Supporting Information for:

A Novel Homobimetallic Nickel Complex for Asymmetric Direct Mannich Reaction of Imines: A Practical Method on a Multi-Gram Scale

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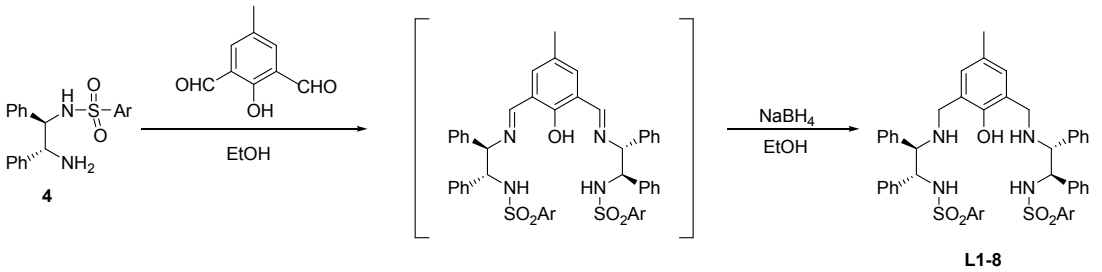
Contents:

1. General information

All reagents were obtained from Acros, Adamas, or TCI etc. without further purification unless otherwise noted. High resolution mass spectra were recorded with a Bruker SolariX FT-ICR-MS system. NMR spectra were recorded on commercial instruments and operating at 500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 or $(CD_3)_2SO$ δ = 2.50) in ^{1}H NMR spectra and Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0 or $(CD_3)_2SO$ δ = 39.5) in ^{13}C NMR spectra. Spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment. The enantiomeric excess (*ee*) was determined by HPLC analysis. Analytical HPLC was performed on a Shimadzu liquid chromatography, using a chiral DAICEL CHIRALCEL OD-H or OJ-H or CHIRALPAK IA or AD-H column at 220 nm. Optical rotations were measured on a commercial polarimeter and are reported as follows: $[\alpha]_D^T$ (*c* = g/100 mL, solvent).

2. General preparation procedure and characterization of the ligands



To a solution of **4** (3.6 mmol) in 50 mL ethanol was slowly added the dialdehyde (1.8 mmol), and the mixture was stirred at room temperature until the reaction proceed completely detected by TLC. Sodium borohydride (14.4 mmol) was then added in small portions at 0 °C. And then the reaction was allowed to warm to ambient temperature and detected by TLC. It was poured over 120 mL of water and extracted with CH_2Cl_2. The combined organic phase was washed with Sat. NaCl and dried with anhydrous Na_2SO_4, and the solvents were removed in vacuo and purified through column chromatography (petroleum ether /AcOEt = 4 : 1) on silica gel to obtain **L1-8**.

L9 and **L10** were synthesized by the analogy of **L1-8**.

L1: White solid; $[\alpha]_D^{25}$ = -51.8 (*c* 0.74, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1, 4H), 7.18-7.13 (m, 6H), 7.06 (d, *J* = 6.4, 4H), 6.95-6.86 (m, 10H), 6.77 (d, *J* = 7.0, 4H), 6.66 (s, 2H), 4.40 (d, *J* = 9.3, 2H), 3.92 (d, *J* = 9.4, 2H), 3.74 (d, *J* = 12.9, 2H), 3.60 (d, *J* = 12.9, 2H), 2.24

(s, 6H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 141.2, 137.7, 136.5, 136.1, 127.72, 127.65, 126.9, 126.6, 126.4, 126.2, 126.14, 126.11, 125.7, 125.6, 122.6, 66.5, 62.5, 48.0, 20.0, 19.0; ESI-HRMS calcd for $C_{51}H_{53}N_4O_5S_2^+$ $[M + H]^+$: 865.3452, found 865.3454.

L2: White solid; $[\alpha]_D^{25}$ = -48.9 (*c* 0.92, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9, 4H), 7.16-7.05 (m, 15H), 6.86-6.79 (m, 6H), 6.69 (s, 6H), 4.34 (d, *J* = 9.4, 2H), 4.01 (d, *J* = 9.5, 2H), 3.74 (d, *J* = 12.8, 2H), 3.61 (d, *J* = 12.8, 2H), 2.18 (s, 3H), 1.20 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 153.8, 138.1, 136.5, 136.2, 128.1, 127.2, 127.0, 126.7, 126.5, 126.4, 126.4, 125.9, 125.9, 124.3, 122.9, 66.7, 63.0, 48.4, 33.8, 30.0, 19.3; ESI-HRMS calcd for $C_{57}H_{65}N_4O_5S_2^+$ $[M + H]^+$: 949.4391, found 949.4347.

L3: White solid; $[\alpha]_D^{25}$ = -62.0 (*c* 0.64, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4, 4H), 7.17-7.15 (m, 6H), 7.05 (d, *J* = 6.4, 4H), 6.93-6.89 (m, 6H), 6.76 (d, *J* = 6.7, 4H), 6.66 (s, 2H), 6.57 (d, *J* = 8.4, 4H), 4.36 (d, *J* = 9.2, 2H), 3.69 (d, *J* = 9.3, 2H), 3.73 (d, *J* = 13.0, 2H), 3.70 (s, 6H), 3.59 (d, *J* = 12.9, 2H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 153.6, 138.0, 136.8, 131.1, 128.1, 128.0, 127.2, 126.9, 126.8, 126.5, 126.5, 126.4, 126.0, 123.0, 112.6, 66.8, 62.9, 54.4, 48.3, 19.3; ESI-HRMS calcd for $C_{51}H_{53}N_4O_7S_2^+$ $[M + H]^+$: 897.3350, found 897.3318.

L4: Yellow solid; $[\alpha]_D^{25}$ = -33.8 (*c* 0.40, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2, 4H), 7.69 (d, *J* = 8.2, 4H), 7.24-7.14 (m, 6H), 7.06 (d, *J* = 5.9, 4H), 6.99-6.91 (m, 6H), 6.84 (d, *J* = 7.1, 4H), 6.64 (s, 2H), 4.50 (d, *J* = 8.7, 2H), 3.94 (d, *J* = 8.7, 2H), 3.76 (d, *J* = 12.8, 2H), 3.63 (d, *J* = 12.8, 2H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 148.3, 145.2, 137.4, 136.2, 128.2, 127.5, 127.2, 127.1, 127.0, 126.8, 126.6, 126.5, 122.9, 122.5, 66.9, 62.9, 48.8, 19.3; ESI-HRMS calcd for $C_{49}H_{47}N_6O_9S_2^+$ $[M + H]^+$: 927.2840, found 927.2834.

L5: Yellow solid; $[\alpha]_D^{25}$ = -21.6 (*c* 0.44, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 2H), 8.09 (d, *J* = 8.1, 2H), 7.91 (d, *J* = 7.7, 2H), 7.33 (t, *J* = 7.8, 2H), 7.16-7.2 (m, 6H), 7.08 (d, *J* = 6.6, 4H), 6.90-6.84 (m, 10H), 6.65 (s, 2H), 4.53 (d, *J* = 9.0, 2H), 3.96 (d, *J* = 9.0, 2H), 3.76 (d, *J* = 12.8, 2H), 3.65 (d, *J* = 12.9, 2H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 146.5, 141.5, 137.5, 135.9, 131.5, 128.7, 128.2, 127.5, 127.1, 126.9, 126.8, 126.7, 126.5, 125.3, 122.9, 121.4, 66.9, 63.0, 48.8, 19.3; ESI-HRMS calcd for $C_{49}H_{47}N_6O_9S_2^+$ $[M + H]^+$: 927.2840, found 927.2849.

L6: White solid; $[\alpha]_D^{25}$ = -38.7 (*c* 0.78, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6, 4H), 7.26-7.23 (m, 2H), 7.15-7.03 (m, 14H), 6.89-6.83 (m, 6H), 6.74 (d, *J* = 6.9, 4H), 6.65 (s, 2H), 4.39 (d, *J* = 9.2, 2H), 3.97 (d, *J* = 9.3, 2H), 3.73 (d, *J* = 12.9, 2H), 3.59 (d, *J* = 12.8, 2H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 139.3, 138.0, 136.6, 130.9, 128.1, 127.4, 127.3, 126.9, 126.8, 126.6, 126.5, 126.4, 126.1, 126.0, 122.9, 66.8, 62.9, 48.4, 19.3; ESI-HRMS calcd for

$C_{49}H_{49}N_4O_5S_2^+$ [M + H]$^+$: 837.3139, found 837.3100.

L7: White solid; $[\alpha]_D^{25}$ = +53.3 (*c* 0.40, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.5, 2H), 7.94 (d, *J* = 7.1, 2H), 7.76 (d, *J* = 8.0, 2H), 7.69 (d, *J* = 8.0, 2H), 7.36 (t, *J* = 7.0, 2H), 7.22-7.16 (m, 4H), 7.08 (s, 6H), 6.94-6.93 (m, 4H), 6.91-6.72 (m, 2H), 6.67-6.65 (m, 10H), 4.36 (d, *J* = 8.9, 2H), 3.88 (d, *J* = 8.9, 2H), 3.75 (d, *J* = 12.9, 2H), 3.60 (d, *J* = 13.0, 2H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 137.8, 136.3, 134.1, 132.8, 132.6, 128.4, 127.9, 127.4, 127.2, 127.0, 126.8, 126.7, 126.5, 126.4, 126.4, 126.1, 125.9, 125.4, 123.7, 123.1, 122.7, 66.8, 62.9, 48.5, 19.4; ESI-HRMS calcd for $C_{57}H_{53}N_4O_5S_2^+$ [M + H]$^+$: 937.3452, found 937.3408.

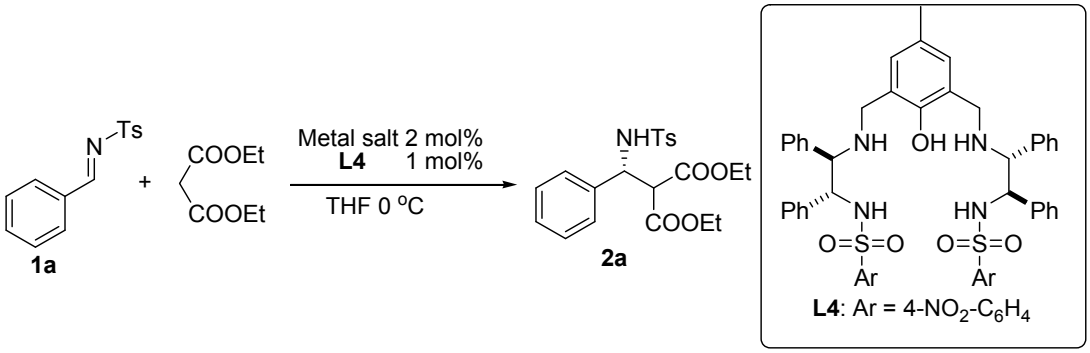
L8: White solid; $[\alpha]_D^{25}$ = -90.0 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7..68 (d, *J* = 8.0, 2H), 7.57 (d, *J* = 8.1, 4H), 7.52-7.47 (m, 4H), 7.44-7.41 (m, 2H), 7.15-7.04 (m, 10H), 6.78-6.69 (m, 12H), 4.48 (d, *J* = 9.2, 2H), 4.02 (d, *J* = 9.3, 2H), 3.76 (d, *J* = 12.9, 2H), 3.65 (d, *J* = 12.9, 2H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7, 138.0, 136.6, 136.3, 133.3, 130.7, 128.0, 127.7, 127.4, 127.2, 126.8, 126.7, 126.6, 126.5, 126.4, 126.4, 126.0, 125.9, 123.1, 121.3, 66.9, 63.0, 48.5, 19.3; ESI-HRMS calcd for $C_{57}H_{53}N_4O_5S_2^+$ [M + H]$^+$: 937.3452, found 937.3464.

L9: Pale yellow solid; $[\alpha]_D^{25}$ = +164.6 (*c* 0.47, CH_3OH); ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 8.01 (d, *J* = 8.0, 2H), 7.66 (d, *J* = 7.8, 2H), 7.10-7.02 (m, 6H), 6.94-6.82 (m, 6H), 6.73 (d, *J* = 7.6, 1H), 6.67-6.65 (m, 1H), 4.44 (d, *J* = 7.6, 1H), 3.85 (d, *J* = 7.9, 1H), 3.39 (s, 2H); ^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 156.0, 148.7, 146.7, 139.5, 138.6, 128.6, 128.1, 127.8, 127.8, 127.4, 127.0, 126.6, 125.2, 123.7, 118.5, 115.0, 66.7, 63.4, 47.2; ESI-HRMS calcd for $C_{27}H_{26}N_3O_5S^+$ [M + H]$^+$: 504.1588, found 504.1587.

L10: Yellow solid; $[\alpha]_D^{25}$ = +32.6 (*c* 0.86, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2, 2H), 7.63 (d, *J* = 8.2, 2H), 7.23 (s, 1H), 7.18 (s, 3H), 7.02-6.90 (m, 5H), 6.70 (d, *J* = 7.2, 2H), 6.65 (s, 1H), 4.71 (d, *J* = 7.9, 1H), 3.89 (d, *J* = 7.9, 1H), 3.83 (d, *J* = 13.3, 1H), 3.56 (d, *J* = 13.3, 1H), 1.47 (s, 9H), 1.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 148.4, 144.9, 140.0, 135.7, 135.3, 134.9, 127.6, 127.2, 127.2, 127.1, 127.0, 126.9, 126.5, 122.7, 122.3, 120.4, 65.2, 61.8, 49.8, 33.9, 33.1, 30.6, 28.6; ESI-HRMS calcd for $C_{35}H_{42}N_3O_5S^+$ [M + H]$^+$: 616.2840, found 616.2830.

3. Other optimizations of the Mannich reaction

Table S1: Metal effects.[a]



Entry	Metal salt	Yield[b] (%)	*ee*[c] (%)
1	$Ni(OAc)_2$	94	96
2	$Fe(OAc)_2$	14	1
3	$Cu(OAc)_2$	21	5
4	$Co(OAc)_2$	38	3
5	CuOAc	30	3
6	$Mn(OAc)_2$	54	1
7	$Mn(OAc)_3$	37	3
8	$Zn(OAc)_2$	26	13

[a] Unless otherwise noted, all reactions were performed with metal salt (2 mol%) and ligand (1 mol%), **1a** (1.0 mmol), and diethyl malonate (1.0 mmol) in THF (5.0 mL) under air atmosphere at 0 °C for 16-17h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S2: Solvent effects.[a]

Entry	Solvent	Yield[b] (%)	*ee*[c] (%)
1	THF	94	96
2	CH_2Cl_2	10	5
3	AcOEt	56	58
4	CH_3OH	50	14
5	Toluene	6	22

[a] Unless otherwise noted, all reactions were performed with $Ni(OAc)_2 \cdot 4H_2O$ (2 mol%) and **L4** (1 mol%), **1a** (1.0 mmol), and diethyl malonate (1.0 mmol) in the specified solvent (5.0 mL) under air atmosphere at 0 °C for 16-17h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S3: The effects of concentration of imine.[a]

Entry	The concentration of imine (M)	Yield[b] (%)	*ee*[c] (%)
1	0.20	94	96
2	0.25	92	97
3	0.33	88	91
4	0.50	84	90
5	1.0	89	83

[a] Unless otherwise noted, all reactions were performed with $Ni(OAc)_2 \cdot 4H_2O$ (2 mol%) and **L4** (1 mol%), **1a** (1.0 mmol), and diethyl malonate (1.0 mmol) in THF (5.0-1.0 mL) under air atmosphere at 0 °C for 16-17h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S4: The effects of the molar ratio of the imine / diethyl malonate.[a]

Entry	The molar ratio of the imine / diethyl malonate.	Yield[b] (%)	*ee*[c] (%)
1	1:1	92	97
2	1:1.2	94	97
3	1:1.4	95	96

[a] Unless otherwise noted, all reactions were performed with $Ni(OAc)_2 \cdot 4H_2O$ (2 mol%) and **L4** (1 mol%), **1a** (1.0 mmol), and diethyl malonate (1.0-1.4 mmol) in THF (4.0 mL) under air atmosphere at 0 °C for 16-17h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S5: The effects of the reaction temperature.[a]

Entry	T (°C).	Time (h)	Yield[b] (%)	ee[c] (%)
1	0	16	92	97
2	-15	40	89	89

[a] Unless otherwise noted, all reactions were performed with $Ni(OAc)_2 \cdot 4H_2O$ (2 mol%) and **L4** (1 mol%), **1a** (1.0 mmol), and diethyl malonate (1.2 mmol) in THF (4.0 mL) under air atmosphere at 0 °C for 16-17h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S6: Additive effects.[a]

Entry	Additive.	Yield[b] (%)	*ee*[c] (%)
1	none	85	96
2	3Å MS (15.0 mg)[d]	90	95

3	4Å MS (15.0 mg)[d]	90	97
4	5Å MS (15.0 mg)[d]	92	95
5	4-*t*Bu-phenol (0.5 mol%)	91	94

[a] The reaction was performed with $Ni(OAc)_2 \cdot 4H_2O$ (1 mol%) and **L4** (0.5 mol%), **1a** (2.0 mmol) and diethyl malonate (2.4 mmol) in THF (8.0 mL) under air atmosphere at 0 °C for 16-17h. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] 1.5 g/mmol, relative to the ligand.

4. General procedure for the catalytic Mannich reaction

4.1 (5 mmol scale): The mixture of $Ni(OAc)_2 \cdot 4H_2O$ (0.01 mmol, 0.2 mol%), 4Å MS (7.5 mg) and **L4** (0.005 mmol, 0.1 mol%) was stirred in THF (15.0 mL) at 35 °C for 1.5 h. The mixture was cooled to 0 °C, then the imine **1** (5.0 mmol) and THF (3.0 mL) were added. After stirring for 30 min at 0 °C, diethyl malonate (6.0 mmol) and THF (2.0 mL) were added. The mixture continued to stir at 0 °C for the time indicated in Table 2. The resulting solution concentrated under reduced pressure and purified by column chromatography (petroleum ether / AcOEt, 5:1 to 8:1) on silica gel to afford the products.

4.2 (20 mmol scale): The mixture of $Ni(OAc)_2 \cdot 4H_2O$ (0.04 mmol, 0.2 mol%), 4Å MS (30 mg) and **L4** (0.02 mmol, 0.1 mol%) was stirred in THF (60 mL) at 35 °C for 1.5 h. The mixture was cooled to 0 °C, and then the imine **1h** (20.0 mmol) and THF (10.0 mL) were added. After stirring for 30 min at 0 °C, diethyl malonate (24.0 mmol) and THF (10.0 mL) were added. The mixture continued to stir at 0 °C for 24 h. The resulting solution was filtered through a short pad of silica gel (15 g) and washed with CH_2Cl_2, and the solution concentrated under reduced pressure. The crude product was recrystallized from petroleum ether and AcOEt to afford **2h**.

4.3 (50 mmol scale): The mixture of $Ni(OAc)_2 \cdot 4H_2O$ (0.1 mmol, 0.2 mol%), 4Å MS (75 mg) and **L4** (0.05 mmol, 0.1 mol%) was stirred in THF (160 mL) at 35 °C for 1.5 h. The mixture was cooled to 0 °C, and then the imine **1h** (50.0 mmol) and THF (20.0 mL) were added. After stirring for 30 min at 0 °C, diethyl malonate (60.0 mmol) and THF (20.0 mL) were added. The mixture continued to stir at 0 °C for 96 h. The reaction mixture was diluted by CH_2Cl_2/ petroleum ether (400 mL, 1:1, *v*/*v*) and filtered through a short pad of silica gel (70 g). The resulting solution was concentrated to 15-20 mL under reduced pressure, then petroleum ether (200 mL) was added to the residue with vigorous stirring to afford the crude product (97% *ee*). The crude product was recrystallized from petroleum ether and AcOEt to afford **2h**.

5. General procedure for the synthesis of azirdines[1]

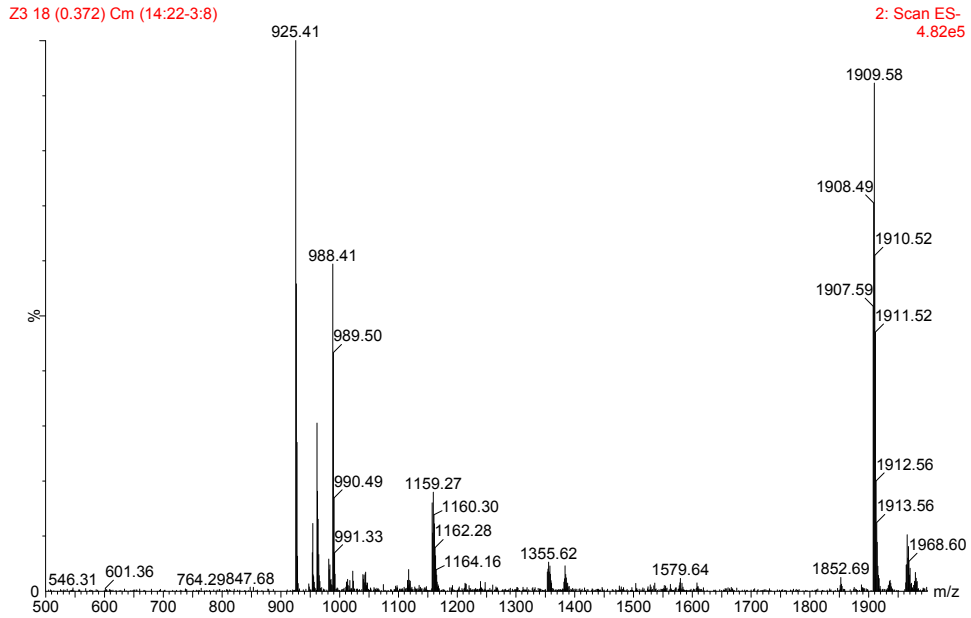
To the solution of **2** (0.2 mmol) in anhydrous CH_3CN (1.0 mL), $PhI(OAc)_2$ (0.4 mmol) and Bu_4NBr (0.4 mmol) were added. The resulted mixture was warmed up and stirred at 30 °C for 30-40 min. The mixture directly purified by column chromatography (petroleum ether / AcOEt, 10:1 to 15:1) on silica gel to provide the corresponding aziridine.

[1] R. Fan, Y. Ye, *Adv. Synth. Catal.* **2008**, *350*, 1526-1530.

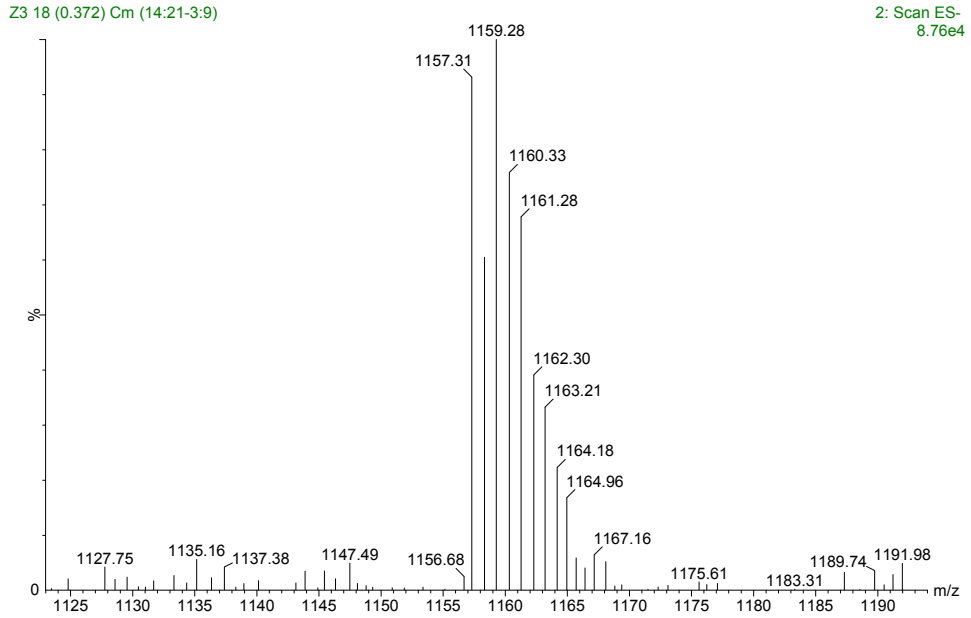
6. Miscellaneous analyses of the complexes

6.1 ESI-MS analysis of the complexes

(a)



(b)

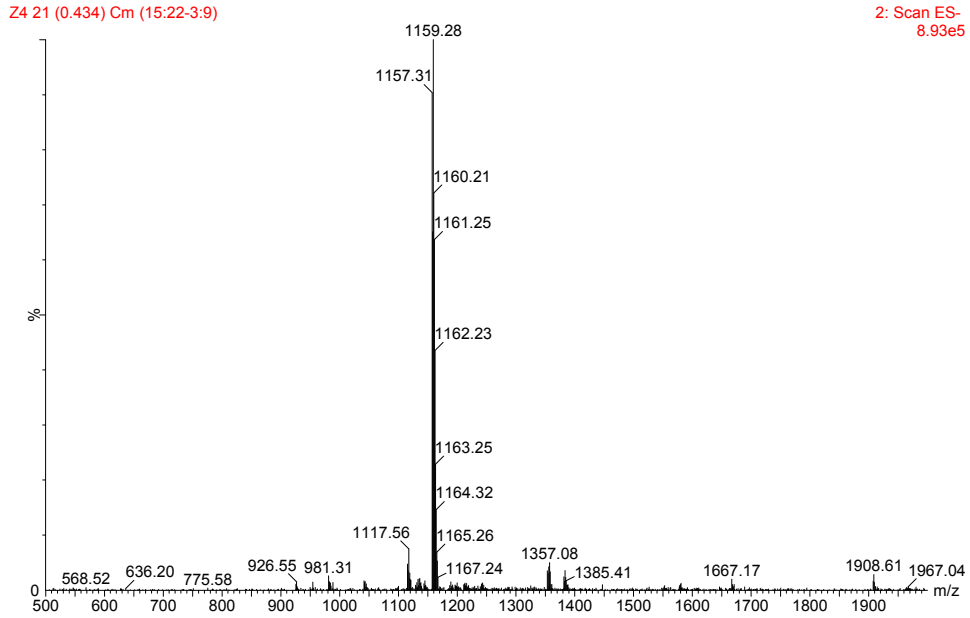


Calcd. $C_{53}H_{49}N_6Ni_2O_{13}S_2$ [$M_{\mathbf{L4}}$ -2H + $Ni_2(OAc)_2$ -H]$^-$: 1157.15

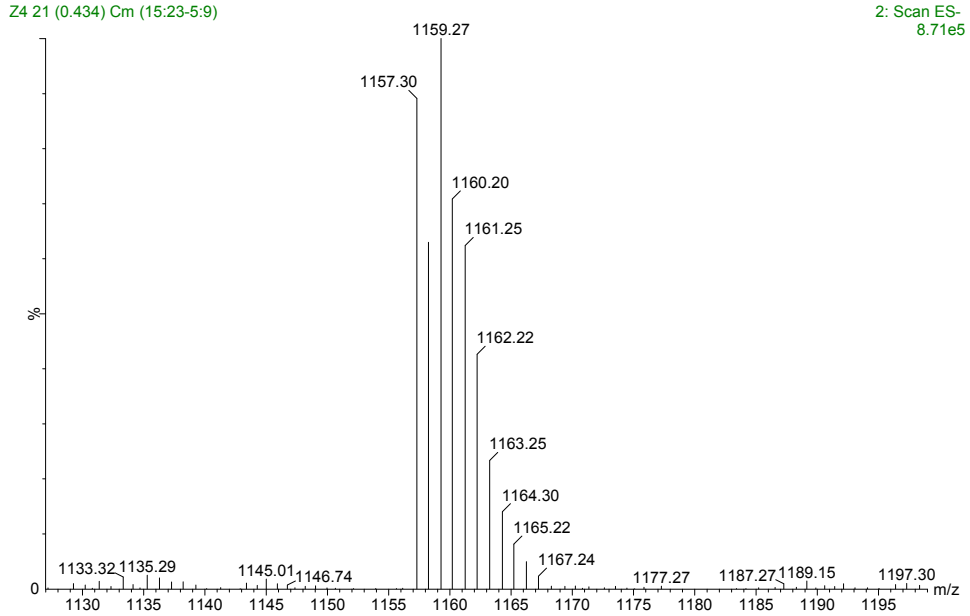
Found: 1157.31

Figure S1. ESI-MS of $Ni(OAc)_2$/**L4** = 1:1 mixture generated in THF (a, b)

(c)



(d)



Calcd. $C_{53}H_{49}N_6Ni_2O_{13}S_2$ [$M_{\mathbf{L4}}$ -2H + $Ni_2(OAc)_2$ -H]$^-$: 1157.15

Found: 1157.30

Figure S2. ESI-MS of $Ni(OAc)_2$/**L4** = 2:1 mixture generated in THF (c, d)

(e)

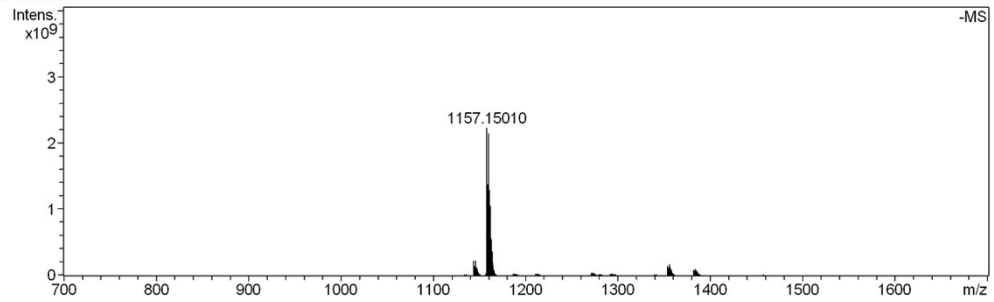
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\201611\Z10-161124_000004.d	Acquisition Date	11/24/2016 2:13:50 PM
Method	4_17_Mass_range_pos_7T	Operator	
Sample Name	Z10-161124	Instrument	solariX
Comment			

Acquisition Parameter

Polarity	Negative	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	100.4 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	3000.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Thu Nov 17 02:55:09 2016
Source Accumulation	0.010 sec	n/a	n/a	Data Acquisition Size	1048576
Ion Accumulation Time	0.100 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.002 sec				



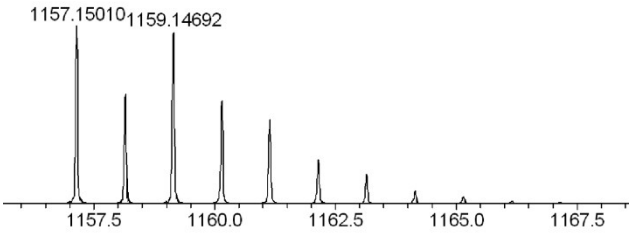
Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1157.15010	1	C 53 H 49 N 6 Ni 2 O 13 S 2	100.00	1157.15115	0.91	0.02	29.8	32.5	even	ok

Calcd. $C_{53}H_{49}N_6Ni_2O_{13}S_2$ [$M_{\mathbf{L4}}$ -2H + $Ni_2(OAc)_2$ -H]$^-$: 1157.15115

Found: 1157.15010

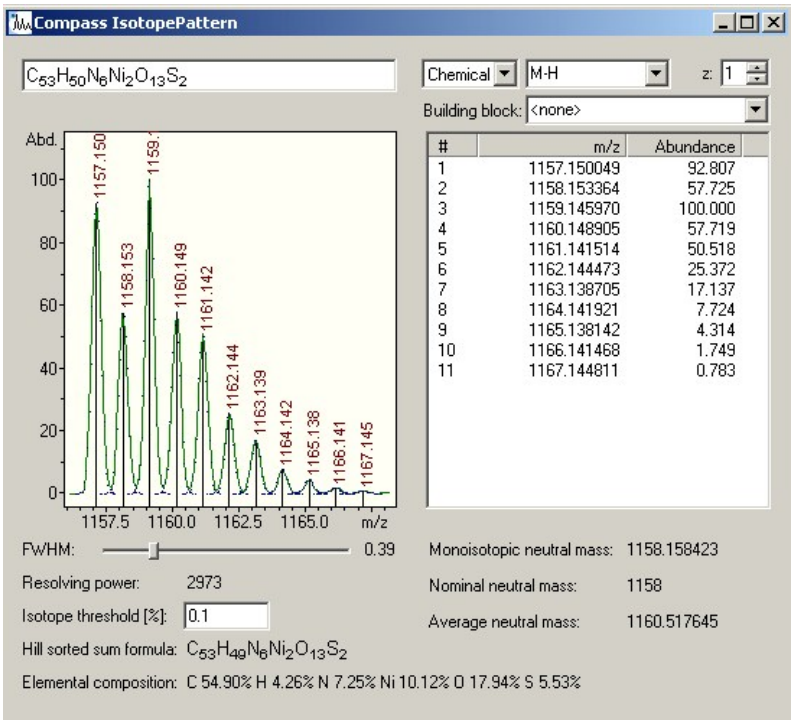
Figure S3. ESI-HRMS of $Ni(OAc)_2$/**L4** = 2:1 mixture generated in THF (e)

(f) Observed



m/z	z	I	Res.
1157.15010		2233938432	25992
1158.15340		1371616256	25453
1159.14692		2160866816	24954
1160.14900		1308342144	25304
1161.14481		1048525184	23693
1162.14679		552893312	25584
1163.14313		364420448	23523
1164.14642		161591120	24961
1165.14247		90892592	23098
1166.14623		38756116	25407
1167.14565		16353530	18416

(g) Calculated



(h)

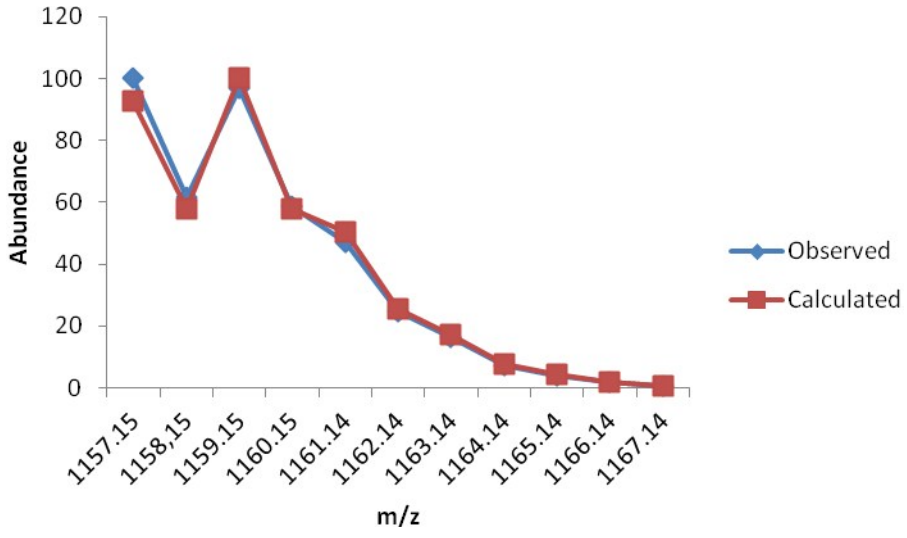
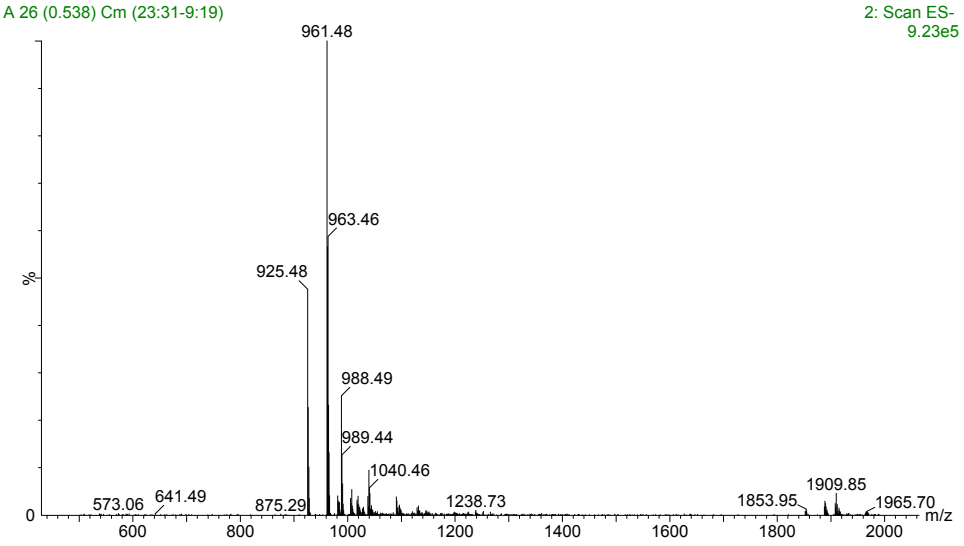


Figure S4. The observed distribution pattern of *m/z* 1157 and the calculated distribution pattern of $C_{53}H_{49}N_6Ni_2O_{13}S_2$ (f, g, h)



(i)

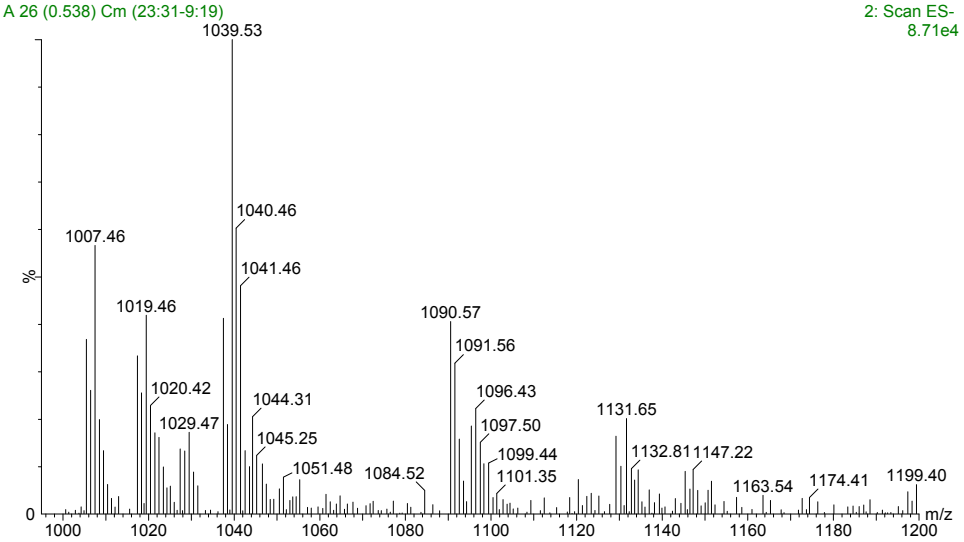
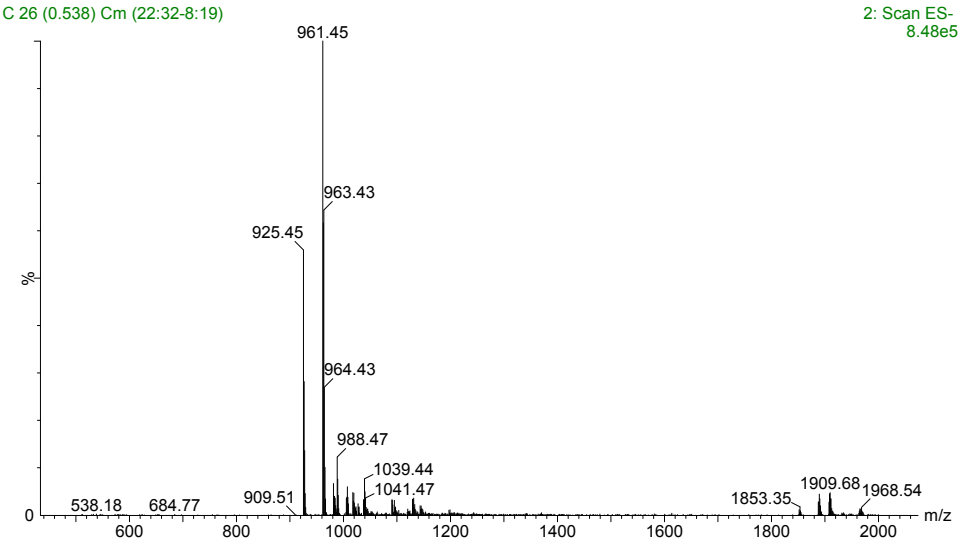


Figure S5. ESI-MS of $Ni(OAc)_2$/**L4** = 2:1 mixture generated in CH_2Cl_2 (i)



(j)

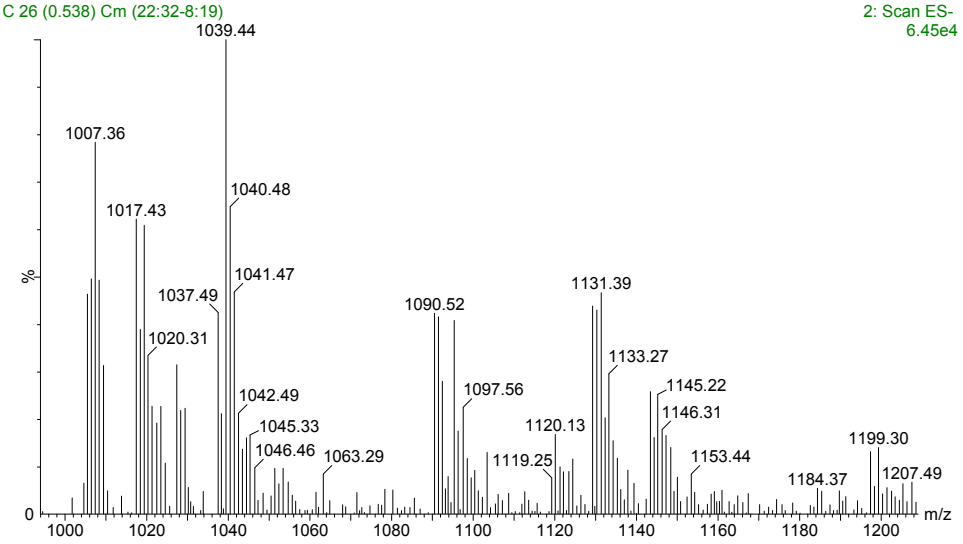


Figure S6. ESI-MS of $Ni(OAc)_2$/**L4** = 2:1 mixture generated in toluene (j)

6.2 The structure of the dinuclear Ni-aminophenol sulfonamide complex optimized by DFT

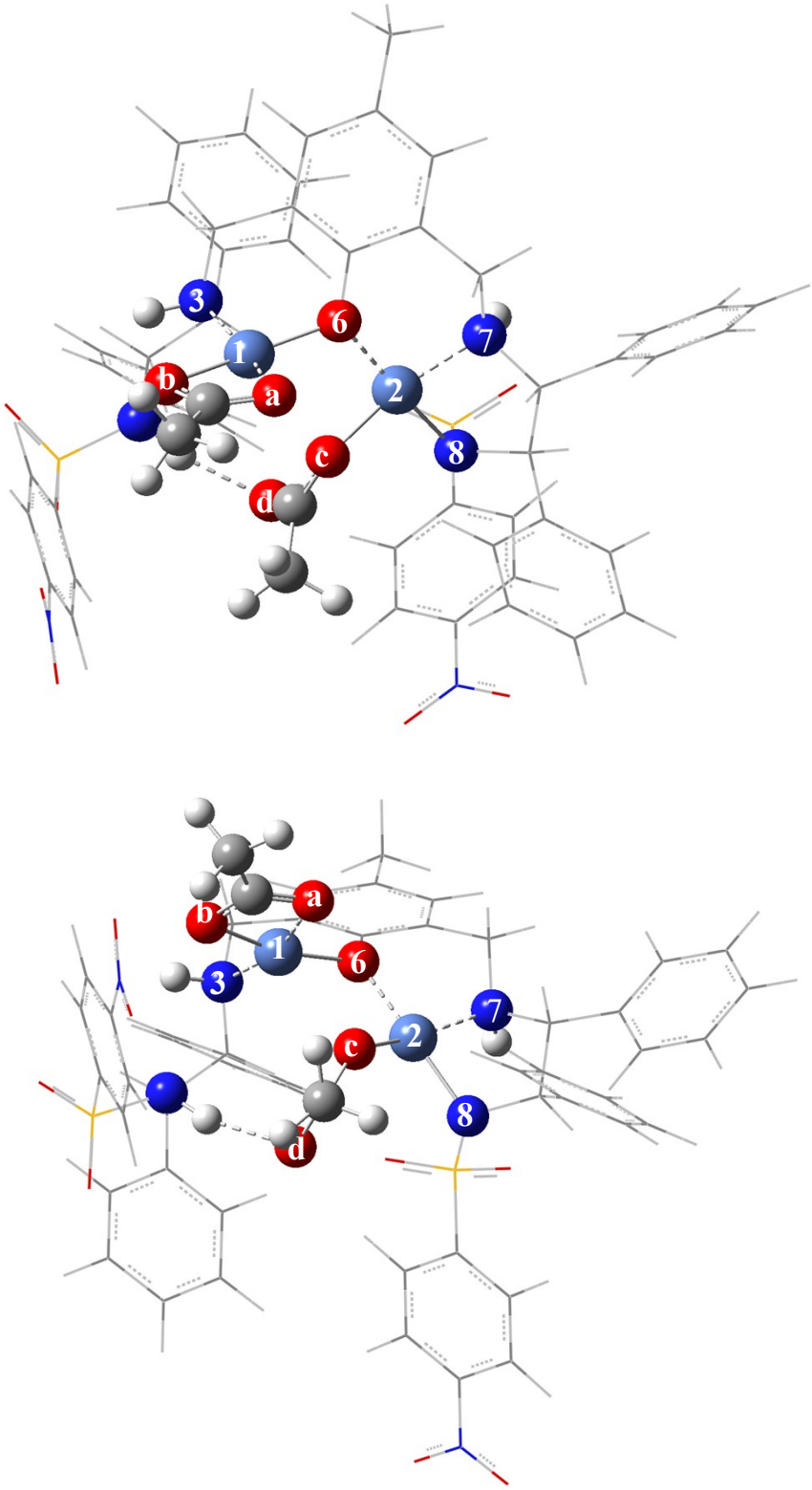


Figure S7. The geometry of Ni_2/**L4** optimized by density functional theory (DFT)

Computational Methods: DFT calculations were carried out using the Gaussian 09 software package[2]. Considering both the desired precision of structures and available computer resources, the geometry optimizations were performed using the Becke's three-parameter nonlocal exchange function[3] and the Lee, Yang, and Parr nonlocal correlation function (LYP)[4] at a mixed basis set level. The Lan2DZ basis set[5] with the associated effective core potential was used for Ni, while the 6-31G(d) basis set[6] was used for all other atoms (C, H, O, N, S).

