Supplementary Information (SI) for Green Chemistry.

Supporting Information

Organocatalytic electrochemical synthesis of *α*-quaternary amino aldehydes

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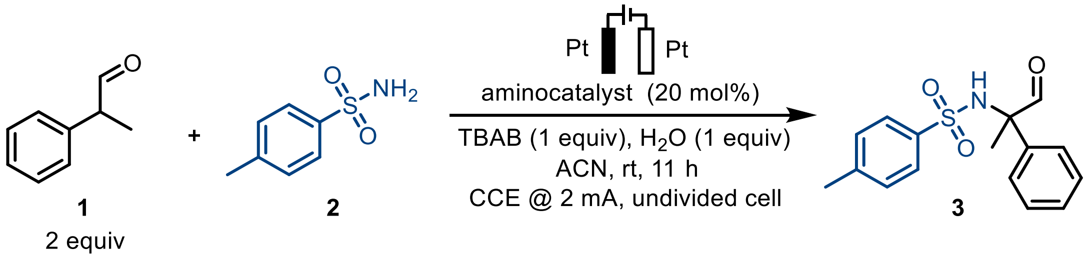
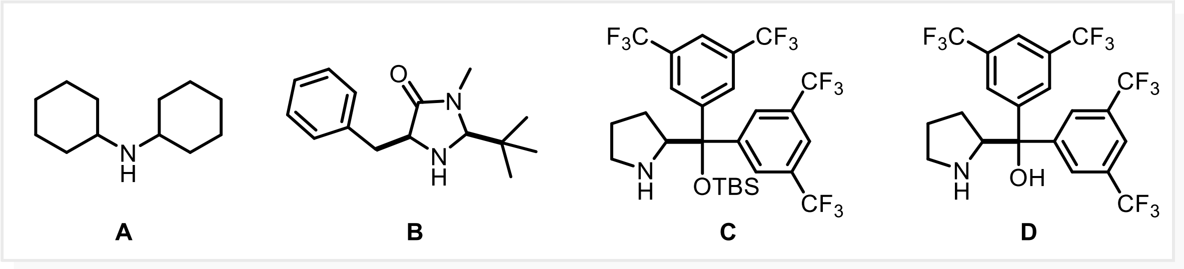
I. General Information

Electroreductive reactions were carried out in undivided electrochemical cells (10 mL) using pre-dried glassware, if not noted otherwise. Platinum electrodes (10 mm × 15 mm × 0.20 mm, 99.9%; obtained from Chuxi, Shanghai, China) were connected using stainless steel adapters. Electroreduction was conducted using an HSPY-36-03 potentiostat in constant current mode. Cyclic Voltammetry studies were performed using a Shanghai Chenhua CHI630E workstation and Nova 2.0 software. Flash column chromatography was performed over silica gel (200-300 mesh) purchased from Qindao Haiyang Chemical Co., China. Anhydrous tetrahydrofuran were purchased from Energy Chemical or Adamas. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. ^{1}H and ^{13}C spectra were collected on a Bruker AV 300 MHz, 400 MHz or 800 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm, Acetone-d_6 at 2.09 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm, DMSO-d_6 at 39.5 ppm, Acetone-d_6 at 30.6 ppm). High resolution mass spectrometric data were obtained on Waters G2-XS QTOf UPLC/MS spectrometer (ESI-TOF), AB_Triple TOF 5600 UPLC/MS spectrometer (ESI-TOF), and FTICR-mass spectrometer.

II. Optimization of the reaction conditions

Table S1. Optimization of aminocatalyst.[a]

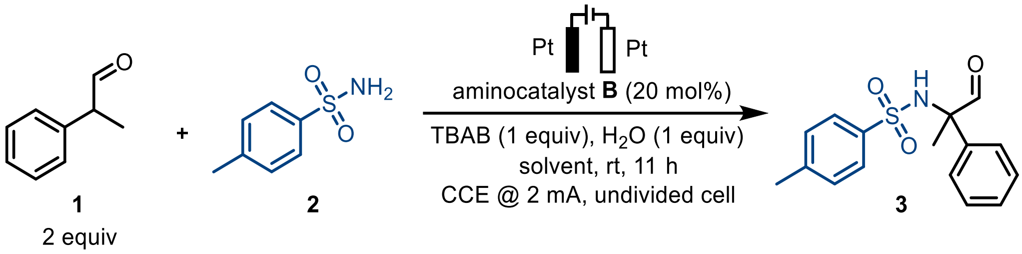




Entry	Aminocatalyst	Yield of **3** (%)[b]	Recovery of **2** (%)[b]
1	**A**	58	4
2	**B**	**82**	**0**
3	**C**	14	25
4	**D**	40	21

[a] Reaction conditions: undivided cell, 2-phenylpropanal **1** (0.4 mmol), *p*-toluenesulfonamide **2** (0.2 mmol), TBAB (0.2 mmol), H_2O (0.2 mmol), and racemic aminocatalyst (0.04 mmol) were stirred in ACN (2 mL) under 2 mA constant current in argon atmosphere at room temperature for 11 h with platinum plates (each 1.0 × 1.5 cm^2) as anode and cathode. [b] NMR yield determined by NMR using mesitylene as the internal standard.

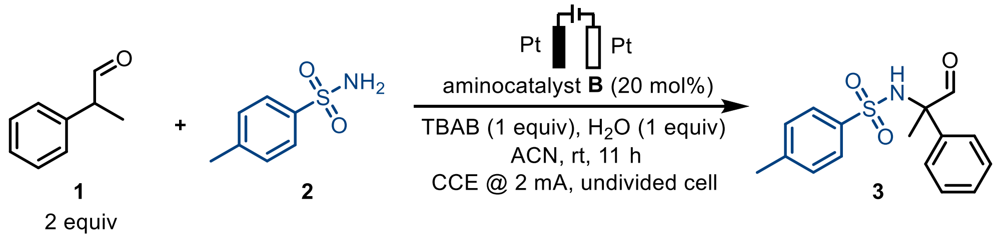
Table S2. Optimization of the solvent.[a]



Entry	Solvent	Yield of **3** (%)[b]	Recovery of **2** (%)[b]
1	**ACN**	**82**	**0**
2	DCM	70	5
3	THF	64	24
4	DMSO	15	50
5	DMF	21	67
6	DCE	46	0

[a] Reaction conditions: undivided cell, 2-phenylpropanal **1** (0.4 mmol), *p*-toluenesulfonamide **2** (0.2 mmol), TBAB (0.2 mmol), H_2O (0.2 mmol), and racemic aminocatalyst **B** (0.04 mmol) were stirred in solvent (2 mL) under 2 mA constant current in argon atmosphere at room temperature for 11 h with platinum plates (each 1.0 × 1.5 cm^2) as anode and cathode. [b] NMR yield determined by NMR using mesitylene as the internal standard.

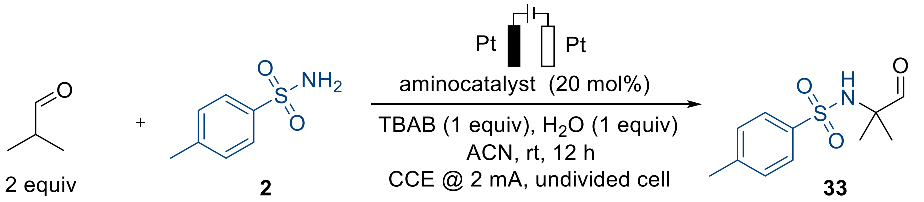
Table S3. Further optimization.[a]

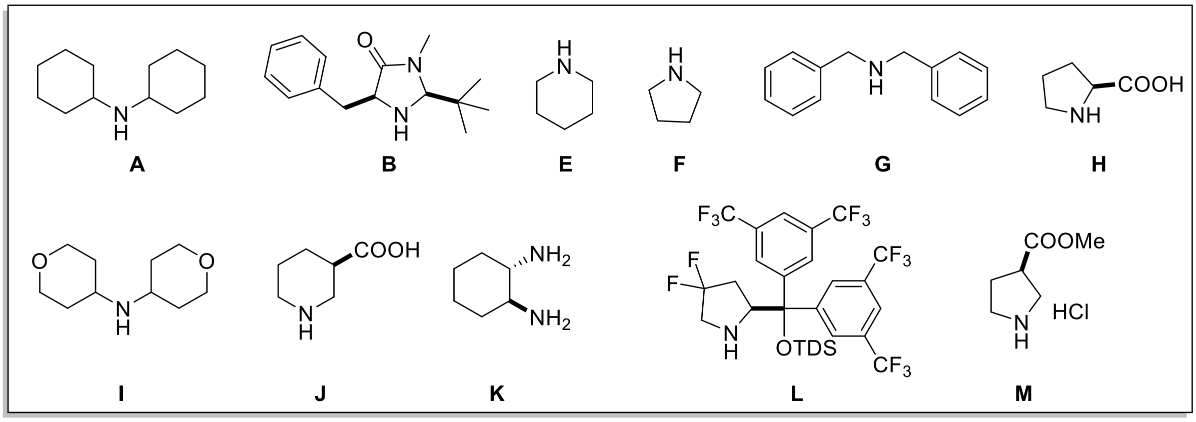


Entry	*Variation from the standard conditions*	Yield of **3** (%)[b]	Recovery of **2** (%)[b]
1	-	**82**	0
2	No electricity	0	94
3	No Catalyst	40	50
4	No H_2O	35	23
5	Ferrocene as mediator	0	50
6	TEMPO as mediator	36	27
7	GF as anode	3	70
8	CF as anode	1	58
9	Cu as anode	0	81
10	Pb as cathode	5	91
11	TEAB as electrolyte	67	29
12	TBAP as electrolyte	0	98
13	TBAI as electrolyte	28	37
14	$n\text{Bu}_4\text{PF}_6$ as electrolyte	0	99
15	TBABF_4 as electrolyte	0	95
16	1 mA (12 h)	17	75
17	3 mA (8 h)	51	33

[a] Reaction conditions: undivided cell, 2-phenylpropanal **1** (0.4 mmol), *p*-toluenesulfonamide **2** (0.2 mmol), TBAB (0.2 mmol), H_2O (0.2 mmol), and racemic aminocatalyst **B** (0.04 mmol) were stirred in ACN (2 mL) under 2 mA constant current in argon atmosphere at room temperature for 11 h with platinum plates (each 1.0 × 1.5 cm^2) as anode and cathode. [b] NMR yield determined by NMR using mesitylene as the internal standard.

Table S4. Optimization for *α*,*α*-dialkyl substituted aldehydes.[a]



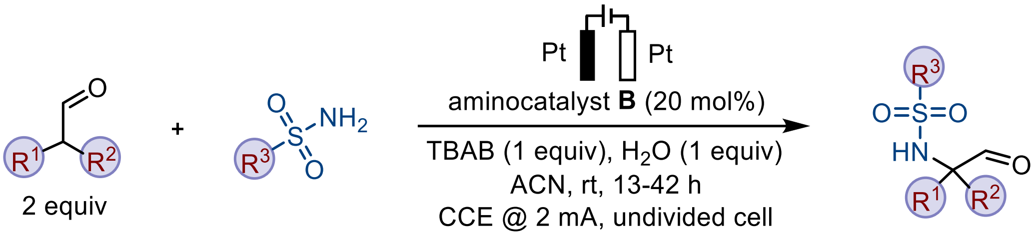


Entry	Aminocatalyst	Concentraction (mol/L)	Yield of **33** (%)[b]	Recovery of **2** (%)[b]
1	**A**	0.05	56	13
2	**E**	0.05	6	48
3	**F**	0.05	8	42
4	**G**	0.05	5	55
5	**A**	0.1	59	3
6	**B**	0.1	6	90
7	**H**	0.1	17	45
8	**I**	0.1	56	5
9	**J**	0.1	42	38
10	**K**	0.1	36	31
11	**L**	0.1	6	50
12	**M**	0.1	6	40
13	**A (30 mol%)**	**0.1**	**70**	**0**
14	-	0.1	13	51

[a] Reaction conditions: undivided cell, isobutyraldehyde (0.4 mmol), *p*-toluenesulfonamide **2** (0.2 mmol), TBAB (0.2 mmol), H_2O (0.2 mmol), and racemic aminocatalyst (0.04 mmol) were stirred in ACN (2 or 4 mL) under 2 mA constant current in argon atmosphere at room temperature for 12 h with platinum plates (each 1.0 × 1.5 cm^2) as anode and cathode. [b] NMR yield determined by NMR using mesitylene as the internal standard.

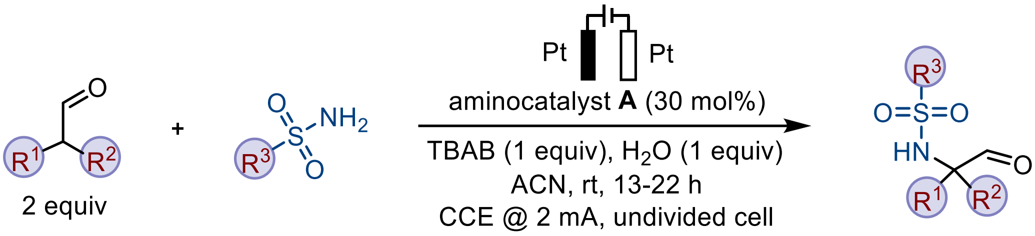
III. Products Purification and Characterization Data

General Procedure I.



The electrocatalysis was carried out in an undivided cell with a platinum plate anode (10.0 mm × 15.0 mm × 0.2 mm) and a platinum plate cathode (10.0 mm × 15.0 mm × 0.2 mm). Under argon, to a 10 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added sulfonamide (0.4 mmol, 1.0 equiv), racemic aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), tetrabutylammonium bromide (128.9 mg, 0.4 mmol, 1.0 equiv). Then H_2O (0.4 mmol, 1.0 equiv, 7.2 uL), aldehyde (0.8 mmol, 2.0 equiv), and ACN (4 mL) were added. The electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 13-42 h. After the reaction was completed, the solution was concentrated and purified by silica gel flash column chromatography to afford the pure product.

General Procedure II.



The electrocatalysis was carried out in an undivided cell with a platinum plate anode (10.0 mm × 15.0 mm × 0.2 mm) and a platinum plate cathode (10.0 mm × 15.0 mm × 0.2 mm). Under argon, to a 10 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added sulfonamide (0.4 mmol, 1.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), tetrabutylammonium bromide (128.9 mg, 0.4 mmol, 1.0 equiv). Then H_2O (0.4 mmol, 1.0 equiv, 7.2 uL), aldehyde (0.8 mmol, 2.0 equiv), and ACN (4 mL) were added. The electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 13-22 h. After the reaction was completed, the solution was concentrated and purified by silica gel flash column chromatography to afford the pure product.

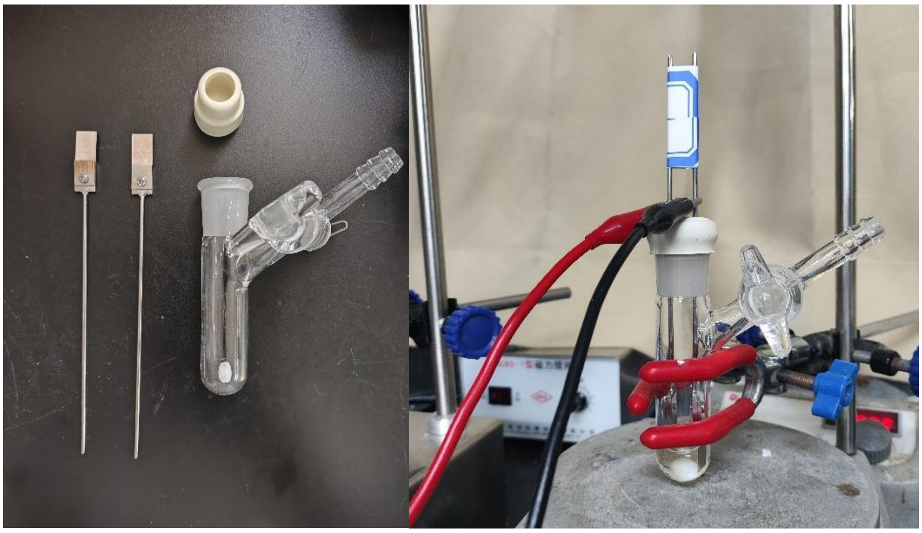
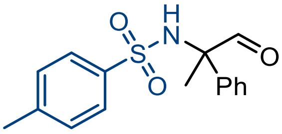


Figure S1. Electrolysis set-up.

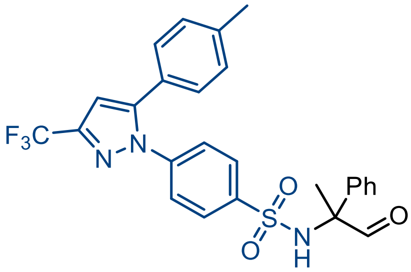


3

4-Methyl-*N*-(1-oxo-2-phenylpropan-2-yl)benzenesulfonamide (3) was prepared as a white solid from 4-methylbenzenesulfonamide **2** (69.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (129.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1, 103.7 mg, 85% yield). The NMR data are in consistent with the reported literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.25-7.10 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.03 (s, 1H), 2.34 (s, 3H), 1.87 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3, 142.7, 139.0, 134.0, 129.1, 128.7, 128.5, 127.4, 126.5, 66.7, 21.3, 19.9 ppm.



4

N**-(1-Oxo-2-phenylpropan-2-yl)-4-(5-(*****p*****-tolyl)-3-(trifluoromethyl)-1*****H*****-pyrazol-1-yl)benzenesulfonamide (4)** was prepared as a white solid from Celecoxib (153.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (130.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 42 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 10/1 to 5/1, 174.6 mg, 85% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.27-7.13 (m, 7H), 7.14-7.02 (m, 4H), 6.72 (s, 1H), 6.17 (s, 1H), 2.37 (s, 3H), 1.90 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.0, 145.0, 143.8 (q, *J* = 38.3 Hz), 141.8, 141.3, 139.7, 133.5, 129.6, 129.0, 128.9, 128.6, 127.6, 127.5, 125.7, 124.9, 121.6 (q, *J* = 267.0 Hz), 106.2, 66.8, 21.2, 19.9 ppm.

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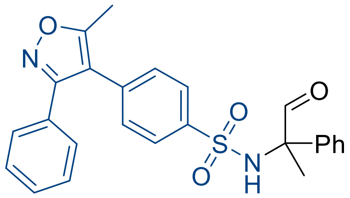
[1] H. Vogt, T. Baumann, M. Nieger and S. Bräse, *Eur. J. Org. Chem.*, 2006, **23**, 5315–5338.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 ppm.

HRMS (ESI) m/z Calcd for $C_{26}H_{23}F_3N_3O_3S$ [M$^+$+H]: 514.1407, Found: 514.1408.



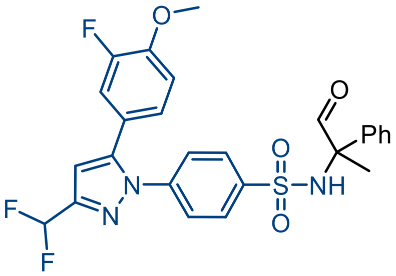
5

4-(5-Methyl-3-phenylisoxazol-4-yl)-*N*-(1-oxo-2-phenylpropan-2-yl)benzenesulfonamide (5) was prepared as a white solid from Valdecoxib (126.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (130.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 10/1 to 6/1, 170.8 mg, 84% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.46-7.29 (m, 7H), 7.21-7.10 (m, 5H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.21 (s, 1H), 2.45 (s, 3H), 1.94 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1, 167.0, 160.9, 140.9, 134.3, 133.7, 129.6, 128.67, 128.65, 128.6, 128.4, 128.3, 127.7, 126.9, 114.4, 66.7, 20.0, 11.6 ppm.

HRMS (ESI) m/z Calcd for $C_{25}H_{22}N_2NaO_4S$ [M$^+$+Na]: 469.1192, Found: 469.1194.



6

4-(3-(Difluoromethyl)-5-(3-fluoro-4-methoxyphenyl)-1*H*-pyrazol-1-yl)-*N*-(1-oxo-2-

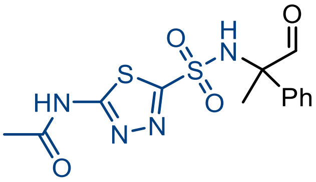
phenylpropan-2-yl)benzenesulfonamide (6) was prepared as a white solid from Deracoxib (159.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (130.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 6/1 to 4/1, 186.3 mg, 86% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.26-7.16 (m, 5H), 7.15-7.08 (m, 2H), 6.99-6.84 (m, 3H), 6.76 (t, *J* = 54.8 Hz, 1H), 6.68 (s, 1H), 6.23 (s, 1H), 3.89 (s, 3H), 1.89 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.0, 151.9 (d, *J* = 246.8 Hz), 148.4 (d, *J* = 9.8 Hz), 148.0 (t, *J* = 29.6 Hz), 143.5, 141.8, 141.1, 133.6, 128.9, 128.8, 127.5, 125.0 (d, *J* = 3.0 Hz), 124.6, 121.6 (d, *J* = 6.8 Hz), 116.4 (d, *J* = 20.3 Hz), 113.5 (d, *J* = 1.5 Hz), 110.9 (t, *J* = 233.3 Hz), 105.6, 66.7, 56.1, 19.8 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -112.2, -133.4 ppm.

HRMS (ESI) m/z Calcd for $C_{26}H_{23}F_3N_3O_4S$ [M^++H]: 530.1356, Found: 530.1359.



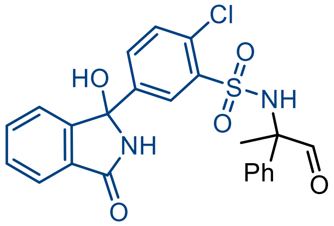
7

***N*-(5-(*N*-(1-Oxo-2-phenylpropan-2-yl)sulfamoyl)-1,3,4-thiadiazol-2-yl)acetamide (7)** was prepared as a white solid from Acetazolamide (89.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), TBAB (130.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 10/1, 72.3 mg, 51% yield).

^{1}H NMR (300 MHz, Acetone-*d*$_6$) *δ* 12.15 (s, 1H), 9.66 (s, 1H), 8.32 (s, 1H), 7.54-7.27 (m, 5H), 2.37 (s, 3H), 1.92 (s, 3H) ppm.

^{13}C NMR (75 MHz, Acetone-*d*$_6$) *δ* 196.8, 170.5, 165.5, 163.4, 137.9, 130.4, 130.1, 128.8, 69.6, 23.4, 21.8 ppm.

HRMS (ESI) m/z Calcd for $C_{13}H_{15}N_4O_4S_2$ [M$^+$+H]: 355.0529, Found: 355.0527.



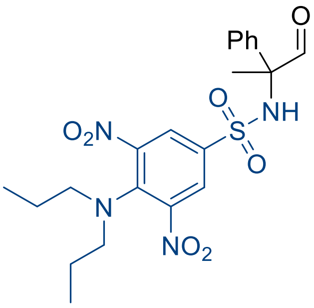
8

2-Chloro-5-(1-hydroxy-3-oxoisoindolin-1-yl)-*N*-(1-oxo-2-phenylpropan-2-yl)benzenesulfonamide (8) was prepared as a white solid from Chlortalidone (137.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.8 mg, 0.08 mmol, 0.2 equiv), TBAB (131.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 2/1 to 9/7, 177.1 mg, 94% yield, dr: 1/1).

^{1}H NMR (300 MHz, DMSO-*d*$_6$) *δ* [9.59 (s, 0.45H), 9.53 (s, 0.49H), 1H], 9.36 (d, *J* = 1.4 Hz, 1H), [8.86 (s, 0.44H), 8.76 (s, 0.46H), 1H], [7.90 (d, *J* = 1.9 Hz, 0.48H), 7.87 (d, *J* = 2.1 Hz, 0.5H), 1H], 7.73-7.50 (m, 5H), 7.34-7.04 (m, 7H), [1.59 (s, 1.5H), 1.52 (s, 1.39H), 3H] ppm.

^{13}C NMR (75 MHz, DMSO-*d*$_6$) *δ* 197.0, 196.6, 168.34, 168.31, 149.8, 142.0, 141.91, 139.5, 139.4, 136.6, 136.3, 132.7, 131.74, 131.71, 131.2, 131.1, 130.61, 130.56, 129.9, 129.4, 128.4, 128.3, 128.2, 126.8, 126.74, 126.71, 122.81, 122.77, 86.61, 86.60, 67.4, 67.3, 21.14, 21.09 ppm.

HRMS (ESI) m/z Calcd for $C_{23}H_{19}ClN_2NaO_5S$ [M$^+$+Na]: 493.0595, Found: 493.0599.



9

4-(Dipropylamino)-3,5-dinitro-*N*-(1-oxo-2-phenylpropan-2-yl)benzenesulfonamide (9) was prepared as a reddish-brown solid from Oryzalin (139.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.6 mg, 0.08 mmol, 0.2 equiv), TBAB (129.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 36 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1, 102.0 mg, 53% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.60 (s, 2H), 7.22-7.13 (m, 3H), 7.10-7.01 (m, 2H), 6.34 (s, 1H), 2.97 (dt, J_1 = 14.3 Hz, J_2 = 7.1 Hz, 2H), 2.81 (dt, J_1 = 13.7 Hz, J_2 = 7.4 Hz, 2H), 2.04 (s, 3H), 1.58 (h, J = 7.3 Hz, 4H), 0.90 (t, J = 7.4 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 144.0, 140.8, 131.9, 131.8, 129.4, 128.8, 128.2, 128.1, 66.4, 54.0, 20.7, 19.8, 11.2 ppm.

HRMS (ESI) m/z Calcd for $C_{21}H_{27}N_4O_7S$ [M^++H]: 479.1595, Found: 479.1597.

10

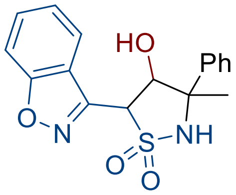
5-(Dimethylamino)-*N*-(1-oxo-2-phenylpropan-2-yl)naphthalene-1-sulfonamide (10) was prepared as a yellow solid from Dansylamide (100.1 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (129.1 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2

uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 5.0 mA, 13 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 10/1, 107.4 mg, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.32 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.6 Hz, 1H), 7.65-7.55 (m, 2H), 7.19-6.99 (m, 3H), 6.94-6.80 (m, 4H), 6.26 (s, 1H), 2.86 (s, 6H), 1.88 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1, 151.8, 136.5, 133.0, 129.7, 129.4, 129.0, 128.8, 128.5, 128.4, 128.2, 127.2, 123.0, 118.4, 114.9, 66.7, 45.3, 19.9 ppm.

HRMS (ESI) m/z Calcd for $C_{21}H_{23}N_2O_3S$ [M^++H]: 383.1424, Found: 383.1424.



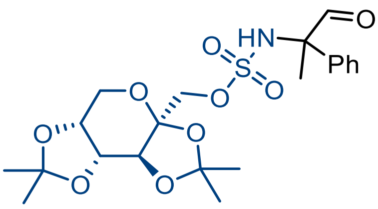
11

5-(Benzo[*d*]isoxazol-3-yl)-4-hydroxy-3-methyl-3-phenylisothiazolidine 1,1-dioxide (11) was prepared as a white solid from Zonisamide (85.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (130.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 42 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 7/1 to 5/1, 102.0 mg, 87% yield, dr: 11.5/1).

^{1}H NMR (300 MHz, Acetone-d_6) δ [8.22 (d, *J* = 8.2 Hz, 0.08H), 7.98 (d, *J* = 8.0 Hz, 0.92H), 1H], 7.82-7.60 (m, 4H), 7.47-7.22 (m, 5H), [5.78 (d, *J* = 6.3 Hz, 0.84H), 5.62 (d, *J* = 5.0 Hz, 0.07H), 1H], 5.37 (dd, J_1 = 10.6 Hz, J_2 = 6.2 Hz, 1H), [5.25 (d, *J* = 10.6 Hz, 1H), 4.83 (d, *J* = 3.9 Hz, 0.07H), 1H], [1.92 (s, 2.73H), 1.78 (s, 0.23H), 3H] ppm.

^{13}C NMR (75 MHz, Acetone-d_6) δ 165.4, 152.2, 147.3, 132.2, 129.9, 128.9, 126.9, 125.6, 124.5, 122.4, 111.4, 79.2, 66.3, 62.8, 24.2 ppm. (only major isomer was reported)

HRMS (ESI) m/z Calcd for $C_{17}H_{17}N_2O_4S$ [M^++H]: 345.0904, Found: 345.0904.



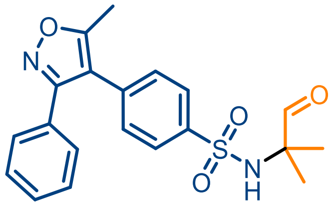
12

((3a*S*,5a*R*,8a*R*,8b*S*)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl (1-oxo-2-phenylpropan-2-yl)sulfamate (12) was prepared as a colorless oil from Topiramate (136.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (130.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1 to 6/1, 97.0 mg, 51% yield, dr: about 1/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.22 (s, 1H), 7.48-7.32 (m, 5H), 6.20 (s, 1H), 4.63-4.55 (m, 1H), 4.25-4.04 (m, 4H), 3.93-3.82 (m, 1H), 3.74 (dd, J_1 = 13.0 Hz, J_2 = 7.0 Hz, 1H), 1.98 (s, 3H), [1.53 (s, 1.52H), 1.52 (s, 1.44H), 3H], 1.45 (s, 3H), 1.37-1.30 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1, 135.5, 129.2, 128.9, 126.94, 126.91, 109.2, 109.13, 109.11, 100.7, 70.7, 70.6, 70.5, 70.4, 70.2, 70.1, 69.8, 67.2, 67.1, 61.3, 61.2, 26.4, 26.3, 25.80, 25.76, 25.1, 25.0, 24.00, 23.97, 18.8, 18.7 ppm.

HRMS (ESI) m/z Calcd for $C_{21}H_{29}NNaO_9S$ [M^++Na]: 494.1455, Found: 494.1456.



13

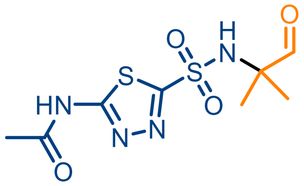
***N*-(2-Methyl-1-oxopropan-2-yl)-4-(5-methyl-3-phenylisoxazol-4-**

yl)benzenesulfonamide (13) was prepared as a white solid from Valdecoxib (127.0 mg, 0.4 mmol, 1.0 equiv), isobutyraldehyde (57.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.3 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 6/1 to 4/1, 108.5 mg, 71% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.44-7.25 (m, 7H), 5.85 (s, 1H), 2.48 (s, 3H), 1.31 (s, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 167.2, 161.0, 141.5, 135.1, 130.2, 129.7, 128.6, 128.4, 127.2, 114.4, 62.4, 22.3, 11.6 ppm.

HRMS (ESI) m/z Calcd for $C_{20}H_{21}N_2O_4S$ [M^++H]: 385.1217, Found: 385.1217.



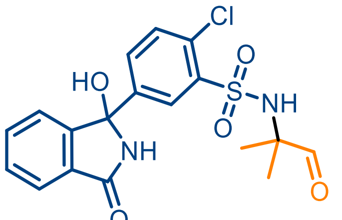
14

***N*-(5-(*N*-(2-Methyl-1-oxopropan-2-yl)sulfamoyl)-1,3,4-thiadiazol-2-yl)acetamide (14)** was prepared as a white solid from Acetazolamide (88.9 mg, 0.4 mmol, 1.0 equiv), isobutyraldehyde (57.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.1 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (15 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 2/1 to 1/1, 79.1 mg, 68% yield).

^{1}H NMR (300 MHz, Acetone-*d*$_6$) δ 11.96 (s, 1H), 9.62 (s, 1H), 8.01 (s, 1H), 2.38 (s, 3H), 1.37 (s, 6H) ppm.

^{13}C NMR (75 MHz, Acetone-*d*$_6$) δ 201.0, 170.6, 165.7, 163.2, 64.7, 23.39, 23.35 ppm.

HRMS (ESI) m/z Calcd for $C_8H_{13}N_4O_4S_2$ [M^++H]: 293.0373, Found: 293.0376.



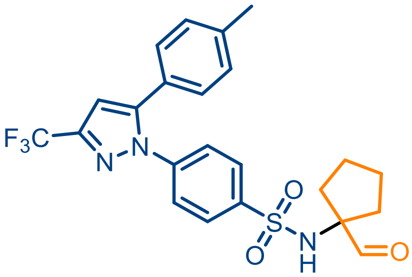
15

2-Chloro-5-(1-hydroxy-3-oxoisoindolin-1-yl)-*N*-(2-methyl-1-oxopropan-2-yl)benzenesulfonamide (15) was prepared as a white solid from Chlortalidone (136.0 mg, 0.4 mmol, 1.0 equiv), isobutyraldehyde (57.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.9 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (17 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 2/1 to 1/1, 132.1 mg, 81% yield).

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 9.47 (s, 2H), 8.70 (s, 1H), 8.09 (s, 1H), 7.75-7.62 (m, 3H), 7.61-7.47 (m, 2H), 7.38-7.23 (m, 2H), 1.05 (s, 6H) ppm.

^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ 200.7, 168.4, 150.0, 142.2, 140.1, 132.8, 132.0, 131.1, 130.6, 130.0, 129.5, 126.9, 122.9, 122.6, 86.6, 61.9, 21.8, 21.6 ppm.

HRMS (ESI) m/z Calcd for $C_{18}H_{17}ClN_2NaO_5S$ [M$^+$+Na]: 431.0439, Found: 431.0440.



16

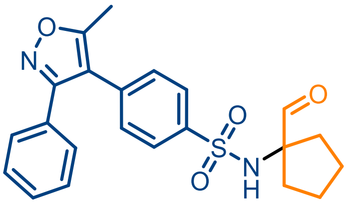
***N*-(1-Formylcyclopentyl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (16)** was prepared as a white solid from Celecoxib (153.0 mg, 0.4 mmol, 1.0 equiv), cyclopentanecarbaldehyde (78.5 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (16 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 9/1, 133.0 mg, 70% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.21-7.05 (m, 4H), 6.75 (s, 1H), 5.84 (s, 1H), 2.37 (s, 3H), 2.06-1.90 (m, 2H), 1.78-1.55 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 145.3, 144.0 (q, *J* = 38.3 Hz), 142.4, 141.4, 139.8, 129.7, 128.7, 127.8, 125.6, 125.5, 121.0 (q, *J* = 267.5 Hz), 106.2, 73.0, 33.9, 23.8, 21.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4 ppm.

HRMS (ESI) m/z Calcd for $C_{23}H_{23}F_3N_3O_3S$ [M$^+$+H]: 478.1407, Found: 478.1410.



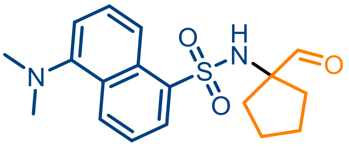
17

***N*-(1-Formylcyclopentyl)-4-(5-methyl-3-phenylisoxazol-4-yl)benzenesulfonamide (17)** was prepared as a white solid from Valdecoxib (126.0 mg, 0.4 mmol, 1.0 equiv), cyclopentanecarbaldehyde (78.5 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.3 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (16 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1 to 4/1, 129.7 mg, 79% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.44-7.23 (m, 7H), 6.02 (s, 1H), 2.49 (s, 3H), 2.05-1.91 (m, 2H), 1.84-1.53 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.7, 167.2, 161.0, 141.0, 135.2, 130.2, 129.7, 128.6, 128.34, 128.26, 127.2, 114.4, 73.0, 33.9, 23.6, 11.7 ppm.

HRMS (ESI) m/z Calcd for $C_{22}H_{23}N_2O_4S$ [M$^+$+H]: 411.1373, Found: 411.1375.



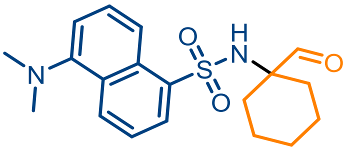
18

5-(Dimethylamino)-*N*-(1-formylcyclopentyl)naphthalene-1-sulfonamide (18) was prepared as a green solid from Dansylamide (100.0 mg, 0.4 mmol, 1.0 equiv), cyclopentanecarbaldehyde (78.5 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.7 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (16 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 9/1, 92.6 mg, 67% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 8.24 (d, *J* = 7.3 Hz, 1H), 7.55 (dt, J_1 = 21.7 Hz, J_2 = 7.9 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.04 (s, 1H), 2.89 (s, 6H), 1.96-1.81 (m, 2H), 1.70-1.56 (m, 2H), 1.54-1.30 (m, 4H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 152.0, 137.0, 130.6, 129.7, 129.4, 128.9, 128.5, 123.2, 118.6, 115.2, 73.1, 45.4, 33.8, 23.5 ppm.

HRMS (ESI) m/z Calcd for $C_{18}H_{22}N_2NaO_3S$ [M$^+$+Na]: 369.1243, Found: 369.1242.



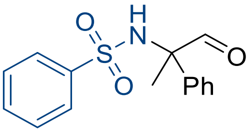
19

5-(Dimethylamino)-*N*-(1-formylcyclohexyl)naphthalene-1-sulfonamide (19) was prepared as a green solid from Dansylamide (100.4 mg, 0.4 mmol, 1.0 equiv), cyclohexanecarbaldehyde (89.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.2 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (16 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 9/1, 124.1 mg, 86% yield).

^{1}H NMR (300 MHz, CDCl$_3$) *δ* 9.69 (s, 1H), 8.55 (d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 8.6 Hz, 1H), 8.28 (d, *J* = 7.3 Hz, 1H), 7.64 (t, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.34 (s, 1H), 2.89 (s, 6H), 1.66 (d, *J* = 13.8 Hz, 2H), 1.51 (t, *J* = 11.4 Hz, 2H), 1.28-1.14 (m, 3H), 1.10-0.78 (m, 3H) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) *δ* 201.3, 151.9, 136.9, 130.5, 129.5, 129.4, 128.9, 128.5, 123.1, 118.4, 115.1, 65.5, 45.3, 29.6, 24.5, 20.2 ppm.

HRMS (ESI) m/z Calcd for $C_{19}H_{24}N_2NaO_3S$ [M$^+$+Na]: 383.1400, Found: 383.1400.



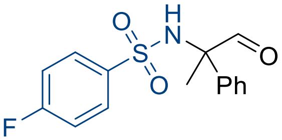
20

***N*-(1-Oxo-2-phenylpropan-2-yl)benzenesulfonamide (20)** was prepared as a colorless oil from benzenesulfonamide (63.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), TBAB (129.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1, 93.9 mg, 81% yield).

^{1}H NMR (300 MHz, CDCl$_3$) *δ* 9.12 (s, 1H), 7.48-7.36 (m, 3H), 7.29-7.07 (m, 7H), 6.10 (s, 1H), 1.90 (s, 3H) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) *δ* 194.2, 141.8, 133.6, 131.9, 128.74, 128.65, 128.5, 127.5, 126.5, 66.7, 19.9 ppm.

HRMS (ESI) m/z Calcd for $C_{15}H_{15}NNaO_3S$ [M$^+$+Na]: 312.0665, Found: 312.0664.



21

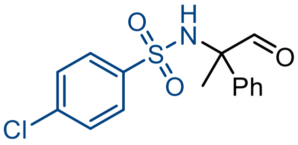
4-Fluoro-*N*-(1-oxo-2-phenylpropan-2-yl)benzenesulfonamide (21) was prepared as a colorless oil from 4-fluorobenzenesulfonamide (70.3 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.8 mg, 0.08 mmol, 0.2 equiv), TBAB (129.3 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 10/1, 104.6 mg, 85% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.41 (dd, J_1 = 8.7 Hz, J_2 = 5.1 Hz, 2H), 7.30-7.12 (m, 3H), 7.12-7.03 (m, 2H), 6.88 (t, J = 8.6 Hz, 2H), 6.17 (s, 1H), 1.92 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.0, 164.4 (d, J = 254.1 Hz), 137.9 (d, J = 3.2 Hz), 133.3, 129.2 (d, J = 9.4 Hz), 128.8, 127.6, 115.6 (d, J = 22.6 Hz), 66.6, 19.9 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -106.3 ppm.

HRMS (ESI) m/z Calcd for $C_{15}H_{14}FNNaO_3S$ [M^++Na]: 330.0571, Found: 330.0572.



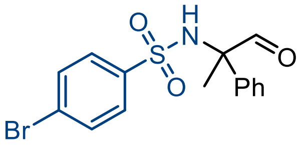
22

4-Chloro-*N*-(1-oxo-2-phenylpropan-2-yl)benzenesulfonamide (22) was prepared as white solid from 4-chlorobenzenesulfonamide (77.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), TBAB (129.1 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) electrocatalysis was performed with a constant current of 2.0 mA according to the General Procedure I (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 10/1, 91.7 mg, 71% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.36-7.29 (m, 2H), 7.28-7.21 (m, 1H), 7.21-7.14 (m, 4H), 7.09-7.03 (m, 2H), 6.17 (s, 1H), 1.93 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 140.3, 138.3, 133.2, 128.8, 128.7, 128.0, 127.7, 66.6, 19.9 ppm.

HRMS (ESI) m/z Calcd for $C_{15}H_{14}ClNNaO_3S$ [M^++Na]: 346.0275, Found: 346.0277.



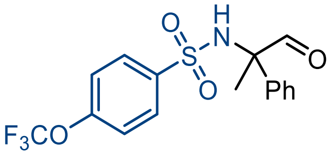
23

4-Bromo-*N*-(1-oxo-2-phenylpropan-2-yl)benzenesulfonamide (23) was prepared as a white solid from 4-bromobenzenesulfonamide (95.0 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), TBAB (129.4 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (18 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1, 109.3 mg, 74% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.38-7.30 (m, 2H), 7.28-7.13 (m, 5H), 7.09-7.01 (m, 2H), 6.16 (s, 1H), 1.93 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 140.8, 133.1, 131.7, 128.8, 128.1, 127.7, 126.8, 66.6, 19.9 ppm.

HRMS (ESI) m/z Calcd for $C_{15}H_{14}BrKNO_3S$ [M^++K]: 405.9509, Found: 405.9512.



24

***N*-(1-Oxo-2-phenylpropan-2-yl)-4-(trifluoromethoxy)benzenesulfonamide (24)** was prepared as a white solid from 4-(trifluoromethoxy)benzenesulfonamide (97.1mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (129.2 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the

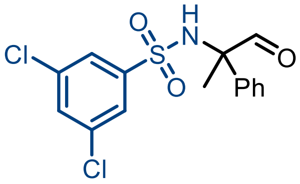
General Procedure I (36 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 10/1, 82.2 mg, 55% yield).

^{1}H NMR (300 MHz, CDCl) *δ* 9.08 (s, 1H), 7.42-7.35 (m, 2H), 7.24-7.17 (m, 1H), 7.16-7.09 (m, 2H), 7.05-6.98 (m, 4H), 6.18 (s, 1H), 1.98 (s, 3H) ppm.

^{13}C NMR (201 MHz, $CDCl_3$) *δ* 193.8, 151.30 (q, *J* = 2.0 Hz), 140.1, 132.7, 128.9, 128.8, 128.6, 127.9, 120.5, 120.2 (q, *J* = 258.6 Hz), 66.5, 19.9 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) *δ* -57.7 ppm.

HRMS (ESI) m/z Calcd for $C_{16}H_{15}F_3NO_4S$ [M$^+$+H]: 374.0668, Found: 374.0669.



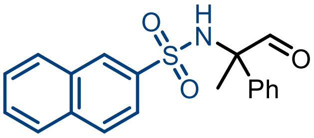
25

3,5-Dichloro-*N*-(1-oxo-2-phenylpropan-2-yl)benzenesulfonamide (25) was prepared as a white solid from 3,5-dichlorobenzenesulfonamide (90.7mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (129.2 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 15/1 to 12/1, 136.1 mg, 95% yield).

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 9.09 (s, 1H), 7.37-7.12 (m, 6H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.33 (s, 1H), 1.99 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 193.6, 144.1, 135.1, 132.1, 131.7, 129.4, 128.6, 127.8, 125.0, 66.5, 19.9 ppm.

HRMS (ESI) m/z Calcd for $C_{15}H_{13}Cl_2NNaO_3S$ [M$^+$+Na]: 379.9885, Found: 379.9888.

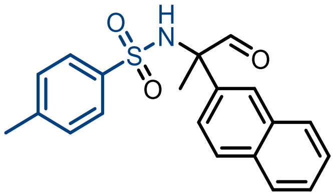


26

***N*-(1-Oxo-2-phenylpropan-2-yl)naphthalene-2-sulfonamide (26)** was prepared as a white solid from naphthalene-2-sulfonamide (83.1 mg, 0.4 mmol, 1.0 equiv), 2-phenylpropanal **1** (107.0 uL, 0.8 mmol, 2.0 equiv, d = 1.002 g/mL), aminocatalyst **B** (19.9 mg, 0.08 mmol, 0.2 equiv), TBAB (129.1 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 9/1, 69.3 mg, 51% yield). The NMR data are in consistent with the reported literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.86-7.72 (m, 3H), 7.68 (d, J = 7.9 Hz, 1H), 7.63-7.48 (m, 3H), 7.10-6.93 (m, 5H), 6.15 (s, 1H), 1.93 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.2, 138.4, 134.3, 133.1, 131.8, 129.2, 128.9, 128.7, 128.53, 128.50, 127.9, 127.6, 127.5, 127.1, 121.8, 66.7, 20.0 ppm.

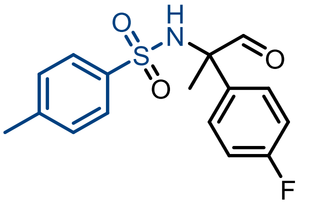


27

4-Methyl-*N*-(2-(naphthalen-2-yl)-1-oxopropan-2-yl)benzenesulfonamide (27) was prepared as a white solid from 4-methylbenzenesulfonamide (69.0 mg, 0.4 mmol, 1.0 equiv), 2-(naphthalen-2-yl)propanal (148.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), TBAB (129.3 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (18 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 10/1 to 9/1, 122.6 mg, 87% yield). The NMR data are in consistent with the reported literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.62 (d, J = 7.1 Hz, 1H), 7.57-7.39 (m, 4H), 7.22 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.7 Hz, 1H), 6.72 (d, J = 8.0 Hz, 2H), 6.19 (s, 1H), 2.11 (s, 3H), 1.98 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3, 142.5, 138.6, 132.8, 132.7, 130.7, 128.7, 128.5, 128.1, 127.5, 127.2, 126.8, 126.4, 126.3, 124.3, 66.7, 21.1, 19.9 ppm.



28

***N*-(2-(4-Fluorophenyl)-1-oxopropan-2-yl)-4-methylbenzenesulfonamide (28)** was prepared as a colorless oil from 4-methylbenzenesulfonamide (69.0 mg, 0.4 mmol, 1.0 equiv), 2-(4-fluorophenyl)propanal (122.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), TBAB (129.2 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (18 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 10/1 to 9/1, 109.2 mg, 85% yield). The NMR data are in consistent with the reported literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 7.1 Hz, 4H), 6.85 (t, J = 8.5 Hz, 2H), 5.98 (s, 1H), 2.36 (s, 3H), 1.90 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 162.8 (d, J = 249.4 Hz), 143.0, 139.0, 129.8 (d, J = 3.3 Hz), 129.6 (d, J = 8.5 Hz), 129.2, 126.6, 115.7 (d, J = 21.8 Hz), 66.2, 21.4, 20.1 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.7 ppm.

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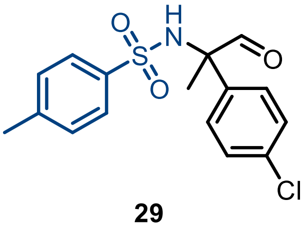
[2] T. Baumann, M. Bächle and S. Bräse, *Org. Lett.*, 2006, **8**, 3797–3800.



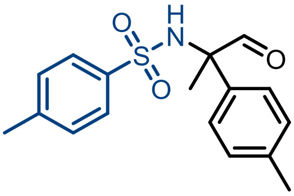
29

***N*-(2-(4-Chlorophenyl)-1-oxopropan-2-yl)-4-methylbenzenesulfonamide (29)** was prepared as a white solid from 4-methylbenzenesulfonamide (68.5 mg, 0.4 mmol, 1.0 equiv), 2-(4-chlorophenyl)propanal (135.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), TBAB (128.5 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (constant current of 3.0 mA, 13 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 12/1 to 10/1, 106.8 mg, 79% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.33 (d, J = 7.9 Hz, 2H), 7.16-6.96 (m, 6H), 6.04 (s, 1H), 2.38 (s, 3H), 1.89 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8, 143.0, 138.8, 135.0, 132.3, 129.2, 129.0, 128.8, 126.6, 66.2, 21.4, 19.9 ppm.

HRMS (ESI) m/z Calcd for $C_{16}H_{17}ClNO_3S$ [M^++H]: 338.0612, Found: 338.0614.

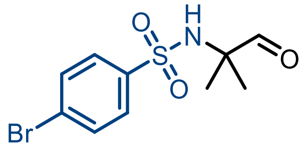


30

4-Methyl-*N*-(1-oxo-2-(*p*-tolyl)propan-2-yl)benzenesulfonamide (30) was prepared as a colorless oil from 4-methylbenzenesulfonamide (68.6 mg, 0.4 mmol, 1.0 equiv), 2-(*p*-tolyl)propanal (119.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **B** (19.8 mg, 0.08 mmol, 0.2 equiv), TBAB (128.9 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (15 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 10/1 to 9/1, 85.1 mg, 67% yield). The NMR data are in consistent with the reported literature.[2]

^{1}H NMR (300 MHz, CDCl$_3$) δ 9.10 (s, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 7.01-6.91 (m, 4H), 5.99 (s, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 1.85 (s, 3H) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) δ 194.3, 142.6, 139.0, 138.6, 130.8, 129.4, 129.0, 127.4, 126.6, 66.4, 21.4, 20.9, 19.8 ppm.



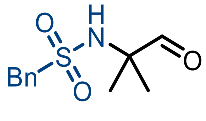
31

4-Bromo-*N*-(2-methyl-1-oxopropan-2-yl)benzenesulfonamide (31) was prepared as a white solid from 4-bromobenzenesulfonamide (94.4 mg, 0.4 mmol, 1.0 equiv), isobutyraldehyde (57.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.1 mg, 0.4 mmol, 1.0 equiv), and H$_2$O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (13 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 7/1 to 5/1, 101.0 mg, 82% yield).

^{1}H NMR (300 MHz, CDCl$_3$) δ 9.44 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H), 5.72 (s, 1H), 1.30 (s, 6H) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) δ 199.1, 141.6, 132.4, 128.3, 127.6, 62.5, 22.4 ppm.

HRMS (ESI) m/z Calcd for $C_{10}H_{12}BrNNaO_3S$ [M$^+$+Na]: 327.9613, Found: 327.9612.



32

***N*-(2-Methyl-1-oxopropan-2-yl)-1-phenylmethanesulfonamide (32)** was prepared as a white solid from phenylmethanesulfonamide (80.5 mg, 0.4 mmol, 1.0 equiv), isobutyraldehyde (57.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.1 mg, 0.4 mmol, 1.0 equiv), and H$_2$O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure

II (20 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 6/1 to 5/1, 58.1 mg, 60% yield).

^{1}**H NMR** (300 MHz, $CDCl_3$) *δ* 9.30 (s, 1H), 7.39 (s, 5H), 5.01 (s, 1H), 4.27 (s, 2H), 1.35 (s, 6H) ppm.

^{13}**C NMR** (75 MHz, $CDCl_3$) *δ* 199.6, 130.8, 129.1, 128.8, 128.7, 62.7, 61.7, 22.8 ppm.

HRMS (ESI) m/z Calcd for $C_{11}H_{16}NO_3S$ [M^++H]: 242.0845, Found: 242.0842.

33

4-Methyl-*N*-(2-methyl-1-oxopropan-2-yl)benzenesulfonamide (33) was prepared as a white solid from 4-methylbenzenesulfonamide (68.5 mg, 0.4 mmol, 1.0 equiv), isobutyraldehyde (57.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (130.1 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 8/1 to 7/1, 67.6 mg, 70% yield). The NMR data are in consistent with the reported literature.[1]

^{1}**H NMR** (300 MHz, $CDCl_3$) *δ* 9.47 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.72 (s, 1H), 2.42 (s, 3H), 1.27 (s, 6H) ppm.

^{13}**C NMR** (75 MHz, $CDCl_3$) *δ* 199.7, 143.5, 139.5, 129.6, 126.8, 62.3, 22.3, 21.4 ppm.

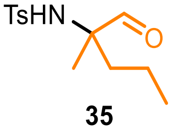
34

***N*-(3-Formylpentan-3-yl)-4-methylbenzenesulfonamide (34)** was prepared as a white solid from 4-methylbenzenesulfonamide (69.0 mg, 0.4 mmol, 1.0 equiv), 2-ethylbutanal (80.1 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (131.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4

mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 8/1 to 7/1, 68.8 mg, 65% yield). The NMR data are in consistent with the reported literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.25 (s, 1H), 2.42 (s, 3H), 2.04 (dq, J_1 = 15.0 Hz, J_2 = 7.5 Hz, 2H), 1.69 (dq, J_1 = 15.3 Hz, J_2 = 7.6 Hz, 2H), 0.59 (t, *J* = 7.5 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 143.3, 139.7, 129.5, 126.8, 70.3, 26.3, 21.5, 7.5 ppm.



35

4-Methyl-*N*-(2-methyl-1-oxopentan-2-yl)benzenesulfonamide (35) was prepared as a white solid from 4-methylbenzenesulfonamide (69.0 mg, 0.4 mmol, 1.0 equiv), 2-methylpentanal (80.1 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (130.1 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 8/1 to 7/1, 78.0 mg, 72% yield). The NMR data are in consistent with the reported literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.66 (s, 1H), 2.42 (s, 3H), 1.83-1.71 (m, 1H), 1.64-1.50 (m, 1H), 1.34-1.15 (m, 4H), 1.12-0.93 (m, 1H), 0.76 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.7, 143.3, 139.7, 129.5, 126.7, 65.5, 37.7, 21.4, 19.8, 16.4, 13.8 ppm.

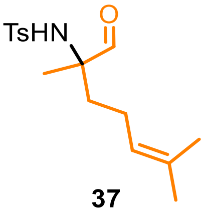
36

4-Methyl-*N*-(2-methyl-1-oxodecan-2-yl)benzenesulfonamide (36) was prepared as a white solid from 4-methylbenzenesulfonamide (69.1 mg, 0.4 mmol, 1.0 equiv), 2-methyldecanal (136.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (128.9 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 18/1 to 15/1, 70.4 mg, 52% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.34 (s, 1H), 2.42 (s, 3H), 1.90-1.75 (m, 1H), 1.64-1.53 (m, 1H), 1.33-1.03 (m, 14H), 1.00-0.82 (m, 4H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 143.3, 139.8, 129.6, 126.8, 65.6, 35.7, 31.8, 29.5, 29.3, 29.1, 23.3, 22.6, 21.5, 20.3, 14.1 ppm.

HRMS (ESI) m/z Calcd for $C_{18}H_{30}NO_3S$ [M$^+$+H]: 340.1941, Found: 340.1943.



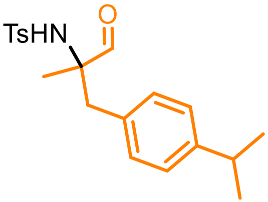
37

***N*-(2,6-Dimethyl-1-oxohept-5-en-2-yl)-4-methylbenzenesulfonamide (37)** was prepared as a colorless oil from 4-methylbenzenesulfonamide (68.6 mg, 0.4 mmol, 1.0 equiv), 2,6-dimethylhept-5-enal (112.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 µL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (131.1 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1 to 8/1, 81.5 mg, 69% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 5.58 (s, 1H), 4.87 (t, *J* = 6.4 Hz, 1H), 2.41 (s, 3H), 2.02-1.87 (m, 2H), 1.86-1.67 (m, 2H), 1.62 (s, 3H), 1.50 (s, 3H), 1.24 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 143.3, 139.8, 133.5, 129.6, 126.7, 122.5, 65.5, 36.0, 25.5, 22.0, 21.4, 20.2, 17.7 ppm.

HRMS (ESI) m/z Calcd for $C_{16}H_{24}NO_3S$ [M^++H]: 310.1471, Found: 310.1471.

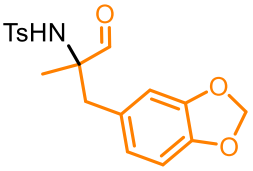


38

***N*-(1-(4-Isopropylphenyl)-2-methyl-3-oxopropan-2-yl)-4-methylbenzenesulfonamide (38)** was prepared as colorless oil from 4-methylbenzenesulfonamide (68.6 mg, 0.4 mmol, 1.0 equiv), 3-(4-isopropylphenyl)-2-methylpropanal (152.2 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (131.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1 to 7/1, 92.1 mg, 64% yield). The NMR data are in consistent with the reported literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 5.14 (s, 1H), 3.02 (s, 2H), 2.88 (hept, *J* = 7.0 Hz, 1H), 2.41 (s, 3H), 1.29 (s, 3H), 1.25 (s, 3H), 1.22 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 148.2, 143.4, 139.8, 131.0, 130.3, 129.6, 126.80, 126.76, 65.6, 42.9, 33.7, 23.9, 21.5, 19.8 ppm.



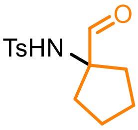
39

***N*-(1-(Benzo[*d*][1,3]dioxol-5-yl)-2-methyl-3-oxopropan-2-yl)-4-methylbenzenesulfonamide (39)** was prepared as a colorless oil from 4-methylbenzenesulfonamide (68.9 mg, 0.4 mmol, 1.0 equiv), 3-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropanal (153.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (130.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (17 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 8/1 to 6/1, 100.0 mg, 75% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.63-6.55 (m, 2H), 5.91 (s, 2H), 5.36 (s, 1H), 3.01 (d, *J* = 14.1 Hz, 1H), 2.95 (d, *J* = 14.1 Hz, 1H), 2.40 (s, 3H), 1.25 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 147.7, 146.9, 143.4, 139.7, 129.6, 127.4, 126.7, 123.6, 110.6, 108.3, 101.0, 65.6, 42.6, 21.4, 19.6 ppm.

HRMS (ESI) m/z Calcd for $C_{18}H_{20}NO_5S$ [M^++H]: 362.1057, Found: 362.1058.



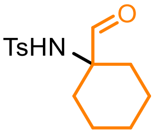
40

***N*-(1-Formylcyclopentyl)-4-methylbenzenesulfonamide (40)** was prepared as a white solid from 4-methylbenzenesulfonamide (68.9 mg, 0.4 mmol, 1.0 equiv), cyclopentanecarbaldehyde (78.5 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.4 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 8/1 to 7/1, 70.0 mg, 65% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.74 (s, 1H), 2.43 (s, 3H), 2.03-1.90 (m, 2H), 1.78-1.56 (m, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 143.6, 139.0, 129.7, 126.8, 72.8, 33.9, 23.8, 21.5 ppm.

HRMS (ESI) m/z Calcd for $C_{13}H_{17}NNaO_3S$ [M^++Na]: 290.0821, Found: 290.0820.

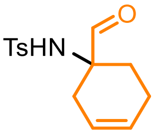


41

***N*-(1-Formylcyclohexyl)-4-methylbenzenesulfonamide (41)** was prepared as a white solid from 4-methylbenzenesulfonamide (68.6 mg, 0.4 mmol, 1.0 equiv), cyclohexanecarbaldehyde (89.7 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.3 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (17 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 8/1 to 7/1, 79.9 mg, 71% yield). The NMR data are in consistent with the reported literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.77 (s, 1H), 2.43 (s, 3H), 1.75-1.55 (m, 4H), 1.49-1.34 (m, 3H), 1.31-1.15 (m, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 143.5, 139.2, 129.6, 126.9, 65.2, 30.0, 24.6, 21.5, 20.5 ppm.



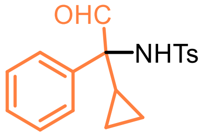
42

***N*-(1-Formylcyclohex-3-en-1-yl)-4-methylbenzenesulfonamide (42)** was prepared as a white solid from 4-methylbenzenesulfonamide (68.7 mg, 0.4 mmol, 1.0 equiv), cyclohex-3-ene-1-carbaldehyde (88.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (130.0 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (17 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1 to 7/1, 73.9 mg, 66% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.69-5.57 (m, 2H), 5.42-5.32 (m, 1H), 2.43 (s, 3H), 2.41-2.30 (m, 1H), 2.17-2.04 (m, 1H), 2.03-1.67 (m, 4H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 200.1, 143.6, 139.0, 129.6, 126.8, 126.4, 121.9, 63.2, 29.8, 26.6, 21.5, 21.1 ppm.

HRMS (ESI) m/z Calcd for $C_{14}H_{17}NNaO_3S$ [M^++Na]: 302.0821, Found: 302.0820.



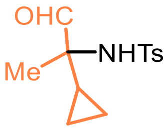
43

***N*-(1-Cyclopropyl-2-oxo-1-phenylethyl)-4-methylbenzenesulfonamide (43)** was prepared as a white solid from 4-methylbenzenesulfonamide (68.6 mg, 0.4 mmol, 1.0 equiv), 2-cyclopropyl-2-phenylacetaldehyde (129.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **B** (19.7 mg, 0.08 mmol, 0.2 equiv), TBAB (129.2 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure I (22 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 10/1, 117.4 mg, 89% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.29-7.11 (m, 7H), 7.02 (d, *J* = 8.2 Hz, 2H), 5.93 (s, 1H), 2.34 (s, 3H), 1.65-1.51 (m, 1H), 0.85 (dq, J_1 = 10.3 Hz, J_2 = 5.4 Hz, 1H), 0.73-0.54 (m, 2H), 0.47 (dq, J_1 = 10.8 Hz, J_2 = 5.5 Hz, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.6, 142.4, 139.3, 133.5, 128.9, 128.8, 128.5, 128.3, 126.4, 69.3, 21.3, 14.9, 2.4, 0.8 ppm.

HRMS (ESI) m/z Calcd for $C_{18}H_{19}NNaO_3S$ [M^++Na]: 352.0978, Found: 352.0976.



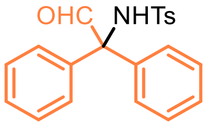
44

***N*-(2-Cyclopropyl-1-oxopropan-2-yl)-4-methylbenzenesulfonamide (44)** was prepared as a white solid from 4-methylbenzenesulfonamide (68.6 mg, 0.4 mmol, 1.0 equiv), 2-cyclopropylpropanal (78.5 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.2 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (16 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 6/1 to 5/1, 81.3 mg, 76% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 5.52 (s, 1H), 2.42 (s, 3H), 1.11 (s, 3H), 0.92 (p, *J* = 7.3 Hz, 1H), 0.54-0.32 (m, 4H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 198.6, 143.3, 139.7, 129.6, 126.8, 64.3, 21.5, 16.6, 16.4, 1.2, 0.5 ppm.

HRMS (ESI) m/z Calcd for $C_{13}H_{17}NNaO_3S$ [M^++Na]: 290.0821, Found: 290.0819.



45

4-Methyl-*N*-(2-oxo-1,1-diphenylethyl)benzenesulfonamide (45) was prepared as a white solid from 4-methylbenzenesulfonamide (68.6 mg, 0.4 mmol, 1.0 equiv), 2,2-diphenylacetaldehyde (157.0 mg, 0.8 mmol, 2.0 equiv), aminocatalyst **A** (24.0 μL, 0.12 mmol, 0.3 equiv, d = 0.912 g/mL), TBAB (129.1 mg, 0.4 mmol, 1.0 equiv), and H_2O (7.2 uL, 0.4 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (4 mL) according to the General Procedure II (constant current of 3.0 mA, 18 h, purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 13/1, 95.2 mg, 65% yield). The NMR data are in consistent with the reported literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 9.36 (s, 1H), 7.36-7.19 (m, 10H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.42 (s, 1H), 2.28 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 190.6, 142.0, 138.9, 134.2, 129.6, 128.7, 128.6, 128.5, 126.1, 74.1, 21.2 ppm.

IV. Gram scale reaction and product Derivatizations

(a) Gram scale reaction

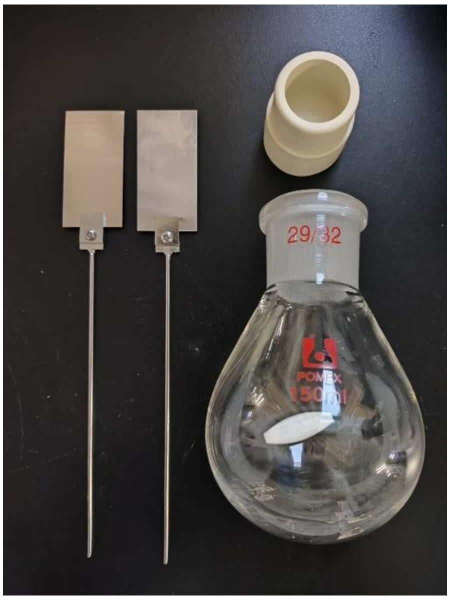
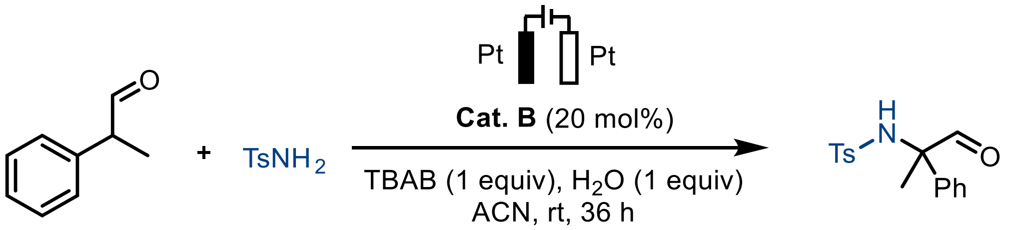


Figure S2. Electrolysis set-up for gram-scale experiment.



