

Supporting Information

for

Photo-Induced Synthesis of β -Sulfonyl Imides from Carboxylic Acids

Linwei Zeng^a, Jian Jin^b, Jixiao He^a, and Sunliang Cui^{*a}

^aInstitute of Drug Discovery and Design, College of Pharmaceutical Sciences, Zhejiang University, 866 Yuhangtang Road, Hangzhou 310058, China

^bCAS Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences

Email: slcui@zju.edu.cn

Content

1. General Information	S2
2. Starting Materials	S3-S4
3. Reaction Optimization	S4-S5
4. Typical Procedure for The Synthesis of 3a.....	S5-S6
5. Gram-Scale Reaction	S6-S7
6. Procedures for The Synthesis of 5, 6 and 7	S7-S8
7. Mechanistic Studies.....	S8-S16
7.1 Radical Scavenging Experiments	S8-S9
7.2 Step-wise Experiment.....	S9
7.3 Stern–Volmer Quenching Experiments	S9-S11
7.4 Light On/Off Experiment.....	S11
7.5 Crossover Reaction	S12
7.6 Cyclic Voltammograms	S13
7.7 UV Sensitizer Experiments	S13-S14
7.8 Determination of The Reaction Quantum Yield	S14-S16
8. Characterization of Products	S16-S49
9. X-ray Crystallographic Data.....	S49-S51
10. HPLC Charts.....	S51-S56
11. Copies of NMR Spectra	S57-S216
12. References	S217

1. General Information

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Column chromatography was performed over silica gel (200–300 mesh).

Melting points were measured with X-4 micro melting point apparatus.

HRMS were performed on Agilent Technologies 6546-LC/Q-TOF LC/MS apparatus (ESI-TOF).

The *ee* values of chiral compounds were determined by HPLC analysis on a CHIRALPAK AD-H column (Department of Chemistry, Zhejiang University).

¹H NMR spectra and ¹³C NMR spectra were recorded on a *Bruker AV-500* spectrometer (Pharmaceutical Informatics Institute, Zhejiang University) or a WNMRI-400 spectrometer (Department of Chemistry, Zhejiang University) in chloroform-*d* (CDCl₃, contain internal TMS) or DMSO-*d*₆. For CDCl₃ as solvent, chemical shifts of ¹H NMR spectra were reported in ppm with the internal TMS signal at 0 ppm as a standard, and chemical shifts of ¹³C NMR spectra were reported in ppm with the chloroform signal at 77.16 ppm as a standard.¹ The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = heptet, dd = double doublet, dt = double of triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration).

Photocatalysts were purchased from Jiangsu Sinocompound Catalysts Co., Ltd.

Solvents, such as Ethyl acetate (EA), petroleum ether (PE) were obtained commercially and used without further purification unless otherwise noted. Acetonitrile (MeCN) was purified by distilling after treating with CaH₂.

2. Starting Materials

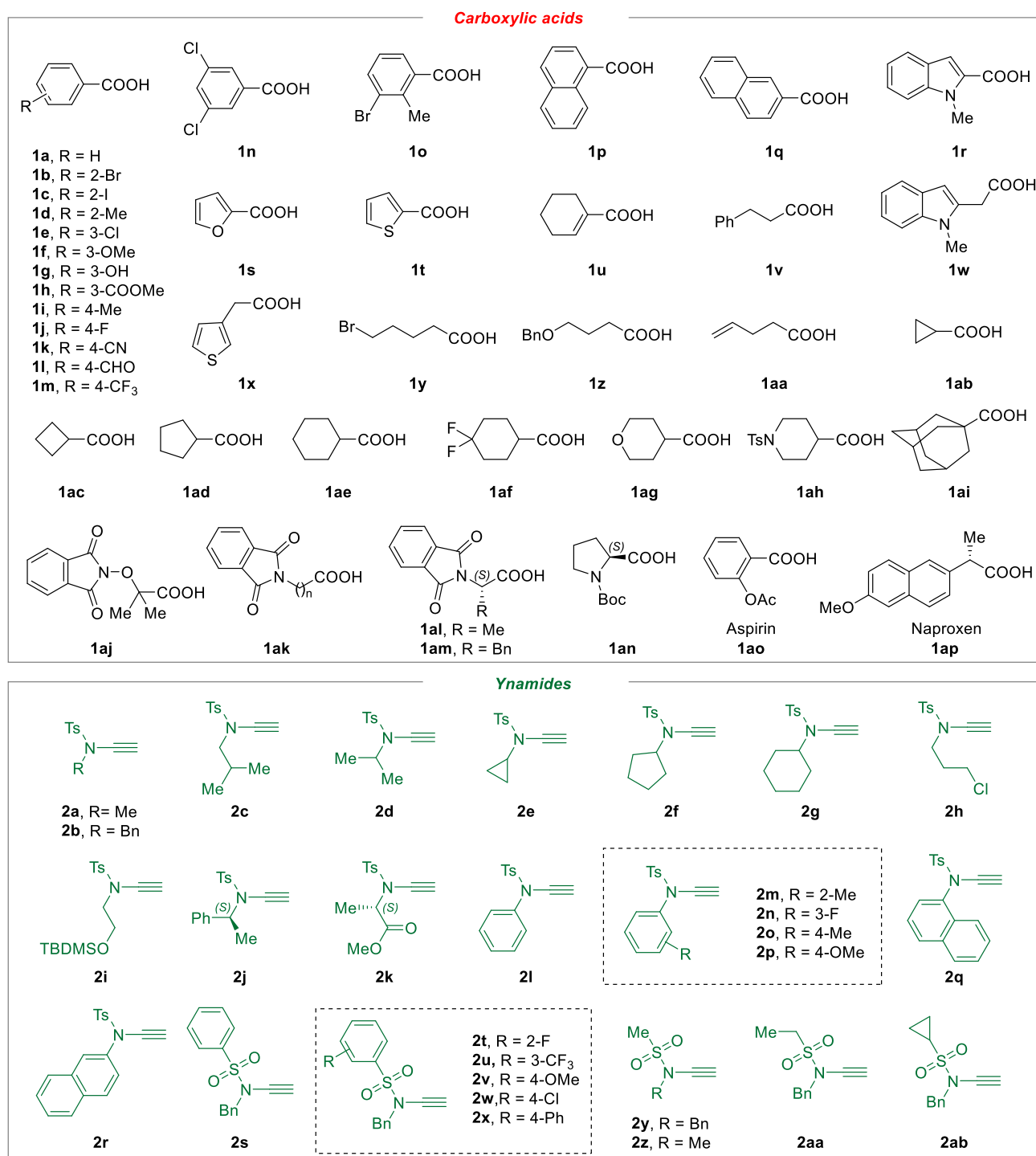


Fig. S1 Starting carboxylic acids and ynamides. Chemical structures of starting materials.

All starting carboxylic acids and ynamides are listed in **Fig. S1**. All starting carboxylic acids, except **1aj**, are commercial available. Carboxylic acid **1aj** was prepared according to the reported procedure.² Starting ynamides are synthesized according to the reported methods. Ynamides **2a-2g**,

2i-2j, **2l-2m**, **2o-2x** were prepared according to the method A,³ Ynamides **2h**, **2k** and **2n** were prepared according to the method B;⁴ and ynamides **2y-2ab** were prepared according to the method C.⁵

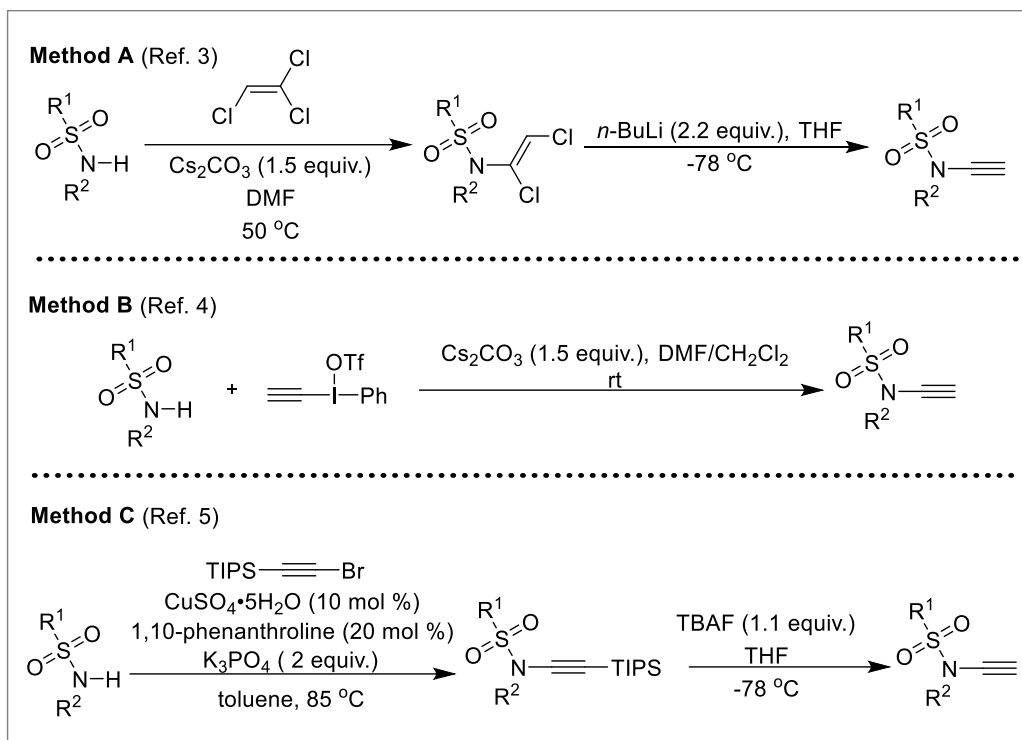
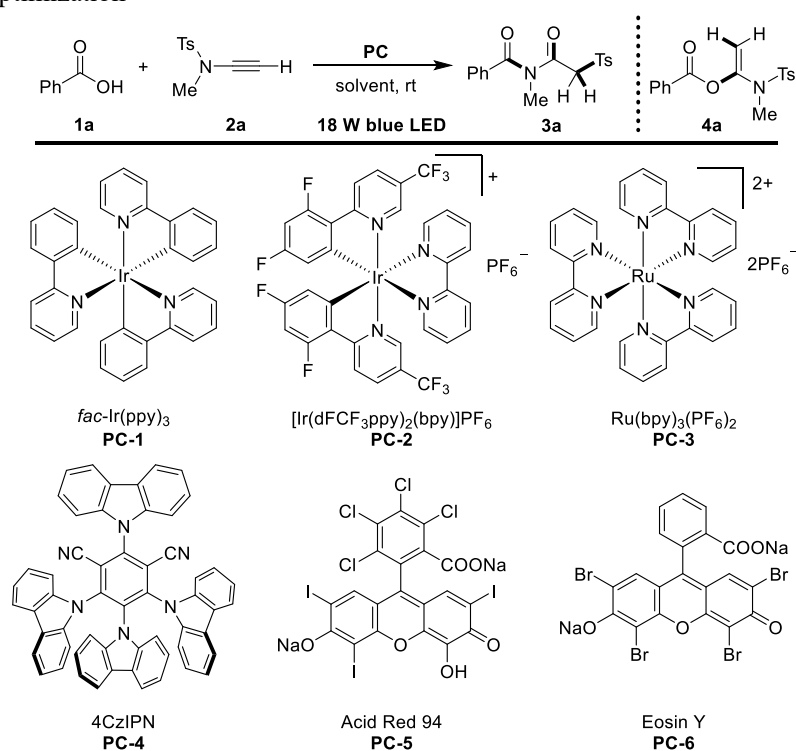


Fig. S2 Synthesis of ynamides. Starting ynamides were prepared according to the reported methods.

3. Reaction Optimization

Table S1. Reaction Optimization



Entry	Photocatalyst	Solvent	Yield (%) ^b
1	PC-1	MeCN	67
2	PC-2	MeCN	96
3	PC-3	MeCN	0 ^c
4 ^d	PC-4	MeCN	85
5 ^d	PC-5	MeCN	0
6 ^d	PC-6	MeCN	31
5	PC-2	CH ₂ Cl ₂	92
6	PC-2	MeOH	63
7	PC-2	MeCN:H ₂ O = 1:1	19
8	none	MeCN	0 ^c
9	PC-2	MeCN	0 ^{c,e}

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), photocatalyst (0.2 mol %), solvent (2 mL), rt, 3 h, argon; 18 W blue LEDs is used. ^b Yield refers to isolated product. ^c Intermediate **4a** was observed. ^d Photocatalyst (2 mol %) is used. ^e Without light irradiation.

4. Typical Procedure for The Synthesis of **3a**

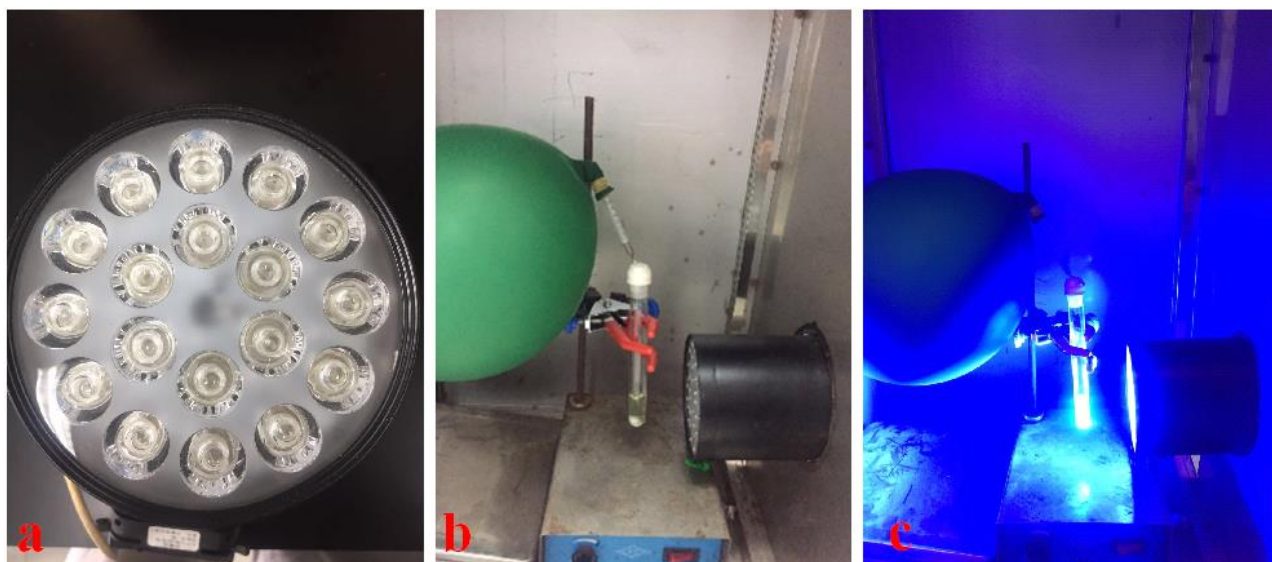
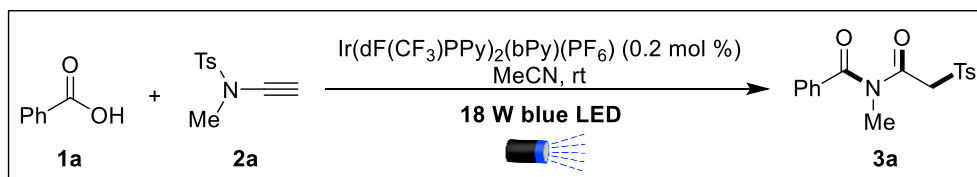


Fig. S3 General reaction apparatus. **a.** 18 W blue LEDs. **b.** Dissolving carboxylic acids (0.2 mmol), ynamides (0.2 mmol) and Ir(dF(CF₃)PPy)₂(bPy)(PF₆) (0.2 mol %) in 2 mL anhydrous MeCN under argon atmosphere. **c.** Irradiating the reaction by blue LED at rt.



An oven-dried culture tube equipped with a magnetic stirrer bar was charged with benzoic acid **1a** (25 mg, 0.2 mmol), ynamide **2a** (42 mg, 0.2 mmol) and Ir(dF(CF₃)PPy)₂(bPy)(PF₆) (0.4 mg, 0.2 mol %), and then purged with argon three times. Anhydrous MeCN (2 mL) was added as solvent and the reaction was stirred at room temperature for 5 h under the irradiation of 18 W Blue LED lamp. The reaction was concentrated under vacuum to obtain the residue, which was further purified by silica gel column chromatography eluting by PE/ EA (3/1, v/v) to give **3a** (63.5 mg, 96% yield) as a white solid.

5. Gram-Scale Reaction

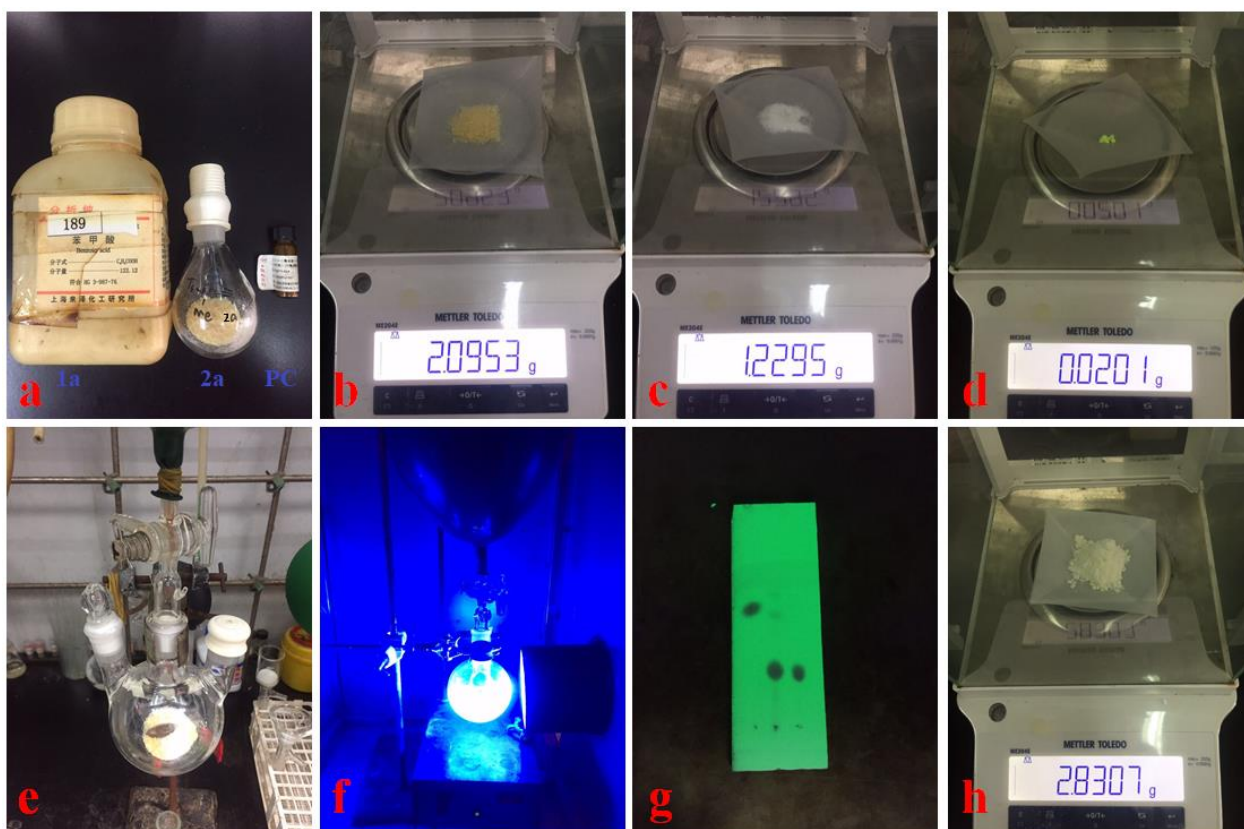
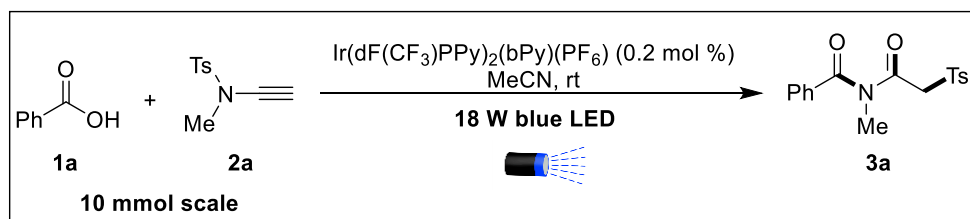
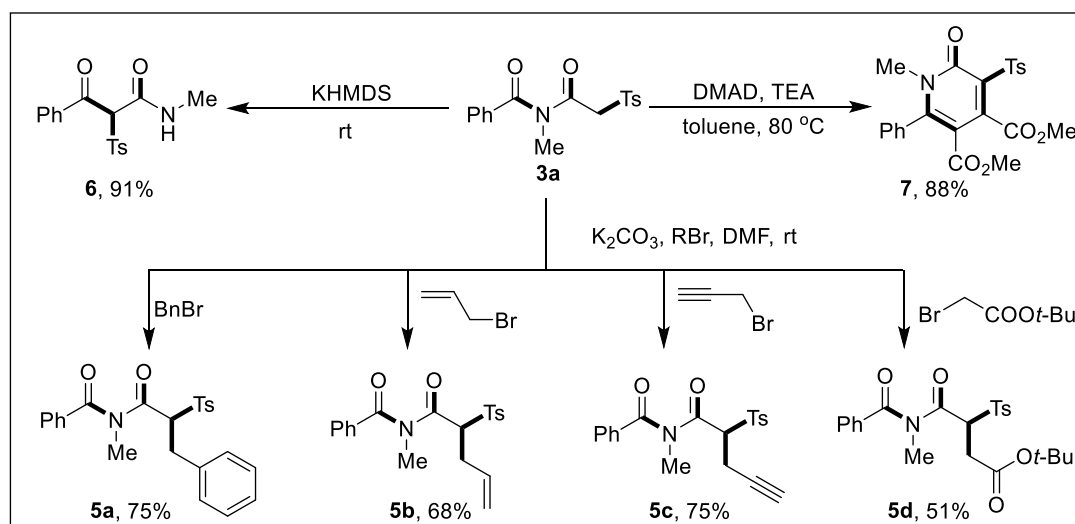


Fig. S4 Gram-scale reaction. **a.** Starting materials and photocatalyst. **b.** 2.09 g of ynamide **2a** was weighed. **c.** 1.22 g of benzoic acid **1a** was weighed. **d.** 20 mg of Ir(dF(CF₃)PPy)₂(bPy)(PF₆) was weighed. **e.** the mixture was under the argon atmosphere and added 100 mL anhydrous MeCN. **f.** The reaction was irradiated by 18 W blue LEDs at rt. **g.** the reaction was analysed by TLC (PE/EA = 3/1, v/v. left: ynamide **2a**; middle: reaction; right: product **3a**). **h.** 2.83 g of product **3a** was isolated.



An oven-dried flask equipped with a magnetic stirrer bar was charged with benzoic acid **1a** (1.22 g, 10 mmol), ynamide **2a** (2.09 g, 10 mmol) and $\text{Ir}(\text{dF}(\text{CF}_3)\text{PPy})_2(\text{bPy})(\text{PF}_6)$ (20 mg, 0.02 mmol), and then purged with argon three times. Anhydrous MeCN (100 mL) was added and the reaction was stirred at room temperature for 5 h under the irradiation of 18 W Blue LED. The reaction was concentrated under vacuum to obtain the residue, which was purified by silica gel column chromatography eluting by PE/ EA (3/1, v/v) to give **3a** (2.83 g, 86% yield) as a white solid.

6. Procedures for The Synthesis of 5, 6 and 7



General procedure for the synthesis 5. An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with **3a** (66 mg, 0.2 mmol) and K_2CO_3 (35 mg, 0.25 mmol), then purged with argon three times. Anhydrous DMF (2 mL) was added as solvent. Alkyl bromides (0.3 mmol, 1.5 equiv.) was added and the reaction was stirred at room temperature for 2 h. The reaction was quenched with aqueous NH_4Cl and extracted with EtOAc (3×10 mL). The combined organic layer was washed by brine, dried over anhydrous Na_2SO_4 , filtered, and the filtrate was concentrated under vacuum to obtain the residue, which was purified by silica gel column chromatography eluting by PE/ EA (5/1, v/v) to give corresponding **5**.

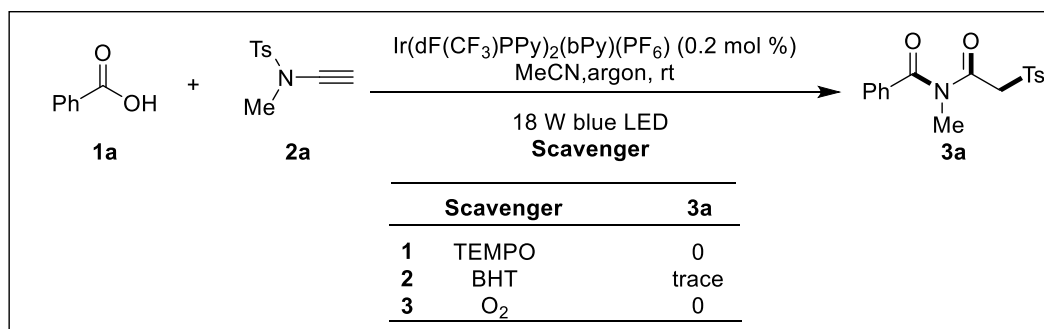
Procedure for the synthesis of 6: An oven-dried Schlenk tube equipped with a magnetic stirrer

bar was charged with **3a** (66 mg, 0.2 mmol), then purged with argon three times. Anhydrous THF (4 mL) was added as solvent. Then KHMDS (0.3 mL, 1 mol/L in THF) was added and the reaction was stirred at room temperature for 1 h. The reaction was quenched with aqueous NH₄Cl and extracted with EtOAc (3×10 mL). The combined organic layer was washed by brine, dried over anhydrous Na₂SO₄, filtered, and the filtrate was concentrated under vacuum to obtain the residue, which was purified by silica gel column chromatography eluting by PE/ EA (1/1, v/v) to give *N*-methyl-3-oxo-3-phenyl-2-tosylpropanamide **6** (60 mg, 91% yield) as a white solid.

Procedure for the synthesis of 7: An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with **3a** (66 mg, 0.2 mmol), then purged with argon three times. Anhydrous toluene (2 mL), DMAD (32 mg, 0.3 mmol) and TEA (55 μL, 0.4 mmol) were added and the reaction was stirred at 80 °C for 12 h. The reaction was concentrated under vacuum to obtain the residue, which was purified by silica gel column chromatography eluting by PE/ EA (2/1, v/v) to give dimethyl 1-methyl-6-oxo-2-phenyl-5-tosyl-1,6-dihydropyridine-3,4-dicarboxylate **7** (80 mg, 88% yield) as a yellow solid.

7. Mechanistic Studies

7.1 Radical Scavenging Experiments



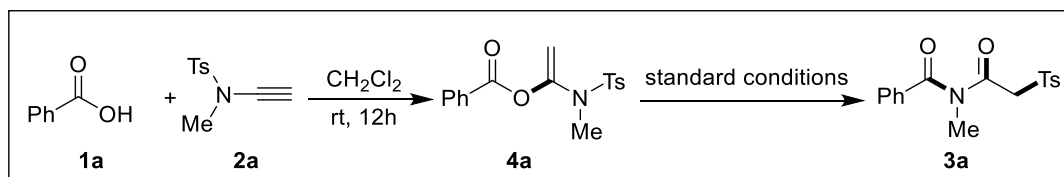
Experiment 1 and 2: An oven-dried culture tube equipped with a magnetic stirrer bar was charged with benzoic acid **1a** (25 mg, 0.2 mmol), ynamide **2a** (42 mg, 0.2 mmol), Ir(dF(CF₃)PPy)₂(bPy)(PF₆) (0.4 mg, 0.2 mol %) and radical scavenger (TEMPO or BHT, 1.5 equiv.), and then purged with argon three times. Anhydrous MeCN (2 mL) was added as solvent and the reaction was stirred at room temperature for 5 h under the irradiation of 18 W Blue LED lamp.

Experiment 3: An oven-dried culture tube equipped with a magnetic stirrer bar was charged with benzoic acid **1a** (25 mg, 0.2 mmol), ynamide **2a** (42 mg, 0.2 mmol) and Ir(dF(CF₃)PPy)₂(bPy)(PF₆)

(0.4 mg, 0.2 mol %), and then purged with oxygen three times. Anhydrous MeCN (2 mL) was added as solvent and the reaction was stirred at room temperature for 5 h under the irradiation of 18 W Blue LED lamp.

The TLC analysis of these reactions showed that TEMPO, BHT and O₂ could completely suppress the imidation reaction, suggesting a radical intermediate was involved in the process.

7.2 Step-wise Experiment



An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with benzoic acid **1a** (25 mg, 0.2 mmol), ynamide **2a** (42 mg, 0.2 mmol) and then purged with argon three times. Anhydrous CH₂Cl₂ (2 mL) was added and the reaction was stirred at room temperature for 12 h. TLC analysis showed the ynamide was consumed completely. The reaction was concentrated to obtain the product **4a** (67 mg, quant.) as a white solid.

The **4a** (67 mg, 0.2 mmol) and Ir(dF(CF₃)PPy)₂(bPy)(PF₆) (0.4 mg, 0.0004 mmol) was dissolved in anhydrous MeCN (2 mL) under argon and then the mixture was stirred under the irradiation of 18 W Blue LED for 5h at room temperature. The reaction was concentrated under vacuum to obtain the residue, which was purified by silica gel column chromatography eluting by PE/ EA (3/1, v/v) to give **3a** (62 mg, 92% yield). The step-wise experiment demonstrates that **4a** is the intermediate of this photo-induced imidation process.

7.3 Stern–Volmer Quenching Experiments

Emission intensities were recorded using Hitachi F-2500 fluorescence spectrometer for all experiments. All Ir(dF(CF₃)PPy)₂(bPy)(PF₆) solutions (0.01 mM) were excited at 390 nm and the emission intensity at 485 nm was collected at room temperature (**Fig. S5**). Samples were prepared by rapidly adding solutions of photocatalyst, quencher, and MeCN to obtain a total volume of 1.5 mL under an argon atmosphere. The sample was shaken for 1 min and then the emission of the sample was collected at fluorescence spectrometer immediately. All the experiments are run in three times (**Table S2-S4**). The data show that **4a** could quench the excited state of the photocatalyst, while **1a** and **2a** are

unable to quench this excited state, further verifying that **4a** is the intermediate of this imidation process (**Fig. S6**).

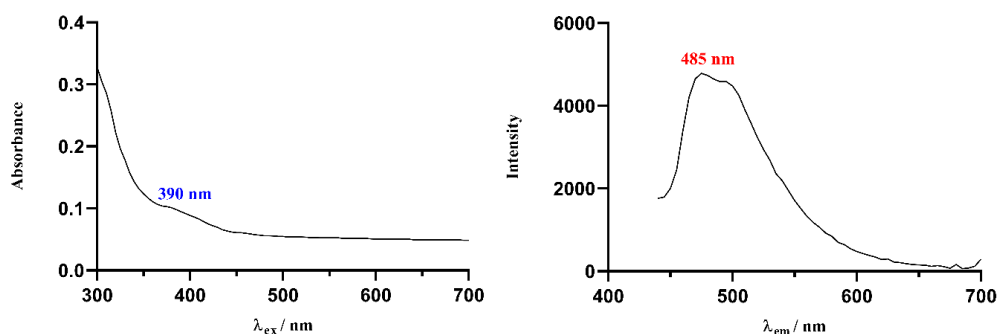


Fig. S5 Absorbance and emission spectra of Ir(dF(CF₃)PPy)₂(bPy)(PF₆). 0.01Mm concentration in MeCN. **Left:** Absorbance of Ir(dF(CF₃)PPy)₂(bPy)(PF₆). **Right:** Emission spectra of Ir(dF(CF₃)PPy)₂(bPy)(PF₆).

Table S2. Stern–Volmer quenching experiment of Ir(dF(CF₃)PPy)₂(bPy)(PF₆) and **4a**

4a /mM	Emission 1	Emission 2	Emission 3	Average	I ₀ /I
0	1261	1250	1241	1250.667	1.004264
0.5	1236	1234	1235	1235	1.017004
1	1179	1146	1167	1164	1.079038
2	1150	1124	1135	1136.333	1.105309
4	989	993	989	990.3333	1.26826

Table S3. Stern–Volmer quenching experiment of Ir(dF(CF₃)PPy)₂(bPy)(PF₆) and **1a**

1a /mM	Emission 1	Emission 2	Emission 3	Average	I ₀ /I
0	1278	1273	1268	1273	1
0.5	1261	1266	1259	1262	1.008716
1	1271	1268	1260	1266.333	1.005265
2	1258	1272	1263	1264.333	1.006855
4	1263	1277	1261	1267	1.004736

Table S4. Stern–Volmer quenching experiment of Ir(dF(CF₃)PPy)₂(bPy)(PF₆) and **2a**

2a /mM	Emission 1	Emission 2	Emission 3	Average	I ₀ /I
0	1261	1268	1271	1266.667	1
0.5	1259	1263	1255	1259	1.00609
1	1263	1266	1256	1261.667	1.003963
2	1243	1249	1251	1247.667	1.015229
4	1251	1249	1249	1249.667	1.013604

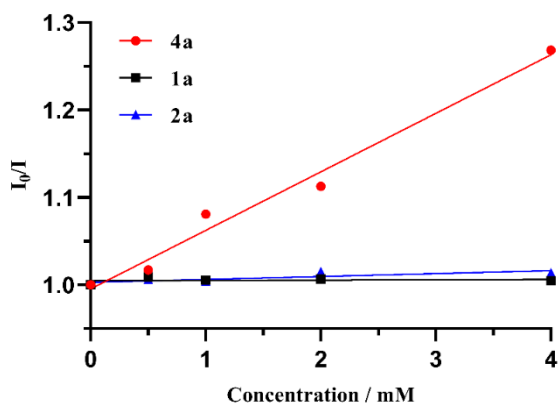


Fig. S6 Results of Stern–Volmer quenching experiment. The data show that **4a** could quench the excited state of the photocatalyst, while **1a** and **2a** are unable to quench this excited state.

7.4 Light On/Off Experiment

An oven-dried 25 mL culture tube equipped with a magnetic stirrer bar was charged with benzoic acid **1a** (74 mg, 0.6 mmol), ynamide **2a** (126 mg, 0.6 mmol) and Ir(dF(CF₃)PPy)₂(bPy)(PF₆) (2.4 mg, 0.2 mol %), and then purged with argon three times. Anhydrous MeCN (12 mL) was added as solvent. The reaction was performed at room temperature under alternating intervals of light and dark (15 mins). The reaction profile is shown below and the yield of product **3a** was determined by ¹H NMR (taking 1mL samples and adding 0.1 mmol 1,3,5-trioxane was used as an internal standard). This experiment indicates that continuous irradiation of blue light is essential for the reaction (**Fig. S7**).

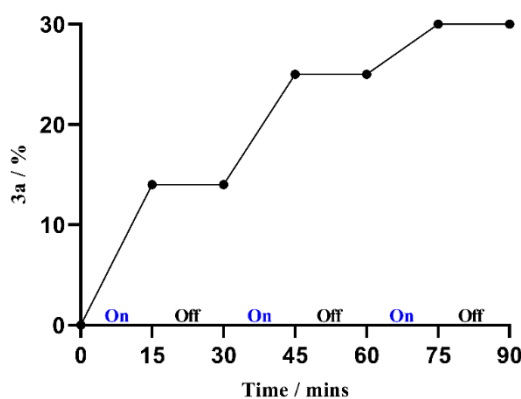
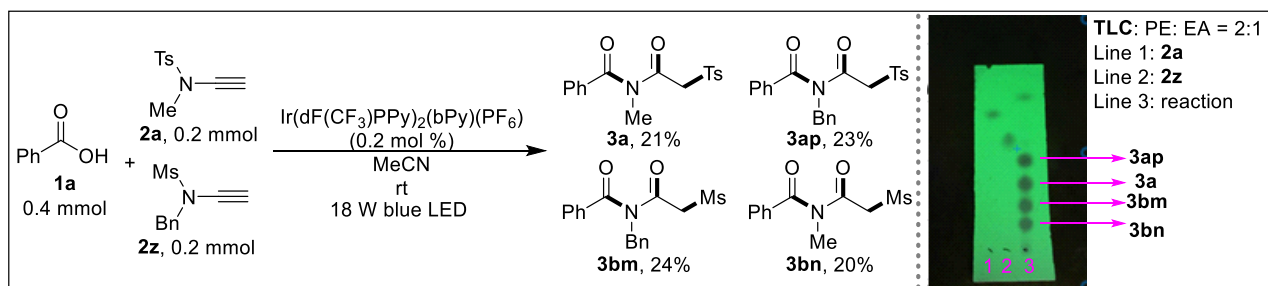


Fig. S7 Light on/off experiment. The result shows the imidation process needs continuous irradiation.

7.5 Crossover Reaction



An oven-dried culture tube equipped with a magnetic stirrer bar was charged with benzoic acid **1a** (49 mg, 0.4 mmol), ynamide **2a** (42 mg, 0.2 mmol), ynamide **2z** (42 mg, 0.2 mmol) and $\text{Ir}(\text{dF}(\text{CF}_3)\text{PPy})_2(\text{bPy})(\text{PF}_6)$ (0.8 mg, 0.2 mol %), and then purged with argon three times. Anhydrous MeCN (4 mL) was added as solvent and the reaction was stirred at room temperature for 5h under the irradiation of a Blue LED lamp (18 W). TLC analysis showed that there were four products formed (**3a**, **3ap**, **3bm** and **3bn**). The mixture was concentrated and the yields of four products were determined by ^1H NMR spectroscopy (0.1 mmol of 1,3,5-trioxane as an internal standard, **Fig. S8**).

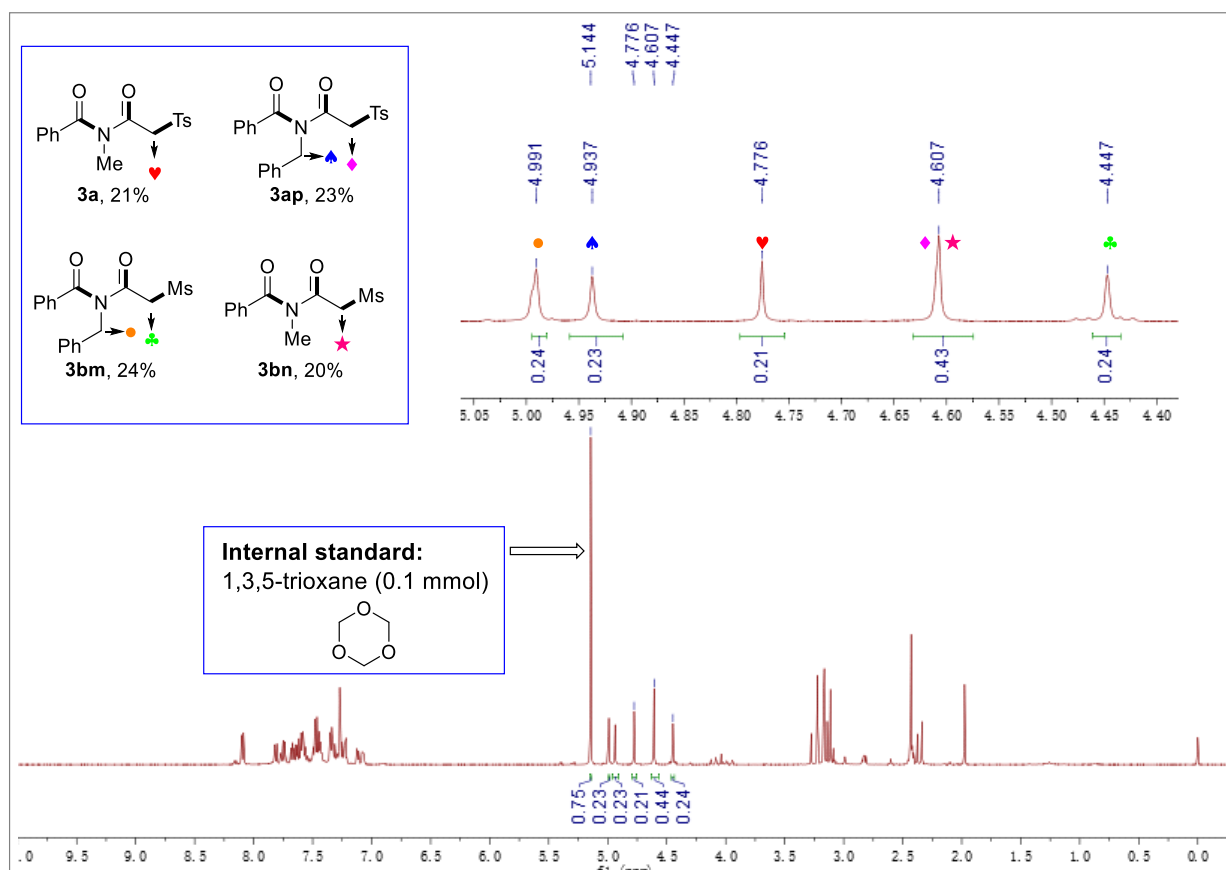


Fig. S8 ^1H NMR (CDCl₃, 500 MHz) of the crossover reaction. The NMR shows **3a**, **3ap**, **3bm** and **3bn** were formed in comparable yields, indicating the intermolecular process in the imidation reaction.

7.6 Cyclic Voltammograms

Cyclic voltammograms were taken on a C-H Instruments 840B potentiostat using a glassy carbon working electrode, a Ag/AgCl reference electrode (SCE), and a Pt wire counter electrode. The pH was not adjusted and voltammograms were taken at room temperature in a 100 mM MeCN solution of tetrabutylammonium hexafluorophosphate containing 10 mM of **4a**. The scan rate was 100 mV/s. The reduction potential of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{bpy})]^+$ ($E_{1/2}[\text{Ir}^{\text{IV}}/*\text{Ir}^{\text{III}}] = -1.00 \text{ V vs SCE}$)⁶ shows not higher than that of intermediate **4a** ($E_{1/2}^{\text{red}} = -1.00 \text{ V}$) (**Fig. S9**), indicating that the reduction of intermediate **4a** by the excited state $*\text{Ir}^{\text{III}}$ was thermodynamically unfavorable.

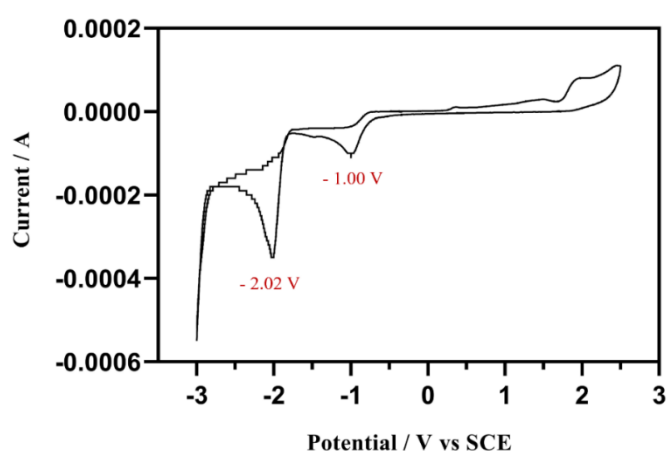
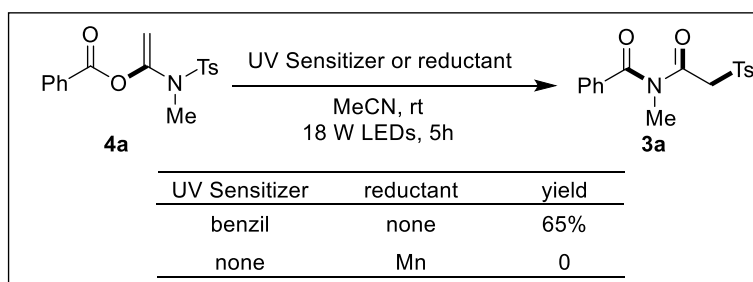


Fig. S9 Cyclic voltammograms. The reduction potential of intermediate **4a** is $E_{1/2}^{\text{red}} = -1.00 \text{ V}$.

7.7 UV Sensitizer Experiments



An oven-dried culture tube equipped with a magnetic stirrer bar was charged with **4a** (33 mg, 0.1 mmol) and benzil (22 mg, 0.1 mmol) or Mn powder (110 mg, 0.2 mmol), and then purged with argon three times. Anhydrous MeCN (1 mL) was added as solvent and the reaction was stirred at room temperature for 5h under the irradiation of 18W Blue LED lamp. The reactions were analysed by TLC, showing the benzyl promoted the imidation, while Mn powder failed to deliver the product. The reaction of benzil was further analysed by ^1H NMR (adding 0.1 mmol 1,3,5-trioxane was used as an internal standard), showing **3a** could be formed in 65% yield (**Fig. S10**).

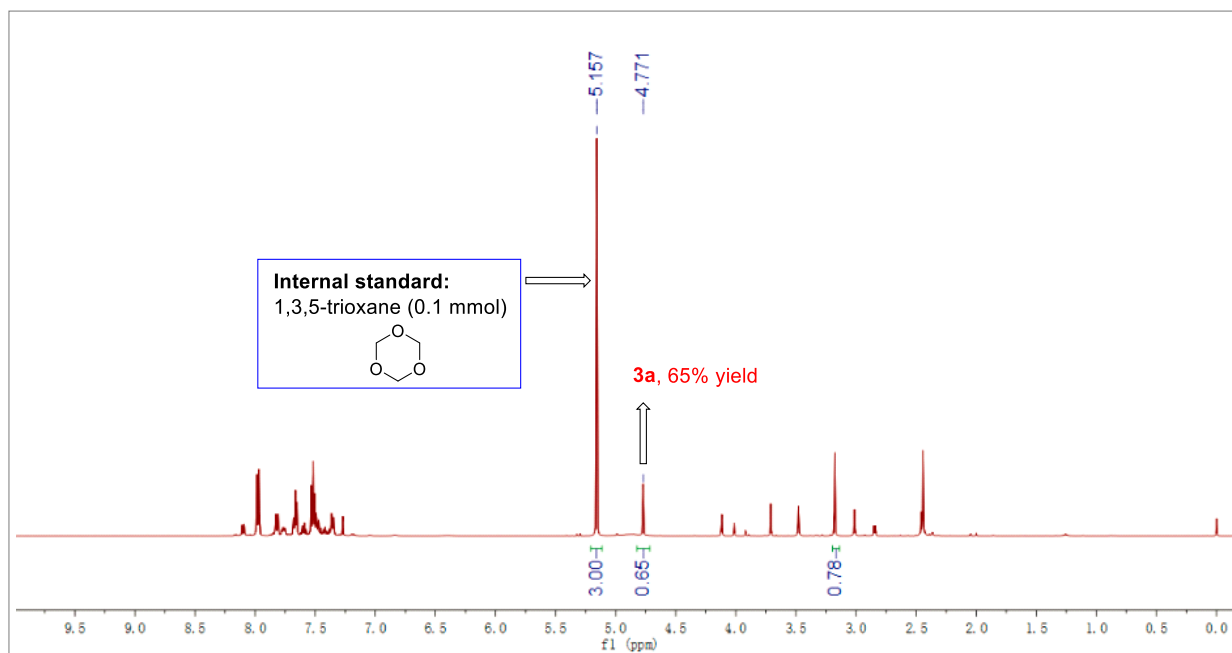


Fig. S10 ^1H NMR (CDCl_3 , 500 MHz) of the benzyl-promoted reaction. The benzil could promote the formation of **3a** in 65% yield.

UV Sensitizer could promote this reaction, strongly suggesting that an energy transfer mechanism is indeed involved. Using Mn powder ($E^\circ = -1.42$ V vs. SCE (saturated calomel electrode))⁷ as an external reductant (comparable to $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2](\text{bpy})^+$ ($E_{1/2}[\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}}] = -1.00$ V vs SCE)⁶ failed to promote the desired reaction, indicating that photoredox pathway was not operative for this transformation.

7.8 Determination of The Reaction Quantum Yield

(1) Determination of the light intensity at 452 nm:

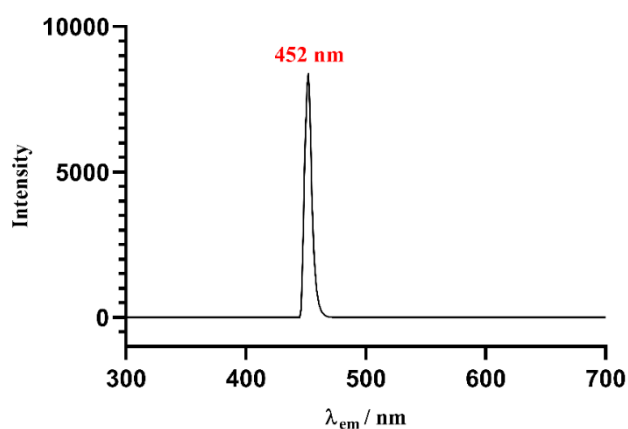


Fig. S11. Emission spectrum of blue LED. $\lambda_{\text{max}} = 452$ nm (Using Hitachi F-2500 fluorescence spectrometer).

Absorbance of samples were recorded using a PERSEE TU-1810 UV-visible spectrophotometer.

According to the procedure of Yoon⁸, the photon flux of the blue LED ($\lambda_{\text{max}} = 452 \text{ nm}$) was determined by standard ferrioxalate actinometry. 2.21 g of potassium ferrioxalate hydrate was dissolved in 30 mL of 0.05 M H_2SO_4 to prepare a 0.15 M solution of ferrioxalate. A buffered solution of 1, 10-phenanthroline was prepared by dissolving 50 mg of 1,10-phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4 . Both solutions were stored in the dark. To determine the photon flux of the blue LED ($\lambda_{\text{max}} = 452 \text{ nm}$, **Fig. S11**), 2.0 mL of the ferrioxalate solution was placed in a 3 mL cuvette and irradiated for 90.0 seconds. After irradiation, 0.35 mL of the 1,10-phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \epsilon} \quad (\text{eq 1})$$

Where V is the total volume (0.00235 L) of the solution after addition of 1,10-phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions (1.541 – 0.786), l is the path length (1.0 cm), and ϵ is the molar absorptivity at 510 nm (11100 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). The photon flux can be calculated using eq 2.

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \times t \times f} \quad (\text{eq 2})$$

Where Φ is the quantum yield for the ferrioxalate actinometer (approximate value: 0.845 for a 0.15 M solution at $\lambda = 458 \text{ nm}$)⁹, t is the time (90.0 s).

f is the fraction of light absorbed at $\lambda = 452 \text{ nm}$, which was calculated using eq 3.

$$f = 1 - 10^{-A(\lambda = 452 \text{ nm})} \quad (\text{eq 3})$$

where A is the measured absorbance of above ferrioxalate solution at 452 nm (1.817).

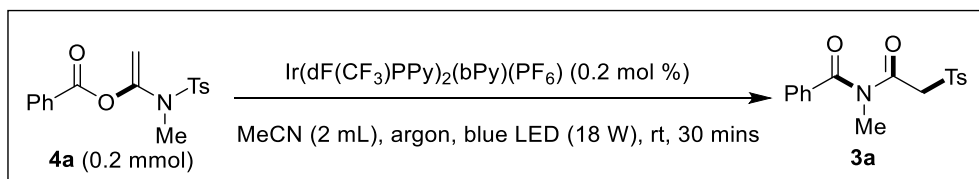
The photon flux calculation:

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \epsilon} = \frac{0.00235 \text{ L} \times (1.541 - 0.786)}{1 \text{ cm} \times 11100 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}} = 1.598423 \times 10^{-7} \text{ mol}$$

$$f = 1 - 10^{-A(\lambda = 452 \text{ nm})} = 1 - 10^{-1.817} = 0.9847595$$

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \times t \times f} = \frac{1.598423 \times 10^{-7} \text{ mol}}{0.845 \times 90 \text{ s} \times 0.9847595} = 2.13 \times 10^{-9} \text{ einstein} \cdot \text{s}^{-1}$$

(2) Determination of the reaction quantum yield:



PC-2 $\text{Ir}(\text{dF}(\text{CF}_3)\text{PPy})_2(\text{bPy})(\text{PF}_6)$ (6.0mg) was dissolved in 30 mL anhydrous MeCN. An oven-dried culture tube equipped with a magnetic stirrer bar was charged with **4a** (66 mg, 0.2 mmol), then purged with argon three times. 2 mL of above **PC** solution was added and the mixture was stirred under the irradiation of 18 W Blue LED for 30 mins (1800 s) at room temperature. The reaction was concentrated under vacuum to obtain the residue, which was analysed by ^1H NMR (adding 0.1 mmol 1,3,5-trioxane was used as an internal standard), showing **3a** could be formed in 30% yield (0.06×10^{-3} mol). The reaction quantum yield (Φ) was determined using eq 4

$$\Phi = \frac{\text{mol of } \mathbf{3a}}{\text{photon flux} \times t \times f} \quad (\text{eq 4})$$

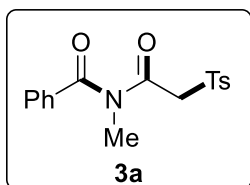
where the photon flux is 2.13×10^{-9} einstein s^{-1} (determined by actinometry as described above), t is the reaction time (1800 s) and f is the fraction of incident light absorbed by the reaction mixture, determined using eq 3. An absorbance of the reaction mixture at 452 nm was measured to be 0.100.

The reaction quantum yield (Φ) calculation:

$$\Phi = \frac{\text{mol of } \mathbf{3a}}{\text{photon flux} \times t \times f} = \frac{0.06 \times 10^{-3} \text{ mol}}{2.13 \times 10^{-9} \text{ einstein} \cdot \text{s}^{-1} \times 1800 \text{ s} \times (1 - 10^{-0.100})} = 76.1$$

The value of quantum yield suggests a radical chain propagation process for the present reaction.

8. Characterization of Products



N-methyl-*N*-(2-tosylacetyl)benzamide

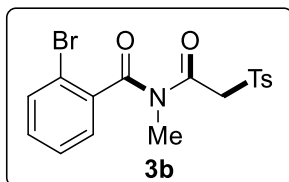
3a: White solid (64 mg, 96% yield), m. p. 97 – 98 °C.

TLC: $R_f = 0.20$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.84 – 7.80 (m, 2H), 7.68 – 7.64 (m, 2H), 7.61 – 7.56 (m, 1H), 7.51 – 7.47 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.77 (s, 2H), 3.17 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.4, 164.7, 145.3, 136.3, 133.7, 133.0, 129.9, 128.9 (129.93), 128.9 (128.86), 128.4, 61.9, 35.5, 21.7.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{17}\text{H}_{18}\text{NO}_4\text{S}$, 332.0957; found, 332.0954.



2-bromo-*N*-methyl-*N*-(2-tosylacetyl)benzamide

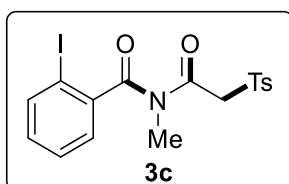
3b: Light yellow oil (80 mg, 98% yield).

TLC: R_f = 0.44 (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.89 – 7.85 (m, 2H), 7.62 (dd, J_1 = 8.0 Hz, J_2 = 0.5 Hz, 1H), 7.46 – 7.34 (m, 5H), 4.96 (s, 2H), 3.05 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 171.6, 164.7, 145.4, 137.0, 136.5, 133.3, 131.9, 129.9, 128.7, 128.1, 127.9, 118.6, 63.0, 33.7, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{17}\text{H}_{17}\text{BrNO}_4\text{S}$, 410.0062; found, 410.0066.



2-iodo-*N*-methyl-*N*-(2-tosylacetyl)benzamide

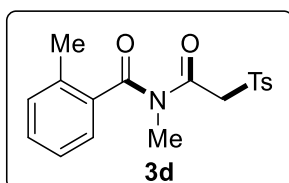
3c: White solid (84 mg, 92% yield), m. p. 87 – 88 °C.

TLC: R_f = 0.46 (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.90 – 7.86 (m, 3H), 7.50 – 7.45 (m, 1H), 7.40 – 7.35 (m, 3H), 7.21 – 7.16 (m, 1H), 4.96 (s, 2H), 3.04 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 172.9, 164.9, 145.4, 141.0, 139.8, 136.6, 131.8, 130.0, 128.8, 128.7, 127.5, 91.5, 63.0, 34.1, 21.9.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{17}\text{H}_{17}\text{INO}_4\text{S}$, 457.9923; found, 457.9919.



N,2-dimethyl-*N*-(2-tosylacetyl)benzamide

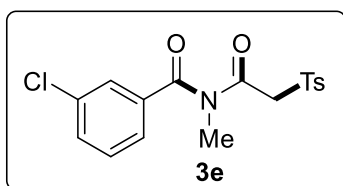
3d: White solid (65 mg, 95% yield), m. p. 97 – 99 °C.

TLC: $R_f = 0.35$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.41 – 7.35 (m, 3H), 7.33 – 7.25 (m, 3H), 4.90 (s, 2H), 3.05 (s, 3H), 2.46 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.1, 164.9, 145.3, 136.5, 135.9, 134.5, 131.3, 131.1, 129.9, 128.6, 126.8, 126.3, 62.9, 34.4, 21.8, 19.4.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{S}$, 346.1113; found, 346.1110.



3-chloro-*N*-methyl-*N*-(2-tosylacetyl)benzamide

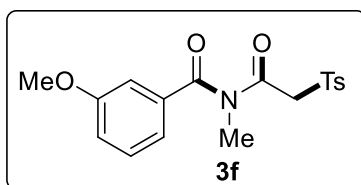
3e: White solid (64 mg, 88% yield), m. p. 88 – 89 °C.

TLC: $R_f = 0.42$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.83 – 7.79 (m, 2H), 7.62 (M, 1H), 7.57 – 7.53 (m, 2H), 7.46 – 7.42 (m, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.79 (s, 2H), 3.17 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 173.0, 164.5, 145.5, 136.2, 135.5, 135.0, 132.8, 130.2, 130.0, 128.8, 128.4, 126.9, 61.9, 35.4, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{17}\text{H}_{17}\text{ClNO}_4\text{S}$, 366.0567; found, 366.0561.



3-methoxy-*N*-methyl-*N*-(2-tosylacetyl)benzamide

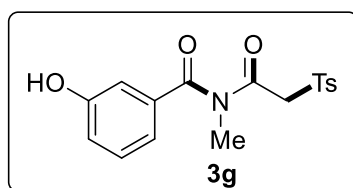
3f: Colourless gum (70 mg, 97% yield).

TLC: $R_f = 0.28$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, $J = 8.5$ Hz, 2H), 7.41 – 7.34 (m, 3H), 7.22 – 7.16 (m, 2H), 7.11 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.5$ Hz, 1H), 4.75 (s, 2H), 3.86 (s, 3H), 3.17 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.2, 164.7, 159.9, 145.4, 136.3, 135.1, 130.0 (130.00), 130.0 (129.97), 128.5, 121.0, 119.0, 113.9, 62.0, 55.6, 35.5, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₁₈H₂₀NO₅S, 362.1062; found, 362.1058.



3-hydroxy-N-methyl-N-(2-tosylacetyl)benzamide

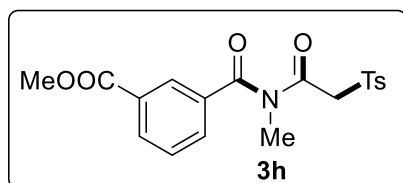
3g: Colourless gum (62 mg, 89% yield).

TLC: R_f = 0.10 (PE: EA = 3:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.16 – 7.11 (m, 2H), 7.08 – 7.03 (m, 1H), 6.92 (br, 1H), 4.77 (s, 2H), 3.15 (s, 3H), 2.42 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 174.3, 164.8, 156.5, 145.7, 136.0 134.8, 130.3, 130.1, 128.5, 120.8, 120.5, 115.6, 62.0, 35.6, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₁₇H₁₈NO₅S, 348.0906; found, 348.0901.



methyl 3-(methyl(2-tosylacetyl)carbamoyl)benzoate

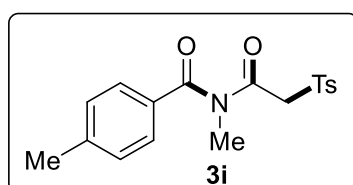
3h: Colourless gum (72 mg, 93% yield).

TLC: R_f = 0.15 (PE: EA = 3:1, v/v).

¹H NMR (400 MHz, CDCl₃) δ 8.33 – 8.29 (m, 1H), 8.27 – 8.23 (m, 1H), 7.89 – 7.85 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.81 (s, 2H), 3.96 (s, 3H), 3.18 (s, 3H), 2.44 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 173.5, 165.8, 164.5, 145.5, 136.2, 134.2, 133.6, 133.0, 131.0, 130.0, 129.9, 129.2, 128.4, 61.9, 52.6, 35.5, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₁₉H₂₀NO₆S, 390.1011; found, 390.1015.



N,4-dimethyl-N-(2-tosylacetyl)benzamide

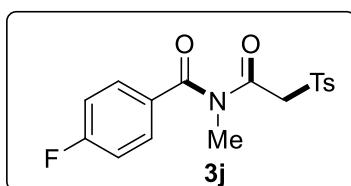
3i: White solid (50 mg, 73% yield), m. p. 97 – 99 °C.

TLC: $R_f = 0.35$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 4.72 (s, 2H), 3.18 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.4, 164.7, 145.3, 144.1, 136.4, 130.8, 129.9, 129.6, 129.3, 128.5, 61.9, 35.6, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{S}$, 346.1113; found, 346.1108.



4-fluoro-*N*-methyl-*N*-(2-tosylacetyl)benzamide

3j: White solid (63 mg, 90% yield), m. p. 95 – 96 °C.

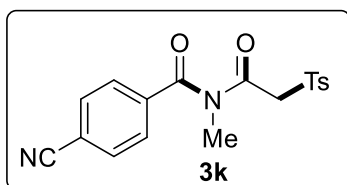
TLC: $R_f = 0.28$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.76 – 7.70 (m, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.21 – 7.15 (m, 2H), 4.75 (s, 2H), 3.19 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 173.5, 165.5 (d, $J = 255.2$ Hz), 164.5, 145.5, 136.3, 131.9 (d, $J = 9.3$ Hz), 130.0, 129.8 (d, $J = 3.2$ Hz), 128.4, 116.2 (d, $J = 22.2$ Hz), 61.8, 35.6, 21.8.

^{19}F NMR (376 MHz, CDCl_3) δ -104.50.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{17}\text{H}_{17}\text{FNO}_4\text{S}$, 350.0862; found, 350.0862.



4-cyano-*N*-methyl-*N*-(2-tosylacetyl)benzamide

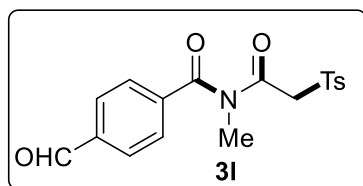
3k: White solid (65 mg, 92% yield), m. p. 117 – 118 °C.

TLC: $R_f = 0.21$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.78 (m, 6H), 7.37 (d, $J = 8.4$ Hz, 2H), 4.81 (s, 2H), 3.18 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 163.3, 144.7, 137.0, 135.1, 131.7, 129.1, 128.3, 127.4, 116.7, 115.1, 60.9, 34.3, 20.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₁₈H₁₇N₂O₄S, 357.0909; found, 357.0903.



4-formyl-*N*-methyl-*N*-(2-tosylacetyl)benzamide

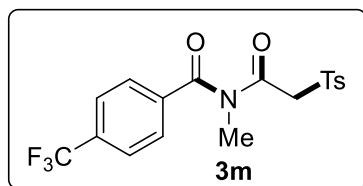
3l: White solid (69 mg, 96% yield), m. p. 125 – 126 °C.

TLC: R_f = 0.14 (PE: EA = 3:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 10.11 (s, 1H), 8.03 – 7.99 (m, 2H), 7.86 – 7.79 (m, 4H), 7.40 – 7.35 (m, 2H), 4.82 (s, 2H), 3.18 (s, 3H), 2.46 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 191.3, 173.5, 164.5, 145.6, 139.1, 138.8, 136.2, 130.1, 130.0, 129.3, 128.4, 62.0, 35.3, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₁₈H₁₈NO₅S, 360.0906; found, 360.0900.



***N*-methyl-*N*-(2-tosylacetyl)-4-(trifluoromethyl)benzamide**

3m: White solid (73 mg, 91% yield), m. p. 68 – 69 °C.

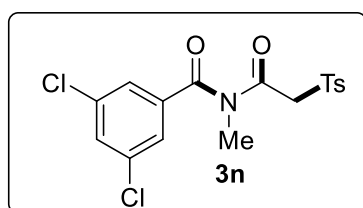
TLC: R_f = 0.36 (PE: EA = 3:1, v/v).

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.71 (m, 6H), 7.37 (d, *J* = 8.4 Hz, 2H), 4.82 (s, 2H), 3.18 (s, 3H), 2.45 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 173.3, 164.4, 145.6, 137.3, 136.2, 134.2 (q, *J* = 32.9 Hz), 130.1, 129.2, 128.4, 126.0 (q, *J* = 3.5 Hz), 123.5 (q, *J* = 272.8 Hz), 62.0, 35.4, 21.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.14.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₁₈H₁₇F₃NO₄S, 400.0830; found, 400.0823.



3,5-dichloro-*N*-methyl-*N*-(2-tosylacetyl)benzamide

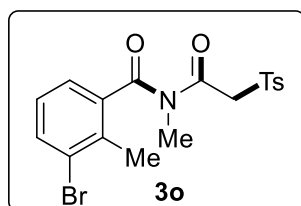
3n: White solid (74 mg, 93% yield), m. p. 137 – 139 °C.

TLC: $R_f = 0.43$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.4$ Hz, 2H), 7.57 – 7.54 (m, 1H), 7.53 – 7.50 (m, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 4.79 (s, 2H), 3.18 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 164.4, 145.7, 136.8, 136.2, 135.9, 132.6, 130.1, 128.5, 127.0, 61.9, 35.4, 21.9.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{17}\text{H}_{16}\text{Cl}_2\text{NO}_4\text{S}$, 400.0177; found, 400.0173.



3-bromo-*N*,2-dimethyl-*N*-(2-tosylacetyl)benzamide

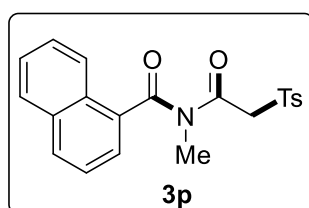
3o: White solid (73 mg, 86% yield), m. p. 164 – 165 °C.

TLC: $R_f = 0.36$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 8.4$ Hz, 2H), 7.68 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.30 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 7.21 – 7.13 (m, 1H), 4.96 (s, 2H), 3.04 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 164.8, 145.5, 136.9, 136.6, 135.1, 134.9, 130.0, 128.6, 127.8, 126.9, 125.4, 63.1, 34.4, 21.9, 20.0.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{18}\text{H}_{19}\text{BrNO}_4\text{S}$, 424.0218; found, 424.0213.



N-methyl-*N*-(2-tosylacetyl)-1-naphthamide

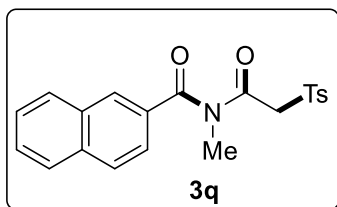
3p: White solid (61 mg, 80% yield), m. p. 145 – 146 °C.

TLC: $R_f = 0.36$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.0$ Hz, 2H), 7.94 – 7.90 (m, 1H), 7.87 (d, $J = 8.4$ Hz, 2H), 7.64 – 7.51 (m, 4H), 7.38 (d, $J = 8.0$ Hz, 2H), 4.99 (s, 2H), 3.07 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 165.0, 145.4, 136.6, 133.7, 132.4, 131.9, 130.0, 129.6, 128.9, 128.7, 128.2, 127.1, 126.0, 125.0, 124.5, 63.0, 34.8, 21.9.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{21}\text{H}_{20}\text{NO}_4\text{S}$, 382.1113; found, 382.1107.



N-methyl-*N*-(2-tosylacetyl)-2-naphthamide

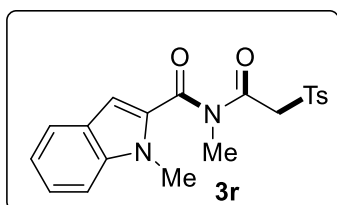
3q: White solid (55 mg, 72% yield), m. p. 174 – 175 °C.

TLC: R_f = 0.36 (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1H), 7.98 – 7.88 (m, 3H), 7.83 (d, J = 8.4 Hz, 2H), 7.69 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.35 (d, J = 8.4 Hz, 2H), 4.79 (s, 2H), 3.25 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 164.8, 145.4, 136.4, 135.4, 132.5, 131.0, 130.6, 130.0, 129.4, 128.9 (128.93), 128.9 (128.86), 128.6, 128.0, 127.4, 124.7, 62.0, 35.7, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{21}\text{H}_{20}\text{NO}_4\text{S}$, 382.1113; found, 382.1109.



N,1-dimethyl-*N*-(2-tosylacetyl)-1*H*-indole-2-carboxamide

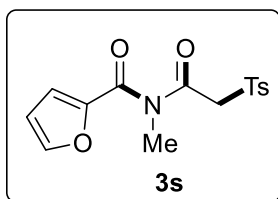
3r: White solid (50 mg, 65% yield), m. p. 127 – 128 °C.

TLC: R_f = 0.35 (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 4.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.23 – 7.16 (m, 1H), 6.96 (s, 1H), 4.60 (s, 2H), 3.99 (s, 3H), 3.36 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 164.6, 145.5, 140.3, 136.1, 130.3, 130.0, 128.6, 126.4, 125.8, 123.1, 121.5, 111.3, 110.6, 62.4, 35.9, 31.7, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_4\text{S}$, 385.1222; found, 385.1219.



***N*-methyl-*N*-(2-tosylacetyl)furan-2-carboxamide**

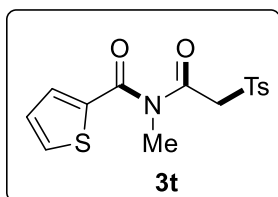
3s: Colourless oil (51 mg, 79% yield).

TLC: $R_f = 0.14$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.64 (dd, $J_1 = 1.5$ Hz, $J_2 = 1.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.30 (dd, $J_1 = 3.5$ Hz, $J_2 = 0.5$ Hz, 1H), 6.61 (dd, $J_1 = 3.5$ Hz, $J_2 = 1.5$ Hz, 1H), 4.71 (s, 2H), 3.33 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 164.4, 162.2, 147.0, 146.6, 145.3, 136.3, 129.9, 128.6, 121.5, 112.8, 61.9, 34.0, 21.8.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$) $^+$ calcd. For $\text{C}_{15}\text{H}_{16}\text{NO}_5\text{S}$, 322.0749; found, 322.0749.



***N*-methyl-*N*-(2-tosylacetyl)thiophene-2-carboxamide**

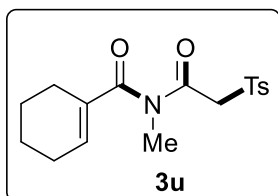
3t: White solid (61 mg, 91% yield), m. p. 107 – 108 °C.

TLC: $R_f = 0.21$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 4.5$ Hz, 1H), 7.63 – 7.59 (m, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.17 – 7.15 (m, 1H), 4.70 (s, 2H), 3.37 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 167.3, 164.4, 145.4, 136.8, 136.3, 134.5, 134.0, 130.0, 128.6, 128.1, 61.8, 35.8, 21.8.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$) $^+$ calcd. For $\text{C}_{15}\text{H}_{16}\text{NO}_4\text{S}_2$, 338.0521; found, 338.0520.



***N*-methyl-*N*-(2-tosylacetyl)cyclohex-1-ene-1-carboxamide**

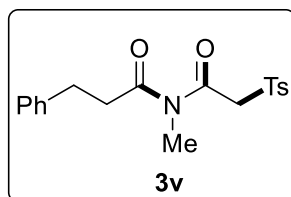
3u: Colourless oil (33 mg, 49% yield).

TLC: $R_f = 0.43$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 6.56 – 6.40 (m, 1H), 4.64 (s, 2H), 3.15 (s, 3H), 2.45 (s, 3H), 2.33 – 2.21 (m, 4H), 1.77 – 1.63 (m, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 175.4, 164.6, 145.3, 139.7, 136.4, 134.3, 129.9, 128.6, 61.9, 34.8, 25.7, 24.7, 21.9, 21.8, 21.4.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{17}\text{H}_{22}\text{NO}_4\text{S}$, 336.1270; found, 336.1273.



***N*-methyl-3-phenyl-*N*-(2-tosylacetyl)propanamide**

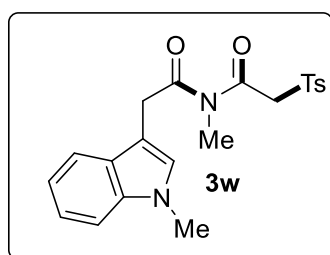
3v: White solid (60 mg, 83% yield), m. p. 105 – 106 °C.

TLC: $R_f = 0.28$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.83 – 7.80 (m, 2H), 7.36 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 4.80 (s, 2H), 3.18 (s, 3H), 2.98 – 2.92 (m, 2H), 2.89 – 2.82 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 175.4, 164.7, 145.3, 140.2, 136.5, 129.9, 128.7, 128.6, 128.5, 126.5, 63.2, 39.1, 31.7, 30.5, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{S}$, 360.1270; found, 360.1267.



***N*-methyl-2-(1-methyl-1*H*-indol-3-yl)-*N*-(2-tosylacetyl)acetamide**

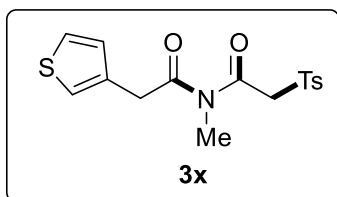
3w: Colourless oil (63 mg, 79% yield).

TLC: $R_f = 0.14$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.0$ Hz, 2H), 7.54 (d, $J = 8.0$ Hz, 1H), 7.34 – 7.22 (m, 4H), 7.17 – 7.11 (m, 1H), 7.04 (s, 1H), 4.82 (s, 2H), 4.03 (s, 2H), 3.77 (s, 3H), 3.25 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 165.0, 145.2, 137.0, 136.7, 129.9, 128.6, 128.0, 127.5, 122.2, 119.6, 118.7, 109.7, 105.4, 63.4, 34.5, 32.9, 32.2, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₂₁H₂₃N₂O₄S, 399.1379; found, 399.1376.



***N*-methyl-2-(thiophen-3-yl)-*N*-(2-tosylacetyl)acetamide**

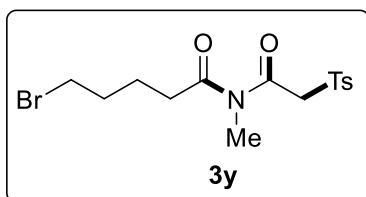
3v: Colourless oil (56 mg, 80% yield).

TLC: R_f = 0.21 (PE: EA = 3:1, v/v).

¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.15 – 7.11 (m, 1H), 6.99 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.2 Hz, 1H), 4.80 (s, 2H), 3.94 (s, 2H), 3.24 (s, 3H), 2.44 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 173.9, 164.8, 145.3, 136.5, 132.5, 129.9, 128.6, 128.4, 126.3, 123.5, 63.2, 38.8, 32.0, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₁₆H₁₈NO₄S₂, 352.0677; found, 352.0673.



5-bromo-*N*-methyl-*N*-(2-tosylacetyl)pentanamide

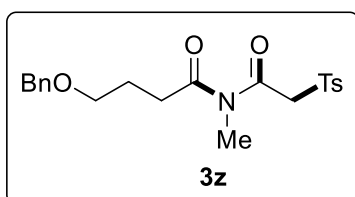
3y: Colourless oil (33 mg, 43% yield).

TLC: R_f = 0.10 (PE: EA = 3:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.81 (s, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 3.23 (s, 3H), 2.61 (t, *J* = 7.0 Hz, 2H), 2.46 (s, 3H), 1.96 – 1.90 (m, 2H), 1.85 – 1.78 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 175.7, 164.7, 145.3, 136.5, 129.9, 128.6, 63.3, 36.2, 33.3, 31.8, 23.0, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For C₁₅H₂₁BrNO₄S, 390.0375; found, 390.0377.



4-(benzyloxy)-*N*-methyl-*N*-(2-tosylacetyl)butanamide

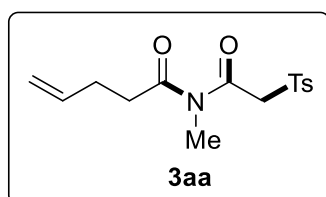
3z: Colourless oil (50 mg, 62% yield).

TLC: $R_f = 0.21$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.83 – 7.79 (m, 2H), 7.36 – 7.26 (m, 7H), 4.80 (s, 2H), 4.49 (s, 2H), 3.53 (t, $J = 6.0$ Hz, 2H), 3.20 (s, 3H), 2.66 (t, $J = 7.0$ Hz, 2H), 2.43 (s, 3H), 1.99 – 1.90 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 176.1, 164.7, 145.2, 138.3, 136.6, 129.8, 128.6, 128.5, 127.8, 73.0, 68.7, 63.3, 33.8, 31.7, 24.6, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{21}\text{H}_{26}\text{NO}_5\text{S}$, 404.1532; found, 404.1531.



***N*-methyl-*N*-(2-tosylacetyl)pent-4-enamide**

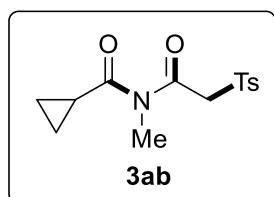
3aa: Colourless oil (37 mg, 60% yield).

TLC: $R_f = 0.36$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 5.88 – 5.78 (m, 1H), 5.11 – 5.06 (m, 1H), 5.05 – 5.02 (m, 1H), 4.81 (s, 2H), 3.23 (s, 3H), 2.68 – 2.62 (m, 2H), 2.45 (s, 3H), 2.42 – 2.36 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 175.5, 164.7, 145.3, 136.6, 136.4, 129.9, 128.6, 116.1, 63.3, 36.5, 31.7, 28.3, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{15}\text{H}_{20}\text{NO}_4\text{S}$, 310.1113; found, 310.1109.



***N*-methyl-*N*-(2-tosylacetyl)cyclopropanecarboxamide**

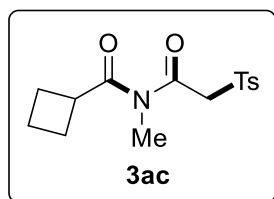
3ab: Colourless oil (39 mg, 66% yield).

TLC: $R_f = 0.21$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.80 (s, 2H), 3.36 (s, 3H), 2.45 (s, 3H), 1.98 – 1.88 (m, 1H), 1.17 – 1.10 (m, 2H), 1.05 – 0.98 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 177.5, 164.4, 145.2, 136.7, 129.9, 128.7, 62.9, 32.1, 21.8, 15.2, 10.9.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{14}\text{H}_{18}\text{NO}_4\text{S}$, 296.0957; found, 296.0966.



***N*-methyl-*N*-(2-tosylacetyl)cyclobutanecarboxamide**

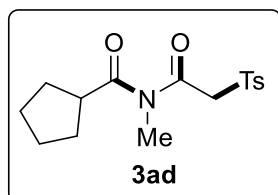
3ac: Colourless oil (31 mg, 50% yield).

TLC: $R_f = 0.28$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.88 (s, 2H), 3.47 – 3.37 (m, 1H), 3.11 (s, 3H), 2.45 (s, 3H), 2.40 – 2.29 (m, 2H), 2.28 – 2.18 (m, 2H), 2.07 – 1.84 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 177.7, 164.8, 145.2, 136.7, 129.8, 128.6, 63.3, 40.4, 31.2, 25.0, 21.8, 17.6.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{15}\text{H}_{20}\text{NO}_4\text{S}$, 310.1113; found, 310.1112.



***N*-methyl-*N*-(2-tosylacetyl)cyclopentanecarboxamide**

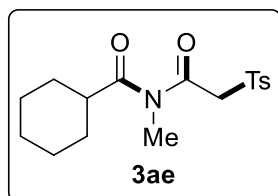
3ad: Colourless oil (44 mg, 68% yield).

TLC: $R_f = 0.36$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.84 (s, 2H), 3.25 (s, 3H), 3.16 – 3.01 (m, 1H), 2.45 (s, 3H), 1.93 – 1.79 (m, 4H), 1.77 – 1.70 (m, 2H), 1.67 – 1.58 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 179.9, 165.2, 145.2, 136.7, 129.9, 128.7, 63.4, 44.9, 32.0, 30.3, 26.2, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{16}\text{H}_{22}\text{NO}_4\text{S}$, 324.1270; found, 324.1268.



***N*-methyl-*N*-(2-tosylacetyl)cyclohexanecarboxamide**

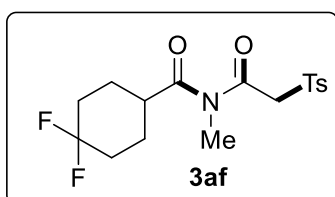
3ae: Colourless oil (38 mg, 57% yield).

TLC: $R_f = 0.43$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.84 – 7.80 (m, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.79 (s, 2H), 3.24 (s, 3H), 2.76 – 2.60 (m, 1H), 2.45 (s, 3H), 1.87 – 1.79 (m, 4H), 1.72 – 1.68 (m, 1H), 1.54 – 1.41 (m, 2H), 1.35 – 1.22 (m, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 179.7, 165.2, 145.2, 136.6, 129.8, 128.6, 63.2, 44.3, 31.9, 29.2, 25.7, 25.6, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{17}\text{H}_{24}\text{NO}_4\text{S}$, 338.1426; found, 338.1428.



4,4-difluoro-*N*-methyl-*N*-(2-tosylacetyl)cyclohexane-1-carboxamide

3af: White solid (67 mg, 90% yield), m. p. 94 – 95 °C.

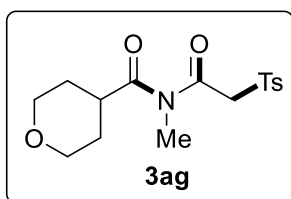
TLC: $R_f = 0.21$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 4.72 (s, 2H), 3.27 (s, 3H), 2.98 – 2.81 (m, 1H), 2.46 (s, 3H), 2.24 – 2.13 (m, 2H), 1.99 – 1.68 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 178.1, 164.9, 145.5, 136.4, 130.0, 128.5, 122.4 (t, $J = 242.4$ Hz), 63.1, 42.1, 32.8 (t, $J = 25.3$ Hz), 32.2, 25.6, 25.5, 21.8.

^{19}F NMR (376 MHz, CDCl_3) δ -93.29 (d, $J = 237.6$ Hz), -101.45 (d, $J = 237.6$ Hz).

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{17}\text{H}_{22}\text{F}_2\text{NO}_4\text{S}$, 374.1238; found, 374.1233.



N-methyl-*N*-(2-tosylacetyl)tetrahydro-2*H*-pyran-4-carboxamide

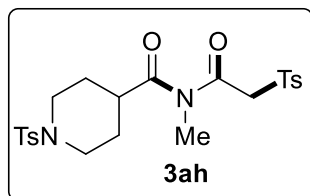
3ag: White solid (62 mg, 92% yield), m. p. 107 – 109 °C.

TLC: $R_f = 0.10$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 4.75 (s, 2H), 4.05 – 3.99 (m, 2H), 3.50 – 3.39 (m, 2H), 3.27 (s, 3H), 3.09 – 2.99 (m, 1H), 2.46 (s, 3H), 1.91 – 1.80 (m, 2H), 1.77 – 1.70 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 178.0, 164.9, 145.4, 136.5, 129.9, 128.5, 67.0, 63.1, 41.7, 32.0, 28.8, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{16}\text{H}_{22}\text{NO}_5\text{S}$, 340.1219; found, 340.1227.



***N*-methyl-1-tosyl-*N*-(2-tosylacetyl)piperidine-4-carboxamide**

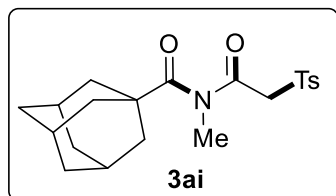
3ah: White solid (87 mg, 88% yield), m. p. 163 – 164 °C.

TLC: R_f = 0.15 (PE: EA = 1:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.38 – 7.31 (m, 4H), 4.64 (s, 2H), 3.84 – 3.73 (m, 2H), 3.20 (s, 3H), 2.83 – 2.70 (m, 1H), 2.44 (s, 6H), 2.41 – 2.30 (m, 2H), 1.93 – 1.77 (m, 4H).

^{13}C NMR (100 MHz, CDCl_3) δ 177.7, 164.8, 145.6, 143.8, 136.3, 132.9, 130.0, 129.8, 128.4, 127.8, 63.0, 45.5, 41.9, 32.2, 27.8, 21.8, 21.6.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{23}\text{H}_{29}\text{N}_2\text{O}_6\text{S}_2$, 493.1467; found, 493.1463.



***N*-methyl-*N*-(2-tosylacetyl)adamantane-1-carboxamide**

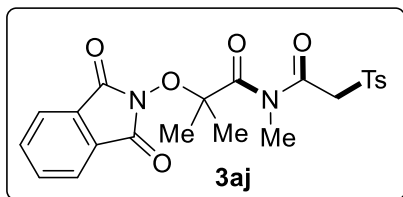
3ai: White solid (43 mg, 56% yield), m. p. 90 – 91 °C.

TLC: R_f = 0.50 (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.47 (s, 2H), 3.21 (s, 3H), 2.45 (s, 3H), 2.12 – 2.02 (m, 9H), 1.81 – 1.70 (m, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 185.5, 164.5, 145.3, 136.3, 129.9, 128.6, 61.4, 45.3, 39.0, 36.4, 33.2, 28.2, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{21}\text{H}_{28}\text{NO}_4\text{S}$, 390.1739; found, 390.1739.



2-((1,3-dioxoisindolin-2-yl)oxy)-N,2-dimethyl-N-(2-tosylacetyl)propanamide

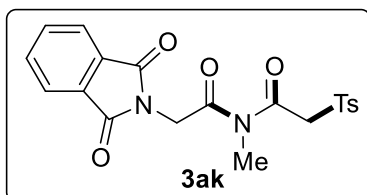
3aj: White solid (82 mg, 90% yield), m. p. 137 – 138 °C.

TLC: $R_f = 0.21$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.87 – 7.77 (m, 6H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.79 (s, 2H), 3.58 (s, 3H), 2.45 (s, 3H), 1.76 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 175.3, 165.6, 164.5, 145.3, 136.4, 135.1, 129.9, 128.8, 128.6, 124.0, 89.7, 62.6, 33.6, 23.9, 21.8.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$) $^+$ calcd. For $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_7\text{S}$, 459.1226; found, 459.1222.



2-(1,3-dioxoisindolin-2-yl)-N-methyl-N-(2-tosylacetyl)acetamide

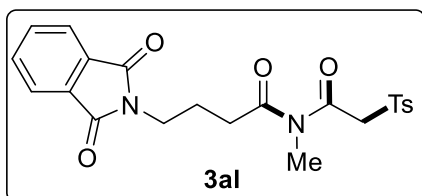
3ak: White solid (79 mg, 96% yield), m. p. 177 – 178 °C.

TLC: $R_f = 0.10$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.73 (m, 6H), 7.39 (d, $J = 8.0$ Hz, 2H), 4.74 (s, 2H), 4.60 (s, 2H), 3.35 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 167.7, 165.0, 145.8, 135.8, 134.4, 132.1, 130.1, 128.7, 123.7, 62.8, 43.3, 31.9, 21.8.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$) $^+$ calcd. For $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_6\text{S}$, 415.0964; found, 415.0962.



4-(1,3-dioxoisindolin-2-yl)-N-methyl-N-(2-tosylacetyl)butanamide

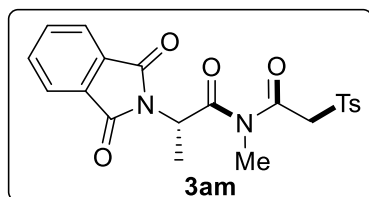
3al: White solid (51 mg, 58% yield), m. p. 150 – 151 °C.

TLC: $R_f = 0.10$ (PE: EA = 3:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.87 – 7.80 (m, 4H), 7.76 – 7.71 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.77 (s, 2H), 3.77 (t, *J* = 6.5 Hz, 2H), 3.20 (s, 3H), 2.62 (t, *J* = 6.5 Hz, 2H), 2.45 (s, 3H), 2.08 – 1.98 (m, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 175.2, 168.6, 164.7, 145.2, 136.7, 134.2, 132.1, 129.9, 128.7, 123.4, 63.2, 37.0, 34.4, 31.7, 23.6, 21.8.

HRMS (ESI-TOF) *m/z*: (M+H)⁺ calcd. For C₂₂H₂₃N₂O₆S, 443.1277; found, 443.1272.



(S)-2-(1,3-dioxoisindolin-2-yl)-N-methyl-N-(2-tosylacetyl)propanamide

3am: Colourless oil (62 mg, 73% yield). Specific optical rotation: [α]²⁰_D = -97.22 (*c* 0.95, CH₃Cl).

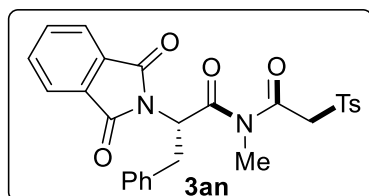
HPLC: The *ee* value was determined by HPLC analysis on a CHIRALPAK AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm) with *t_r* = 22.7 min (minor), 27.5 min (major): > 99% *ee*.

TLC: *R_f* = 0.10 (PE: EA = 3:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.89 – 7.85 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.79 – 7.75 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.32 (q, *J* = 7.0 Hz, 1H), 4.76 (d, *J* = 15.0 Hz, 1H), 4.51 (d, *J* = 15.0 Hz, 1H), 3.13 (s, 3H), 2.44 (s, 3H), 1.62 (d, *J* = 7.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 173.7, 167.3, 165.0, 145.2, 136.8, 134.7, 131.6, 129.8, 128.7, 123.9, 62.2, 49.6, 32.1, 21.8, 15.4.

HRMS (ESI-TOF) *m/z*: (M+H)⁺ calcd. For C₂₁H₂₁N₂O₆S, 429.1120; found, 429.1122.



(S)-2-(1,3-dioxoisindolin-2-yl)-N-methyl-3-phenyl-N-(2-tosylacetyl)propanamide

3an: Colourless oil (61 mg, 61% yield). Specific optical rotation: [α]²⁰_D = -162.32 (*c* 0.75, CH₃Cl).

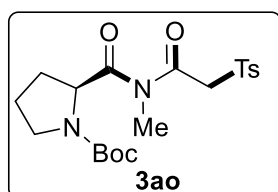
HPLC: The *ee* value was determined by HPLC analysis on a CHIRALPAK AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm) with *t_r* = 20.6 min (major), 30.5 min (minor): > 99% *ee*.

TLC: $R_f = 0.10$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.87 – 7.81 (m, 2H), 7.80 – 7.75 (m, 2H), 7.73 – 7.69 (m, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.20 – 7.12 (m, 5H), 5.54 (dd, $J_1 = 9.5$ Hz, $J_2 = 5.5$ Hz, 1H), 4.76 (d, $J = 15.0$ Hz, 1H), 4.52 (d, $J = 15.0$ Hz, 1H), 3.49 – 3.37 (m, 2H), 3.15 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 172.9, 167.4, 165.0, 145.3, 136.5, 136.3, 134.6, 131.3, 129.9, 129.2, 128.8, 128.7, 127.2, 123.8, 62.3, 55.8, 34.8, 32.3, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}_6\text{S}$, 505.1433; found, 505.1435.



tert-butyl (S)-2-(methyl(2-tosylacetyl)carbamoyl)pyrrolidine-1-carboxylate

3ao: Colourless oil (80 mg, 94% yield). Specific optical rotation: $[\alpha]^{20}_D = -37.99$ (c 0.8, CH_3Cl).

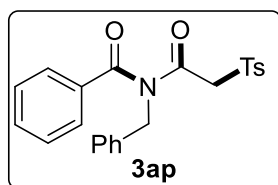
HPLC: The *ee* value was determined by HPLC analysis on a CHIRALPAK AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm) with $t_r = 6.0$ min (minor), 9.7 min (major): > 99% *ee*.

TLC: $R_f = 0.14$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3 , 2 rotamers see, ratio = 6:4) δ 7.82 (d, $J = 8.4$ Hz, 2H), 7.43 – 7.31 (m, 2H), 5.16 (d, $J = 14.4$ Hz, 0.6H), 5.03 (d, $J = 14.4$ Hz, 0.4H), 4.83 – 4.71 (m, 1H), 4.51 (d, $J = 14.4$ Hz, 0.4H), 4.40 (d, $J = 14.4$ Hz, 0.6H), 3.66 – 3.55 (m, 1H), 3.52 – 3.39 (m, 1H), 3.33 and 3.30 (two single peaks, 3H), 2.46 and 2.45 (two single peaks, 3H), 2.35 – 2.20 (m, 1H), 2.06 – 1.87 (m, 3H), 1.45 and 1.38 (two single peaks, 9H)

^{13}C NMR (100 MHz, CDCl_3 , 2 rotamers see) δ 176.2, 176.1, 164.7, 154.5, 153.4, 145.4, 145.2, 136.4 (136.43), 136.4 (136.41), 129.9, 129.8, 128.6, 128.5, 80.1 (80.13), 80.1 (80.10), 63.0 (63.03), 63.0 (62.98), 60.0, 59.9, 46.9, 46.7, 31.7, 31.6, 30.3, 29.4, 28.5, 28.3, 24.1, 23.2, 21.7.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{20}\text{H}_{29}\text{N}_2\text{O}_6\text{S}$, 425.1746; found, 425.1745.



N-benzyl-N-(2-tosylacetyl)benzamide

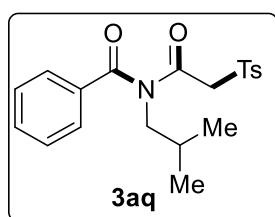
3ap: White solid (71 mg, 87% yield), m. p. 114 – 115 °C.

TLC: $R_f = 0.43$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, $J = 8.5$ Hz, 2H), 7.62 – 7.53 (m, 3H), 7.46 – 7.41 (m, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 7.25 – 7.19 (m, 3H), 7.10 – 7.06 (m, 2H), 4.94 (s, 2H), 4.59 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 164.6, 145.4, 136.2, 136.1, 134.3, 133.0, 130.0, 129.0, 128.9, 128.6, 128.5, 127.9, 127.8, 62.4, 50.5, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{23}\text{H}_{22}\text{NO}_4\text{S}$, 408.1270; found, 408.1270.



***N*-isobutyl-*N*-(2-tosylacetyl)benzamide**

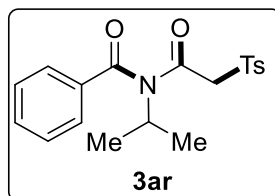
3aq: White solid (58 mg, 78% yield), m. p. 123 – 124 °C.

TLC: $R_f = 0.57$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.75 (m, 2H), 7.71 – 7.66 (m, 2H), 7.62 – 7.57 (m, 1H), 7.52 – 7.46 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.60 (s, 2H), 3.57 (d, $J = 6.8$ Hz, 2H), 2.45 (s, 3H), 2.01 – 1.83 (m, 1H), 0.76 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 175.4, 164.4, 145.4, 136.3, 134.2, 133.1, 130.0, 129.3, 129.0, 128.5, 62.0, 55.0, 28.5, 21.8, 20.1.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{20}\text{H}_{24}\text{NO}_4\text{S}$, 374.1426; found, 374.1442.



