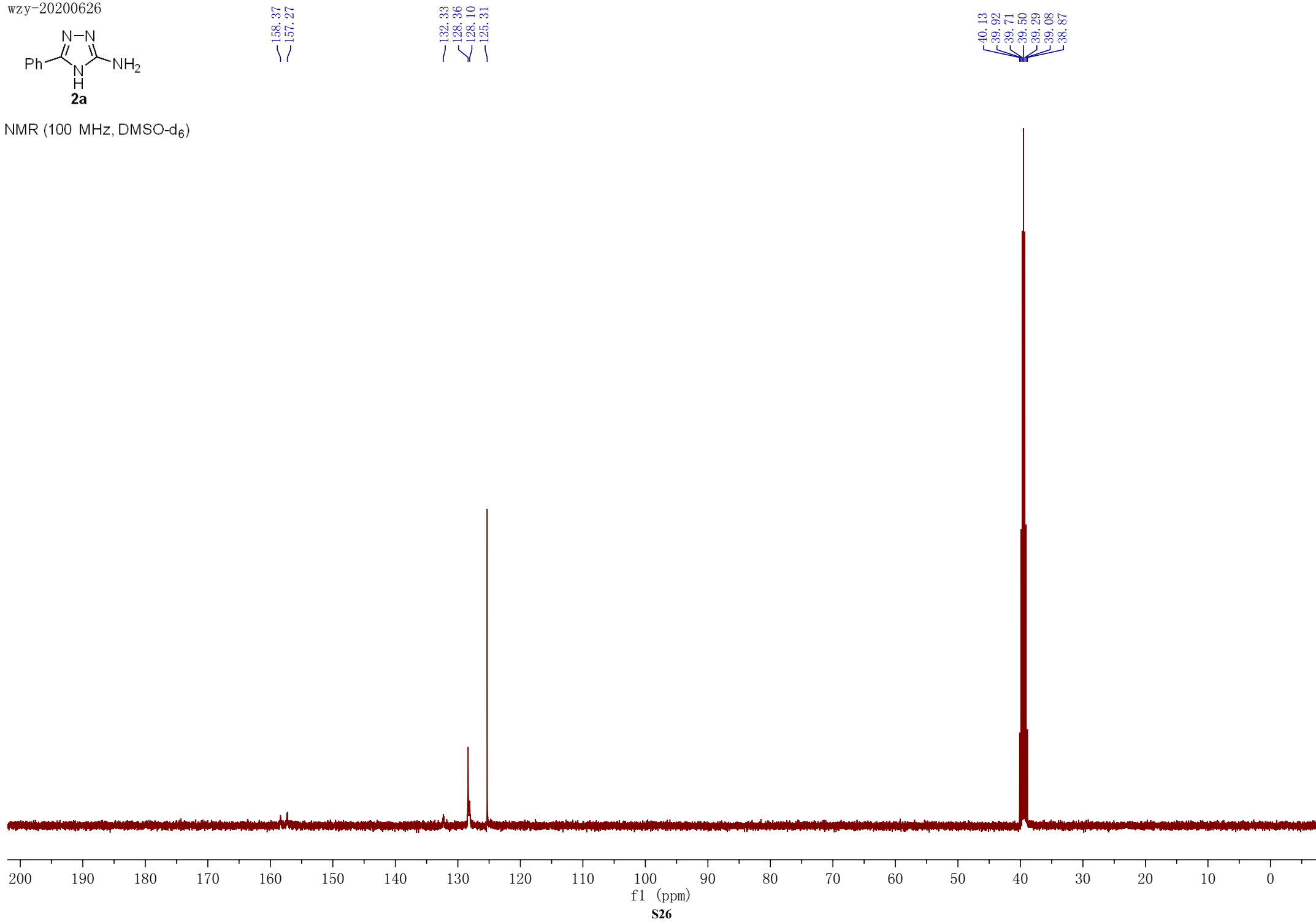
¹H NMR (400 MHz, DMSO-d₆)



wzy-20200626



^{13}C NMR (100 MHz, DMSO- d_6)



wzy-20200710-1

— 11.978

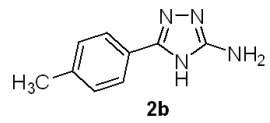
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7.765

7.210
7.192

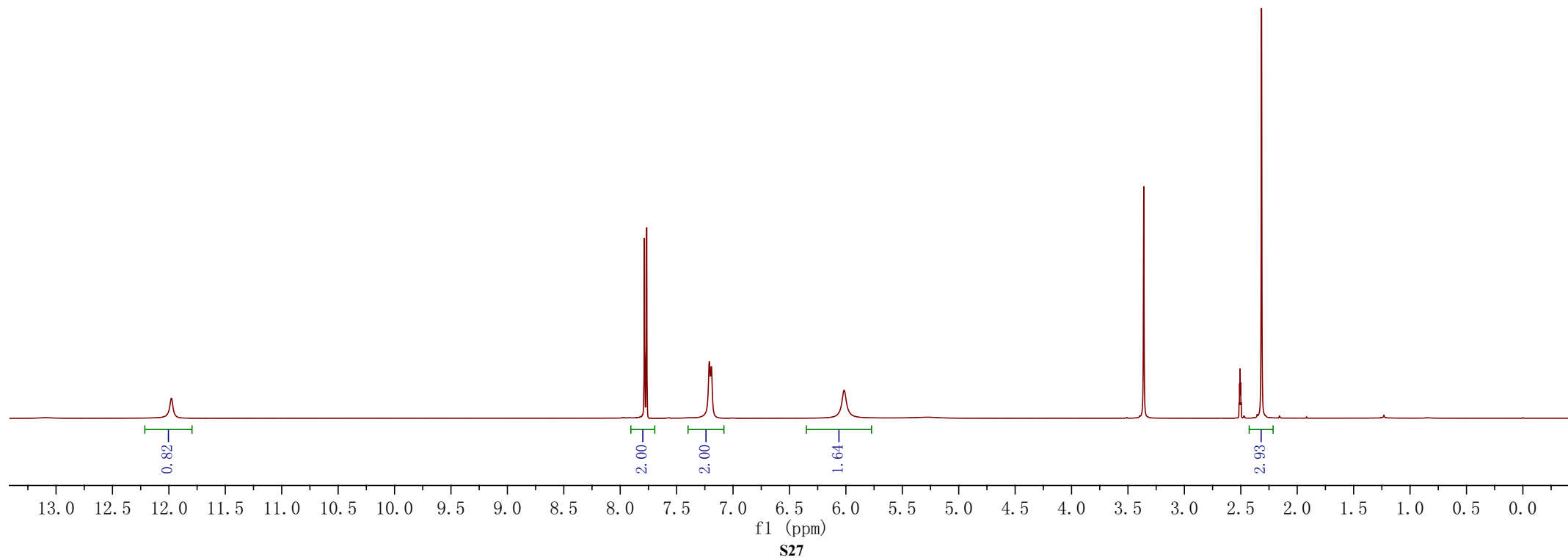
— 6.016

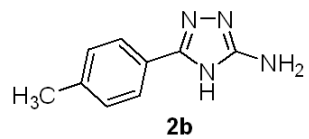
— 3.360

2.511
2.506
2.501
2.316



¹H NMR (400 MHz, DMSO-d₆)





¹³C NMR (100 MHz, DMSO-d₆)

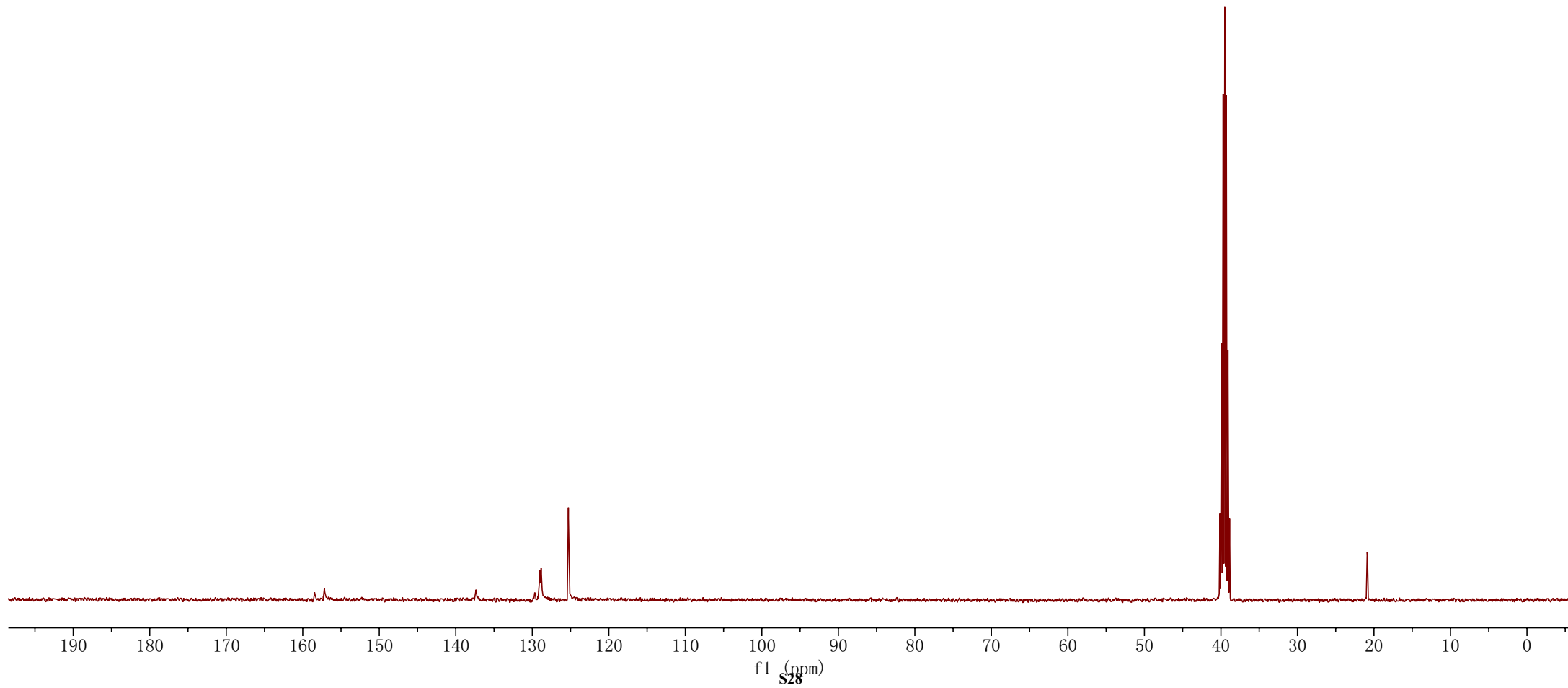
158.43
157.18

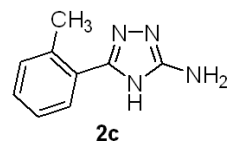
137.36

129.03
128.84
125.28

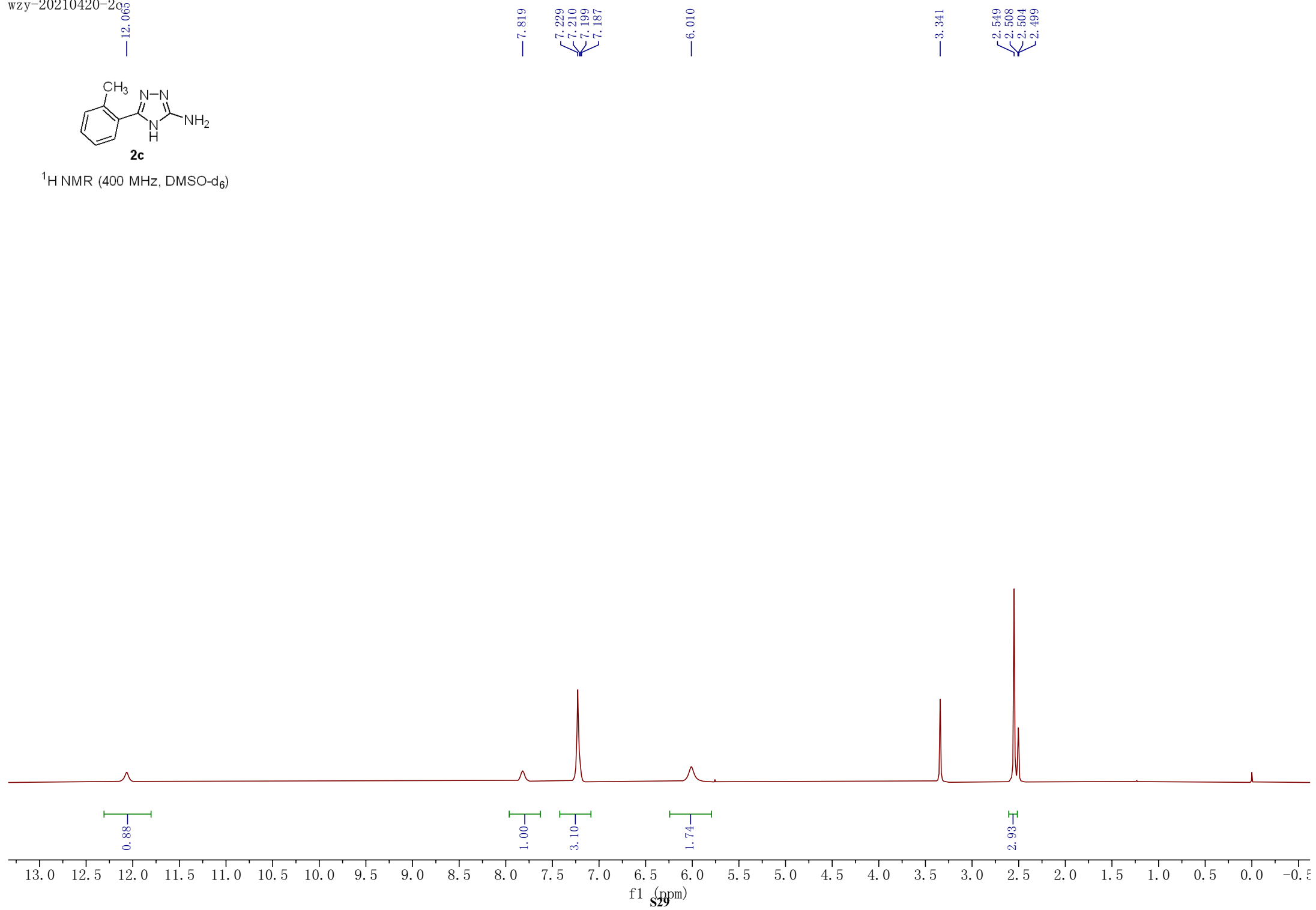
40.13
39.92
39.71
39.50
39.29
39.08
38.87

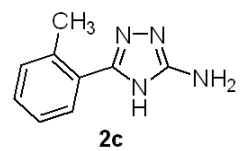
20.88





¹H NMR (400 MHz, DMSO-d₆)





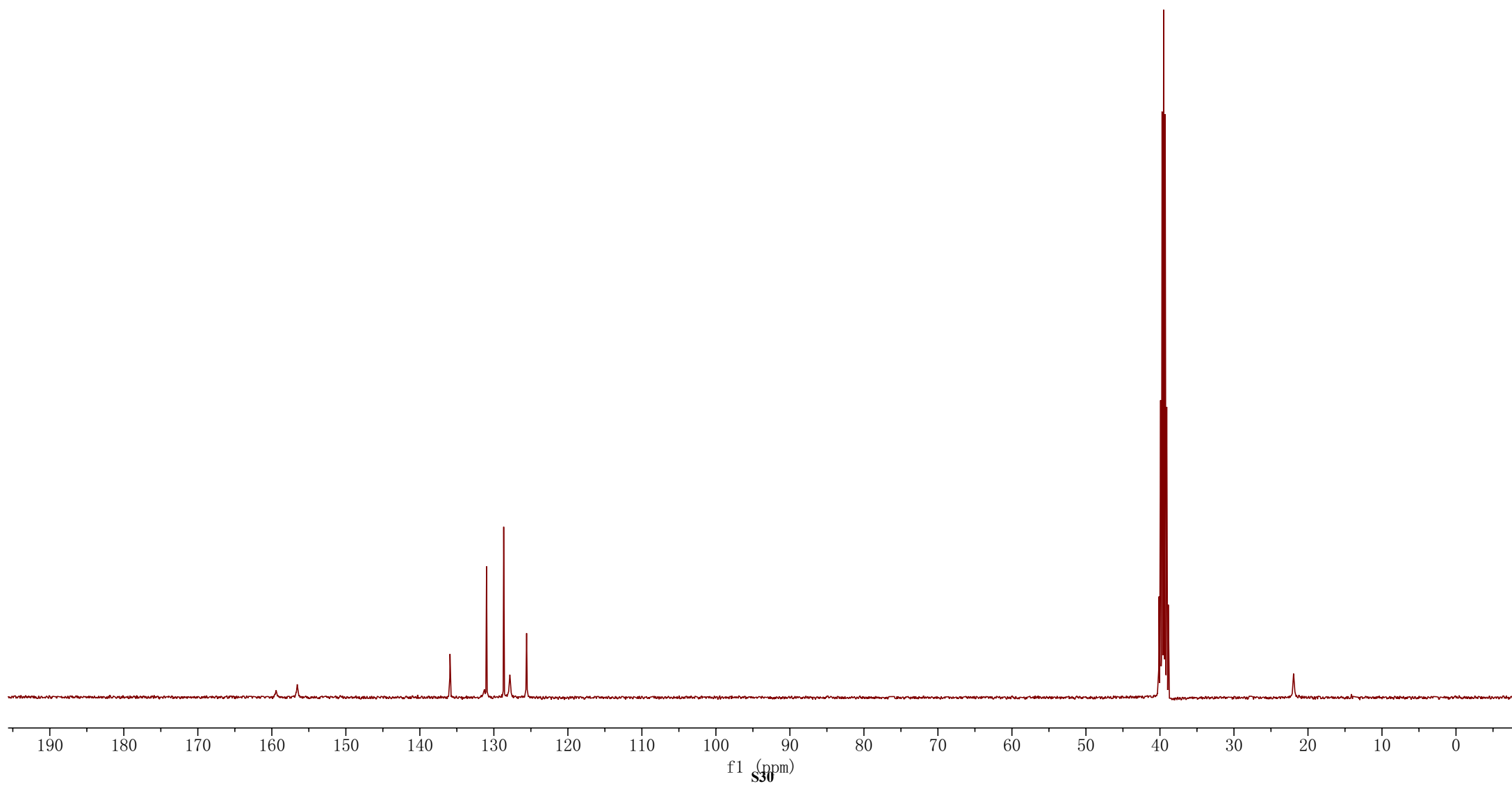
^{13}C NMR (100 MHz, DMSO- d_6)

— 159.43
— 156.57

— 135.93
— 131.32
— 130.99
— 128.67
— 127.84
— 125.58

— 40.13
— 39.92
— 39.71
— 39.50
— 39.29
— 39.08
— 38.87

— 21.94



wzy-20200824-3

11.914

7.829
7.821
7.816
7.805
7.799
7.792

6.961
6.940

5.999

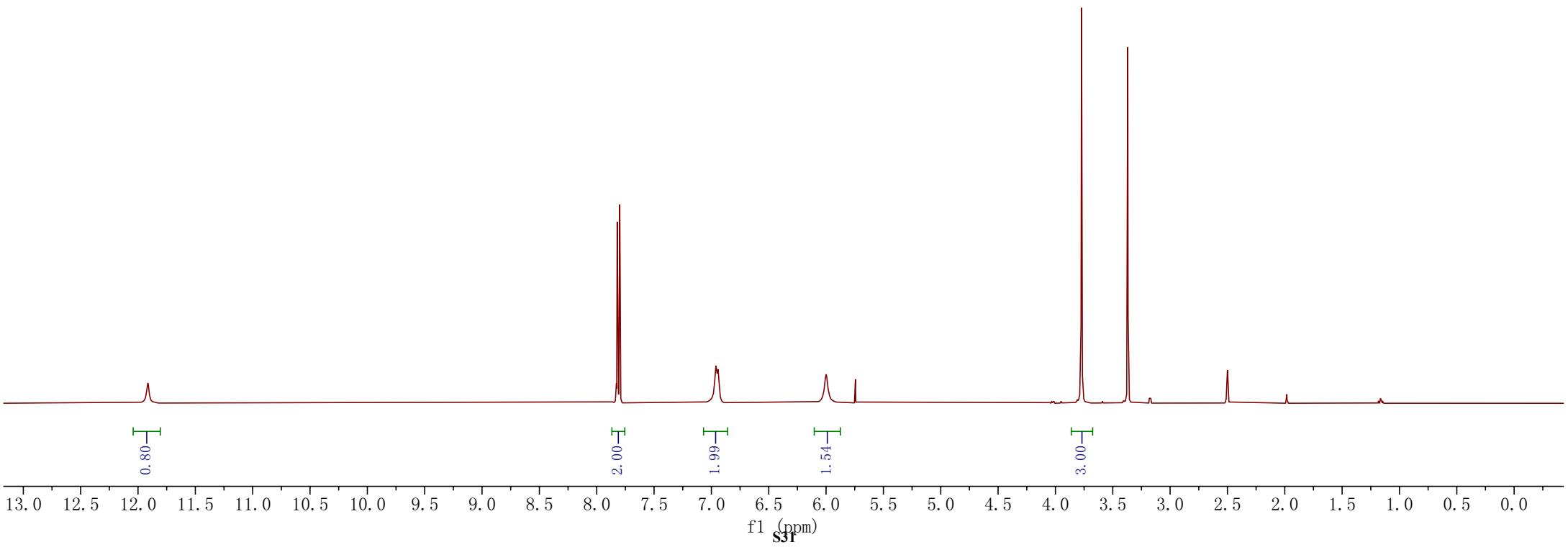
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3.369

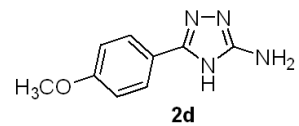
2.505
2.500
2.495



¹H NMR (400 MHz, DMSO-d₆)



wzy-20200824-3



159.32
158.32
157.18

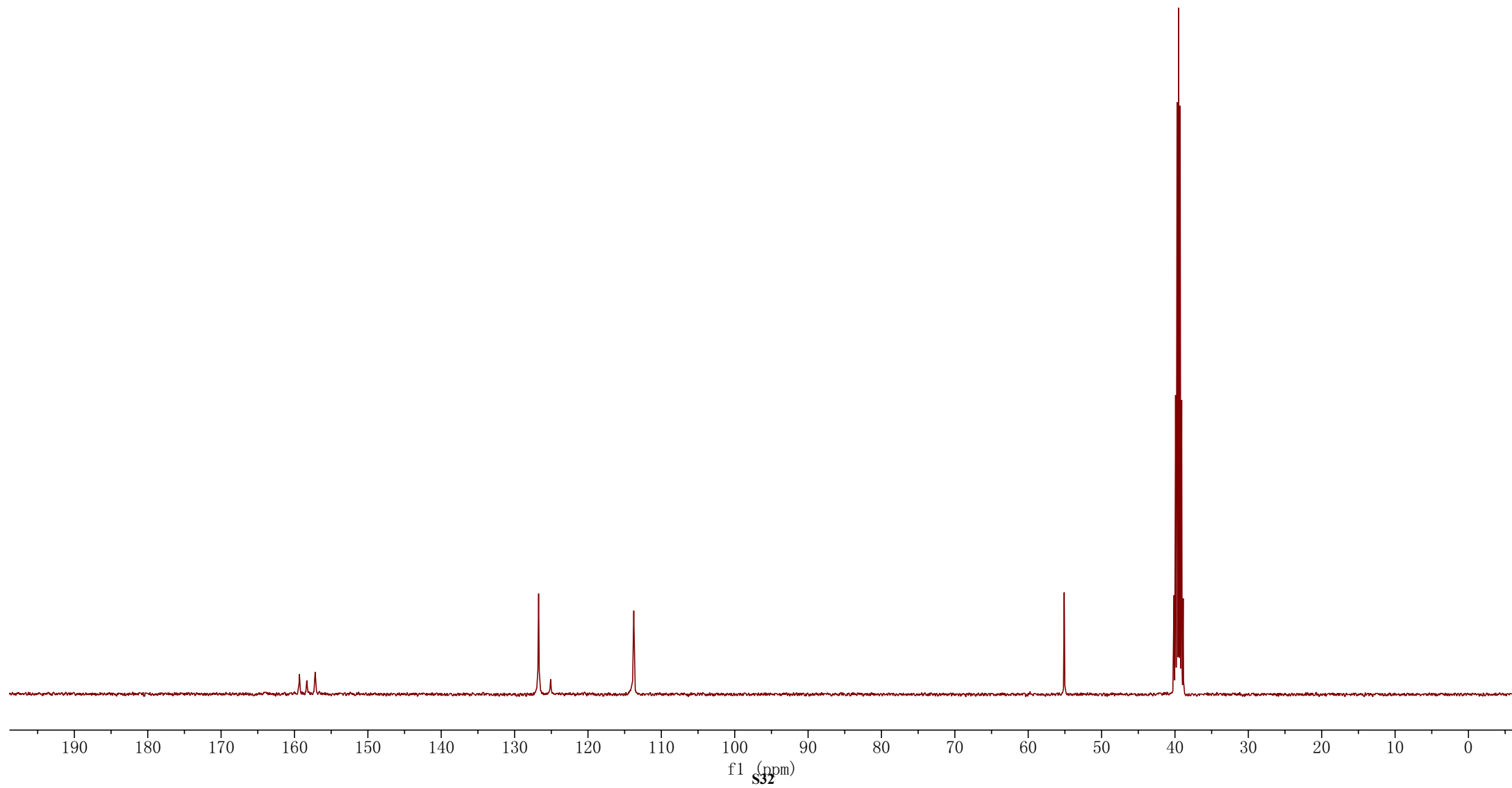
126.73
125.09

113.76

55.09

40.13
39.92
39.71
39.50
39.29
39.09
38.88

¹³C NMR (100 MHz, DMSO-d₆)



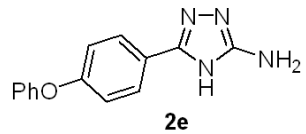
WZY-20200715-8

12.031

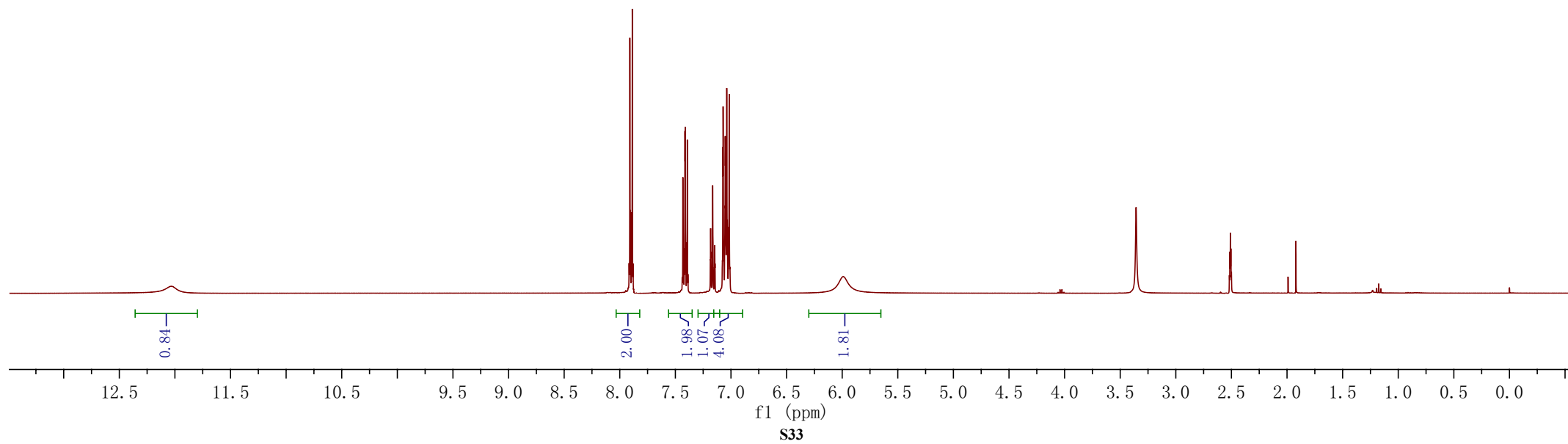
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7.898
7.897
7.892
7.887
7.882
7.880
7.433
7.414
7.411
7.393
7.165
7.073
7.071
7.051
7.049
7.038
7.006

3.357

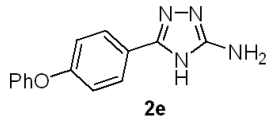
2.514
2.509
2.505



¹H NMR (400 MHz, DMSO-d₆)



WZY-20200715-8

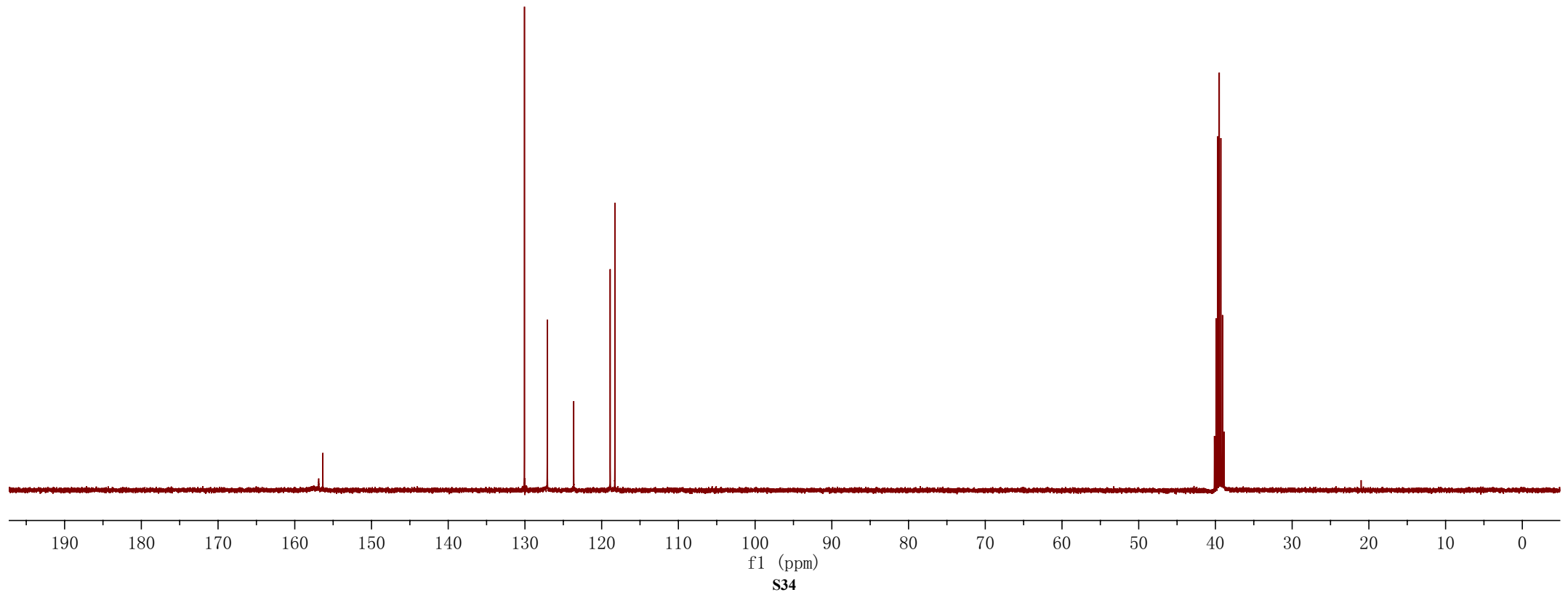


156.88
156.34

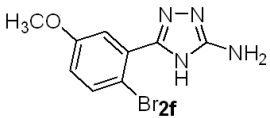
130.06
130.05
127.09
123.64
118.89
118.28

40.13
39.92
39.71
39.50
39.29
39.08
38.87

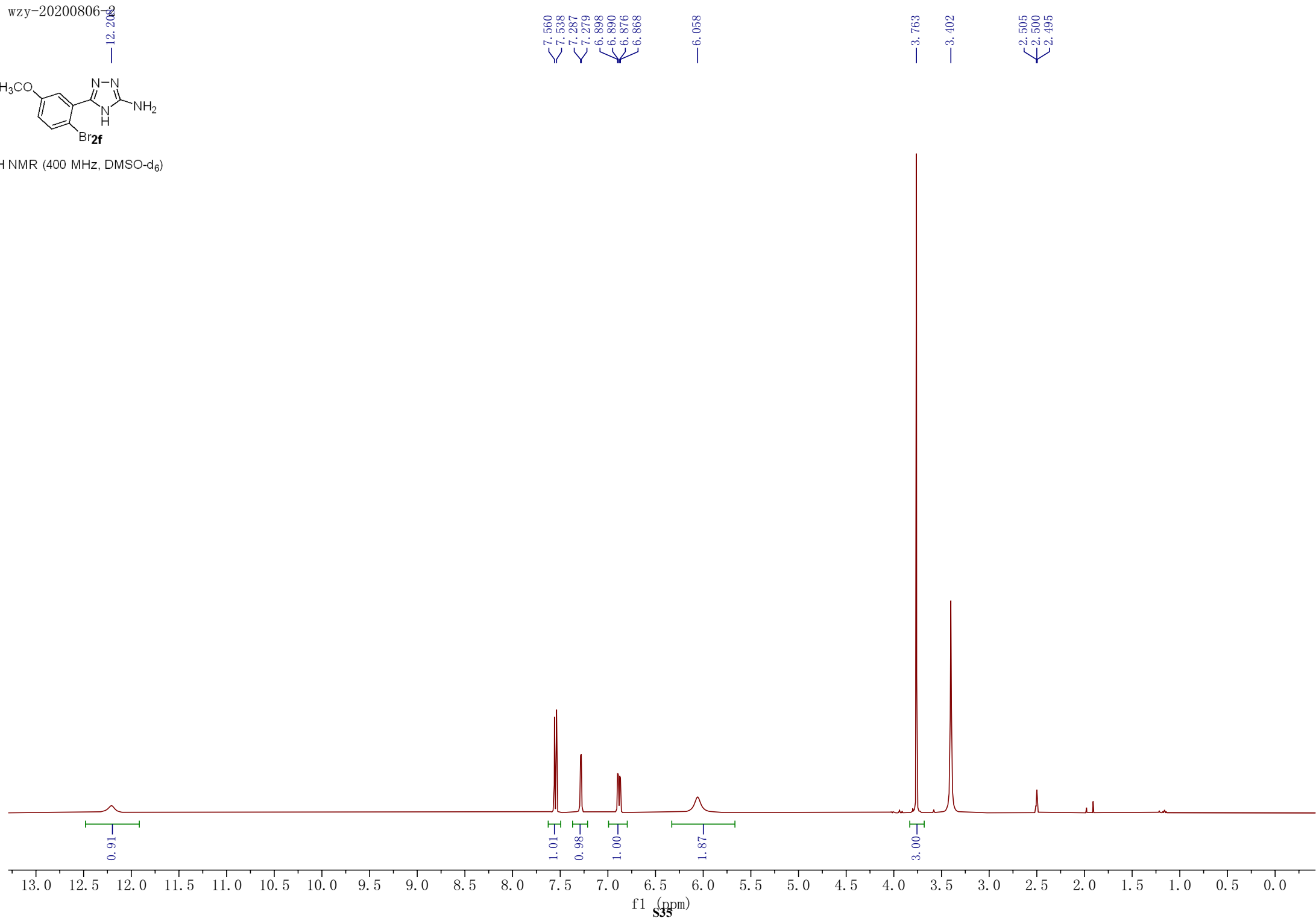
¹³C NMR (100 MHz, DMSO-d₆)



