

Supporting Information

Copper-Catalyzed Decarboxylative Ethynyl Methylene Cyclic Carbamates with Amines: Modular Synthesis of 3-Aminopyrroles

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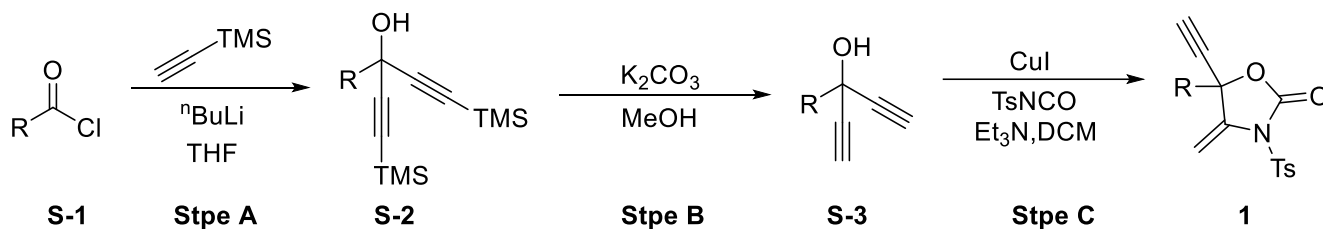
General information

All reactions were carried out using oven-dried glassware with magnetic stirring under argon atmosphere unless otherwise noted. Anhydrous solvents were dried prior to use. Reagents were purchased from Energy Chemical and used without further purification. For column chromatography, 200-300 mesh silica gel was used. Thin layer chromatography (TLC) was performed on Silicycle 250 μ m silica gel 60Å plates. Visualization was accomplished with UV light (254 nm), Iodine, or Potassium Permanganate. Heating by an oil bath.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz (300 MHz for ^1H ; 282 MHz for ^{19}F ; 75 MHz for ^{13}C) spectrometers at ambient temperature. The chemical shifts (δ) are given in parts per million relative to CDCl_3 (7.26 ppm for ^1H) or TMS (0 ppm for ^1H) and CDCl_3 (77.16 ppm for ^{13}C). Coupling constants (J) are reported in Hz, and multiplicity is described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, or combinations thereof. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus.

Amines used in this paper are all commercially available, purchased from company and direct use without further treatment. Ethynyl Methylene Cyclic Carbamates (EMCCs) have been prepared according to the reported literatures.¹ All new compounds, include EMCCs, have been characterized by ^1H NMR, ^{13}C NMR, ^{19}F NMR and HRMS.

General procedure for the synthesis of EMCCs



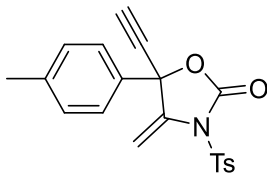
Step A: To a solution of trimethylsilyl acetylene (130 mmol, 2.6 equiv.) in THF (100 mL), a solution of $n\text{-BuLi}$ (50 mL, 2.4 M in hexane, 2.4 equiv.) was added dropwise at $-78\text{ }^\circ\text{C}$ under argon. The mixtures were then warmed to $-20\text{ }^\circ\text{C}$ and stirred for additional 30 min. A solution of S-1 (50 mmol, 1.0 equiv.) in THF (10 mL) was then added dropwise. After stirring for 2 h, the reaction mixtures were quenched with aq NH_4Cl at $-20\text{ }^\circ\text{C}$. The layers were separated and the aqueous layer was extracted with EAOAc (3×100 mL). The combined organic phases were washed with brine (3×100 mL) and dried over NaSO_4 . Removal of the solvent afforded S-2, which was used directly in the next step without further purification.

Step B: To the above crude S-2 (50 mmol, 1.0 equiv.), MeOH (100 mL), K_2CO_3 (50 mmol, 1.0 equiv.) were added and the solution was stirred continuously for 30 min. After completion of the reaction, the solvent was removed under reduced pressure. The residue was diluted by adding H_2O (100 mL) and then the mixtures were extracted with Et_2O (3×100 mL). The combined organic phases were washed with brine (3×100 mL) and dried over NaSO_4 . After concentration, the residue was purified by flash column chromatography to give the desired product S-3, which was used directly in the next step without further purification.

Step C: To a 25 mL round-bottomed flask, CuI (0.25 mmol, 47.5 mg 0.05 equiv.) was added under argon, followed by a dry dichloromethane (4 mL) solution of triethylamine (0.6 mmol, 63 mg, 0.12 equiv.) and S-3 (5.0 mmol, 1.0 equiv.). Then a dry dichloromethane (1 mL) solution of TsNCO (5.5 mmol, 1.1 equiv.) was added dropwise to the solution by syringe at $0\text{ }^\circ\text{C}$. After being stirred for 2-4 h at room temperature, the reaction was filtered by silica gel. Evaporation of the filtrate left a crude product, which was subjected to column chromatography (EtOAc/hexane, 1: 3-1:10) for product EMCCs 1.

The new EMCCs were listed as follows:

5-ethynyl-4-methylene-5-(p-tolyl)-3-tosyloxazolidin-2-one (1b)



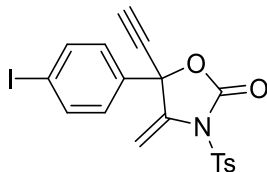
The title compound was prepared through above general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **1b** in 67% yield.

¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.34 (dd, *J* = 13.3, 8.0 Hz, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.70 (d, *J* = 3.2 Hz, 1H), 4.71 (d, *J* = 3.2 Hz, 1H), 2.89 (s, 1H), 2.47 (d, *J* = 2.6 Hz, 3H), 2.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.8, 146.5, 141.6, 140.2, 134.3, 134.2, 130.1, 130.0, 129.5, 128.4, 126.0, 96.0, 80.6, 79.4, 78.4, 21.9, 21.3.

HRMS (ESI) *m/z* calculated for C₂₀H₁₈NO₄S [M+H]⁺ : 368.0951, found: 368.0955.

5-ethynyl-5-(4-iodophenyl)-4-methylene-3-tosyloxazolidin-2-one (1d)



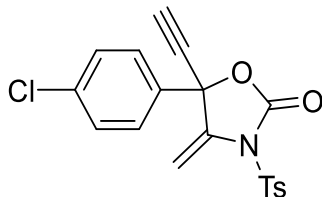
The title compound was prepared through above general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1d** in 70% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 5.72 (d, *J* = 3.4 Hz, 1H), 4.75 (d, *J* = 3.4 Hz, 1H), 2.94 (s, 1H), 2.48 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.5, 146.7, 140.9, 138.0, 137.0, 133.8, 130.1, 128.3, 127.7, 96.5, 96.4, 80.0, 79.0, 78.6, 22.0.

HRMS (ESI) *m/z* calculated for C₁₉H₁₅INO₄S [M+H]⁺ : 479.9761, found: 479.9766.

5-(4-chlorophenyl)-5-ethynyl-4-methylene-3-tosyloxazolidin-2-one (1e)



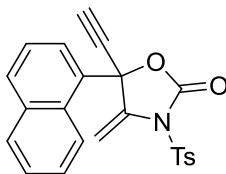
The title compound was prepared through above general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1e** in 65% yield.

¹H NMR (300 MHz, CDCl₃) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.34 (m, 6H), 5.73 (s, 1H), 4.75 (s, 1H), 2.94 (s, 1H), 2.47 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 149.5, 146.7, 141.0, 136.2, 135.7, 133.9, 130.1, 129.1, 128.3, 127.4, 96.5, 79.8, 79.0, 78.8, 21.9.

HRMS (ESI) *m/z* calculated for C₁₉H₁₅ClNO₄S [M+H]⁺ : 388.0405, found: 388.0407.

5-ethynyl-4-methylene-5-(naphthalen-1-yl)-3-tosyloxazolidin-2-one (1l)



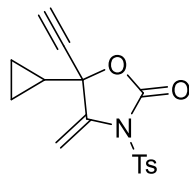
The title compound was prepared through above general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:6) furnished **1l** in 58% yield.

¹H NMR (300 MHz, CDCl₃) δ 7.99 (dd, *J* = 8.5, 1.7 Hz, 3H), 7.91-7.81 (m, 3H), 7.47 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.41-7.29 (m, 4H), 5.90 (d, *J* = 3.2 Hz, 1H), 4.89 (d, *J* = 3.2 Hz, 1H), 2.98 (s, 1H), 2.44 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 149.5, 146.6, 139.8, 134.7, 134.0, 131.9, 130.5, 130.1, 129.9, 129.2, 128.5, 126.7, 126.3, 126.3, 125.2, 124.3, 97.7, 81.7, 79.9, 79.7, 21.9.

HRMS (ESI) *m/z* calculated for C₂₃H₁₈NO₄S [M+H]⁺ : 404.0951, found: 404.0958.

5-cyclopropyl-5-ethynyl-4-methylene-3-tosyloxazolidin-2-one (1q)



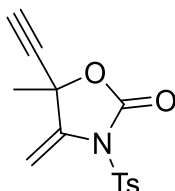
The title compound was prepared through above general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **1q** in 55% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.00-7.91 (m, 2H), 7.41-7.33 (m, 2H), 5.62 (d, *J* = 3.0 Hz, 1H), 4.86 (d, *J* = 3.0 Hz, 1H), 2.64 (s, 1H), 2.46 (s, 3H), 1.26 (tt, *J* = 8.0, 5.2 Hz, 1H), 0.78-0.50 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 149.7, 146.5, 140.8, 134.1, 130.0, 128.3, 93.8, 81.9, 77.0, 21.9, 19.7, 2.9, 1.9.

HRMS (ESI) *m/z* calculated for C₁₆H₁₆NO₄S [M+H]⁺ : 318.0795, found: 318.0791.

5-ethynyl-5-methyl-4-methylene-3-tosyloxazolidin-2-one (1r)



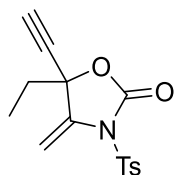
The title compound was prepared through above general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:10) furnished **1r** in 50% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.02-7.85 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 5.62 (d, *J* = 3.3 Hz, 1H), 4.81 (d, *J* = 3.2 Hz, 1H), 2.72 (s, 1H), 2.46 (s, 3H), 1.72 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.5, 146.6, 141.5, 133.9, 130.0, 128.2, 93.0, 80.0, 76.6, 76.1, 29.0, 21.8.

HRMS (ESI) *m/z* calculated for C₁₄H₁₄NO₄S [M+H]⁺ : 292.0638, found: 292.0635.

5-ethyl-5-ethynyl-4-methylene-3-tosyloxazolidin-2-one (1s)



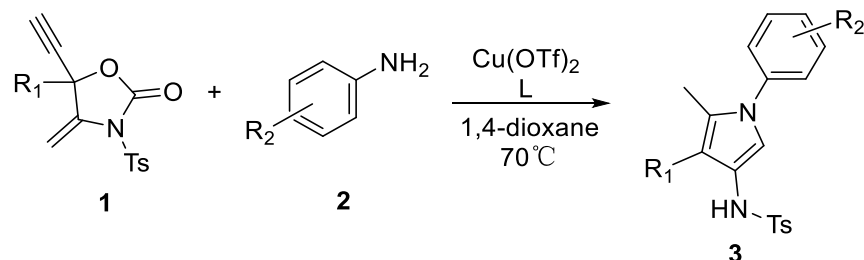
The title compound was prepared through above general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:5) furnished **1s** in 67% yield.

¹H NMR (300 MHz, CDCl₃) δ 8.00-7.88 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.65 (d, *J* = 3.2 Hz, 1H), 4.76 (d, *J* = 3.2 Hz, 1H), 2.73 (s, 1H), 2.45 (s, 3H), 1.91 (ddt, *J* = 24.7, 14.4, 7.2 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 149.7, 146.5, 140.2, 134.0, 130.0, 128.2, 93.1, 80.0, 79.2, 76.6, 35.1, 21.8, 7.3.

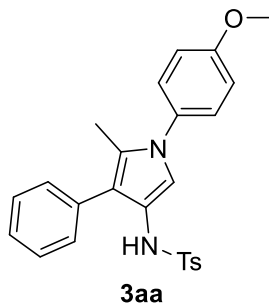
HRMS (ESI) *m/z* calculated for C₁₅H₁₆NO₄S [M+H]⁺ : 306.0795, found: 306.0791.

General procedure for the synthesis of 3-aminopyrroles (3aa-3as)



General procedure A: To a flame dried tube was cooled to rt. and charged with Cu(OTf)₂ (4.0 mg, 0.01mmol, 5 mol%) and L1 (4.0 mg, 0.01mmol, 5 mol%). The tube was added freshly distilled 1,4-dioxane (1.0 mL), and stirred at rt. for 20 min. The compound **1** (0.2 mmol, 1 equiv.), amine **2** (0.3 mmol, 1.5 equiv.) were added and the mixtures were then heated to 70 °C for 5 h. After completion of the reaction, the reaction mixture was concentrated and purified by flash column chromatography using (1:3 ethyl acetate/hexanes) to give the desired product **3aa-3as**.

N-(1-(4-methoxyphenyl)-5-methyl-4-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3aa**)



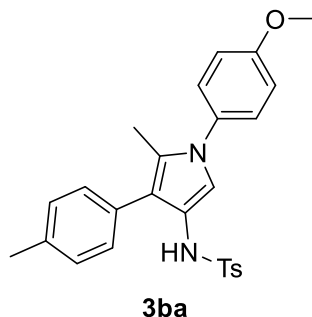
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3aa** (77.7 mg, 90% yield) as colorless solid.

¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.26-7.19 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.90-6.82 (m, 3H), 6.14 (s, 1H), 3.85 (s, 3H), 2.38 (s, 3H), 2.00 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 158.8, 143.3, 136.4, 133.6, 132.7, 129.7, 129.4, 128.6, 127.4, 127.3, 126.5, 125.2, 118.1, 115.8, 114.4, 55.7, 21.7, 11.5.

HRMS (ESI) m/z calculated for $C_{25}H_{25}N_2O_3S$ $[M+H]^+$: 433.1580, found: 433.1582.

N-(1-(4-methoxyphenyl)-5-methyl-4-(*p*-tolyl)-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3ba**)



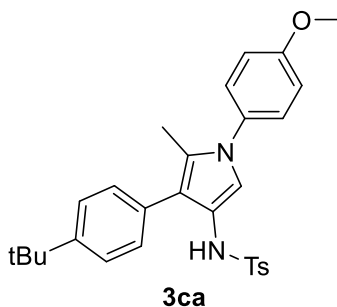
The title compound was prepared from **1b** (73.4 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ba** (74 mg, 83% yield) as colorless solid.

¹H NMR (300 MHz, $CDCl_3$) δ 7.59-7.49 (m, 2H), 7.24-7.18 (m, 2H), 7.14 (d, $J = 7.9$ Hz, 2H), 7.08 (d, $J = 7.6$ Hz, 2H), 6.98-6.91 (m, 2H), 6.84 (s, 1H), 6.81-6.71 (m, 2H), 6.13 (s, 1H), 3.84 (s, 3H), 2.37 (d, $J = 11.4$ Hz, 6H), 1.99 (s, 3H).

¹³C NMR (75 MHz, $CDCl_3$) δ 158.7, 143.3, 136.4, 136.0, 132.8, 130.4, 129.5, 129.4, 129.3, 127.4, 127.2, 125.1, 118.2, 117.8, 115.4, 114.3, 55.6, 21.7, 21.3, 11.5.

HRMS (ESI) m/z calculated for $C_{26}H_{26}N_2O_3S$ $[M+H]^+$: 447.1713, found: 447.1715.

N-(4-(4-(*tert*-butyl)phenyl)-1-(4-methoxyphenyl)-5-methyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3ca**)



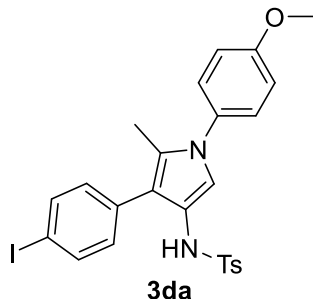
The title compound was prepared from **1c** (81.8 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ca** (83.0mg, 85% yield) as colorless solid.

¹H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, $J = 7.9$ Hz, 2H), 7.31-7.08 (m, 6H), 6.95 (d, $J = 8.3$ Hz, 2H), 6.89-6.71 (m, 3H), 6.19 (s, 1H), 3.84 (s, 3H), 2.38 (s, 3H), 2.00 (s, 3H), 1.34 (s, 9H).

¹³C NMR (75 MHz, $CDCl_3$) δ 158.7, 149.1, 143.2, 136.3, 132.8, 130.4, 129.3, 129.2, 127.3, 127.2, 125.4, 125.1, 118.2, 117.7, 115.5, 114.3, 55.6, 34.5, 31.5, 21.7, 11.5.

HRMS (ESI) m/z calculated for $C_{29}H_{33}N_2O_3S$ $[M+H]^+$:489.2206, found: 489.2208.

N-(4-(4-iodophenyl)-1-(4-methoxyphenyl)-5-methyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide
(3da)



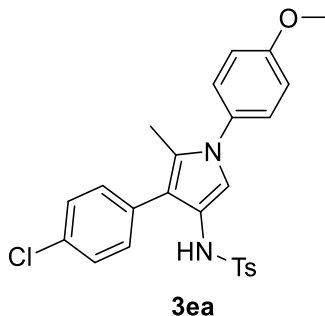
The title compound was prepared from **1d** (95.8 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3da** (93.7mg, 84% yield) as colorless solid.

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.81 (s, 1H), 6.64 (d, *J* = 8.3 Hz, 2H), 6.16 (s, 1H), 3.85 (s, 3H), 2.41 (s, 3H), 1.98 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 158.9, 143.5, 137.5, 136.4, 133.3, 132.5, 131.5, 129.4, 127.3, 127.3, 125.4, 117.8, 117.6, 117.4, 114.4, 91.7, 55.7, 21.7, 11.5.

HRMS (ESI) *m/z* calculated for C₂₅H₂₄IN₂O₃S [M+H]⁺: 559.0547, found: 559.0548.

N-(4-(4-chlorophenyl)-1-(4-methoxyphenyl)-5-methyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide
(3ea)



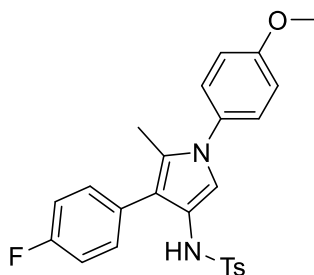
The title compound was prepared from **1e** (77.4 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ea** (76.4mg, 82% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.15 (dd, *J* = 23.9, 8.0 Hz, 6H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 6.33 (s, 1H), 3.84 (s, 3H), 2.39 (s, 3H), 1.98 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 158.9, 143.4, 136.5, 132.5, 132.2, 132.1, 130.9, 129.3, 128.5, 127.3, 127.2, 125.4, 117.8, 117.5, 117.4, 114.3, 55.6, 21.6, 11.5.

HRMS (ESI) m/z calculated for $C_{25}H_{24}ClN_2O_3S$ $[M+H]^+$: 467.1191, found: 467.1193.

***N*-(4-(4-fluorophenyl)-1-(4-methoxyphenyl)-5-methyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3fa)**



3fa

The title compound was prepared from **1f** (74.2 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3fa** (72.0mg, 80% yield) as colorless solid.

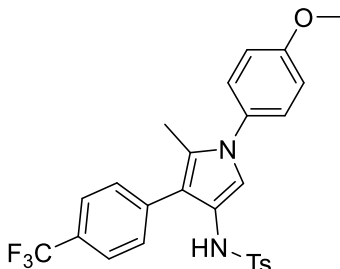
¹H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, $J = 8.0$ Hz, 2H), 7.16 (dd, $J = 18.6, 8.4$ Hz, 4H), 6.99-6.81 (m, 6H), 6.78 (s, 1H), 6.25 (s, 1H), 3.84 (s, 3H), 2.39 (s, 3H), 1.98 (s, 3H).

¹³C NMR (75 MHz, $CDCl_3$) δ 161.6 (d, $J = 246.1$ Hz), 158.8, 143.4, 136.5, 132.6, 131.2 (d, $J = 7.8$ Hz), 129.5, 129.4, 127.4, 127.2, 125.3, 117.7 (d, $J = 5.9$ Hz), 116.7, 115.3 (d, $J = 21.3$ Hz), 114.3, 55.7, 21.6, 11.4.

¹⁹F NMR (282 MHz, $CDCl_3$) δ -116.28.

HRMS (ESI) m/z calculated for $C_{25}H_{24}FN_2O_3S$ $[M+H]^+$: 451.1486, found: 451.1484.

***N*-(1-(4-methoxyphenyl)-5-methyl-4-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3ga)**



3ga

The title compound was prepared from **1g** (84.2 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ga** (75.0mg, 75% yield) as colorless solid.

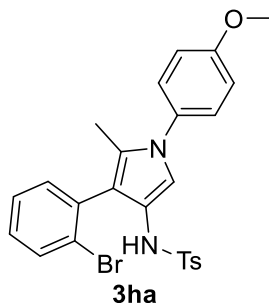
¹H NMR (300 MHz, $CDCl_3$) δ 7.52-7.43 (m, 4H), 7.24-7.18 (m, 2H), 7.05 (dd, $J = 8.2, 2.7$ Hz, 4H), 7.01-6.93 (m, 2H), 6.82 (s, 1H), 6.41 (s, 1H), 3.85 (s, 3H), 2.36 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 159.0, 143.4, 137.7, 136.3, 132.3, 129.7, 129.3, 127.9 (q, $J = 32.3$ Hz), 127.3, 127.3, 125.9, 125.2 (q, $J = 3.8$ Hz), 124.45 (q, $J = 271.9$ Hz), 118.6, 118.1, 117.2, 114.4, 55.6, 21.5, 11.6.

^{19}F NMR (282 MHz, CDCl_3) δ -62.26.

HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 501.1454, found: 501.1456.

N-(4-(2-bromophenyl)-1-(4-methoxyphenyl)-5-methyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3ha**)



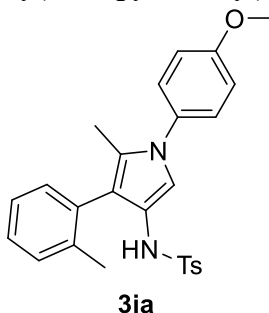
The title compound was prepared from **1h** (86.2 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ha** (84.7mg, 83% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.59-7.50 (m, 1H), 7.48-7.40 (m, 2H), 7.29-7.19 (m, 2H), 7.15-7.03 (m, 4H), 7.00-6.87 (m, 3H), 6.65-6.57 (m, 1H), 6.07 (s, 1H), 3.85 (s, 3H), 2.37 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.8, 143.1, 136.5, 134.6, 132.9, 132.7, 132.6, 129.4, 128.6, 127.2, 127.1, 125.9, 124.9, 118.1, 117.9, 117.1, 114.3, 76.7, 55.7, 21.6, 11.6.

HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{24}\text{BrN}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 511.0686, found: 511.0687.

N-(1-(4-methoxyphenyl)-5-methyl-4-(*o*-tolyl)-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3ia**)



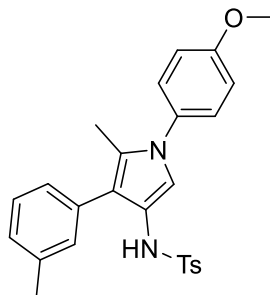
The title compound was prepared from **1i** (73.4 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ia** (77.6mg, 87% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.55-7.44 (m, 2H), 7.24-7.13 (m, 6H), 7.06 (td, $J = 6.8, 6.2, 2.5$ Hz, 1H), 6.99-6.90 (m, 3H), 6.66-6.59 (m, 1H), 5.90 (s, 1H), 3.85 (s, 3H), 2.40 (s, 3H), 1.84 (d, $J = 10.9$ Hz, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.6, 143.3, 138.0, 136.3, 132.9, 132.4, 131.2, 130.2, 129.4, 127.6, 127.4, 127.1, 125.8, 125.0, 118.7, 116.6, 114.3, 114.2, 55.6, 21.6, 19.6, 11.5.

HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 447.1737, found: 447.1735.

N-(1-(4-methoxyphenyl)-5-methyl-4-(*m*-tolyl)-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3ja**)



3ja

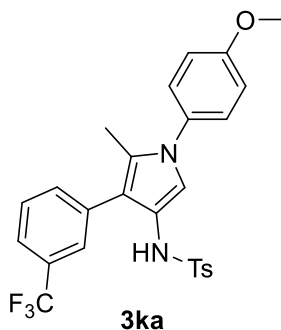
The title compound was prepared from **1j** (73.4 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ja** (80.3mg, 90% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.53 (d, $J = 7.9$ Hz, 2H), 7.18 (dd, $J = 20.5, 8.3$ Hz, 5H), 7.07-6.85 (m, 4H), 6.70 (d, $J = 7.5$ Hz, 1H), 6.58 (s, 1H), 6.20 (s, 1H), 3.84 (s, 3H), 2.33 (d, $J = 32.9$ Hz, 6H), 1.99 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.7, 143.2, 138.0, 136.4, 133.4, 132.7, 130.2, 129.4, 128.4, 127.3, 127.2, 127.2, 126.7, 125.1, 118.1, 118.0, 115.6, 114.3, 55.6, 21.6, 21.5, 11.5.

HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 447.1737, found: 447.1735.

N-(1-(4-methoxyphenyl)-5-methyl-4-(3-(trifluoromethyl)phenyl)-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3ka**)



3ka

The title compound was prepared from **1k** (84.2 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ka** (80.1mg, 80% yield) as colorless solid.

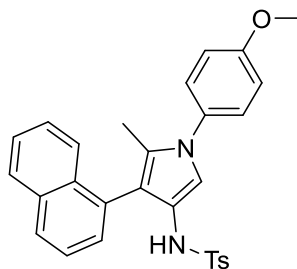
^1H NMR (300 MHz, CDCl_3) δ 7.54-7.35 (m, 4H), 7.25-7.16 (m, 3H), 7.14-7.04 (m, 3H), 7.02-6.92 (m, 2H), 6.87 (s, 1H), 6.23 (s, 1H), 3.85 (s, 3H), 2.36 (s, 3H), 2.00 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 159.0, 143.5, 136.3, 134.6, 133.0, 132.5, 130.6 (q, $J = 32.1$ Hz), 129.4, 128.9, 127.3, 127.3, 126.1 (q, $J = 3.9$ Hz), 125.8, 124.19 (q, $J = 272.5$ Hz), 123.0 (q, $J = 3.8$ Hz), 117.8, 117.6, 117.4, 114.4, 55.7, 21.5, 11.5.

^{19}F NMR (282 MHz, CDCl_3) δ -62.39.

HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 501.1454, found: 501.1456

N-(1-(4-methoxyphenyl)-5-methyl-4-(naphthalen-1-yl)-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3la)



3la

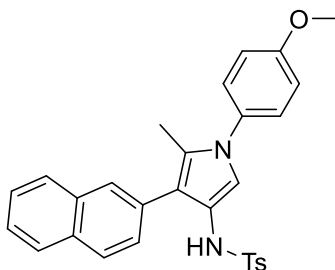
The title compound was prepared from **11** (80.6 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3la** (89.7mg, 93% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.82 (dd, $J = 23.5, 8.2$ Hz, 2H), 7.51-7.27 (m, 7H), 7.05 (s, 1H), 7.03-6.90 (m, 4H), 6.85 (d, $J = 7.0$ Hz, 1H), 5.91 (s, 1H), 3.87 (s, 3H), 2.32 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.8, 143.0, 136.0, 133.8, 132.9, 132.5, 130.8, 129.2, 128.5, 128.4, 127.6, 127.2, 127.2, 126.4, 126.1, 125.8, 125.7, 125.5, 119.2, 115.7, 115.6, 114.4, 55.7, 21.7, 11.6.

HRMS (ESI) m/z calculated for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 483.1737, found: 483.1735.

N-(1-(4-methoxyphenyl)-5-methyl-4-(naphthalen-2-yl)-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3ma)



3ma

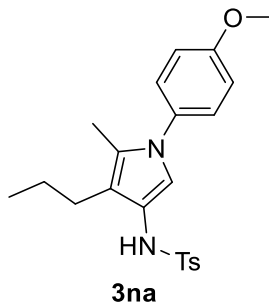
The title compound was prepared from **1m** (80.6 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ma** (86.8mg, 90% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.93-7.62 (m, 3H), 7.46 (m, $J = 7.6$ Hz, 4H), 7.23 (m, 2H), 7.16-6.76 (m, 6H), 6.24 (s, 1H), 3.85 (s, 3H), 2.29 (s, 3H), 2.05 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.9, 143.3, 136.5, 133.6, 132.7, 132.0, 131.2, 129.3, 128.1, 128.0, 127.8, 127.7, 127.3, 127.3, 126.2, 125.8, 125.5, 118.3, 118.1, 116.7, 114.4, 55.7, 21.6, 11.6.

HRMS (ESI) m/z calculated for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 483.1737, found: 483.1735.

N-(1-(4-methoxyphenyl)-5-methyl-4-propyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3na**)



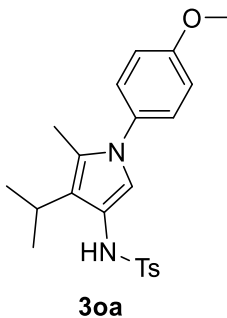
The title compound was prepared from **1n** (63.8 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3na** (45.4mg, 57% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.76-7.65 (m, 2H), 7.23 (d, $J = 0.9$ Hz, 1H), 7.16-7.05 (m, 2H), 6.97-6.87 (m, 2H), 6.45 (s, 1H), 5.88 (s, 1H), 3.84 (s, 3H), 2.40 (s, 3H), 2.23-2.08 (m, 2H), 1.98 (s, 3H), 1.33-1.23 (m, 2H), 0.82 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.6, 137.1, 133.0, 129.5, 127.6, 127.2, 124.8, 118.1, 117.3, 116.5, 114.2, 55.7, 25.6, 24.1, 21.7, 14.2, 10.9.

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 399.1737, found: 399.1738.

N-(4-isopropyl-1-(4-methoxyphenyl)-5-methyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3oa**)



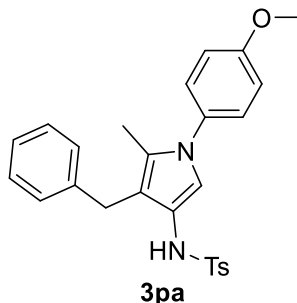
The title compound was prepared from **1o** (63.8 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3oa** (50.2mg, 63% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.85-7.61 (m, 2H), 7.23 (s, 1H), 7.14-7.05 (m, 2H), 6.96-6.84 (m, 2H), 6.43 (s, 1H), 5.92 (s, 1H), 3.83 (s, 3H), 2.75 (p, $J = 7.1$ Hz, 1H), 2.40 (s, 3H), 2.02 (s, 3H), 1.07 (d, $J = 7.1$ Hz, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.6, 143.3, 137.1, 132.8, 129.4, 127.6, 127.5, 123.6, 122.6, 117.3, 116.8, 114.2, 55.6, 24.6, 22.6, 21.6, 11.5.

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 399.1737, found: 399.1735.

N-(4-benzyl-1-(4-methoxyphenyl)-5-methyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3pa**)



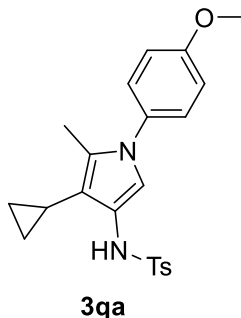
The title compound was prepared from **1p** (73.4 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3pa** (56.2mg, 63% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.77-7.55 (m, 2H), 7.07 (dd, J = 59.0, 26.8 Hz, 10H), 6.55 (s, 1H), 5.77 (s, 1H), 3.82 (s, 3H), 3.50 (s, 2H), 2.40 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.6, 143.4, 140.9, 137.0, 132.9, 129.5, 128.6, 128.1, 127.5, 127.2, 125.9, 125.4, 118.5, 117.1, 115.3, 114.2, 55.6, 29.4, 21.7, 11.0.

HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 447.1737, found: 447.1738.

N-(4-cyclopropyl-1-(4-methoxyphenyl)-5-methyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3qa**)



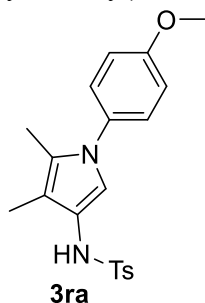
The title compound was prepared from **1q** (63.4 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3qa** (49.9mg, 62% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.78-7.66 (m, 2H), 7.22 (d, 1H), 7.16-7.07 (m, 2H), 6.97-6.88 (m, 2H), 6.63 (s, 1H), 6.15 (s, 1H), 3.84 (s, 3H), 2.40 (s, 3H), 2.02 (s, 3H), 1.01 (td, J = 7.9, 4.1 Hz, 1H), 0.73-0.62 (m, 2H), 0.23 (dt, J = 5.4, 2.9 Hz, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.6, 143.4, 136.8, 133.0, 129.5, 127.5, 127.2, 126.7, 120.3, 115.3, 114.2, 113.7, 55.6, 21.7, 11.0, 4.9, 4.0.

HRMS (ESI) m/z calculated for $C_{22}H_{25}N_2O_3S$ $[M+H]^+$: 397.1580, found: 397.1584.

***N*-(1-(4-methoxyphenyl)-4,5-dimethyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3ra)**



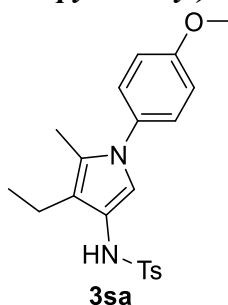
The title compound was prepared from **1r** (58.2 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ra** (49.6mg, 67% yield) as colorless solid.

1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.3 Hz, 2H), 7.23 (s, 1H), 7.08 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 8.9 Hz, 2H), 6.43 (s, 1H), 6.00 (d, J = 13.5 Hz, 1H), 3.83 (s, 3H), 2.40 (s, 3H), 1.97 (s, 3H), 1.73 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 143.3, 137.1, 133.0, 129.4, 127.6, 127.1, 124.8, 118.5, 117.0, 114.2, 113.0, 55.6, 21.6, 10.8, 8.3.

HRMS (ESI) m/z calculated for $C_{20}H_{23}N_2O_3S$ $[M+H]^+$: 371.1424, found: 371.1426.

***N*-(4-ethyl-1-(4-methoxyphenyl)-5-methyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3sa)**



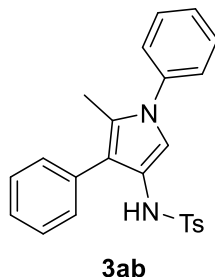
The title compound was prepared from **1s** (61.0 mg, 0.2 mmol, 1 eq.) and **2a** (36.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3sa** (49.9mg, 65% yield) as colorless solid.

1H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.24-7.21 (m, 1H), 7.09 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 6.41 (s, 1H), 6.11 (s, 1H), 3.83 (s, 3H), 2.39 (s, 3H), 2.24 (q, J = 7.6 Hz, 2H), 1.99 (s, 3H), 0.93 (t, J = 7.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5, 143.3, 137.1, 133.0, 129.4, 127.6, 127.2, 124.4, 119.2, 117.9, 116.5, 114.2, 60.5, 55.6, 21.6, 21.2, 16.6, 15.4, 14.3, 10.7.

HRMS (ESI) m/z calculated for $C_{21}H_{25}N_2O_3S$ $[M+H]^+$: 385.1580, found: 385.1582.

4-methyl-N-(5-methyl-1,4-diphenyl-1H-pyrrol-3-yl)benzenesulfonamide (3ab)



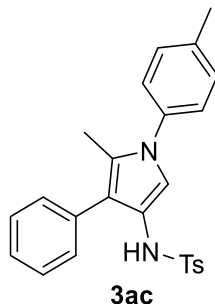
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2b** (27.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ab** (64.3 mg, 80% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.56-7.50 (m, 2H), 7.45 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.40-7.35 (m, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 7.30-7.26 (m, 2H), 7.24-7.21 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.94-6.84 (m, 3H), 6.15 (s, 1H), 2.39 (s, 3H), 2.04 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.3, 139.7, 136.3, 133.4, 129.6, 129.4, 129.4, 129.3, 128.6, 127.4, 127.3, 126.5, 125.9, 124.9, 118.6, 118.5, 115.5, 21.7, 11.7.

HRMS (ESI) *m/z* calculated for C₂₄H₂₃N₂O₂S [M+H]⁺: 403.1475, found: 403.1476.

4-methyl-N-(5-methyl-4-phenyl-1-(*p*-tolyl)-1H-pyrrol-3-yl)benzenesulfonamide (3ac)



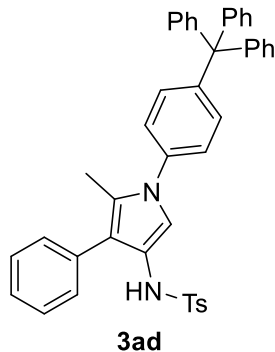
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2c** (32.1 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE=1:3) furnished **3ac** (71.6 mg, 86% yield) as colorless solid.

¹H NMR (400 MHz, CDCl₃) δ 7.57-7.49 (m, 2H), 7.28 (d, *J* = 6.7 Hz, 2H), 7.24 (s, 2H), 7.16 (dd, *J* = 19.8, 8.2 Hz, 4H), 6.90-6.83 (m, 3H), 6.11 (s, 1H), 2.40 (d, *J* = 8.3 Hz, 6H), 2.02 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.3, 137.3, 137.3, 136.4, 133.5, 129.9, 129.7, 129.4, 128.6, 127.4, 126.5, 125.8, 125.0, 118.3, 118.3, 115.6, 21.7, 21.2, 11.6.

HRMS (ESI) *m/z* calculated for C₂₅H₂₄N₂O₂S [M+H]⁺: 417.1631, found: 417.1632.

4-methyl-N-(5-methyl-4-phenyl-1-(4-tritylphenyl)-1H-pyrrol-3-yl)benzenesulfonamide (3ad)



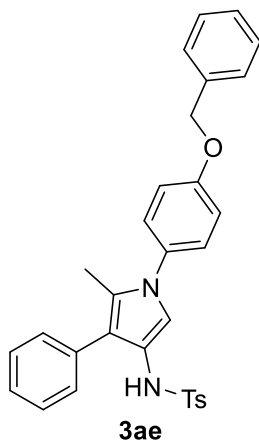
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2d** (100.5 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ad** (109.5 mg, 85% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.30-7.13 (m, 23H), 6.95 (s, 1H), 6.83 (dd, *J* = 7.8, 1.8 Hz, 2H), 6.08 (s, 1H), 2.38 (s, 3H), 2.06 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 146.6, 146.0, 143.4, 137.5, 136.3, 133.4, 132.0, 131.2, 129.7, 129.4, 128.6, 127.8, 127.4, 126.6, 126.3, 124.9, 124.6, 118.5, 118.5, 115.4, 64.8, 21.7, 11.9.

HRMS (ESI) *m/z* calculated for C₄₃H₃₆N₂O₂S [M+H]⁺: 644.2497, found: 644.2499.

N-(1-(4-(benzyloxy)phenyl)-5-methyl-4-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3ae)



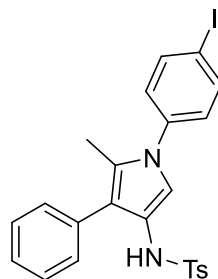
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2e** (59.7 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ae** (80.3 mg, 79% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.54-7.49 (m, 2H), 7.49-7.36 (m, 5H), 7.22 (ddd, *J* = 8.9, 4.5, 2.6 Hz, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.07-6.99 (m, 2H), 6.90-6.82 (m, 3H), 6.11 (s, 1H), 5.10 (s, 2H), 2.38 (s, 3H), 2.00 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 158.0, 143.3, 136.7, 136.4, 133.5, 133.0, 129.6, 129.4, 128.8, 128.6, 128.3, 127.6, 127.4, 127.3, 126.4, 125.2, 118.1, 115.8, 115.3, 70.4, 21.7, 11.5.

HRMS (ESI) *m/z* calculated for C₃₁H₂₉N₂O₂S [M+H]⁺: 509.1893, found: 509.1895.

***N*-(1-(4-iodophenyl)-5-methyl-4-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3af)**



3af

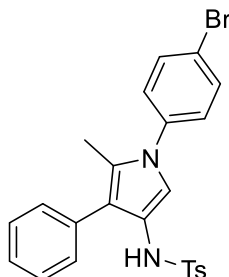
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2f** (65.7 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3af** (85.5 mg, 81% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.81-7.73 (m, 2H), 7.55-7.48 (m, 2H), 7.25 (d, *J* = 2.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.09-7.02 (m, 2H), 6.87 (d, *J* = 2.3 Hz, 2H), 6.84 (t, *J* = 1.6 Hz, 1H), 6.17 (s, 1H), 2.38 (s, 3H), 2.03 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.4, 139.4, 138.4, 136.2, 133.0, 129.6, 129.4, 128.6, 127.5, 127.3, 126.6, 124.7, 119.0, 118.96, 115.0, 92.1, 21.6, 11.6.

HRMS (ESI) *m/z* calculated for C₂₄H₂₁IN₂O₂S [M+H]⁺: 529.0441, found: 529.0443.

***N*-(1-(4-bromophenyl)-5-methyl-4-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3ag)**



3ag

The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2g** (51.3 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished

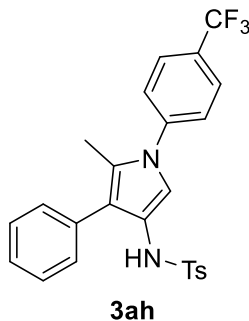
3ag (74.9 mg, 78% yield) as colorless solid.

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.63-7.47 (m, 4H), 7.25 (q, $J = 3.0, 2.5$ Hz, 2H), 7.22-7.10 (m, 4H), 6.92-6.81 (m, 3H), 6.15 (s, 1H), 2.39 (s, 3H), 2.03 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 143.4, 138.7, 136.2, 133.1, 132.4, 129.6, 129.4, 128.6, 127.3, 127.3, 126.6, 124.8, 121.0, 118.9, 118.9, 115.1, 21.6, 11.6.

HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{22}\text{BrN}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 481.0580, found: 481.0582.

4-methyl-N-(5-methyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrrol-3-yl)benzenesulfonamide (3ah)



The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2h** (48.3 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ah** (71.5mg, 76% yield) as colorless solid.

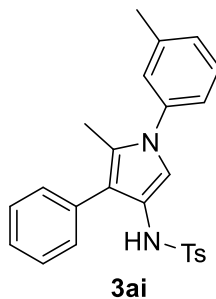
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.3$ Hz, 2H), 7.57-7.51 (m, 2H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 7.4$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 6.94 (s, 1H), 6.87 (dd, $J = 8.0, 1.6$ Hz, 2H), 6.20 (s, 1H), 2.39 (s, 3H), 2.07 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.5, 142.7, 136.3, 132.9, 129.7, 129.5, 129.2 (q, $J = 33.0$ Hz), 128.7, 127.3, 126.8, 126.6 (q, $J = 3.7$ Hz), 125.7, 124.8, 124.0 (q, $J = 272.0$ Hz), 119.6, 119.5, 114.9, 21.7, 11.8.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.33.

HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 471.1349, found: 471.1346.

4-methyl-N-(5-methyl-4-phenyl-1-(m-tolyl)-1H-pyrrol-3-yl)benzenesulfonamide (3ai)



The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2i** (32.1 mg, 0.3 mmol, 1.5 eq.)

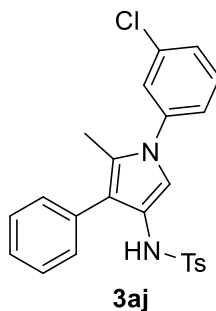
via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ai** (69.1 mg, 83% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.52 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.24 (s, 2H), 7.13 (q, *J* = 9.8, 9.1 Hz, 5H), 6.95-6.77 (m, 3H), 6.13 (s, 1H), 2.40 (d, *J* = 8.6 Hz, 6H), 2.04 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.3, 139.6, 139.3, 136.3, 133.4, 129.6, 129.4, 129.0, 128.5, 128.1, 127.3, 126.5, 126.4, 124.8, 122.9, 118.4, 118.3, 115.5, 21.6, 21.4, 11.7.

HRMS (ESI) *m/z* calculated for C₂₅H₂₅N₂O₂S [M+H]⁺: 417.1631, found: 417.1633.

N-(1-(3-chlorophenyl)-5-methyl-4-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3aj**)



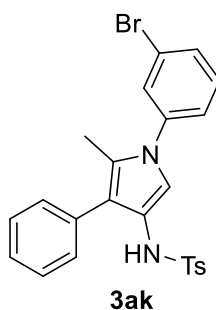
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2j** (38.1 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3aj** (74.1 mg, 85% yield) as colorless solid.

¹H NMR (400 MHz, CDCl₃) δ 7.55-7.49 (m, 2H), 7.42-7.28 (m, 4H), 7.21 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.90 (s, 1H), 6.88-6.82 (m, 2H), 6.13 (s, 1H), 2.40 (s, 3H), 2.05 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.4, 140.8, 136.2, 134.8, 133.0, 130.3, 129.6, 129.4, 128.6, 127.5, 127.3, 126.7, 126.0, 124.8, 124.0, 119.1, 119.0, 115.1, 21.7, 11.7.

HRMS (ESI) *m/z* calculated for C₂₄H₂₂ClN₂O₂S [M+H]⁺: 437.1085, found: 437.1087.

N-(1-(3-bromophenyl)-5-methyl-4-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3ak**)

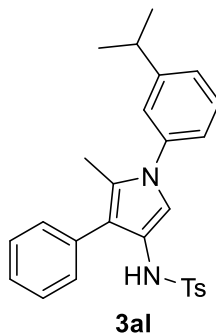


The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2k** (51.0 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ak** (83.5 mg, 87% yield) as colorless solid.

¹H NMR (400 MHz, CDCl₃) δ 7.56-7.45 (m, 4H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.90 (s, 1H), 6.85 (dd, *J* = 7.9, 1.7 Hz, 2H), 6.10 (s, 1H), 2.40 (s, 3H), 2.05 (s, 3H).
¹³C NMR (101 MHz, CDCl₃) δ 143.5, 140.9, 136.2, 133.0, 130.6, 130.4, 129.7, 129.5, 128.9, 128.7, 127.3, 126.7, 124.9, 124.5, 122.7, 119.2, 118.9, 115.1, 21.7, 11.7.

HRMS (ESI) *m/z* calculated for C₂₄H₂₂BrN₂O₂S [M+H]⁺: 481.0580, found: 481.0581.

***N*-(1-(3-isopropylphenyl)-5-methyl-4-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3al)**



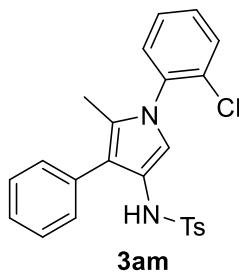
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2l** (40.5 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3al** (71.1 mg, 80% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.28 (s, 1H), 7.23 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.18-7.08 (m, 4H), 6.93-6.85 (m, 3H), 6.12 (s, 1H), 2.97 (p, *J* = 6.9 Hz, 1H), 2.39 (s, 3H), 2.05 (s, 3H), 1.29 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 150.4, 143.3, 139.7, 136.3, 133.5, 129.7, 129.4, 129.1, 128.6, 127.4, 126.5, 125.5, 124.9, 124.0, 123.2, 118.4, 118.3, 115.6, 34.1, 24.0, 21.6, 11.7.

HRMS (ESI) *m/z* calculated for C₂₇H₂₉N₂O₂S [M+H]⁺: 445.1944, found: 445.1946.

***N*-(1-(2-chlorophenyl)-5-methyl-4-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3am)**



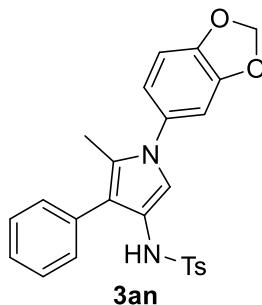
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2m** (38.1 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3am** (68.0 mg, 78% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.58-7.48 (m, 3H), 7.38 (q, *J* = 4.0 Hz, 3H), 7.23 (s, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 6.82-6.73 (m, 2H), 6.12 (s, 1H), 2.39 (s, 3H), 1.88 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 143.4, 137.3, 135.9, 133.2, 132.8, 130.4, 129.9, 129.9, 129.6, 129.3, 128.6, 127.7, 127.4, 126.5, 126.1, 118.6, 117.6, 115.6, 21.7, 10.8.

HRMS (ESI) *m/z* calculated for C₂₄H₂₂ClN₂O₂S [M+H]⁺: 437.1085, found: 437.1087.

N-(1-(benzo[d][1,3]dioxol-4-yl)-5-methyl-4-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3an**)



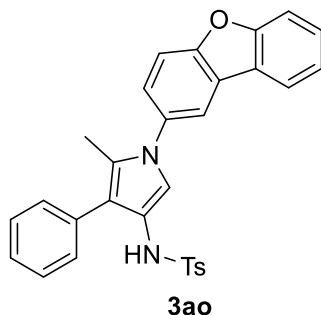
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2n** (41.1 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3an** (64.2 mg, 72% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.26-7.20 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.89-6.82 (m, 4H), 6.76 (d, *J* = 7.8 Hz, 2H), 6.09 (s, 1H), 6.04 (s, 2H), 2.39 (s, 3H), 2.00 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.0, 147.0, 143.3, 136.3, 133.7, 133.4, 129.6, 129.4, 128.6, 127.3, 126.4, 125.2, 119.5, 118.1, 118.1, 115.7, 108.2, 107.5, 101.9, 21.6, 11.4.

HRMS (ESI) *m/z* calculated for C₂₅H₂₃N₂O₄S [M+H]⁺: 447.1373, found: 447.1375.

N-(1-(dibenzo[*b,d*]furan-2-yl)-5-methyl-4-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (**3ao**)



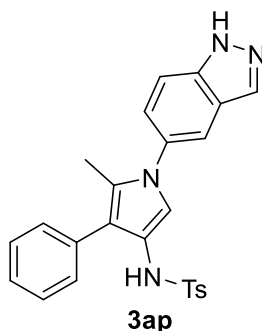
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2o** (54.9 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ao** (44.3 mg, 45% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 8.00-7.94 (m, 1H), 7.88 (d, *J* = 2.2 Hz, 1H), 7.64-7.51 (m, 5H), 7.43-7.36 (m, 2H), 7.29 (s, 1H), 7.26 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.99 (s, 1H), 6.94-6.86 (m, 2H), 6.15 (s, 1H), 2.40 (s, 3H), 2.06 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 157.1, 155.0, 143.3, 136.4, 135.0, 133.5, 129.7, 129.5, 128.6, 128.1, 127.4, 126.5, 125.5, 125.4, 125.1, 123.8, 123.3, 121.0, 118.5, 118.4, 118.3, 116.2, 112.1, 21.7, 11.6.

HRMS (ESI) *m/z* calculated for C₃₀H₂₅N₂O₃S [M+H]⁺: 493.1580, found: 493.1582.

***N*-(1-(1*H*-indazol-5-yl)-5-methyl-4-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3ap)**



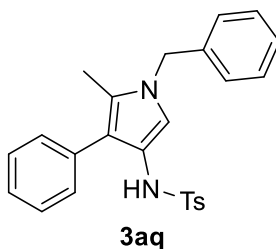
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2p** (40.0 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ap** (44.2 mg, 50% yield) as colorless solid.

¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.67 (d, *J* = 2.1 Hz, 1H), 7.56 (t, *J* = 8.5 Hz, 3H), 7.35-7.27 (m, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.94 (s, 1H), 6.93-6.87 (m, 2H), 6.45 (s, 1H), 5.30 (s, 1H), 2.39 (s, 3H), 2.03 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.4, 136.5, 133.6, 133.4, 129.7, 129.5, 128.6, 127.4, 126.5, 126.0, 125.5, 118.3, 118.3, 118.2, 116.3, 110.5, 21.7, 11.6.

HRMS (ESI) *m/z* calculated for C₂₅H₂₃N₄O₂S [M+H]⁺: 443.1536, found: 443.1538.

***N*-(1-benzyl-5-methyl-4-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3aq)**



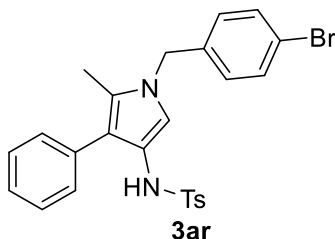
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2q** (32.0 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3aq** (34.9 mg, 42% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.32-7.25 (m, 5H), 7.09 (dd, *J* = 5.1, 1.9 Hz, 3H), 6.96-6.83 (m, 6H), 6.05 (s, 1H), 4.62 (d, *J* = 16.6 Hz, 1H), 4.32 (d, *J* = 16.6 Hz, 1H), 2.30 (s, 3H), 2.08 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 142.3, 138.4, 137.6, 134.4, 129.9, 129.0, 128.7, 127.8, 127.4, 127.0, 127.0, 126.6, 125.5, 120.4, 120.0, 119.1, 47.8, 21.6, 11.2.

HRMS (ESI) *m/z* calculated for C₂₅H₂₅N₂O₂S [M+H]⁺: 417.1631, found: 417.1632.

***N*-(1-(4-bromobenzyl)-5-methyl-4-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3ar)**



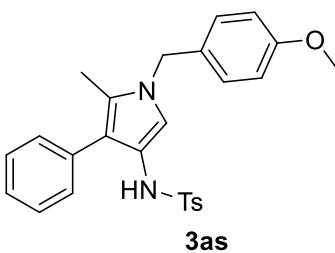
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2r** (55.5 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ar** (30.2 mg, 34% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.42-7.35 (m, 2H), 7.31-7.25 (m, 2H), 7.15-7.05 (m, 3H), 6.96-6.84 (m, 4H), 6.76 (dd, *J* = 8.8, 2.2 Hz, 2H), 6.34 (s, 1H), 4.71-4.32 (m, 2H), 2.31 (s, 3H), 2.00 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 142.5, 137.5, 137.1, 134.0, 131.7, 129.8, 129.1, 128.5, 128.0, 127.0, 126.8, 125.7, 121.2, 120.7, 120.4, 119.0, 47.6, 21.6, 11.2.

