Supplementary Materials for

Palladium-Catalyzed Asymmetric Allylic Alkylation (AAA) with Alkyl Sulfones as Nucleophiles

Barry M. Trost*, Zhiwei Jiao*, Hadi Gholami

Table of contents

I. General information

All experiments were performed under argon. To guarantee exclusion of air and moisture, all glassware was flame-dried under high vacuum and afterwards filled with argon. Tetrahydrofuran (THF) and toluene were refluxed and distilled over sodium/benzophenone. Anhydrous diethylether and anhydrous methanol were purchased from Acros Organics in AcroSeal bottles and were used as received. Chloroform-*d* was stored over potassium carbonate. If not stated otherwise, all starting materials were synthesized according to literature procedures or used in the form they were purchased commercially. The synthesized material was stored under argon at -10 ℃ until further use.

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded at 300 MHz using a Varian Inova 300 spectrometer, at 400 MHz using either a Varian 400 or Varian Mercury 400 spectrometer, at 500MHz using a Varian Inova 500 spectrometer, or at 600 MHz using a Varian Inova 600 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to the residual solvent peak (7.26 ppm for $CDCl_3$, 7.16 ppm for C_6D_6). Multiplets were assigned with the assistance of the multiplet tool in Mestrenova, and are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, app. = apparent. Carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded at 75 MHz using a Varian Inova 300 spectrometer, at 101 MHz using either a Varian 400 or Varian Mercury 400 spectrometer, or at 126 MHz using a Varian Inova 500 spectrometer. All ^{13}C chemical shifts are reported in ppm relative to the center of the residual solvent peak (77.16 ppm for $CDCl_3$).

Purification by flash column chromatography (FCC) was performed on silica gel (Fisher Scientific, 230−400 mesh, grade 60) using bulk solvent. Analytical thin layer chromatography (TLC) and preparative thin layer chromatography (PTLC) were performed on glass-backed silica-coated plates (Merck TLC Silicagel 60 F_{254}).

Visualization was done by UV light ($\lambda = 254$ nm) and/or basic potassium permanganate ($KMnO_4$).

Infrared (IR) spectra were obtained using a Nicolet IR100 FT-IR spectrometer and were measured as thin films from CH_2Cl_2 on NaCl plates and all values are given as wavenumbers in cm^{-1}. Enantiomeric excess (ee) was determined by high performance liquid chromatography (HPLC) using an Agilent 1200 series HPLC system. Individual retention times and separation conditions are specified for the compounds analyzed by HPLC. High resolution mass spectrometry (HRMS) was performed at University of Illinois at Urbana-Champaign. Crystal structure determination was performed at University of Notre Dame.

II. Substrate scope of different sulfone donors

General procedure: A 5 mL vial was flame-dried with a magnetic stir bar inside, (*R*, *R*, *S*, *S*, *R*, *R*)-Cy-Tom ligand **L1** (8.4 mg, 6 mmol %.), CpPd(η3–C_3H_5) (2 mg, 5 mmol%), (phenylsulfonylmethyl)trimethylsilane **1a** (68 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were added and the system was placed under an atmosphere of argon. The system was then dissolved in dry *t*-BuOMe (0.5 mL) and stirred at RT for 10 min, and then the mixture was placed in an oil bath maintained at 50 ^oC for 6-12 h. The crude mixture was subjected to flash silica column chromatography (petroleum ether/EtOAc 80:20) to yield the compound (**3a**, 50 mg, 80% yield) as a white solid. The ee value of the pure compound is 94% which was determined by HPLC.

For the non-enantioselective transformations, the same conditions were applied with SPhos (**L6**, CAS: 657408-07-6) as the supporting ligand.

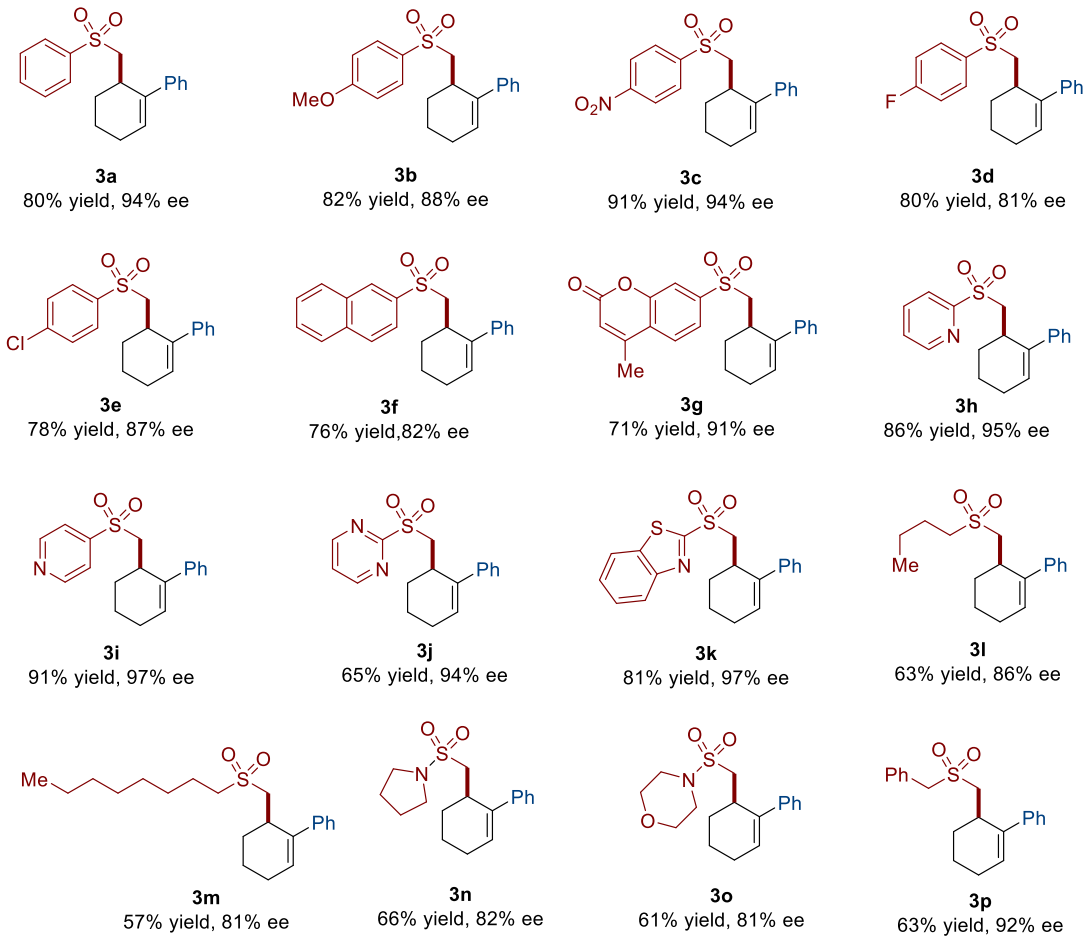
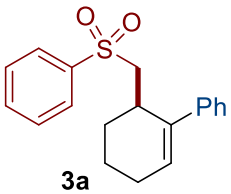


Figure S-1. Substrate scope of different sulfone donors



(*R*)-2-((Phenylsulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.67-7.63 (m, 1H), 7.55-7.51 (m, 2H), 7.18-7.16 (m, 3H), 7.01-6.99 (m, 2H), 6.05-6.03 (m, 1H), 3.27-3.23 (m, 1H), 3.09 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.97-2.93 (m, 1H), 2.30-2.24 (m, 1H), 2.19-2.15 (m, 2H), 1.94-1.86 (m, 1H), 1.74-1.69 (m, 1H), 1.63-1.55 (m, 1H).

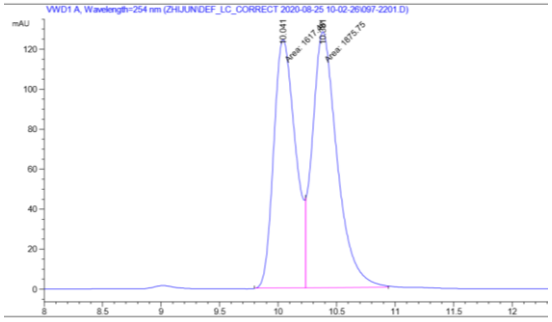
^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.2, 139.5, 138.0, 133.7, 129.4, 129.1, 128.6, 128.2, 127.2, 126.0, 58.1, 30.9, 26.7, 25.8, 17.7.

HRMS-ESI $(M+Na)^+$: 335.1082, found: 335.1074.

IR (cm^{-1}): 1439, 1296, 1143, 1080, 806, 756, 737, 686.

$[\alpha]^{23}_{D}$ = +88.6 (*c* = 5.3, $CHCl_3$).

Enantiomeric excess of the product (ee = 94%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 10.28 min), minor enantiomer (t_R = 9.99 min).



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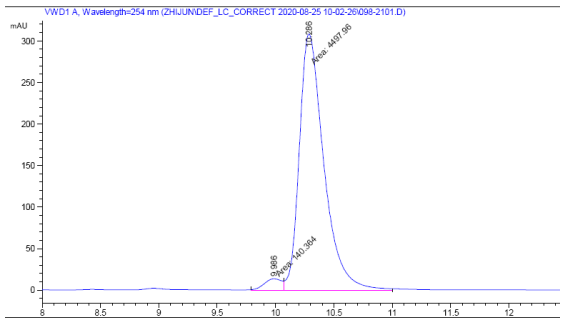

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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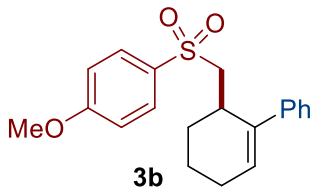


3b

(*R*)-2-(((4-Methoxyphenyl)sulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl.

The reaction was performed on 0.2 mmol scale, ((4-methoxyphenyl)sulfonyl)methyl)trimethylsilane (77 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.4 mg) was used as the supporting ligand. The product **3b** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (56 mg, 82% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.19-7.17 (m, 3H), 7.03-7.00 (m, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.03 (t, *J* = 4.0 Hz, 1H), 3.89 (s, 3H), 3.24-3.21 (m, 1H), 3.05 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.92 (d, *J* = 16.0 Hz, 1H), 2.27-2.15 (m, 3H), 1.90-1.85 (m, 1H), 1.72-1.68 (m, 1H), 1.59-1.54 (m, 1H).

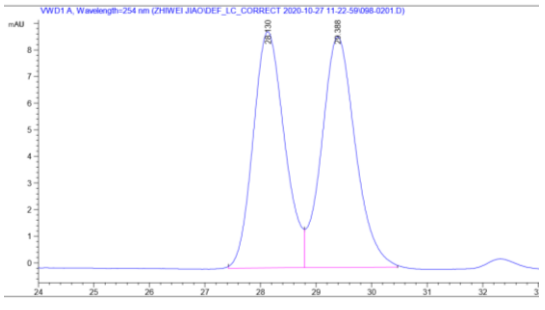
^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.7, 140.3, 138.17, 131.15, 130.3, 128.9, 128.6, 127.2, 126.1, 114.5, 58.4, 55.8, 31.0, 26.7, 25.9, 17.8.

HRMS-ESI $(M+Na)^+$: 365.1187, found: 365.1183.

IR (cm^{-1}): 1587, 1489, 1288, 1254, 1139, 1083, 756, 744, 695.

$[\alpha]^{23}_D$ = +94.6 (*c* = 5.1, $CHCl_3$).

Enantiomeric excess (ee = 88%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 29.30min), minor enantiomer (t_R = 28.04 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	28.130	BV	0.6000	347.84262		8.87424	48.7943
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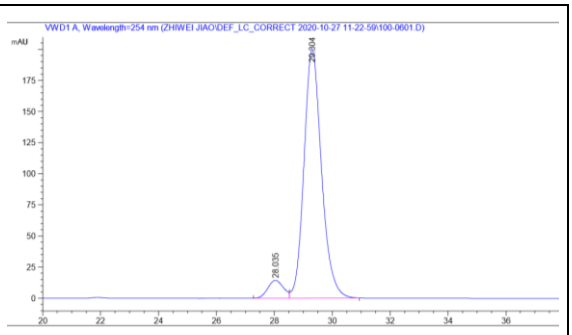
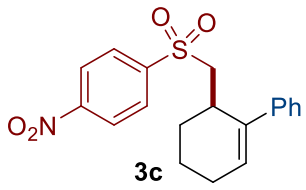


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	28.035	BV	0.5774	539.11902		14.37204	6.0125
2	29.304	VB	0.6465	8427.47461		199.79187	93.9875



3c

(*R*)-2-(((4-Nitrophenyl)sulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl.

The reaction was performed on 0.2 mmol scale, trimethyl(((4-nitrophenyl)sulfonyl)methyl)silane (82 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.4 mg) was used as the supporting ligand. The product **3c** was obtained by flash silica column chromatography (petroleum ether/EtOAc 85:15) (65 mg, 91% yield) as a pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.0 Hz, 2H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.20-7.15 (m, 3H), 7.02-7.00 (m, 2H), 6.01 (t, *J* = 4.0 Hz, 1H), 3.27-3.10 (m, 1H),

3.13 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.98 (d, *J* = 16.0 Hz, 1H), 2.27-2.16 (m, 3H), 1.98-1.90 (m, 1H), 1.77-1.72 (m, 1H), 1.62-1.55 (m, 1H).

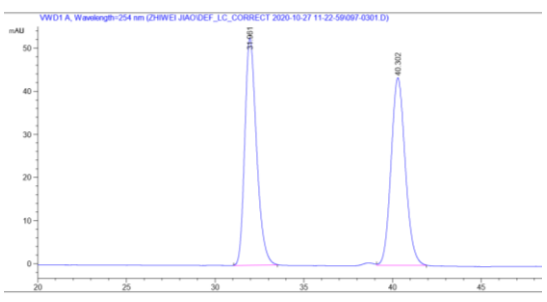
^{13}C-NMR (101 MHz, $CDCl_3$): δ 150.8, 145.2, 140.2, 137.7, 129.52, 129.50, 128.6, 127.4, 126.2, 124.5, 58.1, 31.1, 26.9, 25.7, 17.6.

HRMS -ESI $(M+Na)^+$: 380.0932, found: 380.0927.

IR (cm^{-1}): 1629, 1603, 1526, 1342, 1302, 1143, 1079, 850, 754, 733, 692, 679.

$[\alpha]^{24}_D$ = +90.0 (*c* = 5.7, $CHCl_3$).

Enantiomeric excess (ee = 94%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 40.23 min), minor enantiomer (t_R = 31.97 min).



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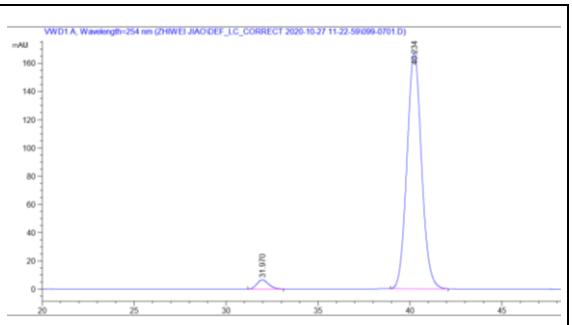

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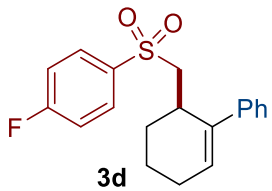


3d

(*R*)-2-(((4-Fluorophenyl)sulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl.

The reaction was performed on 0.2 mmol scale, (((4-fluorophenyl)sulfonyl)methyl)trimethylsilane (74 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3c** was obtained by flash silica column chromatography (petroleum ether/EtOAc 85:15) (53 mg, 80% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.21-7.17 (m, 5H), 7.03-7.00 (m, 2H), 6.03 (t, *J* = 4.0 Hz, 1H), .25-3.22 (m, 1H), 3.07 (dd,, *J* = 16.0, 8.0 Hz, 1H), 2.93 (d, *J* = 16.0 Hz, 1H), 2.28-2.22 (m, 1H), 2.19-2.16 (m, 2H), 1.94-1.87 (m, 1H), 1.75-1.68 (m, 1H), 1.61-1.54 (m, 1H).

^{19}F NMR (376.6 MHz, CDCl3): δ -104.15.

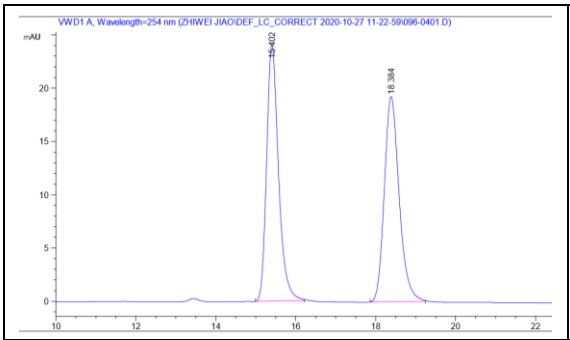
^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.9 (d, *J* = 256.5 Hz), 140.3, 138.1, 135.7 (d, *J* = 3.0 Hz), 131.0 (d, *J* = 9.1 Hz), 129.2, 128.6, 127.3, 126.1, 116.6 (d, *J* = 22.2 Hz), 58.3, 31.1, 26.8, 25.8, 17.7.

HRMS -ESI $(M+Na)^+$: 353.0987, found: 353.0983.

IR (cm^{-1}): 1637, 1538, 1486, 1283, 1142, 833, 744, 695.

$[\alpha]^{24}_D$ = +71.3 (*c* = 2.8, $CHCl_3$).

Enantiomeric excess (ee = 81%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 18.32 min), minor enantiomer (t_R = 15.41 min).



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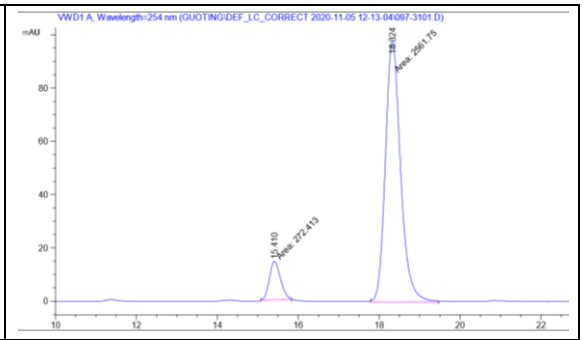

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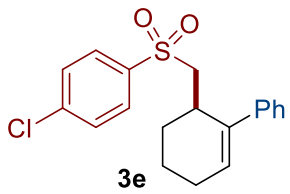


3e

(*R*)-2-(((4-Chlorophenyl)sulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl.

The reaction was performed on 0.2 mmol scale, (((4-chlorophenyl)sulfonyl)methyl)trimethylsilane (79 mg, 0.3 mmol) and

2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3e** was obtained by flash silica column chromatography (petroleum ether/EtOAc 85:15) (54 mg, 78% yield) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 3H), 7.01-6.99 (m, 2H), 6.02 (t, *J* = 4.0 Hz, 1H), 3.22-3.21 (m, 1H), 3.07 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.92 (d, *J* = 16.0 Hz 1H), 2.28-2.21 (m, 1H), 2.19-2.15 (m, 1H), 1.94-1.87 (m, 1H), 1.75-1.70 (m, 1H), 1.61-1.54 (m, 1H).

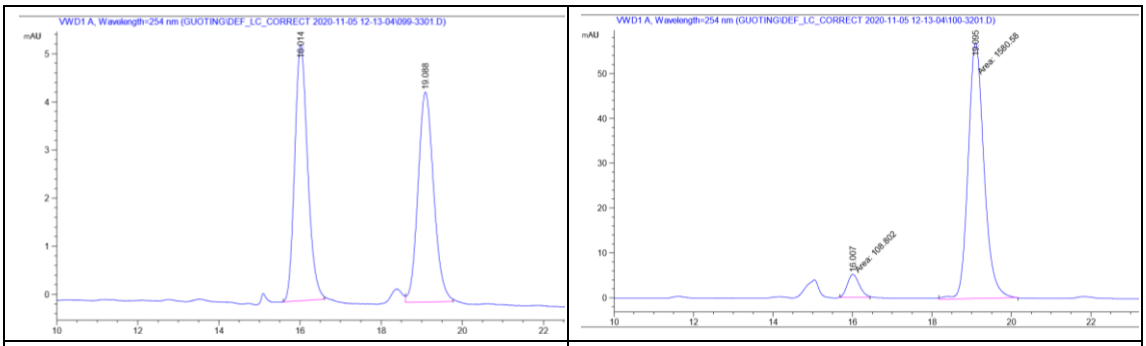
^{13}C-NMR (101 MHz, $CDCl_3$):δ 140.5, 140.3, 138.0, 129.69, 129.66, 129.66, 129.2, 128.6, 127.3, 126.1, 58.2, 31.1, 26.8, 25.8, 17.7.

HRMS-ESI $(M+Na)^+$: 369.0692, found: 369.0680.

IR (cm^{-1}): 1581, 1475, 1395, 1311, 1278, 1, 1088, 1013, 810, 758, 735, 698, 624.

$[\alpha]^{24}_D$ = +163.8 (*c* = 3.0, $CHCl_3$).

Enantiomeric excess (ee = 87%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 19.10 min), minor enantiomer (t_R = 16.01 min).



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1	16.014	BB	0.3421	117.56873	5.32406	50.0775
2	19.088	VB	0.4110	117.20483	4.36178	49.9225

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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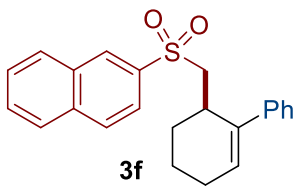
2	19.095	MM	0.4623	1580.57788	56.97678	93.5596



3f

(*R*)-2-(((2,3,4,5-Tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)naphthalene

The reaction was performed on 0.2 mmol scale, trimethyl((naphthalen-2-ylsulfonyl)methyl)silane (84 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.4 mg) was used as the supporting ligand. The product **3f** was obtained by flash silica column chromatography (petroleum ether/EtOAc 85:15) (55 mg, 76% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 7.97-7.94 (m, 3H), 7.75-7.64 (m, 3H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 8.0 Hz, 2H), 6.92-6.90 (m, 2H), 6.01 (t, *J* = 4.0 Hz, 1H), 3.28-3.25 (m, 1H), 3.15 (dd. *J* = 16.0, 12.0 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.34-2.28 (m, 1H), 2.18-2.15 (m, 1H), 1.97-1.88 (m, 1H), 1.75-1.69 (m, 1H), 1.63-1.59 (m, 1H).

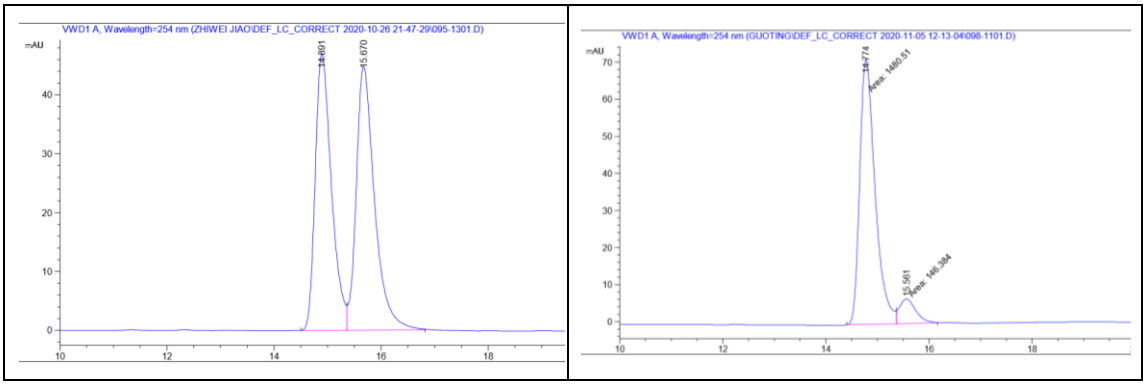
^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.2, 138.1, 136.3, 135.4, 132.3, 129.9, 129.64, 129.58, 129.4, 129.0, 128.5, 128.1, 127.8, 127.1, 126.0, 122.9, 58.2, 31.1, 26.8, 25.9, 17.8.

HRMS -ESI $(M+Na)^+$: 385.1238, found: 385.1235.

IR (cm^{-1}): 1447, 1346, 1304, 1268, 1242, 1189, 1148, 1125, 1072, 908, 870, 818, 754, 698, 658, 614.

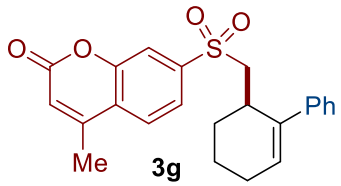
$[\alpha]^{24}_D$ = +97.6 (*c* = 3.4, $CHCl_3$).

Enantiomeric excess (ee = 82%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.6 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 15.56 min), minor enantiomer (t_R = 14.77 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.037	BB	0.4031	2894.45313	108.97269	50.8622
2	27.289	BB	0.9670	2796.32397	42.66730	49.1378

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.774	MF	0.3450	1480.51392	71.51909	91.0023
2	15.561	FM	0.3657	146.38376	6.67154	8.9977



3g

(*R*)-4-Methyl-7-(((2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)-2*H*-chromen-2-one.

The reaction was performed on 0.2 mmol scale, 6-(((trimethylsilyl)methyl)sulfonyl)-2H-chromen-2-one (89 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand, as the solubility of this sulfone is not very good in *t*-BuOMe, 1,4-dioxane was used as solvent. The product **3g** was obtained by flash silica column chromatography (petroleum ether/EtOAc 60:40) (56 mg, 71% yield) as a yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73-7.66 (m, 3H), 7.17-7.13 (m, 3H), 7.03-7.01 (m, 2H), 6.45 (s, 1H), 6.00 (t, *J* = 4.0 Hz, 1H), 3.28-3.26 (m, 1H), 3.11 (dd, *J* = 16.0, 12.0 Hz, 1H), 2.98 (d, *J* = 16.0 Hz, 1H), 2.49 (s, 3H), 2.24-2.15 (m, 3H), 1.97-1.90 (m, 1H), 1.73-1.70 (m, 1H), 1.62-1.53 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 159.3, 153.4, 151.0, 142.3, 140.3, 137.9, 129.3, 128.5, 127.31, 126.2, 125.9, 124.0, 123.2, 118.0, 117.1, 58.2, 31.1, 26.9, 25.73, 18.9, 17.7.

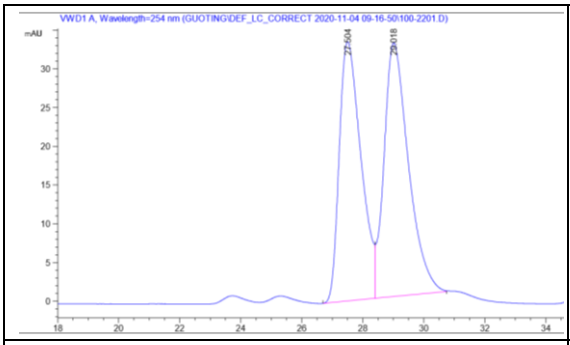
HRMS-ESI $(M+H)^+$: 395.1317, found: 395.1304.

IR (cm^{-1}): 1742, 1627, 1444, 1403, 1328, 1308, 1246, 1223, 1177, 1145, 1086, 958, 870, 758, 700, 651, 622.

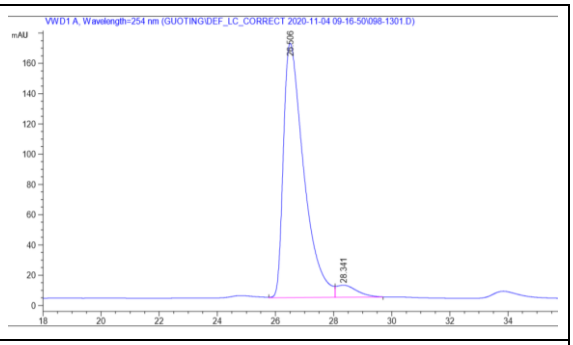
$[\alpha]^{24}_{D}$ = +96.9 (*c* = 4.1, $CHCl_3$).

Enantiomeric excess (ee = 91%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 80:20, 254 nm absorbance), retention times: major

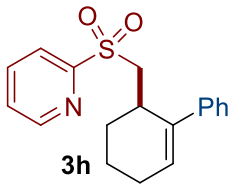
enantiomer (t_R = 26.51 min), minor enantiomer (t_R = 28.34 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.504	BV	0.7586	1650.67749	33.48201	47.4406
2	29.018	VB	0.8306	1828.78198	32.75014	52.5594



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.506	VB	0.7286	8188.30811	168.04630	95.4509
2	28.341	BB	0.6819	390.24307	8.01069	4.5491



3h

(*R*)-2-(((2,3,4,5-Tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3h** was obtained by flash silica column chromatography (petroleum ether/EtOAc 60:40) (54 mg, 86% yield) as a white solid. The compound was recrystallized for acetone/hexanes to afford the single crystal, which was subjected to X-ray diffraction.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.93-7.90 (m, 1H), 7.53-7.50 (m, 1H), 7.24-7.19 (m, 3H), 7.16-7.14 (m 2H), 6.03 (t, *J* = 4.0 Hz, 1H), 3.41-3.40 (m, 1H), 3.38 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.26 (d, *J* = 12.0 Hz, 1H), 2.19-2.14 (m, 3H), 1.90-1.84 (m, 1H), 1.70-1.61 (m, 2H).

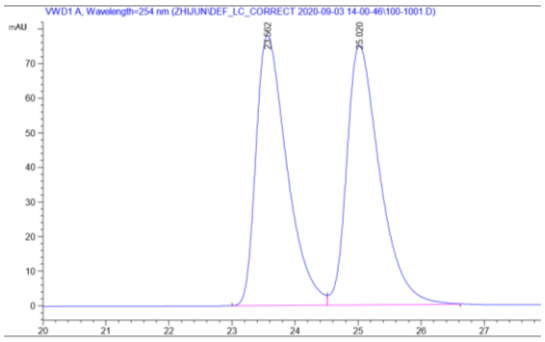
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.6, 150.3, 140.4, 138.22, 138.20, 129.1, 128.6, 127.3, 127.2, 126.2, 122.2, 54.2, 30.7, 26.9, 25.8, 17.6.

HRMS-ESI $(M+Na)^+$: 336.1034, found: 336.1027.

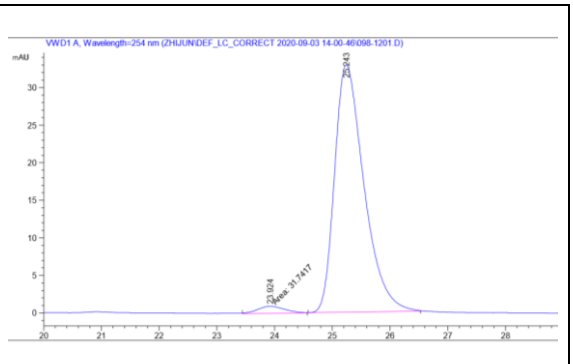
IR (cm^{-1}): 1577, 1451, 1427, 1306, 1162, 1111, 1081, 809, 751, 698.

$[\alpha]^{23}_{D}$ = +75.4 (*c* = 0.6, $CHCl_3$).

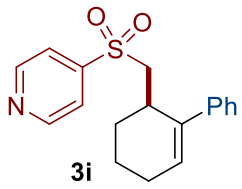
Enantiomeric excess (ee = 95%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 25.24 min), minor enantiomer (t_R = 23.92 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.562	BV	0.5177	2657.99097	78.13873	49.3488
2	25.020	VB	0.5492	2728.14087	75.06833	50.6512



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.924	MM	0.5527	31.74166	9.57106e-1	2.6512
2	25.243	VB	0.5414	1165.52380	32.90414	97.3488



3i

(*R*)-4-(((2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 4-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3i** was obtained by flash silica column chromatography (petroleum ether/EtOAc 50:50) (57 mg, 91% yield) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.84 (d, *J* = 4.0 Hz, 2H), 7.62 (d, *J* = 4.0 Hz, 2H), 7.20-7.18 (m, 3H), 7.02-6.99 (m, 1H), 6.02 (t, *J* = 4.0 Hz, 1H), 3.26-3.23 (m, 1H), 3.10 (dd, *J* = 16.0, 12.0 Hz, 1H), 2.95 (d, *J* = 12.0 Hz, 1H), 2.27-2.15 (m, 3H), 1.98-1.89 (m, 1H), 1.74-1.71 (m, 1H), 1.61-1.54 (m, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 151.3, 147.4, 140.1, 137.7, 129.4, 128.7, 127.4,

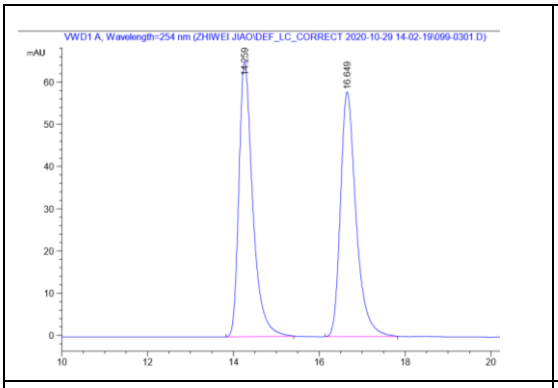
126.1, 121.2, 57.6, 31.0, 26.8, 25.7, 17.6.

HRMS-ESI $(M+H)^+$: 314.1216, found: 314.1215.

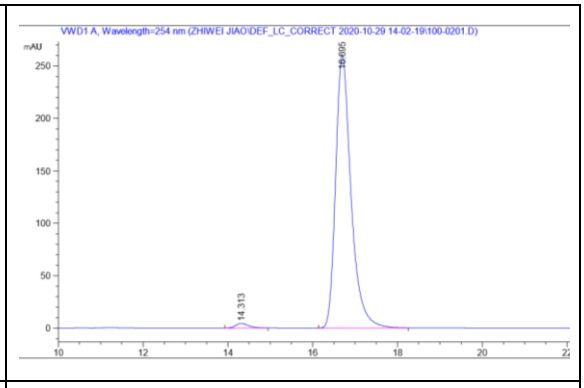
IR (cm^{-1}): 2921, 1631, 1565, 1396, 1305, 1148, 1093, 813, 749, 696.

$[\alpha]^{23}_D$ = +85.6 (*c* = 6.2, $CHCl_3$).

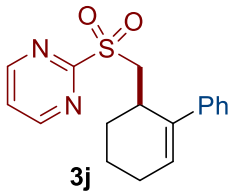
Enantiomeric excess (ee = 97%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 16.703 min), minor enantiomer (t_R = 14.31 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.259	BB	0.3368	1461.35571	65.29304	49.9376
2	16.649	BB	0.3822	1465.00879	57.97651	50.0624



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.313	BB	0.3312	97.34240	4.42035	1.4564
2	16.695	BB	0.3826	6586.57715	260.31570	98.5436



3j

(*R*)-2-(((2,3,4,5-Tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)pyrimidine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyrimidine (69 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3j** was obtained by flash silica column chromatography (petroleum ether/EtOAc 50:50) (41 mg, 65% yield) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.25-7.20 (m, 5H), 6.05 (t, *J* = 4.0 Hz, 1H), 3.53-3.52 (m, 1H), 3.49 (t, *J* = 12.0 Hz, 1H), 3.42 (d, *J* =

12.0 Hz, 1H), 2.23-2.18 (m, 1H), 1.97-1.90 (m, 1H), 1.73-1.58 (m, 2H).

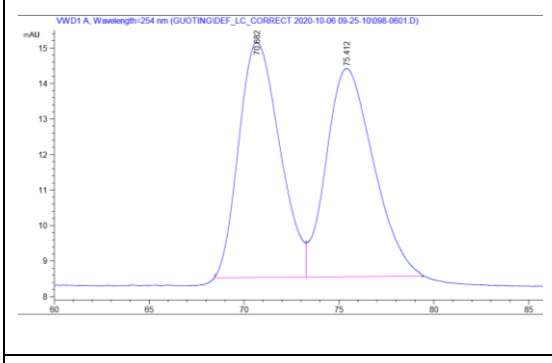
^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.1, 158.7, 140.5, 138.3, 129.3, 128.6, 127.3, 126.4, 123.7, 53.6, 30.7, 27.1, 25.8.

HRMS-ESI $(M+Na)^+$: 337.0987 found: 337.0977.

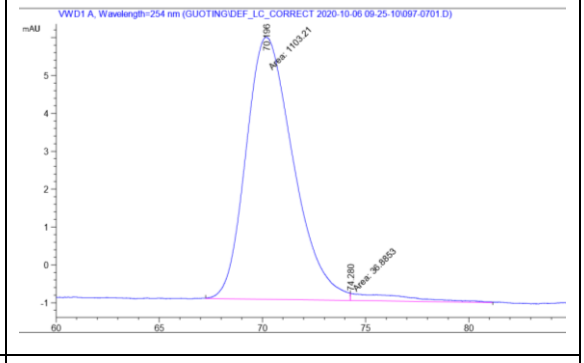
IR (cm^{-1}): 1670, 1565, 1445, 1386, 1312, 1250, 1213, 1123, 989, 814, 758, 699, 613.

$[\alpha]^{24}_D$ = +116.1 (*c* = 2.5, $CHCl_3$).

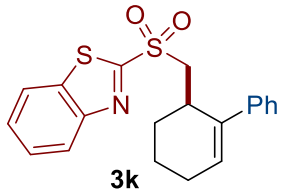
Enantiomeric excess (ee = 94%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (OD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 70.20 min), minor enantiomer (t_R = 74.28 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	70.682	BV	1.7513	988.66327	6.61919	49.3485
2	75.412	VB	2.0316	1014.76855	5.86088	50.6515



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	70.196	MF	2.6567	1103.20935	6.92093	96.7647
2	74.280	FM	3.2396	36.88529	1.89762e-1	3.2353



3k

(*R*)-2-(((2,3,4,5-Tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)benzo[*d*]thiazole.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)benzo[*d*]thiazole (86 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3k** was obtained by flash silica column chromatography (petroleum ether/EtOAc 85:15) (60 mg, 81% yield) as a yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.67-7.58 (m, 2H), 7.12-7.01 (m, 5H), 6.04 (t, *J* = 4.0 Hz, 1H), 3.52-3.48 (m, 1H), 3.45-3.36 (m, 2H), 2.29-2.23 (m, 1H), 2.21-2.19 (m, 2H), 2.00-1.93 (m, 1H), 1.76-1.71 (m, 1H), 1.68-1.60 (m, 1H).

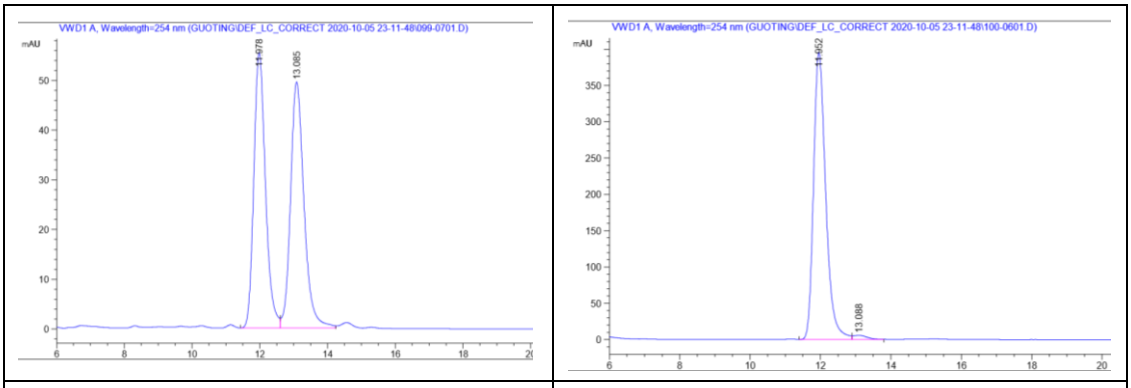
^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.0, 152.8, 140.1, 137.9, 137.0, 129.4, 128.5, 128.1, 127.7, 127.3, 126.2, 125.7, 122.4, 57.1, 31.1, 27.0, 25.8, 17.5.

HRMS-ESI $(M+H)^+$: 370.0935, found: 370.0927.

IR (cm^{-1}): 1642, 1548, 1486, 1464, 1416, 1329, 1310, 1231, 1184, 1144, 1078, 1018, 864, 847, 756, 726, 694, 623.

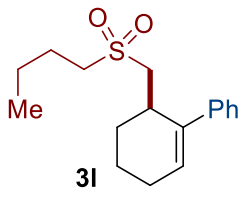
$[\alpha]^{24}_D$ = +106.0 (*c* = 5.6, $CHCl_3$).

Enantiomeric excess (ee = 97%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (OD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 13.09 min), minor enantiomer (t_R = 11.95 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.978	VV	0.3675	1325.07935	55.47977	49.1735
2	13.085	VB	0.4202	1369.62329	49.52304	50.8265

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.952	VV	0.3695	9517.98828	395.63358	98.4450
2	13.088	VB	0.3950	150.34297	5.59503	1.5550



3l

(*R*)-2-((Butylsulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl.

The reaction was performed on 0.2 mmol scale, ((butylsulfonyl)methyl)trimethylsilane (62 mg, 0.3 mmol) and

2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3l** was obtained by flash silica column chromatography (petroleum ether/EtOAc 90:10) (37 mg, 63% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (m, 4H), 7.20-7.17 (m, 1H), 5.99 (t, *J* = 4.0 Hz, 1H), 3.41 (brs, 1H), 2.85-2.72 (m, 4H), 2.18-2.11 (m, 3H), 1.94-1.90 (m, 1H), 1.58-1.49 (m, 4H), 1.32-1.23 (m, 2H), 0.80 (t, *J* = 8.0 Hz, 3H).

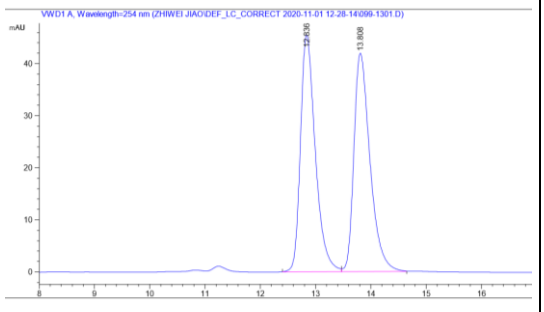
^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.7, 138.4, 129.1, 128.8, 127.5, 126.4, 54.6, 53.8, 30.5, 27.3, 25.8, 24.0, 21.8, 17.7, 13.6.

HRMS-ESI $(M+Na)^+$: 315.1395, found: 315.1397

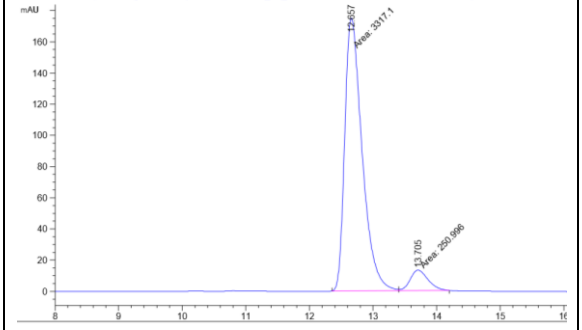
IR (cm^{-1}): 1451, 1312, 1295, 1271, 1130, 1099, 1066, 752, 694.

$[\alpha]^{24}_D$ = +78.4 (*c* = 3.2, $CHCl_3$).

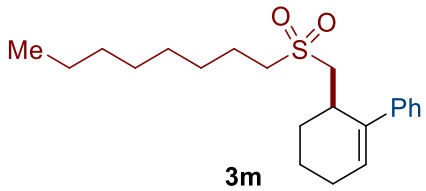
Enantiomeric excess (ee = 86%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 98:2, 254 nm absorbance), retention times: major enantiomer (t_R = 12.66 min), minor enantiomer (t_R = 13.71 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	12.836	BV	0.2833	849.12177	45.49051	50.0678	
2	13.808	VB	0.3070	846.82288	41.92700	49.9322	



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	12.657	MF	0.3160	3317.10352	174.94426	92.9656	
2	13.705	FM	0.3204	250.99594	13.05635	7.0344	



3m

(*R*)-2-((Octylsulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl.

The reaction was performed on 0.2 mmol scale, trimethyl((octylsulfonyl)methyl)silane (79 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3m** was obtained by flash silica column chromatography (petroleum ether/EtOAc 90:10) (40 mg, 57% yield) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34-7.33 (m, 4H), 7.28-7.25 (m, 1H), 6.07 (t, *J* = 4.0 Hz, 1H), 3.48 (brs, 1H), 2.93-2.79 (m, 4H), 2.25-2.19 (m, 3H), 1.74-1.64 (m, 1H), 1.62-1.55 (m, 4H), 1.30-1.24 (m, 10H), 0.87 (t, *J* = 8.0 Hz, 3H).

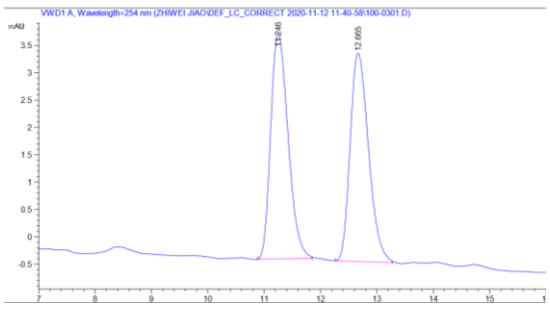
^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.8, 138.5, 129.2, 128.8, 127.5, 126.5, 54.6, 54.1, 31.8, 30.6, 29.1, 29.0, 28.6, 27.4, 25.9, 22.7, 22.1, 17.8, 14.2.

HRMS-ESI $(M+Na)^+$: 371.2021, found: 371.2015.

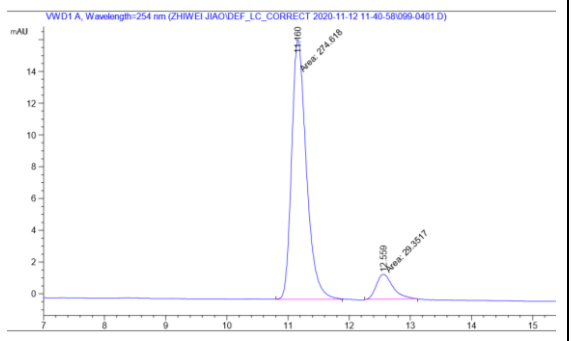
IR (cm^{-1}): 1467, 1299, 1259, 1132, 757, 699, 618.

$[\alpha]^{24}_{D}$ = +56.3 (*c* = 1.0, $CHCl_3$).

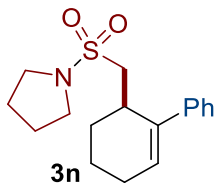
Enantiomeric excess (ee = 81%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 98:2, 254 nm absorbance), retention times: major enantiomer (t_R = 11.16 min), minor enantiomer (t_R = 12.56 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.246	BB	0.3409	88.29968	4.10983	50.5559
2	12.665	BB	0.3549	86.35781	3.80678	49.4441



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.160	MM	0.2797	274.61835	16.36478	90.3439
2	12.559	MM	0.3121	29.35171	1.56732	9.6561



3n

(*R*)-1-(((2,3,4,5-Tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)pyrrolidine.

The reaction was performed on 0.2 mmol scale, 1-(((trimethylsilyl)methyl)sulfonyl)pyrrolidine (66 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3n** was obtained by flash silica column chromatography (petroleum ether/EtOAc 85:15) (40 mg, 66% yield) as a pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 737-7.30 (m, 4H), 7.27-7.23 (m, 1H), 6.08 (t, *J* = 4.0 Hz, 1H), 3.39 (brs,1H), 3.22-3.17 (m, 4H), 2.87 (d, *J* = 4.0 Hz, 2H), 2.29-2.17 (m, 3H), 1.98-1.92 (m, 1H), 1.86-1.82 (m, 4H), 1.76-1.71 (m, 1H), 1.66-1.59 (m, 1H).

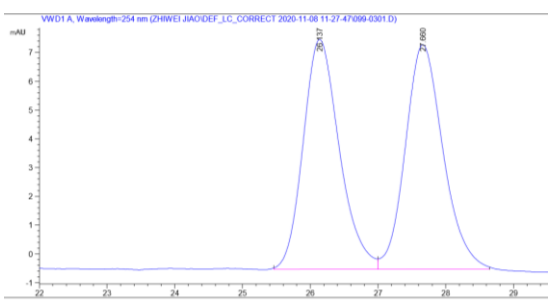
^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.8, 138.6, 128.7, 128.7, 127.3, 126.4, 51.4, 47.7, 31.6, 26.9, 26.0, 25.9, 17.9.