1
2 equiv

2
5 mmol

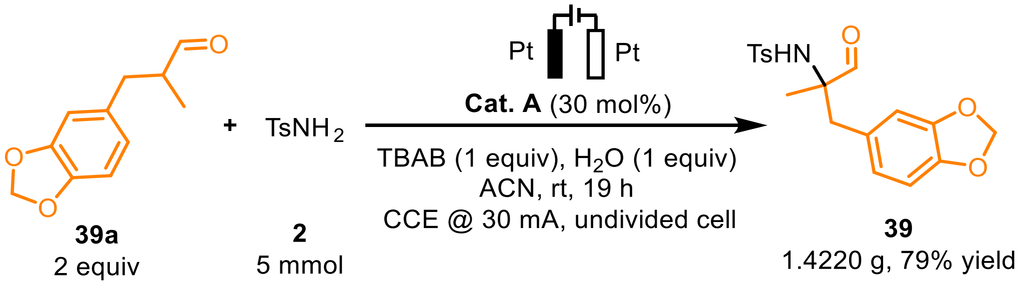
3
1.2751 g, 84% yield

The electrocatalysis was carried out in an undivided cell with a platinum plate anode (20.0 mm × 50.0 mm × 0.2 mm) and a platinum plate cathode (20.0 mm × 50.0 mm × 0.2 mm). The dimensions of the platinum plate immersed in the reaction solution are approximately 20.0 mm × 20.0 mm. Under argon, to a 150 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added 4-methylbenzenesulfonamide **2** (857.0 mg, 5.0 mmol, 1.0 equiv), aminocatalyst **B** (247.0 mg, 1.0 mmol, 0.2 equiv), tetrabutylammonium bromide (1.6140 g, 5.0 mmol, 1.0 equiv), then H_2O (5.0 mmol, 1.0 equiv, 90.0 uL), 2-phenylpropanal **1** (10.0 mmol, 2.0

equiv, 1.340 mL) and ACN (50.0 mL) were added. The electrocatalysis was performed at room temperature with a constant current of 30.0 mA maintained for 36 h. After the reaction was completed, the solution was concentrated and purified by silica gel flash column chromatography to afford the pure product (purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1, 1.2751 g, white solid, 84% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.26-7.07 (m, 5H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.02 (s, 1H), 2.34 (s, 3H), 1.87 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3, 142.7, 139.0, 134.1, 129.1, 128.7, 128.5, 127.4, 126.5, 66.7, 21.3, 19.9 ppm.



39a 2 equiv

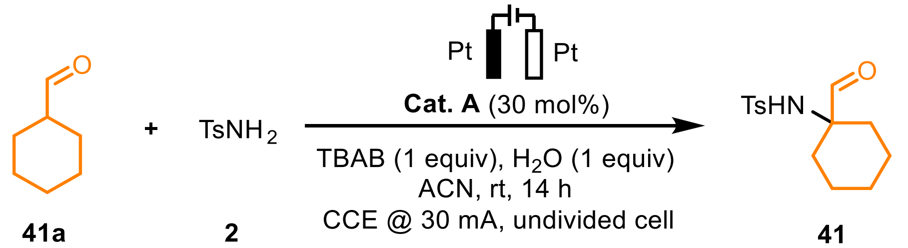
2 5 mmol

39 1.4220 g, 79% yield

The electrocatalysis was carried out in an undivided cell with a platinum plate anode (20.0 mm × 50.0 mm × 0.2 mm) and a platinum plate cathode (20.0 mm × 50.0 mm × 0.2 mm). The dimensions of the platinum plate immersed in the reaction solution are approximately 20.0 mm × 20.0 mm. Under argon, to a 150 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added 4-methylbenzenesulfonamide **2** (855.0 mg, 5.0 mmol, 1.0 equiv), aminocatalyst **A** (298.0 uL, 1.5 mmol, 0.3 equiv), tetrabutylammonium bromide (1.6150 g, 5.0 mmol, 1.0 equiv), then H_2O (5.0 mmol, 1.0 equiv, 90.0 uL), 3-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropanal (1.654 mL, 10.0 mmol, 2.0 equiv) and ACN (50.0 mL) were added. The electrocatalysis was performed at room temperature with a constant current of 30.0 mA maintained for 19 h. After the reaction was completed, the solution was concentrated and purified by silica gel flash column chromatography to afford the pure product (purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 6/1 to 4/1, 1.4220 g, colorless oil, 79% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.63-6.55 (m, 2H), 5.92 (s, 2H), 5.29 (s, 1H), 3.01 (d, *J* = 14.1 Hz, 1H), 2.95 (d, *J* = 14.1 Hz, 1H), 2.41 (s, 3H), 1.26 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 147.7, 146.9, 143.4, 139.7, 129.6, 127.4, 126.7, 123.6, 110.6, 108.3, 101.1, 65.6, 42.7, 21.4, 19.7 ppm.



41a
2 equiv

2
5 mmol

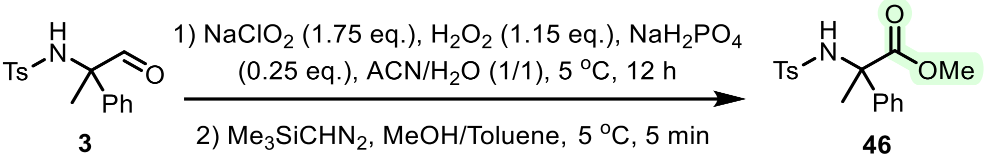
41
1.1220 g, 80% yield

The electrocatalysis was carried out in an undivided cell with a platinum plate anode (20.0 mm × 50.0 mm × 0.2 mm) and a platinum plate cathode (20.0 mm × 50.0 mm × 0.2 mm). The dimensions of the platinum plate immersed in the reaction solution are approximately 20.0 mm × 20.0 mm. Under argon, to a 150 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added 4-methylbenzenesulfonamide **2** (858.0 mg, 5.0 mmol, 1.0 equiv), aminocatalyst **A** (298.0 uL, 1.5 mmol, 0.3 equiv), tetrabutylammonium bromide (1.6170 g, 5.0 mmol, 1.0 equiv), then H_2O (5.0 mmol, 1.0 equiv, 90.0 uL), cyclohexanecarbaldehyde (1.210 mL, 10.0 mmol, 2.0 equiv) and ACN (50.0 mL) were added. The electrocatalysis was performed at room temperature with a constant current of 30.0 mA maintained for 14 h. After the reaction was completed, the solution was concentrated and purified by silica gel flash column chromatography to afford the pure product (purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 9/1 to 6/1, 1.2200 g, white solid, 80% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 5.90 (s, 1H), 2.43 (s, 3H), 1.74-1.55 (m, 4H), 1.51-1.35 (m, 3H), 1.31-1.12 (m, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 201.0, 143.5, 139.2, 129.6, 126.8, 65.2, 29.9, 24.6, 21.5, 20.5 ppm.

(b) Synthetic transformations

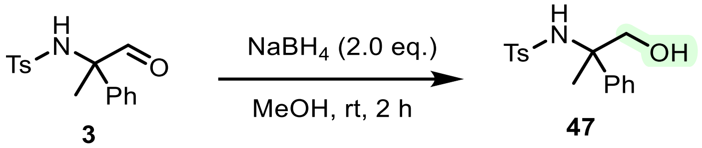


Methyl 2-((4-methylphenyl)sulfonamido)-2-phenylpropanoate (46)

To a solution of **3** (0.455 g, 1.50 mmol, 1.0 equiv) in ACN (5 mL) was added an aqueous solution of NaH_2PO_4 (0.05 g, 0.42 mmol, 0.25 equiv) in water (2 mL), follow by 35% H_2O_2 (140.0. μL). Subsequently, an aqueous solution of $NaClO_2$ (0.2270 g, 2.60 mmol, 1.75 equiv) in water (3 mL) was added dropwise to the resulting mixture, keeping the temperature of the mixture at 5 °C. After the mixture was stirred for 12 h, Na_2SO_3 (0.0301 g) was added and the resulting mixture was acidified (pH = 2-3) with 10% aqueous hydrochloric acid. The reaction mixture was extracted with DCM (20 mL×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. Then the residue was dissolved in toluene/methanol 1: 2 and treated with trimethylsilyldiazomethane (0.8 mL) at 0 °C for 5 min until bubbling subsided. The excess trimethylsilyldiazomethane was quenched with a few drops of acetic acid and the solution was concentrated and purified by silica gel flash column chromatography to afford the pure product. (purified by flash column chromatography, eluent: *n*-hexane/ethyl acetate = 10/1, 0.4400 g, white solid, 88% yield). The NMR data are in consistent with the reported literature.[2]

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.50 (d, *J* = 8.2 Hz, 2H), 7.29-7.08 (m, 7H), 5.99 (s, 1H), 3.64 (s, 3H), 2.36 (s, 3H), 1.91 (s, 3H) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) *δ* 173.3, 142.8, 139.3, 139.0, 129.2, 128.4, 128.0, 126.8, 125.8, 64.3, 53.2, 23.7, 21.3 ppm.

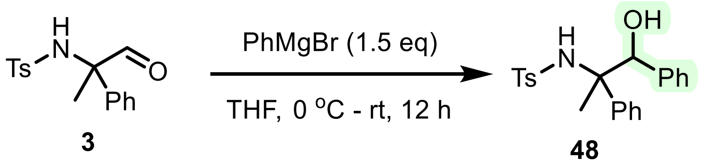


To a solution of **3** (61.0 mg, 0.2 mmol, 1.0 equiv) in MeOH (2 mL) was added sodium borohydride (15.0 mg, 0.4 mmol, 2.0 equiv). The reaction mixture was stirred at room temperature for 2 h. After the completion of the reaction determined by TLC, the reaction mixture was quenched by water (5 mL) and extracted with DCM (20 mL×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 5/1 to 3/1, white solid, 48.9 mg, 80% yield) to give ***N*-(1-Hydroxy-2-phenylpropan-2-yl)-4-methylbenzenesulfonamide (47)**.

^{1}H NMR (300 MHz, CDCl$_3$) *δ* 7.61 (d, *J* = 8.2 Hz, 2H), 7.37-7.13 (m, 7H), 5.52 (s, 1H), 3.86 (d, *J* = 11.4 Hz, 1H), 3.65 (d, *J* = 11.3 Hz, 1H), 2.39 (s, 3H), 2.25 (s, 1H), 1.56 (s, 3H) ppm.

^{13}C NMR (75 MHz, CDCl$_3$) *δ* 143.0, 141.8, 139.5, 129.4, 128.4, 127.4, 126.9, 126.1, 70.3, 62.4, 23.2, 21.4 ppm.

HRMS (ESI) m/z Calcd for $C_{16}H_{19}NNaO_3S$ [M$^+$+Na]: 328.0978, Found: 328.0977.

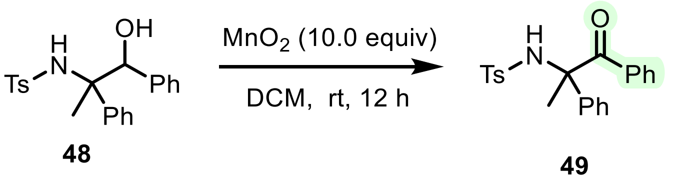


At 0 °C, to a solution of **3** (121.0 mg, 0.4 mmol, 1.0 equiv) in anhydrous THF (2 mL) was added PhMgBr (0.6 mL, 0.6 mmol, 1.0 mol/L in THF, 1.5 equiv) under argon. The reaction mixture was warmed up to room temperature naturally and stirred for 12 h. After the completion of the reaction determined by TLC, the reaction mixture was quenched by saturated aqueous solution of NH_4Cl (5 mL) and extracted with EA (10 mL×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel flash column chromatography (eluent: *n*-hexane /ethyl acetate = 7/1, white solid, 123.1 mg, 81% yield, dr: about 1/1) to give ***N*-(1-Hydroxy-1,2-diphenylpropan-2-yl)-4-methylbenzenesulfonamide (48)**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.32-7.25 (m, 1H), 7.23-7.01 (m, 9H), 6.97 (d, *J* = 7.1 Hz, 1H), 6.75 (d, *J* = 7.3 Hz, 1H), [5.95 (s, 0.45H), 5.82 (s, 0.50H), 1H], [4.83 (s, 0.50H), 4.77 (s, 0.45H), 1H], [2.66 (s, 0.50H), 2.57 (s, 0.45H), 1H], [2.35 (s, 1.5 H), 2.33 (s, 1.4H), 3H], [1.59 (s, 1.56H), 1.47 (s, 1.39H), 3H] ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.8, 142.5, 141.8, 139.8, 139.5, 139.4, 138.1, 129.2, 129.0, 128.1, 128.0, 127.9, 127.6, 127.54, 127.51, 127.48, 127.4, 127.3, 127.2, 127.0, 126.9, 126.7, 81.2, 80.9, 65.1, 64.3, 21.6, 21.38, 21.36, 19.7 ppm.

HRMS (ESI) m/z Calcd for $C_{22}H_{23}NNaO_3S$ [M^++Na]: 404.1291, Found: 404.1293.

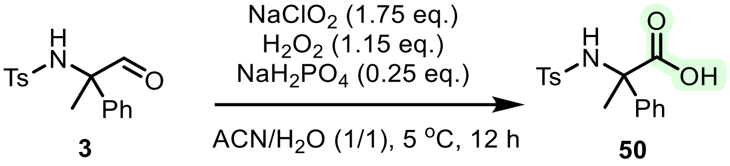


To a solution of **48** (76.4 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) was added MnO_2 (174.0 mg, 2.0 mmol, 10.0 equiv). The reaction mixture was stirred at room temperature for 12 h. After the completion of the reaction determined by TLC. Upon completion, the reaction mixture was filtered through a pad of celite, the residue was washed with EA (15 mL×3), the filtrate was combined and concentrated. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 12/1 to 10/1, white solid, 48.9 mg, 76% yield) to give **4-Methyl-*N*-(1-oxo-1,2-diphenylpropan-2-yl)benzenesulfonamide (49)**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.34 (m, 3H), 7.24-7.12 (m, 7H), 7.11-7.02 (m, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.82 (s, 1H), 2.30 (s, 3H), 2.15 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 141.9, 139.4, 136.6, 133.2, 132.8, 130.0, 128.8, 128.6, 128.3, 128.2, 127.5, 126.3, 67.3, 24.9, 21.3 ppm.

HRMS (ESI) m/z Calcd for $C_{22}H_{21}NNaO_3S$ [M$^+$+Na]: 402.1134, Found: 402.1136.



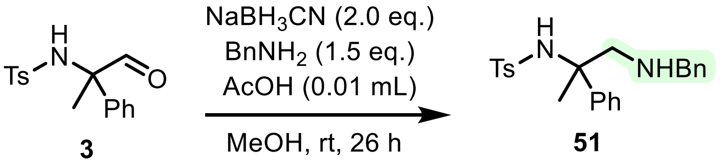
2-((4-Methylphenyl)sulfonamido)-2-phenylpropanoic acid (50)

To a solution of **3** (60.9 mg, 0.2 mmol, 1.0 equiv) in ACN (1 mL) was added an aqueous solution of NaH_2PO_4 (6.0 mg, 0.05 mmol, 0.25 equiv) in water (0.5 mL), follow by 35% H_2O_2 (1.5 μL). Subsequently, an aqueous solution of $NaClO_2$ (26.2 mg, 0.35 mmol, 1.75 equiv) in water (0.5 mL) was added dropwise to the resulting mixture, keeping the temperature of the mixture at 5 °C. After the mixture was stirred for 12 h, Na_2SO_3 (10.0 mg) was added and the resulting mixture was acidified (pH = 2-3) with 10% aqueous hydrochloric acid. The reaction mixture was extracted with DCM (10 mL×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 2/1 to 1/1, white solid, 58.1 mg, 91% yield).

^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 8.04 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.42-7.12 (m, 8H), 2.35 (s, 3H), 1.68 (s, 3H) ppm.

^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ 173.5, 142.0, 141.0, 140.6, 129.2, 127.9, 127.4, 126.3, 126.1, 63.8, 24.2, 21.0 ppm.

HRMS (ESI) m/z Calcd for $C_{16}H_{17}NO_4S$ [M$^+$+Na]:342.0770, Found:342.0774.



To a solution of **3** (60.7 mg, 0.2 mmol, 1.0 equiv) in MeOH (2 mL) was added Benzylamine (32.0 mg, 0.3 mmol, 1.5 equiv). After stirring the reaction mixture at room temperature for 20 minutes, adjust the pH to 6 using 0.1 mL of acetic acid, then add sodium cyanoborohydride (25.0 mg, 0.4 mmol, 2.0 equiv). After the completion of the reaction determined by TLC, the reaction mixture was quenched by water (5 mL) and extracted with DCM (20 mL×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 6/1 to 5/1) to give ***N*-(1-(benzylamino)-2-phenylpropan-2-yl)-4-methylbenzenesulfonamide (51)** (white oil, 67.2 mg, 85% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.44-7.09 (m, 12H), 6.32 (s, 1H), 3.71 (d, J = 13.4 Hz, 1H), 3.62 (d, J = 13.4 Hz, 1H), 2.90 (d, J = 11.9 Hz, 1H), 2.54 (d, J = 11.9 Hz, 1H), 2.37 (s, 3H), 1.51 (s, 3H), 1.26 (s, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5, 142.4, 140.5, 139.6, 129.2, 128.5, 128.2, 128.1, 127.2, 126.9, 126.6, 125.8, 60.6, 60.0, 53.4, 24.0, 21.4 ppm.

HRMS (ESI) m/z Calcd for $C_{23}H_{27}N_2O_2S$ [M^++H]: 395.1788, Found: 395.1788.

V. Mechanistic Studies

Cyclic voltammetry studies

The cyclic voltammetry was carried out with a Shanghai Chenhua CHI630E workstation in 10 mL electrolytic cell (inner diameter 26 mm). A glassy-carbon electrode (3 mm-diameter, disc-electrode) was used as the working electrode, a Pt plate (10 mm × 10 mm × 0.1 mm) was used as the auxiliary electrode and an Ag/AgCl electrode was used as a reference electrode. The sample should be bubbled with Ar for 5 min before testing. The measurements were carried out at a scan rate of 100 mV s^{-1} in ACN/$^{n}Bu_4NBF_4$ (0.1 M).

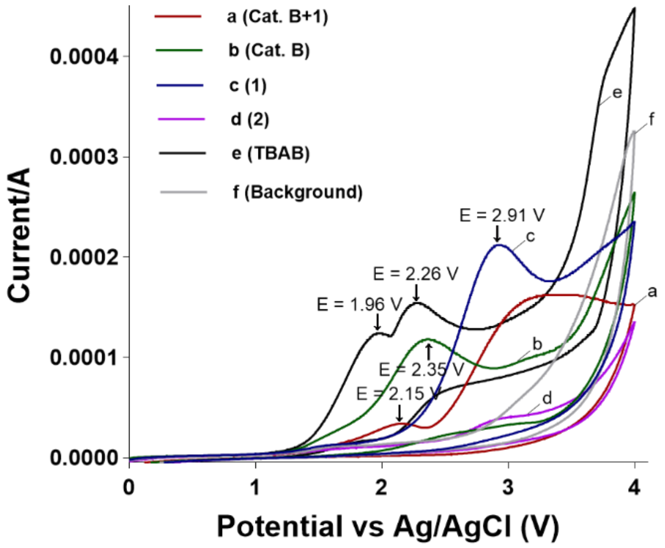


Figure S3. Cyclic voltammograms of **1** and related compounds in 0.1 M ACN/$^{n}Bu_4NBF_4$ using a glass-carbon working electrode, Pt plate, and Ag/AgCl as counter and reference electrodes at 100 mV s^{-1} scan rate. (a) Cat. **B** (0.002 M) and **1** (0.01M), (b) Cat. **B** (0.01 M), (c) **1** (0.01 M), (d) **2** (0.01 M), (e) TBAB (0.01 M), (f) Background.

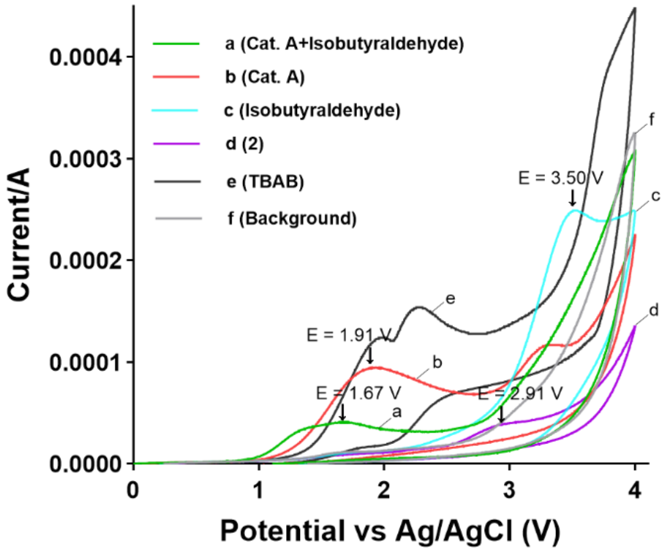


Figure S4. Cyclic voltammograms of Isobutyraldehyde and related compounds in 0.1 M ACN/^{n}Bu$_4$NBF$_4$ using a glass-carbon working electrode, Pt plate, and Ag/AgCl as counter and reference electrodes at 100 mV s^{-1} scan rate. (a) Cat. **A** (0.002 M) and Isobutyraldehyde (0.01 M), (b) Cat. **A** (0.01 M), (c) Isobutyraldehyde (0.01 M), (d) **2** (0.01M), (e) TBAB (0.01 M), (f) Background.

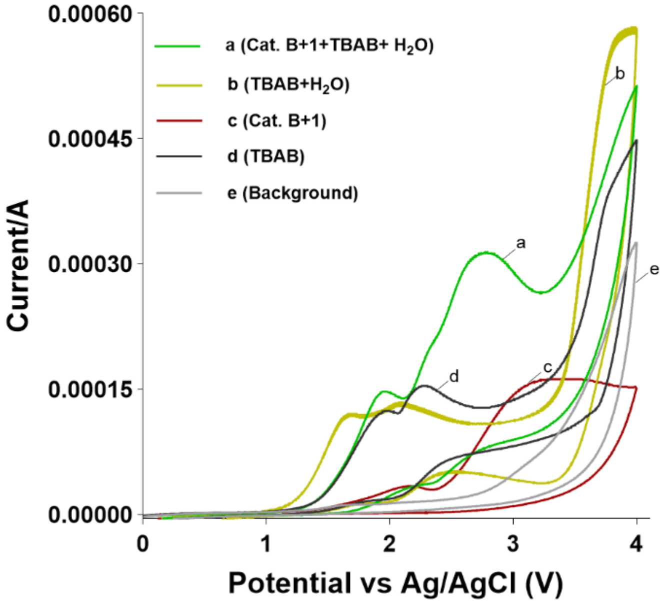


Figure S5. Cyclic voltammograms of **1** and related compounds in 0.1 M ACN/$^{n}Bu_4NBF_4$ using a glass-carbon working electrode, Pt plate, and Ag/AgCl as counter and reference electrodes at 100 mV s^{-1} scan rate. (a) Cat. **B** (0.002 M), **1** (0.01 M), TBAB (0.01 M) and H_2O (0.01 M), (b) TBAB (0.01 M) and H_2O (0.01 M), (c) Cat. **B** (0.002 M) and **1** (0.01 M), (d) TBAB (0.01 M), (e) Background.

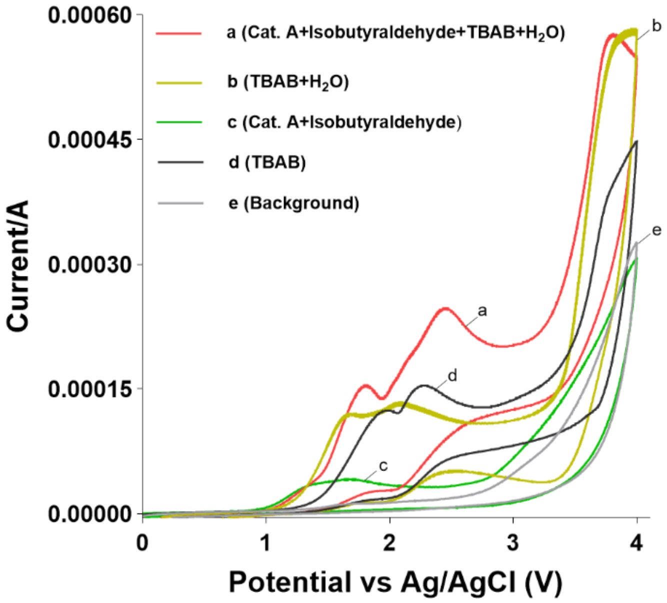
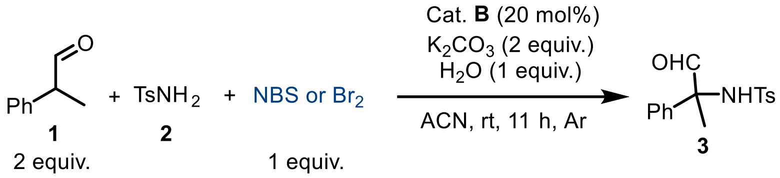


Figure S6. Cyclic voltammograms of Isobutyraldehyde and related compounds in 0.1 M ACN/$^{n}Bu_4NBF_4$ using a glass-carbon working electrode, Pt plate, and Ag/AgCl as counter and reference electrodes at 100 mV s^{-1} scan rate. (a) Cat. **A** (0.002 M), Isobutyraldehyde (0.01 M), TBAB (0.01 M) and H_2O (0.01 M), (b) TBAB (0.01 M) and H_2O (0.01 M), (c) Cat. **A** (0.002 M) and Isobutyraldehyde (0.01 M), (d) TBAB (0.01 M), (e) Background.

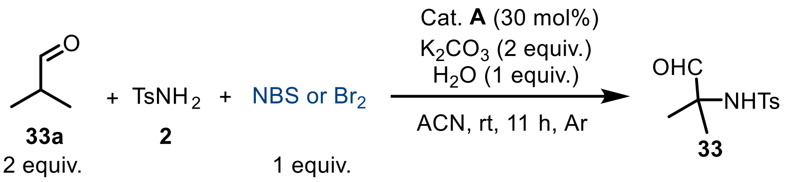
Control experiments with Br_2 and NBS



Entry	[Br]	K_2CO_3	H_2O	Yield of **3** (%)[a]	Recovery of **2** (%)[a]
1	NBS	x	x	0	72
2	NBS	√	x	0	10
3	NBS	x	√	0	72
4	NBS	√	√	35	22
5	Br_2	x	x	0	66
6	Br_2	√	x	2	46
7	Br_2	x	√	0	62
8	Br_2	√	√	3	44

[a] Determined by NMR using mesitylene as the internal standard

To a solution of **1** (53.5 uL, 0.4 mmol, 2.0 equiv, d = 1.002 g/mL), **2** (34.2 mg, 0.2 mmol, 1.0 equiv), Cat. **B** (9.8 mg, 0.04 mmol, 0.2 equiv), K_2CO_3 (56.0 mg, 0.4 mmol, 2.0 equiv), H_2O (3.6 uL, 0.2 mmol, 1.0 equiv) in ACN (2 mL) was added Br_2 (10.0 uL, 0.2 mmol, 1.0 equiv) or NBS (35.6 mg, 0.2 mmol, 1.0 equiv) or under argon. The reaction was stirred at room temperature for 11 h, then the reaction mixture was filtered through a short pad of silica gel and washed with EA (20 mL×3). After concentrated, a crude NMR analysis was conducted with 14 μL of mesitylene as internal standard.

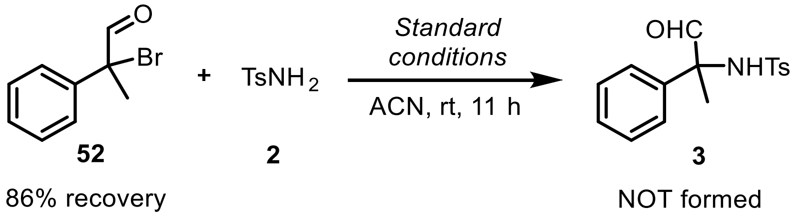


Entry	[Br]	K_2CO_3	H_2O	Yield of **33** (%)[a]	Recovery of **2** (%)[a]
1	NBS	x	x	0	87
2	NBS	√	x	0	0
3	NBS	x	√	0	69
4	NBS	√	√	14	83
5	Br_2	x	x	0	30
6	Br_2	√	x	1	32
7	Br_2	x	√	5	40
8	Br_2	√	√	3	78

[a] Determined by NMR using mesitylene as the internal standard

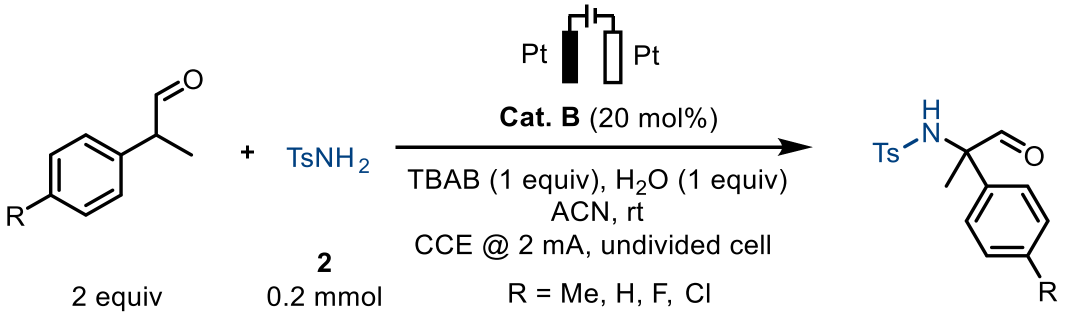
To a solution of isobutyraldehyde (28.8 mg, 0.4 mmol, 2.0 equiv), **2** (34.2 mg, 0.2 mmol, 1.0 equiv), Cat. **A** (12.0 μL, 0.06 mmol, 0.3 equiv, d = 0.912 g/mL), K_2CO_3 (56.0 mg, 0.4 mmol, 2.0 equiv), H_2O (3.6 uL, 0.2 mmol, 1.0 equiv) in ACN (2 mL) was added Br_2 (10.0 uL, 0.2 mmol, 1.0 equiv) or NBS (35.6 mg, 0.2 mmol, 1.0 equiv) under argon. The reaction was stirred at room temperature for 11 h, then the reaction mixture was filtered through a short pad of silica gel and washed with EA (20 mL×3). After concentrated, a crude NMR analysis was conducted with 14 μL of mesitylene as internal standard.

Control experiment with *α*-bromoaldehyde



Under argon, to a 10 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added 2-bromo-2-phenylpropanal **52**[3] (85.1 mg, 0.4 mmol, 2.0 equiv), **2** (34.3 mg, 0.2 mmol, 1.0 equiv), Cat. **B** (9.8 mg, 0.04 mmol, 0.2 equiv), TBAB (64.5 mg, 0.2 mmol, 1.0 equiv), and H_2O (3.6 uL, 0.2 mmol, 1.0 equiv, d = 1.000 g/mL) in ACN (2 mL) according to the General Procedure I. The electrocatalysis was performed at room temperature for 11 h, then the reaction mixture was filtered through a short pad of silica gel and washed with EA (20 mL×3). After concentrated, a crude NMR analysis was conducted with 14 μL of mesitylene as internal standard. As a result, **3** was not found, the recovery of **52** was calculated to be 86%.

Hammett analysis



The electrocatalysis was carried out in an undivided cell with a platinum plate anode (10.0 mm × 15.0 mm × 0.2 mm) and a platinum plate cathode (10.0 mm × 15.0 mm × 0.2 mm). Under argon, to a 10 mL pre-dried undivided electrochemical cell equipped with a magnetic bar were added **2** (34.2 mg, 0.2 mmol, 1.0 equiv), racemic aminocatalyst **B** (9.85 mg, 0.04 mmol, 0.2 equiv), tetrabutylammonium bromide (64.5 mg, 0.2 mmol, 1.0 equiv). Then H_2O (0.2 mmol, 1.0 equiv, 3.6 uL), aldehyde (0.4 mmol, 2.0 equiv), and ACN (2 mL) were added. The electrocatalysis was performed at room temperature with a constant current of 2.0 mA maintained for 0.33-1.67 h. The crude reaction mixture was concentrated, and Mesitylene (14.0 μL, 0.1 mmol) was added.

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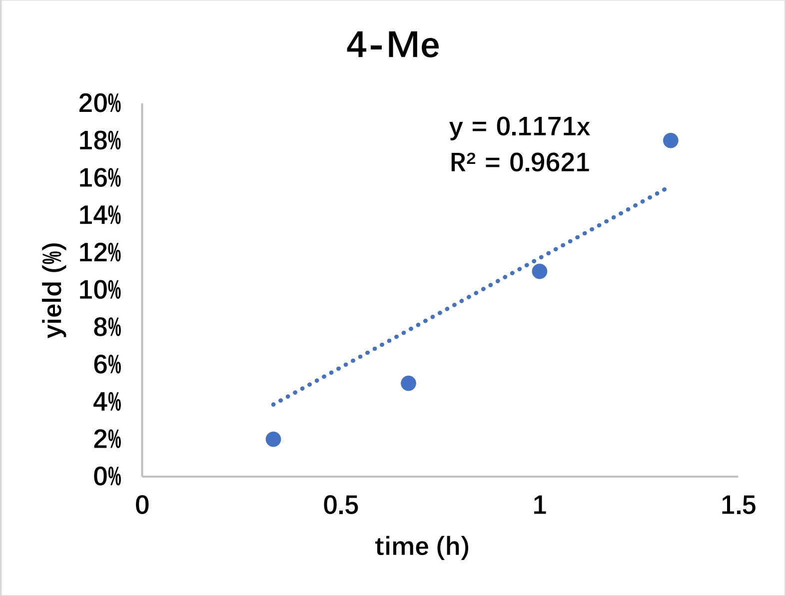
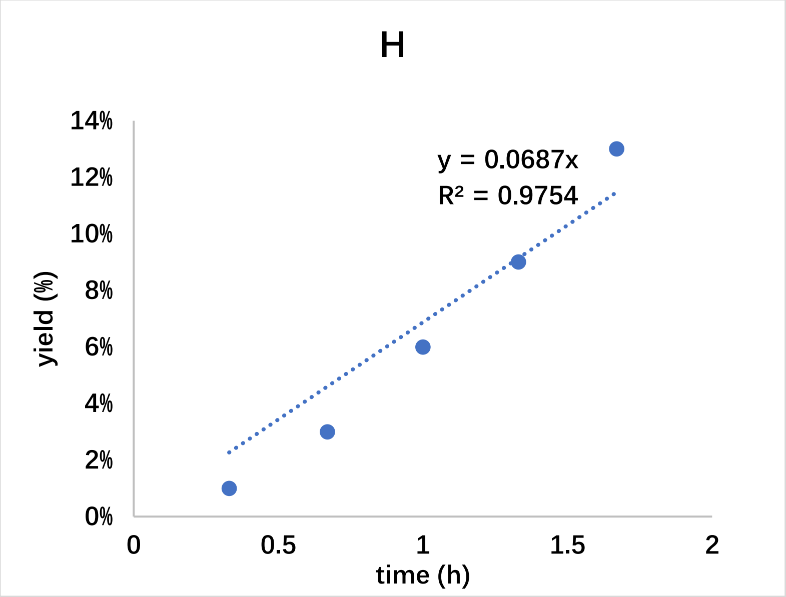
[3] G. Hutchinson, C. Alamillo-Ferrer, M. Fernández-Pascual and J. Burés, *J. Org. Chem.*, 2022, **87**, 7968–7974.

The yield dependence on substituent R and time was measured by ^{1}H NMR and is listed in the following table.

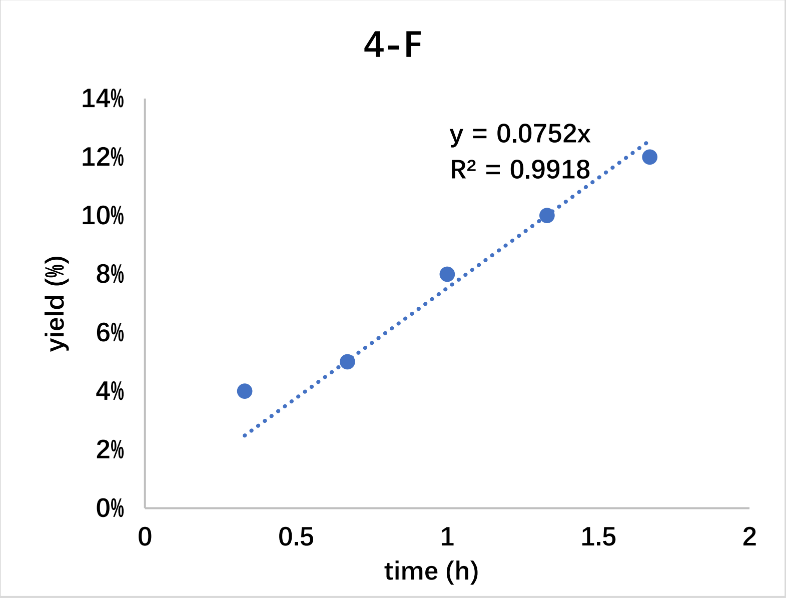
Time (h)	Yield (4-Me)
0.33	2%
0.67	5%
1	11%
1.33	18%
1.67	24% (delete)



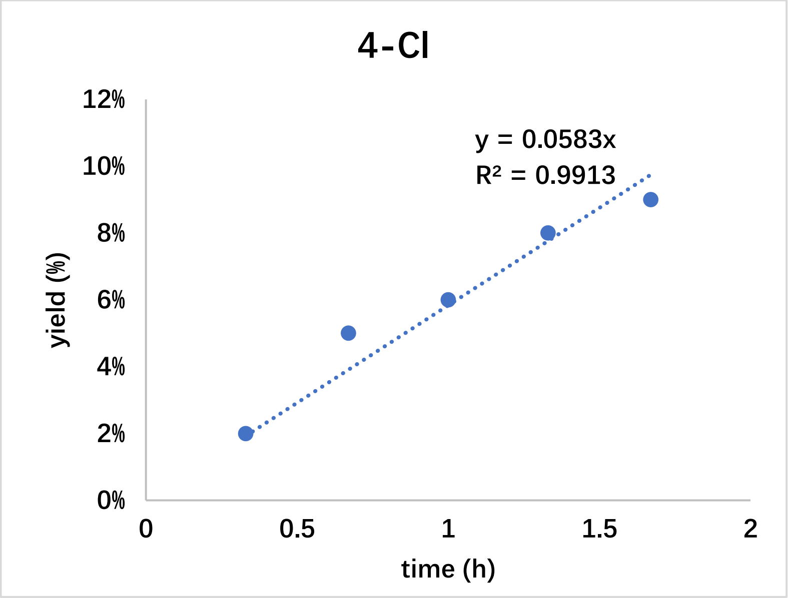
Time (h)	Yield (H)
0.33	1%
0.67	3%
1	6%
1.33	9%
1.67	13%



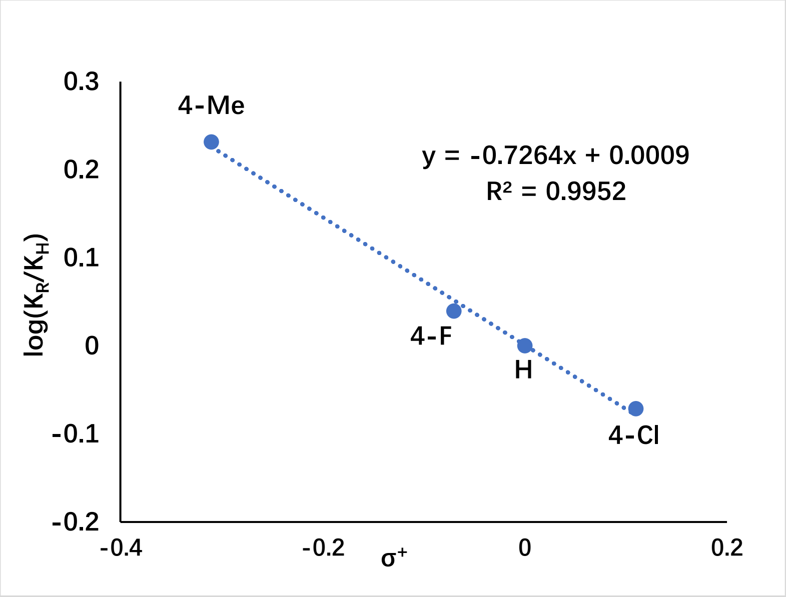
Time (h)	Yield (4-F)
0.33	4%
0.67	5%
1	8%
1.33	10%
1.67	12%



Time (h)	Yield (4-Cl)
0.33	2%
0.67	5%
1	6%
1.33	8%
1.67	9%

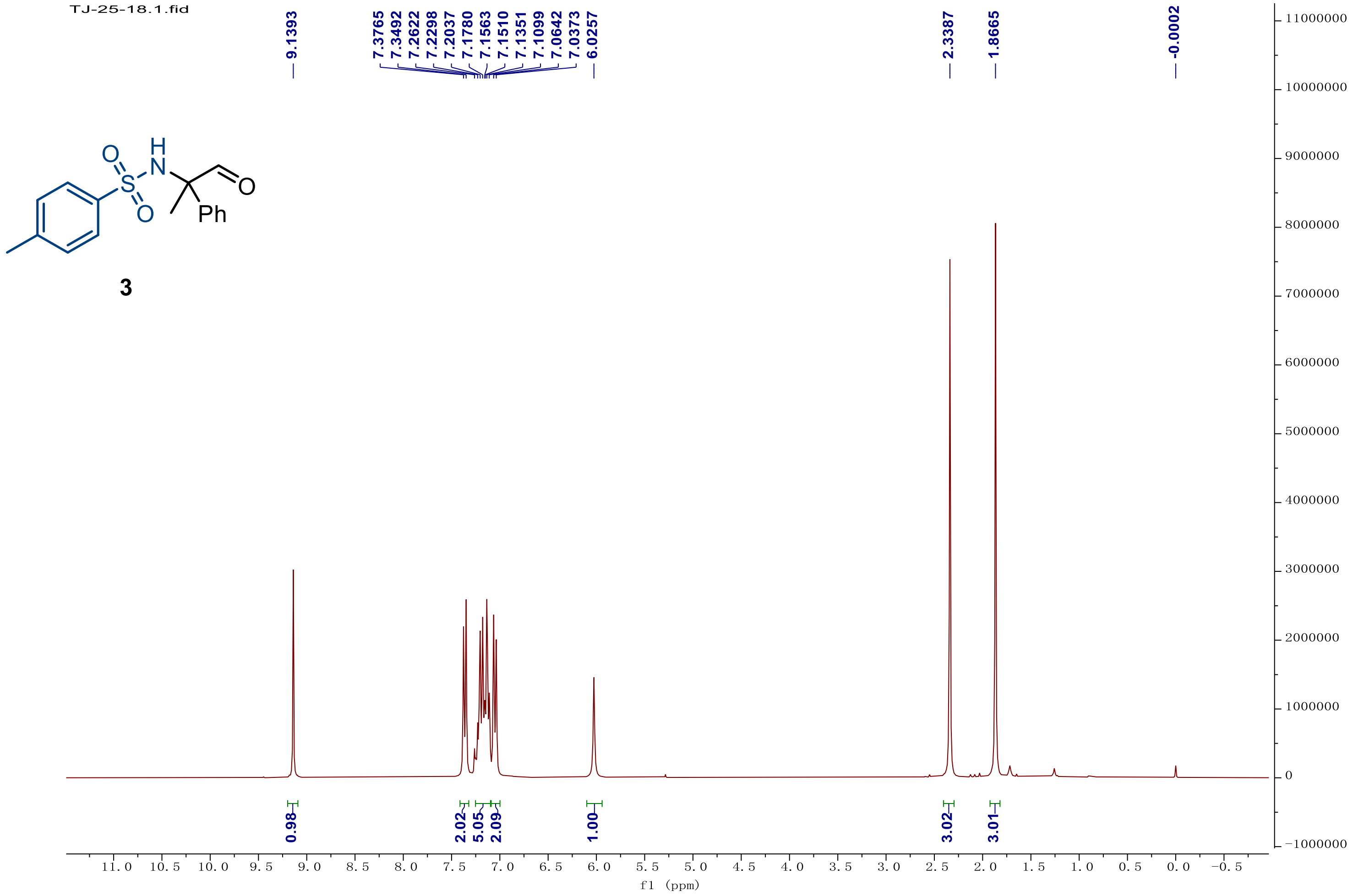


R	4-Me	H	4-F	4-Cl
σ^+	-0.31	0	-0.07	0.11
K_R/K_H	1.7045	1	1.095	0.8486
$\text{Log}(K_R/K_H)$	0.232	0	0.039	-0.071

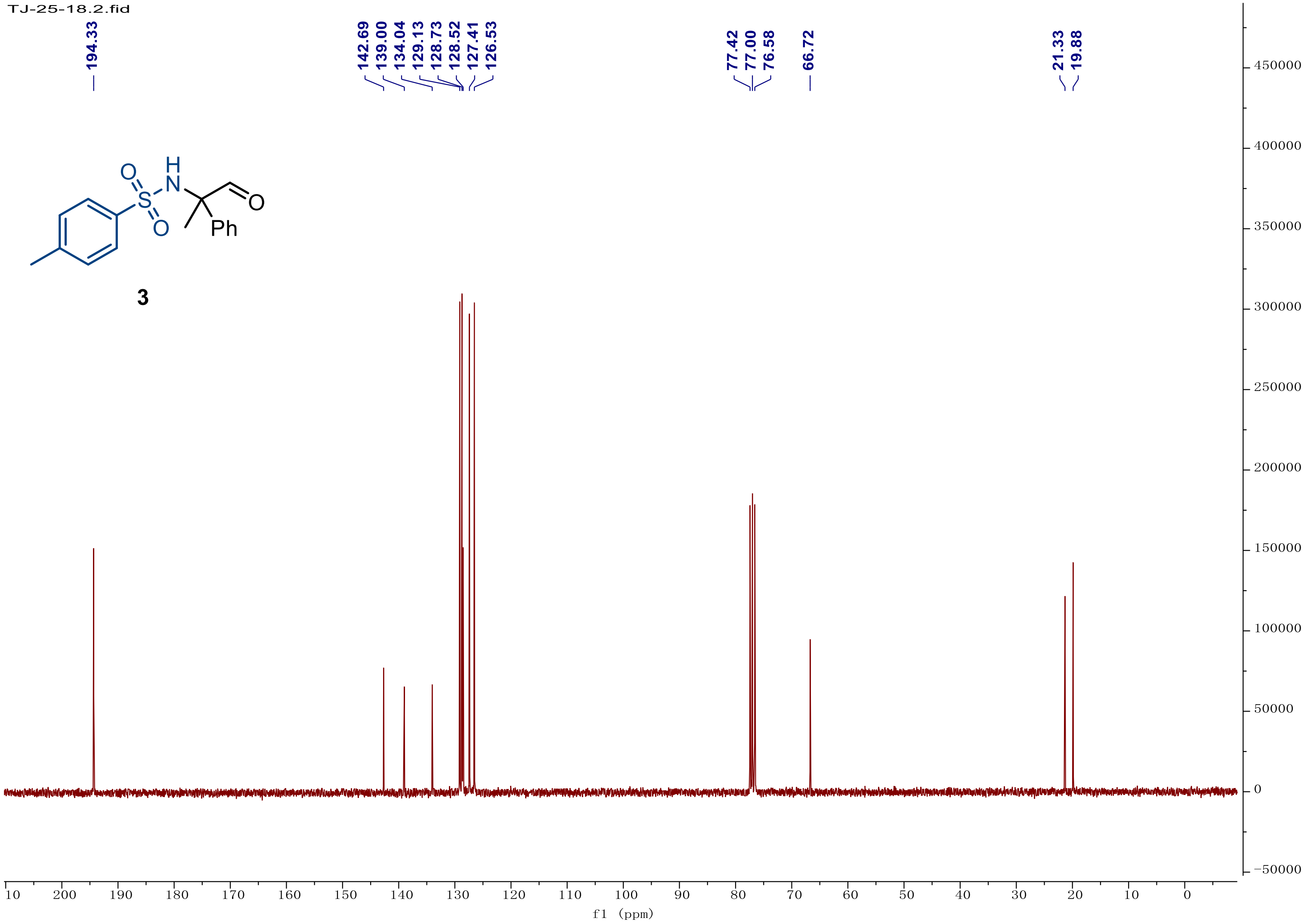

0.3
0.2
0.1
0
-0.1
-0.2
log(K_R/K_H)
-0.4
-0.2
0
0.2
σ+
4-Me
4-F
H
4-Cl
y = -0.7264x + 0.0009
R² = 0.9952

VI. NMR Spectra

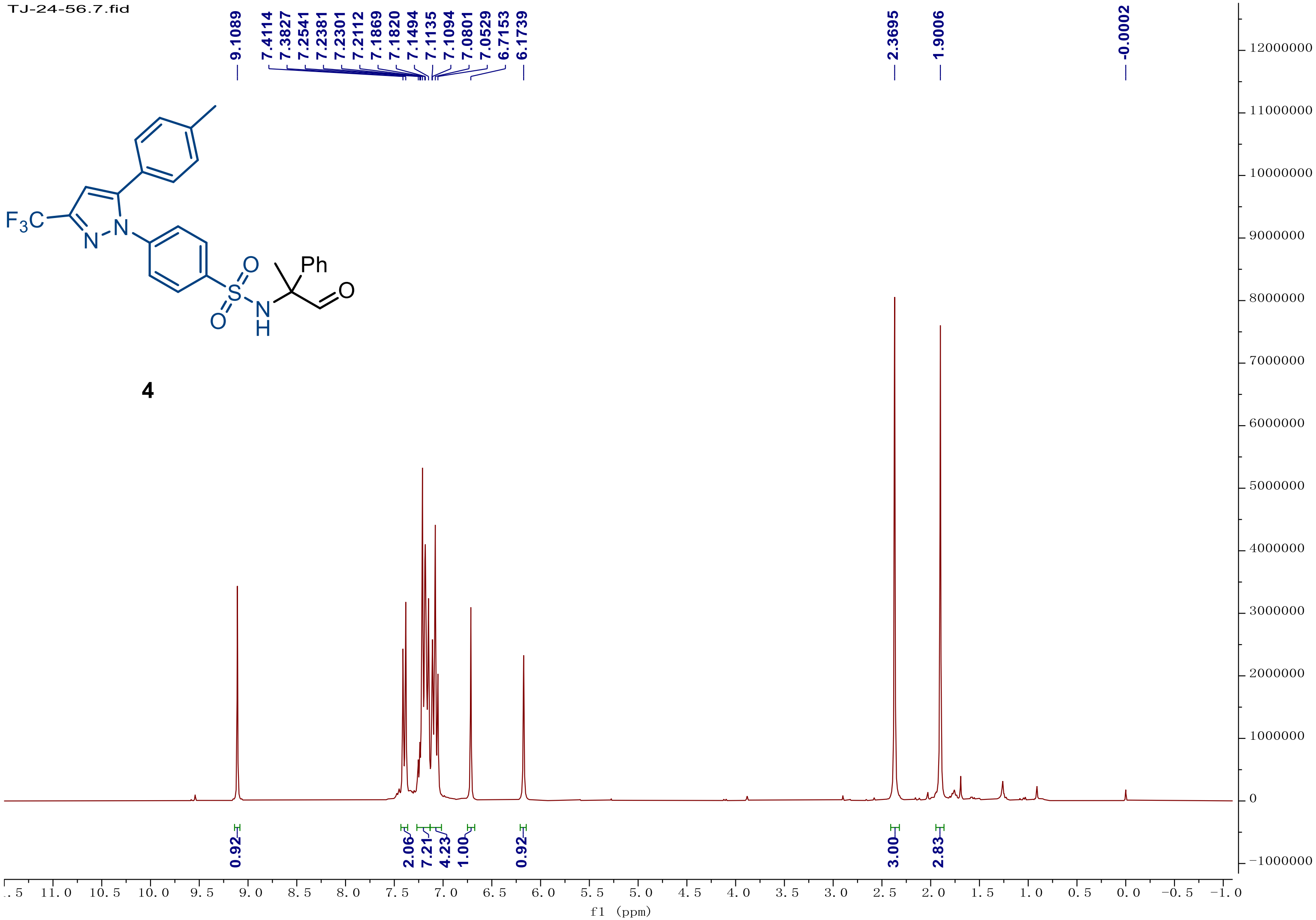
^{1}**H NMR** spectrum of compound **3** (300 MHz, $CDCl_3$)



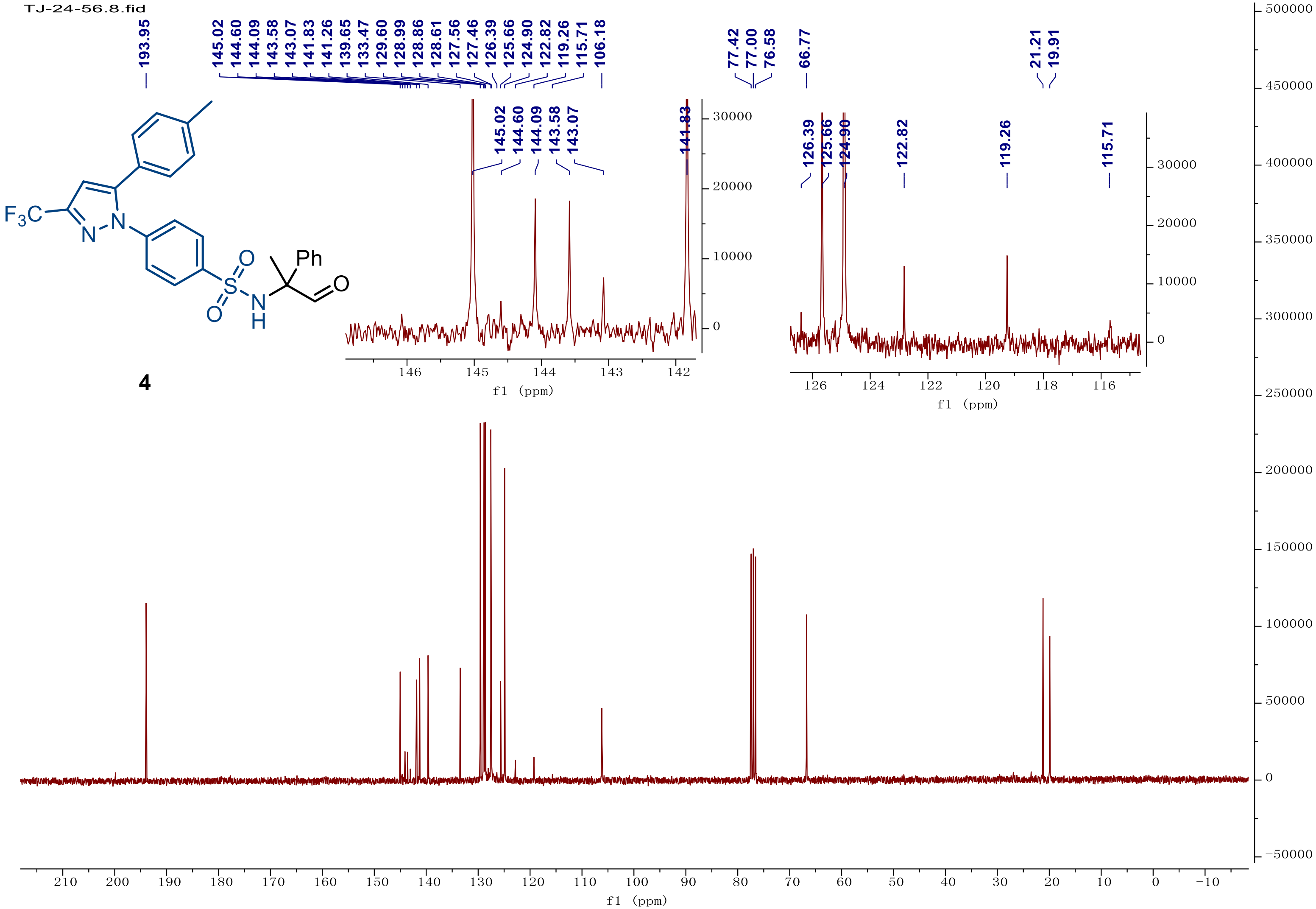
^{13}C **NMR** spectrum of compound **3** (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound 4 (300 MHz, CDCl$_3$)

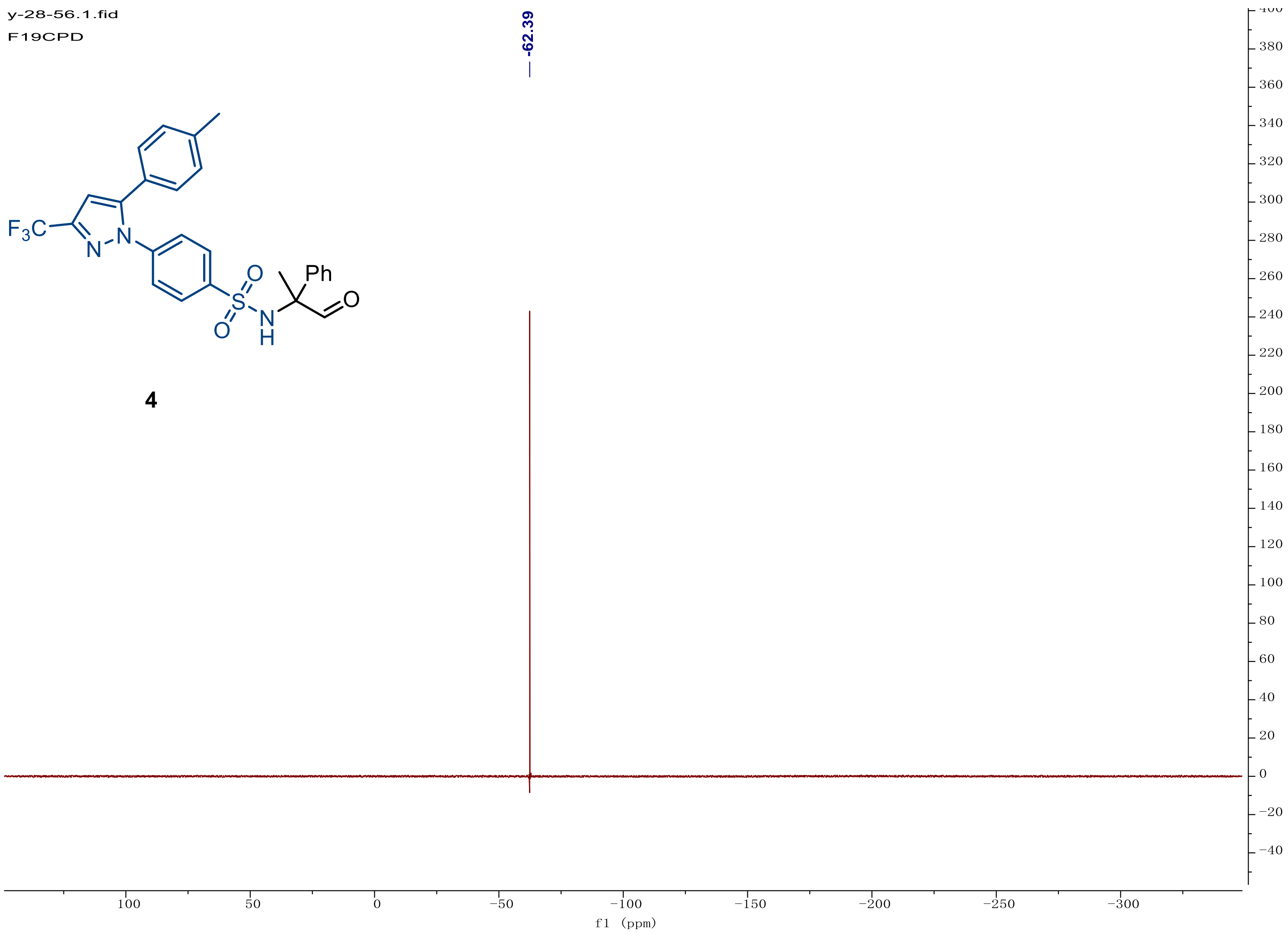


^{13}C NMR spectrum of compound 4 (75 MHz, $CDCl_3$)

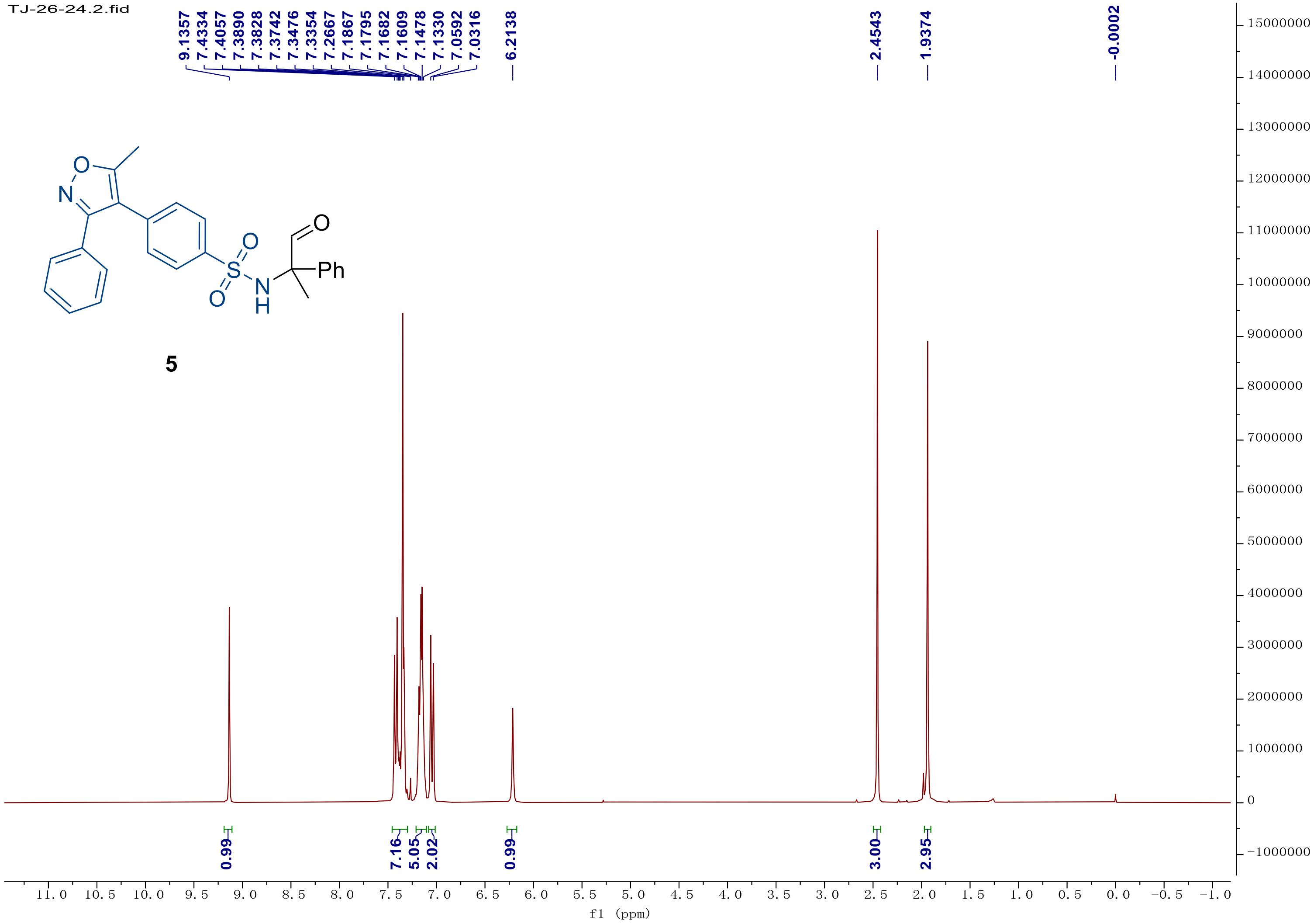


4

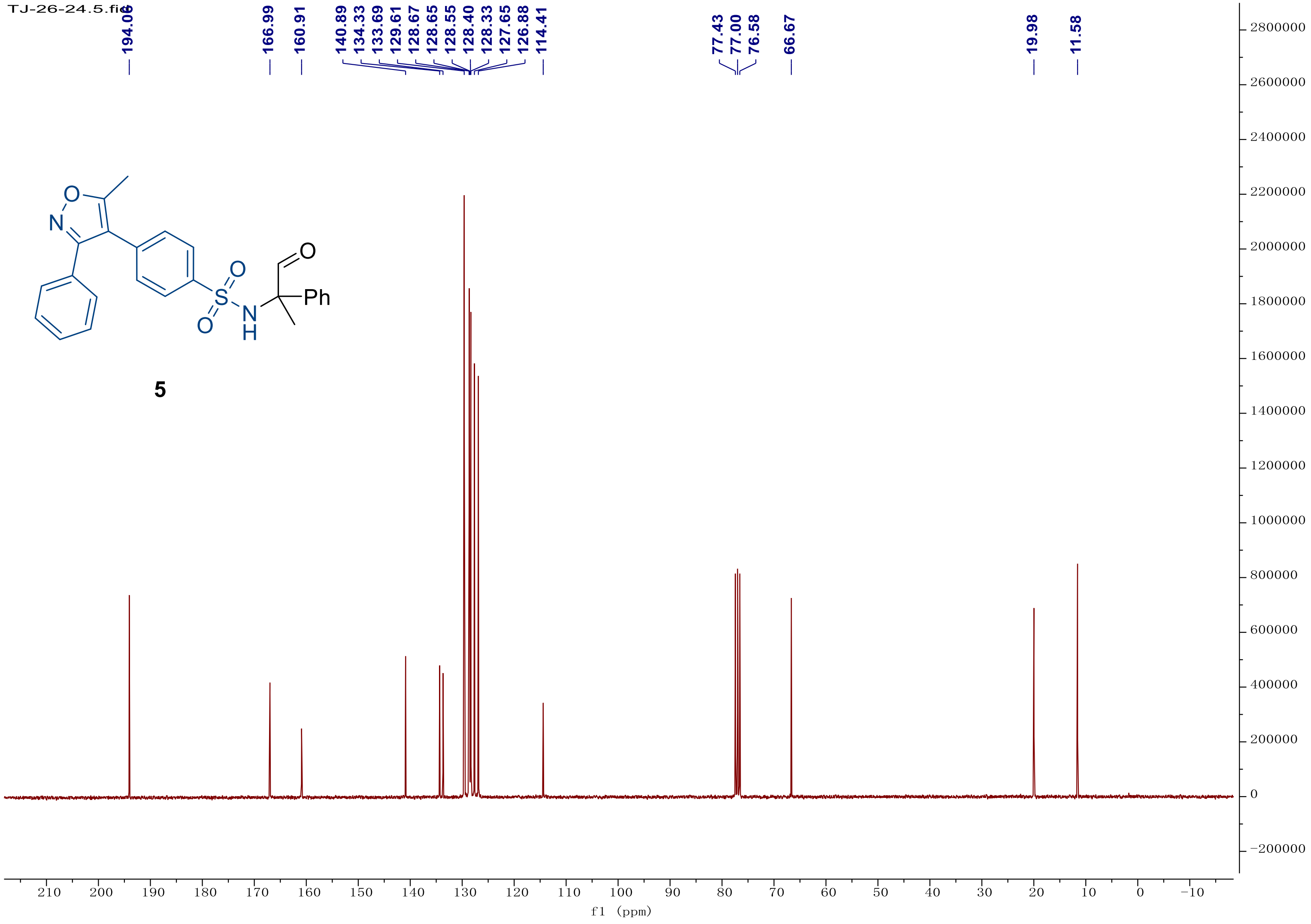
^{19}F NMR spectrum of compound **4** (376 MHz, $CDCl_3$)