6.2.1 Selected bond length (nm)

Ni_1-N_3	Ni_1-O_a	Ni_1-O_6	Ni_2-O_6	Ni_2-N_7	Ni_2-N_8	Ni_2-O_c	Ni_1-O_b	Ni_1-Ni_2
0.1962	0.1955	0.1878	0.1932	0.1948	0.1917	0.1893	0.1916	0.3185

6.2.2 Selected dihedral angles (°)

∠$Ni_1N_3N_4O_5$	∠$N_3N_4O_5O_6$	∠$Ni_2O_6N_7N_8$	∠$O_6N_7N_8O_9$	∠$Ni_1O_6Ni_2O_9$	∠$N_3N_4O_6O_9$	∠$N_3Ni_1O_6Ni_2$
123.71	-13.90	4.11	68.74	91.42	-121.54	-107.89

[2] M. J. Frisch, G. W. , H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingform, CT, 2009.

[3] W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, *100*, 12974-12980.

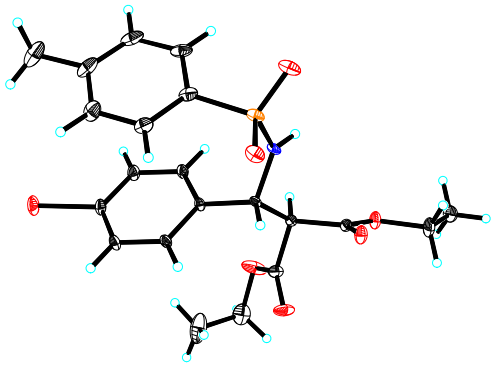
[4] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

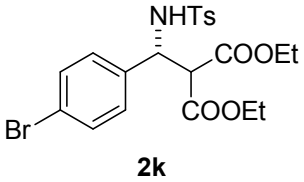
[5] (a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270-283. (b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284-298. (c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.

[6] P. C. Hariharan, J. A. Pople, *Theoretica. Chimica. Acta.* **1973**, *28*, 213-222.

7. The X-ray data for 2k

Crystal data for **2k**: $C_{21}H_{24}BrNO_6S$, M = 498.38, a = 9.7594(11) Å, b = 12.6345(14) Å, c = 17.835(2) Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, V = 2199.1(4) Å^3, T = 100(2) K, space group $P212121$, Z = 4, μ(MoKα) = 2.001 mm^{-1}, 24629 reflections measured, 6517 independent reflections (R_{int} = 0.0415). The final R_1 values were 0.0446 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1001 ($I > 2\sigma(I)$). The final R_1 values were 0.0596 (all data). The final $wR(F^2)$ values were 0.1059 (all data). The goodness of fit on F^2 was 1.072. Flack parameter = 0.020(4).





2k

CCDC No. 1567111

Figure S8. View of a molecule of **2k** with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level.

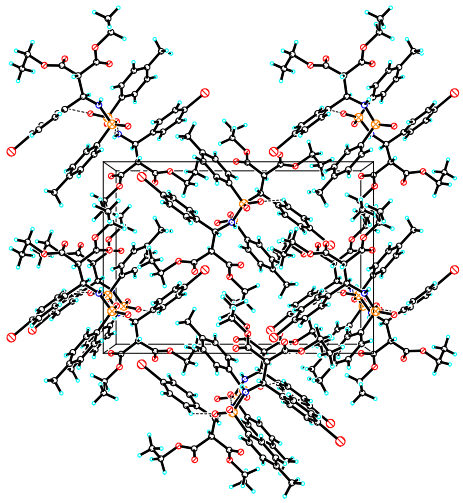


Figure S7. View of the pack drawing of **2k**. Hydrogen-bonds are shown as dashed

lines.

8. Postulated working model

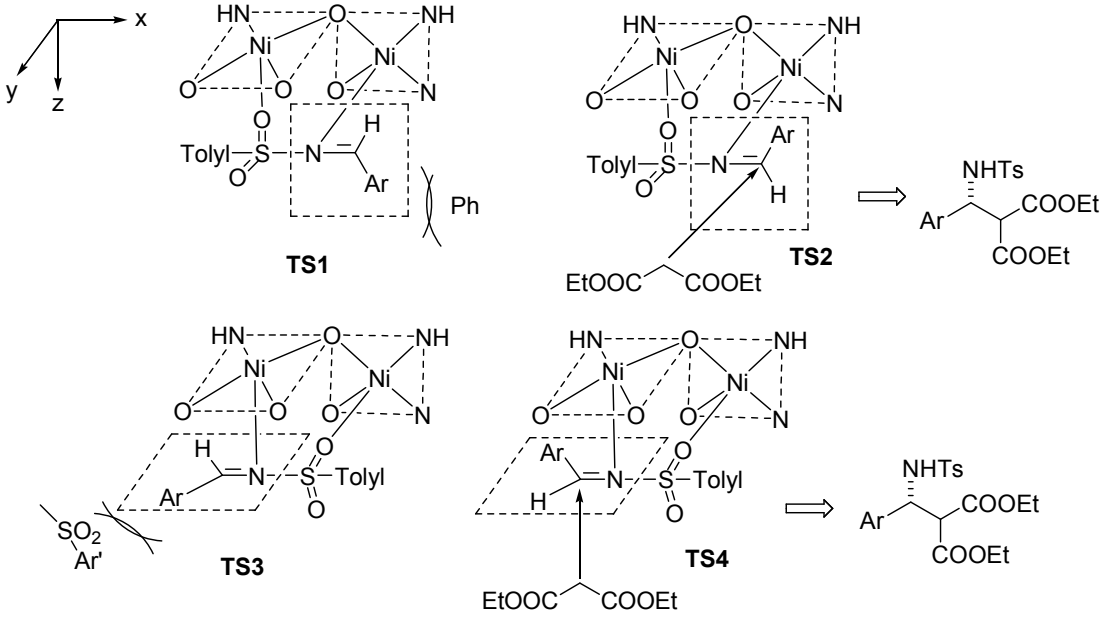
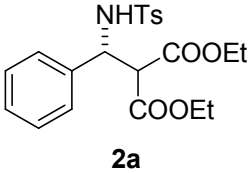


Figure S8. The proposed working model

Based on the geometry of Ni_2/**L4** optimized by DFT and the absolute configuration of the products, four plausible transition states **TS1-4** (Figure S8) were proposed to elucidate the asymmetric induction. **TS2** and **TS4** were speculated to be more favorable than **TS2** or **TS4** due to the steric repulsion between Ar and the complex, affording (*R*)-**2**.

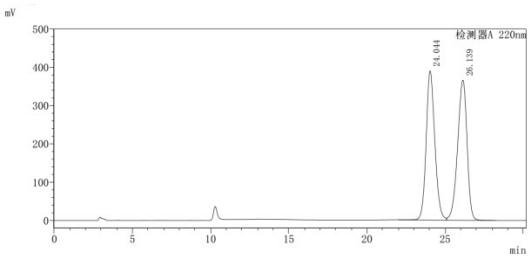
9. Characterization of products

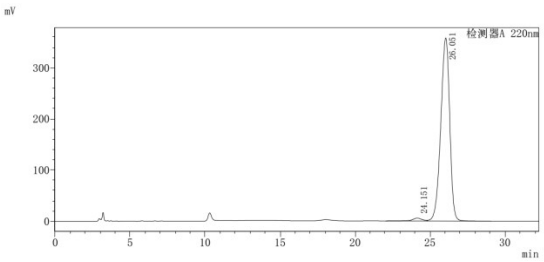
The absolute configuration of **2k** was determined by X-ray crystallographic analysis. The absolute configuration of **2a**-**2j**, **2l**-**2n** was determined by analogy.



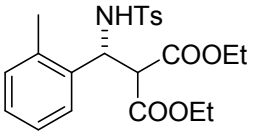
2a

2a: White solid; 1.975 g, 94% yield, 96% *ee*; $[\alpha]_D^{25}$ = + 29.6 (*c* 0.69, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7, 2H), 7.10 (s, 5H), 7.04 (d, *J* = 7.7, 2H), 6.43 (d, *J* = 9.5, 1H), 5.16-5.13 (m, 1H), 4.15-3.95 (m, 4H), 3.76 (d, *J* = 5.6, 1H), 2.29 (s, 3H), 1.17-1.11 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 165.4, 144.9, 136.8, 136.5, 128.1, 127.3, 126.7, 125.9, 125.7, 61.1, 60.9, 56.9, 56.0, 20.4, 12.8, 12.8; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 85/15, flow rate = 1.0 mL/min, 220 nm, t_r = 24.15 min (minor) and t_r = 26.05 min (major); ESI-HRMS Calcd for $C_{21}H_{25}NNaO_6S^+$ $[M + Na]^+$: 442.1295, found 442.1293.



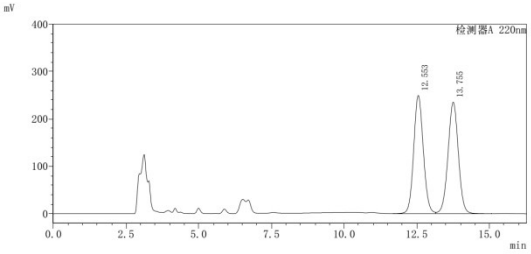


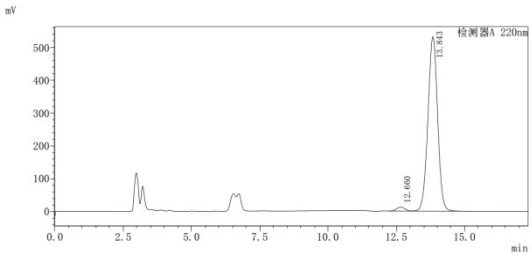
Peak#	Ret Time	Area	Height	Area%
1	24.151	258267	5580	1.709
2	26.051	14852579	357985	98.291



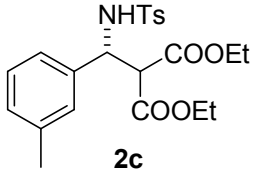
2b

2b: White solid; 2.121 g, 98% yield, 96% *ee*; $[\alpha]_D^{25}$ = +22.9 (c 0.87, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.9, 2H), 7.01-6.97 (m, 5H), 6.87 (t, *J* = 7.2, 1H), 6.48 (d, *J* = 9.1, 1H), 5.39-5.36 (m, 1H), 4.17-4.02 (m, 4H), 3.67 (d, *J* = 5.5, 1H), 2.33 (s, 3H), 2.28 (s, 3H), 1.19-1.12 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 166.5, 142.9, 137.9, 135.6, 134.9, 130.5, 129.1, 127.7, 126.8, 126.5, 126.1, 62.2, 62.0, 56.4, 53.3, 21.4, 19.1, 13.9, 13.9; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 12.66 min (minor) and t_r = 13.84 min (major); ESI-HRMS Calcd for $C_{22}H_{27}NNaO_6S^+$ $[M + Na]^+$: 456.1451 , found 456.1451.





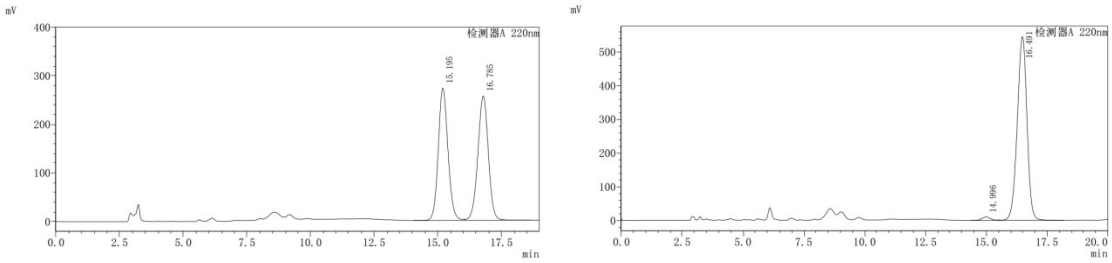
Peak#	Ret Time	Area	Height	Area%
1	12.660	258372	12112	1.927
2	13.843	13148502	533570	98.073



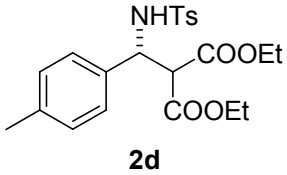
2c

2c: White solid; 2.152 g, 99% yield, 96% *ee*; $[\alpha]_D^{25}$ = +26.7 (c 0.60, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0, 2H), 7.06-7.00 (m, 3H), 6.92-6.90 (m, 2H), 6.79 (s, 1H), 6.33 (d, *J* = 9.5, 1H), 5.13-5.09

(m, 1H), 4.13-4.03 (m, 4H), 3.75 (d, *J* = 5.5, 1H), 2.31 (s, 3H), 2.14 (s, 3H), 1.20-1.12 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 165.4, 141.8, 136.9, 136.8, 136.3, 128.0, 127.4, 127.2, 126.4, 126.0, 122.8, 61.1, 60.8, 56.8, 56.0, 20.3, 20.2, 12.9, 12.8; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 80/20, flow rate = 1.0 mL/min, 220 nm, t_r = 14.99 min (minor) and t_r = 16.49 min (major); ESI-HRMS Calcd for $C_{22}H_{27}NNaO_6S^+$ $[M + Na]^+$: 456.1451, found 456.1462.

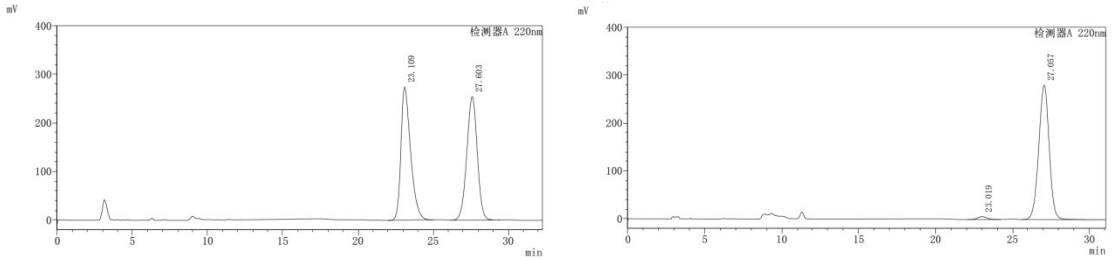


Peak#	Ret Time	Area	Height	Area%
1	14.996	256329	9941	1.662
2	16.491	15167245	545335	98.338



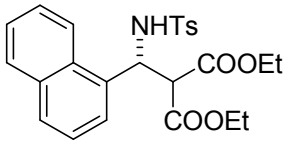
2d

2d: White solid; 1.949 g, 90% yield, 96% *ee*; $[\alpha]_D^{25}$ = +36.0 (*c* 0.70, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.7, 2H), 7.05 (d, *J* = 7.7, 2H), 6.97 (d, *J* = 7.5, 2H), 6.91 (d, *J* = 7.6, 2H), 6.35 (d, *J* = 9.4, 1H), 5.09 (t, *J* = 7.4, 1H), 4.14-3.96 (m, 4H), 3.74 (d, *J* = 5.6, 1H), 2.31(s, 3H), 2.23 (s, 3H), 1.15 (m, 6.53, 6H); ^{13}C NMR (125 MHz, CDCl3) δ 166.1, 164.8, 141.1, 136.2, 135.7, 132.9, 127.4, 127.3, 125.3, 125.0, 60.4, 60.2, 56.2, 55.1, 19.7, 19.3, 12.2, 12.2; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 80/20, flow rate = 1.0 mL/min, 220 nm, t_r = 23.02 min (minor) and t_r = 27.06 min (major); ESI-HRMS Calcd for $C_{22}H_{27}NNaO_6S^+$ $[M + Na]^+$: 456.1451, found 456.1443.



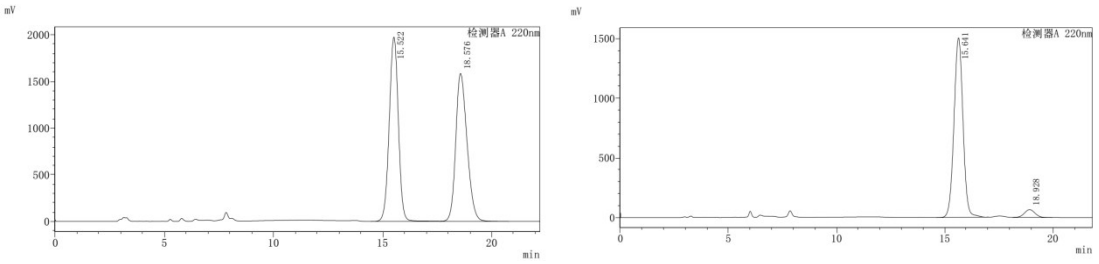
Peak#	Ret Time	Area	Height	Area%

1	23.019	254068	6054	1.878
2	27.057	13271744	281134	98.122



2e

2e: White solid; 2.280 g, 97% yield, 90% *ee*; $[\alpha]_D^{25}$ = -12.9 (*c* 0.86, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5, 1H), 7.74 (d, *J* = 8.1, 1H), 7.59 (d, *J* = 8.2, 1H), 7.51 (t, *J* = 7.5, 1H), 7.42 (t, *J* = 7.4, 1H), 7.38 (d, *J* = 8.0 , 2H), 7.33 (d, *J* = 7.2, 1H), 7.15 (t, *J* = 7.7, 1H), 6.94 (d, *J* = 9.5, 1H), 6.80 (d, *J* = 4.7, 2H), 6.06-6.02 (m, 1H), 4.13-4.01 (m, 4H), 4.0-3.94 (m, 1H), 2.15 (s, 3H), 1.13 (t, *J* = 7.1, 3H), 1.05 (t, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 166.7, 142.8, 137.7, 133.6, 132.9, 130.0, 129.0, 128.9, 128.5, 126.9, 126.8, 125.8, 125.0, 125.0, 122.0, 62.3, 61.9, 56.8, 53.1, 21.3, 13.9, 13.9; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 15.64 min (major) and t_r = 18.93 min (minor); ESI-HRMS Calcd for $C_{25}H_{27}NNaO_6S^+$ $[M + Na]^+$: 492.1451, found 492.1457.



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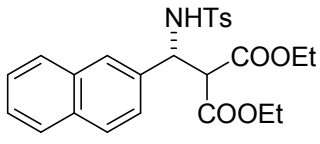
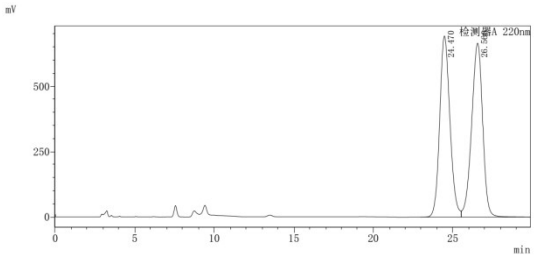
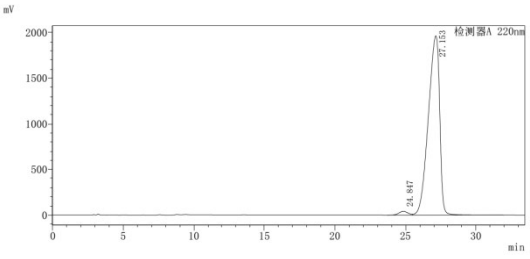
2	18.928	2231239	65718	4.874



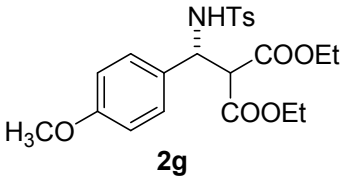
2f

2f: White solid; 2.210 g, 94% yield, 97% *ee*; $[\alpha]_D^{25}$ = +56.3 (c 1.26, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.72 (m, 1H), 7.62-7.59 (m, 2H), 7.47-7.41 (m, 5H), 7.24 (d, *J* = 8.5, 1H), 6.86 (d, *J* = 7.8, 2H), 6.53 (d, *J* = 9.5, 1H), 5.34-5.31 (m, 1H), 4.16-4.01 (m, 4H), 3.89 (d, *J* = 5.5, 1H), 2.09 (s, 3H), 1.18 (t, *J* = 7.1, 3H), 1.12 (t, *J* = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 165.4, 141.9, 136.7, 133.5, 131.8, 131.6, 128.0, 127.2, 126.9, 126.4, 125.9, 125.4, 125.2, 125.1, 123.2, 61.2, 60.9, 56.7, 56.2, 20.1, 12.9, 12.8; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 80/20, flow rate = 1.0 mL/min, 220 nm, t_r = 24.85 min (minor) and t_r = 27.15 min (major); ESI-HRMS Calcd for $C_{25}H_{27}NNaO_6S^+$ $[M + Na]^+$: 492.1451, found 492.1439.



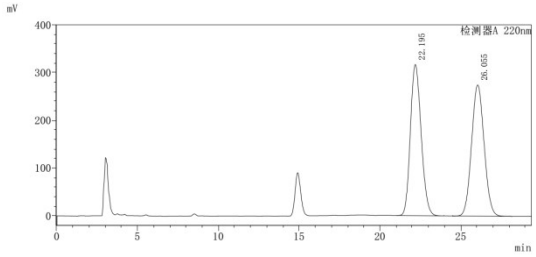


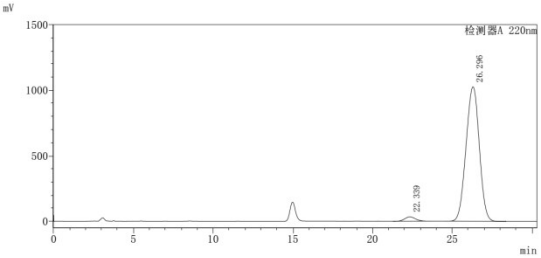
Peak#	Ret Time	Area	Height	Area%
1	24.847	1849960	41045	1.658
2	27.153	109699000	1966771	98.342



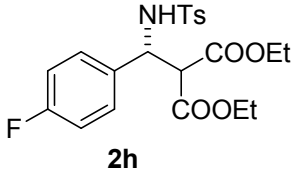
2g

2g: White solid; 1.798 g, 80% yield, 95% *ee*; $[\alpha]_D^{25}$ = +35.9 (c 0.74, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.9, 2H), 7.02 (d, *J* = 7.85, 2H), 6.98 (d, *J* = 8.2, 2H), 6.58 (d, *J* = 8.3, 2H), 6.37 (d, *J* = 9.4, 1H), 5.07-5.04 (m, 1H), 4.13-3.95 (m, 4H), 3.74 (d, *J* = 6.6, 1H), 3.66 (s, 3H), 2.27 (s, 3H), 1.15-1.08 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 164.3, 157.0, 140.7, 135.9, 127.6, 127.1, 126.1, 125.0, 111.6, 59.9, 59.8, 56.1, 54.6, 53.1, 19.3, 11.8, 11.8; The *ee* was determined by HPLC analysis using a CHIRALPAK AD-H column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 22.34 min (minor) and t_r = 26.30 min (major); ESI-HRMS Calcd for $C_{22}H_{27}NNaO_7S^+$ [M + Na]$^+$: 472.1400, found 472.1394.





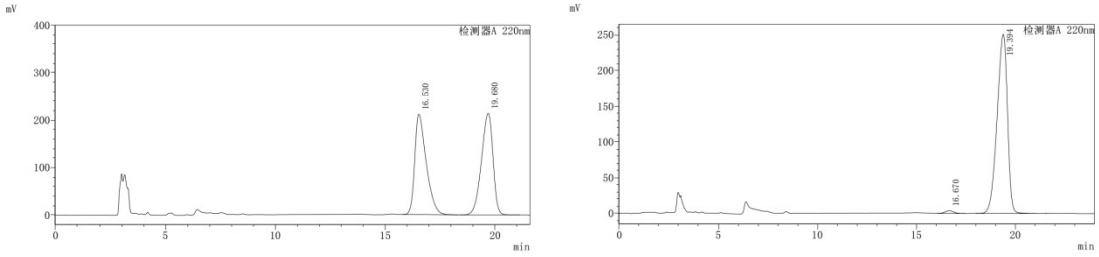
Peak#	Ret Time	Area	Height	Area%
1	22.339	1533253	32876	2.518
2	26.296	59360076	1025443	97.482



2h

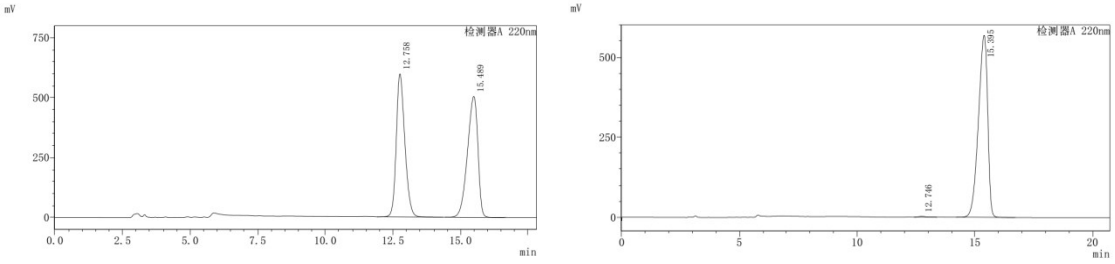
2h: White solid; 2.106 g, 96% yield, 97% *ee*; $[\alpha]_D^{25}$ = +22.6 (*c* 0.59, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9, 2H), 7.10-7.06 (m, 4H), 6.78 (t, *J* = 8.4, 2H), 6.45 (d, *J* = 9.3 1H), 5.12-5.09 (m,

1H), 4.16-3.95 (m, 4H), 3.73 (d, J = 6.2, 1H), 2.31 (s, 3H), 1.14 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 165.2, 161.1 (d, J = 245.4), 142.1, 136.7, 132.4 (d, J = 3.0), 128.2, 127.7, 127.7, 126.0, 114.2, 114.1, 61.1, 61.0, 56.9, 55.4, 20.4, 12.8; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 16.67 min (minor) and t_r = 19.39 min (major); ESI-HRMS Calcd for $C_{21}H_{24}FNNaO_6S^+$ $[M + Na]^+$: 460.1201, found 460.1208.

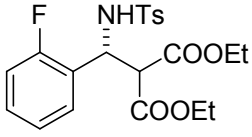


Peak#	Ret Time	Area	Height	Area%
1	16.670	114236	3887	1.235
2	19.394	9132991	250877	98.765

2h: White solid; 99% ee, $[\alpha]_D^{25}$ = +24.5 (*c* 0.40, CH_2Cl_2); The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 12.75 min (minor) and t_r = 15.40 min (major).



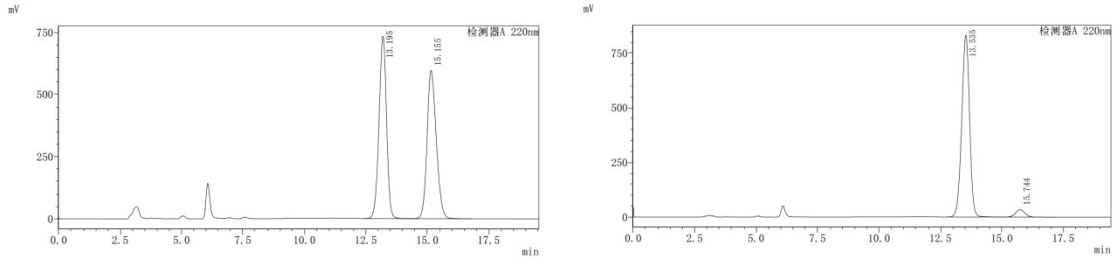
Peak#	Ret Time	Area	Height	Area%
1	12.746	40628	2047	0.260
2	15.395	15556490	569147	99.740



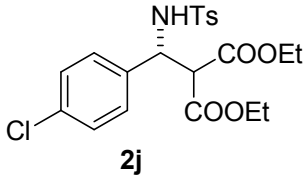
2i

2i: White solid; 2.078 g, 95% yield, 91% *ee*; $[\alpha]_D^{25}$ = +21.6 (c 2.20, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8, 2H), 7.12-7.09 (m, 2H), 7.03 (d, J = 7.8, 2H), 6.86-6.80 (m, 2H), 6.27 (d, J = 9.9, 1H), 5.36-5.33 (m, 1H), 4.14-3.90 (m, 4H), 3.84 (d, J = 6.5, 1H), 2.26 (s, 3H), 1.14-1.08 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 165.1, 158.7 (d, J = 244.6), 142.1, 136.6,

128.6 (d, J = 8.4), 128.2, 128.1 (d, J = 3.4), 126.0, 123.7 (d, J = 12.6), 123.0 (d, J = 3.2), 114.3 (d, J = 21.4), 61.1, 60.9, 55.4, 50.9, 20.3, 12.8, 12.8 ppm. The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 13.54 min (major) and t_r = 15.74 min (minor); ESI-HRMS Calcd for $C_{21}H_{24}FNNaO_6S^+$ $[M + Na]^+$: 460.1201, found 460.1209.

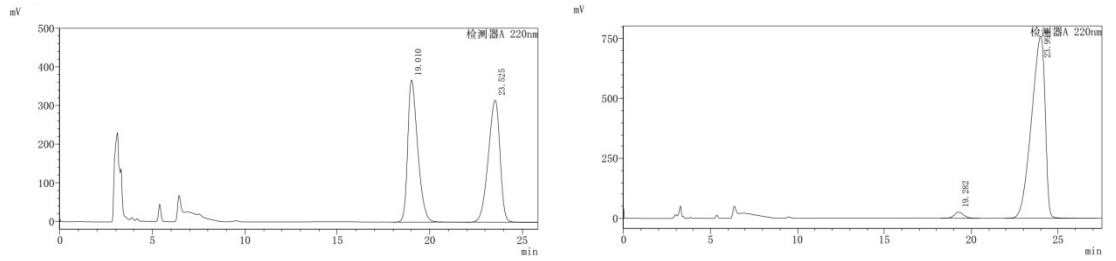


Peak#	Ret Time	Area	Height	Area%
1	13.535	18435529	832944	95.356
2	15.744	897783	34437	4.644

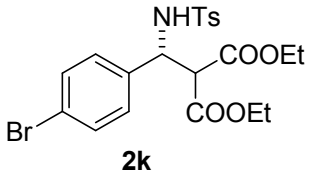


2j

2j: White solid; 2.256 g, 99% yield, 95% *ee*; $[\alpha]_D^{25}$ = +29.8 (*c* 0.88, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.0, 2H), 7.06-7.03 (m, 6H), 6.48 (d, J = 9.4, 1H), 5.10-5.07 (m, 1H), 4.16-3.94 (m, 4H), 3.74 (d, J = 6.4, 1H), 2.31 (s, 3H), 1.13 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 165.2, 142.2, 136.7, 135.2, 132.6, 128.2, 127.5, 127.4, 126.0, 61.1, 61.1, 56.7, 55.5, 20.4, 12.8; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 19.28 min (minor) and t_r = 23.99 min (major); ESI-HRMS Calcd for $C_{21}H_{24}ClNNaO_6S^+$ $[M + Na]^+$: 476.0905, found 476.0927.

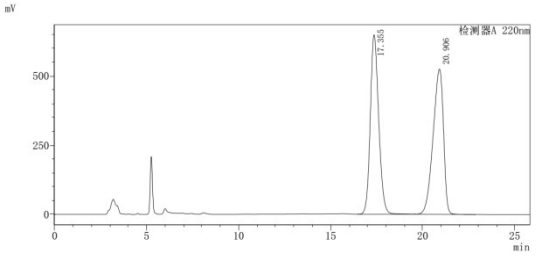


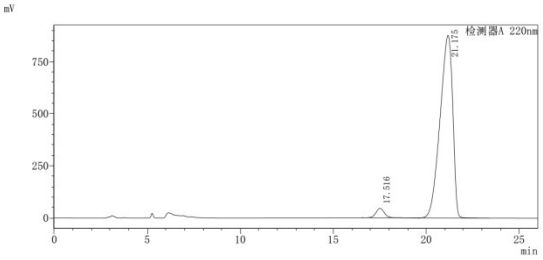
Peak#	Ret Time	Area	Height	Area%
1	19.282	943038	25240	2.230
2	23.994	41341347	760197	97.770



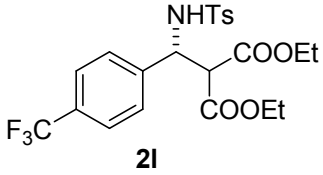
2k

2k: White solid; 2.400 g, 96% yield, 93% *ee*; $[\alpha]_D^{25}$ = +27.0 (c 0.99, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.9, 2H), 7.22 (d, *J* = 8.2, 2H), 7.07 (d, *J* = 7.9, 2H), 6.98 (d, *J* = 8.2, 2H), 6.43 (d, *J* = 9.4, 1H), 5.10-5.06 (m, 1H), 4.18-3.97 (m, 4H), 3.72 (d, *J* = 5.8, 1H), 2.34 (s, 3H), 1.16 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 166.2, 143.3, 137.7, 136.7, 131.5, 129.3, 128.8, 127.0, 121.9, 62.3, 62.1, 57.6, 56.6, 21.5, 13.9, 13.9; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 17.52 min (minor) and t_r = 21.18 min (major); ESI-HRMS Calcd for $C_{21}H_{24}BrNNaO_6S^+$ $[M + Na]^+$: 520.0400, found 520.0393.



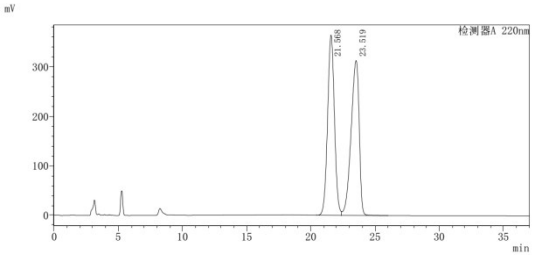


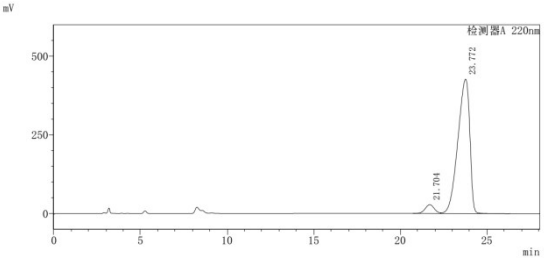
Peak#	Ret Time	Area	Height	Area%
1	17.516	1467603	45375	3.414
2	21.175	41520285	876707	96.586



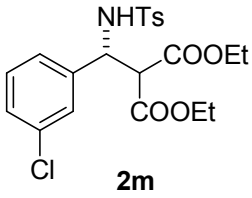
2l

2l: White solid; 2.386 g, 98% yield, 90% *ee*; $[\alpha]_D^{25}$ = +14.6 (c 3.80, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6, 2H), 7.33 (d, *J* = 7.7, 2H), 7.22 (d, *J* = 7.7, 2H), 7.01 (d, *J* = 7.7, 2H), 6.57 (d, *J* = 9.5, 1H), 5.20-5.17 (m, 1H), 4.19-3.98 (m, 4H), 3.77 (d, *J* = 5.7, 1H), 2.28 (s, 3H), 1.15 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 165.1, 142.3, 140.5, 136.5, 128.2, 126.6, 125.9, 124.2 (d, *J* = 3.7), 61.3, 61.2, 56.5, 55.7, 20.2, 12.8, 12.8; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 80/20, flow rate = 1.0 mL/min, 220 nm, t_r = 21.70 min (minor) and t_r = 23.77 min (major); ESI-HRMS Calcd for $C_{22}H_{24}F_3NNaO_6S^+$ $[M + Na]^+$: 510.1167, found 510.1164.