HRMS-ESI $(M+Na)^+$: 328.1347, found: 328.1339.

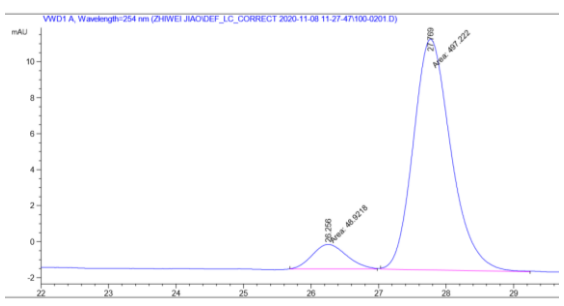
IR (cm^{-1}): 1453, 1316, 1253, 1197, 1143, 1063, 1010, 795, 759, 695, 620.

$[\alpha]^{24}_{D}$ = +34.9 (*c* = 1.2, $CHCl_3$).

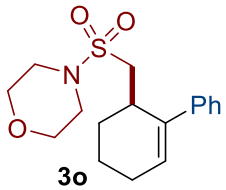
Enantiomeric excess (ee = 82%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 99:1, 254 nm absorbance), retention times: major enantiomer (t_R = 27.77 min), minor enantiomer (t_R = 26.26 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.137	BV	0.5673	296.76645	7.98884	49.5828
2	27.660	VB	0.5898	301.76016	7.79757	50.4172



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.256	MM	0.5925	48.92182	1.37623	8.9577
2	27.769	MM	0.6463	497.22153	12.82295	91.0423



3o

(*R*)-4-(((2,3,4,5-Tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)morpholine.

The reaction was performed on 0.2 mmol scale, 4-(((trimethylsilyl)methyl)sulfonyl)morpholine (71 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3o** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (39 mg, 61% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35-7.33 m, 4H), 7.29-7.24 (m, 1H), 6.09 (t, *J* = 4.0 Hz, 1H), 3.68 (t, *J* = 4.0 Hz, 4H), 3.41 (brs, 1H), 3.08 (t, *J* = 4.0 Hz, 4H), 2.81-2.78 (m, 2H), 2.26-2.19 (m, 3H), 2.00-1.93 (m, 1H), 1.75-1.72 (m, 1H), 1.65-1.61 (m, 1H).

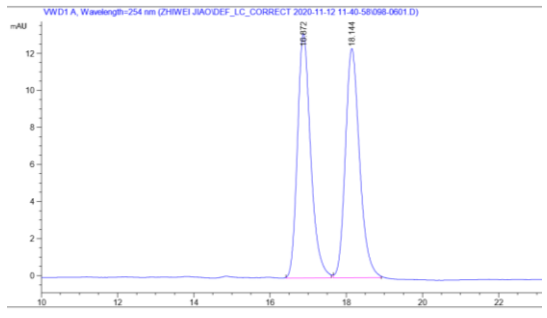
^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.8, 138.7, 129.0, 128.8, 127.5, 126.4, 66.6, 50.4, 45.7, 31.4, 26.9, 25.9, 17.9.

HRMS-ESI $(M+Na)^+$: 344.1296, found: 344.1288.

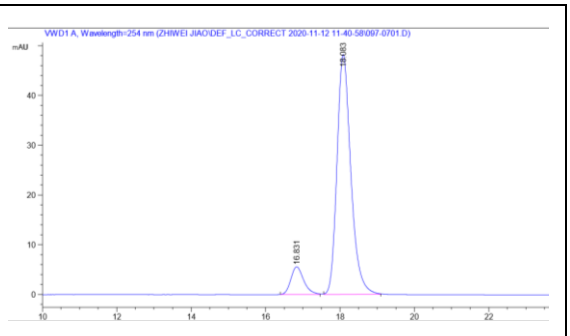
IR (cm^{-1}): 1452, 1345, 1318, 1261, 1154, 1114, 1073, 950, 755, 697.

$[\alpha]^{24}_{D}$ = +23.8 (*c* = 1.5, $CHCl_3$).

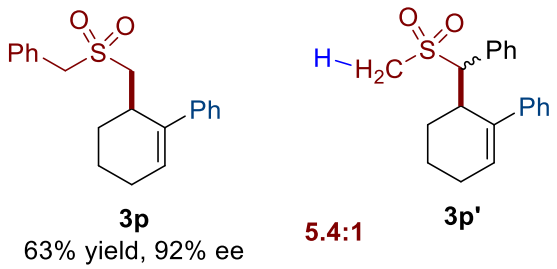
Enantiomeric excess (ee = 81%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 18.08 min), minor enantiomer (t_R = 16.83 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.872	BB	0.3698	319.07388	13.18115	49.8516
2	18.144	BB	0.3974	320.97296	12.36785	50.1484



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.831	BB	0.3673	133.66444	5.56958	9.6882
2	18.083	BB	0.3948	1245.99890	48.19700	90.3118



(*R*)-2-((benzylsulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl

The reaction was performed on 0.2 mmol scale, ((benzylsulfonyl)methyl)trimethylsilane (73 mg, 0.3 mmol) and 2-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (35 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **3p** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (41 mg, 63% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 8H), 7.17-7.15 (m, 2H), 6.04 (t, d, *J* = 4.0 Hz, 1H), 4.07 (s, 2H), 3.48 (brs, 1H), 2.83-2.78 (m, 2H), 2.19-2.15 (m, 3H), 2.01-1.96 (m, 1H), 1.71-1.67 (m, 1H), 1.55-1.50 (m, 1H).

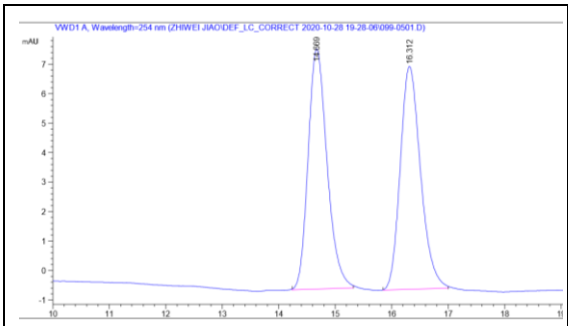
^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.6, 138.3, 130.7, 129.1, 129.0, 128.9, 128.8, 128.0, 127.4, 126.4, 60.8, 53.3, 30.4, 27.3, 25.8, 17.8.

IR (cm^{-1}): 1494, 1454, 1302, 1247, 1136, 1116, 781, 760, 698.

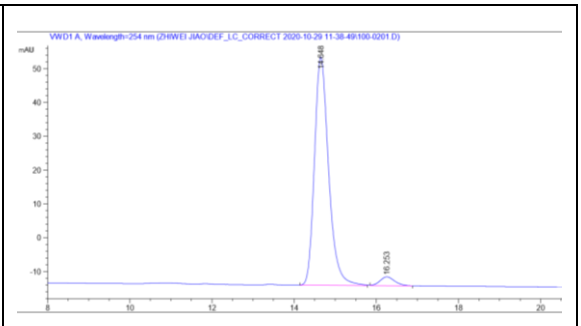
HRMS-ESI $(M+Na)^+$: 349.1238, found: 349.1227.

$[\alpha]^{24}_D$ = +151.0 (*c* = 4.6, $CHCl_3$).

Enantiomeric excess (ee = 92%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 98:2, 254 nm absorbance), retention times: major enantiomer (t_R = 14.65 min), minor enantiomer (t_R = 16.25 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	14.669	BB	0.3611	190.29311	8.15449	50.1464	
2	16.312	BB	0.3833	189.18187	7.56948	49.8536	



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	14.648	BB	0.3674	1622.34888	67.58199	96.1426	
2	16.253	BB	0.3719	65.09137	2.61549	3.8574	

III. Substrate scope of different allylic acceptors

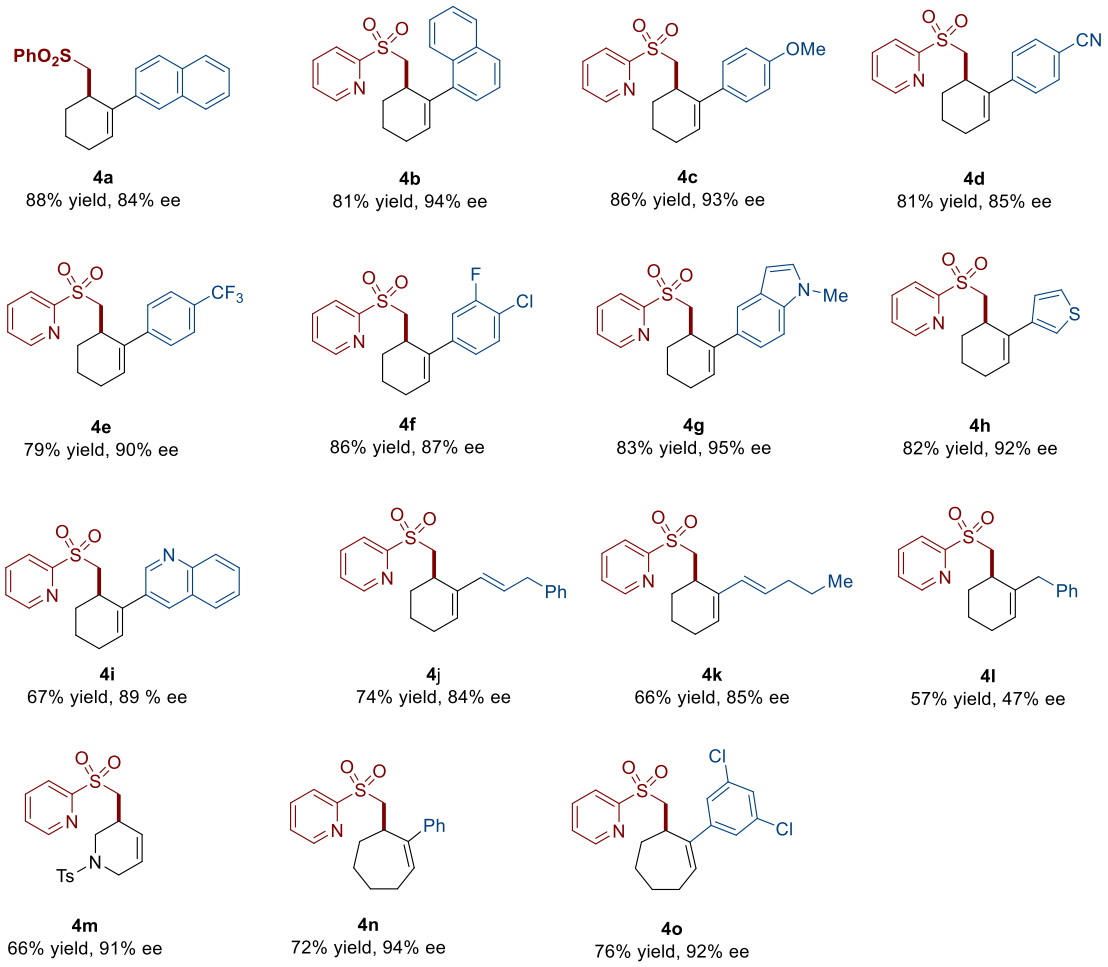
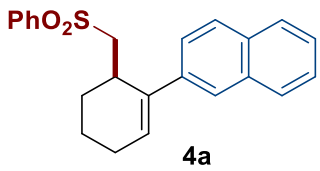


Figure S-2. Substrates scope of different allylic acceptors.



4a

(*R*)-2-((benzylsulfonyl)methyl)-2,3,4,5-tetrahydro-1,1'-biphenyl

The reaction was performed on 0.2 mmol scale, trimethyl((phenylsulfonyl)methyl)silane (68 mg, 0.3 mmol) and 2-(6-fluorocyclohex-1-en-1-yl)naphthalene (45 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4a** was obtained by flash silica column chromatography (petroleum ether/EtOAc 85:15) (64 mg, 88% yield) as a yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.80-7.77 (m, 3H), 7.68-7.62 (m, 3H), 7.50-7.44 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.19 (t, *J* = 4.0 Hz, 1H), 3.42 (brs, 1H), 3.11 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.02 (d, *J* = 16.0 Hz, 1H), 2.39-2.32 (m, 1H), 2.24-2.23 (m, 1H), 2.01-1.92 (m, 1H), 1.79-1.74 (m, 1H), 1.69-1.62 (m, 1H).

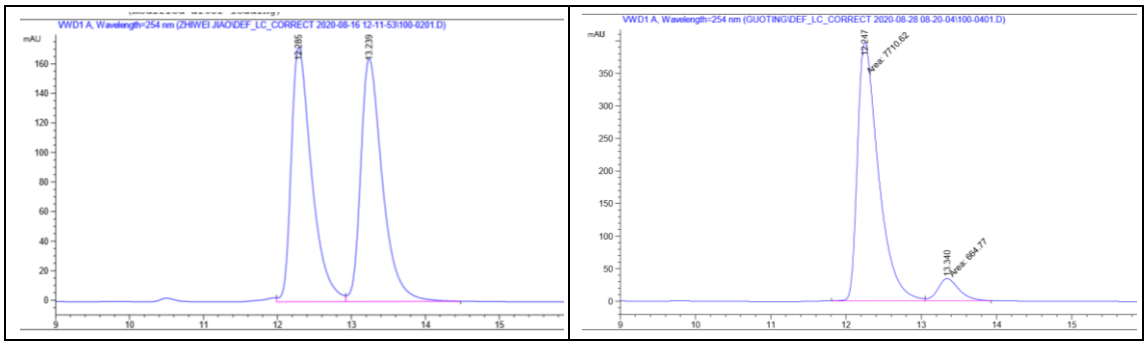
^{13}C-NMR (101 MHz, $CDCl_3$): δ 139.5, 138.0, 137.5, 133.7, 133.4, 132.7, 129.8, 129.4, 128.2, 128.1, 127.6, 126.3, 125.9, 124.6, 124.5, 58.1, 30.9, 26.7, 26.0, 17.8.

IR (cm^{-1}): 1596, 1543, 1447, 1303, 1149, 859, 810, 752, 688.

HRMS-ESI $(M+Na)^+$: 385.1238, found: 385.1235.

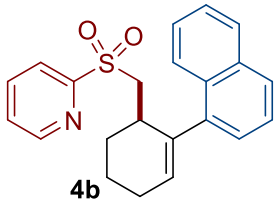
$[\alpha]^{24}_D$ = +24.8 (*c* = 1.5, $CHCl_3$).

Enantiomeric excess (ee = 84%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 12.25 min), minor enantiomer (t_R = 13.34 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.285	VV	0.2895	3308.65723	172.34094	49.6402
2	13.239	VB	0.3079	3356.61670	164.53307	50.3598

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.247	MF	0.3230	7710.61768	397.80652	92.0628
2	13.340	FM	0.3259	664.77002	34.00153	7.9372



4b

(*R*)-2-(((2-(Naphthalen-1-yl)cyclohex-2-en-1-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 1-(6-fluorocyclohex-1-en-1-yl)naphthalene (45 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4b** was obtained by flash silica column chromatography (petroleum ether/EtOAc 60:40) (59 mg, 81% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.79-7.77 (m, 1H), 7.74-7.71 (m, 2H), 7.62 (s, 1H), 7.46-7.40 (m, 3H), .34 (d, *J* = 8.0 Hz, 1H), 6.18 (t, *J* = 4.0 Hz, 1H), 3.57 (brs, 1H), 3.42 (dd, *J* = 16.0, 12.0 Hz, 1H), 3.33 (d, *J* = 16.0 Hz, 1H), 2.29-2.23 (m, 3H), 2.00-1.92 (m, 1H), 1.75-1.63 (m, 2H).

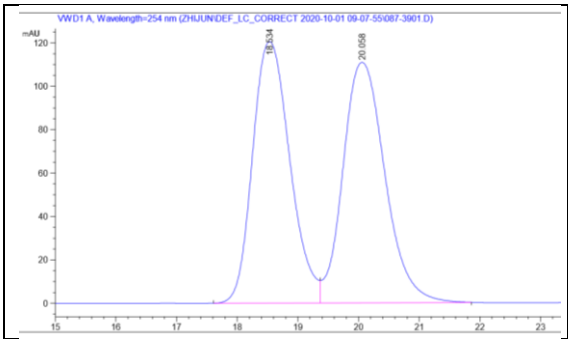
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.6, 150.2, 138.3, 138.1, 137.8, 133.5, 132.7, 129.7, 128.3, 128.2, 127.6, 127.3, 126.2, 125.9, 124.83, 124.82, 122.0, 54.2, 30.7, 27.1, 25.9, 17.6.

IR (cm^{-1}): 1578, 1451, 1427, 1306, 1162, 1110, 1081, 859, 809, 748.

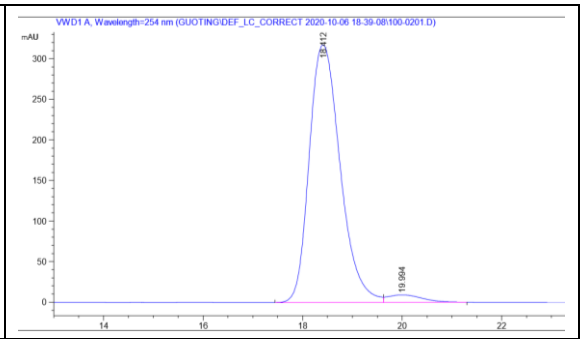
HRMS-ESI $(M+H)^+$: 364.1371, found: 364.1361.

$[\alpha]^{24}_{D}$ = +47.4 (*c* = 2.5, $CHCl_3$).

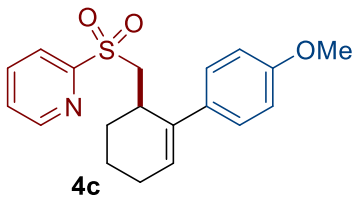
Enantiomeric excess (ee = 94%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IA column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 18.41 min), minor enantiomer (t_R = 19.99 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.534	BV	0.6698	5160.95898	120.55130	49.1376
2	20.058	VB	0.7516	5342.11719	110.83054	50.8624



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.412	BV	0.6752	1.37431e4	317.61960	96.8565
2	19.994	VB	0.7449	446.03165	9.19728	3.1435



4c

(*R*)-2-(((4'-Methoxy-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 2-fluoro-4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (41 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4c** was obtained by flash silica column chromatography (petroleum ether/EtOAc 60:40) (59 mg, 86% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.96 (t, *J* = 4.0 Hz, 1H), 3.79 (s, 3H), 3.40 (s, 1H), 3.36 (d, *J* = 12.0 Hz, 1H), 3.26 (d, *J* = 12.0 Hz, 1H), 2.17-2.15 (m, 3H), 1.89-1.82 (m, 1H), 1.70-1.60 (m, 2H).

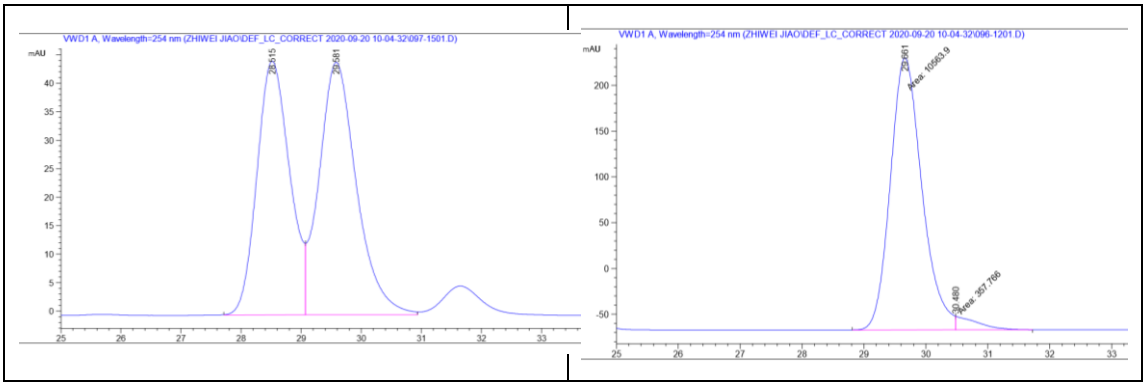
^{13}C-NMR (101 MHz, $CDCl_3$): δ 158.9, 157.8, 150.3, 138.2, 137.7, 132.9, 127.7, 127.3, 122.2, 114.0, 55.4, 54.2, 30.7, 27.0, 25.8, 17.6.

IR (cm^{-1}): 1606, 1577, 1511, 1453, 1427, 1305, 1285, 1245, 1179, 1162, 1111, 1034, 838, 813, 790, 769, 748.

HRMS-ESI $(M+Na)^+$: 366.1140, found: 366.1133.

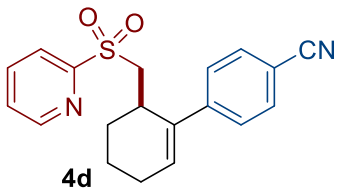
$[\alpha]^{24}_{D}$ = +123.1 (*c* = 1.0, $CHCl_3$).

Enantiomeric excess (ee = 93%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 85:15, 254 nm absorbance), retention times: major enantiomer (t_R = 29.66 min), minor enantiomer (t_R = 30.48 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.515	BV	0.5795	1684.63318	44.55140	46.7358
2	29.581	VB	0.6539	1919.95605	44.32549	53.2642

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.661	MF	0.5924	1.05639e4	297.21210	96.7243
2	30.480	FM	0.4004	357.76599	14.89371	3.2757



4d

(*R*)-2'-((Pyridin-2-ylsulfonyl)methyl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 2'-fluoro-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (40 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4d** was obtained by flash silica column chromatography (petroleum ether/EtOAc 60:40) (55 mg, 81% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.56-7.53 (m, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.18 (t, *J* = 4.0 Hz, 1H), 3.48-3.47 (m, 1H), 3.37 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.17 (d, *J* = 16.0 Hz, 1H), 2.23-2.15 (m, 3H), 1.94-1.85 (m, 1H), 1.74-1.70 (m, 1H), 1.67-1.60 (m, 1H).

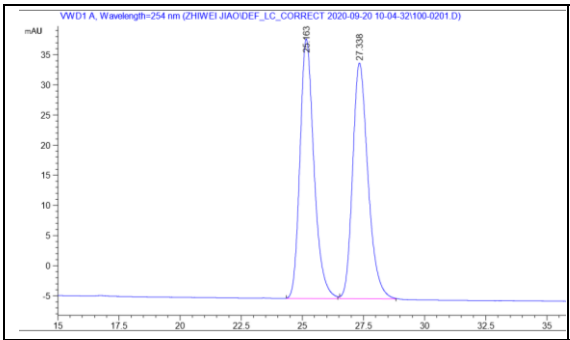
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.7, 150.3, 144.9, 138.4, 137.1, 132.5, 132.3, 127.5, 126.8, 122.1, 119.0, 110.8, 53.9, 30.1, 27.0, 25.9, 17.4.

IR (cm^{-1}): 2226, 1603, 1578, 1452, 1427, 1306, 1162, 1111, 991, 846, 814, 761.

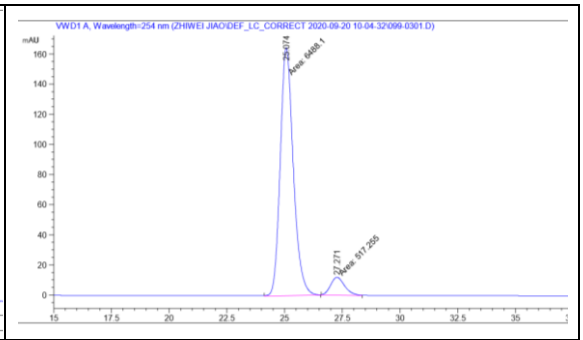
HRMS-ESI $(M+H)^+$: 339.1167, found: 339.1162.

$[\alpha]^{24}_D$ = +79.9 (*c* = 1.6, $CHCl_3$).

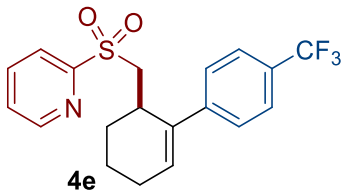
Enantiomeric excess (ee = 85%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 80:20, 254 nm absorbance), retention times: major enantiomer (t_R = 25.07 min), minor enantiomer (t_R = 27.27 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	25.163	BB	0.6103	1720.41895		43.06130	50.1230
2	27.338	BB	0.6676	1711.97595		39.13585	49.8770



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	25.074	MM	0.6568	6488.10059		164.65155	92.6163
2	27.271	MM	0.7180	517.25543		12.00654	7.3837



4e

(*R*)-2-(((4'-(Trifluoromethyl)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 2-fluoro-4'-(trifluoromethyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (49 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4e** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (60 mg, 79% yield) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 4.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H),

7.94 (td, *J* = 8.0, 4.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.11 (t, *J* = 4.0 Hz, 1H), 3.41 (brs, 1H), 3.36 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.22 (d, *J* = 16.0 Hz, 1H), 2.21-2.16 (m, 3H), 1.93-1.87 (m, 1H), 1.74-1.62 (m, 2H).

^{19}F NMR (376.6 MHz, CDCl3): δ -62.88.

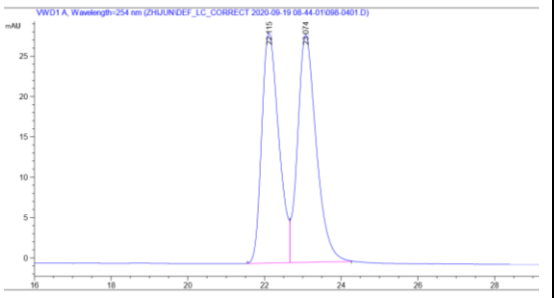
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.6, 150.3, 144.1, 138.3, 137.4, 131.1, 129.2 (q, *J* = 32.3 Hz), 127.5, 126.6, 126.6 (overlap), 125.6 (m), 122.2, 54.0, 30.6, 27.0, 25.8, 17.5.

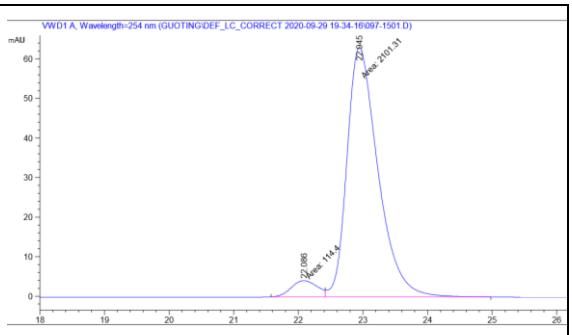
IR (cm^{-1}): 1614, 1579, 1428, 1327, 1164, 1113, 1069, 848.

HRMS-ESI $(M+H)^+$: 382.1089, found: 382.1086.

$[\alpha]^{24}_D$ = +85.4 (*c* = 1.5, $CHCl_3$).

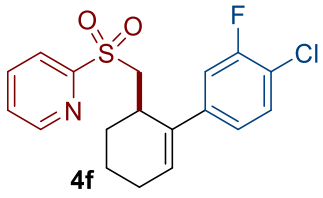
Enantiomeric excess (ee = 90%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 22.94 min), minor enantiomer (t_R = 22.09 min).





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.115	BV	0.4741	877.35876	28.50819	47.8627
2	23.074	VB	0.5097	955.71350	28.24763	52.1373

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.086	MF	0.4632	114.40047	4.11669	5.1632
2	22.945	FM	0.5558	2101.30737	63.00615	94.8368



4f

(*R*)-2-(((4'-Chloro-3'-fluoro-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale,

2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 4'-chloro-2,3'-difluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (46 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4f** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (60 mg, 82% yield) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.96 (td, *J* = 8.0, 4.0 Hz, 1H), 7.56-7.53 (m, 1H), 7.27-7.23 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.08 (t, *J* = 4.0 Hz, 1H), 3.34-3.23 (m, 3H), 2.23-2.18 (m, 3H), 1.89-1.83 (m, 1H), 1.73-1.56 (m, *J* = 4.0 Hz, 2H).

^{19}F NMR (376.6 MHz, CDCl3): δ -115.6.,

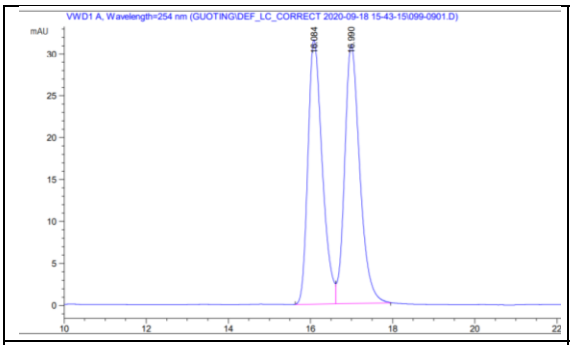
^{13}C-NMR (101 MHz, $CDCl_3$): δ 159.3, 157.1 (d, *J* = 65.6 Hz), 150.4, 141.2 (d, *J* = 6.1 Hz), 138.3, 136.6 (d, *J* = 2.0 Hz), 130.6 (d, *J* = 4.0 Hz), 127.5, 122.7 (d, *J* = 4.0 Hz), 122.2, 119.6 (d, *J* = 17.2 Hz), 114.3 (d, *J* = 22.2 Hz), 54.0, 30.6, 26.8, 25.8, 17.3.

IR (cm^{-1}): 1569, 1489, 1452, 1427, 1307, 1248, 1182, 1162, 1111, 1061, 991, 855, 807, 748.

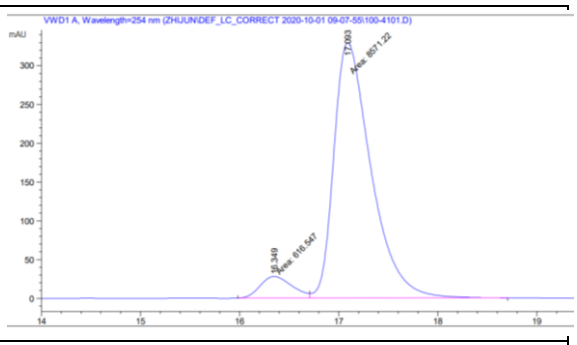
HRMS-ESI $(M+H)^+$: 366.0731, found: 366.0723.

$[\alpha]^{24}_D$ = +81.3 (*c* = 2.8, $CHCl_3$).

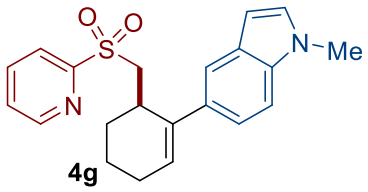
Enantiomeric excess (ee = 88%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 17.09 min), minor enantiomer (t_R = 16.35 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.084	BV	0.3692	762.65460	31.57228	49.0157
2	16.990	VB	0.3893	793.28467	30.95080	50.9843



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.349	MF	0.3697	616.54730	27.79153	6.7105
2	17.093	FM	0.4339	8571.21582	329.23553	93.2895



4g

(*R*)-2-(((4'-Chloro-3'-fluoro-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 5-(6-fluorocyclohex-1-en-1-yl)-1-methyl-1*H*-indole (46 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4g** was obtained by flash silica column chromatography (petroleum ether/EtOAc 50:50) (61 mg, 83% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.96 (td, *J* = 8.0, 4.0 Hz, 1H), 7.56-7.53 (m, 1H), 7.27-7.23 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.86 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.08 (t, *J* = 4.0 Hz, 1H), 3.34-3.23 (m, 3H), 2.23-2.18 (m, 3H), 1.89-1.83 (m, 1H), 1.73-1.56 (m, *J* = 4.0 Hz, 2H).

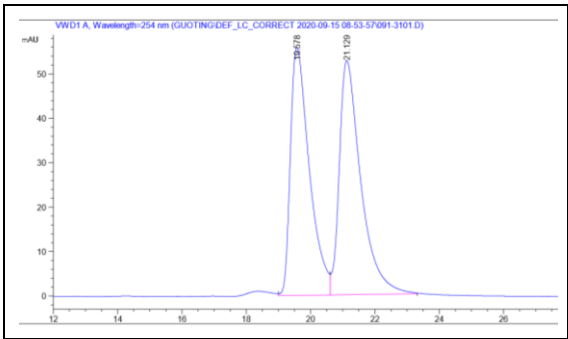
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.7, 150.2, 139.2, 138.1, 136.2, 132.1, 129.3, 128.6, 127.6, 127.2, 122.1, 120.7, 118.5, 109.3, 101.3, 54.4, 33.0, 31.4, 27.1, 25.9, 17.8.

IR (cm^{-1}): 1579, 1512, 1489, 1427, 1305, 1249, 1161, 1110, 992, 756.

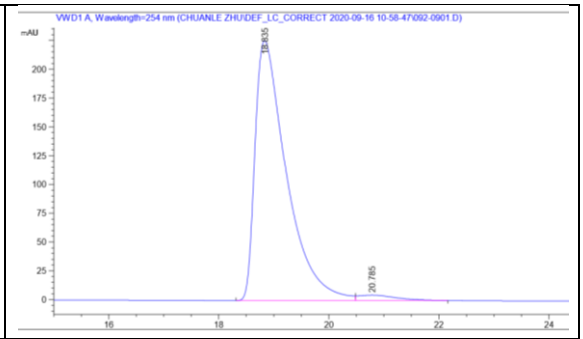
HRMS-ESI $(M+Na)^+$: 389.1300, found: 389.1295.

$[\alpha]^{24}_D$ = +56.7 (*c* = 1.7, $CHCl_3$).

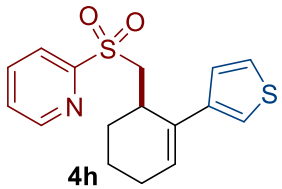
Enantiomeric excess (ee = 95%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 80:20, 254 nm absorbance), retention times: major enantiomer (t_R = 18.84 min), minor enantiomer (t_R = 20.79 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	19.578	VV	0.6099	2279.33057	55.86737	48.2443	
2	21.129	VB	0.6897	2445.22534	52.71227	51.7557	



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	18.835	BB	0.5870	8929.25293	225.57776	97.5141	
2	20.785	BB	0.6711	227.63516	4.77552	2.4859	



4h

(*R*)-2-(((2-(Thiophen-3-yl)cyclohex-2-en-1-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 3-(6-fluorocyclohex-1-en-1-yl)thiophene (36 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4h** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (52 mg, 82% yield) as a brown solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.96 (td, *J* = 8.0, 4.0 Hz, 1H), 7.56-7.53 (m, 1H), 7.23-7.21 (m, 1H), 7.15-7.14 (m, 1H), 7.09 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.19 (t, *J* = 4.0 Hz, 1H), 3.53-3.38 (m, 3H), 2.21-2.15 (m, 3H), 1.80-1.76 (m, 1H), 1.69-1.60 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.9, 150.4, 141.4, 138.3, 133.1, 127.5, 127.4, 125.9, 125.4, 122.1, 119.3, 54.1, 30.4, 26.5, 25.5, 17.2.

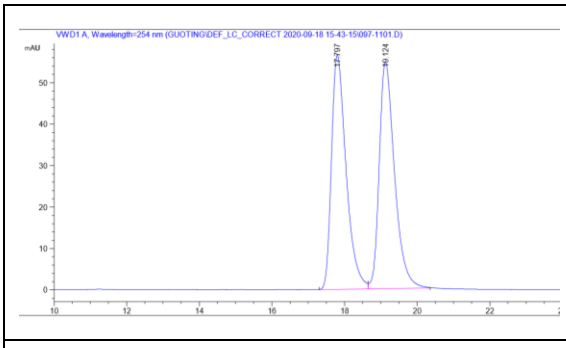
IR (cm^{-1}): 1578, 1452, 1427, 1329, 1304, 1246, 1162, 1111, 1081, 991, 851, 780, 763, 653.

HRMS-ESI $(M+Na)^+$: 342.0598, found: 342.0596.

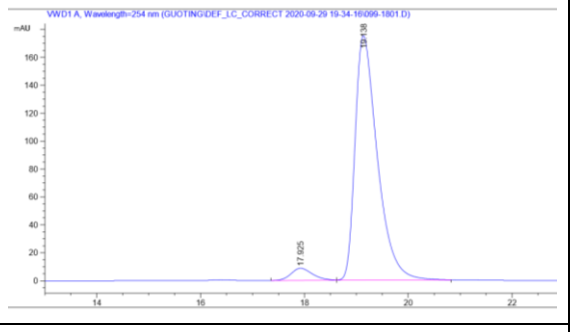
$[\alpha]^{24}_D$ = +105.8 (*c* = 2.2, $CHCl_3$).

Enantiomeric excess (ee = 91%) was determined by high-performance liquid

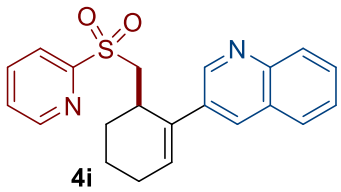
chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 19.14 min), minor enantiomer (t_R = 17.93 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.797	BV	0.4251	1579.67542	56.50927	49.6382
2	19.124	VB	0.4450	1602.70276	54.73921	50.3618



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.925	BV	0.4364	254.73068	8.76990	4.6389
2	19.138	VB	0.4536	5236.50439	175.16827	95.3611



4i

(*R*)-3-(6-((Pyridin-2-ylsulfonyl)methyl)cyclohex-1-en-1-yl)quinolone.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 3-(6-fluorocyclohex-1-en-1-yl)quinoline (45 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4i** was obtained by flash silica column chromatography (petroleum ether/EtOAc 50:50) (48 mg, 66% yield) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 4.0 Hz, 1H), 8.47 (d, *J* = 4.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.88 (t, 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.44 (td, *J* = 8.0, 4.0 Hz, 1H), 6.25 (t, *J* = 4.0 Hz, 1H), 3.54 (brs, 1H), 3.45-3.31 (m, 1H), 2.32-2.25 (m, 3H), 1.99-1.92 (m, 1H), 1.79-1.67 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 150.3, 149.7, 138.2, 135.6, 132.9, 132.2, 131.5, 129.4, 129.2, 128.2, 127.9, 127.5, 127.0, 122.0, 53.9, 30.5, 27.0, 26.0, 17.3.

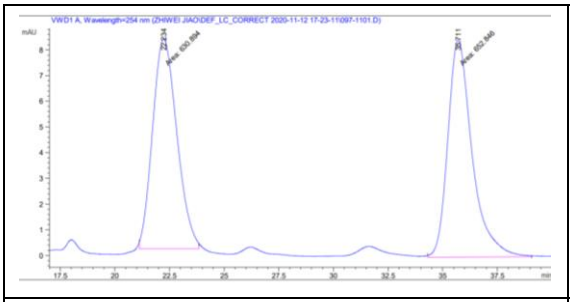
IR (cm^{-1}): 2926, 1492, 1452, 1427, 1306, 1258, 1162, 1111, 1082, 1022, 991, 973,

908, 849, 788, 754, 698, 664.

HRMS-ESI $(M+H)^+$: 365.1324, found: 365.1317.

$[\alpha]^{24}_D$ = +5.9 (*c* = 1.7, $CHCl_3$).

Enantiomeric excess (ee = 89%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 85:15, 254 nm absorbance), retention times: major enantiomer (t_R = 35.84 min), minor enantiomer (t_R = 21.80 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
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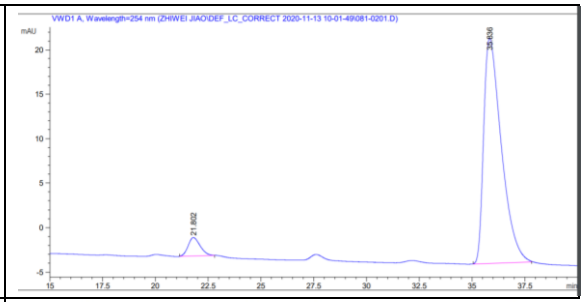
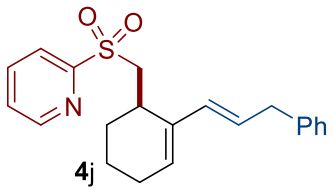
2	35.711	MM	1.2883	652.84570		8.44606	50.8550



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	21.802	BB	0.5758	82.58546		2.07771	5.2959
2	35.836	BB	0.8637	1476.83630		25.32944	94.7041



4j

(*R*,*E*)-2-(((2-(3-Phenylprop-1-en-1-yl)cyclohex-2-en-1-yl)methyl)sulfonyl)pyridine

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and (*E*)-(3-(6-fluorocyclohex-1-en-1-yl)allyl)benzene (43 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4j** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (52 mg, 74% yield) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.88 (td, *J* = 8.0, 4.0 Hz, 1H), 7.46-7.43 (m, 1H), 7.29-7.25 (m, 2H), 7.21-7.17 (m, 1H), 7.15-7.13 (m, 2H), 5.89 (d, *J* = 16.0 Hz, 1H), 5.73 (t, *J* = 4.0 Hz, 1H), 5.66-5.59 (m, 2H), 3.52 (d, *J* = 12.0 Hz, 1H), 3.42 (d, *J* = 12.0, 8.0 Hz, 1H), 3.36 (d, *J* = 8.0 Hz,

2H), 3.15 (d, J = 12.0 Hz, 1H), 2.16-2.12 (m, 3H), 1.66-1.55 (m, 3H).

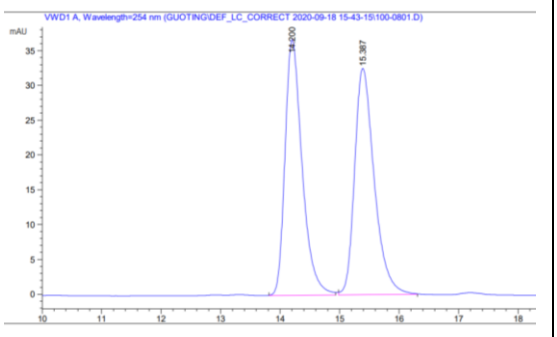
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.8, 150.3, 140.6, 138.2, 136.0, 132.3, 130.9, 128.7, 128.5, 127.4, 126.1, 122.3, 54.0, 39.3, 28.0, 25.7, 25.5, 17.1.

IR (cm^{-1}): 1658, 1639, 1580, 1550, 1511, 1494, 1452, 1428, 1407, 1307, 1163, 1111, 991, 853, 756, 701.

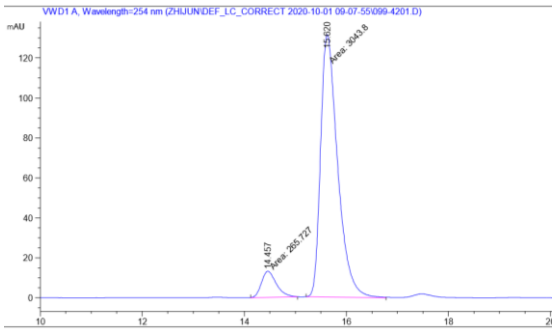
HRMS-ESI $(M+Na)^+$: 376.1525, found: 376.1531.

$[\alpha]^{24}_D$ = +39.1 (c = 3.6, $CHCl_3$).

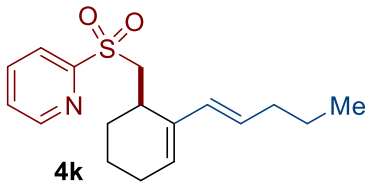
Enantiomeric excess (ee = 84%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 15.62 min), minor enantiomer (t_R = 14.46 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.200	BB	0.3031	733.83301	36.70916	49.6159
2	15.387	BB	0.3489	745.19464	32.52158	50.3841



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.457	MM	0.3386	265.72742	13.07886	8.0292
2	15.620	MM	0.3865	3043.79663	131.24077	91.9708



4k

(*R*,*E*)-2-(((2-(Pent-1-en-1-yl)cyclohex-2-en-1-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and (*E*)-6-fluoro-1-(pent-1-en-1-yl)cyclohex-1-ene (34 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4k** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (40 mg, 66% yield) as

a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 4.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.97 (t, *J* = 8.0 Hz, 1H), 7.57-7.53 (m, 1H), 5.81 (d, *J* = 16.0 Hz, 1H), 5.67 (t, *J* = 4.0 Hz, 1H), 5.58-5.51 (m, 1H), 3.53-3.40 (m, 2H), 3.16 (d, *J* = 8.0 Hz, 1H), 2.09 (brs, 1H), 2.06-1.97 (m, 2H), 1.65-1.55 (m, 3H), 1.40-1.31 (m, 2H), 0.87 (t, *J* = 8.0 Hz, 3H).

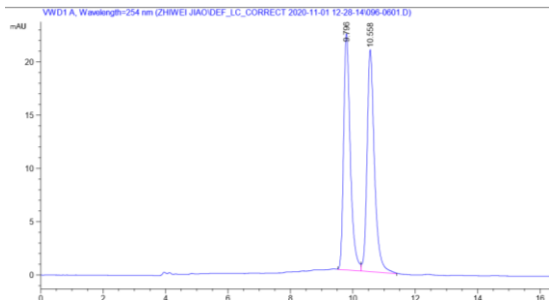
^{13}C-NMR (101 MHz, $CDCl_3$): δ 158.1, 150.3, 138.3, 136.2, 131.0, 129.7, 128.0, 127.4, 122.2, 53.9, 35.1, 27.9, 25.8, 25.4, 22.7, 17.2, 13.8.

IR (cm^{-1}): 1578, 1453, 1427, 1307, 1163, 1111, 990, 971, 783, 757, 618.

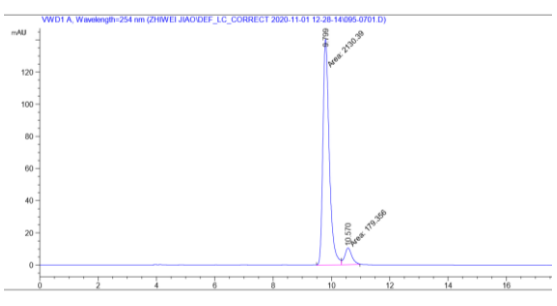
HRMS-ESI $(M+Na)^+$: 328.1347, found: 328.1340.

$[\alpha]^{24}_D$ = +59.6 (*c* = 3.5, $CHCl_3$).

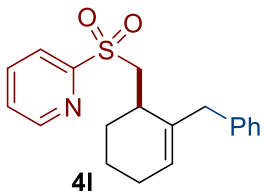
Enantiomeric excess (ee = 85%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 9.80 min), minor enantiomer (t_R = 10.57 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.796	BV	0.2242	329.30450	22.17315	48.9929
2	10.558	VB	0.2457	342.84308	20.85203	51.0071



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.799	MF	0.2529	2130.38525	140.37639	92.2348
2	10.570	FM	0.2860	179.35590	10.45259	7.7652



4l

(*R*)-2-(((2-Benzylcyclohex-2-en-1-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale,

2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and ((6-fluorocyclohex-1-en-1-yl)methyl)benzene (38 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4l** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (37 mg, 57% yield) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.92 (td, *J* = 8.0, 4.0 Hz, 1H), 7.54-7.51 (m, 1H), 7.23-7.14 (m, 3H), 7.03 (d , *J* = 8.0 Hz, 2H), 5.51 (s, 1H), 3.60 (d, *J* = 16.0 Hz, 1H), 3.36 (dd, *J* = 16.0, 12.0 Hz, 1H), 3.27 (d, *J* = 16.0 Hz, 1H), 3.14 (d, *J* = 8.0 Hz, 1H), 3.55 (d, *J* = 8.0 Hz, 1H), 2.04-1.95 (m, 3H), 1.60-1.52 (m, 2H).

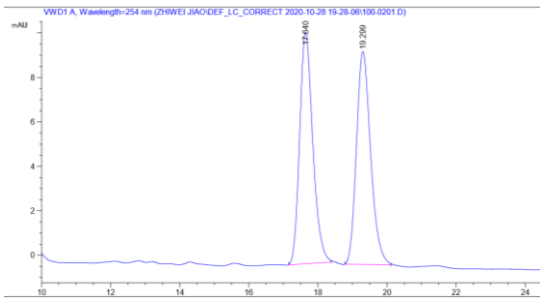
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.6, 150.3, 139.5, 138.2, 136.9, 128.9, 128.3, 127.4, 127.2, 126.1, 122.3, 53.8, 41.6, 31.0, 26.8, 25.1, 17.3.

IR (cm^{-1}): 1578, 1452, 1428, 1306, 1163, 1110, 991, 65, 747, 701.

