

Supporting Information for

**Coupling of Carboxylic Acids with Ynamides and Subsequent
Rearrangement for the Synthesis of Imides/Amides**

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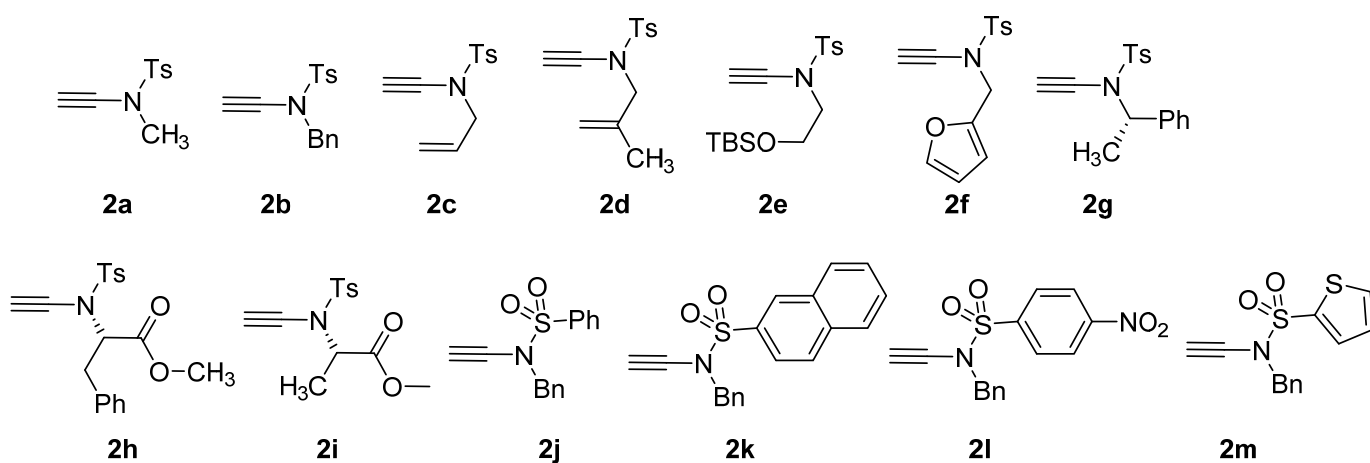
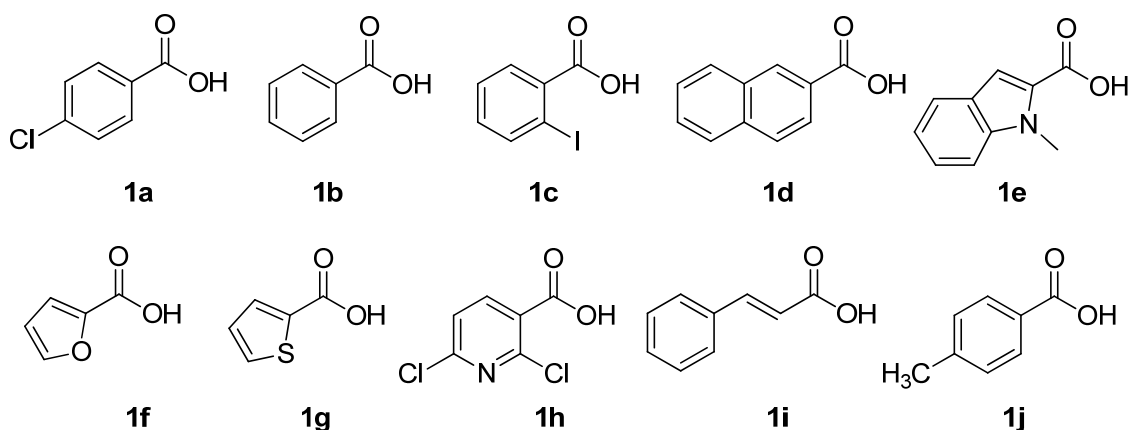
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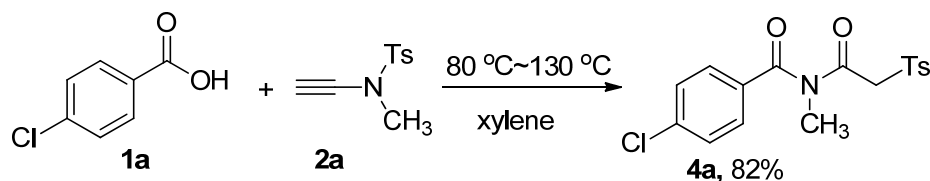
1. General Information

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

Ethyl acetate (EA), acetonitrile, toluene, petroleum ether (PE) carboxylic acid (**1a-1e**, **1g-1j**) were commercial available, **1f**¹ and ynamides (**2a-2u**)^{2,3} were prepared according to the reported literature.

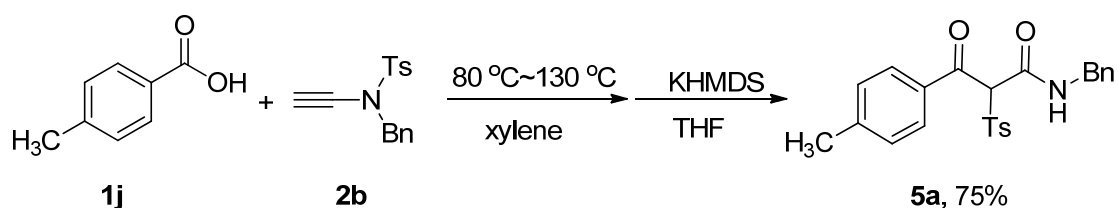


2. Typical Procedure for the Synthesis of 4a



A schlenk tube was added *p*-toluic acid **1a** (31.3 mg, 0.2 mmol), ynamide **2a** (41.8 mg, 0.2 mmol), and exchanged with argon for three tiems, xylene (2 mL) was followed as solvent. The solution was stirred under 80 °C until the starting materials was fully converted to intermediate product, then the temperature was raised to 130 °C and kept for 8 hours. After the reaction, the solution was concentrated and residue was subject to flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **4a** as a white solid (60 mg, 82% yield).

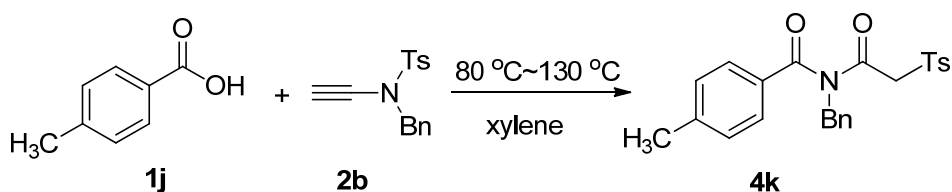
3. Typical Procedure for the Synthesis of 5a



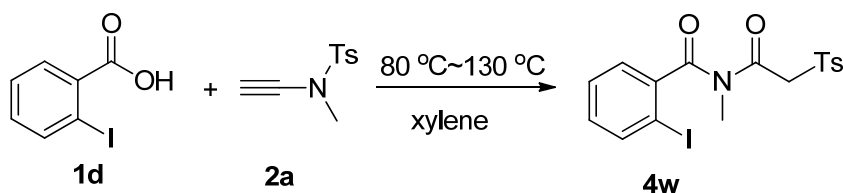
A schlenk tube was added *p*-toluic acid **1c** (27.2 mg, 0.2 mmol), ynamide **2b** (57 mg, 0.2 mmol), and exchanged with argon for three times, xylene (2 mL) was followed as solvent. The solution was stirred under 80 °C until the starting materials was fully converted to intermediate product, then the temperature was raised to 130 °C for about 8 hours. As a one-pot reaction, THF (2 mL) was added to enhance the solubility while KHMDS (1M in THF, 0.3 mL, 0.3 mmol) was slowly added at room temperature. After one hour, saturated ammonium chloride solution (1 mL) was added to quench the reaction. aqueous phase was extracted by EA, The combined organic layer was washed with water, brine and then dried over MgSO₄, The solution was concentrated and residue was recrystallized from ethyl acetate/petroleum ether (v/v, 1:2) to give **5a** as a white solid (63 mg, 75% yield).

It seemed that the product **5** was easily adhered on silica gel, so the purification was conducted using the method of recrystallization.

4. Procedure of the Gram-scale Reaction

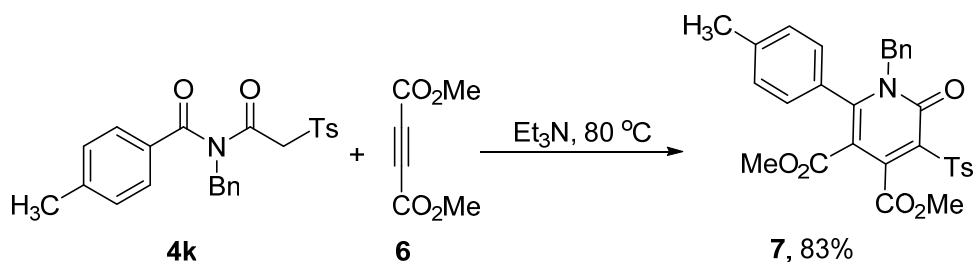


A three neck bottle was added *p*-toluic acid **1c** (0.544 g, 4.0 mmol), ynamide **2b** (1.14 g, 4.0 mmol), and exchanged with argon for three tiems, xylene (30 mL) was followed as solvent. The solution was stirred under 80 °C until the starting materials was fully converted to intermediate product, then the temperature was raised to 130 °C and kept for 8 hours. After the reaction, sodium bicarbonate aqueous solution (10%, 10 mL) was added, organic layer was washed with water, brine and then dried over MgSO₄, The solution was concentrated and residue was recrystallized from ethyl acetate/petroleum ether (v/v, 1:10) to give **4k** as light yellow solid (1.52 g, 90% yield).

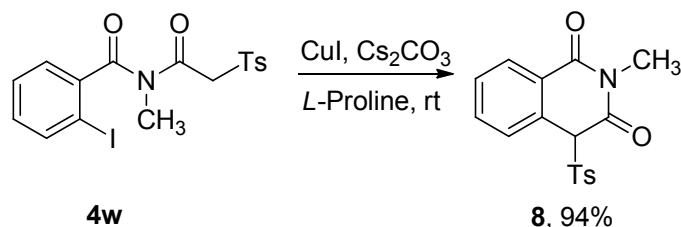


A three neck bottle was added 2-iodobenzoic acid **1d** (0.744 g, 3 mmol), ynamide **2a** (0.627 g, 3 mmol), and exchanged with argon for three tiems, xylene (30 mL) was followed as solvent. The solution was stirred under 80 °C until the starting materials was fully converted to intermediate product, then the temperature was raised to 130 °C and kept for 8 hours. After the reaction, sodium bicarbonate aqueous solution (10%, 10 mL) was added, organic layer was washed with water, brine and then dried over MgSO₄, The solution was concentrated and residue was recrystallized from ethyl acetate/petroleum ether (v/v, 1:10) to give **4w** as light yellow solid (1.19 g, 87% yield).

5. Procedure for the Synthesis of 7 and 8 ⁴

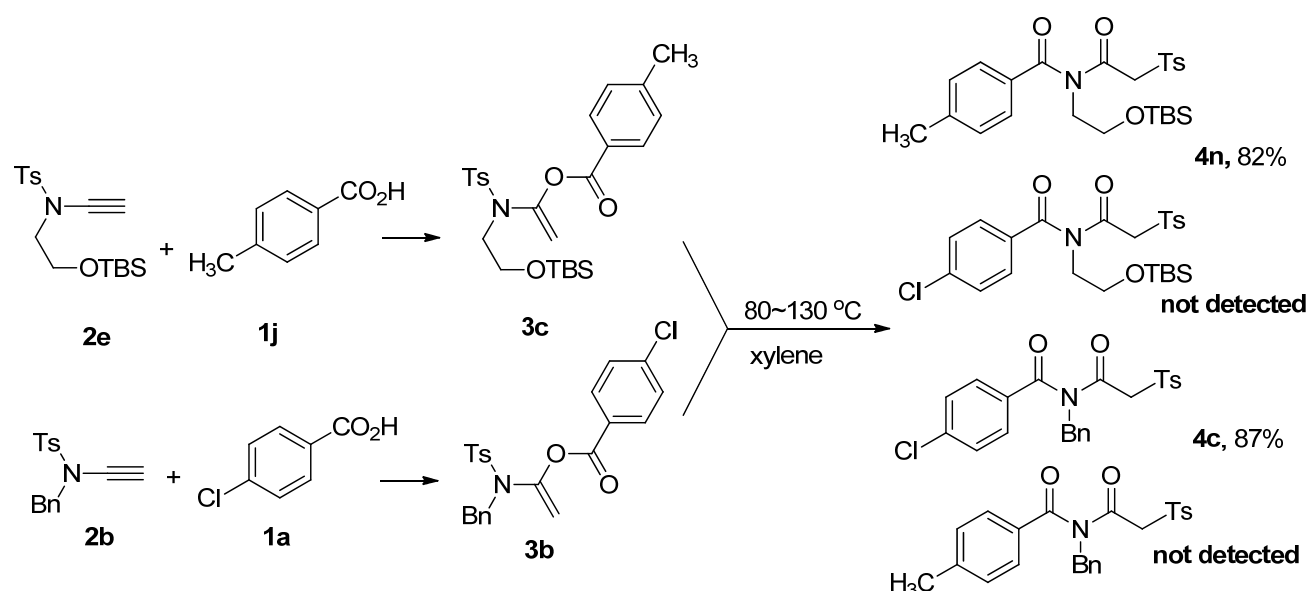


A schlenk tube was added **4k** (42 mg, 0.1 mmol), dimethyl acetylenedicarboxylate (DMAD, 21 mg, 0.15 mmol), and exchanged with argon for three times, toluene (2 mL) and Et₃N (20 mg, 0.2 mmol) were followed. The solution was stirred under 80 °C about 4 hours. After the reaction, the solution was concentrated and residue was subject to flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **7** as white solid (45 mg, 83% yield).

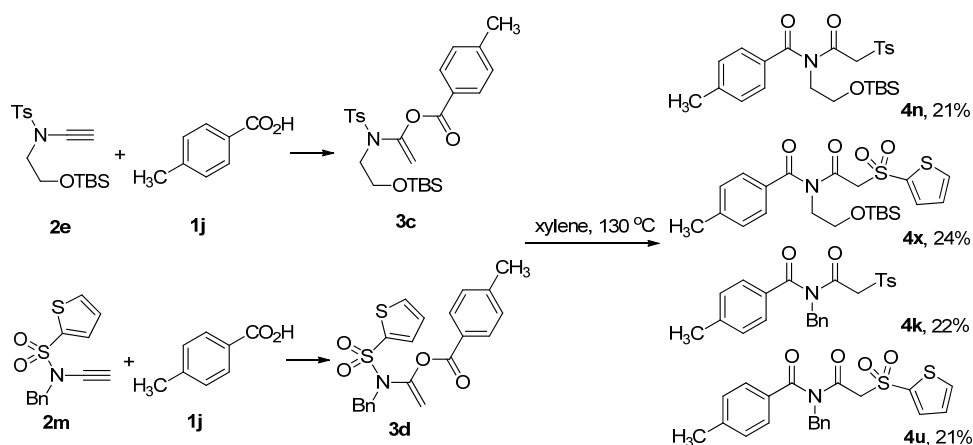


A schlenk tube was added **4w** (45.7 mg, 0.1 mmol), CuI (4 mg, 20% mmol), *L*-proline (2.4 mg, 20% mmol), Cs₂CO₃ (49 mg, 0.15 mmol), exchanged with argon for three times, and DMSO (2 mL) was added by follow. The solution was stirred at room temperature over night. After the reaction, water was added, aqueous phase was extracted by EA, combined organic layer was washed with water, brine and then dried over MgSO₄, The solution was concentrated and residue was subjected to flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:4) as eluent to give **8** as white solid (31 mg, 94% yield).

6. Procedure for the Crossover Reaction

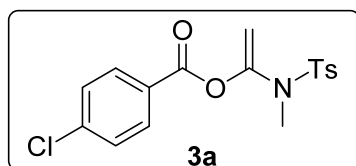


A schlenk tube was added *p*-toluic acid **1j** (13.6 mg, 0.1 mmol), ynamide **2e** (35.3 mg, 0.1 mmol), and exchanged with argon for three times, CH₂Cl₂ (1 mL) was followed as solvent. When the reaction was completed, the solution was concentrated and residue (**3c**) was directly used in next step. Another schlenk tube contained **1a** (15.6 mg, 0.1 mmol) and **2b** (28.5 mg, 0.1 mmol) was conducted similarly to attain **3b**. **3b** and **3c** were added to xylene (1 mL) and kept at 130 °C for 8 hours. Then the solution was concentrated and residue was subject to flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **4n** (40 mg, 82% yield) and **4c** (38 mg, 87% yield) as white solids.



A schlenk tube was added *p*-toluic acid **1j** (13.6 mg, 0.1 mmol), ynamide **2e** (35.3 mg, 0.1 mmol), and exchanged with argon for three times, CH₂Cl₂ (1 mL) was followed as solvent. After the reaction, the solution was concentrated and residue (**3c**) was directly used in next step. Another schlenk tube contained **1j** (13.6 mg, 0.1 mmol) and **2m** (27.7 mg, 0.1 mmol) was conducted similarly to attain **3d**. **3c** and **3d** were combined to stir under 130 °C for about 8 hours using xylene (1 mL) as solvent. Then the solution was concentrated and residue was subject to flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **4n** (18.9 mg, 21% yield), **4x** (21.7 mg, 24% yield), **4k** (19.9 mg, 22% yield), **4u** (19.0 mg, 21% yield) as white solids.

7. Characterization of 3, 4, 5, 7 and 8



1-((N,4-Dimethylphenyl)sulfonamido)vinyl 4-chlorobenzoate (3a)

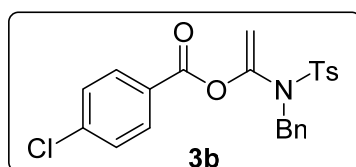
White solid, m. p. 80-82 °C, R_f = 0.2 (EtOAc/Petroleum ether 1:10).

^1H NMR (CDCl_3 , 400MHz) δ 7.83 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.02 (d, J = 2.4 Hz, 1H), 4.82 (d, J = 2.4 Hz, 1H), 3.10 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 163.3, 147.1, 144.2, 140.4, 134.1, 131.6, 129.7, 129.0, 128.1, 127.2, 101.7, 37.5, 21.7.

IR (KBr) ν 2946, 1691, 1600, 1422, 1321, 1210, 1070, 810, 640 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_4\text{S}$ (M^+): 365.0489; Found: 365.0489.



1-((N-Benzyl-4-methylphenyl)sulfonamido)vinyl 4-chlorobenzoate (3b)

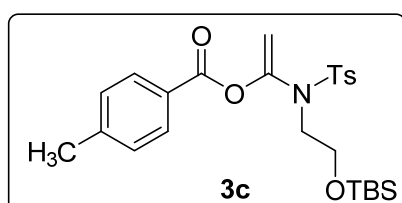
White solid, m. p. 84-86 °C, R_f = 0.2 (EtOAc/Petroleum ether 1:10).

^1H NMR (CDCl_3 , 400MHz) δ 7.76 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.36-7.22 (m, 9H), 5.09 (d, J = 1.6 Hz, 1H), 4.86 (d, J = 1.6 Hz, 1H), 4.61 (s, 2H), 2.37 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 162.6, 150.9, 144.1, 143.6, 140.3, 136.3, 135.6, 131.4, 129.7, 128.9, 128.6, 128.1, 127.8, 127.2, 105.6, 53.1, 21.6.

IR (KBr) ν 2945, 1690, 1600, 1423, 1320, 1214, 1070, 808, 636 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}_4\text{S}$ (M^+): 441.0802; Found: 441.0802.



1-((N-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-4-methylphenyl)sulfonamido)vinyl

4-methylbenzoate (3c)

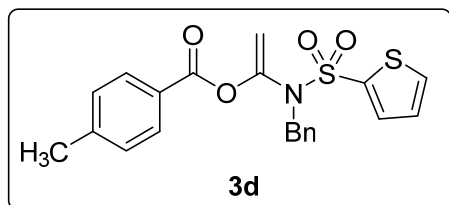
White solid, m. p. 77-79 °C, $R_f = 0.2$ (EtOAc/Petroleum ether 1:10).

^1H NMR (CDCl_3 , 400MHz) δ 7.76 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 5.18 (d, $J = 2.0$ Hz, 1H), 5.14 (d, $J = 2.0$ Hz, 1H), 3.85 (t, $J = 6.4$ Hz, 2H), 3.51 (t, $J = 6.4$ Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H), 0.87 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (CDCl_3 , 100MHz) δ 163.7, 144.7, 144.3, 143.8, 136.3, 130.2, 129.6, 129.2, 127.9, 126.0, 104.9, 61.2, 50.5, 26.0, 21.8, 21.6, 18.4, -5.3.

IR (KBr) ν 2945, 1690, 1602, 1433, 1321, 1220, 1060, 826, 633 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{25}\text{H}_{35}\text{NO}_5\text{SSi}$ (M^+): 489.2005; Found: 489.2003.



1-(N-Benzylthiophene-2-sulfonamido)vinyl 4-methylbenzoate (3d)

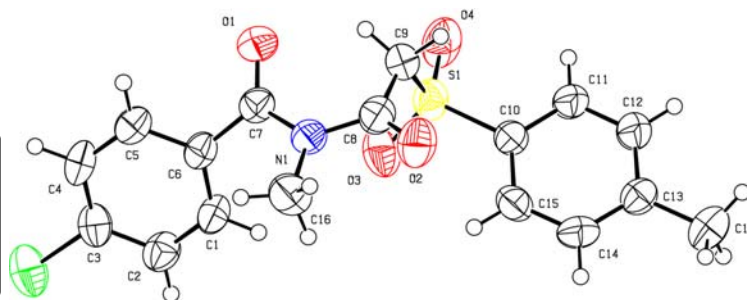
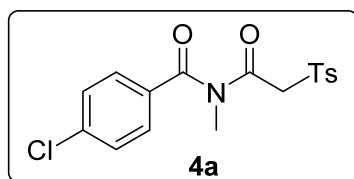
White solid, m. p. 72-74 °C, $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl_3 , 400MHz) δ 7.69 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 3.2$ Hz, 1H), 7.57 (d, $J = 4.8$ Hz, 1H), 7.38-7.25 (m, 5H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.03 (t, $J = 4.4$ Hz, 1H), 5.14 (d, $J = 1.6$ Hz, 1H), 4.93 (d, $J = 2.0$ Hz, 1H), 4.64 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 163.5, 144.9, 143.2, 139.7, 135.4, 133.4, 132.6, 130.2, 129.4, 129.0, 128.6, 128.2, 127.4, 125.9, 106.1, 52.8, 21.9.

IR (KBr) ν 2945, 1690, 1600, 1432, 1321, 1230, 1060, 811, 636 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_4\text{S}_2$ (M^+): 413.0755; Found: 413.0750.



4-Chloro-*N*-methyl-*N*-(2-tosylacetyl)benzamide (4a)

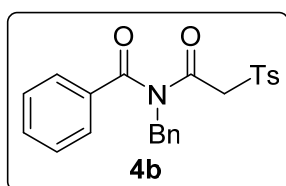
White solid, m. p. 89-91 °C (60 mg, 82% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl₃, 400MHz) δ 7.89 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 7.6$ Hz, 2H), 7.48 (d, $J = 8.8$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.76 (s, 2H), 3.18 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 173.6, 164.5, 145.6, 139.5, 136.3, 132.1, 130.6, 130.1, 129.3, 128.5, 61.8, 35.6, 21.9.

IR (KBr) ν 2945, 1700, 1601, 1432, 1321, 1220, 1060, 808, 636 cm⁻¹.

HRMS (EI) calcd for C₁₇H₁₆ClNO₄S (M⁺): 365.0489; Found: 356.0488.



N-Benzyl-*N*-(2-tosylacetyl)benzamide (4b)

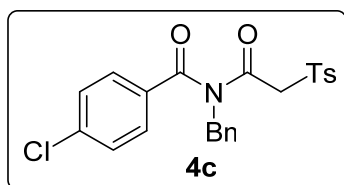
White solid, m. p. 85-87 °C (70 mg, 86% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl₃, 400MHz) δ 7.74 (d, $J = 8.0$ Hz, 2H), 7.61-7.55 (m, 3H), 7.44 (t, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.26-7.22 (m, 3H), 7.09-7.07 (m, 2H), 4.94 (s, 2H), 4.59 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 174.7, 164.7, 145.4, 136.3, 136.2, 134.4, 133.0, 130.0, 129.0, 128.9, 128.7, 128.5, 127.9, 127.8, 62.4, 50.6, 21.8.

IR (KBr) ν 2955, 1716, 1600, 1560, 1339, 1201, 1038, 861, 546 cm⁻¹.

HRMS (EI) calcd for C₂₃H₂₁NO₄S (M⁺): 407.1191; Found: 407.1190.



N-Benzyl-4-chloro-*N*-(2-tosylacetyl)benzamide (4c)

White solid, m. p. 94-96 °C (74 mg, 84% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

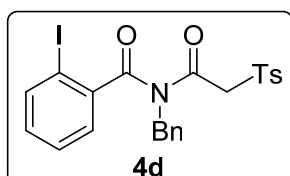
^1H NMR (CDCl₃, 400MHz) δ 7.75 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.26-7.23 (m, 3H), 7.07-7.05 (m, 2H), 4.93 (s, 2H), 4.63 (s, 2H),

2.44 (s, 3H).

¹³C NMR (CDCl₃, 100MHz) δ 173.9, 164.4, 145.5, 139.4, 136.1, 136.0, 132.6, 130.4, 130.0, 129.2, 128.8, 128.4, 127.9, 127.7, 62.2, 50.5, 21.8.

IR (KBr) ν 2956, 1710, 1600, 1554, 1347, 1214, 1046, 825, 631, 547 cm⁻¹.

HRMS (EI) calcd for C₂₃H₂₀ClNO₄S (M⁺): 441.0802; Found: 441.0805.



***N*-Benzyl-2-iodo-*N*-(2-tosylacetyl)benzamide (4d)**

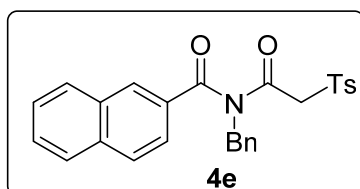
White solid, m. p. 85-87 °C (93 mg, 87% yield), R_f = 0.2 (EtOAc/Petroleum ether 1:5).

¹H NMR (CDCl₃, 400MHz) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 8.4 Hz, 2H), 7.46-7.27 (m, 6H), 7.20-7.16 (m, 2H), 7.00-6.98 (m, 2H), 4.92 (s, 2H), 4.83 (s, 2H), 2.49 (s, 3H).

¹³C NMR (CDCl₃, 100MHz) δ 173.3, 165.1, 145.3, 140.1, 139.7, 136.5, 135.9, 131.9, 129.9, 128.9, 128.73, 128.65, 128.3, 127.8, 127.7, 92.4, 62.9, 49.7, 21.8.