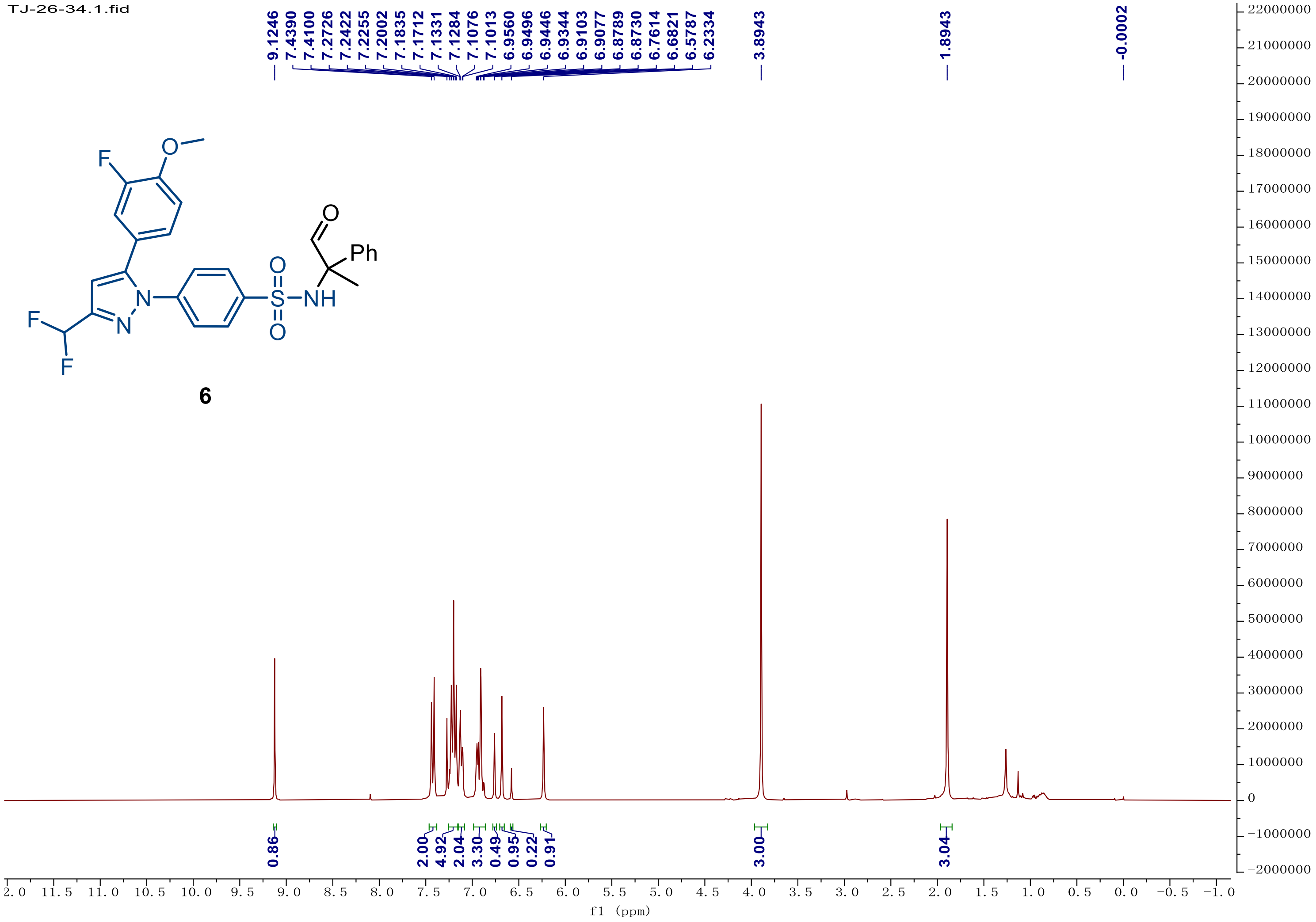
^{1}**H NMR** spectrum of compound **5** (300 MHz, CDCl$_3$)



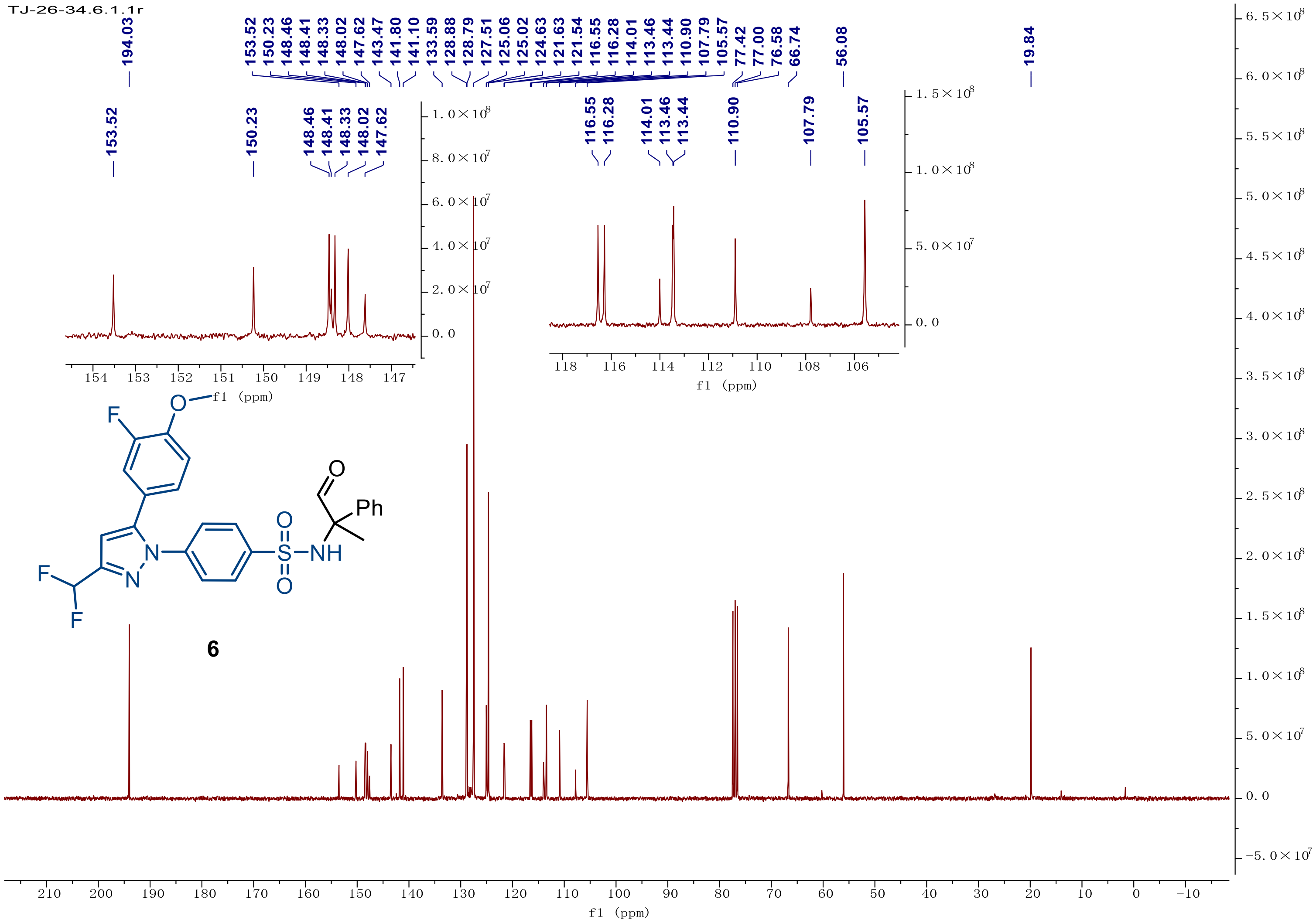
^{13}C **NMR** spectrum of compound **5** (75 MHz, CDCl$_3$)



^{1}**H NMR** spectrum of compound **6** (300 MHz, $CDCl_3$)

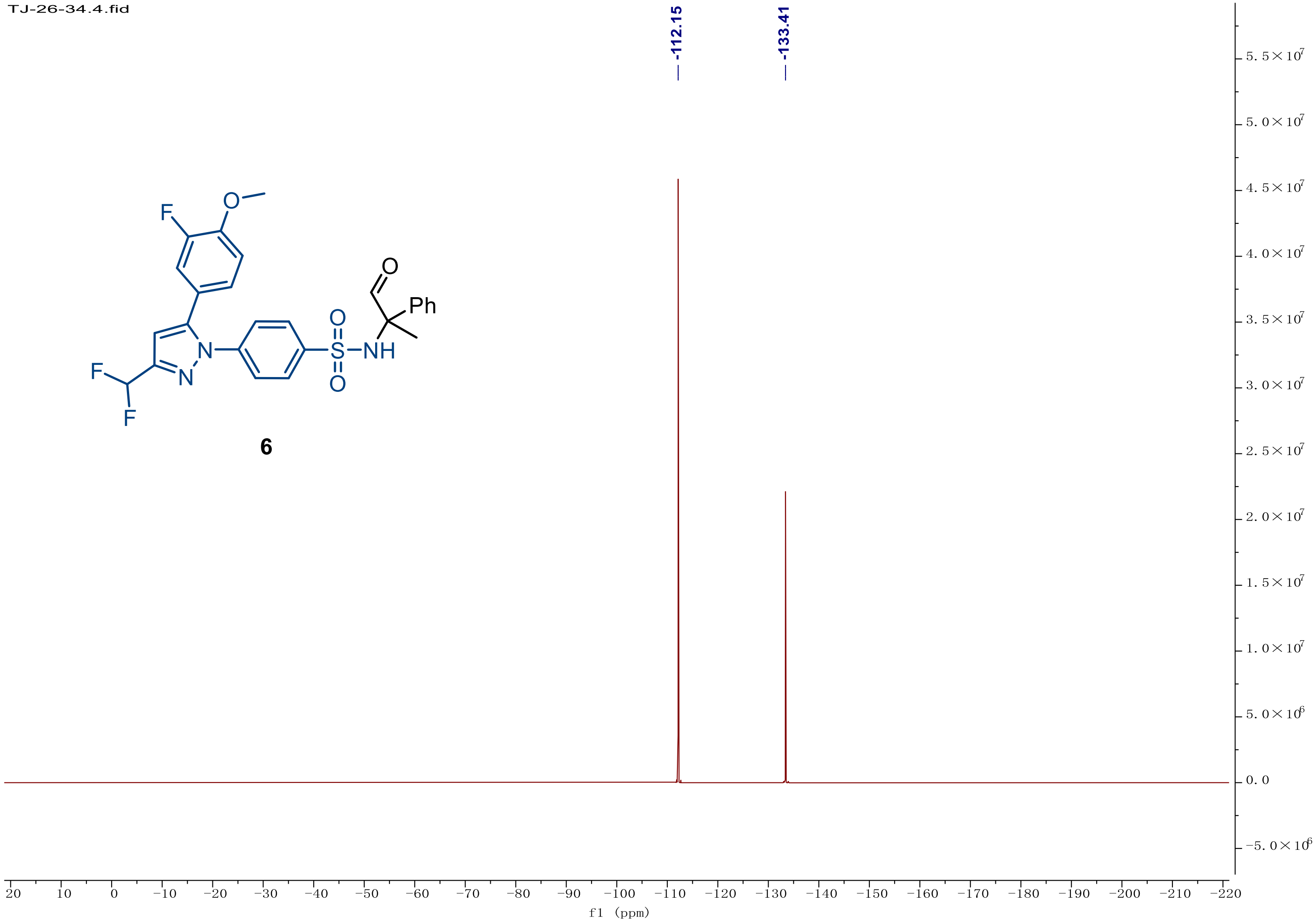


^{13}C **NMR** spectrum of compound **6** (75 MHz, CDCl$_3$)

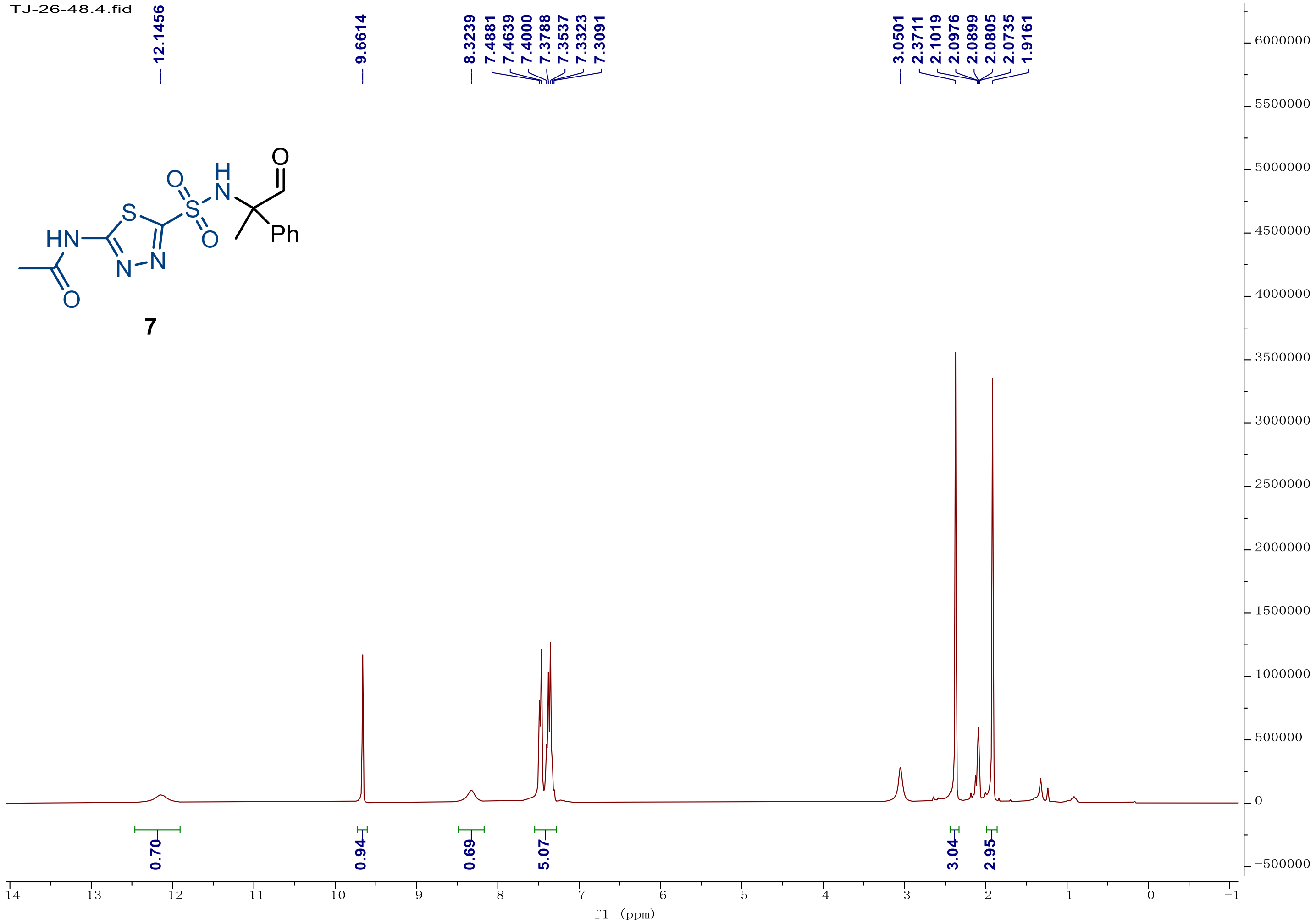


6

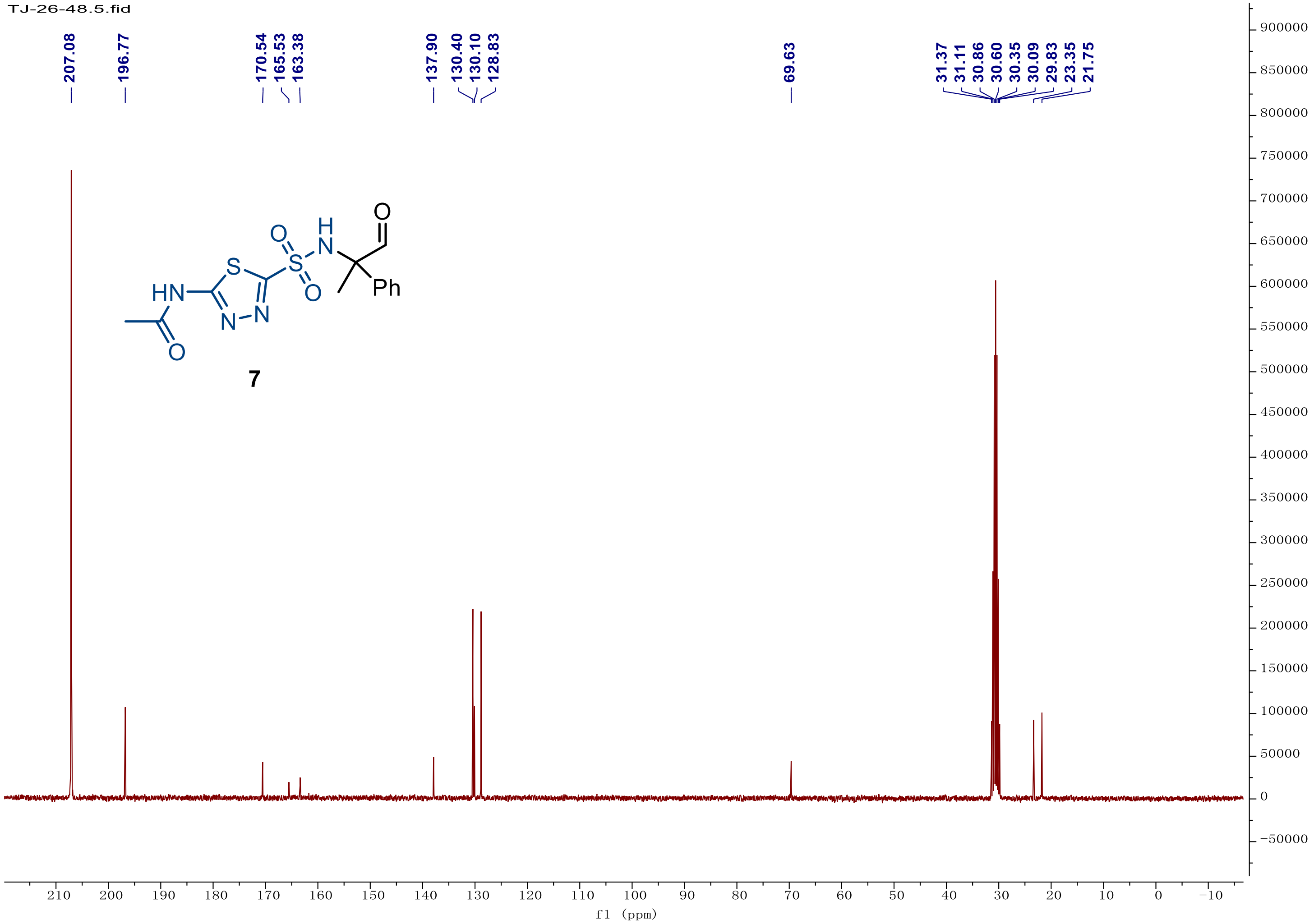
^{19}F NMR spectrum of compound 6 (282 MHz, CDCl$_3$)



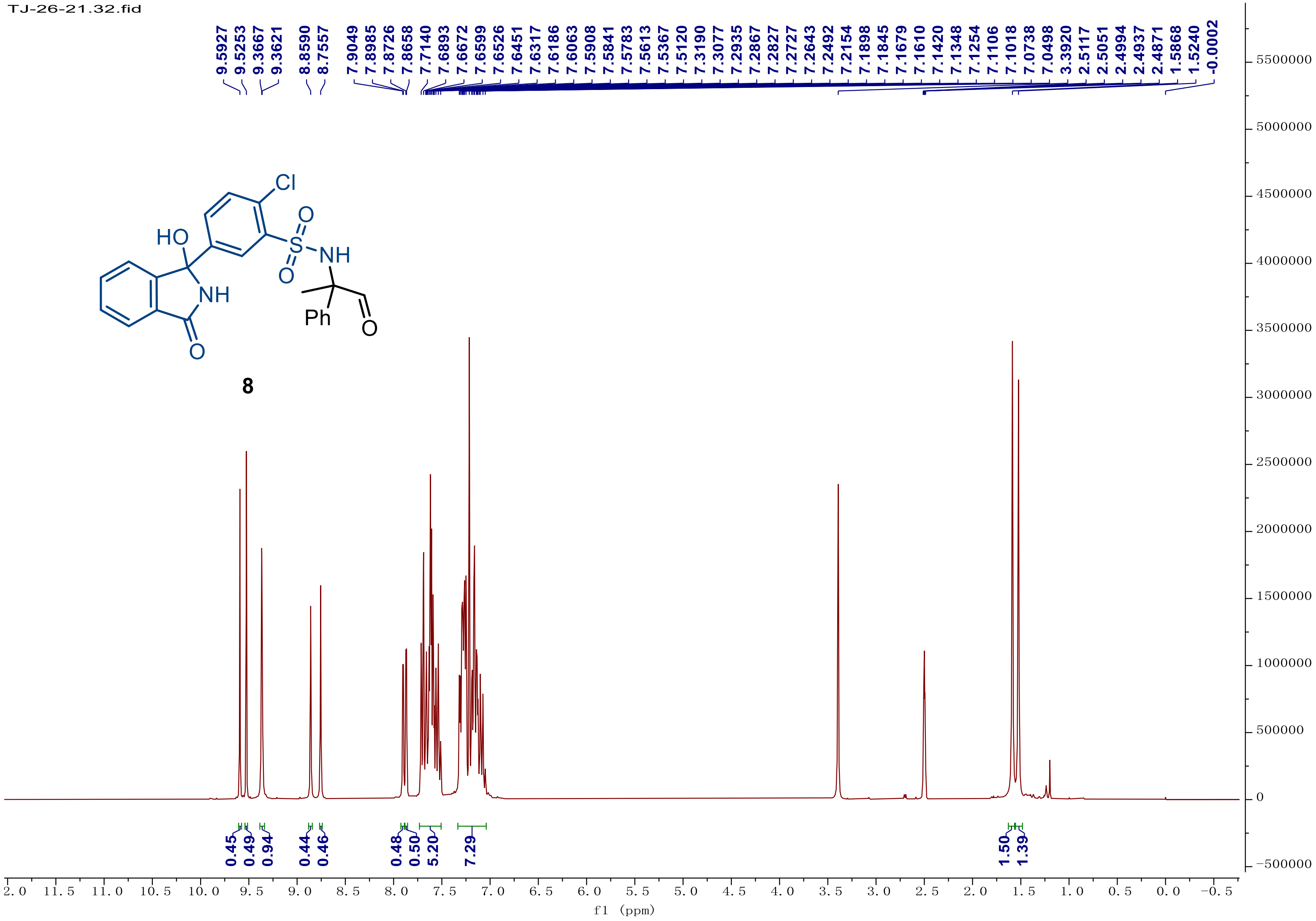
^{1}**H NMR** spectrum of compound **7** (300 MHz, Acetone-*d*$_6$)



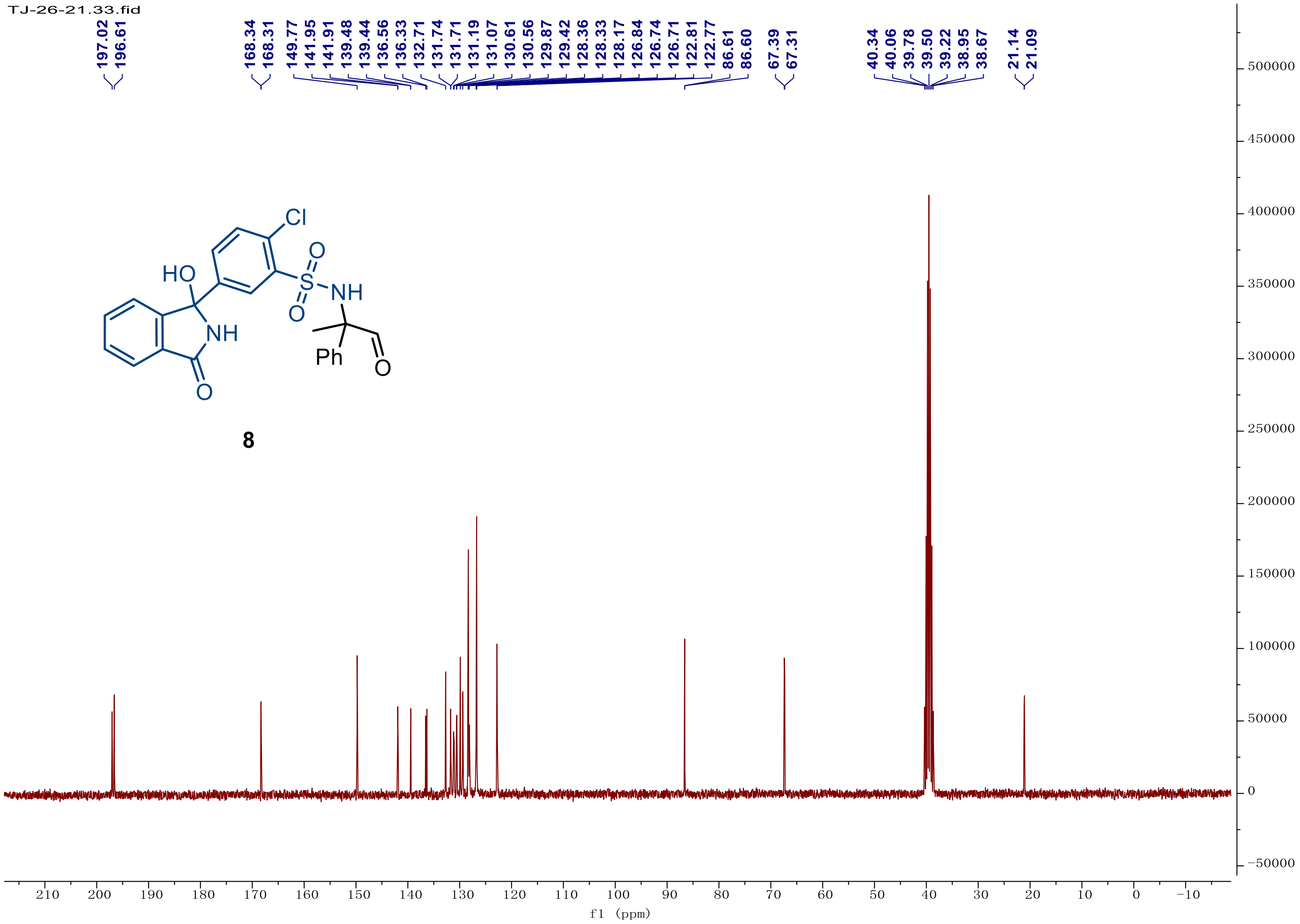
^{13}**C NMR** spectrum of compound **7** (75 MHz, Acetone-*d*$_6$)



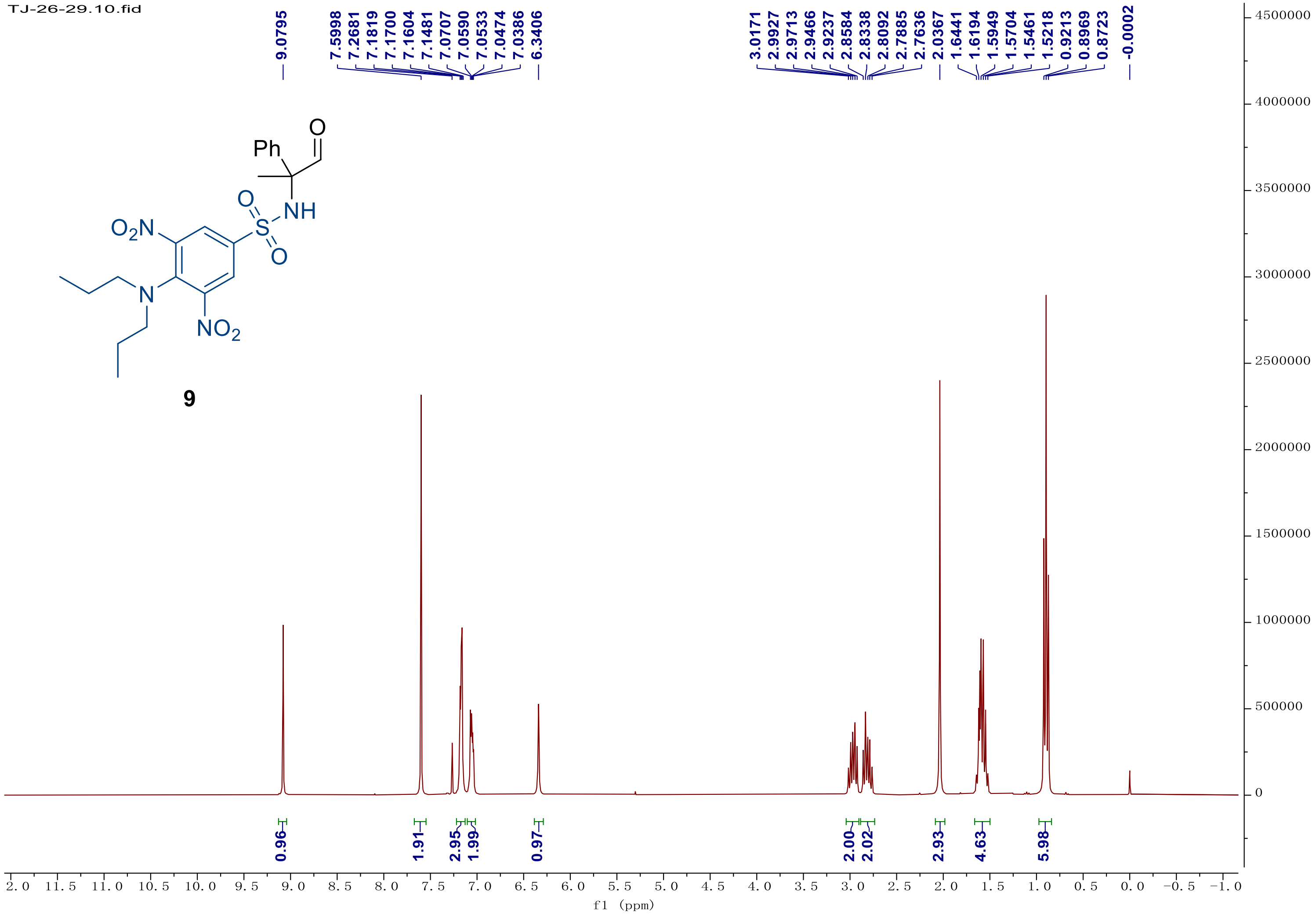
^{1}**H NMR** spectrum of compound **8** (300 MHz, DMSO-d_6)



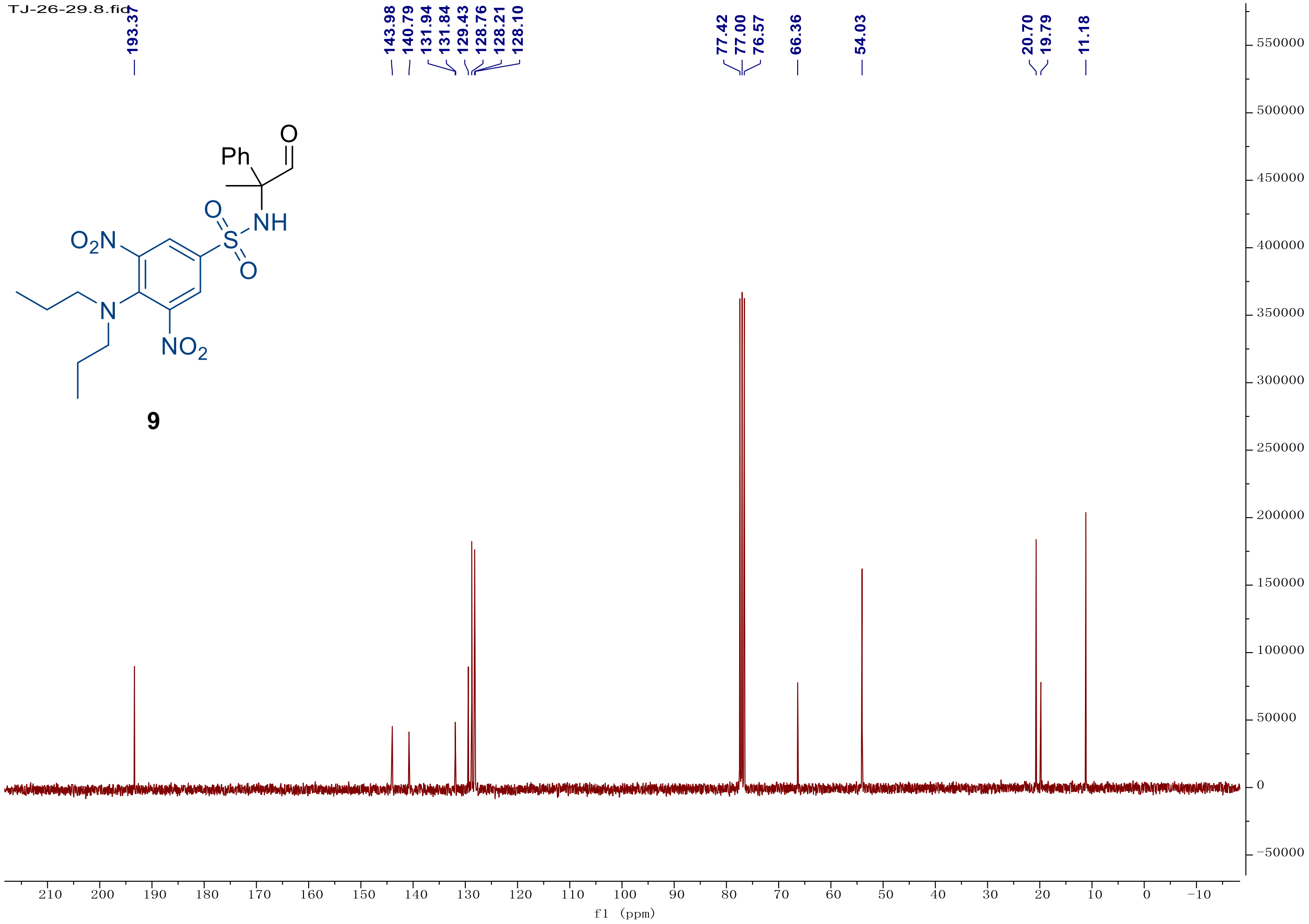
^{13}C NMR spectrum of compound **8** (75 MHz, DMSO-d_6)



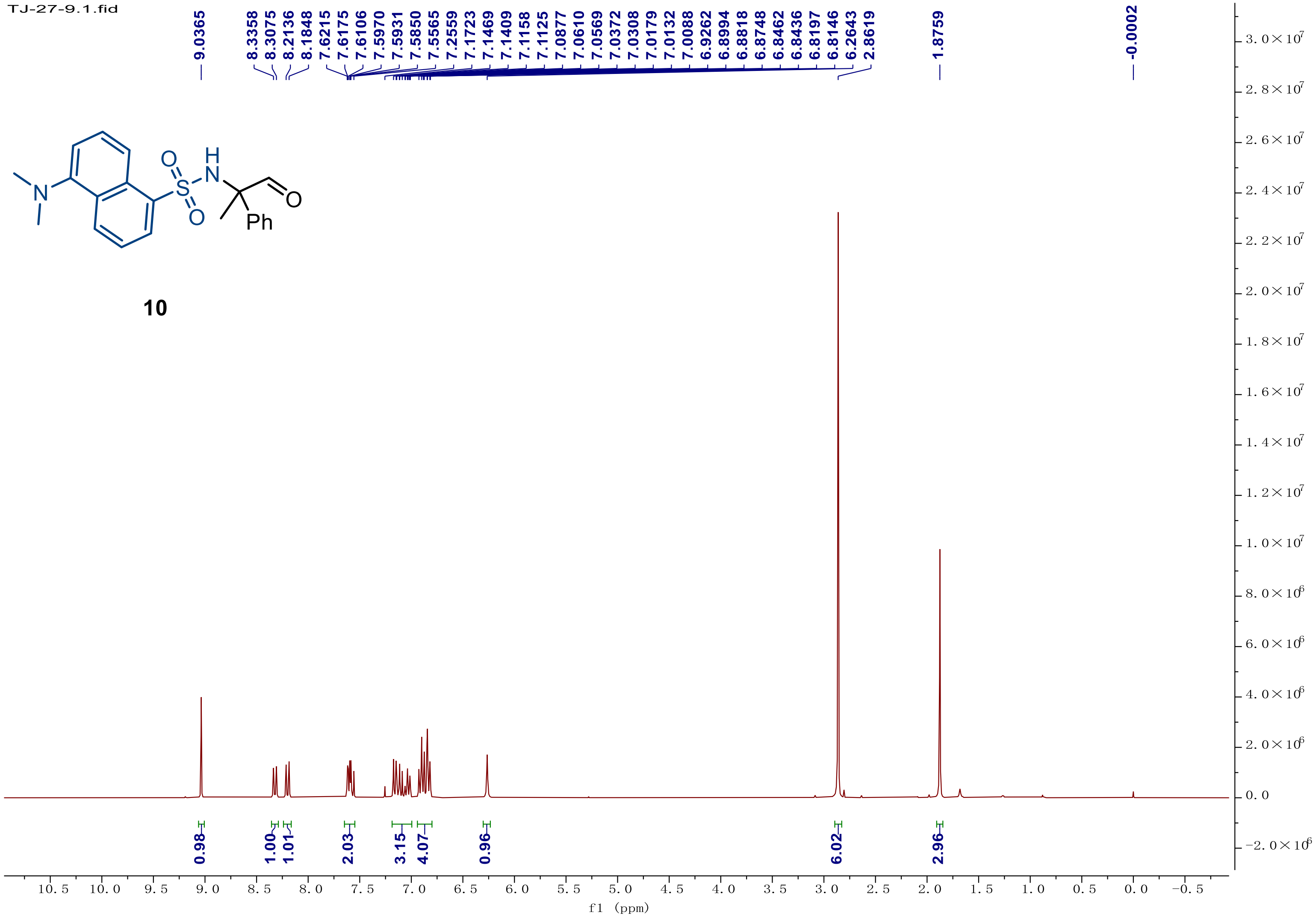
^{1}H NMR spectrum of compound 9 (300 MHz, $CDCl_3$)



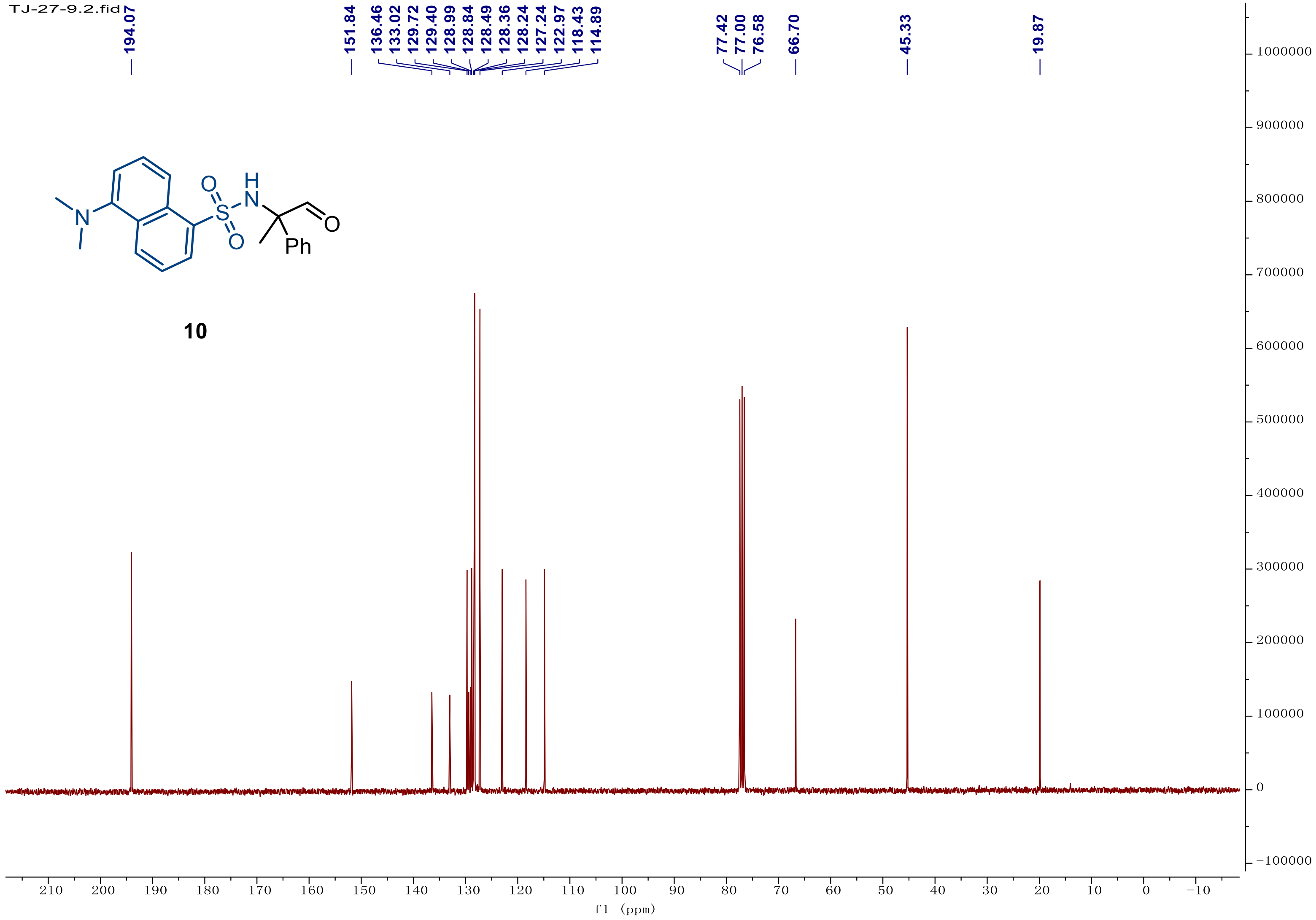
^{13}**C NMR** spectrum of compound **9** (75 MHz, CDCl$_3$)



^{1}H NMR spectrum of compound 10 (300 MHz, CDCl$_3$)

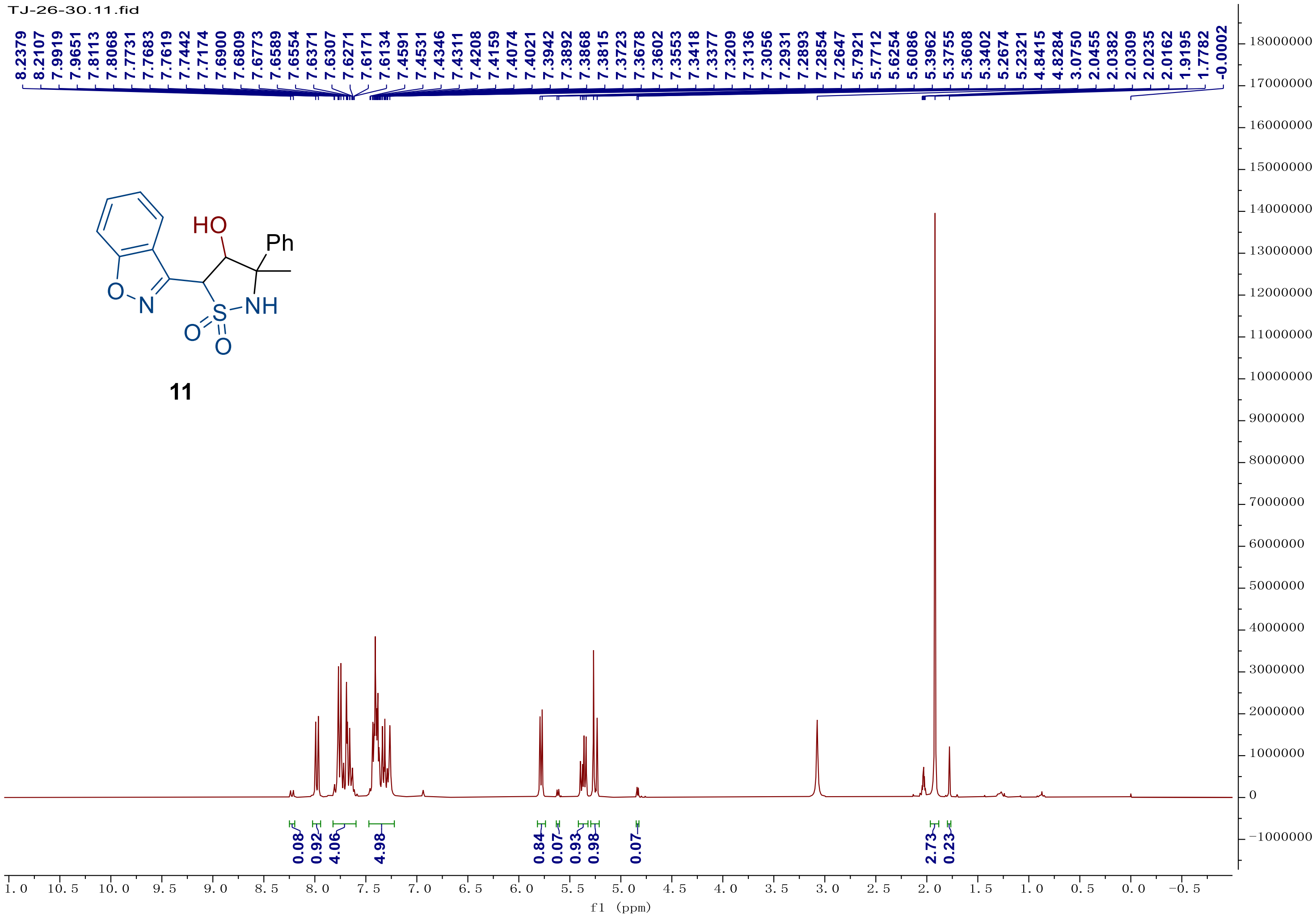


^{13}C **NMR** spectrum of compound **10** (75 MHz, CDCl$_3$)

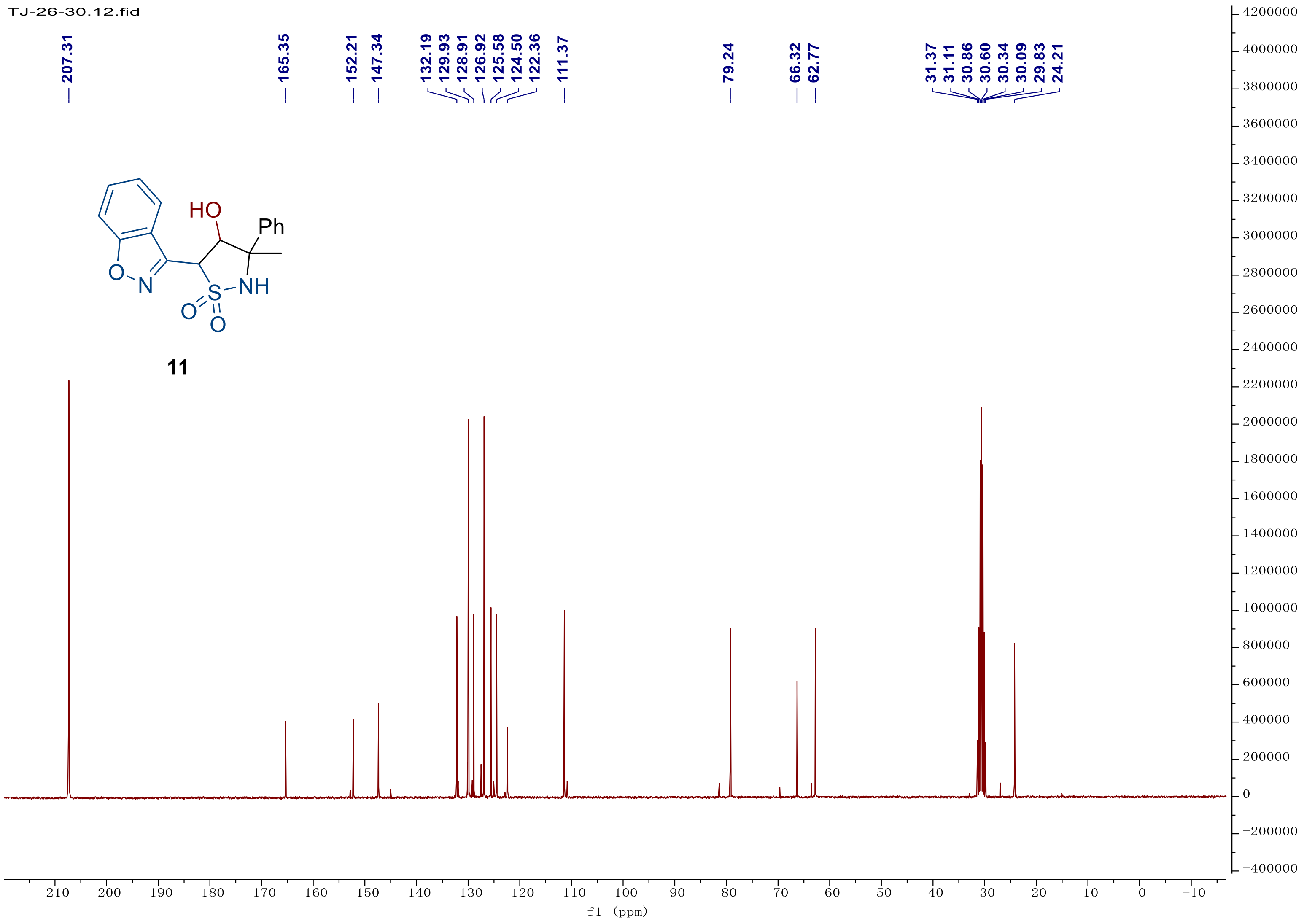


10

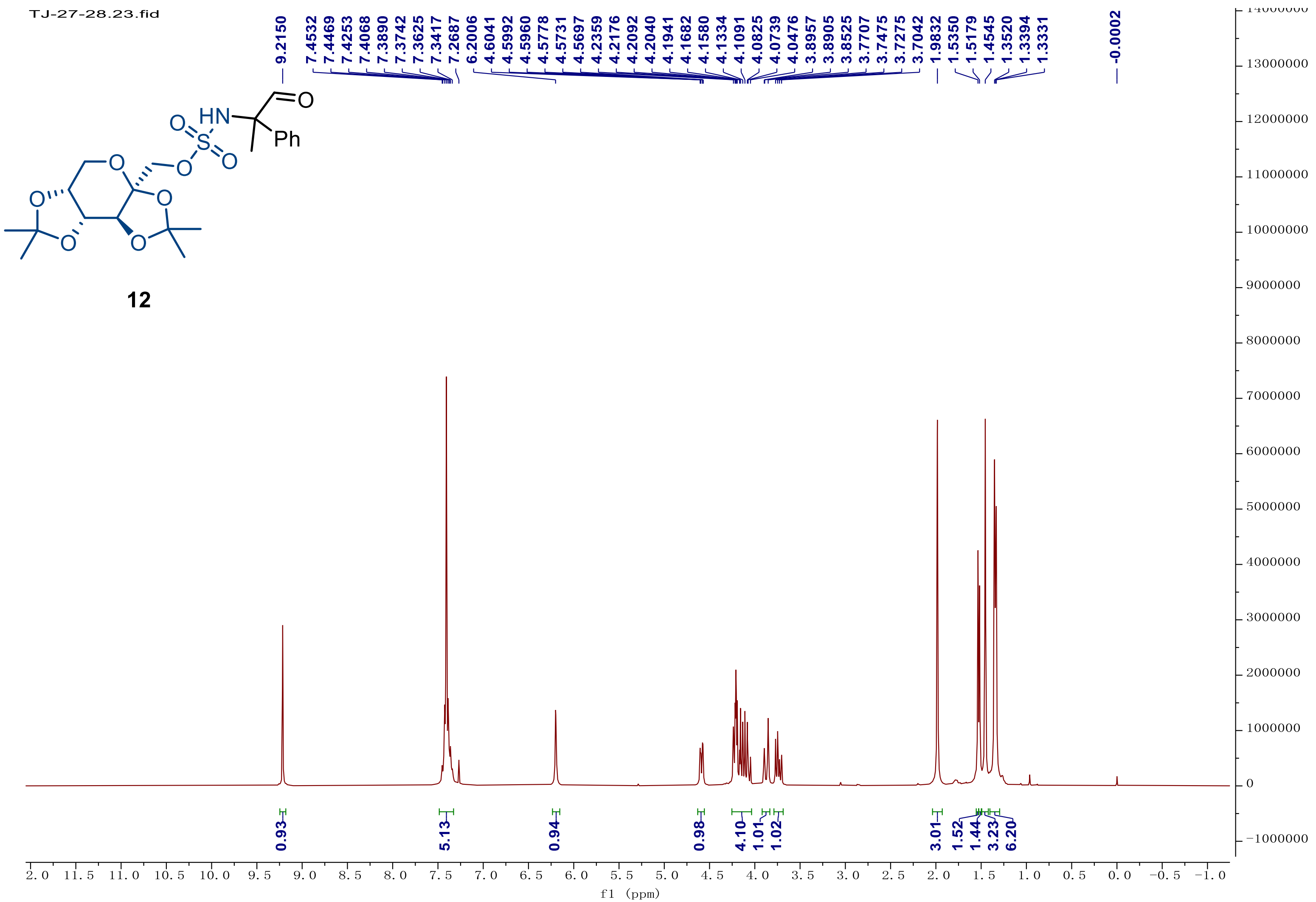
^{1}**H NMR** spectrum of compound **11** (300 MHz, Acetone-d_6)



^{13}C **NMR** spectrum of compound **11** (75 MHz, Acetone-*d*$_6$)

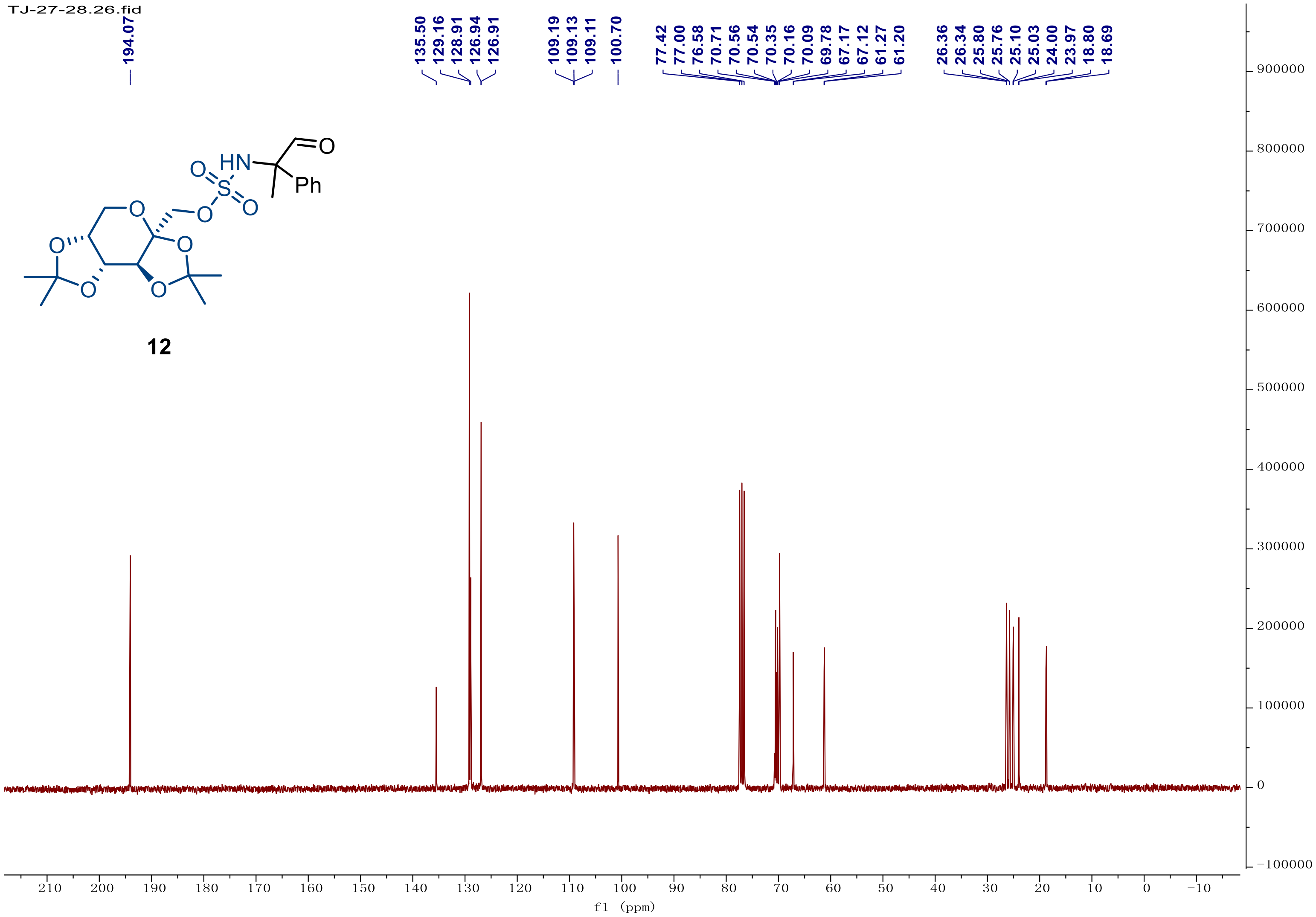


^{1}**H NMR** spectrum of compound **12** (300 MHz, $CDCl_3$)



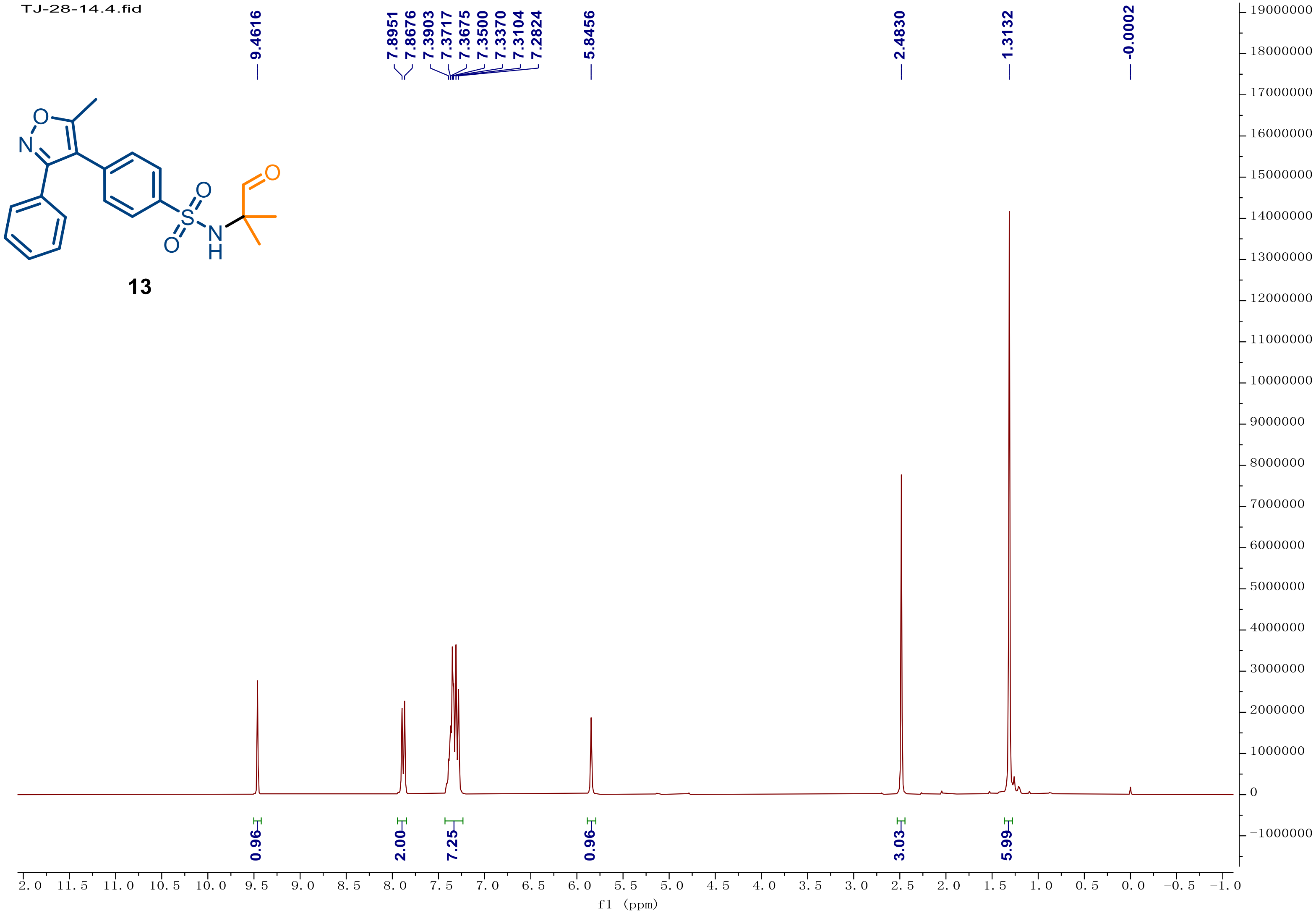
12

^{13}C NMR spectrum of compound **12** (75 MHz, $CDCl_3$)

