Supplementary Information

Pd/Cu-Catalyzed Cascade Heck-Type Reactions of Alkenyl Halides with Terminal Alkynes toward Substituted Pyrrolidine Analogues

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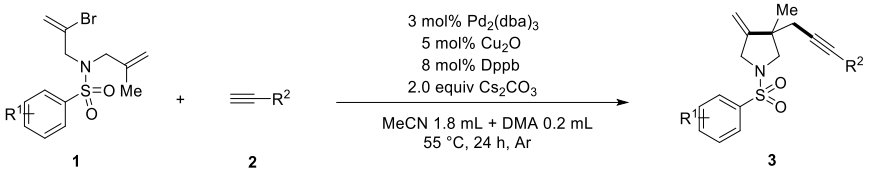
1. General Information

Unless otherwise noted, all reactions were carried out under argon atmosphere; materials obtained from commercial suppliers were used directly without further purification. ^{1}H NMR spectra, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on an Agilent 400 or on a Bruker 400 MHz spectrometer in $CDCl_3$. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (*d* 7.26 or 77.0 ppm) as the internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant (s) in Hz, integration). All the solvents were used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Copies of NMR were processed with MestReNova Software. All melting points were uncorrected.

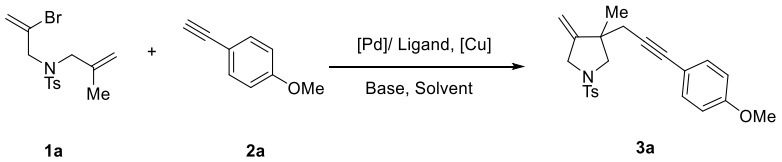
2. Synthesis and Reaction

2.1 General Procedure for the Synthesis of Pyrrolidines 3



A sealed tube equipped with a magnetic stir bar was charged with 2-bromo-1,6-diene **1** (0.30 mmol, 1.0 equiv.), terminal alkynes **2** (0.60 mmol, 2.0 equiv.), $Pd_2(dba)_3$ (8.2 mg, 0.009 mmol, 0.03 equiv.), Cu_2O (2.2 mg, 0.015 mmol, 0.05 equiv.), 1,4-bis(diphenylphosphino)butane (10.2 mg, 0.024 mmol, 0.08 equiv.), Cs_2CO_3 (195.5 mg, 0.60 mmol, 2.0 equiv.) and solvent (2.0 mL). The tube was sealed with a Teflon lined cap. Degassed solvent and backfilled with argon for 3 times at -78 ºC. The reaction mixture was stirred at 55 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

2.2 Table S1. Optimization of Reaction Conditions[a]

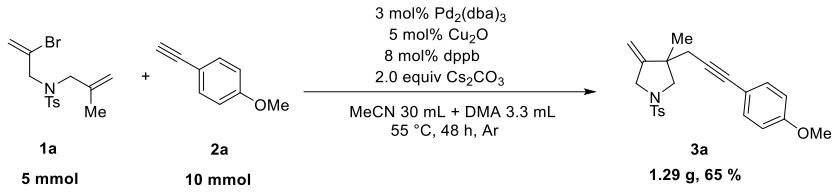


Entry	[Pd]	[Cu]	Ligand	Solvent	Yield (%)[b]
1	$Pd_2(dba)_3$	-	Dpephos	MeCN	10
2	$Pd_2(dba)_3$	-	Xphos	MeCN	27
3	$Pd_2(dba)_3$	-	Xantphos	MeCN	N.R
4	$Pd_2(dba)_3$	-	PPh_3	MeCN	N.R
5	$Pd_2(dba)_3$	-	Dppf	MeCN	N.R
6	$Pd_2(dba)_3$	-	Dppb	MeCN	31
7	$Pd_2(dba)_3$	CuI	Dppb	MeCN	13
8	$Pd_2(dba)_3$	CuO	Dppb	MeCN	69
9	$Pd_2(dba)_3$	Cu_2O	Dppb	MeCN	70
10	$Pd_2(dba)_3$	Cu_2O	Dppb	Toluene	17

11	$Pd_2(dba)_3$	Cu_2O	Dppb	DCE	42
12	$Pd_2(dba)_3$	Cu_2O	Dppb	THF	10
13[c]	$Pd_2(dba)_3$	Cu_2O	Dppb	M.S.	70
14[e]	$Pd_2(dba)_3$	Cu_2O	Dppb	M.S.	74
15[c,d]	$Pd(OAc)_2$	Cu_2O	Dppb	M.S.	59
16[c,d]	$PdCl_2$	Cu_2O	Dppb	M.S.	62
17[c,d]	$Pd(MeCN)_2Cl_2$	Cu_2O	Dppb	M.S.	10
18[c,d]	$Pd(acac)_2$	Cu_2O	Dppb	M.S.	39

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), Cs_2CO_3 (2.0 equiv.), 3 mol% of Pd catalyst, 8 mol% of Ligand, and 5 mol% of Cu catalyst in the solvent (2.0 mL) at 55 °C under Ar for 24 h. [b] Isolated yield. [c] M.S.= MeCN : DMA (2.0 mL, 9:1 ratio). [d] 6 mol% of Pd catalyst. [e] **1a** (0.3 mmol, 1.0 equiv.), **2a** (0.6 mmol, 2.0 equiv.), Cs_2CO_3 (2.0 equiv.), 3 mol% of $Pd_2(dba)_3$, 8 mol% of Dppb, and 5 mol% of Cu_2O in the dry MeCN/dry DMA (2.0 mL, 9:1 ratio) at 55 °C under Ar for 24 h; N.R, no reaction.

2.3 Gram-Scale Synthesis of 3a

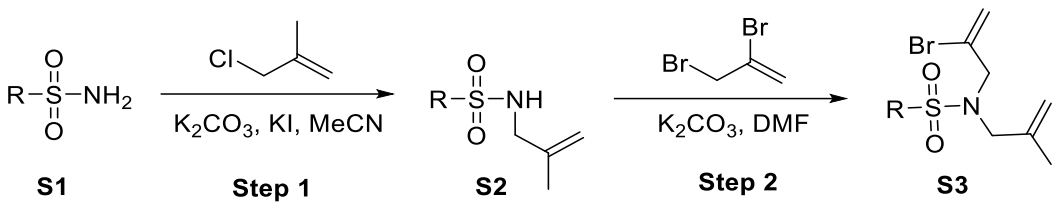


1a **2a** **3a**

5 mmol **10 mmol** **1.29 g, 65 %**

An oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar was charged with $Pd_2(dba)_3$ (137.4 mg, 0.15 mmol, 0.03 equiv.), Cu_2O (35.8 mg, 0.25 mmol, 0.05 equiv.), 1,4-bis(diphenylphosphino)butane (170.6 mg, 0.40 mmol, 0.08 equiv.), Cs_2CO_3 (3.2582 g, 10.0 mmol, 2.0 equiv.), **1a** (1.7213 g, 5 mmol), **2a** (1.3216 g, 10 mmol), dry MeCN (30.0 mL) and dry *N*,*N*-dimethylacetamide (3.3 mL) were added sequentially. Degassed solvent and backfilled with argon for 3 times at -78 °C. The reaction mixture was stirred at 55 °C for 48 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **3a** 1.29g in 65% yield.

2.4 General Procedure for Preparation of Substrates 1a-1l.[1-4]

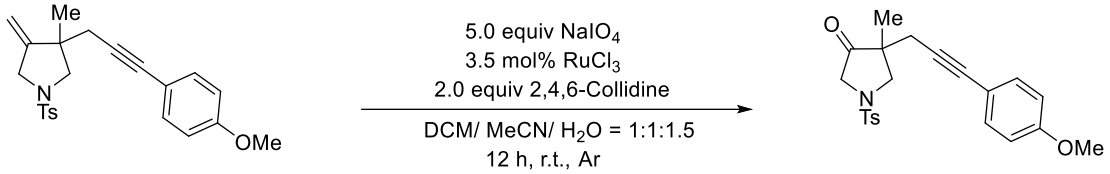


S1 S2 S3

Step 1 To a solution of **S1** (1.2 equiv.), K_2CO_3 (2.0 equiv.) and KI (0.5 equiv.) in CH_3CN was added 3-chloro-2-methylpropene (1.0 equiv.) slowly. The reaction mixture was stirred at 60 °C for 12 h. After completion, the reaction was quenched with water, extracted with EtOAc for three times. The combined organic layer was washed with water and brine for three times, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure.

Step 2 The residue **S2** was dissolved in DMF, K_2CO_3 (2.0 equiv.) and 2,3-dibromopropene (1.2 equiv.) were added. The reaction mixture was stirred at room temperature for 2 h. After completion, it was diluted with water, extracted with EtOAc for three times, and washed with water and brine for three times, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford target product **S3**.

2.5 Experimental Procedure for Synthesis of 5[5]

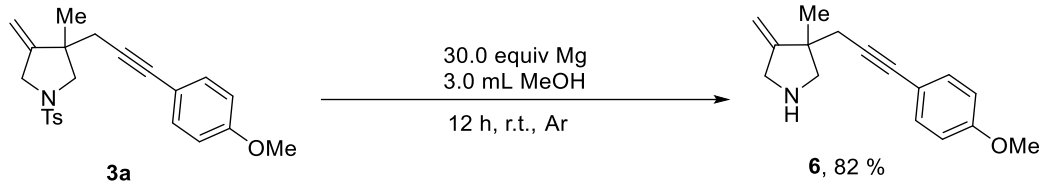


3a **5**, 48 %

A dried round bottle flask equipped with a magnetic stir bar was charged with product **3a** (0.2 mmol, 1.0 equiv.) and 2.4 mL solvent (V_{DCM}:V_{MeCN} = 1:1) under nitrogen. And then, 2,4,6-Collidine (48.5 mg, 0.4 mmol, 2.0 equiv.), water (1.8 mL), sodium periodate (215.9 mg, 1.0 mmol, 5.0 equiv.) and ruthenium (III) trichloride hydrate (1.5 mg, 0.007mmol, 3.5 mol%) were added in order. The reaction mixture was stirred at room temperature overnight. The resulting mixture was then diluted with water and extracted with DCM for three times. The organic extracts were combined, washed with brine and dried over Na_2SO_4. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl

acetate as eluent to give the desired product **5** (38.5 mg, 48%) as a yellow oil.

2.6 Experimental procedure for synthesis of 6[1]

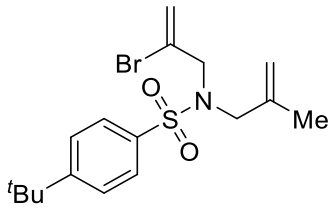


3a **6**, 82 %

A dried round bottle flask equipped with a magnetic stir bar was charged with product **3a** (0.2 mmol, 1.0 equiv.), Mg turnings (145.9 mg, 6.0 mmol, 30.0 equiv.) and 3.0 mL MeOH under nitrogen. The reaction mixture was ultrasonicated for 5 minutes, and then stirred at room temperature overnight. The white suspension was treated with Et_3N and filtered through a short pad of celite, washed with Et_2O and MeOH. The filtrate was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with a gradient eluant of EA/MeOH (10:1) and Et_3N to give the desired product **6** (39.6 mg, 82%) as a white oil.

3. Characterization Data

***N*-(2-bromoallyl)-4-(*tert*-butyl)-*N*-(2-methylallyl)benzenesulfonamide (1c)**



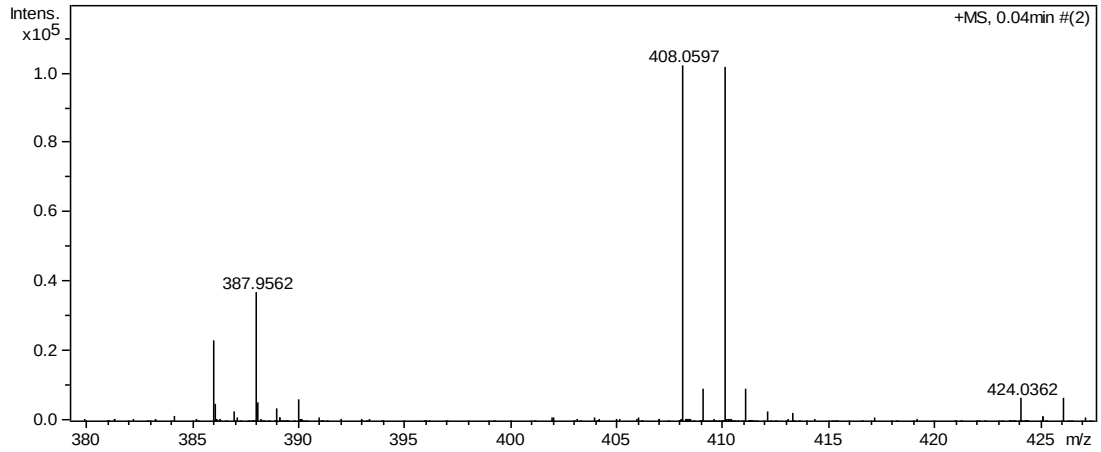
1c

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 20:1) gave the product **1c** (2.0g, 31% yield) as a white solid; m.p.: 70-73 ºC.

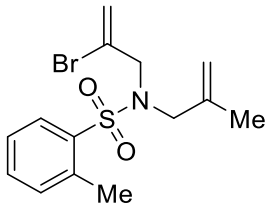
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 5.75-5.74 (m, 1H), 5.55-5.54 (m, 1H), 4.92 (s, 1H), 4.83 (s, 1H), 4.04 (s, 2H), 3.82 (s, 2H), 1.63 (s, 3H), 1.33 (s, 9H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.5, 139.5, 137.1, 127.7, 127.2, 125.9, 119.4, 115.4, 54.0, 53.5, 35.1, 31.0, 19.8;

HRMS Calcd (ESI) m/z for $C_{17}H_{24}BrNNaO_2S$ $[M + Na]^+$: 408.0603, found: 408.0597.



***N*-(2-bromoallyl)-2-methyl-*N*-(2-methylallyl)benzenesulfonamide (1d)**



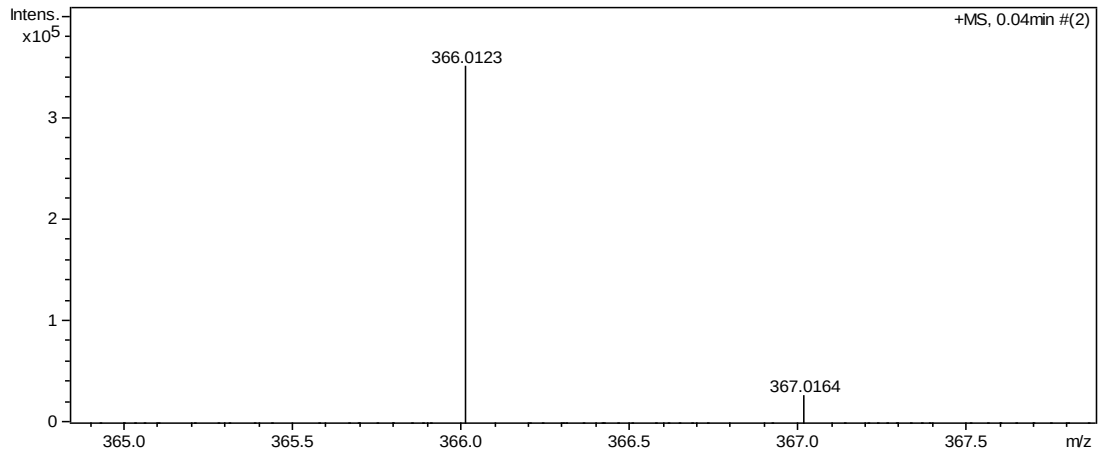
1d

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 20:1) gave the product **1d** (2.8g, 64% yield) as a yellow oil.

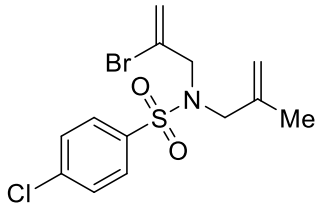
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, J = 8.0 Hz, 1H), 7.37-7.34 (m, 1H), 7.23-7.19 (m, 2H), 5.69-5.68 (m, 1H), 5.47 (s, 1H), 4.87 (s, 1H), 4.81 (s, 1H), 3.99 (s, 2H), 3.83 (s, 2H), 2.54 (s, 3H), 1.49 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.1, 137.8, 137.6, 132.8, 132.5, 130.1, 127.2, 125.9, 120.3, 115.7, 53.0, 52.3, 20.6, 19.6;

HRMS Calcd (ESI) m/z for $C_{14}H_{18}BrNNaO_2S$ $[M + Na]^+$: 366.0134, found: 366.0123.



***N*-(2-bromoallyl)-4-chloro-*N*-(2-methylallyl)benzenesulfonamide (1f)**



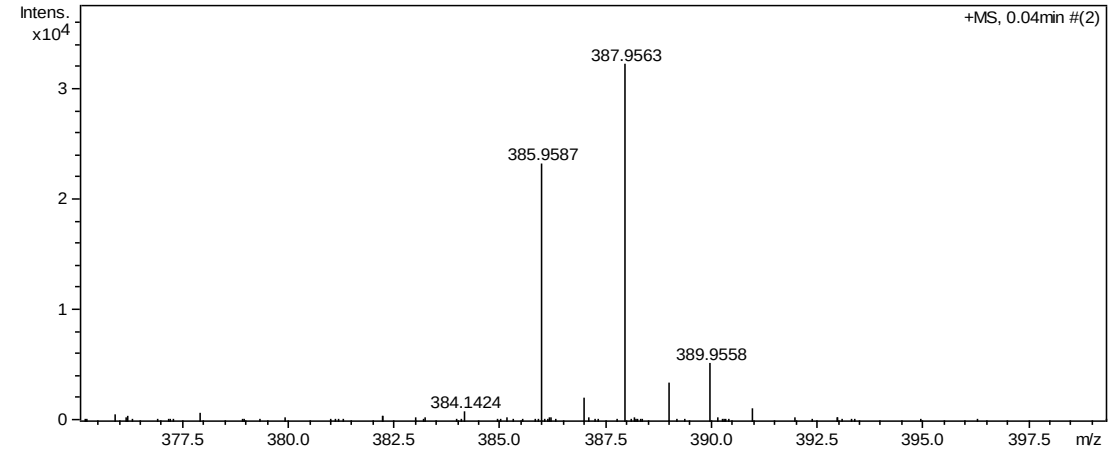
1f

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 20:1) gave the product **1f** (4.1g, 28% yield) as a yellow oil.

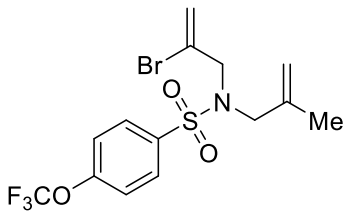
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 5.75-5.74 (m, 1H), 5.57-5.56 (m, 1H), 4.95 (s, 1H), 4.84 (s, 1H), 4.07 (s, 2H), 3.85 (s, 2H), 1.65 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.1 (2C), 139.0, 129.2, 128.8, 127.3, 120.2, 115.6, 53.8, 53.3, 19.9;

HRMS Calcd (ESI) m/z for $C_{13}H_{15}BrClNNaO_2S$ $[M + Na]^+$: 385.9588, found: 385.9587.



***N*-(2-bromoallyl)-*N*-(2-methylallyl)-4-(trifluoromethoxy)benzenesulfonamide (1h)**



1h

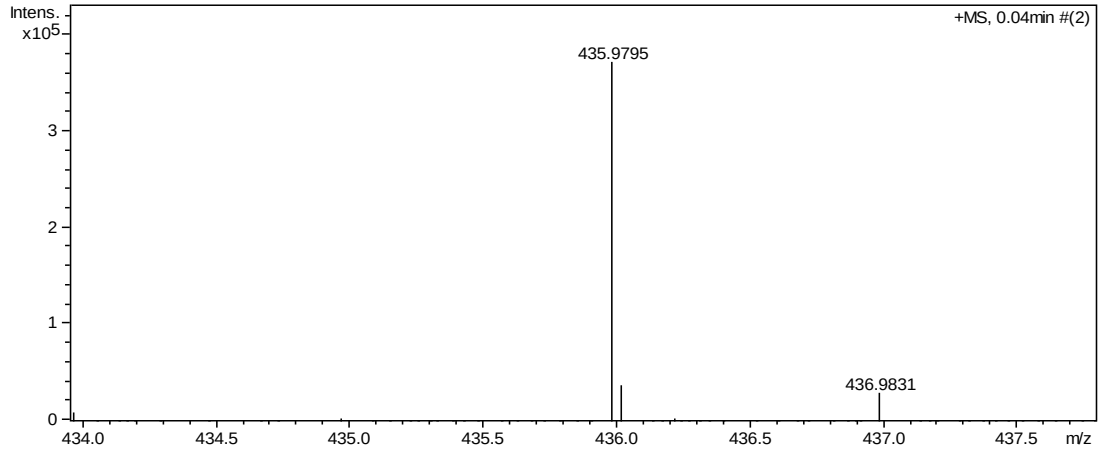
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 20:1) gave the product **1h** (2.1g, 50% yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.88 (d, *J* = 9.2 Hz, 2H), 7.30 (d, *J* = 9.2 Hz, 2H), 5.74-5.73 (m, 1H), 5.54-5.53 (m, 1H), 4.92 (s, 1H), 4.82 (s, 1H), 4.06 (s, 2H), 3.85 (s, 2H), 1.62 (s, 3H);

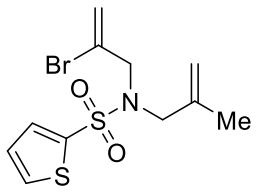
^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 139.0, 138.9, 129.4, 127.3, 120.8, 120.3, 120.2 (q, *J* = 257.9 Hz), 115.5, 53.8, 53.3, 19.8;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -57.7;

HRMS Calcd (ESI) m/z for $C_{14}H_{15}BrF_3NNaO_3S$ $[M + Na]^+$: 435.9800, found: 435.9795.



***N*-(2-bromoallyl)-*N*-(2-methylallyl)thiophene-2-sulfonamide (1i)**



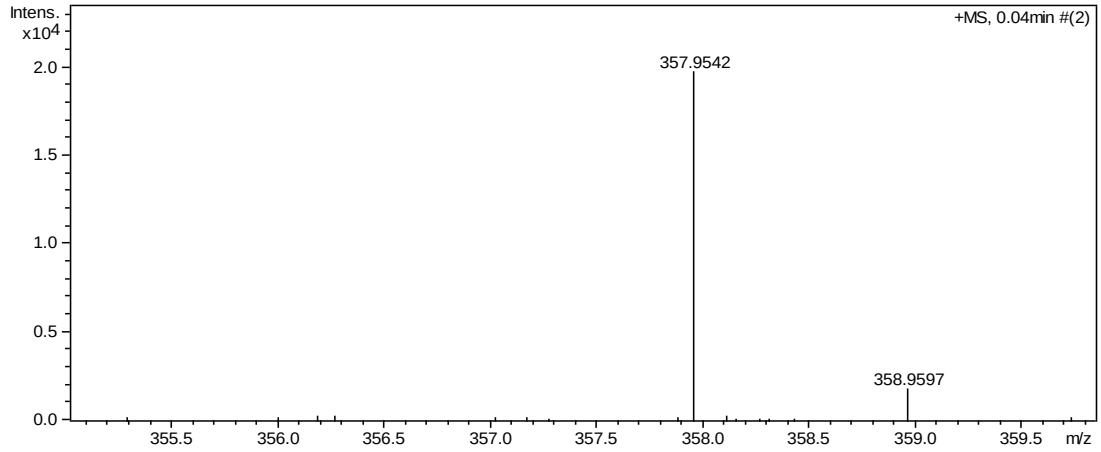
1i

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 20:1) gave the product **1i** (2.5g, 59% yield) as a yellow oil.

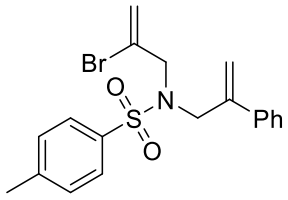
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.56-7.55 (m, 2H), 7.06-7.04 (m, 1H), 5.77-5.76 (m, 1H), 5.55-5.54 (m, 1H), 4.91 (s, 1H), 4.84 (s, 1H), 4.03 (s, 2H), 3.81 (s, 2H), 1.64 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.5, 139.0, 132.0, 131.6, 127.2, 127.1, 119.7, 115.4, 54.2, 53.7, 19.7;

HRMS Calcd (ESI) m/z for $C_{11}H_{14}BrNNaO_2S_2$ $[M + Na]^+$: 357.9542, found: 357.9542.



***N*-(2-bromoallyl)-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1l)**



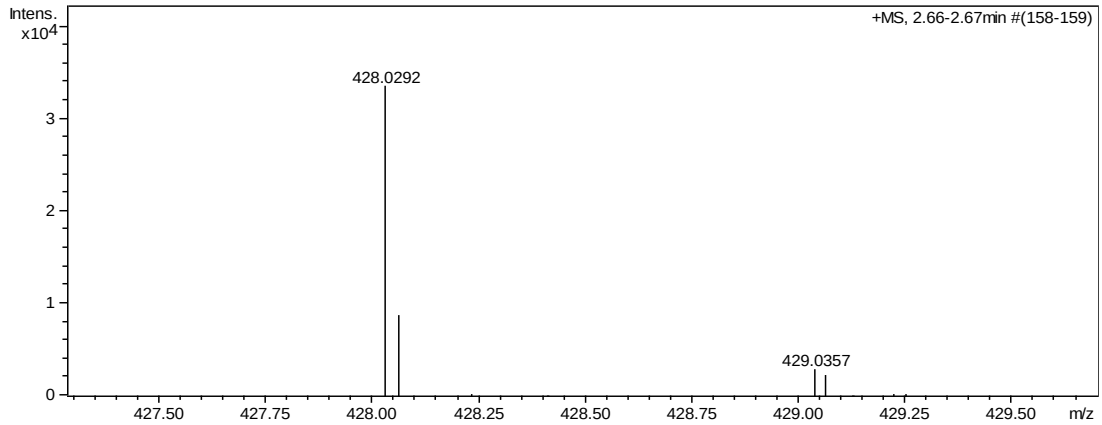
1l

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 20:1) gave the product **1l** (0.3g, 18% yield) as a yellow solid; m.p.: 37-40 °C.

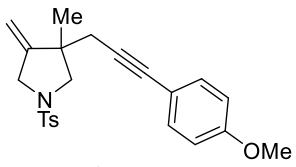
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67-7.64 (m, 2H), 7.34-7.25 (m, 7H), 5.63 (s, 1H), 5.46-5.43 (m, 2H), 5.19 (s, 1H), 4.32 (s, 2H), 3.99 (s, 2H), 2.43 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4, 141.9, 138.2, 136.5, 129.5, 128.3, 127.9, 127.3, 127.2, 126.3, 119.2, 116.9, 54.1, 51.4, 21.4;

HRMS Calcd (ESI) m/z for $C_{19}H_{20}BrNNaO_2S$ $[M + Na]^+$: 428.0290, found: 428.0292.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-tosylpyrrolidine (3a)



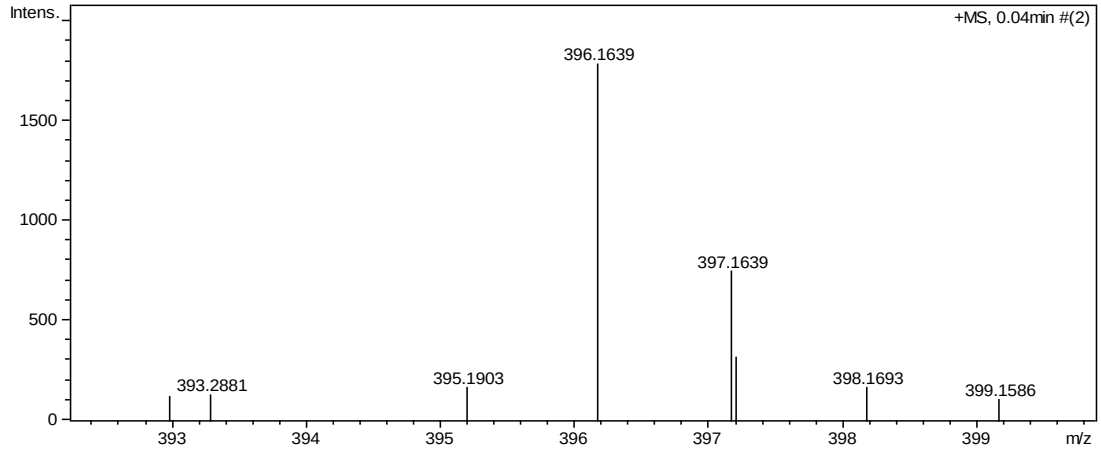
3a

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 9:1) gave the product **3a** (88.0mg, 74% yield) as a yellow solid; m.p.: 77-80 ºC.

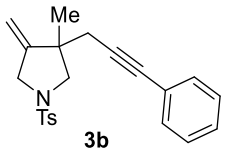
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.95-4.94 (m, 2H), 3.95-3.84 (m, 2H), 3.80 (s, 3H), 3.44 (d, *J* = 9.2 Hz, 1H), 3.02 (d, *J* = 9.6 Hz, 1H), 2.47-2.37 (m, 5H), 1.24 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.2, 150.7, 143.6, 132.9, 132.4, 129.6, 127.8, 115.4, 113.8, 106.4, 84.7, 82.3, 58.7, 55.2 (2C), 45.3, 30.0, 23.4, 21.5;

HRMS Calcd (ESI) m/z for $C_{23}H_{26}NO_3S$ $[M + H]^+$: 396.1628, found: 396.1639.



3-Methyl-4-methylene-3-(3-phenylprop-2-yn-1-yl)-1-tosylpyrrolidine (3b)



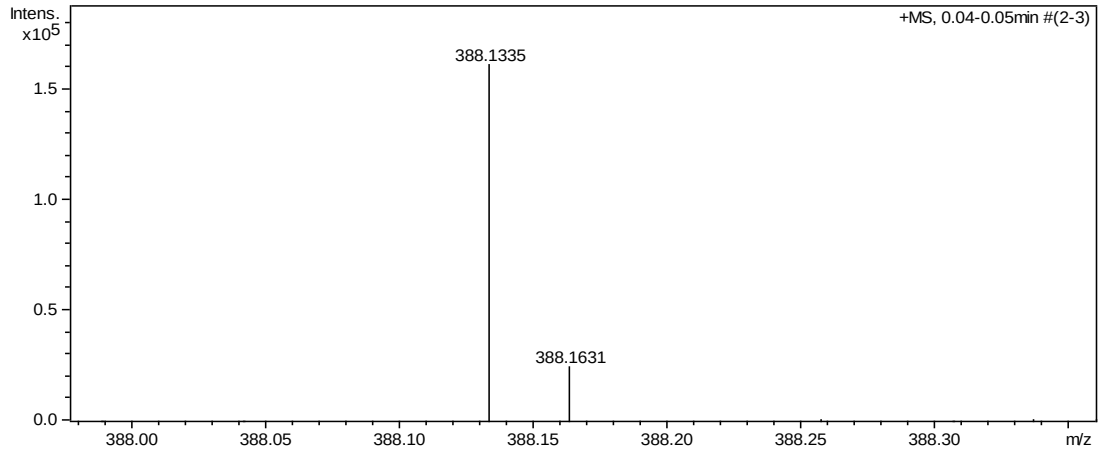
3b

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 9:1) gave the product **3b** (73.6 mg, 67% yield) as a yellow solid; m.p.: 47-49 ºC.

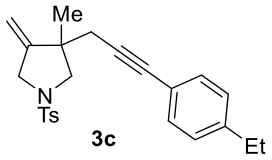
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.31-7.26 (m, 7H), 4.96-4.95 (m, 2H), 3.94-3.85 (m, 2H), 3.44 (d, *J* = 9.2 Hz, 1H), 3.03 (d, *J* = 9.6 Hz, 1H), 2.49-2.39 (m, 5H), 1.24 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 143.6, 132.4, 131.4, 129.6, 128.1, 127.7 (2C), 123.3, 106.4, 86.3, 82.5, 58.6, 52.2, 45.2, 29.9, 23.4, 21.4;

HRMS Calcd (ESI) m/z for $C_{22}H_{23}NNaO_2S$ $[M + Na]^+$: 388.1342, found: 388.1335.



3-(3-(4-Ethylphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-tosylpyrrolidine (3c)



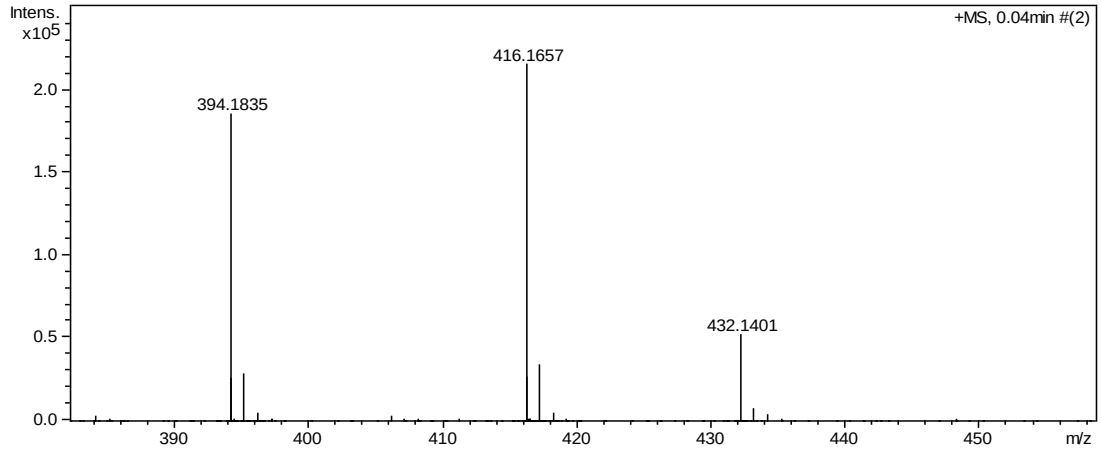
3c

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 15:1) gave the product **3c** (87.1 mg, 74% yield) as a yellow oil.

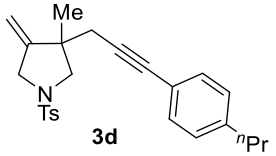
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.96-4.94 (m, 2H), 3.95-3.85 (m, 2H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.03 (d, *J* = 9.2 Hz, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.48-2.38 (m, 5H), 1.24-1.21 (m, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 144.2, 143.6, 132.4, 131.5, 129.6, 127.8, 127.7, 120.5, 106.4, 85.6, 82.6, 58.7, 52.3, 45.3, 30.0, 28.7, 23.5, 21.5, 15.4;

HRMS Calcd (ESI) m/z for $C_{24}H_{27}NNaO_2S$ $[M + Na]^+$: 416.1655, found: 416.1657.



3-Methyl-4-methylene-3-(3-(4-propylphenyl)prop-2-yn-1-yl)-1-tosylpyrrolidine (3d)



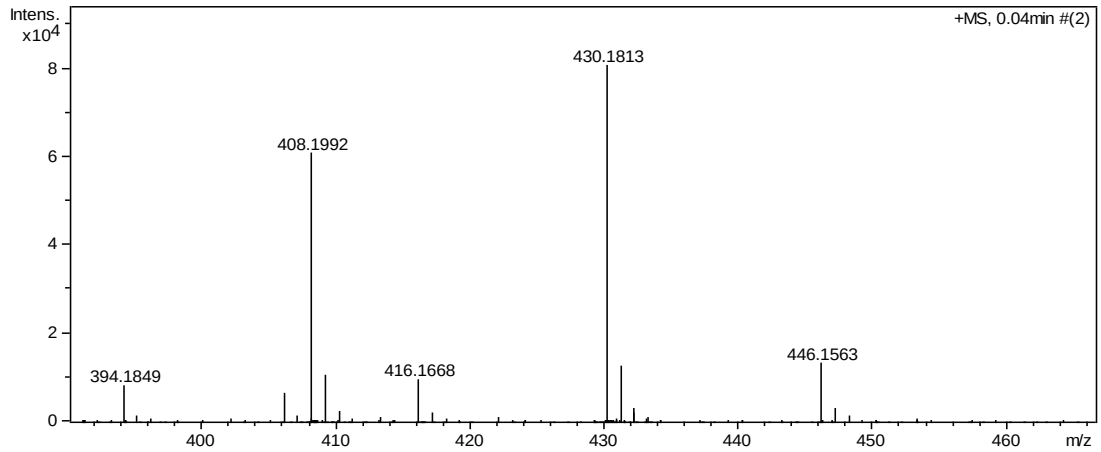
3d

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 15:1) gave the product **3d** (88.4 mg, 72% yield) as a yellow oil.

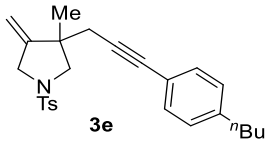
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 4.95 (s, 2H), 3.94-3.85 (m, 2H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.03 (d, *J* = 9.6 Hz, 1H), 2.59-2.55 (m, 2H), 2.48-2.38 (m, 5H), 1.67-1.58 (m, 2H), 1.24 (s, 3H), 0.95-0.91 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 143.6, 142.6, 132.4, 131.3, 129.6, 128.3, 127.8, 120.5, 106.4, 85.5, 82.6, 58.7, 52.2, 45.3, 37.8, 30.0, 24.3, 23.4, 21.5, 13.7;

HRMS Calcd (ESI) m/z for $C_{25}H_{29}NNaO_2S$ $[M + Na]^+$: 430.1811, found: 430.1813.



3-(3-(4-Butylphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-tosylpyrrolidine (3e)

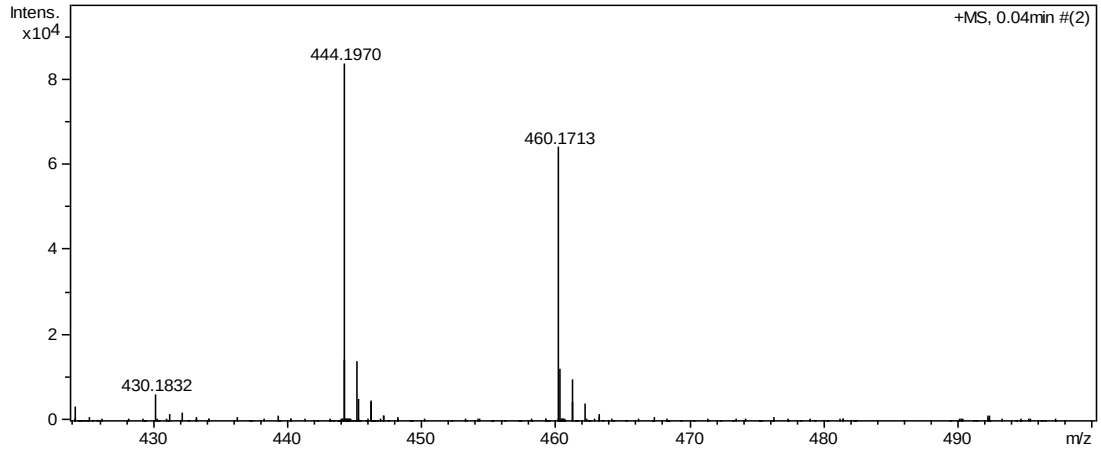


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 15:1) gave the product **3e** (86.8 mg, 69% yield) as a yellow oil.

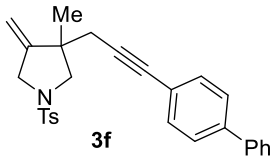
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.96-4.95 (m, 2H), 3.95-3.85 (m, 2H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.03 (d, *J* = 9.2 Hz, 1H), 2.61-2.57 (m, 2H), 2.48-2.38 (m, 5H), 1.62-1.58 (m, 2H), 1.39-1.30 (m, 2H), 1.24 (s, 3H), 0.94-0.91 (m, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.7, 143.6, 142.9, 132.5, 131.4, 129.6, 128.3, 127.8, 120.4, 106.4, 85.6, 82.7, 58.7, 52.3, 45.3, 35.5, 33.4, 30.0, 23.5, 22.2, 21.5, 13.9;

HRMS Calcd (ESI) m/z for $C_{26}H_{31}NNaO_2S$ $[M + Na]^+$: 444.1968, found: 444.1970.



3-(3-([1,1'-Biphenyl]-4-yl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-tosylpyrrolidine (3f)



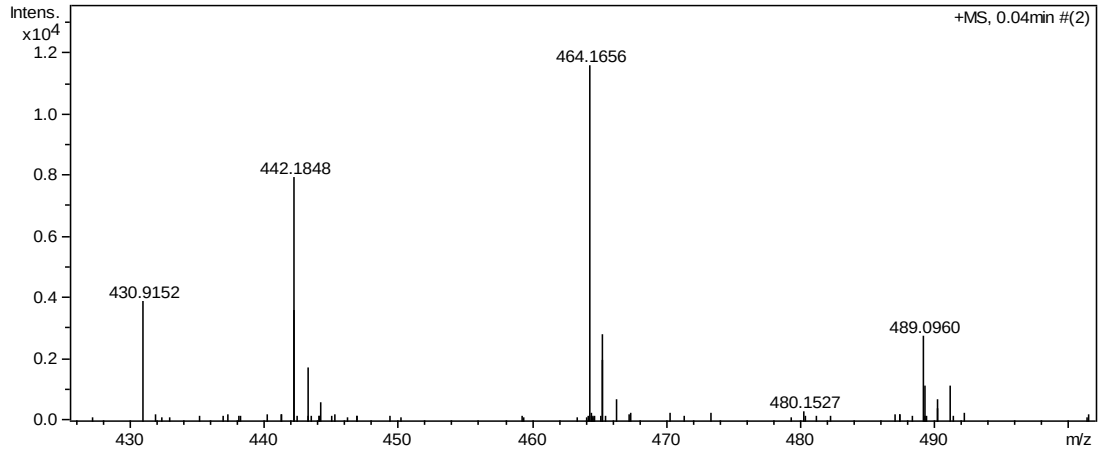
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10:1) gave the product **3f** (80.6 mg, 61% yield) as a yellow solid; m.p.: 106-109 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.47-7.36 (m, 5H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.99-4.98 (m, 2H),

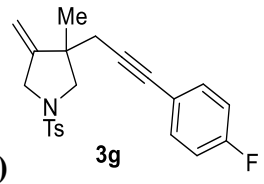
3.98-3.87 (m, 2H), 3.48 (d, J = 9.6 Hz, 1H), 3.06 (d, J = 9.2 Hz, 1H), 2.54-2.44 (m, 2H), 2.41 (s, 3H), 1.28 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 143.6, 140.6, 140.3, 132.5, 131.9, 129.6, 128.8, 127.8, 127.5, 126.9, 126.8, 122.3, 106.5, 87.1, 82.5, 58.7, 52.3, 45.3, 30.1, 23.5, 21.5;

HRMS Calcd (ESI) m/z for $C_{28}H_{27}NNaO_2S$ $[M + Na]^+$: 464.1655, found: 464.1656.



3-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-tosylpyrrolidine(3g)



3g

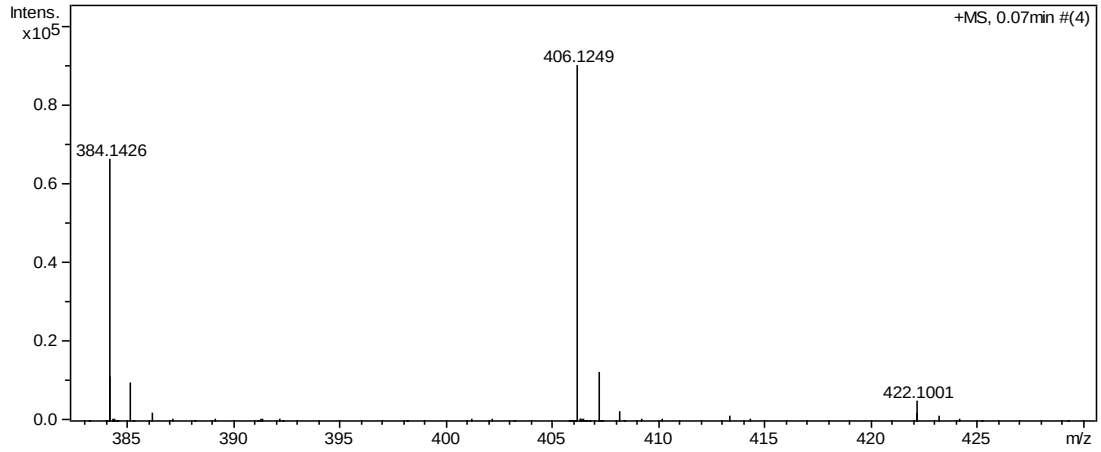
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 11:1) gave the product **3g** (54.8 mg, 48% yield) as a brown solid; m.p.: 60-63 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, J = 8.0 Hz, 2H), 7.32-7.28 (m, 4H), 6.99-6.95 (m, 2H), 4.97-4.94 (m, 2H), 3.96-3.91 (m, 1H), 3.87-3.83 (m, 1H), 3.44 (d, J = 9.2 Hz, 1H), 3.01 (d, J = 9.2 Hz, 1H), 2.49-2.39 (m, 5H), 1.23 (s, 3H);

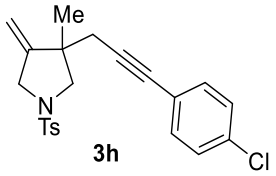
^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.2 (d, J = 247.6 Hz), 150.6, 143.7, 133.3(d, J = 8.2 Hz), 132.4, 128.7 (d, J = 180.6 Hz), 119.4 (d, J = 3.6 Hz), 115.4 (d, J = 21.9 Hz), 110.0, 106.5, 86.0, 81.5, 58.7, 52.2, 45.3, 30.0, 23.4, 21.5;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -111.6;

HRMS Calcd (ESI) m/z for $C_{22}H_{22}FNNaO_2S$ $[M + Na]^+$: 406.1247, found: 406.1249.



3-(3-(4-Chlorophenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-tosylpyrrolidine (3h)



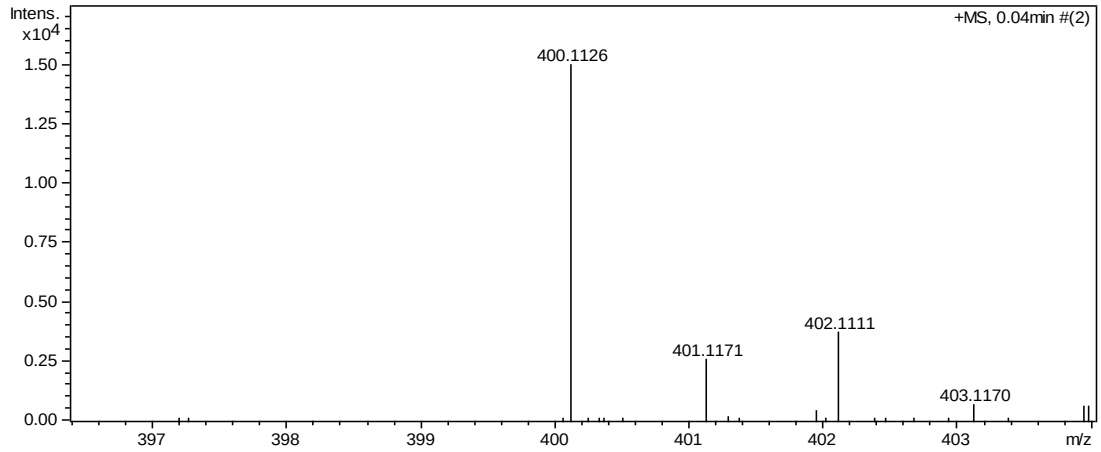
3h

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 11:1) gave the product **3h** (90.2 mg, 75% yield) as a yellow oil.

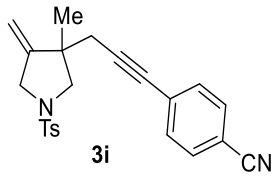
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (s, 4H), 4.97-4.94 (m, 2H), 3.96-3.91 (m, 1H), 3.87-3.83 (m, 1H), 3.43 (d, *J* = 9.2 Hz, 1H), 3.01 (d, *J* = 9.6 Hz, 1H), 2.51-2.41 (m, 5H), 1.23 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.5, 143.7, 133.7, 132.7, 132.4, 129.6, 128.4, 127.8, 121.8, 106.5, 87.5, 81.5, 58.7, 52.2, 45.2, 30.0, 23.4, 21.5;

HRMS Calcd (ESI) m/z for $C_{22}H_{23}ClNO_2S$ $[M + H]^+$: 400.1133, found: 400.1126.



4-(3-(3-Methyl-4-methylene-1-tosylpyrrolidin-3-yl)prop-1-yn-1-yl)benzonitrile (3i)



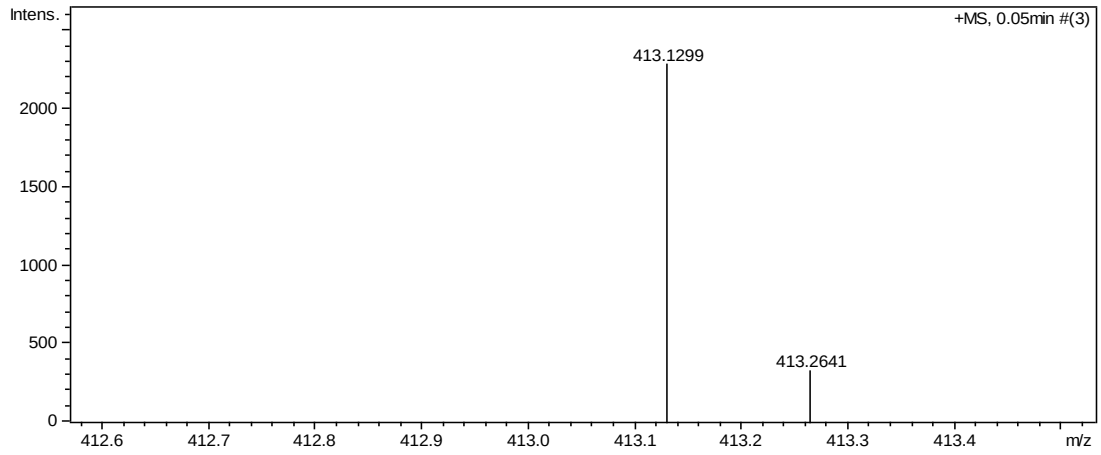
3i

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 5:1) gave the product **3i** (71.6 mg, 61% yield) as a brown oil.