IR (KBr) ν 2956, 1713, 1600, 1559, 1346, 1211, 1039, 841, 632, 541 cm⁻¹.

HRMS (EI) calcd for C₂₃H₂₀INO₄S (M⁺): 533.0158; Found: 533.0156.



***N*-Benzyl-*N*-(2-tosylacetyl)-1-naphthamide (4e)**

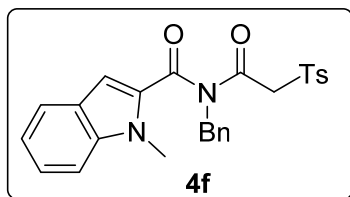
White solid, m. p. 90-92 °C (50 mg, 55% yield), R_f = 0.2 (EtOAc/Petroleum ether 1:5).

¹H NMR (CDCl₃, 400MHz) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.90 (t, *J* = 9.2 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.56-7.50 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.16-7.12 (m, 3H), 6.96-6.94 (m, 2H), 4.88 (s, 2H), 4.79 (s, 2H), 2.45 (s, 3H).

¹³C NMR (CDCl₃, 100MHz) δ 174.0, 165.0, 145.4, 136.4, 133.7, 132.3, 132.2, 129.98, 129.93, 128.7, 128.6, 128.5, 128.1, 128.0, 127.7, 127.0, 126.8, 124.7, 124.5, 123.1, 63.1, 50.3, 21.8.

IR (KBr) ν 2956, 1710, 1599, 1559, 1346, 1221, 1039, 841, 632, 551 cm⁻¹.

HRMS (EI) calcd for C₂₇H₂₃NO₄S (M⁺): 457.1348; Found: 457.1350.



***N*-Benzyl-1-methyl-*N*-(2-tosylacetyl)-1*H*-indole-2-carboxamide (4f)**

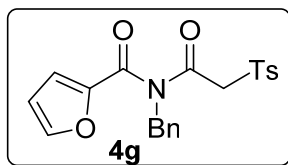
White solid, m. p. 102-104 °C (69 mg, 75% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl₃, 400MHz) δ 7.68 (d, $J = 8.0$ Hz, 2H), 7.83 (d, $J = 8.4$ Hz, 1H), 7.42-7.16 (m, 10H), 6.87 (s, 1H), 5.07 (s, 2H), 4.45 (s, 2H), 3.82 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 166.6, 164.4, 145.5, 140.3, 136.4, 135.7, 131.7, 130.0, 128.7, 128.6, 127.9, 126.4, 125.8, 123.1, 121.4, 110.8, 110.6, 63.1, 50.9, 31.4, 21.8.

IR (KBr) ν 2951, 1710, 1599, 1555, 1347, 1219, 1036, 829, 629 cm⁻¹.

HRMS (EI) calcd for C₂₆H₂₄N₂O₄S (M⁺): 460.1457; Found: 460.1457.



***N*-Benzyl-*N*-(2-tosylacetyl)furan-2-carboxamide (4g)**

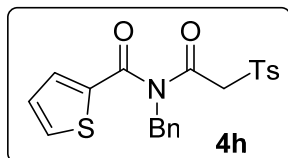
White solid, m. p. 75-78 °C (61 mg, 77% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl₃, 400MHz) δ 7.73 (d, $J = 8.0$ Hz, 2H), 7.60 (s, 1H), 7.36-7.27 (m, 3H), 7.25-7.18 (m, 5H), 6.56-6.55 (m, 1H), 5.09 (s, 2H), 4.57 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 164.5, 162.4, 146.9, 145.3, 136.3, 136.0, 129.9, 128.9, 128.7, 128.0, 127.7, 127.6, 121.3, 113.1, 62.3, 49.5, 21.8.

IR (KBr) ν 2952, 1695, 1599, 1425, 1308, 1069, 862, 579 cm⁻¹.

HRMS (EI) calcd for C₂₁H₁₉NO₅S (M⁺): 397.0984; Found: 397.0983.



***N*-Benzyl-*N*-(2-tosylacetyl)thiophene-2-carboxamide (4h)**

White solid, m. p. 74-77 °C (69 mg, 83% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

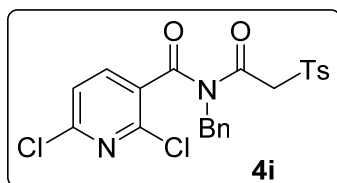
^1H NMR (CDCl₃, 400MHz) δ 7.75 (d, $J = 8.4$ Hz, 2H), 7.69 (d, $J = 4.8$ Hz, 1H), 7.53 (d, $J =$

3.6 Hz, 1H), 7.33-7.25 (m, 5H), 7.18 (d, $J = 6.8$ Hz, 2H), 7.09 (d, $J = 4.4$ Hz, 1H), 5.07 (s, 2H), 4.58 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 167.6, 164.3, 145.4, 137.3, 136.1, 136.1, 134.7, 133.8, 130.0, 128.8, 128.6, 128.2, 127.8, 127.6, 62.3, 51.0, 21.8.

IR (KBr) ν 2950, 1696, 1595, 1509, 1308, 1147, 1077, 892, 767, 576 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_4\text{S}_2$ (M^+): 413.0755; Found: 413.0756.



***N*-Benzyl-2,6-dichloro-*N*-(2-tosylacetyl)nicotinamide (4i)**

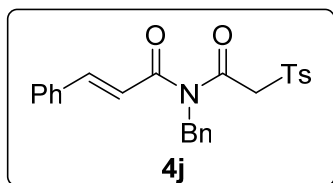
White solid, m. p. 100-102 °C 65 mg, 68% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:3).

^1H NMR (CDCl_3 , 400MHz) δ 7.78 (d, $J = 8.0$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.28-7.20 (m, 4H), 7.01-7.00 (m, 2H), 4.93 (s, 2H), 4.81 (s, 2H), 2.46 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 169.2, 164.4, 152.0, 146.4, 145.8, 139.5, 136.2, 135.5, 130.3, 130.1, 129.1, 128.5, 128.2, 127.2, 123.0, 62.8, 49.0, 21.9.

IR (KBr) ν 2951, 1702, 1599, 1565, 1341, 1210, 1036, 828, 557 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_4\text{S}$ (M^+): 476.0364; Found: 476.0364.



***N*-Benzyl-*N*-(2-tosylacetyl)cinnamamide (4j)**

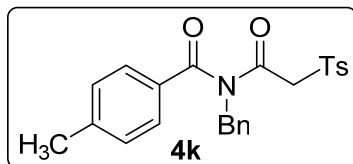
White solid, m. p. 88-91 °C (59 mg, 68% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl_3 , 400MHz) δ 7.79 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 15.2$ Hz, 1H), 7.43-7.29 (m, 10H), 7.24 (d, $J = 7.6$ Hz, 2H), 6.79 (d, $J = 15.2$ Hz, 1H), 5.06 (s, 2H), 4.88 (s, 2H), 2.38 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 169.6, 164.9, 147.5, 145.2, 136.4, 136.3, 134.1, 131.1, 129.8, 129.0, 128.74, 128.65, 128.5, 127.8, 126.7, 118.4, 62.7, 48.0, 21.7.

IR (KBr) ν 2954, 1715, 1600, 1561, 1328, 1210, 1037, 851 547 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_4\text{S}$ (M^+): 433.1348; Found: 433.1349.



***N*-Benzyl-4-methyl-*N*-(2-tosylacetyl)benzamide (4k)**

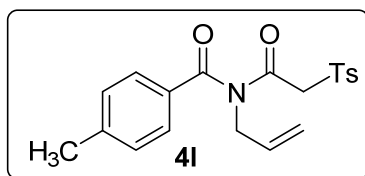
White solid, m. p. 84-86 °C (75 mg, 89% yield), R_f = 0.2 (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl₃, 400MHz) δ 7.73 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.26-7.23 (m, 5H), 7.11 (d, J = 7.2 Hz, 2H), 4.94 (s, 2H), 4.53 (s, 2H), 2.44 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 174.6, 164.6, 145.4, 144.2, 136.4, 136.1, 131.5, 130.0, 129.8, 129.3, 128.7, 128.6, 128.0, 127.8, 62.6, 50.6, 21.8.

IR (KBr) ν 2945, 1690, 1604, 1432, 1321, 1220, 1060, 808, 636 cm⁻¹.

HRMS (EI) calcd for C₂₄H₂₃NO₄S (M⁺): 421.1348; Found: 421.1346.



***N*-Allyl-4-methyl-*N*-(2-tosylacetyl)benzamide (4l)**

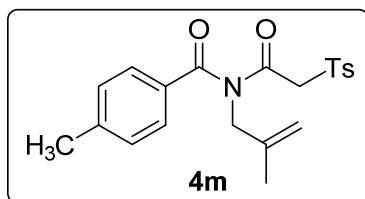
White solid, m. p. 90-92 °C (56 mg, 75% yield), R_f = 0.3 (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl₃, 400MHz) δ 7.80 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.81-5.72 (m, 1H), 5.15-5.02 (m, 2H), 4.62 (s, 2H), 4.29 (d, J = 5.6 Hz, 2H), 2.45 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 174.7, 164.6, 145.4, 144.1, 136.3, 132.0, 131.1, 130.0, 129.6, 129.2, 128.6, 118.3, 62.3, 49.7, 21.8.

IR (KBr) ν 2951, 1715, 1675, 1604, 1348, 1208, 1139, 822, 626, 545 cm⁻¹.

HRMS (EI) calcd for C₂₀H₂₁NO₄S (M⁺): 371.1191; Found: 371.1195.



4-Methyl-*N*-(2-methylallyl)-*N*-(2-tosylacetyl)benzamide (4m)

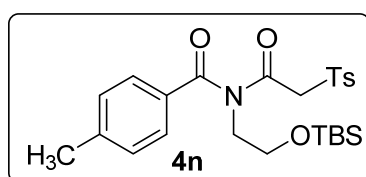
White solid, m. p. 87-89 °C (69 mg, 90% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl_3 , 400MHz) δ 7.80 (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 4.82 (s, 1H), 4.69 (s, 1H), 4.66 (s, 2H), 4.26 (s, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 1.59 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 174.8, 164.5, 145.3, 143.9, 139.8, 136.3, 131.1, 129.9, 129.5, 129.0, 128.5, 112.3, 62.1, 52.2, 21.8, 20.4.

IR (KBr) ν 2949, 1718, 1695, 1606, 1326, 1142, 836, 629, 545 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4\text{S}$ (M^+): 385.1348; Found: 385.1348.



***N*-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-4-methyl-*N*-(2-tosylacetyl)benzamide**

(4n)

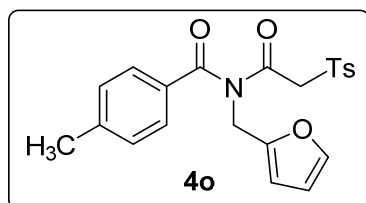
White solid, m. p. 75-77 °C (80 mg, 82% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl_3 , 400MHz) δ 7.79 (d, $J = 7.6$ Hz, 2H), 7.58 (d, $J = 7.2$ Hz, 2H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.26 (d, $J = 6.0$ Hz, 2H), 4.61 (s, 2H), 3.90 (t, $J = 4.8$ Hz, 2H), 3.70 (t, $J = 4.8$ Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 0.79 (s, 9H), -0.06 (s, 6H).

^{13}C NMR (CDCl_3 , 100MHz) δ 174.7, 164.7, 145.3, 143.8, 136.4, 131.3, 130.0, 129.7, 129.5, 128.5, 61.9, 61.3, 50.3, 25.9, 21.8, 18.4, -5.5.

IR (KBr) ν 2951, 1695, 1604, 1465, 1338, 1158, 1092, 831, 656 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{25}\text{H}_{35}\text{NO}_5\text{SSi}$ (M^+): 489.2005; Found: 489.2006.



***N*-(Furan-2-ylmethyl)-4-methyl-*N*-(2-tosylacetyl)benzamide (4o)**

White solid, m. p. 92-94 °C (63 mg, 77% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

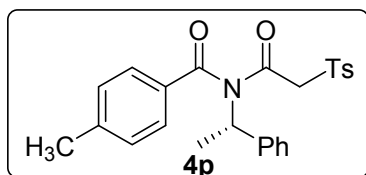
^1H NMR (CDCl_3 , 400MHz) δ 7.74 (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J =$

8.0 Hz, 2H), 7.29-7.26 (m, 3H), 6.27-6.26 (m, 1H), 6.18 (d, $J=2.8$ Hz, 1H), 4.90 (s, 2H), 4.57 (s, 2H), 2.44 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 174.2, 164.3, 149.6, 145.4, 144.2, 142.4, 136.1, 131.1, 130.0, 129.7, 129.3, 128.6, 110.6, 109.3, 62.2, 43.6, 21.8.

IR (KBr) ν 3031, 1685, 1645, 1599, 1330, 1194, 1059, 796, 626 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_5\text{S}$ (M^+): 411.1140; Found: 411.1140.



(S)-4-Methyl-N-(1-phenylethyl)-N-(2-tosylacetyl)benzamide (4p)

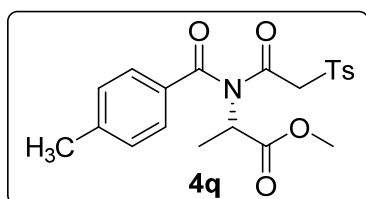
White solid, m. p. 95-97 °C (64 mg, 74% yield), $R_f = 0.3$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl_3 , 400MHz) δ 7.60 (t, $J = 8.8$ Hz, 4H), 7.35 (d, $J = 7.6$ Hz, 2H), 7.30-7.21 (m, 7H), 5.56 (q, $J = 6.8$ Hz, 1H), 4.28 (d, $J = 14.4$ Hz, 1H), 4.07 (d, $J = 14.0$ Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H), 1.77 (d, $J = 7.2$ Hz, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 174.6, 163.9, 145.3, 144.7, 140.0, 135.9, 132.6, 130.0, 129.9, 129.4, 128.6, 128.4, 127.6, 63.3, 57.3, 21.9, 17.5.

IR (KBr) ν 2955, 1695, 1655, 1600, 1324, 1253, 1153, 816, 526 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_4\text{S}$ (M^+): 435.1504; Found: 435.1504.



Methyl N-(4-methylbenzoyl)-N-(2-tosylacetyl)-L-alaninate (4q)

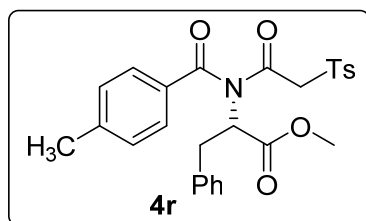
White solid, m. p. 90-93 °C (51 mg, 61% yield), $R_f = 0.3$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl_3 , 400MHz) δ 7.75 (d, $J = 8.0$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.34-7.29 (m, 4H), 4.68 (q, $J = 7.2$ Hz, 1H), 4.43 (d, $J = 14.0$ Hz, 1H), 4.27 (d, $J = 14.0$ Hz, 1H), 3.69 (s, 3H), 2.43 (s, 6H), 1.53 (d, $J = 6.8$ Hz, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 173.7, 170.4, 164.3, 145.5, 144.6, 136.0, 131.4, 130.0, 129.9, 129.2, 128.6, 62.6, 56.4, 52.7, 21.8, 14.7.

IR (KBr) ν 2953, 1712, 1682, 1599, 1345, 1156, 863, 684, 554 cm^{-1} .

HRMS (EI) calcd for C₂₁H₂₃NO₆S (M⁺): 417.1246; Found: 417.1245.



Methyl *N*-(4-methylbenzoyl)-*N*-(2-tosylacetyl)-*L*-phenylalaninate (4r)

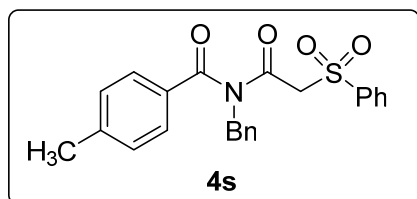
White solid, m. p. 80-82 °C (51 mg, 52% yield), R_f = 0.3 (EtOAc/Petroleum ether 1:5).

¹H NMR (CDCl₃, 400MHz) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.23-7.11 (m, 7H), 6.98 (d, *J* = 6.4 Hz, 2H), 4.86 (q, *J* = 6.4 Hz, 1H), 4.59 (d, *J* = 14.4 Hz, 1H), 4.22 (d, *J* = 14.4 Hz, 1H), 3.80 (s, 3H), 3.47-3.42 (m, 1H), 3.30-3.24 (m, 1H), 2.43 (s, 3H), 2.38 (s, 3H).

¹³C NMR (CDCl₃, 100MHz) δ 173.4, 169.4, 164.7, 145.3, 144.0, 137.0, 136.5, 129.9, 129.8, 129.6, 129.0, 128.8, 128.8, 127.7, 127.2, 62.5, 62.1, 52.9, 35.4, 21.8.

IR (KBr) ν 2956, 1715, 1685, 1600, 1339, 1213, 1086, 859, 747, 552 cm⁻¹.

HRMS (EI) calcd for C₂₇H₂₇NO₆S (M⁺): 493.1559; Found: 493.1559.



***N*-Benzyl-4-methyl-*N*-(2-(phenylsulfonyl)acetyl)benzamide (4s)**

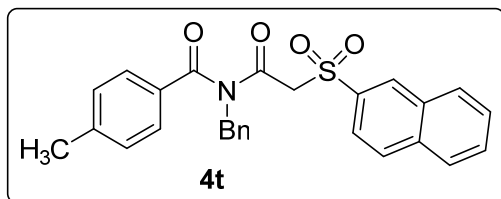
White solid, m. p. 93-95 °C (71 mg, 87% yield), R_f = 0.2 (EtOAc/Petroleum ether 1:5).

¹H NMR (CDCl₃, 400MHz) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.56-7.51 (m, 4H), 7.26-7.23 (m, 5H), 7.12-7.10 (m, 2H), 4.94 (s, 2H), 4.55 (s, 2H), 2.42 (s, 3H).

¹³C NMR (CDCl₃, 100MHz) δ 174.6, 164.5, 144.3, 139.1, 136.3, 134.3, 131.4, 129.8, 129.4, 129.3, 128.7, 128.6, 128.0, 127.8, 62.4, 50.7, 21.9.

IR (KBr) ν 2957, 1711, 1600, 1554, 1346, 1211, 1049, 829, 626, 543 cm⁻¹.

HRMS (EI) calcd for C₂₃H₂₁NO₄S (M⁺): 407.1191; Found: 407.1190.



***N*-Benzyl-4-methyl-*N*-(2-(naphthalen-2-ylsulfonyl)acetyl)benzamide (4t)**

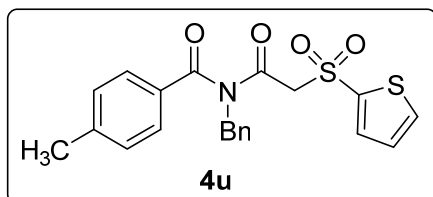
White solid, m. p. 99-101 °C (72 mg, 79% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl₃, 400MHz) δ 8.47 (s, 1H), 7.97 (d, $J = 8.8$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.70-7.61 (m, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.22-7.20 (m, 5H), 7.10-7.08 (m, 2H), 4.94 (s, 2H), 4.67 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (CDCl₃, 151MHz) δ 174.5, 164.5, 144.2, 136.3, 136.0, 135.6, 132.1, 131.3, 130.5, 129.7, 129.7, 129.63, 129.59, 129.2, 128.6, 128.1, 127.9, 127.8, 127.7, 123.0, 62.3, 50.6, 21.8.

IR (KBr) ν 3042, 1718, 1601, 1554, 1348, 1193, 1049, 829, 561 cm⁻¹.

HRMS (EI) calcd for C₂₇H₂₃NO₄S (M⁺): 457.1348; Found: 457.1348.



***N*-Benzyl-4-methyl-*N*-(2-(thiophen-2-ylsulfonyl)acetyl)benzamide (4u)**

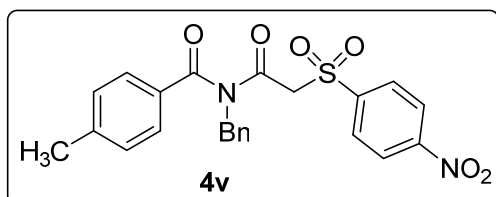
White solid, m. p. 85-88 °C (66 mg, 80% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl₃, 400MHz) δ 7.74 (d, $J = 5.2$ Hz, 1H), 7.66 (d, $J = 3.2$ Hz, 1H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.27-7.23 (m, 5H), 7.15-7.11 (m, 3H), 4.96 (s, 2H), 4.64 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 174.5, 164.5, 144.4, 139.7, 136.3, 135.5, 135.0, 131.3, 129.8, 129.3, 128.7, 128.0, 127.8, 63.5, 50.7, 21.9.

IR (KBr) ν 2958, 1700, 1601, 1554, 1346, 1211, 1049, 829, 626, 547 cm⁻¹.

HRMS (EI) calcd for C₂₁H₁₉NO₄S₂ (M⁺): 413.0755; Found: 413.0756.



***N*-Benzyl-4-methyl-*N*-(2-((4-nitrophenyl)sulfonyl)acetyl)benzamide (4v)**

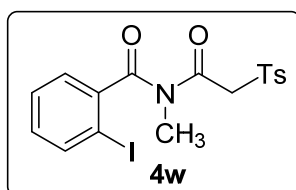
White solid, m. p. 100-102 °C (83 mg, 92% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:3).

^1H NMR (CDCl_3 , 400MHz) δ 8.30 (d, $J = 9.2$ Hz, 2H), 8.00 (d, $J = 8.8$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.24-7.20 (m, 5H), 7.08-7.05 (m, 2H), 4.90 (s, 2H), 4.58 (s, 2H), 2.41 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 174.4, 164.1, 151.0, 144.8, 144.4, 136.0, 130.9, 130.4, 129.9, 129.3, 128.8, 128.03, 127.99, 124.4, 62.2, 50.8, 21.9.

IR (KBr) ν 2957, 1721, 1610, 1559, 1329, 1203, 1049, 886, 733, 558 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_6\text{S}$ (M^+): 452.1042; Found: 452.1042.



2-Iodo-N-methyl-N-(2-tosylacetyl)benzamide (4w)

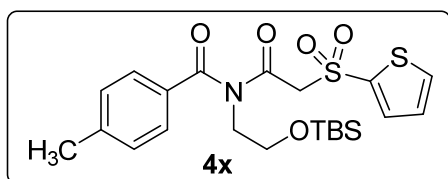
White solid, m. p. 85-87 °C, (1.19 g, 87% yield) $R_f = 0.2$ (EtOAc/Petroleum ether 1:5).

^1H NMR (CDCl_3 , 600MHz) δ 7.87 (d, $J = 8.4$ Hz, 3H), 7.46 (td, $J = 7.8$ Hz, $J = 1.2$ Hz, 1H), 7.38-7.35 (m, 3H), 7.18 (td, $J = 7.8$ Hz, $J = 1.8$ Hz, 1H), 4.95 (s, 2H), 3.03 (s, 3H), 2.54 (s, 3H).

^{13}C NMR (CDCl_3 , 151MHz) δ 172.9, 164.9, 145.4, 141.0, 139.8, 136.6, 131.8, 130.0, 128.8, 128.7, 127.5, 91.5, 63.0, 34.1, 21.9.

IR (KBr) ν 2952, 1701, 1589, 1427, 1330, 1219, 1138, 1057, 819, 566 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{17}\text{H}_{16}\text{INO}_4\text{S}$ (M^+): 456.9845; Found: 456.9844.



N-(2-((tert-Butyldimethylsilyl)oxy)ethyl)-4-methyl-N-(2-(thiophen-2-ylsulfonyl)acetyl)benzamide (4x)

White solid, m. p. 89-91 °C, $R_f = 0.2$ (EtOAc/Petroleum ether 1:4).

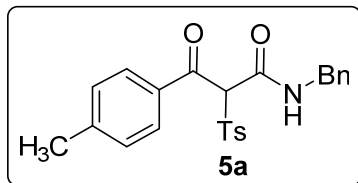
^1H NMR (CDCl_3 , 400MHz) δ 7.75 (d, $J = 4.4$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 7.2$ Hz, 2H), 7.16 (t, $J = 4.0$ Hz, 1H), 4.72 (s, 2H), 3.92 (t, $J = 4.8$ Hz, 2H), 3.71 (t, $J = 4.8$ Hz, 2H), 2.43 (s, 3H), 0.70 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (CDCl_3 , 100MHz) δ 174.6, 164.6, 143.9, 140.1, 135.3, 134.9, 131.2, 129.7, 129.6,

128.0, 63.1, 61.3, 50.3, 26.0, 21.8, 18.4, -5.5.

IR (KBr) ν 2955, 1712, 1600, 1575, 1347, 1219, 1036, 829, 565 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_5\text{S}_2\text{Si}$ (M^+): 481.1413; Found: 481.1414.



***N*-Benzyl-3-oxo-3-(*p*-tolyl)-2-tosylpropanamide (5a)**

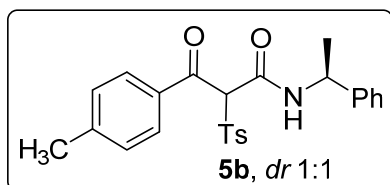
White solid, m. p. 162-165 °C (63 mg, 75% yield), R_f = 0.2 (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl_3 , 400MHz) δ 7.85-7.80 (m, 3H), 7.65 (d, J = 8.4 Hz, 2H), 7.37-7.28 (m, 6H), 7.26-7.21 (m, 3H), 5.99 (s, 1H), 4.52 (dd, J = 15.2 Hz, J = 6.4 Hz, 1H), 4.38 (dd, J = 14.8 Hz, J = 5.6 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 188.1, 159.5, 146.3, 146.1, 137.3, 134.3, 133.9, 130.0, 129.8, 129.6, 129.4, 128.9, 128.0, 126.6, 75.6, 44.4, 21.9, 21.9.

IR (KBr) ν 3367, 3046, 1670, 1600, 1534, 1328, 1153, 881, 690 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_4\text{S}$ (M^+): 421.1348; Found: 421.1348.



3-Oxo-*N*-((*S*)-1-phenylethyl)-3-(*p*-tolyl)-2-tosylpropanamide (5b)

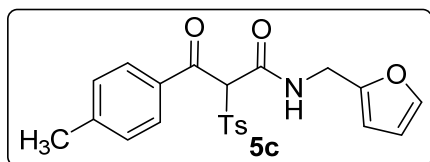
White solid, m. p. 171-173 °C (58 mg, 67% yield), R_f = 0.2 (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl_3 , 400MHz) δ 7.89 (d, J = 8.0 Hz, 1H), 7.84-7.72 (m, 2H), 7.47-7.23 (m, 10H), 7.07 (d, J = 8.0 Hz, 1H), 5.93 and 5.88 (s, 1H), 5.05-4.98 (m, 1H), 2.43 (s, 3H), 2.40 and 2.34 (s, 3H), 1.53 and 1.51 (d, J = 12.0 Hz, 3H).