HRMS (ESI) *m/z* calculated for C₂₅H₂₄BrN₂O₂S [M+H]⁺: 495.0736, found: 495.0738.

***N*-(1-(4-methoxybenzyl)-5-methyl-4-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3as)**



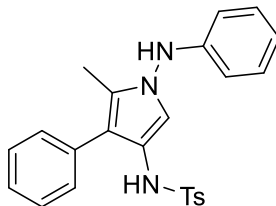
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2s** (41.0 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3as** (44.5 mg, 45% yield) as colorless solid.

¹H NMR (300 MHz, CDCl₃) δ 7.34-7.22 (m, 2H), 7.19-7.04 (m, 3H), 6.96 (dd, *J* = 7.2, 2.4 Hz, 2H), 6.90-6.77 (m, 6H), 6.09 (s, 1H), 4.58 (d, *J* = 15.6, 1H), 4.26 (d, *J* = 15.6 Hz, 1H), 3.80 (s, 3H), 2.31 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 158.9, 142.3, 137.7, 134.5, 130.5, 129.9, 129.0, 128.1, 127.9, 127.0, 126.5, 125.5, 120.4, 119.9, 119.1, 114.0, 55.5, 47.4, 21.6, 11.2.

HRMS (ESI) m/z calculated for $\text{C}_{26}\text{H}_{27}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 447.1737, found: 447.1734.

4-methyl-N-(5-methyl-4-phenyl-1-(phenylamino)-1H-pyrrol-3-yl)benzenesulfonamide (3at)



3at

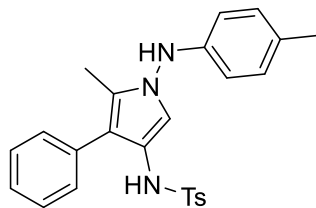
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2t** (32.4 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3at** (50.0 mg, 60% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.59-7.41 (m, 4H), 7.41-7.35 (m, 1H), 7.34-7.21 (m, 5H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.97-6.79 (m, 3H), 6.10 (s, 1H), 2.39 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 143.2, 139.8, 136.4, 133.4, 129.7, 129.4, 129.3, 128.6, 127.4, 127.4, 126.6, 126.0, 125.0, 118.6, 118.5, 115.5, 21.7, 11.7.

HRMS (ESI) m/z calculated for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 418.1584, found: 418.1586.

4-methyl-N-(5-methyl-4-phenyl-1-(p-tolylamino)-1H-pyrrol-3-yl)benzenesulfonamide (3au)



3au

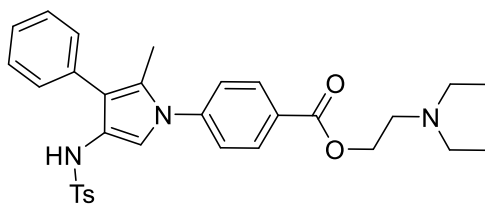
The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2u** (36.6 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3au** (44.8 mg, 52% yield) as colorless solid.

^1H NMR (300 MHz, CDCl_3) δ 7.52 (d, $J = 8.3$ Hz, 2H), 7.27-7.12 (m, 9H), 6.92-6.80 (m, 3H), 6.08 (s, 1H), 2.40 (d, $J = 6.2$ Hz, 6H), 2.02 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 143.4, 137.3, 136.4, 133.5, 129.9, 129.7, 129.4, 128.6, 127.4, 126.5, 125.8, 125.0, 118.3, 115.6, 21.7, 21.2, 11.6.

HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{26}\text{N}_3\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 432.1740, found: 432.1742.

2-(diethylamino)ethyl 4-(2-methyl-4-((4-methylphenyl)sulfonamido)-3-phenyl-1H-pyrrol-1-yl)benzoate (3ax)



3ax

The title compound was prepared from **1a** (76.6 mg, 0.2 mmol, 1 eq.) and **2x** (70.8 mg, 0.3 mmol, 1.5 eq.) via general procedure. Purified by silica gel column chromatography (eluent: EtOAc/PE = 1:3) furnished **3ax** (78.5 mg, 72% yield) as colorless solid.

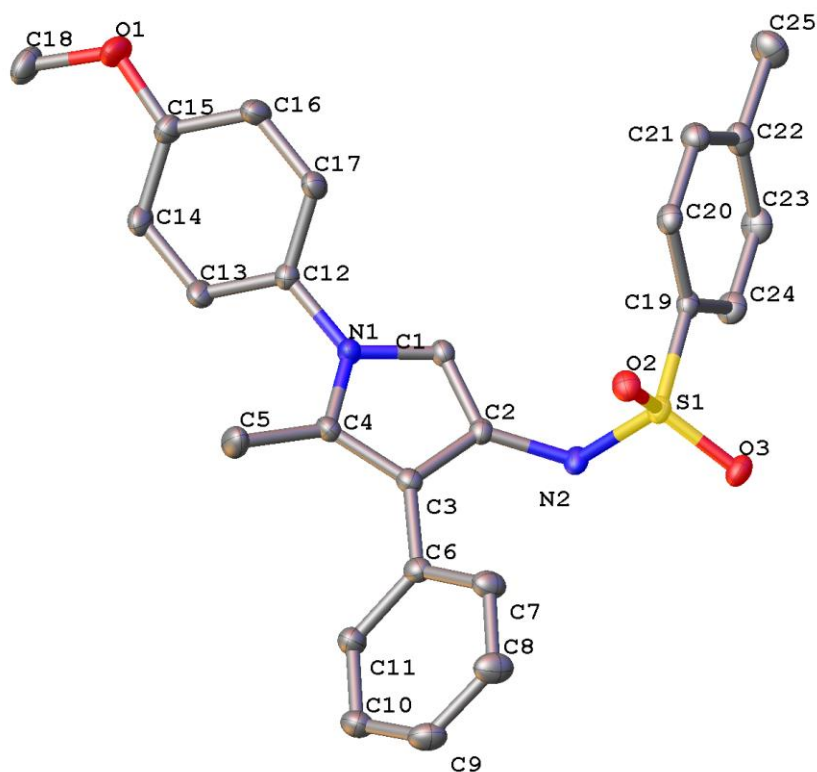
¹H NMR (300 MHz, CDCl₃) δ 8.20-8.09 (m, 2H), 7.57-7.50 (m, 2H), 7.43-7.35 (m, 2H), 7.29 (s, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.97 (s, 1H), 6.85 (dd, *J* = 7.6, 1.9 Hz, 2H), 6.09 (s, 1H), 4.43 (t, *J* = 6.2 Hz, 2H), 2.89 (t, *J* = 6.2 Hz, 2H), 2.66 (q, *J* = 7.1 Hz, 4H), 2.40 (s, 3H), 2.09 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 7H).

¹³C NMR (75 MHz, CDCl₃) δ 165.9, 143.6, 140.8, 136.3, 133.0, 130.9, 129.7, 129.5, 128.8, 128.1, 127.4, 126.9, 125.2, 124.8, 119.6, 119.4, 114.8, 63.6, 57.7, 51.3, 48.0, 39.3, 21.7, 12.0.

HRMS (ESI) *m/z* calculated for C₃₁H₃₆N₃O₄S [M+H]⁺: 546.2421, found: 546.2424.

Determined the configuration **3aa** by X-ray

X-ray of 3aa (method of crystallization: in a 20 mL tube, the compound **3aa** (100 mg) was dissolved in a mixture n-hexane/CH₂Cl₂ (10 mL:3 mL). The tube was sealed with a septum and a needle was inserted into the septum in order to slowly evaporation of CH₂Cl₂). Thermal ellipsoids are shown at the 50% level.



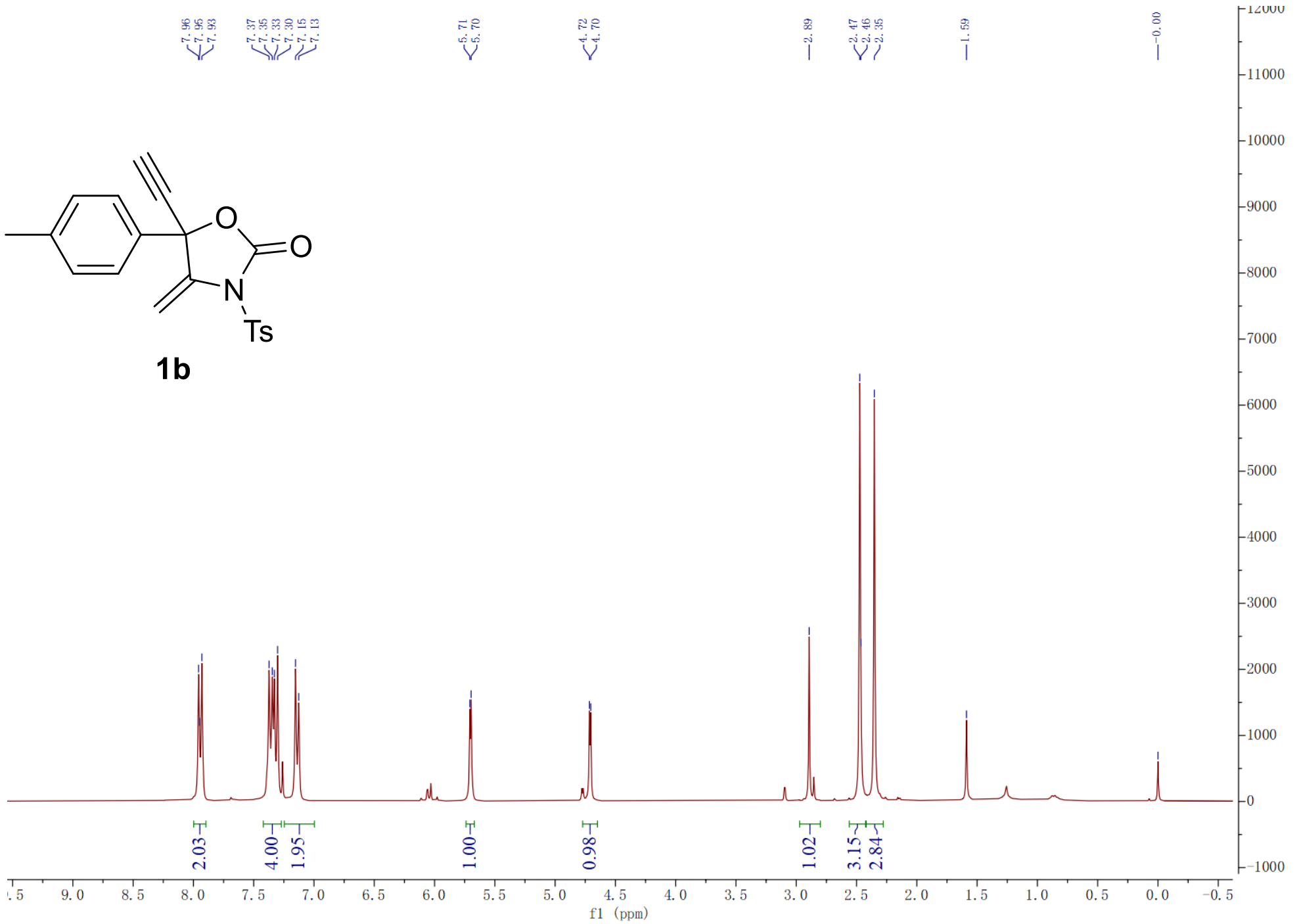
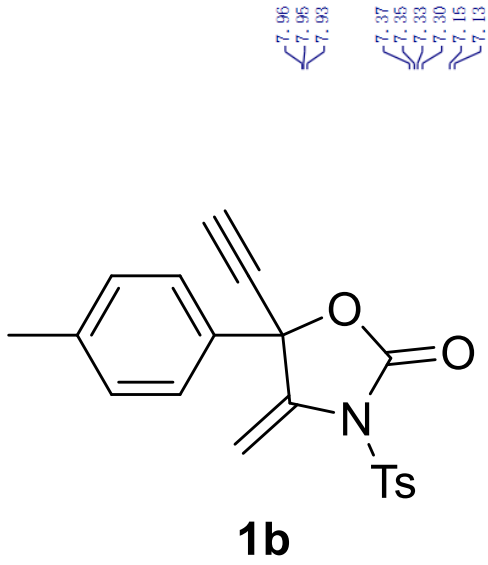
Crystallographic data of **3aa**

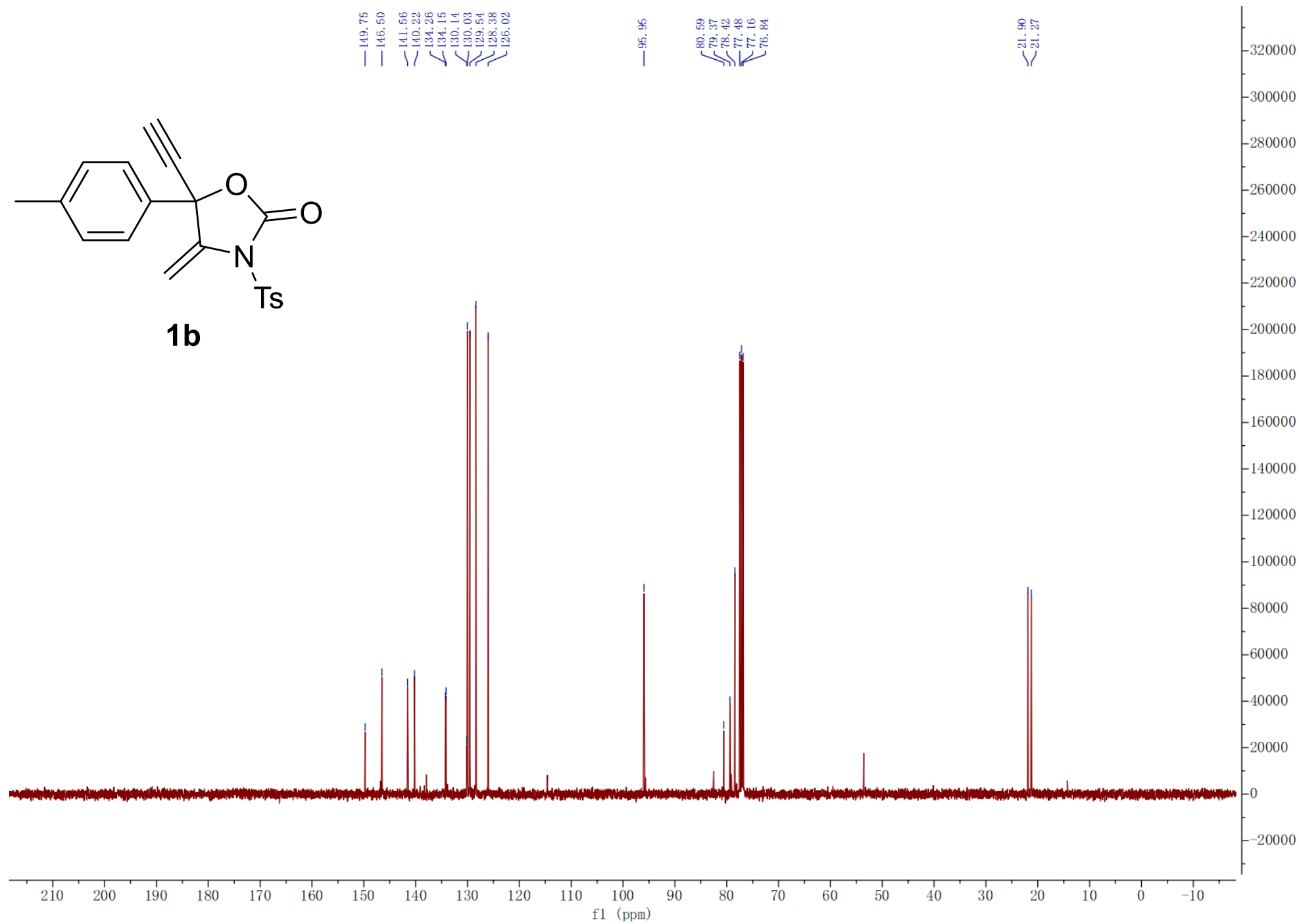
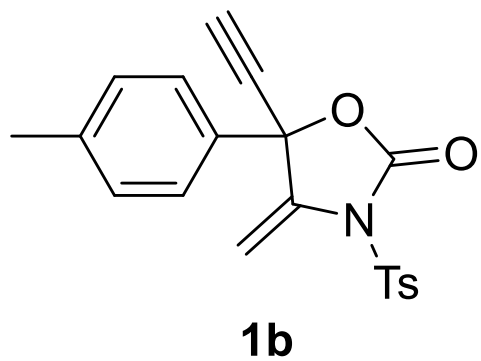
Empirical formula	C ₂₅ H ₂₄ N ₂ O ₃ S
Formula weigh	432.52
Wavelength	1.34139
Crystal system	monoclinic
Space group	P21
a (Å)	9.04750(10)
b (Å)	10.4700(2)
c (Å)	12.6844(2)
α (°)	70.9370(10)
β (°)	82.2400(10)
γ (°)	84.1790(10)
V (Å ³)	1123.16(3)
Z	2
Temperature/K	173
F (000)	456

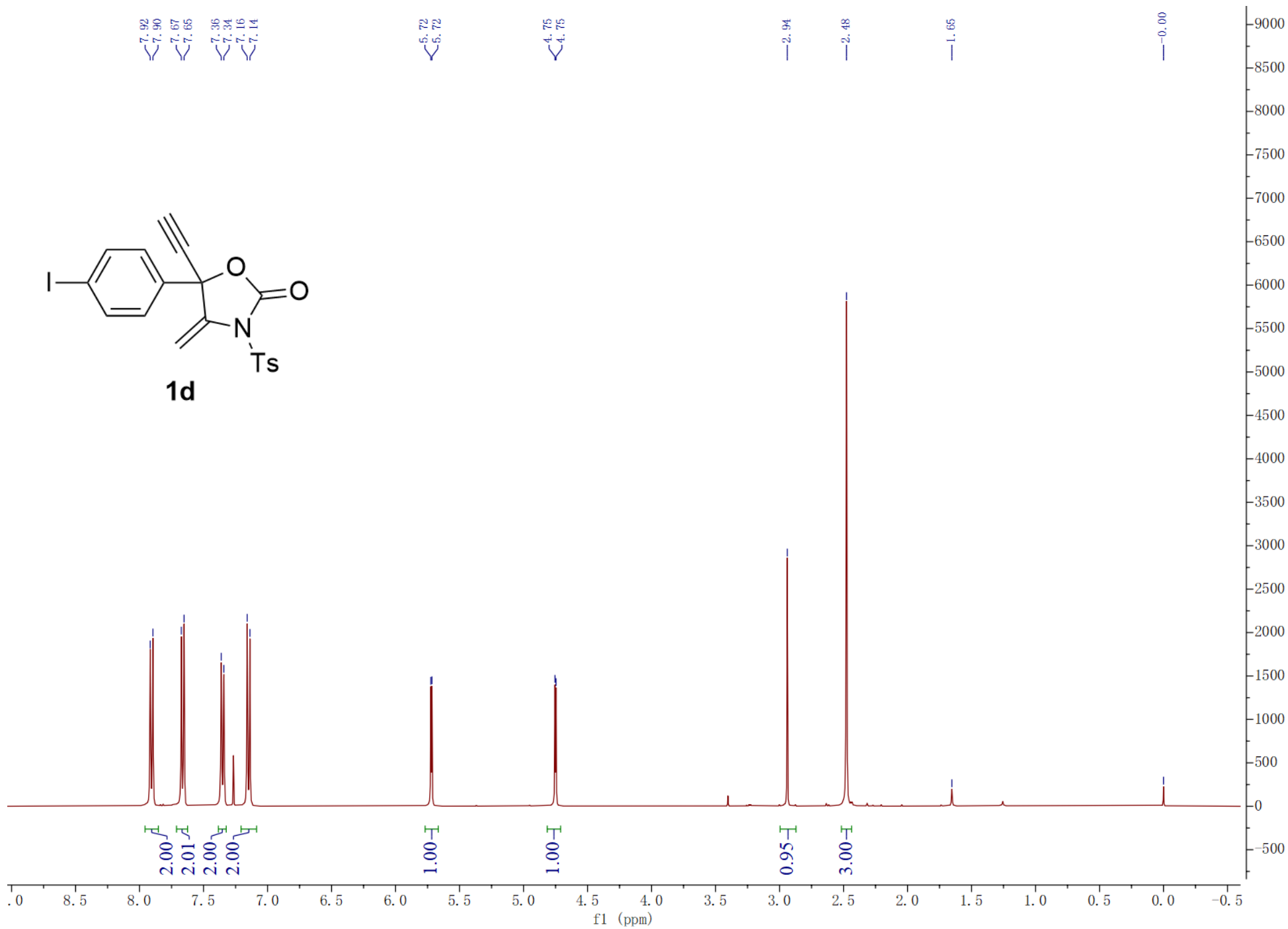
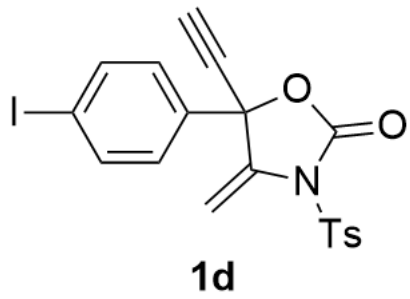
Crystal size/mm ³	0.17x0.17x0.05
θ min, θ max (deg)	3.894, 54.991
Reflections collected	17147
Independent reflections	4221
Data/restraints/parameters	4221 / 0 / 283
Goodness-of-fit on F ²	1.043
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0407, wR2 = 0.1005
Final R indexes [all data]	R1 = 0.0504, wR2 = 0.1067
Largest diff. peak and hole/ e Å ⁻³	0.329/-0.436

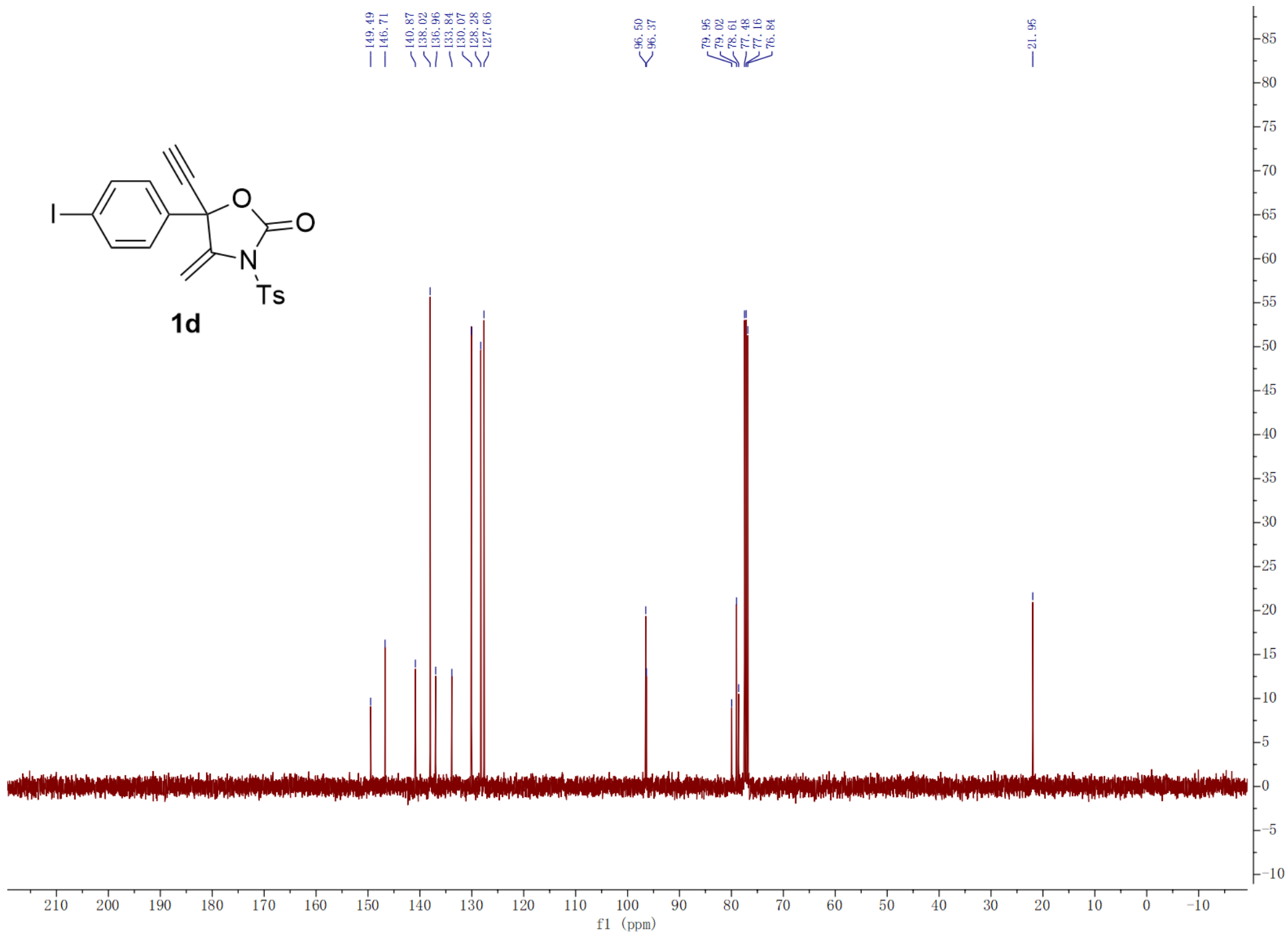
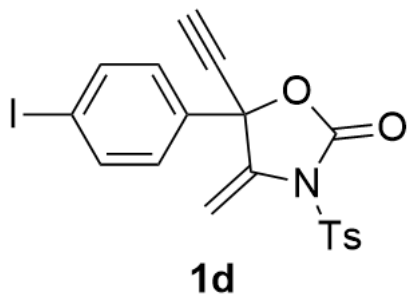
Reference

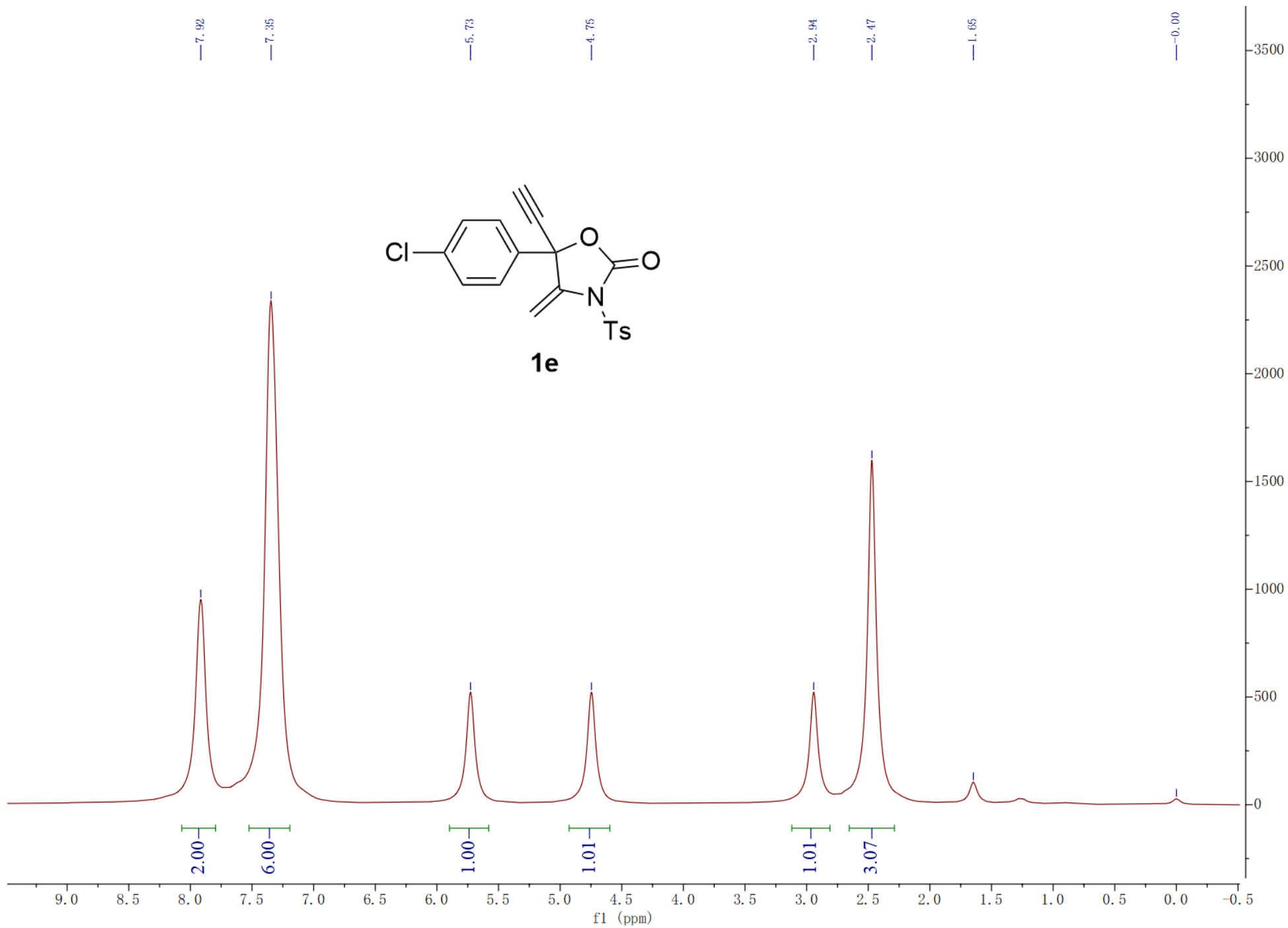
- (a) L. Shen, Z. Lin, B. Guo and W. Zi, Synthesis of cycloheptanoids through catalytic enantioselective (4 + 3)-cycloadditions of 2-aminoallyl cations with dienol silyl ethers, *Nat. Synth.*, **2022**, *1*, 883; (b) L. Shen, Y. Zheng, Z. Lin, T. Qin, Z. Huang and W. Zi, Copper-Catalyzed Enantioselective C1,N-Dipolar (3+2) Cycloadditions of 2-Aminoallyl Cations with Indoles, *Angew. Chem. Int. Ed.*, 2023, **62**, e202217051.

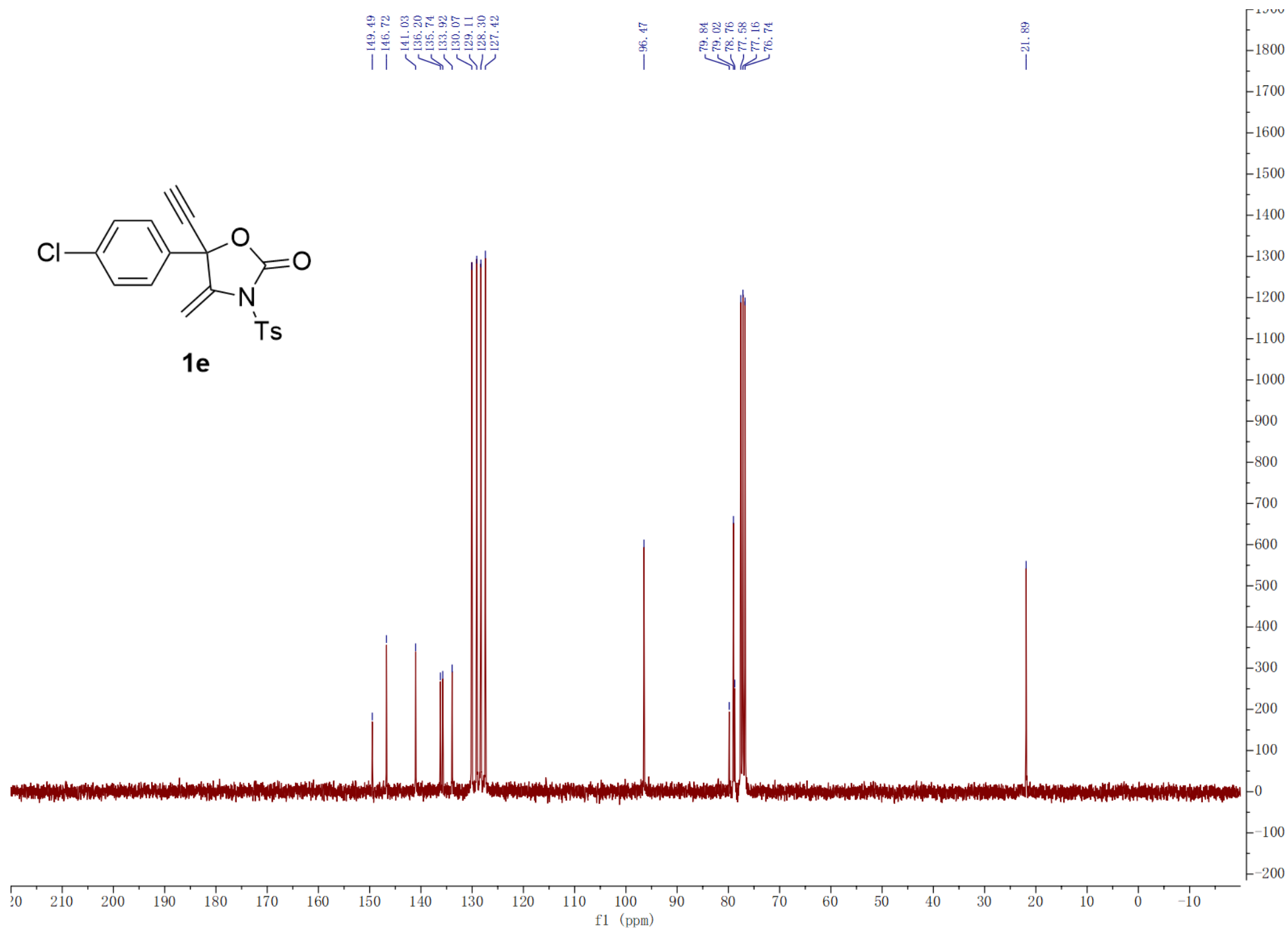
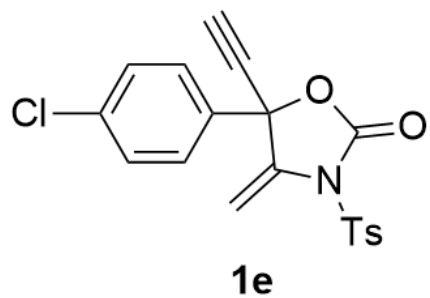


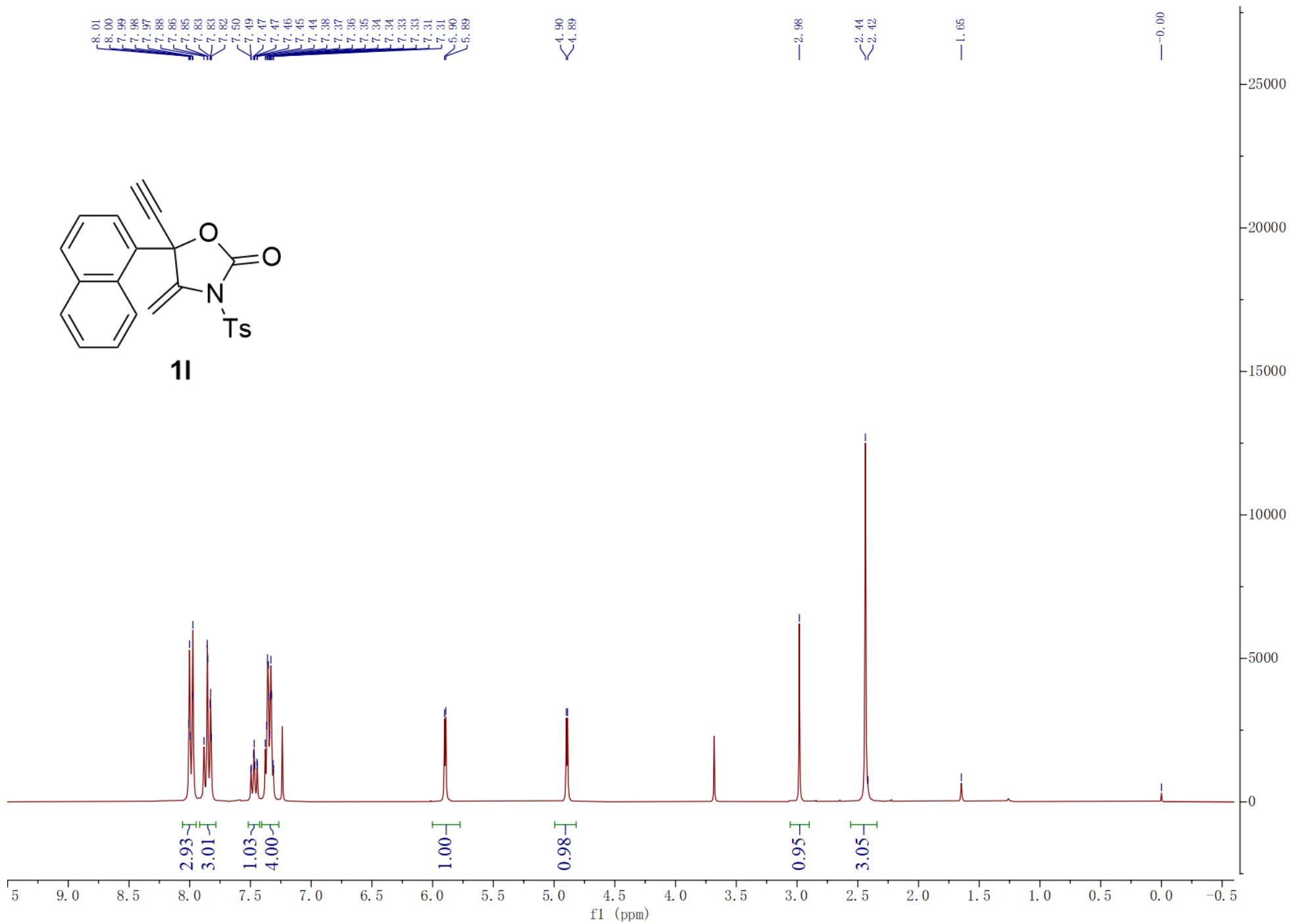
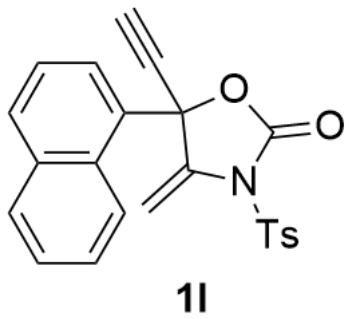


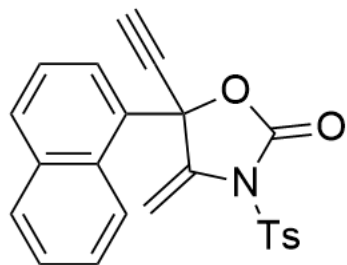




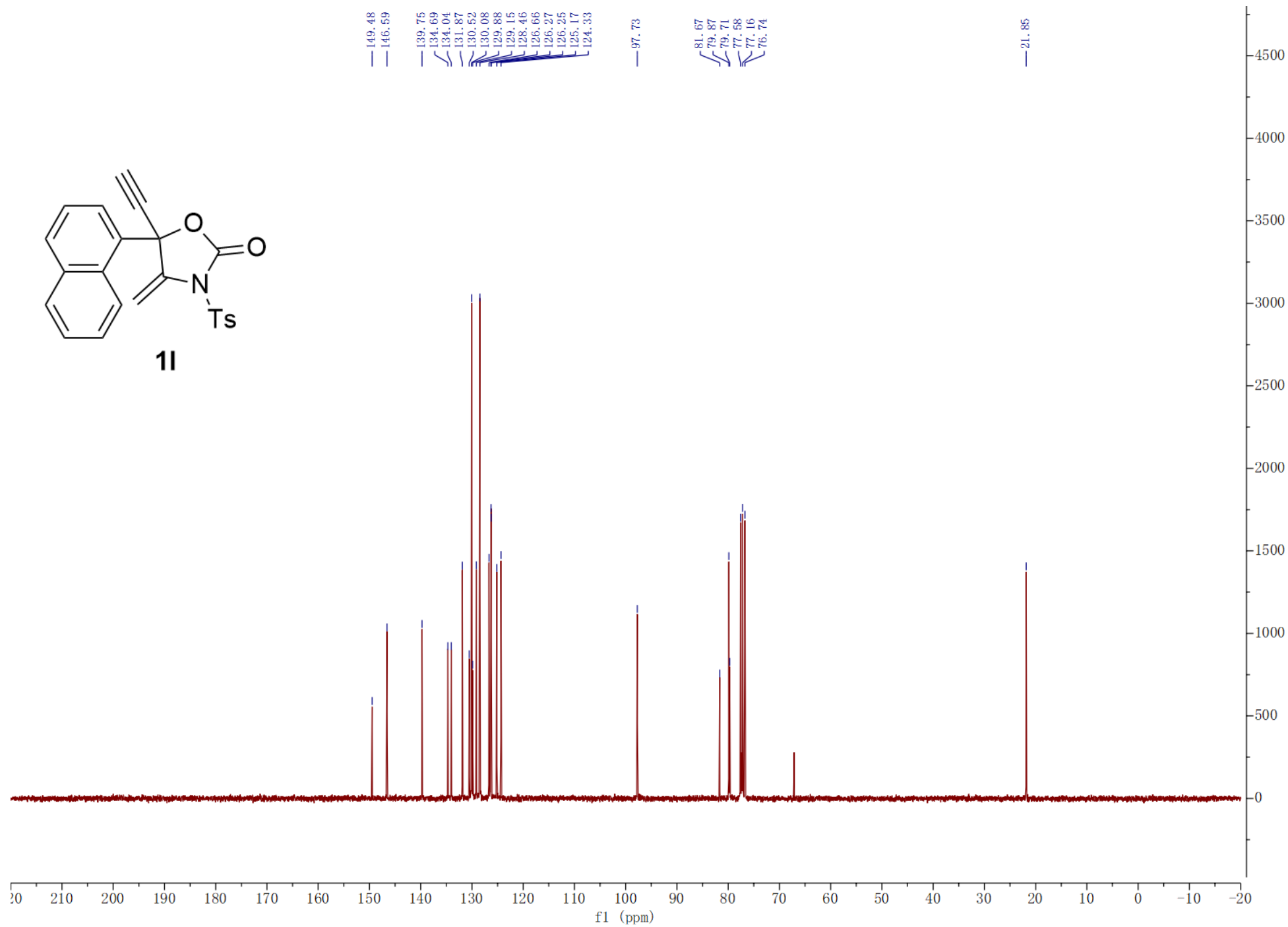


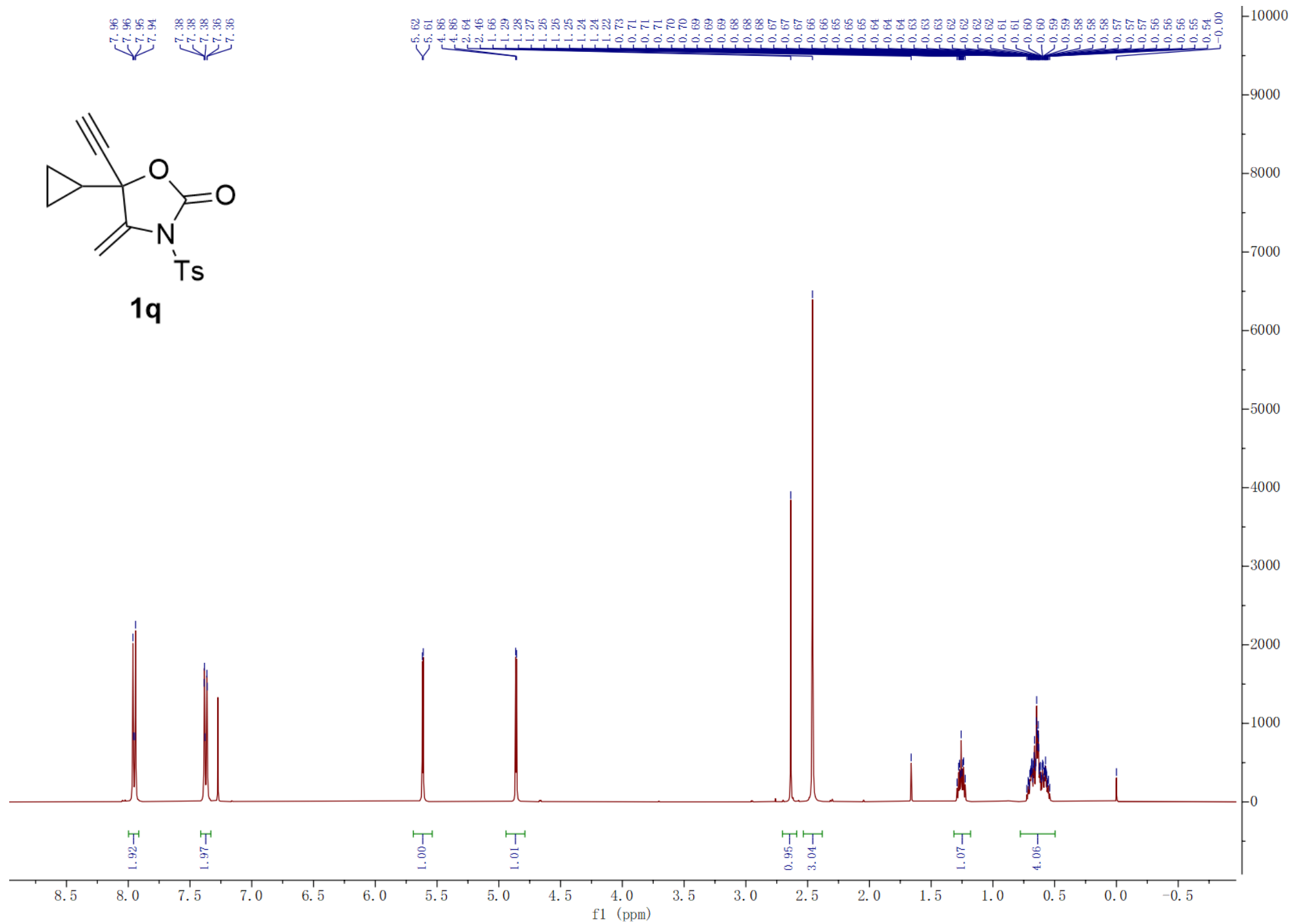
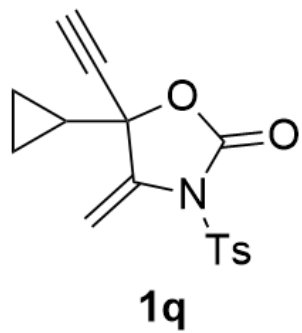


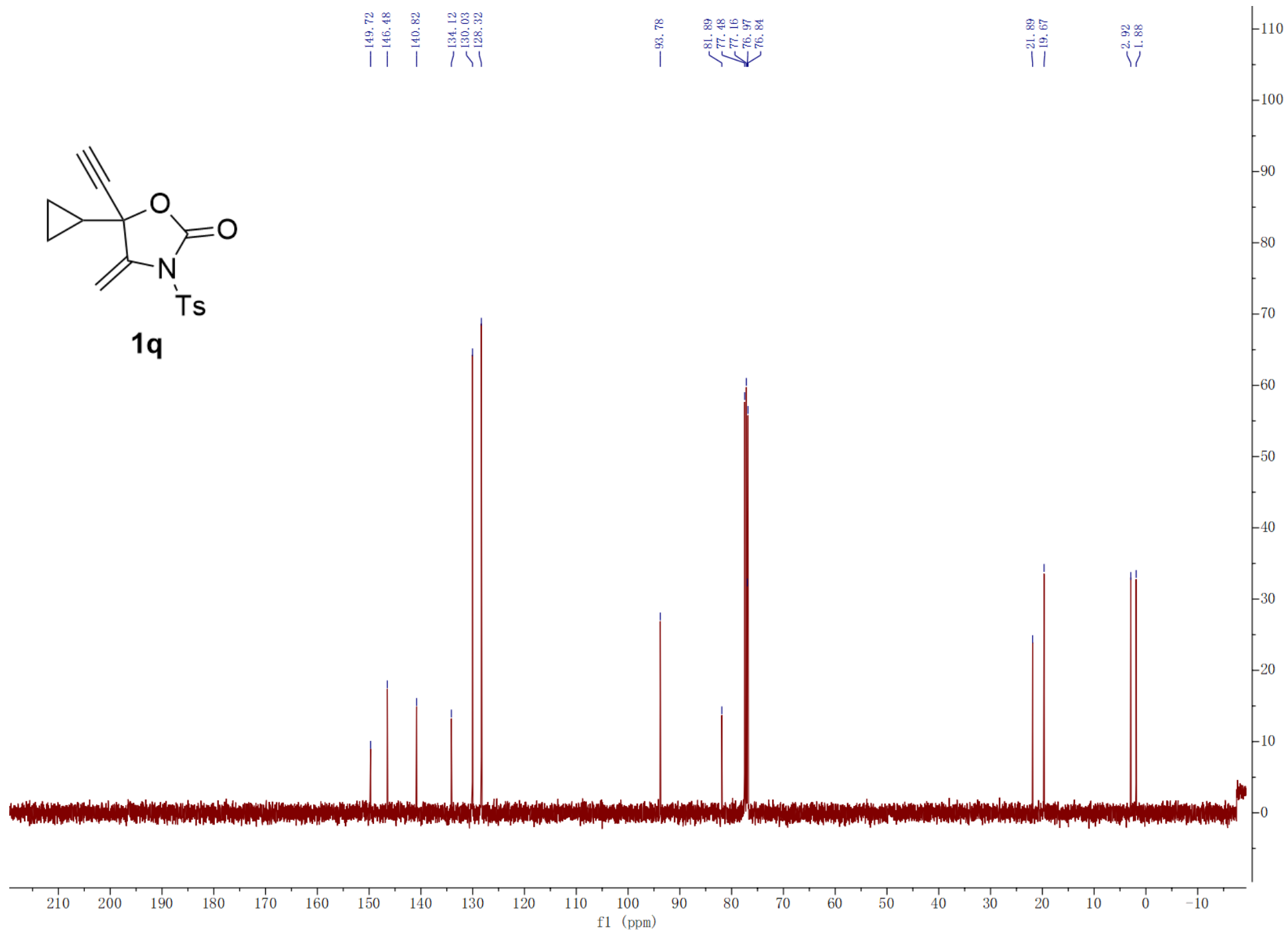
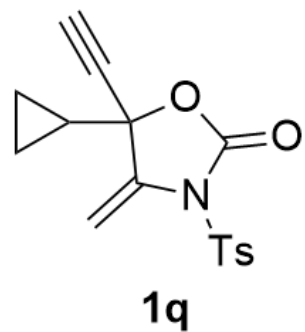


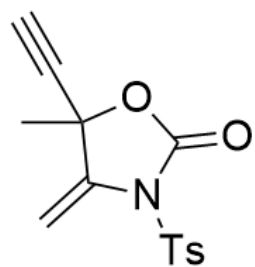


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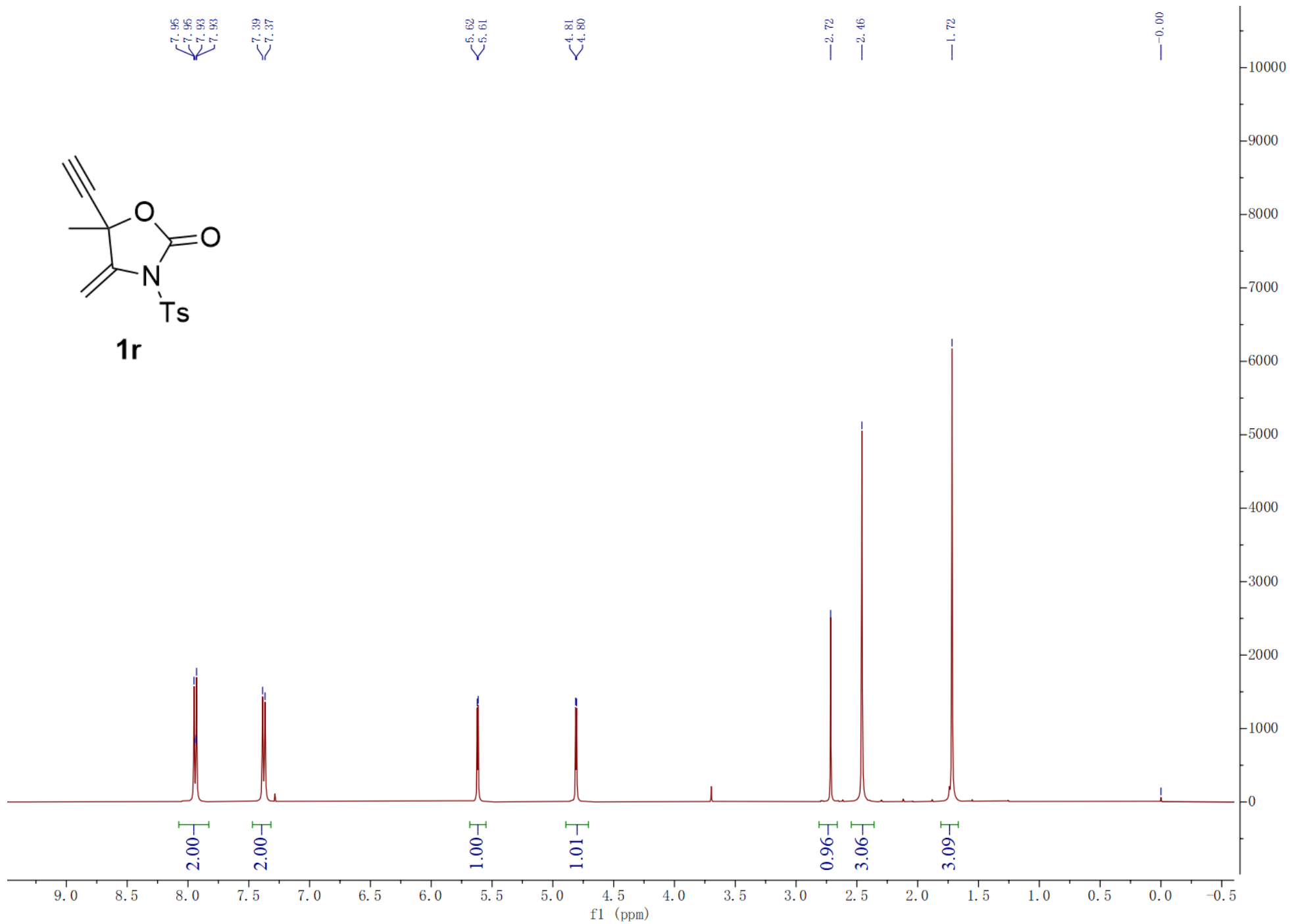