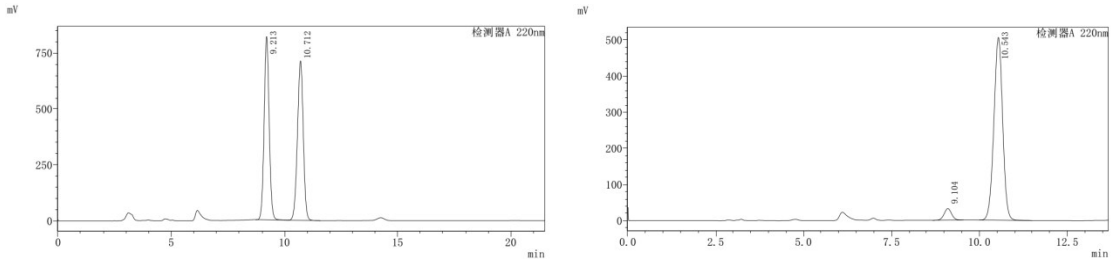


Peak#	Ret Time	Area	Height	Area%
1	21.704	1043607	28276	4.859
2	23.772	20433254	427576	95.141

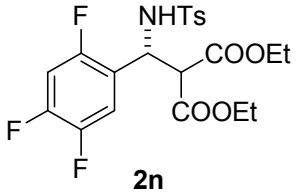


2m

2m: White solid; 2.220 g, 98% yield, 90% *ee*; $[\alpha]_D^{25}$ = +28.3 (c 3.30, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6, 2H), 7.08-7.04 (m, 5H), 6.96 (s, 1H), 6.42 (d, *J* = 9.3, 1H), 5.12-5.09 (m, 1H), 4.18-4.00 (m, 4H), 3.73 (d, *J* = 4.5, 1H), 2.32 (s, 3H), 1.20-1.14 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 166.2, 143.3, 139.5, 137.6, 134.3, 129.7, 129.3, 128.0, 127.2, 127.0, 125.2, 62.4, 62.2, 57.6, 56.6, 21.5, 13.9, 13.9; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 9.10 min (minor) and t_r = 10.54 min (major); ESI-HRMS Calcd for $C_{21}H_{24}ClNNaO_6S^+$ [M + Na]$^+$: 476.0905, found 476.0907.

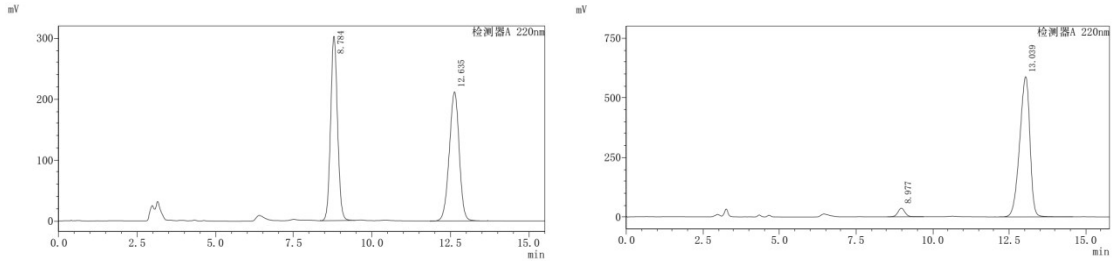


Peak#	Ret Time	Area	Height	Area%
1	9.104	475704	31994	5.135
2	10.543	8787826	505583	94.865

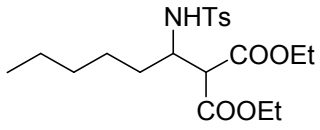


2n

2n: White solid; 2.180 g, 92% yield, 92% *ee*; $[\alpha]_D^{25}$ = +16.8 (*c* 2.00, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0, 2H), 7.12 (d, *J* = 7.9, 2H), 7.00-6.94 (m, 1H), 6.78-6.72(m, 1H), 6.36 (d, *J* = 9.7, 1H), 5.30-5.26 (m, 1H), 4.18-3.95 (m, 4H), 3.79 (d, *J* = 6.3, 1H), 2.32(s, 3H), 1.16 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 164.9, 142.6, 136.4, 128.3, 125.9, 116.4 (d, *J* = 4.8), 116.2 (d, *J* = 4.9), 104.6, 104.4 (d, *J* = 6.7), 104.3, 61.3, 61.2, 55.0, 49.9, 20.3, 12.8; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 8.98 min (minor) and t_r = 13.04 min (major); ESI-HRMS Calcd for $C_{21}H_{22}F_3NNaO_6S^+$ [M + Na]$^+$: 496.1012, found 496.1003.

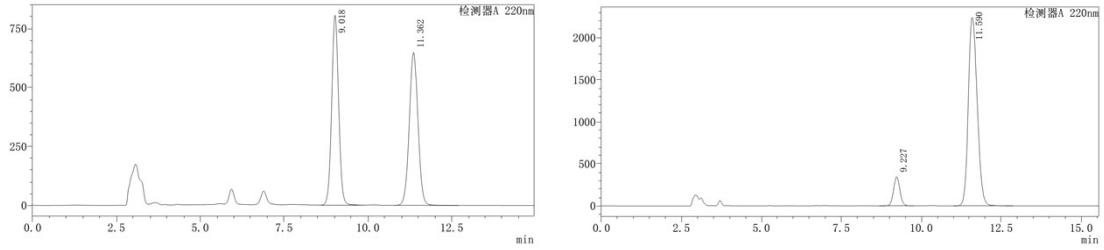


Peak#	Ret Time	Area	Height	Area%
1	8.977	564297	35655	3.973
2	13.039	13639619	587321	96.027

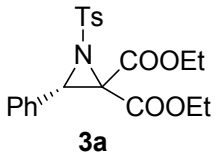


2o

2o: White solid; 70.0 mg, 85% yield, 80% *ee*; $[\alpha]^{25}_{D}$ = -18.7 (*c* 0.46, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2, 2H), 7.24 (d, *J* = 7.9, 2H), 5.52 (d, *J* = 9.8, 1H), 4.17-4.13 (m, 2H), 4.04-4.00 (m, 1H), 3.96-3.92 (m, 1H), 3.84-3.80 (m, 1H), 3.53 (d, *J* = 4.0, 1H), 2.37 (s, 3H), 1.55-1.49 (m, 1H), 1.47-1.41 (m, 1H), 1.25-1.20 (m, 5H), 1.16 (t, *J* = 7.1, 3H), 1.13-1.05 (m, 4H); 0.76 (t, *J* = 7.0, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.0, 167.4, 143.1, 138.5, 129.4, 126.9, 61.7, 61.6, 54.8, 53.5, 33.6, 31.1, 25.6, 22.3, 21.4, 13.9, 13.9, 13.8; The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 85/15, flow rate = 1.0 mL/min, 220 nm, t_r = 9.23 min (minor) and t_r = 11.59 min (major); ESI-HRMS Calcd for $C_{20}H_{31}NNaO_6S^+$ $[M + Na]^+$: 436.1764, found 436.1761.



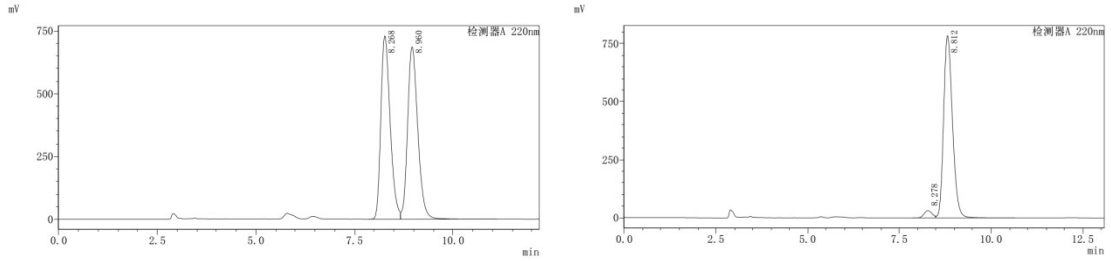
Peak#	Ret Time	Area	Height	Area%
1	9.227	4814832	346798	9.973
2	11.590	43461534	2239275	90.027



3a

3a: Colorless oil; 78.0 mg, 93% yield, 93% *ee*; $[\alpha]_D^{25}$ = -4.6 (*c* 1.15, CH_2Cl_2); ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.93 (d, *J* = 7.9, 2H), 7.46 (d, *J* = 7.8, 2H), 7.29-7.24 (m, 5H), 4.91 (s, 1H), 4.32-4.31 (m, 2H), 3.91-3.90 (m, 2H), 2.39

(s, 3H), 1.27 (t, J = 6.8, 3H), 0.78 (t, J = 6.8, 3H); The *ee* was determined by HPLC analysis using a Chiralcel OD-H column, hexane/2-propanol 90/10, flow rate = 1.0 mL/min, 220 nm, t_r = 8.28 min (minor) and t_r = 8.81 min (major).



Peak#	Ret Time	Area	Height	Area%
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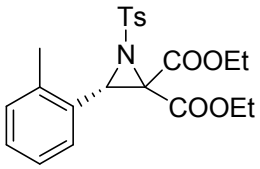
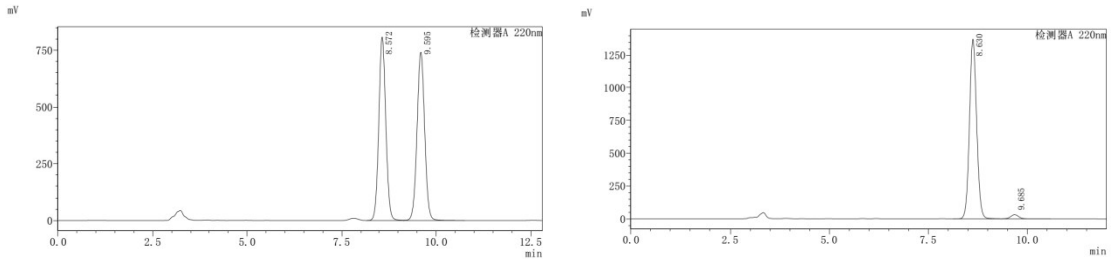
2	8.812	13194858	784859	96.486



3b

3b: White solid; 77.7 mg, 90% yield, 94% *ee*; $[\alpha]_D^{25}$ = +12.3 (*c* 0.90 CH_2Cl_2); ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.96 (d, J = 8.3, 2H), 7.50 (d, J = 8.1, 2H), 7.21-7.15 (m, 2H), 7.04 (t, J = 7.1, 1H), 6.89 (d, J = 7.7, 1H), 4.83 (s, 1H), 4.31 (q, J = 7.0, 2H), 3.83 (q, J = 7.1, 2H), 2.41 (s, 3H), 2.38 (s, 3H), 1.26 (t, J = 7.1, 3H), 0.67 (t, J = 7.1, 3H) ppm. The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 90/10, flow rate = 1.0 mL/min, 220 nm, t_r = 8.63 min (major) and t_r = 9.69 min (minor).



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1	8.630	17354728	1370731	97.358
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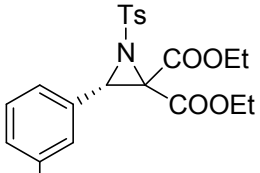
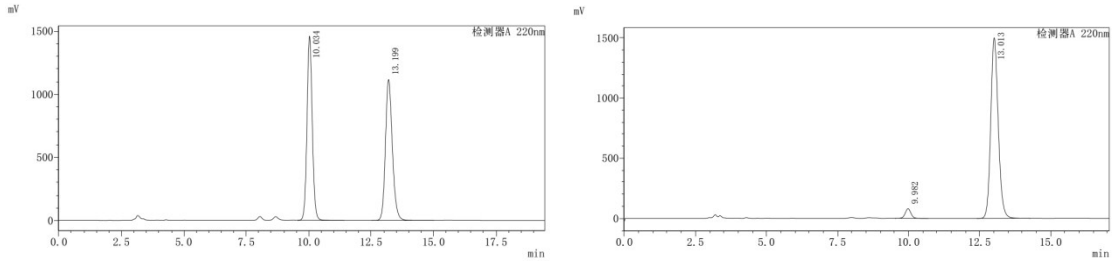


3c

3c: Colorless oil; 78.5 mg, 91% yield, 92% *ee*; $[\alpha]_D^{25}$ = -5.4 (*c* 0.94, CH_2Cl_2); ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.92 (d, J = 7.7, 2H), 7.47 (d, J = 7.7, 2H), 7.20-6.99 (m, 4H), 4.83 (s, 1H), 4.31-4.29 (m, 2H), 3.94-

3.92 (m, 2H), 2.40 (s, 3H), 2.21 (s, 3H), 1.26 (t, *J* = 6.7, 3H), 0.80 (t, *J* = 6.7, 3H); The *ee* was determined by HPLC analysis using a CHIRALPAK IA column, hexane/2-propanol 90/10, flow rate = 1.0 mL/min, 220 nm, t_r = 9.98 min (minor) and t_r = 13.01 min (major).



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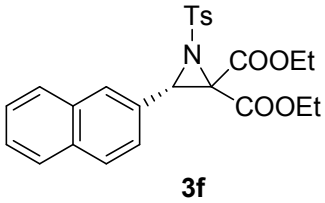
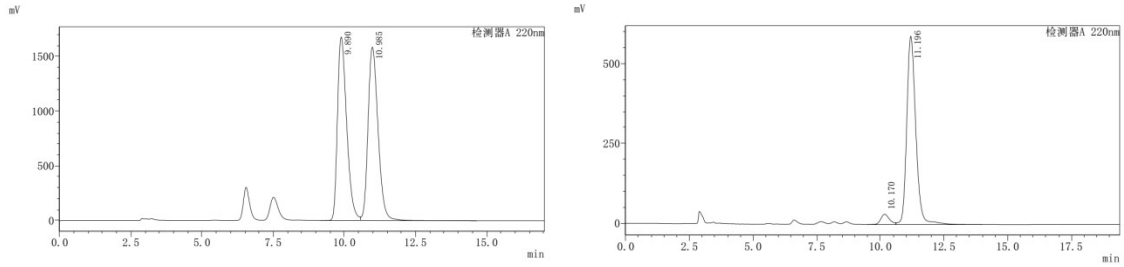


3f

3f: Colorless oil; 87.9 mg, 94% yield, 90% *ee*; $[\alpha]_D^{25}$ = -4.8 (c 0.66, CH_2Cl_2); ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.98 (d, *J* = 8.3, 2H), 7.87-7.82 (m, 4H), 7.51-7.47 (m, 4H), 7.34-7.32 (m, 1H), 5.07 (s, 1H), 4.39-4.28 (m, 2H), 3.93-3.81 (m, 2H), 2.38 (s, 3H), 1.28 (t, *J* = 7.1, 3H), 0.71 (t, *J* = 7.1, 3H); The *ee* was determined by HPLC analysis using a Chiralcel OD-H column, hexane/2-propanol 90/10, flow rate = 1.0 mL/min, 220 nm, t_r = 10.17 min (minor) and t_r = 11.20 min (major).



Peak#	Ret Time	Area	Height	Area%
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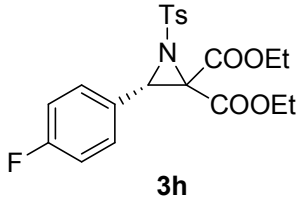
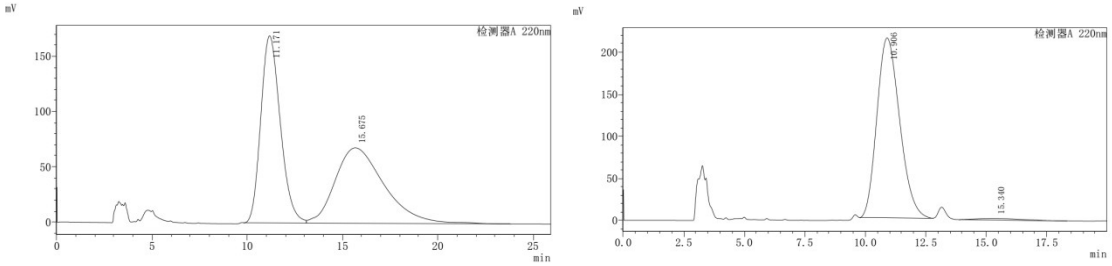
2	11.196	14588686	588308	95.063



3h

3h: Colorless oil; 81.2 mg, 93% yield, 96% *ee*; $[\alpha]_D^{25}$ = -5.0 (c 0.90, CH_2Cl_2); ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 7.93 (d, *J* = 7.8, 2H), 7.4 (d, *J* = 7.7, 2H), 7.36-7.26 (m, 2H), 7.13 (t, *J* = 8.1, 2H), 4.95 (s, 1H),

4.32-4.29 (m, 2H), 3.95-3.92 (m, 2H), 2.38 (s, 3H), 1.26 (t, J = 6.9, 3H), 0.81 (t, J = 6.8, 3H) ppm. The *ee* was determined by HPLC analysis using a Chiralcel OJ-H column, hexane/2-propanol 70/30, flow rate = 1.0 mL/min, 220 nm, t_r = 10.91 min (major) and t_r = 15.34 min (minor).



Peak#	Ret Time	Area	Height	Area%
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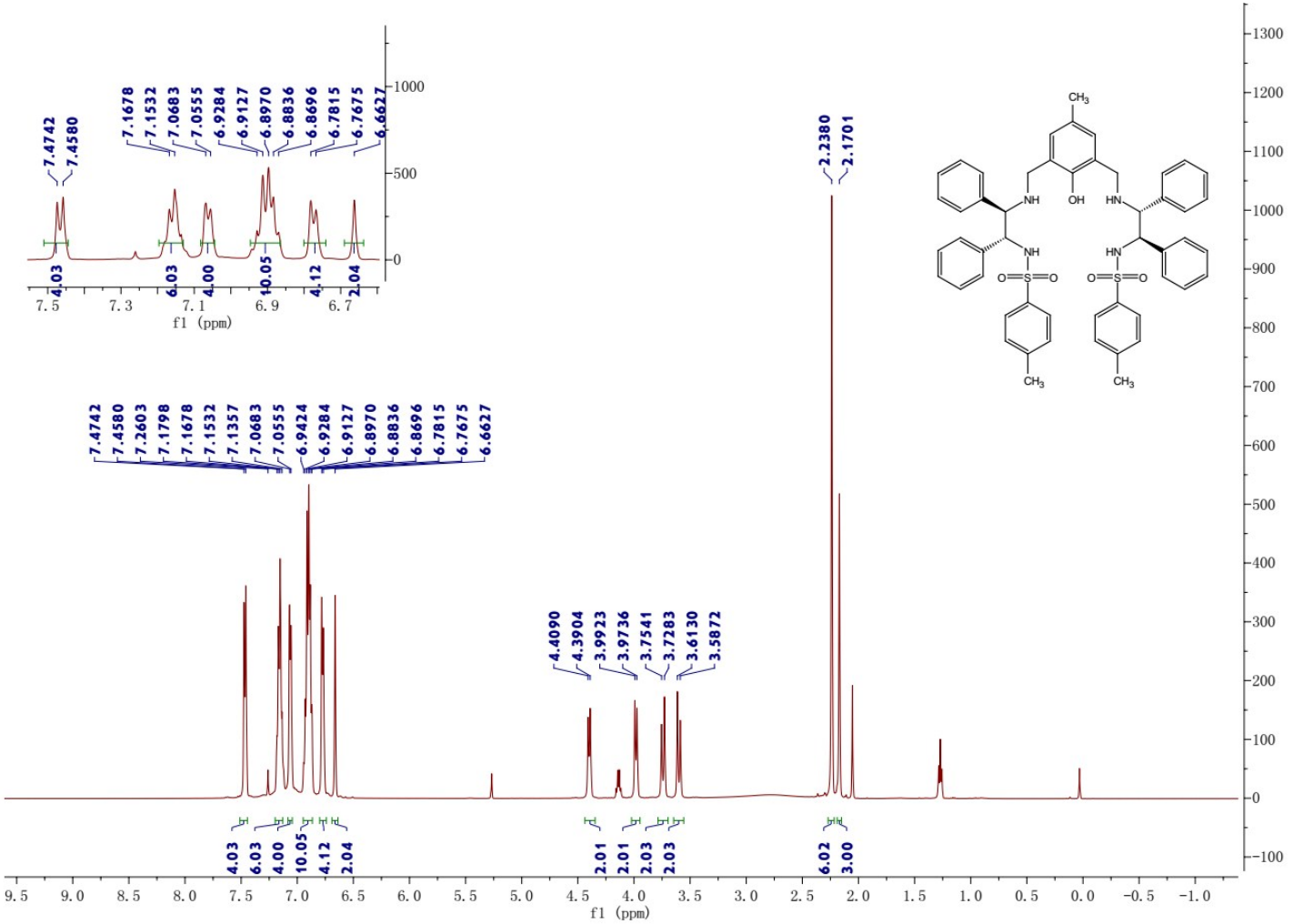
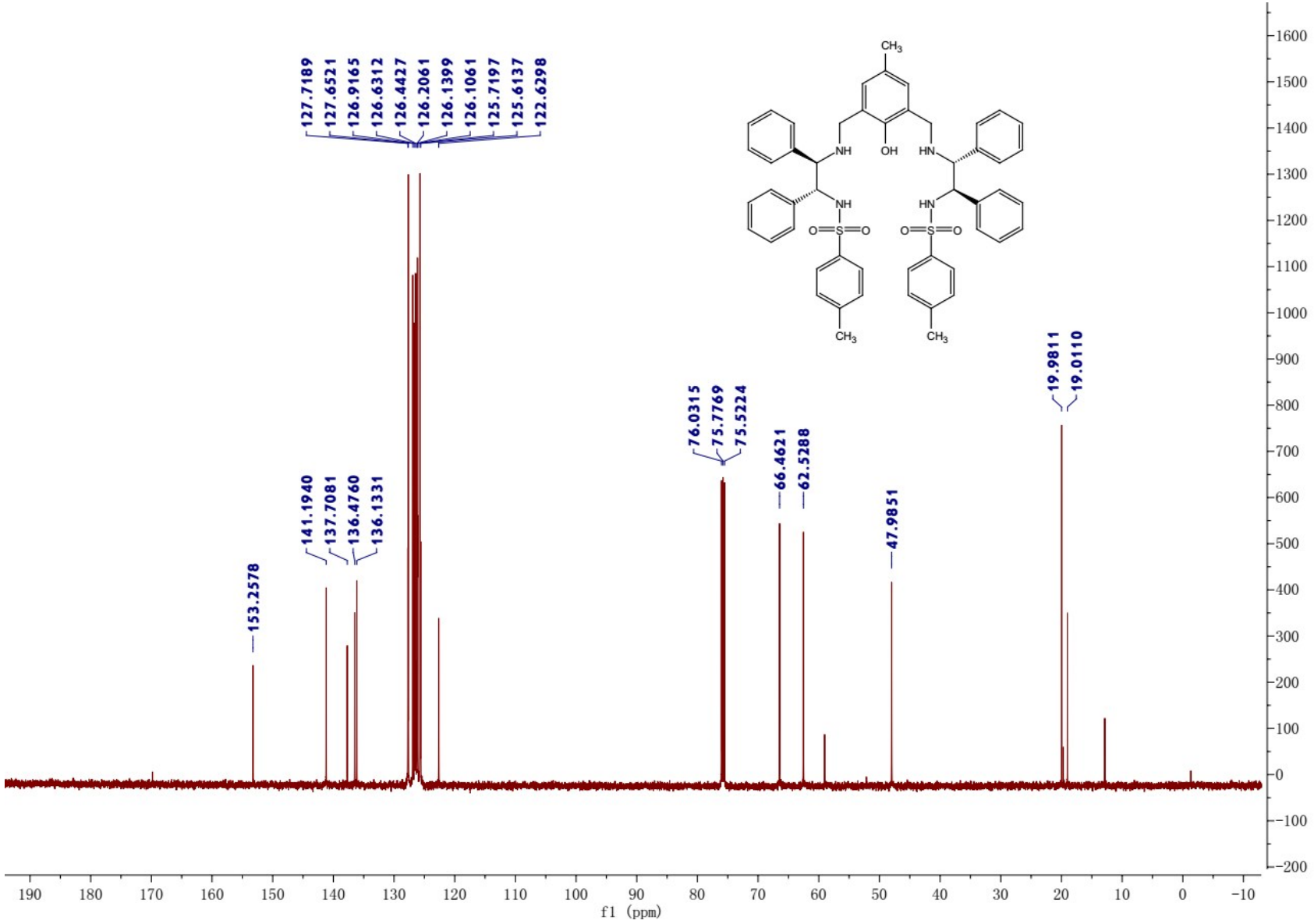
2	15.340	244104	1904	1.712

10. Copies of NMR spectra

L1



L1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122.6298
153.2578
141.1940
137.7081
136.4760
136.1331
76.0315
75.7769
75.5224
66.4621
62.5288
47.9851
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OH
HN
NH
HN
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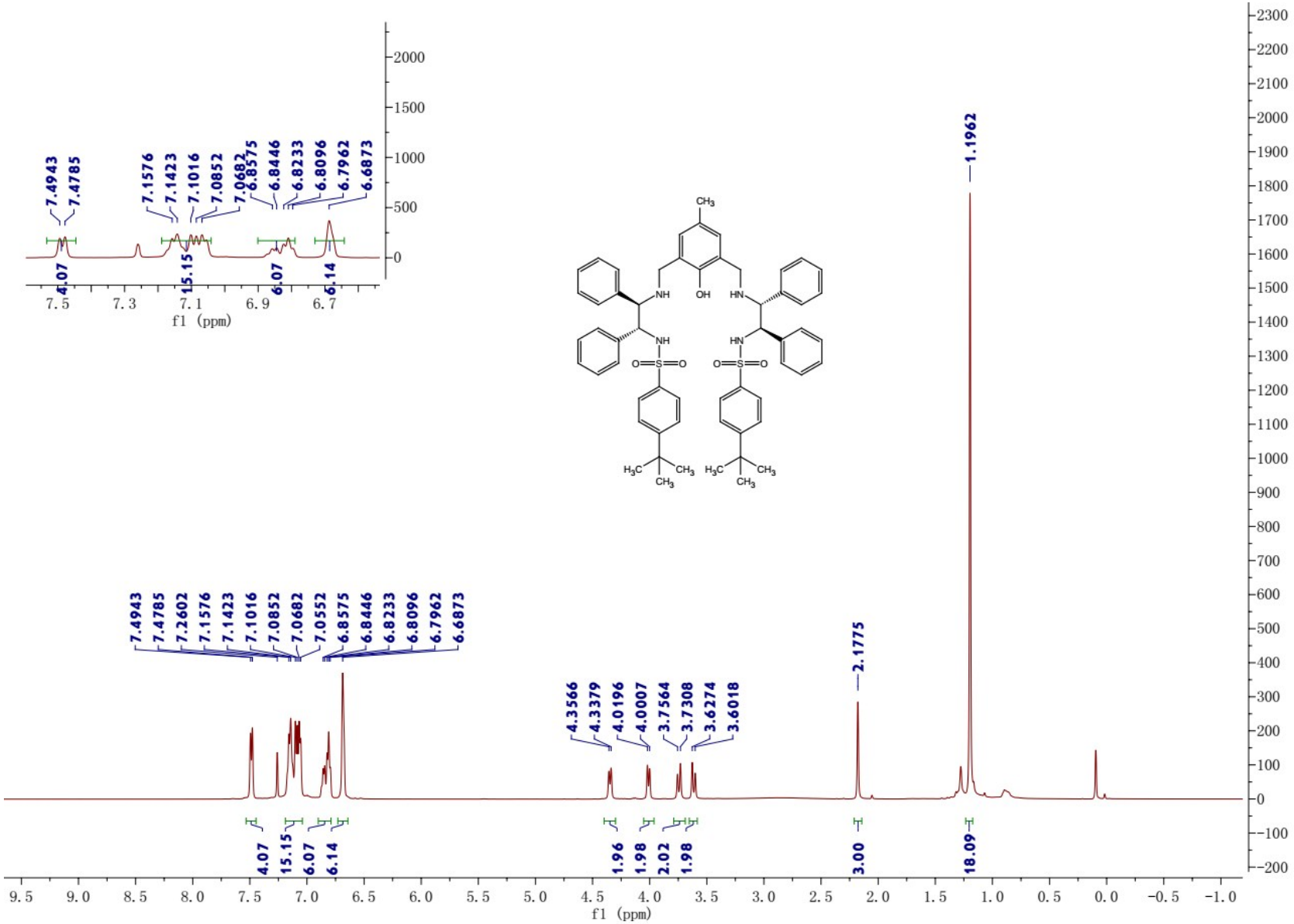
O=S=O
CH3
CH3
f1 (ppm)

L2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4.07
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6.07
6.14
f1 (ppm)
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OH
HN
O=S=O
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4.0007
3.7564
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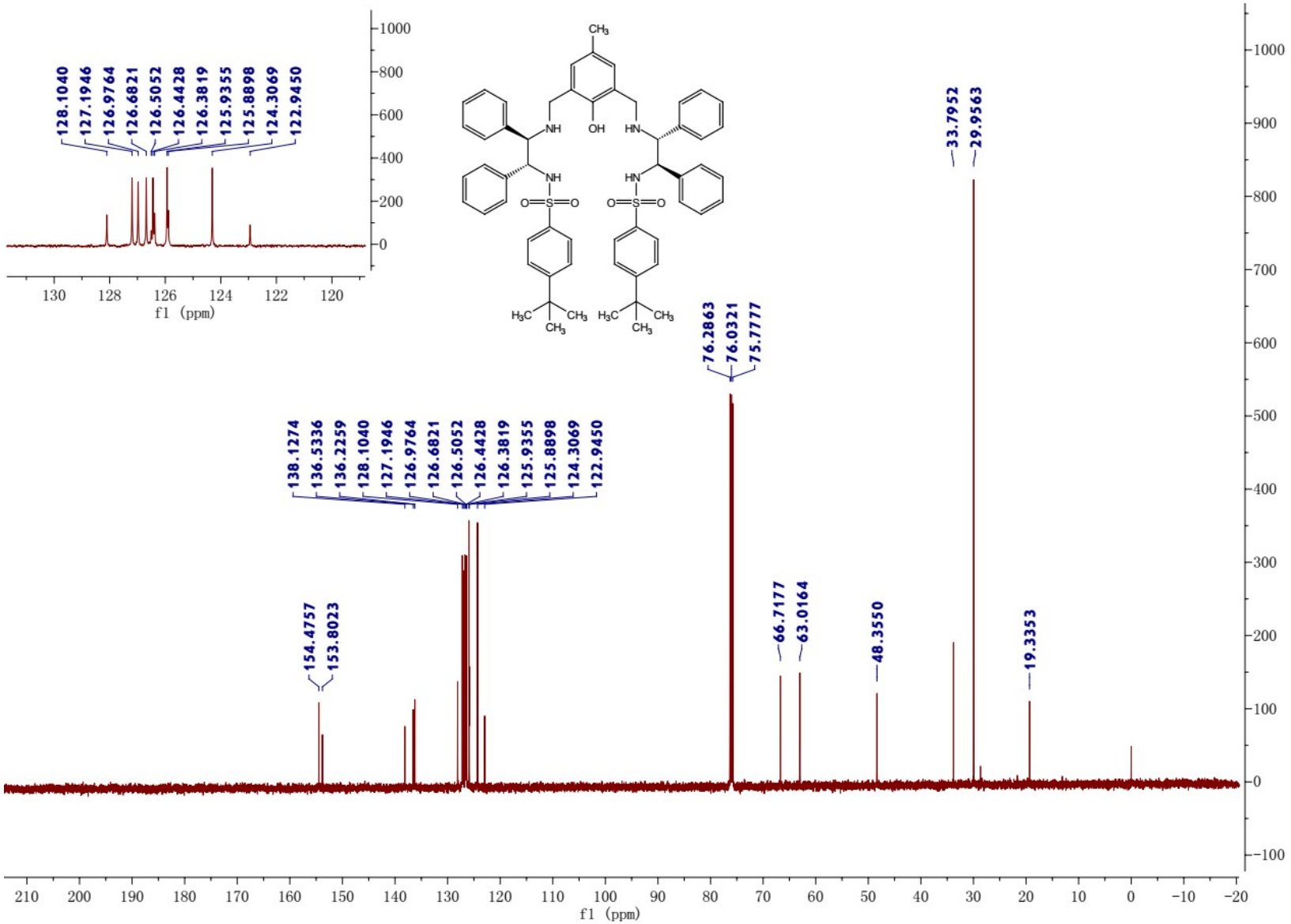
2.02
1.98
3.00
18.09

L2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f1 (ppm)
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NH
OH
HN
O=S=O
H3C
CH3
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136.2259
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127.1946
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126.4428
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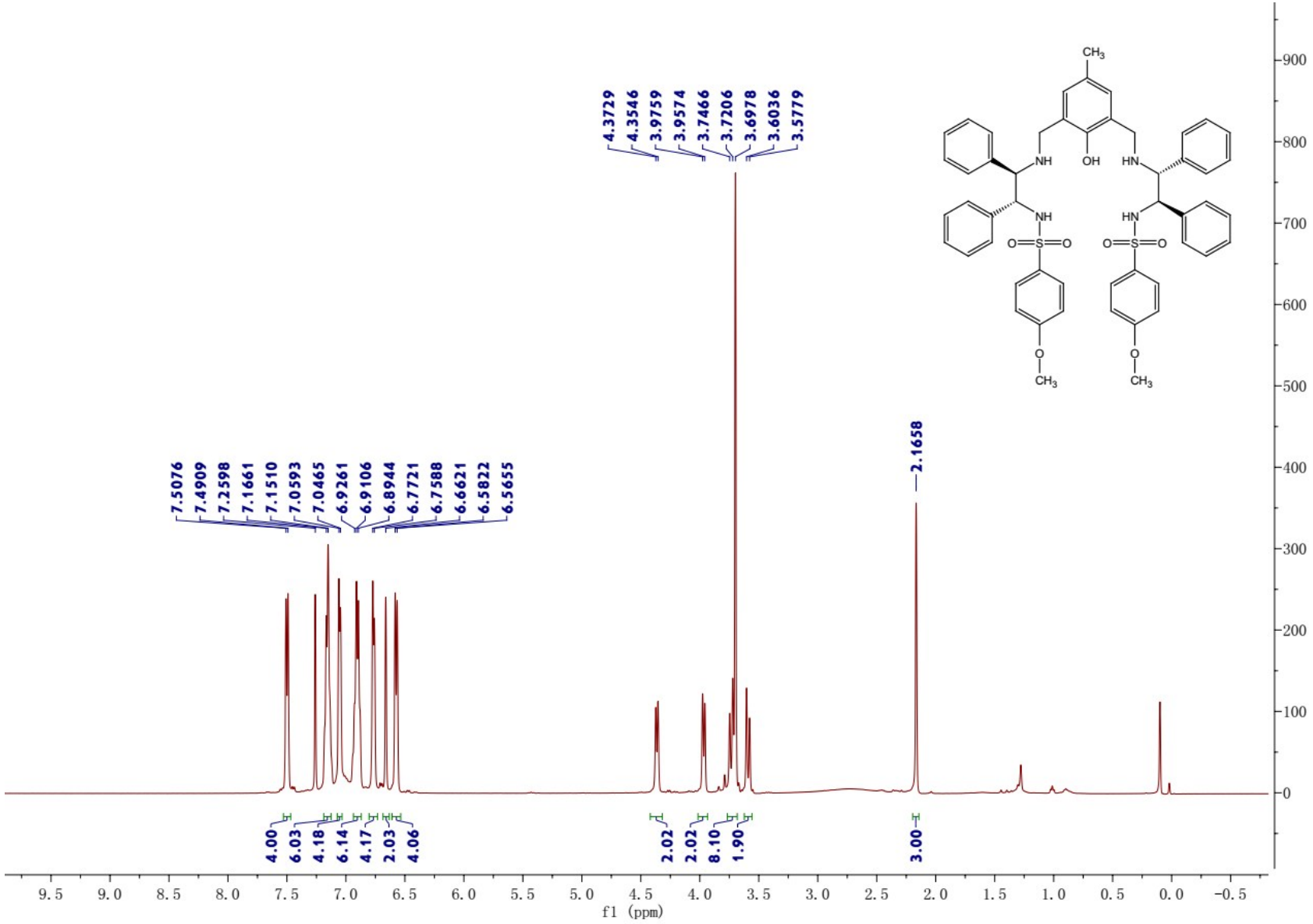
f1 (ppm)

L3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6.7588
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2.03
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2.02
2.02
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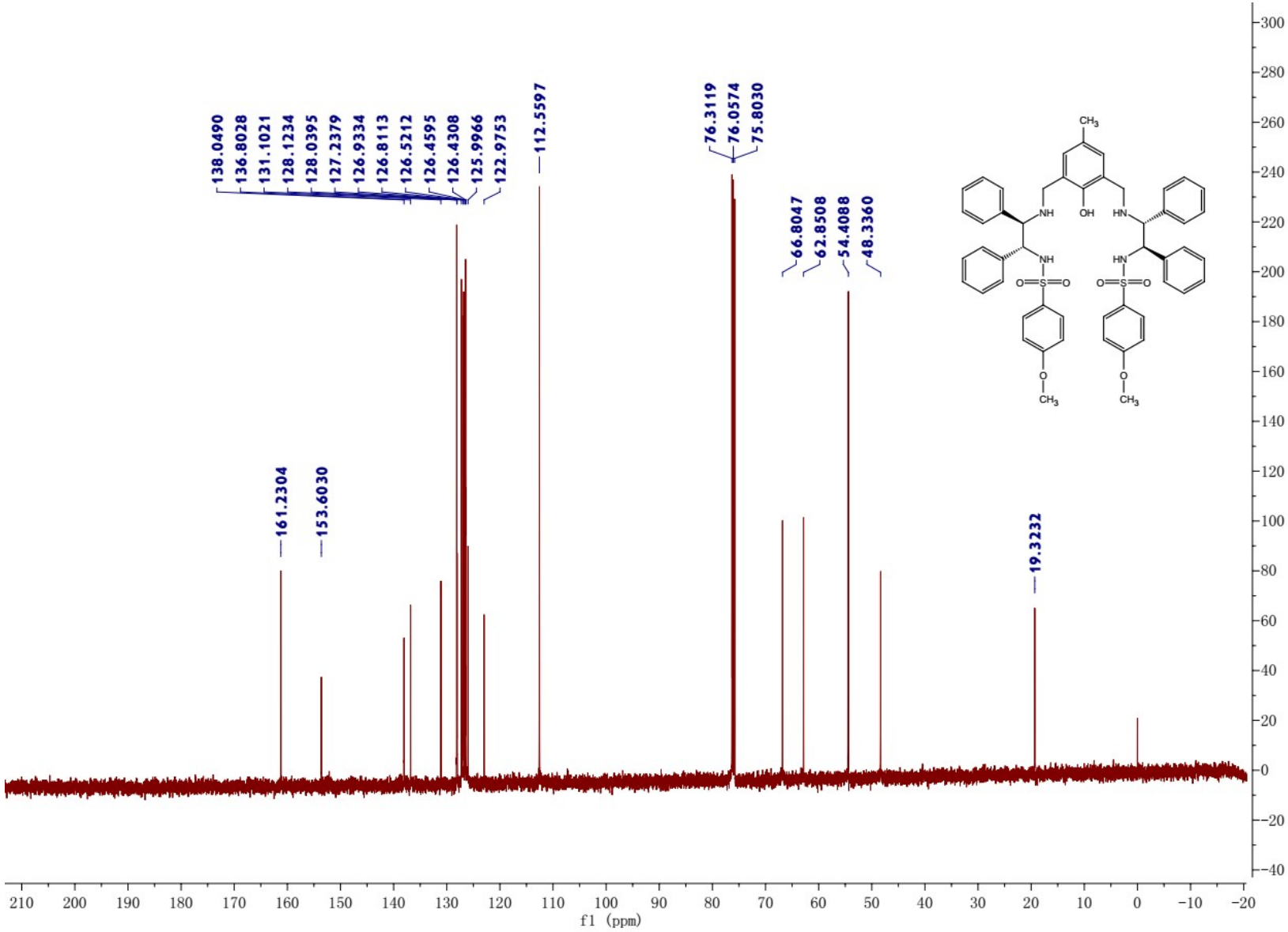
f1 (ppm)