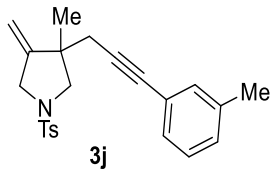
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.98-4.94 (m, 2H), 3.99-3.94 (m, 1H), 3.83-3.79 (m, 1H), 3.44 (d, *J* = 9.6 Hz, 1H), 2.97 (d, *J* = 9.6 Hz, 1H), 2.57-2.45 (m, 2H), 2.41 (s, 3H), 1.23 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.4, 143.7, 132.4, 132.1, 131.9, 129.7, 128.3, 127.8, 118.4, 111.2, 106.7, 91.5, 81.3, 58.7, 52.1, 45.2, 30.2, 23.2, 21.5;

HRMS Calcd (ESI) m/z for $C_{23}H_{22}N_2NaO_2S$ $[M + Na]^+$: 413.1294, found: 413.1299.



3-Methyl-4-methylene-3-(3-(m-tolyl)prop-2-yn-1-yl)-1-tosylpyrrolidine (3j)



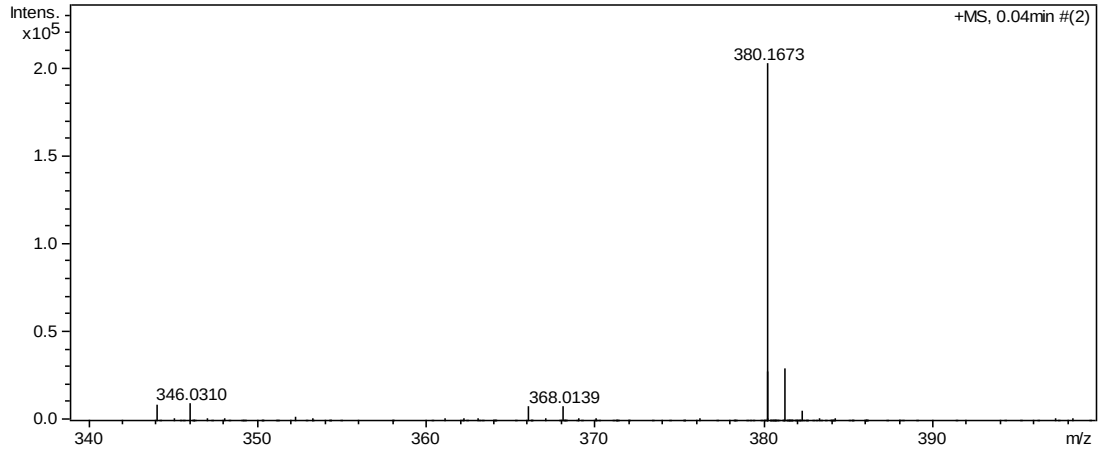
3j

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 11:1) gave the product **3j** (85.3 mg, 75% yield) as a yellow oil.

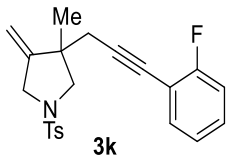
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19-7.09 (m, 4H), 4.96-4.95 (m, 2H), 3.96-3.84 (m, 2H), 3.44 (d, *J* = 9.6 Hz, 1H), 3.03 (d, *J* = 9.6 Hz, 1H), 2.49-2.39 (m, 5H), 2.32 (s, 3H), 1.25 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.7, 143.6, 137.8, 132.5, 132.1, 129.6, 128.7, 128.6, 128.1, 127.8, 123.1, 106.5, 86.0, 82.7, 58.7, 52.2, 45.3, 30.0, 23.4, 21.5, 21.2;

HRMS Calcd (ESI) m/z for $C_{23}H_{26}NO_2S$ $[M + H]^+$: 380.1679, found: 380.1673.



3-(3-(2-Fluorophenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-tosylpyrrolidine(3k)



3k

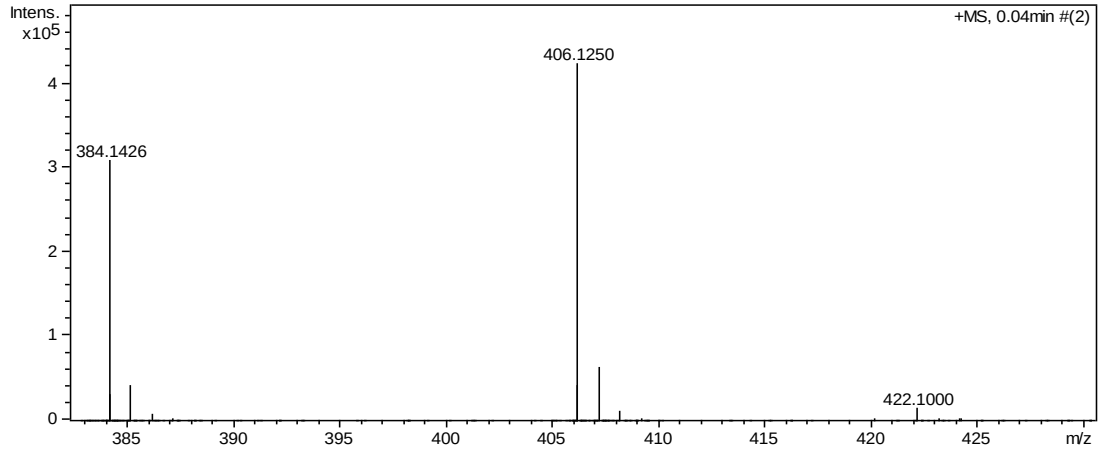
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10:1) gave the product **3k** (70.1 mg, 61% yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.34-7.30 (m, 3H), 7.28-7.23 (m, 1H), 7.08-7.01 (m, 2H), 4.98-4.97 (m, 2H), 3.96-3.91 (m, 1H), 3.89-3.85 (m, 1H), 3.45 (d, *J* = 9.6 Hz, 1H), 3.04 (d, *J* = 9.6 Hz, 1H), 2.48-2.47 (m, 2H), 2.40 (s, 3H), 1.26 (s, 3H);

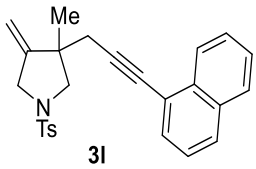
^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.8 (d, *J* = 249.3 Hz), 150.4, 143.6, 133.3 (d, *J* = 1.3 Hz), 132.4, 129.6, 129.4 (d, *J* = 7.8 Hz), 127.7, 123.7 (d, *J* = 3.7 Hz), 115.3 (d, *J* = 20.8 Hz), 111.8 (d, *J* = 15.7 Hz), 106.6, 91.9 (d, *J* = 3.3 Hz), 75.9 (d, *J* = 0.6 Hz), 58.7, 52.2, 45.2, 30.1, 23.2, 21.5;

^{19}F NMR ($CDCl_3$, 376 MHz) δ -110.6;

HRMS Calcd (ESI) m/z for $C_{22}H_{22}FNNaO_2S$ $[M + Na]^+$: 406.1247, found: 406.1250.



3-Methyl-4-methylene-3-(3-(naphthalen-1-yl)prop-2-yn-1-yl)-1-tosylpyrrolidine (3l)



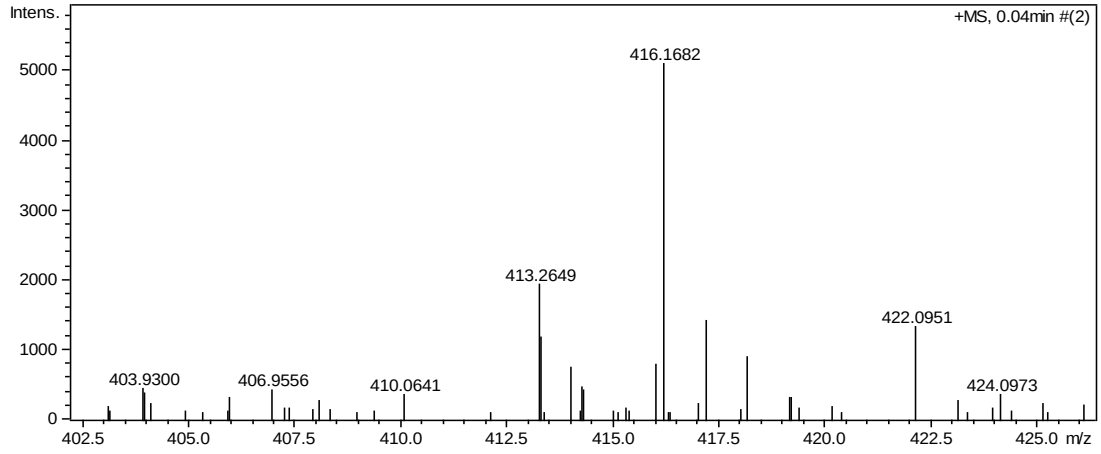
3l

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10:1) gave the product **3l** (97.3 mg, 78% yield) as a yellow oil.

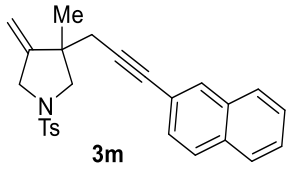
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.86-7.79 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.58-7.50 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.03-5.02 (m, 2H), 4.02-3.91 (m, 2H), 3.56 (d, *J* = 9.6 Hz, 1H), 3.11 (d, *J* = 9.6 Hz, 1H), 2.69-2.58 (m, 2H), 2.33 (s, 3H), 1.34 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 143.6, 133.3, 133.1, 132.4, 130.2, 129.6, 128.2 (2C), 127.7, 126.6, 126.2, 126.0, 125.1, 121.0, 106.6, 91.3, 80.6, 58.7, 52.3, 45.4, 30.3, 23.6, 21.4;

HRMS Calcd (ESI) m/z for $C_{26}H_{26}NO_2S$ $[M + H]^+$: 416.1679, found: 416.1682.



3-Methyl-4-methylene-3-(3-(naphthalen-2-yl)prop-2-yn-1-yl)-1-tosylpyrrolidine (3m)



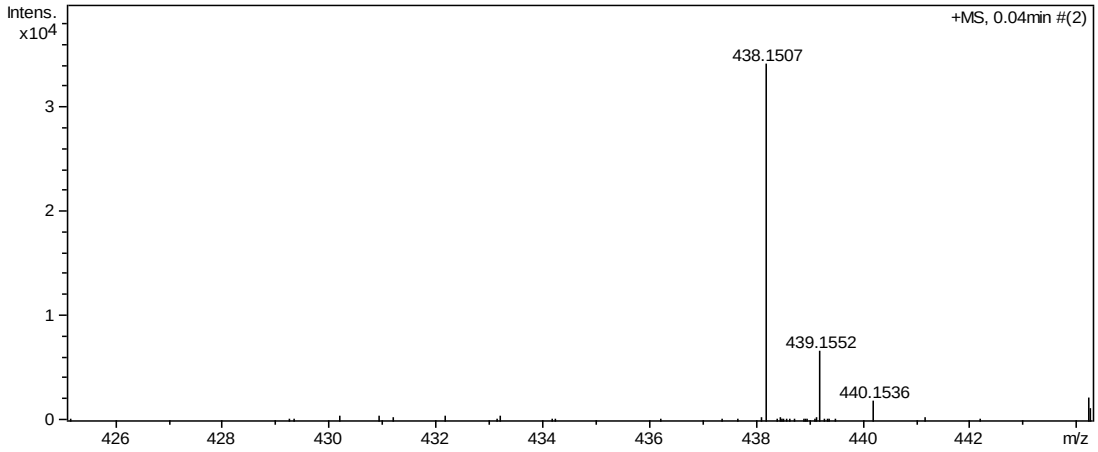
3m

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10:1) gave the product **3m** (67.2 mg, 54% yield) as a yellow solid; m.p.: 82-85 ºC.

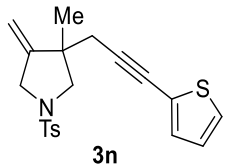
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (s, 1H), 7.81-7.73 (m, 5H), 7.51-7.45 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 5.00-4.99 (m, 2H), 3.99-3.87 (m, 2H), 3.50 (d, *J* = 9.6 Hz, 1H), 3.07 (d, *J* = 9.2 Hz, 1H), 2.56-2.46 (m, 2H), 2.35 (s, 3H), 1.29 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.8, 143.7, 132.9, 132.5, 132.4, 131.1, 129.6, 128.5, 127.8 (2C), 127.7, 127.5, 126.5, 126.4, 120.6, 106.6, 86.8, 83.0, 58.8, 52.3, 45.3, 30.1, 23.5, 21.5;

HRMS Calcd (ESI) m/z for $C_{26}H_{25}NNaO_2S$ $[M + Na]^+$: 438.1498, found: 438.1507.



3-Methyl-4-methylene-3-(3-(thiophen-3-yl)prop-2-yn-1-yl)-1-tosylpyrrolidine (3n)



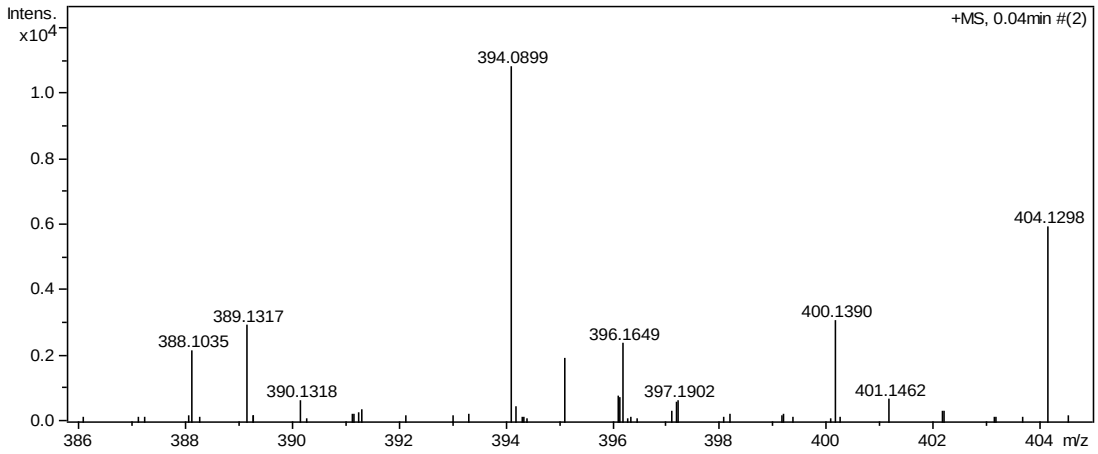
3n

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) gave the product **3n** (66.5 mg, 60% yield) as a yellow solid; m.p.: 53-57 ºC.

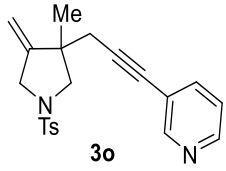
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.33-7.29 (m, 3H), 7.24-7.22 (m, 1H), 7.01-6.99 (m, 1H), 4.96-4.93 (m, 2H), 3.94-3.83 (m, 2H), 3.43 (d, *J* = 9.2 Hz, 1H), 3.01 (d, *J* = 9.2 Hz, 1H), 2.48-2.38 (m, 5H), 1.23 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.6, 143.7, 132.4, 129.9, 129.6, 128.0, 127.8, 125.1, 122.3, 106.5, 85.9, 77.6, 58.7, 52.2, 45.2, 30.0, 23.5, 21.5;

HRMS Calcd (ESI) m/z for $C_{20}H_{21}NNaO_2S_2$ $[M + Na]^+$: 394.0906, found: 394.0899.



3-(3-(3-Methyl-4-methylene-1-tosylpyrrolidin-3-yl)prop-1-yn-1-yl)pyridine (3o)



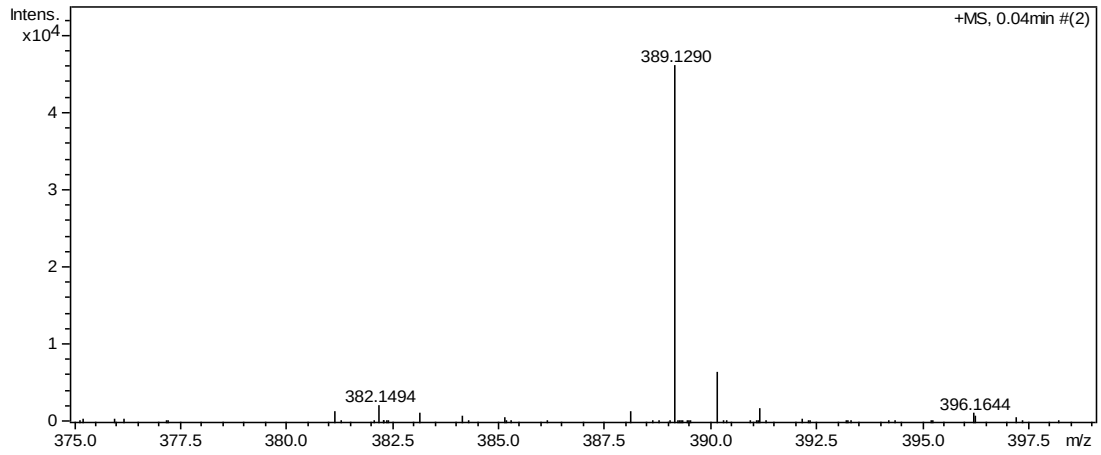
3o

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 3:1) gave the product **3o** (70.8 mg, 64% yield) as a yellow solid; m.p.: 59-63 °C.

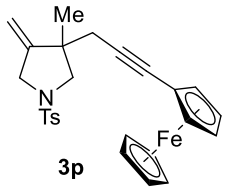
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.52 (d, *J* = 15.2 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23-7.20 (m, 1H), 4.96 (d, *J* = 8.0 Hz, 2H), 3.96-3.82 (m, 2H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.00 (d, *J* = 9.2 Hz, 1H), 2.55-2.44 (m, 2H), 2.41 (s, 3H), 1.24 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.2, 150.4, 148.2, 143.8, 138.5, 132.2, 129.7, 127.8, 122.9, 120.4, 106.7, 90.1, 79.4, 58.6, 52.2, 45.2, 30.1, 23.3, 21.6;

HRMS Calcd (ESI) m/z for $C_{21}H_{22}N_2NaO_2S$ $[M + Na]^+$: 389.1294, found: 389.1290.



3-Methyl-4-methylene-3-(3-ferrocylprop-2-yn-1-yl)-1-tosylpyrrolidine (3p)



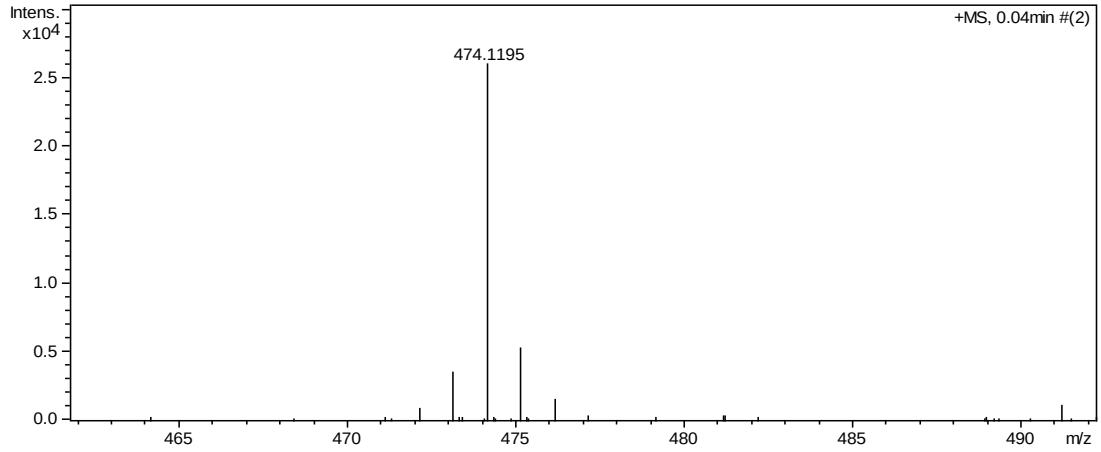
3p

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 11:1) gave the product **3p** (83.7 mg, 59% yield) as a yellow solid; m.p.: 104-108 °C.

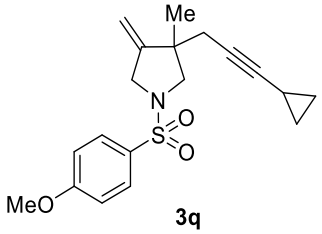
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.96-4.95 (m, 2H), 4.31 (d, *J* = 12.0 Hz, 2H), 4.17-4.11 (m, 7H), 3.94-3.84 (m, 2H), 3.42 (d, *J* = 9.2 Hz, 1H), 3.01 (d, *J* = 9.2 Hz, 1H), 2.43 (s, 3H), 2.40-2.29 (m, 2H), 1.23 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.7, 143.6, 132.5, 129.7, 127.8, 106.4, 82.3, 80.5, 71.2, 69.7, 68.2, 65.6, 58.7, 52.2, 45.2, 30.1, 23.5, 21.5;

HRMS Calcd (ESI) m/z for $C_{26}H_{28}FeNO_2S$ $[M + H]^+$: 474.1185, found: 474.1195.



3-(3-Cyclopropylprop-2-yn-1-yl)-1-((4-methoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3q)



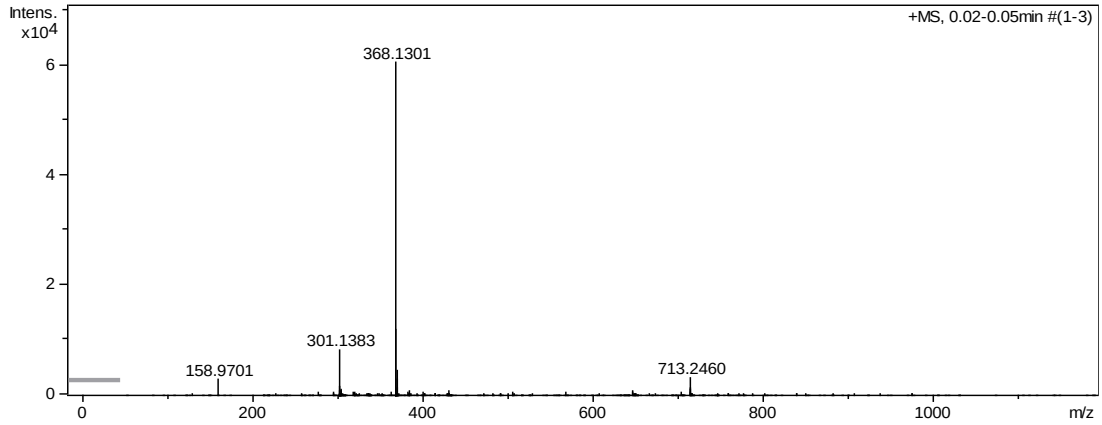
3q

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 5:1) gave the product **3q** (25.9 mg, 25% yield) as a yellow oil.

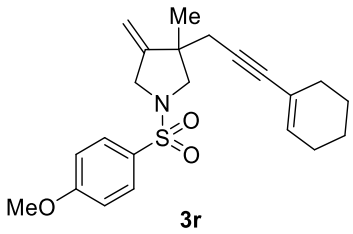
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 4.88 (d, *J* = 18.0 Hz, 2H), 3.88-3.83 (m, 5H), 3.30 (d, *J* = 9.2 Hz, 1H), 2.95 (d, *J* = 9.2 Hz, 1H), 2.20-2.10 (m, 2H), 1.25 (s, 1H), 1.15 (s, 3H), 0.70-0.68 (m, 2H), 0.53 (s, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.0, 150.9, 129.9, 127.3, 114.2, 106.1, 85.6, 71.7, 58.6, 55.6, 52.3, 45.2, 29.5, 23.4, 8.0 (2C), -0.6;

HRMS Calcd (ESI) m/z for $C_{19}H_{23}NNaO_3S$ $[M + Na]^+$: 368.1291, found: 368.1301.



3-(3-(Cyclohex-1-en-1-yl)prop-2-yn-1-yl)-1-((4-methoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (3r)



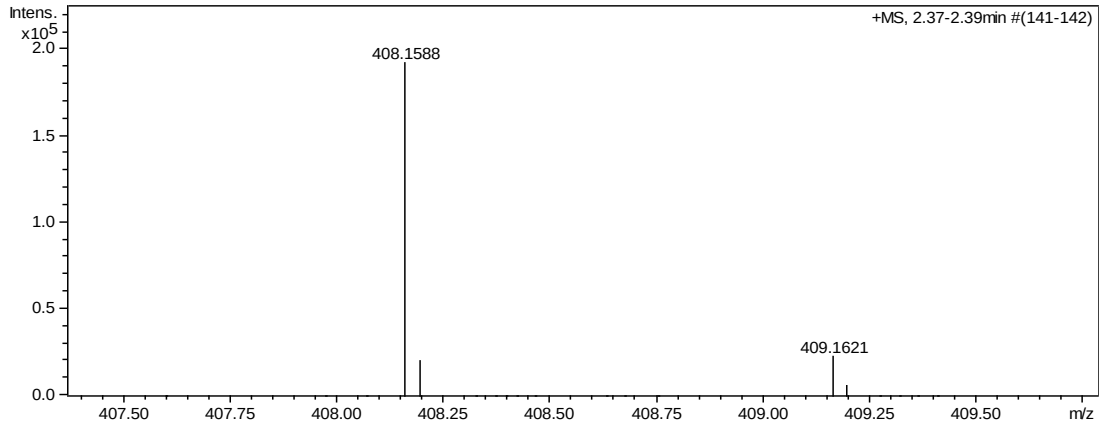
3r

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 7:1) gave the product **3r** (72.2 mg, 62% yield) as a yellow oil.

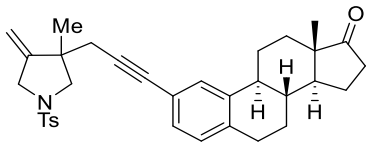
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 5.94 (s, 1H), 4.91 (d, *J* = 11.2 Hz, 2H), 3.86-3.84 (m, 5H), 3.33 (d, *J* = 9.6 Hz, 1H), 2.98 (d, *J* = 9.6 Hz, 1H), 2.36-2.26 (m, 2H), 2.05-2.01 (m, 4H), 1.61-1.55 (m, 4H), 1.18 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.0, 150.8, 133.7, 129.9, 127.2, 120.6, 114.1, 106.3, 84.4, 83.4, 58.7, 55.5, 52.3, 45.2, 29.9, 29.4, 25.5, 23.5, 22.3, 21.5;

HRMS Calcd (ESI) m/z for $C_{22}H_{27}NNaO_3S$ $[M + Na]^+$: 408.1604, found: 408.1588.



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-2-(3-(3-methyl-4-methylene-1-tosylpyrrolidin-3-yl)prop-1-yn-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (3s)



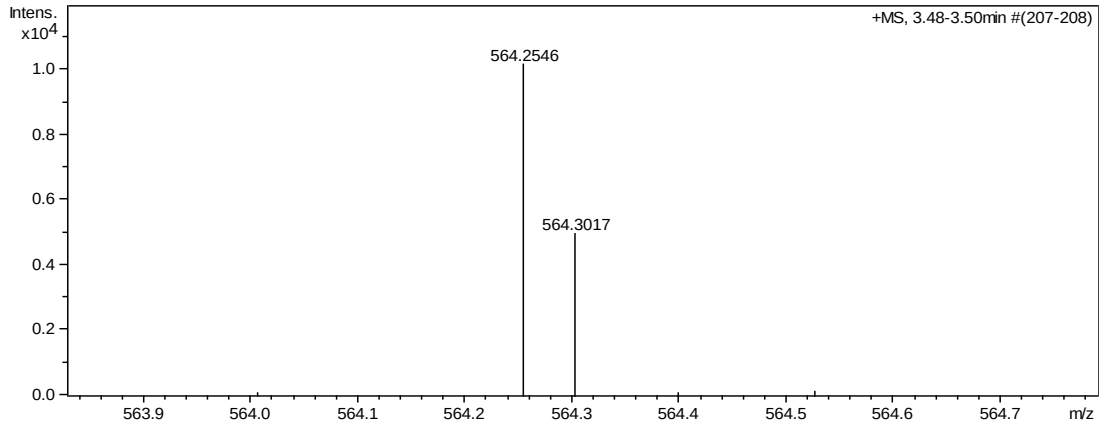
3s

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 5:1) gave the product **3s** (84.7 mg, 52% yield) as a yellow solid; m.p.: 198-201 ºC.

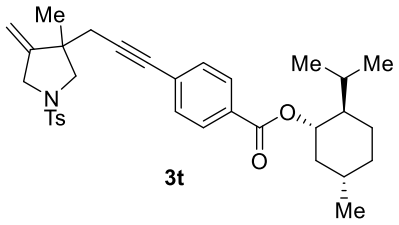
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 6.8 Hz, 2H), 4.94 (s, 2H), 3.93 (d, *J* = 14.4 Hz, 1H), 3.84 (d, *J* = 14.0 Hz, 1H), 3.43 (d, *J* = 9.2 Hz, 1H), 3.00 (d, *J* = 9.2 Hz, 1H), 2.88-2.85 (m, 2H), 2.53-2.46 (m, 1H), 2.42-2.37 (m, 5H), 2.29-2.25 (m, 1H), 2.18-1.94 (m, 5H), 1.67-1.57 (m, 2H), 1.52-1.37 (m, 4H), 1.23 (s, 3H), 0.90 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 220.6, 150.6, 143.6, 139.7, 136.4, 132.4, 131.9, 129.6, 128.8, 127.7, 125.2, 120.6, 106.4, 85.6, 82.5, 58.7, 52.1, 50.3, 47.8, 45.2, 44.3, 37.9, 35.7, 31.4, 30.0, 29.0, 26.2, 25.5, 23.2, 21.5, 13.7, 0.9;

HRMS Calcd (ESI) m/z for $C_{34}H_{39}NNaO_3S$ $[M + Na]^+$: 564.2543, found: 564.2546.



(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl-4-(3-(3-methyl-4-methylene-1-tosylpyrrolidin-3-yl)prop-1-yn-1-yl)benzoate (3t)



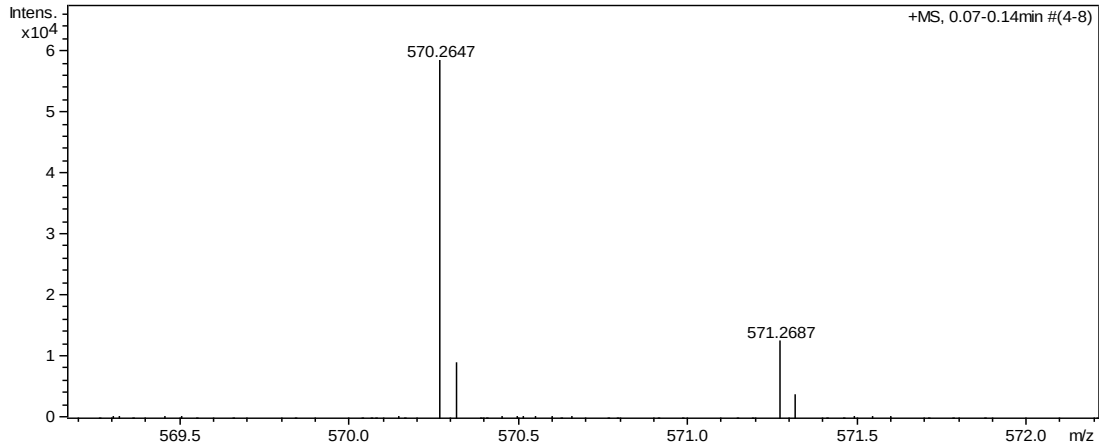
3t

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10:1) gave the product **3t** (100.5 mg, 61% yield) as a yellow oil.

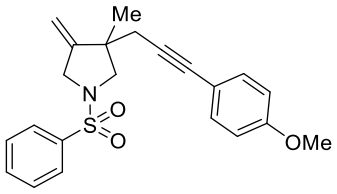
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.36-7.30 (m, 4H), 4.96 (d, *J* = 7.2 Hz, 2H), 4.92-4.89 (m, 1H), 3.93 (d, *J* = 14.0 Hz, 1H), 3.85 (d, *J* = 14.0 Hz, 1H), 3.43 (d, *J* = 9.6 Hz, 1H), 3.01 (d, *J* = 9.6 Hz, 1H), 2.54-2.43 (m, 2H), 2.40 (s, 3H), 2.11 (d, *J* = 12.0 Hz, 1H), 1.95-1.90 (m, 1H), 1.72 (d, *J* = 11.2 Hz, 2H), 1.57-1.52 (m, 2H), 1.25 (s, 3H), 1.17-1.05 (m, 3H), 0.93-0.90 (m, 6H), 0.79 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.5, 150.5, 143.7, 132.3, 131.4, 129.8, 129.6, 129.3, 127.8, 106.6, 89.6, 82.1, 75.0, 58.7, 52.2, 47.2, 45.3, 40.9, 34.2, 31.4, 30.1, 26.5, 23.6, 23.5, 22.0, 21.5, 20.7, 16.5;

HRMS Calcd (ESI) m/z for $C_{33}H_{41}NNaO_4S$ $[M + Na]^+$: 570.2649, found: 570.2647.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-(phenylsulfonyl)pyrrolidine (4a)



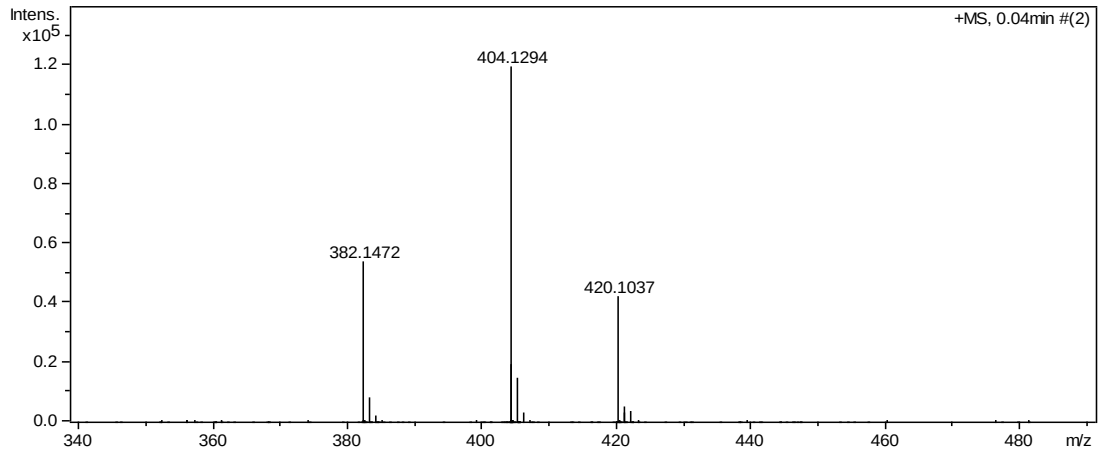
4a

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10:1) gave the product **4a** (82.6 mg, 72% yield) as a yellow solid; m.p.: 71-74 °C.

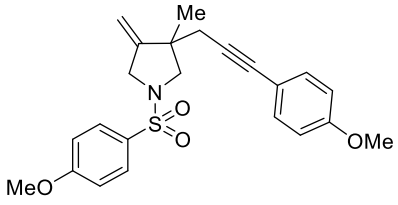
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.52-7.42 (m, 3H), 7.17 (d, *J* = 6.8 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 4.87 (s, 2H), 3.88-3.79 (m, 2H), 3.72 (s, 3H), 3.39 (d, *J* = 9.2 Hz, 1H), 2.97 (d, *J* = 9.2 Hz, 1H), 2.37-2.28 (m, 2H), 1.15 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.2, 150.5, 135.4, 132.8 (2C), 129.0, 127.6, 115.4, 113.7, 106.5, 84.6, 82.3, 58.6, 55.2, 52.2, 45.3, 29.9, 23.3;

HRMS Calcd (ESI) m/z for $C_{22}H_{23}NNaO_3S$ $[M + Na]^+$: 404.1291, found: 404.1294.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-1-((4-methoxyphenyl)sulfonyl)-3-methyl-4-methylenepyrrolidine (4b)



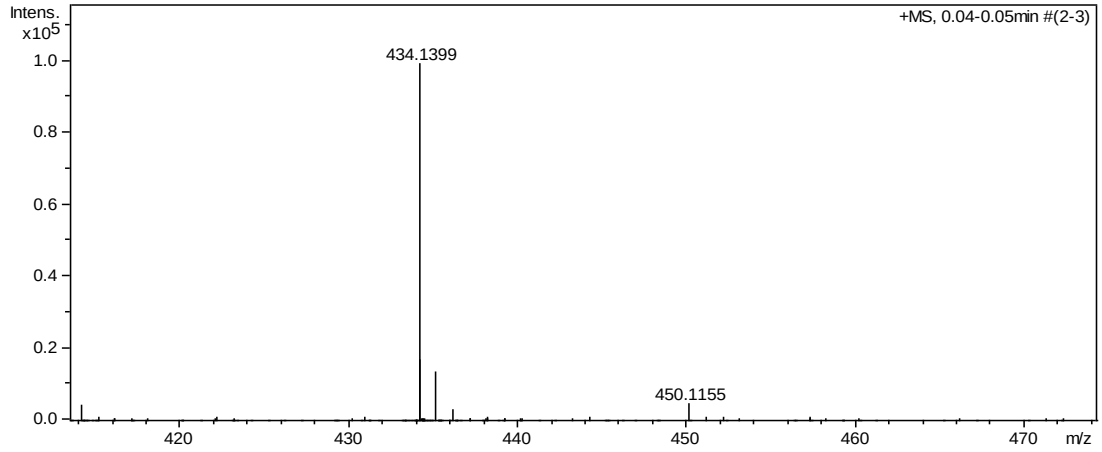
4b

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 5:1) gave the product **4b** (84.0 mg, 68% yield) as a yellow oil.

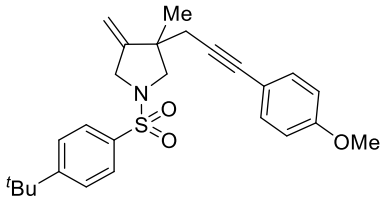
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 9.2 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 4.95-4.94 (m, 2H), 3.89-3.87 (m, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.42 (d, *J* = 9.6 Hz, 1H), 3.02 (d, *J* = 9.6 Hz, 1H), 2.47-2.37 (m, 2H), 1.24 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.9, 159.1, 150.7, 132.8, 129.8, 126.9, 115.4, 114.1, 113.7, 106.3, 84.7, 82.3, 58.6, 55.5, 55.1, 52.3, 45.2, 29.9, 23.6;

HRMS Calcd (ESI) m/z for $C_{23}H_{25}NNaO_4S$ $[M + Na]^+$: 434.1397, found: 434.1399.



1-((4-(*Tert*-butyl)phenyl)sulfonyl)-3-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylenepyrrolidine (4c)



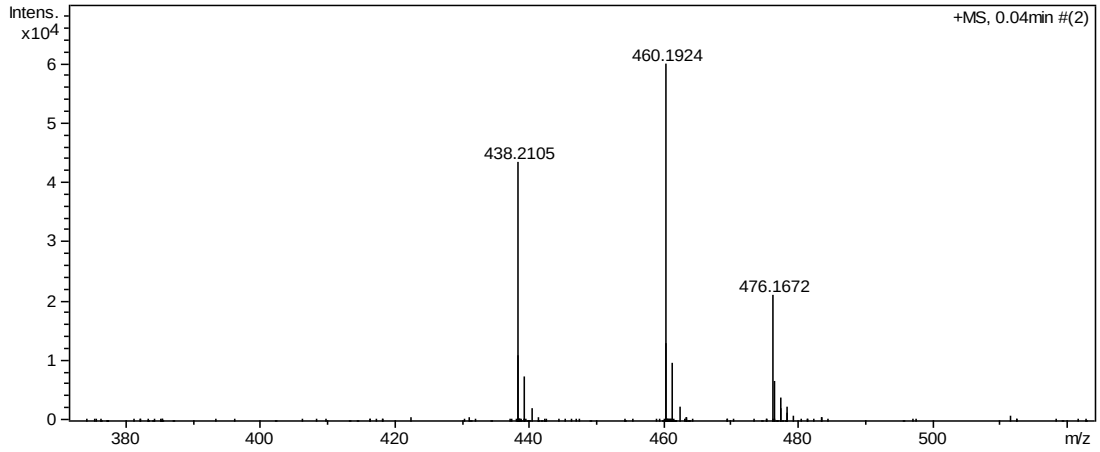
4c

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 12:1) gave the product **4c** (94.3 mg, 72% yield) as a yellow solid; m.p.: 85-89 ºC.

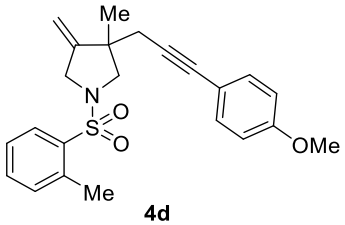
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.96-4.95 (m, 2H), 3.99-3.94 (m, 1H), 3.90-3.85 (m, 1H), 3.80 (s, 3H), 3.46 (d, *J* = 9.6 Hz, 1H), 3.04 (d, *J* = 9.2 Hz, 1H), 2.47-2.37 (m, 2H), 1.33 (s, 9H), 1.24 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.2, 156.5, 150.8, 132.9, 132.7, 127.6, 126.0, 115.5, 113.8, 106.4, 84.8, 82.3, 58.7, 55.2, 52.2, 45.3, 35.1, 31.0, 30.0, 23.2;

HRMS Calcd (ESI) m/z for $C_{26}H_{31}NNaO_3S$ $[M + Na]^+$: 460.1917, found: 460.1924.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-(o-tolylsulfonyl)pyrrolidine (4d)



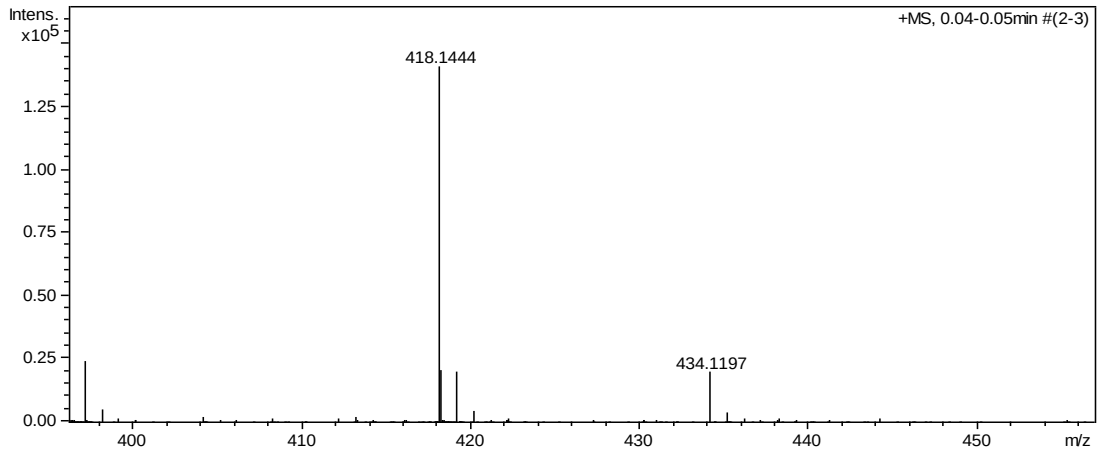
4d

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 15:1) gave the product **4d** (73.4 mg, 62% yield) as a yellow oil.

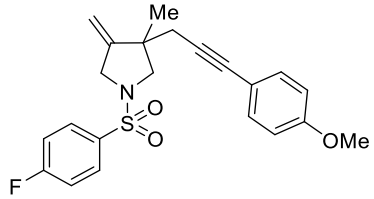
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95-7.93 (m, 1H), 7.46-7.42 (m, 1H), 7.32-7.28 (m, 2H), 7.27-7.24 (m, 2H), 6.80 (d, *J* = 9.2 Hz, 2H), 5.00-4.98 (m, 2H), 3.99-3.98 (m, 2H), 3.79 (s, 3H), 3.51 (d, *J* = 9.2 Hz, 1H), 3.16 (d, *J* = 9.6 Hz, 1H), 2.66 (s, 3H), 2.55-2.43 (m, 2H), 1.28 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.2, 150.7, 138.1, 135.9, 132.8 (2C), 132.7, 129.9, 126.0, 115.4, 113.7, 106.4, 84.6, 82.3, 58.1, 55.2, 51.6, 45.3, 30.0, 23.2, 20.7;

HRMS Calcd (ESI) m/z for $C_{23}H_{25}NNaO_3S$ $[M + Na]^+$: 418.1447, found: 418.1444.



1-((4-Fluorophenyl)sulfonyl)-3-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylenepyrrolidine (4e)



4e

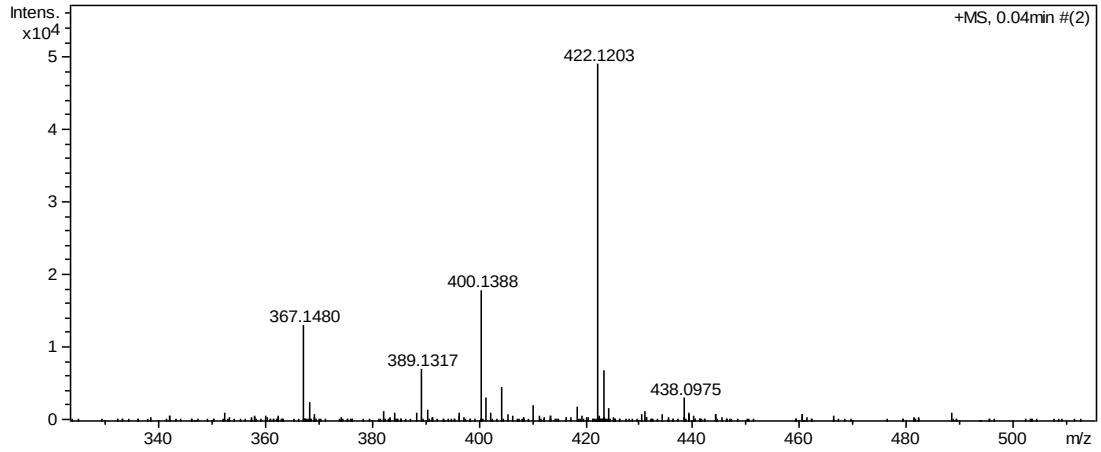
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10:1) gave the product **4e** (78.6 mg, 66% yield) as a yellow solid; m.p.: 87-91 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87-7.83 (m, 2H), 7.27-7.17 (m, 4H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.98-4.97 (m, 2H), 3.92-3.91 (m, 2H), 3.80 (s, 3H), 3.45 (d, *J* = 9.2 Hz, 1H), 3.05 (d, *J* = 9.2 Hz, 1H), 2.47-2.38 (m, 2H), 1.25 (s, 3H);

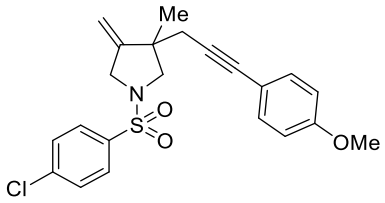
^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.2 (d, *J* = 253.7 Hz), 159.3, 150.4, 132.9, 131.8, 130.4 (d, *J* = 9.2 Hz), 116.3 (d, *J* = 22.3 Hz), 115.3, 113.8, 106.7, 84.6, 82.5, 58.7, 55.3, 52.3, 45.4, 30.0, 23.6;

^{19}F NMR ($CDCl_3$, 376 MHz) -104.8;

HRMS Calcd (ESI) m/z for $C_{22}H_{22}FNNaO_3S$ $[M + Na]^+$: 422.1197, found: 422.1203.



1-((4-Chlorophenyl)sulfonyl)-3-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylenepyrrolidine (4f)



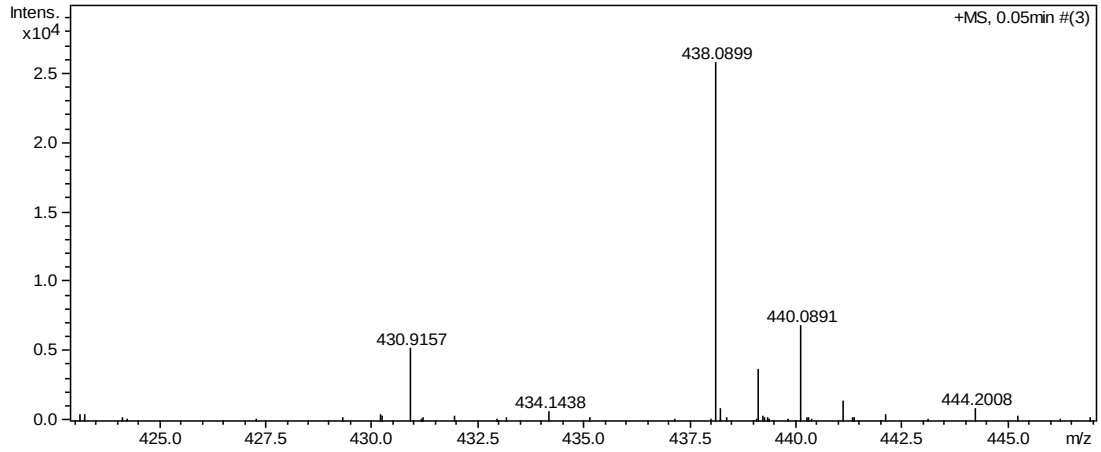
4f

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 12:1) gave the product **4f** (83.2 mg, 64% yield) as a yellow oil.