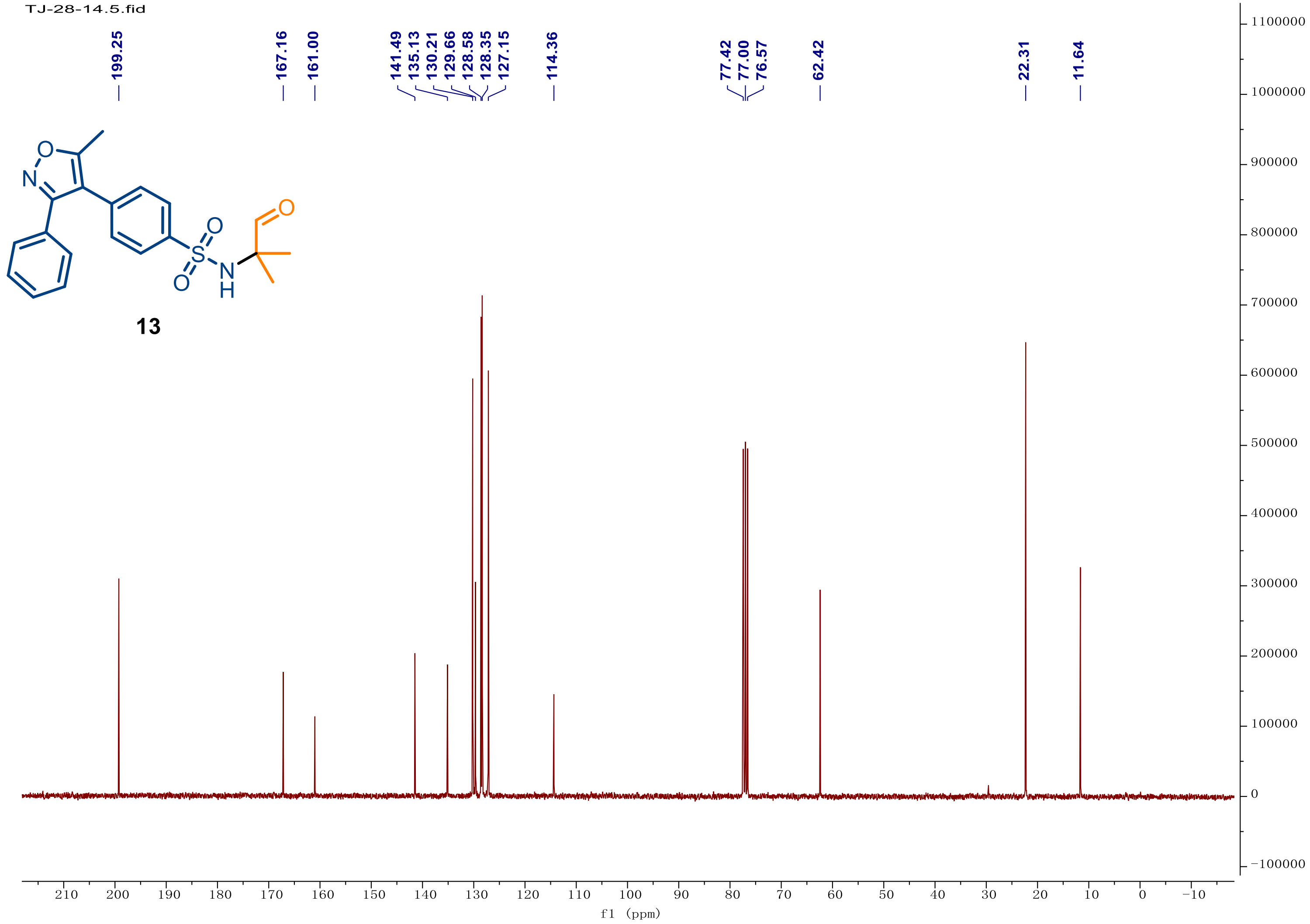


12

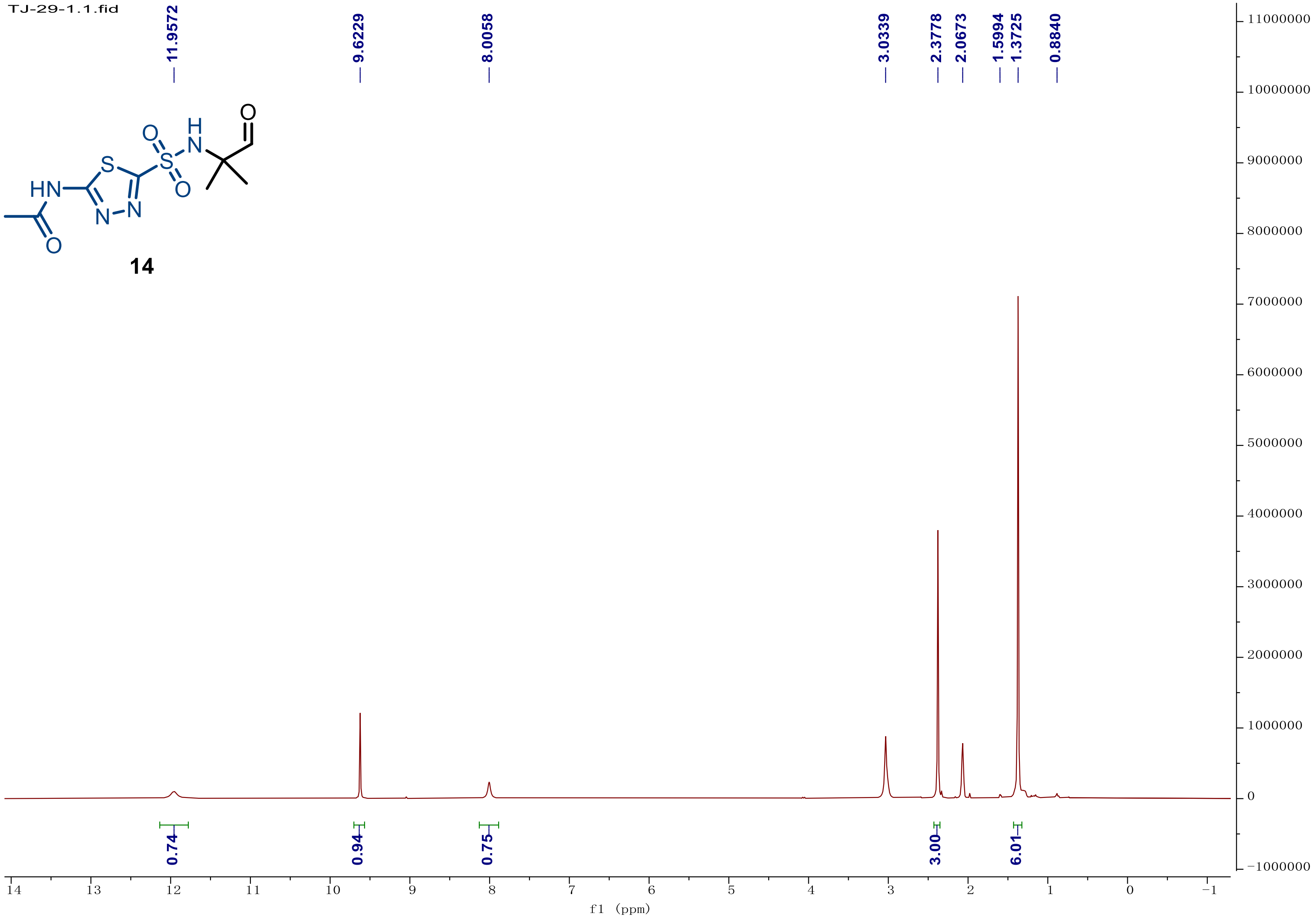
^{1}**H NMR** spectrum of compound **13** (300 MHz, CDCl$_3$)



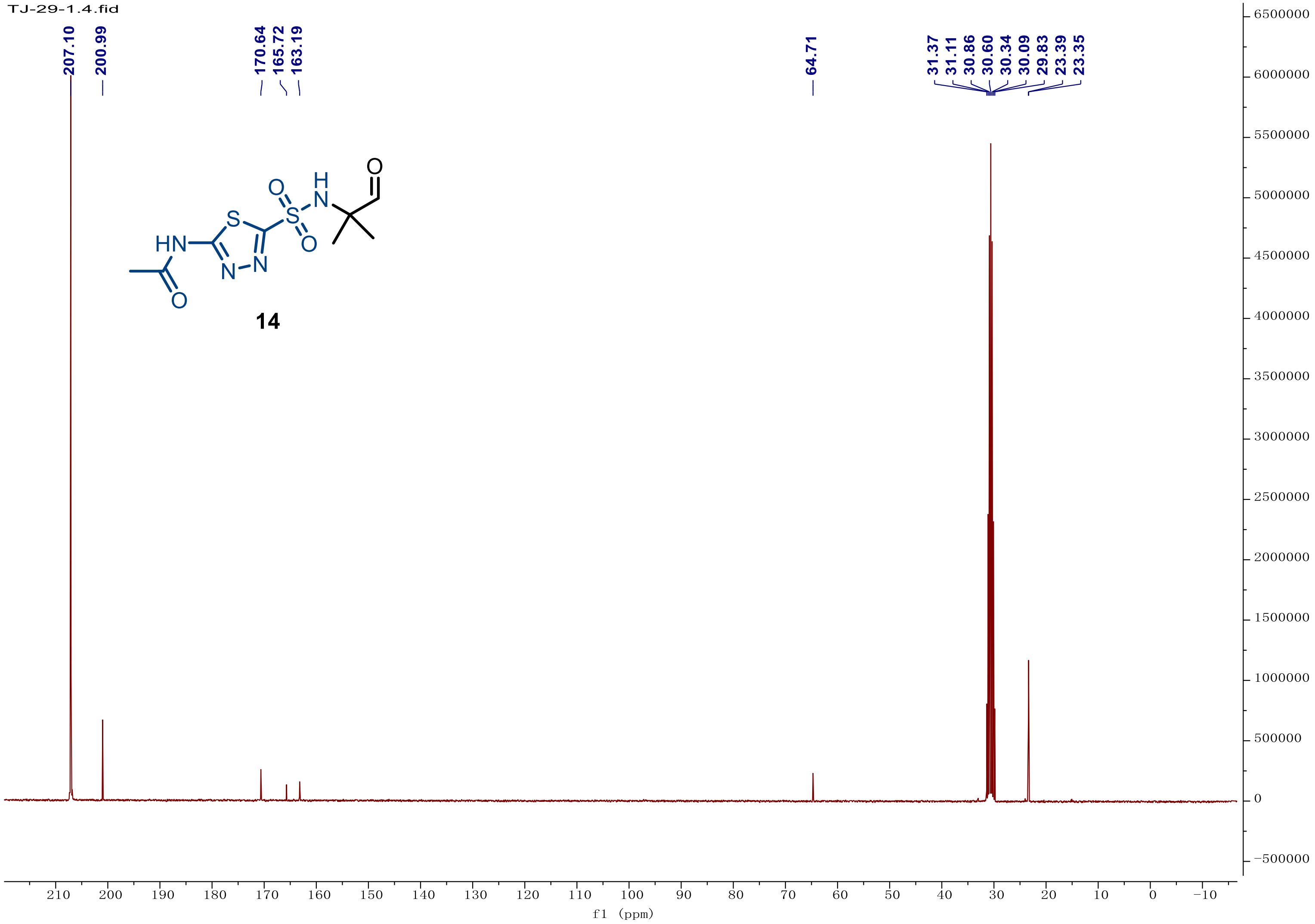
^{13}C **NMR** spectrum of compound **13** (75 MHz, $CDCl_3$)



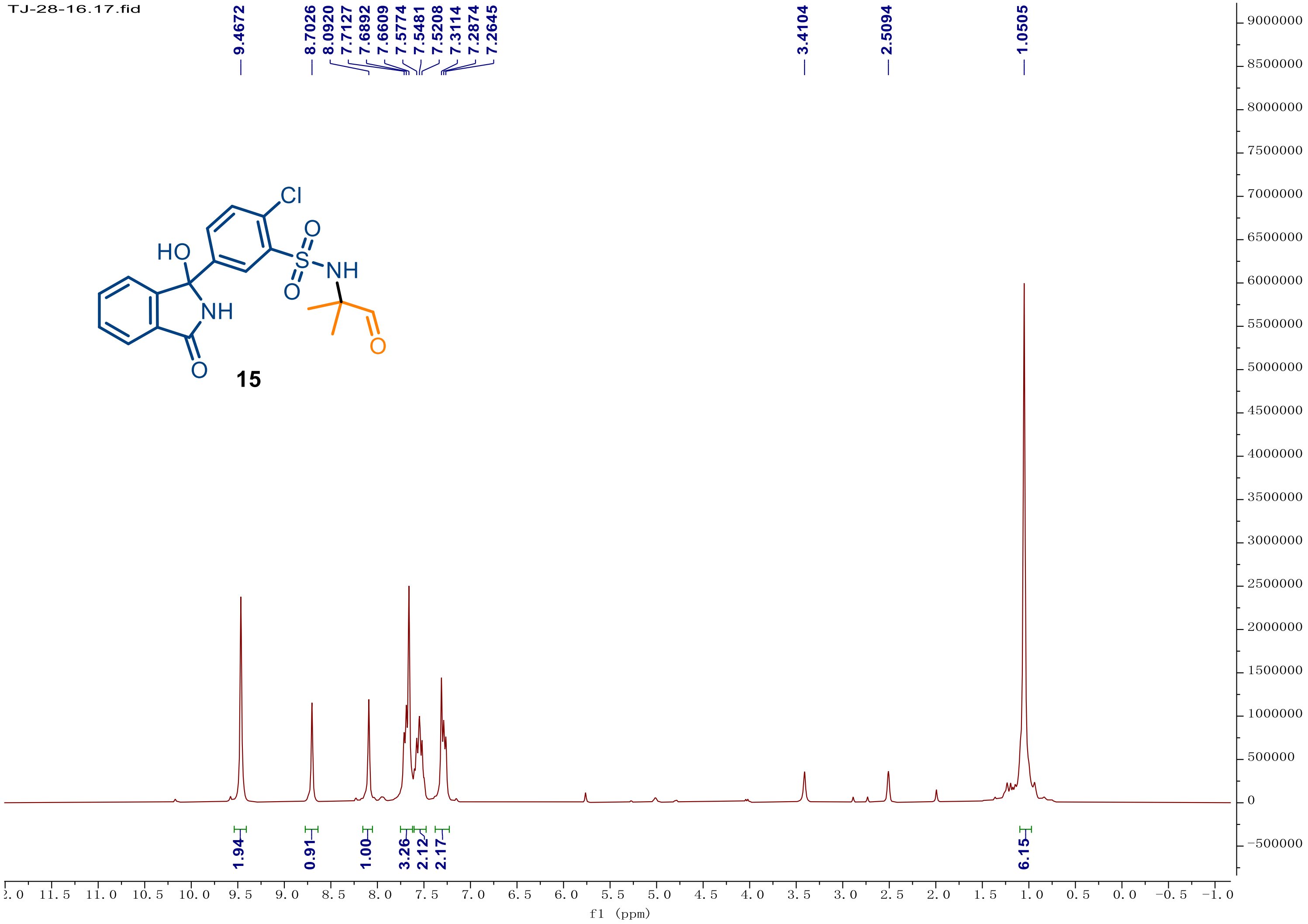
^{1}H NMR spectrum of compound **14** (300 MHz, Acetone-d_6)



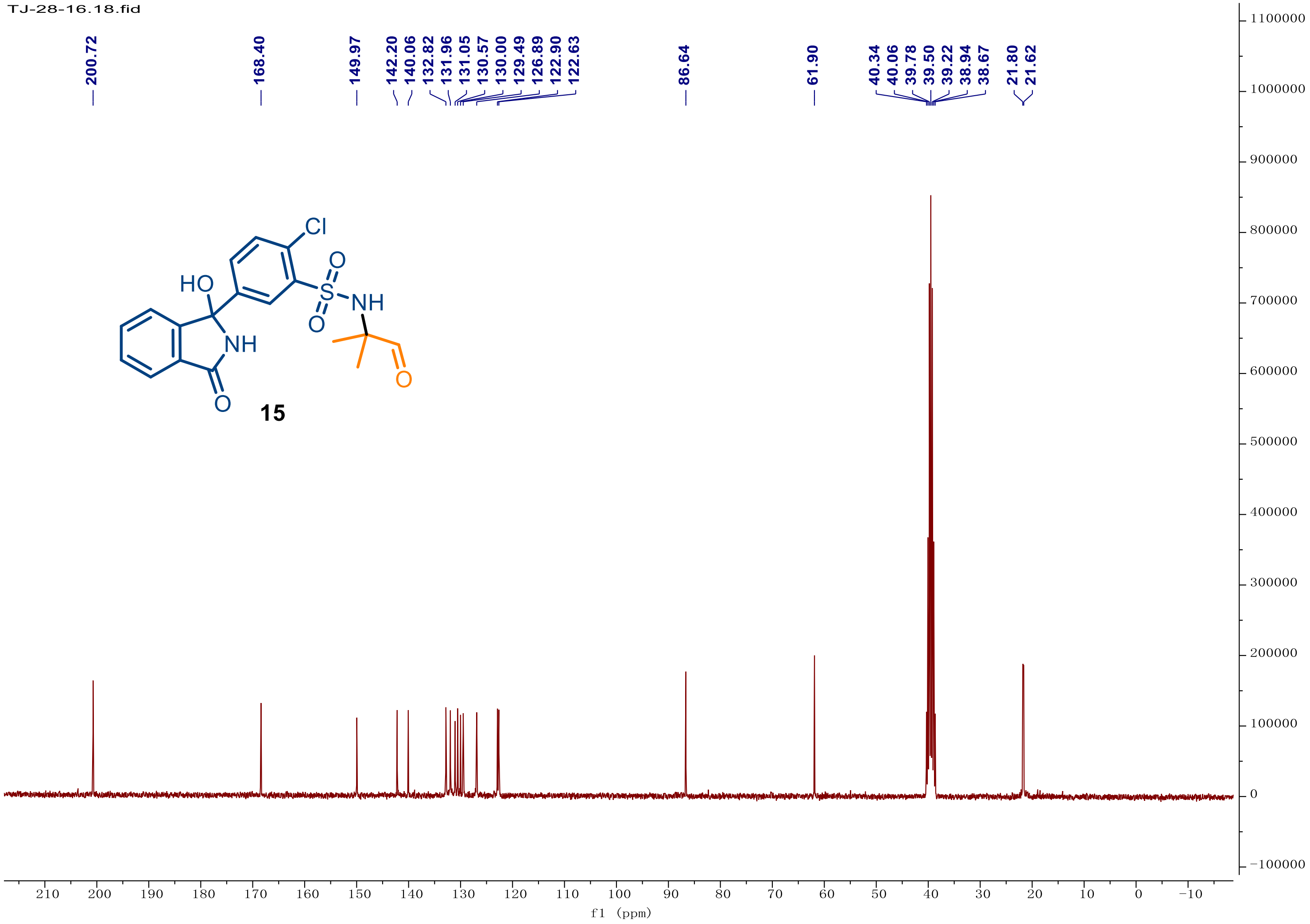
^{13}C **NMR** spectrum of compound **14** (75 MHz, Acetone-d_6)



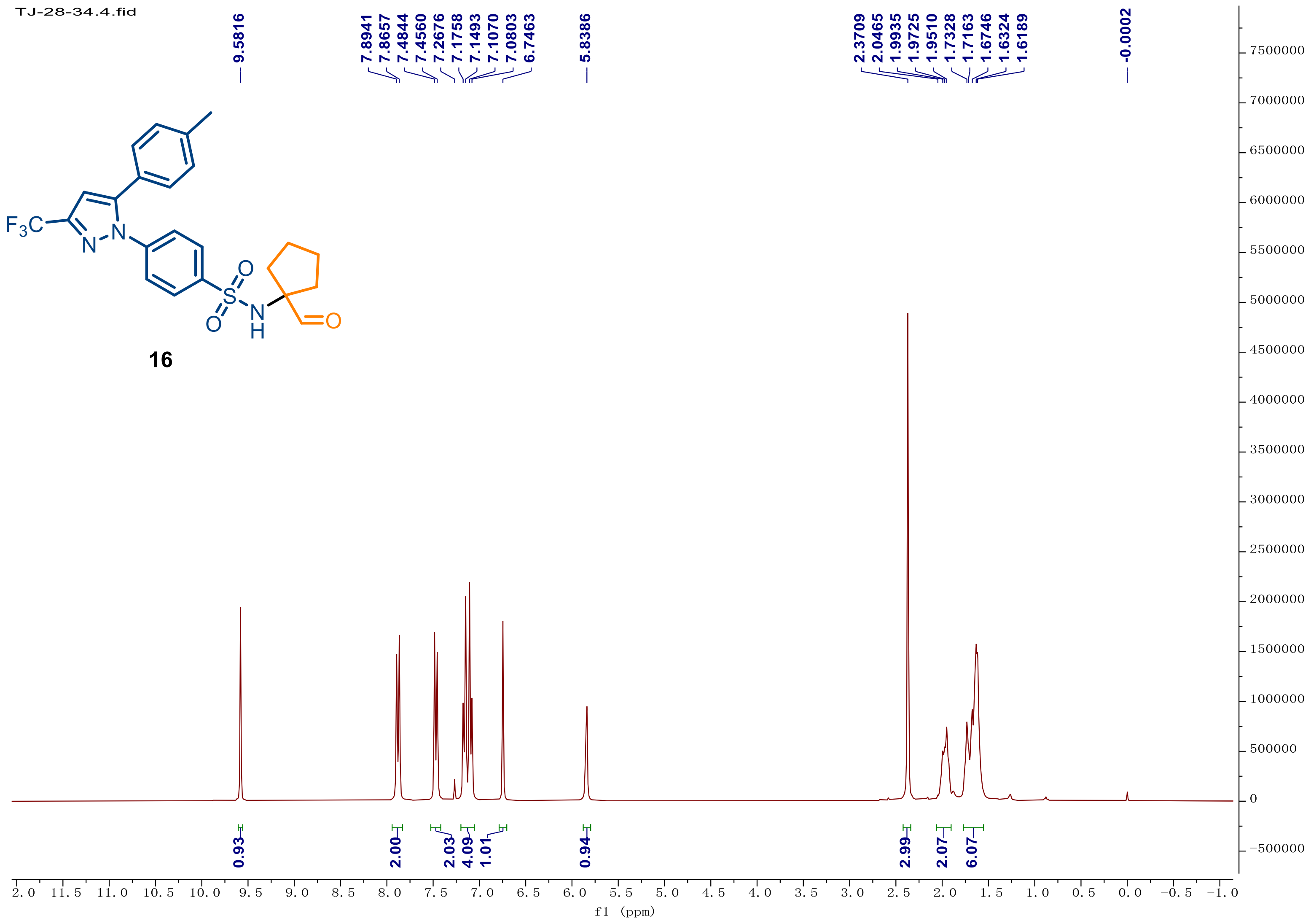
^{1}H NMR spectrum of compound 15 (300 MHz, DMSO-d_6)



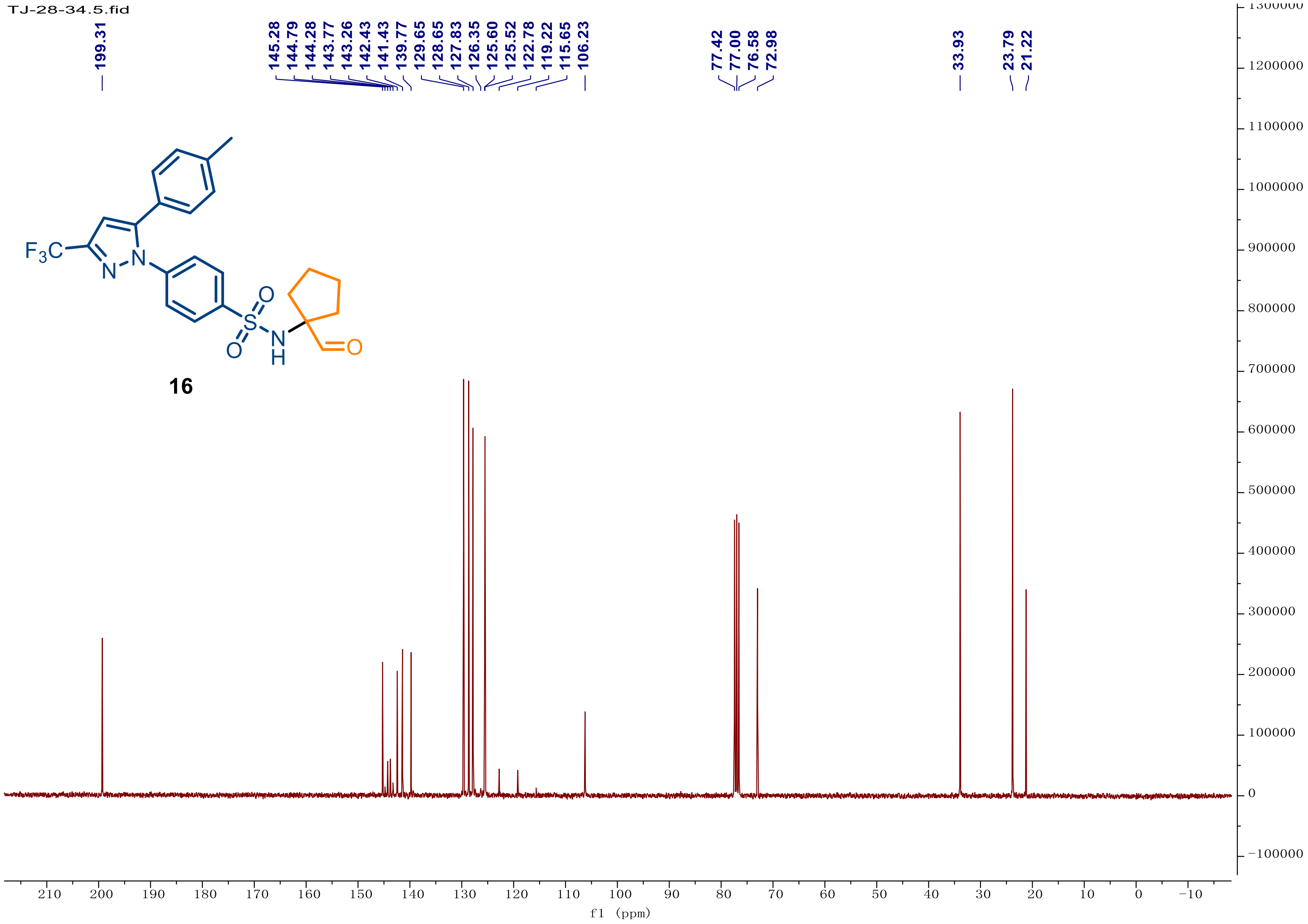
^{13}**C NMR** spectrum of compound **15** (75 MHz, DMSO-d_6)



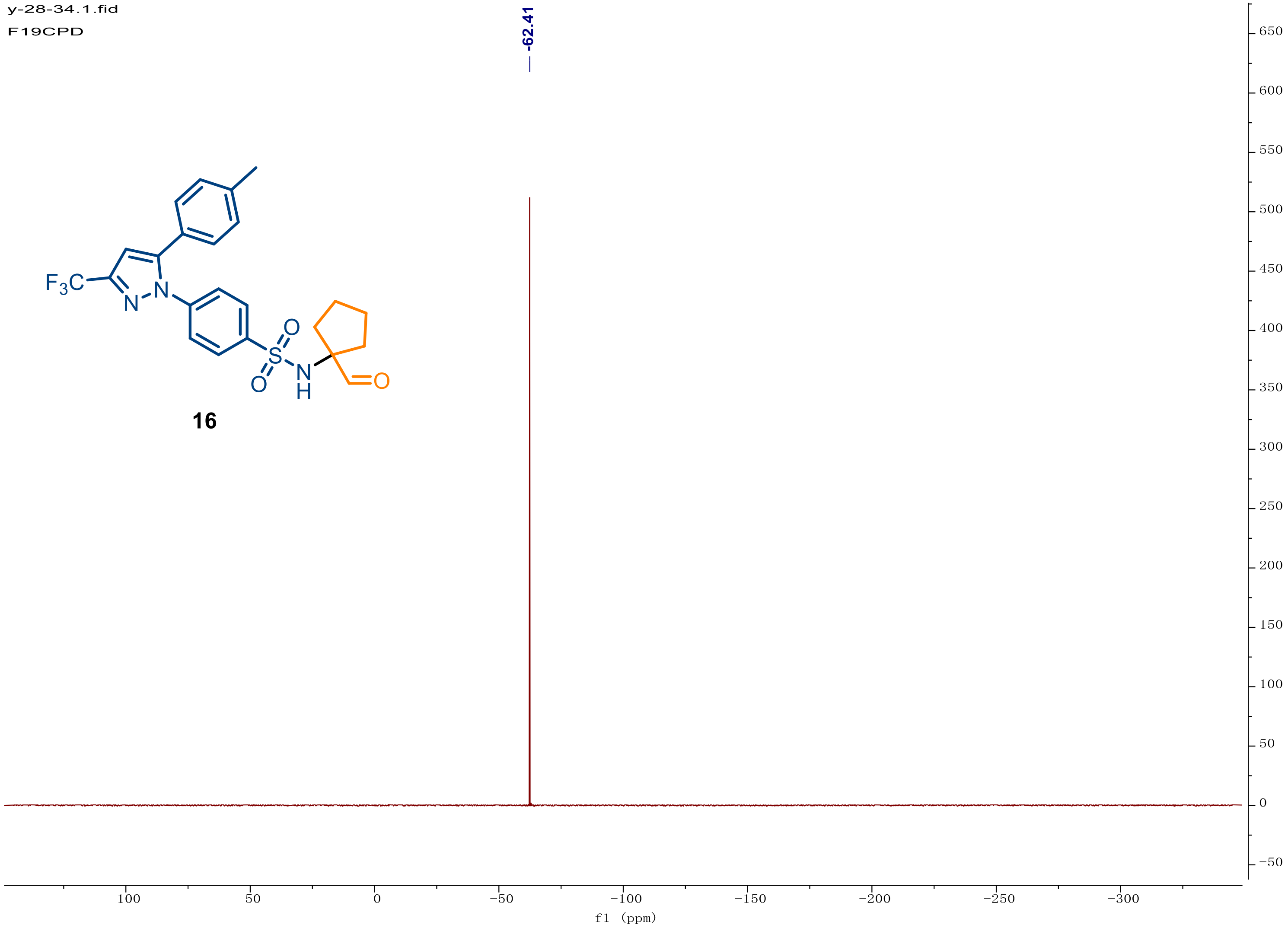
^{1}H NMR spectrum of compound **16** (300 MHz, $CDCl_3$)



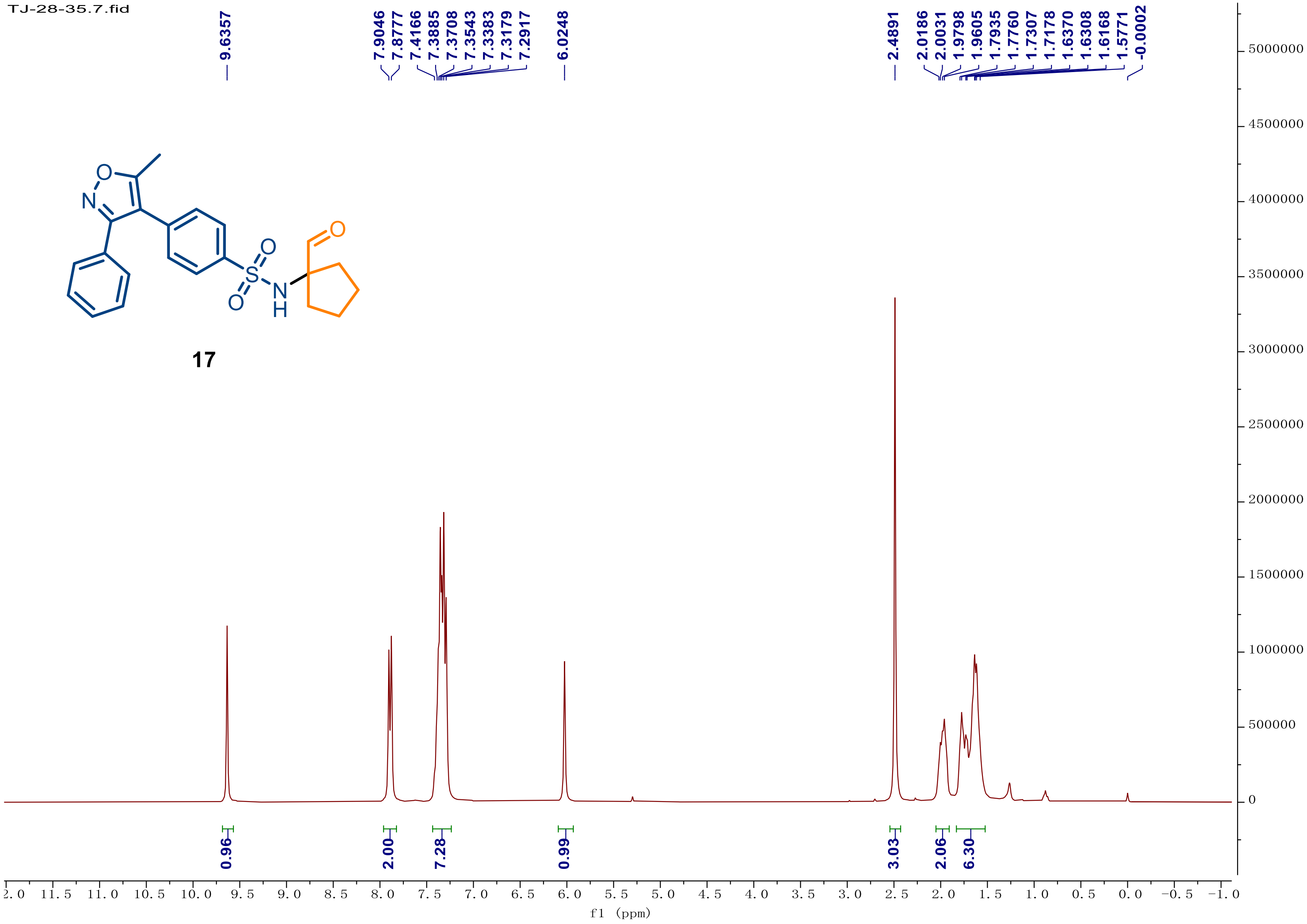
^{13}C NMR spectrum of compound 16 (75 MHz, CDCl$_3$)



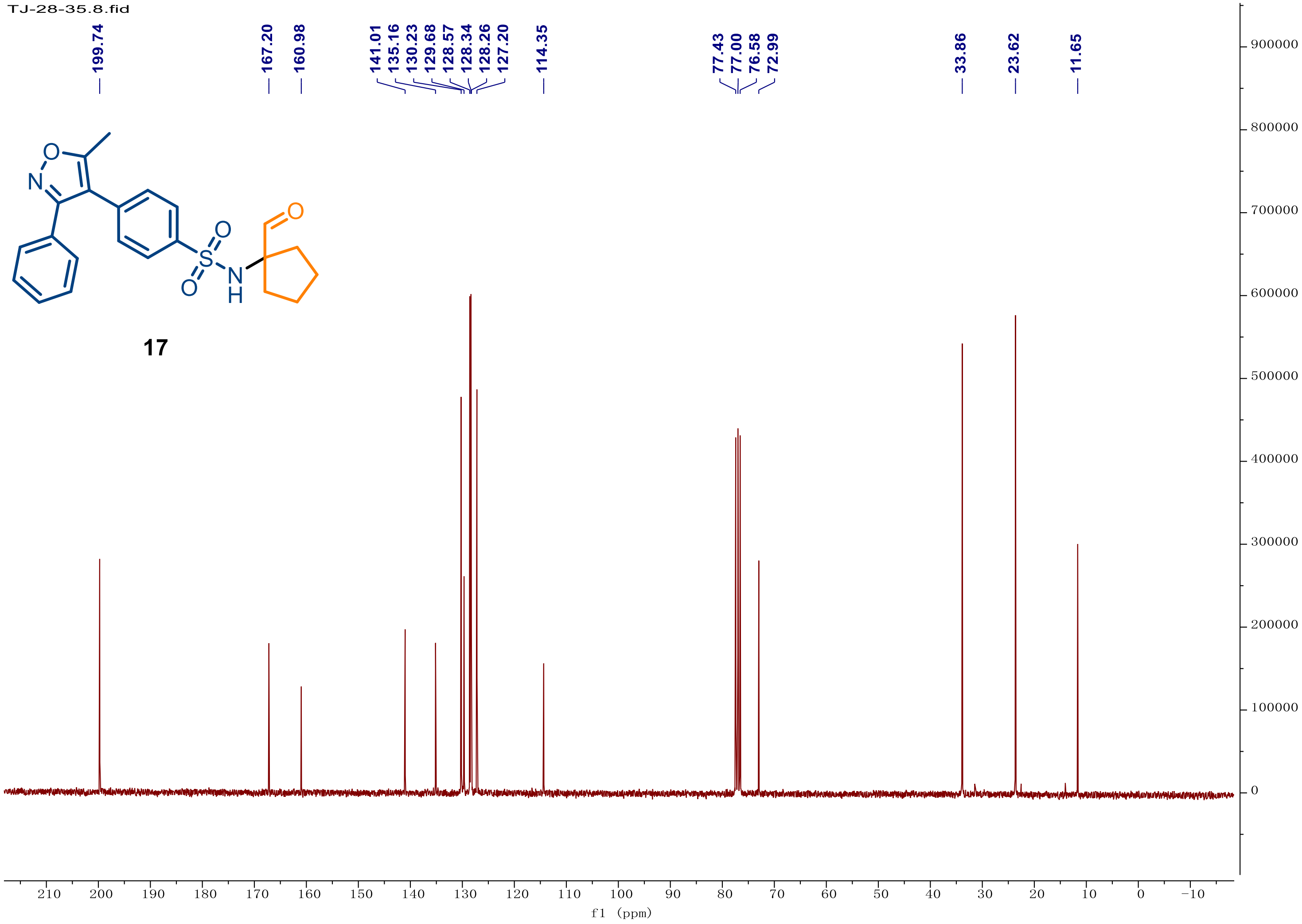
^{19}**F NMR** spectrum of compound **16** (376 MHz, CDCl$_3$)



^{1}**H NMR** spectrum of compound **17** (300 MHz, $CDCl_3$)

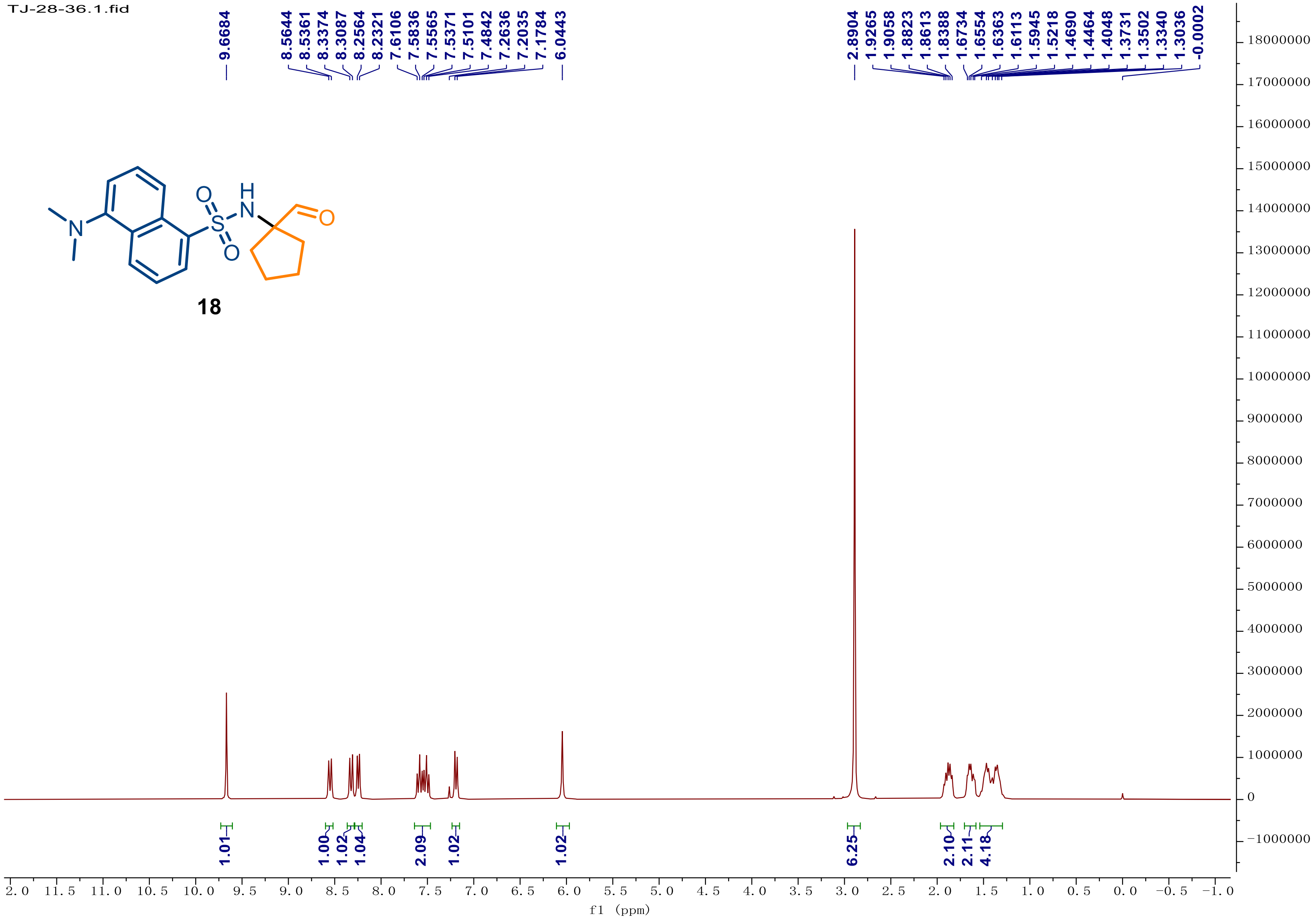


^{13}C **NMR** spectrum of compound **17** (75 MHz, CDCl$_3$)

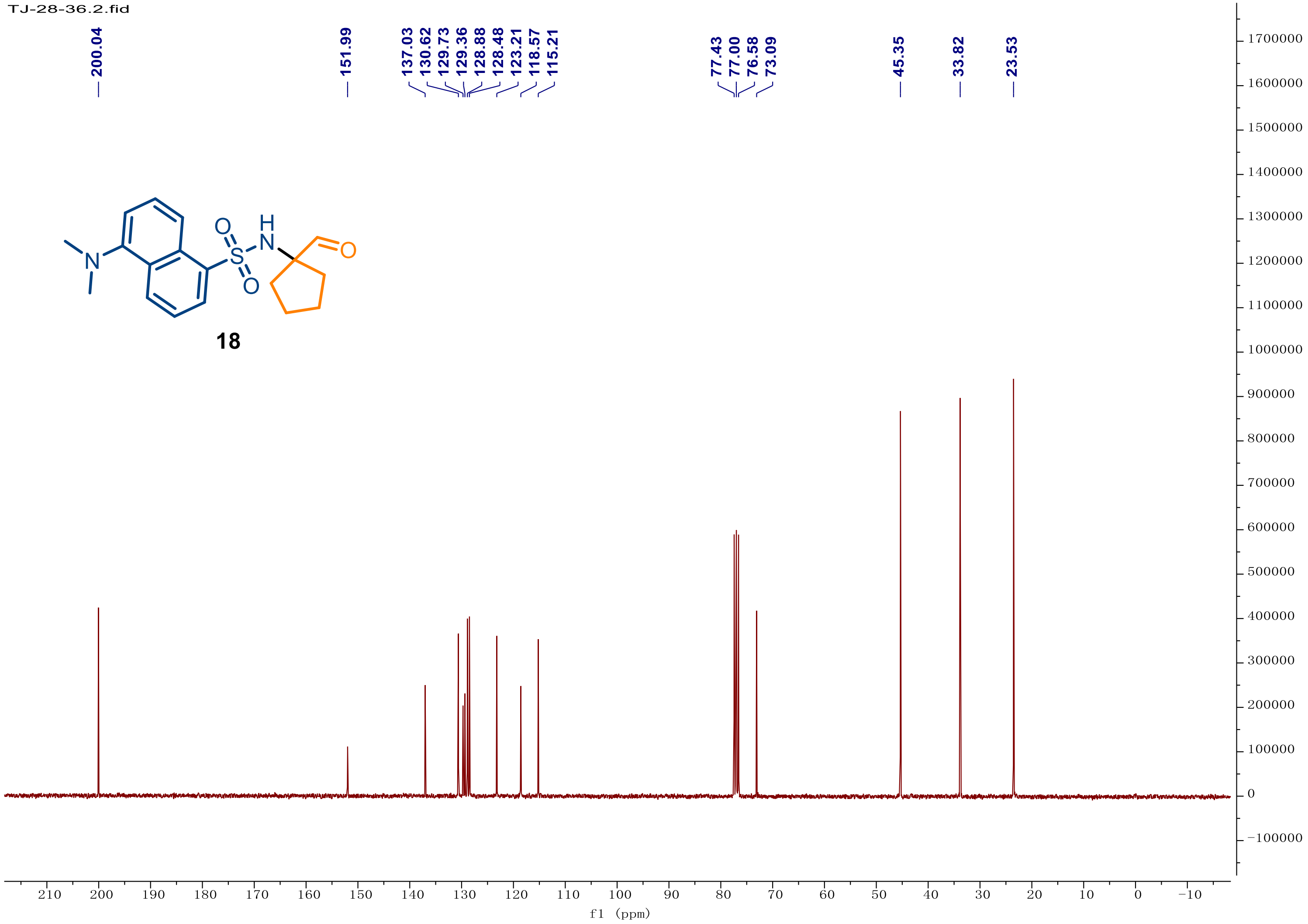


17

^{1}H NMR spectrum of compound **18** (300 MHz, $CDCl_3$)

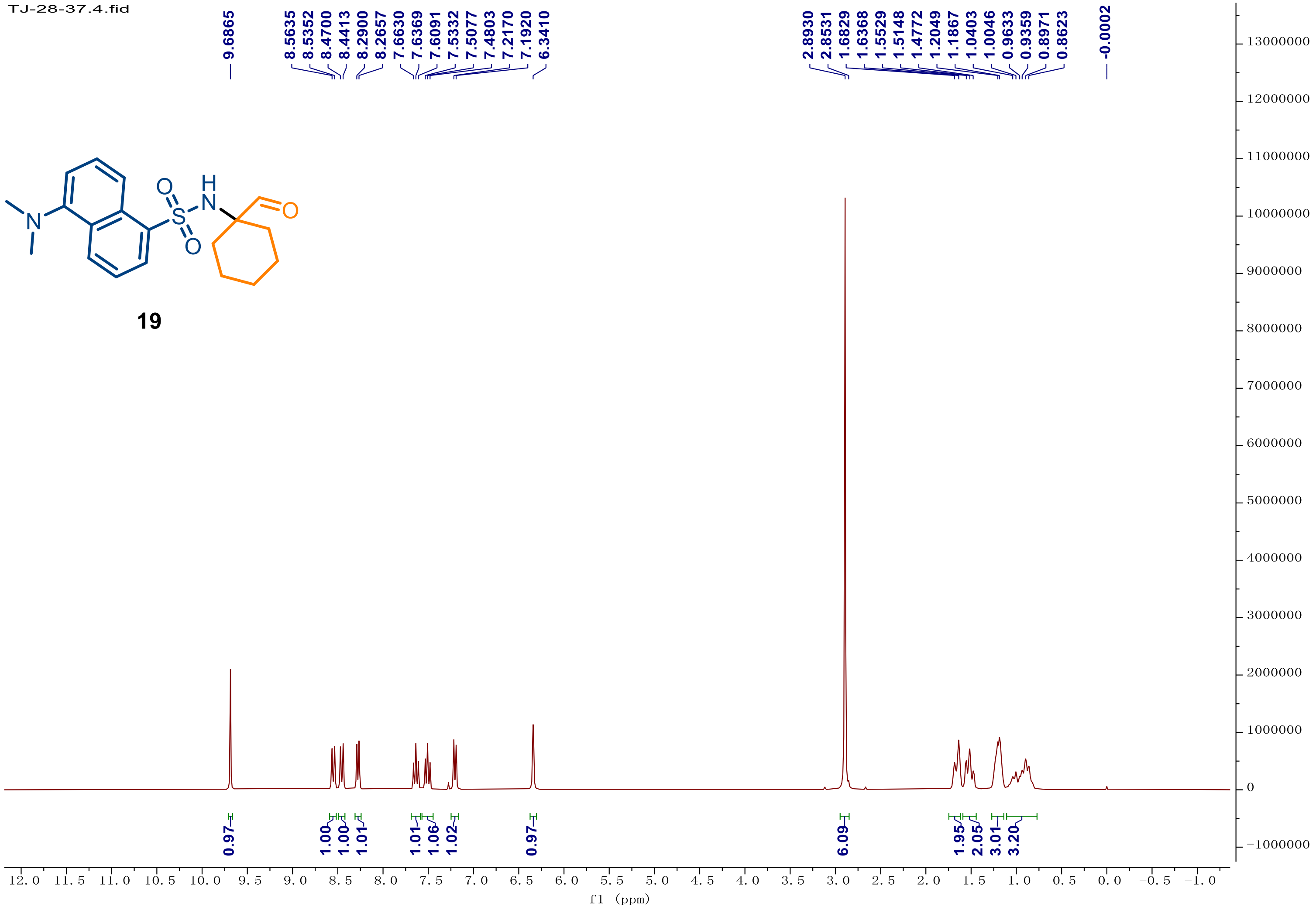


^{13}C **NMR** spectrum of compound **18** (75 MHz, $CDCl_3$)

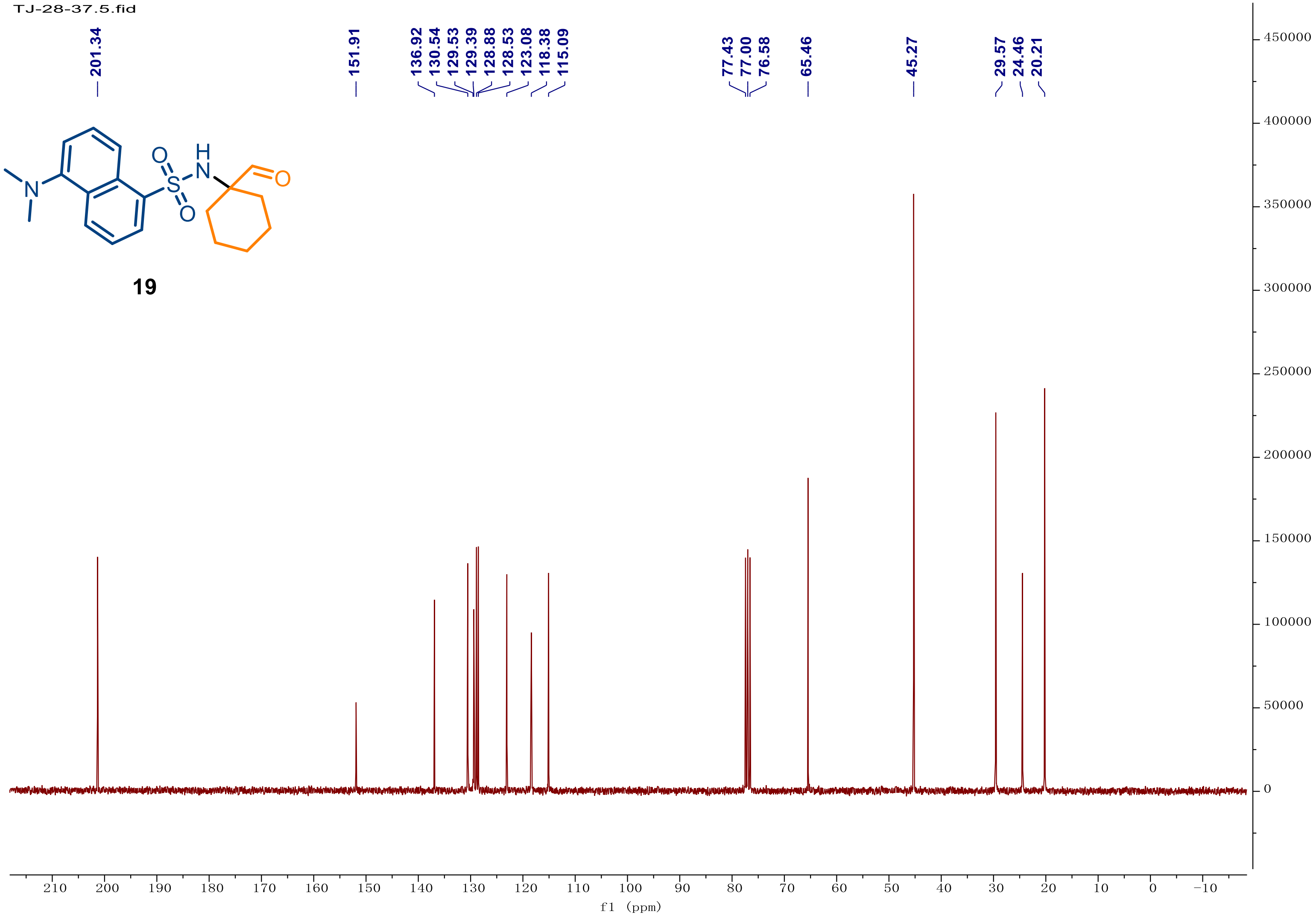


18

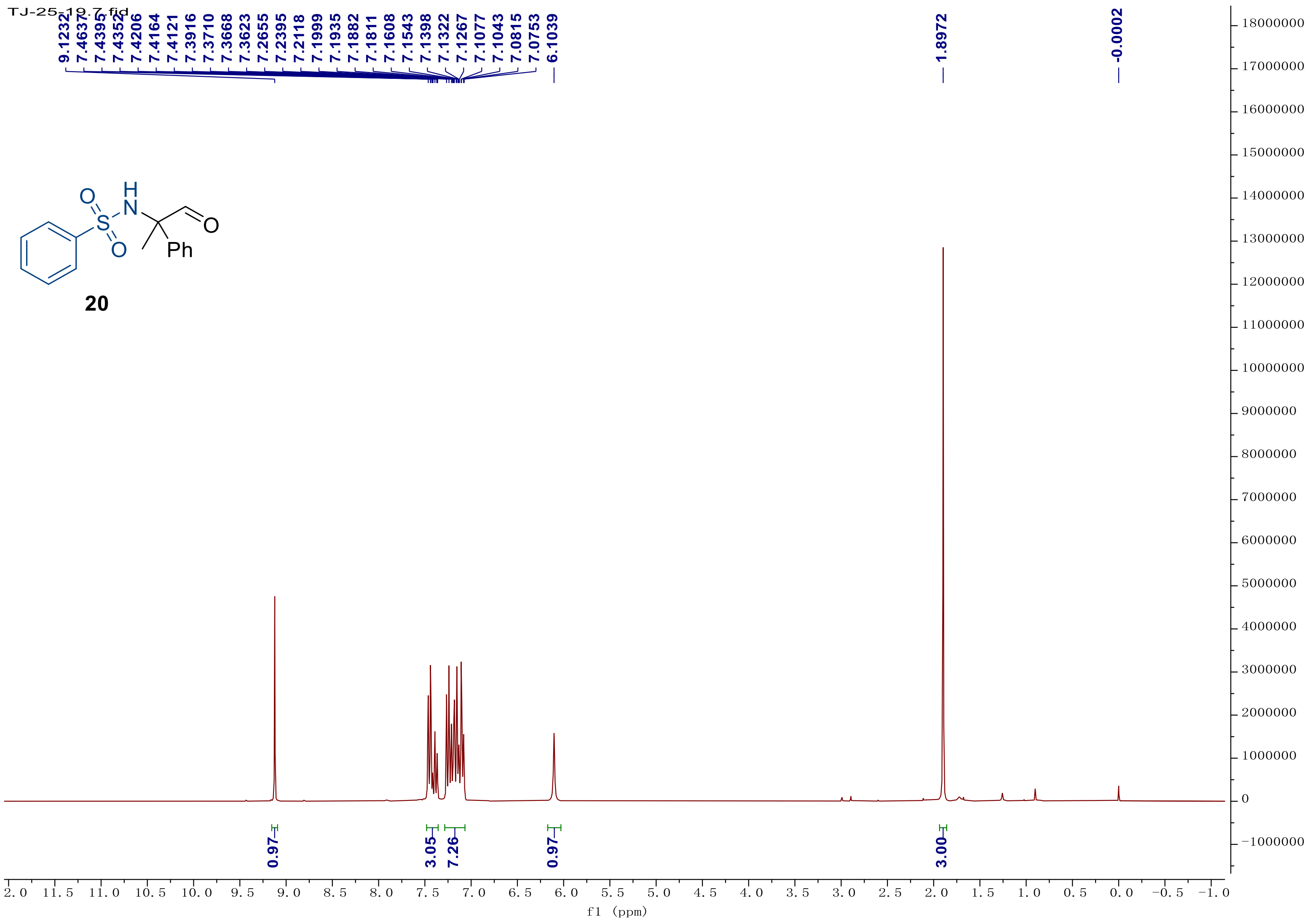
¹H NMR spectrum of compound **19** (300 MHz, $CDCl_3$)



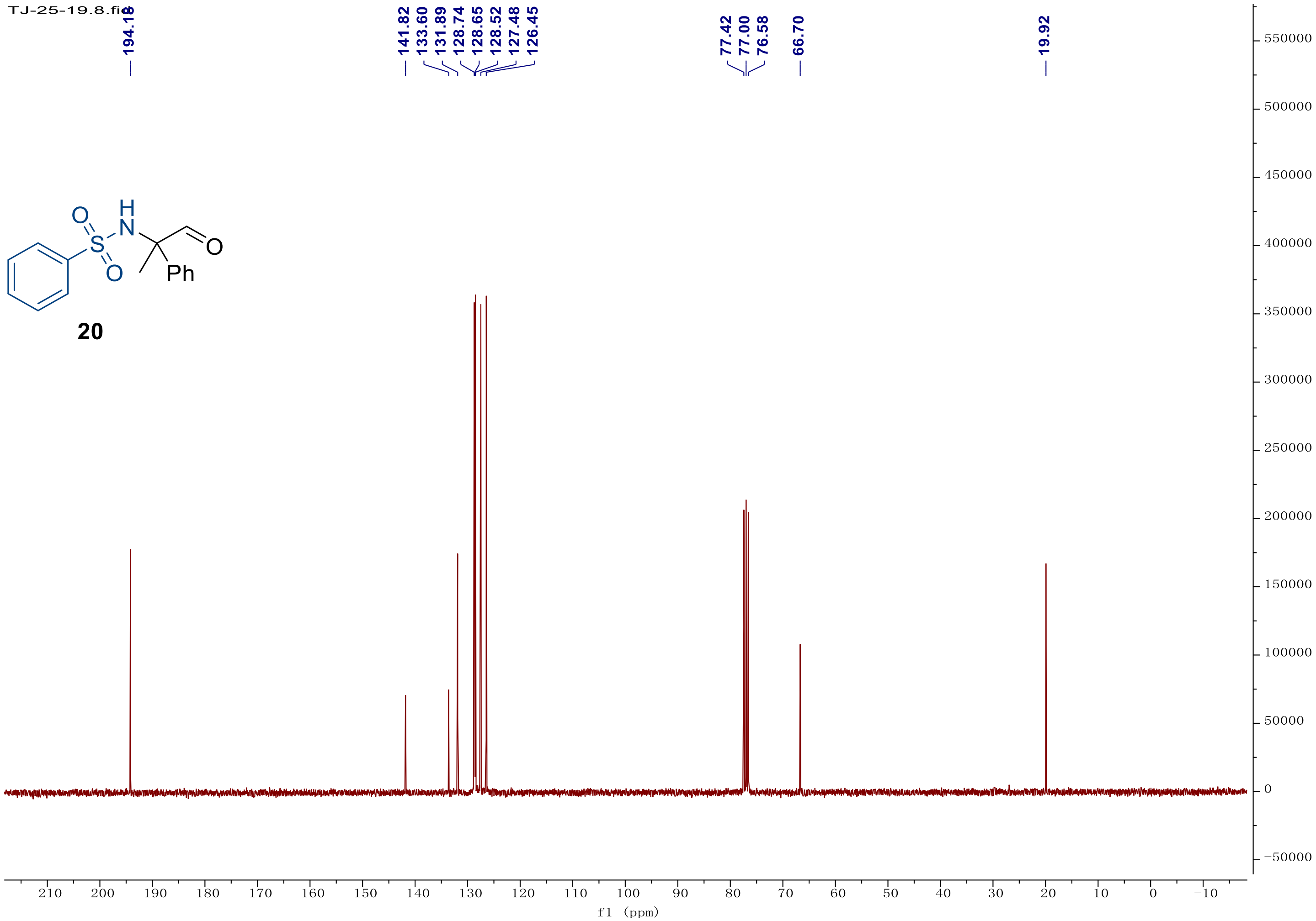
^{13}C **NMR** spectrum of compound **19** (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **20** (300 MHz, $CDCl_3$)

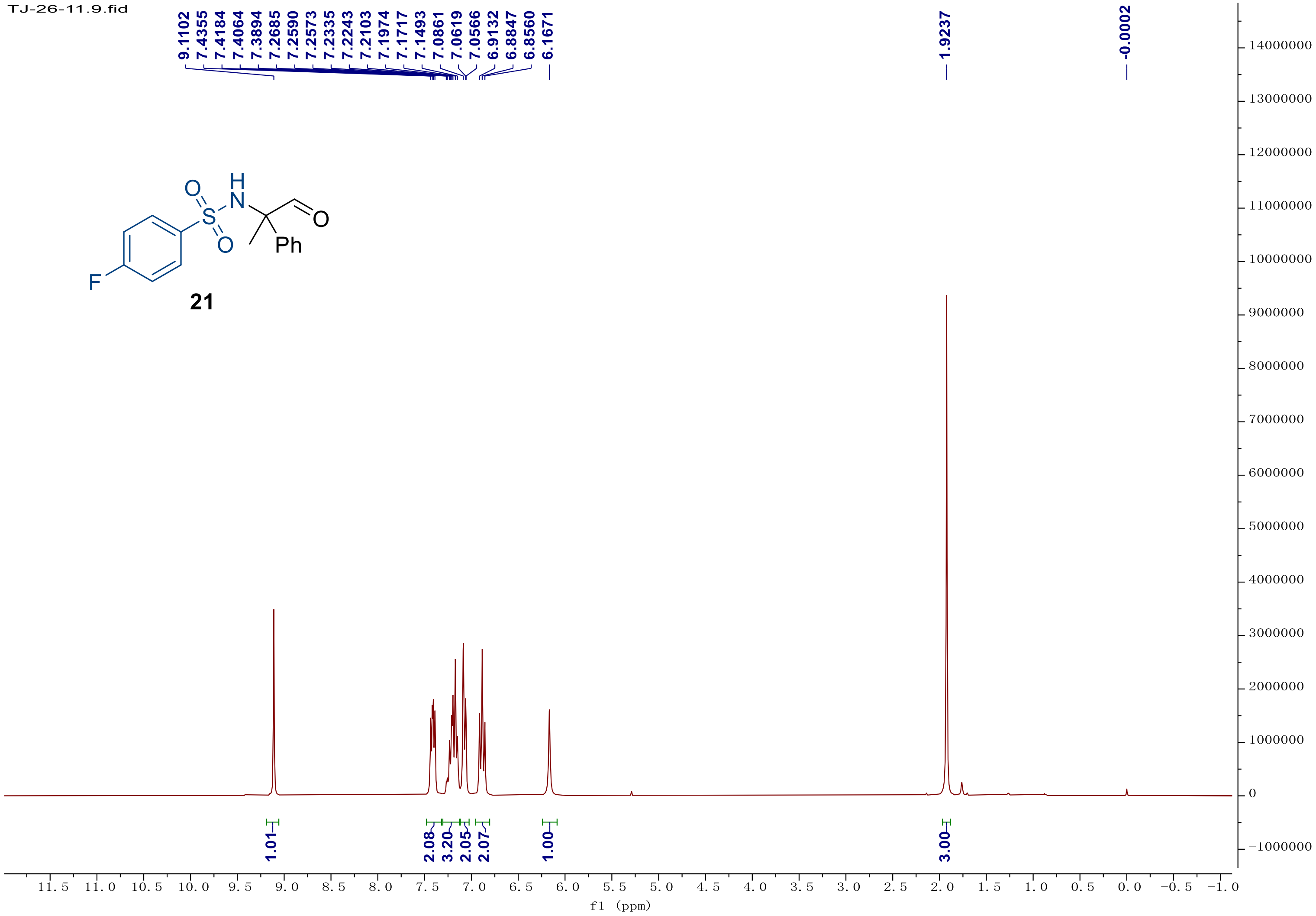


^{13}**C NMR** spectrum of compound **20** (75 MHz, CDCl$_3$)

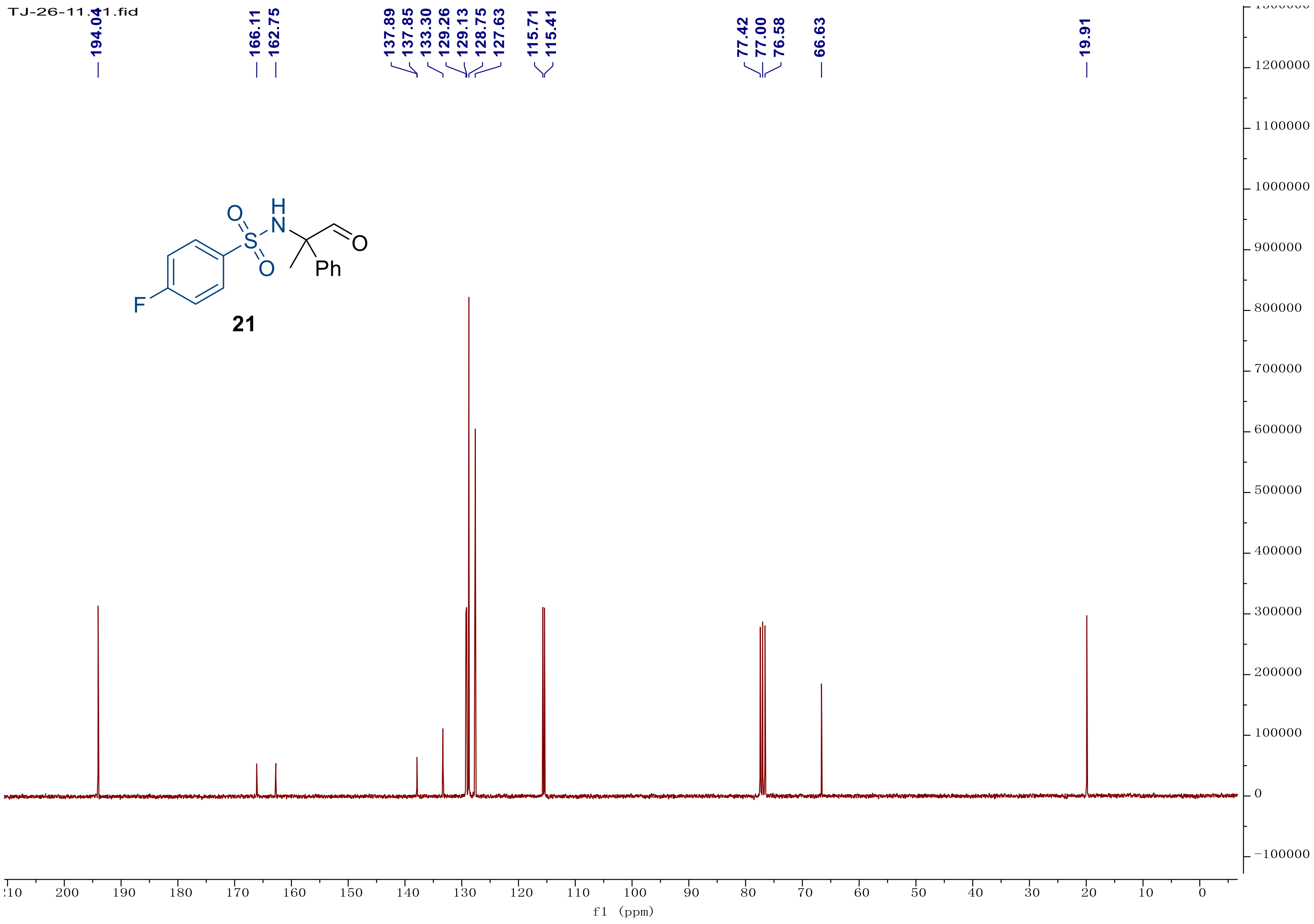


^{1}H NMR spectrum of compound **21** (300 MHz, $CDCl_3$)