L3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126.4308
125.9966
122.9753
112.5597
76.3119
76.0574
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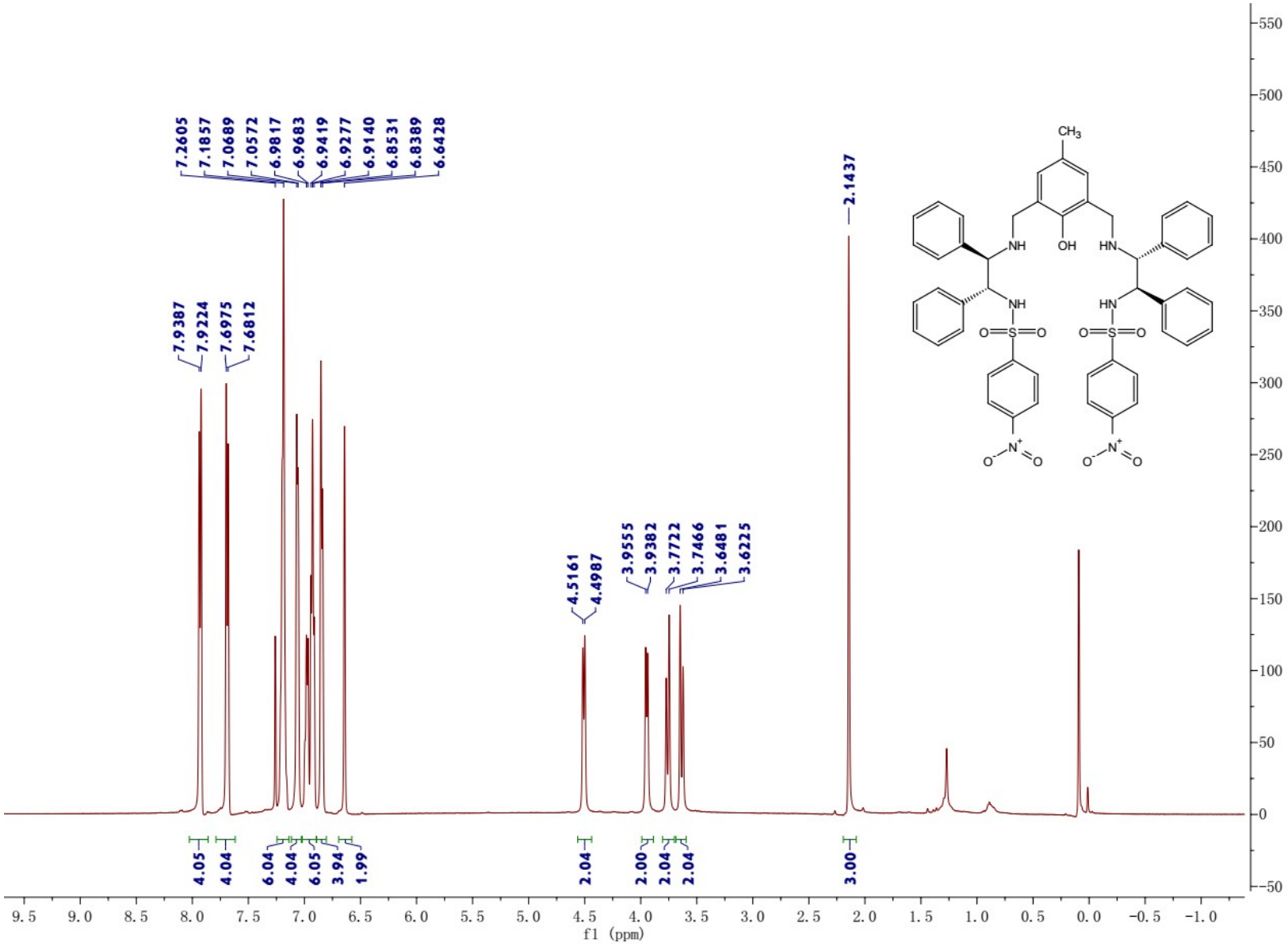
f1 (ppm)

L4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7.9224
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7.6812
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4.4987
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3.9382
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3.7466
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3.6225
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4.05
4.04
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4.04
6.05
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2.04
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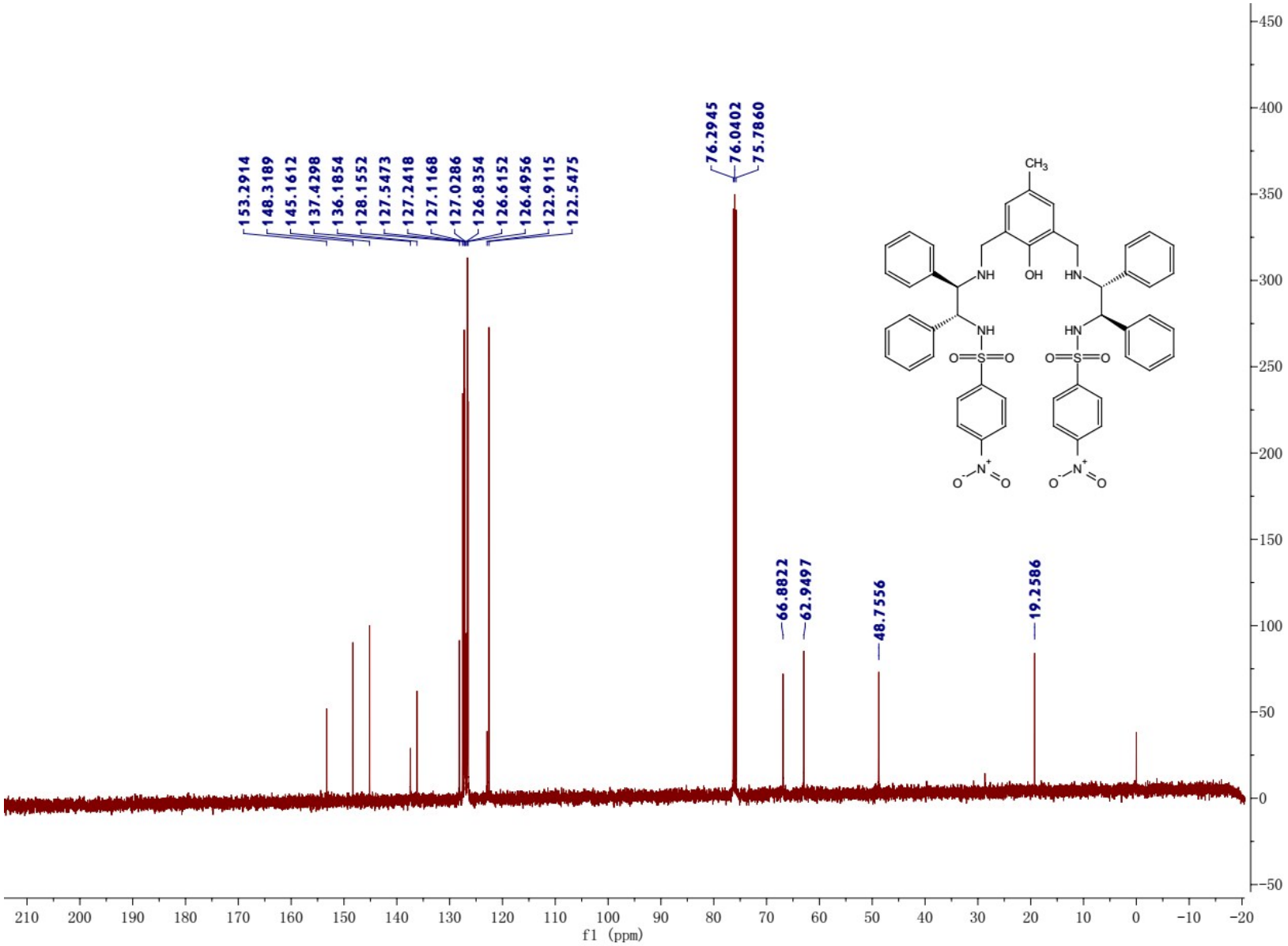
2.04
2.04
3.00
f1 (ppm)

L4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122.5475
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76.0402
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HN
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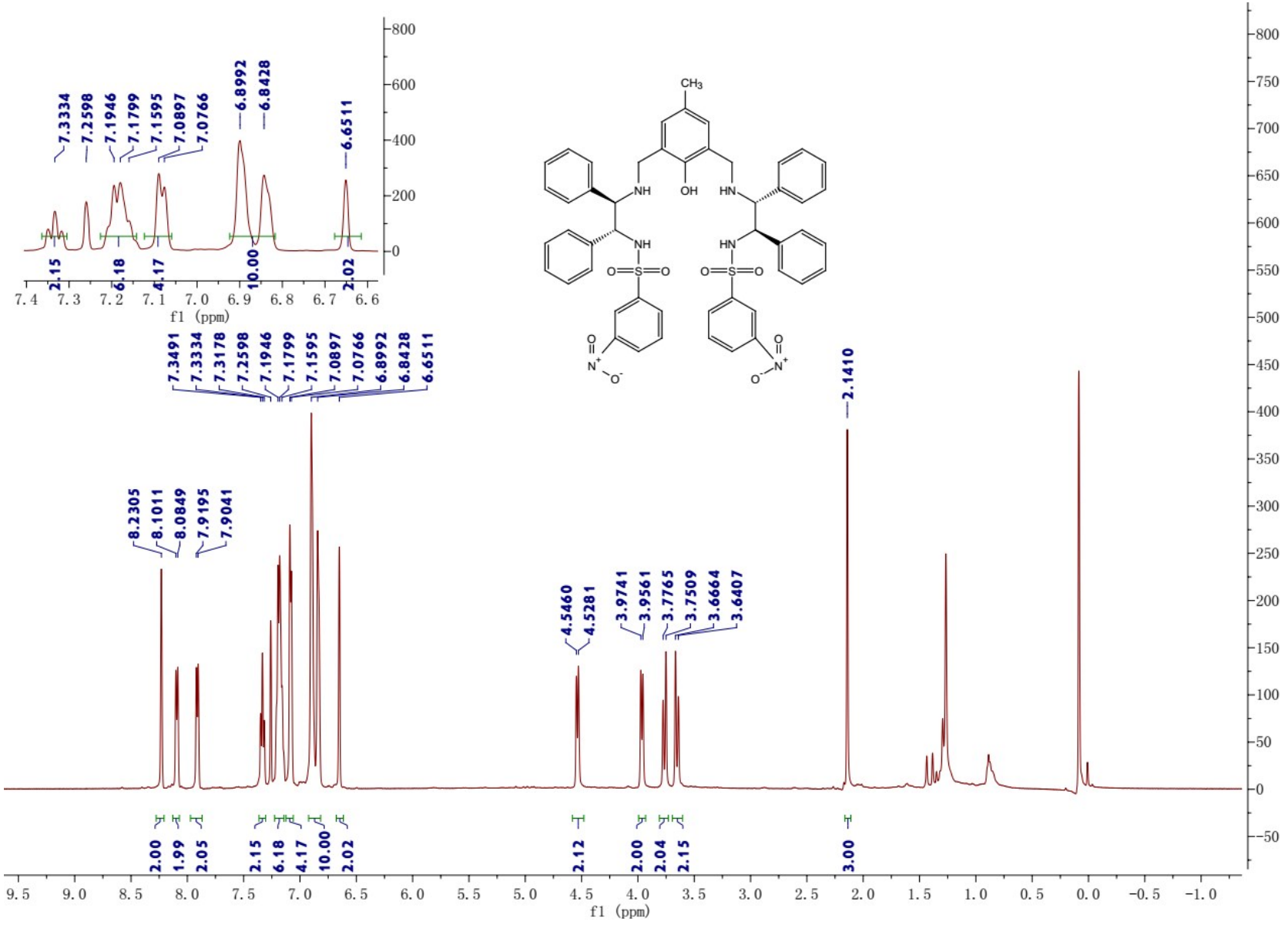
O=S=O
f1 (ppm)

L5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f1 (ppm)
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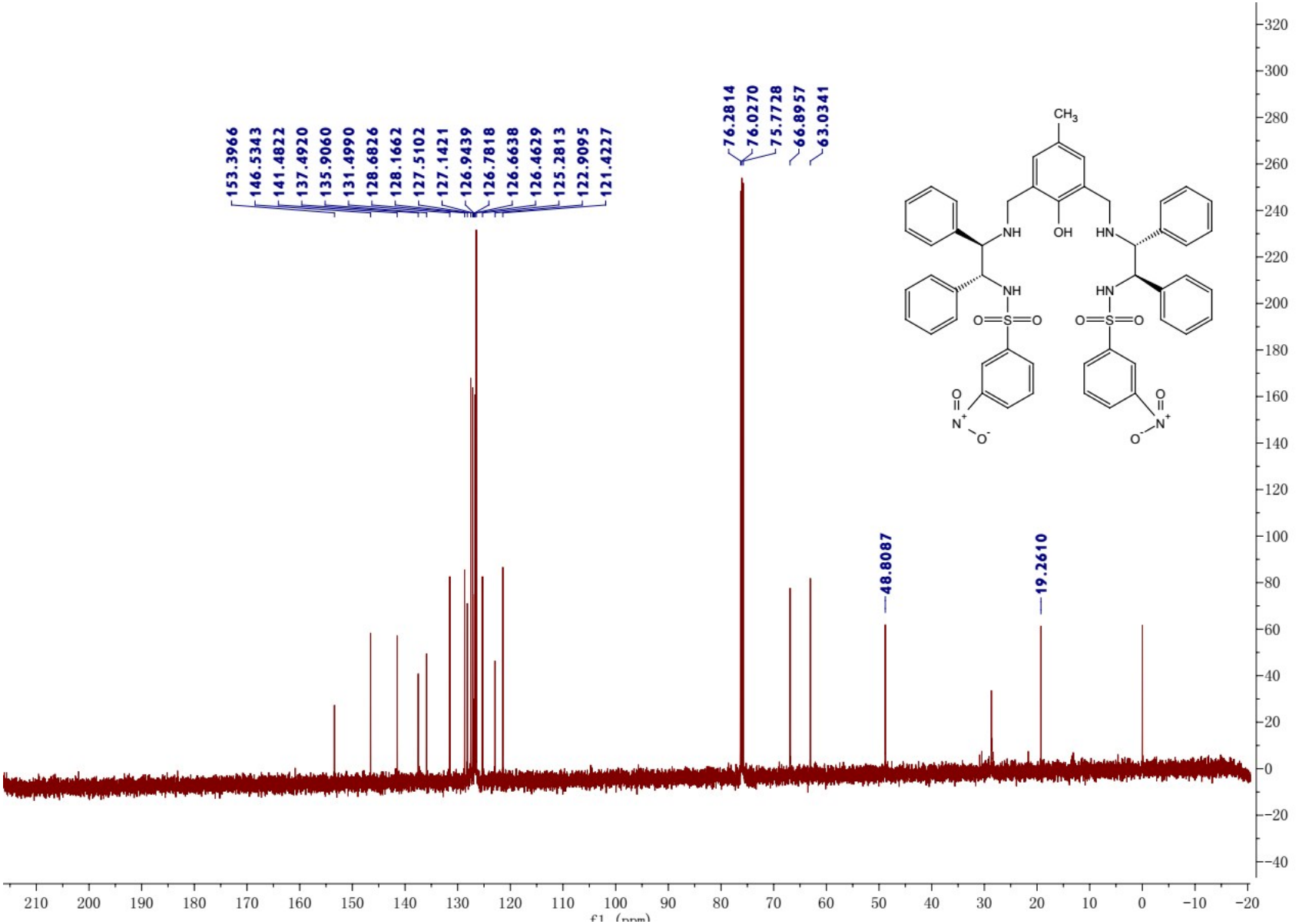
3.00
f1 (ppm)

L5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OH
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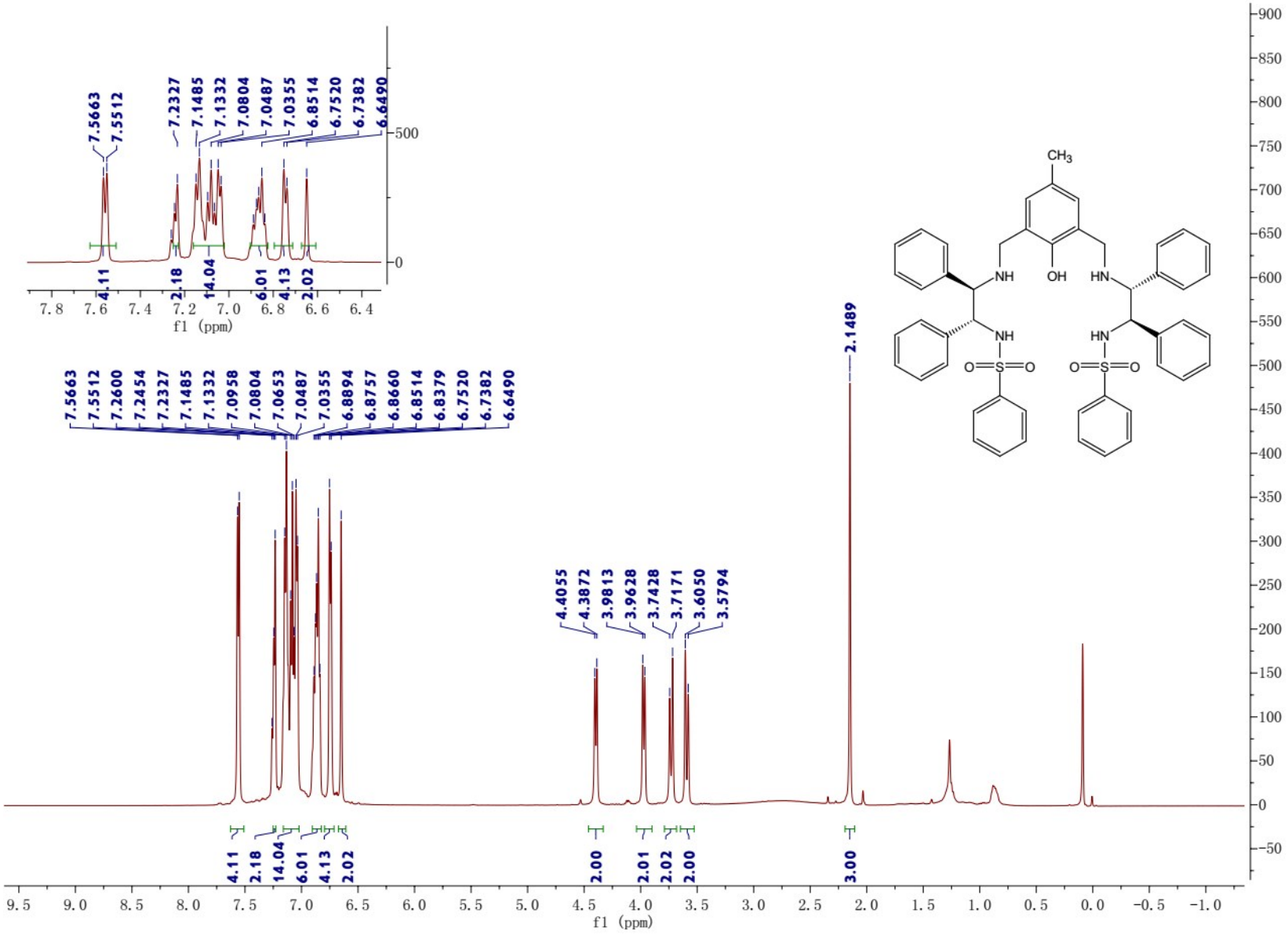
O=S=O
N+
O-
f1 (ppm)

L6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6.6490
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3.9628
3.7428
3.7171
3.6050
3.5794
2.1489
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14.04
6.01
4.13
2.02
2.00
2.01
2.02
2.00
3.00
f1 (ppm)
CH3
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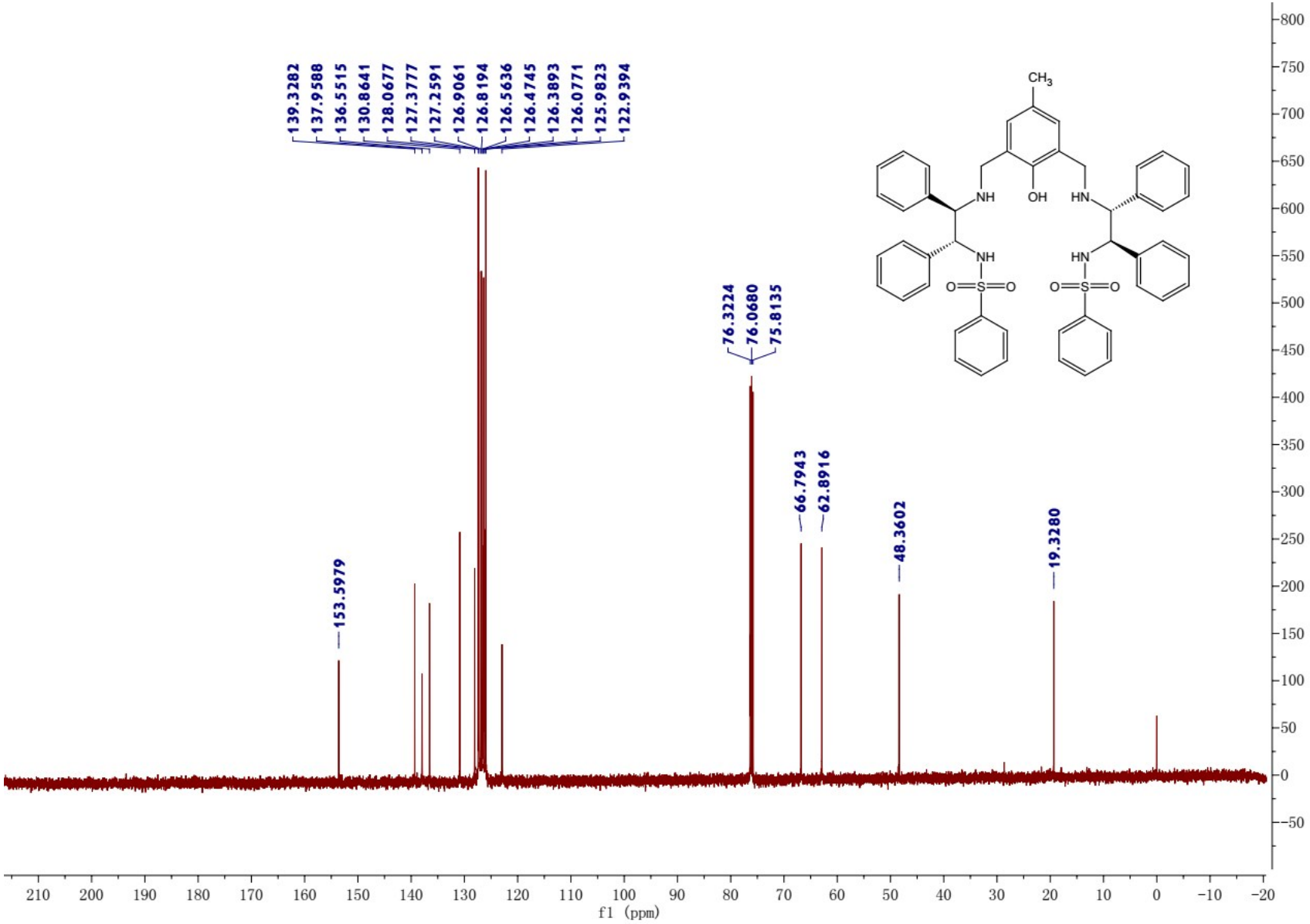
OH
HN
O=S=O

L6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75.8135
66.7943
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CH3
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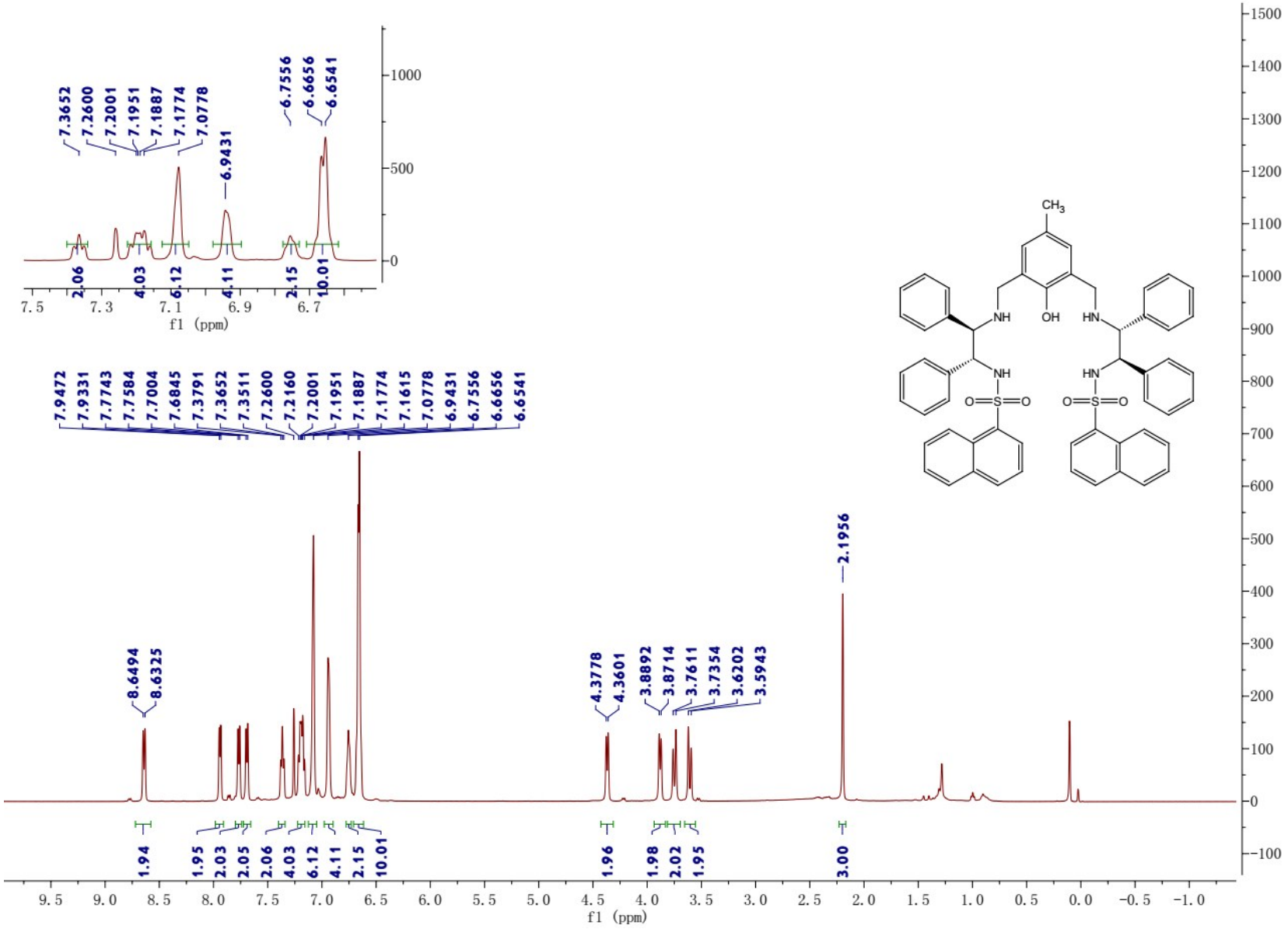
OH
HN
NH
HN
O=S=O
O=S=O
f1 (ppm)

L7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6.6541
2.06
4.03
6.12
4.11
2.15
10.01
f1 (ppm)
CH3
NH
OH
HN
O=S=O
8.6494
8.6325
4.3778
4.3601
3.8892
3.8714
3.7611
3.7354
3.6202
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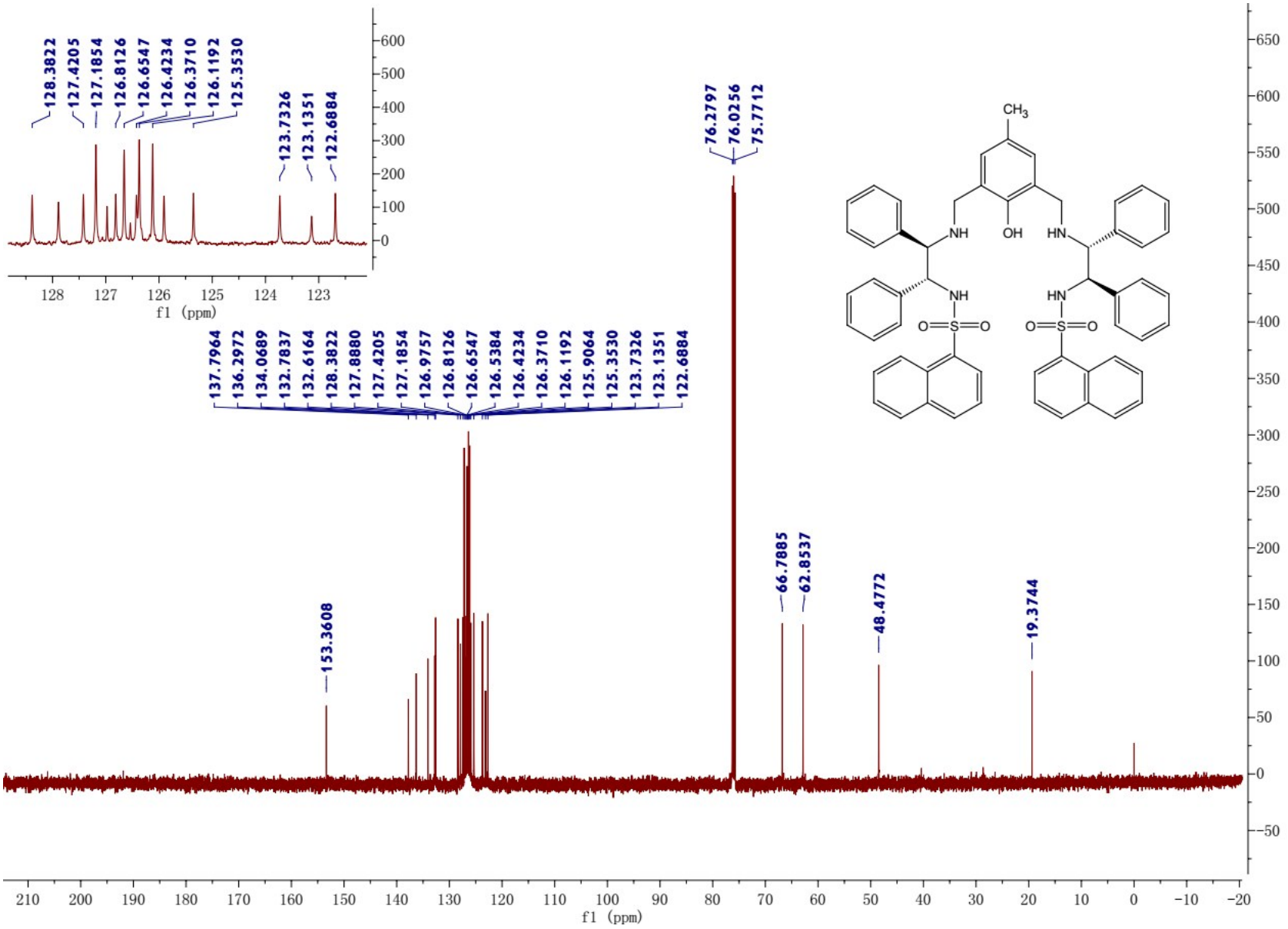
2.02
1.95
3.00
f1 (ppm)

L7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f1 (ppm)
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132.7837
132.6164
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127.4205
127.1854
126.9757
126.8126
126.6547
126.5384
126.4234
126.3710
126.1192
125.9064
125.3530
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123.1351
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75.7712
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66.7885
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OH
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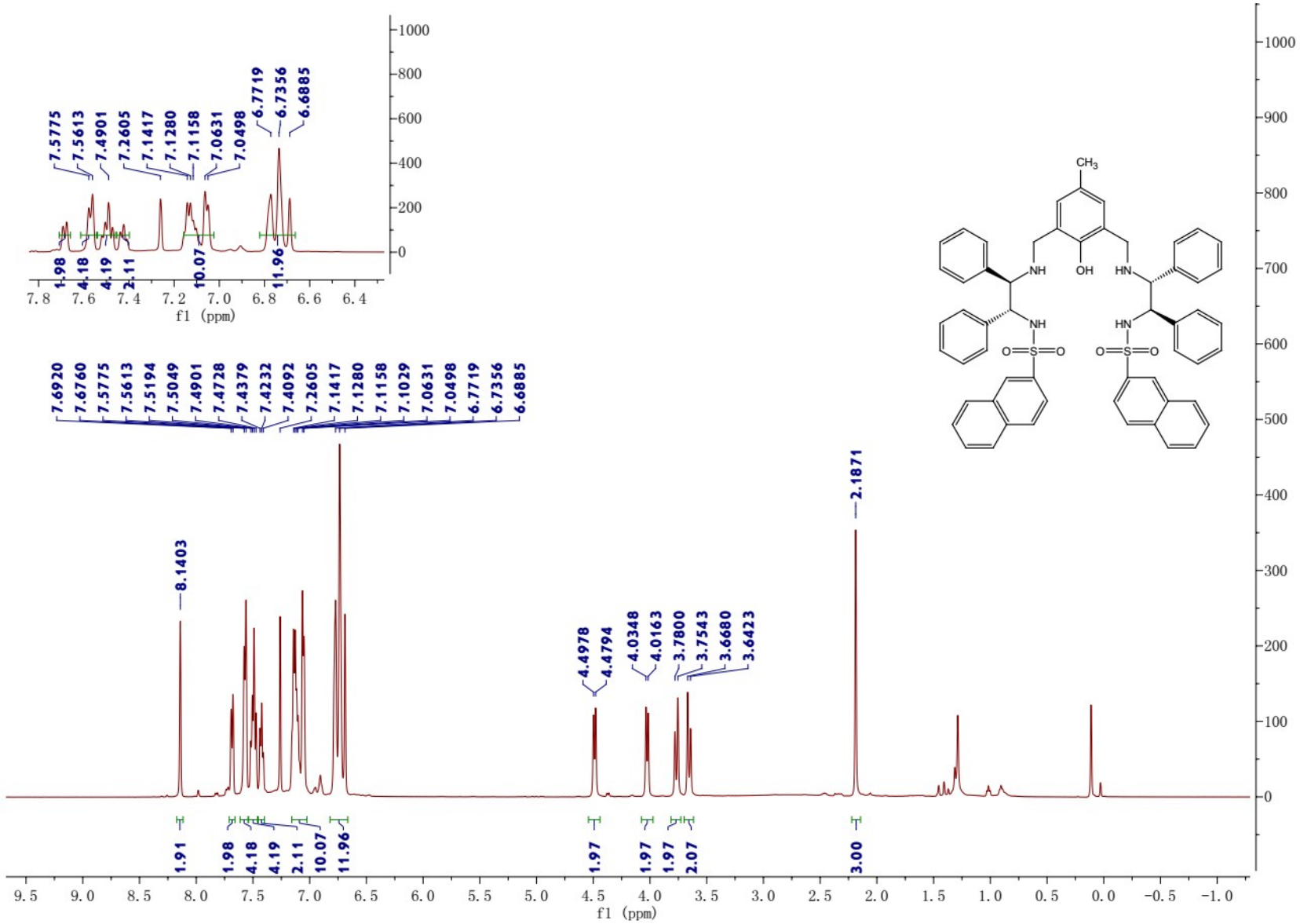
NH
HN
O=S=O
O=S=O
f1 (ppm)

L8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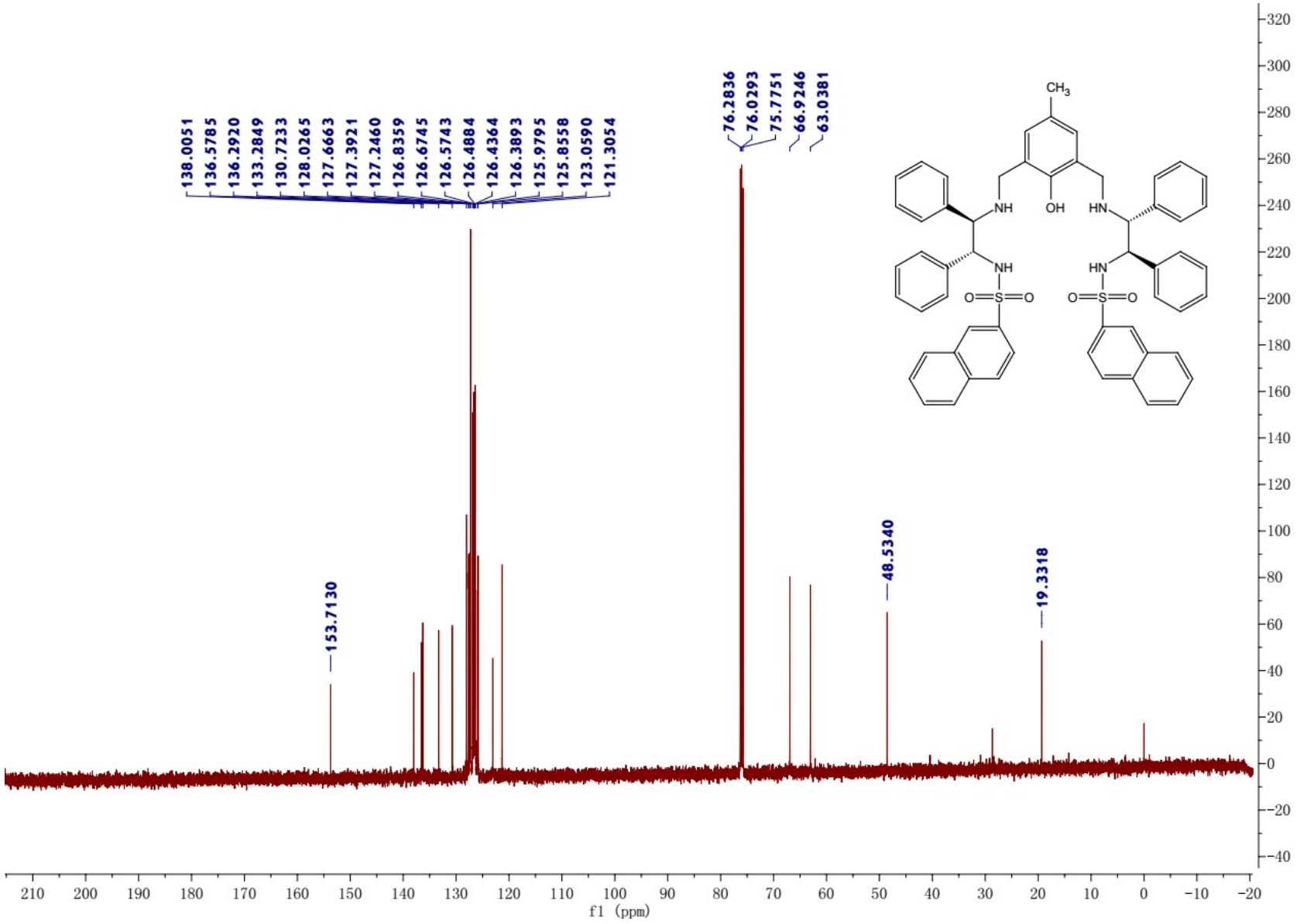
7.2605
7.1417
7.1280
7.1158
7.0631
7.0498
1.98
4.18
4.19
2.11
10.07
11.96
f1 (ppm)
CH3
NH
OH
HN
O=S=O
8.1403
2.1871
4.4978
4.4794
4.0348
4.0163
3.7800
3.7543
3.6680
3.6423
1.91
1.98
4.18
4.19
2.11
10.07
11.96
1.97
1.97
1.97
2.07
3.00
f1 (ppm)