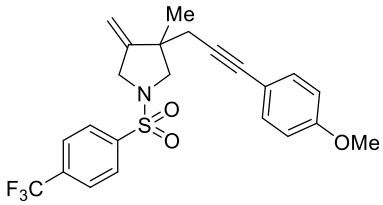
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 4.90-4.89 (m, 2H), 3.84-3.83 (m, 2H), 3.73 (s, 3H), 3.38 (d, *J* = 9.6 Hz, 1H), 2.98 (d, *J* = 9.6 Hz, 1H), 2.40-2.30 (m, 2H), 1.17 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 150.3, 139.3, 134.2, 132.8, 129.3, 129.1, 115.3, 113.8, 106.7, 84.5, 82.5, 58.6, 55.2, 52.2, 45.4, 30.0, 23.5;

HRMS Calcd (ESI) m/z for $C_{22}H_{22}ClNNaO_3S$ $[M + Na]^+$: 438.0901, found: 438.0899.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-((4-(trifluoromethyl)phenyl)sulfonyl)pyrrolidine (4g)



4g

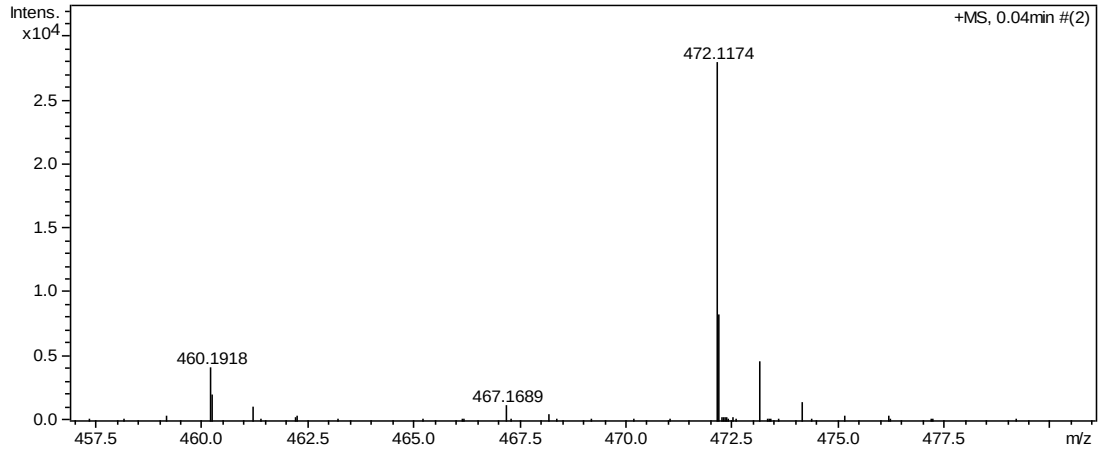
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10:1) gave the product **4g** (67.0 mg, 50% yield) as a brown solid; m.p.: 98-101 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 6.4 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.98-4.97 (m, 2H), 4.00-3.90 (m, 2H), 3.80 (s, 3H), 3.50 (d, *J* = 9.6 Hz, 1H), 3.07 (d, *J* = 9.6 Hz, 1H), 2.47-2.38 (m, 2H), 1.25 (s, 3H);

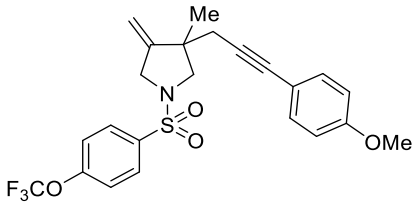
^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 150.0, 139.5, 134.4 (q, *J* = 32.9 Hz), 132.8, 128.1, 126.2 (q, *J* = 3.6 Hz), 123.2 (q, *J* = 271.6 Hz), 115.3, 113.8, 106.9, 84.4, 82.6, 58.7, 55.24, 52.2, 45.5, 29.9, 23.4;

^{19}F NMR ($CDCl_3$, 376 MHz) -63.0;

HRMS Calcd (ESI) m/z for $C_{23}H_{22}F_3NNaO_3S$ $[M + Na]^+$: 472.1165, found: 472.1174.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-((4-(trifluoromethoxy)phenyl)sulfonyl)pyrrolidine (4h)



4h

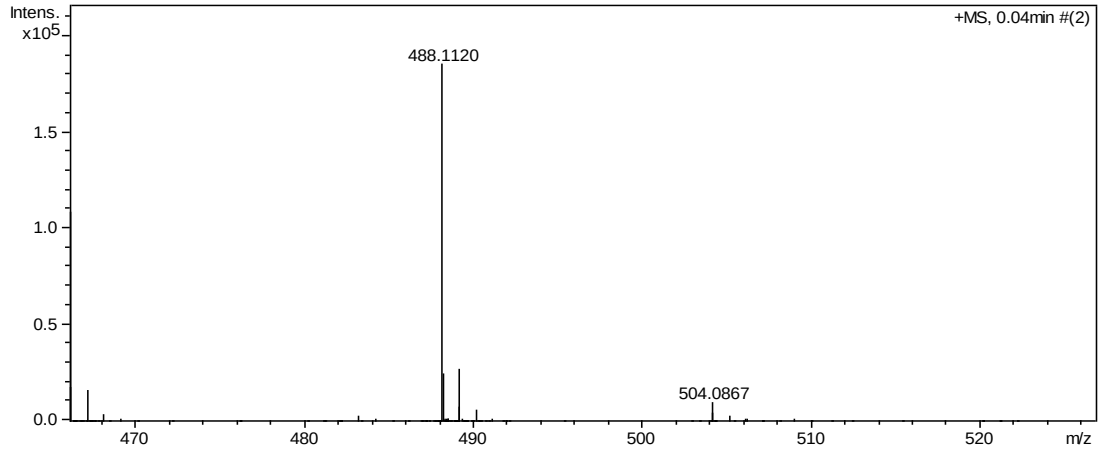
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 10: 1) gave the product **4h** (84.0 mg, 60% yield) as a yellow solid; M.p.: 70-73 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.99-4.98 (m, 2H), 3.98-3.89 (m, 2H), 3.80 (s, 3H), 3.48 (d, *J* = 9.2 Hz, 1H), 3.07 (d, *J* = 9.2 Hz, 1H), 2.47-2.38 (m, 2H), 1.26 (s, 3H);

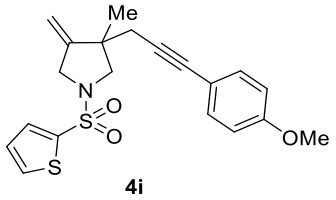
^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 152.3, 152.2, 150.2, 134.2, 132.8, 129.8, 120.8, 120.2 (q, J = 258.2 Hz), 115.3, 113.8, 106.8, 84.5, 82.5, 58.7, 55.2, 52.2, 45.4, 30.0, 23.4;

^{19}F NMR ($CDCl_3$, 376 MHz) -57.6;

HRMS Calcd (ESI) m/z for $C_{23}H_{22}F_3NNaO_4S$ $[M + Na]^+$: 488.1114, found: 488.1120.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-(thiophen-2-ylsulfonyl)pyrrolidine (4i)



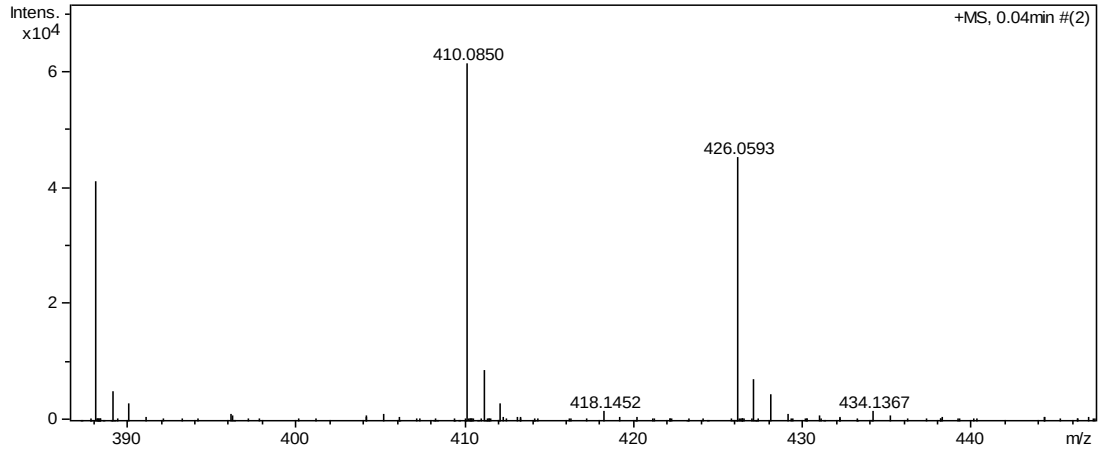
4i

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 8:1) gave the product **4i** (83.8 mg, 72% yield) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61-7.58 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.14-7.12 (m, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.99-4.97 (m, 2H), 4.04-3.93 (m, 2H), 3.80 (s, 3H), 3.51 (d, *J* = 9.6 Hz, 1H), 3.10 (d, *J* = 9.6 Hz, 1H), 2.48-2.38 (m, 2H), 1.25 (s, 3H);

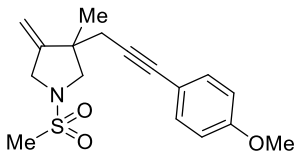
^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.2, 150.3, 135.6, 132.9, 132.5, 132.0, 127.6, 115.4, 113.8, 106.7, 84.6, 82.4, 58.8, 55.2, 52.4, 45.5, 30.0, 23.4;

HRMS Calcd (ESI) m/z for $C_{20}H_{21}NNaO_3S_2$ $[M + Na]^+$: 410.0855, found: 410.0850.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylene-1-(methylsulfonyl)

pyrrolidine (4j)



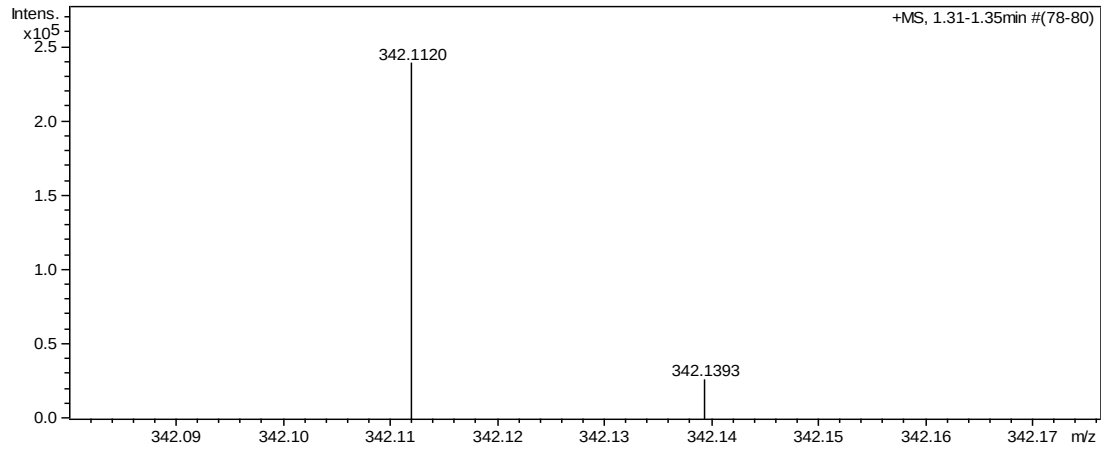
4j

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 4: 1) gave the product **4j** (30.7 mg, 33% yield) as a brown solid; m.p.: 57-60 ^{o}C.

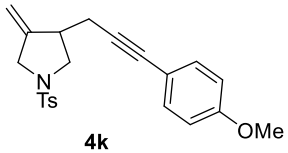
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.06-5.05 (m, 2H), 4.11-4.02 (m, 2H), 3.79 (s, 3H), 3.55 (d, *J* = 9.6 Hz, 1H), 3.20 (d, *J* = 9.6 Hz, 1H), 2.85 (s, 3H), 2.62-2.50 (m, 2H), 1.34 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 150.6, 132.9, 115.4, 113.9, 106.8, 84.6, 82.5, 58.7, 55.3, 52.2, 45.6, 34.7, 30.1, 23.4;

HRMS Calcd (ESI) m/z for $C_{17}H_{21}NNaO_3S$ $[M + Na]^+$:342.1134, found:.342.1120.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-4-methylene-1-tosylpyrrolidine (4k)



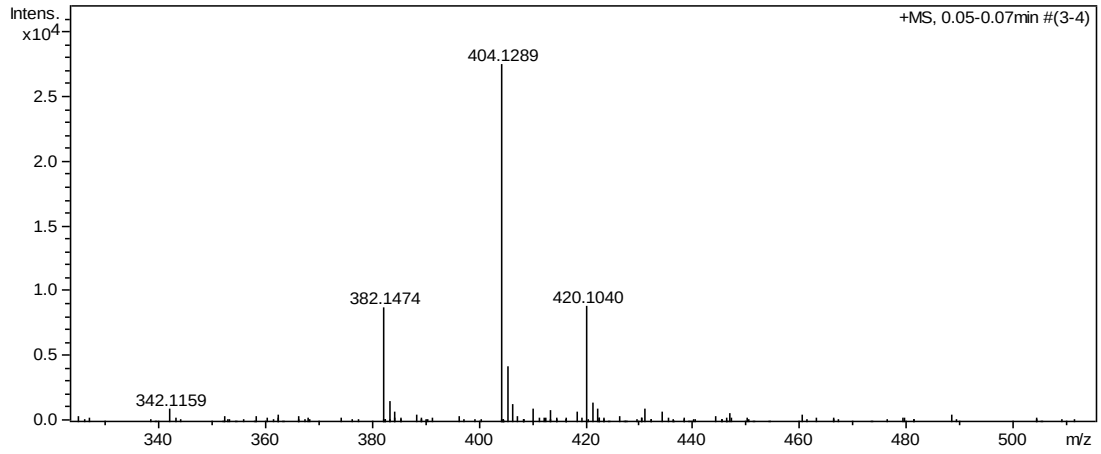
4k

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 8:1) gave the product **4k** (30.0 mg, 26% yield) as a yellow oil.

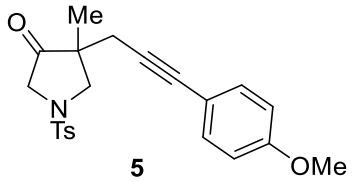
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26-7.24 (m, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.03-5.00 (m, 2H), 3.90-3.80 (m, 5H), 3.59-3.55 (m, 1H), 3.19-3.15 (m, 1H), 2.92-2.86 (m, 1H), 2.58-2.52 (m, 1H), 2.44-2.37 (m, 4H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 146.4, 143.7, 132.9, 132.5, 129.7, 127.9, 115.4, 113.8, 107.8, 85.2, 81.7, 55.3, 53.0, 52.3, 42.2, 22.8, 21.5;

HRMS Calcd (ESI) m/z for $C_{22}H_{23}NNaO_3S$ $[M + Na]^+$: 404.1291, found: 404.1289.



4-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-4-methyl-1-tosylpyrrolidin-3-one (5)



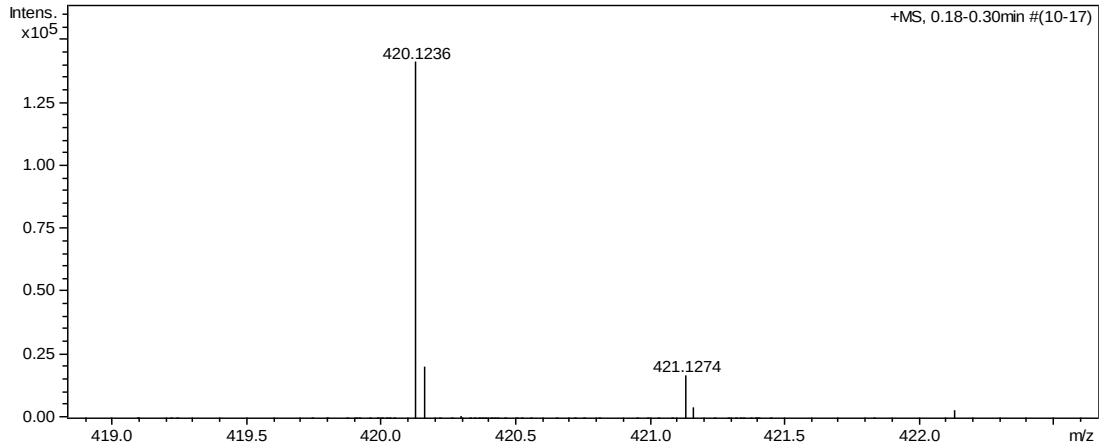
5

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 5:1) gave the product **5** (38.5 mg, 48% yield) as a yellow oil.

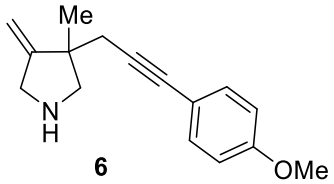
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.80-3.72 (m, 4H), 3.57-3.54 (m, 1H), 3.46-3.39 (m, 2H), 2.61-2.56 (m, 1H), 2.47-2.42 (m, 1H), 2.39 (s, 3H), 1.26 (s, 3H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 210.9, 159.4, 144.3, 132.9, 131.3, 129.9, 128.0, 114.8, 113.8, 83.3, 82.6, 55.9, 55.3, 53.7, 49.7, 25.8, 21.6, 20.9;

HRMS Calcd (ESI) m/z for $C_{22}H_{23}NNaO_4S$ $[M + Na]^+$: 420.1240, found: 420.1236.



3-(3-(4-Methoxyphenyl)prop-2-yn-1-yl)-3-methyl-4-methylenepyrrolidine (6)



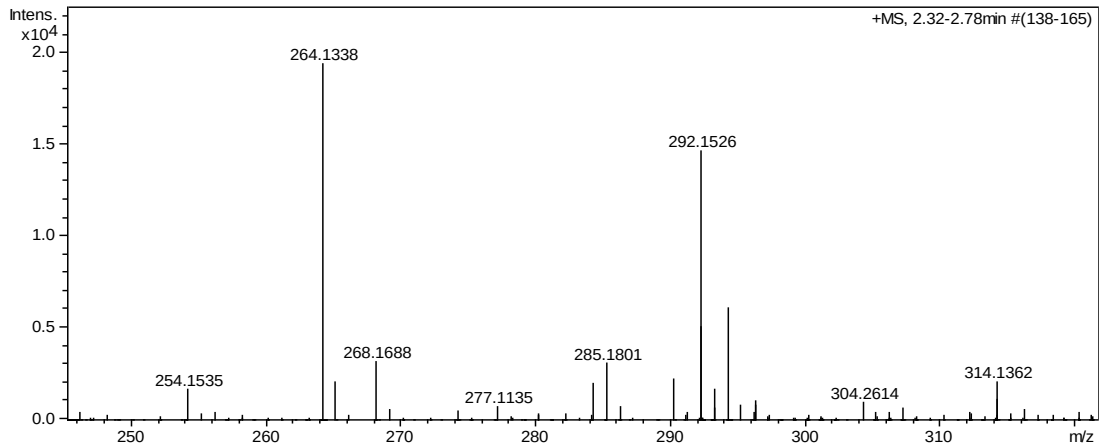
6

Flash column chromatography on a silica gel (ethyl acetate: Methanol, 10:1) gave the product **6** (39.6 mg, 82% yield) as a white oil.

^{1}H NMR ($(CD_3)_2SO$, 400 MHz) δ 7.31 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.92 (s, 2H), 3.75 (s, 3H), 3.55-3.44 (m, 2H), 2.97 (d, *J* = 10.8 Hz, 1H), 2.64 (d, *J* = 10.8 Hz, 1H), 2.54-2.40 (m, 2H), 1.18 (s, 3H);

^{13}C NMR ($(CD_3)_2SO$, 100 MHz) δ 159.0, 157.2, 132.7, 115.3, 114.2, 103.6, 86.9, 81.4, 58.8, 55.3, 52.1, 45.1, 29.6, 23.9;

HRMS Calcd (ESI) m/z for $C_{16}H_{19}NNaO$ $[M + Na]^+$: 264.1359, found: 264.1338.



4. Single Crystal X-Ray Diffraction

Crystals of **3b** were obtained by slow diffusion from a solution of the compounds in $CHCl_3$ layered with petroleum ether at room temperature for several days (Figure S1). Crystal data and details of the structure determination are presented in Table S2.

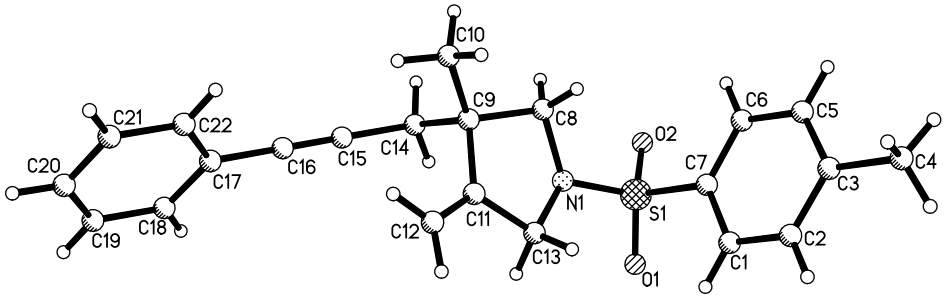


Figure S1. Crystal structure of **3b**

Table S2 The single crystal date of compounds **3b**

Phase	**3b**
Identification code	XSJ20220725
Empirical formula	$C_{22}H_{23}NO_2S$
Formula weight	365.47
Temperature/K	296(2)
Wavelength/ Å	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
a / Å	16.6490(11)
b / Å	6.3815(5)
c / Å	18.6164(12)
α (°)	90
β (°)	95.783(2)
γ (°)	90
Volume ($Å^3$)	1967.8(2)
Z	4
Calculated density ($mg·m^{-3}$)	1.234
Absorption coefficient (mm^{-1})	0.180
F(000)	776
Crystal size (mm)	0.280 x 0.240 x 0.200
θ range for data collection (deg)	3.130 to 25.997
Limiting indices	-20<=h<=20, -7<=k<=7, -22<=l<=22
Reflections collected/unique	26735 / 3844 [R(int) = 0.0520]
Completeness to theta	99.8 %
Max. and min. transmission	0.7456 and 0.6907
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3844 / 0 / 237
Goodness-of-fit on F^2	1.040
Final *R* indices[I>2sigma(I)]	R1 = 0.0479, wR2 = 0.1058
R indices (all data)	R1 = 0.0827, wR2 = 0.1214
Largest diff. peak and hole / ($e·Å^{-3}$)	0.213 and -0.239

5. References

1. J.-B. Qiao, Y.-Q. Zhang, Q.-W. Yao, Z.-Z. Zhao, X. Peng and X.-Z. Shu, *J. Am. Chem. Soc.,* 2021, **143**, 12961–7157.

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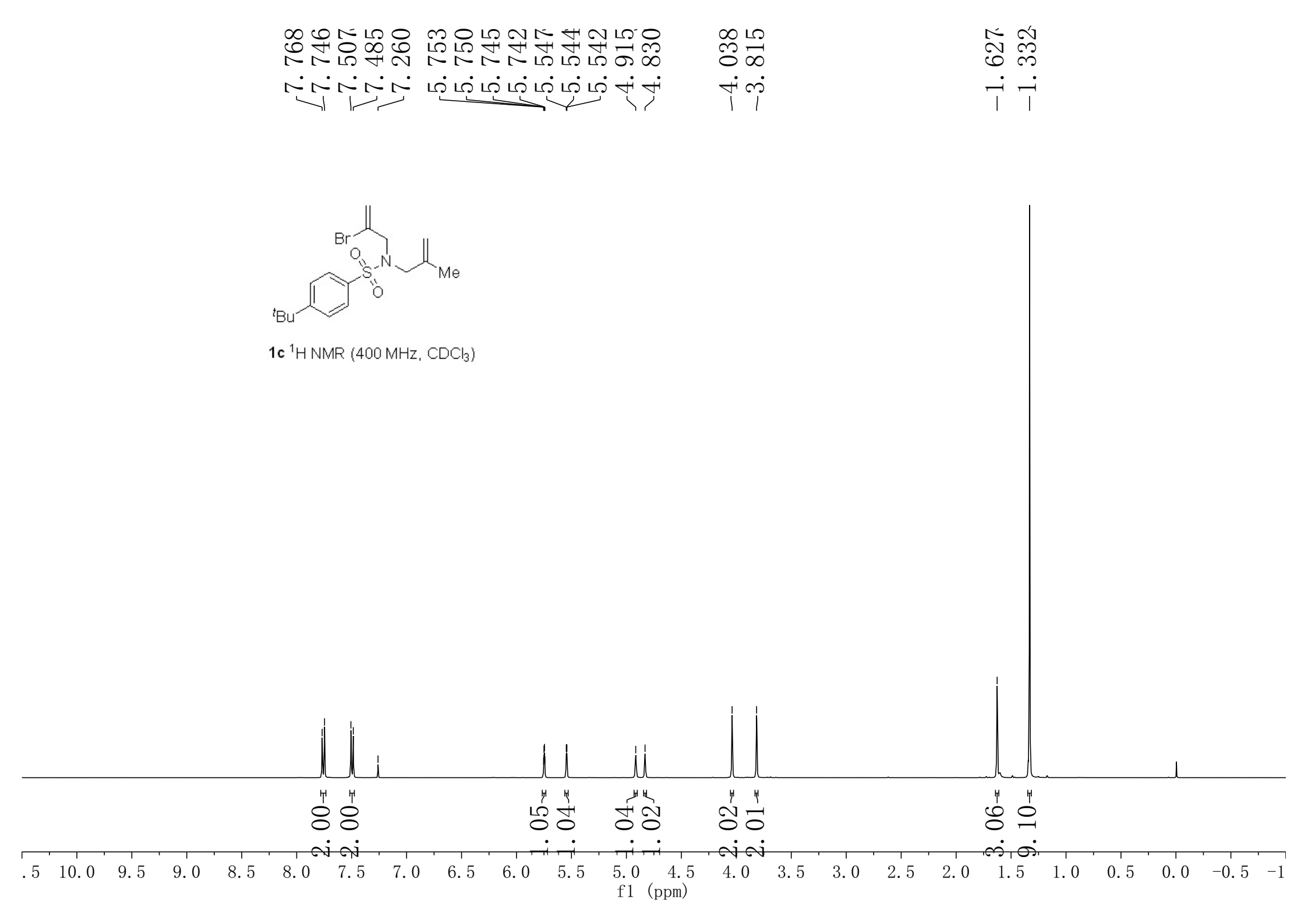
3. C.-W. Lee, K. S. Oh, K. S. Kim and K. H. Ahn, *Org. Lett.,* 2000, **2**, 1213–1216.

4. A. Padwa, H. Nimmesgern and G. S. K. Wong, *Tetrahedron Lett.,* 1985, 957-960.

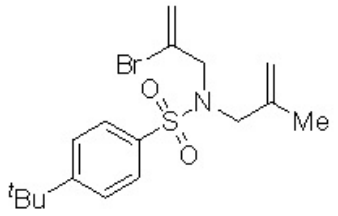
5. W.-B. Xu, M. Sun, M. Shu and C. Li, *J. Am. Chem. Soc.,* 2021. **143**, 8255–8260.

6. Copies of NMR Spectra

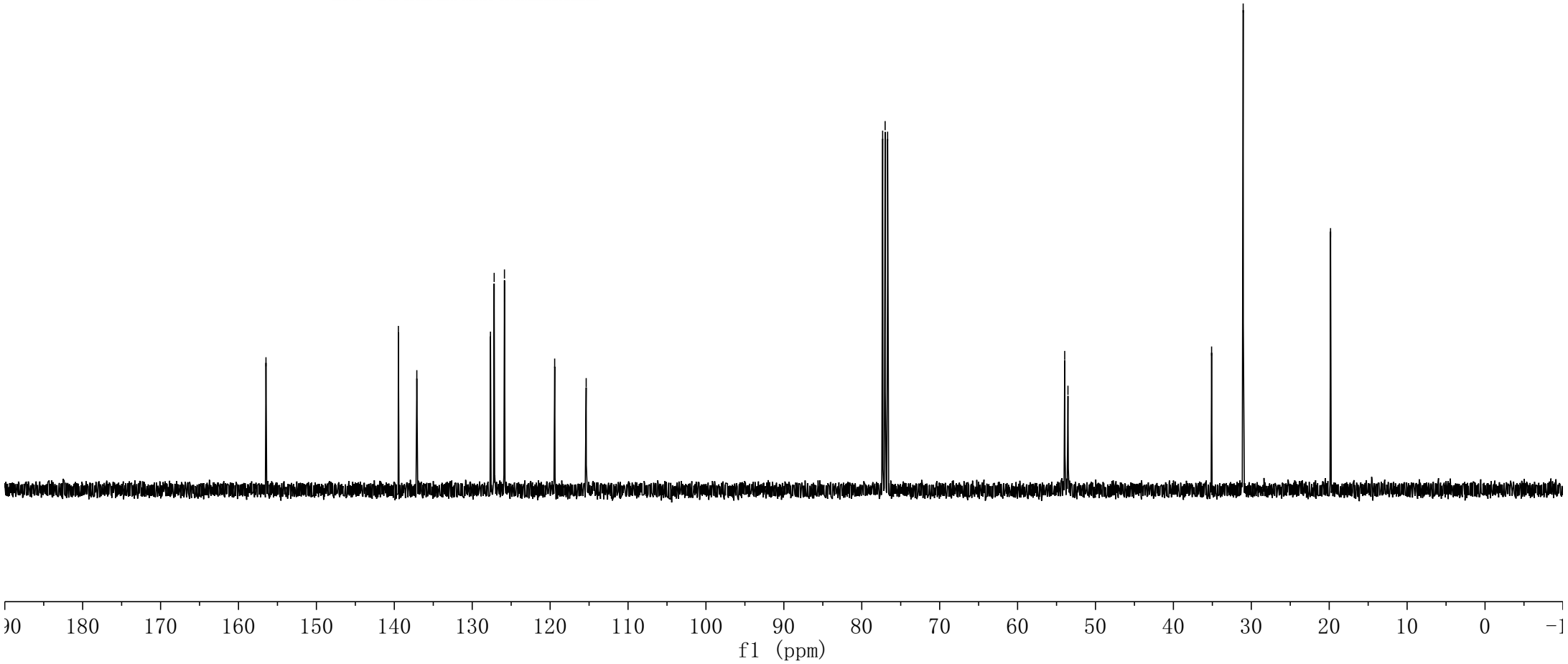


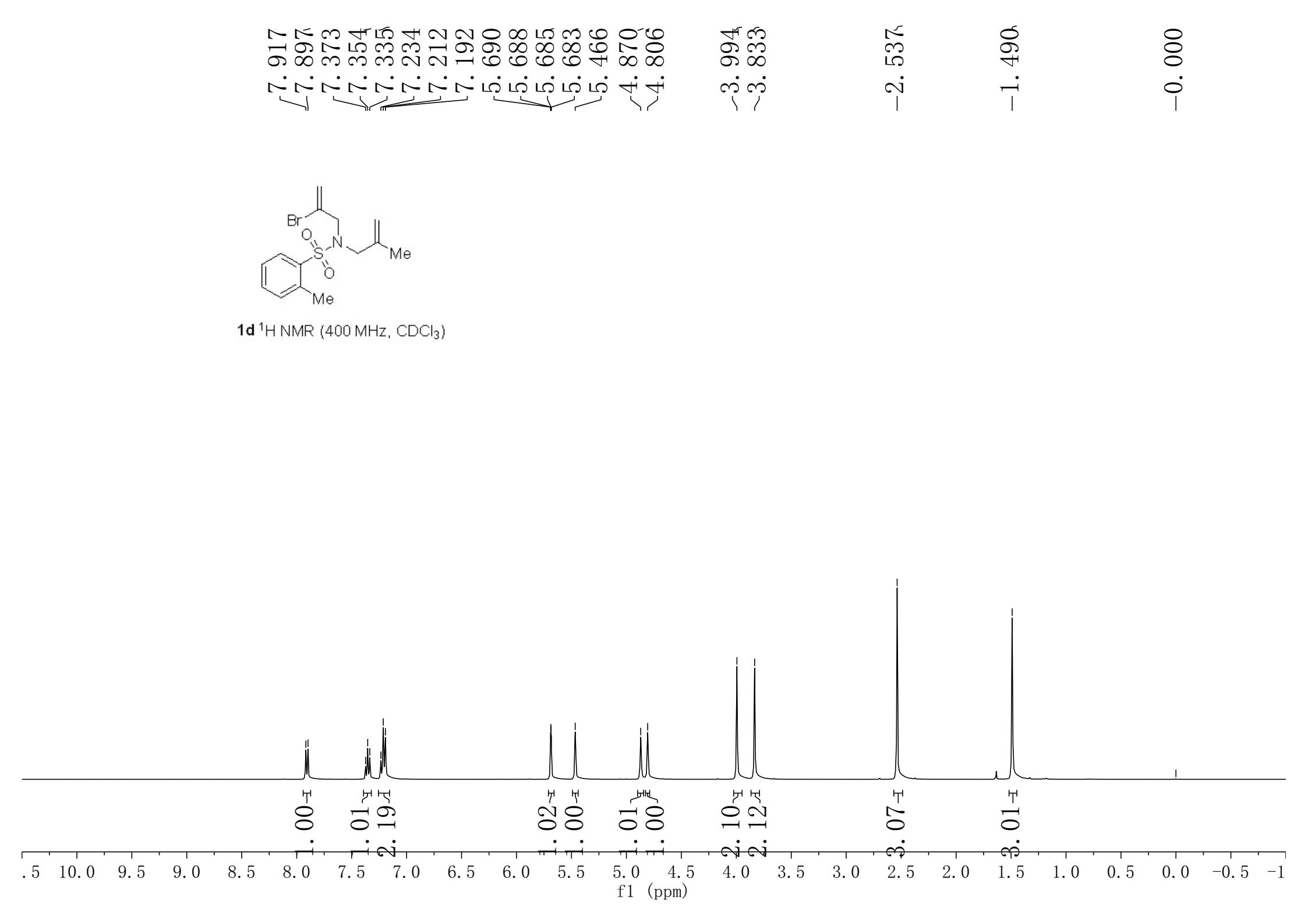
1c ^{1}H NMR (400 MHz, $CDCl_3$)

156.473
139.478
137.111
127.658
127.183
125.862
119.416
115.371
77.319
77.000
76.682
53.951
53.533
35.097
31.043
19.828

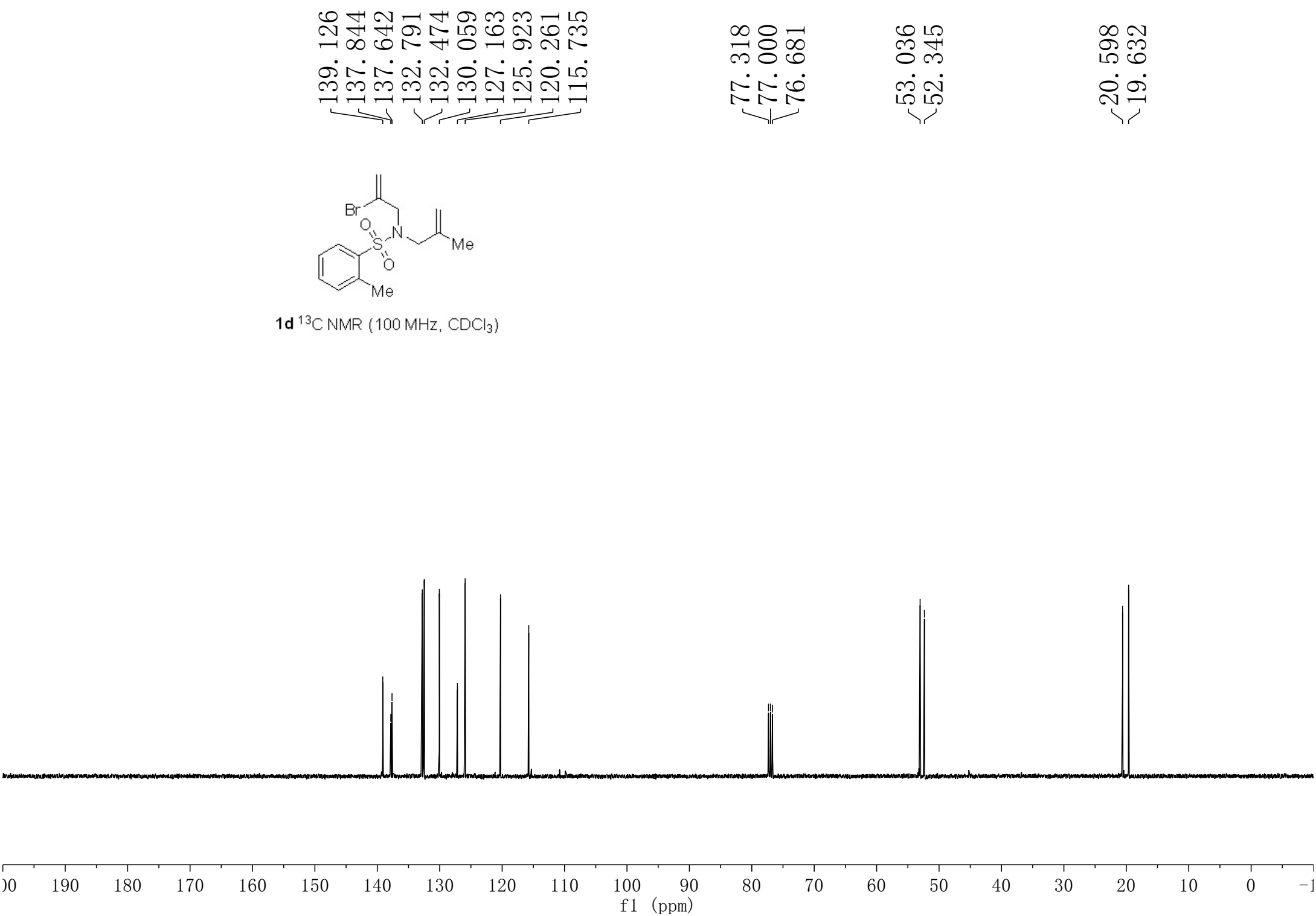


1c ^{13}C NMR (100 MHz, $CDCl_3$)

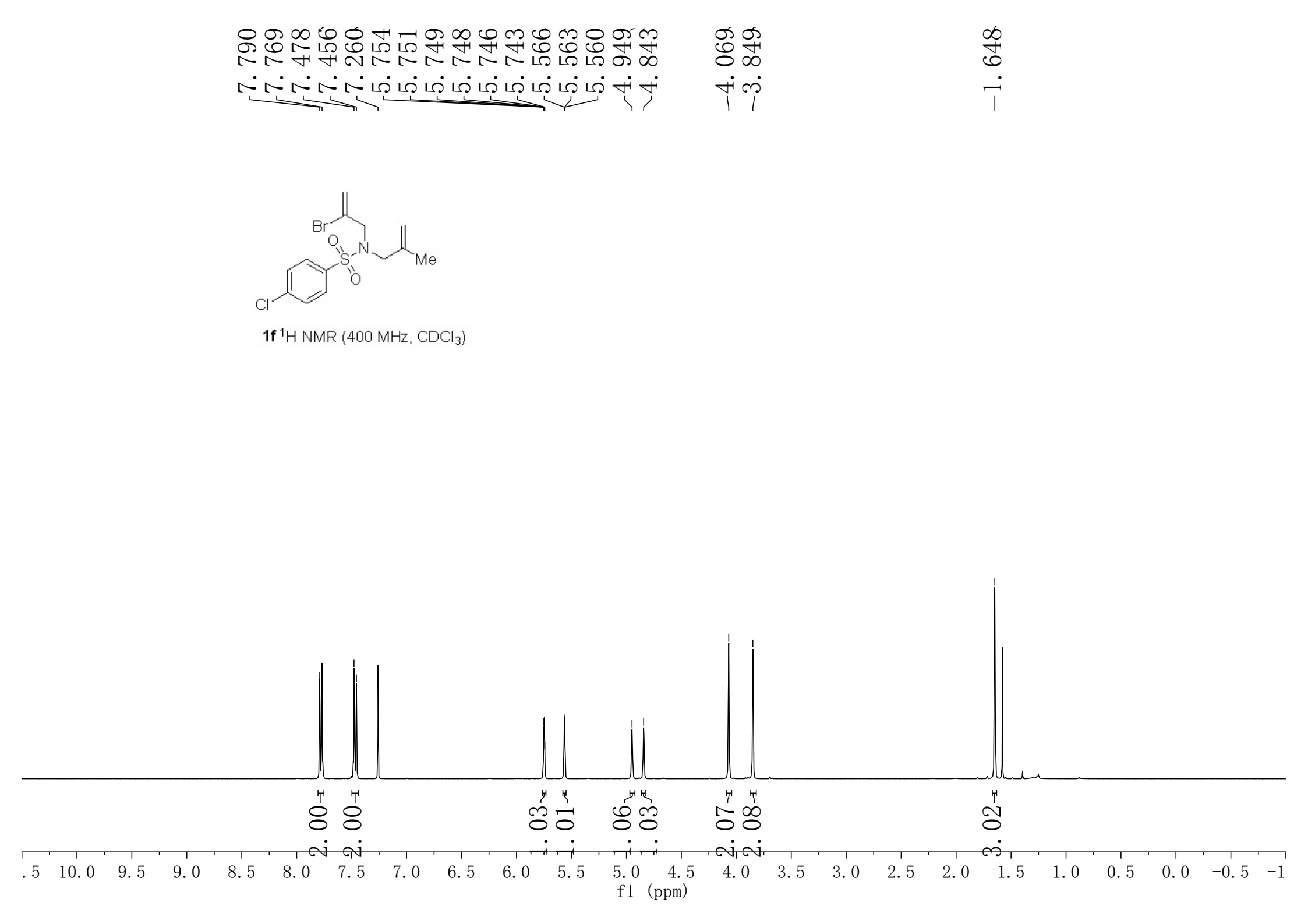




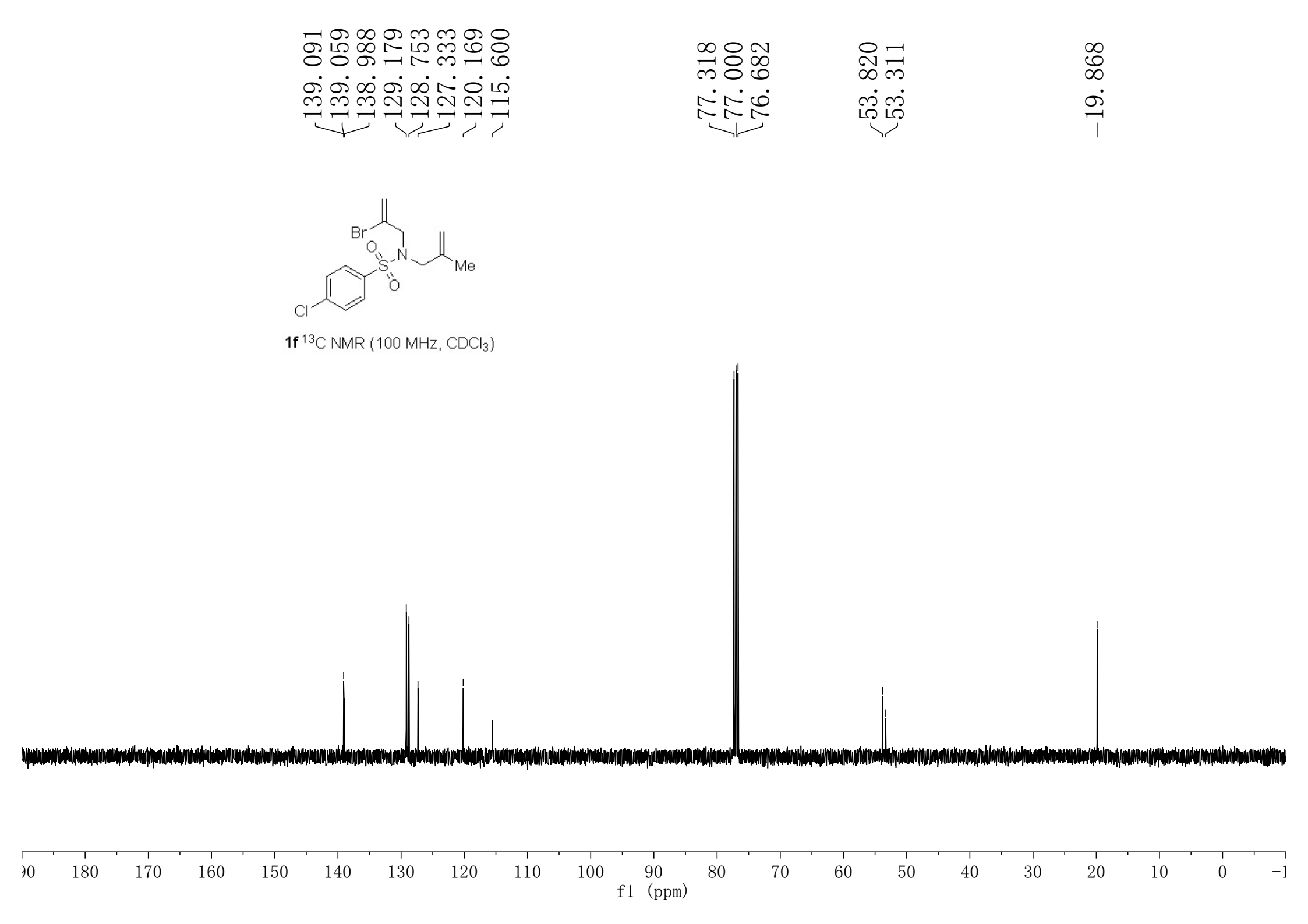
1d ^{1}H NMR (400 MHz, $CDCl_3$)

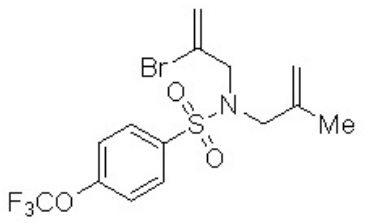


1d ^{13}C NMR (100 MHz, $CDCl_3$)

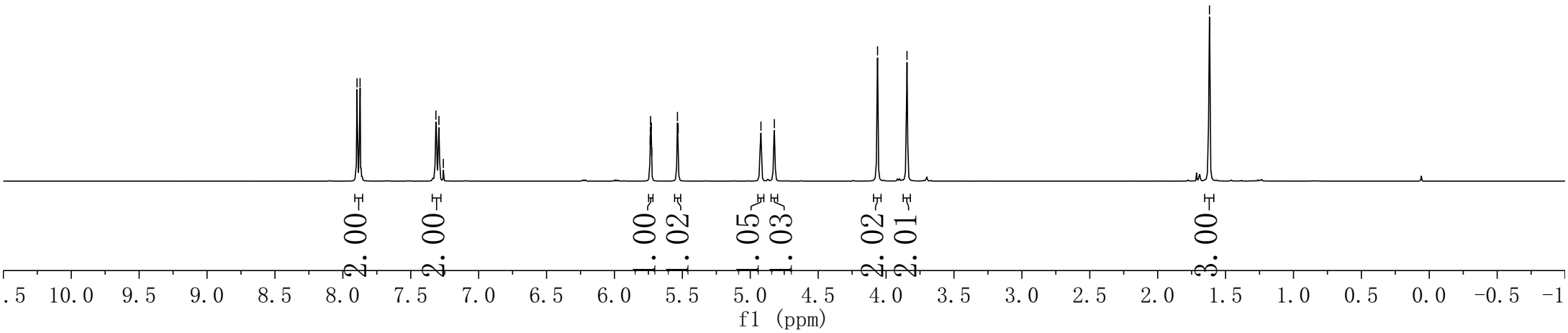


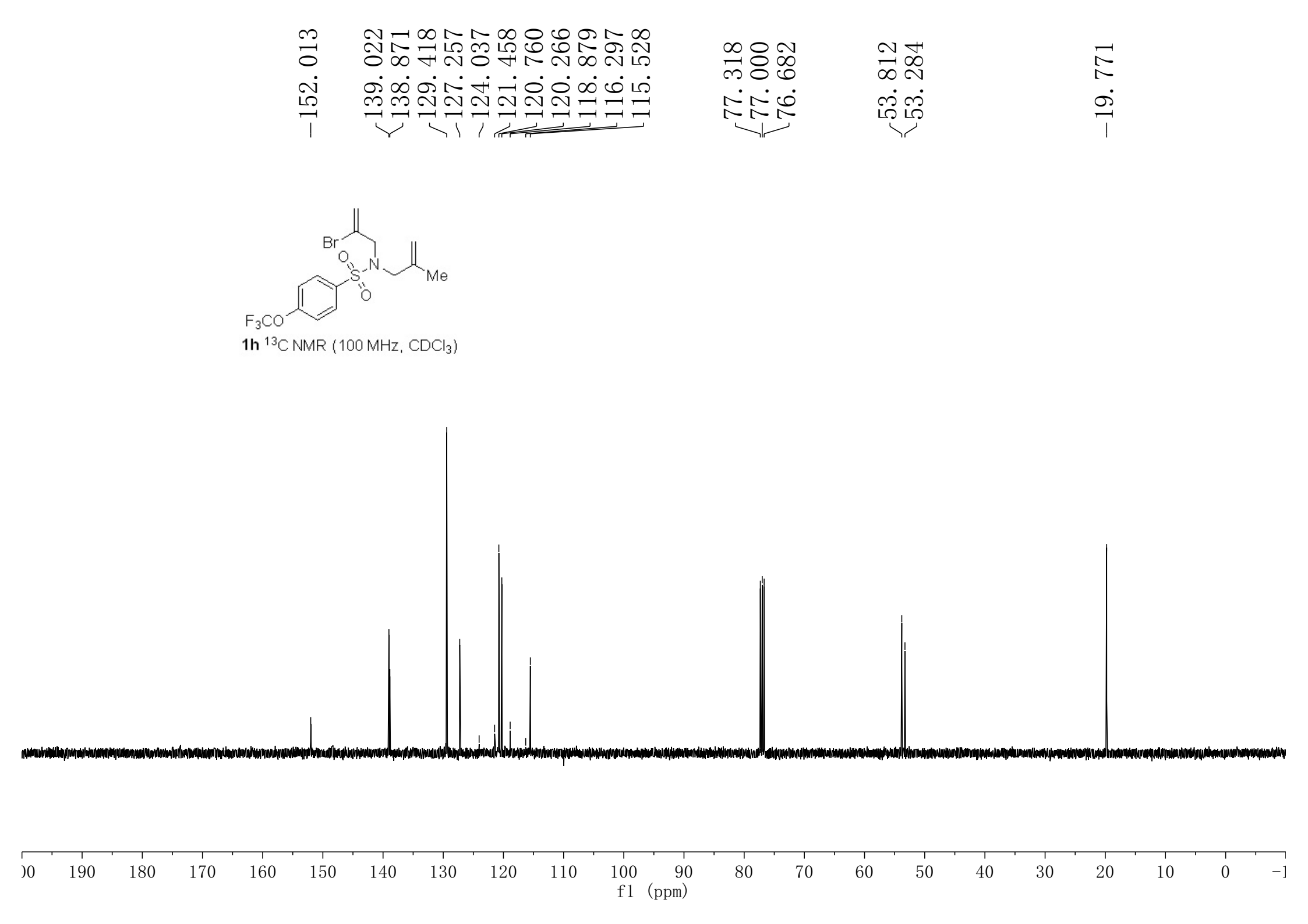
1f ^{1}H NMR (400 MHz, $CDCl_3$)