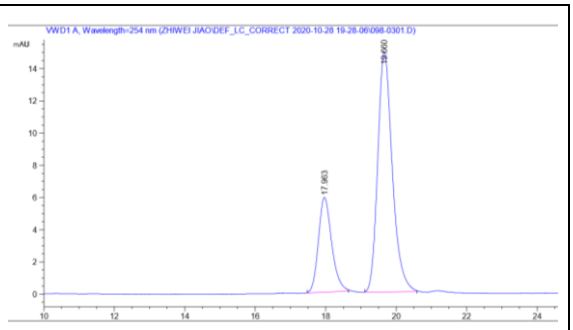
HRMS-ESI $(M+Na)^+$: 350.1191, found: 350.1183.

$[\alpha]^{24}_D$ = +21.3 (*c* = 3.2, $CHCl_3$).

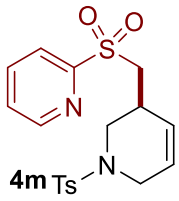
Enantiomeric excess (ee = 47%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 90:10, 254 nm absorbance), retention times: major enantiomer (t_R = 19.66 min), minor enantiomer (t_R = 17.96 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.640	BB	0.4038	274.07343	10.39235	50.1599
2	19.299	BB	0.4351	272.32632	9.57779	49.8401



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.963	BB	0.3972	154.21675	5.89048	26.4893
2	19.660	BB	0.4367	427.96887	14.91436	73.5107



(*S*)-2-(((1-Tosyl-1,2,3,6-tetrahydropyridin-3-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 3-fluoro-1-tosyl-1,2,3,6-tetrahydropyridine (51 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4m** was obtained by flash silica column chromatography (petroleum ether/EtOAc 50:50) (52 mg, 66% yield) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 4.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.59-7.57 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.85-5.82 (m, 1H), 5.72-5.70 (m, 1H), 3.72 (d, *J* = 16.0 Hz, 1H), 3.57-3.46 (m, 2H), 3.42-3.32 (m, 2H), 3.04-3.01 (m, 2H), 2.43 (s, 3H).

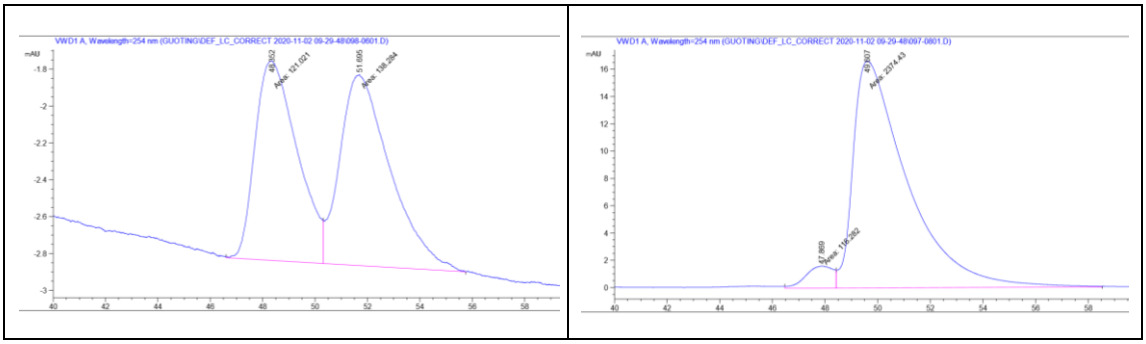
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.6, 150.4, 144.0, 138.5, 133.1, 129.9, 127.8, 127.7, 127.0, 124.8, 122.2, 54.7, 47.2, 44.9, 30.3, 21.7.

IR (cm^{-1}): 1428, 1348, 1307, 1165, 1110, 976, 818, 759, 713, 696.

HRMS-ESI $(M+H)^+$: 393.0943, found: 393.0935.

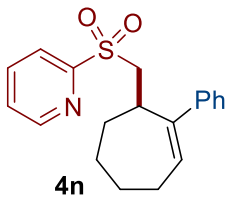
$[\alpha]^{24}_D$ = +99.4 (*c* = 1.4, $CHCl_3$).

Enantiomeric excess (ee = 91%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 80:20, 254 nm absorbance), retention times: major enantiomer (t_R = 49.61 min), minor enantiomer (t_R = 47.87 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	48.352	MF	1.8627	121.02113	1.08282	46.6712
2	51.695	FM	2.2251	138.28441	1.03578	53.3288

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	47.869	MF	1.2057	116.28219	1.60736	4.6686
2	49.607	FM	2.3786	2374.42944	16.63745	95.3314



4n

(*R*)-2-(((2-Phenylcyclohept-2-en-1-yl)methyl)sulfonyl)pyridine.

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 7-fluoro-1-phenylcyclohept-1-ene (38 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4n** was obtained by flash silica column chromatography (petroleum ether/EtOAc 75:25) (47 mg, 72% yield) as a pale yellow solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.86 (td, *J* = 8.0, 4.0 Hz, 1H), 7.49-7.45 (m, 1H), 7.21-7.18 (m, 3H), 7.16-7.14 (m, 2H), 5.96(t , *J* = 8.0 Hz, 1H), 3.82 (dd, *J* = 16.0, 12.0 Hz, 1H), 3.62 (dd, *J* = 16.0, 4.0 Hz, 1H), 3.51-3.47 (m, 1H), 2.34-2.24 (m, 2H), 2.15-2.10 (m, 1H), 1.94-1.81 (m, 3H), 1.78-1.73 (m, 1H), 1.51-1.41 (m, 1H).

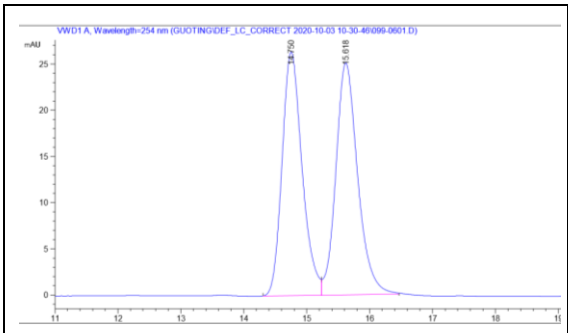
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.5, 150.2, 145.0, 143.7, 138.1, 132.4, 128.3, 127.3, 126.9, 126.4, 122.2, 52.5, 37.6, 29.7, 27.9, 26.9, 25.7.

IR (cm^{-1}): 1578, 1447, 1427, 1309, 1162, 1110, 757, 700.

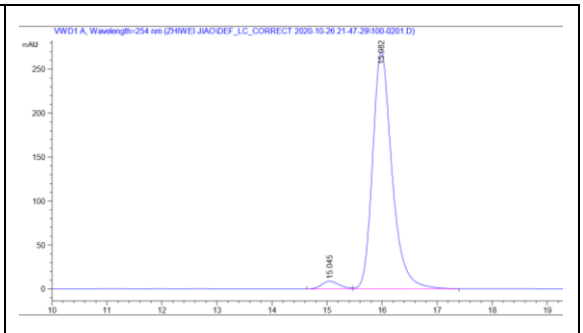
HRMS-ESI $(M+Na)^+$: 350.1911, found: 350.1200.

$[\alpha]^{24}_D$ = +29.8 (*c* = 1.7, $CHCl_3$).

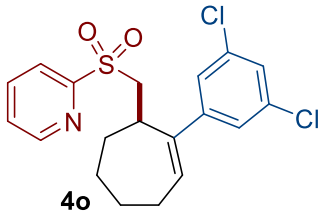
Enantiomeric excess (ee = 94%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (AD-H column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 85:15, 254 nm absorbance), retention times: major enantiomer (t_R = 15.98 min), minor enantiomer (t_R = 15.05 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	14.750	BV	0.3383	583.37836	26.35814	49.1147	
2	15.618	VB	0.3654	604.40869	25.09696	50.8853	



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	15.045	BV	0.3371	194.88681	8.84620	2.8622	
2	15.982	VB	0.3721	6613.99561	269.59860	97.1378	



4o

(*R*)-2-(((2-(3,5-Dichlorophenyl)cyclohept-2-en-1-yl)methyl)sulfonyl)pyridine

The reaction was performed on 0.2 mmol scale, 2-(((trimethylsilyl)methyl)sulfonyl)pyridine (69 mg, 0.3 mmol) and 1-(3,5-dichlorophenyl)-7-fluorocyclohept-1-ene (49 mg, 0.2 mmol) were used and **L1** (8.3 mg) was used as the supporting ligand. The product **4o** was obtained by flash silica column chromatography (petroleum ether/EtOAc 80:20) (60 mg, 76% yield) as a pale yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89 (td, *J* = 8.0, 4.0 Hz, 1H), 7.52-7.49 (m, 1H), 7.16 (t, *J* = 4.0 Hz, 1H), 6.97 (d, *J* = 4.0 Hz, 2H), 5.97 (t, *J* = 8.0 Hz, 1H),3.32 (d, *J* = 8.0 Hz, 1H), 3.27-3.23 (m, 1H), 2.36-2.23 (m, 2H), 2.21-2.11 (m, 1H), 1.94-1.87 (m, 2H), 1.83-1.76 (m, 2H), 1.48-1.38 (m, 1H).

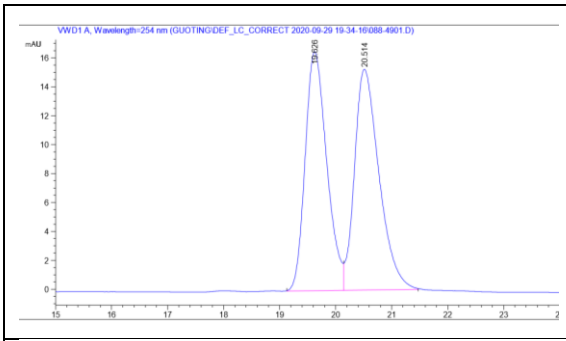
^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.0, 150.3, 146.9, 143.0, 138.1, 134.74, 134.67, 127.5, 126.8, 125.1, 122.2, 52.3, 37.6, 29.8, 27.9, 26.7, 25.6.

IR (cm^{-1}): 1580, 1557, 1450, 1427, 1313, 1162, 1110, 855, 797, 757, 687.

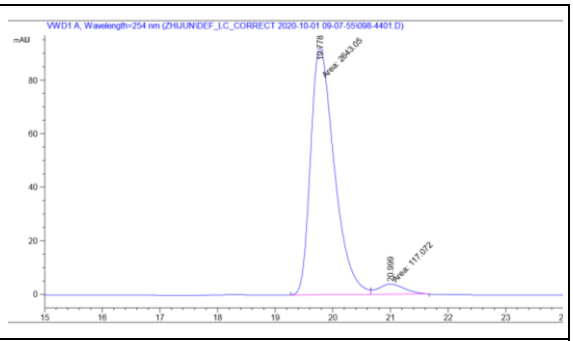
HRMS-ESI $(M+H)^+$: 396.0592, found: 396.0583.

$[\alpha]^{24}_D$ = +29.4 (*c* = 1.4, $CHCl_3$).

Enantiomeric excess (ee = 92%) was determined by high-performance liquid chromatography (HPLC) using a chiral stationary phase (IB column, flow rate = 0.8 mL min^{-1}, eluent: Hept/*i*-PrOH = 95:5, 254 nm absorbance), retention times: major enantiomer (t_R = 19.78 min), minor enantiomer (t_R = 21.00 min).

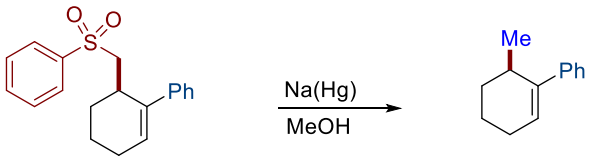


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.626	BV	0.4124	442.15533	16.53913	48.7035
2	20.514	VB	0.4634	465.69592	15.27786	51.2965



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.778	MF	0.4771	2643.04907	92.33620	95.7584
2	20.999	FM	0.5156	117.07218	3.78402	4.2416

IV. Functional groups transformations



3a **5a** 70% yield

3a (62 mg, 0.2 mmol) was dissolved in MeOH (5 mL) and then was treated with 10% Na(Hg) (115 mg) and Na_2HPO_4 (93 mg, 0.6 mmol). The resulting suspension was stirred for 6 h at room temperature before it was quenched with aqueous NH_4Cl (5 mL) and extracted with Et_2O (50 mL x 2), and the combined organic phase was washed with brine (15 mL x 3) and dried (MgSO4), filtered, and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 100:1), to afford **5a** (24 mg, 79% yield) as a colorless oil.

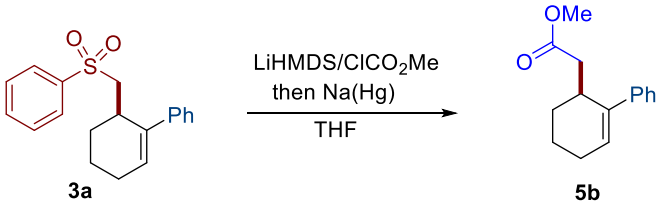
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (m, 4H), 7.24-7.19 (m, 1H), 5.88 (t, d, *J* = 4.0 Hz, 1H), 2.83 (brs, 1H), 2.17-2.15 (m, 1H), 1.89-1.86 (m, 1H), 1.71-1.55 (m, 3H), 0.94 (d, *J* = 8.0 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 143.1, 142.9, 128.2, 126.5, 126.4 125.6, 77.5, 77.2, 76.8, 31.2, 30.6, 26.4, 20.3, 19.0.

IR (cm^{-1}): 1598, 1542, 1493, 144, 1361, 997, 880, 75, 697.

HRMS-EI $(M)^+$: 172.1252, found: 172.1254.

$[\alpha]^{24}_D$ = +62.8 (*c* = 1.1, $CHCl_3$).



3a **5b**
82% yield

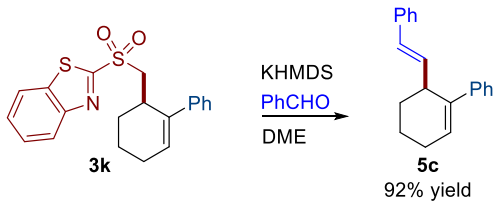
To a solution of sulfone **3a** (62 mg, 0.2 mmol) in THF (1 mL) was added LiHMDS (300 uL, 1.0M in THF) at -78 ℃. The resulting orange solution was stirred at -78 ℃ for 30 min before methyl chloroformate (18 µL, 0.24 mmol) was added. The mixture was stirred at -78 ℃ for 2 h, and then saturated aqueous NH_4Cl (2 mL) was added. The organic phase was separated, and the aqueous layer was extracted with EtOAc (30 mL × 3 mL). The combined organic phase was washed with brine (15 mL x 3), dried over (MgSO4), and then filtered and concentrated. The crude compound was dissolved in MeOH (5 mL) and then was treated with 10% Na(Hg) (115 mg) and Na_2HPO_4 (93 mg, 0.6 mmol). The resulting suspension was stirred for 1 h at room temperature before it was quenched with aqueous NH_4Cl (5 mL) and extracted with Et_2O (50 mL x 3), and the combined organic phase was washed with brine (25 mL x 3) and dried (MgSO4), filtered, and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 95:5) to afford **5b** (38 mg, 82% yield over two steps) as colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 4H), 7.24-7.21 (m, 1H), 5.97 (t, *J* = 4.0 Hz, 1H), 3.59 (s, 3H), 3.26 (brs, 1H), 2.37 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.20-2.16 (m, 3H), 1.88-1.84 (m, 1H), 1.70-1.61 (m, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 173.7, 141.8, 140.3, 128.5, 127.5, 127.0, 126.4, 51.6, 38.4, 32.8, 27.9, 26.2, 18.4.

IR (cm^{-1}): 1737, 1543, 1493, 1435, 1351 1281, 1169, 759, 699.

$[\alpha]^{24}_D$ = +75.9 (*c* = 0.8, $CHCl_3$).



To a solution of sulfone **3k** (74 mg, 0.2 mmol) in DME (1 mL) was added KHMDS (300 uL, 1.0M in THF) at -78 ℃. The resulting orange clear solution was stirred at -78 ℃ for 30 min and then fresh distilled benzaldehyde (31 uL, 0.3 mmol) was added. The mixture was stirred at -78 ℃ for 2 h, and then saturated aqueous NH_4Cl (2 mL) was added. The organic phase was separated, and the aqueous layer was extracted with EtOAc (15 mL × 3 mL). The combined organic phase was washed with brine (15 mL x 3), dried over (MgSO4), and then filtered and concentrated. The residue was purified by flash chromatography (pure hexanes) to afford **5c** (48 mg, 92% yield) as a colorless oil.

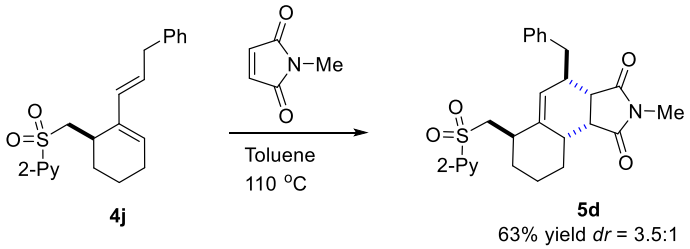
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.29-7.22 (m, 6H), 7.19-7.14 (m, 2H), 6.33-6.22 (m, 2H), 6.20 (t, *J* = 4.0 Hz, 1H), 3.55 (s, 1H), 2.26-2.25 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 142.2, 138.6, 137.9, 133.8, 131.0, 128.5, 128.3, 127.1, 127.0, 126.6, 126.2, 126.1, 39.5, 29.7, 26.2, 18.1.

IR (cm^{-1}): 3023, 2861, 1494, 1445, 965, 757, 744, 693.

HRMS-EI $(M)^+$: 260.1565, found: 260.1569.

$[\alpha]^{24}_D$ = +116.9 (*c* = 2.5, $CHCl_3$).



To a solution of sulfone **4j** (38 mg, 0.12 mmol) in dry toluene (1.0 mL) was added 1-methyl-1*H*-pyrrole-2,5-dione (27 mg, 0.24 mmol) and then the mixture was heated at 110 °C for 12 hours. The mixture was purified by flash chromatography (hexanes/EtOAc 50:50) to afford **5d** as a mixture (35 mg, 63% yield, *dr* = 3.5:1) as

pale yellow foam.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.06-8.01 (m, 1H), 7.94 (t, *J* = 8.0 Hz, 1H), 7.55-7.52 (m, 1H), 7.30-7.26 (m, 5H), 7.24-7.20 (m, 1H), 5.39 (s, 1H), 3.75 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.37-3.21 (m, 2H), 2.96-2.82 (m, 3H), 2.90 (m, 3H), 2.44 (brs, 1H), 2.29 (brs, 1H), 2.02-1.94 (m, 2H), 1.83-1.80 (m, 2H), 1.43-1.27 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 177.9, 177.4, 158.1, 150.2, 142.3, 140.3, 138.4, 129.3, 129.3, 128.6, 127.5, 126.4, 123.6, 121.9, 53.6, 44.0, 42.7, 38.7, 37.3, 37.0, 32.4, 28.0, 24.7, 23.5, 20.6.

IR (cm^{-1}): 1696, 1431, 1382, 1308, 1163, 1111, 992, 754, 703.

HRMS-ESI $(M+H)^+$: 465.1848, found: 465.1844.

$[\alpha]^{24}_D$ = -2.1 (*c* = 2.5, $CHCl_3$)

V. Synthesis of the substrates

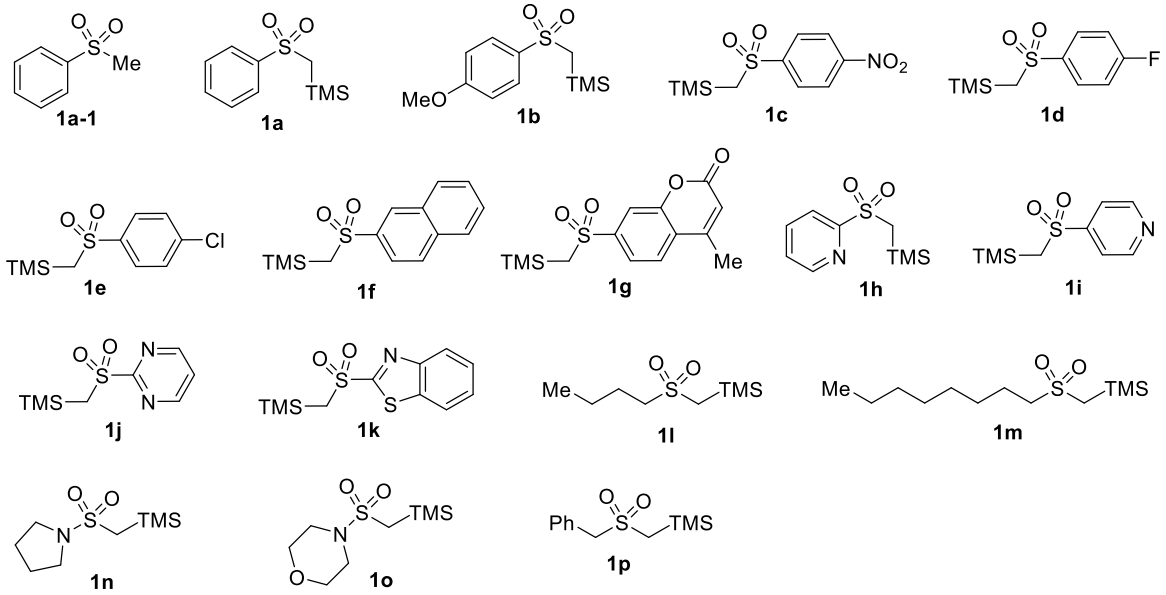
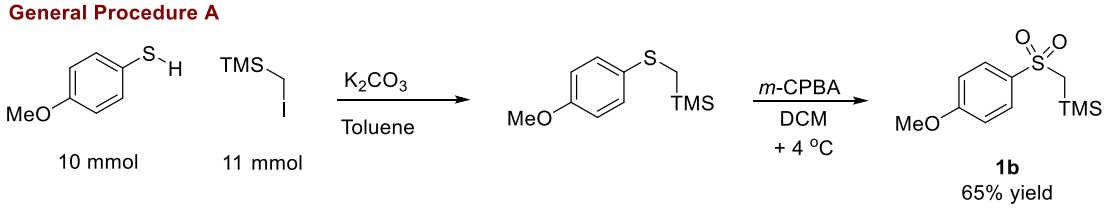


Figure S-3. Summary of different sulfone donors.

Methyl phenyl sulfone **1a-1** (CAS: 3112-85-4) and (phenylsulfonylmethyl)trimethylsilane **1a** (CAS: 17872-92-3) are commercial compounds in Aldrich; all the allylic compounds (**2a-2p**) were synthesized according

to our previous procedure (*J. Am. Chem. Soc.* **2019**, *141*, 11446−11451).



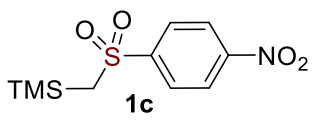
General procedure A: To a flame-dried 100 mL flask was added 4-methoxybenzenethiol (1.23 mL, 10 mmol), $TMSCH_2I$ (1.63 mL, 11 mmol), K_2CO_3 (3.4 g, 25 mmol), 18-crown-6 (100 mg, cat.) and fresh distilled toluene (30 mL). The reaction mixture was heated to 110 ^oC and stirred for another for 6 hours, then the mixture was cooled to room temperature and the solid was removed via a short column on celite and the filtrate was concentrated under vacuum and the residue was used for the next steps.

Above residue was dissolved in DCM (30 mL) and *m*-CPBA (4.9 g, 77% Aldrich, 22 mmol) was added portion wise at 0 ^oC and the mixture was stirred at this temperature for another 30 min. The reaction was quenched with aqueous K_2CO_3 (20 mL) and extracted with EA (50 mL x 3), the combined organic solution was washed with $Na_2S_2O_3$ (15 mL x 2), brine (20 mL x 3) and then dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was dissolved in EA/DCM (1:1, 2 mL) and hexanes (10 mL) was added to the mixture, the white solid was filtered which is pure enough for the further asymmetric transformation. (1.67 g, 75% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H), 2.76 (s, 2H), 0.25 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.1, 135.8, 128.9, 114.3, 55.8, 49.0, -0.60.

HRMS-EI $(M)^+$: 258.0746, found: 258.0755.



Trimethyl(((4-nitrophenyl)sulfonyl)methyl)silane.

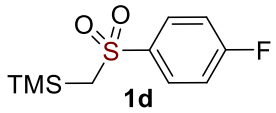
This compound was synthesized according to "**General Procedure A**" from

4-nitrobenzenethiol (930 mg, 6.0 mmol), and **1c** was obtained as a pale yellow solid (980 mg, 60% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.0 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 2.80 (s, 2H), 0.33 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 149.2, 129.1, 128.3, 124.6, 48.3, -0.45.

HRMS-ESI $(M+H)^+$: 274.0576, found: 274.0574.



1d

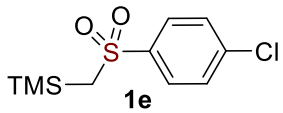
(((4-Fluorophenyl)sulfonyl)methyl)trimethylsilane.

This compound was synthesized according to "**General Procedure A**" from 4-fluorobenzenethiol (640 uL, 6.0 mmol), and **1d** was obtained as a white solid (910 mg, 62% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.92-7.89 (m, 2H), 7.20-7.16 (m, 2H), 2.77 (s, 2H), 0.27 (s, 9H).

^{19}F NMR (376.6 MHz, CDCl3): δ -105.6.

^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.3 (d, *J* = 256.5 Hz), 140.0 (d, *J* = 3.0 Hz), 129.6 (d, *J* = 9.1 Hz), 116.4 (d, *J* = 22.2 Hz), 48.8, -0.58.



1e

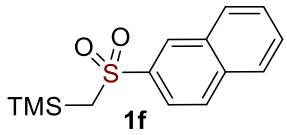
(((4-Chlorophenyl)sulfonyl)methyl)trimethylsilane.

This compound was synthesized according to "**General Procedure A**" from 4-chlorobenzenethiol (858 mg, 6.0 mmol), and **1c** was obtained as a white solid (1.1 g, 70% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 2.76 (s, 2H), 0.29 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 142.4, 139.5, 129.5, 128.4, 48.7, -0.52.

HRMS -ESI $(M+Na)^+$: 285.0148, found: 285.0150.



1f

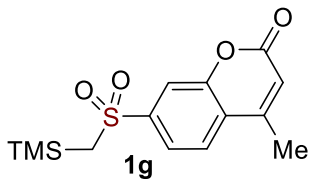
Trimethyl((naphthalen-2-ylsulfonyl)methyl)silane.

This compound was synthesized according to "**General Procedure A**" from naphthalene-2-thiol (960 mg, 6.0 mmol), and **1f** was obtained as a white solid (1.1 g, 66% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.98-7.96 (m, 2H), 7.91-7.87 (m, 2H), 7.66-7.58 (m, 2H), 2.86 (s, 2H), 0.31 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 140.7, 135.0, 132.3, 129.6, 129.4, 128.9, 128.0, 127.9, 127.7, 122.2, 48.6, -0.49.

HRMS-EI $(M)^+$: 278.0797, found: 278.0805.



1g

4-Methyl-7-(((trimethylsilyl)methyl)sulfonyl)-2*H*-chromen-2-one.

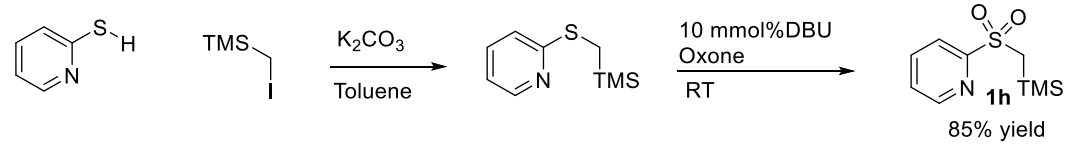
This compound was synthesized according to "**General Procedure A**" from 7-mercapto-4-methyl-2*H*-chromen-2-one (960 mg, 6.0 mmol), and **1g** was obtained as a pink solid (967 mg, 52% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.80-7.73 (m, 3H), 6.39 (s, 1H), 2.80 (s, 2H), 2.47 (s, 3H), 0.30 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 159.4, 153.2, 151.0, 146.3, 125.8, 123.3, 121.9, 117.5, 115.6, 48.2, 18.7, -0.62.

HRMS-ESI $(M+H)^+$: 295.0460, found: 295.0463.

General Procedure B



1h

85% yield

General procedure B: To a flame-dried 100 mL flask was added pyridine-2-thiol (1.1

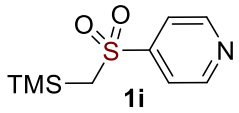
g, 10 mmol), $TMSCH_2I$ (1.63 mL, 11 mmol), K_2CO_3 (3.4 g, 25 mmol), 18-crown-6 (100 mg, cat.) and fresh distilled toluene (30 mL). The reaction mixture was heated to 110 ^oC and stirred for another for 6 hours, then the mixture was cooled to room temperature and the solid was removed via a short column on celite and the filtrate was concentrated under vacuum and the residue was used for the next steps.

Above residue was dissolved in CH_3CN/H_2O (21 mL, 1:3) and Oxone (15 g, 25 mmol) and DBU (149 uL, 1.0 mmol) were added at room temperature, the mixture was stirred for another 10 mins. The reaction was extracted with EA (50 mL x 3), the combined organic solution was washed with $Na_2S_2O_3$ (15 mL x 2), brine (20 mL x 3) and then dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was dissolved in EA/DCM (1:1, 2 mL) and hexanes (15 mL) was added to the mixture, the white solid was filtered which is pure enough for the further asymmetric transformation. (1.94 g, 85% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.68-8.66 (m, 1H), 8.02-7.99 (m, 1H), 7.93-7.81 (m, 1H), 7.50-7.40 (m, 1H), 2.99 (s, 3H), 0.25 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 160.0, 149.9, 138.2, 127.0, 120.5, 42.9, -0.58.

HRMS-ESI $(M+H)^+$: 230.0671, found: 230.0669.



1i

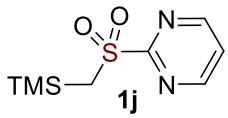
4-(((Trimethylsilyl)methyl)sulfonyl)pyridine.

This compound was synthesized according to "**General Procedure A**" from pyridine-4-thiol (666 mg, 6.0 mmol), and **1i** was purified by flash silica column chromatography (petroleum ether/ EtOAc 50: 50), affording the title compound (577 mg, 42% yield over two steps) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 2.75 (s, 2H), 0.27 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 151.2, 120.0., 47.6, -0.54.

HRMS-ESI $(M+H)^+$: 230.0671, found: 230.0665.



1j

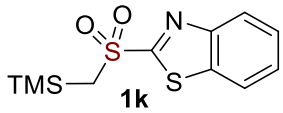
2-(((Trimethylsilyl)methyl)sulfonyl)pyrimidine

This compound was synthesized according to "**General Procedure B**" from pyrimidine-2-thiol (672 mg, 6.0 mmol), and **1j** was purified by flash silica column chromatography (petroleum ether/ EtOAc 40: 60), affording the title compound (1.13 g, 82% yield over two steps) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 4.0 Hz, 2H), 7.51 (t, *J* = 4.0 Hz, 1H), 3.05 (s, 2H), 0.21 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 167.2, 158.5, 123.6, 41.9, -0.67.

HRMS-ESI $(M+H)^+$: 231.0623, found: 231.0621.



1k

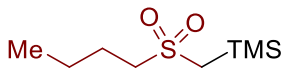
2-(((Trimethylsilyl)methyl)sulfonyl)benzo[*d*]thiazole.

This compound was synthesized according to "**General Procedure B**" from benzo[*d*]thiazole-2-thiol (996 mg, 6.0 mmol), and **1k** was obtained as a white solid (1.0 g, 58% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.0 Hz, 1H), 7.95 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.60-7.51 (m, 2H), 3.19 (s, 2H), 0.34 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 169.2, 152.5, 136.3, 127.8, 127.5, 125.2, 122.4, 45.8, -0.50.

HRMS-ESI $(M+H)^+$: 286.0392, found: 286.0395.



1l

((Butylsulfonyl)methyl)trimethylsilane.

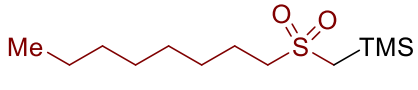
This compound was synthesized according to "**General Procedure A**" from benzo[*d*]thiazole-2-thiol (996 mg, 6.0 mmol), and **1l** was purified by flash silica

column chromatography (petroleum ether/ EtOAc 85: 15), affording the title compound (470 mg, 38% yield over two steps) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.92 (t, *J* = 8.0 Hz, 2H), 2.56 (s, 2H), 1.79-1.72 (m, 2H), 1.44-1.36 (m, 2H), 0.90 (t, *J* = 8.0 Hz, 3H), 0.23 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 57.1, 43.3, 24.8, 21.7, 13.6, -0.60.

HRMS-ESI $(M+Na)^+$: 231.0851, found: 231.0847.



1m

Trimethyl((octylsulfonyl)methyl)silane.

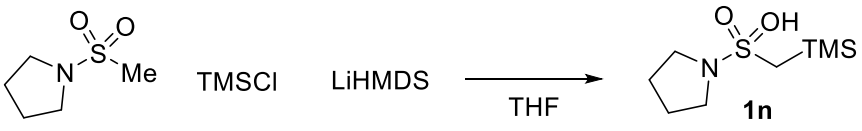
This compound was synthesized according to "**General Procedure A**" from octane-1-thiol (1.0 mL, 6.0 mmol), and **1m** was purified by flash silica column chromatography (petroleum ether/ EtOAc 90: 10), affording the title compound (740 mg, 47% yield over two steps) as a white solid

^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.94 (t, *J* = 8.0 Hz, 2H), 2.57 (s, 2H), 1.81-1.77 (m, 2H), 1.39-1.38 (m, 2H), 1.30-1.20 (m, 8H), 0.85 (t, *J* = 8.0 Hz, 3H), 0.25 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 57.4, 43.4, 31.8, 29.1, 29.0, 28.5, 22.9, 22.6, 14.1, -0.53.

HRMS-EI $(M)^+$: 264.1579, found: 264.1583.

General Procedure C



5.0 mmol 6.0 mmol 6.0 mmol **1n** 55% yield

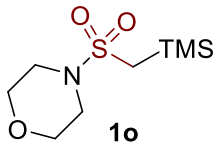
General Procedure C: To a solution of 1-(methylsulfonyl)pyrrolidine (750 mg, 5.0 mmol) in THF (10 mL) was added LiHMDS (6.0 mL, 1.0M in THF) at -78 ℃. The resulting orange solution was stirred at -78 ℃ for 1 hour before TMSCl (760 μL, 6.0 mmol) was added. The mixture was stirred at -78 ℃ for 1 h, and then saturated

aqueous NH_4Cl (10 mL) was added. The organic phase was separated, and the aqueous layer was extracted with EtOAc (50 mL × 3 mL). The combined organic phase was washed with brine (25 mL x 3), dried over ($MgSO_4$), and then filtered and concentrated. The residue was purified by flash chromatography (hexanes/EtOAc 90:10) to afford **1n** (607 mg, 55% yield) as a white solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.94 (t, *J* = 8.0 Hz, 2H), 2.57 (s, 2H), 1.81-1.77 (m, 2H), 1.39-1.38 (m, 2H), 1.30-1.20 (m, 8H), 0.85 (t, *J* = 8.0 Hz, 3H), 0.25 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 47.1, 46.3, 25.7, 1.00.

HRMS-ESI $(M+H)^+$: 222.0984, found: 222.0979.



1o

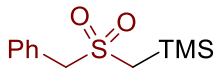
((Butylsulfonyl)methyl)trimethylsilane.

This compound was synthesized according to "**General Procedure C**" from 4-(methylsulfonyl)morpholine (830 mg, 5.0 mmol), and **1o** was purified by flash silica column chromatography (petroleum ether/ EtOAc 80: 20), affording the title compound (663 mg, 56% yield over two steps) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.75 (t, *J* = 4.0 Hz, 2H), 3.09 (t, *J* = 4.0 Hz, 2H), 2.37 (s, 2H), 0.24 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 66.3, 46.0, 35.7, -0.83.

HRMS-ESI $(M+H)^+$: 238.0933, found: 238.0928.



1p

((Benzylsulfonyl)methyl)trimethylsilane.

This compound was synthesized according to "**General Procedure A**" from 4-nitrobenzenethiol (930 mg, 6.0 mmol), and **1p** was obtained as a white solid (1.02 g, 70% yield over two steps).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.07 (s, 2H), 2.32 (s, 2H), 0.10 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ 130.7, 129.4, 129.1, 128.9, 63.8, 41.9, -0.48.

HRMS-ESI $(M+Na)^+$: 265.0694, found: 265.0693.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) zjd783

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: zjd783

```
Bond precision:  C-C = 0.0031 A          Wavelength=1.54178

Cell:            a=9.1212(5)    b=8.4842(4)        c=20.1475(10)
                 alpha=90       beta=90.270(2)     gamma=90
Temperature:     120 K
```

	Calculated	Reported
Volume	1559.12(14)	1559.12(14)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C18 H19 N O2 S	C18 H19 N O2 S
Sum formula	C18 H19 N O2 S	C18 H19 N O2 S
Mr	313.40	313.40
Dx,g cm-3	1.335	1.335
Z	4	4
Mu (mm-1)	1.894	1.894
F000	664.0	664.0
F000’	667.07	
h,k,lmax	11,10,24	11,10,24
Nref	5962[3197]	5761
Tmin,Tmax	0.775,0.899	0.688,1.000
Tmin’	0.613	

```
Correction method= # Reported T Limits: Tmin=0.688 Tmax=1.000
AbsCorr = NUMERICAL

Data completeness= 1.80/0.97      Theta(max)= 70.362

R(reflections)= 0.0258( 5643)     wR2(reflections)= 0.0652( 5761)

S = 1.022                 Npar= 397
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT987_ALERT_1_C The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

Alert level G

```
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.046 Note
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels .........          2 Note
PLAT791_ALERT_4_G Model has Chirality at C8          (Sohnke SpGr)         R Verify
PLAT791_ALERT_4_G Model has Chirality at C8A         (Sohnke SpGr)         R Verify
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600        22 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.        11 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   5 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

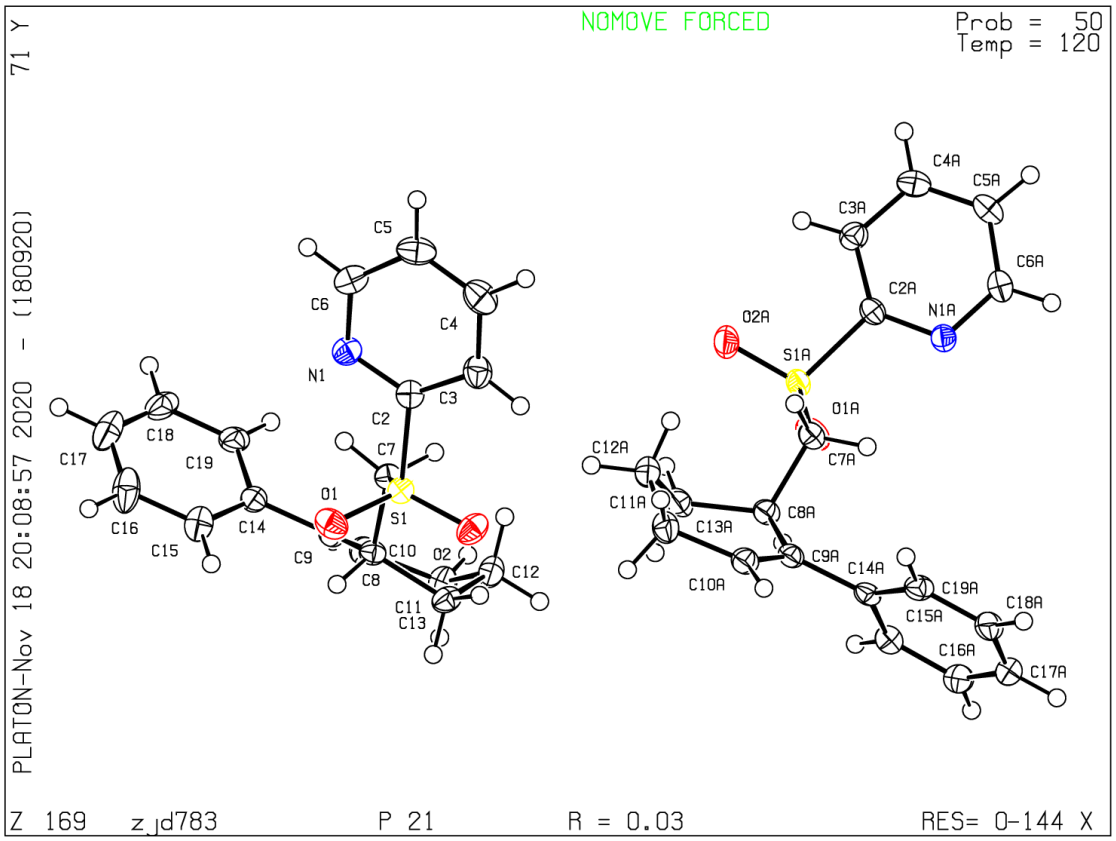
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

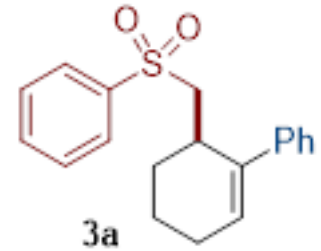
Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 18/09/2020; check.def file version of 20/08/2020

Datablock zjd783 - ellipsoid plot

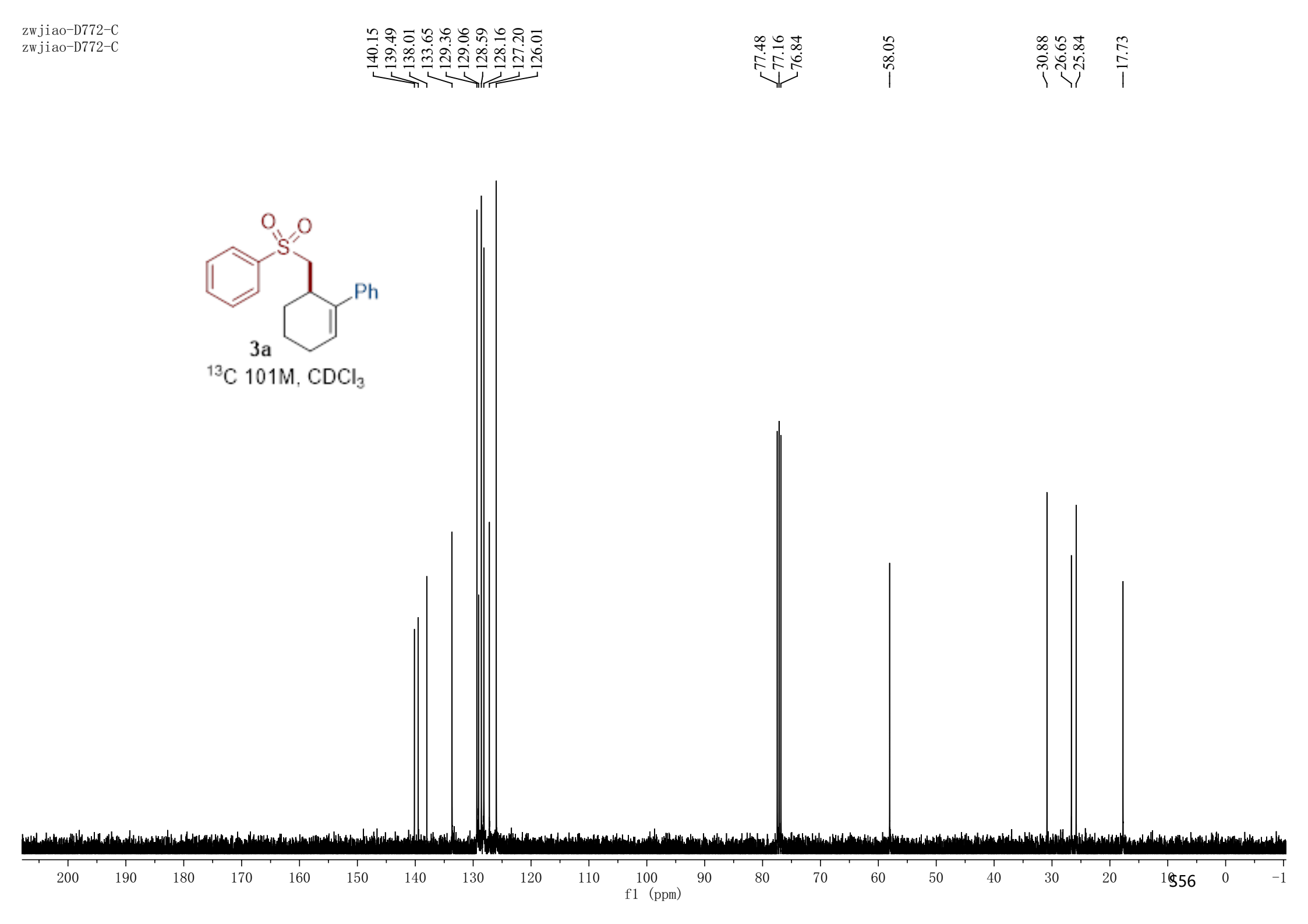


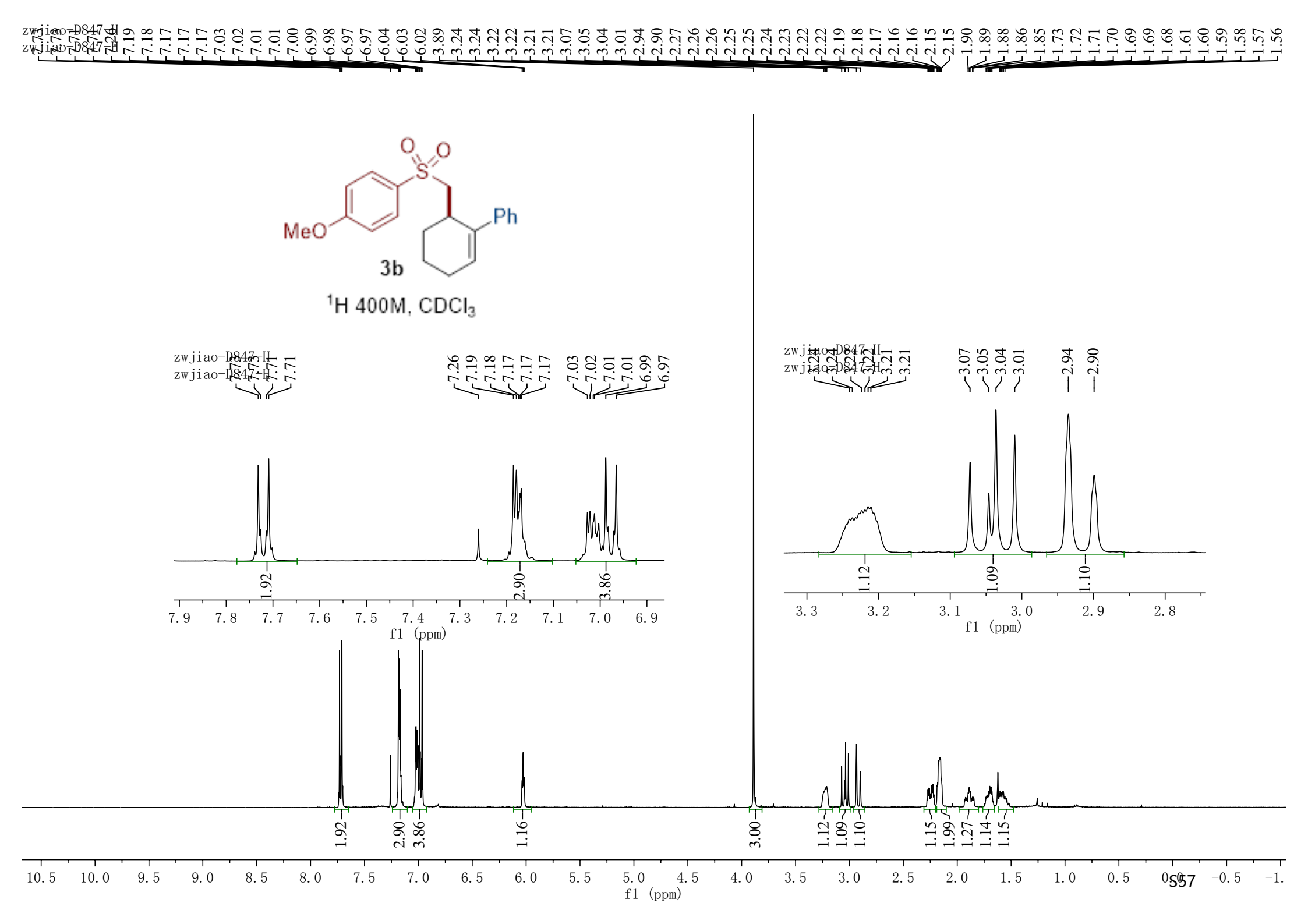


3a

^{1}H 400M, $CDCl_3$

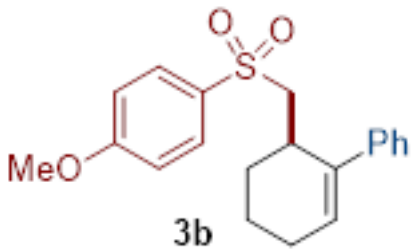
zwjiao-D772-C
zwjiao-D772-C




MeO
Ph
3b
1H 400M, CDCl3
f1 (ppm)