L8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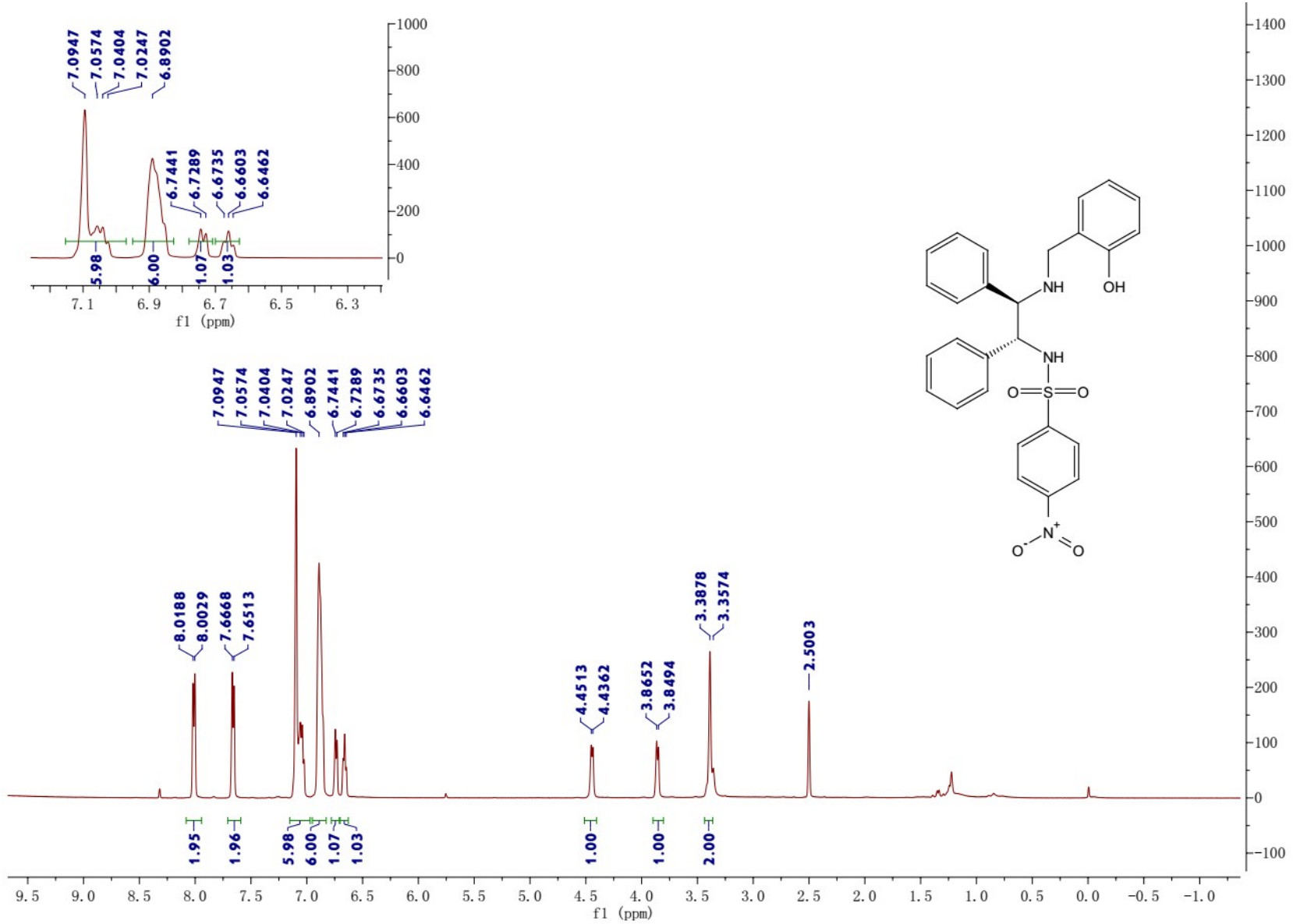
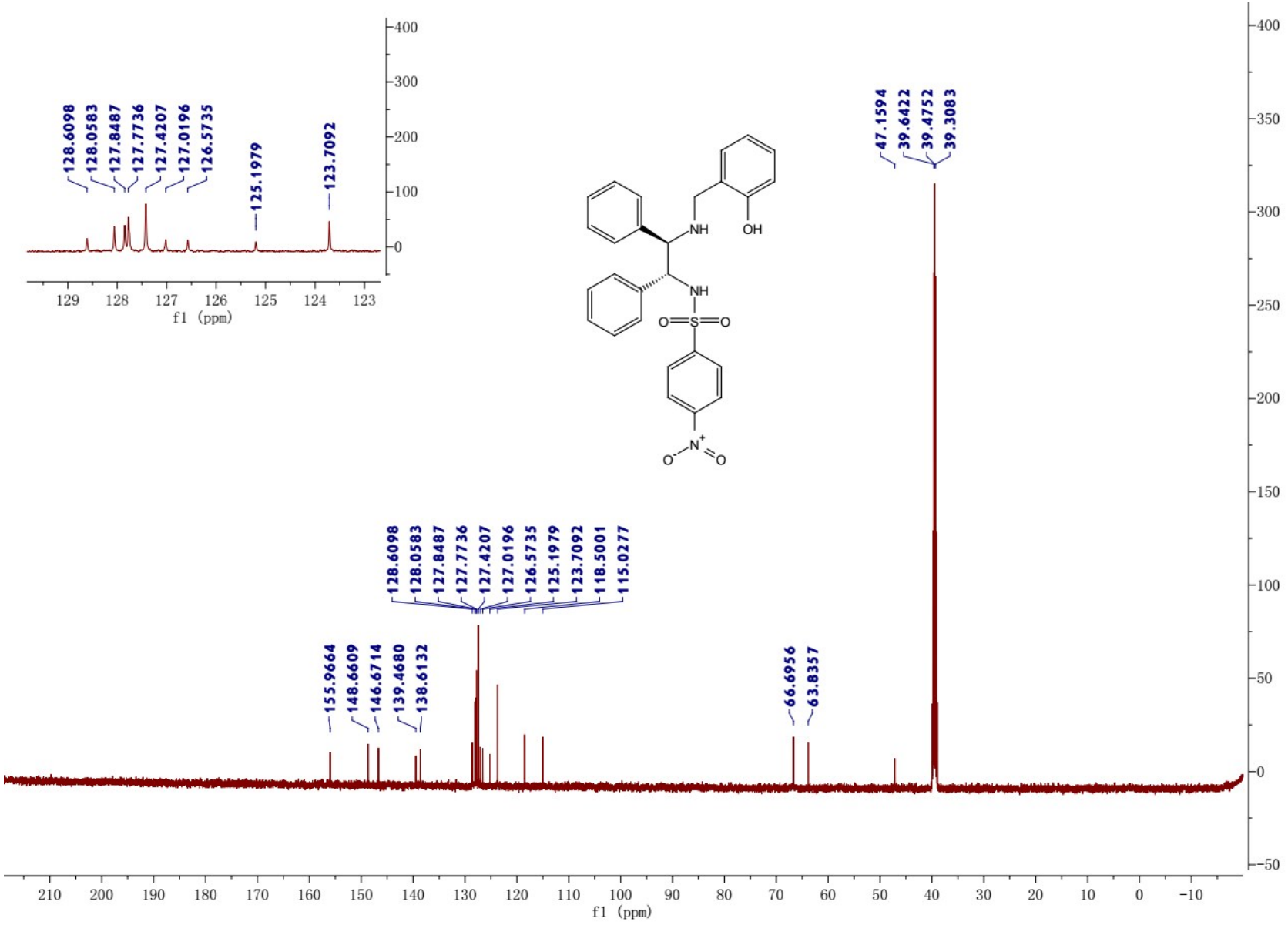
136.5785
136.2920
133.2849
130.7233
128.0265
127.6663
127.3921
127.2460
126.8359
126.6745
126.5743
126.4884
126.4364
126.3893
125.9795
125.8558
123.0590
121.3054
76.2836
76.0293
75.7751
66.9246
63.0381
153.7130
48.5340
19.3318
CH3
NH
OH
HN
NH
HN
O=S=O
O=S=O
f1 (ppm)

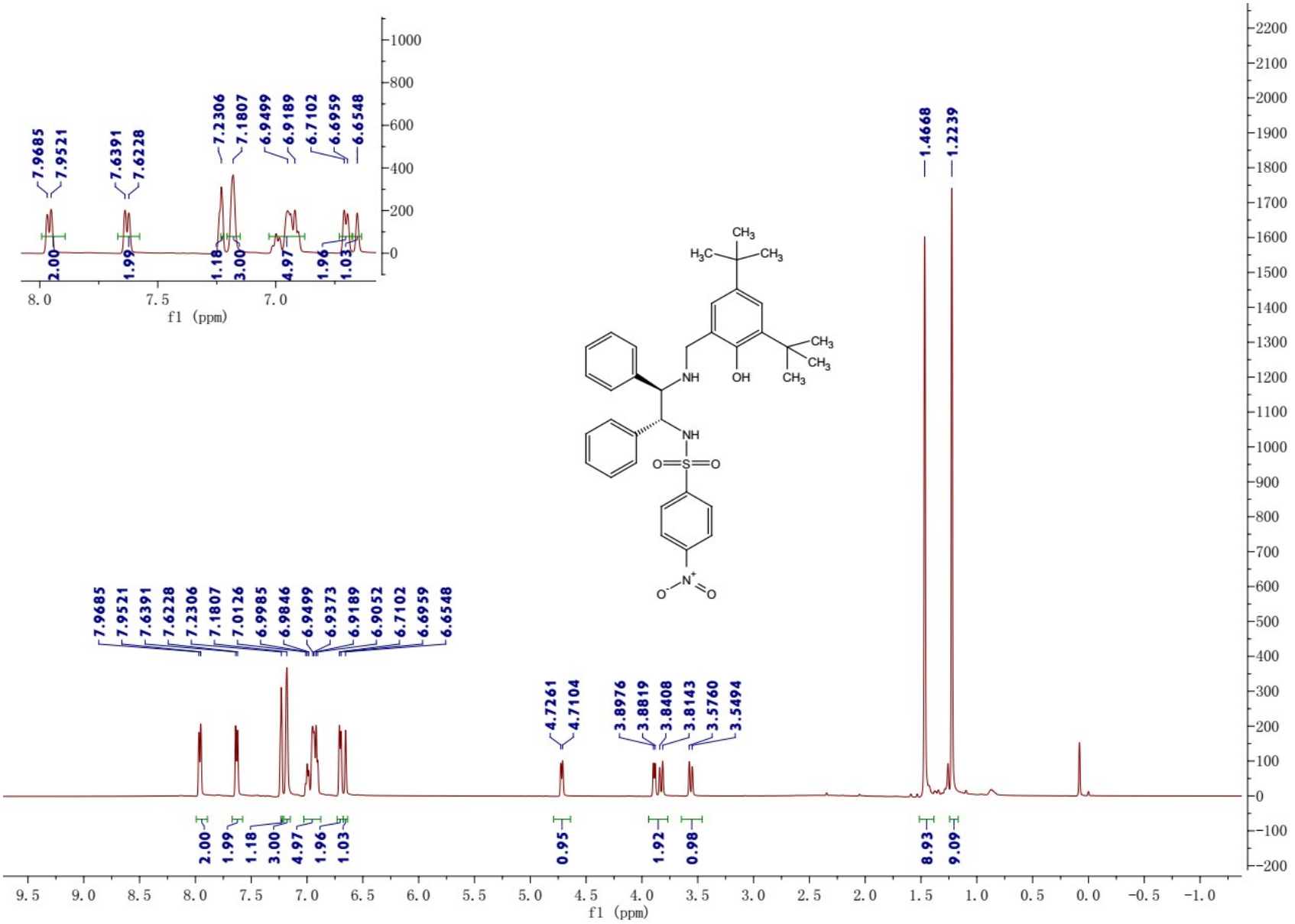
L9


7.0947
7.0574
7.0404
7.0247
6.8902
6.7441
6.7289
6.6735
6.6603
6.6462
5.98
6.00
1.07
1.03
f1 (ppm)
8.0188
8.0029
7.6668
7.6513
4.4513
4.4362
3.8652
3.8494
3.3878
3.3574
2.5003
1.95
1.96
1.00
1.00
2.00
NH
OH
NH
O=S=O
O
N+
O
f1 (ppm)

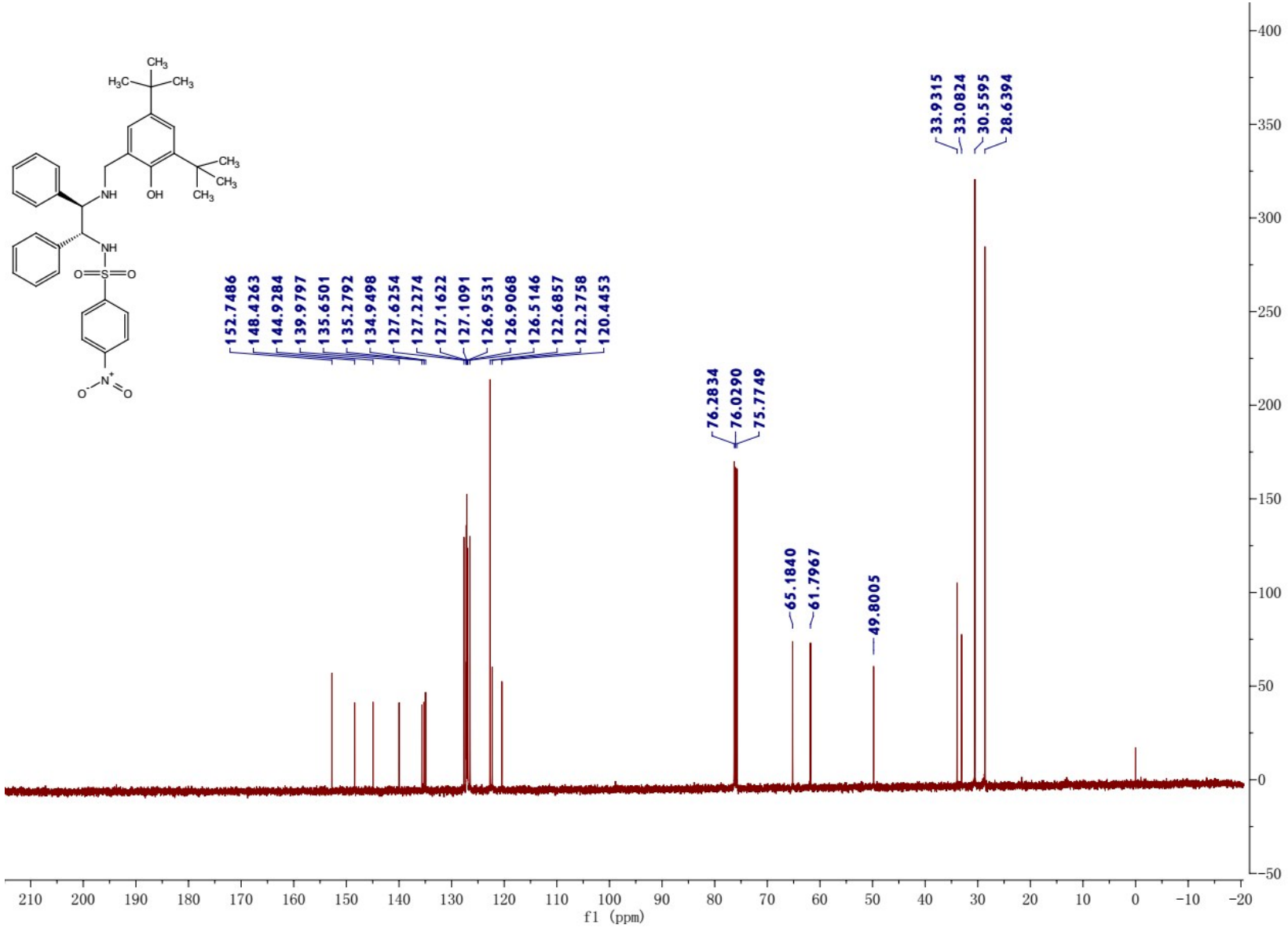
L9


128.6098
128.0583
127.8487
127.7736
127.4207
127.0196
126.5735
125.1979
123.7092
f1 (ppm)
NH
OH
NH
O=S=O
O
N+
O
47.1594
39.6422
39.4752
39.3083
128.6098
128.0583
127.8487
127.7736
127.4207
127.0196
126.5735
125.1979
123.7092
118.5001
115.0277
155.9664
148.6609
146.6714
139.4680
138.6132
66.6956
63.8357
f1 (ppm)

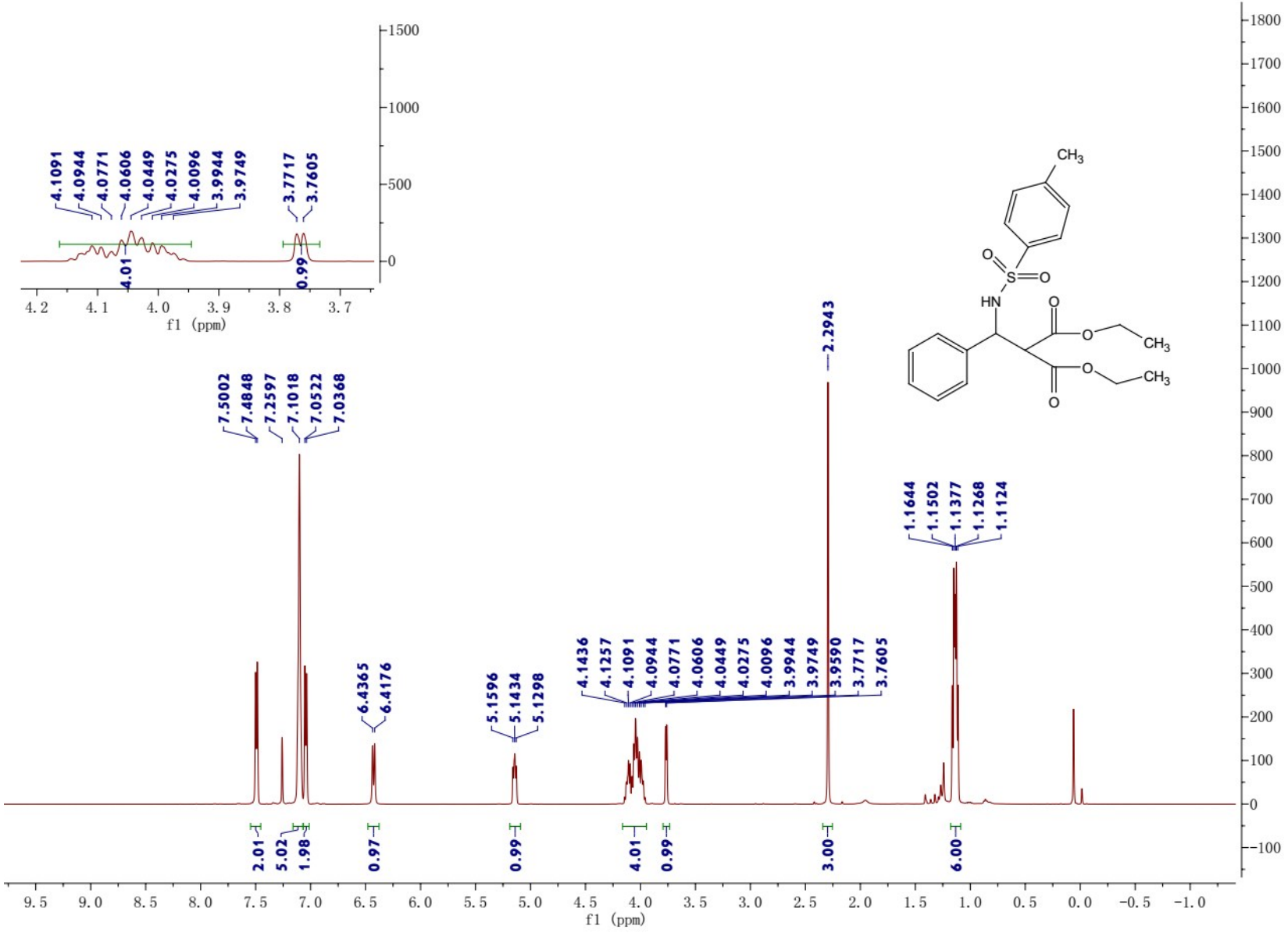
L10


7.9685
7.9521
7.6391
7.6228
7.2306
7.1807
6.9499
6.9189
6.7102
6.6959
6.6548
2.00
1.99
1.18
3.00
4.97
1.96
1.03
f1 (ppm)
CH3
H3C
CH3
CH3
CH3
CH3
NH
OH
NH
O=S=O
O
N+
O
7.0126
6.9985
6.9846
6.9373
6.9052
4.7261
4.7104
3.8976
3.8819
3.8408
3.8143
3.5760
3.5494
1.4668
1.2239
0.95
1.92
0.98
8.93
9.09

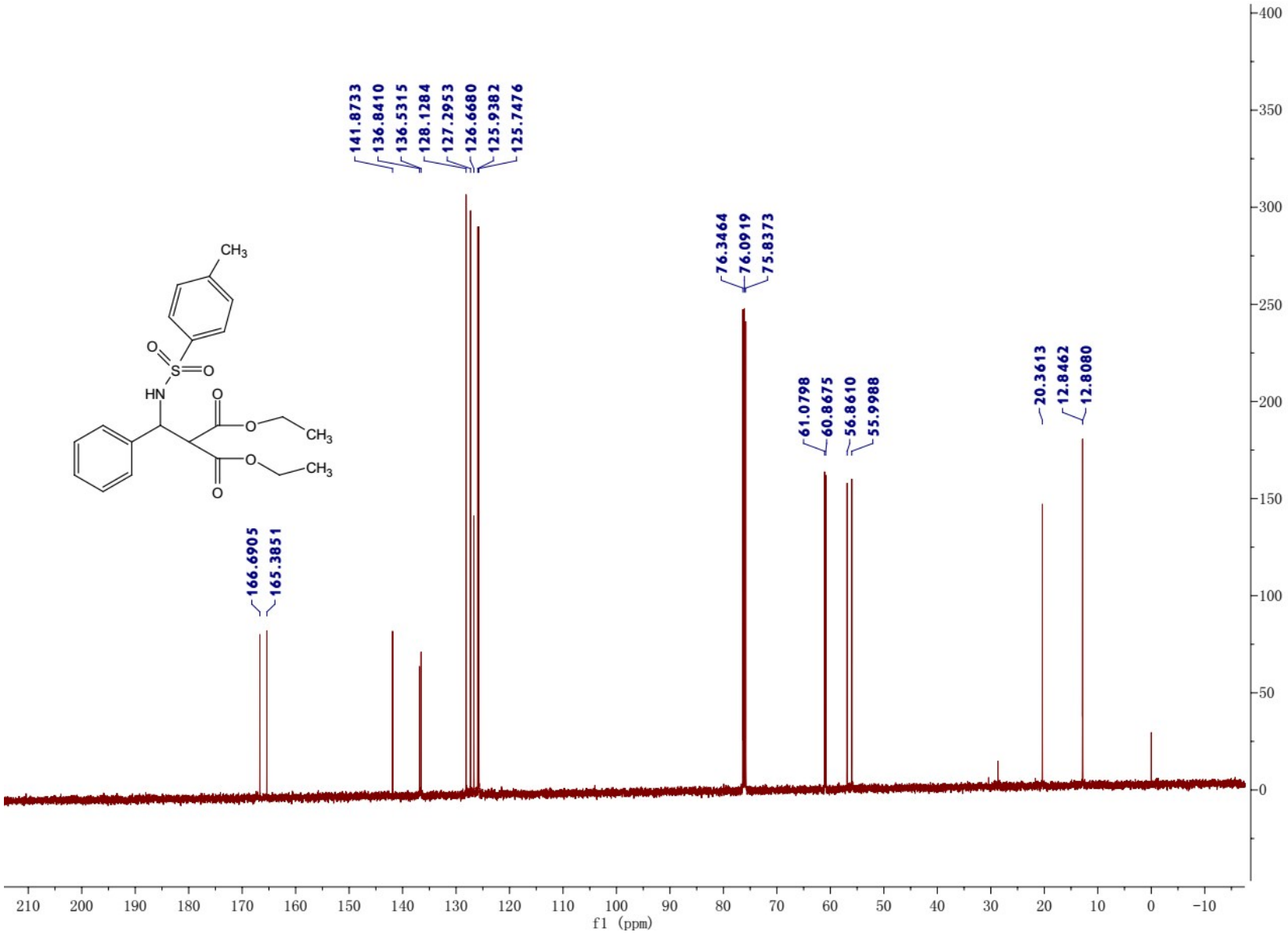
L10


152.7486
148.4263
144.9284
139.9797
135.6501
135.2792
134.9498
127.6254
127.2274
127.1622
127.1091
126.9531
126.9068
126.5146
122.6857
122.2758
120.4453
76.2834
76.0290
75.7749
65.1840
61.7967
49.8005
33.9315
33.0824
30.5595
28.6394
f1 (ppm)

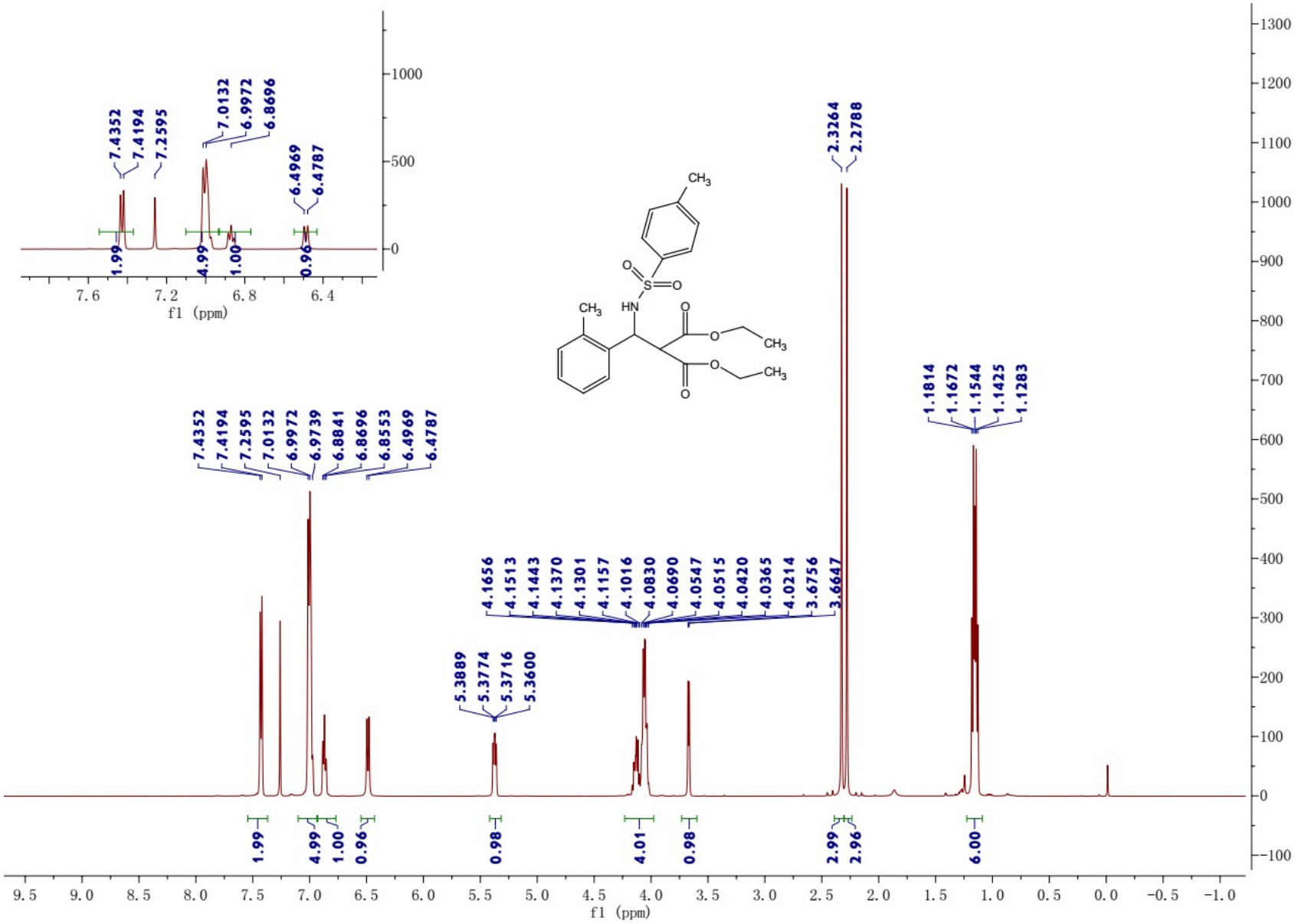
2a


4.1091
4.0944
4.0771
4.0606
4.0449
4.0275
4.0096
3.9944
3.9749
3.7717
3.7605
4.01
0.99
f1 (ppm)
7.5002
7.4848
7.2597
7.1018
7.0522
7.0368
6.4365
6.4176
5.1596
5.1434
5.1298
4.1436
4.1257
4.1091
4.0944
4.0771
4.0606
4.0449
4.0275
4.0096
3.9944
3.9749
3.9590
3.7717
3.7605
2.2943
1.1644
1.1502
1.1377
1.1268
1.1124
2.01
5.02
1.98
0.97
0.99
4.01
0.99
3.00
6.00
f1 (ppm)
CH3
HN
O
S
O
O
O
O
CH3
O
CH3

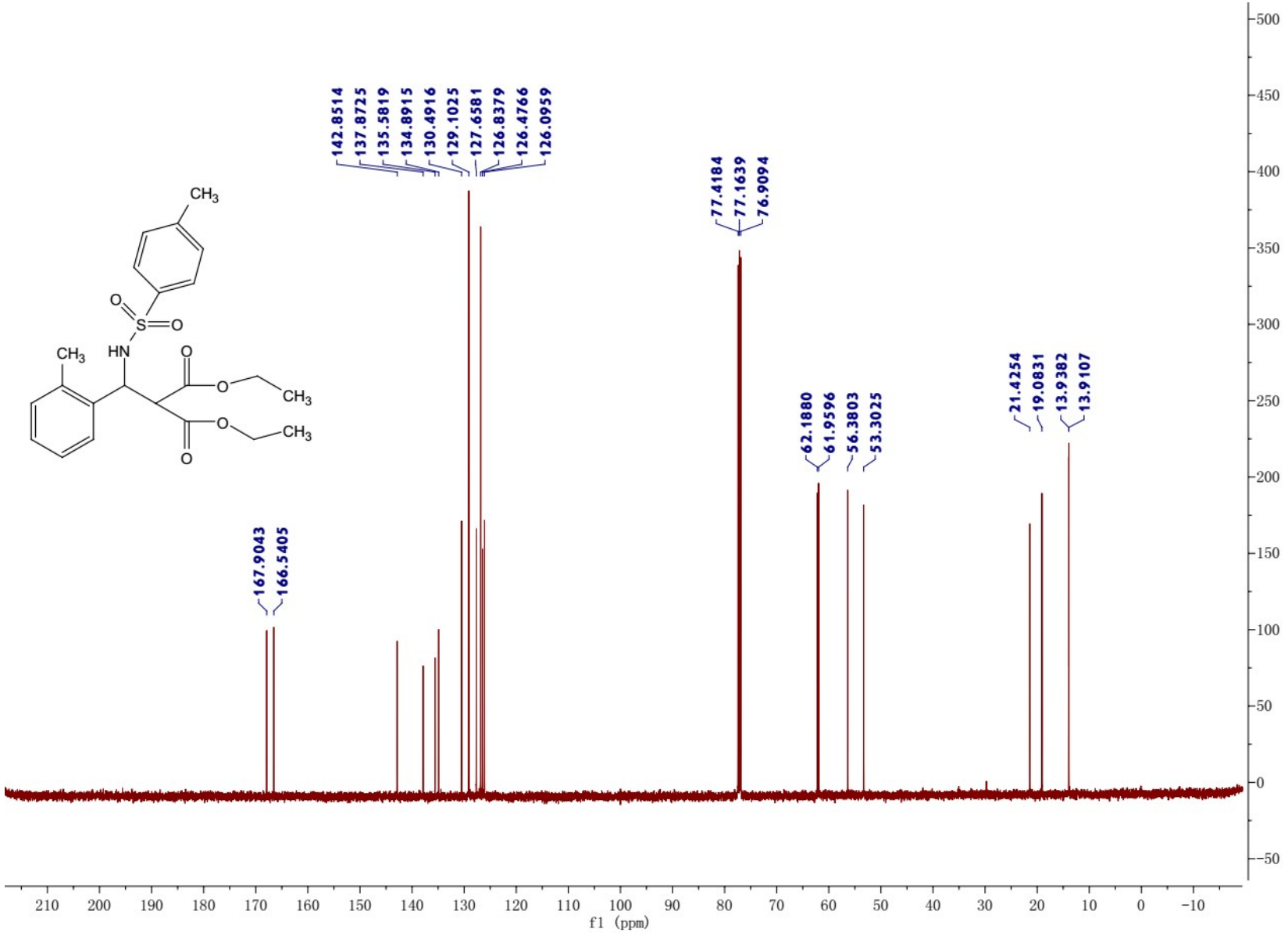
2a


141.8733
136.8410
136.5315
128.1284
127.2953
126.6680
125.9382
125.7476
76.3464
76.0919
75.8373
61.0798
60.8675
56.8610
55.9988
20.3613
12.8462
12.8080
166.6905
165.3851
CH3
O
S
O
HN
O
O
CH3
O
O
CH3
O
400
350
300
250
200
150
100
50
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

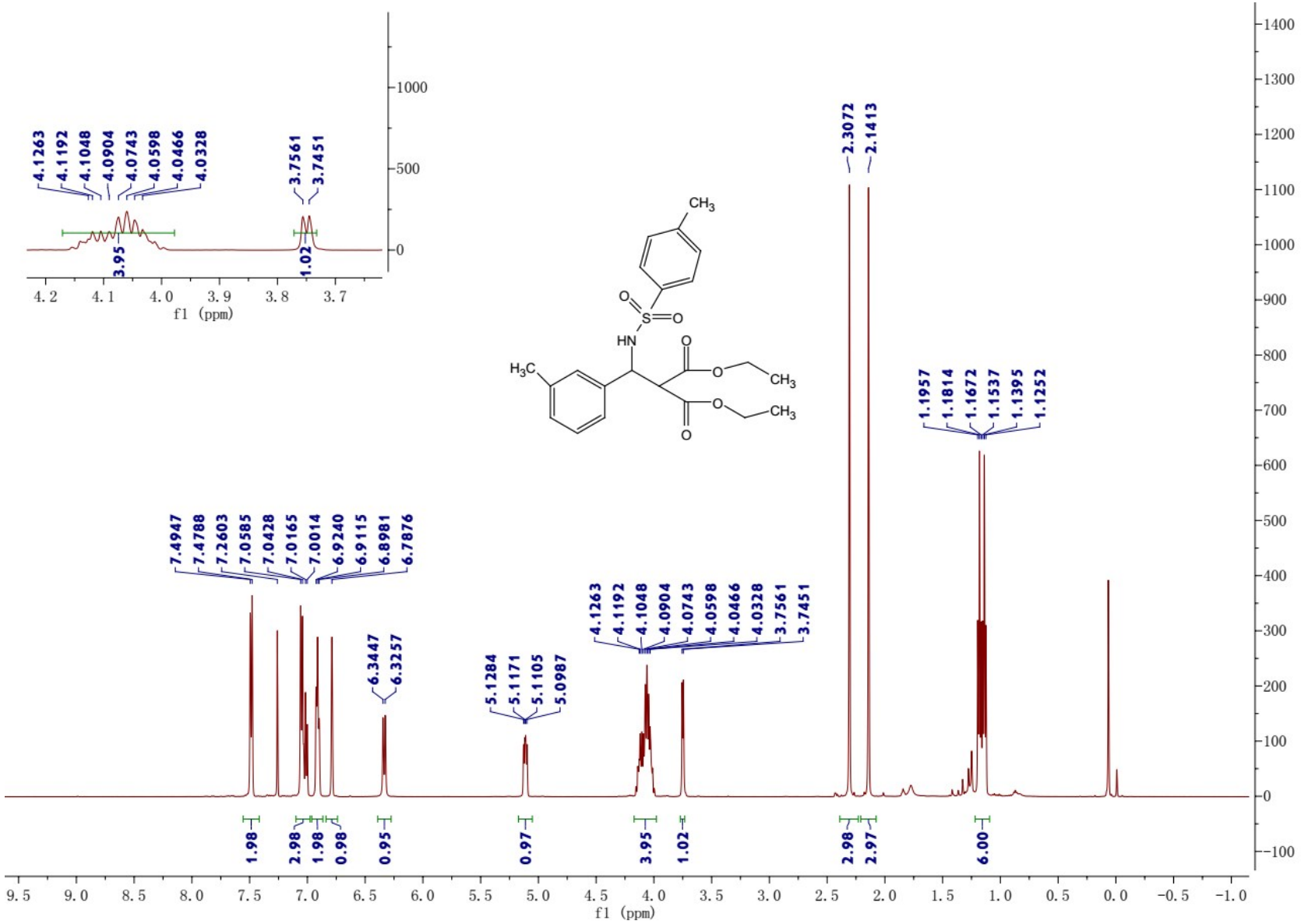
2b


7.4352
7.4194
7.2595
7.0132
6.9972
6.8696
6.4969
6.4787
1.99
4.99
1.00
0.96
f1 (ppm)
CH3
O
S
O
HN
CH3
O
O
CH3
O
O
CH3
2.3264
2.2788
1.1814
1.1672
1.1544
1.1425
1.1283
6.9739
6.8841
6.8553
4.1656
4.1513
4.1443
4.1370
4.1301
4.1157
4.1016
4.0830
4.0690
4.0547
4.0515
4.0420
4.0365
4.0214
3.6756
3.6647
5.3889
5.3774
5.3716
5.3600
1.99
4.99
1.00
0.96
0.98
4.01
0.98
2.99
2.96
6.00
f1 (ppm)

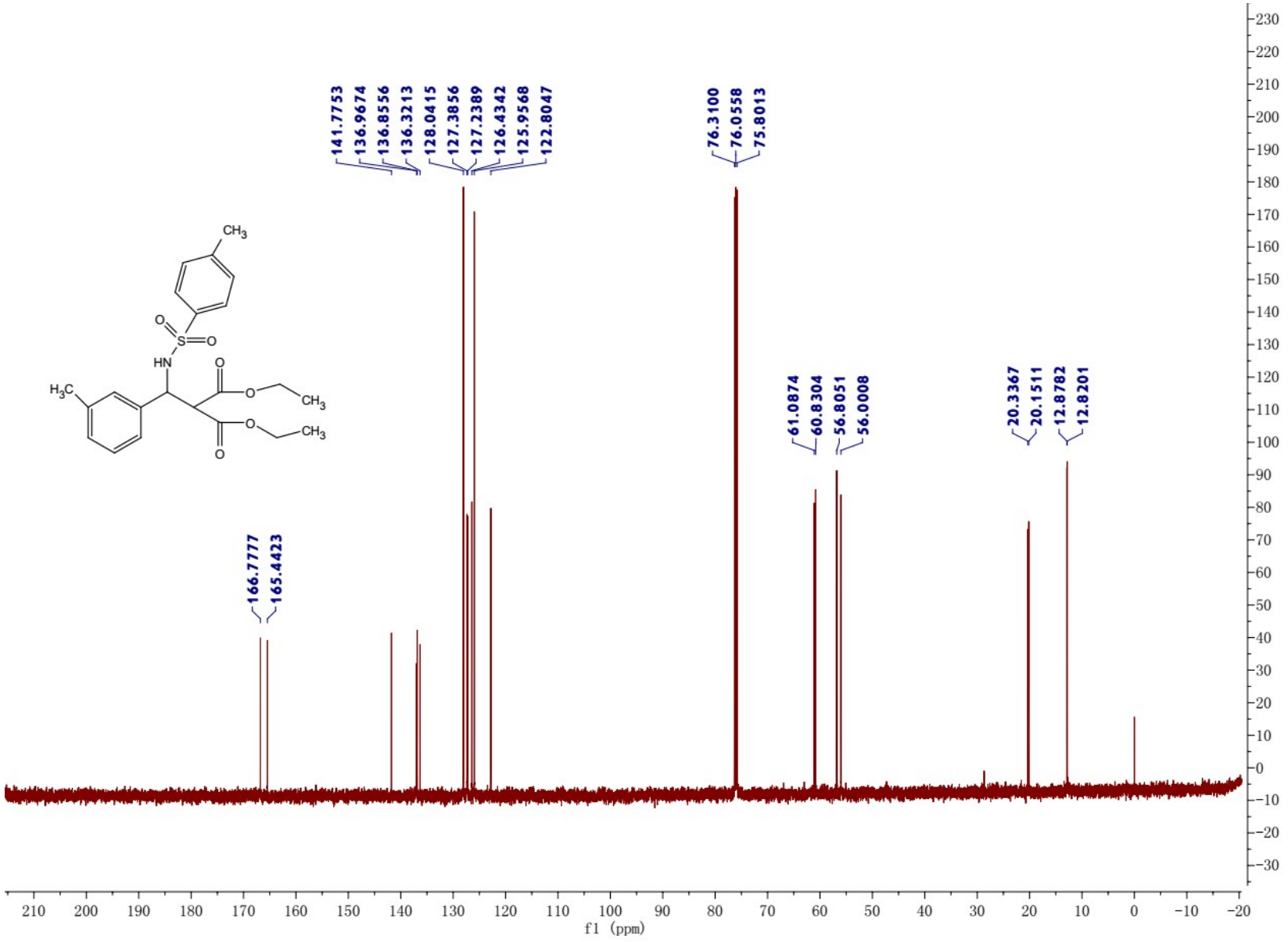
2b


142.8514
137.8725
135.5819
134.8915
130.4916
129.1025
127.6581
126.8379
126.4766
126.0959
77.4184
77.1639
76.9094
62.1880
61.9596
56.3803
53.3025
21.4254
19.0831
13.9382
13.9107
167.9043
166.5405
CH3
HN
O
S
f1 (ppm)

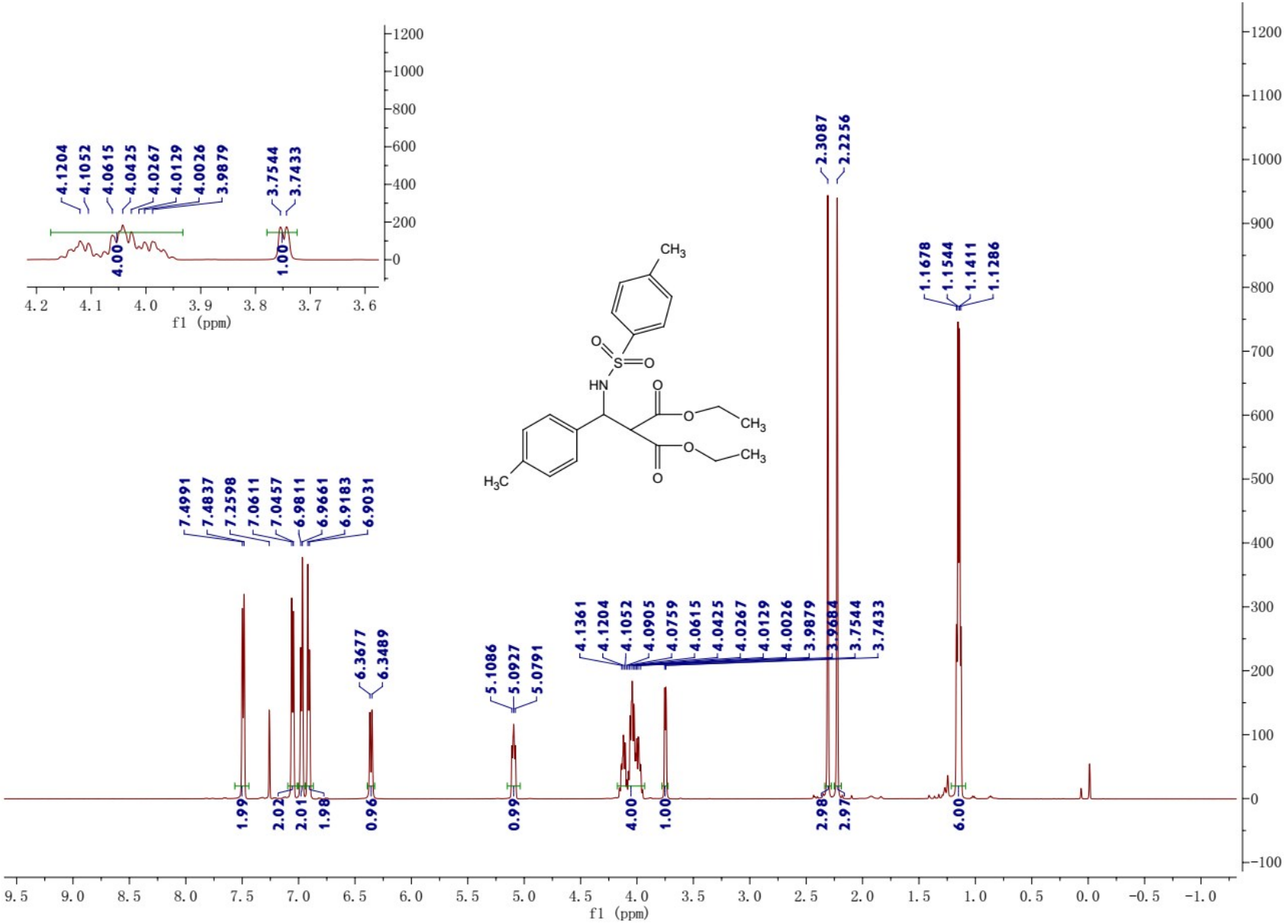
2c


4.1263
4.1192
4.1048
4.0904
4.0743
4.0598
4.0466
4.0328
3.7561
3.7451
3.95
1.02
f1 (ppm)
CH3
O
S
O
HN
O
O
CH3
H3C
O
O
CH3
O
2.3072
2.1413
1.1957
1.1814
1.1672
1.1537
1.1395
1.1252
7.4947
7.4788
7.2603
7.0585
7.0428
7.0165
7.0014
6.9240
6.9115
6.8981
6.7876
6.3447
6.3257
5.1284
5.1171
5.1105
5.0987
1.98
2.98
1.98
0.98
0.95
0.97
3.95
1.02
2.98
2.97
6.00
f1 (ppm)