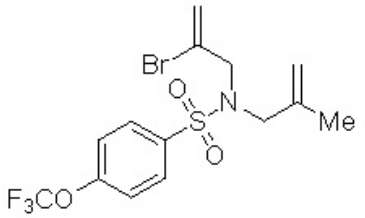

139.091
139.059
138.988
129.179
128.753
127.333
120.169
115.600
77.318
77.000
76.682
53.820
53.311
19.868
Br
O
S
O
N
Me
Cl
1f 13C NMR (100 MHz, CDCl3)
f1 (ppm)



1h ^{1}H NMR (400 MHz, $CDCl_3$)

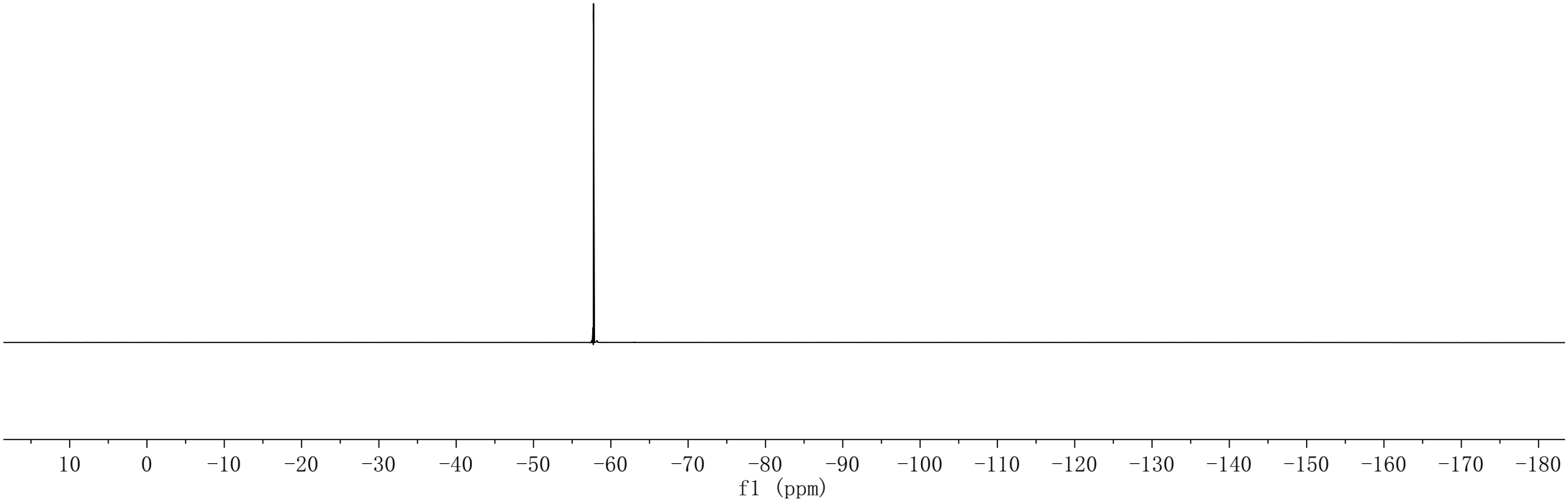


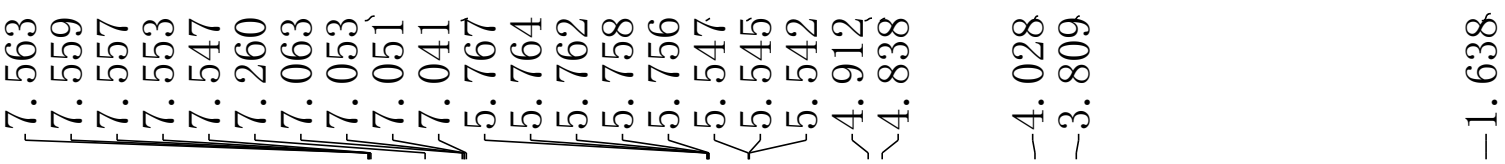

152.013
139.022
138.871
129.418
127.257
124.037
121.458
120.760
120.266
118.879
116.297
115.528
77.318
77.000
76.682
53.812
53.284
19.771
Br
O
S
O
N
Me
F3CO
1h 13C NMR (100 MHz, CDCl3)
f1 (ppm)

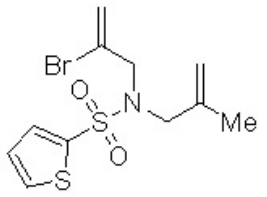


1h ^{19}F NMR (376 MHz, $CDCl_3$)

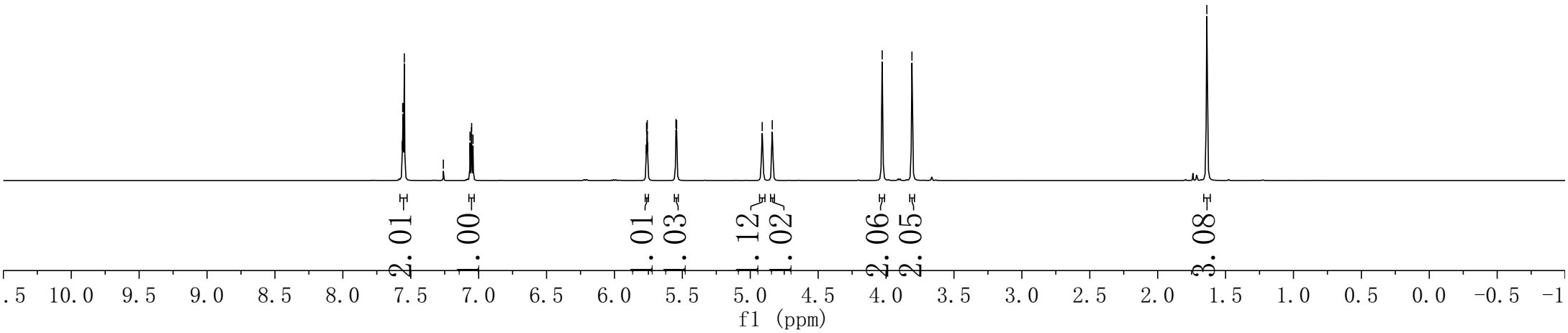
−57.747







1i ^{1}H NMR (400 MHz, $CDCl_3$)

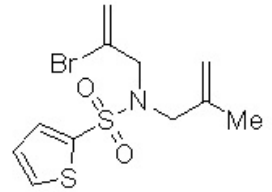


140.456
139.033
132.021
131.633
127.164
127.084
119.709
115.415

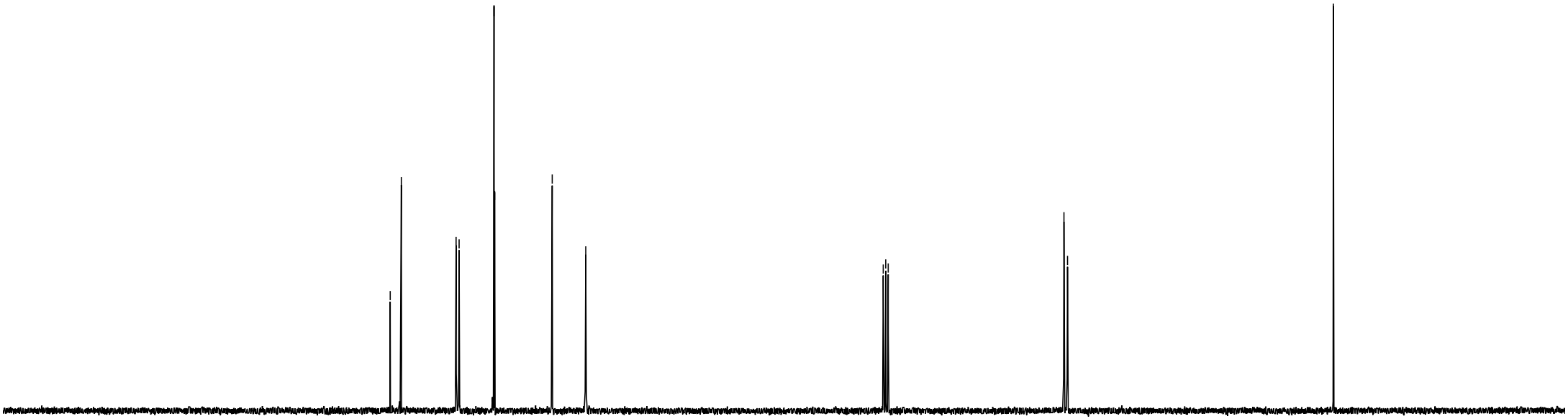
77.319
77.000
76.681

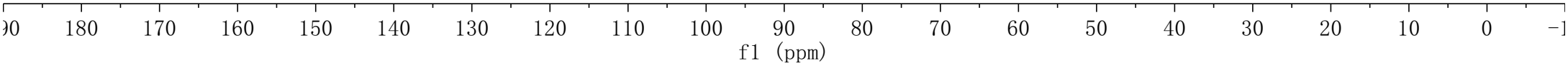
54.176
53.718

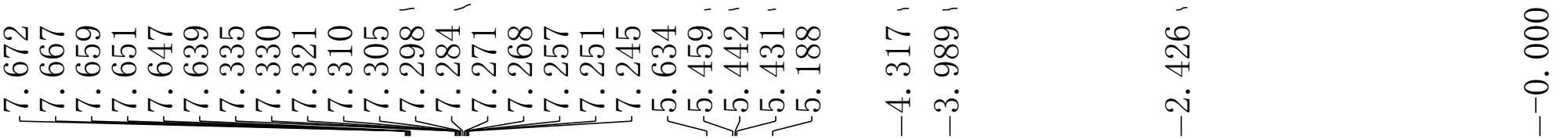
19.675

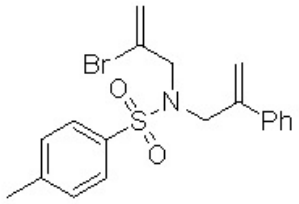


1i ^{13}C NMR (100 MHz, $CDCl_3$)

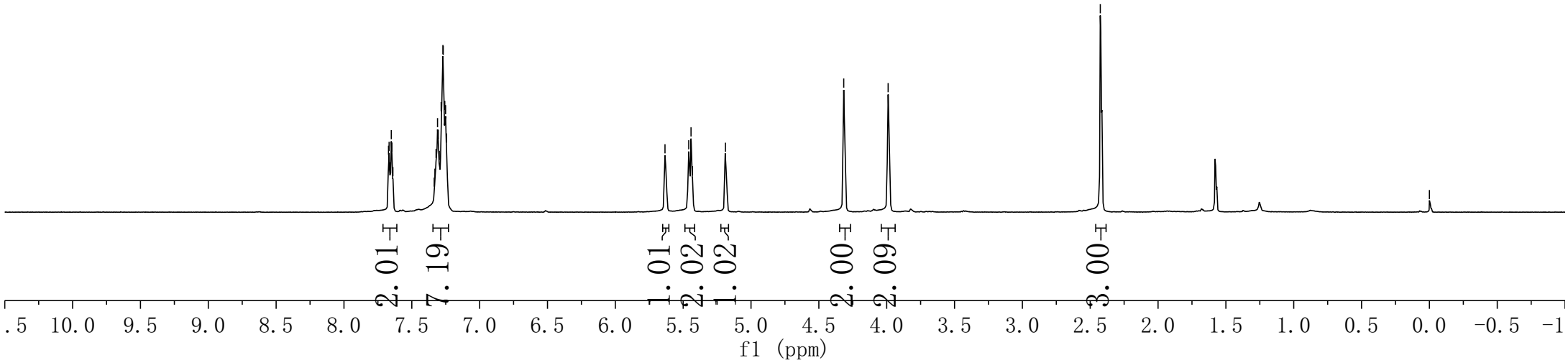








1l ^{1}H NMR (400 MHz, $CDCl_3$)

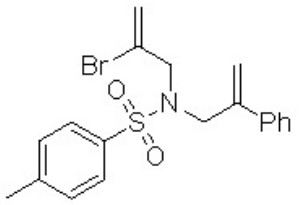


143.421
141.941
138.195
136.515
129.506
128.282
127.934
127.297
127.164
126.264
119.201
116.897

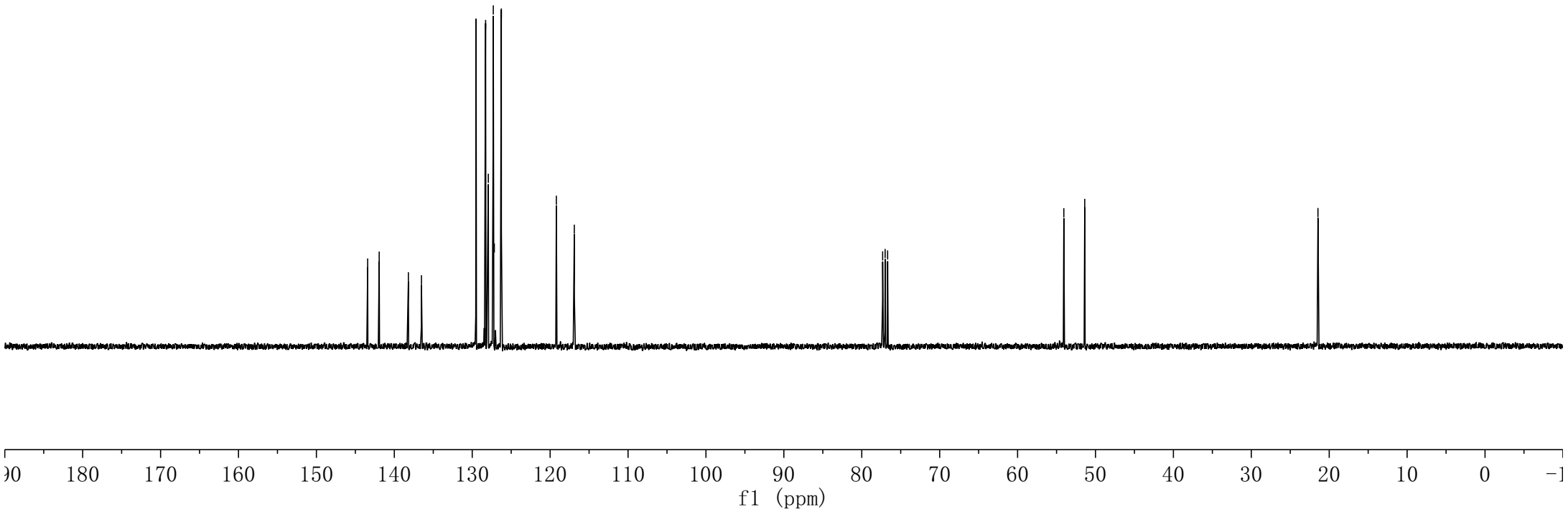
77.318
77.000
76.682

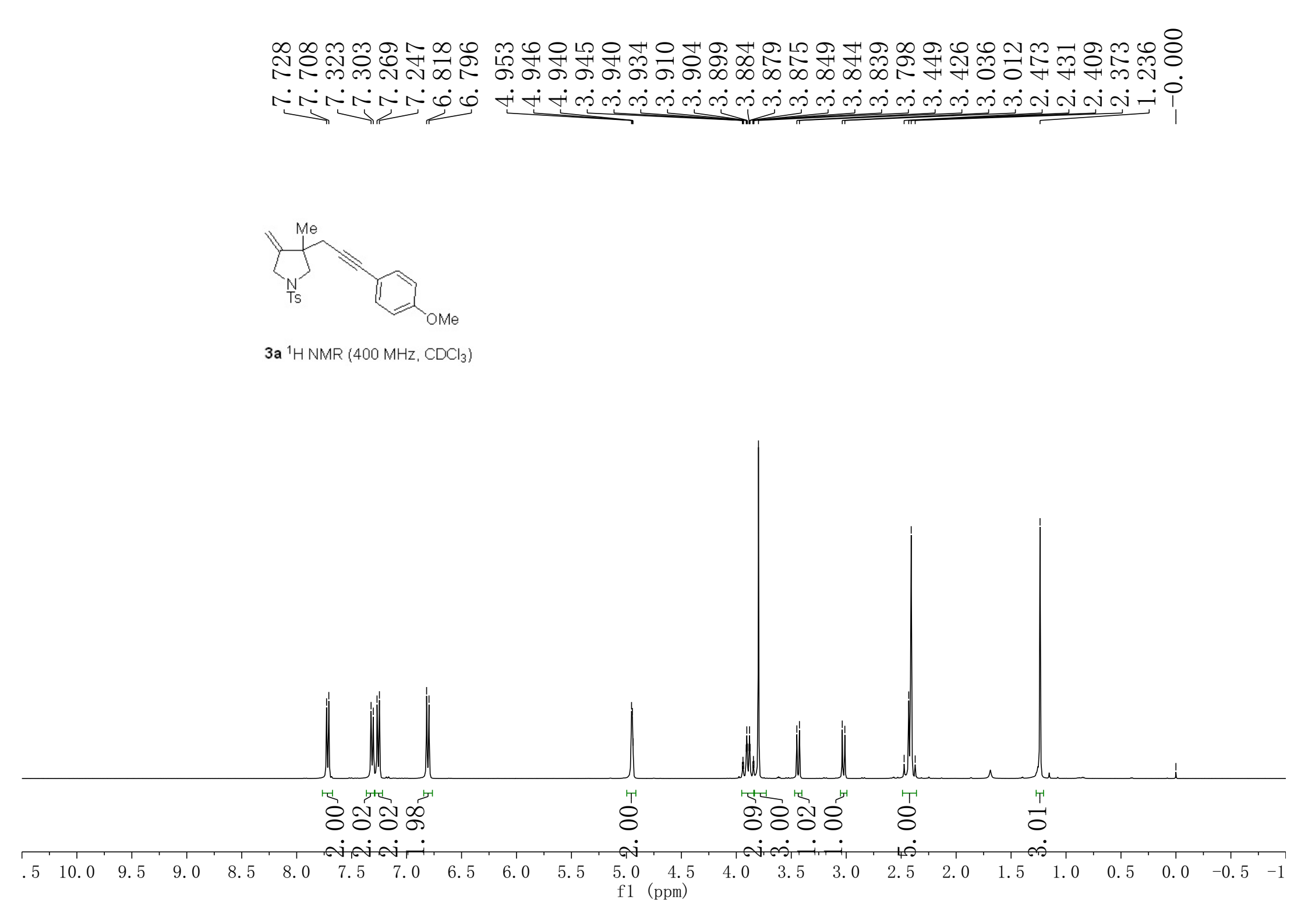
54.063
51.380

21.445

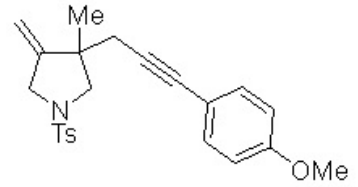


1l ^{13}C NMR (100 MHz, $CDCl_3$)

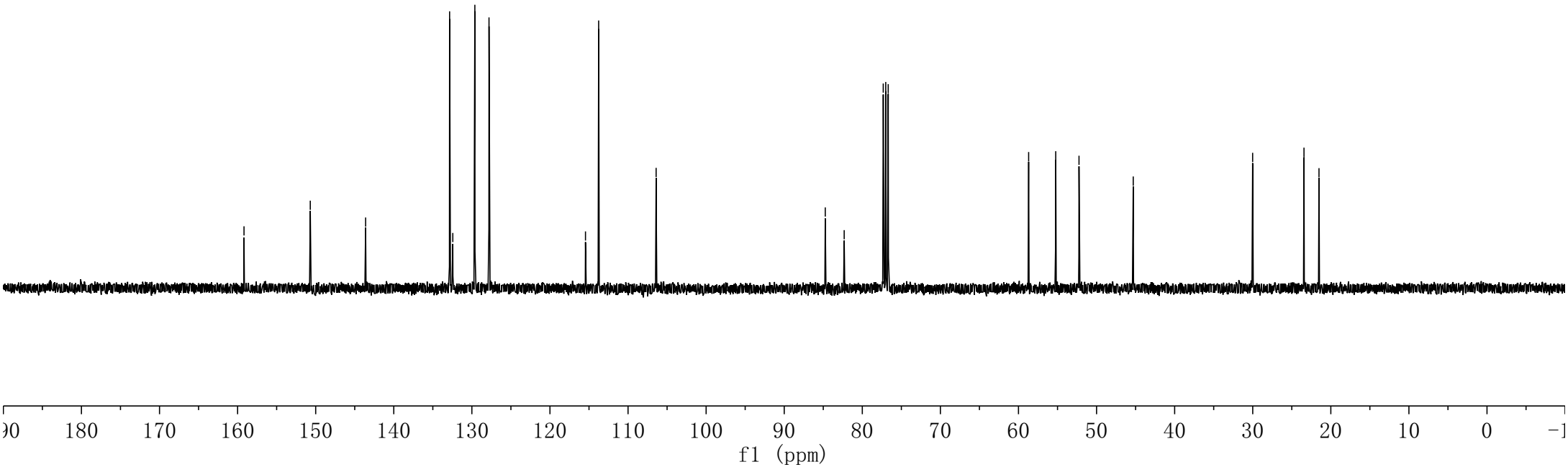


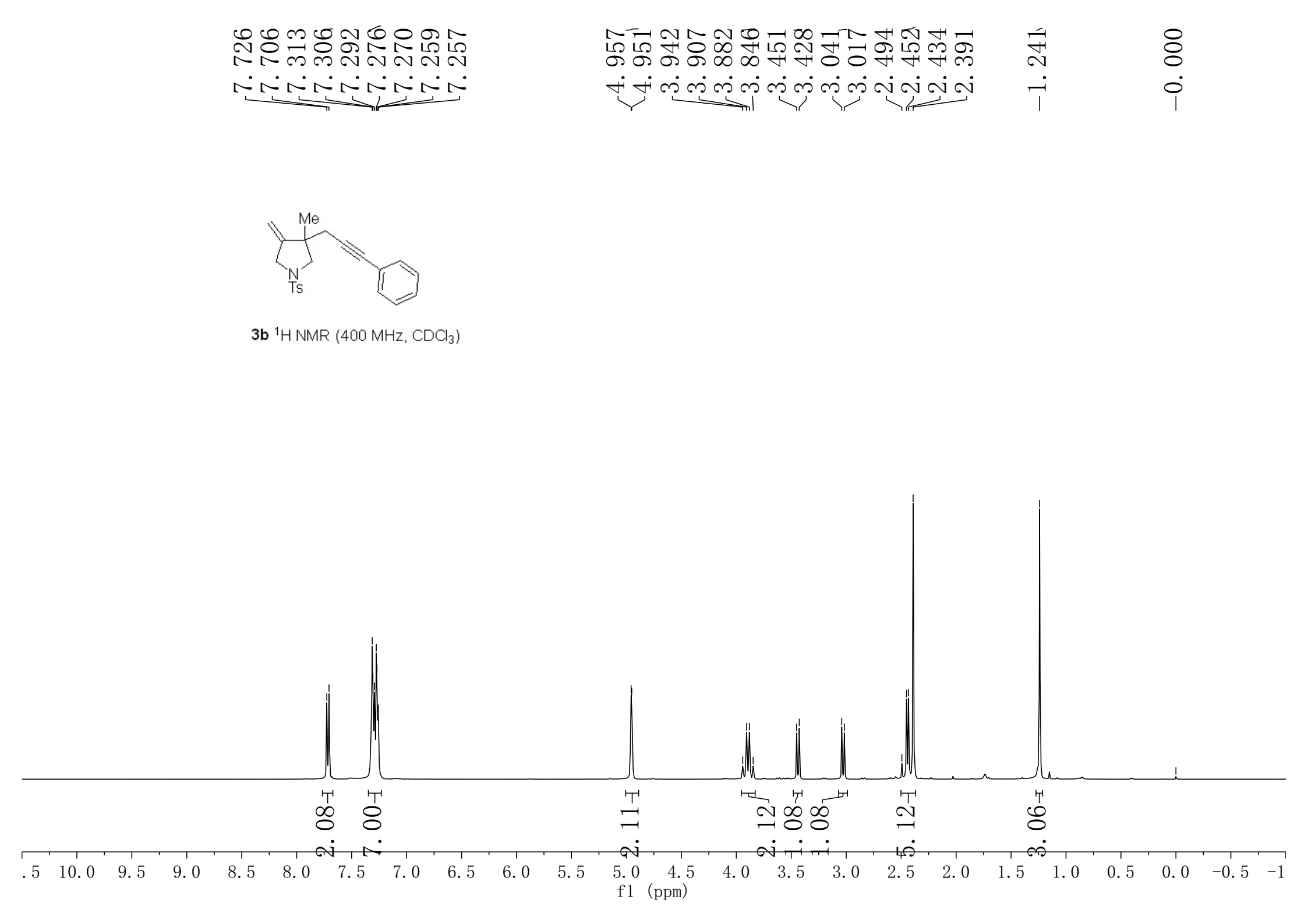

7.728
7.708
7.323
7.303
7.269
7.247
6.818
6.796
4.953
4.946
4.940
3.945
3.940
3.934
3.910
3.904
3.899
3.884
3.879
3.875
3.849
3.844
3.839
3.798
3.449
3.426
3.036
3.012
2.473
2.431
2.409
2.373
1.236
0.000
Me
N
Ts
OMe
3a 1H NMR (400 MHz, CDCl3)
2.00
2.02
2.02
1.98
2.00
2.09
3.00
1.02
1.00
5.00
3.01
f1 (ppm)

159.179
150.694
143.606
132.851
132.441
129.618
127.806
115.449
113.763
106.404
84.744
82.320
77.318
77.000
76.682
58.698
55.229
52.249
45.304
30.013
23.437
21.516



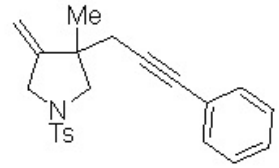
3a ^{13}C NMR (100 MHz, $CDCl_3$)



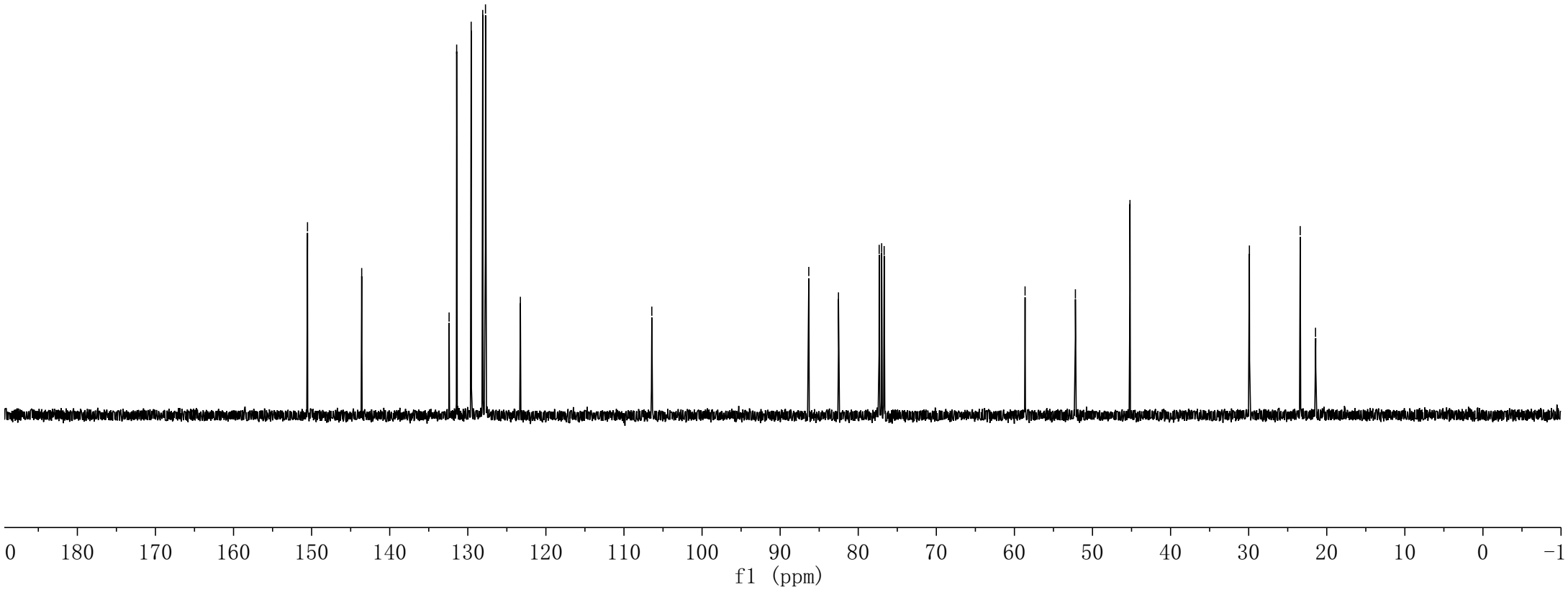


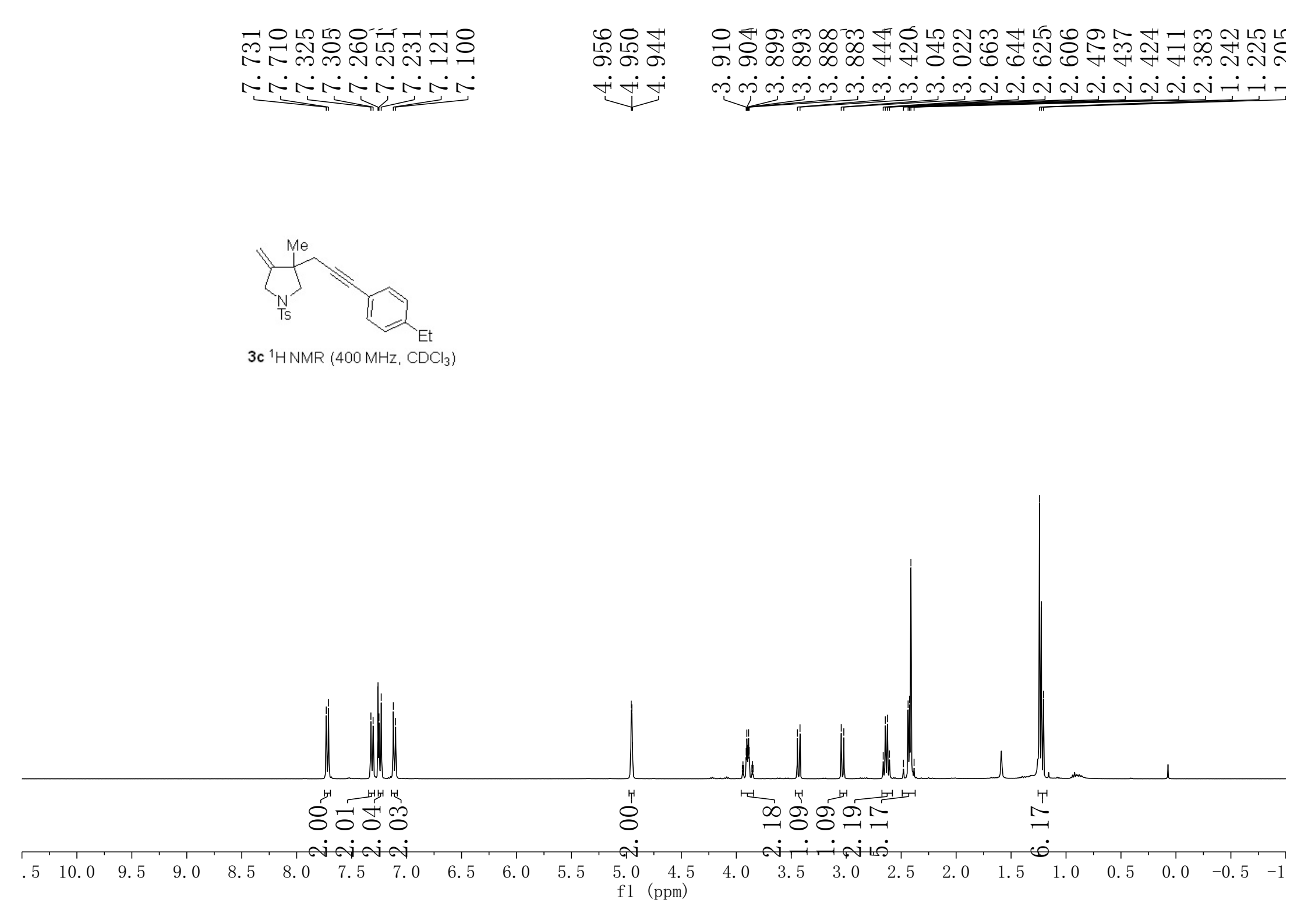
3b ^{1}H NMR (400 MHz, $CDCl_3$)

150.527
143.586
132.395
131.425
129.568
128.091
127.735
123.265
106.434
86.333
82.532
77.318
77.000
76.681
58.636
52.190
45.202
29.907
23.401
21.439



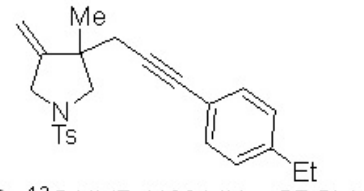
3b ^{13}C NMR (100 MHz, $CDCl_3$)



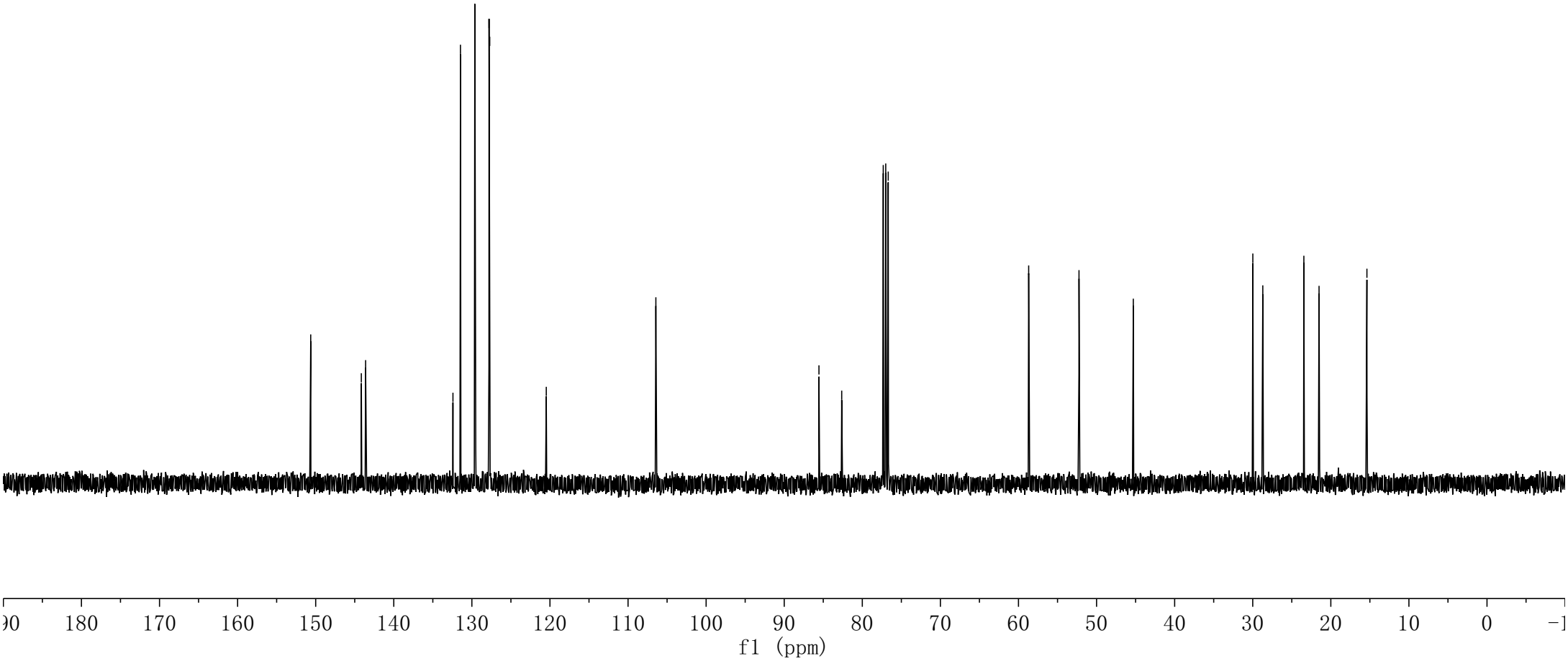


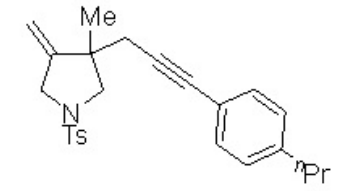
3c ^{1}H NMR (400 MHz, $CDCl_3$)

150.638
144.156
143.607
132.422
131.461
129.620
127.802
127.712
120.471
106.437
85.551
82.637
77.318
77.000
76.681
58.695
52.250
45.294
29.987
28.712
23.453
21.508
15.377

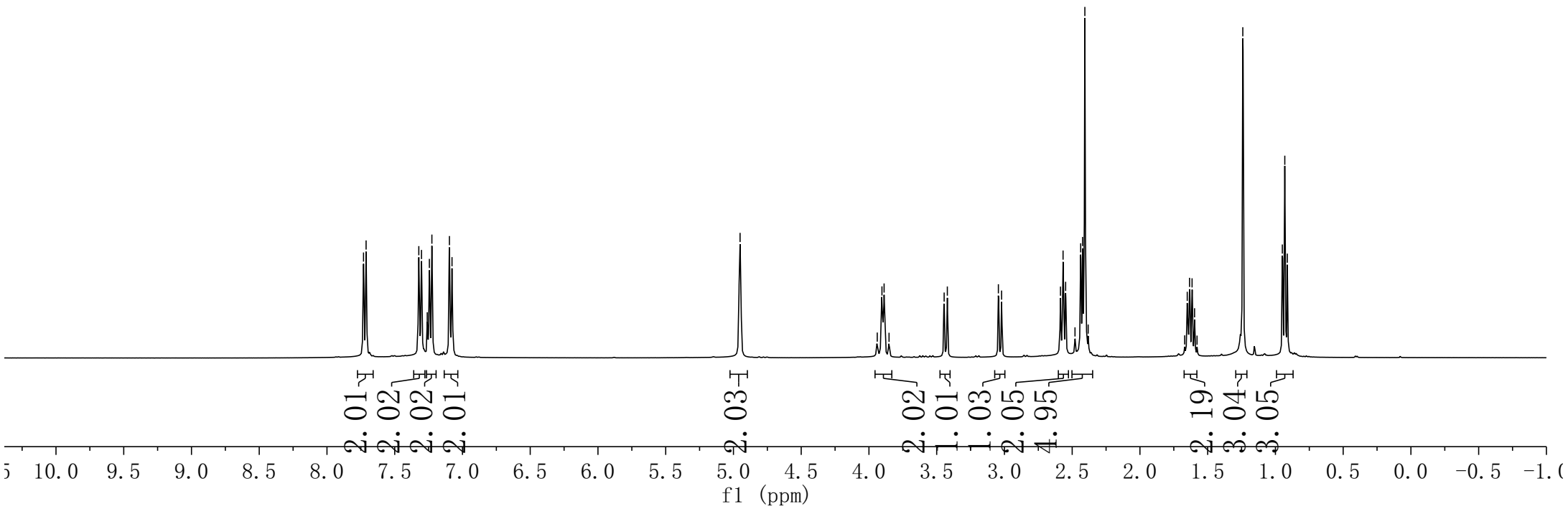


3c ^{13}C NMR (100 MHz, $CDCl_3$)

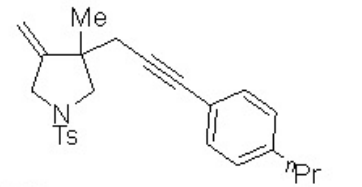




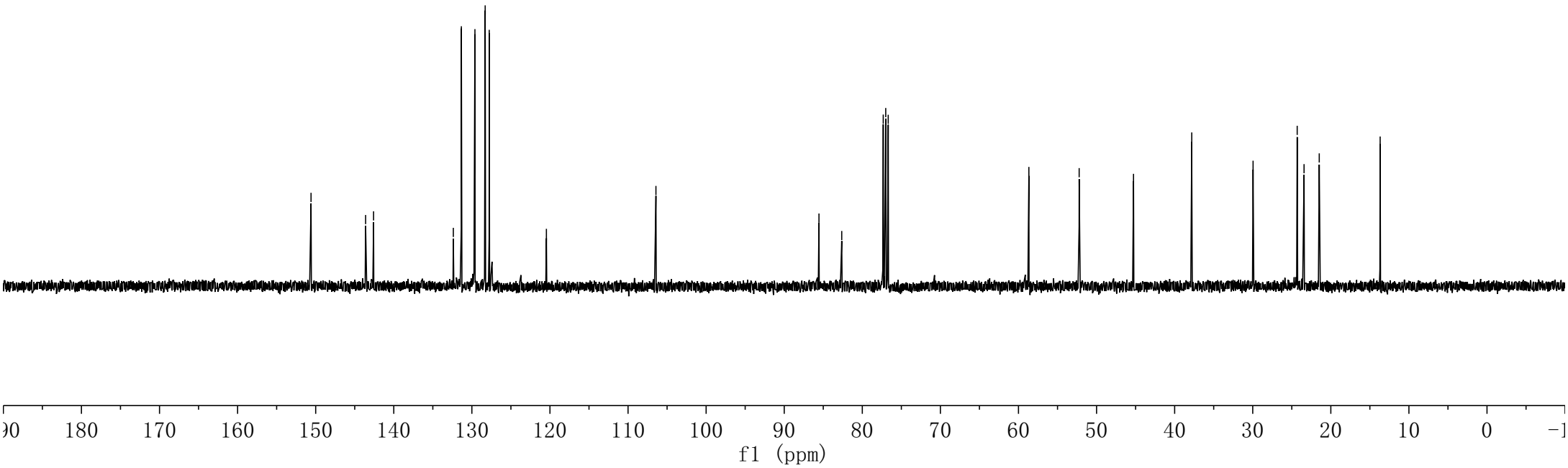
3d ^{1}H NMR (400 MHz, $CDCl_3$)

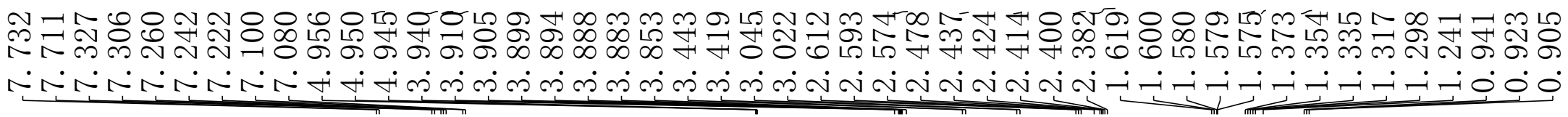


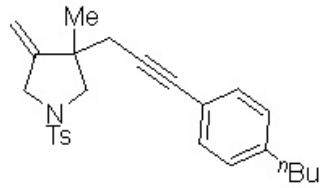
150.596
143.607
142.588
132.375
131.346
129.608
128.295
127.776
120.455
106.428
85.549
82.634
77.319
77.000
76.682
58.669
52.228
45.268
37.810
29.957
24.306
23.428
21.483
13.683



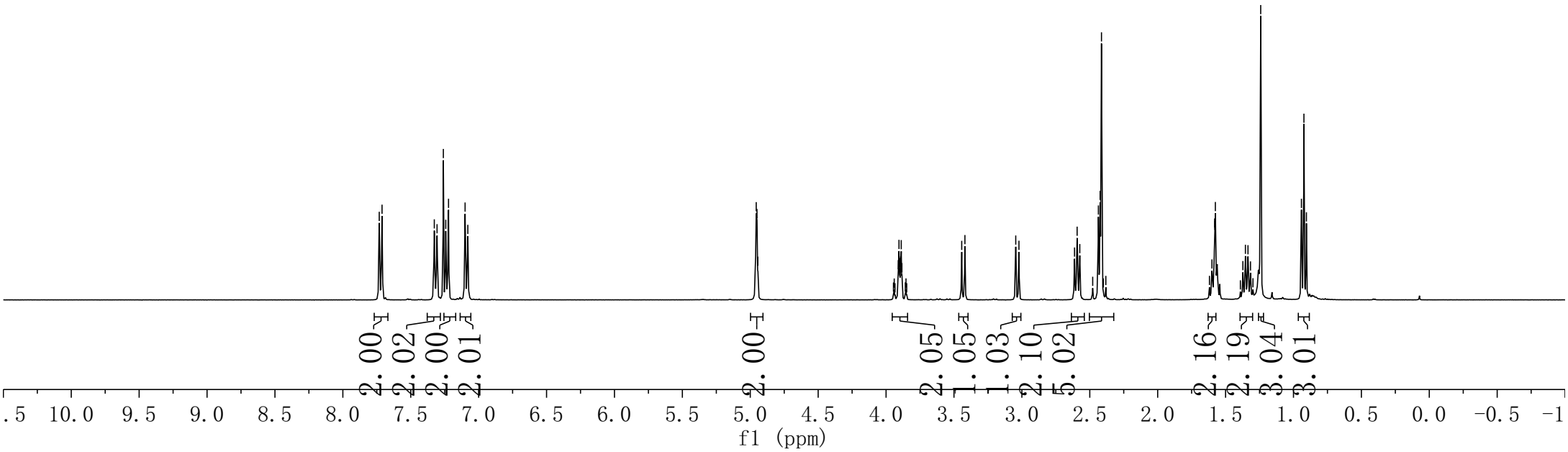
3d ^{13}C NMR (100 MHz, $CDCl_3$)



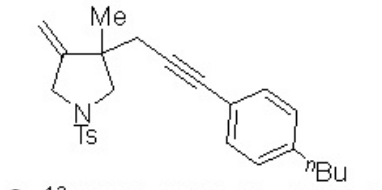




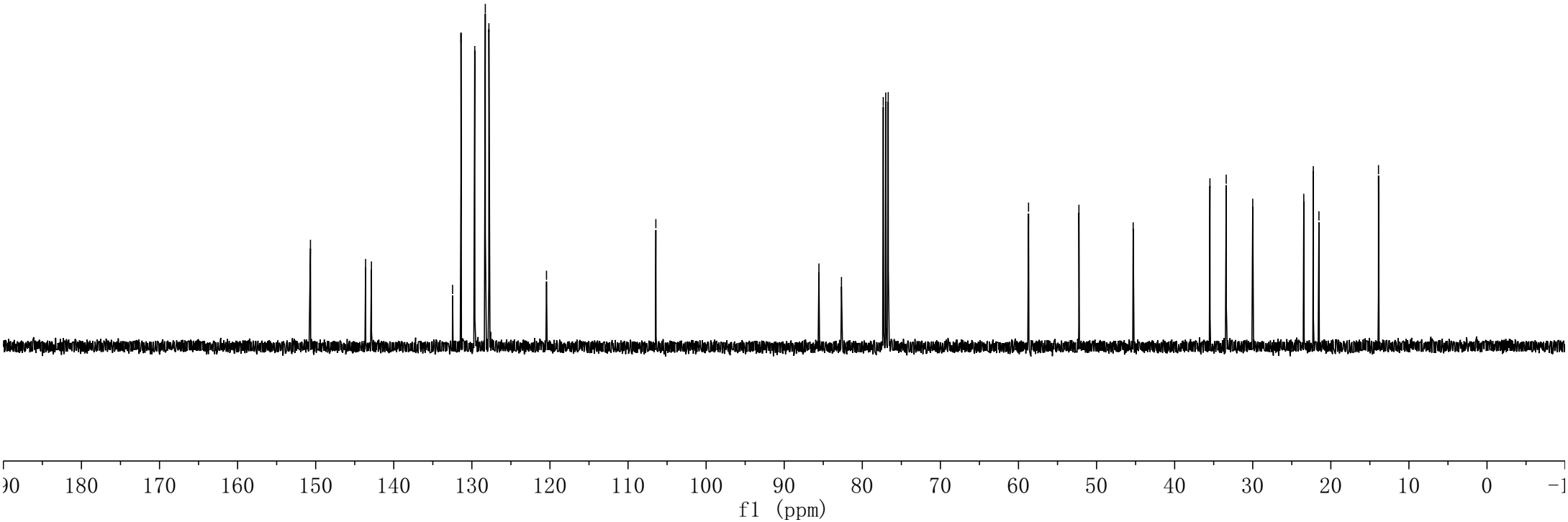
3e ^{1}H NMR (400 MHz, $CDCl_3$)