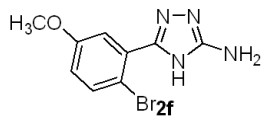
wzy-20200806



¹H NMR (400 MHz, DMSO-d₆)



wzy-20200806-2



158.25
157.70
156.83

134.46
133.77

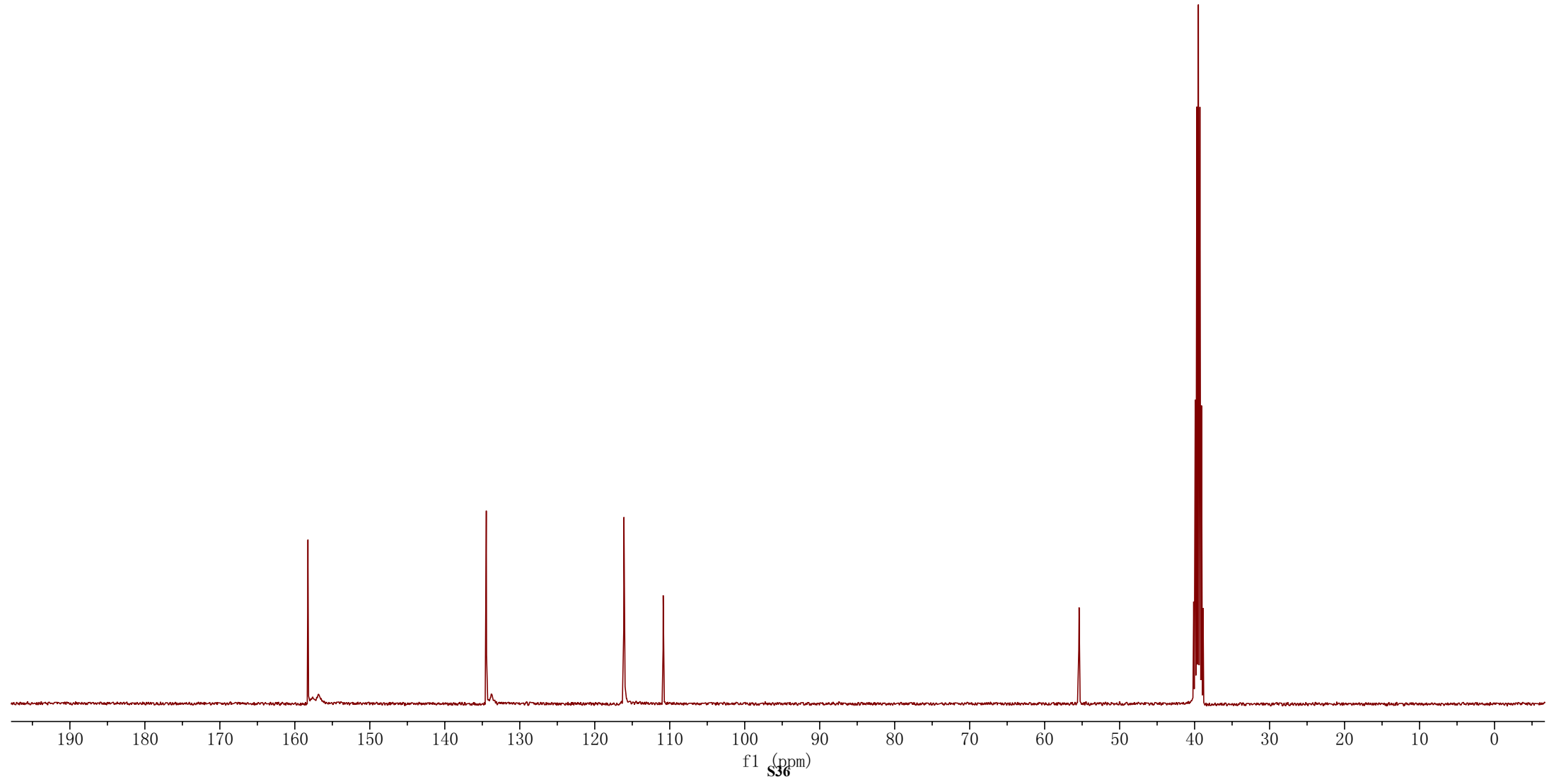
116.11

110.87

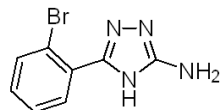
55.40

40.13
39.92
39.71
39.50
39.29
39.08
38.87

^{13}C NMR (100 MHz, DMSO- d_6)



wzy-20200715-6



2g

¹H NMR (400 MHz, DMSO-d₆)

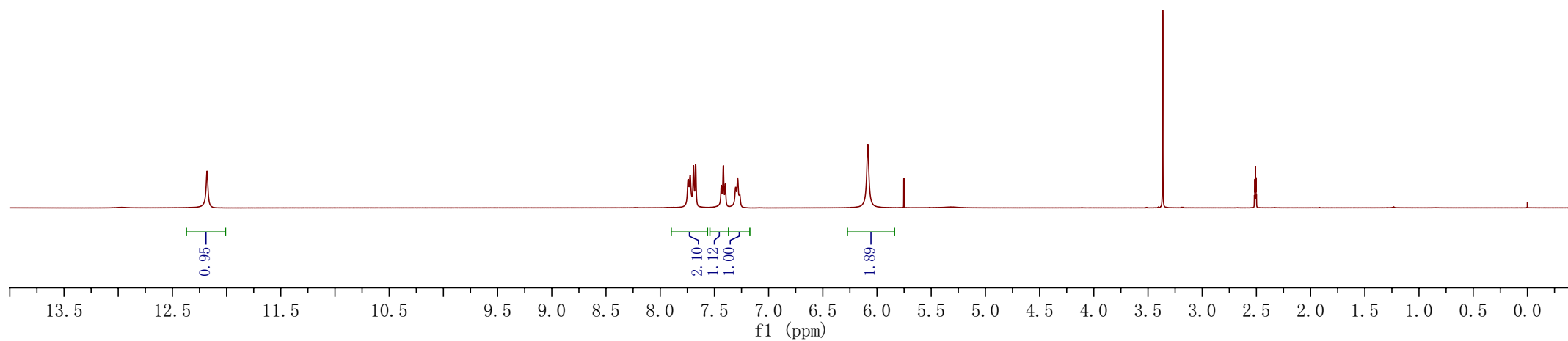
12.180

7.742
7.724
7.693
7.673
7.436
7.418
7.399
7.304
7.285
7.268

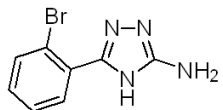
6.085

3.364

2.518
2.514
2.509
2.504
2.500



wzy-20200715-6



2g

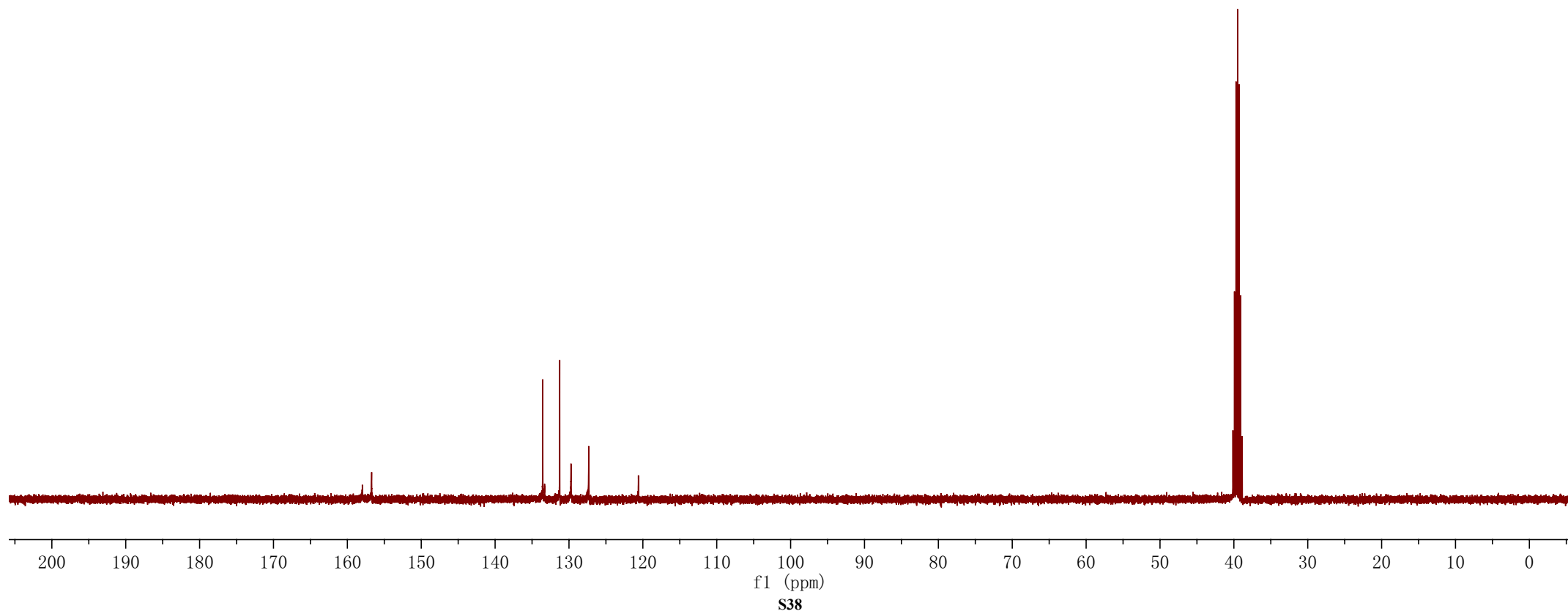
157.97
156.71

133.55
133.30
131.25
129.73
127.33

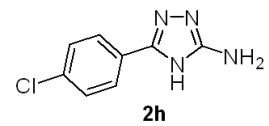
120.60

40.13
39.92
39.71
39.50
39.29
39.08
38.87

¹³C NMR (100 MHz, DMSO-d₆)



wzy-20200715-3



12.138

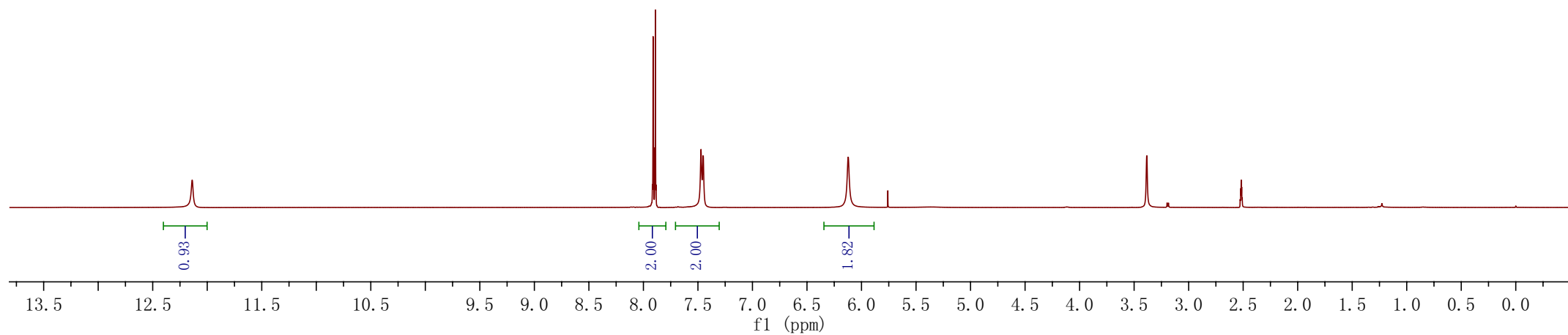
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7.911
7.906
7.895
7.890
7.472
7.452

6.122

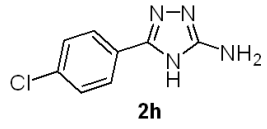
3.384

2.527
2.522
2.518
2.513
2.509

¹H NMR (400 MHz, DMSO-d₆)



wzy-20200715-3

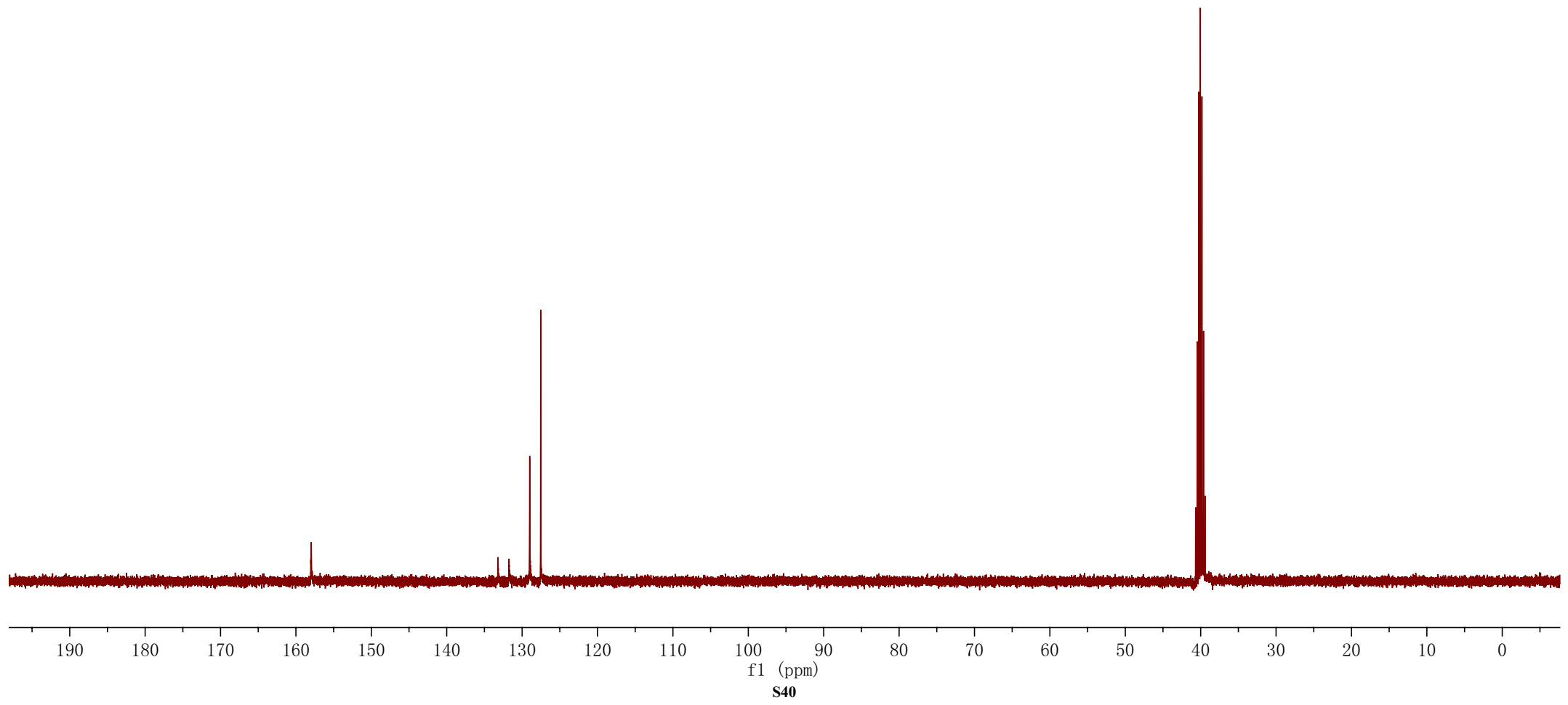


158.03
157.98

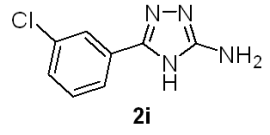
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131.73
128.99
127.54

40.67
40.46
40.25
40.04
39.83
39.62
39.41

¹³C NMR (100 MHz, DMSO-d₆)



wzy-20200710-4



12.194

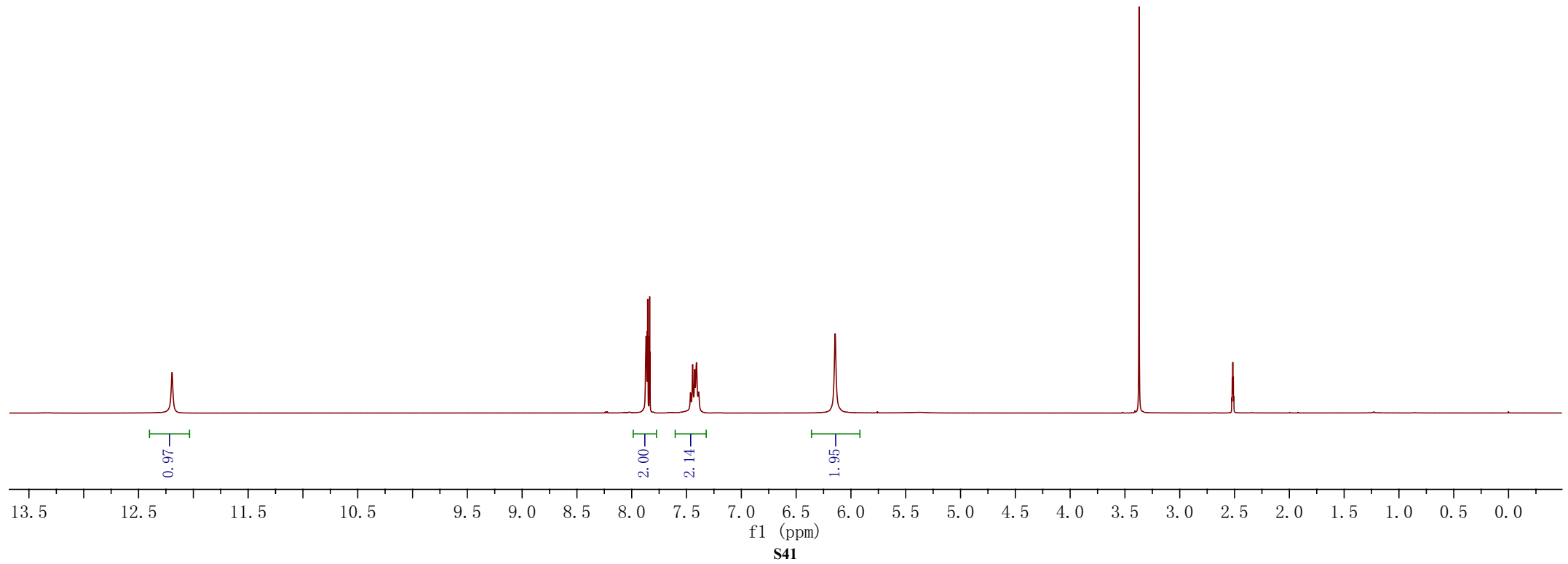
7.869
7.858
7.855
7.851
7.840
7.836
7.833
7.464
7.444
7.425
7.410
7.390

6.144

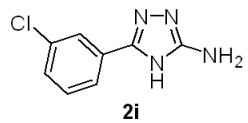
3.371

2.525
2.521
2.516
2.511
2.507

¹H NMR (400 MHz, DMSO-d₆)



wzy-20200710-4

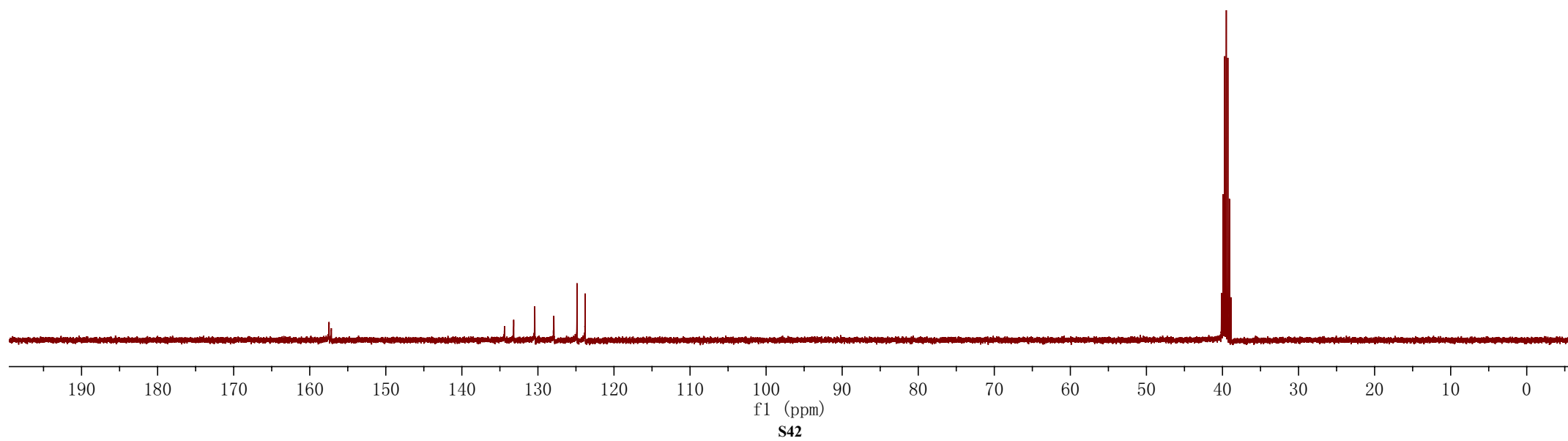


157.47
157.16

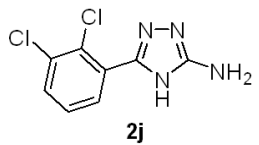
134.39
133.19
130.42
127.91
124.86
123.79

40.13
39.92
39.71
39.50
39.29
39.08
38.87

¹³C NMR (100 MHz, DMSO-d₆)



12.278



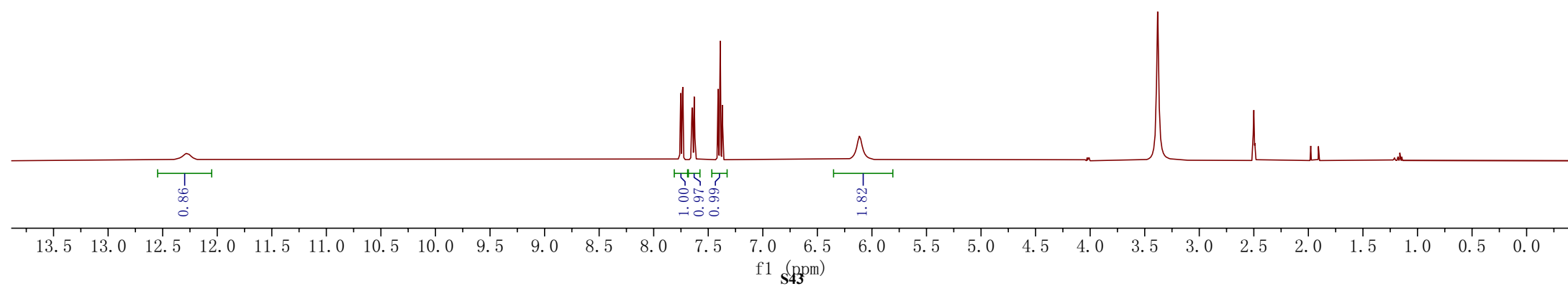
¹H NMR (400 MHz, DMSO-d₆)

7.756
7.752
7.737
7.733
7.649
7.645
7.629
7.625
7.410
7.390
7.370

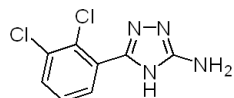
6.114

3.381

2.510
2.505
2.500
2.496
2.491



wzy-20200806-1



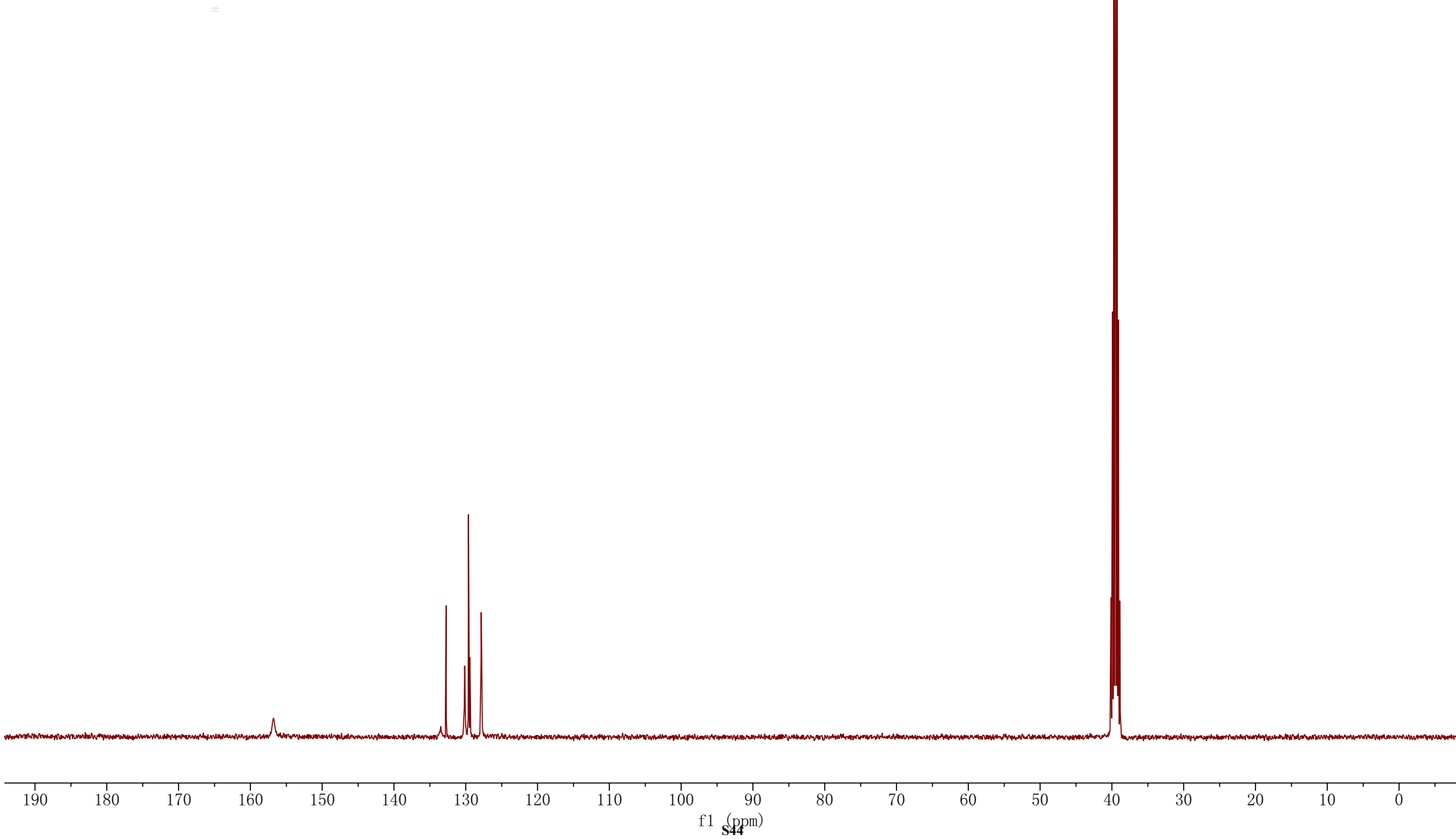
2j

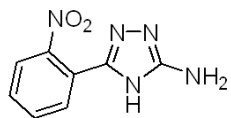
— 156.79

133.50
132.75
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129.43
127.84

39.92
39.71
39.60
39.29
39.09

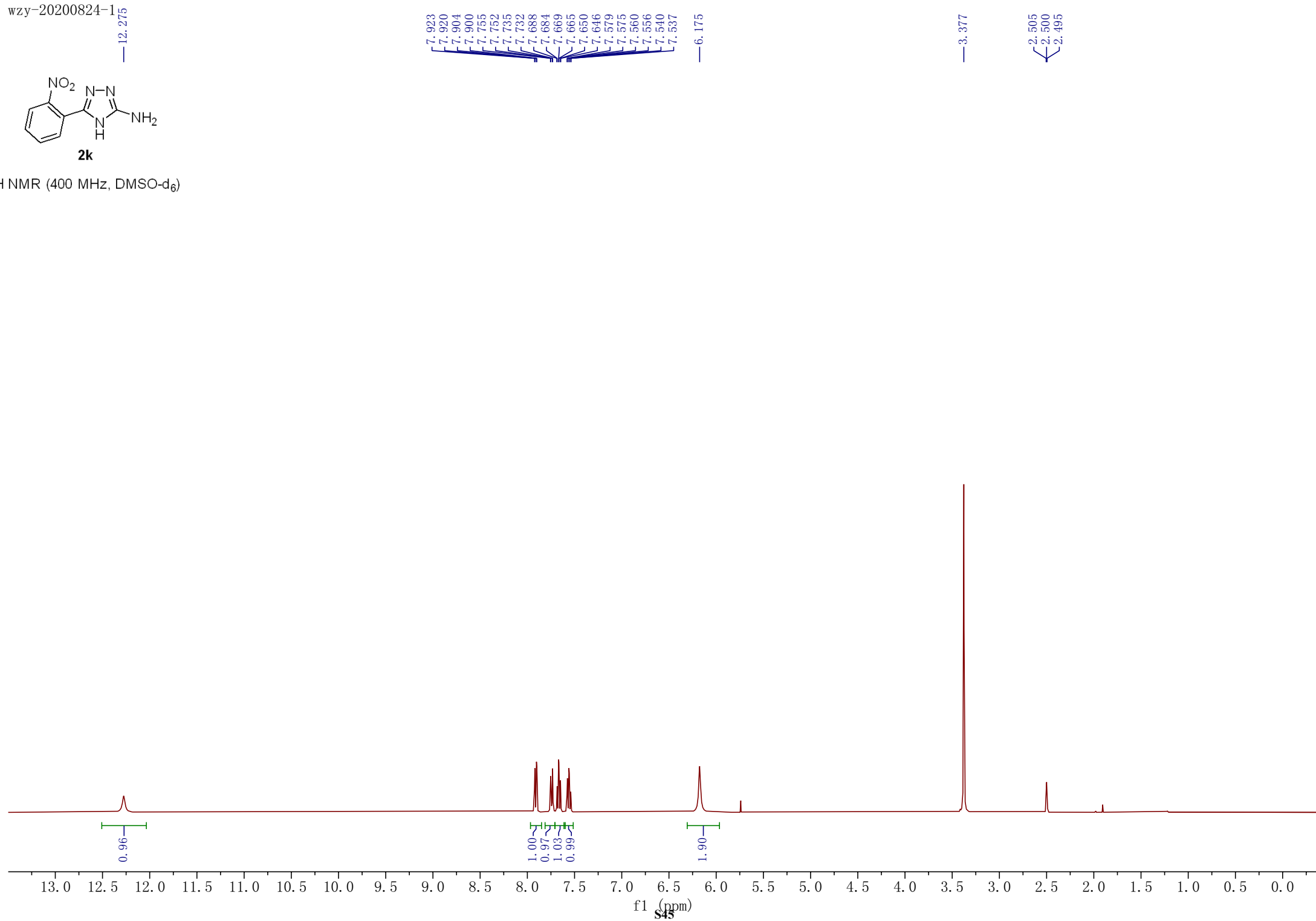
¹³C NMR (100 MHz, DMSO-d₆)



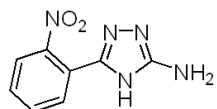


2k

¹H NMR (400 MHz, DMSO-d₆)



wzy-20200824-1



2k

^{13}C NMR (100 MHz, DMSO- d_6)

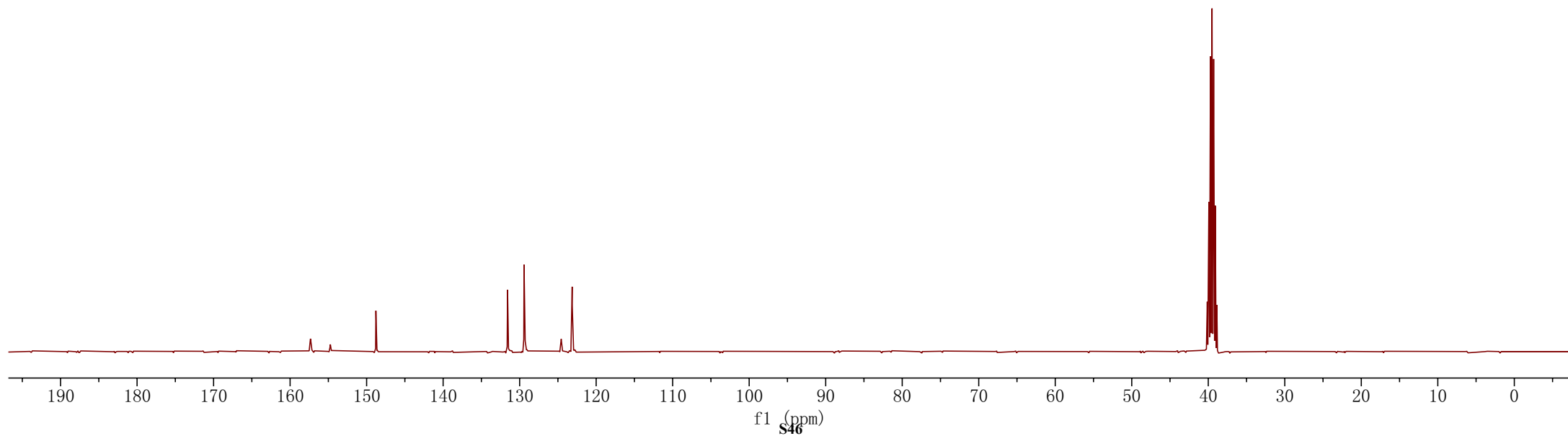
— 157.34
— 154.74

— 148.78

— 131.58
— 129.43
— 129.34

— 124.56
— 123.13

— 40.13
— 39.92
— 39.71
— 39.50
— 39.29
— 39.09
— 38.88



WZY-20200710-5

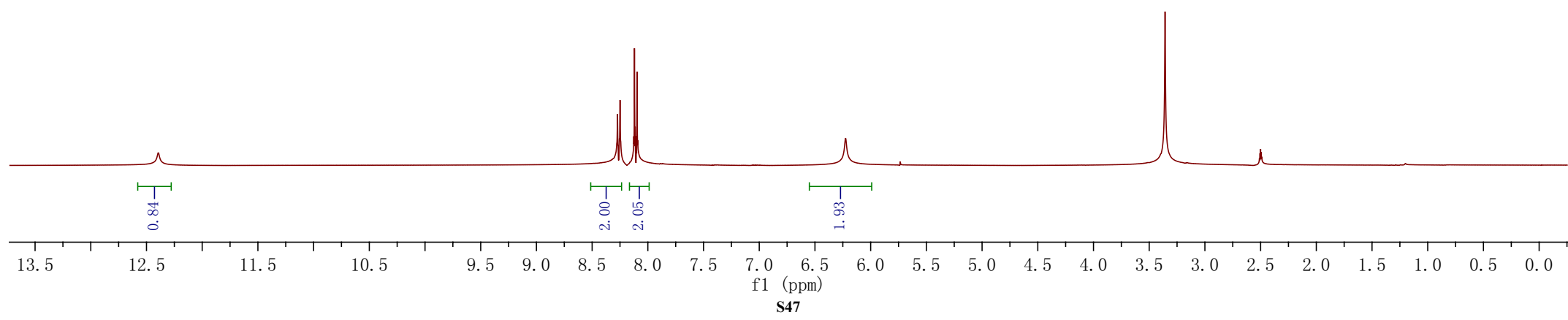
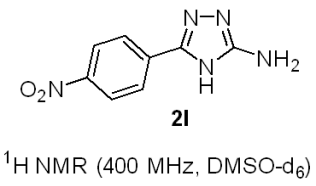
12.394

8.273
8.250
8.126
8.120
8.114
8.103
8.097

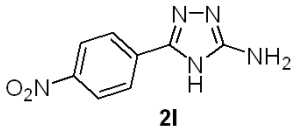
6.225

3.358

2.505
2.500
2.495



WZY-20200710-5



157.79
156.84

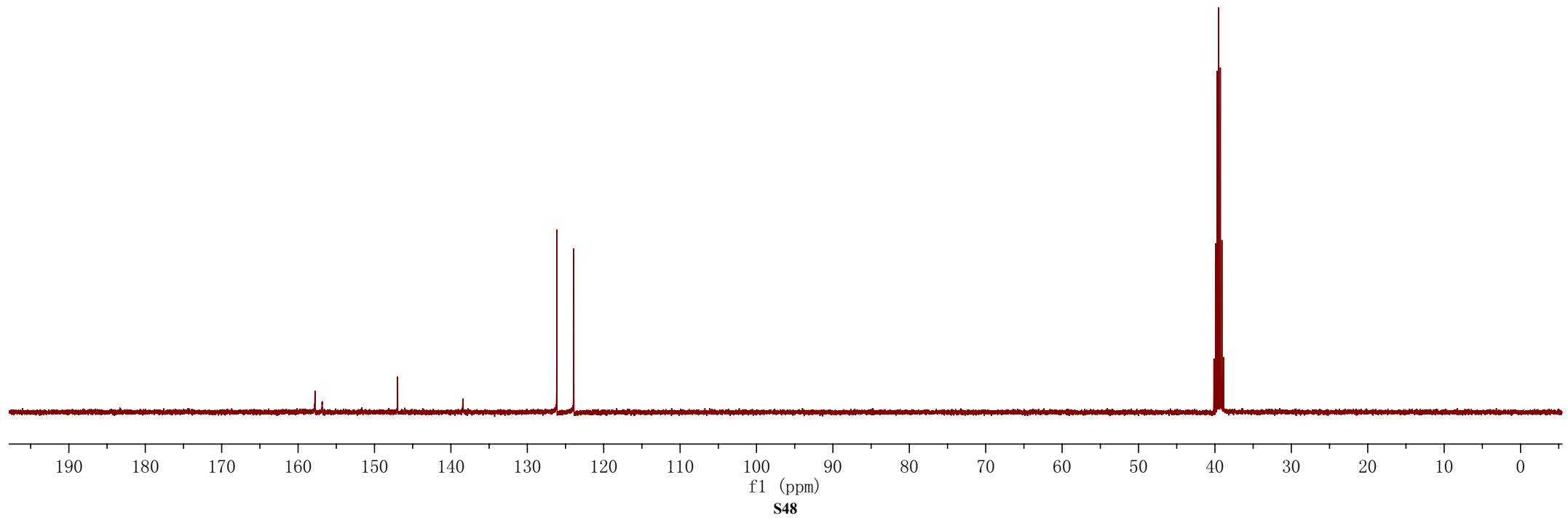
146.97

138.42

126.13
123.92

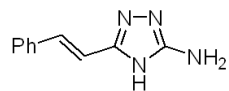
40.13
39.92
39.71
39.50
39.29
39.08
38.87

¹³C NMR (100 MHz, DMSO-d₆)



wzy-20200824-1

12.018



2m

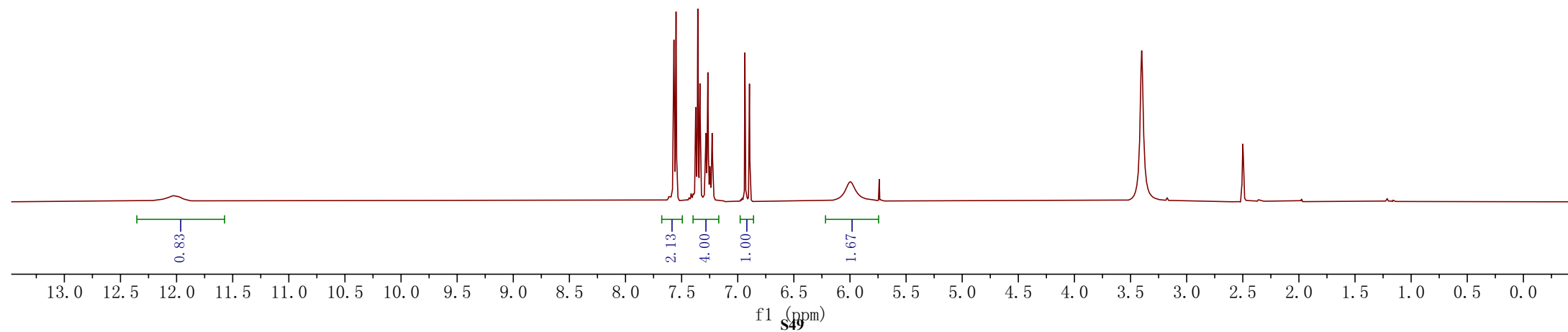
¹H NMR (400 MHz, DMSO-d₆)