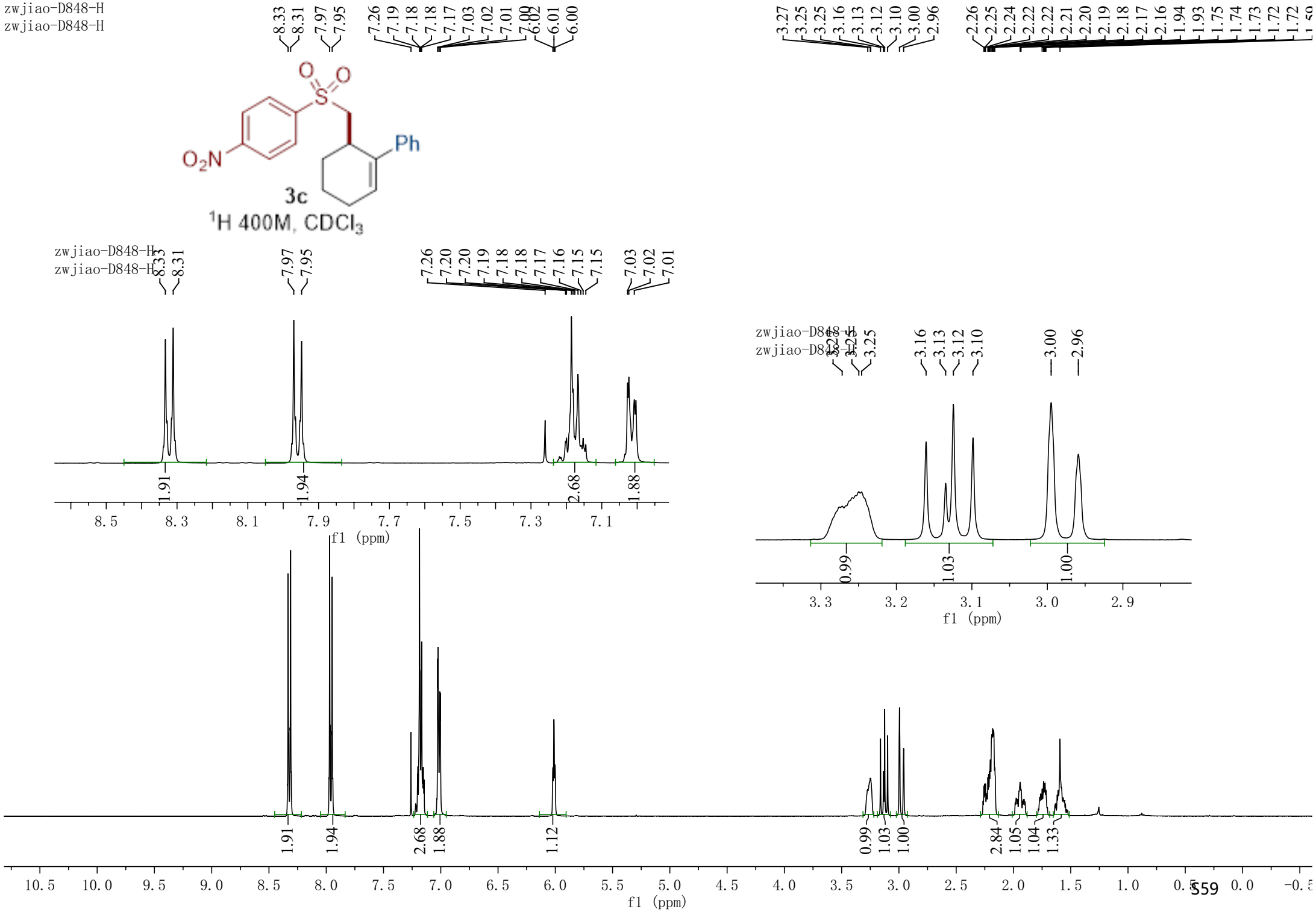
zwjiao-D847-C
zwjiao-D847-C

163.74
140.27
138.17
131.15
130.32
128.93
128.55
127.16
126.09
114.51
77.48
77.16
76.84
58.39
55.83
31.04
26.69
25.86
17.79



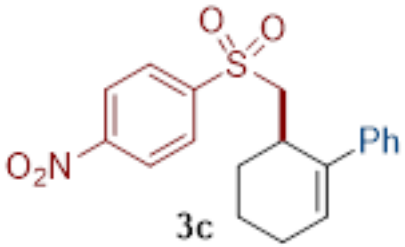
3b

^{13}C 101M, $CDCl_3$


zwjiao-D848-H
zwjiao-D848-H
8.33
8.31
7.97
7.95
7.26
7.19
7.18
7.18
7.17
7.03
7.02
7.01
7.00
6.02
6.01
6.00
3.27
3.25
3.25
3.16
3.13
3.12
3.10
3.00
2.96
2.26
2.25
2.24
2.22
2.22
2.21
2.20
2.19
2.18
2.17
2.16
1.94
1.93
1.75
1.74
1.73
1.72
1.72
O
O
S
O2N
Ph
3c
1H 400M, CDCl3
zwjiao-D848-H
zwjiao-D848-H
8.33
8.31
7.97
7.95
7.26
7.20
7.20
7.19
7.18
7.18
7.17
7.16
7.15
7.15
7.03
7.02
7.01
1.91
1.94
2.68
1.88
8.5
8.3
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
zwjiao-D848-H
zwjiao-D848-H
3.25
3.25
3.16
3.13
3.12
3.10
3.00
2.96
0.99
1.03
1.00
3.3
3.2
3.1
3.0
2.9
f1 (ppm)
1.91
1.94
2.68
1.88
1.12
0.99
1.03
1.00
2.84
1.05
1.04
1.33
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

zwjiao-D848-C
zwjiao-D848-C

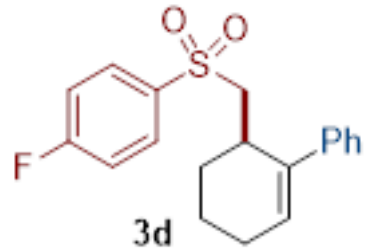
150.81
145.15
140.21
137.73
129.52
129.50
128.64
127.44
126.18
124.51
77.48
77.16
76.84
58.11
31.12
26.91
25.69
17.63



3c

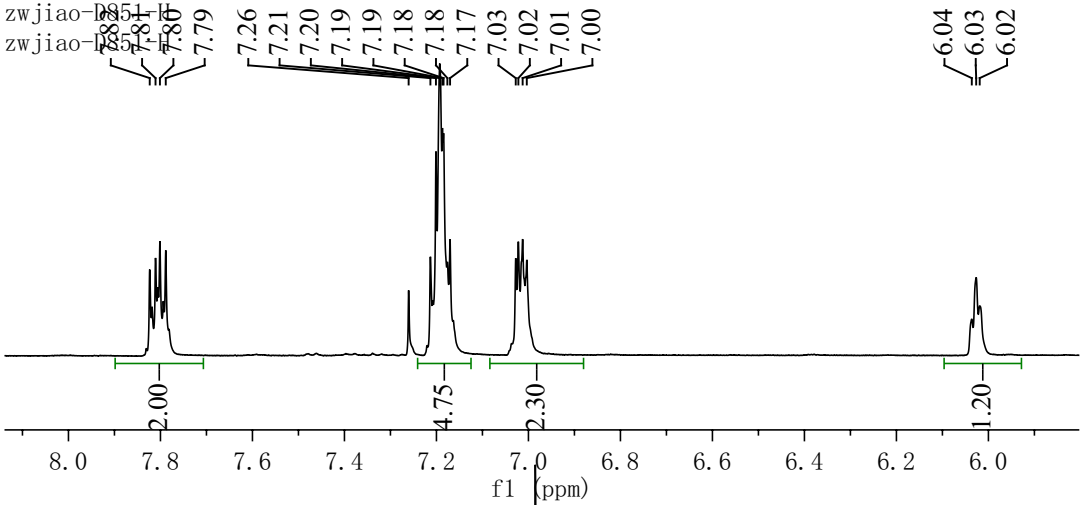
^{13}C 101M, $CDCl_3$

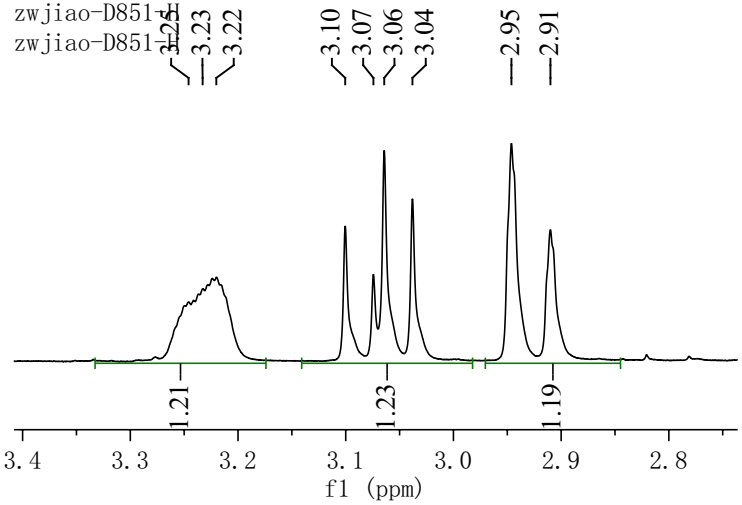
zwjiao-D851-H
zwjiao-D851-H

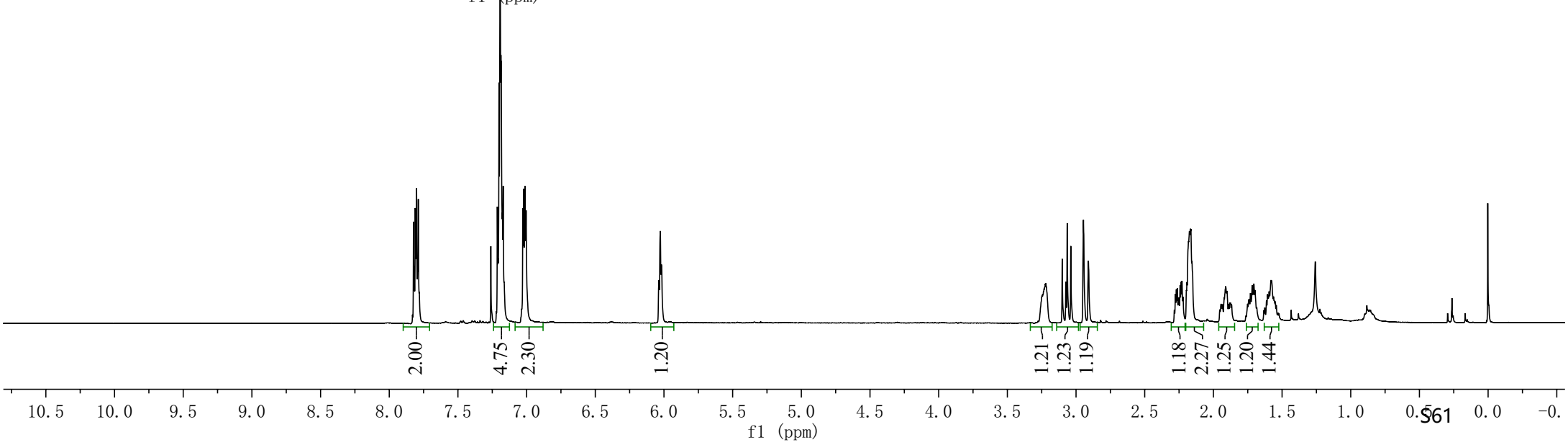


3d

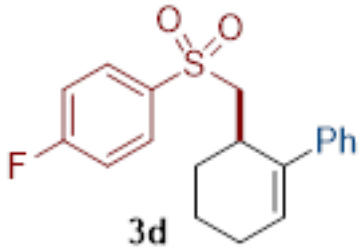
^{1}H 400M, $CDCl_3$







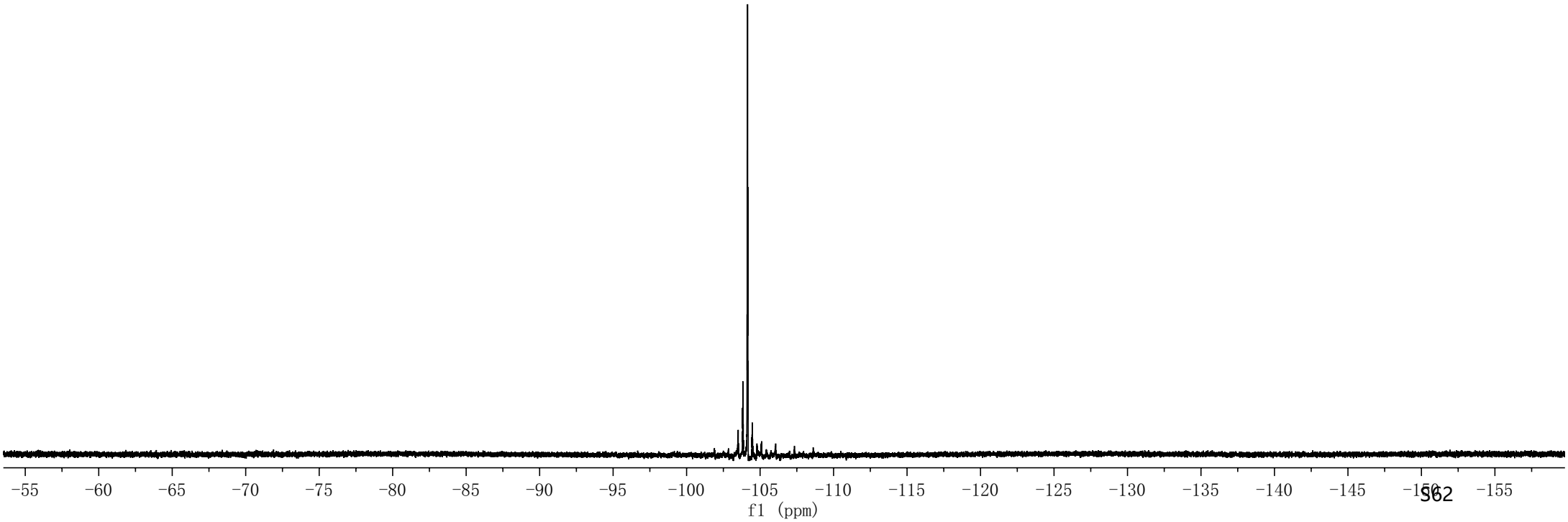
zwjiao-D851-F
zwjiao-D851-F



3d

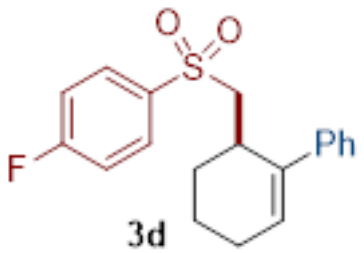
^{19}F 376.6M, $CDCl_3$

-104.15



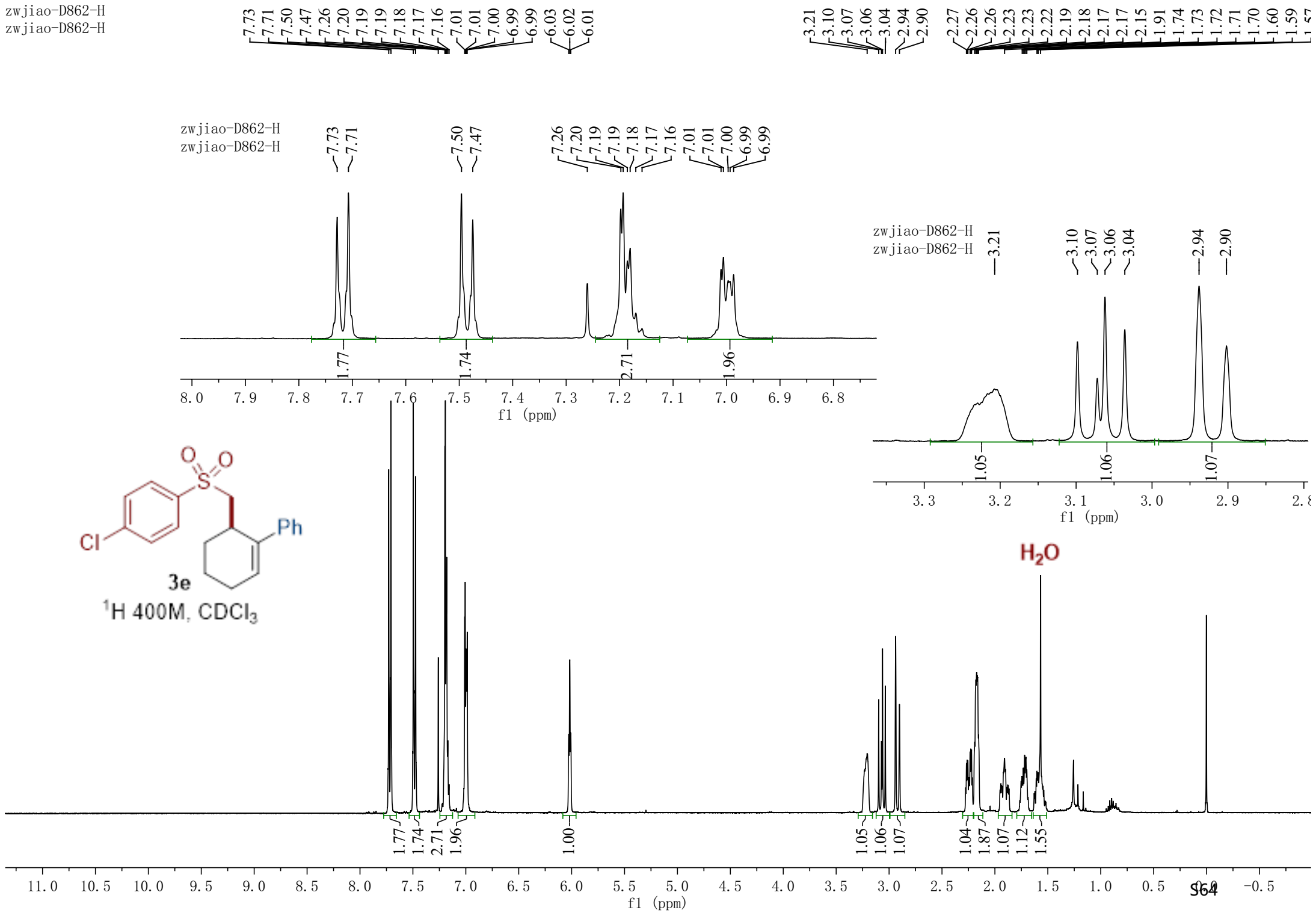
zwjiao-D851-C
zwjiao-D851-C

167.14
164.60
140.27
138.01
135.68
135.65
131.06
130.97
129.20
128.62
127.31
126.11
116.76
116.54
77.48
77.16
76.84
58.30
31.07
26.76
25.82
17.73

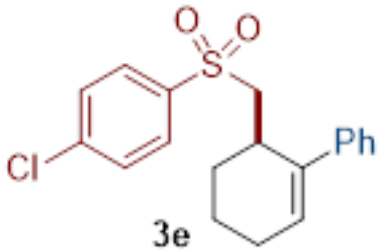


3d

^{13}C 101M, $CDCl_3$


zwjiao-D862-H
zwjiao-D862-H
7.73 7.71 7.50 7.47 7.26 7.20 7.19 7.19 7.18 7.17 7.16 7.01 7.01 7.00 6.99 6.99 6.03 6.02 6.01
3.21 3.10 3.07 3.06 3.04 2.94 2.90 2.27 2.26 2.26 2.23 2.23 2.22 2.19 2.18 2.17 2.17 2.15 1.91 1.74 1.73 1.72 1.71 1.70 1.60 1.59
1.77 1.74 2.71 1.96
f1 (ppm)
1.05 1.06 1.07
Cl
Ph
3e
1H 400M, CDCl3
H2O
1.77 1.74 2.71 1.96 1.00 1.05 1.06 1.07 1.04 1.87 1.07 1.12 1.55
f1 (ppm)

zwjiao-D862-C
zwjiao-D862-C



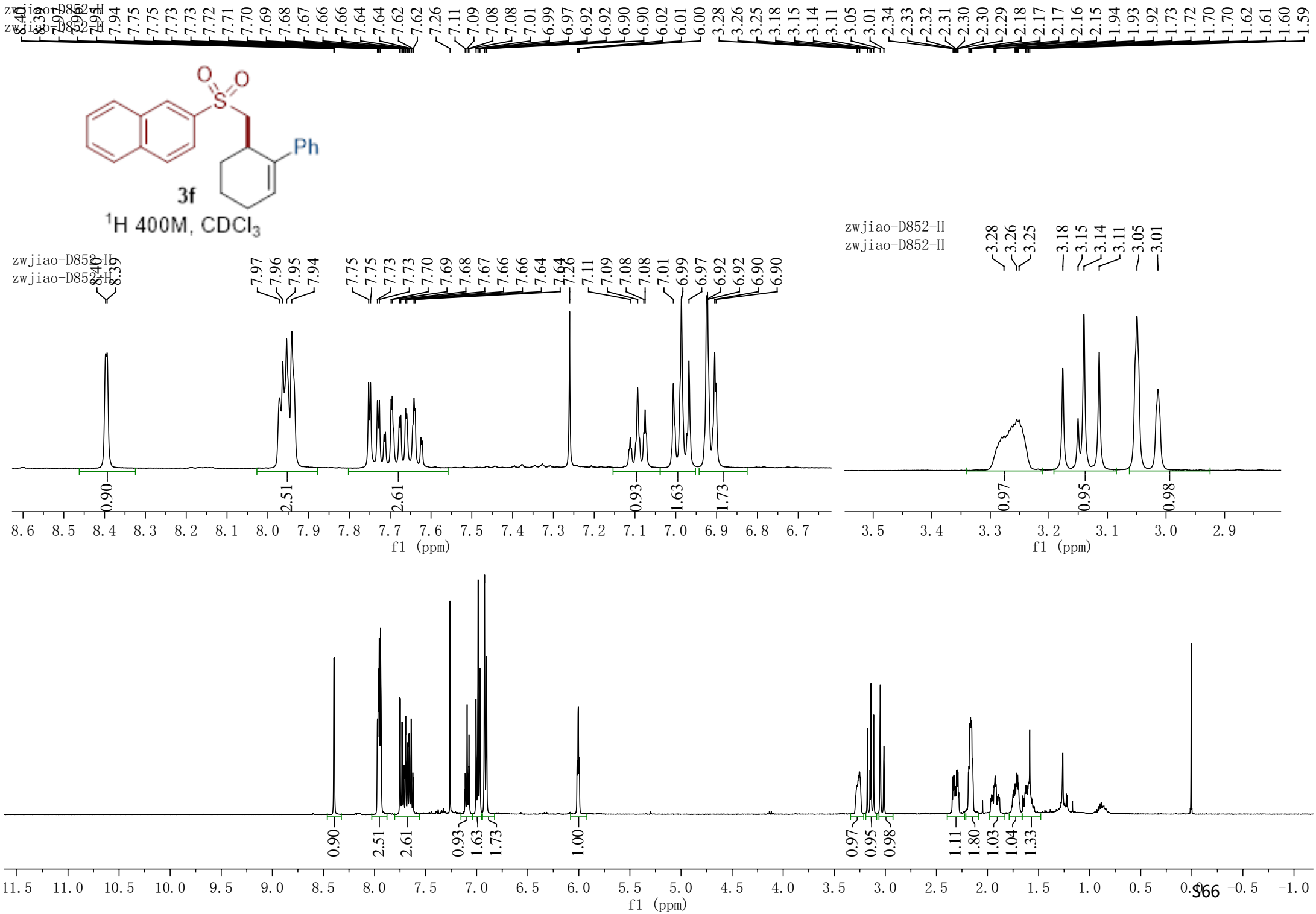
3e

^{13}C 101M, $CDCl_3$

140.46
140.25
138.00
129.69
129.66
129.66
129.21
128.63
127.31
126.13
77.48
77.16
76.84
58.23
31.08
26.79
25.80
17.71

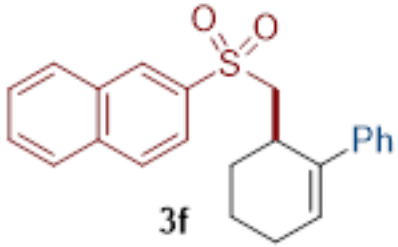
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


zwjiao-D852-H
zwjiao-D852-H
8.40 8.39 7.97 7.96 7.95 7.94 7.75 7.75 7.73 7.73 7.72 7.71 7.70 7.69 7.68 7.67 7.66 7.66 7.64 7.64 7.62 7.62 7.26 7.11 7.09 7.08 7.08 7.01 6.99 6.97 6.92 6.92 6.90 6.90 6.02 6.01 6.00 3.28 3.26 3.25 3.18 3.15 3.14 3.11 3.05 3.01 2.34 2.33 2.32 2.31 2.30 2.30 2.29 2.18 2.17 2.17 2.16 2.15 1.94 1.93 1.92 1.73 1.72 1.70 1.70 1.62 1.61 1.60 1.59
O
O
S
Ph
3f
^{1}H 400M, $CDCl_3$
0.90 2.51 2.61 0.93 1.63 1.73
f1 (ppm)
0.97 0.95 0.98
f1 (ppm)
0.90 2.51 2.61 0.93 1.63 1.73 1.00 0.97 0.95 0.98 1.11 1.80 1.03 1.04 1.33
f1 (ppm)

zwjiao-D852-C
zwjiao-D852-C

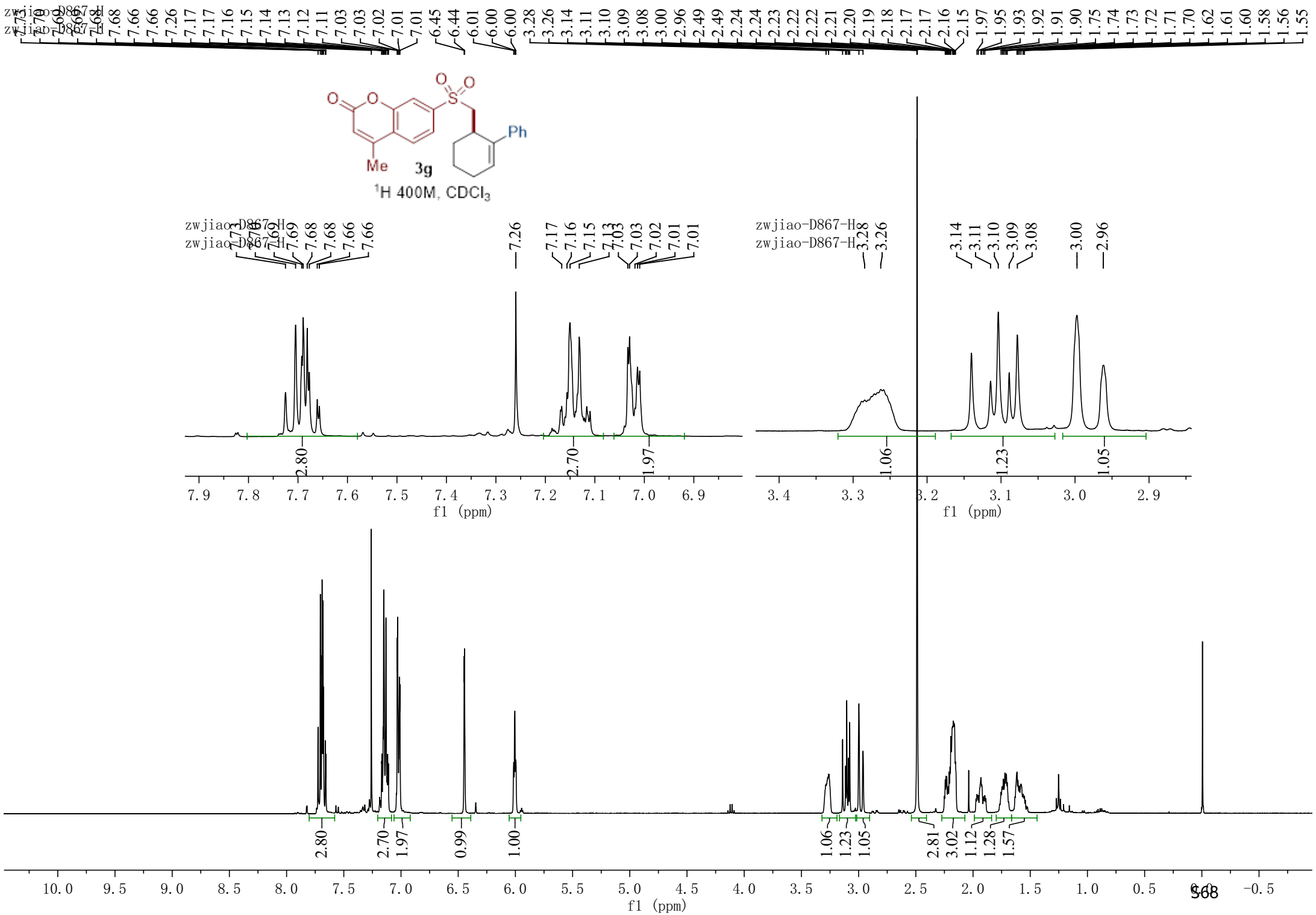
140.17
138.14
136.33
135.37
132.32
129.92
129.64
129.58
129.38
129.00
128.46
128.07
127.80
127.14
126.04
122.94
77.48
77.16
76.84
58.19
31.08
26.78
25.85
17.77



3f

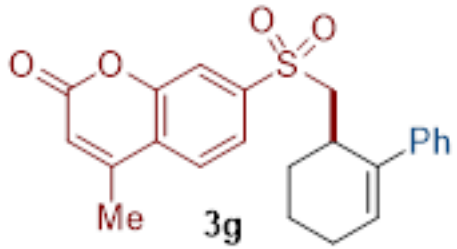
^{13}C 101M, $CDCl_3$

f1 (ppm)


zwjiao-D867-H
Me
3g
Ph
1H 400M, CDCl3
f1 (ppm)

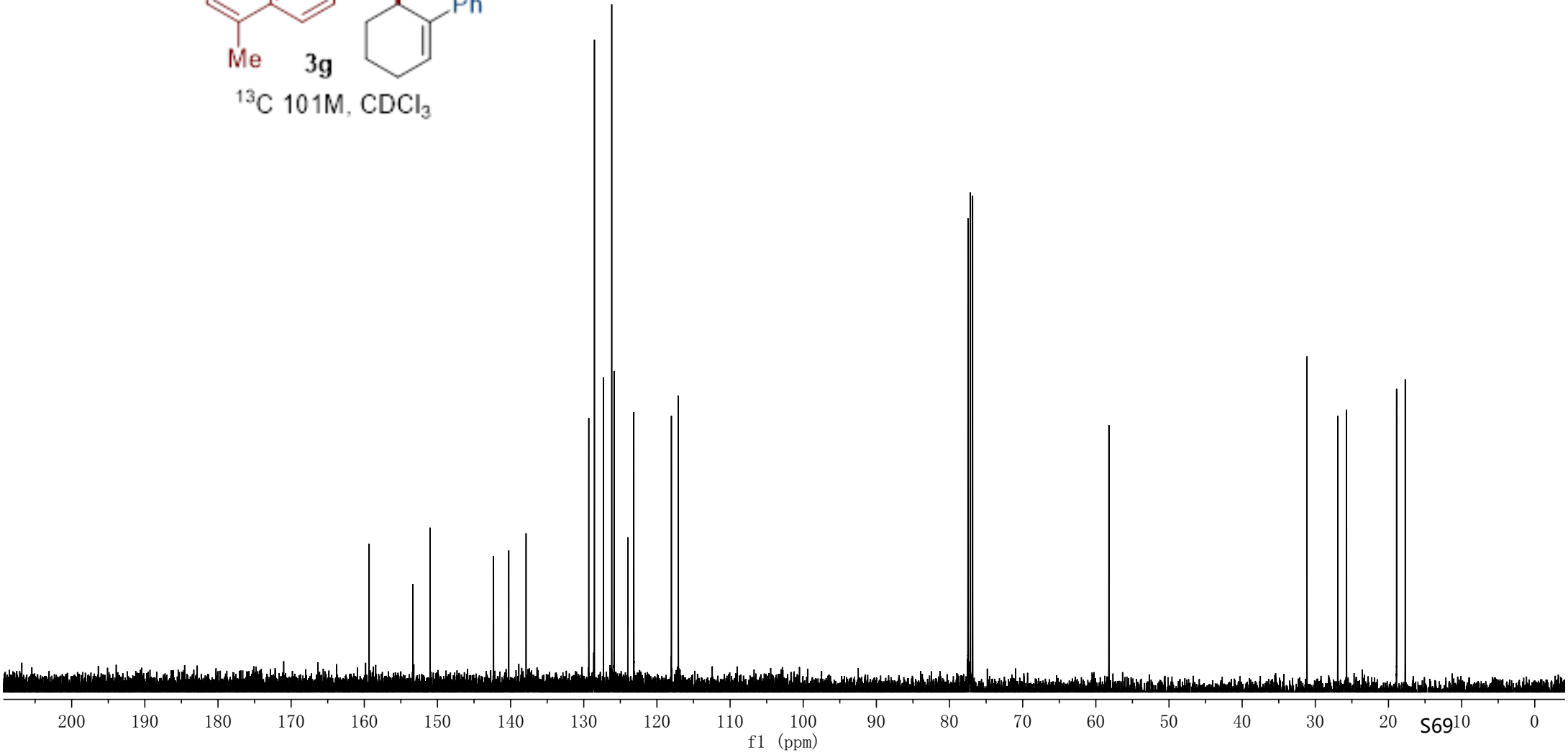
zwjiao-D867-C
zwjiao-D867-C

159.33
153.36
151.01
142.33
140.25
137.88
129.31
128.54
127.31
126.17
125.86
123.98
123.15
118.02
117.06
77.48
77.16
76.84
58.22
31.14
26.93
25.73
18.89
17.71

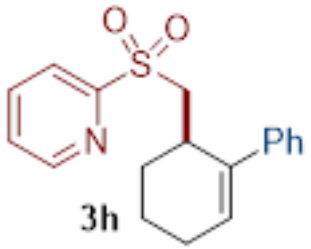


3g

^{13}C 101M, $CDCl_3$



zwjiao-D783-H
zwjiao-D783-H



3h

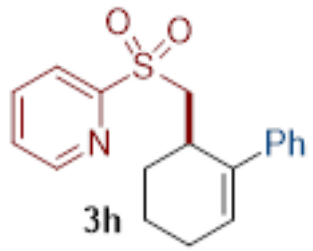
^{1}H 400M, $CDCl_3$

H_2O

f1 (ppm)

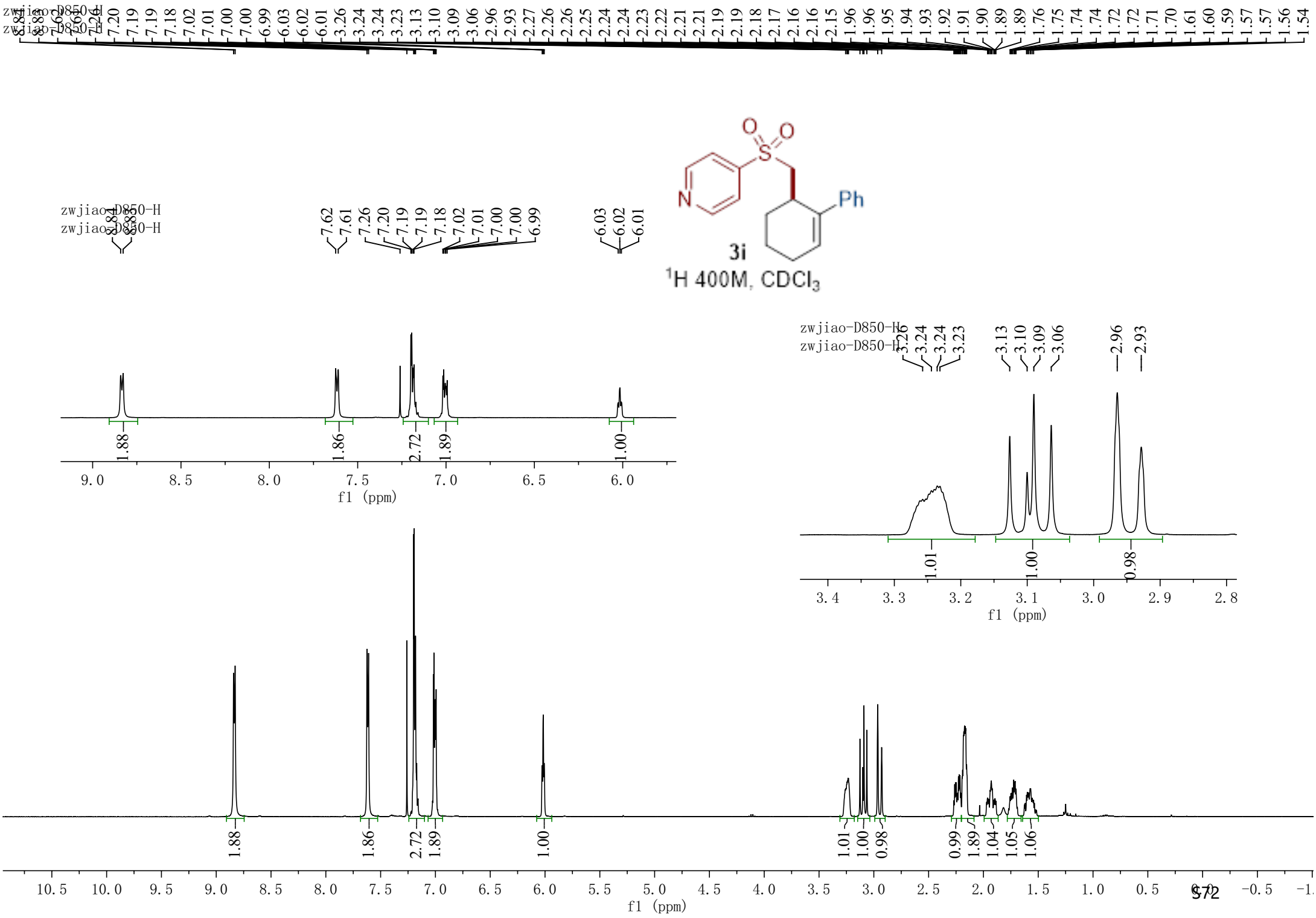
zwjiao-D783-C-3
zwjiao-D783-C

157.63
150.30
140.36
138.22
138.20
129.09
128.58
127.34
127.21
126.22
122.16
77.48
77.16
76.84
54.15
30.66
26.89
25.79
17.58



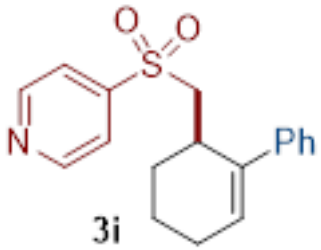
3h

^{13}C 101M, $CDCl_3$


zwjiao-D850-H
zwjiao-D850-H
3i
^{1}H 400M, $CDCl_3$
f1 (ppm)
f1 (ppm)
f1 (ppm)

zwjiao-D850-C
zwjiao-D850-C

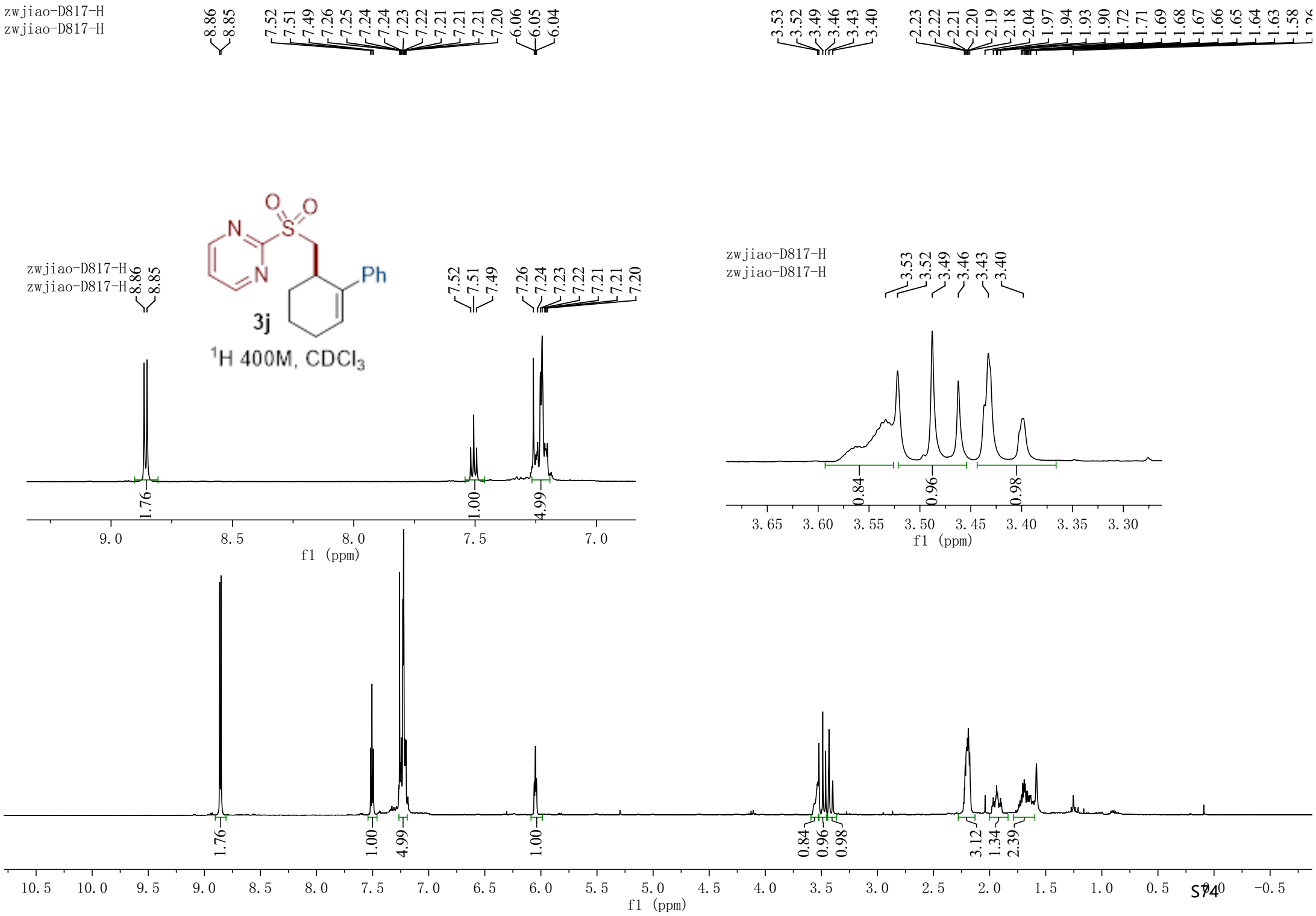
151.33
147.44
140.12
137.72
129.42
128.68
127.42
126.08
121.18
77.48
77.16
76.84
57.63
30.95
26.81
25.70
17.60



3i

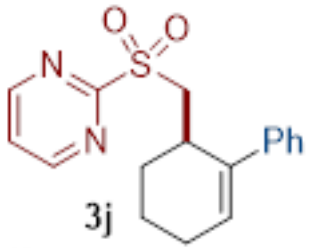
^{13}C 101M, $CDCl_3$

f1 (ppm)


zwjiao-D817-H
zwjiao-D817-H
8.86
8.85
7.52
7.51
7.49
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.21
7.21
7.20
6.06
6.05
6.04
3.53
3.52
3.49
3.46
3.43
3.40
2.23
2.22
2.21
2.20
2.19
2.18
2.04
1.97
1.94
1.93
1.90
1.72
1.71
1.69
1.68
1.67
1.66
1.65
1.64
1.63
1.58
O
O
N
S
N
Ph
3j
1H 400M, CDCl3
1.76
1.00
4.99
1.00
0.84
0.96
0.98
3.12
1.34
2.39
f1 (ppm)