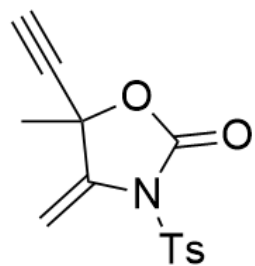




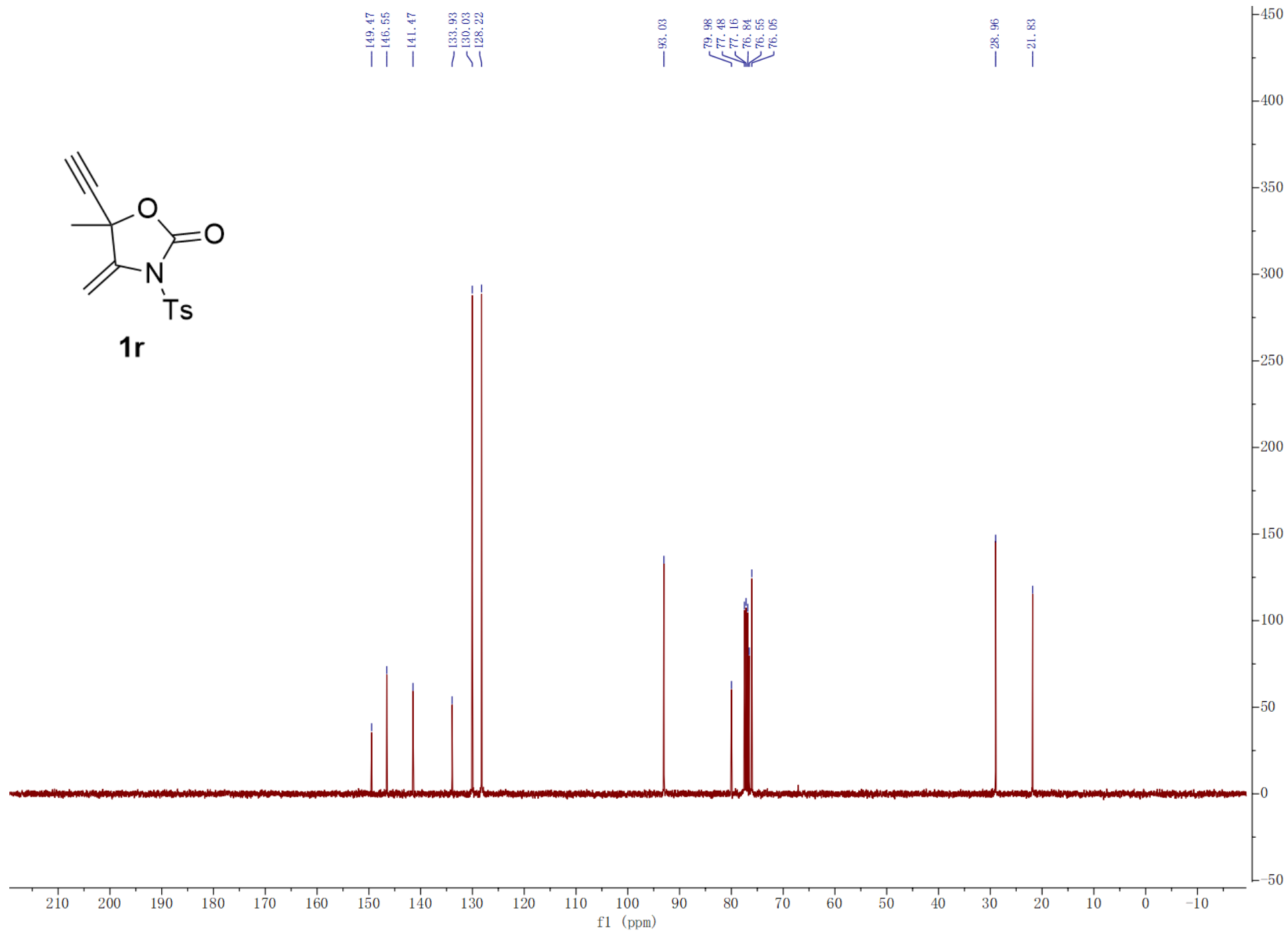


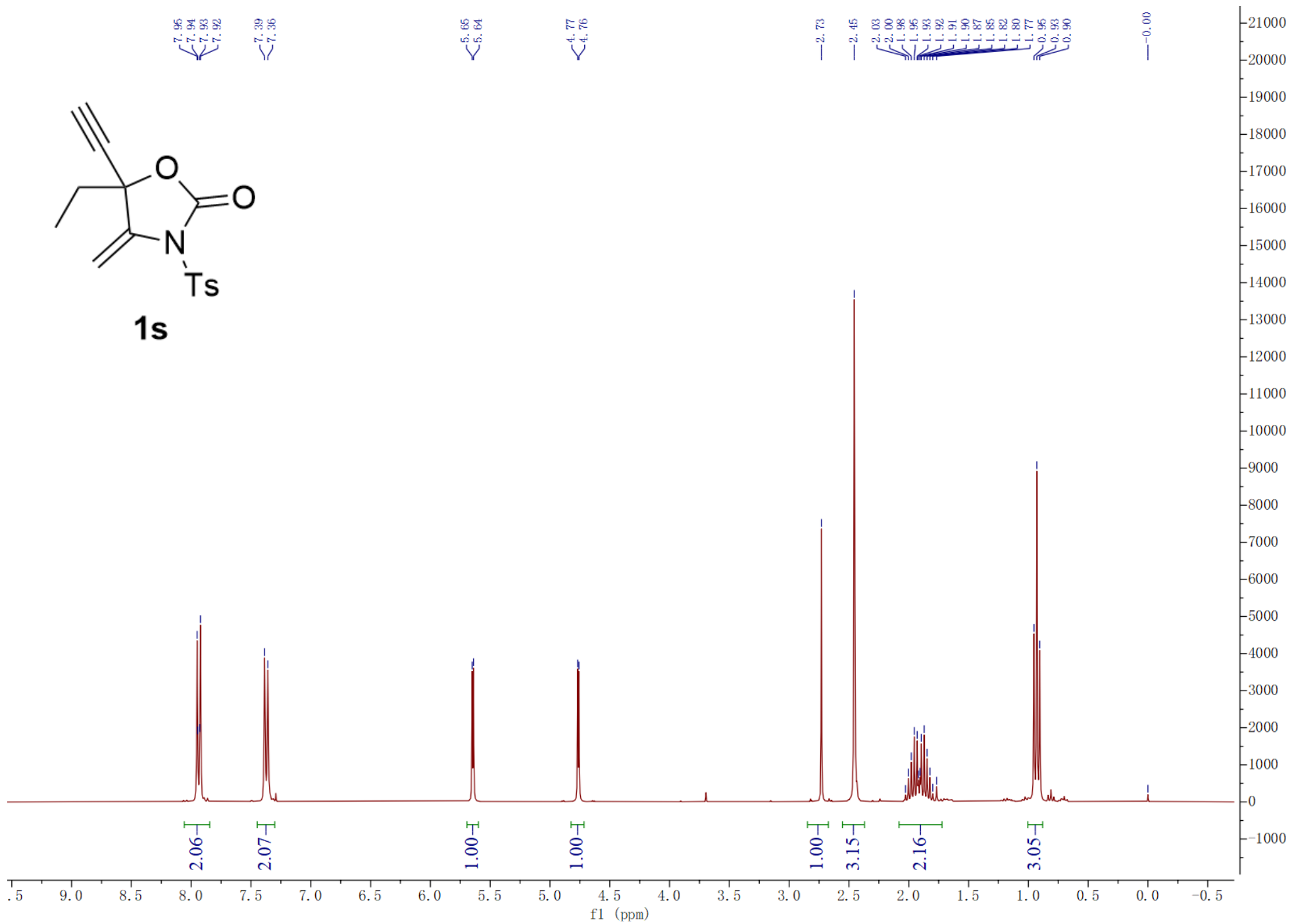
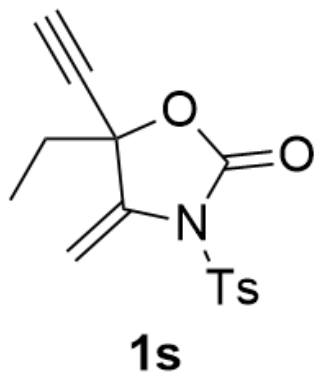
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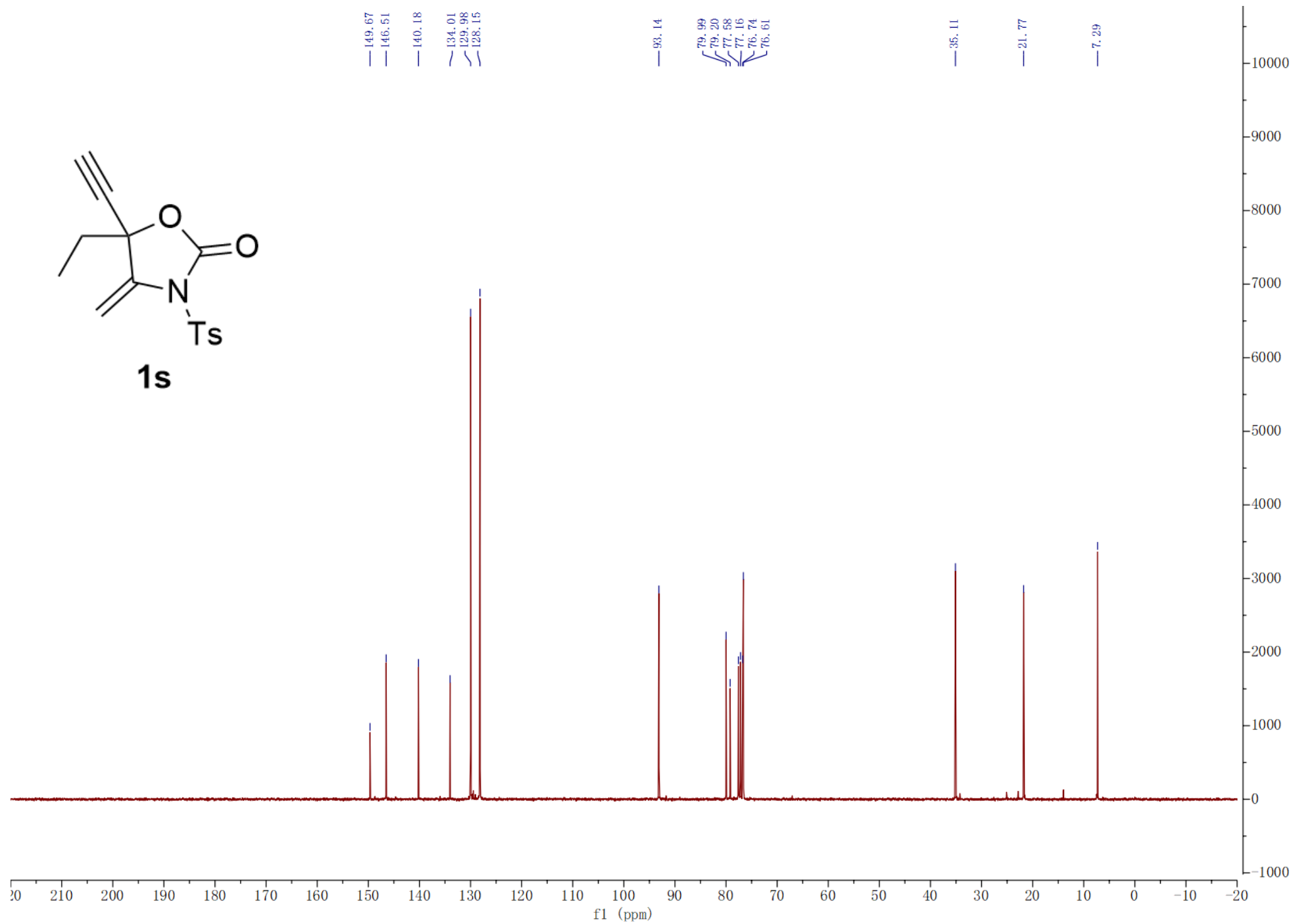
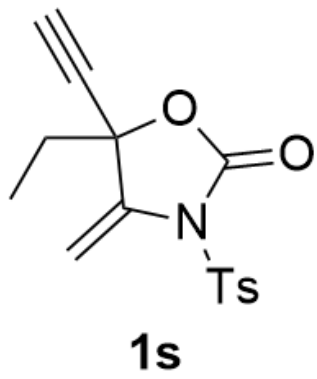


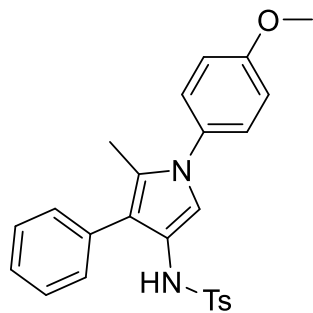


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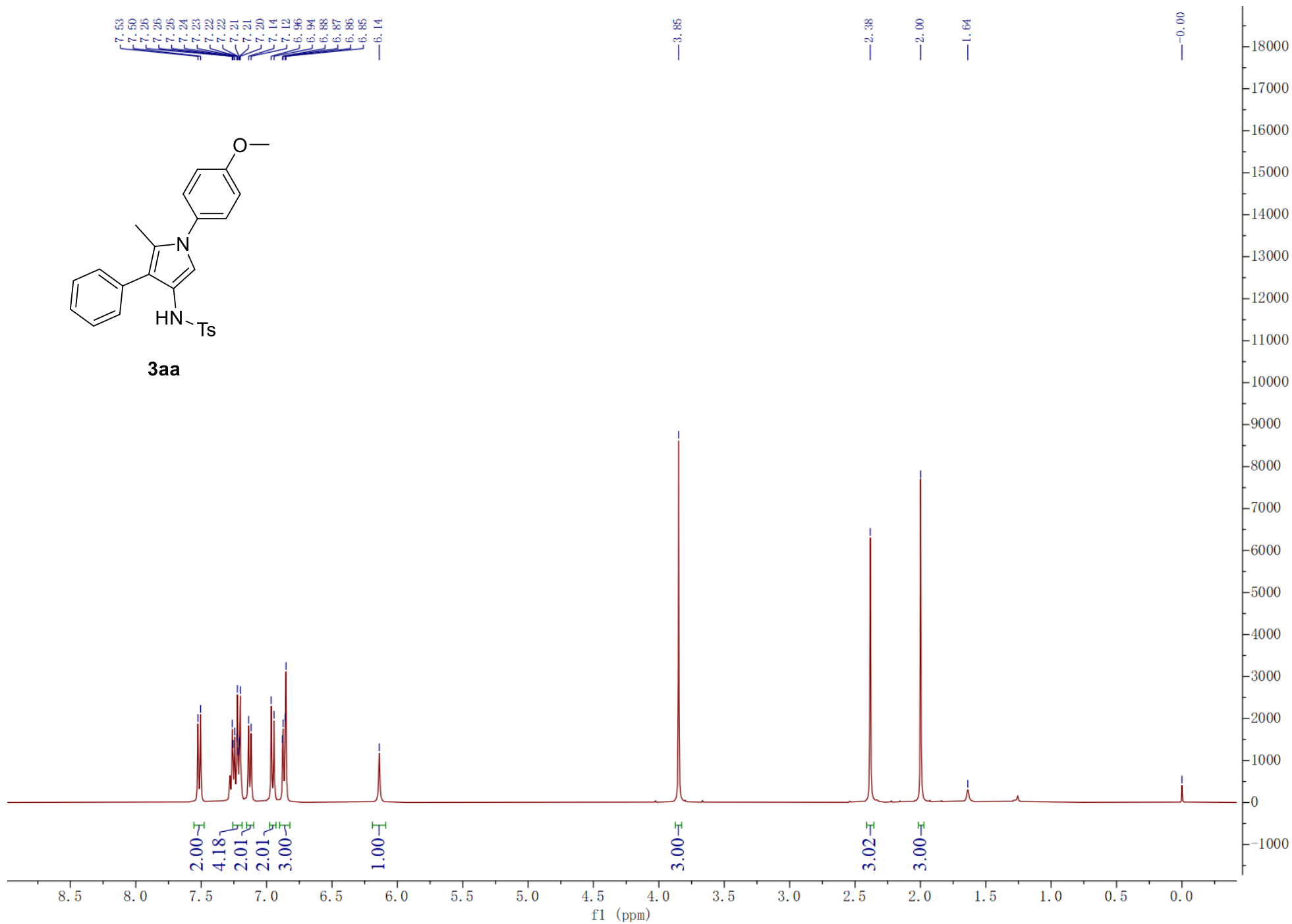


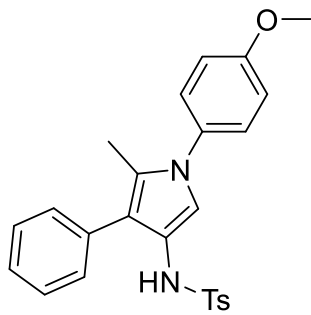




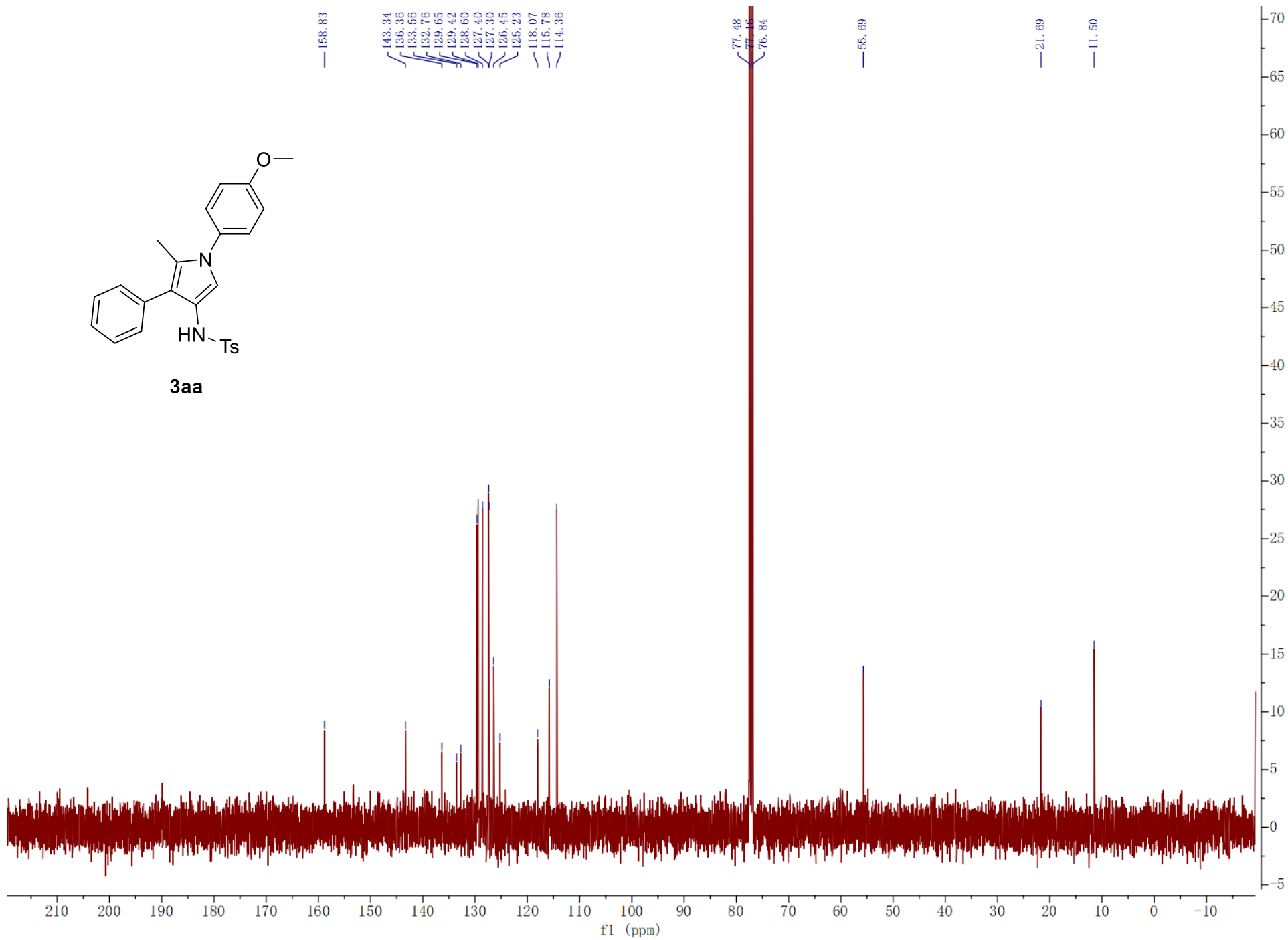


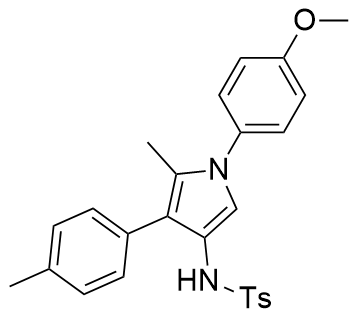
3aa



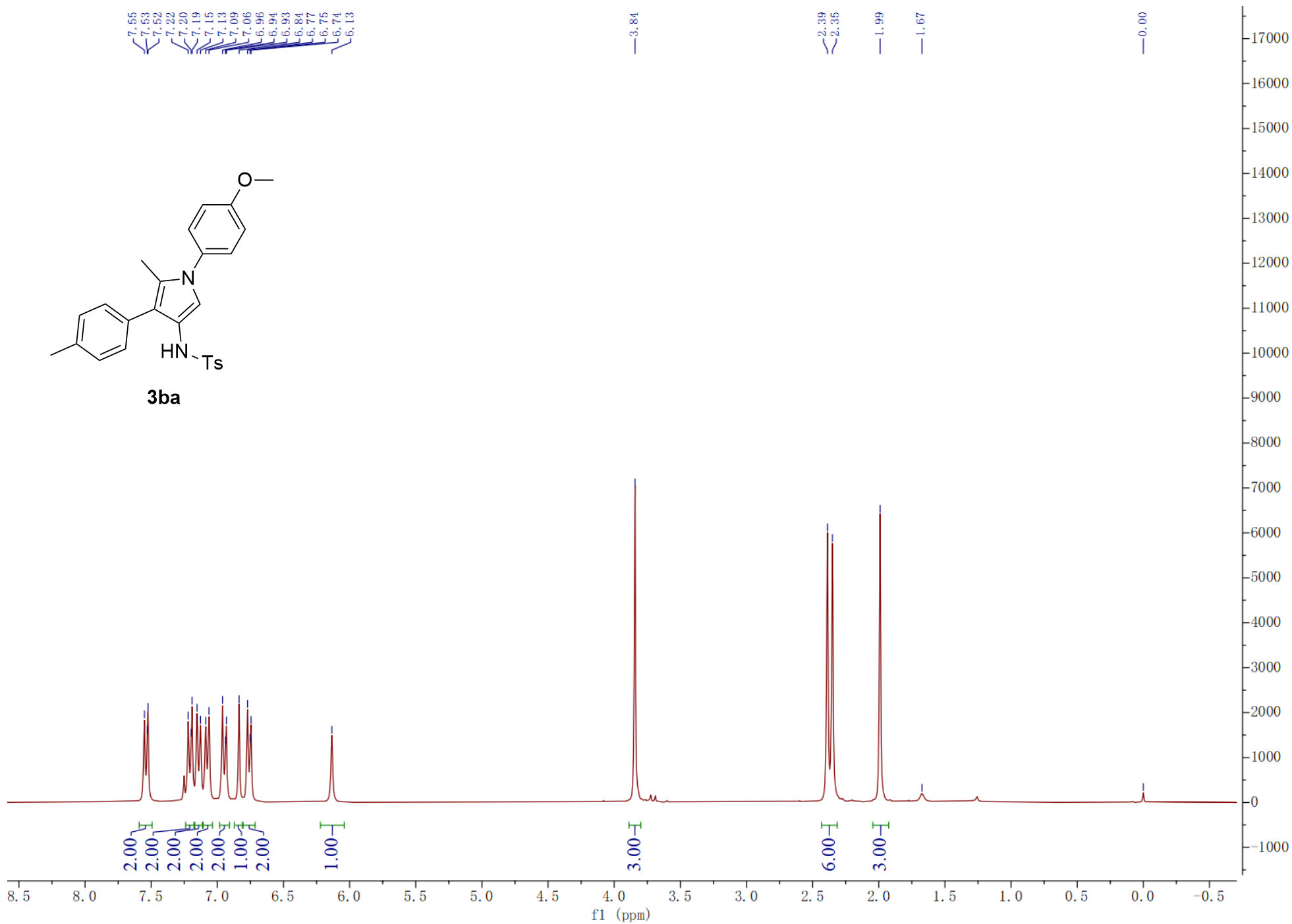


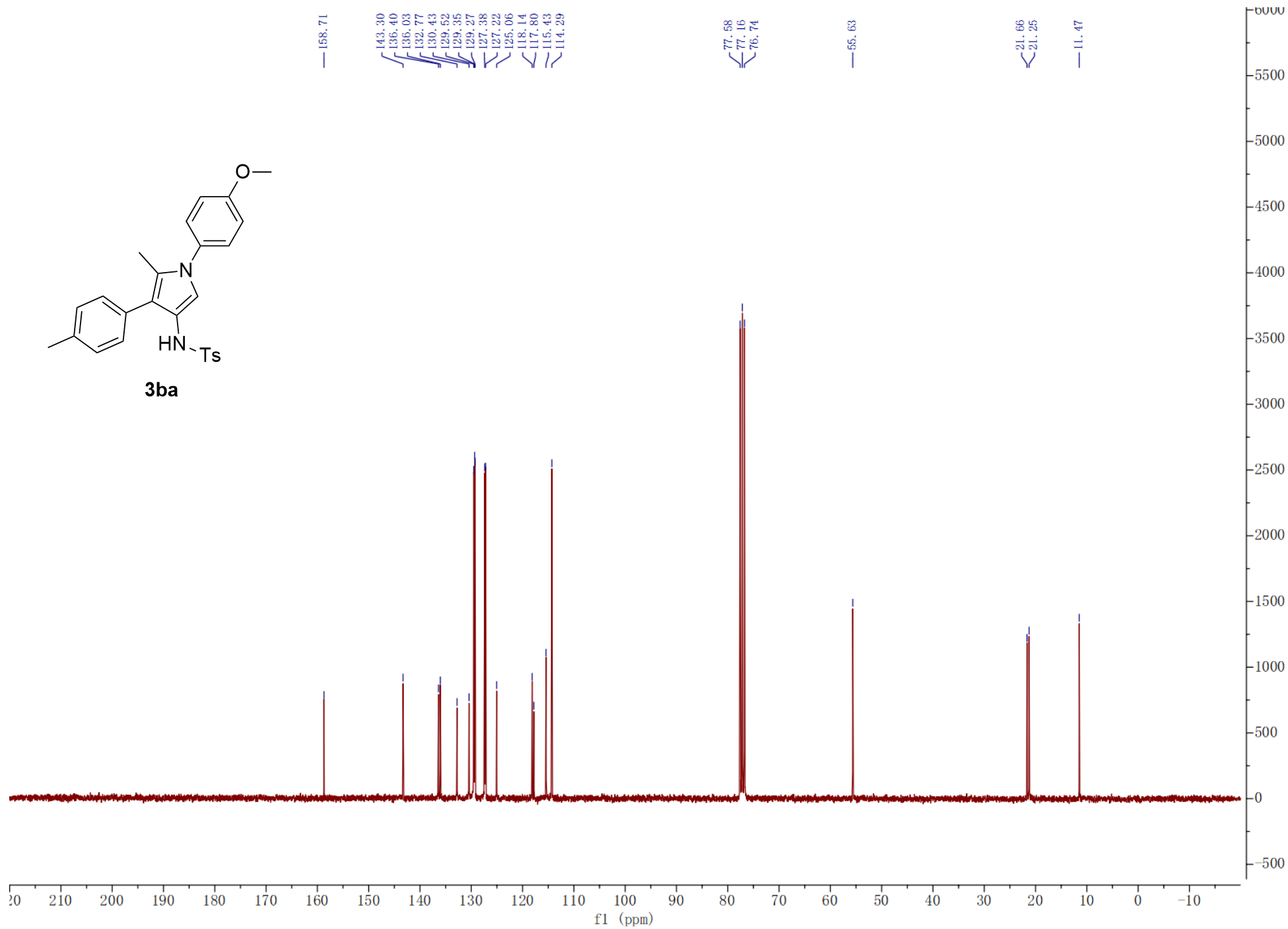
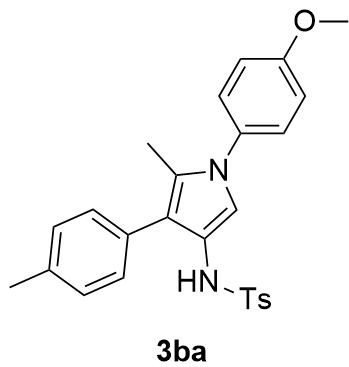
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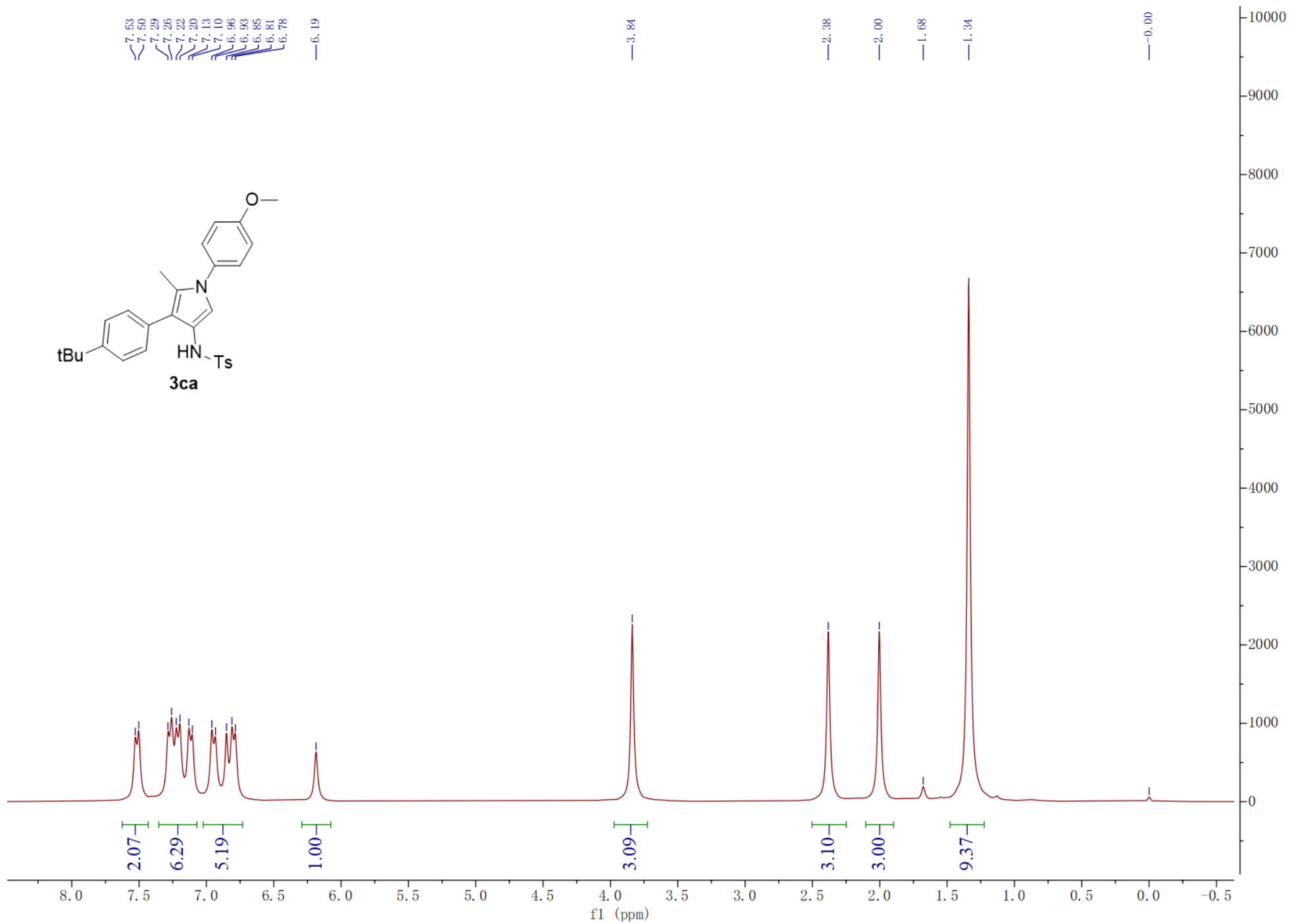
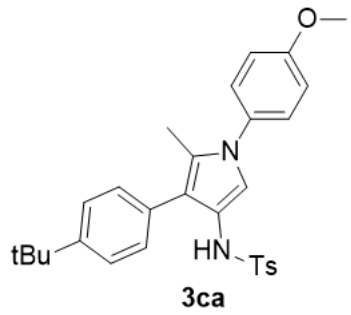


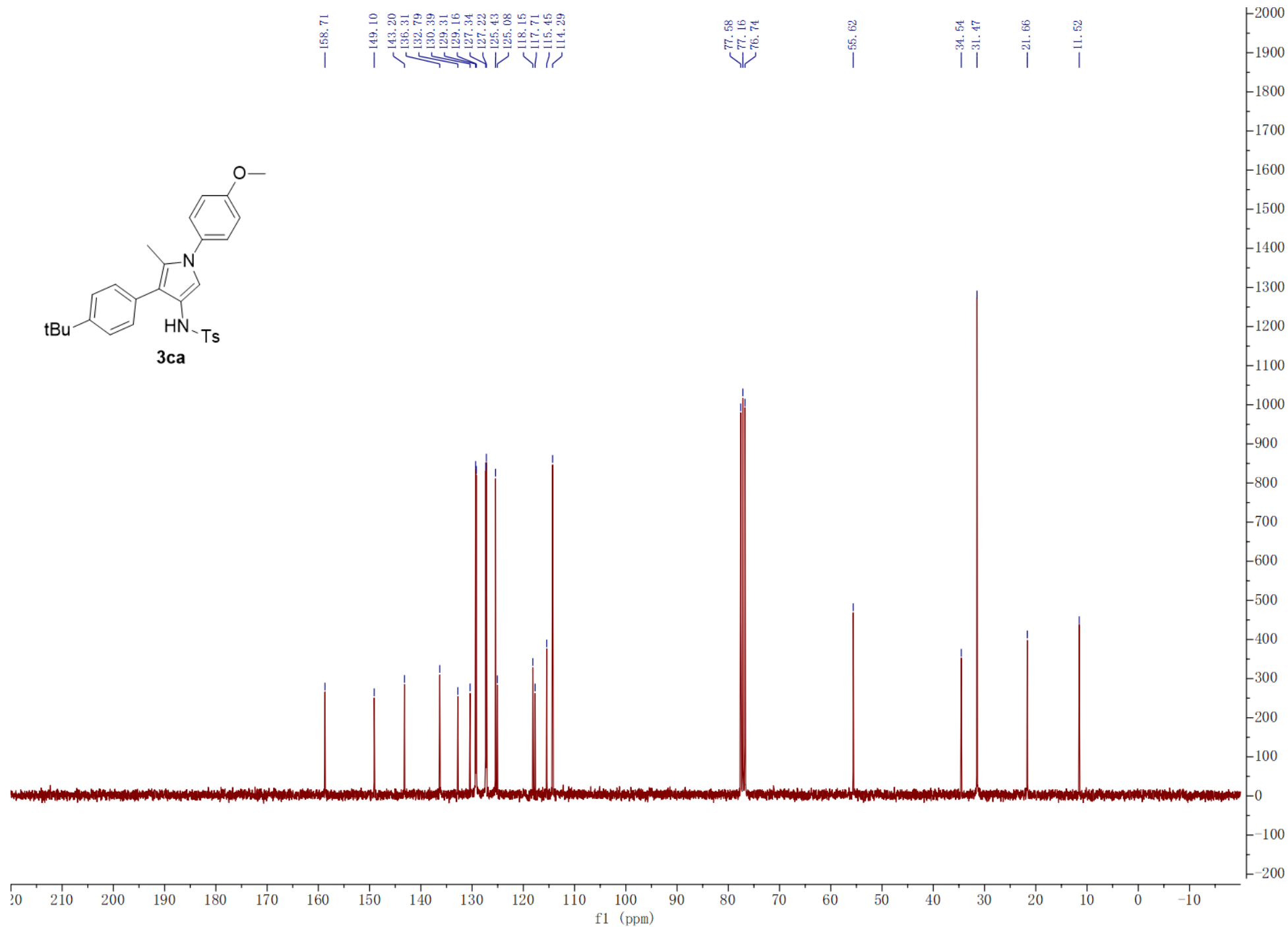
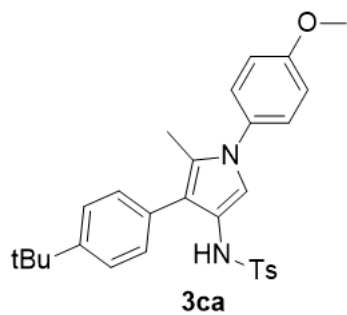


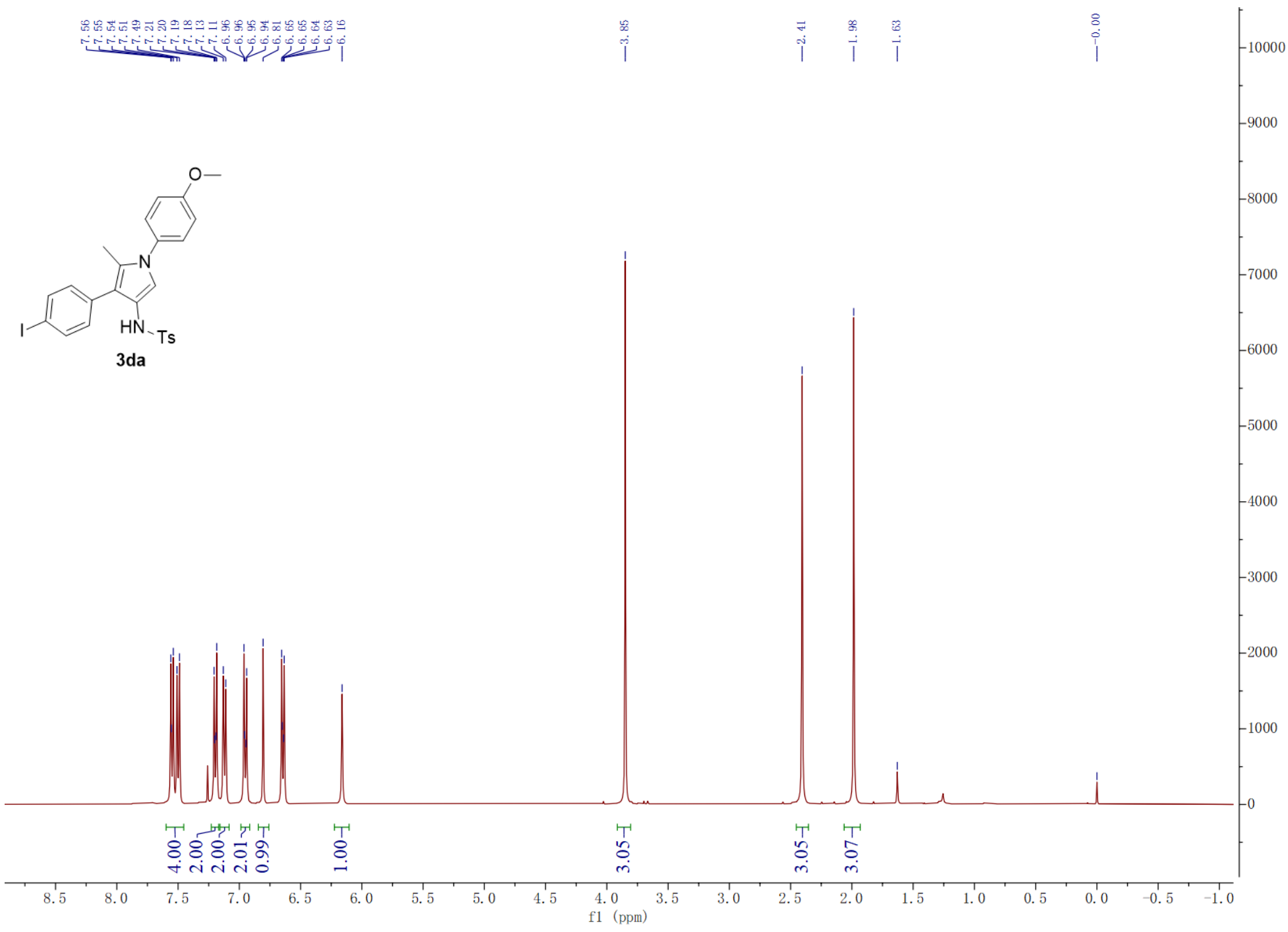
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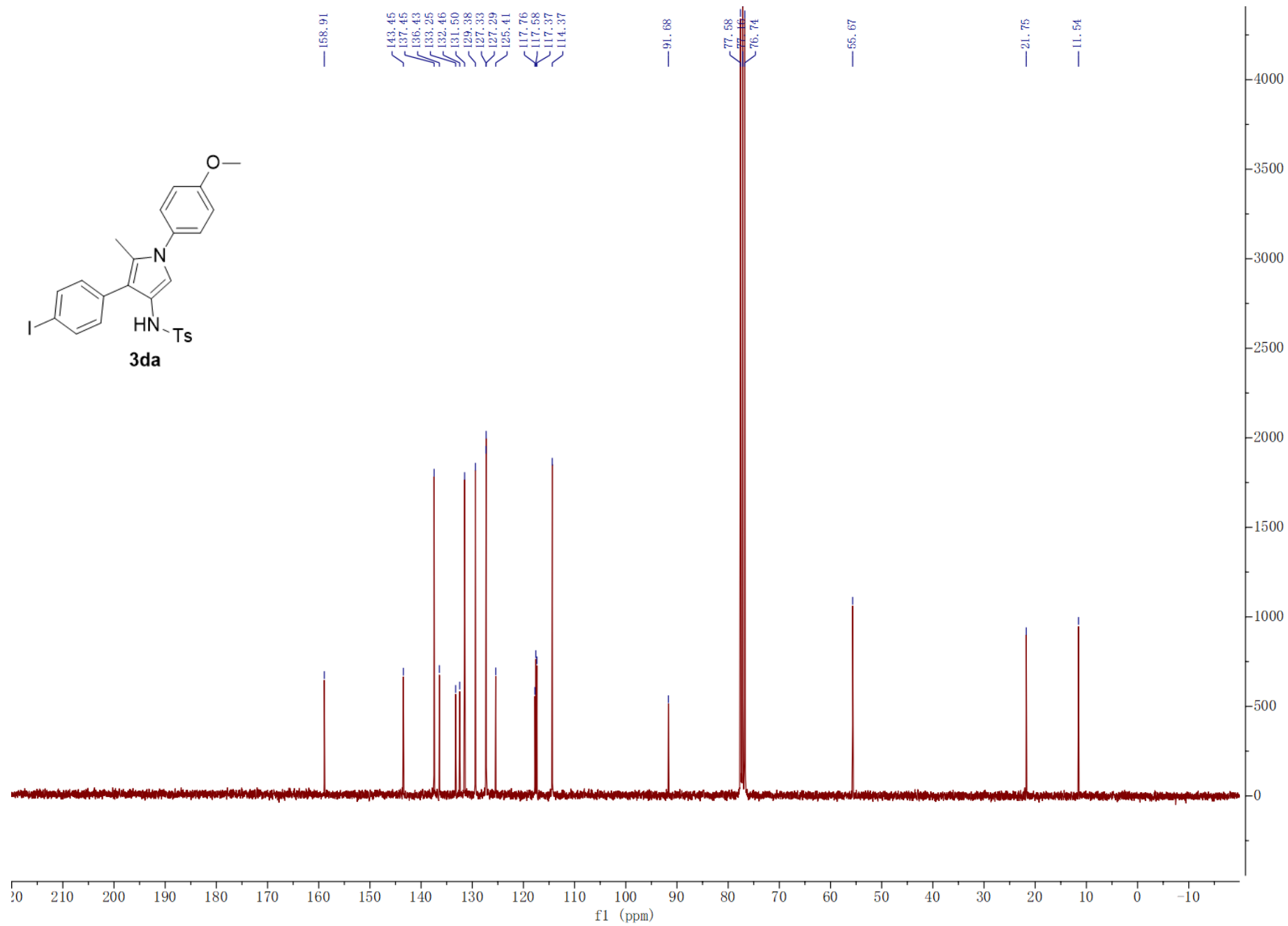
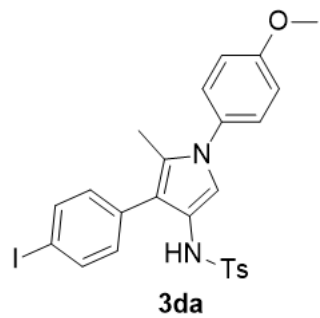


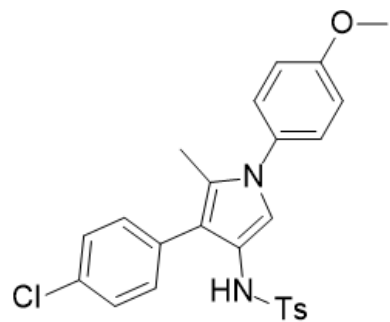




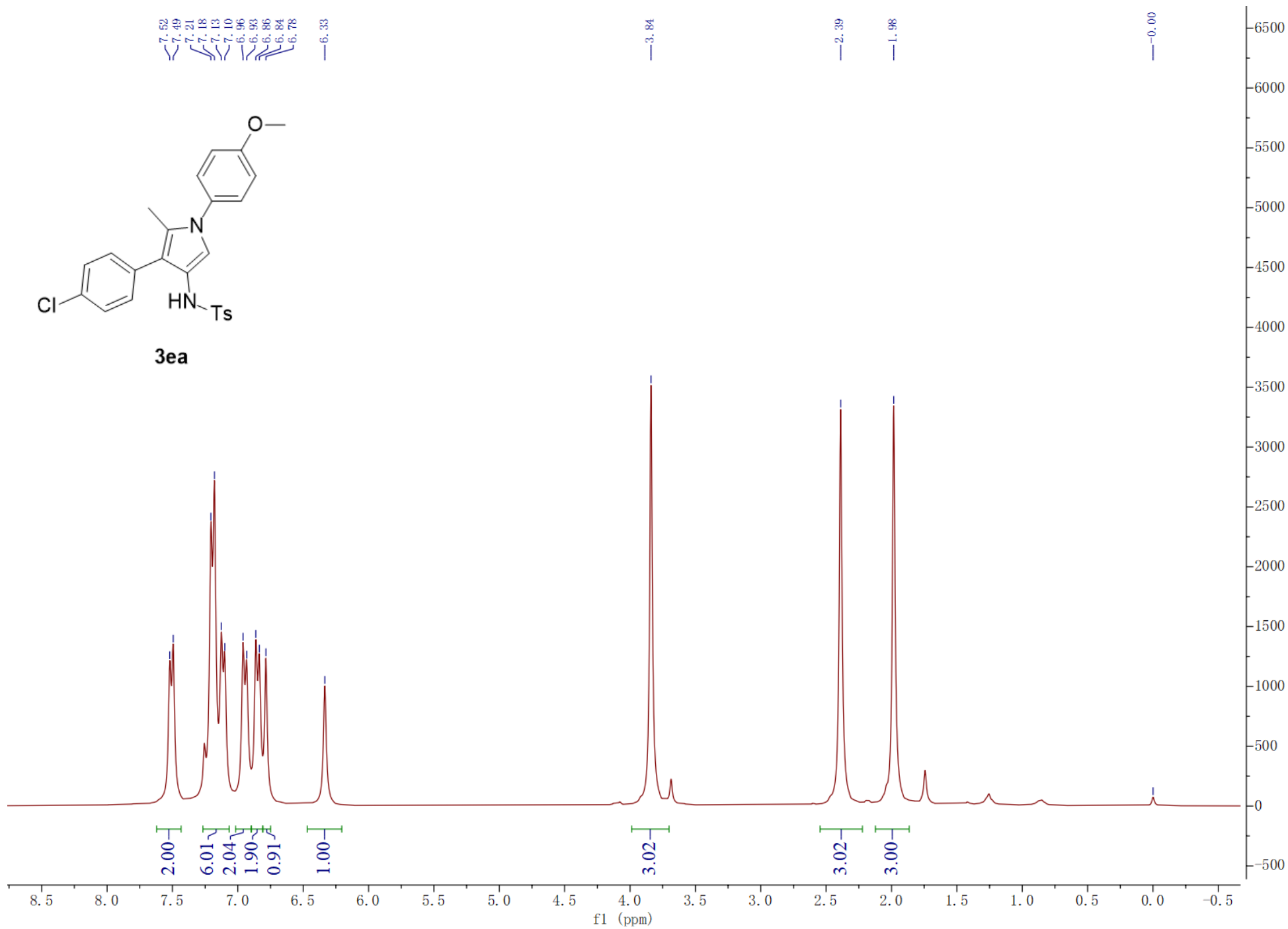


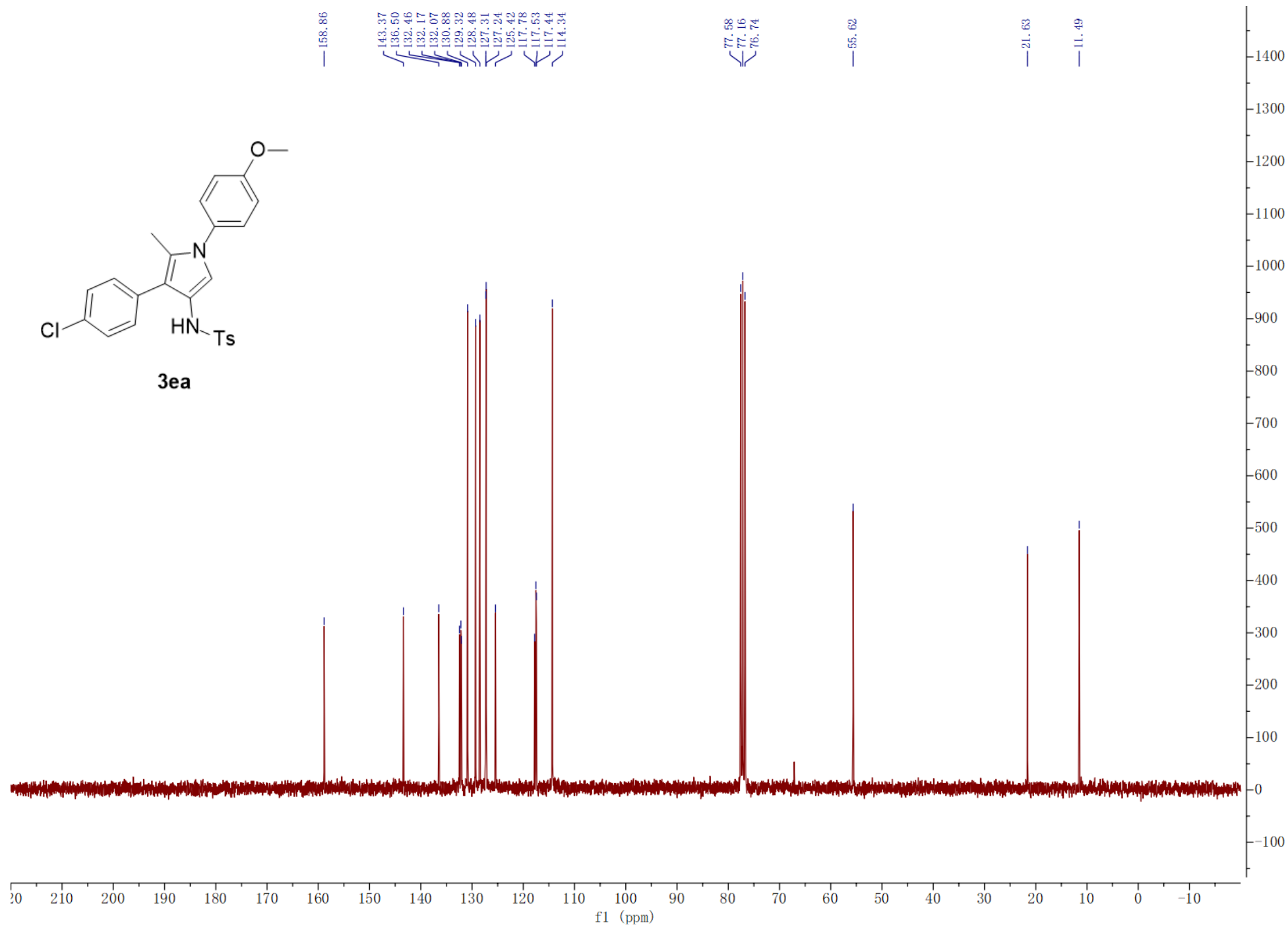
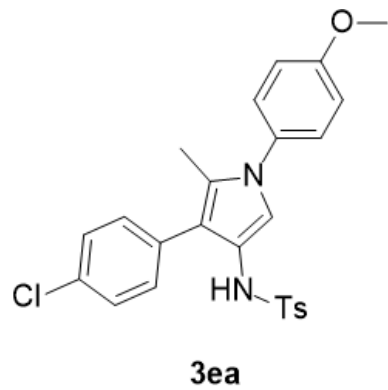