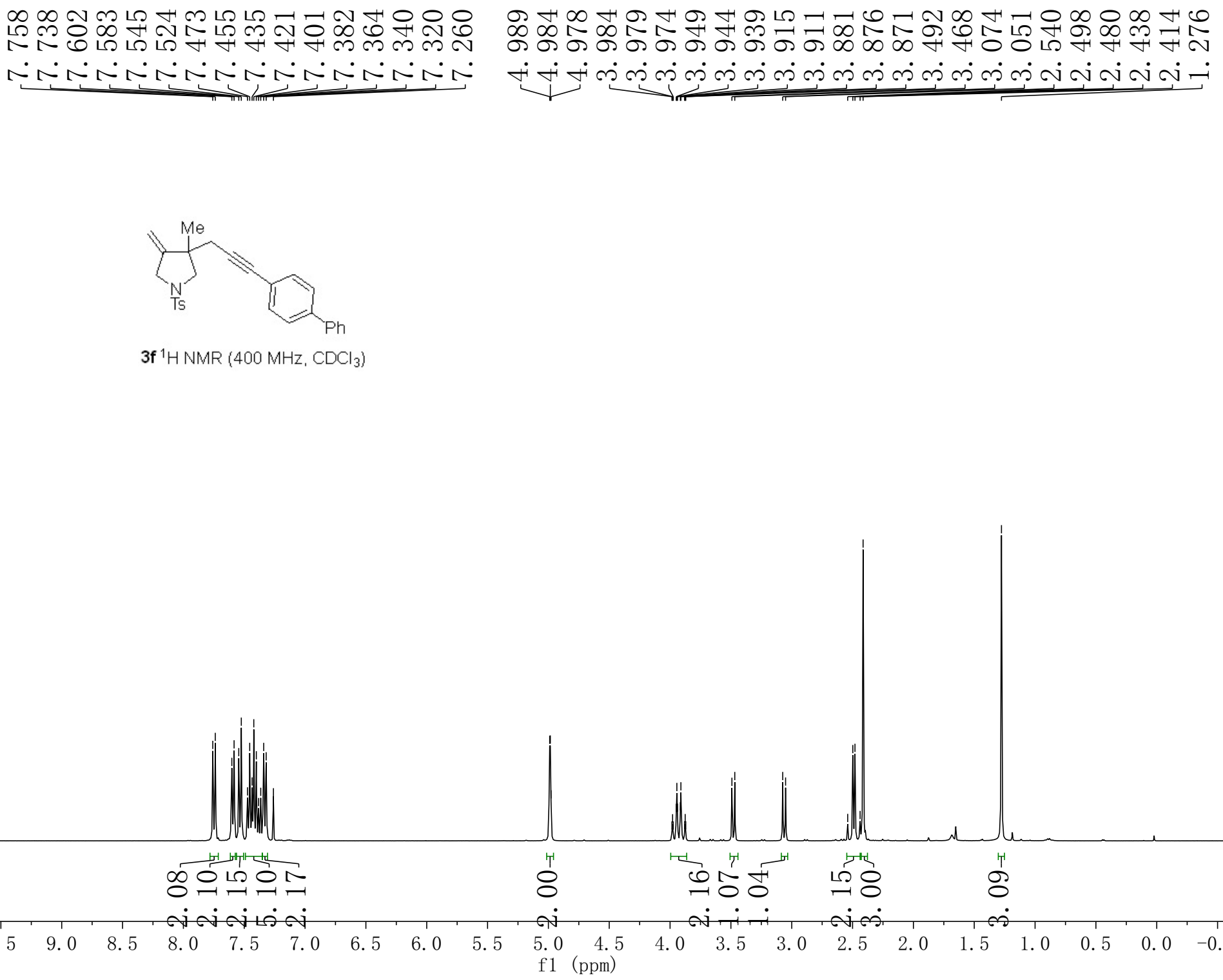


150.671
143.611
142.861
132.471
131.394
129.632
128.279
127.820
120.442
106.438
85.555
82.669
77.318
77.000
76.682
58.711
52.260
45.311
35.482
33.397
30.003
23.462
22.244
21.522
13.895



3e ^{13}C NMR (100 MHz, $CDCl_3$)





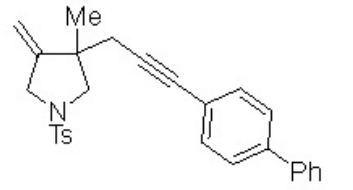
3f ^{1}H NMR (400 MHz, $CDCl_3$)

150.622
143.635
140.568
140.310
132.479
131.927
129.635
128.798
127.819
127.523
126.914
126.841
122.252
106.511

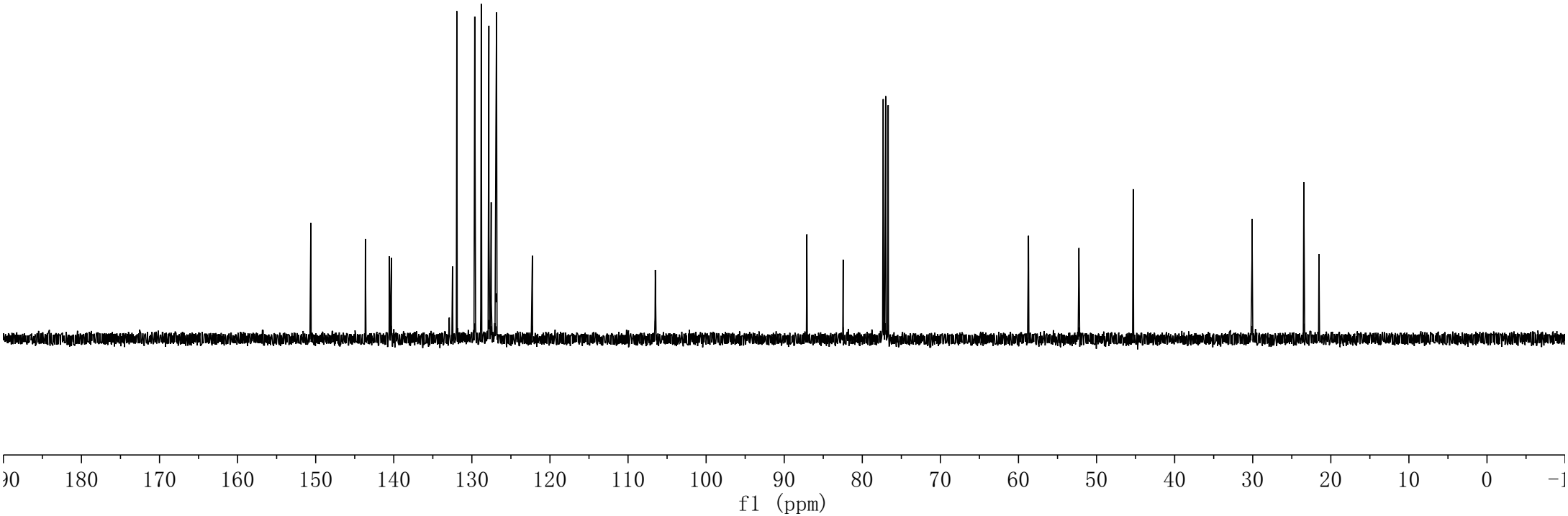
87.097
82.451
77.319
77.000
76.682

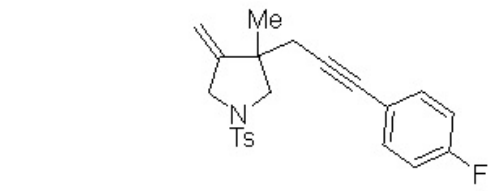
58.721
52.256
45.307

30.089
23.459
21.518

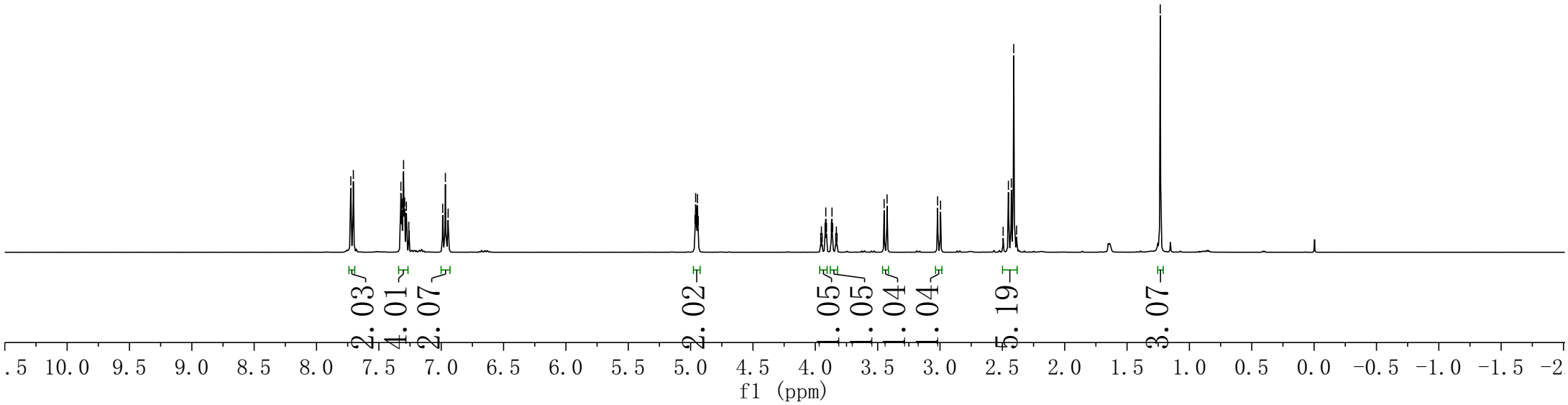


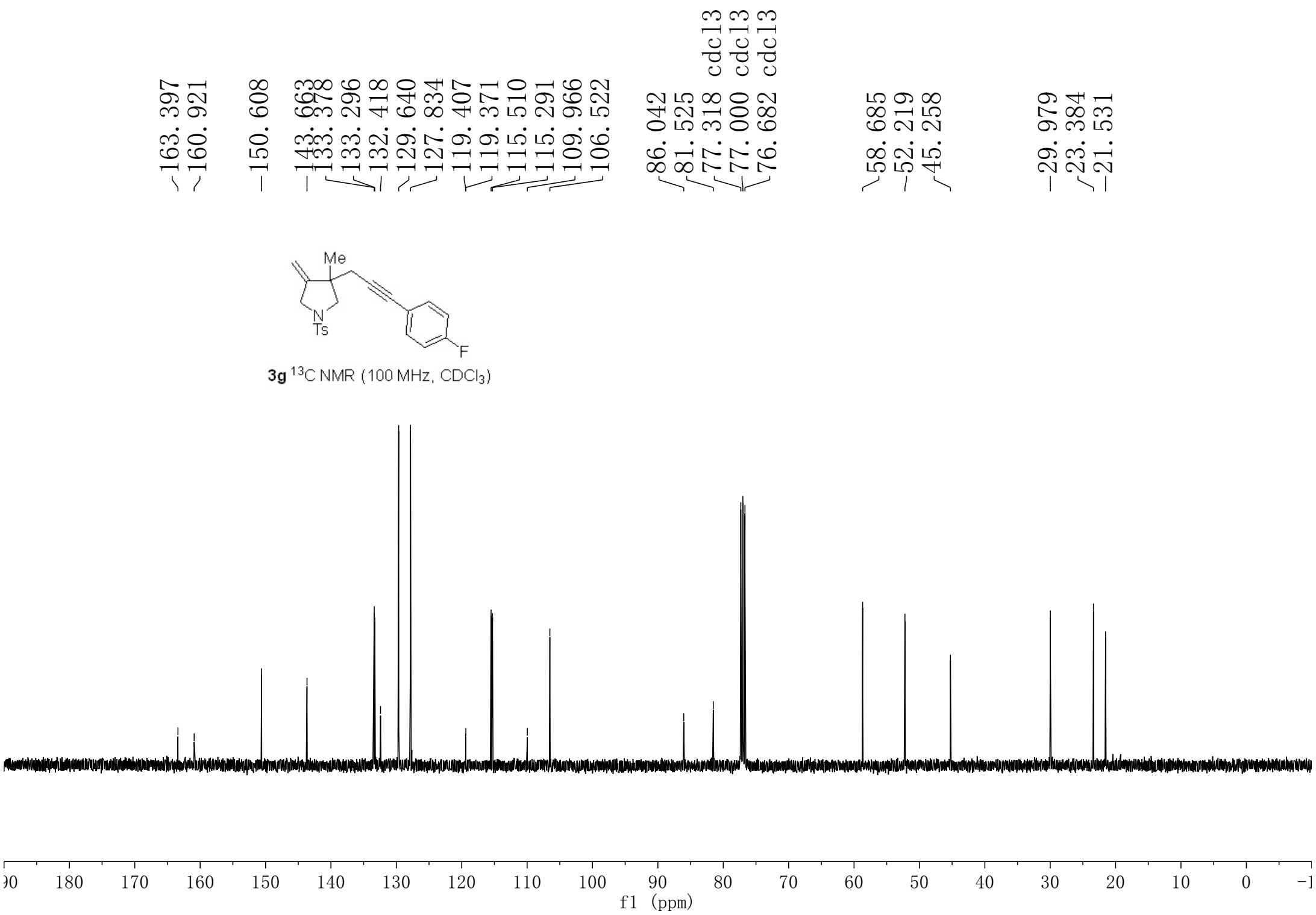
3f ^{13}C NMR (100 MHz, $CDCl_3$)



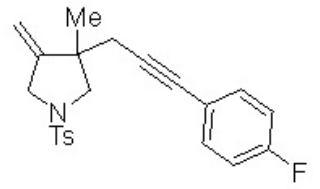


3g ^{1}H NMR (400 MHz, $CDCl_3$)





3g ^{13}C NMR (100 MHz, $CDCl_3$)

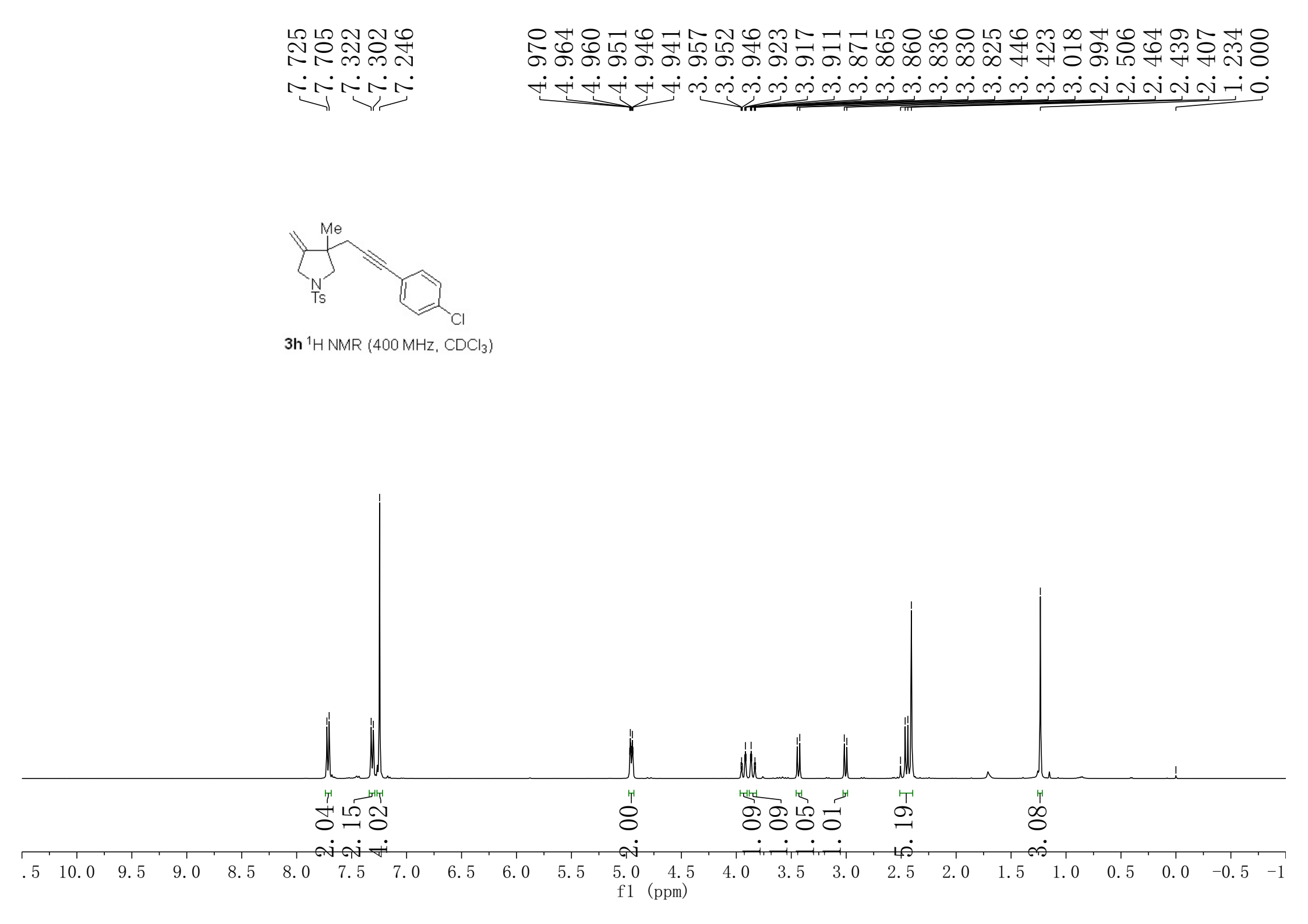


3g ^{19}F NMR (376 MHz, $CDCl_3$)

−111.623

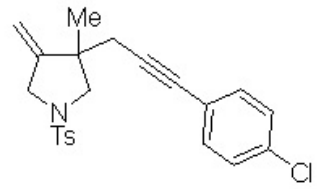
−10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

f1 (ppm)

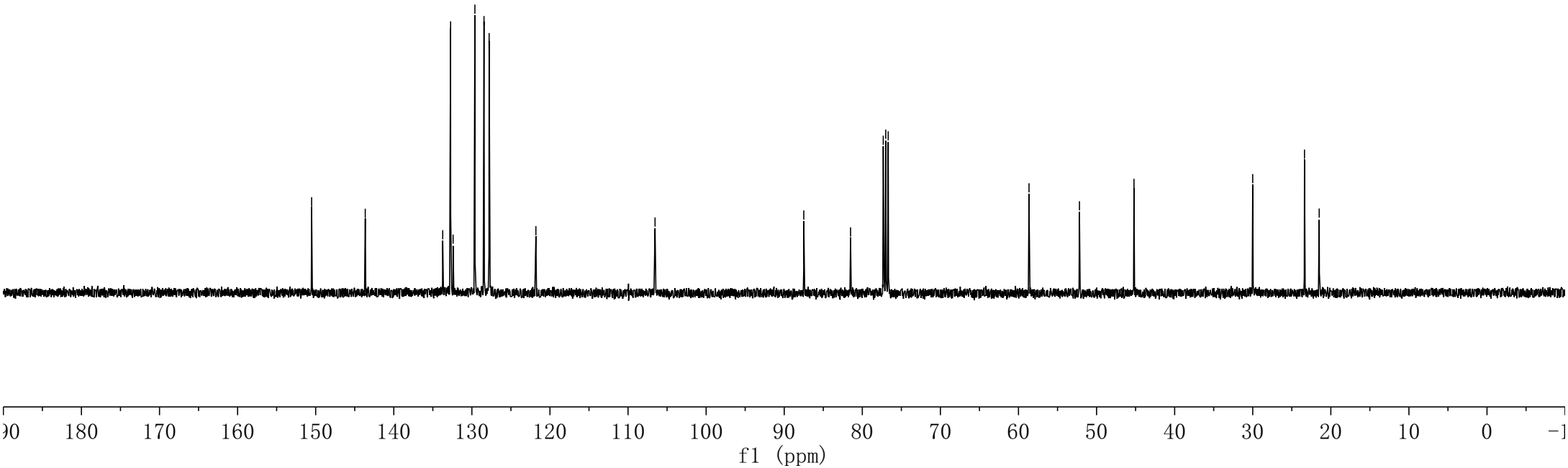


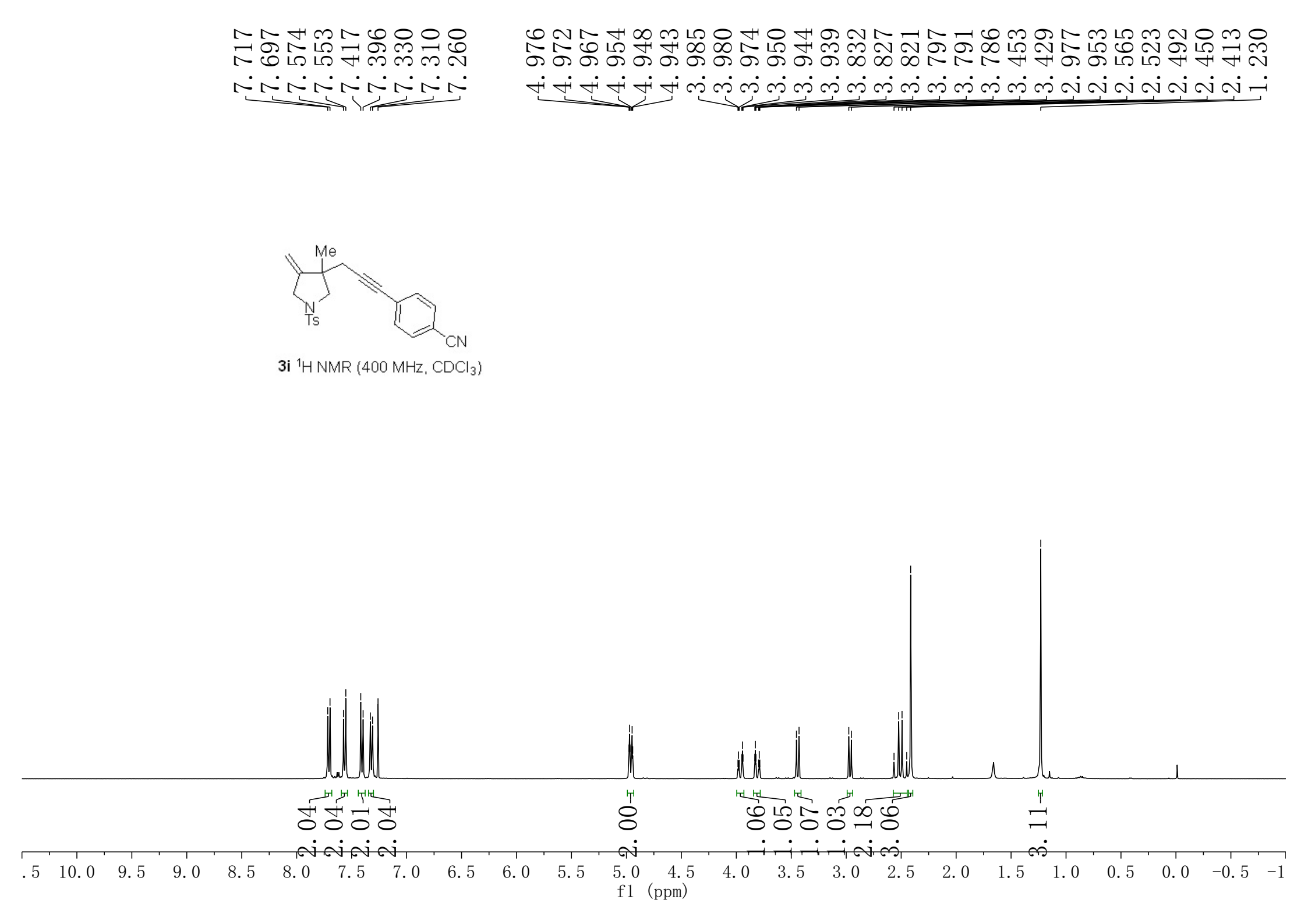
3h ^{1}H NMR (400 MHz, $CDCl_3$)

150.520
143.652
133.732
132.724
132.401
129.613
128.445
127.790
121.802
106.541
87.494
81.504
77.317
77.000
76.682
58.651
52.190
45.209
30.003
23.373
21.488

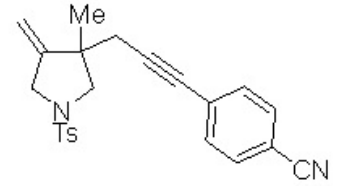


3h ^{13}C NMR (100 MHz, $CDCl_3$)

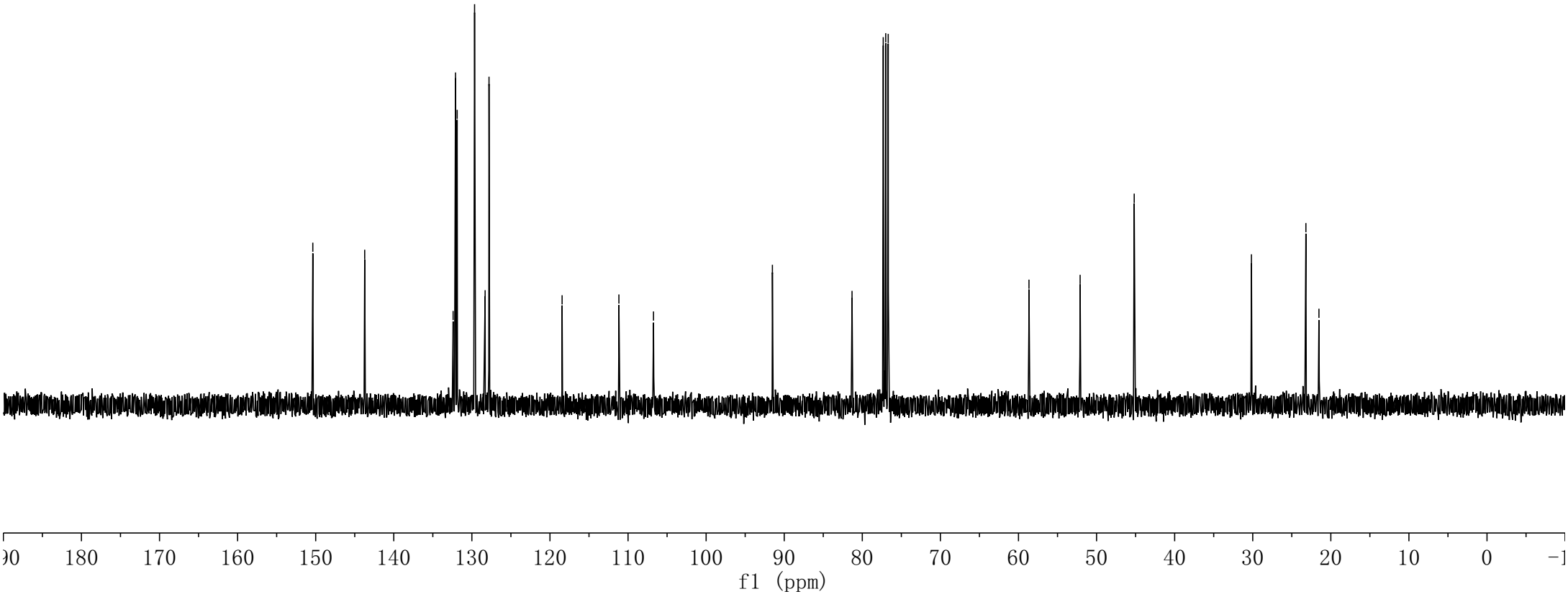


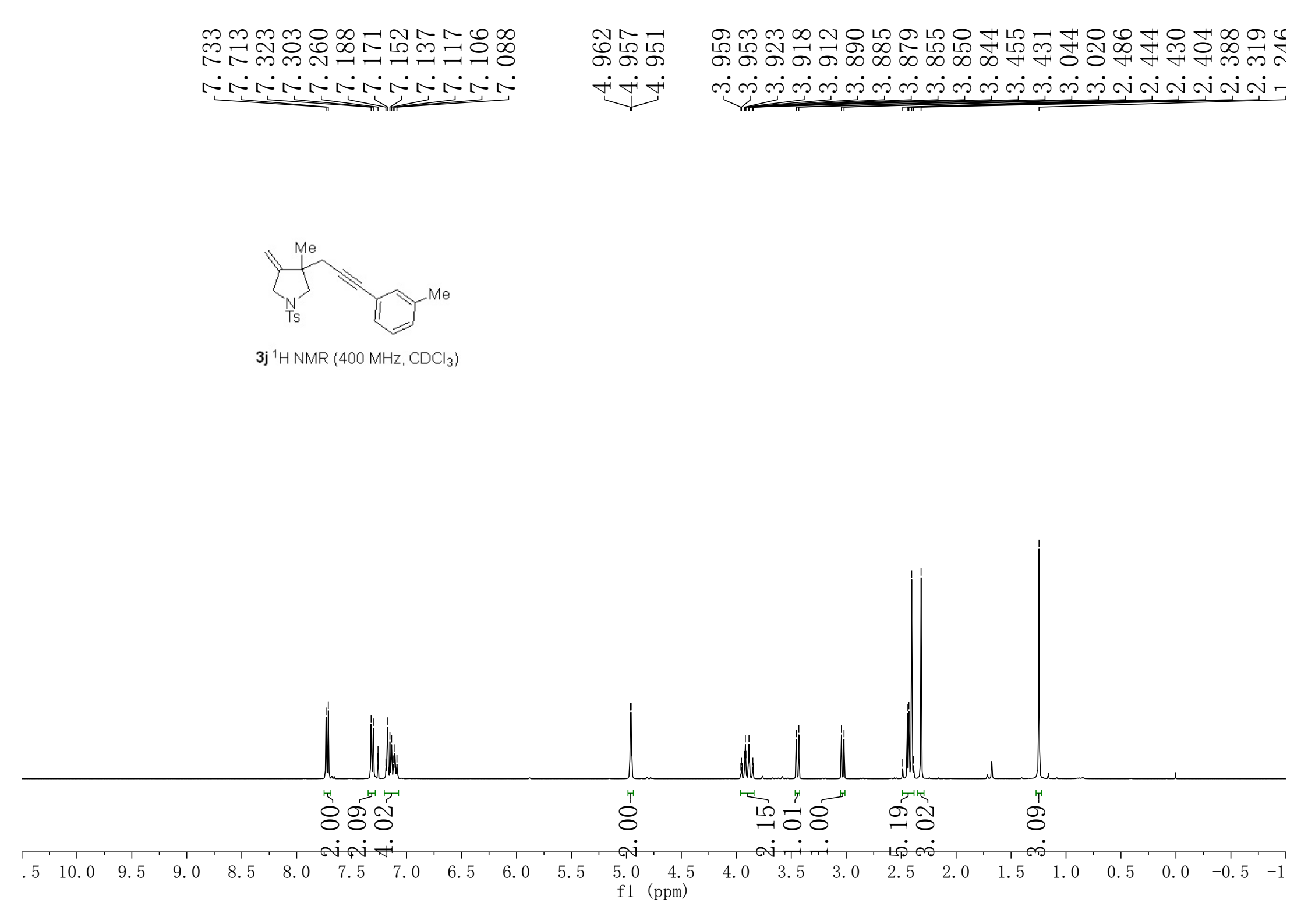

7.717
7.697
7.574
7.553
7.417
7.396
7.330
7.310
7.260
4.976
4.972
4.967
4.954
4.948
4.943
3.985
3.980
3.974
3.950
3.944
3.939
3.832
3.827
3.821
3.797
3.791
3.786
3.453
3.429
2.977
2.953
2.565
2.523
2.492
2.450
2.413
1.230
Me
N
Ts
CN
3i 1H NMR (400 MHz, CDCl3)
2.04
2.04
2.01
2.04
2.00
1.06
1.05
1.07
1.03
2.18
3.06
3.11
f1 (ppm)

150.369
143.724
132.401
132.094
131.883
129.655
128.301
127.804
118.444
111.170
106.740
91.513
81.315
77.318
77.000
76.682
58.655
52.105
45.178
30.167
23.192
21.522



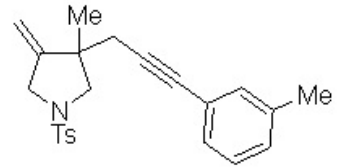
3i ^{13}C NMR (100 MHz, $CDCl_3$)



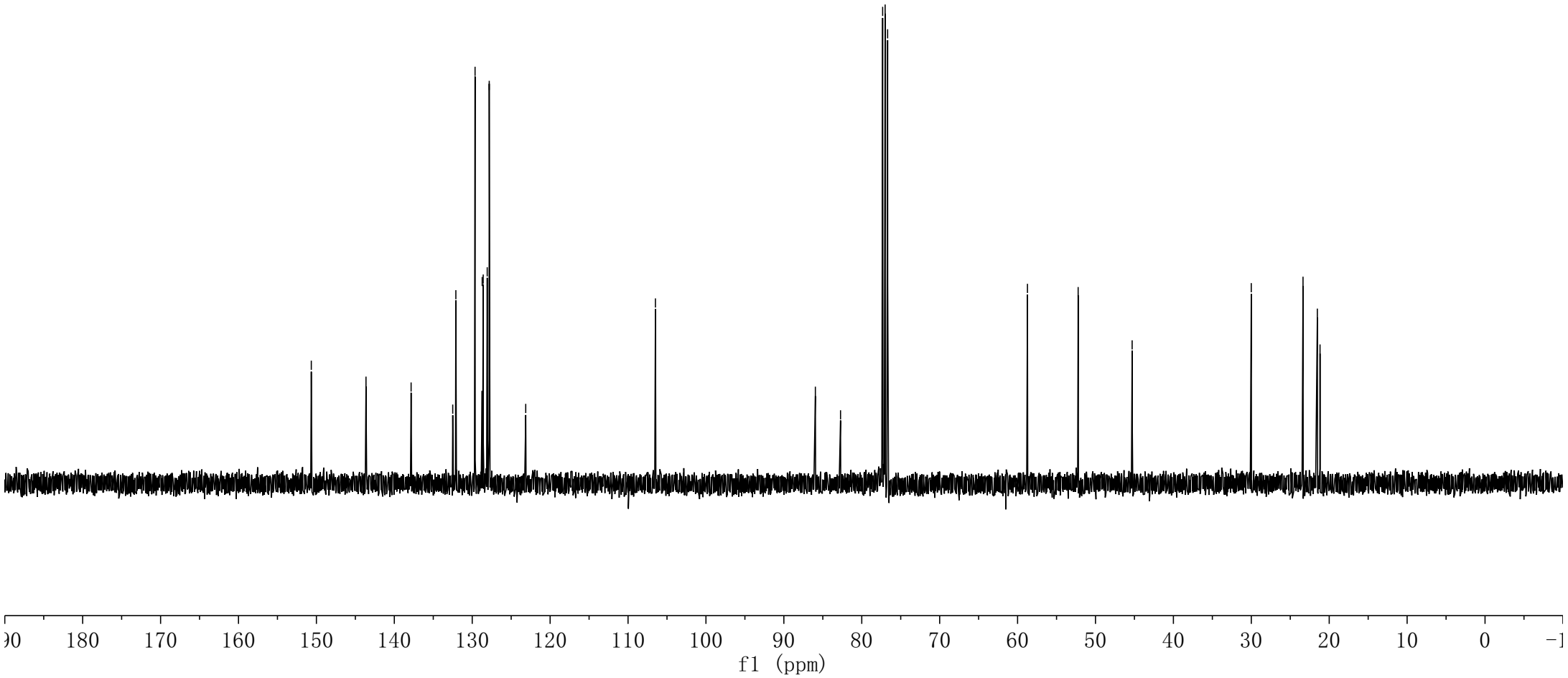


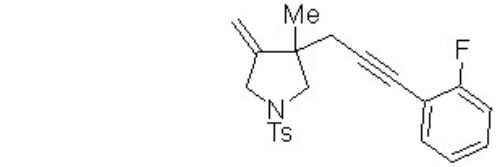
3j ^{1}H NMR (400 MHz, $CDCl_3$)

150.655
143.635
137.844
132.501
132.101
129.635
128.720
128.589
128.075
127.816
123.132
106.485
85.955
82.725
77.318
77.000
76.683
58.731
52.226
45.295
30.005
23.362
21.523
21.179

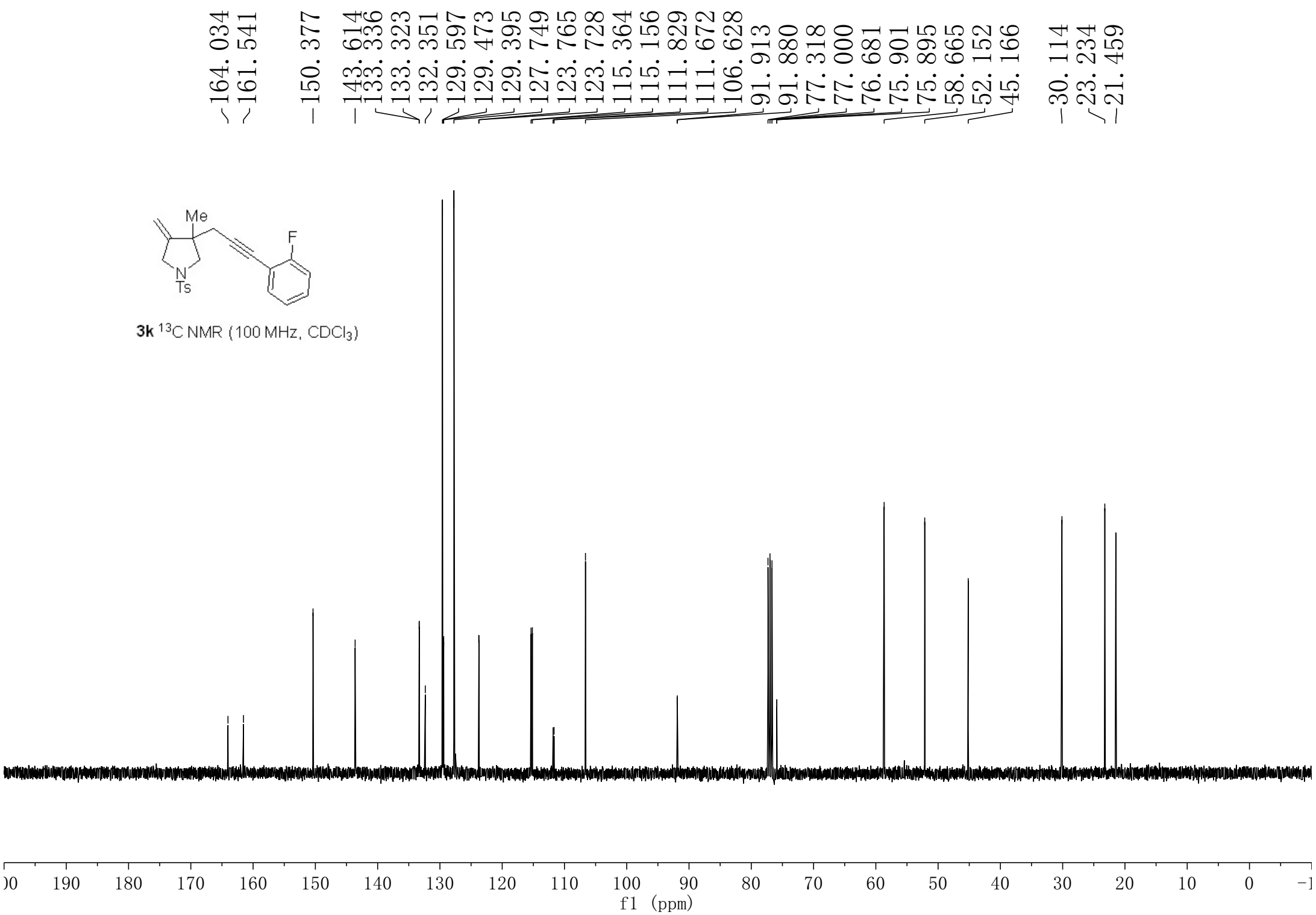


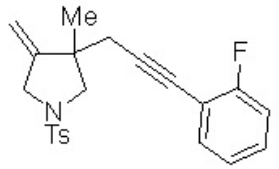
3j ^{13}C NMR (100 MHz, $CDCl_3$)





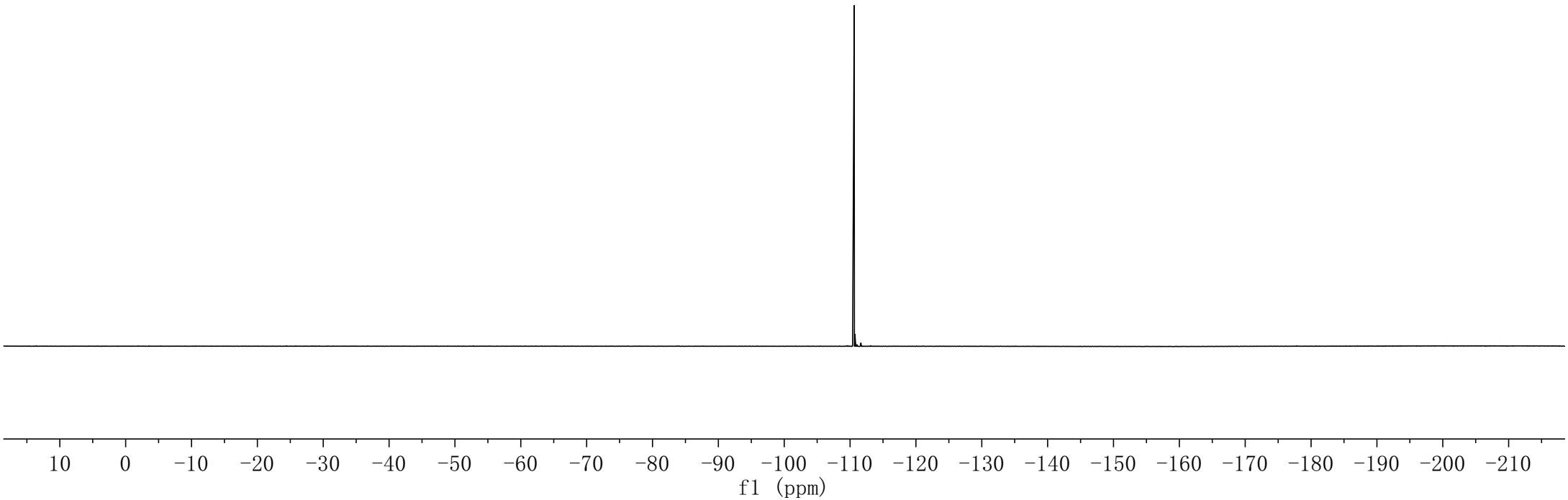
3k ^{1}H NMR (400 MHz, $CDCl_3$)

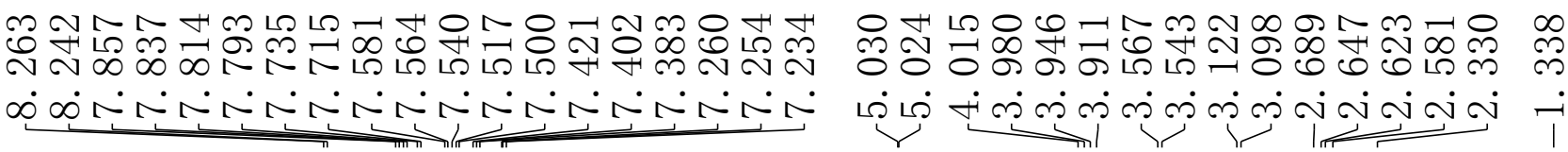

164.034
161.541
150.377
143.614
133.336
133.323
132.351
129.597
129.473
129.395
127.749
123.765
123.728
115.364
115.156
111.829
111.672
106.628
91.913
91.880
77.318
77.000
76.681
75.901
75.895
58.665
52.152
45.166
30.114
23.234
21.459
Me
F
N
Ts
3k 13C NMR (100 MHz, CDCl3)
f1 (ppm)

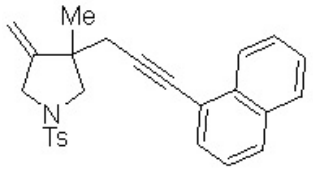


3k ^{19}F NMR (376 MHz, $CDCl_3$)

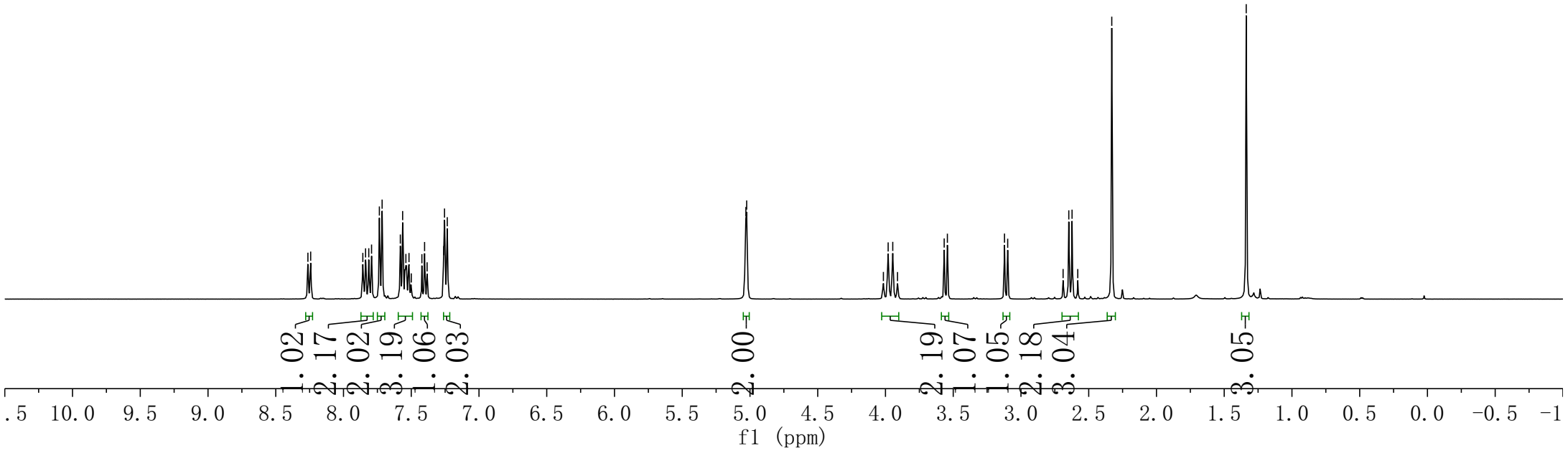
−110.631







3l ^{1}H NMR (400 MHz, $CDCl_3$)



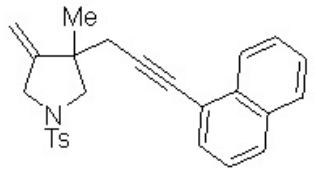
150.611
143.606
133.327
133.069
132.388
130.237
129.567
128.215
128.177
127.736
126.561
126.236
126.013
125.090
120.990
106.611

91.293

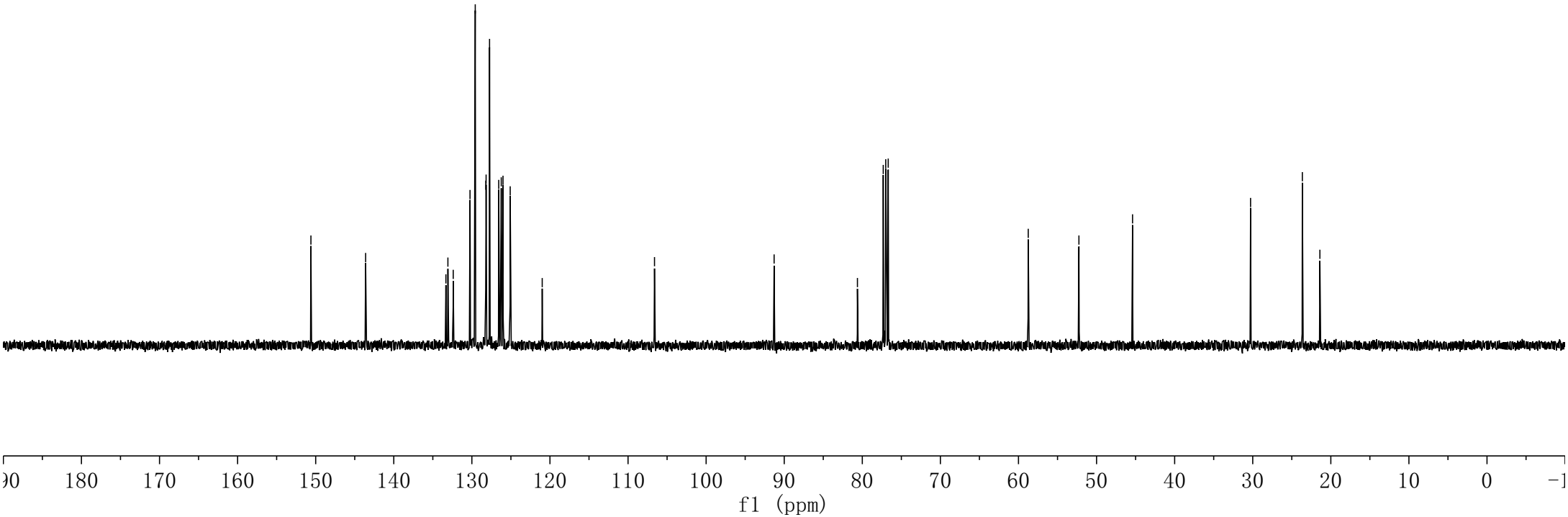
80.623
77.319
77.000
76.682

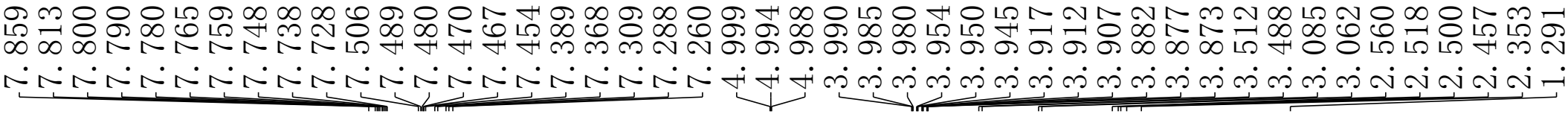
58.749
52.260
45.390

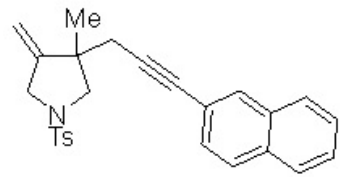
30.277
23.647
21.400



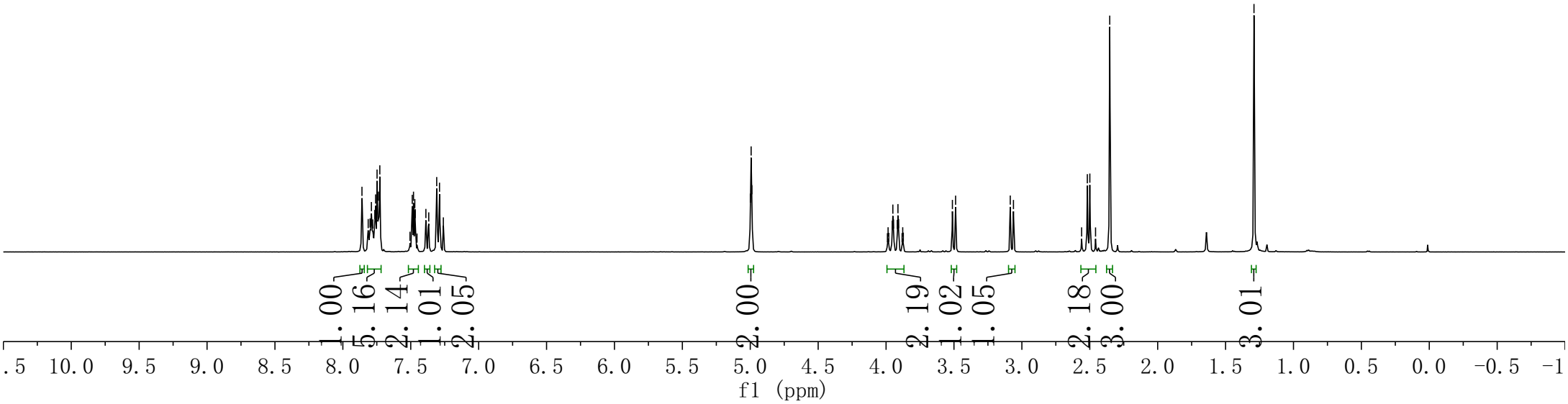
3l ^{13}C NMR (100 MHz, $CDCl_3$)