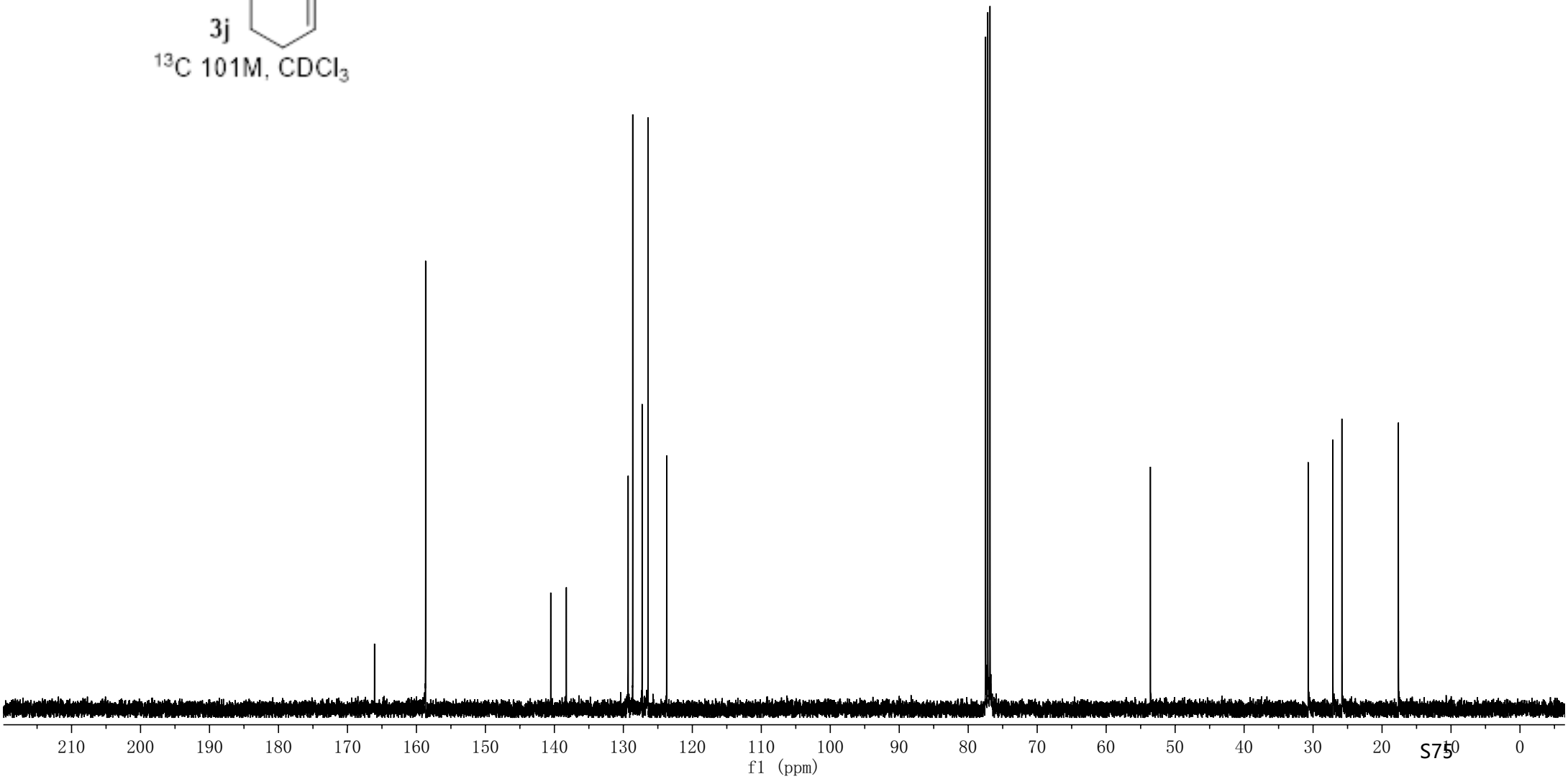
zwjiao-D817-C
zwjiao-D817-C

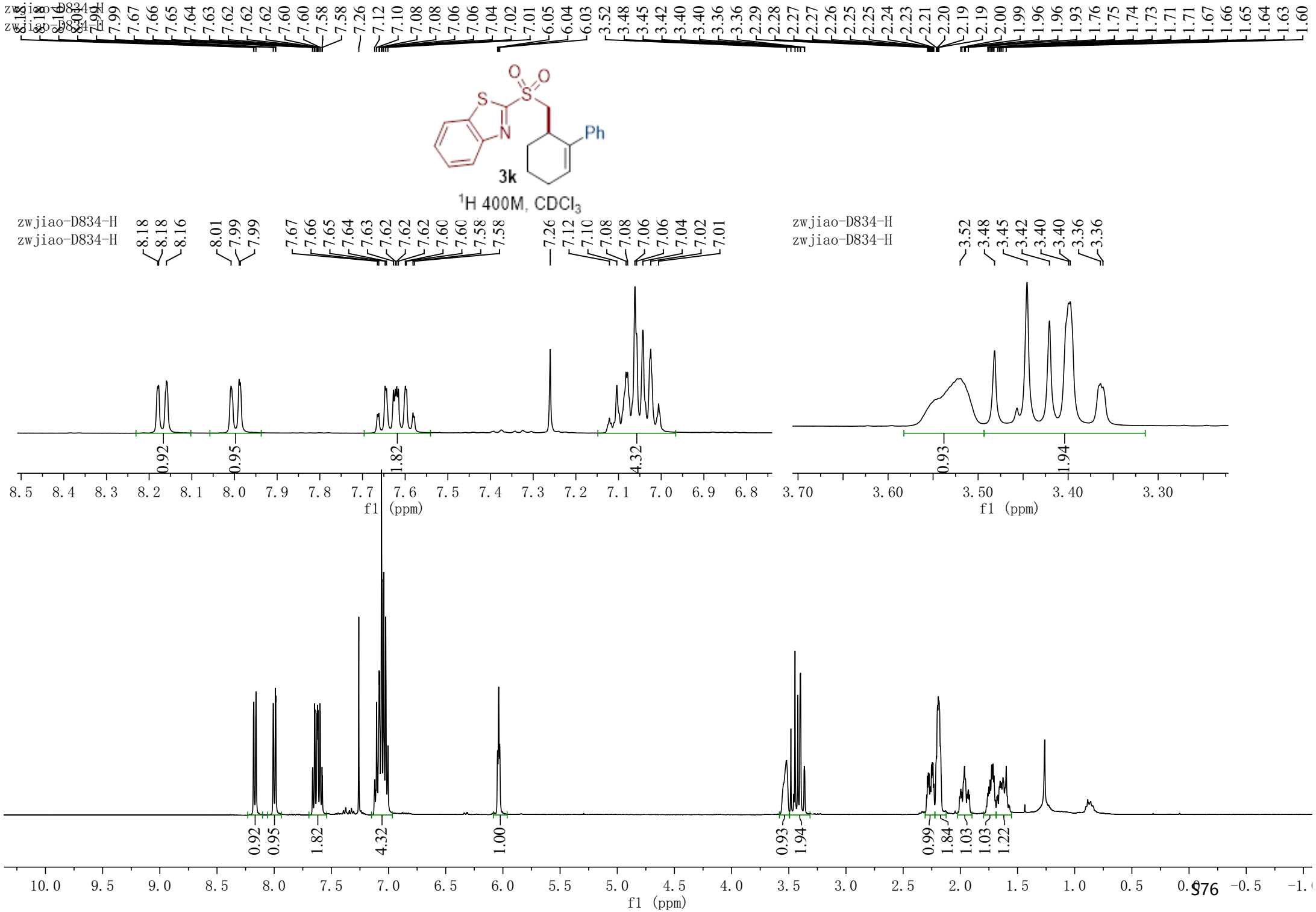
166.08
158.67
140.53
138.27
129.30
128.64
127.28
126.41
123.72
77.48
77.16
76.84
53.59
30.71
27.14
25.82
17.63



3j

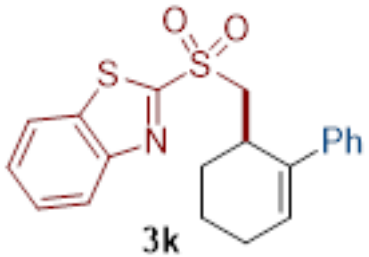
^{13}C 101M, $CDCl_3$




zwjiao-D834-H
zwjiao-D834-H
8.18 8.18 8.16 8.01 7.99 7.99 7.67 7.66 7.65 7.64 7.63 7.62 7.62 7.62 7.60 7.60 7.58 7.58 7.26 7.12 7.10 7.08 7.08 7.06 7.06 7.04 7.02 7.01 6.05 6.04 6.03 3.52 3.48 3.45 3.42 3.40 3.40 3.36 3.36 2.29 2.28 2.27 2.27 2.26 2.25 2.25 2.24 2.23 2.21 2.20 2.19 2.19 2.00 1.99 1.96 1.96 1.93 1.76 1.75 1.74 1.73 1.71 1.71 1.67 1.66 1.65 1.64 1.63 1.60
S
O
O
S
N
Ph
3k
1H 400M, CDCl3
0.92 0.95 1.82 4.32
0.93 1.94
0.92 0.95 1.82 4.32 1.00 0.93 1.94 0.99 1.84 1.03 1.03 1.22
f1 (ppm)

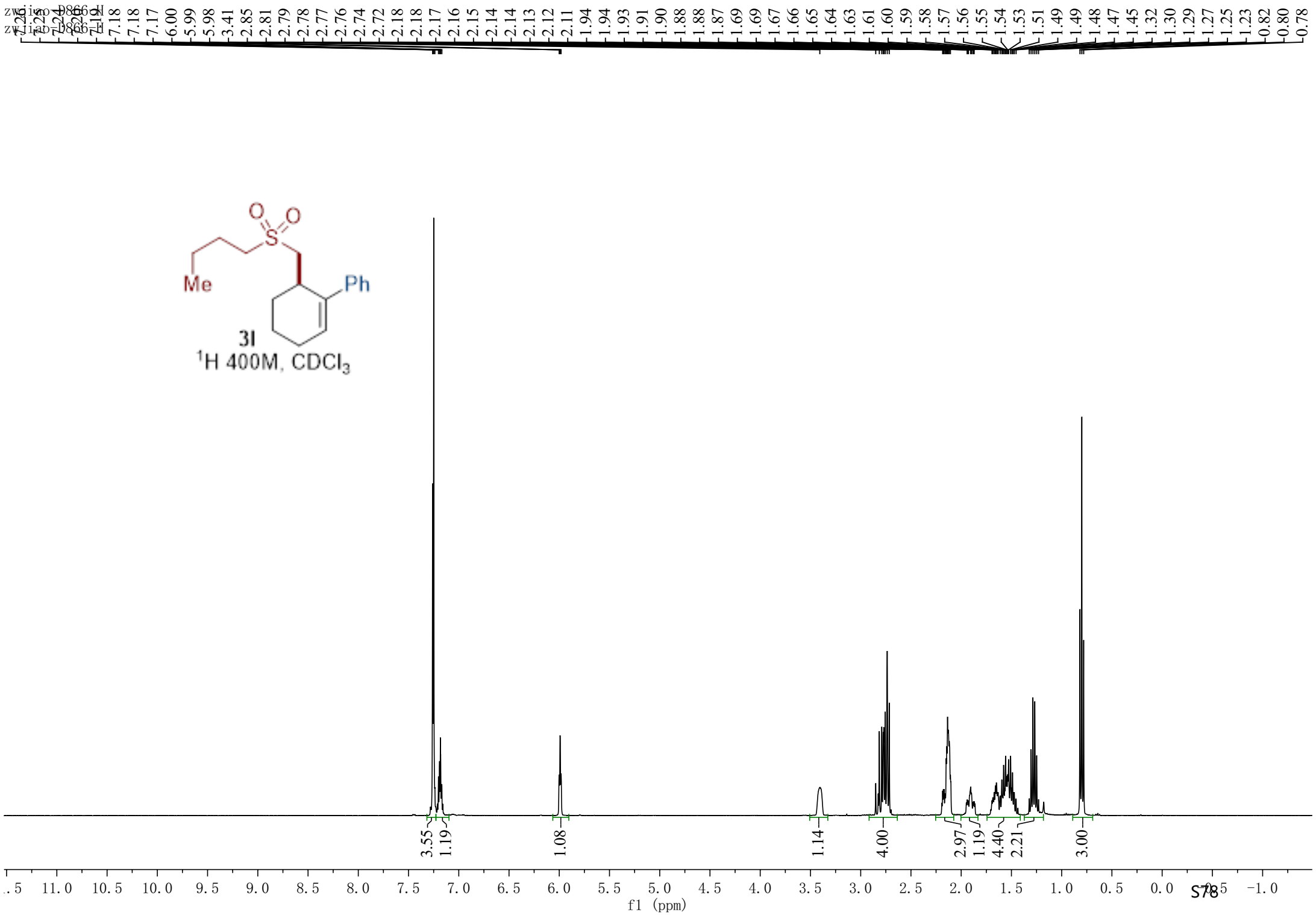
zwjiao-D834-C
zwjiao-D834-C

165.95
152.78
140.12
137.85
137.04
129.42
128.50
128.13
127.71
127.30
126.17
125.68
122.42
77.48
77.16
76.84
57.11
31.05
26.95
25.76
17.54



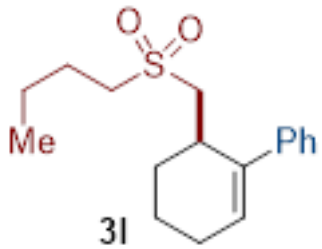
3k

^{13}C 101M, $CDCl_3$


Me
Ph
3l
^{1}H 400M, $CDCl_3$
f1 (ppm)

zwjiao-D866-C
zwjiao-D866-C

140.70
138.41
129.13
128.76
127.45
126.43
77.48
77.16
76.84
54.55
53.81
30.53
27.33
25.81
24.01
21.77
17.74
13.60



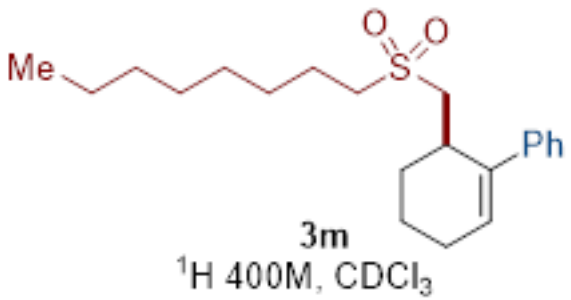
3l

^{13}C 101M, $CDCl_3$

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

zwjiao-D881-H
zwjiao-D881-H



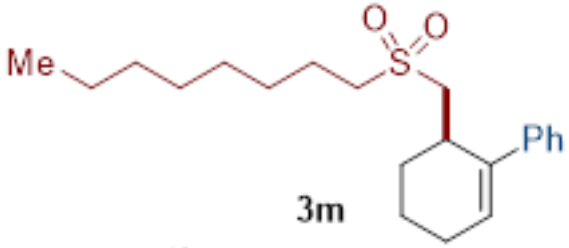
3m

^{1}H 400M, $CDCl_3$

H_2O

f1 (ppm)

zwjiao-D881-C
zwjiao-D881-C



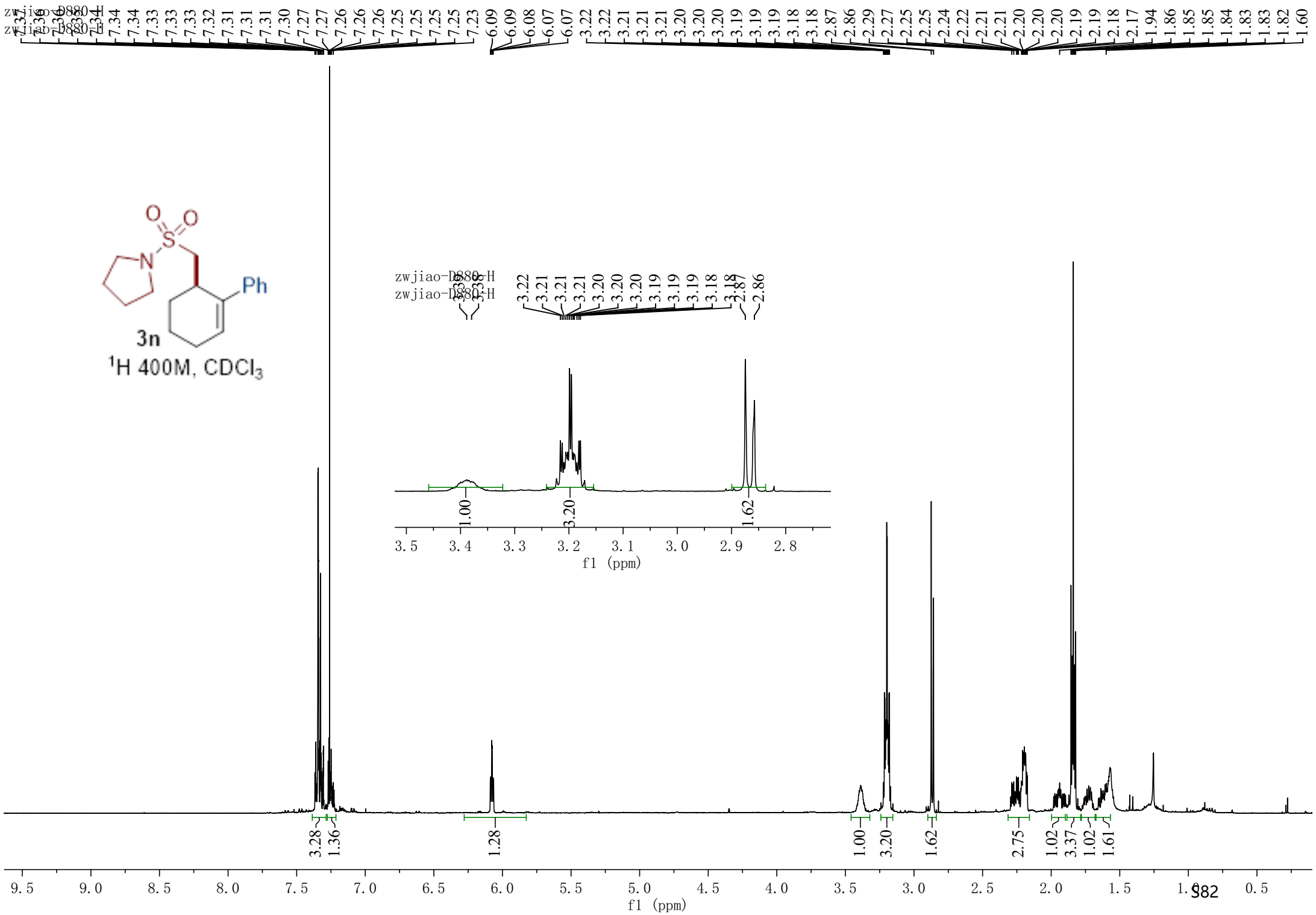
3m

^{13}C 101M, $CDCl_3$

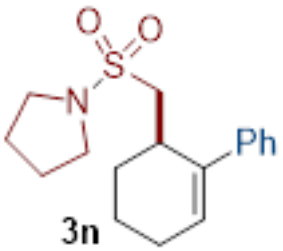
140.75
138.46
129.19
128.81
127.50
126.47
77.48
77.16
76.84
54.60
54.13
31.83
30.58
29.11
29.04
28.55
27.37
25.85
22.72
22.10
17.79
14.21

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


zwjiao-D880-H
zwjiao-D880-H
7.37 7.36 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.25 7.23
6.09 6.09 6.08 6.07 6.07
3.22 3.22 3.21 3.21 3.21 3.20 3.20 3.20 3.19 3.19 3.19 3.18 3.18 2.87 2.86 2.29 2.27 2.25 2.25 2.24 2.22 2.21 2.21 2.20 2.20 2.20 2.19 2.19 2.18 2.17 1.94 1.86 1.85 1.85 1.84 1.83 1.83 1.82 1.60
O
O
S
N
Ph
3n
1H 400M, CDCl3
zwjiao-D880-H
zwjiao-D880-H
3.22 3.21 3.21 3.21 3.20 3.20 3.20 3.19 3.19 3.19 3.18 2.87 2.86
1.00
3.20
1.62
3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8
f1 (ppm)
3.28
1.36
1.28
1.00
3.20
1.62
2.75
1.02
3.37
1.02
1.61
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

zwjiao-D880-C--1
zwjiao-D880-C



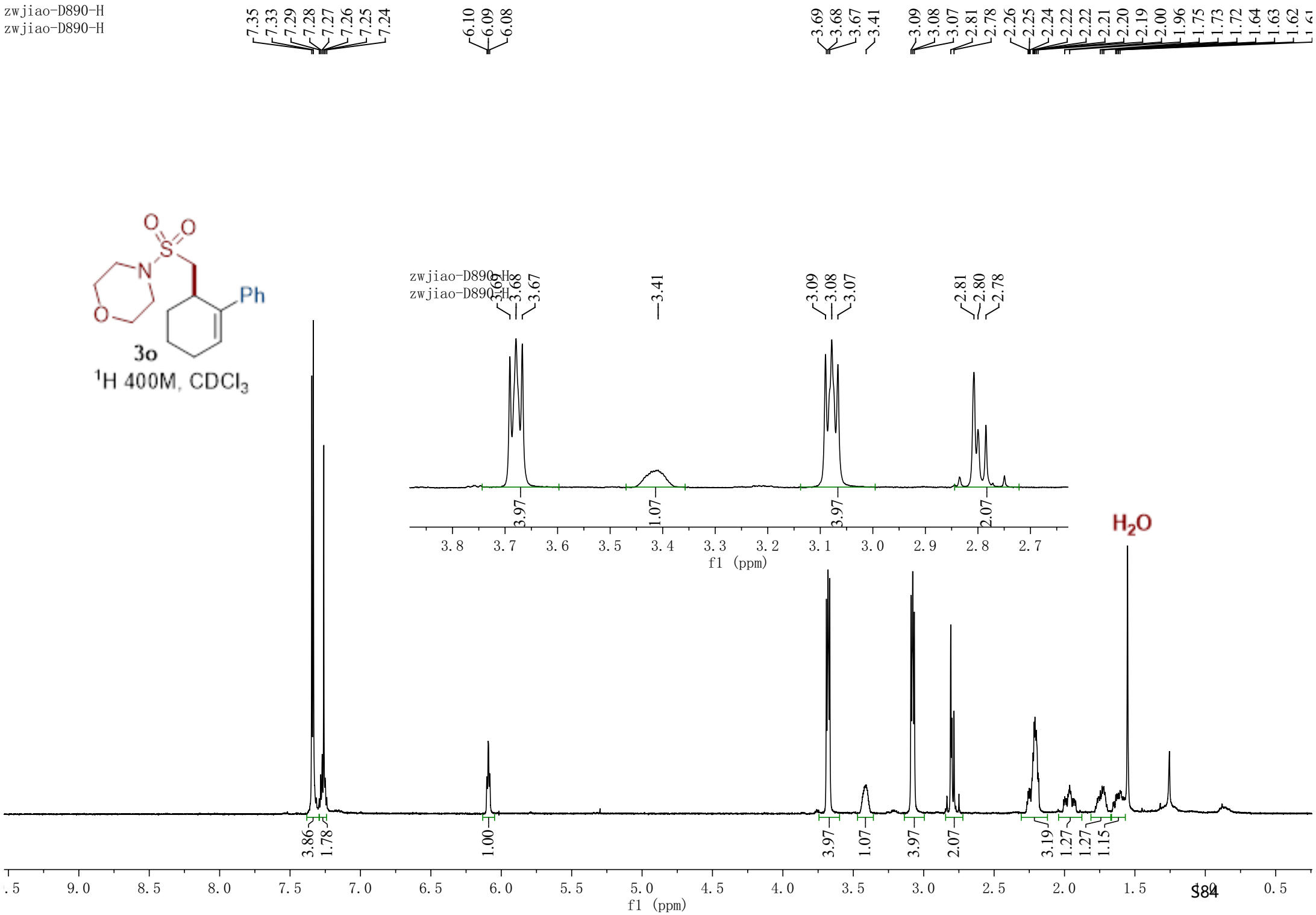
3n

^{13}C 101M, $CDCl_3$

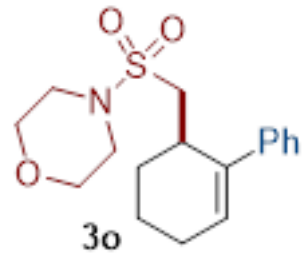
140.81
138.64
128.70
128.67
127.34
126.39
77.48
77.16
76.84
51.41
47.65
31.60
26.87
25.97
25.90
17.92

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


zwjiao-D890-H
zwjiao-D890-H
7.35 7.33 7.29 7.28 7.27 7.26 7.25 7.24
6.10 6.09 6.08
3.69 3.68 3.67 3.41 3.09 3.08 3.07 2.81 2.78 2.26 2.25 2.24 2.22 2.22 2.21 2.20 2.19 2.00 1.96 1.75 1.73 1.72 1.64 1.63 1.62
O
O
S
N
O
Ph
3o
^{1}H 400M, $CDCl_3$
zwjiao-D890-H
zwjiao-D890-H
3.69 3.68 3.67 3.41 3.09 3.08 3.07 2.81 2.80 2.78
3.97 1.07 3.97 2.07
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7
f1 (ppm)
H_2O
3.86 1.78 1.00 3.97 1.07 3.97 2.07 3.19 1.27 1.27 1.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

zwjiao-D890-C
zwjiao-D890-C



3o

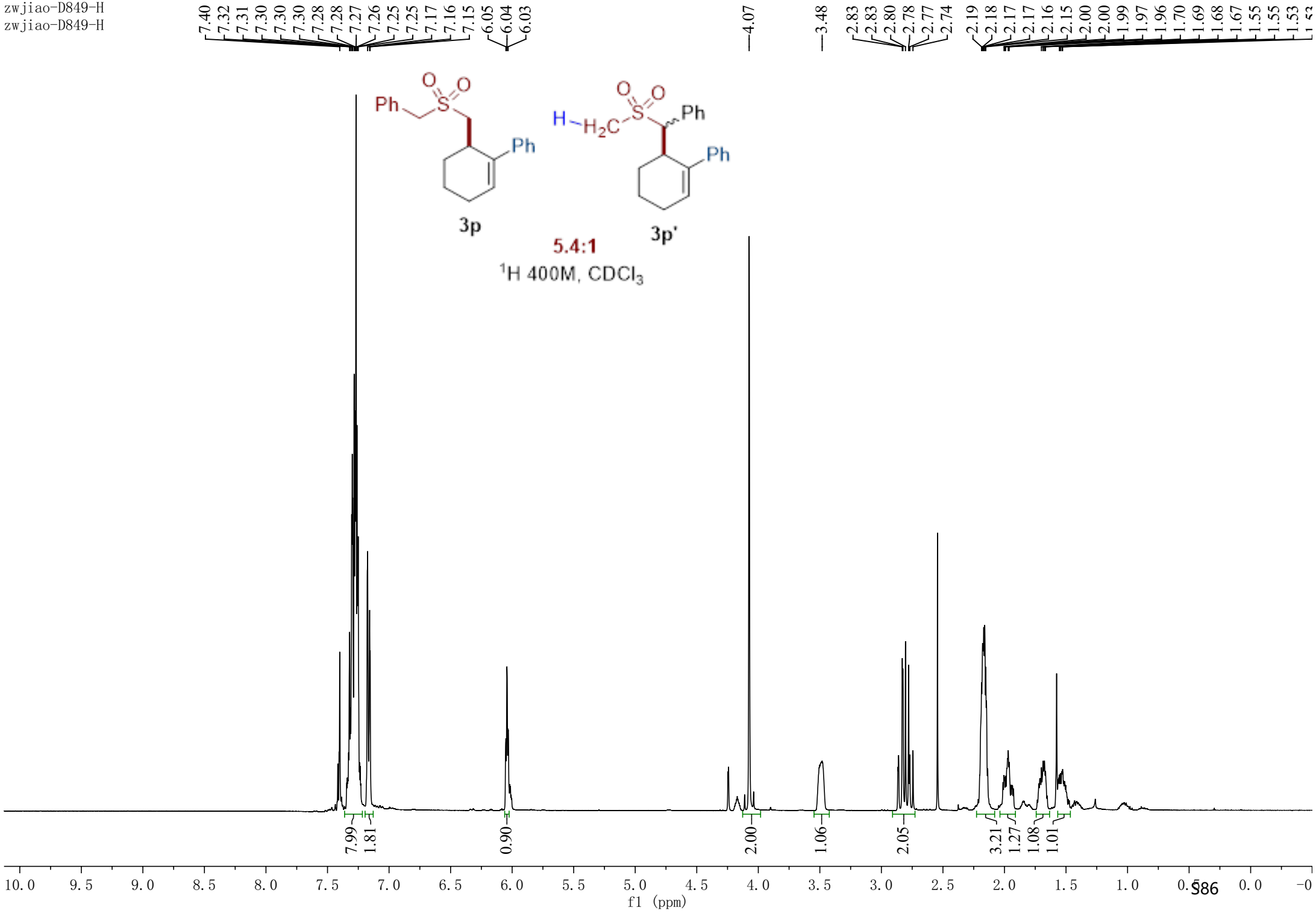
^{13}C 101M, $CDCl_3$

140.78
138.66
128.98
128.77
127.47
126.35
77.48
77.16
76.84
66.60
50.43
45.71
31.37
26.92
25.93
17.93

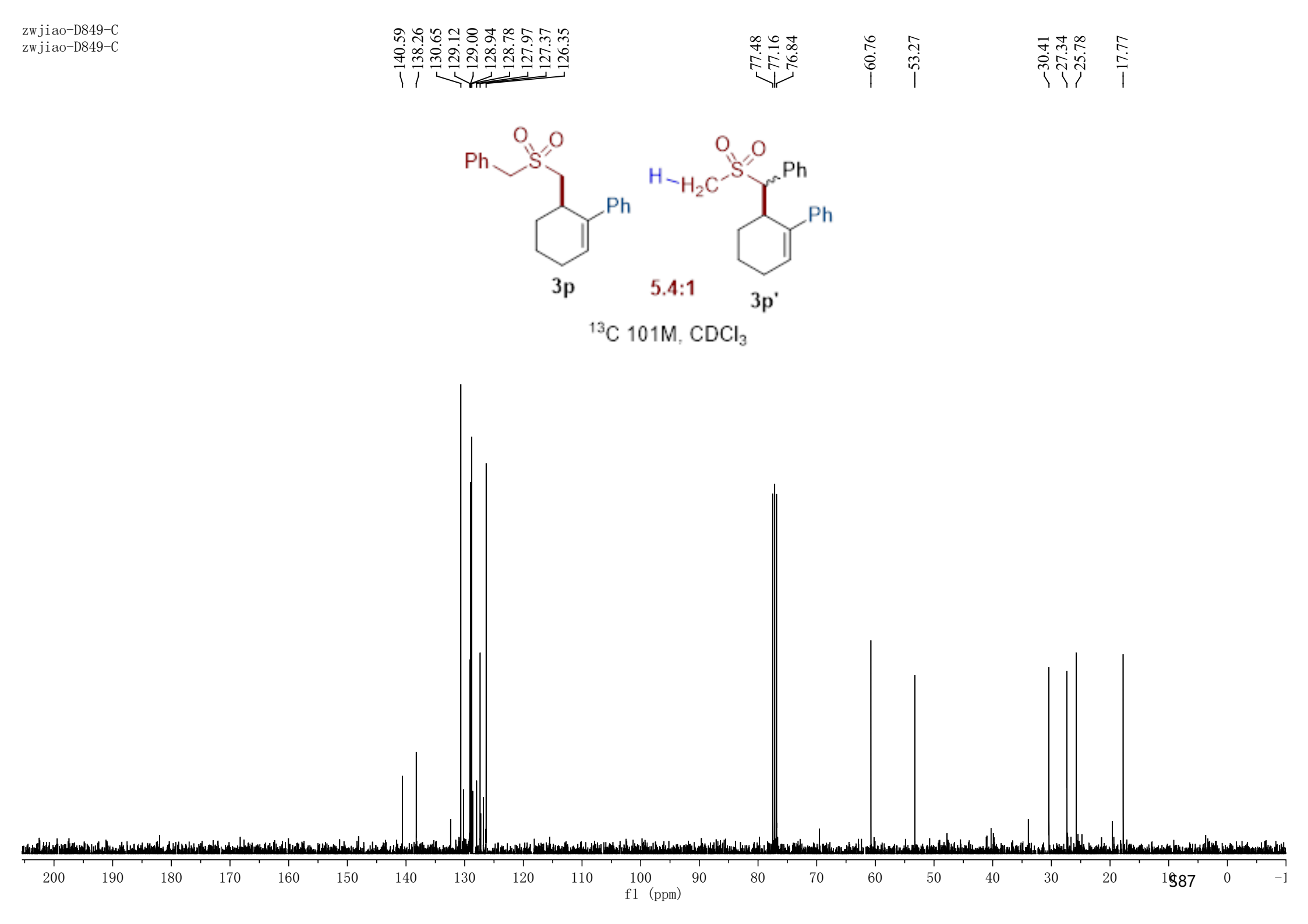
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

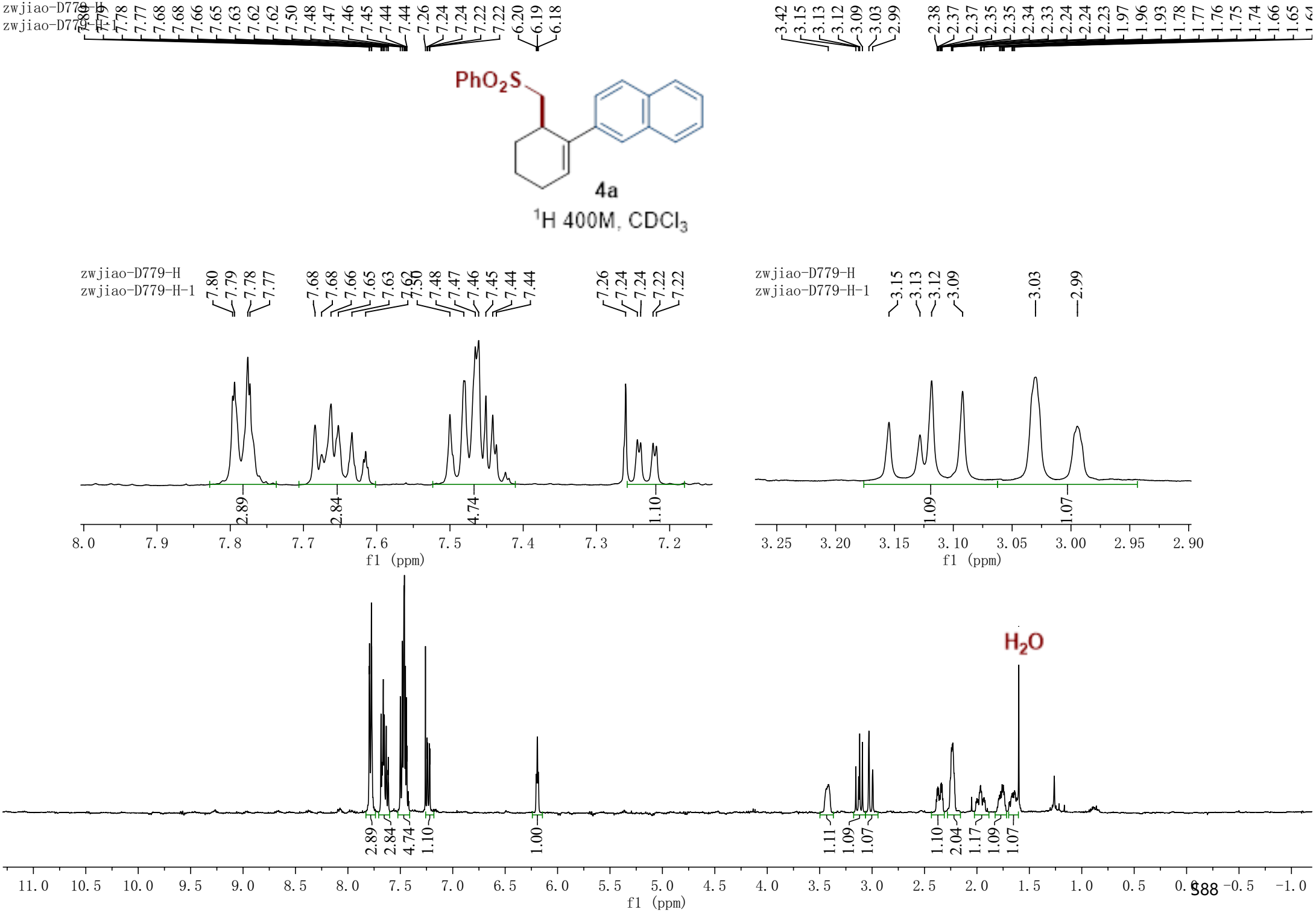
f1 (ppm)

zwjiao-D849-H
zwjiao-D849-H

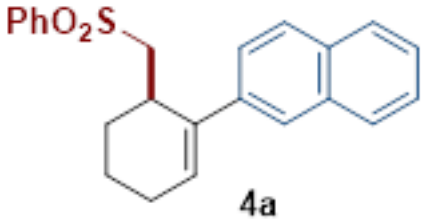


zwjiao-D849-C
zwjiao-D849-C



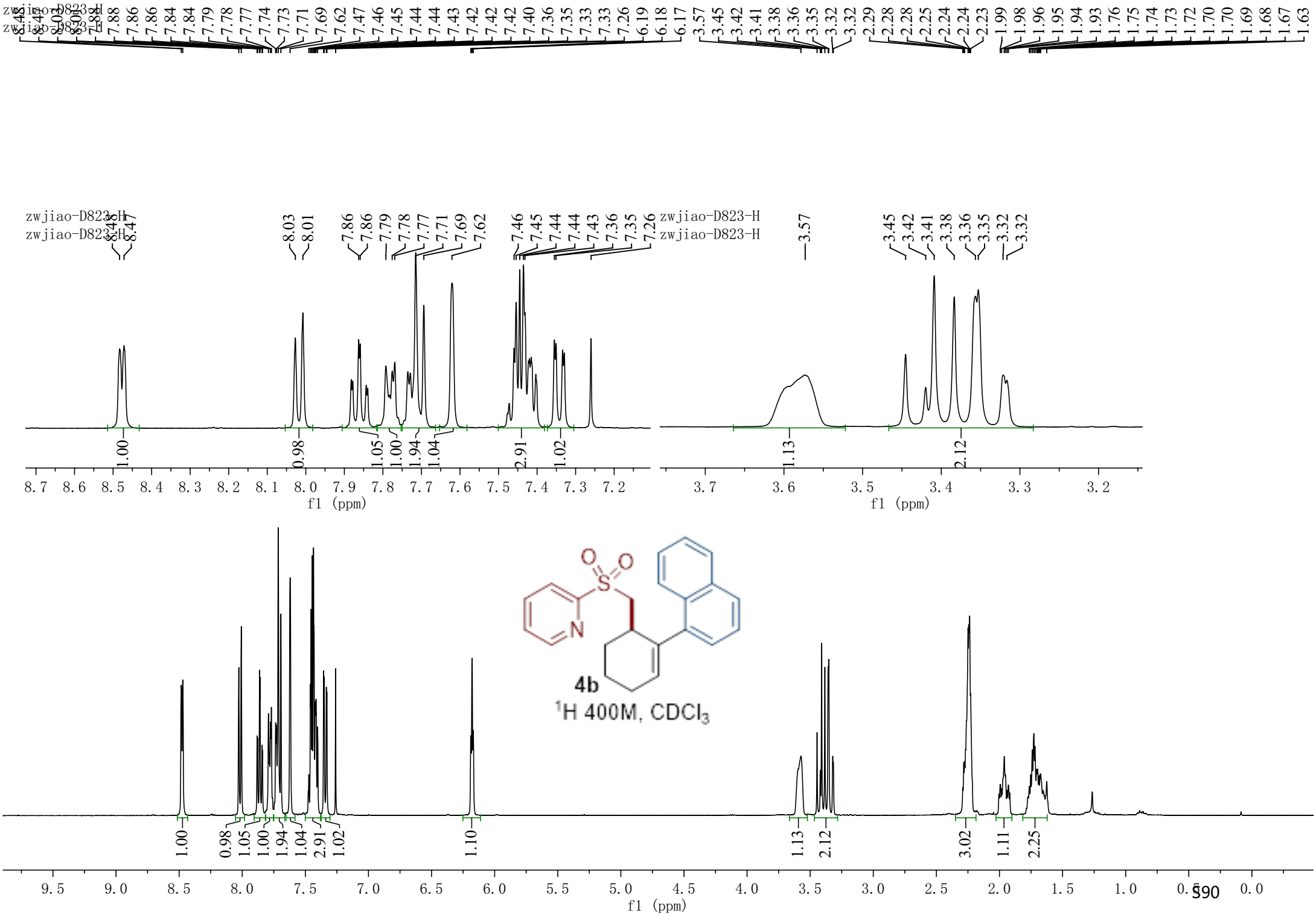

zwjiao-D779-H
zwjiao-D779-H-1
PhO2S
4a
1H 400M, CDCl3
f1 (ppm)
H2O

zwjiao-D779-C
zwjiao-D779-C



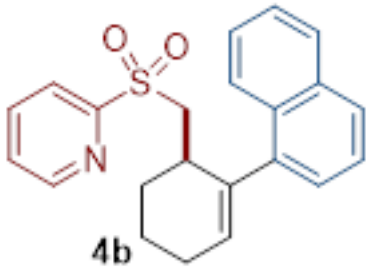
4a

^{13}C 101M, $CDCl_3$


zwjiao-D823-H
zwjiao-D823-H
8.48 8.47 8.03 8.01 7.88 7.86 7.86 7.84 7.84 7.79 7.78 7.77 7.74 7.73 7.71 7.69 7.62 7.47 7.46 7.45 7.44 7.44 7.43 7.42 7.42 7.42 7.40 7.36 7.35 7.33 7.33 7.26 6.19 6.18 6.17 3.57 3.45 3.42 3.41 3.38 3.36 3.35 3.32 3.32 2.29 2.28 2.28 2.25 2.24 2.24 2.23 1.99 1.98 1.96 1.95 1.94 1.93 1.76 1.75 1.74 1.73 1.72 1.70 1.70 1.69 1.68 1.67 1.63
1.00 0.98 1.05 1.00 1.94 1.04 2.91 1.02
f1 (ppm)
1.13 2.12
f1 (ppm)
4b
1H 400M, CDCl3
1.00 0.98 1.05 1.00 1.94 1.04 2.91 1.02 1.10 1.13 2.12 3.02 1.11 2.25
f1 (ppm)

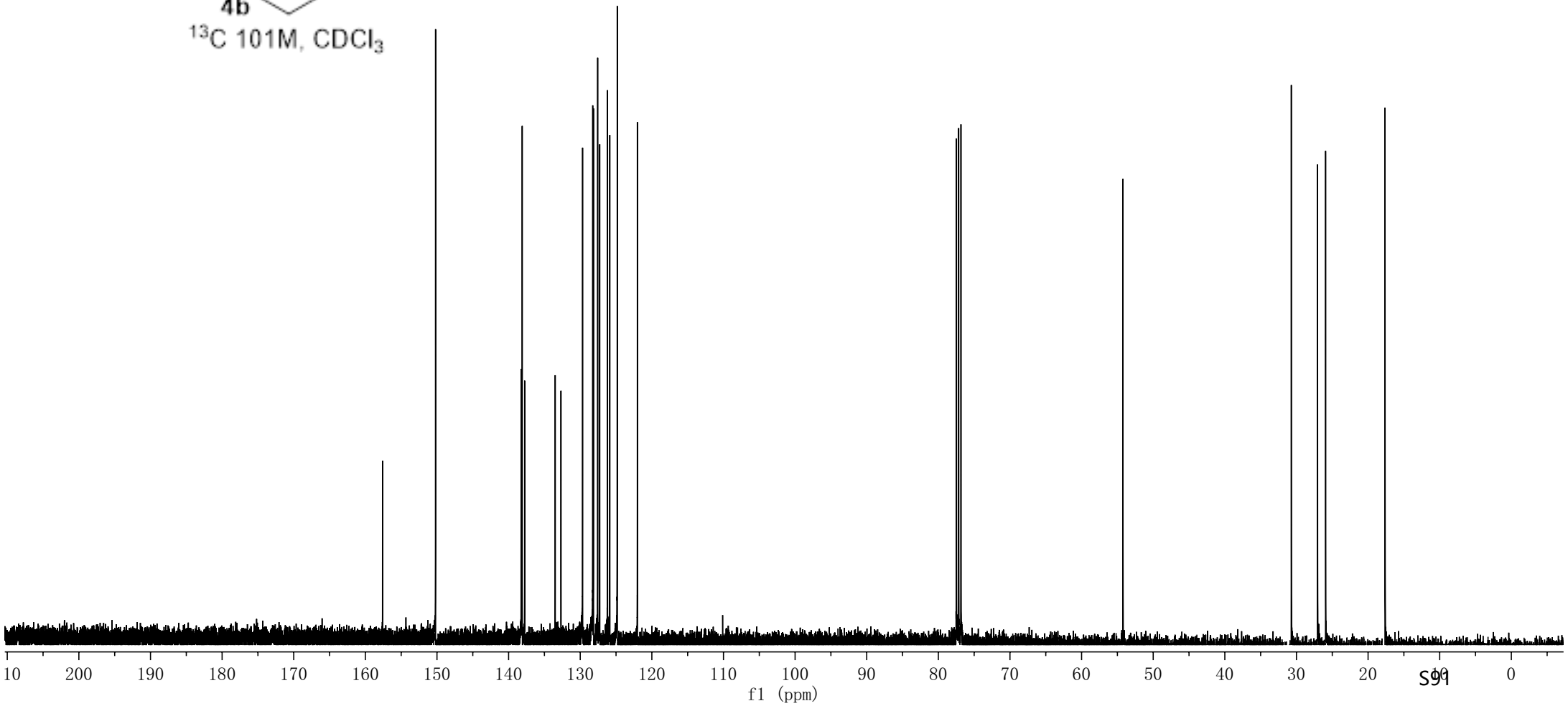
zwjiao-D823-C
zwjiao-D823-C

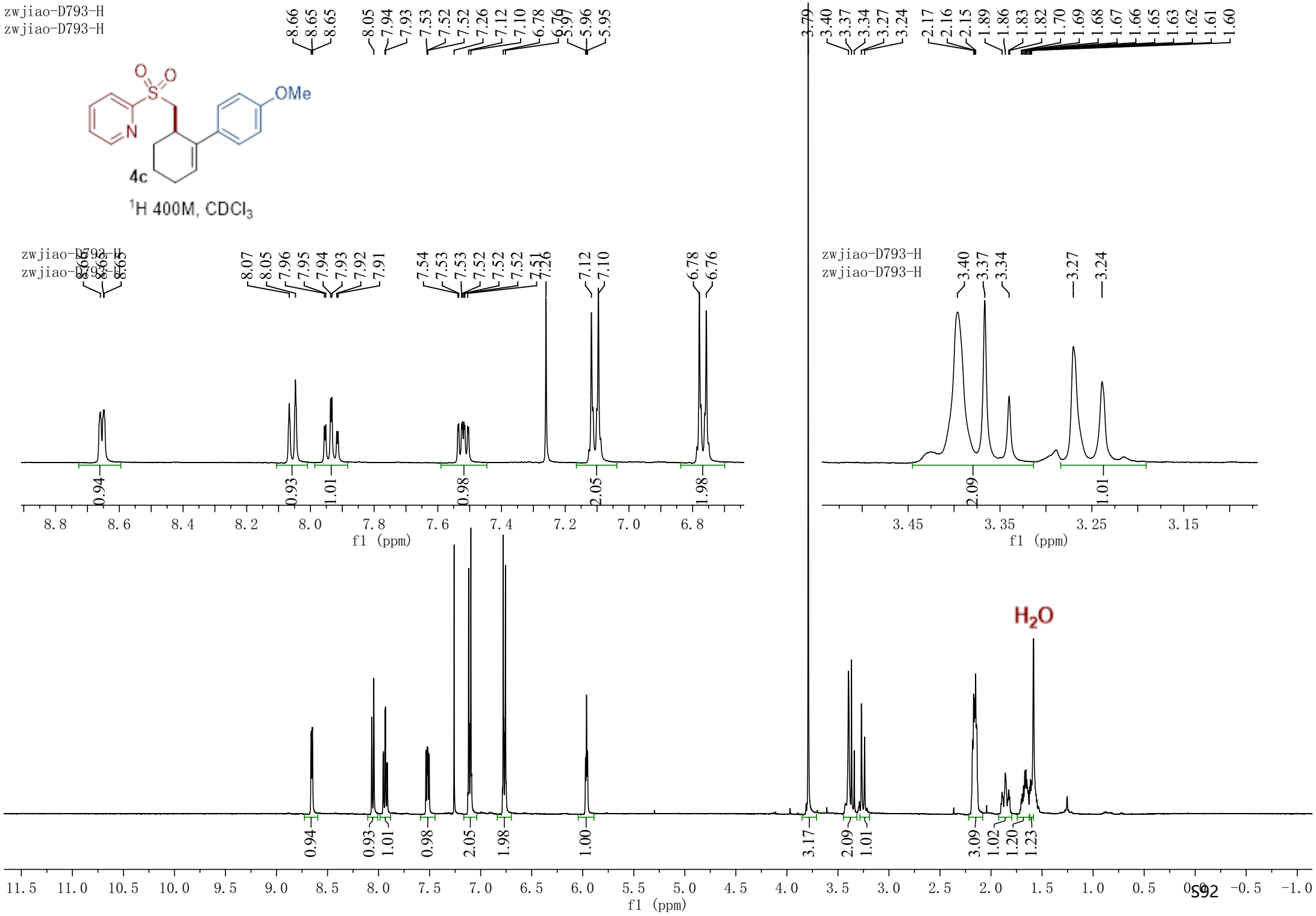
157.60
150.20
138.25
138.10
137.76
133.49
132.69
129.67
128.26
128.15
127.56
127.28
126.19
125.87
124.83
124.82
122.02
77.48
77.16
76.84
54.23
30.72
27.06
25.93
17.63



4b

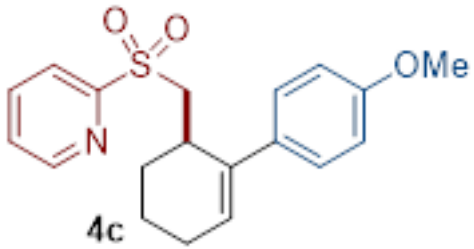
^{13}C 101M, $CDCl_3$




zwjiao-D793-H
zwjiao-D793-H
4c
^{1}H 400M, $CDCl_3$
H$_2$O
f1 (ppm)

zwjiao-D793-C
zwjiao-D793-C

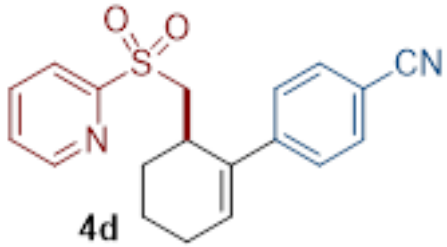
158.91
157.84
150.31
138.22
137.66
132.88
127.67
127.32
122.18
113.99
77.48
77.16
76.84
55.41
54.21
30.69
26.95
25.81
17.59



