

Supporting Information
for
**Reductive Coupling of Alkenes with Unsaturated Imines via
Radical Pathway**

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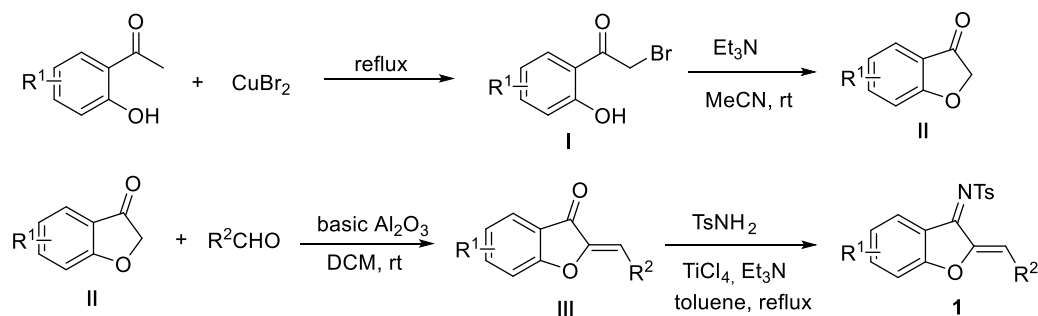
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1. General Information:

Infrared spectra were obtained on a FTIR spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on BRUKER AVANCE III 400 spectrometer, BRUKER AVANCE III 500 spectrometer and BRUKER AVANCE III 600 spectrometer. CDCl_3 were used as solvent. Chemical shifts were referenced relative to residual solvent. The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dq = double quartet. Coupling constants (J) are reported in Hertz (Hz). HRMS were performed on Waters GCT Premier Time of Flight Mass Spectrometer (EI). Melting points were measured with micro melting point apparatus.

$\text{Fe}(\text{acac})_3$, PhSiH_3 , EtOH, THF were commercially available, and the alkenes were commercially available or prepared easily. Unsaturated Imines were prepared according the literature.¹

2. General Synthesis Procedure of Unsaturated Imines¹

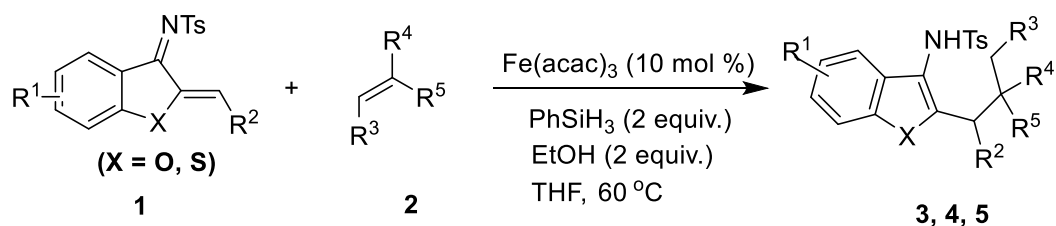


To a solution of *o*-Acetyl phenol (10 mmol, 1eq) in CHCl_3 was added CuBr_2 (11 mmol, 1.1 eq) dissolved in ethyl acetate, the reaction was kept at reflux until the starting material was consumed. The reaction mixture was concentrated under vacuum and the residue was purified by flash chromatography on silica gel to give the desired compound **I**. The compound **I** (5 mmol, 1eq) was dissolved in MeCN, then cooled to 0°C , Et_3N (6.0 mmol, 2eq) was slowly added. The solution was quenched with water (30 mL) and extracted with DCM (3×30 mL). The combined organic phase was dried over NaSO_4 and concentrated. The residue was purified by flash chromatography on silica gel to afford the product **II**.

To a solution of benzofuran-3(2H)-one **II** (5 mmol, 1eq) and aldehyde (5.5 mmol, 1.1eq) in dichloromethane was added aluminum oxide (50 mmol, 10 eq) in three times. The reaction mixture was stirred at rt until benzofuran-3(2H)-one was consumed. The reaction mixture was filtered off. The filtrate was concentrated under vacuum and the residue was purified by flash chromatography on silica gel to give the desired compound **III**.

4-Methylbenzenesulfonamide (3.00 mmol, 1eq) and compound **III** (3.00 mmol, 1eq) were added in a round bottom flask under N_2 , then toluene (40 mL) was added and cooled to 0°C . Et_3N (6.0 mmol, 2eq) and TiCl_4 (3.0 mmol, 1eq) were slowly added and the mixture was kept at reflux under nitrogen overnight. The solution was then cooled to room temperature, quenched with water (30 mL) and extracted with DCM (3×30 mL). The combined organic phase was dried over NaSO_4 and concentrated. The residue was purified by flash chromatography on silica gel to afford unsaturated imines **1**.

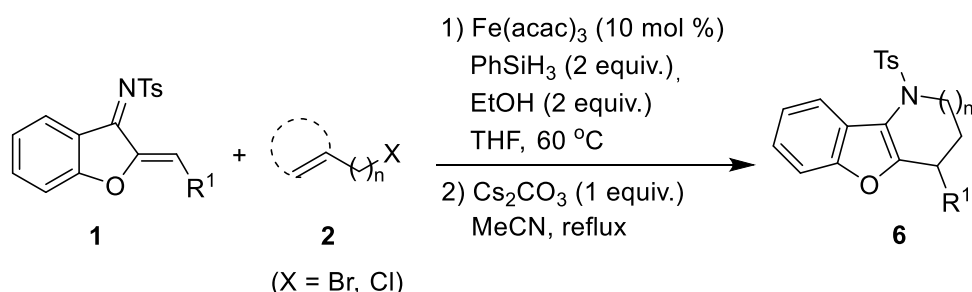
3. General Synthesis Procedure of 3, 4, 5



A Schlenk tube containing $\text{Fe}(\text{acac})_3$ (0.02 mmol, 10 mol %) were evacuated and purged with Argon three times. Afterwards, alkene **2** (0.3mmol, 1.5 eq), unsaturated imine **1** (0.2 mmol, 1.0 eq), PhSiH_3 (0.2 mmol, 1eq) and EtOH (0.4 mmol, 2 eq), THF (2 mL) were added via syringe. The solution was kept at 60 °C until the unsaturated imine was consumed (about 2 hours). Then the solution was evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether.

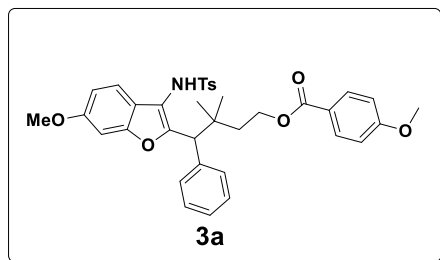
The 1 mmol scale reaction applied for substrate **1a** was performed in the same manner and provided the corresponding product **3a** as a yellow solid (565mg, 90%).

4. General Synthesis Procedure of 6



A Schlenk tube containing $\text{Fe}(\text{acac})_3$ (0.02 mmol, 10 mol %) were evacuated and purged with Argon three times. Afterwards, halogenated olefin **2** (0.3mmol, 1.5 eq), unsaturated imine **1** (0.2 mmol, 1.0 eq), PhSiH_3 (0.2 mmol, 1eq) and EtOH (0.4 mmol, 2 eq), THF (2 mL) were added via syringe. The solution was kept at 60 °C until the unsaturated imine was consumed. (about 2 hours). Then the solution was evaporated under vacuum. Cesium carbonate (0.4 mmol, 2eq) and MeCN (2 mL) were added to the mixture. The solution was kept at reflux about 2 hours. the solution was evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether.

5. Characterization of 3, 4, 5, 6



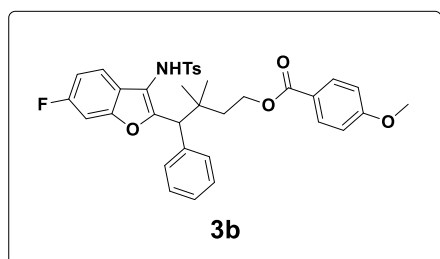
4-(6-methoxy-3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)-3,3-dimethyl-4-phenylbutyl 4-methoxybenzoate

Pale yellow solid (112 mg, 89% yield); m.p. 59-61 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:10).

^1H NMR (600 MHz, CDCl_3) δ 7.95 (d, J = 9.0 Hz, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.32-7.31 (m, 2H), 7.23-7.21 (m, 3H), 7.07 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 2.4 Hz, 2H), 6.95 (d, J = 9.0 Hz, 1H), 6.80-6.88 (m, 2H), 6.71 (s, 1H), 4.44-4.38 (m, 1H), 4.27-4.22 (m, 1H), 4.03 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.32 (s, 3H), 1.74-1.70 (m, 1H), 1.67-1.63 (m, 1H), 1.06 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 166.6, 163.4, 158.0, 155.5, 154.1, 143.8, 138.1, 136.8, 131.7, 130.4, 129.7, 127.8, 127.5, 126.7, 122.8, 119.6, 119.0, 114.3, 113.7, 112.2, 96.1, 62.0, 55.8, 38.9, 37.6, 29.8, 26.0, 25.3, 21.6.

HRMS (EI): calcd for $\text{C}_{36}\text{H}_{37}\text{NO}_7\text{S}$ (M^+): 627.2291; Found: 627.2290.



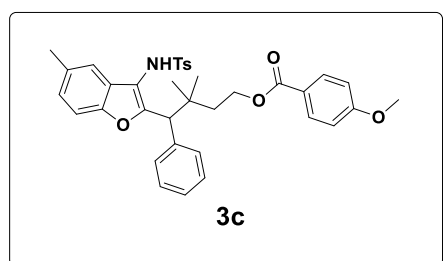
4-(6-fluoro-3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)-3,3-dimethyl-4-phenylbutyl 4-methoxybenzoate

Pale yellow solid (96 mg, 78% yield); m.p. 50-51 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:15).

^1H NMR (600 MHz, CDCl_3) δ 7.88 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.22-7.19 (m, 2H), 7.18-7.14 (m, 3H), 7.12 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.04 (d, J = 7.8 Hz, 2H), 6.99-6.97 (m, 1H), 6.83 (d, J = 9.0 Hz, 2H), 6.78 (td, J_1 = 9.6 Hz, J_2 = 2.4 Hz, 1H), 6.43 (s, 1H), 4.39-35 (m, 1H), 4.18-4.14 (m, 1H), 3.94 (s, 1H), 3.78 (s, 3H), 2.28 (s, 3H), 1.64-1.55 (m, 2H), 0.99 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 166.7, 163.5, 160.0, 157.4, 153.0, 144.1, 137.7, 136.8, 131.8, 130.4, 129.8, 128.0, 127.6, 126.9, 122.8, 119.94 and 119.88, 114.4, 113.7, 111.7, 111.5, 99.5 and 99.3, 61.9, 55.6, 51.9, 39.1, 37.7, 26.1, 25.4, 21.7.

HRMS (EI): calcd for $\text{C}_{35}\text{H}_{34}\text{FNO}_6\text{S}$ (M^+): 615.2091; Found: 615.2089.



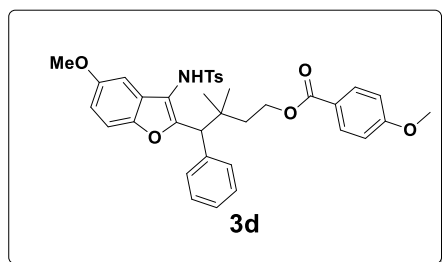
3,3-dimethyl-4-(5-methyl-3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)-4-phenylbutyl 4-methoxybenzoate

Pale yellow solid (90 mg, 74% yield); m.p. 57-59 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:15).

^1H NMR (600 MHz, CDCl_3) δ 7.89-7.86 (m, 2H), 7.52-7.49 (m, 2H), 7.26-7.24 (m, 2H), 7.19-7.13 (m, 4H), 7.05-7.03 (m, 2H), 6.94-6.92 (m, 1H), 6.83-6.81 (m, 2H), 6.61 (s, 1H), 6.27 (bs, 1H), 4.36-4.33 (m, 1H), 4.19-4.16 (m, 1H), 4.00 (s, 1H), 3.78 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H), 1.67-1.52 (m, 2H), 1.00 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 166.6, 163.5, 157.4, 151.7, 143.9, 138.0, 137.1, 132.6, 131.8, 130.5, 129.7, 127.9, 127.8, 126.8, 125.8, 125.5, 122.9, 118.9, 114.0, 113.7, 111.0, 62.0, 55.6, 51.9, 39.0, 37.6, 26.0, 25.4, 21.6, 21.3.

HRMS (EI): calcd for $\text{C}_{36}\text{H}_{37}\text{NO}_6\text{S}$ (M^+): 611.2342; Found: 611.2340.



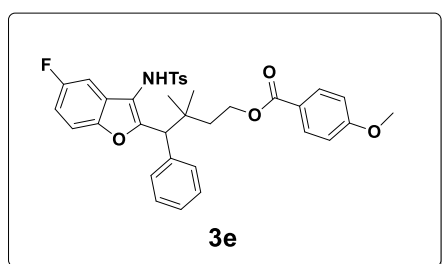
4-(5-methoxy-3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)-3,3-dimethyl-4-phenylbutyl 4-methoxybenzoate

Pale yellow solid (104 mg, 83% yield); m.p. 59-61 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:10).

^1H NMR (600 MHz, CDCl_3) δ 7.96 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.35-7.33 (m, 3H), 7.26-7.23 (m, 3H), 7.13 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 6.81-6.79 (m, 1H), 6.56 (s, 1H), 6.40 (d, J = 2.4 Hz, 1H), 4.46-4.42 (m, 1H), 4.27-4.23 (m, 1H), 4.09 (s, 1H), 3.85 (s, 3H), 3.63 (s, 3H), 2.35 (s, 3H), 1.75-1.72 (m, 1H), 1.68-1.63 (m, 1H), 1.08 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 166.7, 163.4, 158.1, 156.2, 148.0, 143.9, 137.9, 137.1, 131.8, 130.5, 129.8, 127.9, 127.7, 126.8, 126.2, 122.7, 114.4, 113.68, 113.67, 112.2, 100.7, 62.0, 55.7, 55.6, 51.9, 39.0, 37.6, 26.0, 25.3, 21.6.

HRMS (EI): calcd for $\text{C}_{36}\text{H}_{37}\text{NO}_7\text{S}$ (M^+): 627.2291; Found: 627.2290.



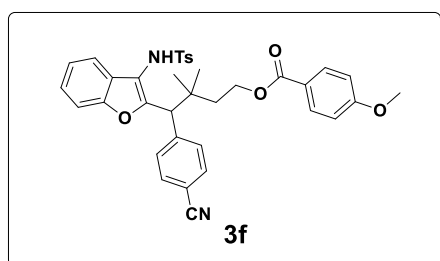
4-(5-fluoro-3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)-3,3-dimethyl-4-phenylbutyl 4-methoxybenzoate

Pale yellow solid (92mg, 75% yield); m.p. 49-51 °C; R_f = 0.3 (EtOAc/Petroleum ether 1:15).

¹H NMR (600 MHz, CDCl₃) δ 7.88 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.32-7.30 (m, 1H), 7.25-7.24 (m, 2H), 7.18-7.15 (m, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.87-6.82 (m, 3H), 6.58-6.56 (m, 1H), 6.43 (s, 1H), 4.40-4.36 (m, 1H), 4.19-4.15 (m, 1H), 4.03 (s, 1H), 3.78 (s, 3H), 2.29 (s, 3H), 1.67-1.57 (m, 2H), 1.01 (s, 3H), 0.93 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 166.6, 163.5, 157.2, 153.2, 143.9, 137.0, 136.4, 134.8, 131.8, 130.3, 129.8, 128.6, 127.6, 125.8, 124.2, 123.1, 122.9, 119.2, 114.2, 113.7, 111.5, 62.0, 55.5, 51.6, 39.0, 37.6, 25.9 and 25.3, 21.6 and 21.5.

HRMS (EI): calcd for C₃₅H₃₄FNO₆S (M⁺): 615.2091; Found: 615.2088.



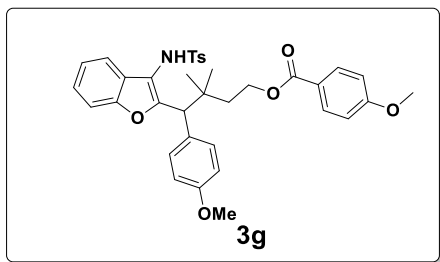
4-(4-cyanophenyl)-3,3-dimethyl-4-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)butyl benzoate

Pale yellow solid (76 mg, 61% yield); m.p. 63-65 °C; *R_f* = 0.5 (EtOAc/Petroleum ether 1:8).

¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.51-7.46 (m, 4H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.82-6.79 (m, 3H), 6.31 (s, 1H), 4.43-4.37 (m, 1H), 4.34 (s, 1H), 4.24-4.18 (m, 1H), 3.76 (s, 3H), 2.26 (s, 3H), 1.74-1.59 (m, 2H), 1.05 (s, 3H), 0.98 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 166.6, 163.6, 155.7, 153.2, 144.1, 143.4, 136.8, 131.8, 131.7, 131.4, 129.7, 127.5, 125.2, 124.7, 123.3, 122.6, 118.9, 115.2, 113.8, 111.6, 110.8, 61.7, 55.6, 51.6, 39.3, 38.1, 26.1, 25.4, 21.7.

HRMS (EI): calcd for C₃₆H₃₄N₂O₆S (M⁺): 622.2138; Found: 622.2135.



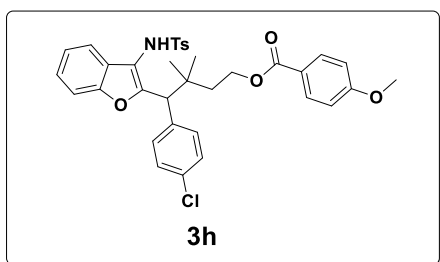
4-(4-methoxyphenyl)-3,3-dimethyl-4-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)butyl 4-methoxybenzoate

Pale yellow solid (100 mg, 80% yield); m.p. 59-61 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:10).

^1H NMR (600 MHz, CDCl_3) δ 7.93 (d, J = 9.0 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.21-7.18 (m, 1H), 7.10-7.03 (m, 4H), 6.88-6.85 (m, 3H), 6.77 (d, J = 8.4 Hz, 2H), 4.41-4.37 (m, 1H), 4.27- 4.23 (m, 1H), 4.10 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.30 (s, 3H), 1.76-1.63 (m, 2H), 1.05 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 166.6, 163.4, 158.4, 157.1, 153.1, 143.8, 136.8, 131.7, 131.5, 130.0, 129.6, 127.5, 125.7, 124.2, 123.0, 122.8, 119.3, 114.2, 113.6, 113.2, 111.4, 62.0, 55.5, 55.2, 51.1, 38.8, 37.7, 25.8, 25.2, 21.5.

HRMS (EI): calcd for $\text{C}_{36}\text{H}_{37}\text{NO}_7\text{S}$ (M^+): 627.2291; Found: 627.2290.



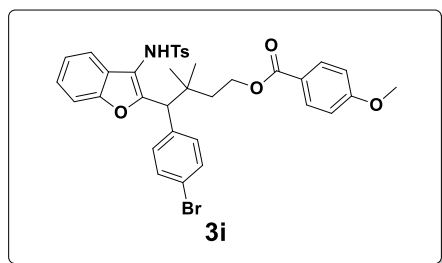
4-(4-chlorophenyl)-3,3-dimethyl-4-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)butyl 4-methoxybenzoate

Pale yellow solid (82 mg, 65% yield); m.p. 53-55 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:15).

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.26-7.19 (m, 4H), 7.07-7.02 (m, 3H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.79 (s, 1H), 4.50-4.42 (m, 1H), 4.32-4.25 (m, 1H), 4.18 (s, 3H), 3.84 (s, 1H), 2.33 (s, 3H), 1.77-1.64 (m, 2H), 1.08 (s, 3H), 1.01 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 166.6, 163.5, 156.0, 153.2, 144.0, 136.9, 136.6, 132.2, 131.7, 130.9, 129.6, 127.5, 125.4, 124.4, 123.2, 122.7, 120.9, 119.3, 114.8, 113.7, 111.5, 61.8, 55.5, 51.1, 38.9, 37.7, 25.9, 25.3, 21.6.

HRMS (EI): calcd for C₃₅H₃₄ClNO₆S (M⁺): 631.1795; Found: 631.1793.



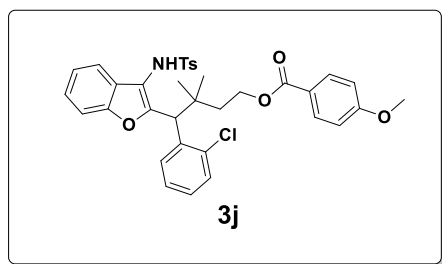
4-(4-bromophenyl)-3,3-dimethyl-4-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)butyl 4-methoxybenzoate

Pale yellow solid (105 mg, 78% yield); m.p. 54-56 °C; *R_f* = 0.5 (EtOAc/Petroleum ether 1:15).

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 9.2 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.37-7.28 (m, 4H), 7.19-7.10 (m, 2H), 7.00-6.95 (m, 4H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.26 (s, 1H), 4.40-4.33 (m, 1H), 4.21-4.16 (m, 1H), 4.11 (s, 1H), 3.76 (s, 3H), 2.26 (s, 3H), 1.70-1.57 (m, 2H), 1.01 (s, 3H), 0.96 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 166.6, 163.5, 156.4, 153.2, 144.0, 136.8, 136.4, 132.8, 131.9, 131.8, 129.7, 128.0, 127.5, 125.5, 124.5, 123.2, 122.7, 119.2, 114.7, 113.7, 111.5, 61.8, 55.6, 51.1, 39.1, 37.8, 26.0, 25.4, 21.7.

HRMS (EI): calcd for C₃₅H₃₄BrNO₆S (M⁺): 675.1290; Found: 675.1290.



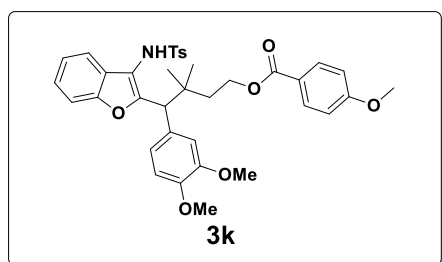
4-(2-chlorophenyl)-3,3-dimethyl-4-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)butyl 4-methoxybenzoate

Pale yellow solid (96 mg, 76% yield); m.p. 50-52 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:15).

^1H NMR (600 MHz, CDCl_3) δ 7.89 (d, J = 8.4 Hz, 2H), 7.6-7.58 (m, 3H), 7.39 (d, J = 8.4 Hz, 1H), 7.28-7.24 (m, 2H), 7.19-7.17 (m, 1H), 7.10-7.05 (m, 5H), 6.83 (d, J = 8.4 Hz, 2H), 6.30 (s, 1H), 4.70 (s, 1H), 4.29-4.24 (m, 1H), 4.16-4.12 (m, 1H), 3.78 (s, 3H), 2.26 (s, 3H), 1.59-1.55 (m, 1H), 1.49-1.45 (m, 1H), 1.01 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 166.5, 163.5, 155.6, 153.3, 144.0, 137.0, 135.9, 134.6, 131.8, 131.7, 130.0, 129.7, 128.2, 127.8, 126.6, 125.6, 124.6, 123.3, 122.8, 120.2, 115.1, 113.7, 111.5, 61.9, 55.6, 46.1, 38.7, 38.6, 25.4, 24.9, 21.6

HRMS (EI): calcd for $\text{C}_{35}\text{H}_{34}\text{ClNO}_6\text{S}$ (M^+): 631.1795; Found: 631.1792.



4-(3,4-dimethoxyphenyl)-3,3-dimethyl-4-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)butyl 4-methoxybenzoate

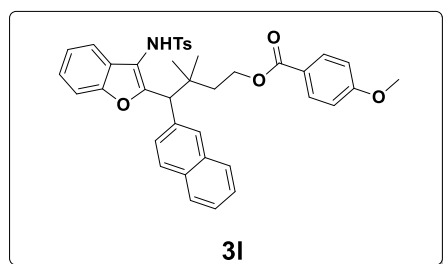
Pale yellow solid (120 mg, 91% yield); m.p. 55-57 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:5).

^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 9.2 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 8.4 Hz, 1H), 7.14-7.12 (m, 1H), 7.01-6.80 (m, 8H), 6.68 (d, J = 8.0 Hz,

1H), 6.58 (bs, 1H), 4.39-4.32 (m, 1H), 4.27-4.17 (m, 1H), 4.08 (s, 1H), 3.78-3.76 (m, 9H), 2.24 (s, 3H), 1.69-1.59 (m, 2H), 1.02 (s, 3H), 0.97 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 166.6, 163.4, 157.1, 153.1, 148.0, 147.8, 143.9, 136.7, 131.7, 130.4, 129.6, 125.5, 124.2, 123.0, 122.8, 122.7, 119.1, 114.2, 114.0, 113.6, 111.4, 110.4, 62.0, 56.0, 55.8, 55.0, 51.2, 39.0, 37.7, 26.0, 25.4, 21.5.

HRMS (EI): calcd for C₃₇H₃₉NO₈S (M⁺): 657.2396; Found: 657.2396.



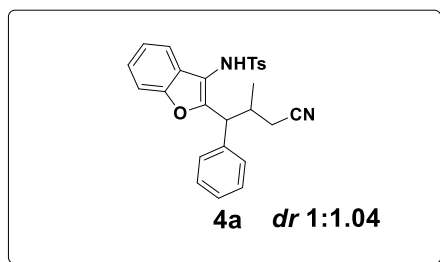
3,3-dimethyl-4-(3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)-4-(naphthalen-2-yl)butyl 4-methoxybenzoate

Pale yellow solid (93 mg, 72% yield); m.p. 59-61 °C; R_f = 0.6 (EtOAc/Petroleum ether 1:3).

¹H NMR (600 MHz, CDCl₃) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.74-7.58 (m, 5H), 7.46-7.36 (m, 6H), 7.02-7.00 (m, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.32 (s, 1H), 4.42-4.38 (m, 1H), 4.24-4.20 (m, 2H), 3.78 (s, 3H), 2.12 (s, 3H), 1.74 -1.63 (m, 2H), 1.07 (s, 3H), 1.00 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 166.7, 163.4, 156.8, 153.2, 143.9, 136.6, 135.5, 133.0, 132.3, 131.8, 129.8, 129.6, 129.2, 128.7, 128.2, 127.5, 127.2, 126.0, 125.9, 125.6, 124.4, 123.2, 122.7, 119.4, 114.6, 113.7, 111.6, 61.9, 55.6, 51.8, 39.0, 38.0, 26.1, 25.4, 21.5.

HRMS (EI): calcd for C₃₉H₃₇NO₆S (M⁺): 647.2342; Found: 647.2340.



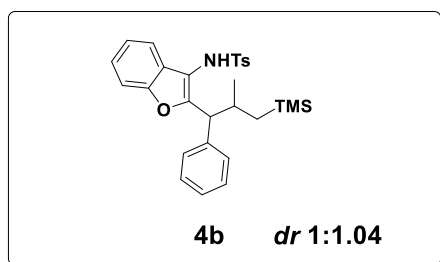
***N*-(2-(3-cyano-2-methyl-1-phenylpropyl)benzofuran-3-yl)-4-methylbenzenesulfonamide**

Pale yellow oil (64 mg, 72% yield); R_f = 0.5 (EtOAc/Petroleum ether 1:20).

^1H NMR (600MHz, CDCl_3) δ 7.57-7.54 (m, 2H), 7.35 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.24-7.17 (m, 4H), 7.16-7.09 (m, 4H), 6.99 and 6.92 (t, J = 7.8 Hz, 1H), 6.95 and 6.69 (d, J = 7.8Hz, 1H), 6.16 and 6.07 (s, 1H), 3.98 and 3.88 (d, J = 10.2 Hz, 1H), 2.77-2.66 (m, 1H), 2.32 and 2.31 (s, 3H), 2.29-2.25 and 2.21-2.18 (m, 1H), 2.13-2.09 and 1.97-1.93 (m, 1H), 0.96 and 0.91 (d, J = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 157.9 and 157.8, 153.23 and 153.20, 144.1 and 144.0, 139.21 and 139.18, 136.8 and 136.7, 130.9, 129.82 and 129.76, 128.67 and 128.64, 128.58, 127.74 and 127.66, 126.92 and 126.86, 126.5, 124.20 and 124.18, 123.1 and 123.0, 119.04 and 118.97, 113.8 and 113.7, 111.5 and 111.4, 55.4 and 55.3, 49.3 and 48.5, 41.7 and 40.7, 40.2 and 39.4, 21.66 and 21.63.

HRMS (EI): calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_3\text{S}$ (M^+): 444.1508; Found: 444.1505.



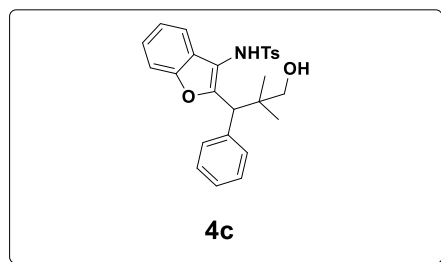
4-methyl-*N*-(2-(2-methyl-1-phenyl-3-(trimethylsilyl)propyl)benzofuran-3-yl)benzenesulfonamide

Pale yellow oil (76 mg, 77% yield); R_f = 0.5 (EtOAc/Petroleum ether 1:50).

¹H NMR (600 MHz, CDCl₃) δ 7.74-7.71 (m, 2H), 7.49-7.47 (m, 1H), 7.36-7.03 (m, 10H), 6.08 (bs, 1H), 3.82 and 3.68 (d, *J* = 10.2 Hz, 1H), 2.59-2.49 (m, 1H), 2.46 (d, *J* = 2.4 Hz, 3H), 0.86 and 0.79 (d, *J* = 6.6 Hz, 3H), 0.63 and 0.41 (d, *J* = 13.8 Hz, 1H), 0.28-0.24 and 0.19-0.14 (m, 1H), 0.03 and 0.01 (m, 9H).

¹³C NMR (150 MHz, CDCl₃) δ 157.9 and 157.6, 153.17 and 153.16, 144.03 and 143.99, 140.8 and 140.7, 136.90 and 136.86, 129.8, 128.9, 128.6, 128.5 and 128.4, 127.83 and 128.77, 126.8, 126.2 and 126.0, 124.2 and 124.1, 123.1 and 123.0, 119.2 and 118.9, 113.6 and 131.1, 111.5 and 111.4, 52.5 and, 52.0, 33.8 and 33.4, 23.2 and 22.7, 21.70 and 21.68, 20.9 and 20.4, -0.56 and -0.63.

HRMS (EI): calcd for C₂₈H₃₃NO₃SSi (M⁺): 491.1950; Found: 491.1953.



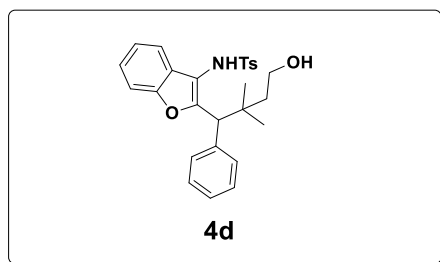
***N*-(2-(3-hydroxy-2,2-dimethyl-1-phenylpropyl)benzofuran-3-yl)-4-methylbenzenesulfonamide**

Pale yellow solid (80 mg, 89% yield); m.p. 169-171 °C; *R_f* = 0.5 (EtOAc/Petroleum ether 1:3).

¹H NMR (600 MHz, CDCl₃) δ 7.65 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.45 (m, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.19-7.18 (m, 1H), 7.15-7.09 (m, 4H), 7.05-7.03 (m, 2H), 6.97 (d, *J* = 7.2 Hz, 2H), 3.79 (s, 1H), 3.19 (d, *J* = 10.8 Hz, 1H), 3.06 (d, *J* = 10.8 Hz, 1H), 2.41 (bs, 1H), 2.26 (s, 3H), 0.86 (s, 3H), 0.74 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 153.6, 153.1, 143.7, 137.0, 136.3, 130.0, 129.8, 127.6, 127.3, 126.7, 125.6, 124.3, 123.2, 120.7, 115.6, 111.3, 71.2, 46.6, 40.4, 24.4, 21.7, 20.8.

HRMS (EI): calcd for C₂₆H₂₇NO₄S (M⁺): 449.1661; Found: 449.1660.



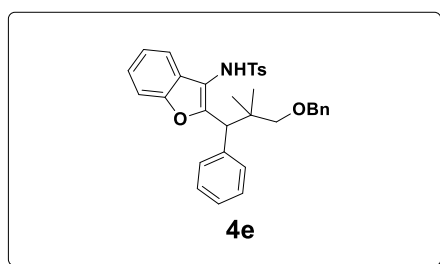
***N*-(2-(4-hydroxy-2,2-dimethyl-1-phenylbutyl)benzofuran-3-yl)-4-methylbenzenesulfonamide**

Pale yellow solid (84 mg, 91% yield); m.p. 135-137 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:3).

^1H NMR (600 MHz, CDCl_3) δ 7.54-7.49 (m, 1H), 7.47-7.45(m, 3H), 7.27-7.14 (m, 7H), 6.99 (d, J = 7.2 Hz, 2H), 4.08 (s, 1H), 3.90-3.86 (m, 1H), 3.78-3.74 (m, 1H), 2.29 (s, 3H), 1.64-1.59 (m, 1H), 1.34-1.28 (m, 1H), 1.04 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 154.4, 153.5, 143.6, 138.0, 136.2, 130.5, 129.7, 127.5, 127.3, 126.4, 125.7, 124.3, 123.1, 120.4, 115.1, 111.3, 60.2, 60.0, 42.0, 38.1, 26.1, 25.8, 21.7.

HRMS (EI): calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_4\text{S}$ (M^+): 463.1817; Found: 463.1815.



***N*-(2-(3-(benzyloxy)-2,2-dimethyl-1-phenylpropyl)benzofuran-3-yl)-4-methylbenzenesulfonamide**

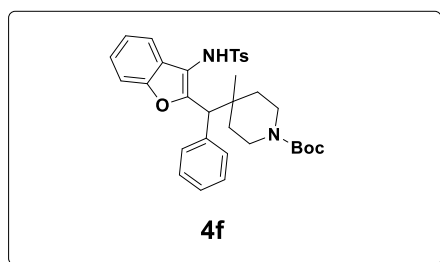
Pale yellow solid (82 mg, 76% yield); m.p. 47-48 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:15).

^1H NMR (600 MHz, CDCl_3) δ 7.83-7.82 (m, 1H), 7.44-7.42 (m, 5H), 7.38-7.37 (m, 1H), 7.31-7.27 (m, 5H), 7.16-7.12 (m, 3H), 7.03-7.01 (m, 2H), 6.93 (d, J = 7.8 Hz,

2H), 4.62 (d, $J = 11.4$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 3.72 (s, 1H), 3.00 (d, $J = 9.6$ Hz, 1H), 2.95 (d, $J = 9.6$ Hz, 1H), 2.29 (s, 3H), 0.89 (s, 3H), 0.82 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 153.6, 152.3, 143.4, 137.4, 136.8, 136.1, 130.5, 129.6, 128.8, 128.5, 128.3, 127.5, 127.1, 126.6, 125.6, 124.3, 123.2, 121.1, 115.7, 111.2, 78.5, 74.2, 46.9, 40.3, 24.7, 21.7, 21.3.