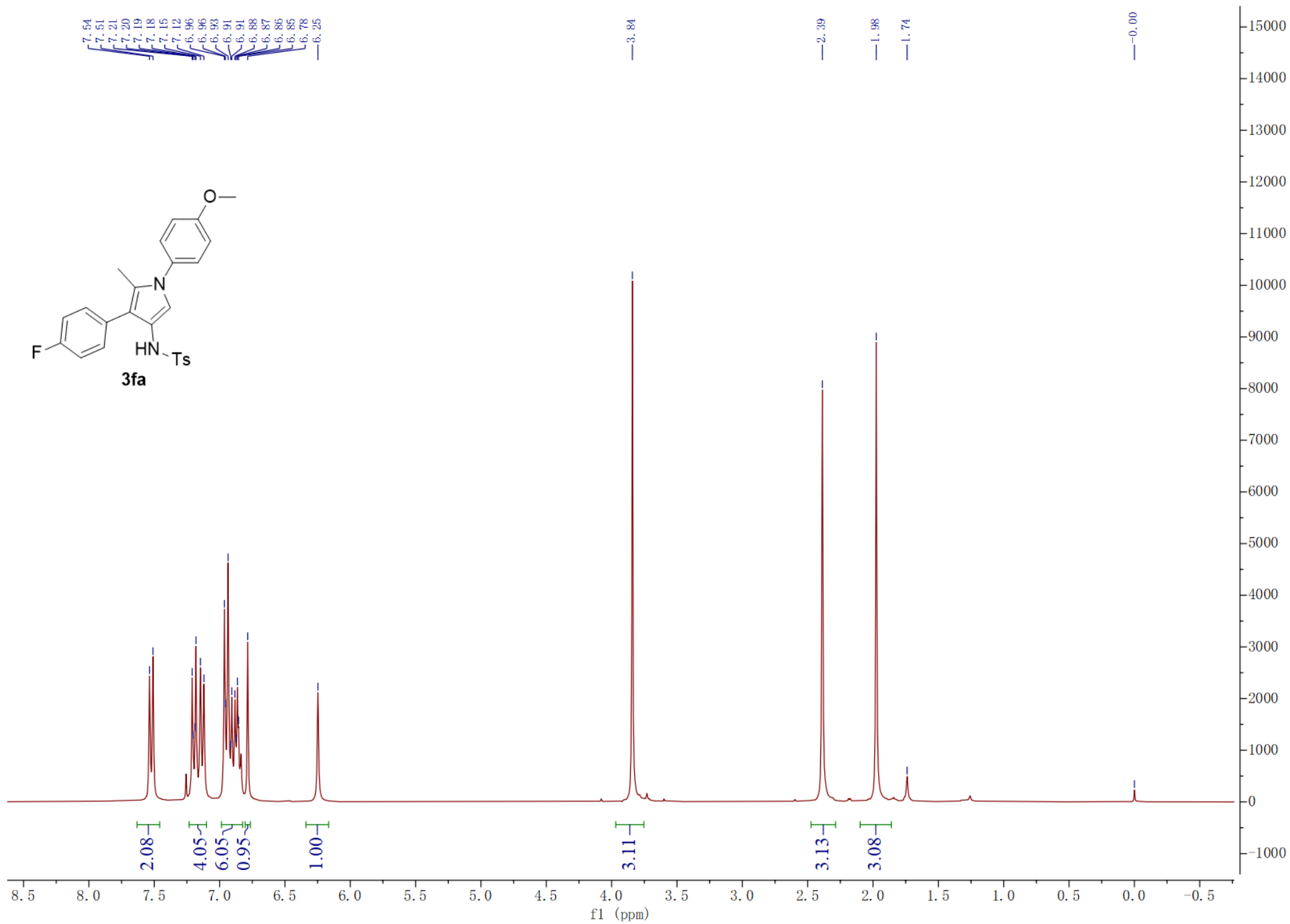
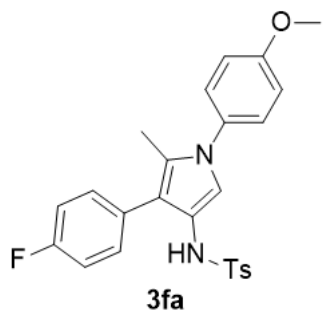


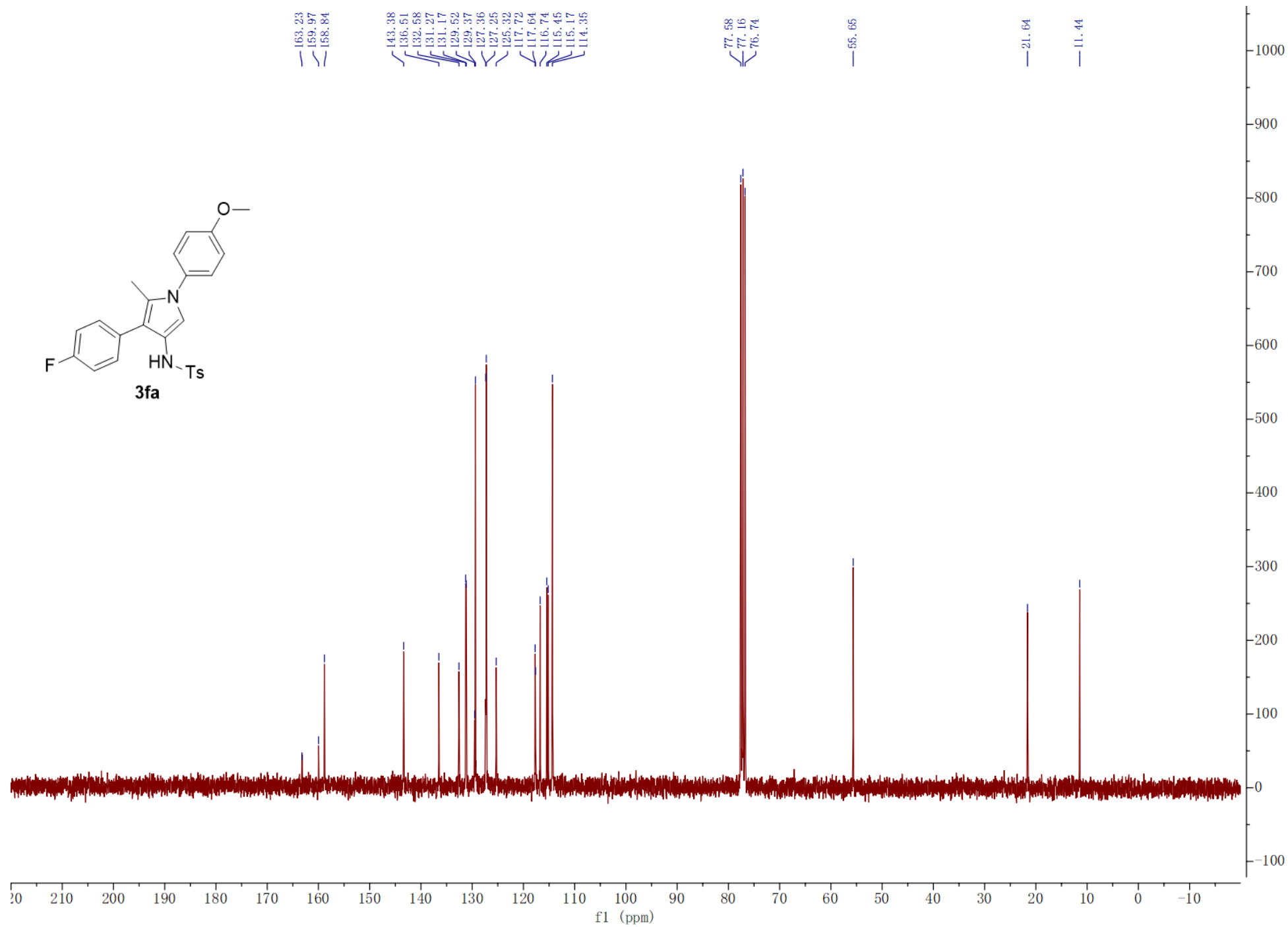
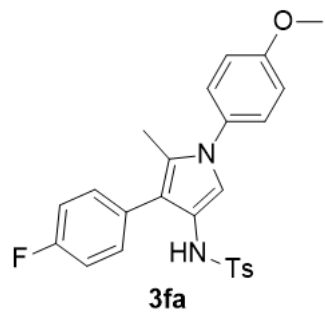


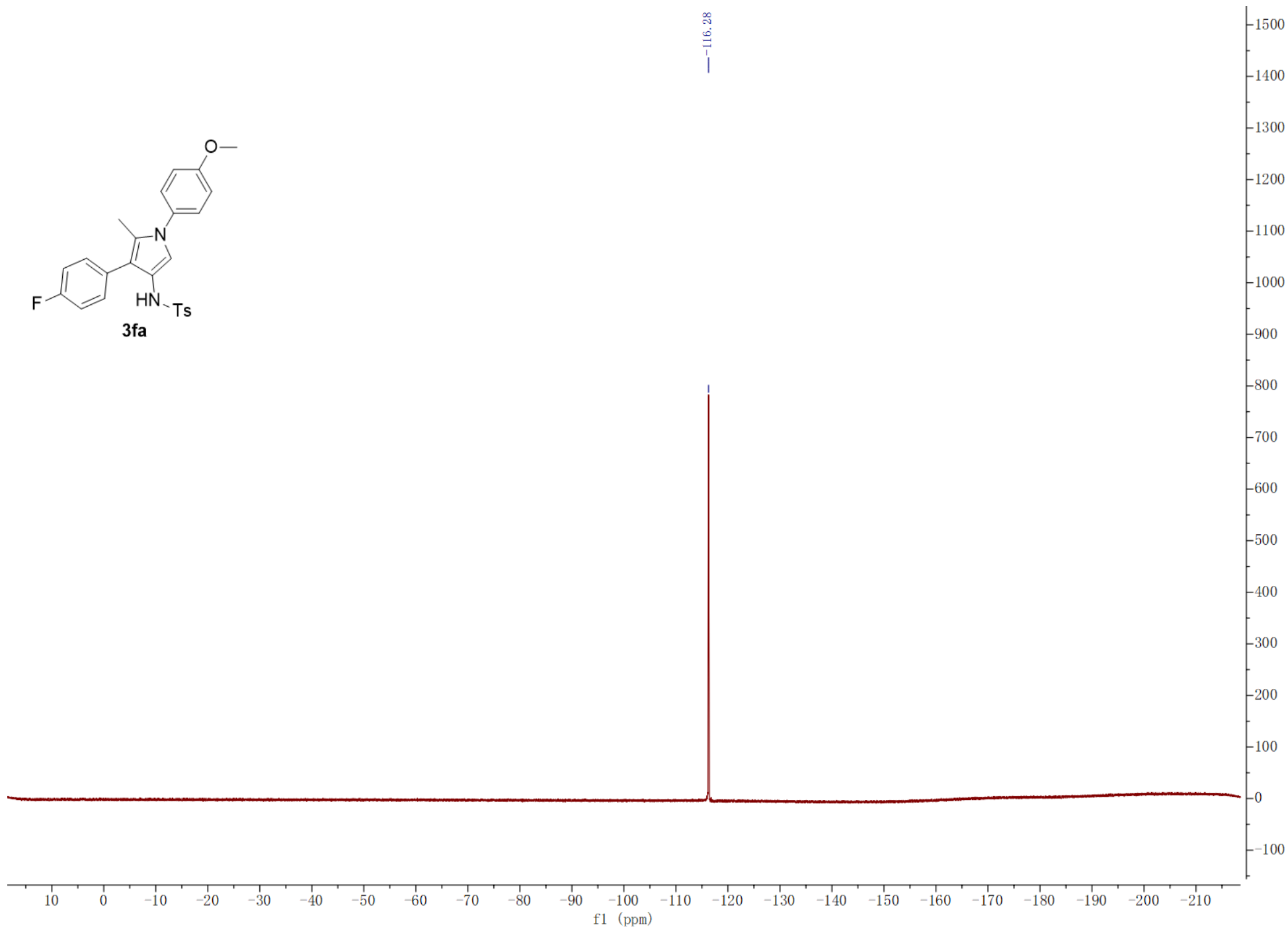
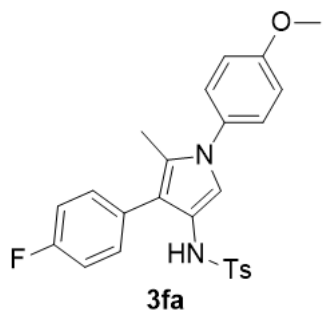
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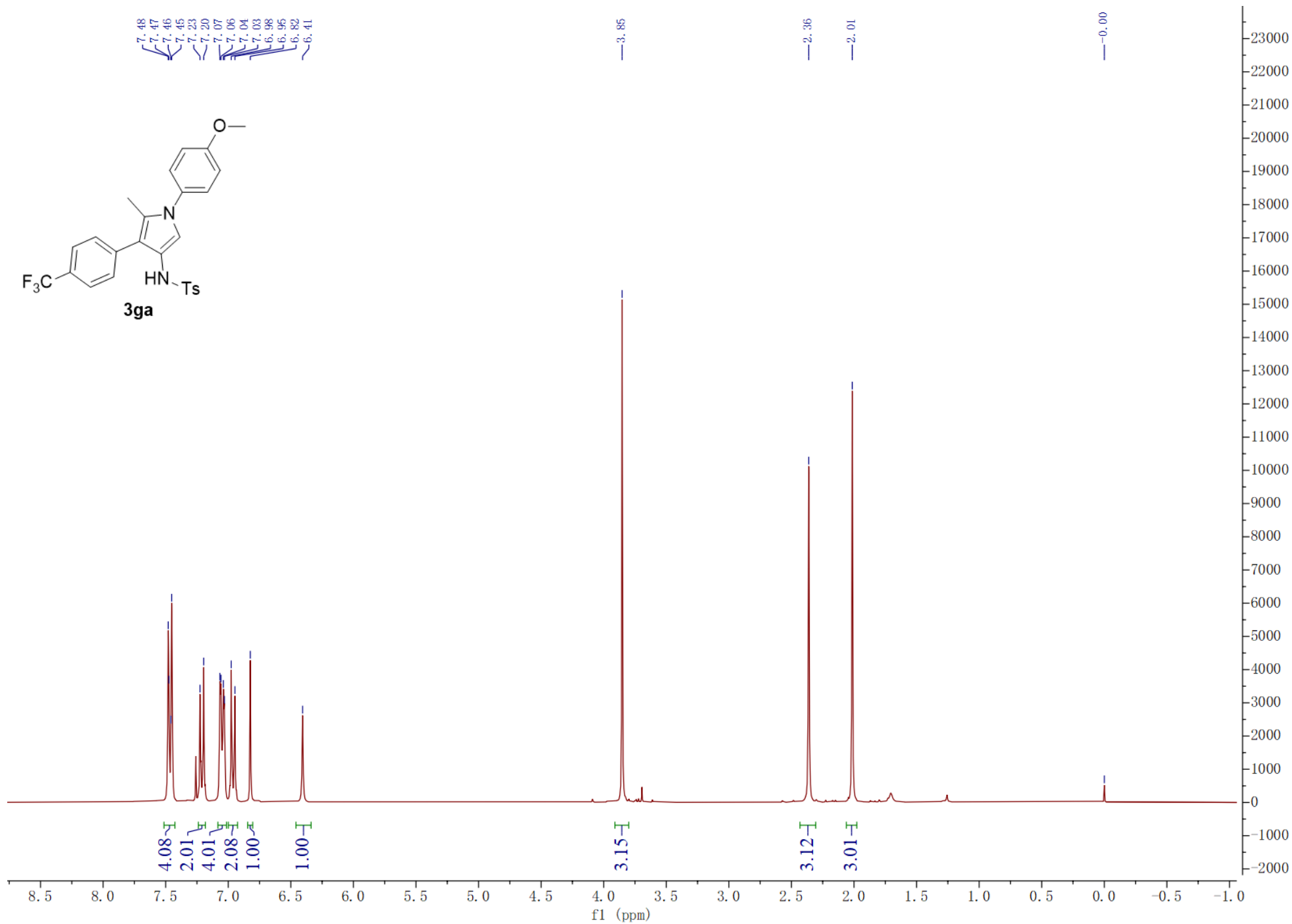
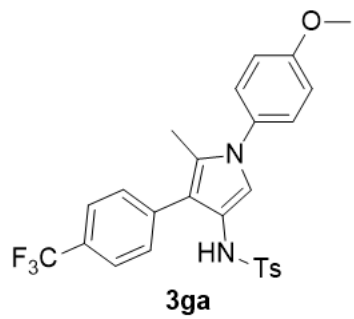


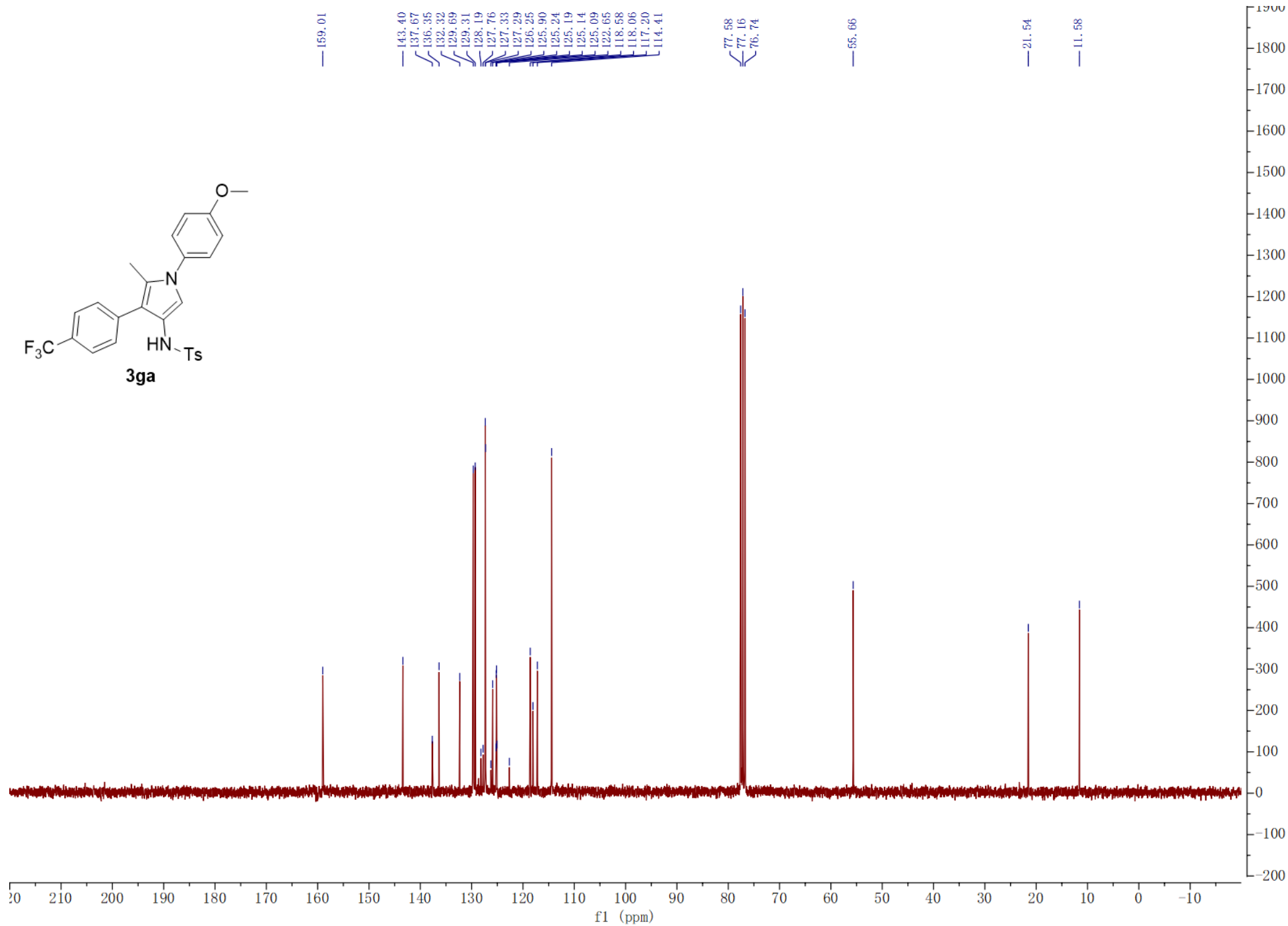
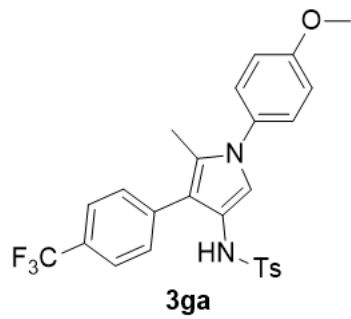


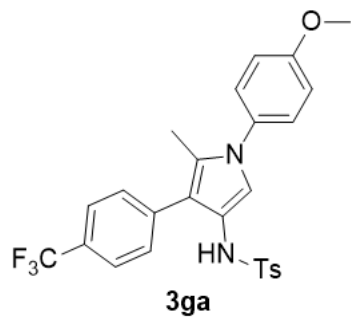




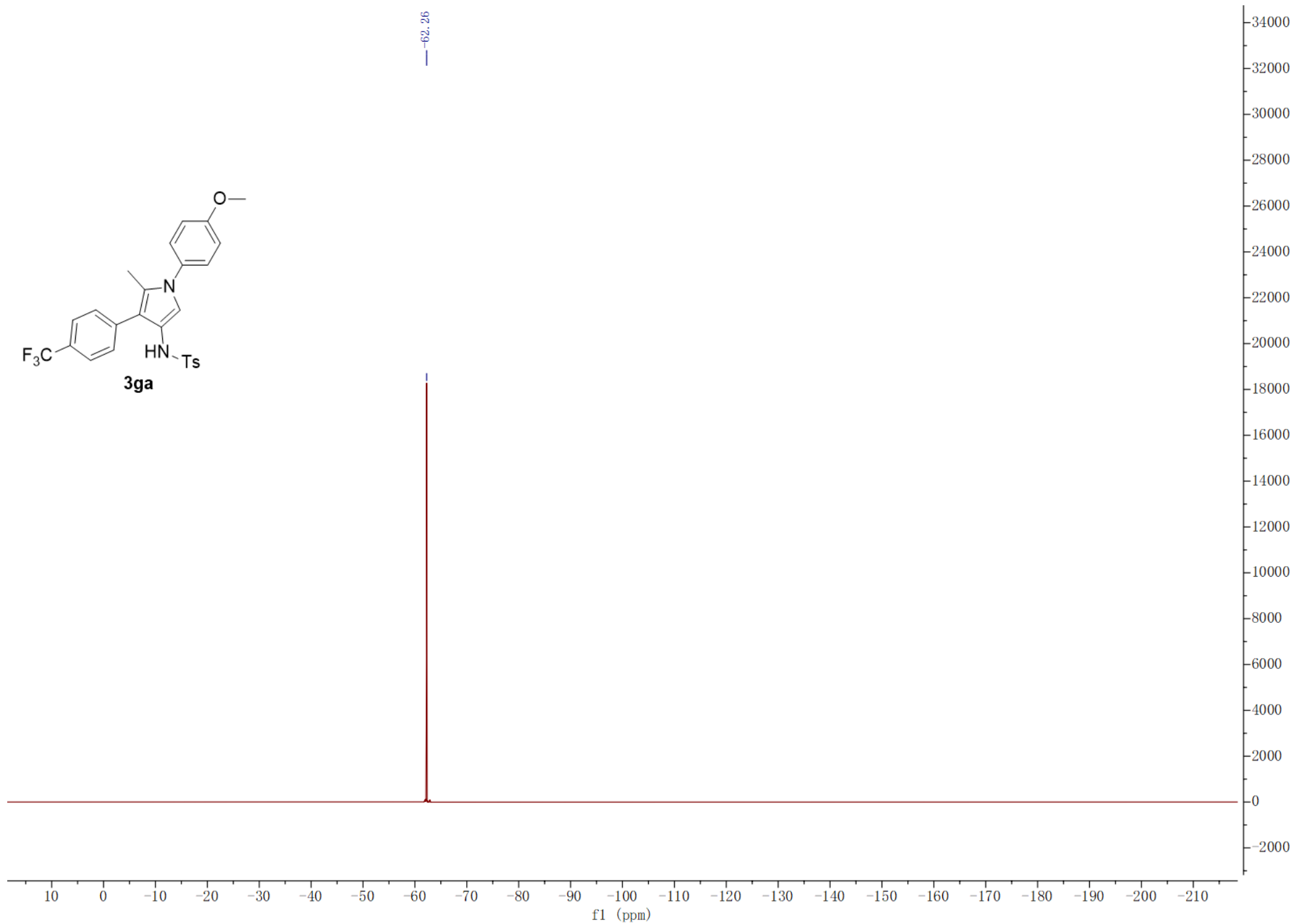


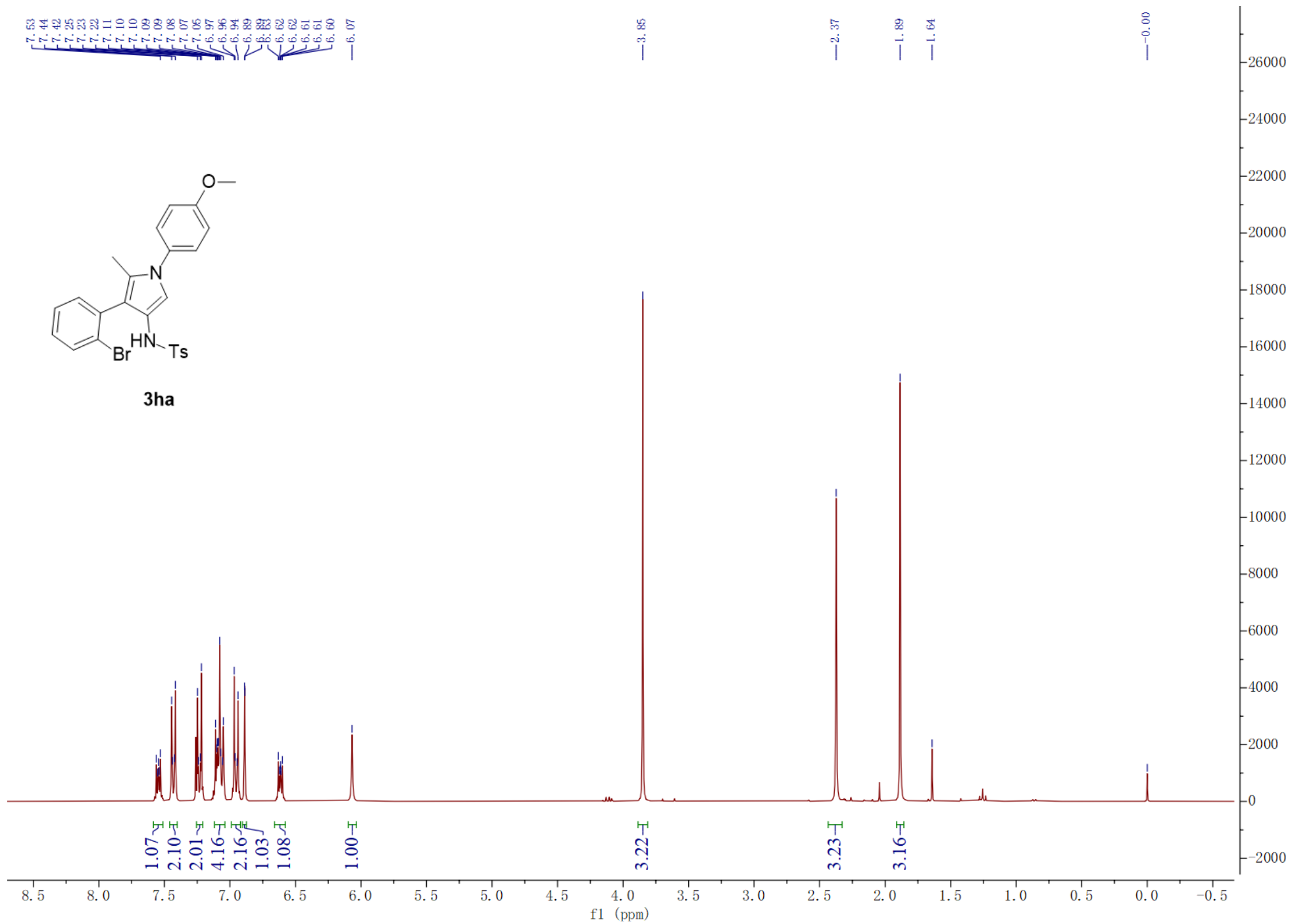


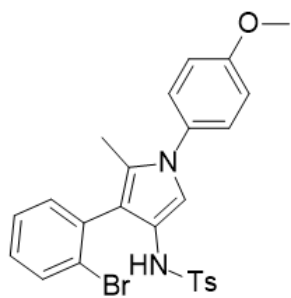




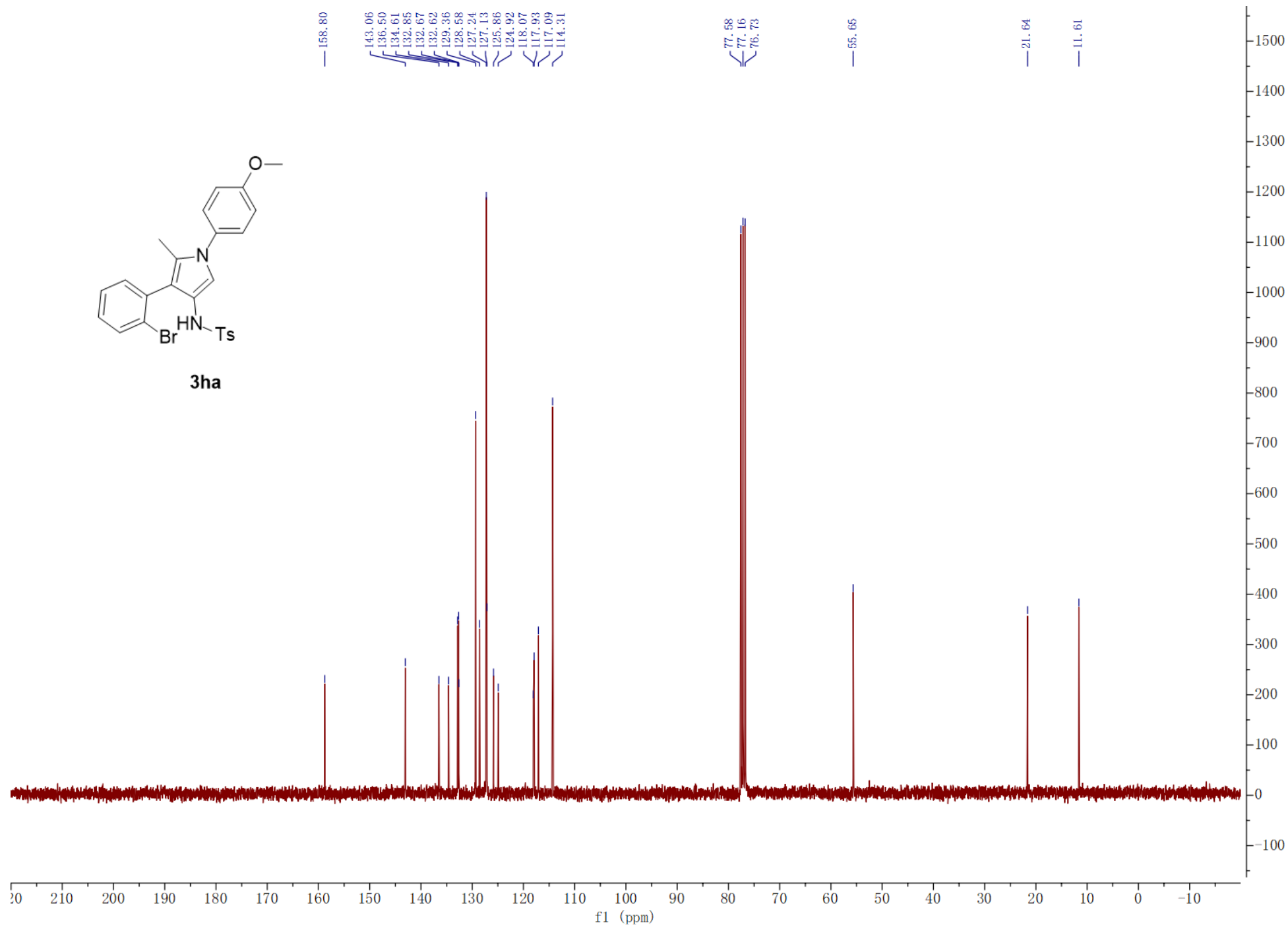
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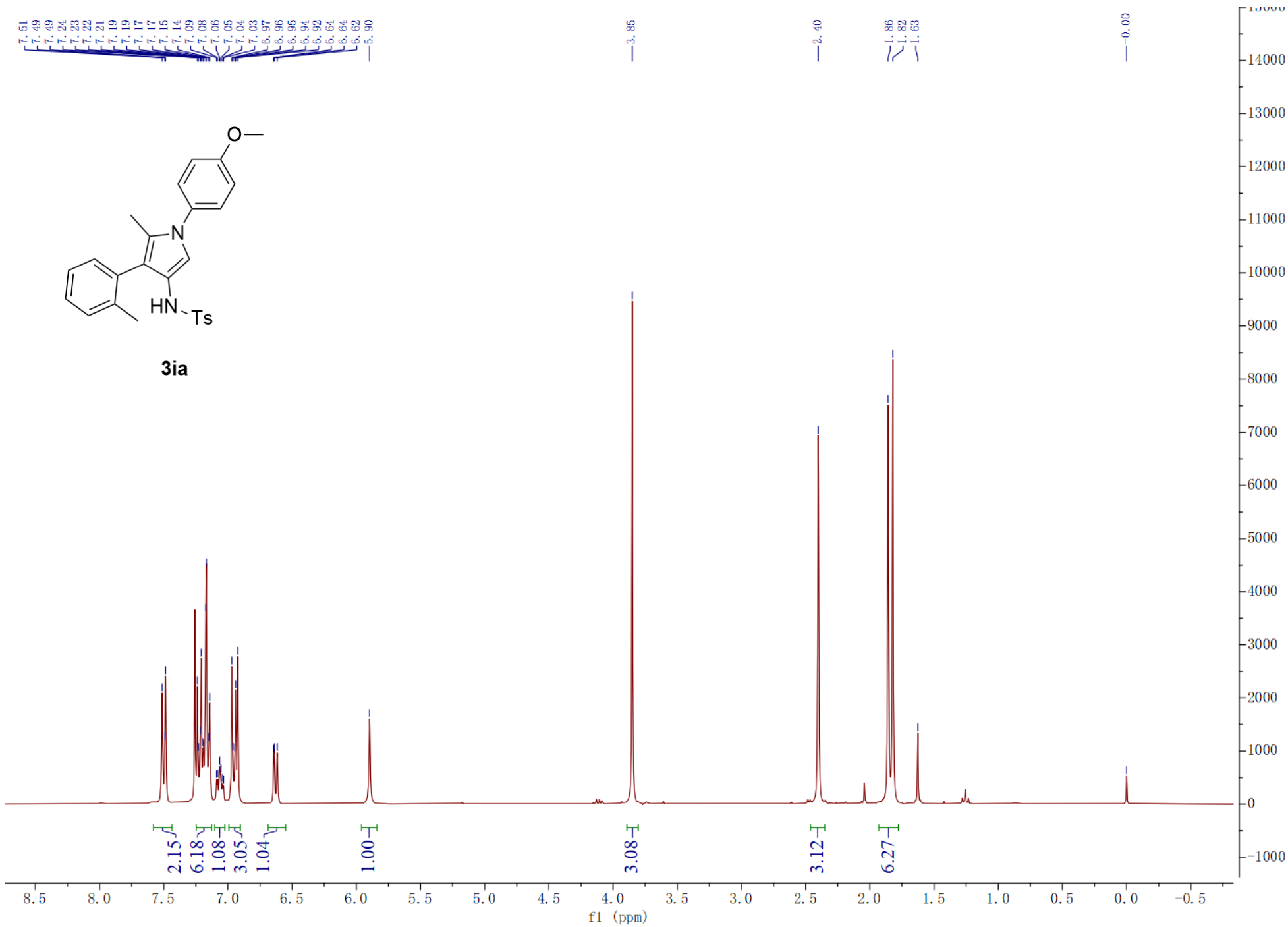


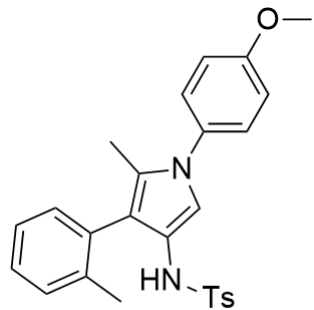




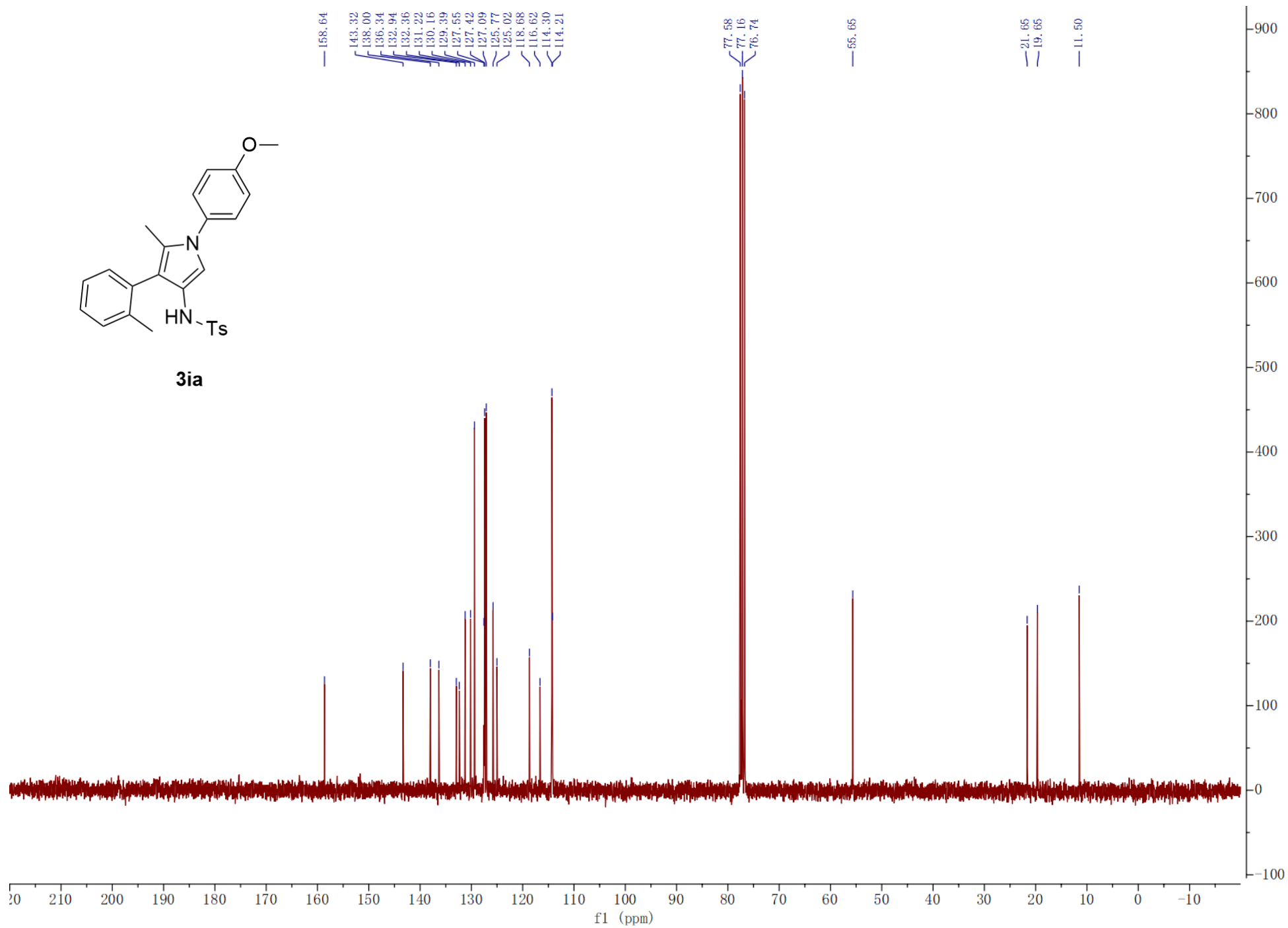
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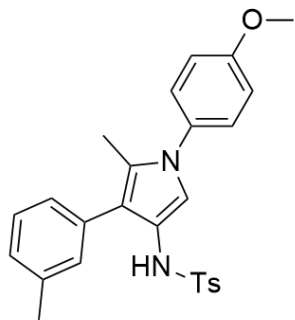




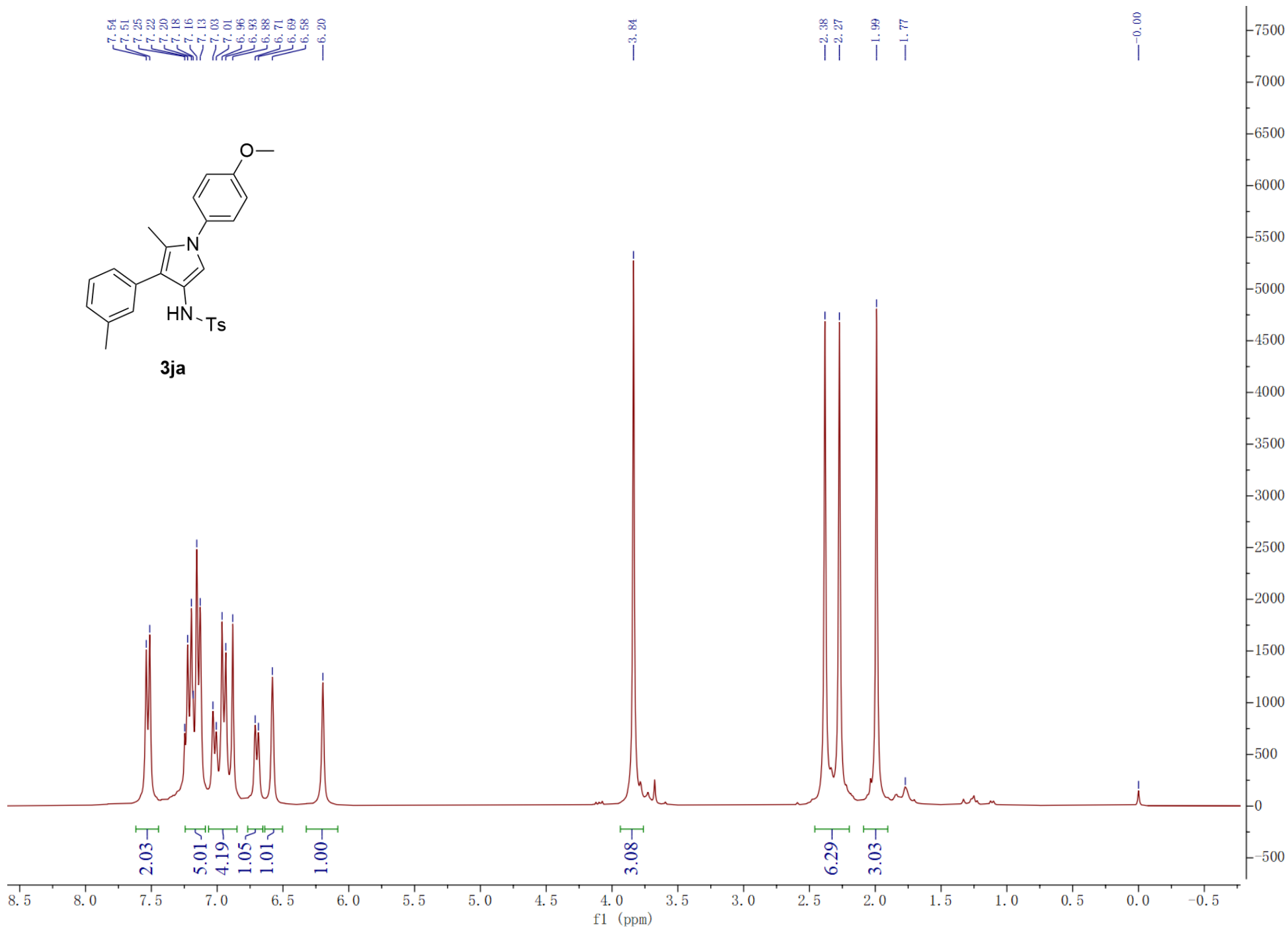


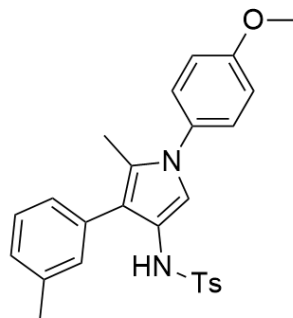
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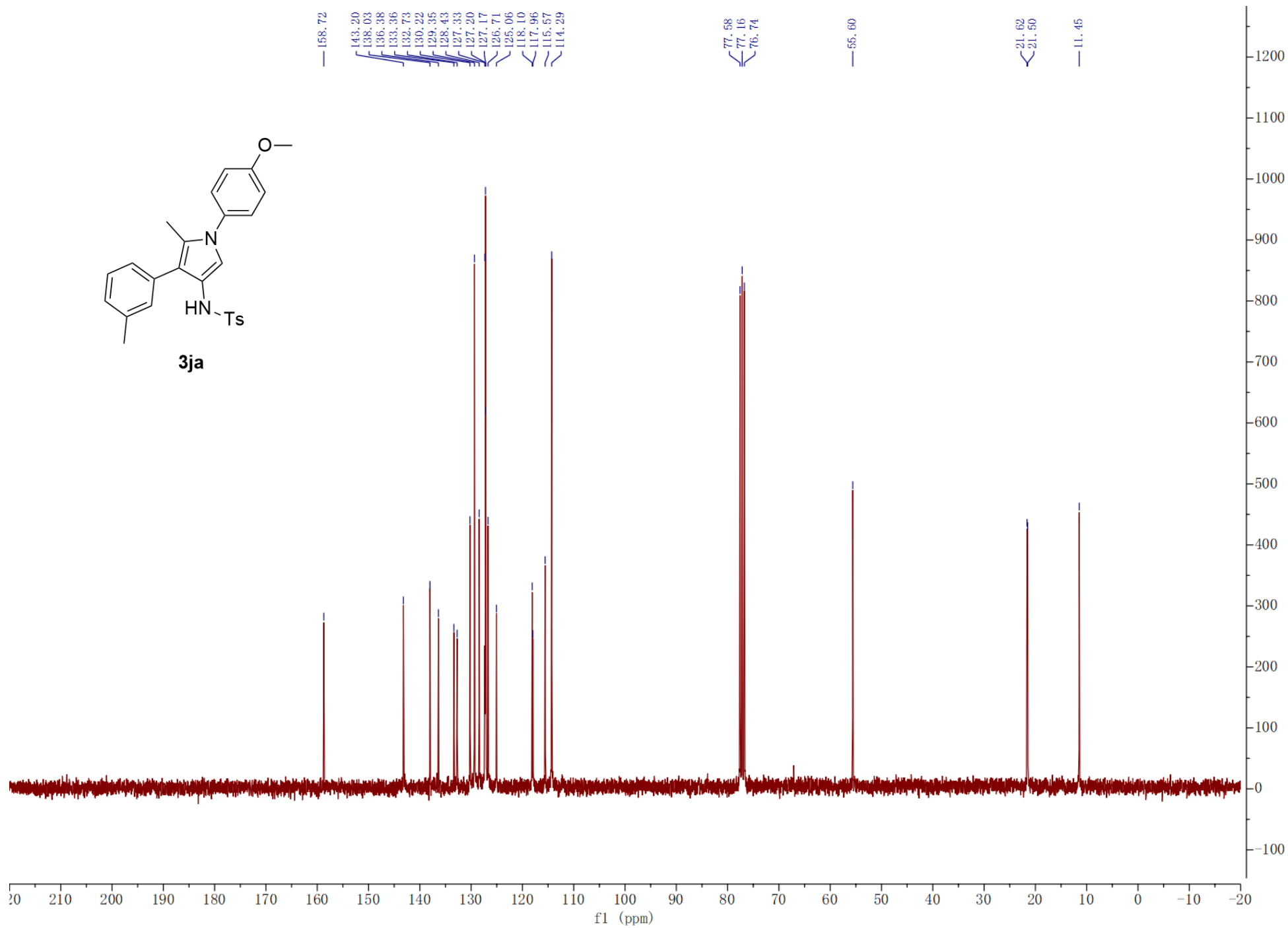