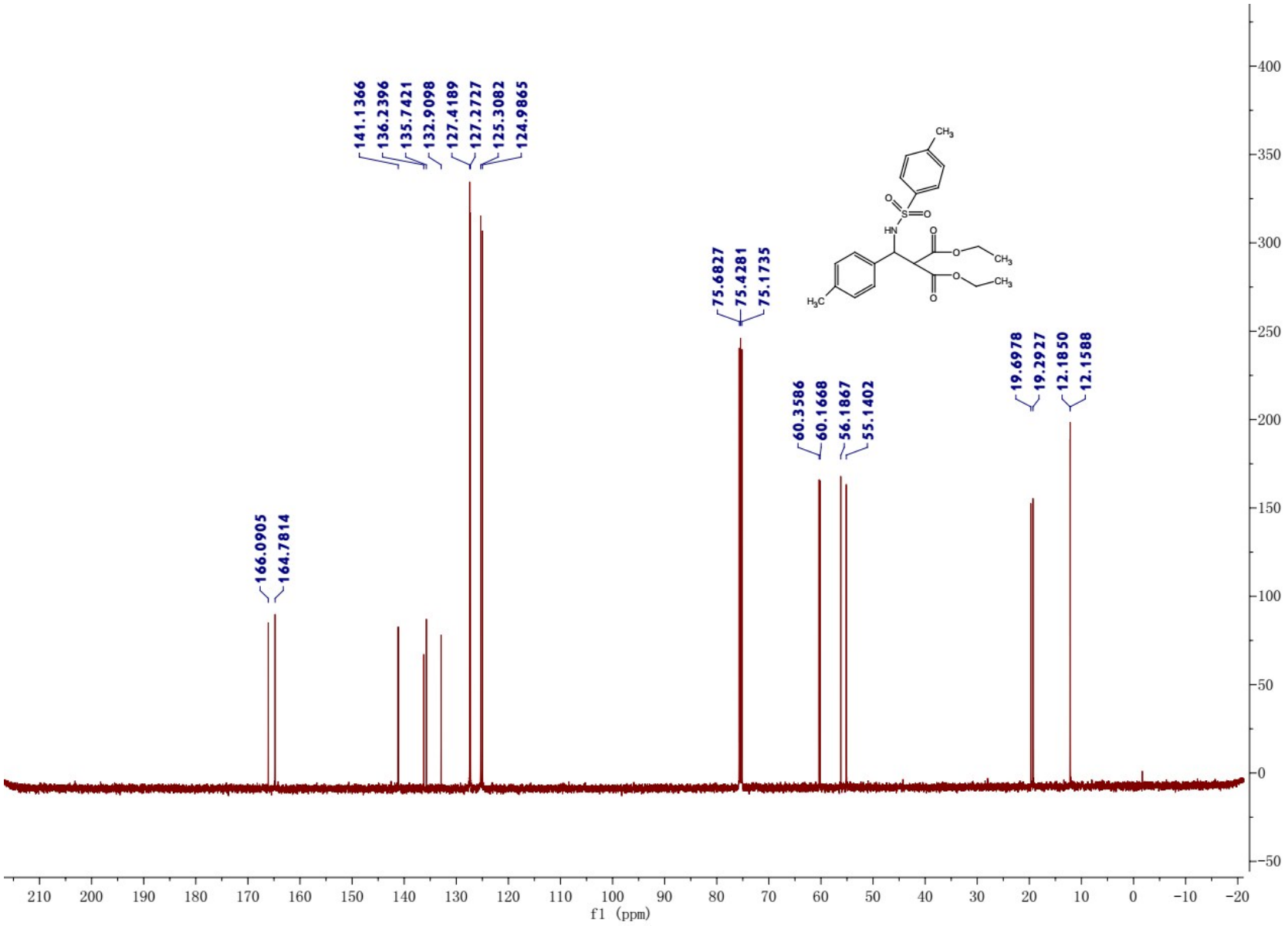
2c


141.7753
136.9674
136.8556
136.3213
128.0415
127.3856
127.2389
126.4342
125.9568
122.8047
76.3100
76.0558
75.8013
61.0874
60.8304
56.8051
56.0008
20.3367
20.1511
12.8782
12.8201
166.7777
165.4423
f1 (ppm)

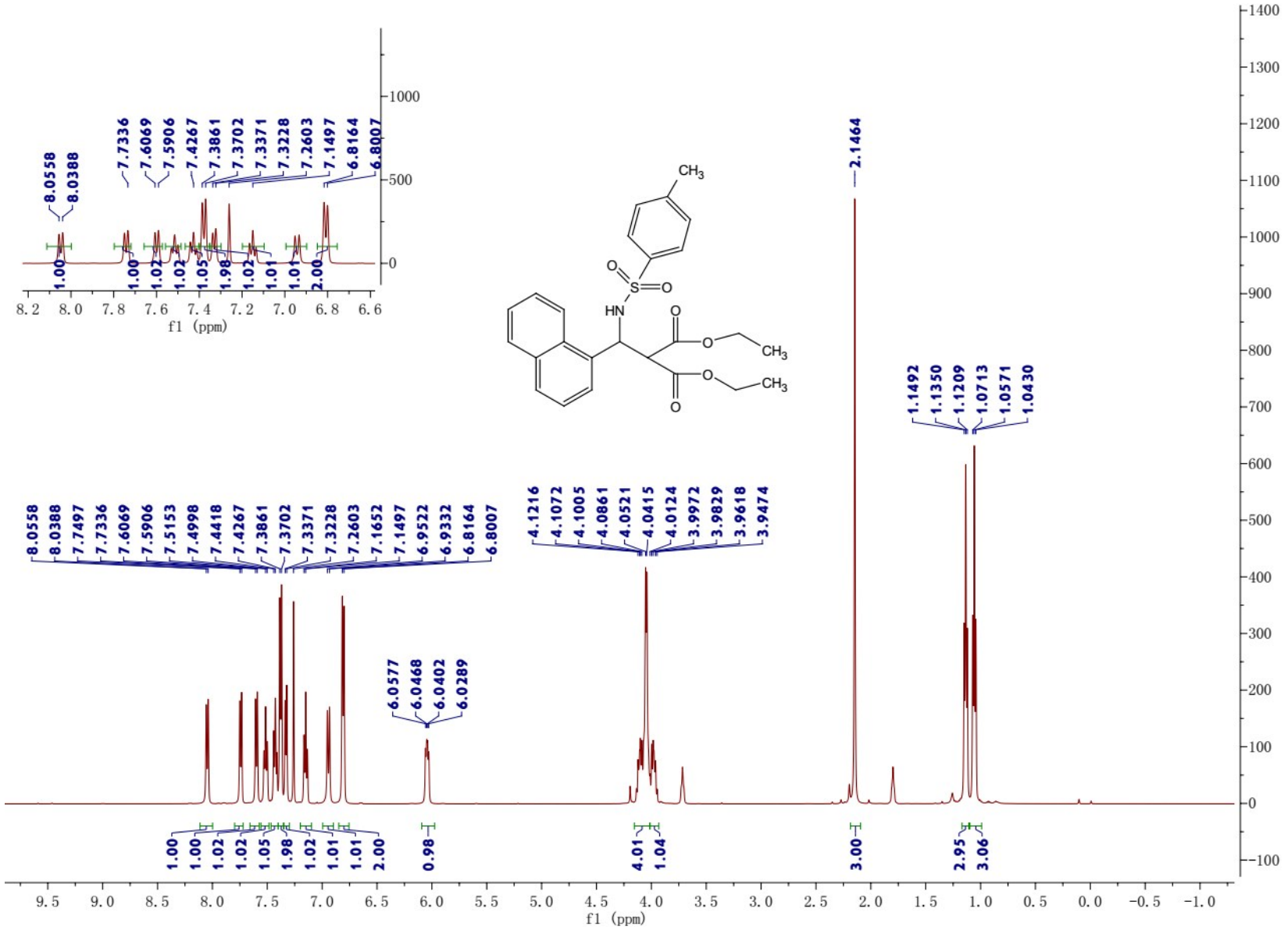
2d


4.1204
4.1052
4.0615
4.0425
4.0267
4.0129
4.0026
3.9879
3.7544
3.7433
4.00
1.00
f1 (ppm)
CH3
O
S
O
HN
O
O
CH3
O
CH3
H3C
2.3087
2.2256
1.1678
1.1544
1.1411
1.1286
7.4991
7.4837
7.2598
7.0611
7.0457
6.9811
6.9661
6.9183
6.9031
6.3677
6.3489
5.1086
5.0927
5.0791
4.1361
4.1204
4.1052
4.0905
4.0759
4.0615
4.0425
4.0267
4.0129
4.0026
3.9879
3.9684
3.7544
3.7433
1.99
2.02
2.01
1.98
0.96
0.99
4.00
1.00
2.98
2.97
6.00
f1 (ppm)

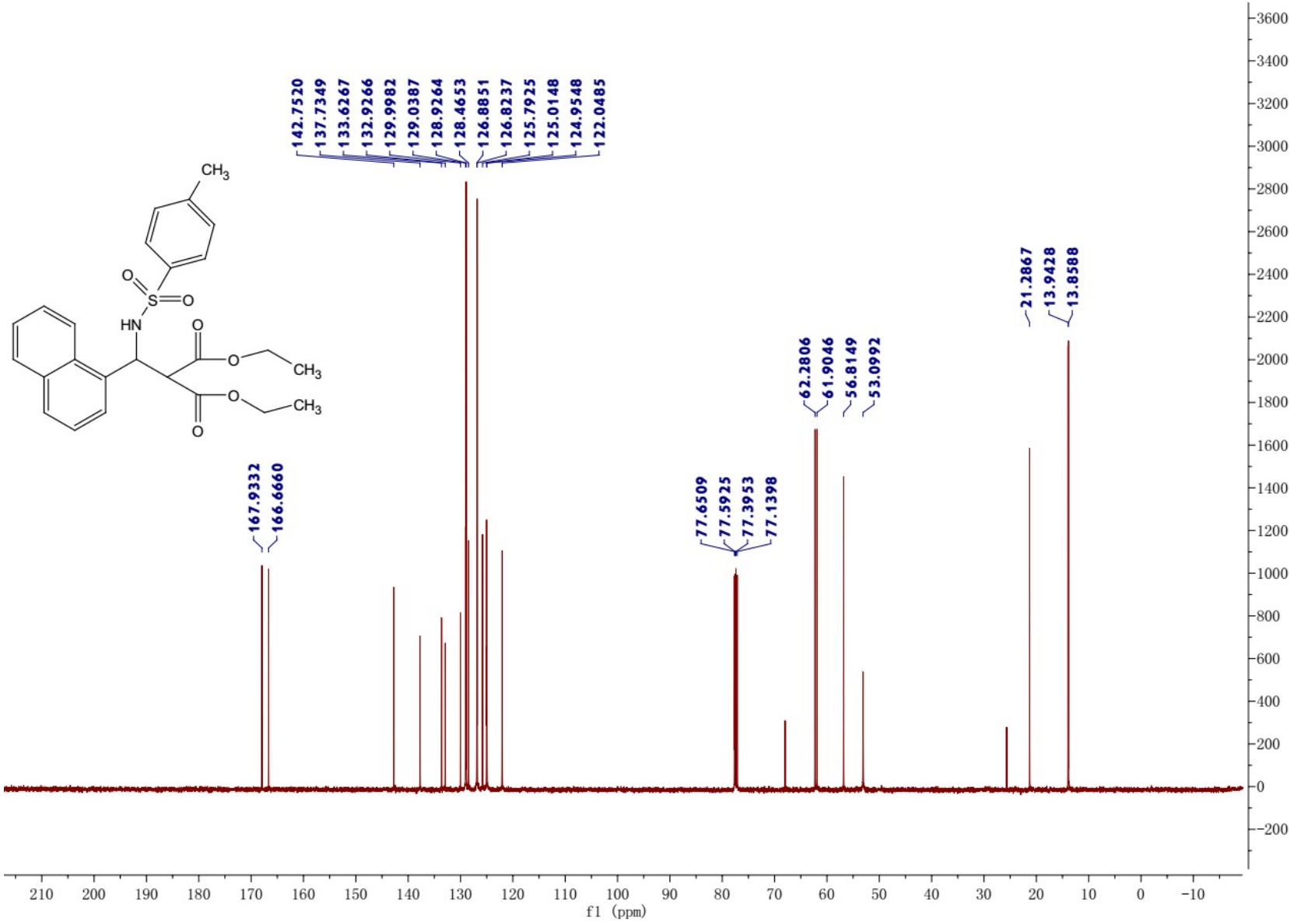
2d


141.1366
136.2396
135.7421
132.9098
127.4189
127.2727
125.3082
124.9865
75.6827
75.4281
75.1735
60.3586
60.1668
56.1867
55.1402
19.6978
19.2927
12.1850
12.1588
166.0905
164.7814
f1 (ppm)

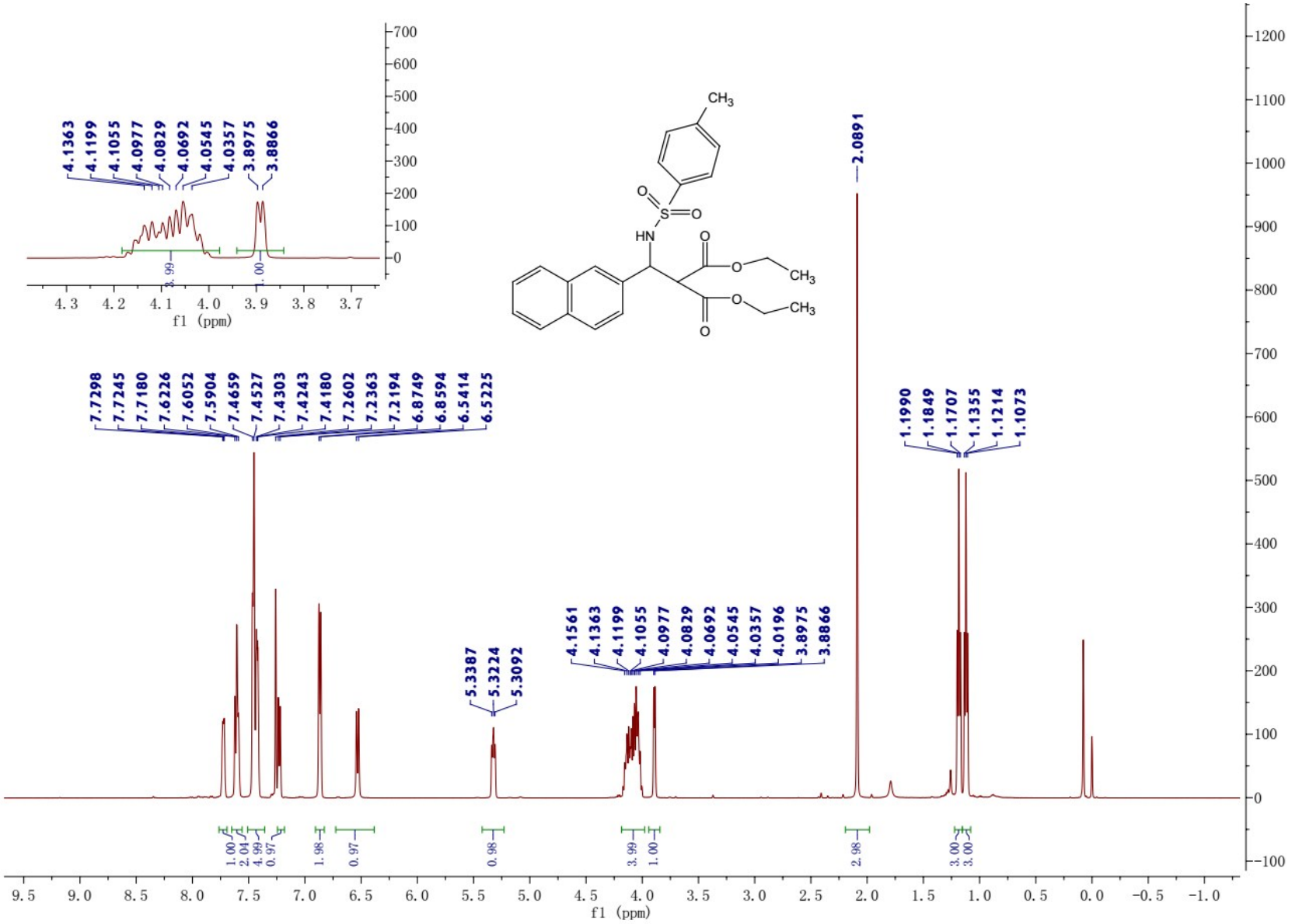
2e


8.0558
8.0388
7.7336
7.6069
7.5906
7.4267
7.3861
7.3702
7.3371
7.3228
7.2603
7.1497
6.8164
6.8007
f1 (ppm)
CH3
O
S
O
HN
O
O
CH3
O
O
CH3
2.1464
1.1492
1.1350
1.1209
1.0713
1.0571
1.0430
4.1216
4.1072
4.1005
4.0861
4.0521
4.0415
4.0124
3.9972
3.9829
3.9618
3.9474
7.1652
6.9522
6.9332
6.0577
6.0468
6.0402
6.0289
1.00
1.00
1.02
1.02
1.05
1.98
1.02
1.01
1.01
2.00
0.98
4.01
1.04
3.00
2.95
3.06
f1 (ppm)

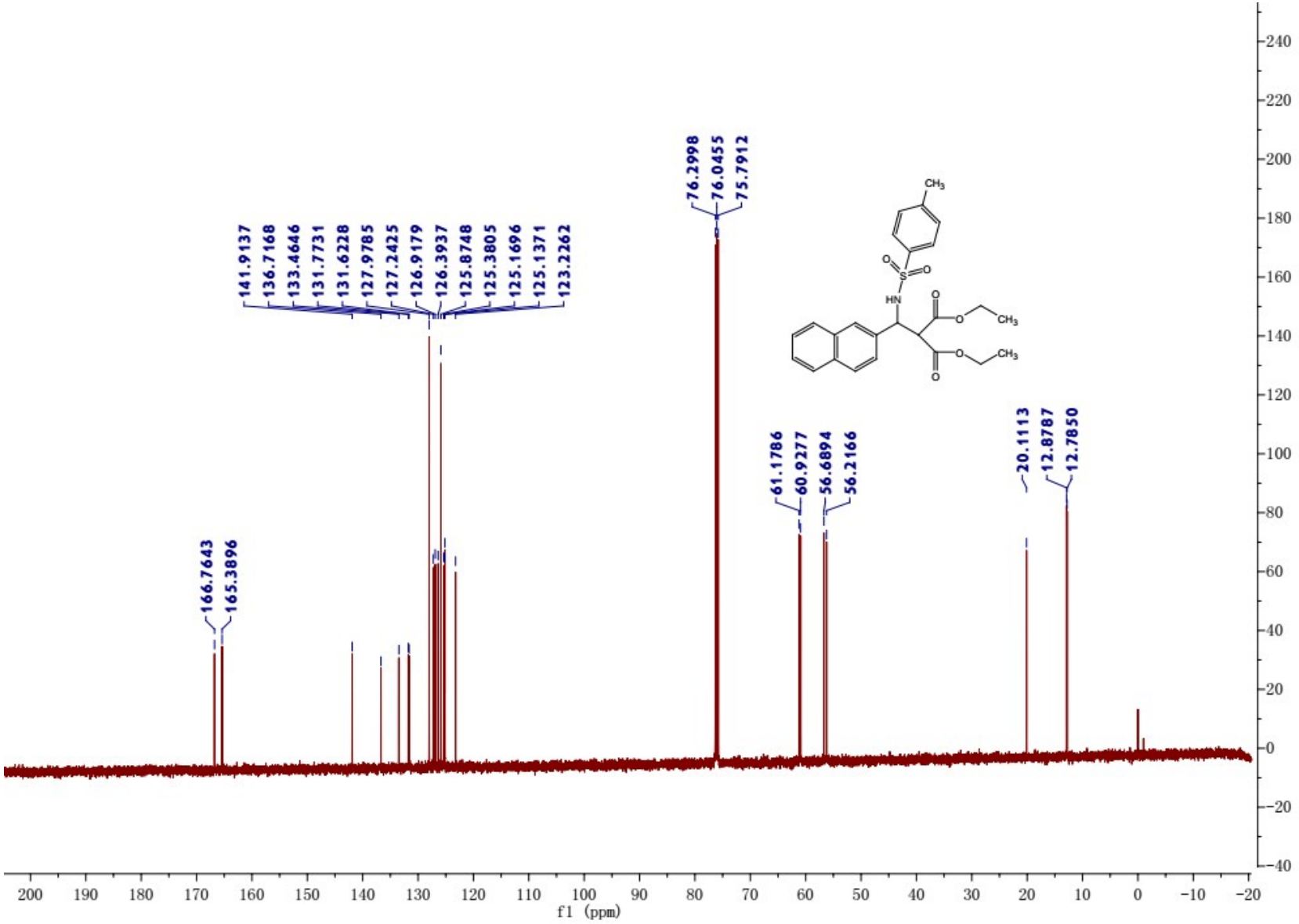
2e


142.7520
137.7349
133.6267
132.9266
129.9982
129.0387
128.9264
128.4653
126.8851
126.8237
125.7925
125.0148
124.9548
122.0485
167.9332
166.6660
77.6509
77.5925
77.3953
77.1398
62.2806
61.9046
56.8149
53.0992
21.2867
13.9428
13.8588
f1 (ppm)

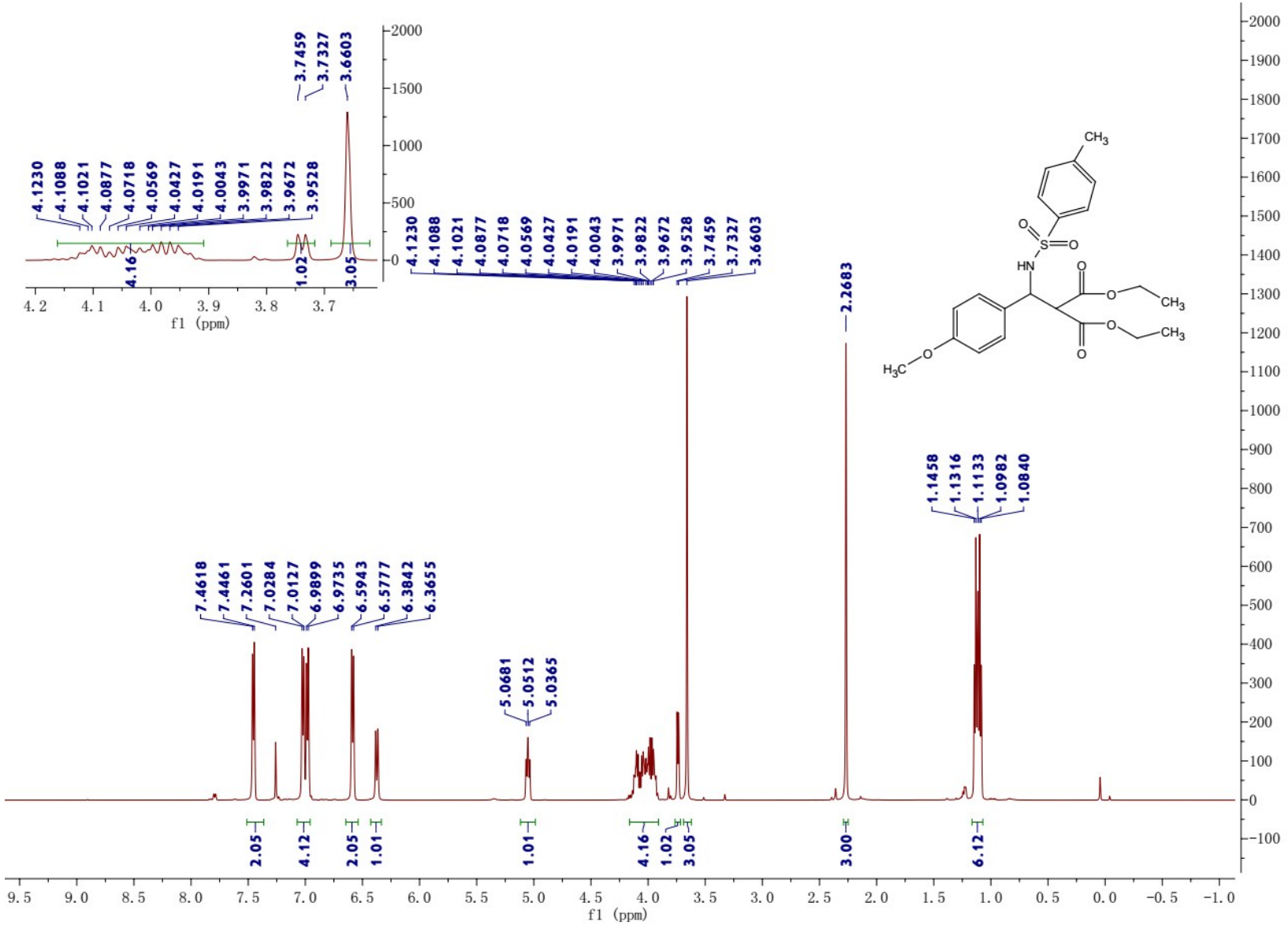
2f


4.1363
4.1199
4.1055
4.0977
4.0829
4.0692
4.0545
4.0357
3.8975
3.8866
f1 (ppm)
CH3
O
S
O
HN
O
O
CH3
O
O
CH3
2.0891
7.7298
7.7245
7.7180
7.6226
7.6052
7.5904
7.4659
7.4527
7.4303
7.4243
7.4180
7.2602
7.2363
7.2194
6.8749
6.8594
6.5414
6.5225
1.1990
1.1849
1.1707
1.1355
1.1214
1.1073
5.3387
5.3224
5.3092
4.1561
4.1363
4.1199
4.1055
4.0977
4.0829
4.0692
4.0545
4.0357
4.0196
3.8975
3.8866
1.00
2.04
4.99
0.97
1.98
0.97
0.98
3.99
1.00
2.98
3.00
3.00
f1 (ppm)

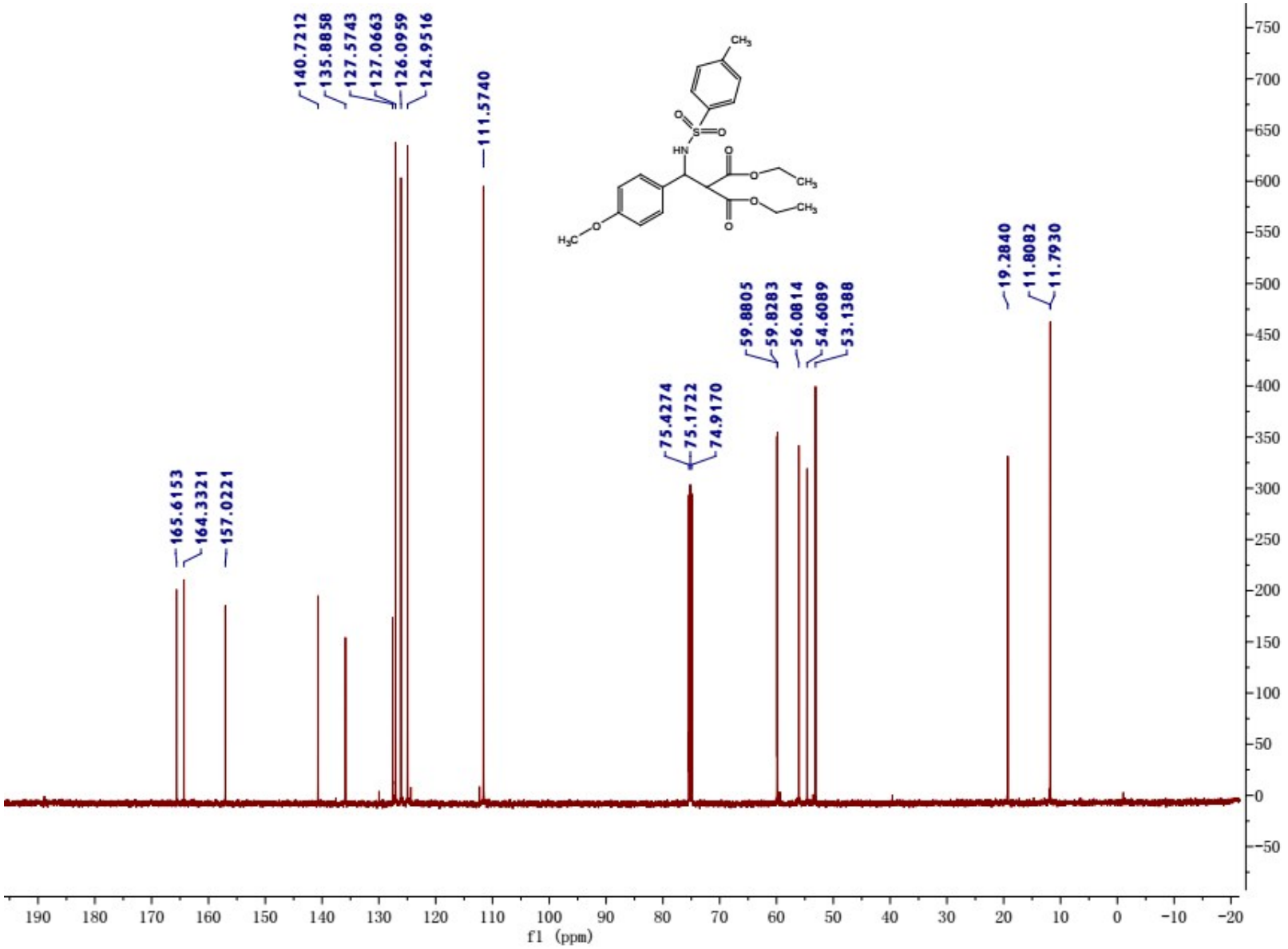
2f


141.9137
136.7168
133.4646
131.7731
131.6228
127.9785
127.2425
126.9179
126.3937
125.8748
125.3805
125.1696
125.1371
123.2262
76.2998
76.0455
75.7912
61.1786
60.9277
56.6894
56.2166
20.1113
12.8787
12.7850
166.7643
165.3896
f1 (ppm)

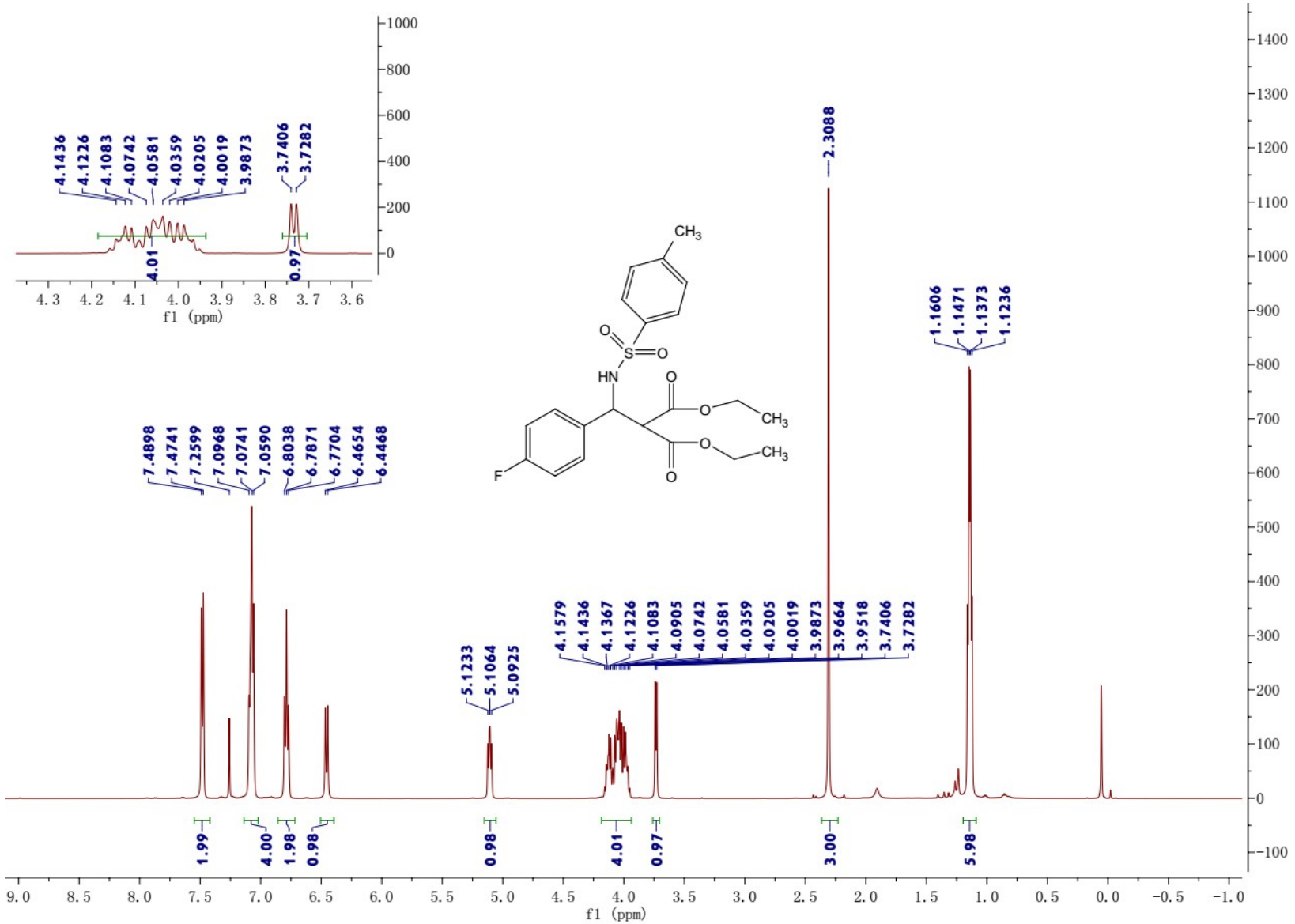
2g


7.4618
7.4461
7.2601
7.0284
7.0127
6.9899
6.9735
6.5943
6.5777
6.3842
6.3655
5.0681
5.0512
5.0365
4.1230
4.1088
4.1021
4.0877
4.0718
4.0569
4.0427
4.0191
4.0043
3.9971
3.9822
3.9672
3.9528
3.7459
3.7327
3.6603
2.2683
1.1458
1.1316
1.1133
1.0982
1.0840
2.05
4.12
2.05
1.01
1.01
4.16
1.02
3.05
3.00
6.12
f1 (ppm)

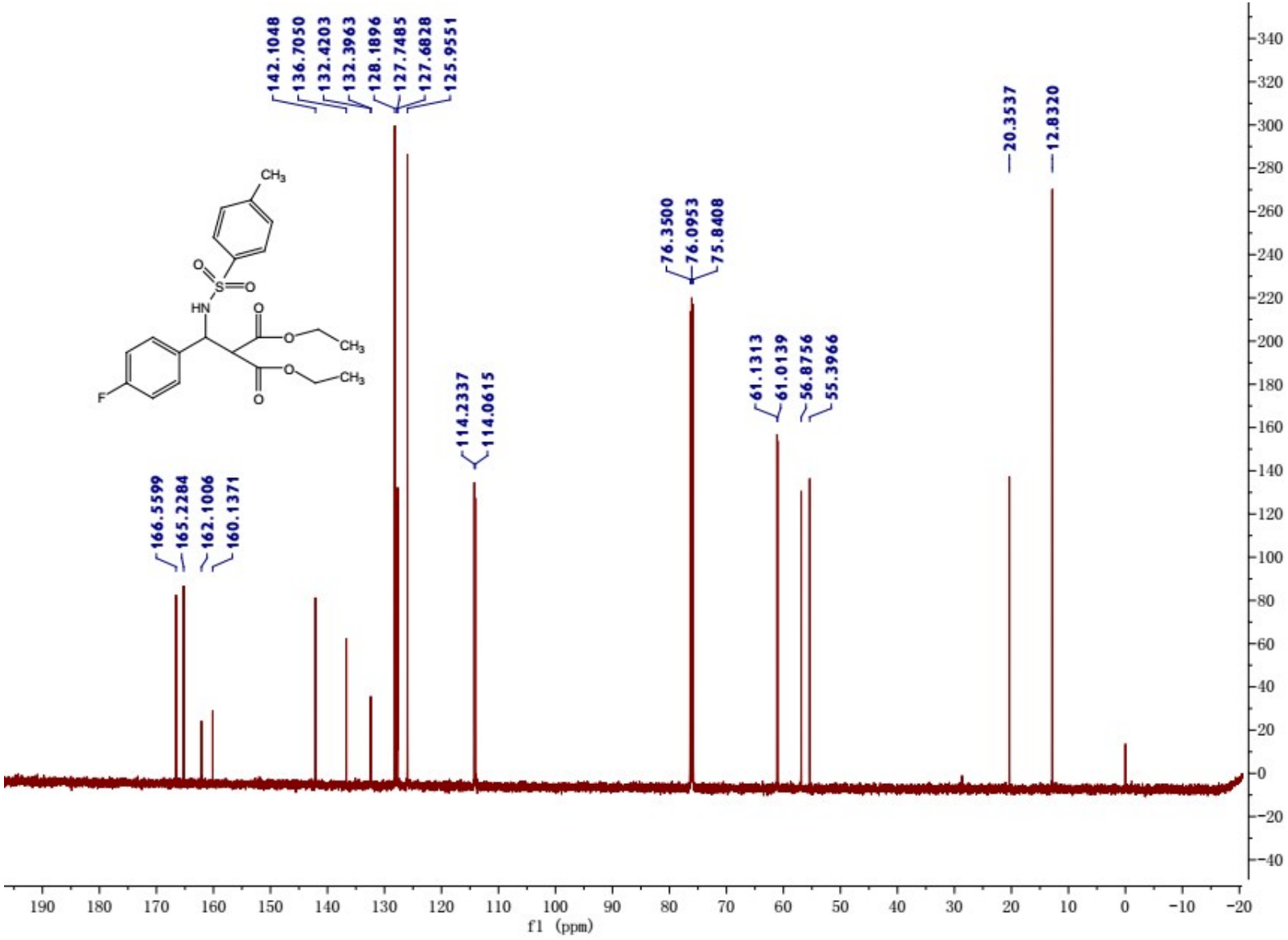
2g


140.7212
135.8858
127.5743
127.0663
126.0959
124.9516
111.5740
165.6153
164.3321
157.0221
75.4274
75.1722
74.9170
59.8805
59.8283
56.0814
54.6089
53.1388
19.2840
11.8082
11.7930
f1 (ppm)