7.572
7.568
7.550
7.375
7.370
7.356
7.337
7.288
7.284
7.266
7.248
7.228
6.936
6.895

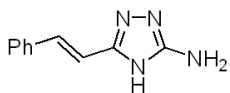
5.997

3.401

2.504
2.500
2.495



wzy-20200824-1



2m

158.43
156.97

136.46

130.97

128.64

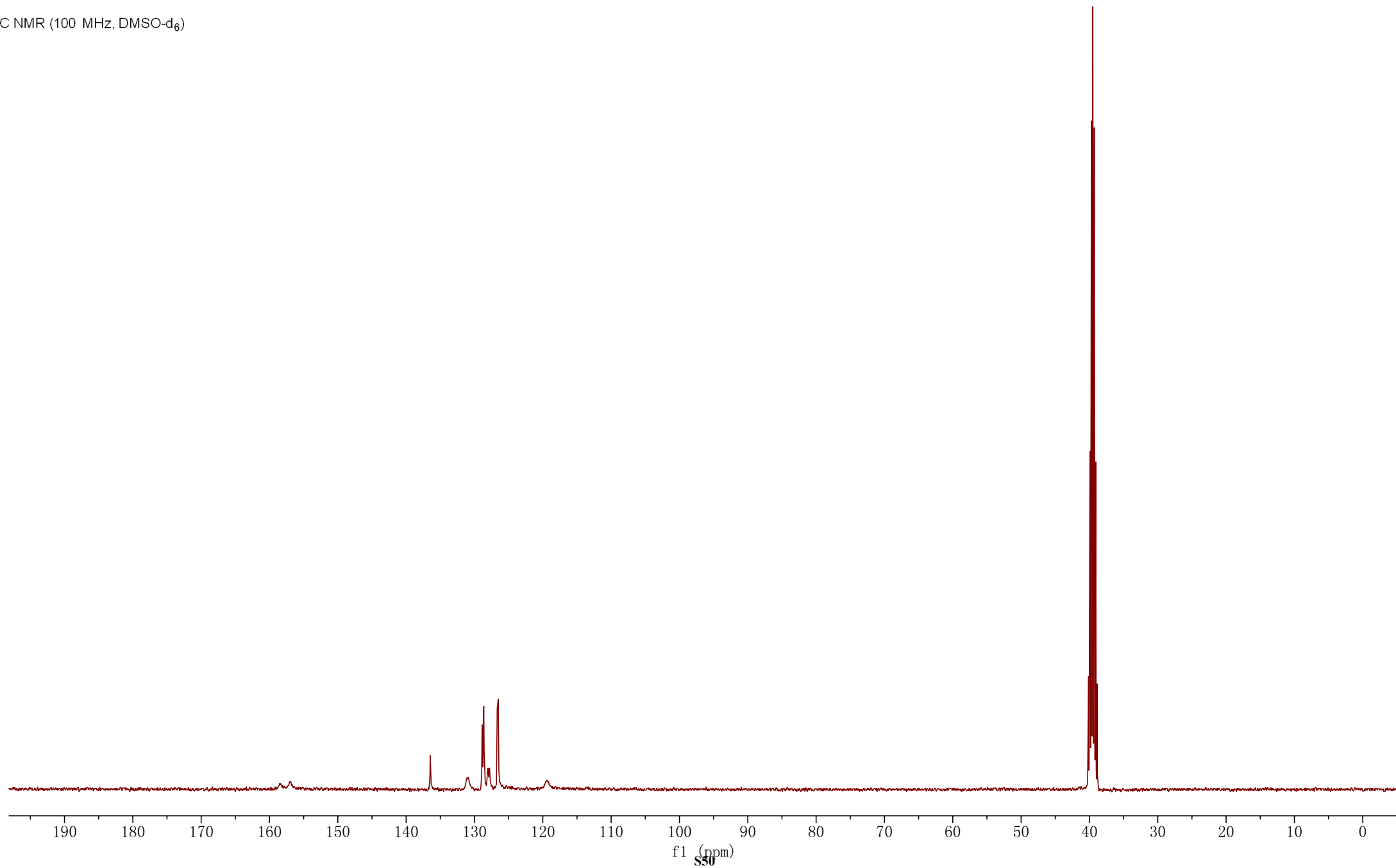
127.79

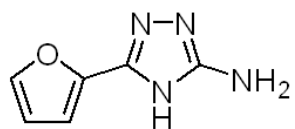
126.52

119.38

39.92
39.71
39.50
39.29
39.08

^{13}C NMR (100 MHz, DMSO- d_6)

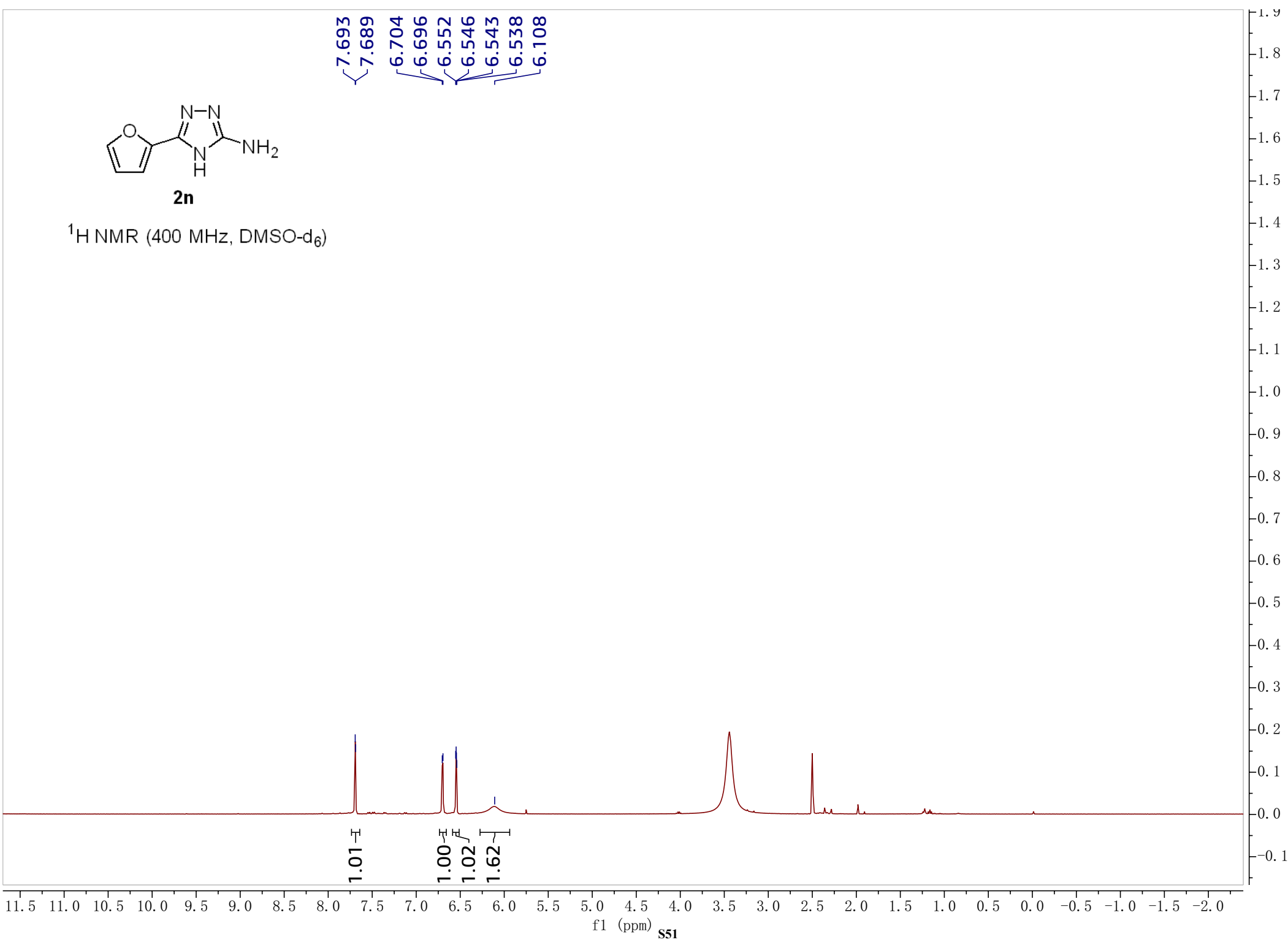




2n

¹H NMR (400 MHz, DMSO-d₆)

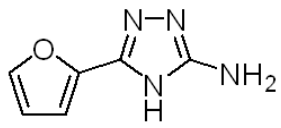
7.693
7.689
6.704
6.696
6.552
6.546
6.543
6.538
6.108



1.01
1.00
1.02
1.62

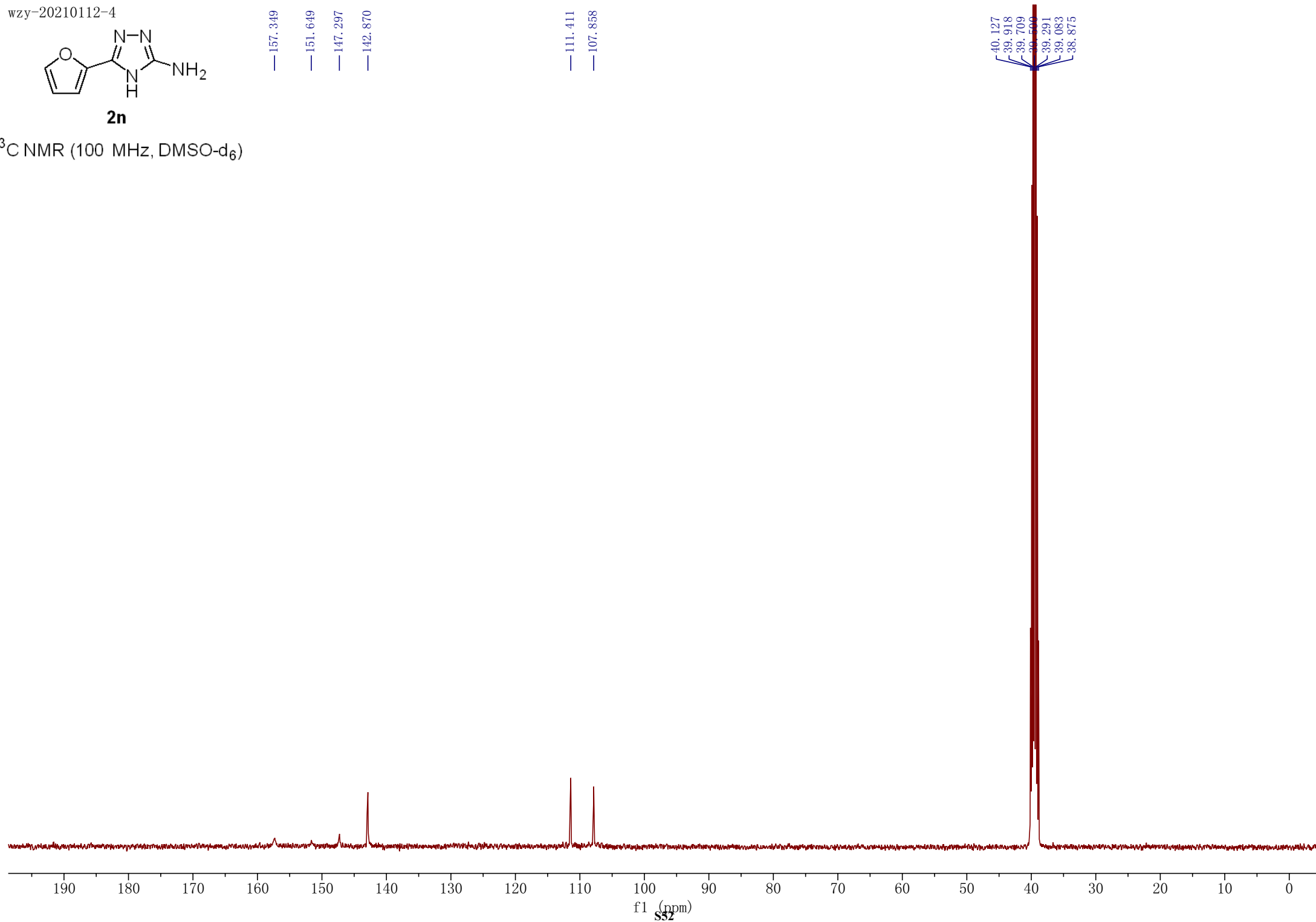
f1 (ppm) S51

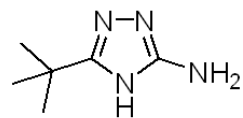
wzy-20210112-4



2n

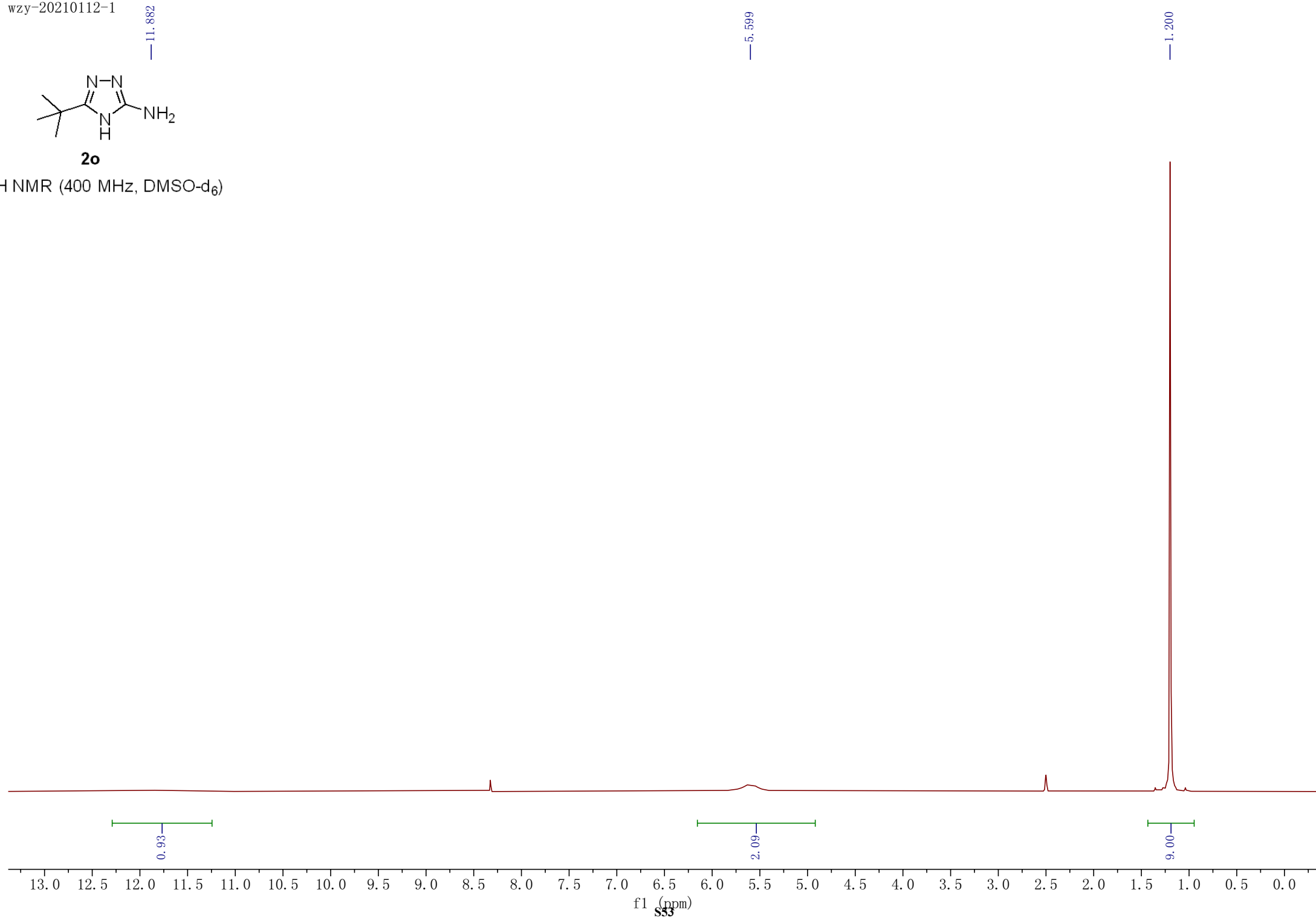
^{13}C NMR (100 MHz, DMSO- d_6)



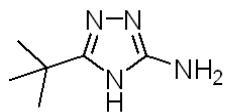


2o

¹H NMR (400 MHz, DMSO-d₆)



wzy-20210112-1



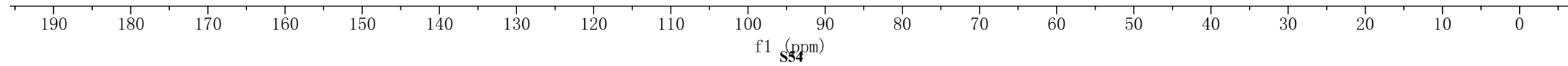
2o

^{13}C NMR (100 MHz, DMSO- d_6)

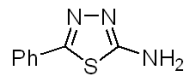
— 164.82

— 158.08

40.12
39.92
39.71
39.50
39.29
39.08
38.87
32.00
29.34



wzy-0827

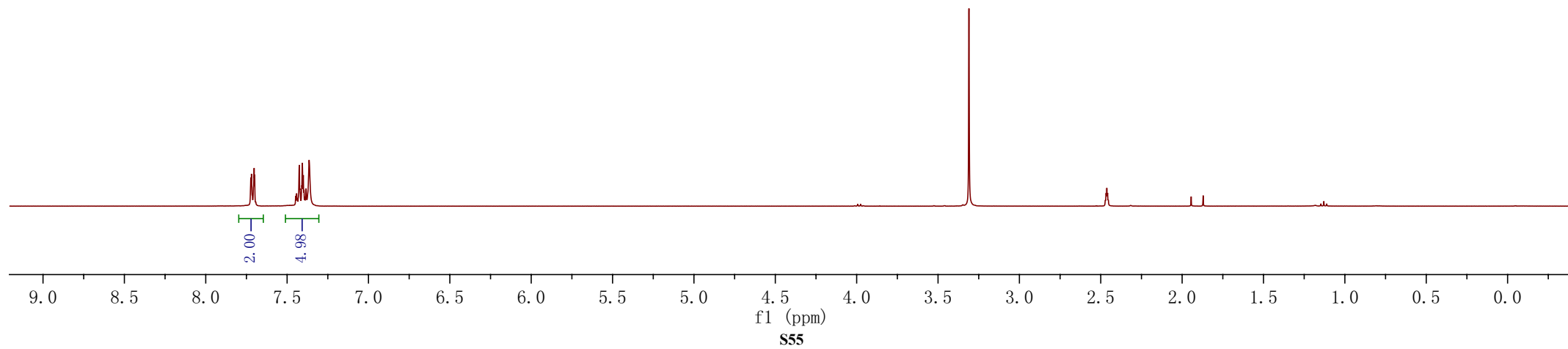


3a

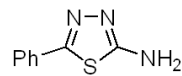
¹H NMR (400 MHz, DMSO-d₆)

7.723
7.719
7.714
7.703
7.699
7.447
7.442
7.437
7.425
7.422
7.410
7.407
7.400
7.397
7.391
7.384
7.365

3.310



wzy-0827



3a

^{13}C NMR (100 MHz, DMSO- d_6)

168.51

156.36

130.98

129.55

129.11

126.29

40.13

39.92

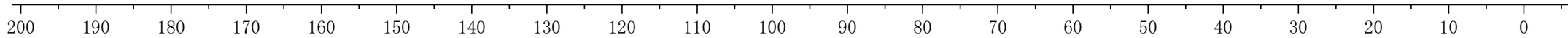
39.71

39.50

39.29

39.08

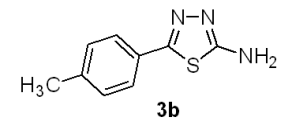
38.87



f1 (ppm)

S56

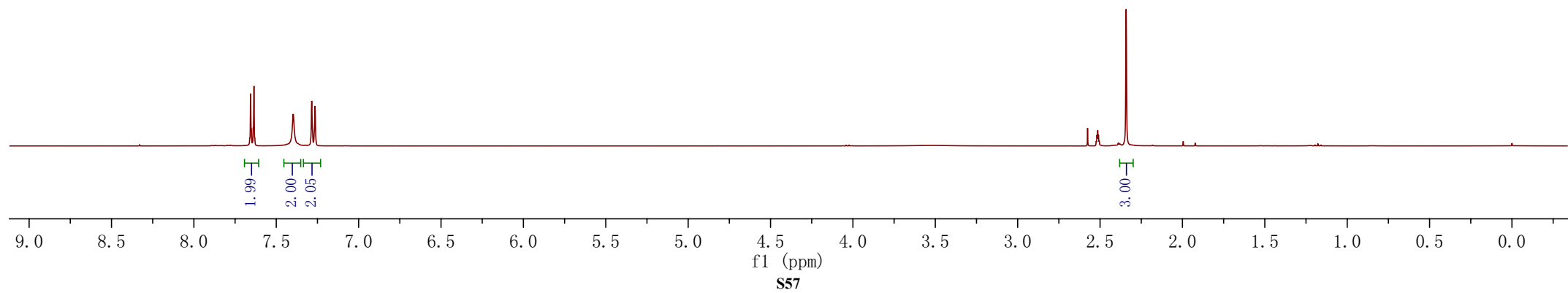
wzy-191114



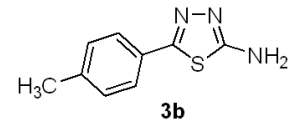
7.660
7.656
7.652
7.640
7.635
7.631
7.397
7.285
7.265

2.342

¹H NMR (400 MHz, DMSO-d₆)



wzy-191114



^{13}C NMR (100 MHz, DMSO- d_6)

— 168.21

— 156.47

— 139.32

— 129.66

— 128.30

— 126.25

39.92

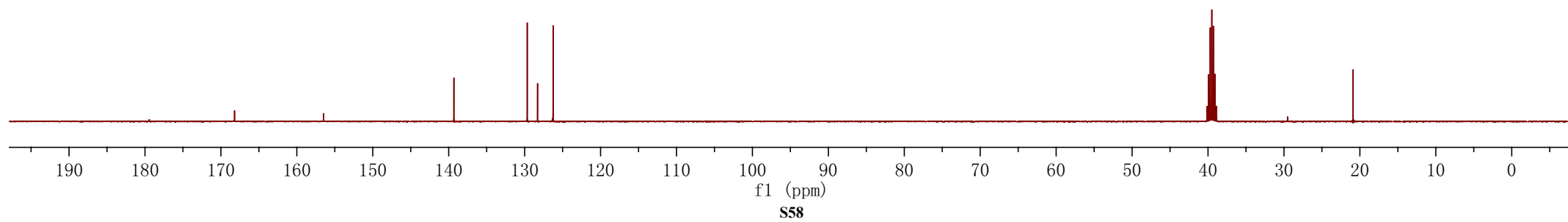
39.71

39.50

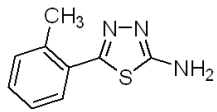
39.29

39.08

— 20.90

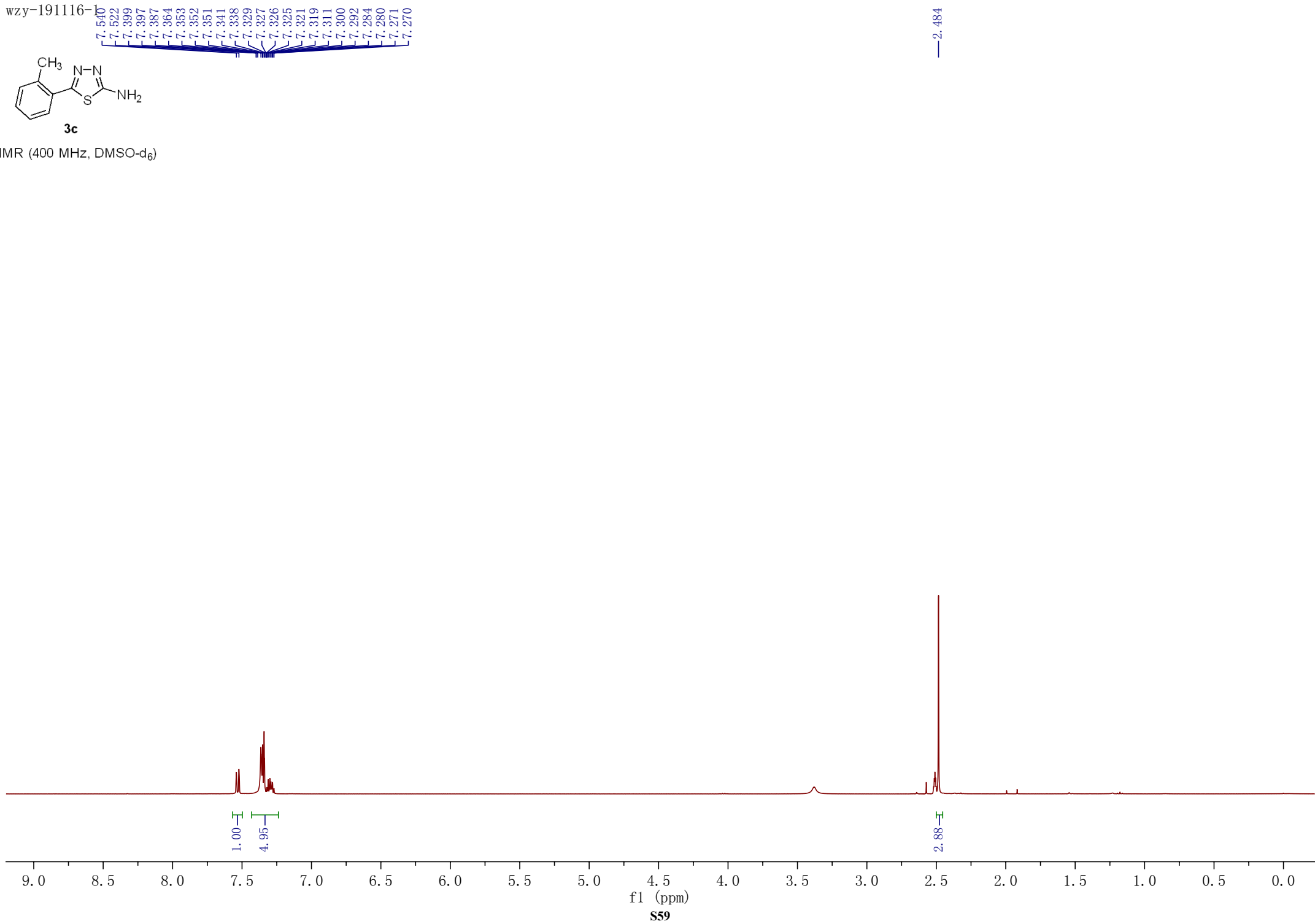


wzy-191116-1

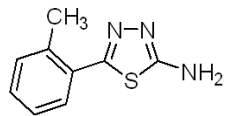


3c

¹H NMR (400 MHz, DMSO-d₆)



wzy-191116-1



3c

^{13}C NMR (100 MHz, DMSO- d_6)

168.79

155.65

135.86

131.37

129.96

129.75

129.14

126.28

39.92

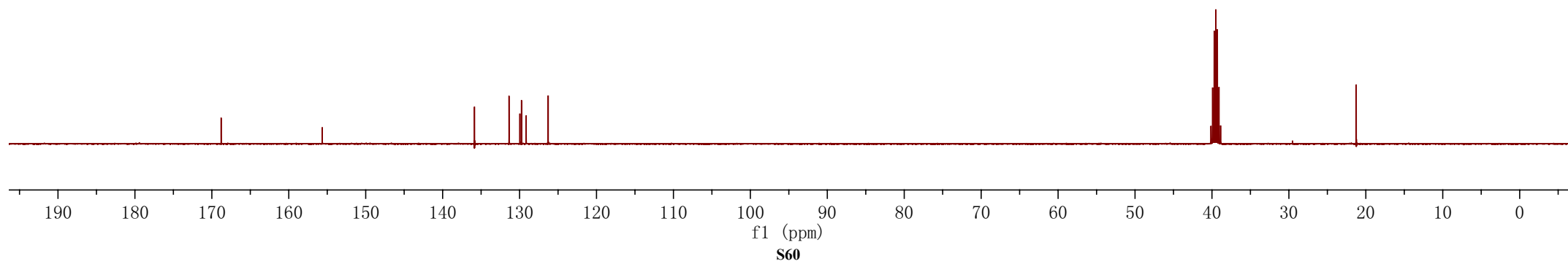
39.71

39.50

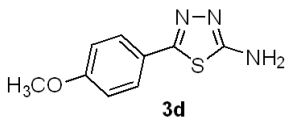
39.29

39.08

21.24



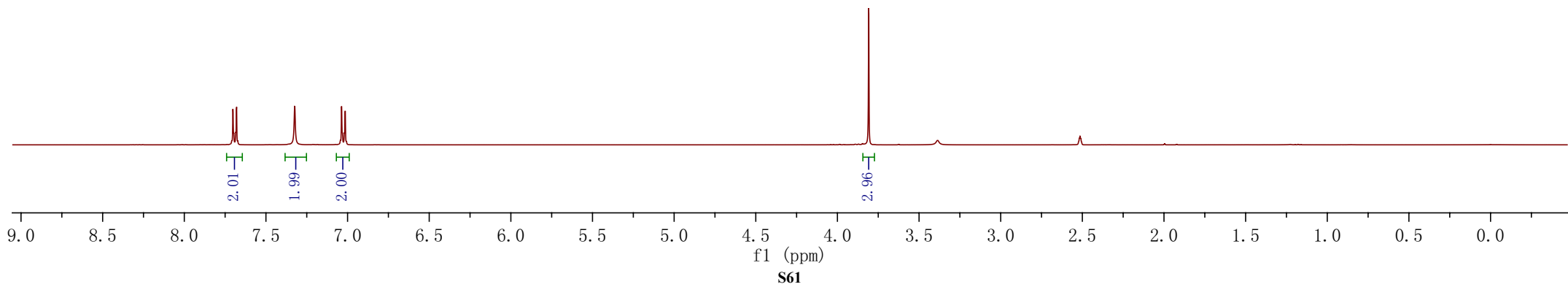
WZY-191127-1



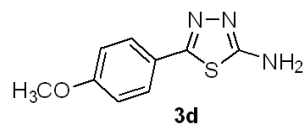
7.702
7.697
7.685
7.680
7.324
7.037
7.032
7.019
7.014

3.808

¹H NMR (400 MHz, DMSO-d₆)



WZY-191127-1



— 167.90

— 160.28

— 156.27

— 127.83

— 123.64

— 114.51

— 55.33

— 40.13

— 39.92

— 39.71

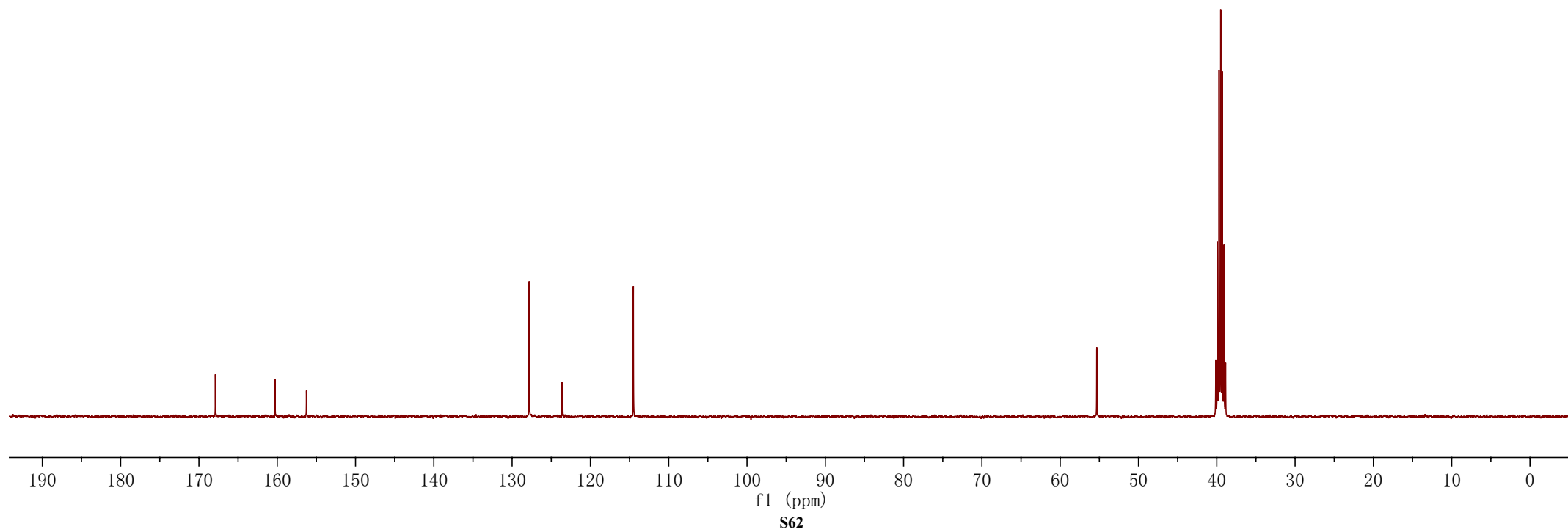
— 39.50

— 39.29

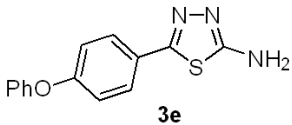
— 39.08

— 38.87

¹³C NMR (100 MHz, DMSO-d₆)

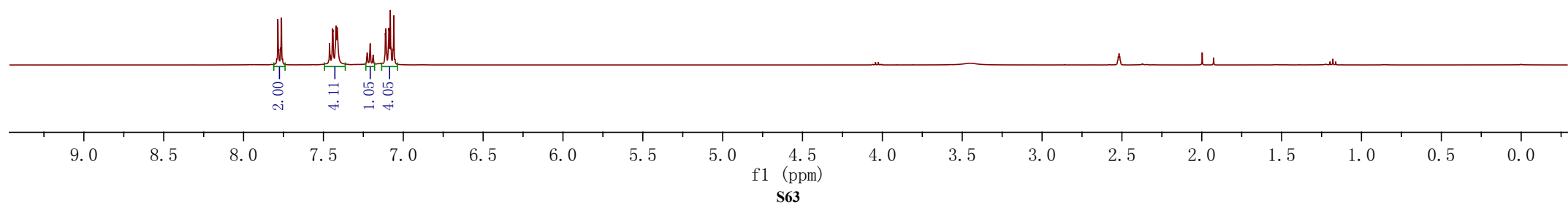


WZY-191127-2

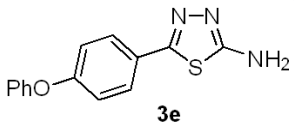


7.792
7.785
7.780
7.768
7.763
7.756
7.467
7.461
7.457
7.443
7.441
7.421
7.414
7.226
7.207
7.189
7.112
7.109
7.104
7.090
7.088
7.081
7.076
7.064
7.059
7.052

¹H NMR (400 MHz, DMSO-d₆)



WZY-191127-2



— 168.31

— 157.98

— 155.83

— 130.23

— 128.17

— 126.05

— 124.14

— 119.30

— 118.60

— 39.92

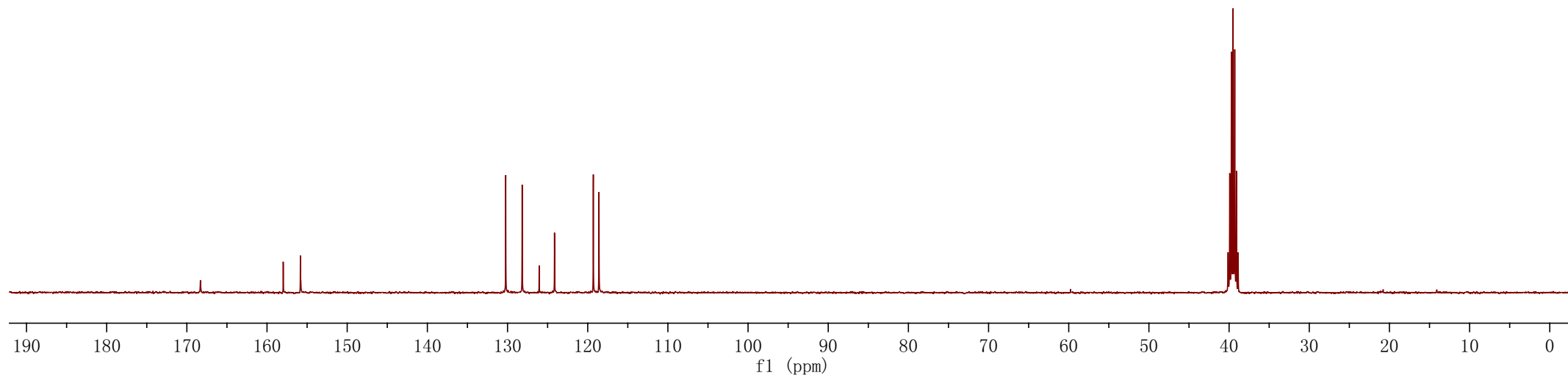
— 39.71

— 39.50

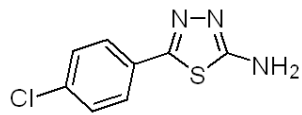
— 39.29

— 39.08

¹³C NMR (100 MHz, DMSO-d₆)