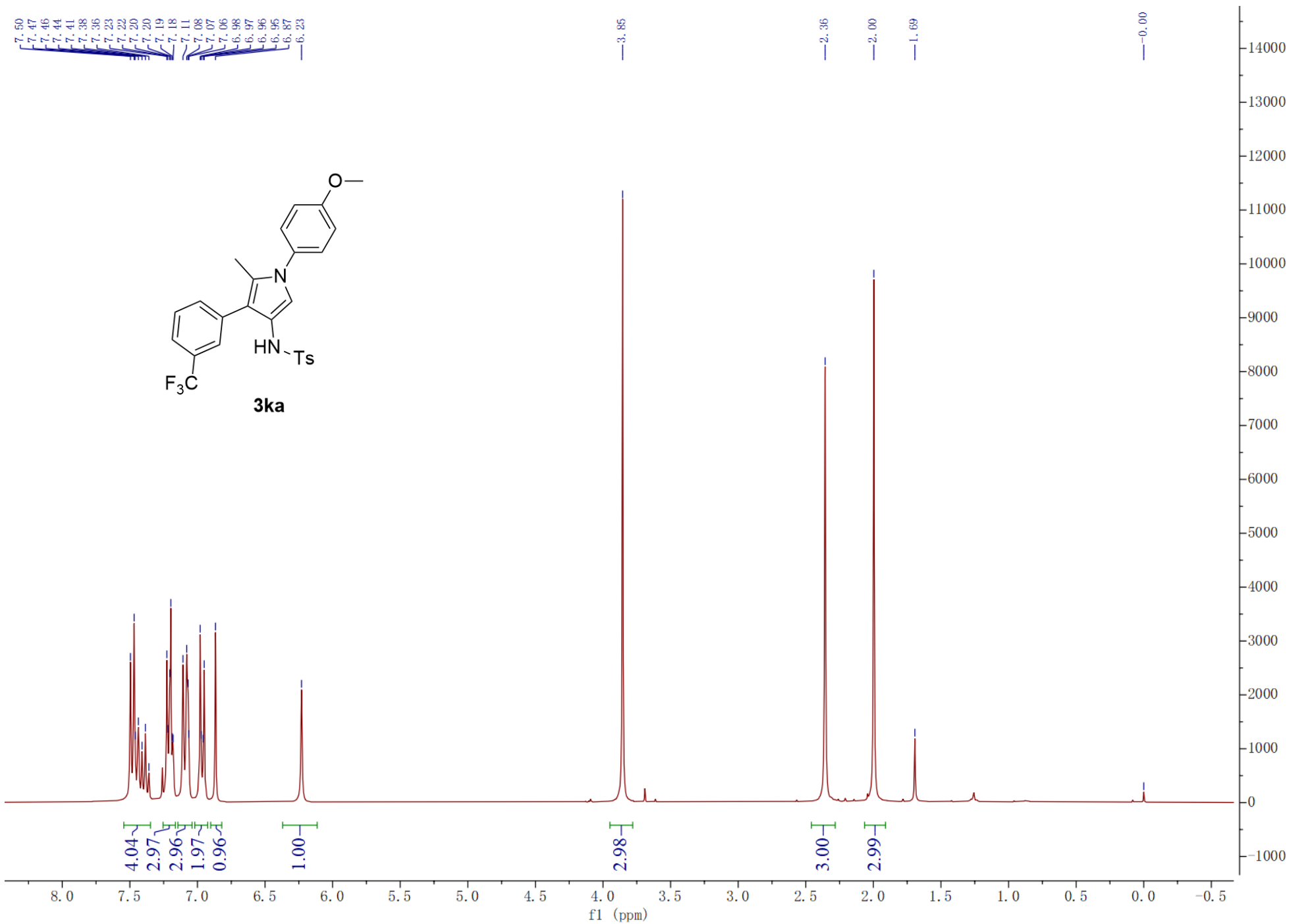
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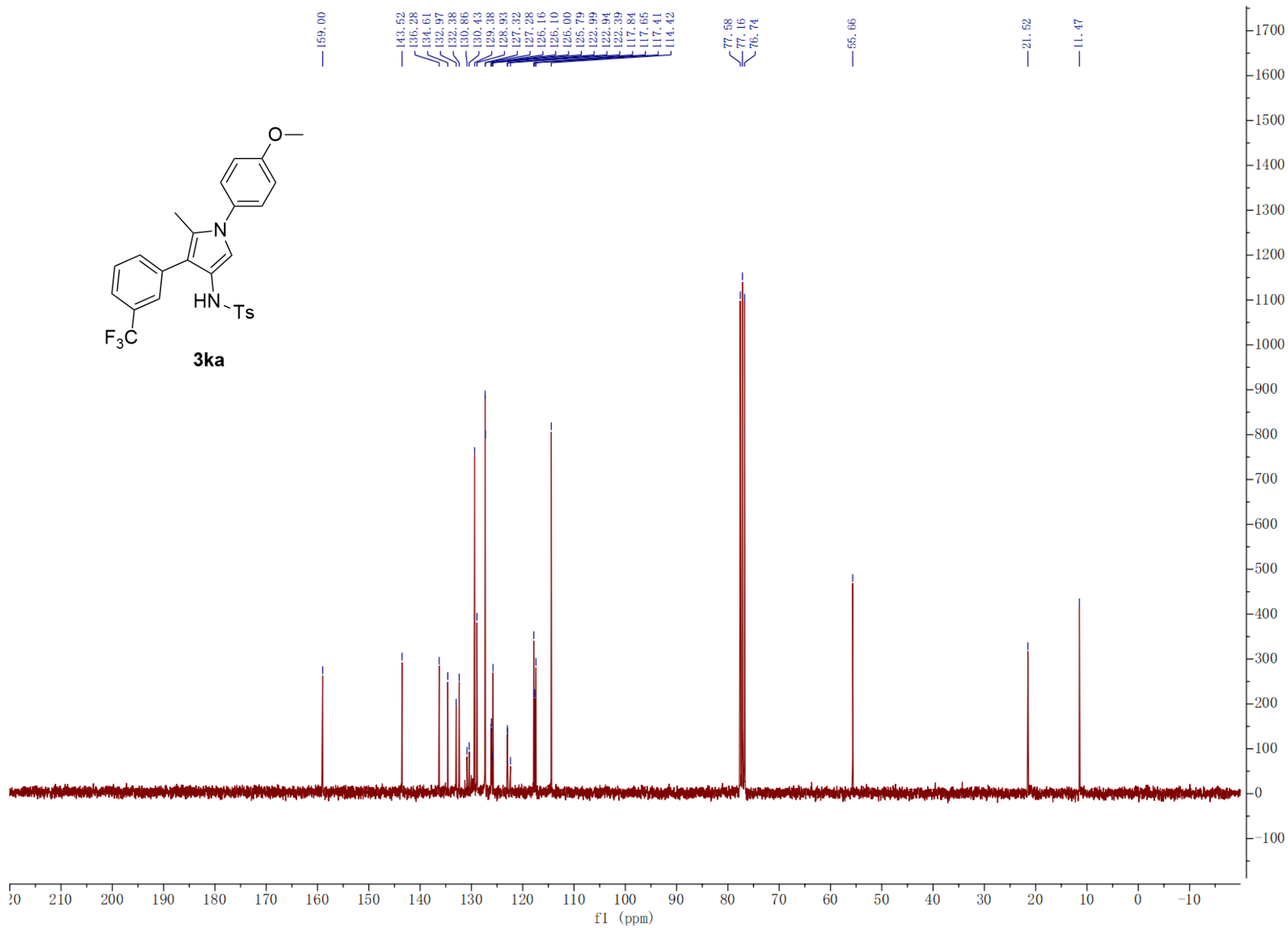
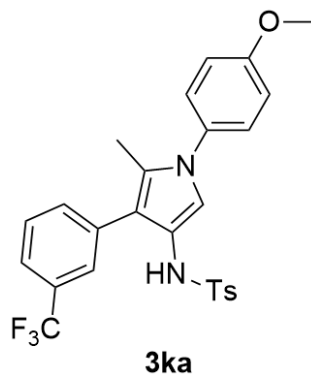


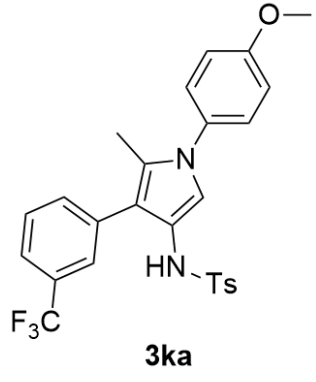


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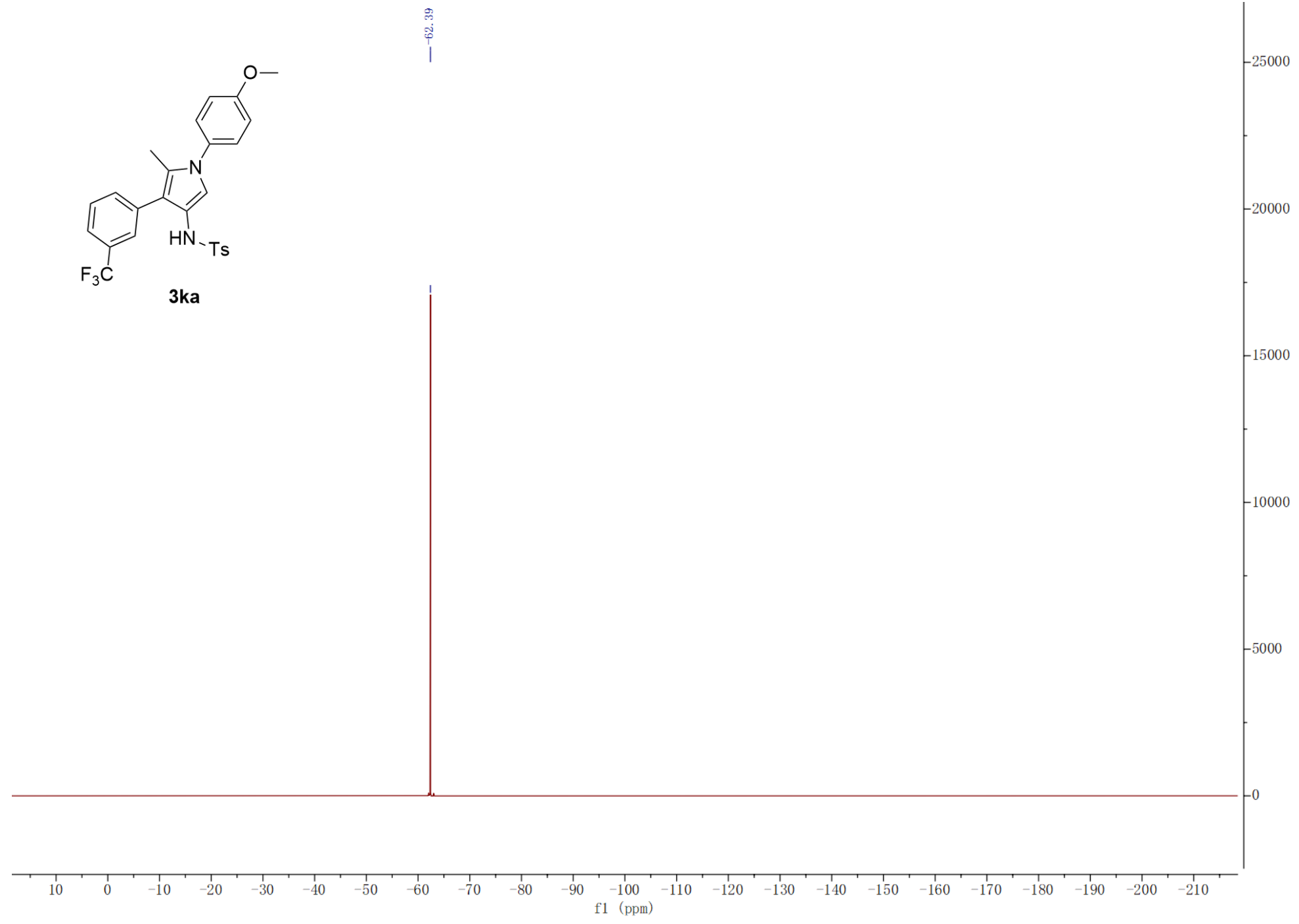


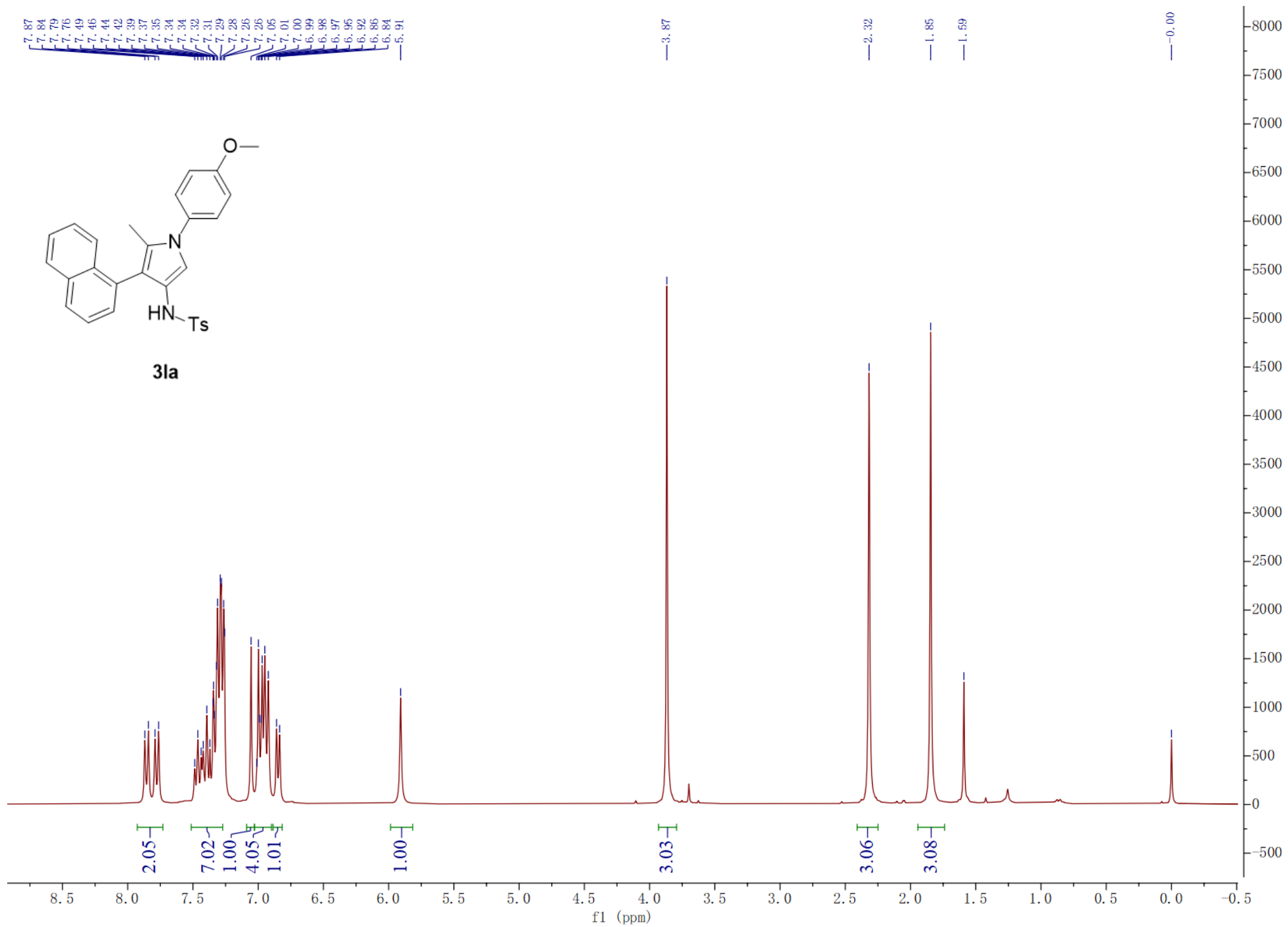


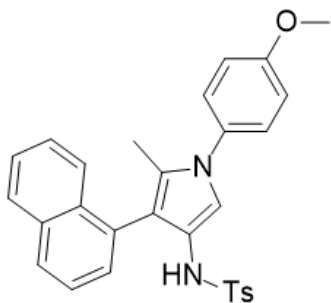




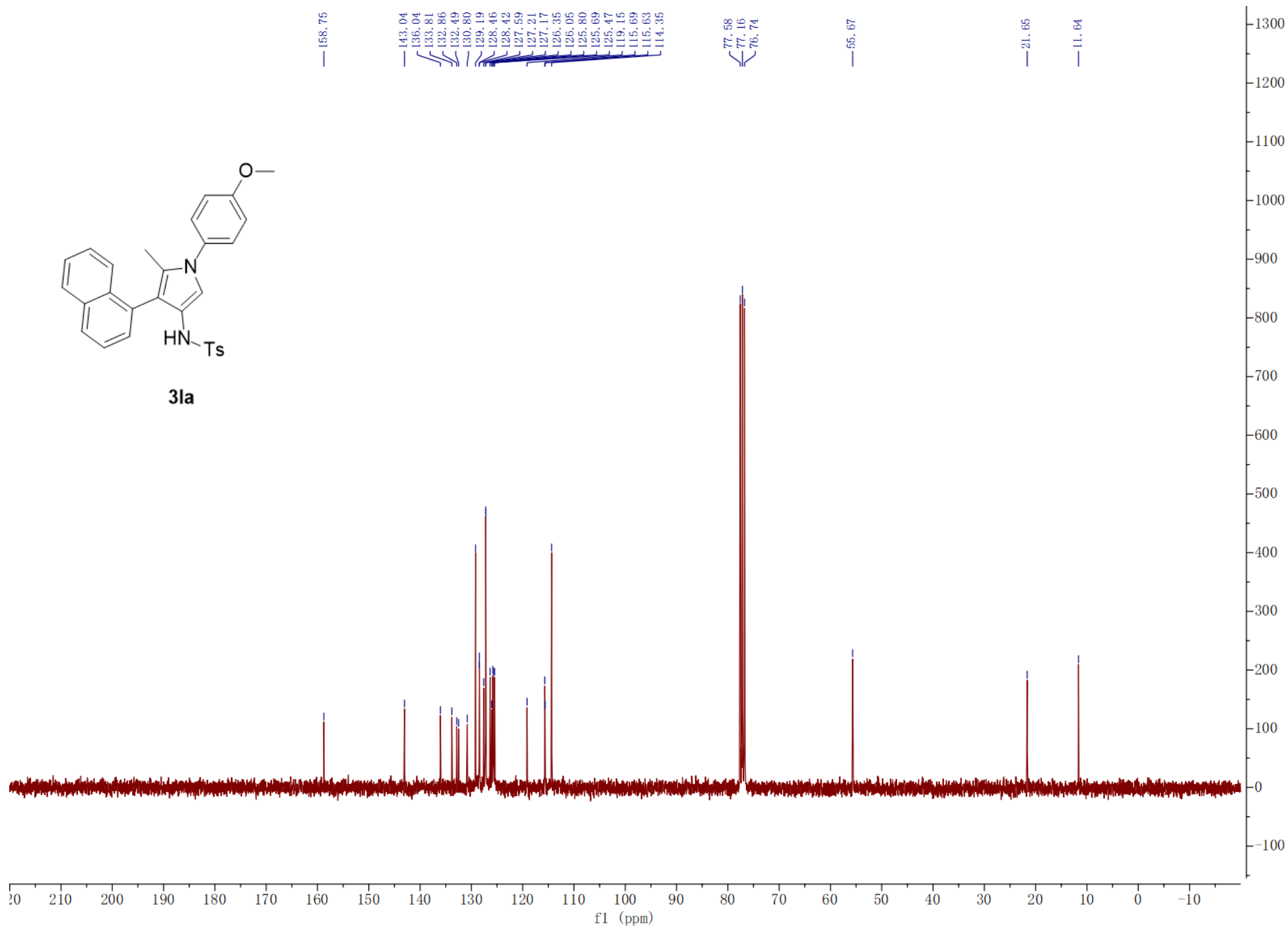
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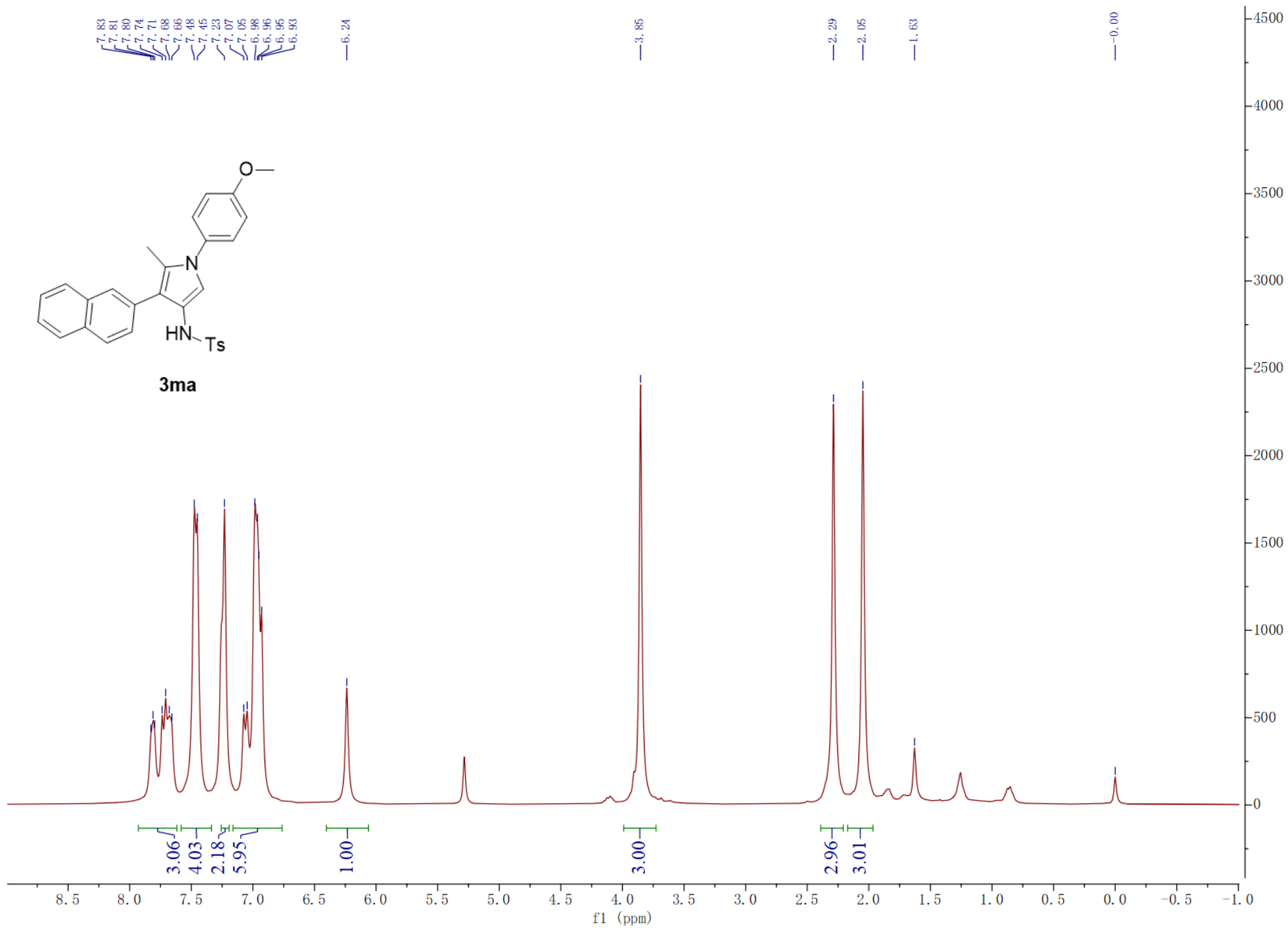


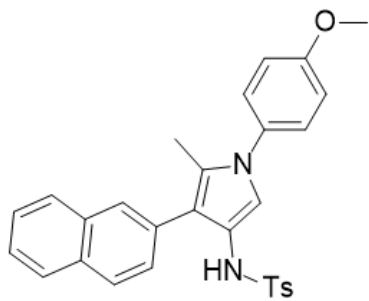




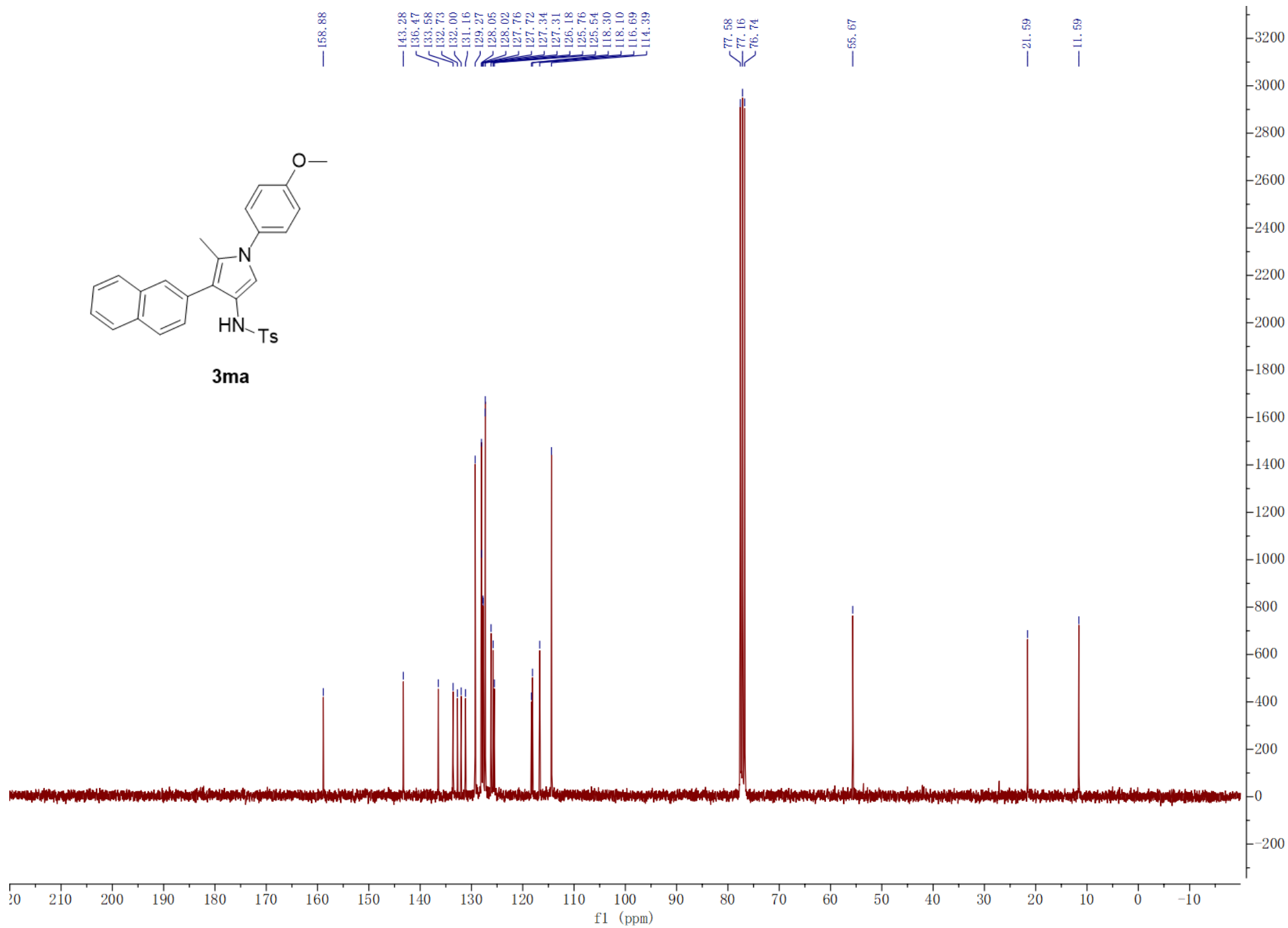
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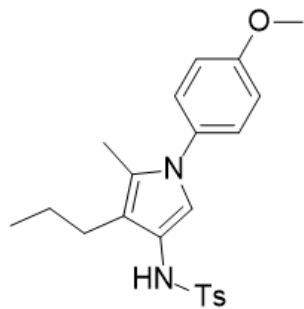




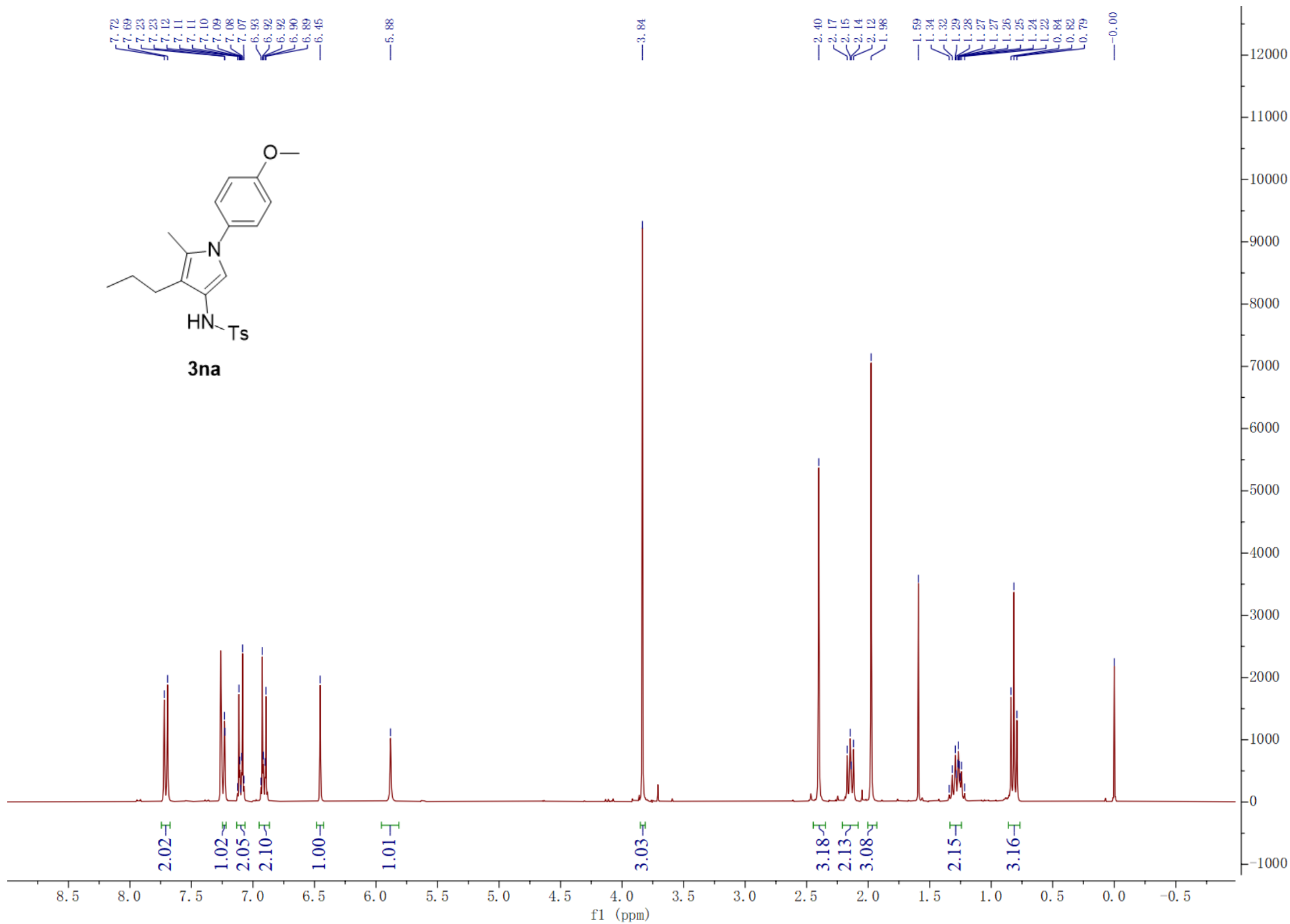


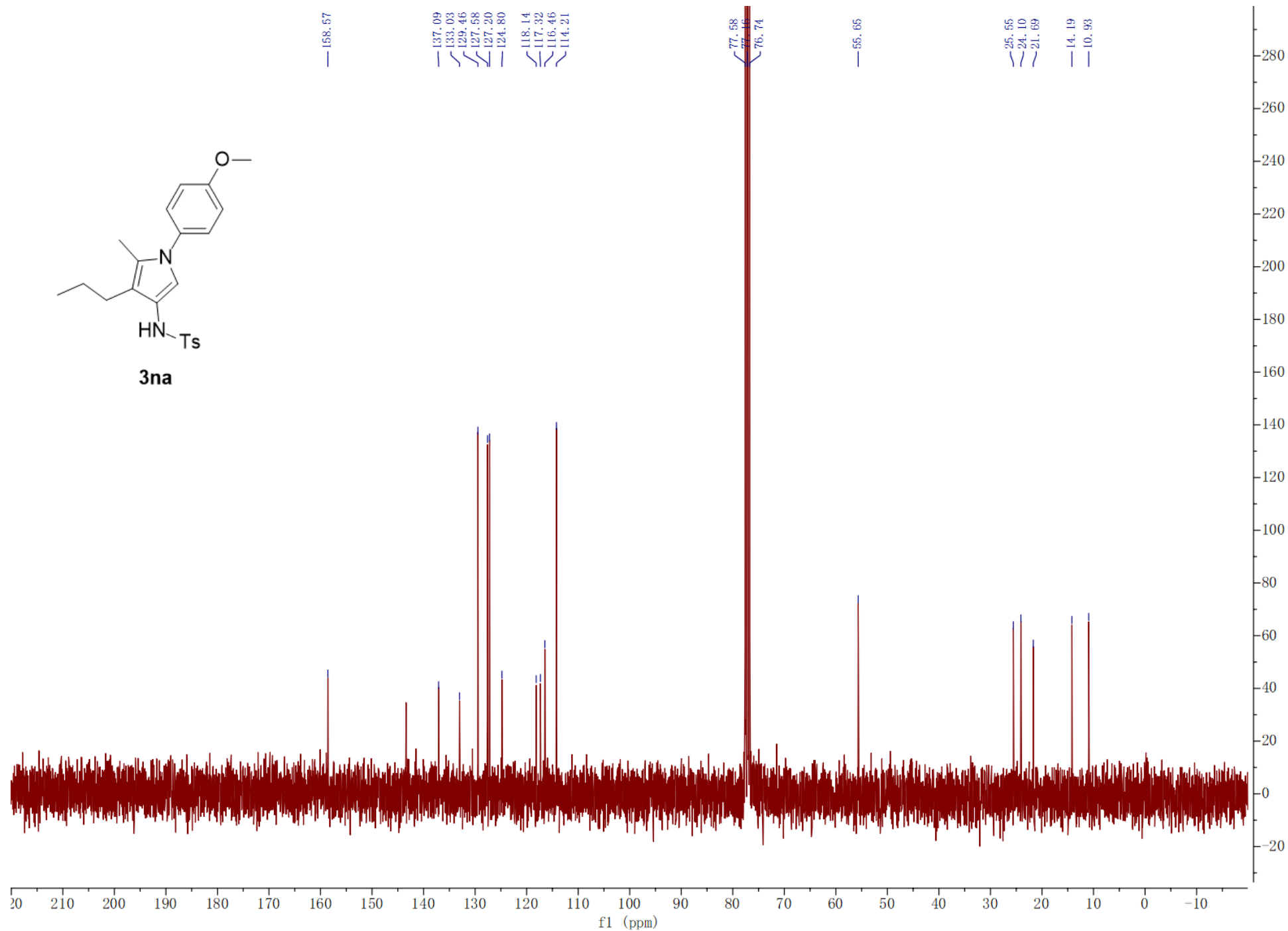
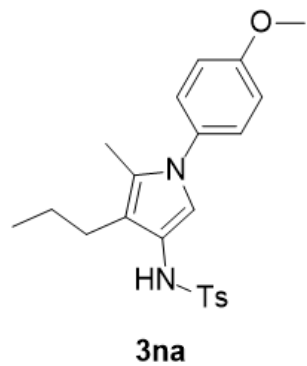
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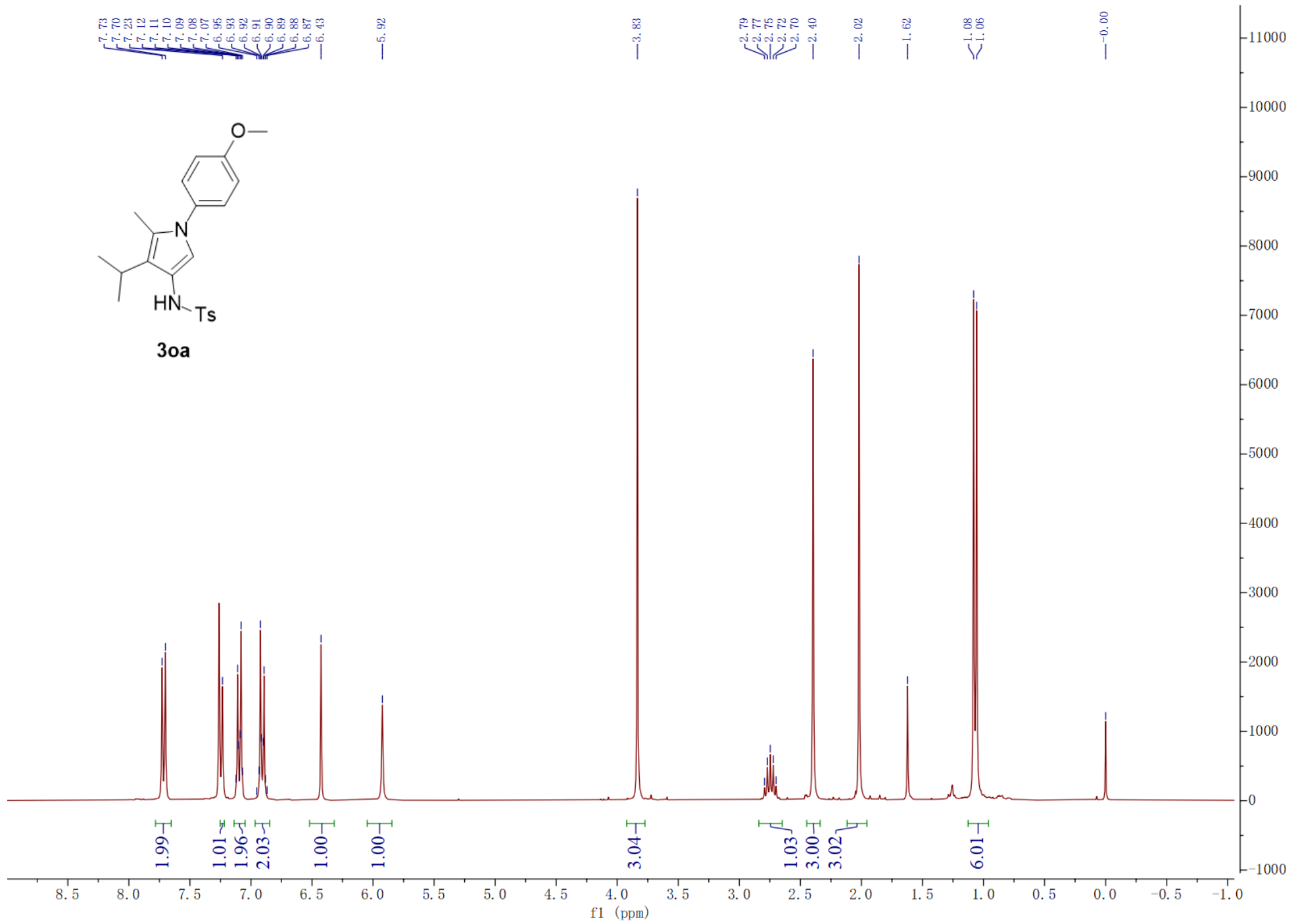
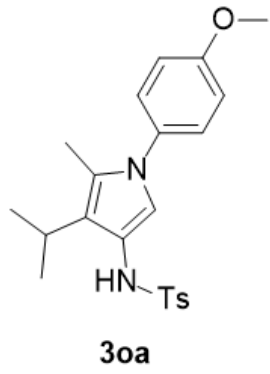


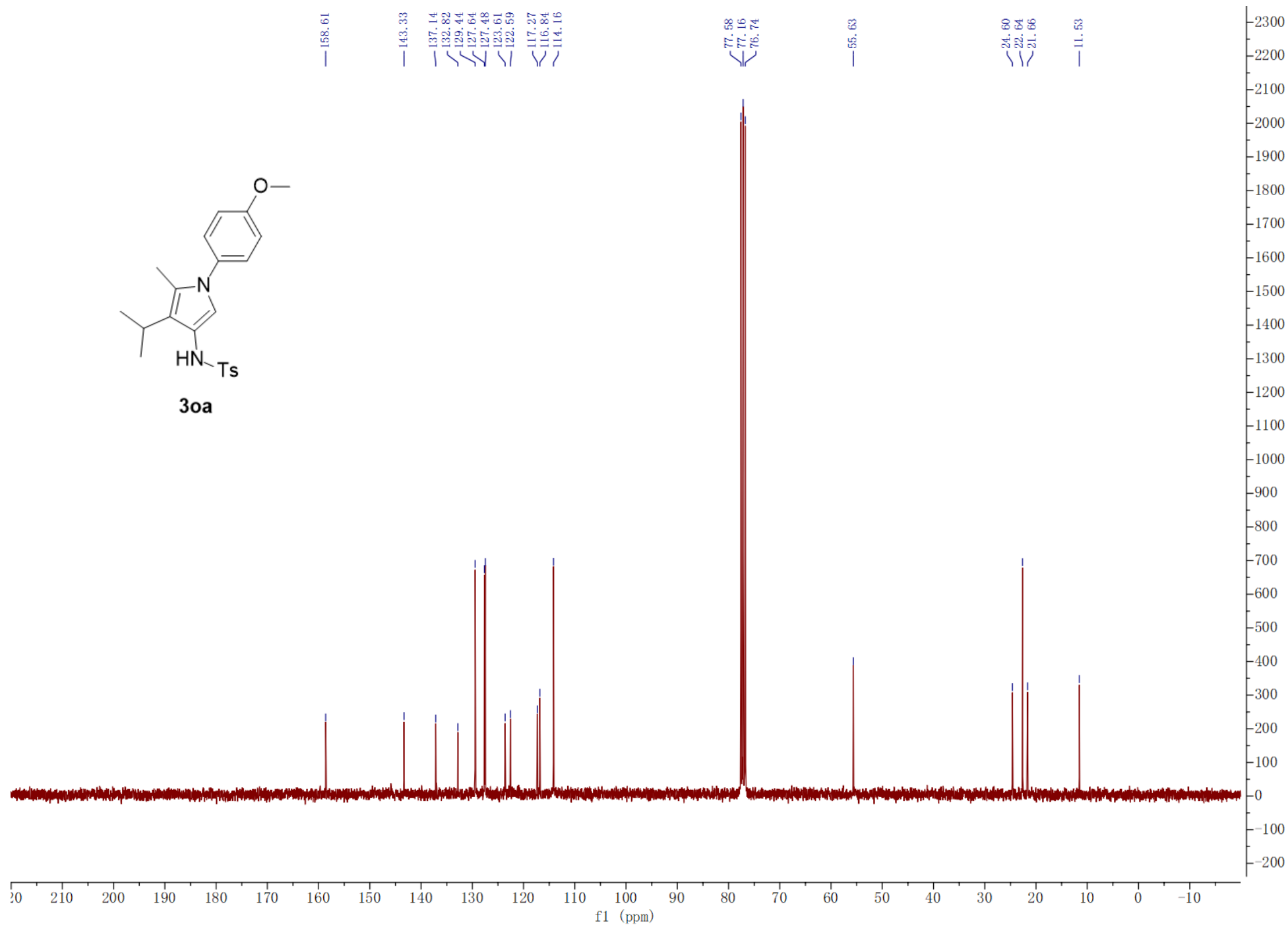
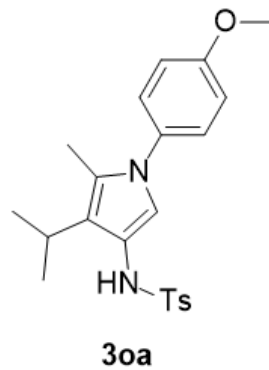


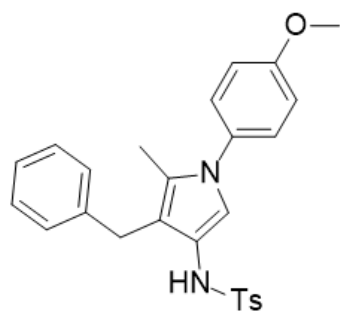
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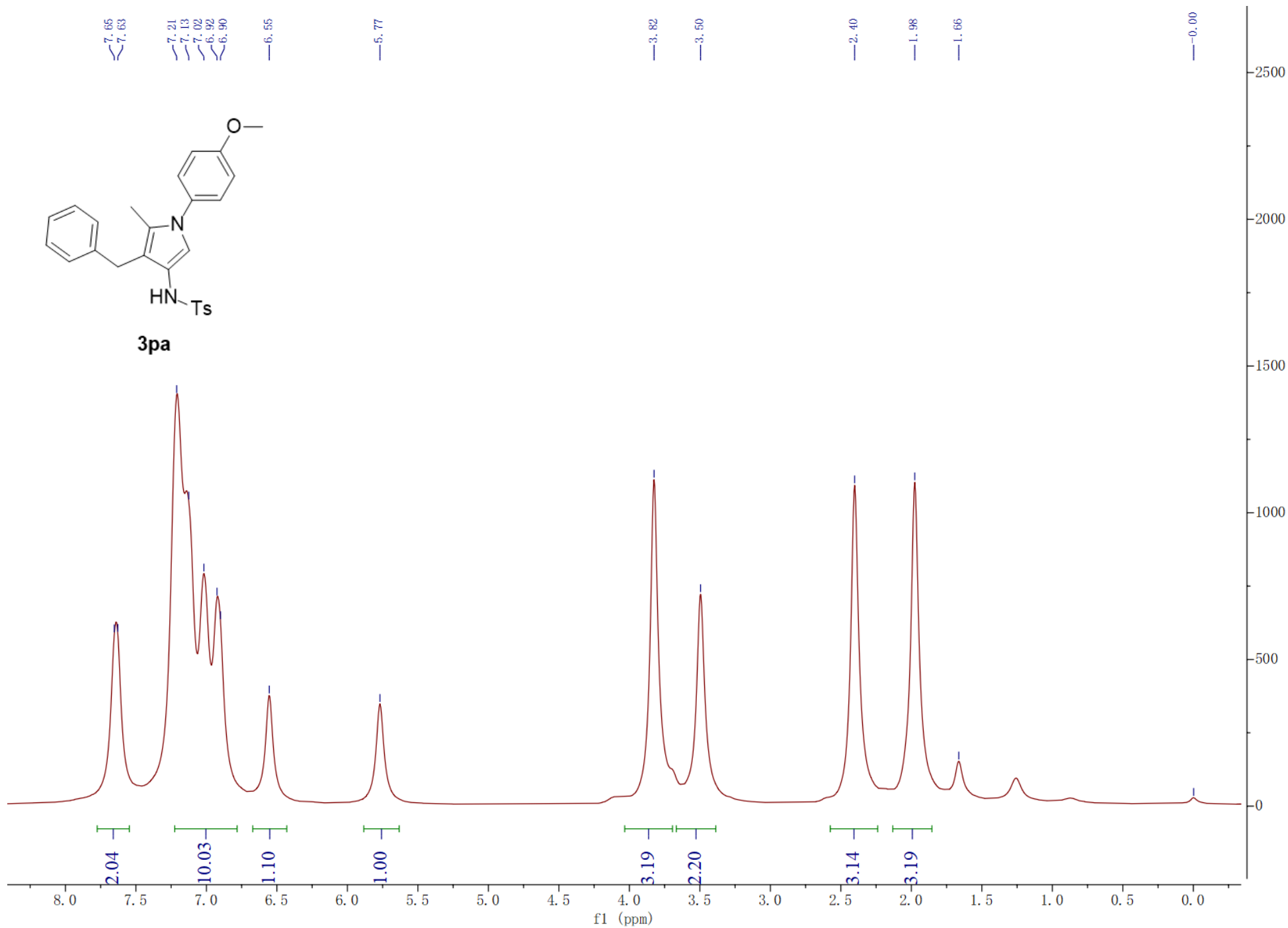


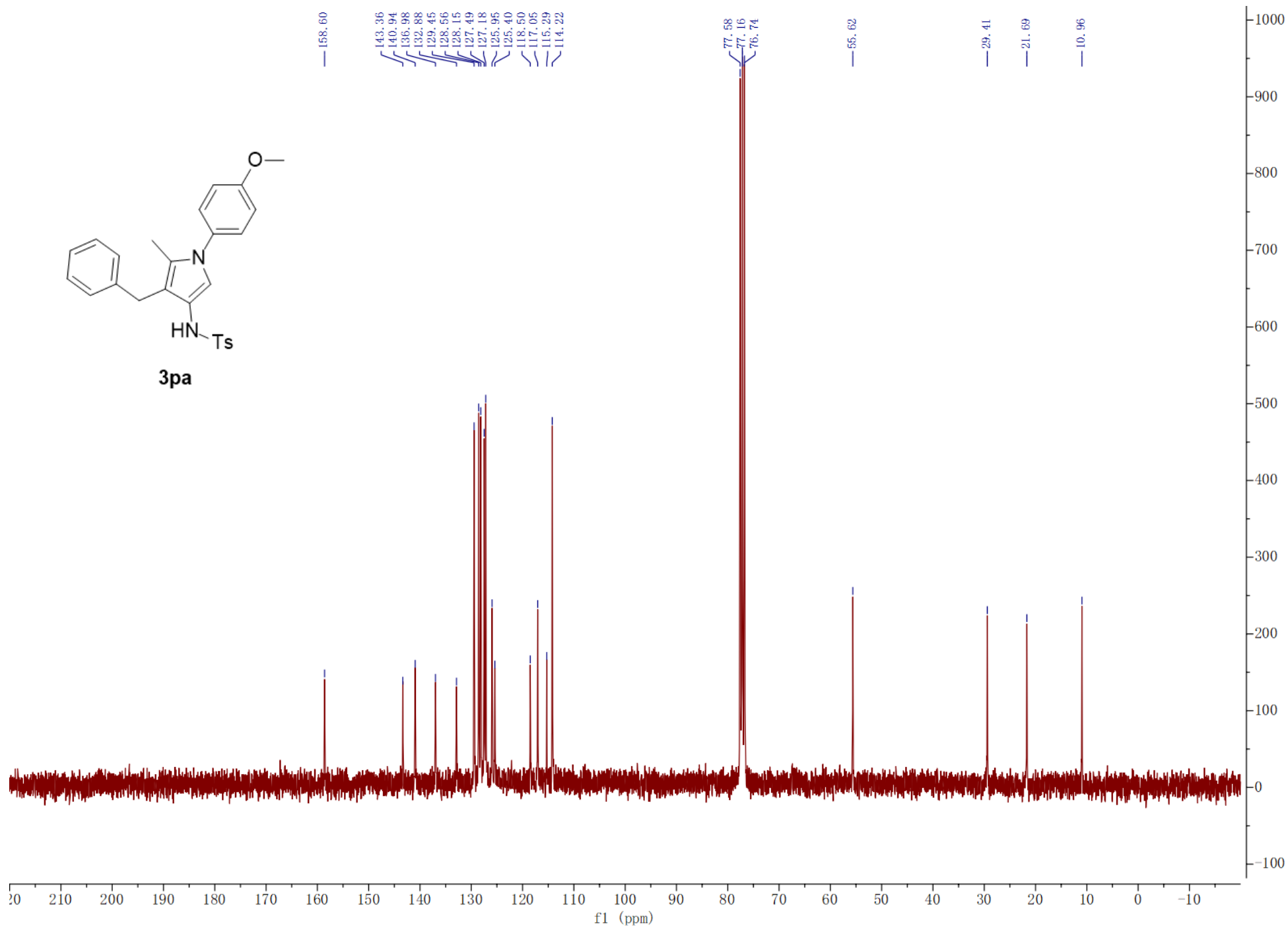
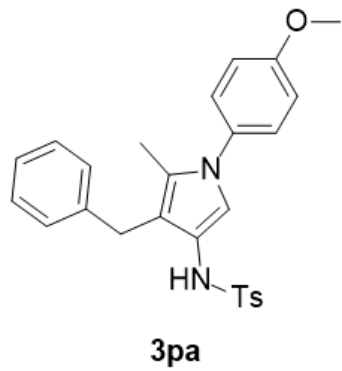


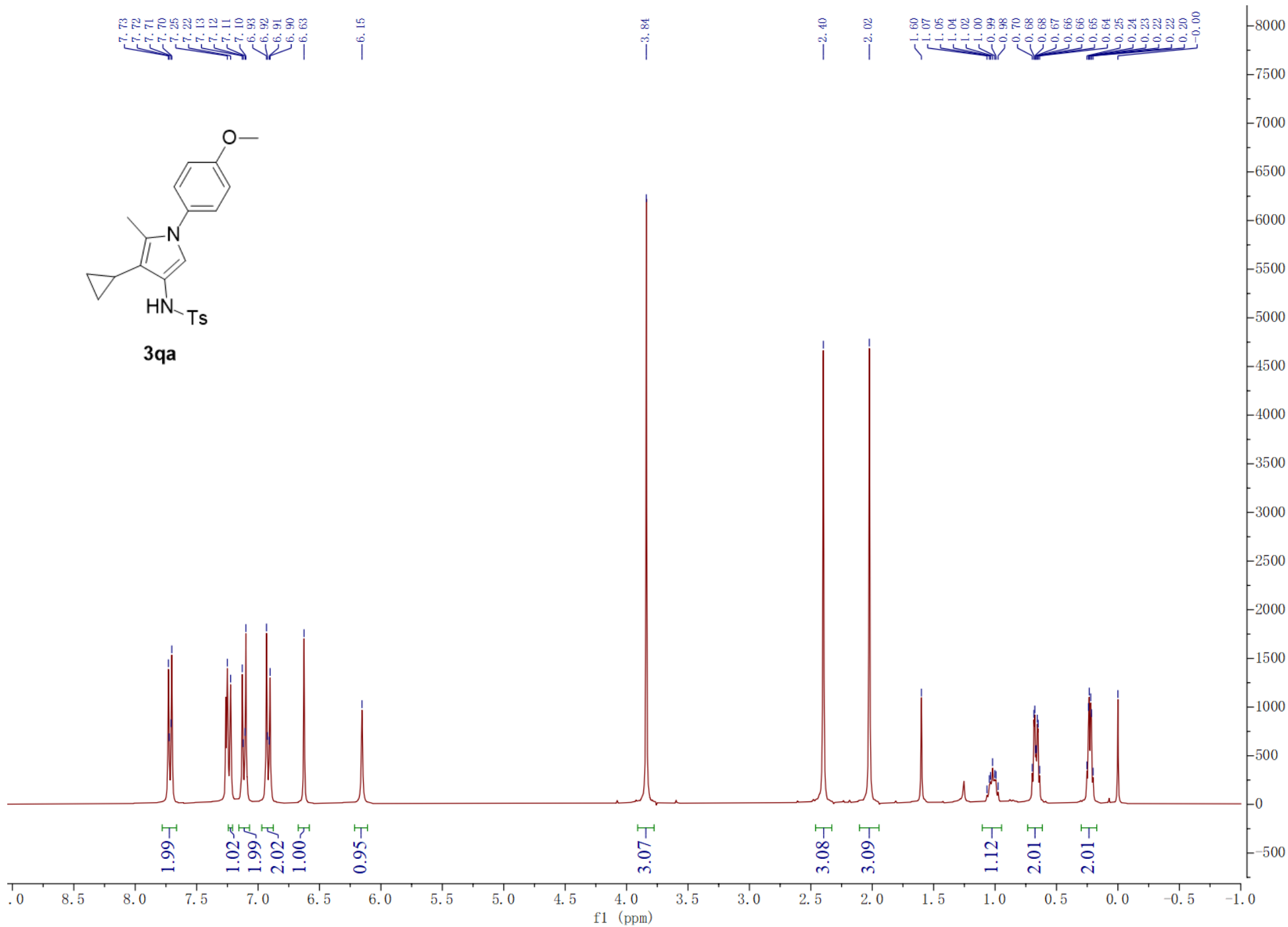
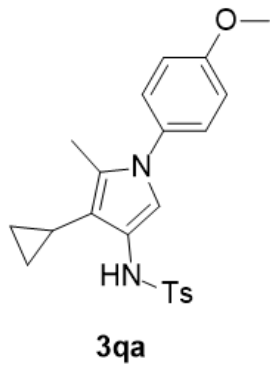