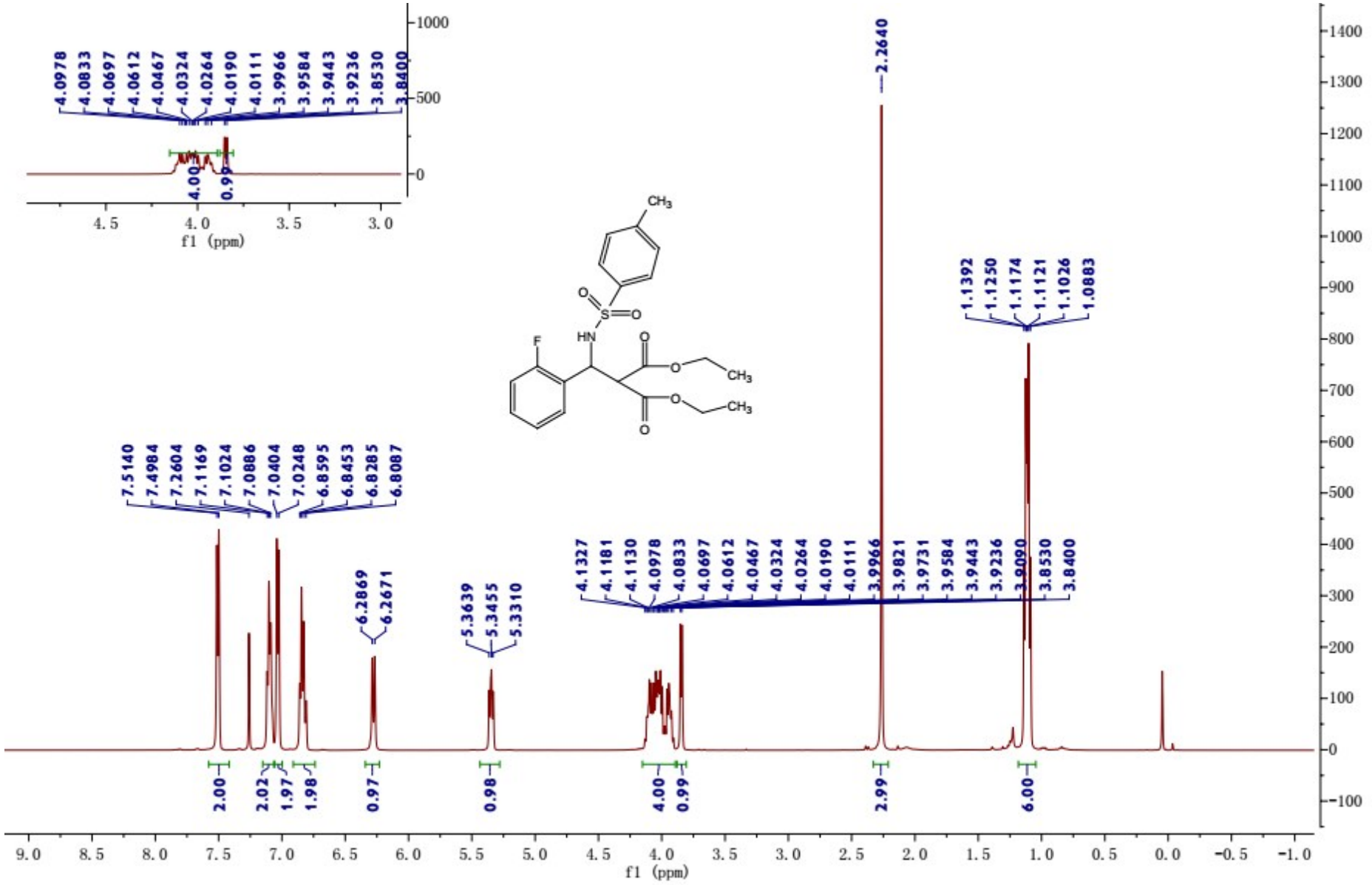
2h


4.1436
4.1226
4.1083
4.0742
4.0581
4.0359
4.0205
4.0019
3.9873
3.7406
3.7282
4.01
0.97
f1 (ppm)
CH3
O
S
O
HN
O
O
CH3
O
O
CH3
F
2.3088
1.1606
1.1471
1.1373
1.1236
7.4898
7.4741
7.2599
7.0968
7.0741
7.0590
6.8038
6.7871
6.7704
6.4654
6.4468
5.1233
5.1064
5.0925
4.1579
4.1436
4.1367
4.1226
4.1083
4.0905
4.0742
4.0581
4.0359
4.0205
4.0019
3.9873
3.9664
3.9518
3.7406
3.7282
1.99
4.00
1.98
0.98
0.98
4.01
0.97
3.00
5.98
f1 (ppm)

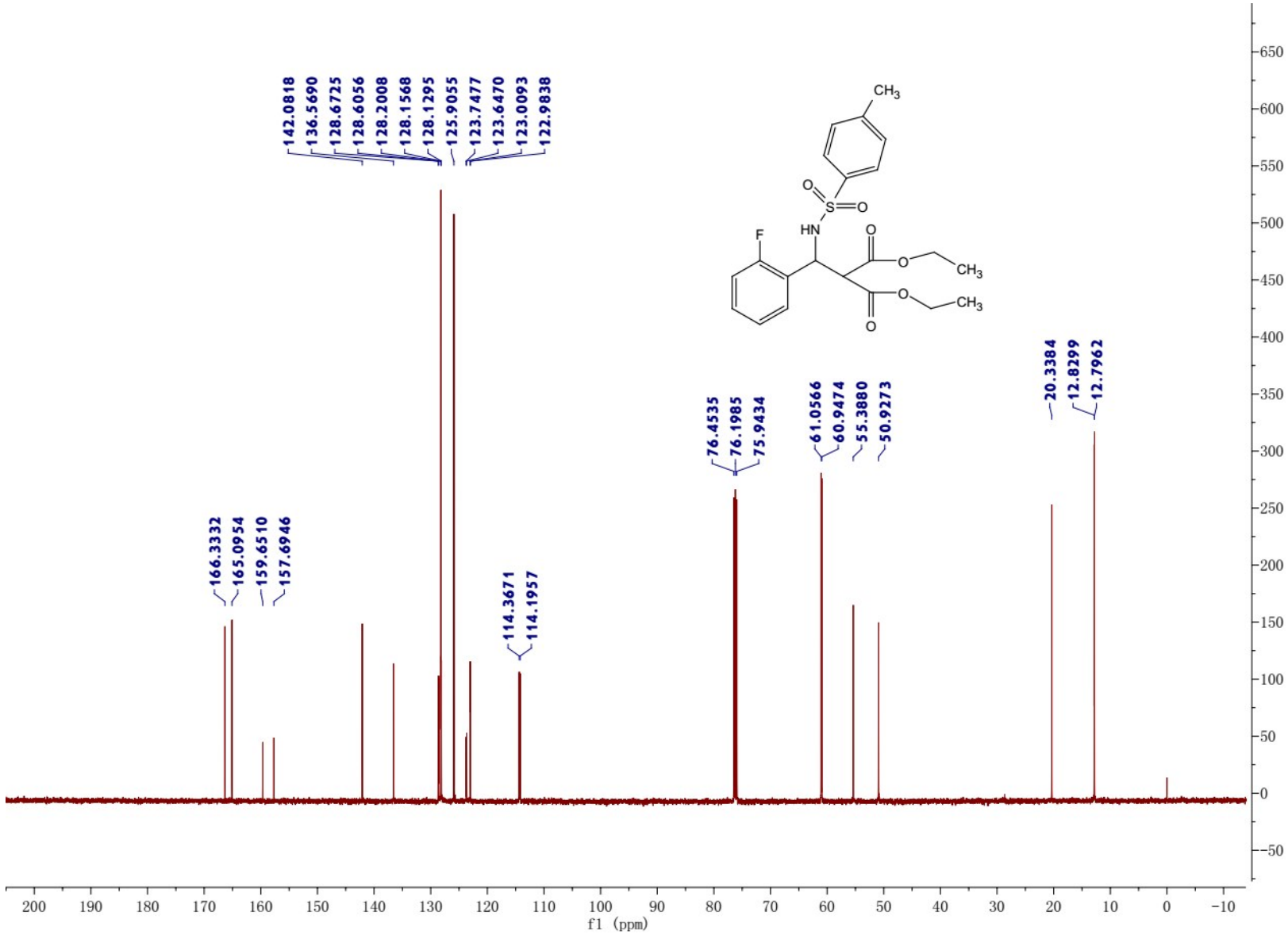
2h


142.1048
136.7050
132.4203
132.3963
128.1896
127.7485
127.6828
125.9551
114.2337
114.0615
76.3500
76.0953
75.8408
61.1313
61.0139
56.8756
55.3966
20.3537
12.8320
166.5599
165.2284
162.1006
160.1371
HN
F
f1 (ppm)

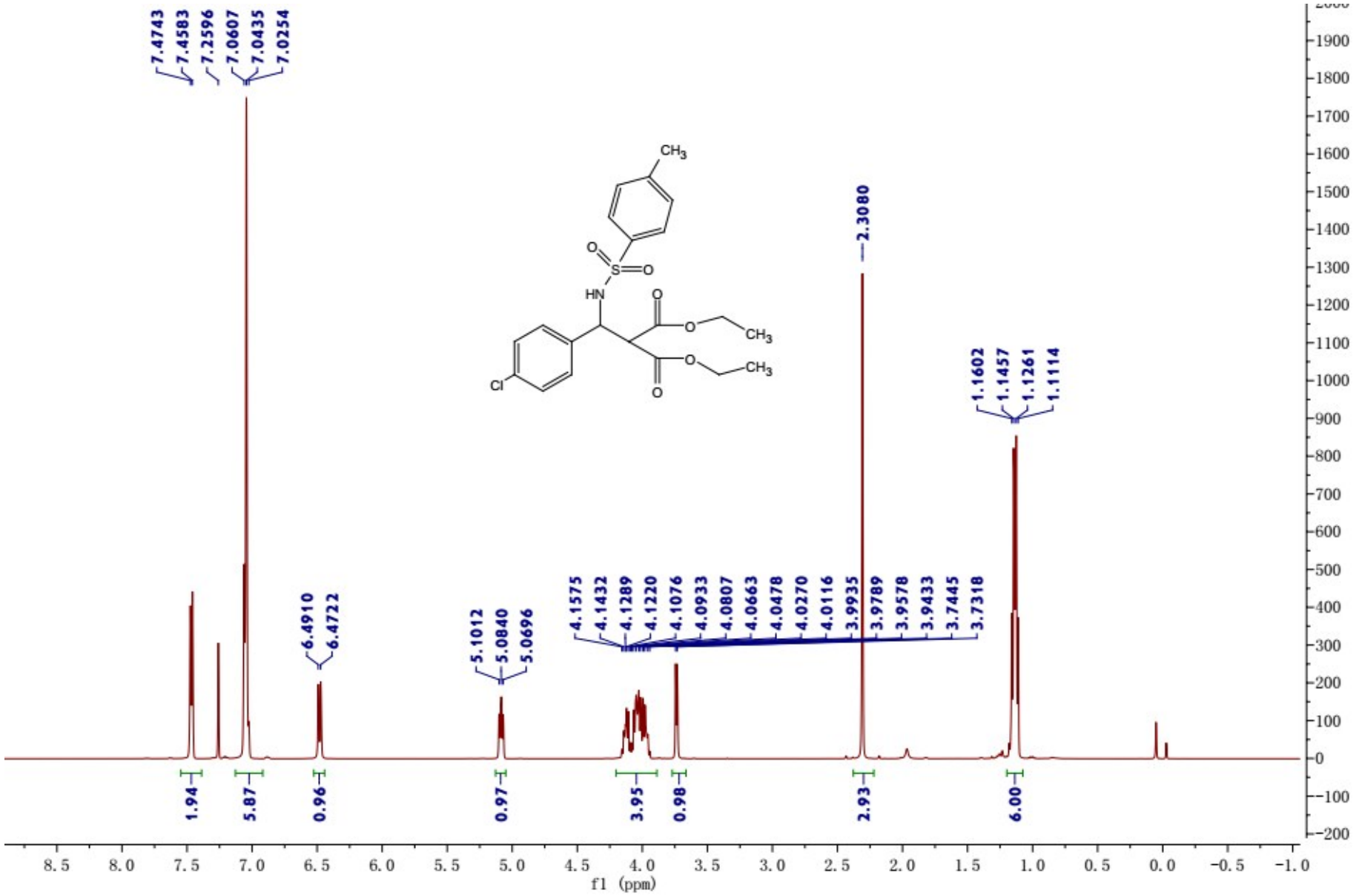
2i


4.0978
4.0833
4.0697
4.0612
4.0467
4.0324
4.0264
4.0190
4.0111
3.9966
3.9584
3.9443
3.9236
3.8530
3.8400
4.00
0.99
f1 (ppm)
CH3
O
S
O
HN
F
O
O
CH3
O
O
CH3
7.5140
7.4984
7.2604
7.1169
7.1024
7.0886
7.0404
7.0248
6.8595
6.8453
6.8285
6.8087
6.2869
6.2671
5.3639
5.3455
5.3310
4.1327
4.1181
4.1130
4.0978
4.0833
4.0697
4.0612
4.0467
4.0324
4.0264
4.0190
4.0111
3.9966
3.9821
3.9731
3.9584
3.9443
3.9236
3.9090
3.8530
3.8400
2.2640
1.1392
1.1250
1.1174
1.1121
1.1026
1.0883
2.00
2.02
1.97
1.98
0.97
0.98
4.00
0.99
2.99
6.00
f1 (ppm)

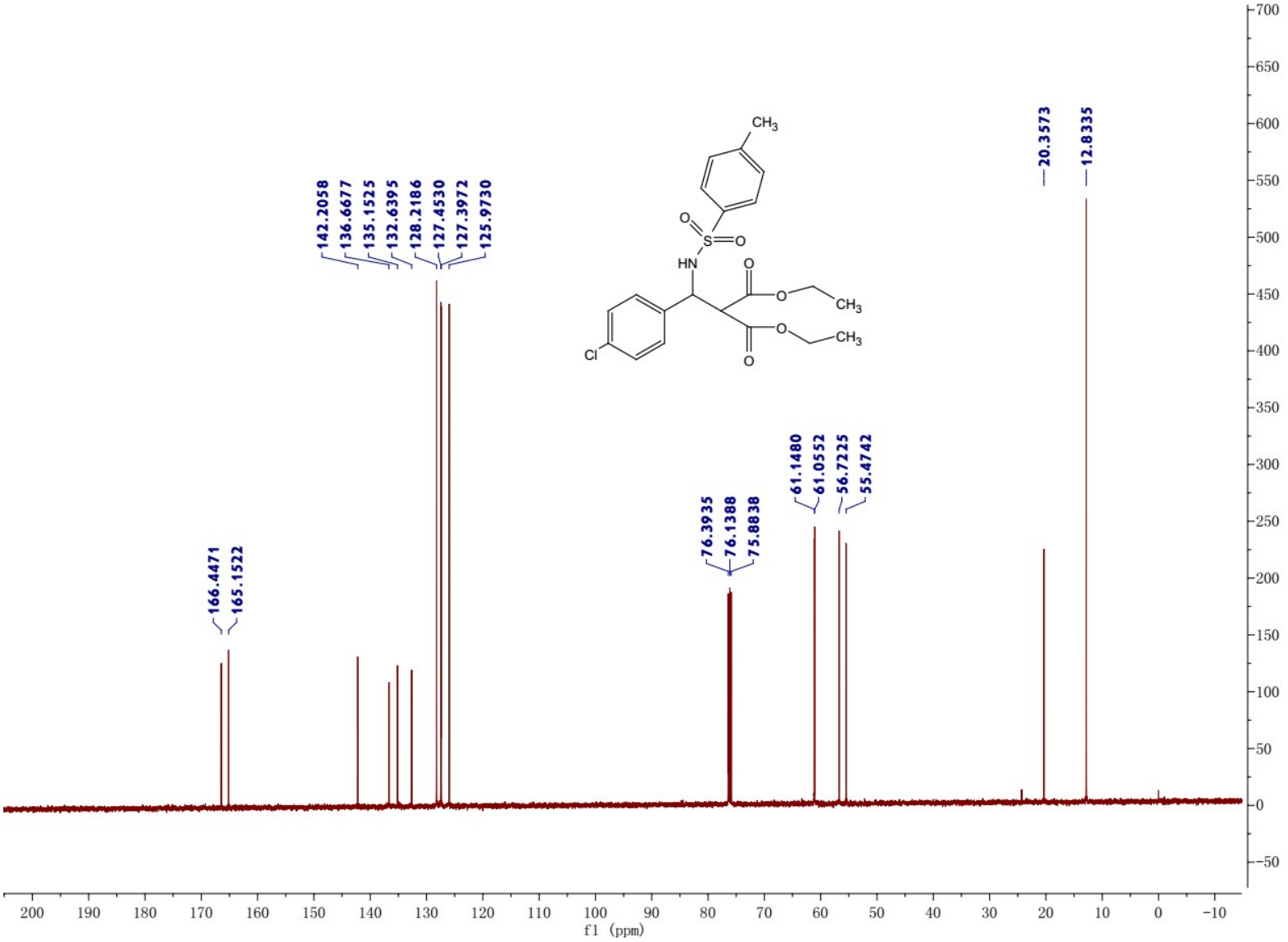
2i


142.0818
136.5690
128.6725
128.6056
128.2008
128.1568
128.1295
125.9055
123.7477
123.6470
123.0093
122.9838
166.3332
165.0954
159.6510
157.6946
114.3671
114.1957
76.4535
76.1985
75.9434
61.0566
60.9474
55.3880
50.9273
20.3384
12.8299
12.7962
CH3
O
S
O
HN
F
O
O
CH3
O
O
CH3
O
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

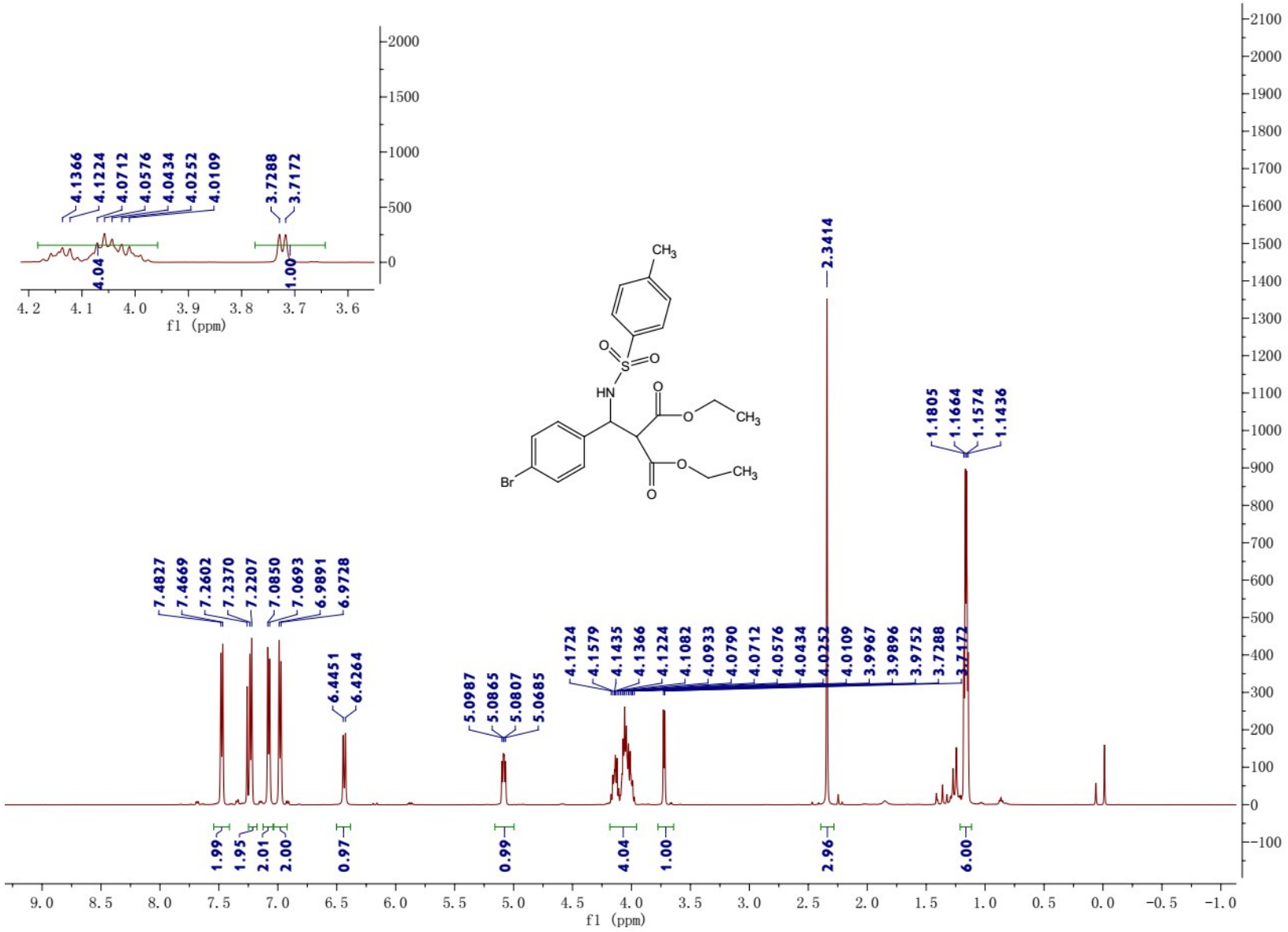
2j


7.4743
7.4583
7.2596
7.0607
7.0435
7.0254
6.4910
6.4722
5.1012
5.0840
5.0696
4.1575
4.1432
4.1289
4.1220
4.1076
4.0933
4.0807
4.0663
4.0478
4.0270
4.0116
3.9935
3.9789
3.9578
3.9433
3.7445
3.7318
2.3080
1.1602
1.1457
1.1261
1.1114
1.94
5.87
0.96
0.97
3.95
0.98
2.93
6.00
f1 (ppm)

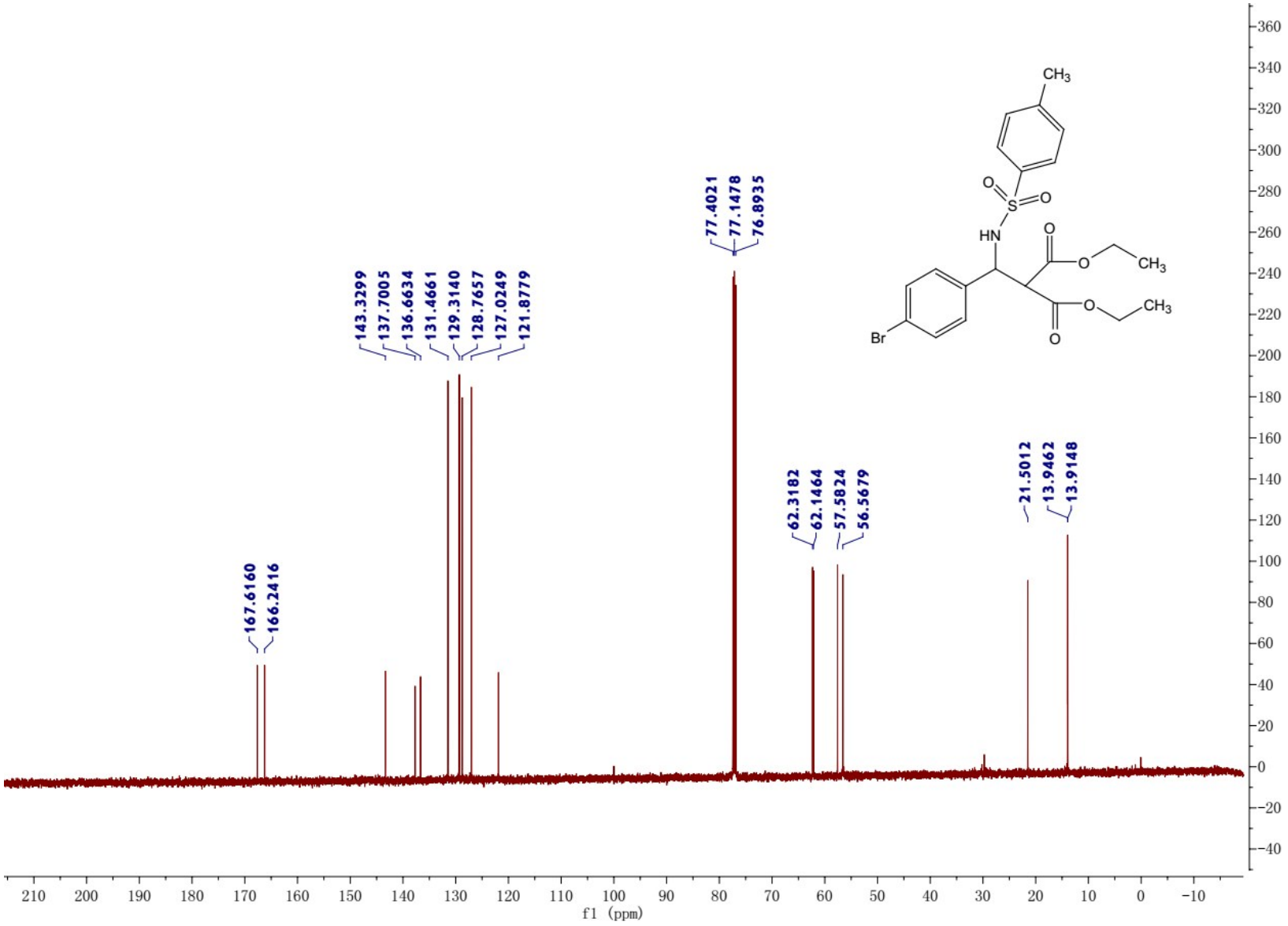
2j


142.2058
136.6677
135.1525
132.6395
128.2186
127.4530
127.3972
125.9730
166.4471
165.1522
76.3935
76.1388
75.8838
61.1480
61.0552
56.7225
55.4742
20.3573
12.8335
f1 (ppm)

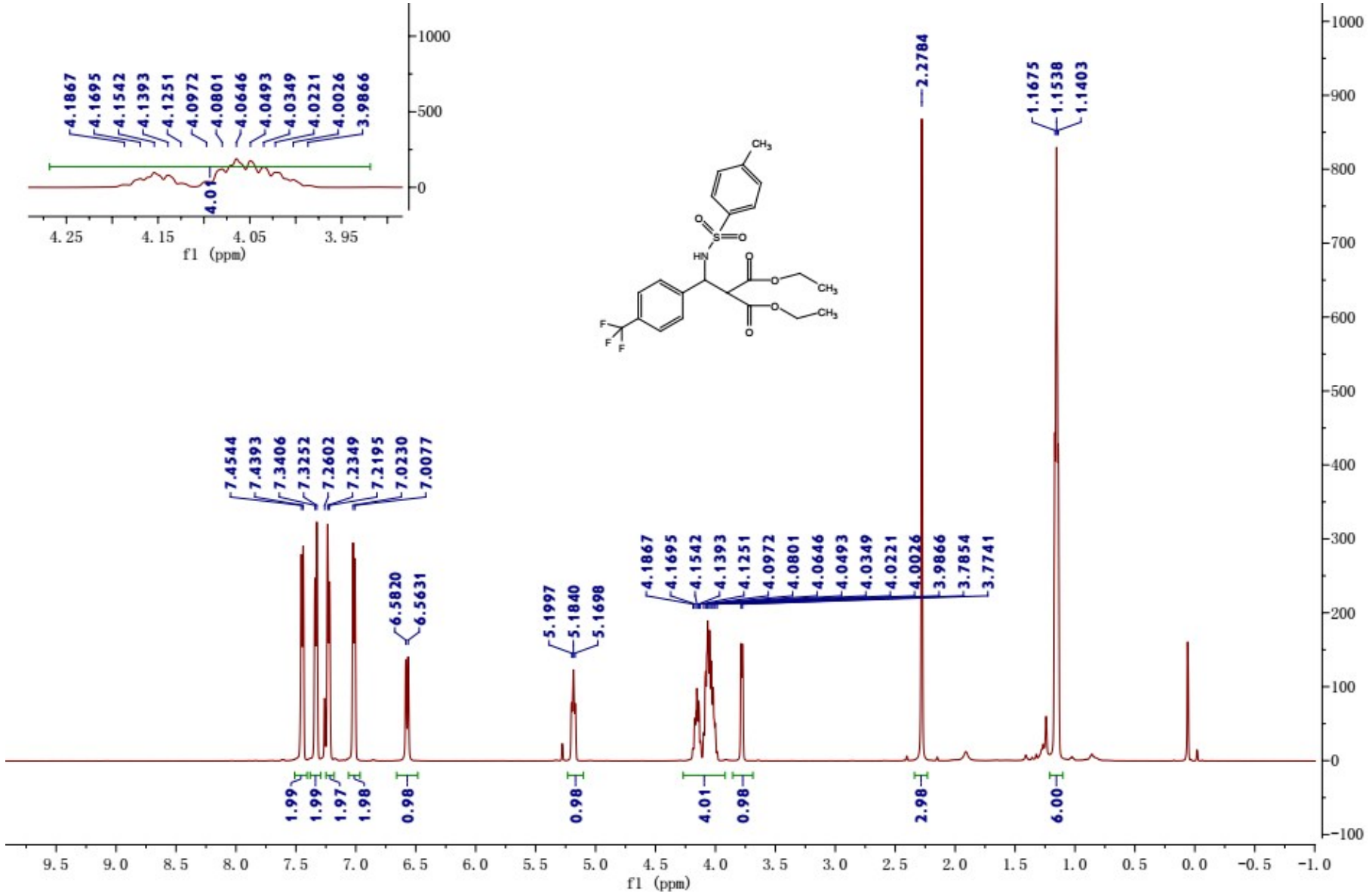
2k


4.1366
4.1224
4.0712
4.0576
4.0434
4.0252
4.0109
3.7288
3.7172
4.04
1.00
f1 (ppm)
CH3
O
S
O
HN
O
O
CH3
O
O
CH3
Br
2.3414
1.1805
1.1664
1.1574
1.1436
7.4827
7.4669
7.2602
7.2370
7.2207
7.0850
7.0693
6.9891
6.9728
6.4451
6.4264
5.0987
5.0865
5.0807
5.0685
4.1724
4.1579
4.1435
4.1366
4.1224
4.1082
4.0933
4.0790
4.0712
4.0576
4.0434
4.0252
4.0109
3.9967
3.9896
3.9752
3.7288
3.7172
1.99
1.95
2.01
2.00
0.97
0.99
4.04
1.00
2.96
6.00
f1 (ppm)

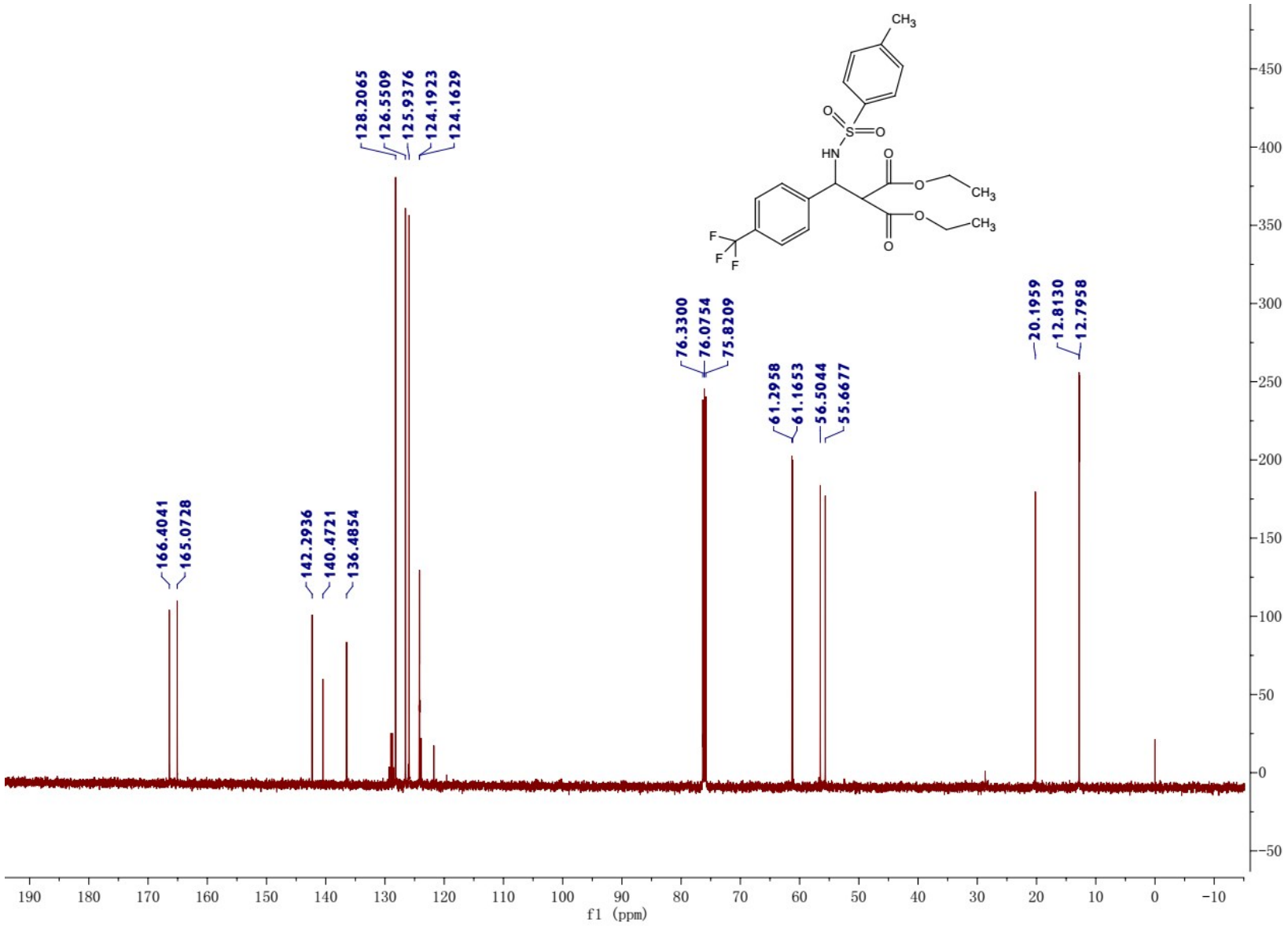
2k


167.6160
166.2416
143.3299
137.7005
136.6634
131.4661
129.3140
128.7657
127.0249
121.8779
77.4021
77.1478
76.8935
62.3182
62.1464
57.5824
56.5679
21.5012
13.9462
13.9148
CH3
O
S
O
HN
O
O
CH3
O
O
CH3
Br
f1 (ppm)

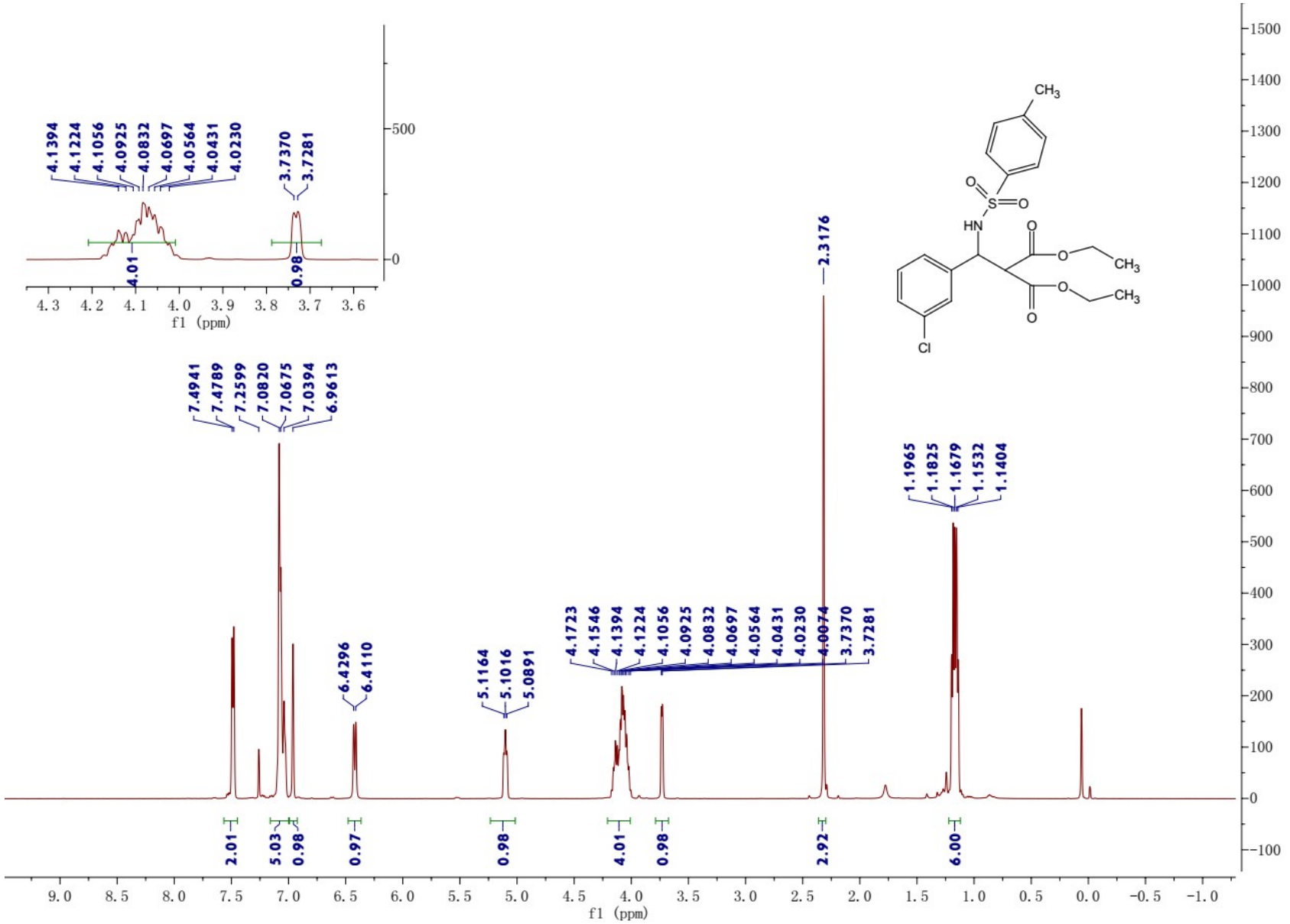
2l


4.1867
4.1695
4.1542
4.1393
4.1251
4.0972
4.0801
4.0646
4.0493
4.0349
4.0221
4.0026
3.9866
4.01
f1 (ppm)
7.4544
7.4393
7.3406
7.3252
7.2602
7.2349
7.2195
7.0230
7.0077
6.5820
6.5631
5.1997
5.1840
5.1698
3.9866
3.7854
3.7741
2.2784
1.1675
1.1538
1.1403
1.99
1.99
1.97
1.98
0.98
0.98
4.01
0.98
2.98
6.00
f1 (ppm)

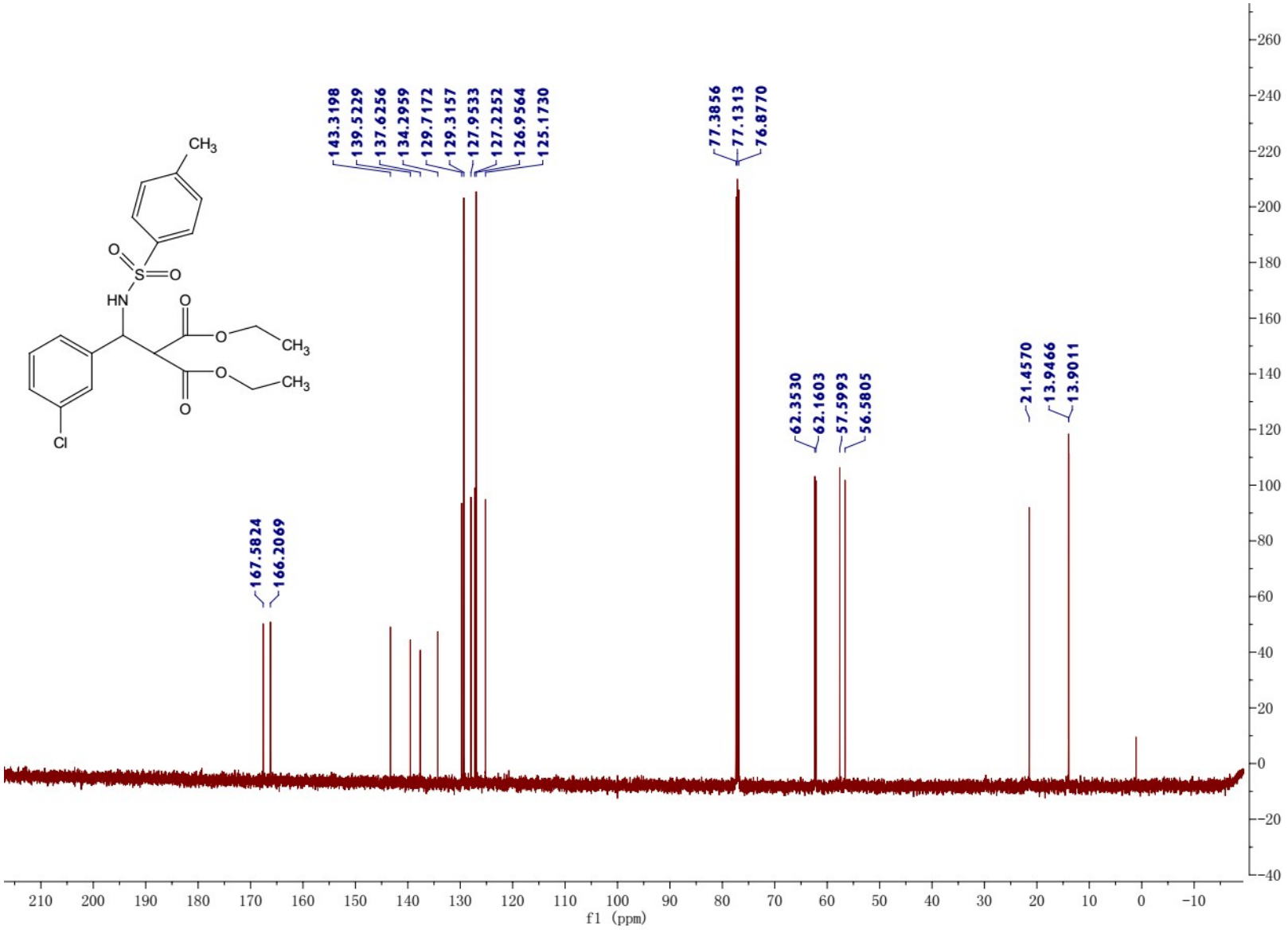
2l


128.2065
126.5509
125.9376
124.1923
124.1629
166.4041
165.0728
142.2936
140.4721
136.4854
76.3300
76.0754
75.8209
61.2958
61.1653
56.5044
55.6677
20.1959
12.8130
12.7958
f1 (ppm)