***N*-isopropyl-*N*-(2-tosylacetyl)benzamide**

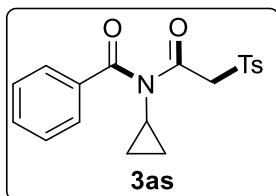
3ar: White solid (60 mg, 83% yield), m. p. 113 – 115 °C.

TLC: $R_f = 0.50$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.79 – 7.72 (m, 4H), 7.64 – 7.58 (m, 1H), 7.53 – 7.47 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.36 – 4.22 (m, 3H), 2.45 (s, 3H), 1.38 (d, $J = 6.8$ Hz, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 175.3, 164.3, 145.4, 136.1, 135.0, 133.4, 129.9, 129.2, 129.1, 128.5, 63.0, 52.6, 21.8, 20.0.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{19}\text{H}_{22}\text{NO}_4\text{S}$, 360.1270; found, 360.1279.



N-cyclopropyl-*N*-(2-tosylacetyl)benzamide

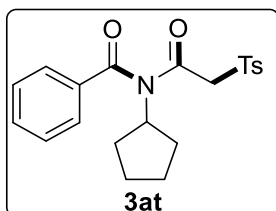
3as: White solid (56 mg, 78% yield), m. p. 91 – 92 °C.

TLC: R_f = 0.28 (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.84 – 7.80 (m, 2H), 7.79 – 7.75 (m, 2H), 7.61 – 7.56 (m, 1H), 7.50 – 7.45 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.73 (s, 2H), 2.88 – 2.79 (m, 1H), 2.43 (s, 3H), 0.87 – 0.76 (m, 2H), 0.55 – 0.47 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.3, 164.6, 145.4, 136.4, 134.7, 133.1, 130.0, 129.25, 128.7, 128.6, 61.5, 30.3, 21.8, 10.1.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{19}\text{H}_{20}\text{NO}_4\text{S}$, 358.1113; found, 358.1124.



N-cyclopentyl-*N*-(2-tosylacetyl)benzamide

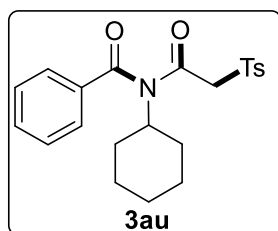
3at: White solid (75 mg, 97% yield), m. p. 99 – 100 °C.

TLC: R_f = 0.57 (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.82 – 7.73 (m, 4H), 7.64 – 7.59 (m, 1H), 7.55 – 7.47 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.45 (s, 2H), 4.24 – 4.14 (m, 1H), 2.44 (s, 3H), 2.10 – 1.97 (m, 2H), 1.90 – 1.74 (m, 4H), 1.49 – 1.38 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 175.6, 163.6, 145.3, 136.3, 134.5, 133.4, 129.9, 129.4, 129.0, 128.5, 62.6, 61.4, 29.2, 25.3, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{21}\text{H}_{24}\text{NO}_4\text{S}$, 386.1426; found, 386.1440.



***N*-cyclohexyl-*N*-(2-tosylacetyl)benzamide**

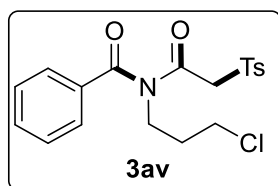
3au: White solid (74 mg, 93% yield), m. p. 99 – 100 °C.

TLC: $R_f = 0.58$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.79 – 7.73 (m, 4H), 7.64 – 7.59 (m, 1H), 7.53 – 7.47 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.23 (s, 2H), 4.01 – 3.87 (m, 1H), 2.44 (s, 3H), 2.07 – 1.93 (m, 2H), 1.80 – 1.71 (m, 4H), 1.58 – 1.49 (m, 1H), 1.21 – 1.06 (m, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 175.1, 164.0, 145.3, 136.0, 135.1, 133.6, 129.9, 129.3, 129.2, 128.6, 63.0, 60.4, 29.8, 26.3, 25.1, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{22}\text{H}_{26}\text{NO}_4\text{S}$, 400.1583; found, 400.1590.



***N*-(3-chloropropyl)-*N*-(2-tosylacetyl)benzamide**

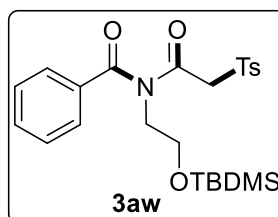
3av: White solid (63 mg, 80% yield), m. p. 119 – 120 °C.

TLC: $R_f = 0.36$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.80 – 7.77 (m, 2H), 7.70 – 7.66 (m, 2H), 7.63 – 7.59 (m, 1H), 7.53 – 7.48 (m, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.58 (s, $J = 7.0$ Hz, 2H), 3.85 (t, 2H), 3.45 (t, $J = 6.0$ Hz, 2H), 2.45 (s, 3H), 2.08 – 1.99 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 164.7, 145.5, 136.2, 133.8, 133.2, 130.0, 129.1, 129.0, 128.5, 62.2, 45.5, 42.0, 31.2, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{19}\text{H}_{21}\text{ClNO}_4\text{S}$, 394.0880; found, 394.0873.



***N*-2-((*tert*-butyldimethylsilyloxy)ethyl)-*N*-(2-tosylacetyl)benzamide**

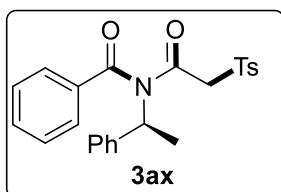
3aw: White solid (60 mg, 63% yield), m. p. 83 – 84 °C.

TLC: $R_f = 0.64$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.71 – 7.66 (m, 2H), 7.59 – 7.53 (m, 1H), 7.49 – 7.44 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.65 (s, 2H), 3.90 (t, $J = 5.2$ Hz, 2H), 3.70 (t, $J = 5.2$ Hz, 2H), 2.44 (s, 3H), 0.79 (s, 9H), -0.05 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3) δ 174.8, 164.7, 145.4, 136.3, 134.2, 132.7, 130.0, 129.4, 128.8, 128.5, 61.9, 61.3, 50.2, 25.9, 21.8, 18.4, -5.5.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$)⁺ calcd. For $\text{C}_{24}\text{H}_{34}\text{NO}_5\text{SSi}$, 476.1927; found, 476.1930.



***(S)*-*N*-(1-phenylethyl)-*N*-(2-tosylacetyl)benzamide**

3ax: White solid (67 mg, 80% yield), m. p. 141 – 142 °C, Specific optical rotation: $[\alpha]^{20}_D = -14.44$ (c 0.5, CH_3Cl).

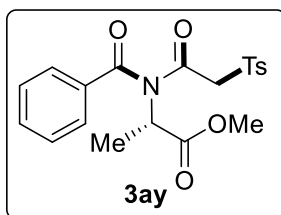
HPLC: The *ee* value was determined by HPLC analysis on a CHIRALPAK AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm) with $t_r = 12.4$ min (major), 15.0 min (minor): > 95% *ee*.

TLC: $R_f = 0.43$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.71 – 7.67 (m, 2H), 7.65 – 7.62 (m, 2H), 7.60 – 7.56 (m, 1H), 7.49 – 7.43 (m, 2H), 7.35 – 7.67 (m, 2H), 7.30 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 5.54 (q, $J = 7.5$ Hz, 1H), 4.35 (d, $J = 14.0$ Hz, 1H), 4.13 (d, $J = 14.0$ Hz, 1H), 2.43 (s, 3H), 1.78 (d, $J = 7.5$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 175.0, 164.0, 145.4, 139.8, 135.9, 135.4, 133.4, 129.9, 129.2, 129.1, 128.6, 128.4, 127.6, 127.5, 63.2, 57.4, 21.8, 17.4.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$)⁺ calcd. For $\text{C}_{24}\text{H}_{24}\text{NO}_4\text{S}$, 422.1426; found, 422.1422.



methyl *N*-benzoyl-*N*-(2-tosylacetyl)-*L*-alaninate

3ay: Colourless oil (44 mg, 55% yield). Specific optical rotation: $[\alpha]^{20}_D = -19.08$ (c 0.5, CH_3Cl).

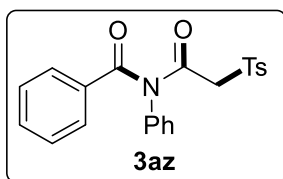
HPLC: The *ee* value was determined by HPLC analysis on a CHIRALPAK AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm) with $t_r = 11.2$ min (major), 11.9 min (minor): 99% *ee*.

TLC: $R_f = 0.28$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.81 – 7.75 (m, 4H), 7.65 – 7.60 (m, 1H), 7.55 – 7.49 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.67 (q, $J = 6.8$ Hz, 1H), 4.50 (d, $J = 14.0$ Hz, 1H), 4.30 (d, $J = 14.0$ Hz, 1H), 3.71 (s, 3H), 2.44 (s, 3H), 1.56 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 173.9, 170.4, 164.3, 145.6, 136.0, 134.3, 133.5, 130.0, 129.4, 129.0, 128.6, 62.6, 56.5, 52.8, 21.8, 14.7.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{20}\text{H}_{22}\text{NO}_6\text{S}$, 404.1168; found, 404.1174.



***N*-phenyl-*N*-(2-tosylacetyl)benzamide**

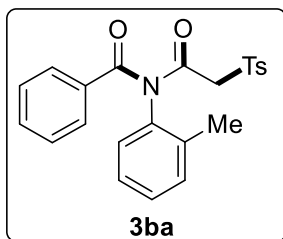
3az: White solid (56 mg, 72% yield), m. p. 127 – 128 °C.

TLC: $R_f = 0.36$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.87 – 7.83 (m, 2H), 7.67 – 7.63 (m, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7.22 (m, 7H), 7.18 – 7.12 (m, 2H), 4.75 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 173.1, 165.3, 145.5, 138.6, 136.4, 133.7, 132.6, 130.0, 129.9, 129.6, 128.6, 128.5, 128.3, 62.2, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{22}\text{H}_{20}\text{NO}_4\text{S}$, 394.1113; found, 394.1110.



***N*-(*o*-tolyl)-*N*-(2-tosylacetyl)benzamide**

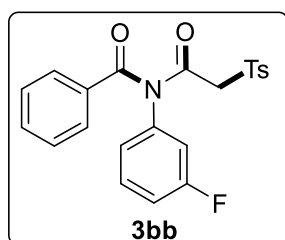
3ba: White solid (55 mg, 68% yield), m. p. 140 – 141 °C.

TLC: $R_f = 0.43$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 7.6$ Hz, 2H), 7.45 – 7.39 (m, 1H), 7.35 – 7.28 (m, 4H), 7.23 – 7.10 (m, 4H), 4.74 (d, $J = 14.4$ Hz, 1H), 4.63 (d, $J = 14.4$ Hz, 1H), 2.42 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 173.0, 165.0, 145.4, 137.4, 136.4, 136.3, 134.0, 132.5, 131.7, 130.0, 129.4, 129.3, 129.2, 128.7, 128.3, 127.3, 62.2, 21.8, 18.2.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{23}\text{H}_{22}\text{NO}_4\text{S}$, 408.1270; found, 408.1270.



***N*-(3-fluorophenyl)-*N*-(2-tosylacetyl)benzamide**

3bb: White solid (37 mg, 45% yield), m. p. 143 – 144 °C.

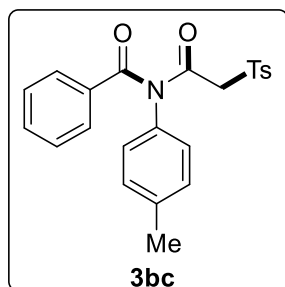
TLC: $R_f = 0.43$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, $J = 8.5$ Hz, 2H), 7.68 – 7.62 (m, 2H), 7.46 – 7.41 (m, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.34 – 7.23 (m, 3H), 7.00 – 6.87 (m, 3H), 4.76 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 172.8, 165.3, 162.9 (d, $J = 248.9$ Hz), 145.7, 139.9 (d, $J = 9.8$ Hz), 136.3, 133.3, 132.9, 130.7 (d, $J = 9.0$ Hz), 130.1, 129.9, 128.6, 128.5, 124.4 (d, $J = 3.3$ Hz), 116.0 (d, $J = 23.3$ Hz), 115.8 (d, $J = 21.0$ Hz), 62.3, 21.8.

^{19}F NMR (376 MHz, CDCl_3) δ -110.95.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{22}\text{H}_{19}\text{FNO}_4\text{S}$, 412.1019; found, 412.1014.



***N*-(*p*-tolyl)-*N*-(2-tosylacetyl)benzamide**

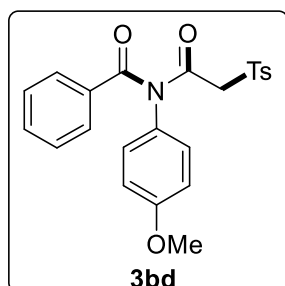
3bc: White solid (57 mg, 70% yield), m. p. 146 – 147 °C.

TLC: $R_f = 0.40$ (PE: EA = 3:1, v/v).

¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.36 – 7.24 (m, 4H), 7.14 – 7.08 (m, 2H), 7.05 – 7.00 (m, 2H), 4.72 (s, 2H), 2.41 (s, 3H), 2.28 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 173.1, 165.4, 145.4, 138.7, 136.4, 135.8, 133.8, 132.5, 130.3, 130.0, 129.9, 128.6, 128.3, 128.2, 62.2, 21.8, 21.2.

HRMS (ESI-TOF) *m/z*: (M+H)⁺ calcd. For C₂₃H₂₂NO₄S, 408.1270; found, 408.1278.



N-(4-methoxyphenyl)-*N*-(2-tosylacetyl)benzamide

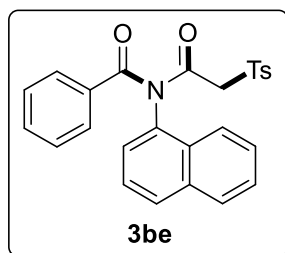
3bd: Colourless gum (68 mg, 80% yield).

TLC: R_f = 0.25 (PE: EA = 3:1, v/v).

¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.76 – 7.66 (m, 2H), 7.48 – 7.41 (m, 1H), 7.39 – 7.28 (m, 4H), 7.14 – 7.08 (m, 2H), 6.89 – 6.82 (m, 2H), 4.75 (s, 2H), 3.78 (s, 3H), 2.46 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 173.1, 165.5, 159.4, 145.5, 136.4, 133.8, 132.5, 131.1, 130.0, 129.8, 129.6, 128.6, 128.4, 114.9, 62.1, 55.5, 21.8.

HRMS (ESI-TOF) *m/z*: (M+H)⁺ calcd. For C₂₃H₂₂NO₅S, 424.1219; found, 422.1233.



N-(naphthalen-1-yl)-*N*-(2-tosylacetyl)benzamide

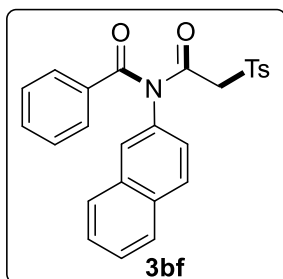
3be: White solid (47 mg, 53% yield), m. p. 179 – 180 °C.

TLC: R_f = 0.36 (PE: EA = 3:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.88 – 7.79 (m, 4H), 7.73 – 7.68 (m, 2H), 7.65 – 7.59 (m, 1H), 7.56 – 7.51 (m, 1H), 7.41 – 7.29 (m, 5H), 7.25 – 7.19 (m, 2H), 4.79 (d, *J* = 14.0 Hz, 1H), 4.60 (d, *J* = 14.0 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 173.6, 165.3, 145.5, 136.3, 134.8, 134.6, 134.0, 132.7, 130.5, 130.1, 130.0, 129.0, 128.8, 128.7, 128.3, 128.1, 127.5, 126.9, 125.5, 122.5, 62.3, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{26}\text{H}_{22}\text{NO}_4\text{S}$, 444.1270; found, 444.1272.



***N*-(naphthalen-2-yl)-*N*-(2-tosylacetyl)benzamide**

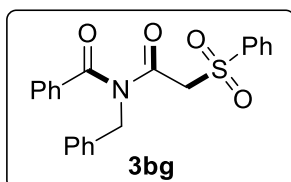
3bf: White solid (59 mg, 67% yield), m. p. 137 – 138 °C.

TLC: R_f = 0.36 (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.5 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.73 – 7.68 (m, 3H), 7.52 (d, J = 1.5 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.39 – 7.32 (m, 4H), 7.28 – 7.22 (m, 2H), 4.79 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 173.2, 165.5, 145.6, 136.4, 136.0, 133.6, 133.4, 132.7, 132.7, 130.1, 130.0, 129.8, 128.6, 128.4, 128.1, 127.9, 127.4, 127.2, 126.9, 125.9, 62.3, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{26}\text{H}_{22}\text{NO}_4\text{S}$, 444.1270; found, 444.1272.



***N*-benzyl-*N*-(2-(phenylsulfonyl)acetyl)benzamide**

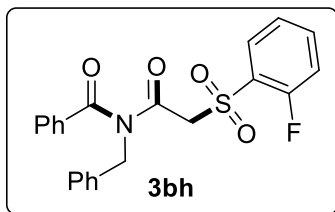
3bg: White solid (68 mg, 87% yield), m. p. 113 – 114 °C.

TLC: R_f = 0.35 (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.91 – 7.84 (m, 2H), 7.69 – 7.63 (m, 1H), 7.62 – 7.51 (m, 5H), 7.49 – 7.42 (m, 2H), 7.26 – 7.20 (m, 3H), 7.11 – 7.04 (m, 2H), 4.94 (s, 2H), 4.62 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 164.5, 139.1, 136.2, 134.3 (134.32), 134.3 (134.29), 133.1, 129.4, 129.0, 128.9, 128.7, 128.5, 127.9, 127.8, 62.3, 50.6.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{22}\text{H}_{20}\text{NO}_4\text{S}$, 394.1113; found, 394.1115.



***N*-benzyl-*N*-(2-((2-fluorophenyl)sulfonyl)acetyl)benzamide**

3bh: Colourless oil (28 mg, 34% yield).

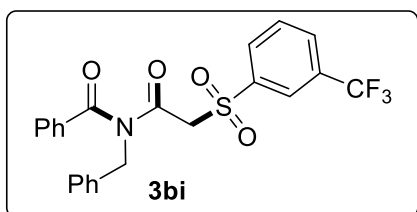
TLC: $R_f = 0.36$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.90 – 7.85 (m, 1H), 7.69 – 7.55 (m, 4H), 7.48 – 7.43 (m, 2H), 7.34 – 7.29 (m, 1H), 7.27 – 7.19 (m, 4H), 7.08 – 7.02 (m, 2H), 4.91 (s, 2H), 4.78 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 164.5, 159.7 (d, $J = 256.1$ Hz), 136.8 (d, $J = 8.6$ Hz), 136.2, 134.2, 133.2, 130.7, 129.1, 129.0, 128.7, 127.9, 127.8, 127.0 (d, $J = 14.2$ Hz), 124.9 (d, $J = 3.7$ Hz), 117.3 (d, $J = 21.1$ Hz), 61.7 (d, $J = 2.6$ Hz), 50.5.

^{19}F NMR (376 MHz, CDCl_3) δ -109.44.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{22}\text{H}_{19}\text{FNO}_4\text{S}$, 412.1019; found, 412.1030.



***N*-benzyl-*N*-(2-((3-(trifluoromethyl)phenyl)sulfonyl)acetyl)benzamide**

3bi: White solid (60 mg, 65% yield), m. p. 80 – 81 °C.

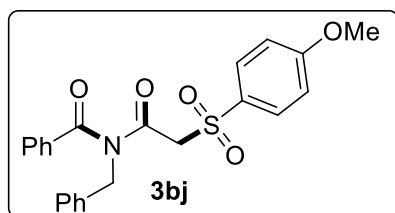
TLC: $R_f = 0.43$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.19 (s, 1H), 8.06 (d, $J = 9.0$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.72 – 7.66 (m, 1H), 7.63 – 7.57 (m, 3H), 7.49 – 7.43 (m, 2H), 7.26 – 7.21 (m, 3H), 7.09 – 7.02 (m, 2H), 4.94 (s, 2H), 4.66 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 164.3, 140.3, 136.0, 134.0, 133.3, 132.2, 132.0 (q, $J = 33.7$ Hz), 131.0 (q, $J = 3.4$ Hz), 130.2, 129.1, 128.9, 128.8, 127.9, 127.8, 125.8 (q, $J = 3.8$ Hz), 123.2 (q, $J = 273.0$ Hz), 62.3, 50.6.

^{19}F NMR (376 MHz, CDCl_3) δ -110.95.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{23}\text{H}_{19}\text{F}_3\text{NO}_4\text{S}$, 462.0987; found, 462.0981.



***N*-benzyl-*N*-(2-((4-methoxyphenyl)sulfonyl)acetyl)benzamide**

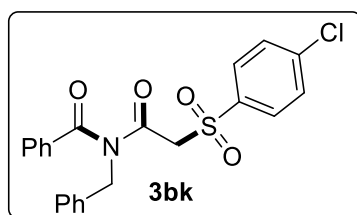
3bj: White solid (73 mg, 86% yield), m. p. 78 – 79 °C.

TLC: $R_f = 0.27$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.81 – 7.76 (m, 2H), 7.62 – 7.54 (m, 3H), 7.48 – 7.40 (m, 2H), 7.27 – 7.19 (m, 3H), 7.13 – 7.05 (m, 2H), 7.01 – 6.94 (m, 2H), 4.94 (s, 2H), 4.57 (s, 2H), 3.86 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 164.7, 164.2, 136.3, 134.3, 133.0, 130.8, 130.4, 129.0, 128.9, 128.6, 127.9, 127.7, 114.5, 62.6, 55.8, 50.5.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{23}\text{H}_{22}\text{NO}_5\text{S}$, 424.1219; found, 424.1215.



***N*-benzyl-*N*-(2-((4-chlorophenyl)sulfonyl)acetyl)benzamide**

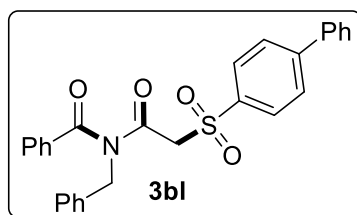
3bk: White solid (70 mg, 82% yield), m. p. 113 – 114 °C.

TLC: $R_f = 0.50$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.82 – 7.76 (m, 2H), 7.62 – 7.55 (m, 3H), 7.50 – 7.43 (m, 4H), 7.27 – 7.21 (m, 3H), 7.08 – 7.04 (m, 2H), 4.93 (s, 2H), 4.61 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 164.4, 141.1, 137.4, 136.1, 134.1, 133.2, 130.1, 129.6, 129.1, 128.9, 128.7, 127.9, 62.3, 50.6.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{22}\text{H}_{19}\text{ClNO}_4\text{S}$, 428.0723; found, 428.0721.



***N*-(2-([1,1'-biphenyl]-4-ylsulfonyl)acetyl)-*N*-benzylbenzamide**

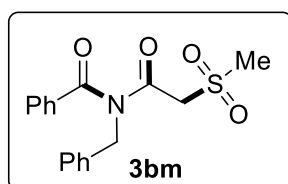
3bl: White solid (63 mg, 67% yield), m. p. 93 – 94 °C.

TLC: $R_f = 0.28$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.96 – 7.89 (m, 2H), 7.78 – 7.69 (m, 2H), 7.63 – 7.54 (m, 5H), 7.51 – 7.40 (m, 5H), 7.26 – 7.19 (m, 3H), 7.12 – 7.05 (m, 2H), 4.96 (s, 2H), 4.66 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 164.6, 147.2, 139.1, 137.6, 136.2, 134.3, 133.1, 129.2, 129.1, 129.0, 128.9 (128.92), 128.9 (128.87), 128.7, 128.0, 127.9, 127.8, 127.5, 62.4, 50.6.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{28}\text{H}_{24}\text{NO}_4\text{S}$, 470.1426; found, 470.1424.



N-benzyl-*N*-(2-(methylsulfonyl)acetyl)benzamide

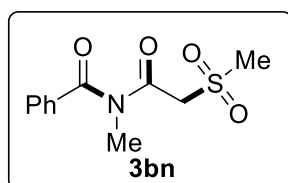
3bm: White solid (47 mg, 71% yield), m. p. 99 – 100 °C.

TLC: $R_f = 0.21$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.65 – 7.56 (m, 3H), 7.49 – 7.43 (m, 2H), 7.30 – 7.22 (m, 3H), 7.15 – 7.10 (m, 2H), 4.99 (s, 2H), 4.42 (d, $J = 0.5$ Hz, 2H), 3.11 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.5, 165.7, 136.1, 133.8, 133.4, 129.1, 129.0, 128.8, 127.9, 127.7, 60.8, 50.6, 42.3.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{17}\text{H}_{18}\text{NO}_4\text{S}$, 332.0957; found, 332.0958.



N-benzyl-*N*-(2-(methylsulfonyl)acetyl)benzamide

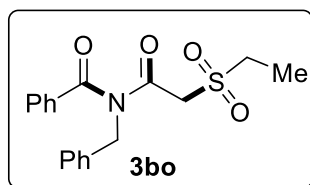
3bn: Colourless oil (36 mg, 70% yield).

TLC: $R_f = 0.15$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.69 – 7.66 (m, 2H), 7.61 – 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 4.62 (s, 2H), 3.22 (s, 3H), 3.17 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.0, 165.6, 133.4, 133.0, 128.0 (128.81), 128.8 (128.80), 60.2, 42.2, 35.2.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{11}\text{H}_{14}\text{NO}_4\text{S}$, 256.0644; found, 256.0646.



***N*-benzyl-*N*-(2-(ethylsulfonyl)acetyl)benzamide**

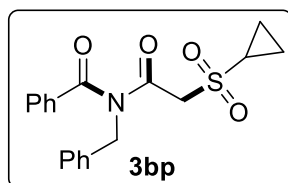
3bo: White solid (50 mg, 72% yield), m. p. 85 – 86 °C.

TLC: $R_f = 0.30$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.66 – 7.62 (m, 2H), 7.60 – 7.55 (m, 1H), 7.49 – 7.43 (m, 2H), 7.30 – 7.22 (m, 3H), 7.15 – 7.11 (m, 2H), 4.99 (s, 2H), 4.39 (s, 2H), 3.24 (q, $J = 7.5$ Hz, 2H), 1.40 (t, $J = 7.5$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 165.6, 136.2, 134.0, 133.3, 129.1, 129.0, 128.8, 127.9, 127.7, 58.0, 50.7, 48.7, 6.8.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$) $^+$ calcd. For $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{S}$, 346.1113; found, 346.1109.



***N*-benzyl-*N*-(2-(cyclopropylsulfonyl)acetyl)benzamide**

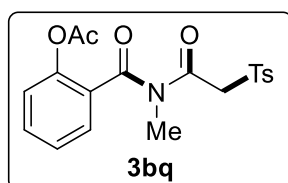
3bp: White solid (56 mg, 78% yield), m. p. 107 – 108 °C.

TLC: $R_f = 0.28$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.66 – 7.61 (m, 2H), 7.60 – 7.55 (m, 1H), 7.49 – 7.42 (m, 2H), 7.30 – 7.21 (m, 3H), 7.18 – 7.10 (m, 2H), 5.00 (s, 2H), 4.47 (s, 2H), 2.82 – 2.70 (m, 1H), 1.31 – 1.20 (m, 2H), 1.11 – 1.00 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 165.4, 136.3, 134.2, 133.2, 129.1, 129.0, 128.8, 127.9, 127.8, 60.1, 50.6, 31.2, 5.6.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$) $^+$ calcd. For $\text{C}_{19}\text{H}_{20}\text{NO}_4\text{S}$, 358.1113; found, 358.1117.



2-(methyl(2-tosylacetyl)carbamoyl)phenyl acetate

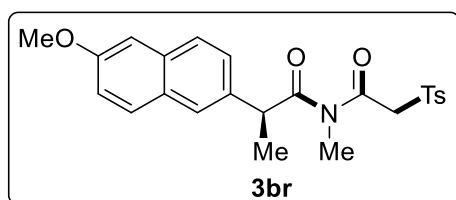
3bq: White solid (68 mg, 87% yield), m. p. 108 – 110 °C.

TLC: $R_f = 0.20$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.83 (m, 2H), 7.62 – 7.53 (m, 2H), 7.42 – 7.34 (m, 3H), 7.23 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 4.85 (s, 2H), 3.16 (s, 3H), 2.47 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 169.5, 164.8, 148.1, 145.3, 136.6, 133.0, 130.0, 128.9, 128.6, 127.7, 126.3, 123.3, 62.4, 34.5, 21.8, 21.1.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$)⁺ calcd. For $\text{C}_{19}\text{H}_{20}\text{NO}_6\text{S}$, 390.1011; found, 390.1008.



(S)-2-(6-methoxynaphthalen-2-yl)-N-methyl-N-(2-tosylacetyl)propanamide

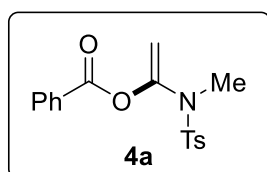
3br: Colourless oil (42 mg, 48% yield).

TLC: $R_f = 0.21$ (PE: EA = 3:1, v/v).

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.4$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.60 (s, 1H), 7.33 – 7.27 (m, 3H), 7.19 – 7.10 (m, 2H), 5.01 (d, $J = 14.8$ Hz, 1H), 4.76 (d, $J = 14.8$ Hz, 1H), 4.19 (q, $J = 6.8$ Hz, 1H), 3.91 (s, 3H), 3.11 (s, 3H), 2.42 (s, 3H), 1.53 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 177.3, 165.2, 158.1, 145.2, 136.7, 134.7, 133.9, 129.8, 129.4, 129.2, 128.7, 128.1, 126.0, 125.8, 119.6, 105.7, 63.6, 55.5, 47.0, 31.9, 21.8, 20.9.

HRMS (ESI-TOF) m/z : ($\text{M}+\text{H}$)⁺ calcd. For $\text{C}_{24}\text{H}_{26}\text{NO}_5\text{S}$, 440.1532; found, 440.1529.



1-((N,4-dimethylphenyl)sulfonamido)vinyl benzoate

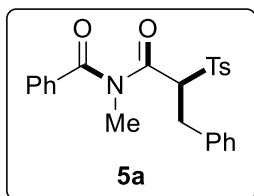
4a: White solid (67 mg, quant.), m. p. 100 – 102 °C.

TLC: $R_f = 0.35$ (PE: EA = 5:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.89 – 7.84 (m, 2H), 7.77 – 7.72 (m, 2H), 7.61 – 7.56 (m, 1H), 7.44 – 7.38 (m, 2H), 7.29 – 7.24 (m, 2H), 5.03 (d, $J = 2.5$ Hz, 1H), 4.89 (d, $J = 2.5$ Hz, 1H), 3.10 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 164.1, 147.0, 144.1, 134.4, 133.9, 130.3, 129.7, 128.7, 128.6, 128.1, 101.8, 37.3, 21.6.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{17}\text{H}_{18}\text{NO}_4\text{S}$, 332.0957; found, 332.0951.



N-methyl-*N*-(3-phenyl-2-tosylpropanoyl)benzamide

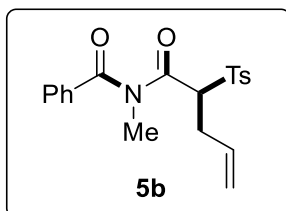
5a: Colorless oil (63 mg, 75%).

TLC: R_f = 0.34 (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.82 – 7.77 (m, 2H), 7.54 – 7.48 (m, 1H), 7.41 – 7.33 (m, 6H), 7.25 – 7.17 (m, 3H), 7.16 – 7.08 (m, 2H), 5.70 (dd, J_1 = 11.0 Hz, J_2 = 4.0 Hz, 1H), 3.34 (dd, J_1 = 13.5 Hz, J_2 = 11.5 Hz, 1H), 3.23 (dd, J_1 = 13.5, J_2 = 4.0 Hz, 1H), 3.04 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.3, 167.6, 145.5, 135.8, 134.3, 134.0, 132.7, 129.8, 129.6, 129.2, 128.8, 128.7, 127.1, 69.2, 35.7, 34.1, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{24}\text{H}_{24}\text{NO}_2\text{S}$, 422.1426; found, 422.1421.



N-methyl-*N*-(2-tosylpent-4-enoyl)benzamide

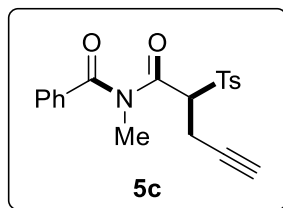
5b: Colorless oil (51 mg, 68%).

TLC: R_f = 0.35 (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.73 (d, J = 8.0 Hz, 2H), 7.69 – 7.65 (m, 2H), 7.61 – 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.77 – 5.67 (m, 1H), 5.46 (dd, J_1 = 11.0, J_2 = 4.0 Hz, 1H), 5.14 (dd, J_1 = 17.0 Hz, J_2 = 1.0 Hz, 1H), 5.08 (dd, J_1 = 10.0 Hz, J_2 = 1.0 Hz, 1H), 3.19 (s, 3H), 2.86 – 2.76 (m, 1H), 2.68 – 2.60 (m, 1H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 167.9, 145.5, 134.1, 134.0, 132.9, 132.2, 129.8, 129.6, 129.0, 128.9, 118.9, 67.6, 35.9, 32.2, 21.8.

HRMS (ESI-TOF) m/z : $(\text{M}+\text{H})^+$ calcd. For $\text{C}_{20}\text{H}_{22}\text{NO}_4\text{S}$, 372.1270; found, 372.1273.



***N*-methyl-*N*-(2-tosylpent-4-ynoyl)benzamide**

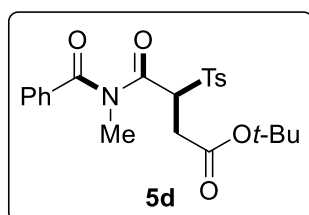
5c: Colorless oil (55 mg, 75%).

TLC: $R_f = 0.35$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.75 – 7.69 (m, 4H), 7.62 – 7.57 (m, 1H), 7.52 – 7.48 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 5.64 (dd, $J_1 = 10.0$, $J_2 = 4.0$ Hz, 1H), 3.25 (s, 3H), 3.04 (ddd, $J_1 = 16.5$ Hz, $J_2 = 10.0$ Hz, $J_3 = 2.5$ Hz, 1H), 2.71 (ddd, $J_1 = 16.5$ Hz, $J_2 = 4.0$ Hz, $J_3 = 2.5$ Hz, 1H), 2.45 (s, 3H), 2.01 (t, $J = 2.5$ Hz, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.5, 166.8, 145.9, 134.1, 133.8, 132.9, 130.0, 129.5, 129.0, 128.9, 78.3, 71.3, 66.5, 36.1, 21.8, 18.2.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{20}\text{H}_{20}\text{NO}_4\text{S}$, 370.1113; found, 370.1117.



***tert*-butyl (*S*)-4-(*N*-methylbenzamido)-4-oxo-3-tosylbutanoate**

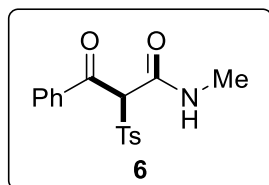
5d: White solid (45 mg, 51% yield), m. p. 160 – 162 °C.

TLC: $R_f = 0.4$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.76 – 7.71 (m, 4H), 7.59 – 7.54 (m, 1H), 7.51 – 7.46 (m, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 6.00 (d, $J = 11.0$ Hz, 1H), 3.25 (s, 3H), 3.19 (dd, $J_1 = 17.0$ Hz, $J_2 = 11.0$ Hz, 1H), 2.71 (dd, $J_1 = 17.0$ Hz, $J_2 = 3.5$ Hz, 1H), 2.44 (s, 3H), 1.39 (s, 9H).

^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 168.8, 167.1, 145.7, 134.8, 134.0, 132.5, 130.0, 129.4, 128.9, 128.7, 82.2, 63.9, 36.2, 34.1, 28.0, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{23}\text{H}_{28}\text{NO}_6\text{S}$, 446.1637; found, 446.1633.



***N*-methyl-3-oxo-3-phenyl-2-tosylpropanamide**

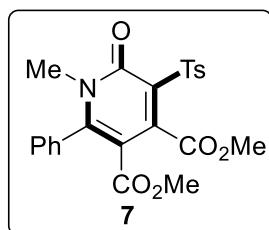
6: White solid (60 mg, 91% yield), m. p. 160 – 162 °C.

TLC: $R_f = 0.15$ (PE: EA = 3:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.94 – 7.89 (m, 2H), 7.80 – 7.74 (m, 2H), 7.64 – 7.58 (m, 1H), 7.50 – 7.39 (m, 3H), 7.32 (d, $J = 8.0$ Hz, 2H), 6.00 (s, 1H), 2.86 (d, $J = 5.0$ Hz, 3H), 2.41 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 188.6, 159.8, 146.2, 136.2, 134.8, 134.4, 130.0, 129.3 (129.33), 129.3 (129.32), 129.0, 75.7, 27.2, 21.8.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{17}\text{H}_{18}\text{NO}_4\text{S}$, 332.0957; found, 332.0965.



dimethyl 1-methyl-6-oxo-2-phenyl-5-tosyl-1,6-dihydropyridine-3,4-dicarboxylate

7: White solid (80 mg, 88% yield), m. p. 231 – 232 °C.

TLC: $R_f = 0.30$ (PE: EA = 1:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, $J = 8.0$ Hz, 2H), 7.54 – 7.46 (m, 3H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.25 – 7.17 (m, 2H), 4.03 (s, 3H), 3.37 (s, 3H), 3.21 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 165.0, 164.7, 157.5, 157.0, 145.8, 144.9, 136.5, 132.9, 130.5, 129.5, 129.4, 129.2, 127.4, 125.3, 110.5, 53.6, 52.6, 35.2, 21.9.

HRMS (ESI-TOF) m/z : (M+H)⁺ calcd. For $\text{C}_{23}\text{H}_{22}\text{NO}_7\text{S}$, 456.1117; found, 456.1133.

9. X-ray Crystallographic Data

Crystals suitable for X-ray diffraction experiments were obtained by following methods: compound **3t** and **3bj** were crystallized from their solution in PE/EA. Intensity data for compounds was collected on ‘Bruke Apex2’ diffractometer at 296(2) (MoK/ α radiation, radiation wavelength = 0.7107). The structures were solved by direct methods and refined by the full-matrix least-squares

method using the SHELX-97 program package.¹⁰ The geometrical parameters and the figures were analyzed using the program OLEX2.¹¹

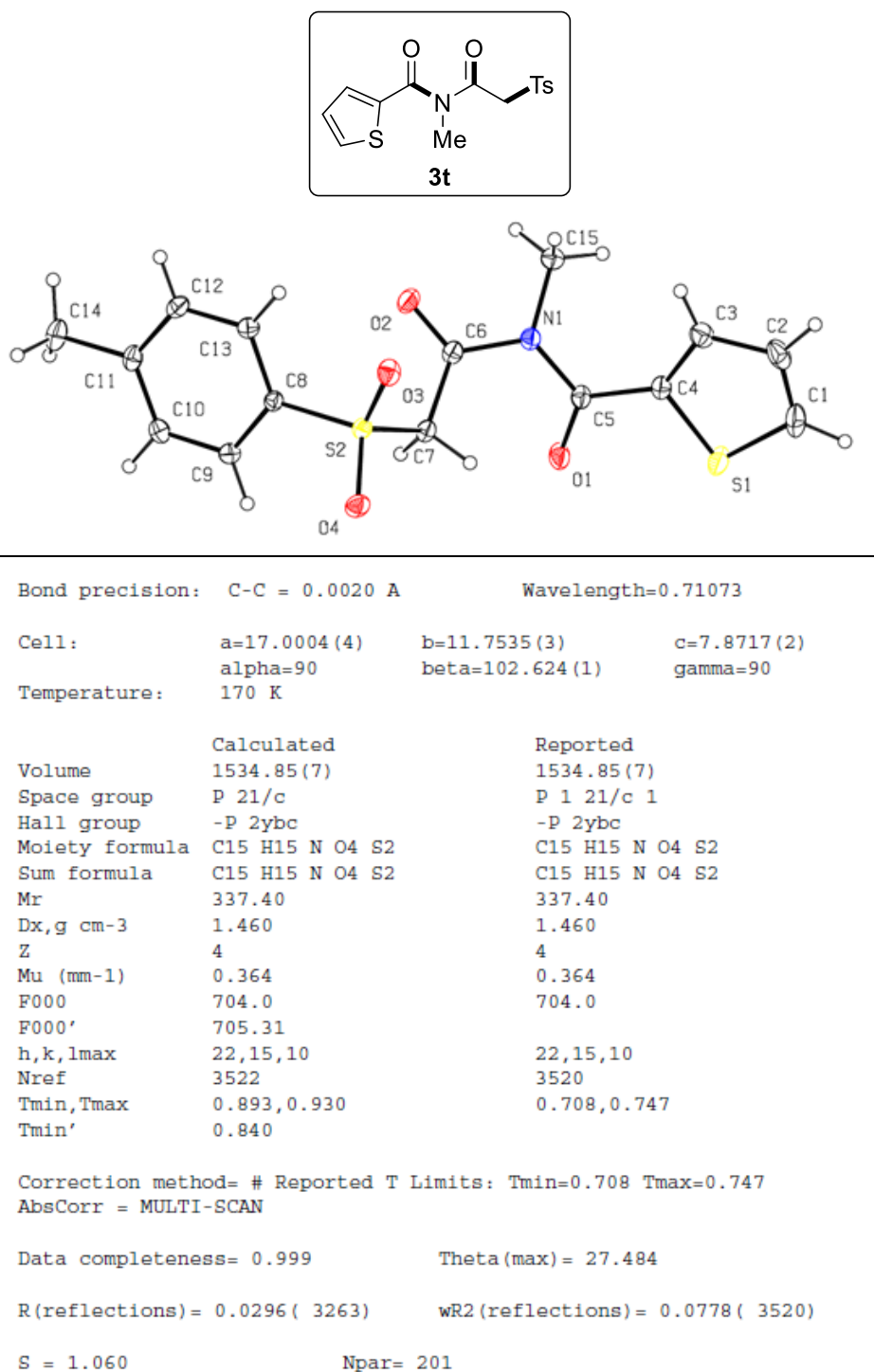
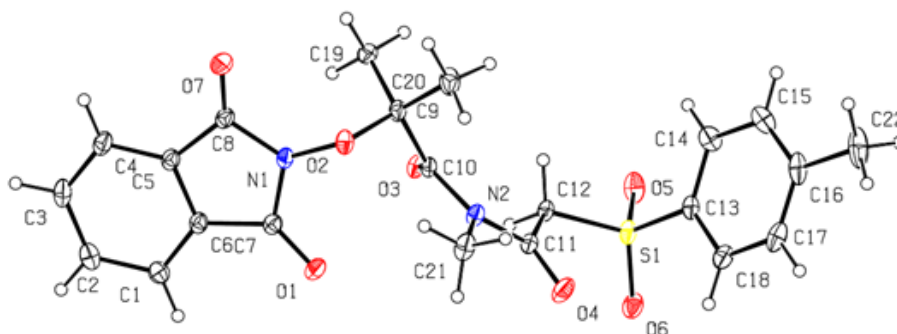
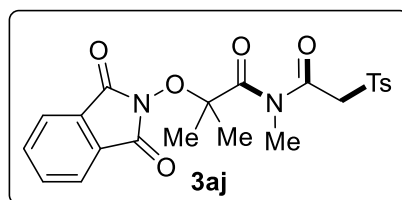


Fig. S12 X-ray analysis of 3t. Detail X-ray crystallographic data of 3t (CCDC 2045517).



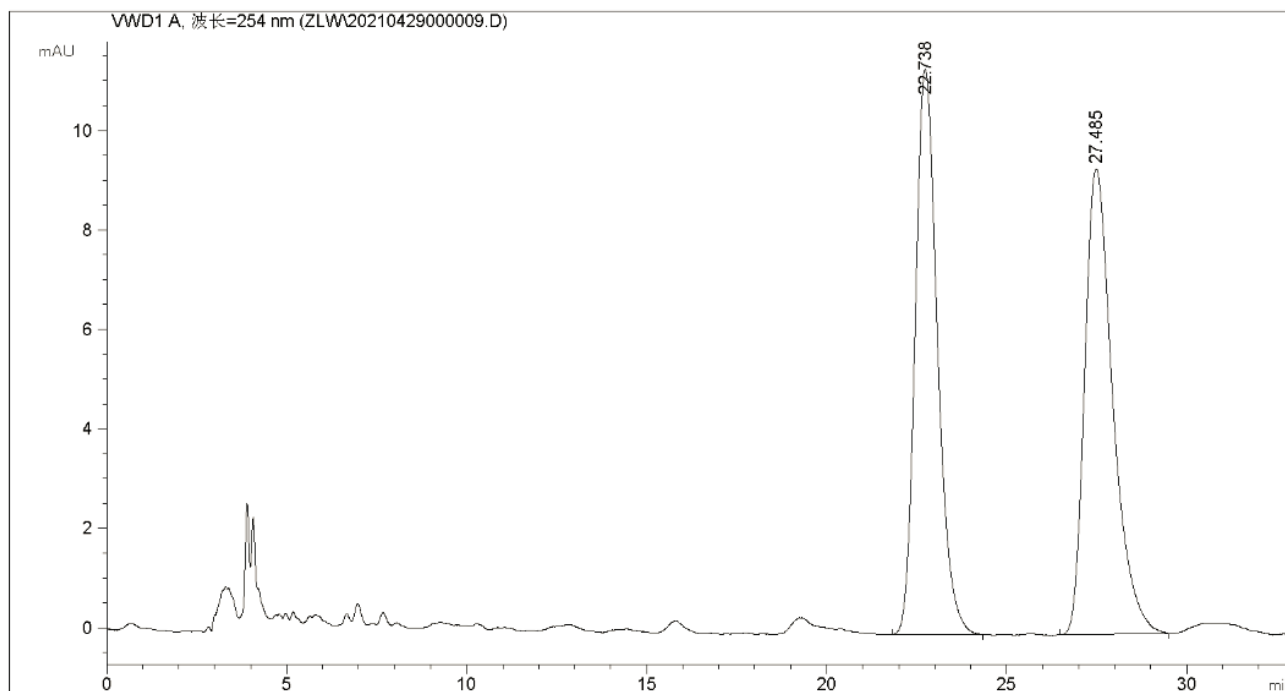
Bond precision:	C-C = 0.0022 Å	Wavelength=0.71073	
Cell:	a=7.266 (3)	b=11.193 (4)	c=14.501 (5)
	alpha=70.164 (13)	beta=79.380 (16)	gamma=81.797 (18)
Temperature:	170 K		
	Calculated	Reported	
Volume	1086.3 (7)	1086.2 (7)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C22 H22 N2 O7 S	C22 H22 N2 O7 S	
Sum formula	C22 H22 N2 O7 S	C22 H22 N2 O7 S	
Mr	458.48	458.47	
Dx, g cm ⁻³	1.402	1.402	
Z	2	2	
Mu (mm ⁻¹)	0.196	0.196	
F000	480.0	480.0	
F000'	480.50		
h, k, lmax	9, 14, 18	9, 14, 18	
Nref	4802	4787	
Tmin, Tmax	0.947, 0.986	0.716, 0.746	
Tmin'	0.928		
Correction method=	# Reported T Limits: Tmin=0.716 Tmax=0.746		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.997	Theta (max)= 27.114	
R (reflections)=	0.0356 (4349)	wR2 (reflections)= 0.0909 (4787)	
S =	1.060	Npar= 293	

Fig. S13 X-ray analysis of 3aj. Detail X-ray crystallographic data of **3aj** (CCDC 2045518).

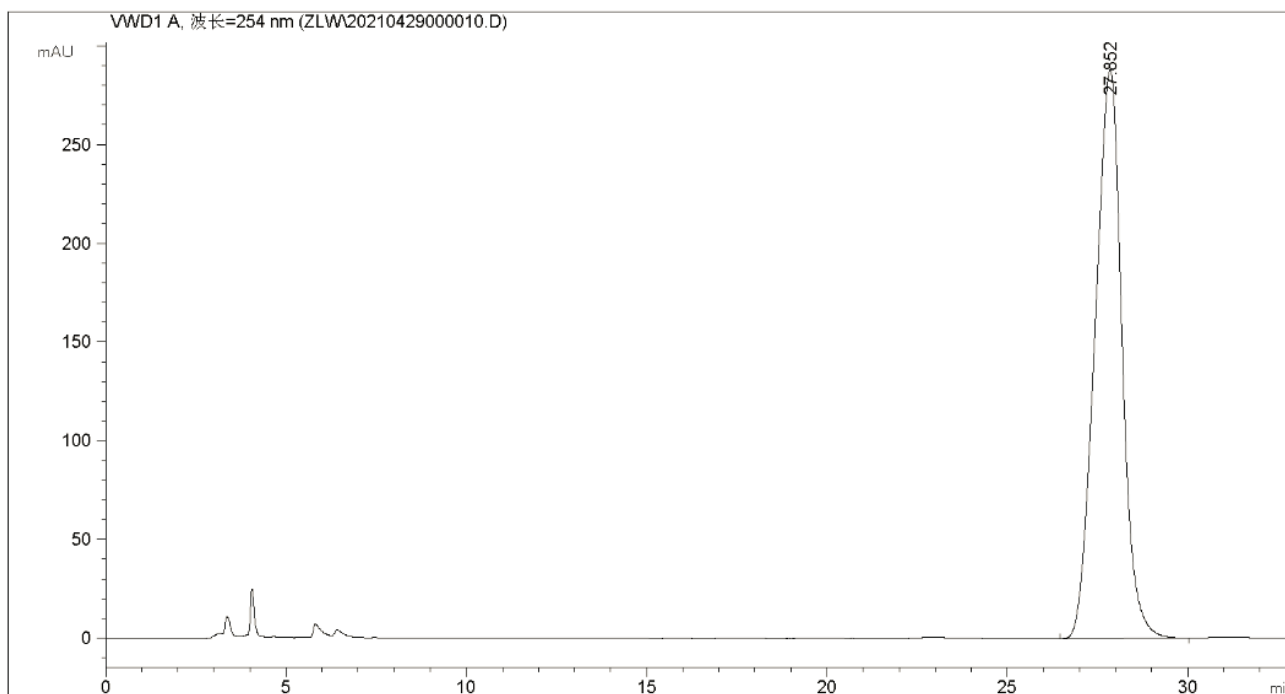
10.HPLC Charts

HPLC analysis was conducted on a CHIRALPAK AD-H column (hexane/isopropanol, 254 nm).

3am: AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm).

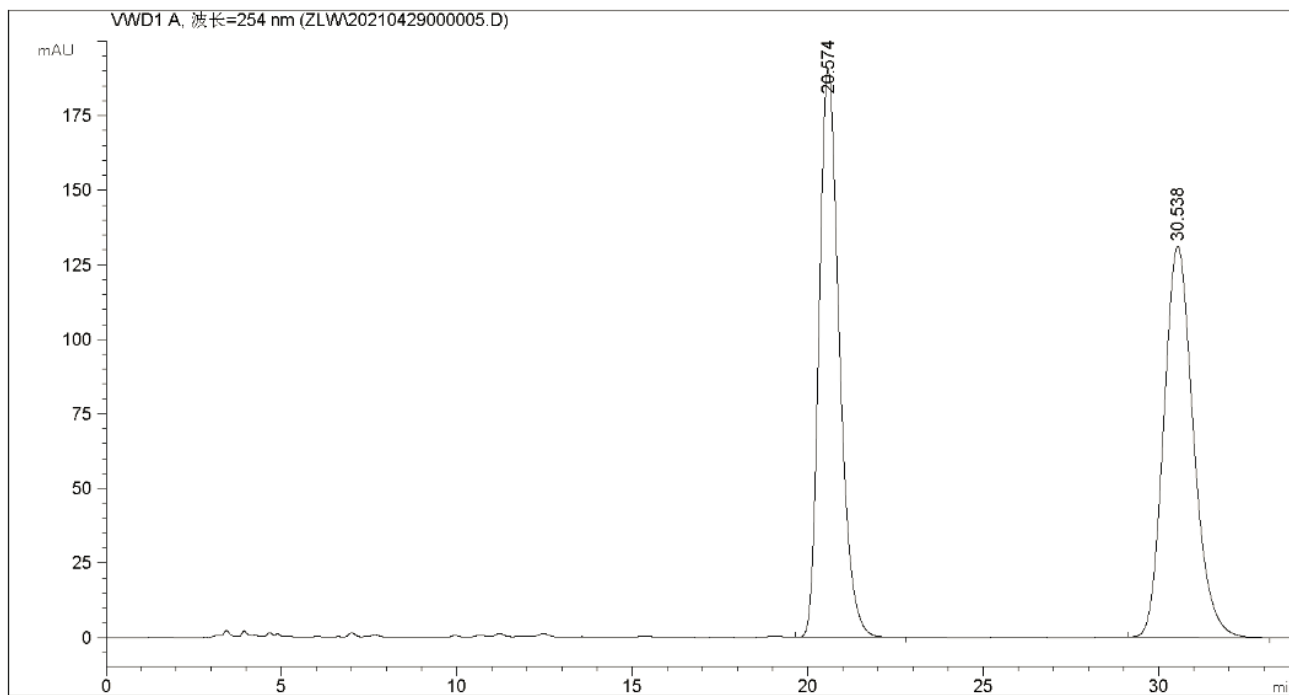


Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	22.738	486.00229	11.36510	48.9761
2	27.485	506.32245	9.36055	51.0239
Totals		992.32474	20.72565	

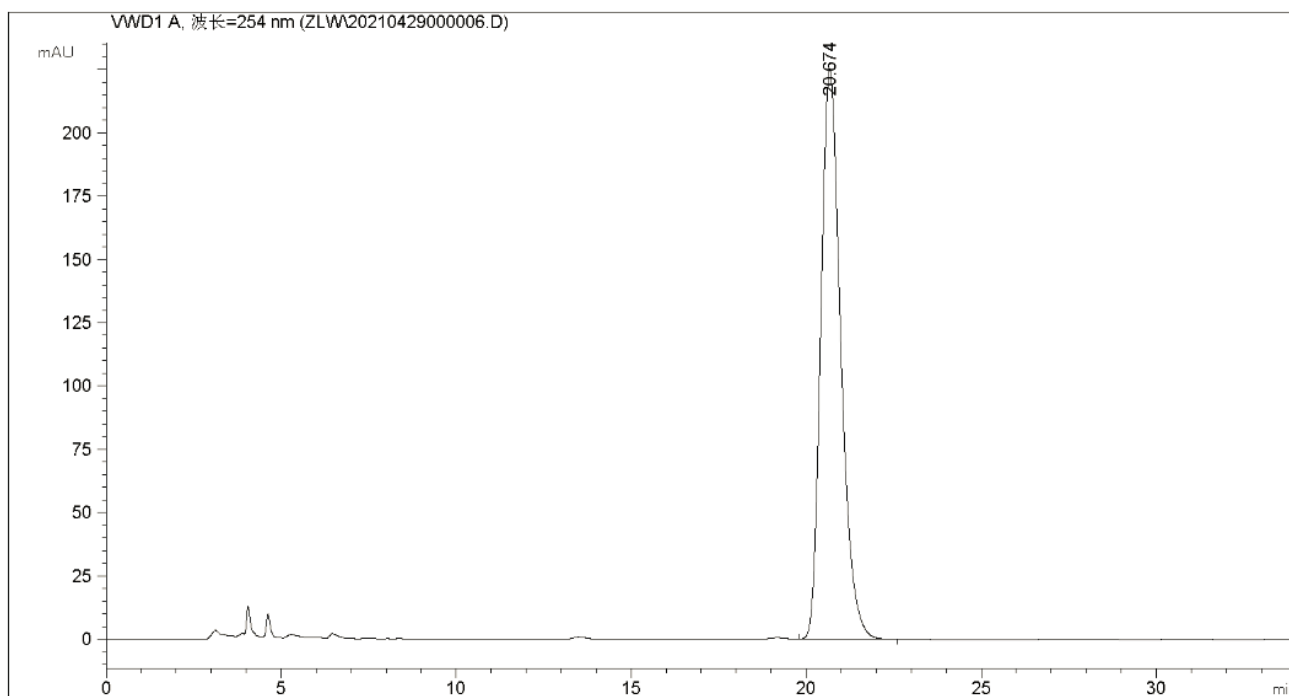


Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	27.852	1.48997e4	287.89261	100
Totals		1.48997e4	287.89261	

3an: AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm).

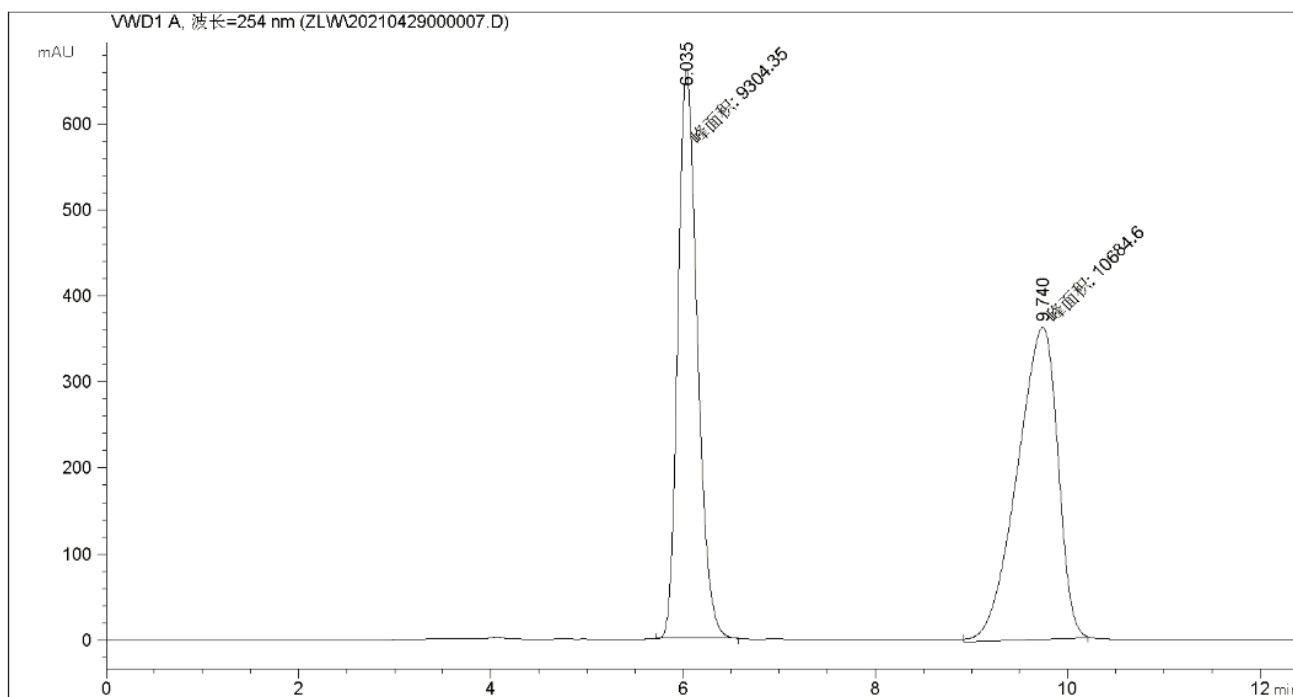


Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	20.574	7650.14990	190.81012	49.9333
2	30.538	7670.59717	131.08847	50.0667
Totals		1.53207e4	321.89859	

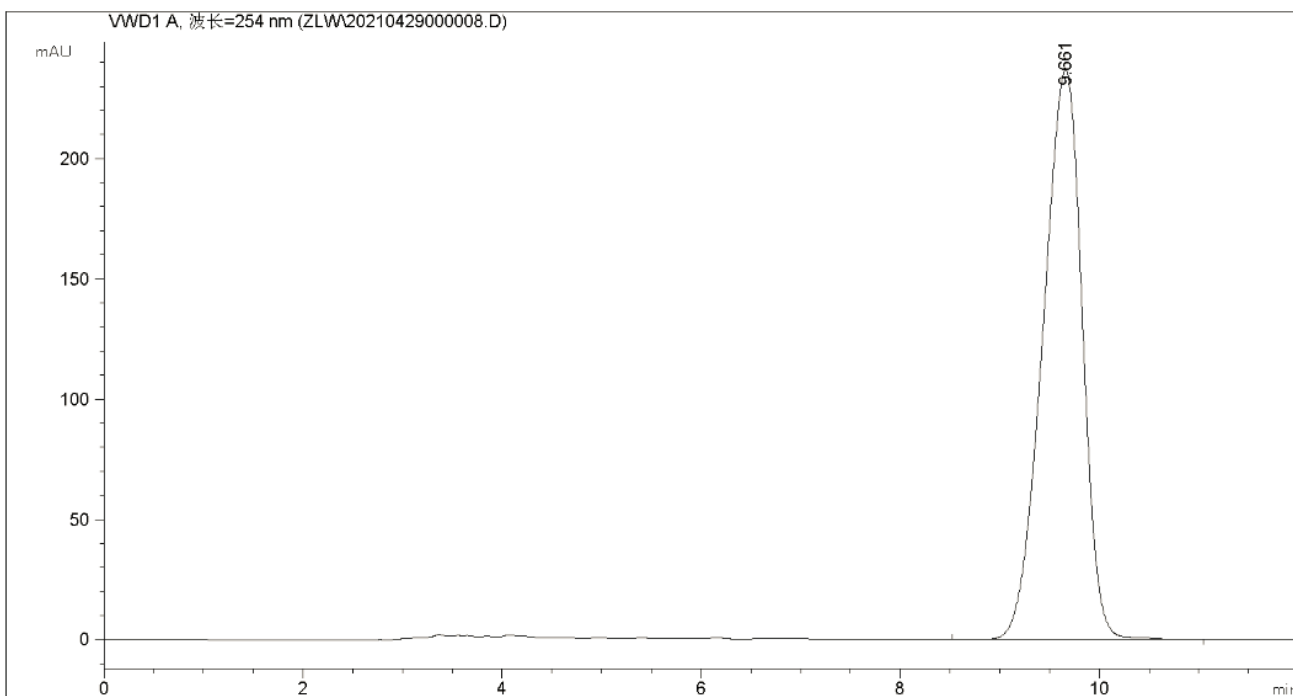


Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	20.674	8897.97461	224.61006	100
Totals		8897.97461	224.61006	

3ao: AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm).

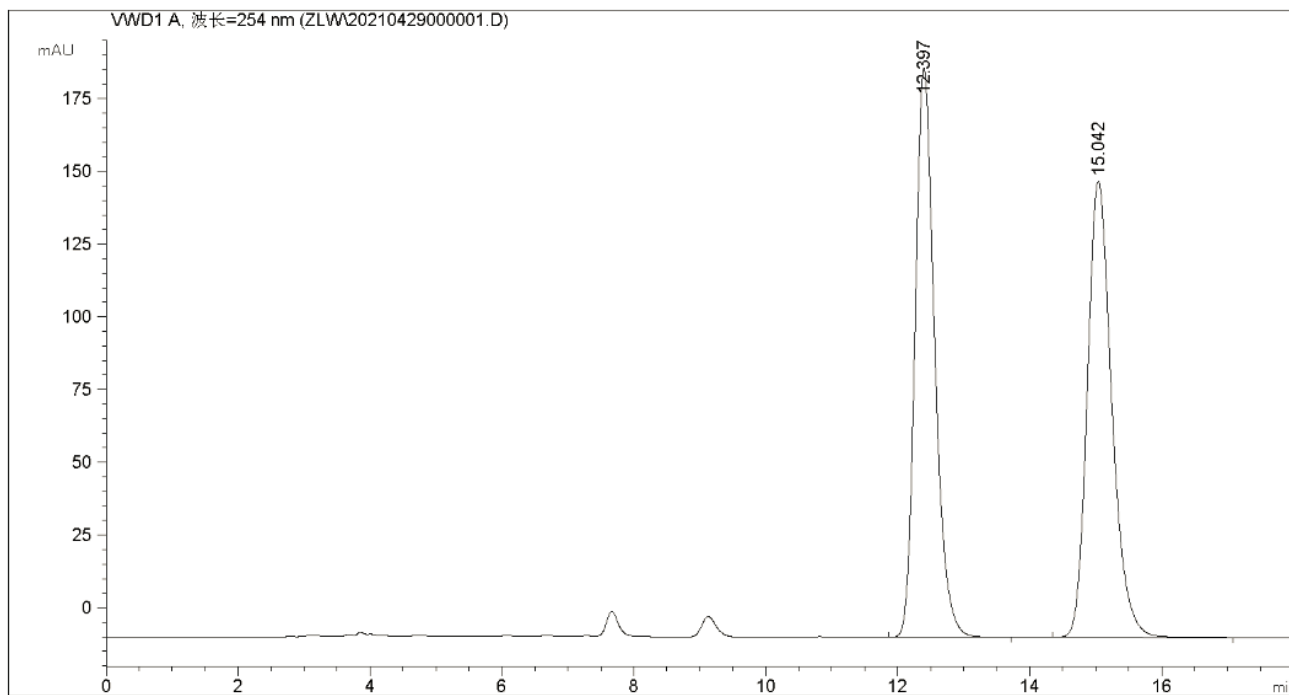


Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	6.035	9304.34766	661.18011	46.5474
2	9.740	1.06846e4	363.54550	53.4526
Totals		1.99890e4	1024.72562	

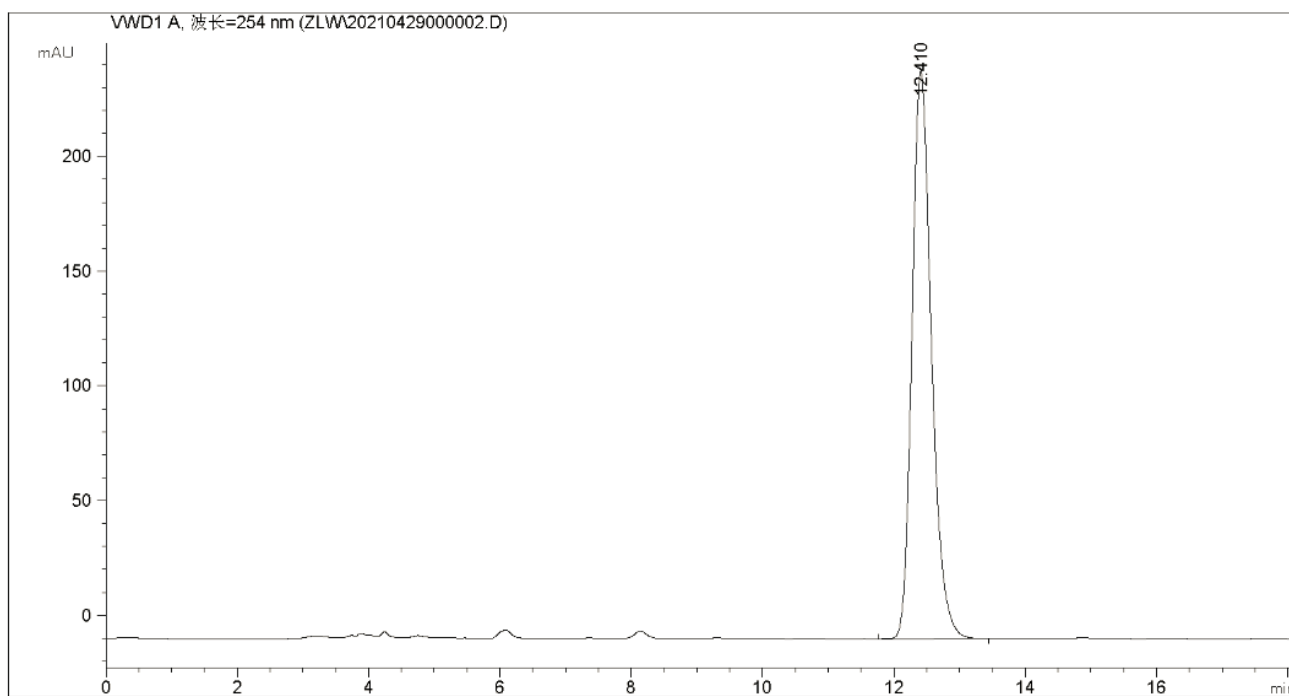


Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	9.661	6507.64258	236.88919	100
Totals		6507.64258	236.88919	

3ax: AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm).

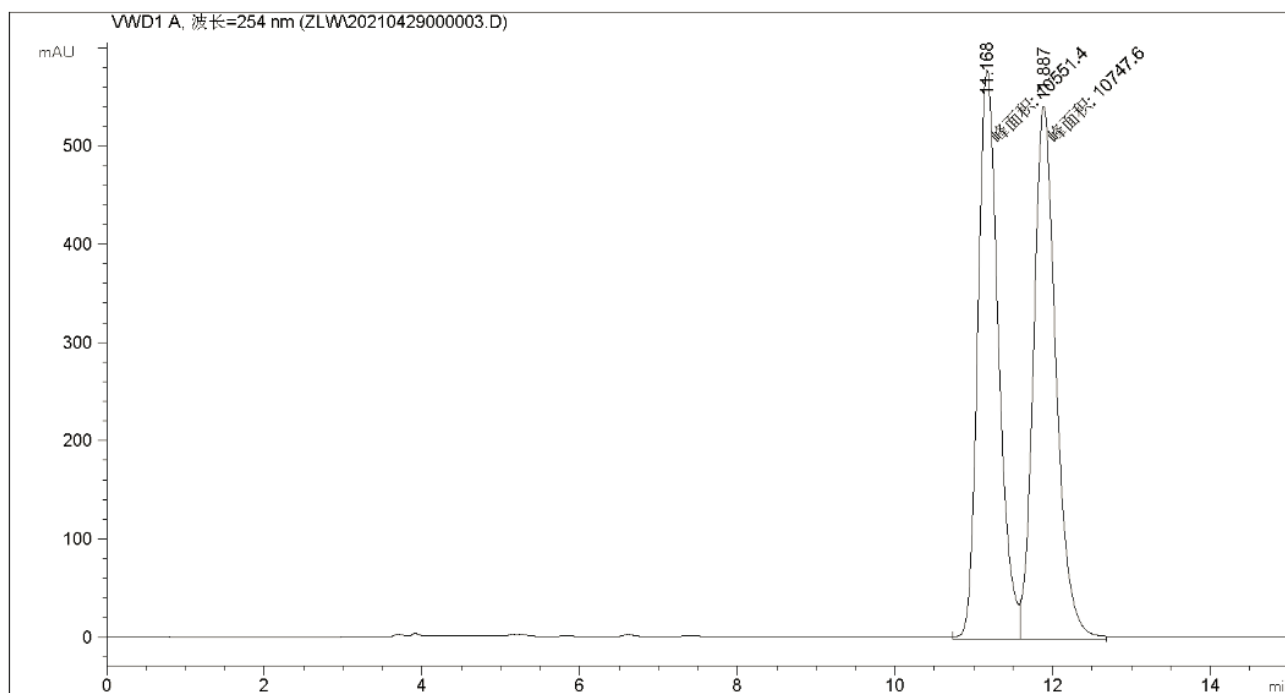


Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	12.397	4021.91676	195.55592	49.9350
2	15.042	4032.39526	156.78488	50.0650
Totals		8054.32202	352.34081	

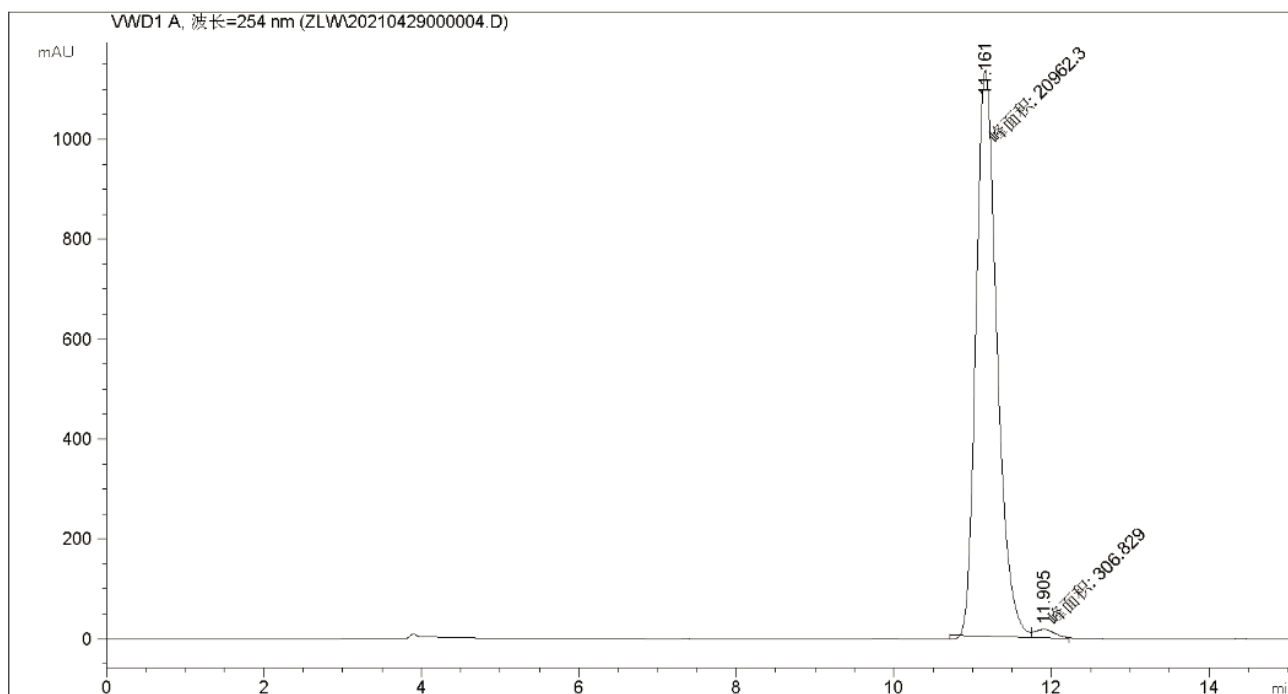


Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	12.410	5080.63379	247.55154	100
Totals		5080.63379	247.55154	

3ay: AD-H column (hexane/isopropanol = 55/45, flow = 1.0 mL/min, 254 nm).

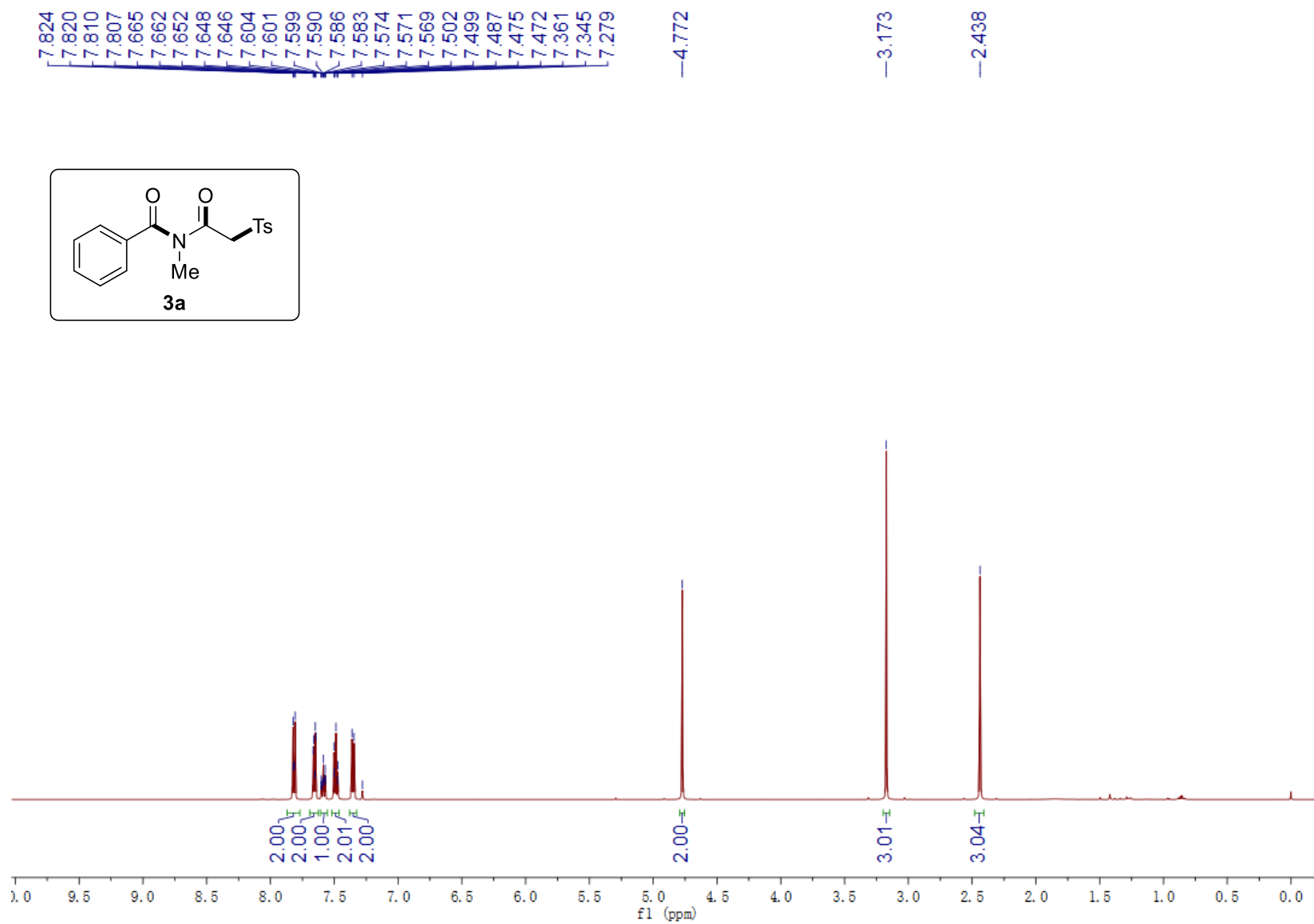


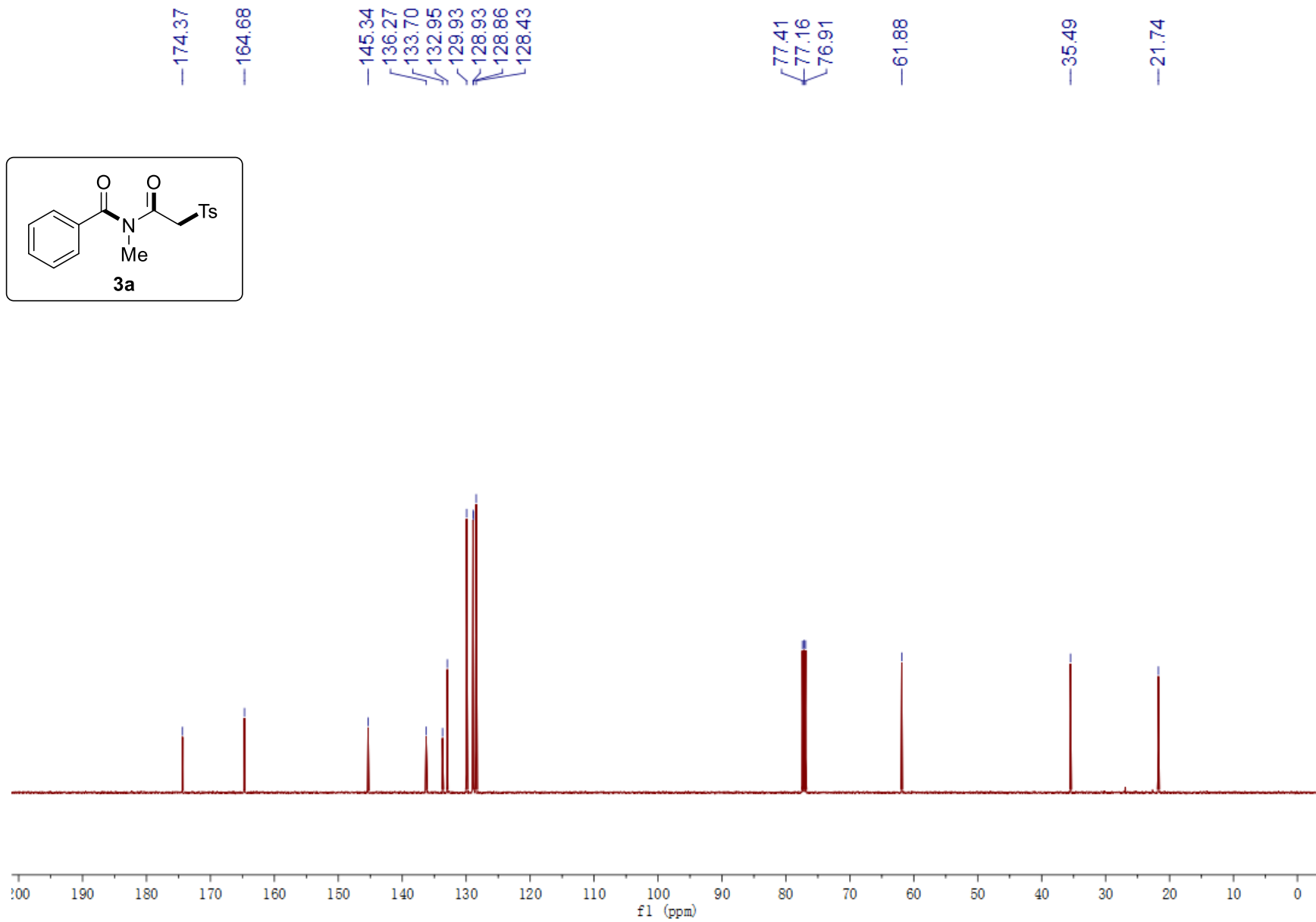
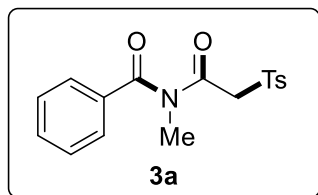
Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	11.168	1.05514e4	579.02026	49.5396
2	11.887	1.07476e4	542.35980	50.4604
Totals		2.12990e4	1121.38007	

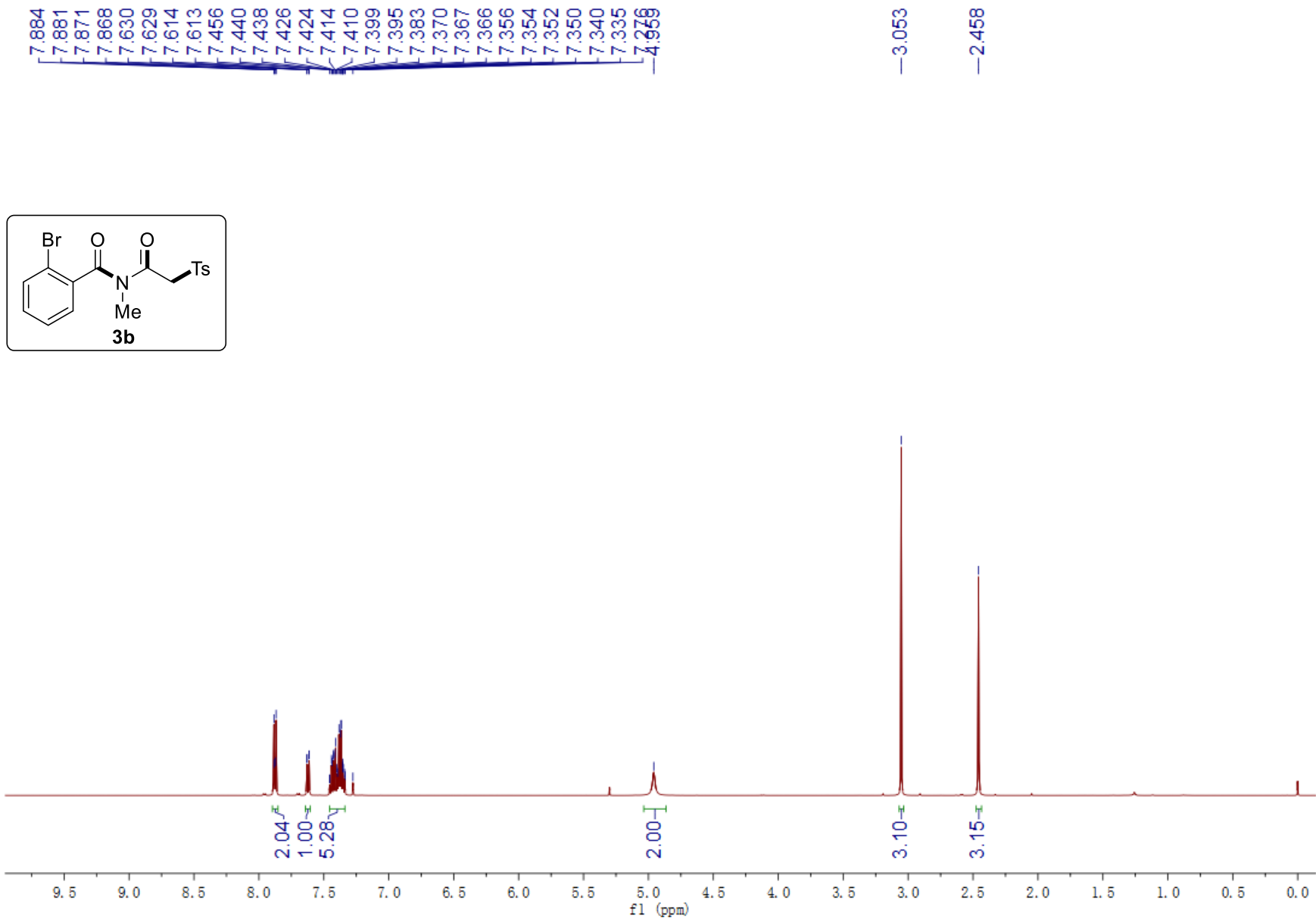


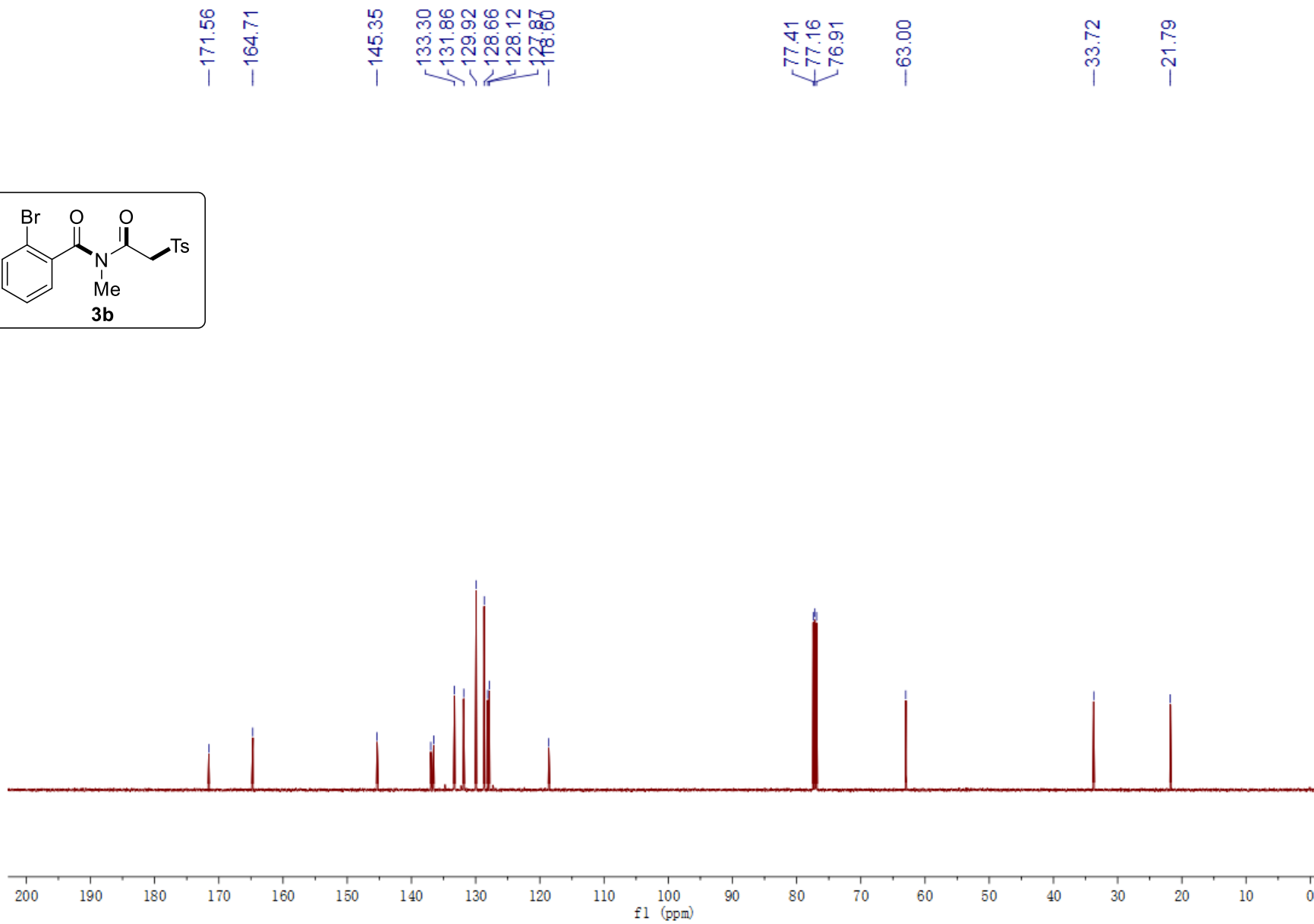
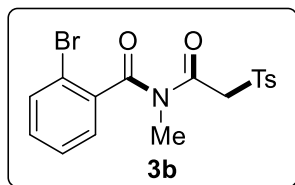
Peak #	Ret. Time (min)	Area (mAU*s)	Height (mAU)	Conc. (%)
1	11.161	2.09623e4	1133.20300	98.5574
2	11.905	306.82938	17.07603	1.4426
Totals		2.12691e4	1150.27904	

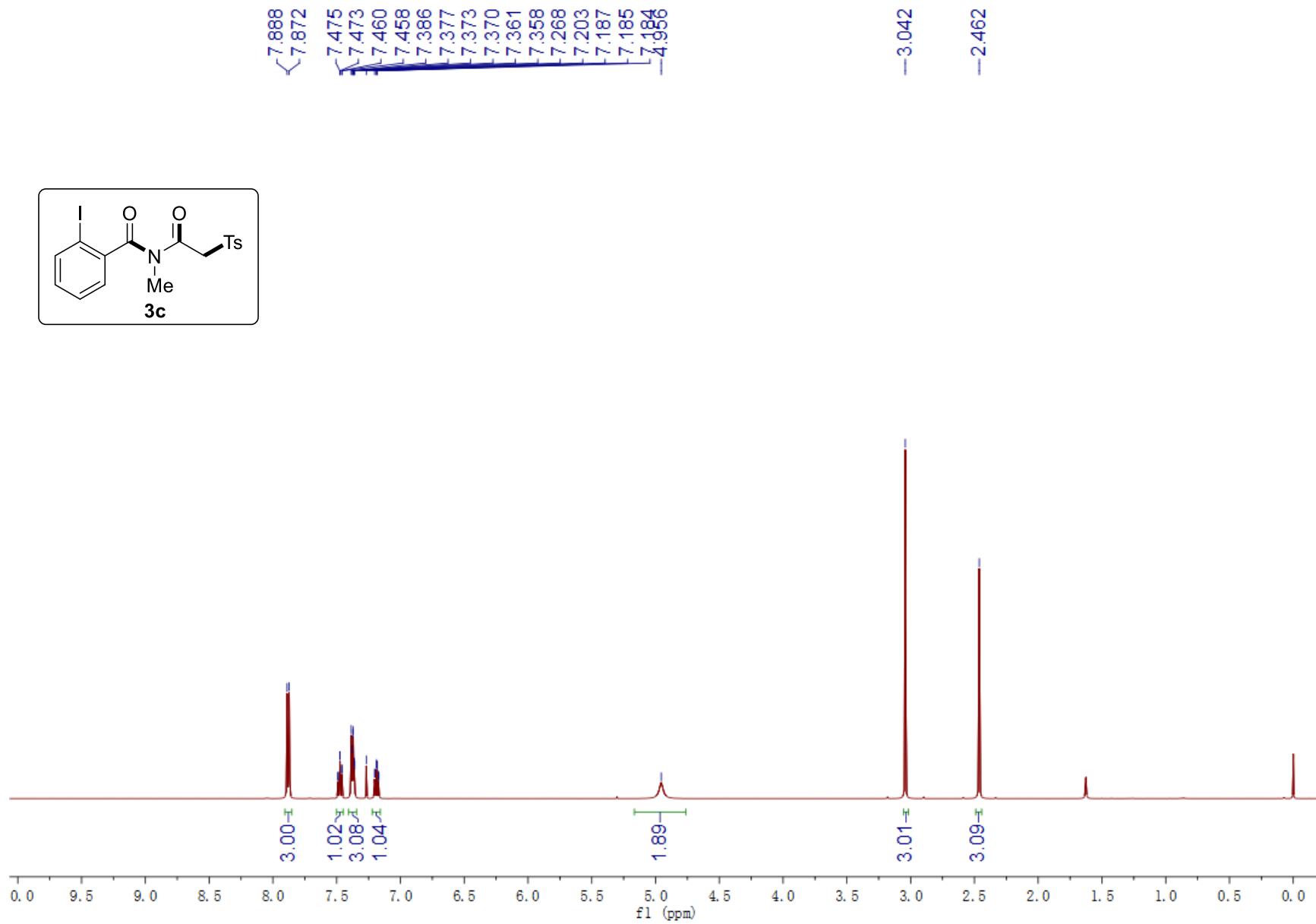
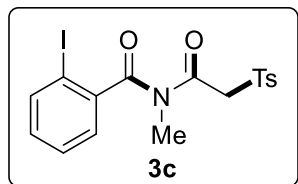
11. Copies of NMR Spectra