^{13}C NMR (CDCl_3 , 151MHz) δ 188.2 and 188.0, 158.53 and 158.50, 146.3 and 145.9, 146.24 and 146.18, 142.6, 134.5 and 133.9, 134.04 and 133.97, 130.0 and 129.8, 129.84 and 129.82, 129.7 and 129.2, 129.6 and 129.5, 128.85 and 128.83, 127.7 and 127.5, 126.7 and 126.0, 75.54 and 75.50, 50.11 and 50.09, 22.2 and 22.1, 22.0 and 21.8, 21.92 and 21.88.

IR (KBr) ν 3366, 3042, 1672, 1599, 1534, 1328, 1150, 880, 692 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_4\text{S}$ (M^+): 435.1504; Found: 435.1503.



***N*-(Furan-2-ylmethyl)-3-oxo-3-(*p*-tolyl)-2-tosylpropanamide (5c)**

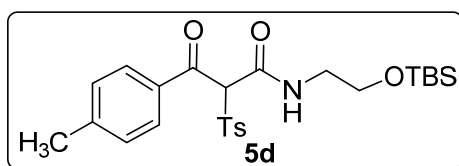
White solid, m. p. 174-176 °C (60 mg, 73% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl₃, 400MHz) δ 7.86 (d, $J = 8.0$ Hz, 2H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.41 (s, 1H), 7.32-7.26 (m, 4H), 6.36 (s, 1H), 6.28 (s, 1H), 5.94 (s, 1H), 4.54 (dd, $J = 15.2$ Hz, $J = 6.4$ Hz, 1H), 4.38 (dd, $J = 15.6$ Hz, $J = 5.2$ Hz, 1H), 2.43 (s, 6H).

^{13}C NMR (CDCl₃, 100MHz) δ 187.9, 159.4, 150.4, 146.4, 146.2, 142.6, 134.1, 133.8, 130.0, 129.8, 129.7, 129.4, 110.6, 108.2, 75.4, 37.2, 22.0, 21.9.

IR (KBr) ν 3357, 3036, 1674, 1601, 1534, 1328, 1153, 891, 682 cm⁻¹.

HRMS (EI) calcd for C₂₂H₂₁NO₅S (M⁺): 411.1140; Found: 411.1140.



***N*-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-3-oxo-3-(*p*-tolyl)-2-tosylpropanamide (5d)**

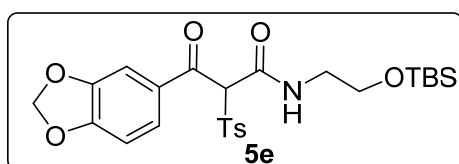
White solid, m. p. 179-181 °C (77 mg, 79% yield), $R_f = 0.3$ (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl₃, 400MHz) δ 7.84 (d, $J = 8.0$ Hz, 2H), 7.80-7.78 (m, 3H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 5.92 (s, 1H), 3.67 (t, $J = 5.2$ Hz, 2H), 3.45-3.30 (m, 2H), 2.43 (s, 3H), 2.42 (s, 3H), 0.92 (s, 9H), 0.082 (s, 3H), 0.077 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 187.8, 159.6, 146.1, 146.1, 134.5, 133.9, 130.0, 129.8, 129.6, 129.5, 75.5, 61.2, 42.7, 26.0, 21.9, 21.9, 18.4, -5.3.

IR (KBr) ν 3357, 2935, 1690, 1603, 1538, 1260, 1155, 856, 679 cm⁻¹.

HRMS (EI) calcd for C₂₅H₃₅NO₅SSi (M⁺): 489.2005; Found: 489.2006.



3-(Benzo[d][1,3]dioxol-5-yl)-N-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-3-oxo-2-tosylpropanamide (5e)

lpropanamide (5e)

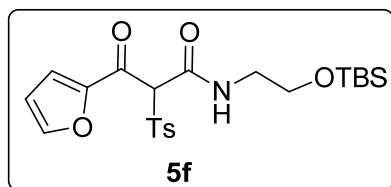
White solid, m. p. 125-127 °C (84 mg, 81% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl₃, 400MHz) δ 7.78 (d, $J = 8.0$ Hz, 3H), 7.54 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 1H), 7.40 (d, $J = 1.2$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 1H), 6.06 (s, 2H), 5.82 (s, 1H), 3.65 (t, $J = 5.6$ Hz, 2H), 3.43-3.29 (m, 2H), 2.43 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H).

^{13}C NMR (CDCl₃, 100MHz) δ 186.1, 159.6, 153.5, 148.7, 146.0, 134.5, 131.2, 129.9, 129.5, 126.8, 108.7, 108.3, 102.5, 75.6, 61.2, 42.7, 26.0, 21.9, 18.3, -5.3.

IR (KBr) ν 3357, 2935, 1680, 1600, 1534, 1263, 1153, 836, 676 cm⁻¹.

HRMS (EI) calcd for C₂₅H₃₃NO₇SSi (M⁺): 519.1747; Found: 519.1745.



N-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-3-(furan-2-yl)-3-oxo-2-tosylpropanamide

(5f)

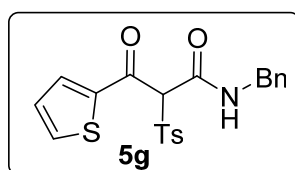
White solid, m. p. 175-178 °C (67 mg, 72% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl₃, 400MHz) δ 7.77 (d, $J = 8.4$ Hz, 2H), 7.69 (br, 1H), 7.61 (s, 1H), 7.34-7.30 (m, 3H), 6.58 (s, 1H), 5.77 (s, 1H), 3.66 (t, $J = 5.2$ Hz, 2H), 3.44-3.30 (m, 2H), 2.42 (s, 3H), 0.91 (s, 9H), 0.075 (s, 3H), 0.070 (s, 3H).

^{13}C NMR (CDCl₃, 100MHz) δ 175.9, 159.1, 152.0, 148.7, 146.1, 134.5, 129.9, 129.5, 121.0, 113.6, 75.8, 61.2, 42.7, 26.0, 21.9, 18.3, -5.3.

IR (KBr) ν 3357, 2936, 1671, 1599, 1535, 1263, 1153, 836, 676 cm⁻¹.

HRMS (EI) calcd for C₂₂H₃₁NO₆SSi (M⁺): 465.1641; Found: 465.1640.



N-Benzyl-3-oxo-3-(thiophen-2-yl)-2-tosylpropanamide (5g)

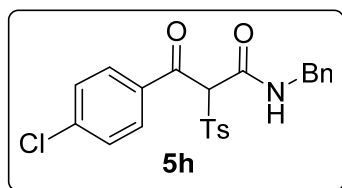
White solid, m. p. 181-183 °C (52 mg, 63% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl_3 , 400MHz) δ 7.79 (d, $J = 4.8$ Hz, 2H), 7.75 (d, $J = 4.0$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.37-7.26 (m, 5H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.14 (t, $J = 4.4$ Hz, 1H), 5.74 (s, 1H), 4.52 (dd, $J = 15.2$ Hz, $J = 6.4$ Hz, 1H), 4.38 (dd, $J = 15.2$ Hz, $J = 5.6$ Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 180.5, 159.1, 146.3, 143.4, 137.7, 137.2, 135.7, 134.0, 130.0, 129.5, 129.0, 128.9, 128.0, 127.8, 77.1, 44.5, 21.9.

IR (KBr) ν 3336, 3039, 1670, 1541, 1330, 1150, 828, 703 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_4\text{S}_2$ (M^+): 413.0755; Found:413.0756.



***N*-Benzyl-3-(4-chlorophenyl)-3-oxo-2-tosylpropanamide (5h)**

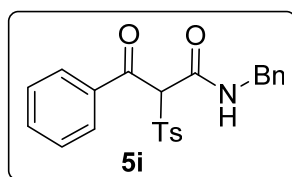
White solid, m. p. 150-154 °C (74 mg, 84% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl_3 , 400MHz) δ 7.92 (d, $J = 8.4$ Hz, 2H), 7.83 (br, 1H), 7.68 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.42-7.28 (m, 7H), 5.97 (s, 1H), 4.56 (dd, $J = 14.8$ Hz, $J = 6.4$ Hz, 1H), 4.42 (dd, $J = 15.2$ Hz, $J = 5.6$ Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 187.4, 159.2, 146.4, 141.7, 137.1, 134.7, 134.2, 130.8, 130.1, 129.5, 129.4, 128.9, 128.1, 127.9, 75.8, 44.5, 21.9.

IR (KBr) ν 3377, 3043, 1665, 1589, 1325, 1148, 1088, 814, 692 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{23}\text{H}_{20}\text{ClNO}_4\text{S}$ (M^+): 441.0802; Found:441.0802.



***N*-Benzyl-3-oxo-3-phenyl-2-tosylpropanamide (5i)**

White solid, m. p. 185-187 °C (71 mg, 87% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:2).

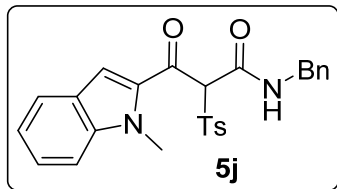
^1H NMR (CDCl_3 , 400MHz) δ 7.94 (d, $J = 8.4$ Hz, 2H), 7.81 (br, 1H), 7.68-7.61 (m, 3H), 7.47 (t, $J = 8.0$ Hz, 2H), 7.38-7.29 (m, 5H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.00 (s, 1H), 4.53 (dd, $J = 14.8$ Hz, $J = 6.0$ Hz, 1H), 4.42 (dd, $J = 14.8$ Hz, $J = 5.6$ Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 188.6, 159.3, 146.2, 137.2, 136.3, 134.9, 134.2, 130.0, 129.4,

129.4, 129.1, 128.9, 128.1, 127.8, 75.7, 44.4, 21.9.

IR (KBr) ν 3292, 3087, 1695, 1645, 1565, 1329, 1137, 1083, 726, 550 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_4\text{S}$ (M^+): 407.1191; Found: 407.1195.



***N*-Benzyl-3-(1-methyl-1*H*-indol-2-yl)-3-oxo-2-tosylpropanamide (5j)**

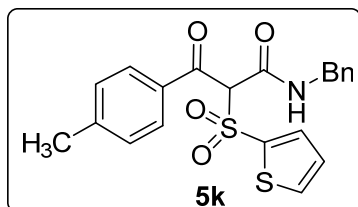
White solid, m. p. 190-192 °C (56 mg, 61% yield), R_f = 0.2 (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl_3 , 400MHz) δ 7.88 (t, J = 5.6 Hz, 1H), 7.70-7.66 (m, 3H), 7.45-7.29 (m, 8H), 7.22 (d, J = 8.0 Hz, 2H), 7.18-7.14 (m, 1H), 5.82 (s, 1H), 4.56 (dd, J = 14.8 Hz, J = 6.4 Hz, 1H), 4.40 (dd, J = 14.8 Hz, J = 4.2 Hz, 1H), 4.03 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 179.9, 159.6, 146.1, 141.6, 137.3, 134.5, 134.4, 130.0, 129.3, 128.9, 128.04, 128.01, 127.8, 125.8, 123.9, 121.6, 116.2, 110.7, 77.4, 44.4, 32.6, 21.8.

IR (KBr) ν 3331, 3037, 1685, 1517, 1326, 1148, 804, 703 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$ (M^+): 460.1457; Found: 460.1455.



***N*-Benzyl-3-oxo-2-(thiophen-2-ylsulfonyl)-3-(*p*-tolyl)propanamide (5k)**

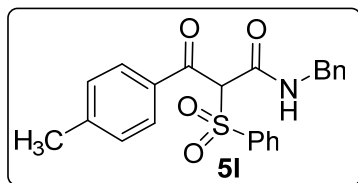
White solid, m. p. 1183-185 °C (43 mg, 52% yield), R_f = 0.2 (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl_3 , 400MHz) δ 7.87 (d, J = 8.4 Hz, 2H), 7.83 (br, 1H), 7.72 (d, J = 5.2 Hz, 1H), 7.55 (d, J = 4.0 Hz, 1H), 7.37-7.27 (m, 7H), 7.04 (t, J = 4.4 Hz, 1H), 6.09 (s, 1H), 4.55 (dd, J = 14.8 Hz, J = 6.0 Hz, 1H), 4.42 (dd, J = 14.8 Hz, J = 6.0 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 187.6, 159.2, 146.6, 137.6, 137.1, 136.7, 136.1, 133.6, 129.9, 129.6, 128.9, 128.2, 128.0, 127.8, 76.2, 44.5, 22.0.

IR (KBr) ν 3371, 3036, 1671, 1596, 1339, 1138, 1086, 818, 696 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_4\text{S}_2$ (M^+): 413.0755; Found: 413.0753.



N-Benzyl-3-oxo-2-(phenylsulfonyl)-3-(p-tolyl)propanamide (5I)

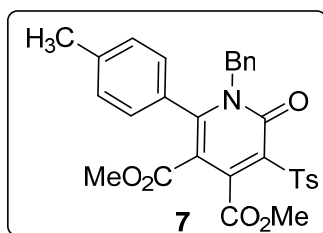
White solid, m. p. 166-168 °C (62 mg, 76% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:2).

^1H NMR (CDCl_3 , 400MHz) δ 7.85-7.76 (m, 5H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.43 (t, $J = 8.0$ Hz, 2H), 7.37-7.24 (m, 7H), 6.00 (s, 1H), 4.52 (dd, $J = 14.8$ Hz, $J = 6.4$ Hz, 1H), 4.38 (dd, $J = 14.8$ Hz, $J = 5.6$ Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 187.9, 159.3, 146.4, 137.2, 137.2, 134.8, 133.7, 129.8, 129.6, 129.342, 129.336, 128.9, 128.0, 127.8, 75.4, 44.4, 21.9.

IR (KBr) ν 3377, 3042, 1670, 1599, 1329, 1142, 1090, 814, 699 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_4\text{S}$ (M^+): 407.1191; Found: 407.1188.



Dimethyl

1-benzyl-6-oxo-2-(p-tolyl)-5-tosyl-1,6-dihydropyridine-3,4-dicarboxylate (7)

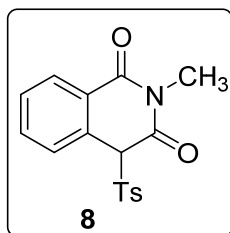
White solid, m. p. 169-171 °C (45 mg, 83% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:3).

^1H NMR (CDCl_3 , 400MHz) δ 8.08 (d, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.16-7.08 (m, 5H), 6.84 (d, $J = 7.2$ Hz, 2H), 6.61 (d, $J = 7.2$ Hz, 2H), 5.03 (s, 2H), 4.03 (s, 3H), 3.58 (s, 3H), 2.44 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (CDCl_3 , 100MHz) δ 165.1, 164.8, 157.5, 157.4, 145.8, 144.8, 140.7, 136.7, 135.2, 129.6, 129.4, 129.3, 129.2, 128.6, 127.9, 127.8, 127.0, 126.0, 111.3, 53.7, 52.7, 49.8, 21.9, 21.6.

IR (KBr) ν 2952, 1717, 1668, 1600, 1326, 1149, 1071, 818, 667 cm^{-1} .

HRMS (EI) calcd for $\text{C}_{30}\text{H}_{27}\text{NO}_7\text{S}$ (M^+): 545.1508; Found: 545.1510.



2-Methyl-4-tosylisoquinoline-1,3(2*H*,4*H*)-dione (**8**)

White solid, m. p. 111-113 °C (31 mg, 94% yield), $R_f = 0.2$ (EtOAc/Petroleum ether 1:4).

^1H NMR (CDCl_3 , 400MHz) δ 8.11 (d, $J = 3.6$ Hz, 1H), 7.68 (d, $J = 7.2$ Hz, 1H), 7.62-7.56 (m, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 2H), 5.25 (s, 1H), 3.23 (s, 3H), 2.44 (s, 3H).

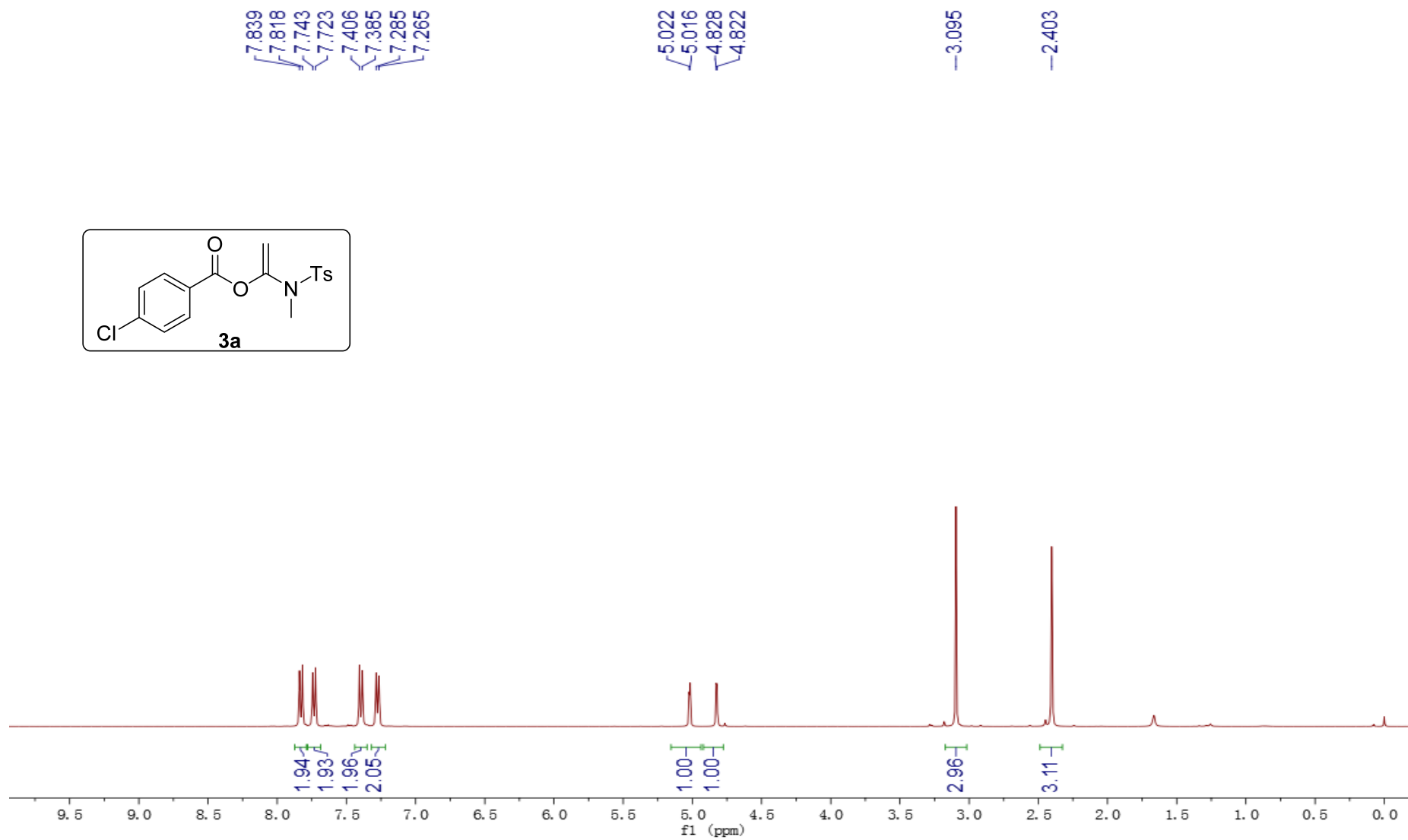
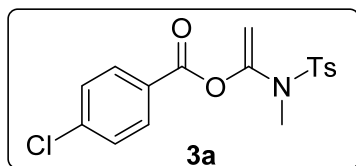
^{13}C NMR (CDCl_3 , 100MHz) δ 164.1, 163.7, 146.5, 133.5, 131.9, 130.5, 130.4, 129.9, 129.5, 129.1, 127.2, 127.1, 72.4, 27.6, 21.9.

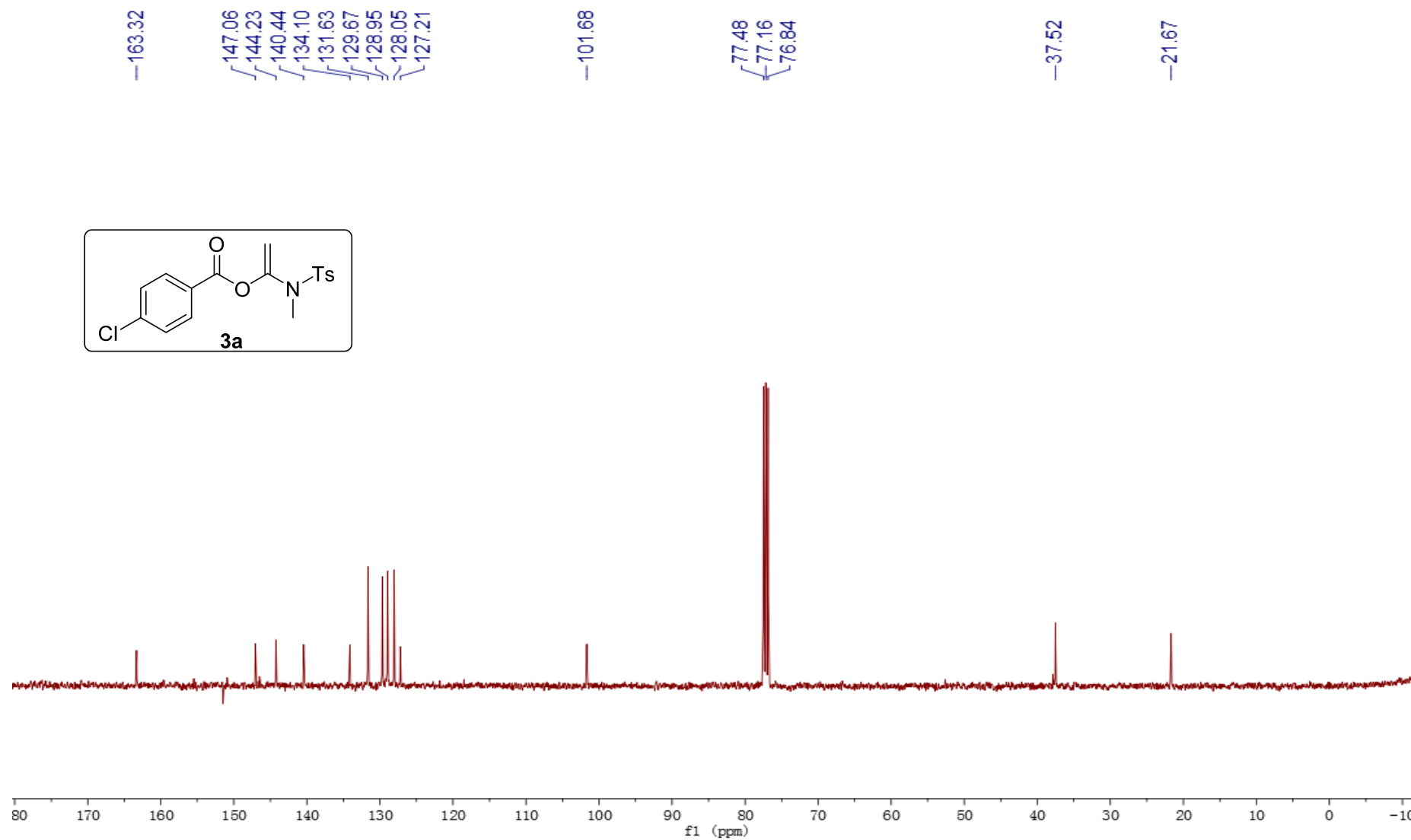
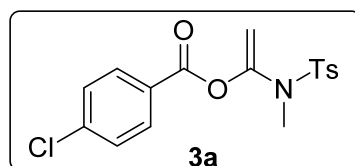
IR (KBr) ν 2951, 1711, 1665, 1604, 1306, 1140, 1079, 808, 661 cm^{-1} .

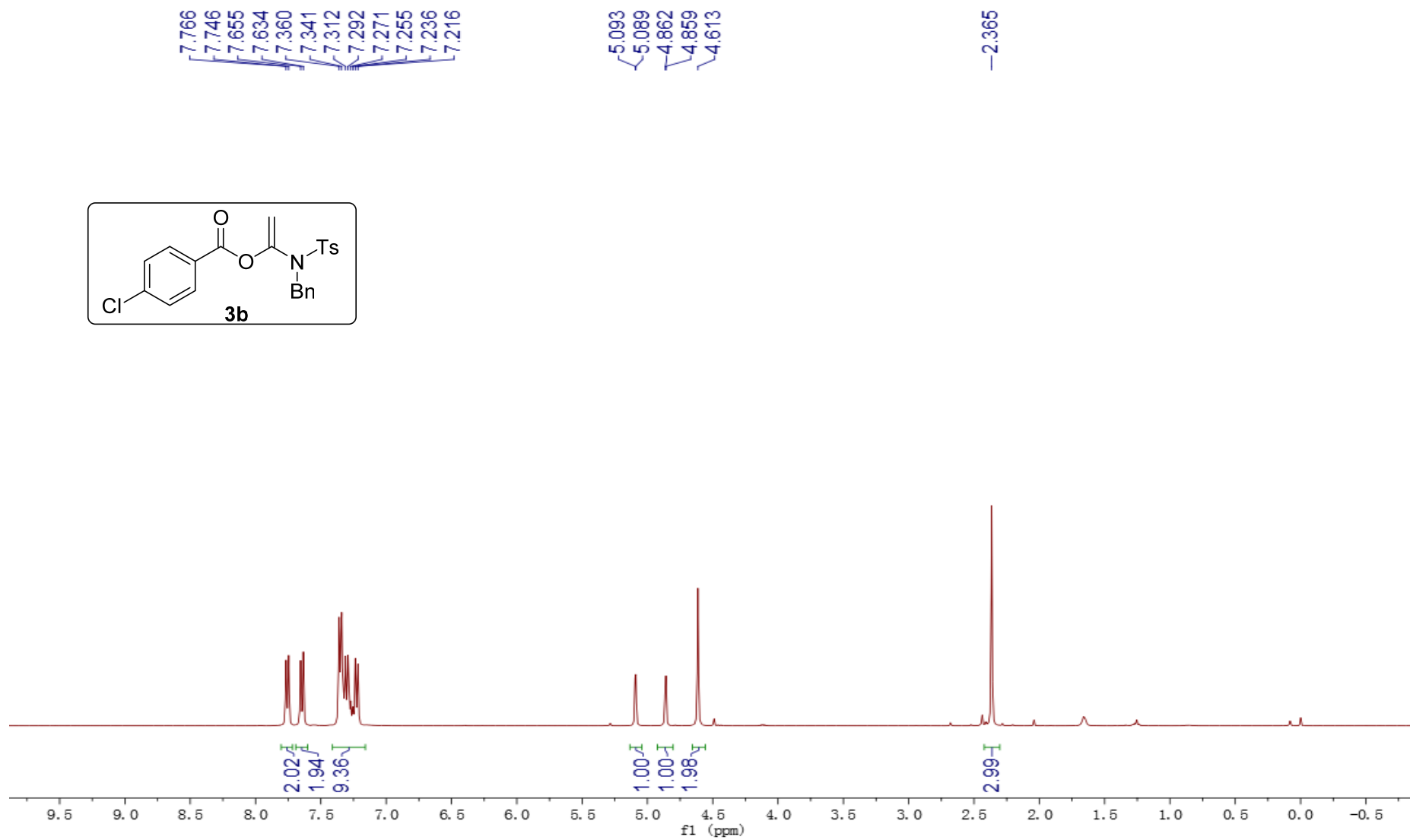
HRMS (EI) calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4\text{S}$ (M^+): 329.0722; Found: 329.0725.