HRMS (EI): calcd for $\text{C}_{33}\text{H}_{33}\text{NO}_4\text{S}$ (M^+): 539.2130 Found: 539.2131.



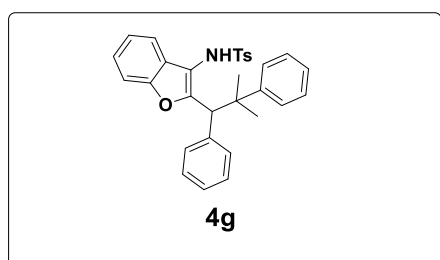
***tert*-butyl 4-methyl-4-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)piperidine-1-carboxylate**

Pale yellow solid (84 mg, 73% yield); m.p. 93-95 °C; $R_f = 0.5$ (EtOAc/Petroleum ether 1:10).

^1H NMR (600 MHz, CDCl_3) δ 7.54-7.53 (m, 2H), 7.45-7.44 (m, 1H), 7.32-7.30 (m, 2H), 7.26-7.20 (m, 4H), 7.09 (d, $J = 7.8$ Hz, 2H), 7.06-7.03 (m, 1H), 7.01-7.00 (m, 1H), 6.19 (bs, 1H), 4.04 (s, 1H), 3.77 (t, $J = 1.2$ Hz, 2H), 2.88 (t, $J = 1.2$ Hz, 2H), 2.34 (s, 3H), 1.43 (s, 9H), 1.40-1.17 (m, 4H), 1.09 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 156.7, 155.1, 153.2, 144.1, 137.3, 136.7, 130.5, 129.7, 127.9, 127.6, 126.9, 125.5, 124.3, 123.2, 119.1, 114.5, 111.5, 79.5, 52.8, 36.9, 31.6, 30.3, 28.6, 21.7, 19.5.

HRMS (EI): calcd for $\text{C}_{33}\text{H}_{38}\text{N}_2\text{O}_5\text{S}$ (M^+): 574.2501; Found: 574.2500.



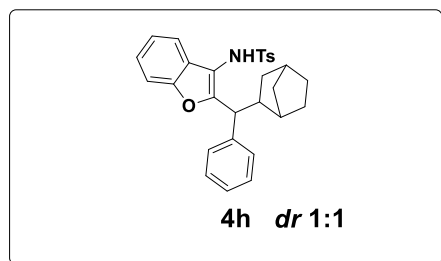
4-methyl-N-(2-(2-methyl-1,2-diphenylpropyl)benzofuran-3-yl)benzenesulfonamide

Pale yellow solid (70 mg, 71% yield); m.p. 45-47 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:20).

^1H NMR (600 MHz, CDCl_3) δ 7.48 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 1H), 7.28-7.01 (m, 15H), 4.93 (bs, 1H), 4.03 (s, 1H), 2.39 (s, 3H), 1.43 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 153.4, 153.1, 148.4, 143.8, 137.4, 136.7, 130.5, 129.8, 128.3, 127.6, 127.4, 126.9, 126.6, 126.5, 125.6, 124.2, 123.1, 119.6, 114.3, 111.3, 54.7, 43.3, 27.3, 24.7, 21.7.

HRMS (EI): calcd for $\text{C}_{31}\text{H}_{29}\text{NO}_3\text{S}$ (M^+): 495.1868; Found: 495.1866.



N-(2-(bicyclo[2.2.1]heptan-2-yl(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide

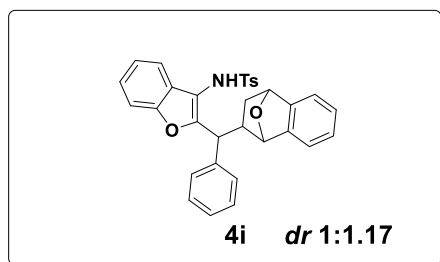
Pale yellow solid (79 mg, 84% yield); m.p. 90-92 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:50).

^1H NMR (600 MHz, CDCl_3) δ 7.60-7.57 (m, 2H), 7.34-7.30 (m, 1H), 7.23-7.21 (m, 1H), 7.19-7.08 (m, 7H), 7.05 and 6.80 (d, J = 7.2 Hz, 1H), 7.01-6.98 and 6.94-6.91 (m, 1H), 5.82 and 5.74 (s, 1H), 3.71 and 3.45 (d, J = 12.0 Hz, 1H), 2.37-2.34 and 2.27-2.23 (m, 1H), 2.33 and 2.32 (s, 3H), 2.11 and 2.02 (t, J = 4.2 Hz, 1H), 1.70-1.68 (m, 1H), 1.39-0.71 (m, 8H).

^{13}C NMR (150 MHz, CDCl_3) δ 158.16 and 157.21, 153.2 and 153.0, 144.2 and 144.1, 141.6 and 139.9, 136.8 and 136.7, 129.9 and 129.8, 129.0 and 128.7, 128.4 and

128.2, 127.64 and 127.62, 126.9 and 126.8, 126.5, 124.1 and 124.0, 123.0 and 122.9, 119.2 and 118.8, 113.4 and 112.5, 111.5 and 111.4, 48.2 and 47.5, 45.7 and 45.1, 40.1 and 38.8, 37.1 and 36.9, 36.6, 35.9 and 35.0, 30.14 and 30.13, 28.84 and 28.76, 21.73 and 21.71.

HRMS (EI): calcd for C₂₉H₂₉NO₃S (M⁺): 471.1868; Found: 471.1866.



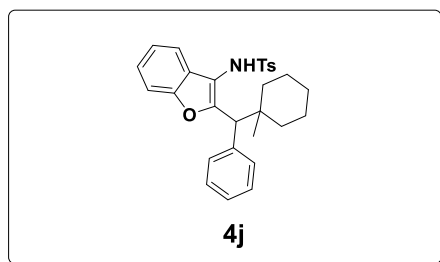
4-methyl-N-(2-(phenyl(1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)methyl)benzofuran-3-yl)benzenesulfonamide

Pale yellow solid (64 mg, 61% yield); m.p. 56-58 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:5).

¹H NMR (600 MHz, CDCl₃) δ 7.65 (t, *J* = 8.4 Hz, 2H), 7.42-7.22 (m, 5H), 7.19-7.08 (m, 10H), 7.04 and 6.63 (s, 1H), 5.34 and 5.23 (d, *J* = 4.2 Hz, 1H), 4.83 (d, *J* = 14.4 Hz, 1H), 4.11 and 4.01 (d, *J* = 12.0 Hz, 1H), 2.71-2.68 and 2.64-2.60 (m, 1H), 2.39 and 2.35 (s, 3H), 1.60-1.57 and 1.45-1.42 (m, 1H), 1.41-1.38 (m, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 155.91 and 155.86, 153.4 and 153.2, 146.0 and 145.9, 145.2 and 145.1, 144.0 and 143.9, 140.4 and 139.6, 136.9 and 136.7, 129.81 and 129.79, 129.0, 128.7, 128.51 and 128.45, 127.6 and 127.5, 127.4 and 127.2, 127.0, 126.8 and 126.6, 126.0, 124.4 and 124.3, 123.12 and 123.06, 119.73 and 119.68, 119.2 and 119.0, 113.9 and 113.4, 111.4 and 111.2, 81.7 and 80.9, 79.8 and 79.7, 46.7 and 46.4, 44.6 and 44.2, 34.0 and 33.5, 21.7 and 21.6.

HRMS (EI): calcd for C₃₂H₂₇NO₄S (M⁺): 521.1661; Found: 521.1661.



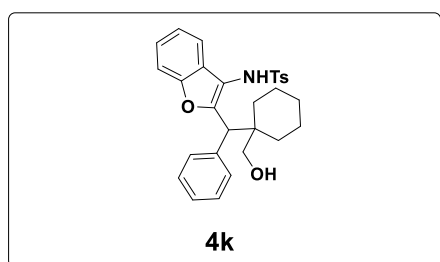
4-methyl-N-(2-((1-methylcyclohexyl)(phenyl)methyl)benzofuran-3-yl)benzenesulfonamide

Pale yellow solid (84 mg, 89% yield); m.p. 50-51 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:50).

^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.8 Hz, 1H), 7.22-7.18 (m, 2H), 7.16-7.09 (m, 5H), 7.04-7.00 (m, 3H), 5.98 (s, 1H), 3.83 (s, 1H), 2.28 (s, 3H), 1.50-1.01 (m, 10H), 0.95 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 157.2, 153.2, 143.9, 138.0, 136.7, 130.5, 129.8, 127.68, 127.65, 126.6, 125.7, 124.2, 123.1, 119.3, 114.1, 111.4, 38.4, 36.8, 36.2, 26.1, 22.2, 21.9, 21.7.

HRMS (EI) : calcd for $\text{C}_{29}\text{H}_{31}\text{NO}_3\text{S}$ (M^+): 473.2025; Found: 473.2023.



N-(2-((1-(hydroxymethyl)cyclohexyl)(phenyl)methyl)benzofuran-3-yl)-4-methylbenzenesulfonamide

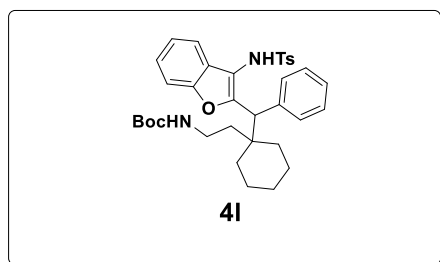
Pale yellow solid (86 mg, 88% yield); m.p. 175-177 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:5).

^1H NMR (600 MHz, CDCl_3) δ 7.87 (s, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 1H), 7.21-7.18 (m, 1H), 7.16-7.13 (m, 1H),

7.11-7.07 (m, 3H), 7.01 (d, $J = 6.6$ Hz, 2H), 6.92 (d, $J = 7.2$ Hz, 2H), 3.88 (d, $J = 11.4$ Hz, 1H), 3.75 (s, 1H), 2.93 (d, $J = 11.4$ Hz, 1H), 2.54 (bs, 1H), 2.24 (s, 3H), 1.49-1.03 (m, 8H), 0.86-0.75 (m, 2H).

^{13}C NMR (150 MHz, CDCl_3) δ 153.6, 152.9, 143.6, 136.3, 136.1, 131.1, 129.8, 127.4, 127.2, 126.6, 125.6, 124.3, 123.2, 120.8, 115.8, 111.2, 63.6, 47.5, 42.7, 29.5, 28.9, 25.5, 21.8, 21.7, 21.6.

HRMS (EI): calcd for $\text{C}_{29}\text{H}_{31}\text{NO}_4\text{S}$ (M^+): 489.1974; Found: 489.1974.



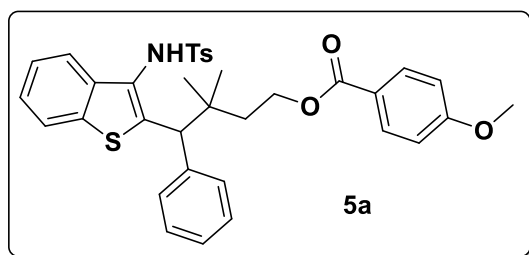
***tert*-butyl (2-(1-((3-((4-methylphenyl)sulfonamido)benzofuran-2-yl)(phenyl)methyl)cyclohexyl)ethyl)carbamate**

Pale yellow solid (81 mg, 67% yield); m.p. 89-90 °C; $R_f = 0.5$ (EtOAc/Petroleum ether 1:5).

^1H NMR (600 MHz, CDCl_3) δ 8.20 (s, 1H), 7.48 (d, $J = 7.8$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.19-7.11(m, 6H), 7.05-6.98 (m, 4H), 4.47-4.45 (m, 1H), 4.14 (s, 1H), 3.45-3.40 (m, 1H), 2.79-2.73 (m, 1H), 2.28 (s, 3H), 1.68-1.63 (m, 2H), 1.45-1.23 (m, 17H), 1.08-1.03 (m, 2H).

^{13}C NMR (150 MHz, CDCl_3) δ 157.0, 156.5, 153.3, 141.3, 138.1, 137.4, 131.0, 129.6, 127.6, 127.4, 126.5, 126.4, 124.0, 122.9, 119.8, 115.0, 111.3, 80.0, 49.6, 40.6, 33.1, 32.7, 32.0, 29.8, 28.5, 25.5, 22.0, 21.8, 21.7.

HRMS (EI): calcd for $\text{C}_{35}\text{H}_{42}\text{N}_2\text{O}_5\text{S}$ (M^+): 602.2814; Found: 602.2812.



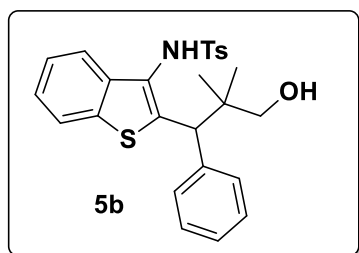
3,3-dimethyl-4-(3-((4-methylphenyl)sulfonamido)benzo[b]thiophen-2-yl)-4-phenylbutyl 4-methoxybenzoate

Pale yellow solid (102 mg, 81% yield); m.p. 55-57°C; R_f = 0.5 (EtOAc/Petroleum ether 1:15).

^1H NMR (600 MHz, CDCl_3) δ 7.95 (d, J = 9.0 Hz, 2H), 7.70 (d, J = 7.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.33-7.32 (m, 2H), 7.27-7.20 (m, 2H), 7.14 (m, 1H), 6.90 (d, J = 9.0 Hz, 2H), 6.23 (s, 1H), 4.44 (s, 1H), 4.39-4.25 (m, 2H), 3.84 (s, 3H), 2.37 (s, 3H), 1.78-1.65 (m, 2H), 1.11 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 166.5, 163.5, 144.2, 144.1, 139.3, 137.8, 136.4, 136.0, 131.7, 130.6, 129.9, 128.2, 127.6, 126.9, 125.5, 124.7, 124.4, 122.9, 122.1, 121.7, 113.7, 62.0, 55.5, 54.9, 39.0, 37.2, 26.0, 25.0, 21.6.

HRMS (EI): calcd for $\text{C}_{35}\text{H}_{35}\text{NO}_5\text{S}_2$ (M^+):613.1957; Found: 613.1955.



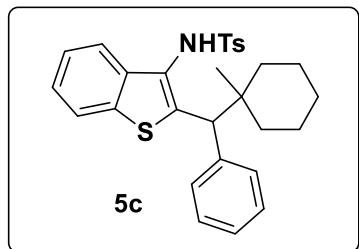
N-(2-(3-hydroxy-2,2-dimethyl-1-phenylpropyl)benzo[b]thiophen-3-yl)-4-methylbenzenesulfonamide

Pale yellow solid (74 mg, 80% yield); m.p. 206-208°C; R_f = 0.5 (EtOAc/Petroleum ether 1:3).

^1H NMR (600 MHz, CDCl_3) δ 8.17 (brs, 1H), 7.78-7.77 (m, 1H), 7.70-7.68 (m, 1H), 7.61-7.59 (m, 2H), 7.28-7.26 (m, 2H), 7.18-7.15 (m, 5H), 6.99-6.97 (m, 2H), 4.34 (s, 1H), 3.24 (d, J = 5.4 Hz, 2H), 2.41 (s, 3H), 1.03 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 143.7, 140.0, 139.4, 137.6, 136.8, 136.1, 130.3, 130.0, 127.8, 127.5, 126.8, 126.6, 124.8, 124.4, 123.4, 121.8, 71.1, 49.5, 40.4, 24.8, 21.7, 20.7.

HRMS (EI): calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_3\text{S}_2$ (M^+):465.1432; Found: 465.1432.



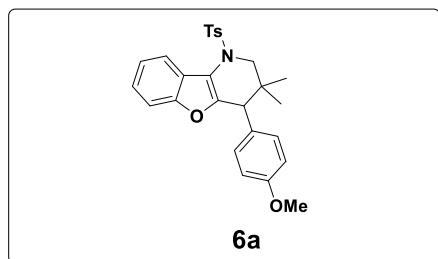
4-methyl-N-(2-(((1-methylcyclohexyl)(phenyl)methyl)benzo[b]thiophen-3-yl)benzenesulfonamide

Pale yellow solid (82 mg, 84% yield); m.p. 52-54 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:20).

^1H NMR (600 MHz, CDCl_3) δ 7.70-7.68 (m, 3H), 7.41(d, J = 7.8 Hz, 1H), 7.25-7.23 (m, 5H), 7.19-7.15 (m, 2H), 5.87 (s, 1H), 4.14 (s, 1H), 2.40 (s, 3H), 1.58-1.28 (m, 8H), 1.15-1.06 (m, 2H), 1.03 (s, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ 144.1, 144.0, 139.3, 137.8, 136.5, 136.1, 130.6, 130.0, 128.0, 127.7, 126.7, 125.3, 124.6, 124.4, 122.0, 121.9, 37.6, 36.9, 36.1, 26.0, 22.1, 21.9, 21.7.

HRMS (EI): calcd for $\text{C}_{29}\text{H}_{31}\text{NO}_2\text{S}_2$ (M^+):489.1796; Found:489.1796.



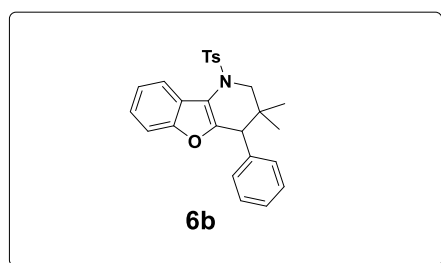
4-(4-methoxyphenyl)-3,3-dimethyl-1-tosyl-1,2,3,4-tetrahydrobenzofuro[3,2-b]pyridine

Pale yellow solid (70 mg, 76% yield); m.p. 134-135 °C; R_f = 0.3 (EtOAc/Petroleum ether 1:10).

^1H NMR (600 MHz, CDCl_3) δ 8.18-8.16 (m, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.24-7.16 (m, 5H), 6.61-6.56 (m, 4H), 3.68 (s, 4H), 3.46 (dd, J_1 = 12.6 Hz, J_2 = 1.2 Hz, 1H), 3.29 (d, J = 12.6 Hz, 1H), 2.35 (s, 3H), 1.01 (s, 3H), 0.65 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 158.8, 154.0, 145.2, 143.8, 135.7, 130.5, 130.4, 129.9, 127.6, 124.4, 123.0, 122.7, 122.1, 118.6, 113.5, 111.5, 55.9, 55.3, 50.1, 34.5, 26.0, 24.0, 21.7.

HRMS (EI): calcd for $\text{C}_{27}\text{H}_{27}\text{NO}_4\text{S}$ (M^+): 461.1661; Found: 461.1660.



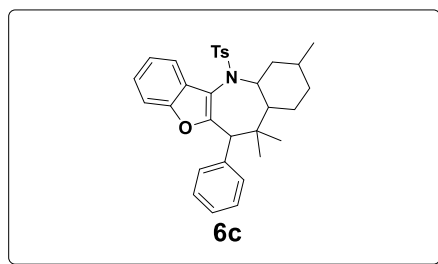
3,3-dimethyl-4-phenyl-1-tosyl-1,2,3,4-tetrahydrobenzofuro[3,2-*b*]pyridine

Pale yellow solid (60 mg, 70% yield); m.p. 150-152 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:10).

^1H NMR (600 MHz, CDCl_3) δ 8.19-8.18 (m, 1H), 7.63-7.17 (d, J = 8.4 Hz, 2H), 7.24-7.22 (m, 1H), 7.21-7.17 (m, 4H), 7.15-7.12 (m, 1H), 7.08-7.05 (m, 2H), 6.65 (d, J = 7.8 Hz, 2H), 3.74 (s, 1H), 3.48 (d, J = 12.6 Hz, 1H), 3.31 (d, J = 12.6 Hz, 1H), 2.36 (s, 3H), 1.04 (s, 3H), 0.65 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 154.1, 144.9, 143.9, 138.6, 135.6, 129.9, 129.4, 128.1, 127.6, 127.3, 124.5, 123.0, 122.8, 122.0, 118.9, 111.5, 55.0, 50.9, 34.5, 27.0, 24.1, 21.7.

HRMS (EI): calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_3\text{S}$ (M^+): 431.1555; Found: 431.1550.



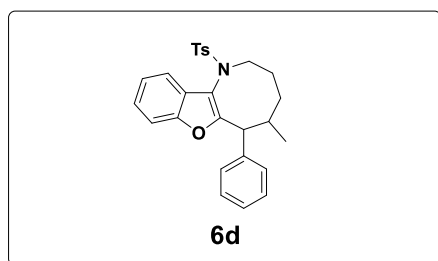
3,12,12-trimethyl-11-phenyl-5-tosyl-2,3,4,4a,5,11,12,12a-octahydro-1H-benzo[b]benzofuro[2,3-f]azepine

Pale yellow solid (84 mg, 82% yield); m.p. 63-65 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:15).

^1H NMR (600 MHz, CDCl_3) δ 7.45-7.41 (m, 2H), 7.38-7.35 (m, 1H), 7.15-7.08 (m, 5H), 7.06-6.98 (m, 4H), 6.00 (d, J = 15.6 Hz, 1H), 5.19-5.12 (m, 1H), 4.00 (d, J = 11.4 Hz, 1H), 2.27 (s, 3H), 1.94-1.80 (m, 3H), 1.65-1.56 (m, 1H), 1.45-1.33 (m, 2H), 1.26-1.12 (m, 2H), 1.00 (d, J = 6.6 Hz, 3H), 0.94 (d, J = 13.2 Hz, 3H), 0.83-0.80 (m, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 156.6 and 156.5, 143.90 and 143.87, 142.3 and 142.2, 138.3 and 138.2, 136.5 and 136.4, 130.34 and 130.32, 129.74 and 129.72, 127.48 and 127.46, 127.4 and 127.3, 126.6 and 126.5, 125.7 and 125.6, 124.20 and 124.15, 123.11 and 123.05, 119.4 and 119.3, 114.1 and 113.9, 111.4 and 111.3, 50.22 and 50.14, 43.79 and 43.76, 34.4, 31.9 and 31.7, 28.22 and 28.18, 25.5, 25.34 and 25.29, 25.1, 24.8, 21.9 and 21.8, 21.7.

HRMS (EI): calcd for $\text{C}_{32}\text{H}_{35}\text{NO}_3\text{S}$ (M^+): 513.2338; Found: 513.2338.



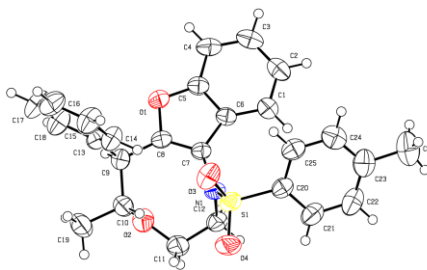
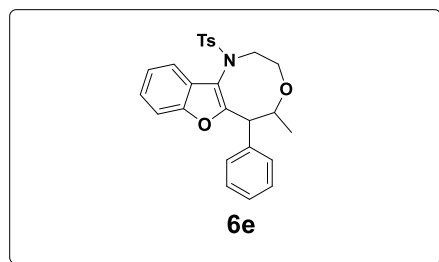
5-methyl-6-phenyl-1-tosyl-1,2,3,4,5,6-hexahydrobenzofuro[3,2-b]azocine

Pale yellow solid (45 mg, 51% yield); m.p. 135-137 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:20).

^1H NMR (600 MHz, CDCl_3) δ 7.59 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 1H), 7.23-7.20 (m, 3H), 7.19-7.17 (m, 2H), 7.14-7.12 (m, 3H), 7.07 (d, J = 7.8 Hz, 2H), 4.33-4.29 (m, 1H), 4.04 (d, J = 4.2 Hz, 1H), 3.31-3.27 (m, 1H), 2.28 (s, 3H), 1.72-1.50 (m, 4H), 1.03-0.97 (m, 1H), 0.67 (d, J = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 158.0, 154.0, 143.5, 138.3, 138.1, 129.8, 129.3, 128.1, 127.2, 126.7, 126.0, 124.3, 123.2, 119.7, 117.8, 111.7, 52.0, 45.7, 37.5, 34.0, 25.4, 21.6, 17.8.

HRMS (EI): calcd for $\text{C}_{27}\text{H}_{27}\text{NO}_3\text{S}$ (M^+): 445.1712; Found: 445.1711.



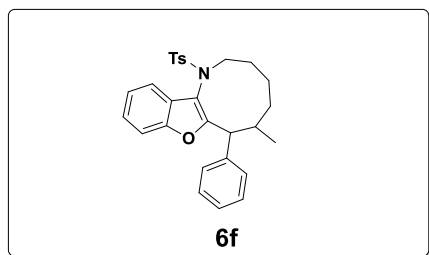
5-methyl-6-phenyl-1-tosyl-2,3,5,6-tetrahydro-1*H*-benzofuro[3,2-*e*][1,4]oxazocine

Pale yellow solid (52 mg, 58% yield); m.p. 162-164 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:20).

^1H NMR (500 MHz, CDCl_3) δ 7.74 (d, J = 8.0 Hz, 2H), 7.48-7.47 (m, 2H), 7.28-7.24 (m, 4H), 7.21-7.16 (m, 2H), 7.04-7.01 (m, 1H), 6.82-6.79 (m, 1H), 6.24-6.23 (m, 1H), 4.77 (s, 1H), 4.11-3.87 (m, 4H), 3.22-3.19 (m, 1H), 2.41 (s, 3H), 0.99 (d, J = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 158.5, 153.2, 144.2, 138.9, 138.4, 130.0, 129.4, 128.9, 127.9, 127.5, 125.7, 124.2, 122.5, 119.0, 117.8, 111.6, 77.8, 70.9, 55.2, 52.8, 21.8, 20.8.

HRMS (EI): calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_4\text{S}$ (M^+): 447.1504; Found: 447.1500.



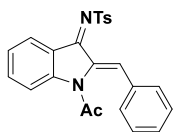
6-methyl-7-phenyl-1-tosyl-2,3,4,5,6,7-hexahydro-1H-benzofuro[3,2-b]azonine

Pale yellow solid (40 mg, 44% yield) m.p.167-169 °C; R_f = 0.5 (EtOAc/Petroleum ether 1:20).

^1H NMR (600 MHz, CDCl_3) δ 7.57(d, J = 8.5 Hz, 2H), 7.52(d, J = 7.0 Hz, 2H), 7.31(t, J = 8.0 Hz, 2H), 7.24-7.19 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.03-6.99 (m, 1H), 6.79-6.76 (m, 1H), 6.15-6.13 (m, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.14-4.09 (m, 1H), 3.25-3.19 (m, 1H), 2.39-2.38 (m, 1H), 2.35 (s, 3H), 2.17-2.10 (m, 1H), 1.91-1.86 (m, 1H), 1.55-1.52 (m, 2H), 1.31-1.21 (m, 1H), 0.91-0.84 (m, 1H), 0.78 (d, J = 7.0 Hz, 3H).

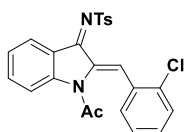
^{13}C NMR (125 MHz, CDCl_3) δ 156.0, 153.1, 144.0, 136.9, 136.6, 132.2, 131.7, 130.9, 129.6, 127.5, 125.4, 124.4, 123.2, 120.9, 113.7, 111.5, 61.8, 55.5, 51.1, 38.9, 37.7, 25.9, 25.3, 21.6.

HRMS (EI): calcd for $\text{C}_{28}\text{H}_{29}\text{NO}_3\text{S}$ (M^+): 459.1868; Found: 459.1866.



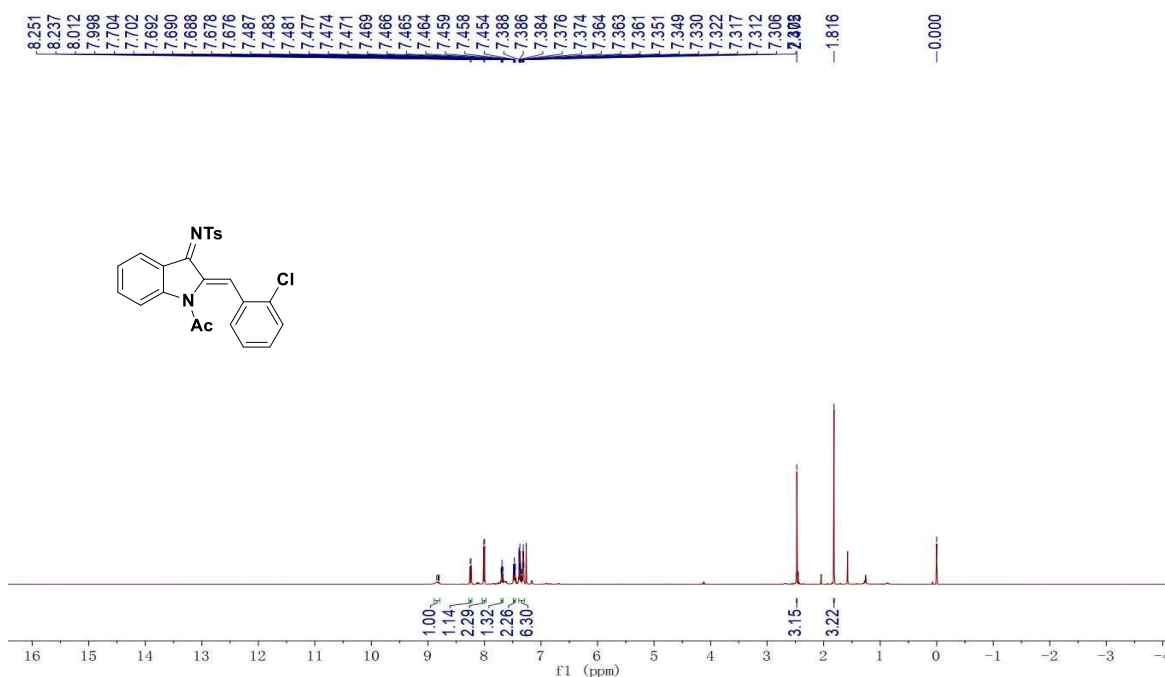
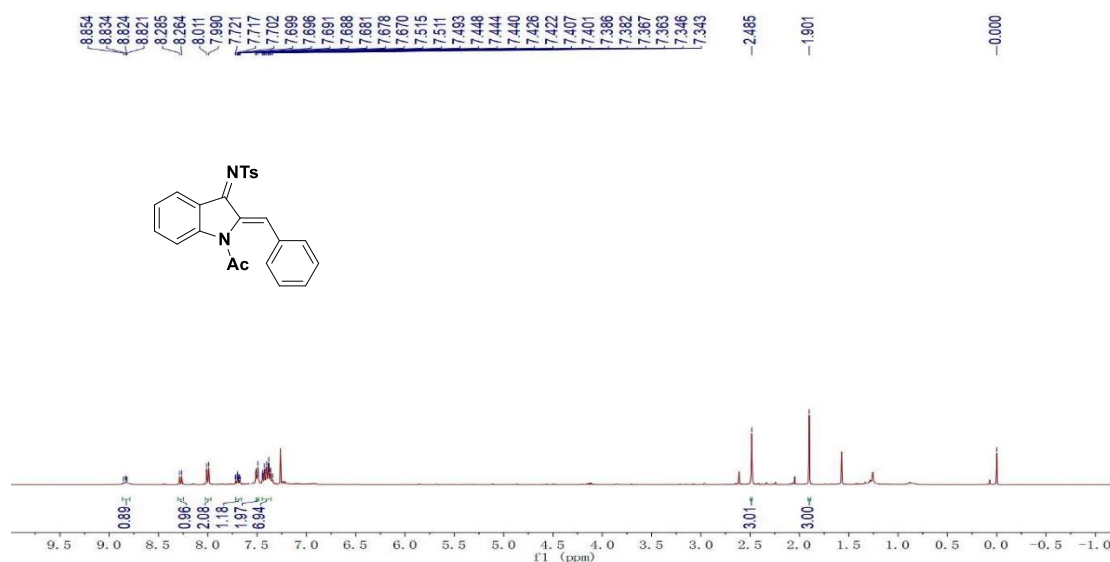
^1H NMR (400 MHz, CDCl_3) δ 8.85-8.82 (m,1H),8.27 (d, J = 8.4 Hz, 1H), 8.01(d, J = 8.4 Hz, 2H), 7.72-7.67 (m, 1H), 7.52-7.49 (m, 2H), 7.45-7.34 (m, 7H), 2.49 (s, 3H), 1.90 (s, 3H).

calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$, LC-MS: $[\text{M}+\text{H}]^+ = 417$



¹HNMR (600 MHz, CDCl₃) δ 8.84-8.80 (m,1H),8.24 (d, *J* = 8.4 Hz, 1H), 8.01(d, *J* = 8.4 Hz, 2H), 7.70-7.68 (m, 1H), 7.49-7.45 (m, 2H), 7.39-7.30 (m, 6H), 2.48 (s, 3H), 1.82 (s, 3H).

calcd for C₂₄H₁₉ClN₂O₃S, LC-MS: [M+H]⁺ =451

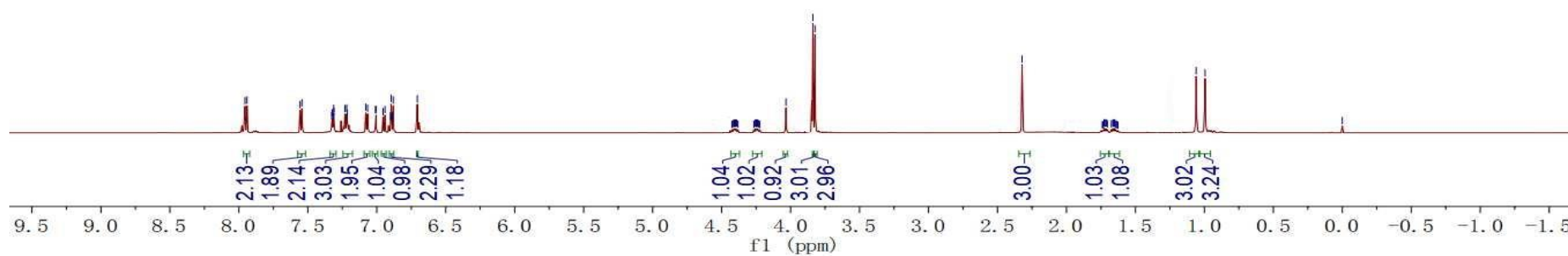
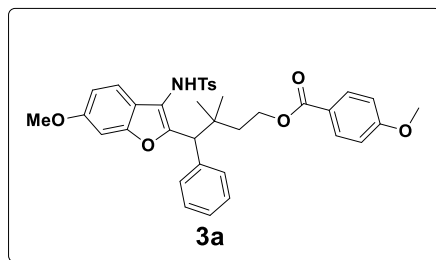