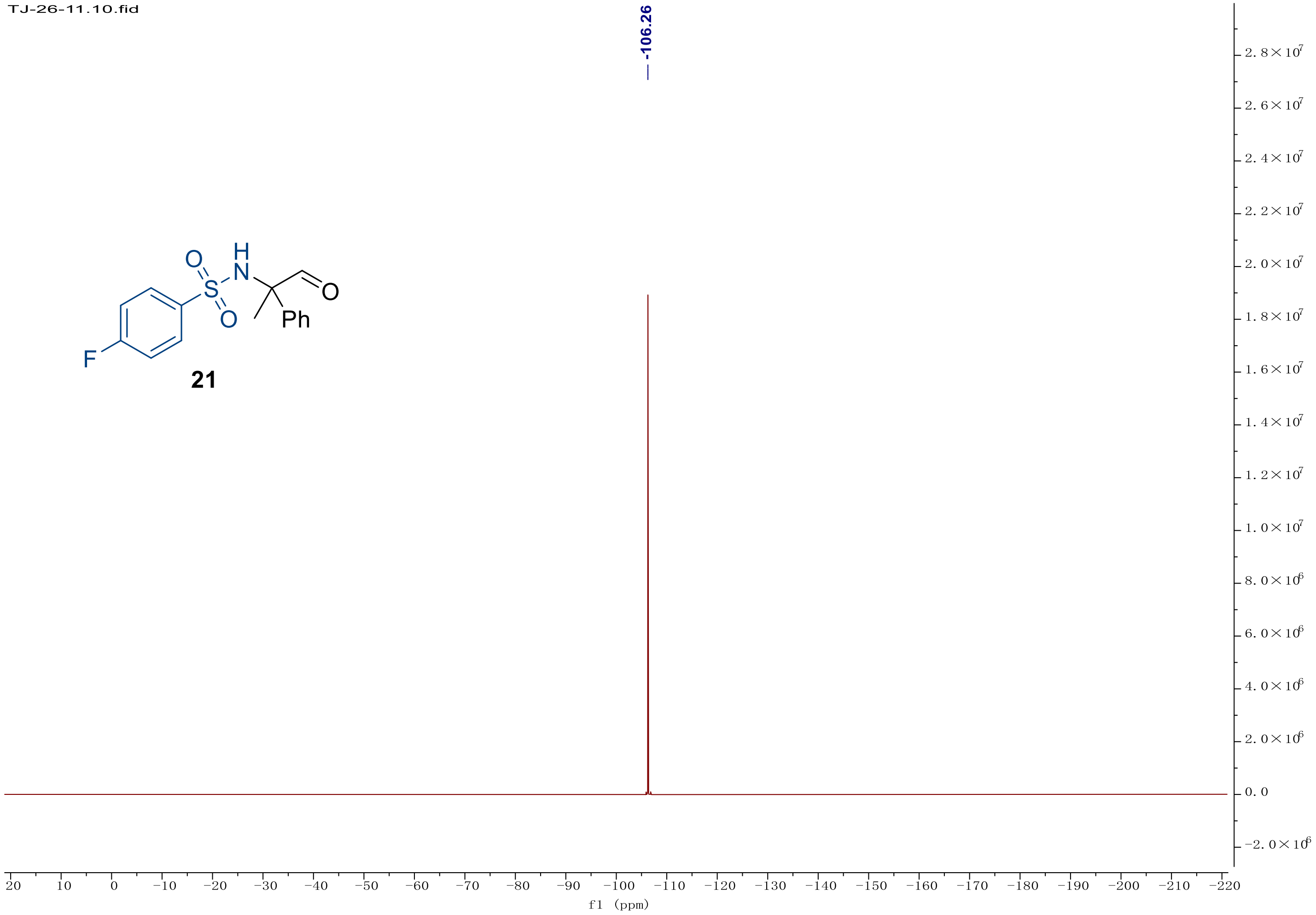
21



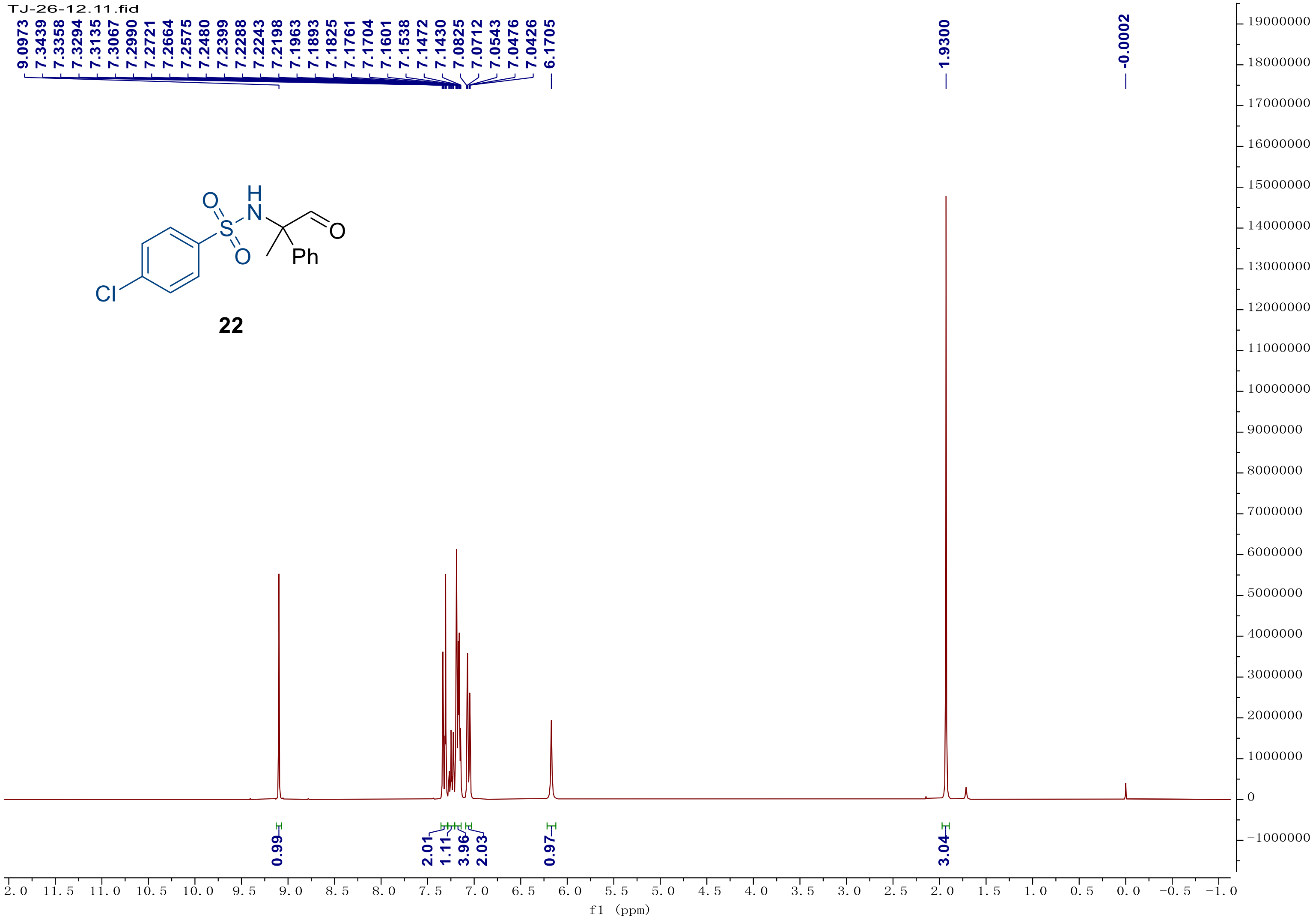
^{13}C NMR spectrum of compound **21** (75 MHz, CDCl$_3$)



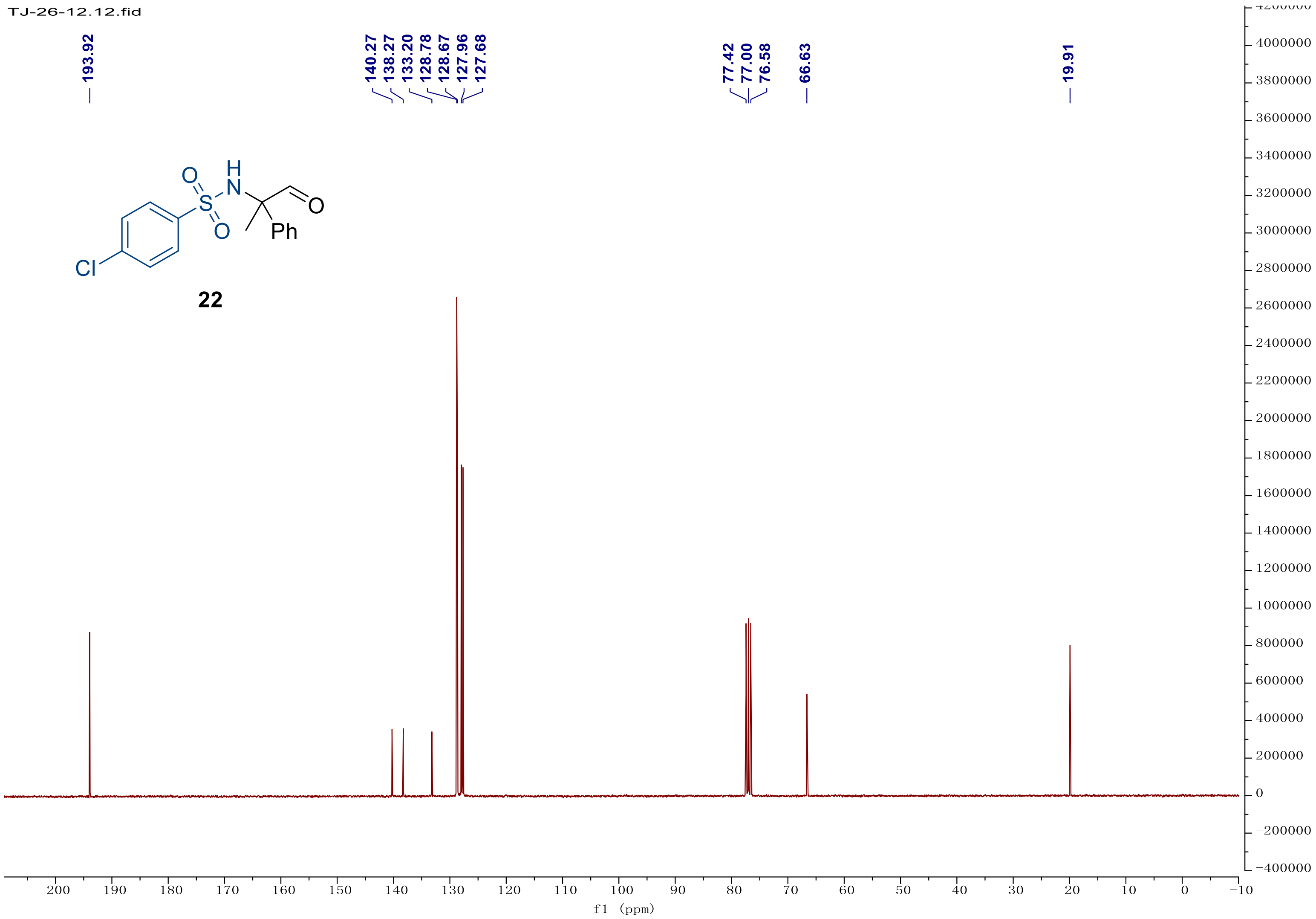
^{19}F **NMR** spectrum of compound **21** (282 MHz, CDCl$_3$)



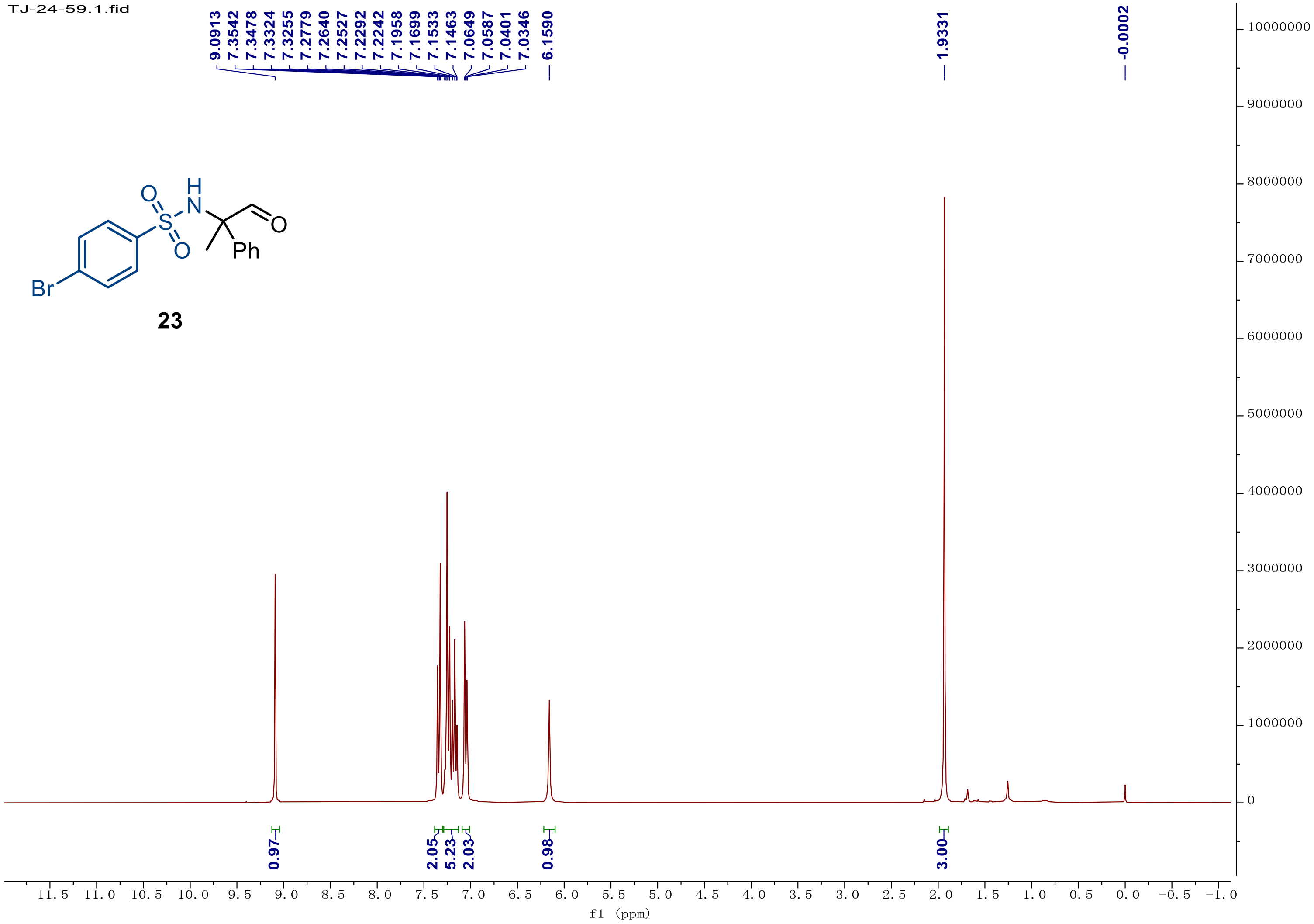
^{1}**H NMR** spectrum of compound **22** (300 MHz, CDCl$_3$)



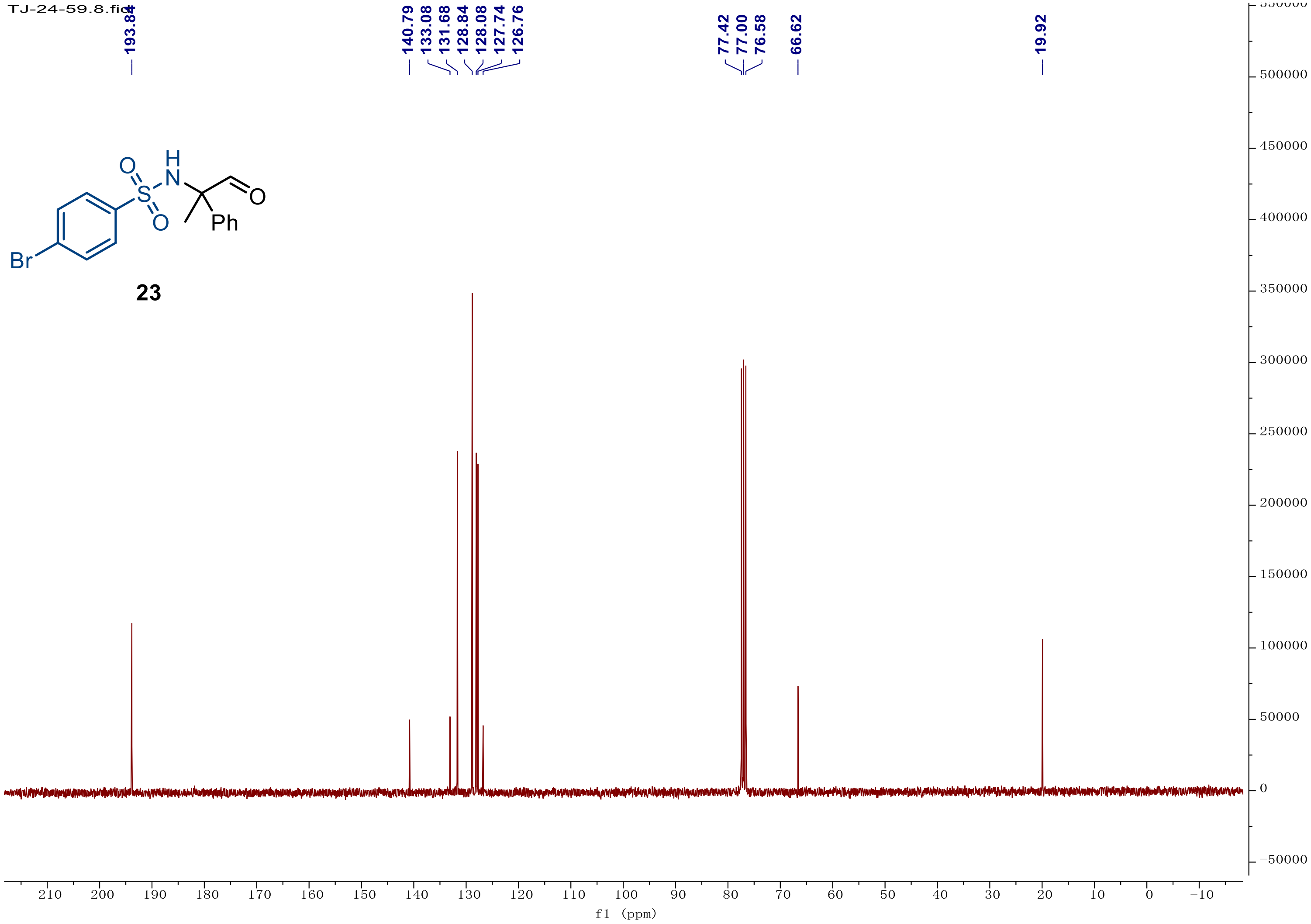
^{13}C NMR spectrum of compound **22** (75 MHz, $CDCl_3$)



^{1}**H NMR** spectrum of compound **23** (300 MHz, $CDCl_3$)

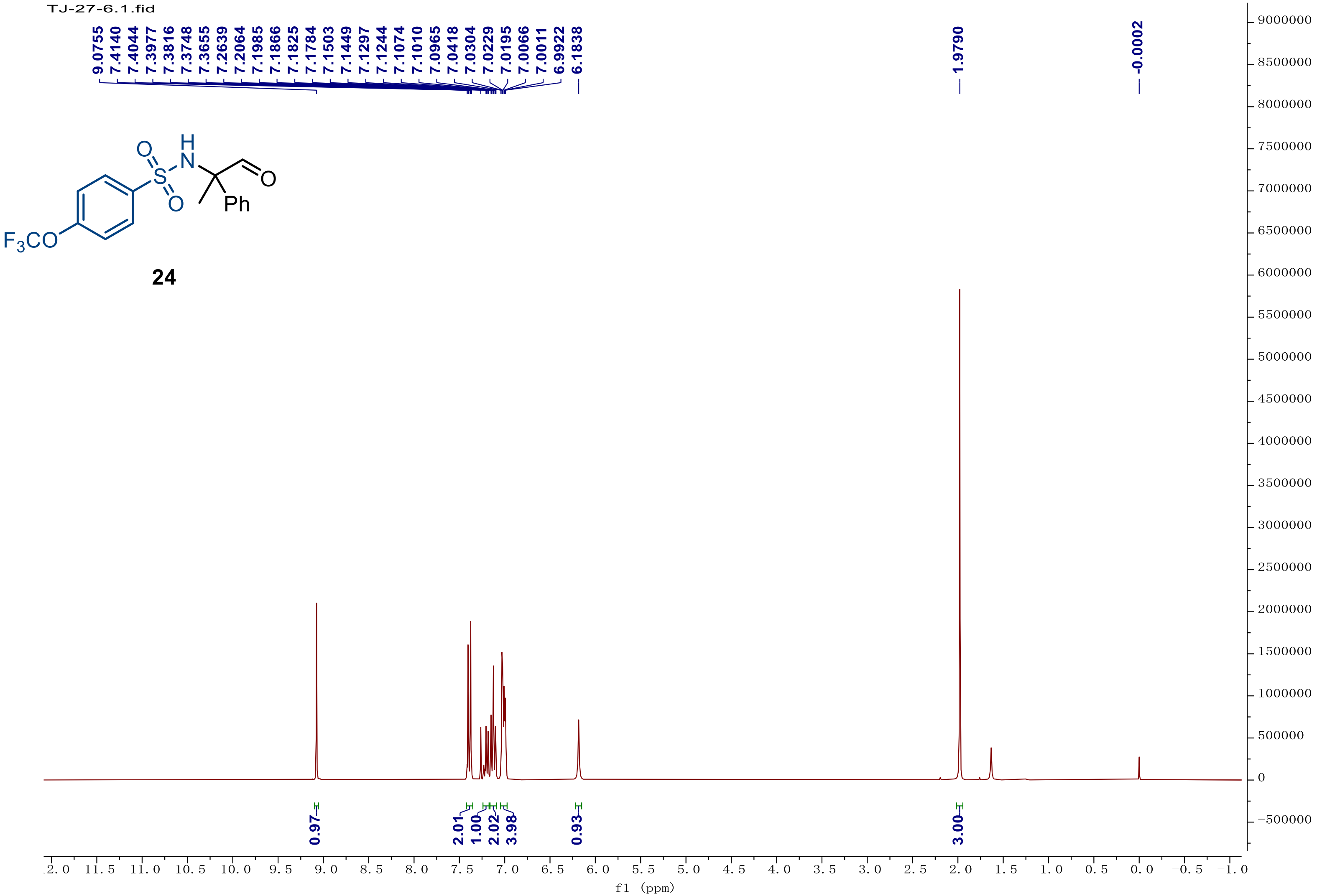


^{13}C NMR spectrum of compound **23** (75 MHz, $CDCl_3$)



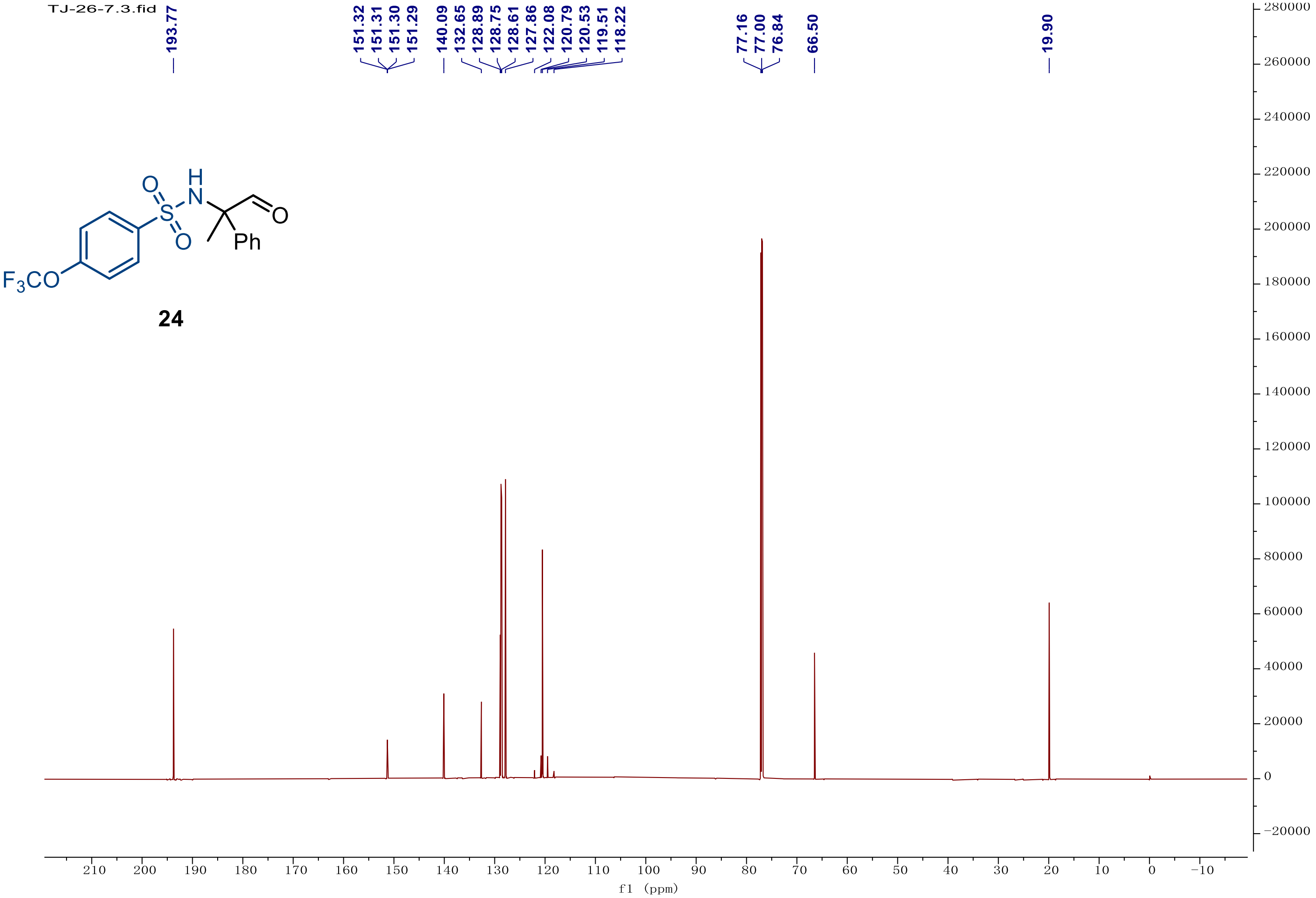
23

^{1}**H NMR** spectrum of compound **24** (300 MHz, $CDCl_3$)

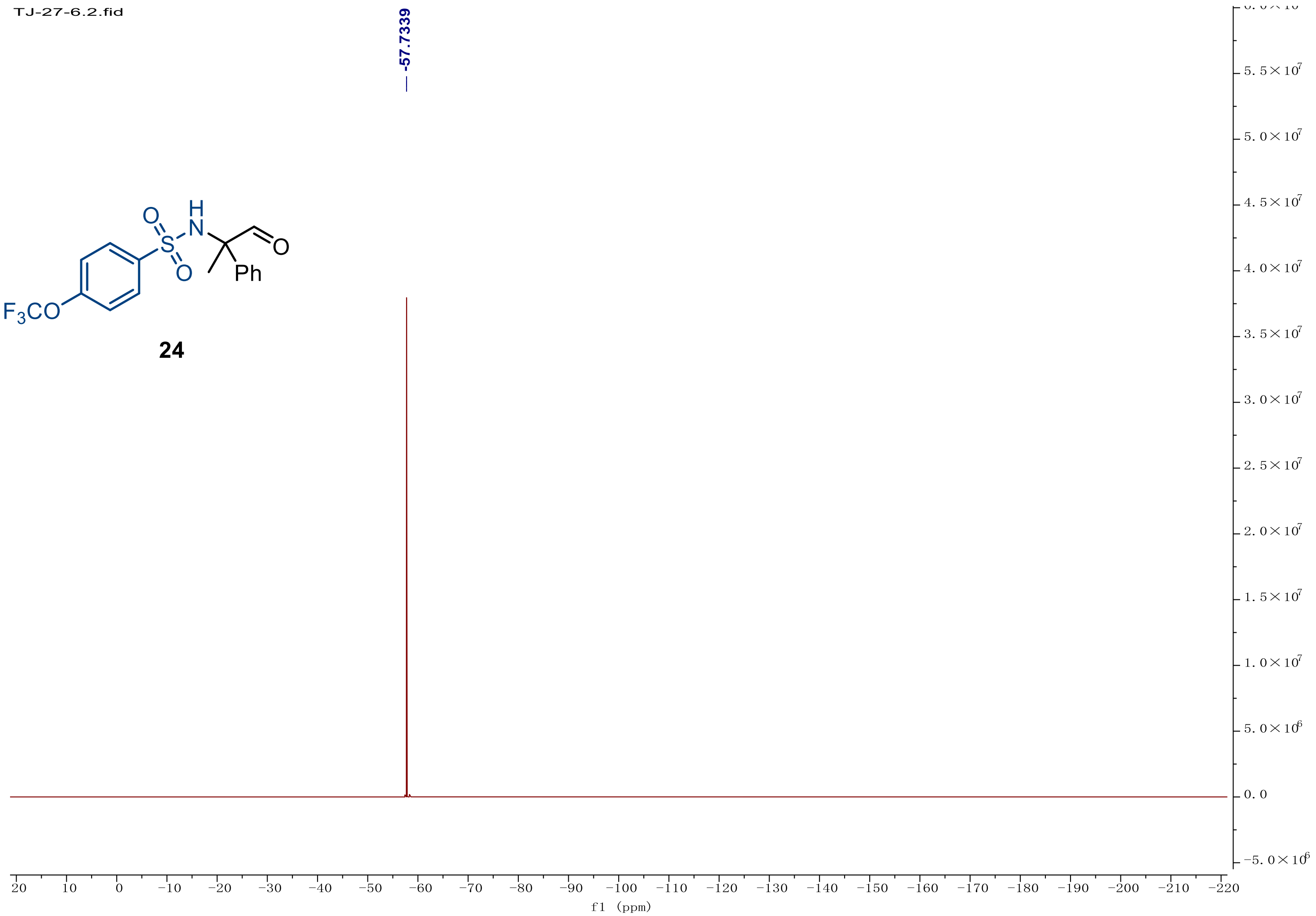


^{13}C NMR spectrum of compound **24** (201 MHz, $CDCl_3$)

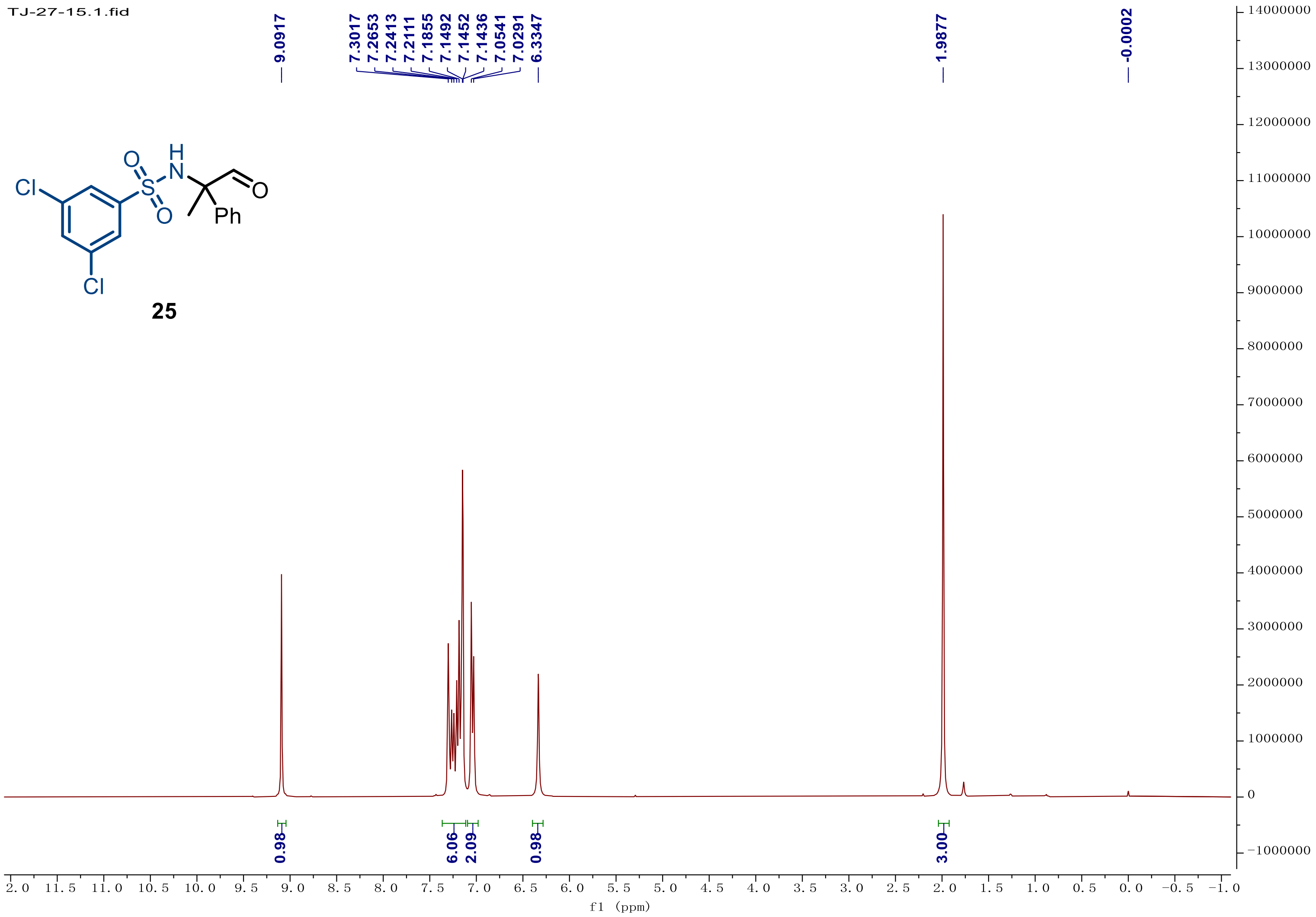
24



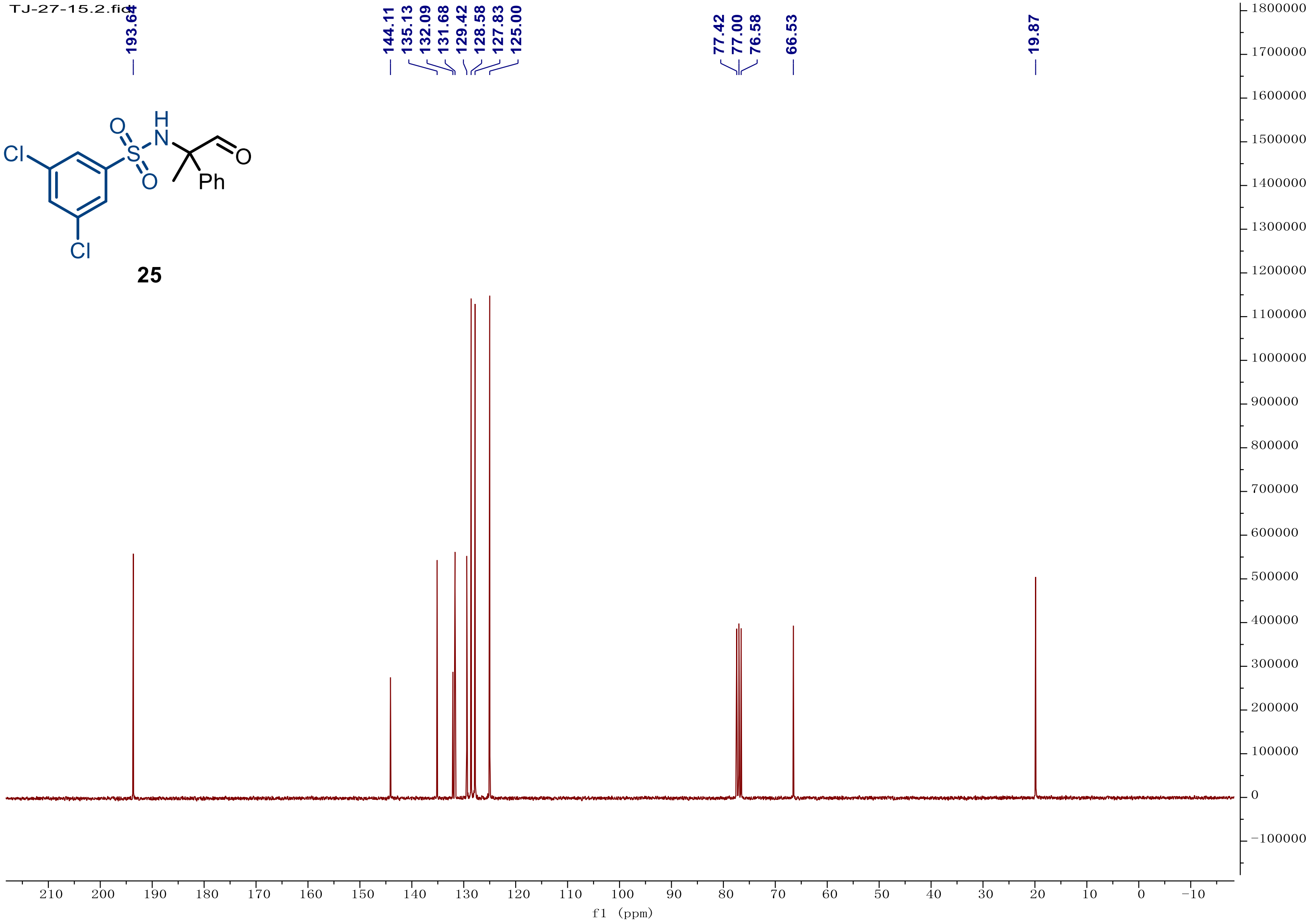
^{19}**F NMR** spectrum of compound **24** (282 MHz, $CDCl_3$)



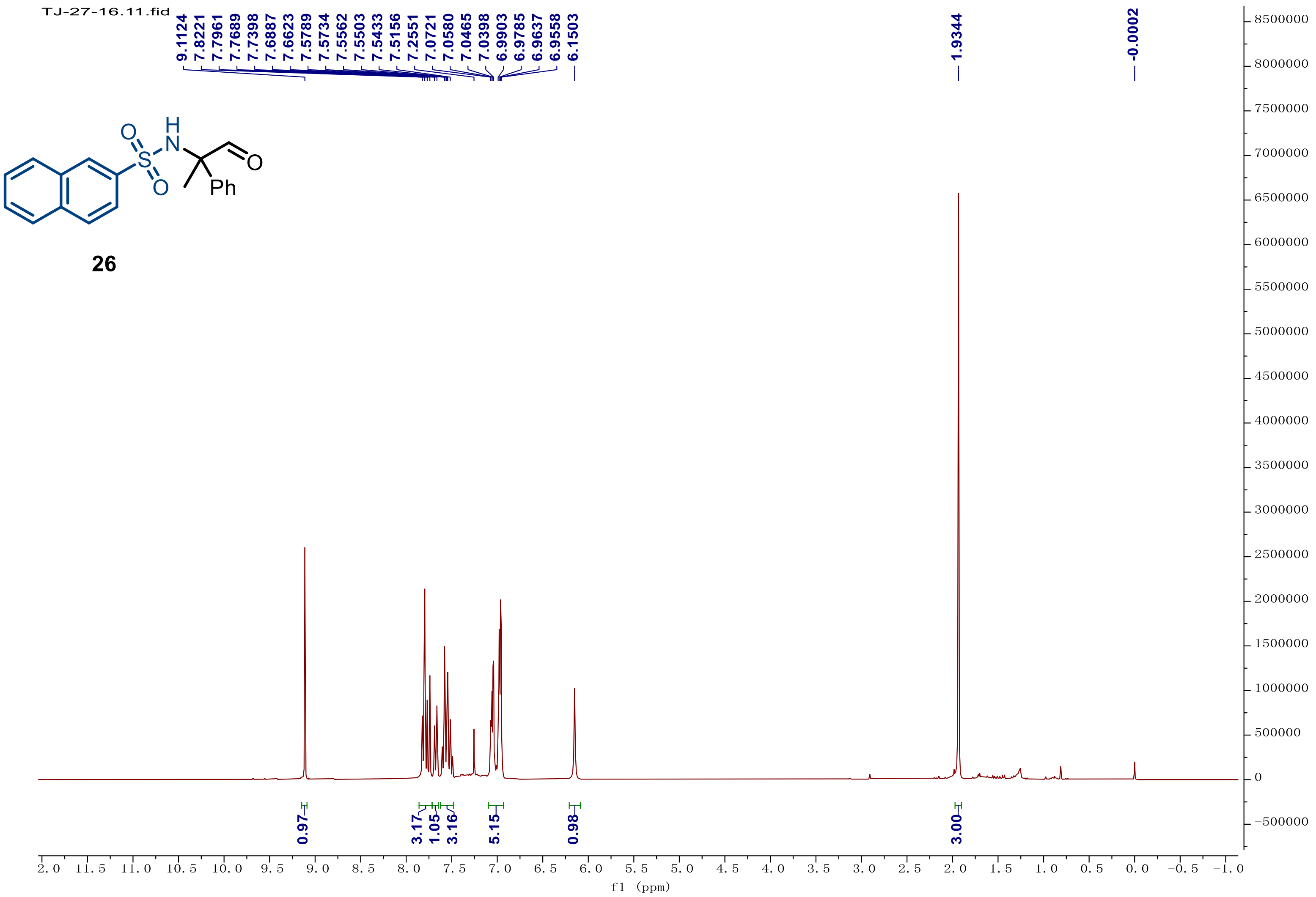
^{1}**H NMR** spectrum of compound **25** (300 MHz, CDCl$_3$)



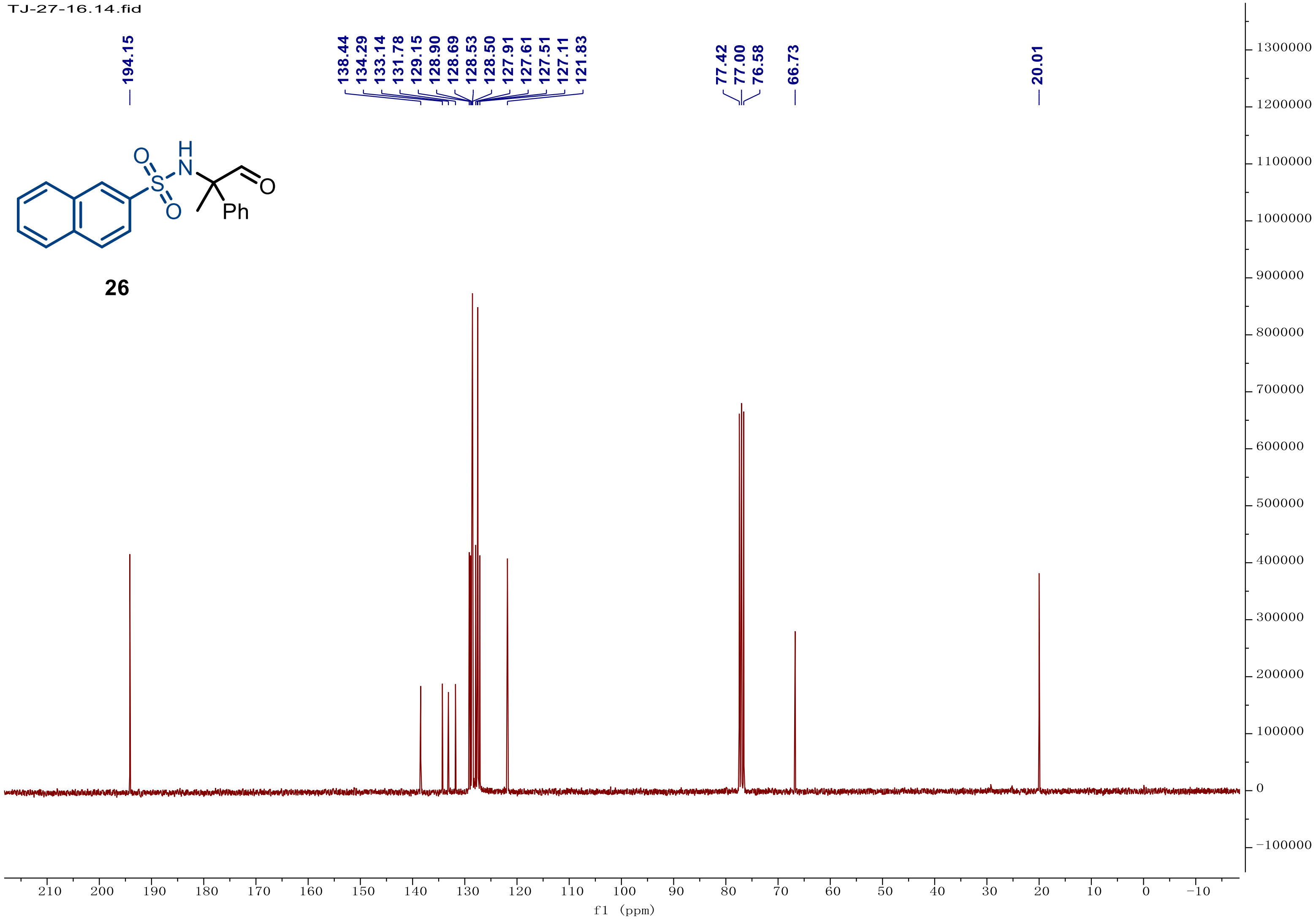
^{13}C **NMR** spectrum of compound **25** (75 MHz, $CDCl_3$)



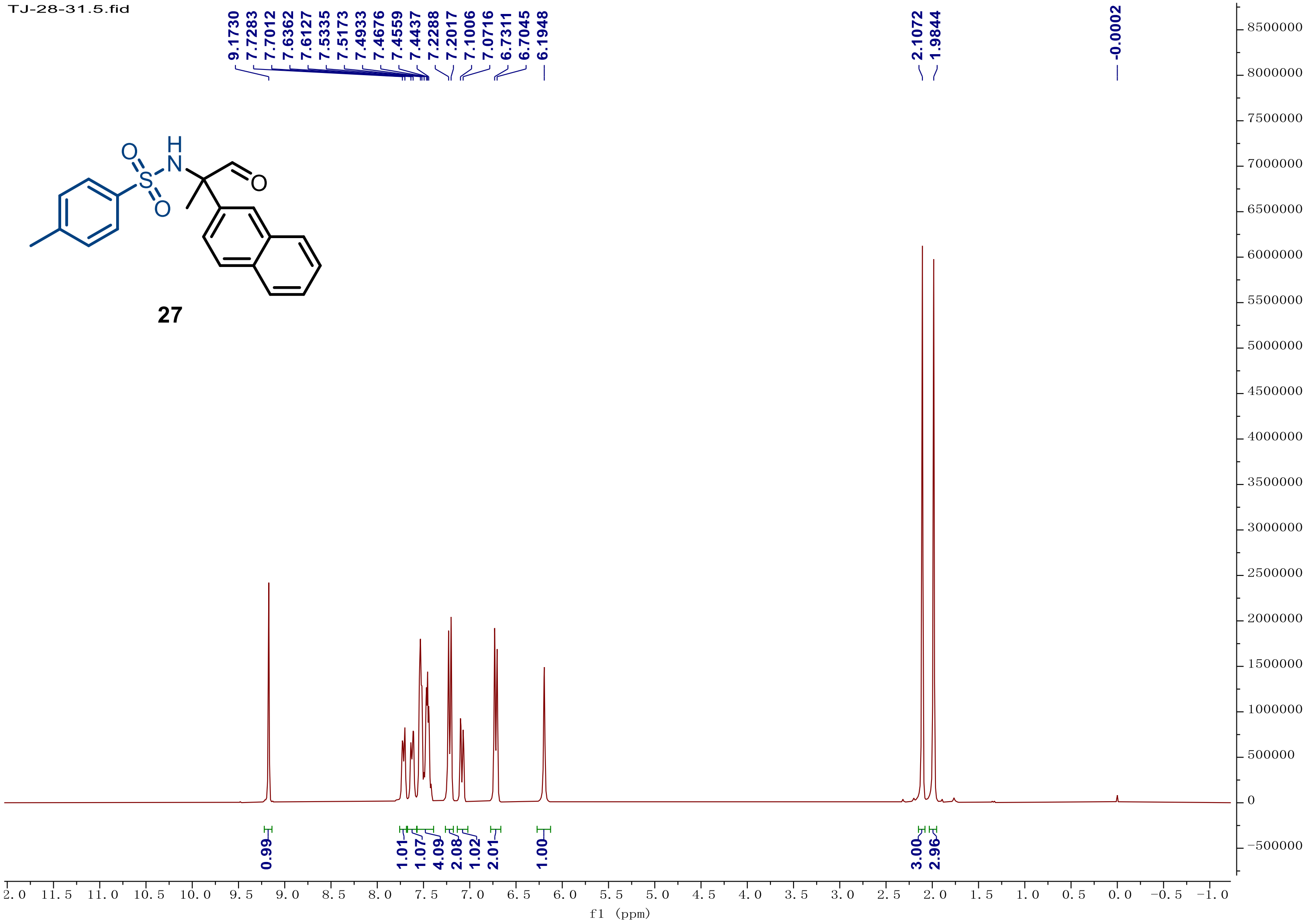
^{1}**H NMR** spectrum of compound **26** (300 MHz, $CDCl_3$)



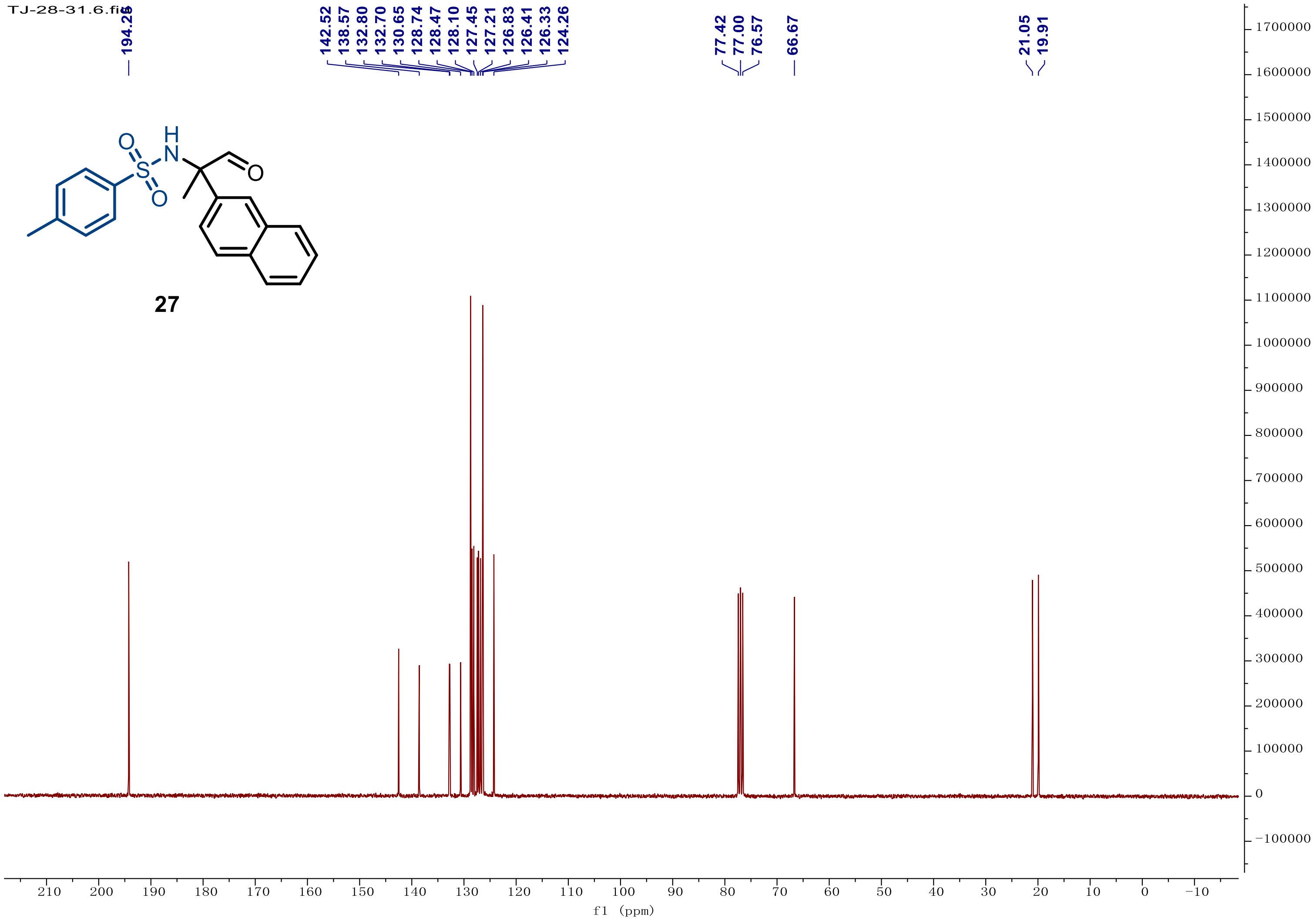
^{13}**C NMR** spectrum of compound **26** (75 MHz, CDCl$_3$)



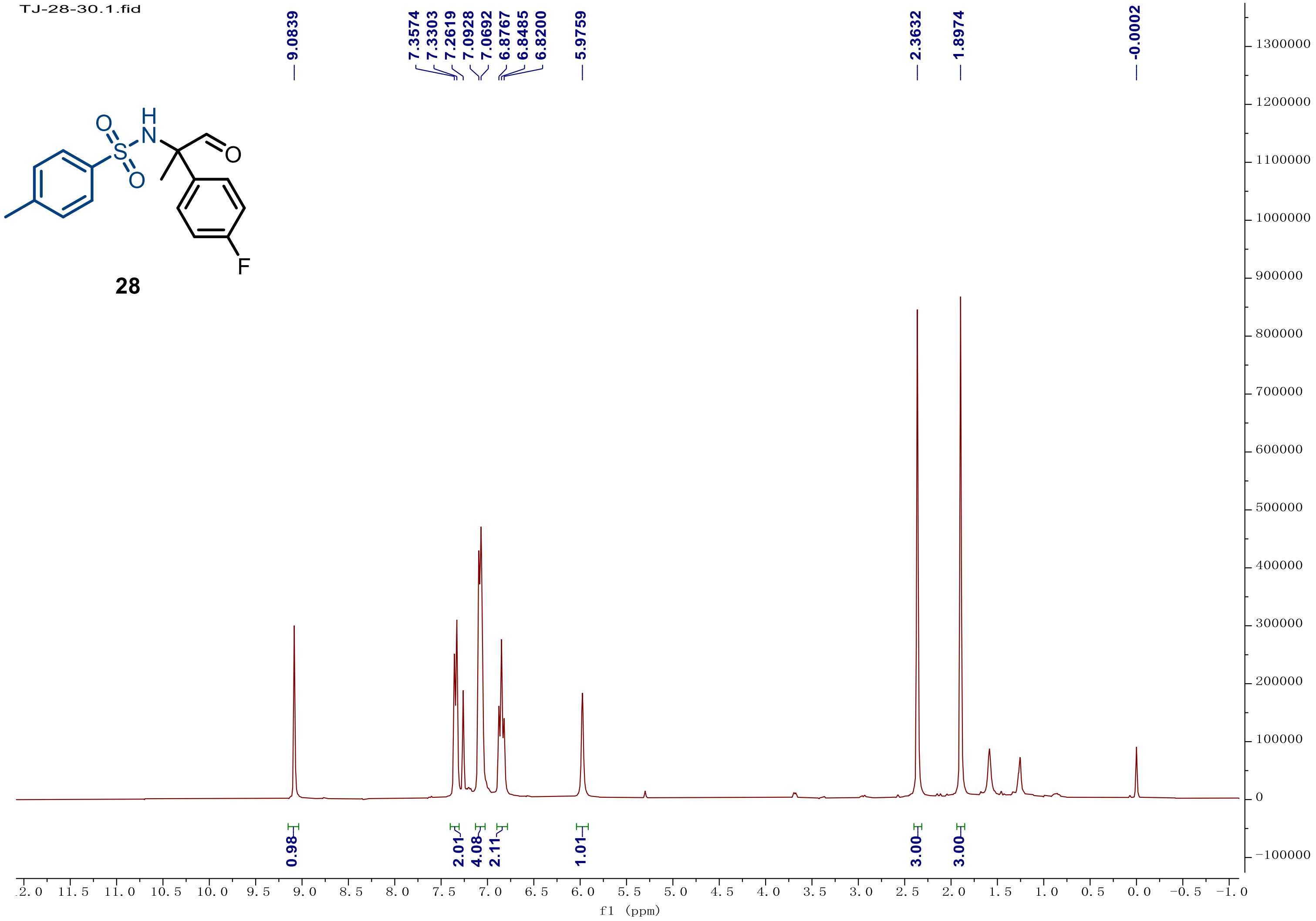
^{1}H NMR spectrum of compound **27** (300 MHz, $CDCl_3$)



^{13}**C NMR** spectrum of compound **27** (75 MHz, CDCl$_3$)

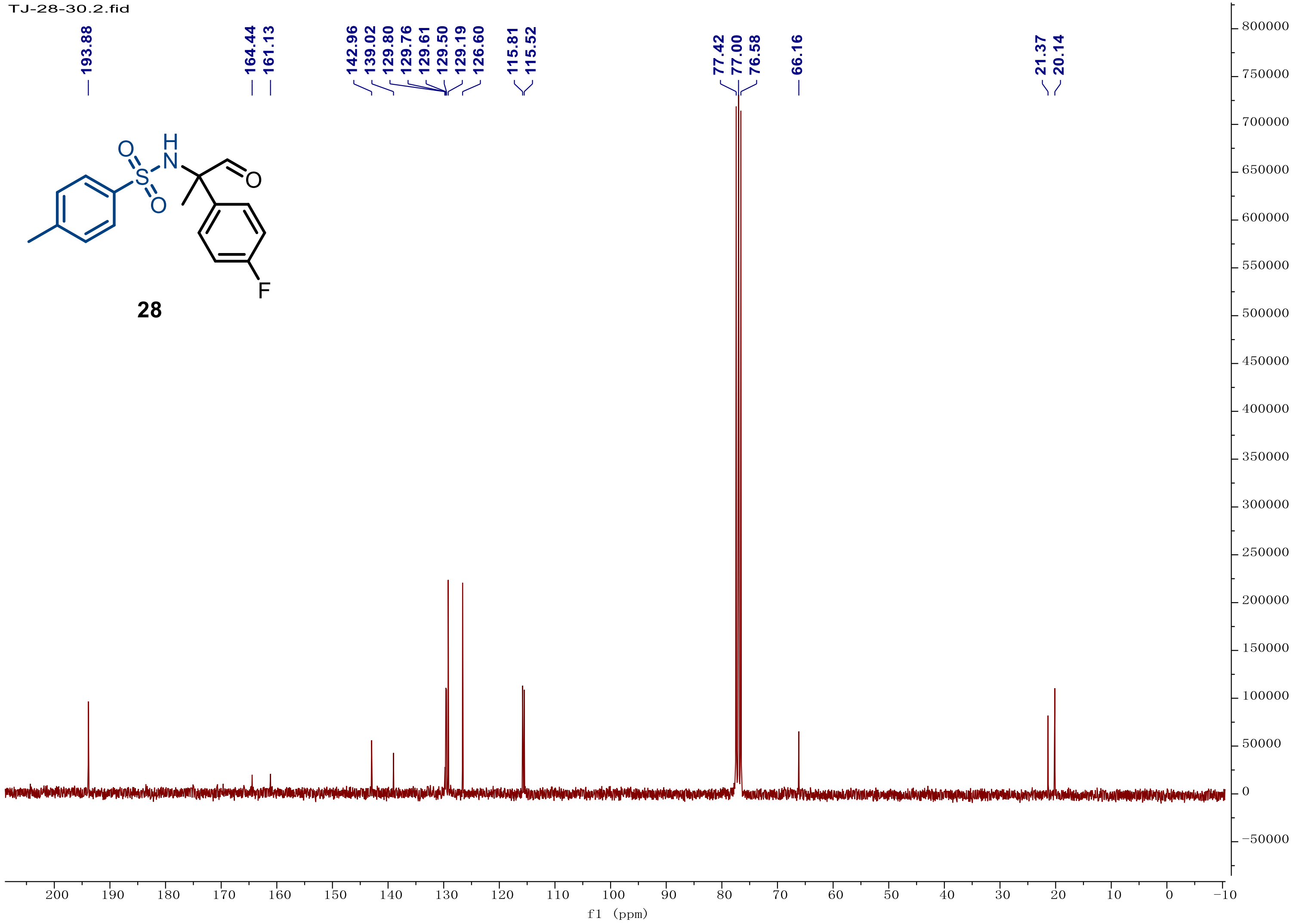


^{1}**H NMR** spectrum of compound **28** (300 MHz, $CDCl_3$)



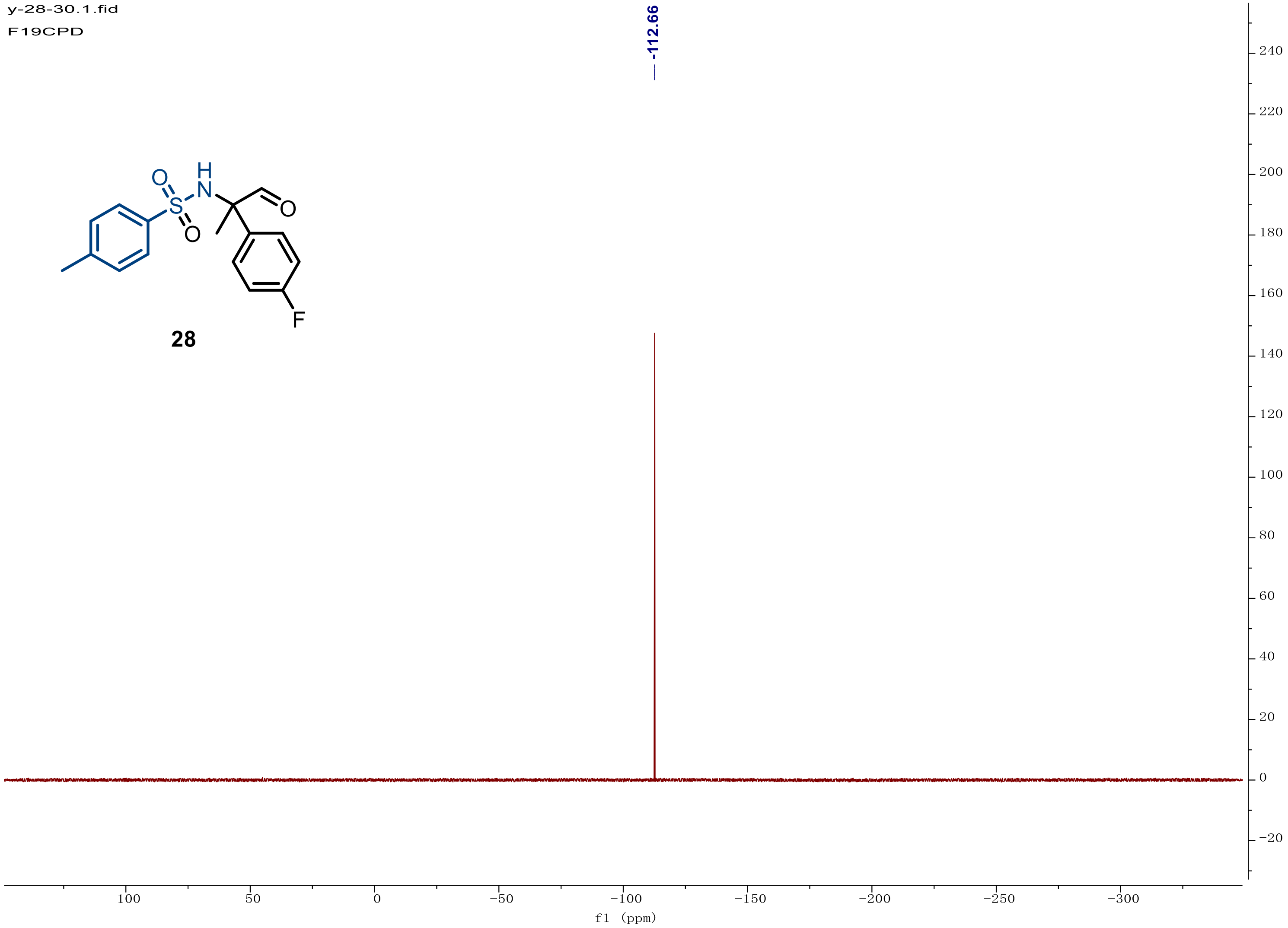
28

^{13}**C NMR** spectrum of compound **28** (75 MHz, CDCl$_3$)