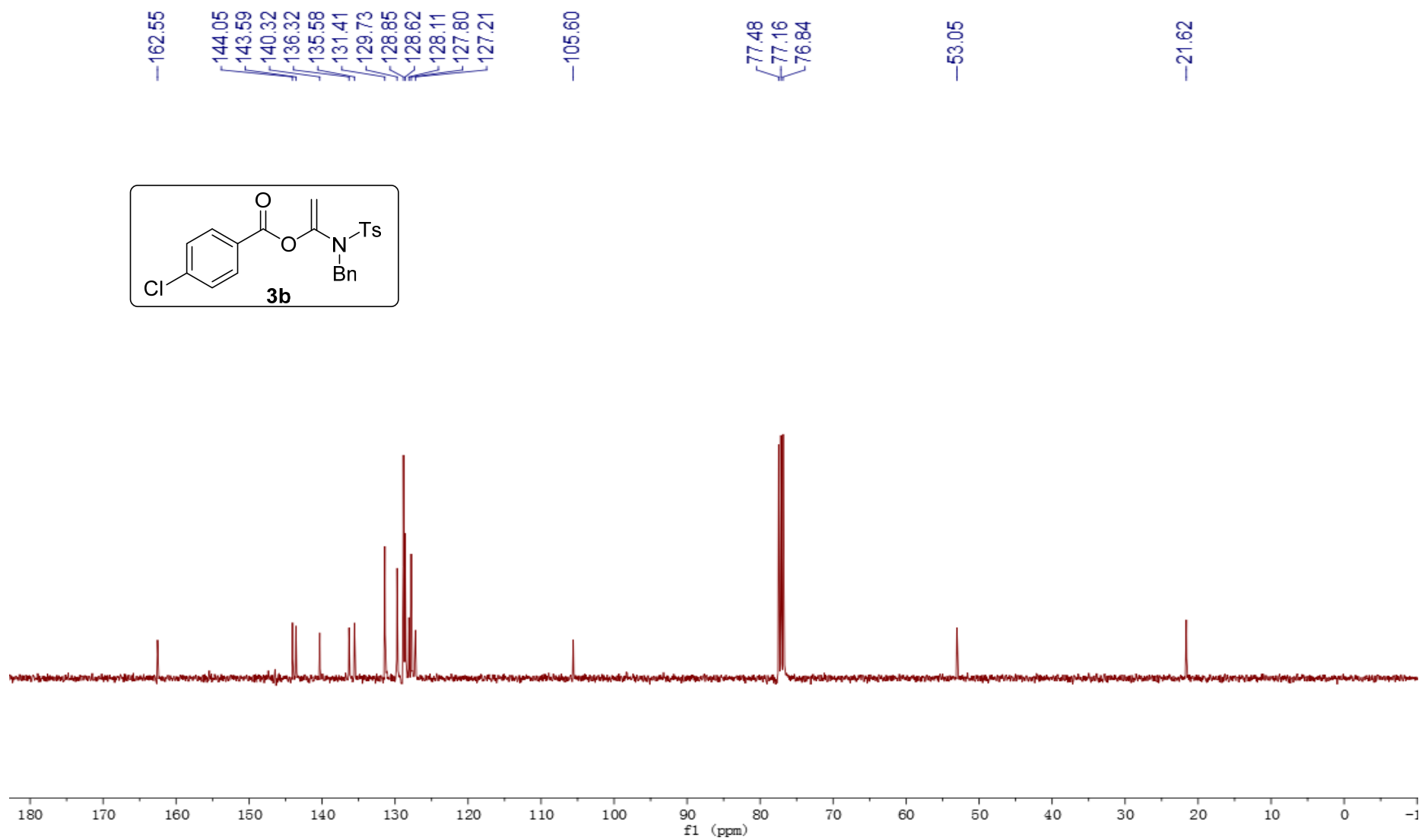
8. References

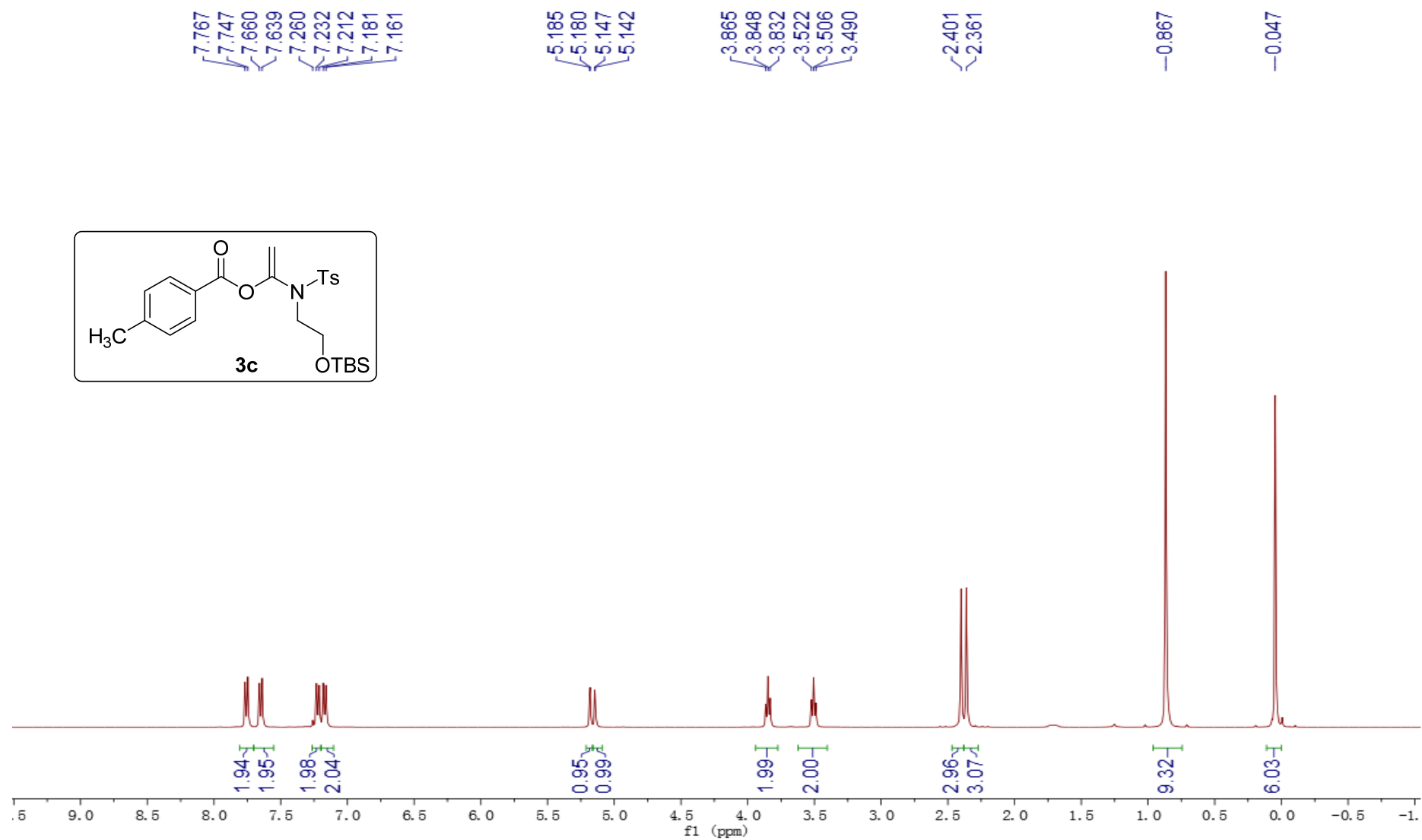
- (1) Hopkins, C. R.; etc. *Bioorg. Med. Chem. Lett.* **2005**, 15, 2734.
- (2) DeKorver, K. A.; Li, H.; Lohse, A. G.; Hayashi, R.; Lu, Z.; Zhang, Y.; Hsung, R. P. *Chem. Rev.* **2010**, 110, 5064.
- (3) Mamidipalli, P.; Yun, S. Y.; Wang, K. P.; et al. *Chem. Sci.* **2014**, 5, 2362.
- (4) Lu, B.; Ma, D. *Org. Lett.* **2006**, 8, 6115.