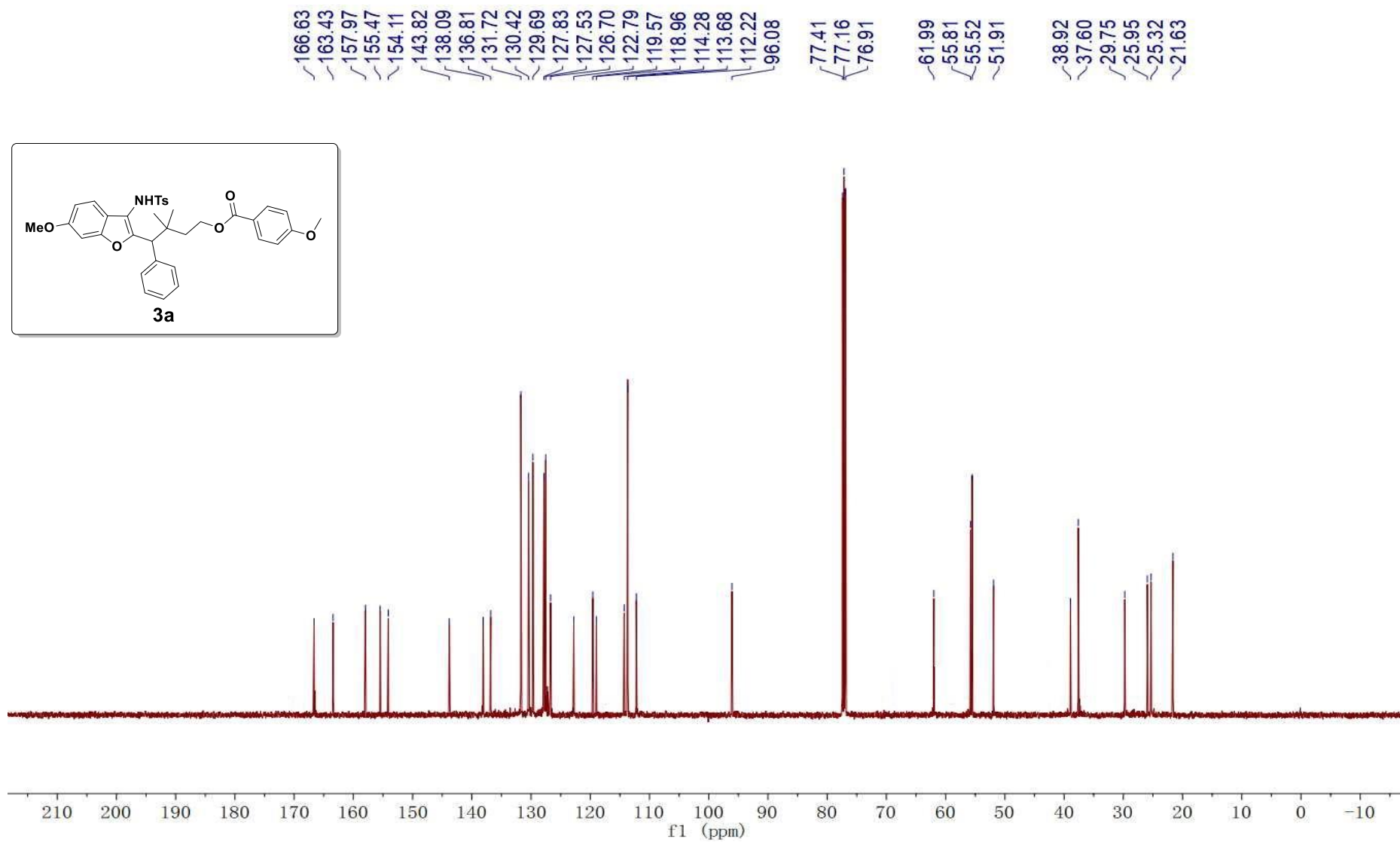
6. Reference

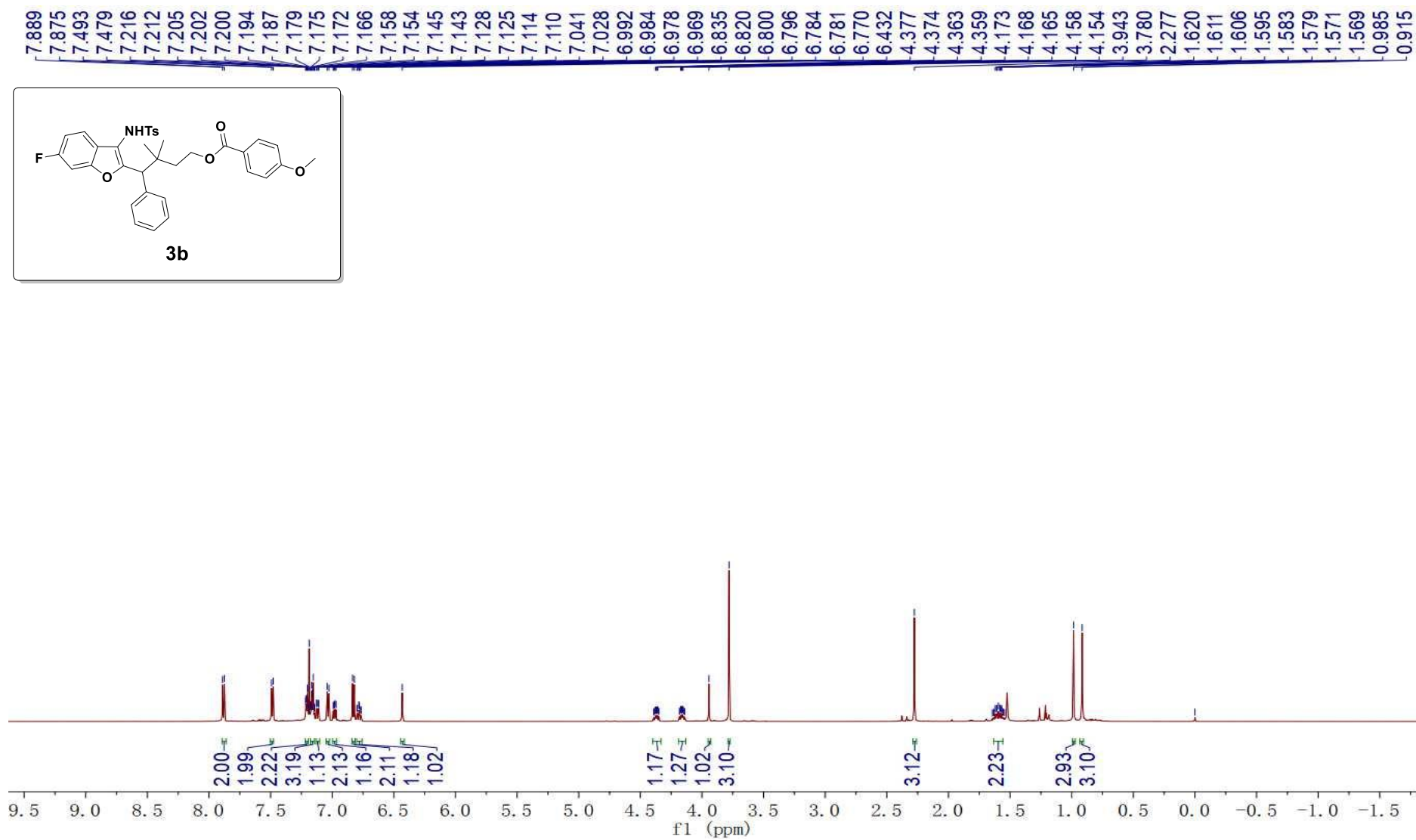
1. a) Z. P. Wang, Y. He, P. L. Shao, *Organic & Biomolecular Chemistry*. 2018,16, 5422. b) Z, Gu, J. J. Xie, G. F. Jiang, Y. G. Zhou, *Asian J. Org. Chem.* 2018, 7, 1561. c)H. Z. Ni, X. D. Tang, W. R. Zheng, W. J. Yao, N. Ullah, Y. X. Lu, *Angew. Chem. Int. Ed.* 2017, 56, 14222.

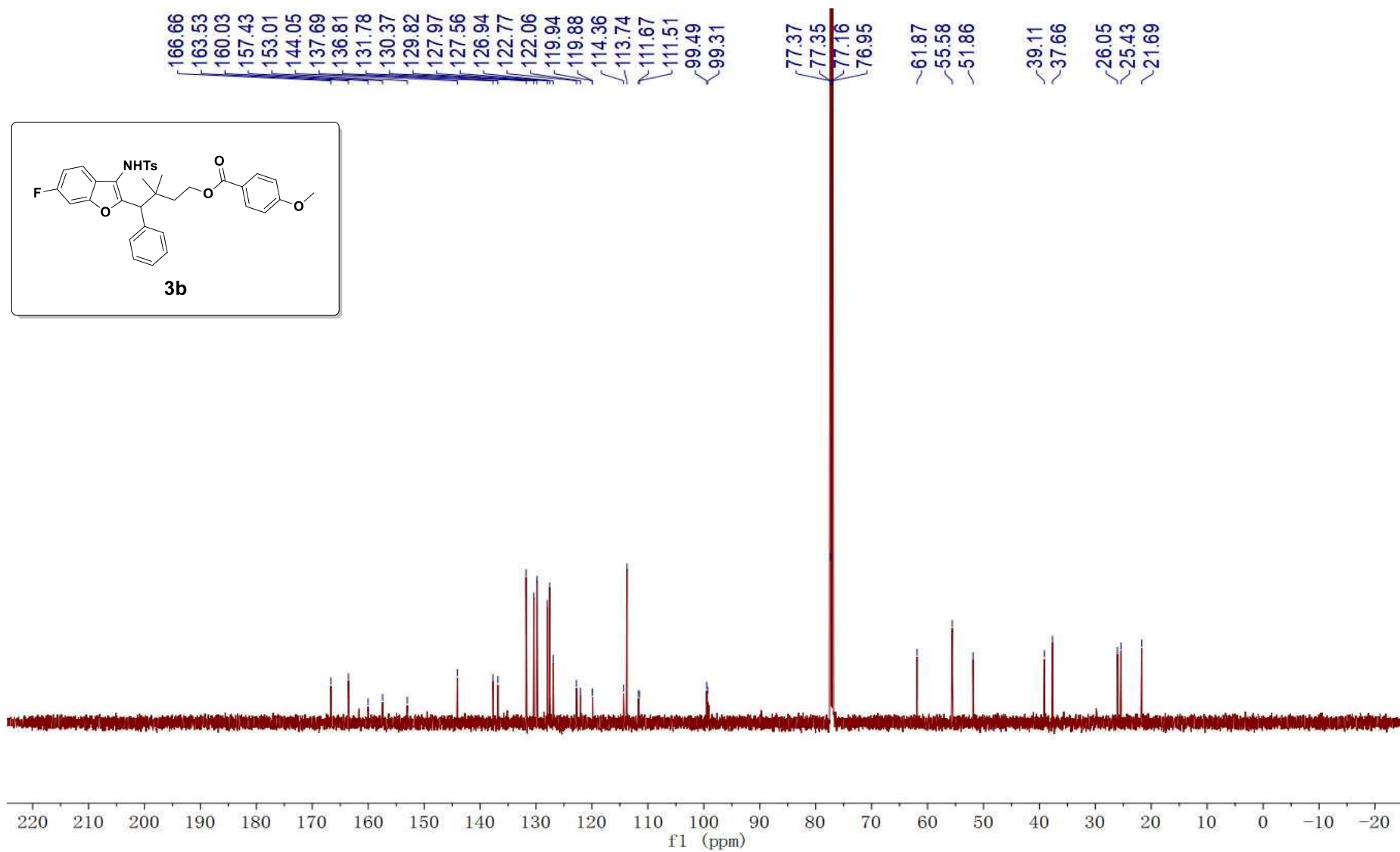
7. Copies of NMR Spectra.

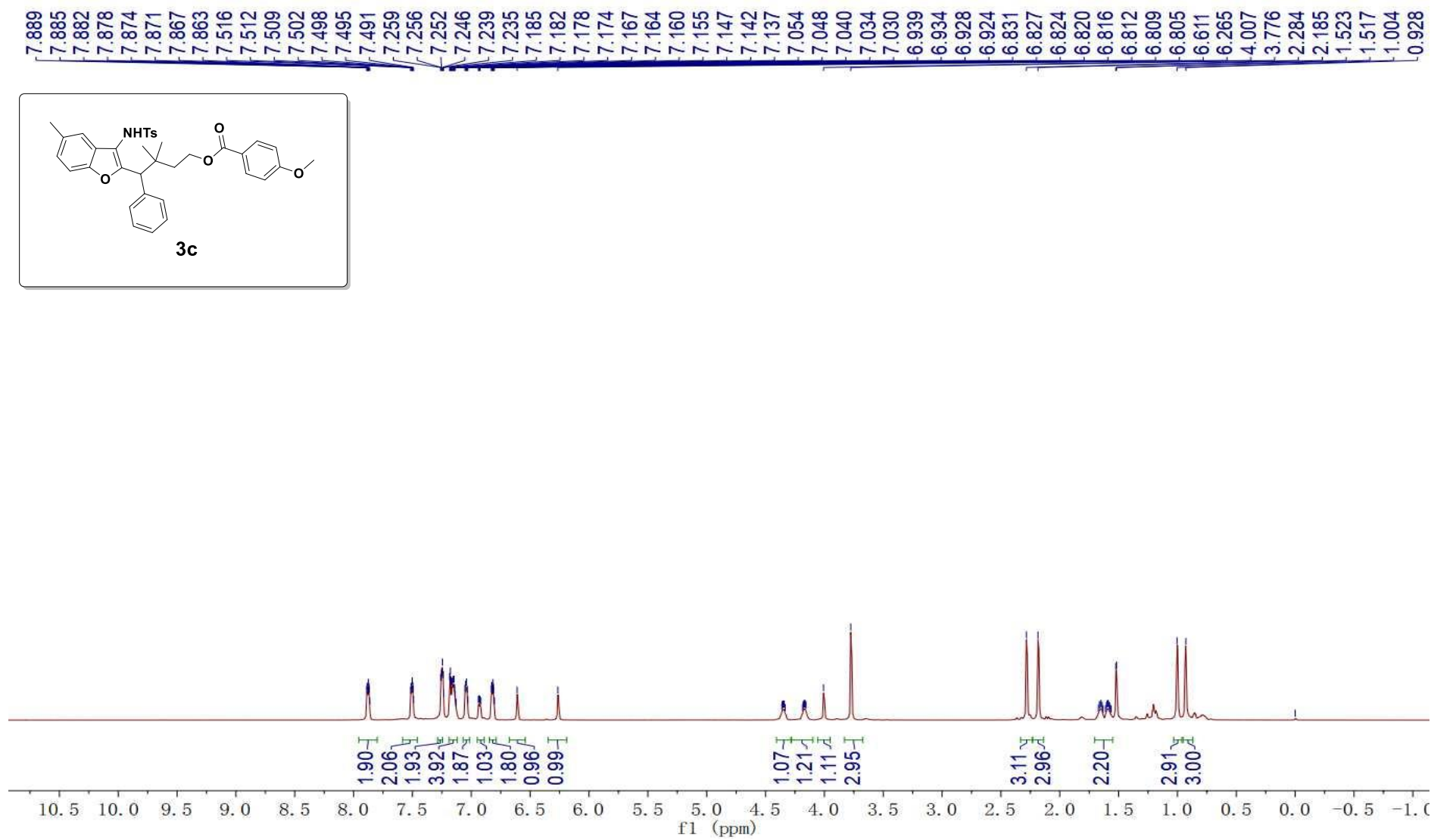
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7.941
7.556
7.543
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7.324
7.316
7.313
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7.230
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7.067
7.009
7.005
6.955
6.940
6.900
6.896
6.892
6.884
6.881
6.706
4.442
4.425
4.415
4.410
4.407
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4.397
4.392
4.382
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1.649
1.641
1.060
0.995
0.000