4c

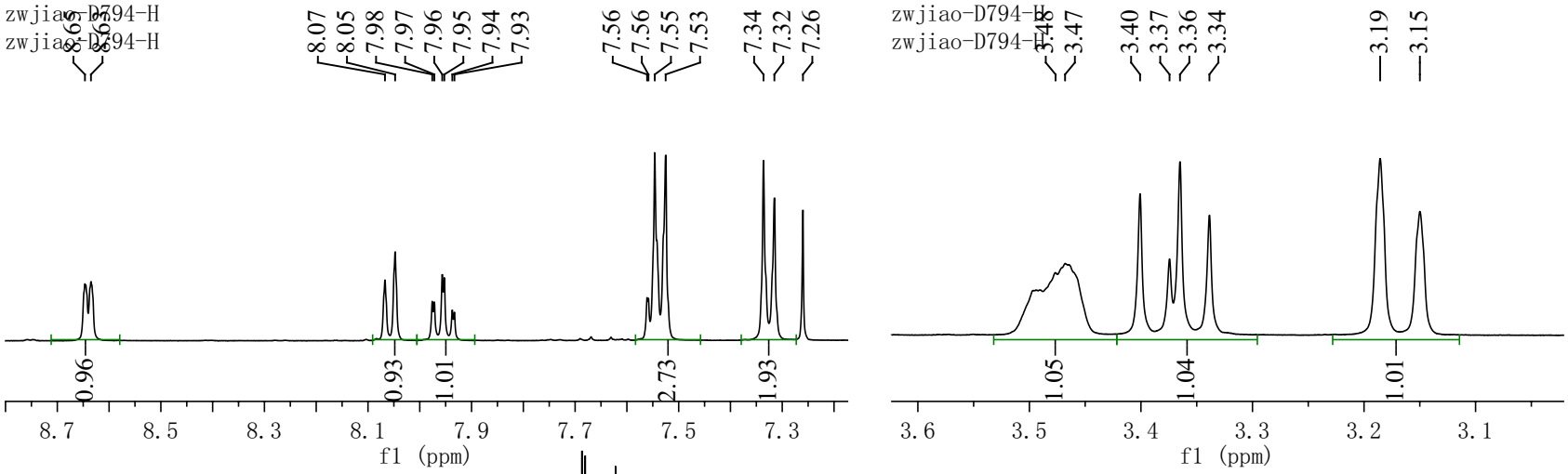
^{13}C 101M, $CDCl_3$

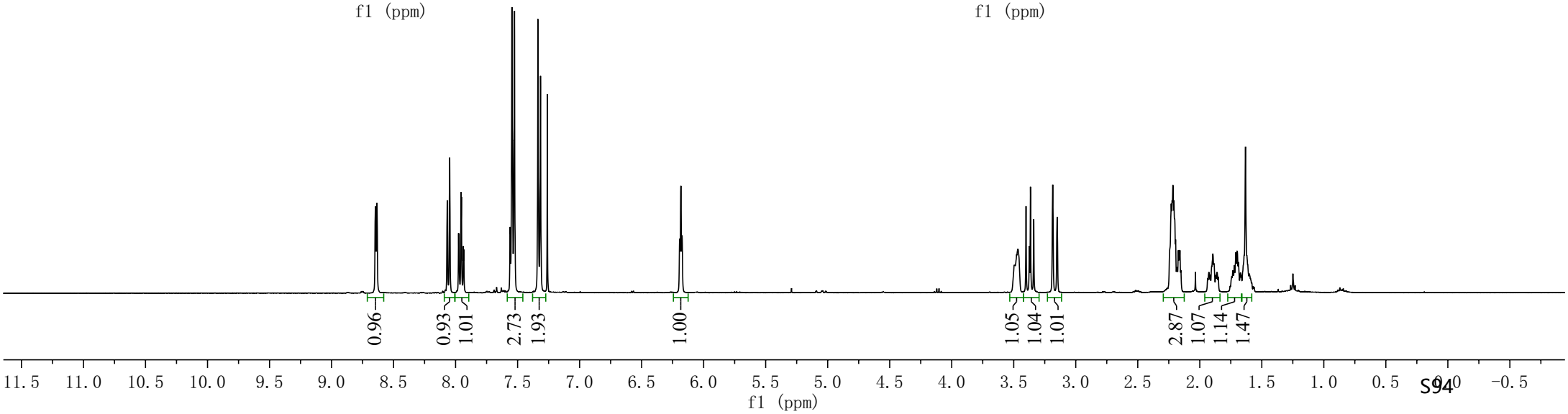
zwjiao-D794-H
zwjiao-D794-H



4d

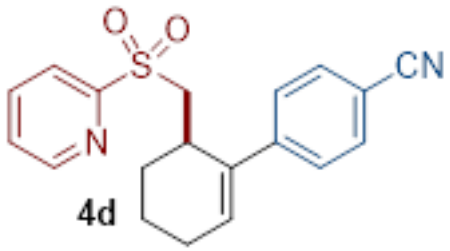
^{1}H 400M, $CDCl_3$





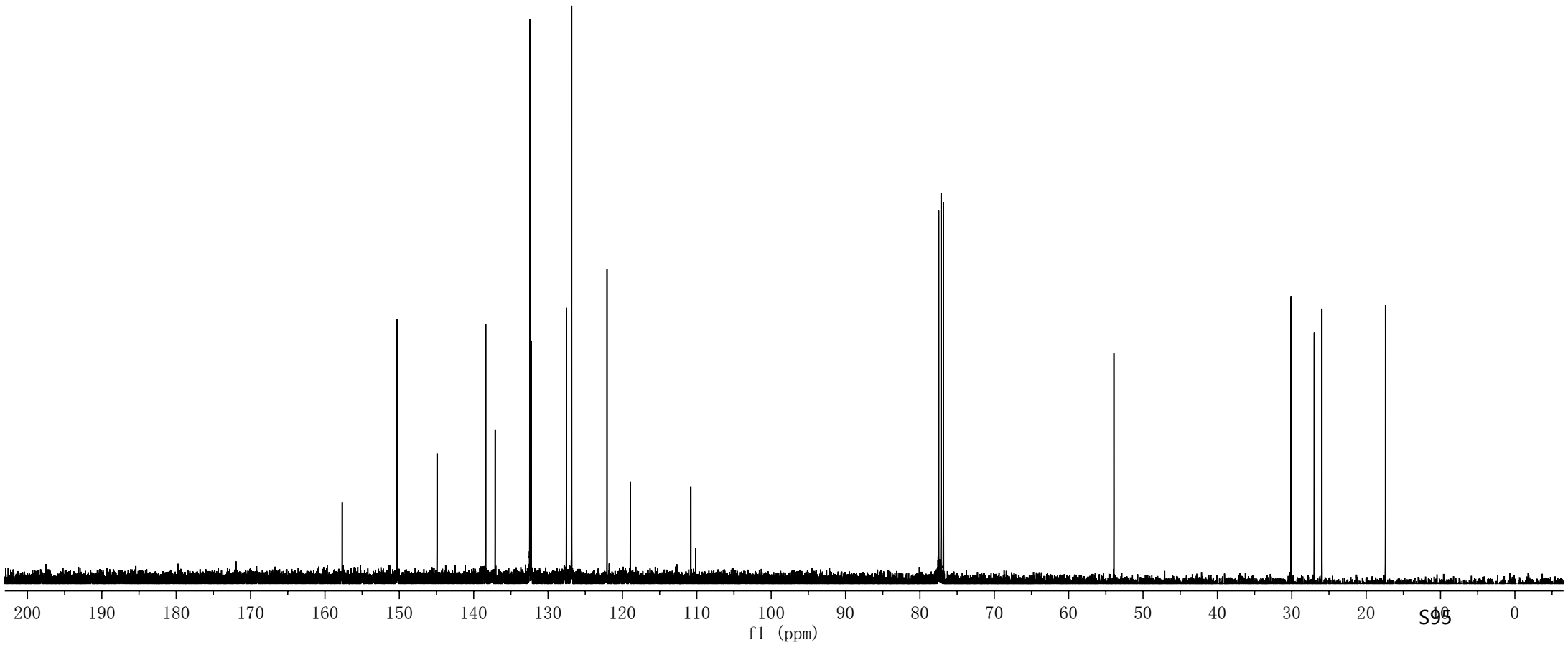
zwjiao-D794-C-1
zwjiao-D794-C

157.68
150.28
144.93
138.38
137.12
132.46
132.27
127.54
126.82
122.07
118.95
110.79
77.48
77.16
76.84
53.91
30.10
26.98
25.94
17.40

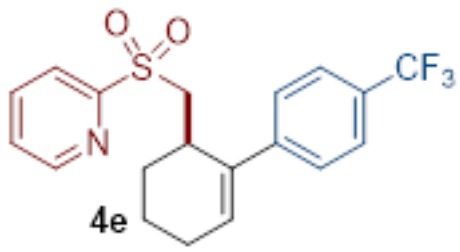


4d

^{13}C 101M, $CDCl_3$

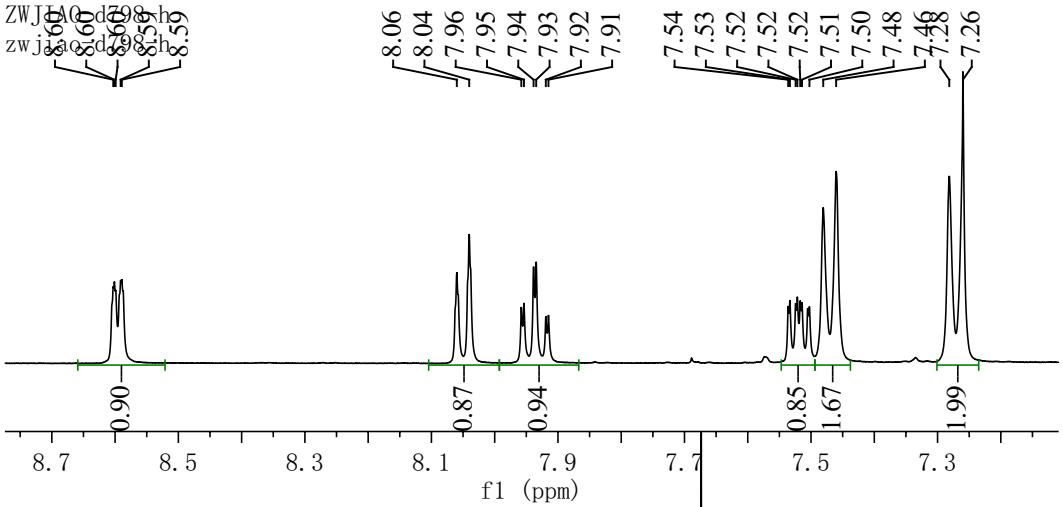


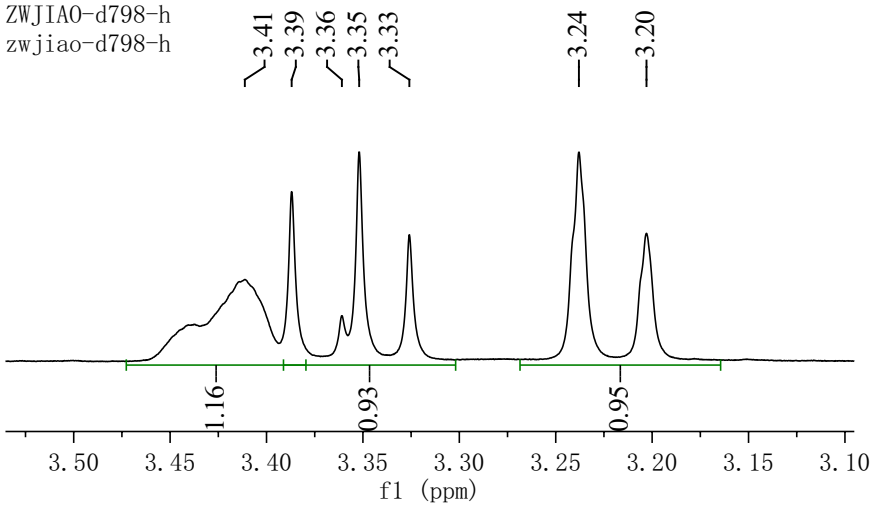
ZWJIAO-d798-h
zwjiao-d798-h

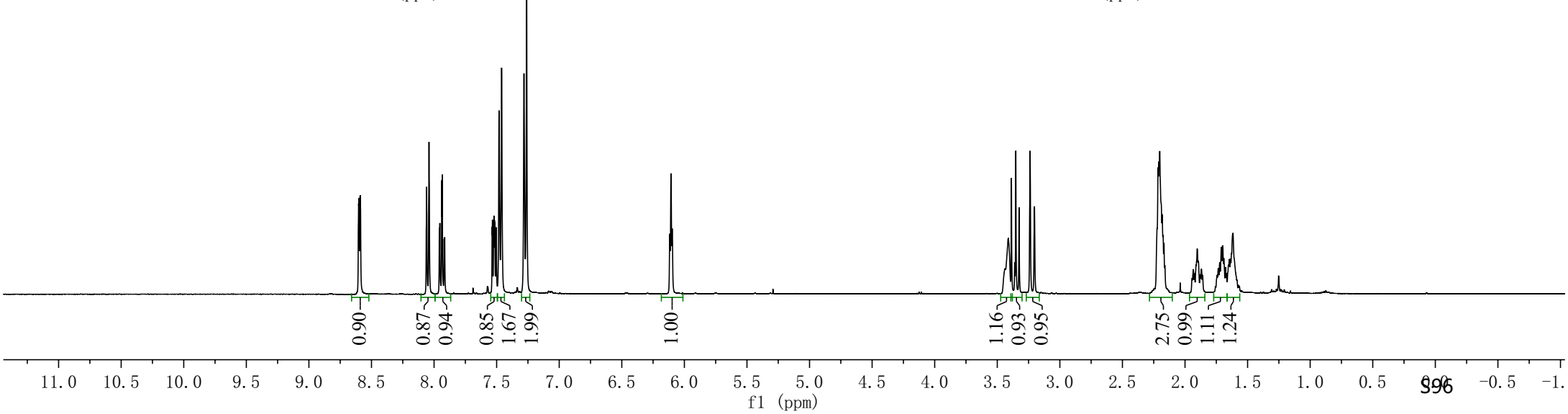


4e

^{1}H 400M, $CDCl_3$

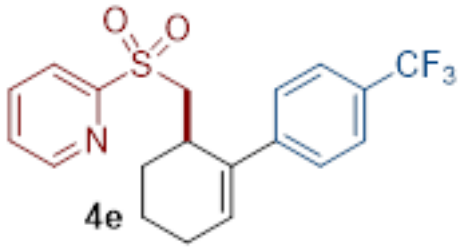






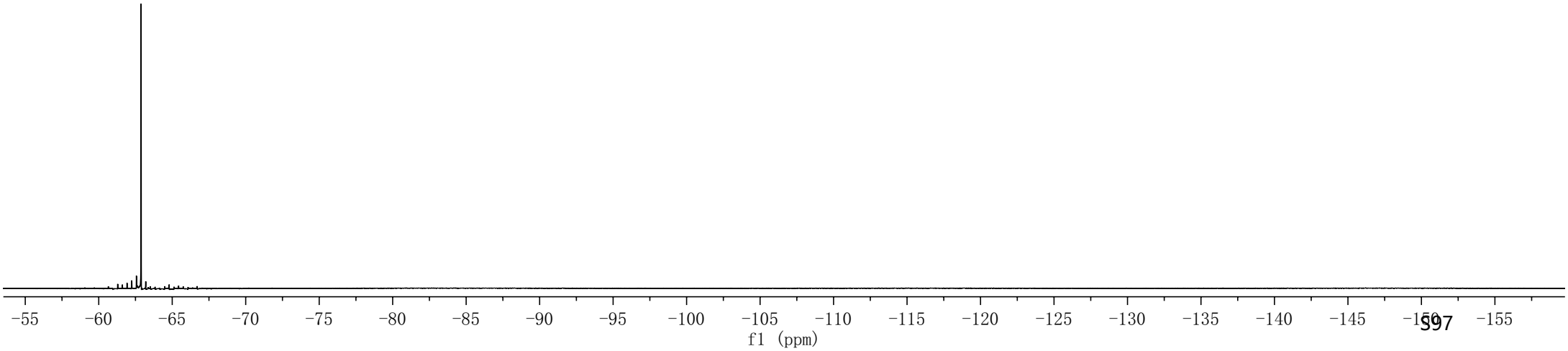
zwjiao-D798-F
zwjiao-D798-F

-62.88



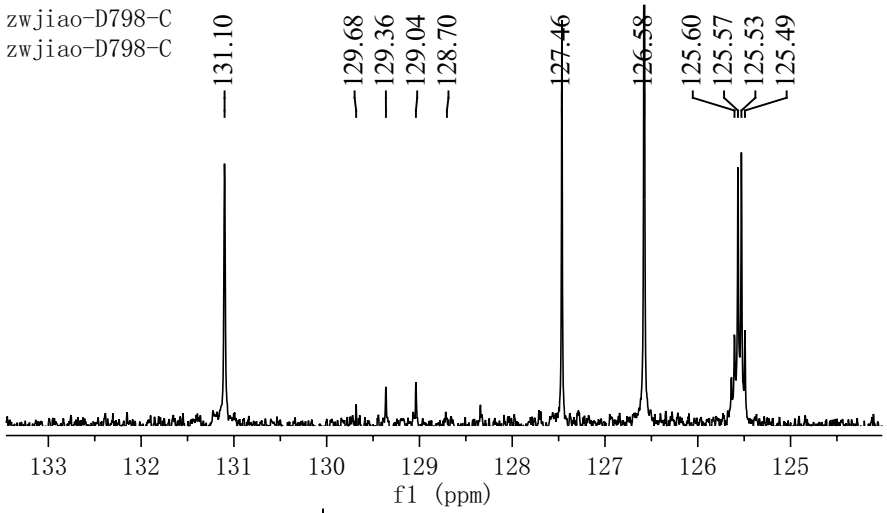
4e

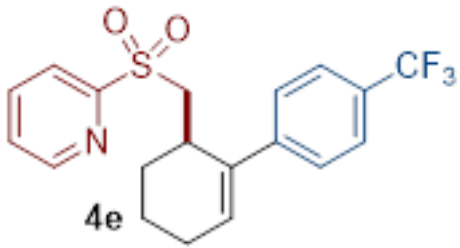
^{19}F 376.6M, $CDCl_3$



zwjiao-D798-C
zwjiao-D798-C

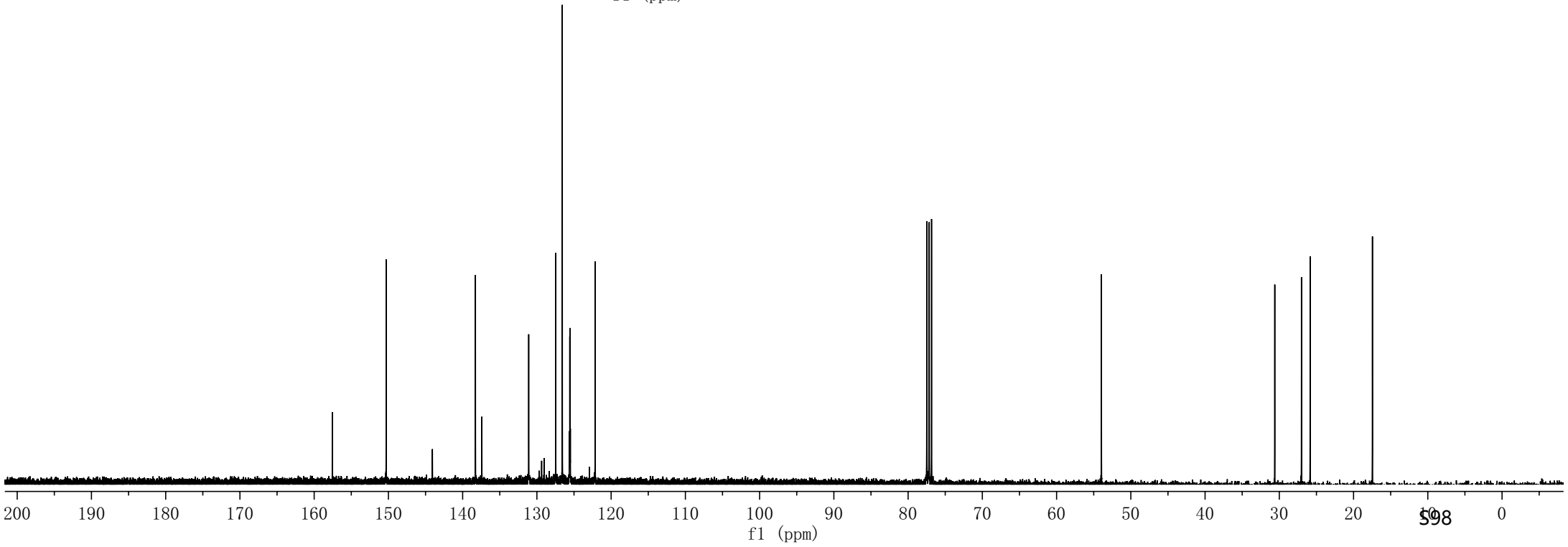
157.56 150.30 144.08 138.28 137.42 131.10 129.68 129.36 129.04 128.70 127.46 126.58 125.60 125.57 125.53 125.49 122.15 77.48 77.16 76.84 53.96 30.61 27.02 25.84 17.46

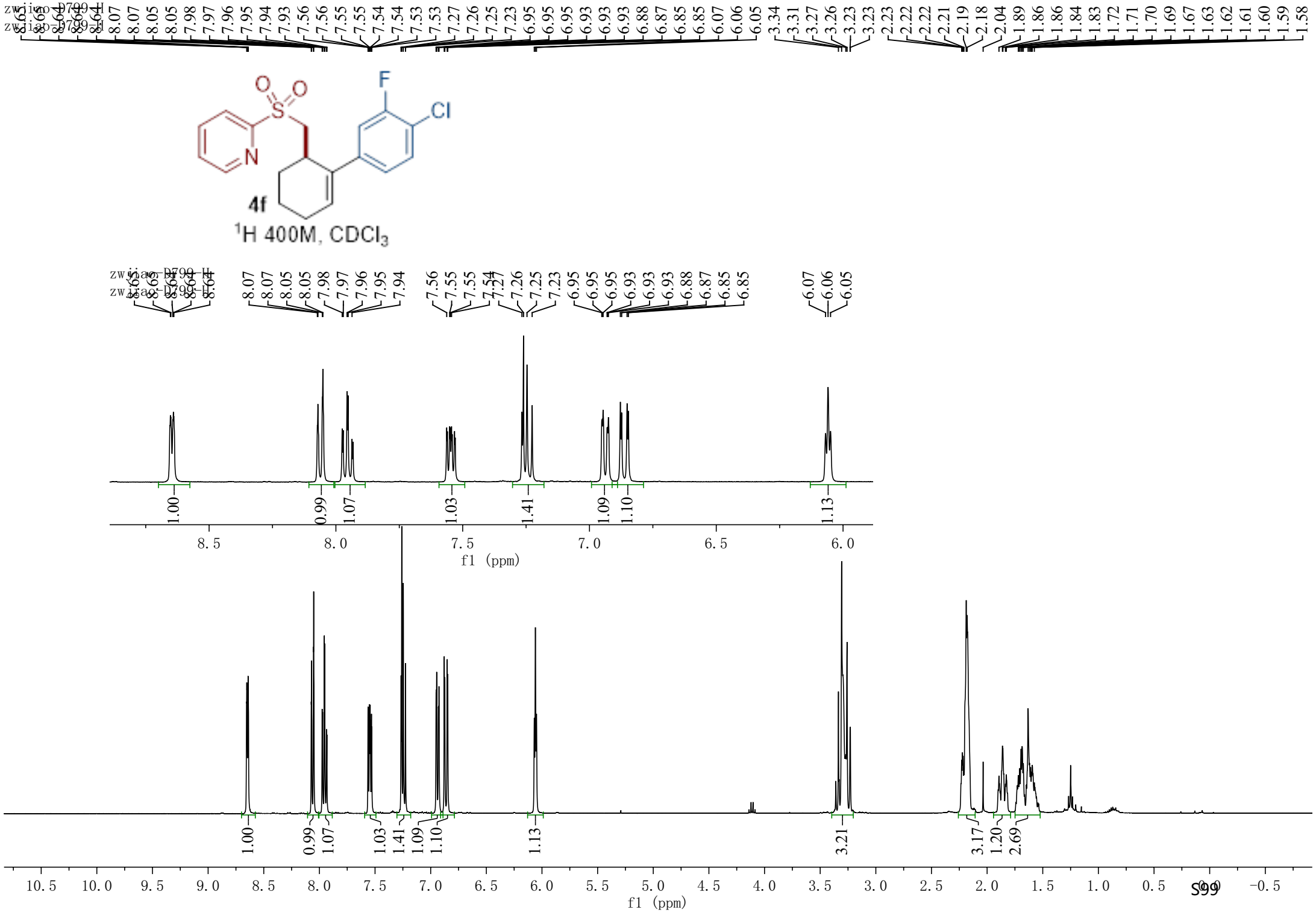




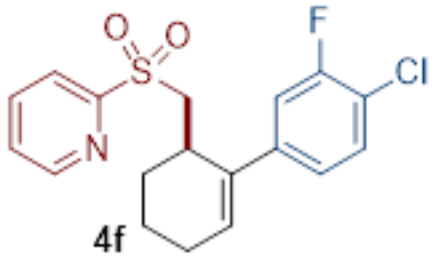
4e

^{13}C 101M, $CDCl_3$




zwjiao-D799-H
zwjiao-D799-H
8.07 8.07 8.05 8.05 7.98 7.97 7.96 7.95 7.94 7.93 7.56 7.56 7.55 7.55 7.54 7.54 7.53 7.53 7.27 7.26 7.25 7.23 6.95 6.95 6.95 6.93 6.93 6.93 6.88 6.87 6.85 6.85 6.07 6.06 6.05 3.34 3.31 3.27 3.26 3.23 3.23 2.23 2.22 2.22 2.21 2.19 2.18 2.04 1.89 1.86 1.86 1.84 1.83 1.72 1.71 1.70 1.69 1.67 1.63 1.62 1.61 1.60 1.59 1.58
O
O
S
N
F
Cl
4f
1H 400M, CDCl3
zwjiao-D799-H
zwjiao-D799-H
8.07 8.07 8.05 8.05 7.98 7.97 7.96 7.95 7.94 7.56 7.55 7.55 7.54 7.27 7.26 7.25 7.23 6.95 6.95 6.95 6.93 6.93 6.93 6.88 6.87 6.85 6.85 6.07 6.06 6.05
1.00 0.99 1.07 1.03 1.41 1.09 1.10 1.13
8.5 8.0 7.5 7.0 6.5 6.0
f1 (ppm)
1.00 0.99 1.07 1.03 1.41 1.09 1.10 1.13 3.21 3.17 1.20 2.69
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

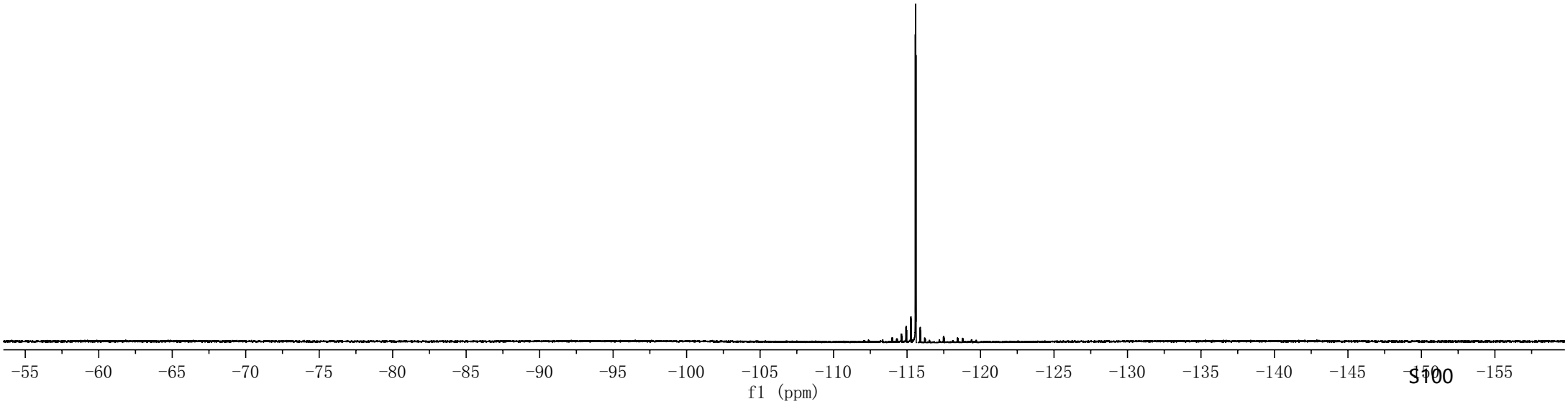
zwjiao-D799-F
zwjiao-D799-F



4f

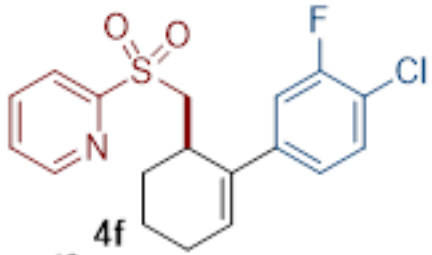
^{19}F 376.6M, $CDCl_3$

-115.58



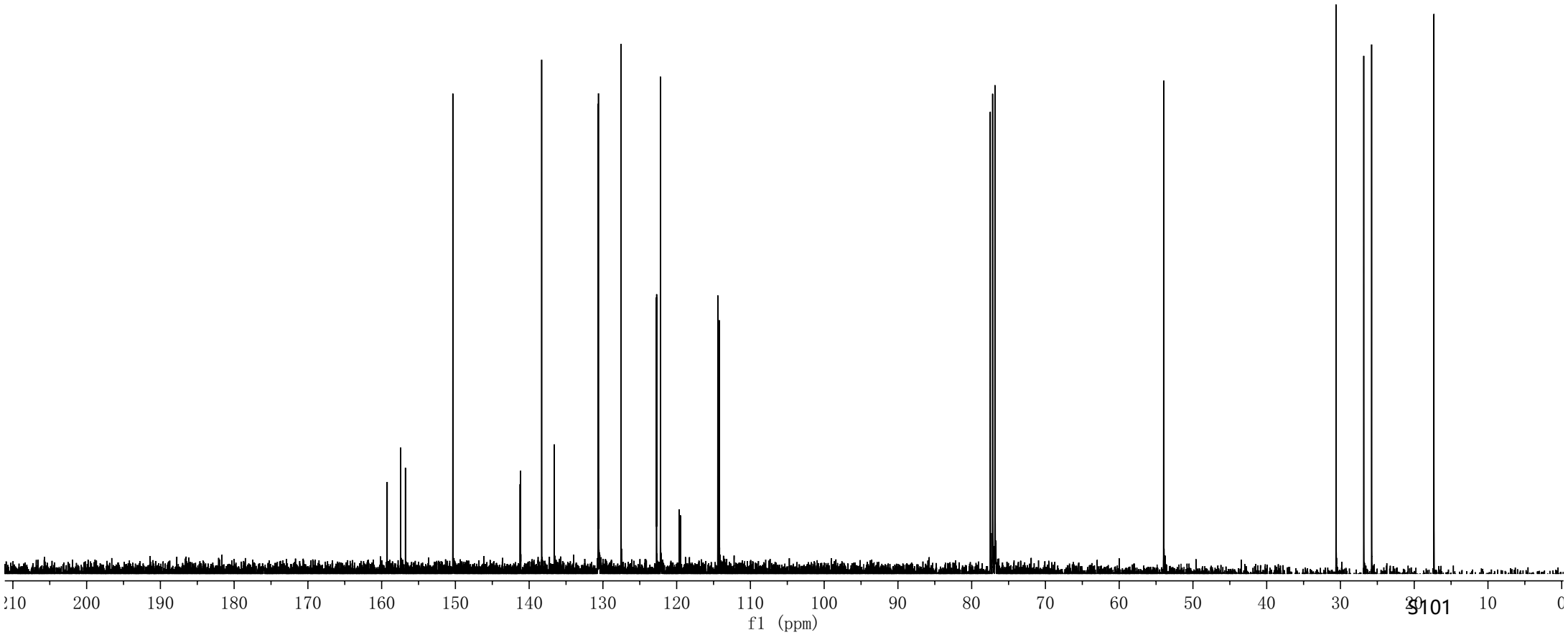
zwjiao-D799-C
zwjiao-D799-C

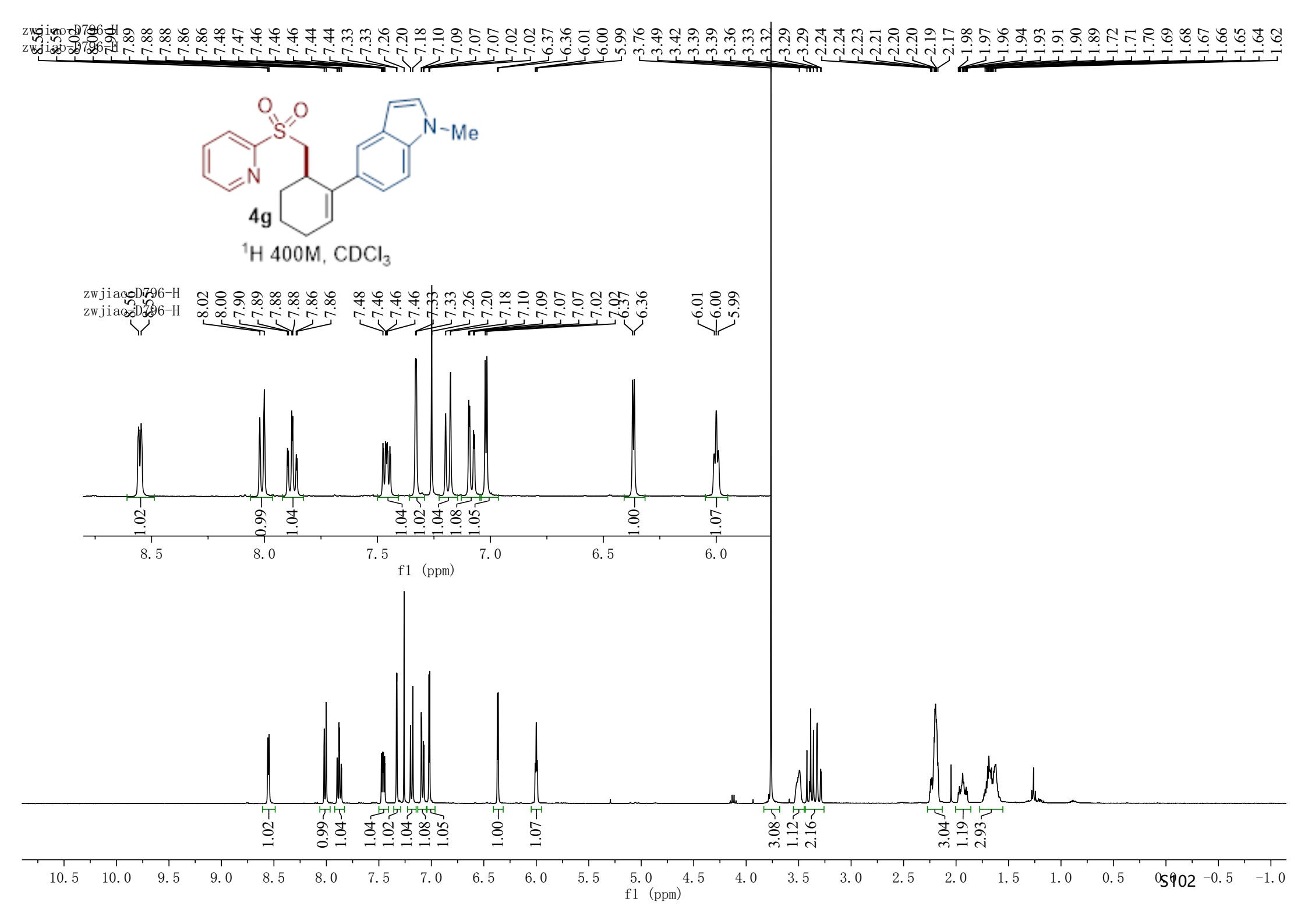
159.25
157.43
156.78
150.35
141.23
141.17
138.30
136.61
136.59
130.65
130.61
127.54
122.75
122.71
122.20
119.66
119.49
114.43
114.21
77.48
77.16
76.84
53.97
30.59
26.84
25.77
17.33



4f

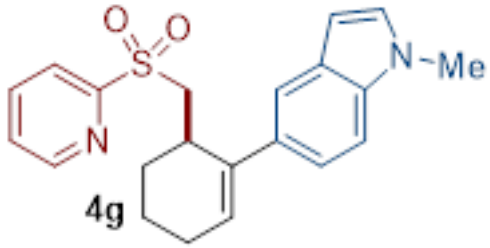
^{13}C 101M, $CDCl_3$




zwjiao-D796-H
zwjiao-D796-H
8.56 8.55 8.02 8.00 7.90 7.89 7.88 7.88 7.86 7.86 7.48 7.47 7.46 7.46 7.46 7.44 7.44 7.33 7.33 7.26 7.20 7.18 7.10 7.09 7.07 7.07 7.02 7.02 6.37 6.36 6.01 6.00 5.99 3.76 3.49 3.42 3.39 3.39 3.36 3.33 3.32 3.29 3.29 2.24 2.24 2.23 2.21 2.20 2.20 2.19 2.17 1.98 1.97 1.96 1.94 1.93 1.91 1.90 1.89 1.72 1.71 1.70 1.69 1.68 1.67 1.66 1.65 1.64 1.62
N-Me
4g
1H 400M, CDCl3
f1 (ppm)
S102

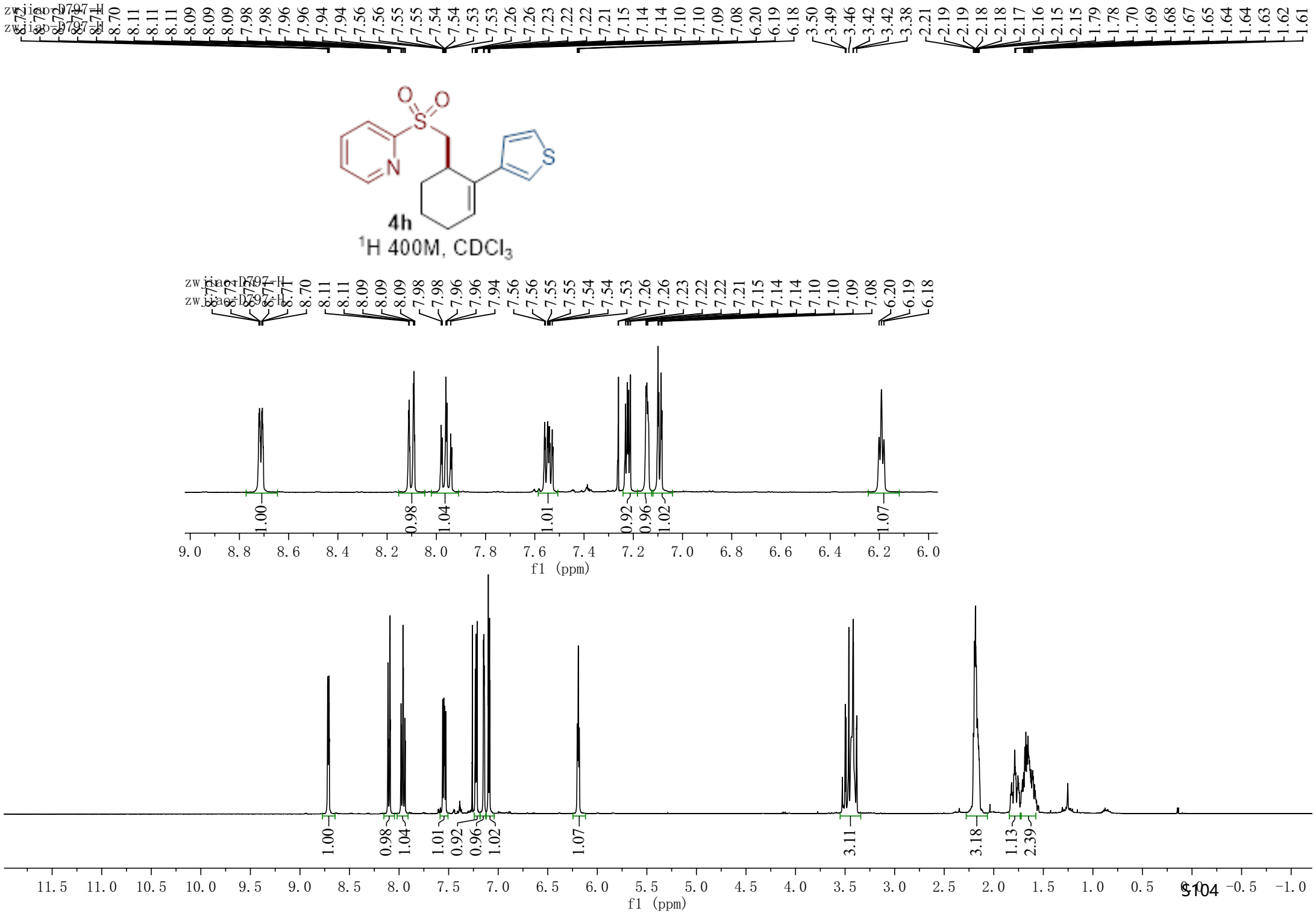
zwjiao-D796-C
zwjiao-D796-C

157.71
150.22
139.20
138.06
136.22
132.05
129.28
128.57
127.64
127.20
122.12
120.69
118.50
109.25
101.28
77.48
77.16
76.84
54.42
32.99
31.38
27.08
25.92
17.80



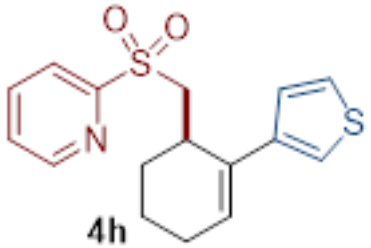
4g

^{13}C 101M, $CDCl_3$


zw.jiao-D797-H
8.72 8.71 8.70 8.11 8.11 8.09 8.09 8.09 7.98 7.96 7.94 7.56 7.55 7.54 7.53 7.26 7.23 7.22 7.21 7.15 7.14 7.10 7.09 7.08 6.20 6.19 6.18 3.50 3.49 3.46 3.42 3.38 2.21 2.19 2.18 2.17 2.16 2.15 1.79 1.78 1.70 1.69 1.68 1.67 1.65 1.64 1.63 1.62 1.61
O
O
S
N
S
4h
1H 400M, CDCl3
1.00 0.98 1.04 1.01 0.92 0.96 1.02 1.07
f1 (ppm)
1.00 0.98 1.04 1.01 0.92 0.96 1.02 1.07 3.11 3.18 1.13 2.39
f1 (ppm)

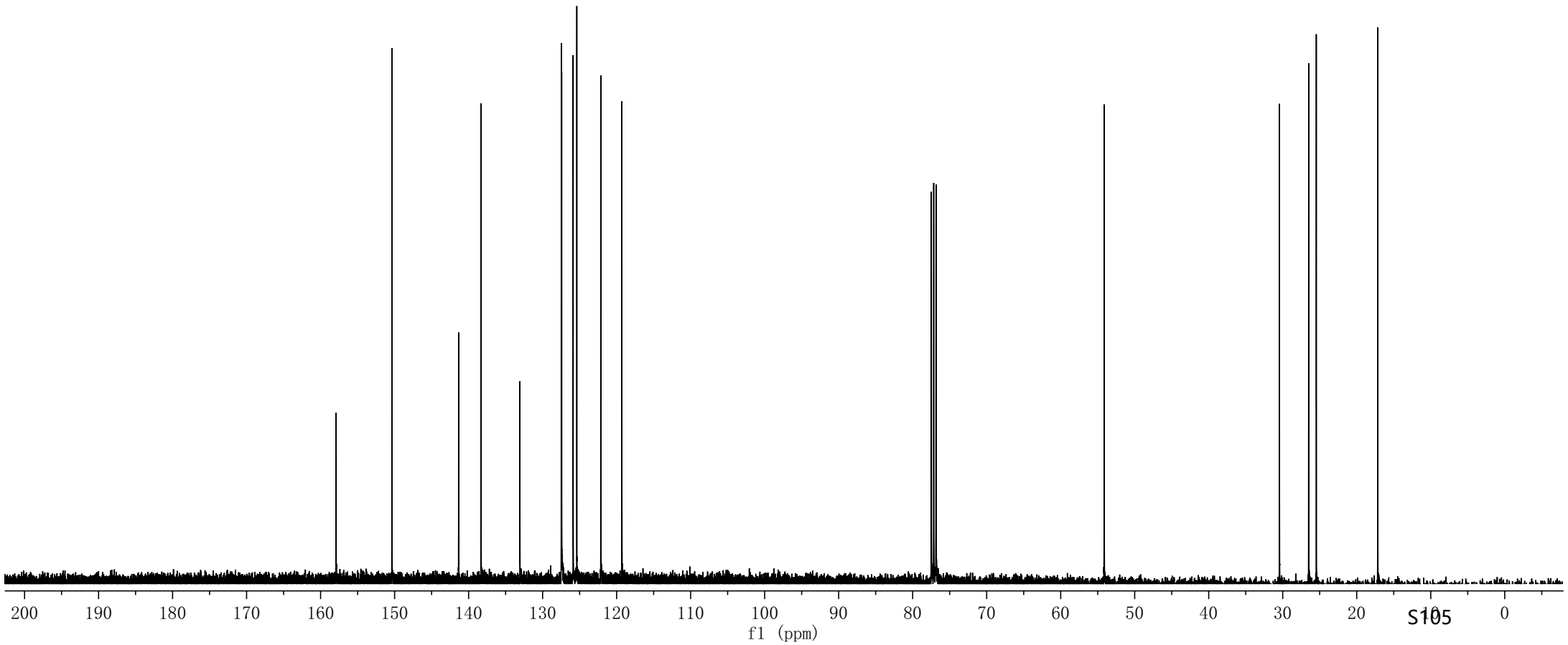
zwjiao-D797-C
zwjiao-D797-H

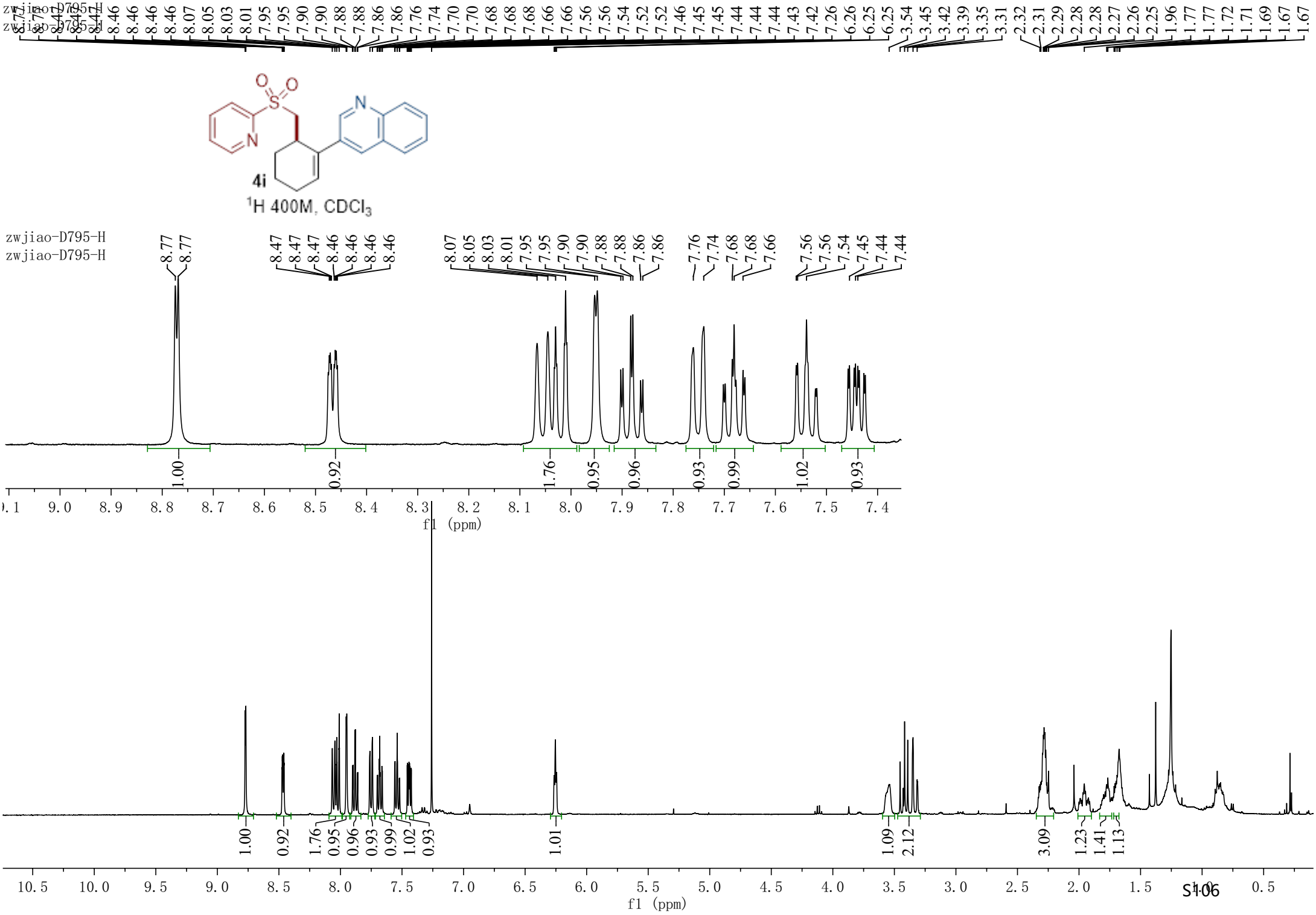
157.90
150.36
141.35
138.33
133.07
127.48
127.43
125.88
125.38
122.14
119.29
77.48
77.16
76.84
54.12
30.44
26.50
25.46
17.16