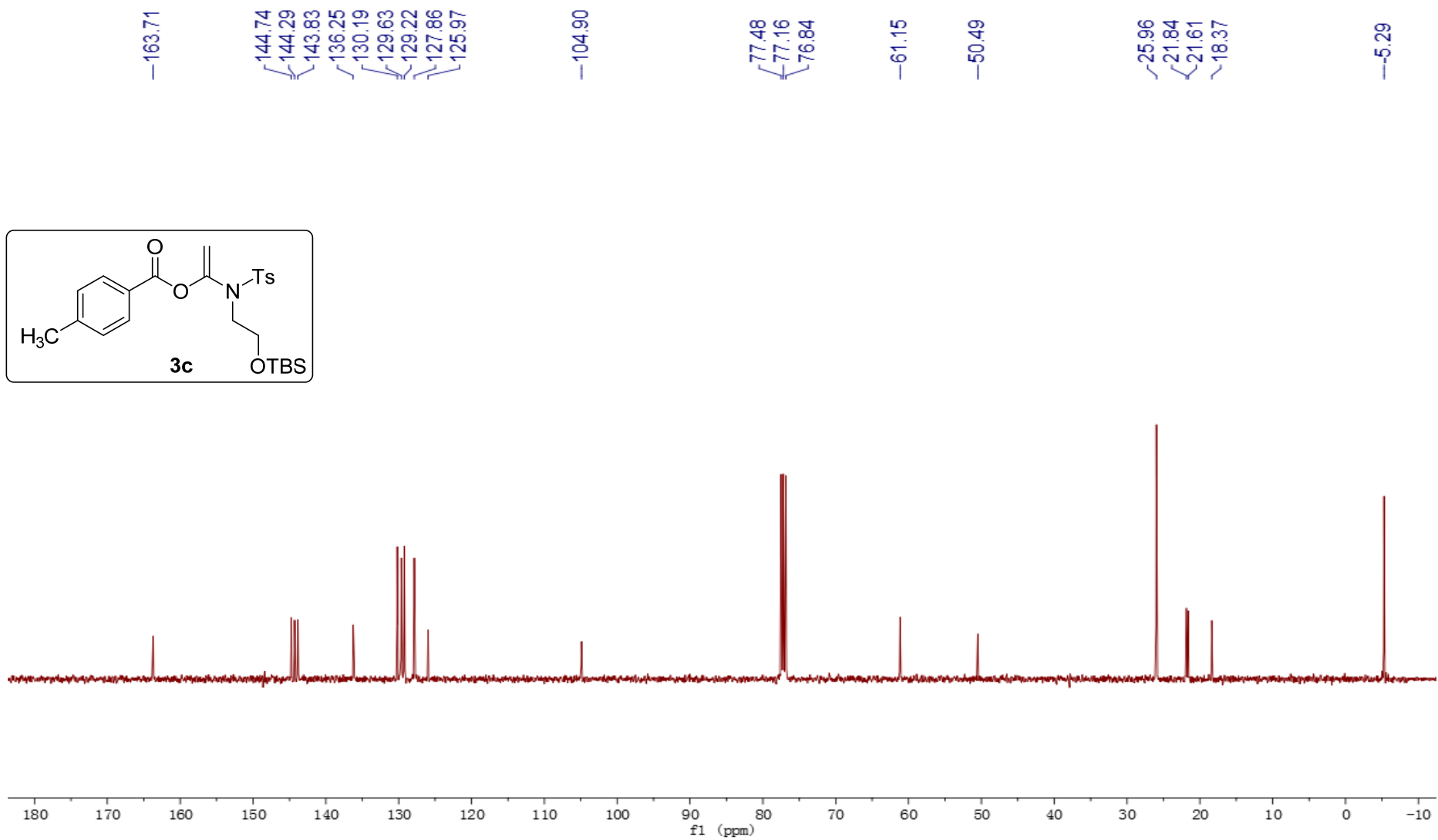


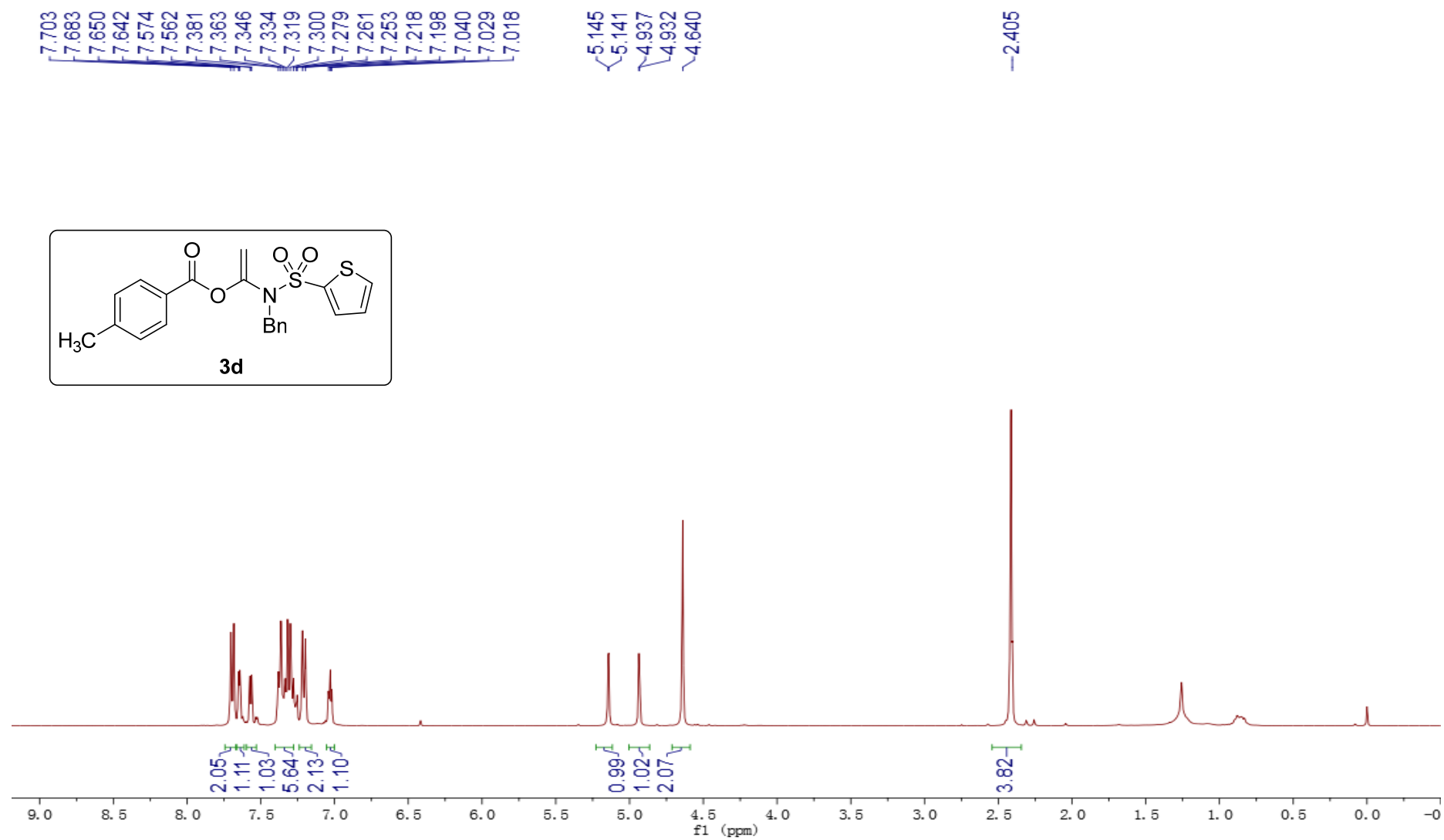


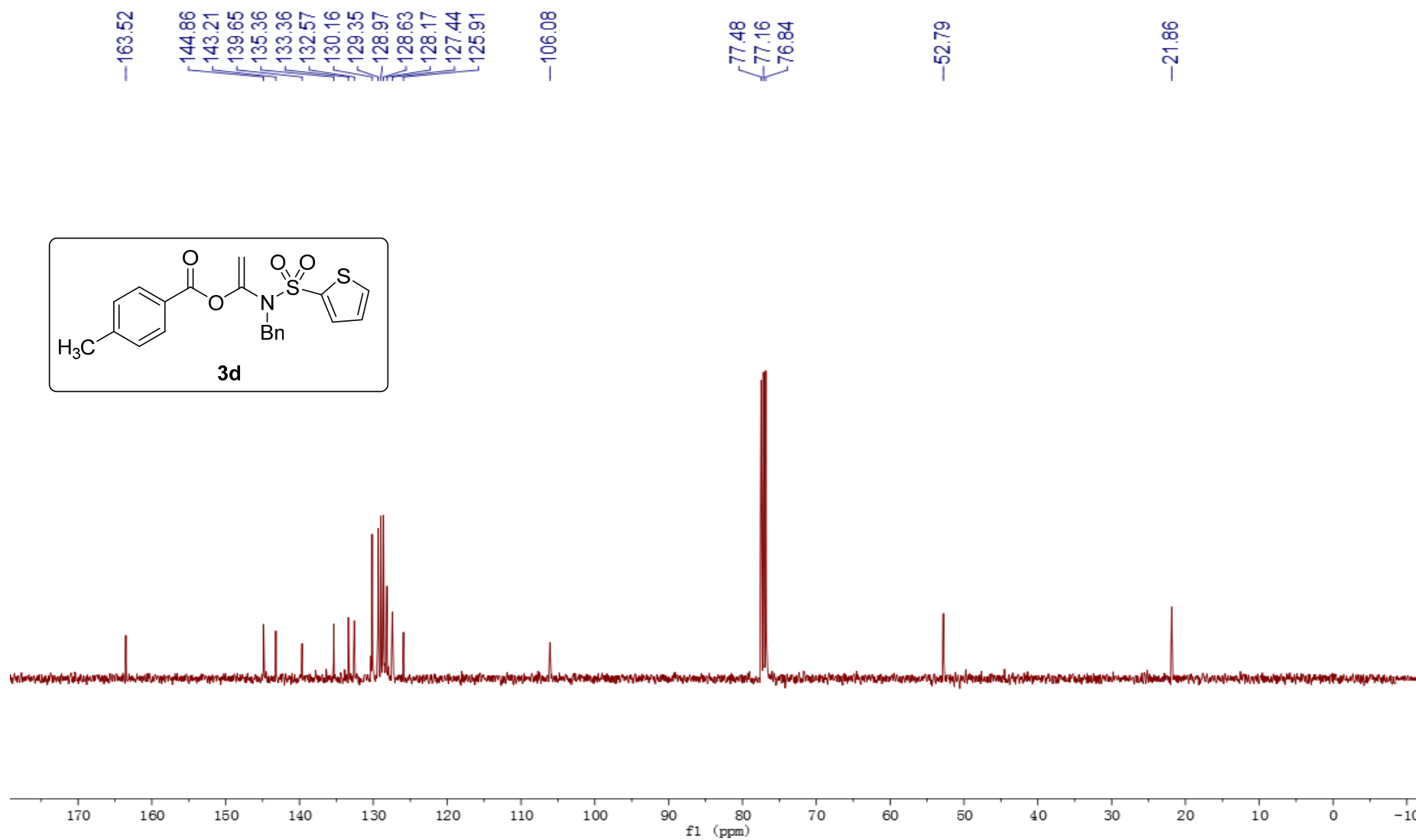


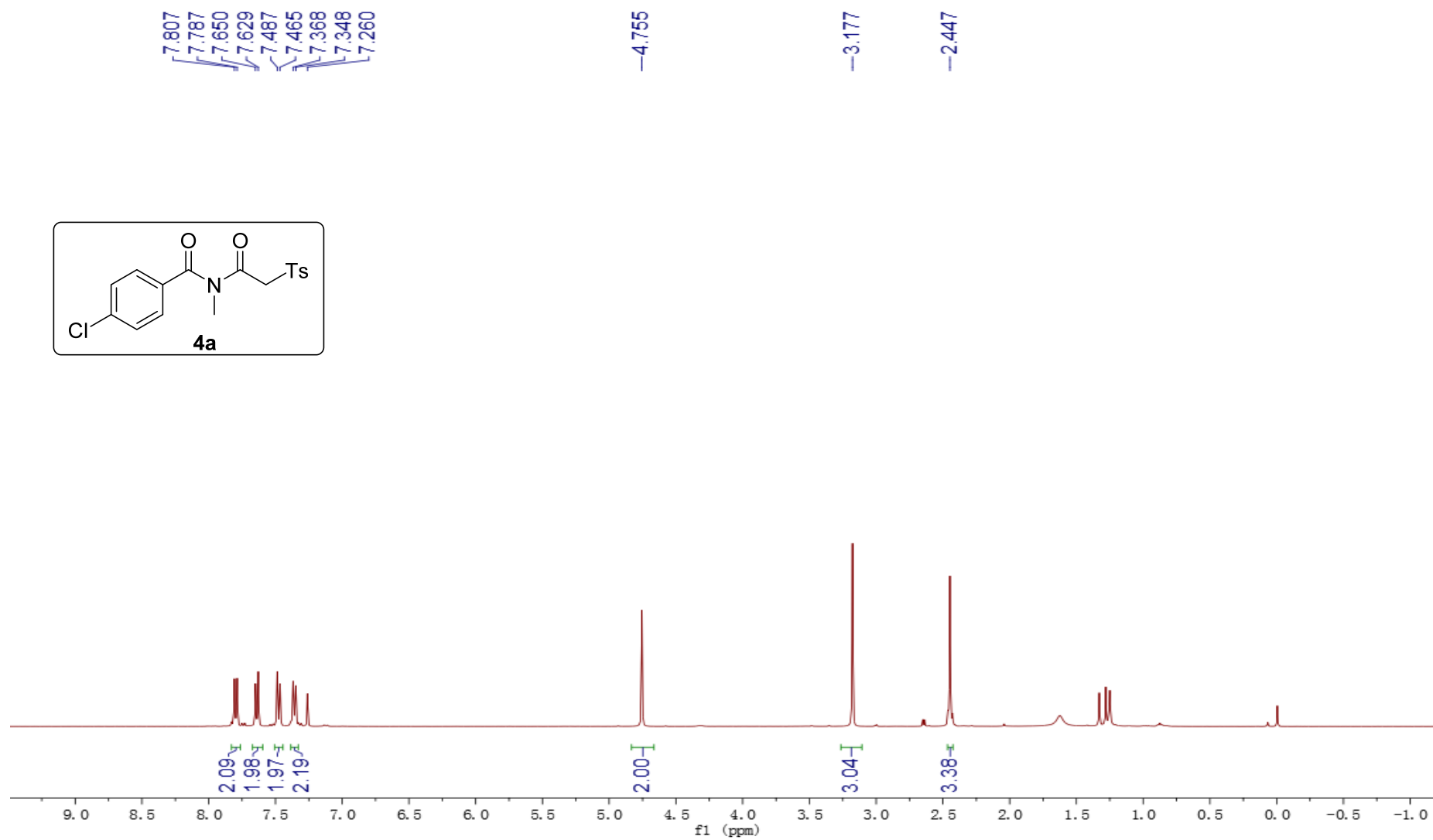


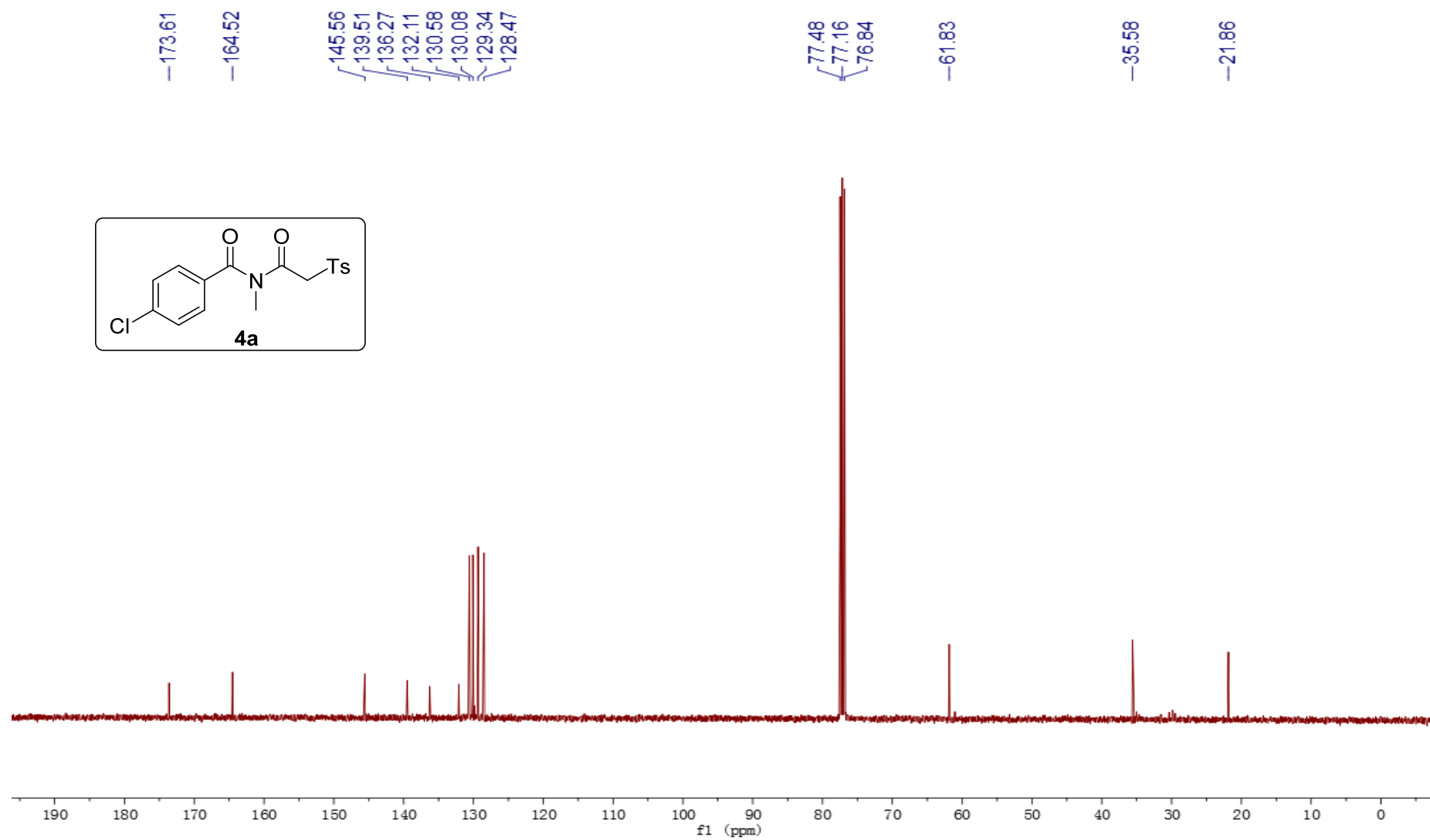


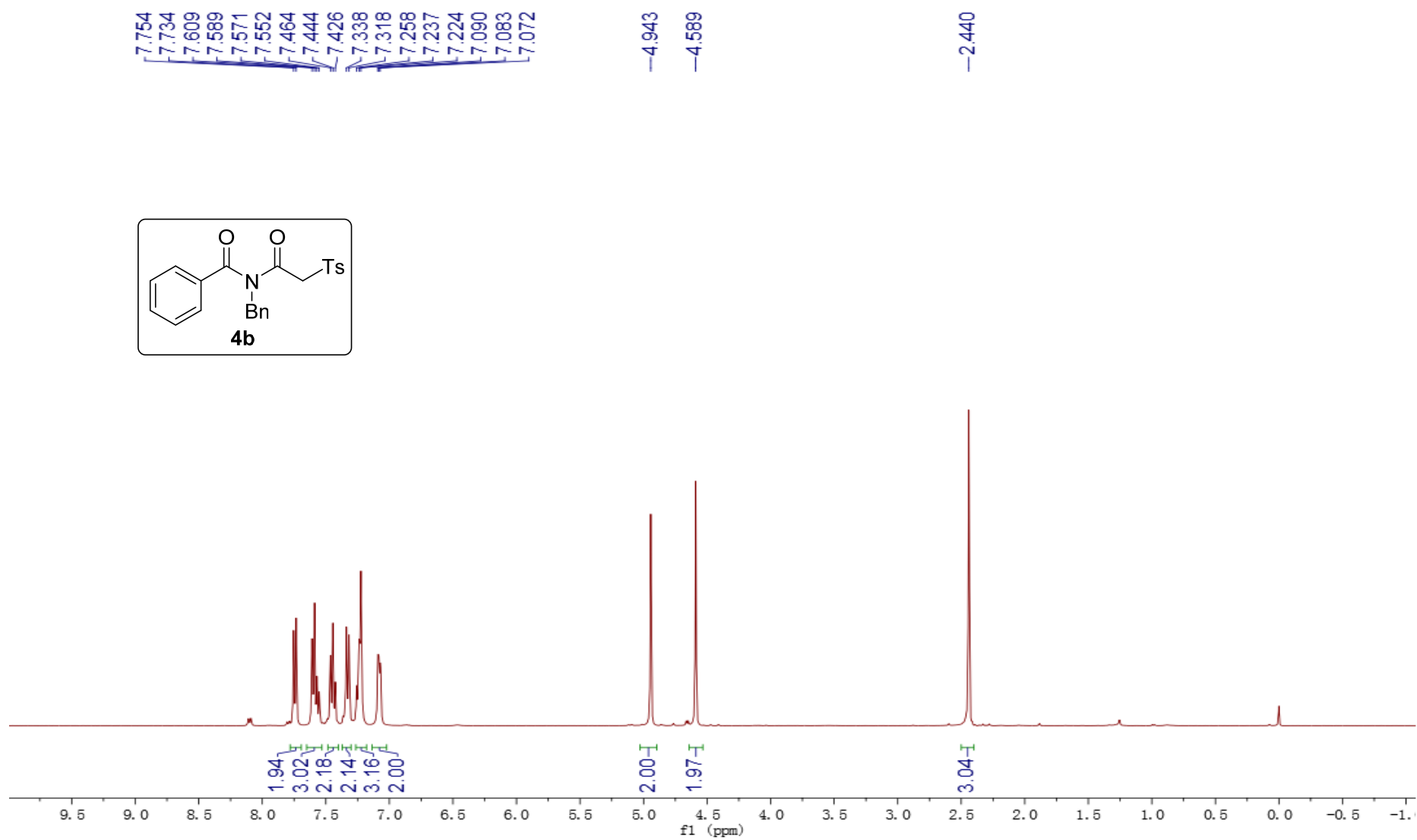


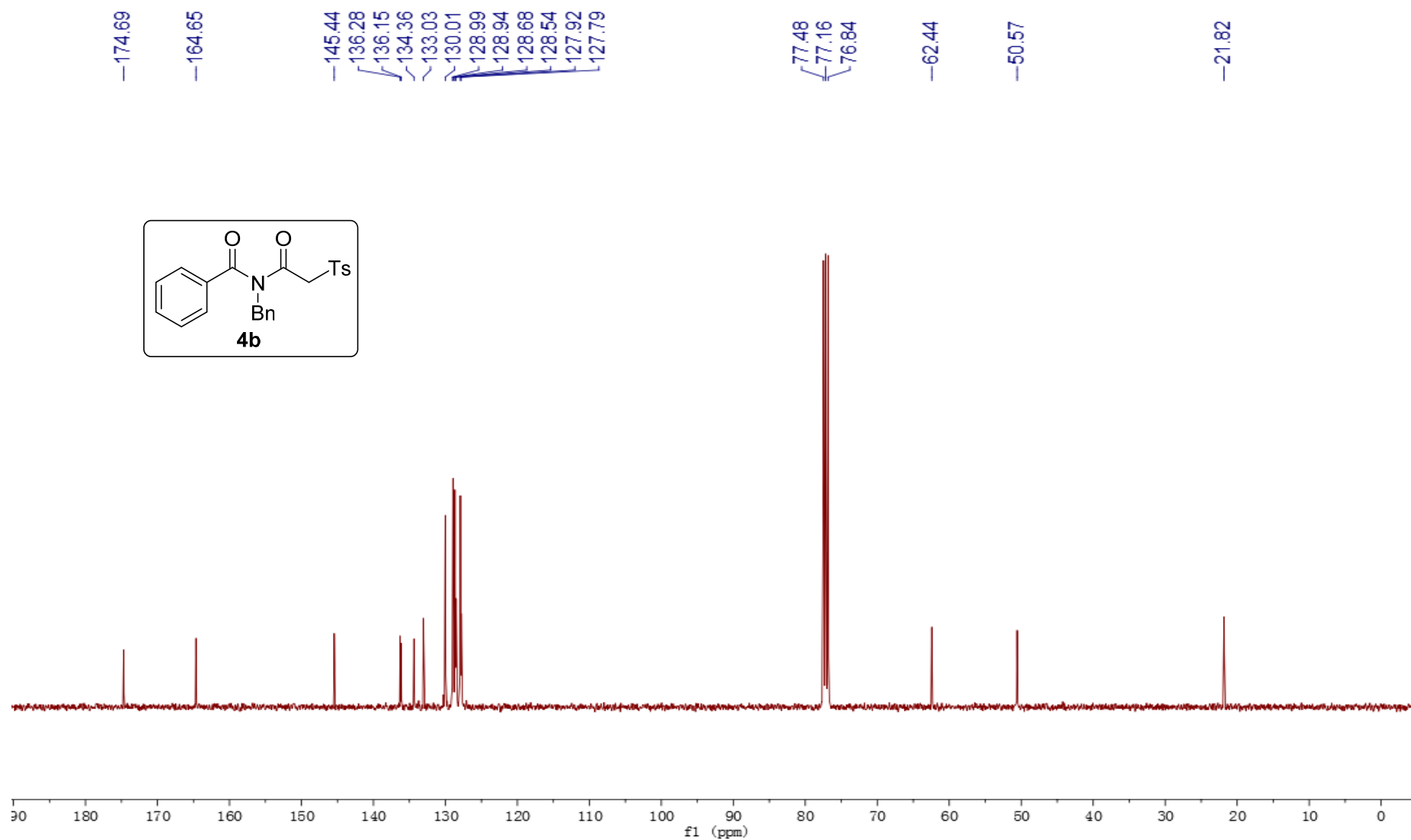


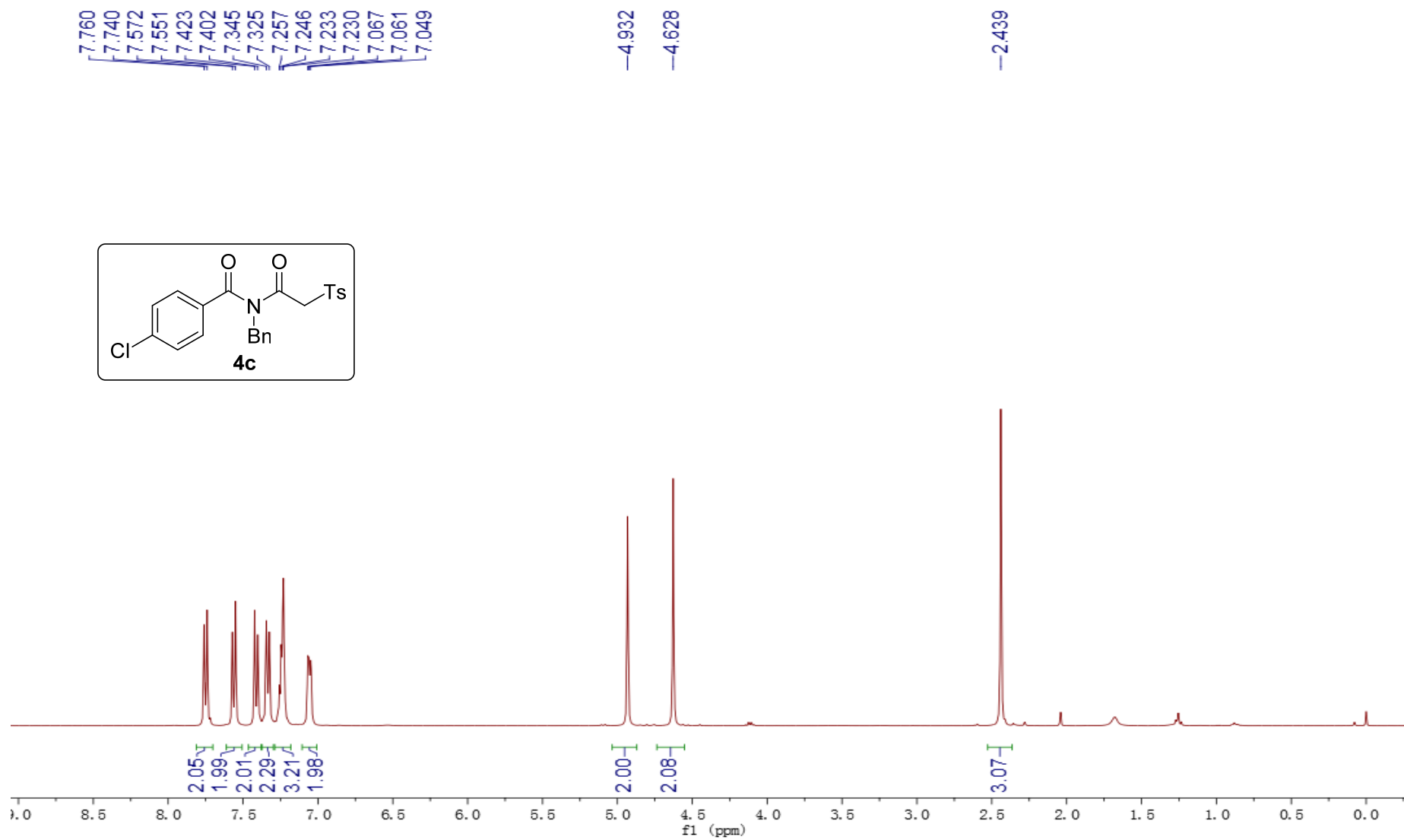


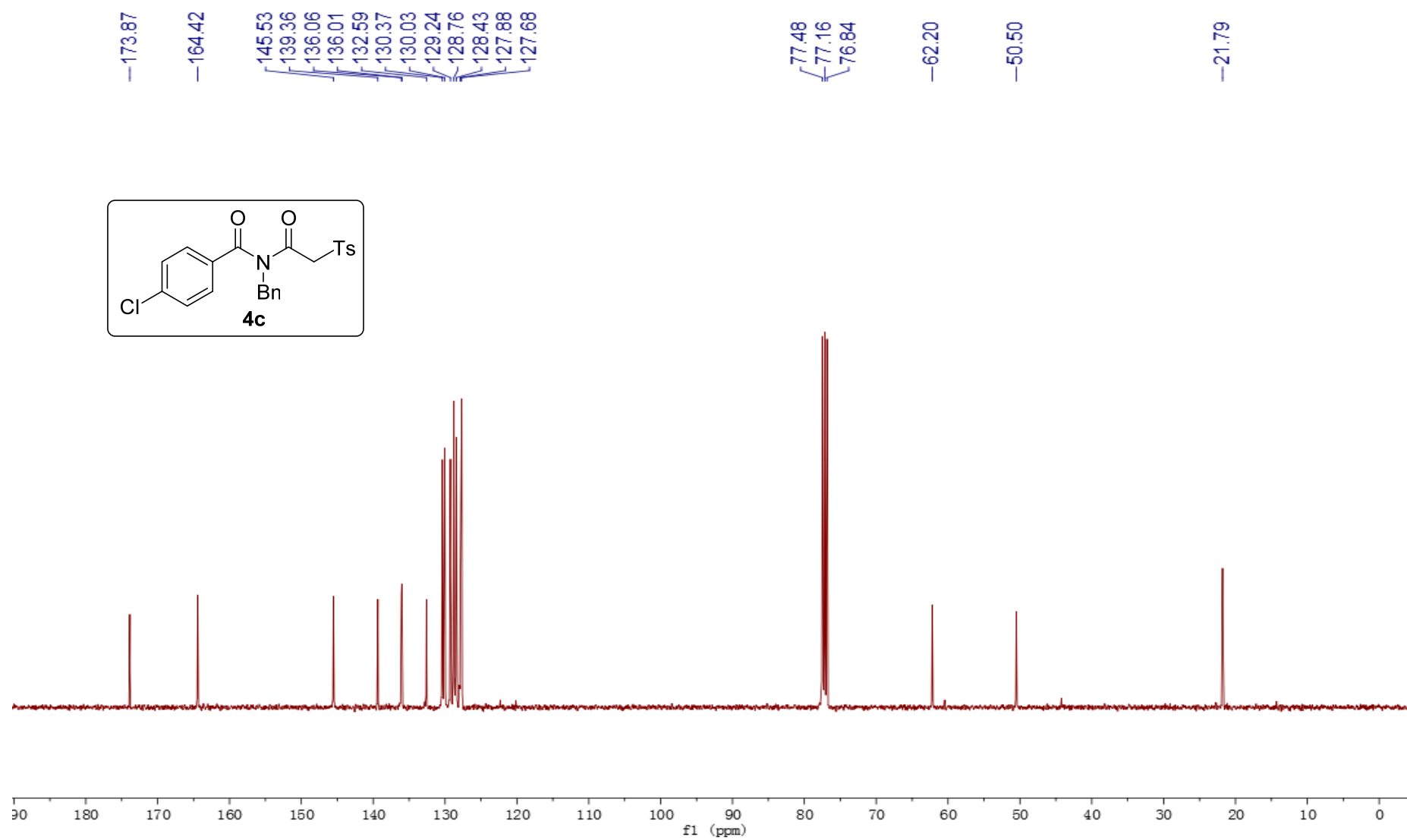


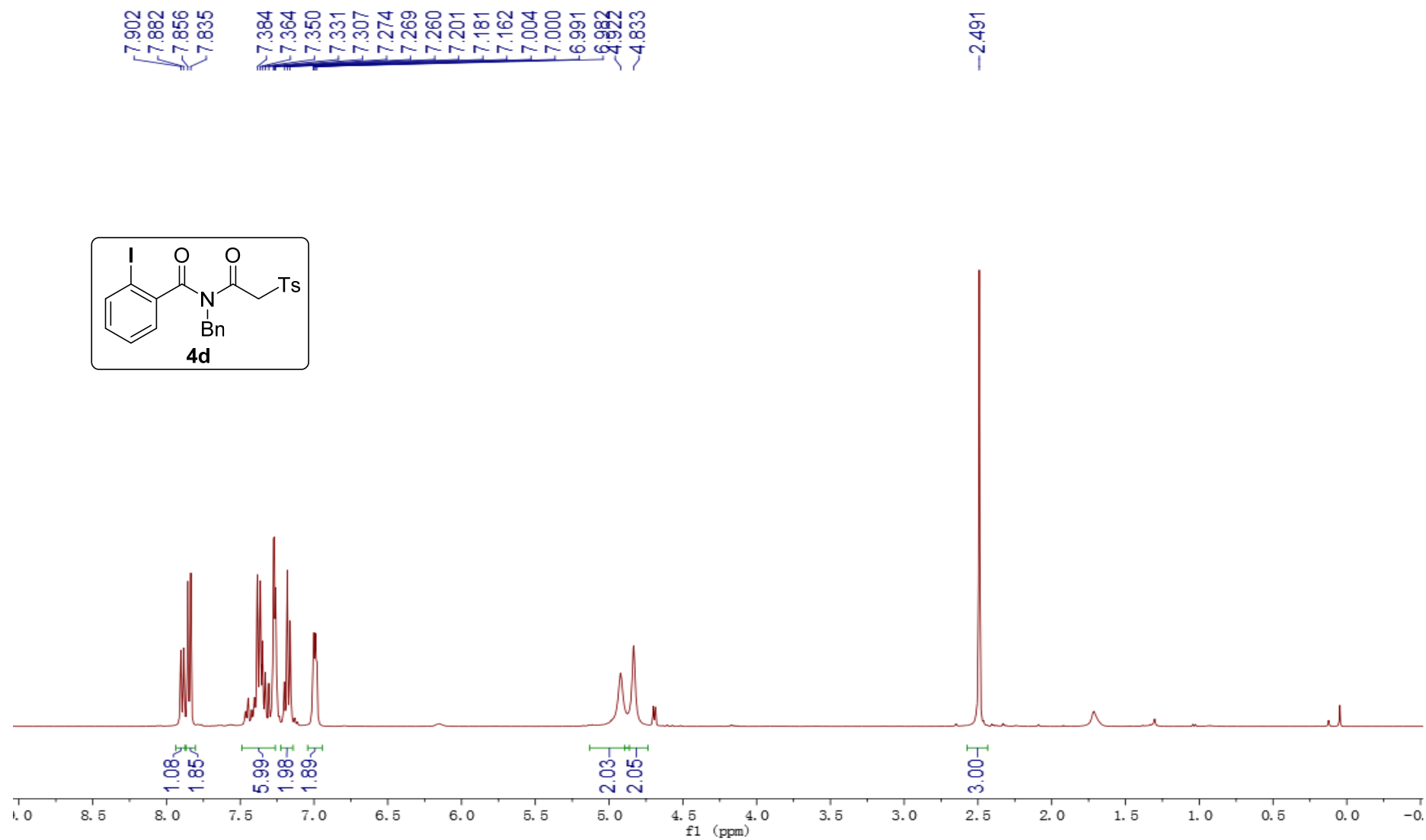


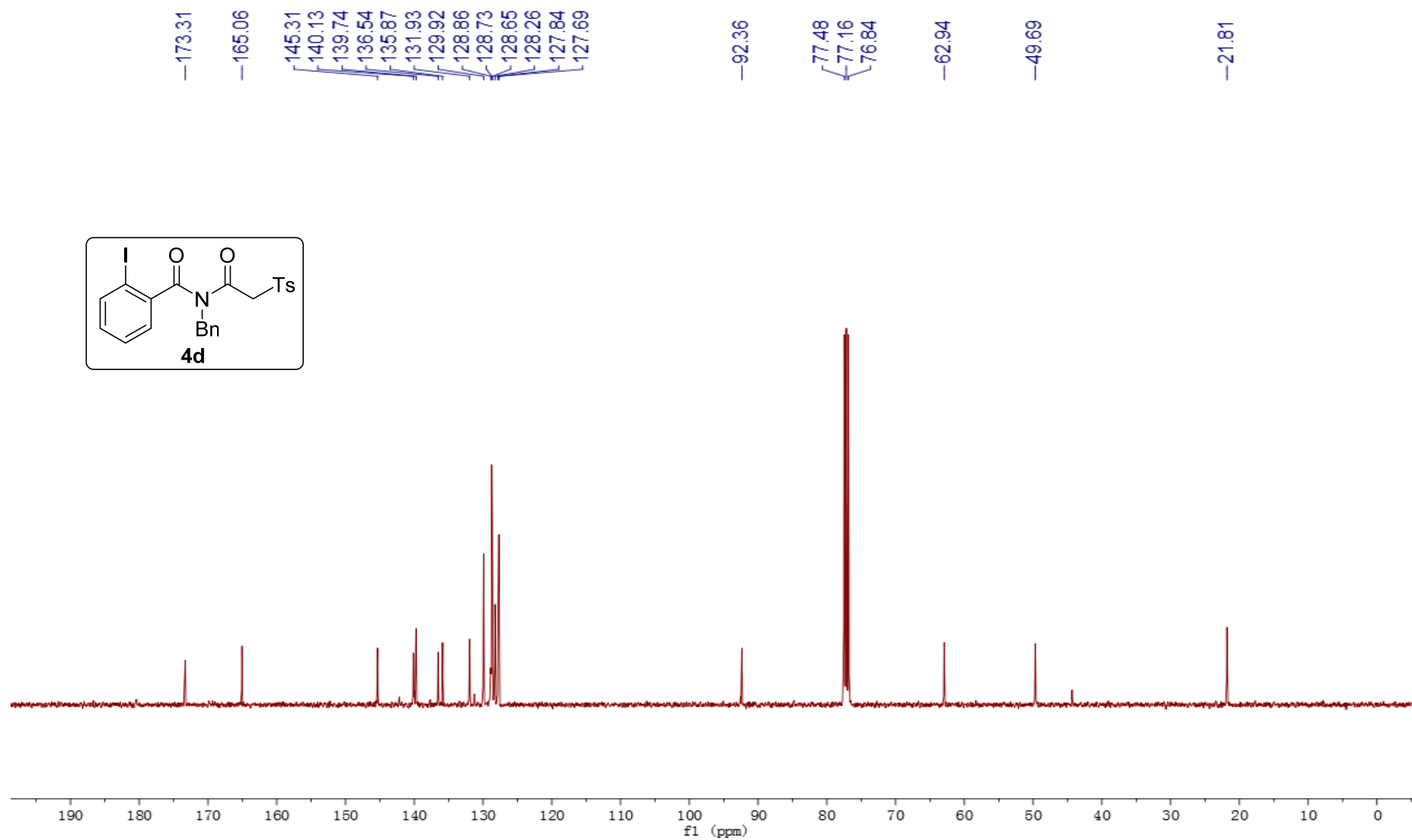