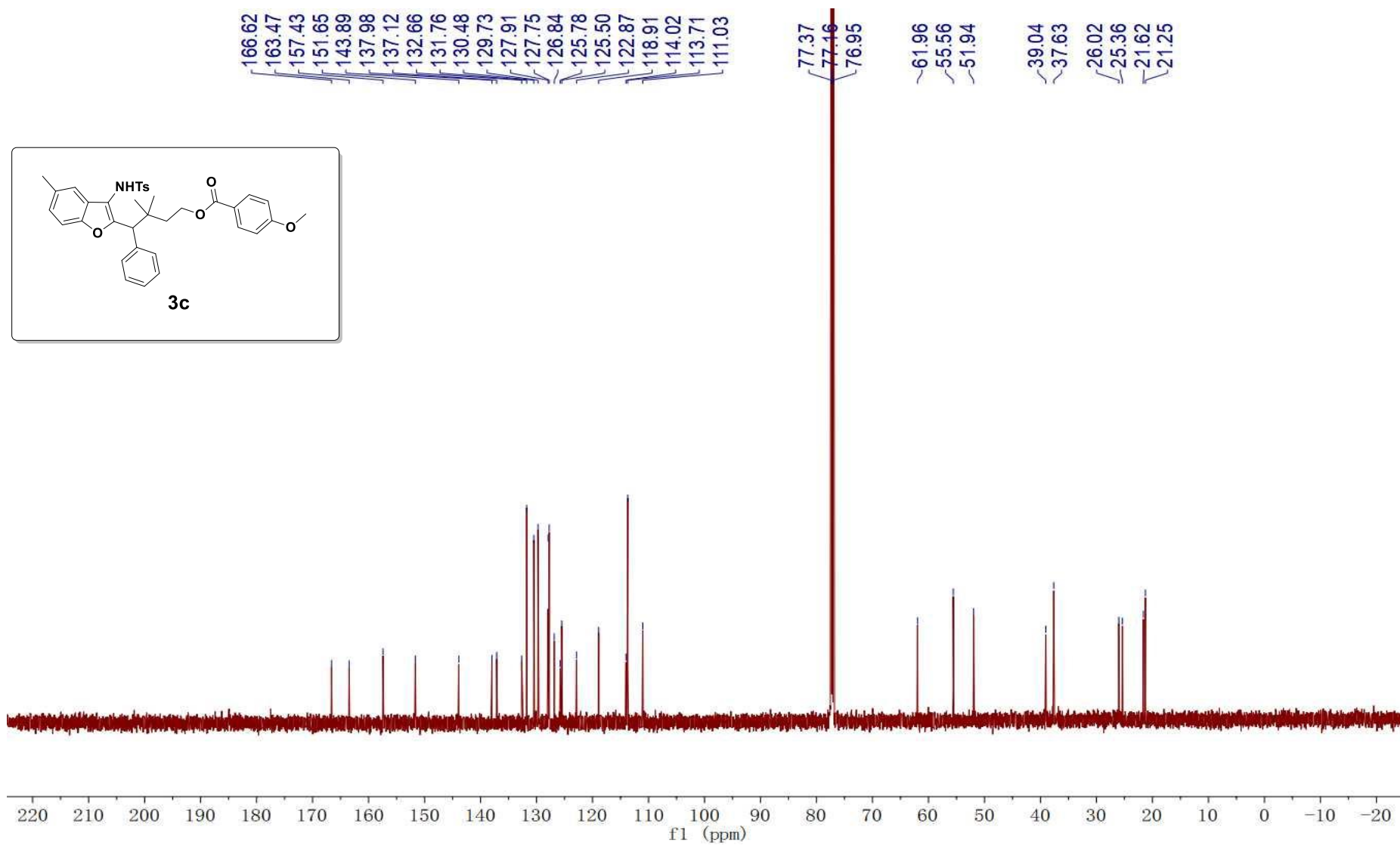


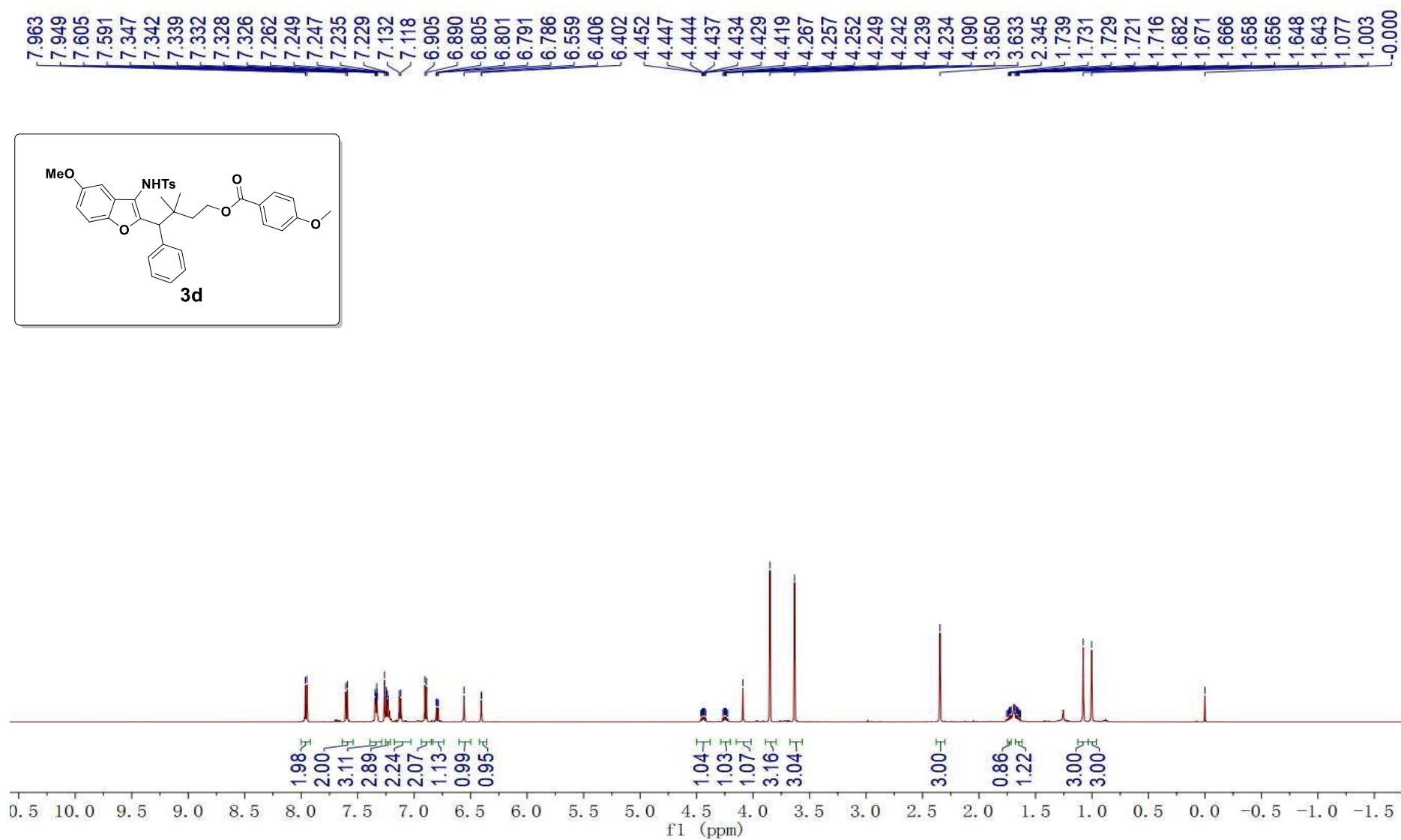


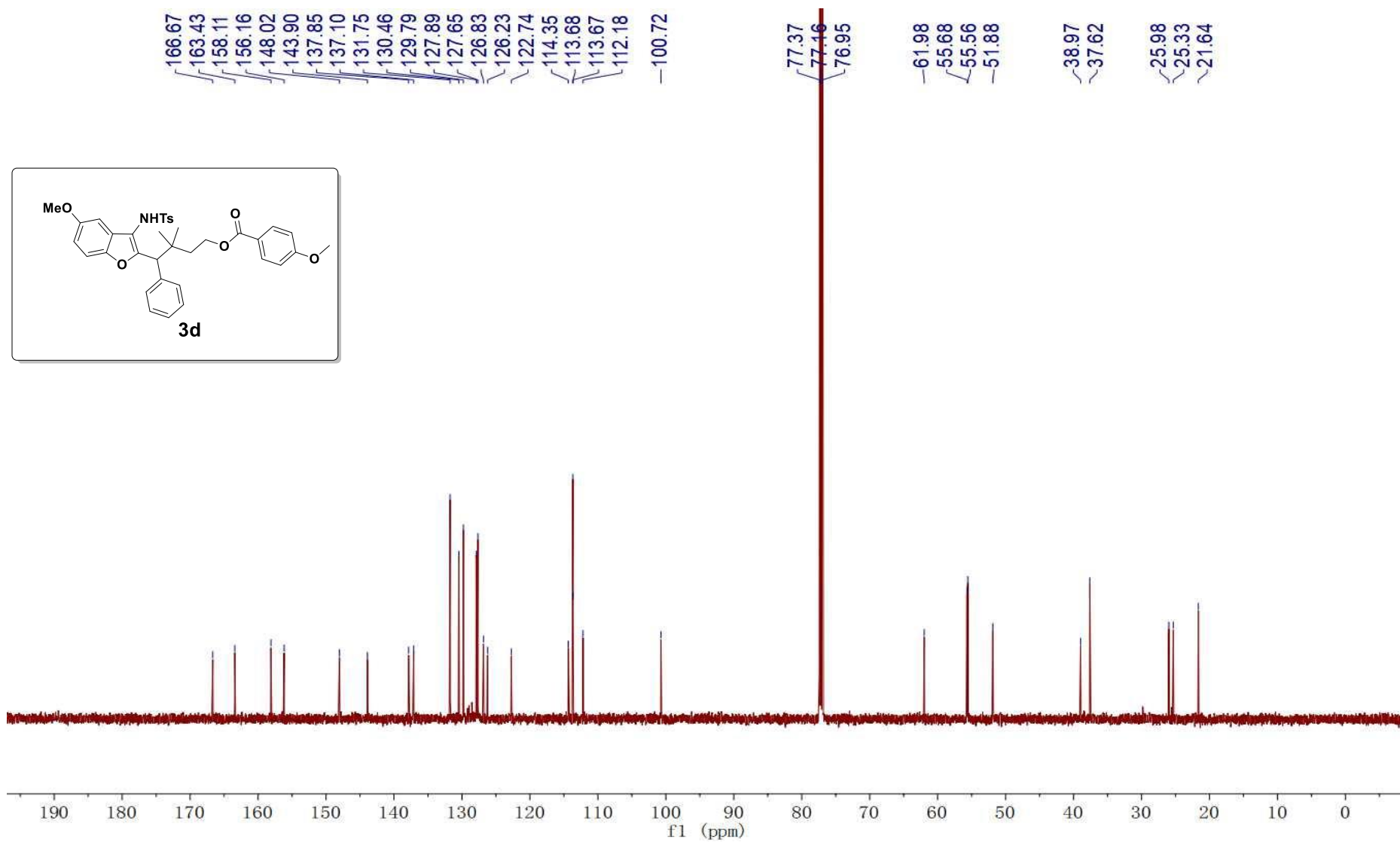


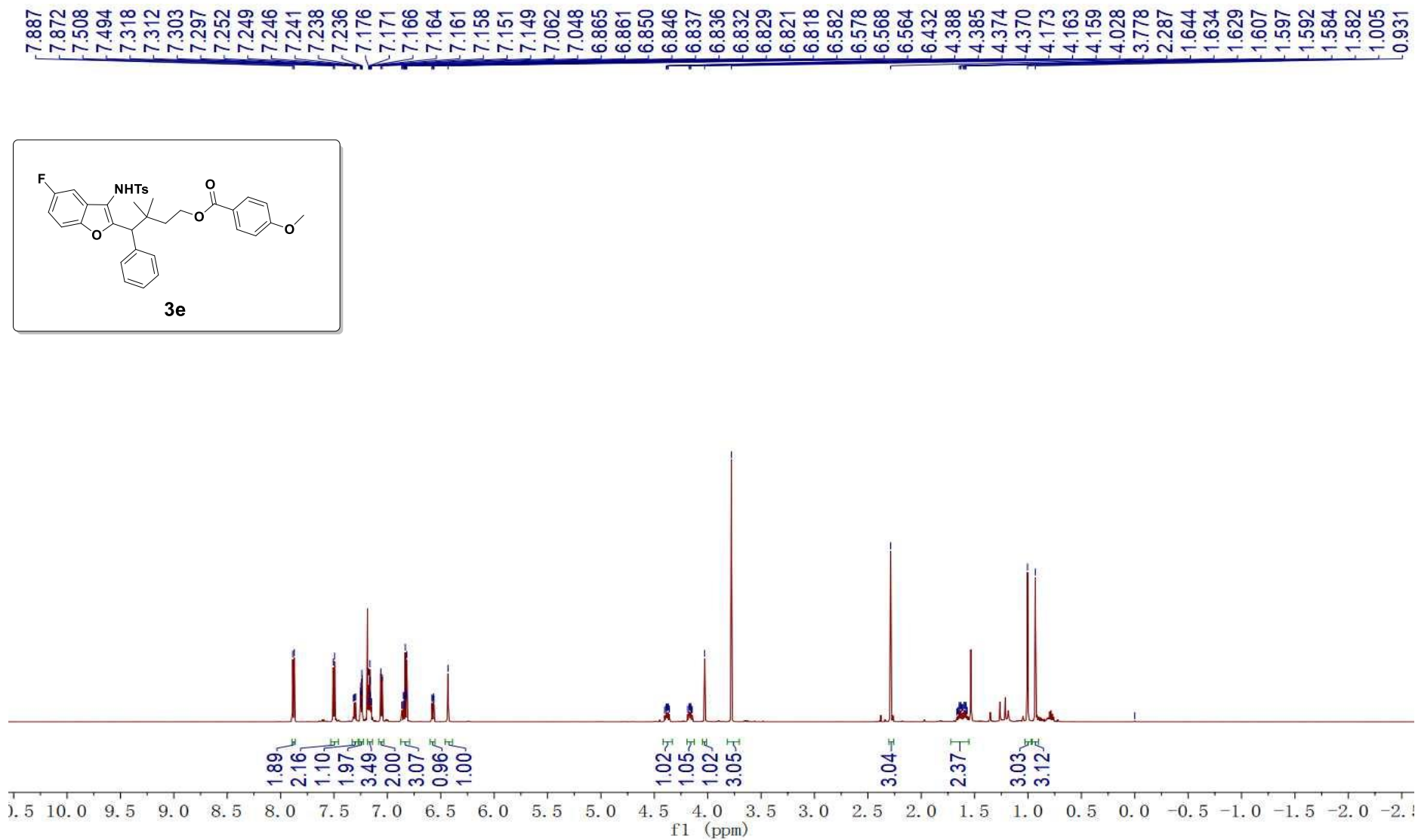


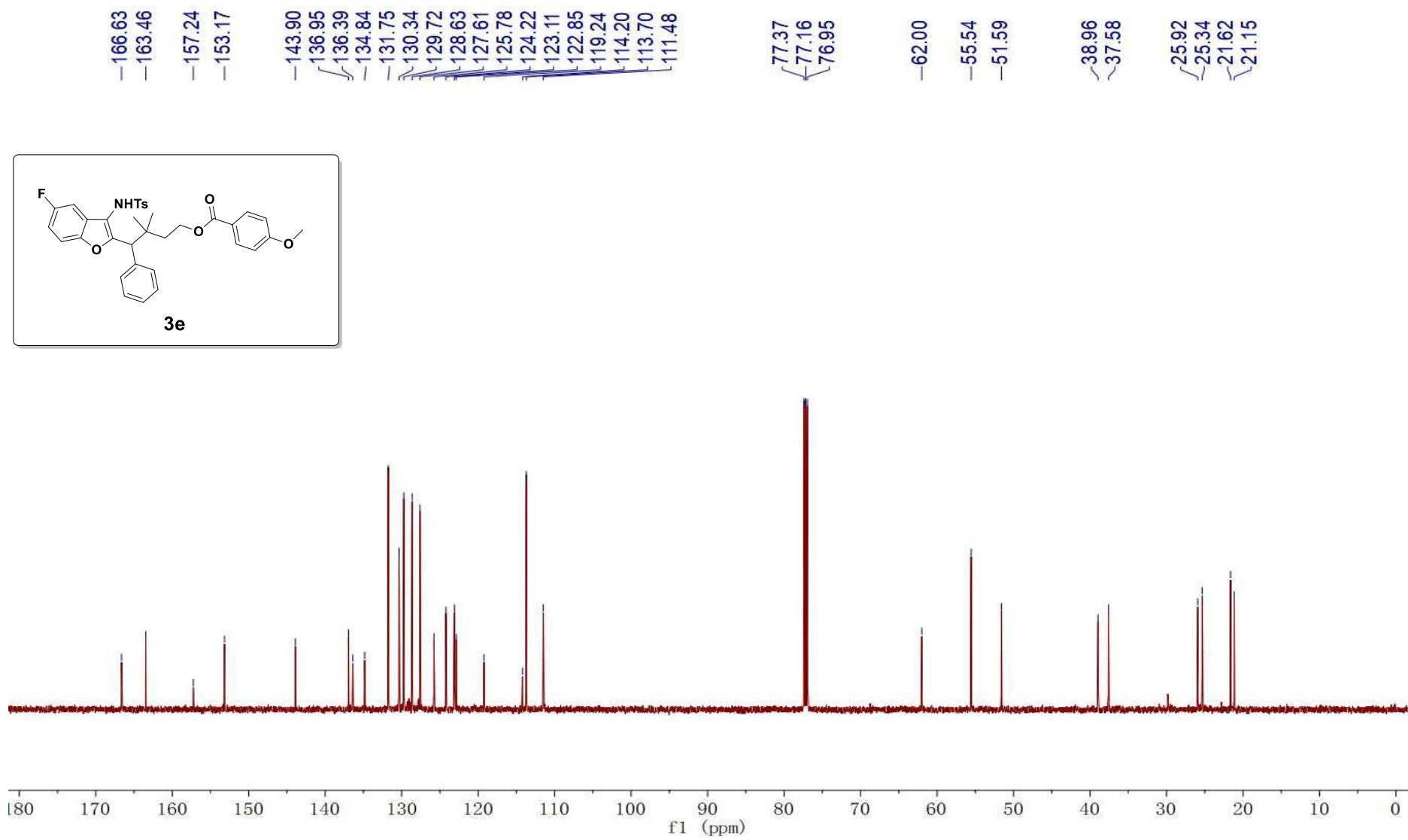


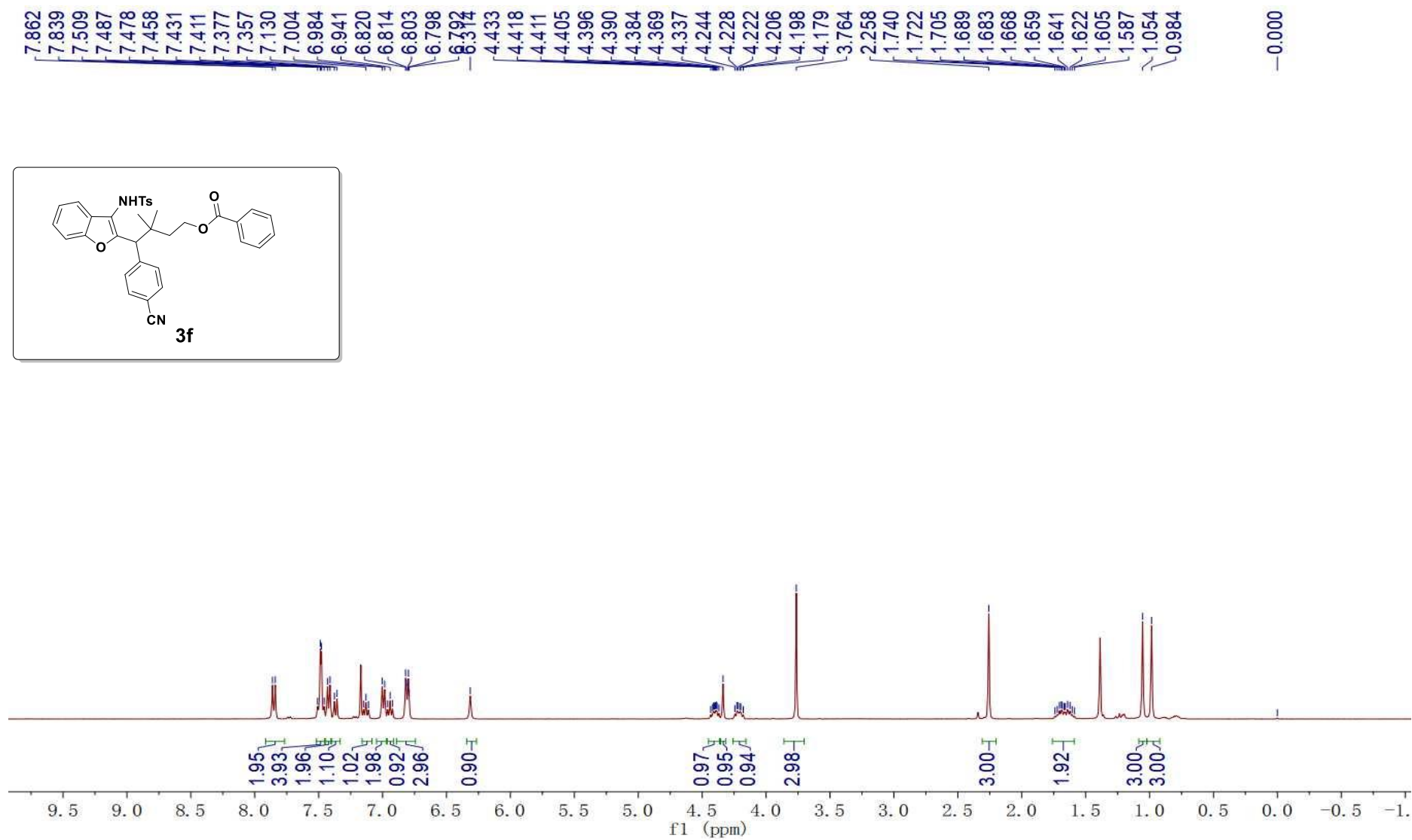


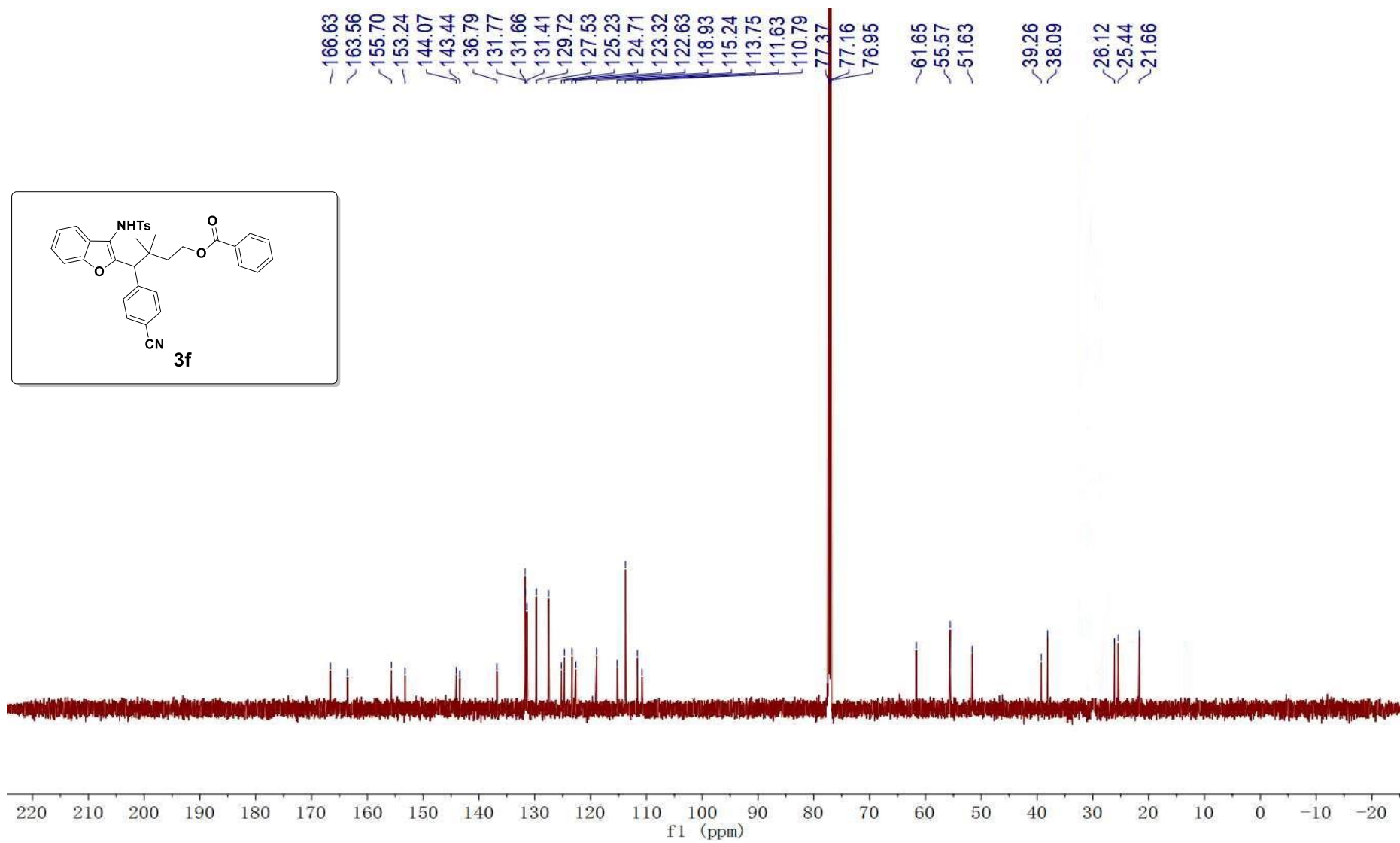


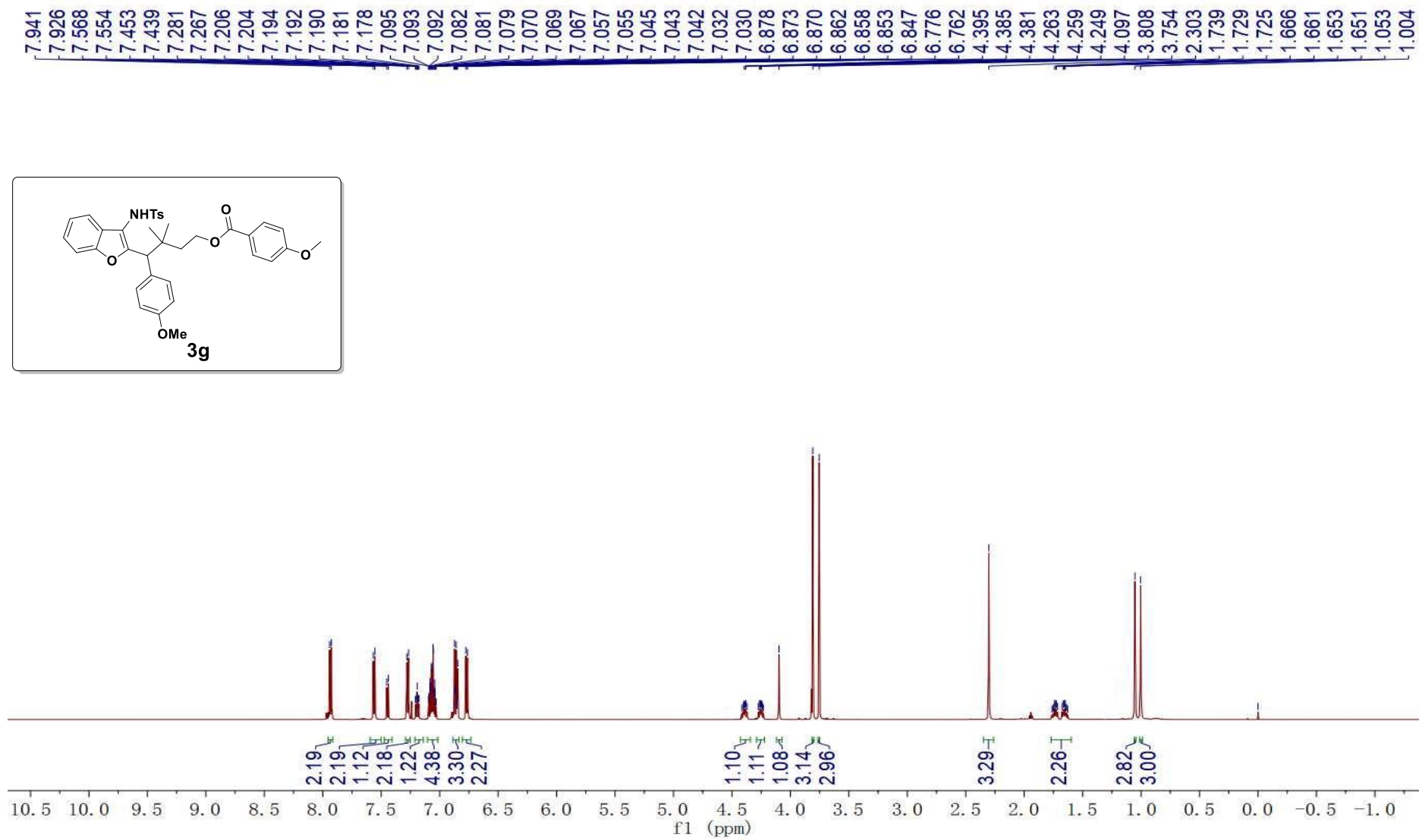


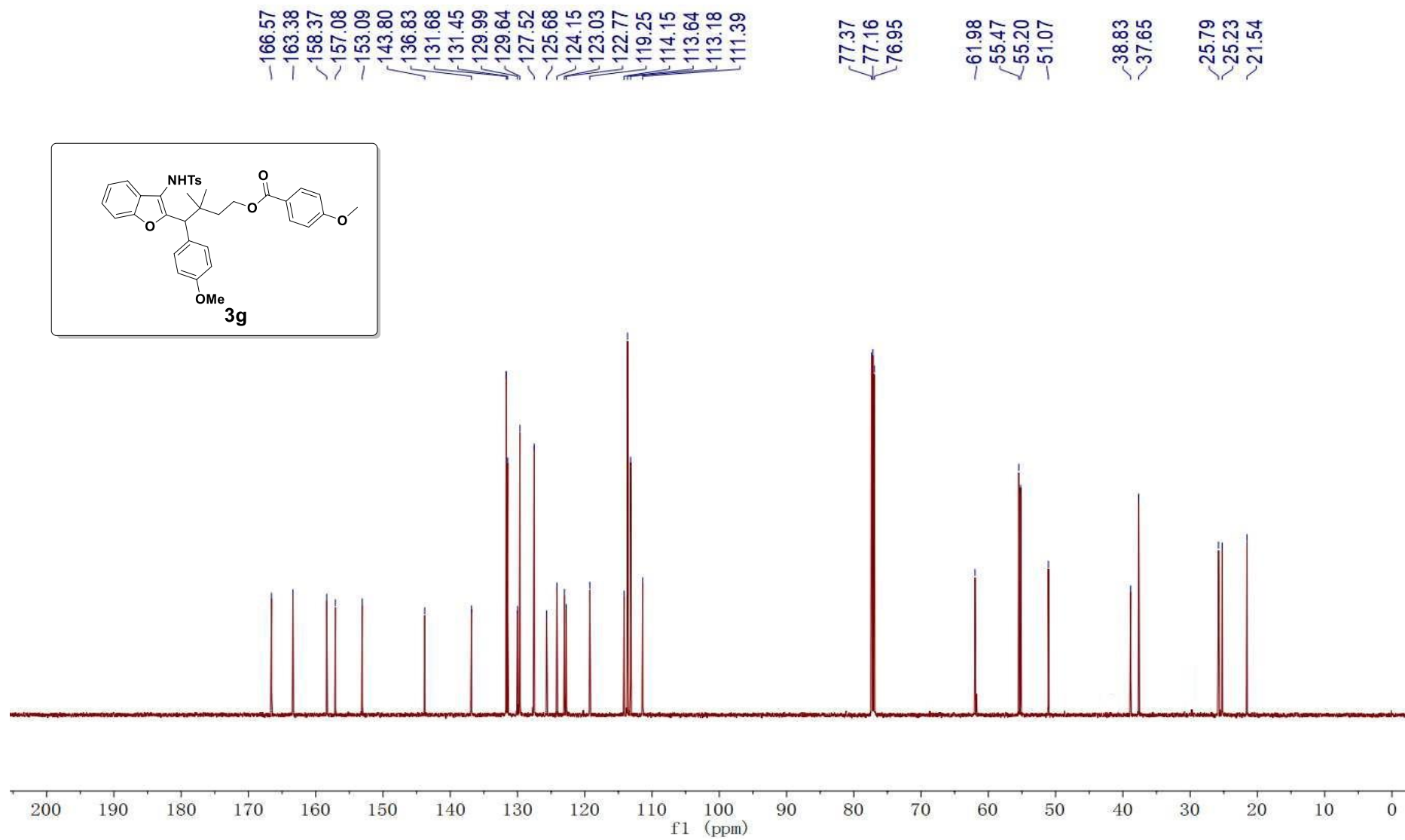