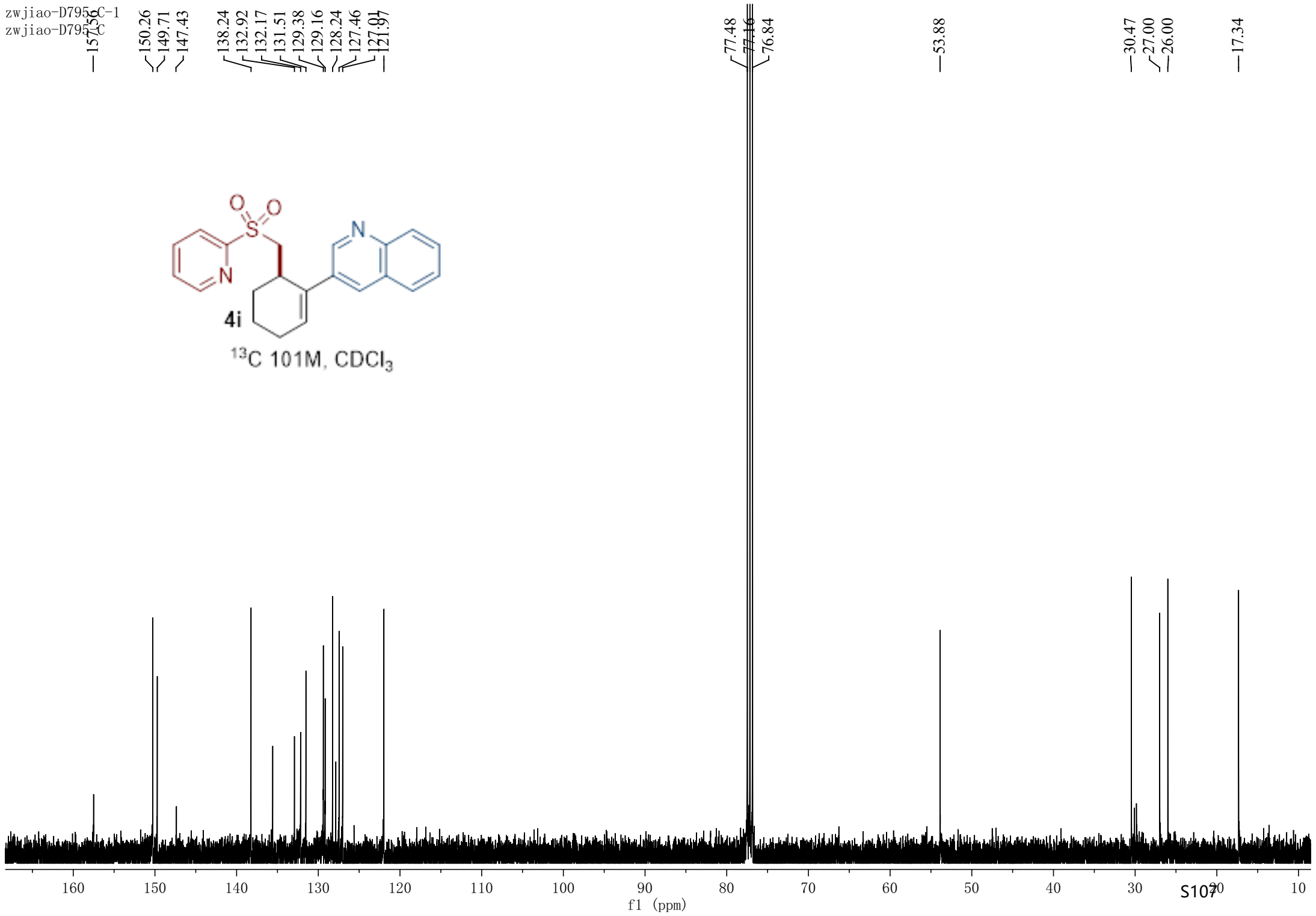


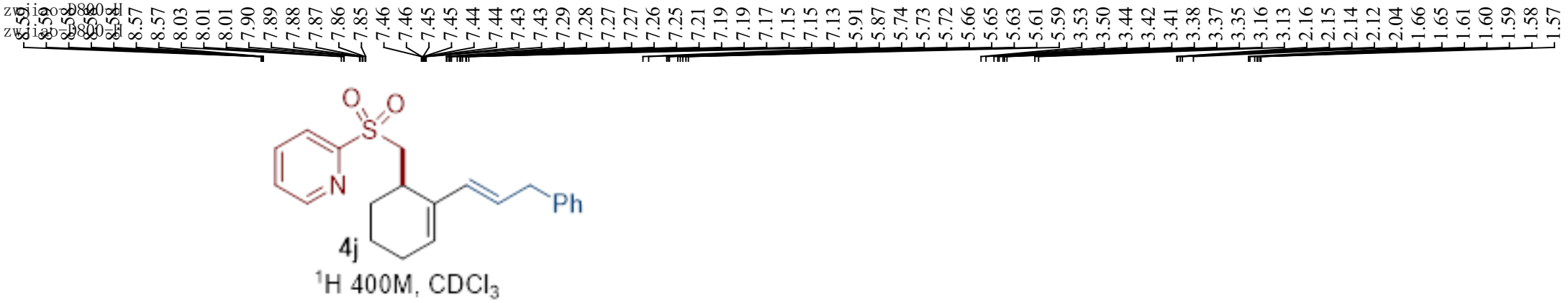
4h

^{13}C 101M, $CDCl_3$



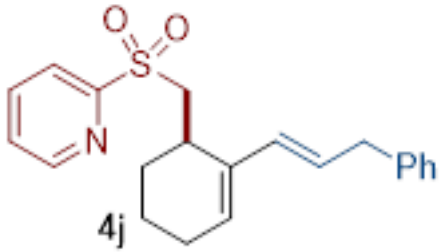

zwjiao-D795-H
zwjiao-D795-H
4i
^{1}H 400M, $CDCl_3$
f1 (ppm)
f1 (ppm)


zwjiao-D795-C-1
zwjiao-D795-C
157.56
150.26
149.71
147.43
138.24
132.92
132.17
131.51
129.38
129.16
128.24
127.46
127.01
121.97
77.48
77.16
76.84
53.88
30.47
27.00
26.00
17.34
4i
13C 101M, CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


zwjiao-D800-H
zwjiao-D800-H
8.59 8.58 8.57 8.57 8.57 8.03 8.01 8.01 7.90 7.89 7.88 7.87 7.86 7.85 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.29 7.28 7.27 7.27 7.26 7.25 7.21 7.19 7.19 7.17 7.15 7.15 7.13 5.91 5.87 5.74 5.73 5.72 5.66 5.65 5.63 5.61 5.59 3.53 3.50 3.44 3.42 3.41 3.38 3.37 3.35 3.16 3.13 2.16 2.15 2.14 2.12 2.04 1.66 1.65 1.61 1.60 1.59 1.58 1.57
O
O
S
N
Ph
4j
1H 400M, CDCl3
zwjiao-D800-H
zwjiao-D800-H
8.59 8.58 8.57 8.57 8.57 8.03 8.01 8.01 7.90 7.89 7.88 7.87 7.86 7.85 7.46 7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.29 7.28 7.27 7.27 7.26 7.25 7.21 7.19 7.15 7.15 7.13
1.00 0.98 1.08 1.06 2.31 1.00 1.89
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
f1 (ppm)
zwjiao-D800-H
zwjiao-D800-H
5.91 5.87 5.74 5.73 5.72 5.66 5.65 5.63 5.61 5.59
1.15 1.08 1.19
6.0 5.9 5.8 5.7 5.6 5.5
f1 (ppm)
1.00 0.98 1.08 1.06 2.31 1.00 1.89 1.15 1.08 1.19 1.10 1.14 1.88 1.13 3.05 3.73
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

zwjiao-D800-C
zwjiao-D800-C

157.82
150.32
140.55
138.22
135.96
132.27
130.87
128.69
128.50
127.38
126.09
122.26
77.48
77.16
76.84
54.00
39.34
27.96
25.71
25.47
17.12

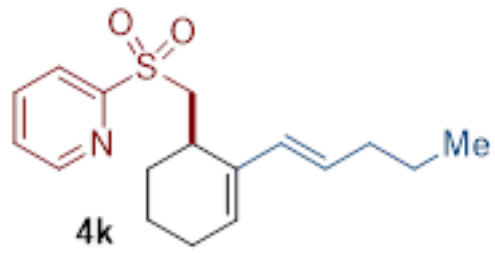


4j

^{13}C 101M, $CDCl_3$

f1 (ppm)

zwjiao-D864-H
zwjiao-D864-H

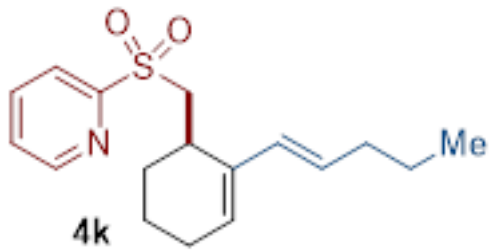


4k

^{1}H 400M, $CDCl_3$

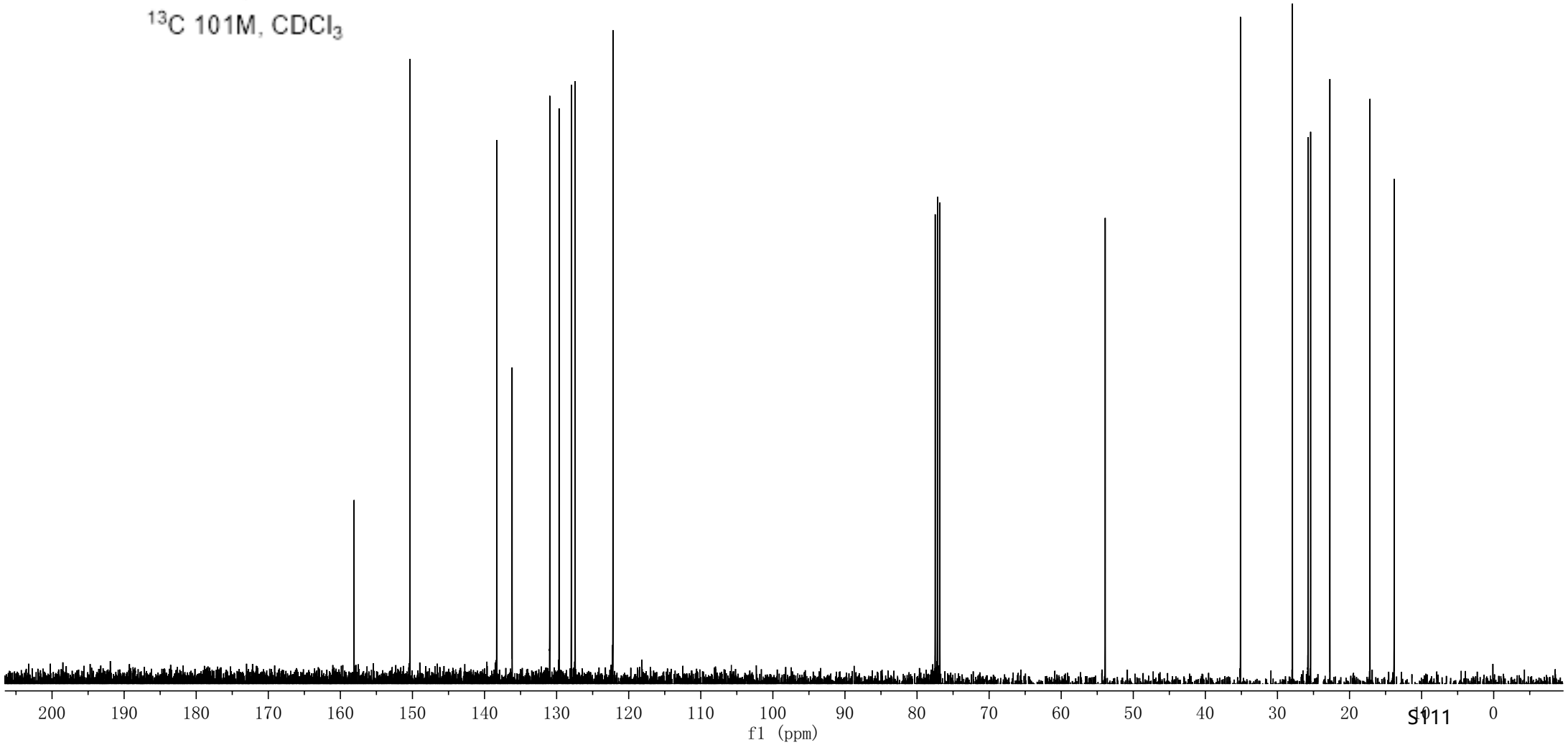
zwjiao-D864-C
zwjiao-D864-C

158.09
150.34
138.31
136.17
130.95
129.66
127.96
127.43
122.19
77.48
77.16
76.84
53.89
35.13
27.92
25.75
25.40
22.72
17.17
13.80

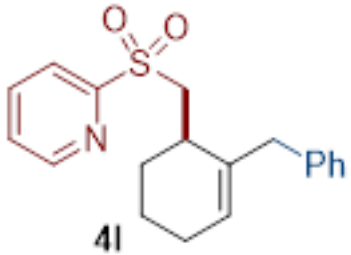


4k

^{13}C 101M, $CDCl_3$

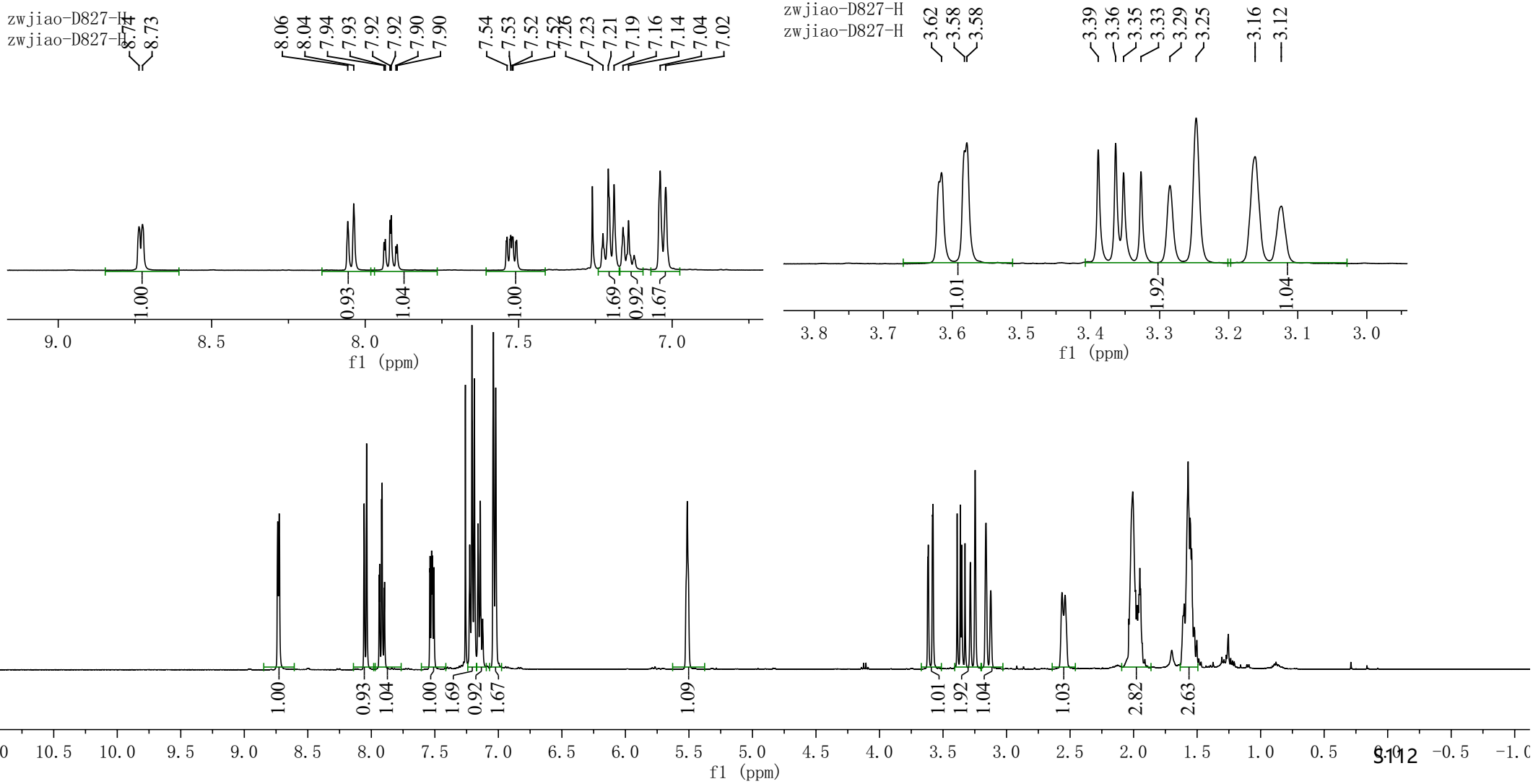


zwjiao-D827-H
zwjiao-D827-H



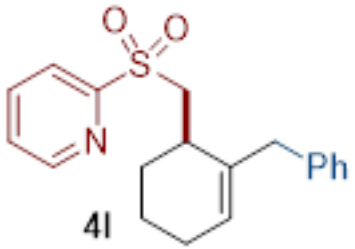
4l

^{1}H 400M, $CDCl_3$



zwjiao-D827-C
zwjiao-D827-C

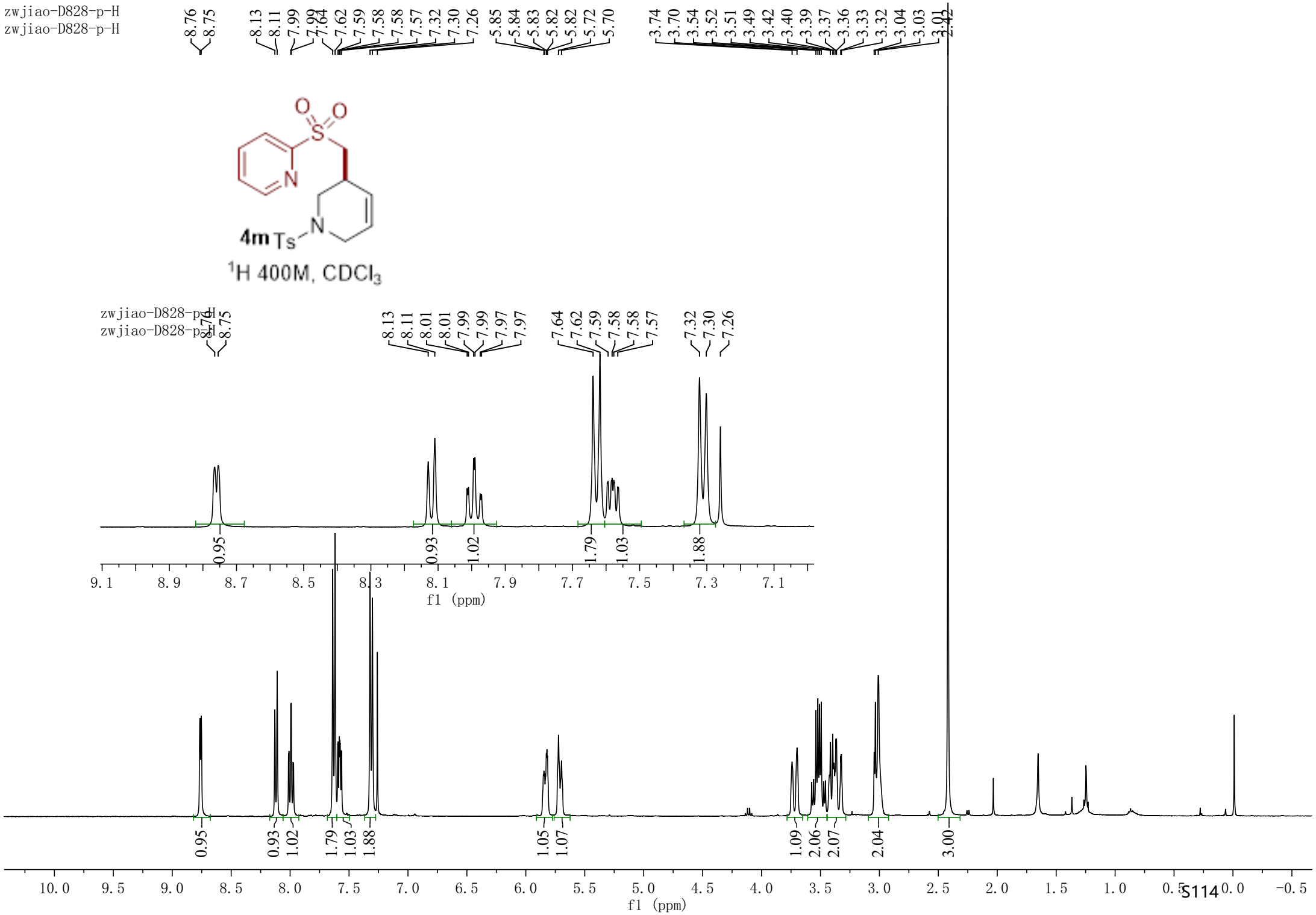
157.58
150.33
139.47
138.22
136.91
128.89
128.34
127.39
127.20
126.14
122.25
77.48
77.16
76.84
53.80
41.60
31.00
26.80
25.05
17.34



4l

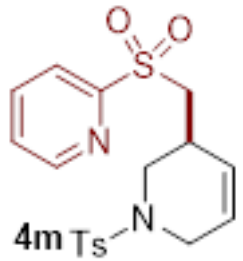
^{13}C 101M, $CDCl_3$

f1 (ppm)


zwjiao-D828-p-H
zwjiao-D828-p-H
4m Ts
^{1}H 400M, $CDCl_3$
f1 (ppm)
f1 (ppm)

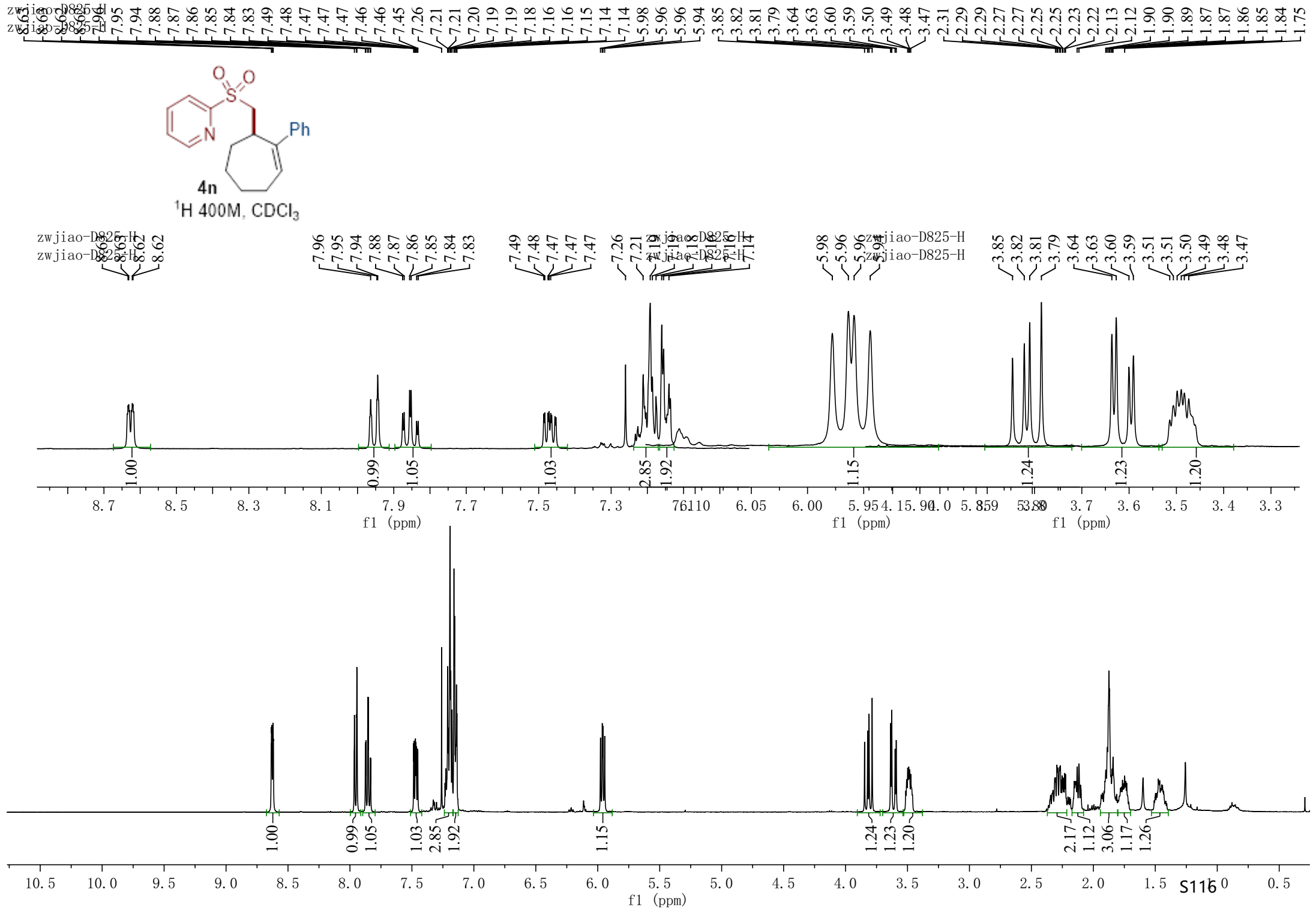
zwjiao-D828-p-C
zwjiao-D828-p-C

157.57
150.44
143.97
138.50
133.05
129.90
127.75
127.70
127.00
124.75
122.22
77.48
77.16
76.84
54.68
47.15
44.93
30.31
21.66



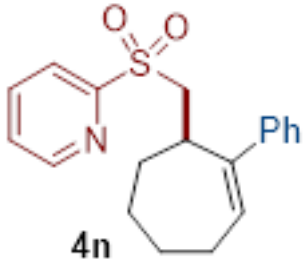
4m

^{13}C 101M, $CDCl_3$


4n
^{1}H 400M, CDCl$_3$
f1 (ppm)

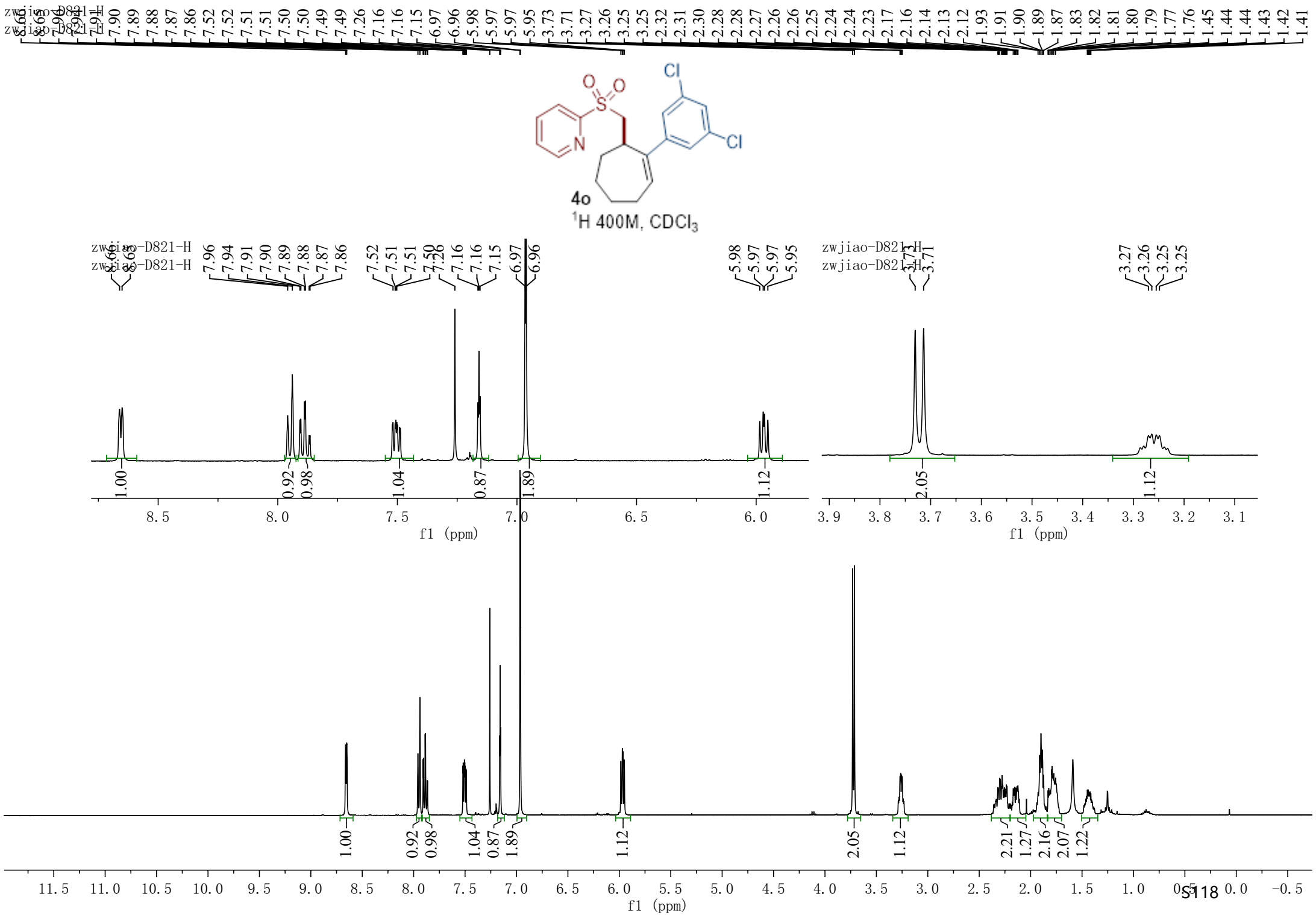
zwjiao-D825-C
zwjiao-d825-C

157.50
150.24
144.98
143.69
138.06
132.37
128.30
127.31
126.90
126.44
122.20
77.48
77.16
76.84
52.46
37.61
29.68
27.91
26.93
25.69



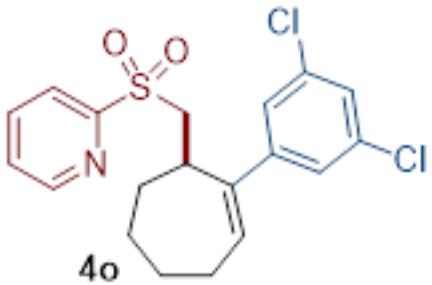
4n

^{13}C 101M, $CDCl_3$


4o
^{1}H 400M, $CDCl_3$
f1 (ppm)

zwjiao-D821-C
zwjiao-D821-C

157.03
150.31
146.87
143.03
138.09
134.74
134.67
127.54
126.84
125.08
122.24
77.48
77.16
76.84
52.28
37.59
29.79
27.93
26.68
25.57

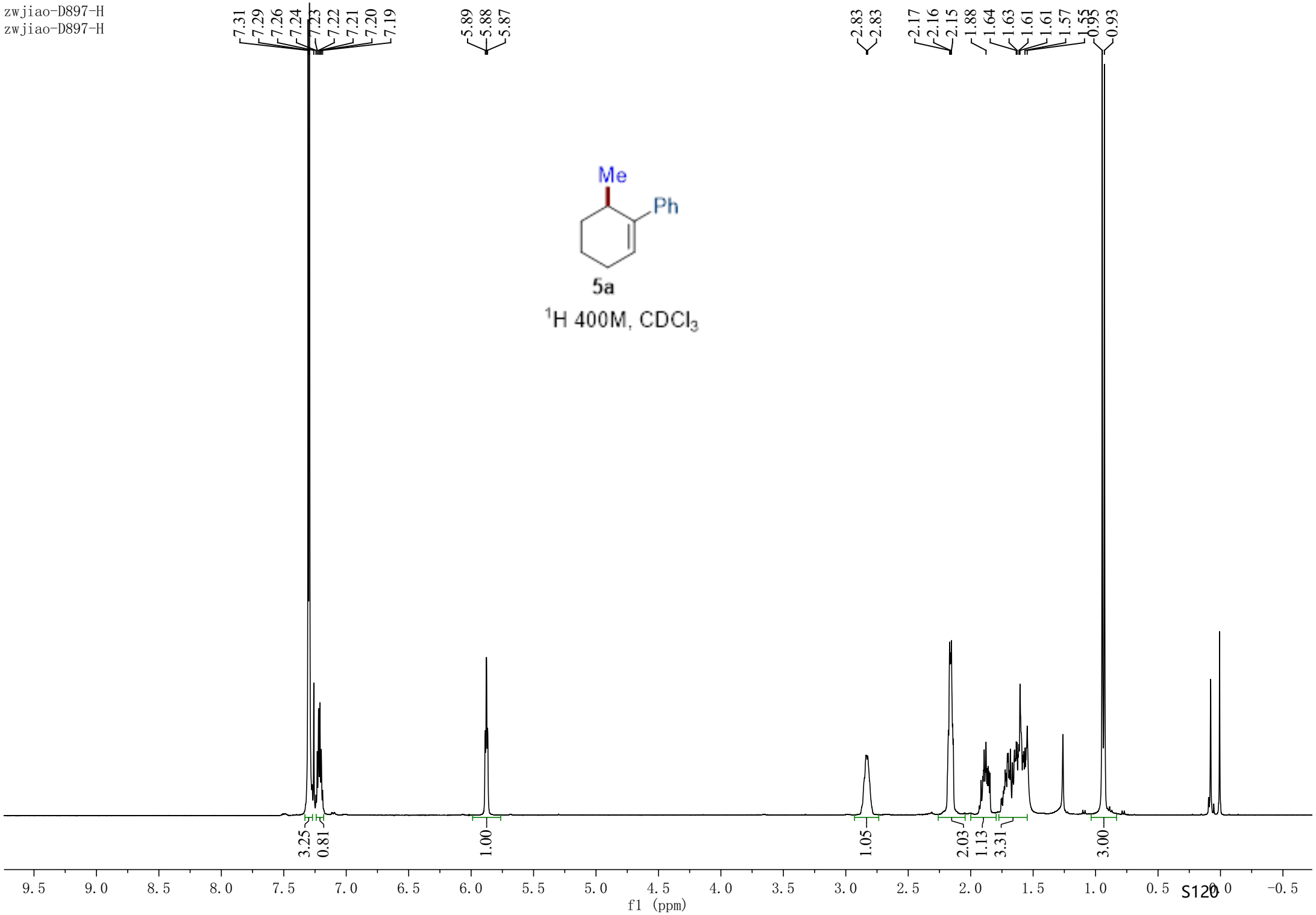


4o

^{13}C 101M, $CDCl_3$

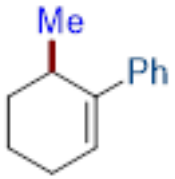
f1 (ppm)

zwjiao-D897-H
zwjiao-D897-H



zwjiao-D897-C
zwjiao-D897-C

143.06
142.89
128.24
126.49
126.37
125.60
77.48
77.16
76.84
31.20
30.58
26.38
20.34
19.02

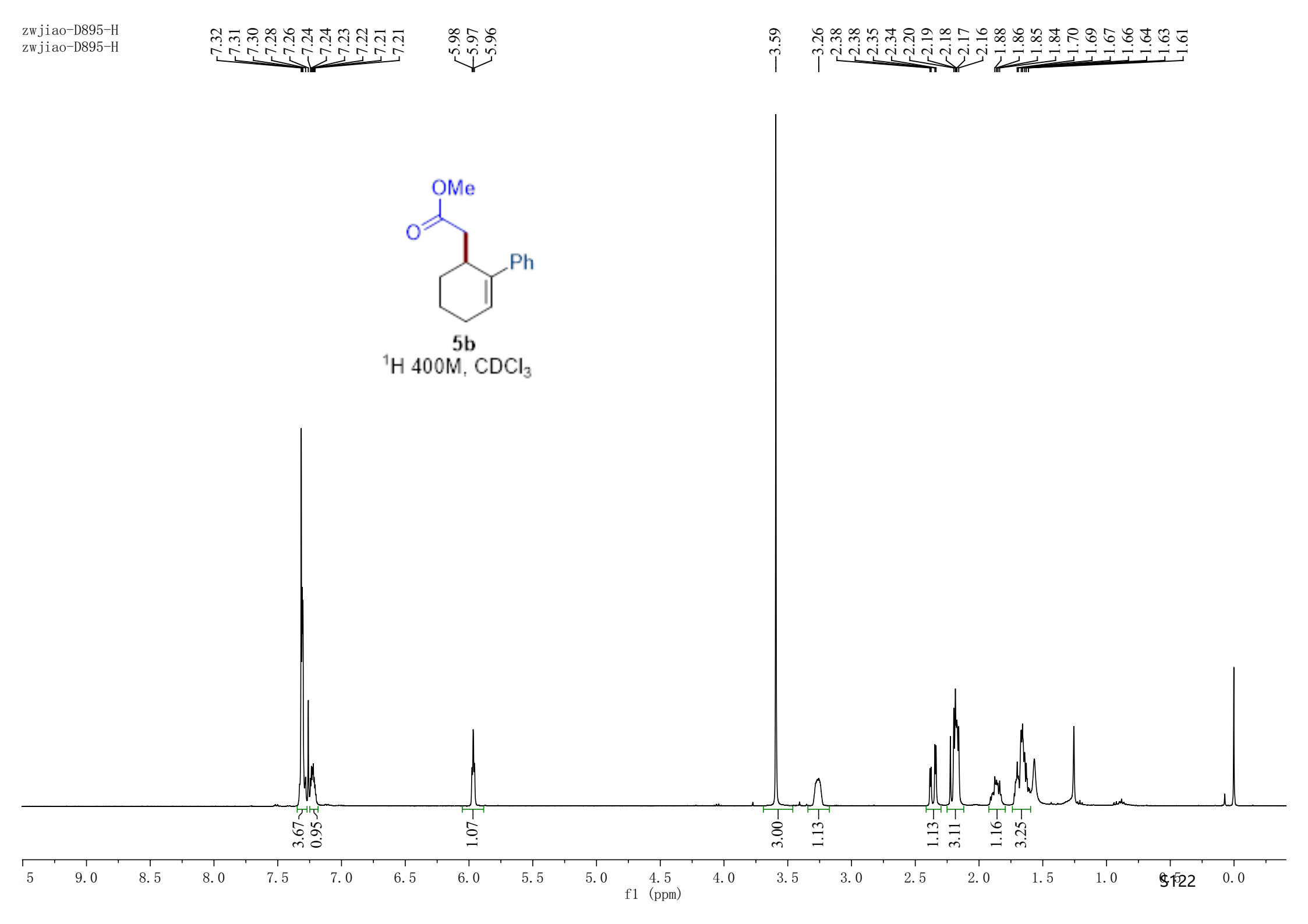


5a

^{13}C 101M, $CDCl_3$

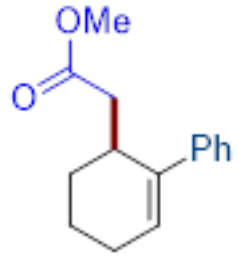
f1 (ppm)

zwjiao-D895-H
zwjiao-D895-H



zwjiao-D895-C
zwjiao-D895-C

173.68
141.75
140.30
128.48
127.47
126.95
126.42
77.48
77.16
76.84
51.58
38.44
32.77
27.89
26.15
18.41

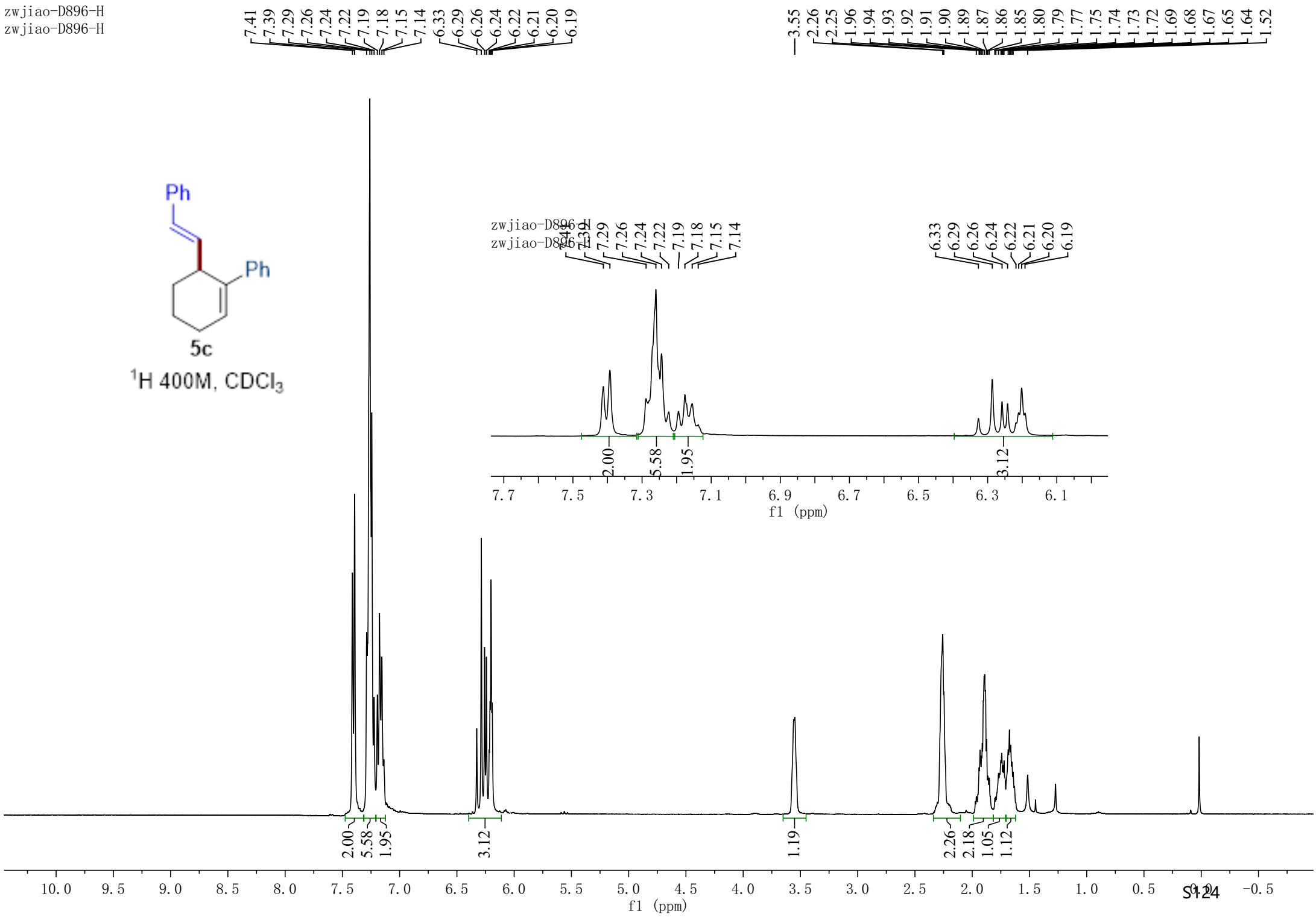


5b

^{13}C 101M, $CDCl_3$

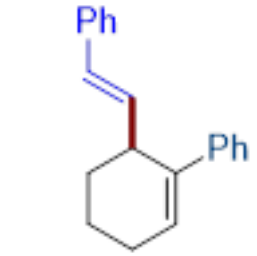
f1 (ppm)

zwjiao-D896-H
zwjiao-D896-H



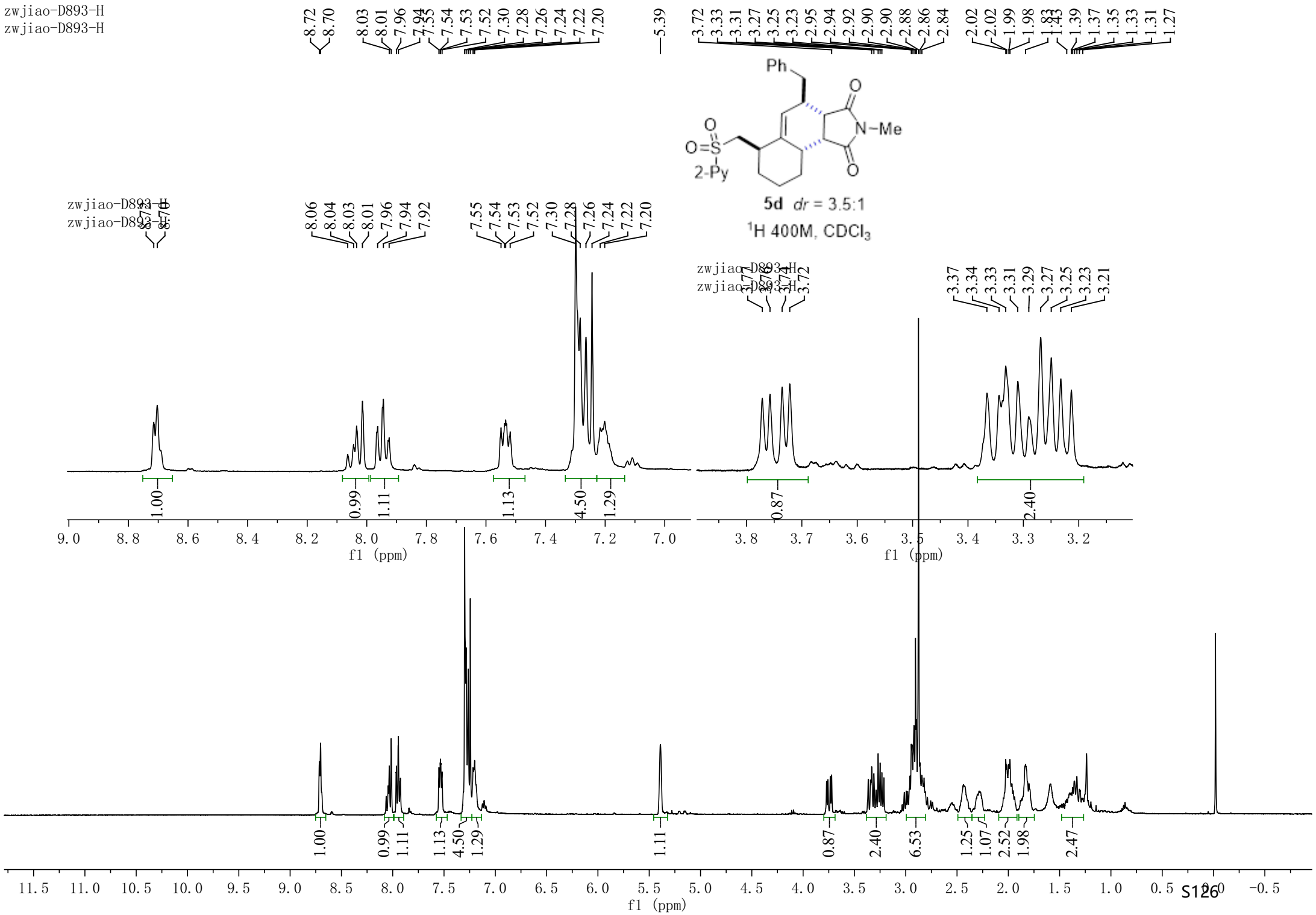
zwjiao-D896-C
zwjiao-D896-C

142.22
138.61
137.88
133.76
130.95
128.50
128.25
127.09
126.97
126.60
126.18
126.12
77.48
77.16
76.84
39.47
29.68
26.19
18.10