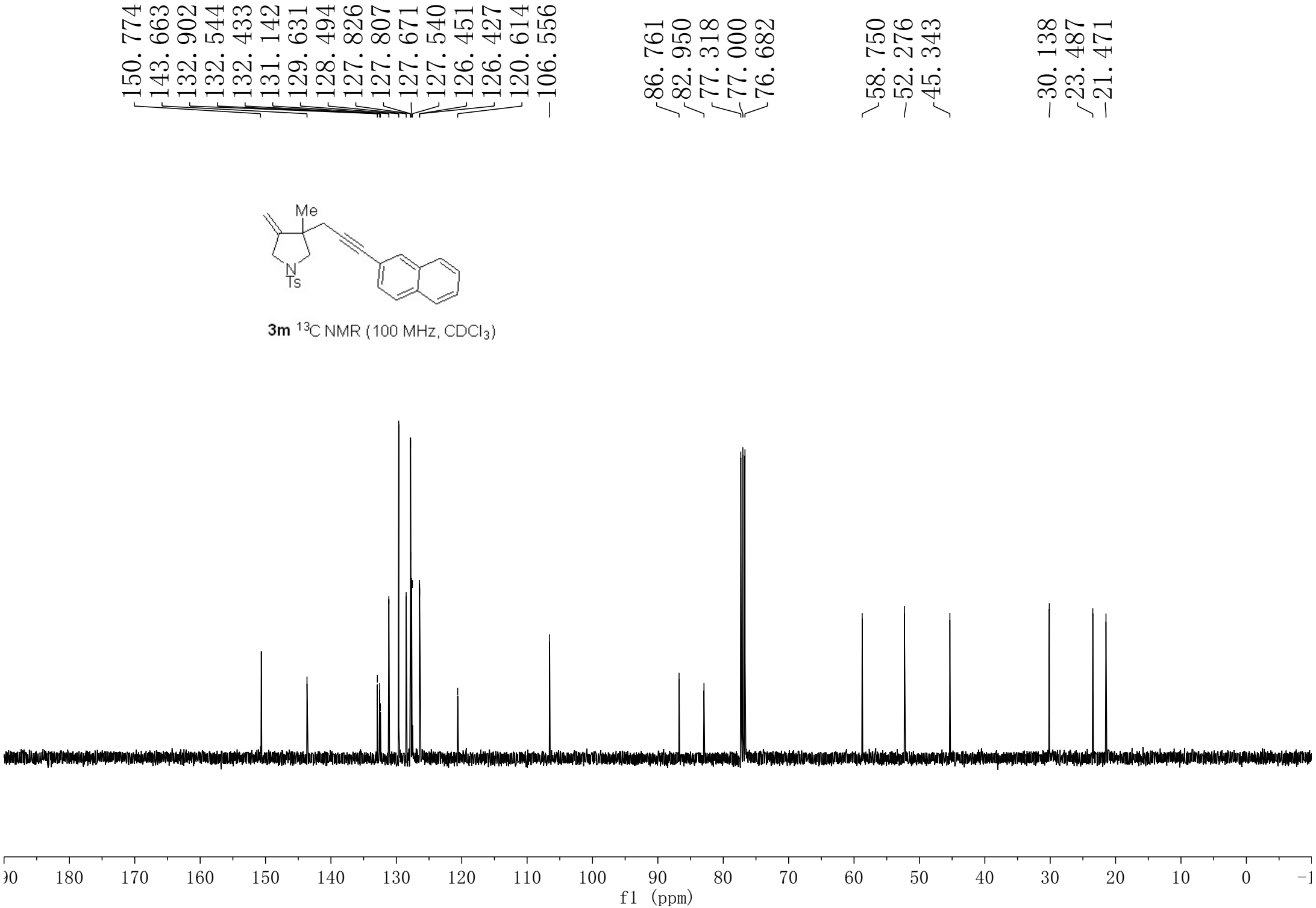




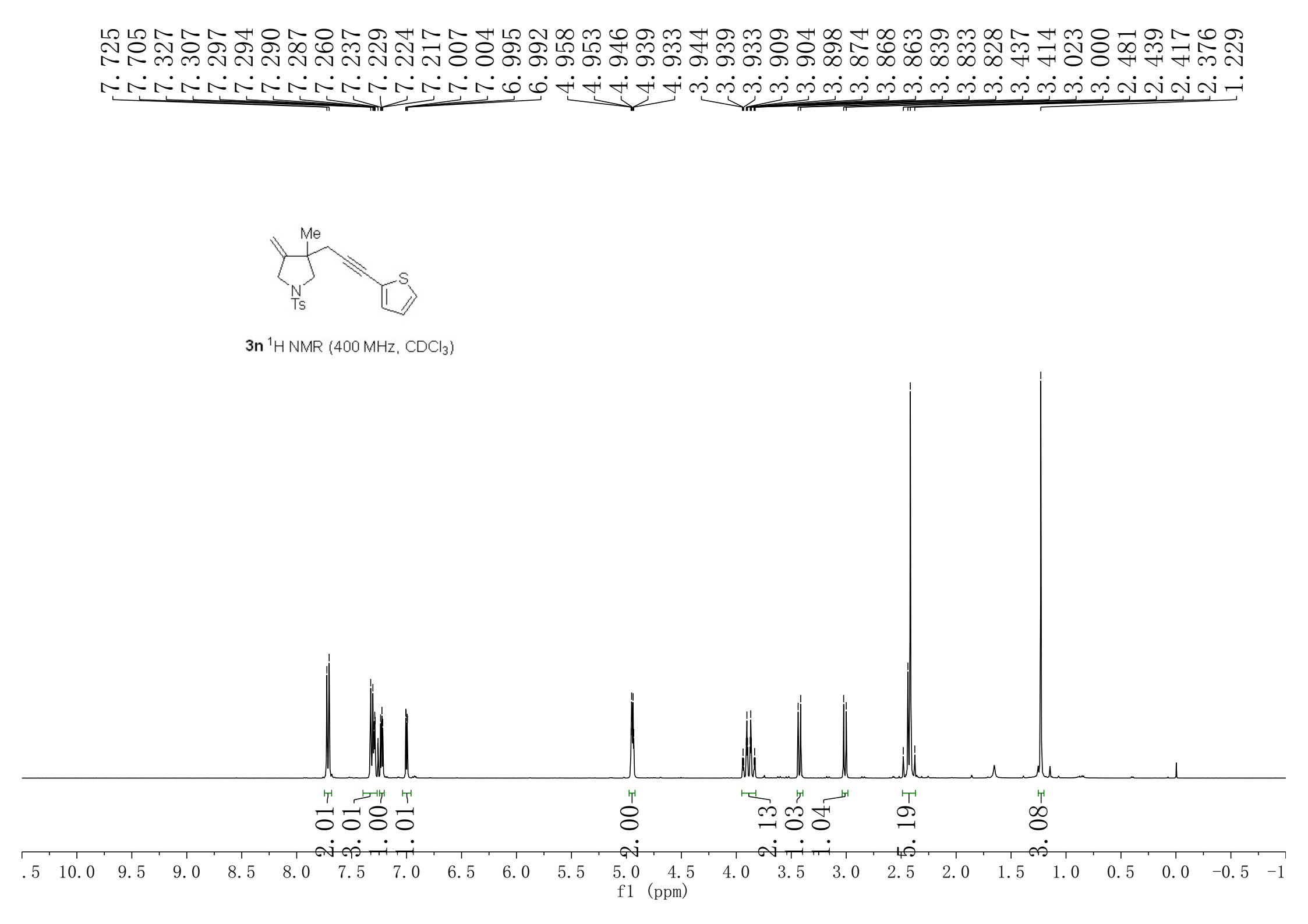


3m ^{1}H NMR (400 MHz, $CDCl_3$)

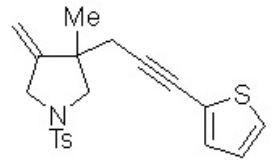




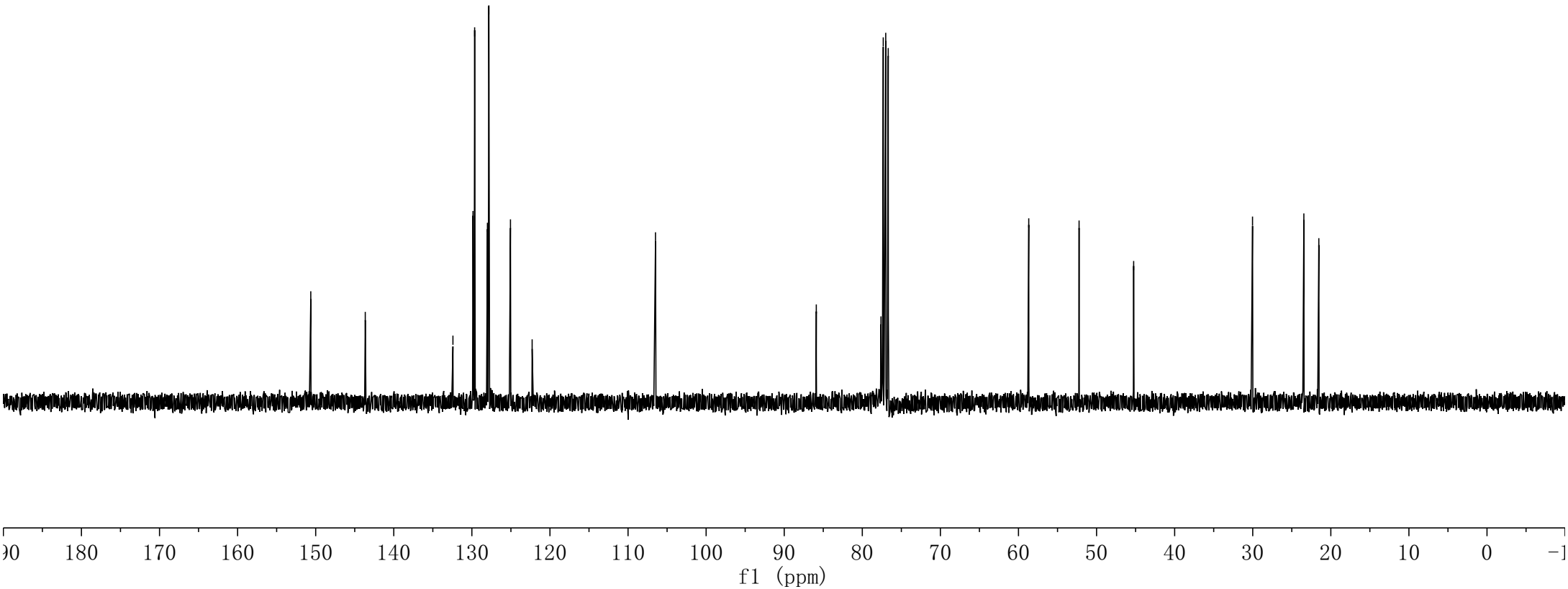
3m ^{13}C NMR (100 MHz, $CDCl_3$)

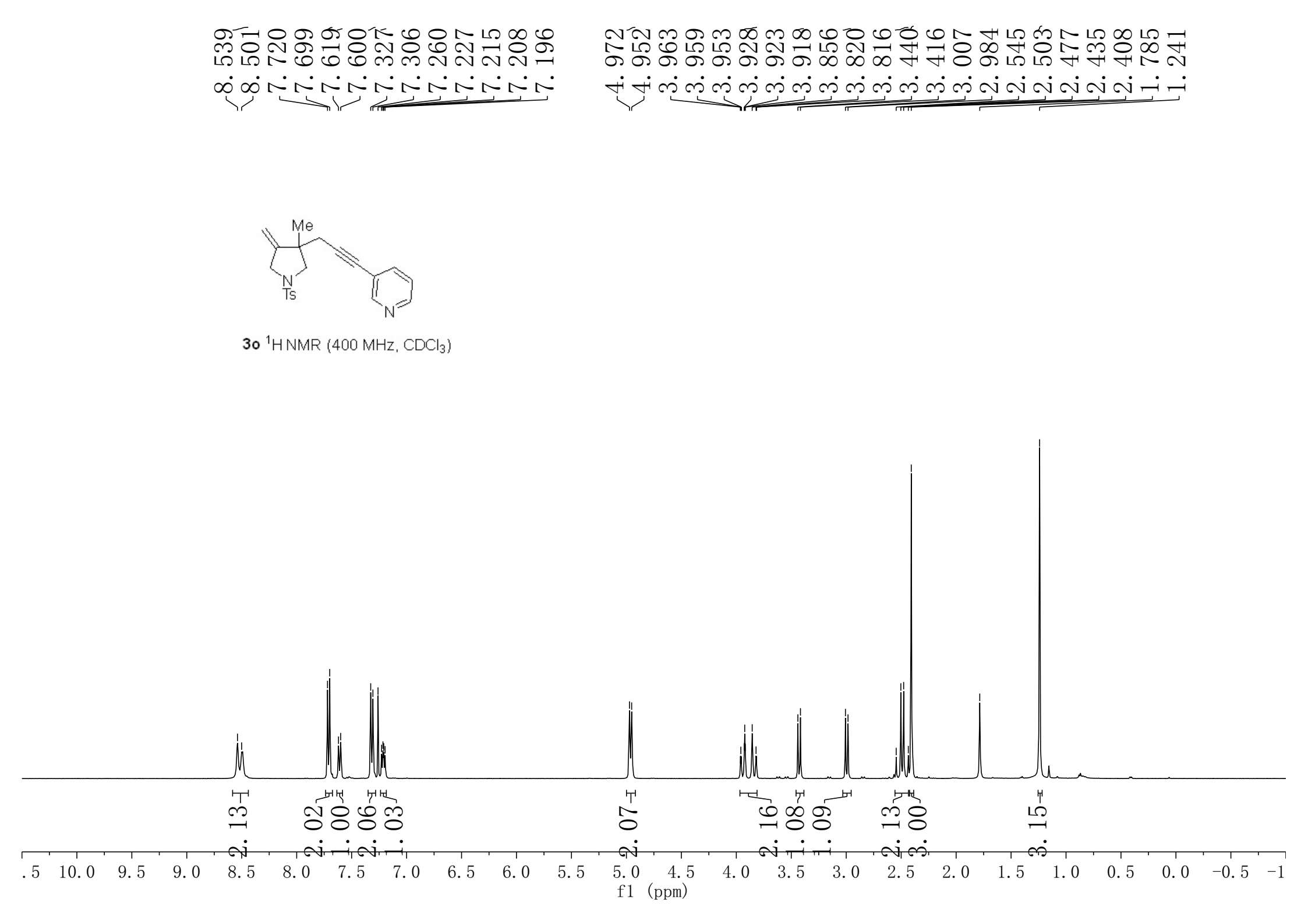

7.725
7.705
7.327
7.307
7.297
7.294
7.290
7.287
7.260
7.237
7.229
7.224
7.217
7.007
7.004
6.995
6.992
4.958
4.953
4.946
4.939
4.933
3.944
3.939
3.933
3.909
3.904
3.898
3.874
3.868
3.863
3.839
3.833
3.828
3.437
3.414
3.023
3.000
2.481
2.439
2.417
2.376
1.229
Me
N
Ts
S
3n 1H NMR (400 MHz, CDCl3)
2.01
3.01
1.00
1.01
2.00
2.13
1.03
1.04
5.19
3.08
f1 (ppm)

150.629
143.652
132.425
129.855
129.644
128.007
127.829
125.056
122.281
106.485
85.892
77.611
77.318
77.000
76.682
58.685
52.239
45.249
30.028
23.453
21.537



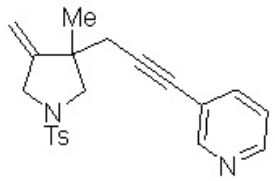
3n ^{13}C NMR (100 MHz, $CDCl_3$)



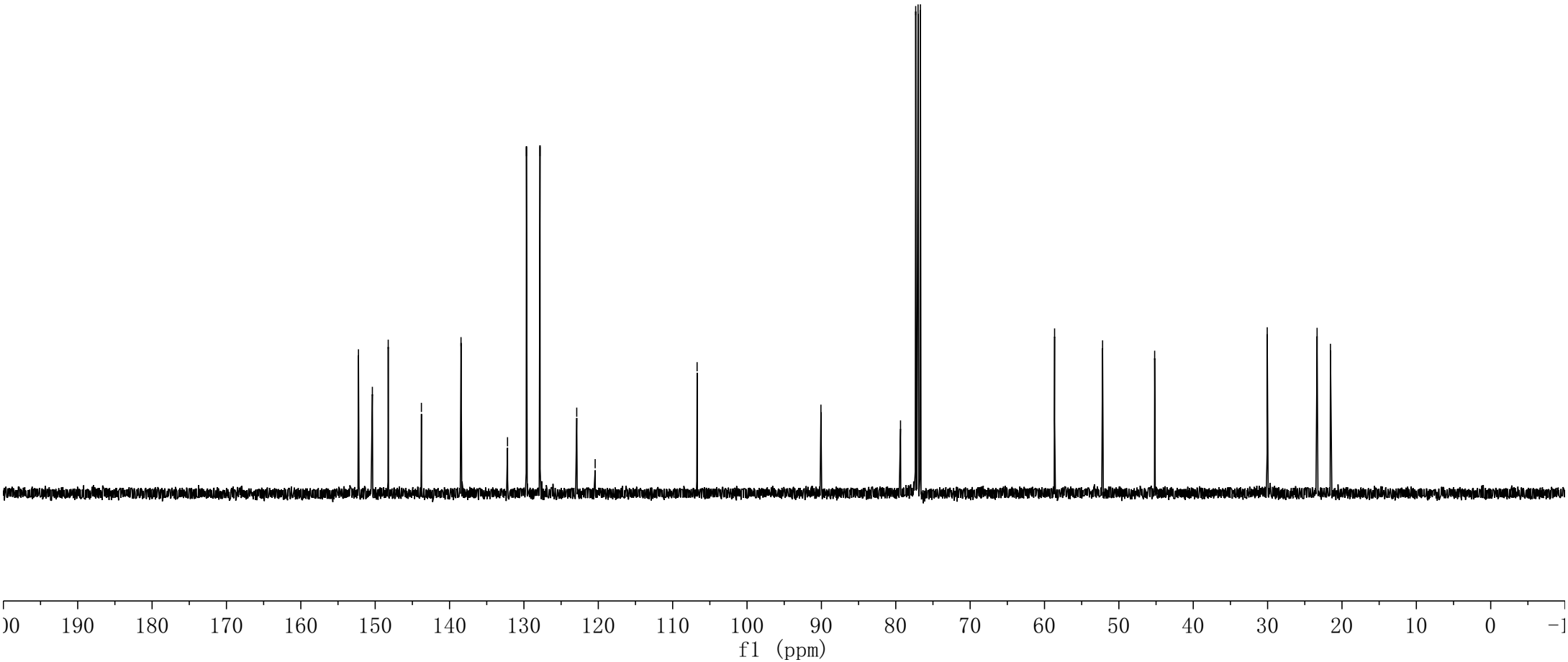


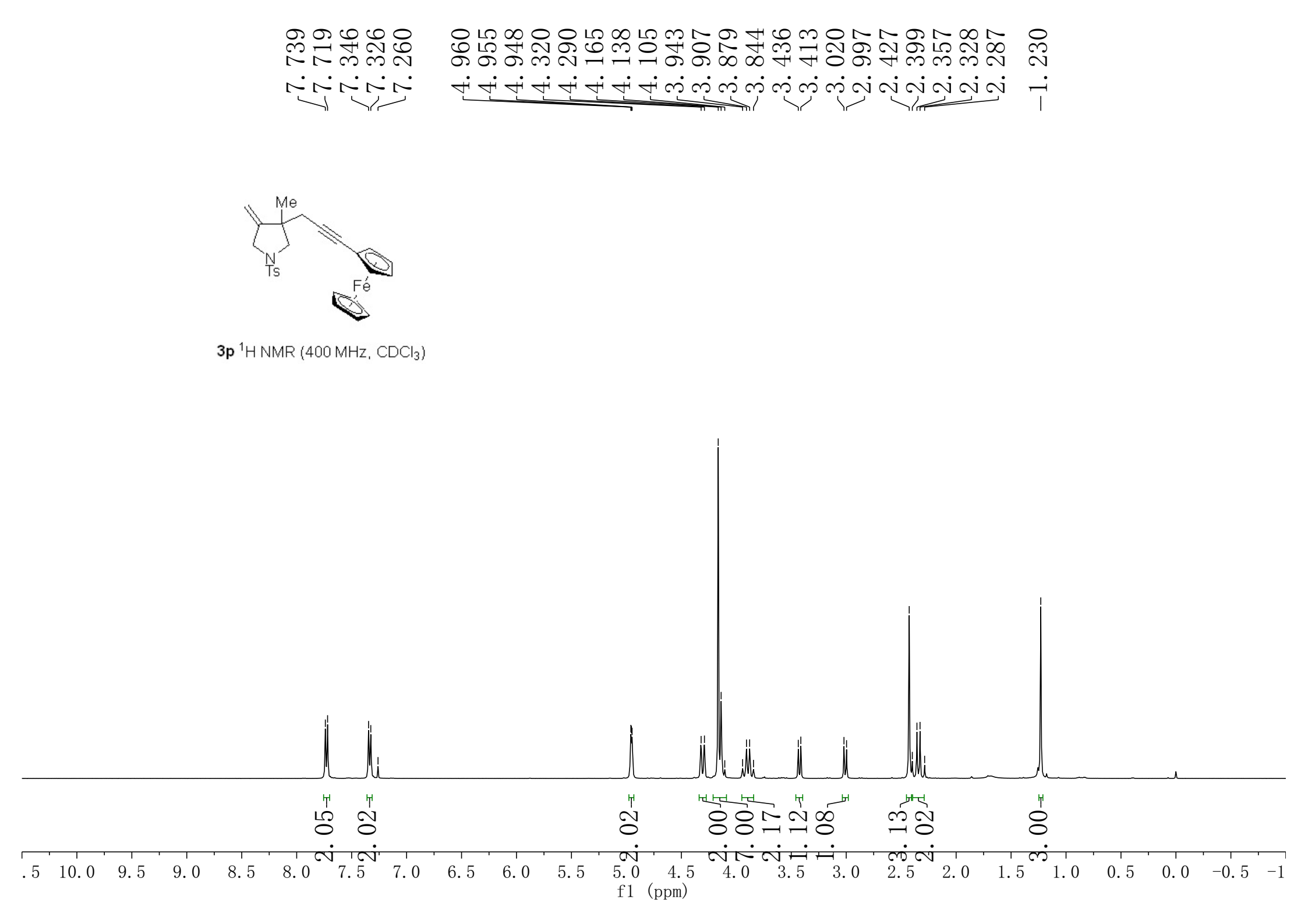
3o ^{1}H NMR (400 MHz, $CDCl_3$)

152.247
150.380
148.247
143.785
138.459
132.205
129.666
127.837
122.899
120.422
106.713
90.063
79.360
77.318
77.000
76.683
58.645
52.189
45.188
30.051
23.347
21.551

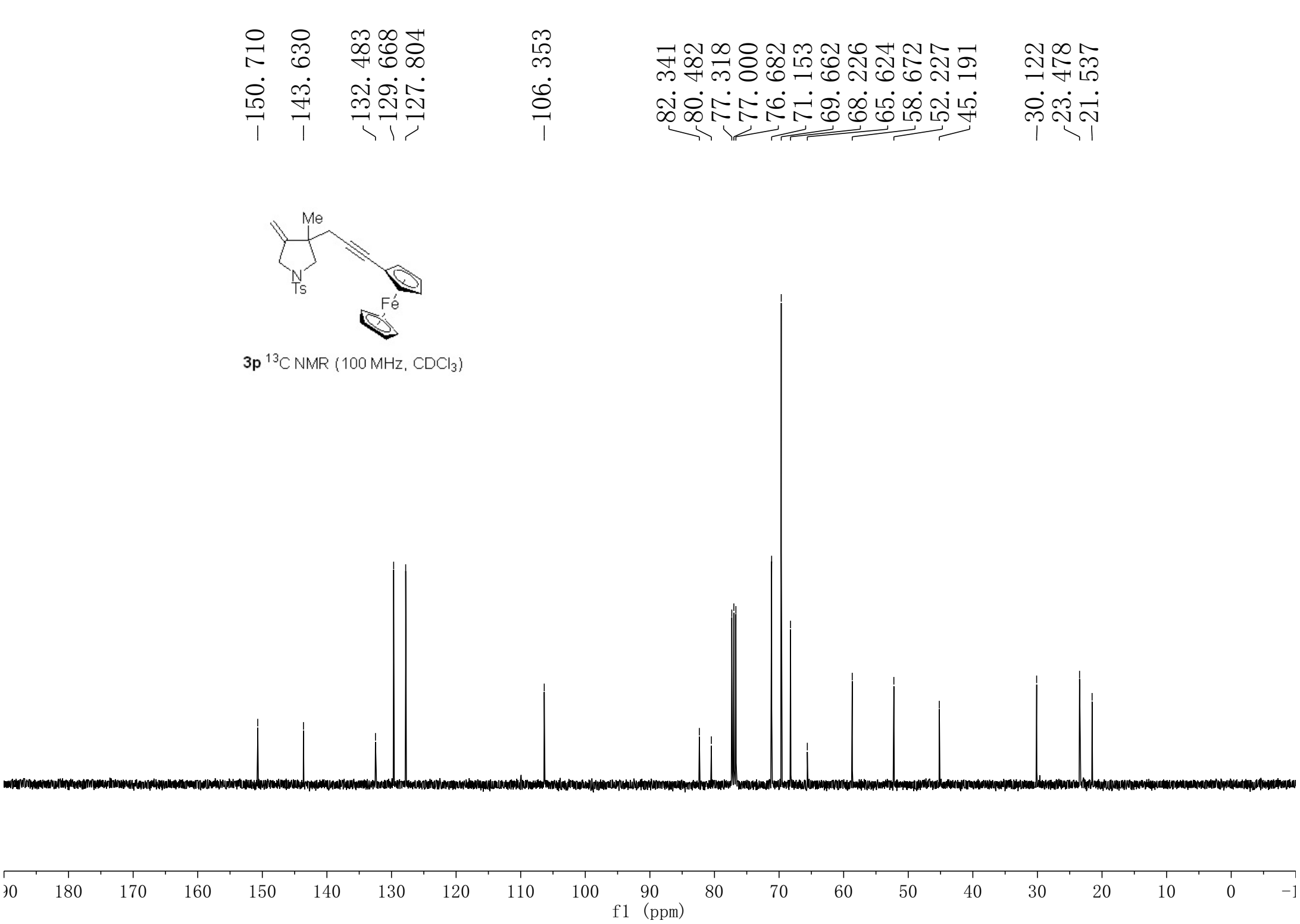


3o ^{13}C NMR (100 MHz, $CDCl_3$)

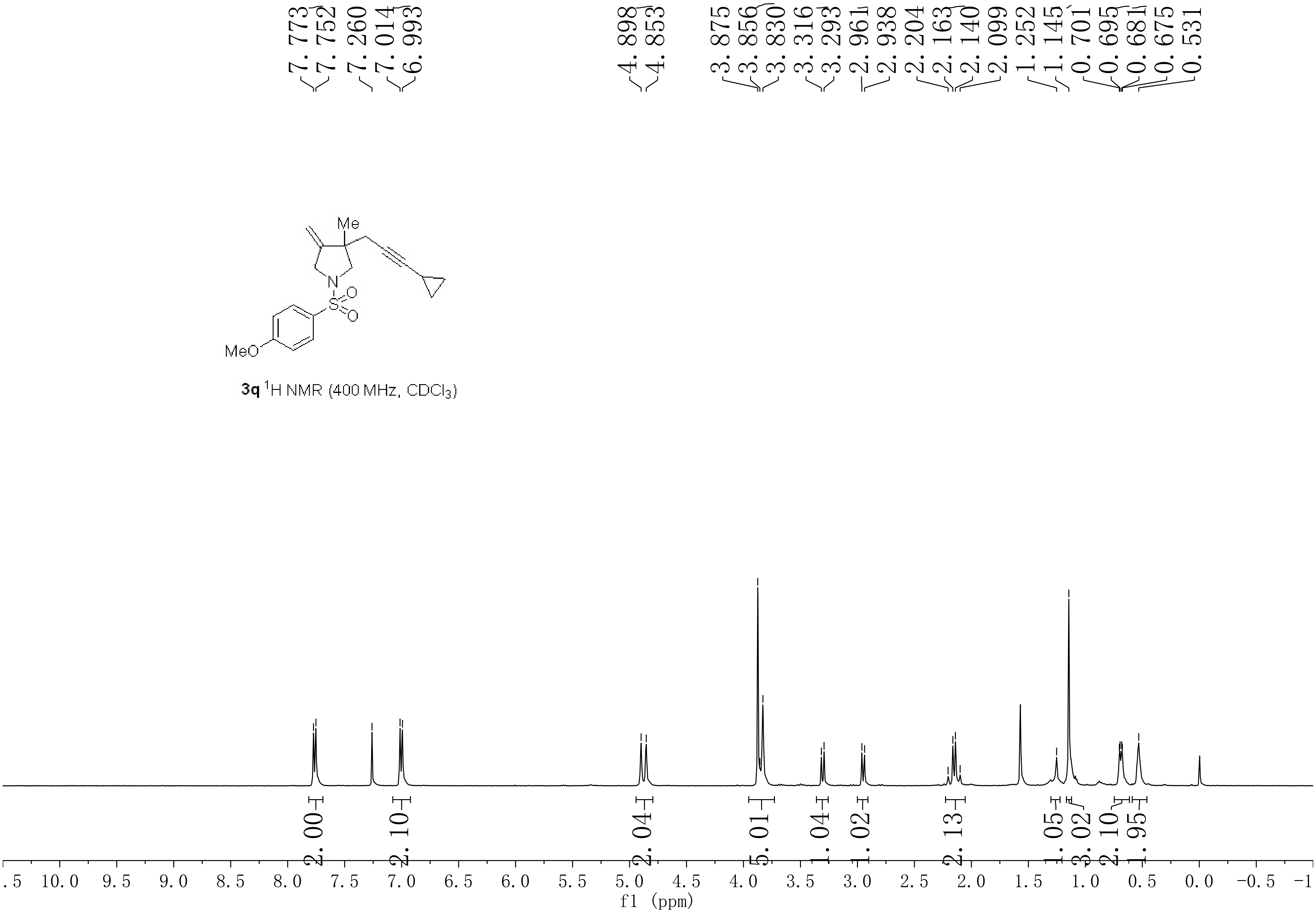




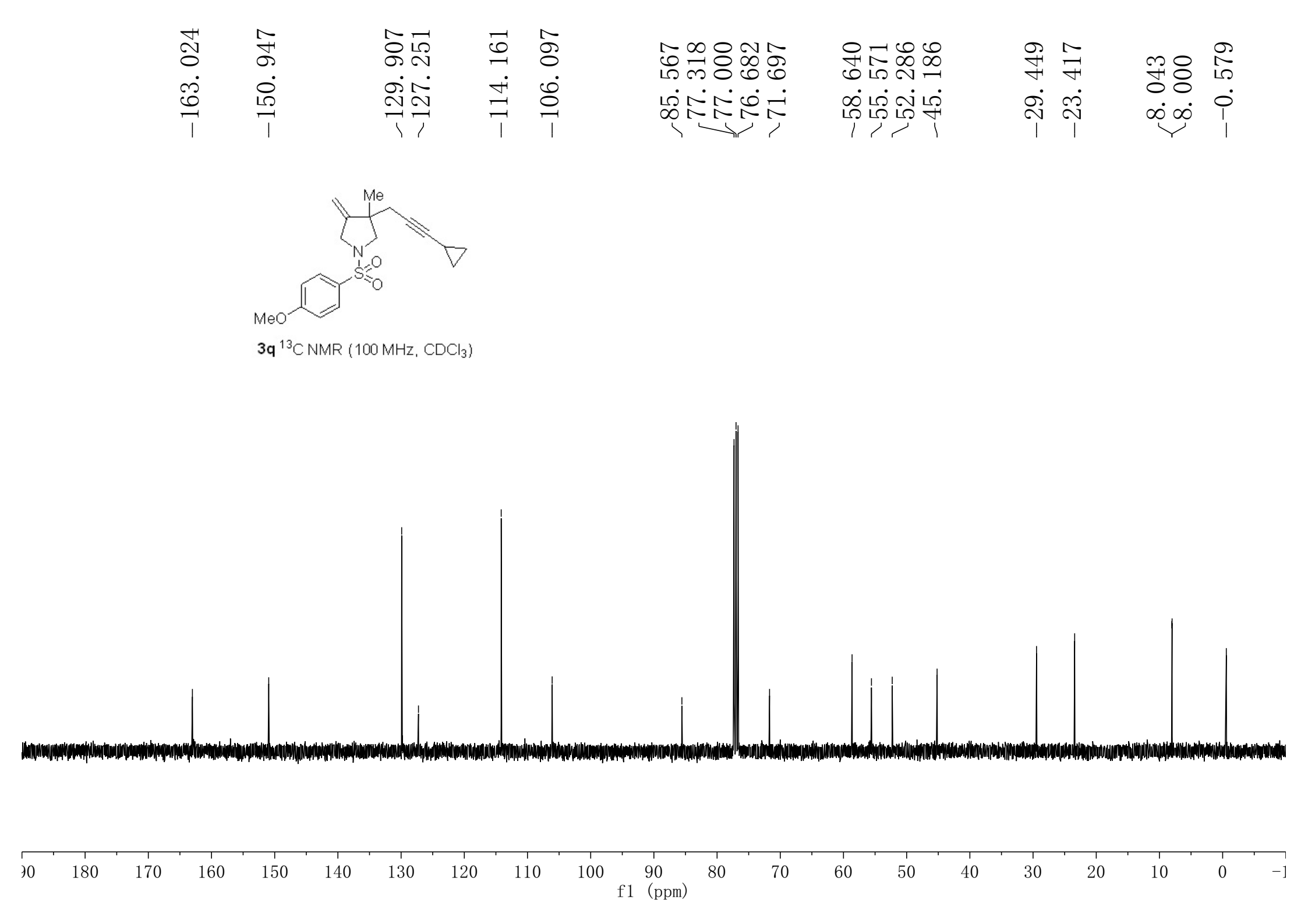
3p ^{1}H NMR (400 MHz, $CDCl_3$)

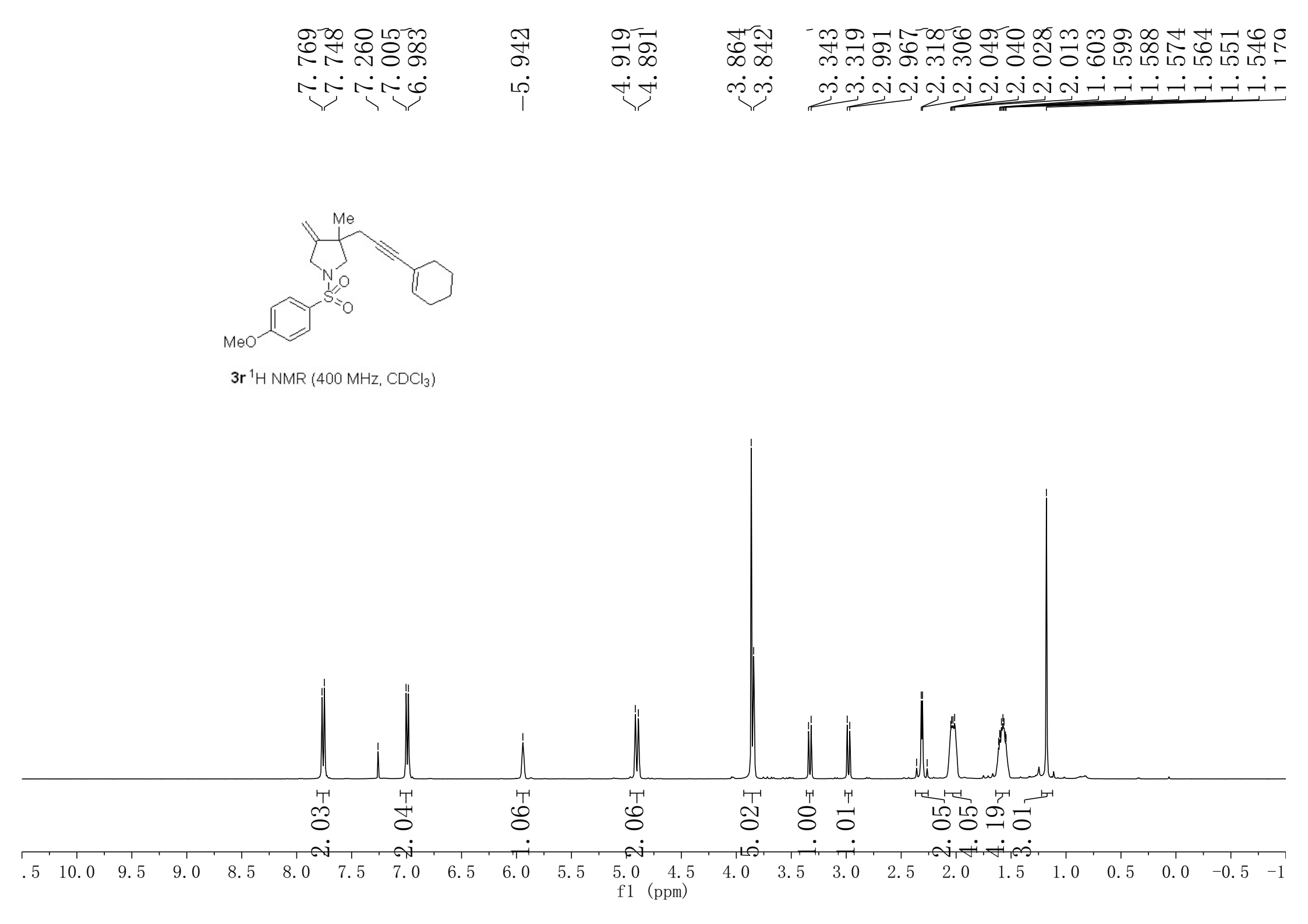


3p ^{13}C NMR (100 MHz, $CDCl_3$)



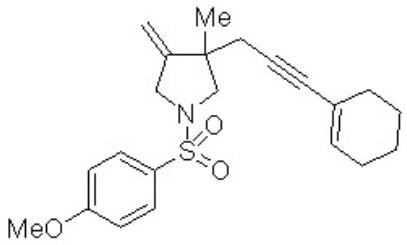
3q ^{1}H NMR (400 MHz, $CDCl_3$)


163.024
150.947
129.907
127.251
114.161
106.097
85.567
77.318
77.000
76.682
71.697
58.640
55.571
52.286
45.186
29.449
23.417
8.043
8.000
-0.579
Me
N
S
O
O
MeO
3q 13C NMR (100 MHz, CDCl3)
f1 (ppm)

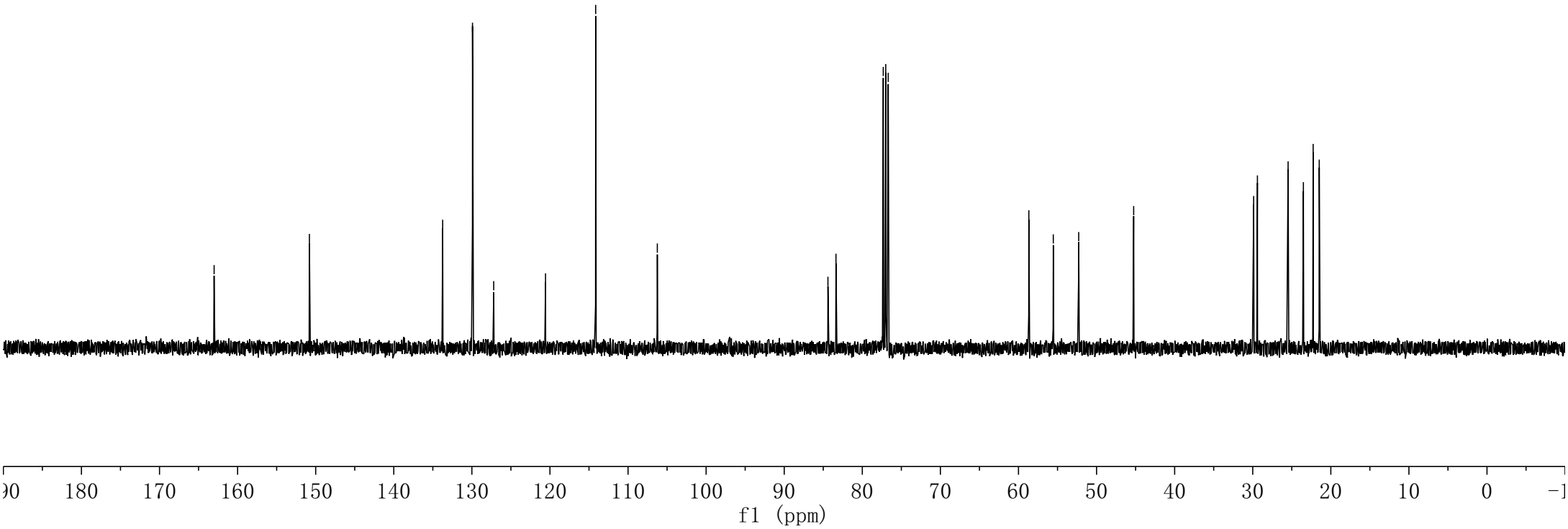


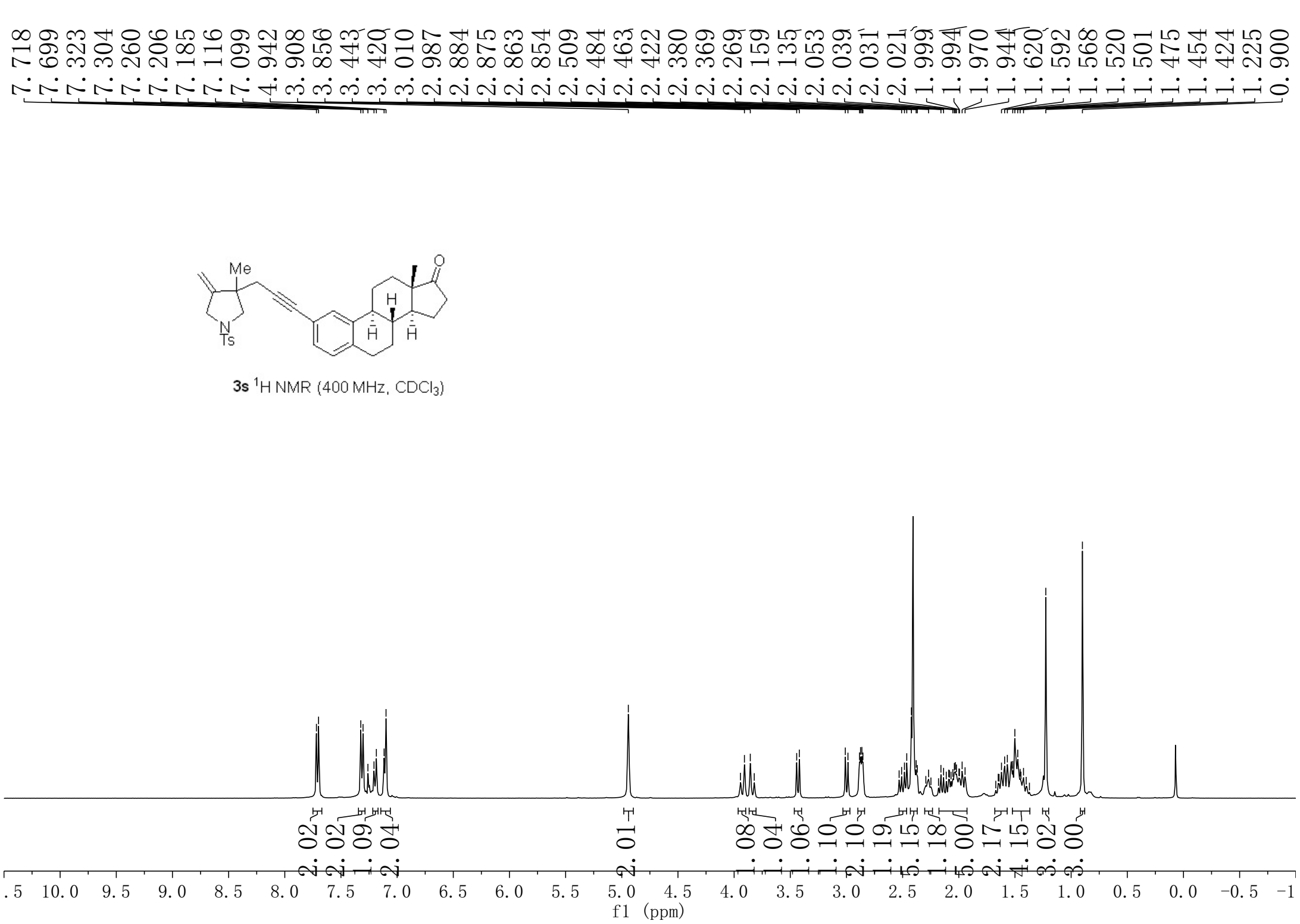
3r ^{1}H NMR (400 MHz, $CDCl_3$)

−163.008
−150.804
133.739
129.919
127.202
120.567
114.143
106.250
84.401
83.372
77.318
77.000
76.682
58.673
55.542
52.286
45.249
29.882
29.401
25.471
23.514
22.264
21.483

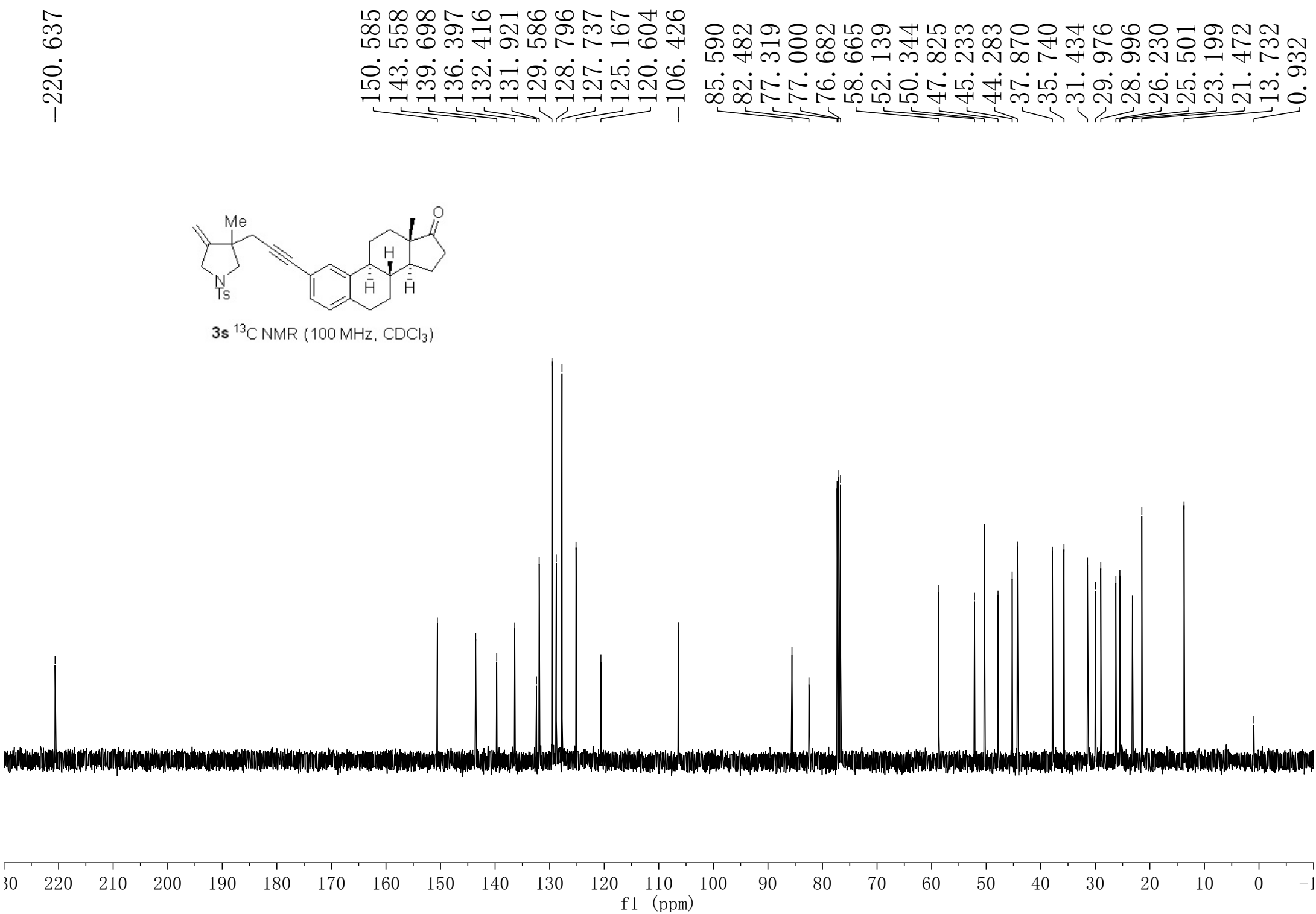


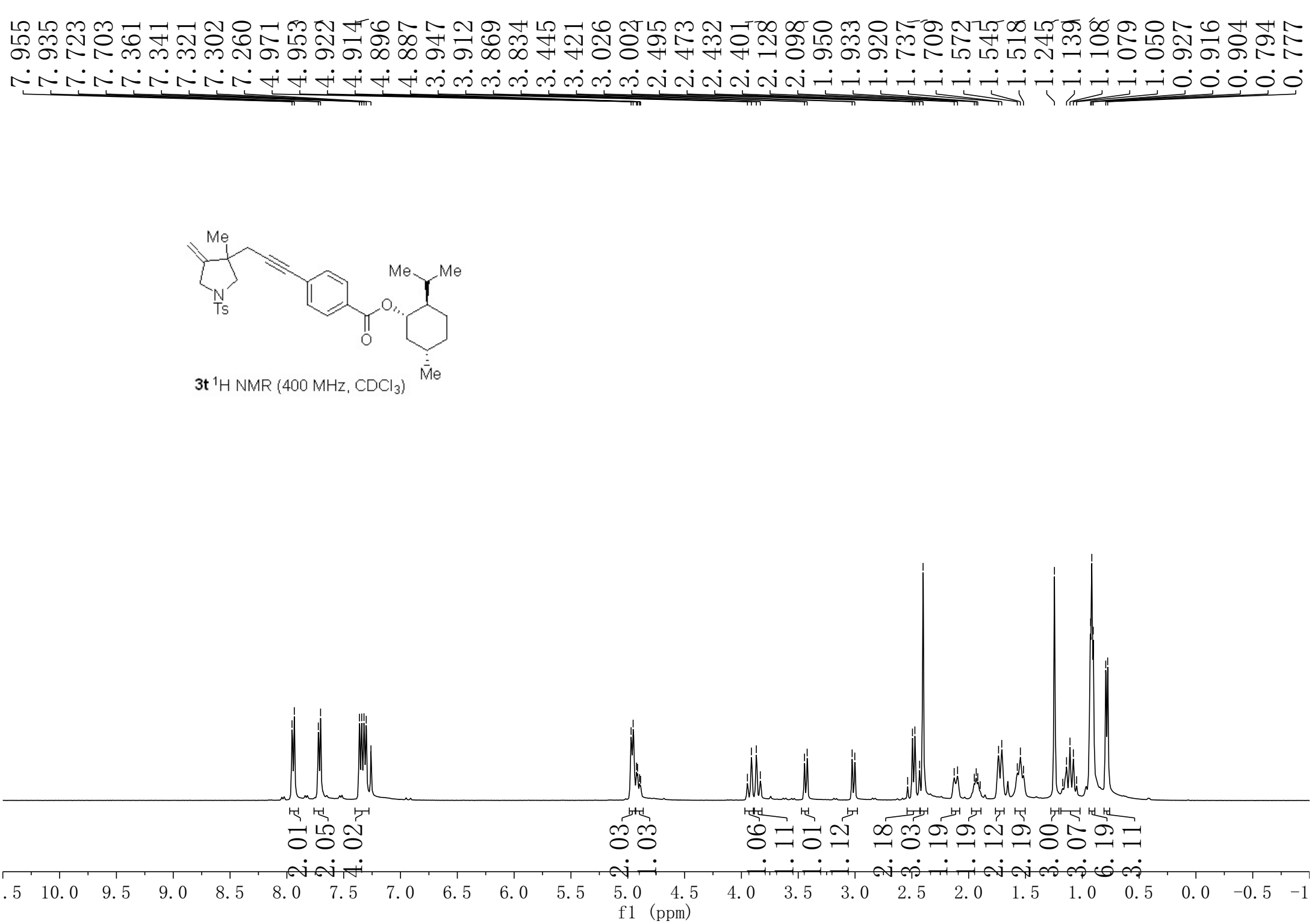
3r ^{13}C NMR (100 MHz, $CDCl_3$)