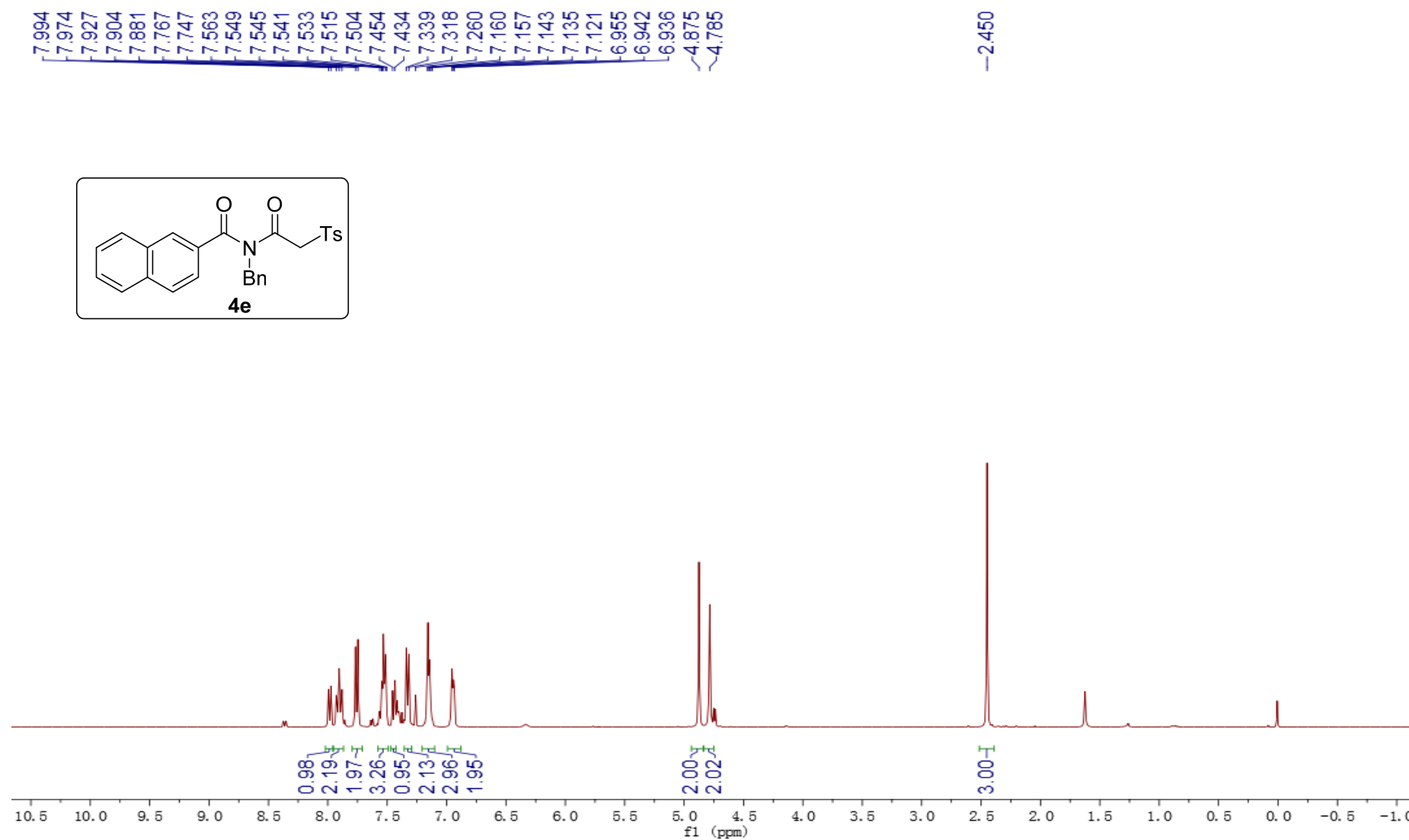


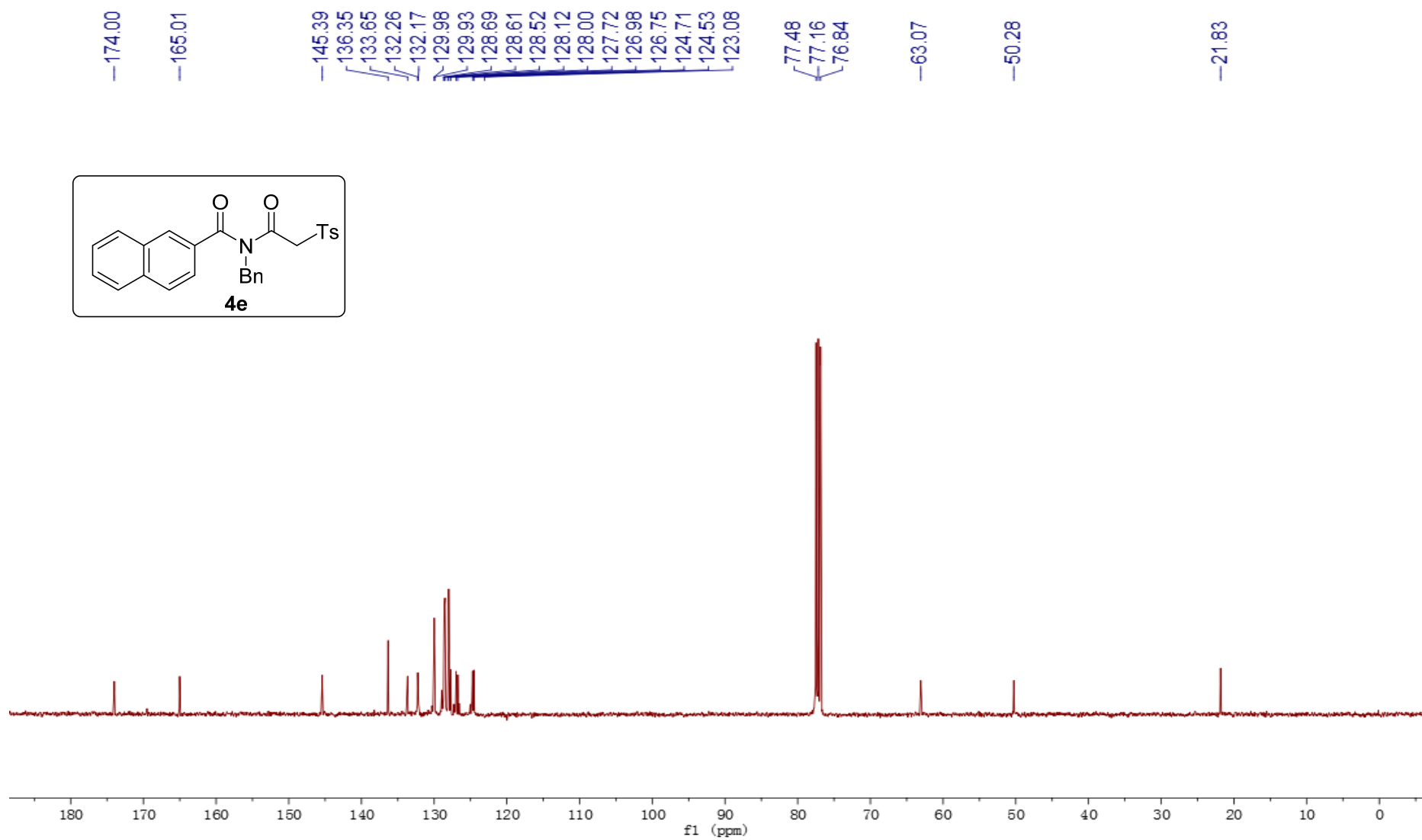


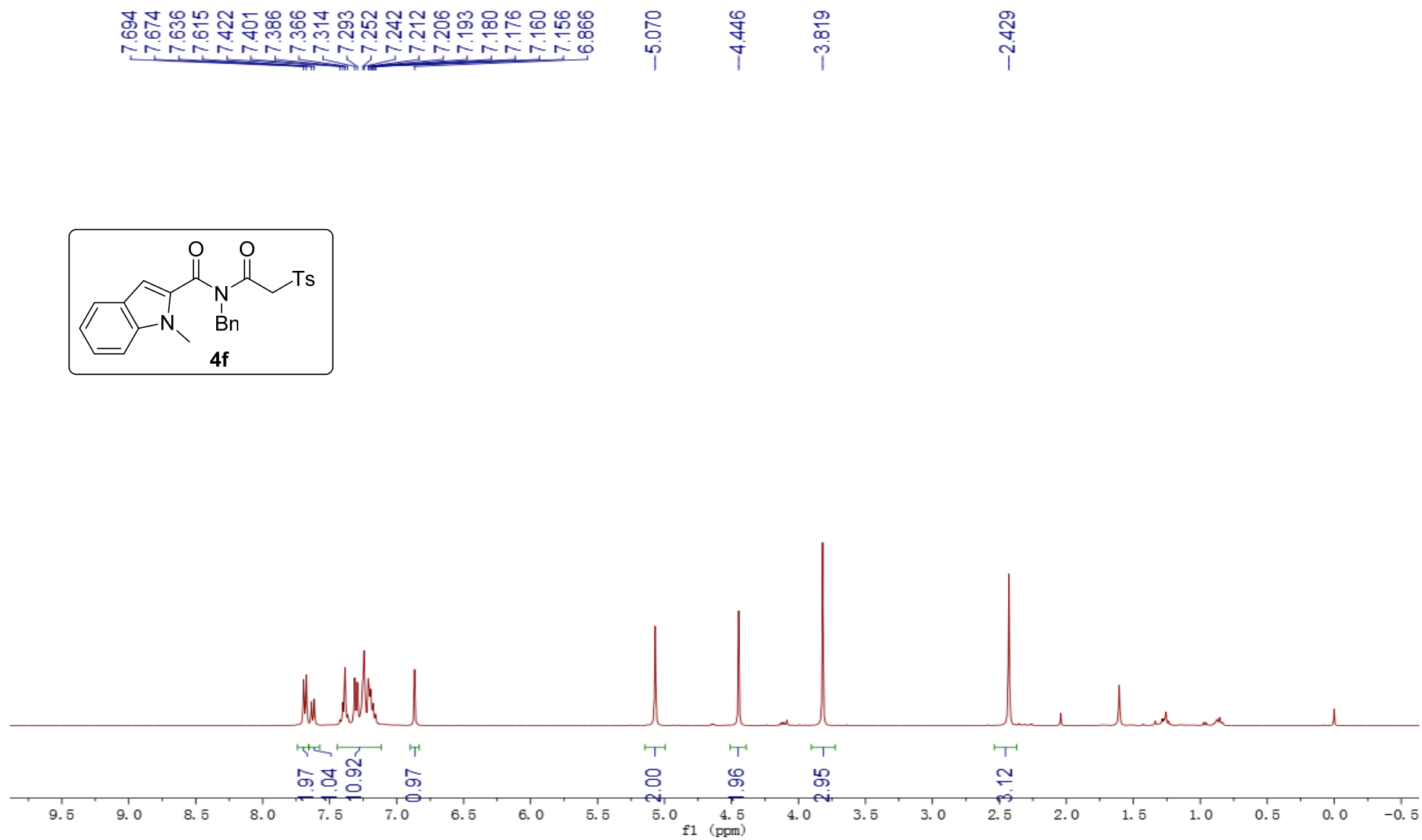
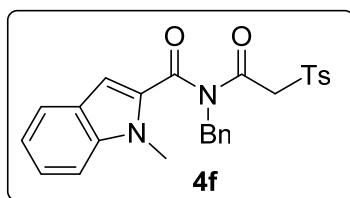


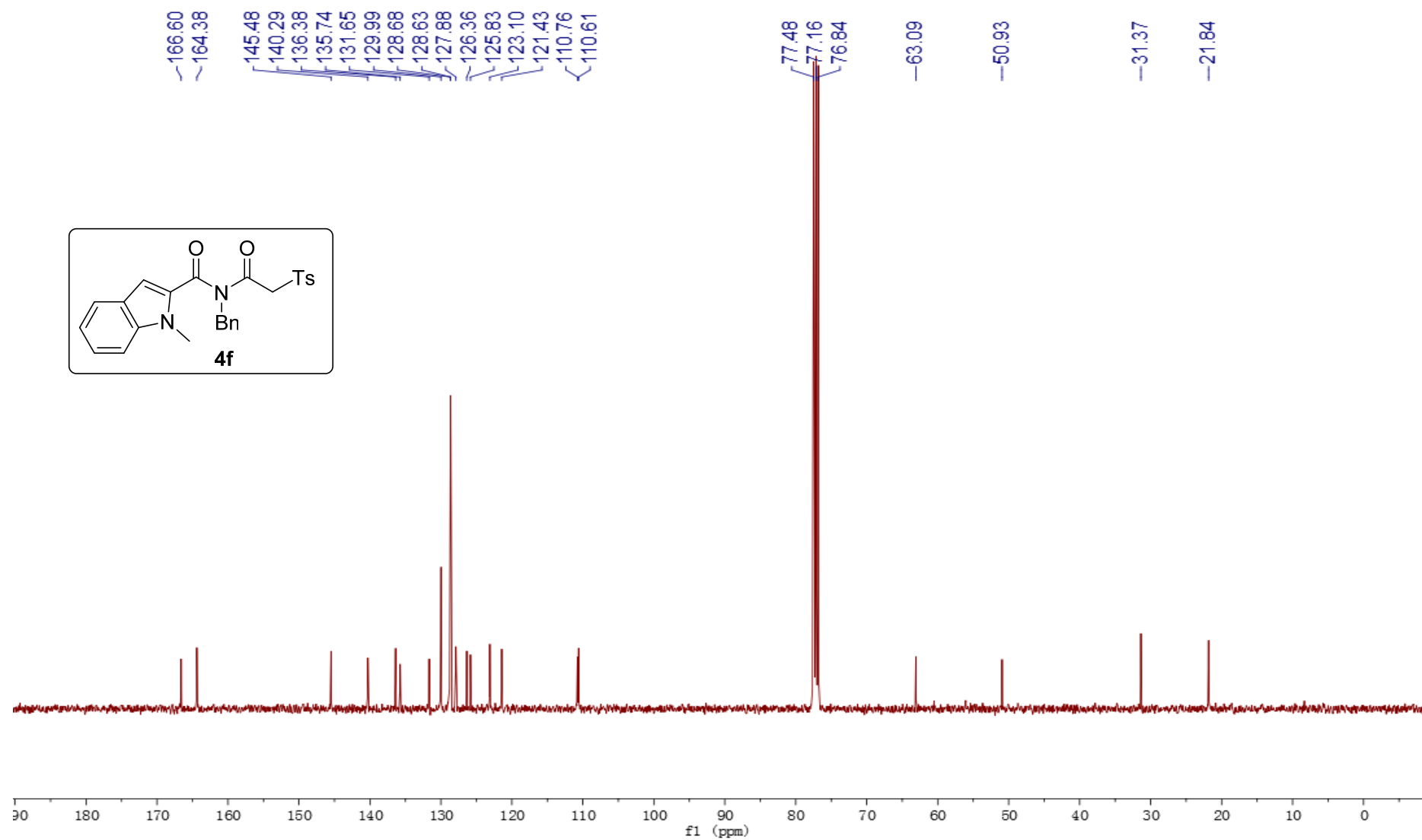


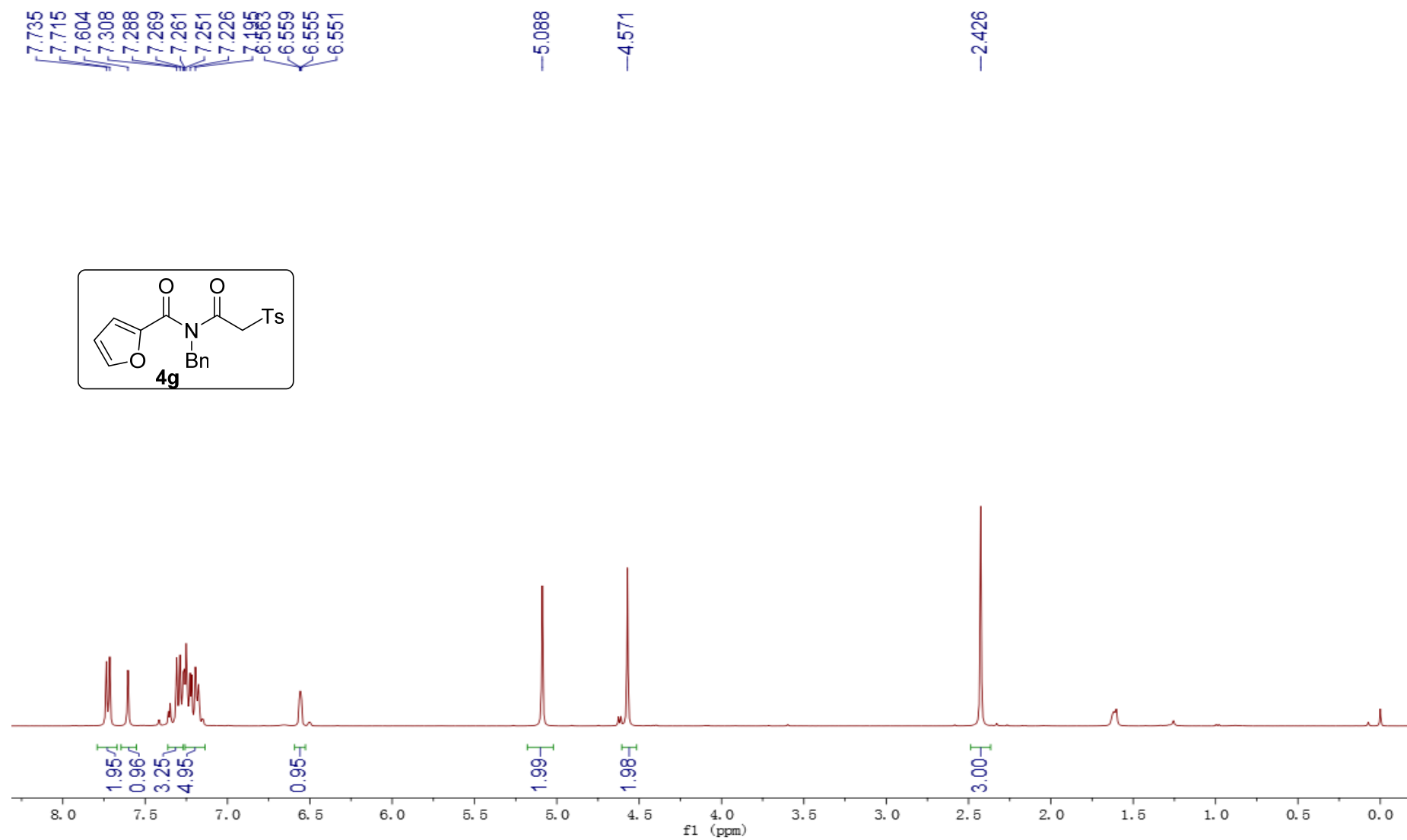


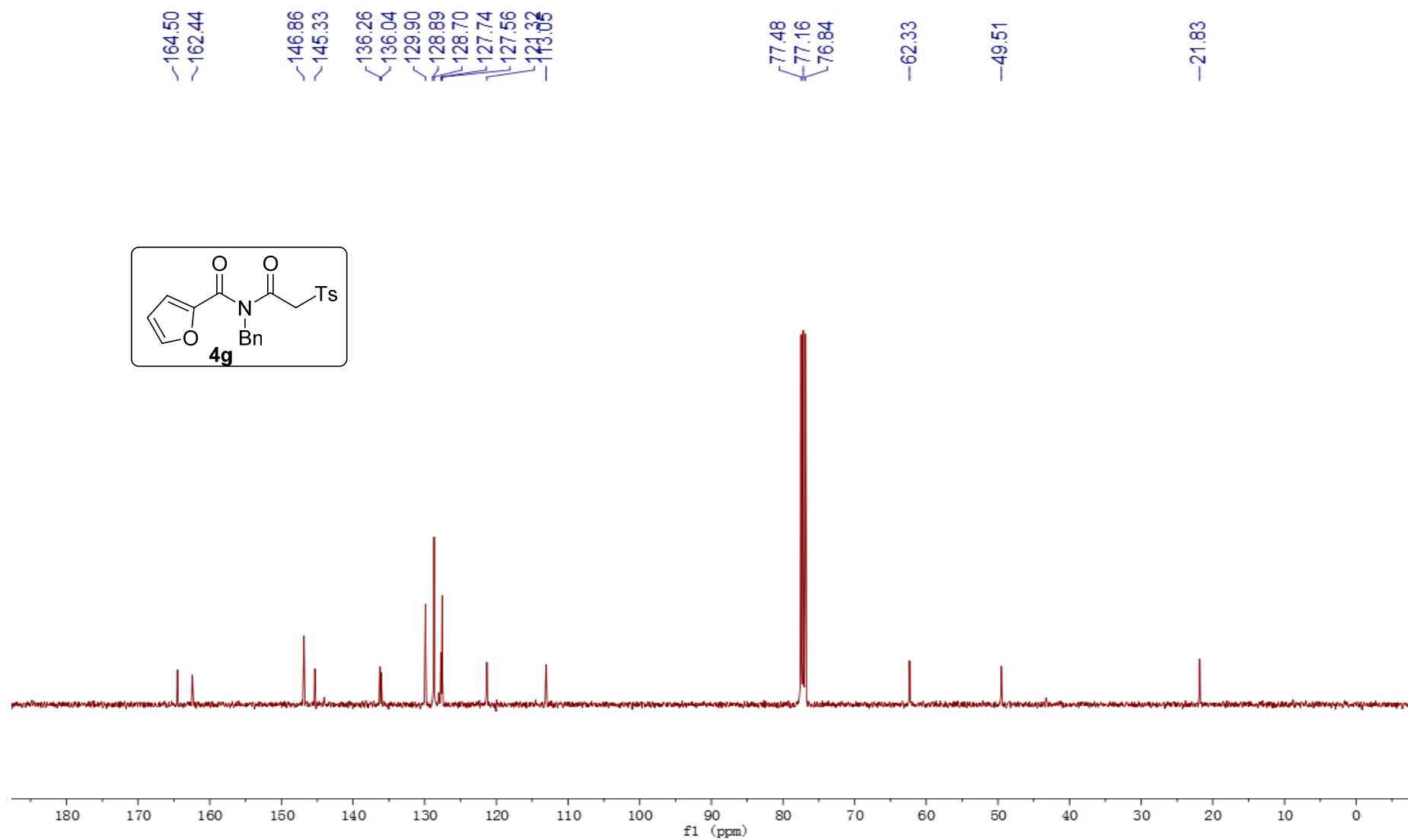


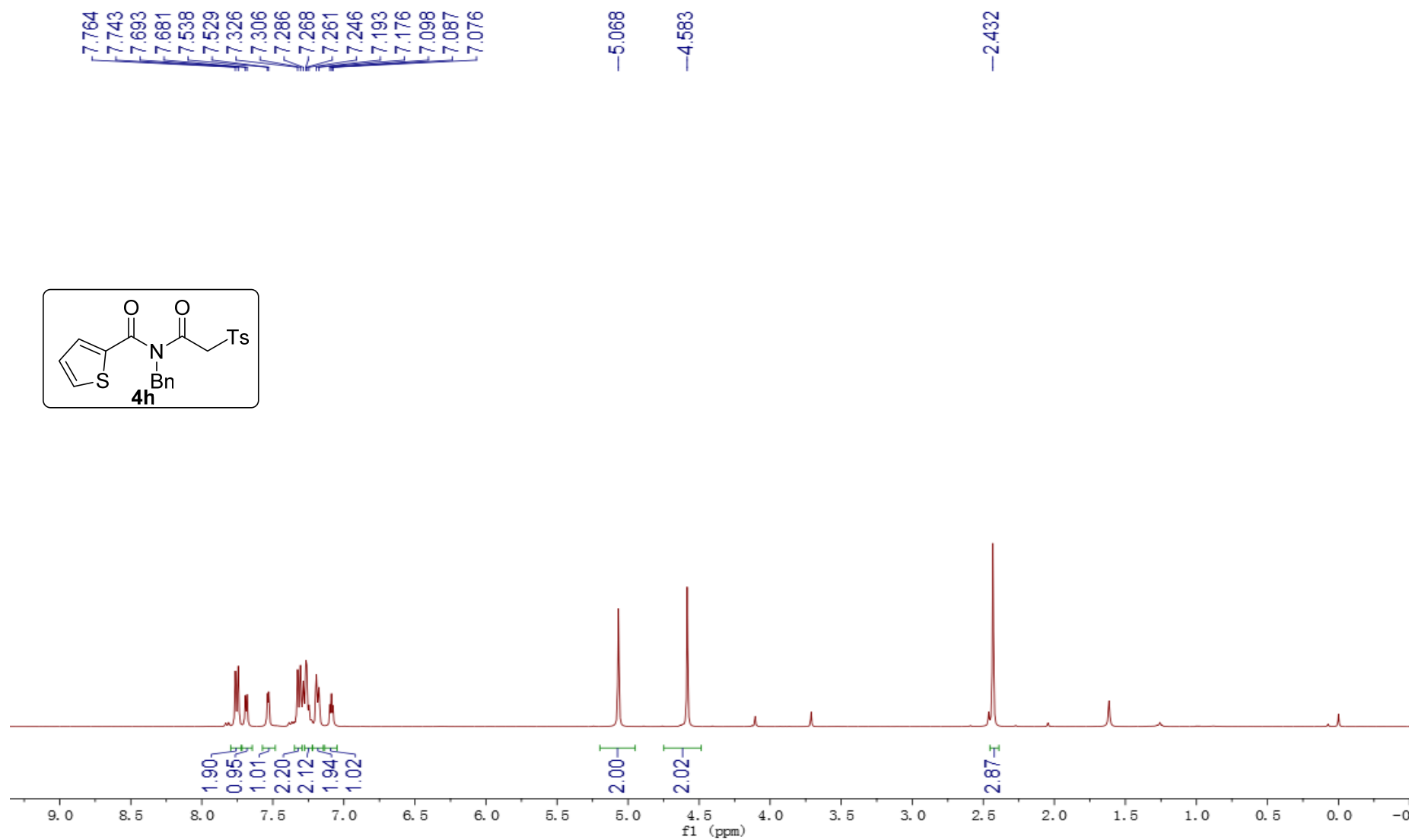


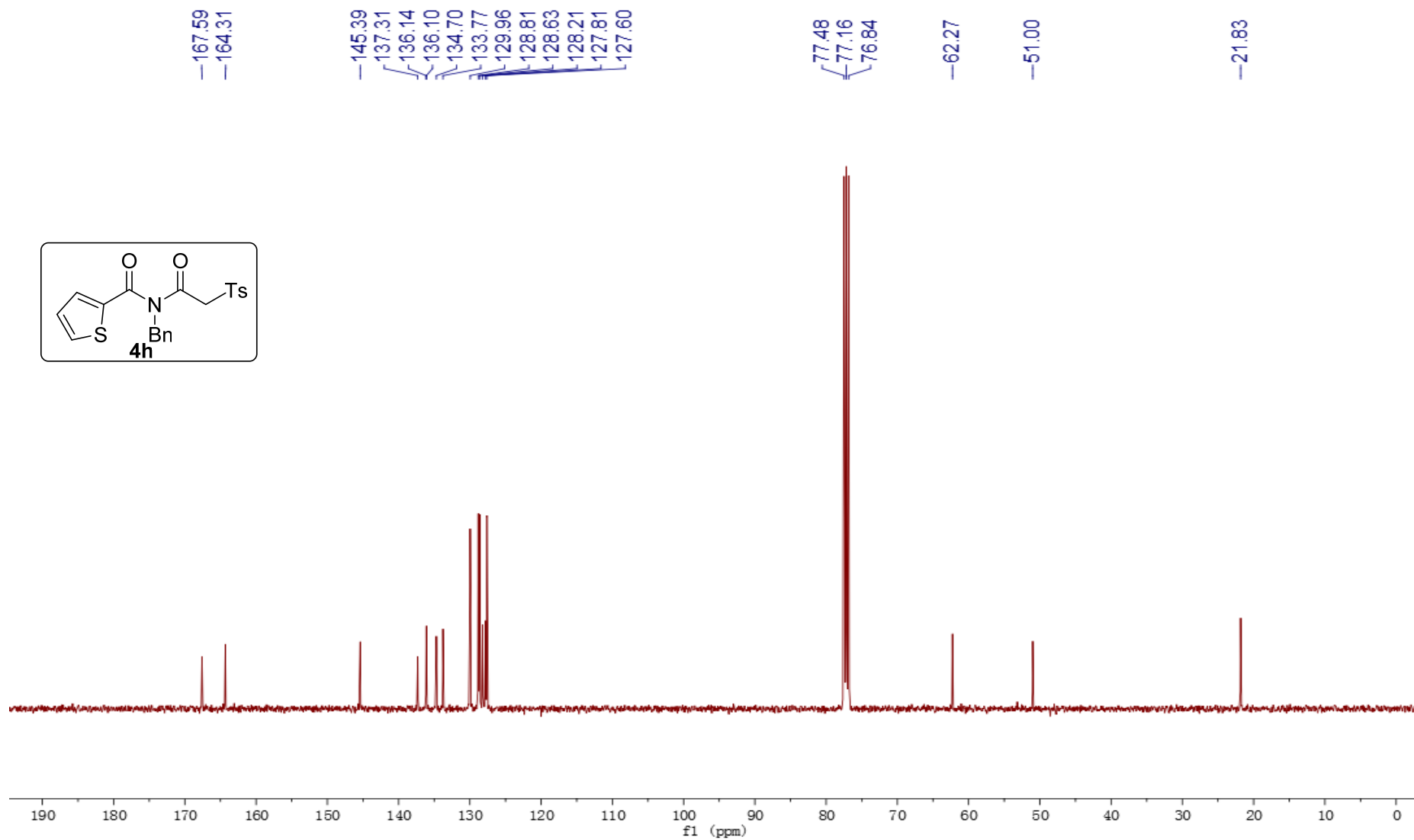
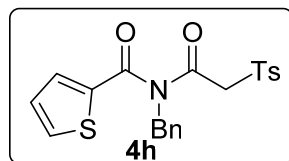