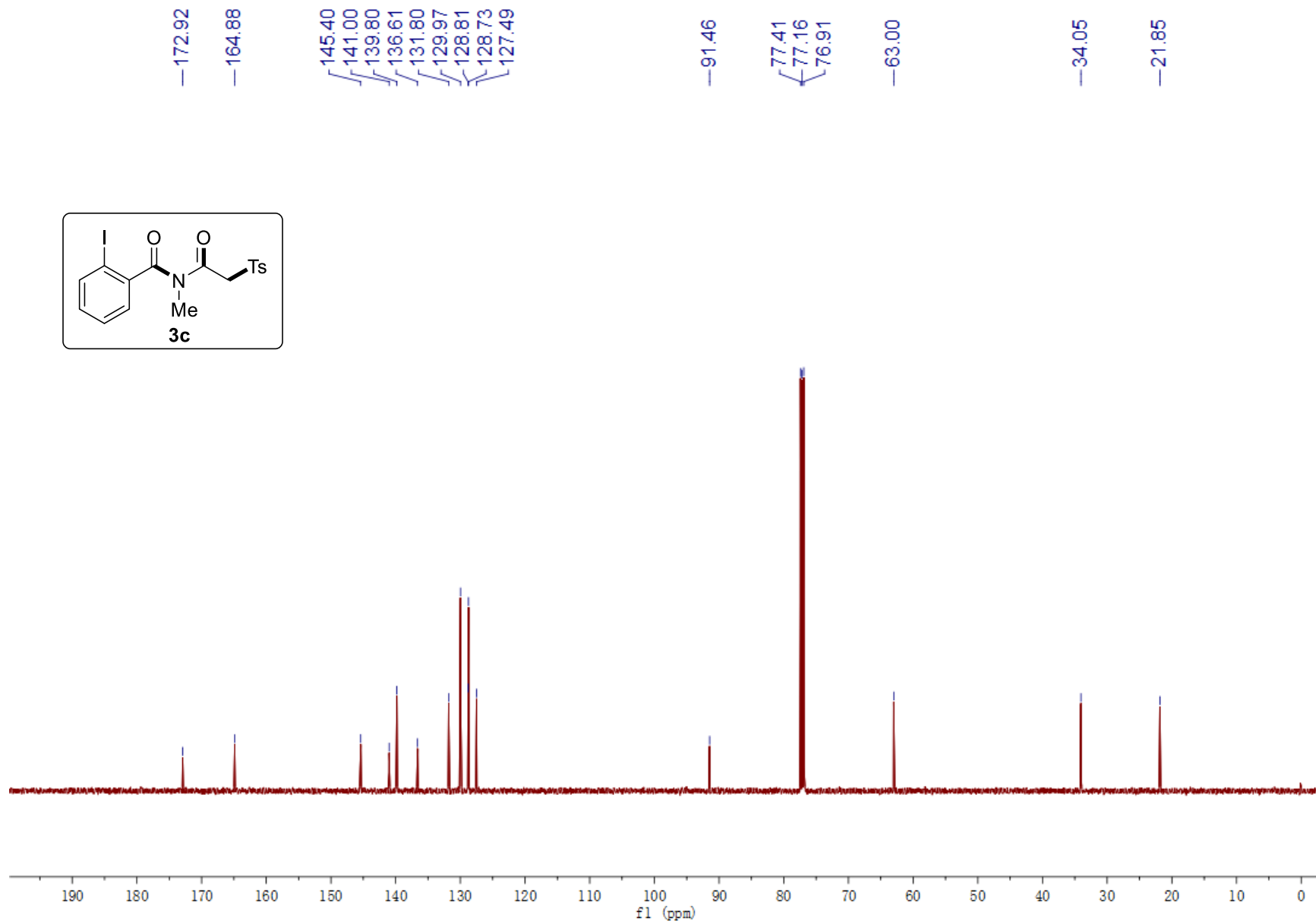
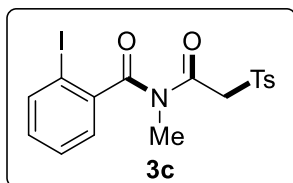


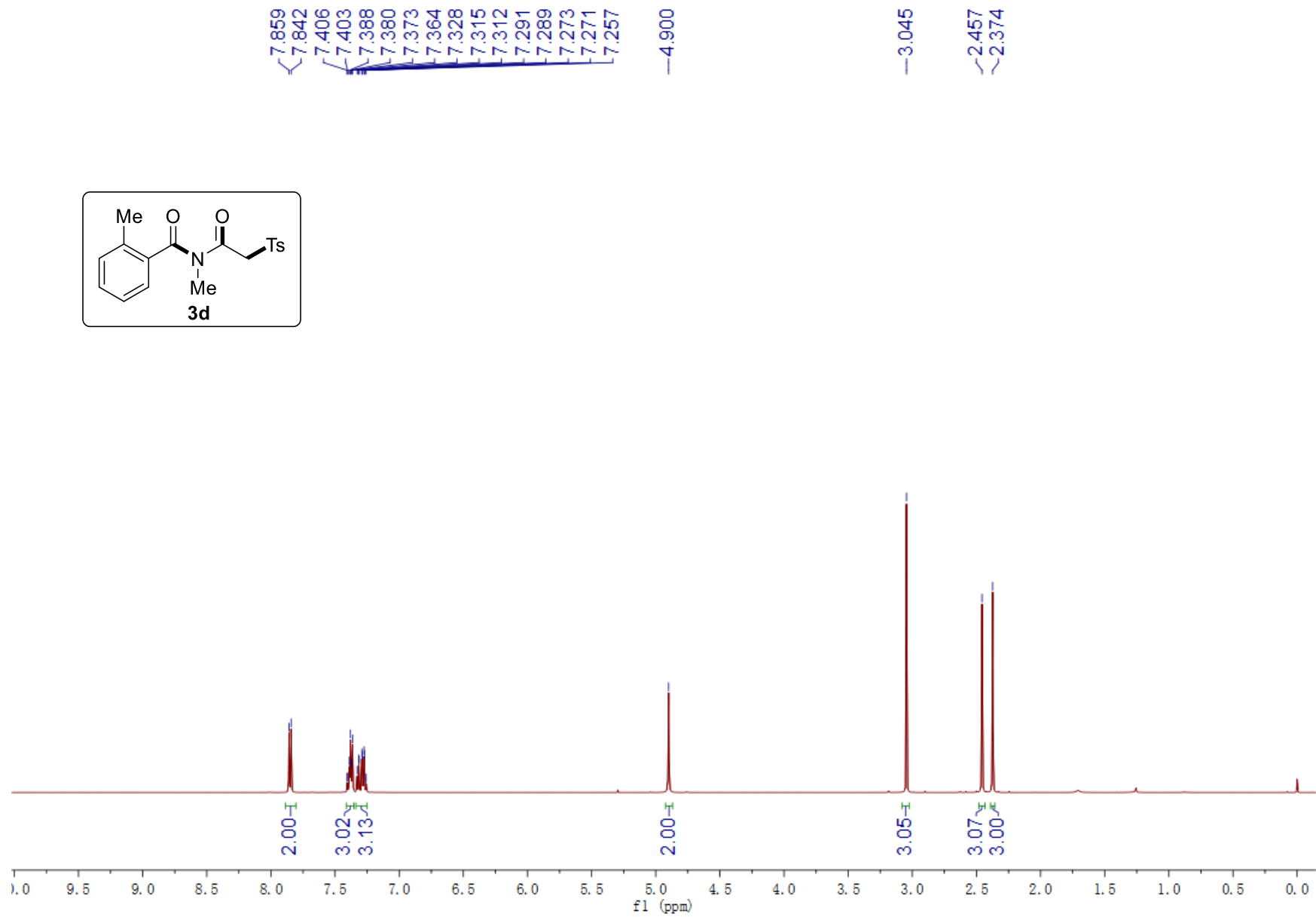
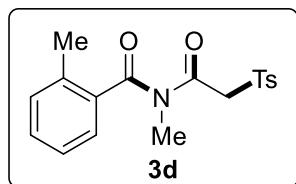


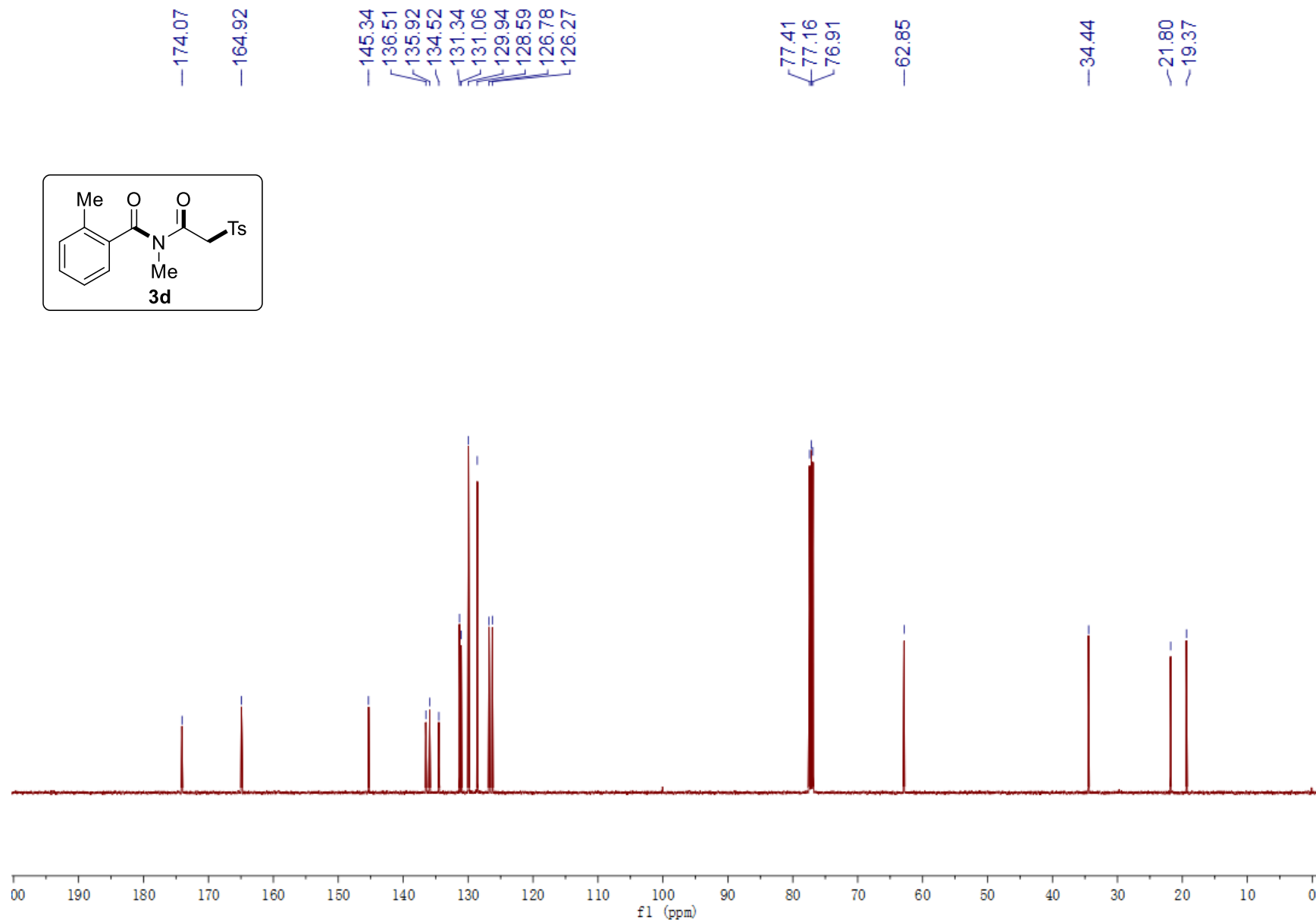
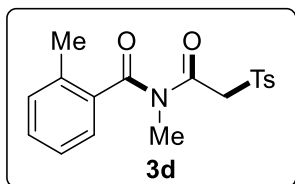


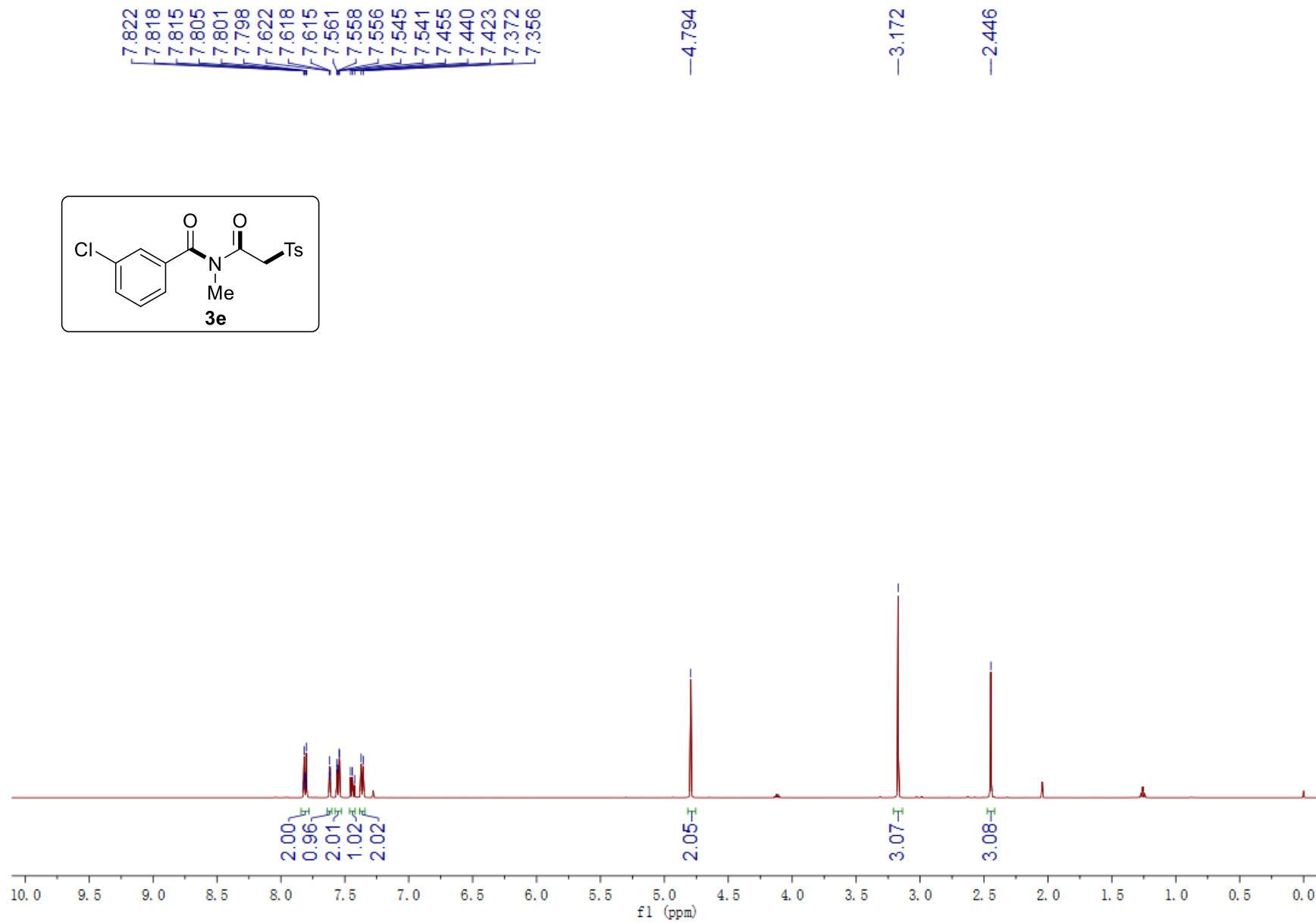
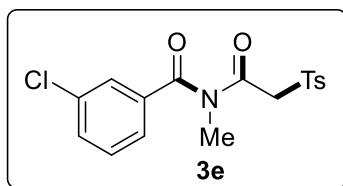


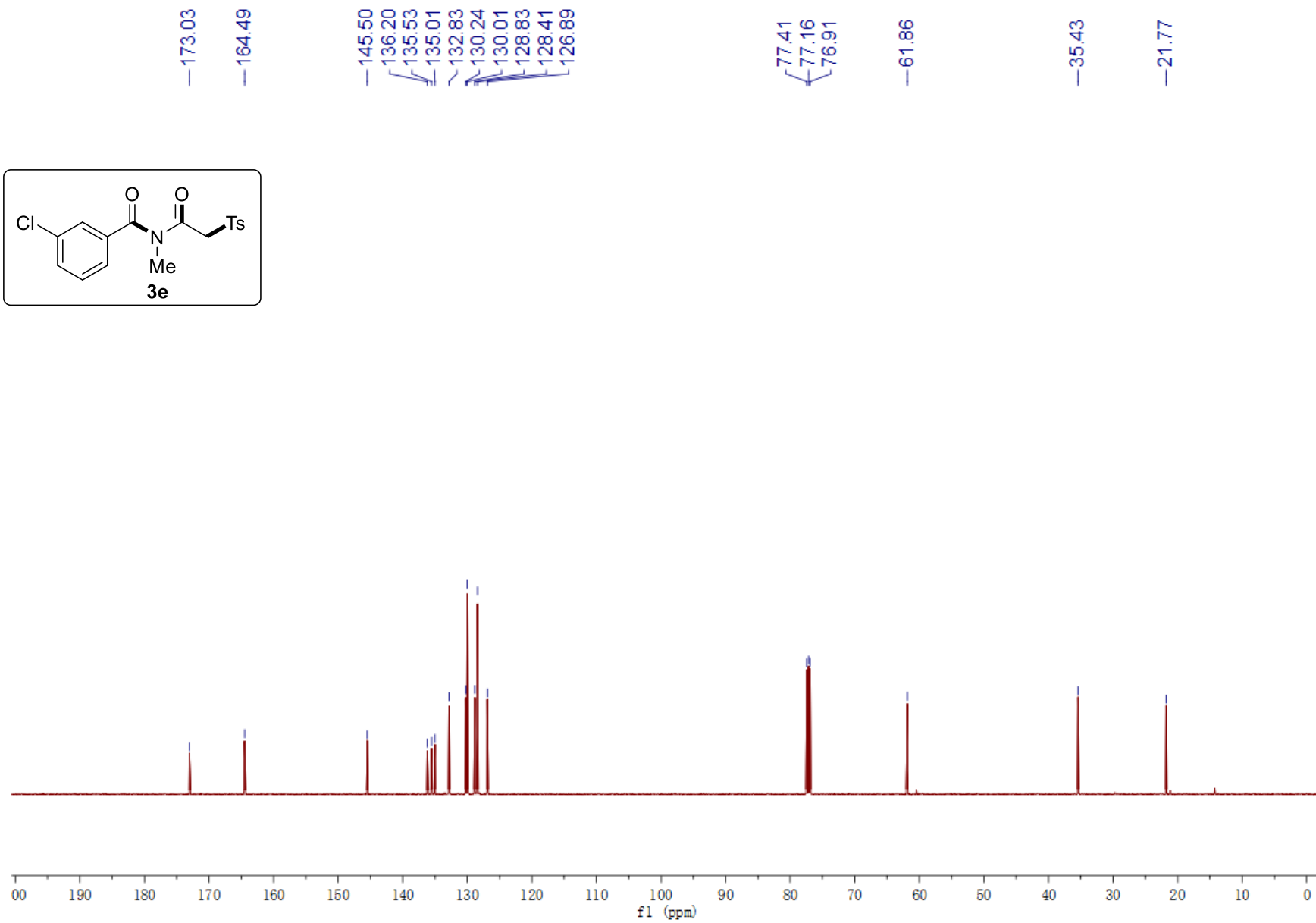
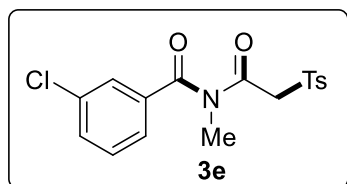


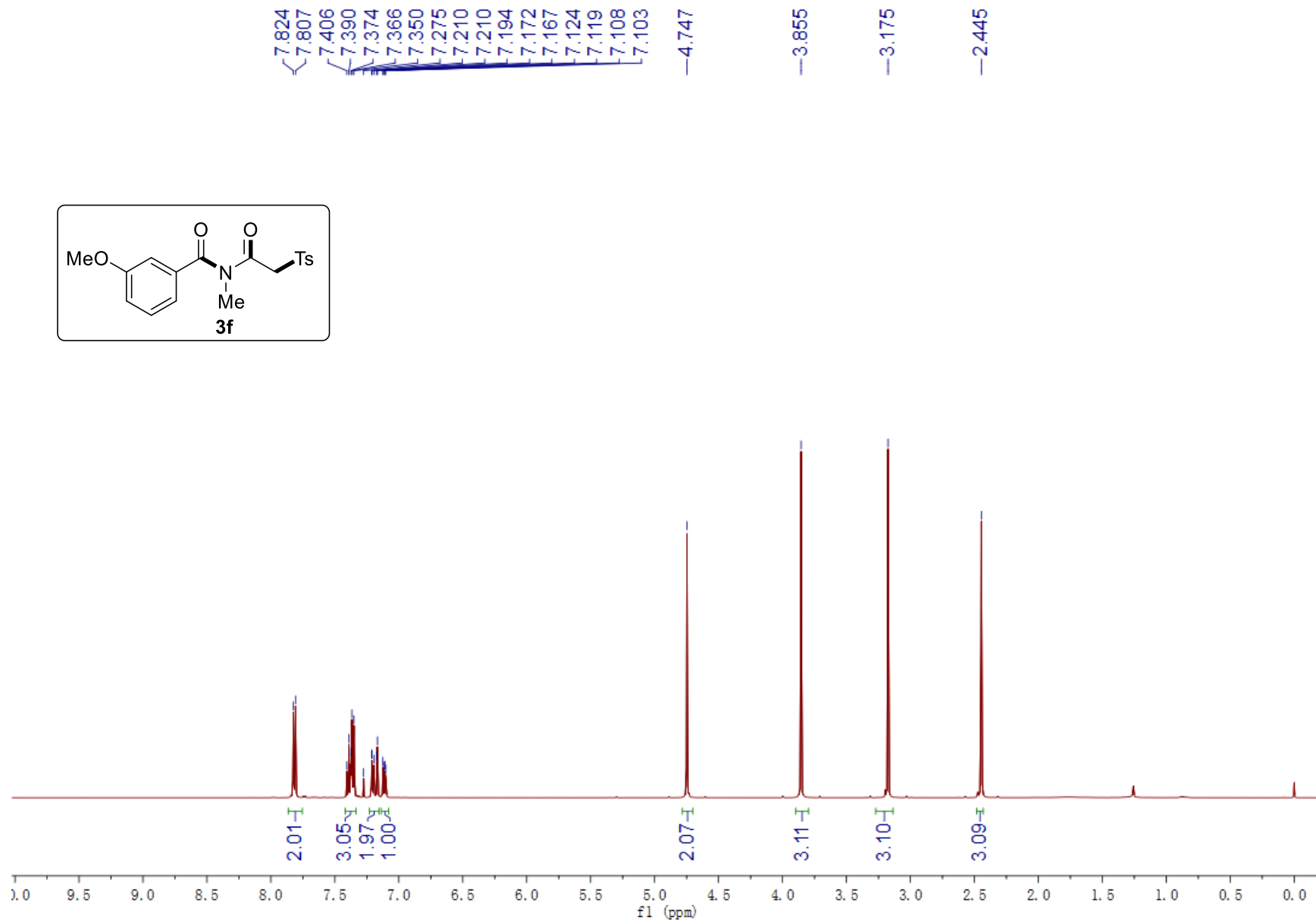
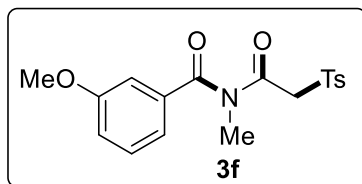


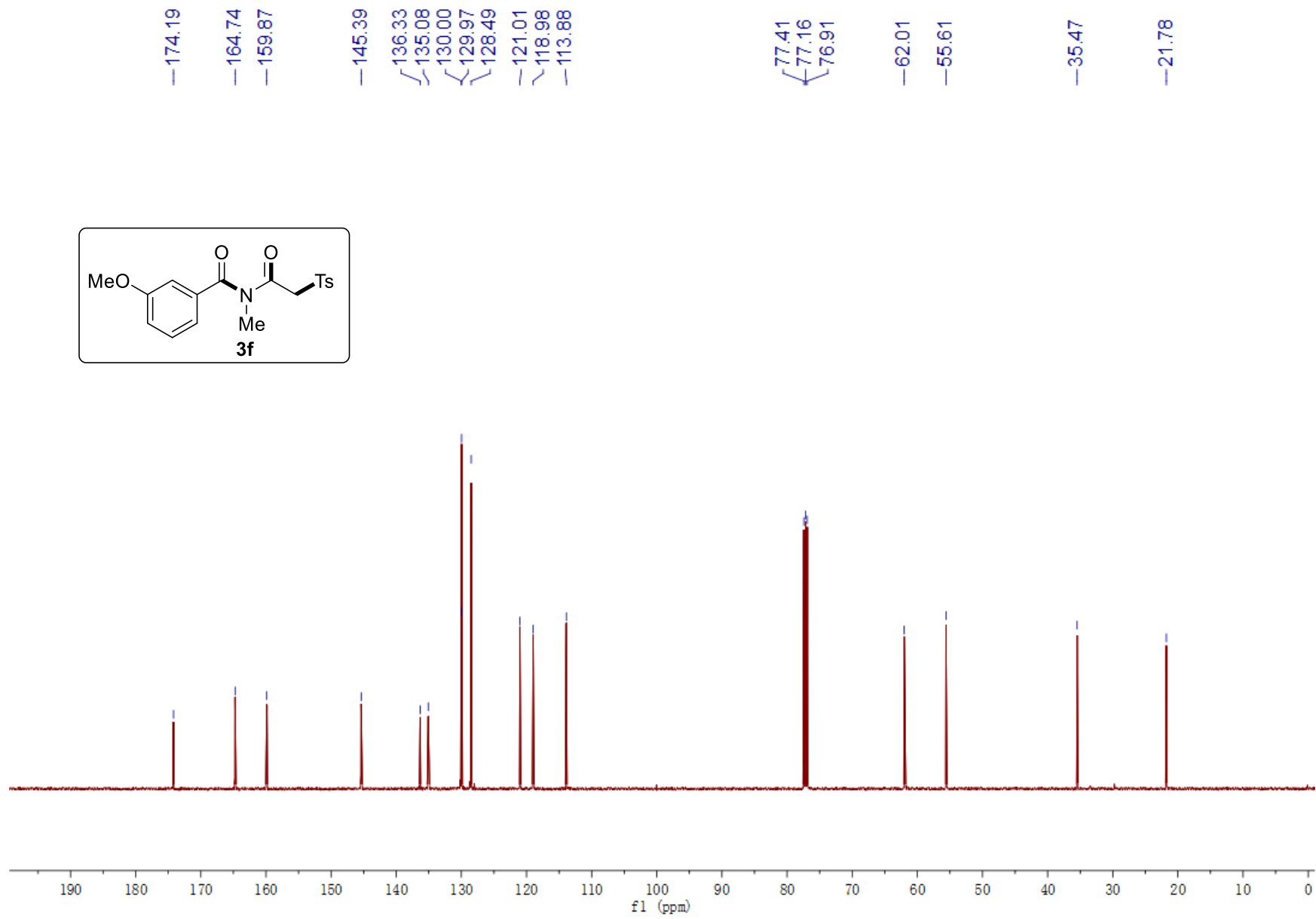
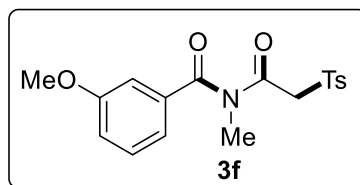




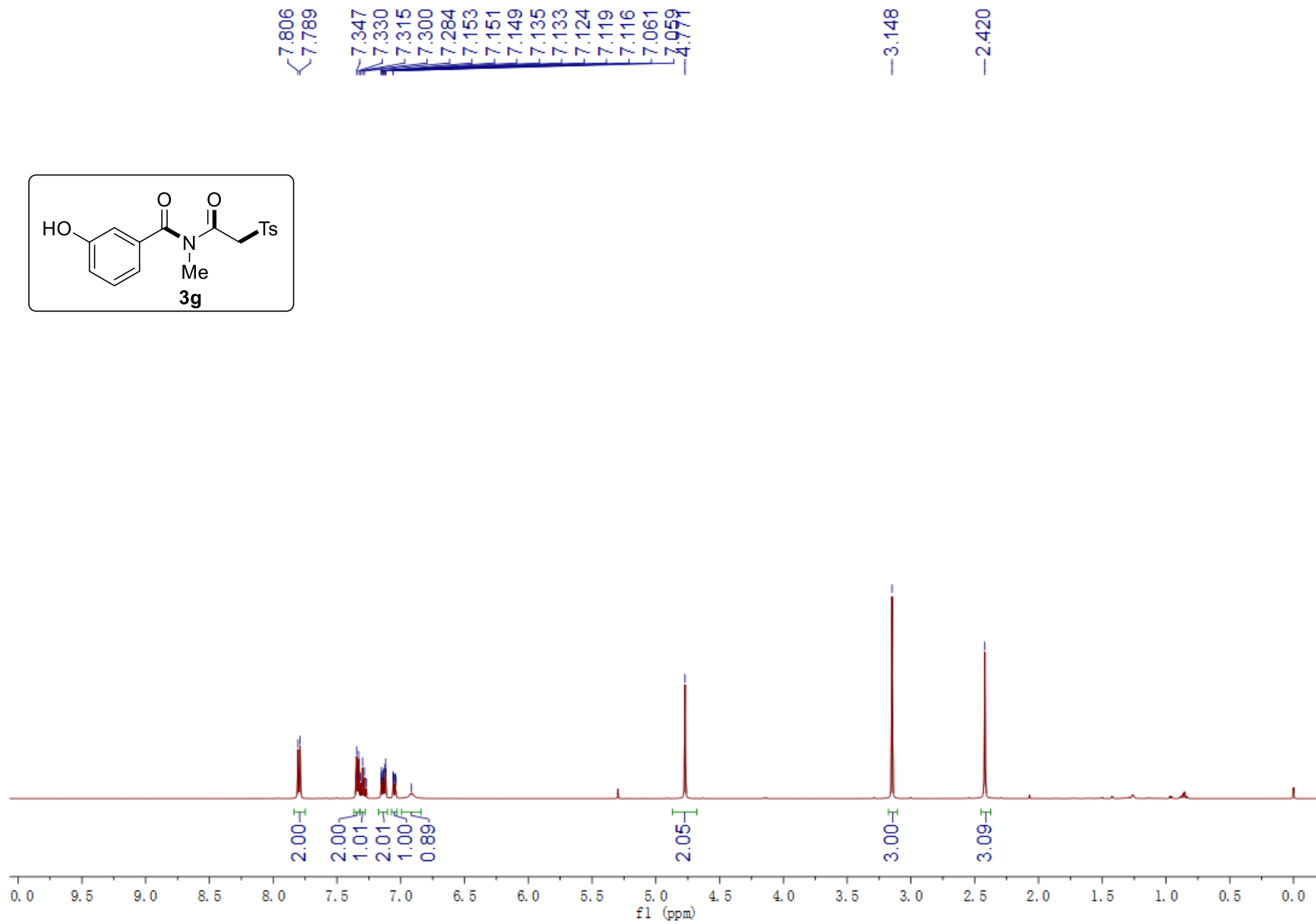
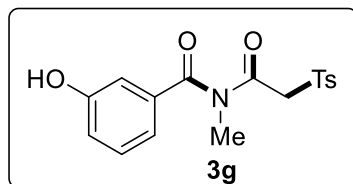


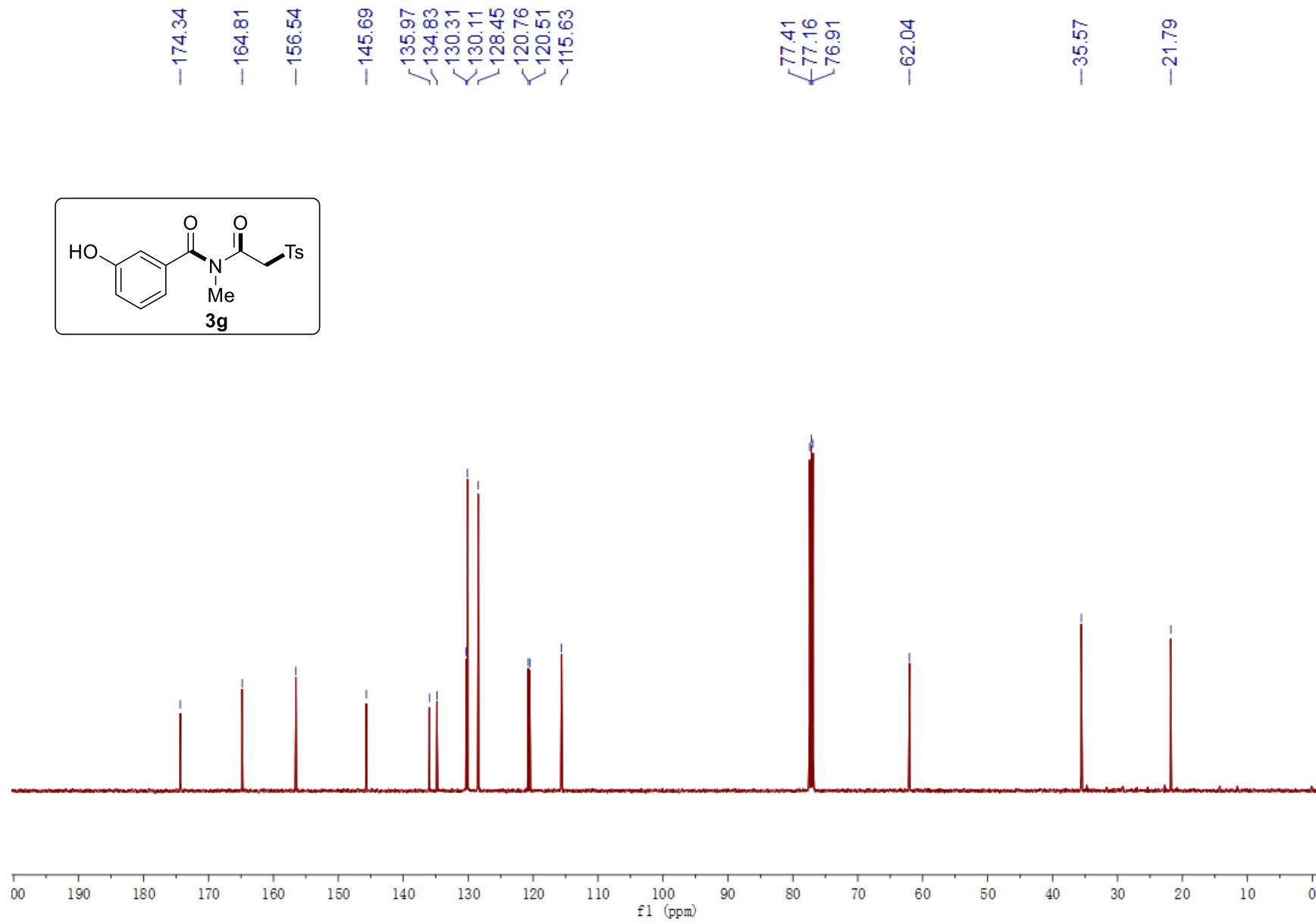
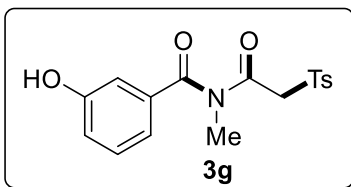




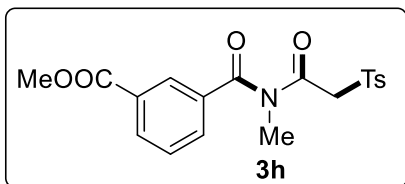


S68

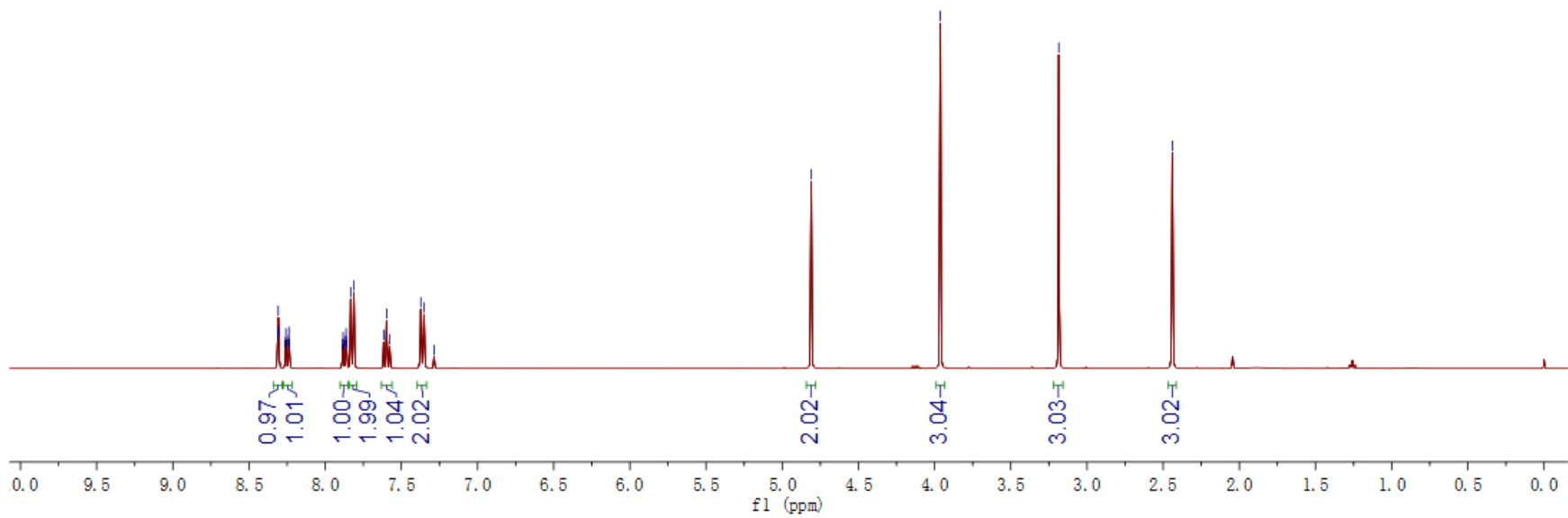


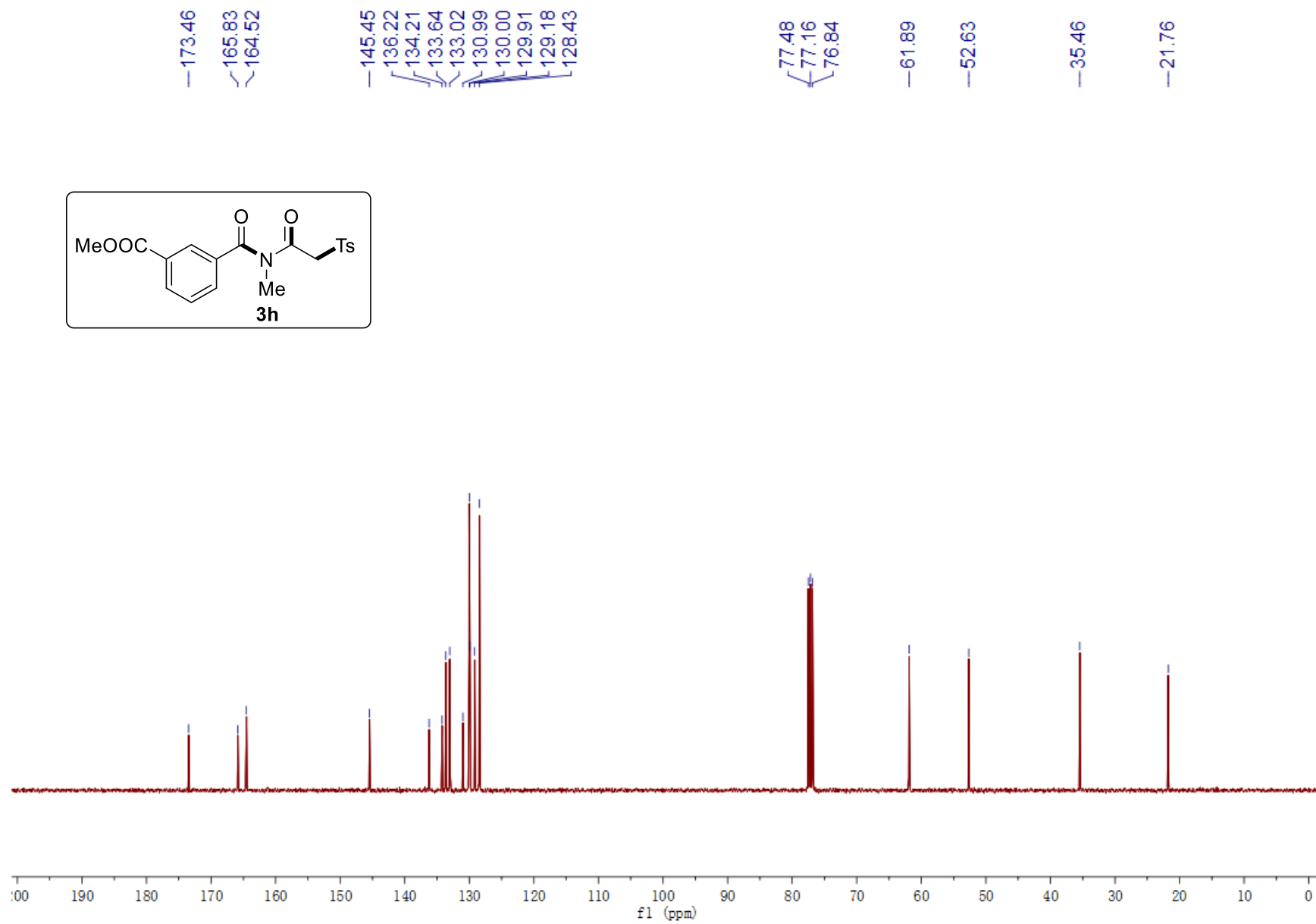
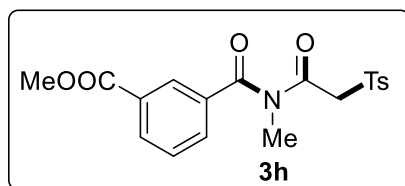


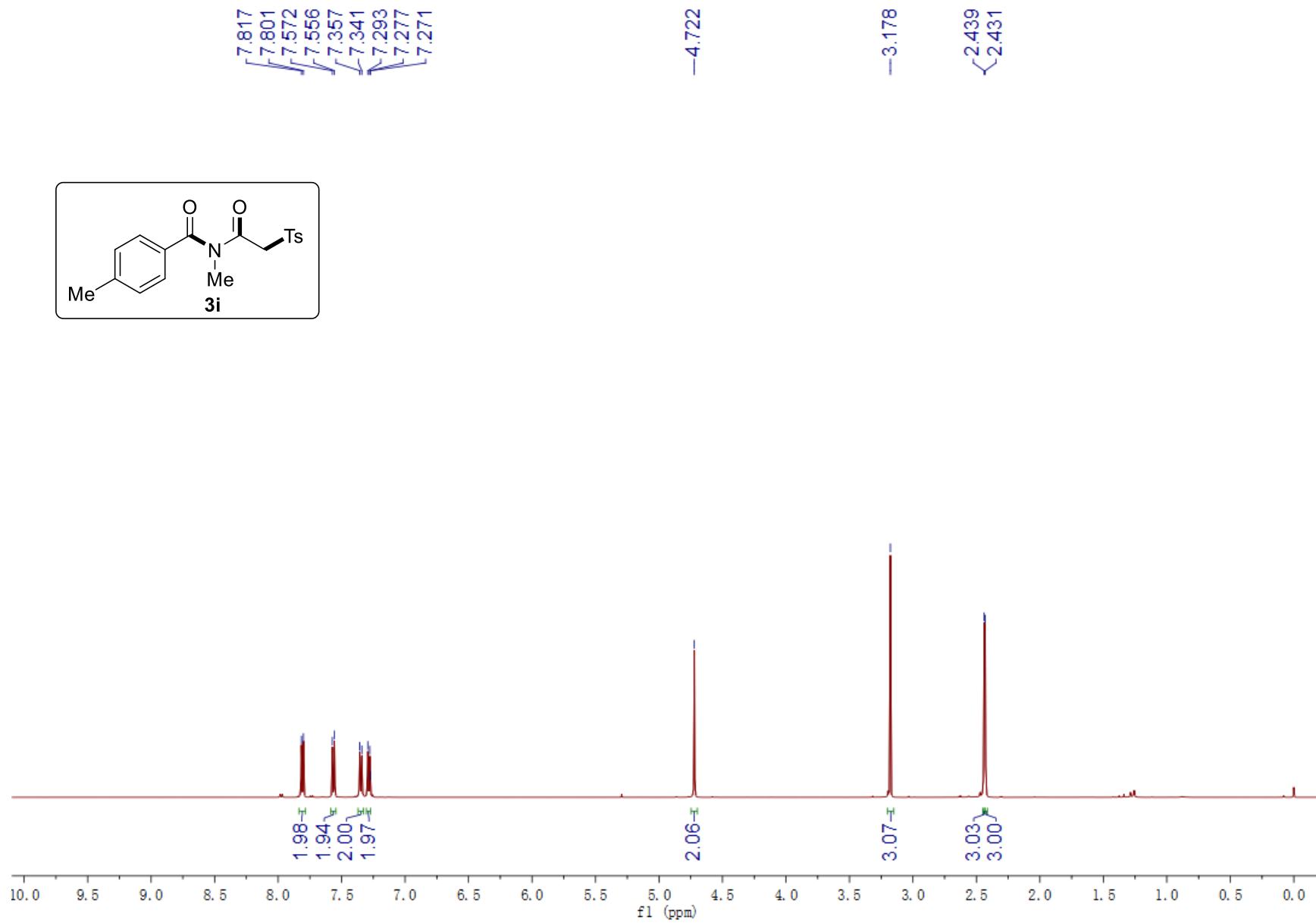
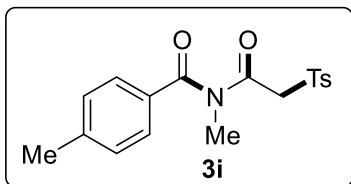
8.312
8.308
8.304
8.261
8.258
8.254
8.242
8.238
8.235
7.886
7.882
7.879
7.867
7.863
7.859
7.832
7.812
7.616
7.597
7.577
7.372
7.352
7.285



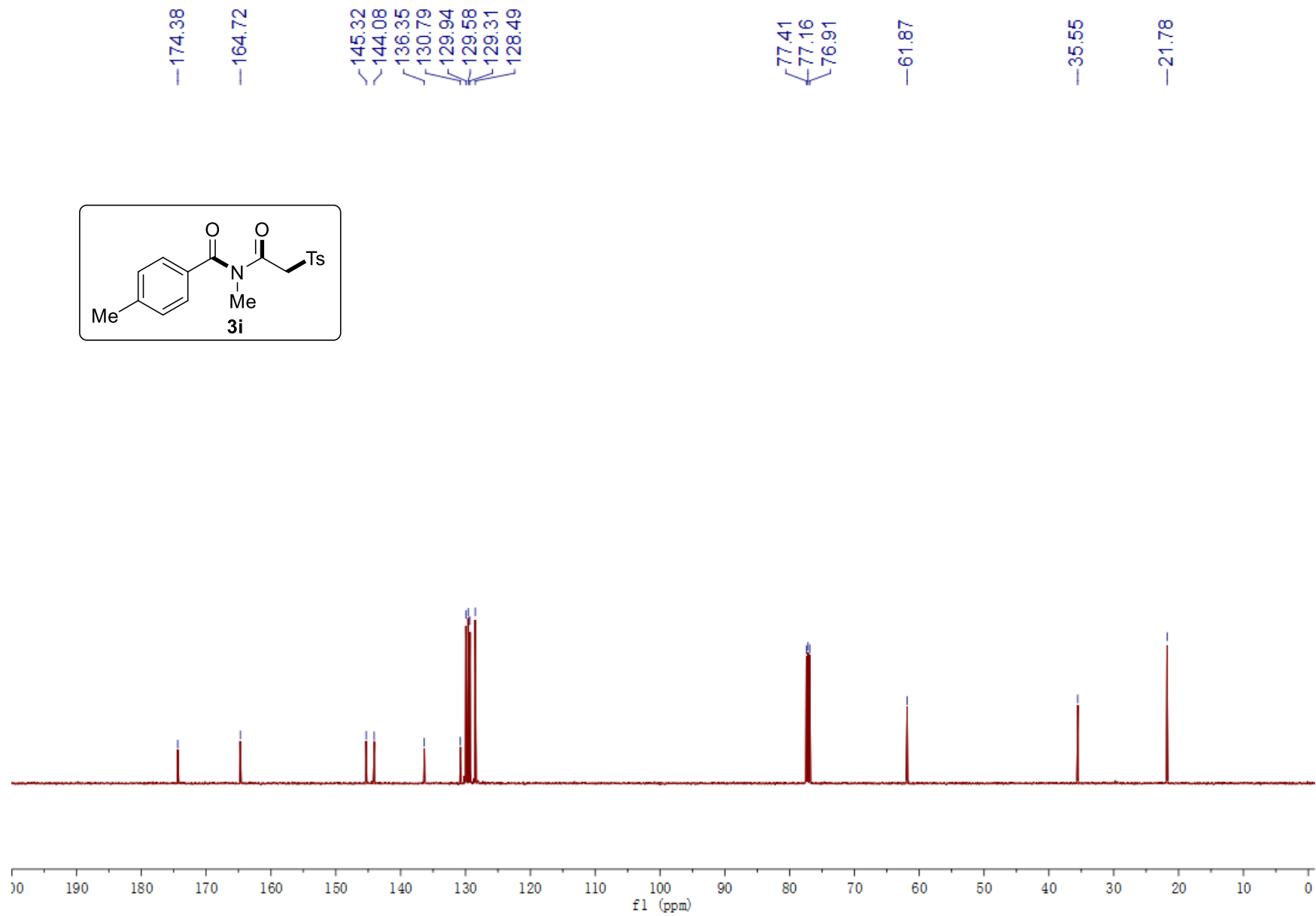
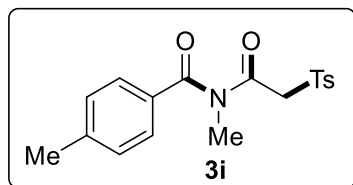
—4.810
—3.963
—3.185
—2.440

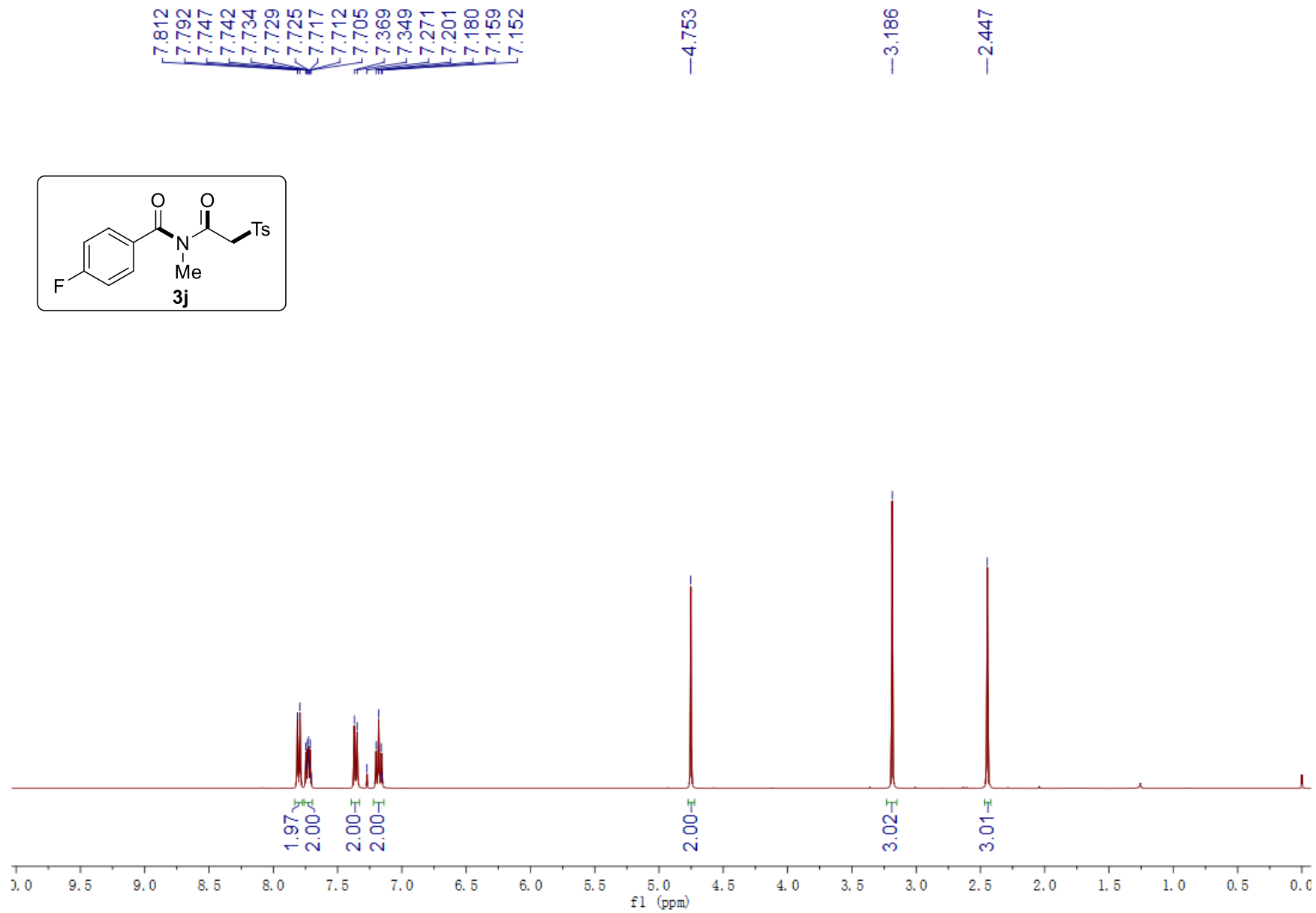
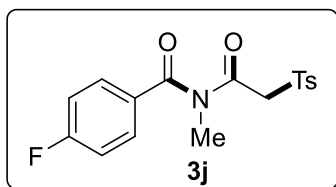


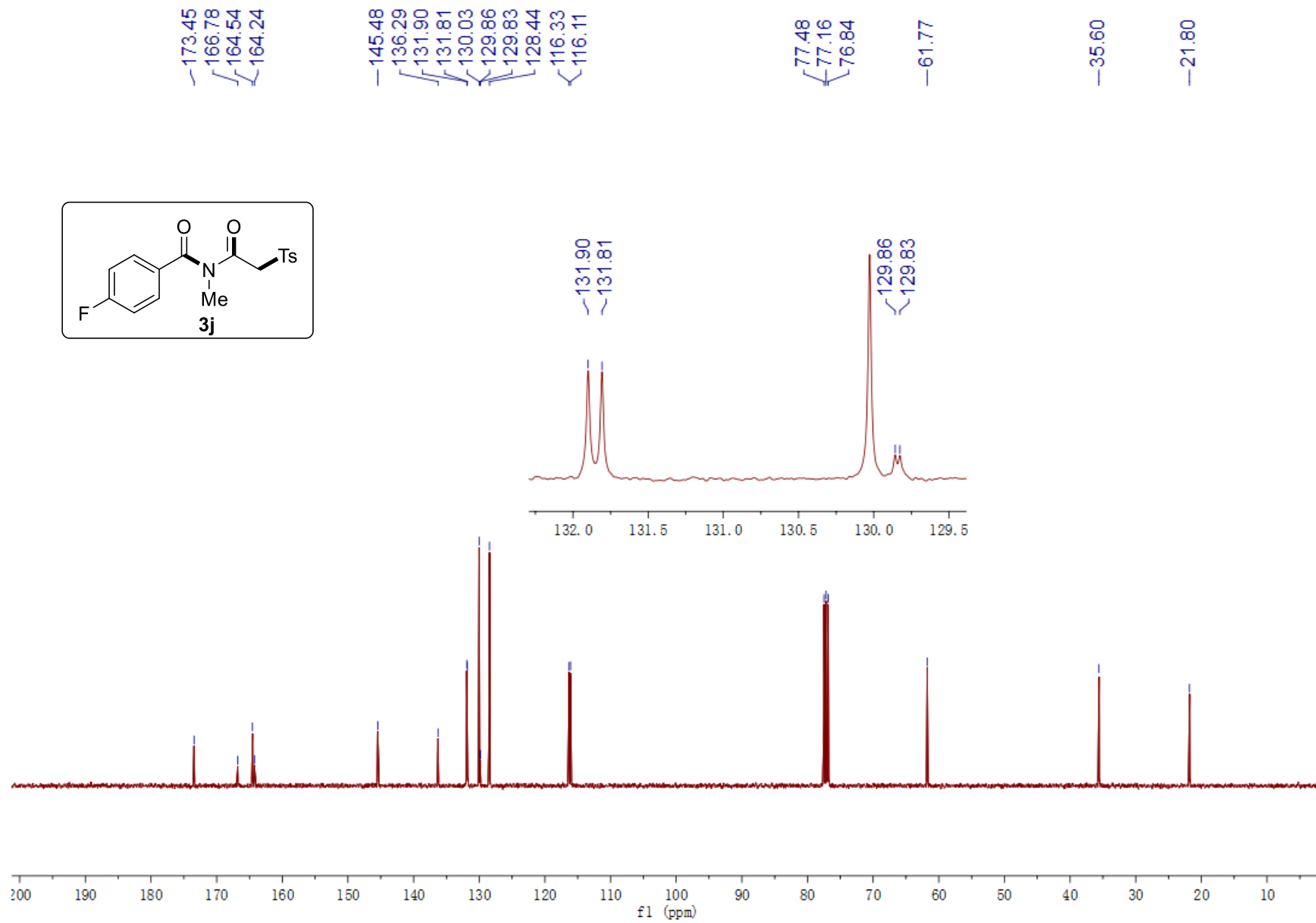
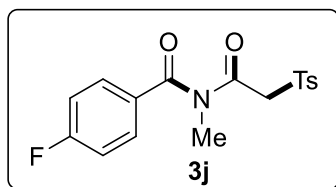


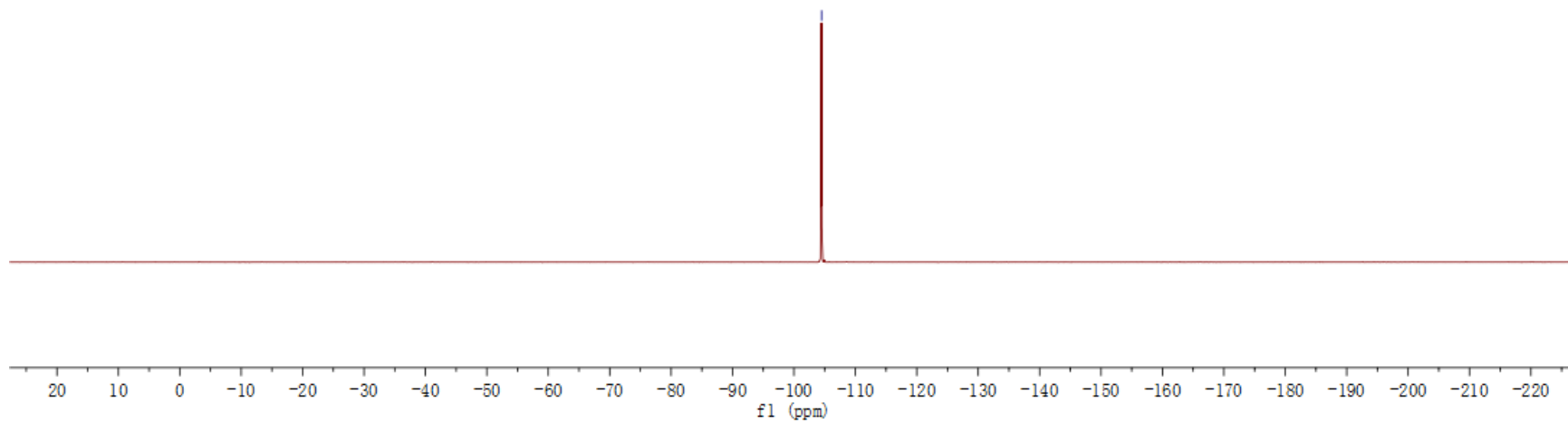
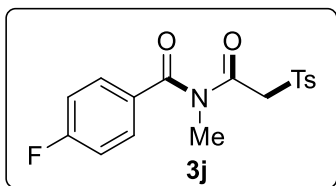


S73

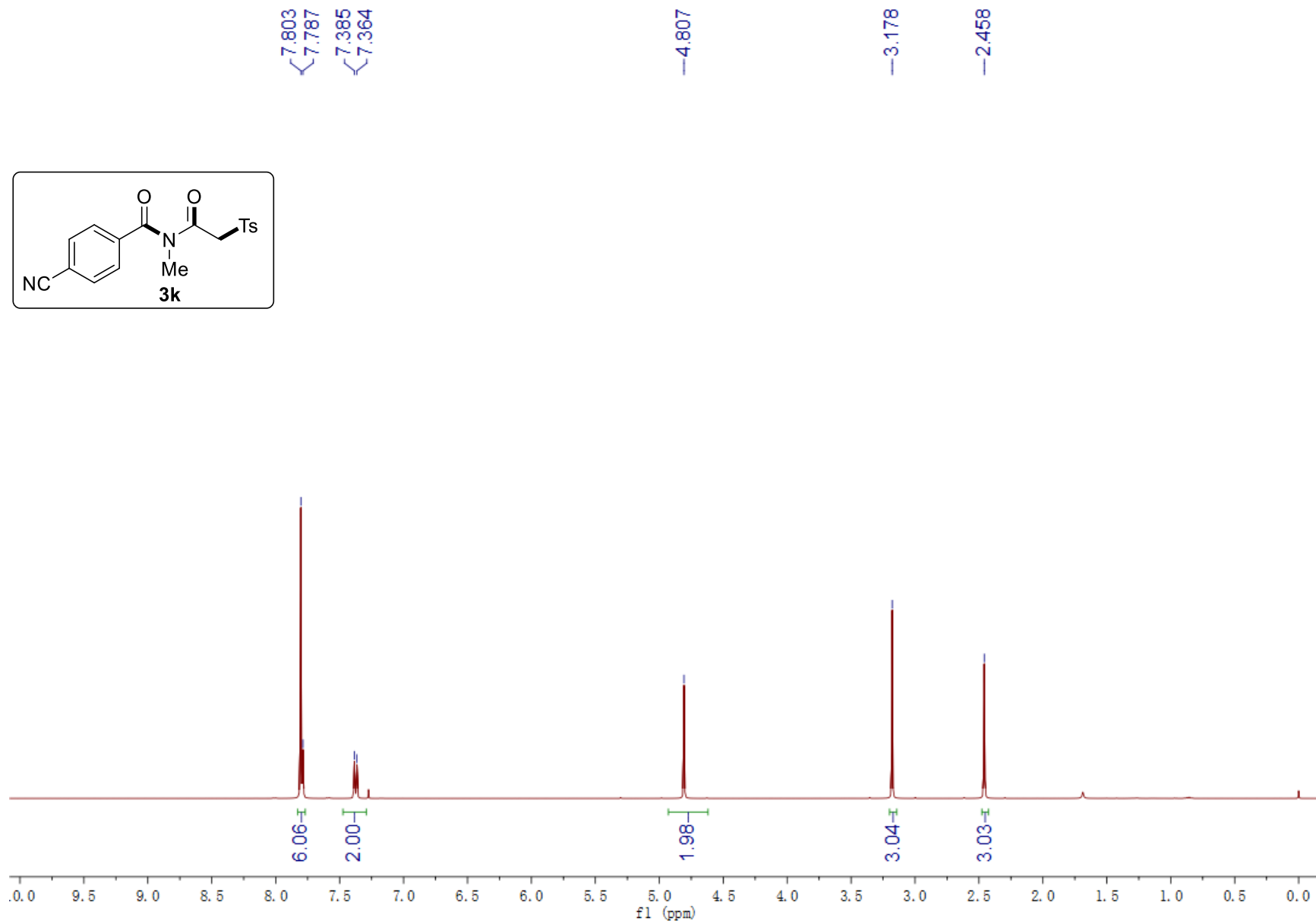
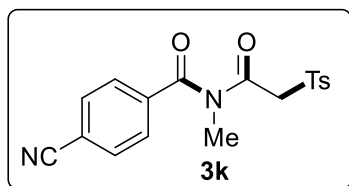


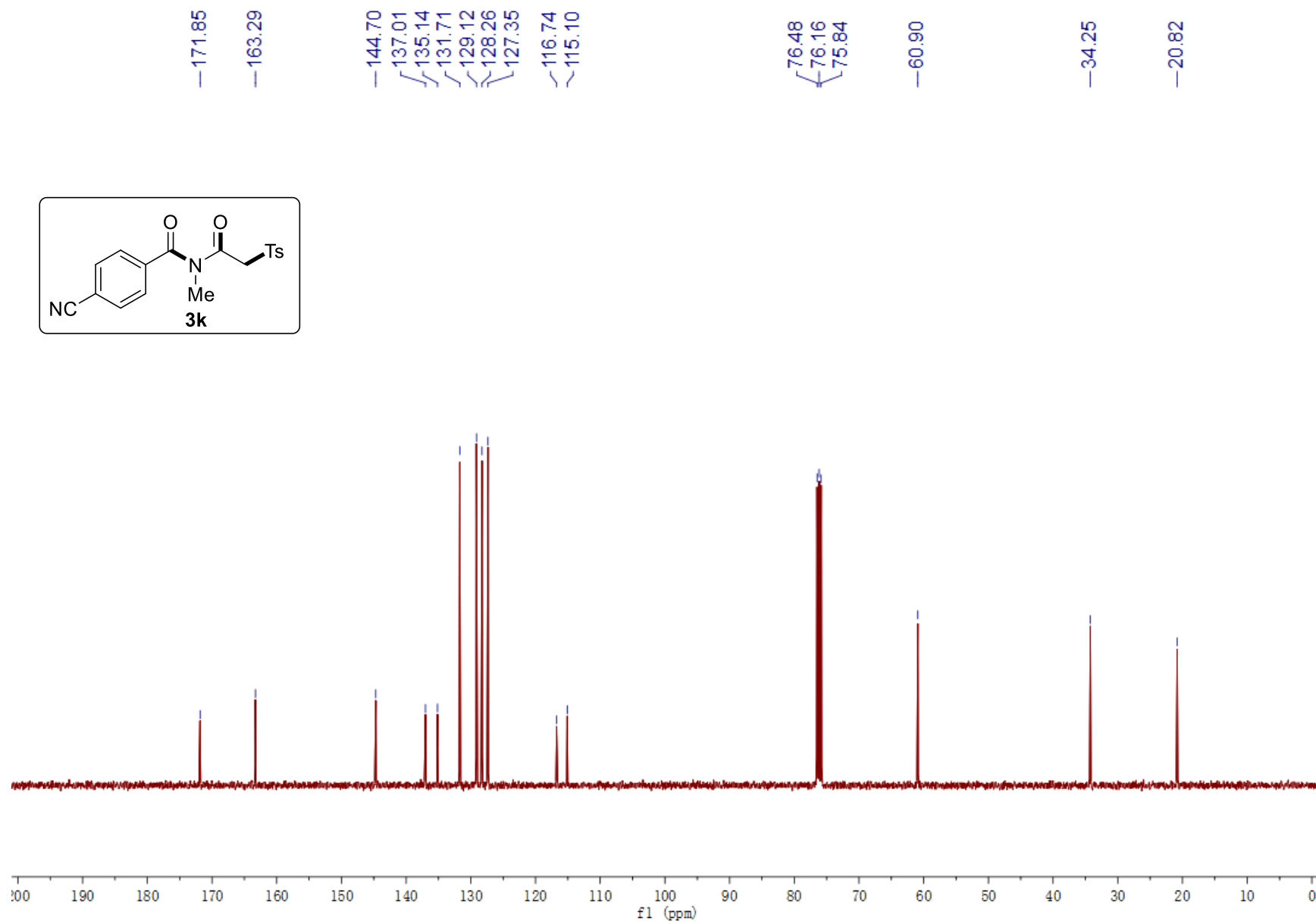
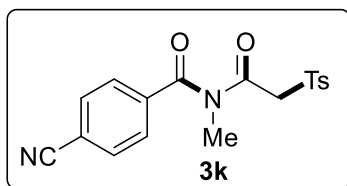


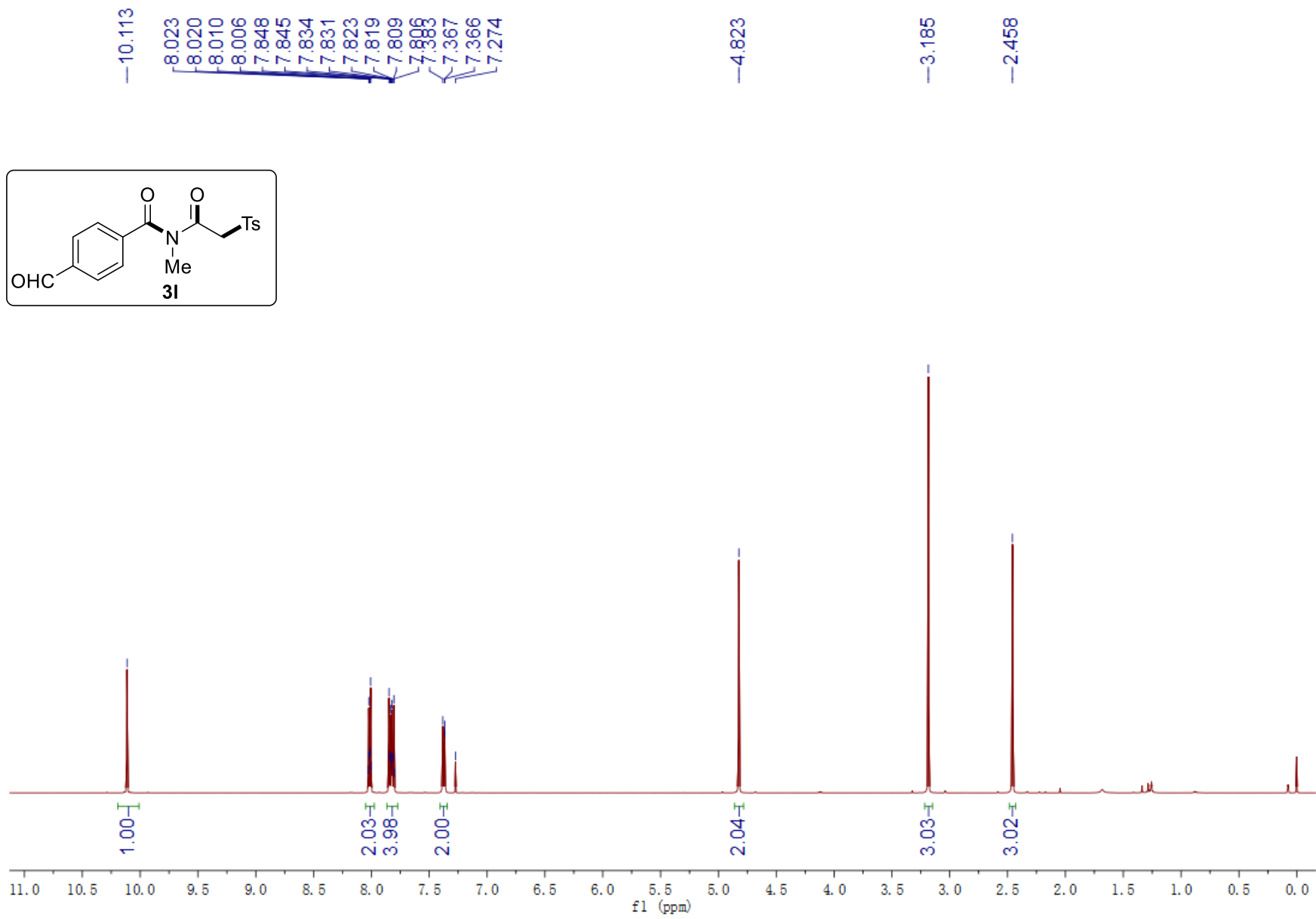


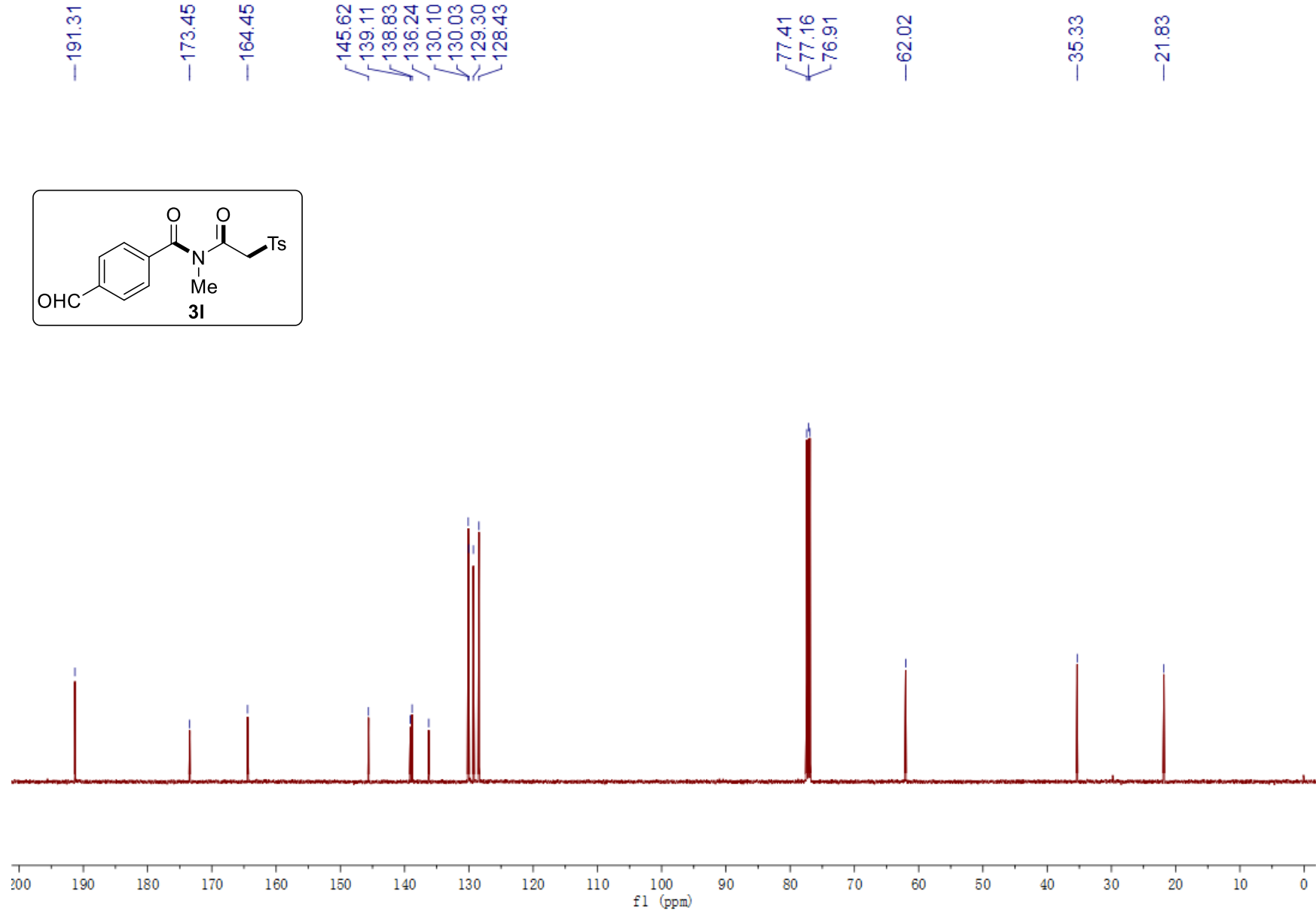
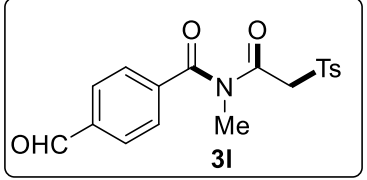


S77

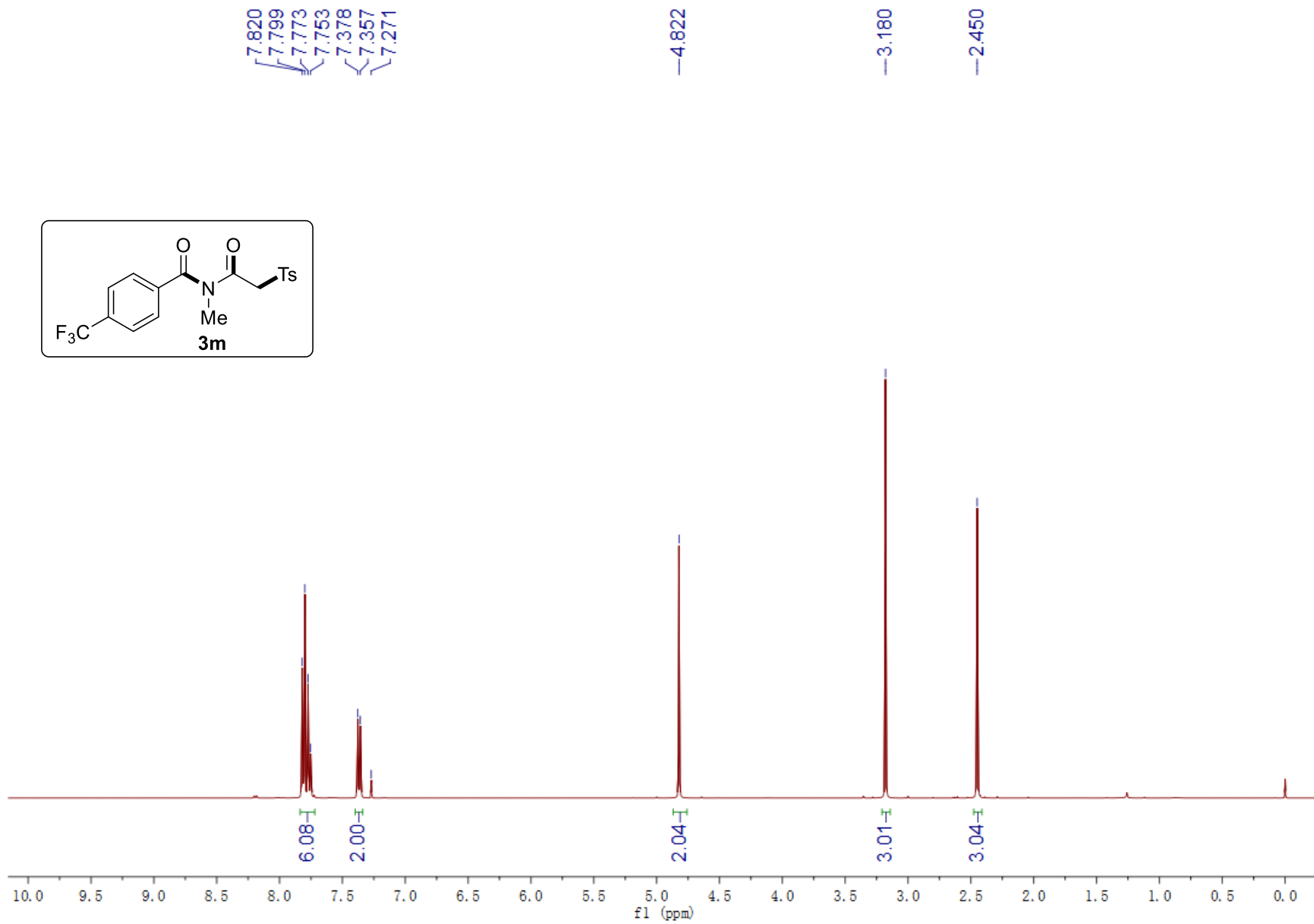
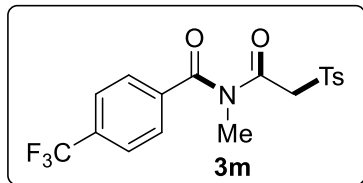




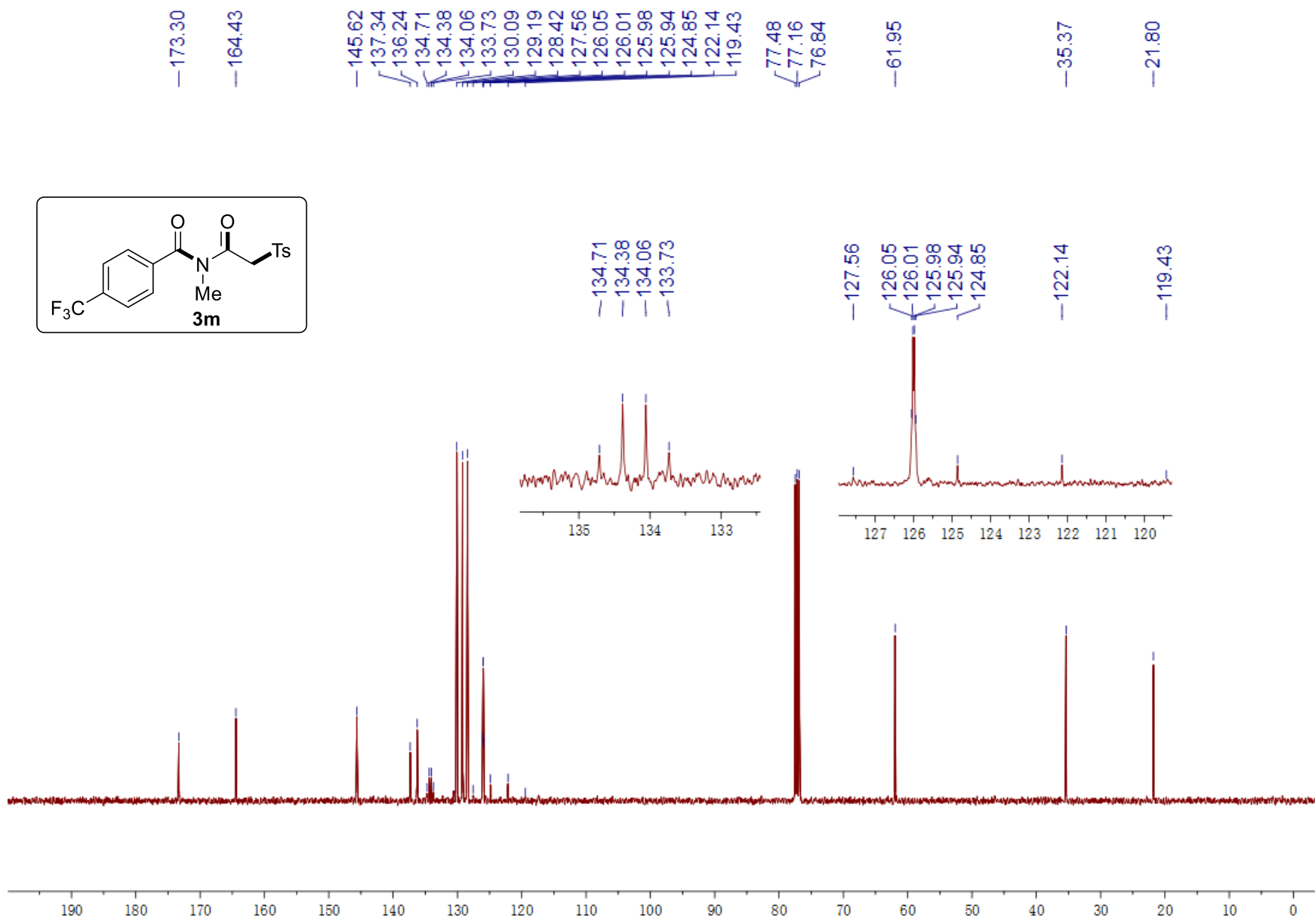


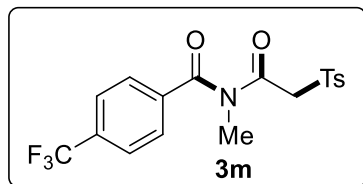


S81

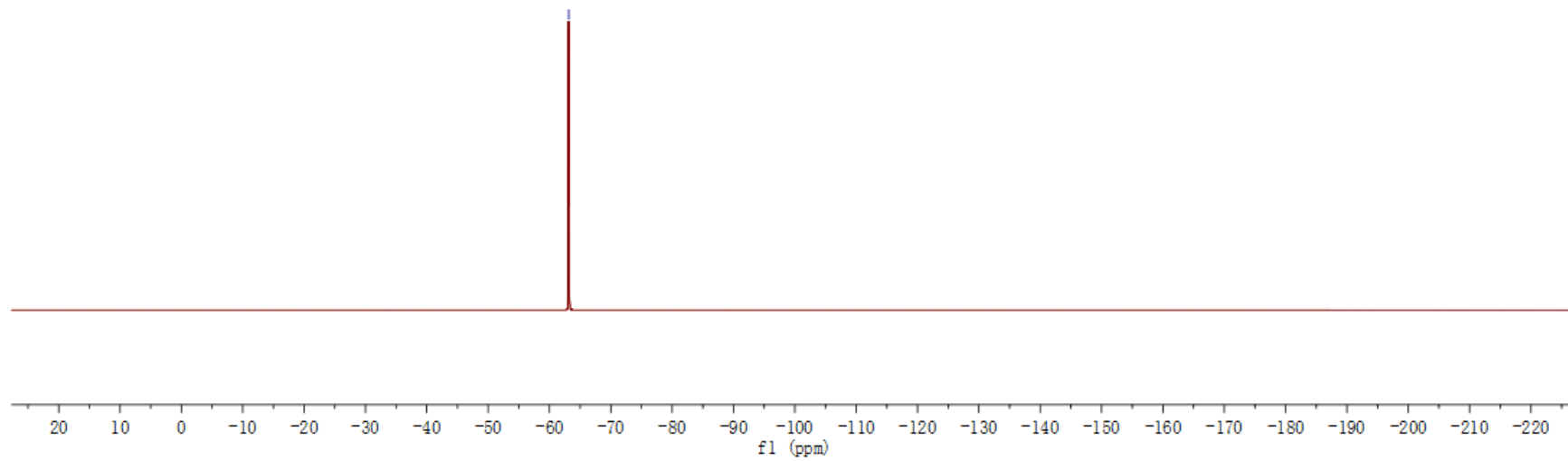


S82

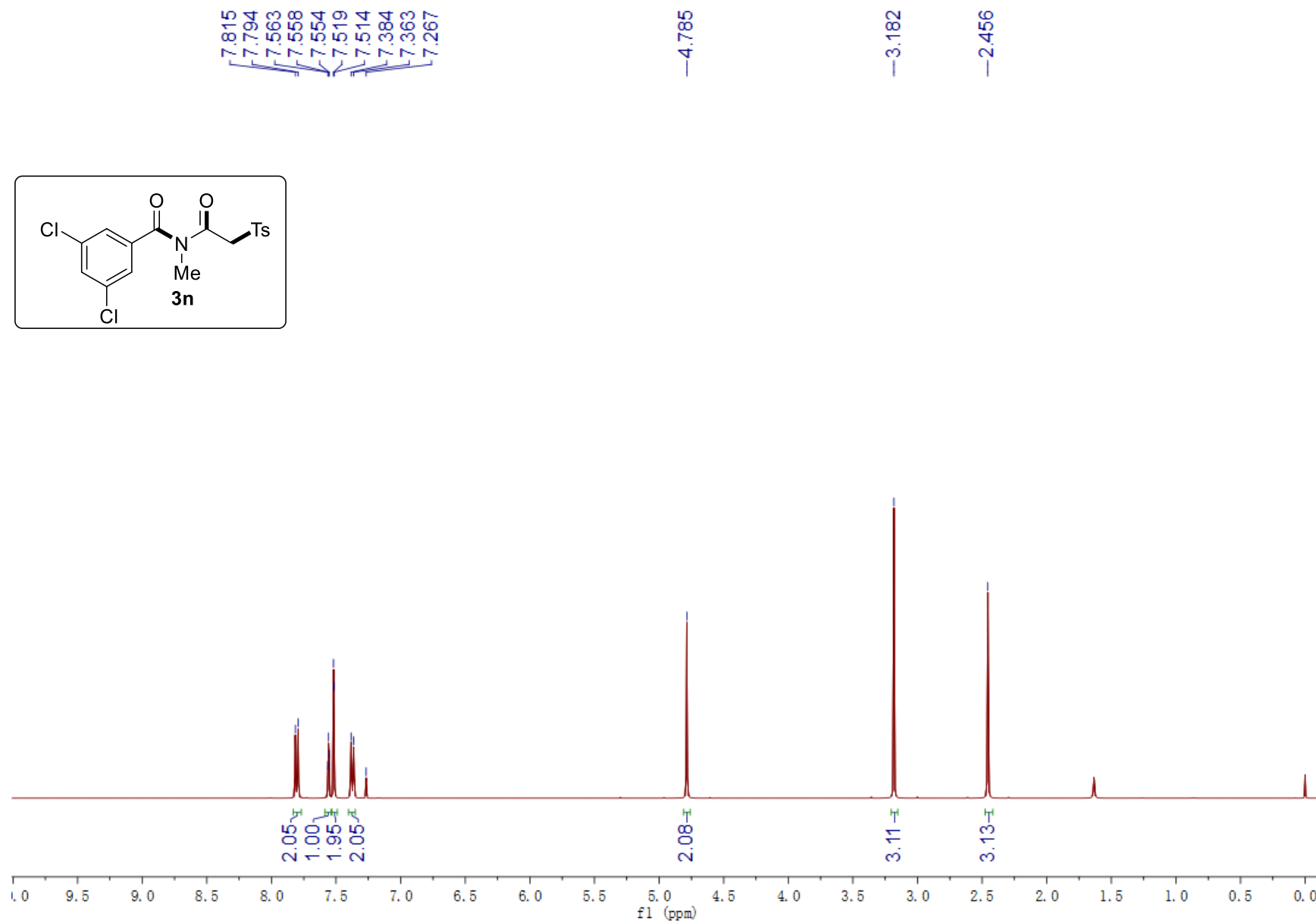
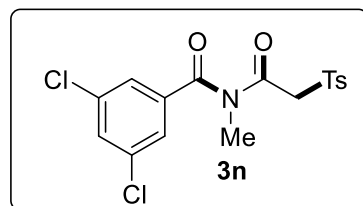




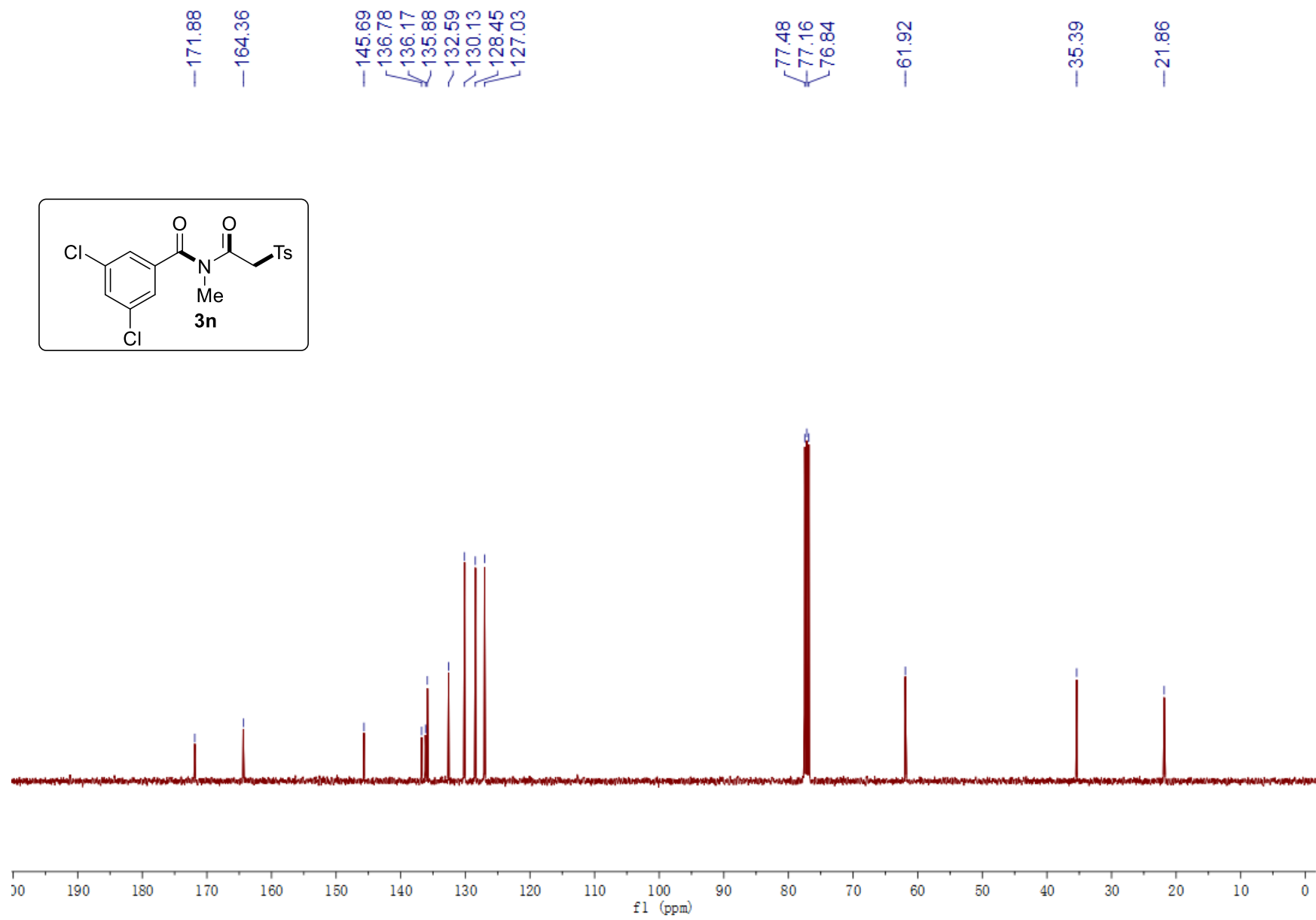
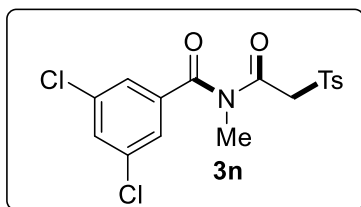
--63.139

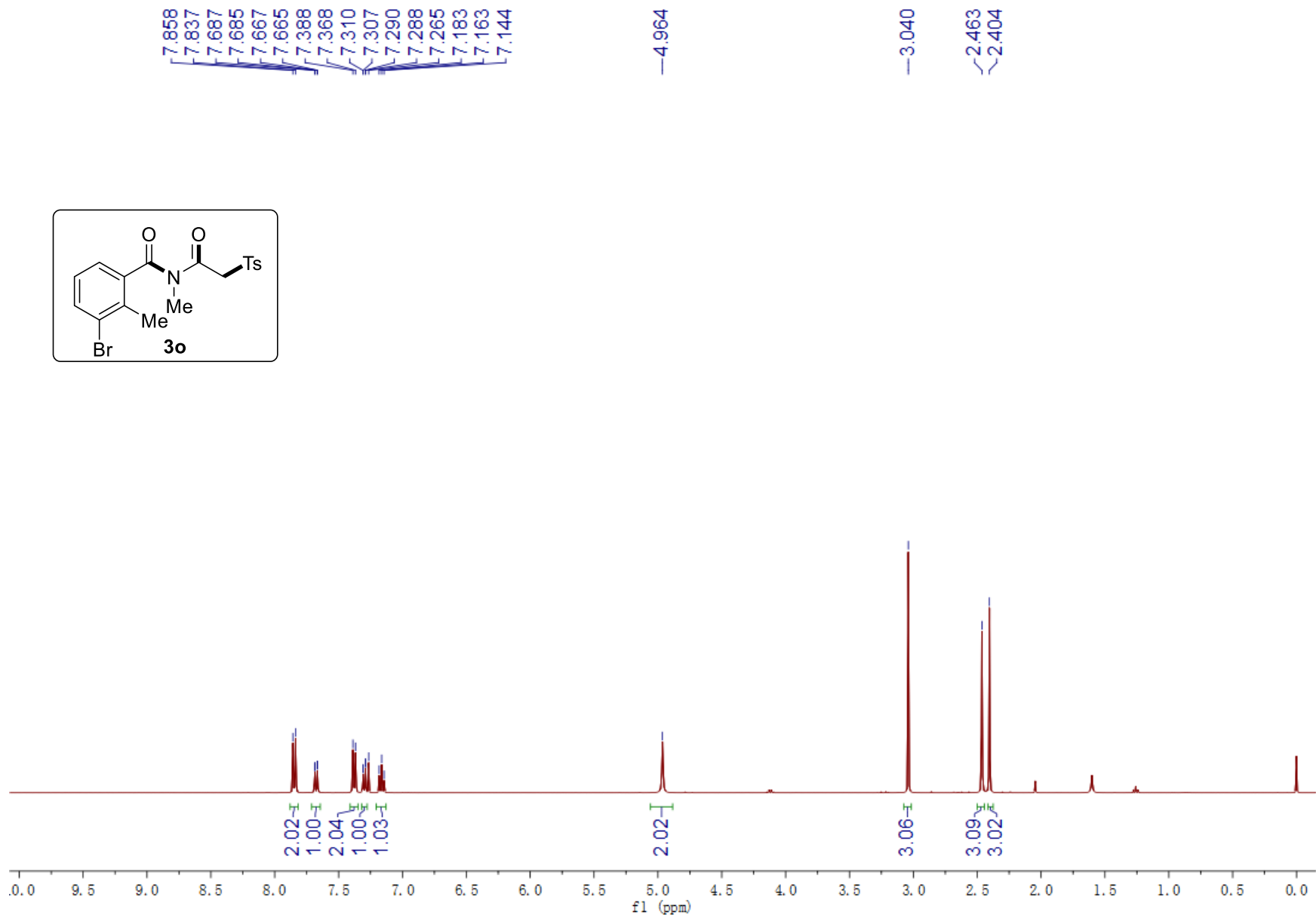
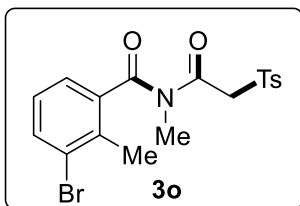