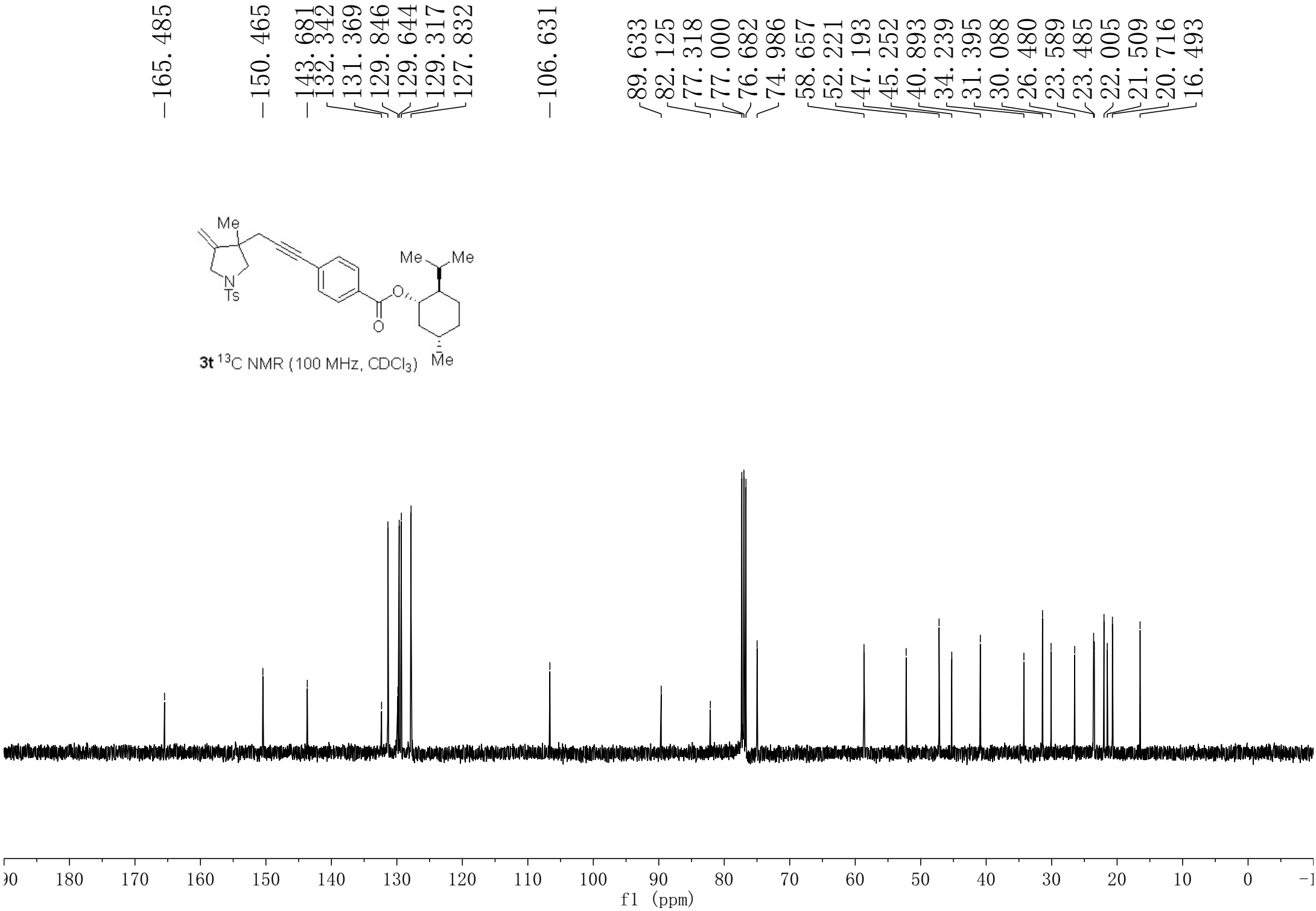


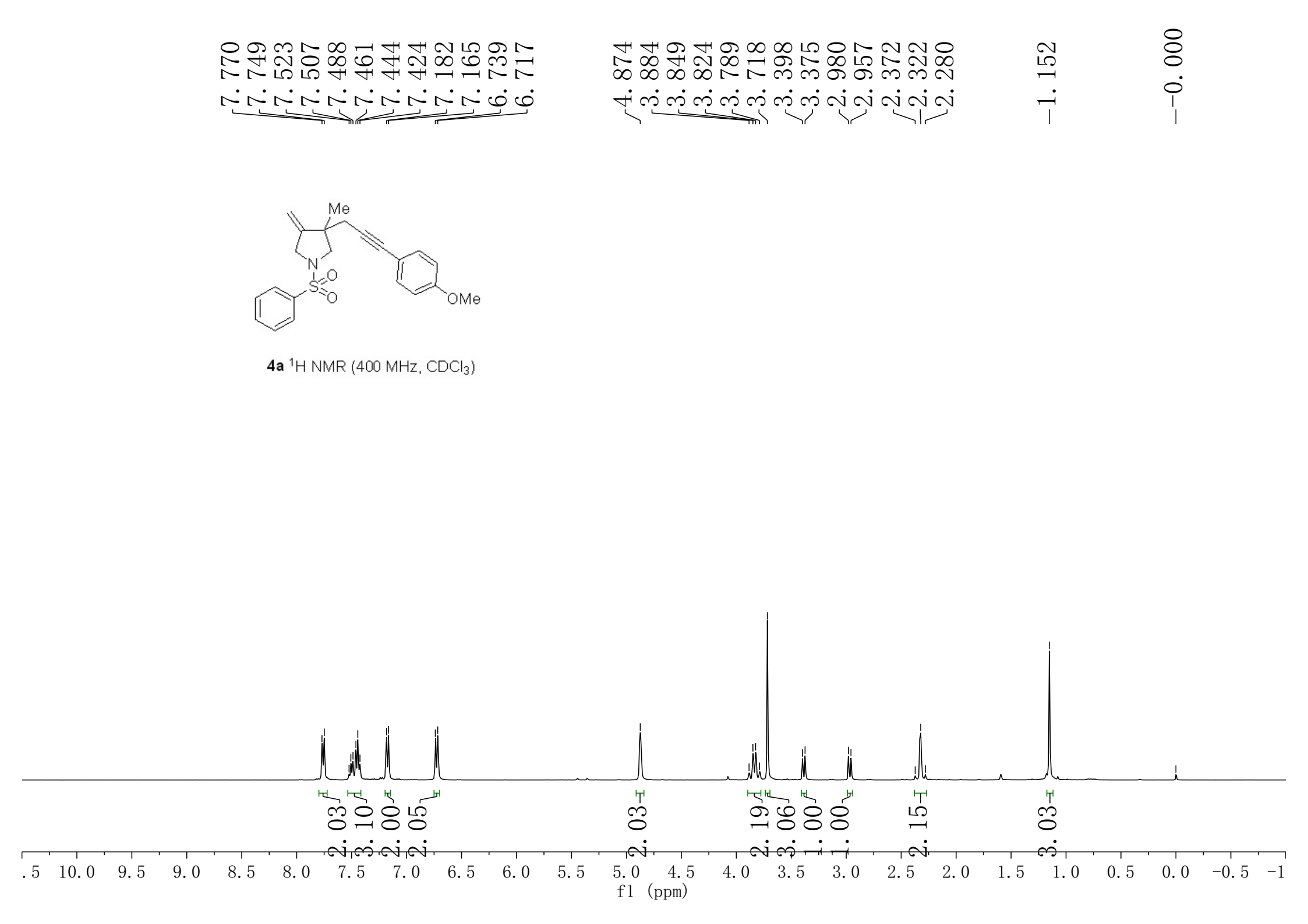
3s ^{1}H NMR (400 MHz, $CDCl_3$)


−220.637
150.585
143.558
139.698
136.397
132.416
131.921
129.586
128.796
127.737
125.167
120.604
−106.426
85.590
82.482
77.319
77.000
76.682
58.665
52.139
50.344
47.825
45.233
44.283
37.870
35.740
31.434
29.976
28.996
26.230
25.501
23.199
21.472
13.732
0.932
Me
N
Ts
H
H
H
O
3s ^{13}C NMR (100 MHz, $CDCl_3$)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



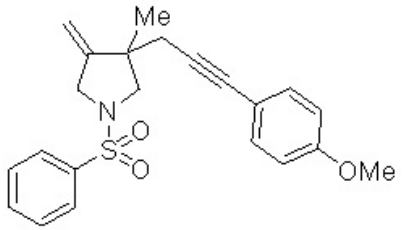
3t ^{1}H NMR (400 MHz, $CDCl_3$)


165.485
150.465
143.681
132.342
131.369
129.846
129.644
129.317
127.832
106.631
89.633
82.125
77.318
77.000
76.682
74.986
58.657
52.221
47.193
45.252
40.893
34.239
31.395
30.088
26.480
23.589
23.485
22.005
21.509
20.716
16.493
Me
N
Ts
O
O
Me
Me
Me
3t ^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

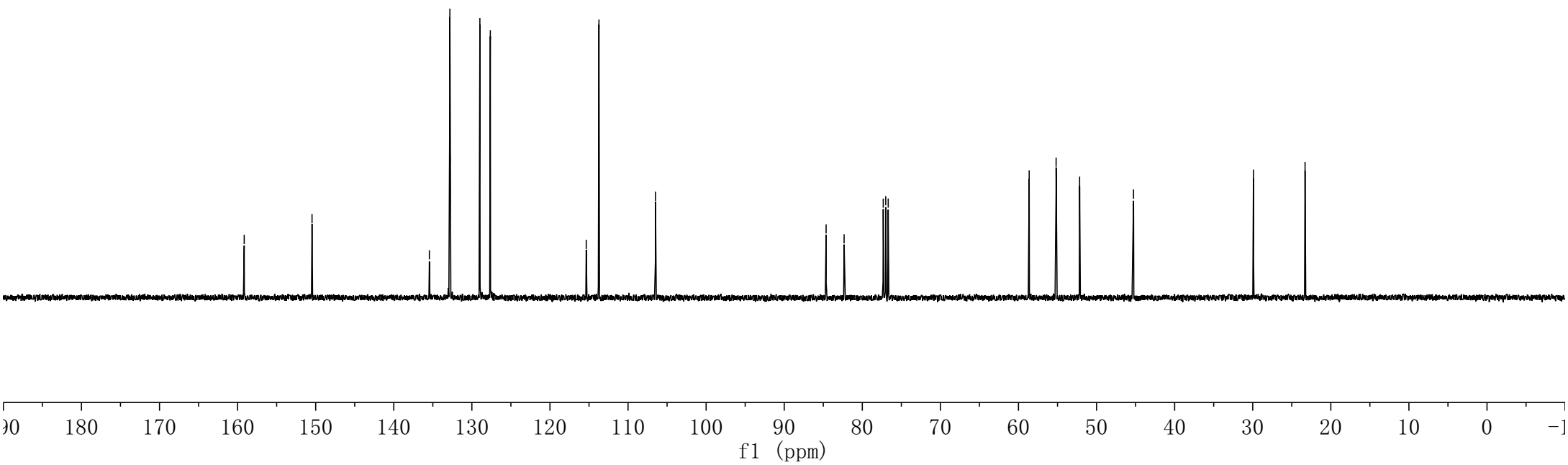


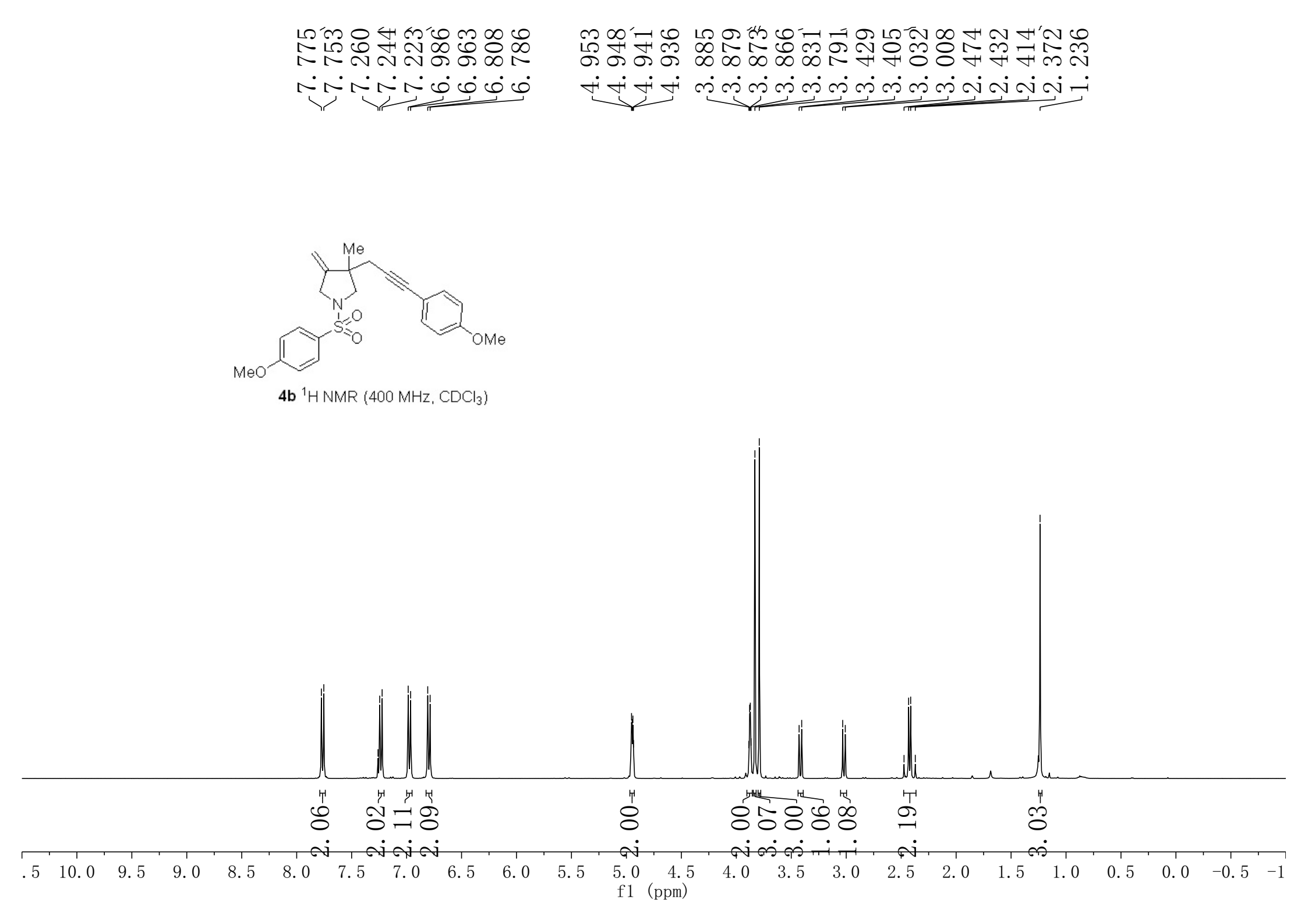
4a ^{1}H NMR (400 MHz, $CDCl_3$)

159.154
150.469
135.441
132.815
132.789
128.974
127.637
115.352
113.724
106.483
84.636
82.331
77.319
77.000
76.682
58.629
55.180
52.172
45.267
29.907
23.300



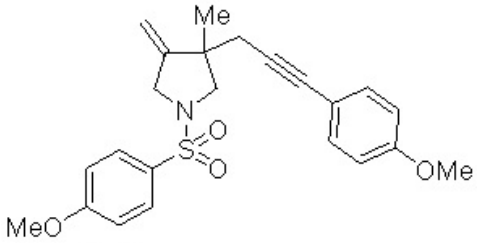
4a ^{13}C NMR (100 MHz, $CDCl_3$)



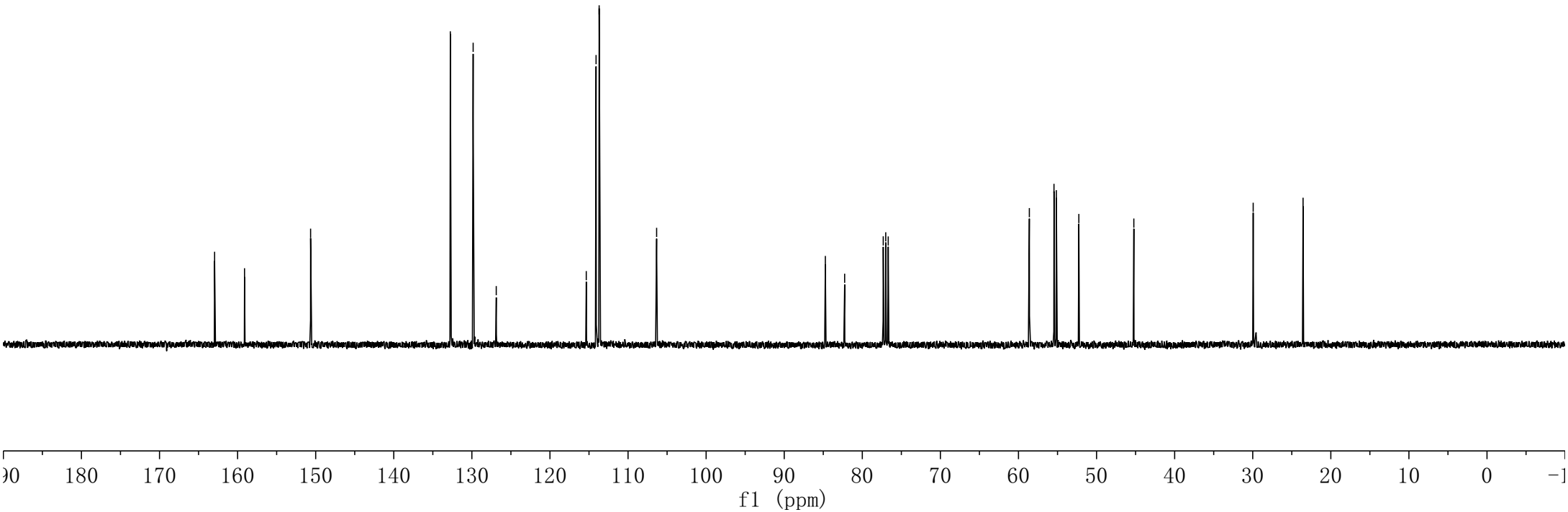


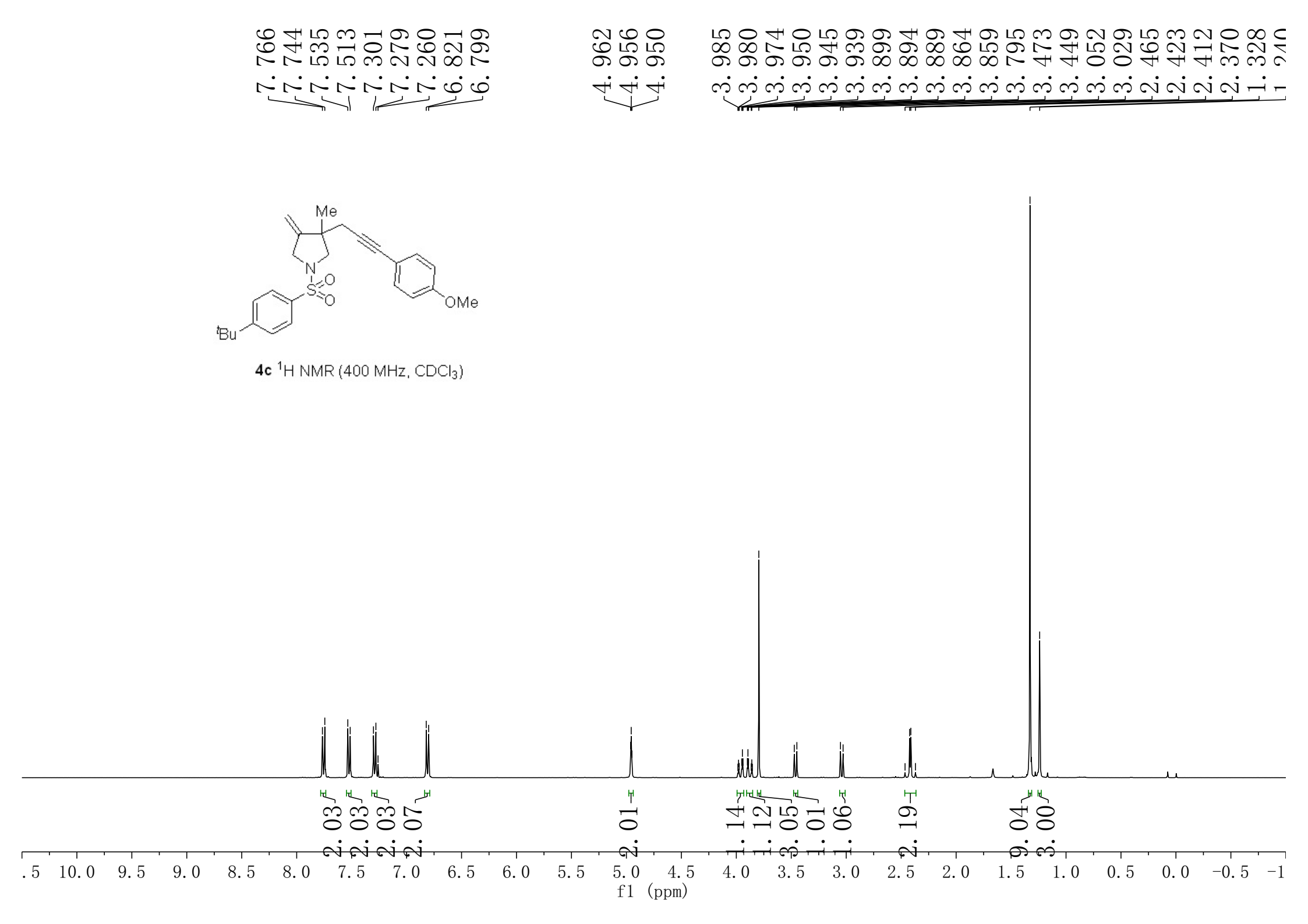
4b ^{1}H NMR (400 MHz, $CDCl_3$)

162.945
159.113
150.653
132.760
129.836
126.878
115.350
114.095
113.699
106.340
84.733
82.261
77.319
77.000
76.681
58.608
55.453
55.149
52.269
45.228
29.943
23.556



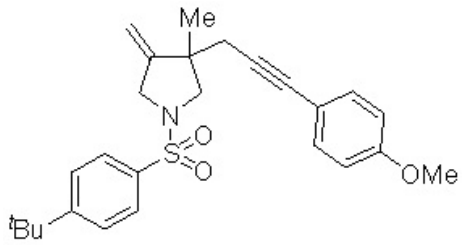
4b ^{13}C NMR (100 MHz, $CDCl_3$)



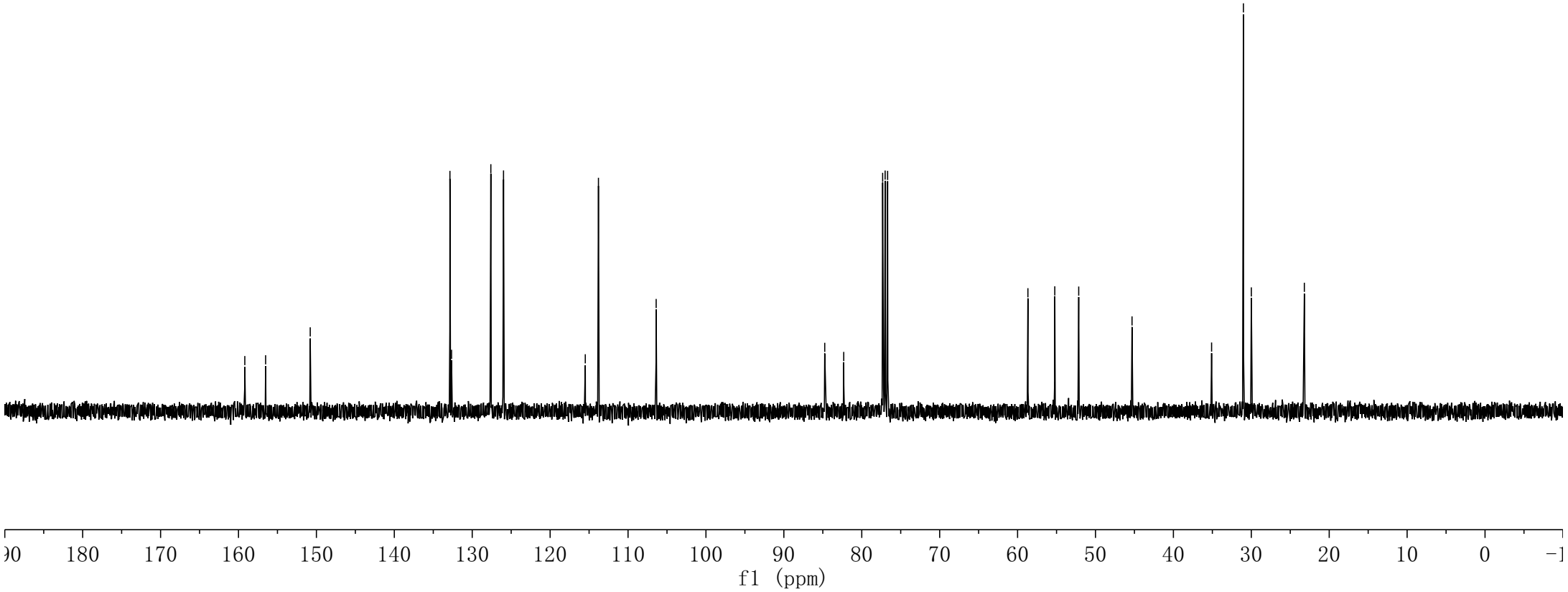


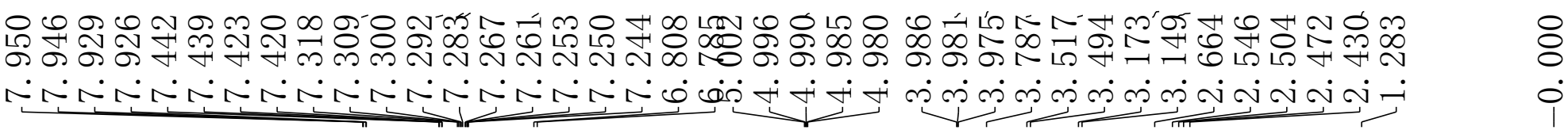
4c ^{1}H NMR (400 MHz, $CDCl_3$)

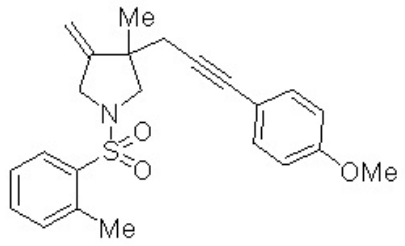
159.190
156.518
150.793
132.861
132.652
127.610
125.982
115.488
113.798
106.390
84.753
82.313
77.319
77.000
76.682
58.674
55.225
52.153
45.310
35.097
31.012
29.996
23.192



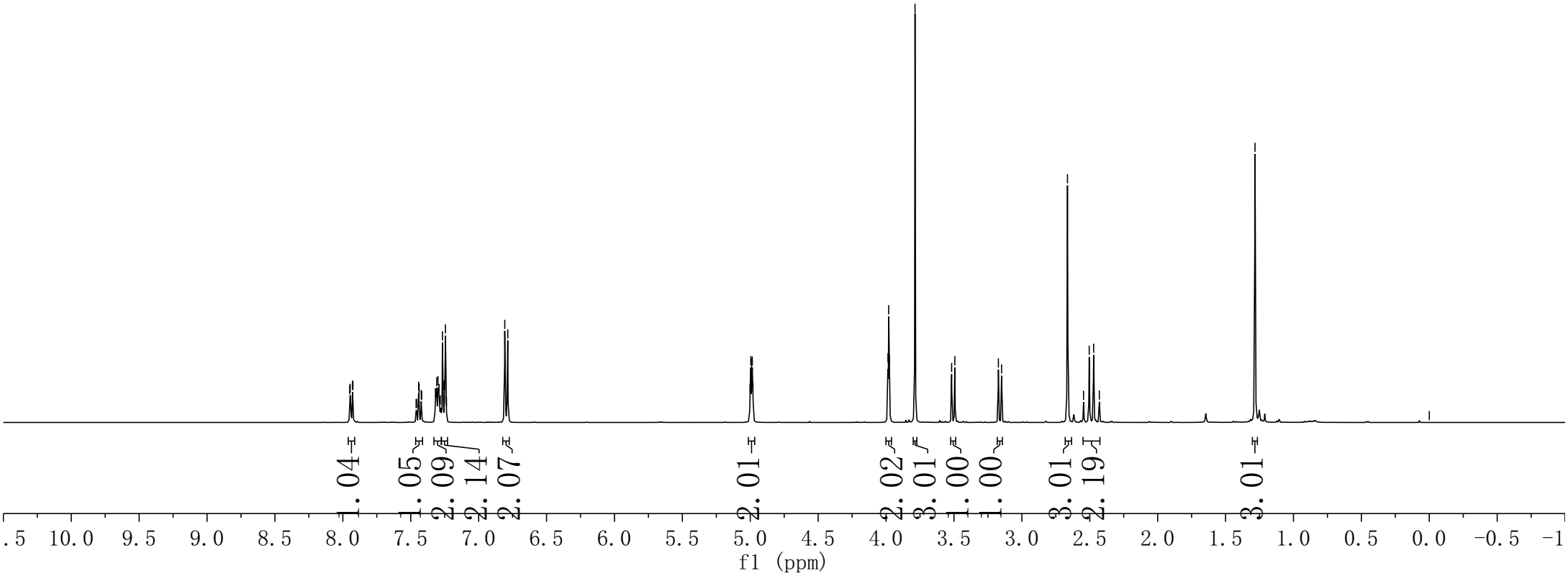
4c ^{13}C NMR (100 MHz, $CDCl_3$)



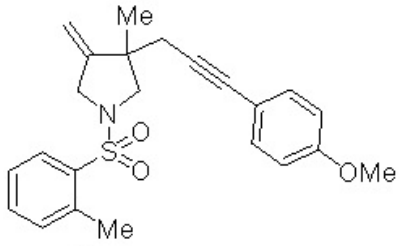




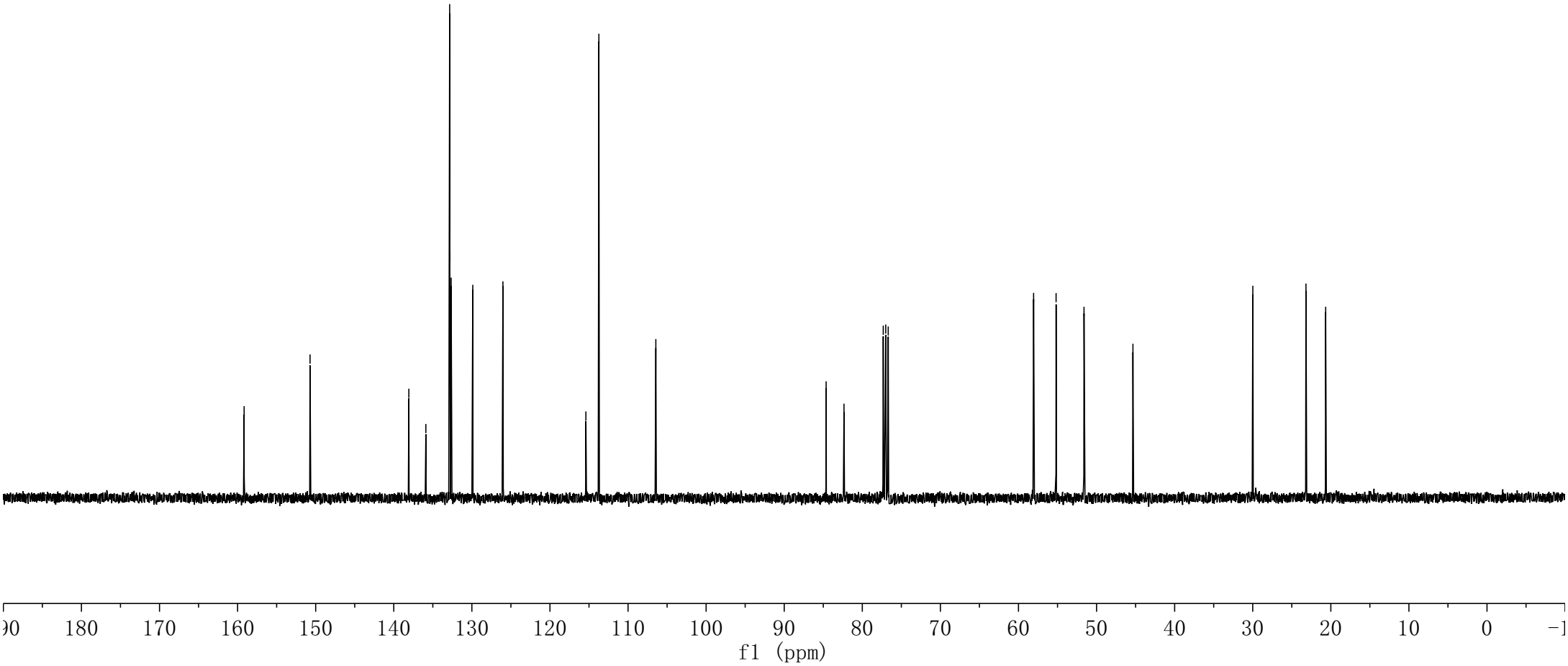
4d ^{1}H NMR (400 MHz, $CDCl_3$)

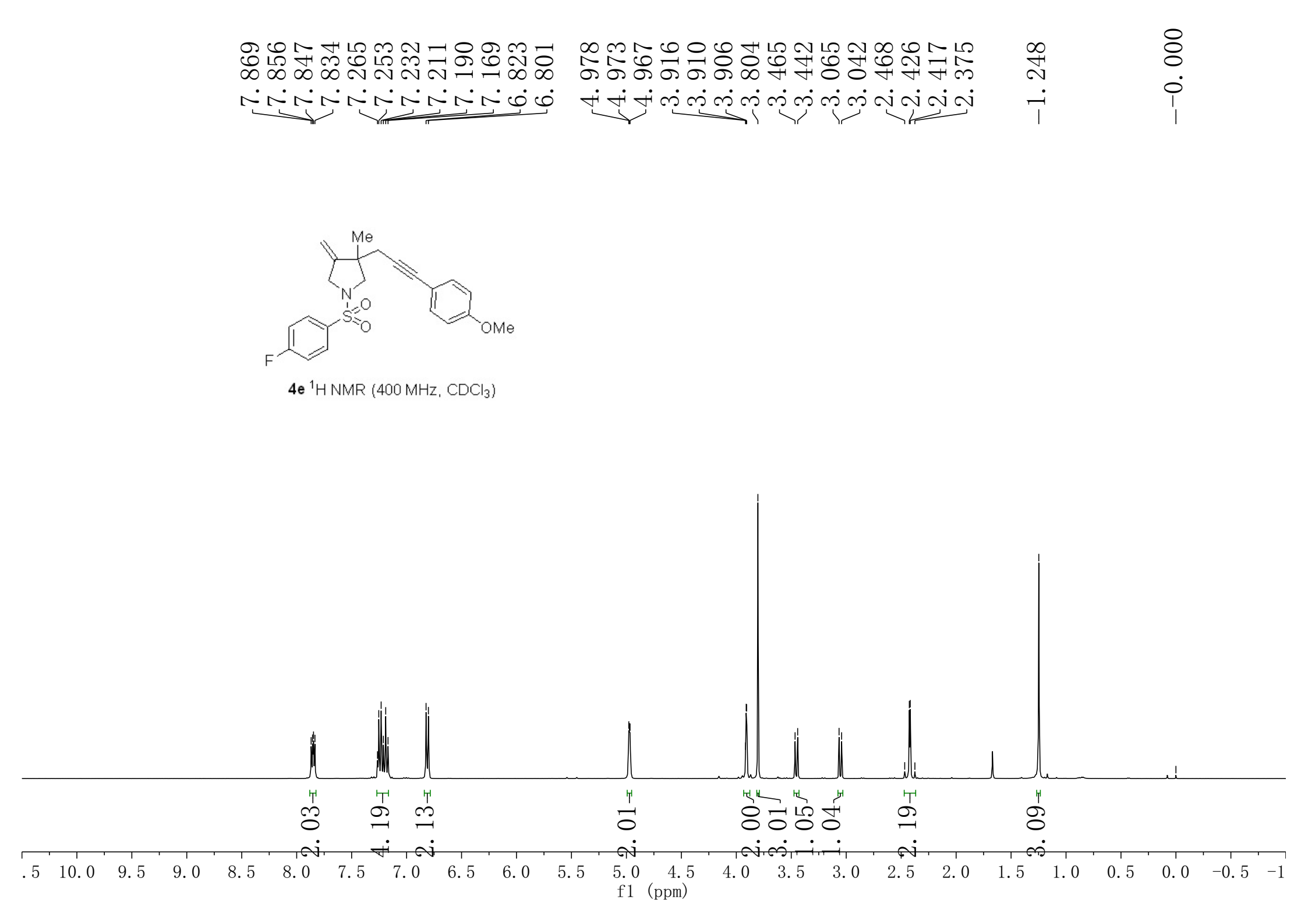


159.164
150.722
138.069
135.892
132.843
132.828
132.652
129.884
126.024
115.398
113.734
106.441
84.632
82.345
77.318
77.000
76.681
58.063
55.184
51.608
45.343
29.989
23.184
20.659

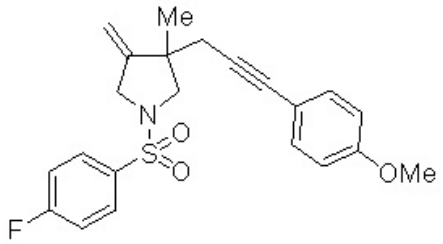


4d ^{13}C NMR (100 MHz, $CDCl_3$)



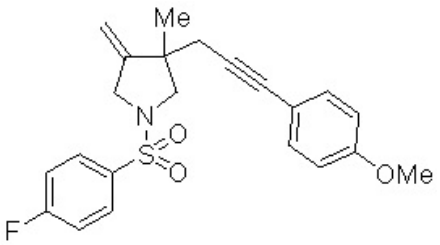

7.869
7.856
7.847
7.834
7.265
7.253
7.232
7.211
7.190
7.169
6.823
6.801
4.978
4.973
4.967
3.916
3.910
3.906
3.804
3.465
3.442
3.065
3.042
2.468
2.426
2.417
2.375
1.248
0.000
Me
N
O
S
O
OMe
F
4e 1H NMR (400 MHz, CDCl3)
2.03
4.19
2.13
2.01
2.00
3.01
1.05
1.04
2.19
3.09
f1 (ppm)

166.494
163.957
159.288
150.399
132.863
131.763
130.454
130.362
116.423
116.200
115.347
113.838
106.695
84.588
82.492
77.318
77.000
76.682
58.685
55.275
52.301
45.353
30.020
23.575



4e ^{13}C NMR (100 MHz, $CDCl_3$)

f1 (ppm)

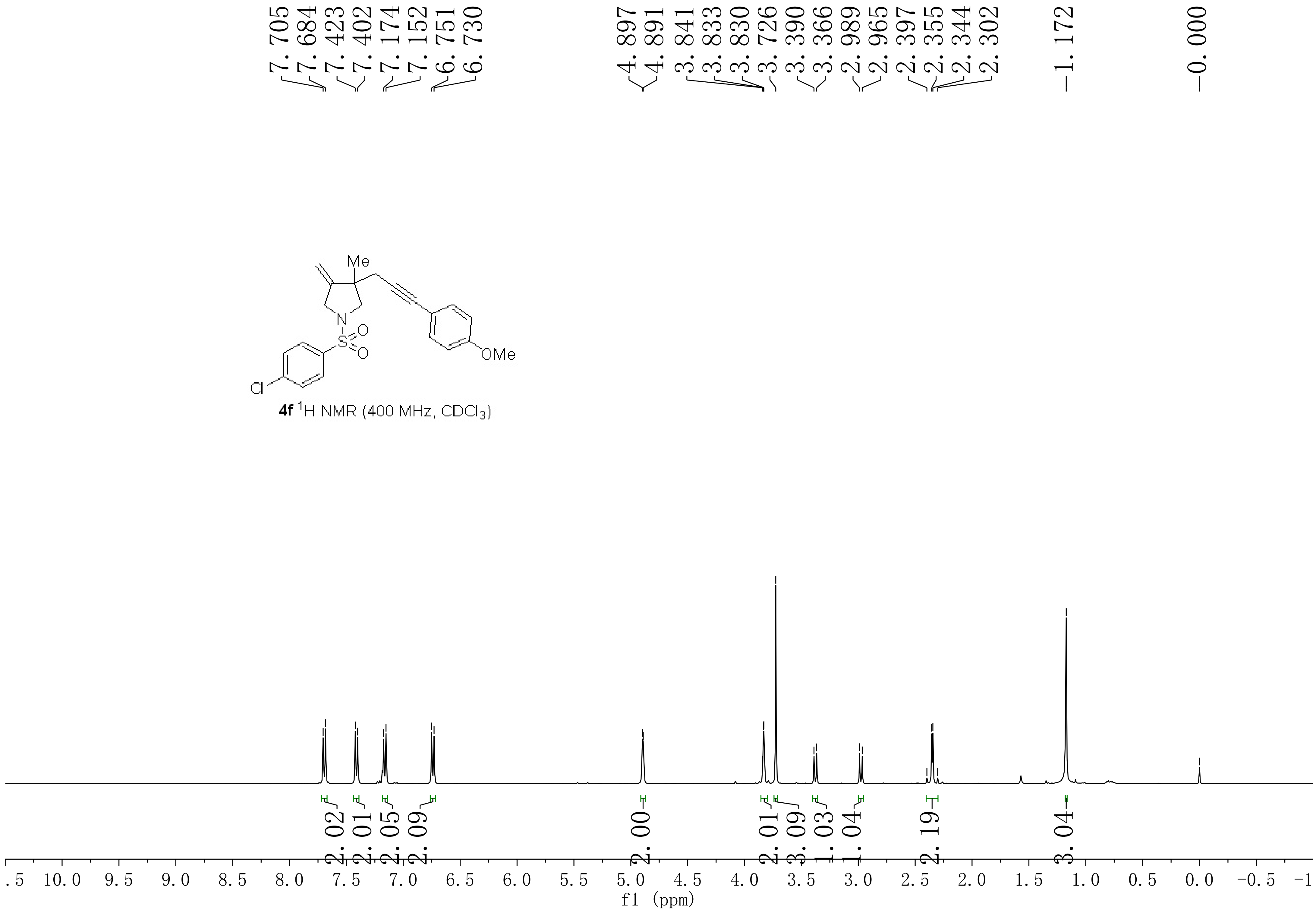


4e ^{19}F NMR (376 MHz, $CDCl_3$)

−104.831

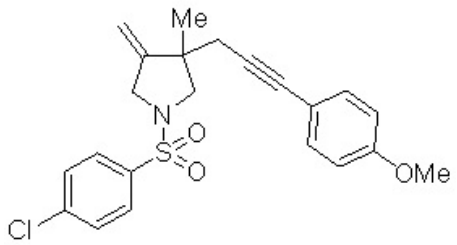
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

f1 (ppm)

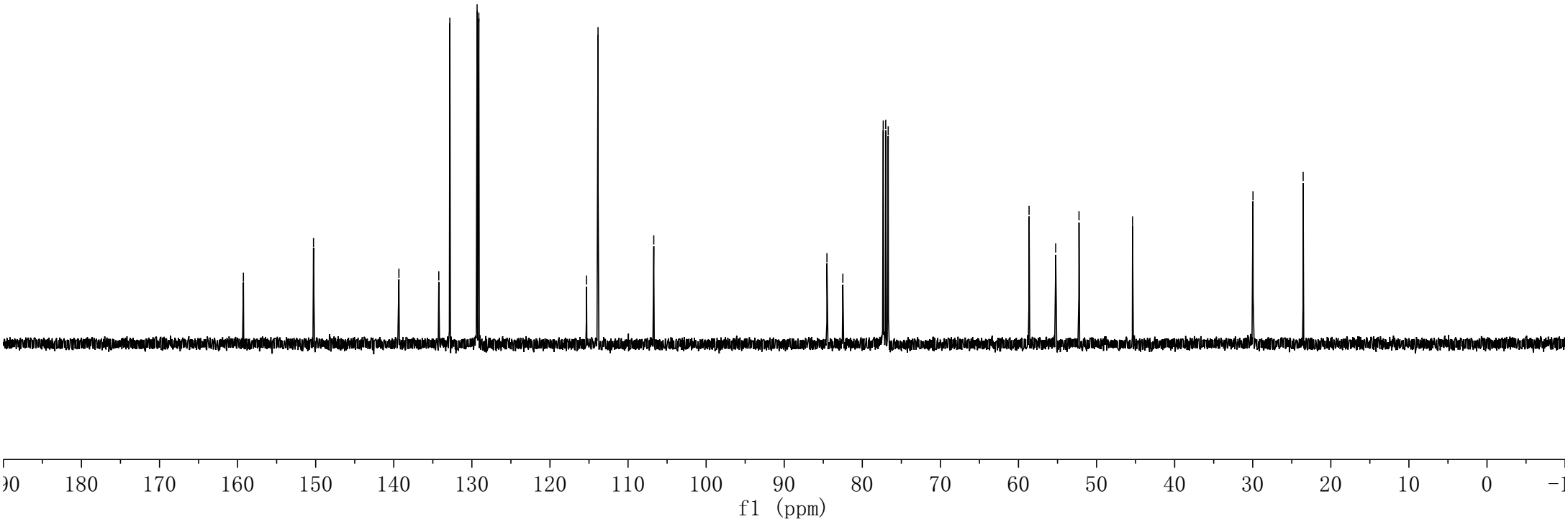


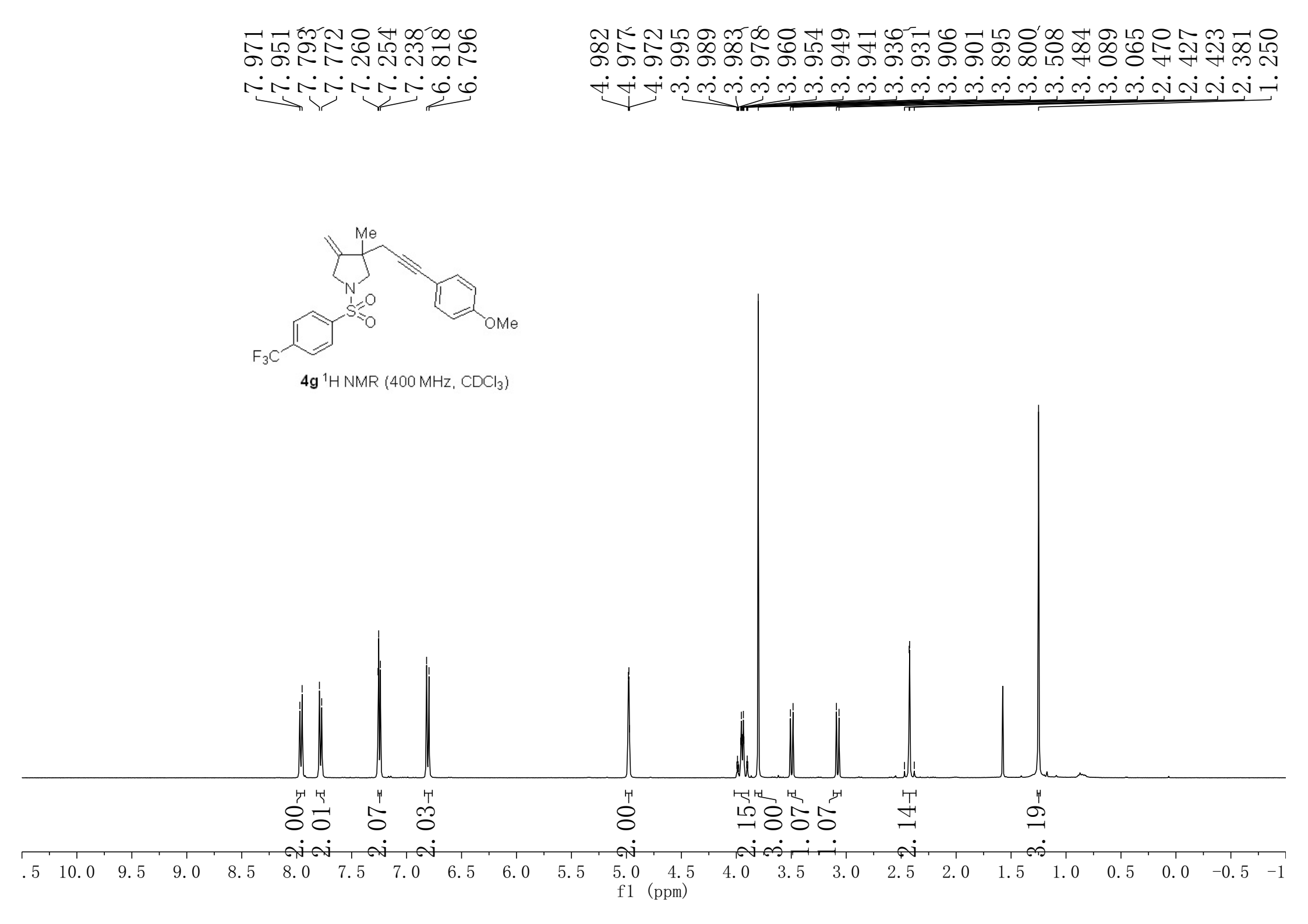
4f ^{1}H NMR (400 MHz, $CDCl_3$)