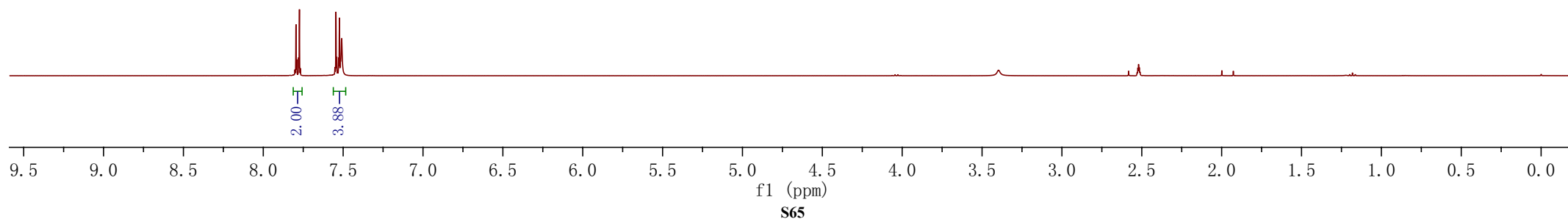
wzy-191116-2



3f

7.795
7.790
7.779
7.774
7.767
7.551
7.545
7.540
7.528
7.523
7.517
7.510

¹H NMR (400 MHz, DMSO-d₆)



wzy-191116-2

168.85

155.12

133.97

129.84

129.17

127.91

40.13

39.92

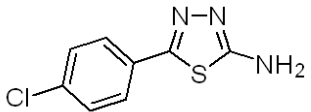
39.71

39.50

39.29

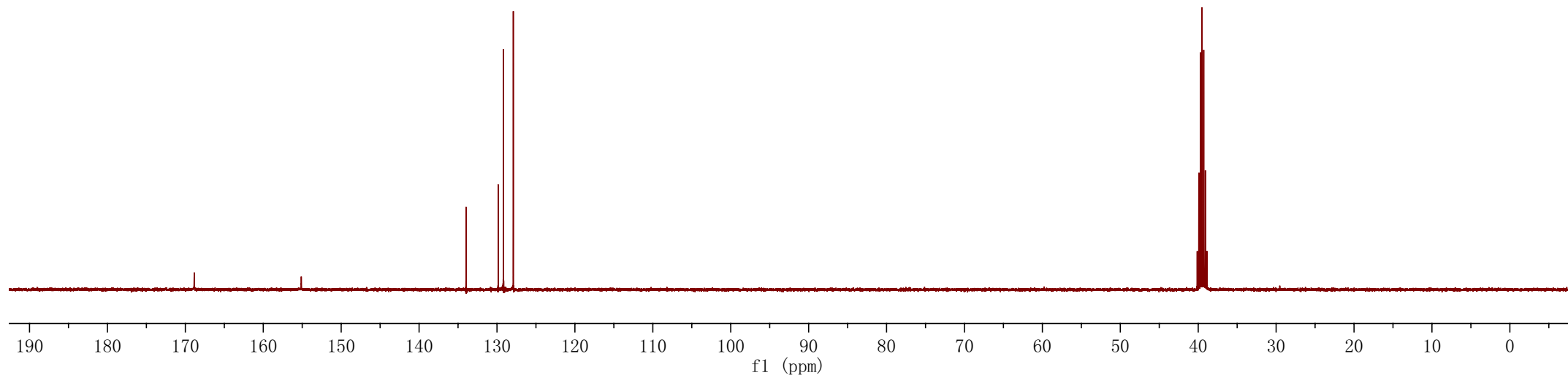
39.08

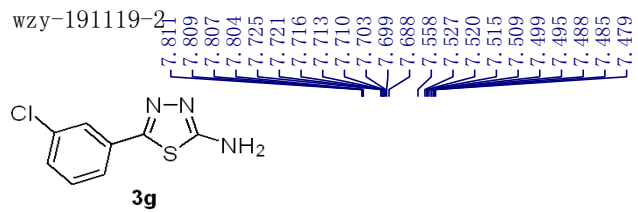
38.87



3f

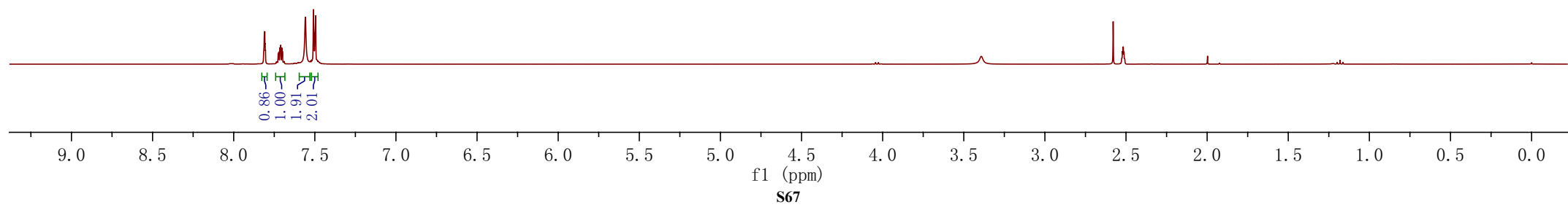
¹³C NMR (100 MHz, DMSO-d₆)



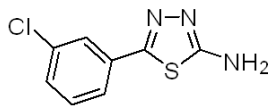


7.811
7.809
7.807
7.804
7.725
7.721
7.716
7.713
7.710
7.703
7.699
7.688
7.558
7.527
7.520
7.515
7.509
7.499
7.495
7.488
7.485
7.479

¹H NMR (400 MHz, DMSO-d₆)



wzy-191119-2



3g

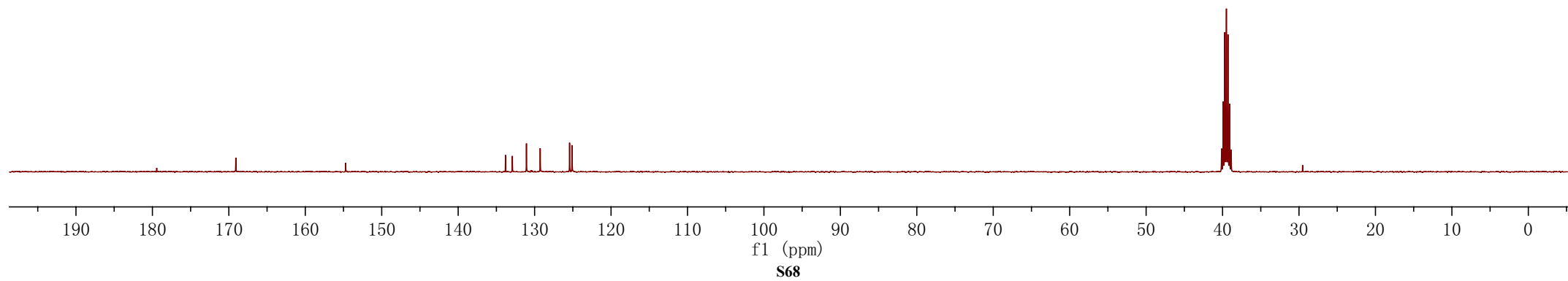
^{13}C NMR (100 MHz, DMSO- d_6)

— 169.09

— 154.72

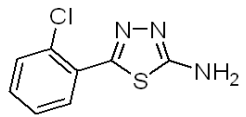
— 133.81
— 132.91
— 131.07
— 129.27
— 125.42
— 125.10

— 40.13
— 39.92
— 39.71
— 39.50
— 39.29
— 39.08
— 38.87



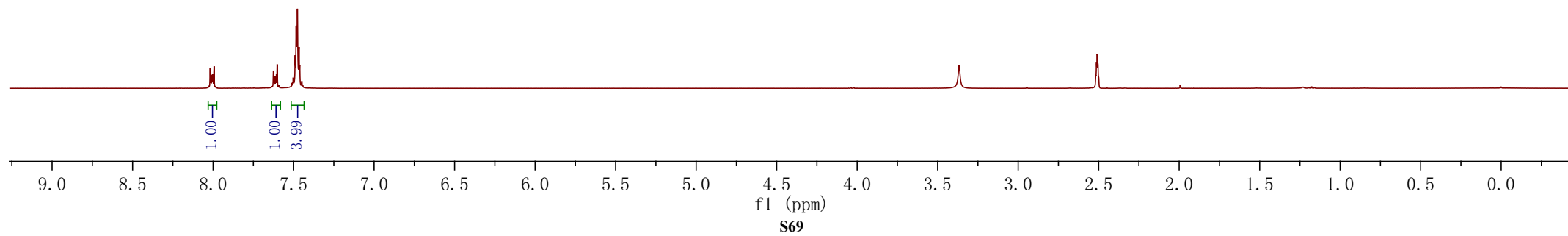
wzy-191119-1

8.018
8.012
8.008
8.003
8.001
7.994
7.625
7.619
7.617
7.611
7.607
7.602
7.503
7.490
7.484
7.476
7.466
7.462

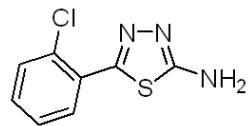


3h

¹H NMR (400 MHz, DMSO-d₆)



wzy-191119-1



3h

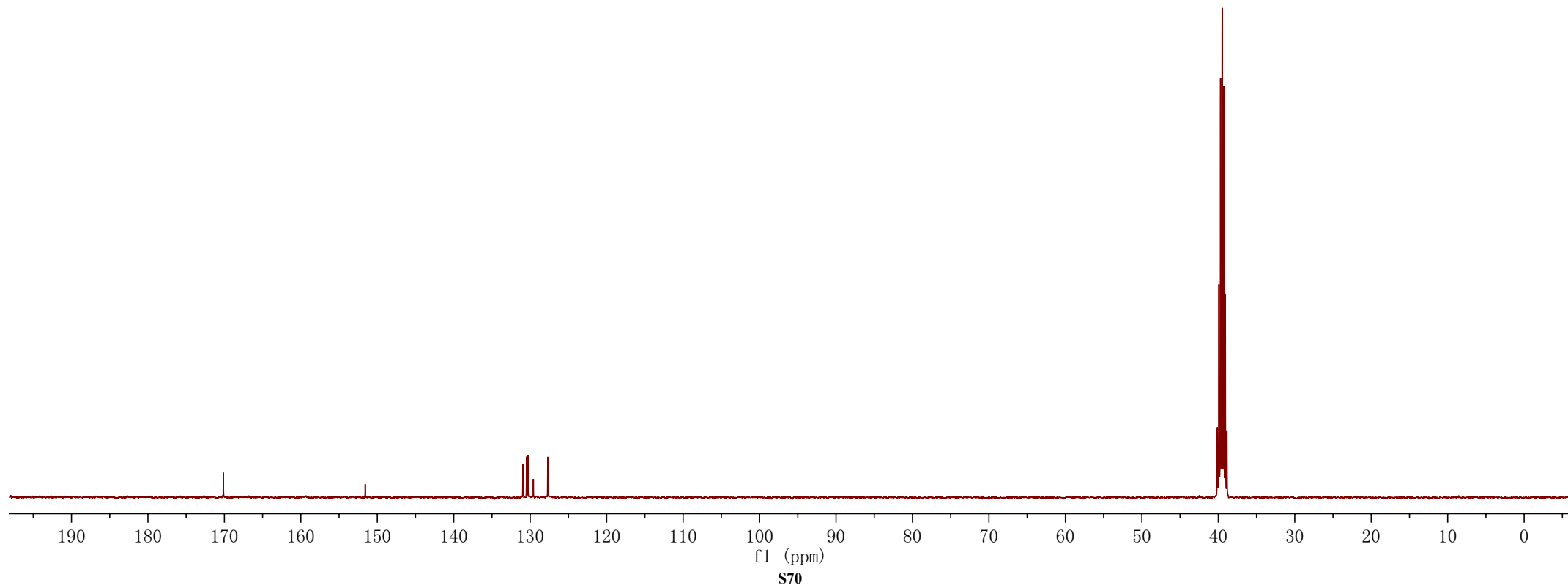
^{13}C NMR (100 MHz, DMSO- d_6)

170.13

151.58

130.96
130.49
130.42
130.30
129.58
127.71

39.92
39.71
39.50
39.29
39.08



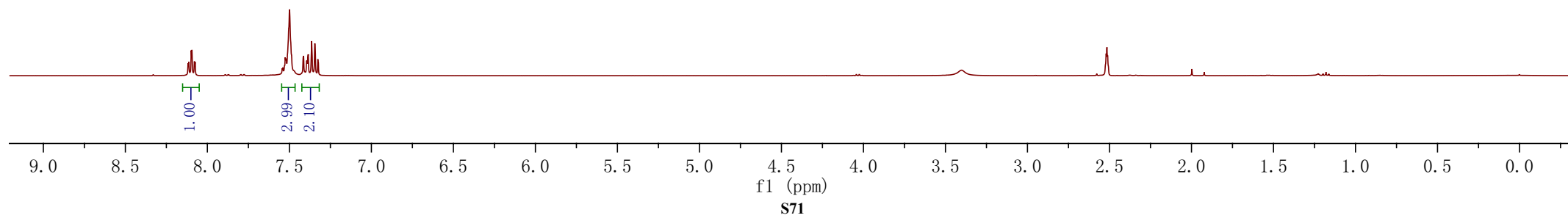
WZY-191202-1

8.117
8.113
8.098
8.094
8.079
8.075
7.544
7.539
7.530
7.525
7.522
7.519
7.499
7.487
7.415
7.414
7.395
7.393
7.385
7.364
7.344
7.326
7.324

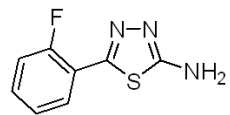


3i

^1H NMR (400 MHz, DMSO- d_6)



WZY-191202-1



3i

^{13}C NMR (100 MHz, DMSO- d_6)

169.96

159.11

156.64

148.46

131.42

131.34

127.67

125.19

125.16

118.76

118.64

116.45

116.23

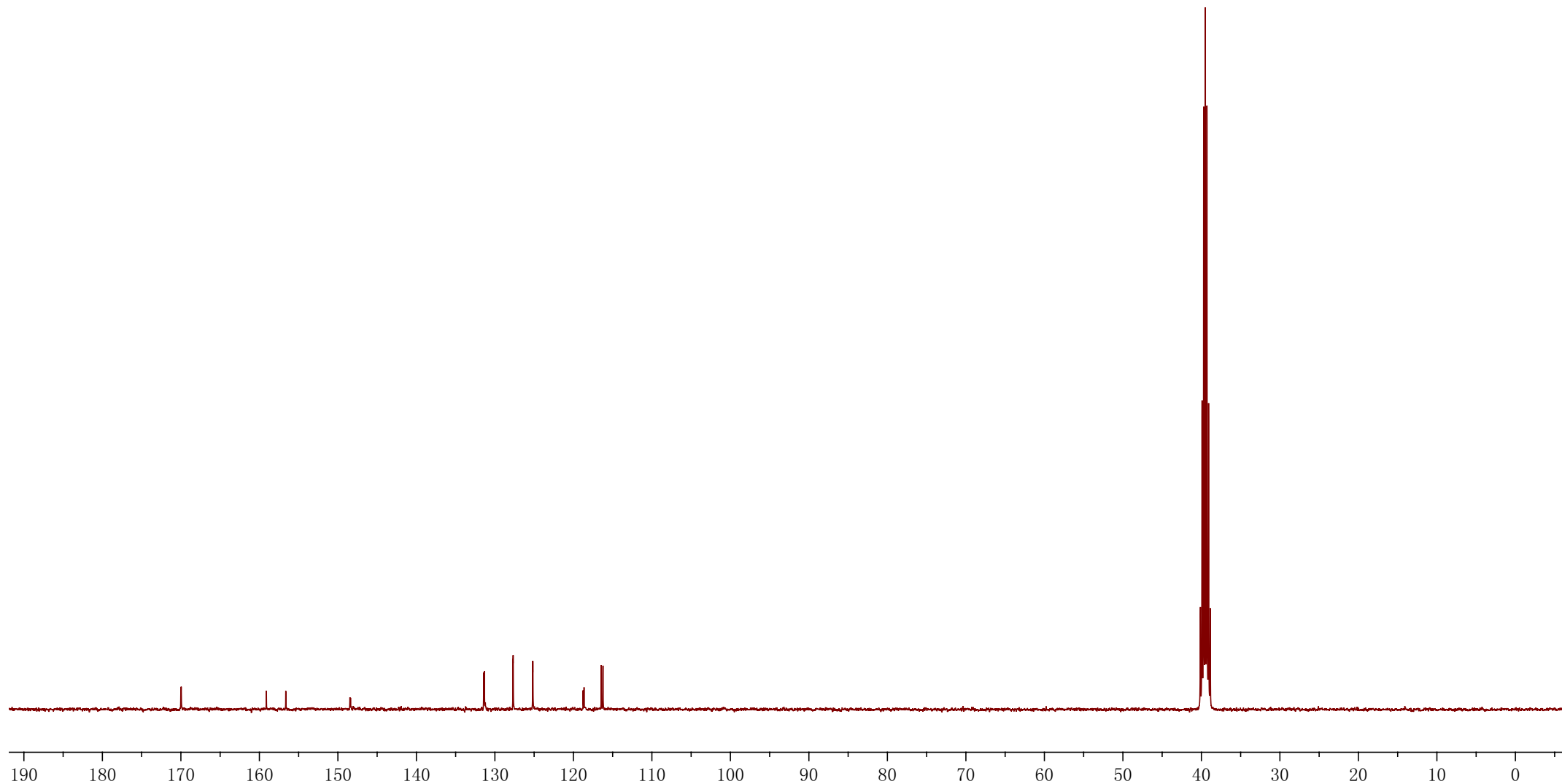
39.92

39.71

39.50

39.29

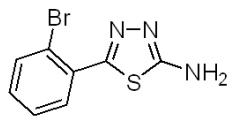
39.08



f1 (ppm)

S72

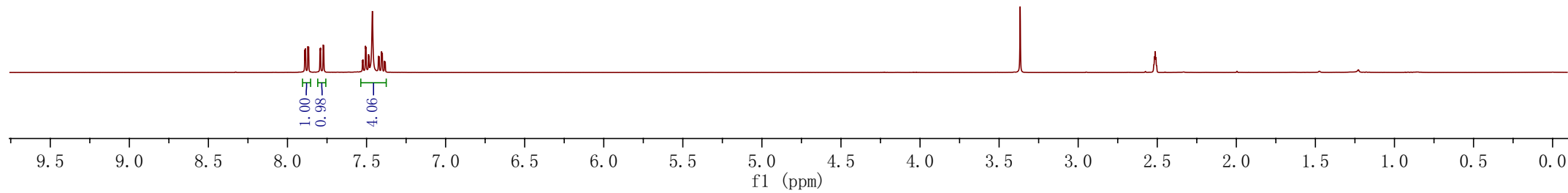
wzy-191202-2



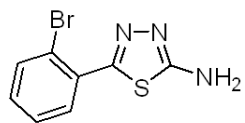
3j

¹H NMR (400 MHz, DMSO-d₆)

7.890
7.886
7.871
7.866
7.794
7.791
7.774
7.771
7.525
7.523
7.506
7.504
7.487
7.485
7.463
7.425
7.420
7.405
7.401
7.386
7.382



wzy-191202-2



169.99

153.05

133.75

131.63

131.21

128.11

120.91

39.92

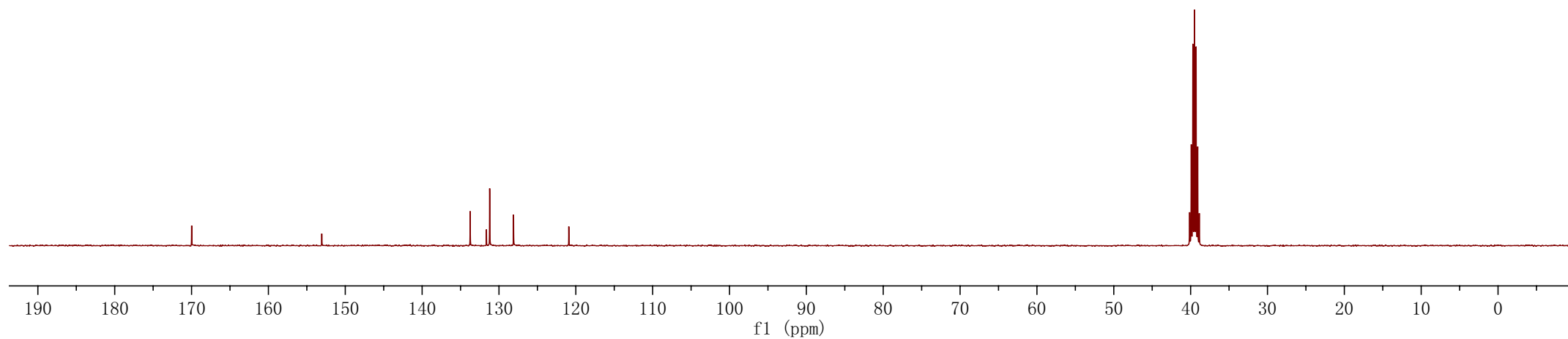
39.71

39.50

39.29

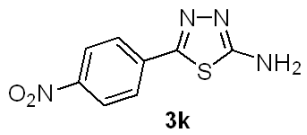
39.08

^{13}C NMR (100 MHz, DMSO- d_6)

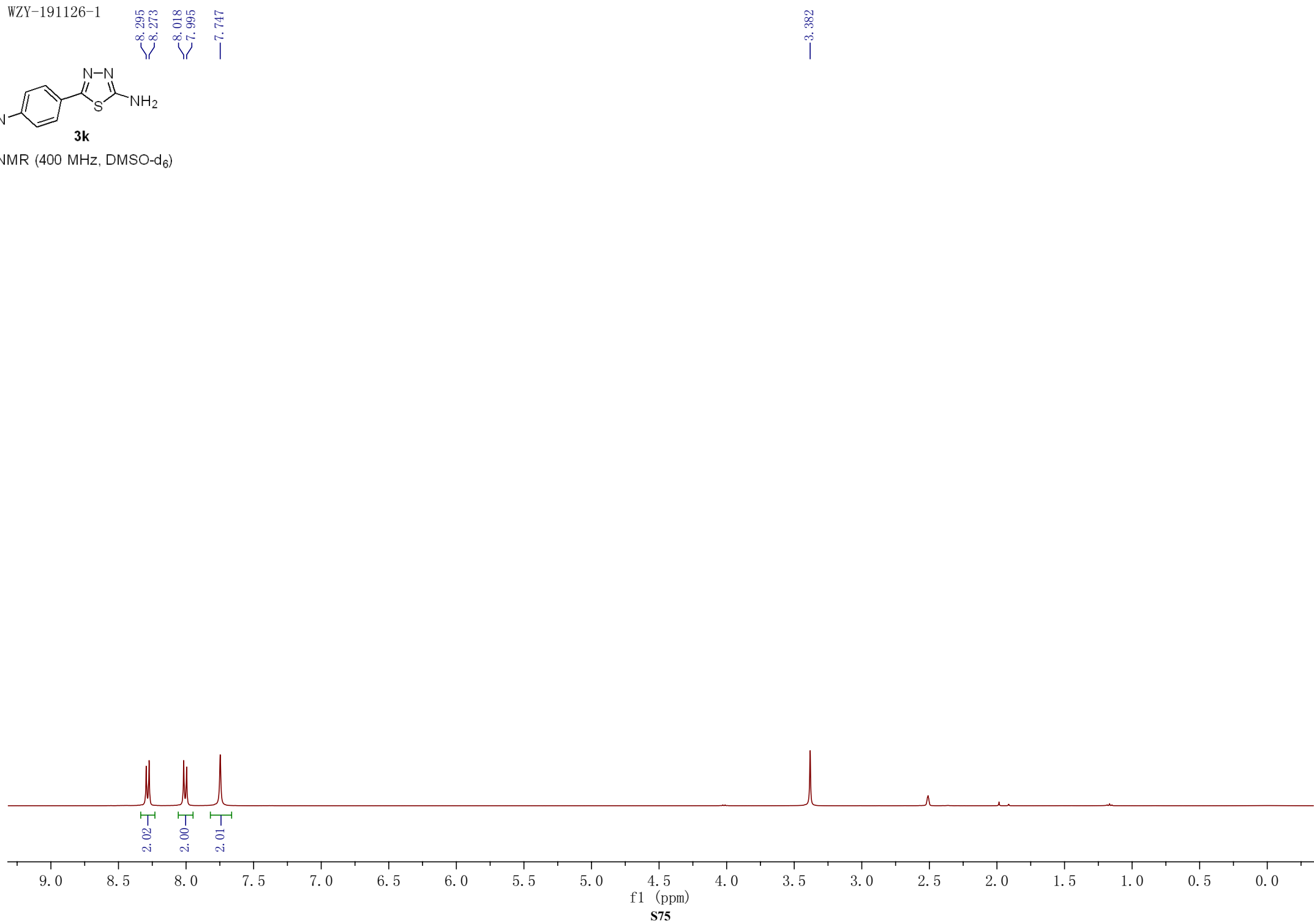


WZY-191126-1

8.295
8.273
8.018
7.995
7.747



¹H NMR (400 MHz, DMSO-d₆)



WZY-191126-1

170.04

154.10

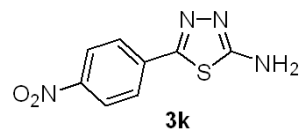
147.36

136.82

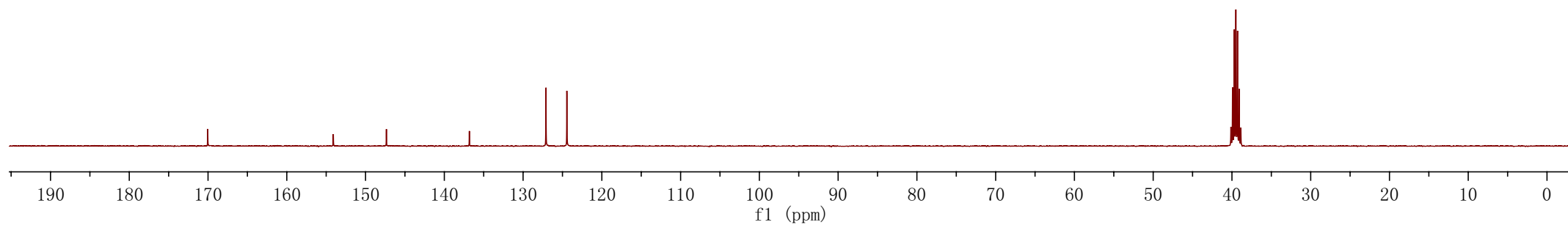
127.10

124.44

39.92
39.71
39.50
39.29
39.08

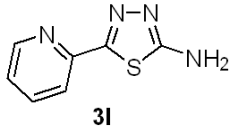


^{13}C NMR (100 MHz, DMSO- d_6)

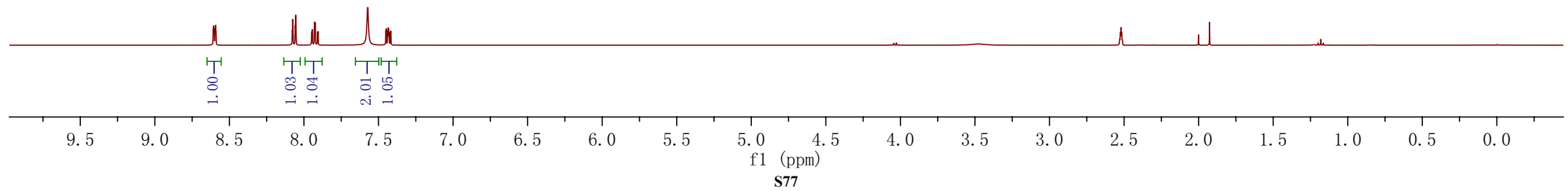


wzy-191219

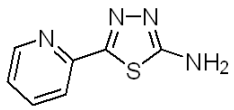
8.608
8.606
8.605
8.602
8.596
8.593
8.076
8.056
8.053
7.929
7.925
7.873
7.451
7.448
7.439
7.436
7.432
7.429
7.420
7.417



¹H NMR (400 MHz, DMSO-d₆)



wzy-191219



3I

^{13}C NMR (100 MHz, DMSO- d_6)

— 170.10

— 158.46

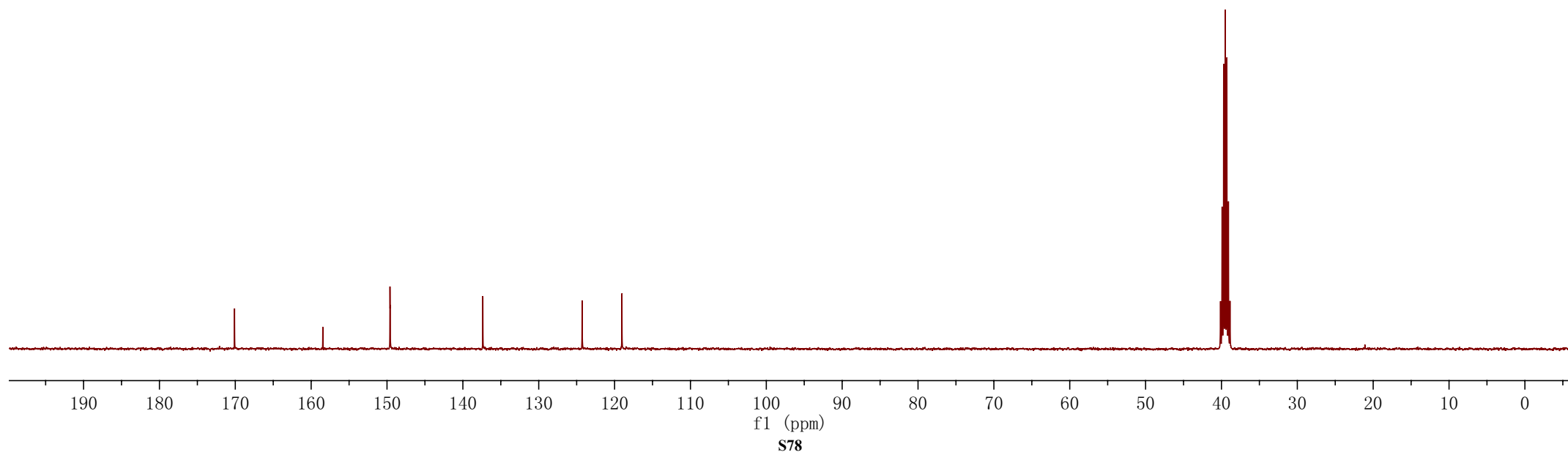
— 149.61

— 137.37

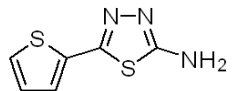
— 124.28

— 119.03

39.92
39.71
39.50
39.29
39.08



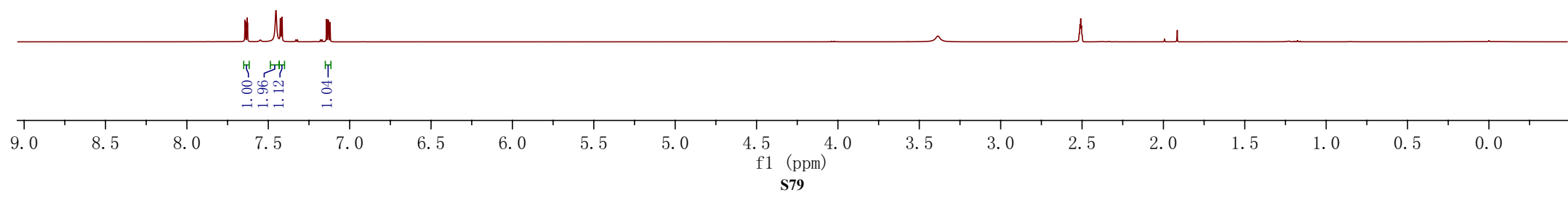
wzy-191213-1



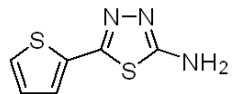
3m

¹H NMR (400 MHz, DMSO-d₆)

7.642
7.640
7.630
7.628
7.453
7.426
7.424
7.417
7.415
7.142
7.133
7.129
7.120



wzy-191213-1



3m

¹³C NMR (100 MHz, DMSO-d₆)

168.11

150.63

133.27

127.99

127.62

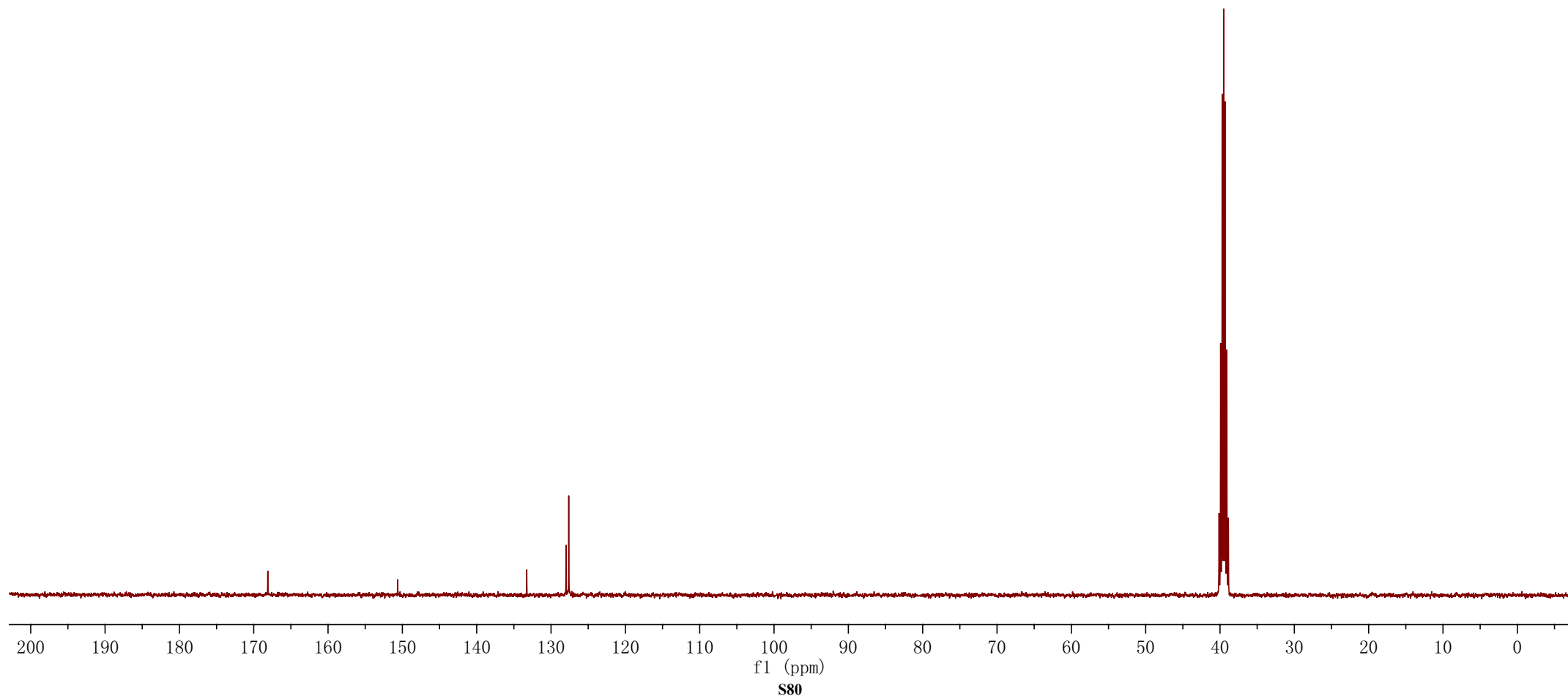
39.92

39.71

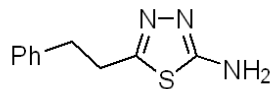
39.50

39.29

39.08



wzy-191209-2

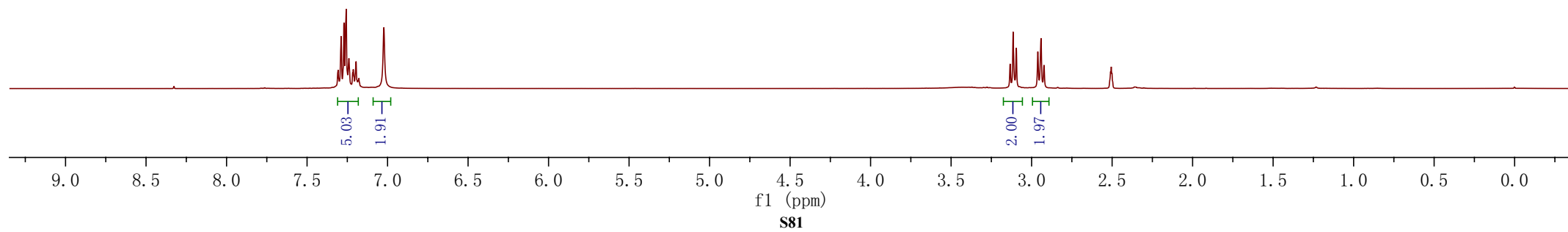


3n

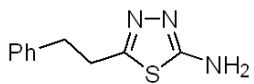
¹H NMR (400 MHz, DMSO-d₆)