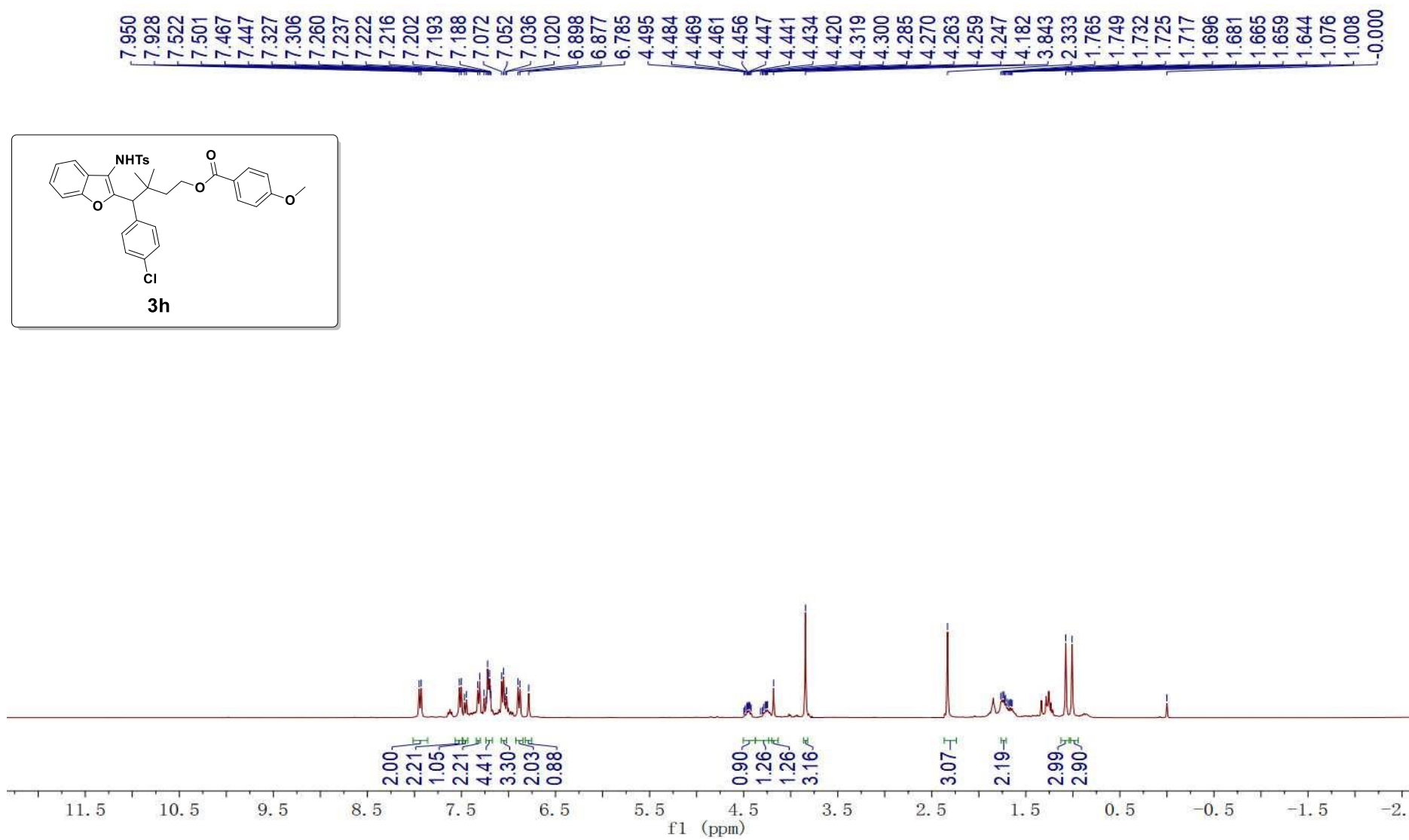


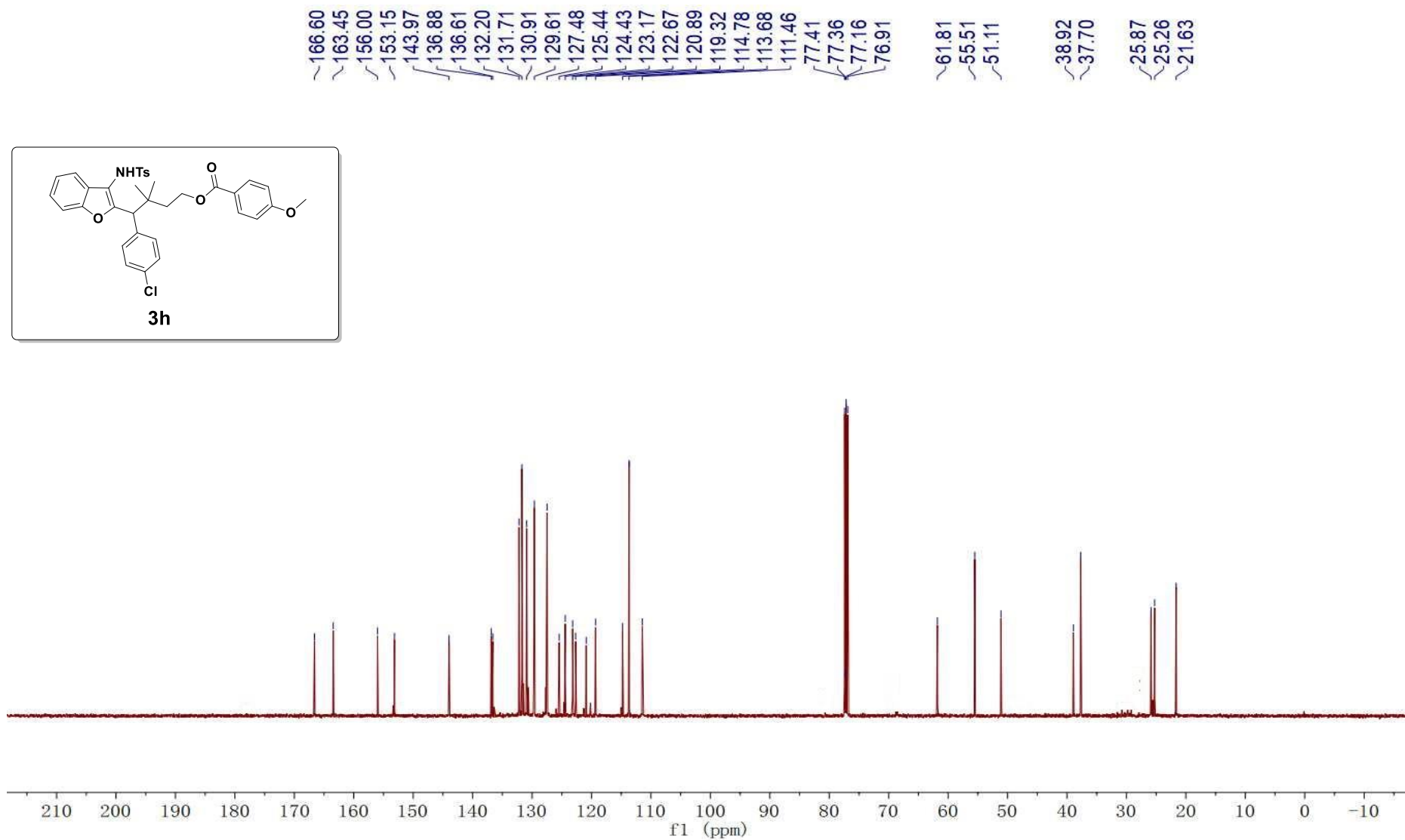


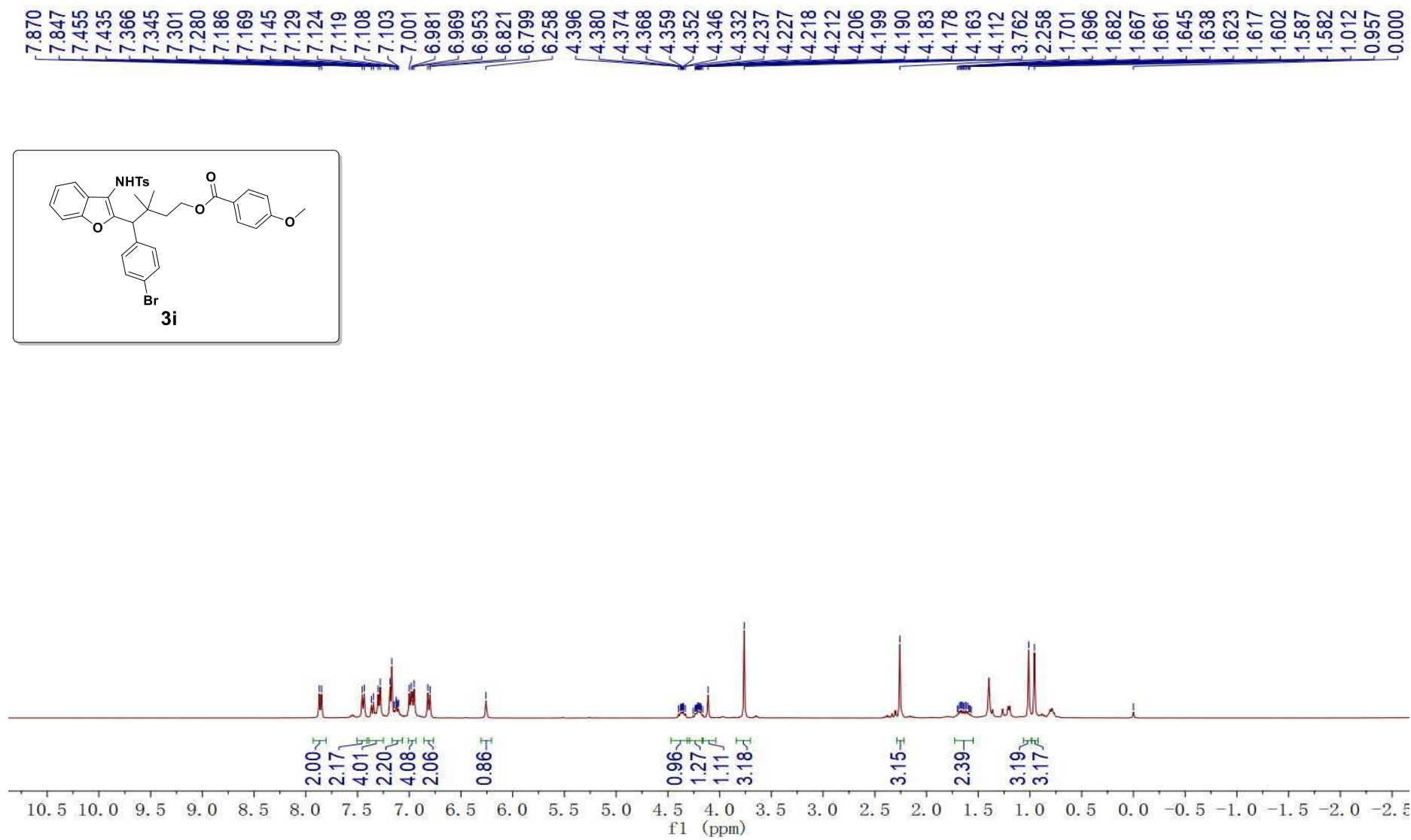


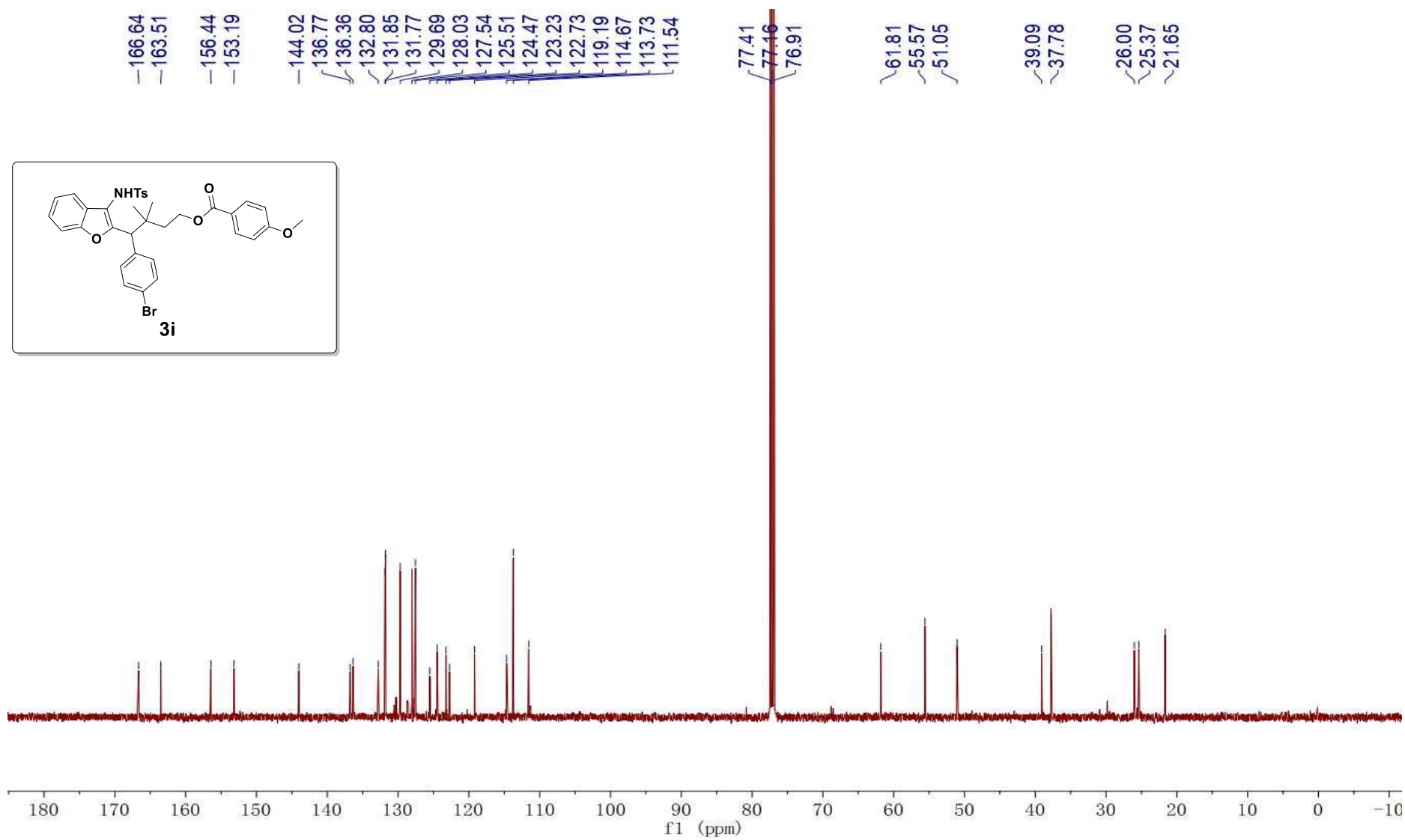


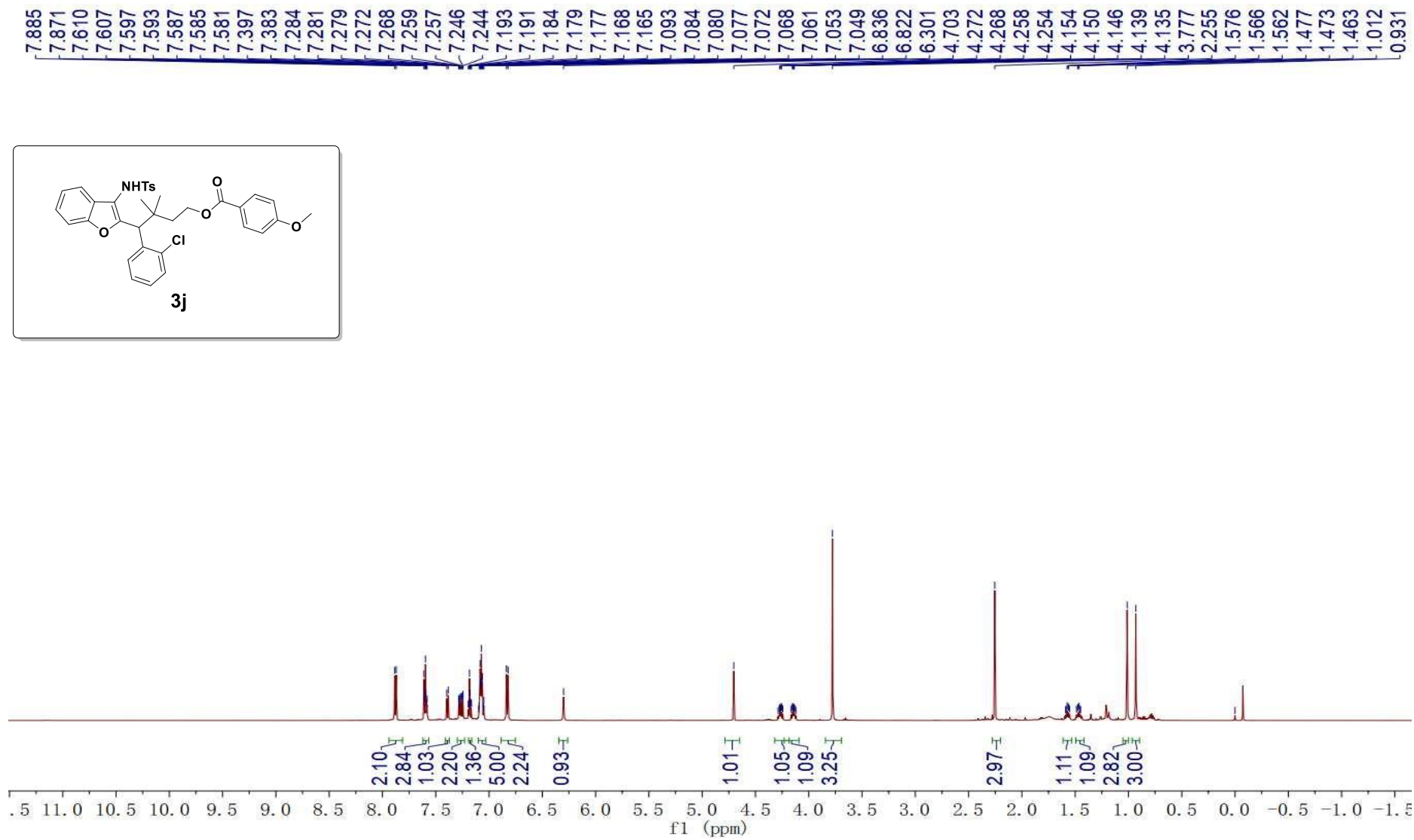


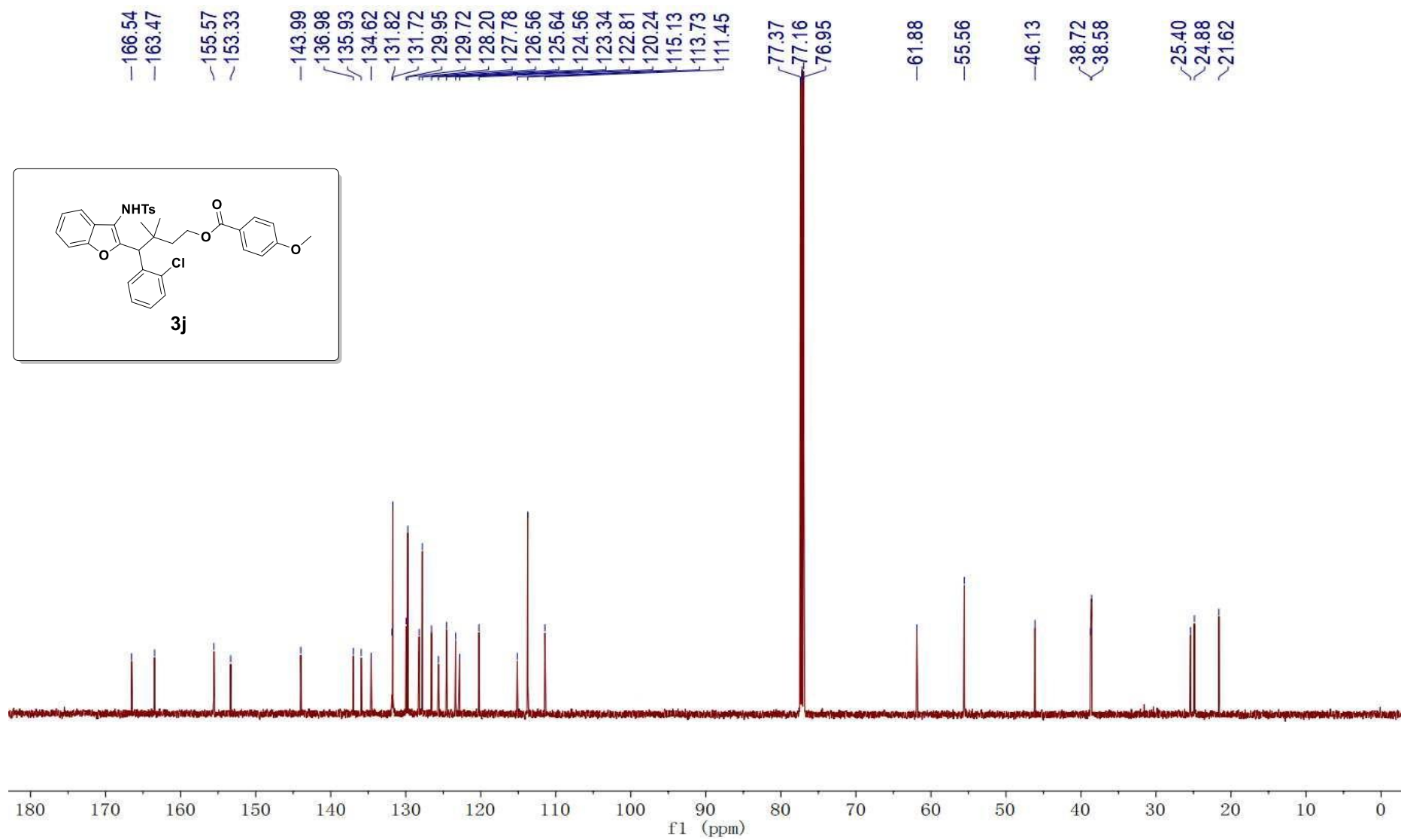


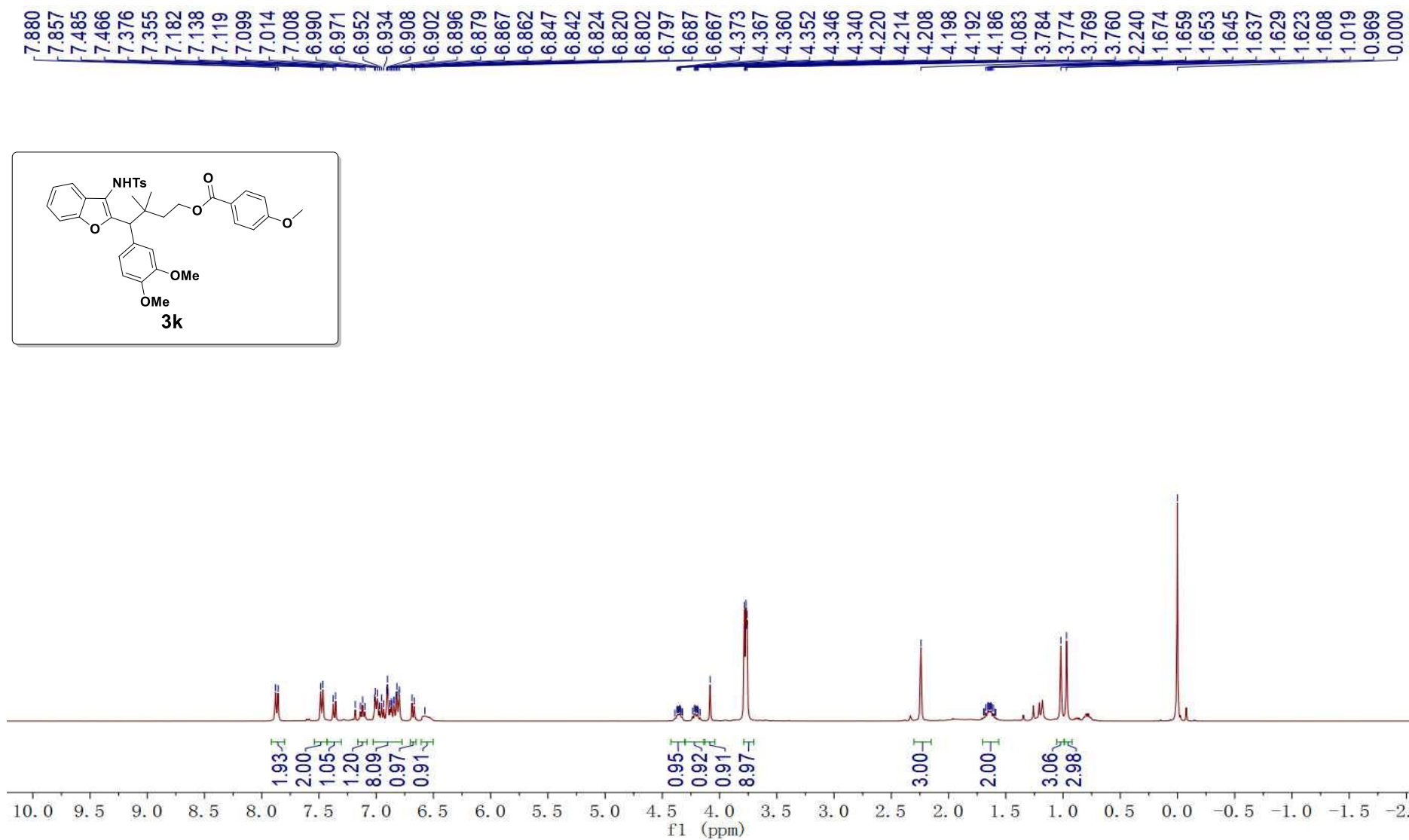


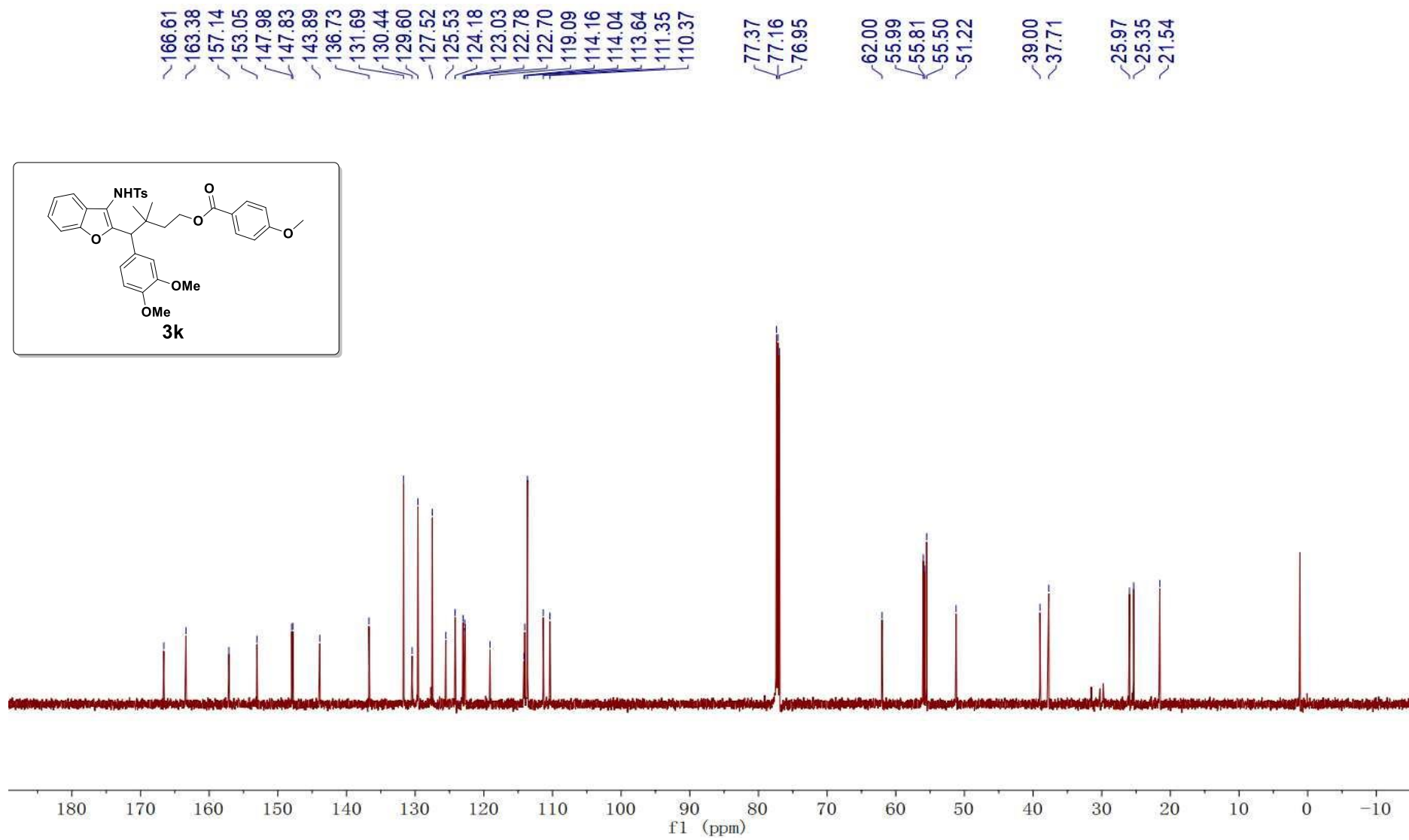


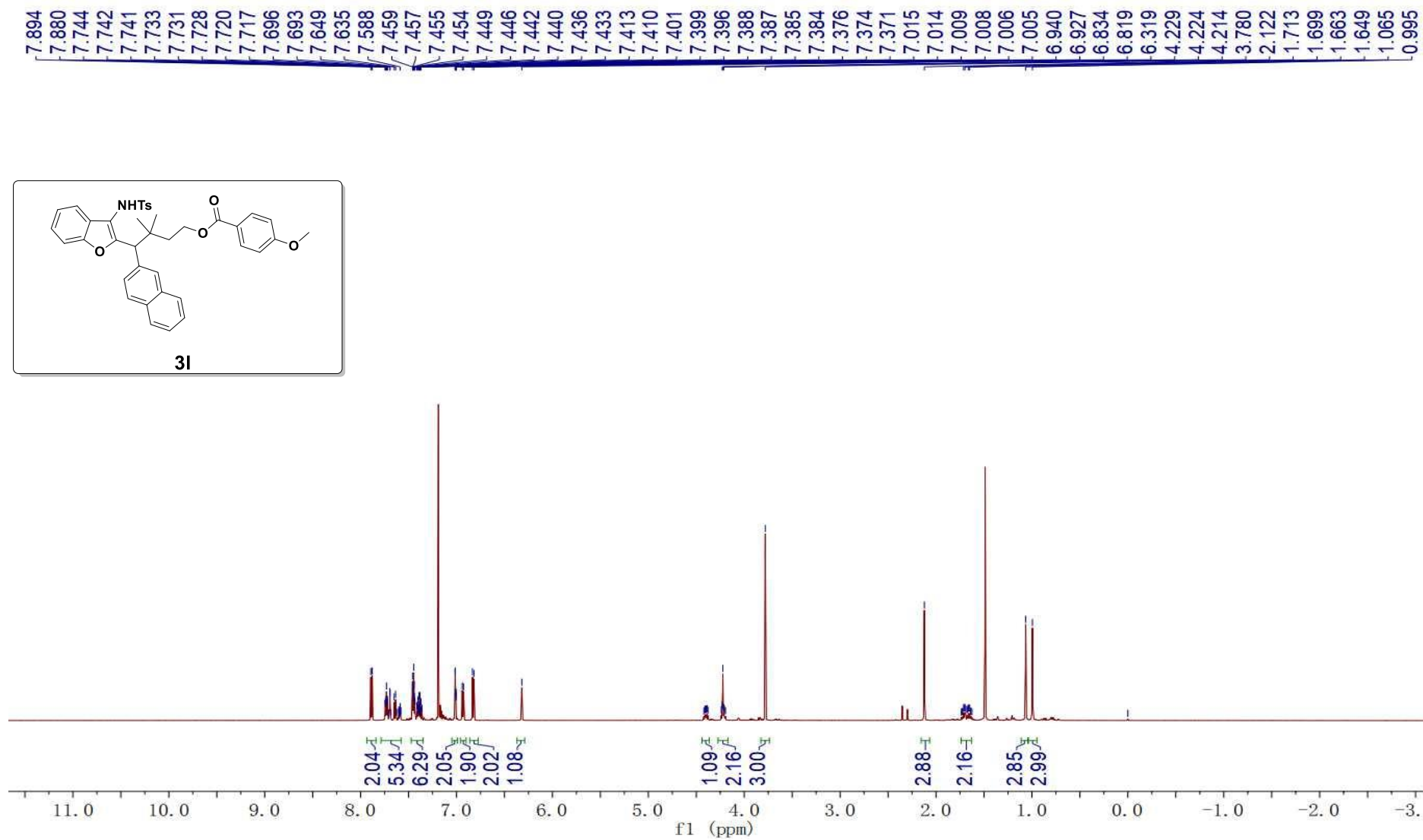


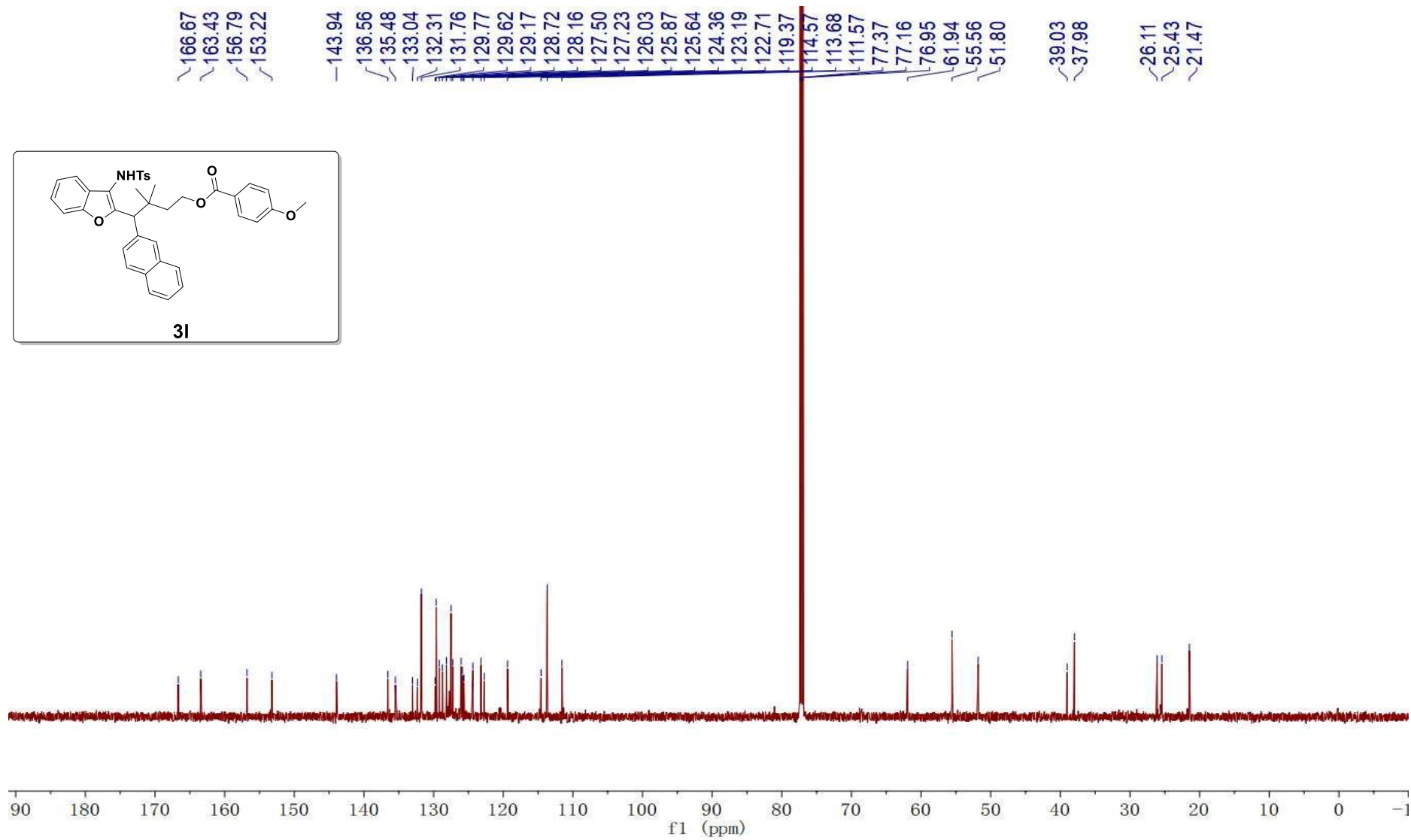