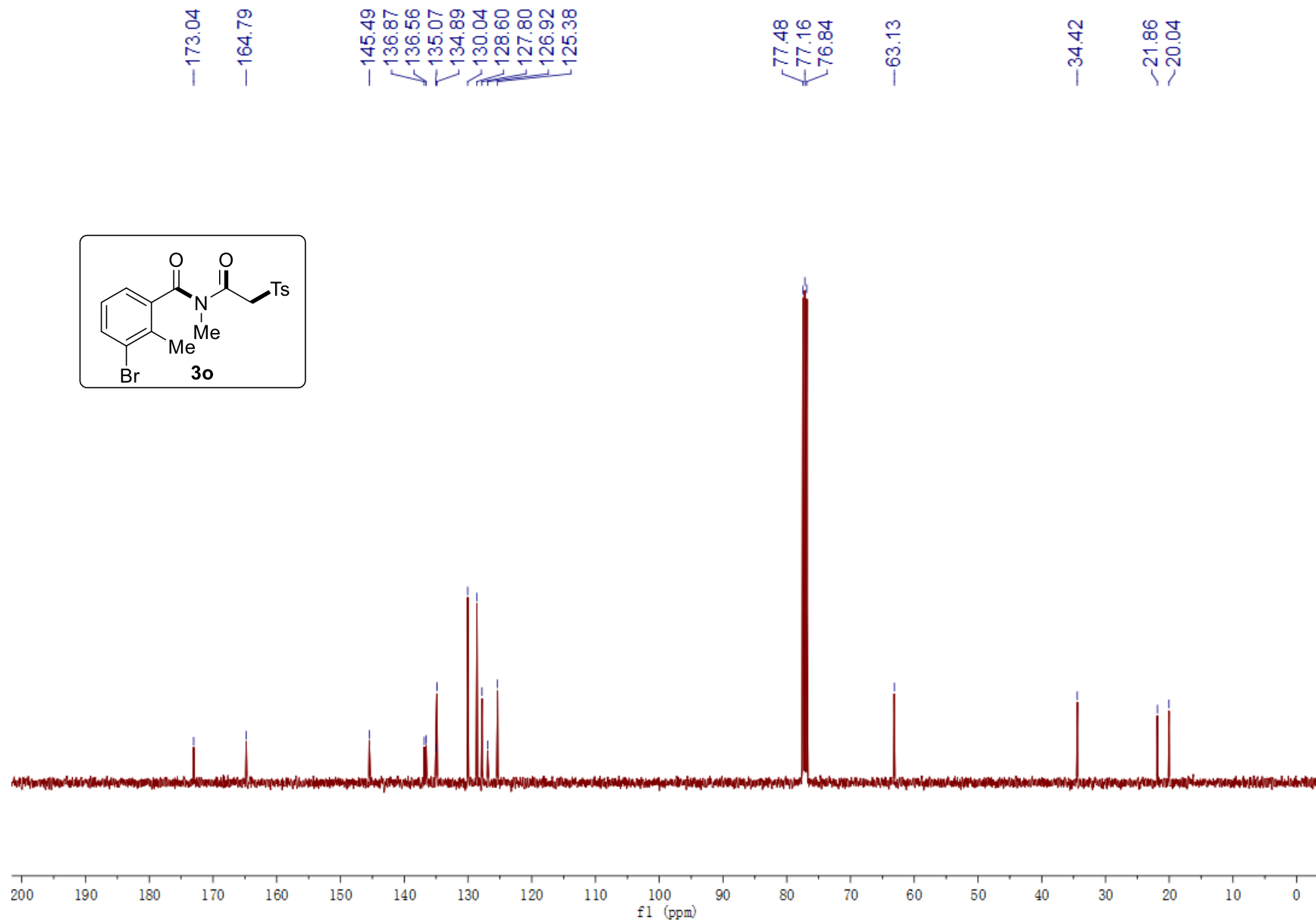
S84

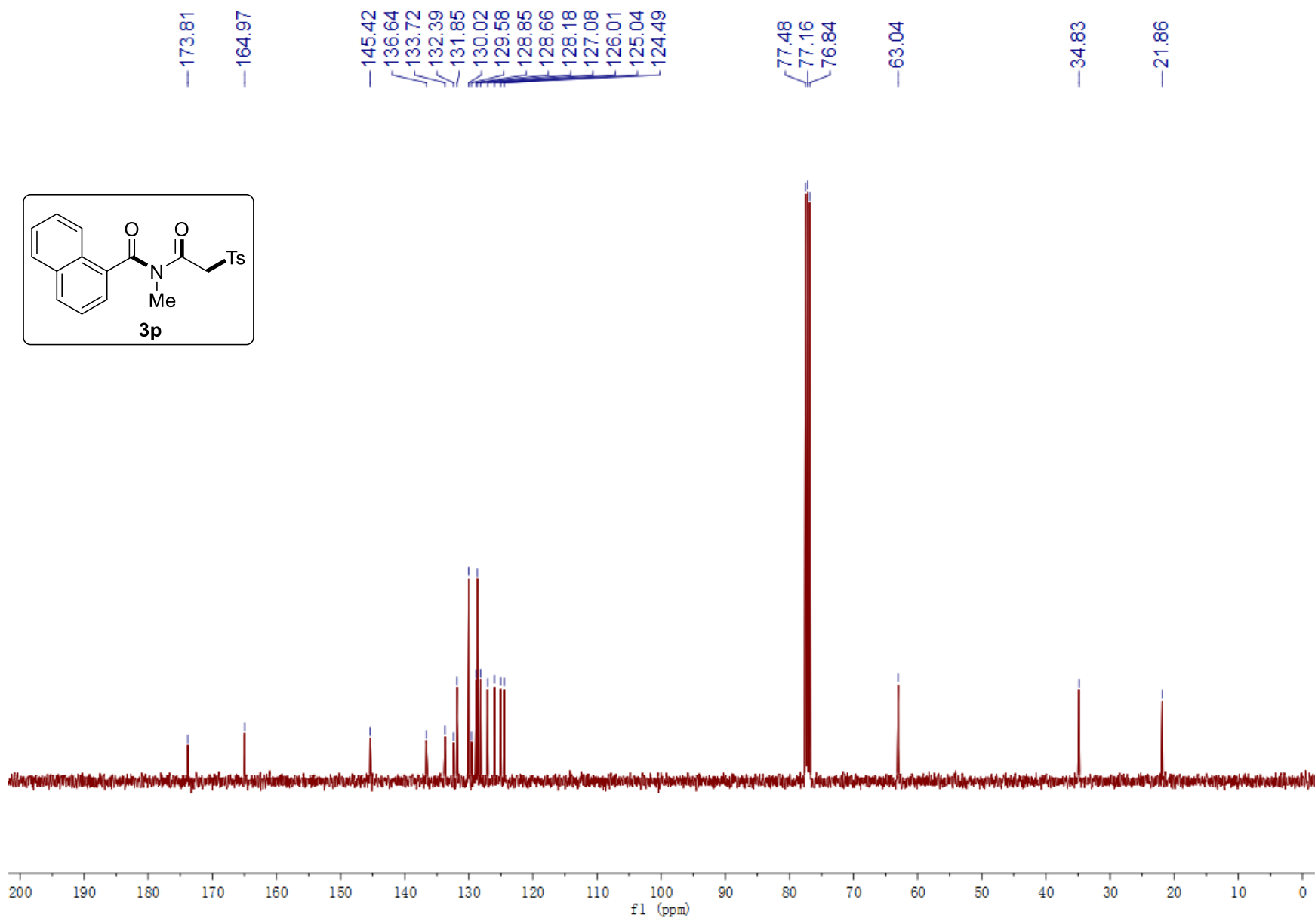


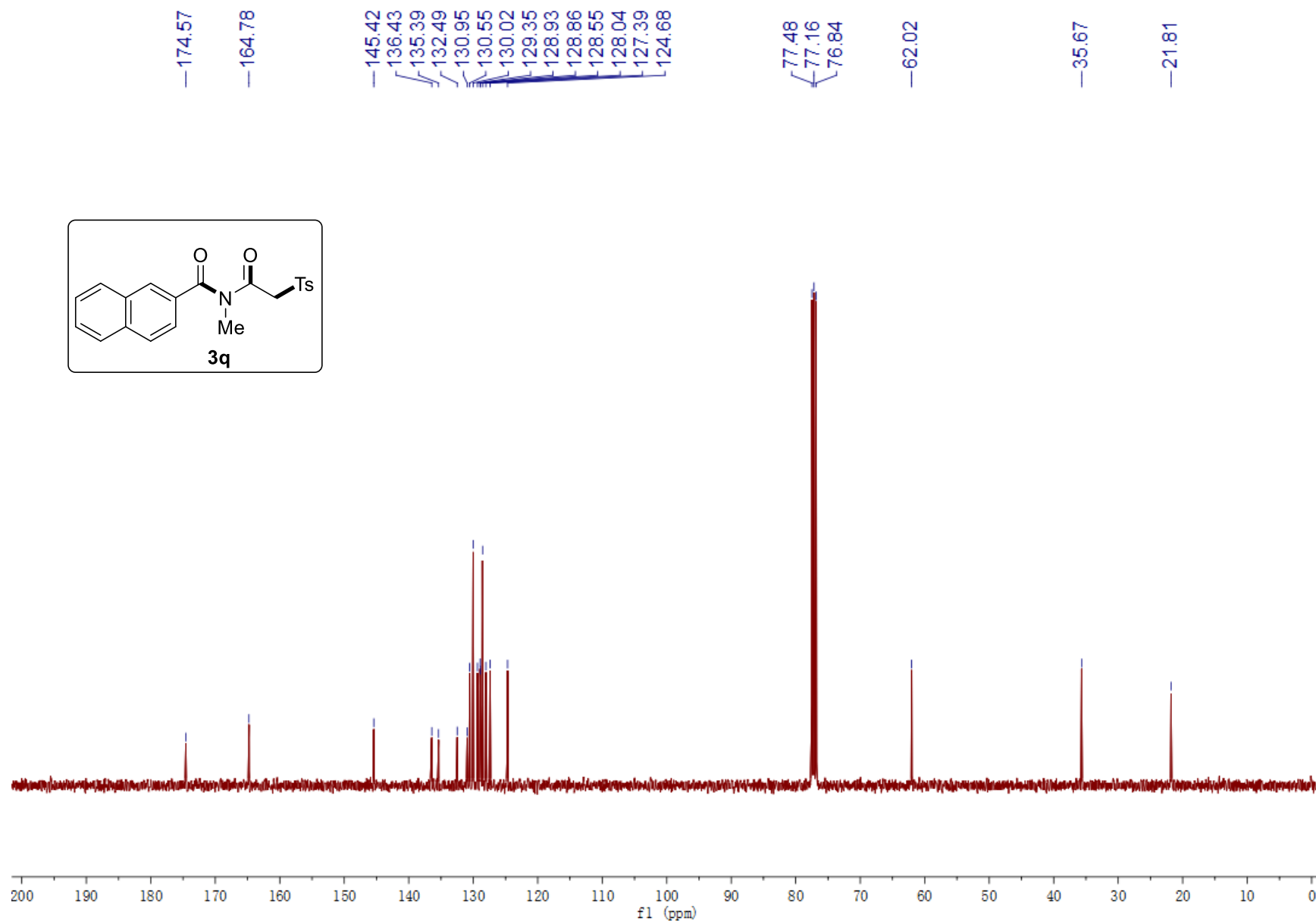
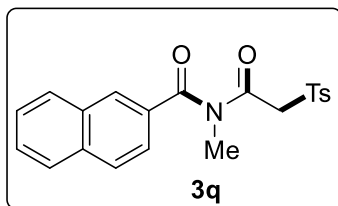
S85

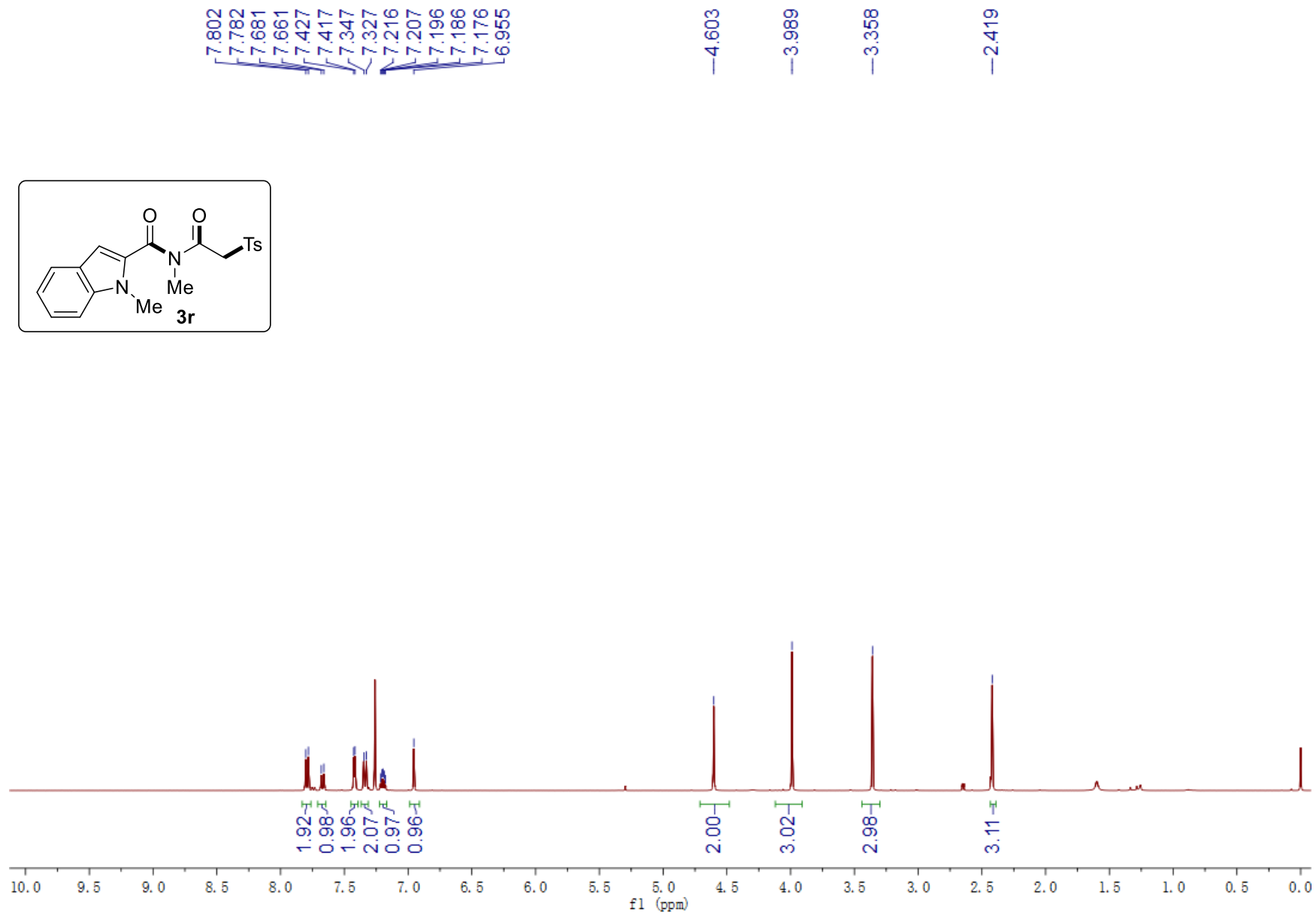
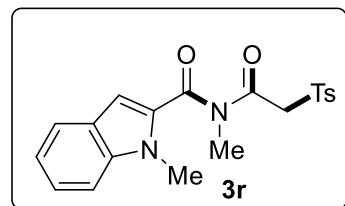


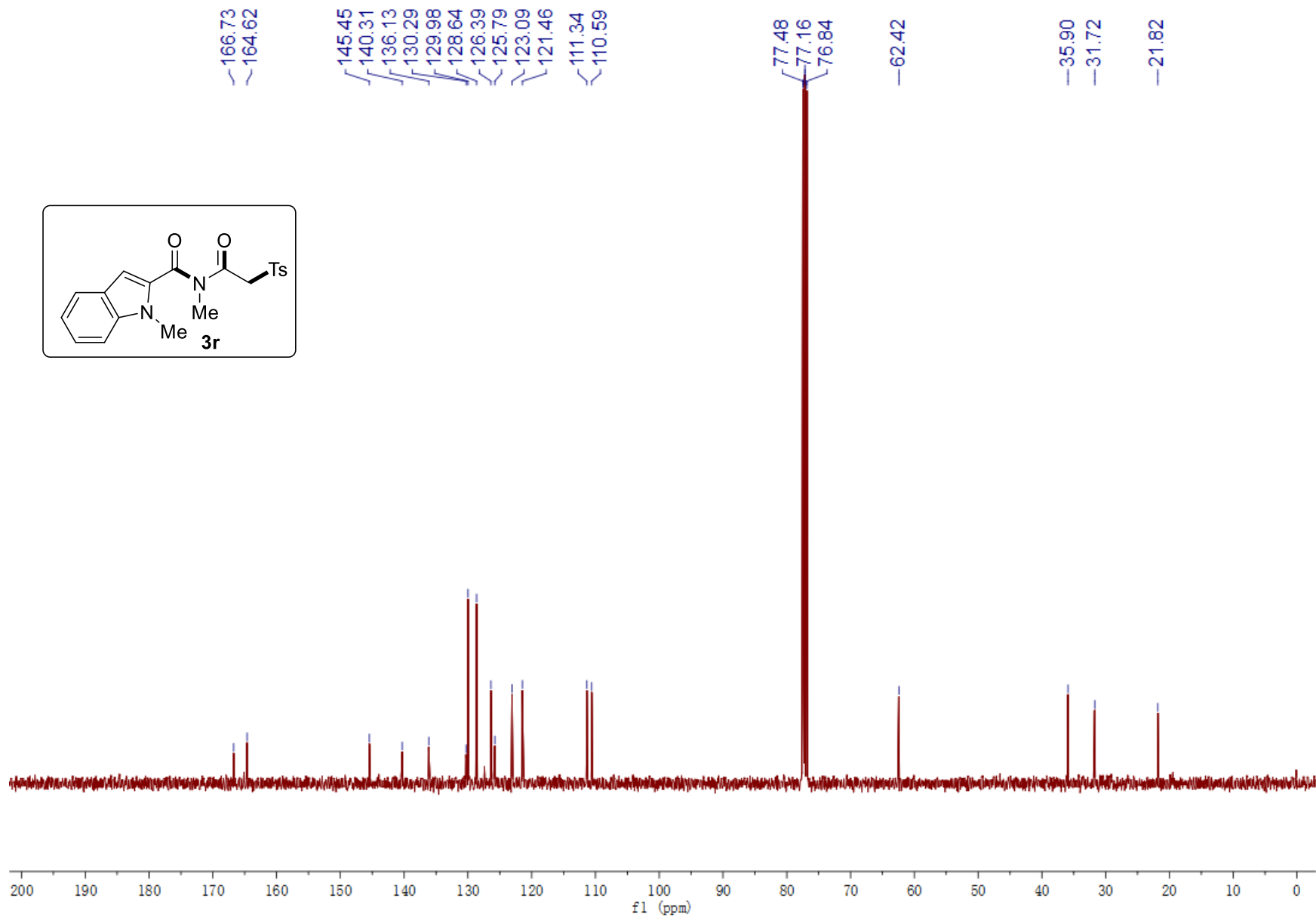
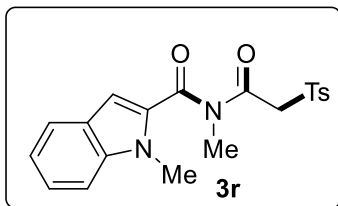


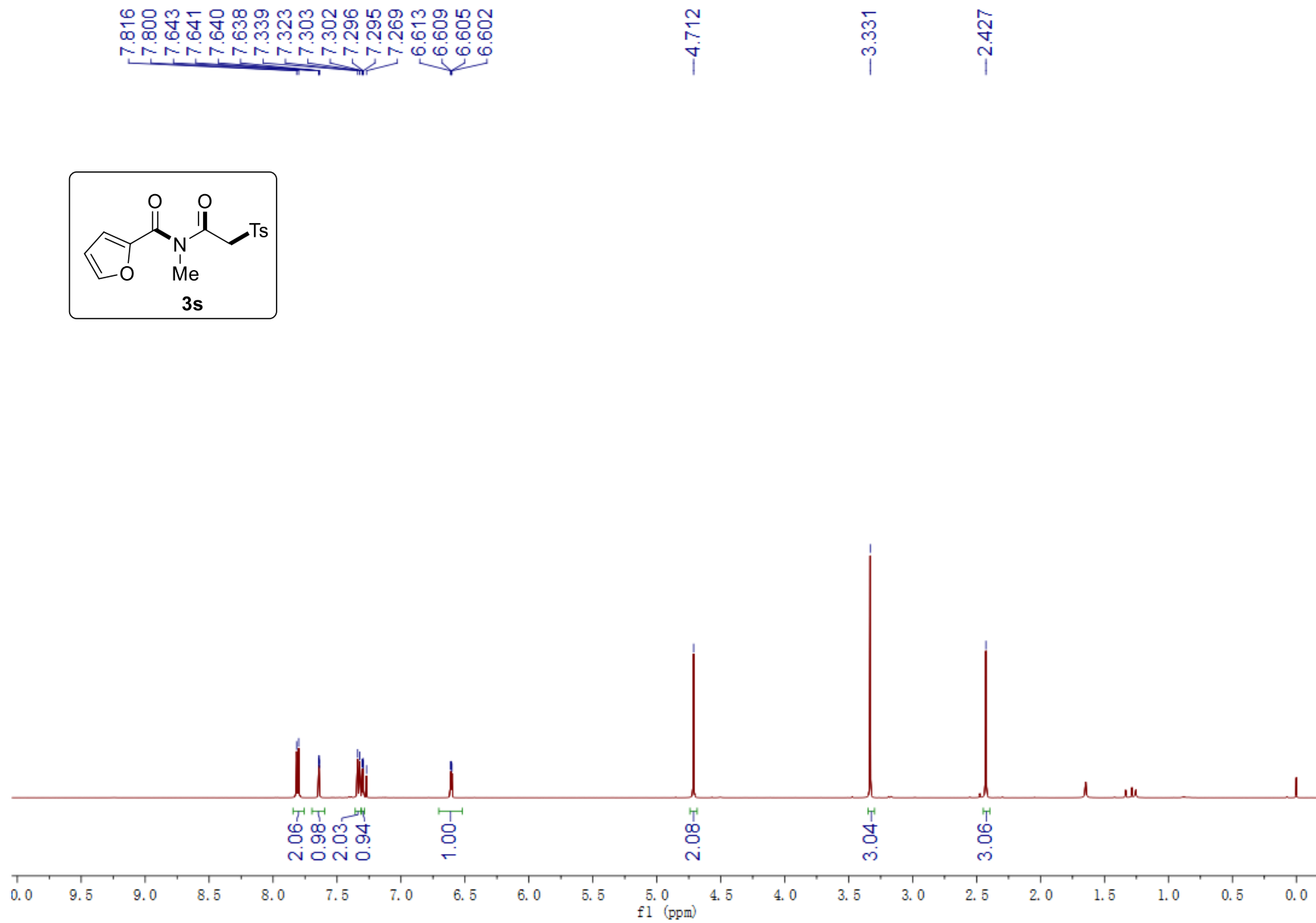
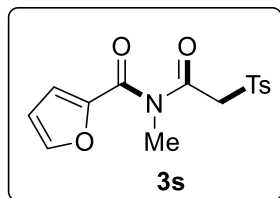


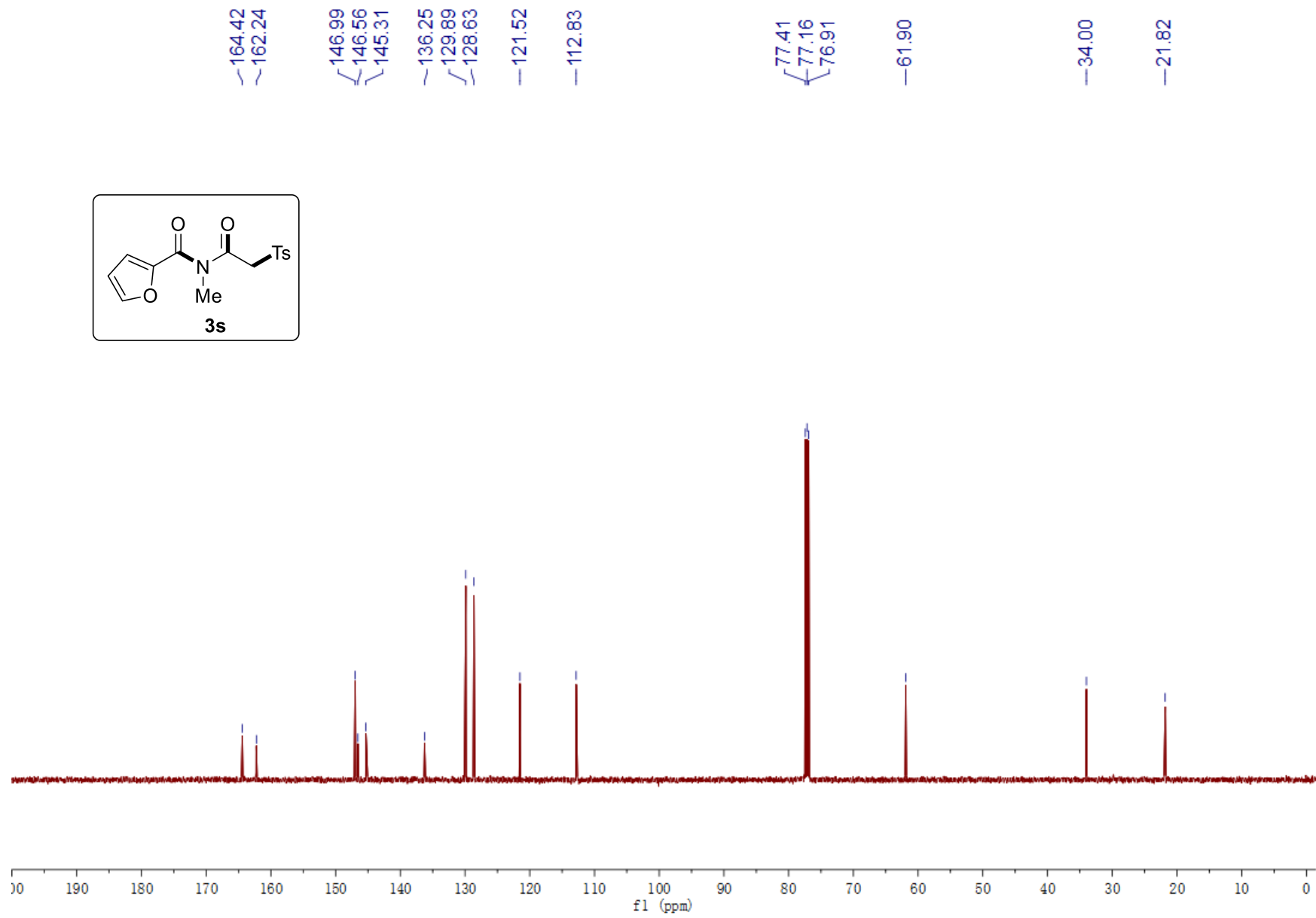
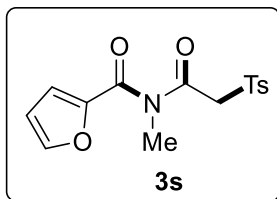


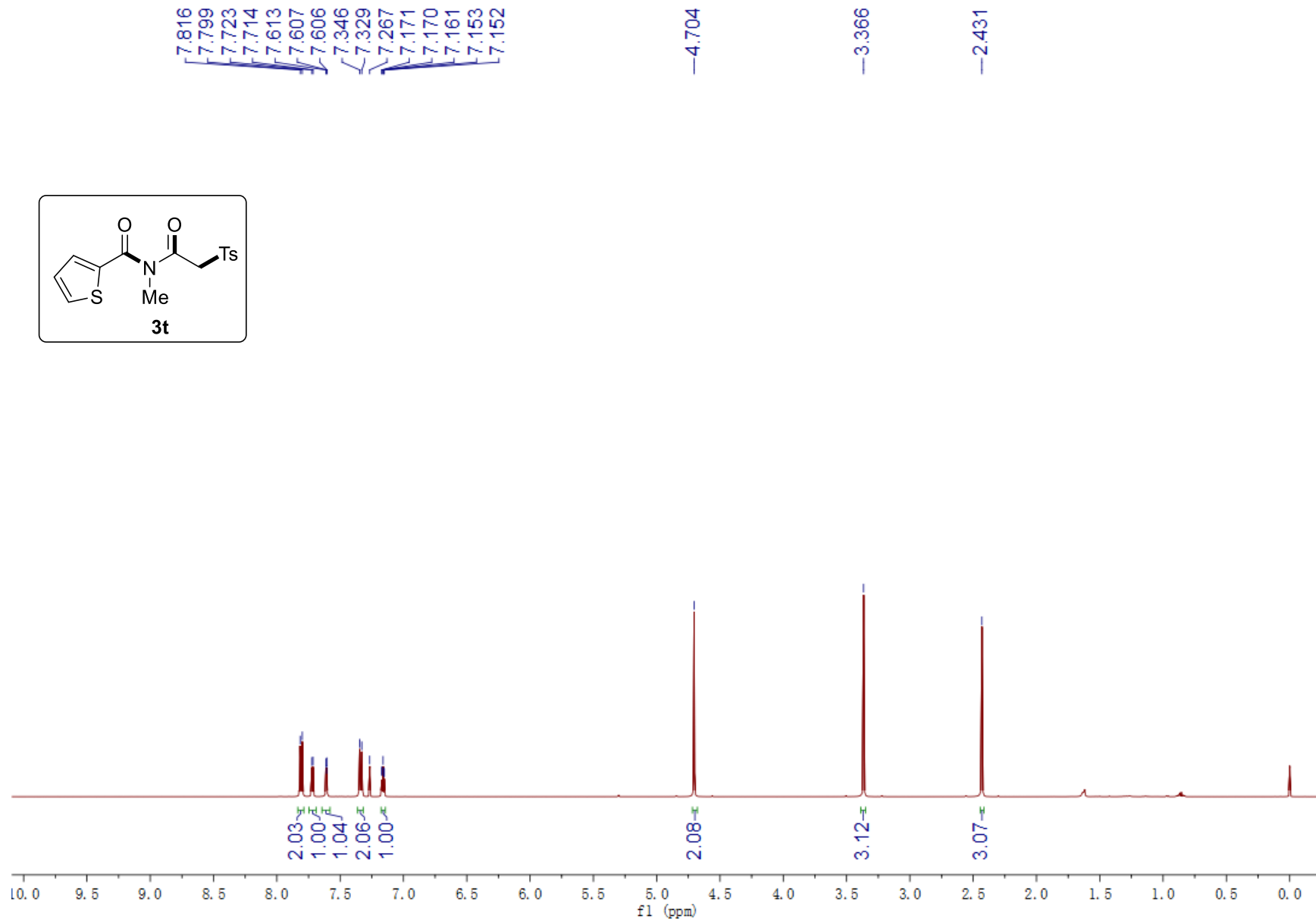
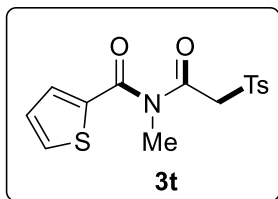


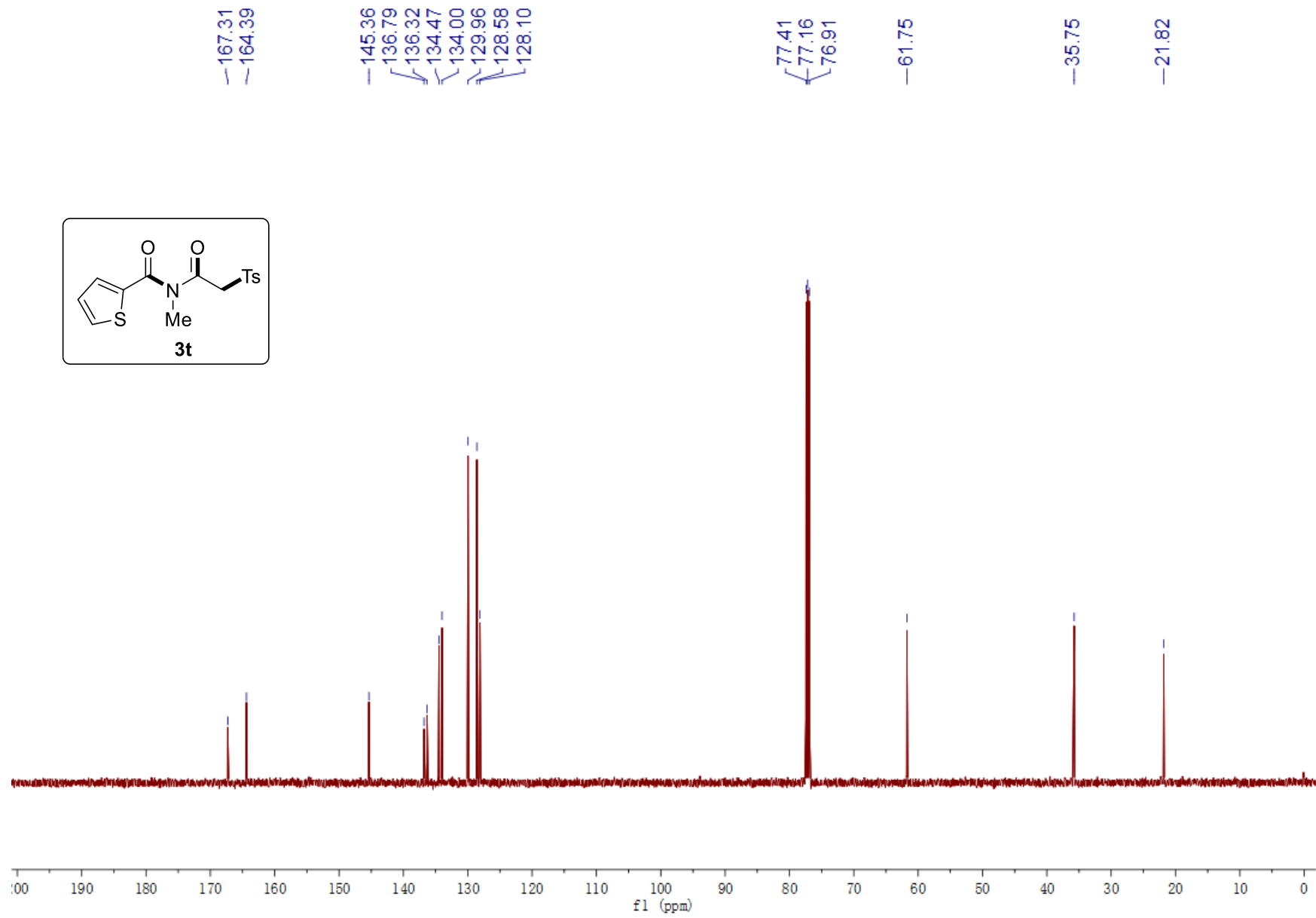
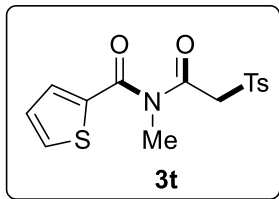


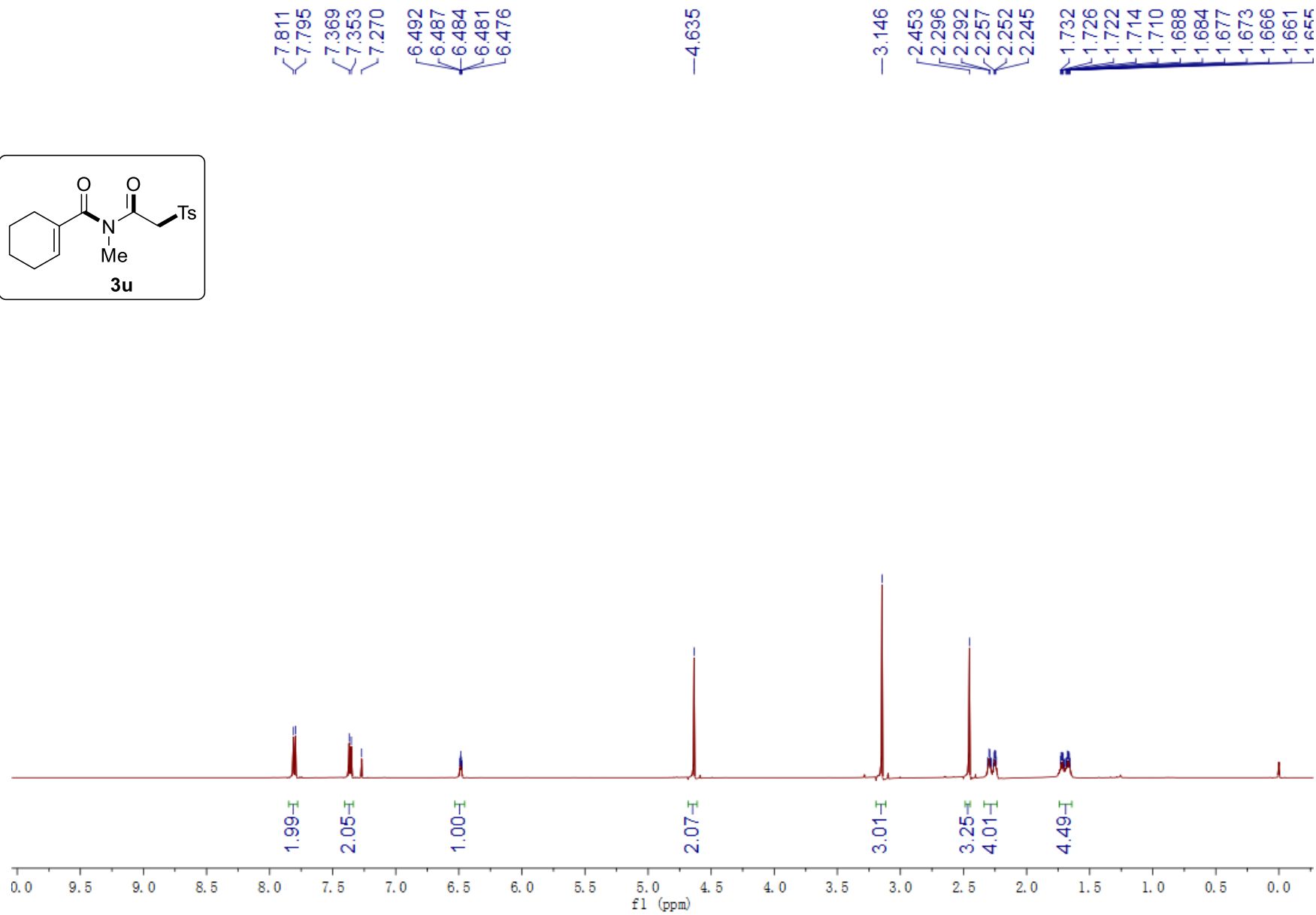
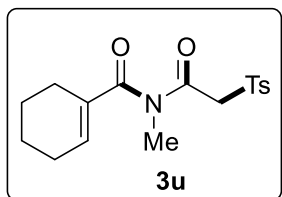


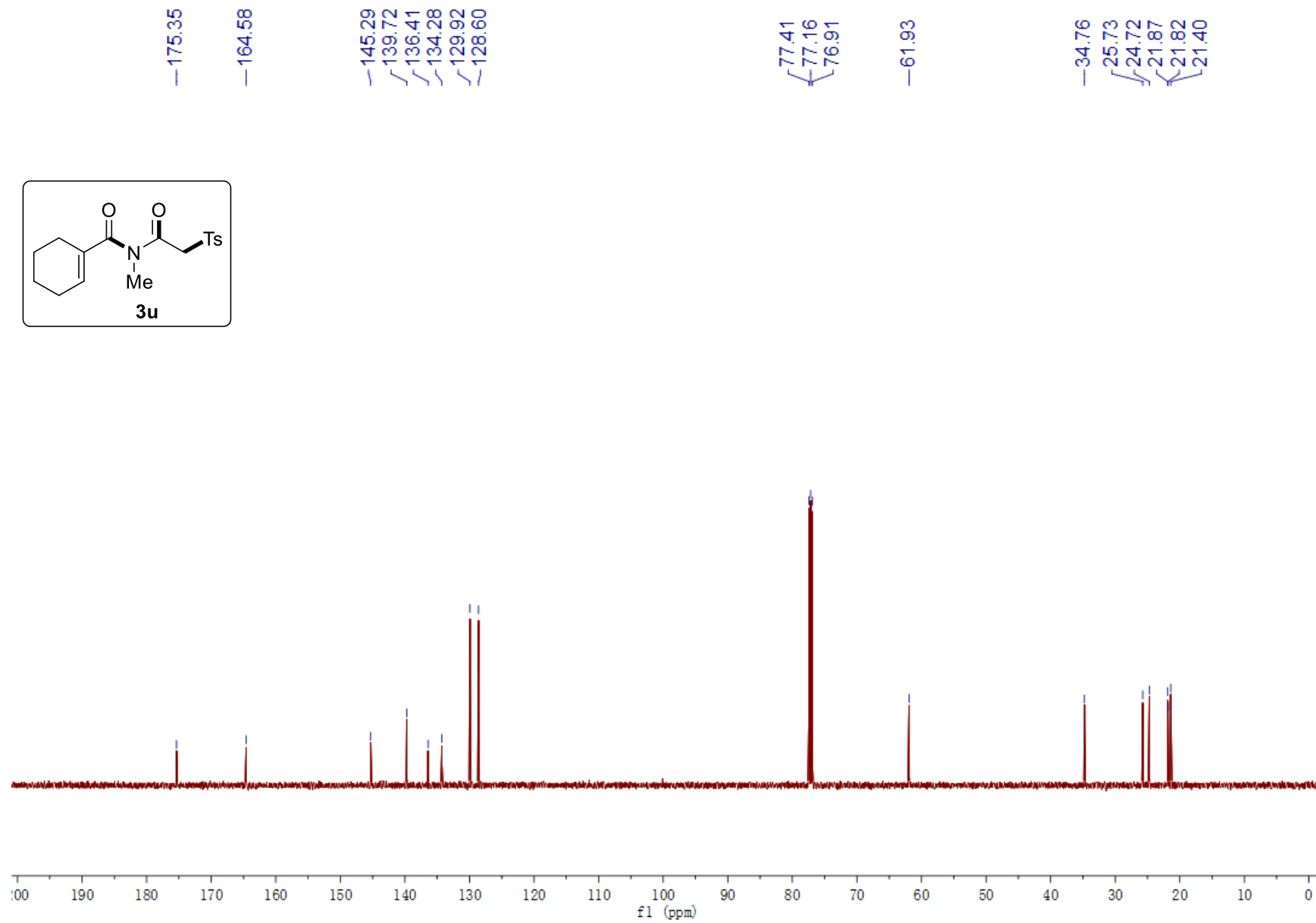
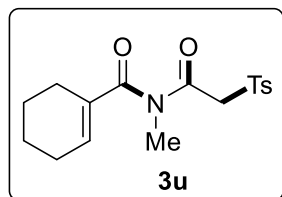




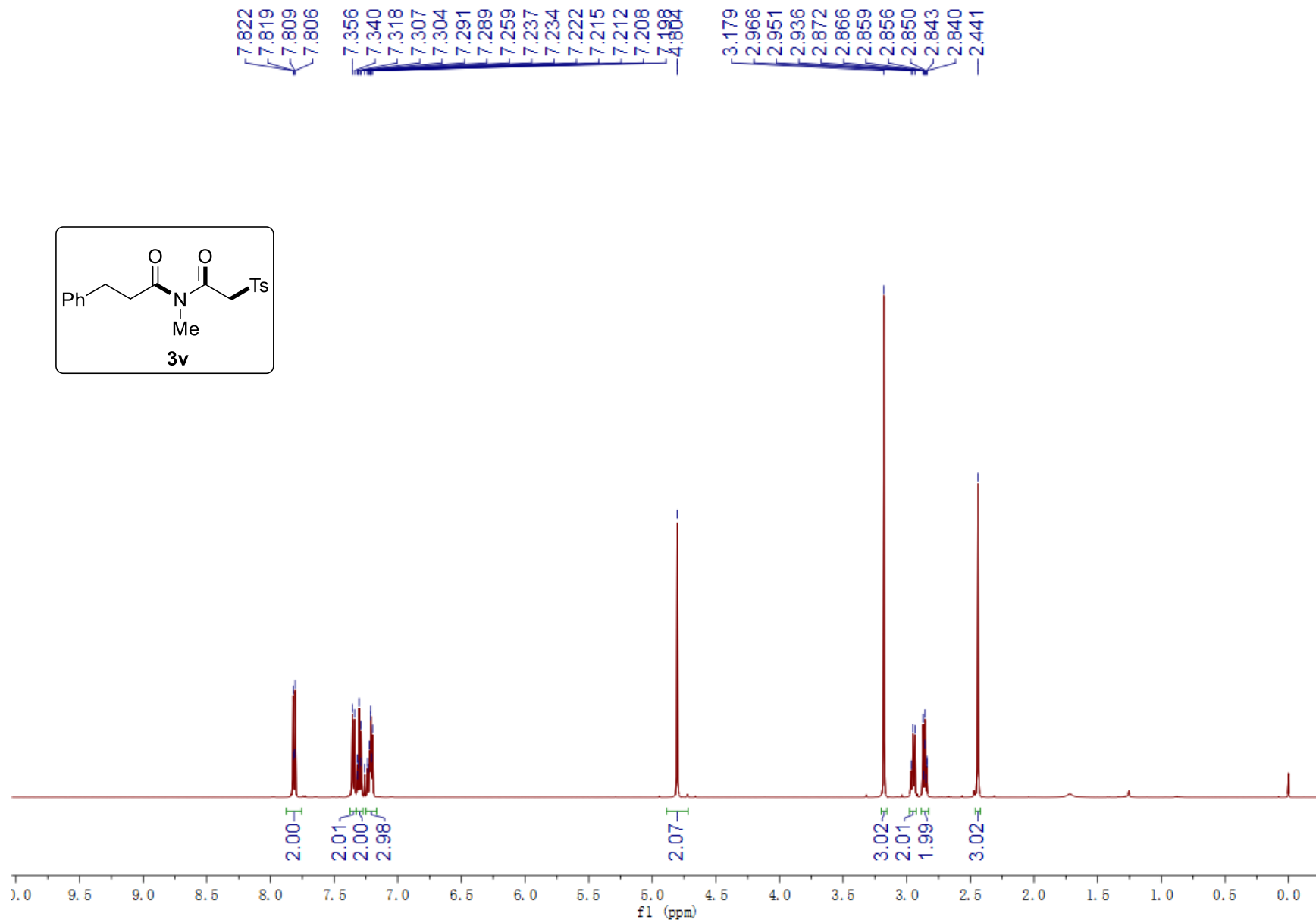
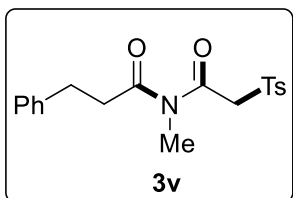




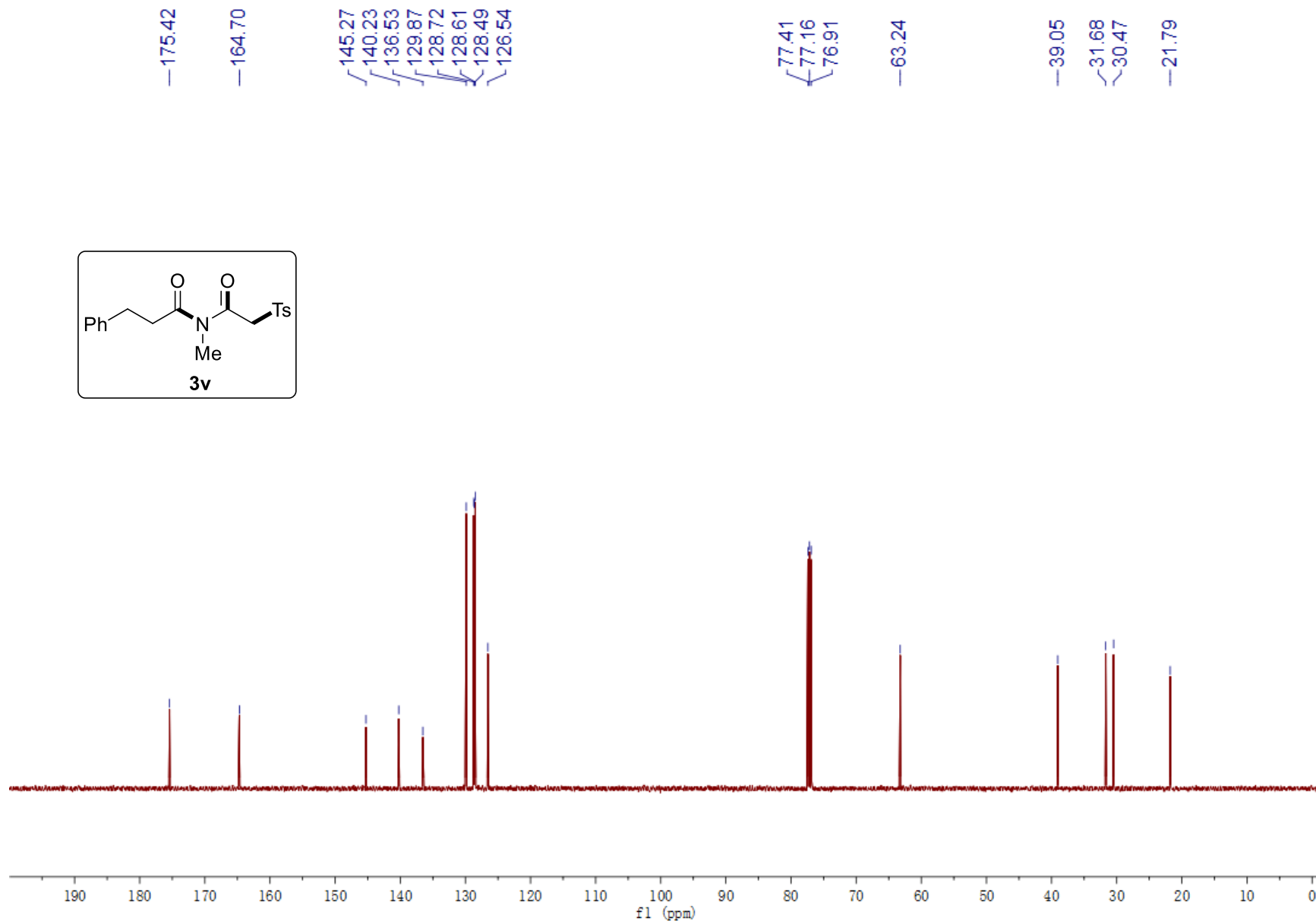
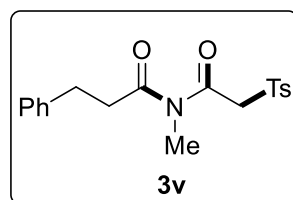




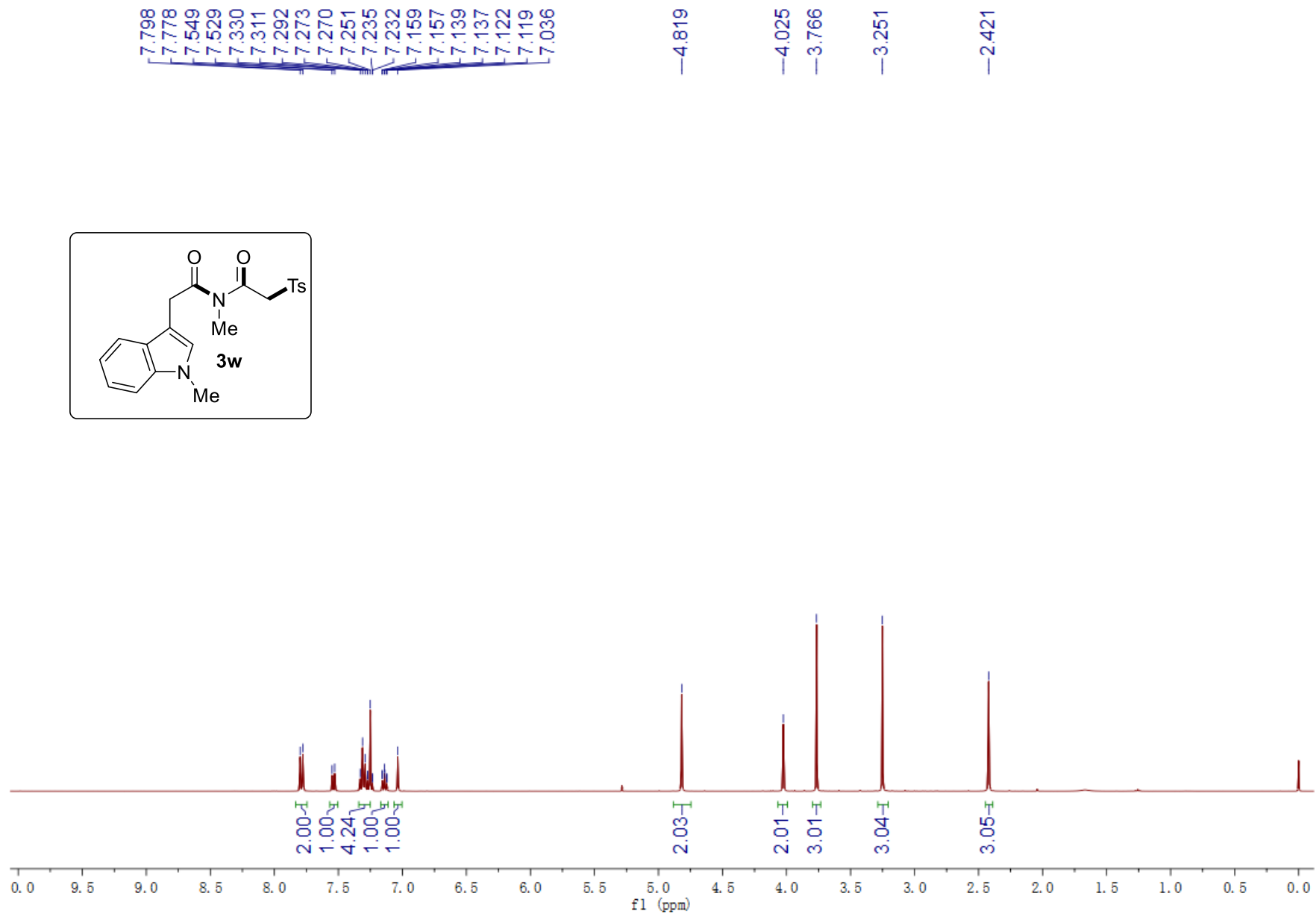
S100



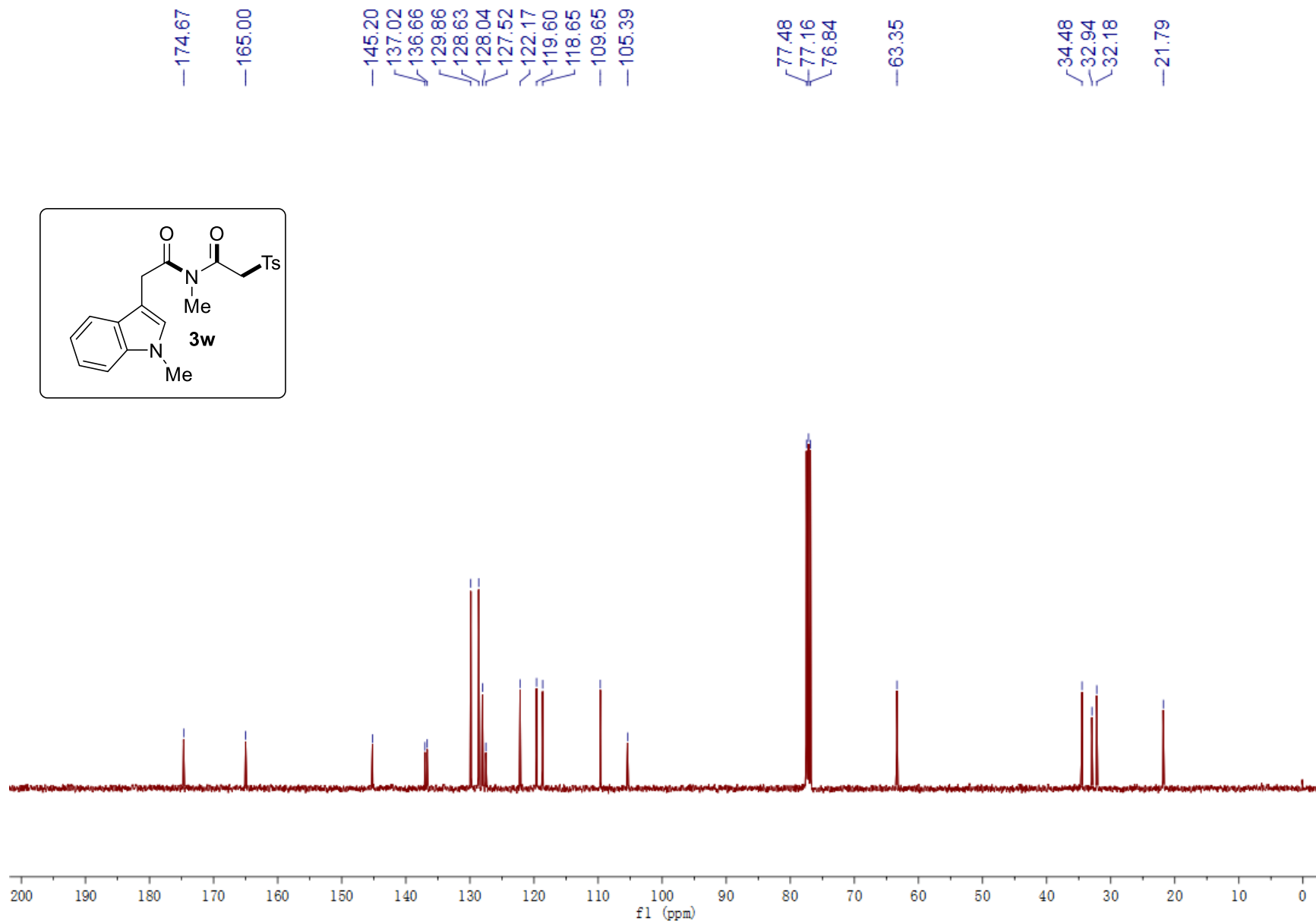
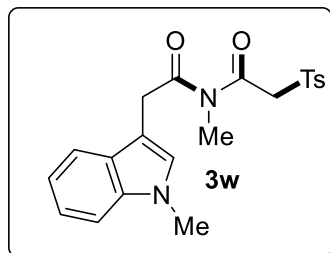
S101



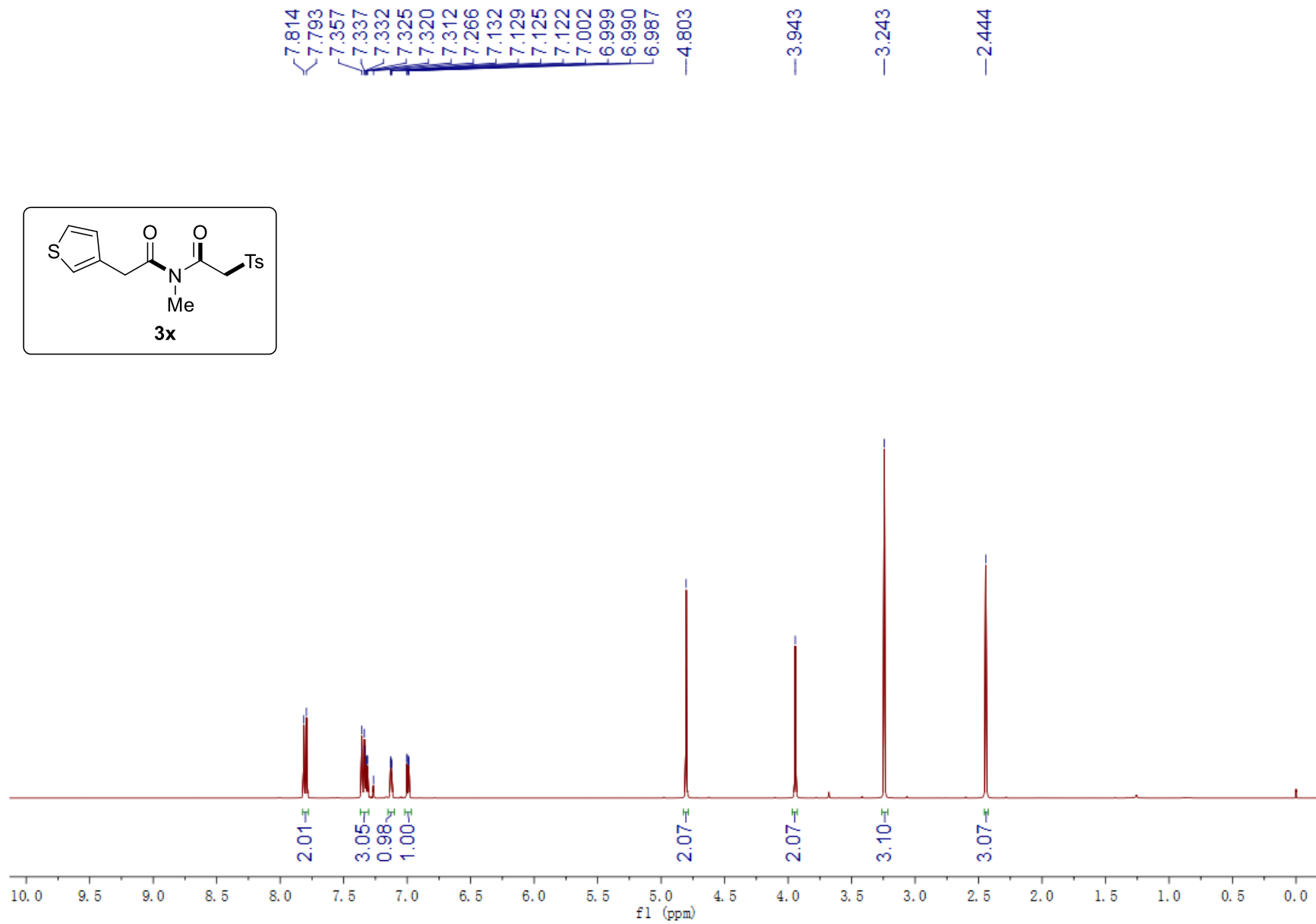
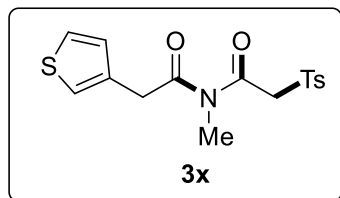
S102



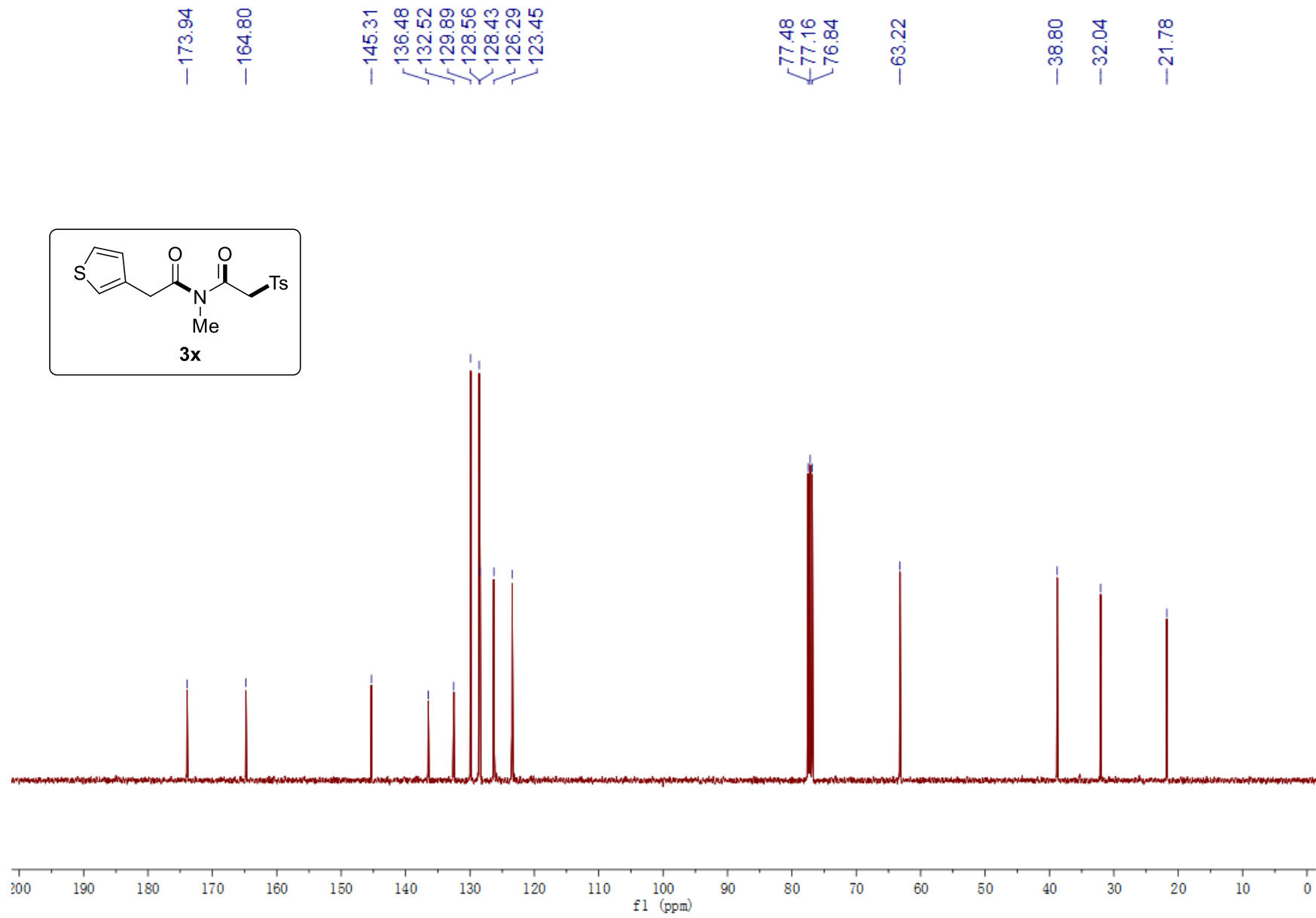
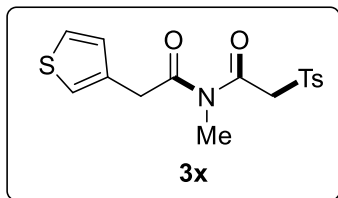
S103



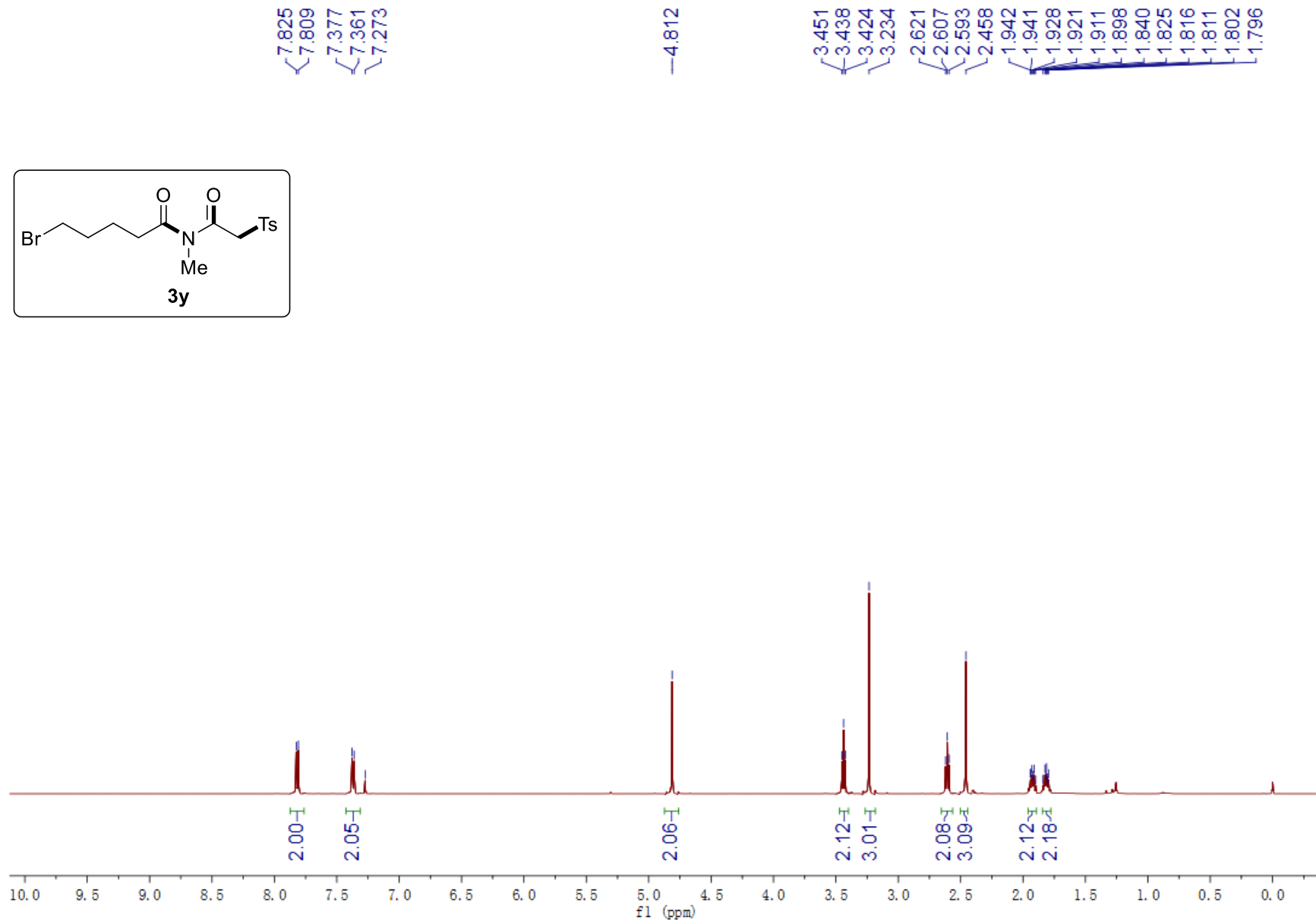
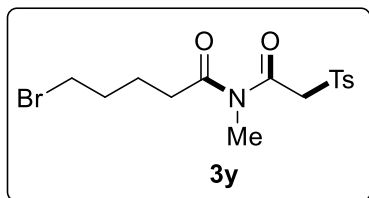
S104



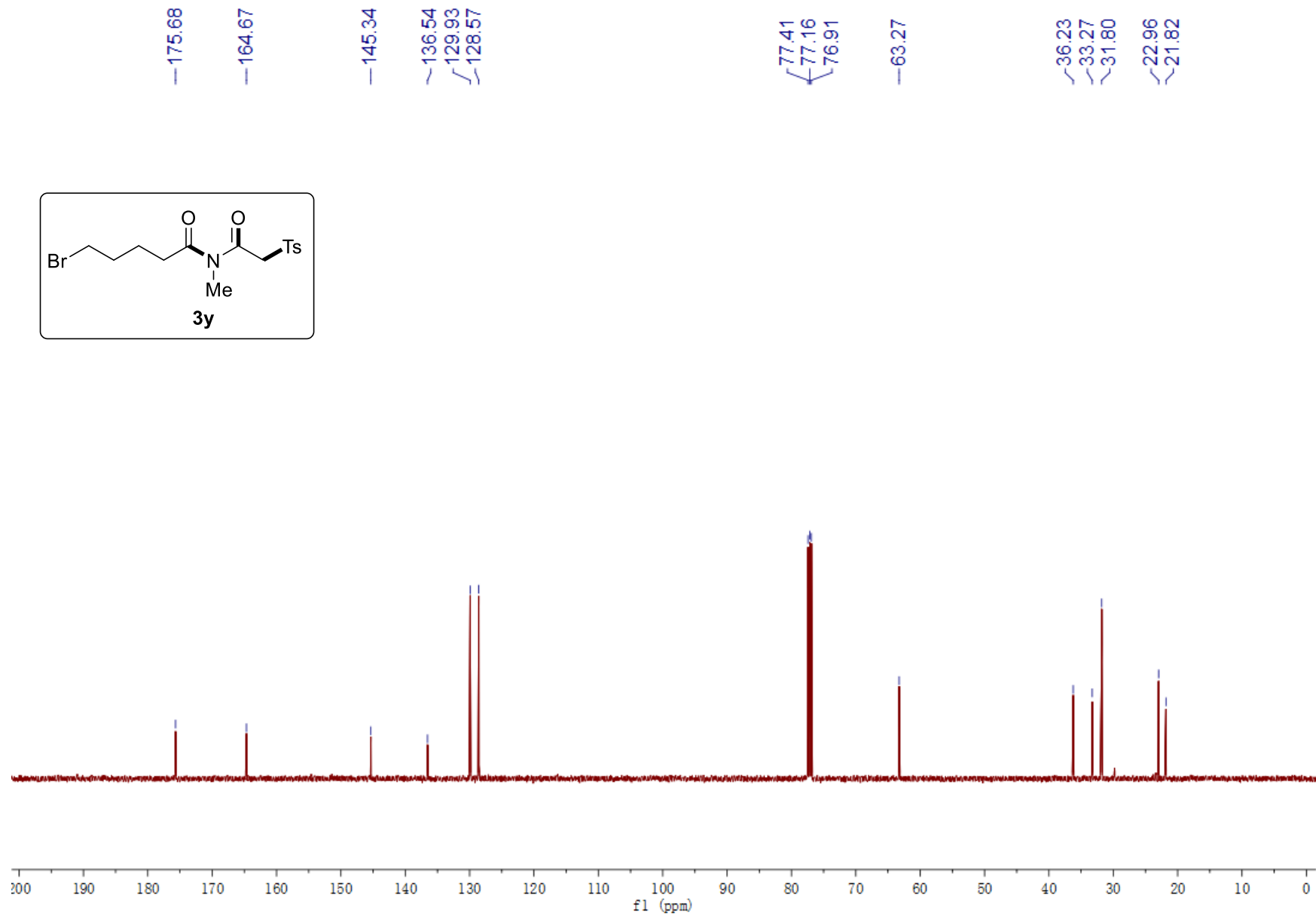
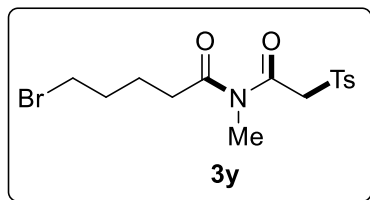
S105



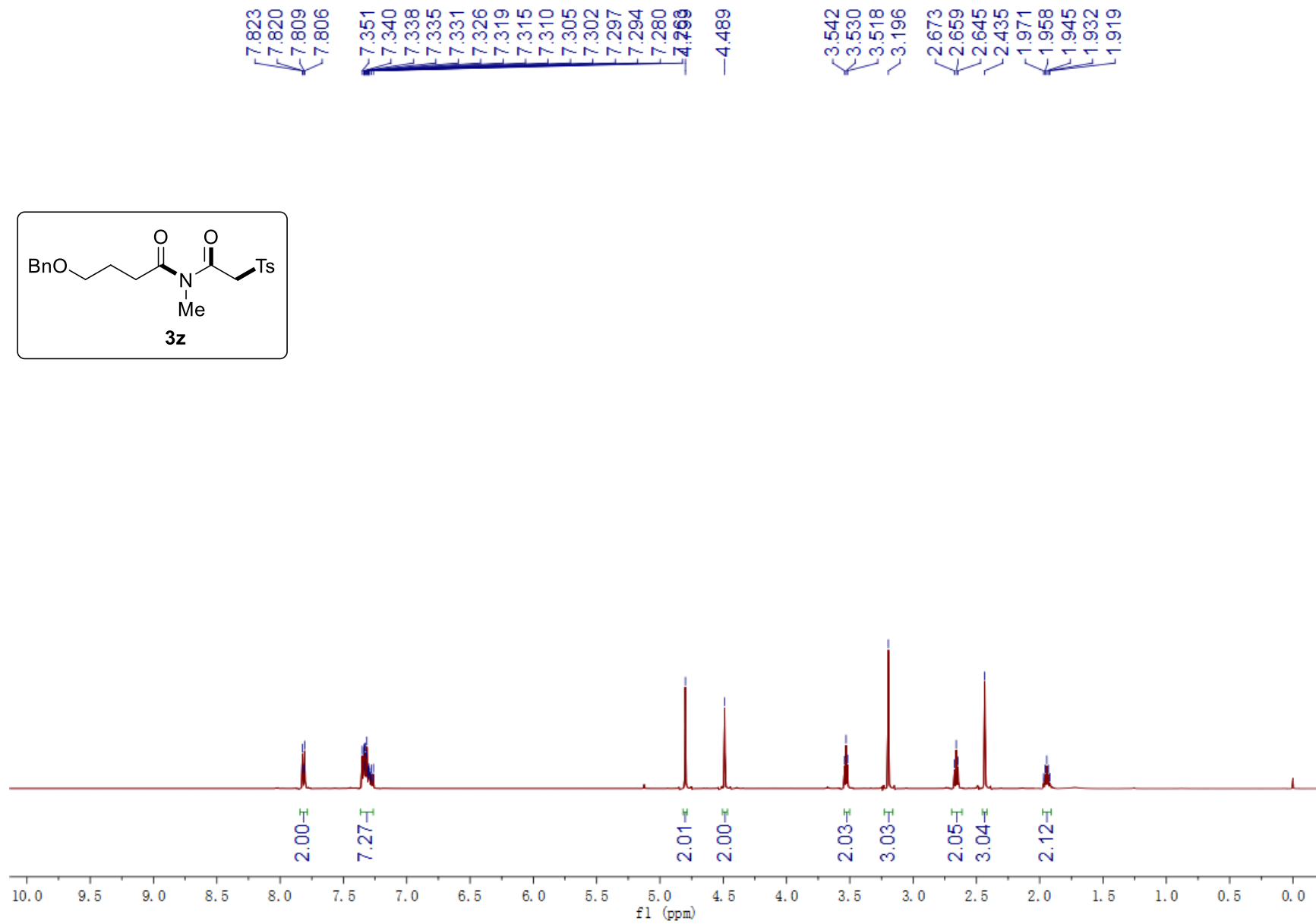
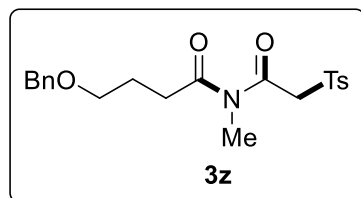
S106

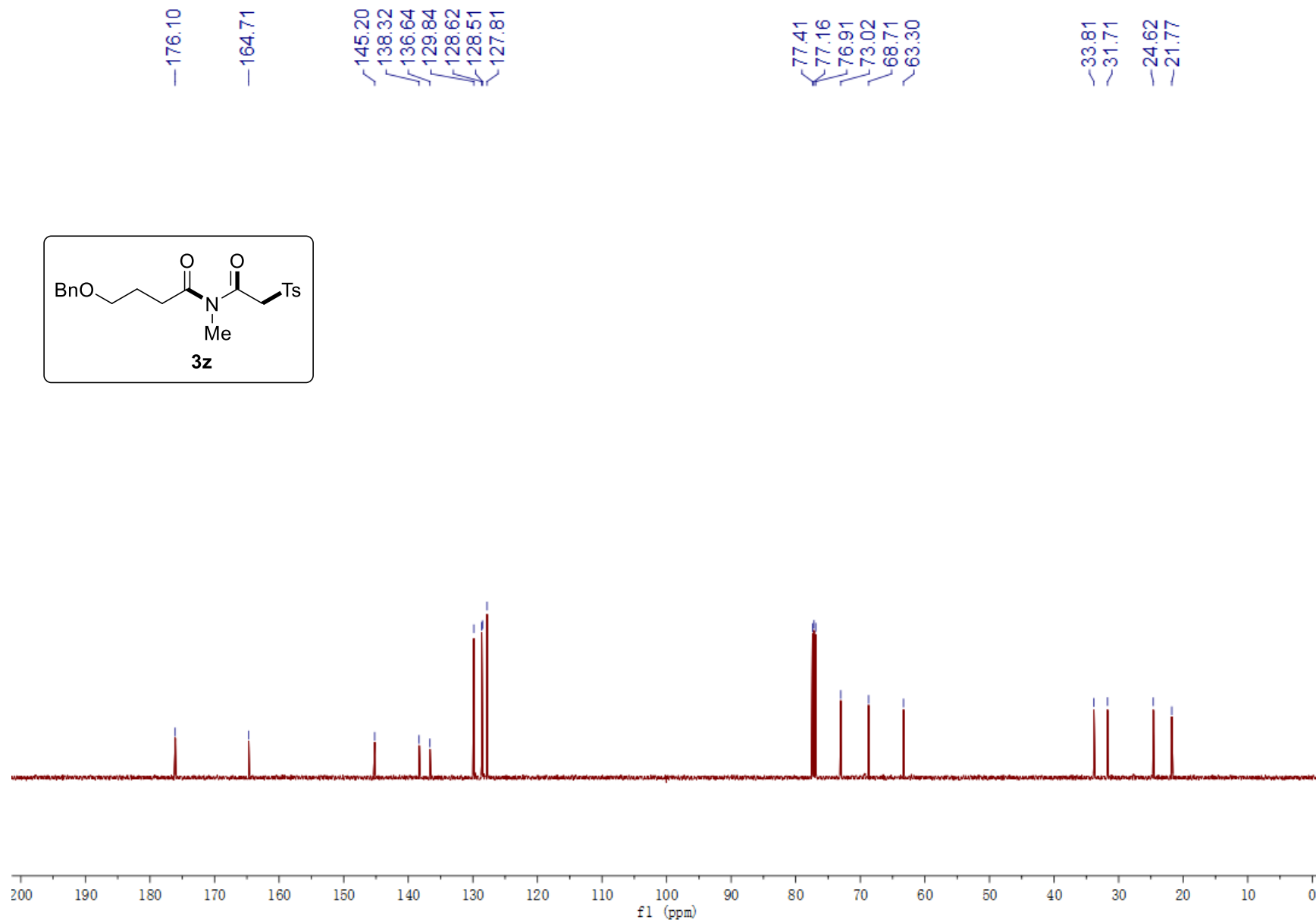
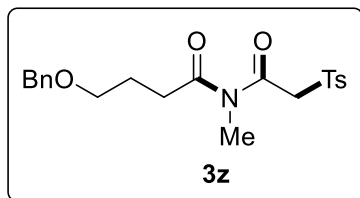


S107

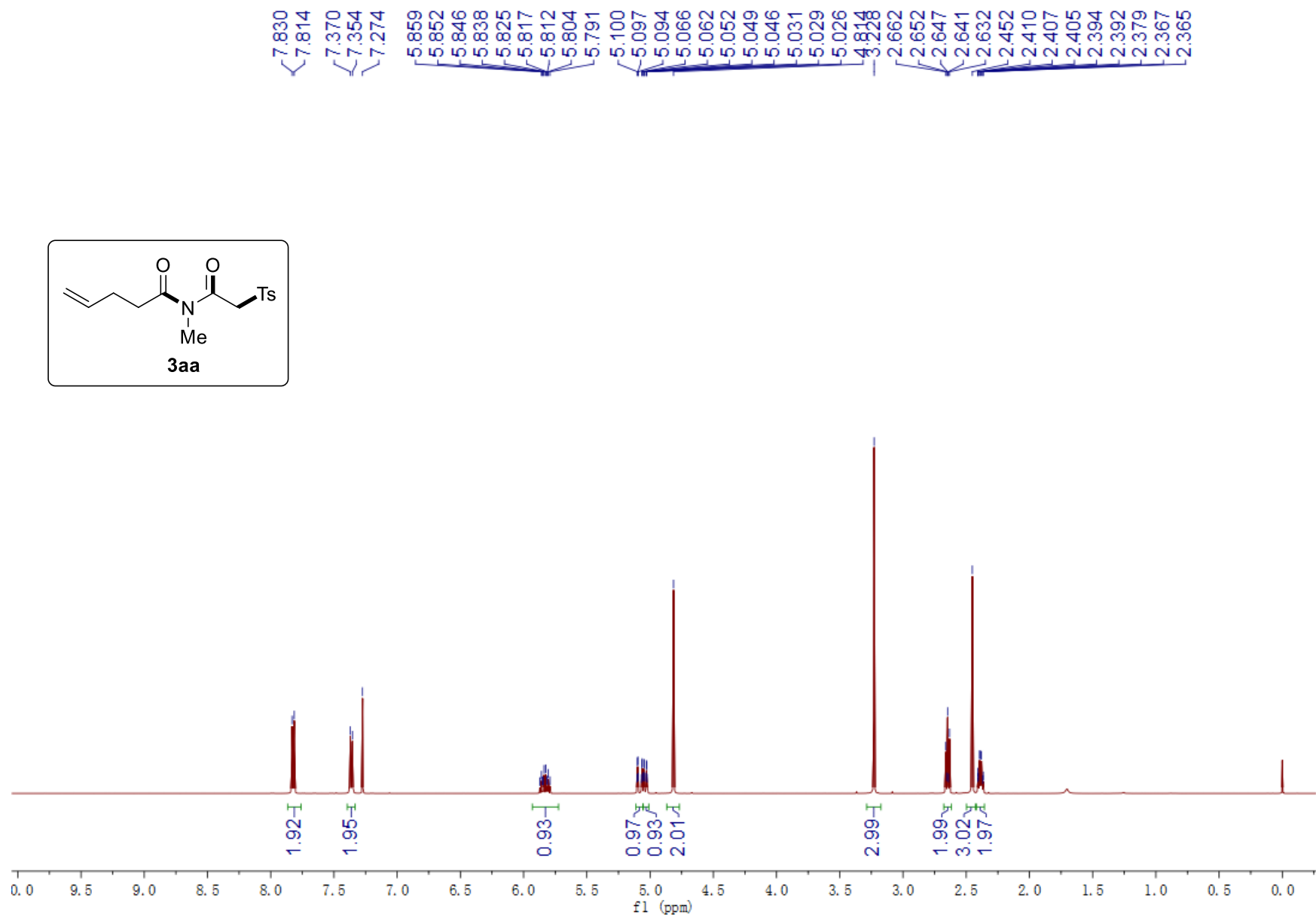
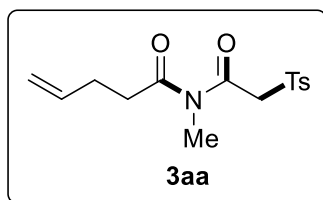


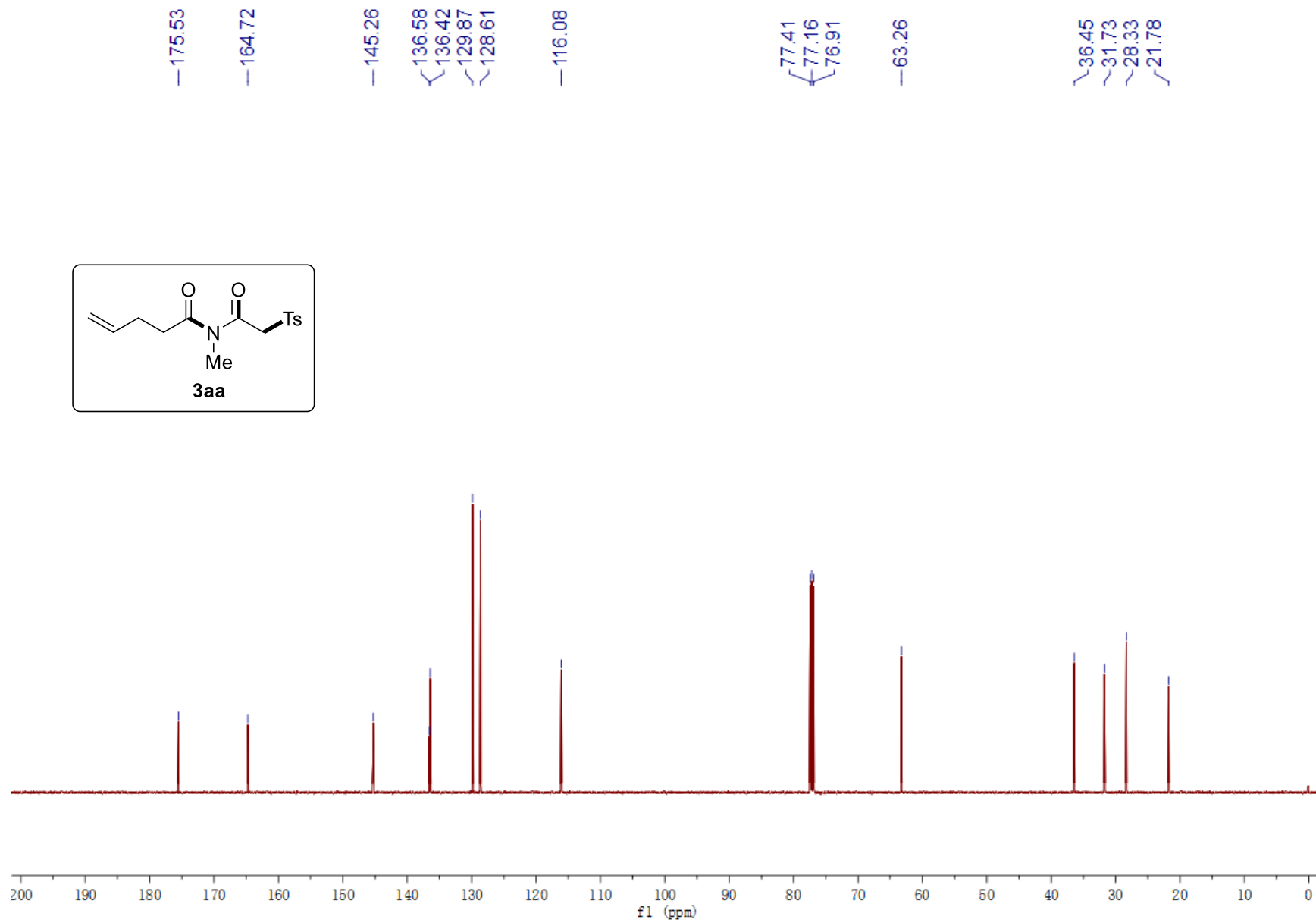
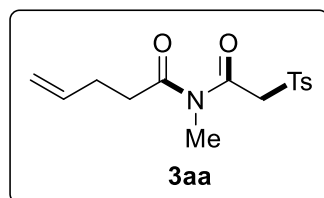
S108



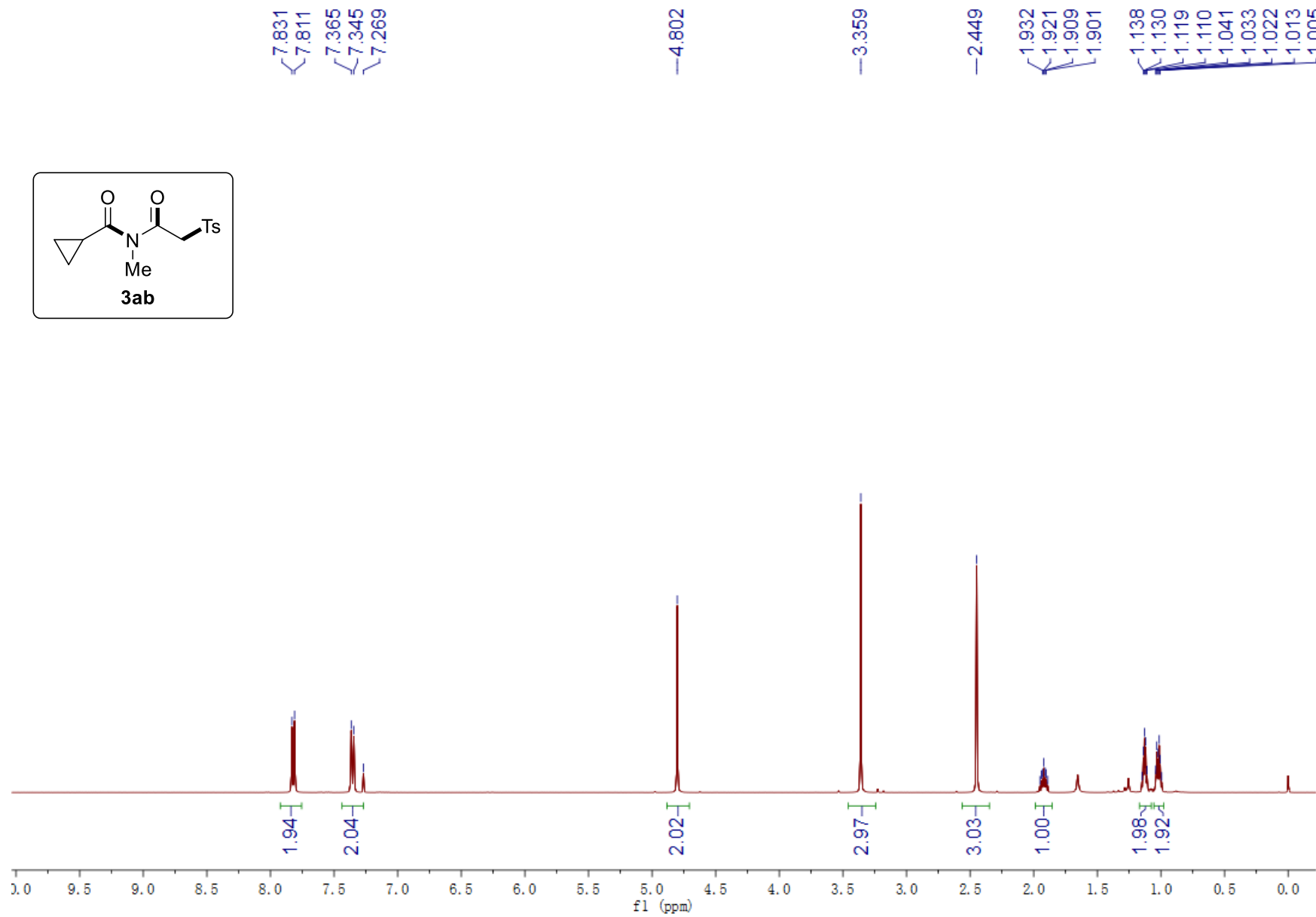
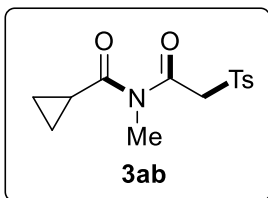