7.307
7.289
7.271
7.257
7.240
7.216
7.213
7.196
7.189
7.182
7.178
7.023

3.133
3.115
3.095
2.961
2.942
2.923



wzy-191209-2



3n

¹³C NMR (100 MHz, DMSO-d₆)

— 168.27

— 157.43

— 140.30

— 128.48

— 128.34

— 126.19

40.13

39.92

39.71

39.50

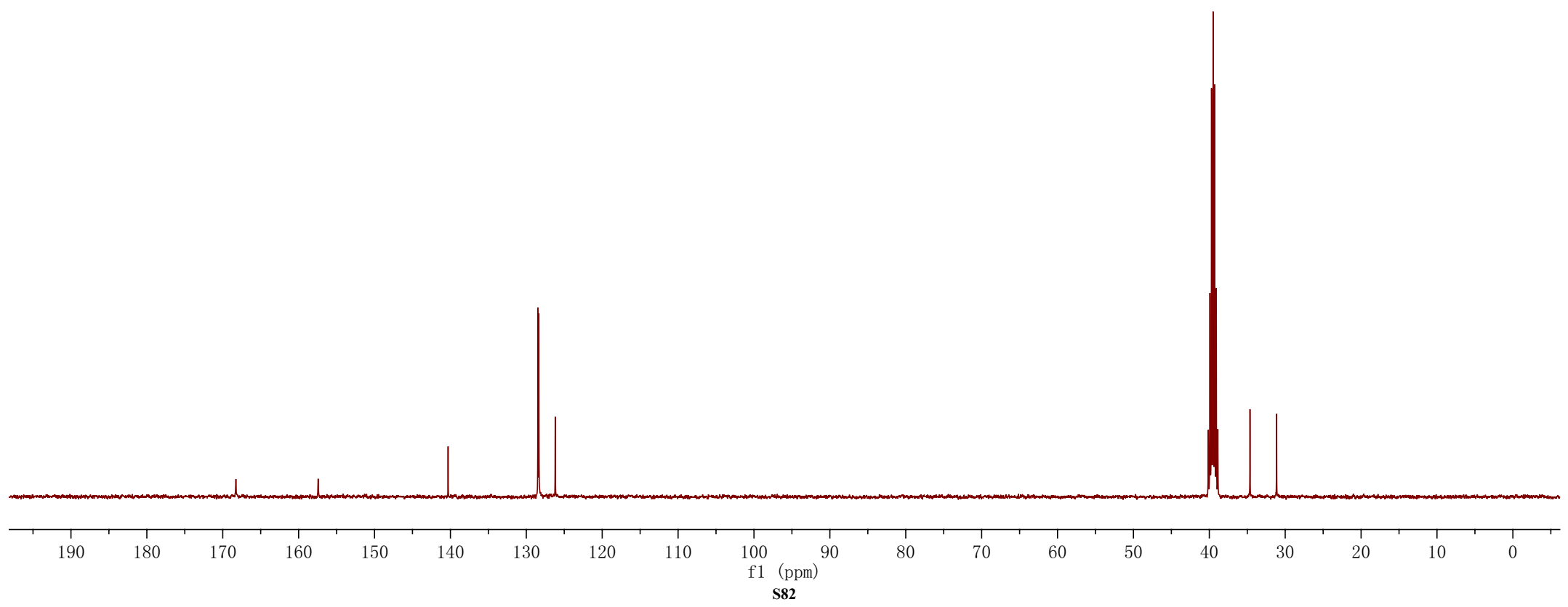
39.29

39.08

38.87

38.64

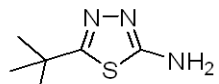
— 31.14



f1 (ppm)

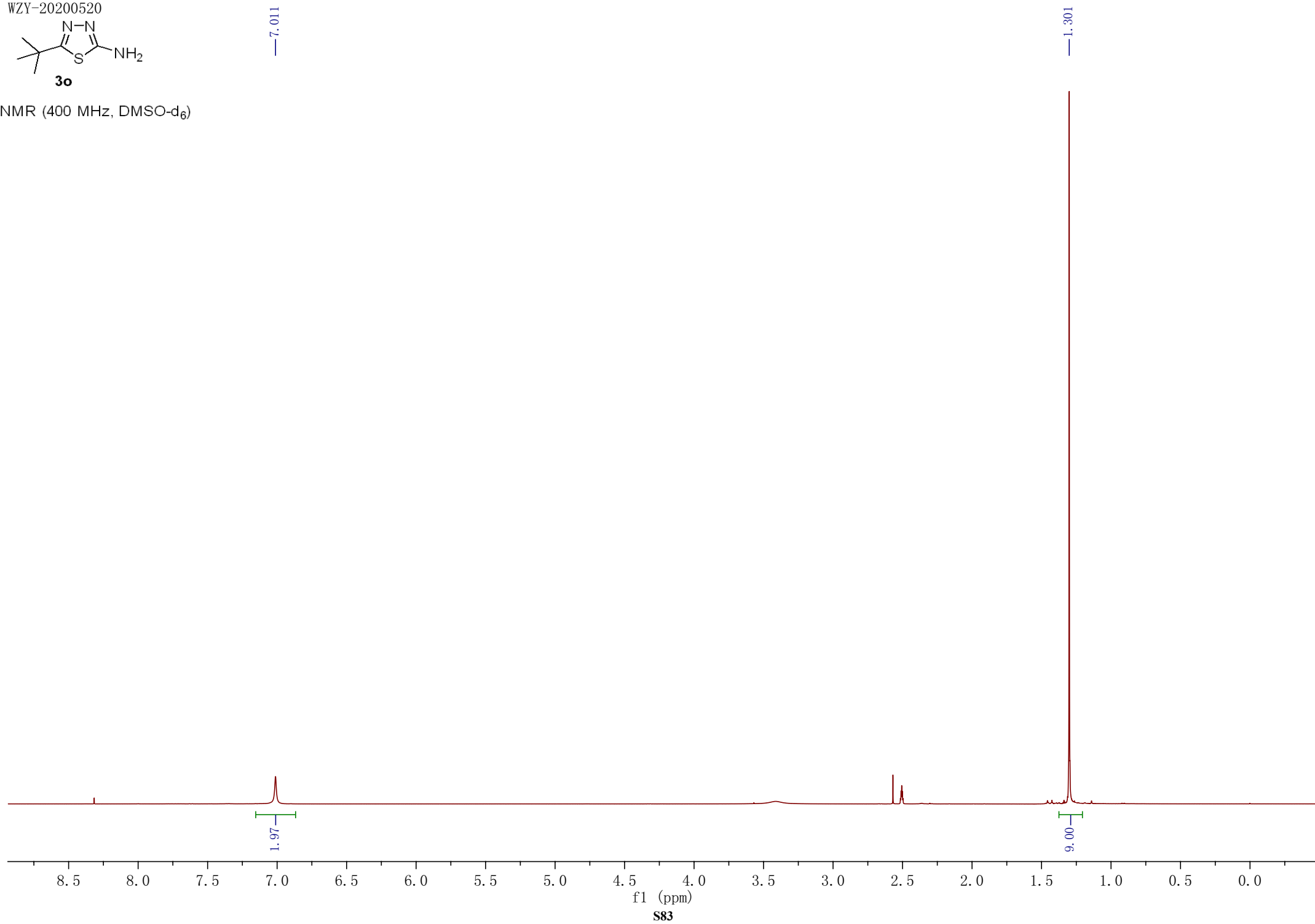
S82

WZY-20200520

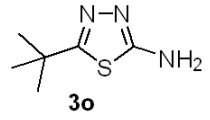


3o

¹H NMR (400 MHz, DMSO-d₆)



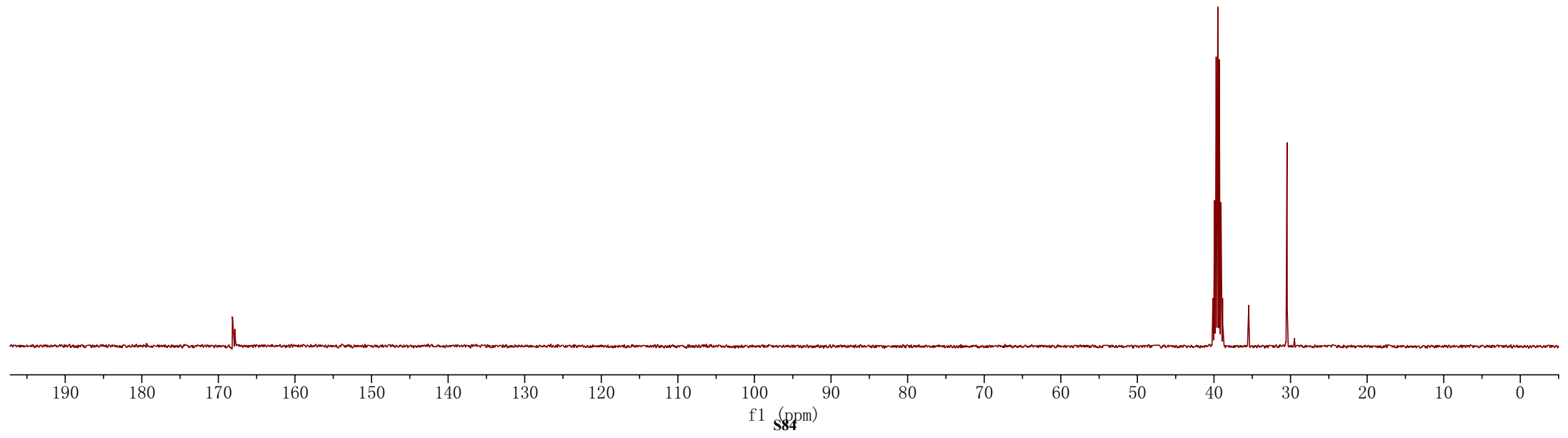
WZY-20200520



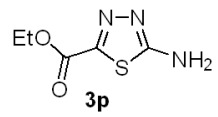
^{13}C NMR (100 MHz, DMSO- d_6)

168.16
167.85

40.13
39.92
39.71
39.50
39.29
39.09
38.88
35.45
30.46



WZY-20200521

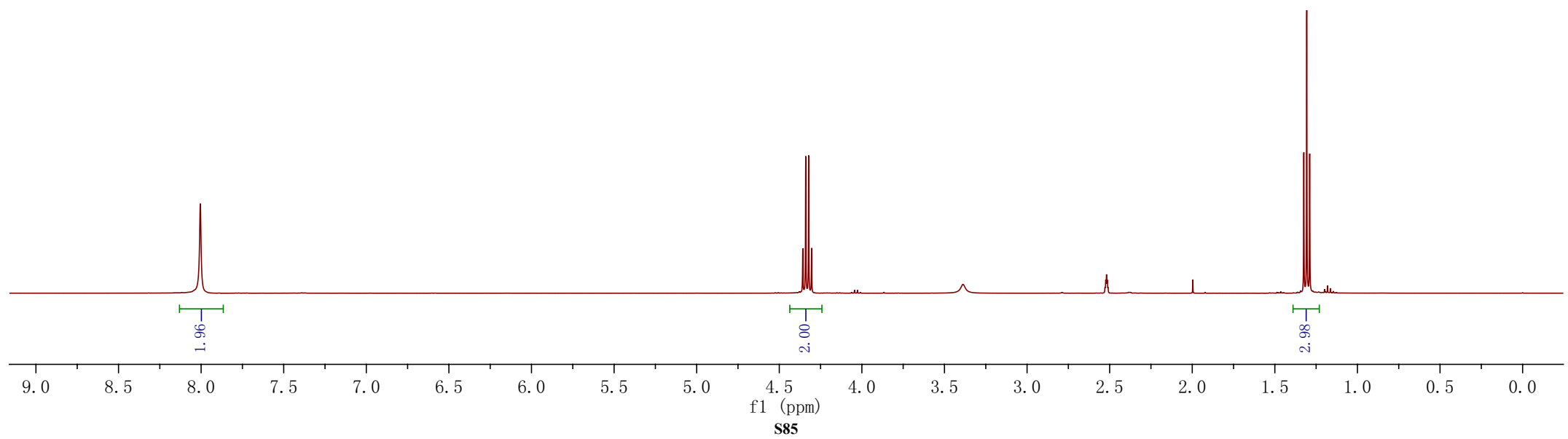


8.005

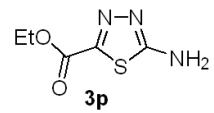
4.358
4.340
4.322
4.304

1.325
1.307
1.289

¹H NMR (400 MHz, DMSO-d₆)



WZY-20200521



— 172.35

— 158.89

— 147.61

— 61.80

39.92

39.71

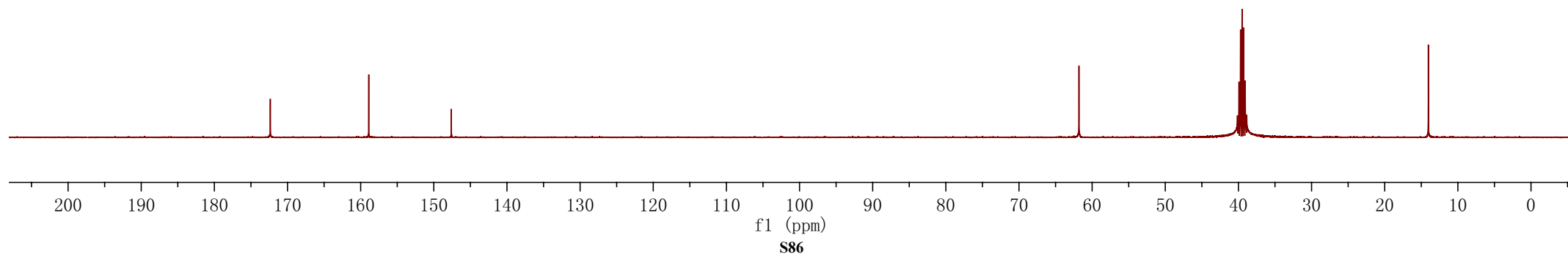
39.50

39.29

39.08

— 14.03

^{13}C NMR (100 MHz, DMSO- d_6)

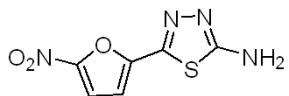


wzy-20201026-5

7.913
7.901
7.844
7.834

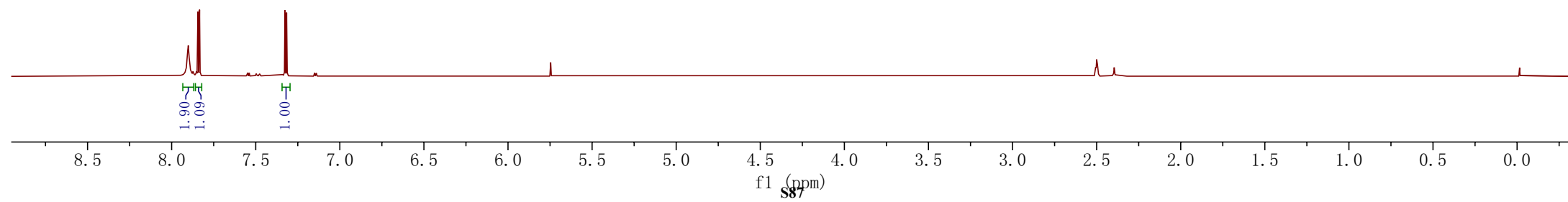
7.327
7.316

2.505
2.500
2.495

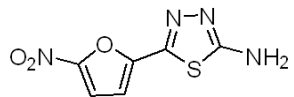


furidiazine

¹H NMR (400 MHz, DMSO-d₆)



wzy-20201026-5



furidiazine

^{13}C NMR (100 MHz, DMSO- d_6)

170.08

151.34

147.86

144.48

115.18

111.67

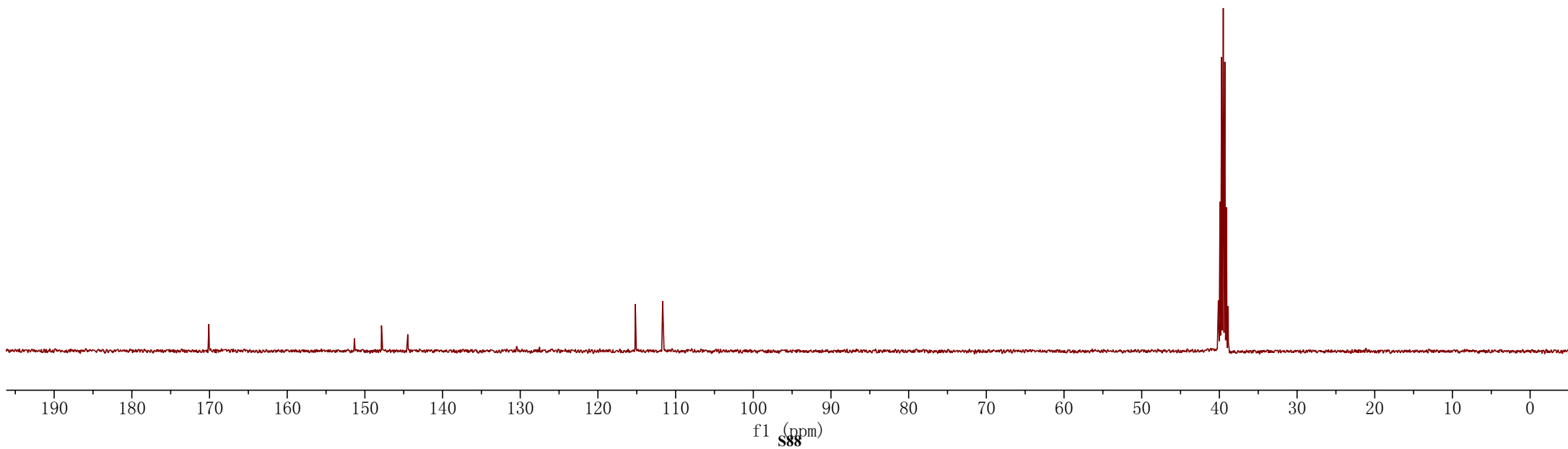
39.92

39.71

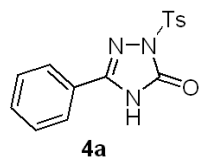
39.50

39.30

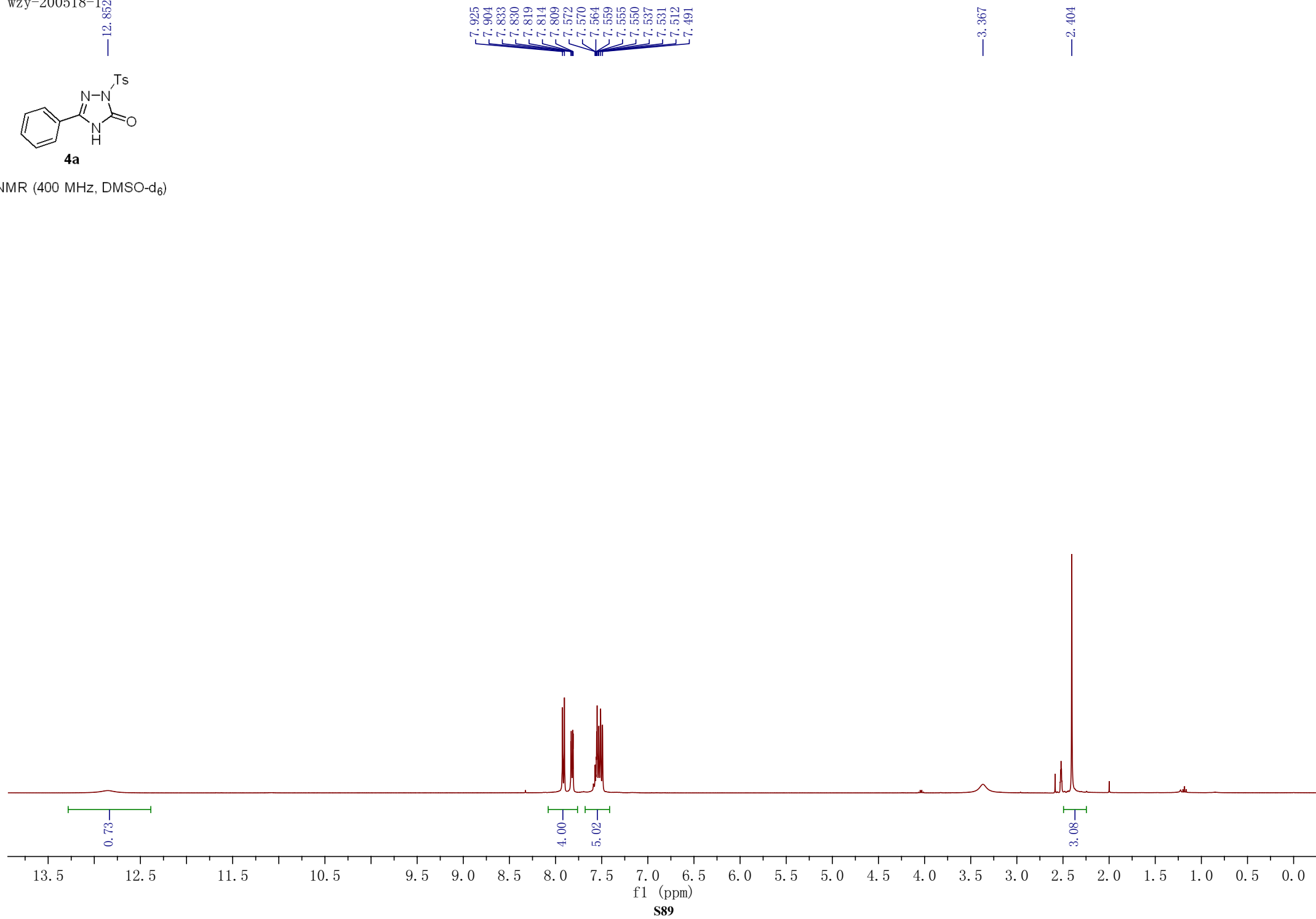
39.09



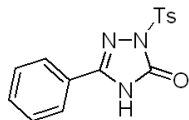
wzy-200518-1



¹H NMR (400 MHz, DMSO-d₆)



wzy-200518-1



4a

¹³C NMR (100 MHz, DMSO-d₆)

— 152.26

— 147.79

— 145.91

— 133.90

— 131.56

— 130.25

— 129.08

— 127.51

— 125.81

— 125.11

40.13

39.92

39.71

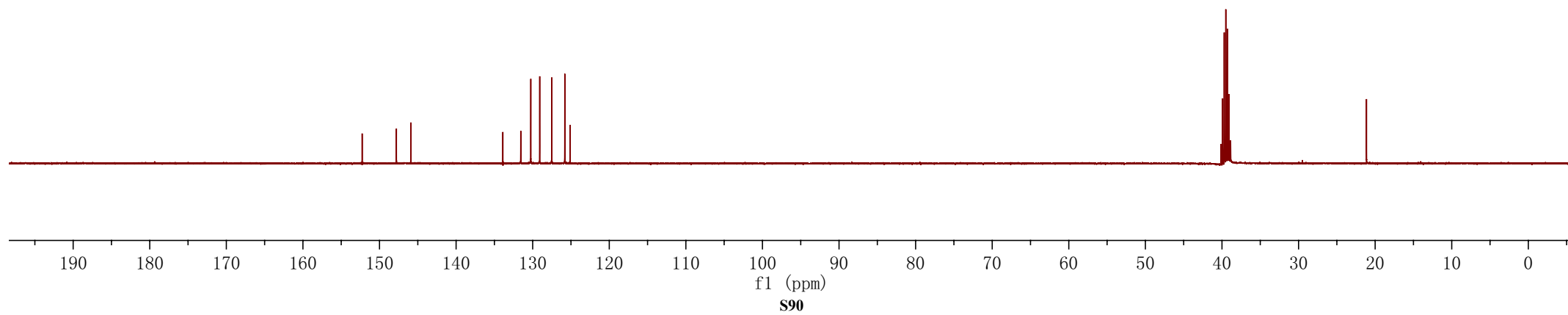
39.50

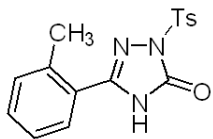
39.29

39.08

38.87

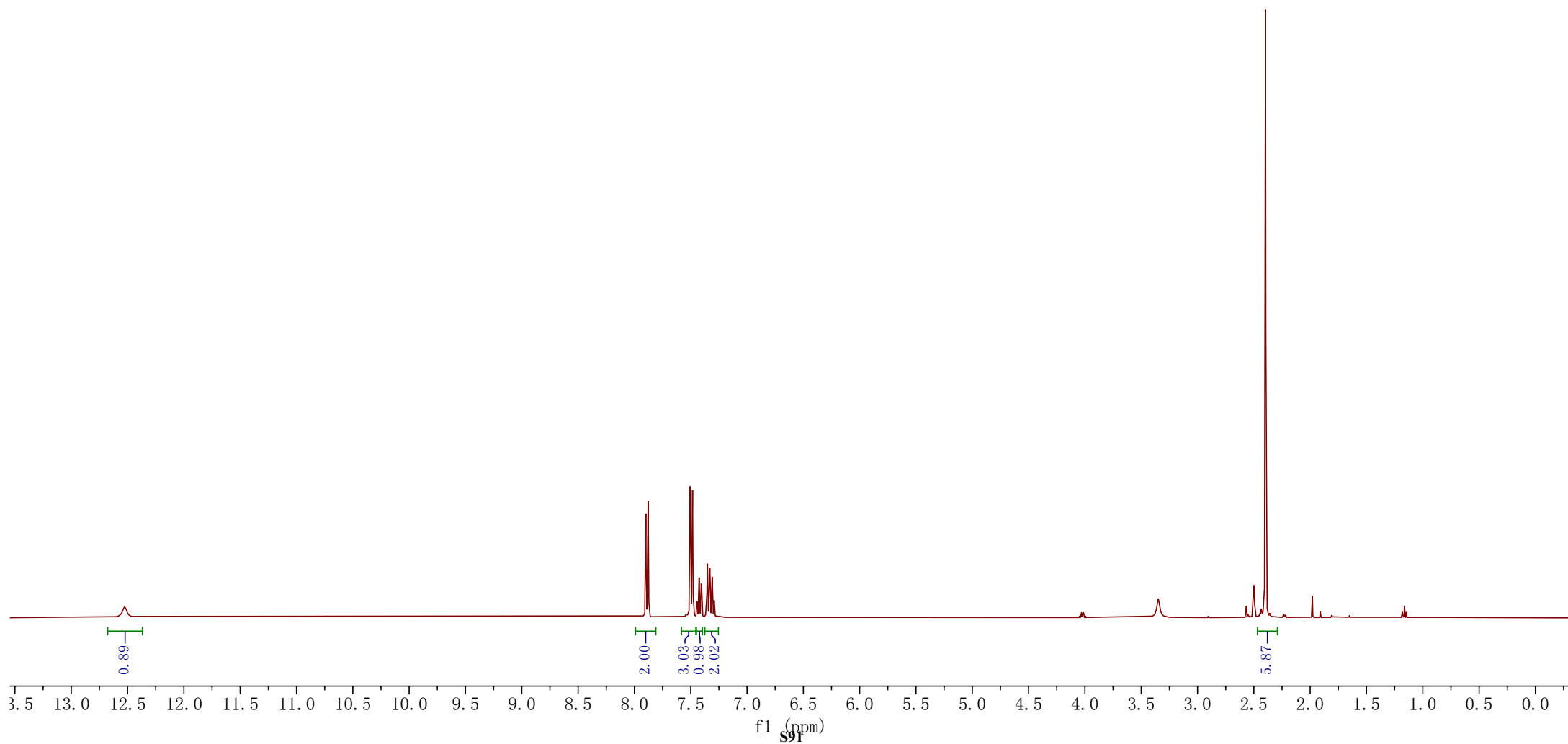
— 21.13



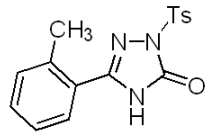


4b

¹H NMR (400 MHz, DMSO-d₆)



ZQI-20200922-1B



4b

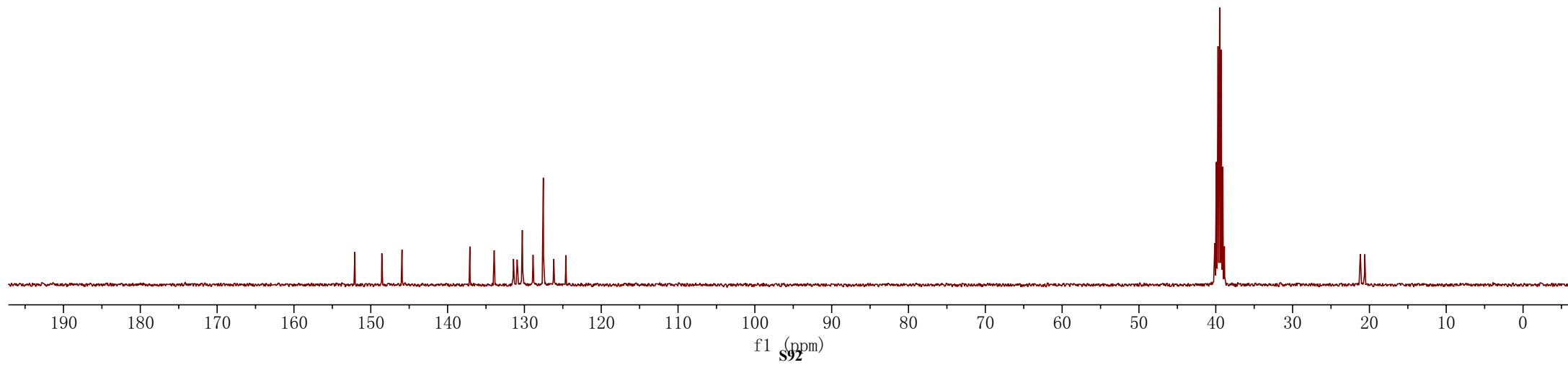
¹³C NMR (100 MHz, DMSO-d₆)

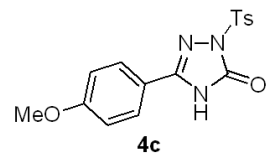
152.07
148.56
145.94

137.10
133.93
131.42
130.94
130.27
128.87
127.54
126.18
124.62

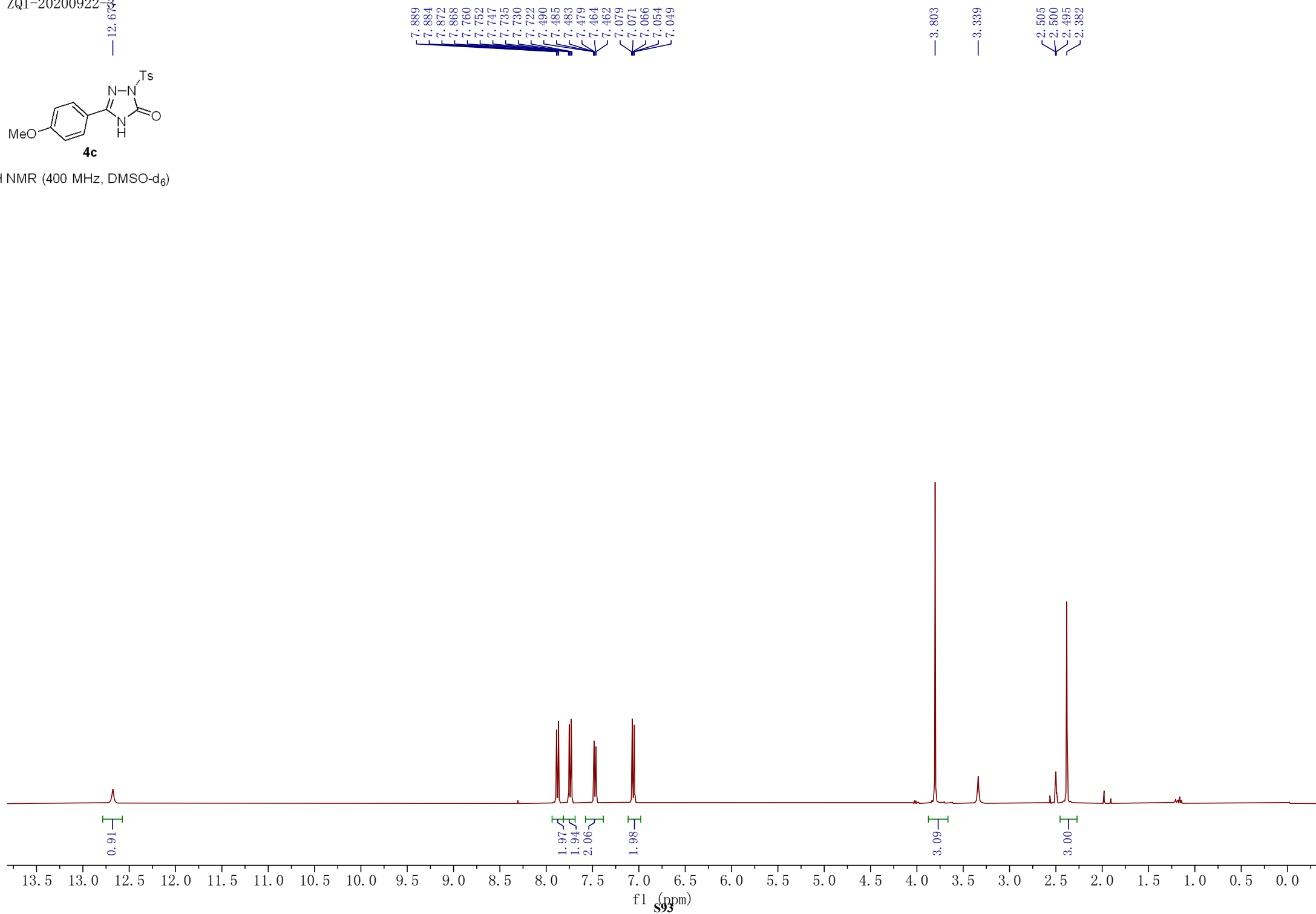
40.13
39.92
39.71
39.50
39.29
39.09
38.88

21.19
20.61

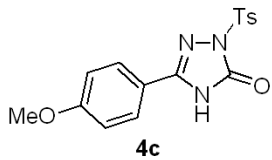




¹H NMR (400 MHz, DMSO-d₆)



ZQI-20200922-3



— 161.73

— 152.37

— 147.70

— 145.82

— 133.97

— 130.22

— 127.55

— 127.46

— 117.33

— 114.53

— 55.44

— 40.13

— 39.92

— 39.71

— 39.50

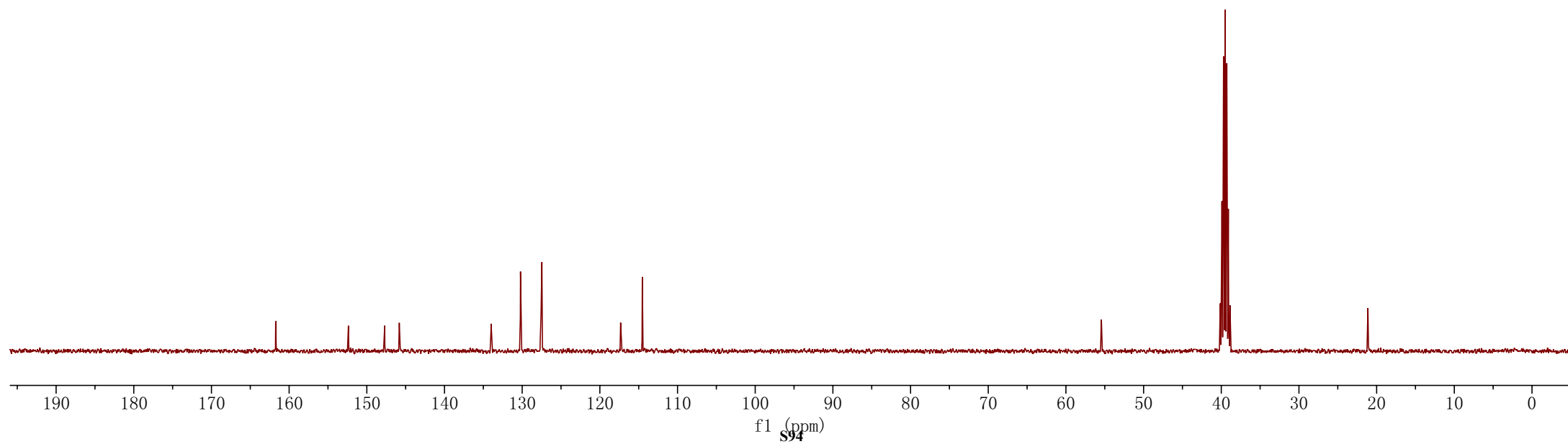
— 39.29

— 39.08

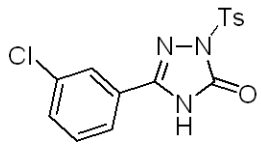
— 38.88

— 21.12

¹³C NMR (100 MHz, DMSO-d₆)