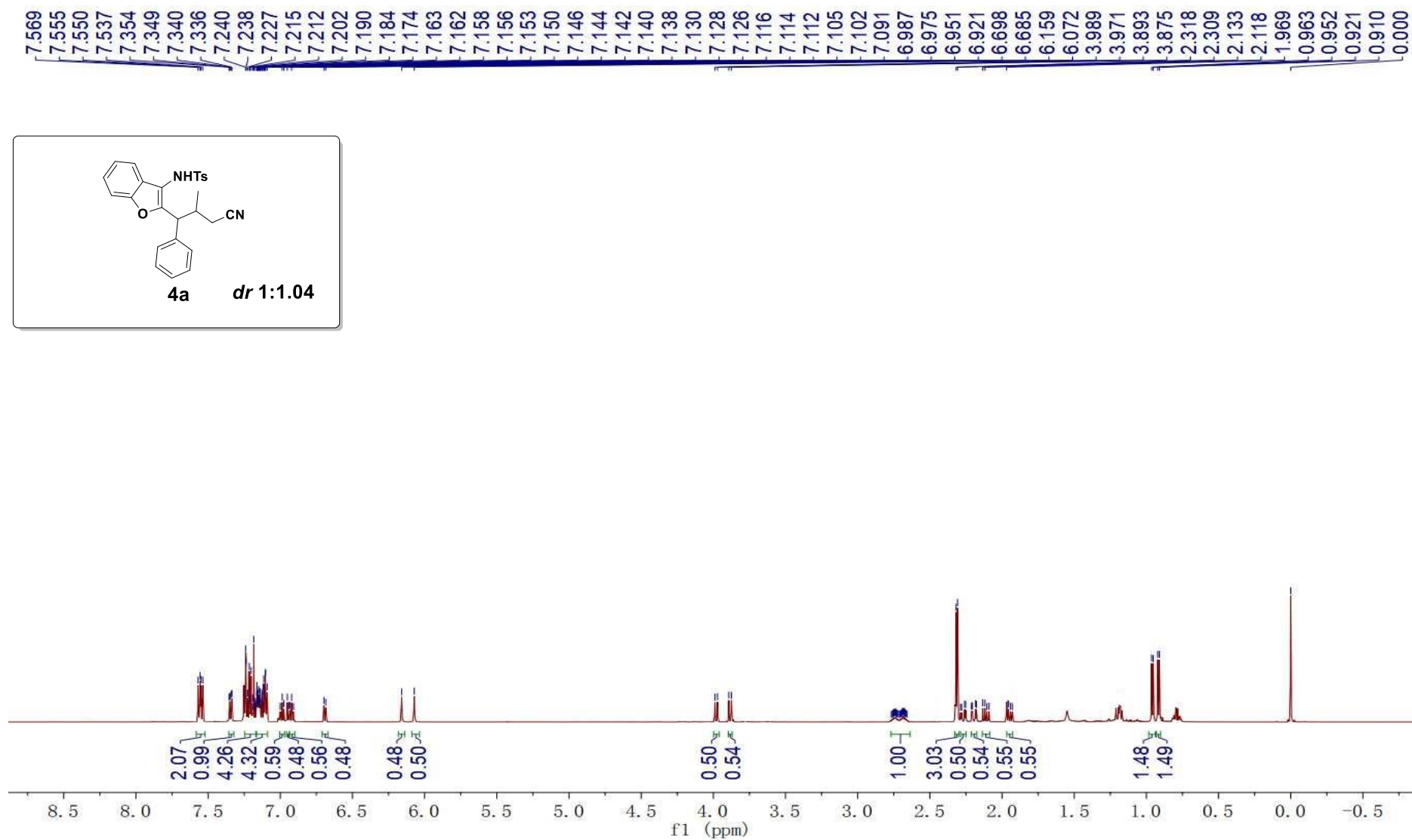


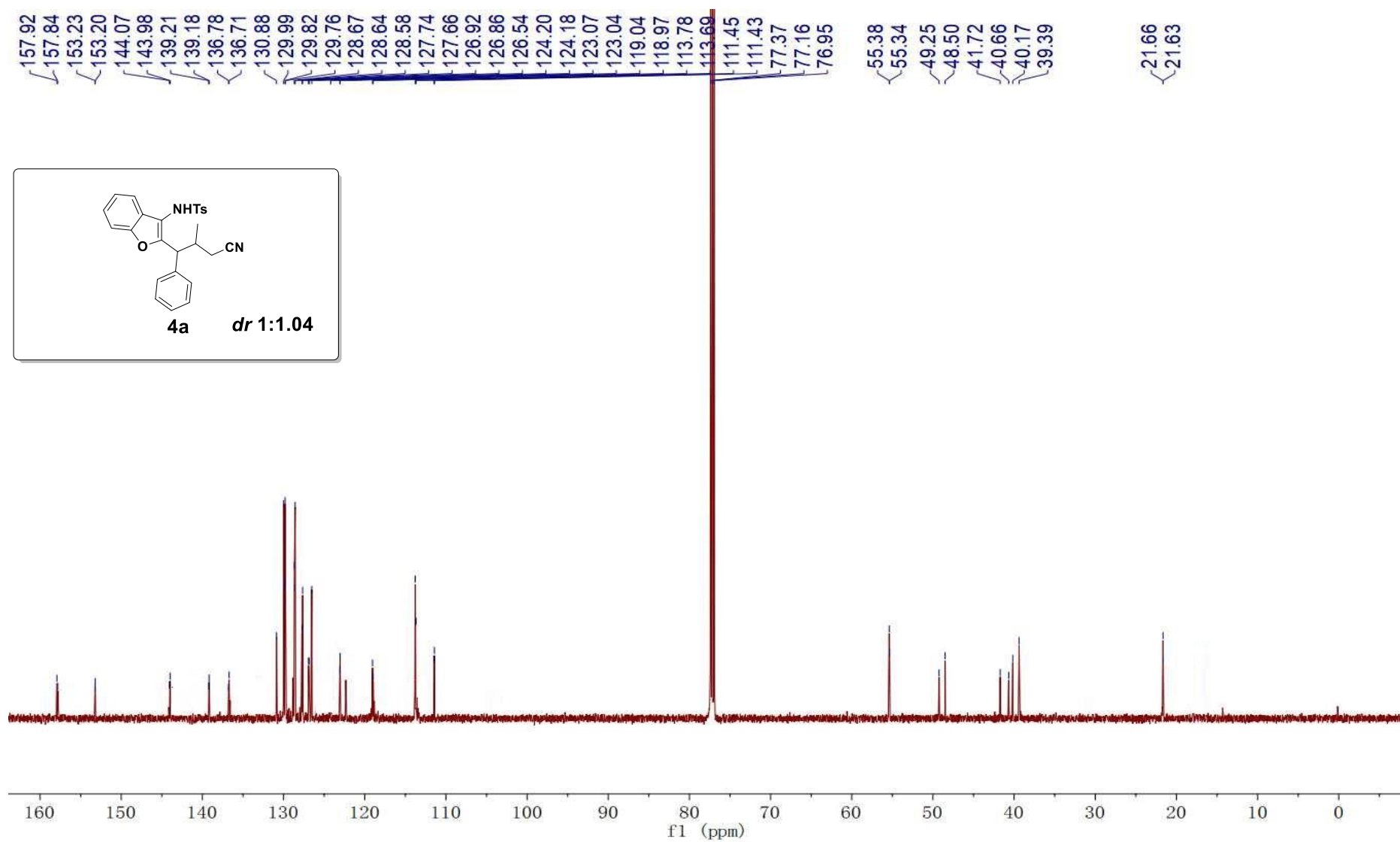


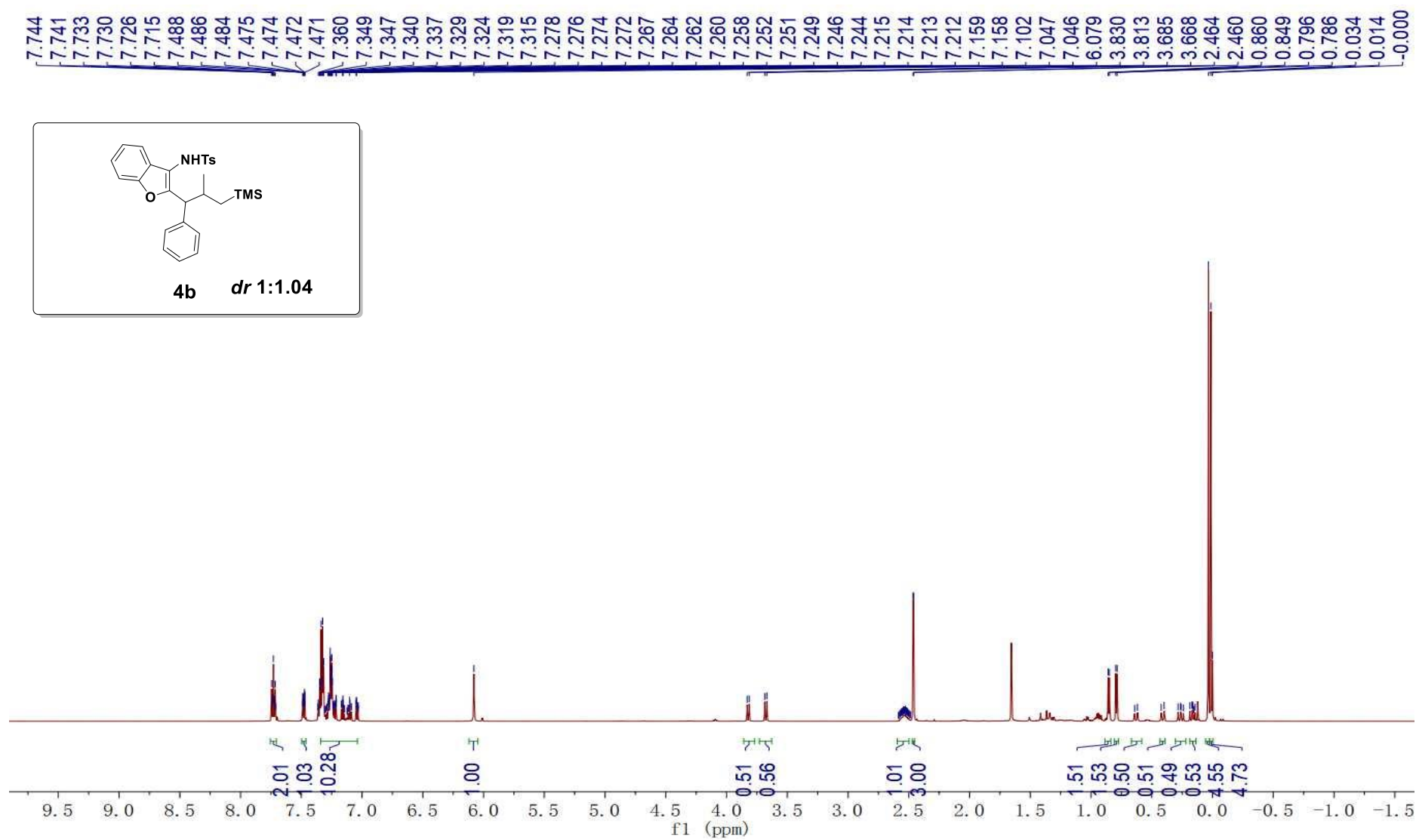


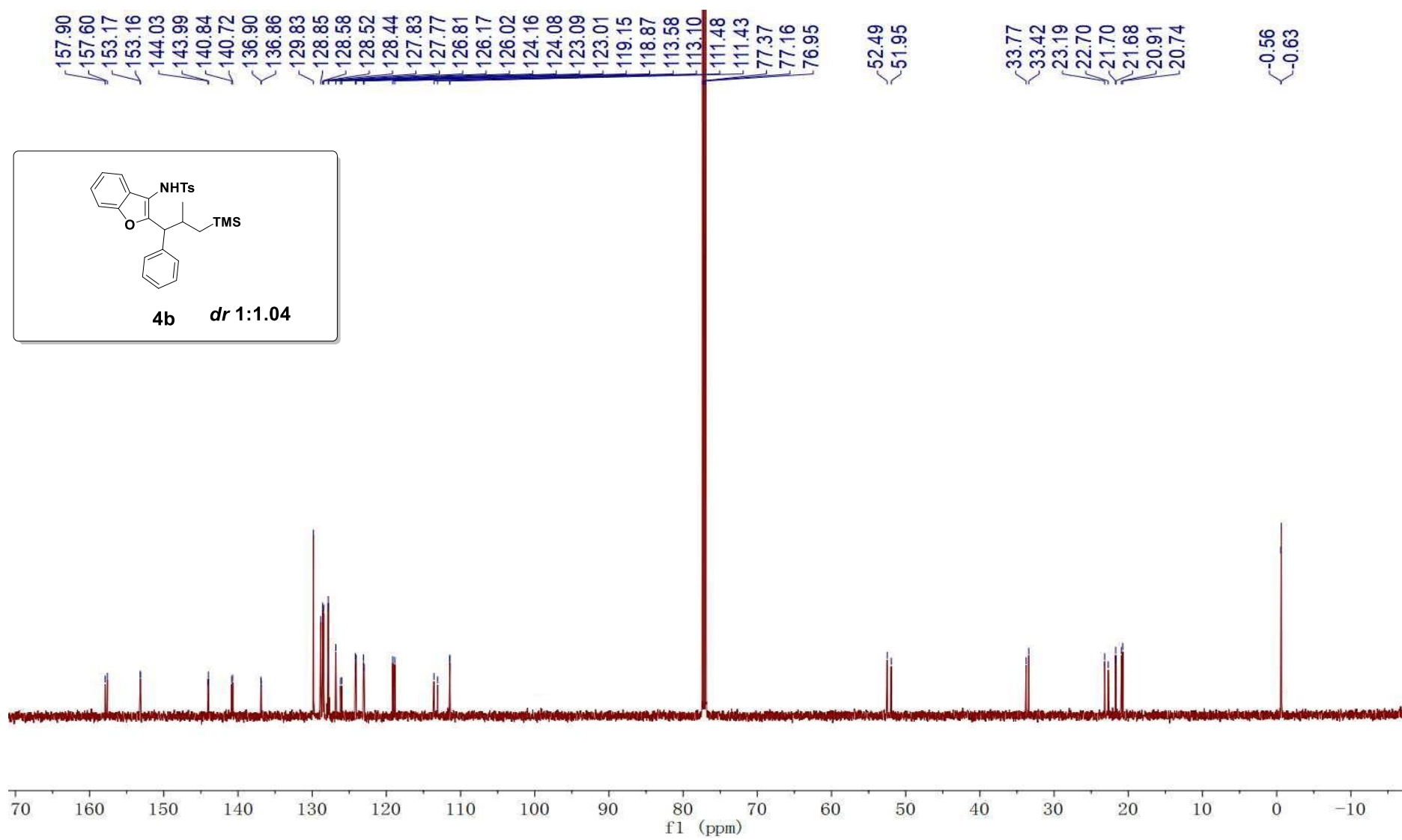


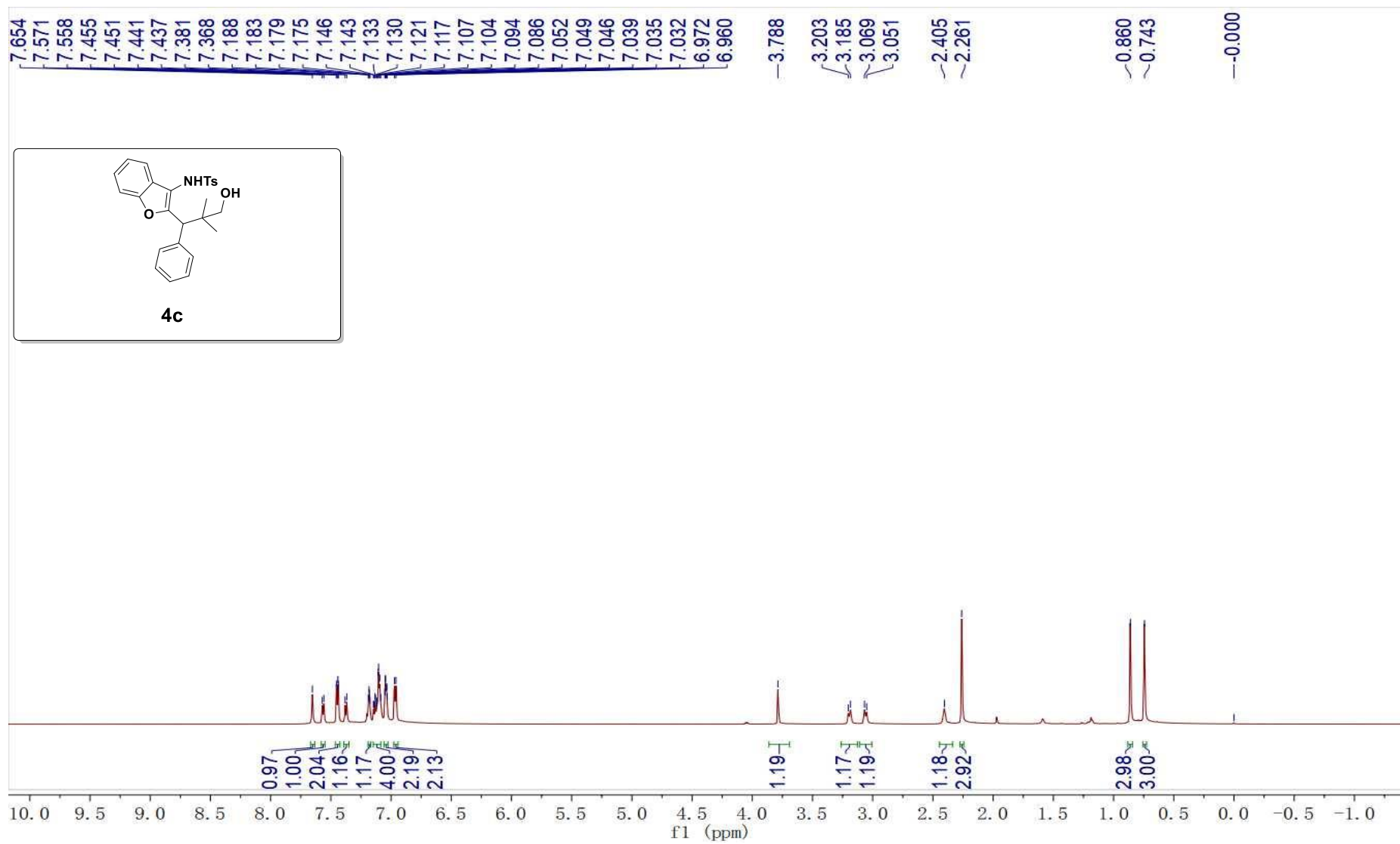


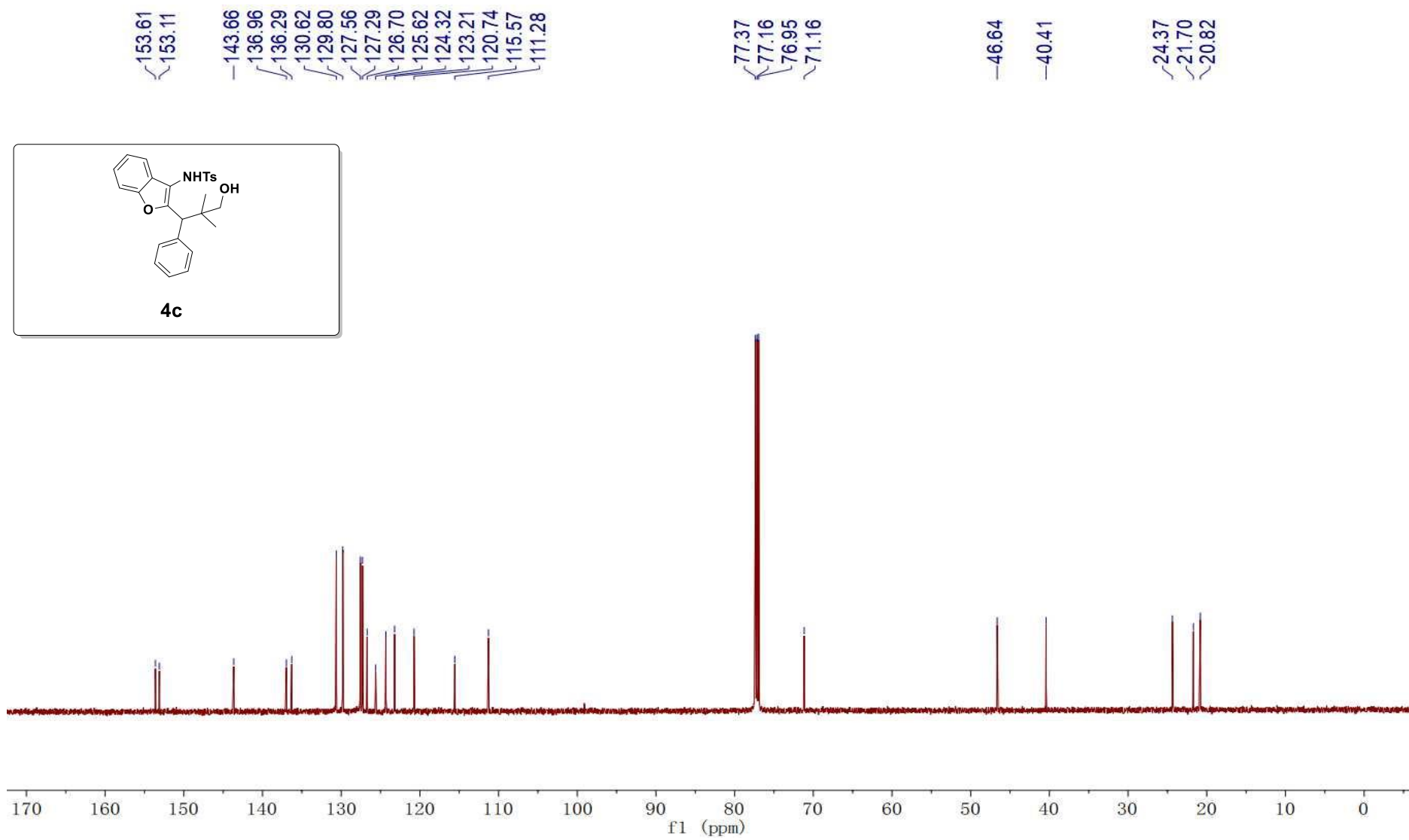


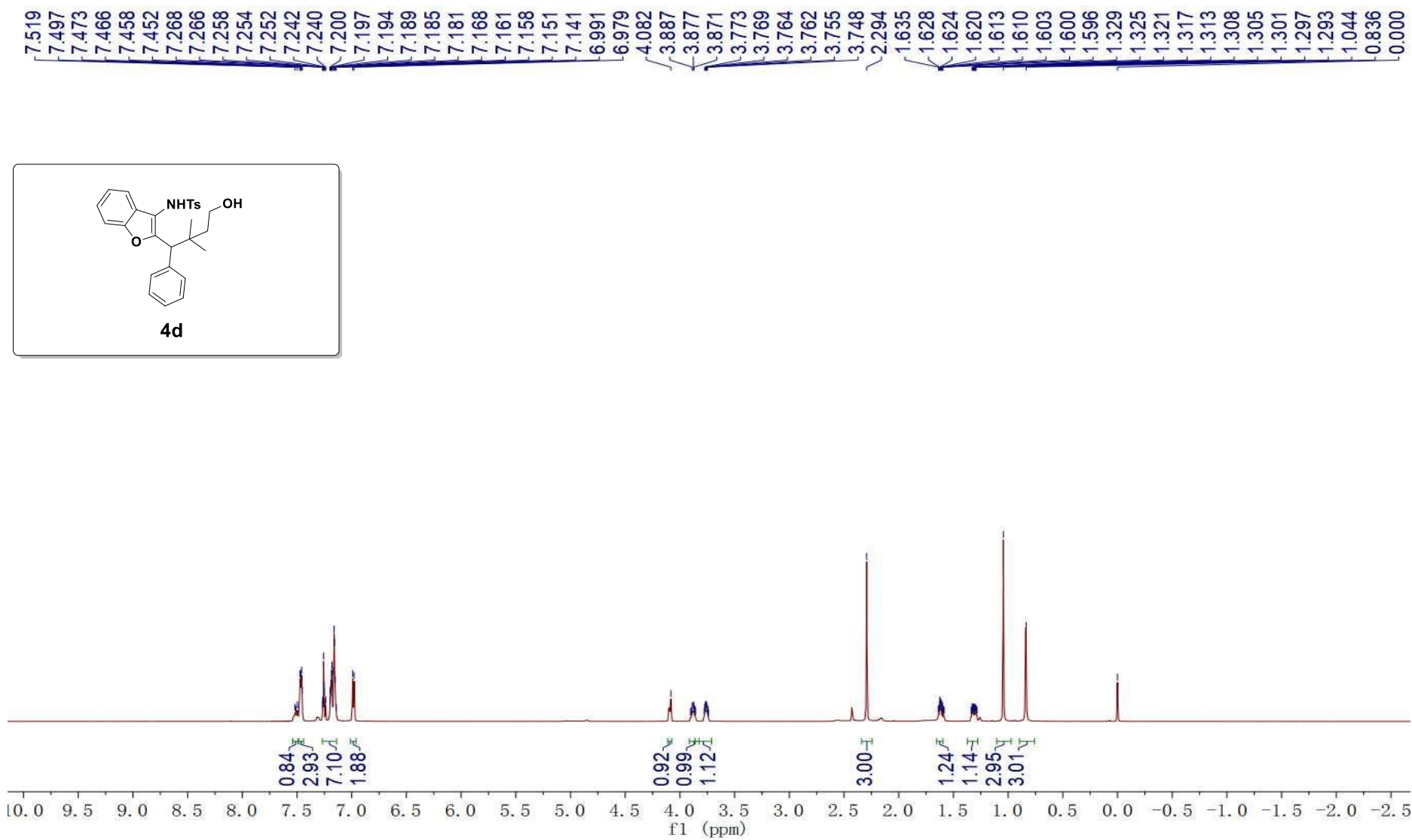


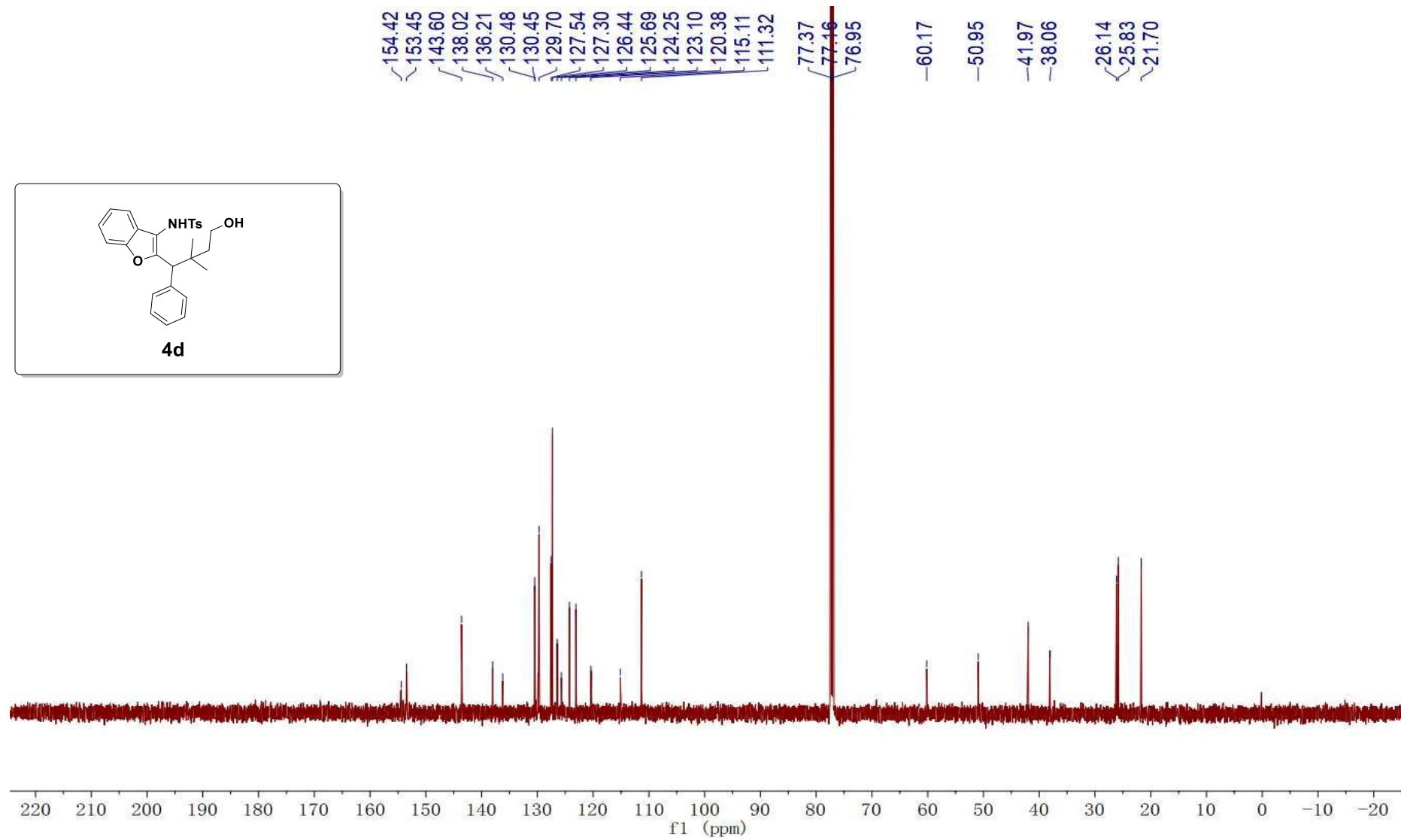
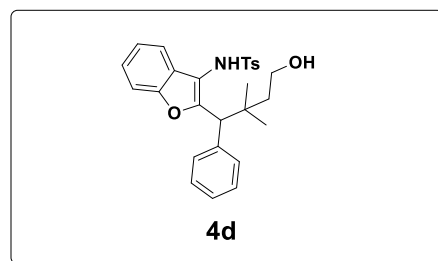