S110

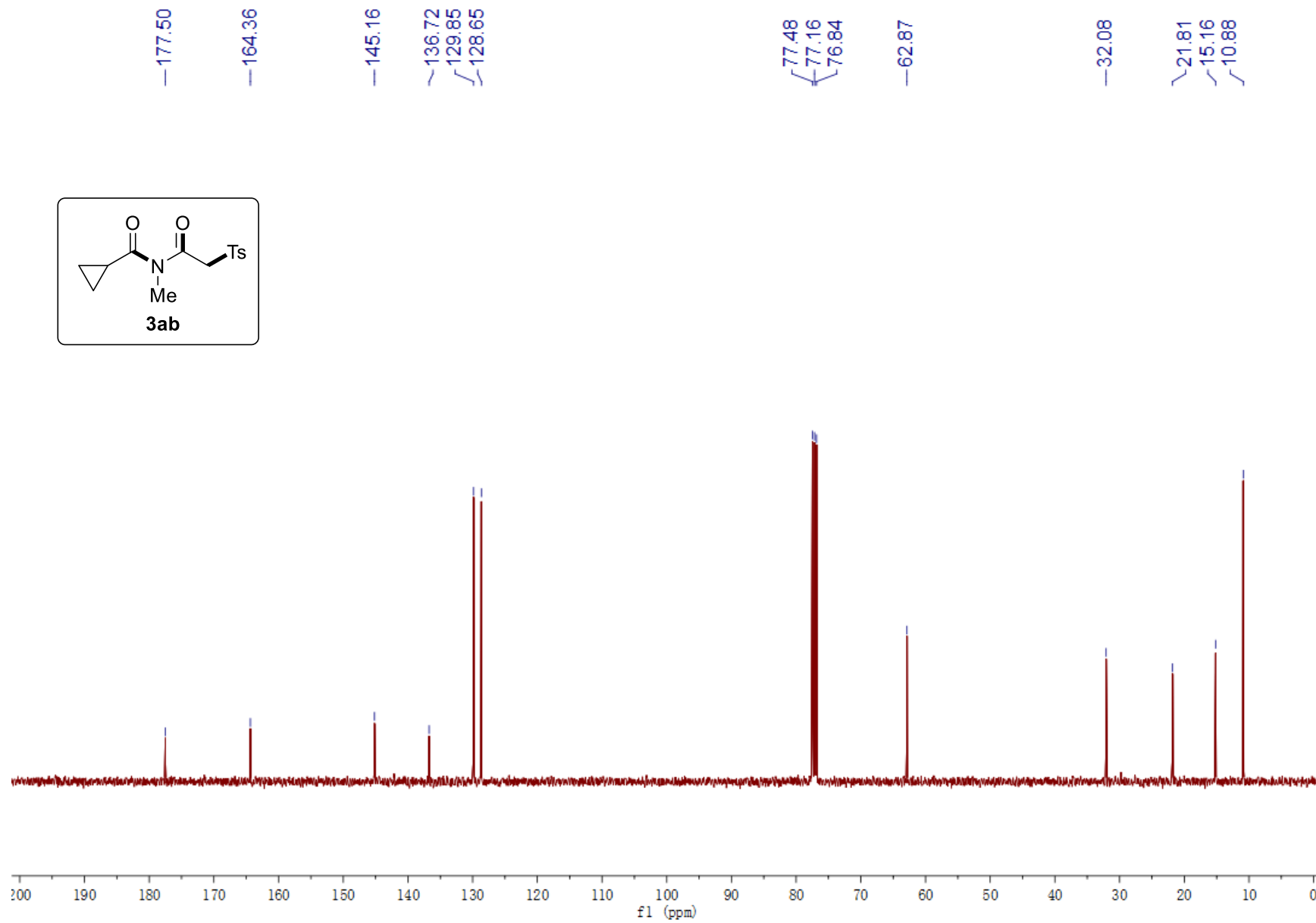
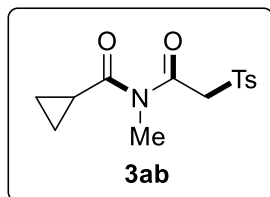


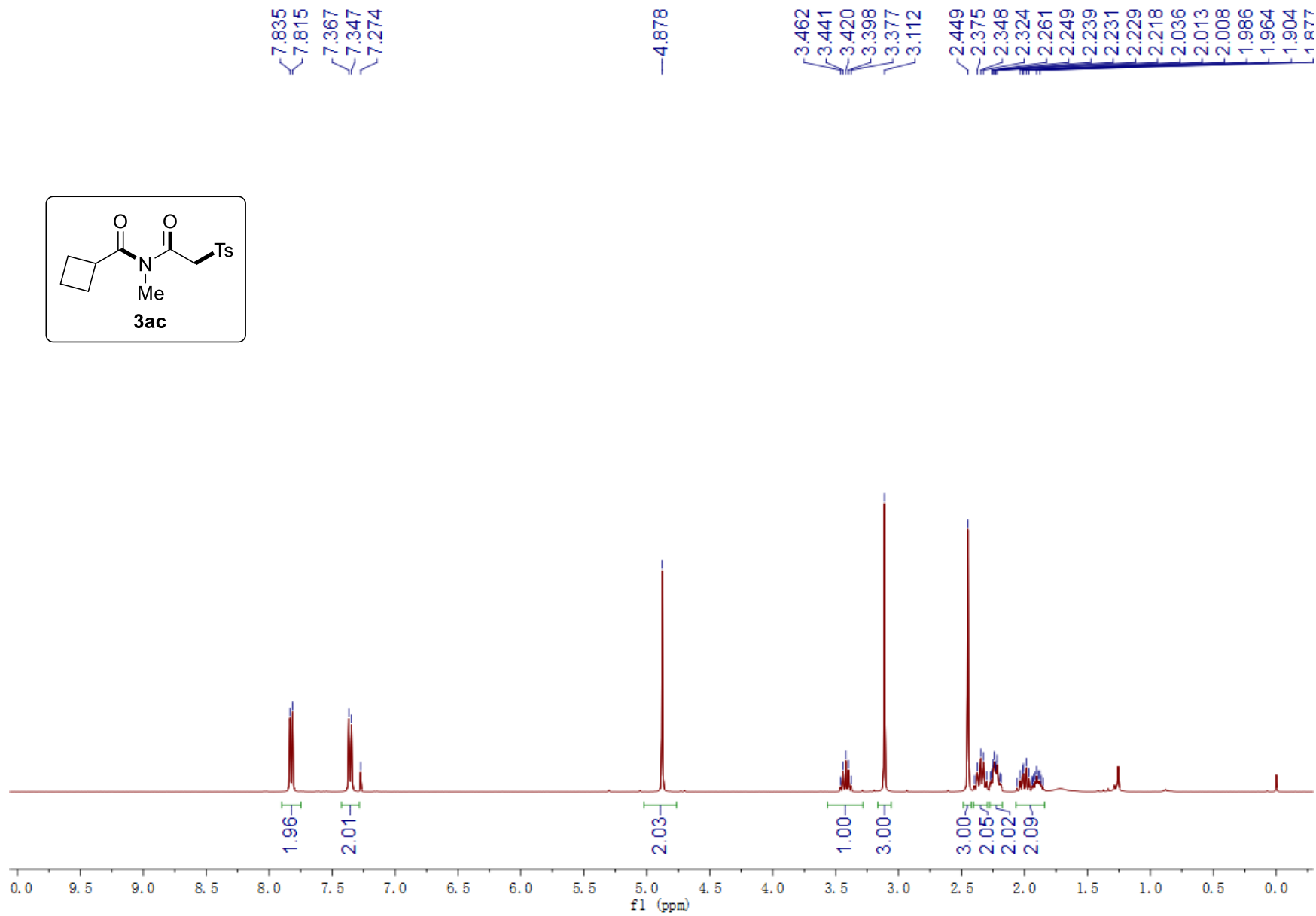
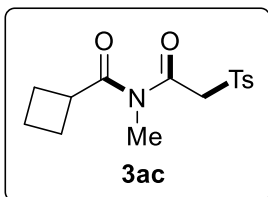


S112

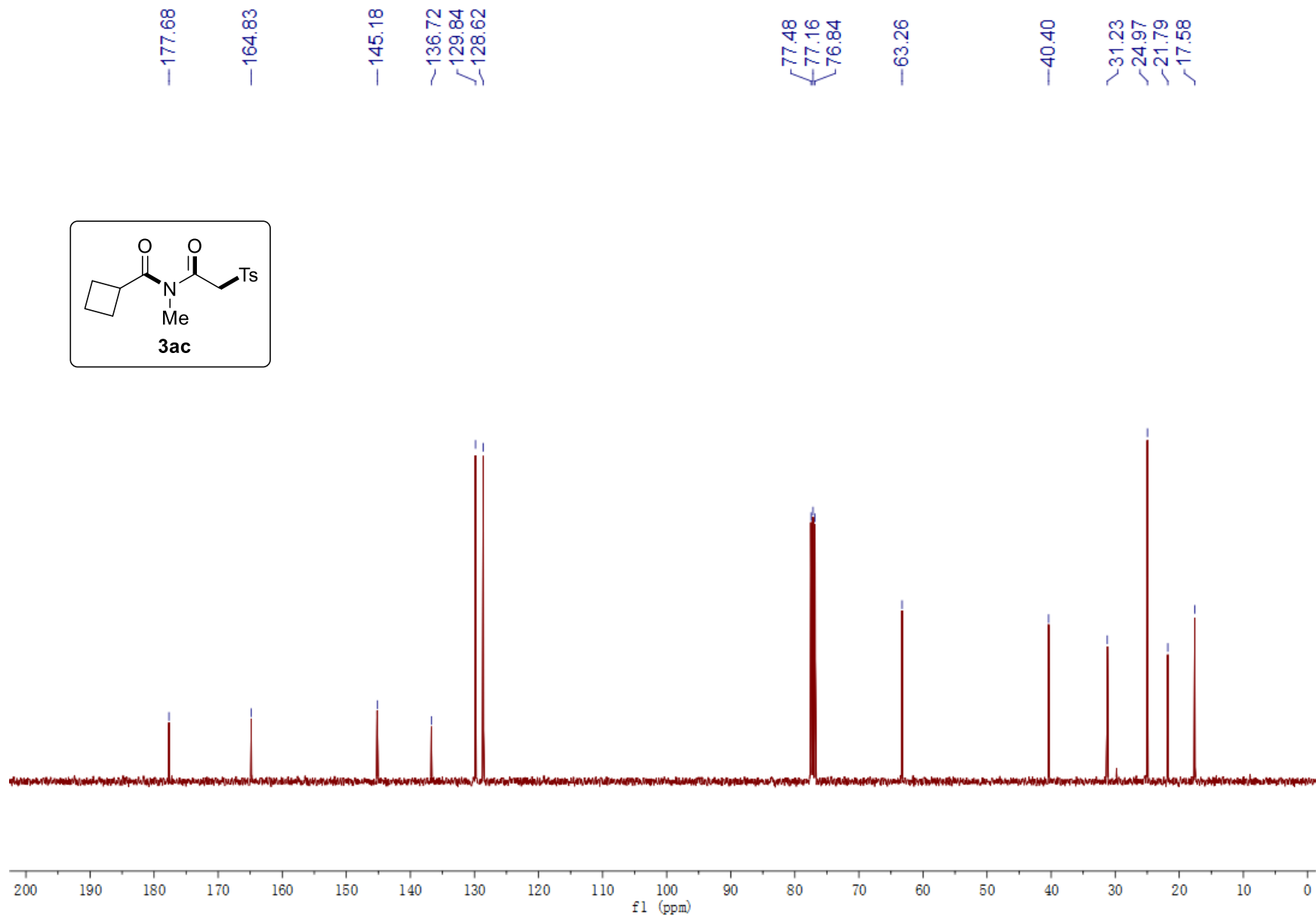
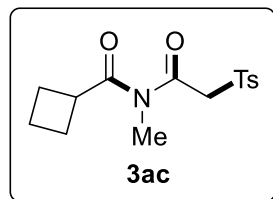


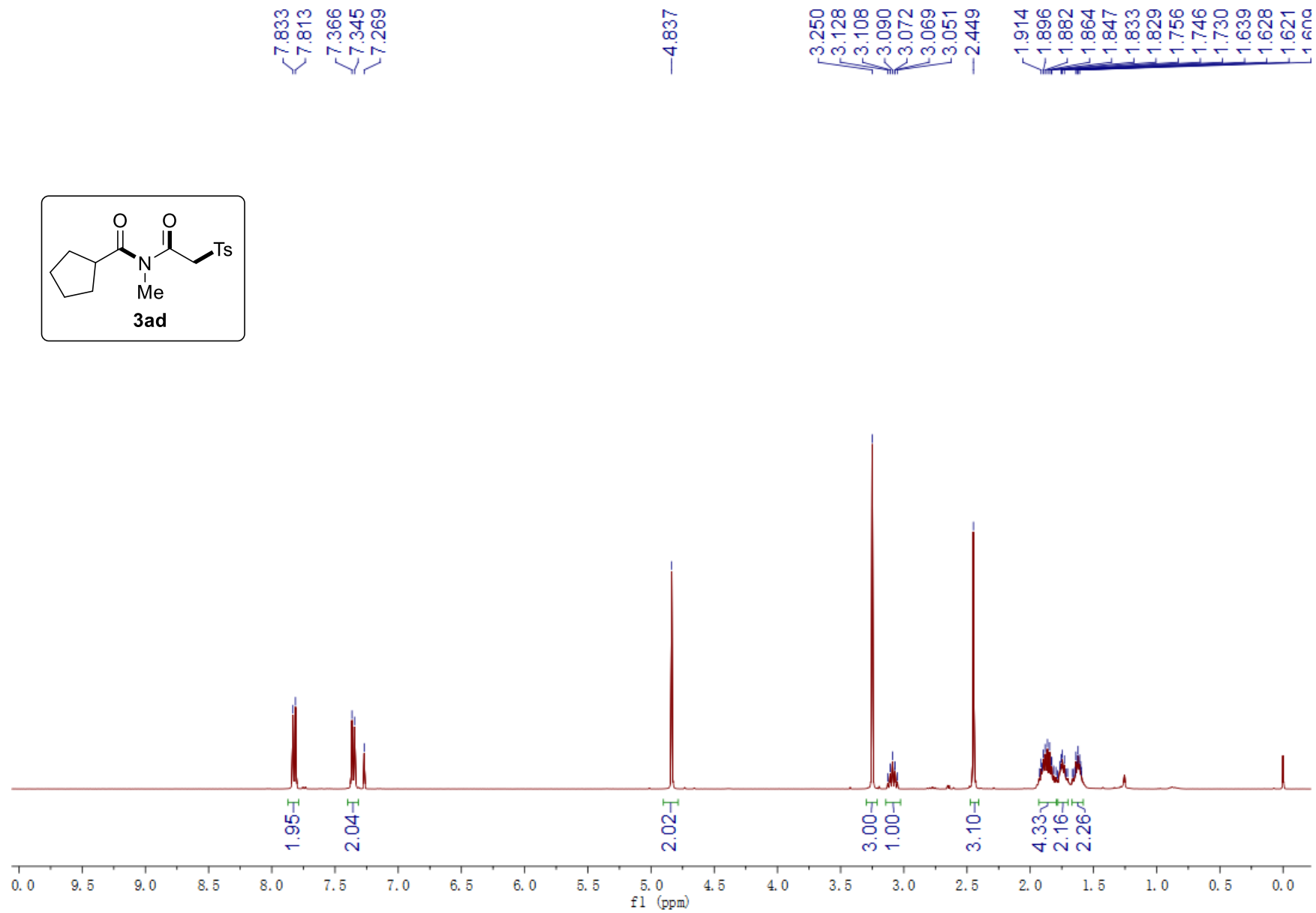
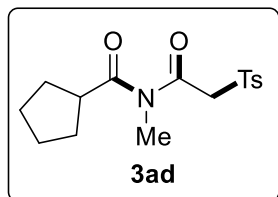
S113



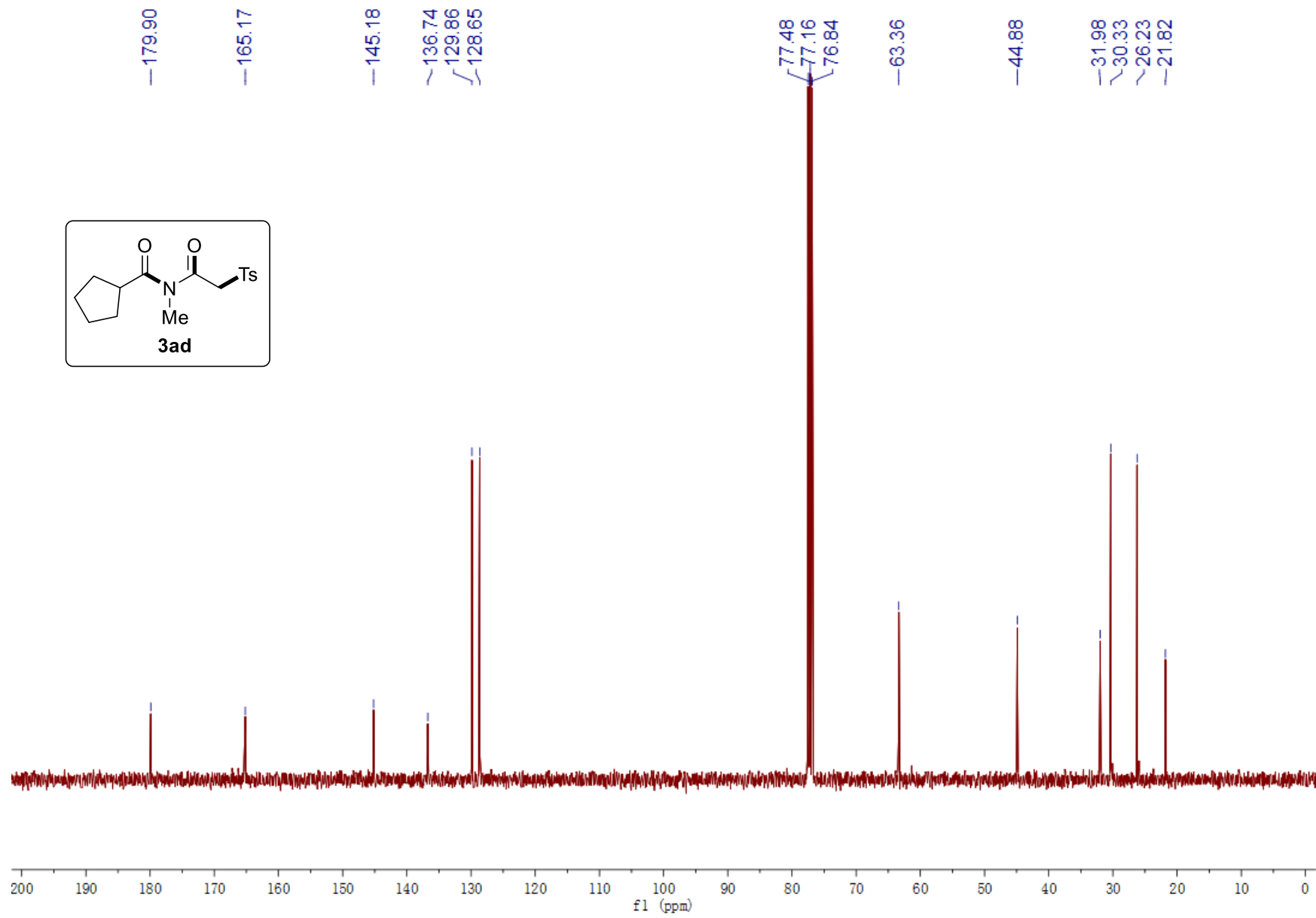
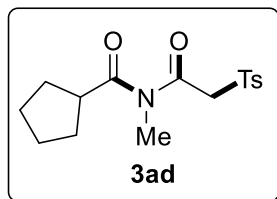


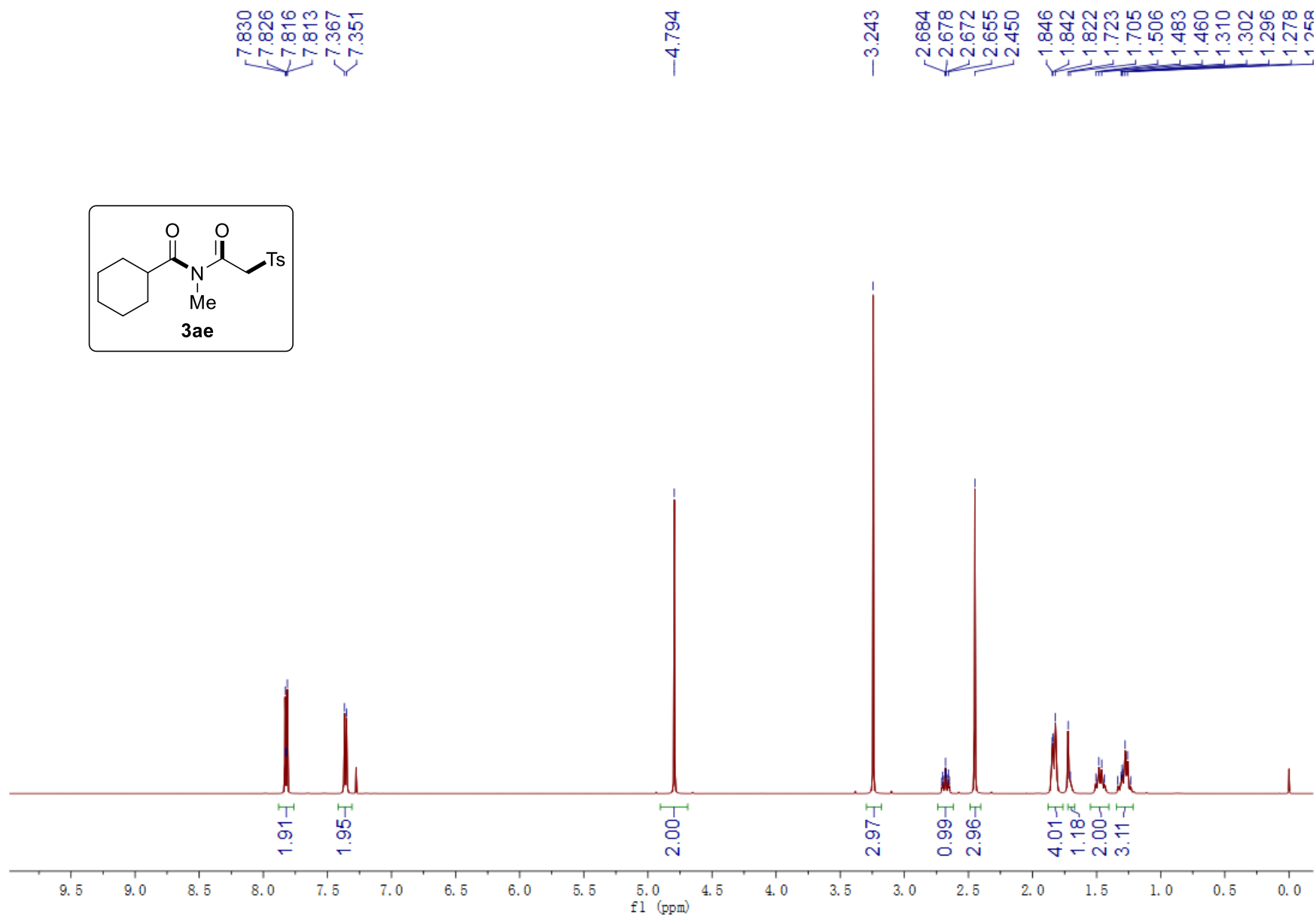
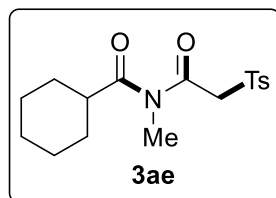
S115

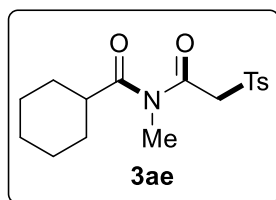




S117







—179.67

—165.16

—145.18

~136.62

~129.84

~128.60

~77.41

~77.16

~76.91

—63.23

—44.33

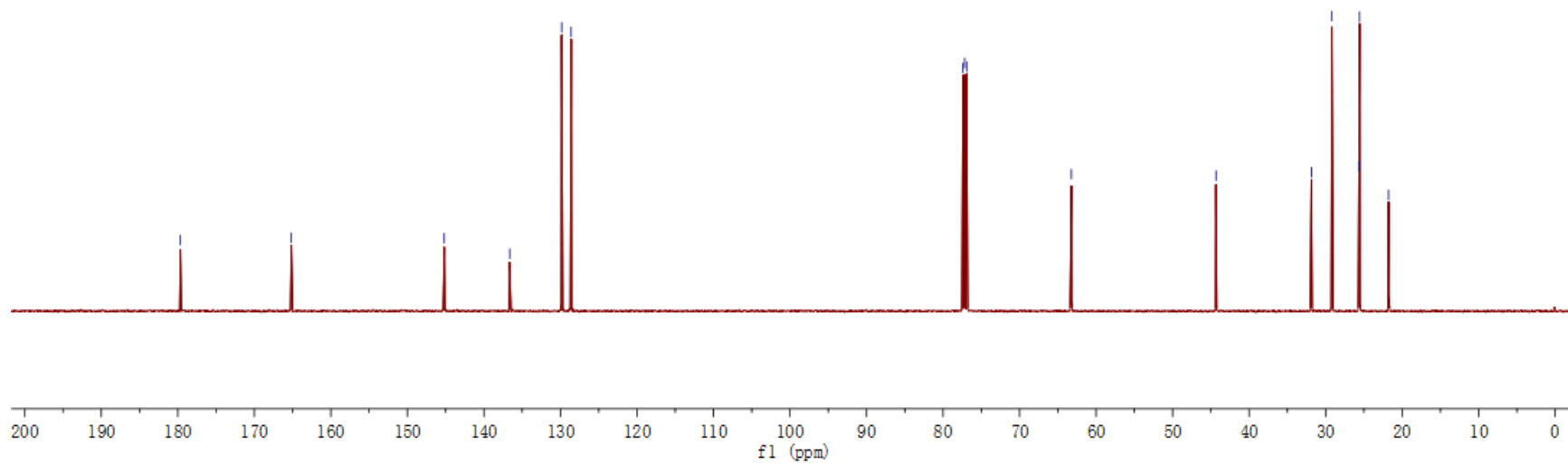
~31.87

~29.19

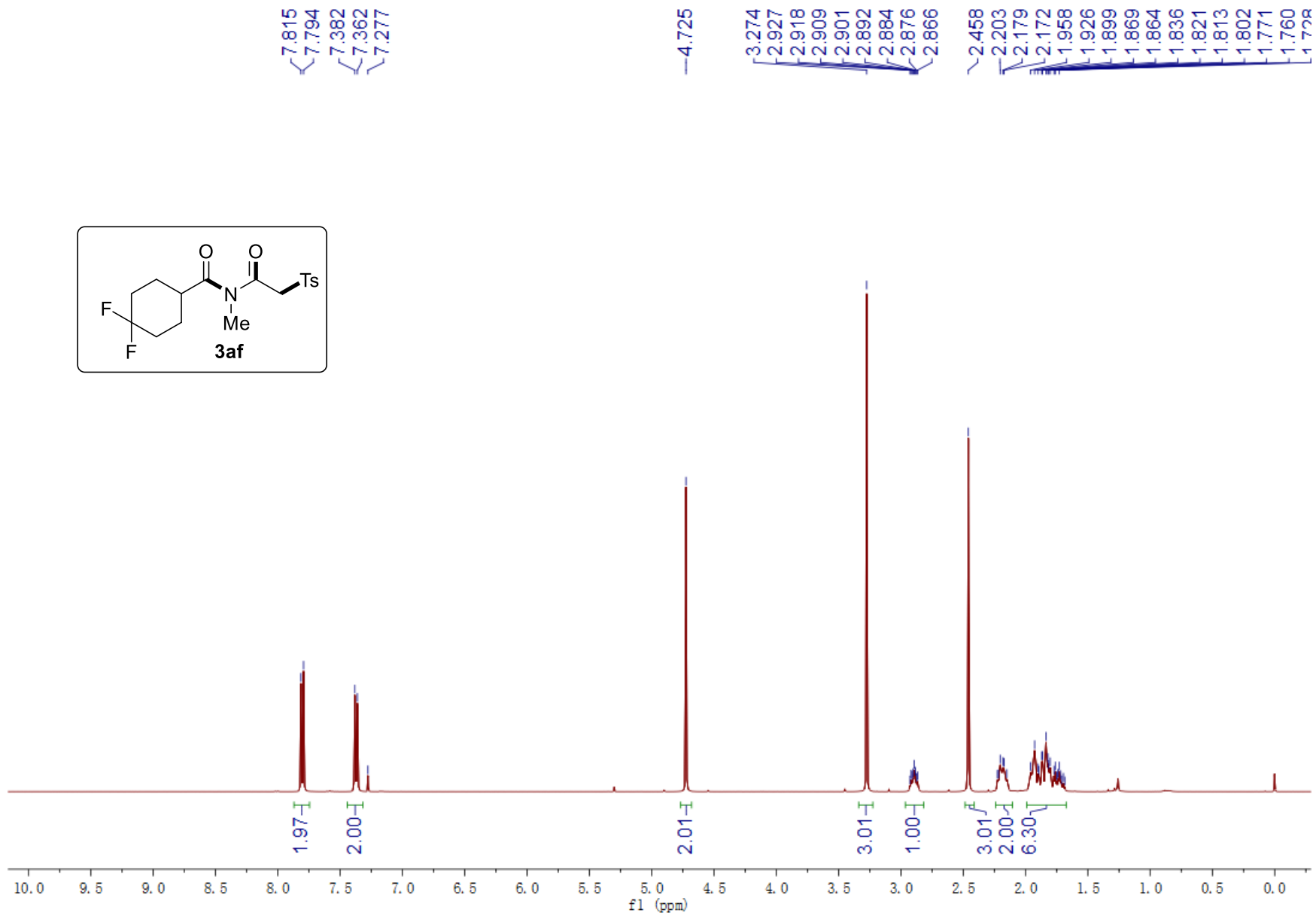
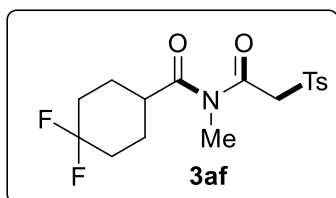
~25.68

~25.57

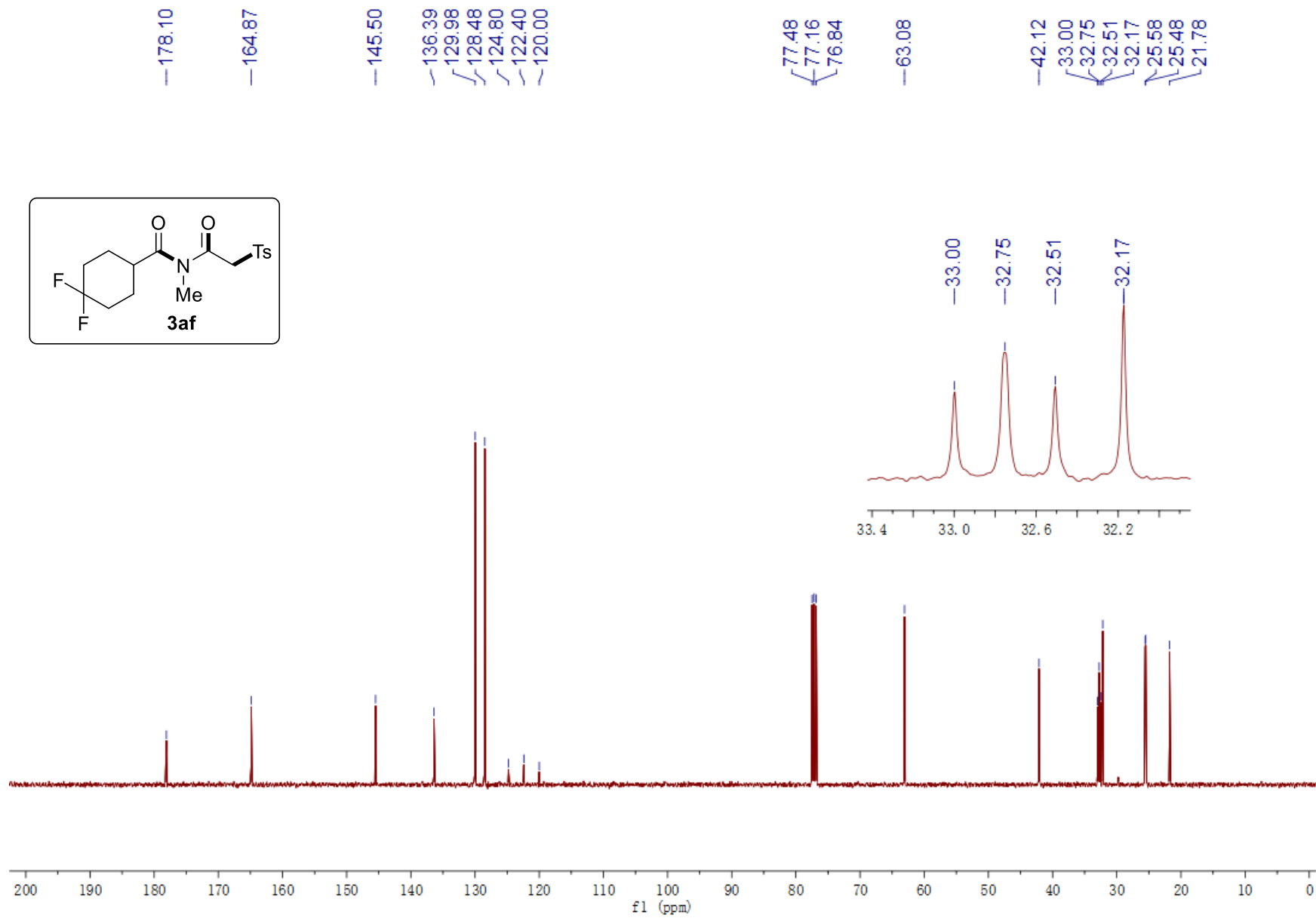
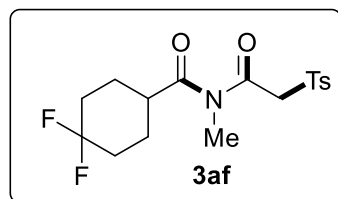
~21.78



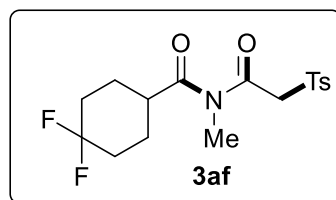
S120



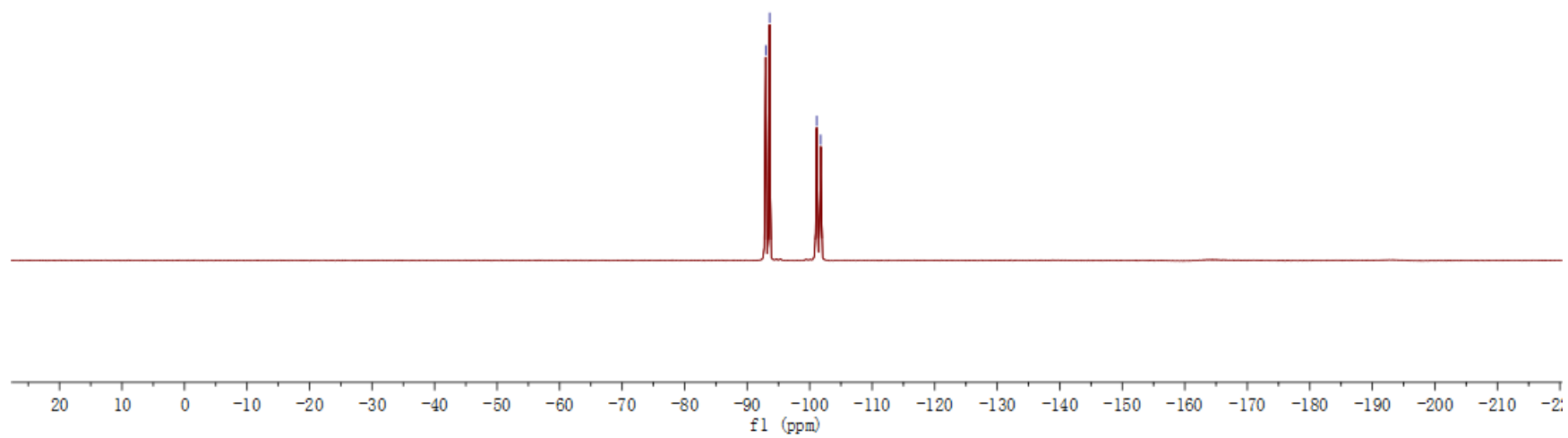
S121



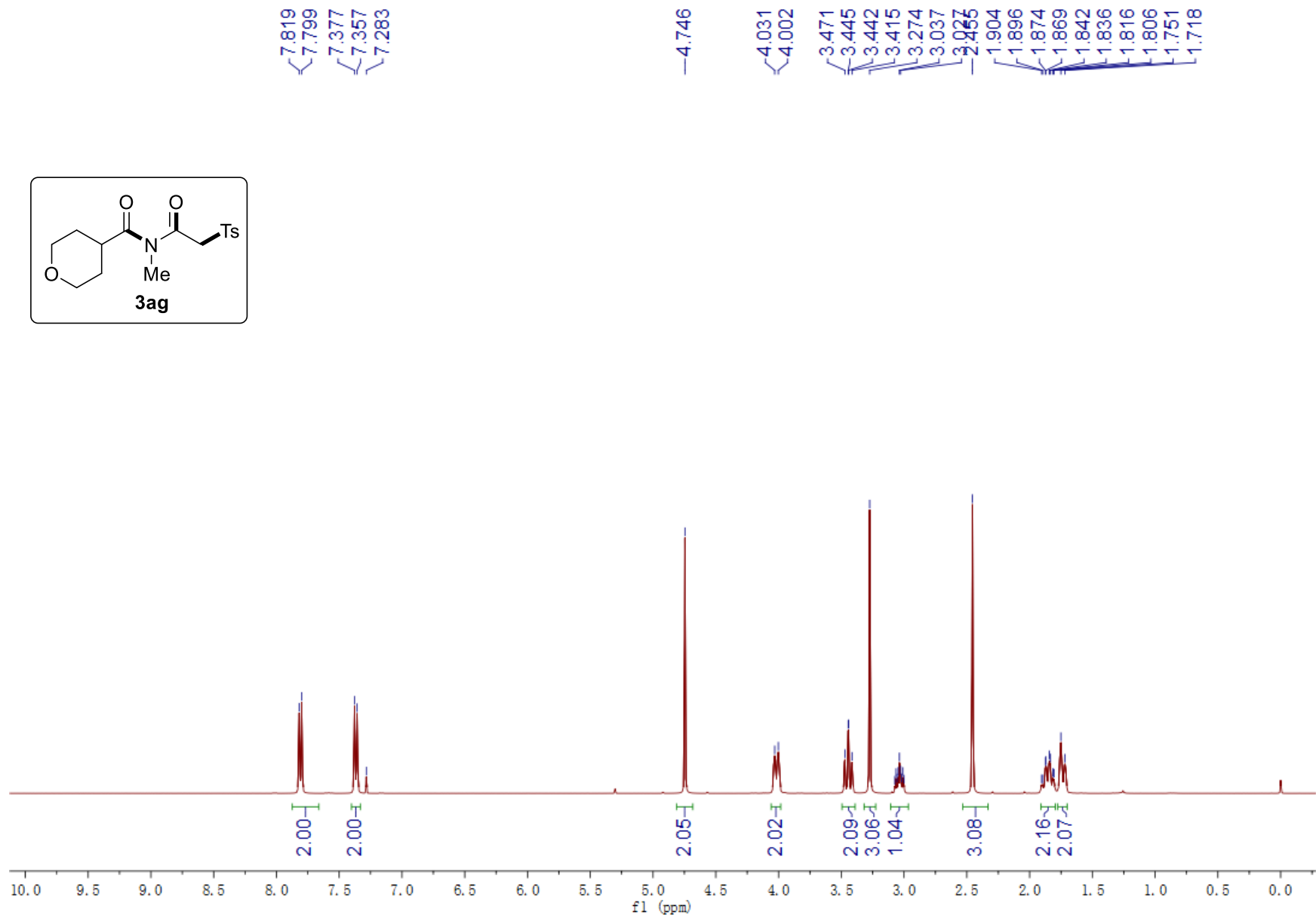
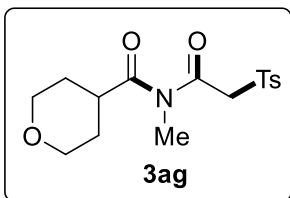
S122

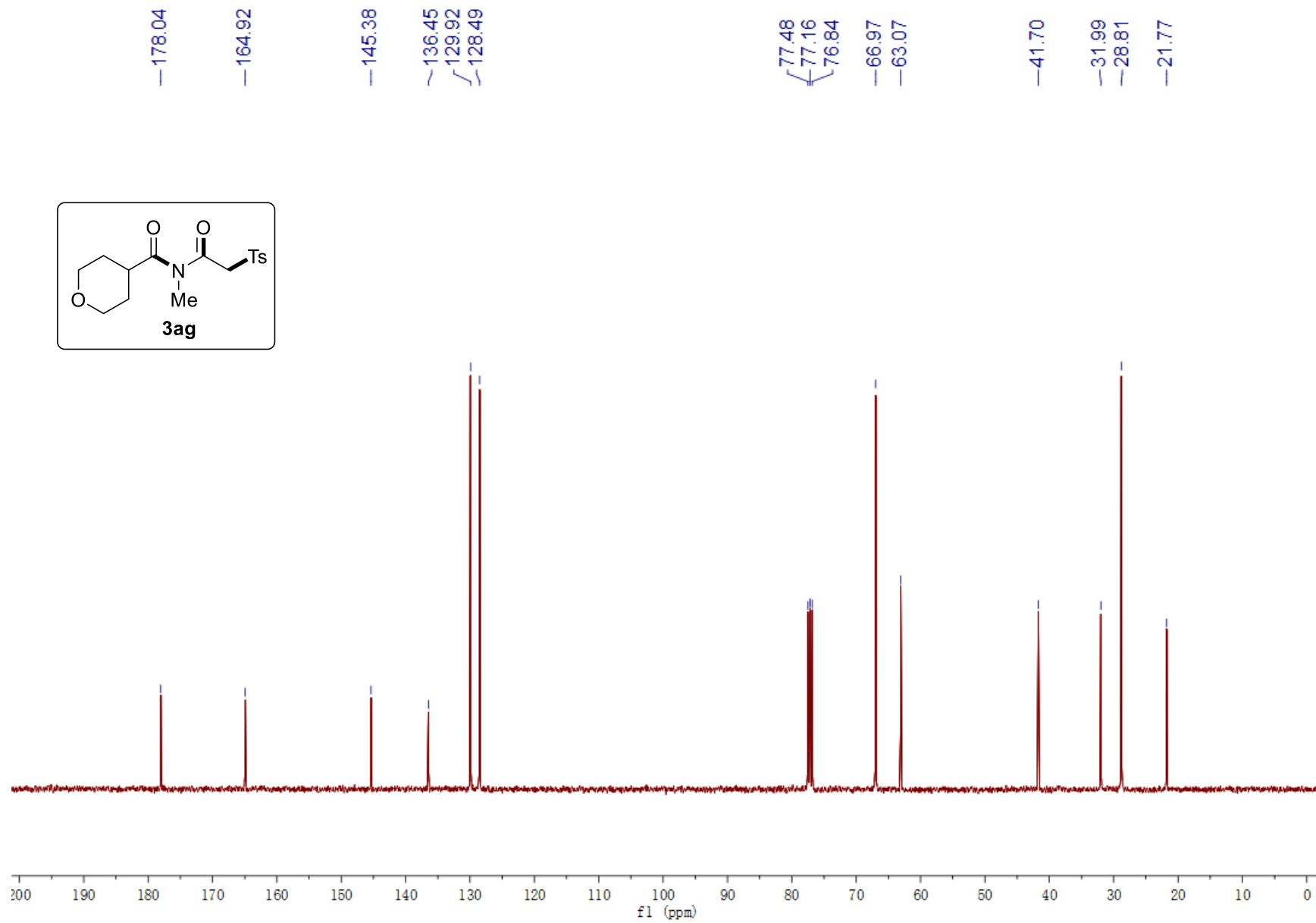
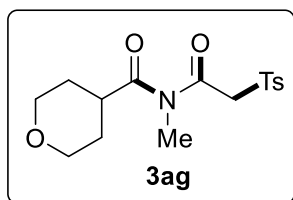


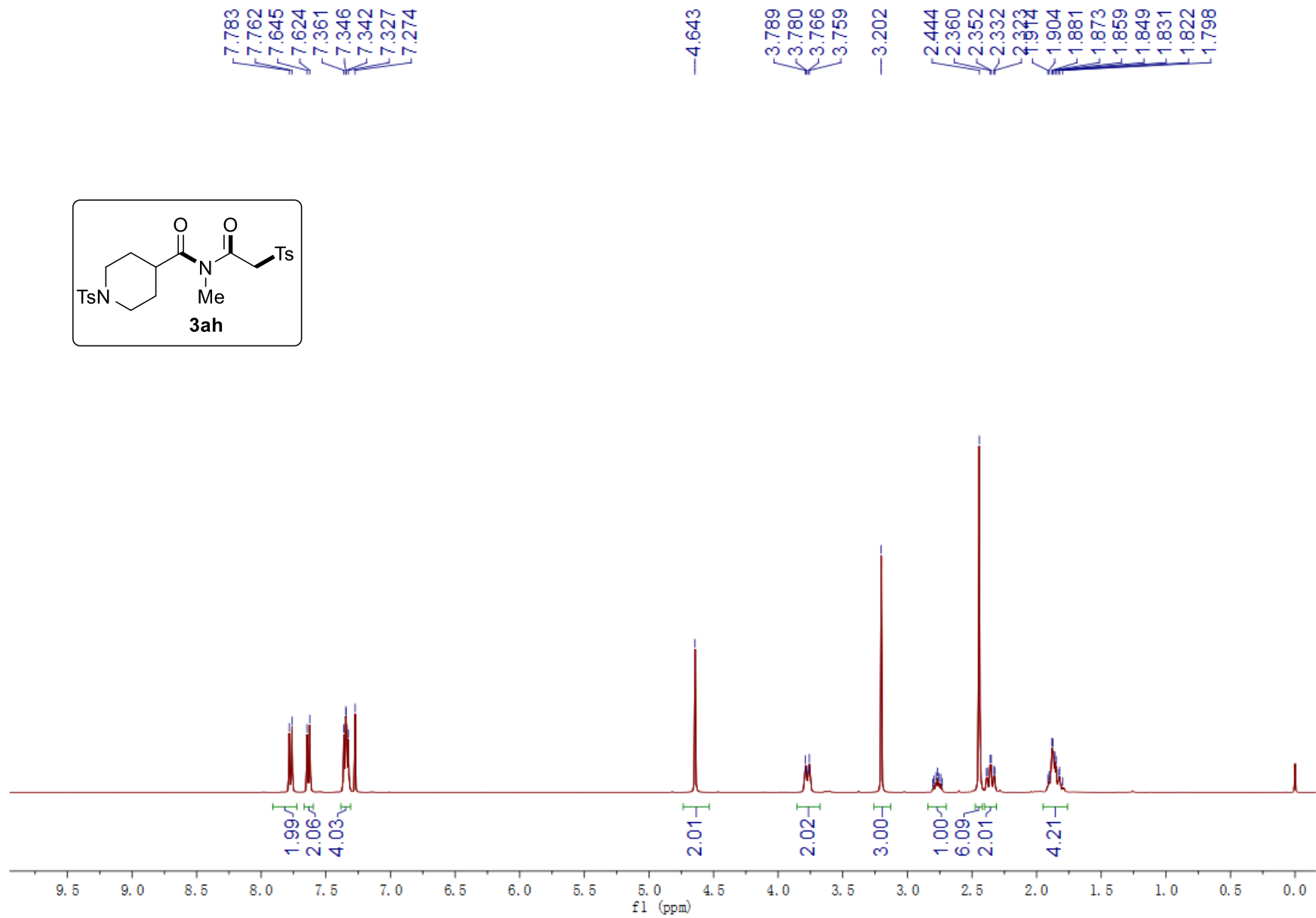
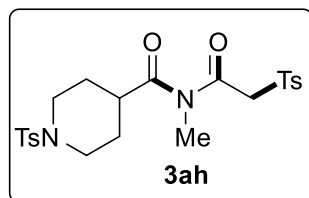
92.97
93.60
101.13
101.76

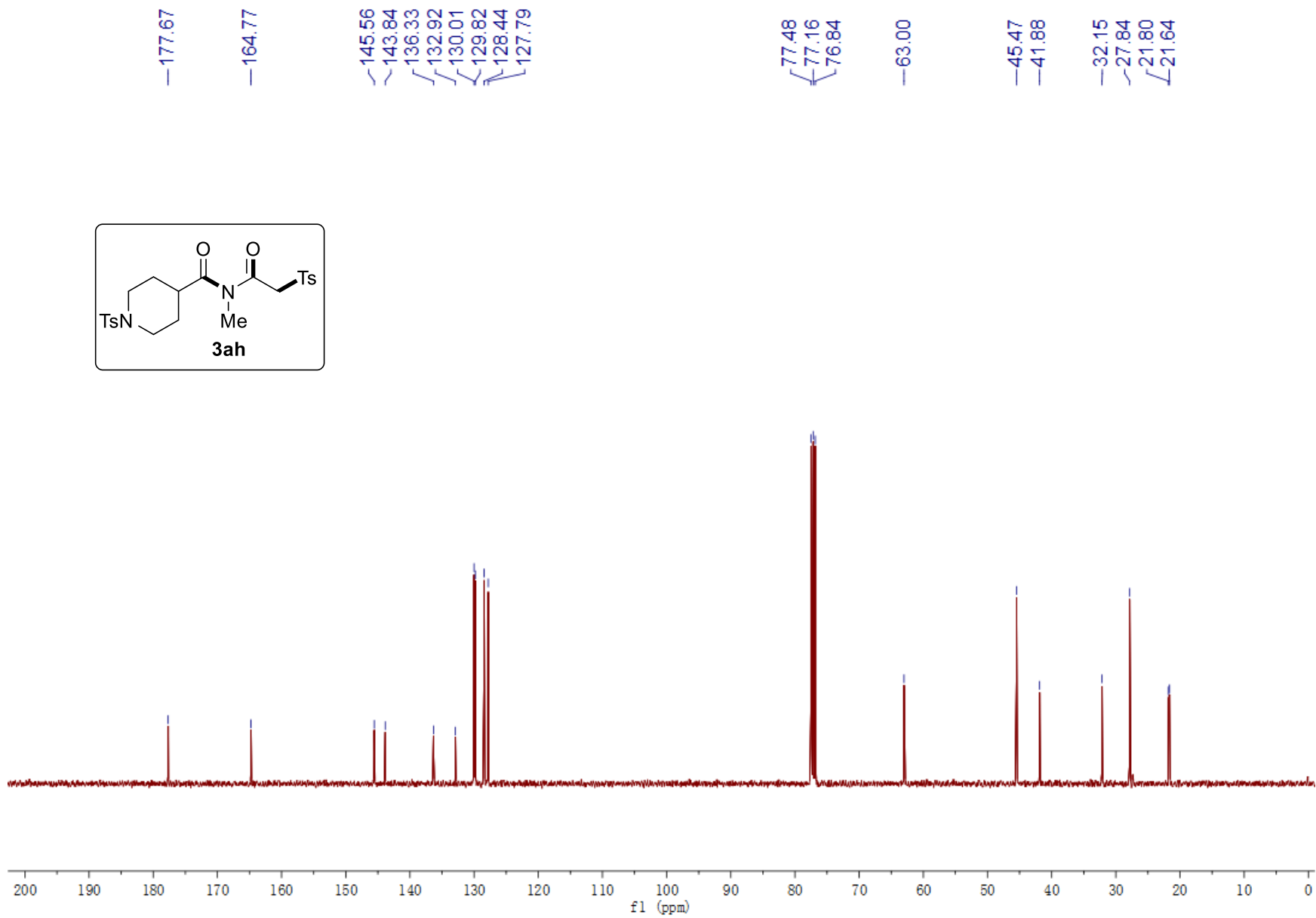
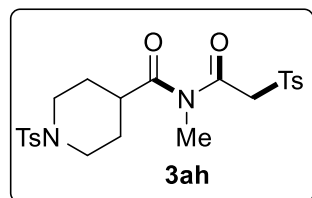


S123

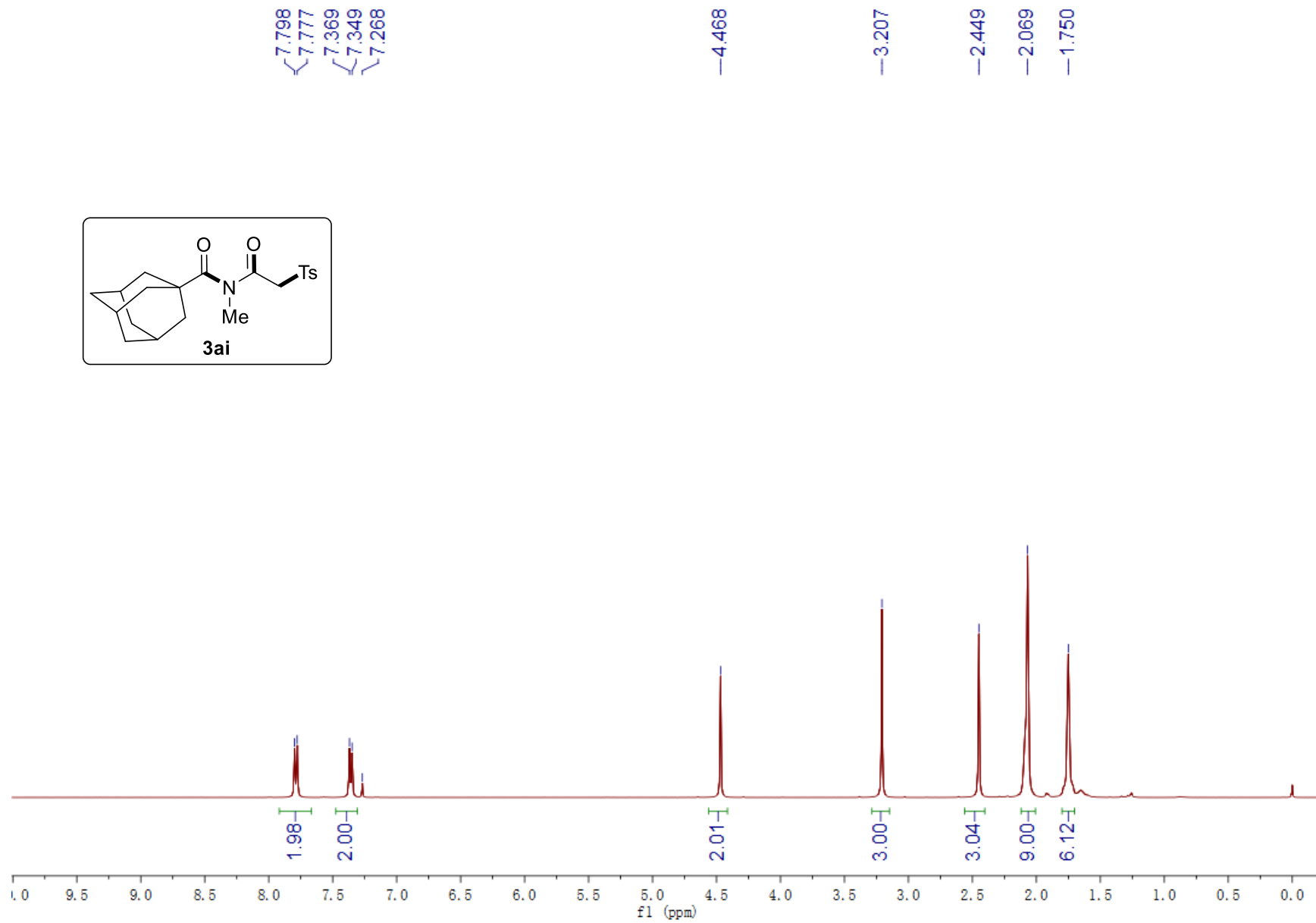
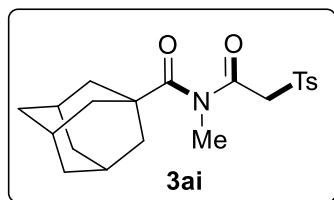








S127



—185.48

—164.47

—145.31

~136.26

~129.92

~128.59

~77.48

~77.16

~76.84

—61.44

~45.29

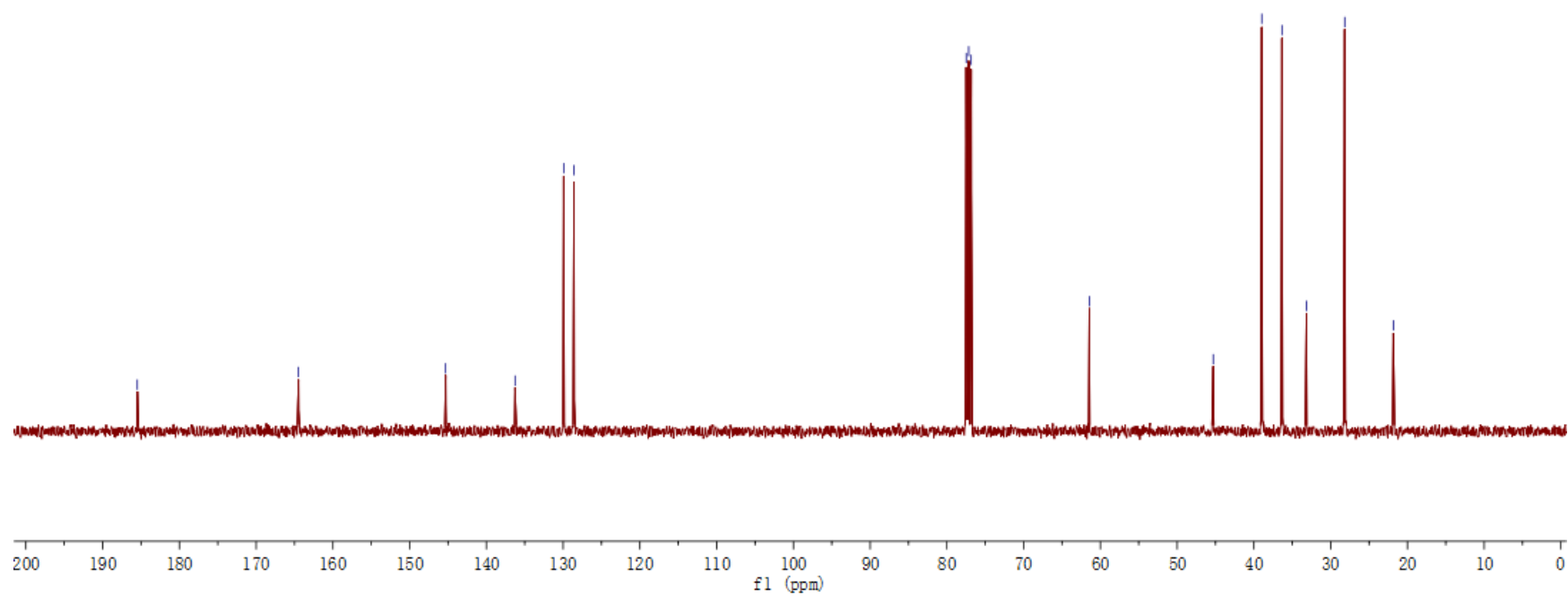
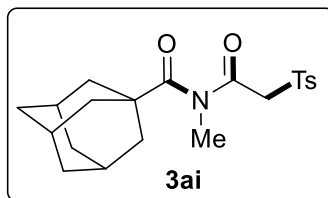
~38.97

~36.35

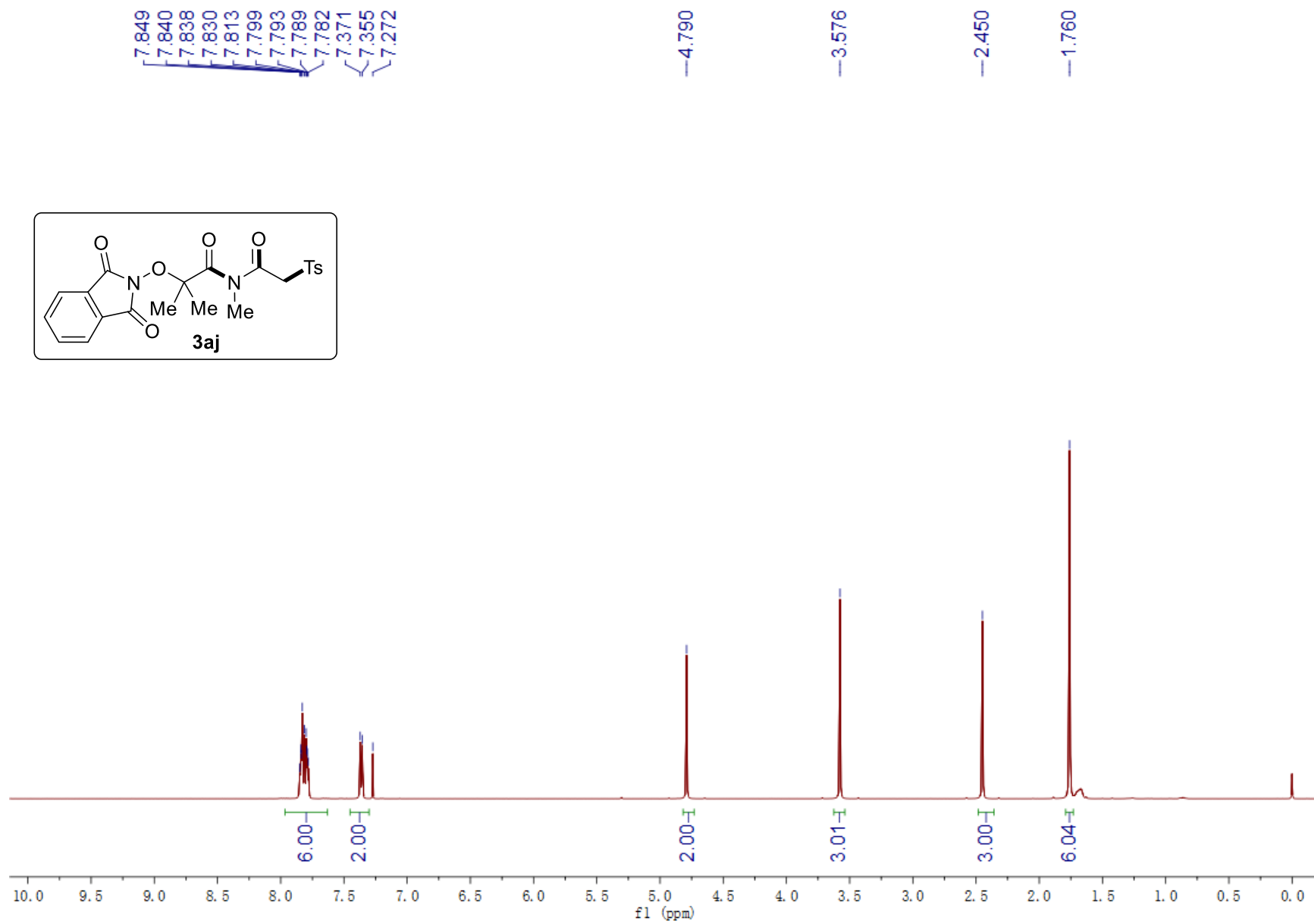
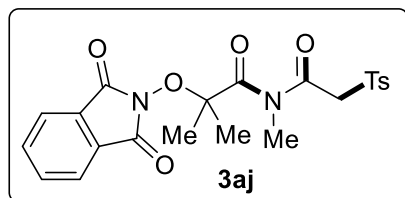
~33.16

~28.17

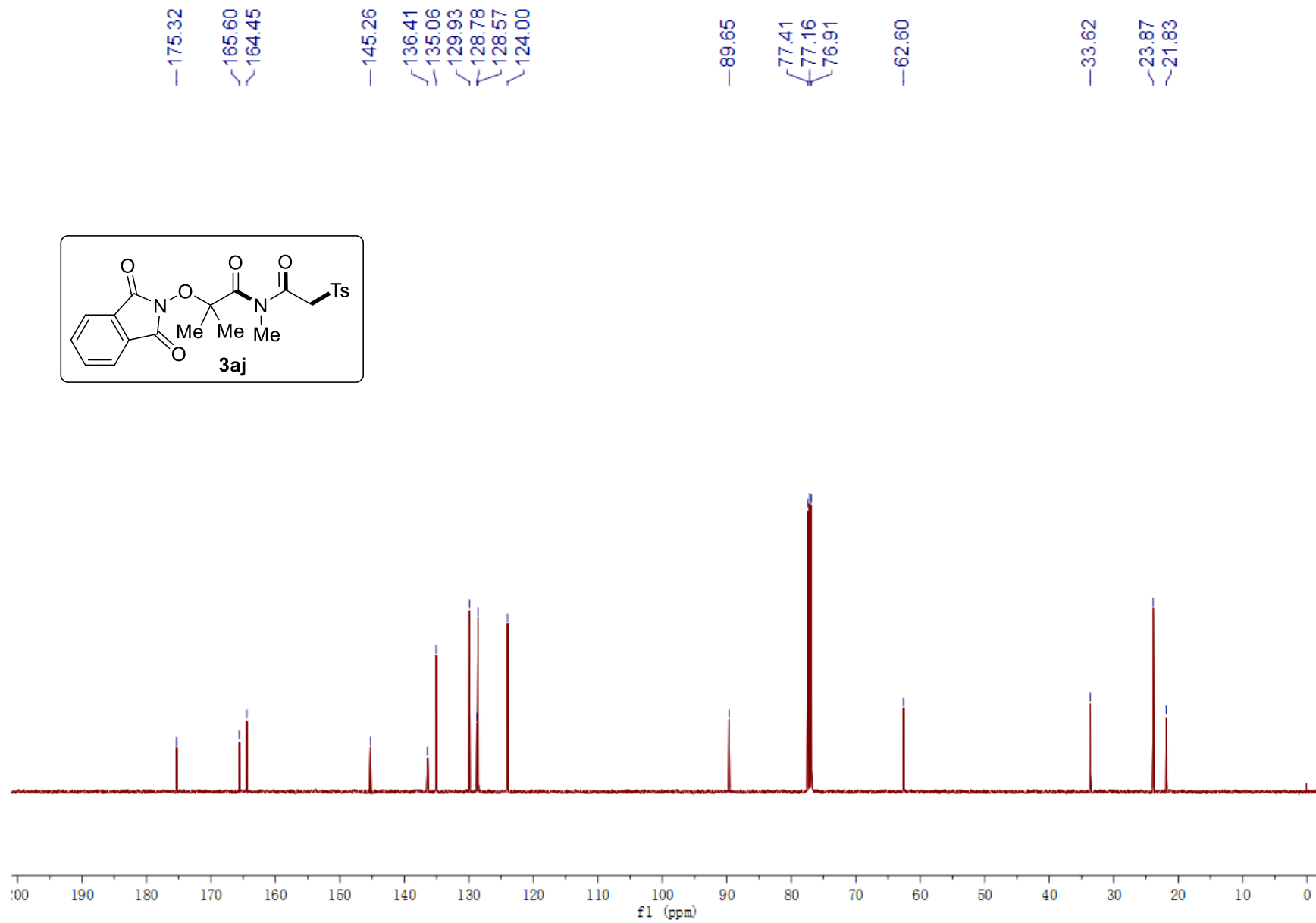
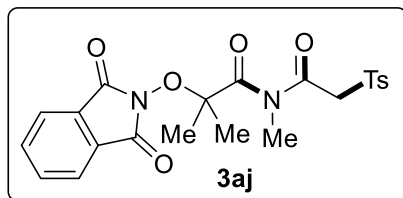
~21.83



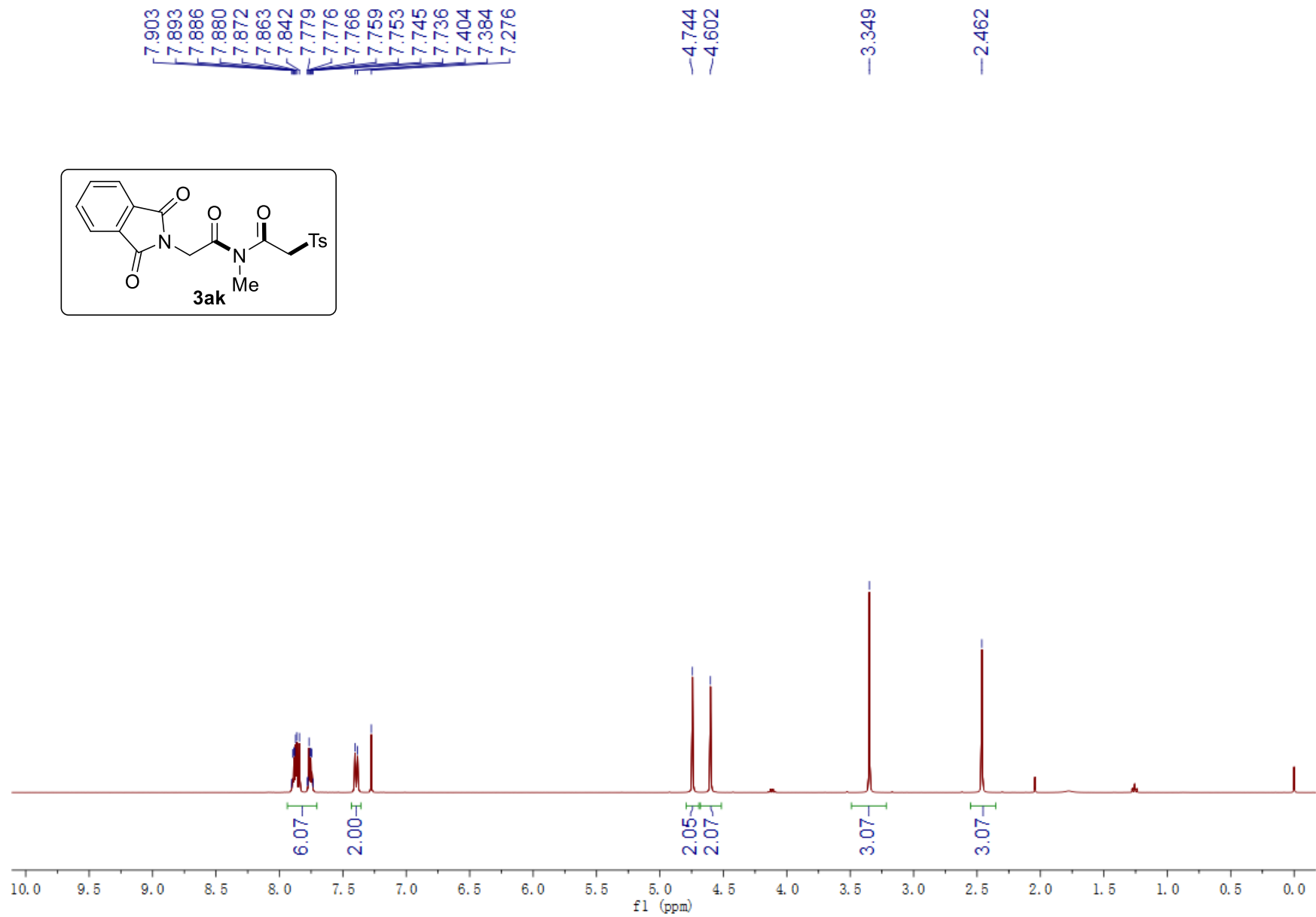
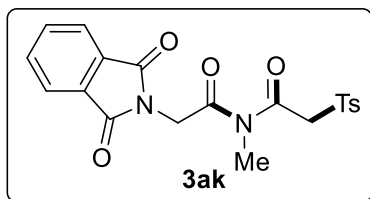
S129



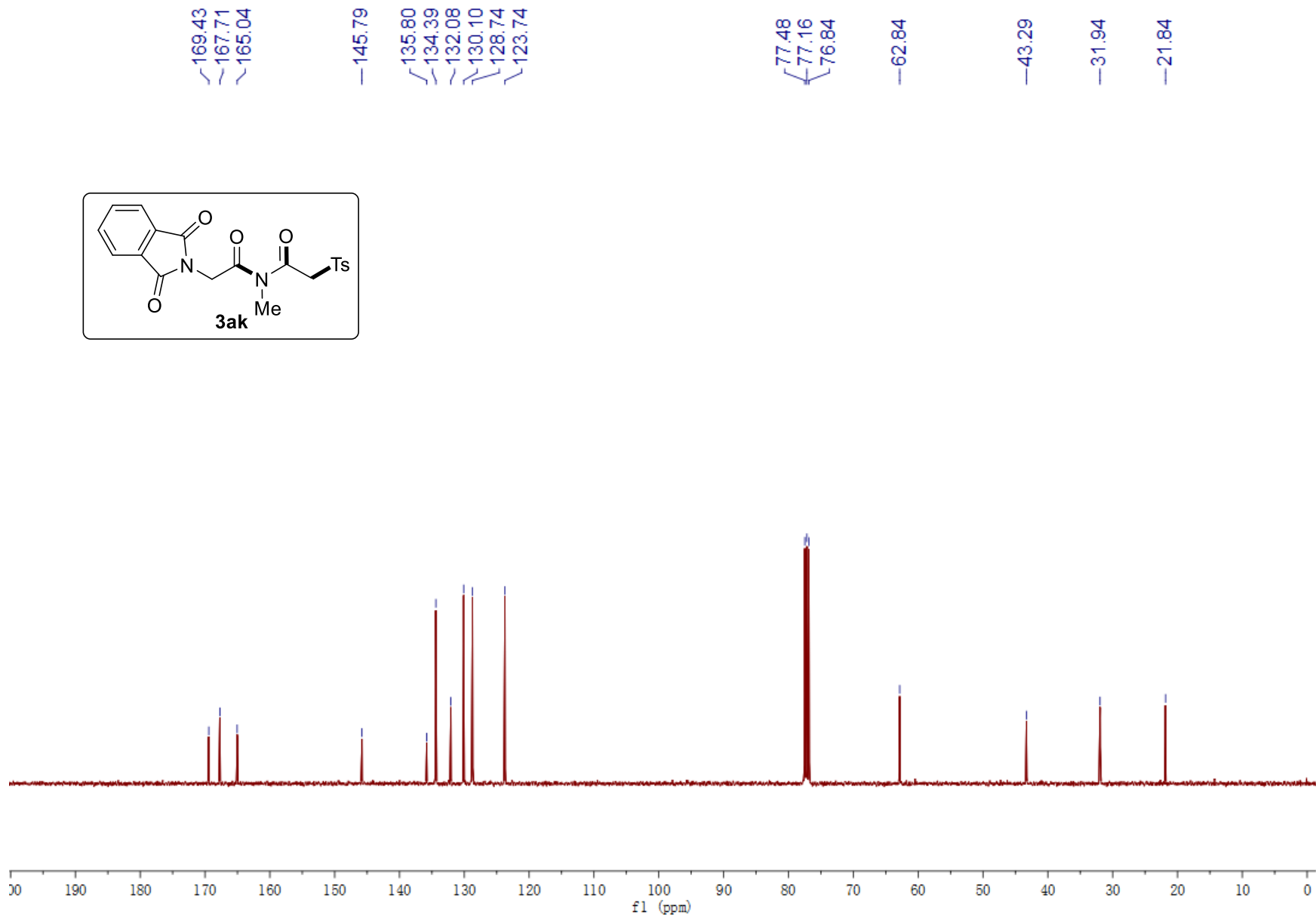
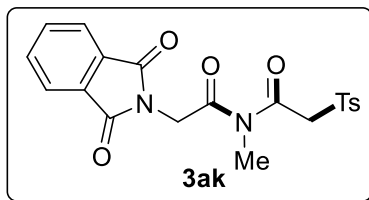
S130



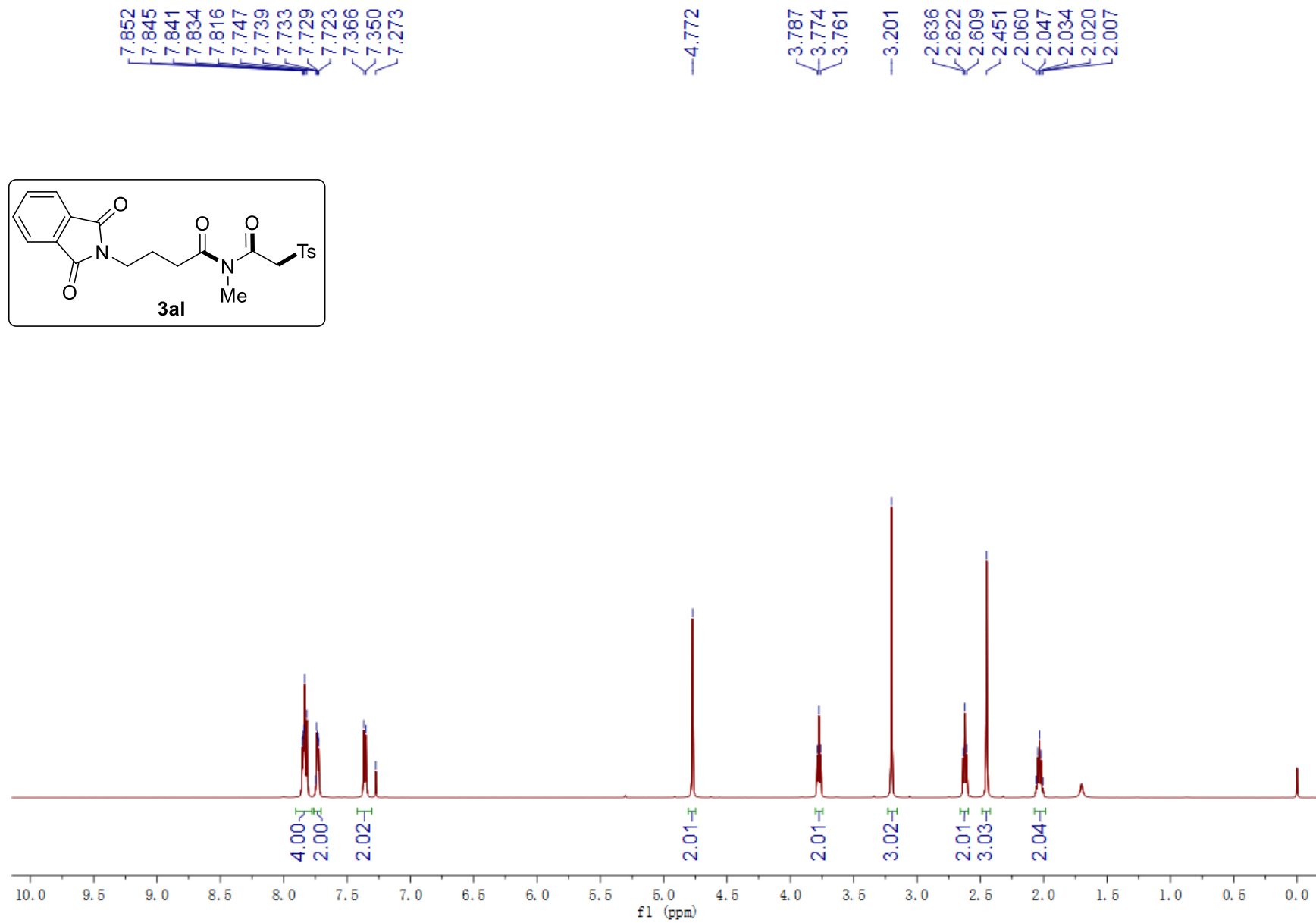
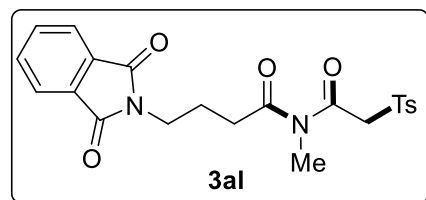
S131

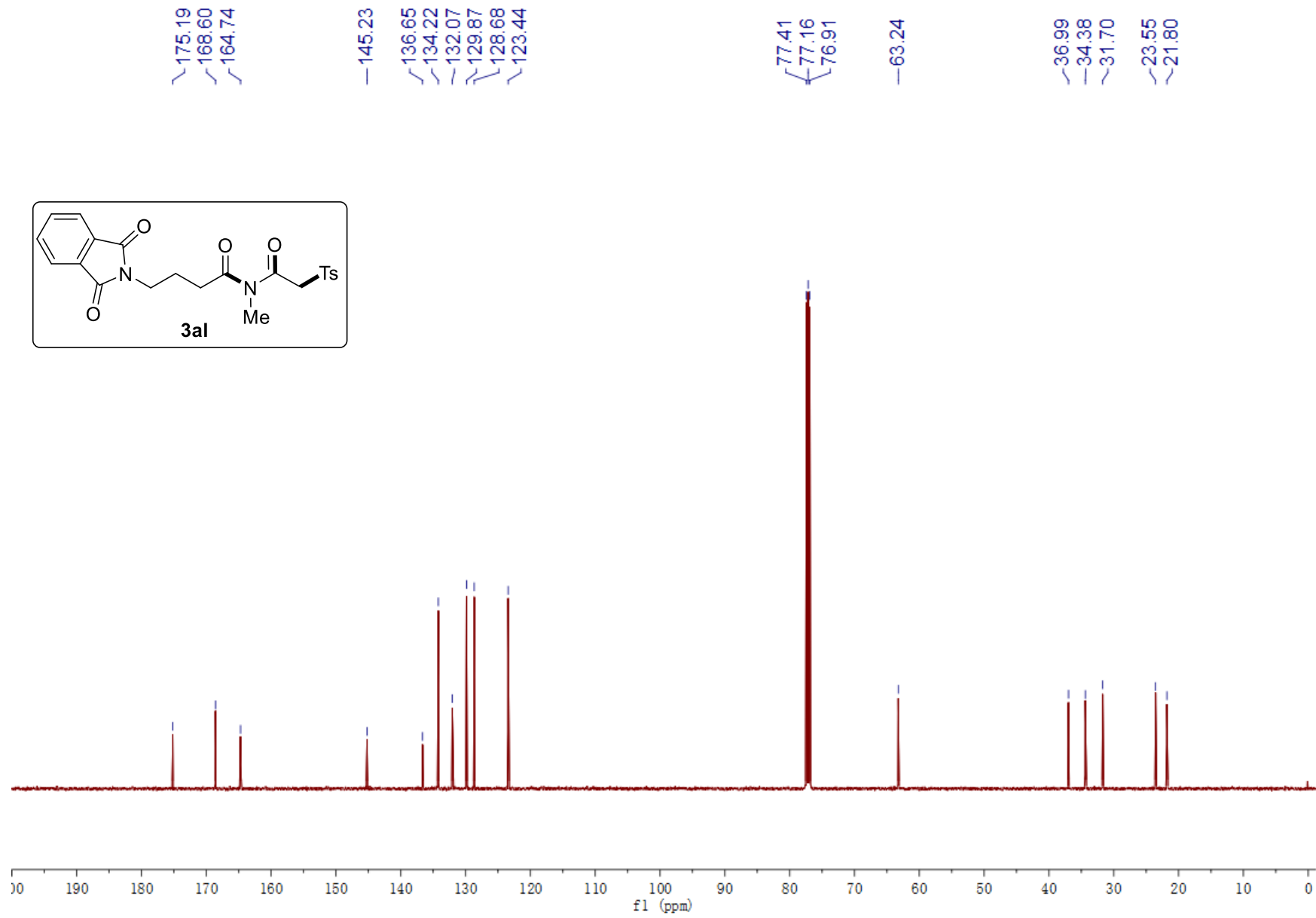
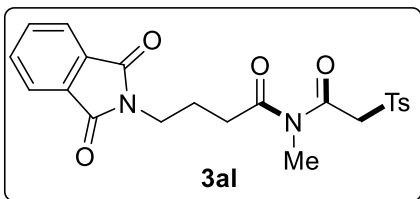


S132

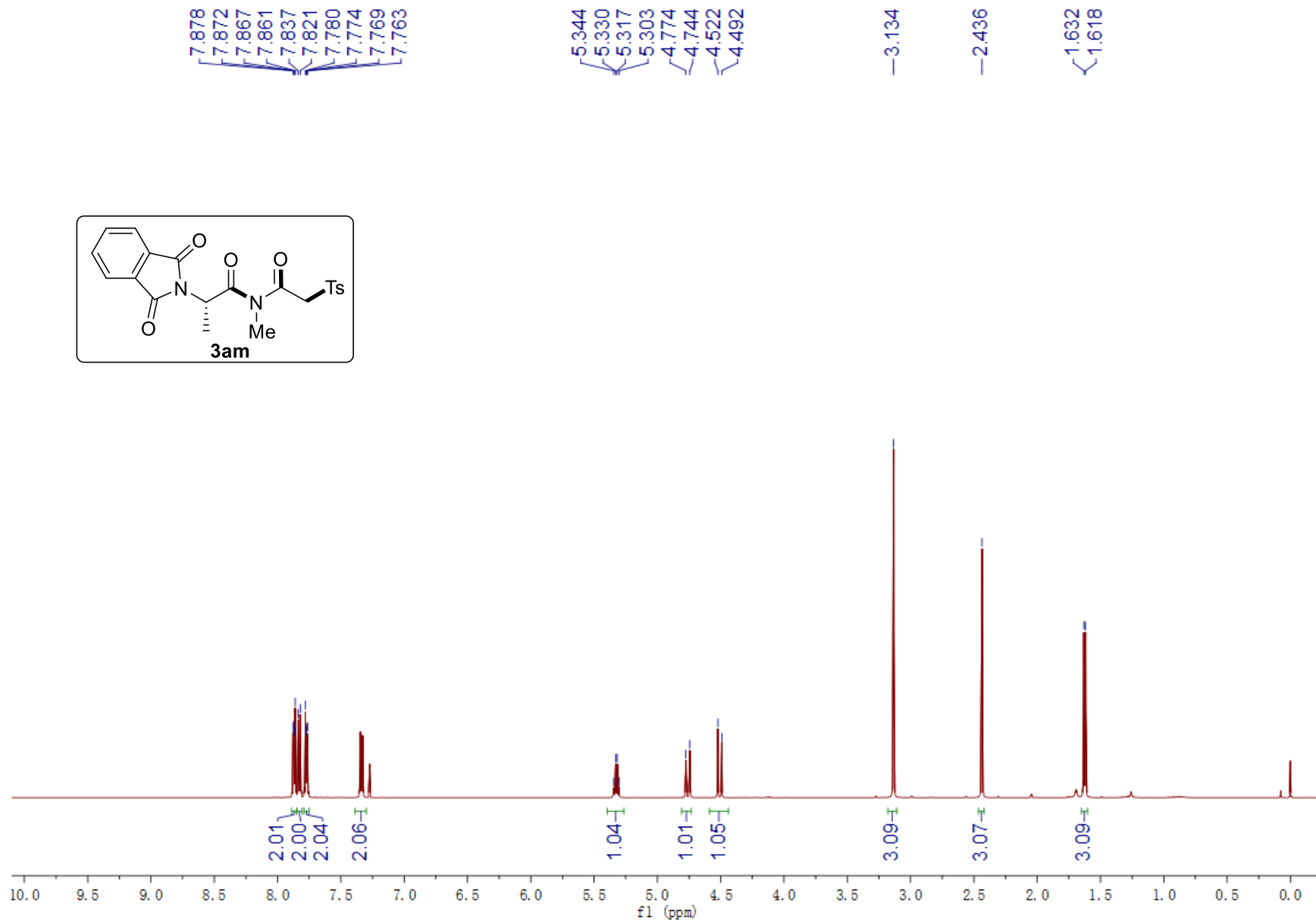
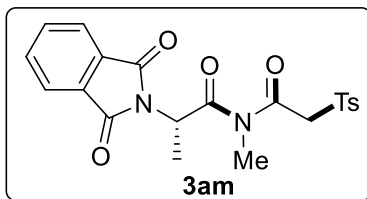


S133

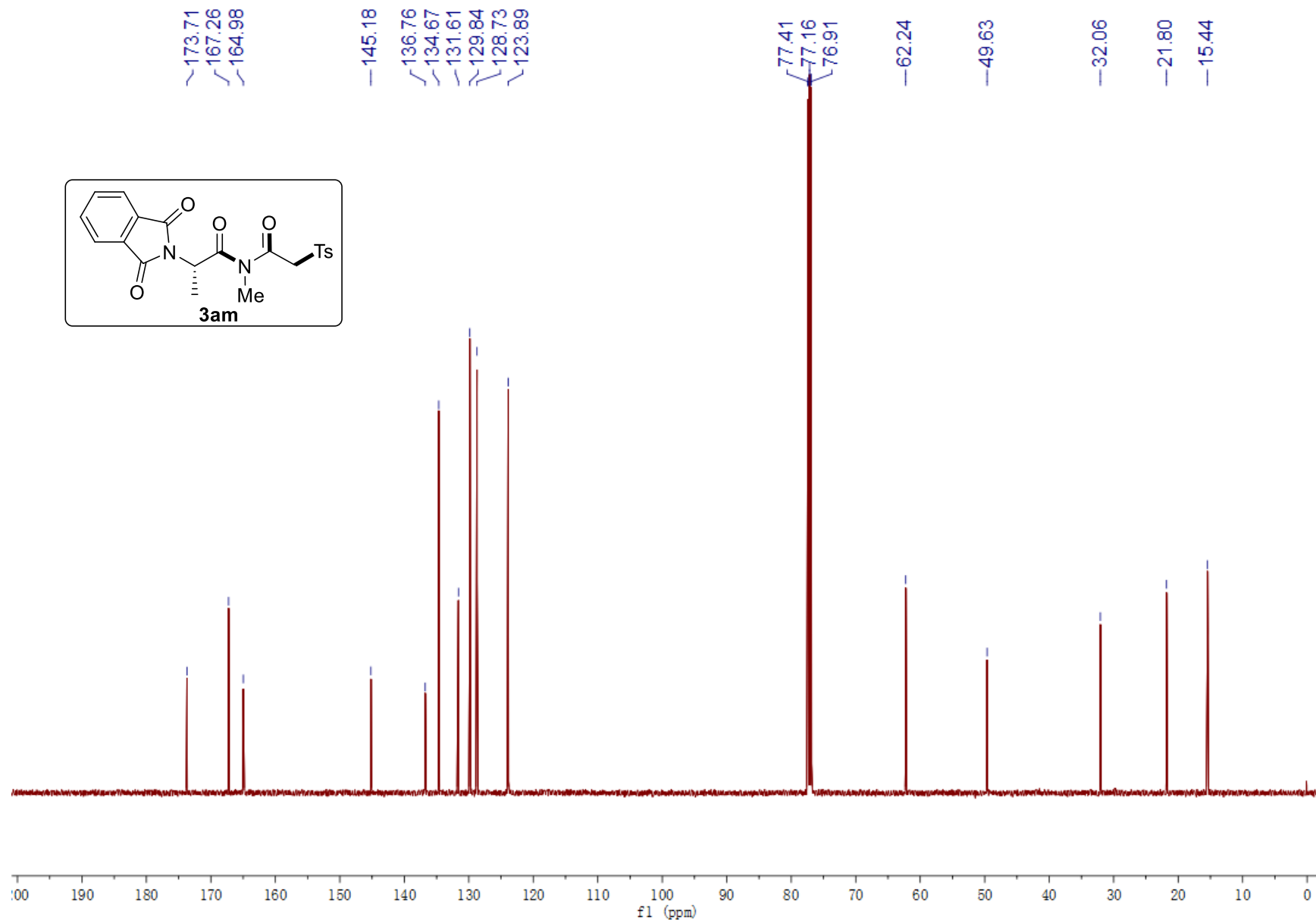




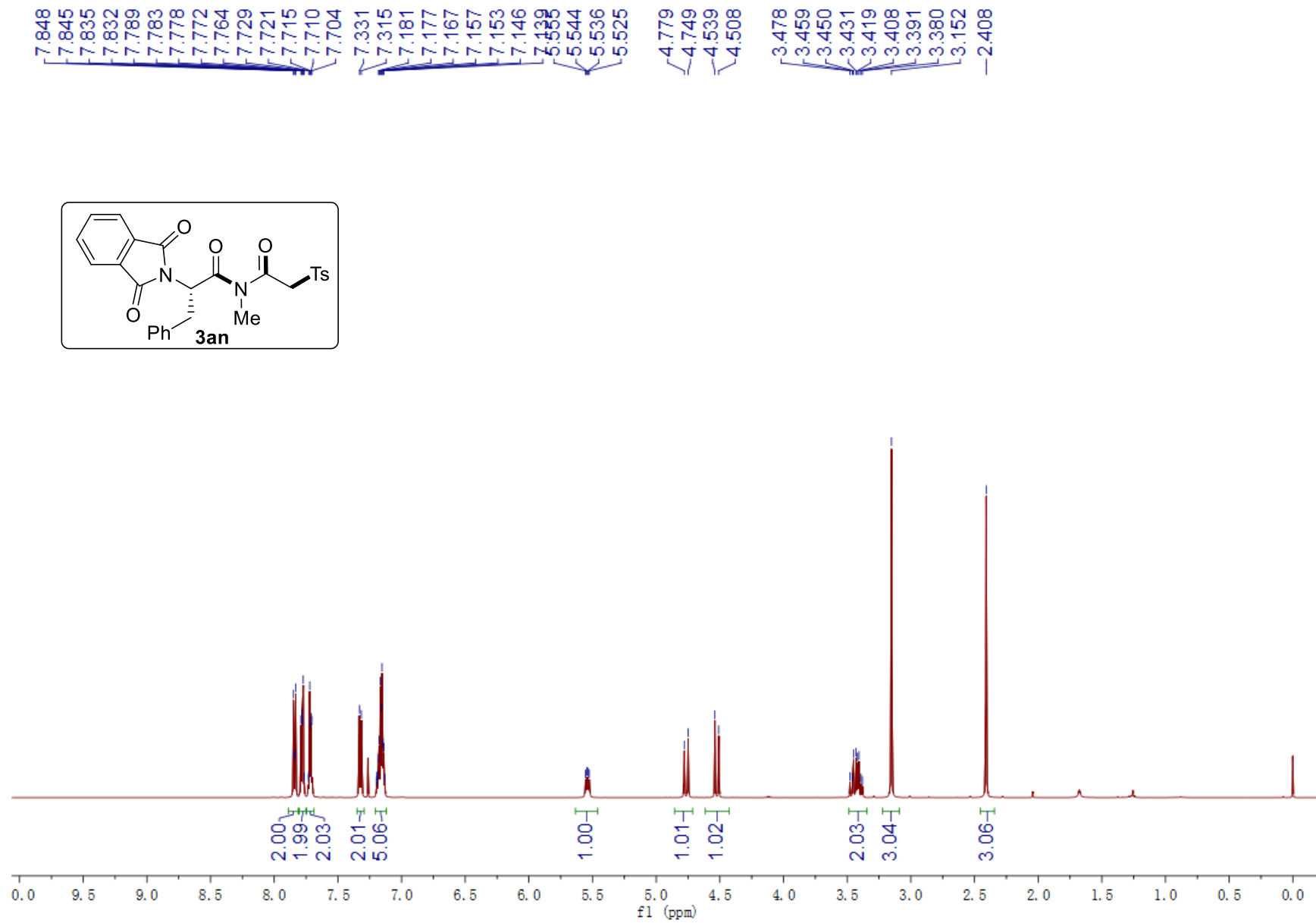
S135



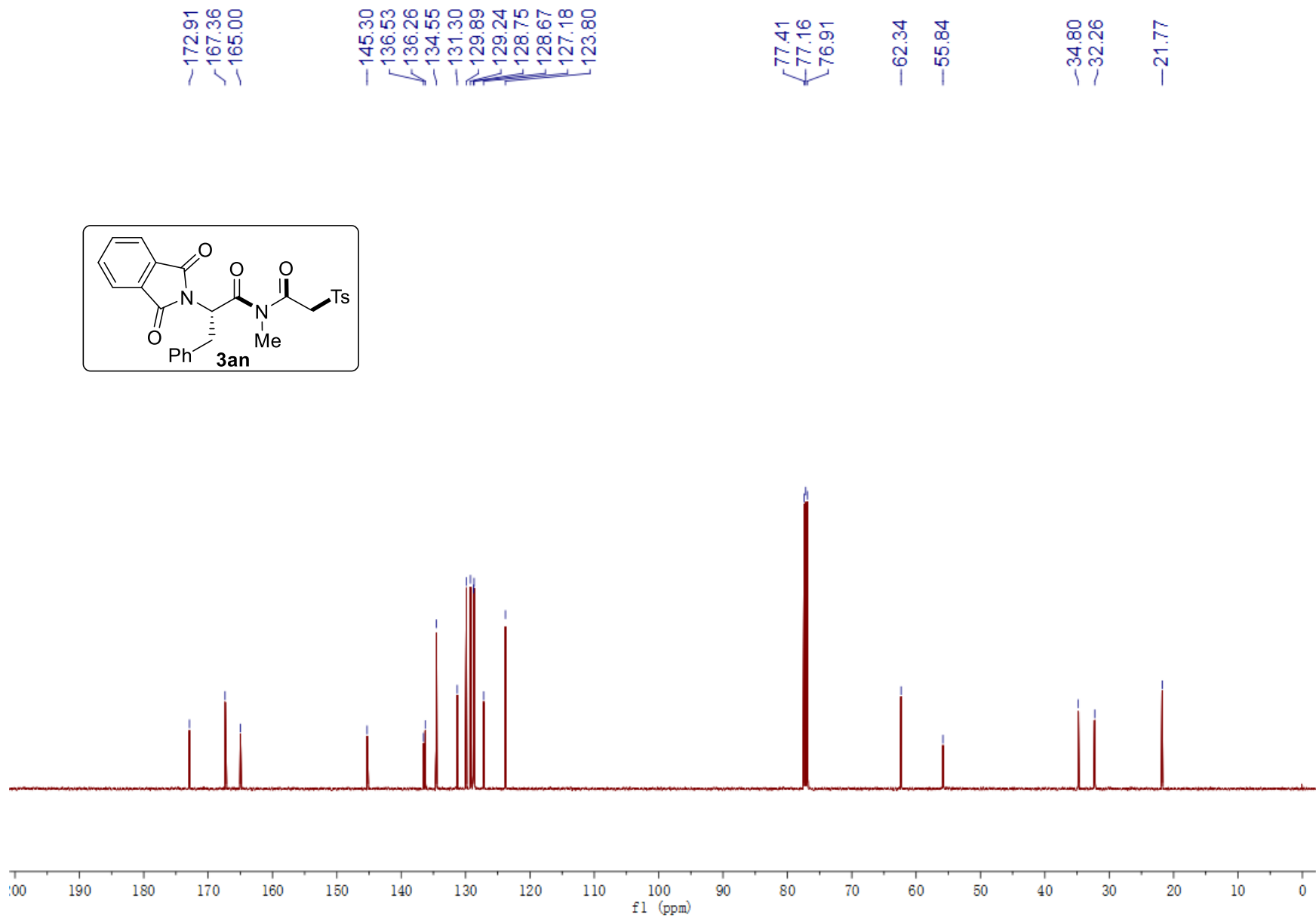
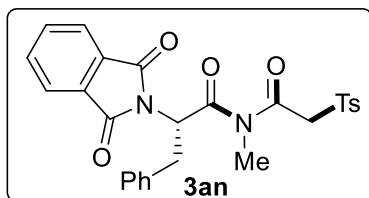
S136