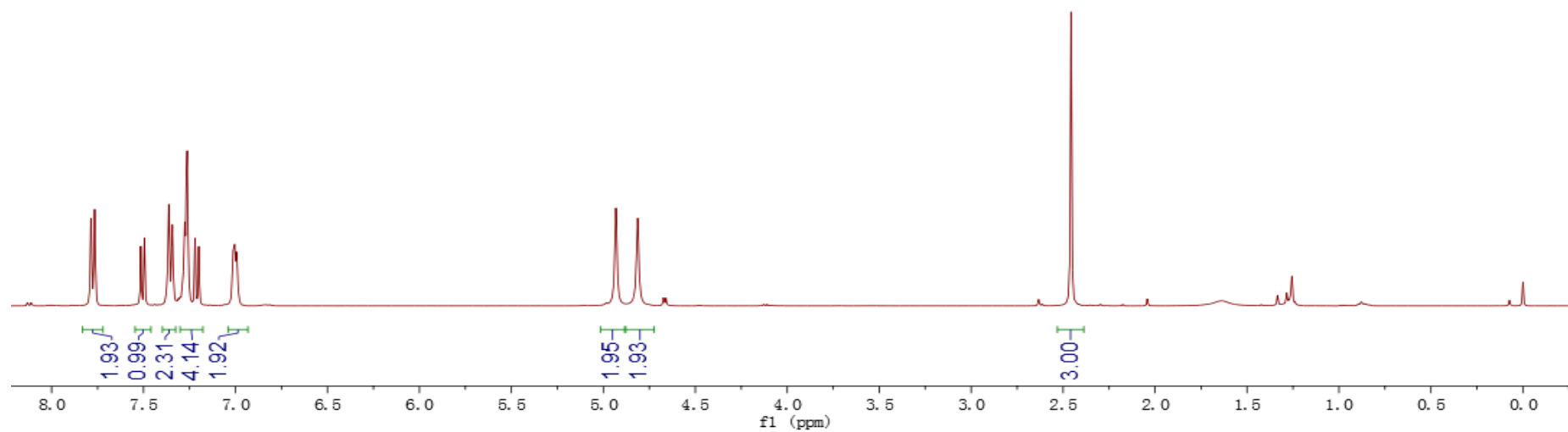
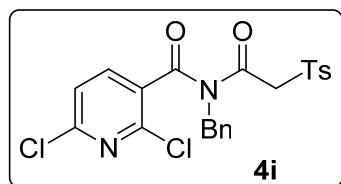


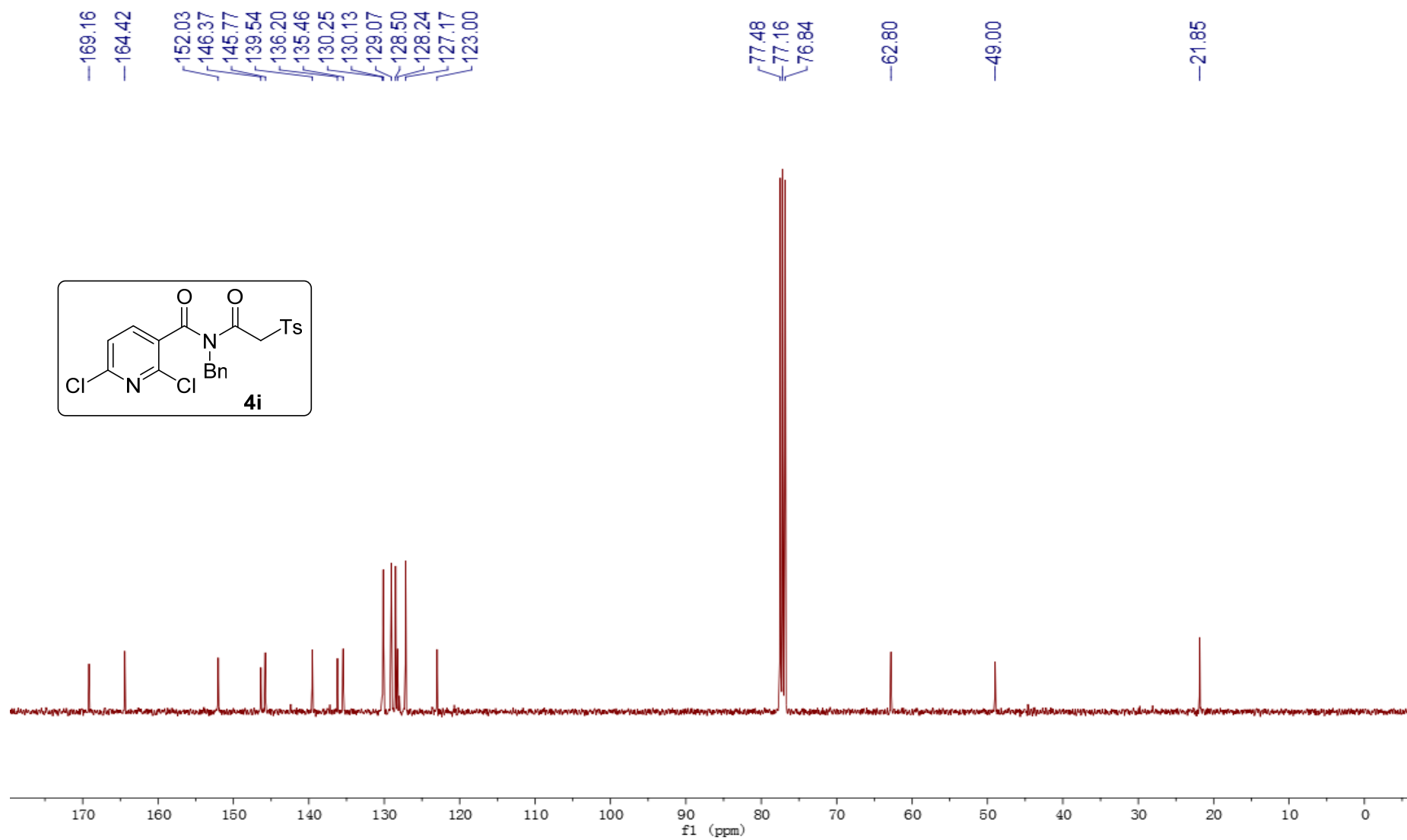


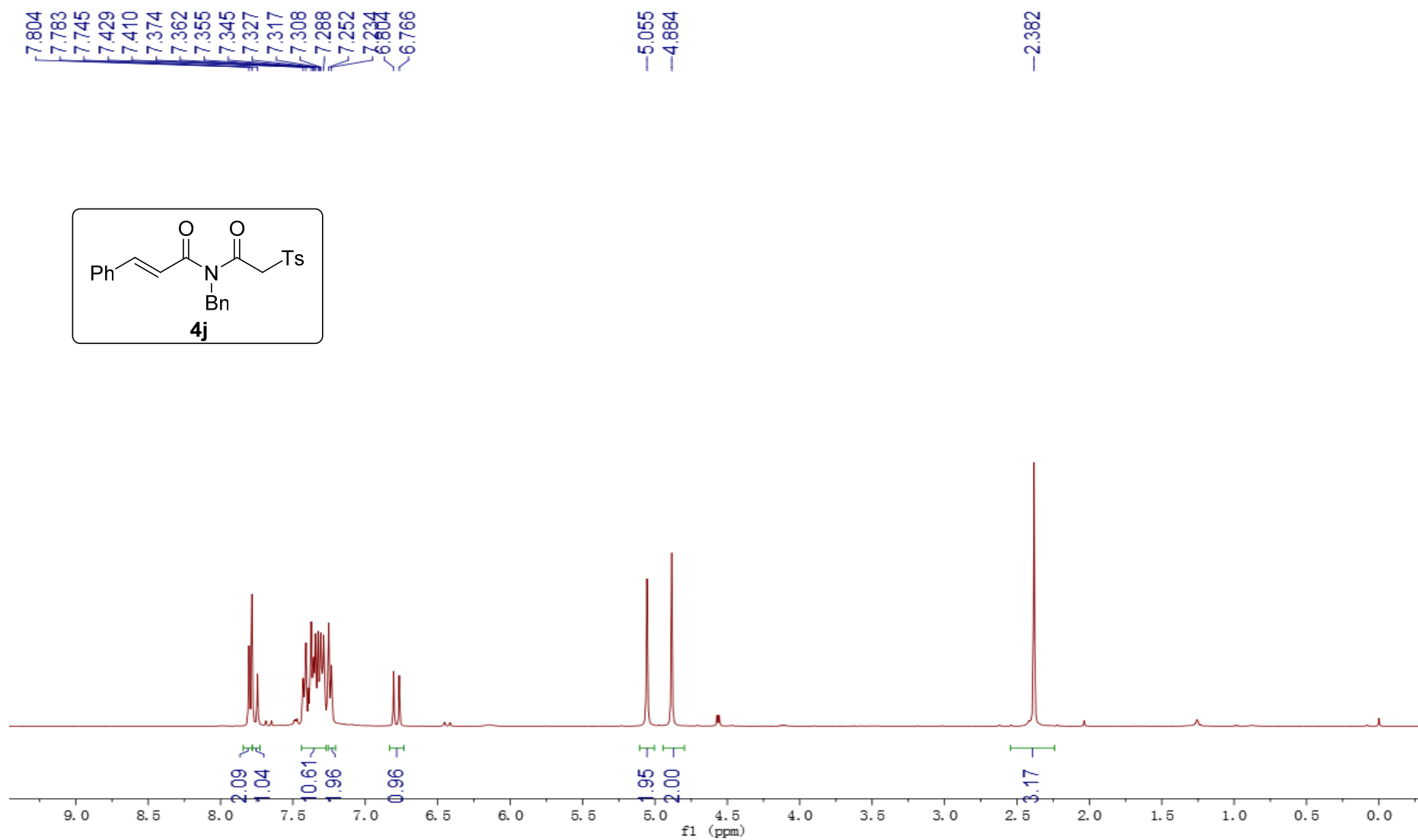
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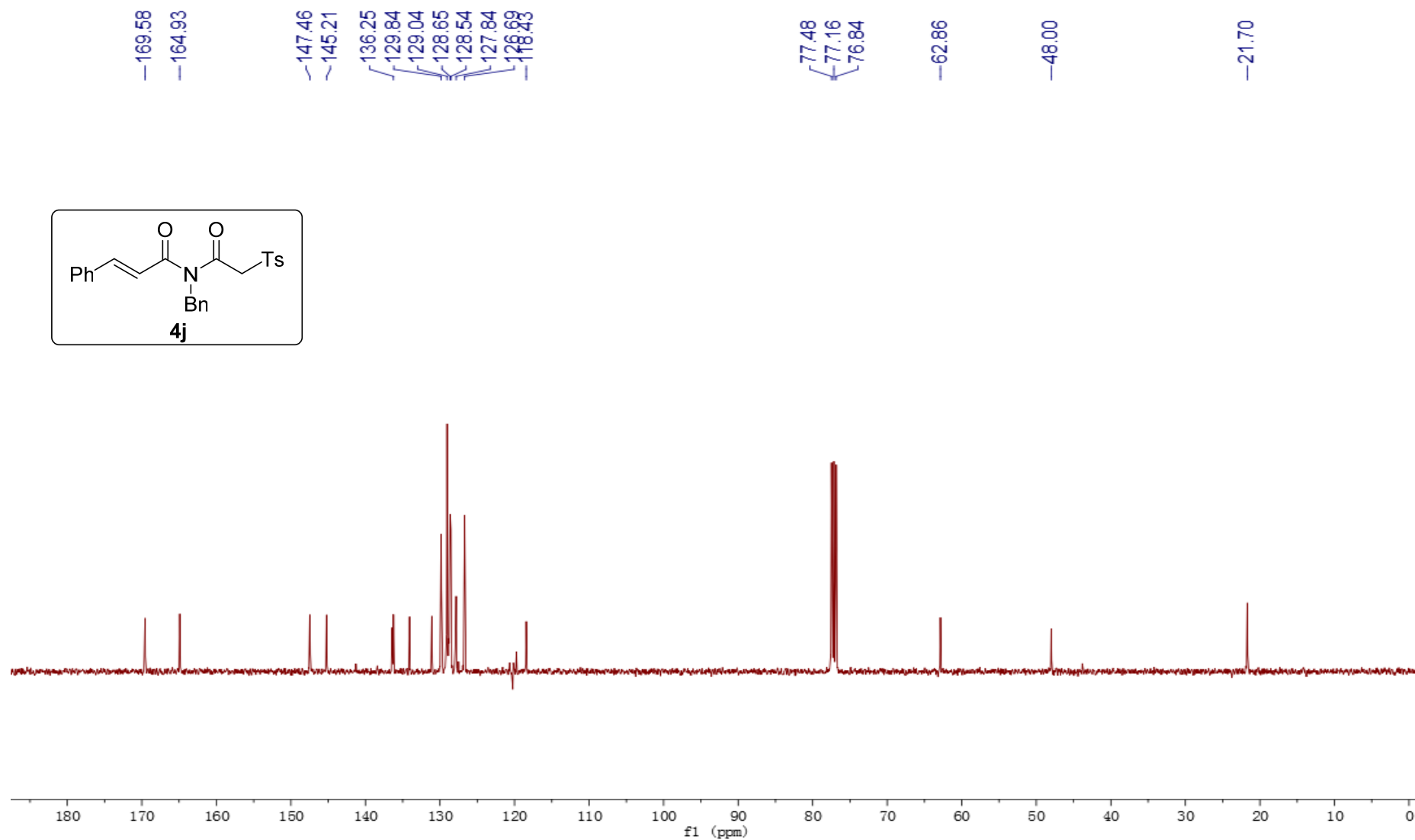
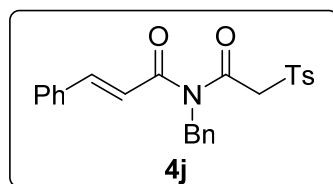
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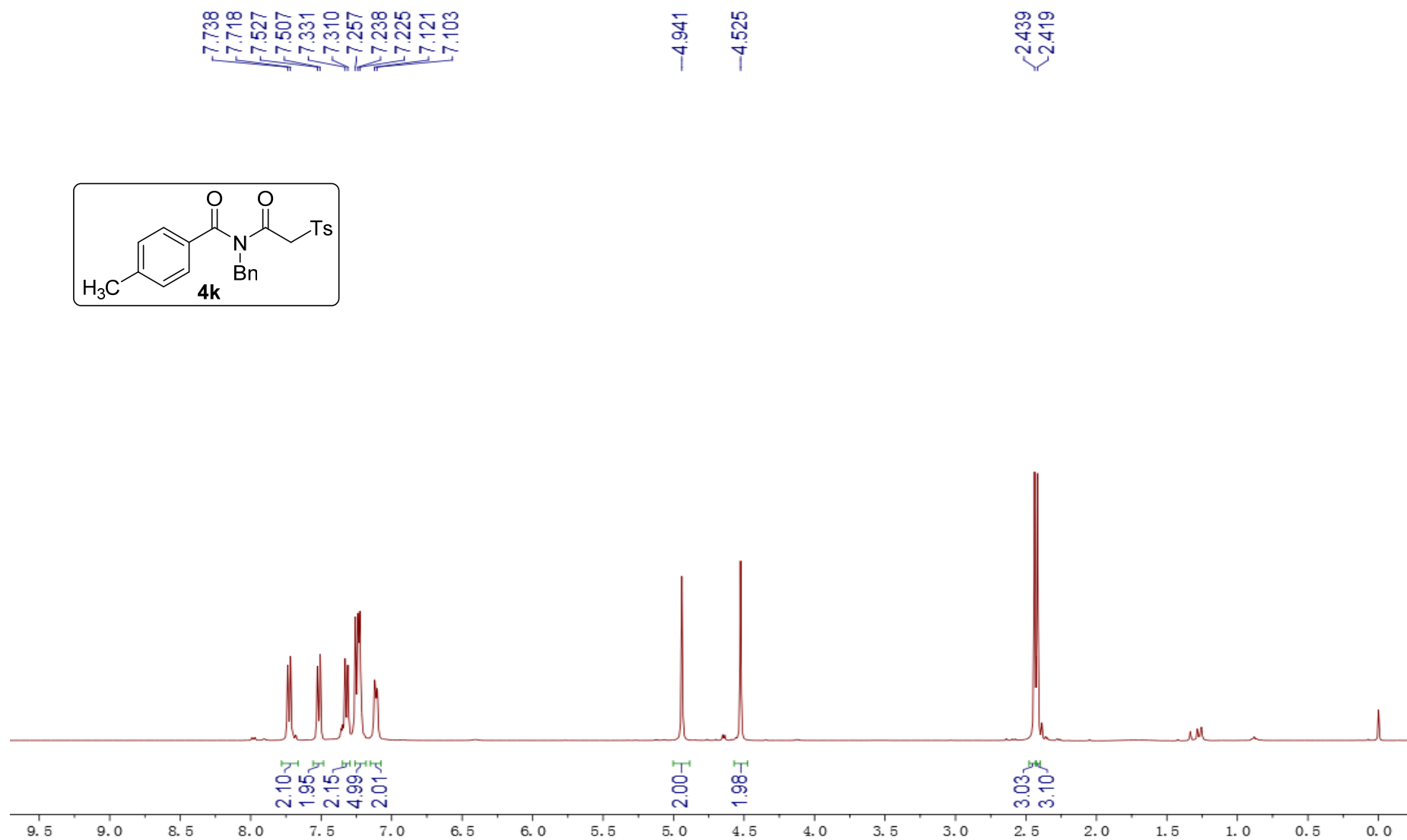
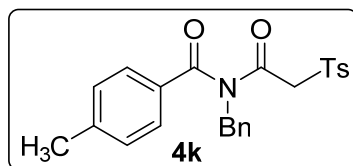
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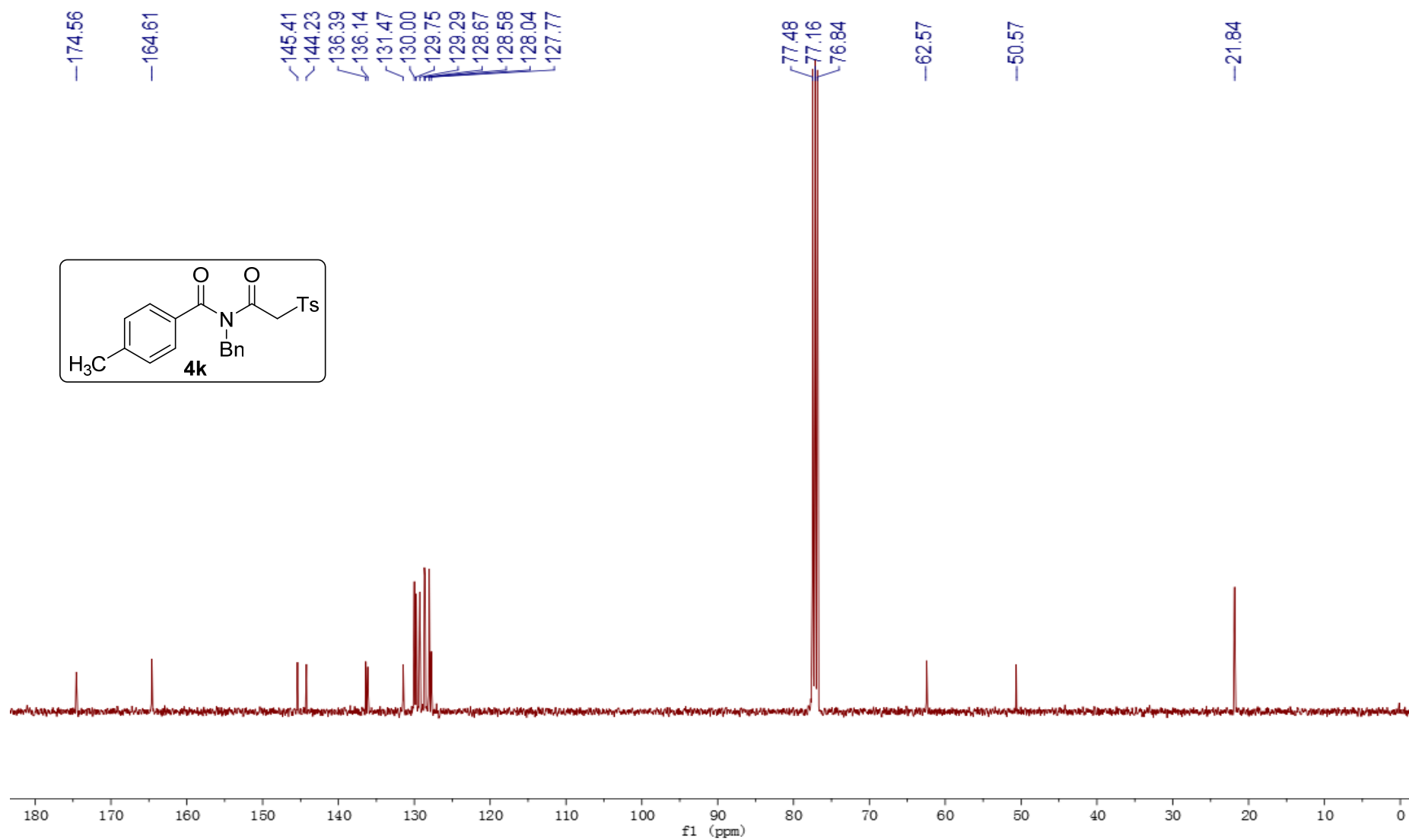