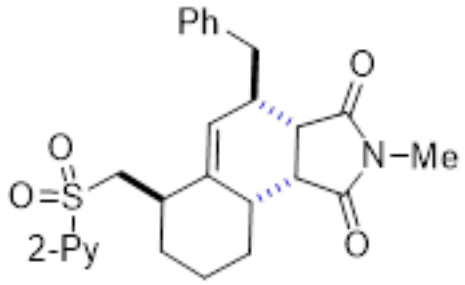
5c

^{13}C 101M, $CDCl_3$


zwjiao-D893-H
zwjiao-D893-H
Ph
O
N–Me
O
O=S
2-Py
O
5d dr = 3.5:1
1H 400M, CDCl3
f1 (ppm)
f1 (ppm)
f1 (ppm)

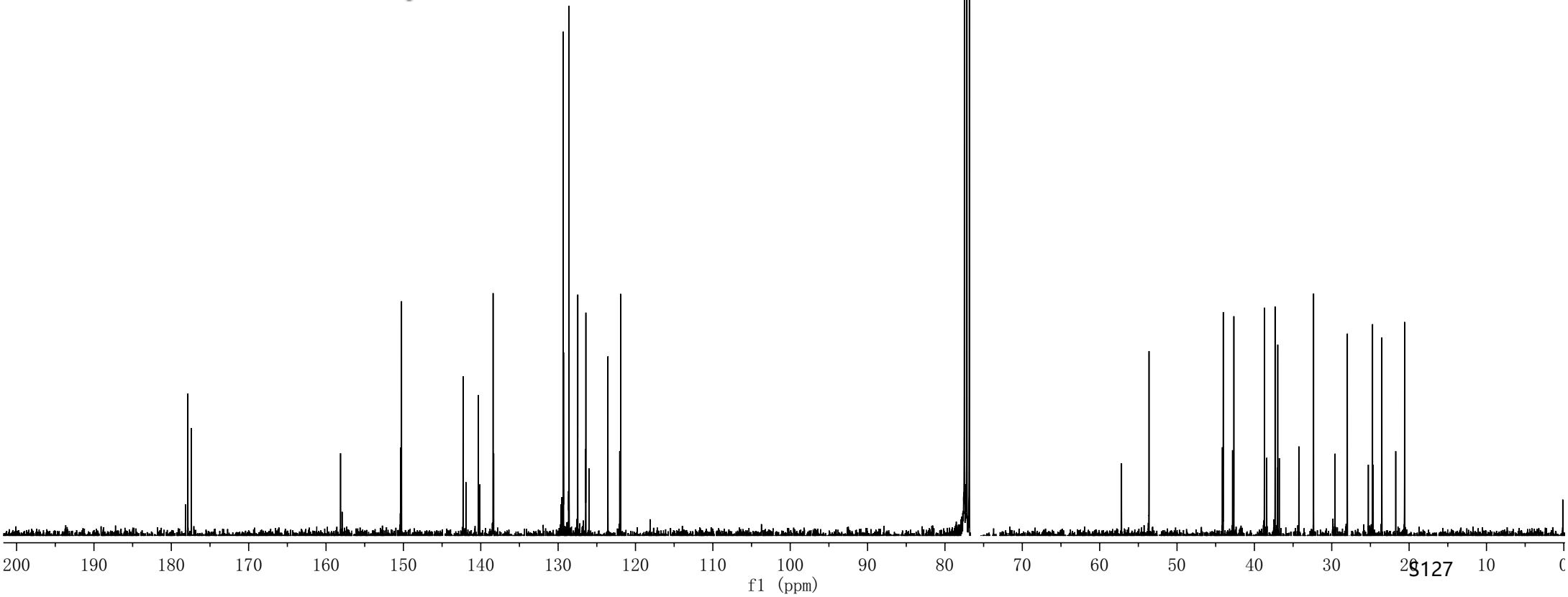
zwjiao-D893-C
zwjiao-D893-C

177.86
177.41
158.13
150.24
142.29
140.31
138.41
129.34
129.30
128.59
127.46
126.41
123.56
121.91
77.48
77.16
76.84
53.62
44.03
42.65
38.71
37.33
36.98
32.35
27.98
24.73
23.52
20.58

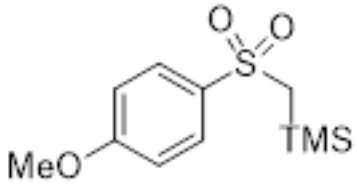


5d *dr* = 3.5:1

^{13}C 101M, $CDCl_3$



zwjiao-D836-H
zwjiao-D836-H

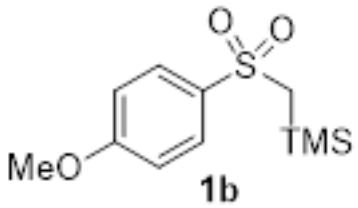


1b

^{1}H 400M, $CDCl_3$

zwjiao-D836-C
zwjiao-D836-C

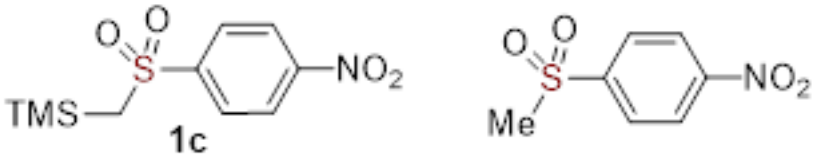
163.12
135.78
128.92
114.30
77.48
77.16
76.84
55.75
49.01
-0.60



1b

^{13}C 101M, $CDCl_3$

zwjiao-D839-H
zwjiao-D839-H

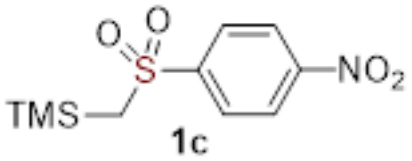


1c

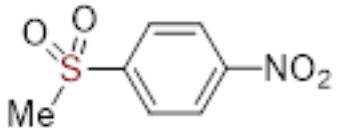
^{1}H 400M, $CDCl_3$

zwjiao-D839-C
zwjiao-D839-C

149.17
129.09
128.29
124.55
77.48
77.16
76.84
48.31
-0.45

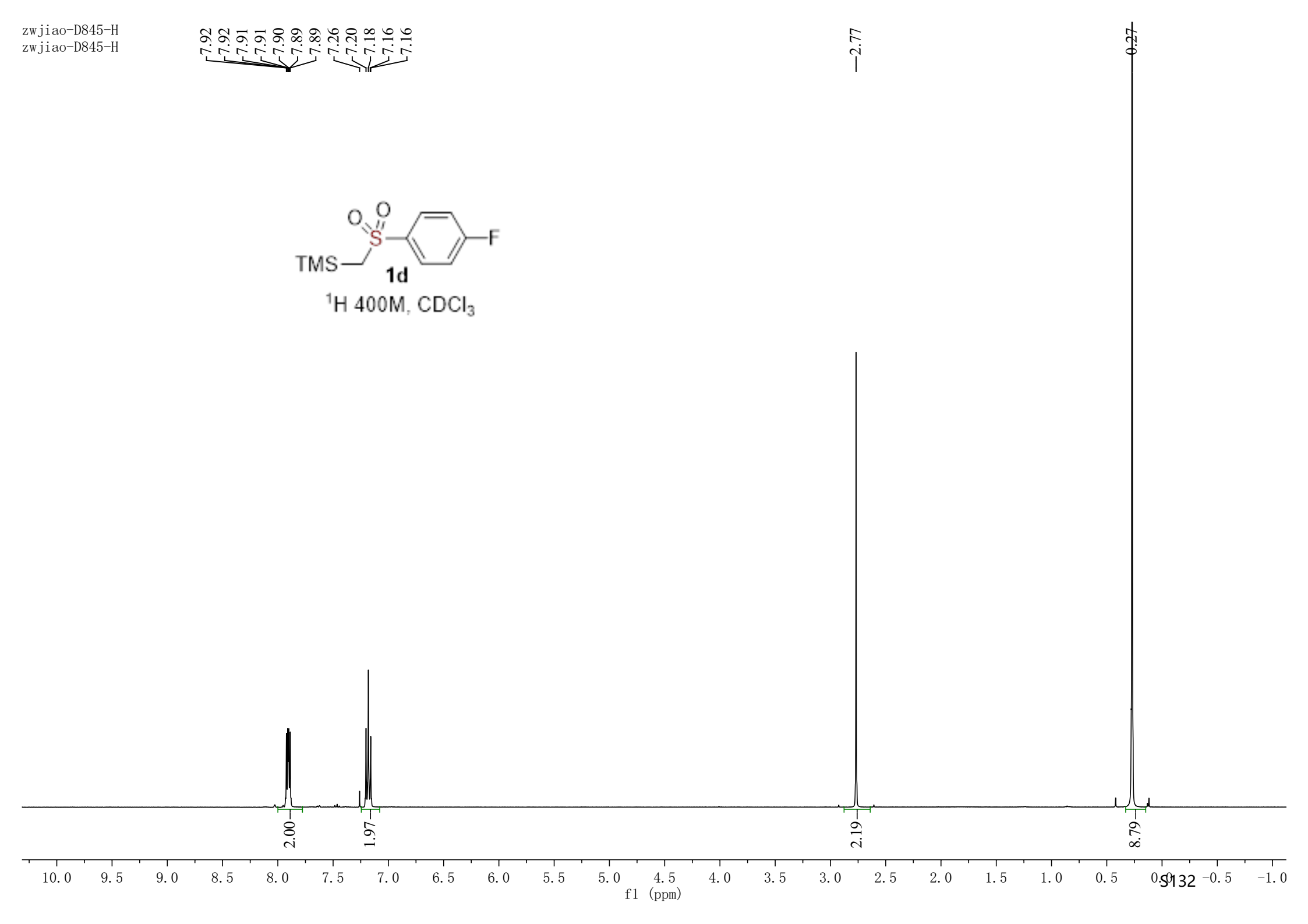


1c



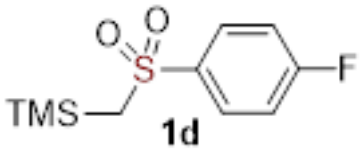
^{13}C 101M, $CDCl_3$

zwjiao-D845-H
zwjiao-D845-H



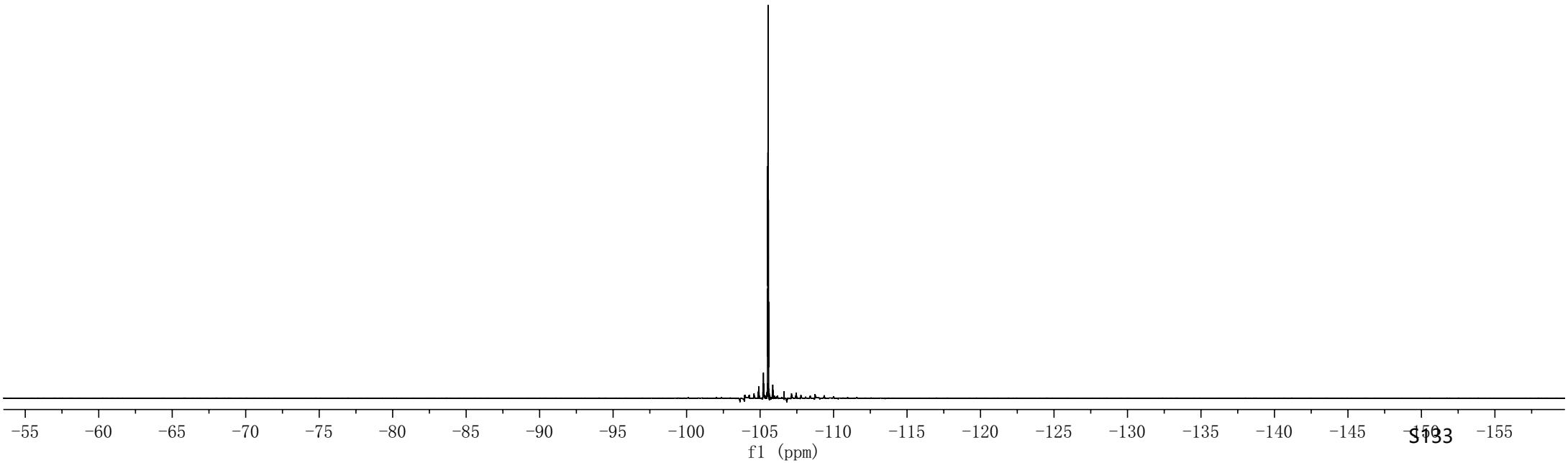
zwjiao-D845-F
zwjiao-D845-F

-105.55



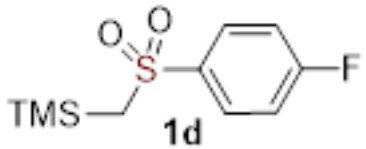
1d

^{19}F 376.6M, $CDCl_3$



zwjiao-D845-C
zwjiao-D845-C

166.56
164.02
140.00
139.97
129.64
129.55
116.50
116.28
77.48
77.16
76.84
48.79
0.58

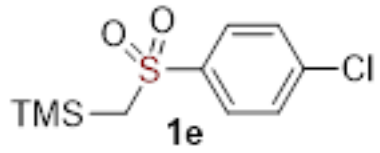


1d

^{13}C 101M, $CDCl_3$

f1 (ppm)

zwjiao-D843-H
zwjiao-D843-H

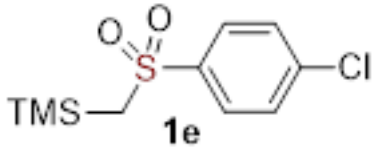


1e

^{1}H 400M, $CDCl_3$

zwjiao-D843-C
zwjiao-D843-C

142.35
139.51
129.52
128.36
77.48
77.16
76.84
48.66
-0.52



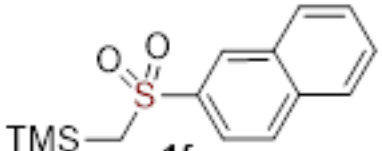
1e

^{13}C 101M, $CDCl_3$

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

zwjiao-D844-H
zwjiao-D844-H



1f

^{1}H 400M, $CDCl_3$

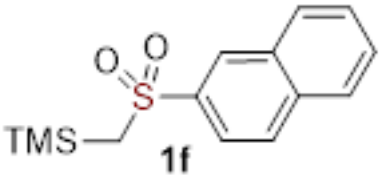
8.47 7.98 7.97 7.96 7.91 7.90 7.89 7.88 7.87 7.66 7.65 7.64 7.64 7.62 7.62 7.60 7.60 7.58 7.26 2.86 0.31

1.00 2.09 2.03 2.09 2.35 9.14

11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.

f1 (ppm)

zwjiao-D844-C
zwjiao-D844-C



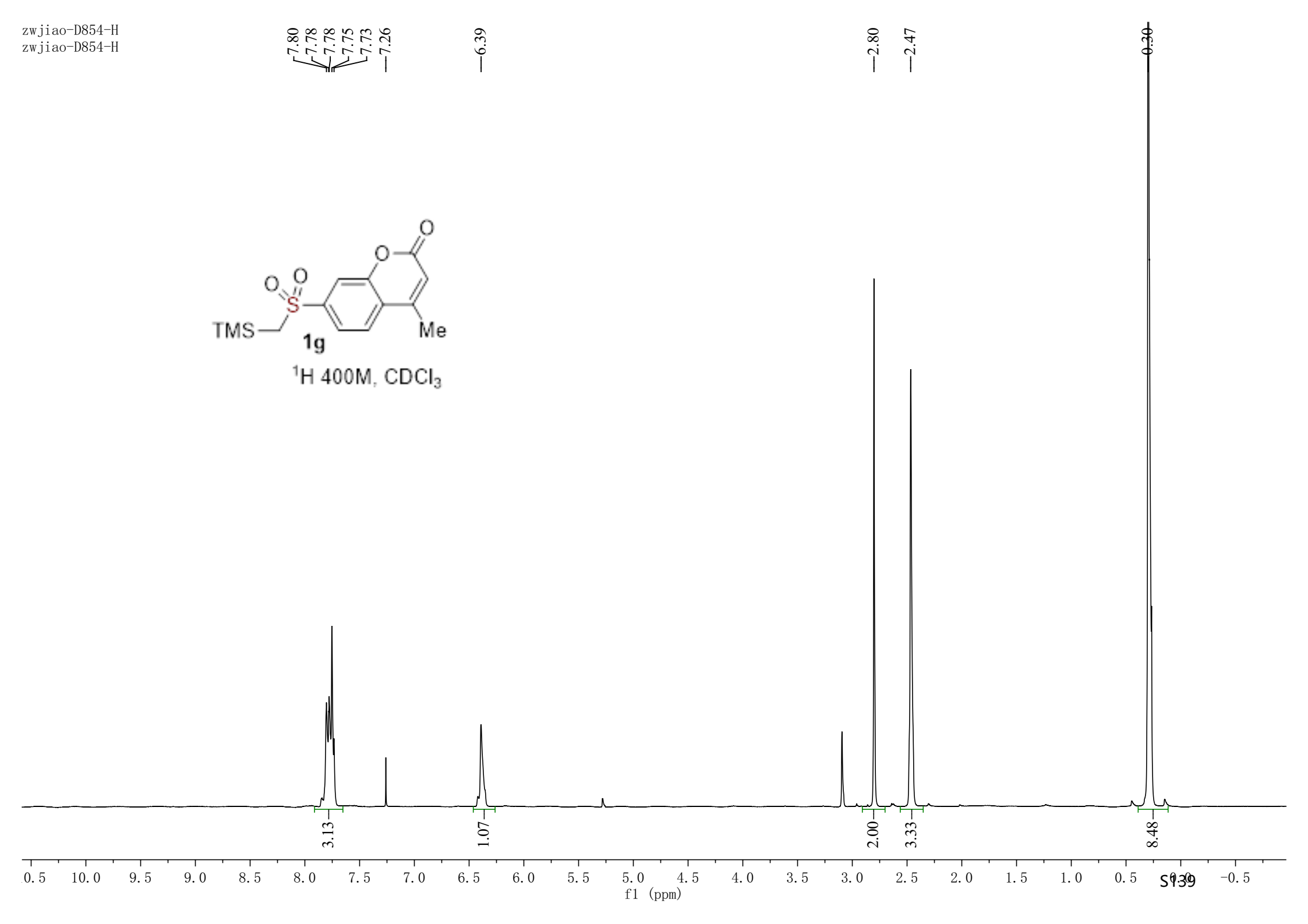
1f

^{13}C 101M, $CDCl_3$

140.71
135.01
132.30
129.56
129.43
128.94
128.03
127.94
127.66
122.17
77.48
77.16
76.84
48.60
0.49

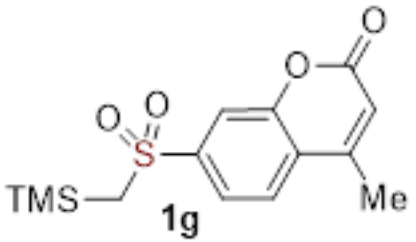
f1 (ppm)

zwjiao-D854-H
zwjiao-D854-H



zwjiao-D854-C
zwjiao-D854-C

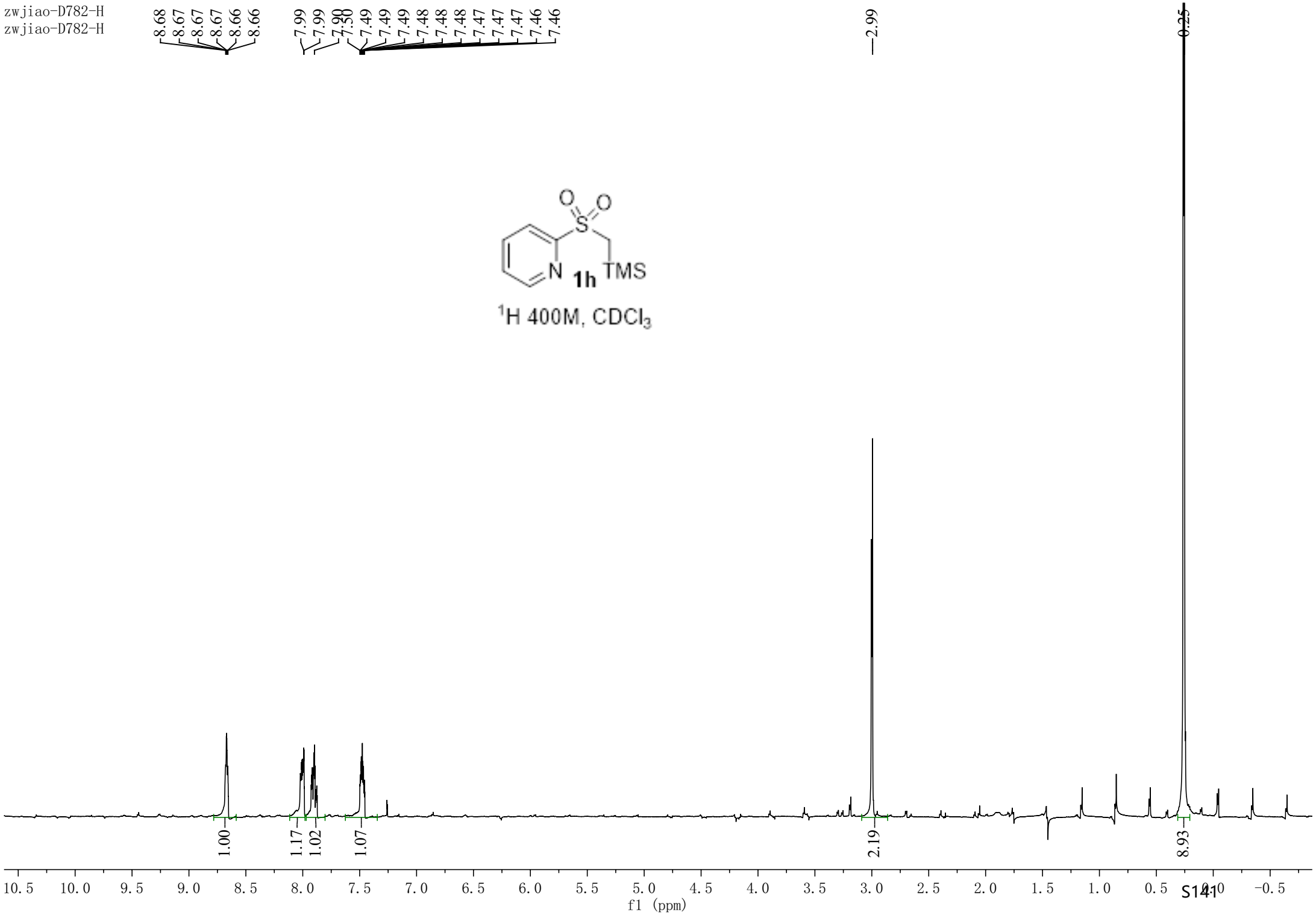
159.43
153.23
150.98
146.32
125.78
123.28
121.89
117.45
115.64
77.35
77.03
76.71
48.22
18.73
0.62



1g

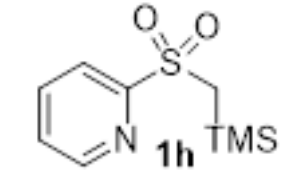
^{13}C 101M, $CDCl_3$

f1 (ppm)


zwjiao-D782-H
zwjiao-D782-H
8.68
8.67
8.67
8.67
8.66
8.66
7.99
7.99
7.90
7.50
7.49
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.46
7.46
2.99
0.25
1h
TMS
1H 400M, CDCl3
1.00
1.17
1.02
1.07
2.19
8.93
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

zwjiao-D782-C
zwjiao-D782-C

159.98
149.93
138.20
126.96
120.48
77.48
77.16
76.84
42.86
-0.58

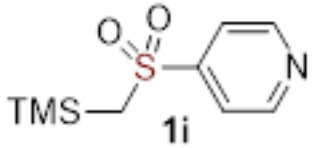


1h

^{13}C 101M, $CDCl_3$

f1 (ppm)

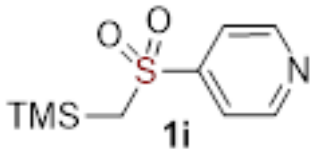
zwjiao-D837-H
zwjiao-D837-H



1i

^{1}H 400M, $CDCl_3$

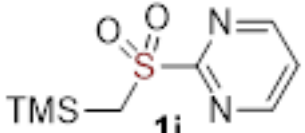
zwjiao-D837-C
zwjiao-D837-C



1i

^{13}C 101M, $CDCl_3$

zwjiao-D816-H
zwjiao-D816-H

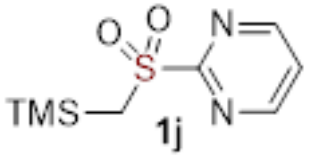


1j

^{1}H 400M, $CDCl_3$

zwjiao-D816-C
zwjiao-D816-C

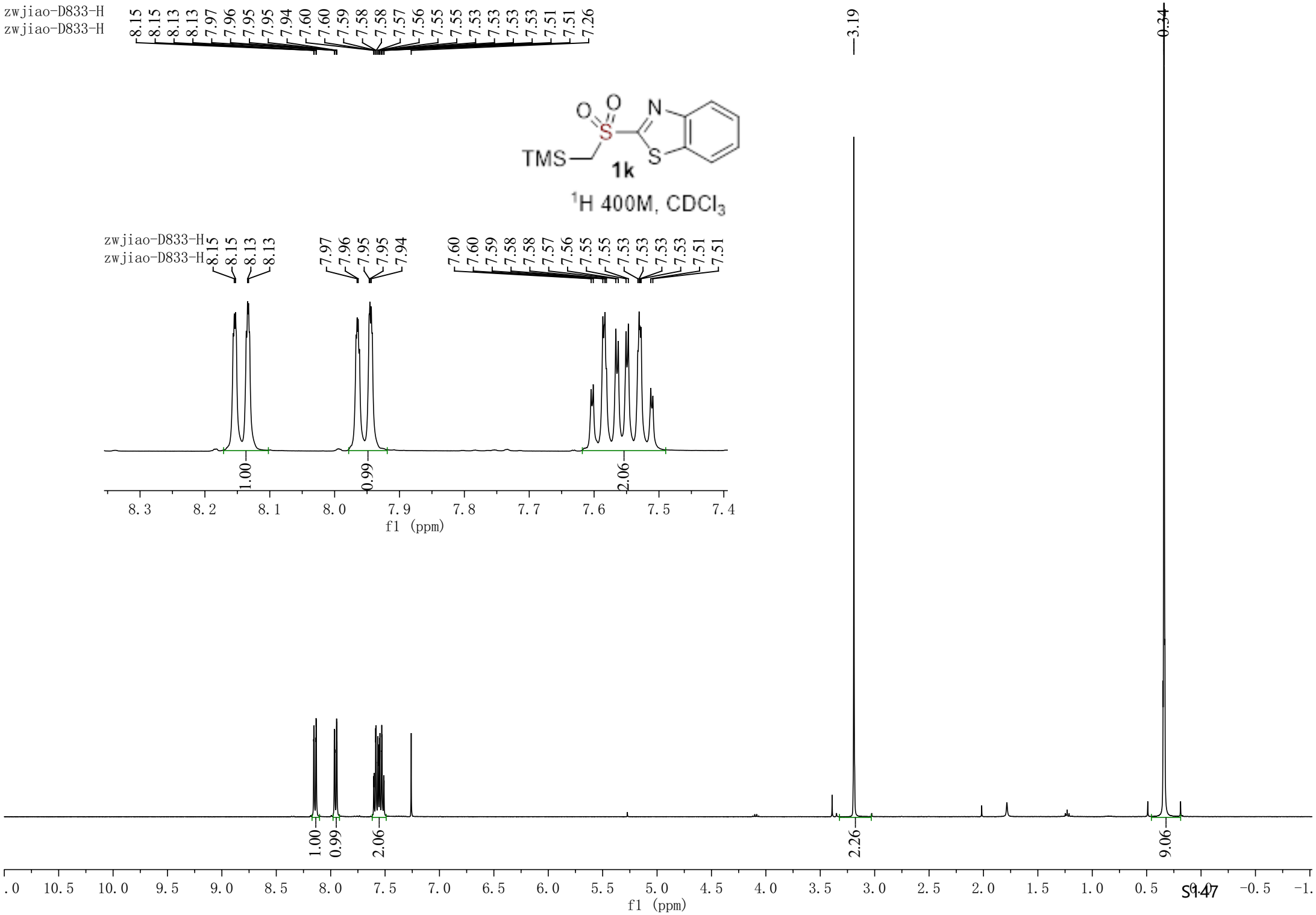
167.19
158.54
123.57
77.54
77.22
76.90
41.88
0.67



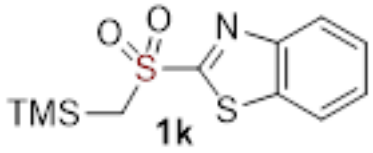
1j

^{13}C 101M, $CDCl_3$

f1 (ppm)


zwjiao-D833-H
zwjiao-D833-H
8.15 8.15 8.13 8.13 7.97 7.96 7.95 7.95 7.94 7.60 7.60 7.59 7.58 7.58 7.57 7.56 7.55 7.55 7.53 7.53 7.53 7.53 7.51 7.51 7.26
3.19
0.34
TMS
1k
^{1}H 400M, CDCl$_3$
1.00
0.99
2.06
2.26
9.06
f1 (ppm)
S147

zwjiao-D833-C-1
zwjiao-D833-C



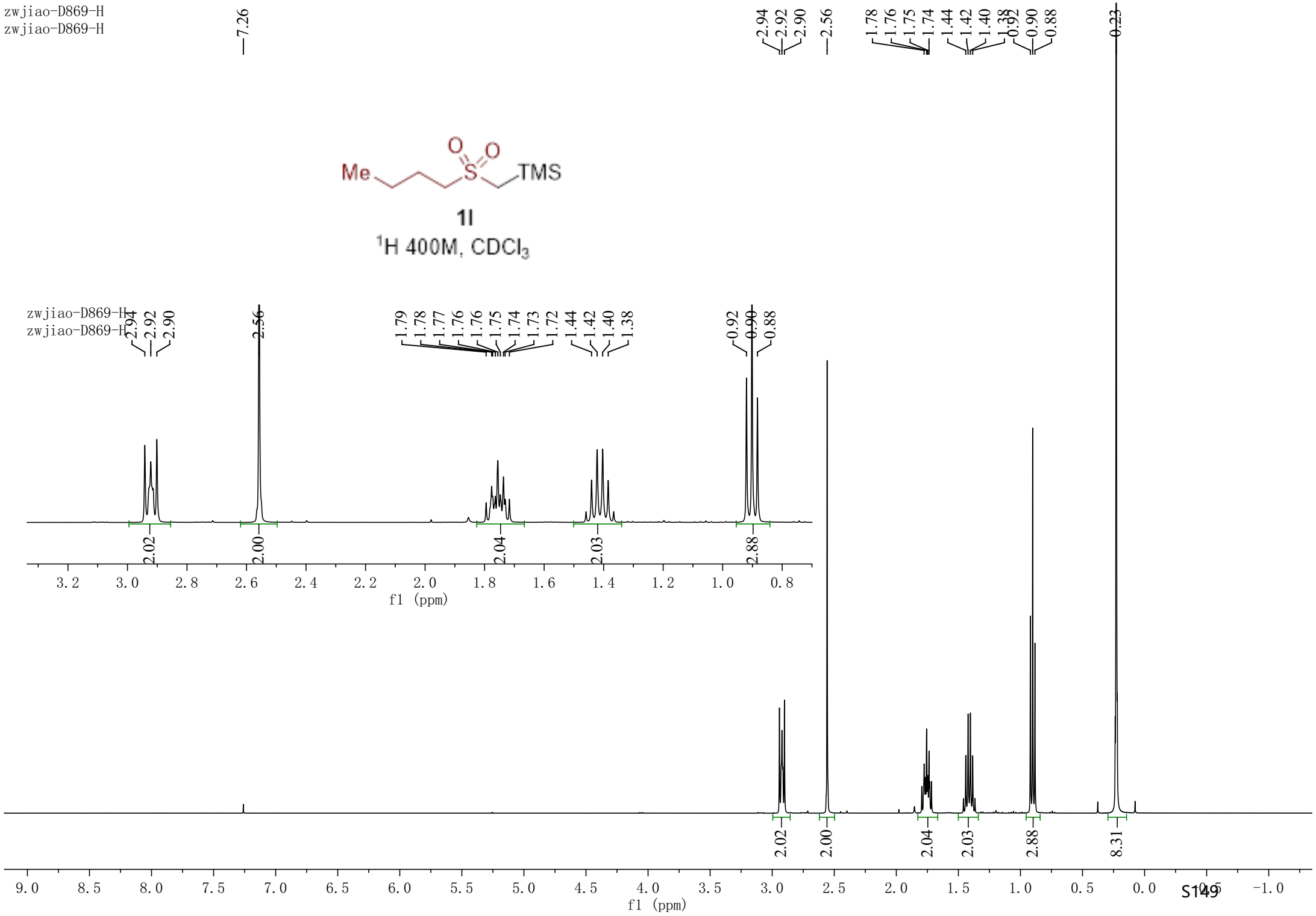
1k

^{13}C 101M, $CDCl_3$

169.19
152.46
136.53
127.78
127.52
125.16
122.40
77.48
77.16
76.84
45.81
0.50

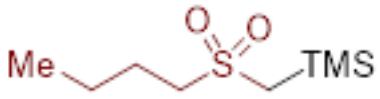
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


zwjiao-D869-H
zwjiao-D869-H
7.26
2.94
2.92
2.90
2.56
1.78
1.76
1.75
1.74
1.44
1.42
1.40
1.38
0.92
0.90
0.88
0.23
Me
TMS
1l
1H 400M, CDCl3
f1 (ppm)
2.02
2.00
2.04
2.03
2.88
8.31

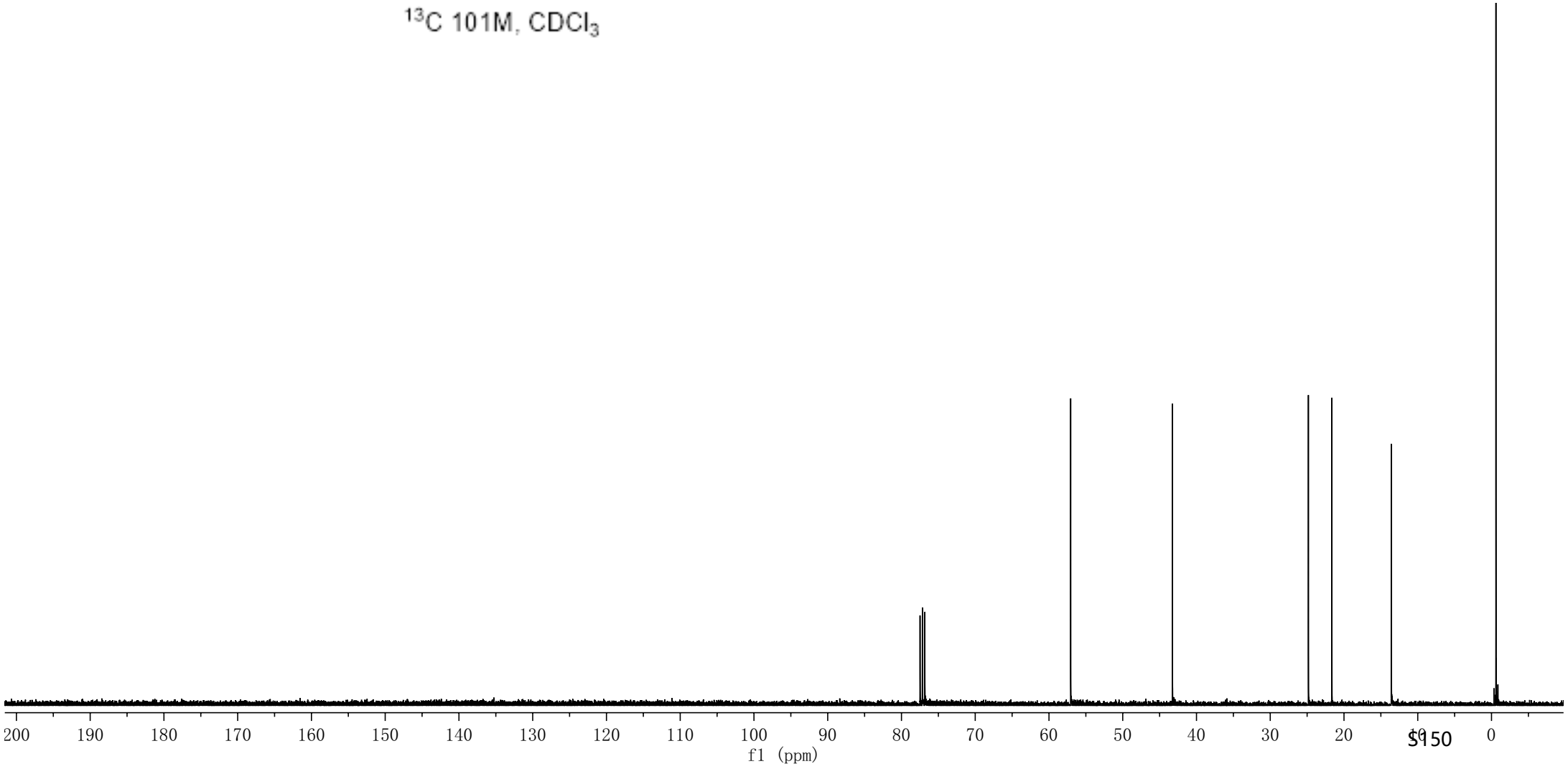
zwjiao-D869-C
zwjiao-D869-C

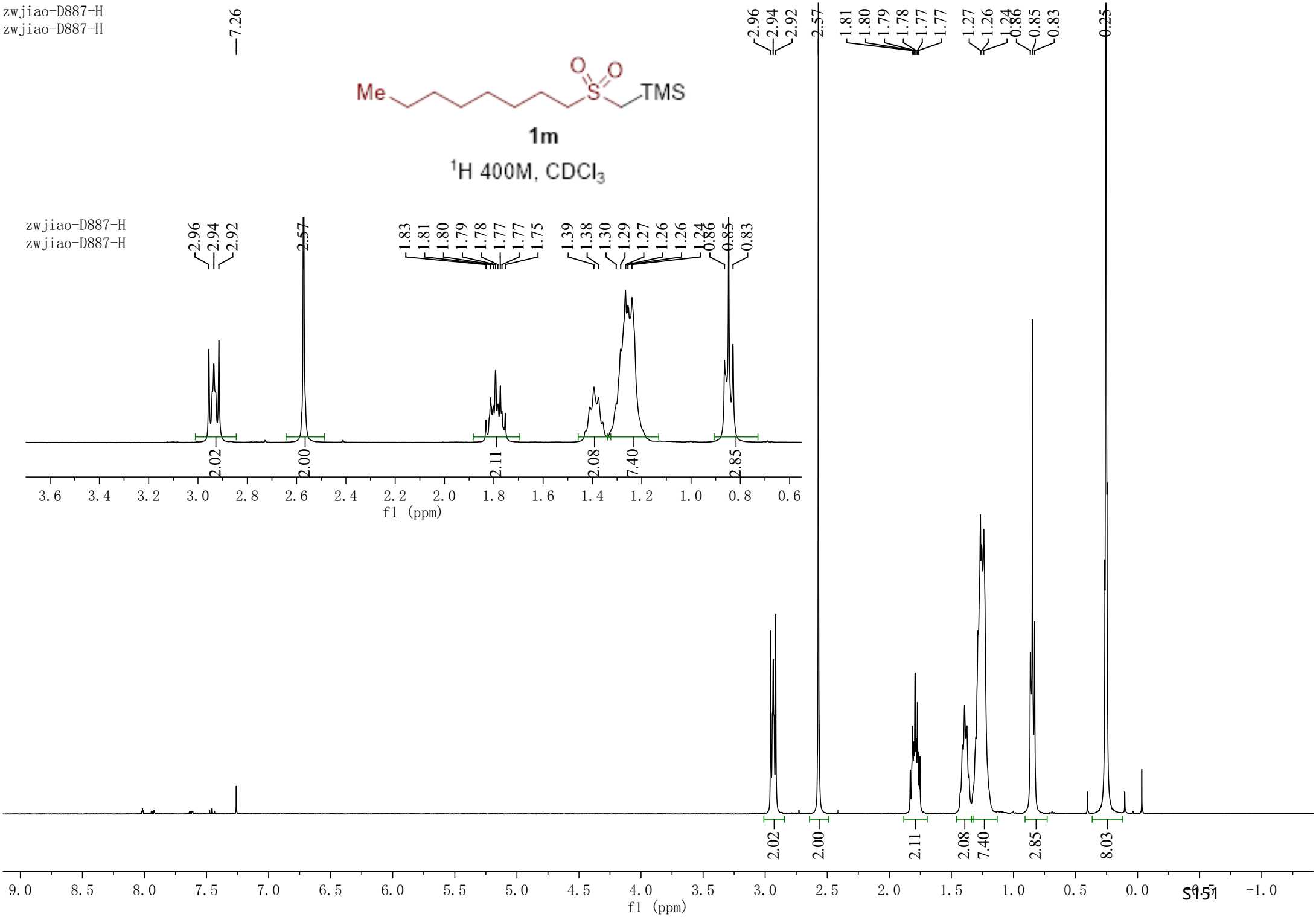
77.48
77.16
76.84
57.06
43.27
24.83
21.65
13.59
-0.60



1l

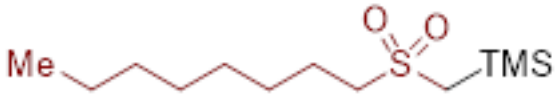
^{13}C 101M, $CDCl_3$




zwjiao-D887-H
zwjiao-D887-H
Me
TMS
1m
1H 400M, CDCl3
f1 (ppm)

zwjiao-D887-C
zwjiao-D887-C

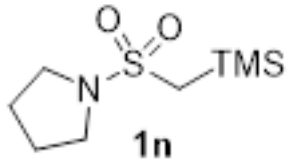
77.48
77.16
76.84
57.42
43.35
31.76
29.13
29.00
28.47
22.91
22.64
14.12
-0.53



1m

^{13}C 101M, $CDCl_3$

zwjiao-D855-H-1
zwjiao-D855-H

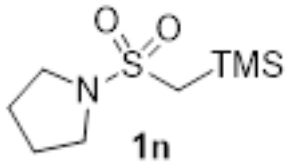


1n

^{1}H 400M, $CDCl_3$

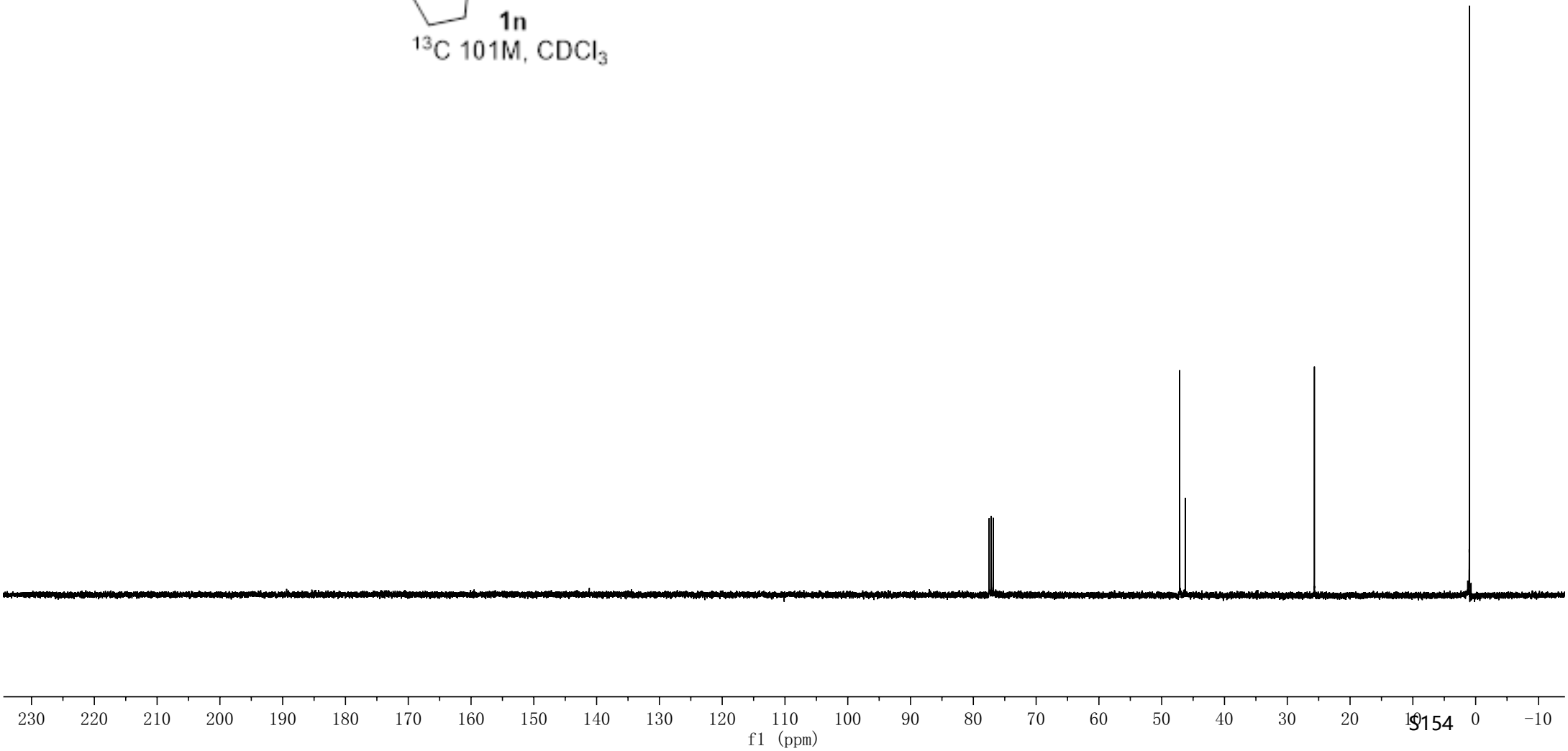
zwjiao-D855-C-1
zwjiao-D855-C

77.48
77.16
76.84
47.13
46.25
25.68
1.00

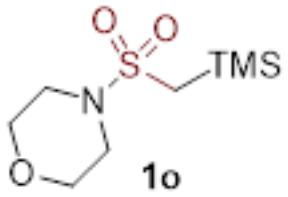


1n

^{13}C 101M, $CDCl_3$



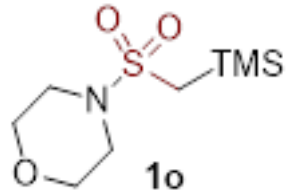
zwjiao-D888-2-H
zwjiao-D888-2-H



1o

^{1}H 400M, $CDCl_3$

zwjiao-D888-2-C
zwjiao-D888-2-C



1o

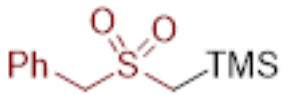
^{13}C 101M, $CDCl_3$

77.48
77.16
76.84
66.29
46.03
35.69
-0.83

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

zwjiao-D853-H
zwjiao-D853-H



1p

^{1}H 400M, $CDCl_3$

zwjiao-D853-C
zwjiao-D853-C