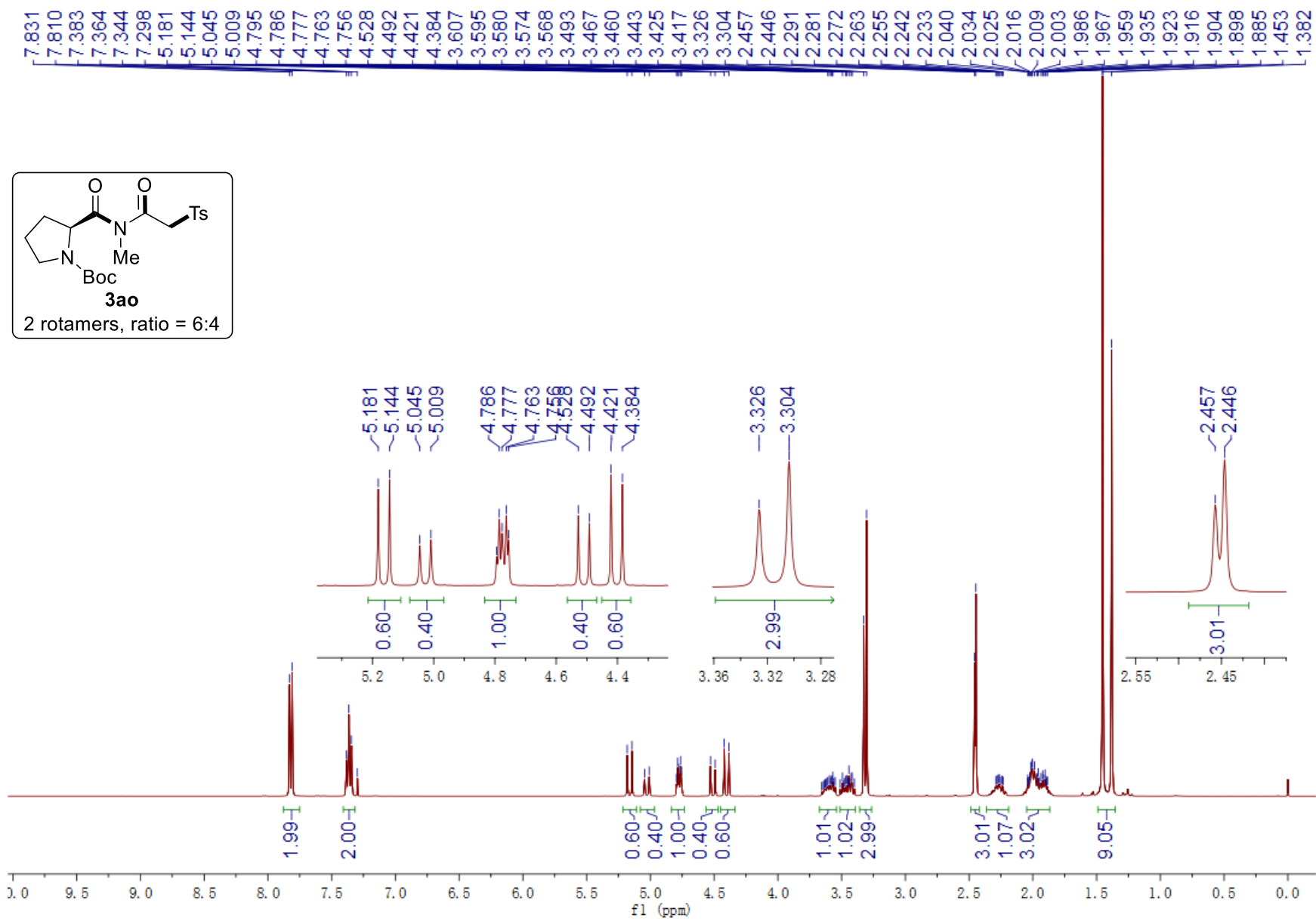
S137



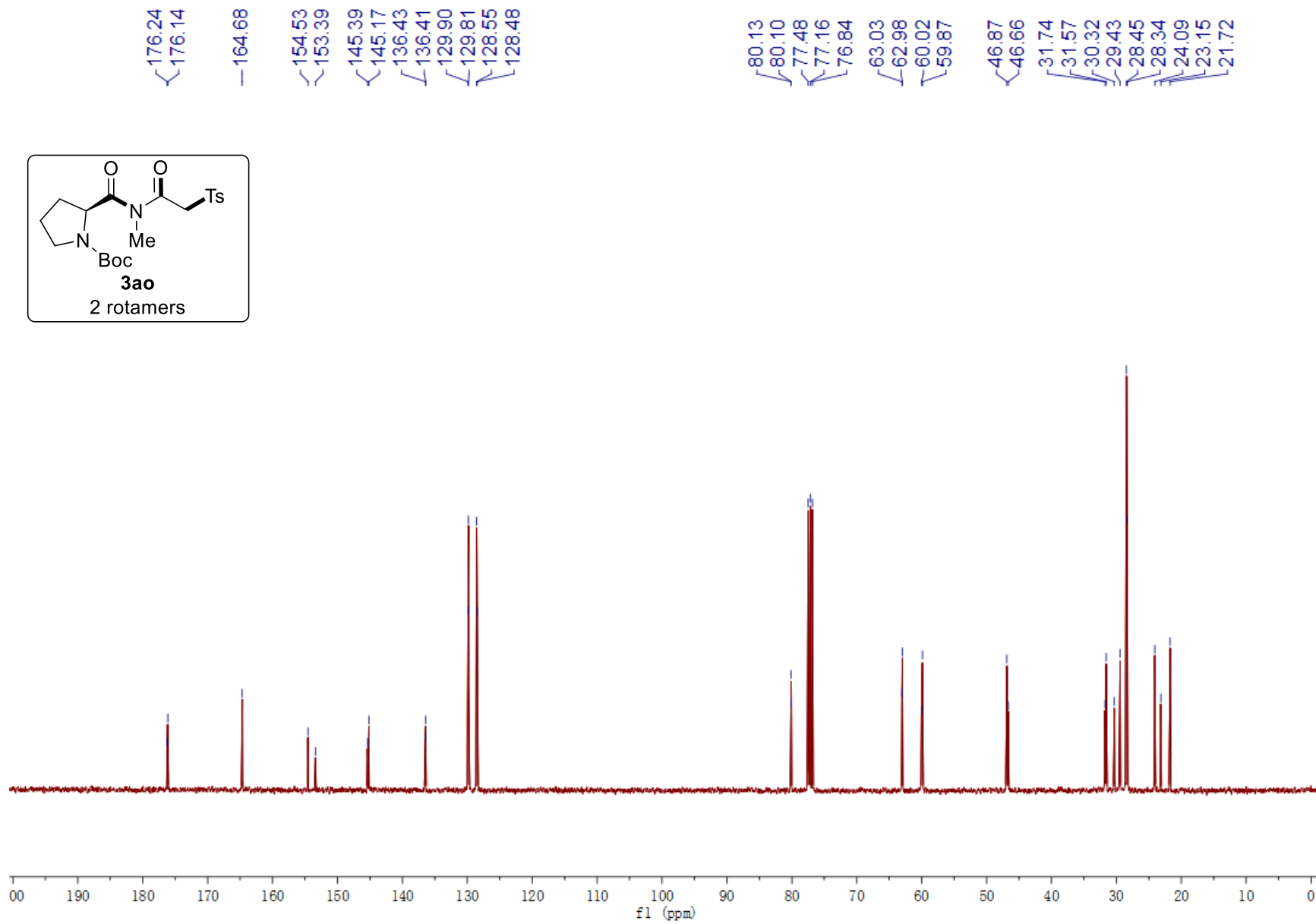
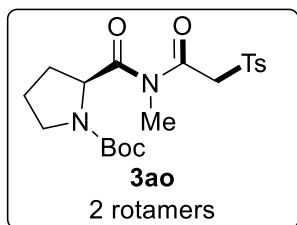
S138



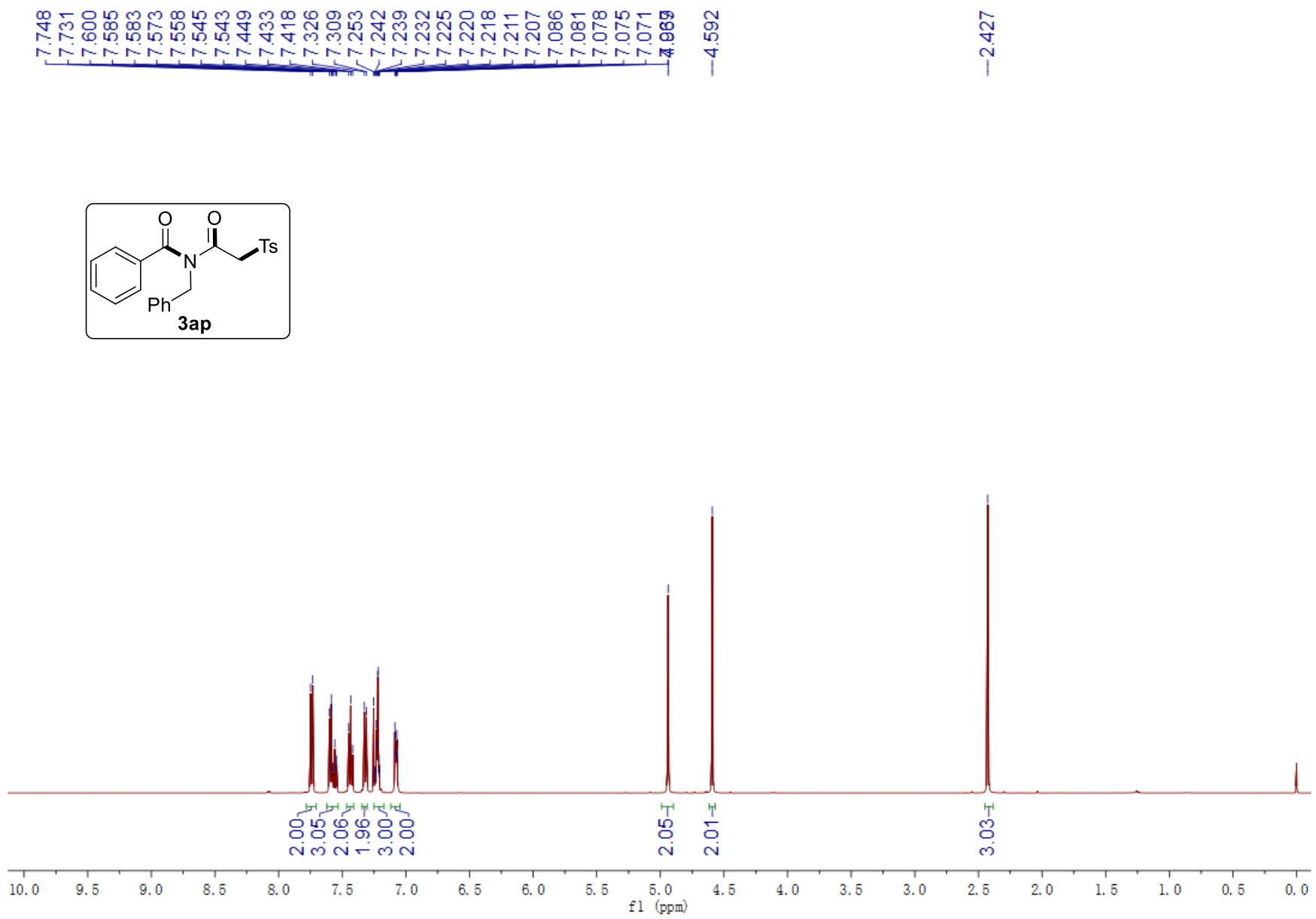
S139



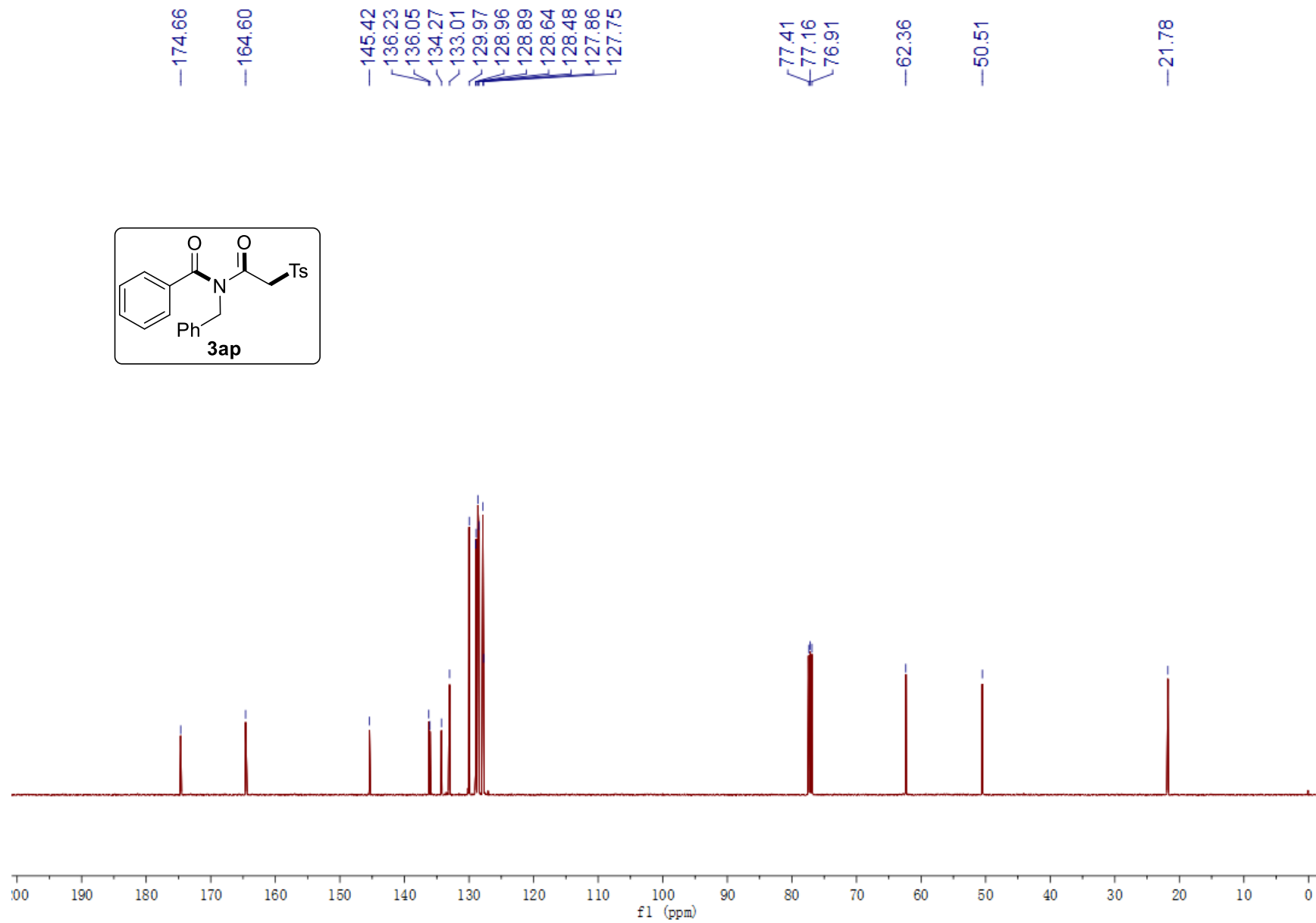
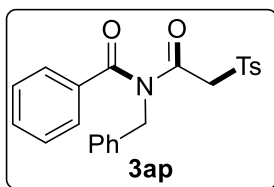
S140



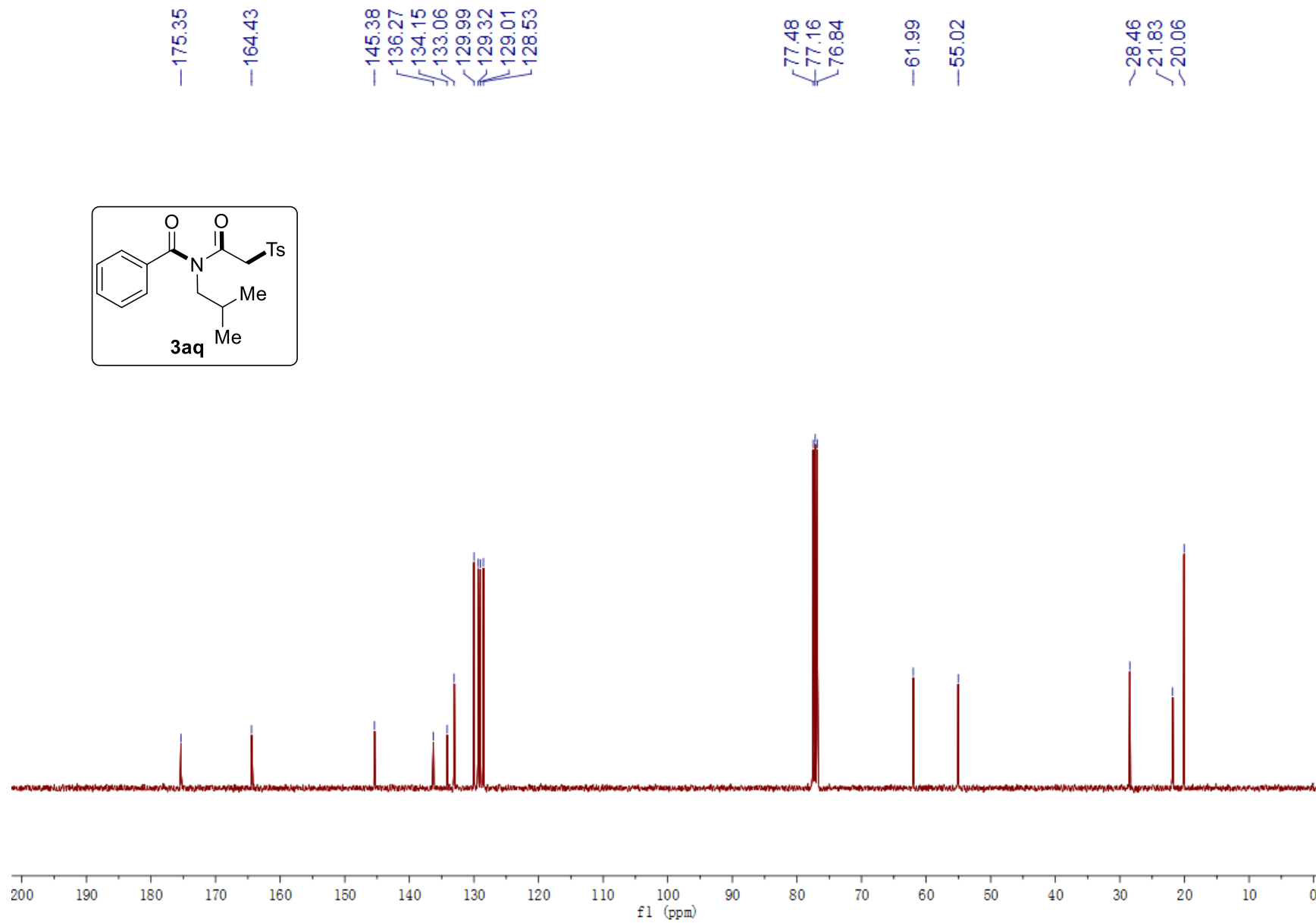
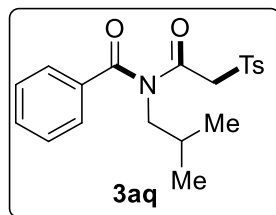
S141



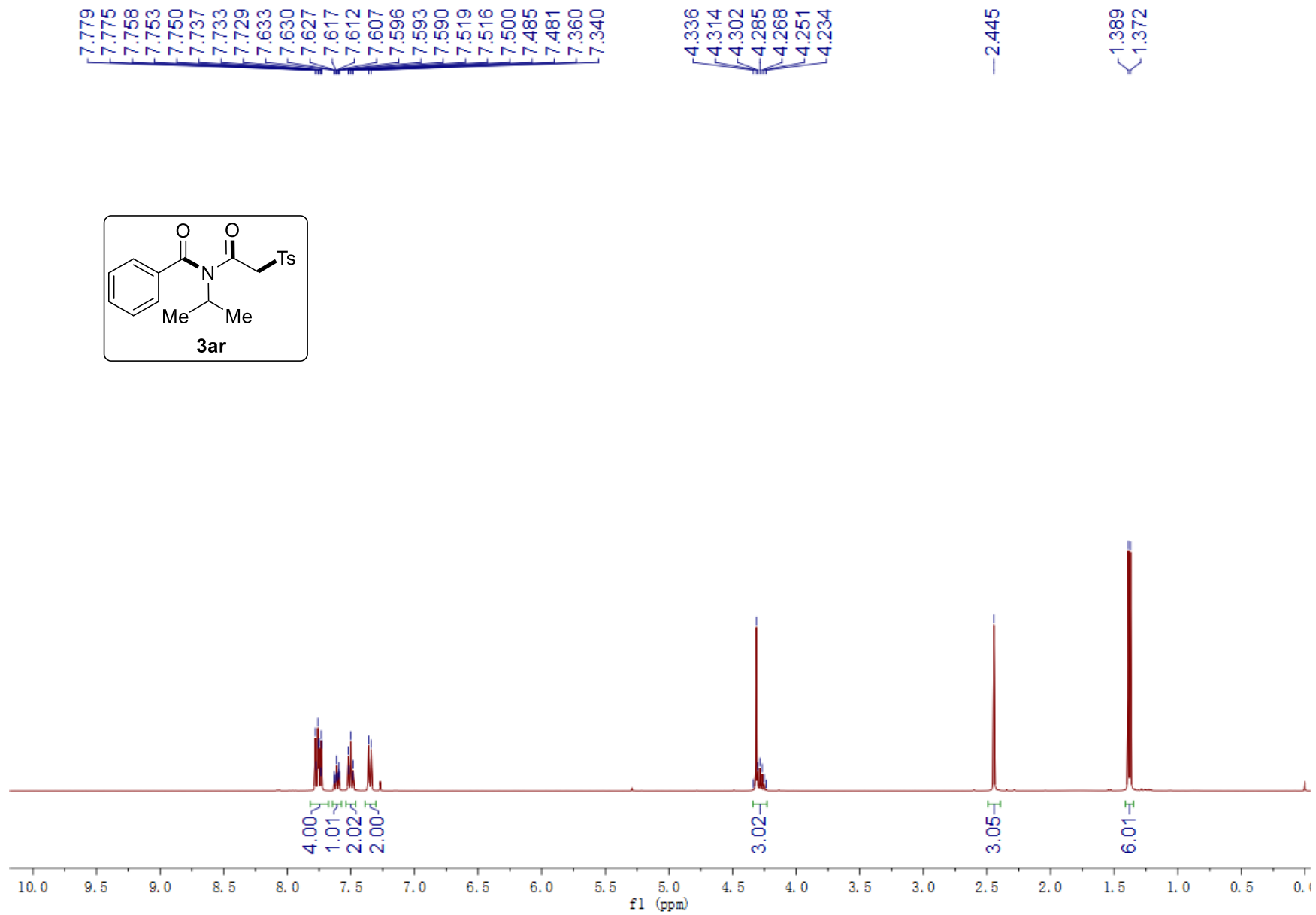
S142

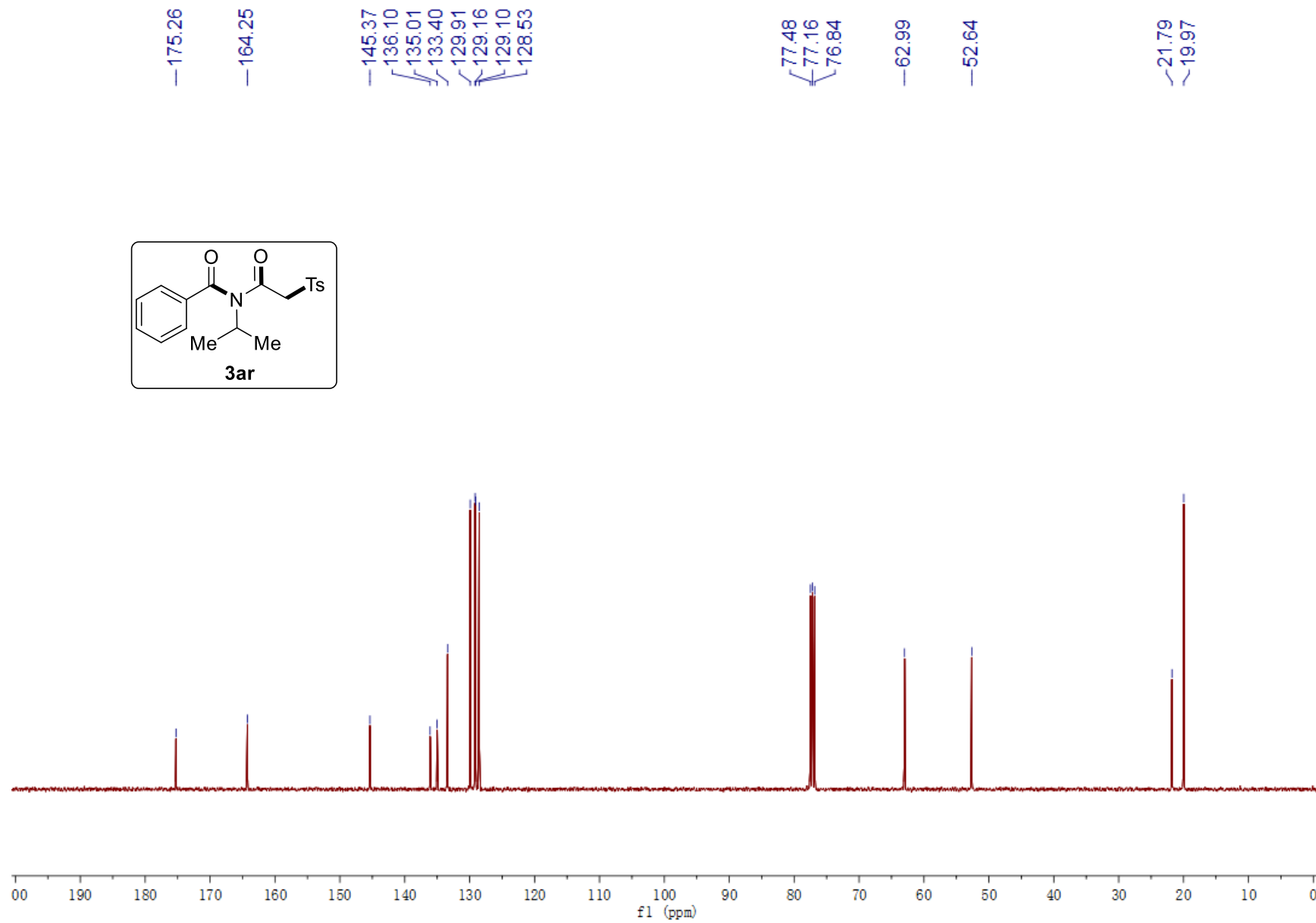
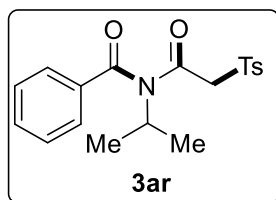


S143

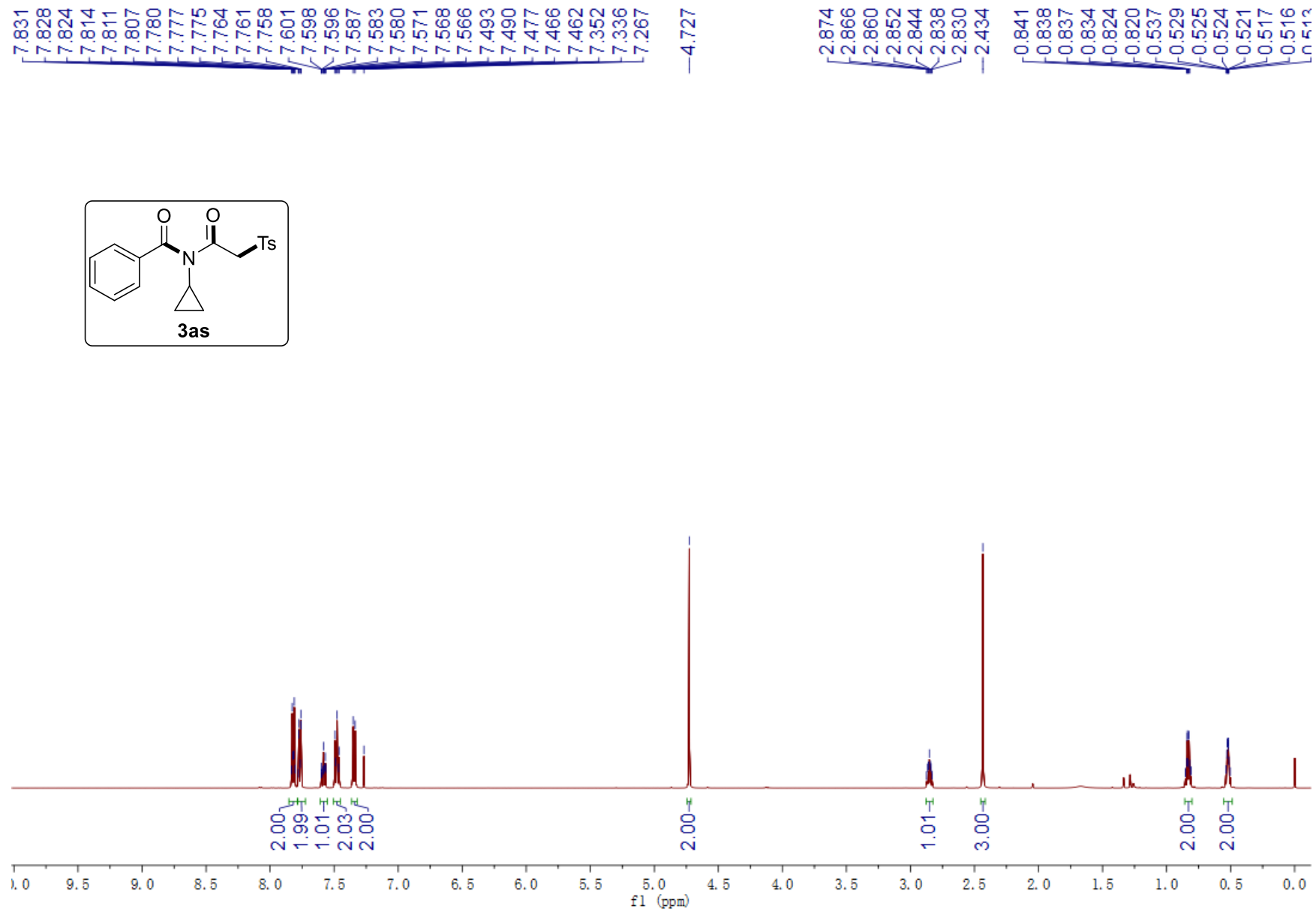


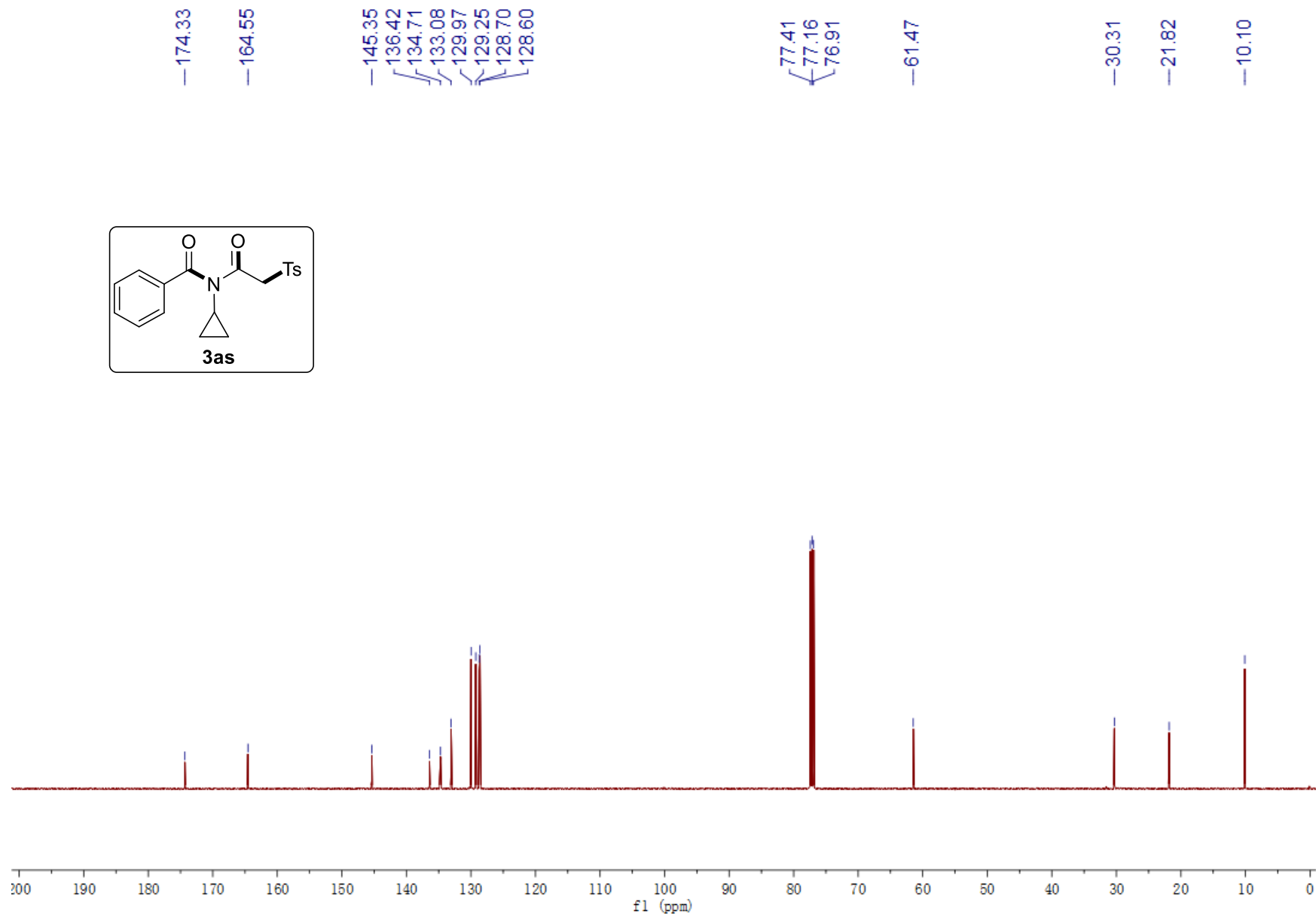
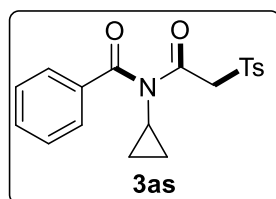
S145



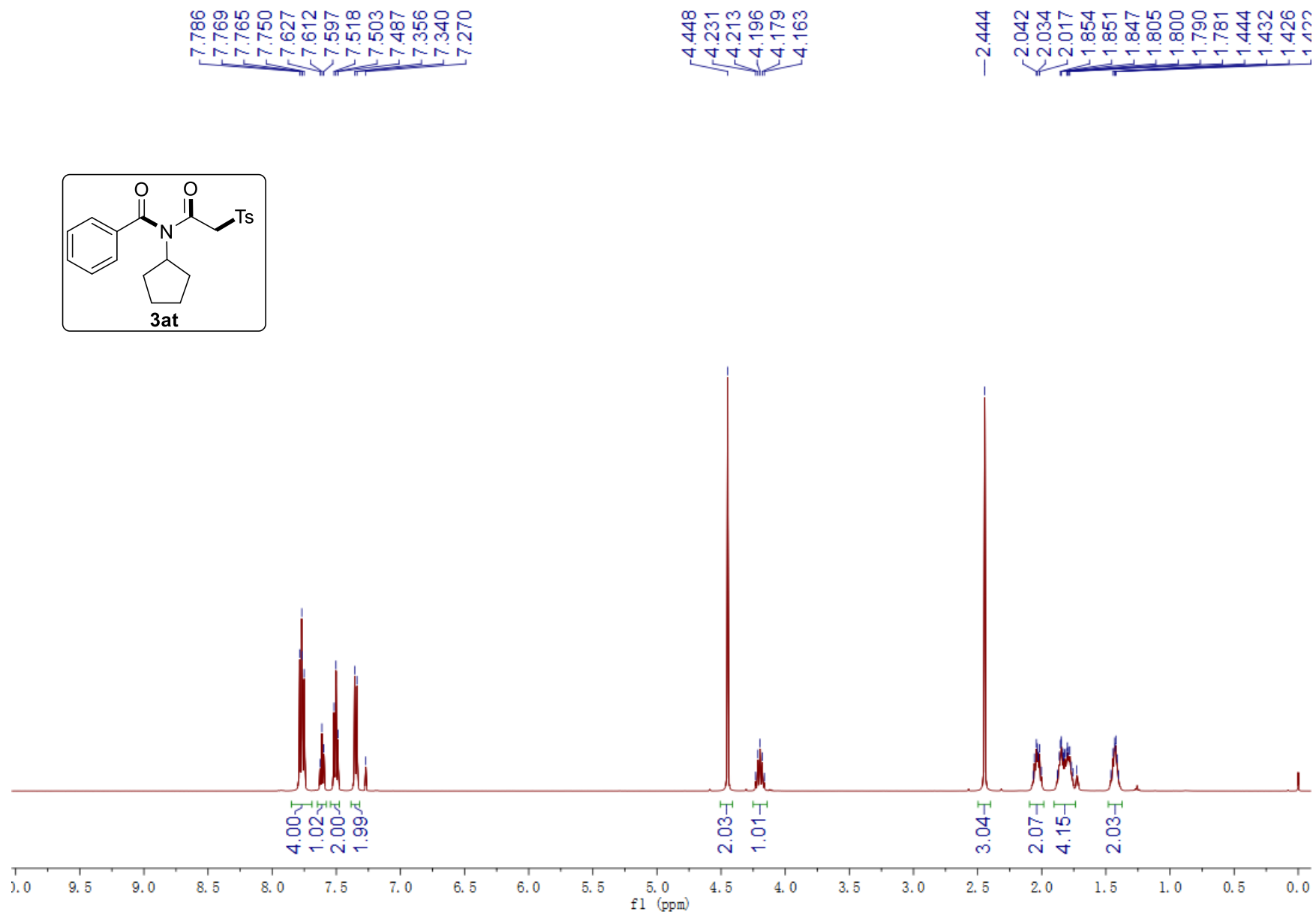
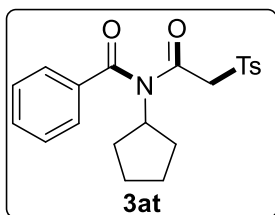


S147

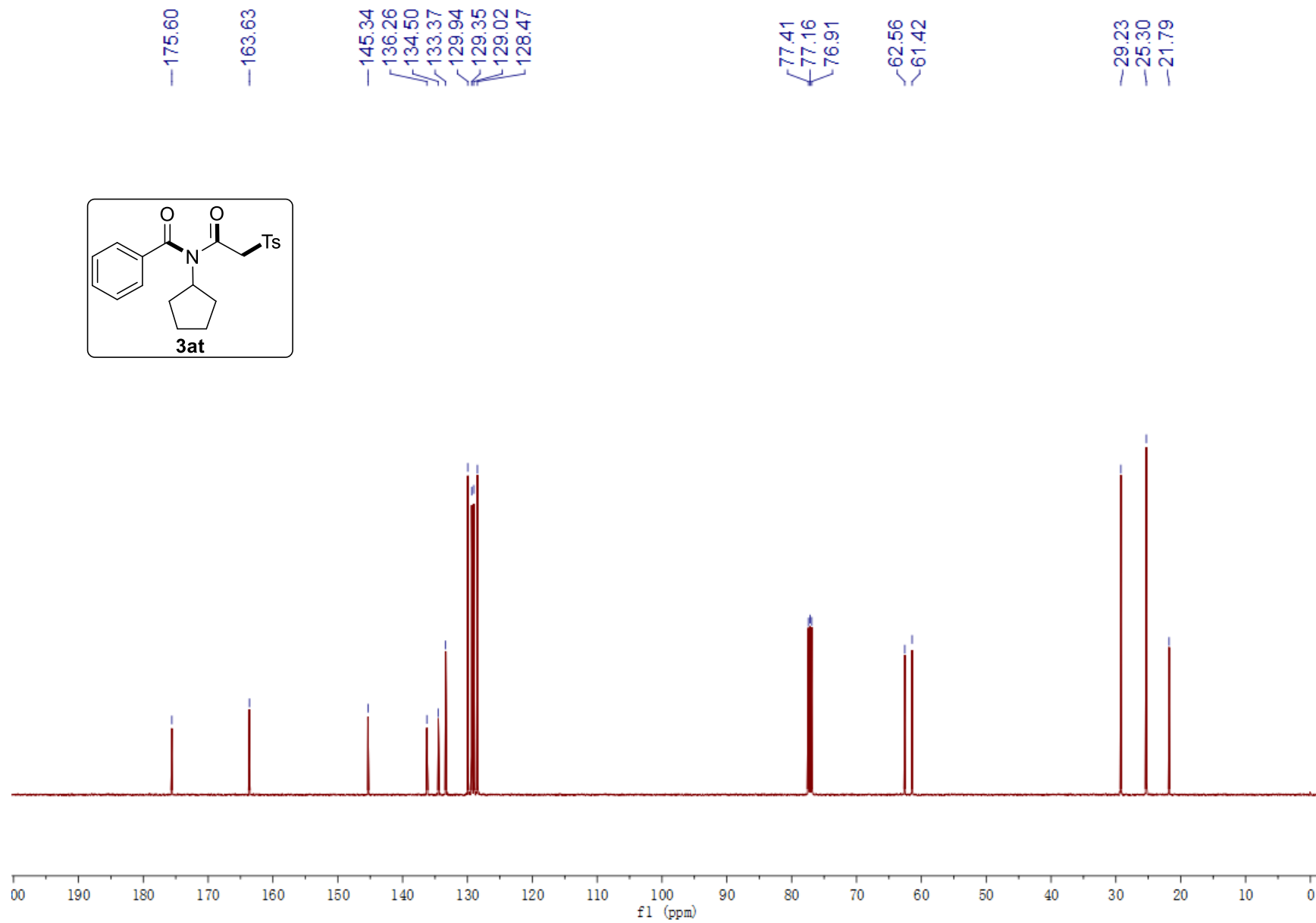
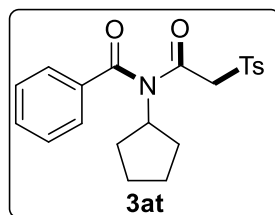




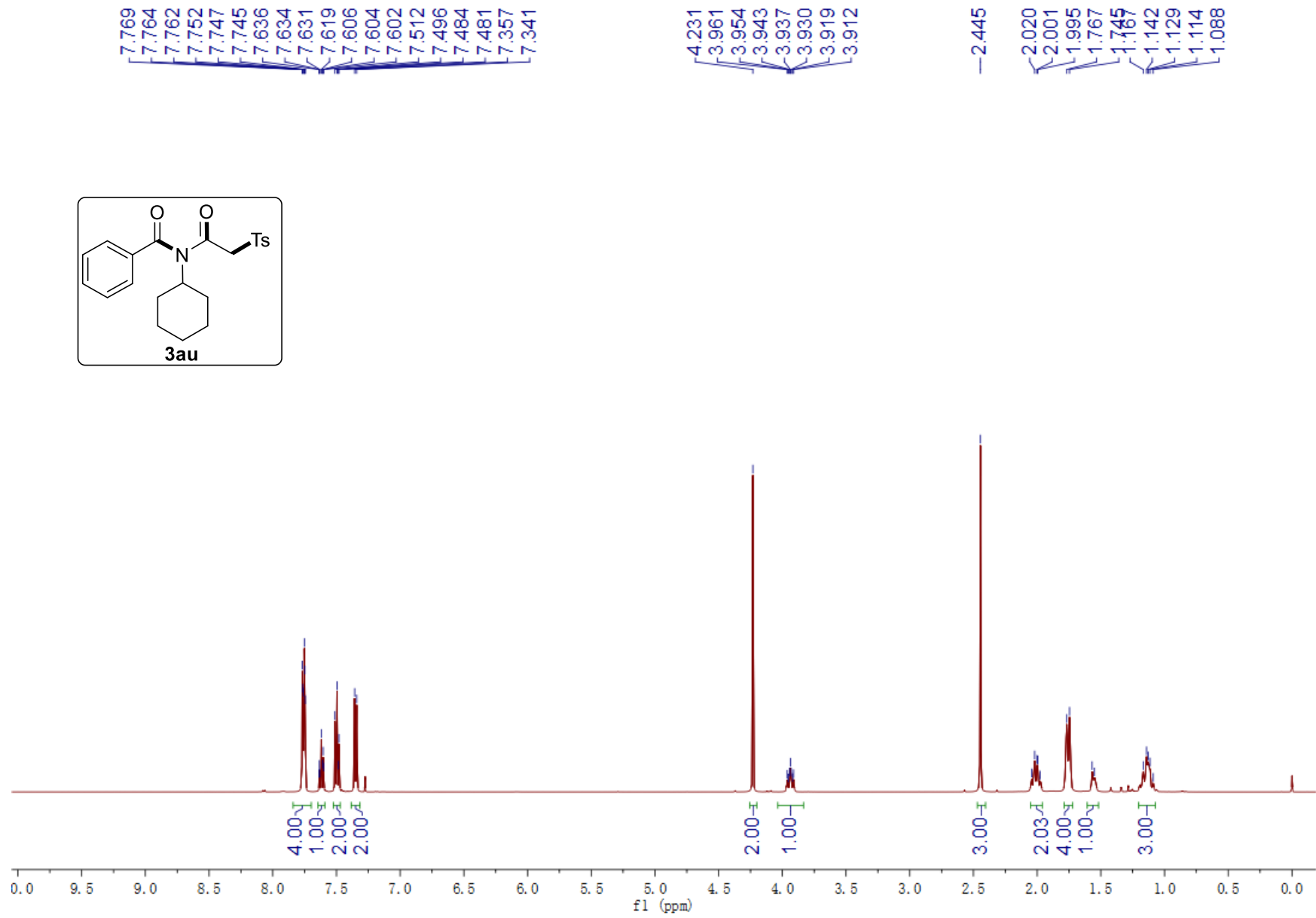
S149



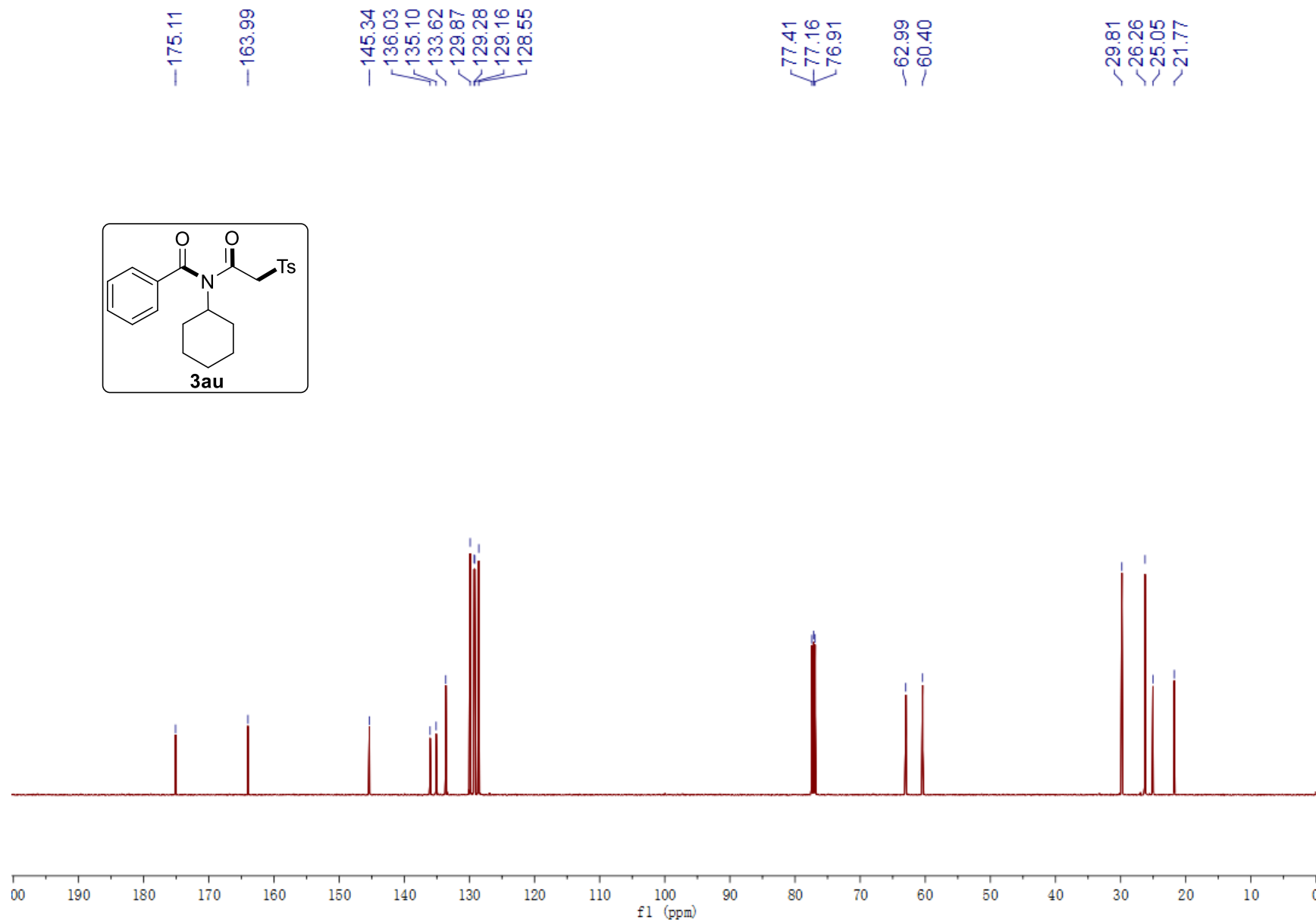
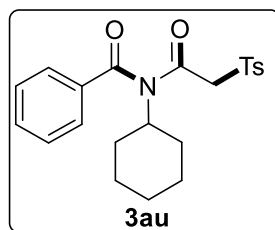
S150



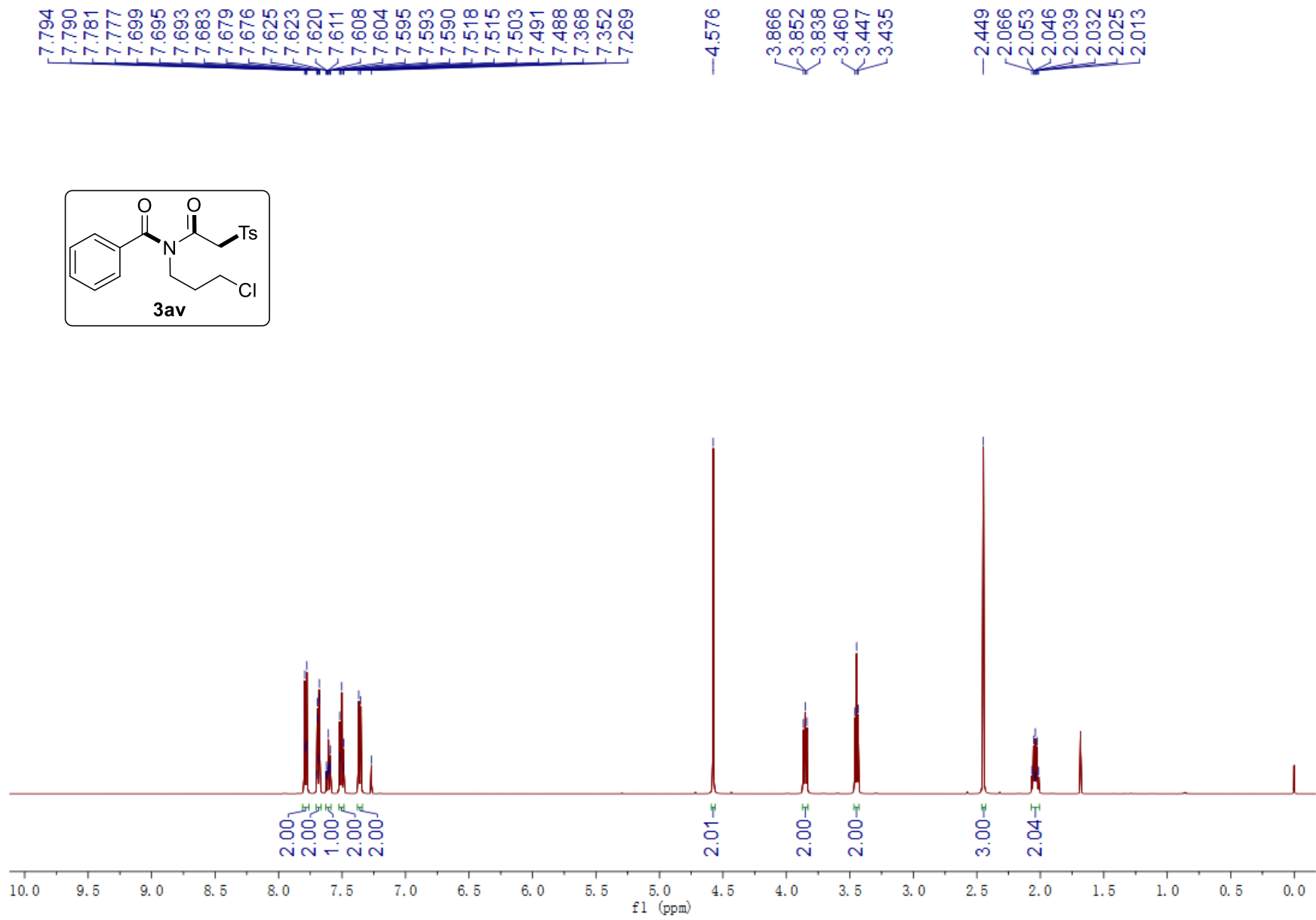
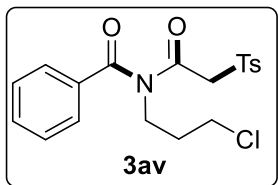
S151



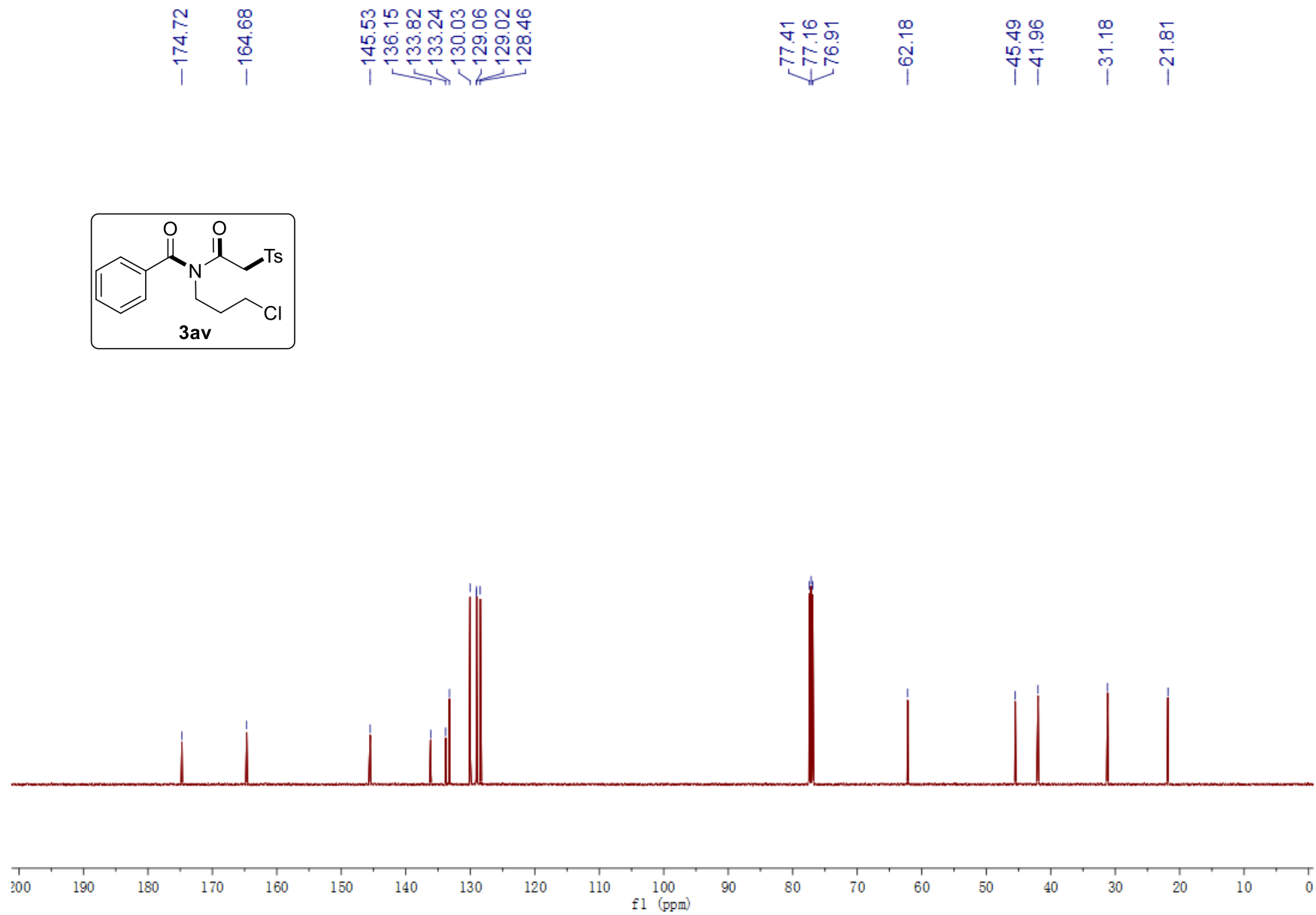
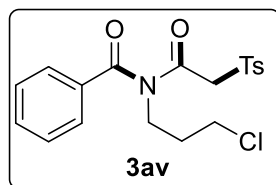
S152



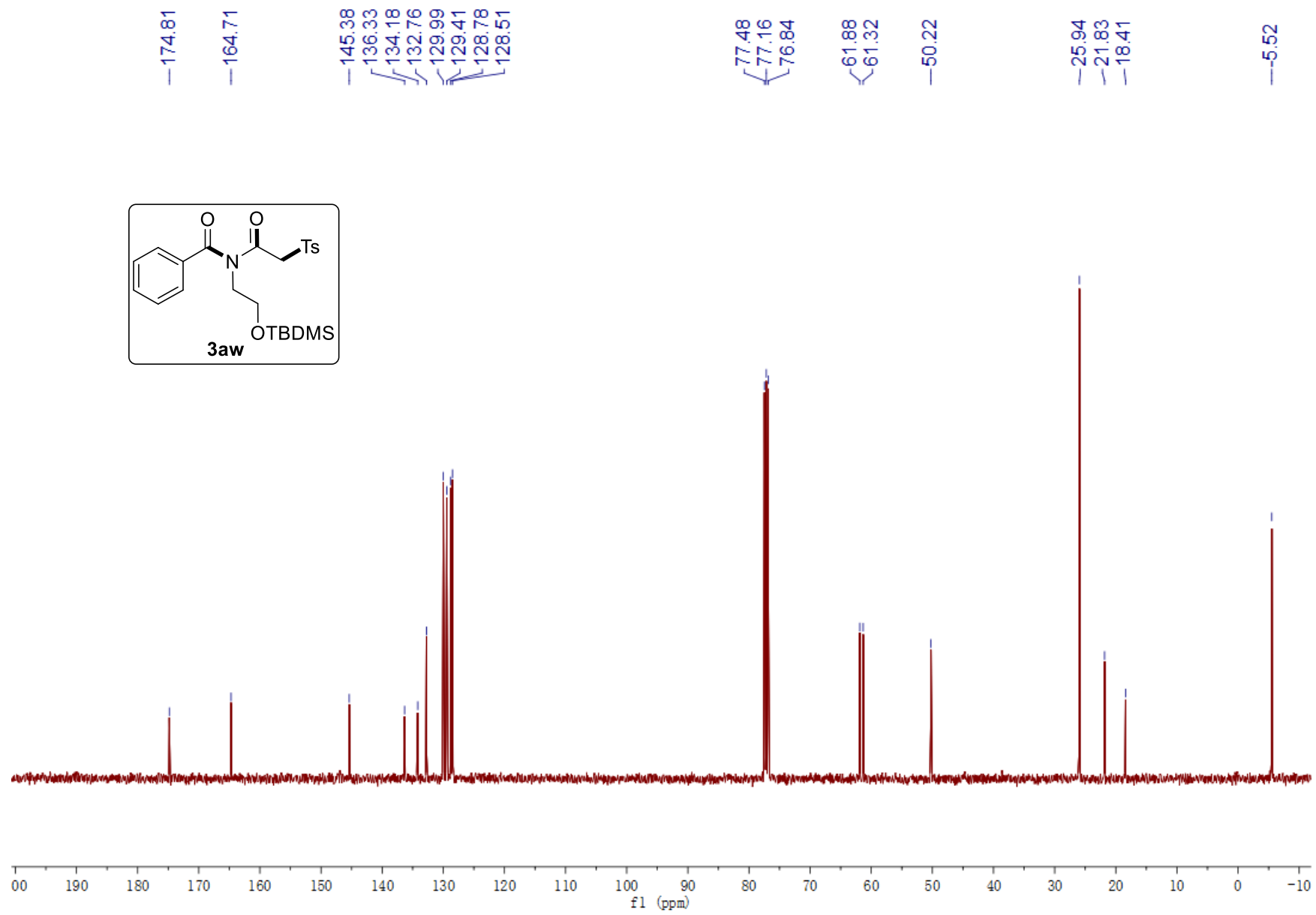
S153



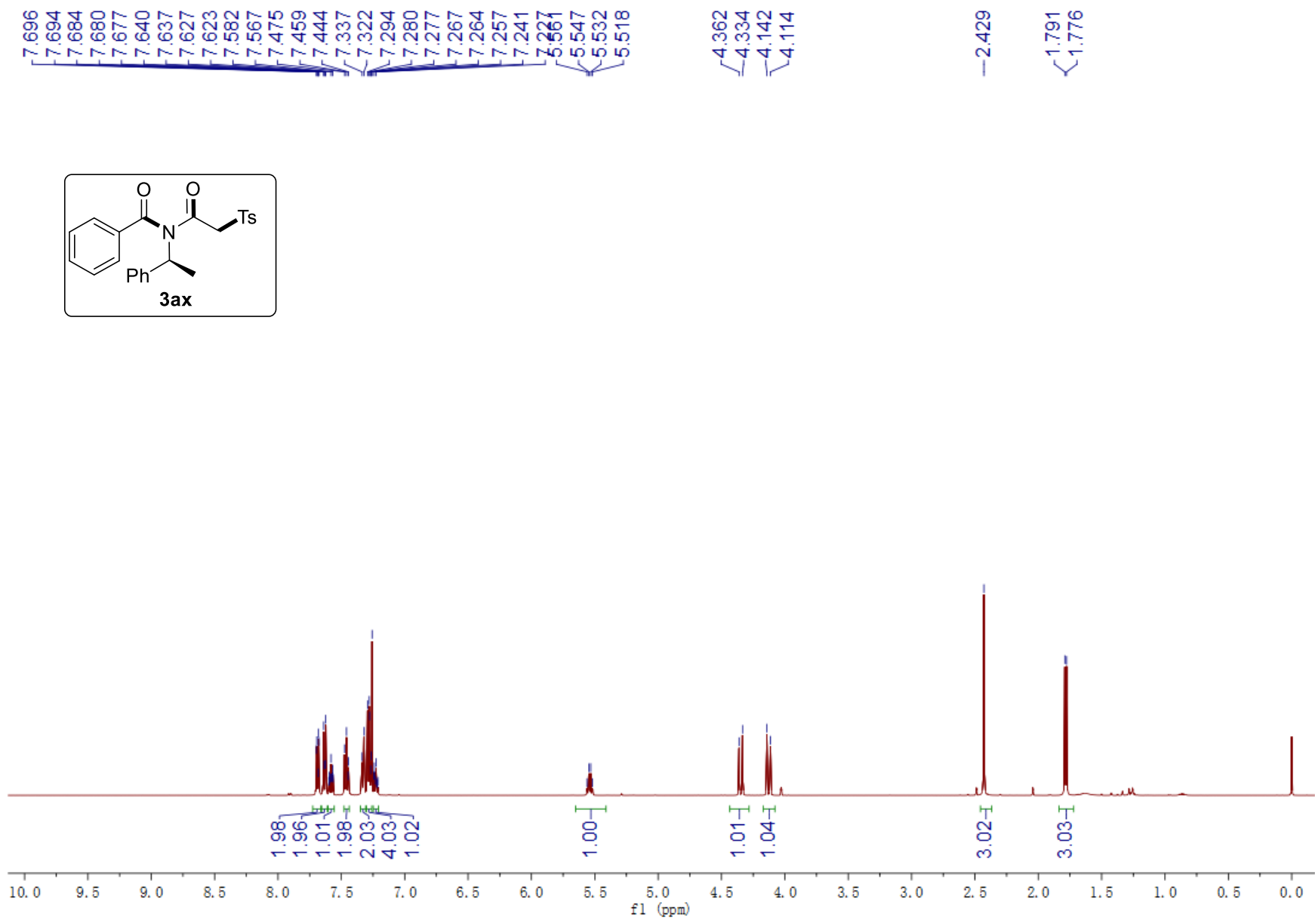
S154

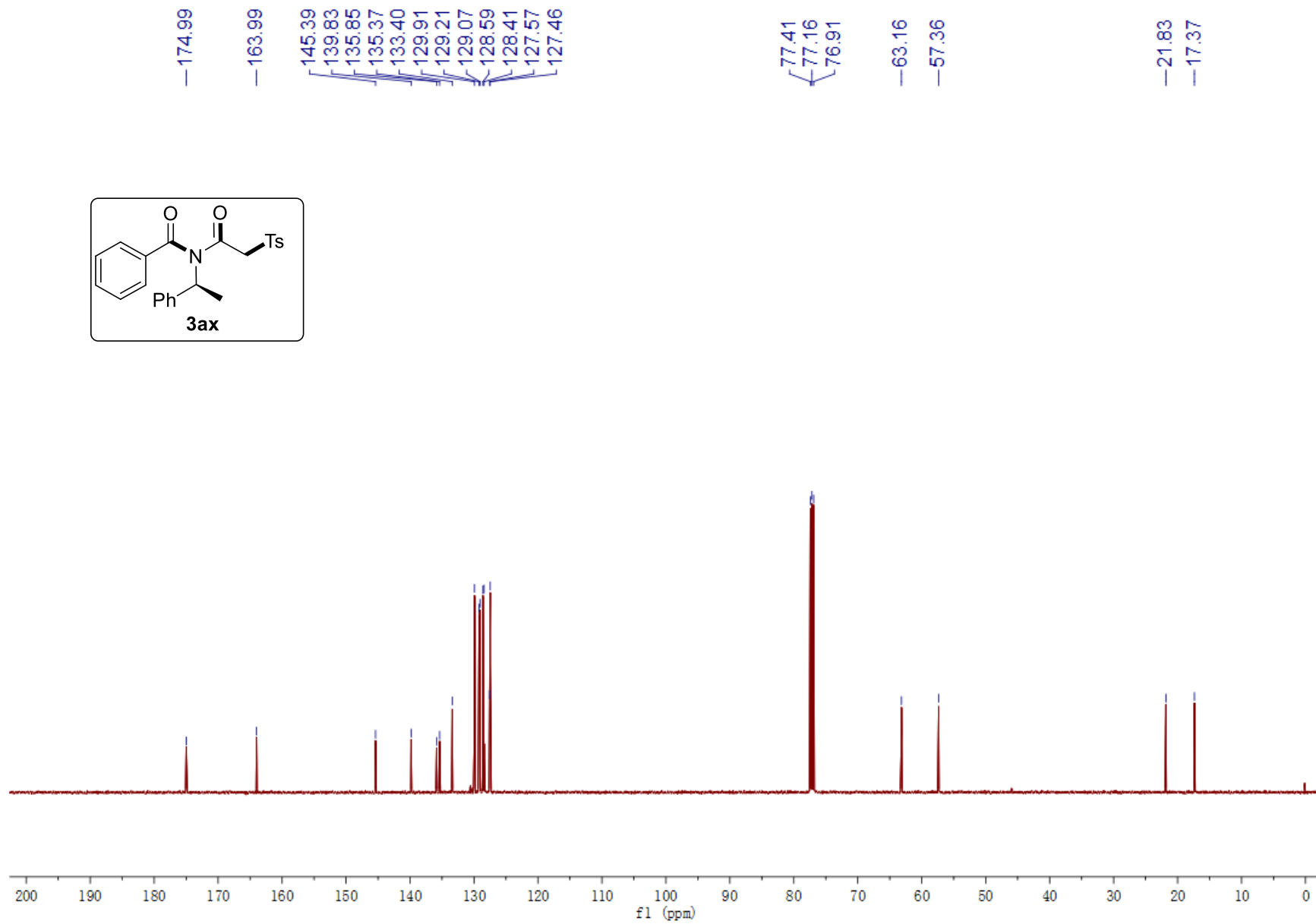
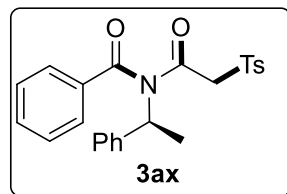


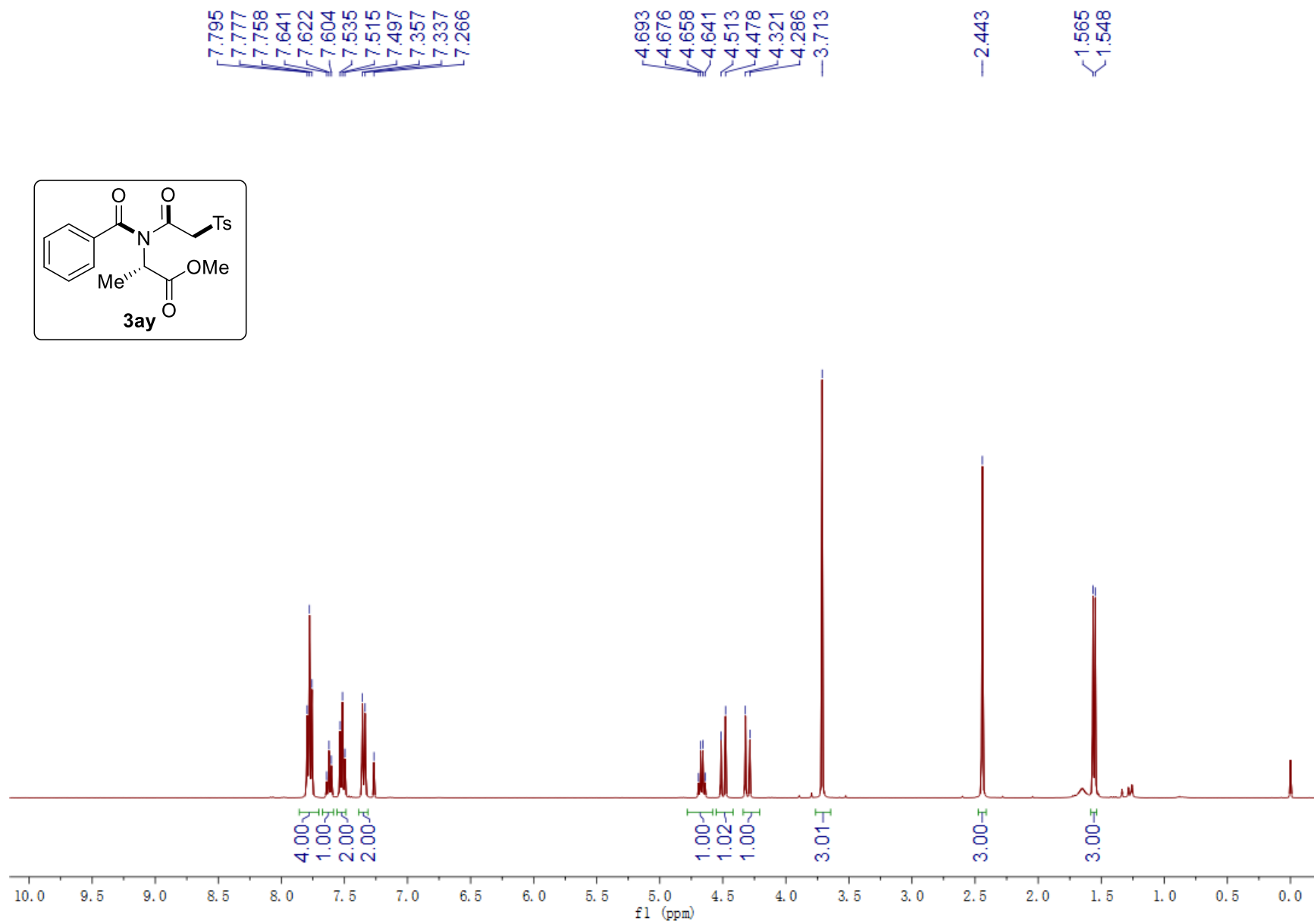
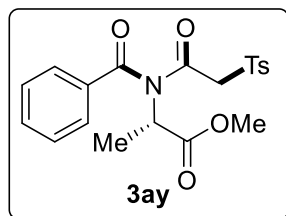
S155



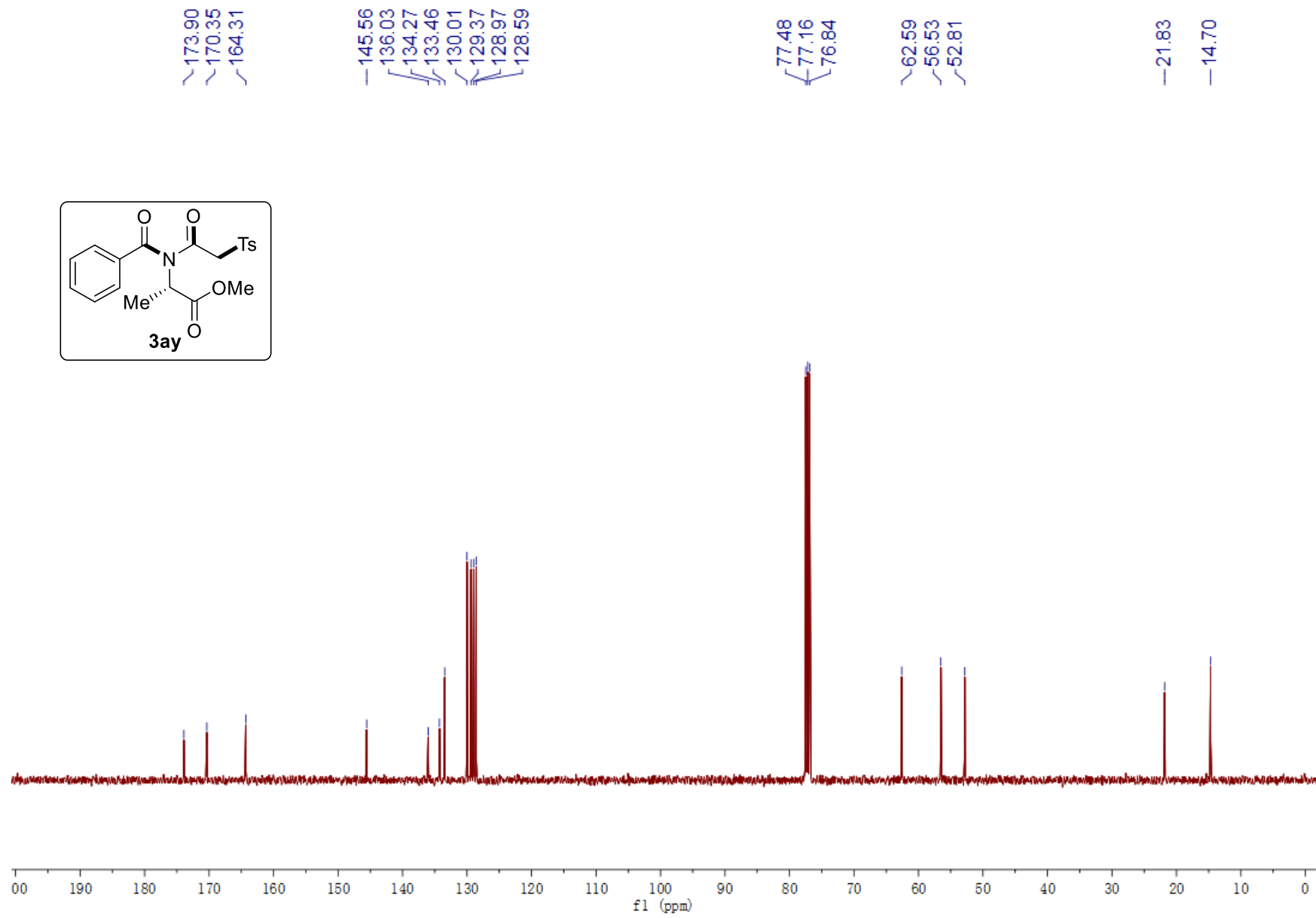
S157



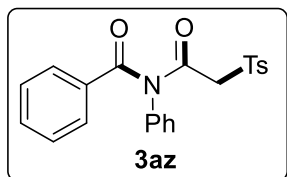
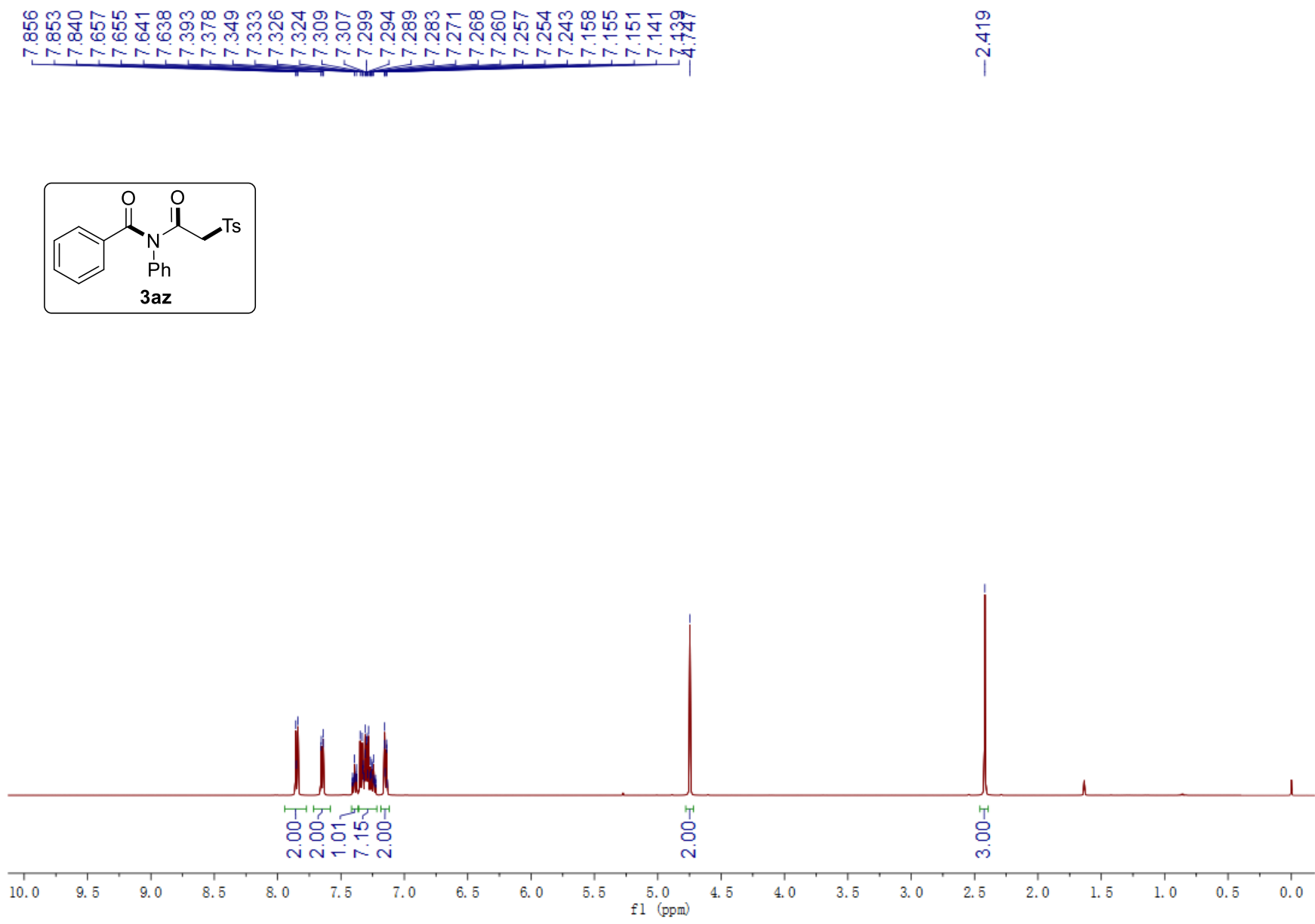


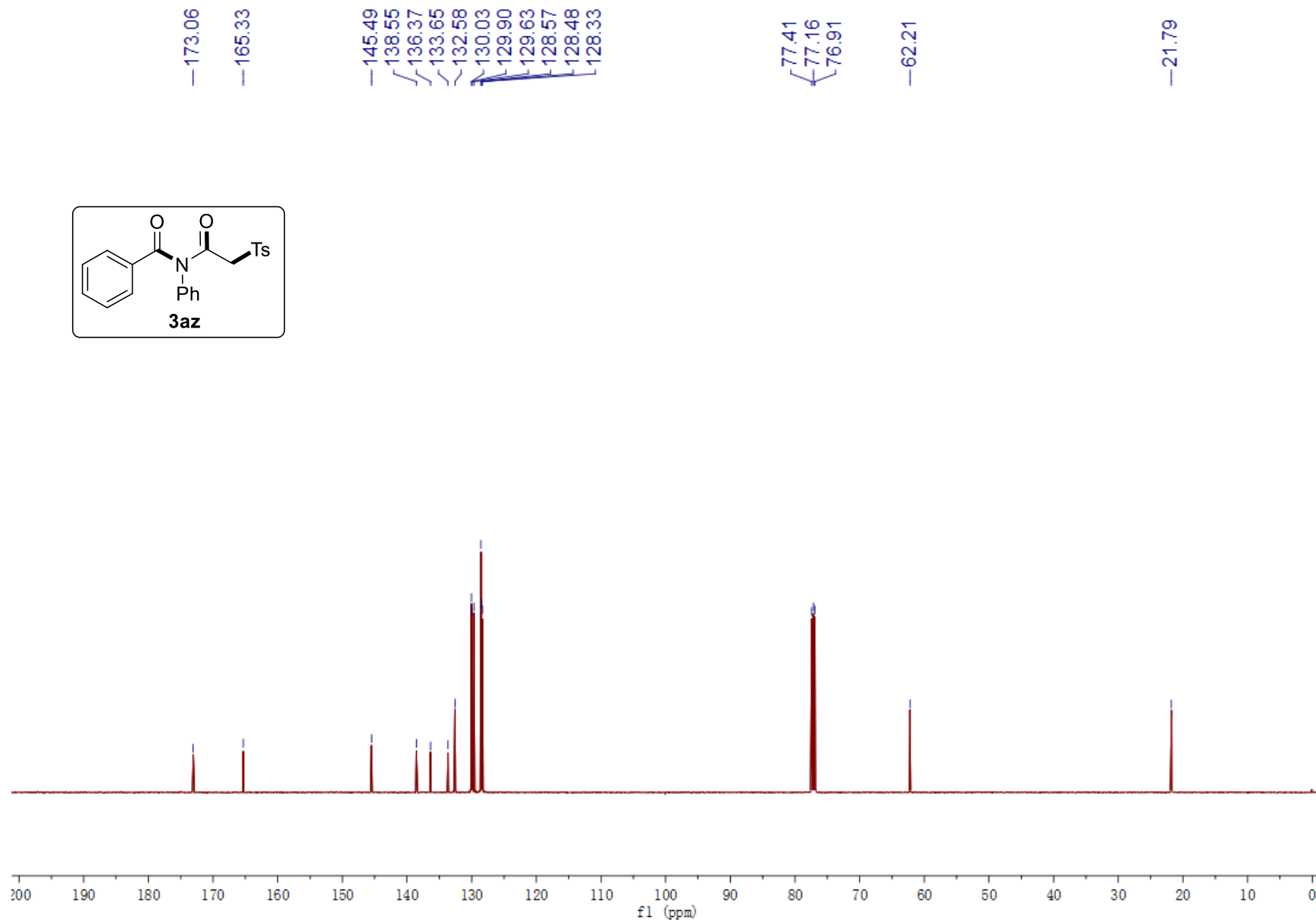
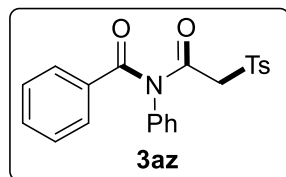


S160

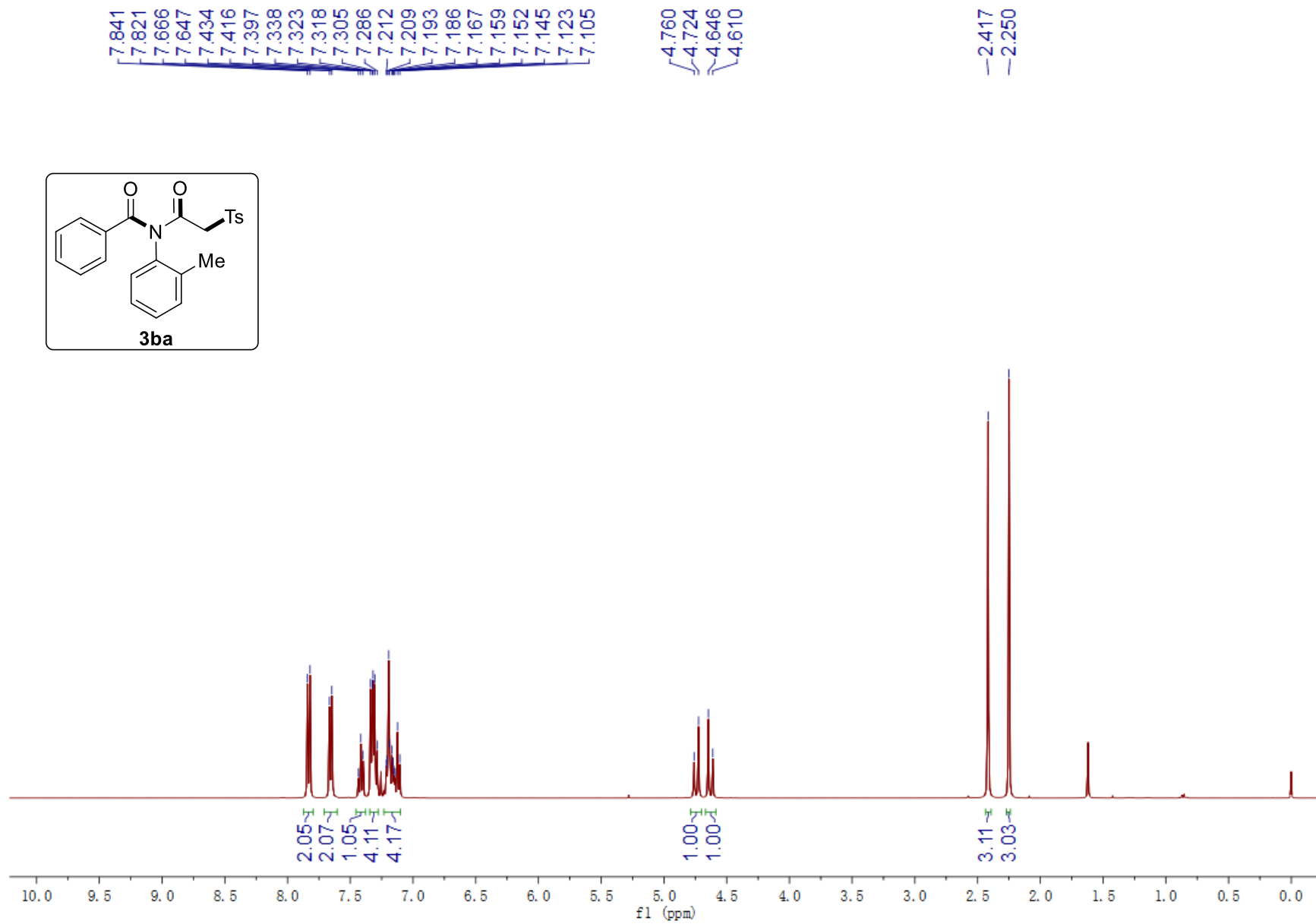
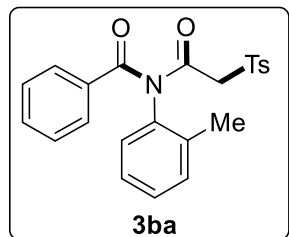


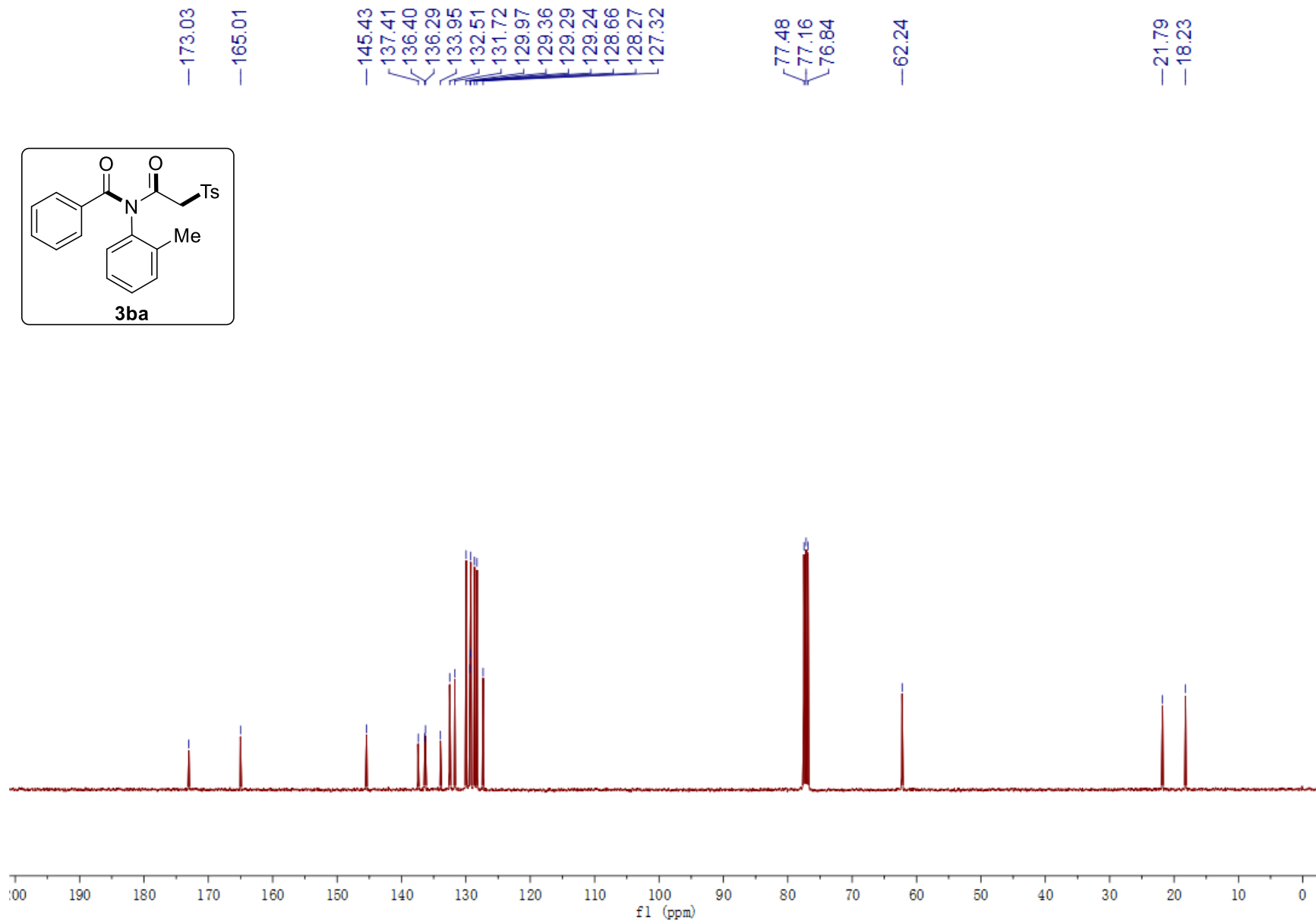
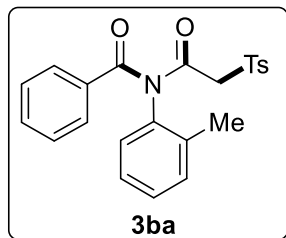
S161