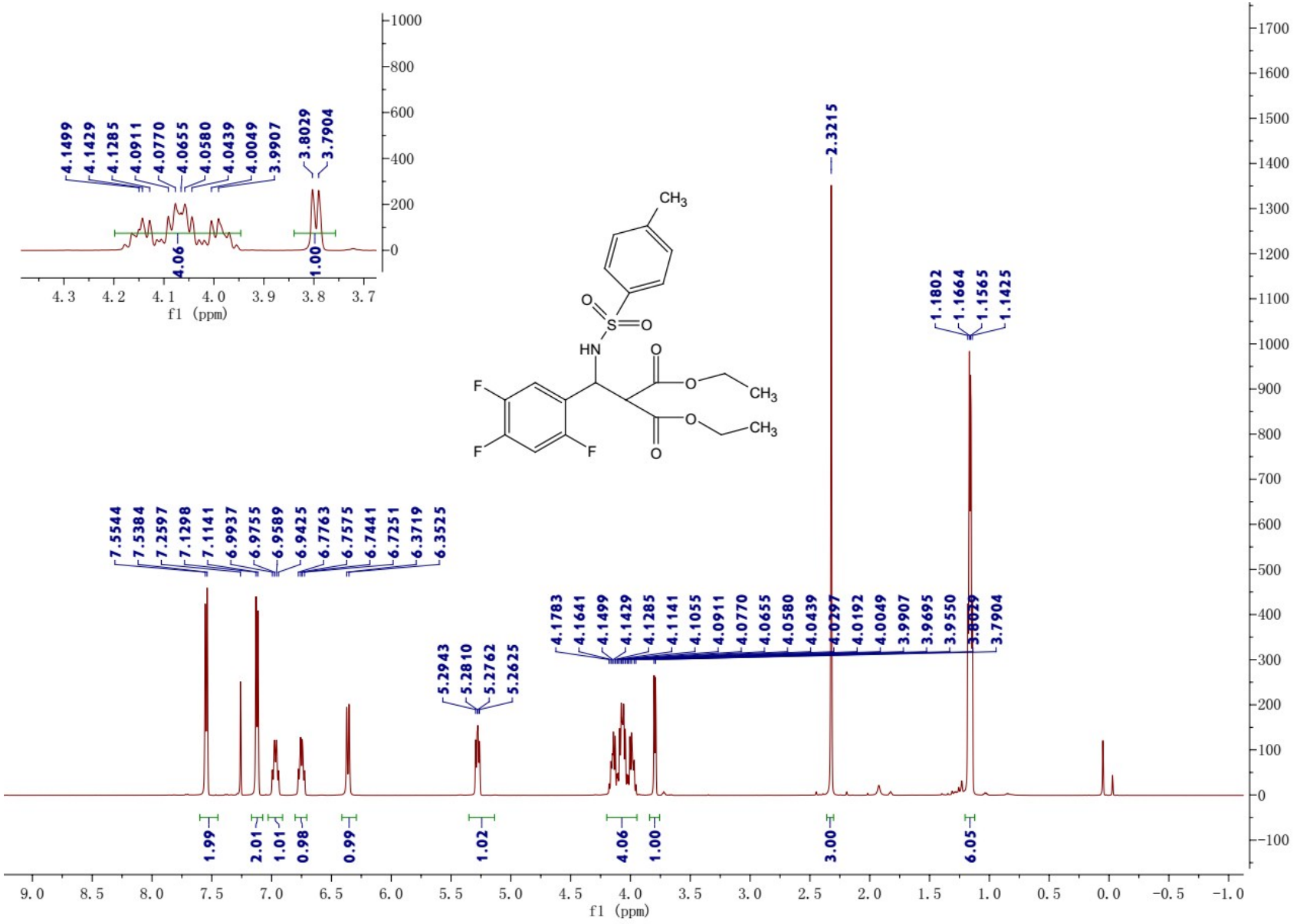
2m


4.1394
4.1224
4.1056
4.0925
4.0832
4.0697
4.0564
4.0431
4.0230
3.7370
3.7281
4.01
0.98
f1 (ppm)
7.4941
7.4789
7.2599
7.0820
7.0675
7.0394
6.9613
6.4296
6.4110
5.1164
5.1016
5.0891
4.1723
4.1546
4.1394
4.1224
4.1056
4.0925
4.0832
4.0697
4.0564
4.0431
4.0230
4.0074
3.7370
3.7281
2.3176
1.1965
1.1825
1.1679
1.1532
1.1404
2.01
5.03
0.98
0.97
0.98
4.01
0.98
2.92
6.00
f1 (ppm)

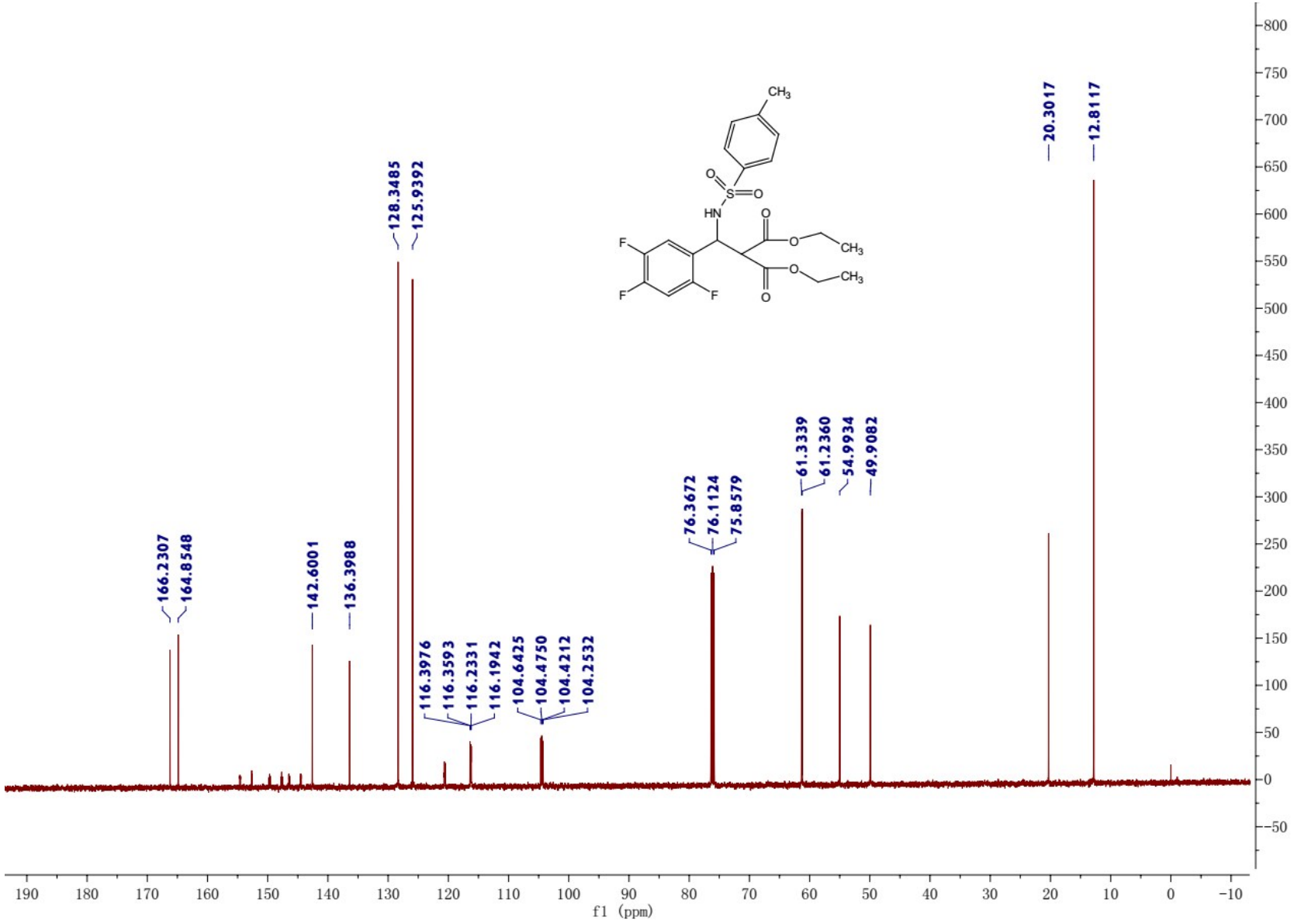
2m


143.3198
139.5229
137.6256
134.2959
129.7172
129.3157
127.9533
127.2252
126.9564
125.1730
77.3856
77.1313
76.8770
62.3530
62.1603
57.5993
56.5805
21.4570
13.9466
13.9011
167.5824
166.2069
CH3
O
S
O
HN
O
O
CH3
O
CH3
O
Cl
f1 (ppm)

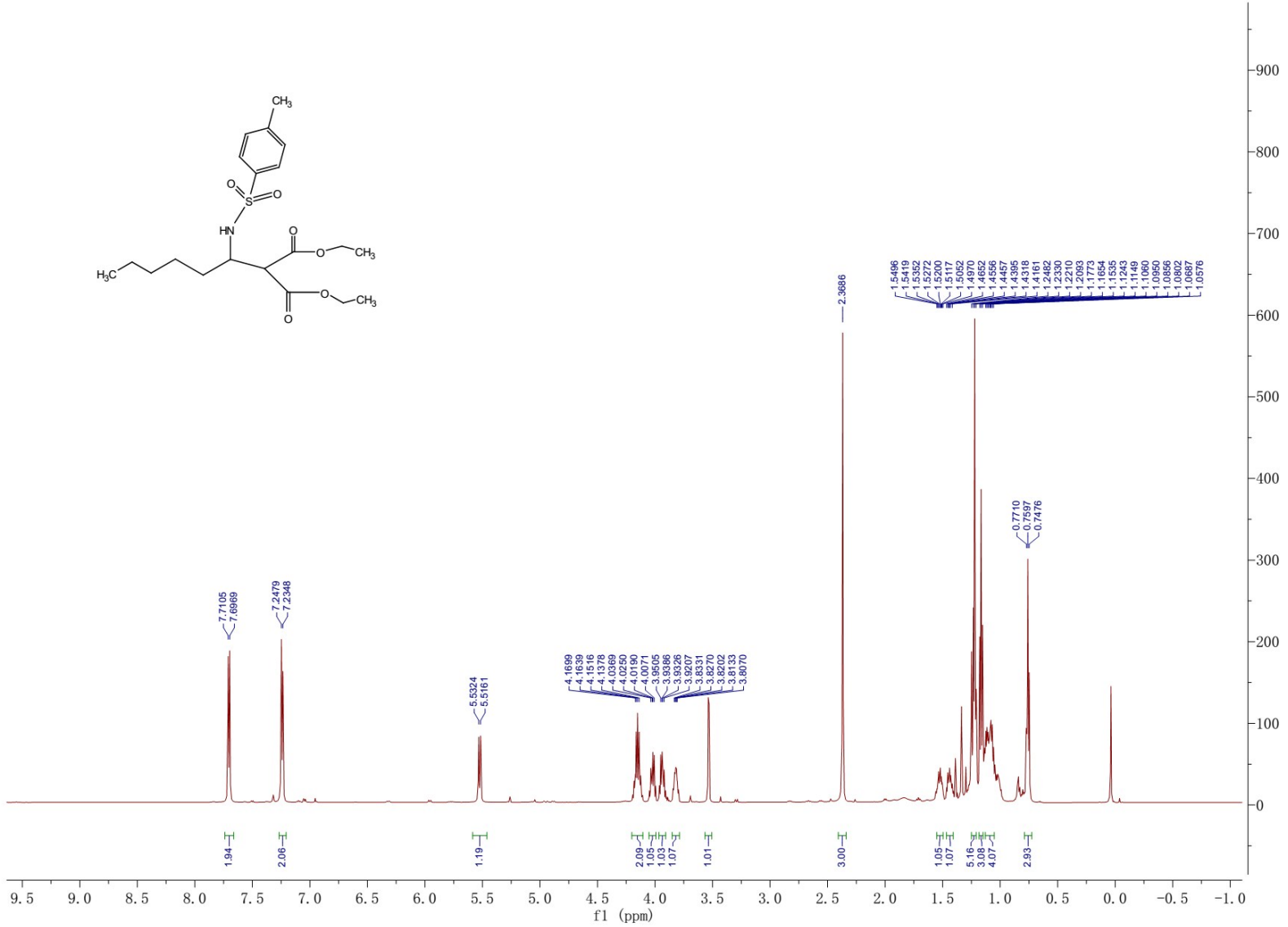
2n


4.1499
4.1429
4.1285
4.0911
4.0770
4.0655
4.0580
4.0439
4.0049
3.9907
3.8029
3.7904
4.06
1.00
f1 (ppm)
CH3
O
S
O
HN
O
O
CH3
O
CH3
F
F
F
O
2.3215
1.1802
1.1664
1.1565
1.1425
7.5544
7.5384
7.2597
7.1298
7.1141
6.9937
6.9755
6.9589
6.9425
6.7763
6.7575
6.7441
6.7251
6.3719
6.3525
5.2943
5.2810
5.2762
5.2625
4.1783
4.1641
4.1499
4.1429
4.1285
4.1141
4.1055
4.0911
4.0770
4.0655
4.0580
4.0439
4.0297
4.0192
4.0049
3.9907
3.9695
3.9550
3.8029
3.7904
1.99
2.01
1.01
0.98
0.99
1.02
4.06
1.00
3.00
6.05
f1 (ppm)

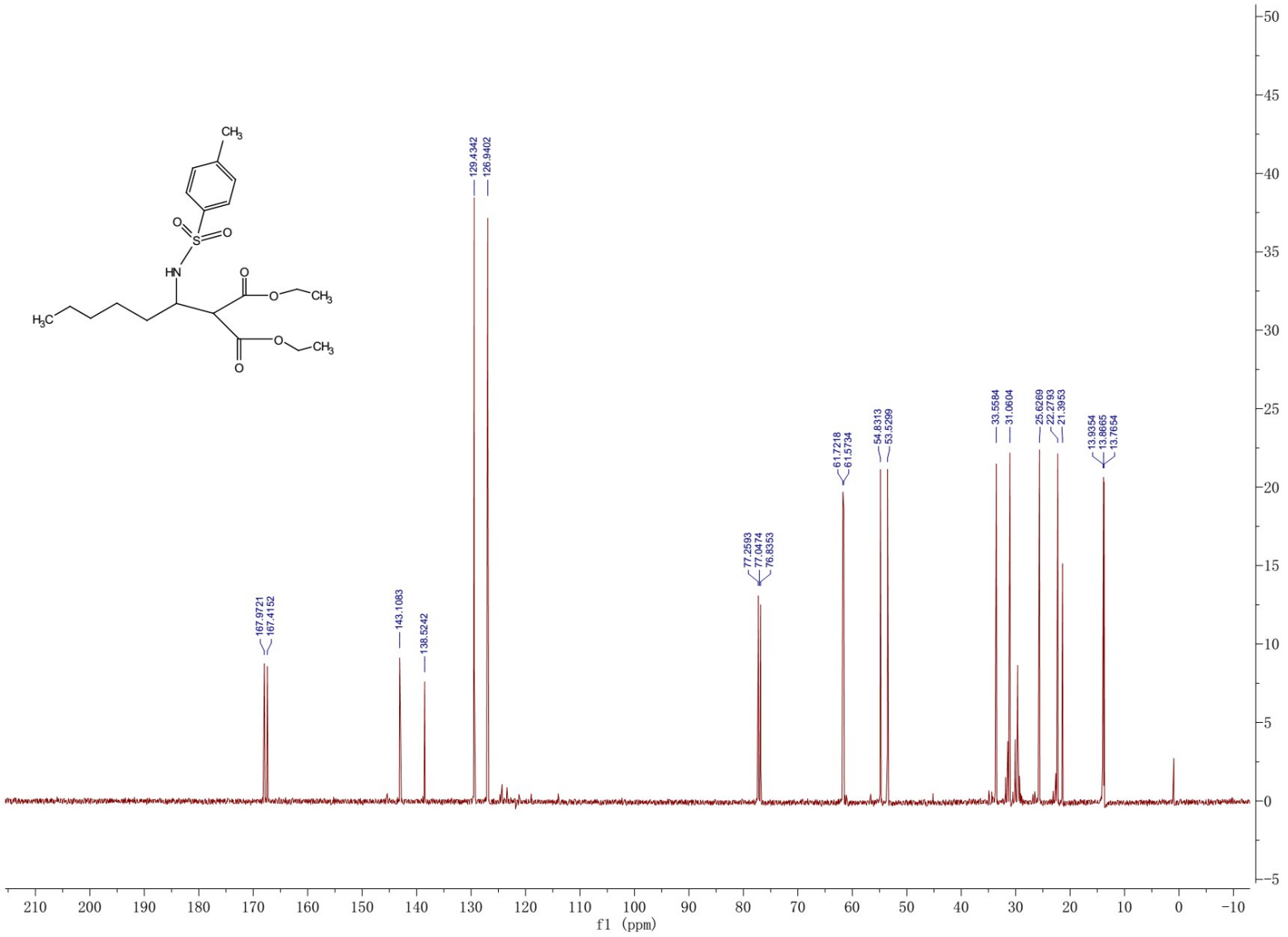
2n


166.2307
164.8548
142.6001
136.3988
128.3485
125.9392
116.3976
116.3593
116.2331
116.1942
104.6425
104.4750
104.4212
104.2532
76.3672
76.1124
75.8579
61.3339
61.2360
54.9934
49.9082
20.3017
12.8117
f1 (ppm)

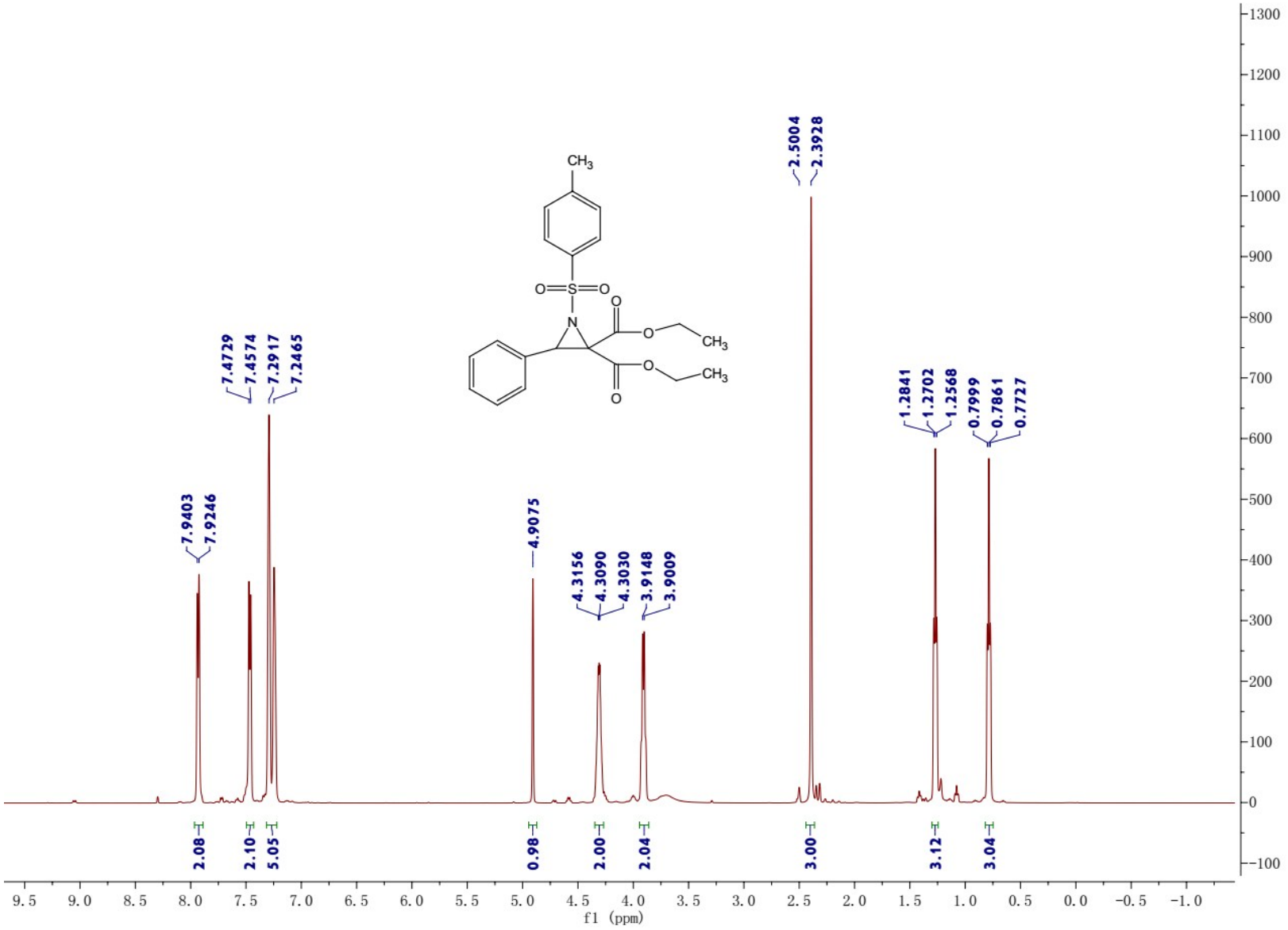
2o


7.7105
7.6969
7.2479
7.2348
5.5324
5.5161
4.1699
4.1639
4.1516
4.1378
4.0369
4.0250
4.0190
4.0071
3.9505
3.9396
3.9326
3.9207
3.8331
3.8270
3.8202
3.8133
3.8070
2.3686
1.5496
1.5419
1.5352
1.5272
1.5200
1.5117
1.5052
1.4970
1.4652
1.4556
1.4457
1.4395
1.4318
1.4161
1.2482
1.2330
1.2210
1.2093
1.1773
1.1654
1.1535
1.1243
1.1149
1.1060
1.0950
1.0856
1.0802
1.0687
1.0576
0.7710
0.7597
0.7476
1.94
2.06
1.19
2.09
1.05
1.03
1.07
1.01
3.00
1.05
1.07
5.16
3.08
4.07
2.93
f1 (ppm)

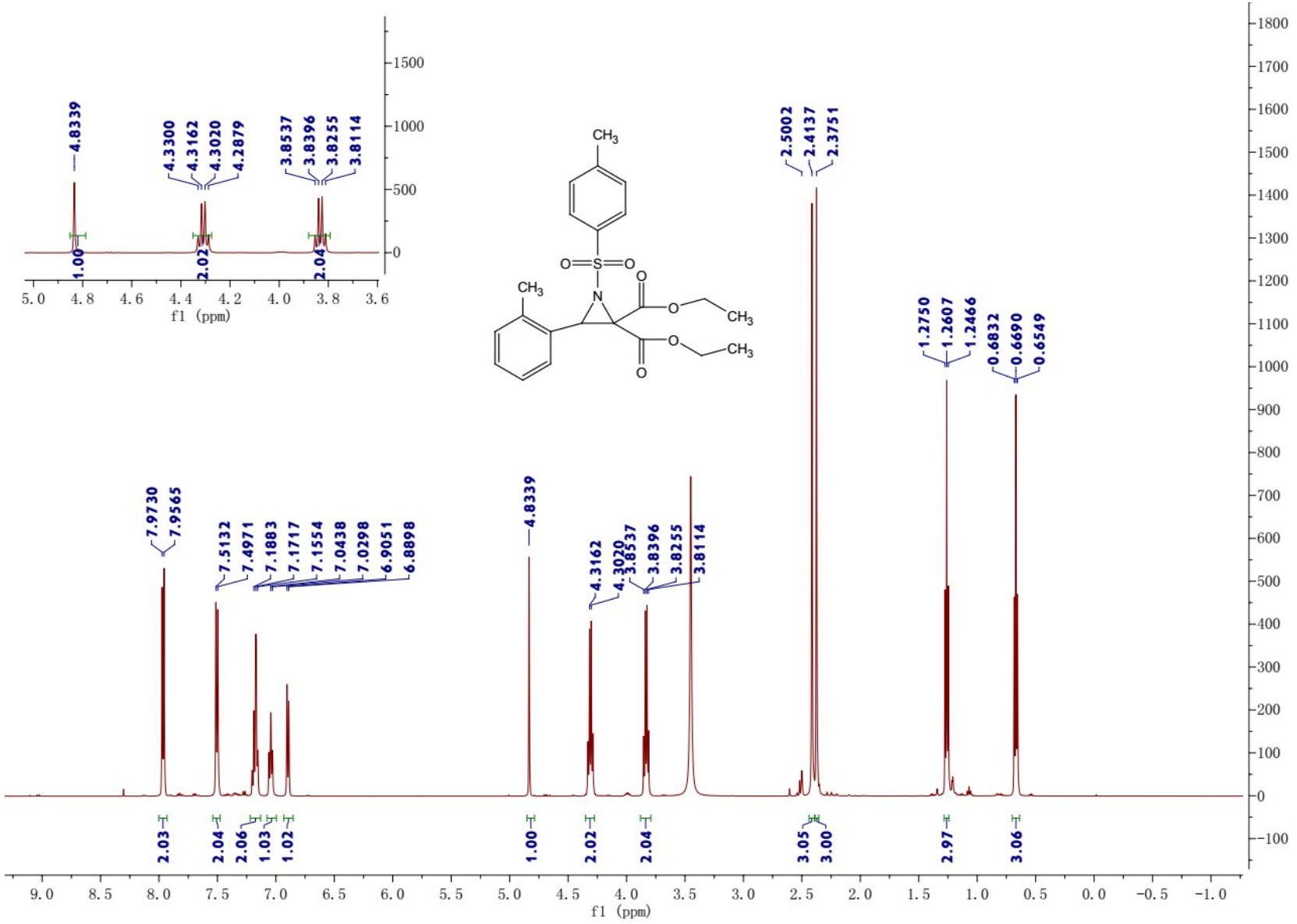
2o


CH3
O
S
O
HN
O
O
CH3
H3C
O
CH3
O
129.4342
126.9402
167.9721
167.4152
143.1083
138.5242
77.2593
77.0474
76.8353
61.7218
61.5734
54.8313
53.5299
33.5584
31.0604
25.6269
22.2793
21.3953
13.9354
13.8665
13.7654
f1 (ppm)

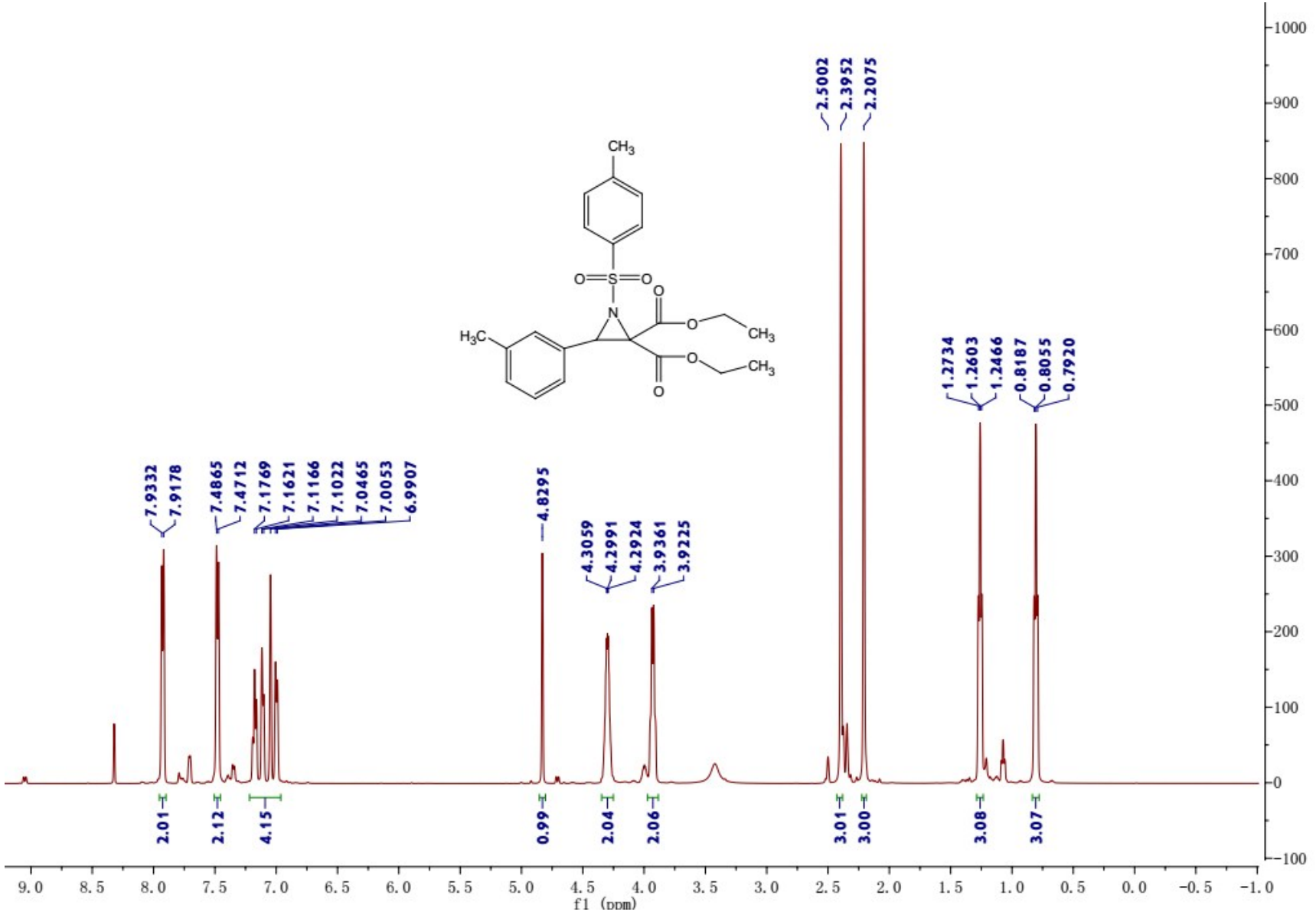
3a


7.9403
7.9246
7.4729
7.4574
7.2917
7.2465
4.9075
4.3156
4.3090
4.3030
3.9148
3.9009
2.5004
2.3928
1.2841
1.2702
1.2568
0.7999
0.7861
0.7727
2.08
2.10
5.05
0.98
2.00
2.04
3.00
3.12
3.04
f1 (ppm)

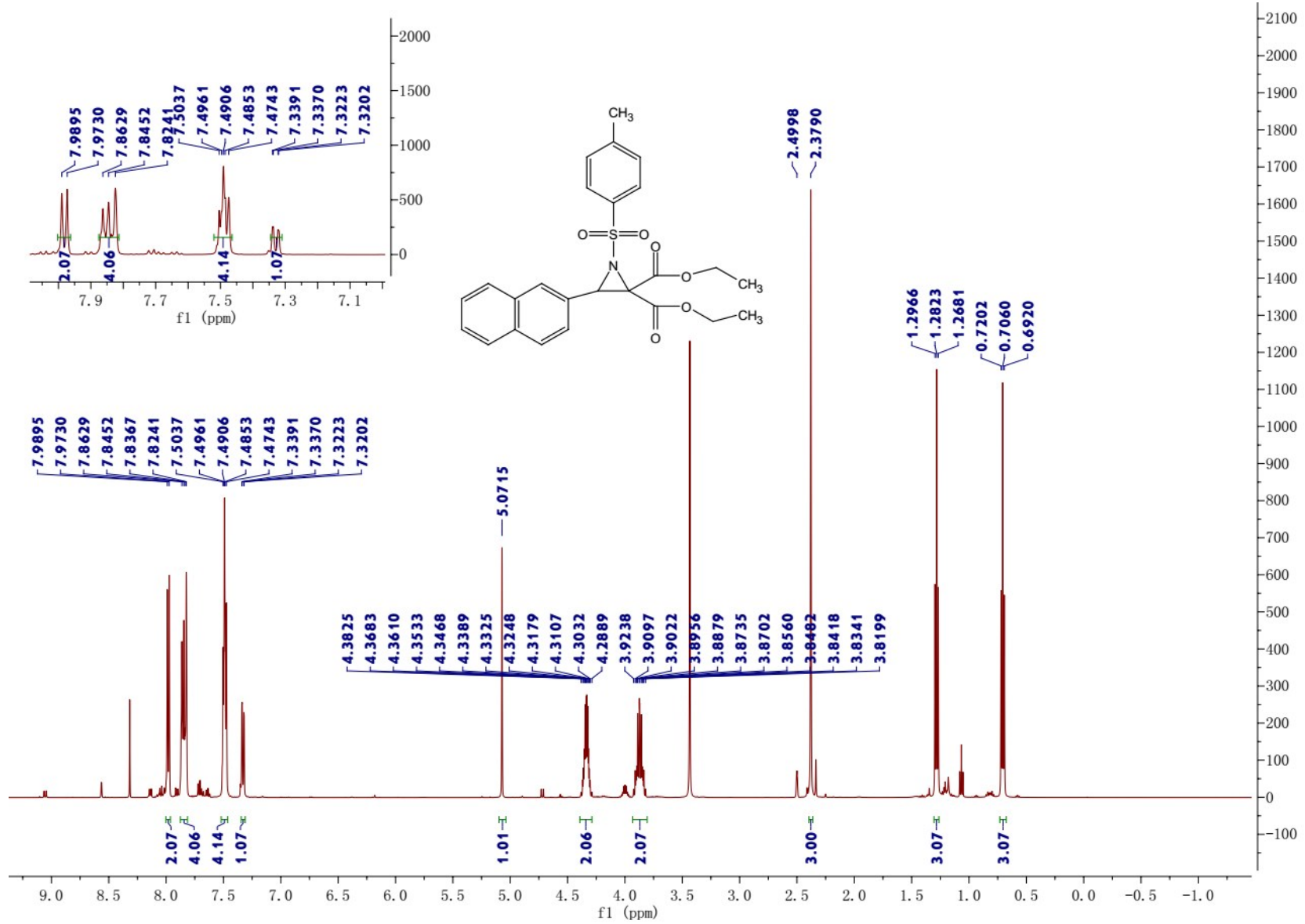
3b


4.8339
4.3300
4.3162
4.3020
4.2879
3.8537
3.8396
3.8255
3.8114
1.00
2.02
2.04
f1 (ppm)
CH3
O=S=O
N
O
O
CH3
O
O
CH3
2.5002
2.4137
2.3751
1.2750
1.2607
1.2466
0.6832
0.6690
0.6549
7.9730
7.9565
7.5132
7.4971
7.1883
7.1717
7.1554
7.0438
7.0298
6.9051
6.8898
4.8339
4.3162
4.3020
3.8537
3.8396
3.8255
3.8114
2.03
2.04
2.06
1.03
1.02
1.00
2.02
2.04
3.05
3.00
2.97
3.06
f1 (ppm)

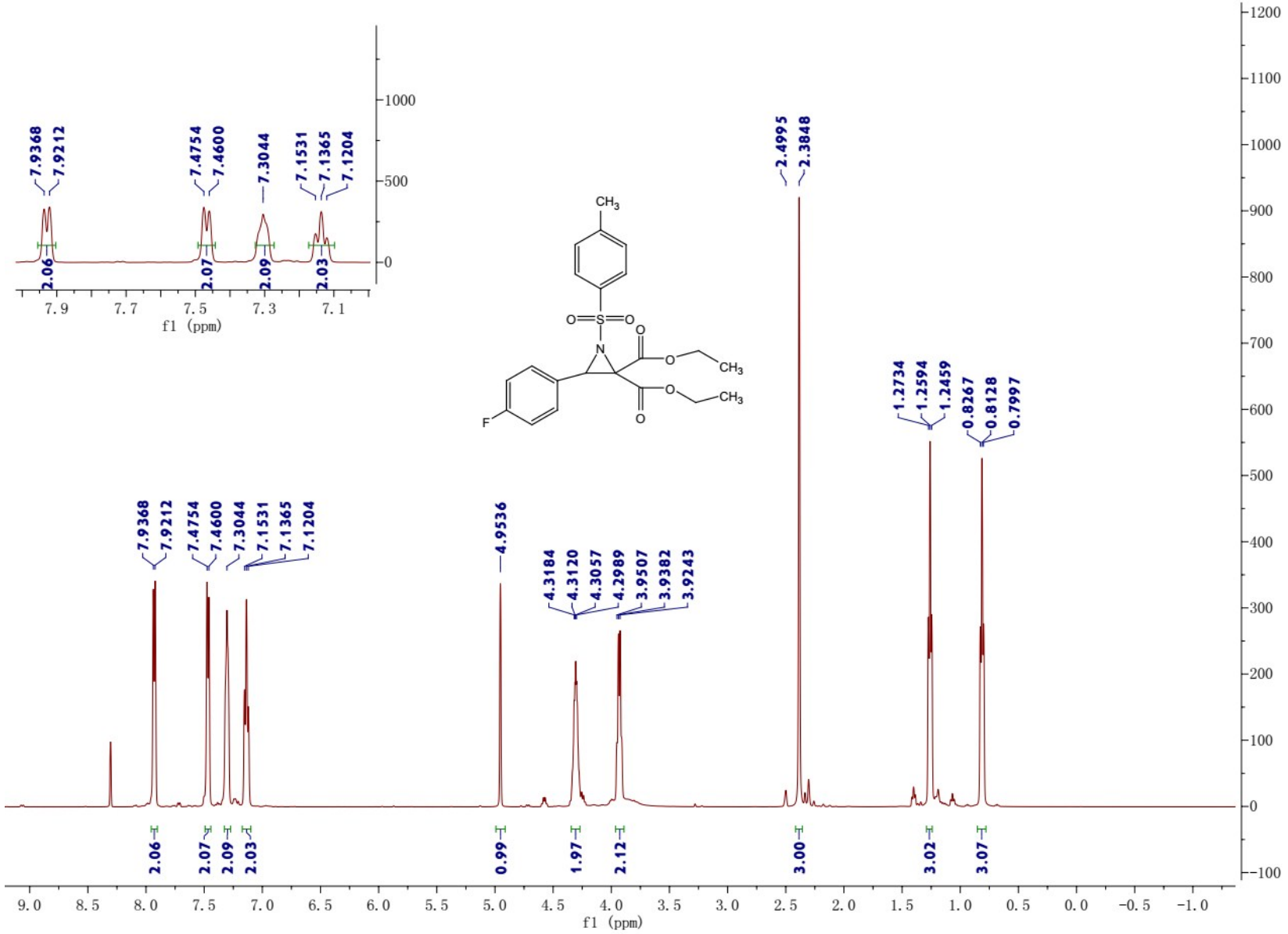
3c


7.9332
7.9178
7.4865
7.4712
7.1769
7.1621
7.1166
7.1022
7.0465
7.0053
6.9907
4.8295
4.3059
4.2991
4.2924
3.9361
3.9225
2.5002
2.3952
2.2075
1.2734
1.2603
1.2466
0.8187
0.8055
0.7920
2.01
2.12
4.15
0.99
2.04
2.06
3.01
3.00
3.08
3.07
f1 (ppm)

3f


7.9895
7.9730
7.8629
7.8452
7.8241
7.5037
7.4961
7.4906
7.4853
7.4743
7.3391
7.3370
7.3223
7.3202
2.07
4.06
4.14
1.07
f1 (ppm)
CH3
O=S=O
N
O
O
O
CH3
O
CH3
2.4998
2.3790
1.2966
1.2823
1.2681
0.7202
0.7060
0.6920
5.0715
4.3825
4.3683
4.3610
4.3533
4.3468
4.3389
4.3325
4.3248
4.3179
4.3107
4.3032
4.2889
3.9238
3.9097
3.9022
3.8956
3.8879
3.8735
3.8702
3.8560
3.8482
3.8418
3.8341
3.8199
2.07
4.06
4.14
1.07
1.01
2.06
2.07
3.00
3.07
3.07
f1 (ppm)

3h


7.9368
7.9212
7.4754
7.4600
7.3044
7.1531
7.1365
7.1204
2.06
2.07
2.09
2.03
f1 (ppm)
CH3
O=S=O
N
O
O
CH3
O
O
CH3
F
2.4995
2.3848
1.2734
1.2594
1.2459
0.8267
0.8128
0.7997
4.9536
4.3184
4.3120
4.3057
4.2989
3.9507
3.9382
3.9243
0.99
1.97
2.12
3.00
3.02
3.07
f1 (ppm)