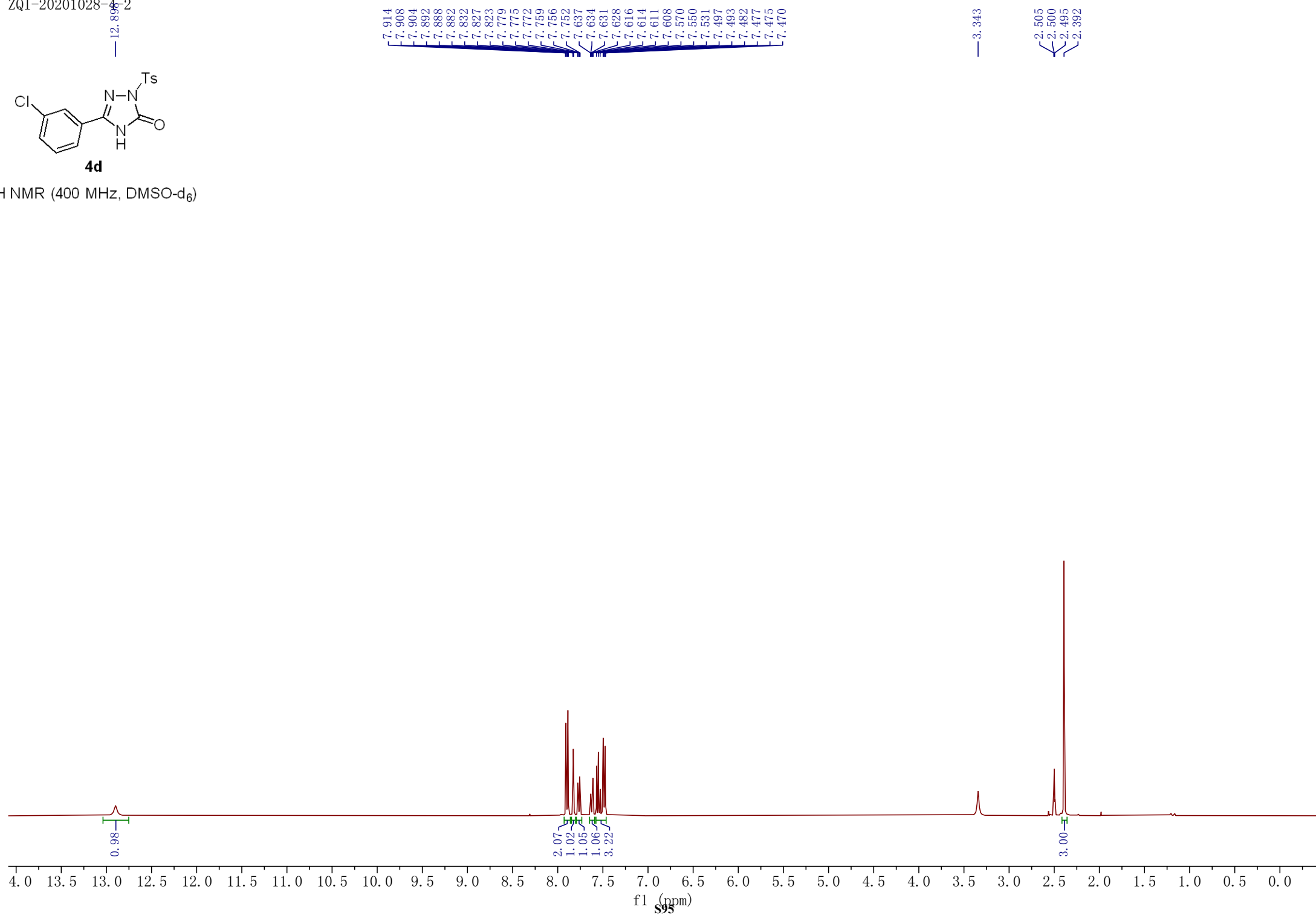


ZQI-20201028-4-2

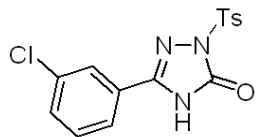


4d

¹H NMR (400 MHz, DMSO-d₆)

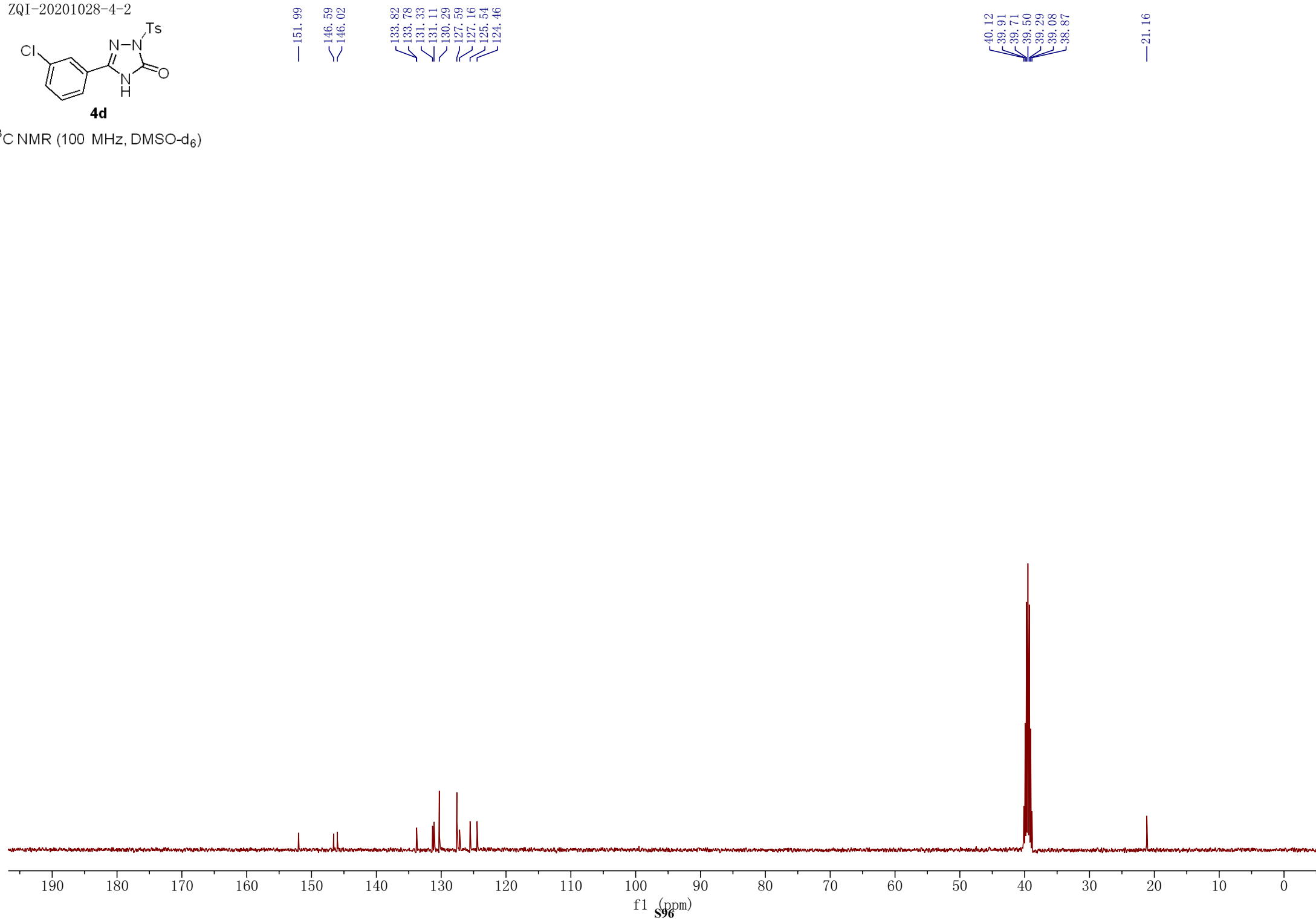


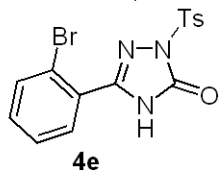
ZQI-20201028-4-2



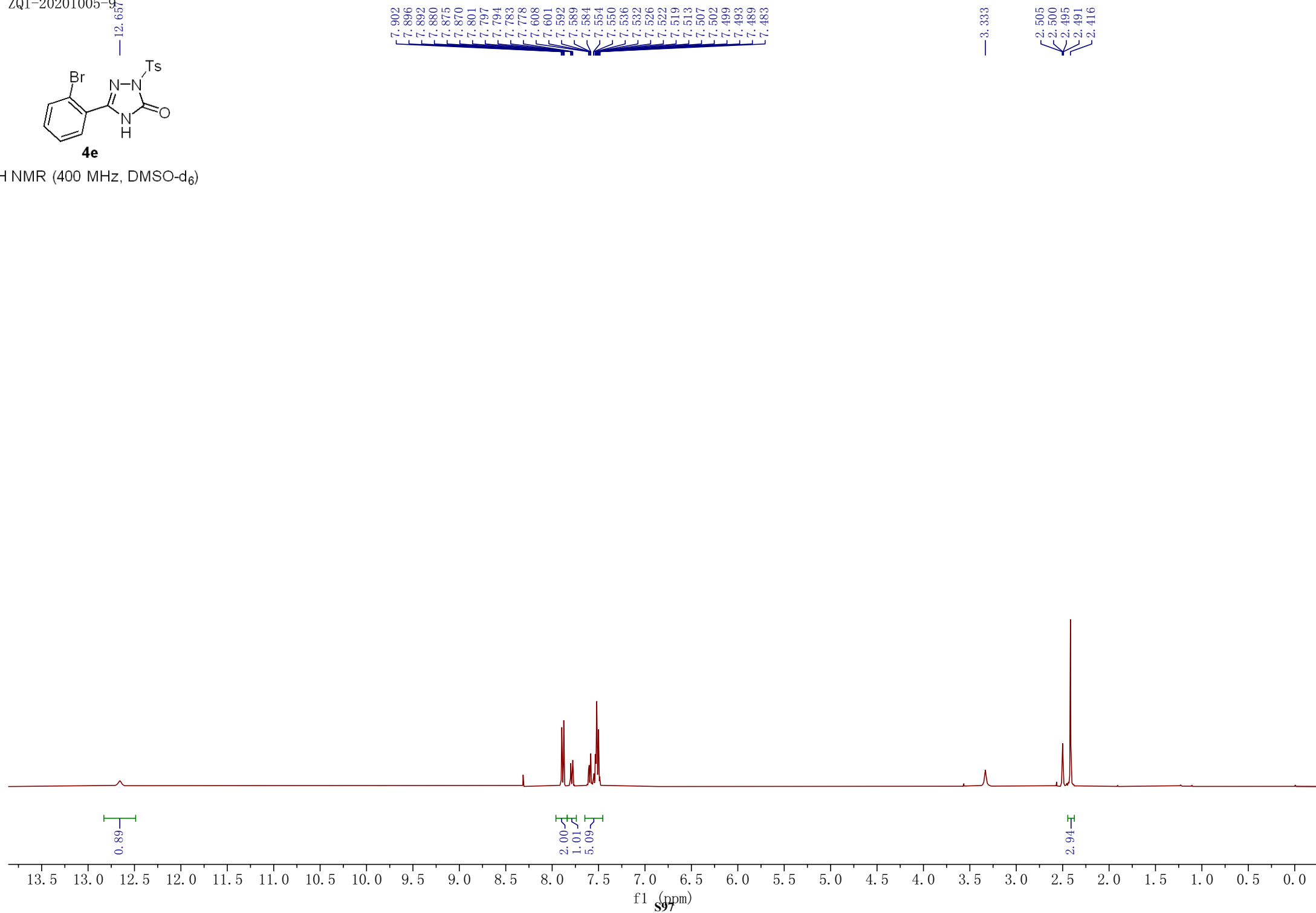
4d

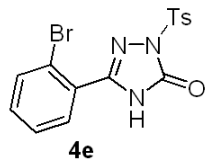
^{13}C NMR (100 MHz, DMSO- d_6)





¹H NMR (400 MHz, DMSO-d₆)





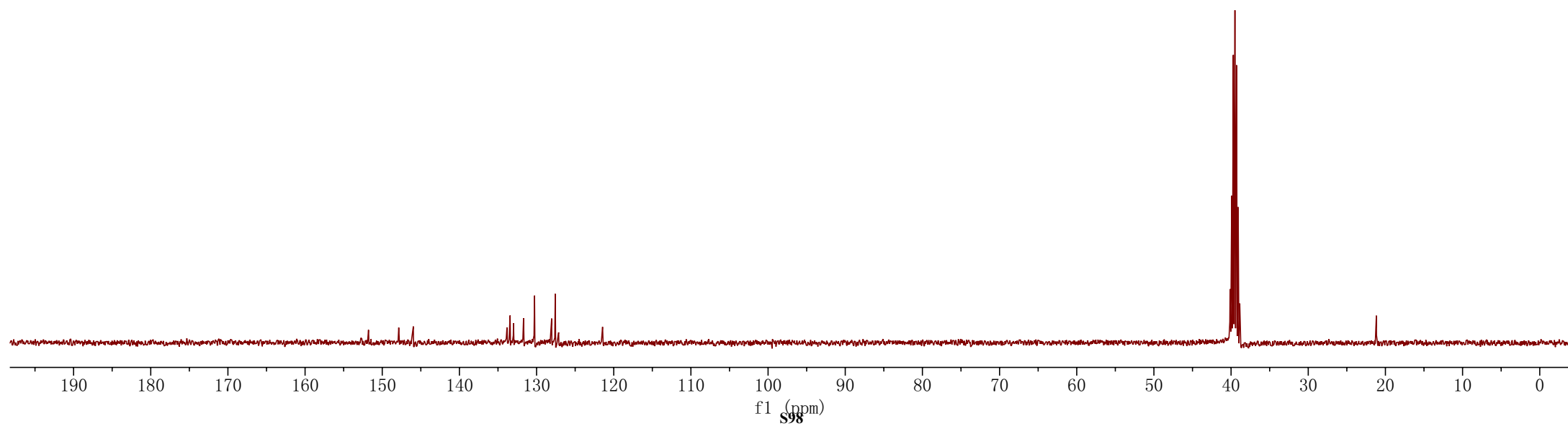
151.78
147.86
145.97

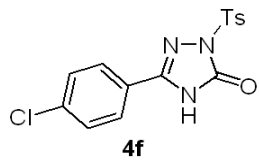
133.84
133.44
132.99
131.69
130.26
128.05
127.58
127.14
121.45

40.13
39.92
39.71
39.50
39.29
39.08
38.88

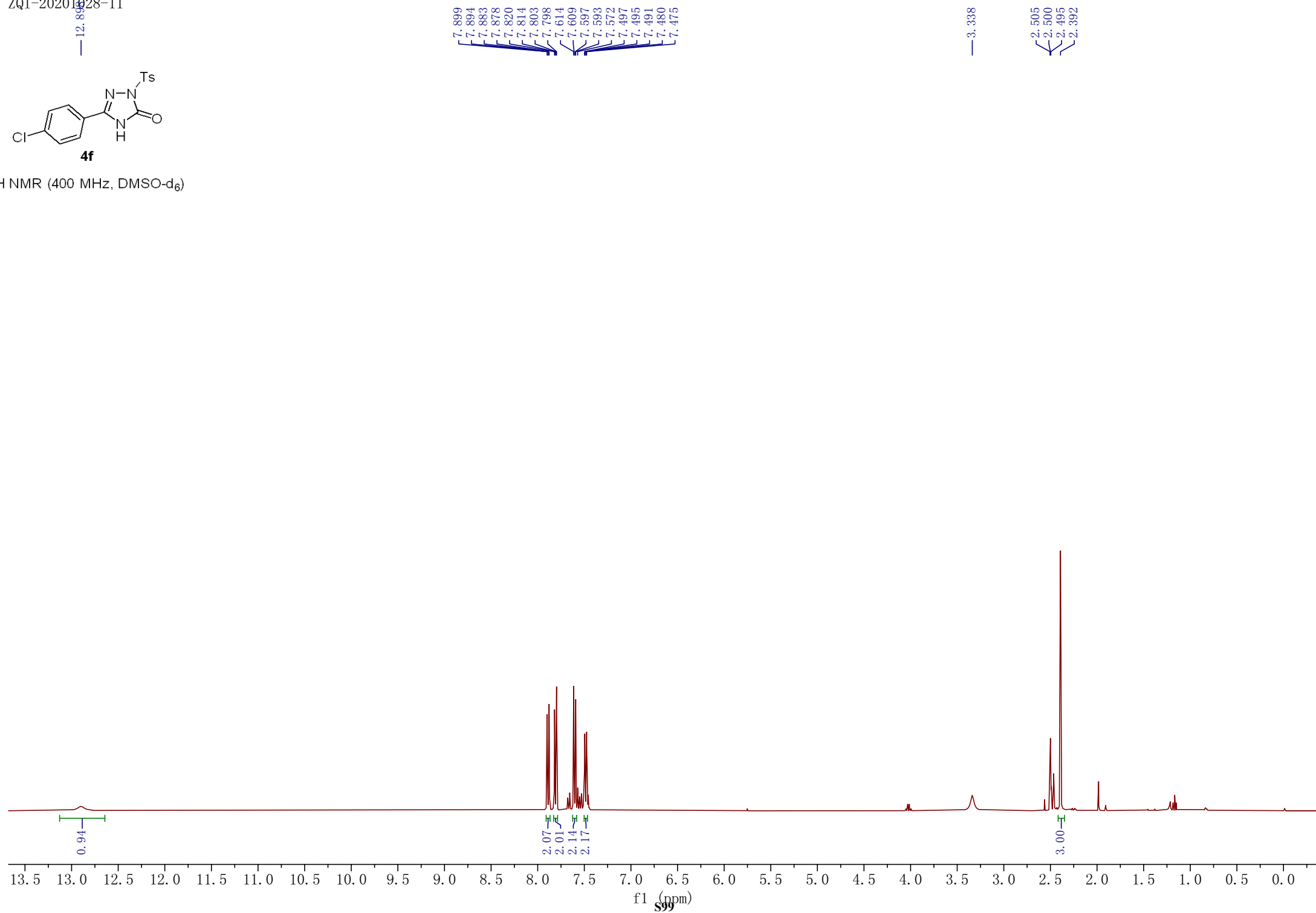
21.17

¹³C NMR (100 MHz, DMSO-d₆)

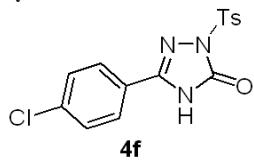




¹H NMR (400 MHz, DMSO-d₆)



ZQI-20201028-11

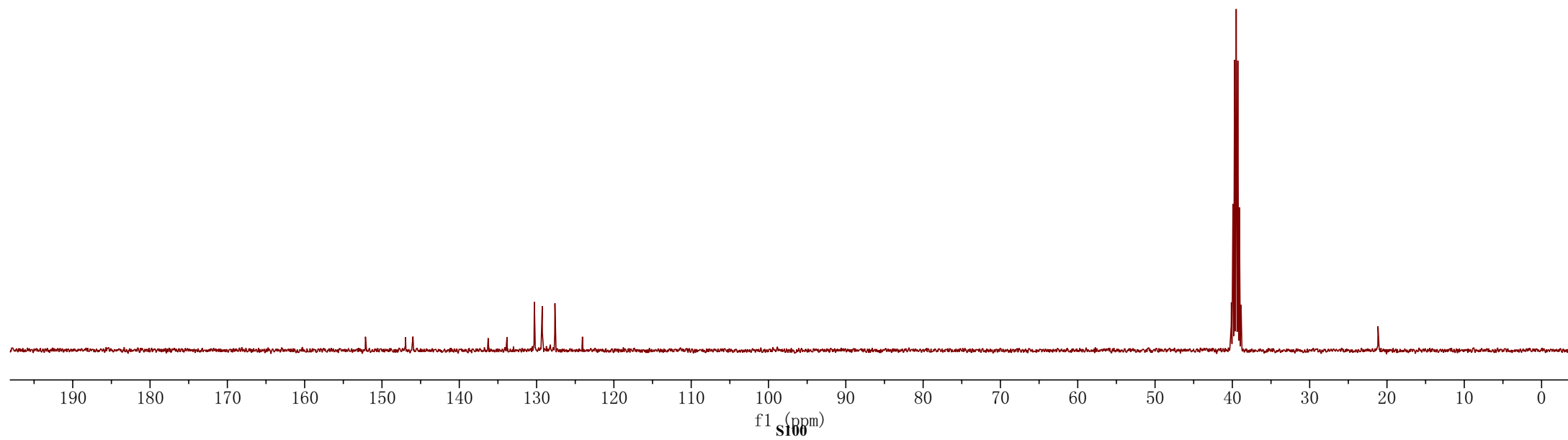


^{13}C NMR (100 MHz, DMSO- d_6)

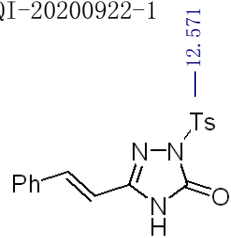
152.13
146.96
145.99
136.27
133.83
130.29
129.27
127.63
127.55
124.07

40.13
39.92
39.71
39.50
39.29
39.08
38.88

21.16

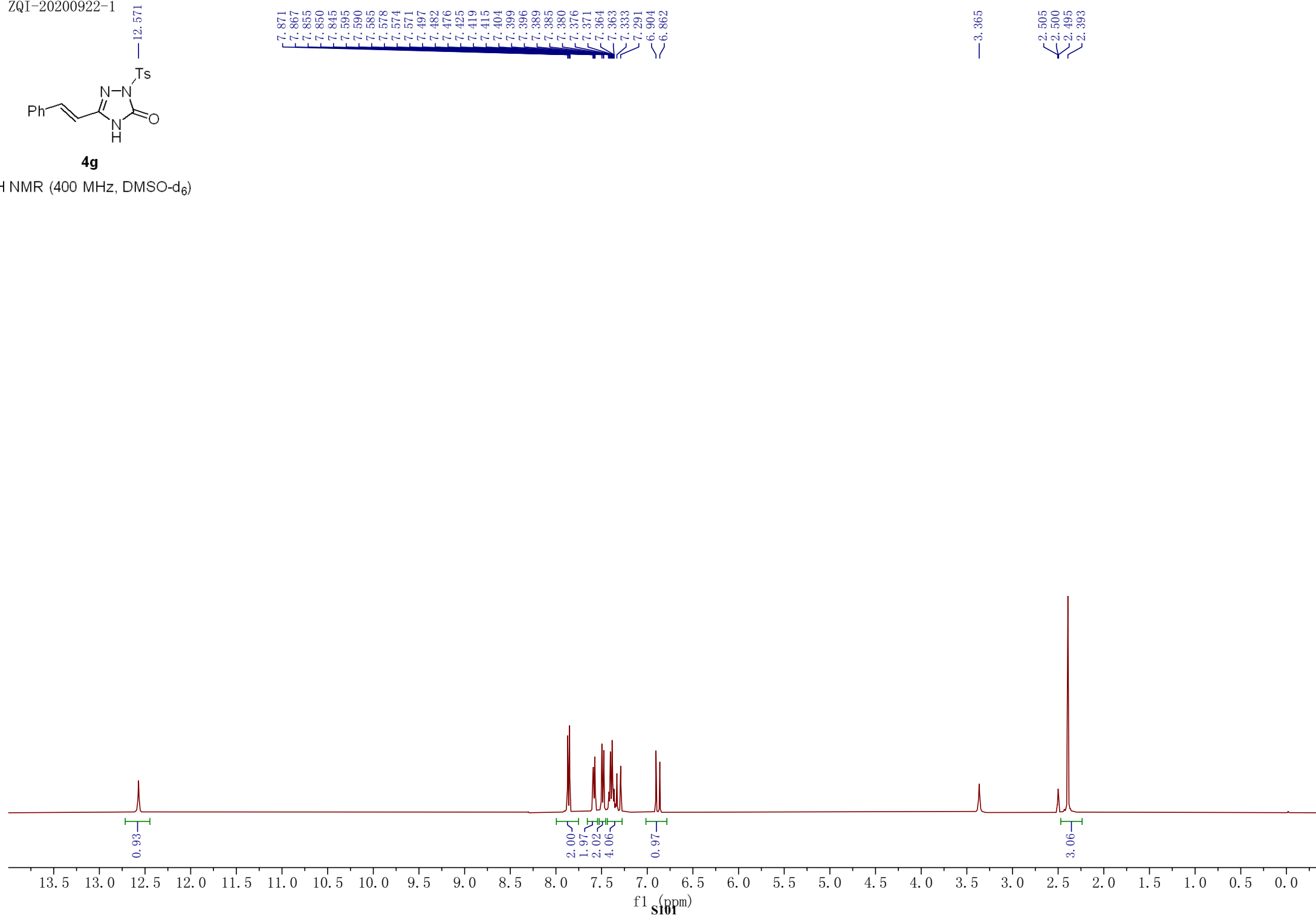


ZQI-20200922-1

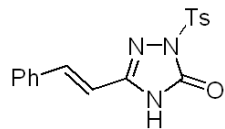


4g

¹H NMR (400 MHz, DMSO-d₆)

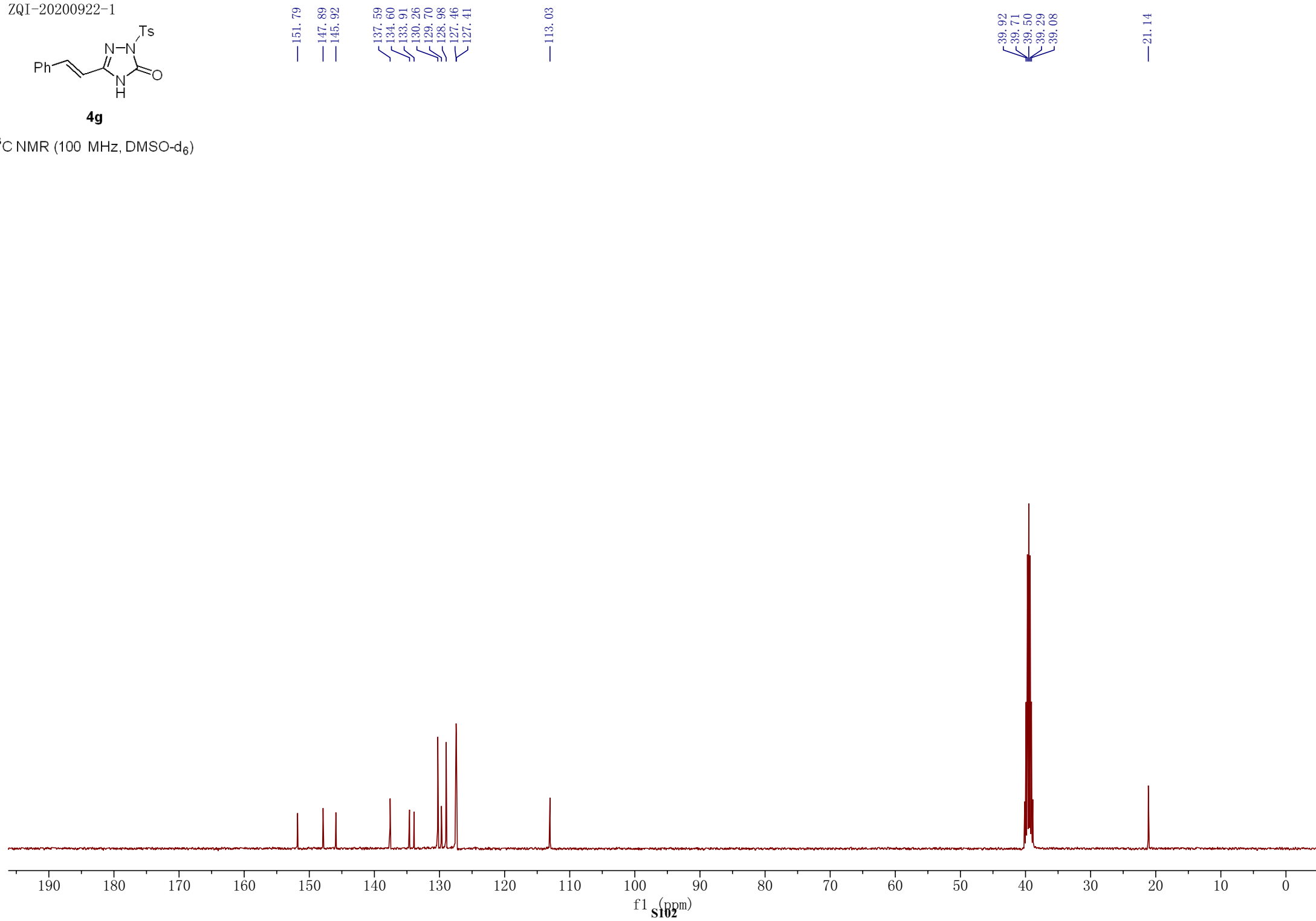


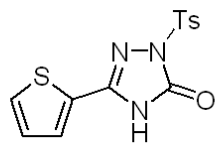
ZQI-20200922-1



4g

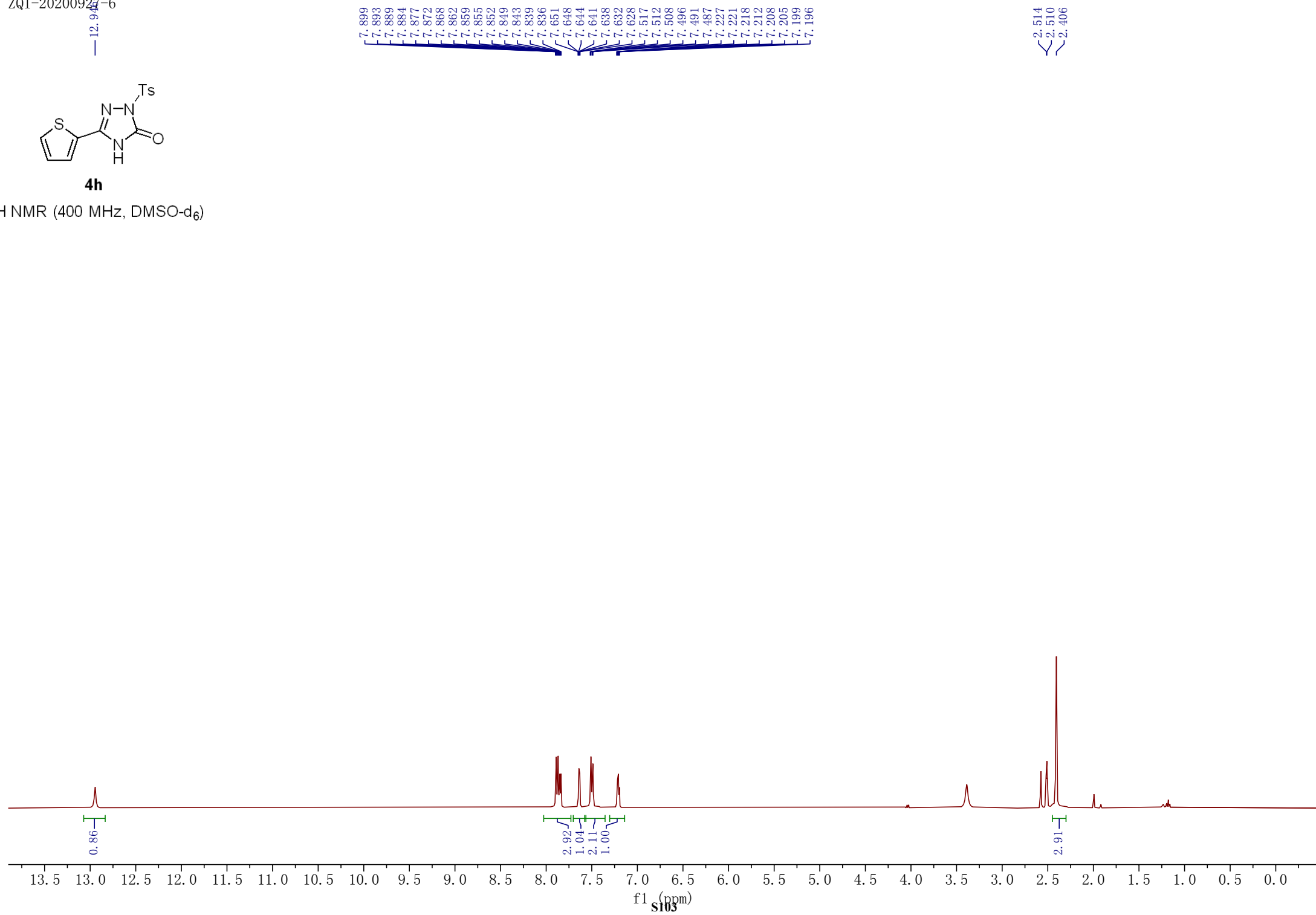
^{13}C NMR (100 MHz, DMSO- d_6)



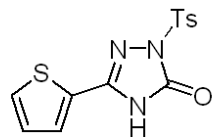


4h

¹H NMR (400 MHz, DMSO-d₆)



ZQI-20200927-6



4h

^{13}C NMR (100 MHz, DMSO- d_6)

151.82

145.97

144.21

133.80

130.67

130.28

129.84

128.21

127.49

126.97

40.13

39.92

39.71

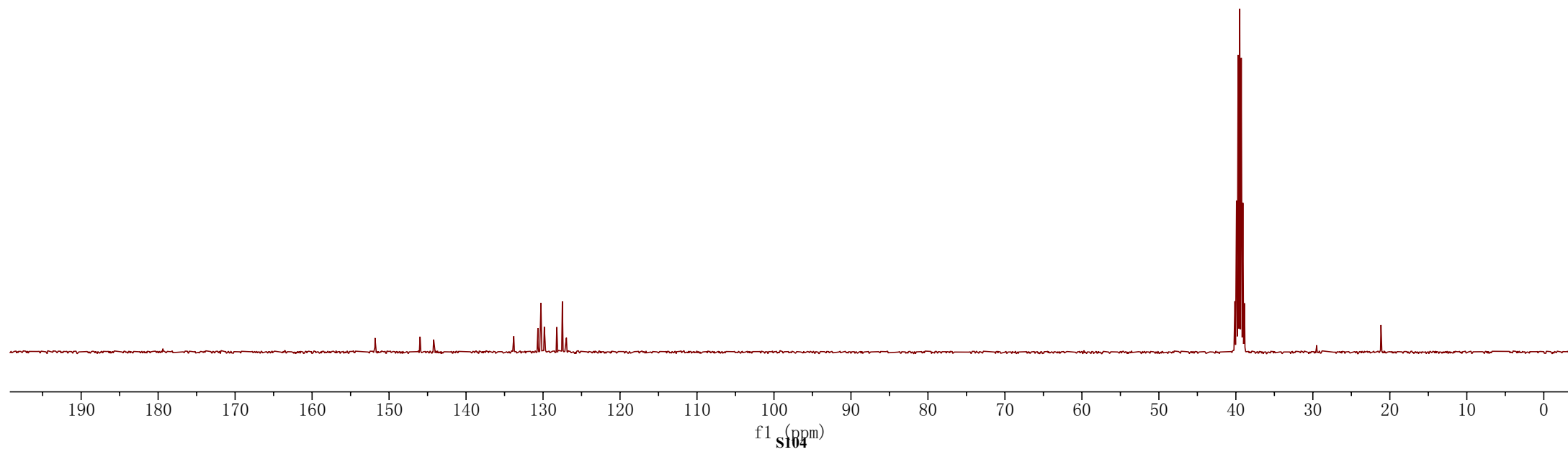
39.50

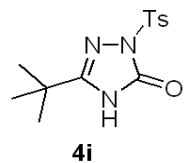
39.29

39.09

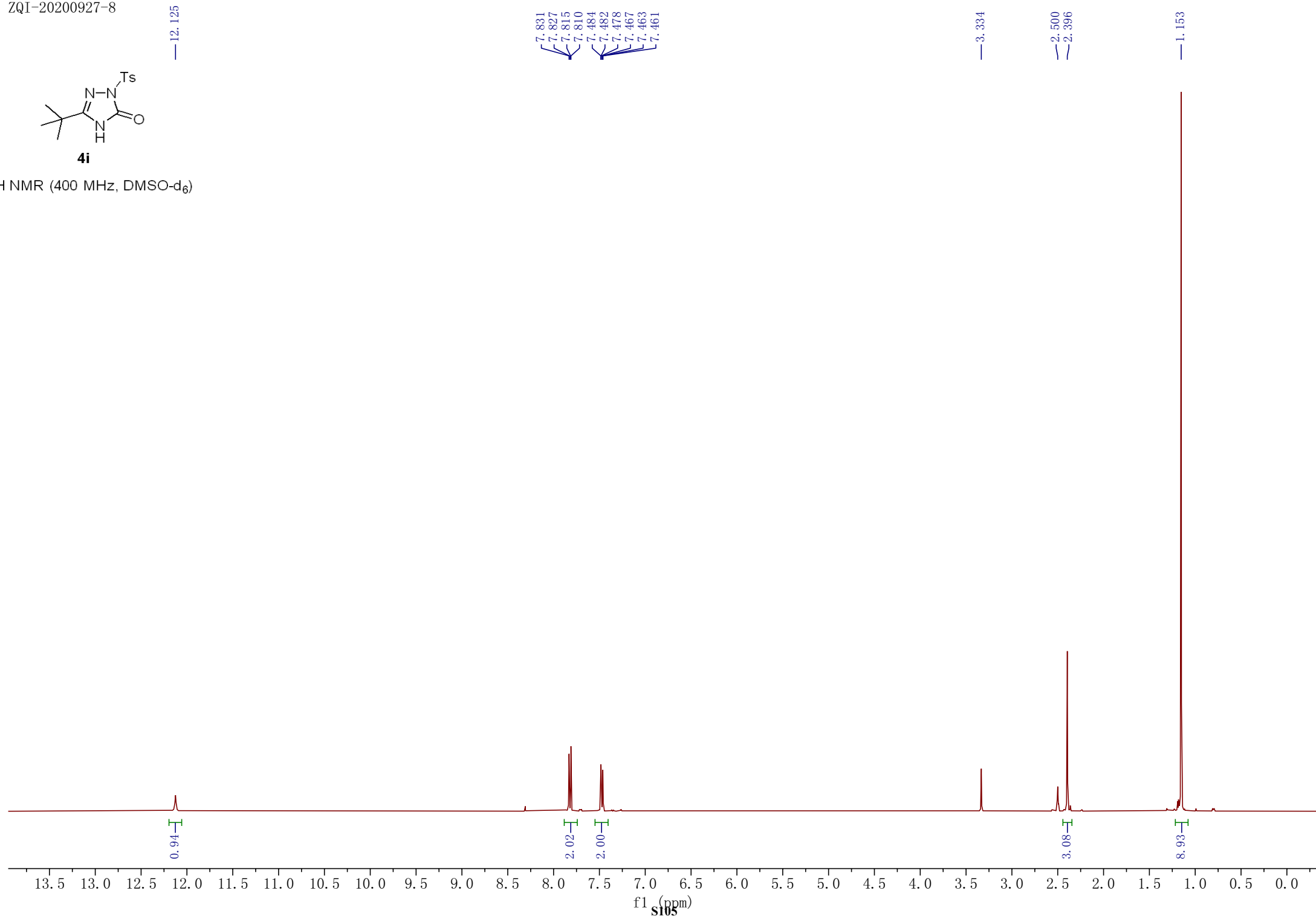
38.87

21.15

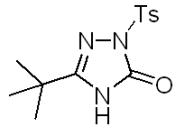




¹H NMR (400 MHz, DMSO-d₆)