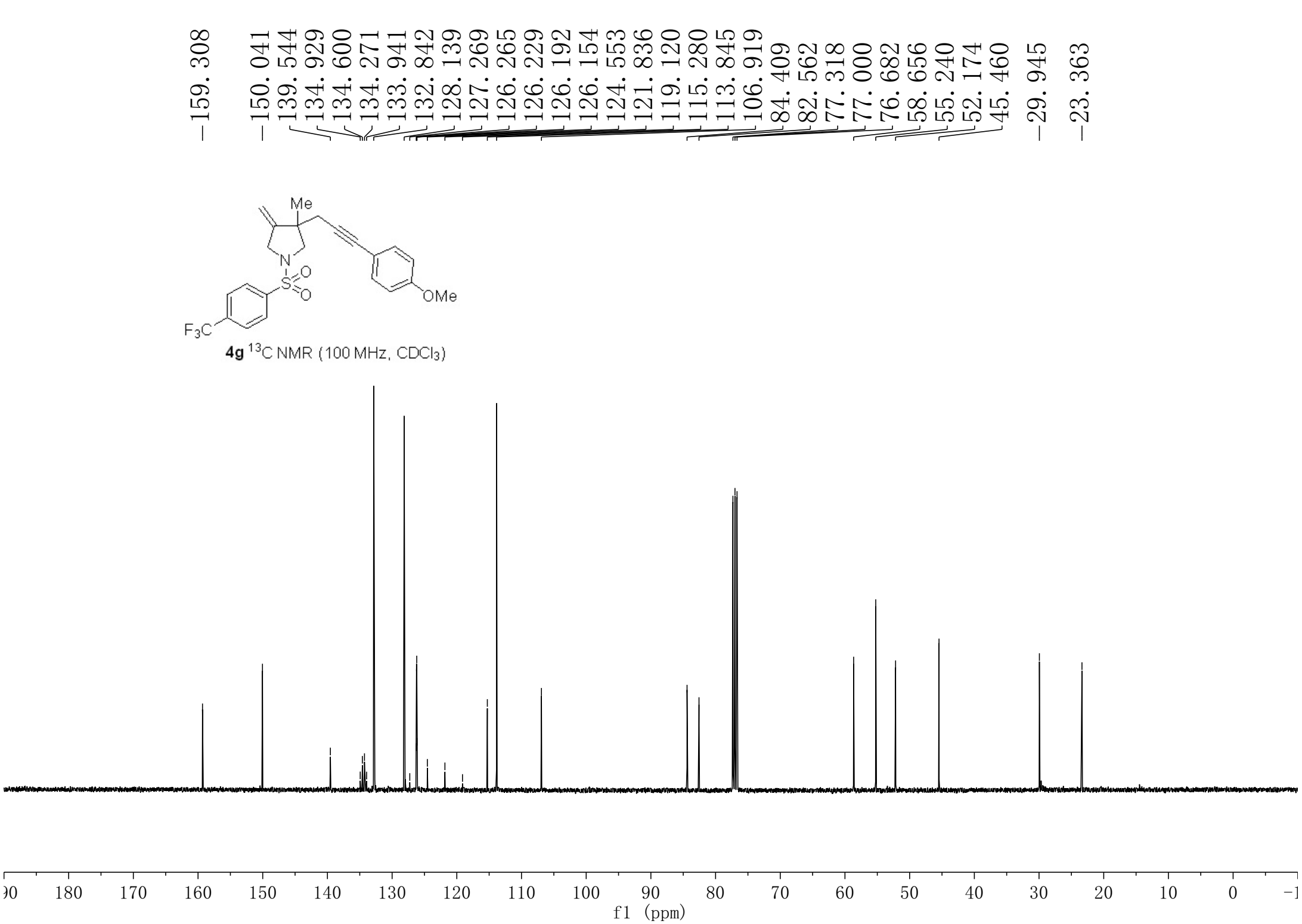
159.257
150.277
139.343
134.236
132.820
129.330
129.112
115.317
113.843
106.704
84.528
82.490
77.319
77.000
76.682
58.643
55.234
52.248
45.392
29.967
23.543

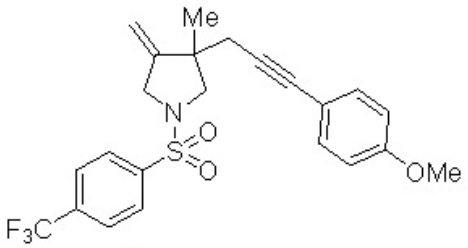


4f ^{13}C NMR (100 MHz, $CDCl_3$)




7.971
7.951
7.793
7.772
7.260
7.254
7.238
6.818
6.796
4.982
4.977
4.972
3.995
3.989
3.983
3.978
3.960
3.954
3.949
3.941
3.936
3.931
3.906
3.901
3.895
3.800
3.508
3.484
3.089
3.065
2.470
2.427
2.423
2.381
1.250
Me
N
S
O
O
OMe
F3C
4g 1H NMR (400 MHz, CDCl3)
2.00
2.01
2.07
2.03
2.00
2.15
3.00
1.07
1.07
2.14
3.19
f1 (ppm)


159.308
150.041
139.544
134.929
134.600
134.271
133.941
132.842
128.139
127.269
126.265
126.229
126.192
126.154
124.553
121.836
119.120
115.280
113.845
106.919
84.409
82.562
77.318
77.000
76.682
58.656
55.240
52.174
45.460
29.945
23.363
Me
N
S
O
O
OMe
F3C
4g 13C NMR (100 MHz, CDCl3)
f1 (ppm)

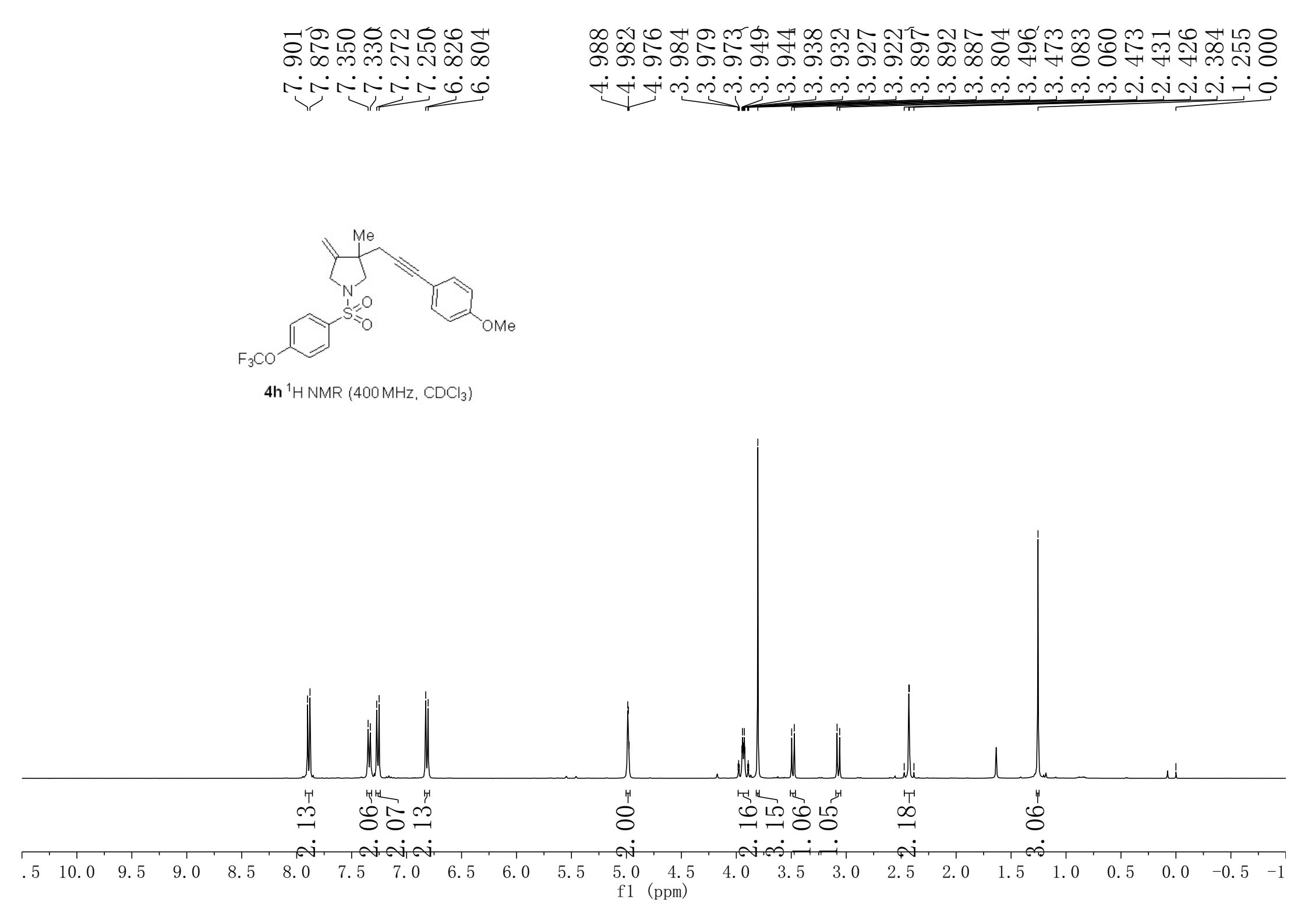


4g ^{19}F NMR (376 MHz, $CDCl_3$)

−63.036

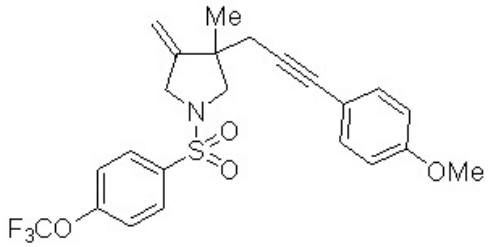
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −1

f1 (ppm)

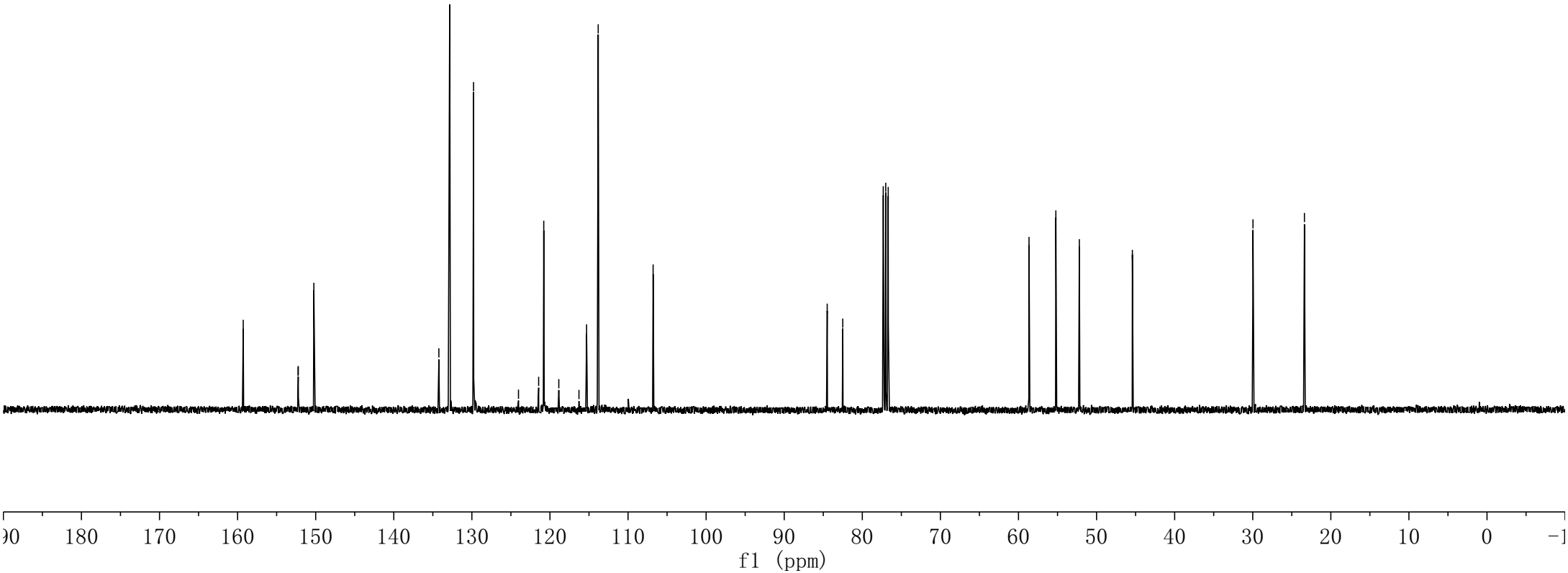


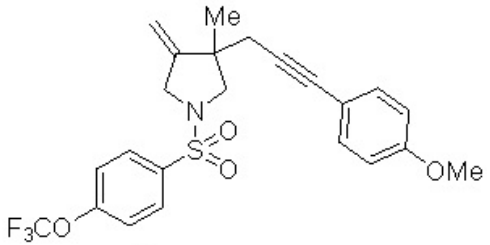
4h ^{1}H NMR (400 MHz, $CDCl_3$)

159.279
152.250
152.233
150.234
134.227
132.837
129.784
124.030
121.448
120.793
118.867
116.286
115.308
113.822
106.788
84.495
82.502
77.318
77.000
76.682
58.651
55.214
52.204
45.414
29.968
23.380



4h ^{13}C NMR (100 MHz, $CDCl_3$)



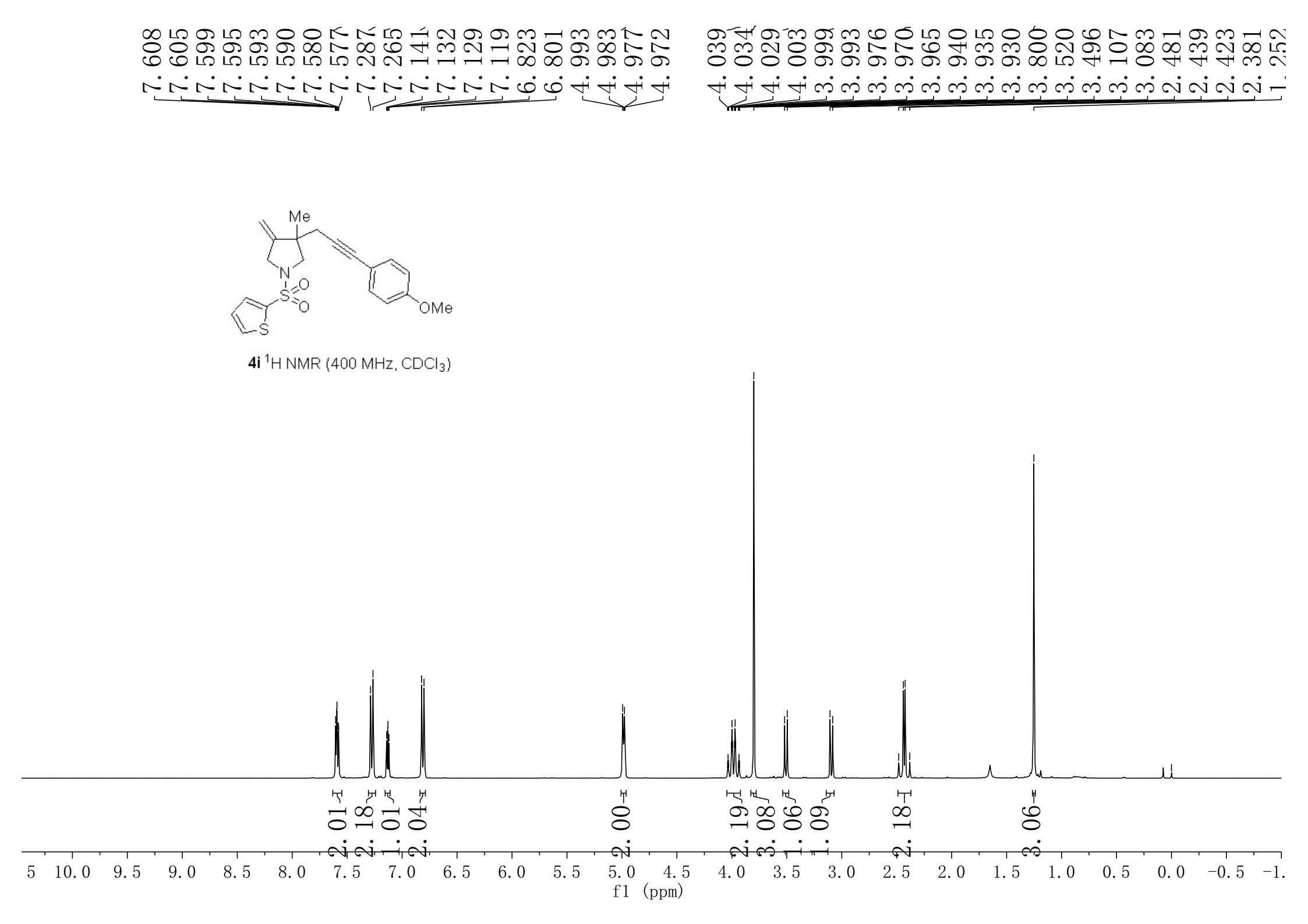


4h ^{19}F NMR (376 MHz, $CDCl_3$)

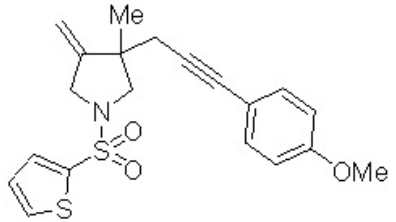
−57.643

10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140

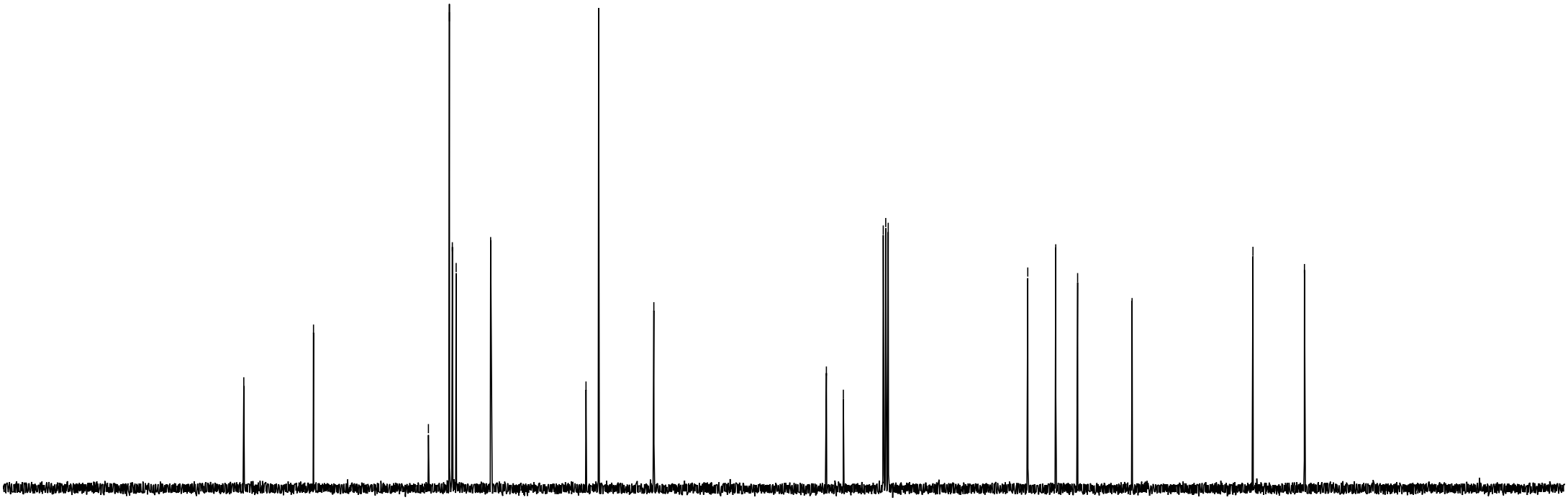
f1 (ppm)

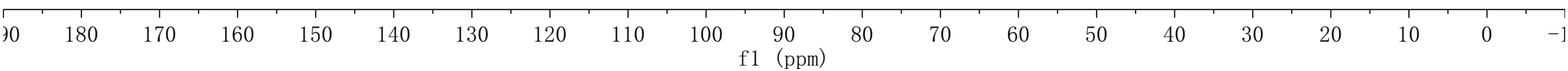

7.608
7.605
7.599
7.595
7.593
7.590
7.580
7.577
7.287
7.265
7.141
7.132
7.129
7.119
6.823
6.801
4.993
4.983
4.977
4.972
4.039
4.034
4.029
4.003
3.999
3.993
3.976
3.970
3.965
3.940
3.935
3.930
3.800
3.520
3.496
3.107
3.083
2.481
2.439
2.423
2.381
Me
N
S
O
O
S
OMe
4i 1H NMR (400 MHz, CDCl3)
2.01
2.18
1.01
2.04
2.00
2.19
3.08
1.06
1.09
2.18
3.06
f1 (ppm)

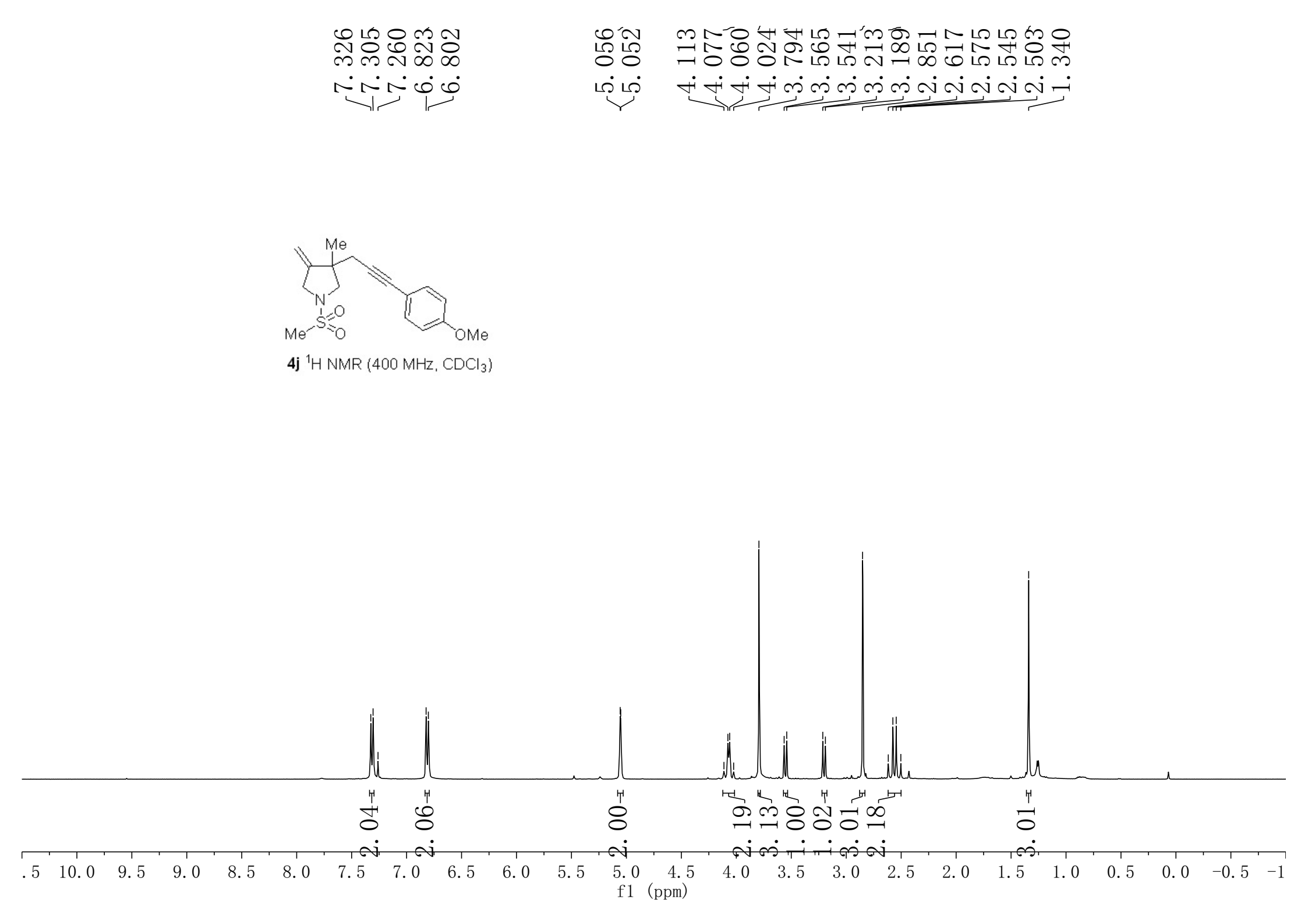
159.206
150.279
135.563
132.880
132.500
132.011
127.597
115.383
113.767
106.695
84.601
82.427
77.318
77.000
76.682
58.809
55.228
52.426
45.453
29.972
23.378



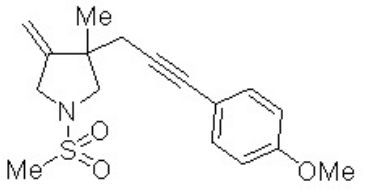
4i ^{13}C NMR (100 MHz, $CDCl_3$)



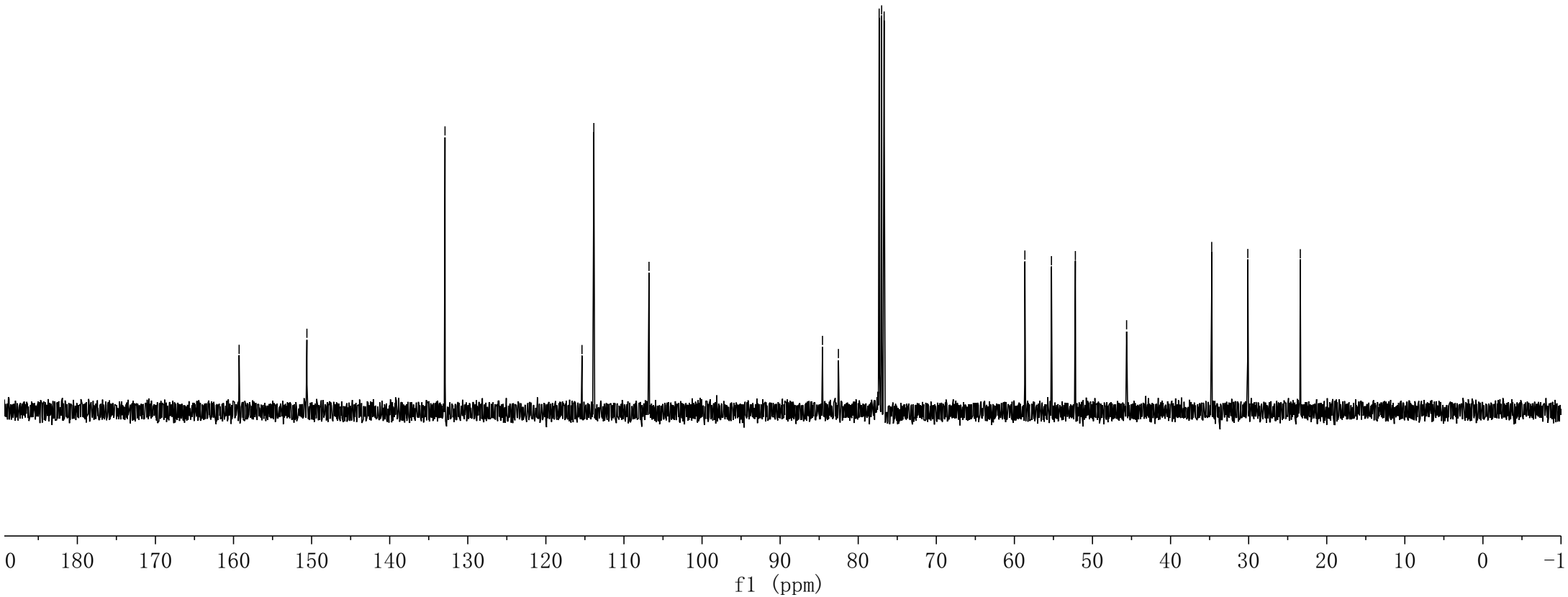


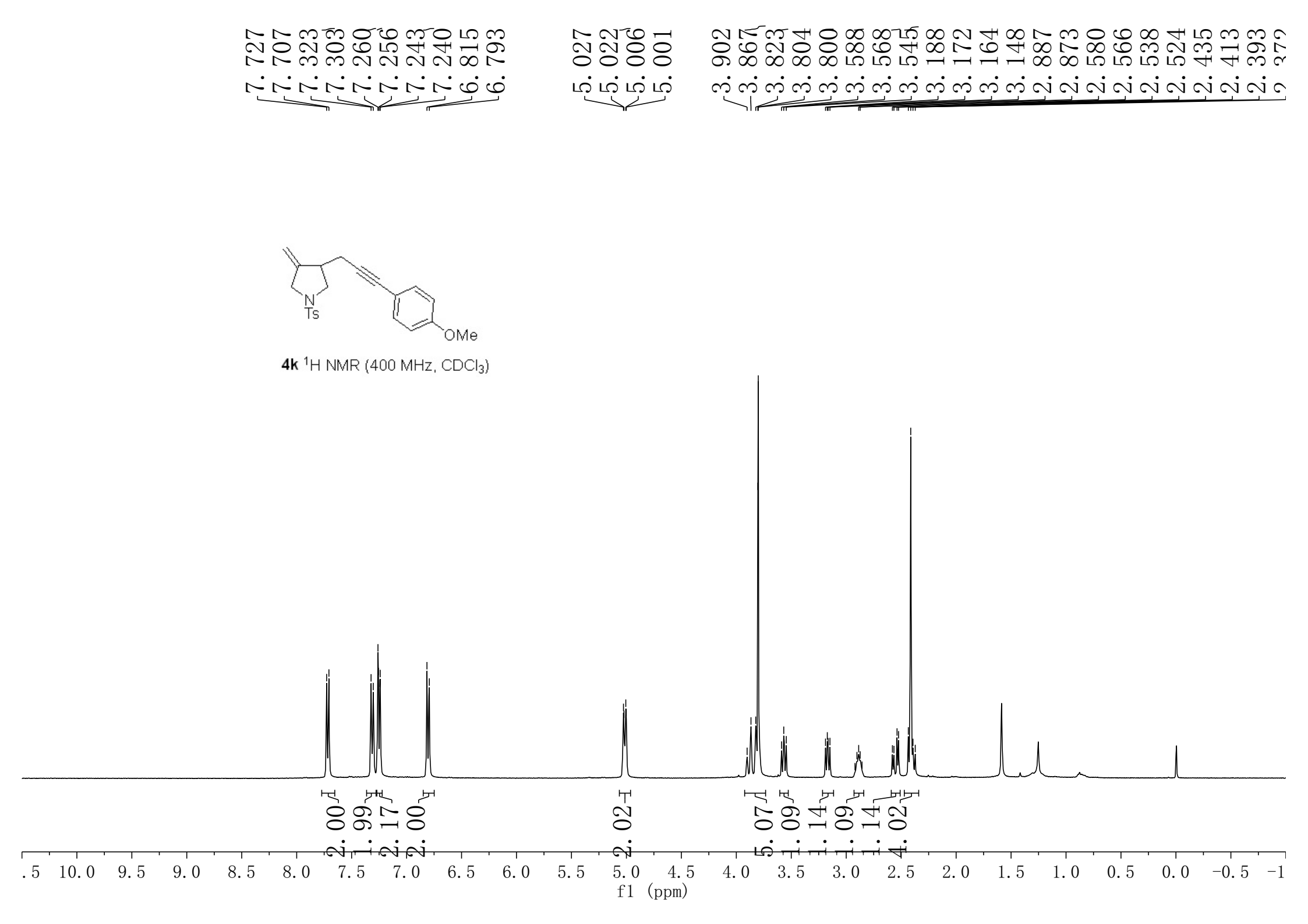

7.326
7.305
7.260
6.823
6.802
5.056
5.052
4.113
4.077
4.060
4.024
3.794
3.565
3.541
3.213
3.189
2.851
2.617
2.575
2.545
2.503
1.340
Me
N
S
O
O
Me
OMe
4j 1H NMR (400 MHz, CDCl3)
2.04
2.06
2.00
2.19
3.13
1.00
1.02
3.01
2.18
3.01
f1 (ppm)

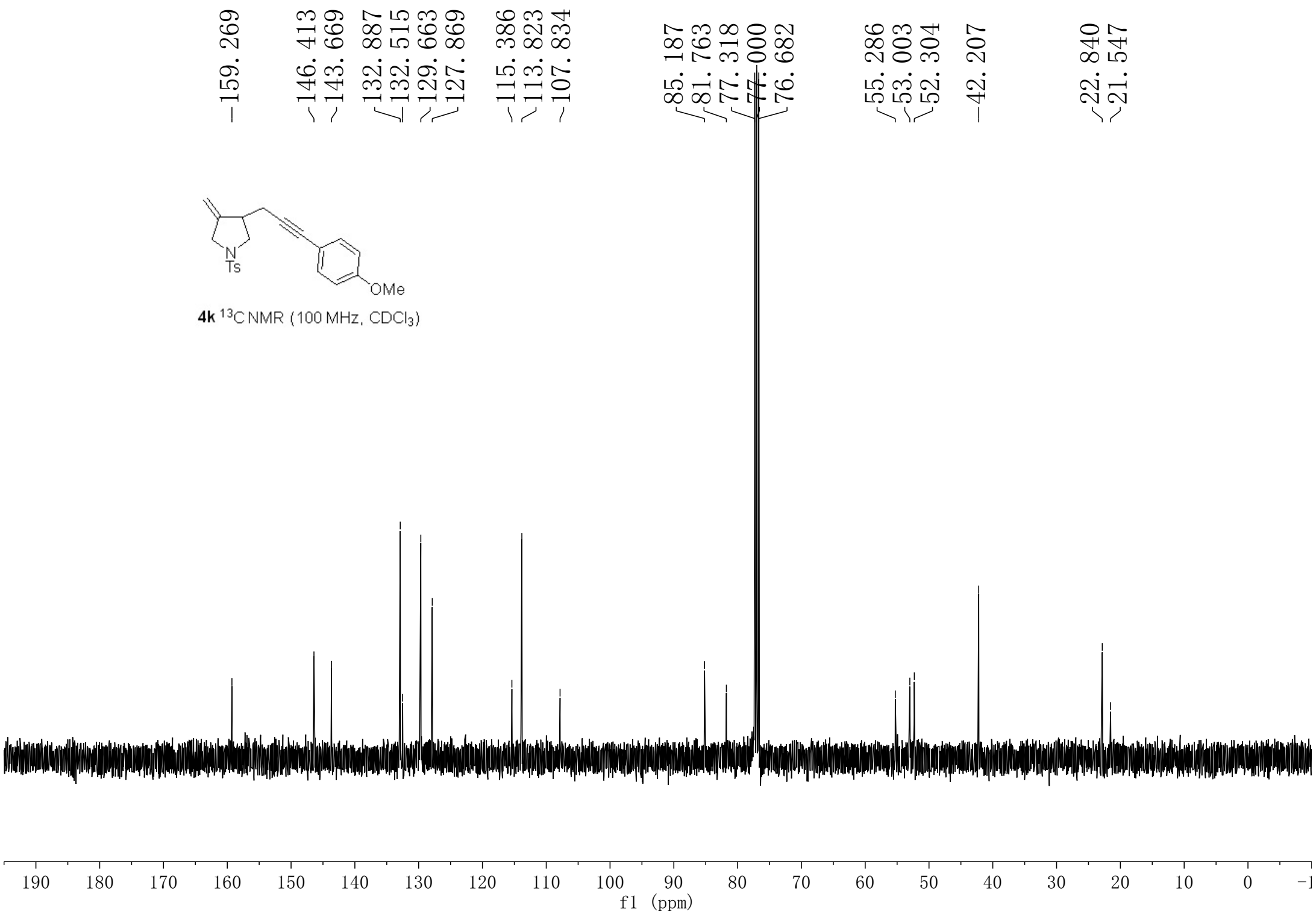
159.282
150.601
132.916
115.376
113.856
106.792
84.574
82.535
77.318
77.000
76.682
58.657
55.255
52.191
45.631
34.732
30.110
23.386



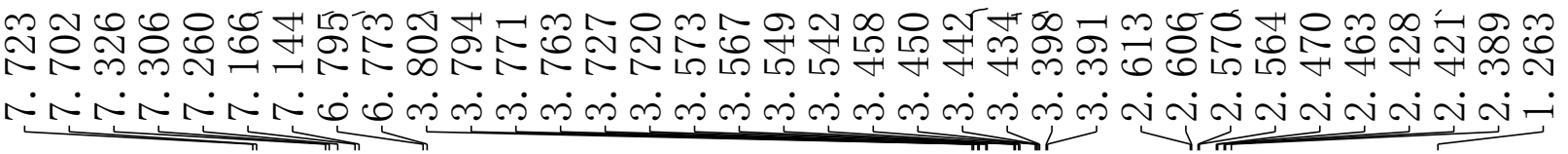
4j ^{13}C NMR (100 MHz, $CDCl_3$)

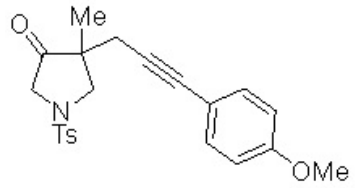



7.727
7.707
7.323
7.303
7.260
7.256
7.243
7.240
6.815
6.793
5.027
5.022
5.006
5.001
3.902
3.867
3.823
3.804
3.800
3.588
3.568
3.545
3.188
3.172
3.164
3.148
2.887
2.873
2.580
2.566
2.538
2.524
2.435
2.413
2.393
N
Ts
OMe
4k 1H NMR (400 MHz, CDCl3)
2.00
1.99
2.17
2.00
2.02
5.07
1.09
1.14
1.09
1.14
4.02
f1 (ppm)

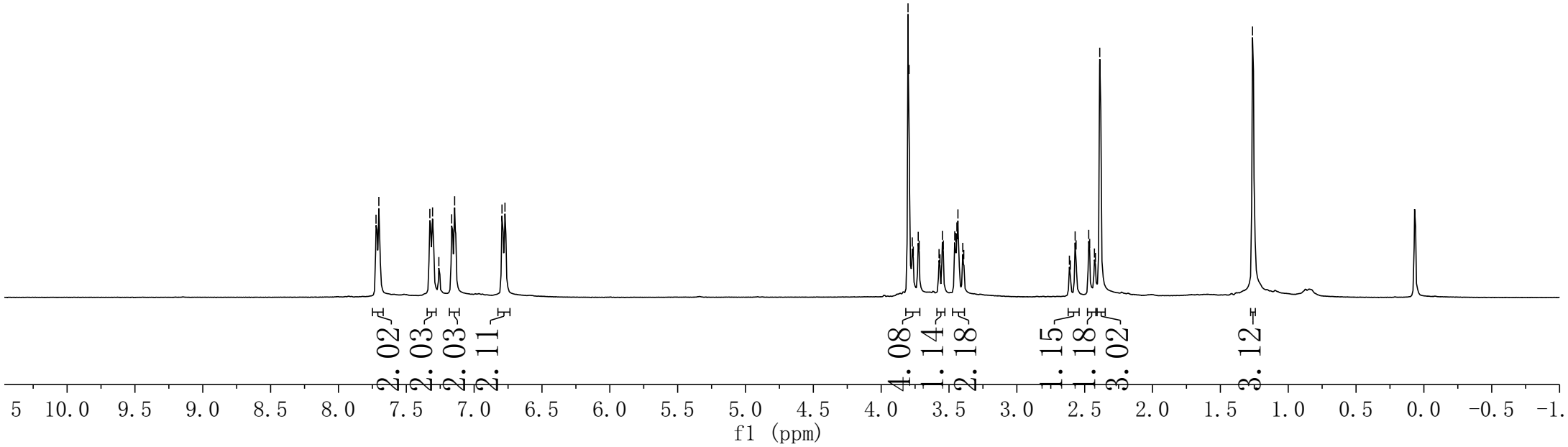


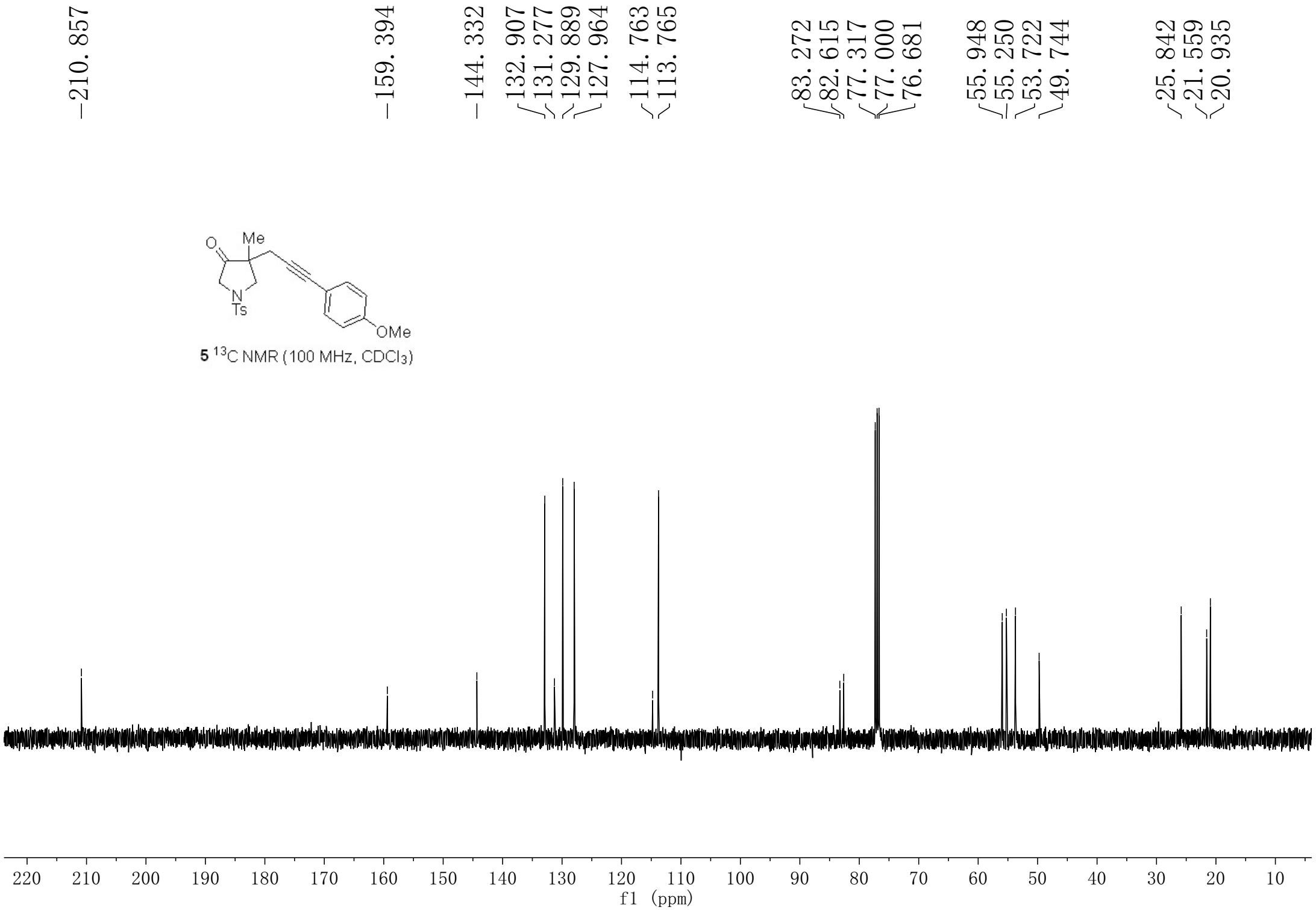
4k ^{13}C NMR (100 MHz, $CDCl_3$)



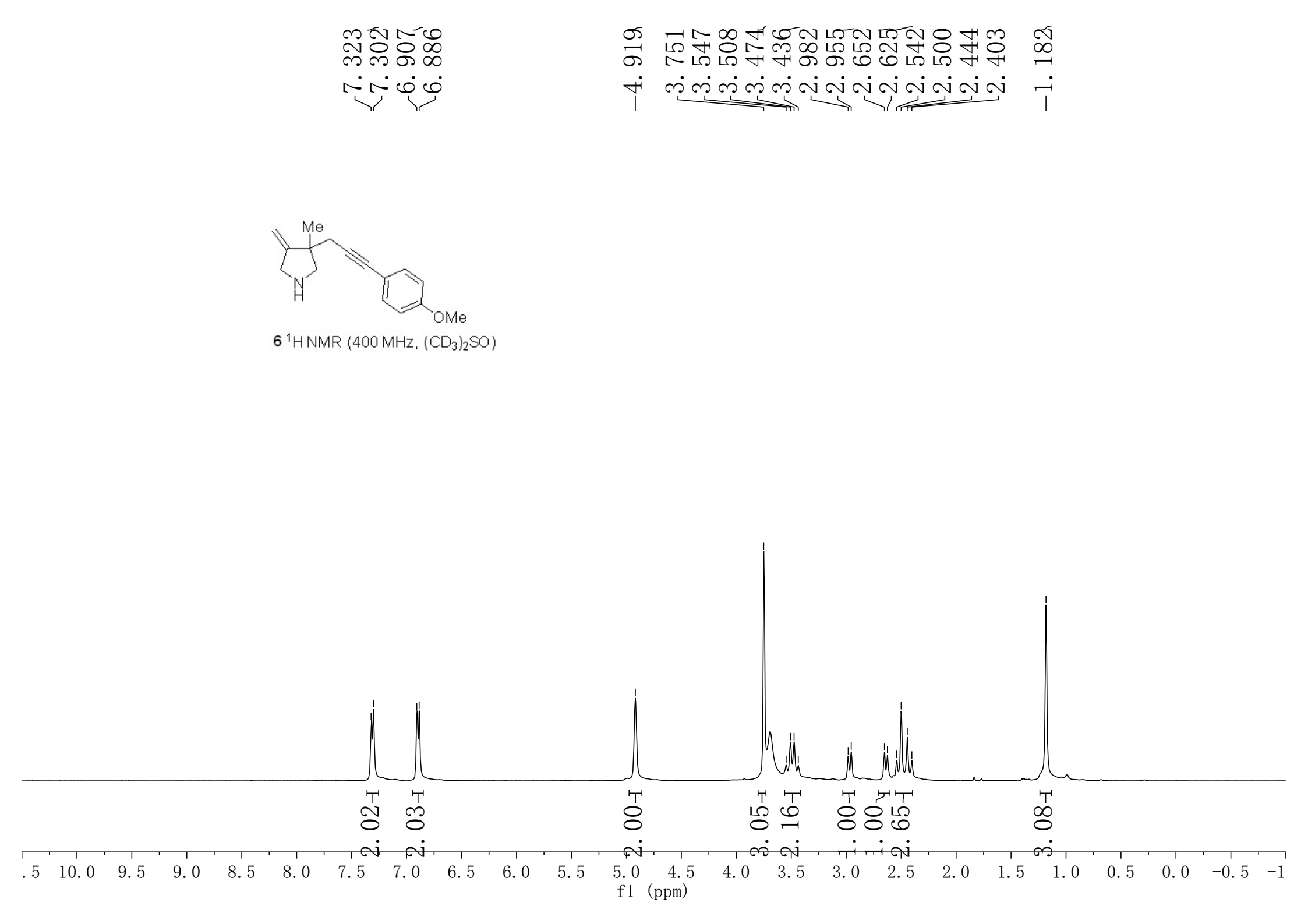


5 ^{1}H NMR (400 MHz, $CDCl_3$)

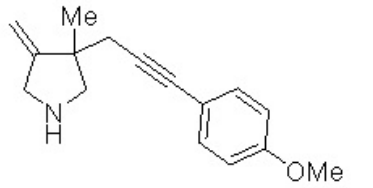




5 ^{13}C NMR (100 MHz, $CDCl_3$)


7.323
7.302
6.907
6.886
4.919
3.751
3.547
3.508
3.474
3.436
2.982
2.955
2.652
2.625
2.542
2.500
2.444
2.403
1.182
Me
N
H
OMe
6 1H NMR (400 MHz, (CD3)2SO)
2.02
2.03
2.00
3.05
2.16
1.00
1.00
2.65
3.08
f1 (ppm)

158.966
157.159
132.734
115.258
114.249
103.594
86.901
81.398
58.838
55.267
52.092
45.096
40.229
40.017
39.809
39.600
39.392
39.183
38.978
29.636
23.945



6 ^{13}C NMR (100 MHz, $(CD_3)_2SO$)

f1 (ppm)