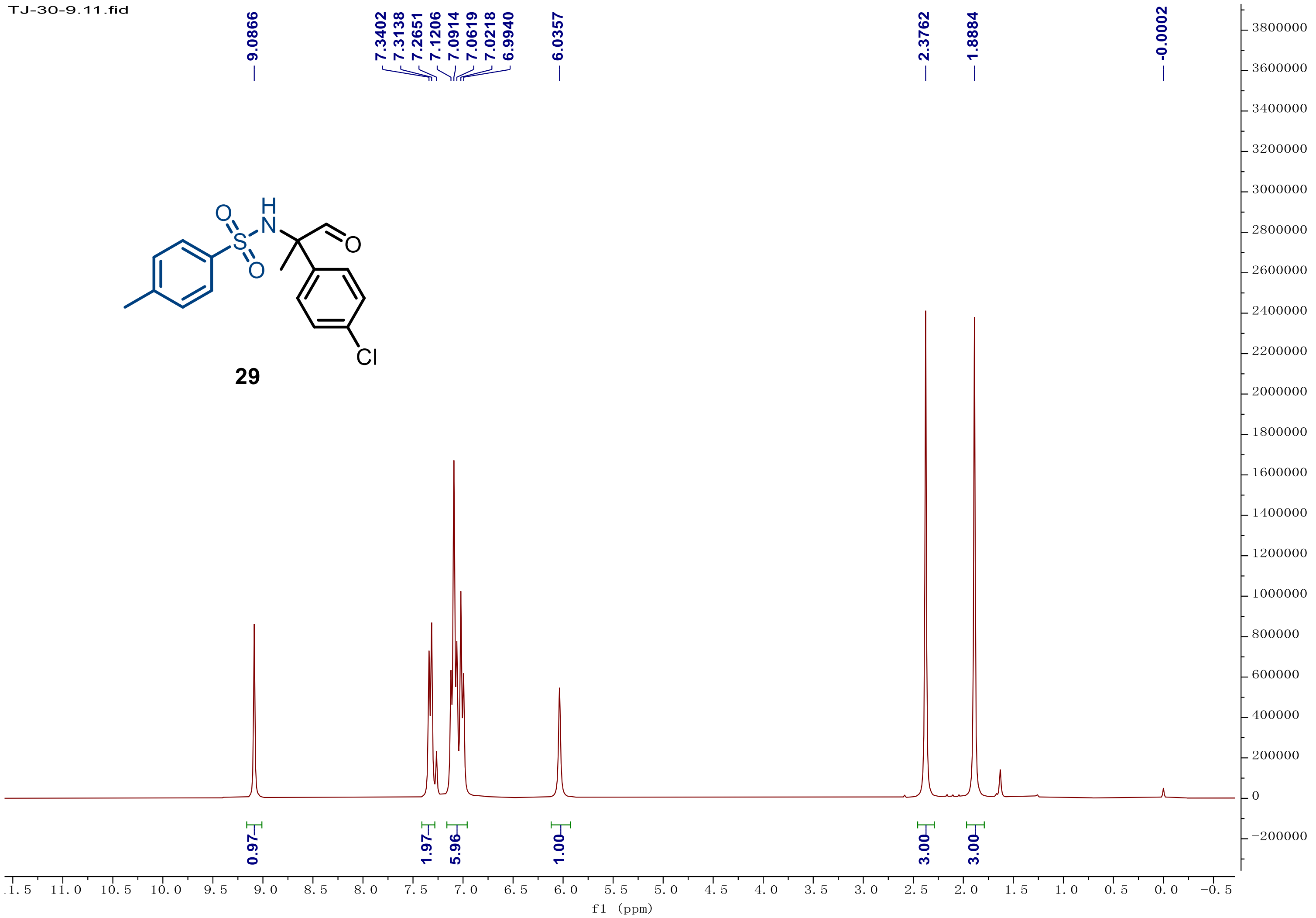


28

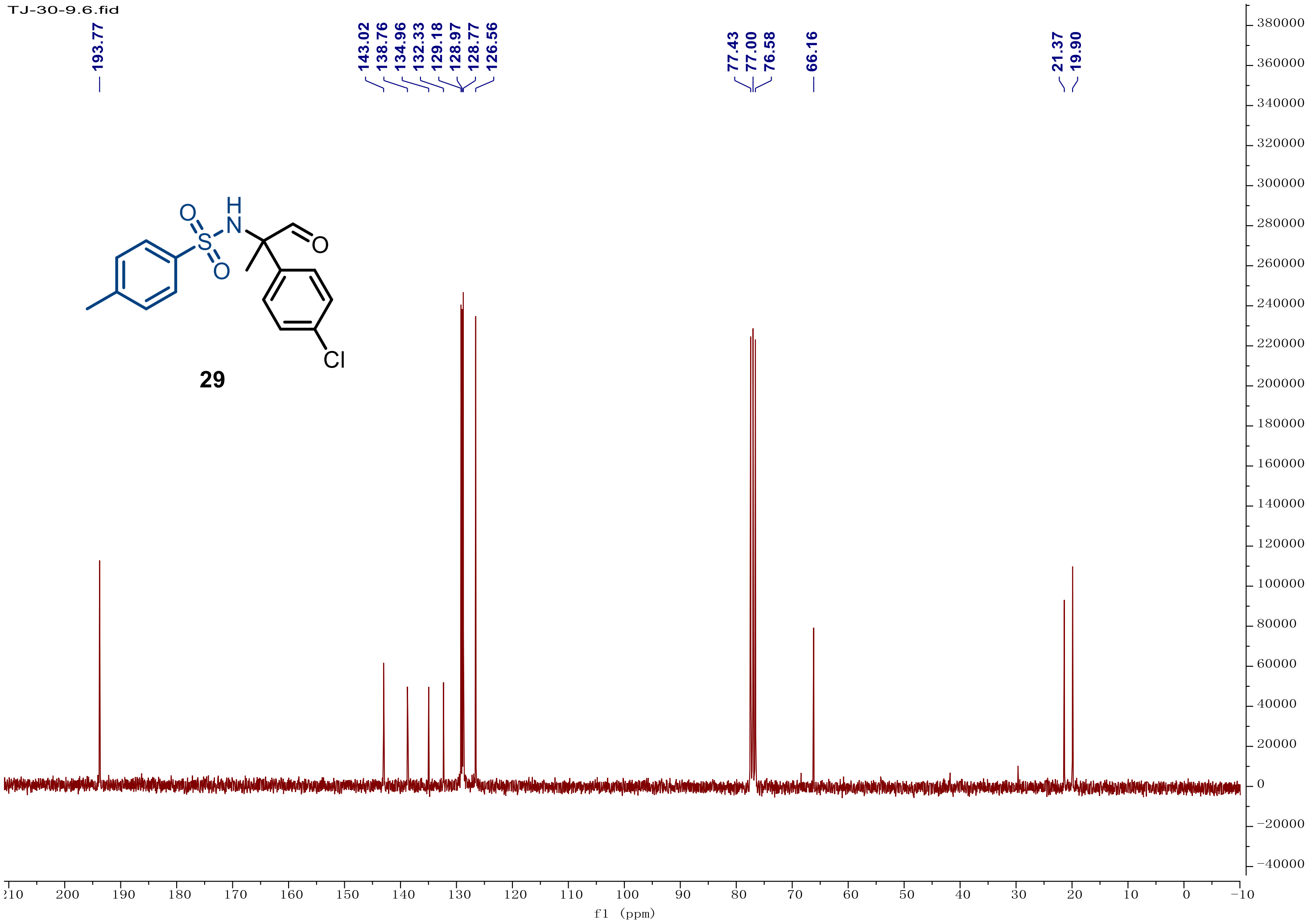
^{19}**F NMR** spectrum of compound **28** (376 MHz, $CDCl_3$)



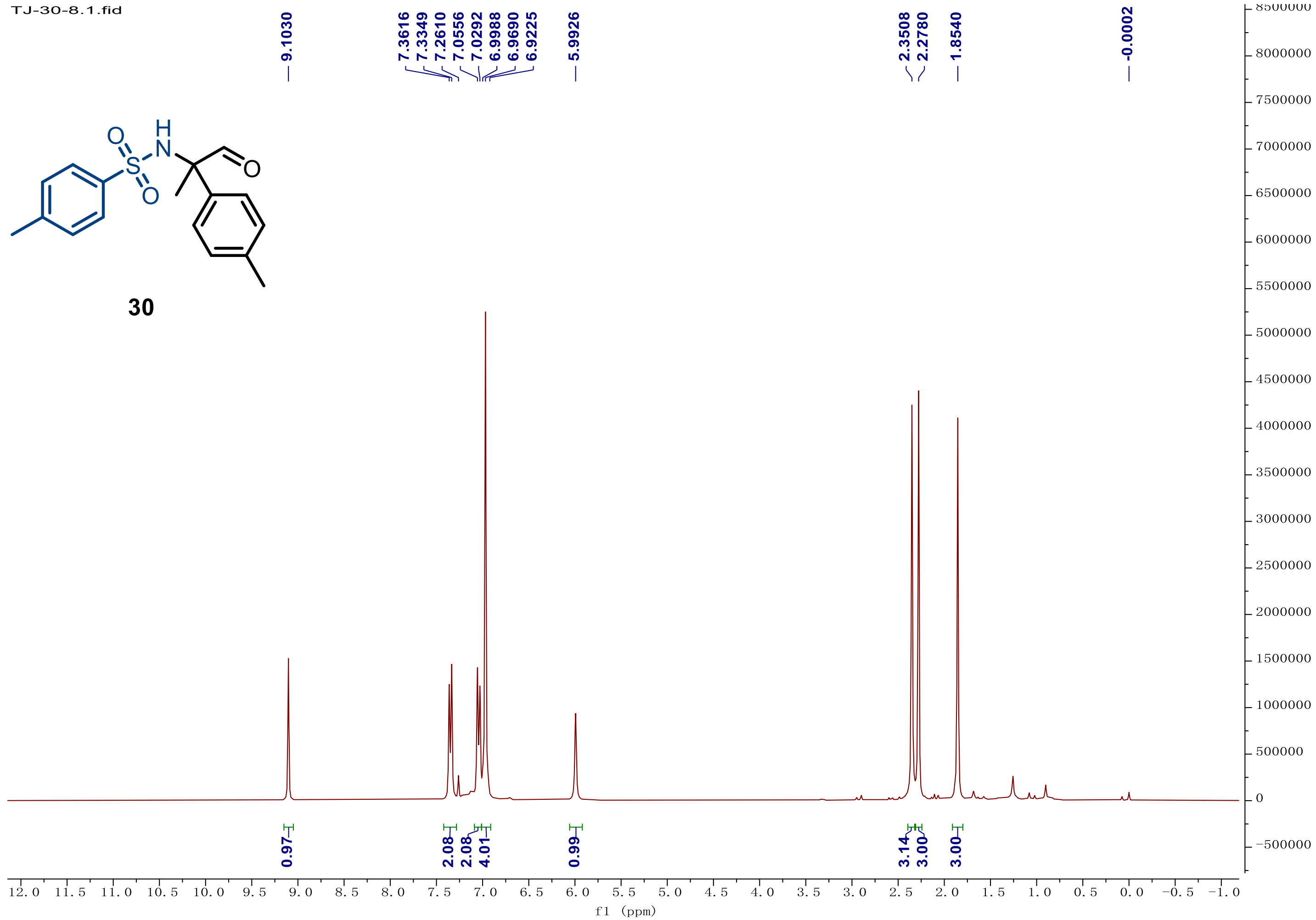
^{1}**H NMR** spectrum of compound **29** (300 MHz, $CDCl_3$)



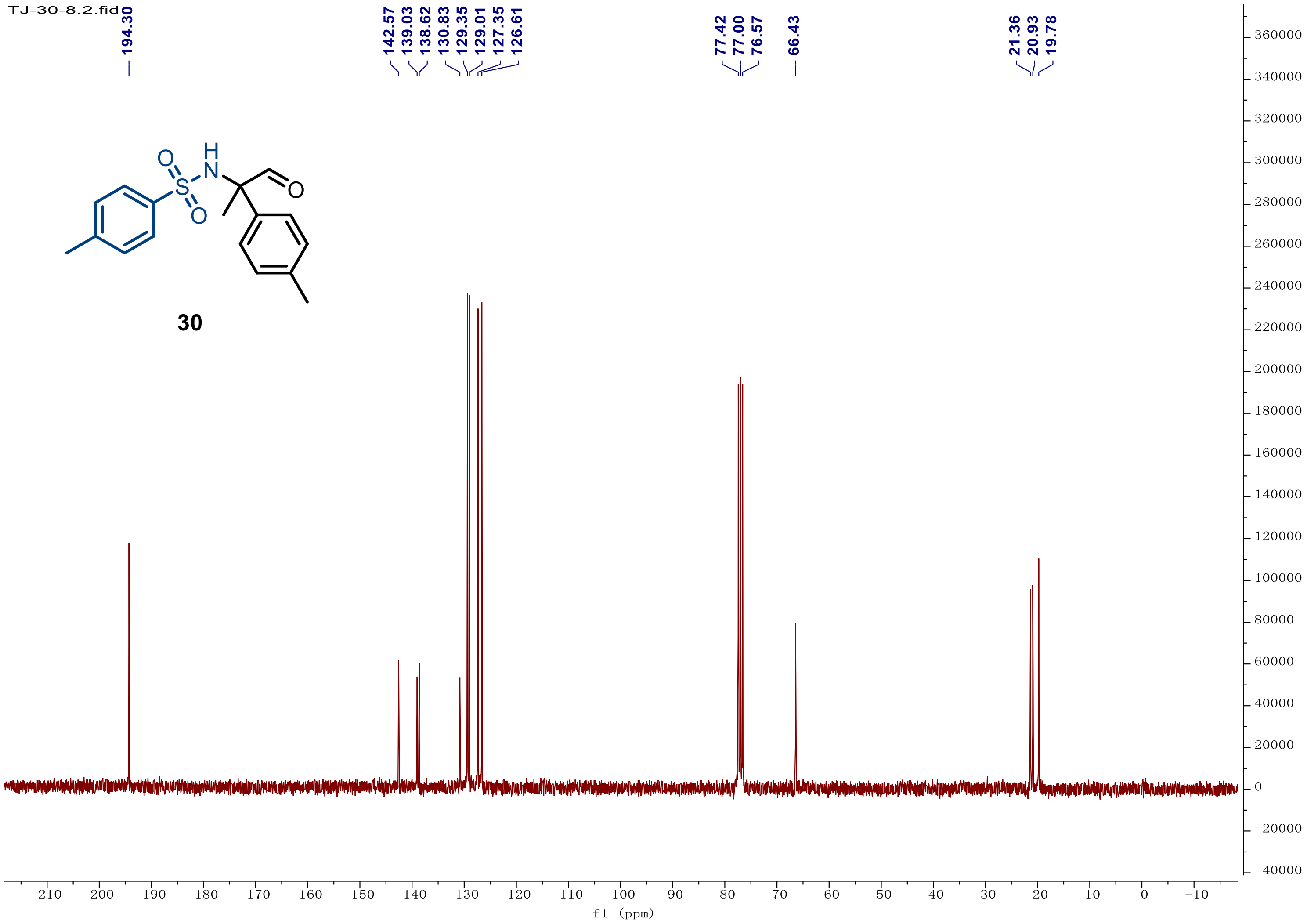
^{13}**C NMR** spectrum of compound **29** (75 MHz, CDCl$_3$)



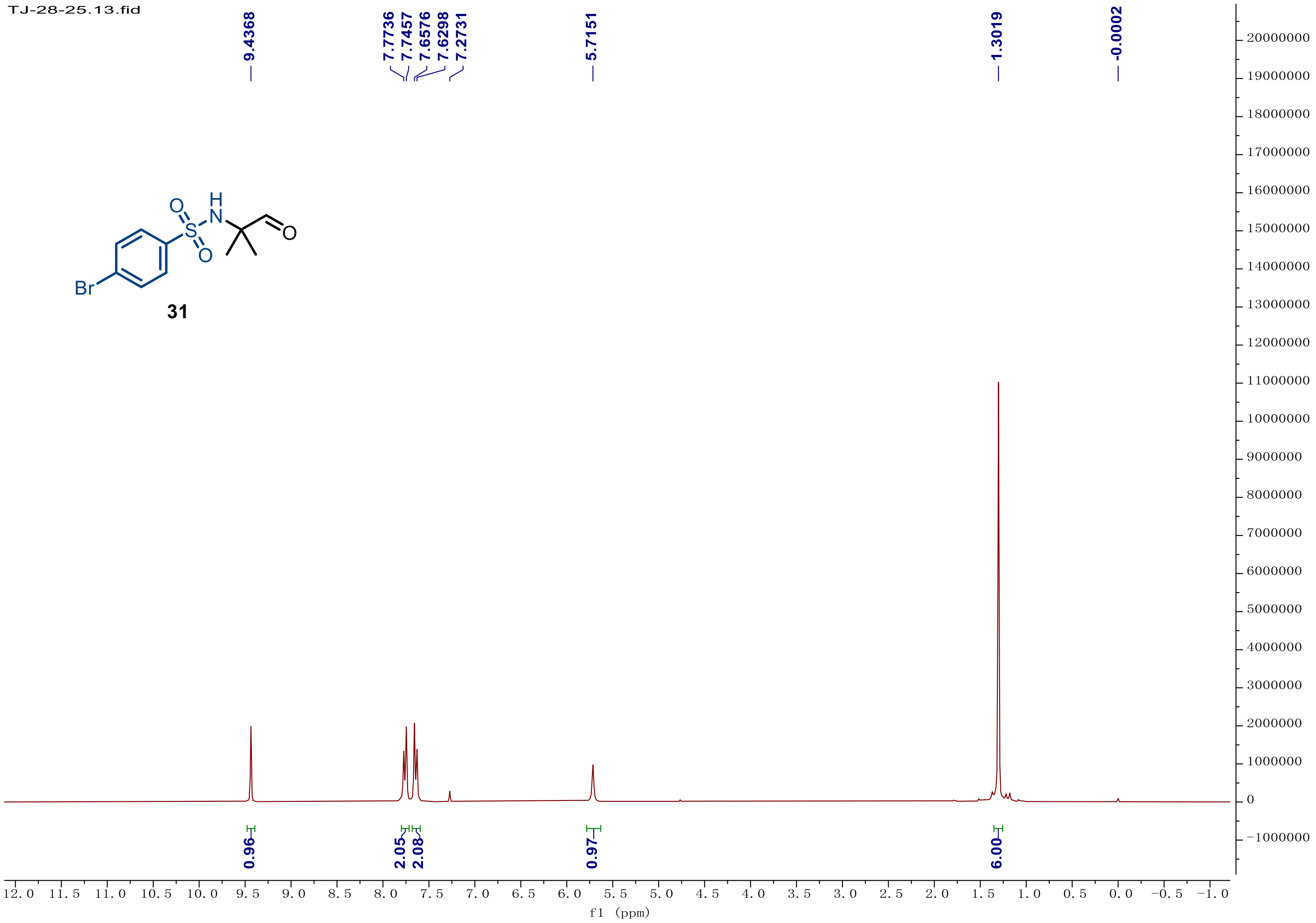
^{1}**H NMR** spectrum of compound **30** (300 MHz, $CDCl_3$)



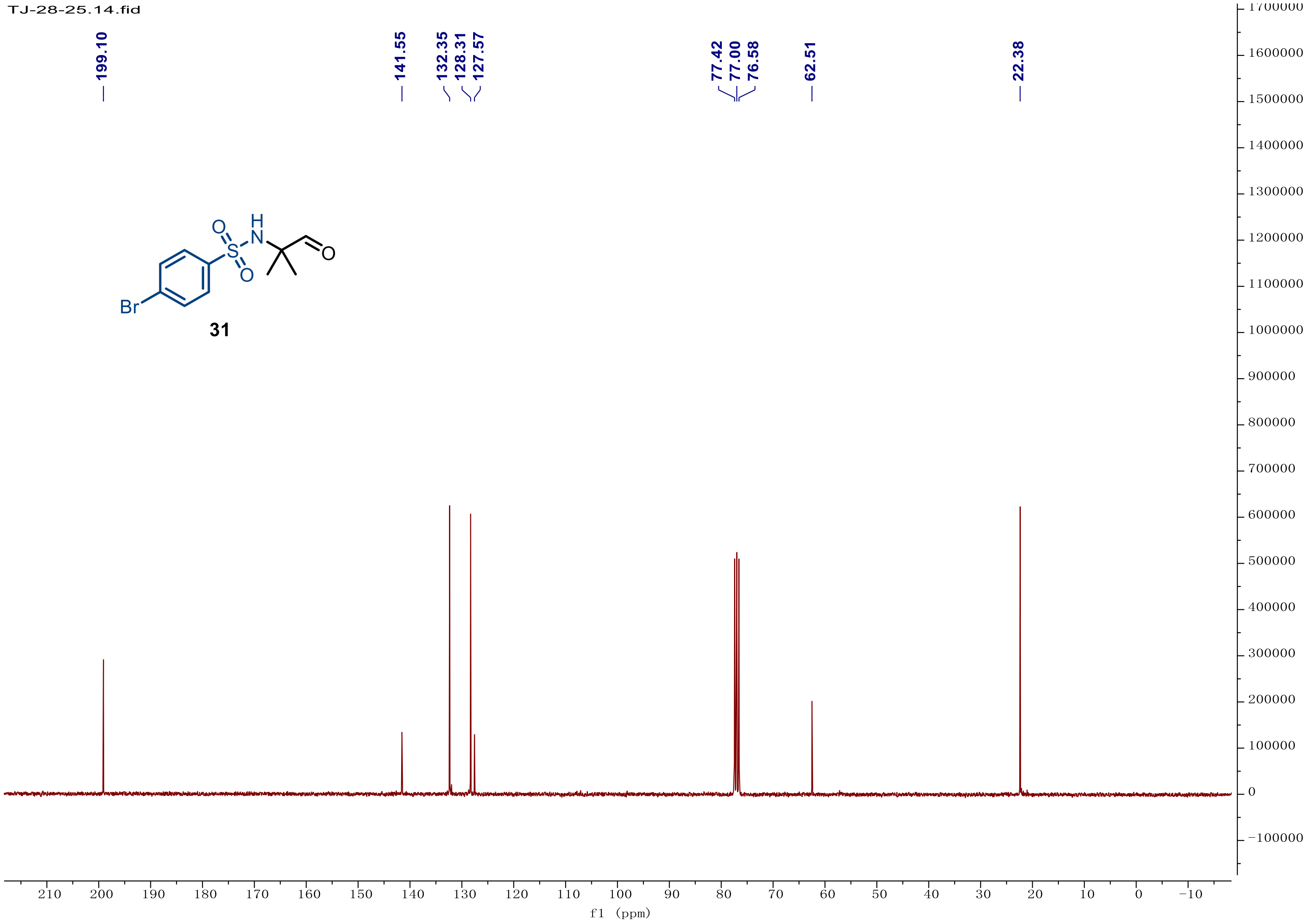
^{13}C **NMR** spectrum of compound **30** (75 MHz, CDCl$_3$)



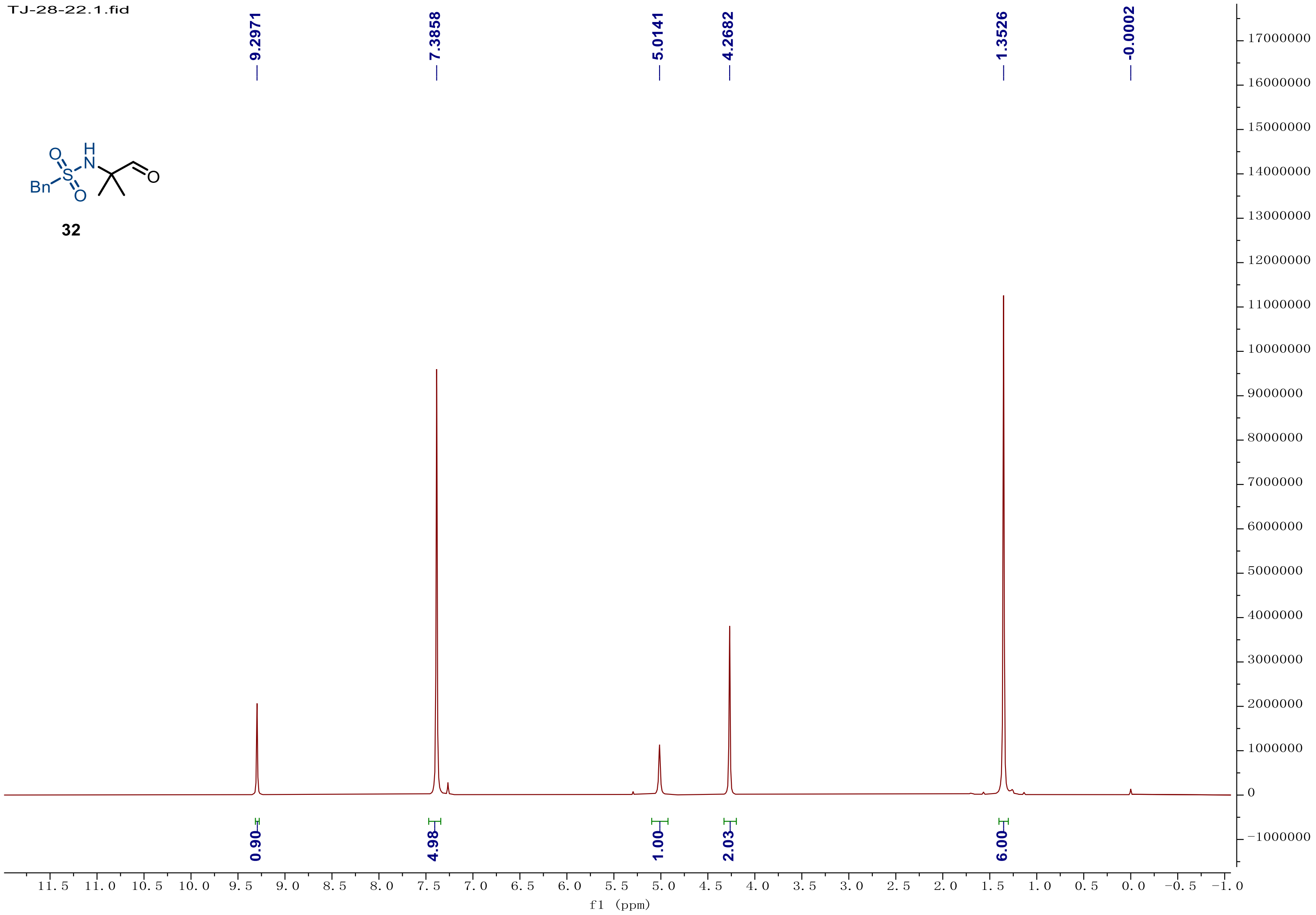
^{1}**H NMR** spectrum of compound **31** (300 MHz, $CDCl_3$)



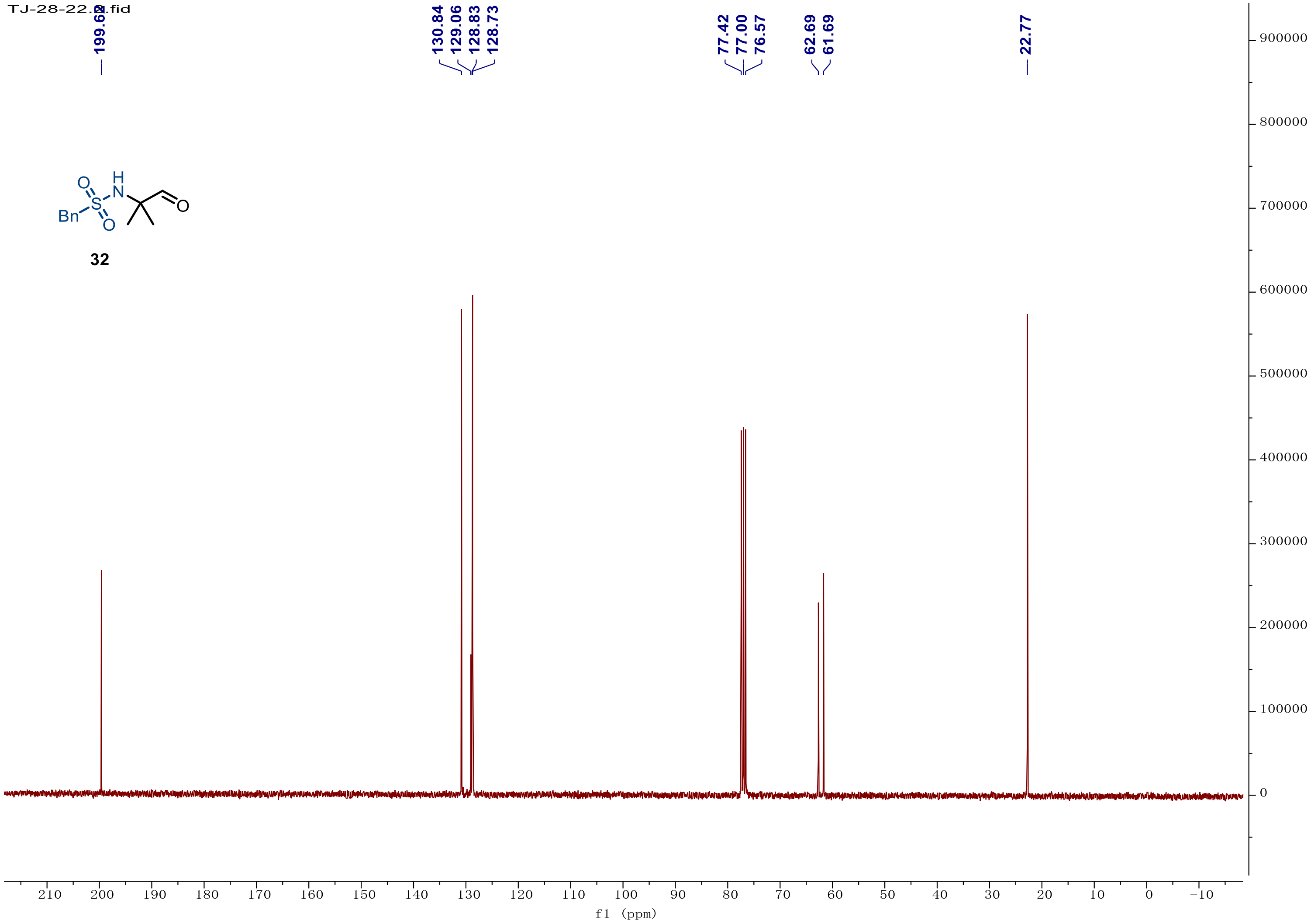
^{13}C **NMR** spectrum of compound **31** (75 MHz, $CDCl_3$)



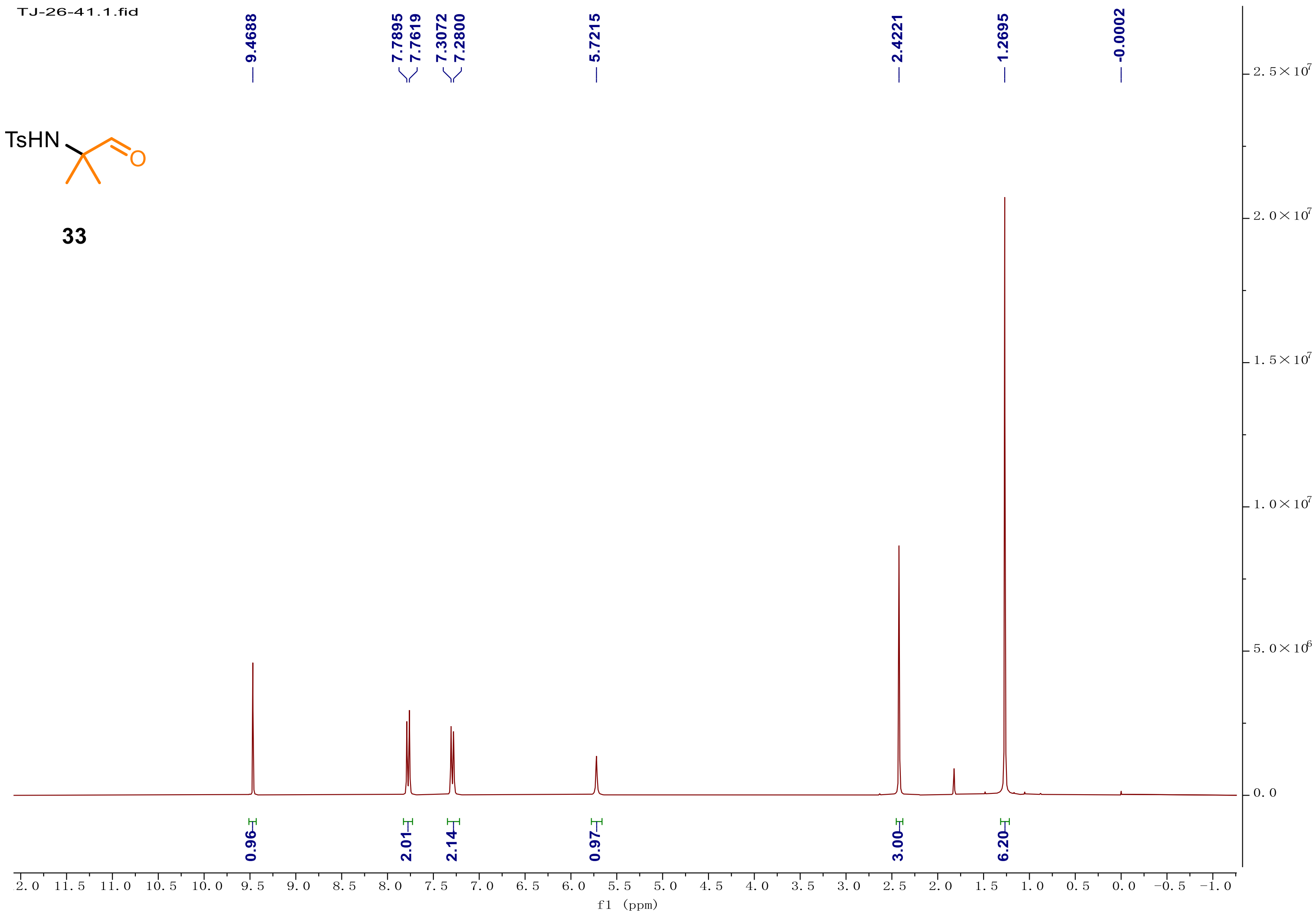
^{1}**H NMR** spectrum of compound **32** (300 MHz, $CDCl_3$)



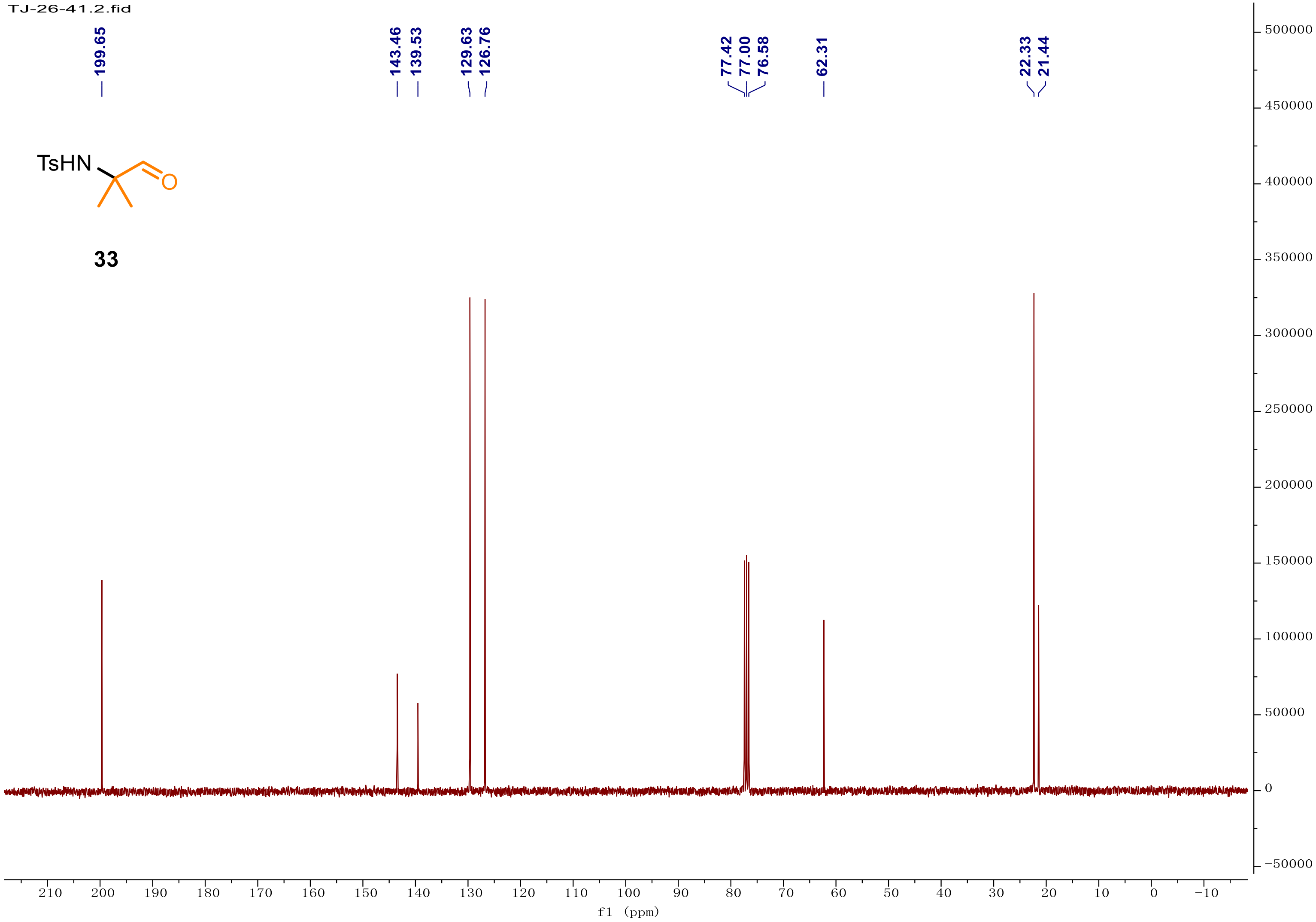
^{13}C **NMR** spectrum of compound **32** (75 MHz, CDCl$_3$)



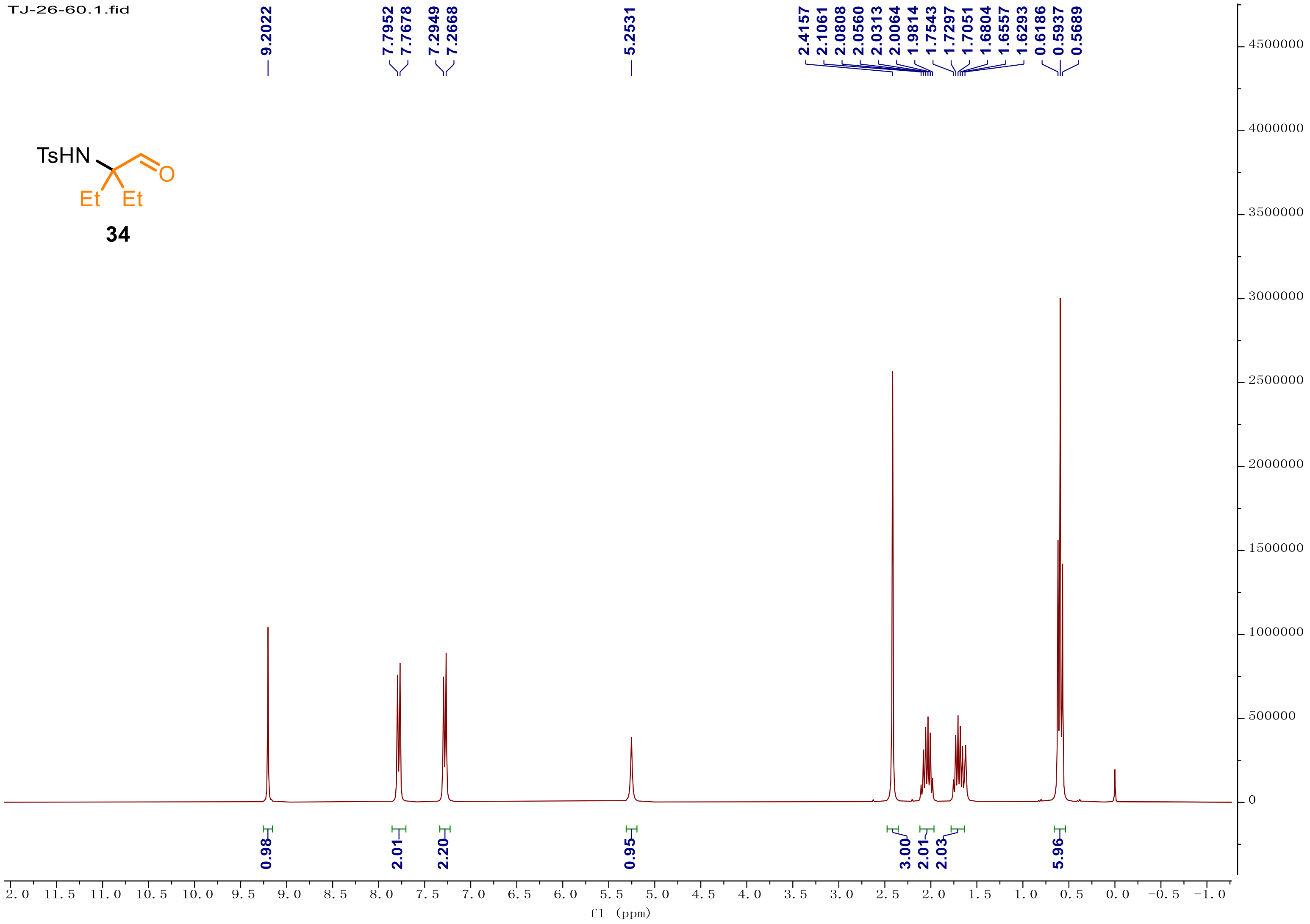
^{1}H NMR spectrum of compound **33** (300 MHz, $CDCl_3$)



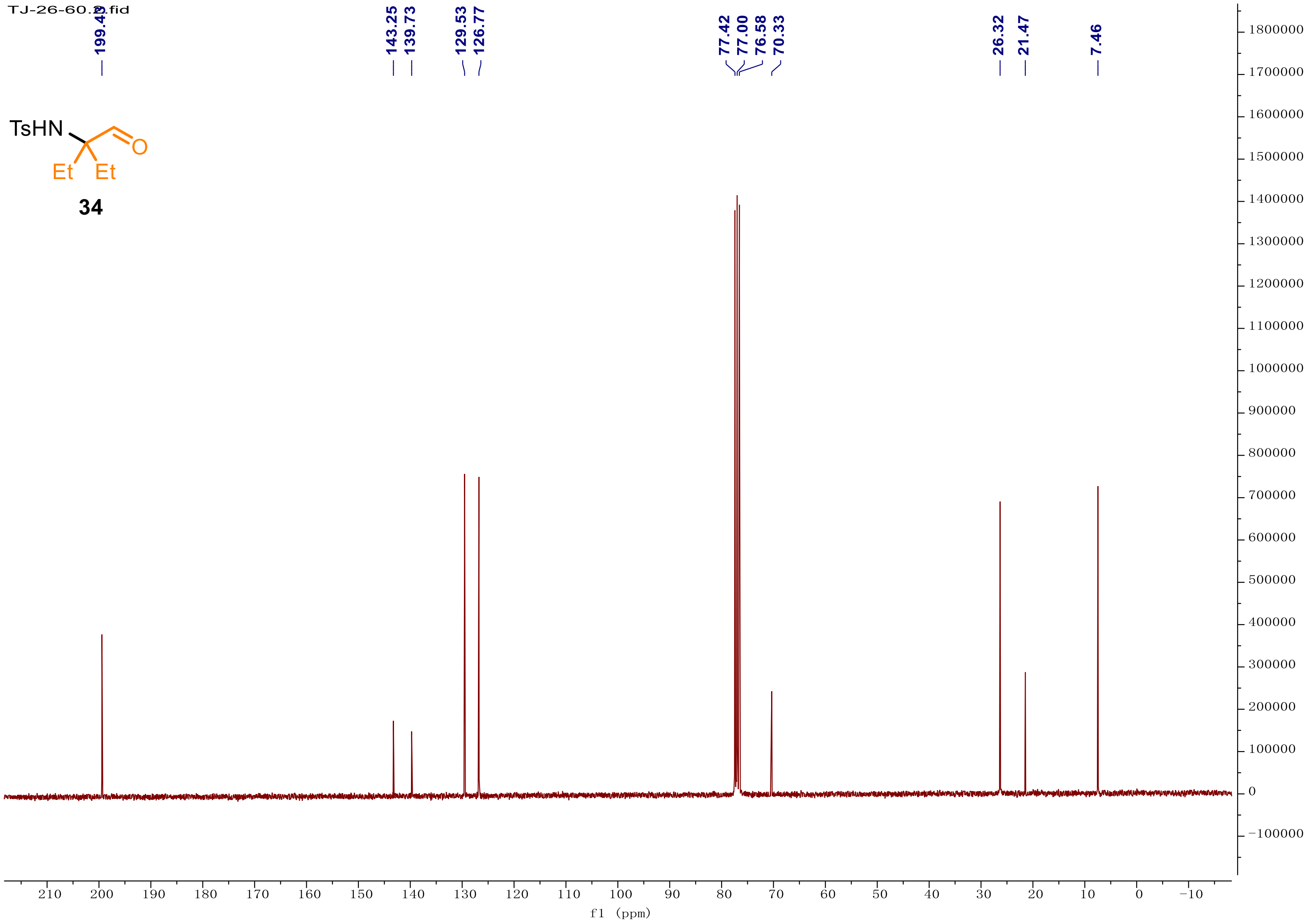
^{13}**C NMR** spectrum of compound **33** (75 MHz, $CDCl_3$)



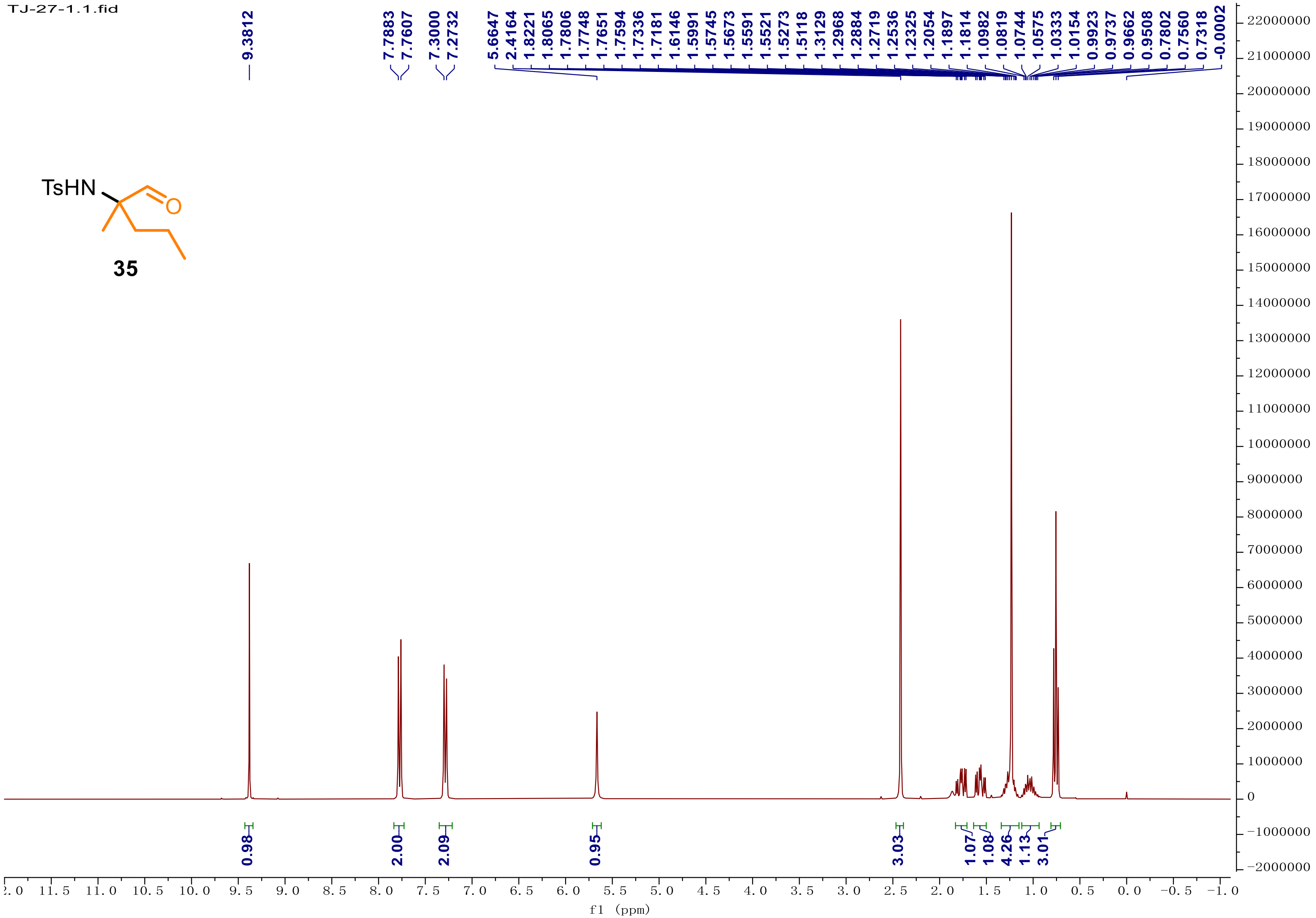
^{1}**H NMR** spectrum of compound **34** (300 MHz, $CDCl_3$)



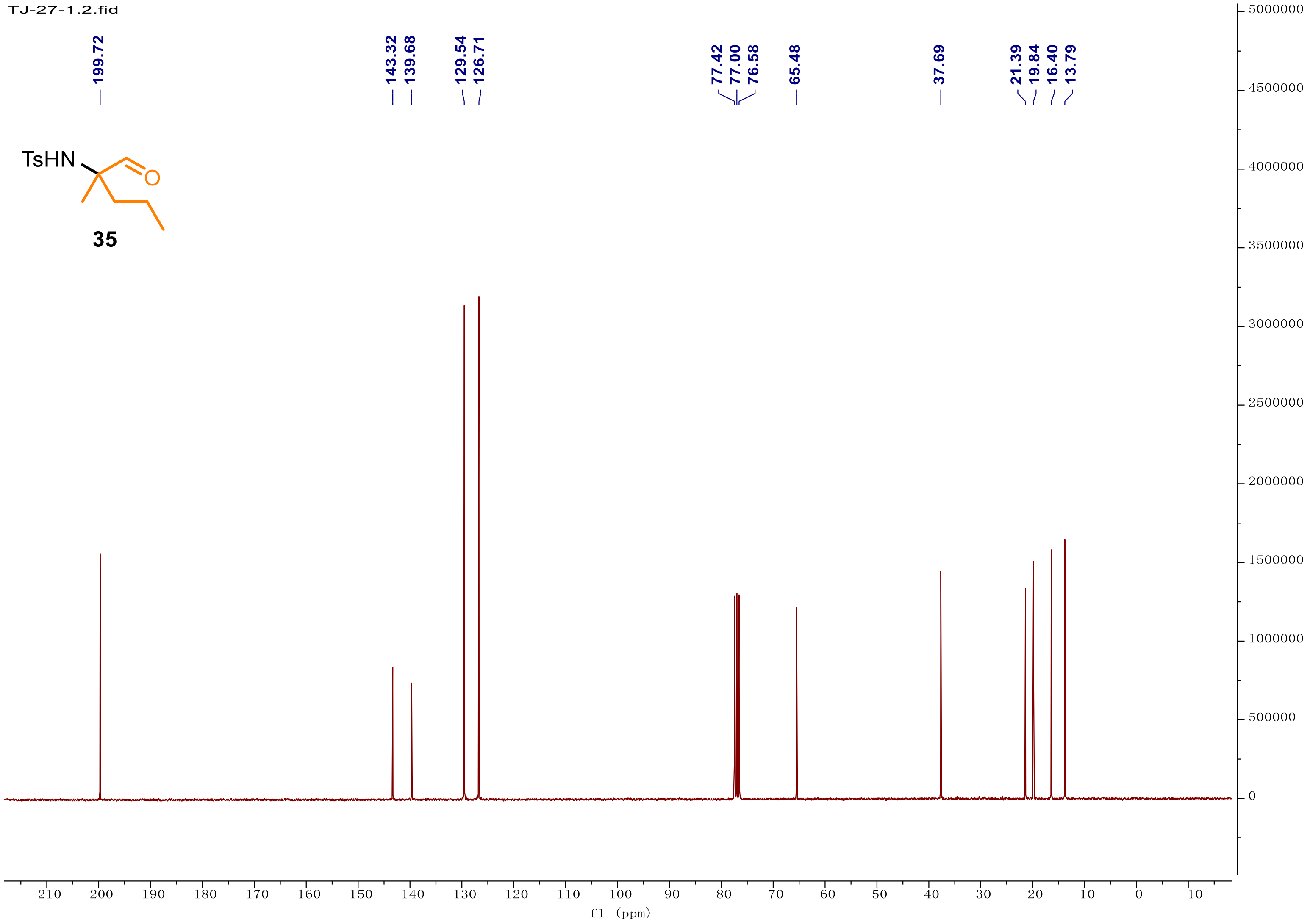
^{13}**C NMR** spectrum of compound **34** (75 MHz, CDCl$_3$)



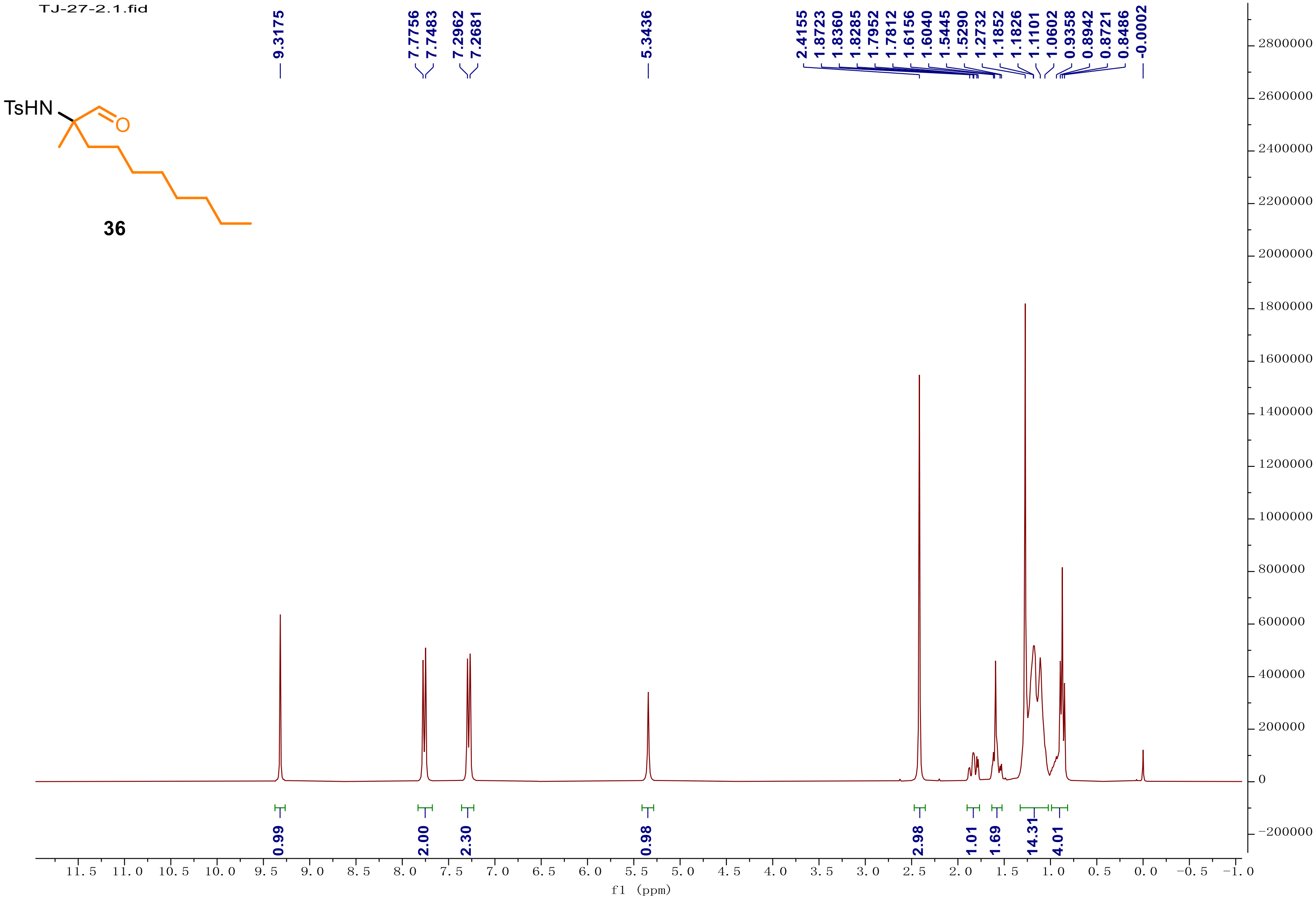
^{1}H NMR spectrum of compound **35** (300 MHz, $CDCl_3$)



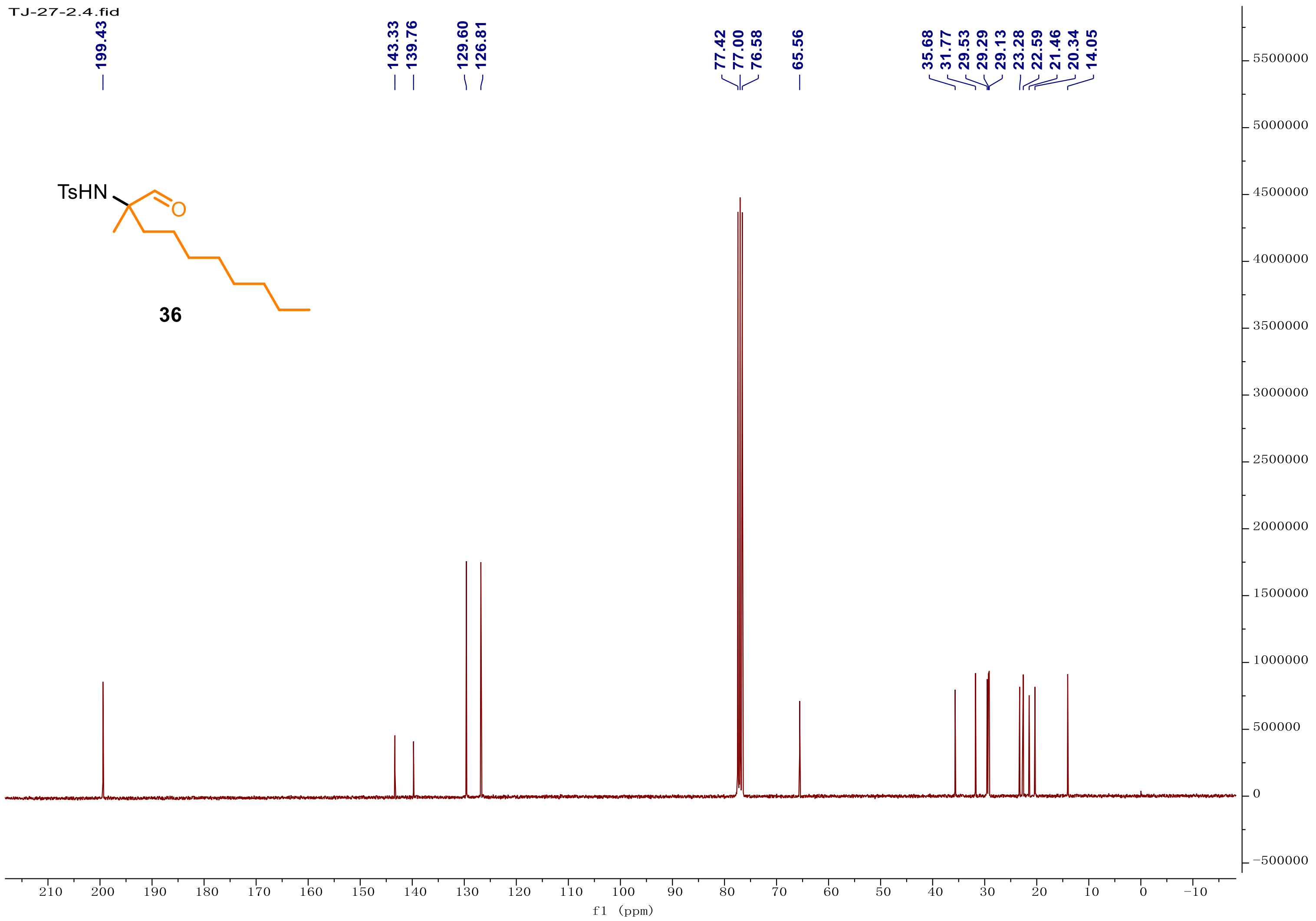
^{13}**C NMR** spectrum of compound **35** (75 MHz, CDCl$_3$)



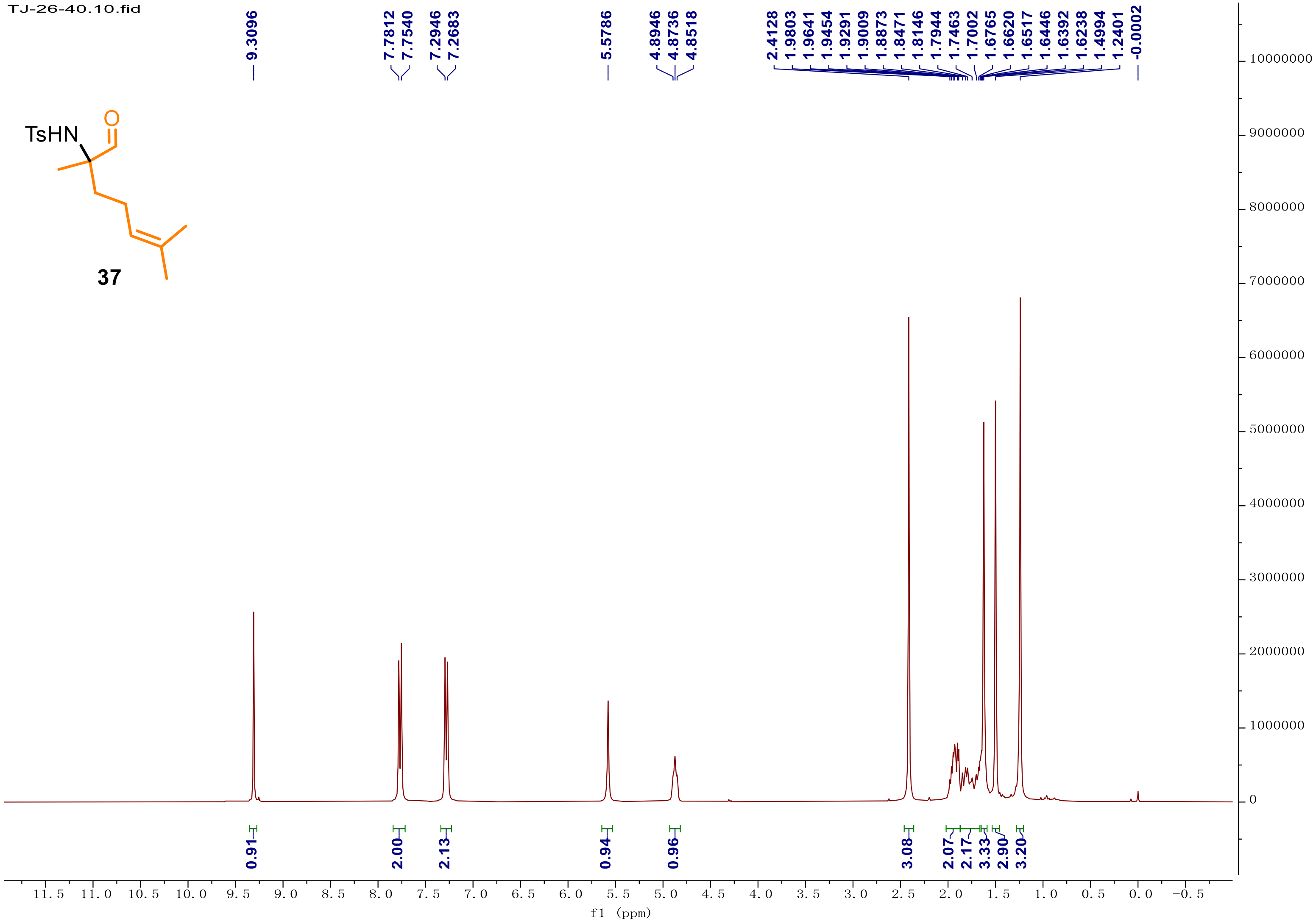
^{1}**H NMR** spectrum of compound **36** (300 MHz, CDCl$_3$)