ZQI-20200927-8

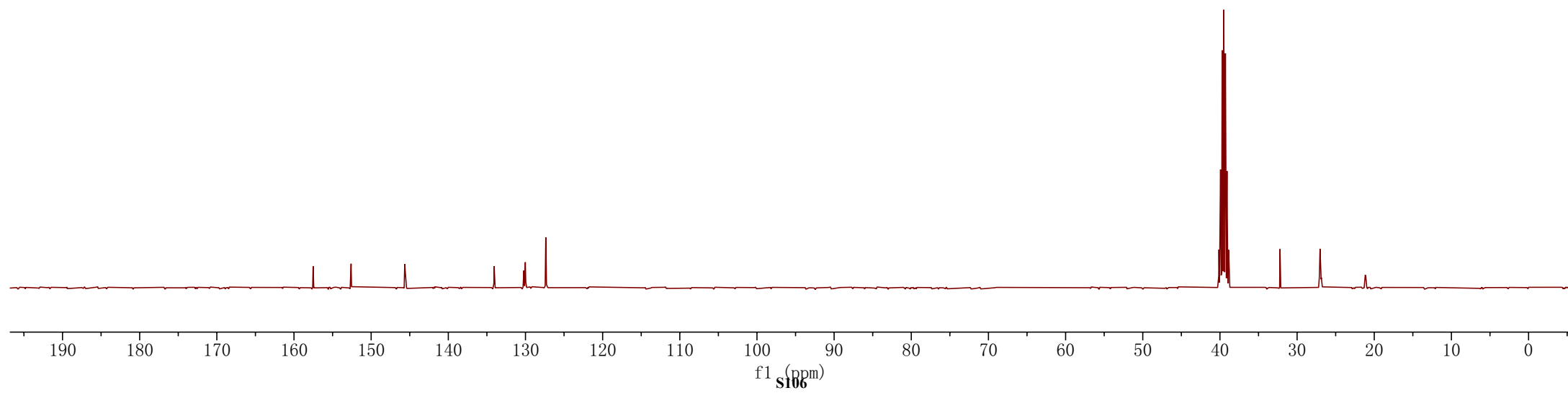


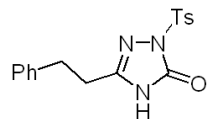
4i

^{13}C NMR (100 MHz, DMSO- d_6)

— 157.52
— 152.60
— 145.65
— 134.06
— 130.02
— 127.37

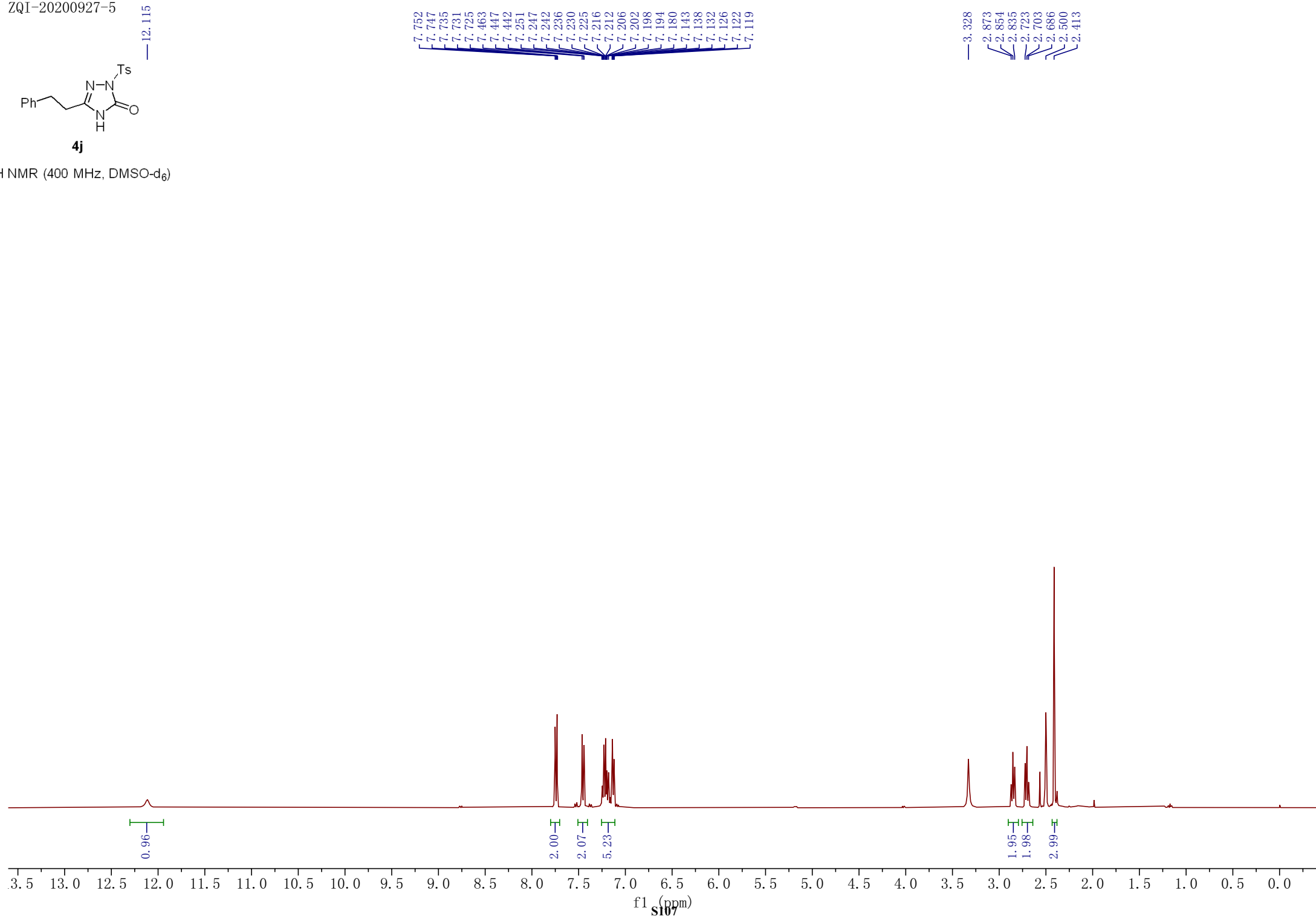
40.13
39.92
39.82
39.71
39.50
39.29
39.08
38.87
32.21
— 26.94
— 21.16



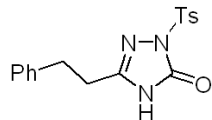


4j

¹H NMR (400 MHz, DMSO-d₆)



ZQI-20200927-5

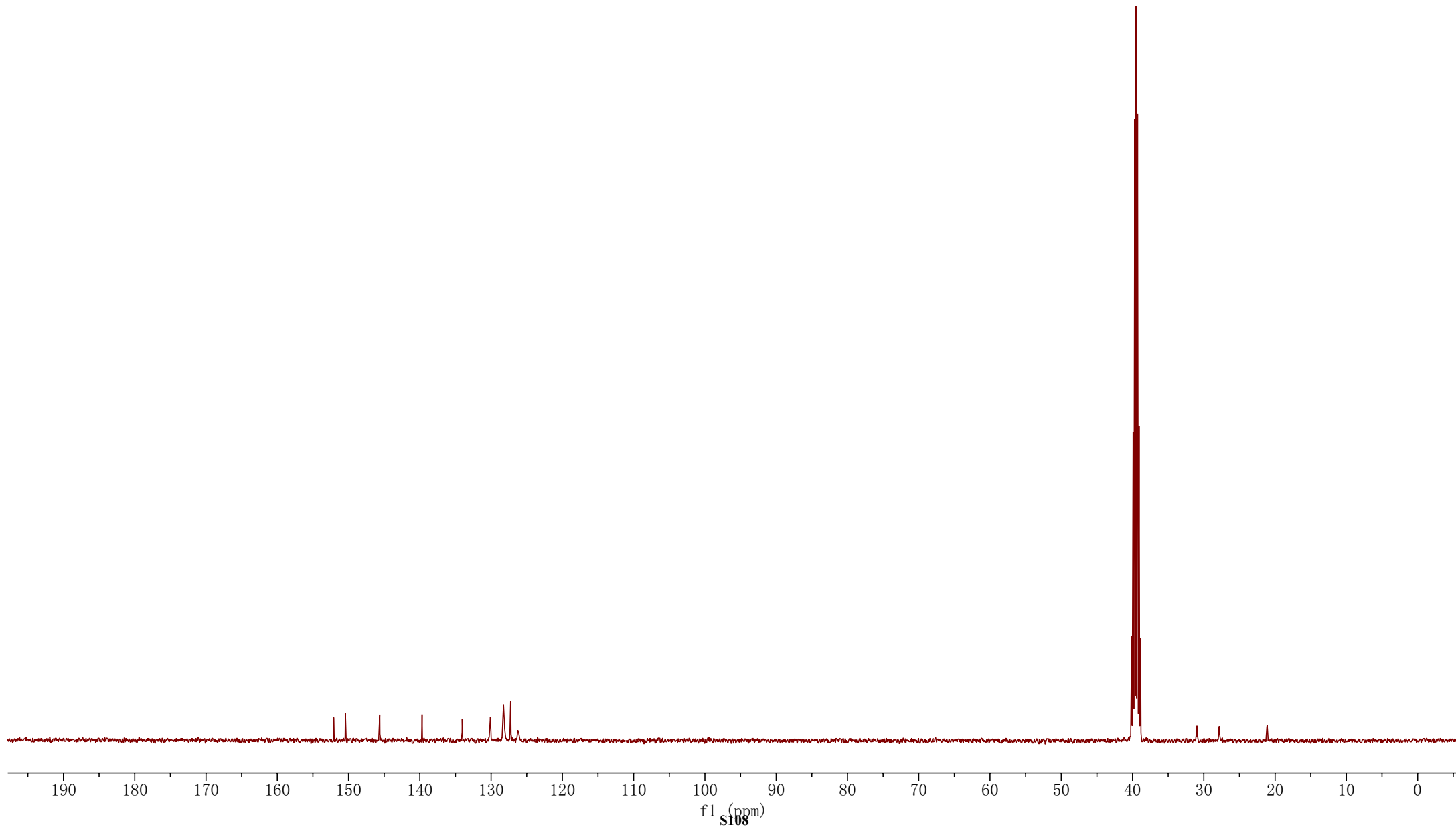


4j

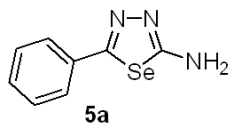
^{13}C NMR (100 MHz, DMSO- d_6)

152.09
150.44
145.61
139.68
134.05
130.20
130.10
128.26
127.26
126.21

40.13
40.01
39.92
39.80
39.71
39.50
39.29
39.08
38.87
30.97
27.84
21.11



WZY-20201004

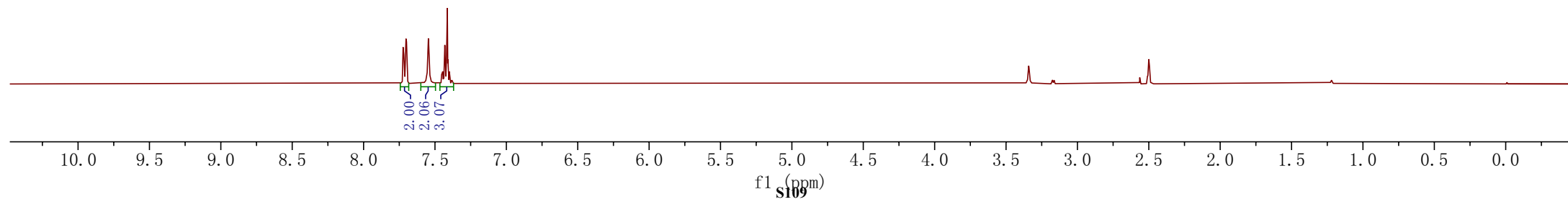


¹H NMR (400 MHz, DMSO-d₆)

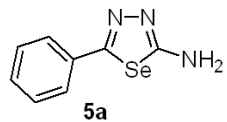
7.727
7.723
7.719
7.717
7.713
7.709
7.707
7.703
7.699
7.546
7.453
7.450
7.445
7.441
7.439
7.437
7.433
7.431
7.427
7.422
7.418
7.413
7.409
7.406
7.400
7.397

— 3.341

2.505
2.500
2.495



WZY-20201004



172.17

161.62

133.88

129.42

129.05

127.09

40.13

39.92

39.71

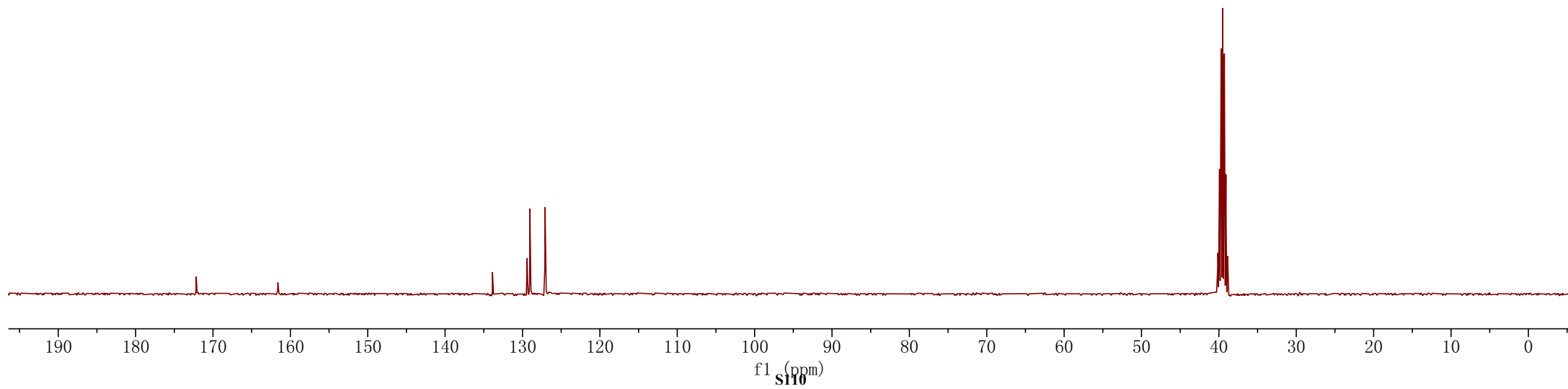
39.50

39.29

39.09

38.88

^{13}C NMR (100 MHz, DMSO- d_6)



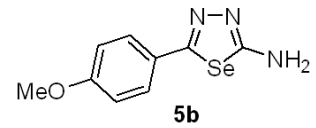
wzy-20201027-2

7.653
7.647
7.636
7.631
7.426
6.993
6.988
6.976
6.971

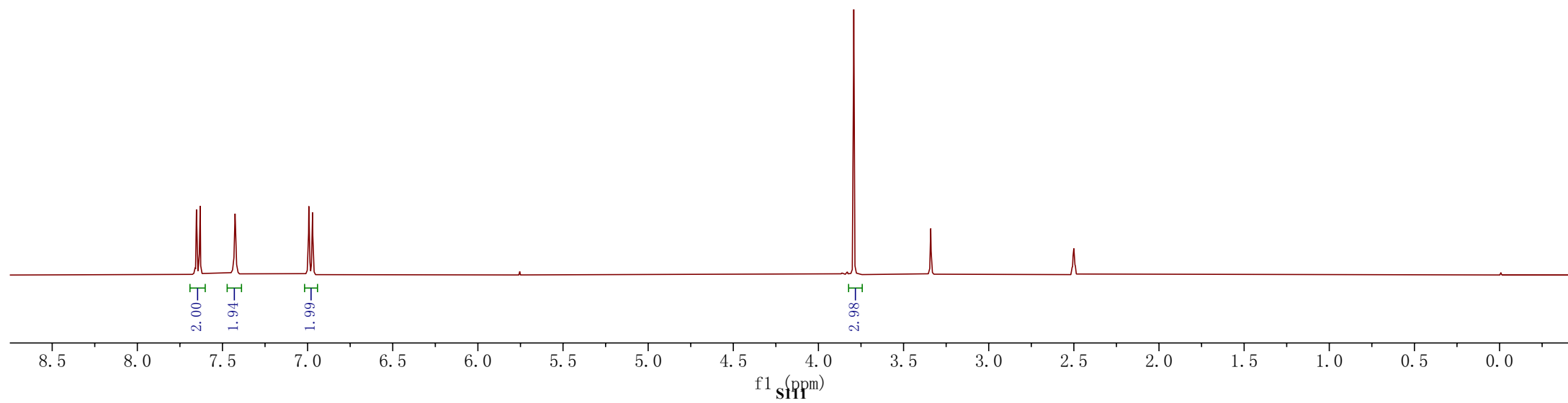
3.793

3.341

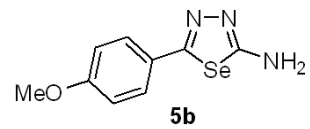
2.505
2.500
2.495



¹H NMR (400 MHz, DMSO-d₆)



wzy-20201027-2



— 171.43

161.41
160.20

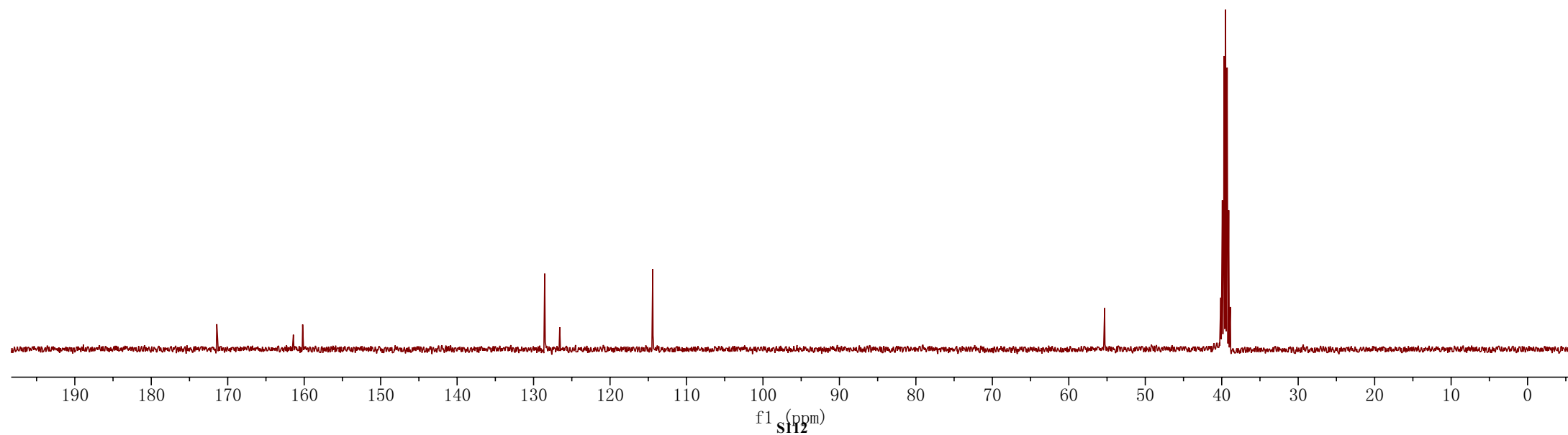
— 128.54
— 126.58

— 114.42

— 55.31

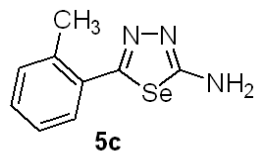
40.13
39.92
39.71
39.50
39.29
39.09
38.88

¹³C NMR (100 MHz, DMSO-d₆)



f1 (ppm)
S112

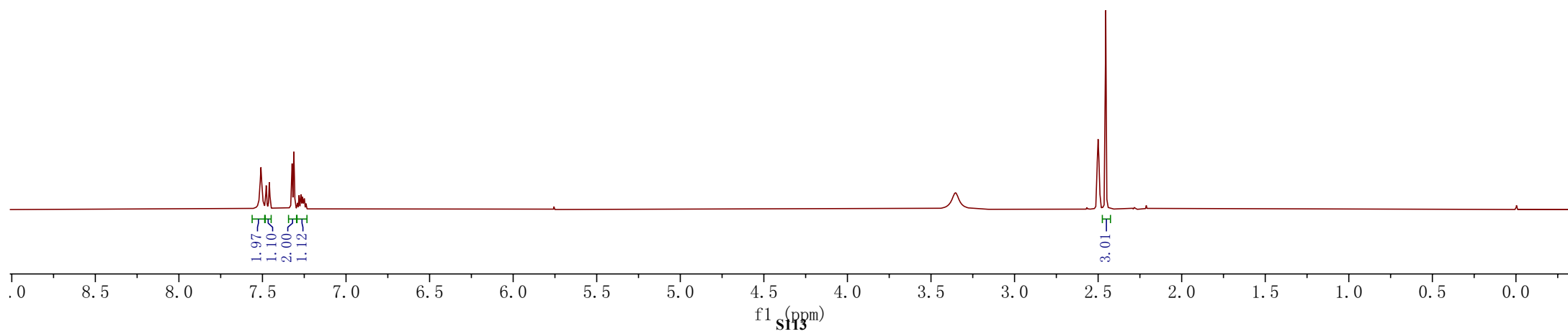
wzy-20201102-3



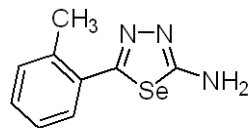
7.509
7.477
7.459
7.325
7.322
7.312
7.308
7.298
7.290
7.281
7.273
7.269
7.261
7.250
7.240

2.500
2.455

^1H NMR (400 MHz, DMSO- d_6)



wzy-20201102-3



— 172.85

— 160.59

— 135.47

— 132.74

— 131.27

— 130.57

— 128.86

— 126.22

— 40.13

— 39.92

— 39.71

— 39.50

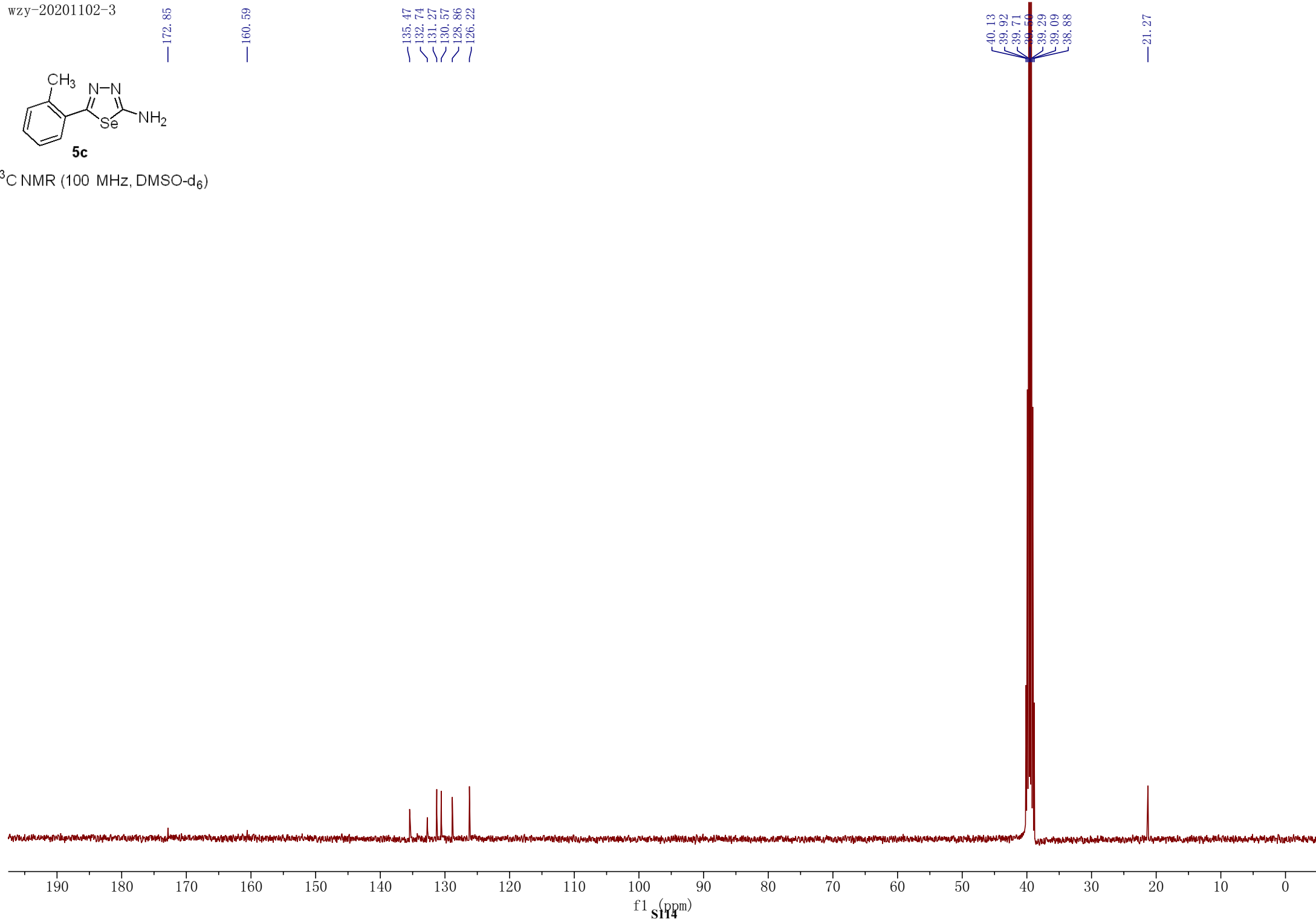
— 39.29

— 39.09

— 38.88

— 21.27

^{13}C NMR (100 MHz, DMSO- d_6)



f1 (ppm)

S114

wzy-20201102-2

— 174.26

— 157.06

— 134.19

— 133.69

— 130.81

— 130.78

— 127.99

— 121.11

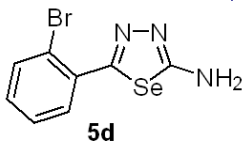
— 39.92

— 39.71

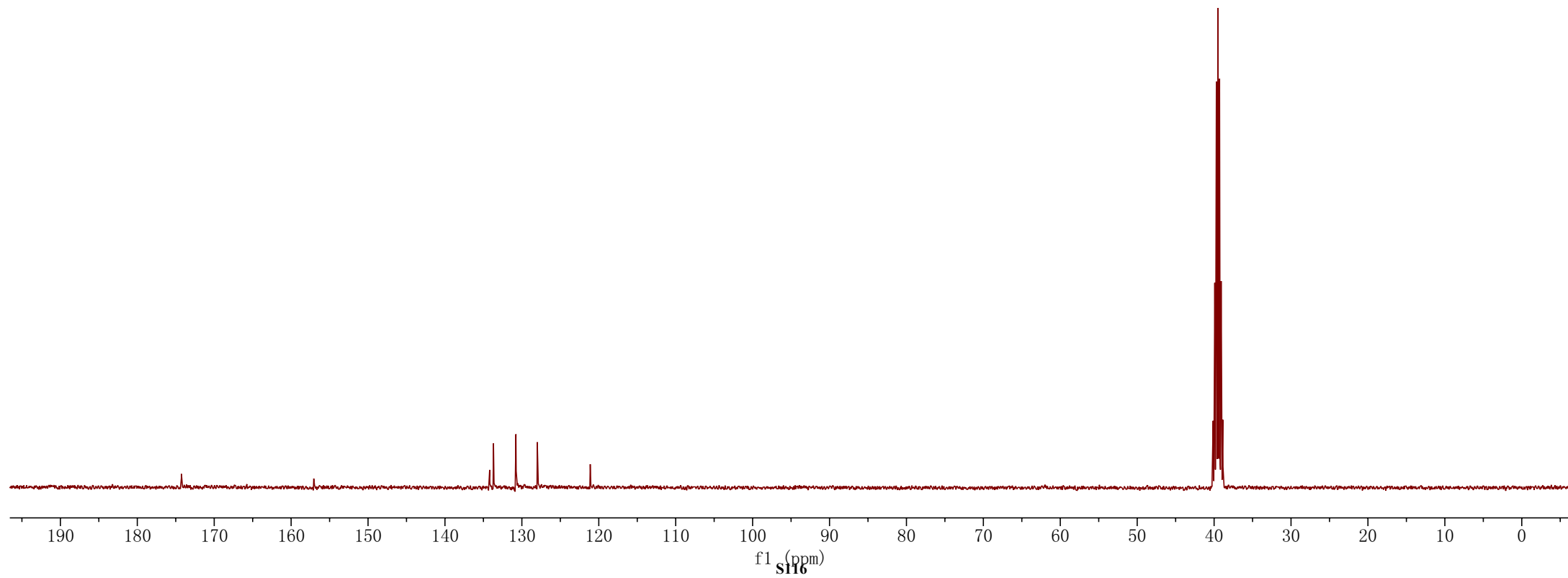
— 39.50

— 39.29

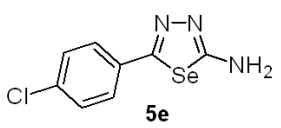
— 39.08



^{13}C NMR (100 MHz, DMSO- d_6)



wzy-20201026-1

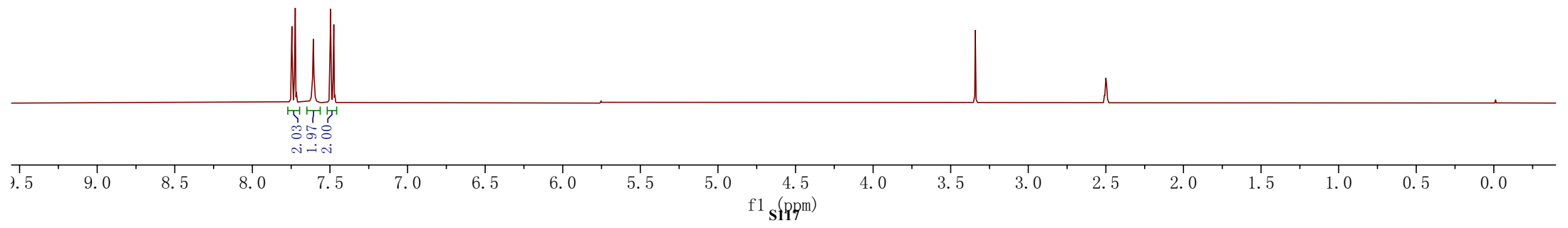


7.752
7.745
7.740
7.729
7.724
7.717
7.607
7.503
7.497
7.492
7.480
7.475
7.469

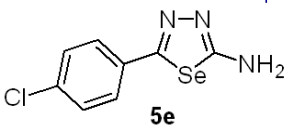
3.342

2.505
2.500
2.495

¹H NMR (400 MHz, DMSO-d₆)



wzy-20201026-1



172.62

160.24

133.78

132.76

129.06

128.62

39.92

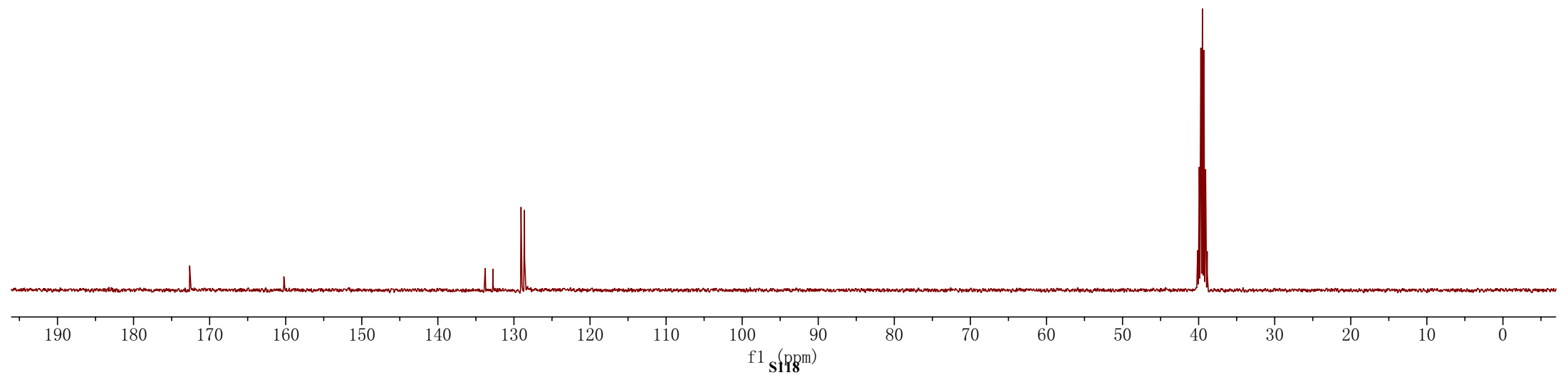
39.71

39.50

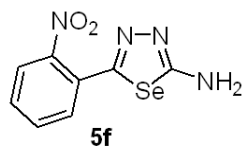
39.29

39.09

¹³C NMR (100 MHz, DMSO-d₆)



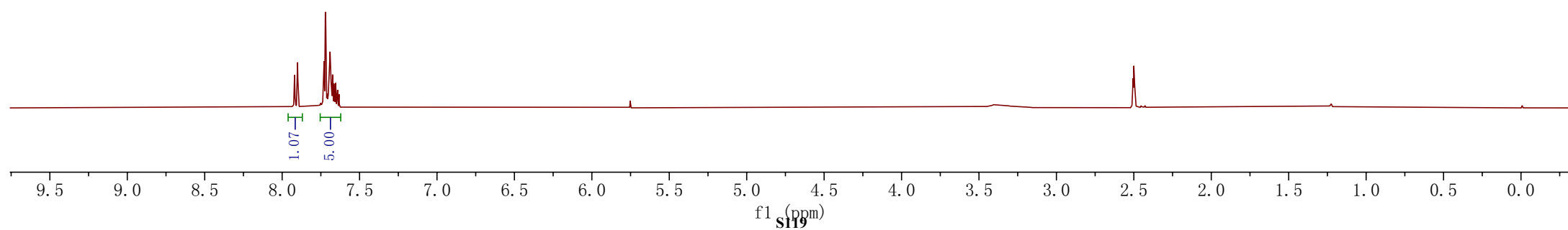
wzy-20201102-1



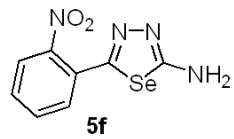
7.922
7.920
7.918
7.903
7.900
7.898
7.735
7.732
7.729
7.721
7.719
7.710
7.691
7.685
7.675
7.666
7.661
7.655
7.652
7.645
7.642
7.632

2.505
2.500
2.495

¹H NMR (400 MHz, DMSO-d₆)



wzy-20201102-1



— 174.08

— 155.18

— 147.86

— 132.52

— 131.95

— 130.31

— 126.29

— 124.05

— 40.12

— 39.92

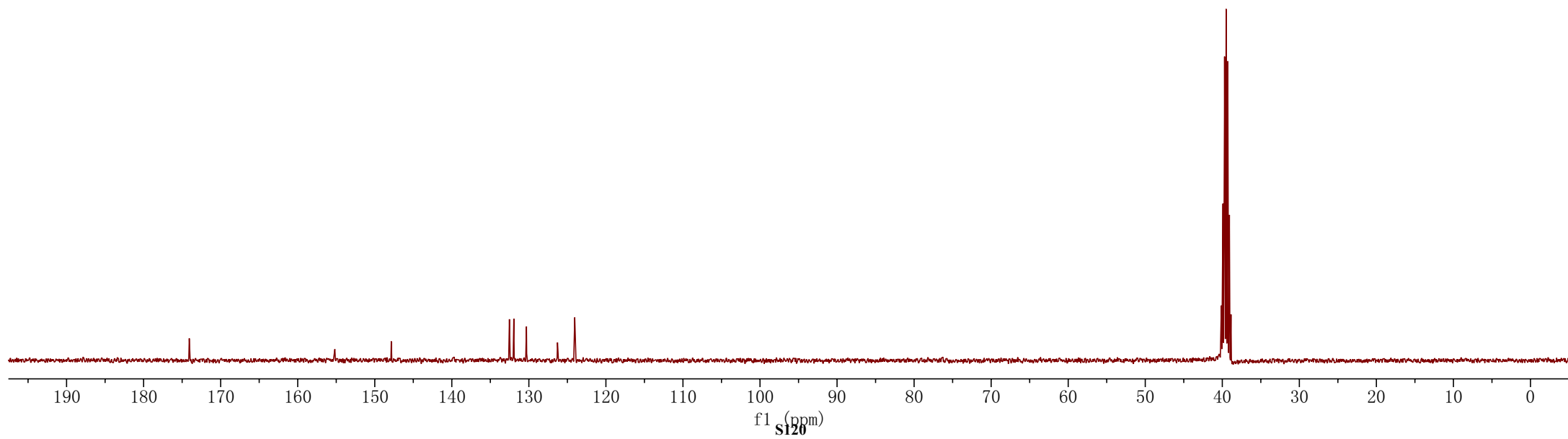
— 39.71

— 39.50

— 39.29

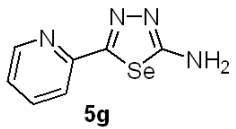
— 39.08

^{13}C NMR (100 MHz, DMSO- d_6)