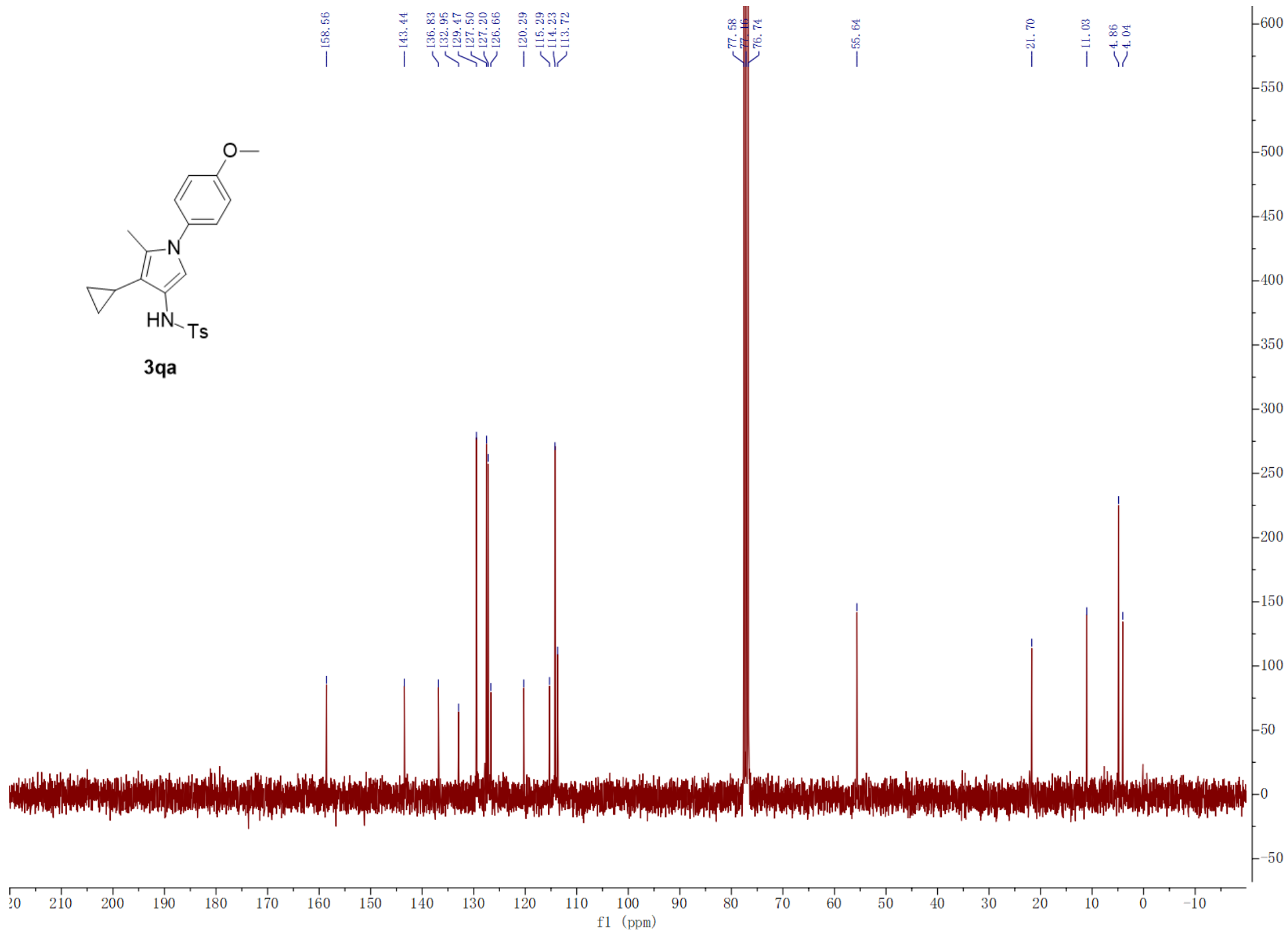
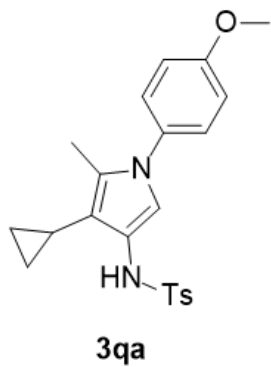


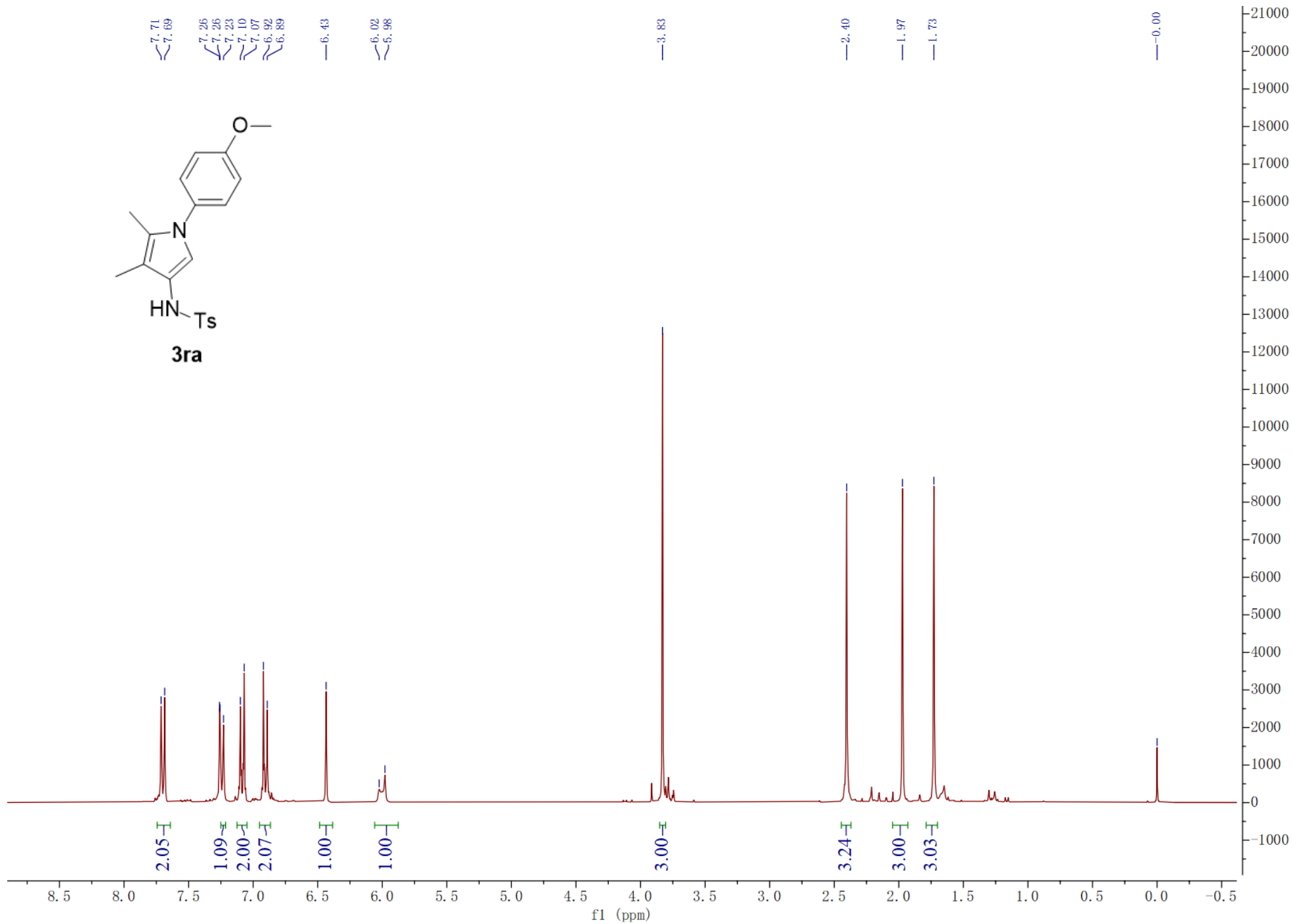
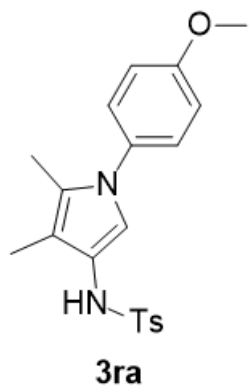
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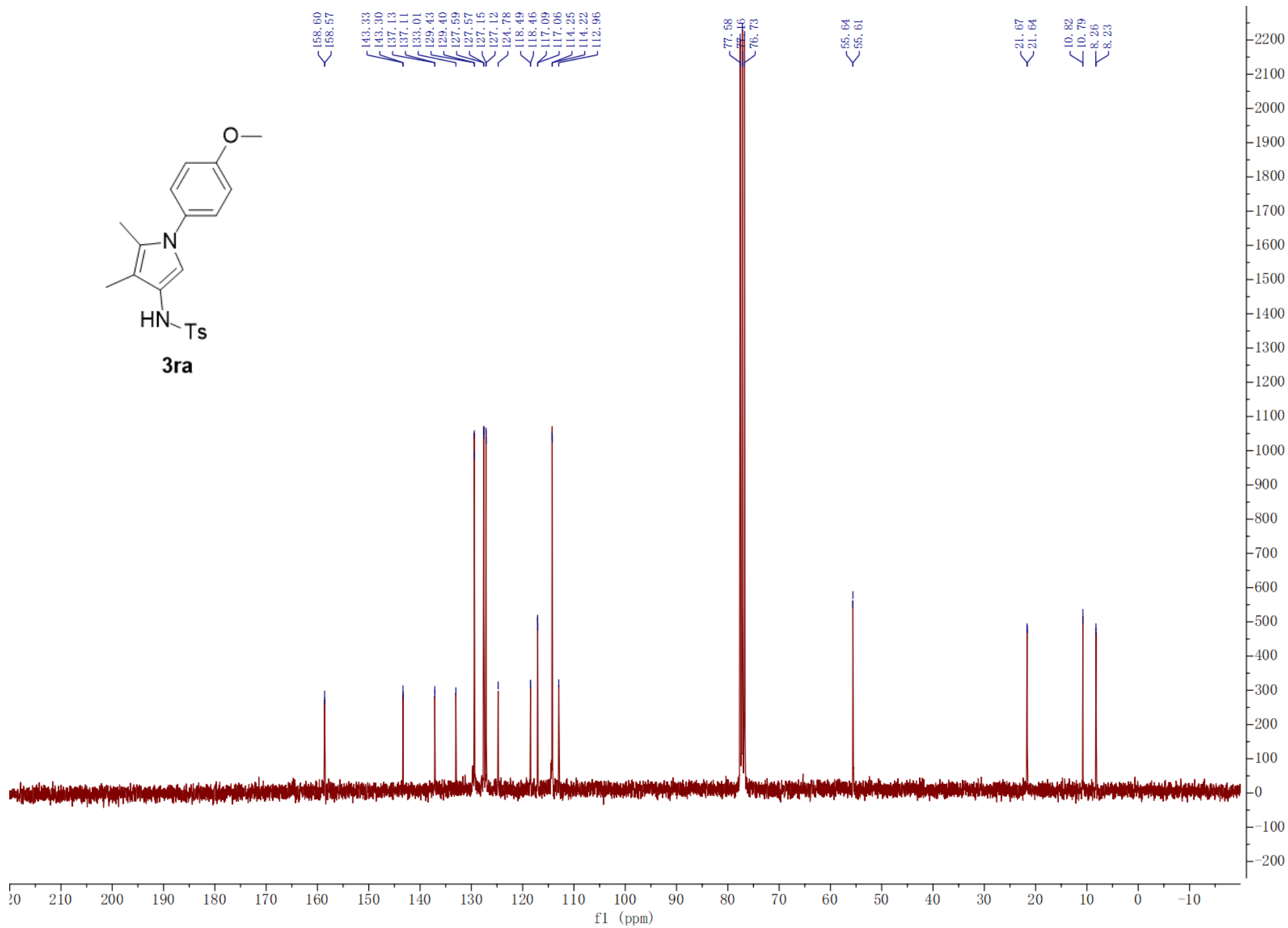
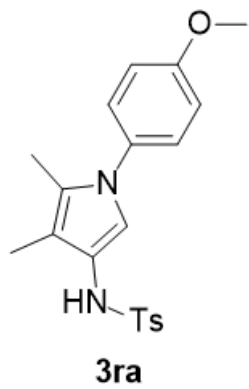


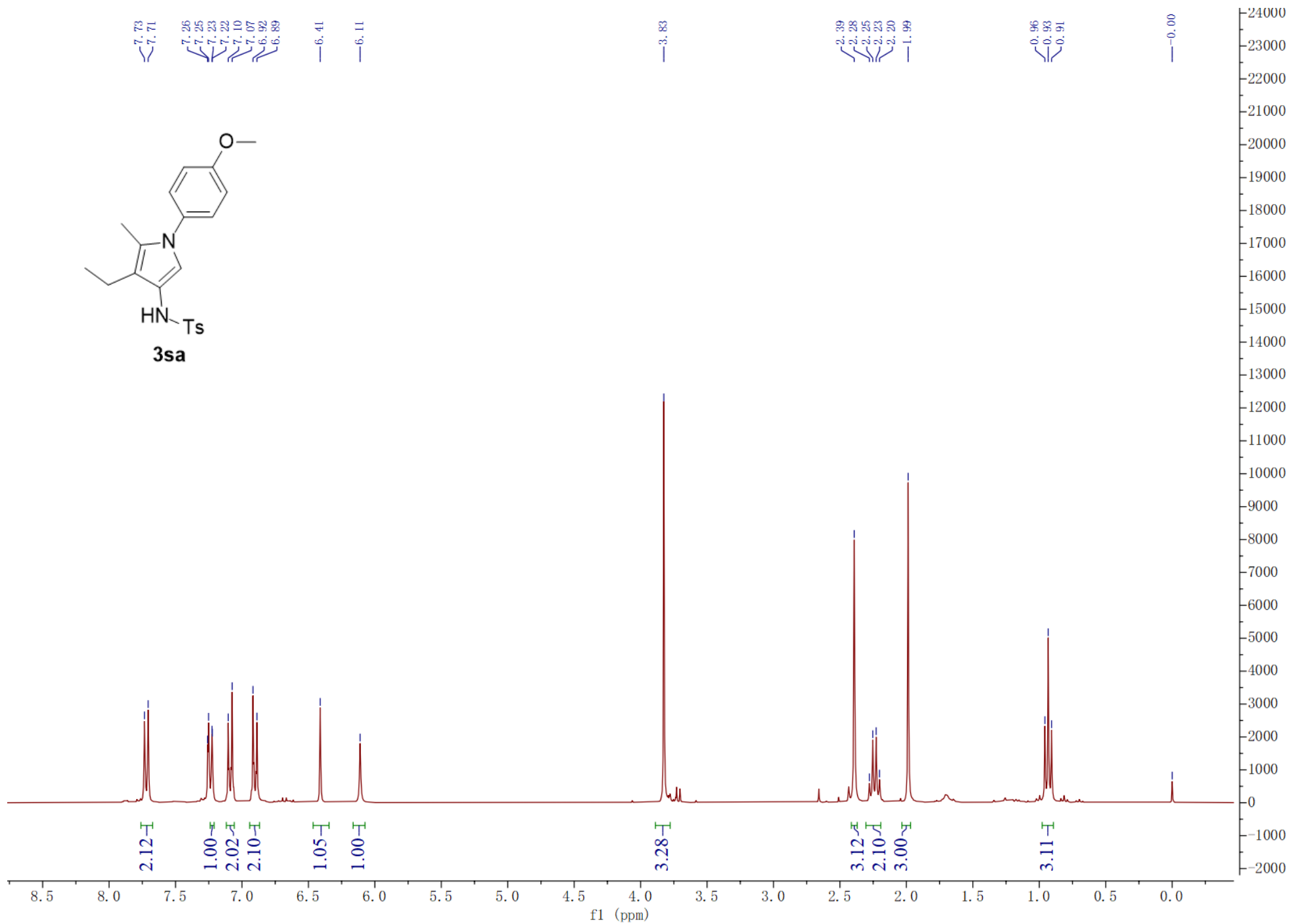
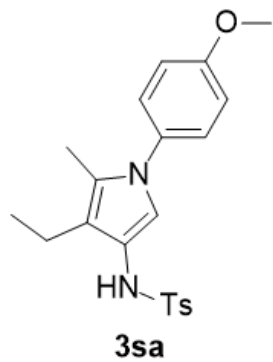


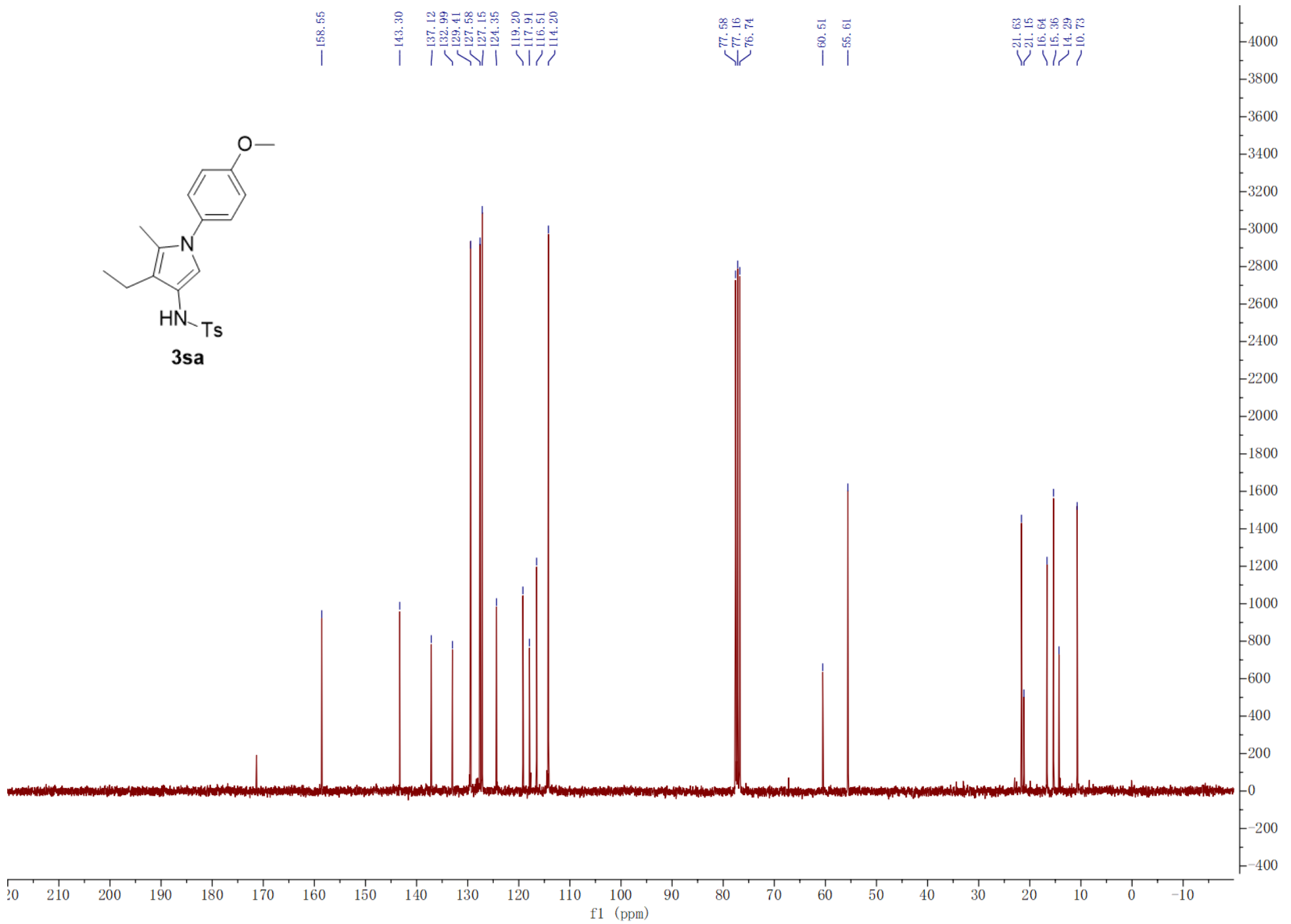
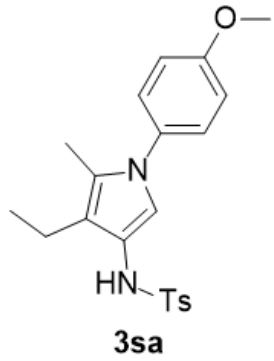


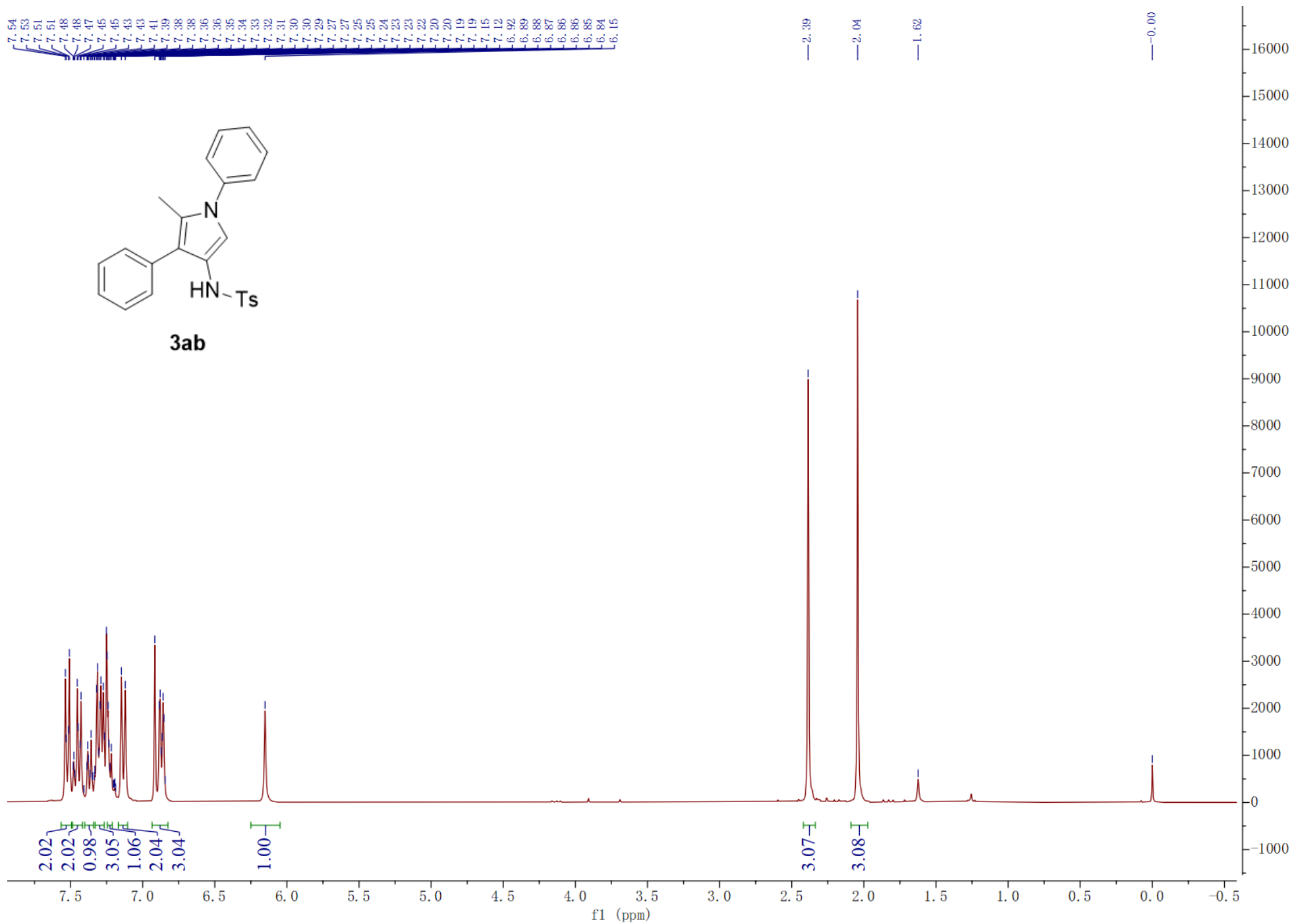


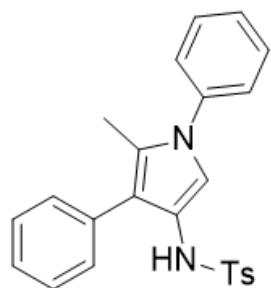




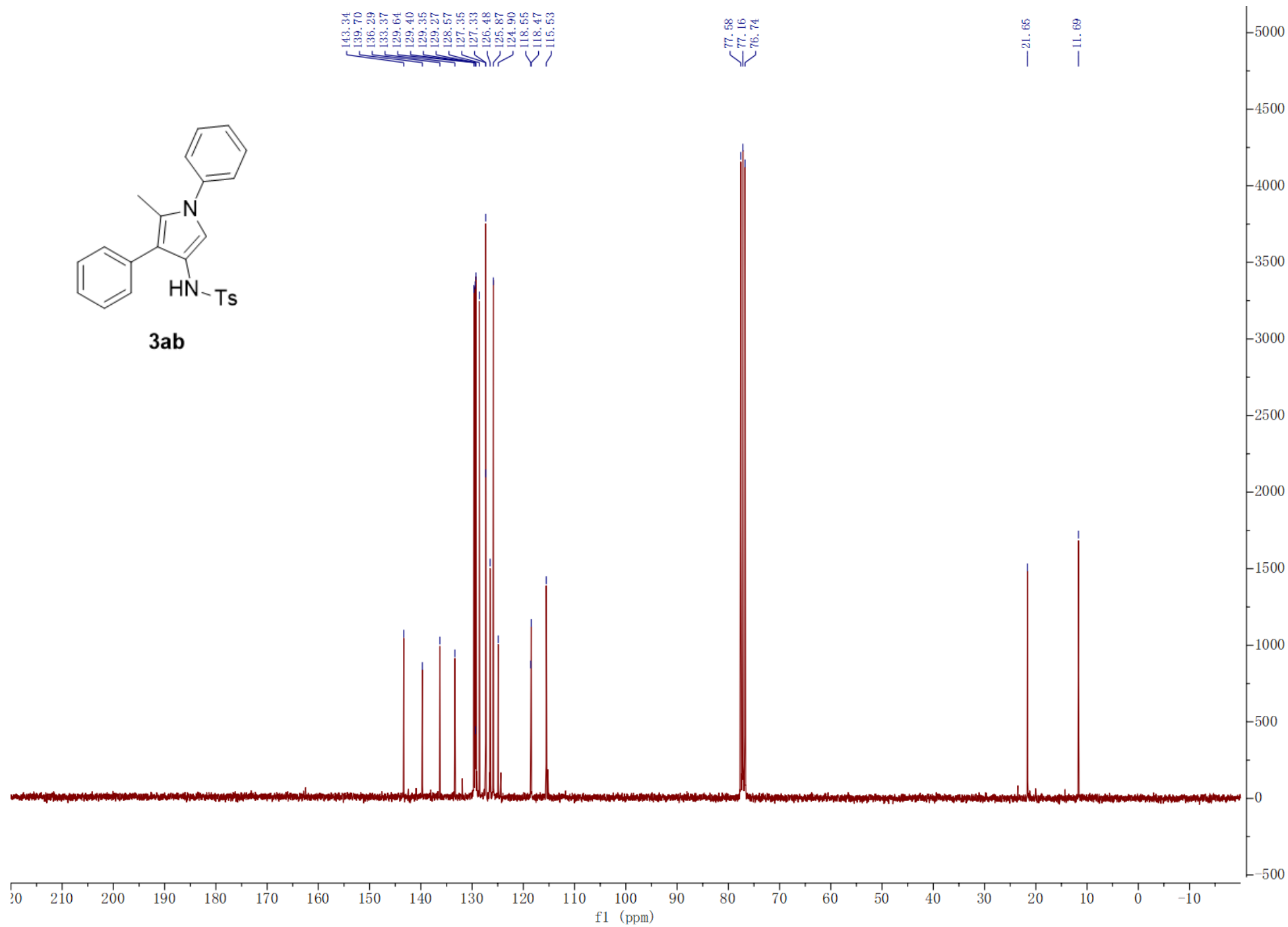




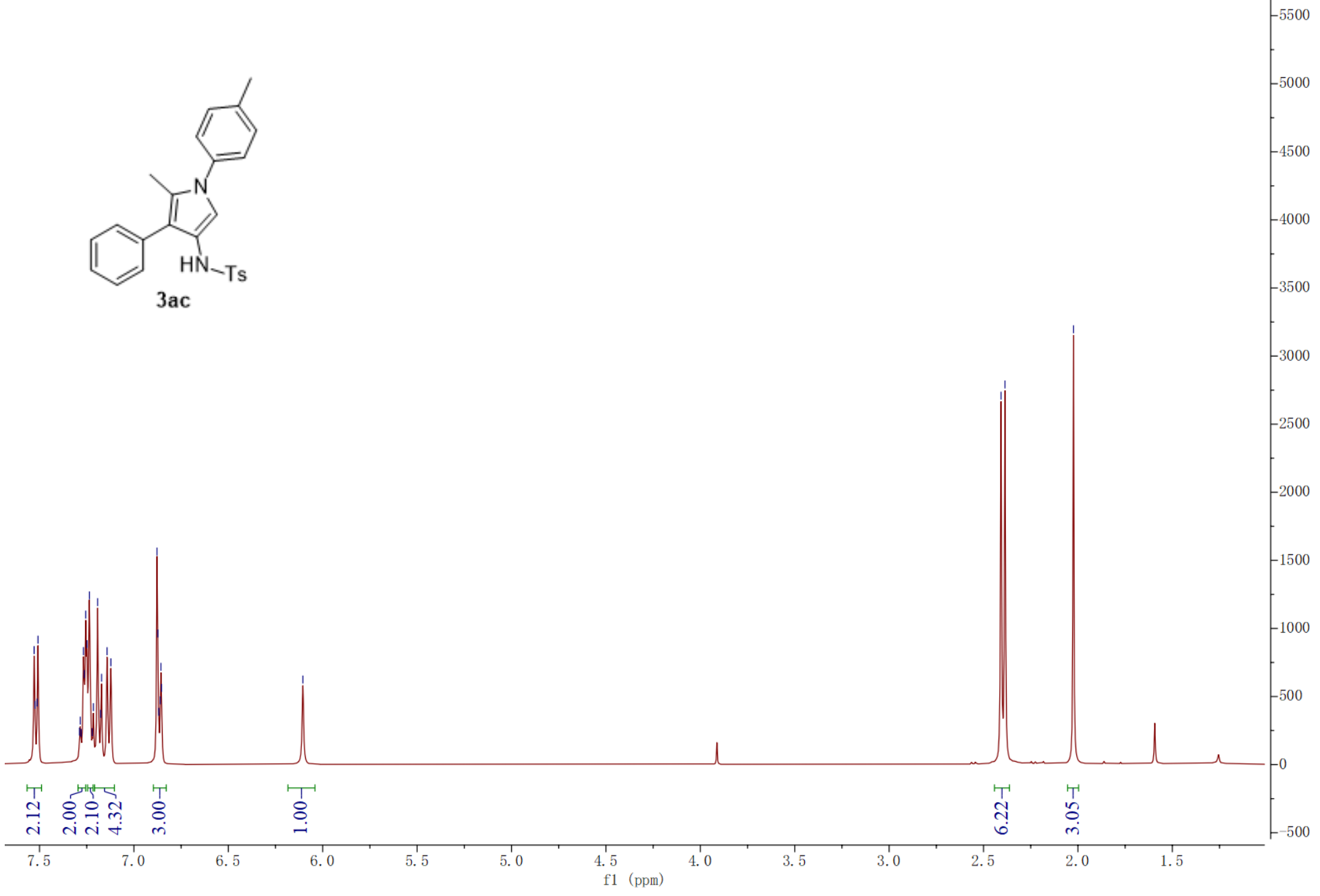
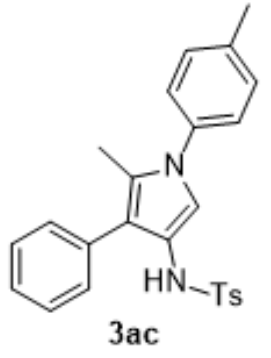


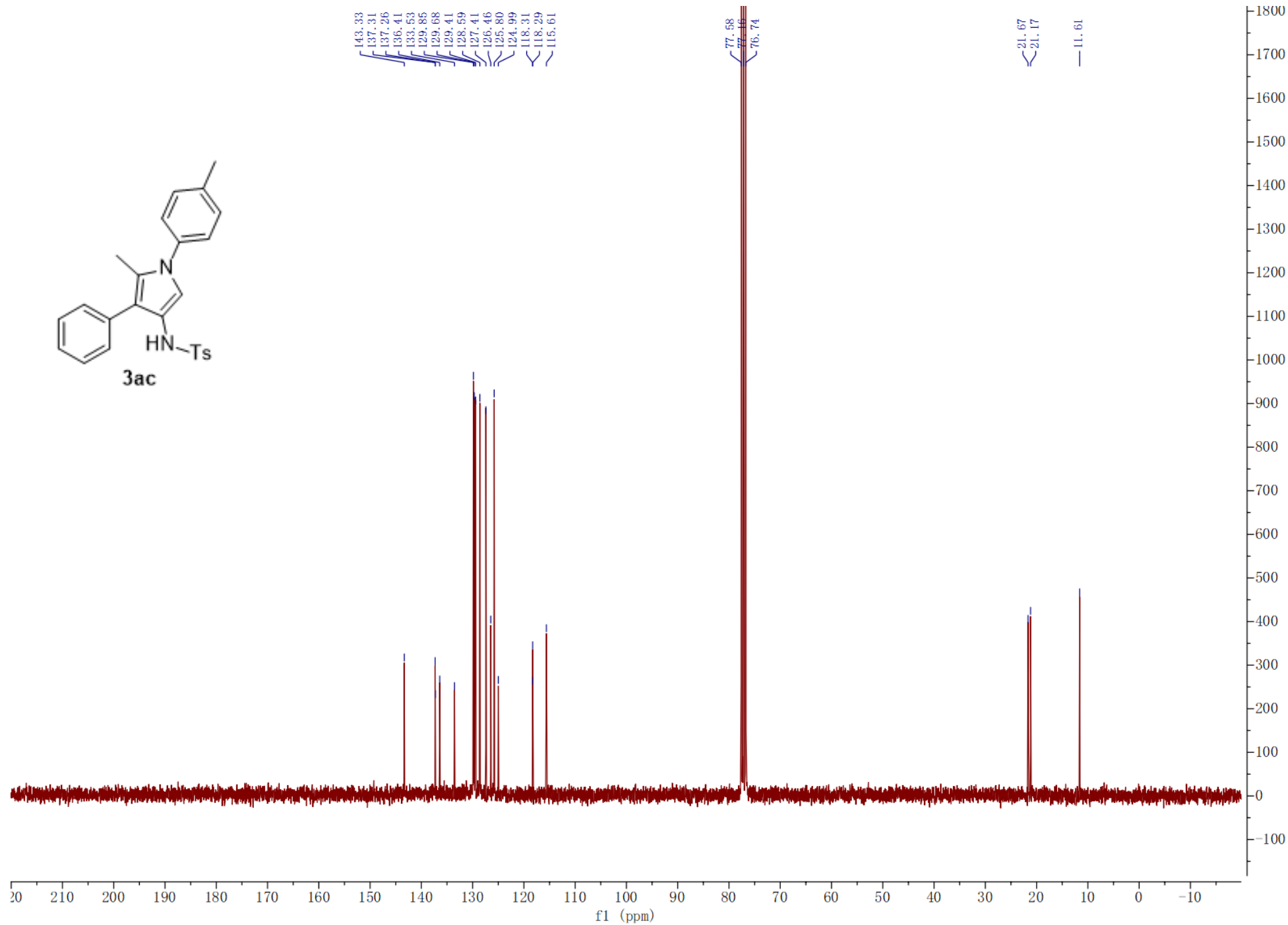


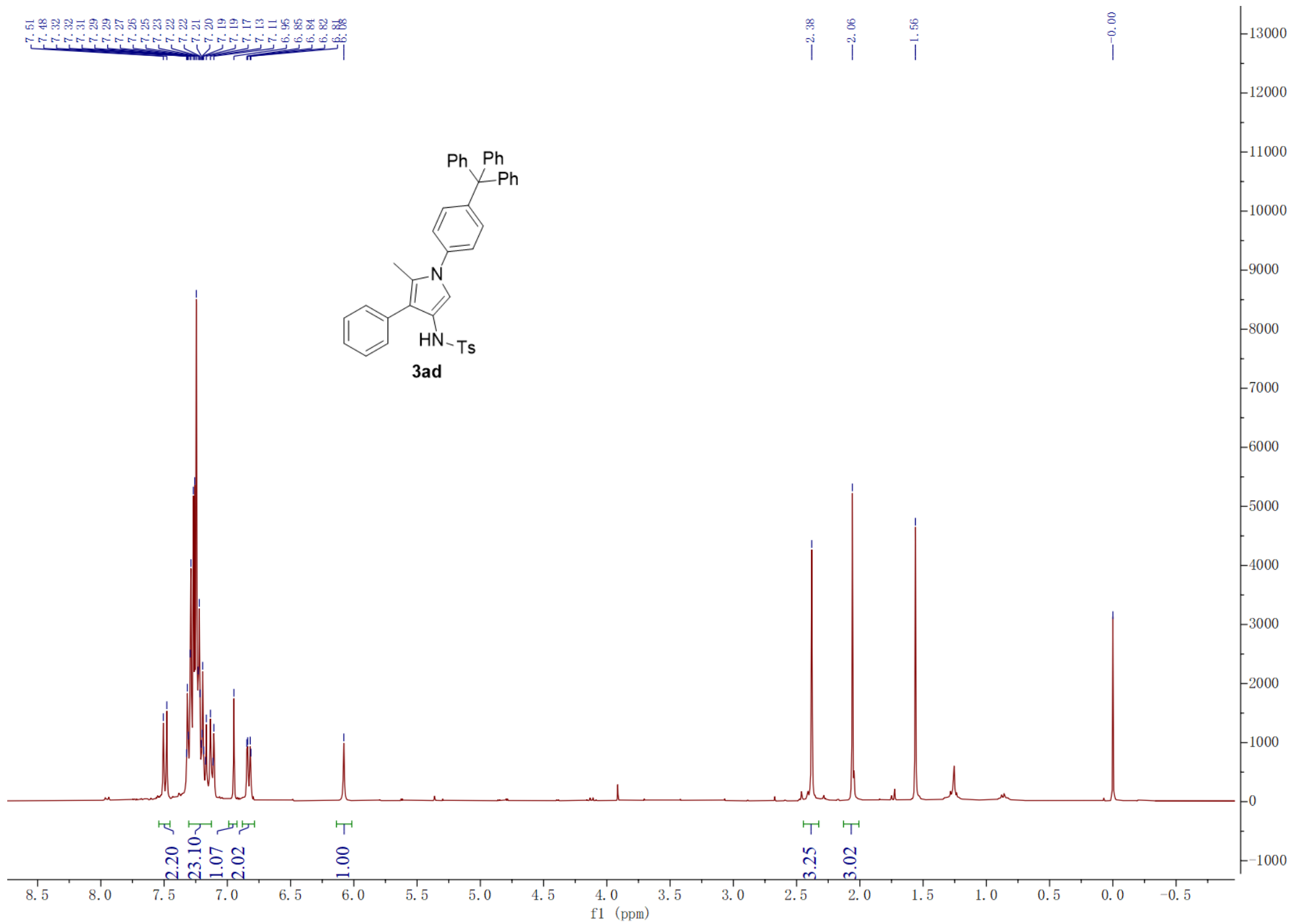
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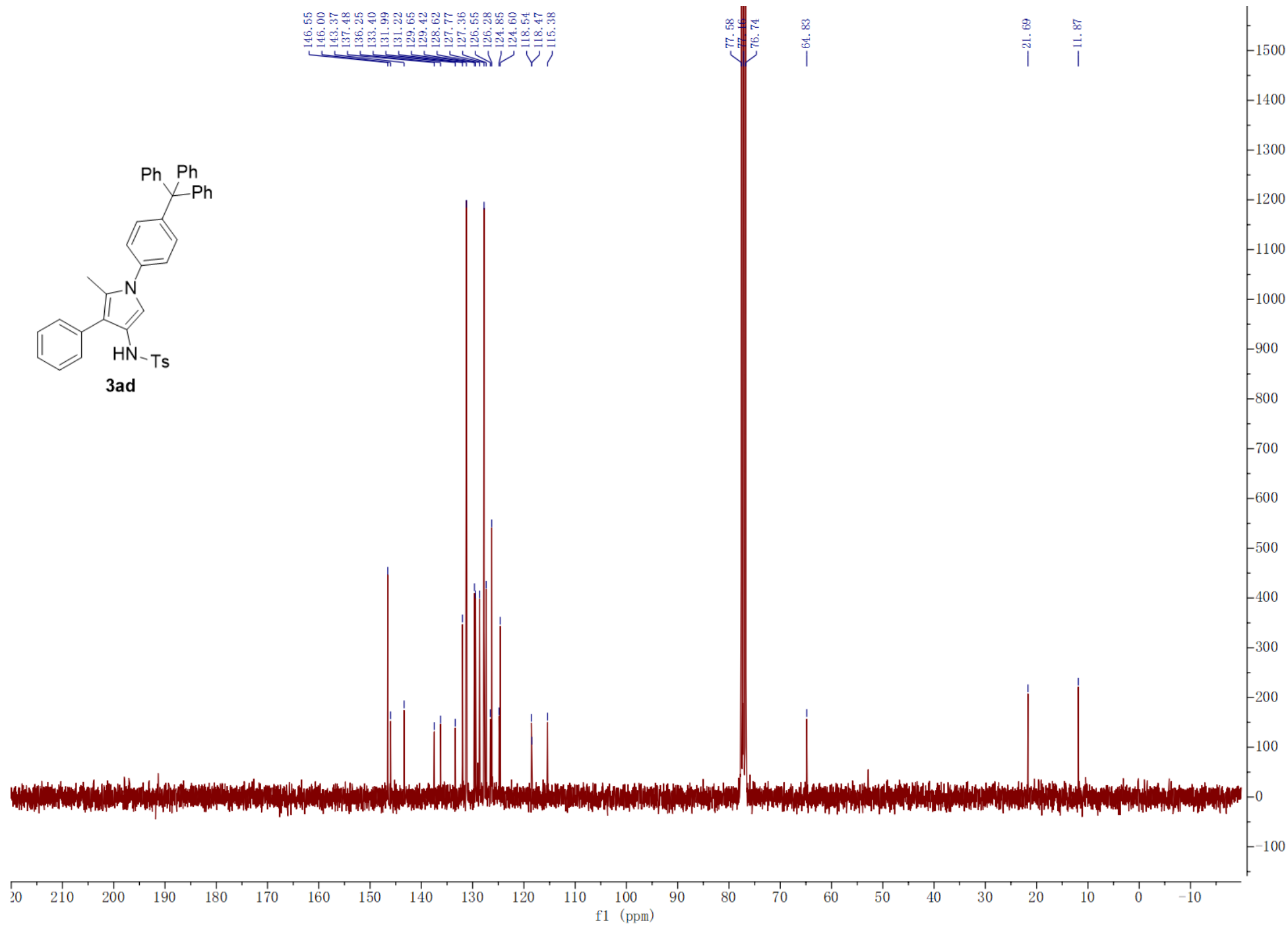
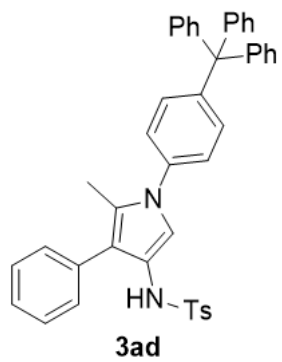


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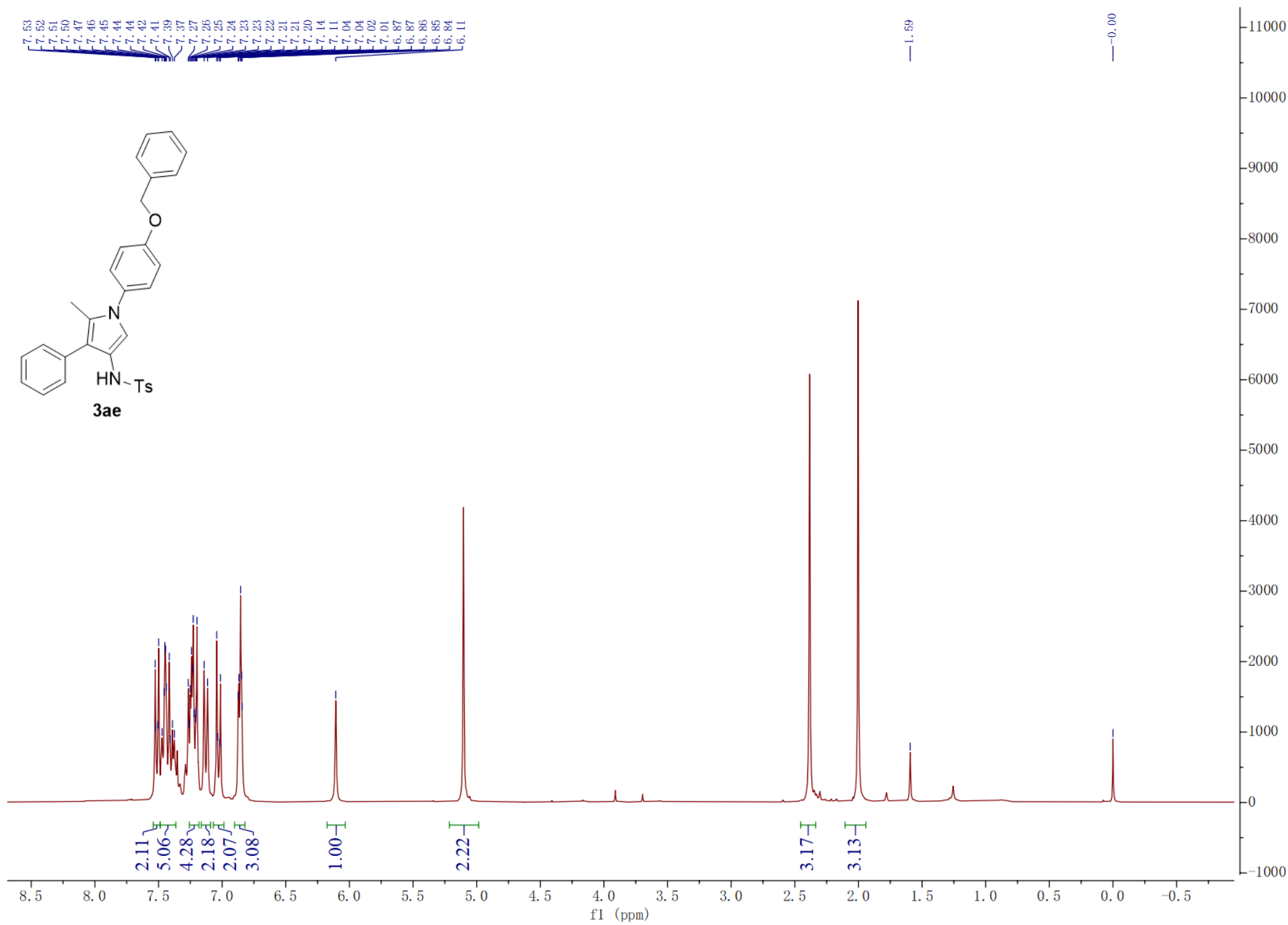
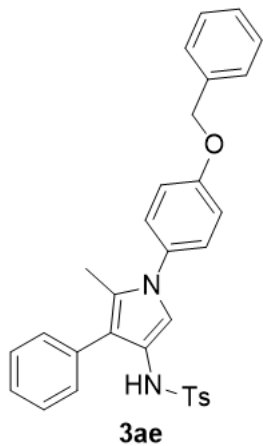


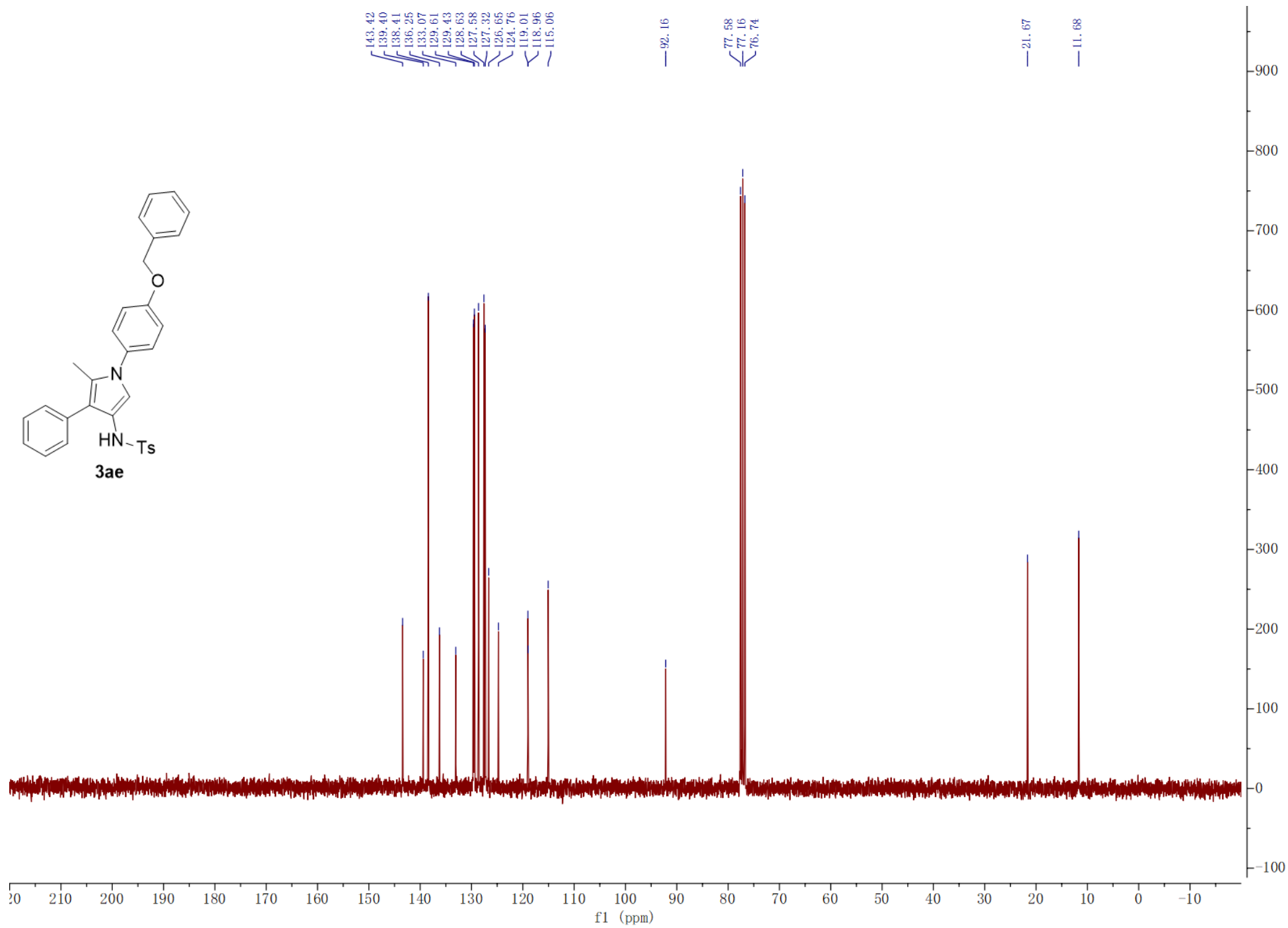
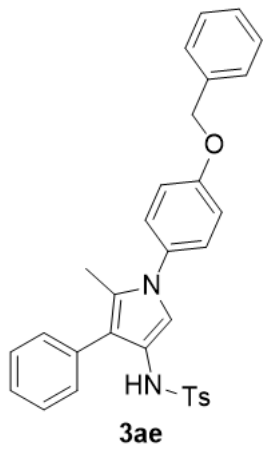