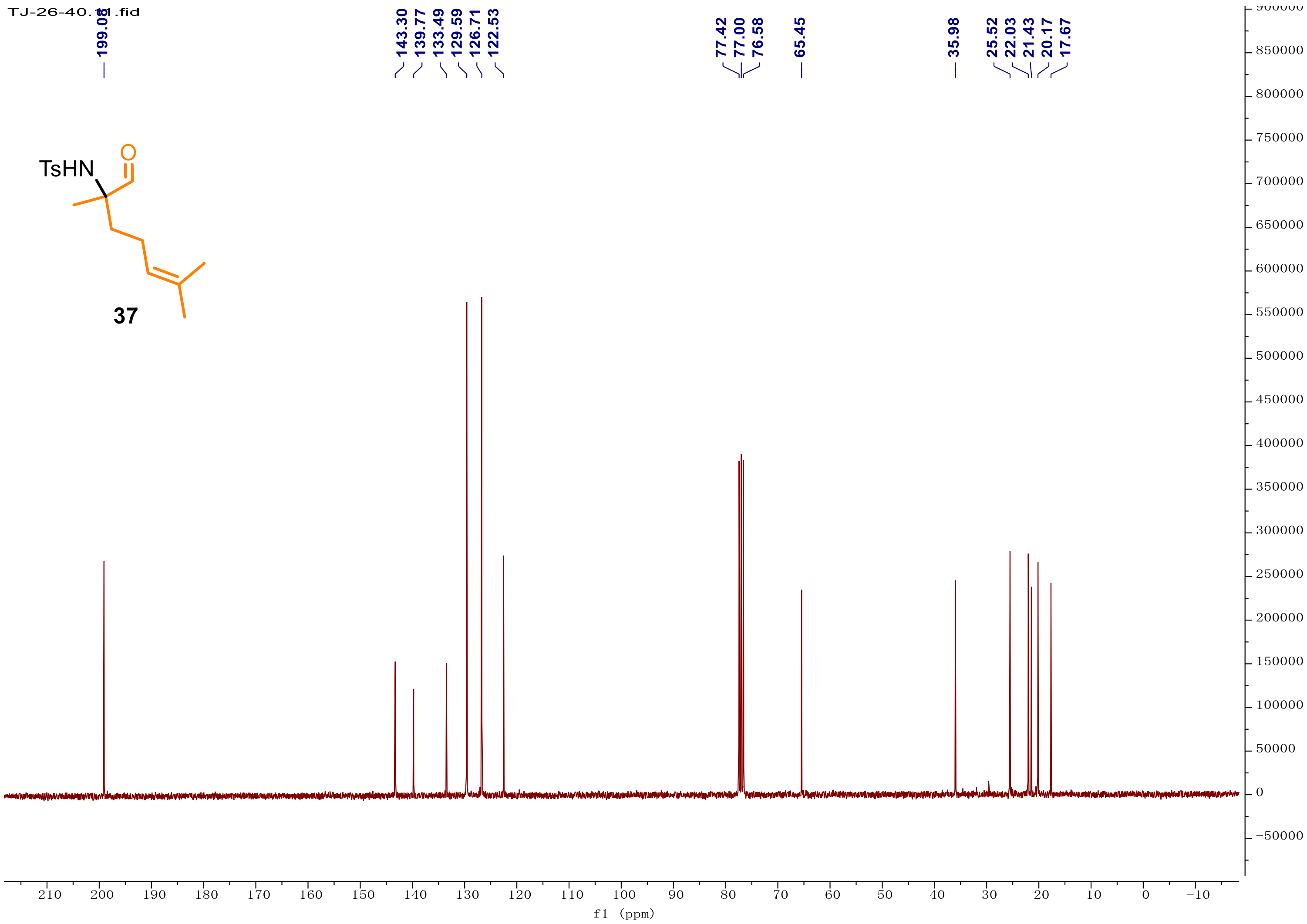
^{13}**C NMR** spectrum of compound **36** (75 MHz, CDCl$_3$)



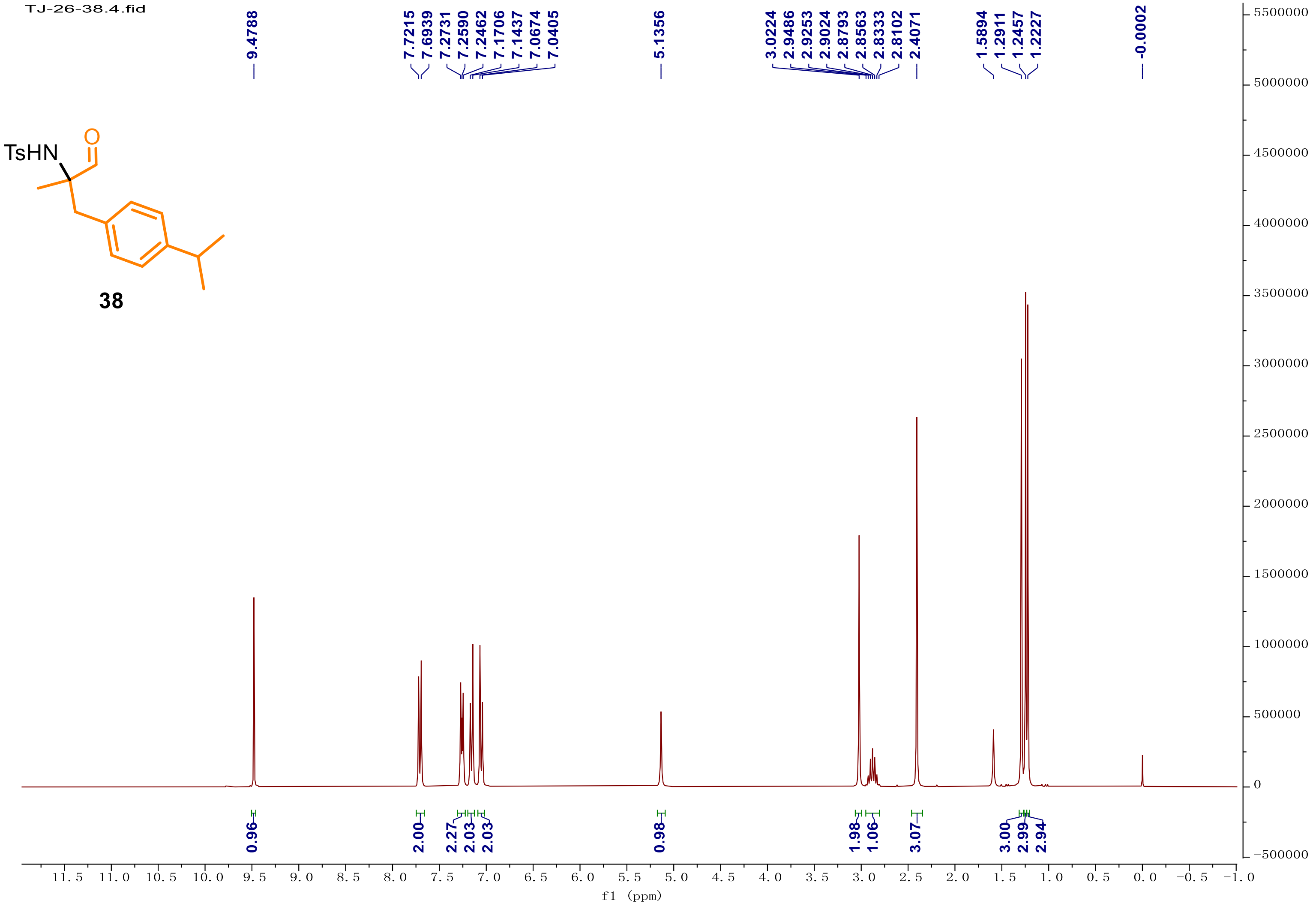
^{1}H NMR spectrum of compound **37** (300 MHz, $CDCl_3$)



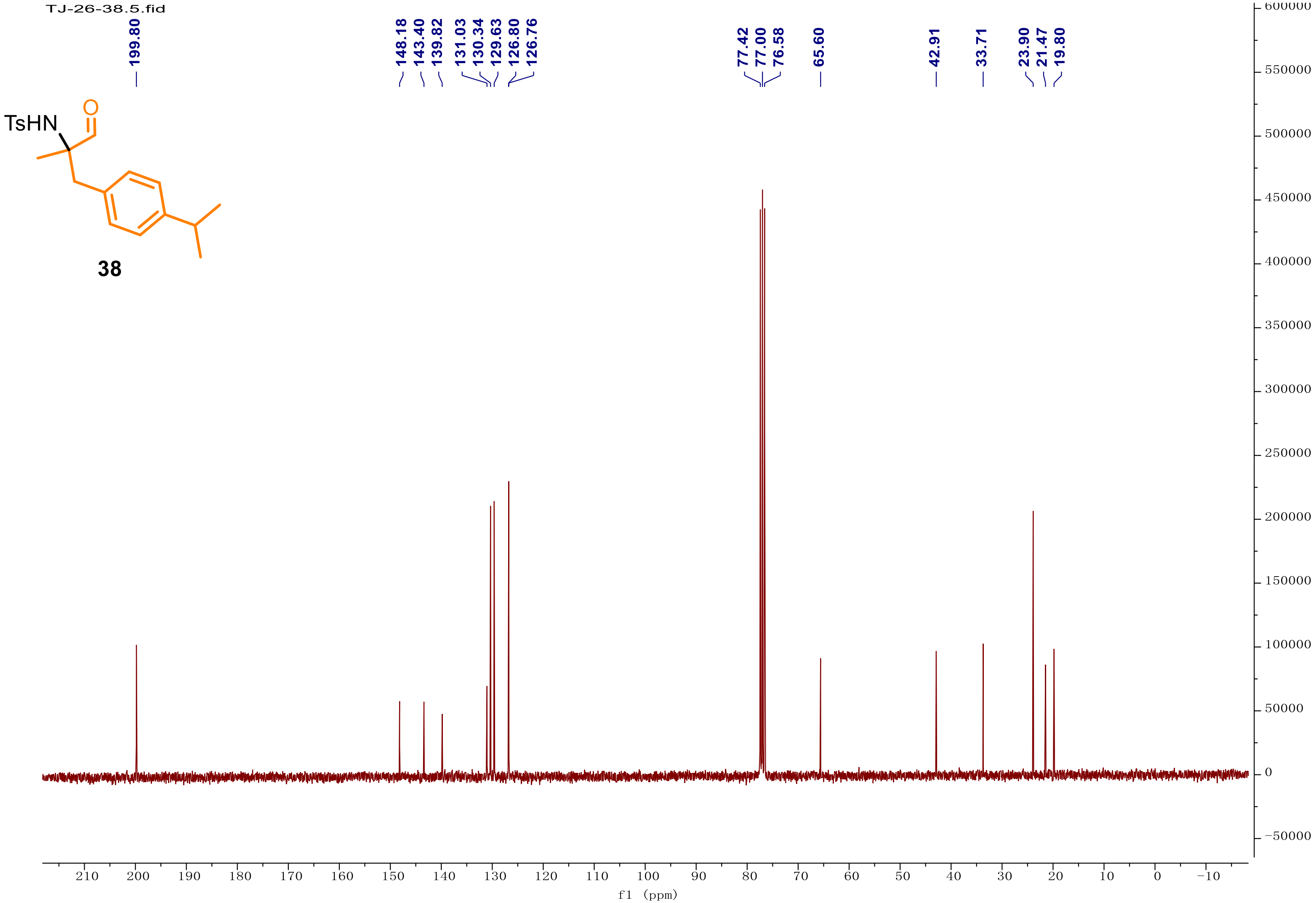
^{13}C **NMR** spectrum of compound **37** (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound 38 (300 MHz, CDCl$_3$)

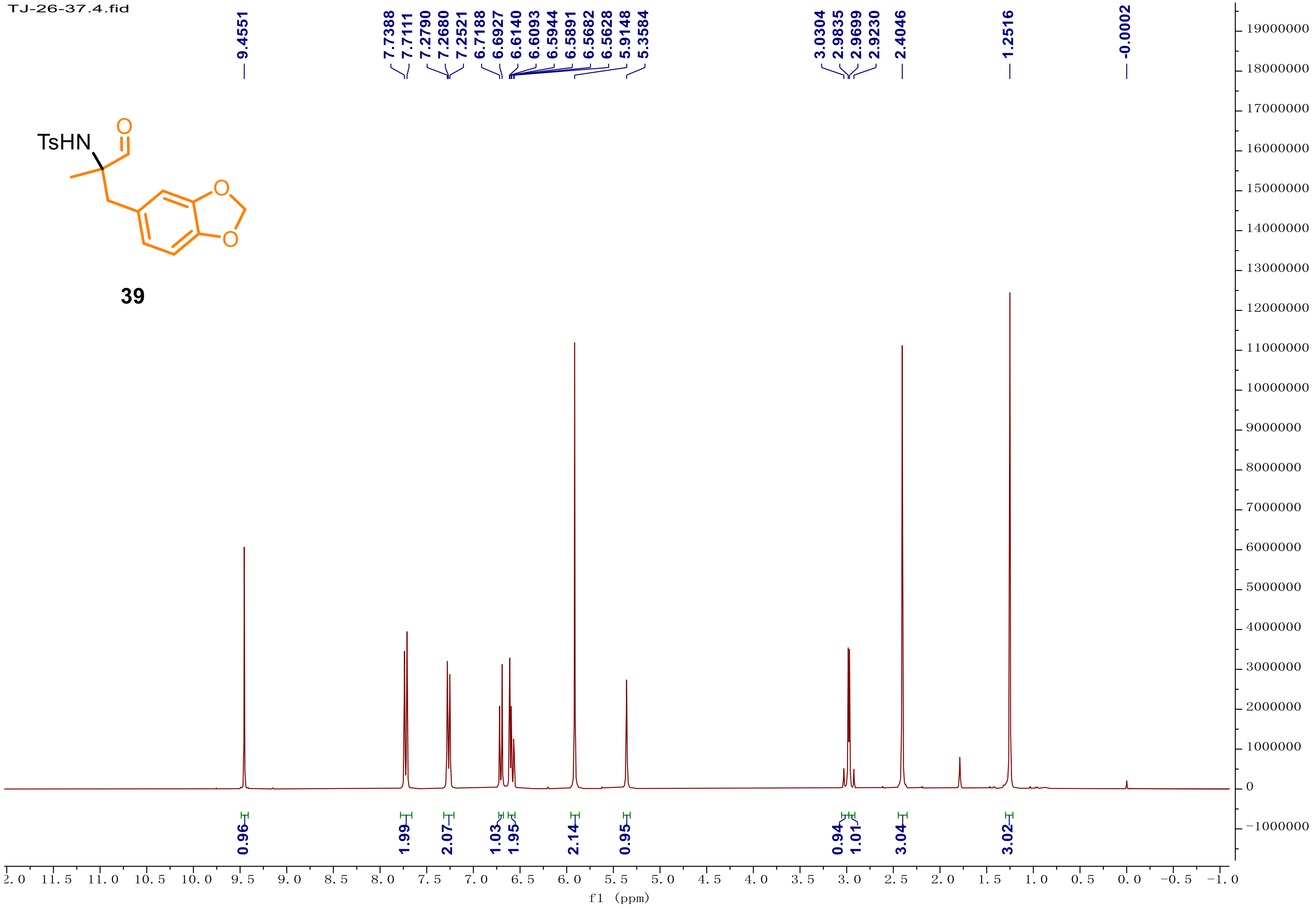


^{13}C NMR spectrum of compound **38** (75 MHz, CDCl$_3$)

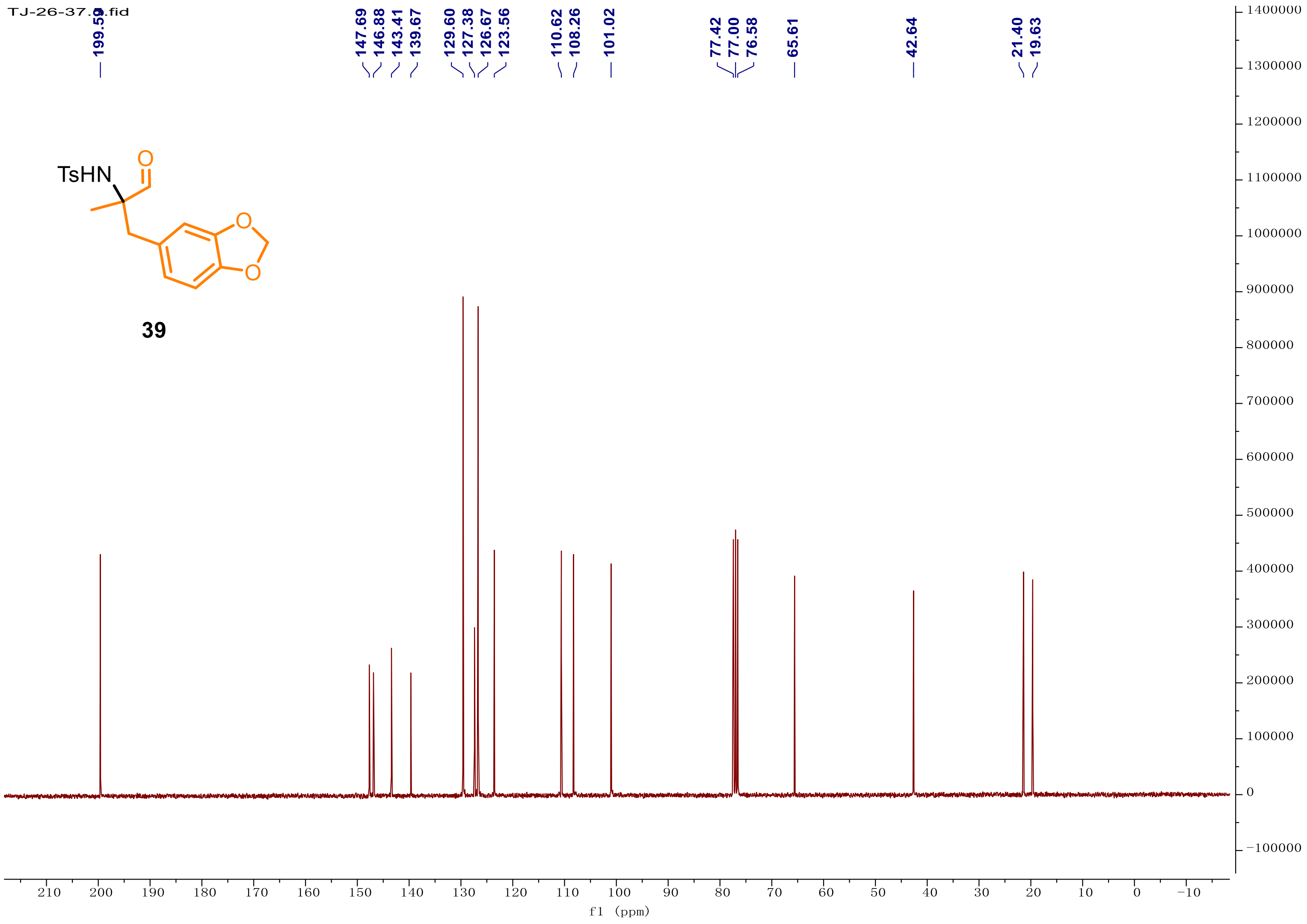


38

^{1}**H NMR** spectrum of compound **39** (300 MHz, $CDCl_3$)

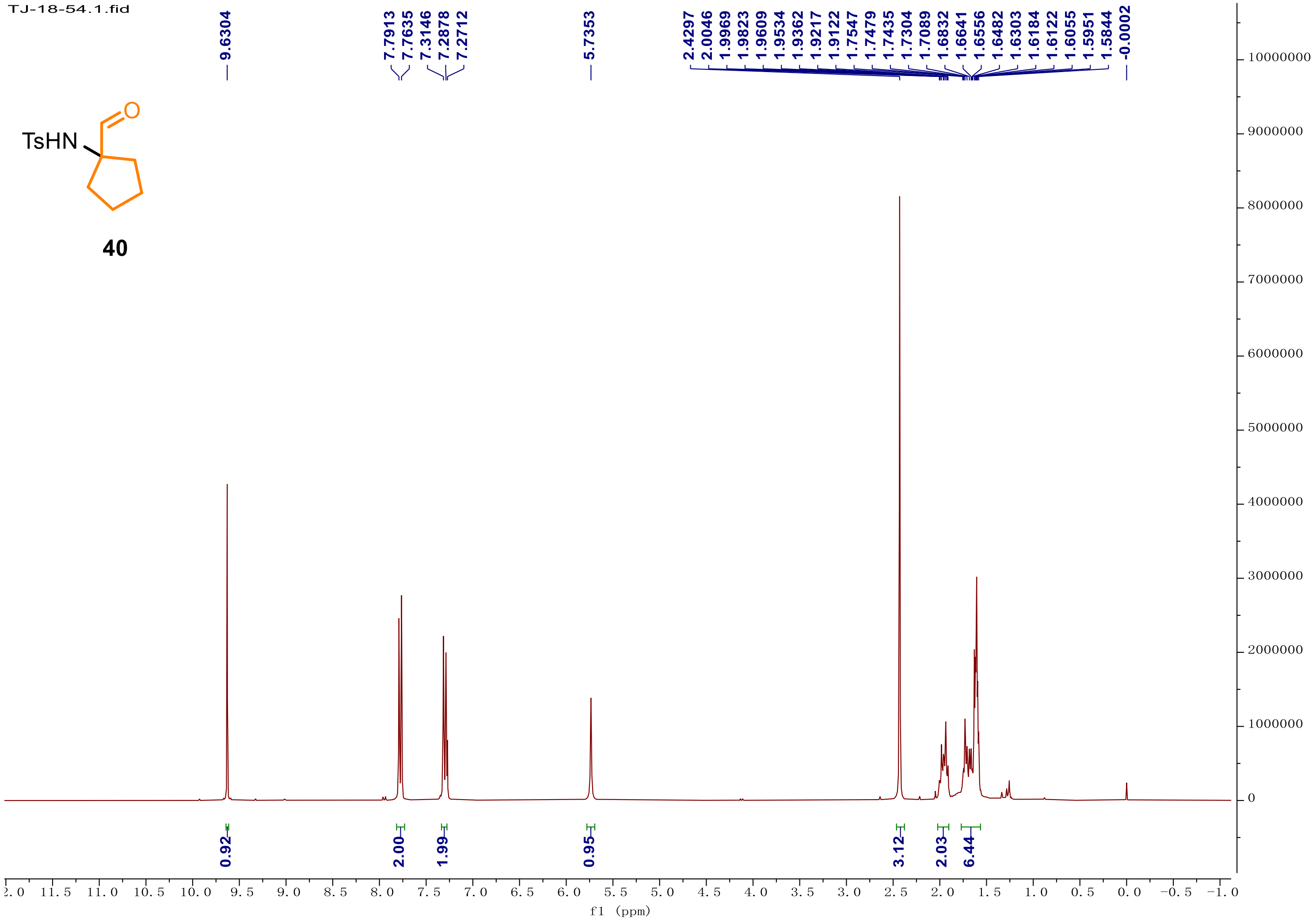


^{13}C NMR spectrum of compound **39** (75 MHz, CDCl$_3$)

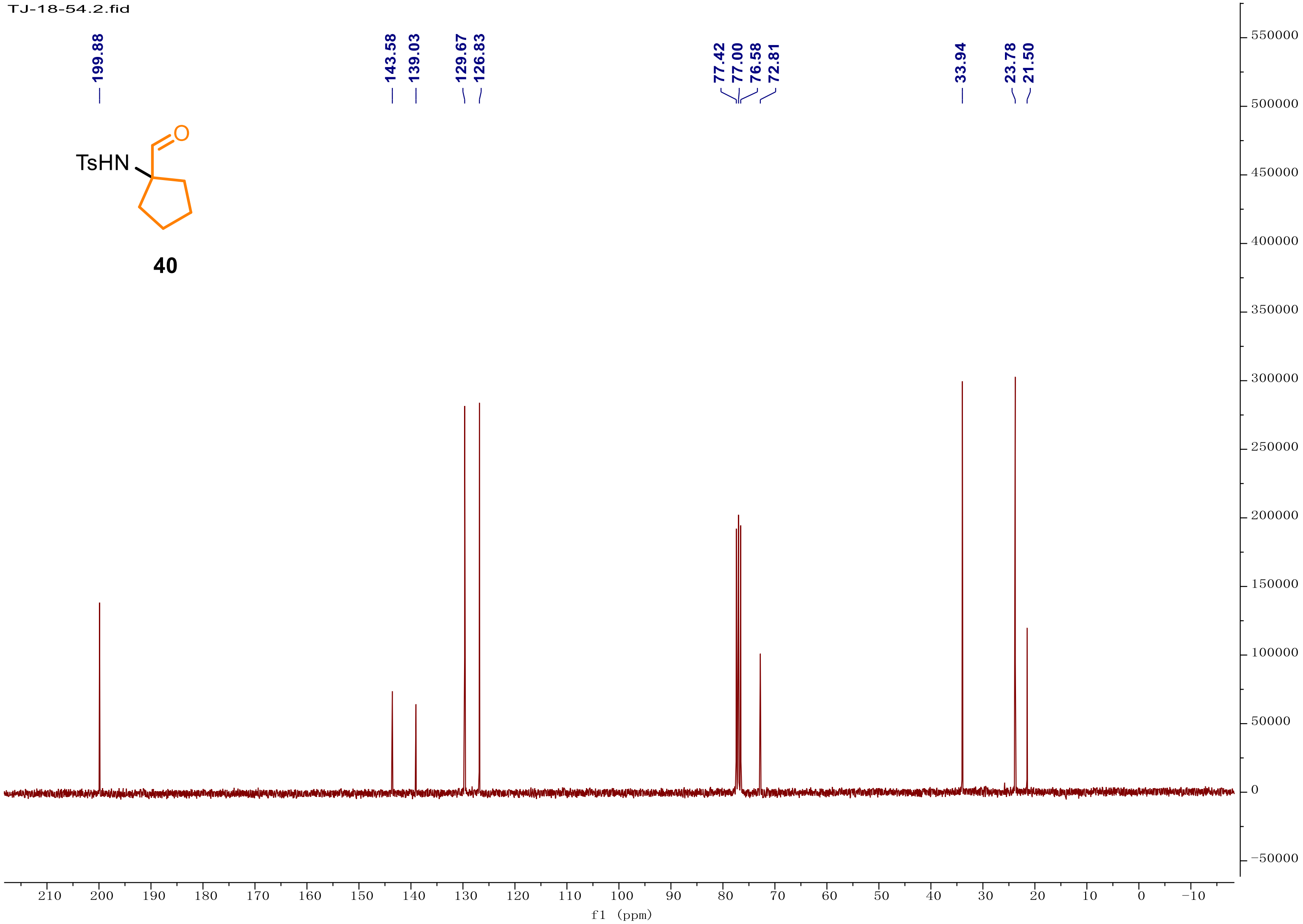


39

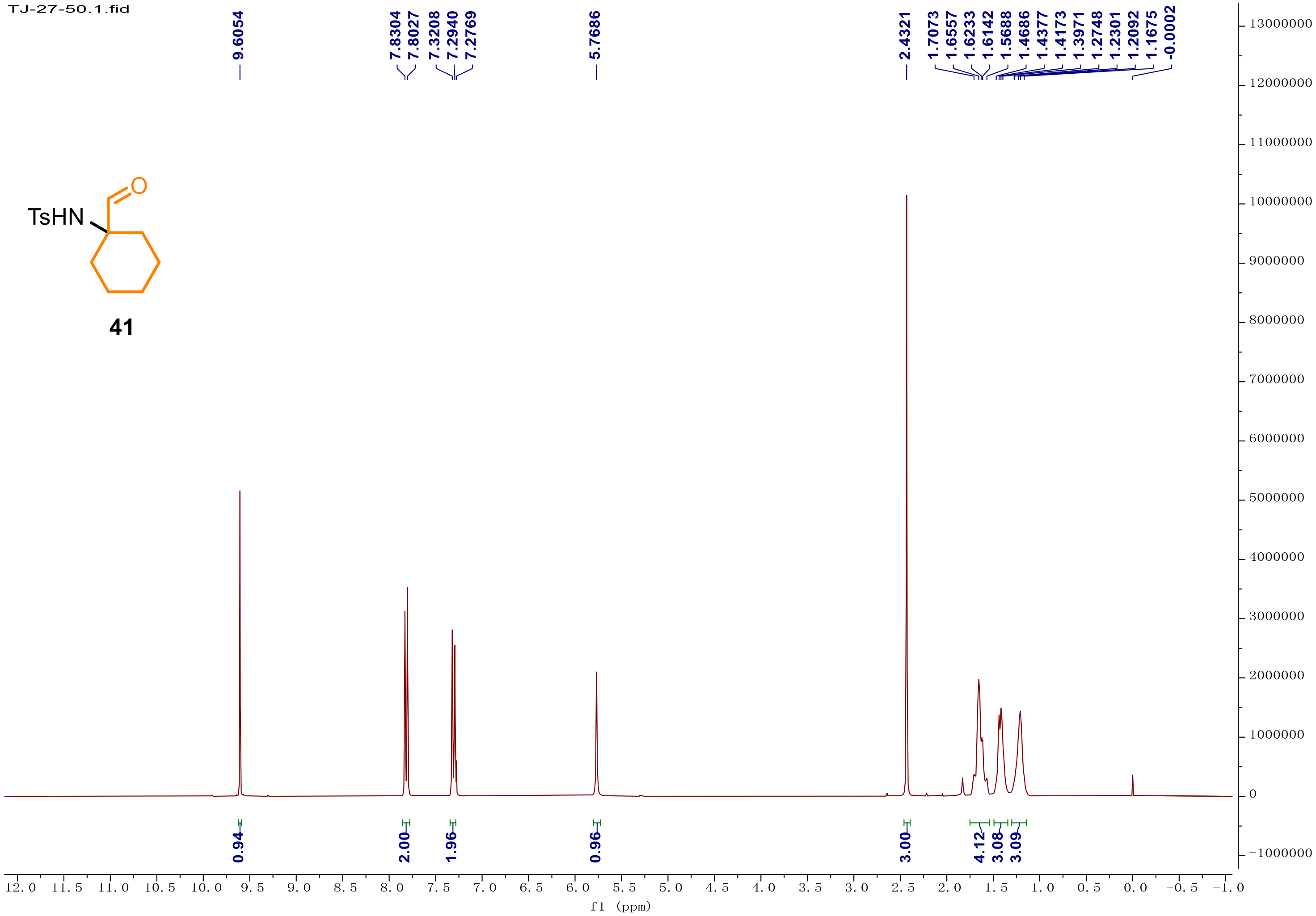
^{1}**H NMR** spectrum of compound **40** (300 MHz, $CDCl_3$)



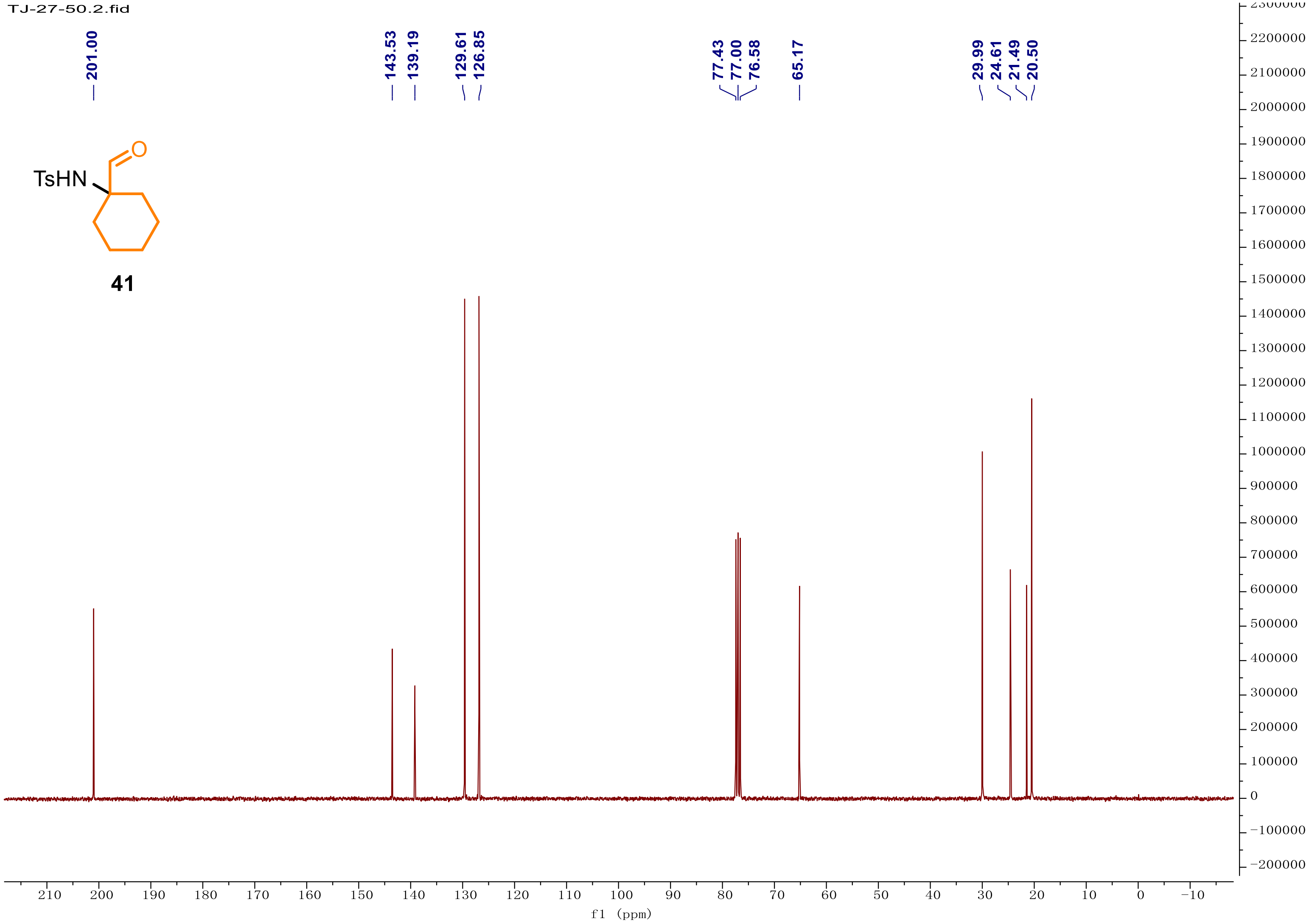
^{13}C NMR spectrum of compound **40** (75 MHz, $CDCl_3$)



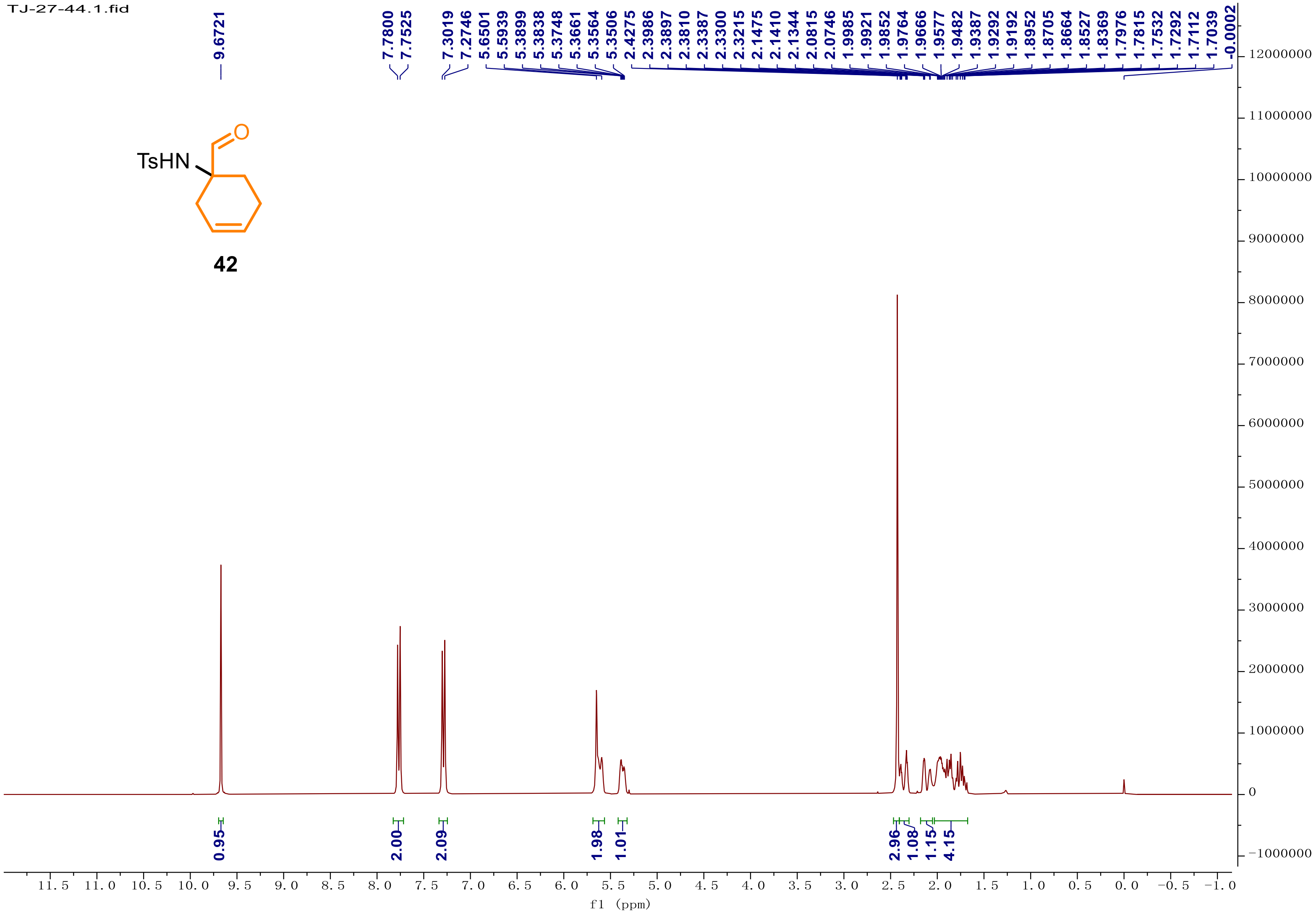
¹H NMR spectrum of compound **41** (300 MHz, $CDCl_3$)



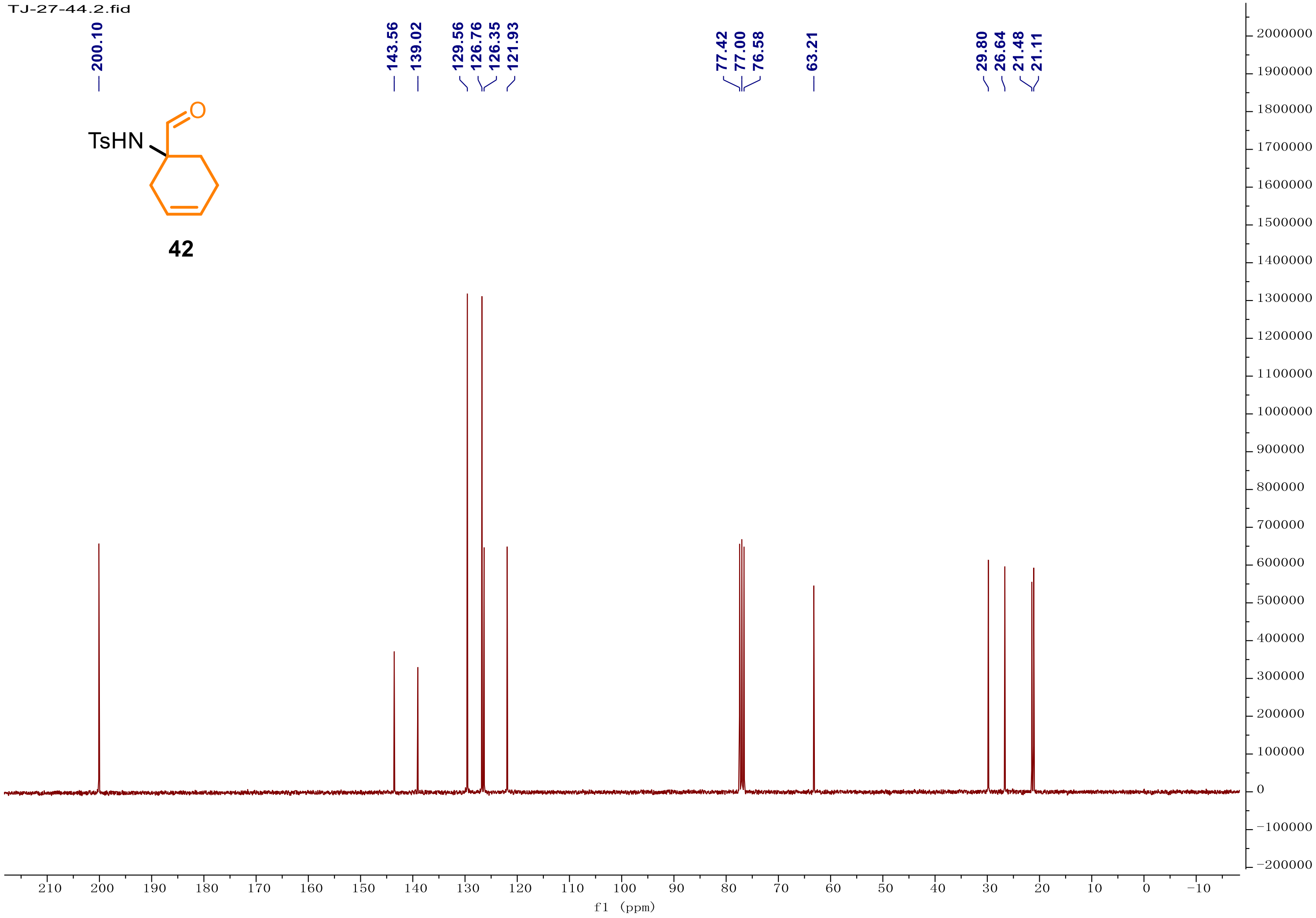
^{13}C **NMR** spectrum of compound **41** (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **42** (300 MHz, CDCl$_3$)

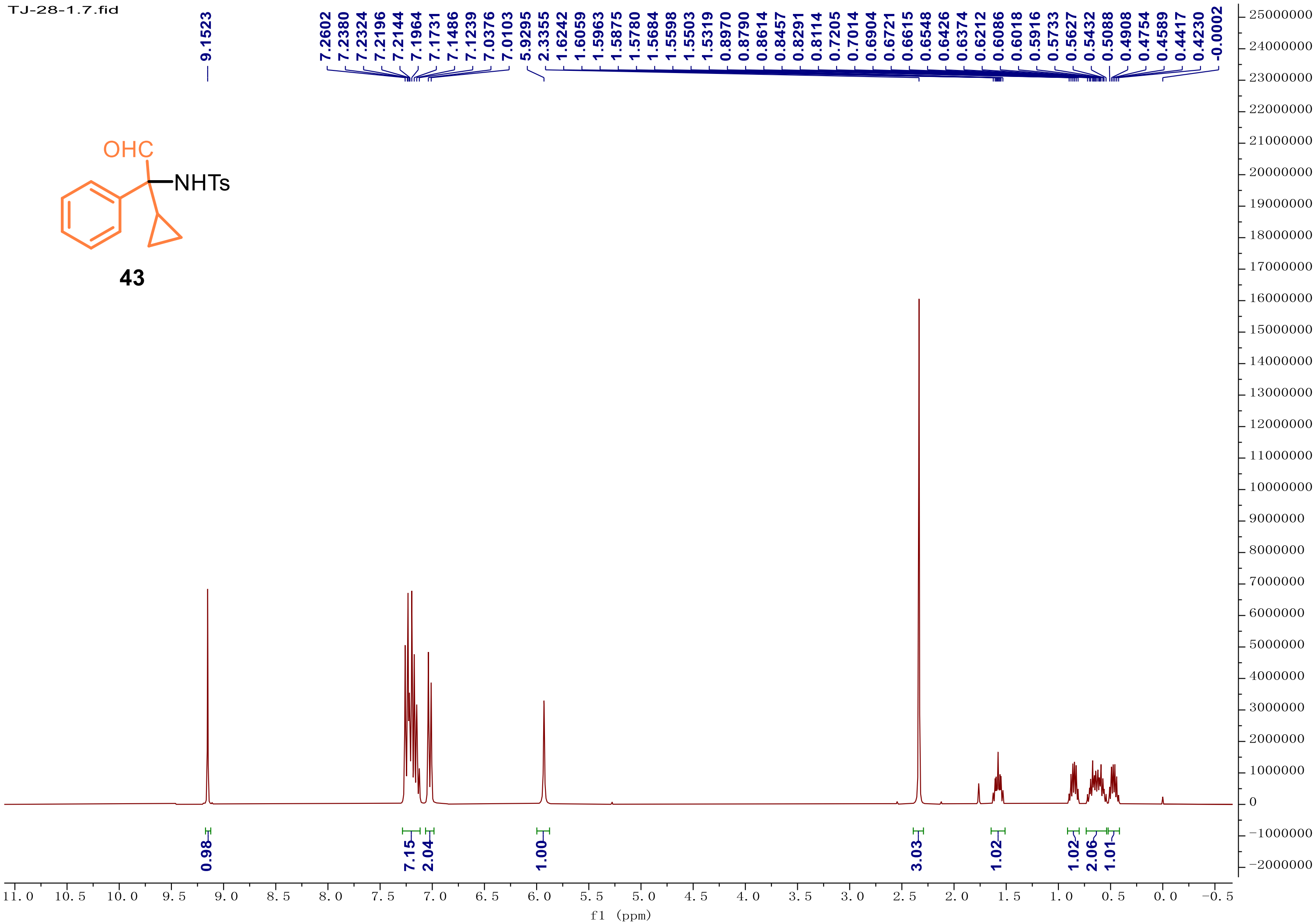


^{13}C NMR spectrum of compound **42** (75 MHz, CDCl$_3$)

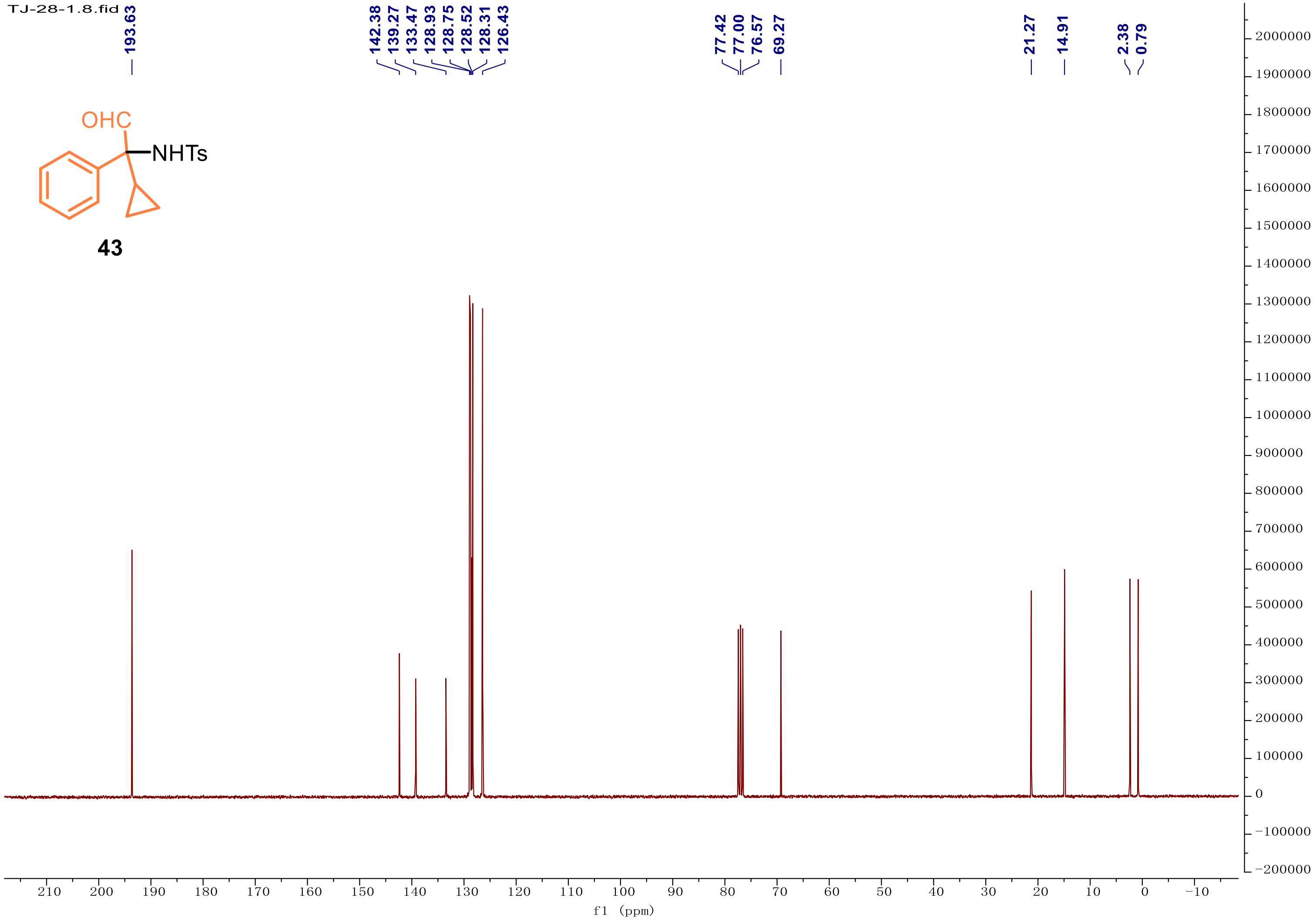


42

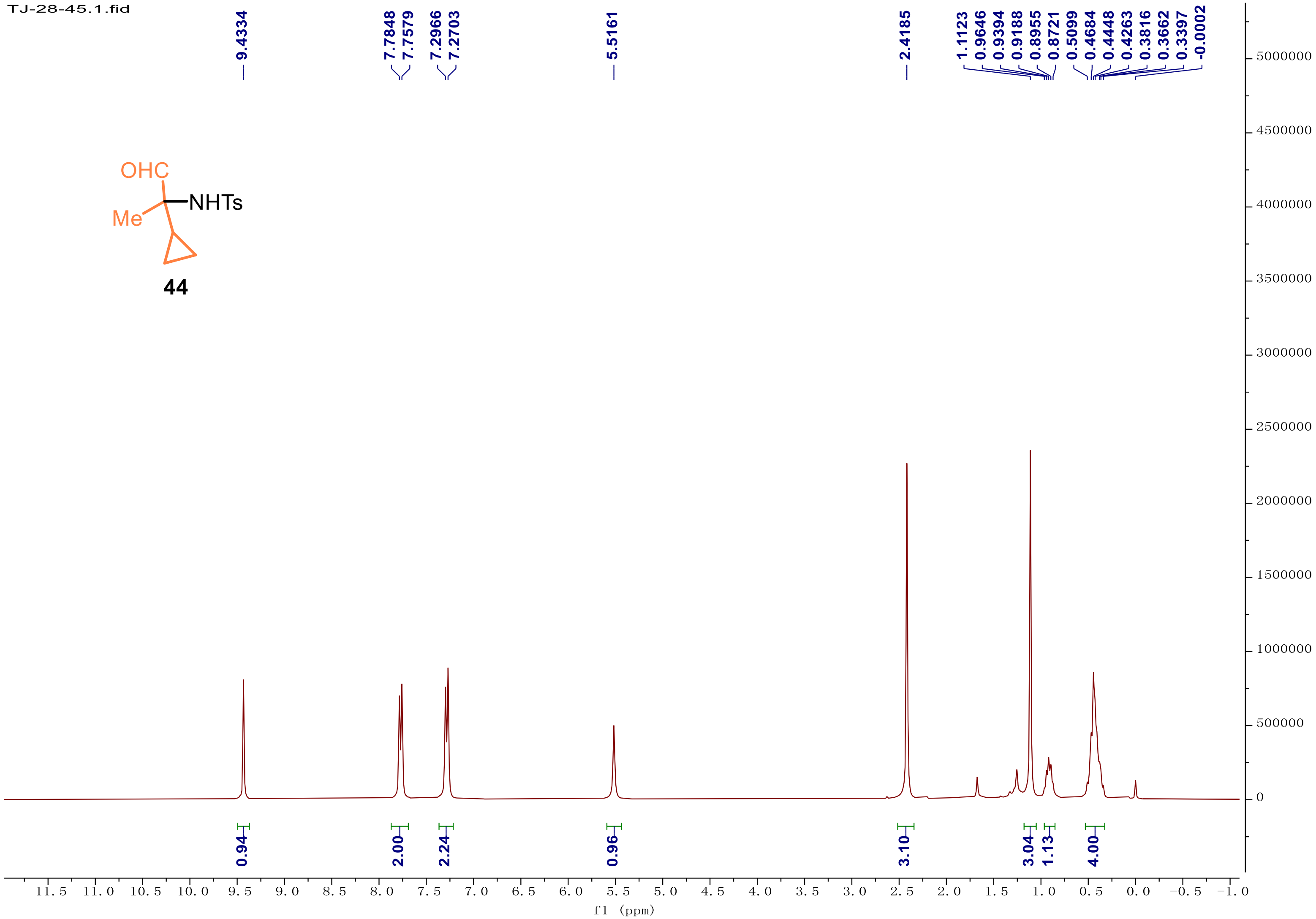
^{1}**H NMR** spectrum of compound **43** (300 MHz, CDCl$_3$)



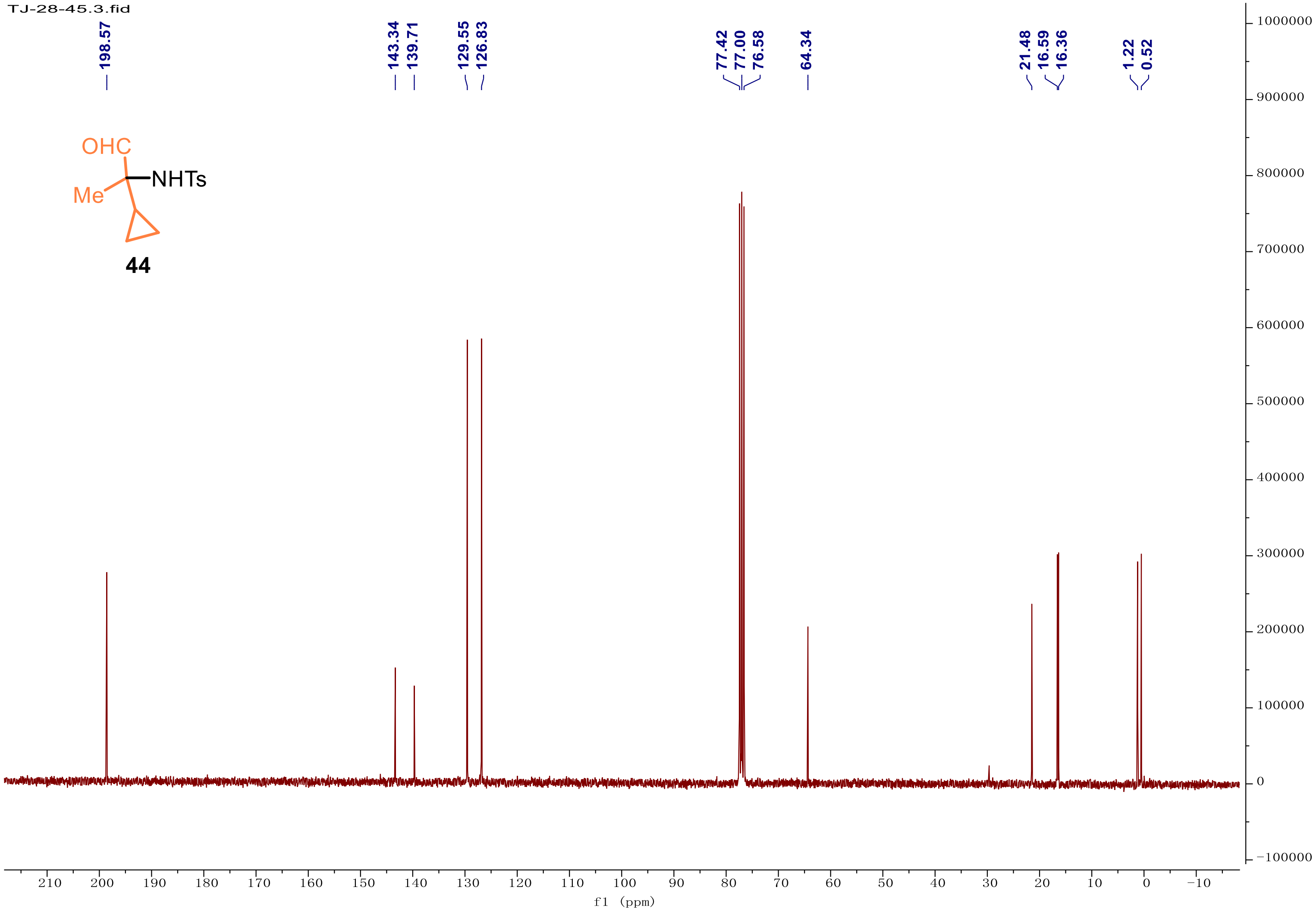
^{13}C **NMR** spectrum of compound **43** (75 MHz, CDCl$_3$)



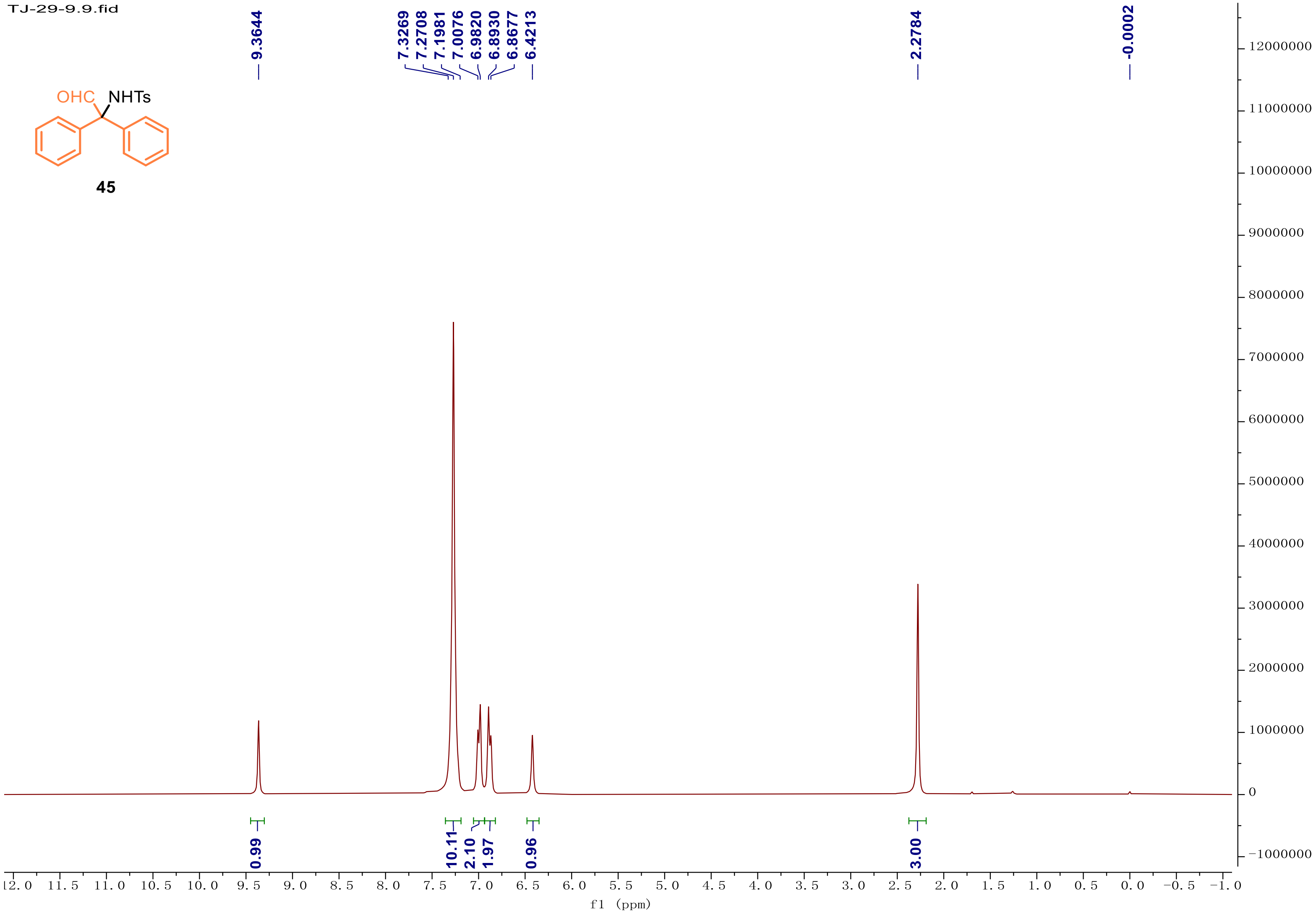
^{1}**H NMR** spectrum of compound **44** (300 MHz, $CDCl_3$)



^{13}C **NMR** spectrum of compound **44** (75 MHz, $CDCl_3$)

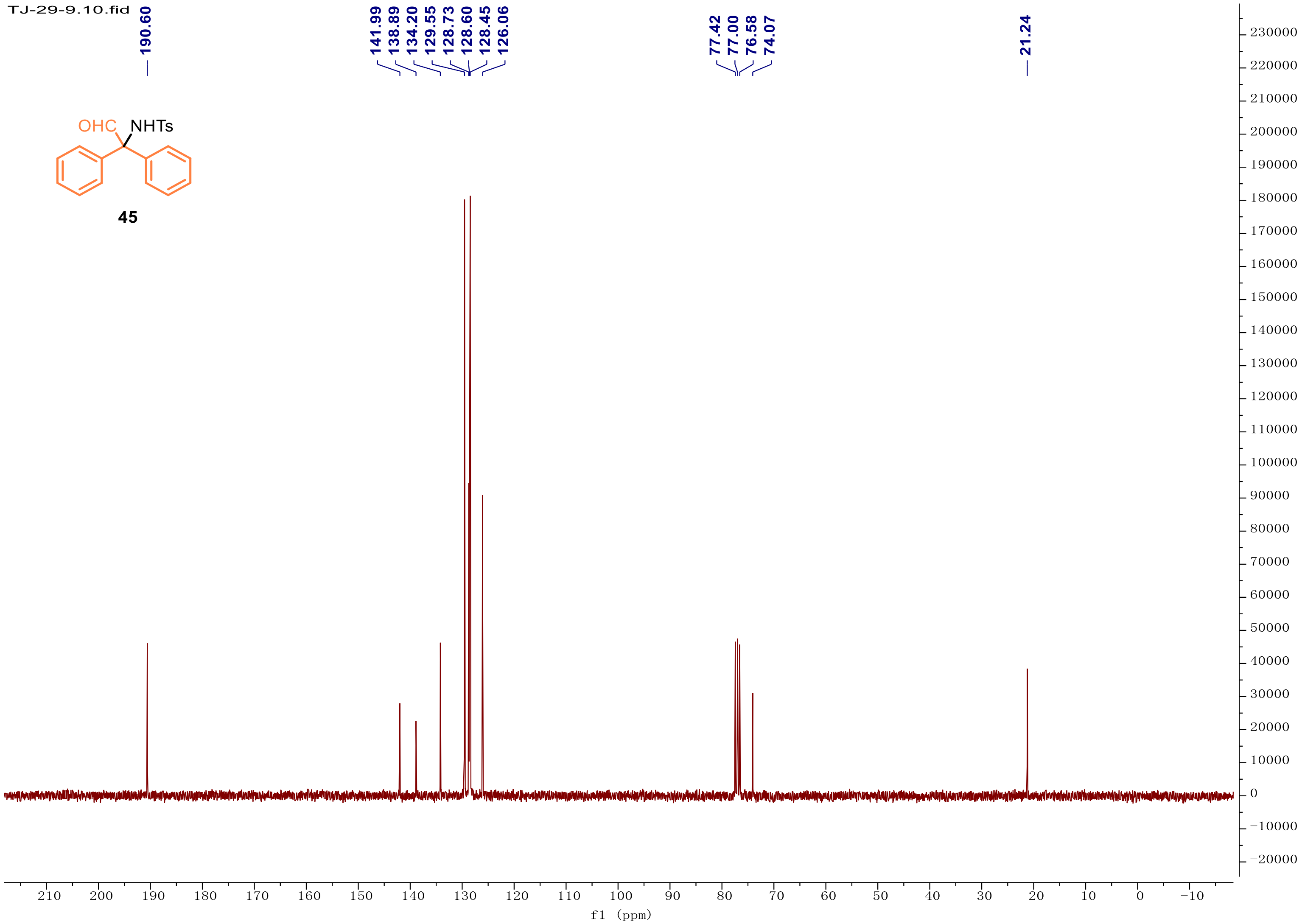


^{1}H NMR spectrum of compound 45 (300 MHz, CDCl$_3$)