S120

wzy-20201107-1

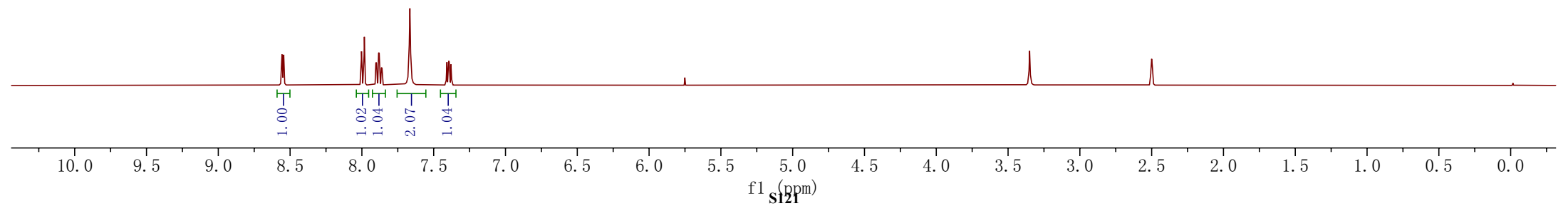


8.561
8.557
8.554
8.548
8.545
8.541
8.006
8.003
8.000
7.986
7.983
7.980
7.903
7.898
7.884
7.879
7.864
7.860
7.666
7.411
7.408
7.399
7.395
7.392
7.389
7.380
7.377

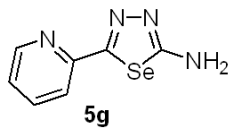
3.350

2.505
2.500
2.495

¹H NMR (400 MHz, DMSO-d₆)



wzy-20201107-1



— 173.40

— 164.05

— 151.80

— 149.71

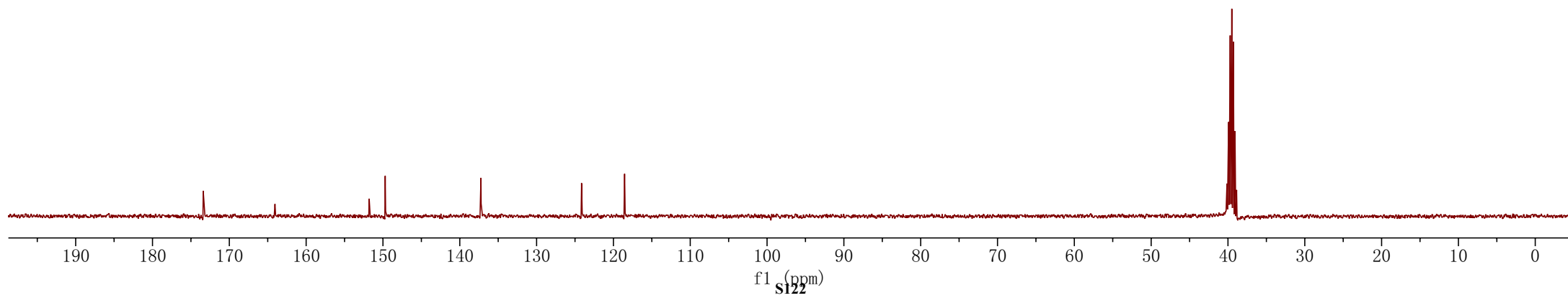
— 137.25

— 124.15

— 118.54

39.92
39.71
39.50
39.30
39.09

¹³C NMR (100 MHz, DMSO-d₆)



f1 (ppm)
S122

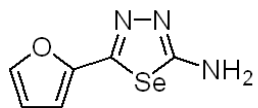
wzy-20201026-3

7.810
7.806
7.804
7.801
7.556

6.921
6.918
6.916
6.912
6.910
6.907
6.641
6.637
6.632
6.628
6.625

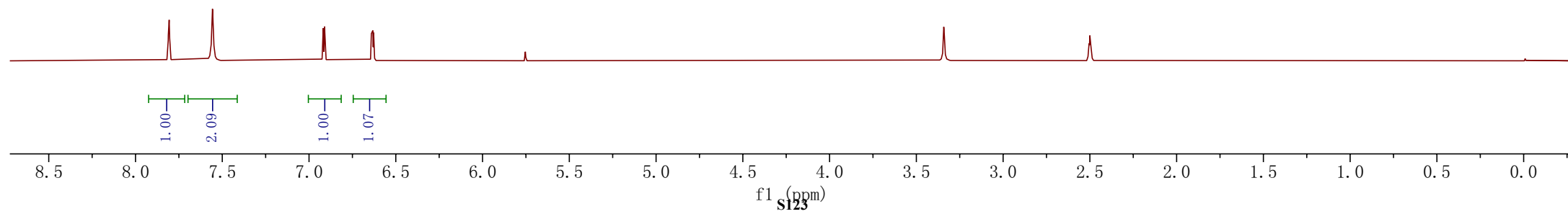
3.341

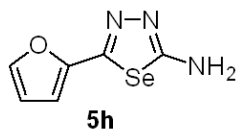
2.505
2.500
2.496
2.491



5h

¹H NMR (400 MHz, DMSO-d₆)





¹³C NMR (100 MHz, DMSO-d₆)

— 171.56

— 151.03

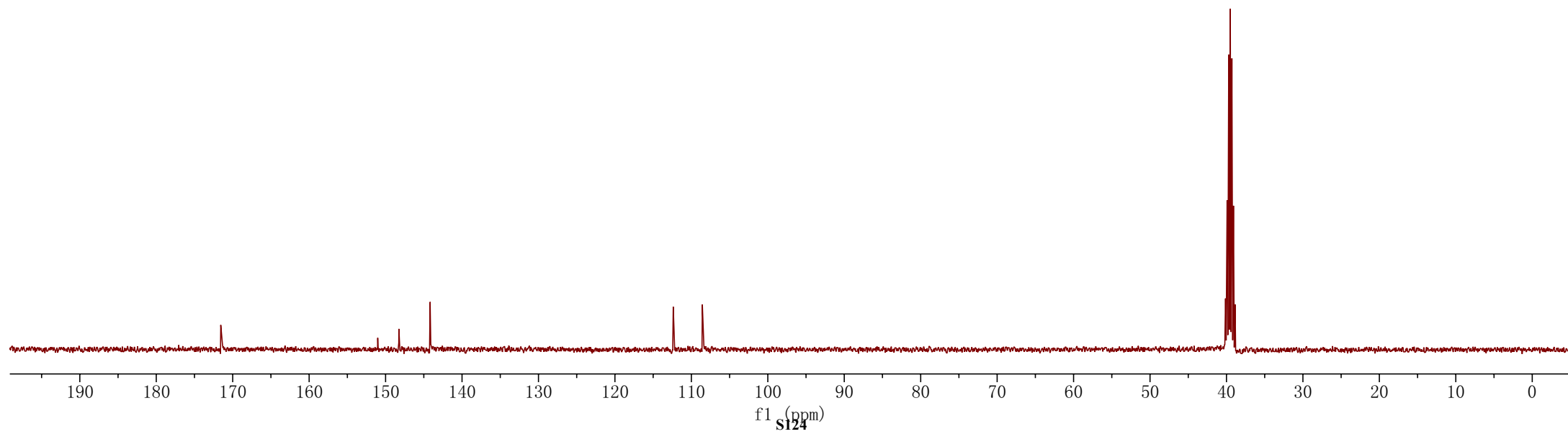
— 148.26

— 144.18

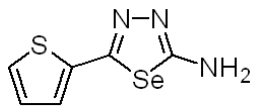
— 112.37

— 108.57

39.92
39.71
39.50
39.29
39.08



wzy-20201027-3

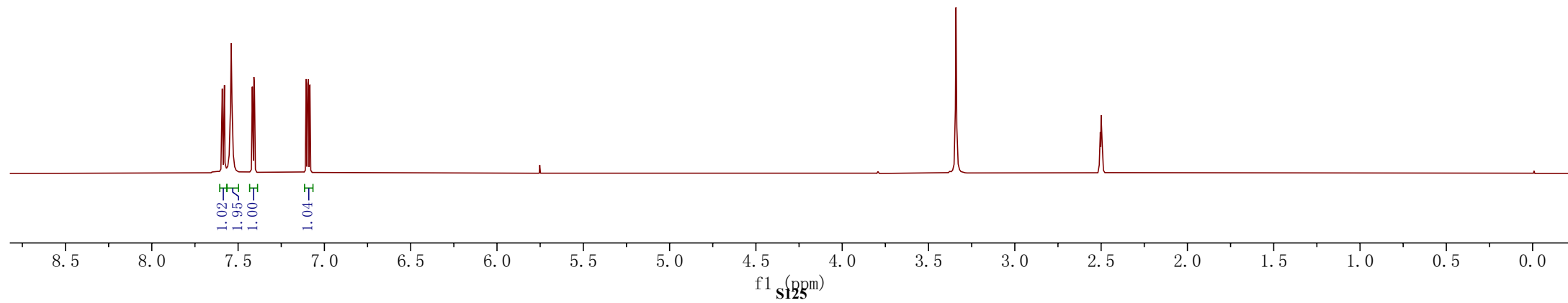


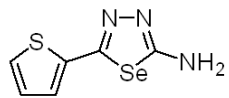
7.595
7.592
7.582
7.579
7.540
7.418
7.415
7.408
7.405
7.106
7.097
7.093
7.084

3.341

2.505
2.500
2.495

¹H NMR (400 MHz, DMSO-d₆)





5i

^{13}C NMR (100 MHz, DMSO- d_6)

— 171.71

— 154.78

— 136.45

— 128.74

— 127.78

— 127.41

— 40.12

— 39.92

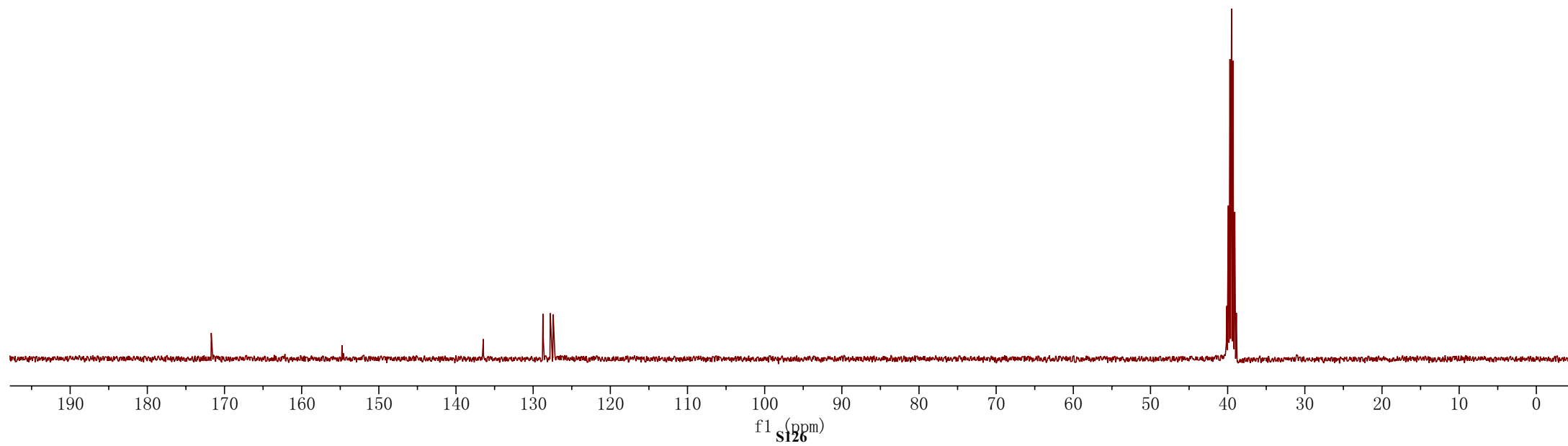
— 39.71

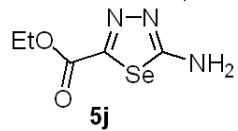
— 39.50

— 39.29

— 39.08

— 38.87





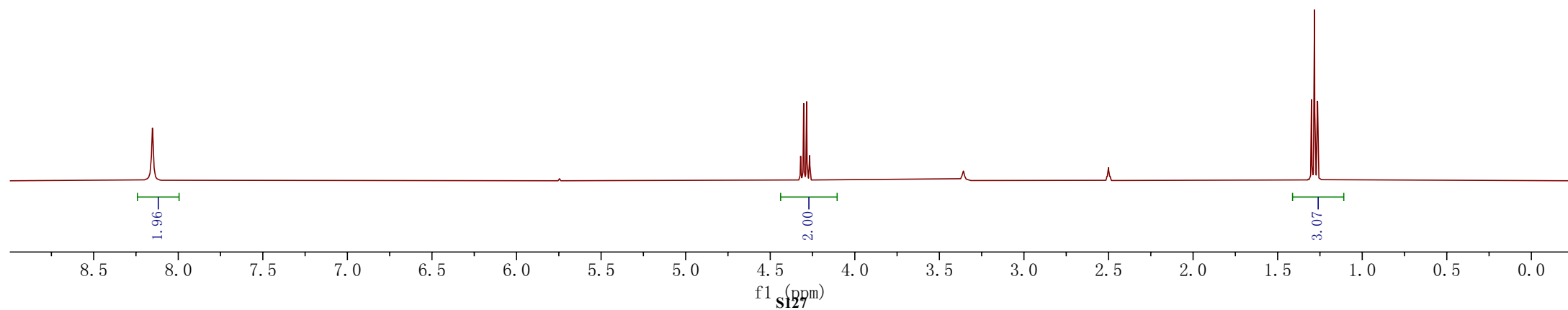
8.153

4.320
4.303
4.285
4.267

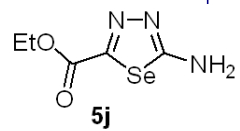
2.505
2.500
2.495

1.300
1.282
1.264

¹H NMR (400 MHz, DMSO-d₆)



wzy-20201107-2



— 176.68

— 160.79

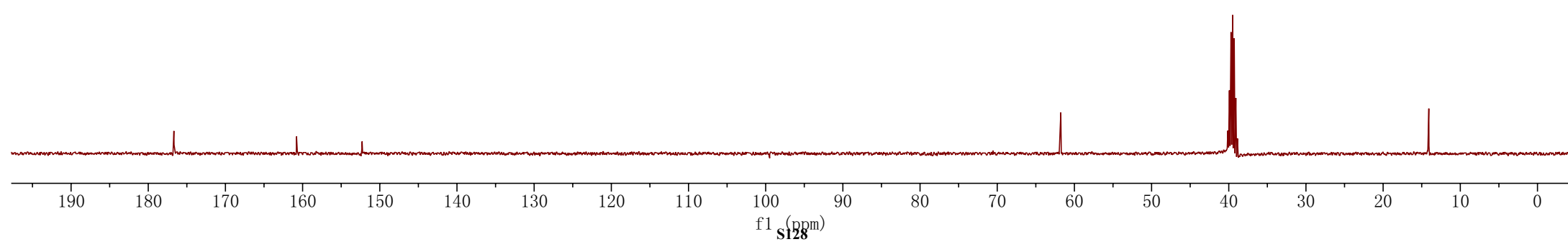
— 152.29

— 61.76

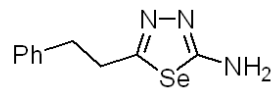
— 39.92
— 39.71
— 39.50
— 39.29
— 39.08

— 14.08

¹³C NMR (100 MHz, DMSO-d₆)



wzy-20201027-4

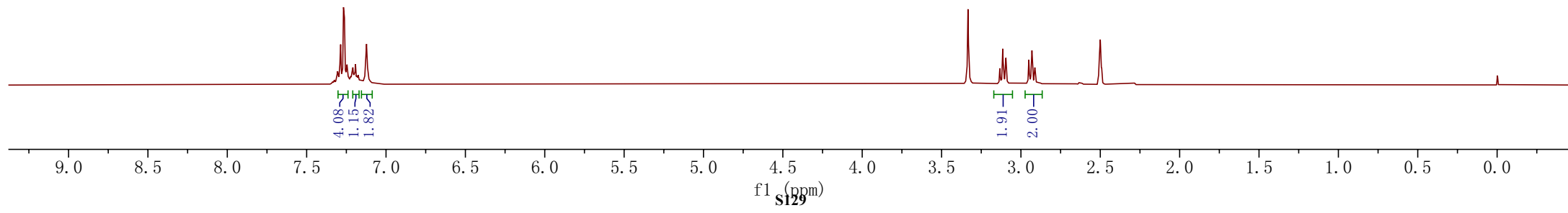


5k

¹H NMR (400 MHz, DMSO-d₆)

7.308
7.305
7.300
7.291
7.286
7.268
7.262
7.254
7.250
7.246
7.241
7.223
7.214
7.209
7.204
7.199
7.192
7.185
7.181
7.176
7.171
7.123

3.334
3.133
3.115
3.111
3.108
3.095
2.950
2.931
2.912
2.505
2.500
2.496



wzy-20201027-4

172.04

162.87

140.37

128.50

128.30

126.14

40.13

39.92

39.71

39.50

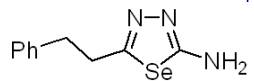
39.29

39.08

38.88

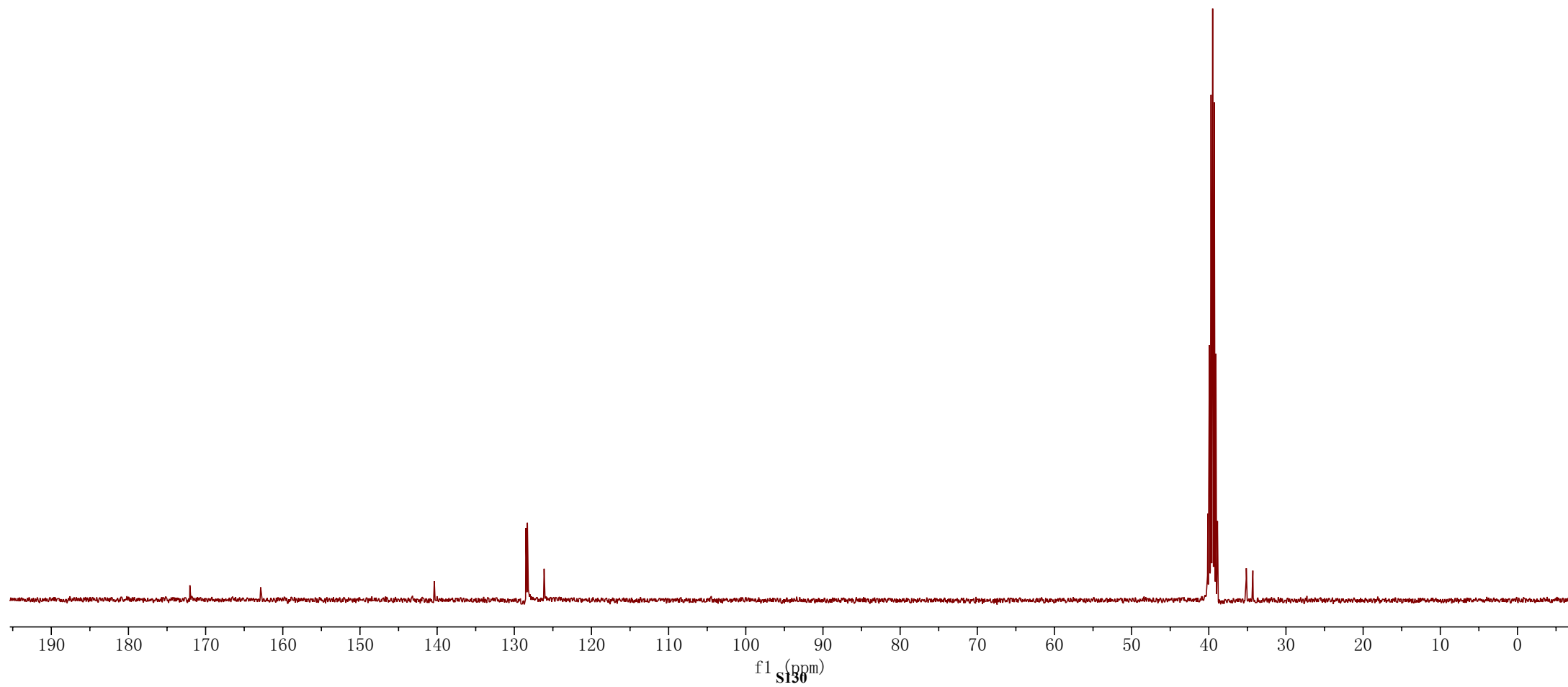
35.14

34.29

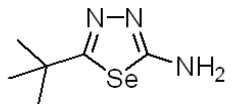


5k

¹³C NMR (100 MHz, DMSO-d₆)



wzy-20201026-2



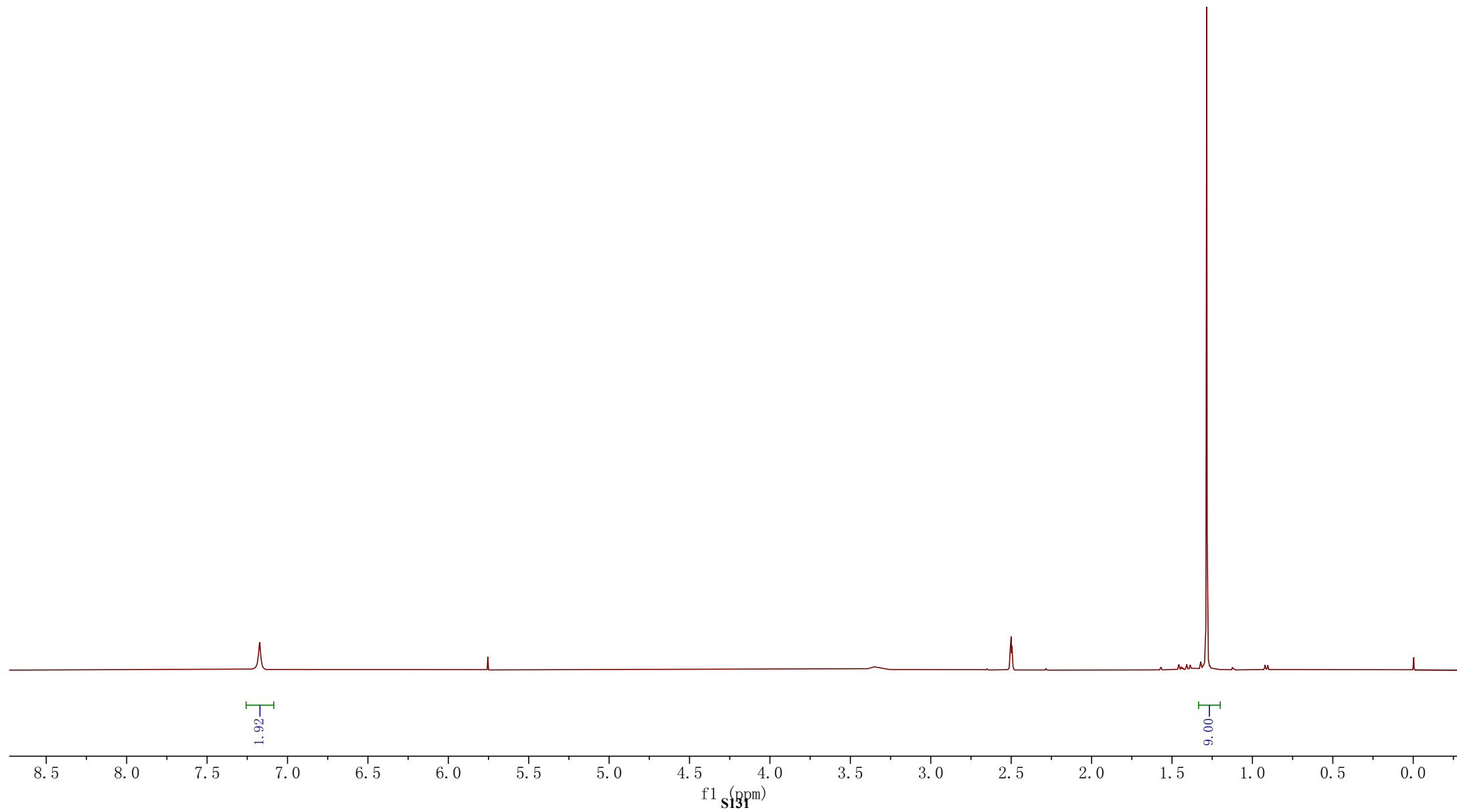
5I

—7.174

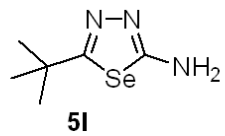
2.509
2.505
2.500
2.495
2.491

—1.284

¹H NMR (400 MHz, DMSO-d₆)



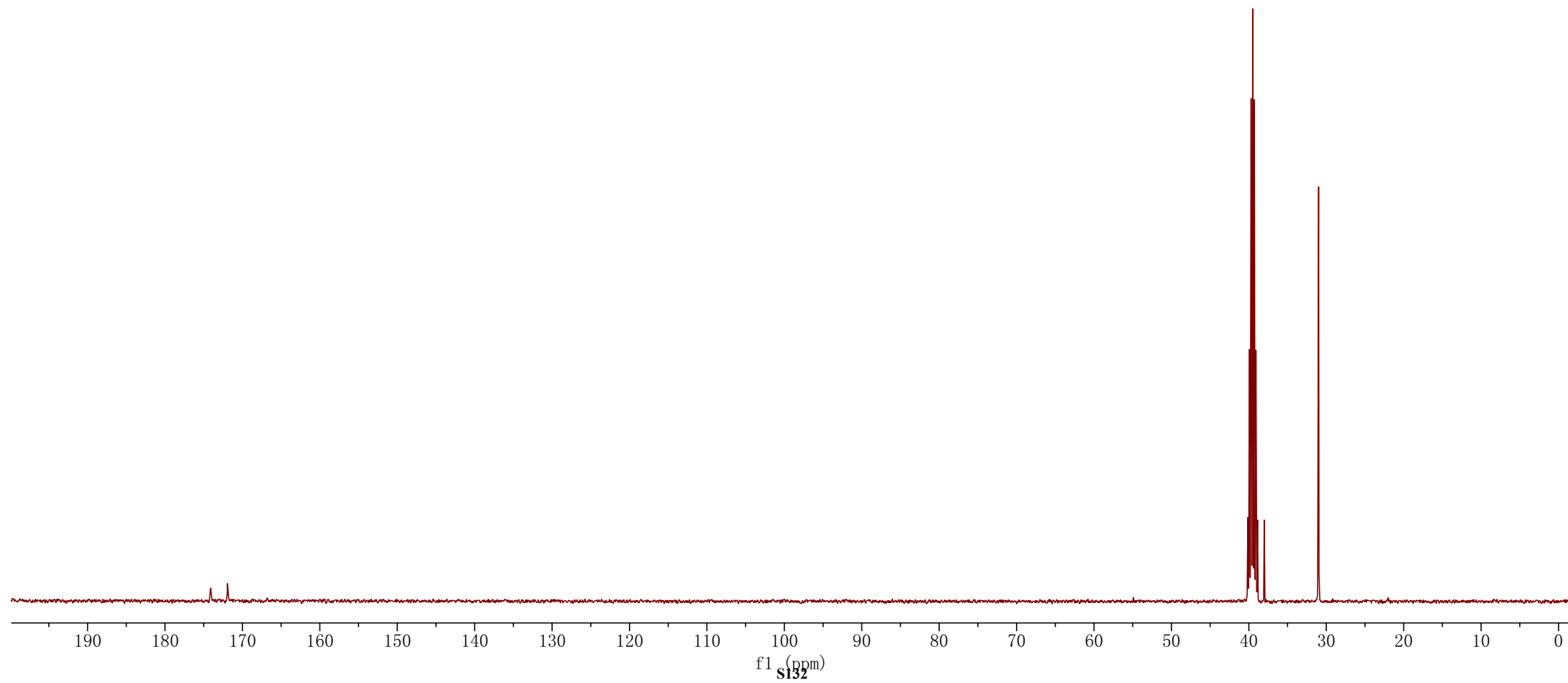
wzy-20201026-2



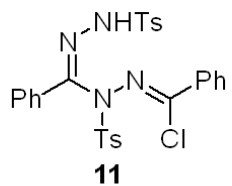
174.11
171.91

39.92
39.71
39.50
39.29
39.08
38.01
30.98

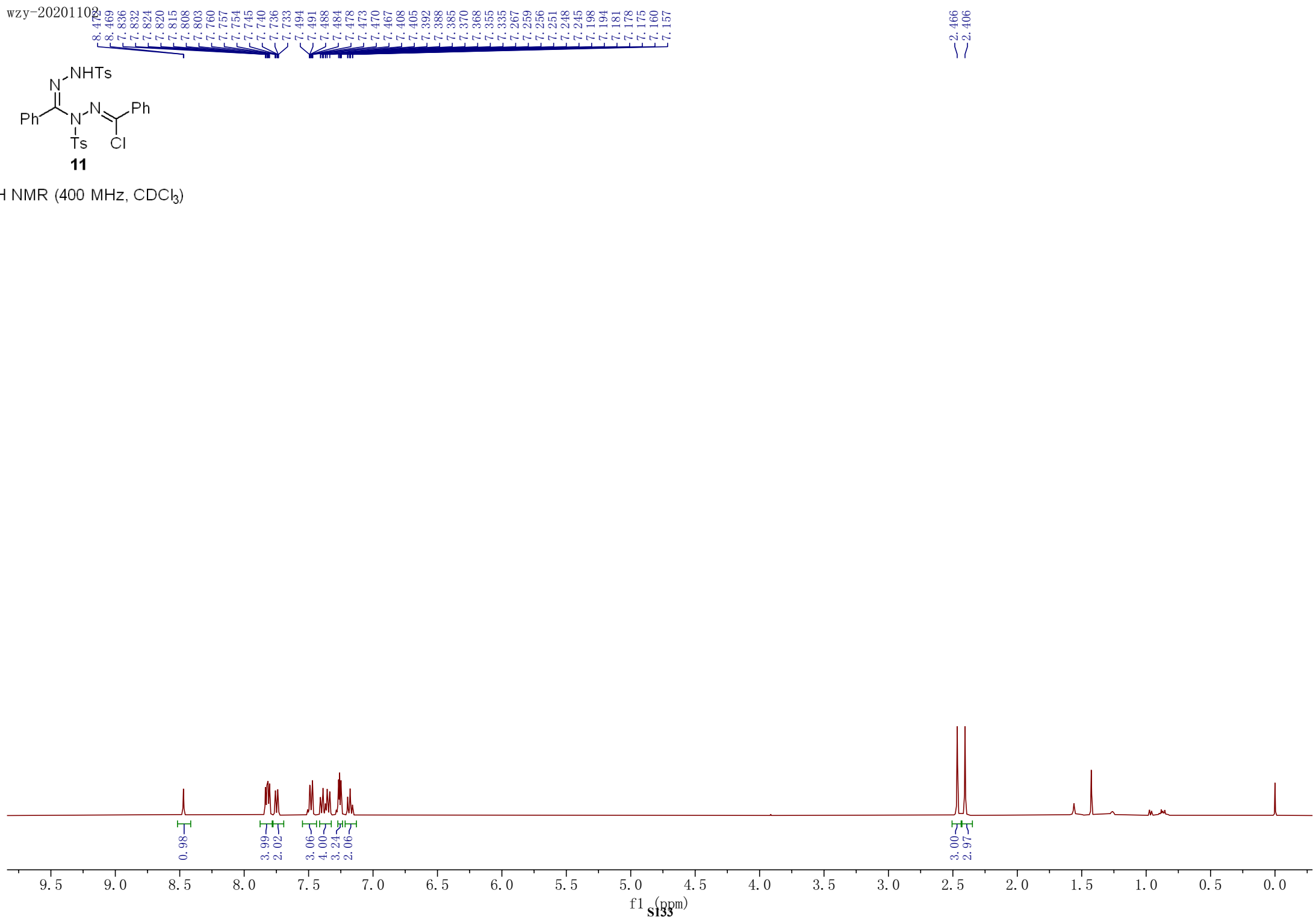
^{13}C NMR (100 MHz, DMSO- d_6)



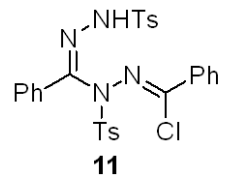
wzy-20201103



¹H NMR (400 MHz, CDCl₃)



wzy-001

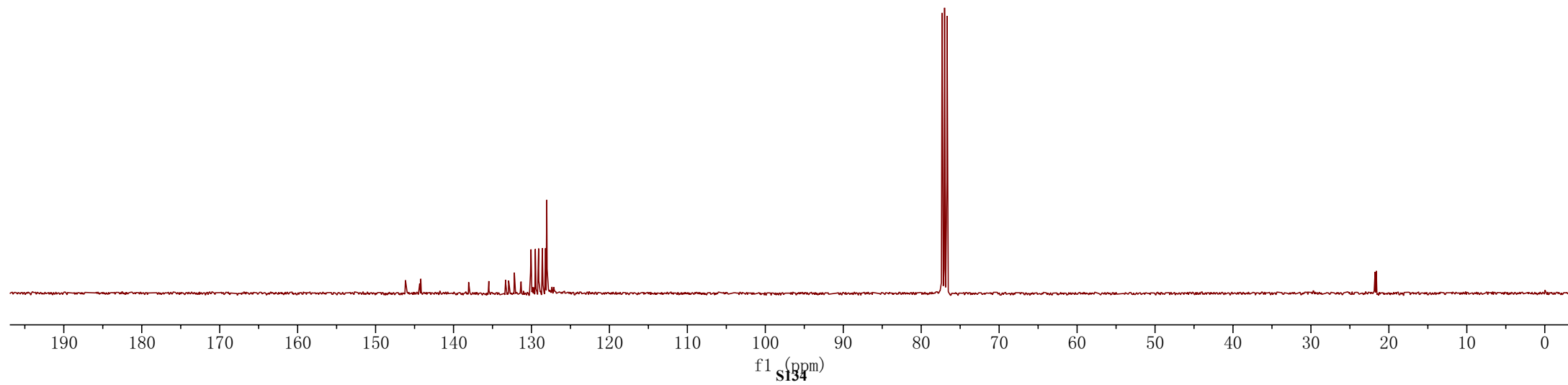


^{13}C NMR (100 MHz, CDCl_3)

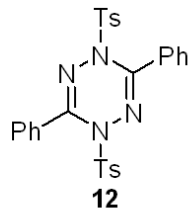
146.17
144.35
144.20
138.06
135.47
133.32
132.93
132.20
131.34
130.12
130.05
129.51
129.08
128.61
128.51
128.20
128.04
128.02

77.32
77.00
76.68

21.77
21.61



wzy-200518-2

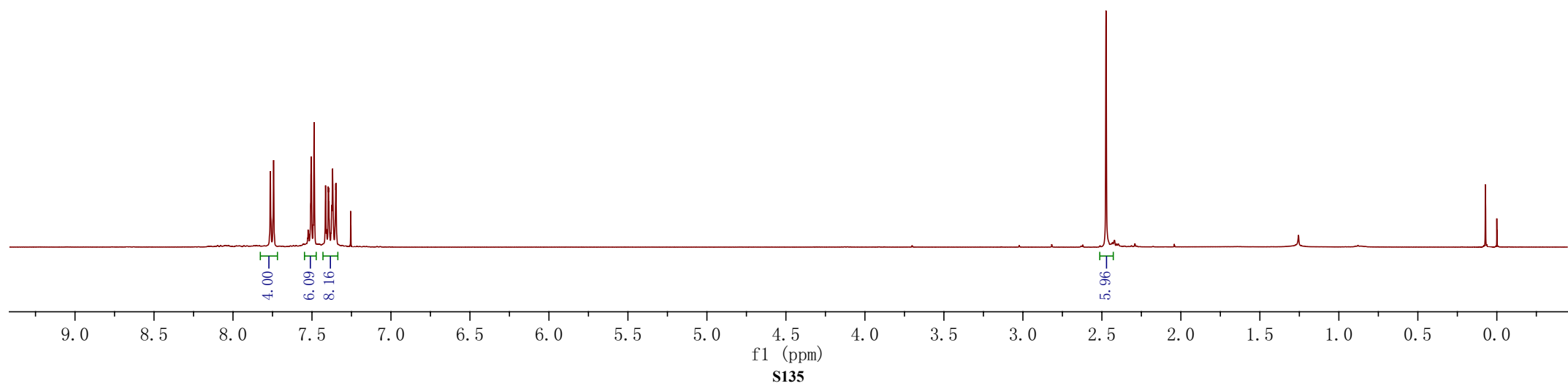


7.764
7.743
7.505
7.504
7.486
7.414
7.397
7.395
7.393
7.376
7.374
7.371
7.369
7.349
7.348
7.255

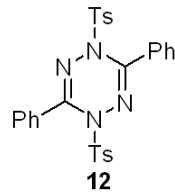
2.474

0.073
0.071
0.000

¹H NMR (400 MHz, CDCl₃)



wzy-200518-2



— 154.61

— 145.61

134.42
131.57
129.72
129.70
128.85
128.64
128.25

77.32
77.00
76.68

— 21.77

¹³C NMR (100 MHz, CDCl₃)