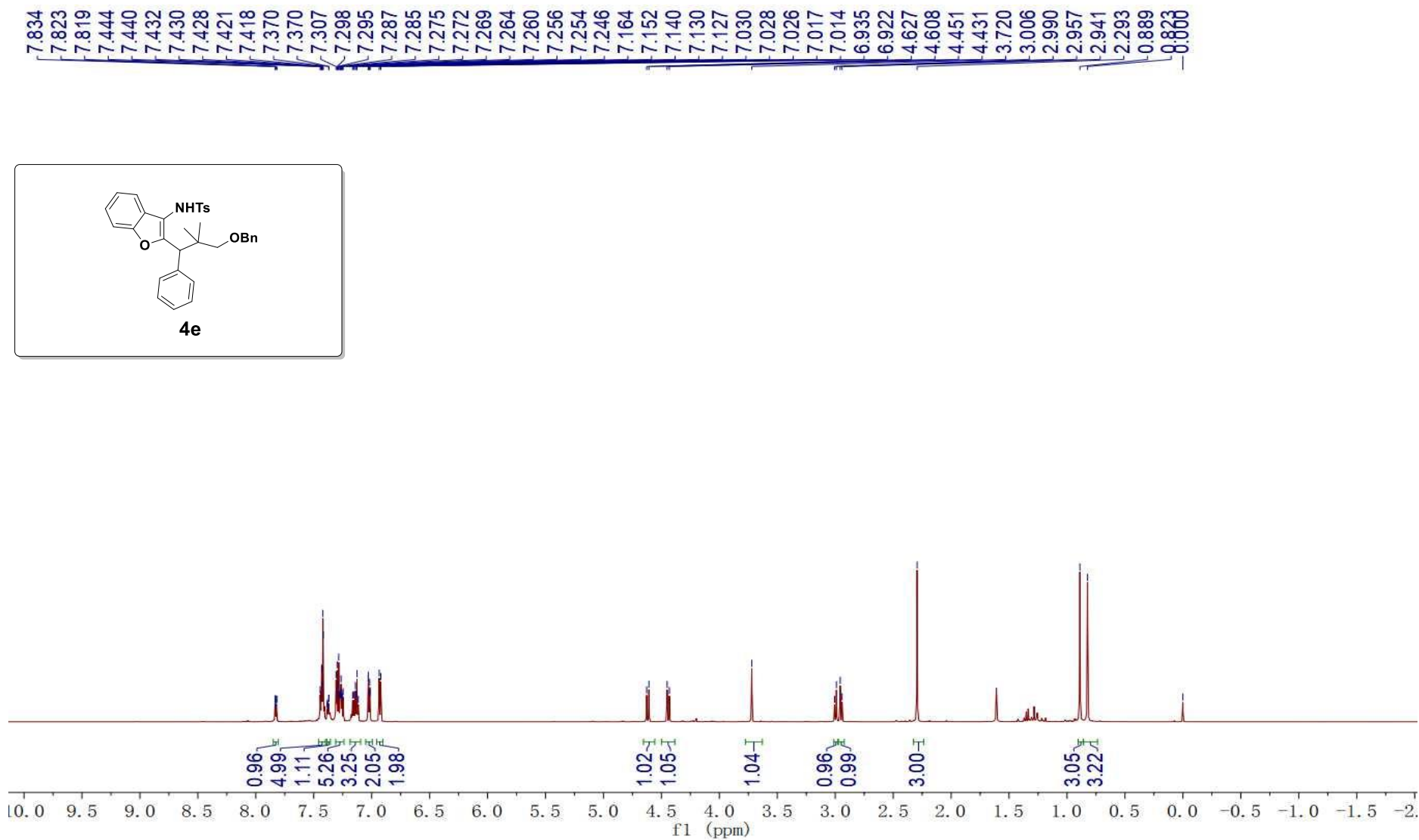


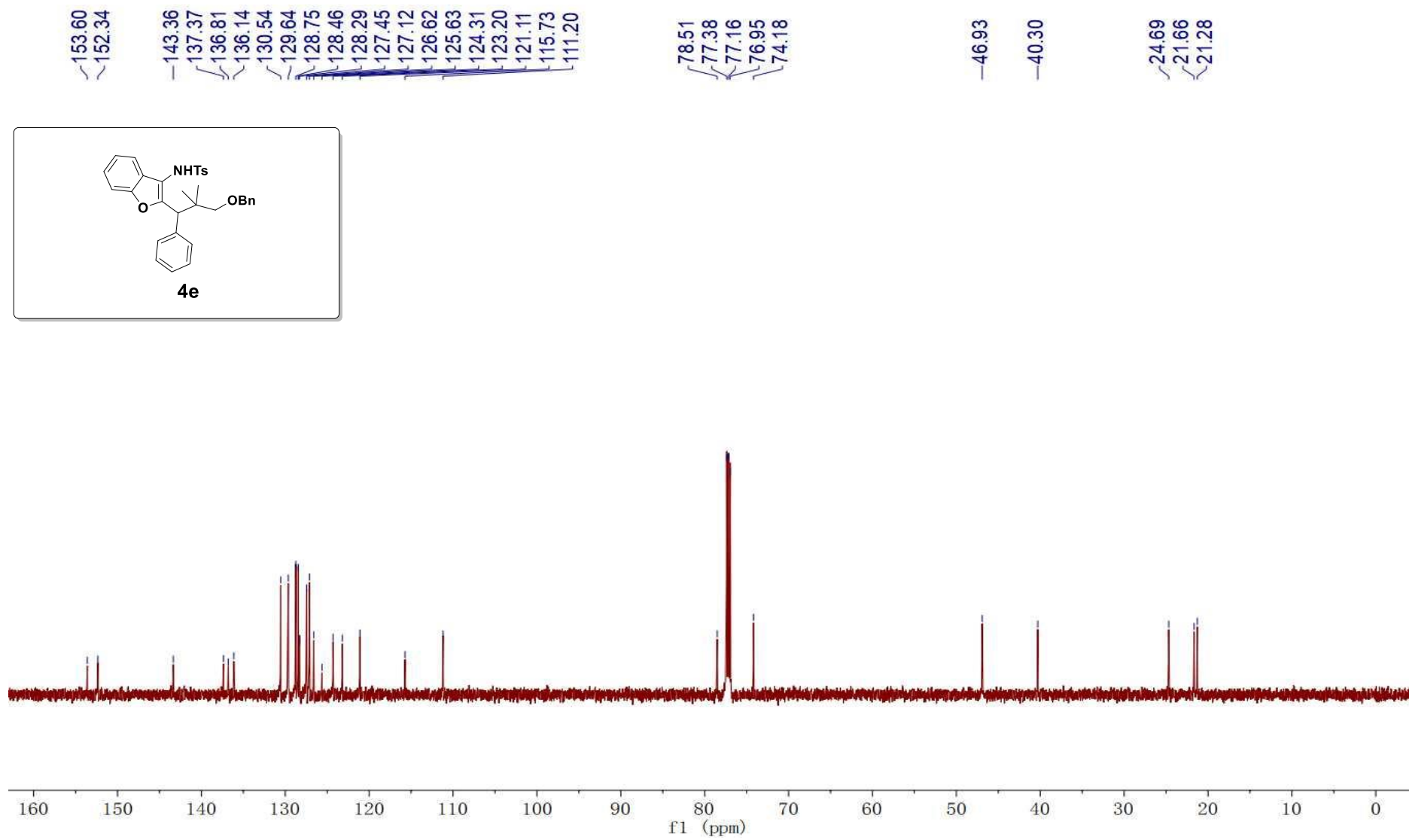


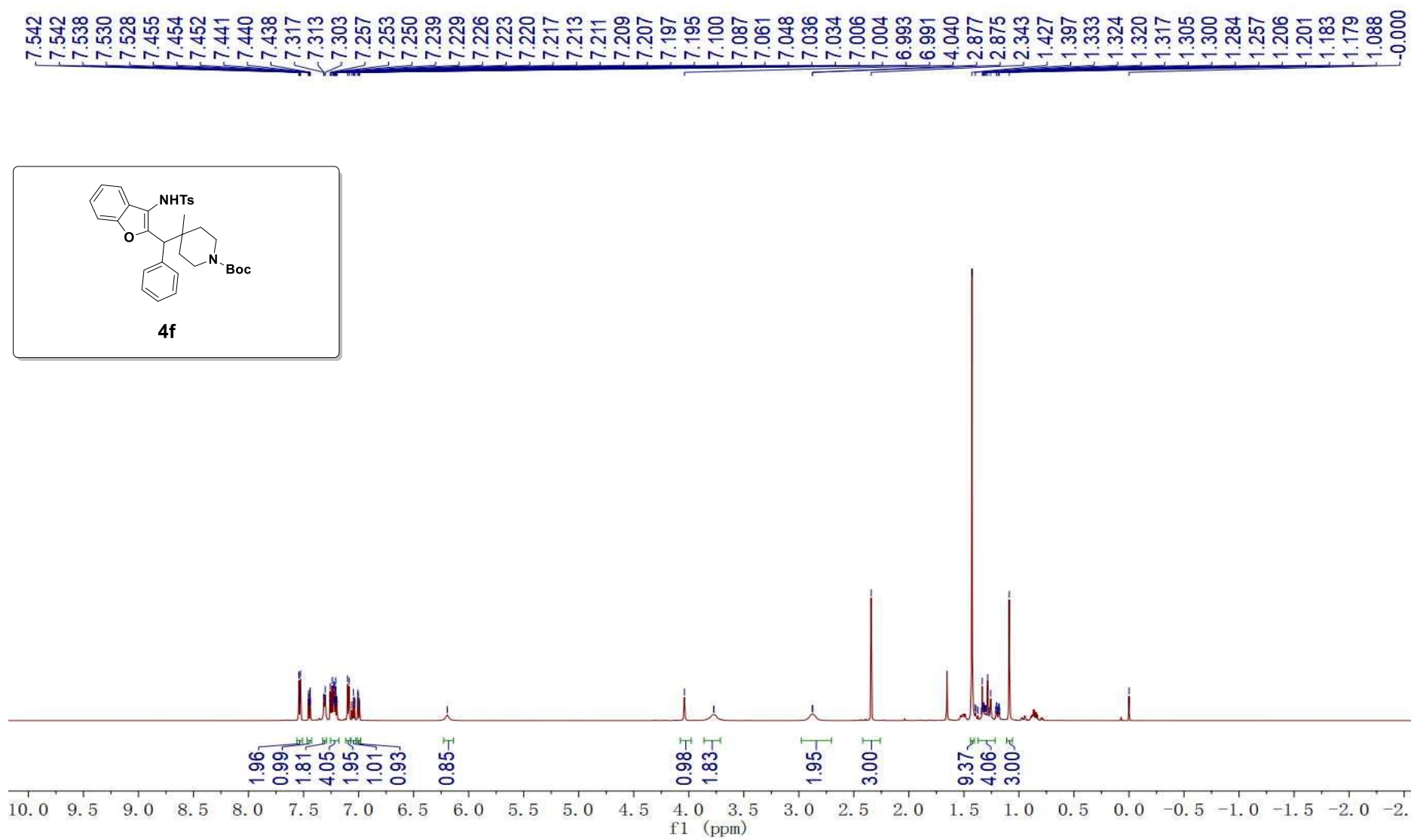


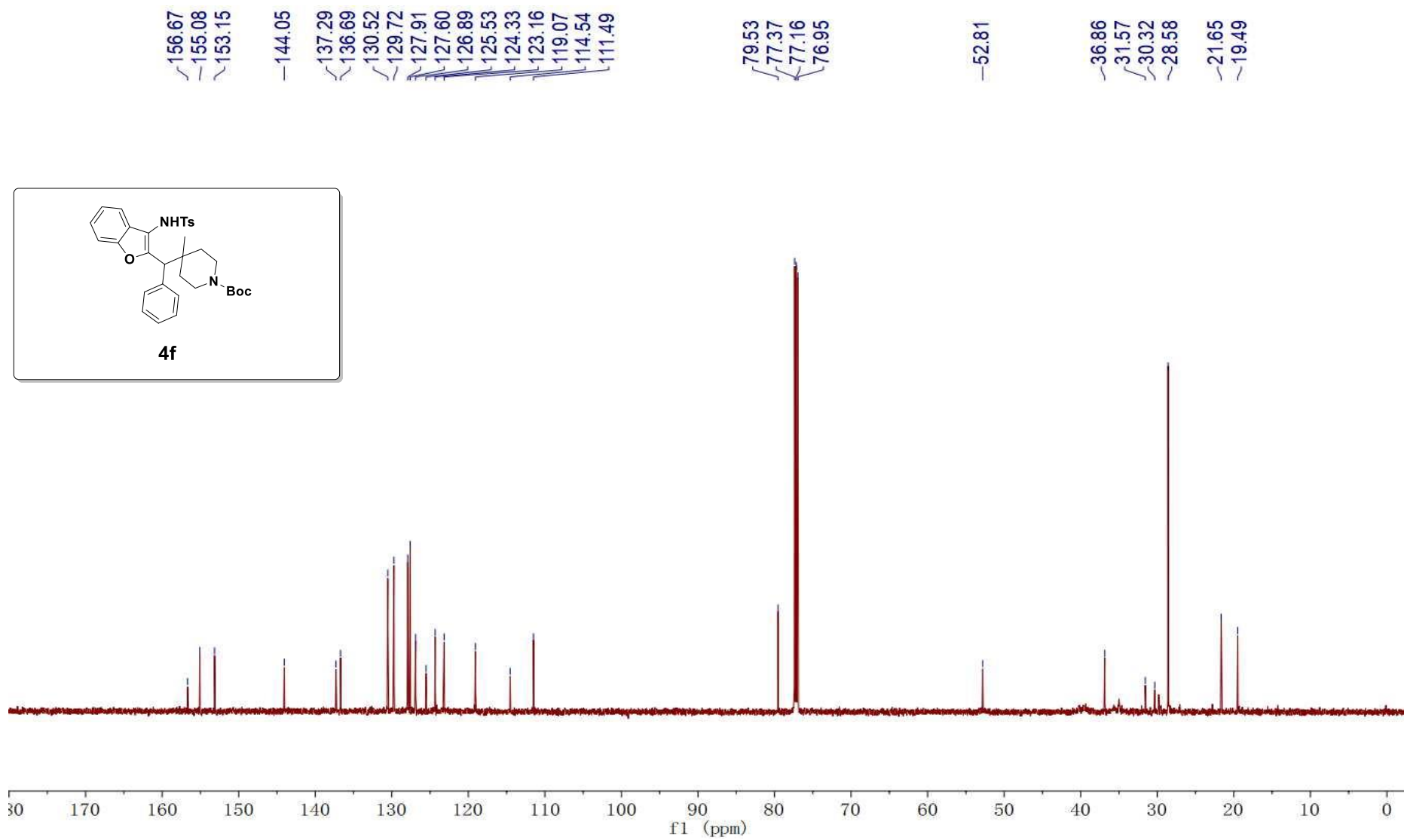


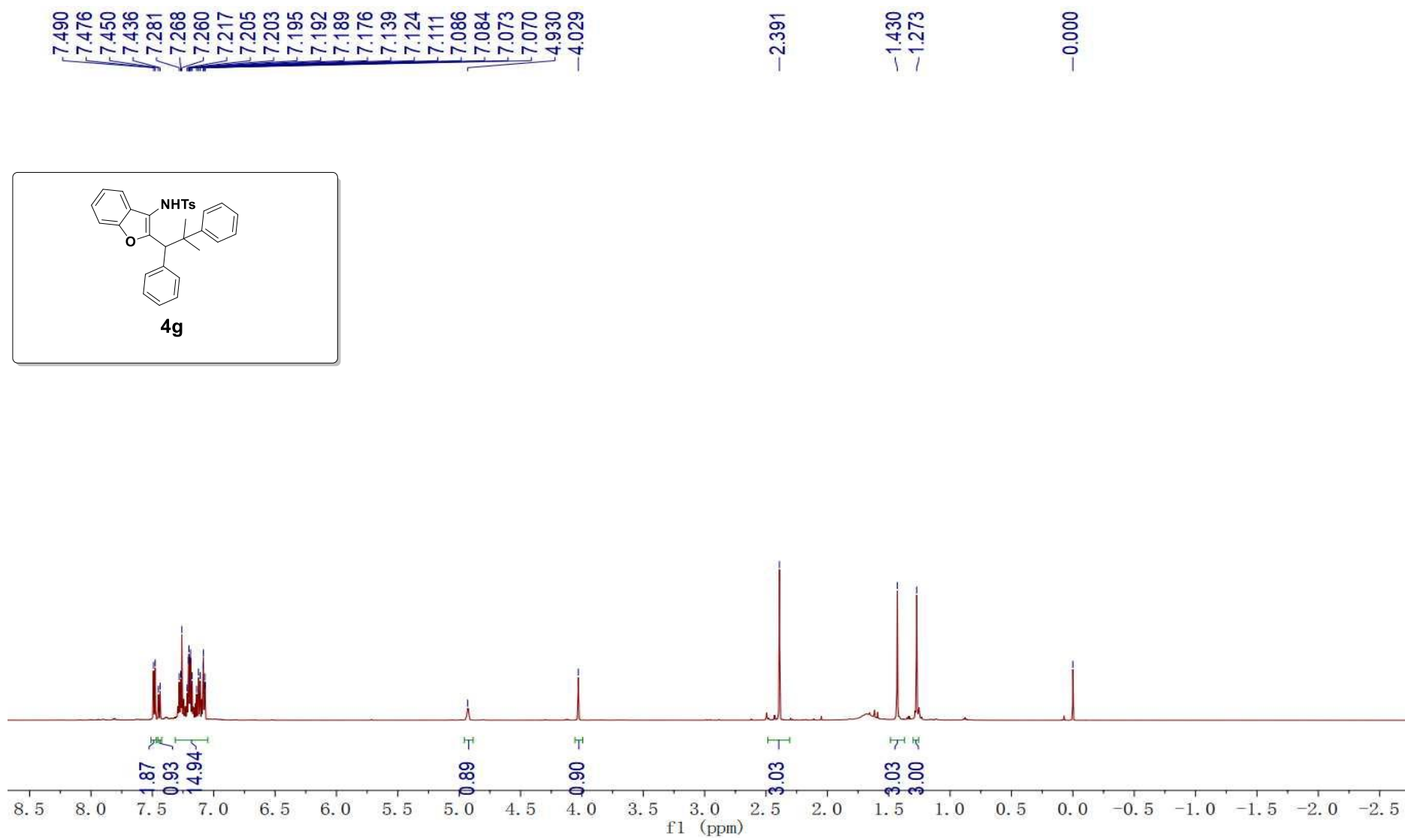


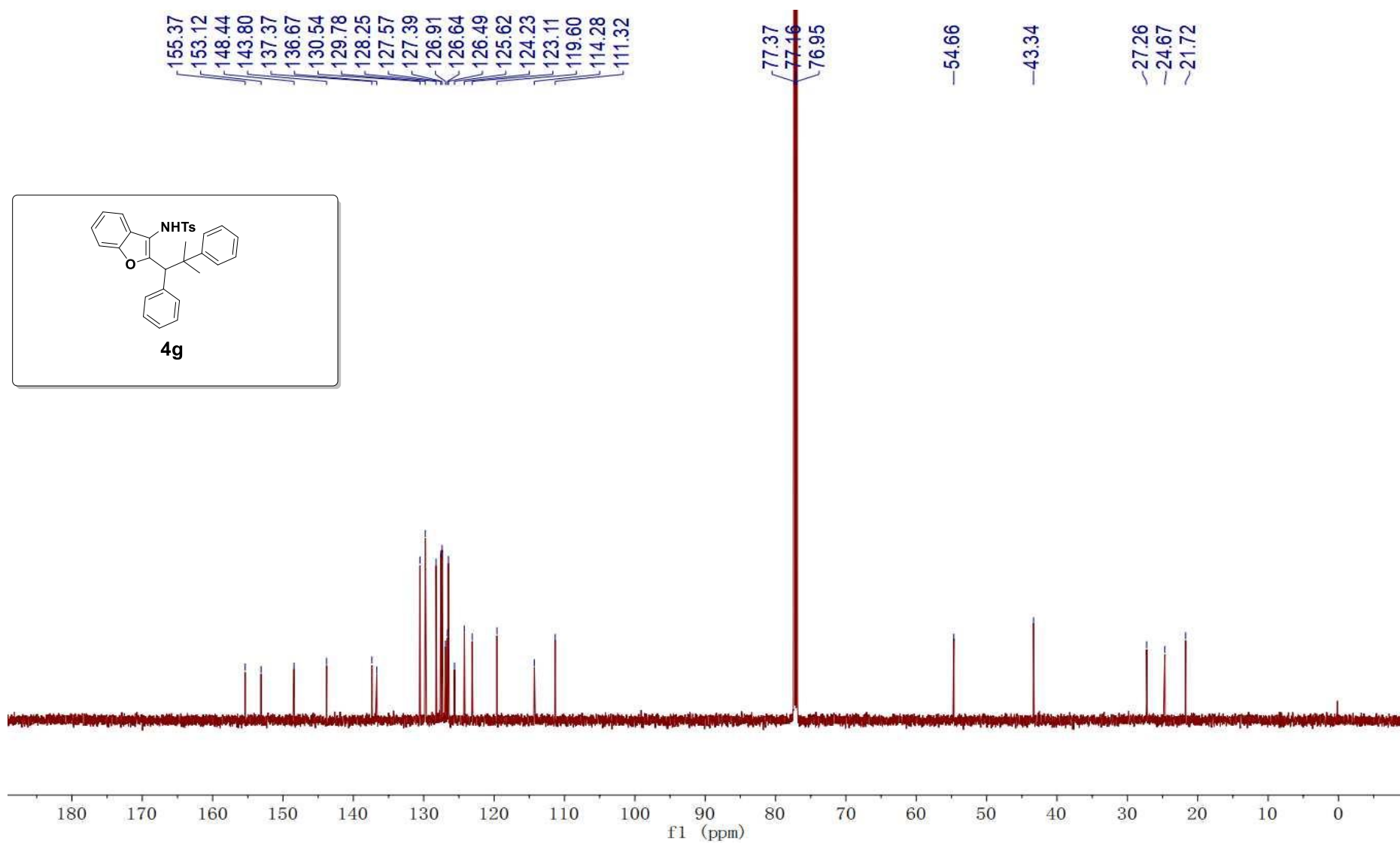


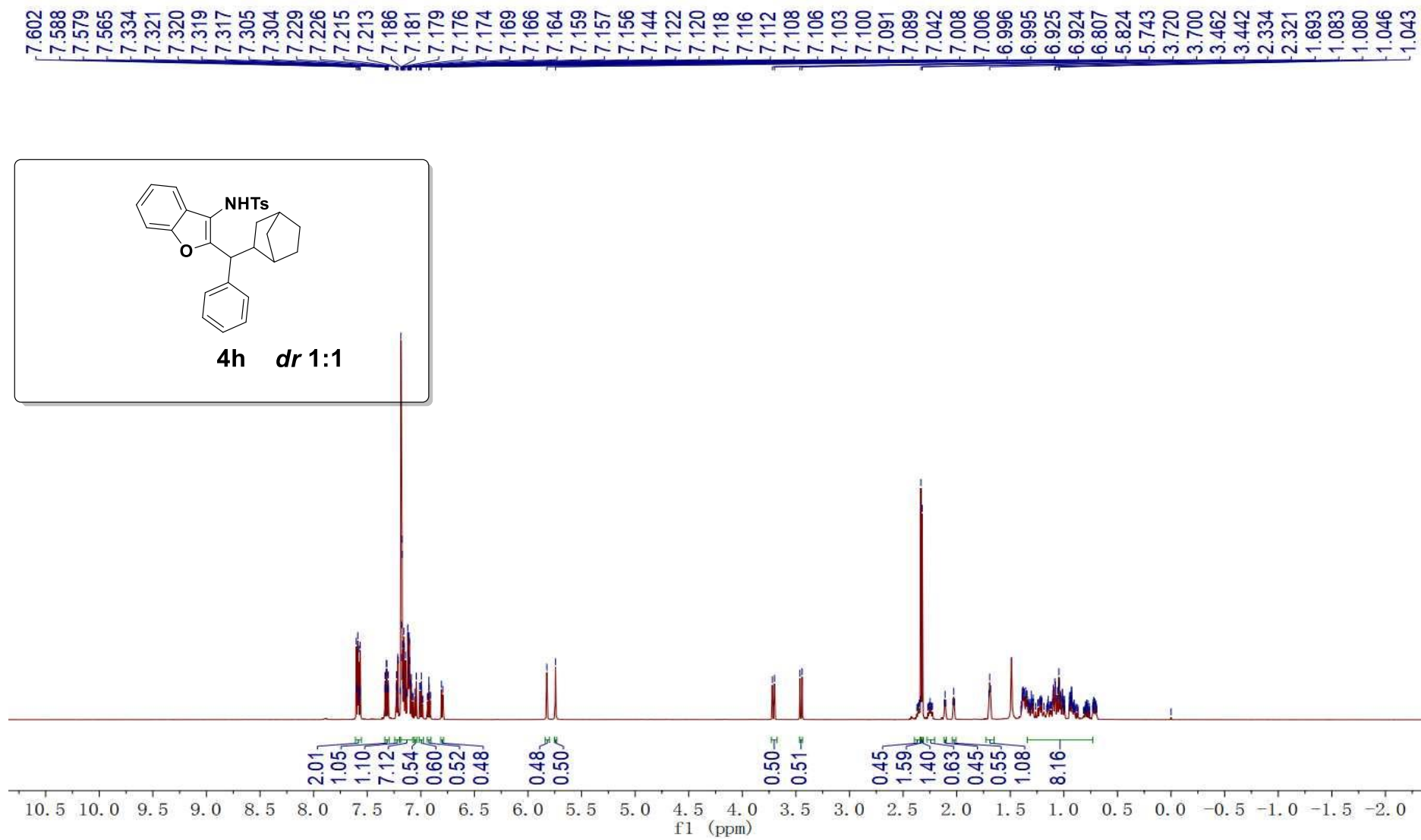


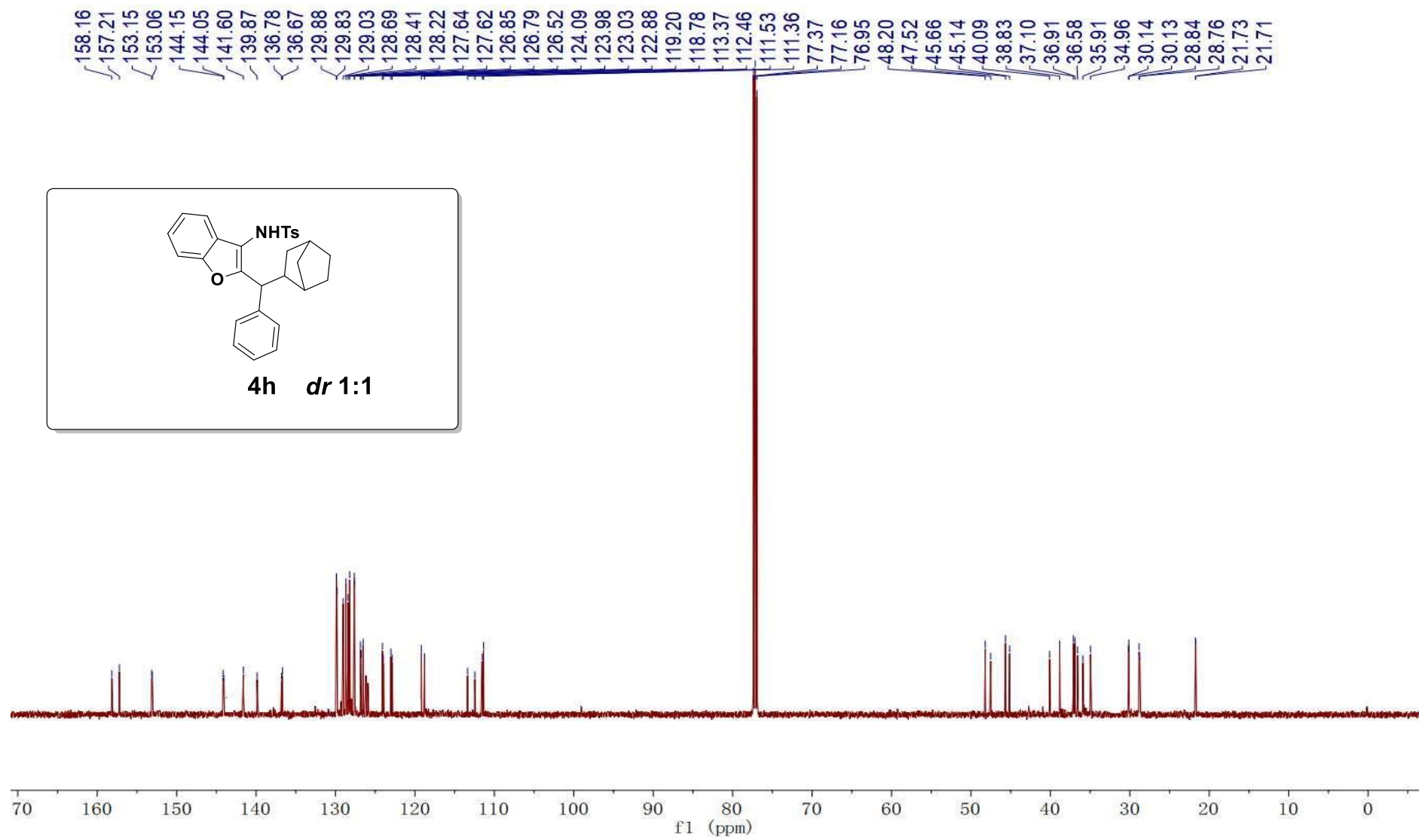


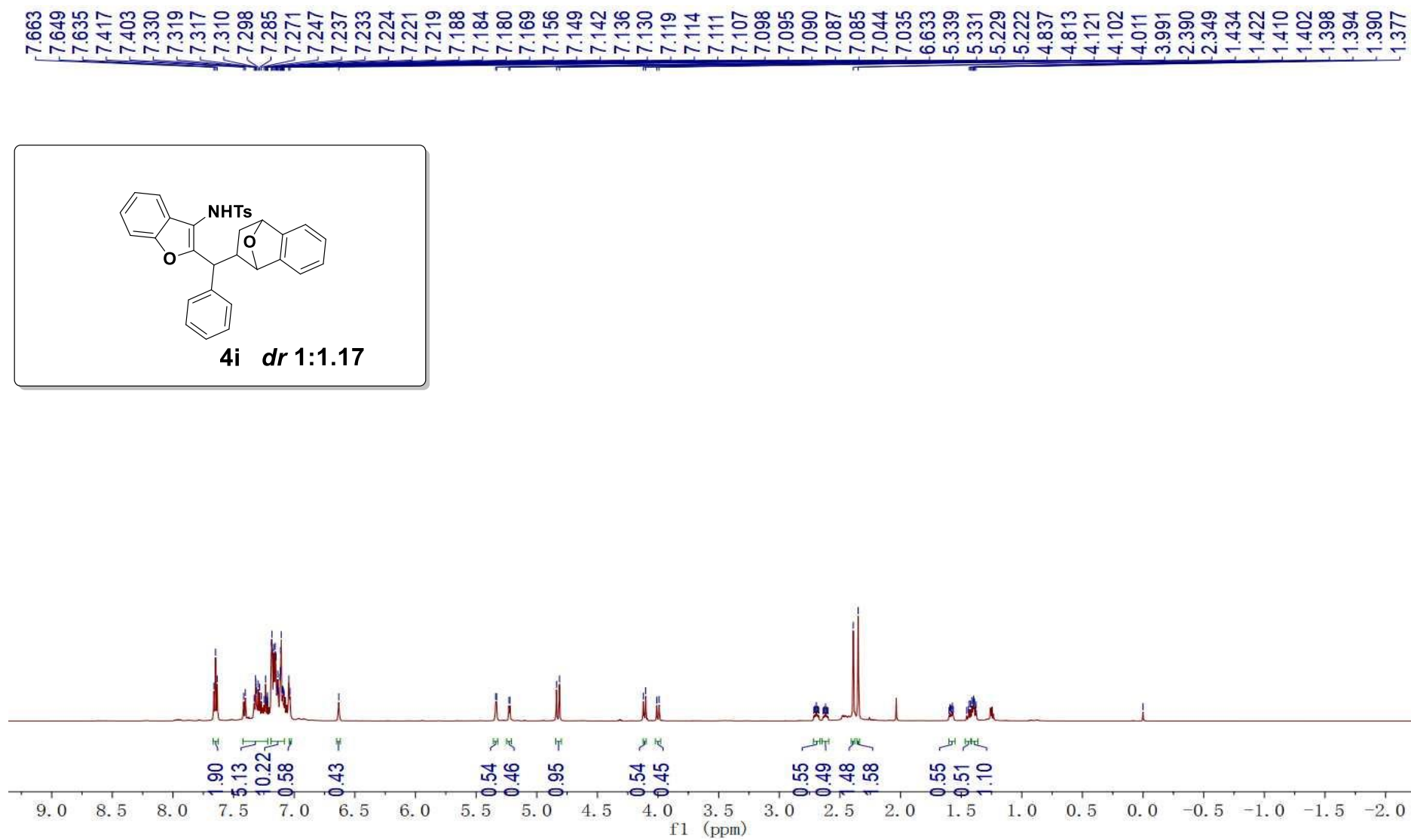


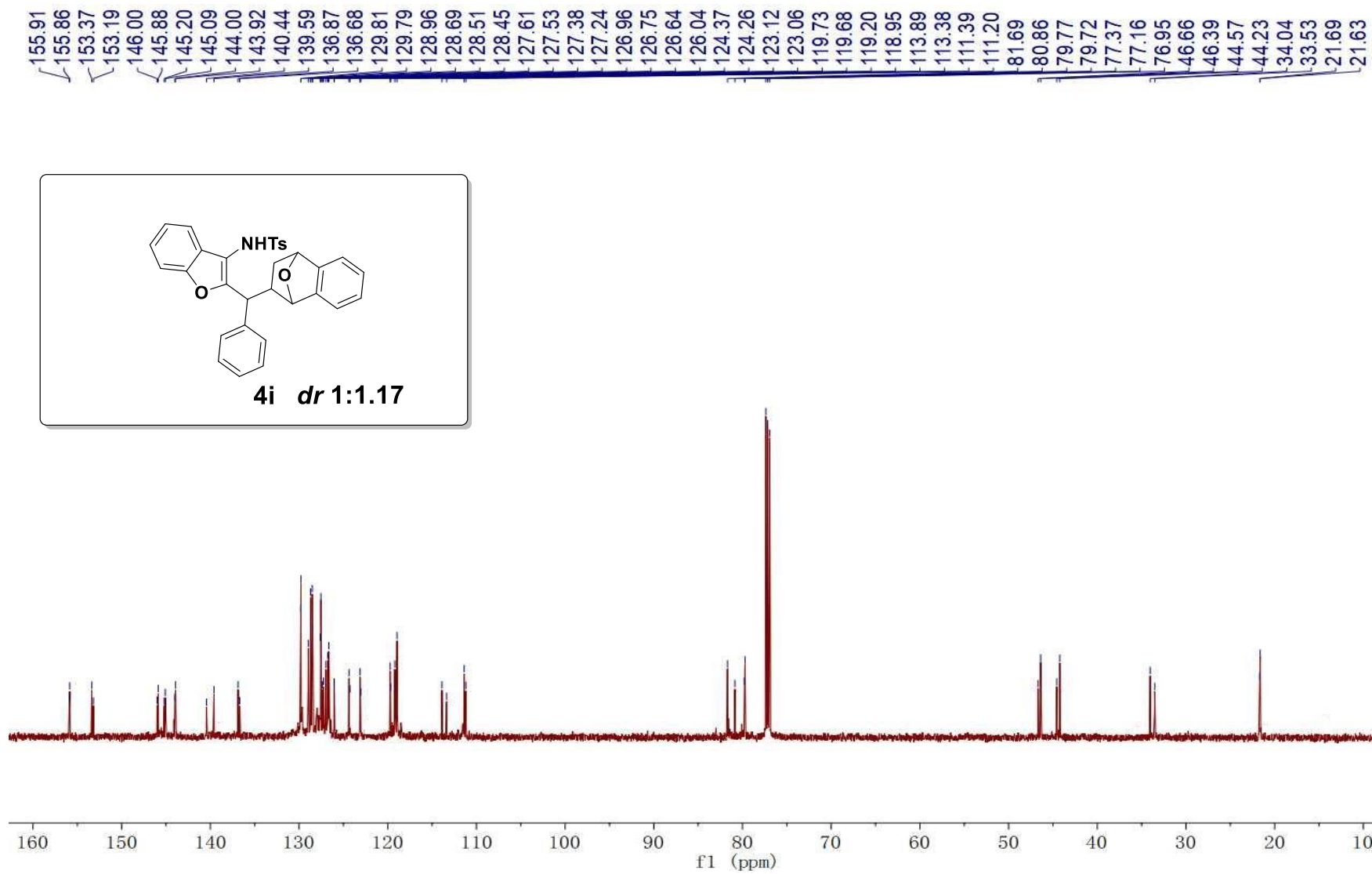


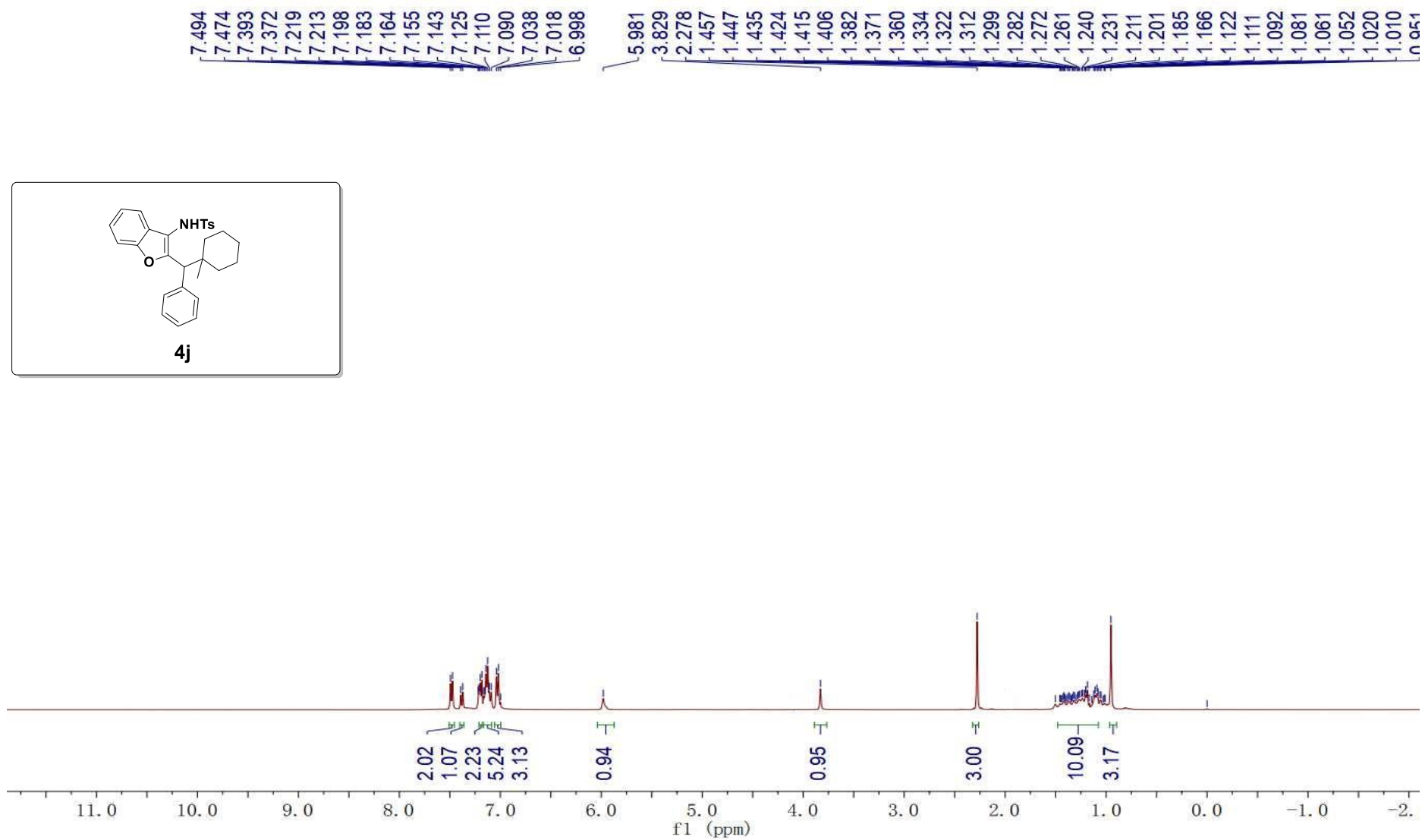


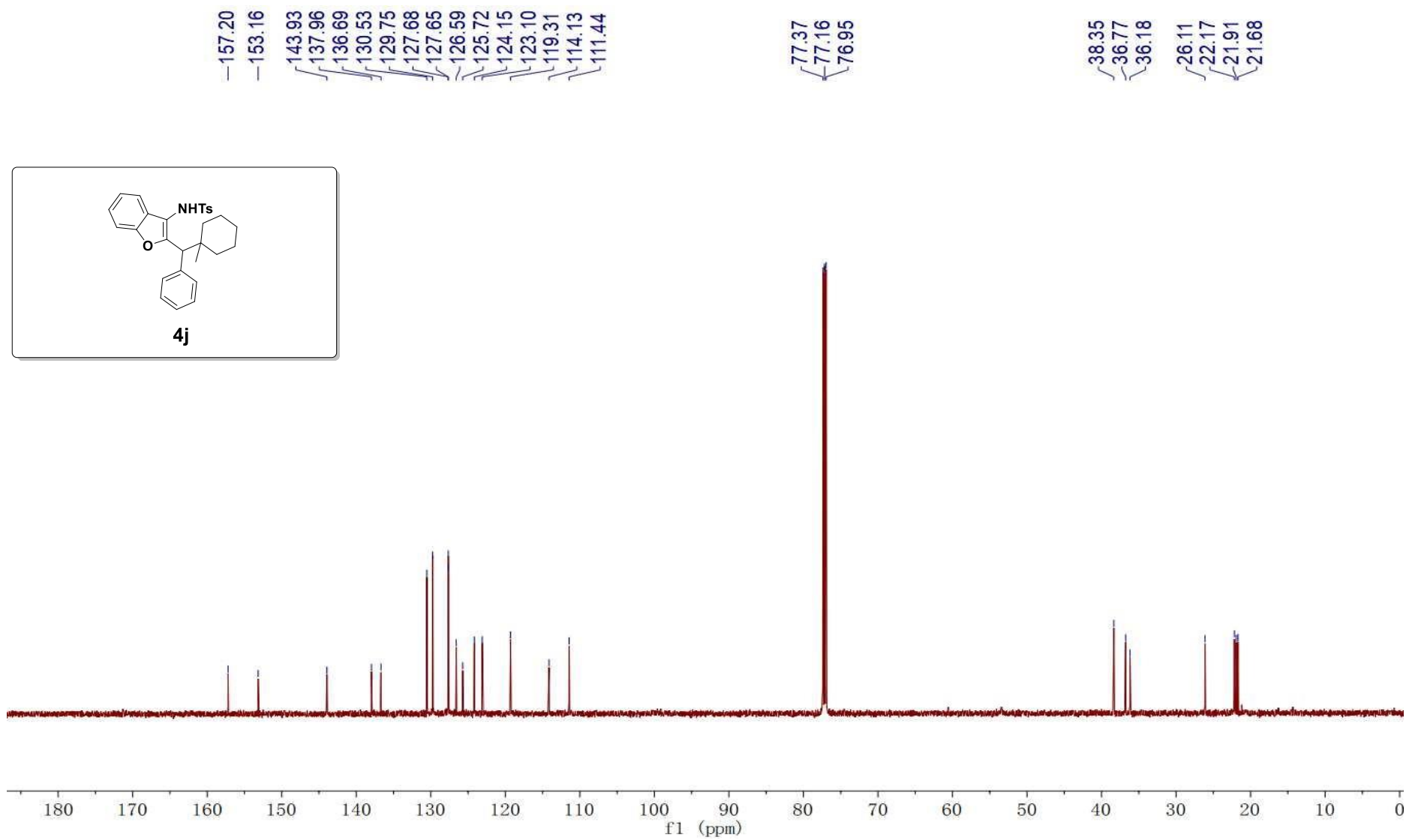


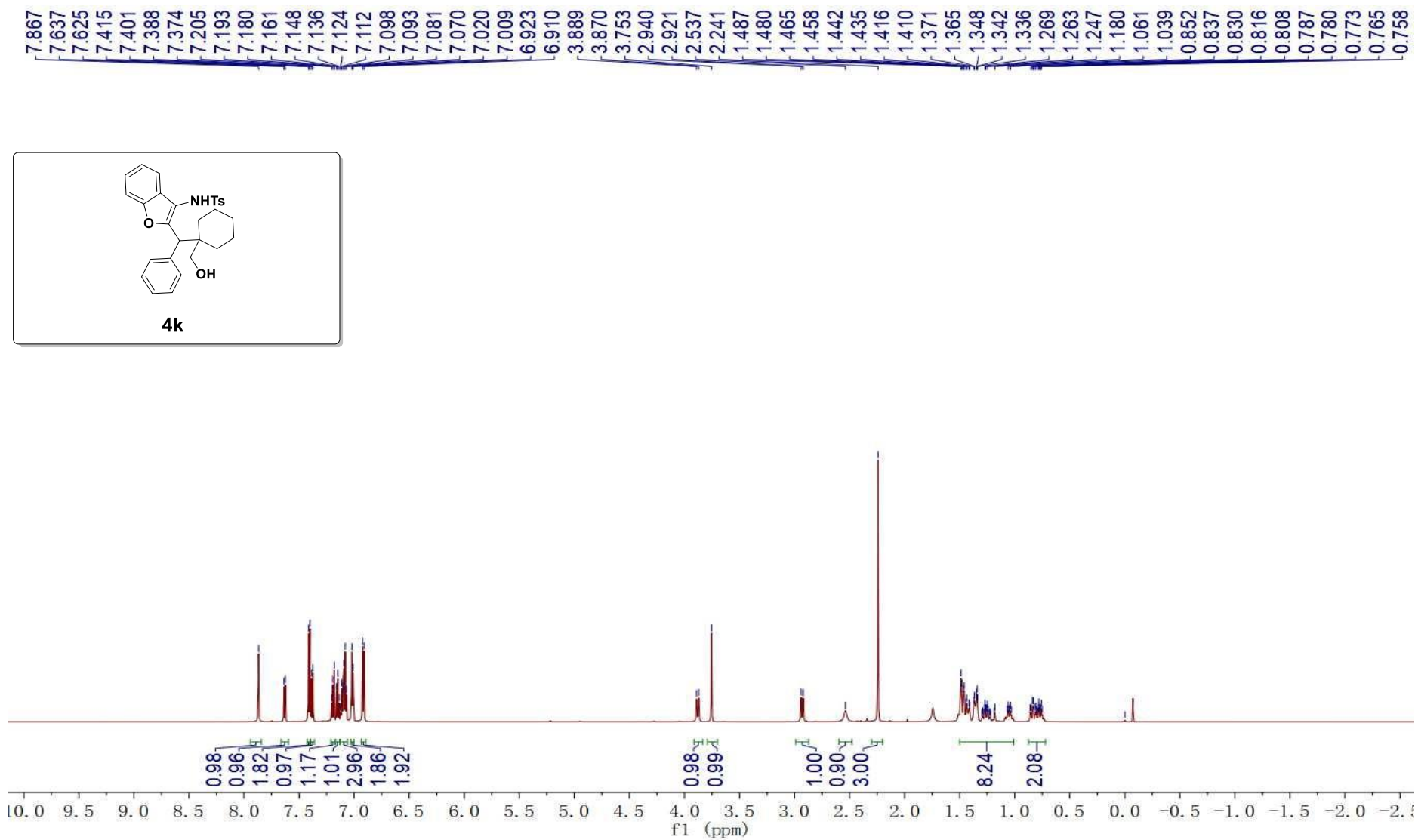


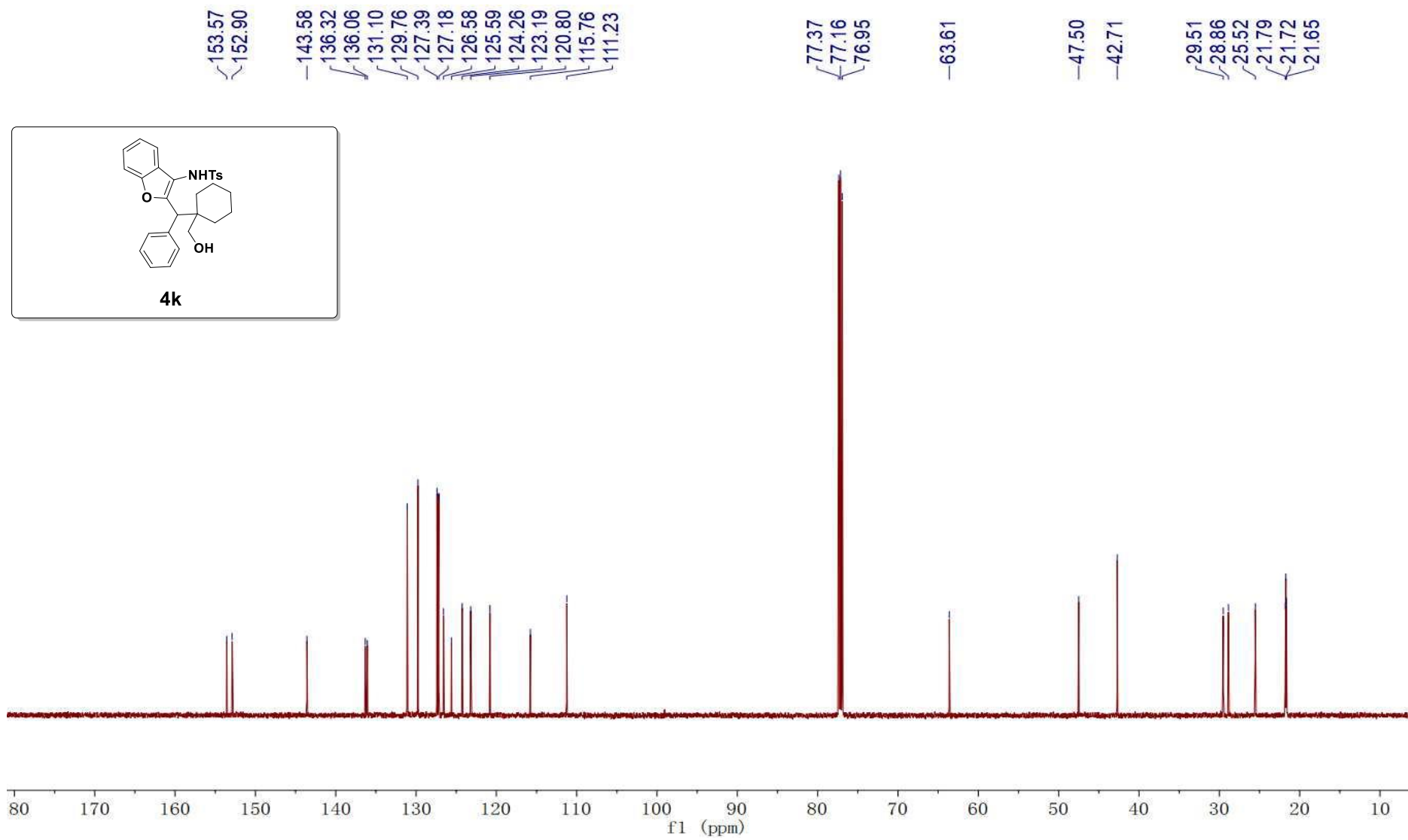