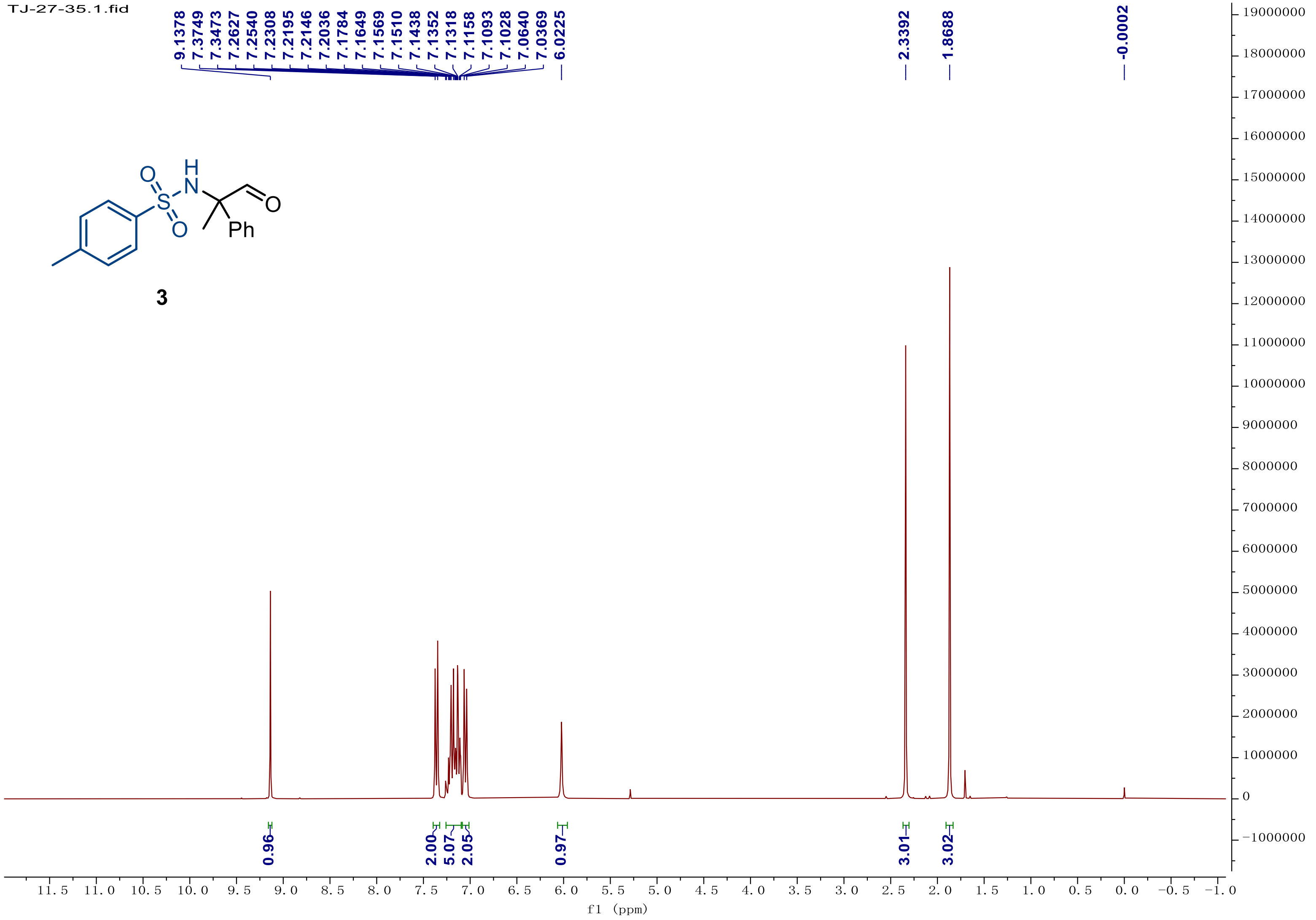


45

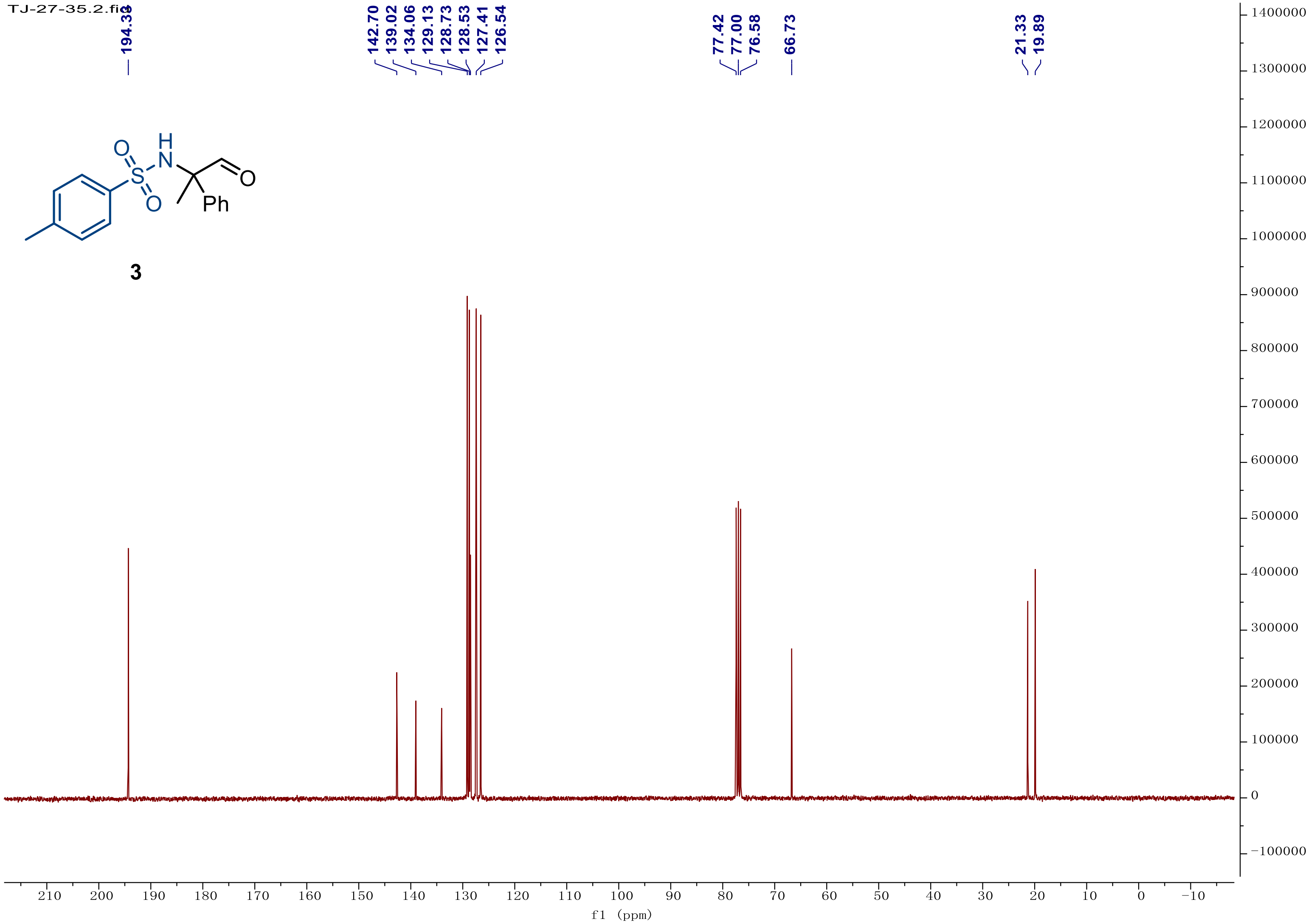
^{13}C **NMR** spectrum of compound **45** (75 MHz, $CDCl_3$)



^{1}**H NMR** spectrum of compound **3** from gram scale reaction (300 MHz, $CDCl_3$)

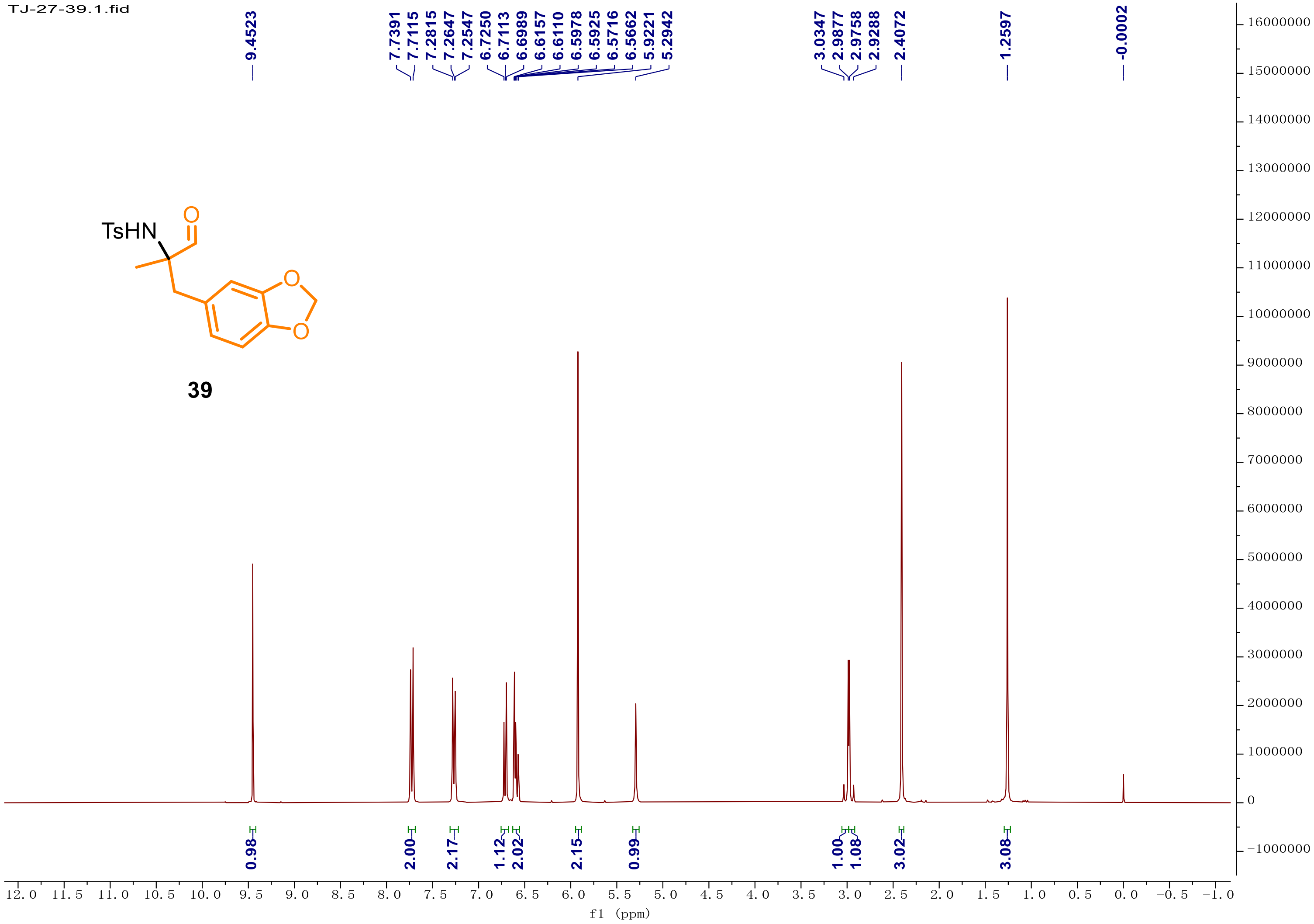


^{13}C NMR spectrum of compound 3 from gram scale reaction (75 MHz, CDCl$_3$)

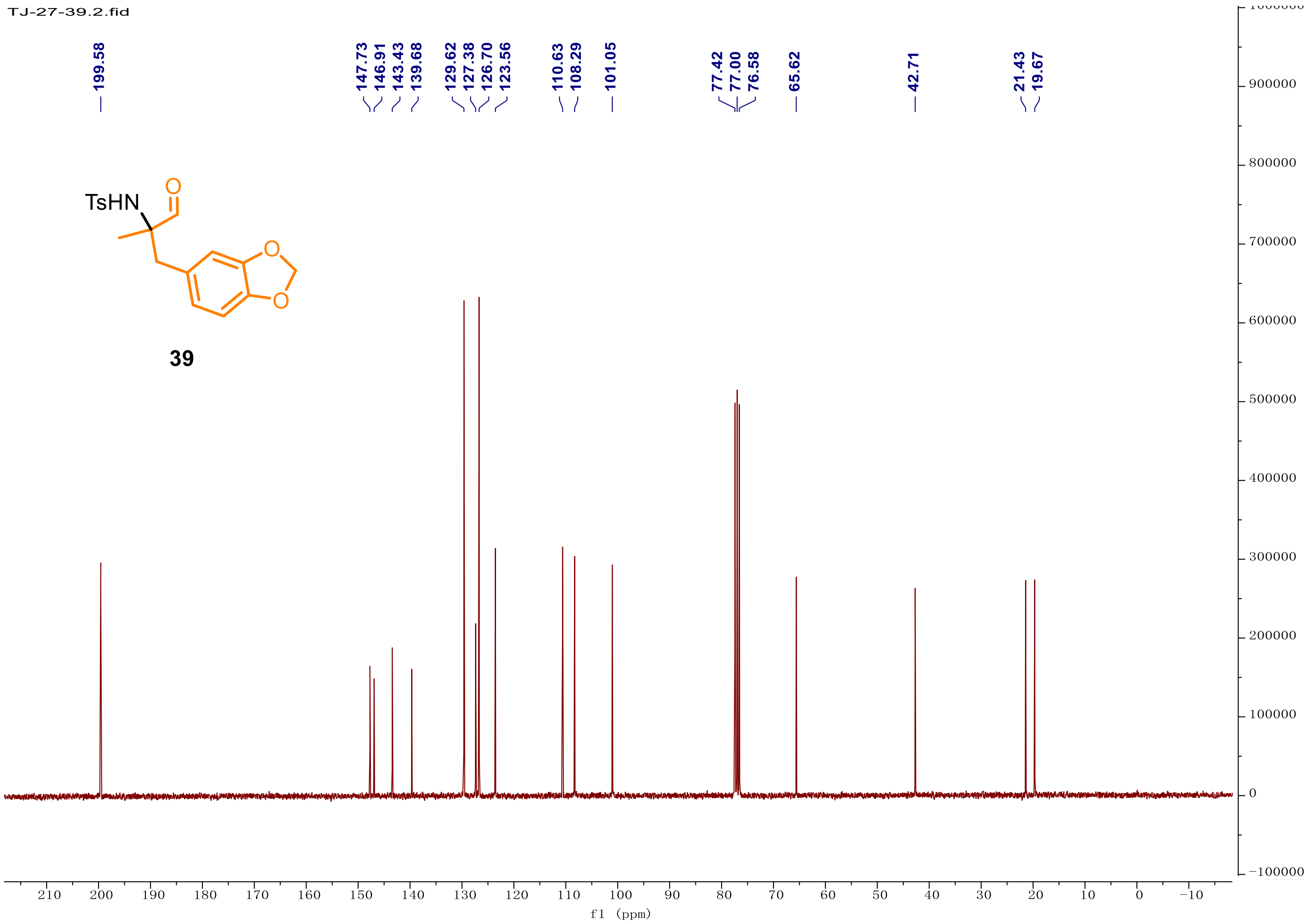


3

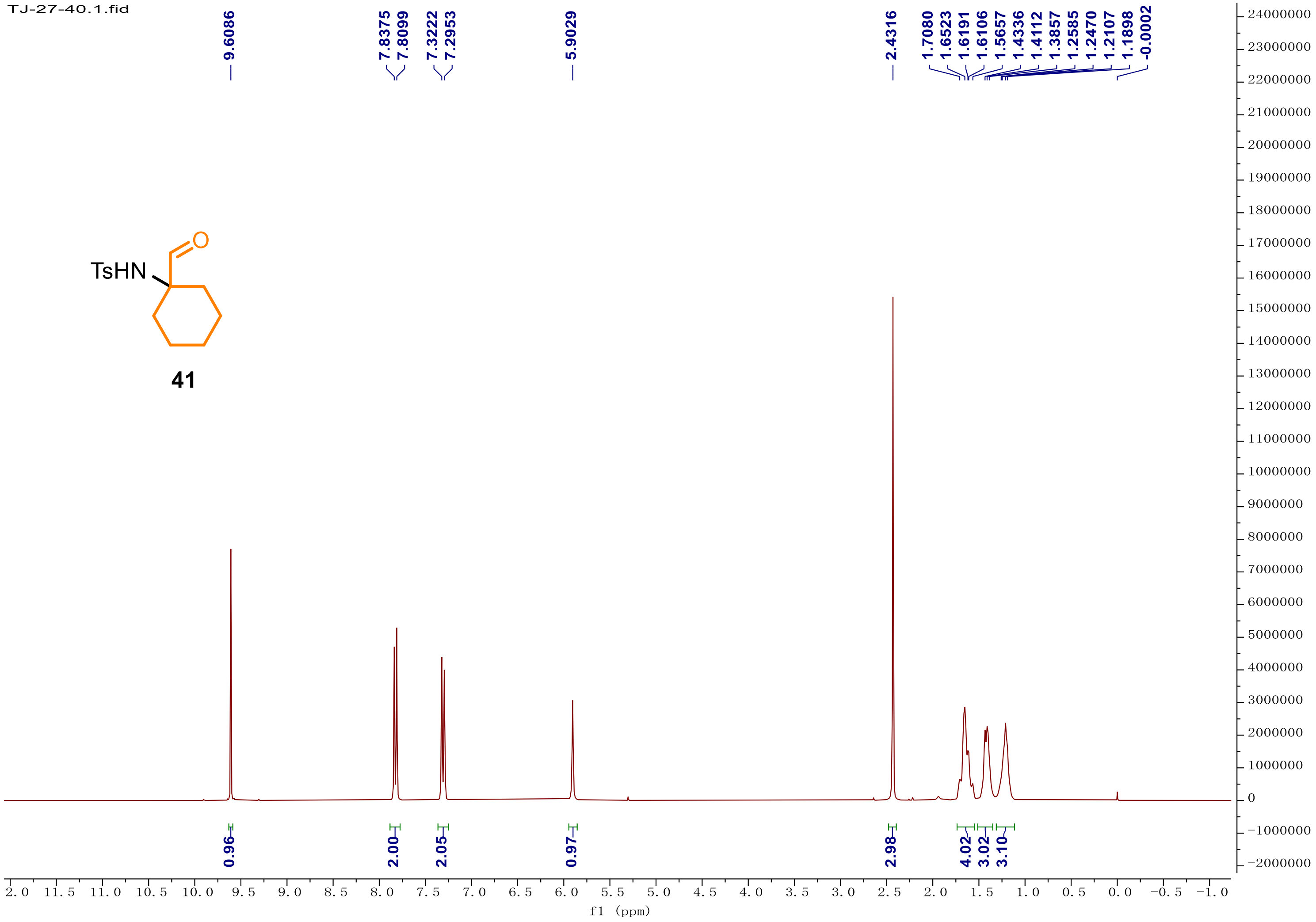
^{1}H NMR spectrum of compound **39** from gram scale reaction (300 MHz, CDCl$_3$)



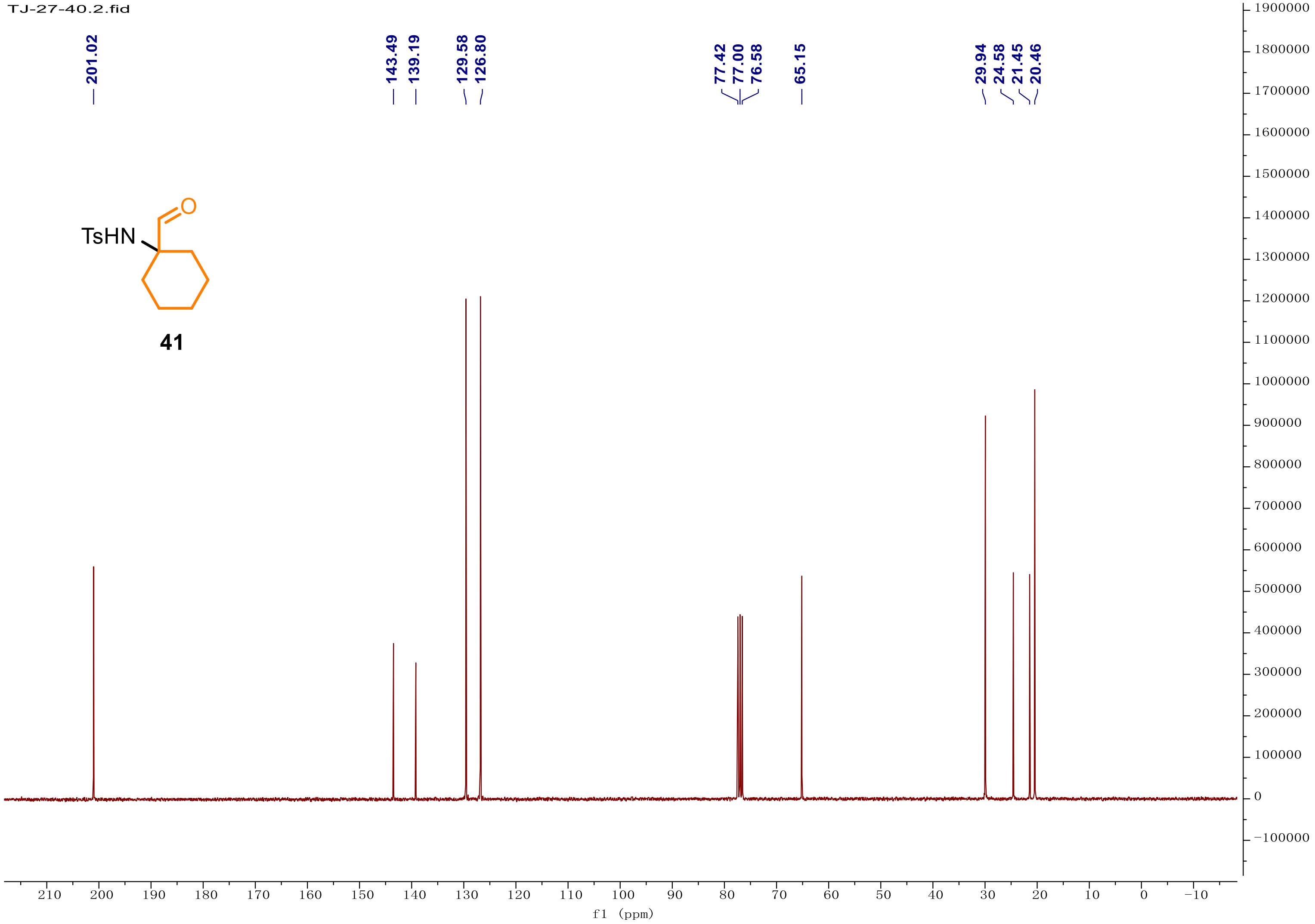
^{13}C **NMR** spectrum of compound **39** from gram scale reaction (75 MHz, $CDCl_3$)



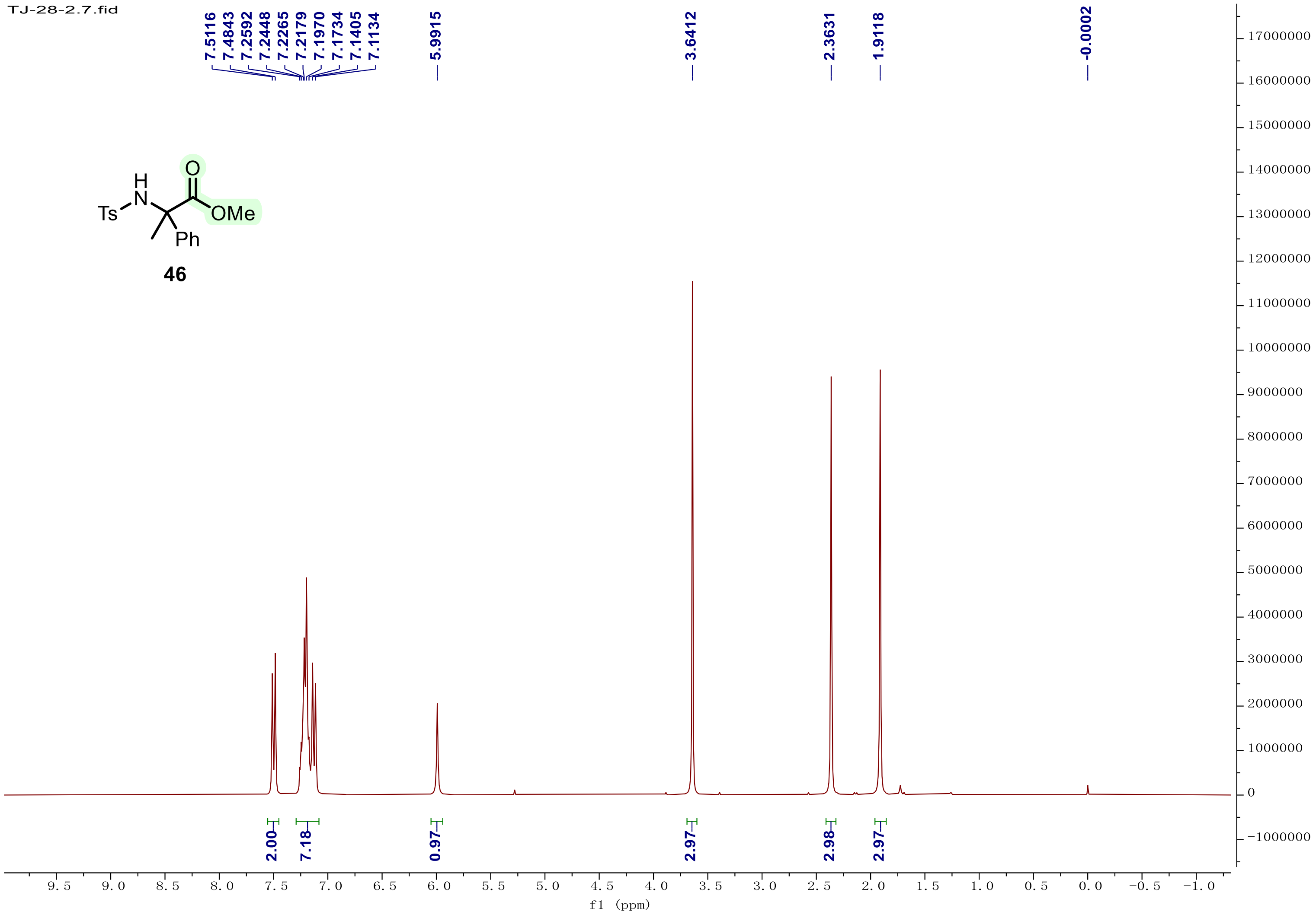
^{1}**H NMR** spectrum of compound **41** from gram scale reaction (300 MHz, CDCl$_3$)



^{13}**C NMR** spectrum of compound **41** from gram scale reaction (75 MHz, $CDCl_3$)

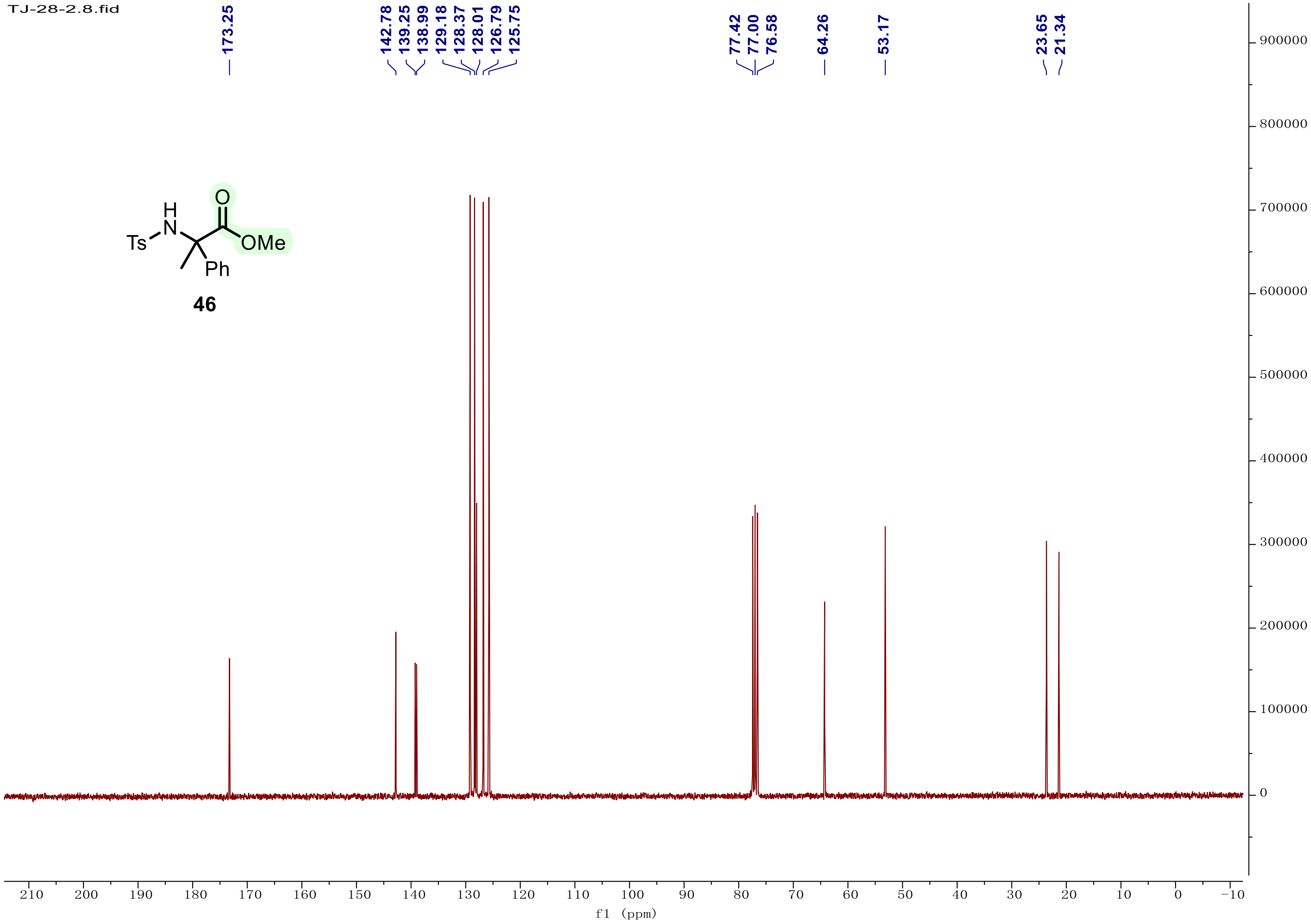


^{1}**H NMR** spectrum of compound **46** (300 MHz, CDCl$_3$)

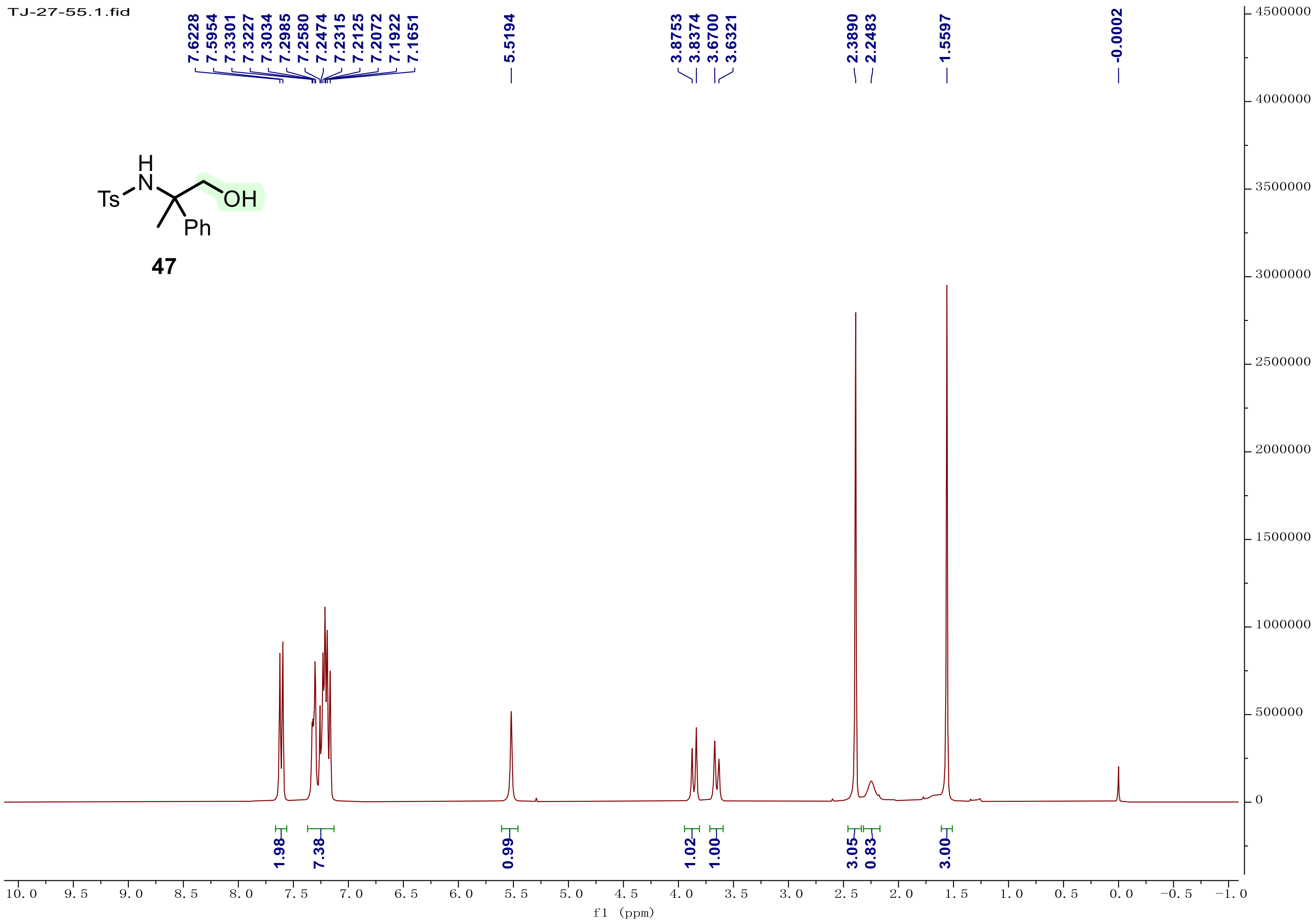


^{13}C NMR spectrum of compound **46** (75 MHz, CDCl$_3$)

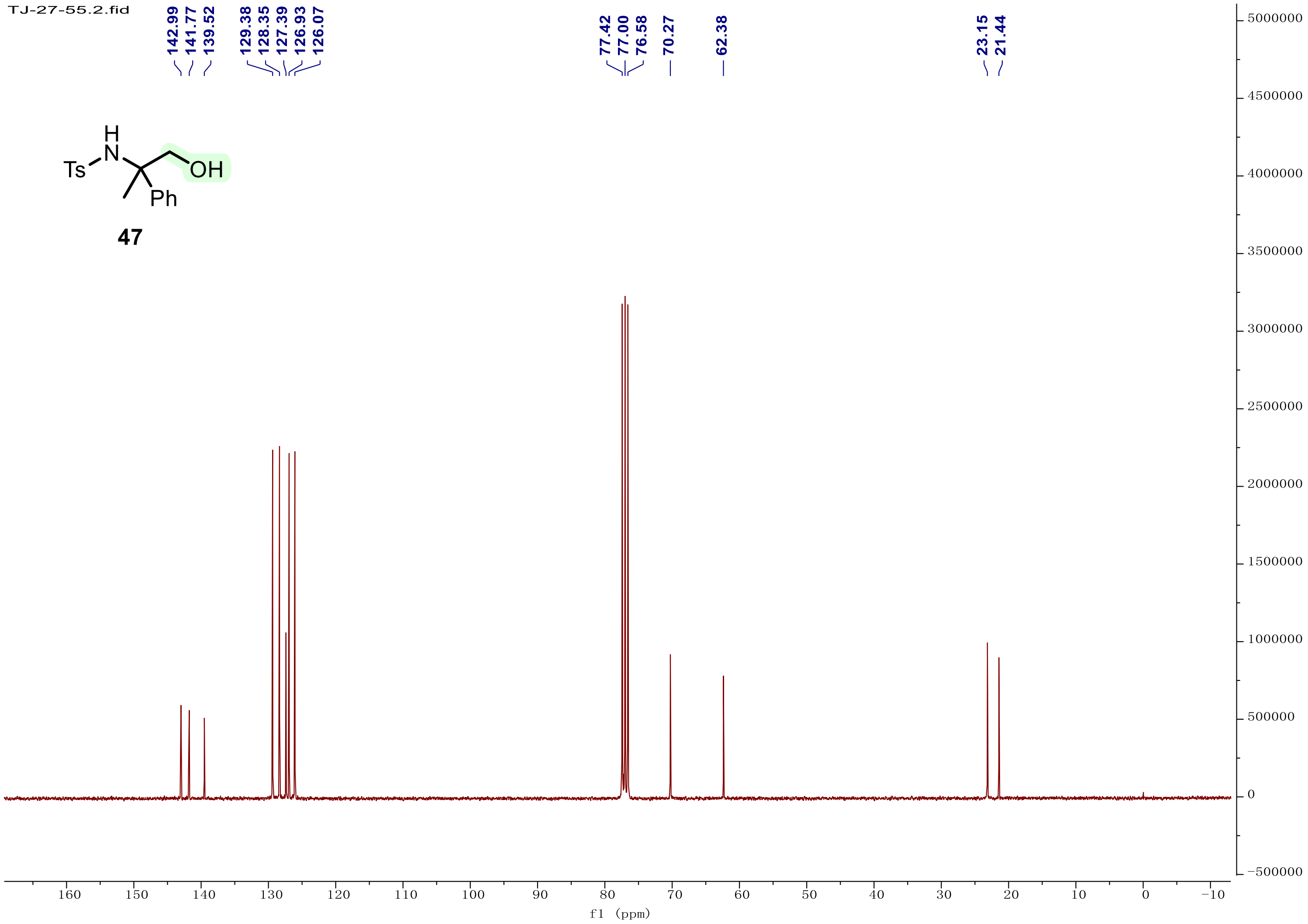
46



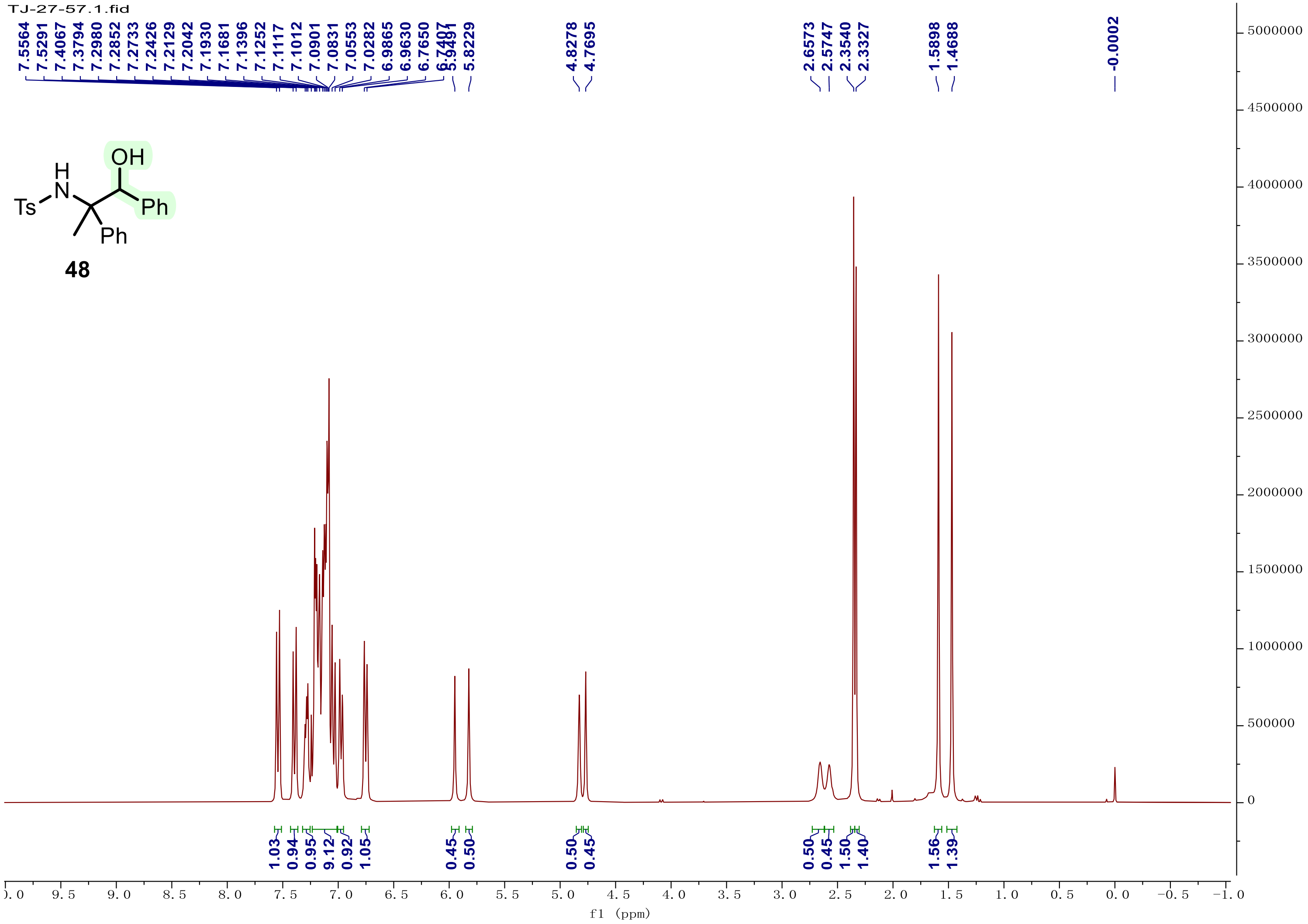
^{1}**H NMR** spectrum of compound **47** (300 MHz, $CDCl_3$)



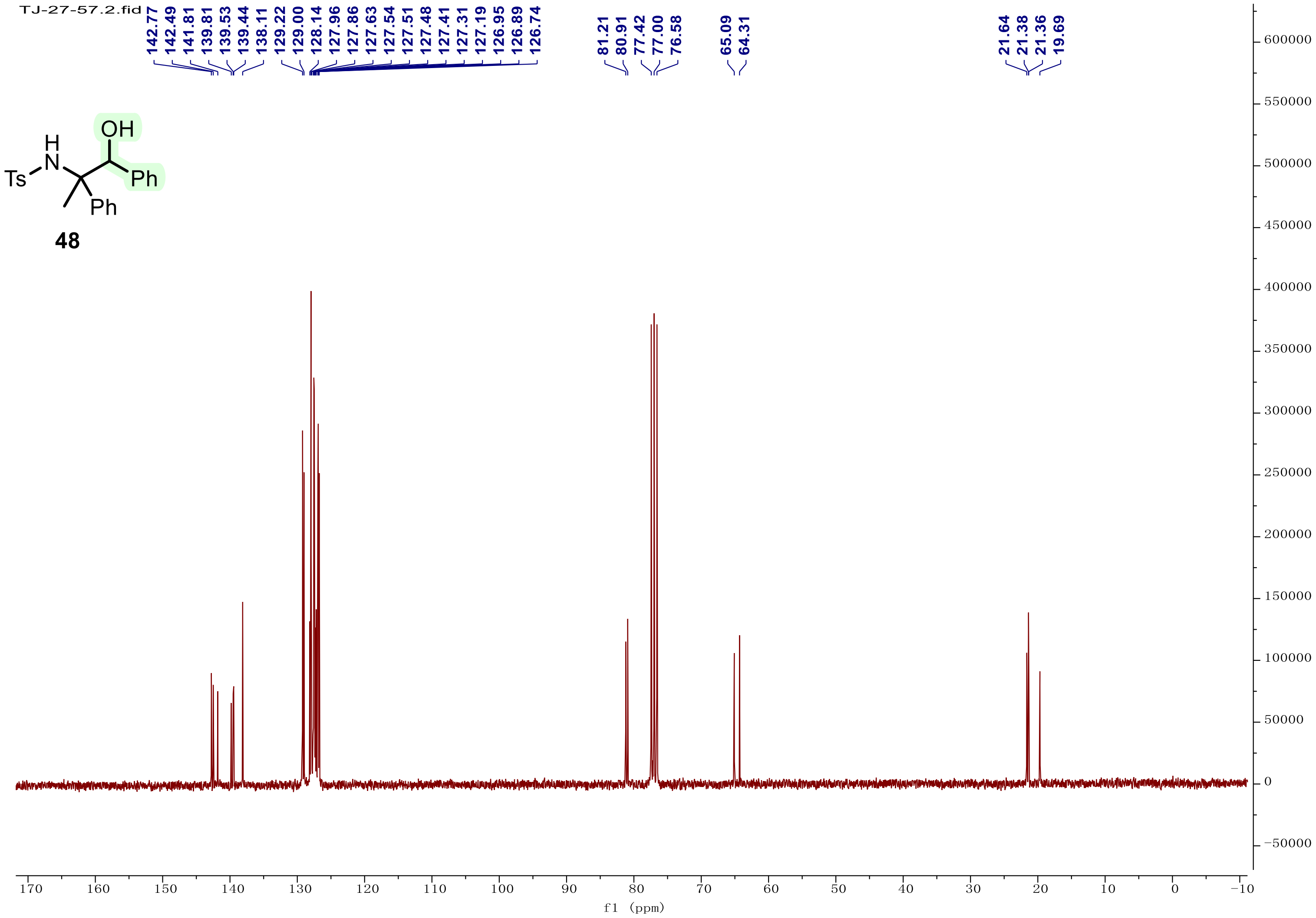
^{13}**C NMR** spectrum of compound **47** (75 MHz, CDCl$_3$)



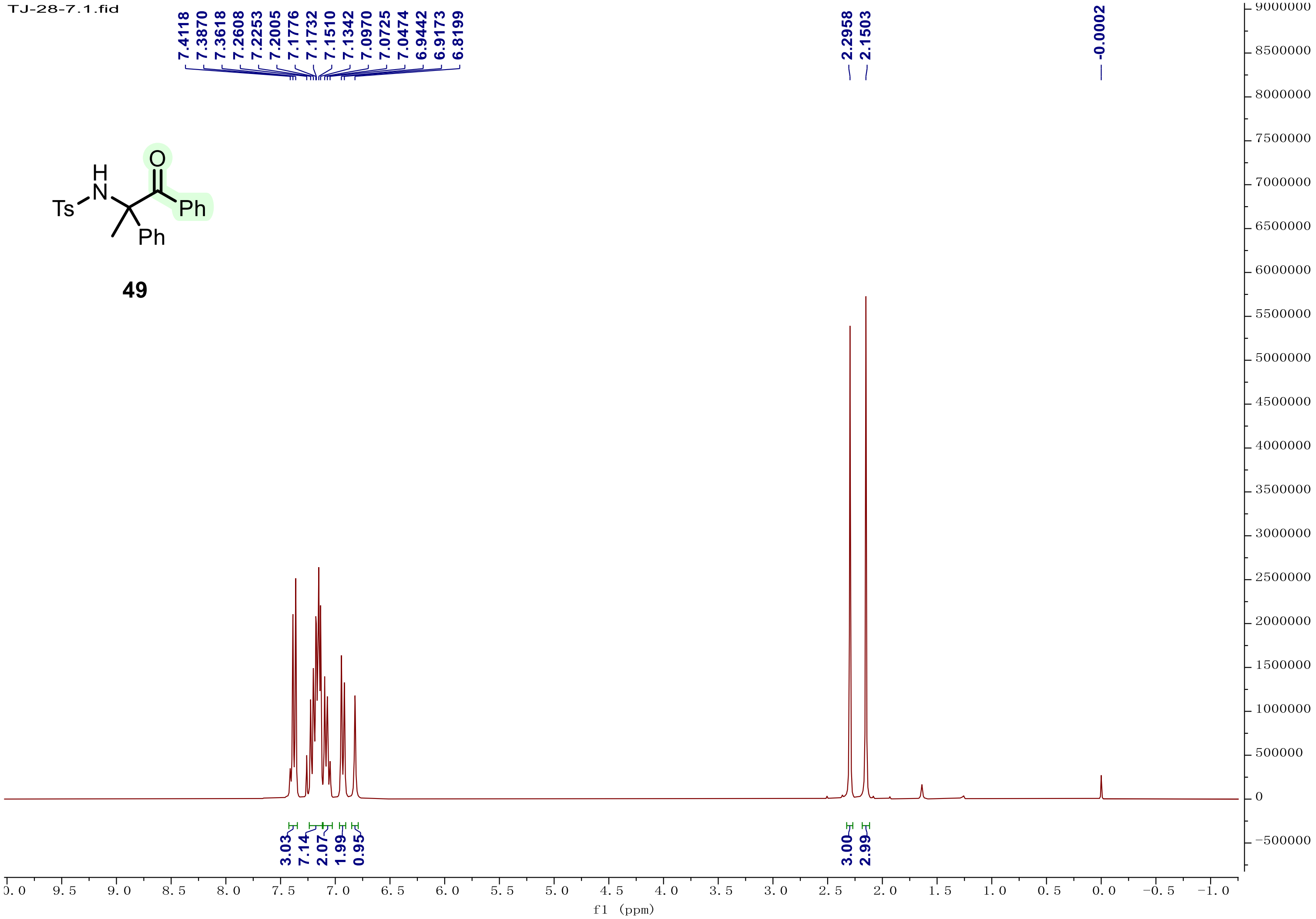
^{1}**H NMR** spectrum of compound **48** (300 MHz, CDCl$_3$)



^{13}C **NMR** spectrum of compound **48** (75 MHz, $CDCl_3$)

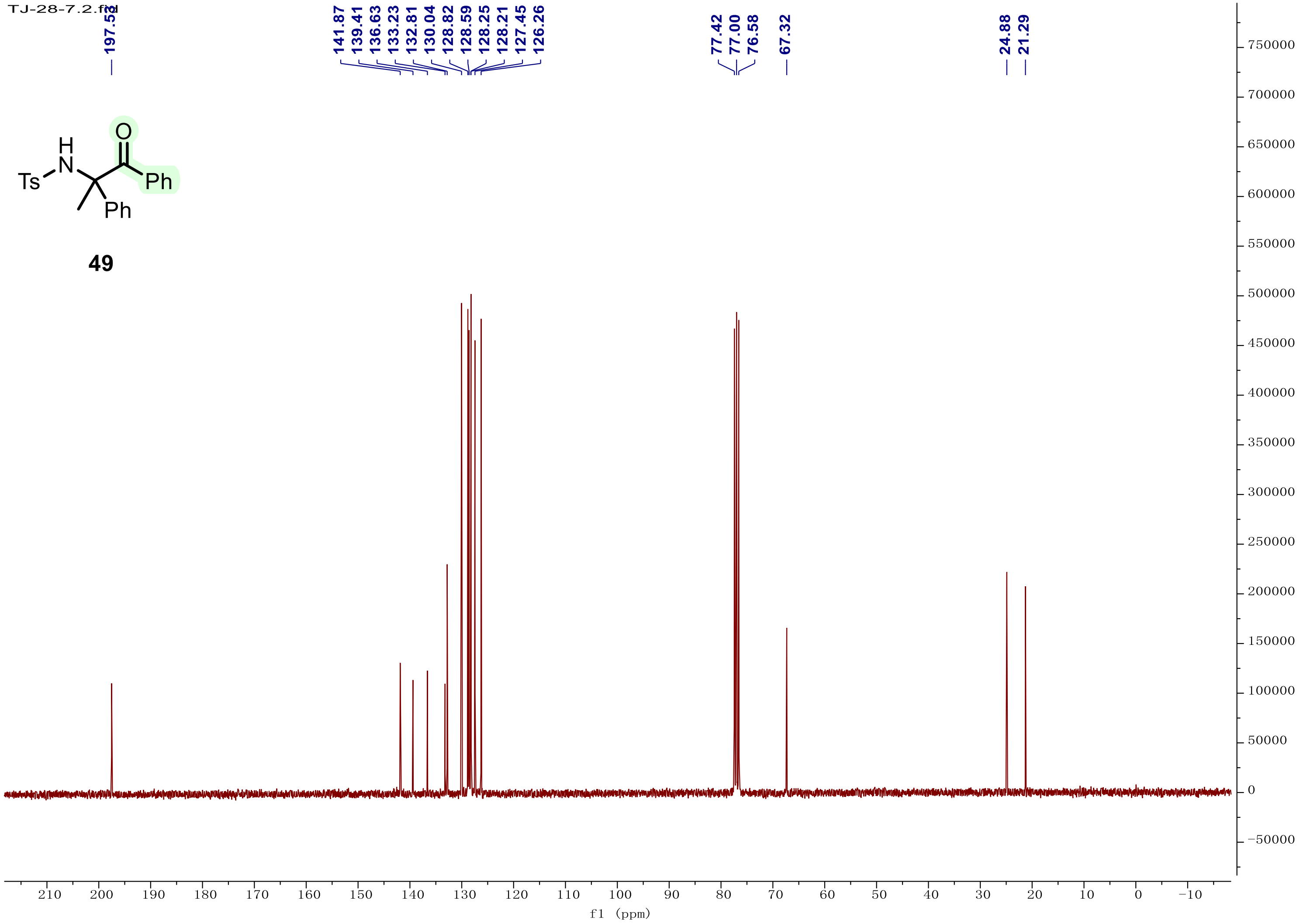


^{1}**H NMR** spectrum of compound **49** (300 MHz, $CDCl_3$)



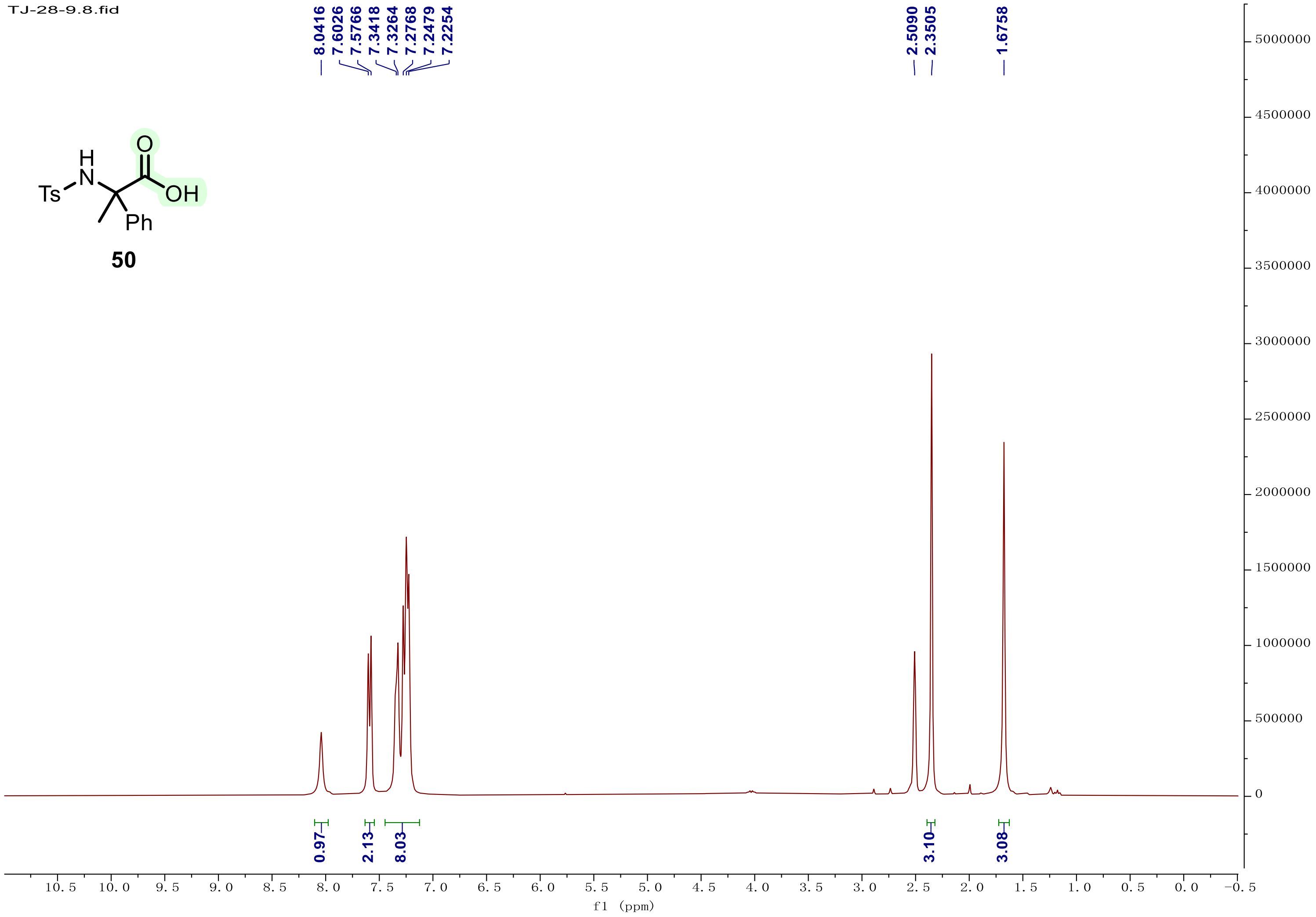
49

^{13}C NMR spectrum of compound 49 (75 MHz, CDCl$_3$)

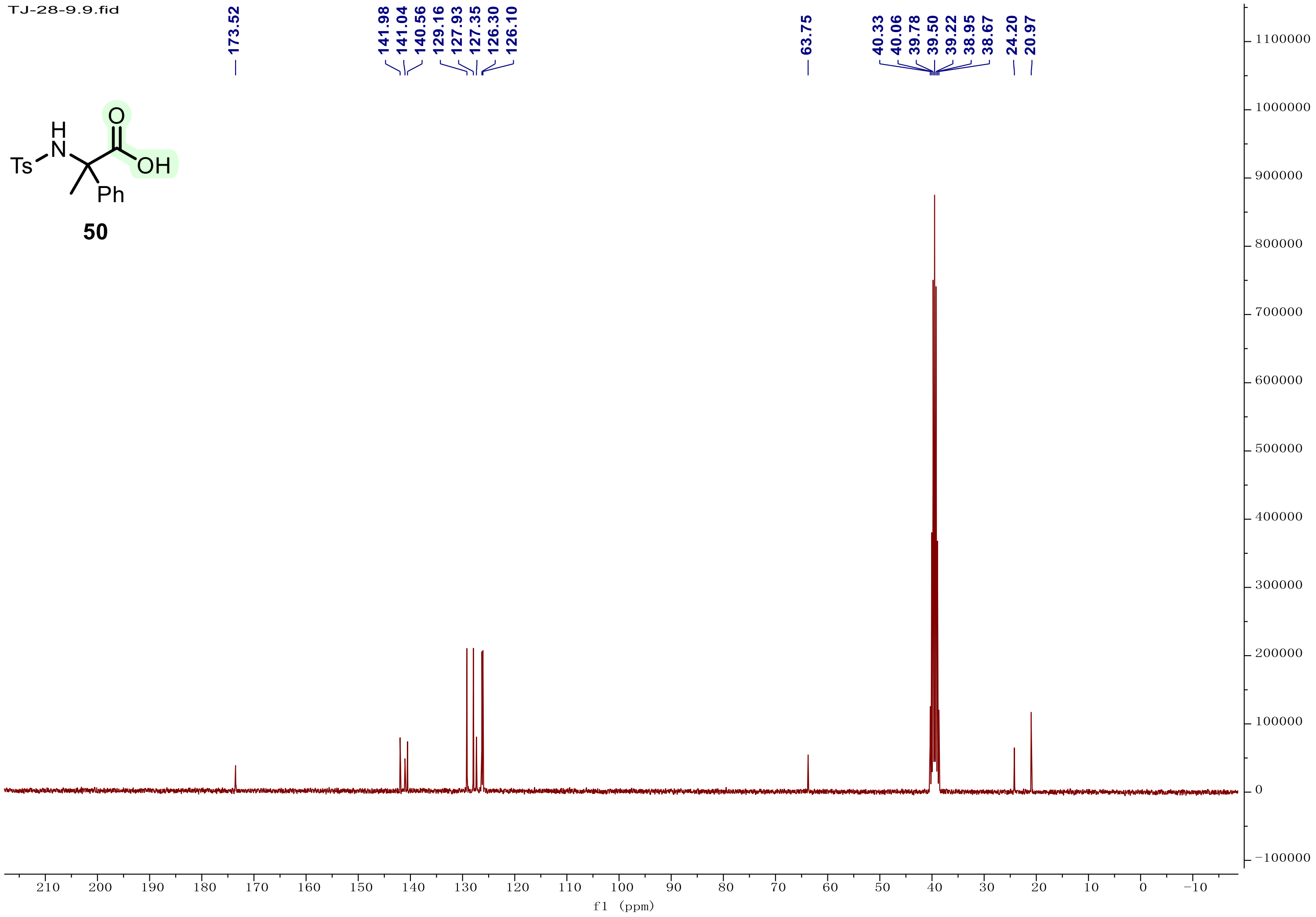


49

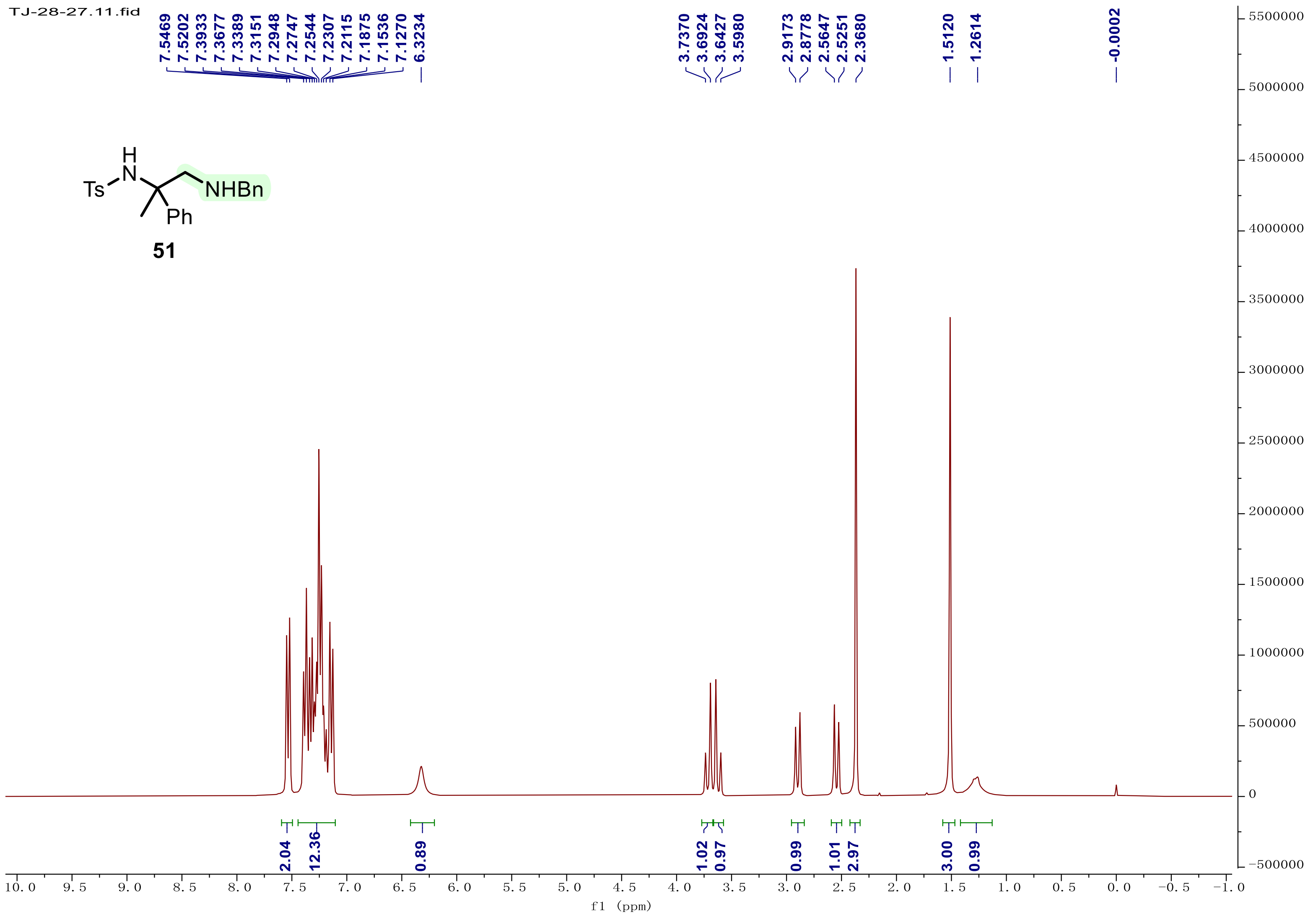
^{1}H NMR spectrum of compound **50** (300 MHz, DMSO-d_6)



^{13}C **NMR** spectrum of compound **50** (75 MHz, DMSO-d_6)



^{1}**H NMR** spectrum of compound **51** (300 MHz, $CDCl_3$)



^{13}C **NMR** spectrum of compound **51** (75 MHz, $CDCl_3$)