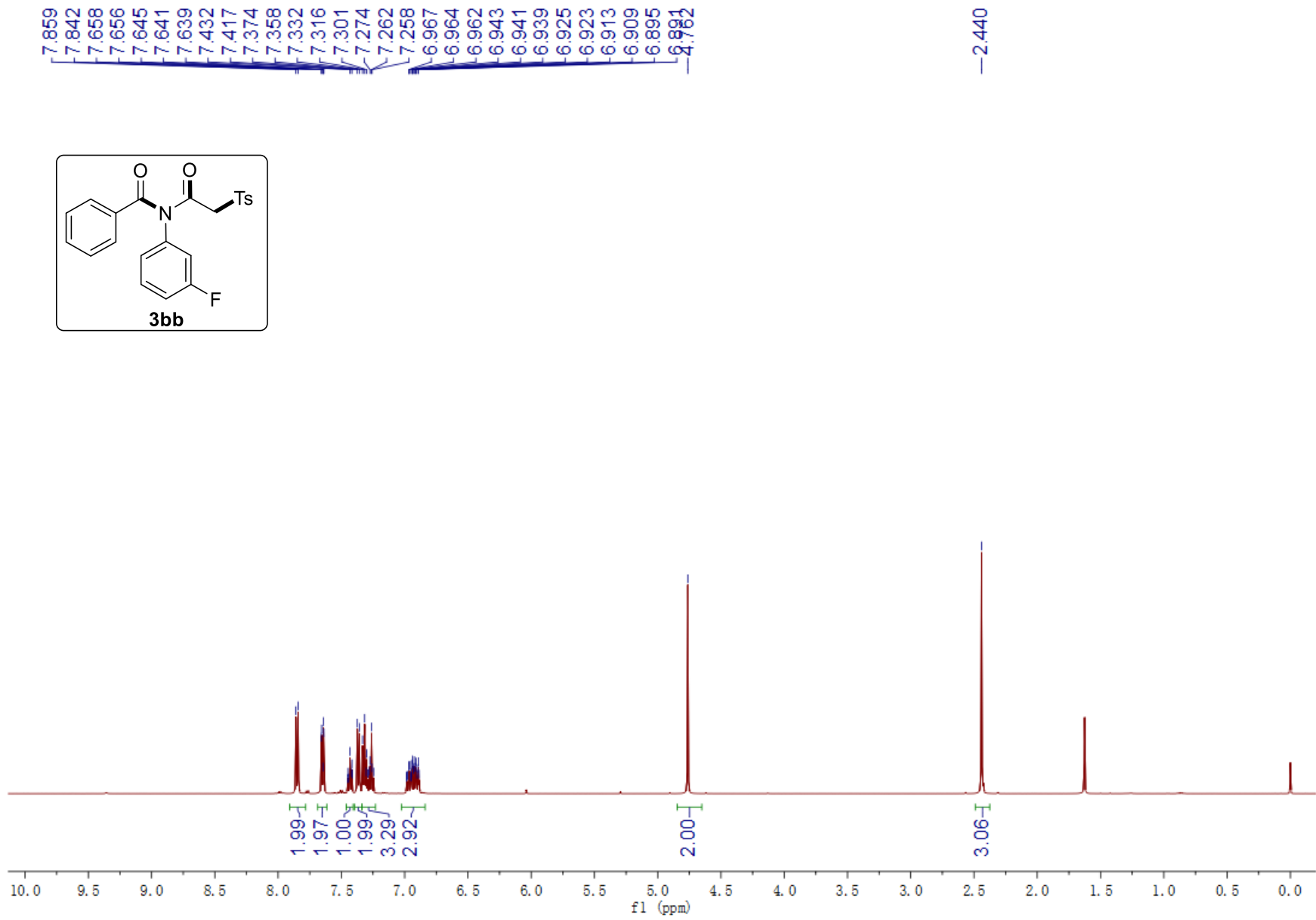




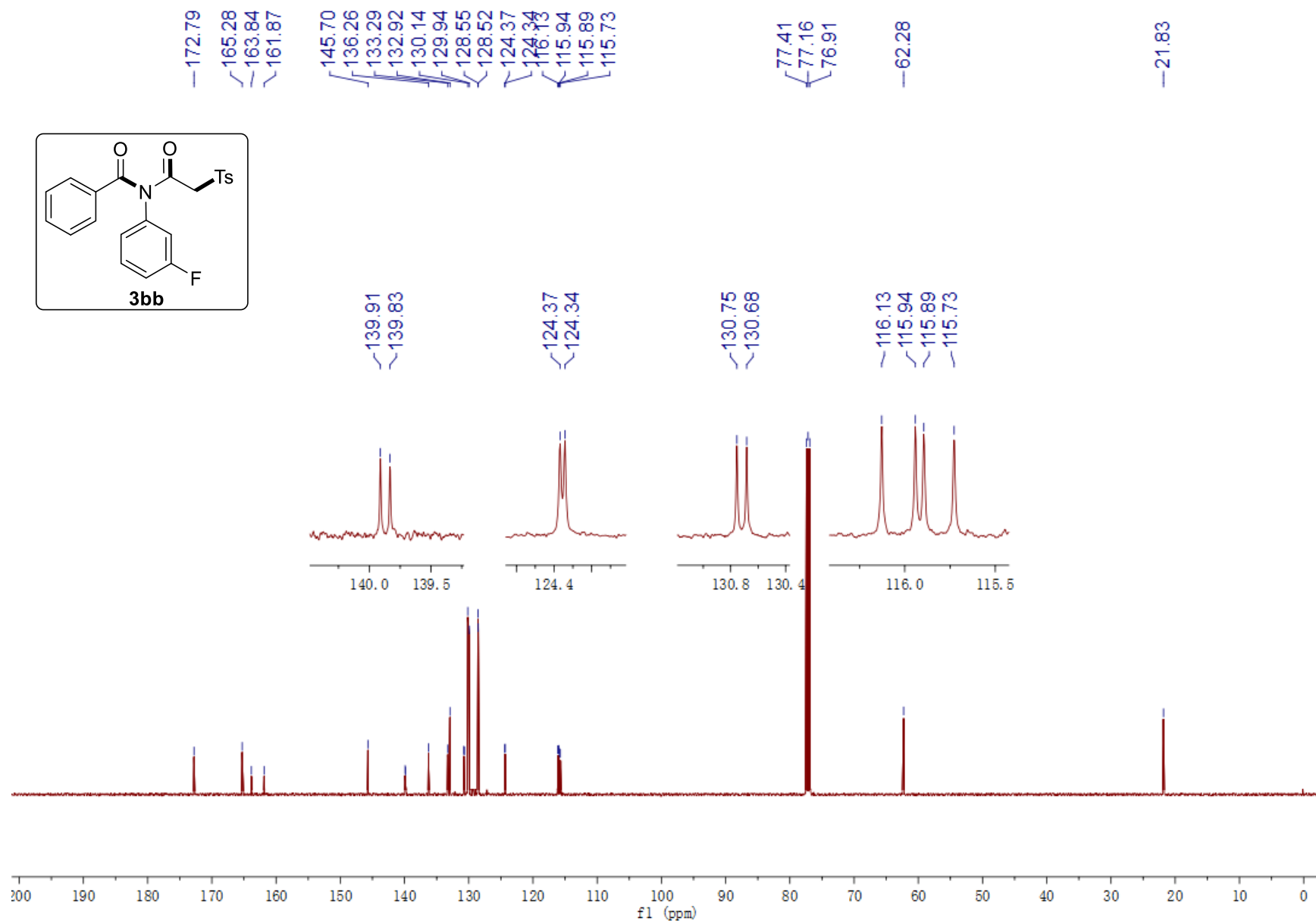
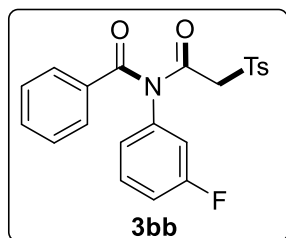
S163

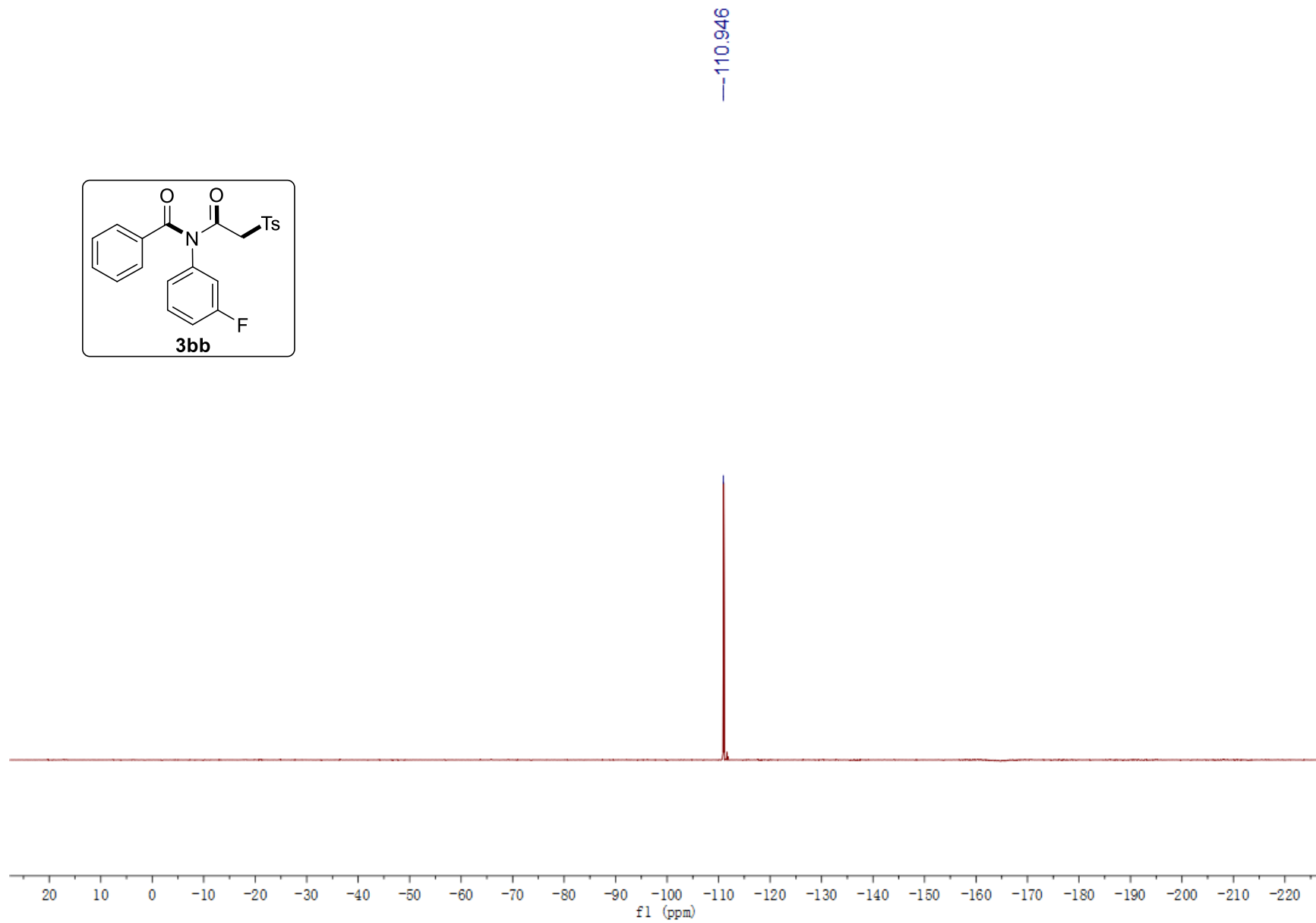
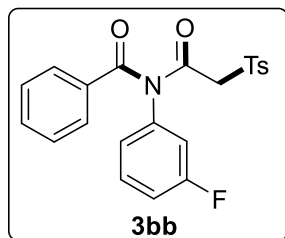




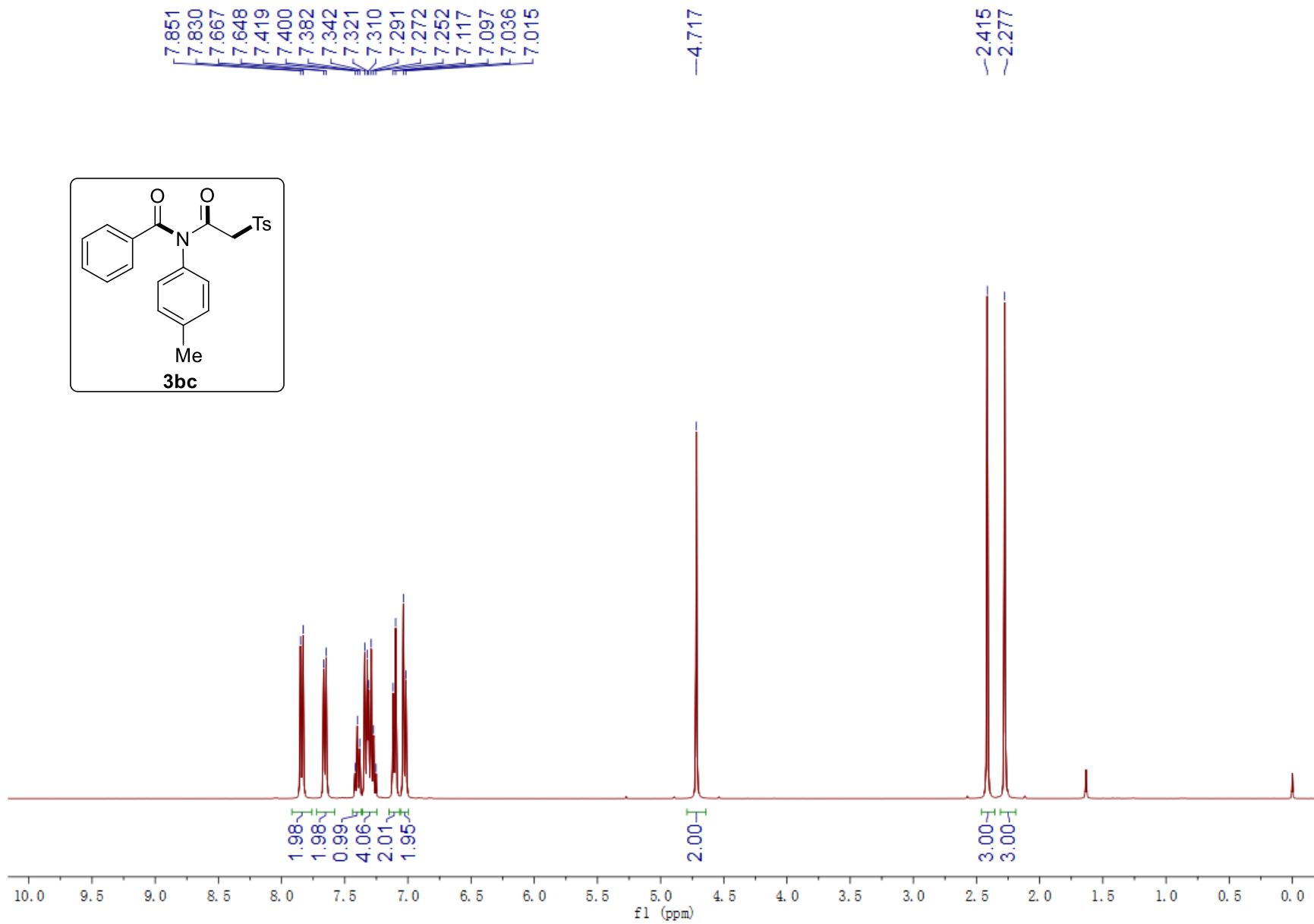
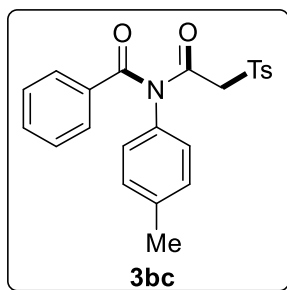


S166

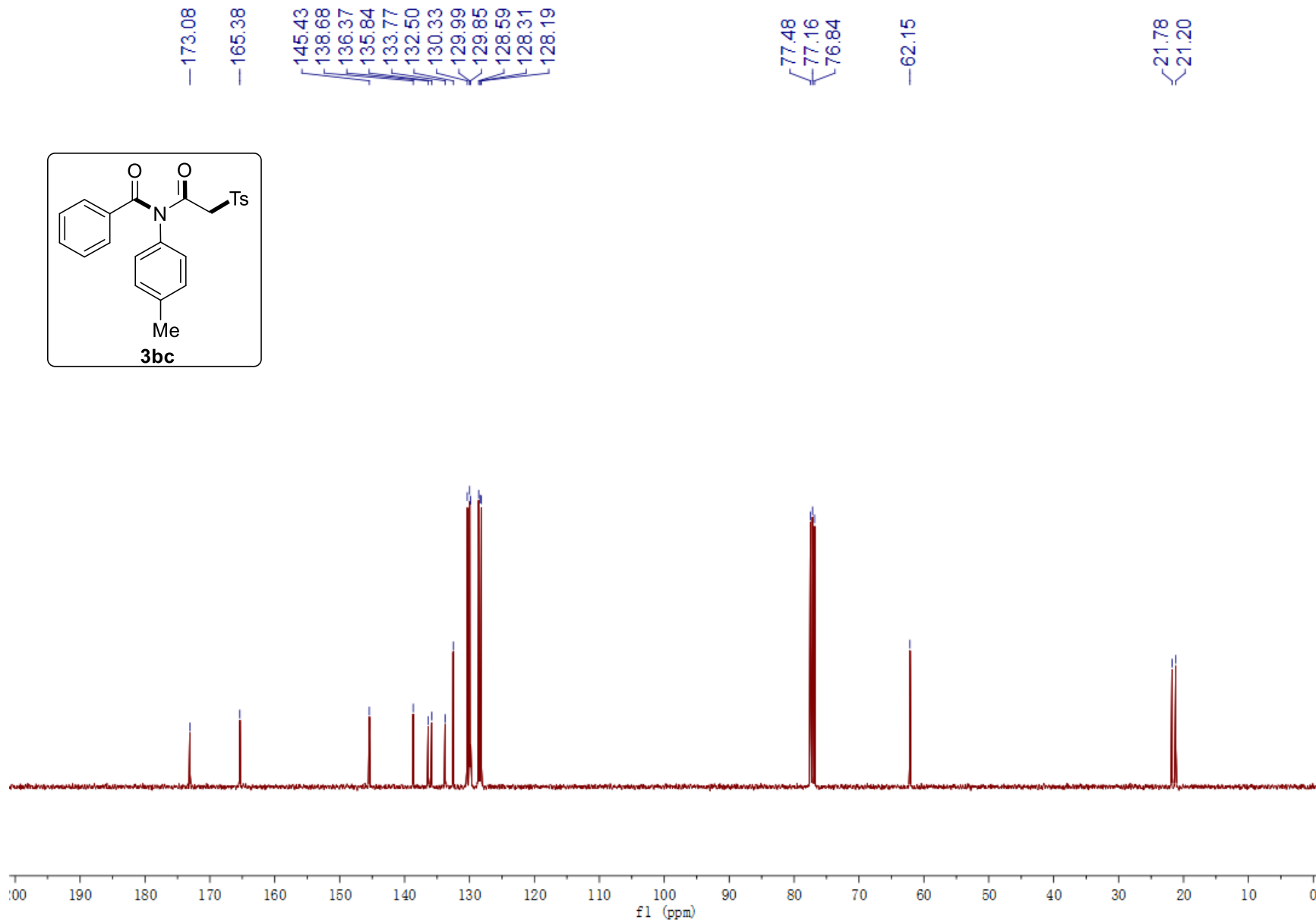
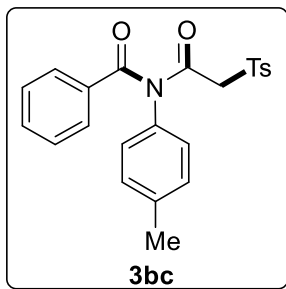




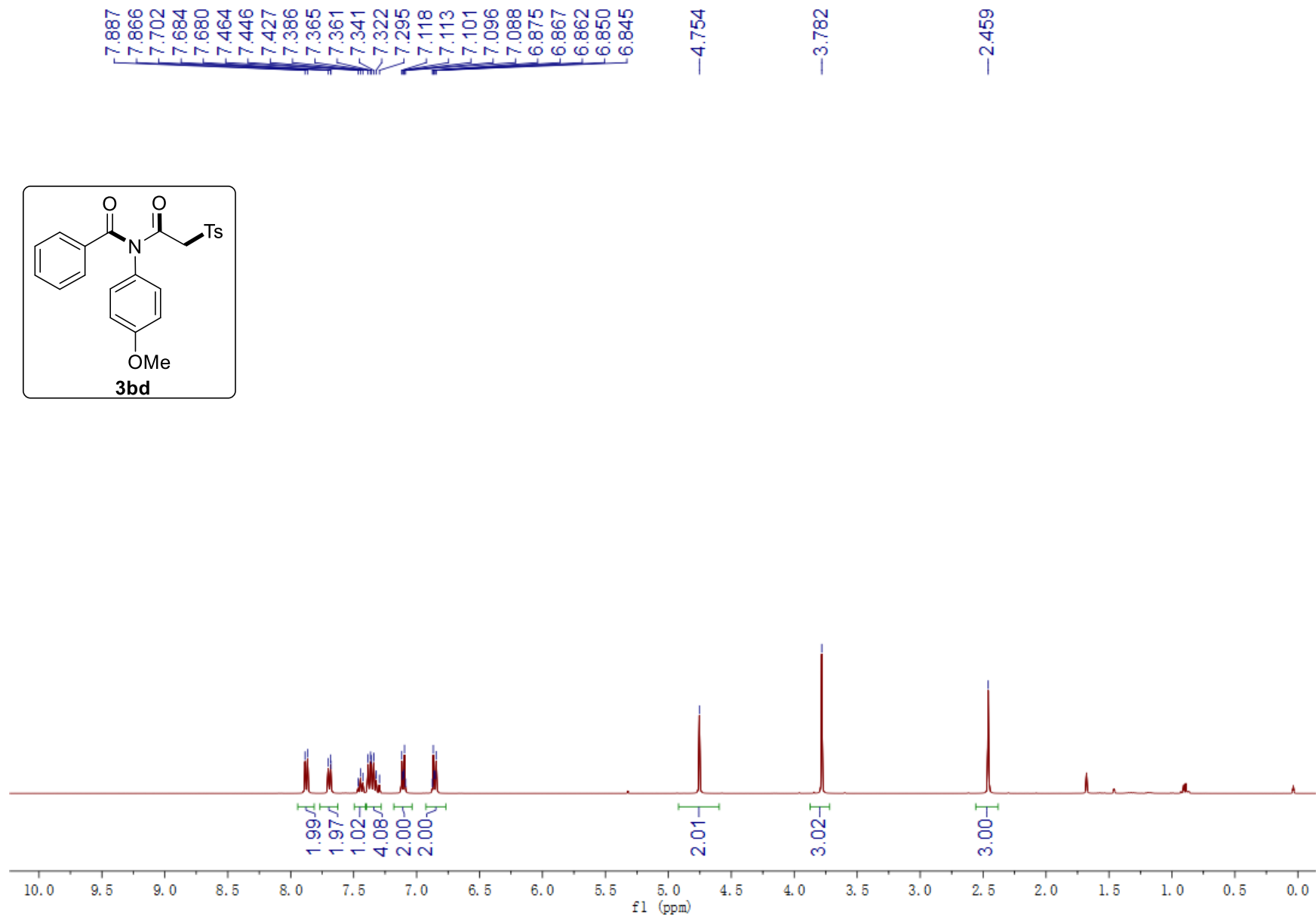
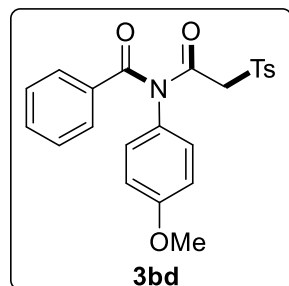
S168



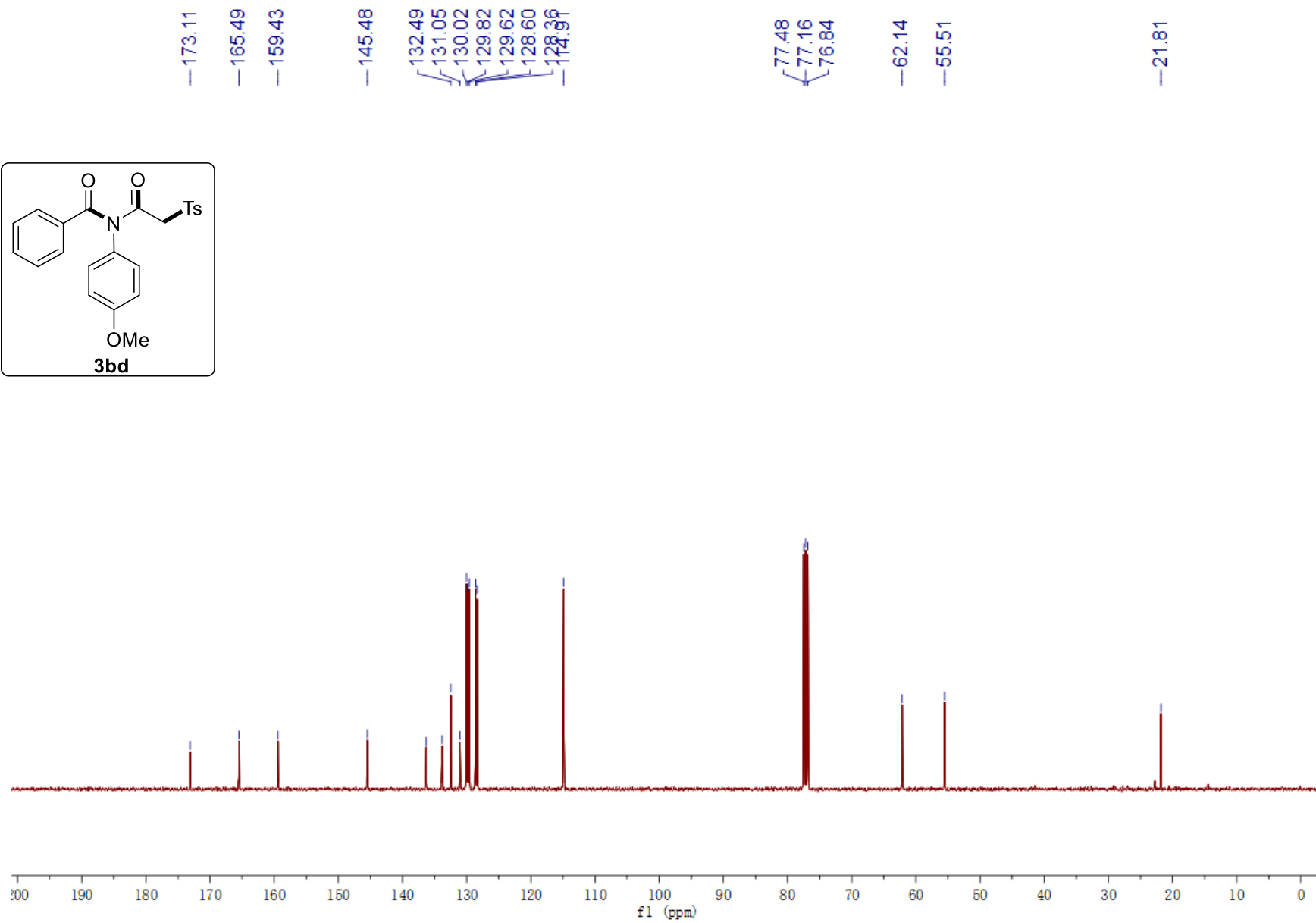
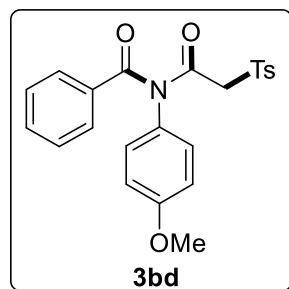
S169



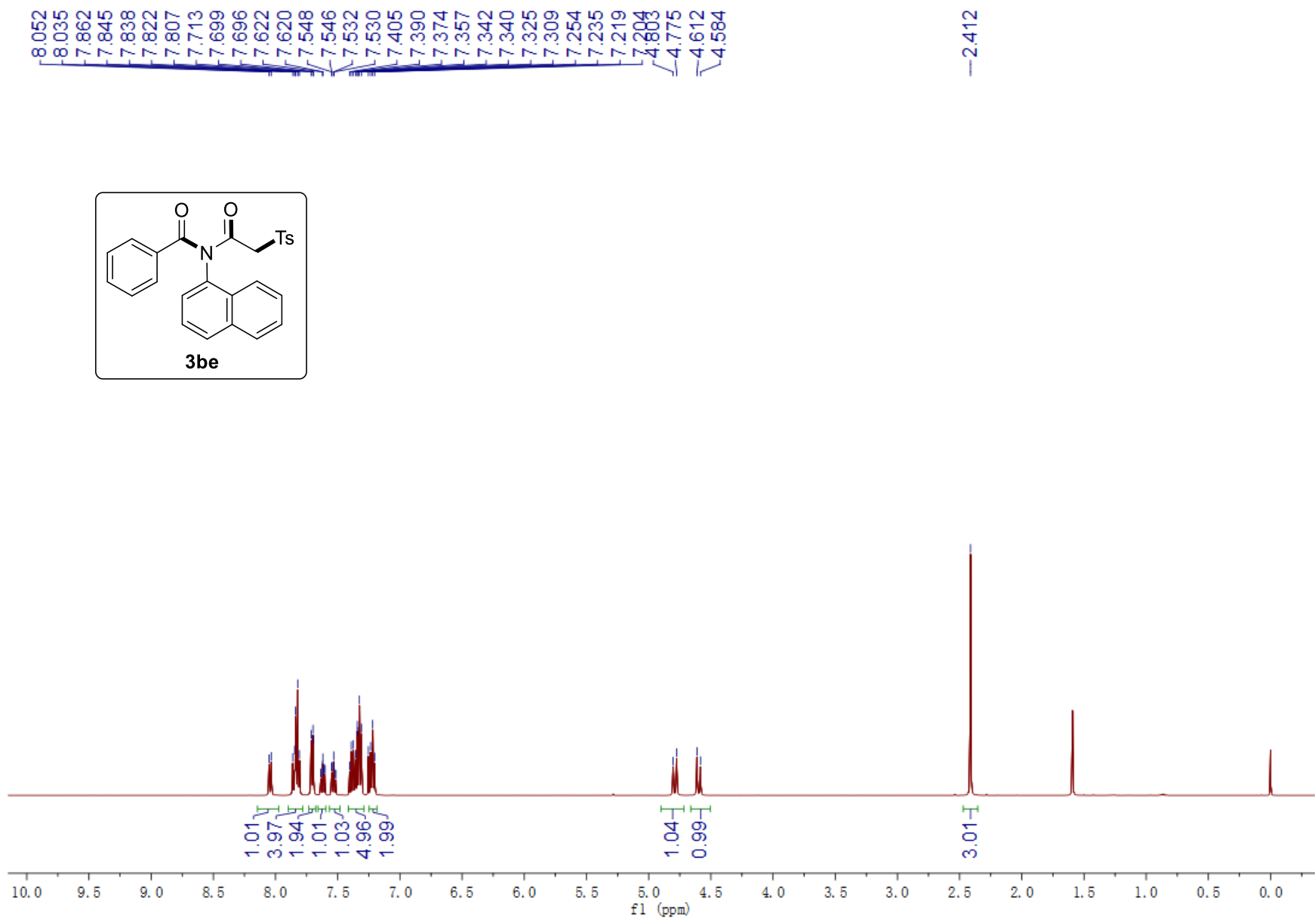
S170

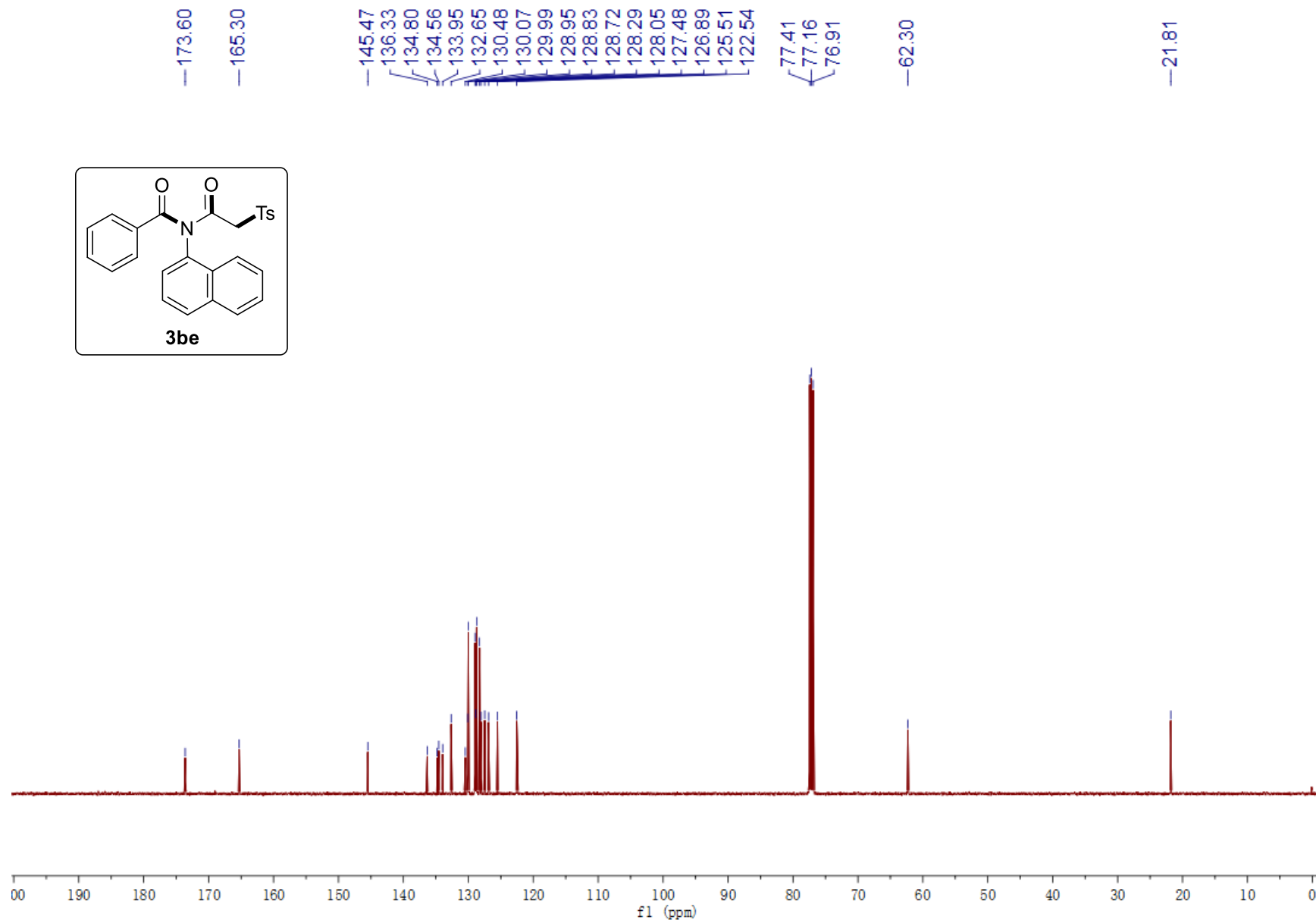
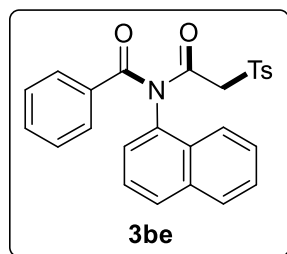


S171

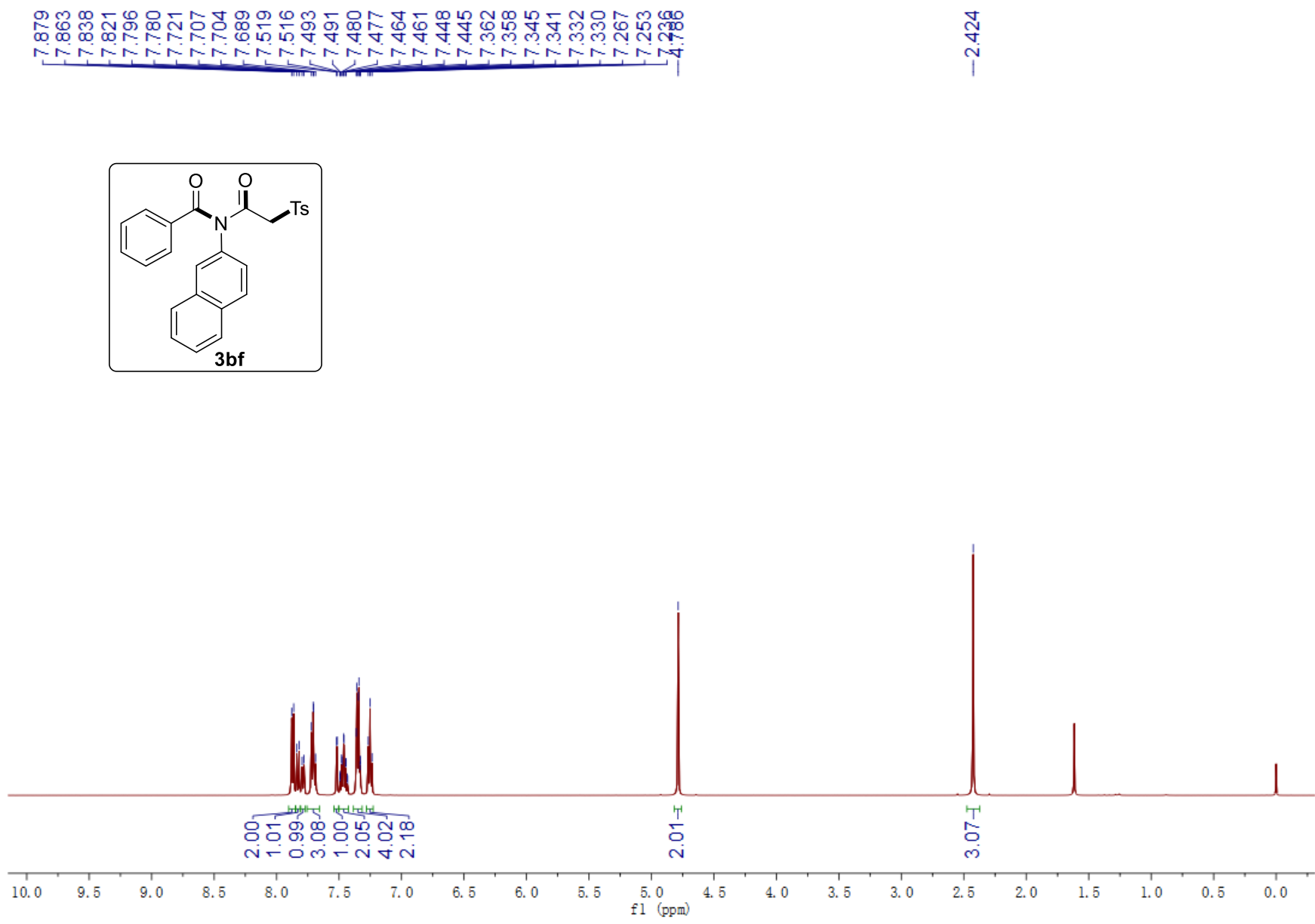


S172

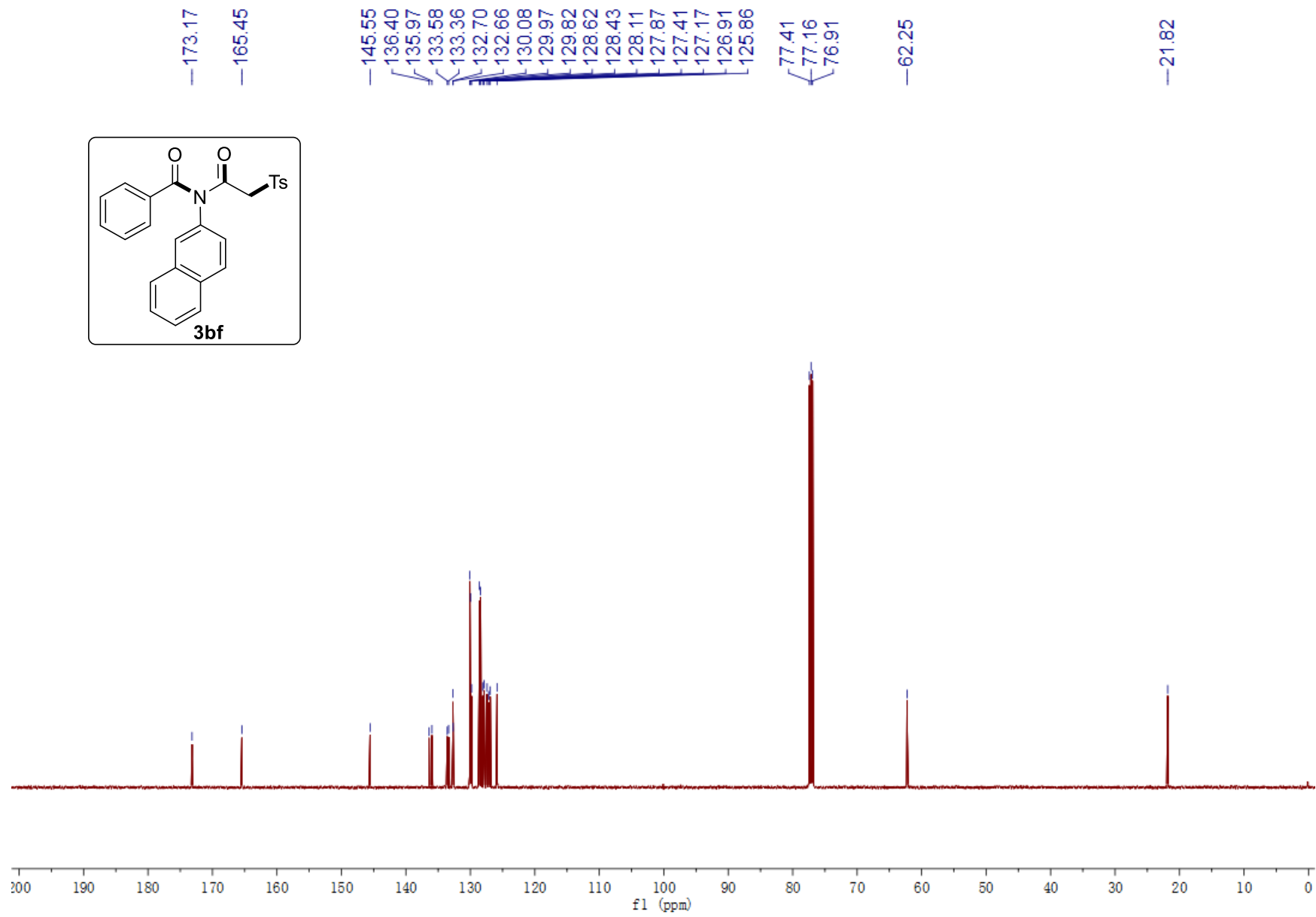
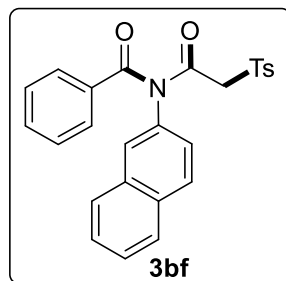




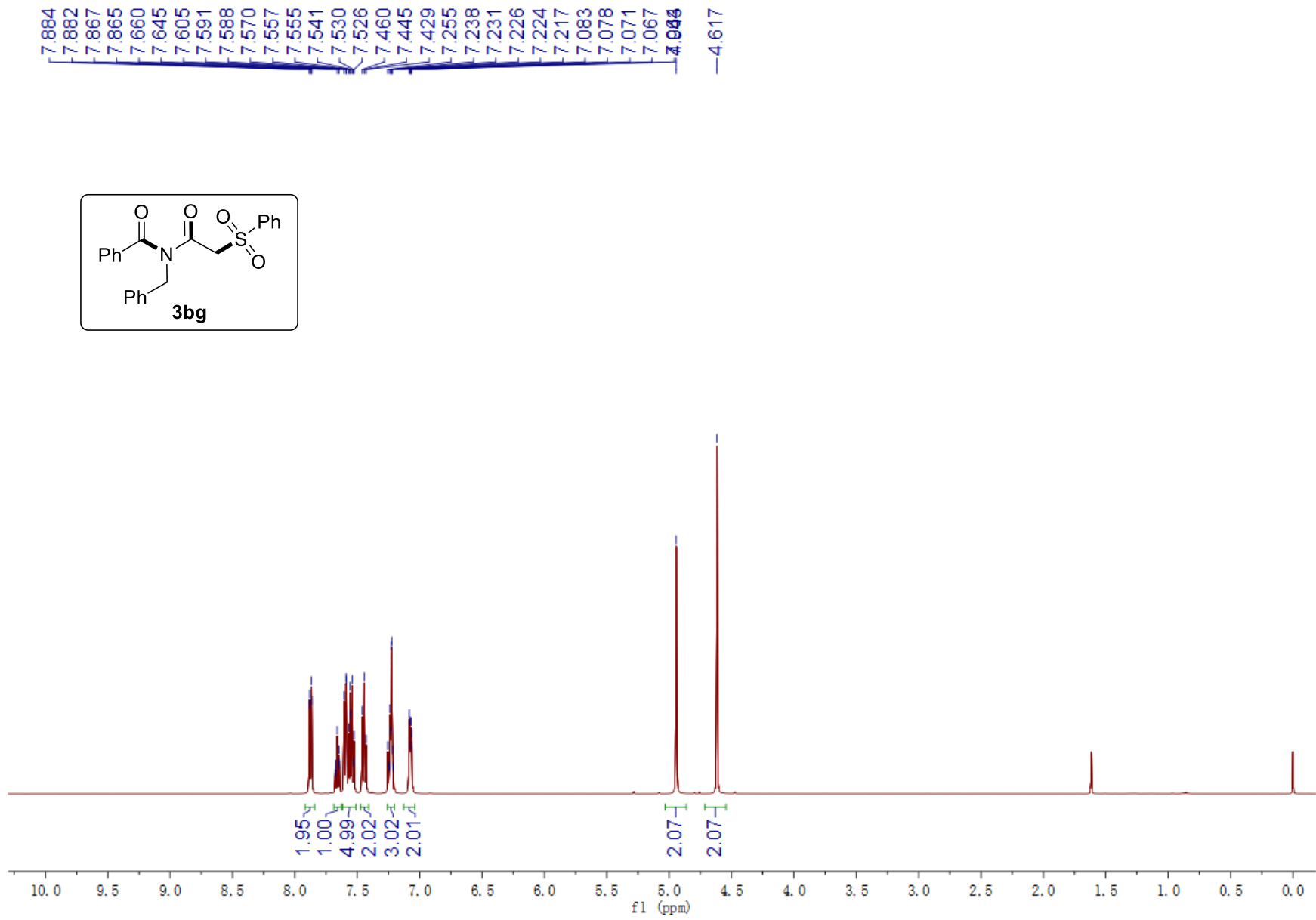
S174



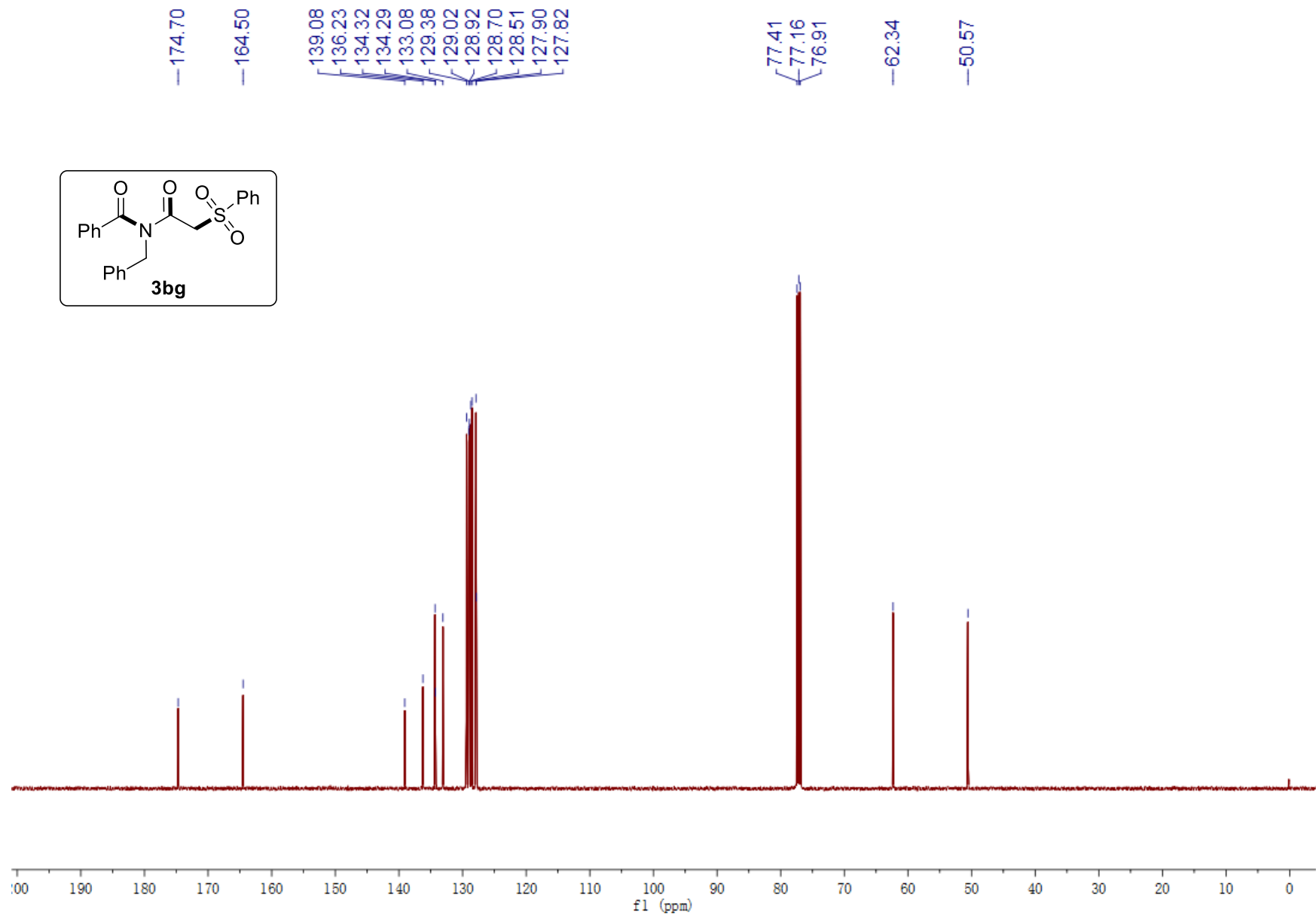
S175



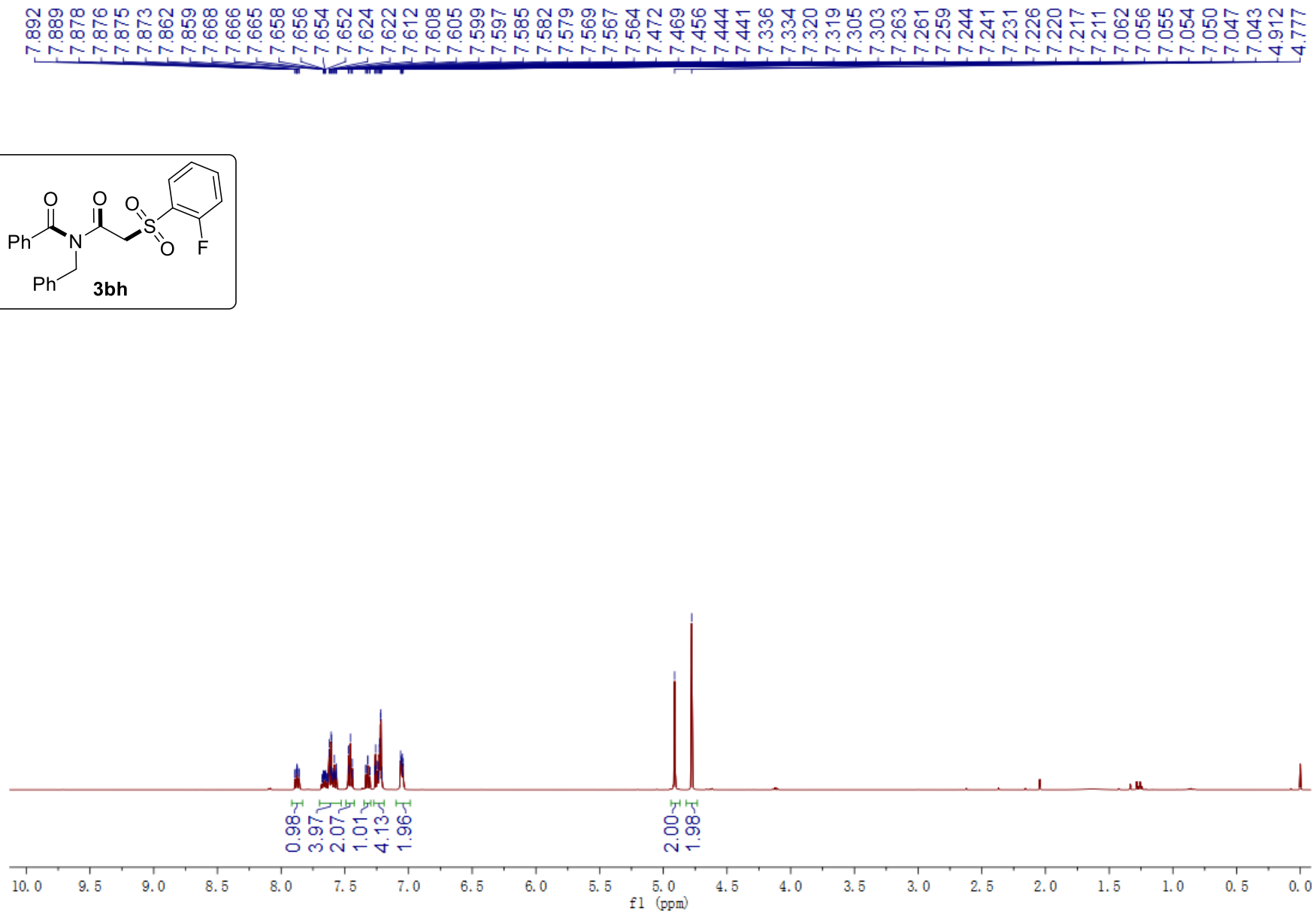
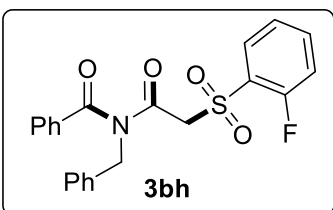
S176



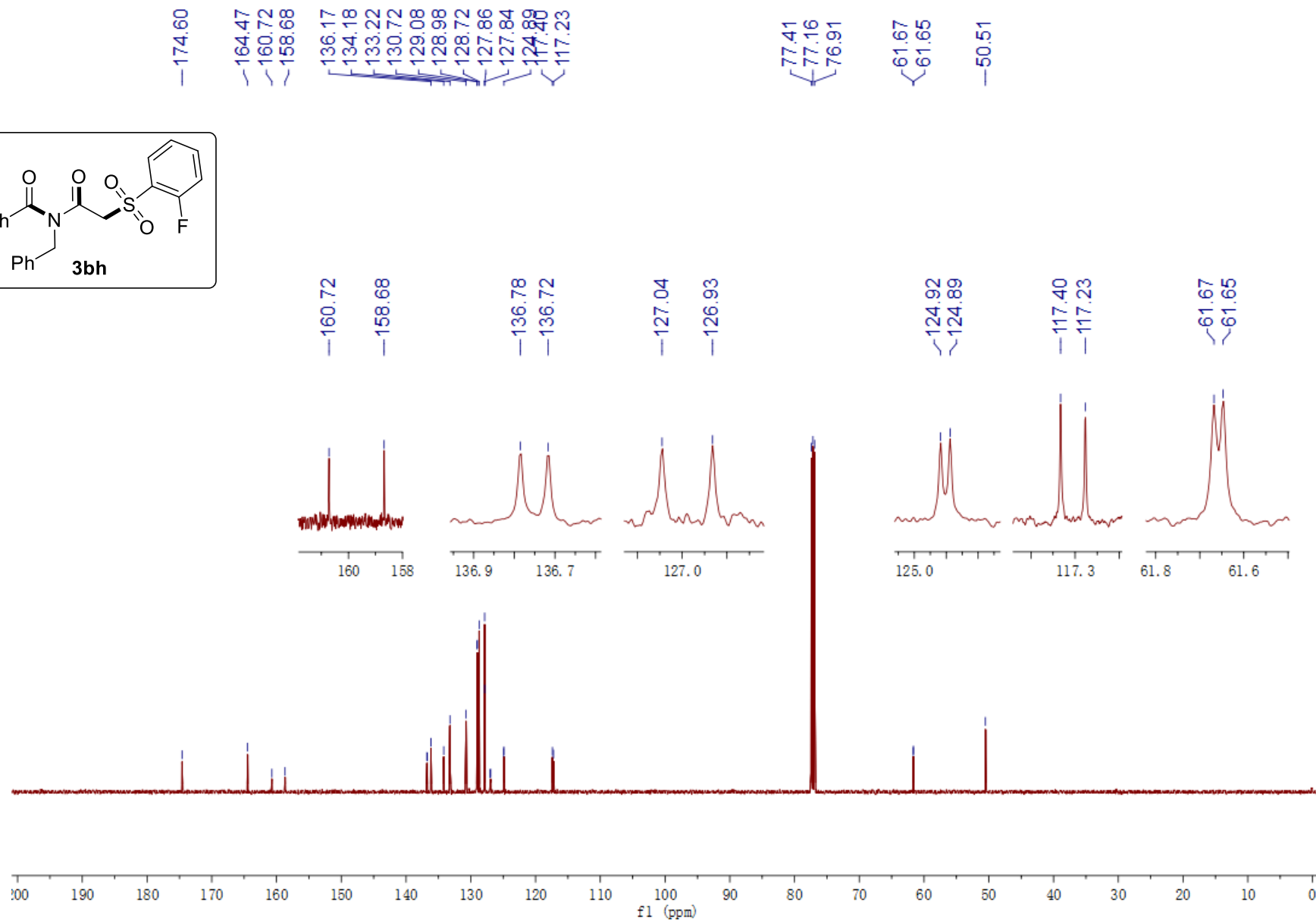
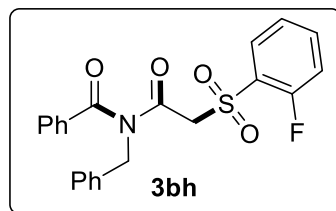
S177



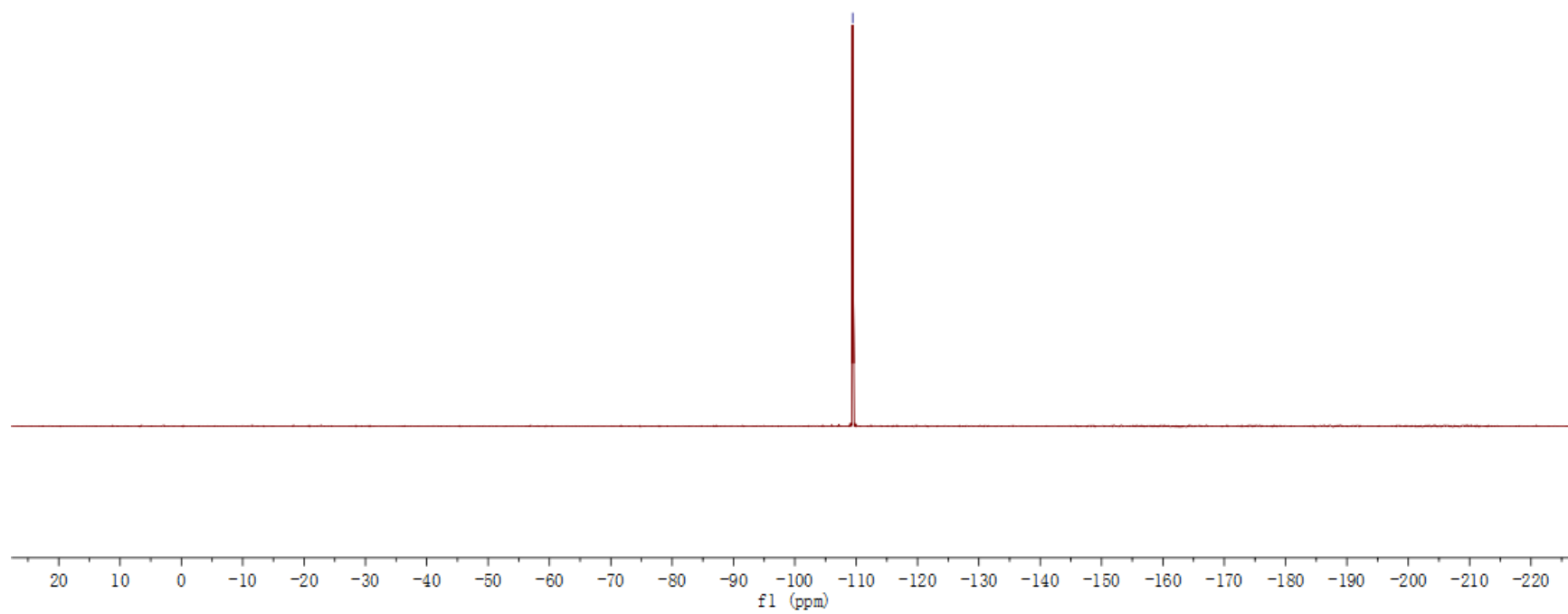
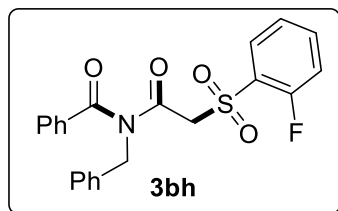
S178



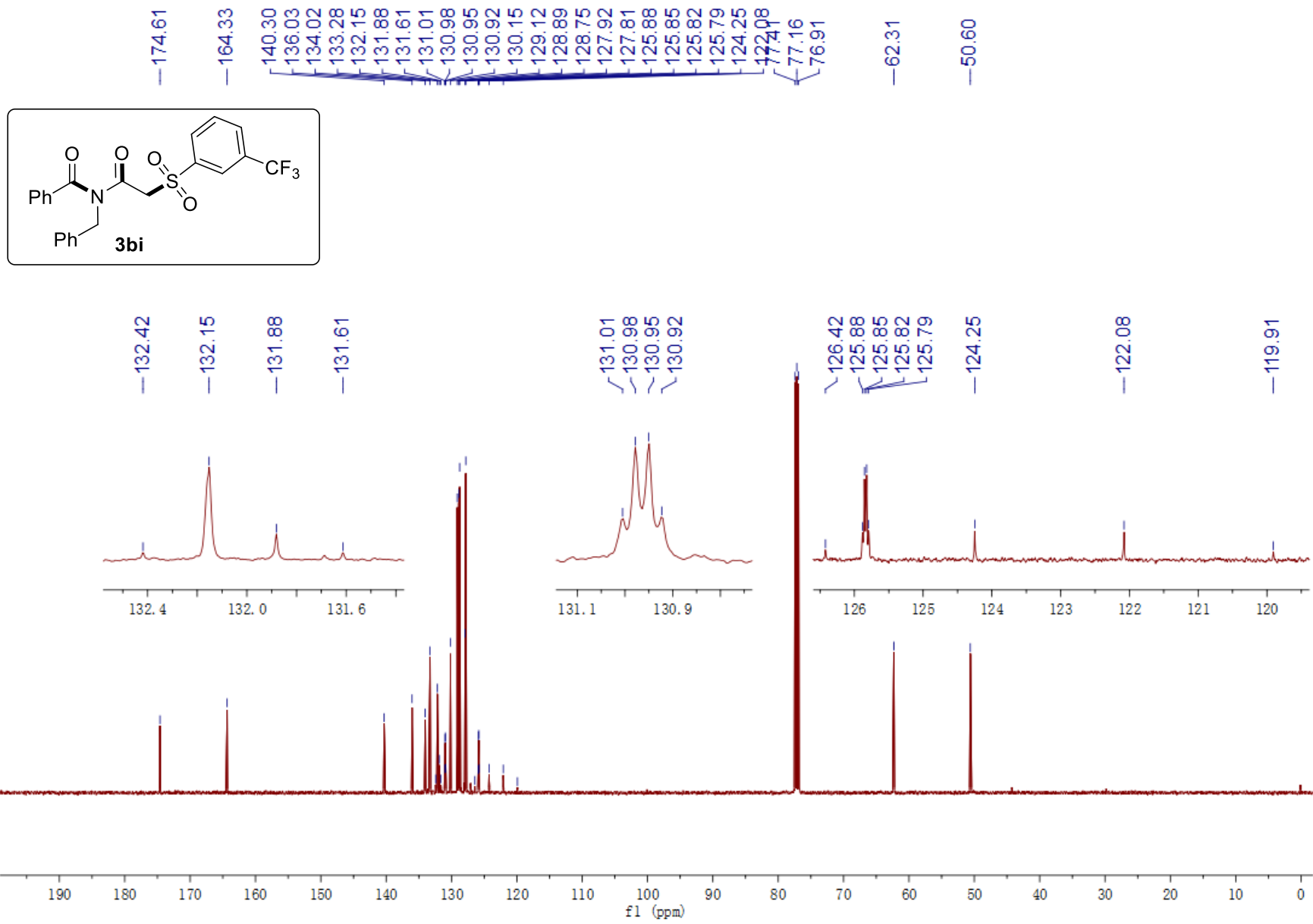
S179

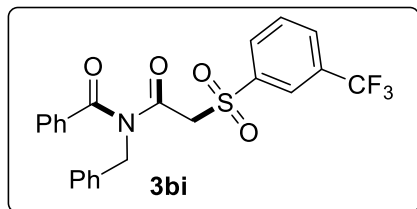


S180

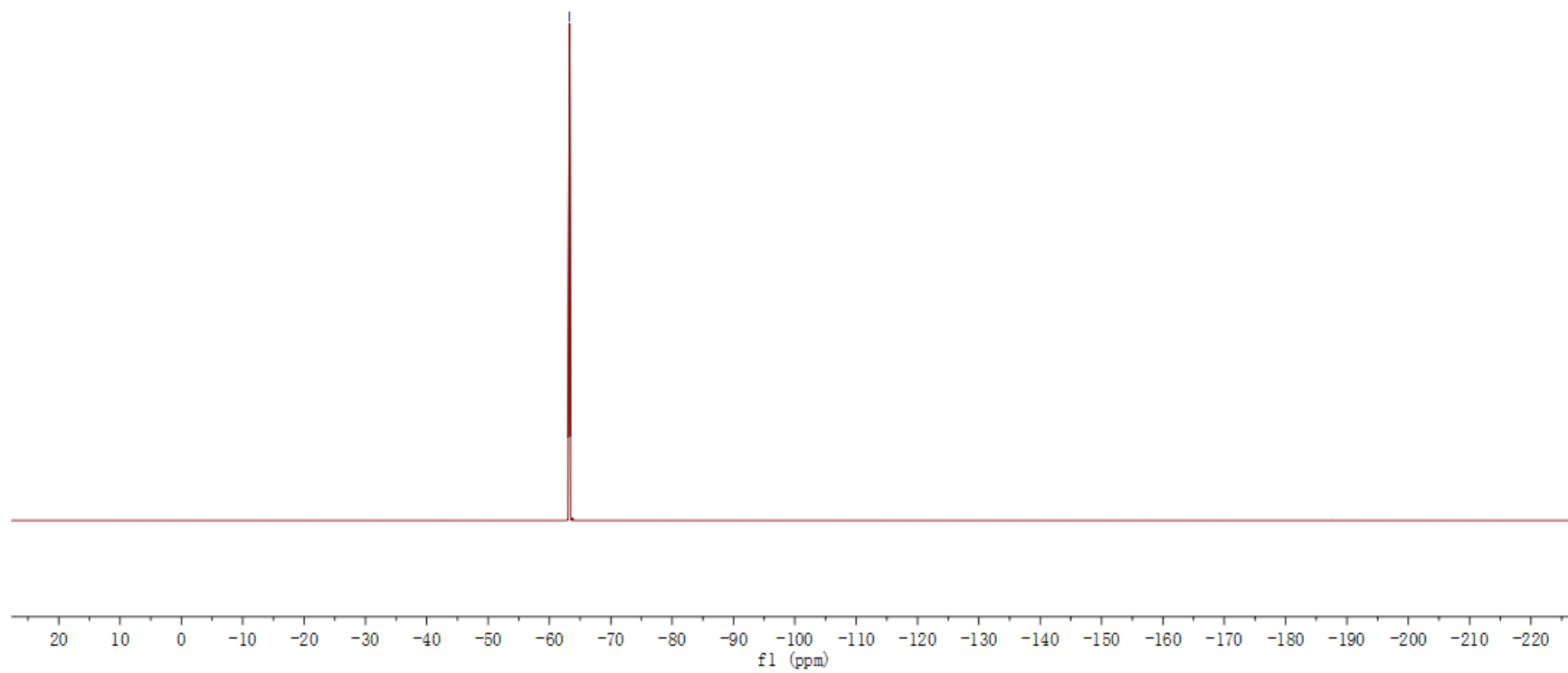


S181

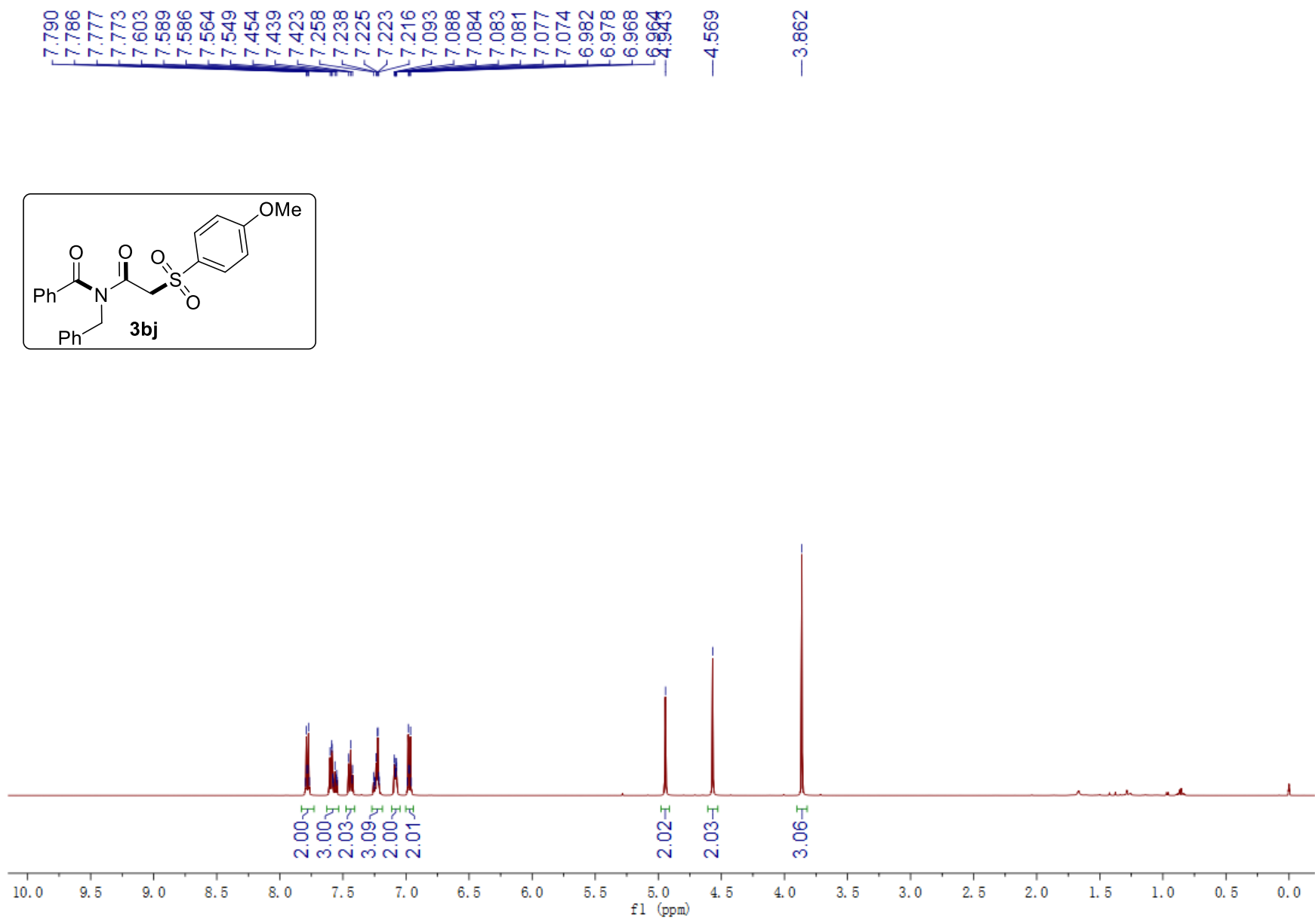


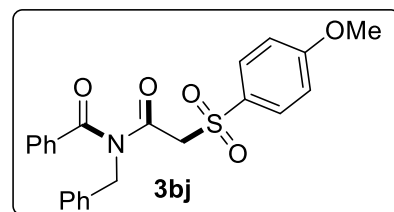


---63.275



S184





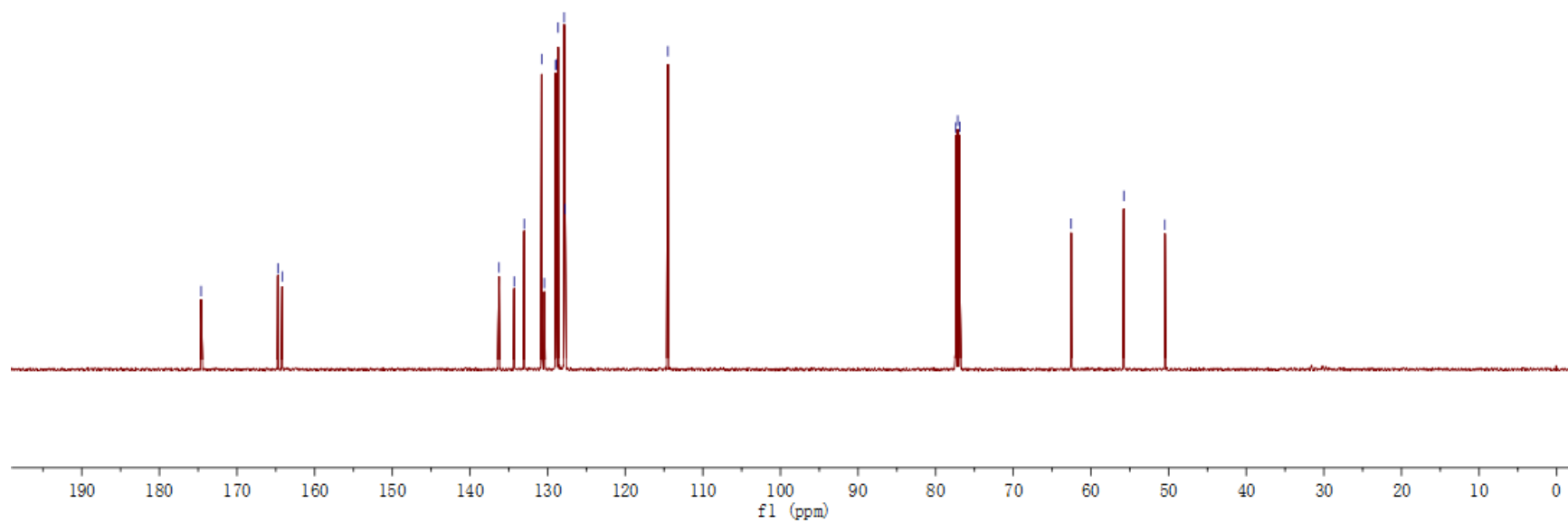
174.63

164.74
164.18

136.26
134.30
133.01
130.76
130.42
128.96
128.88
128.63
127.87
127.74
114.50

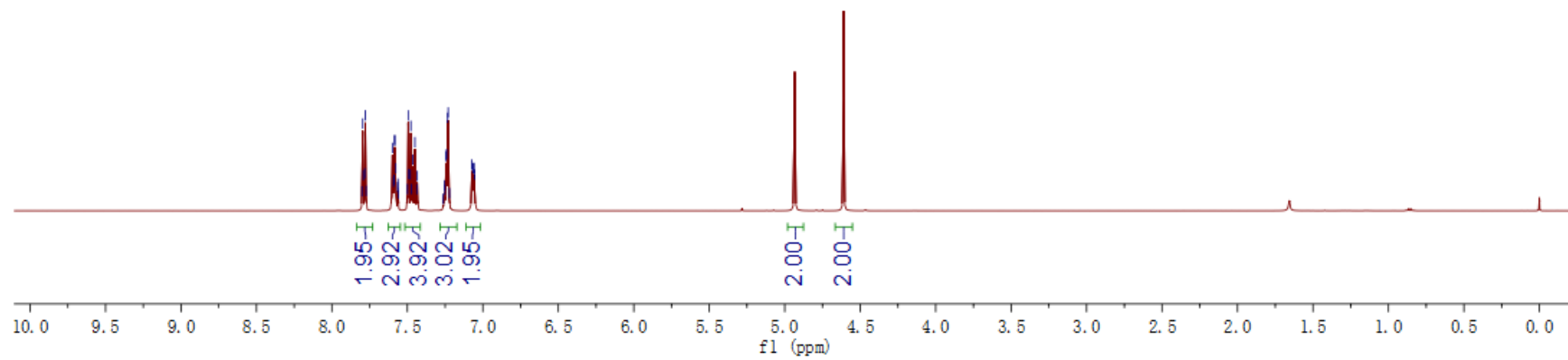
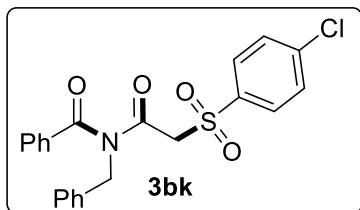
77.41
77.16
76.91

62.55
55.77
50.48

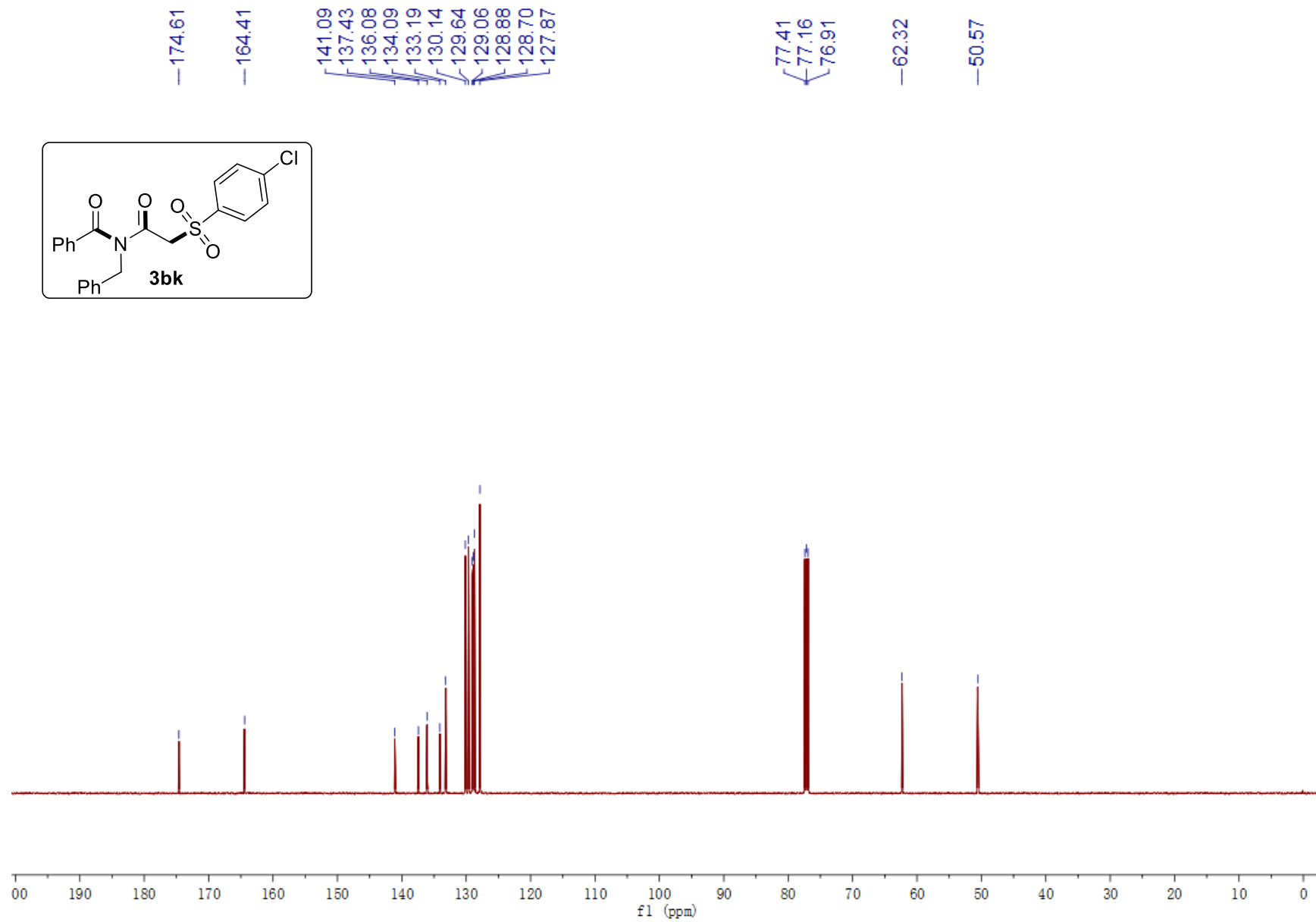
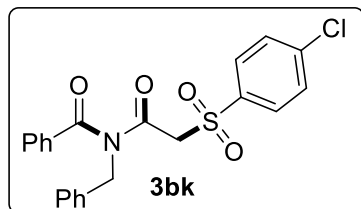


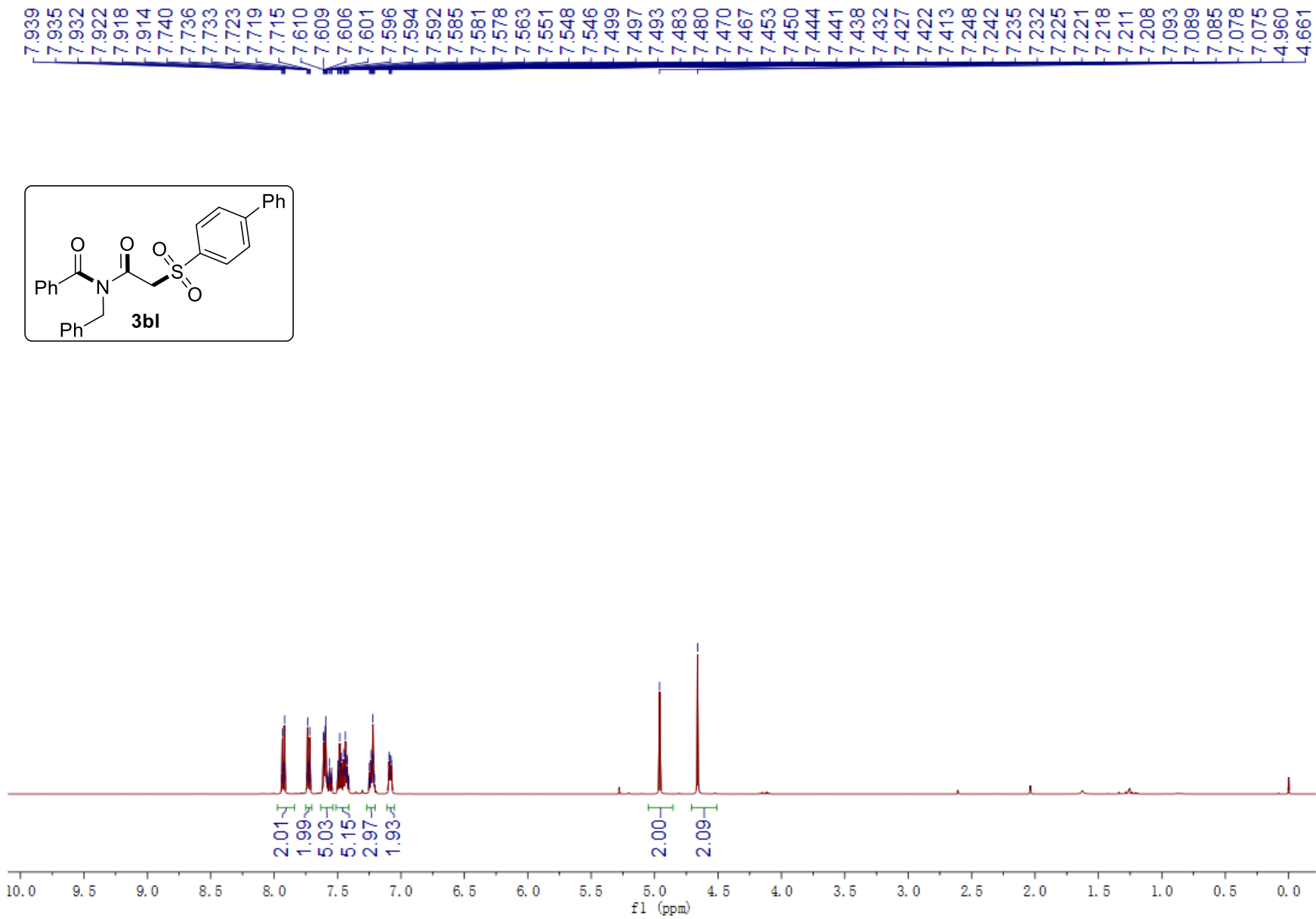
S186

7.801
7.796
7.792
7.782
7.778
7.774
7.599
7.592
7.589
7.585
7.583
7.577
7.564
7.562
7.560
7.499
7.495
7.491
7.481
7.477
7.472
7.465
7.450
7.438
7.434
7.262
7.256
7.252
7.244
7.240
7.234
7.230
7.221
7.073
7.066
7.065
7.058
7.054

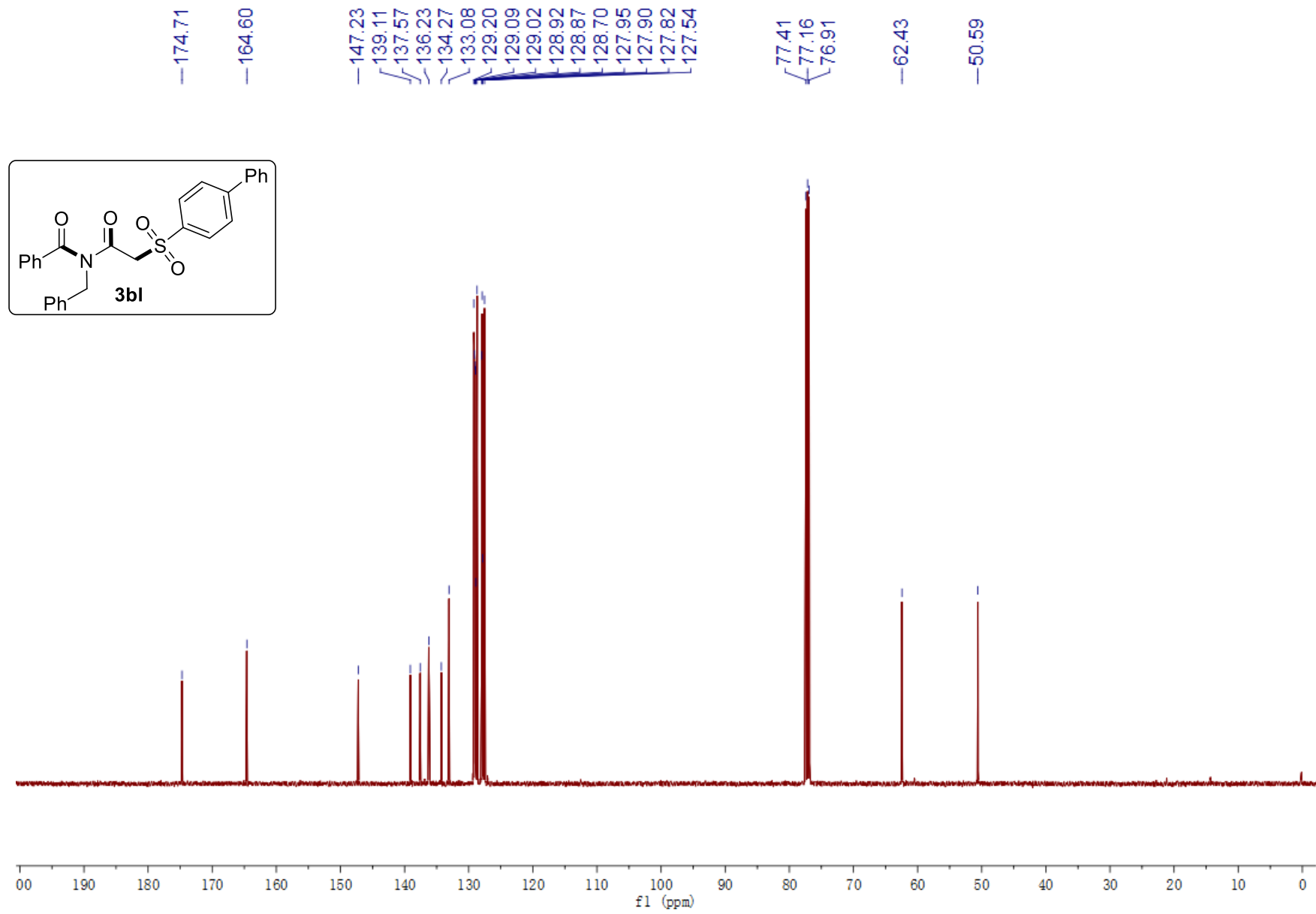


S187



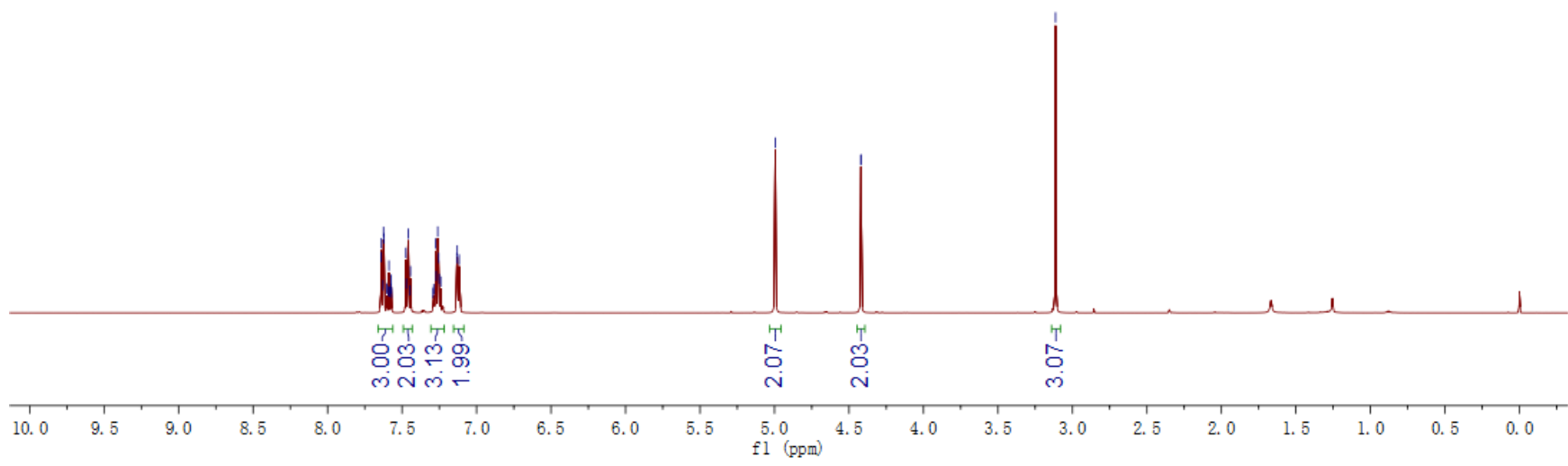
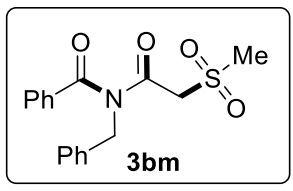