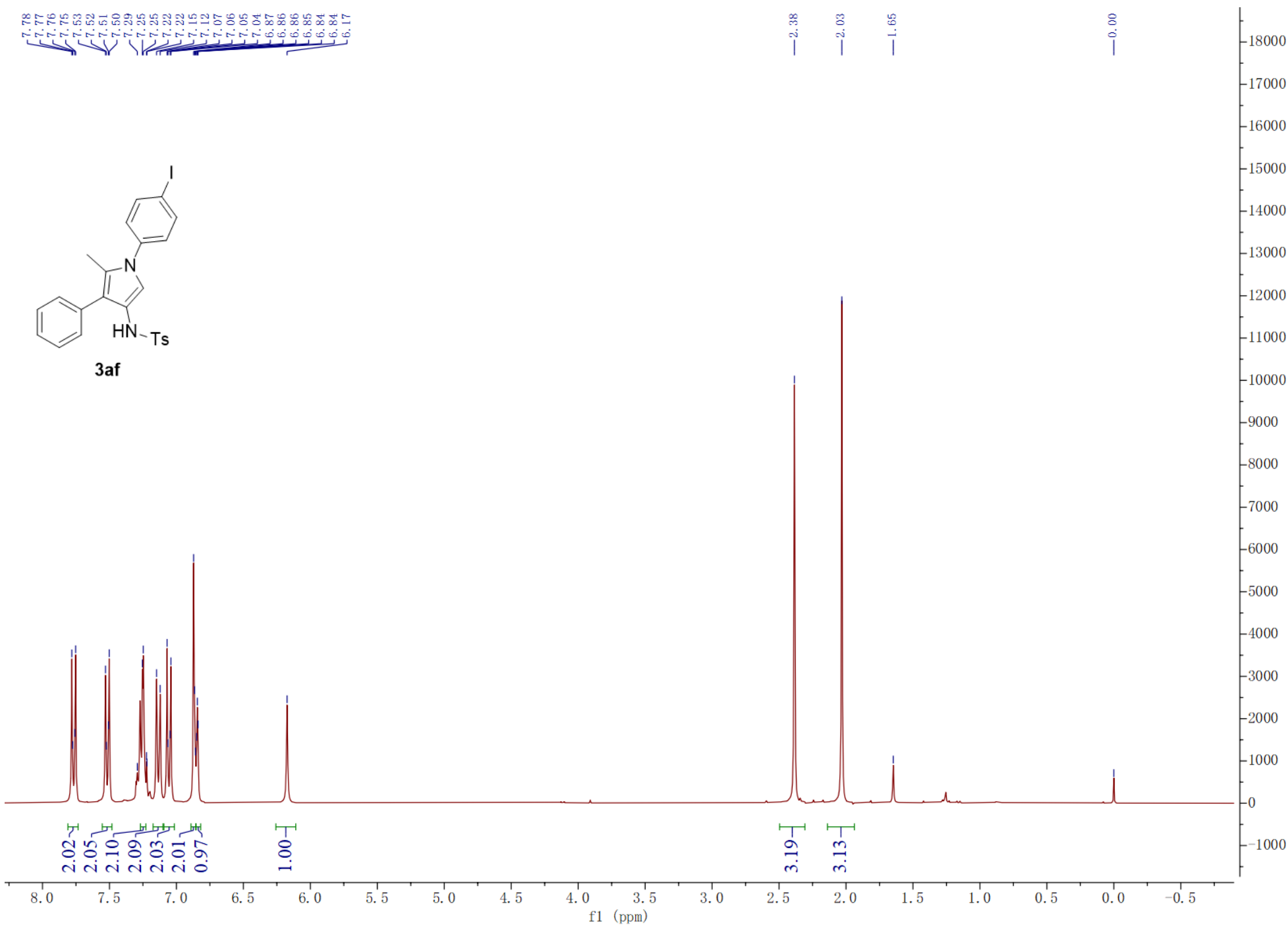


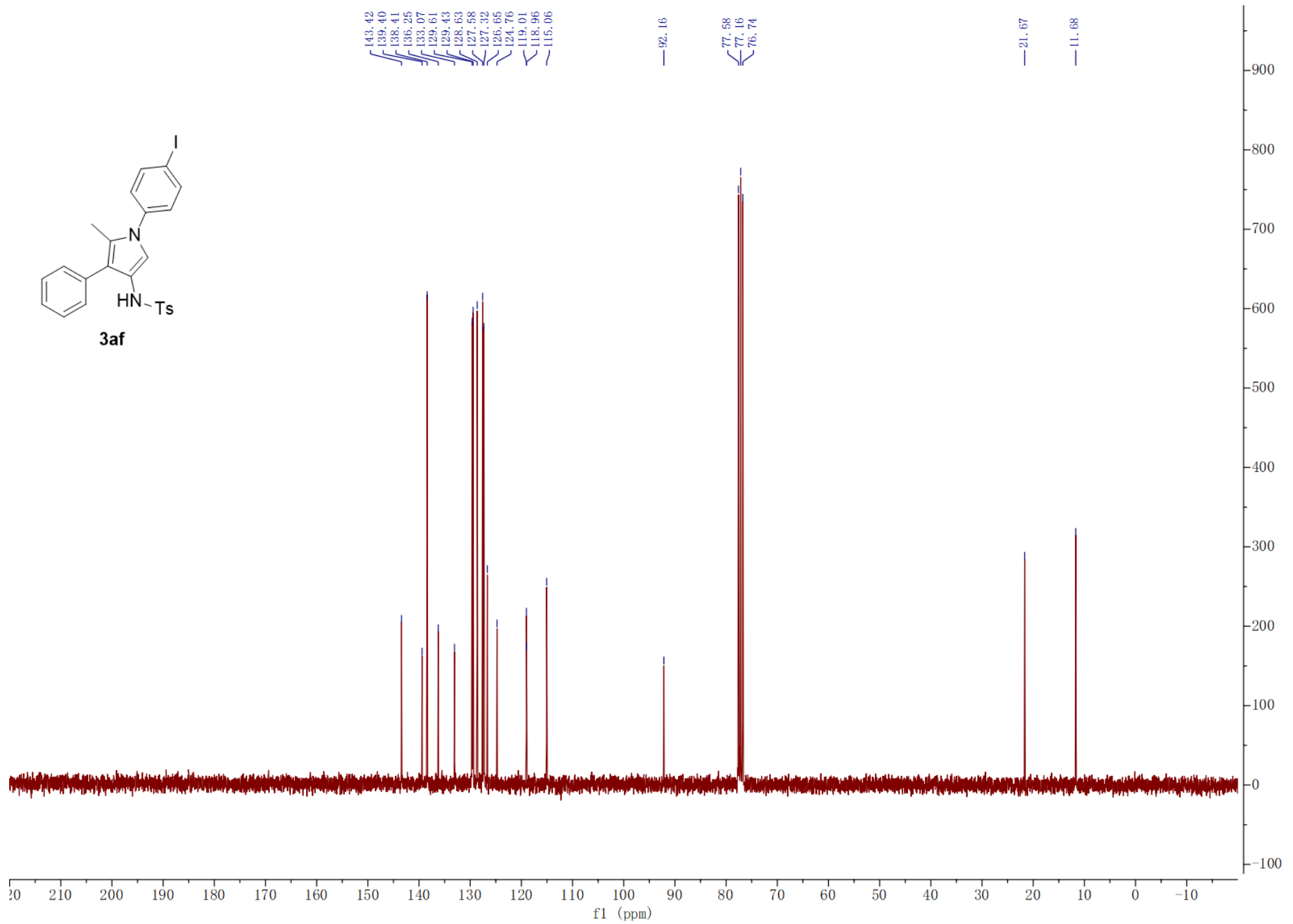
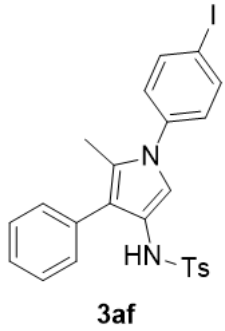


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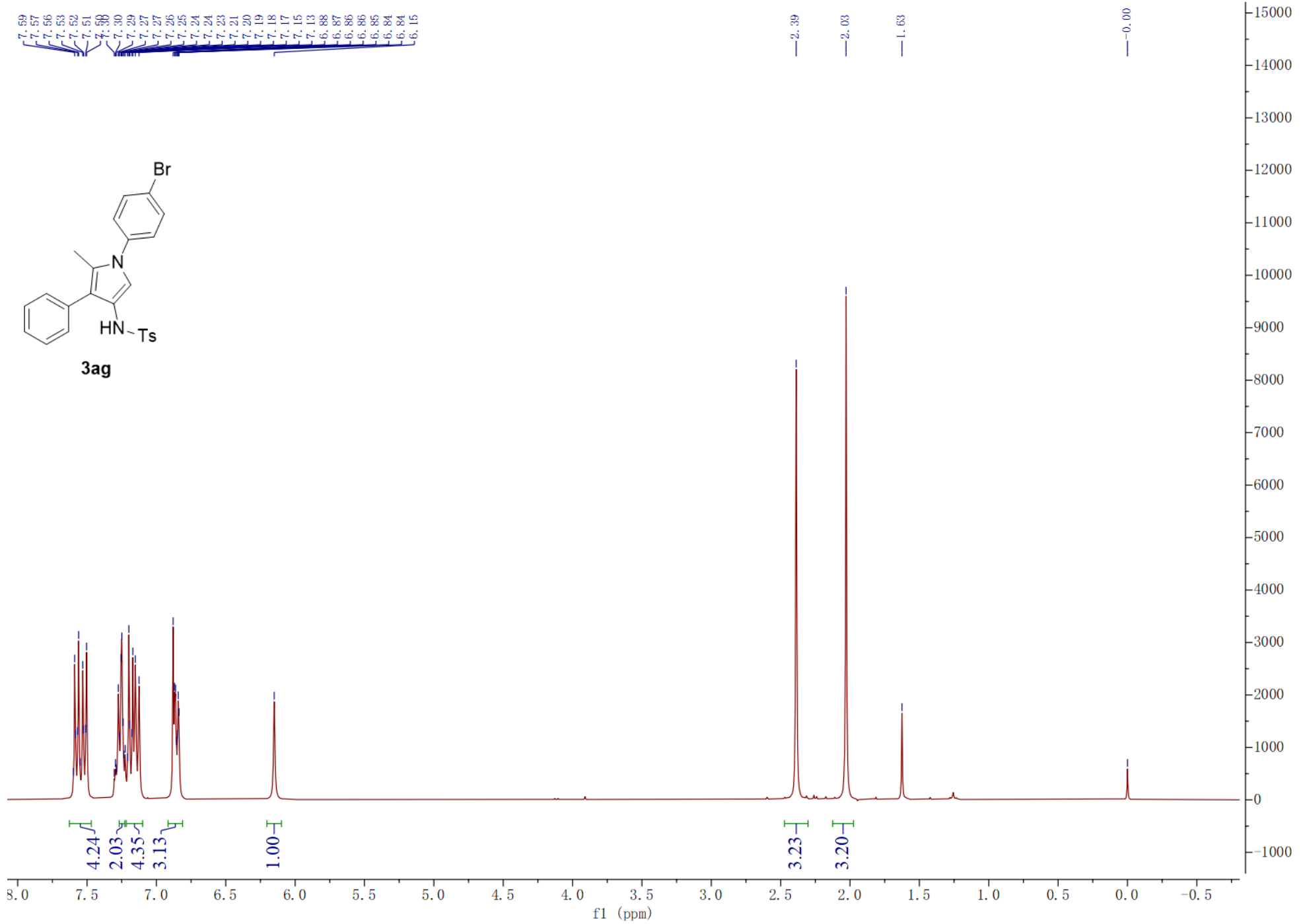
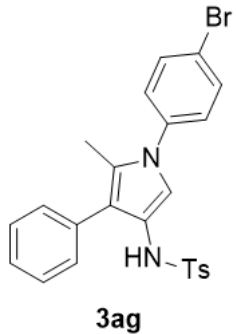


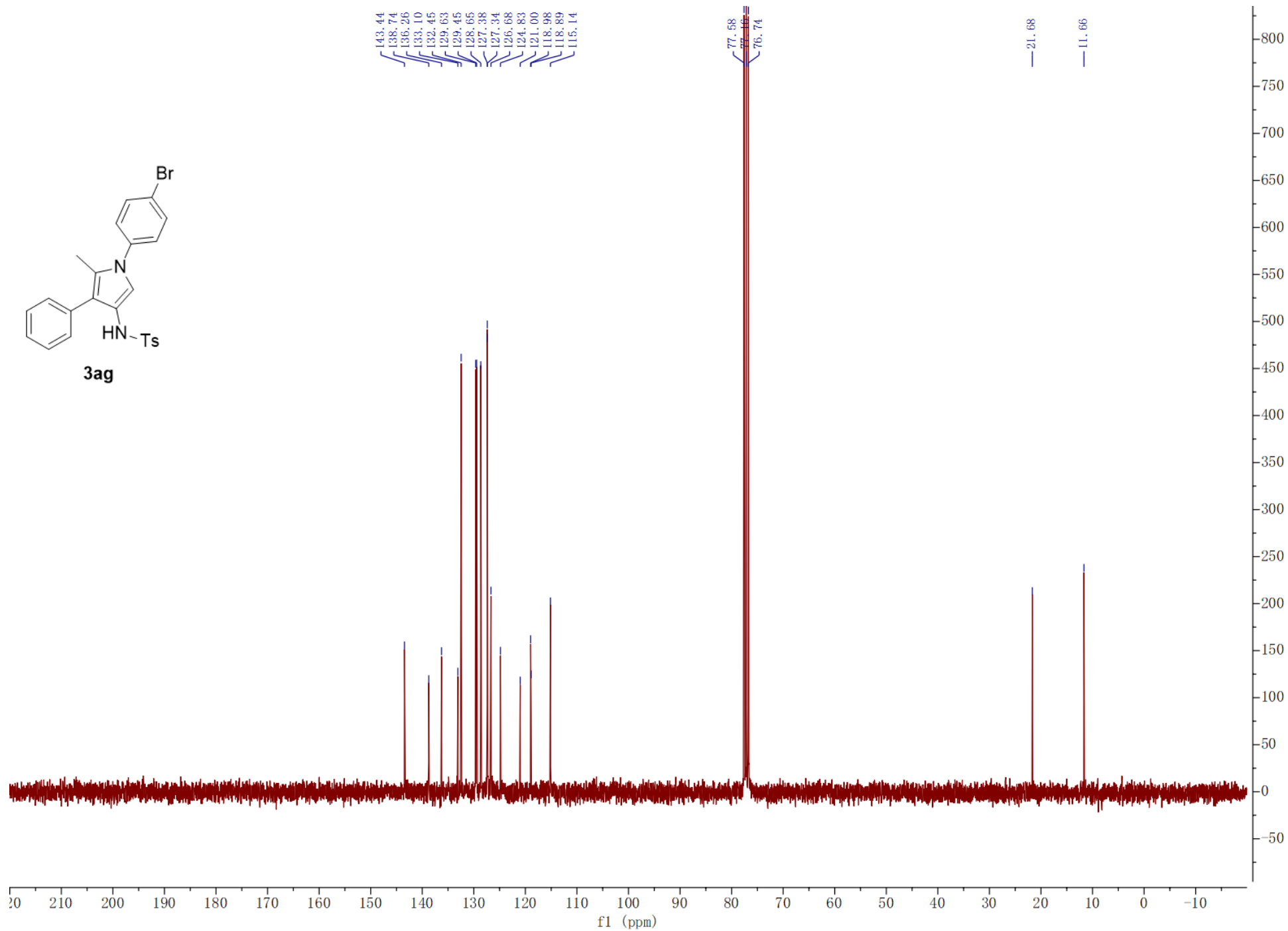
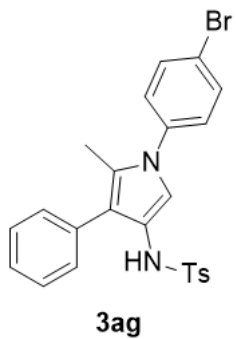


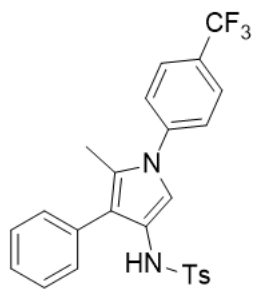


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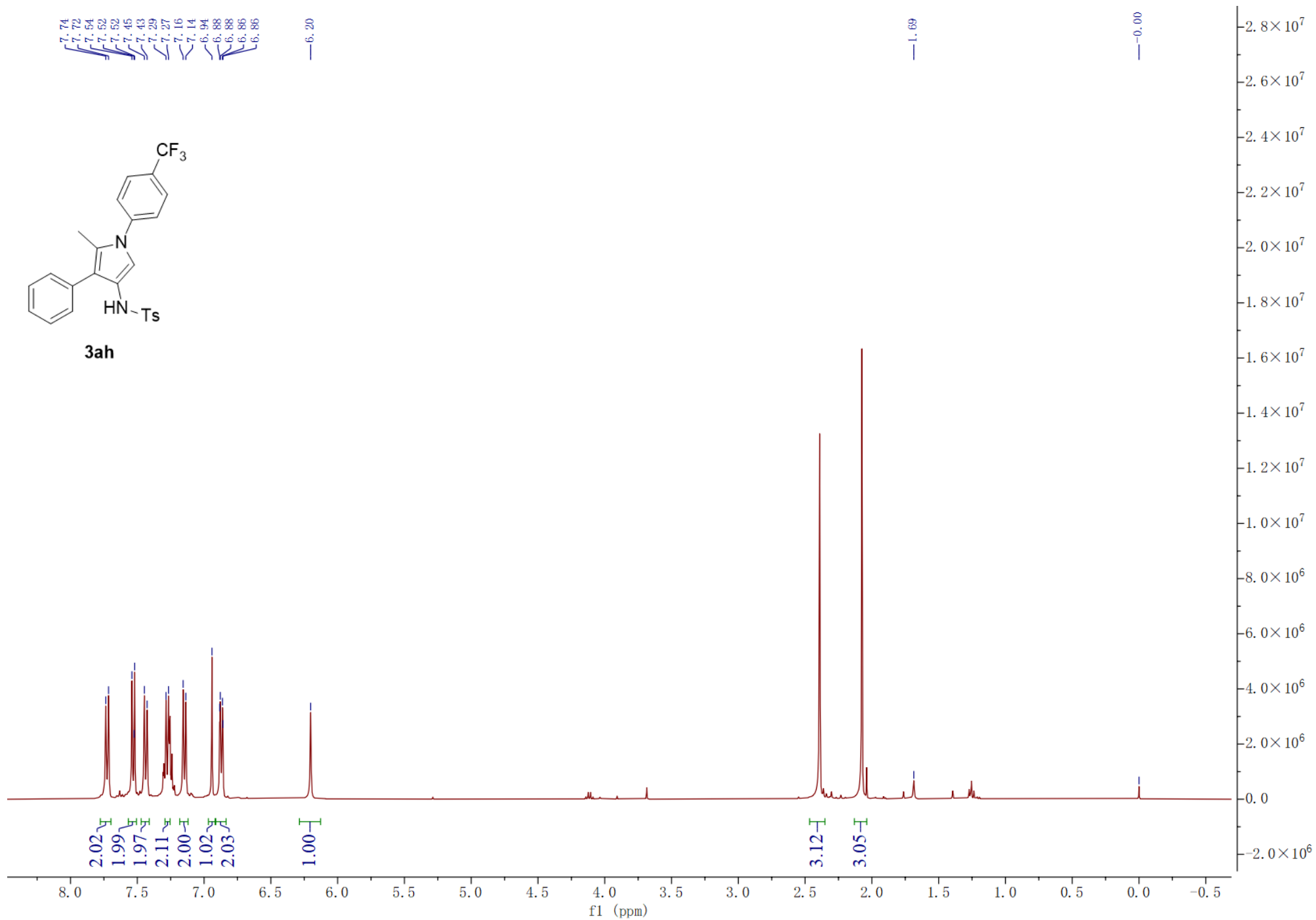
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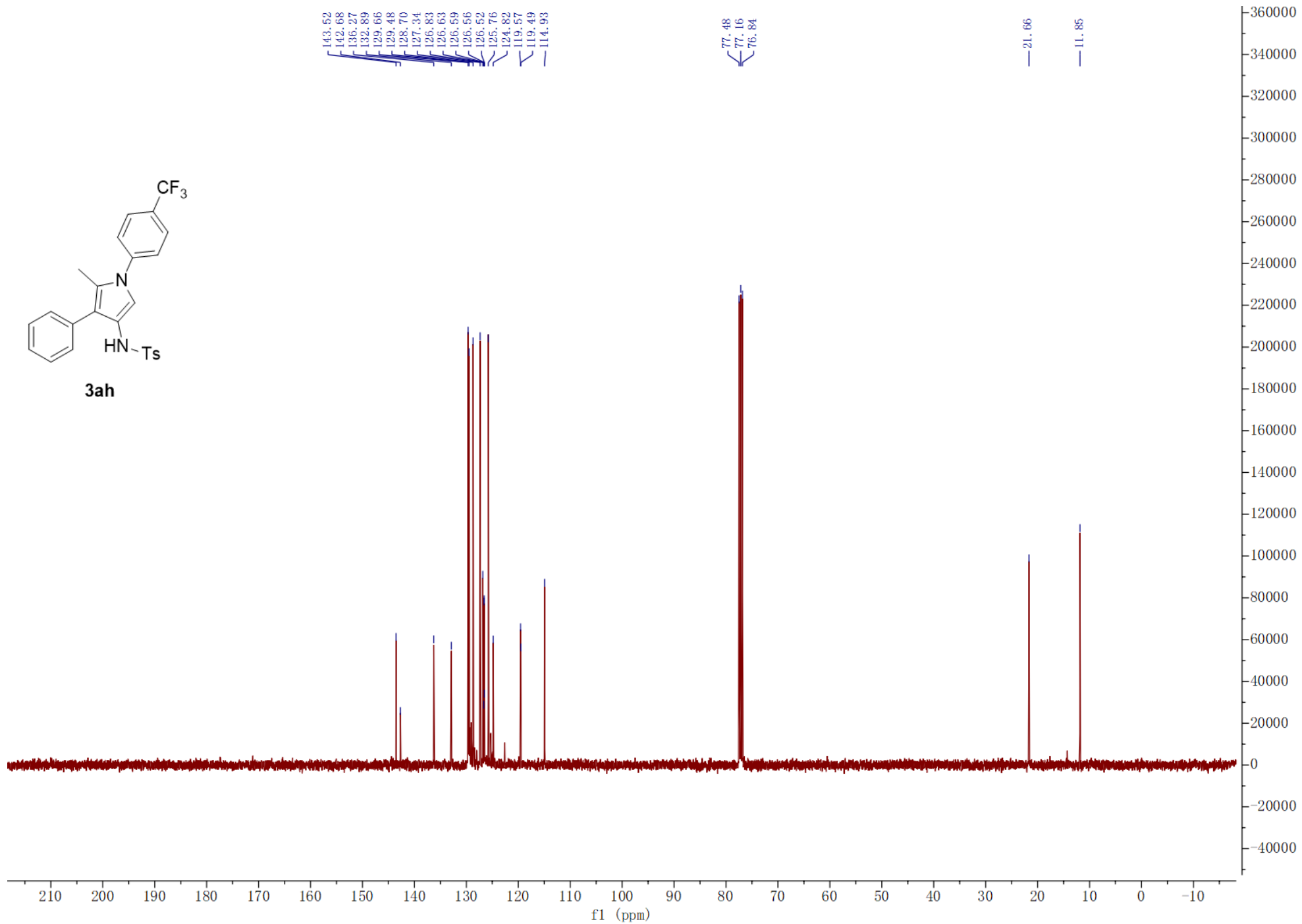
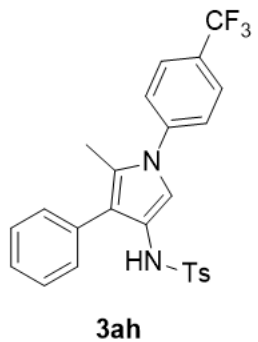


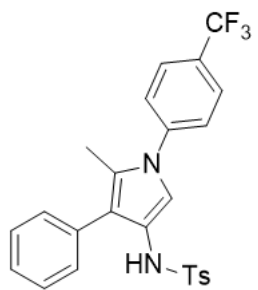




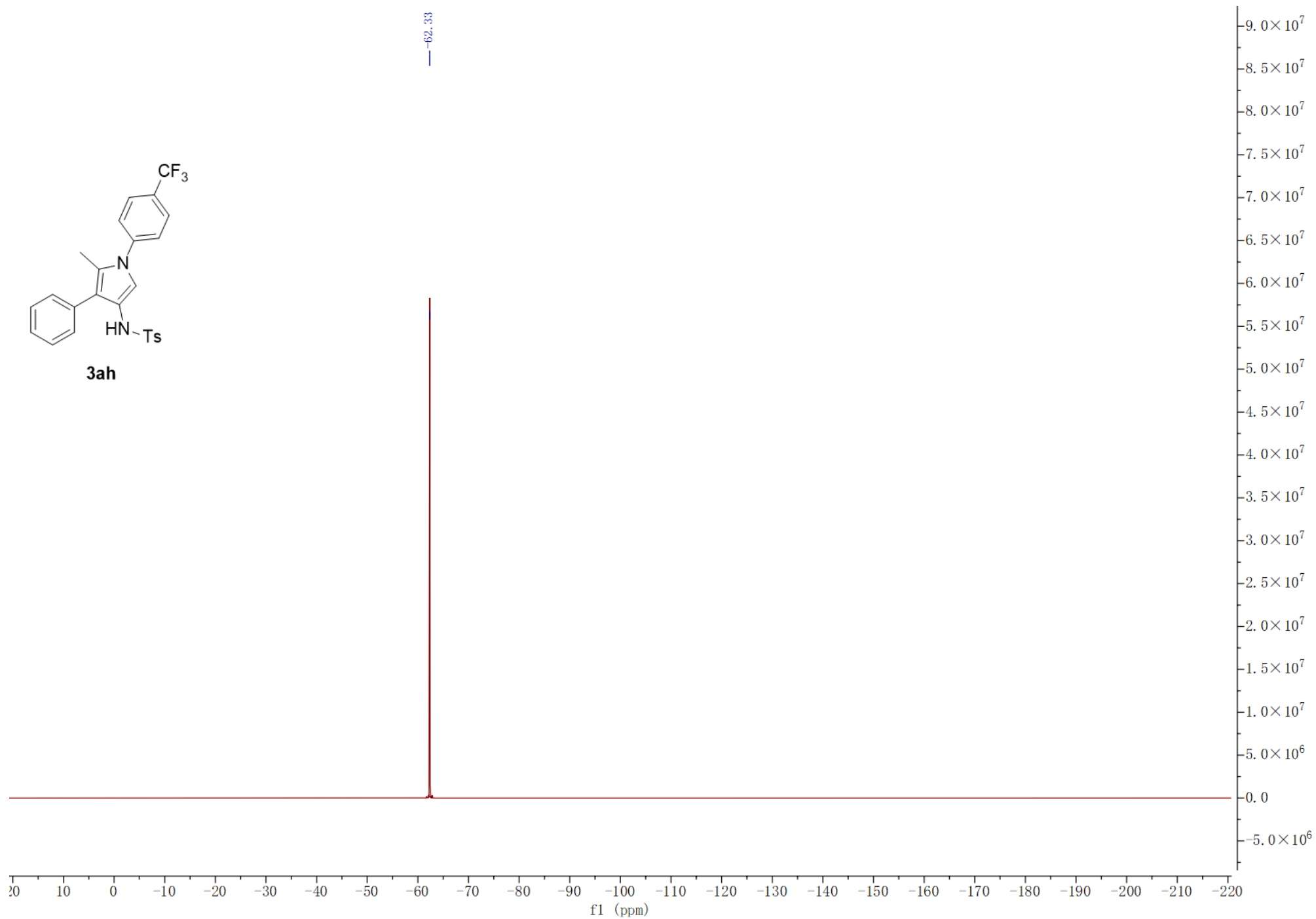
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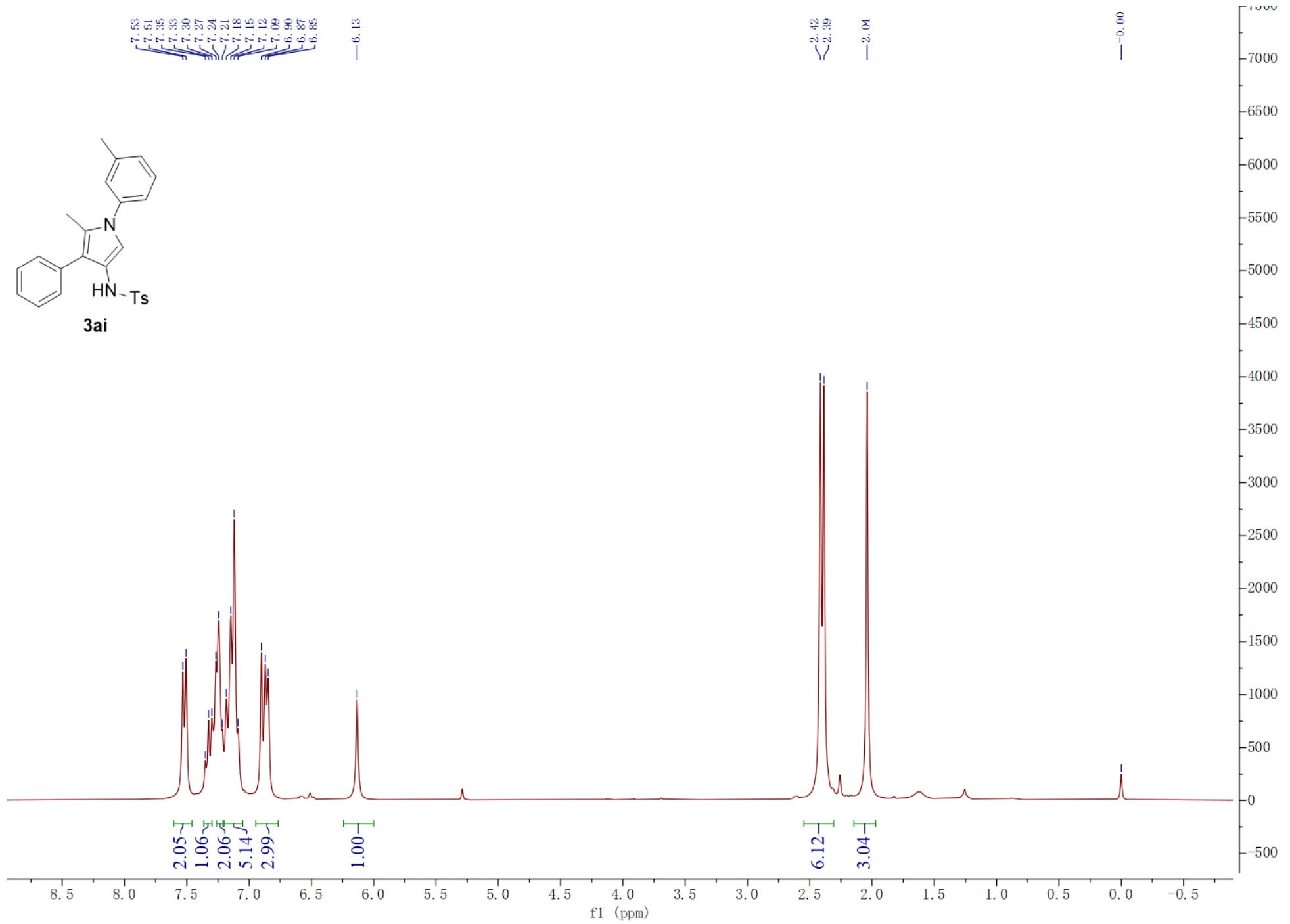
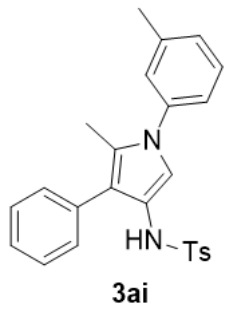


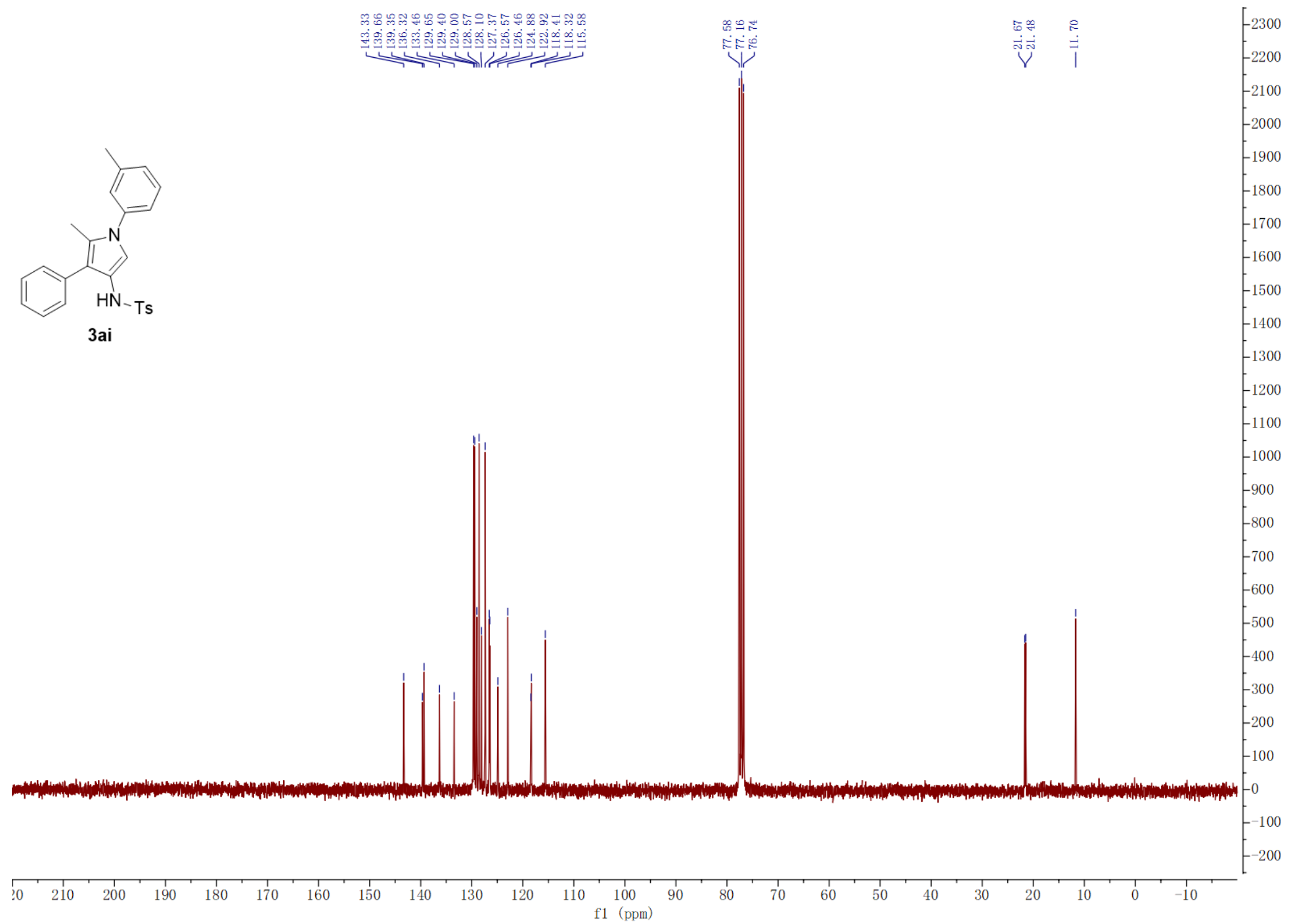
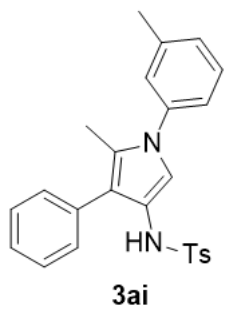




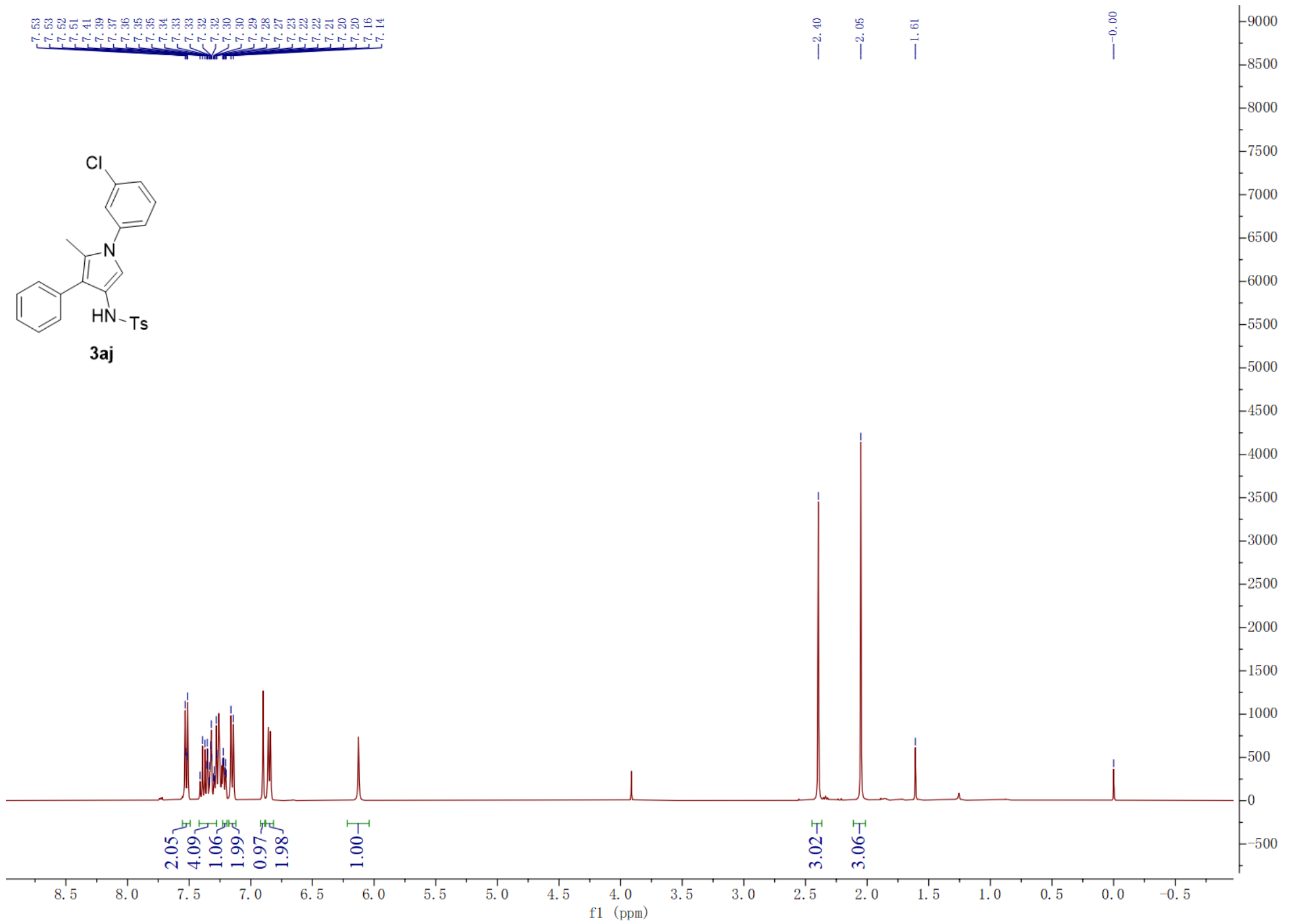
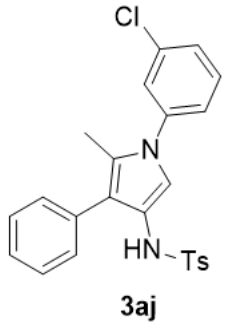
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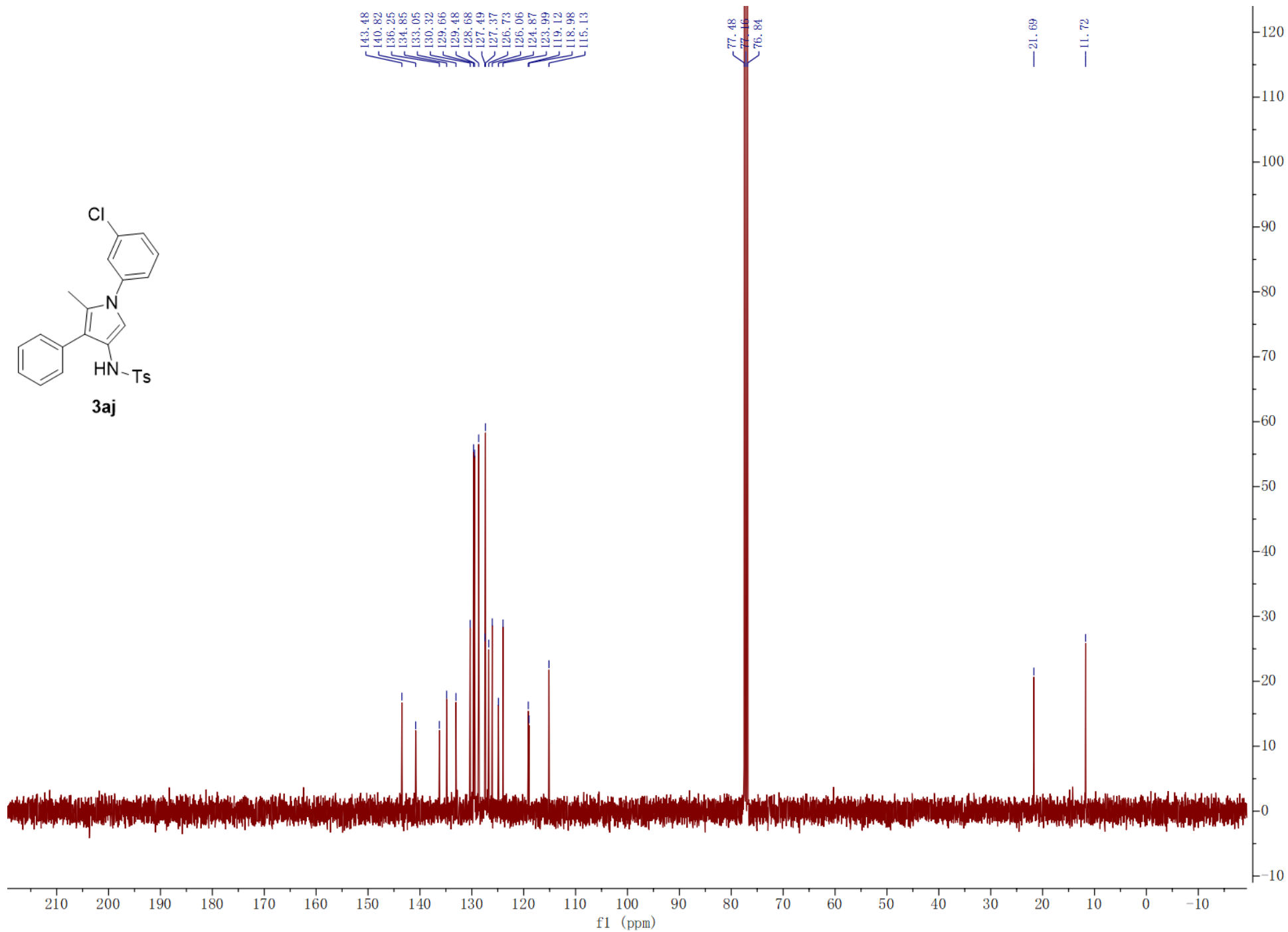
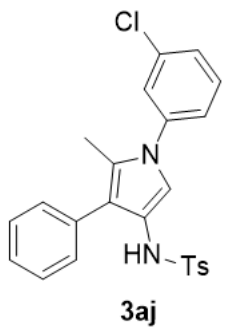