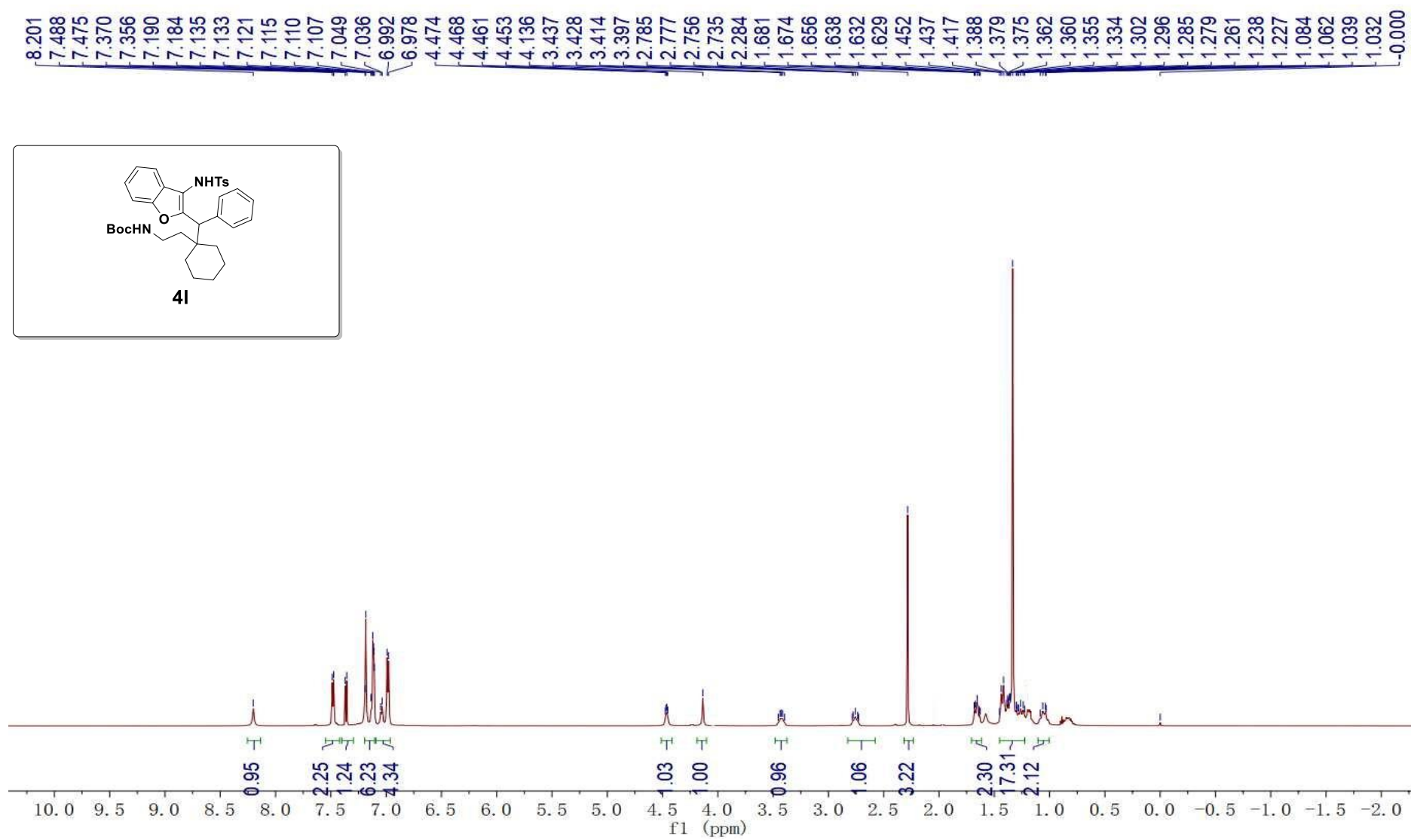


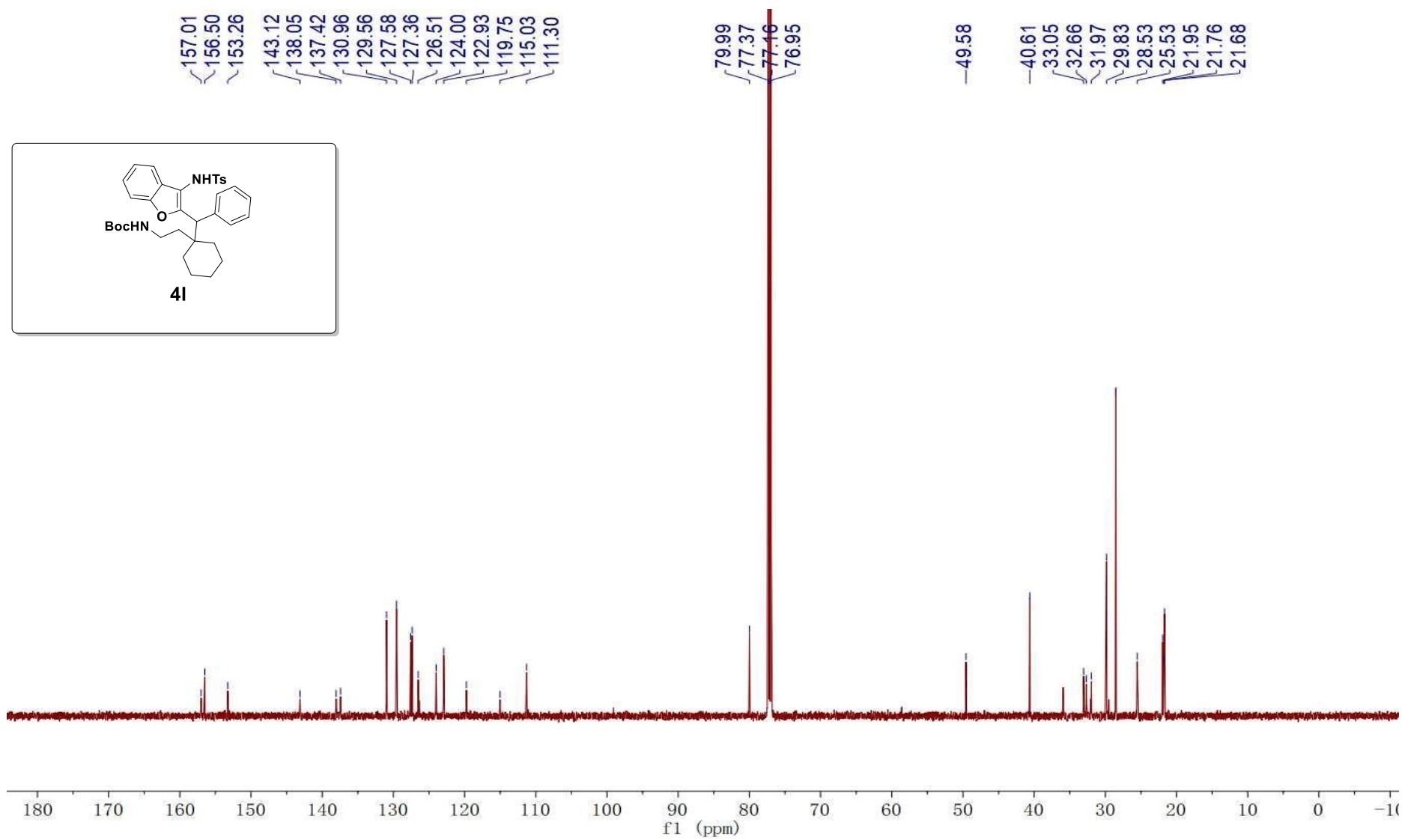


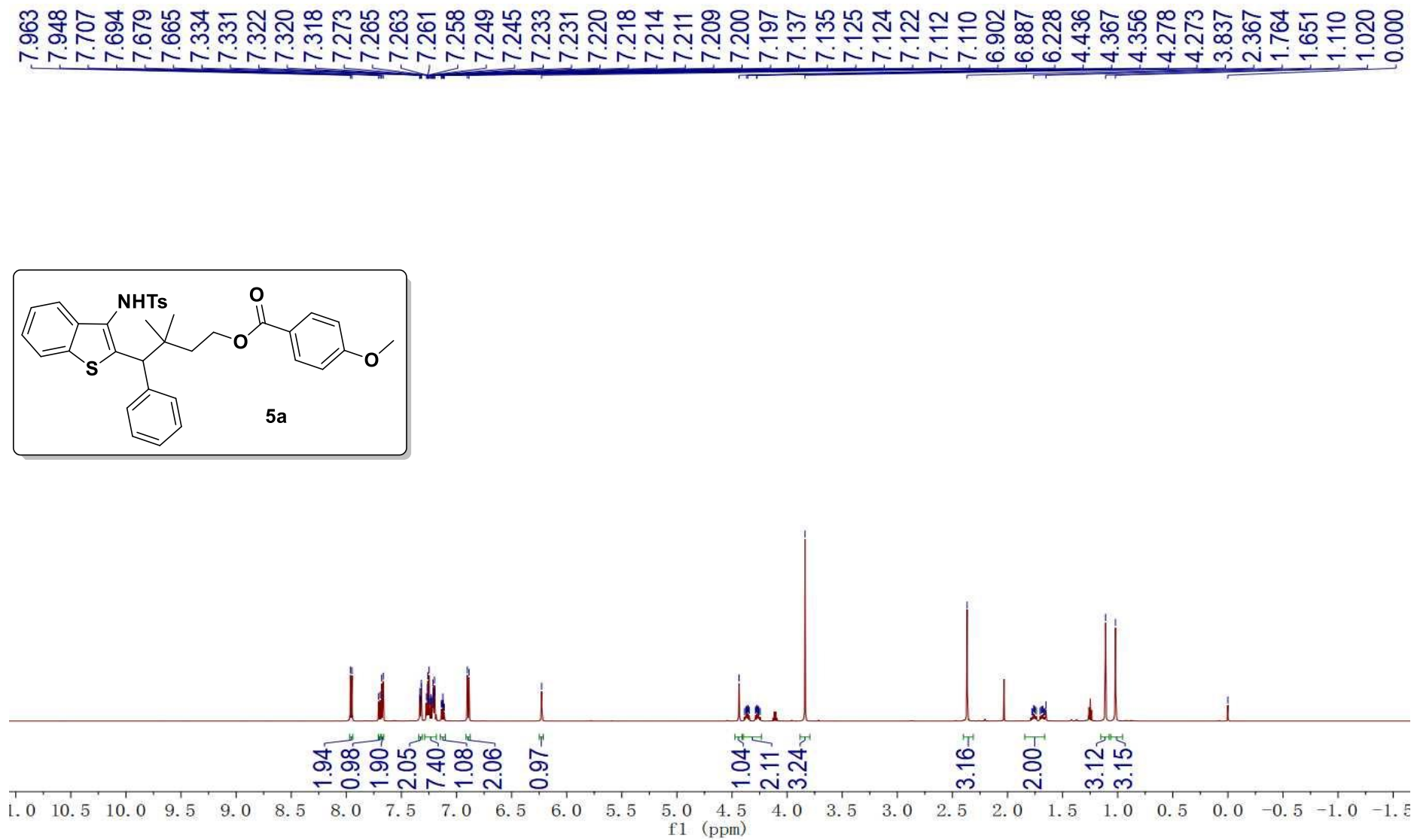


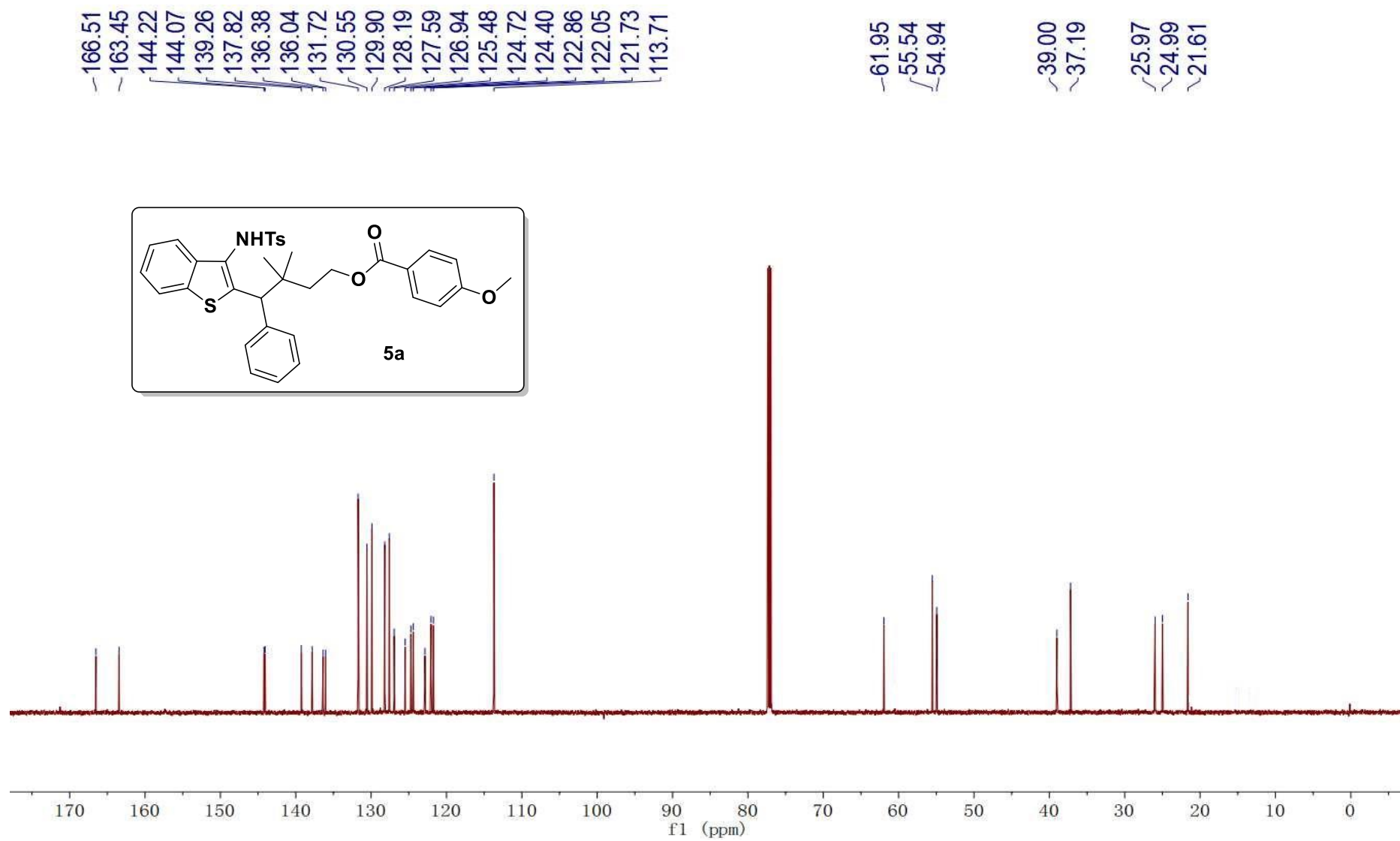


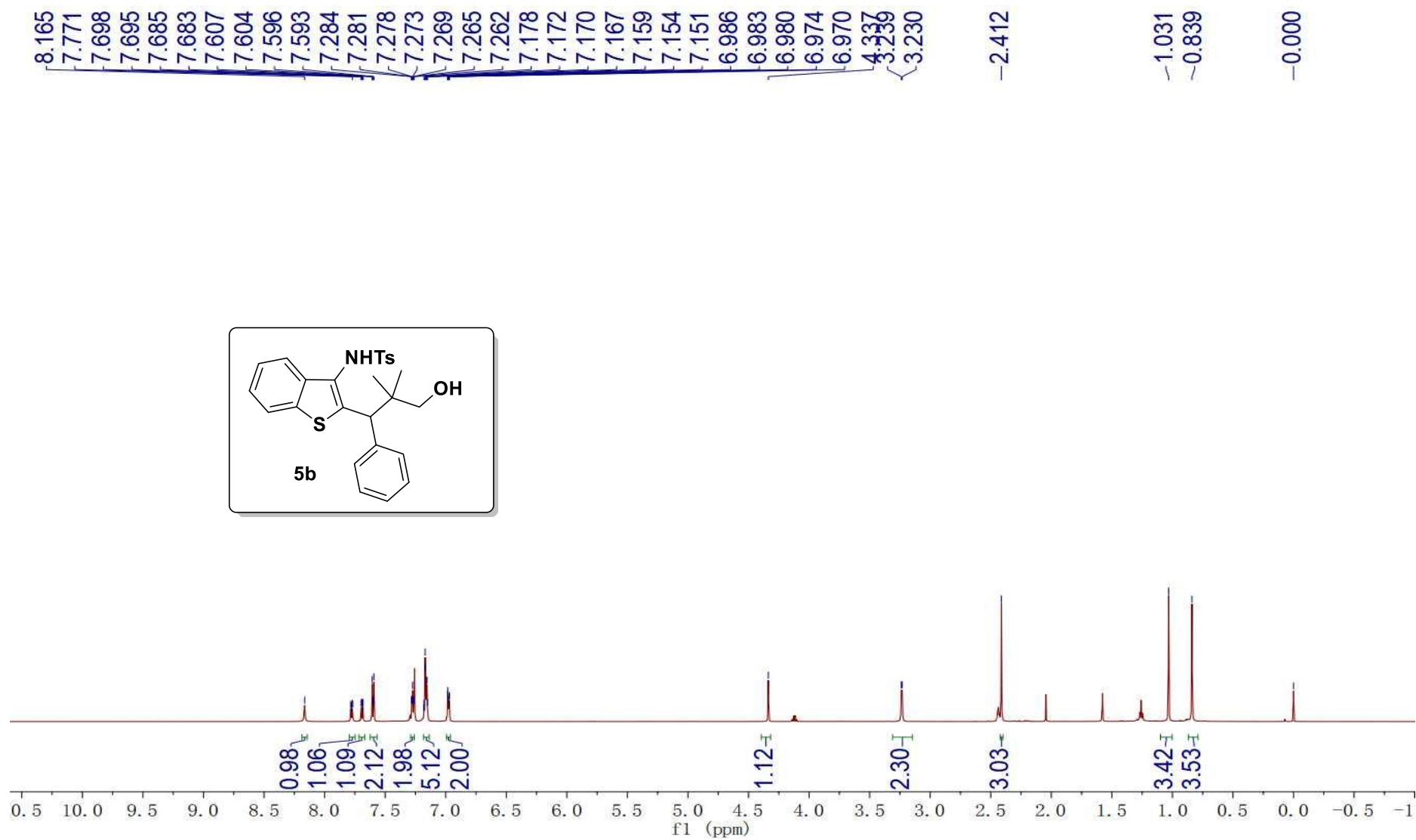


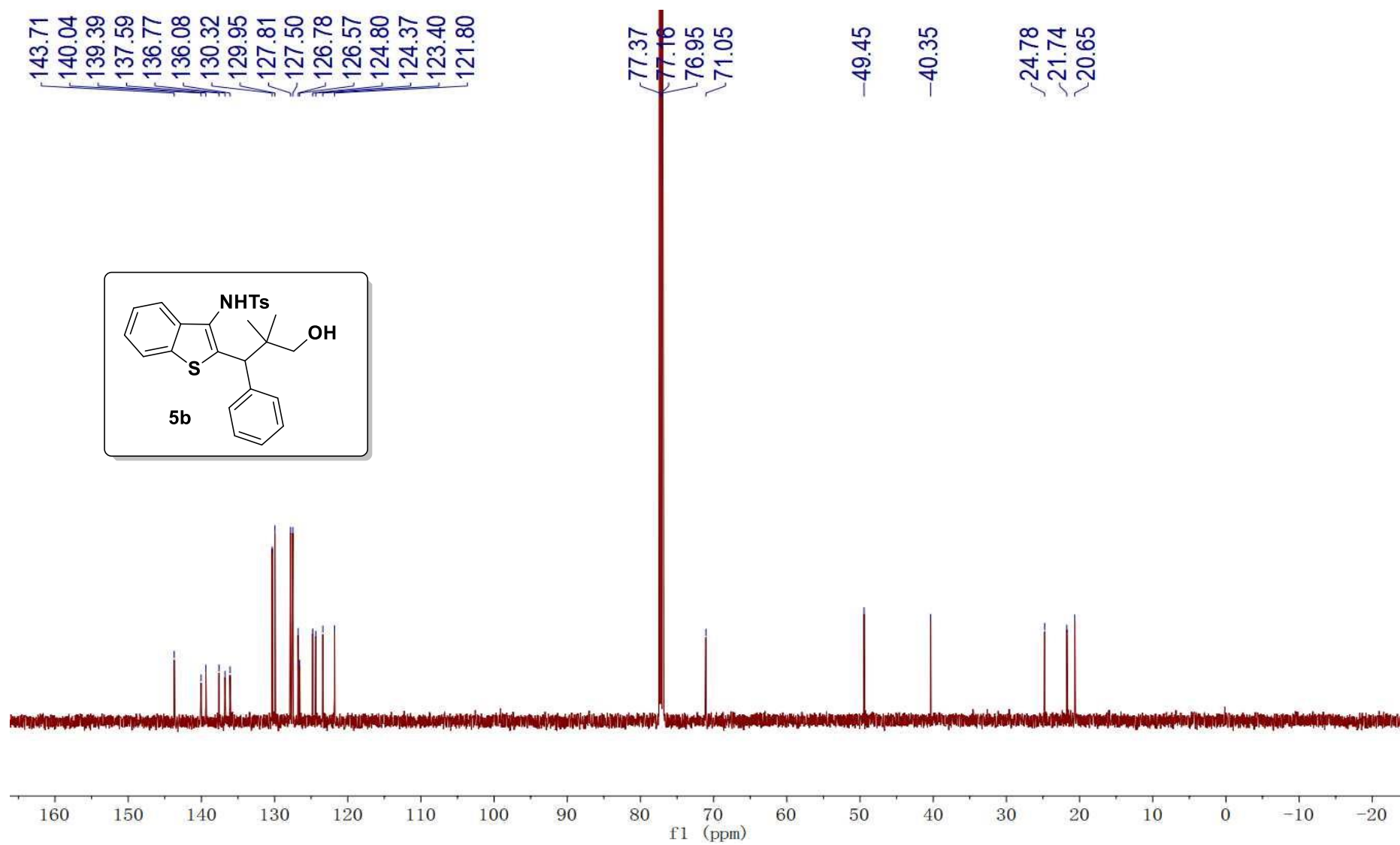


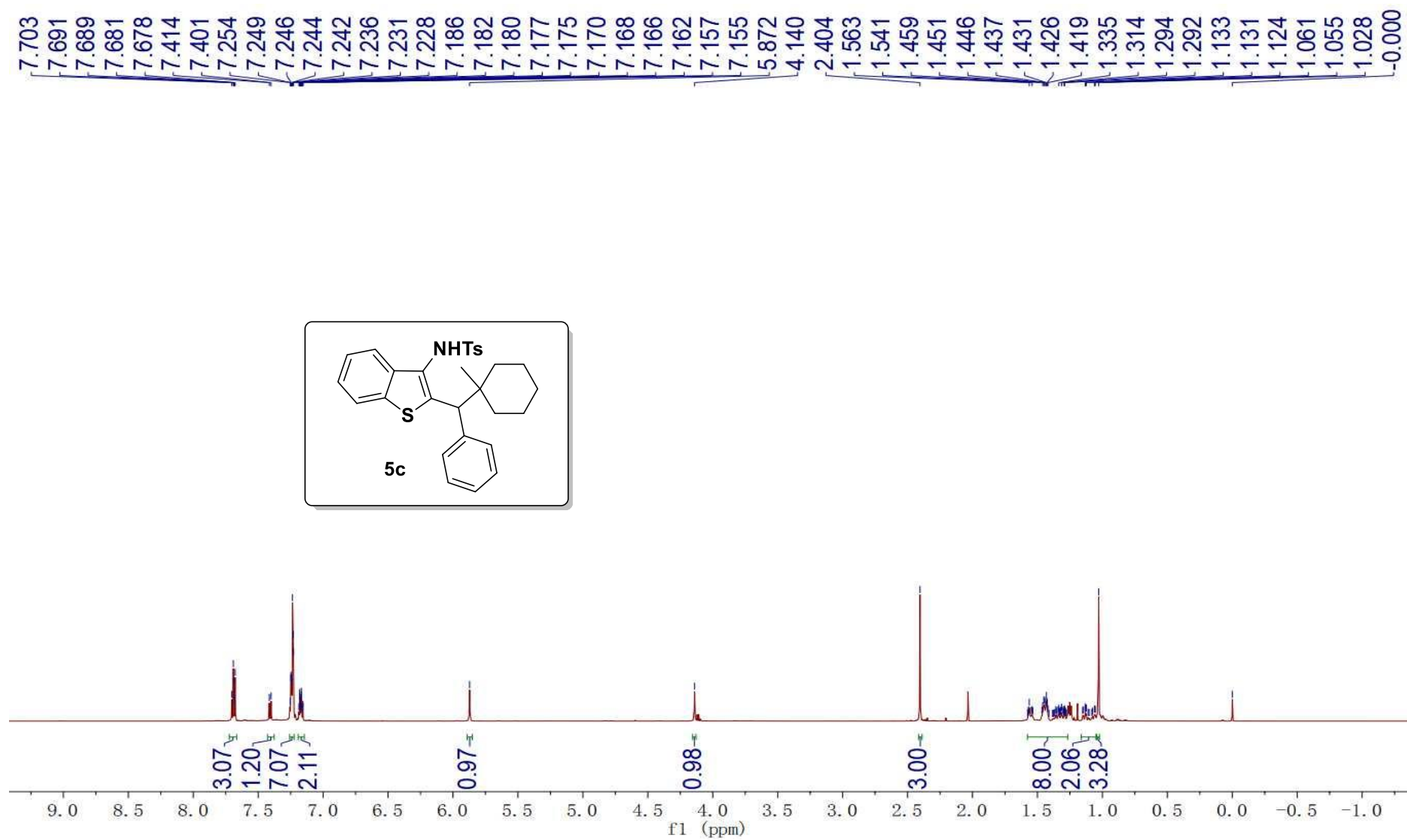


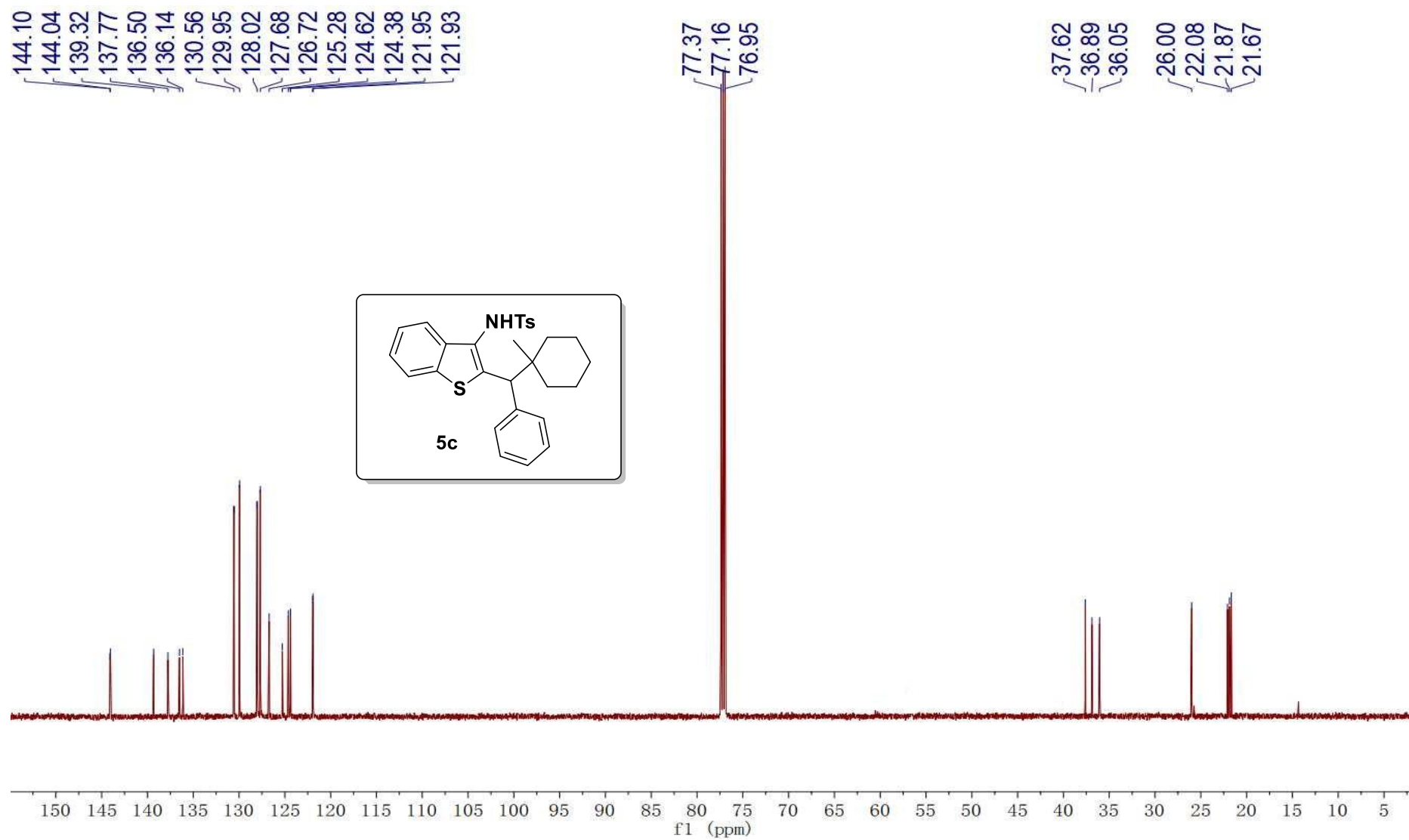


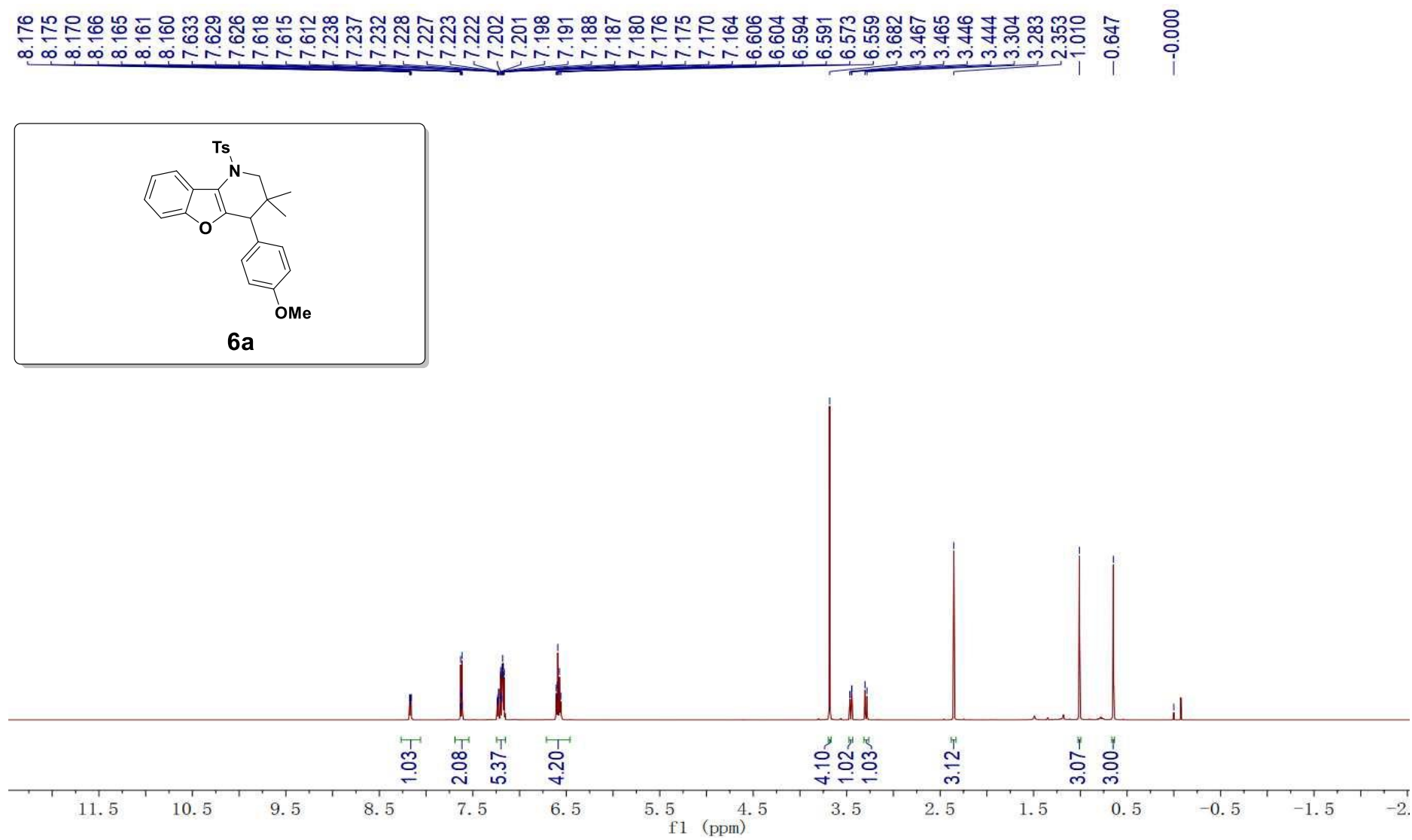


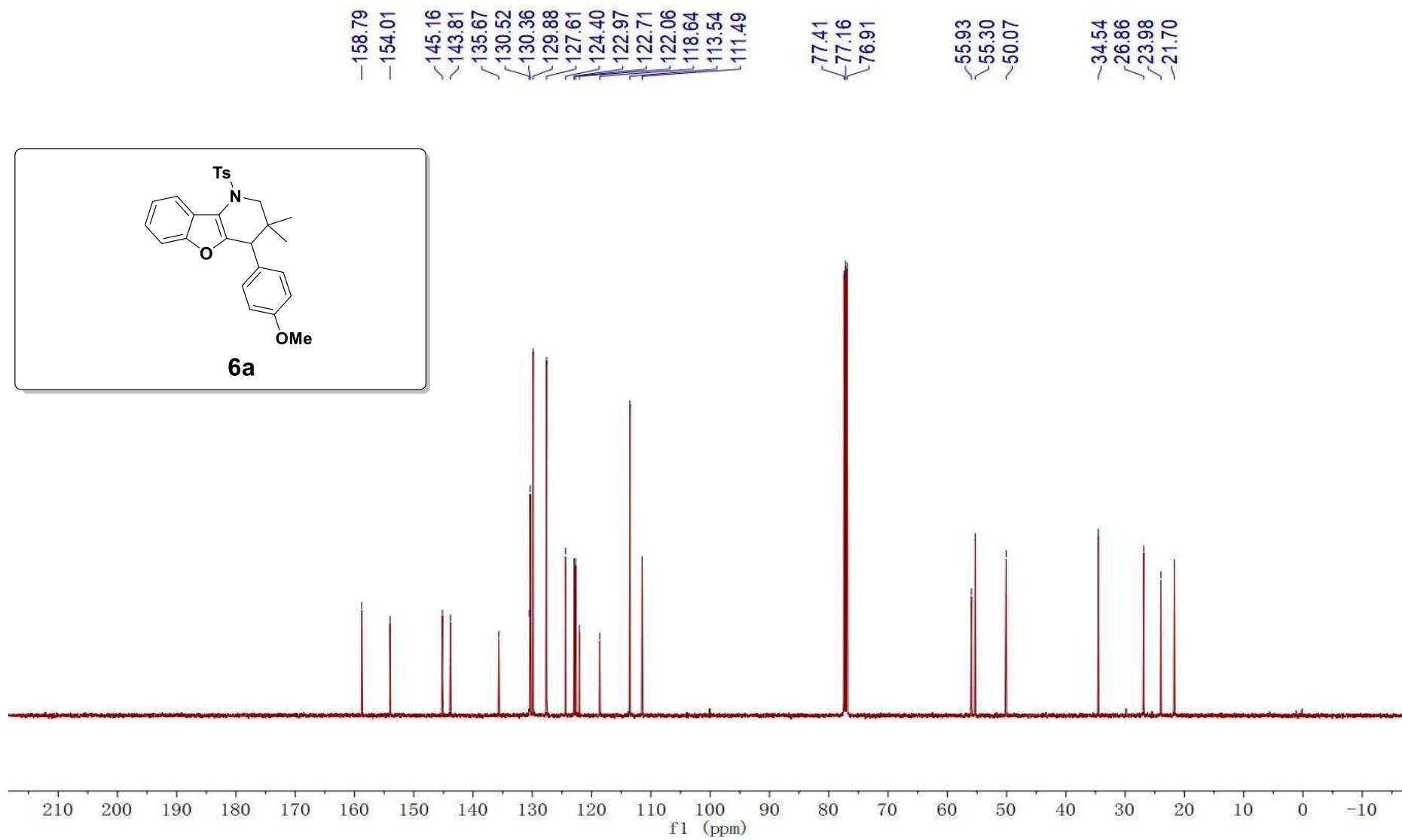


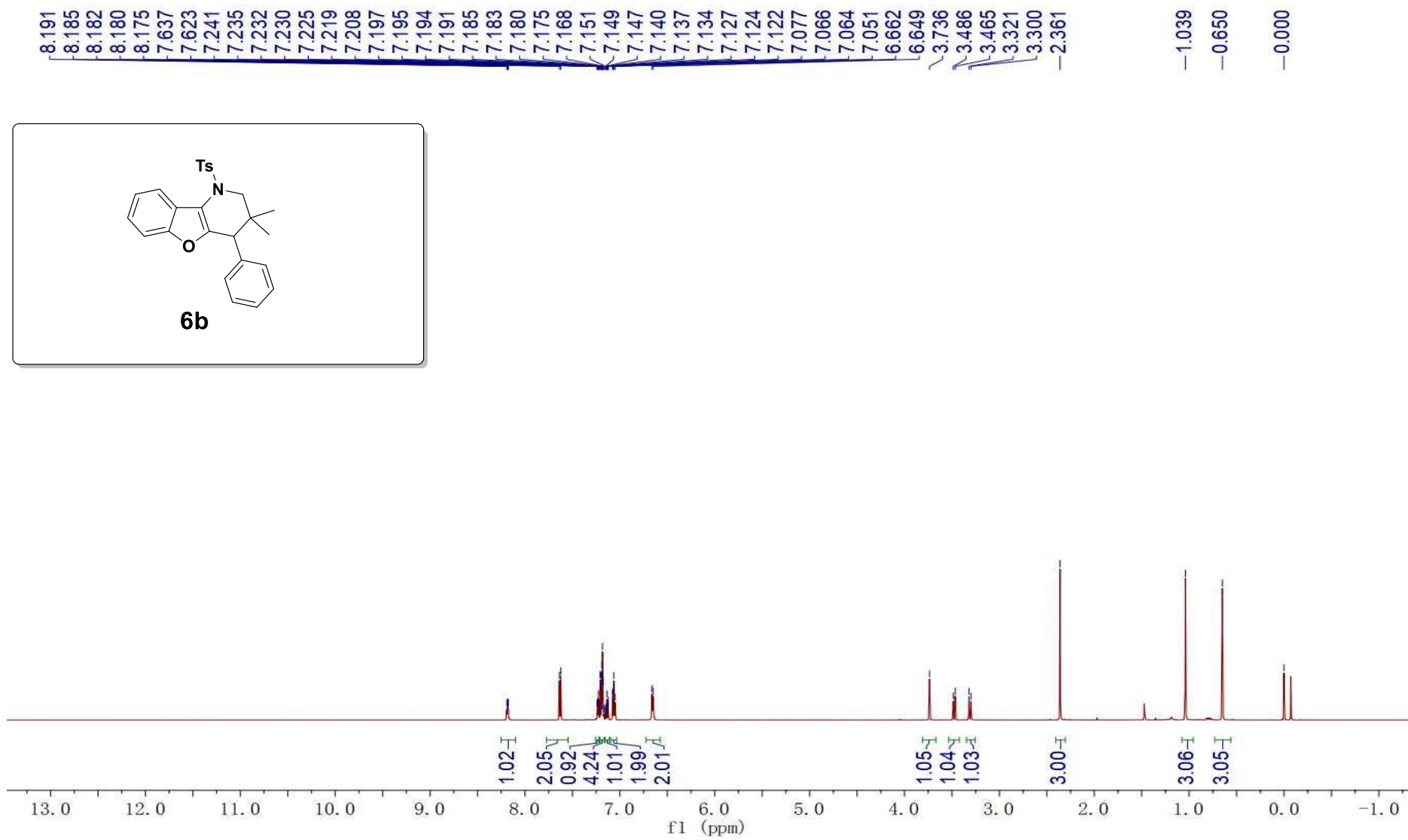


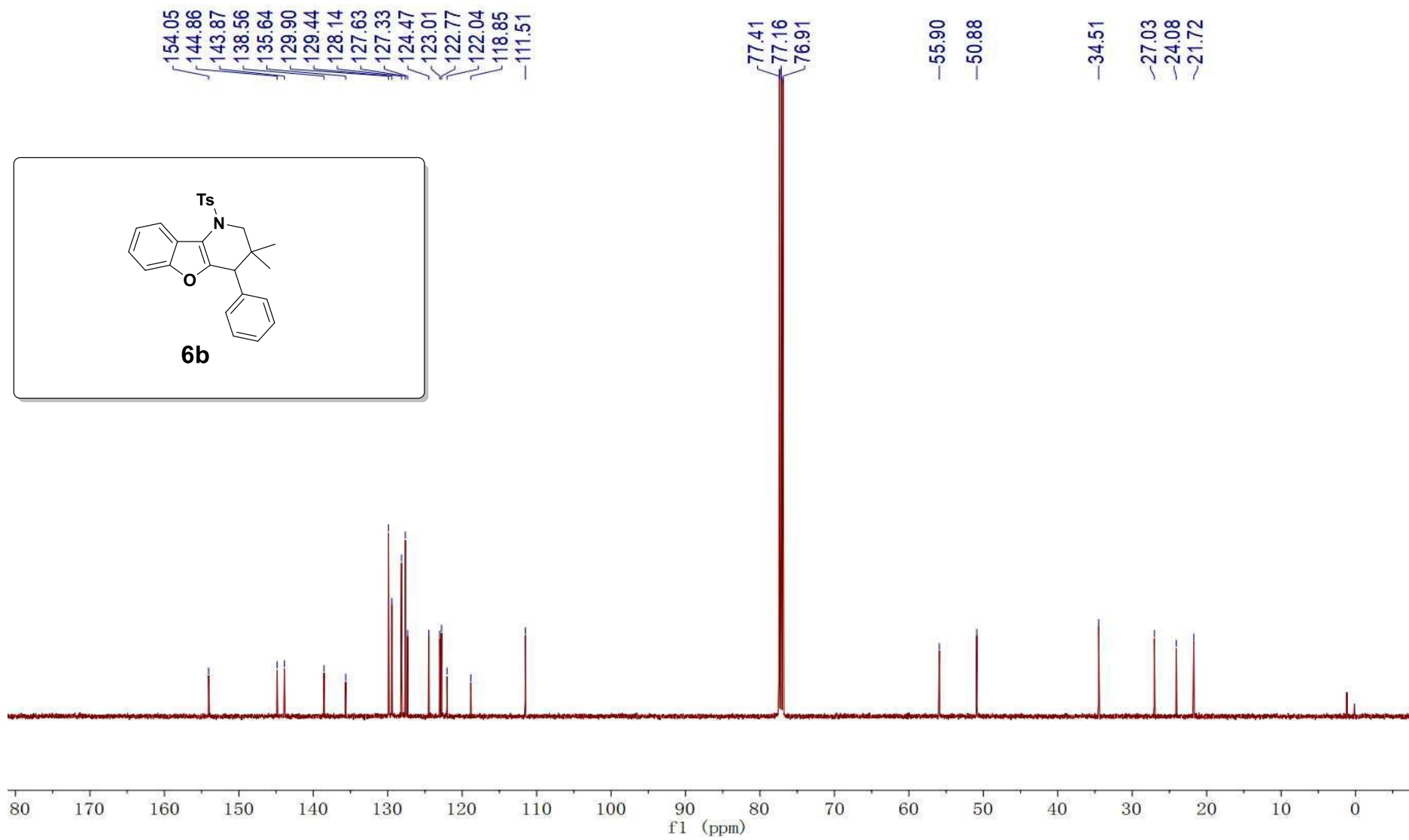












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