S189

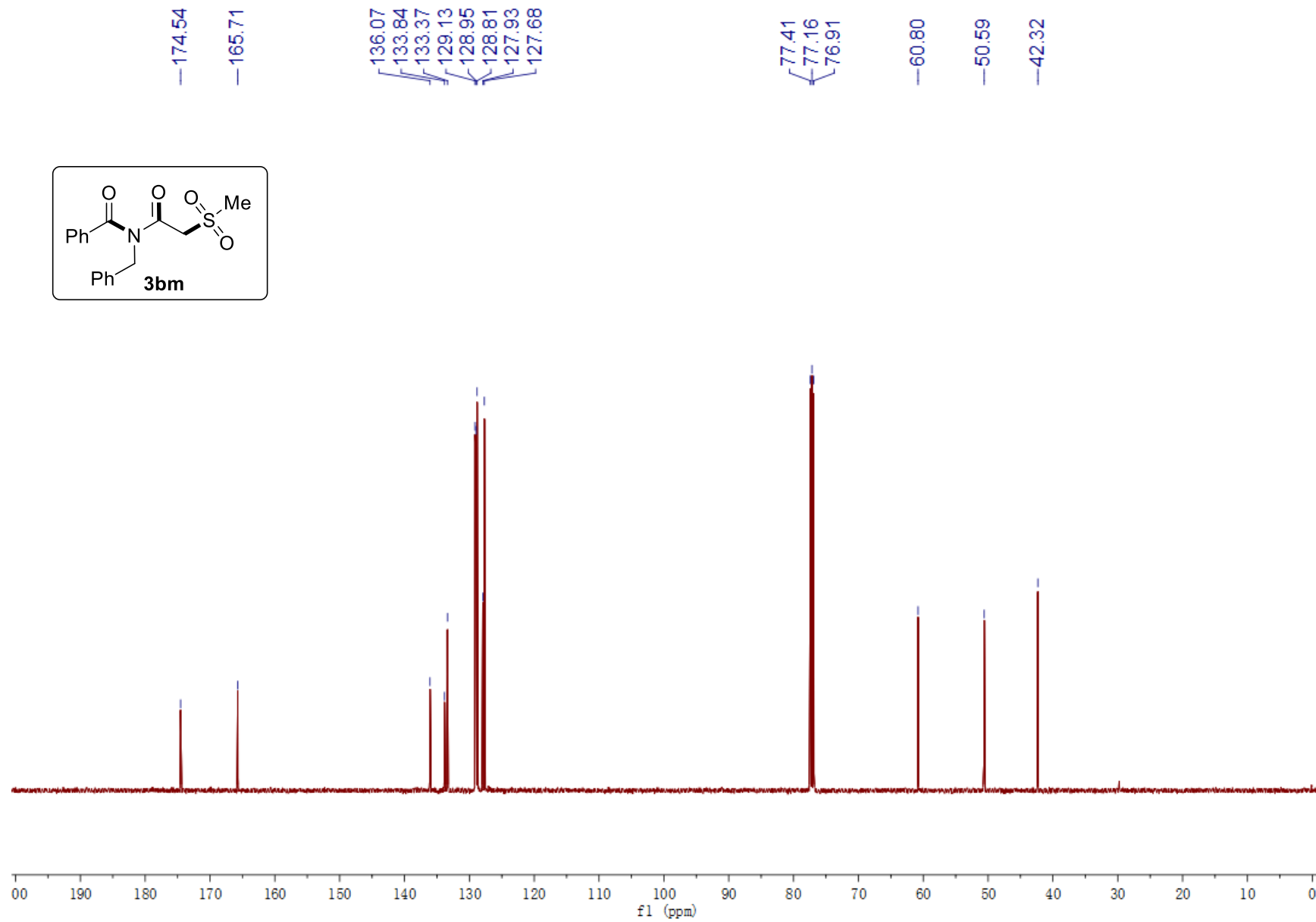
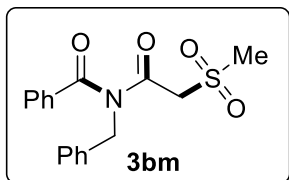


S190

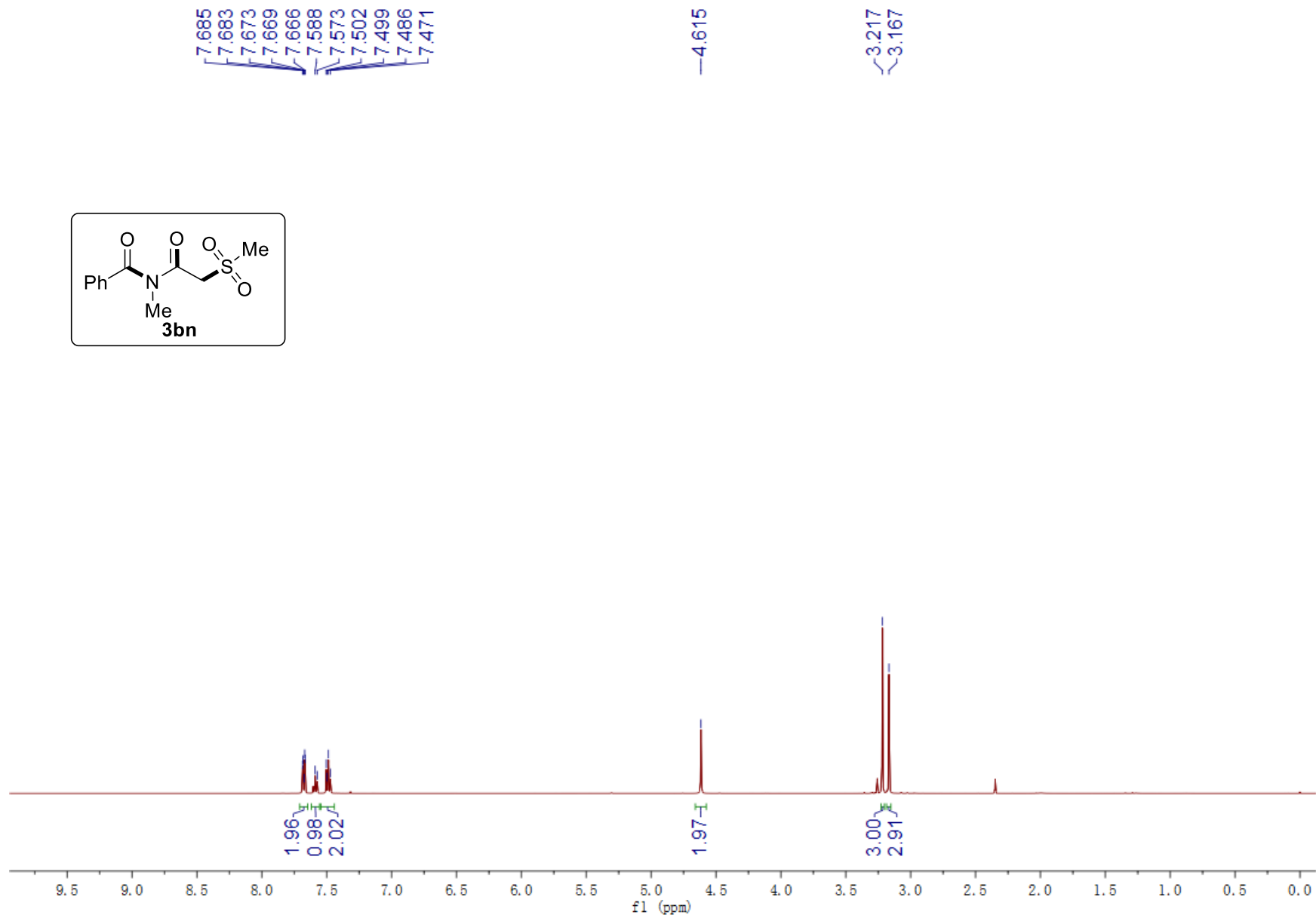
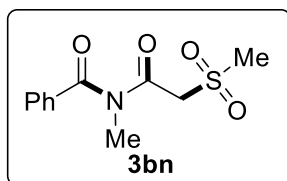
7.641
7.639
7.628
7.625
7.622
7.603
7.591
7.588
7.584
7.575
7.573
7.570
7.474
7.471
7.458
7.447
7.443
7.292
7.287
7.274
7.271
7.260
7.254
7.251
7.240
7.133
7.129
7.116
-4.995
-4.420
-4.419
-3.114



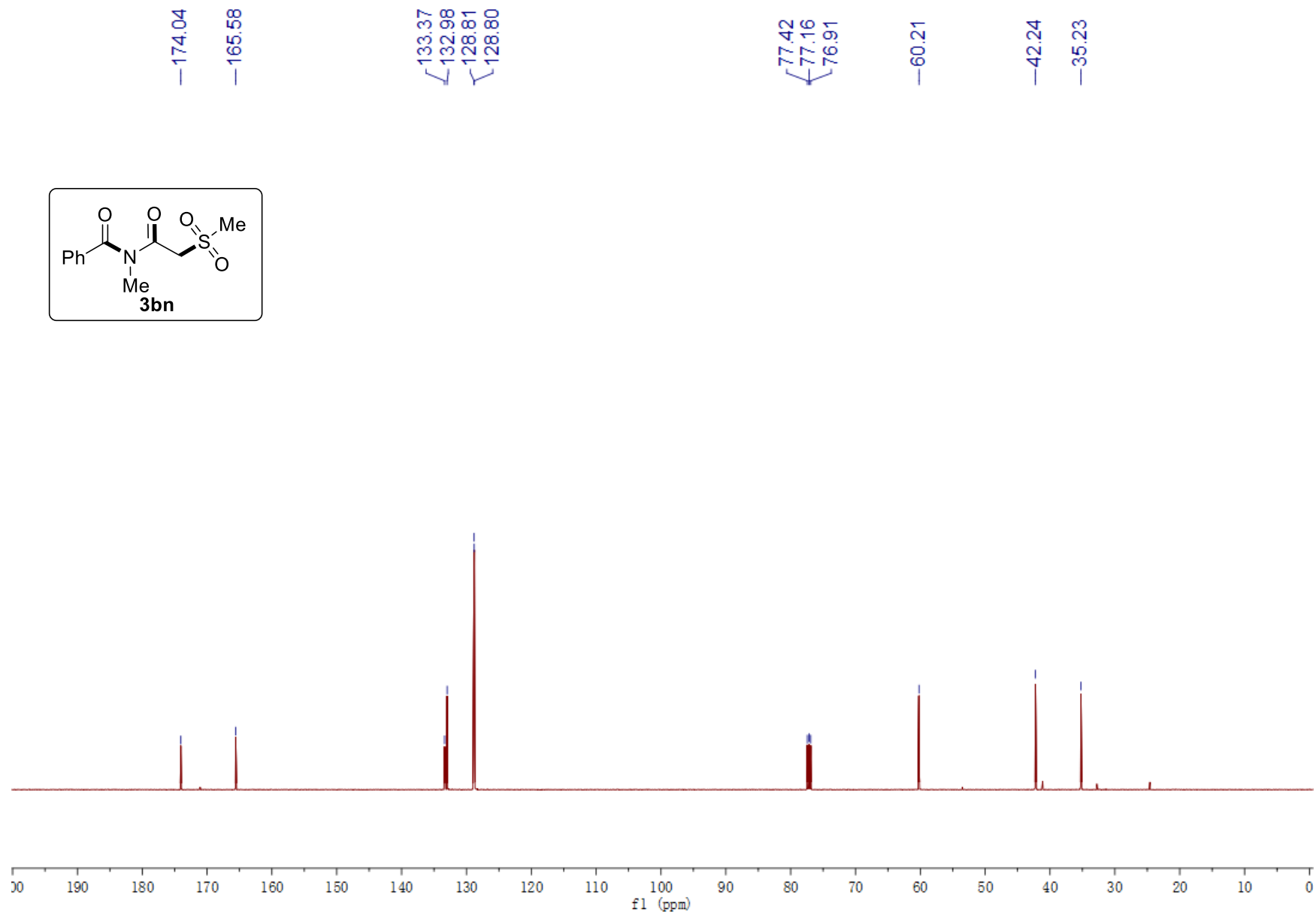
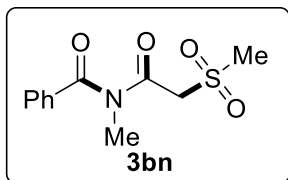
S191

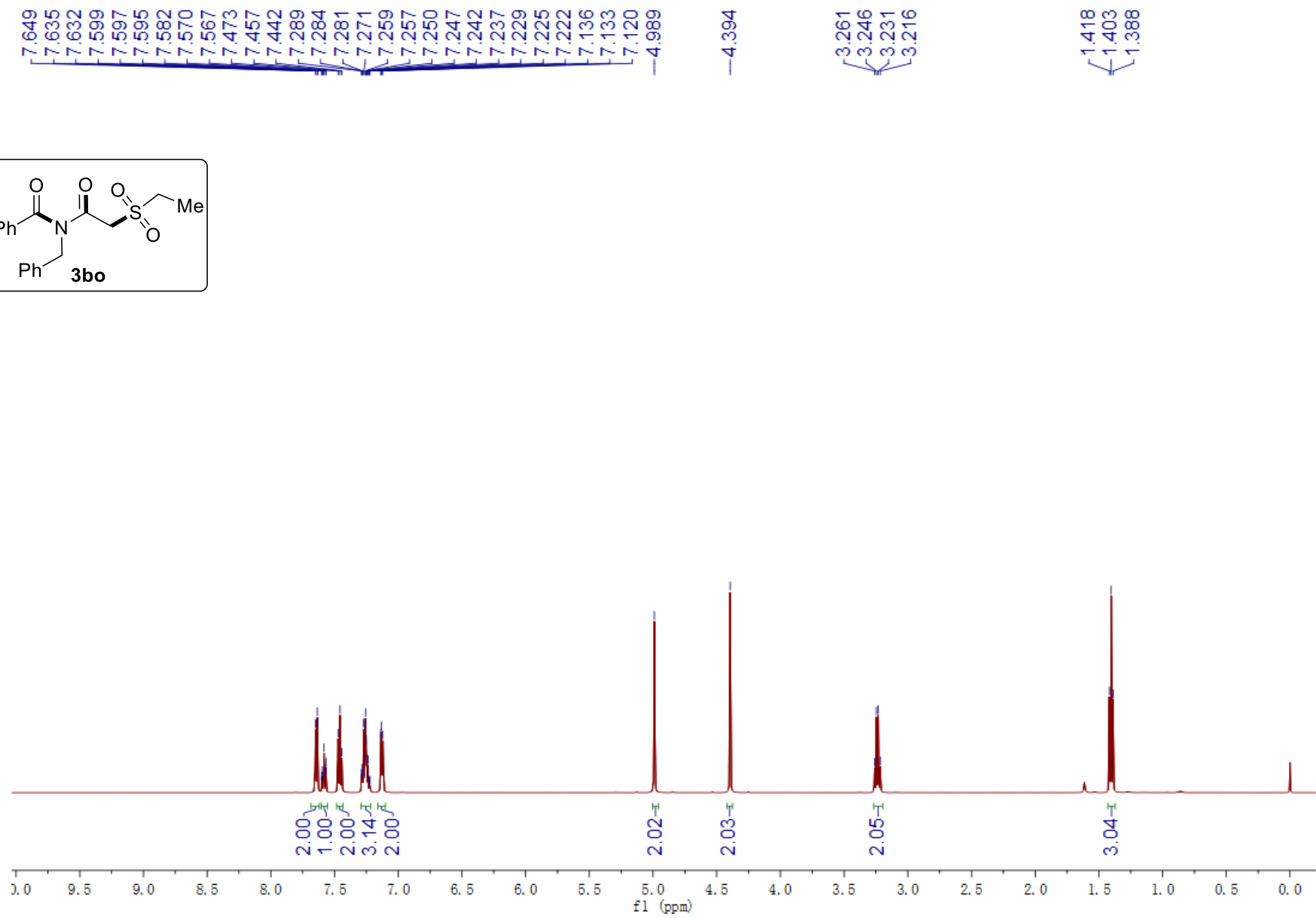
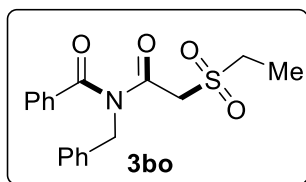


S192

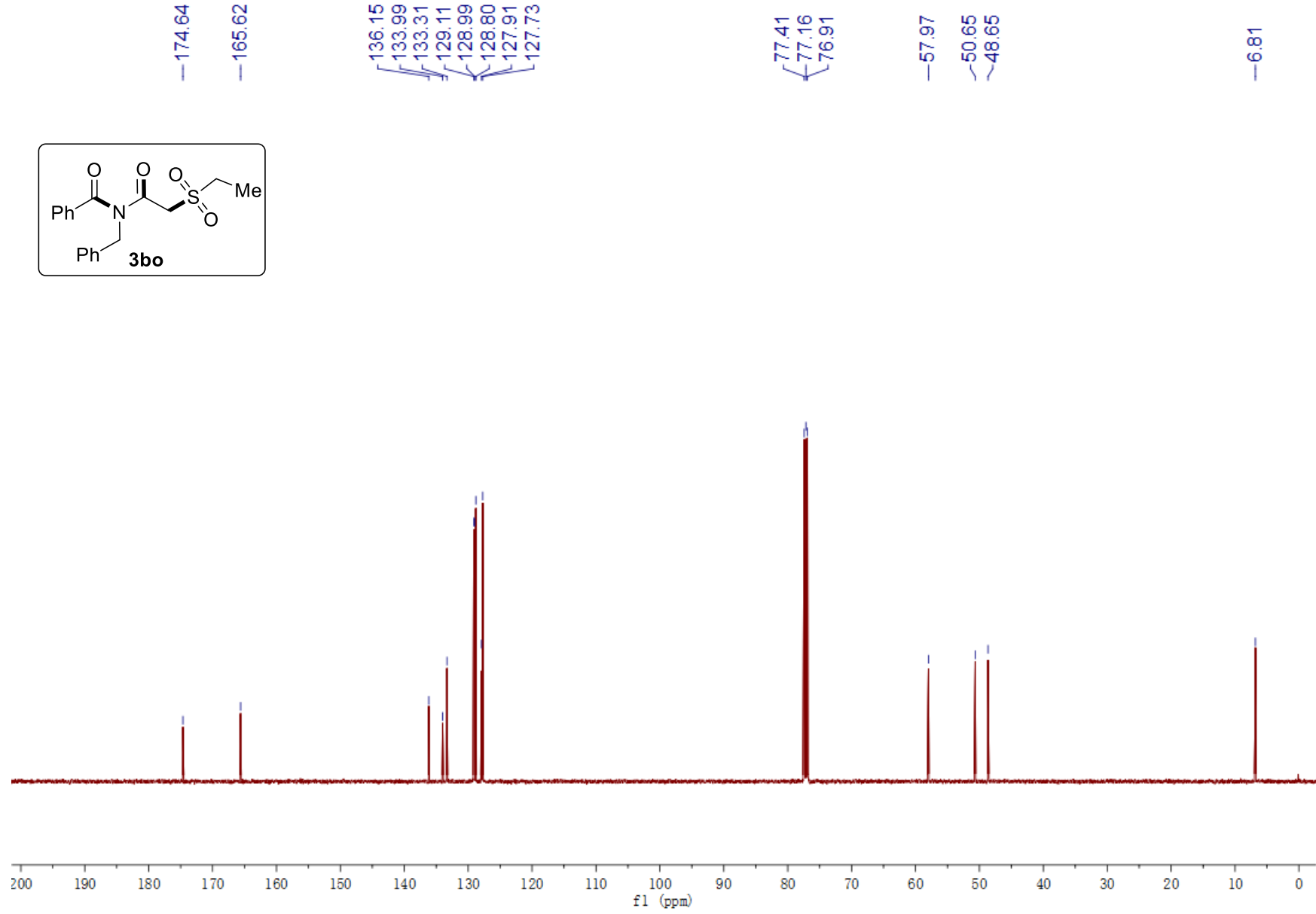
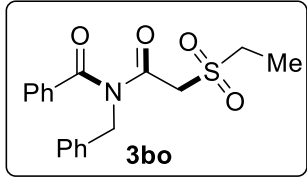


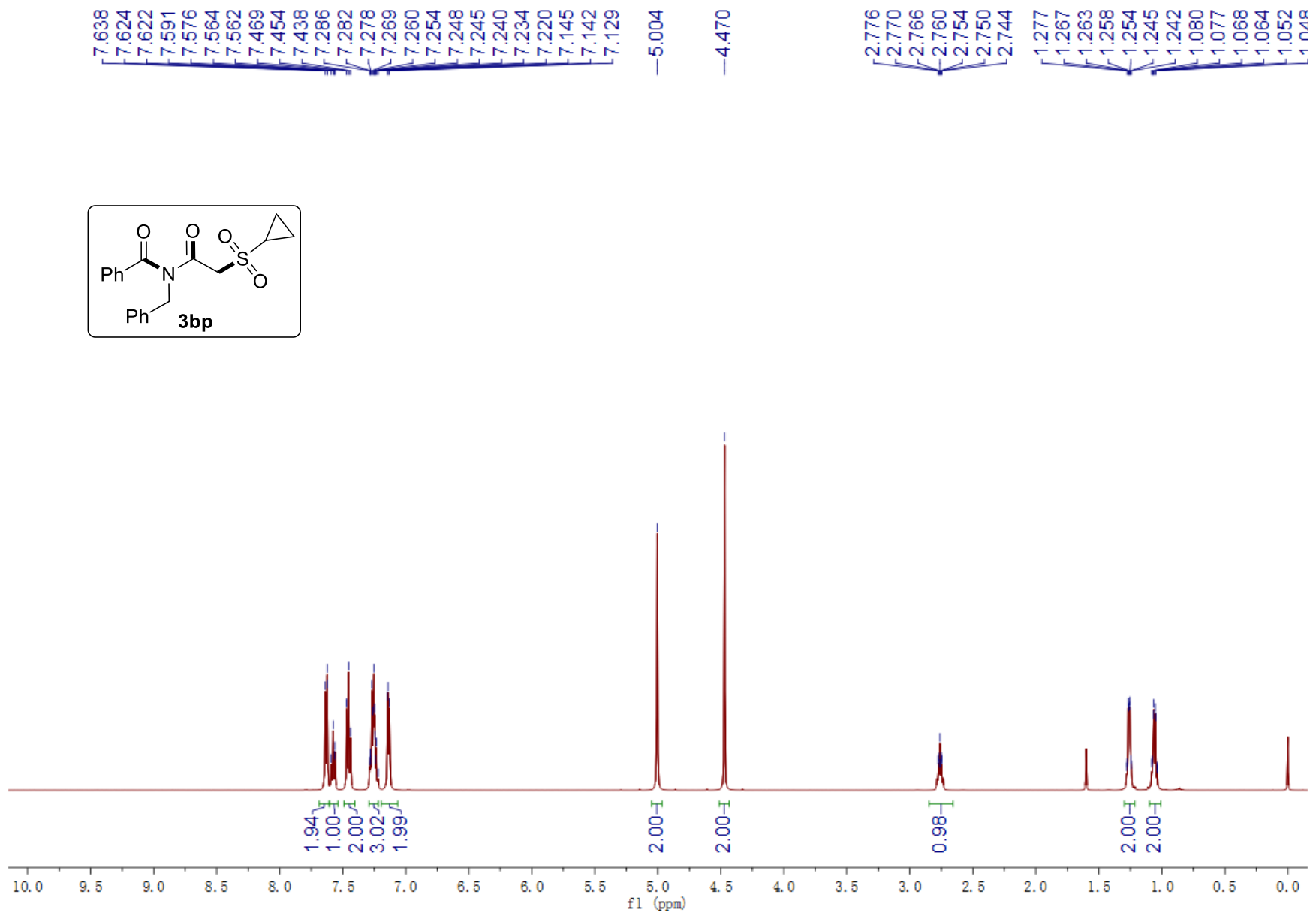
S193



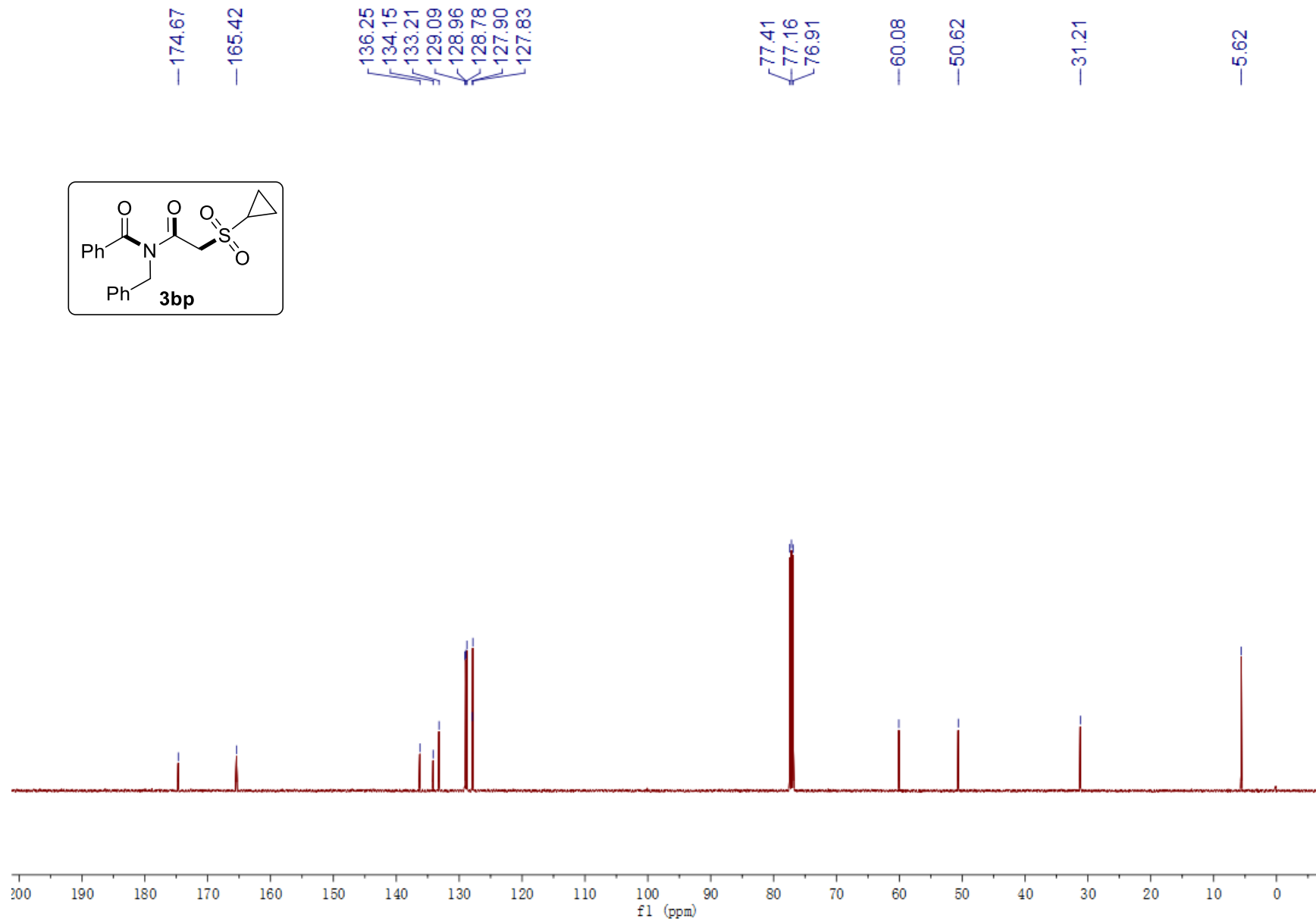
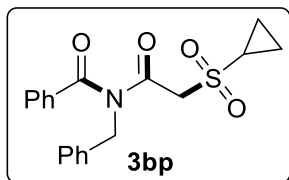


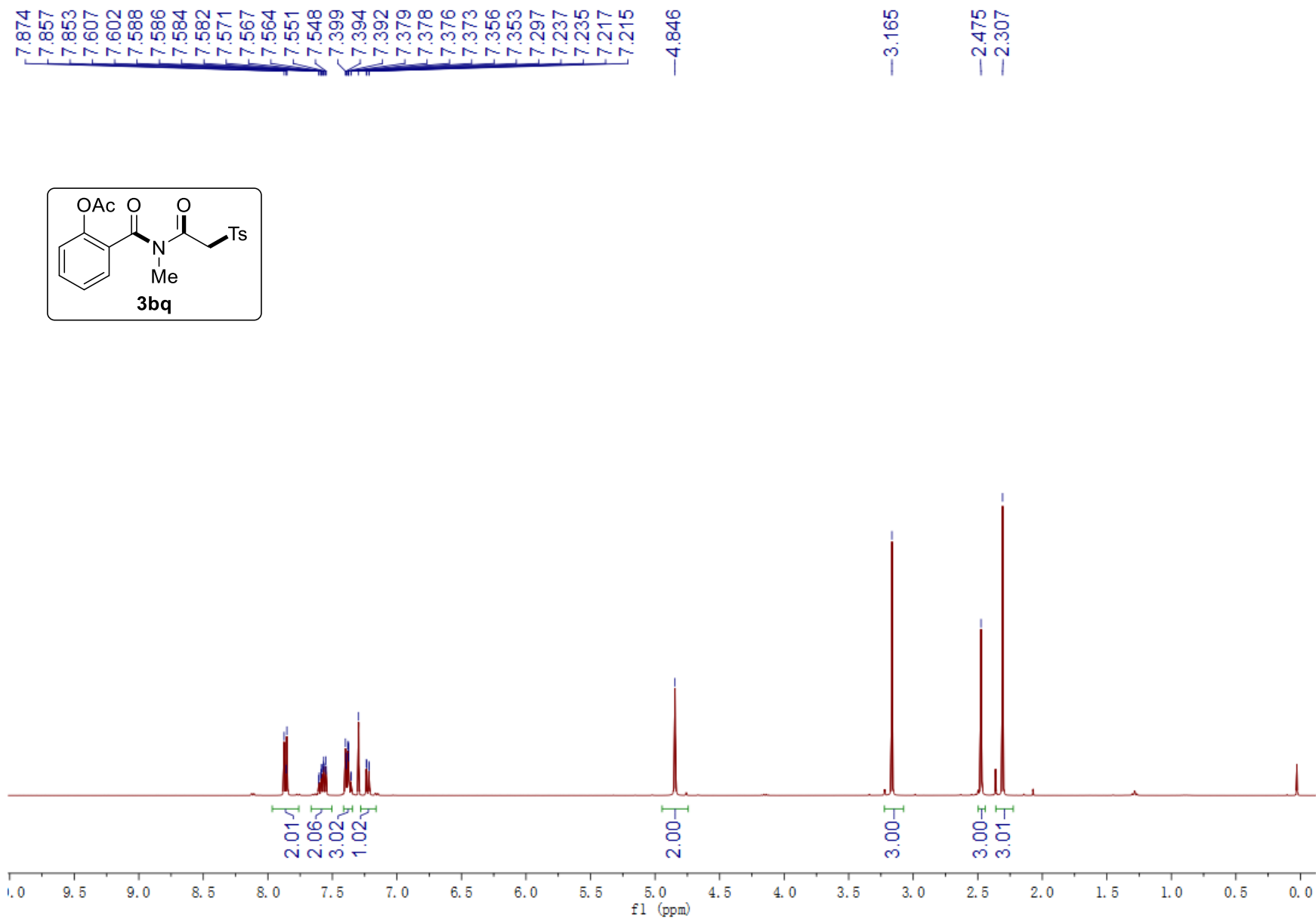
S195



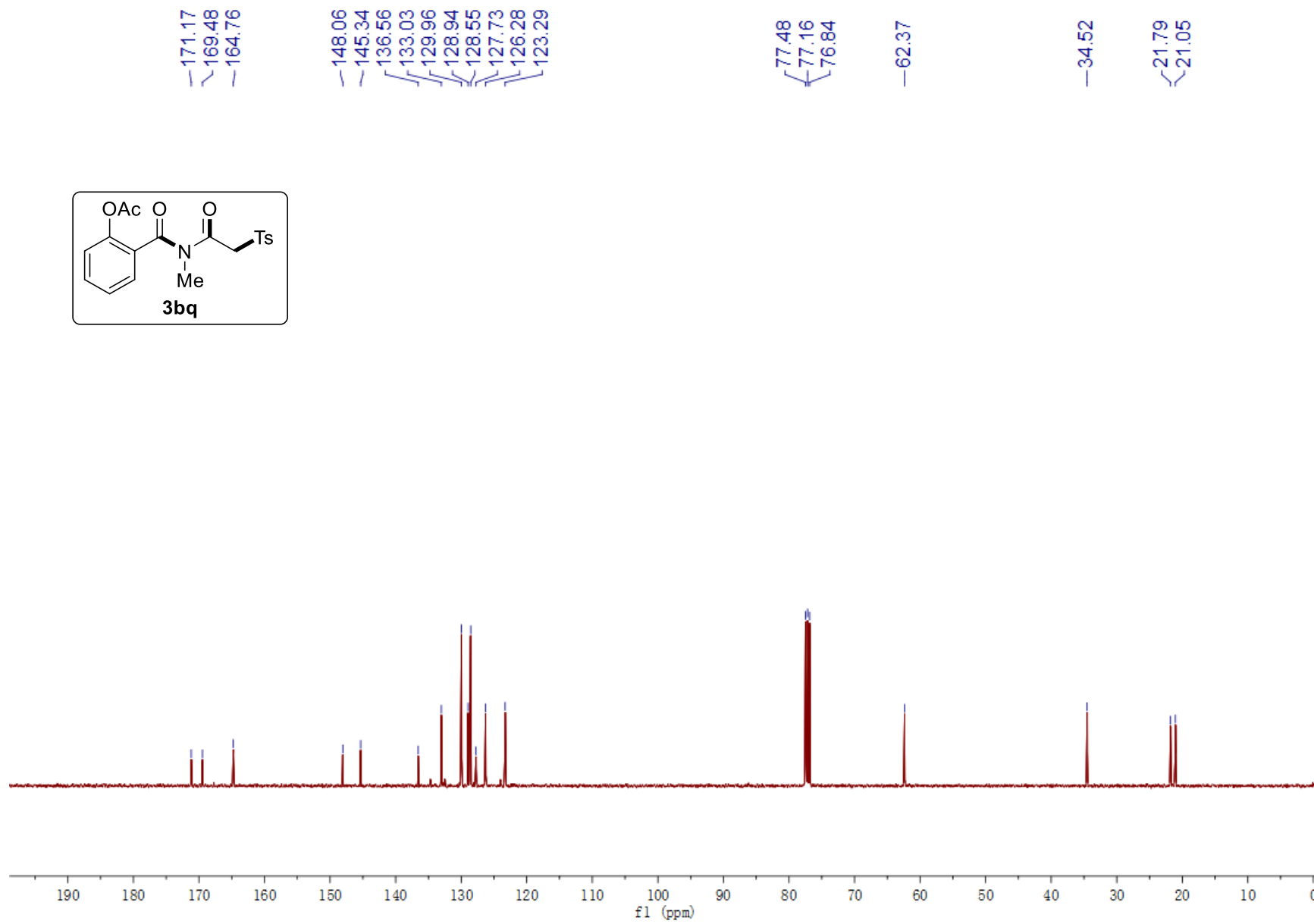
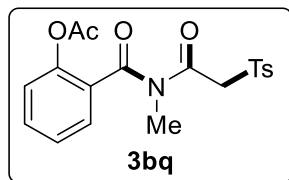


S197

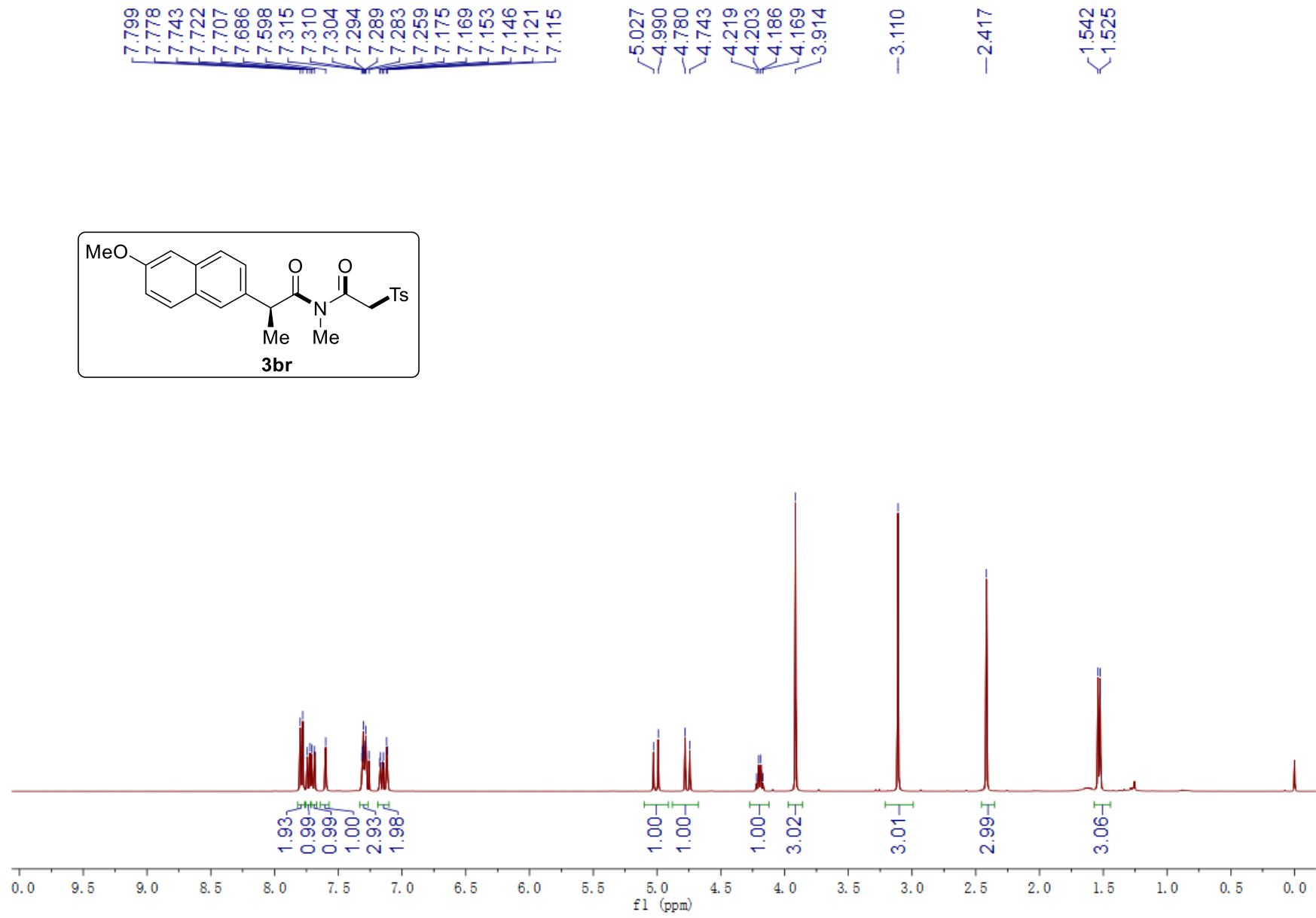




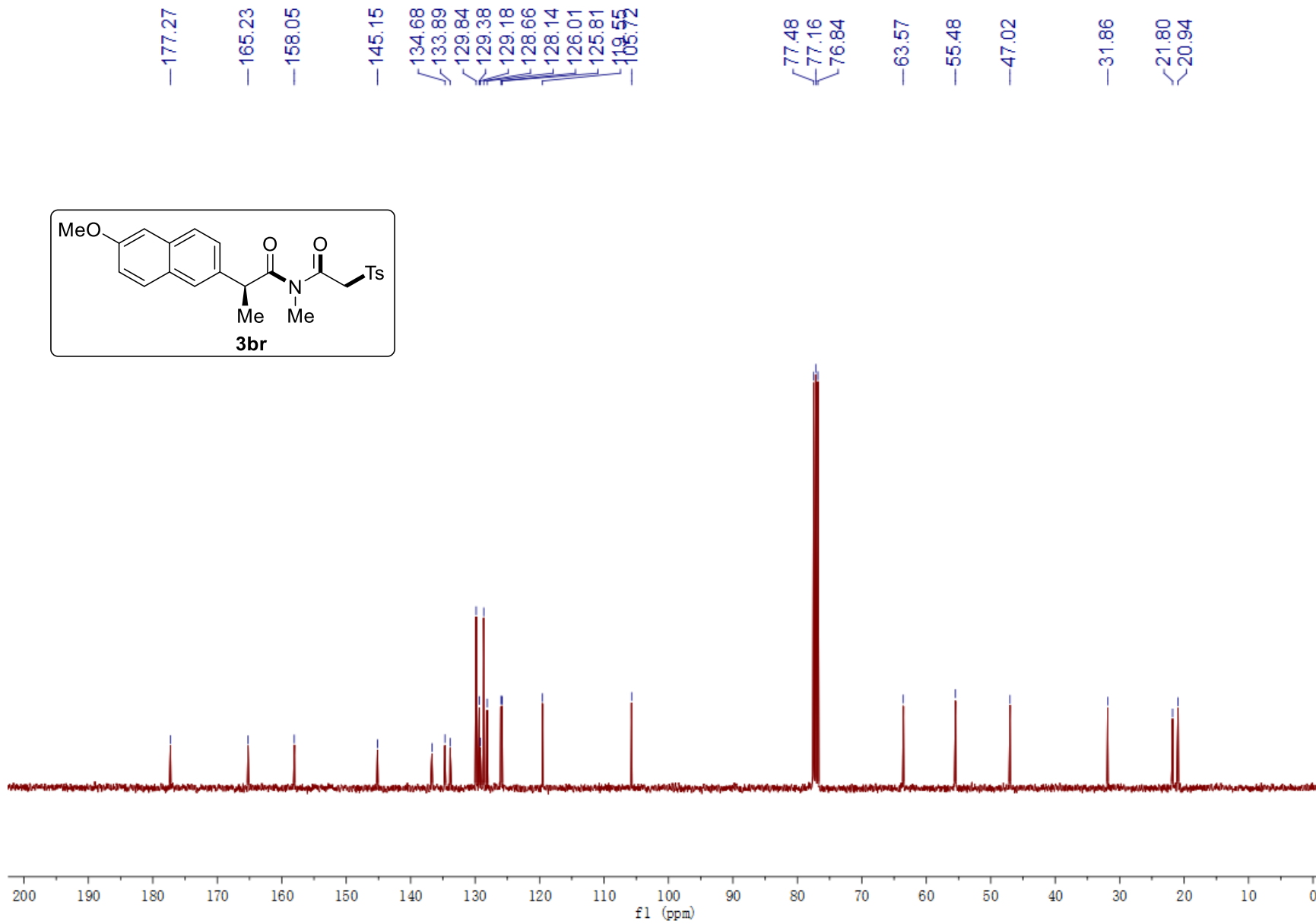
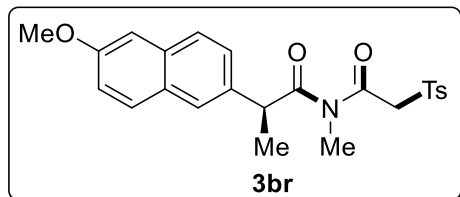
S199



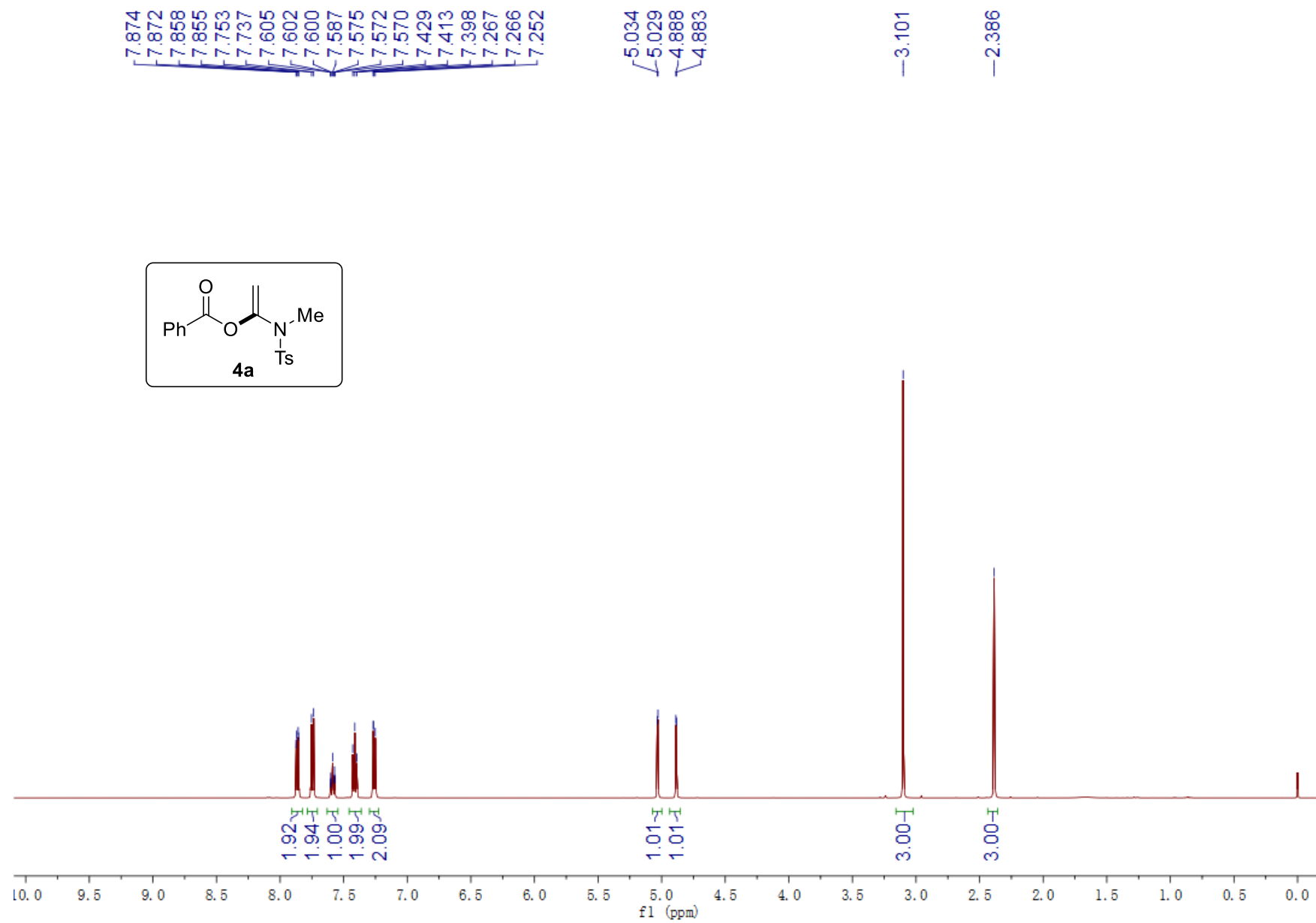
S200



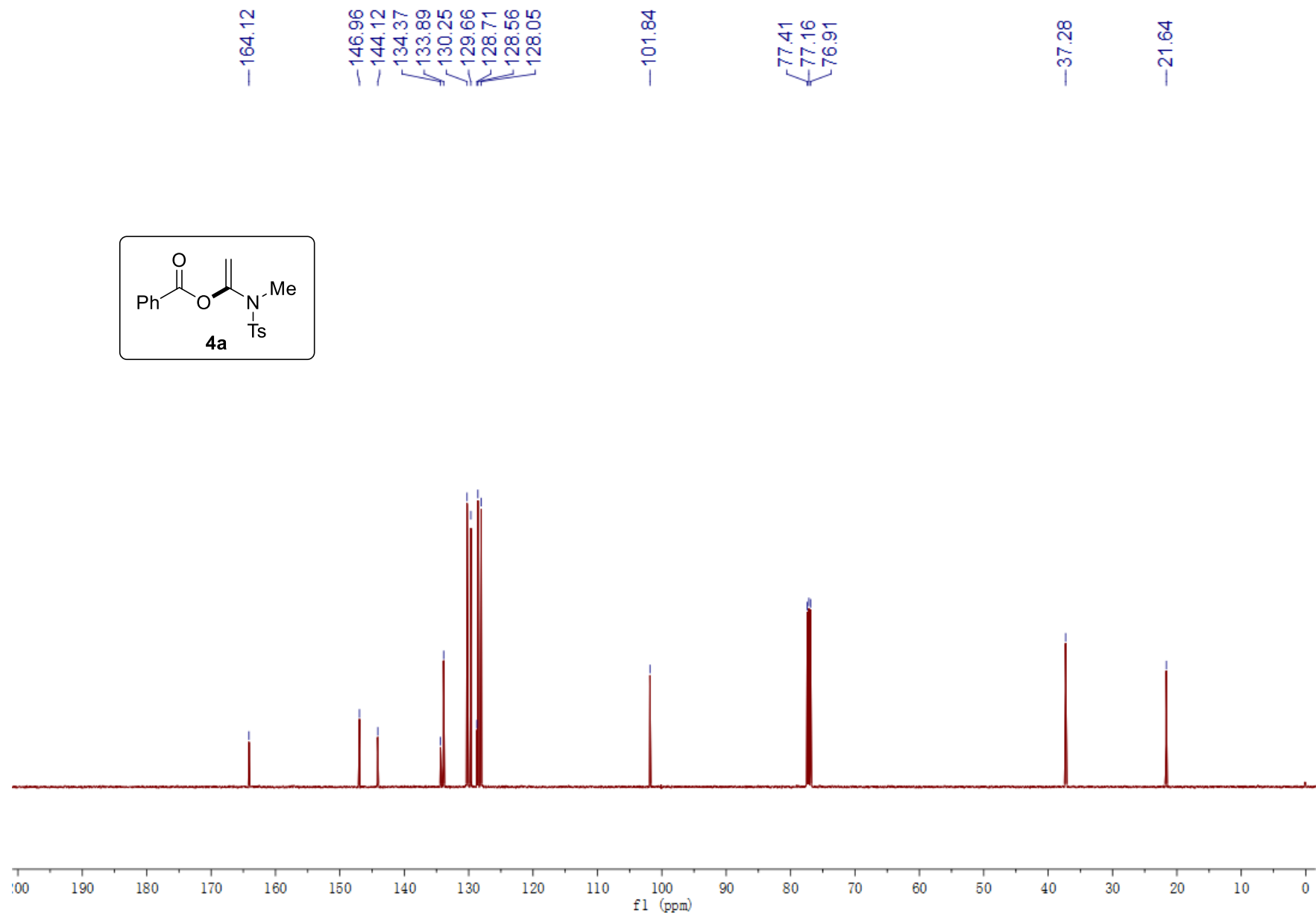
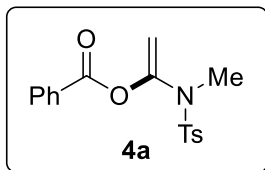
S201



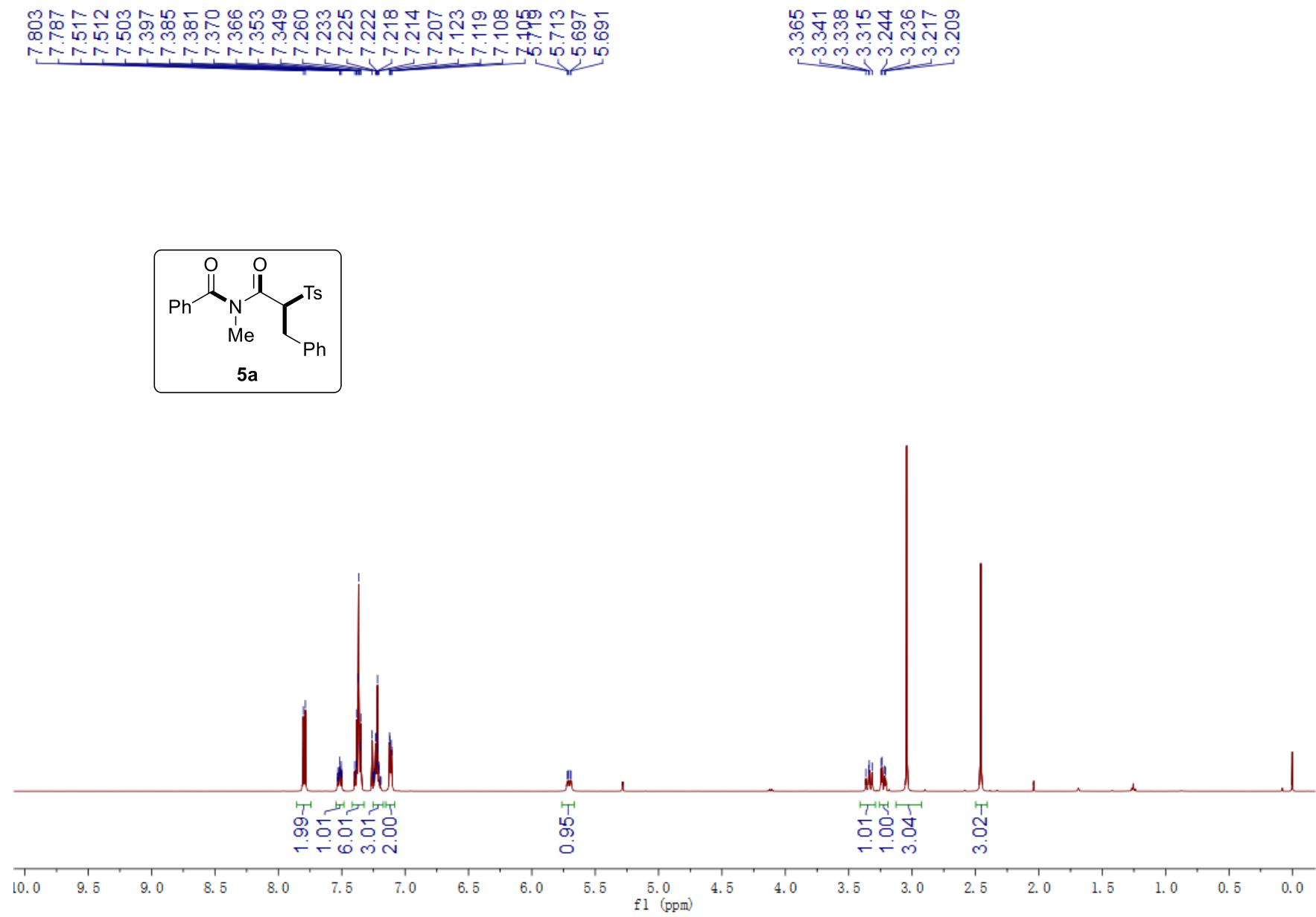
S202



S203



S204



S205

—174.29

—167.57

—145.47

135.80

134.27

134.04

132.70

129.83

129.57

129.19

128.79

128.73

127.13

77.41

77.16

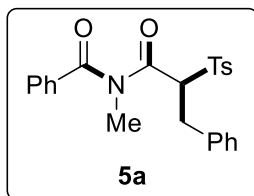
76.91

—69.16

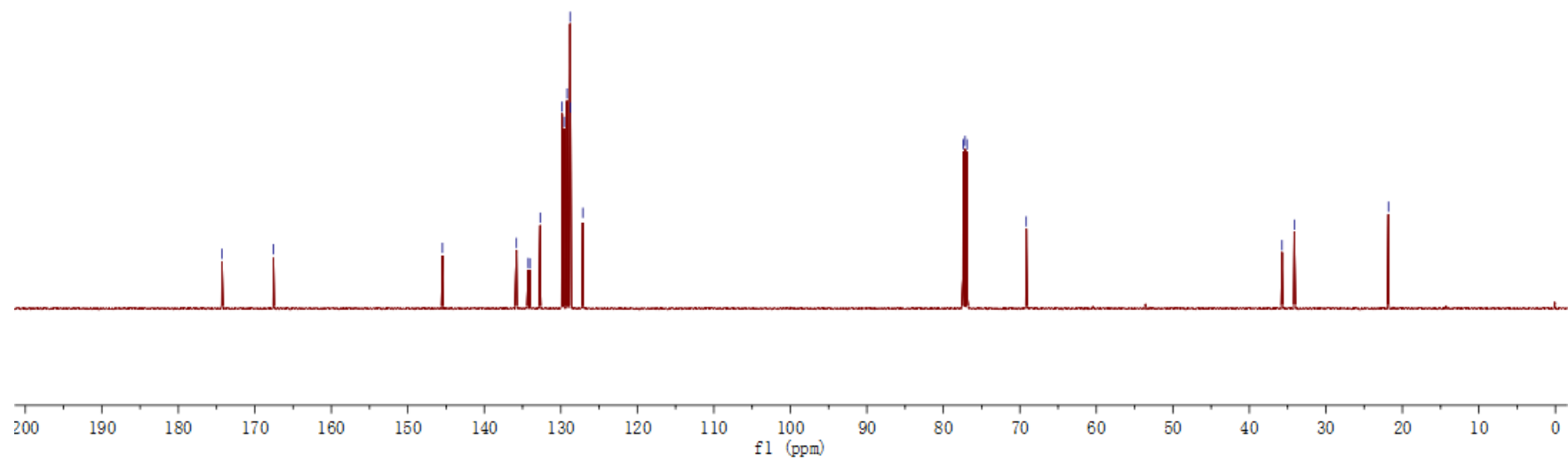
35.73

34.13

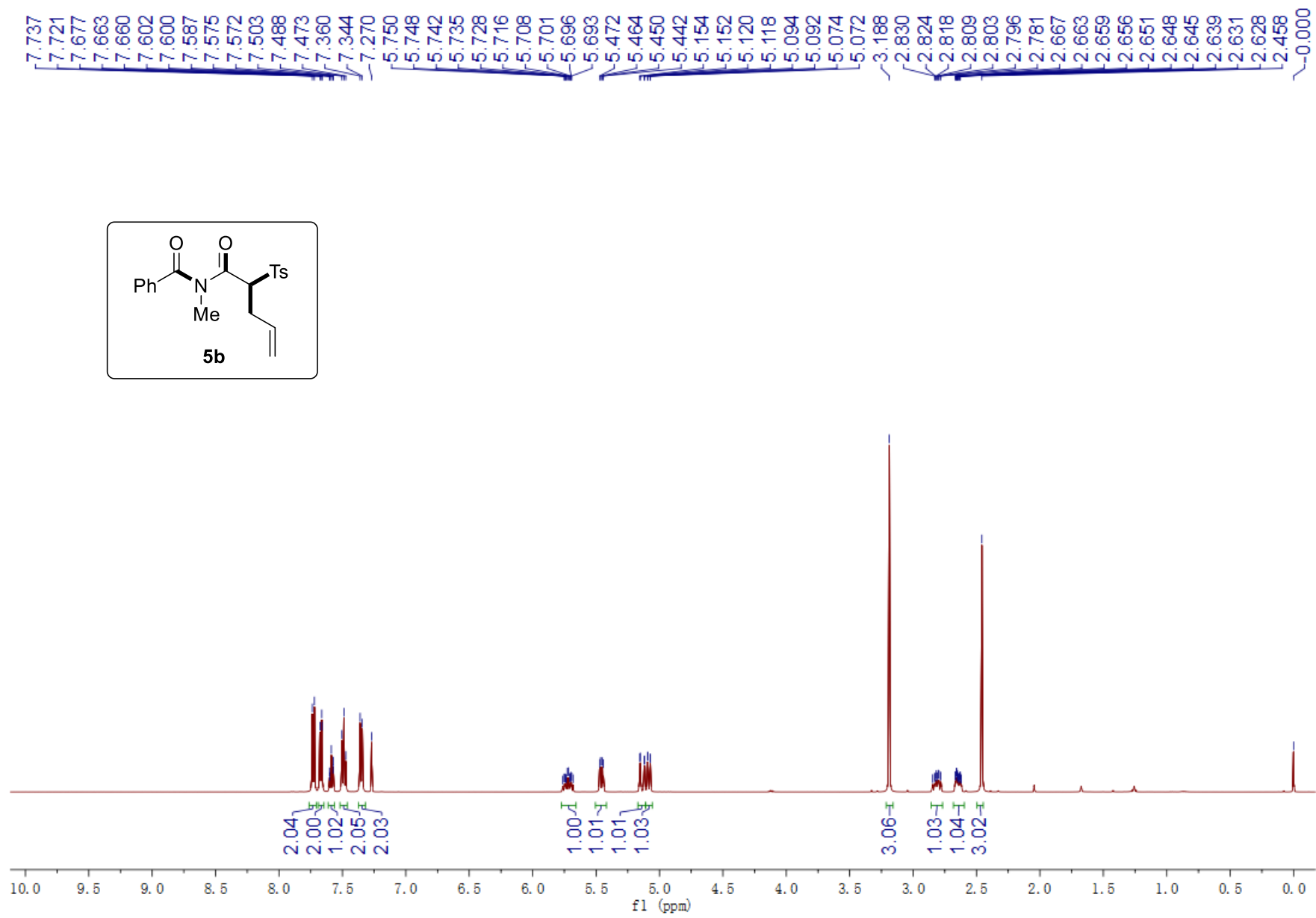
—21.82



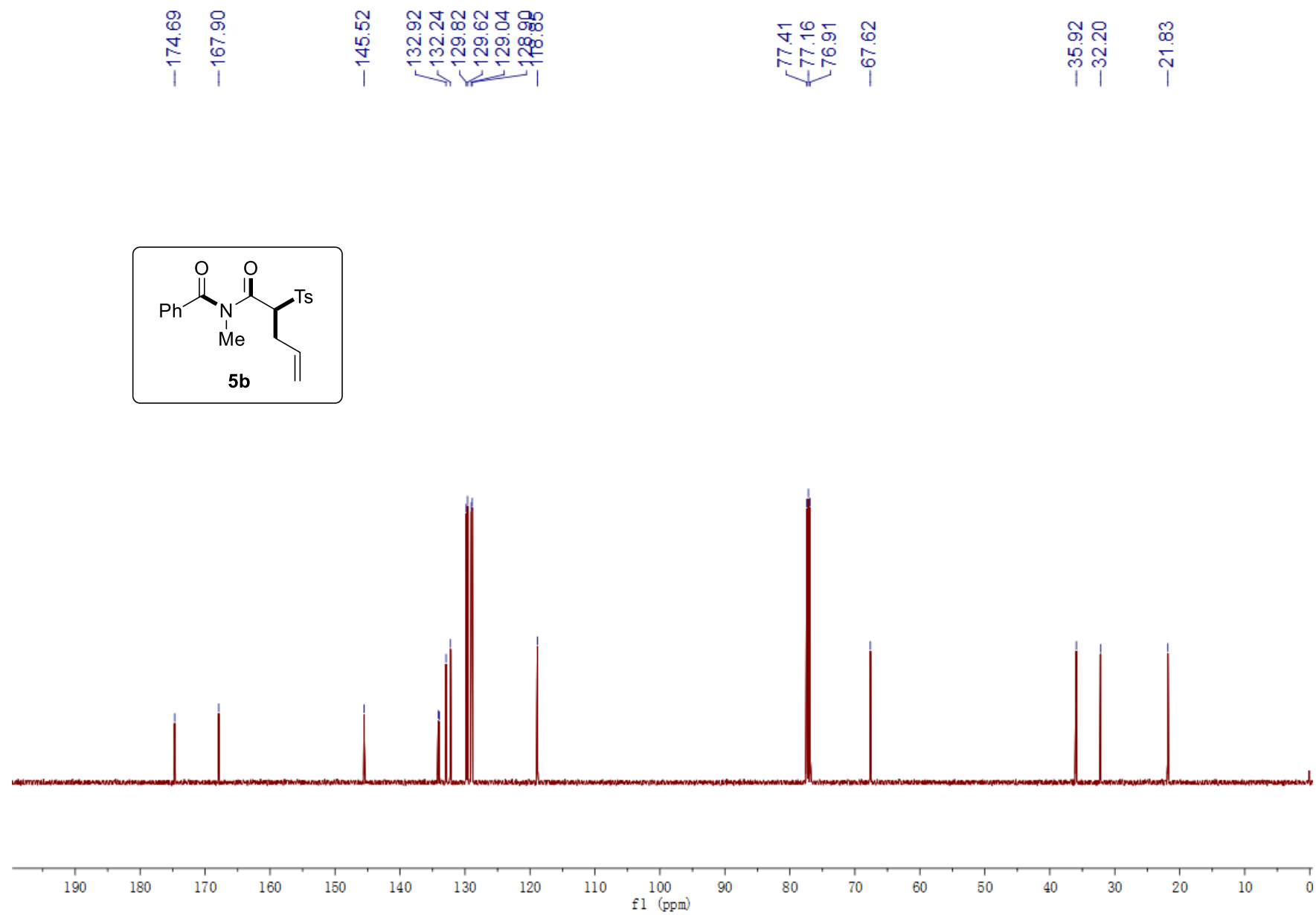
5a



S206



S207

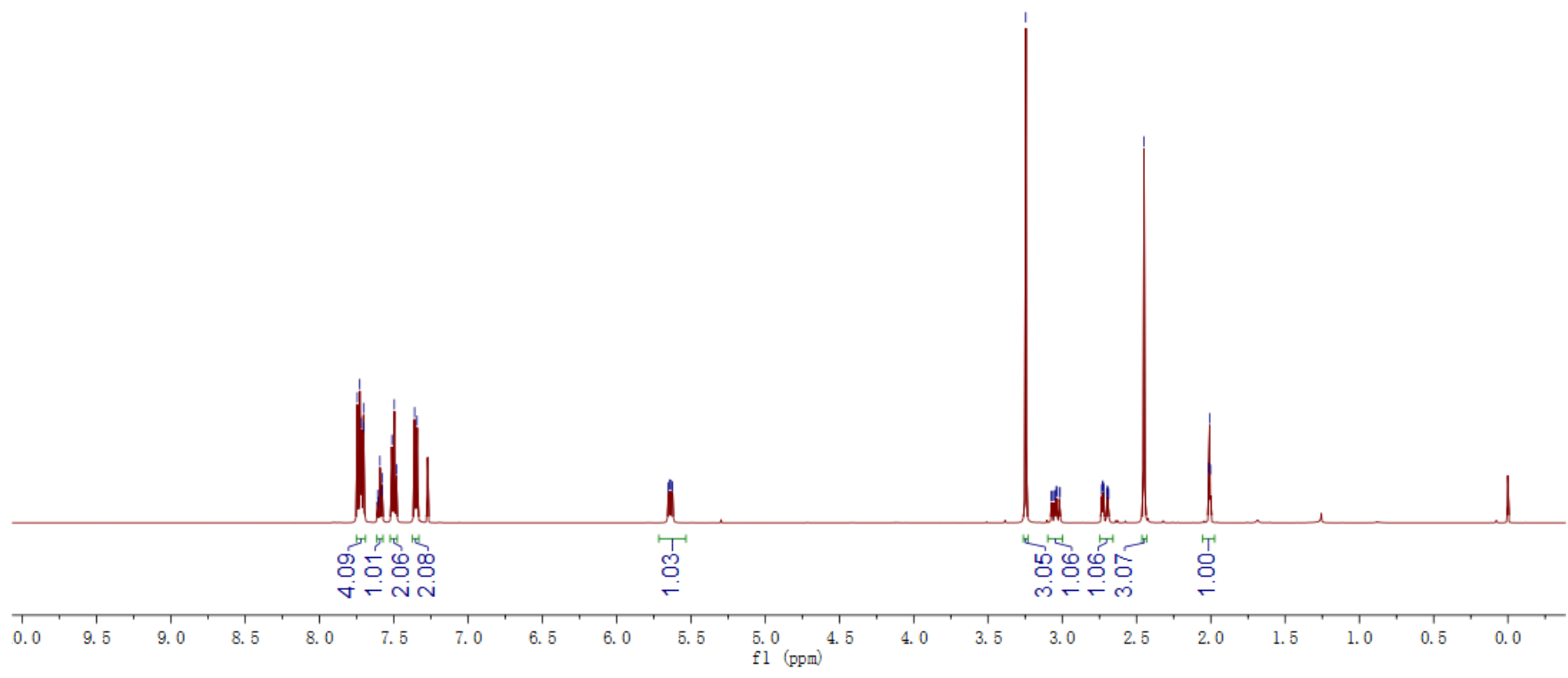
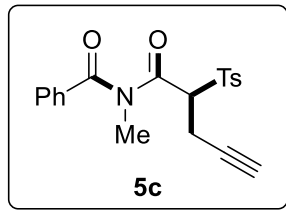


S208

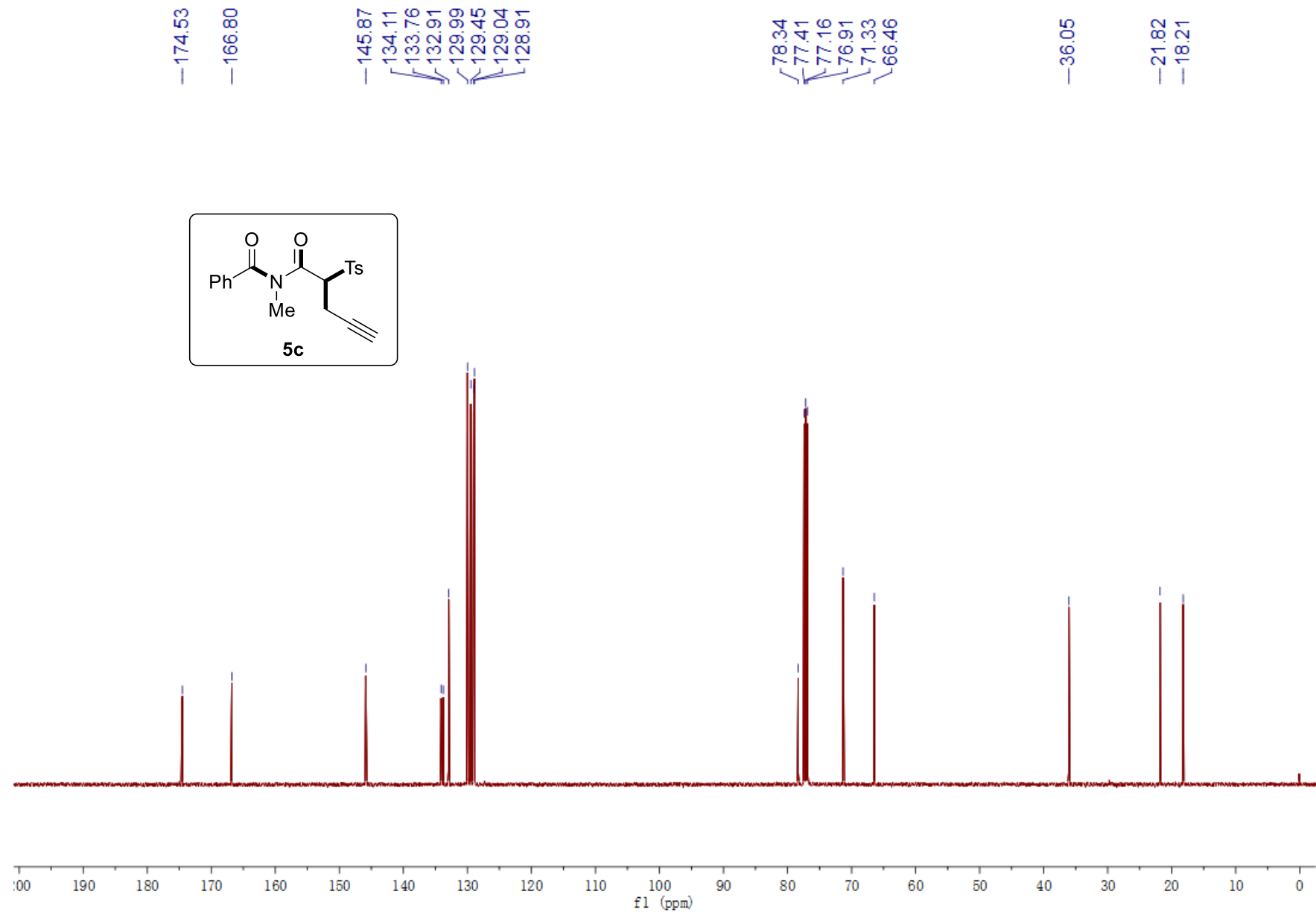
7.745
7.729
7.717
7.703
7.700
7.608
7.606
7.593
7.580
7.578
7.512
7.496
7.481
7.359
7.343

5.652
5.644
5.632
5.623

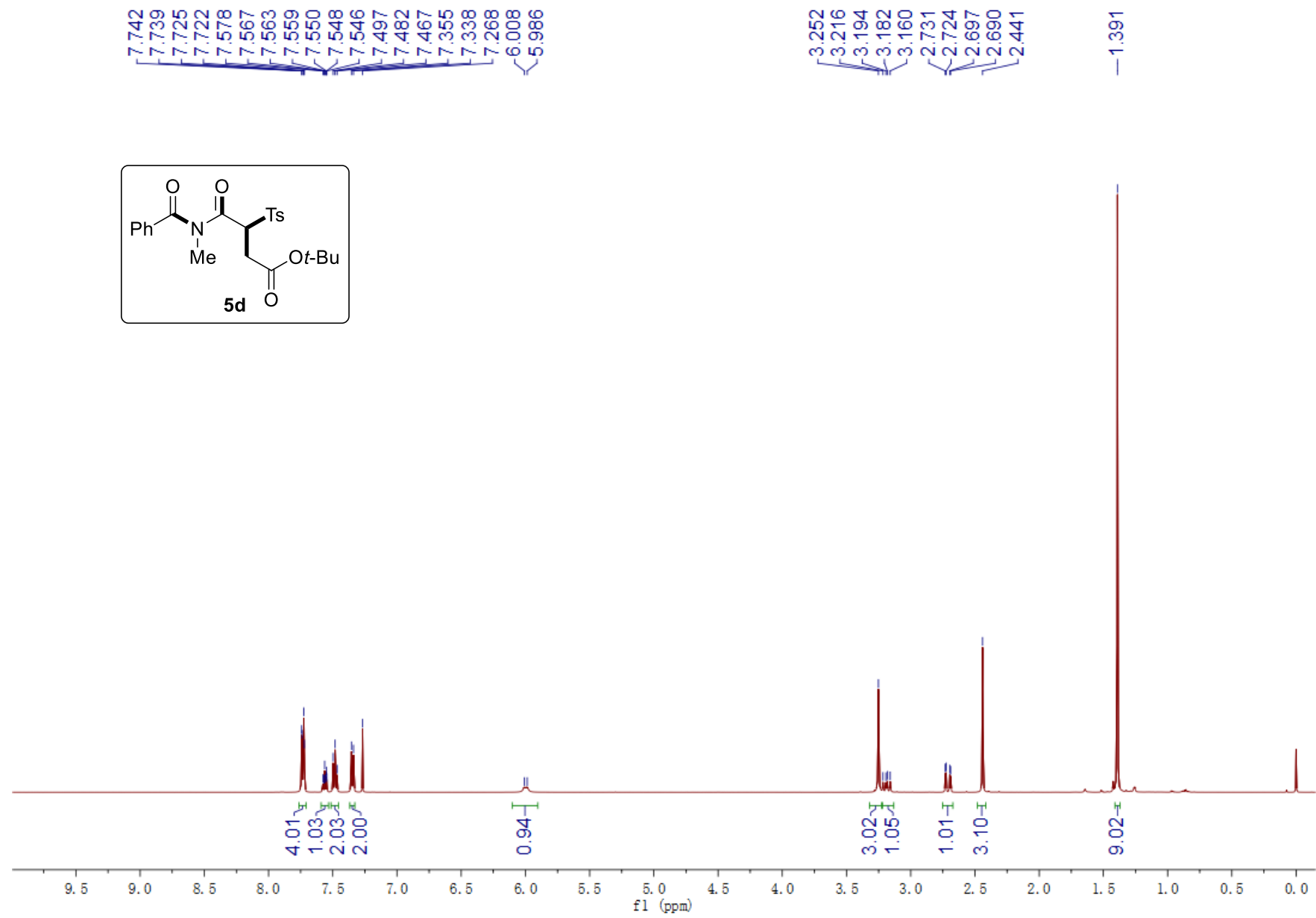
3.246
3.068
3.053
3.048
3.041
3.035
3.020
3.015
2.734
2.729
2.726
2.720
2.701
2.696
2.693
2.687
2.459
2.013
2.008
2.003



S209



S210



S211

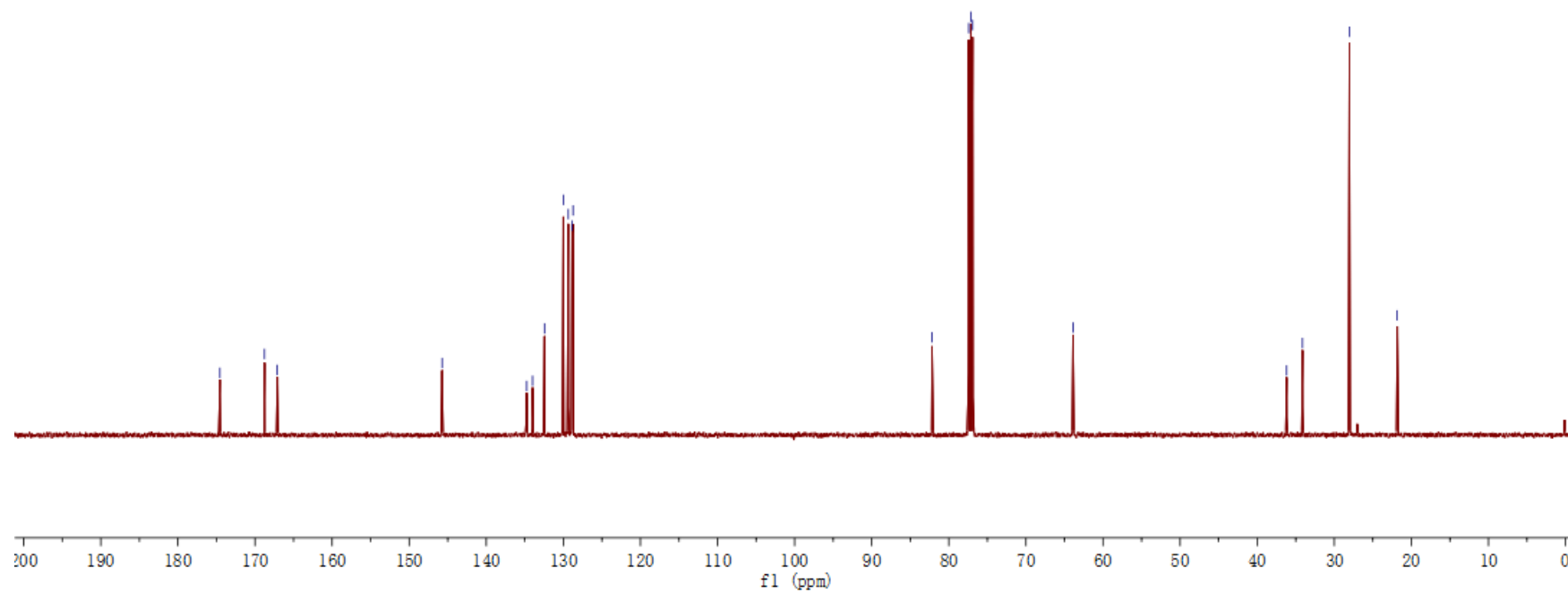
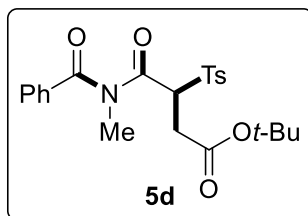
174.56
168.77
167.11

145.73
134.76
134.00
132.45
130.01
129.37
128.88
128.74

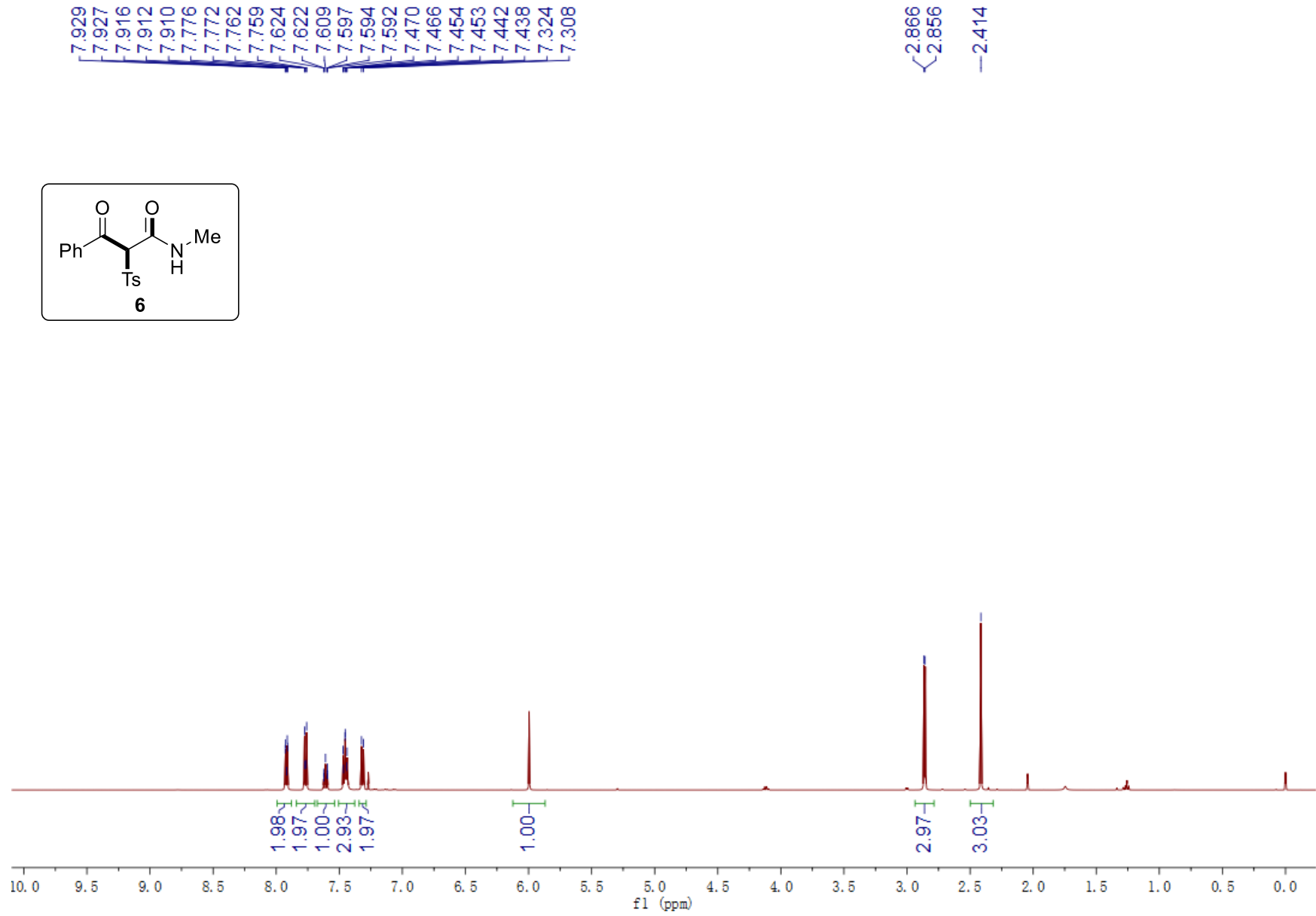
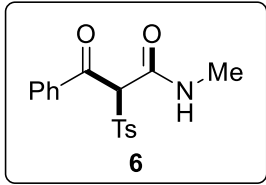
82.17
77.41
77.16
76.91

63.89

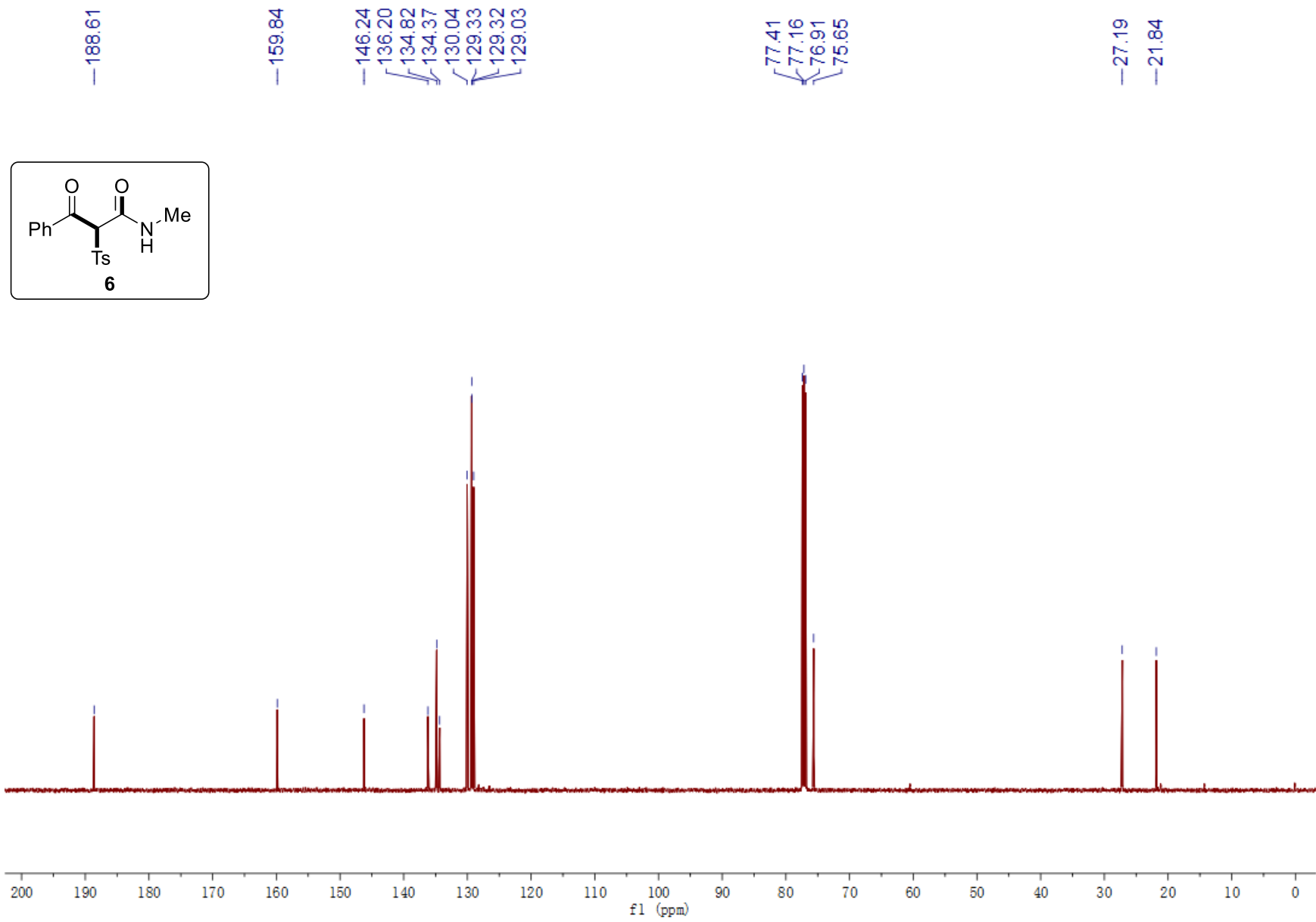
36.18
34.13
28.04
21.84



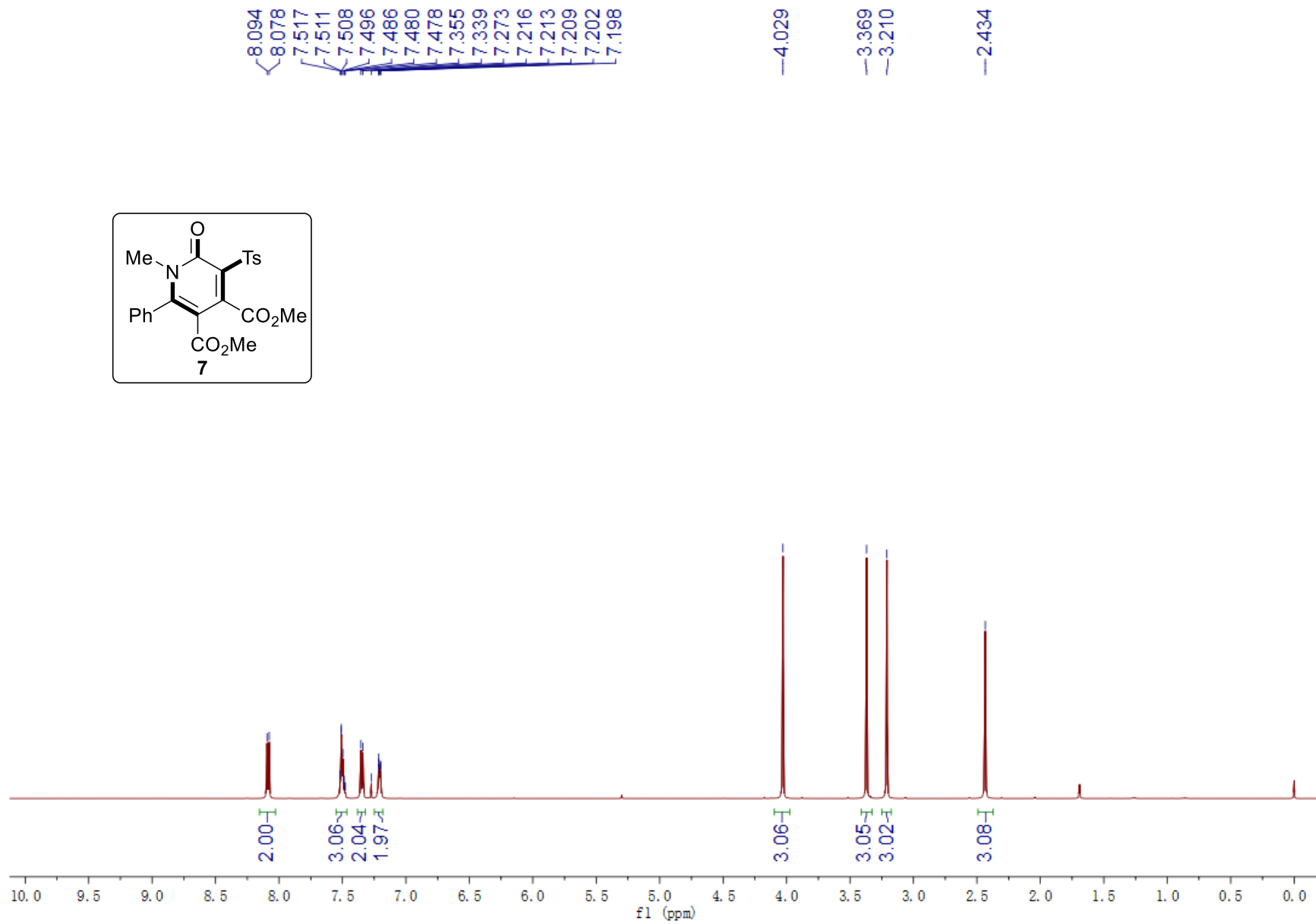
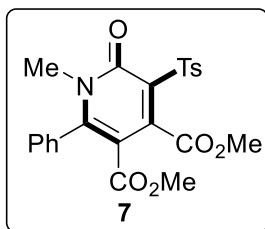
S212



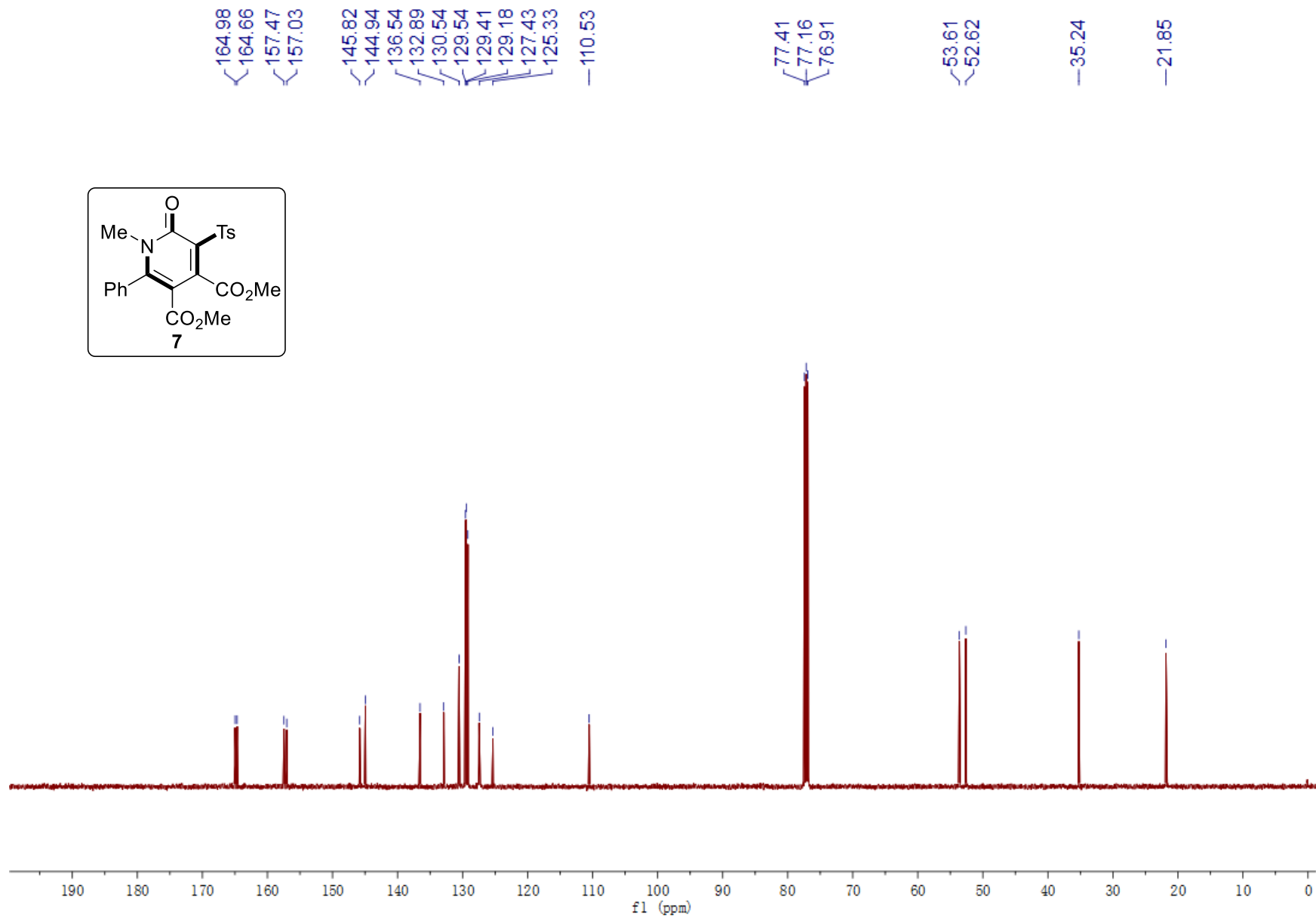
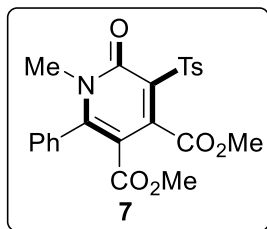
S213



S214



S215



S216

12. References

1. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.
2. Park, H.-S.; Fan, Z.-L.; Zhu, R. -Y.; Yu, J.-Q. *Angew. Chem., Int. Edit.* **2020**, *59*, 12853.
3. Mansfield, S. J.; Campbell, C. D.; Jones, M. W.; Anderson, E. A. *Chem. Commun.* **2015**, *51*, 3316.
4. Witulski, B.; Gossmann, M. *Chem. Commun.* **1999**, 1879.
5. Clavier, H.; Lepronier, A.; Bengobesse-Mintsa, N.; Gatineau, D.; Pellissier, H.; Giordano, L.; Tenaglia, A.; Buono, G. *Adv. Synth. Catal.* **2013**, *35*, 403.
6. Singh, A.; Teegardin, K.; Kelly, M.; Prasad, K. S.; Krishnan, S.; Weaver, J. D. *J. Organomet. Chem.* **2015**, *776*, 51.
7. D. C. Harris, *Quantitative Chemical Analysis*, Freeman, 9th edn, **2015**.
8. Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 6019.
9. Monalti, M., et. al. *Handbook of Photochemistry*, 3rd Ed; Taylor & Francis Group, LLC. Boca Raton, FL, **2006**, 601.
10. Sheldrick, G. M. *Acta Crystallographica Section A: Foundations of Crystallography* **2008**, *64*, 112-122.
11. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. *J. Appl. Crystallogra.* **2009**, *42*, 339- 341.