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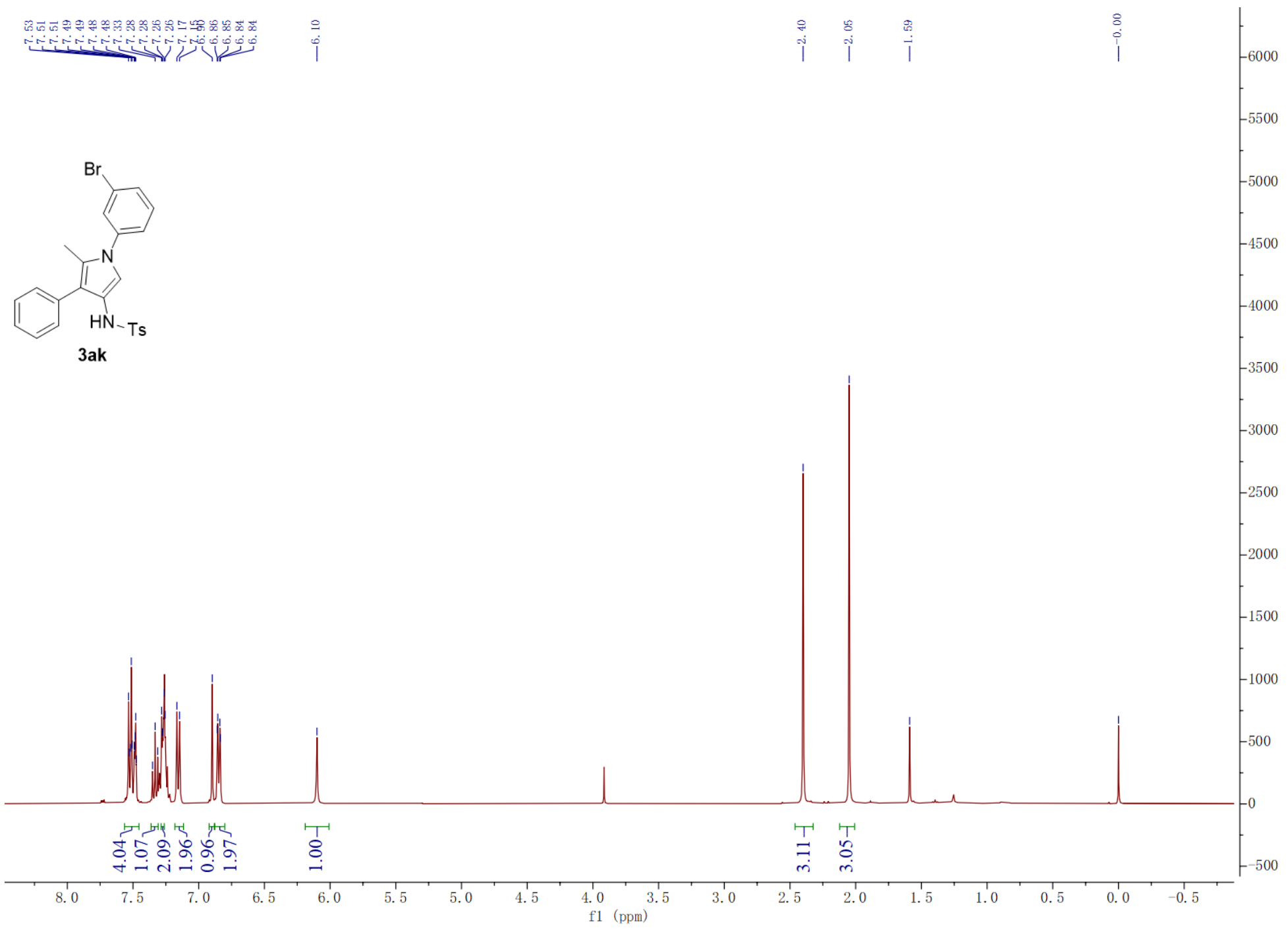
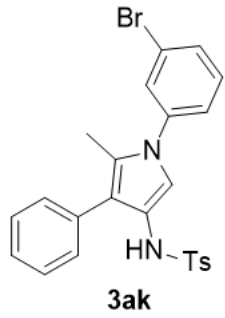
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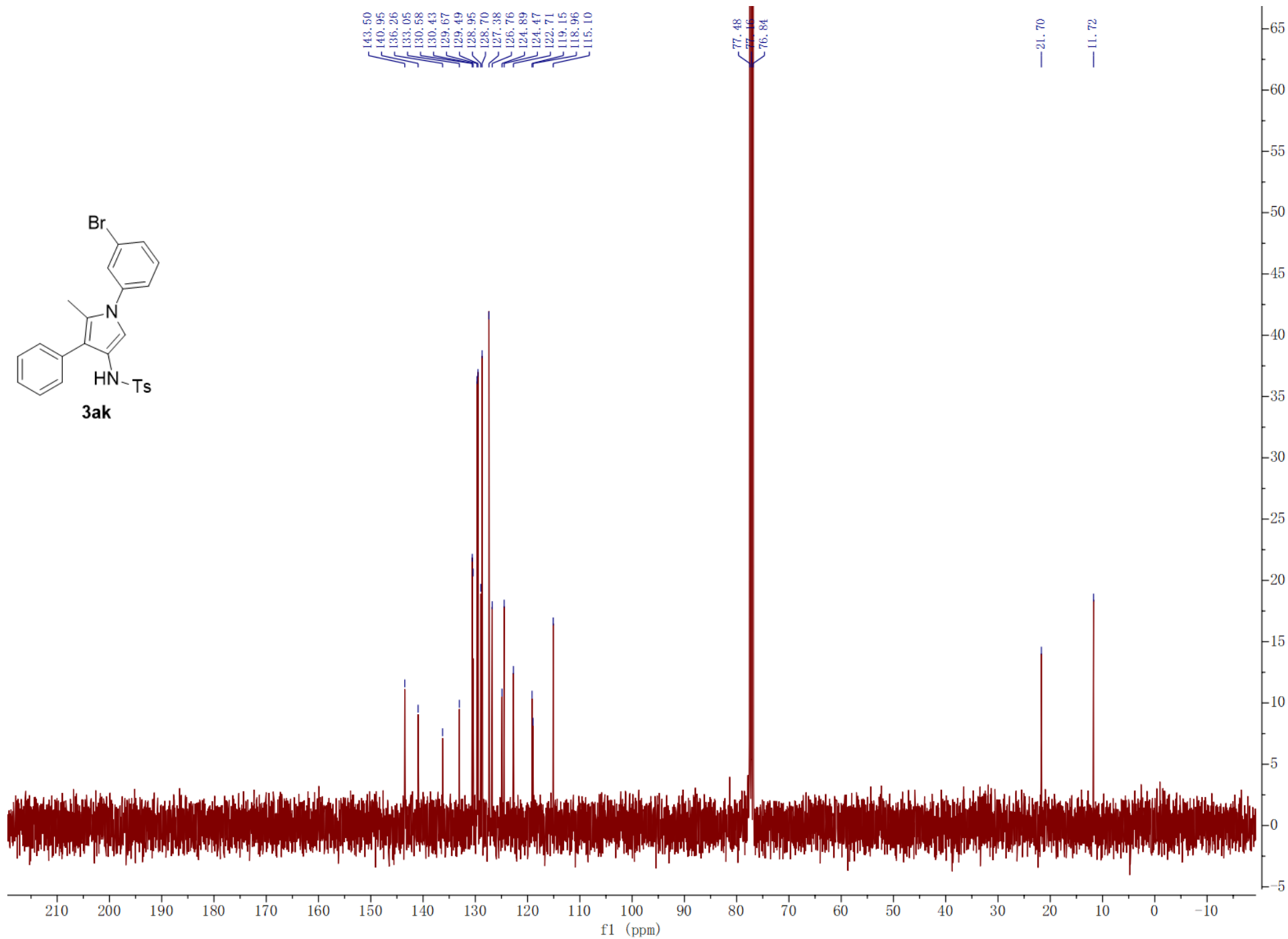
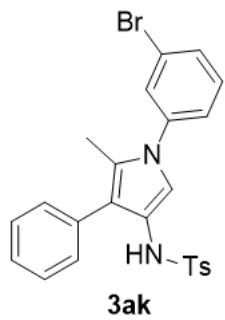
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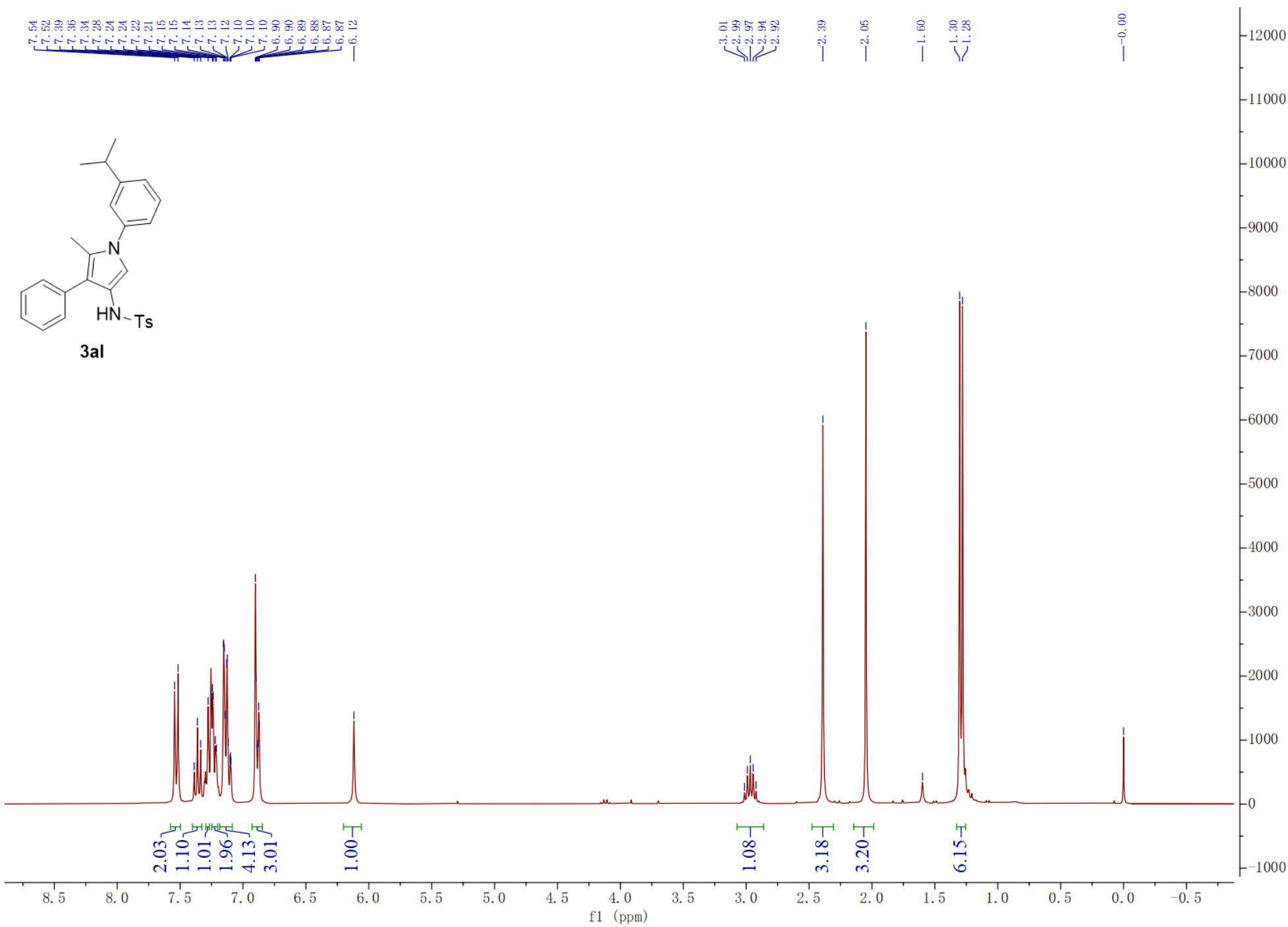
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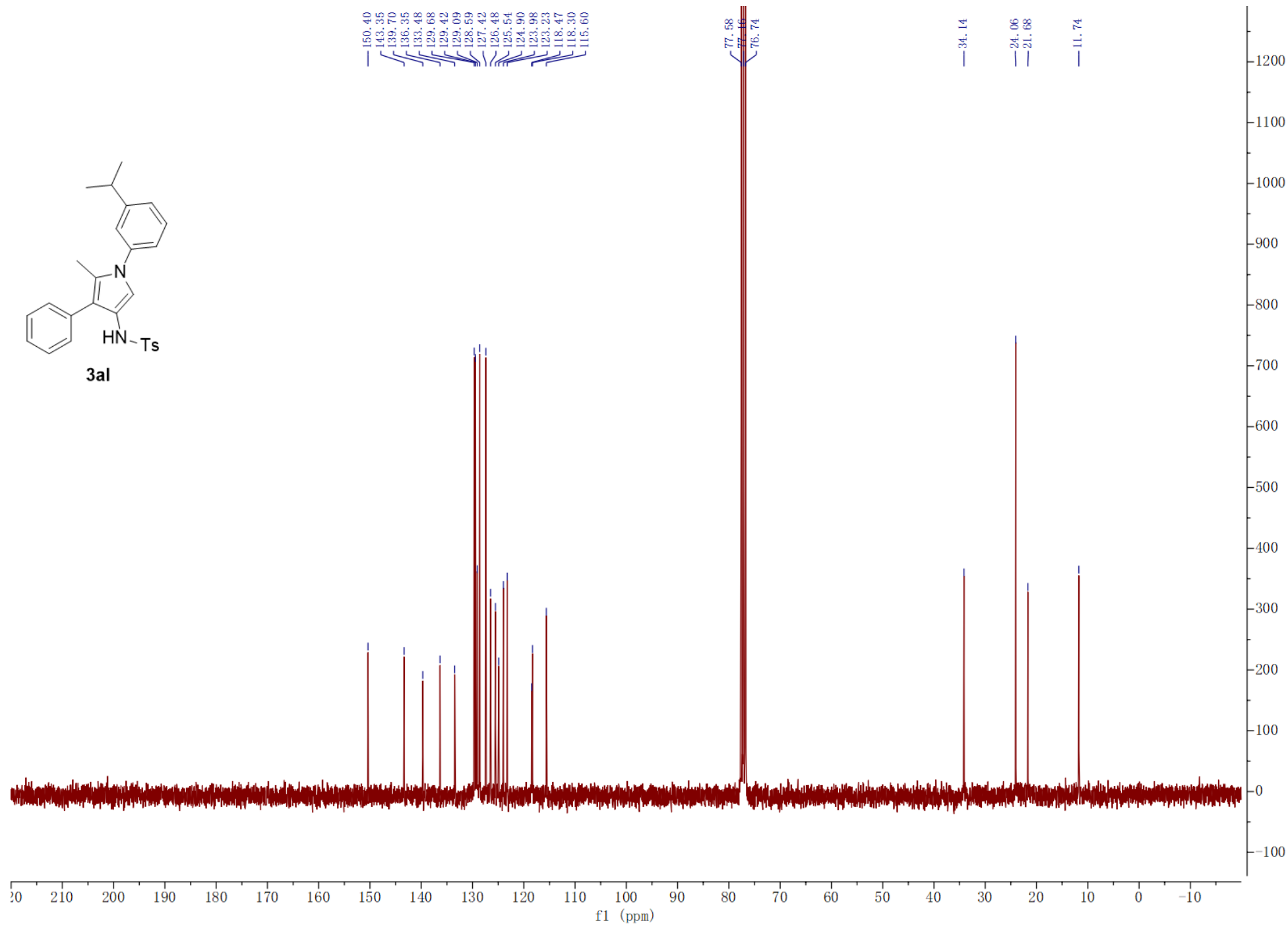
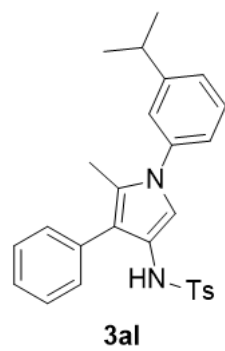
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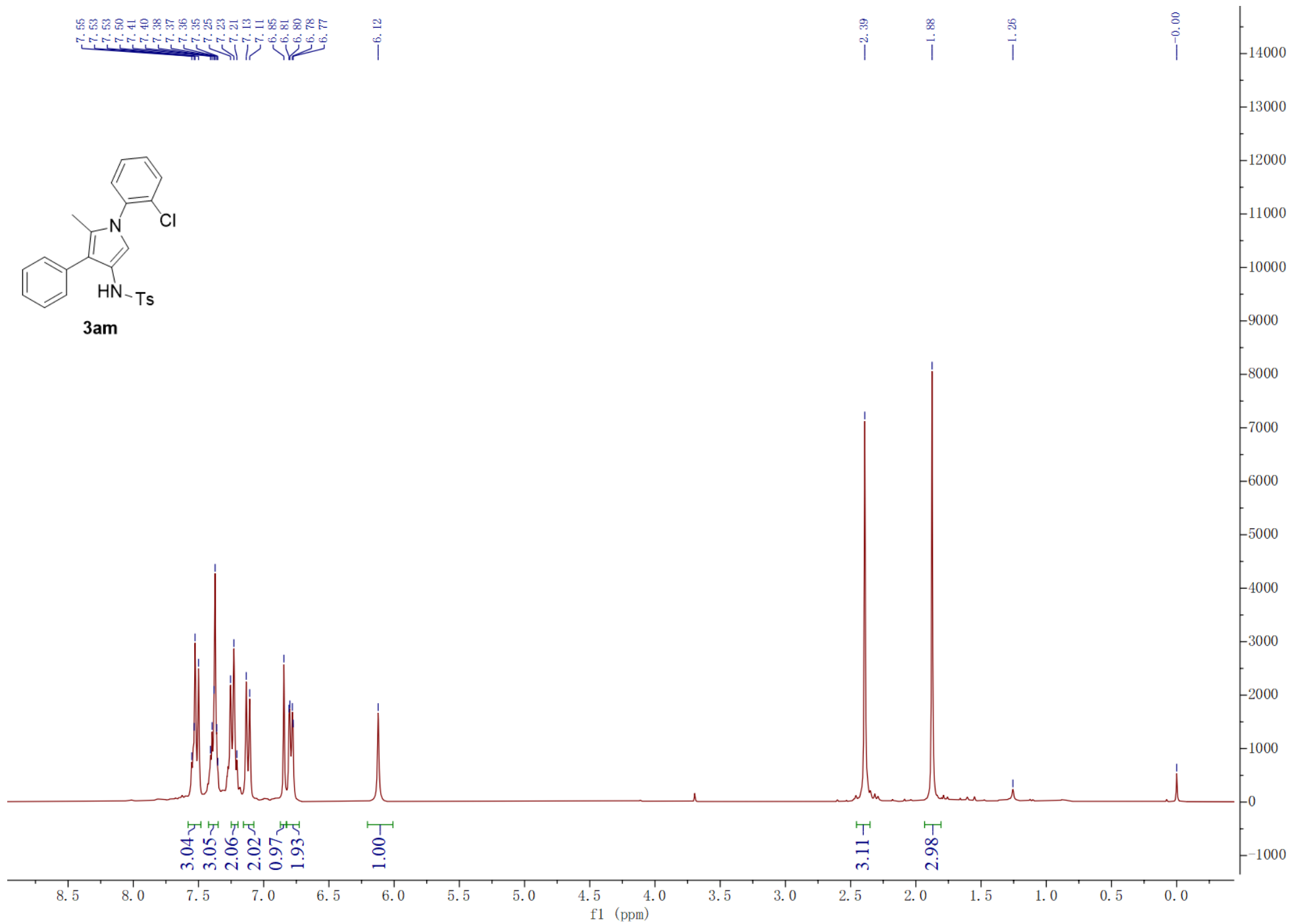
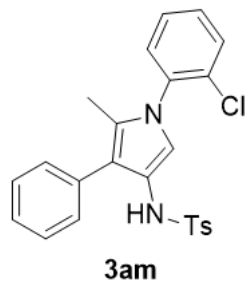
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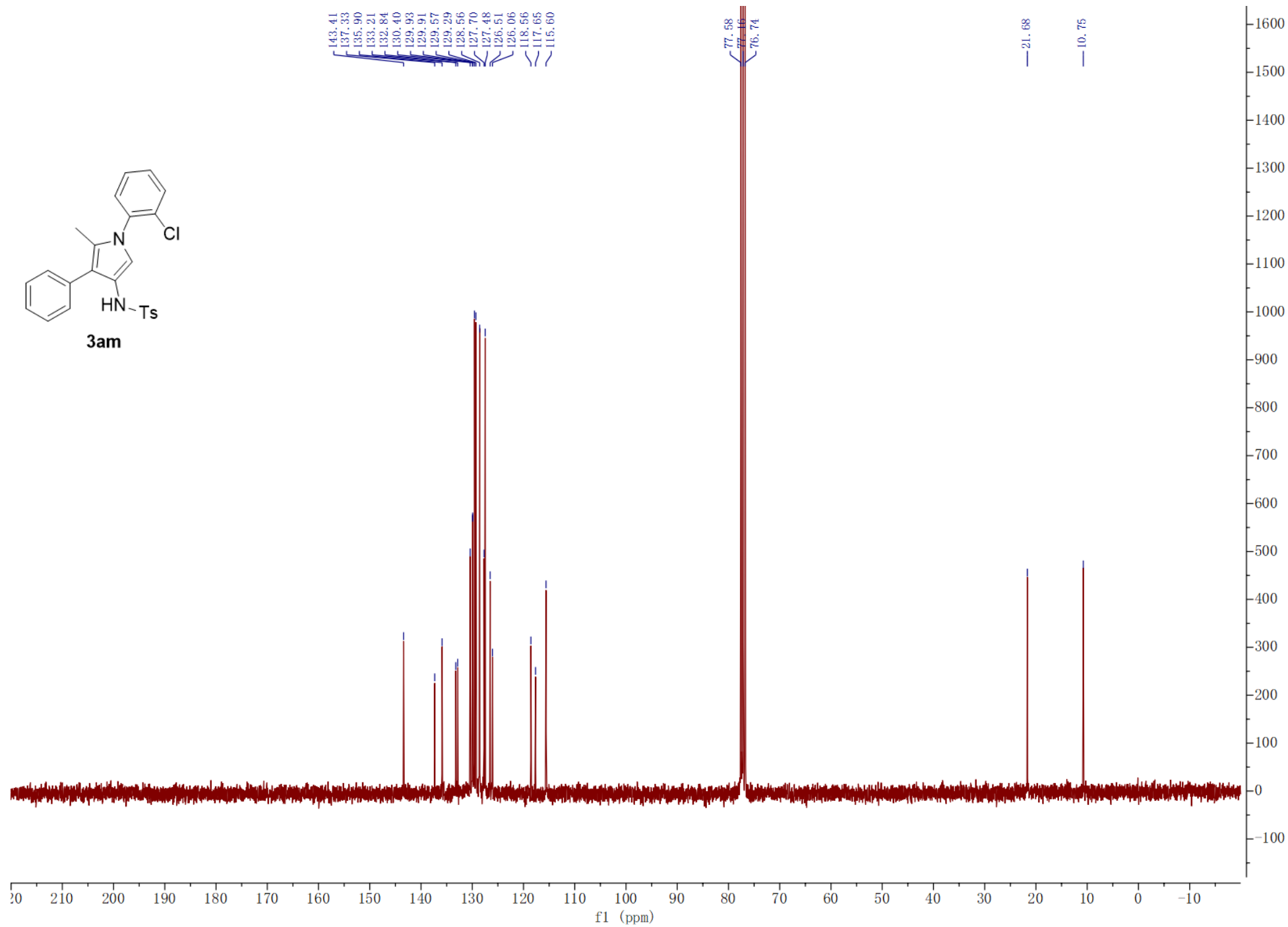
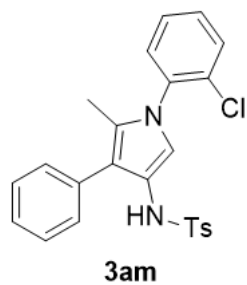


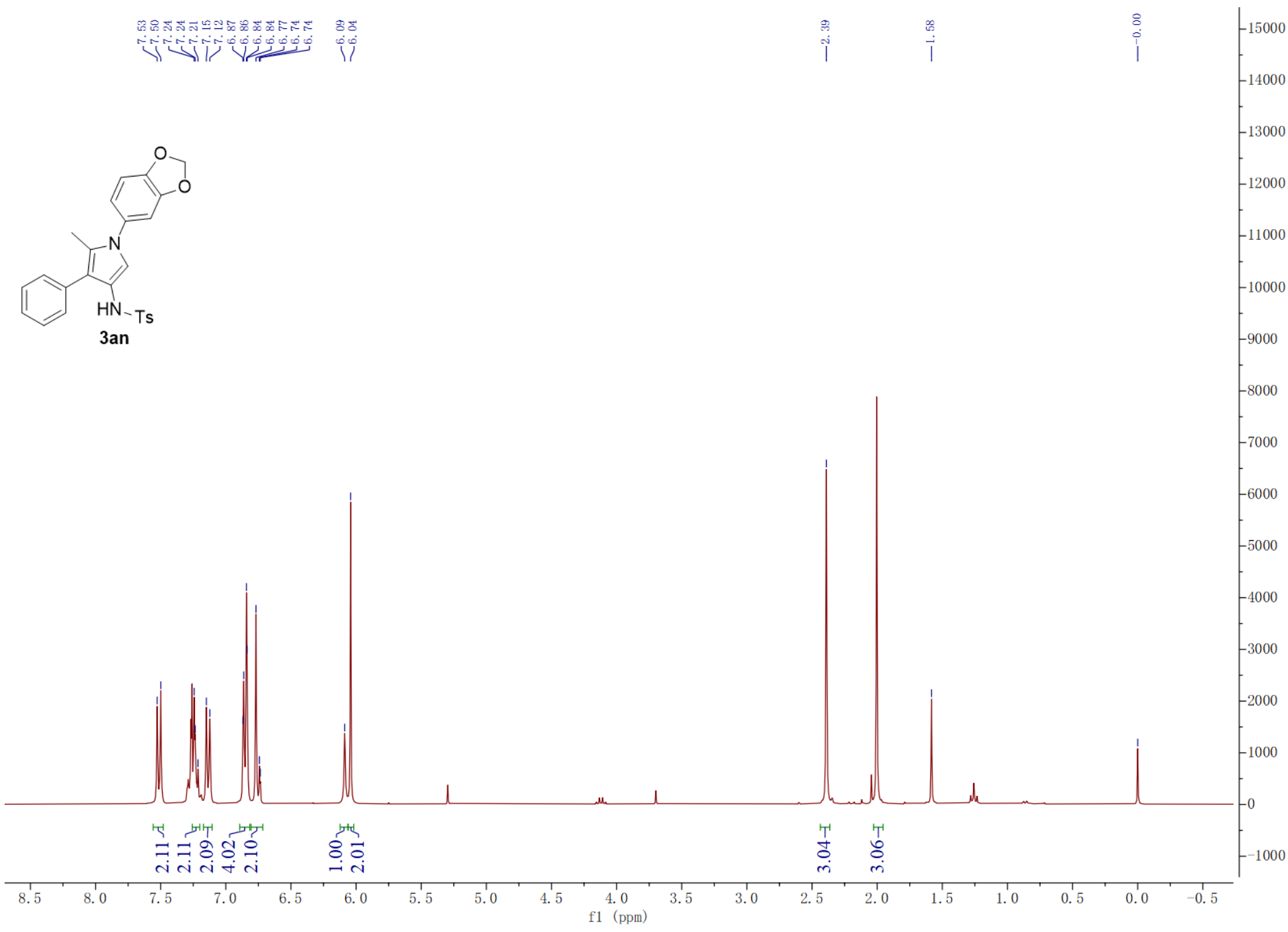


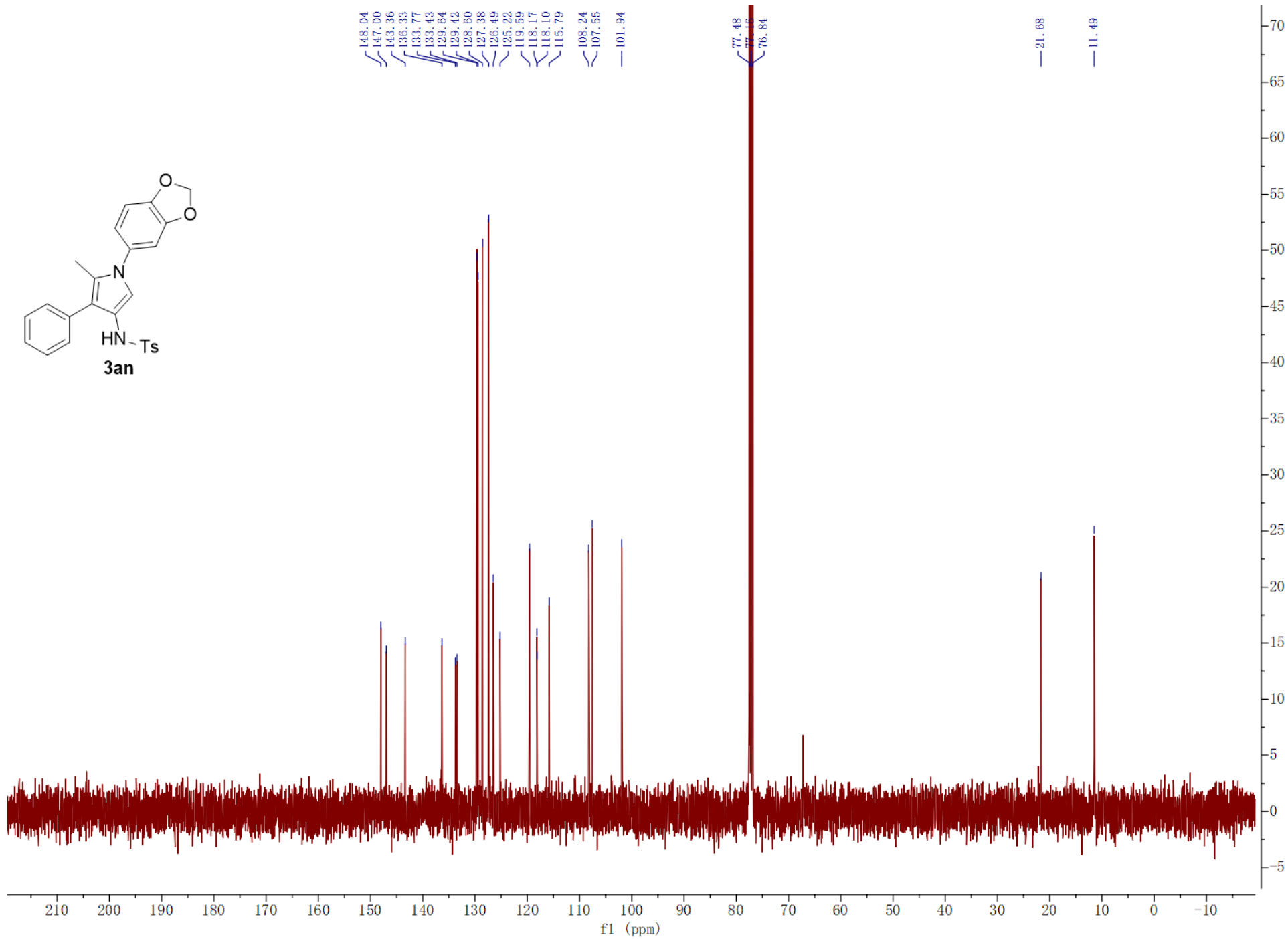
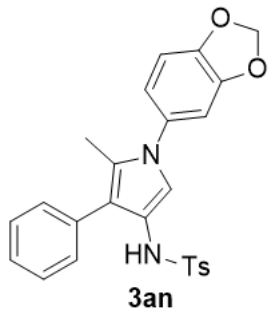


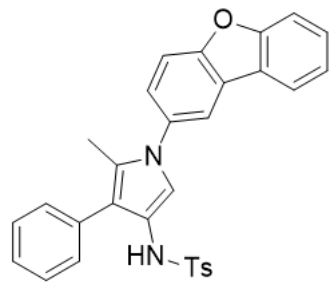




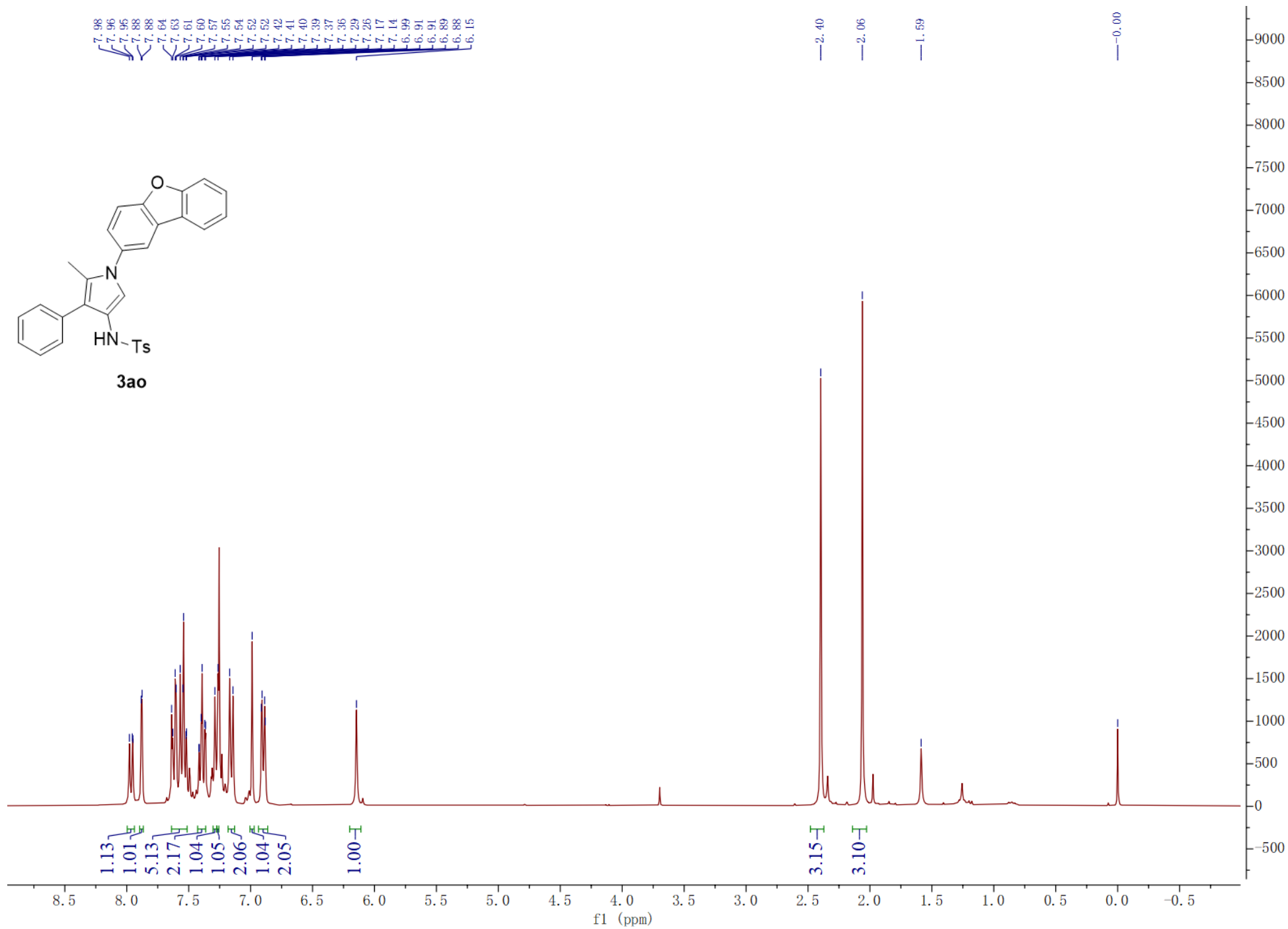


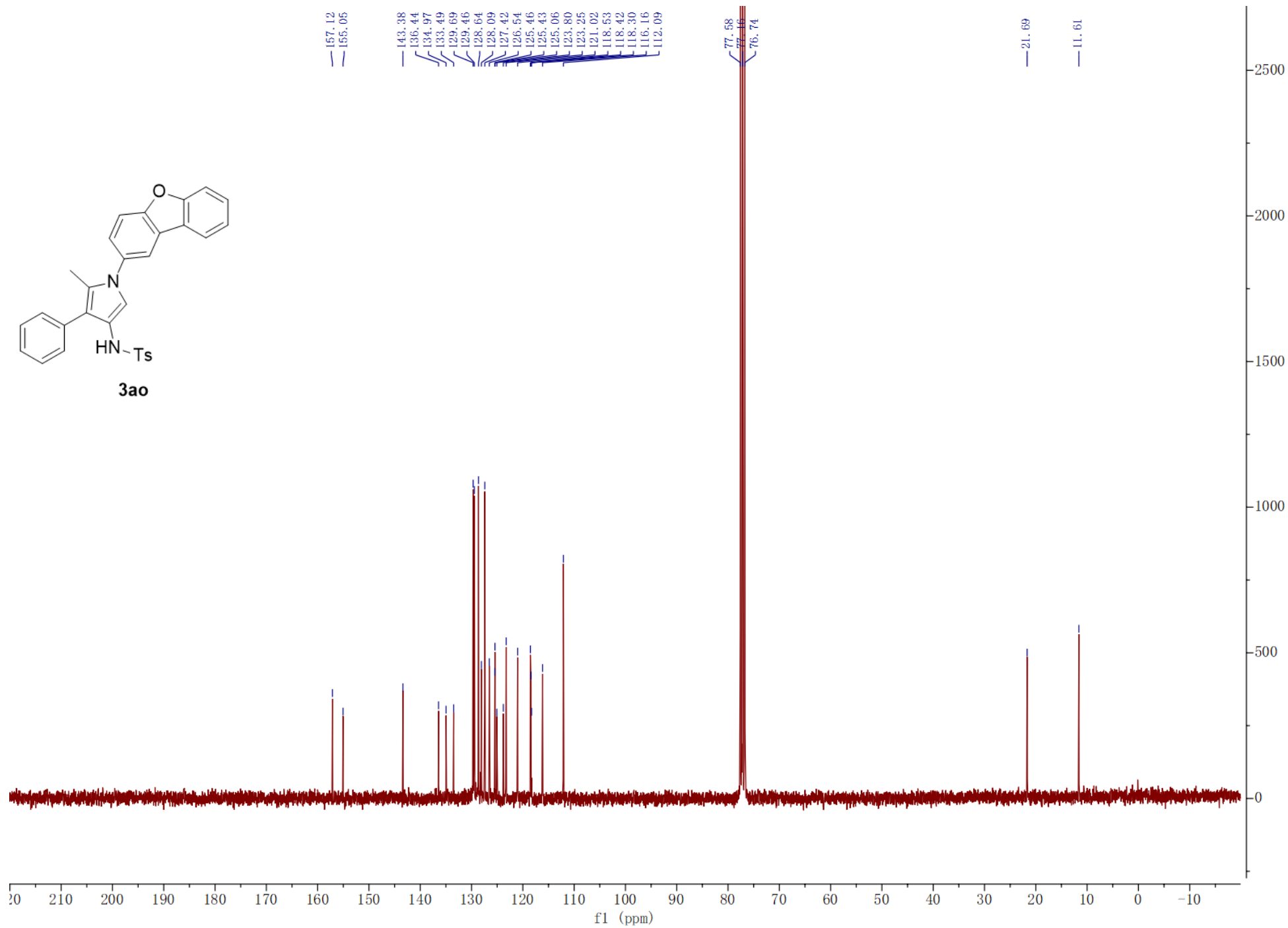
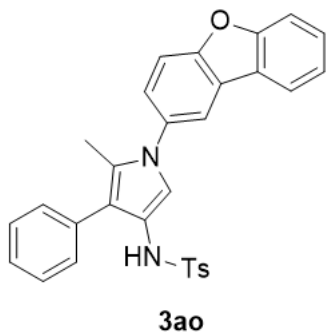


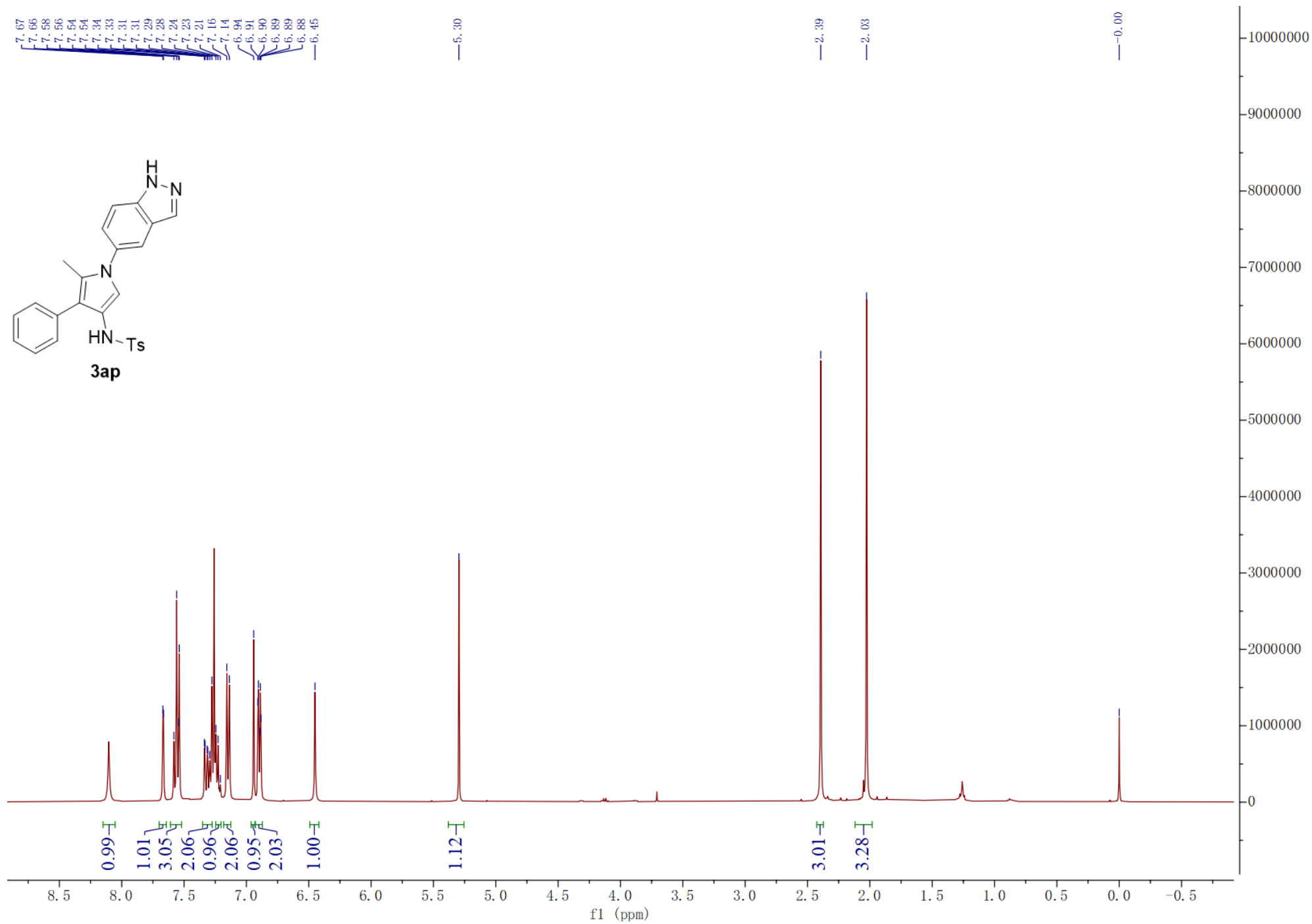
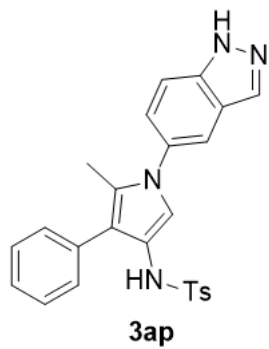


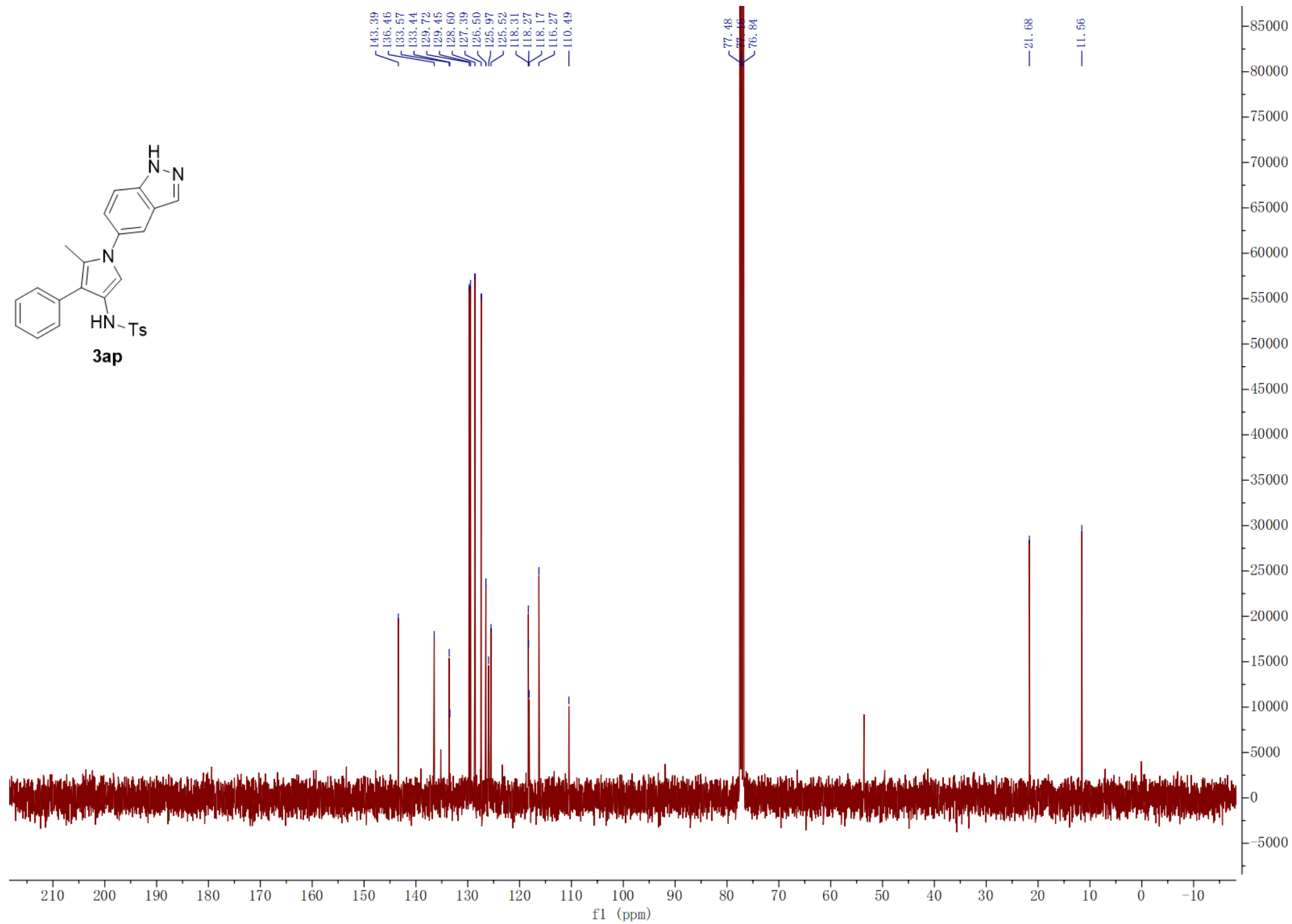
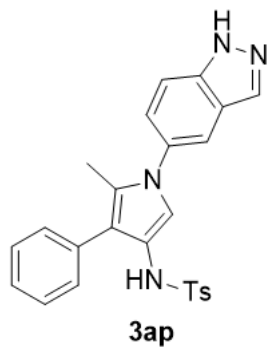


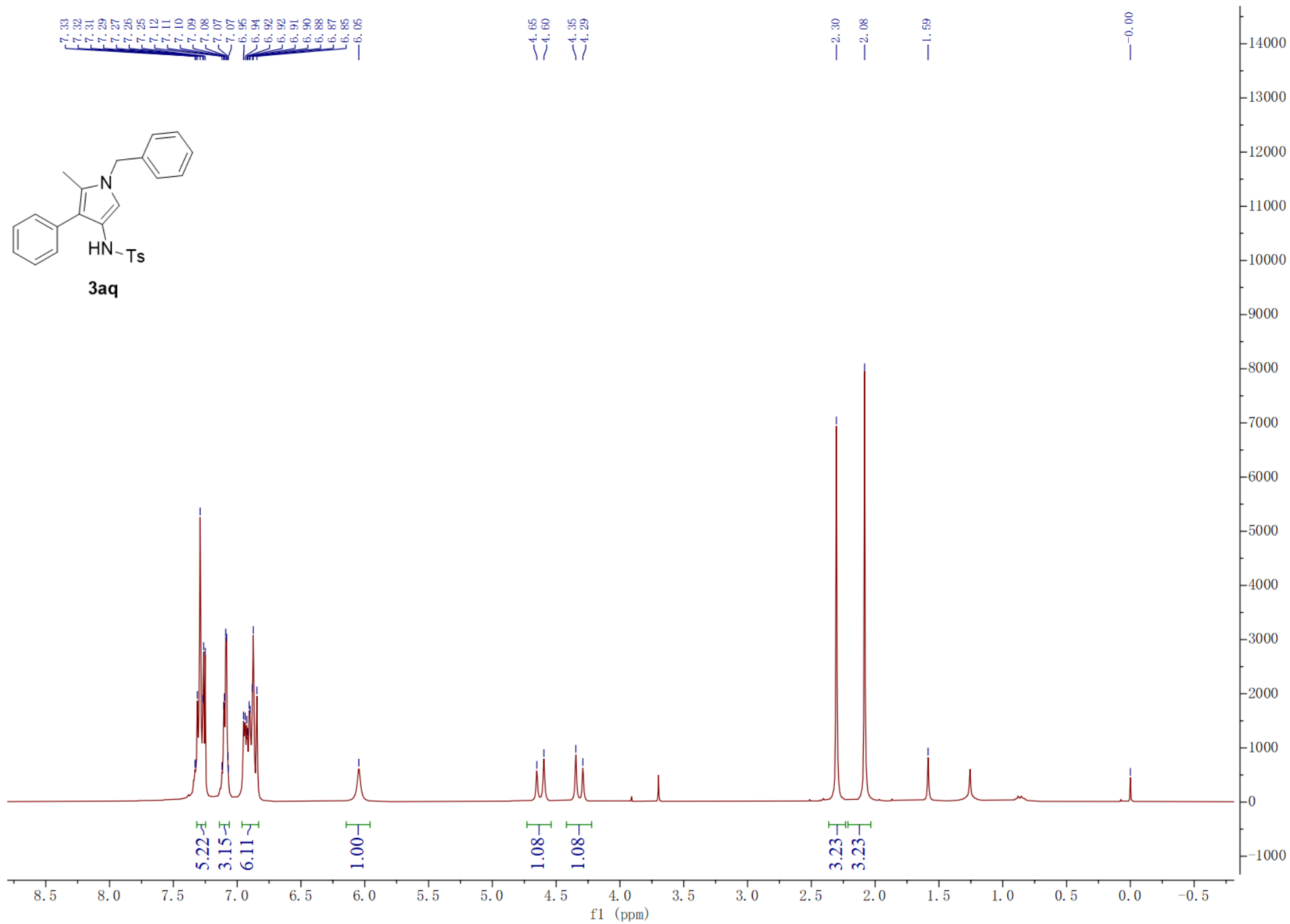
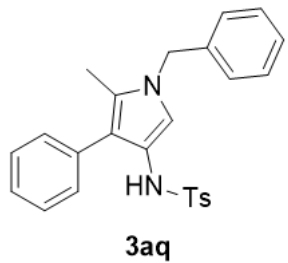
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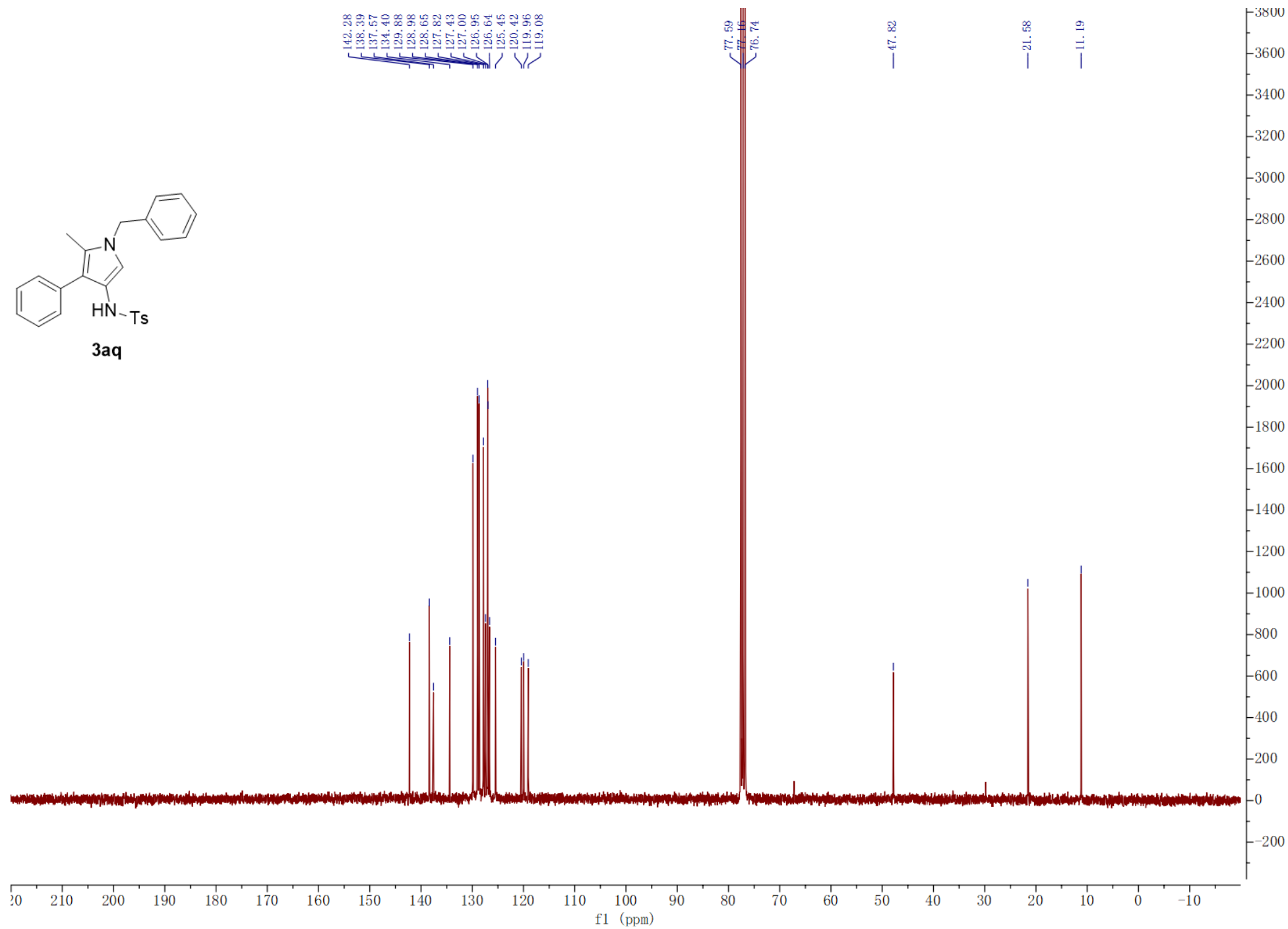
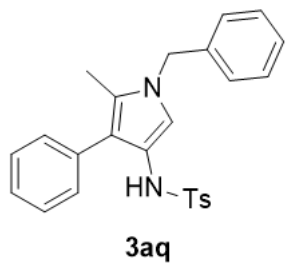


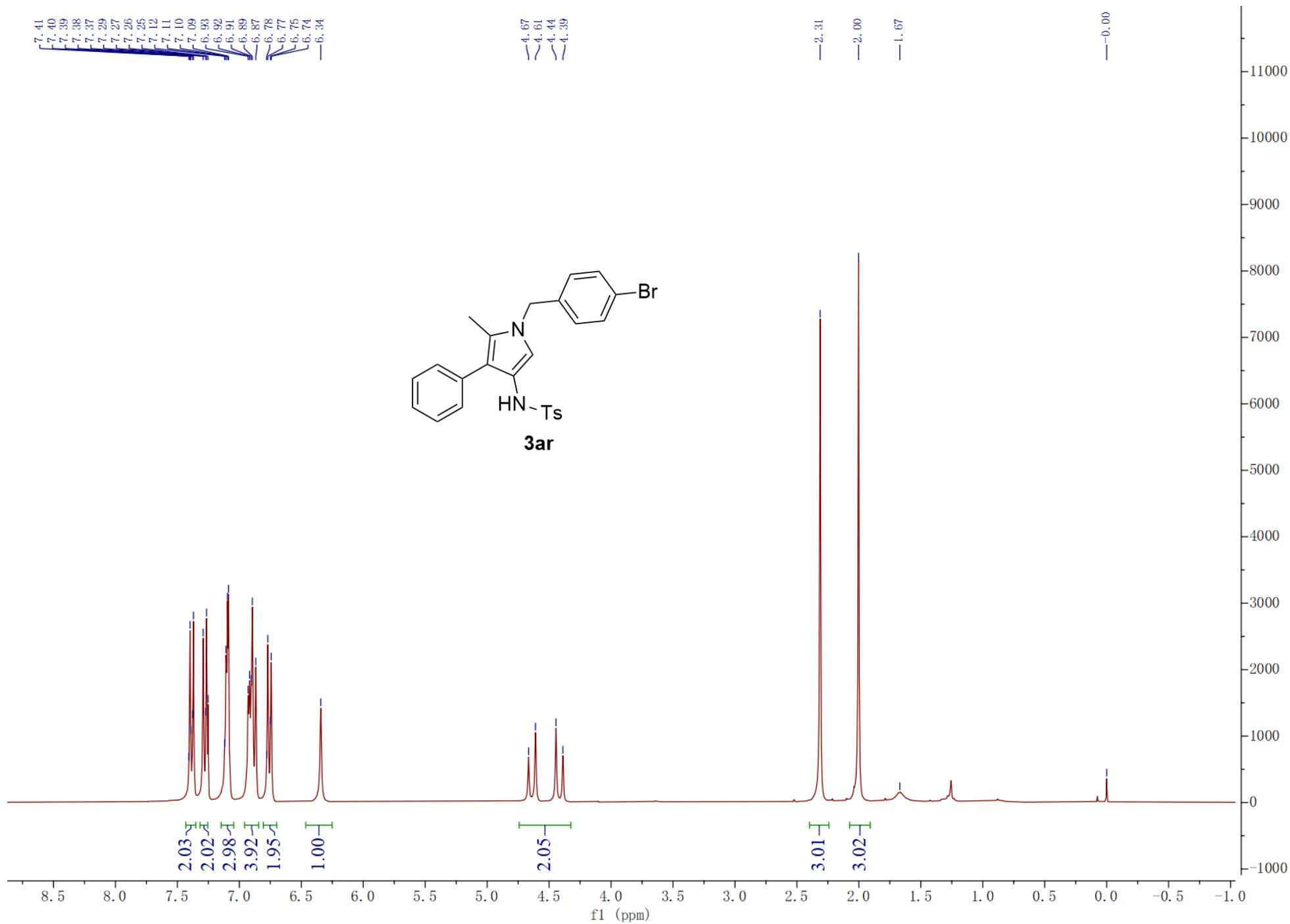
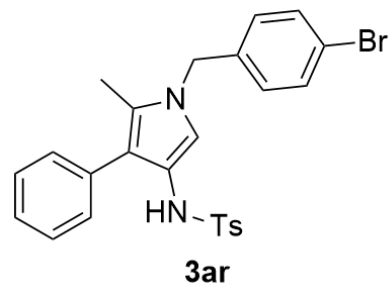


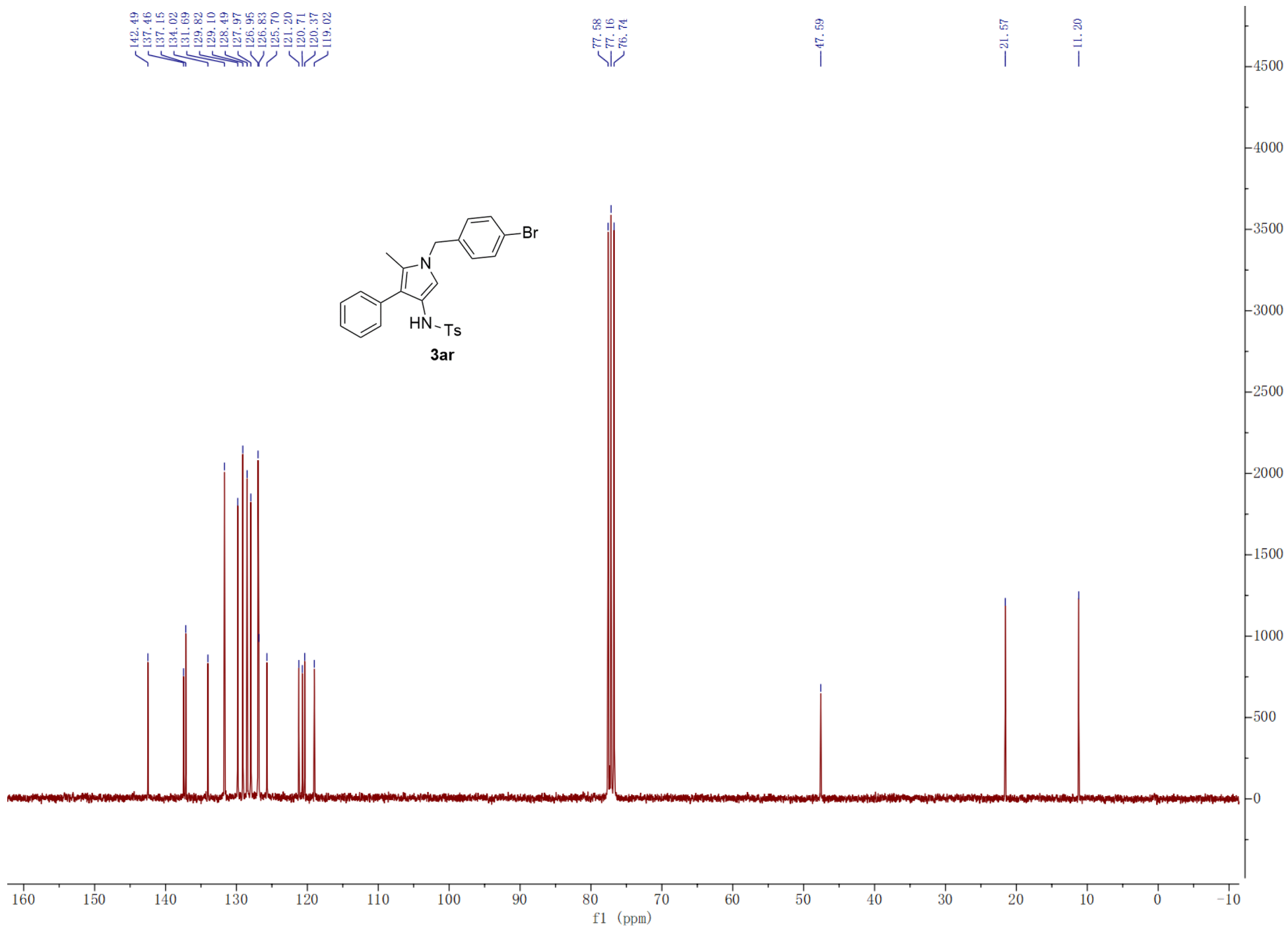












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7.26
7.13
7.12
7.11
7.10
7.09
7.08
6.97
6.96
6.95
6.94
6.88
6.85
6.84
6.83
6.81
6.80
6.77
6.09

4.61
4.56
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2.31
2.08
1.61

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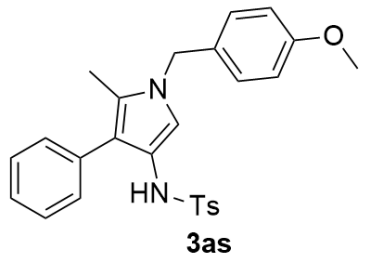
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1.00

1.25
1.07
3.45

3.10
3.06

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

f1 (ppm)