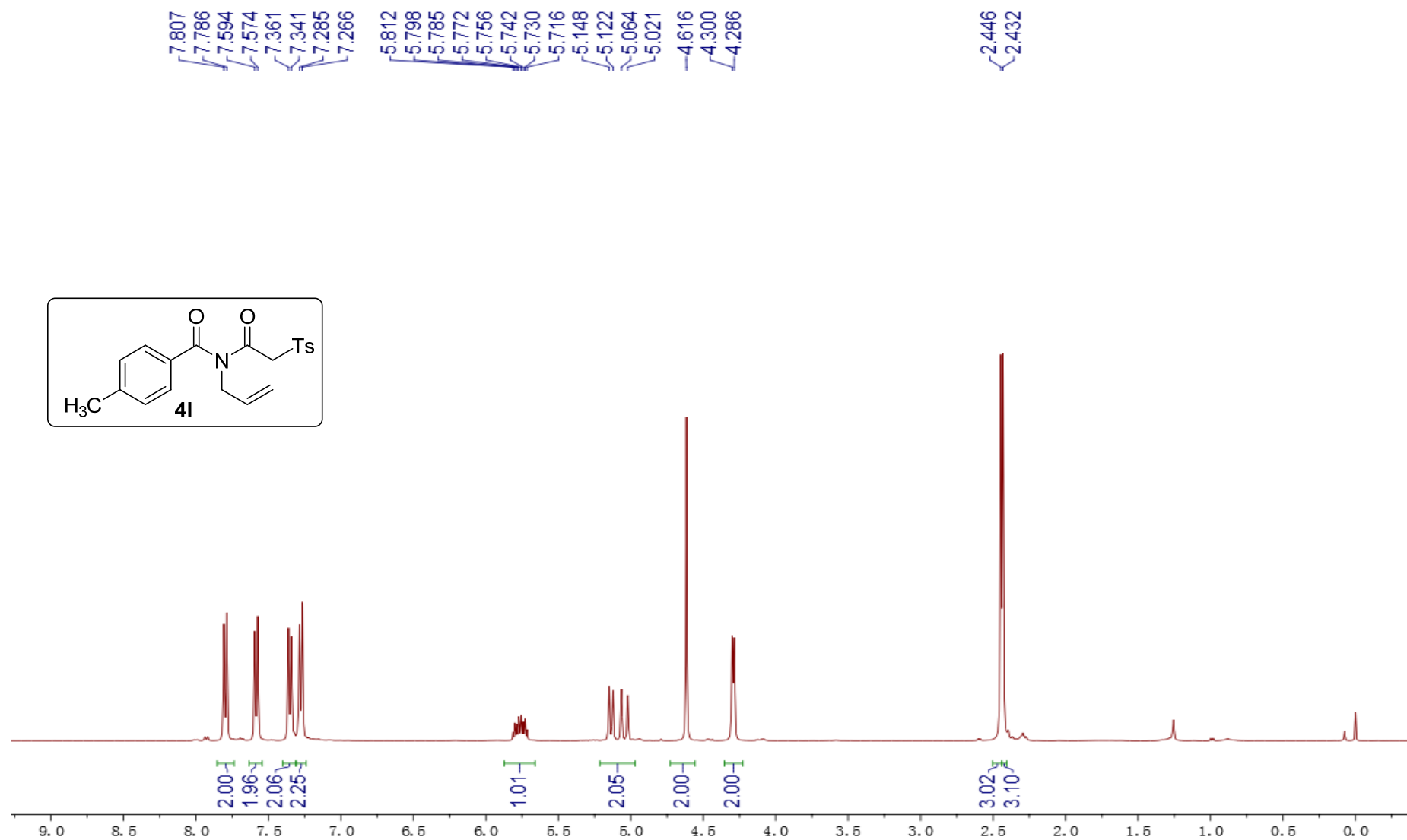


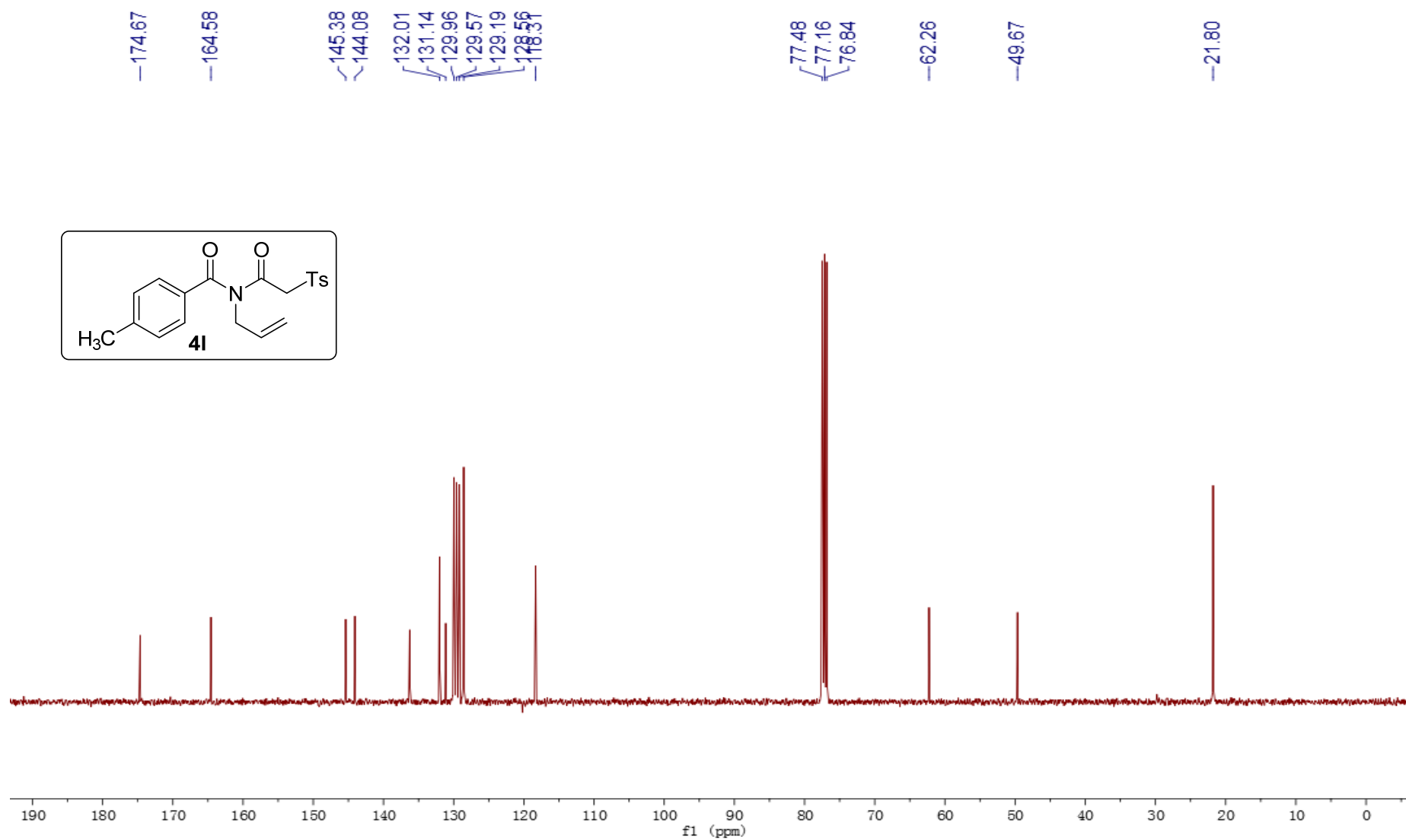


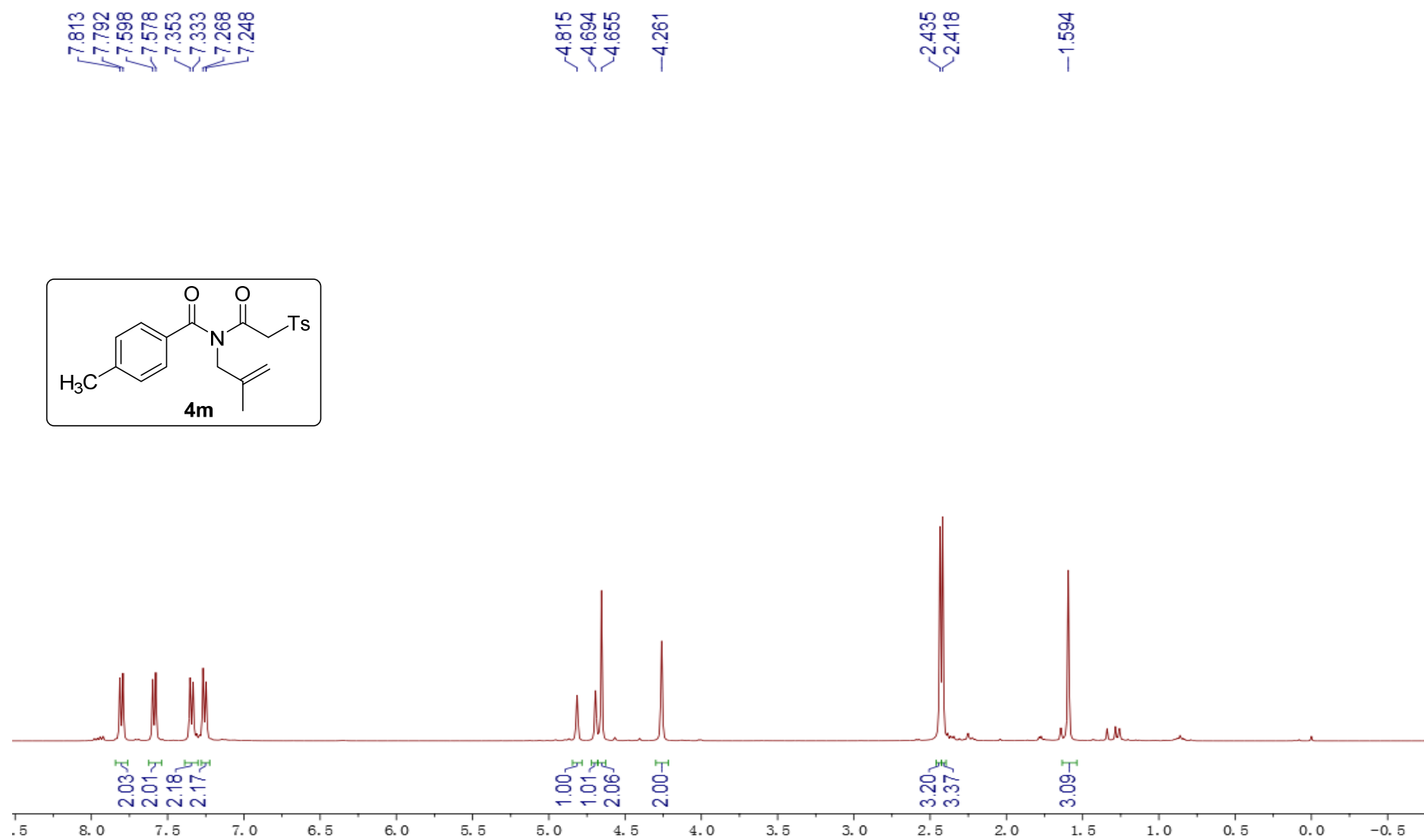


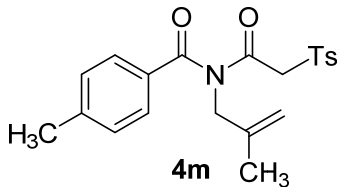


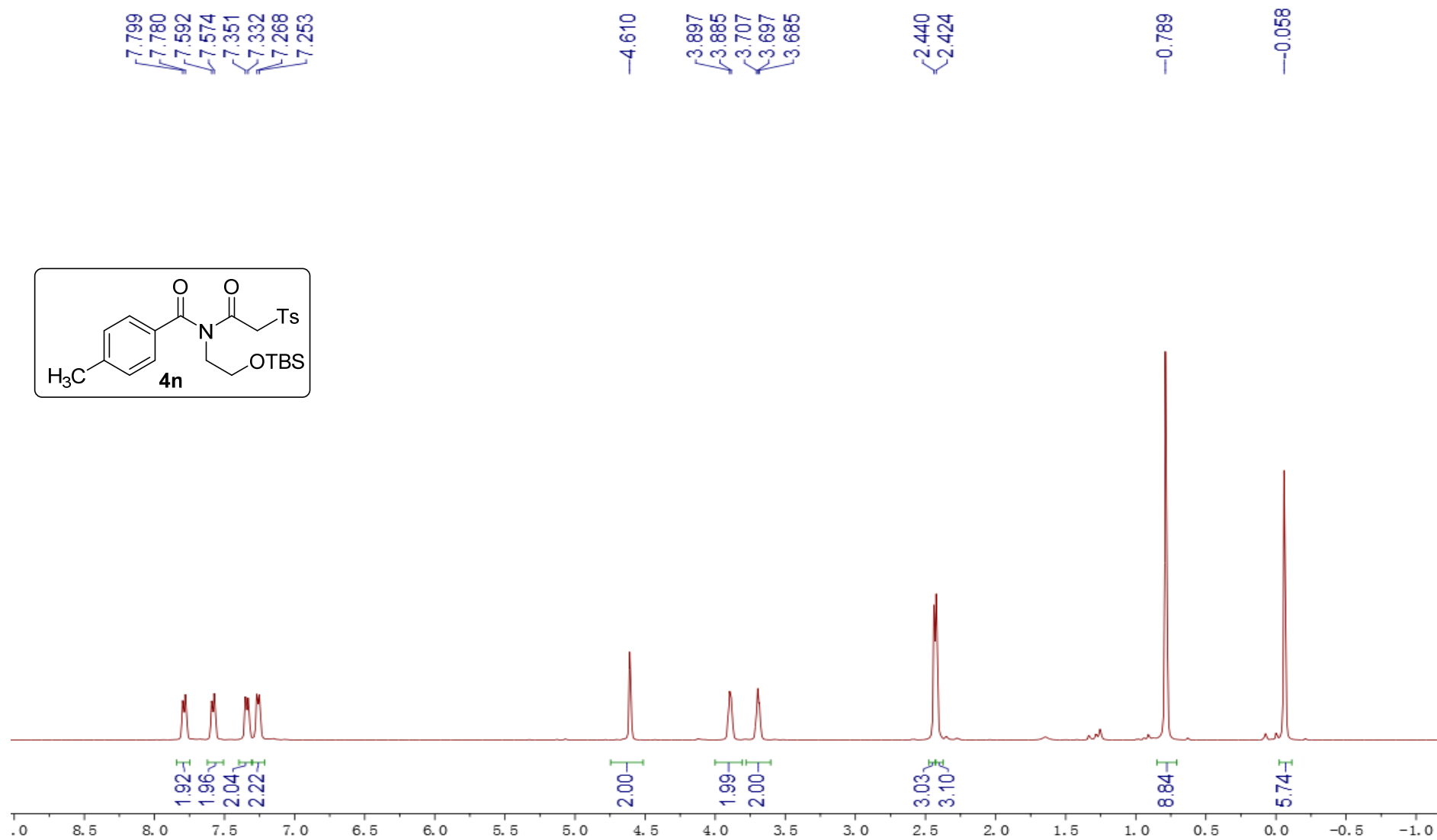


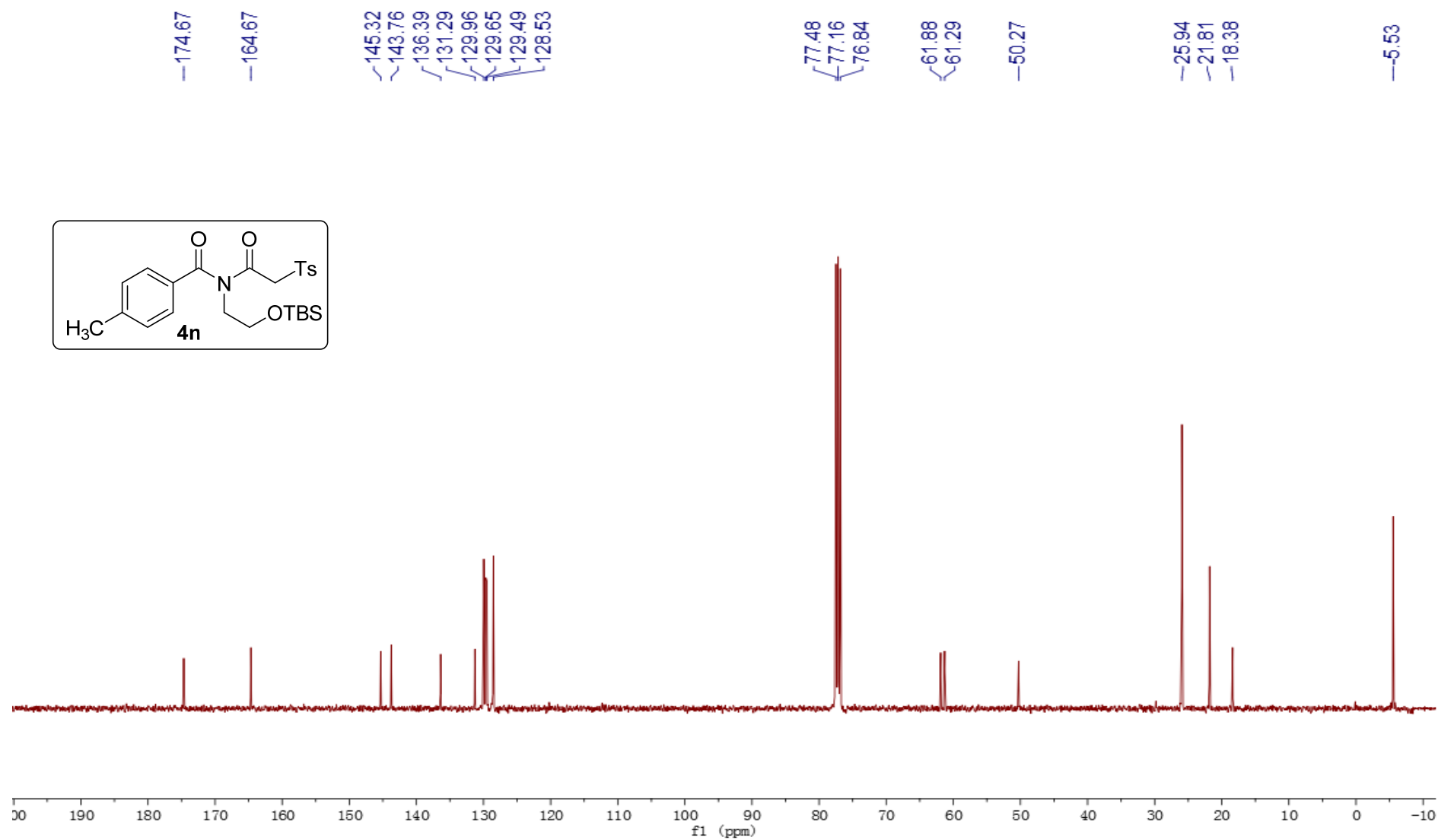


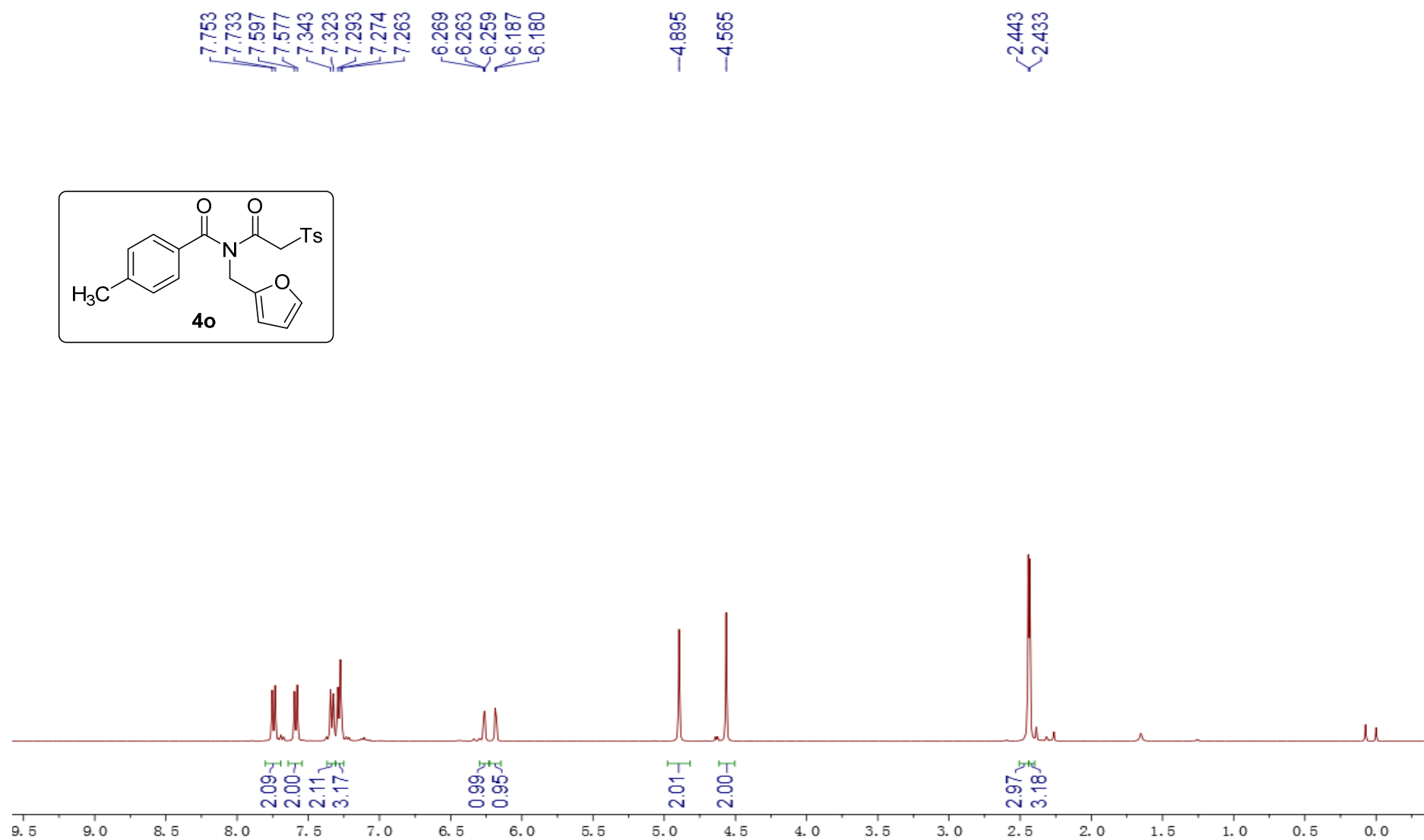
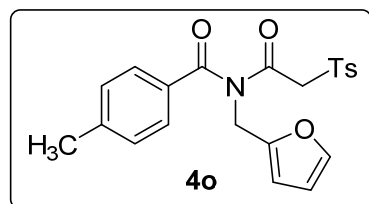


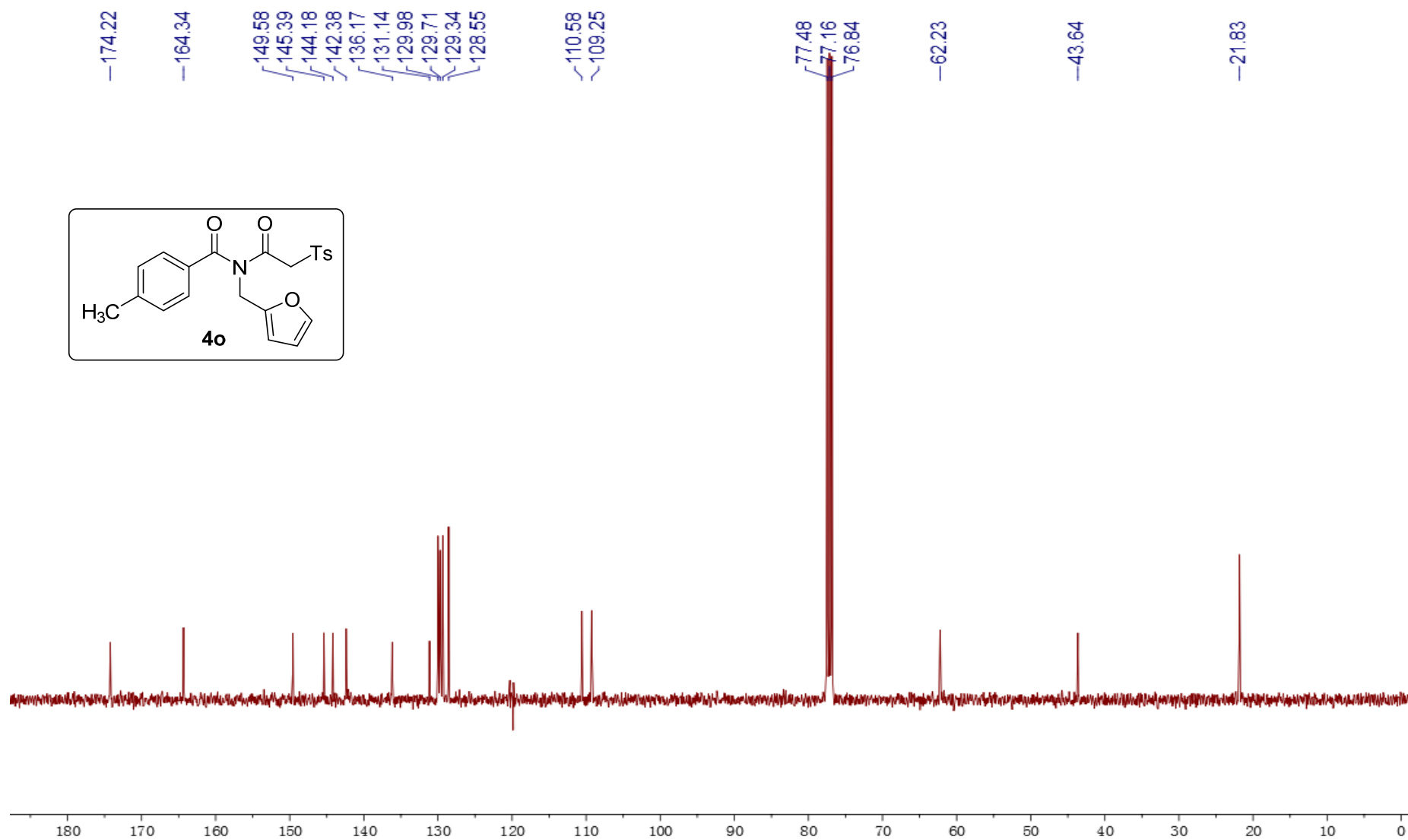












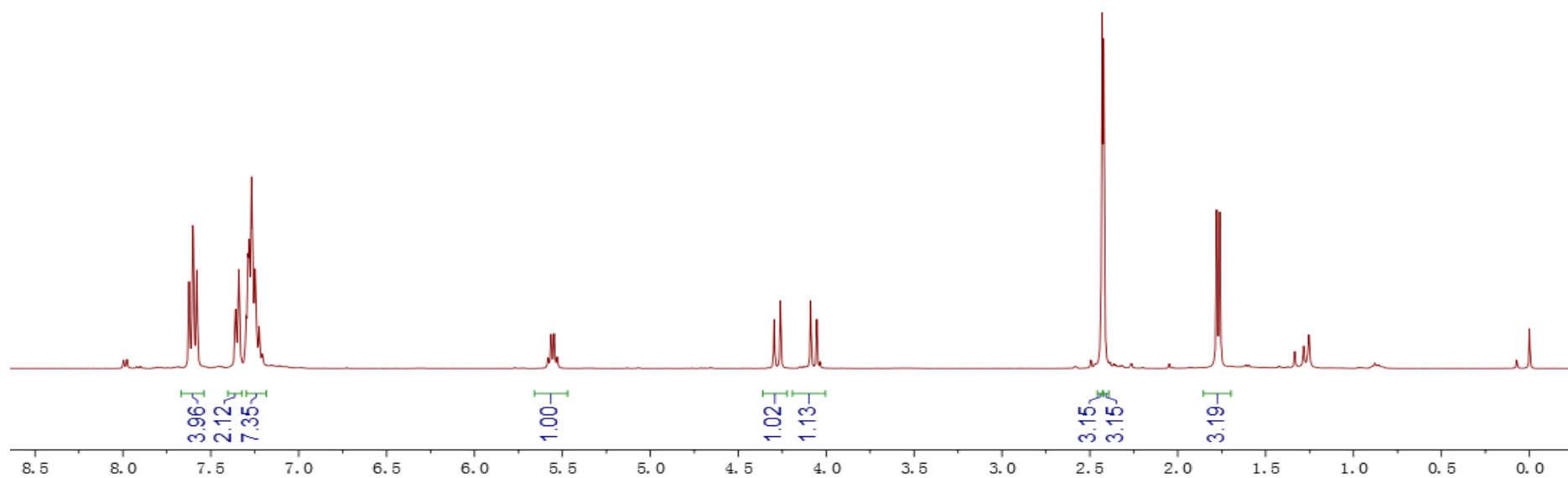
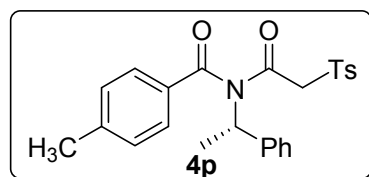
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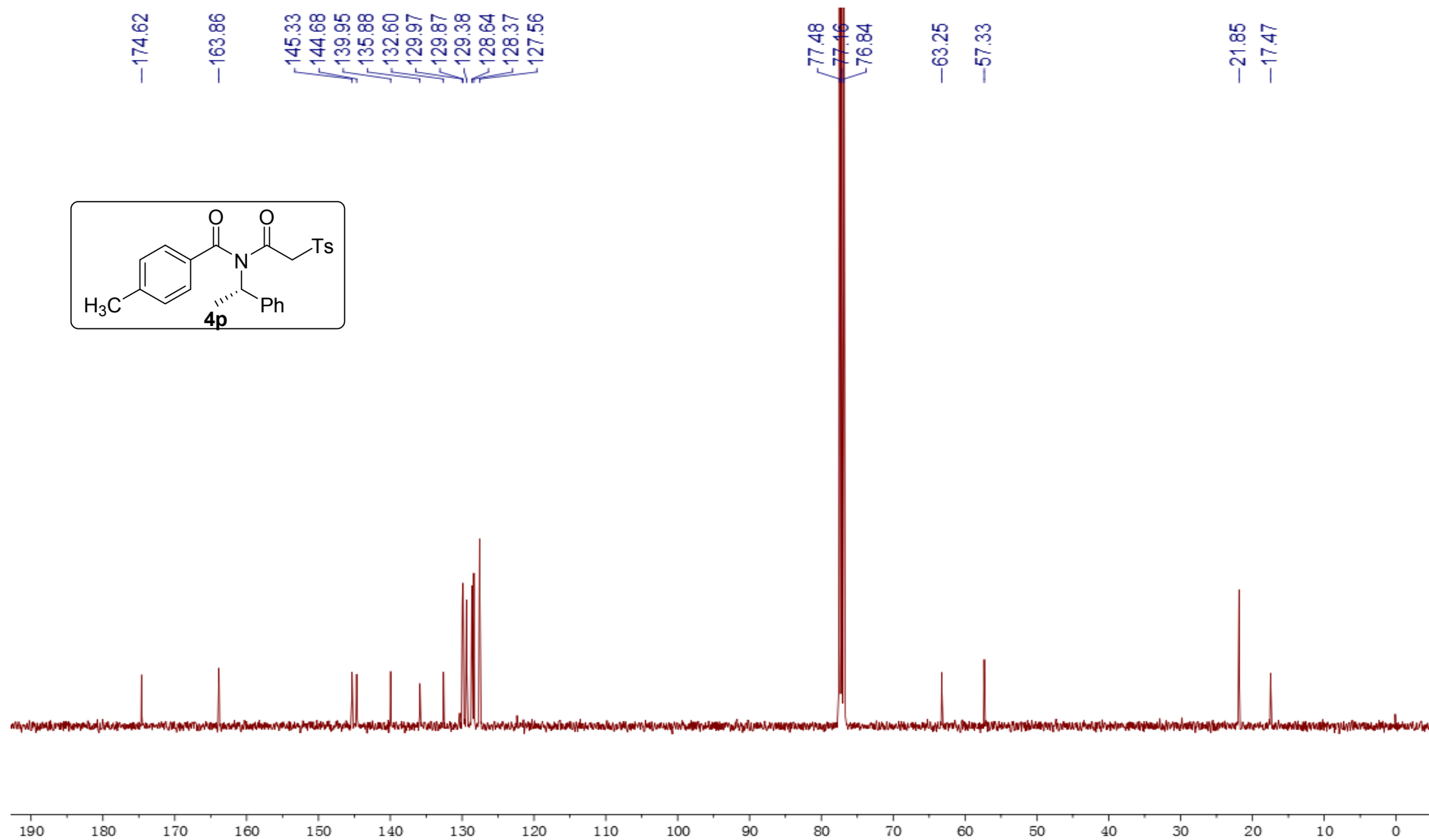
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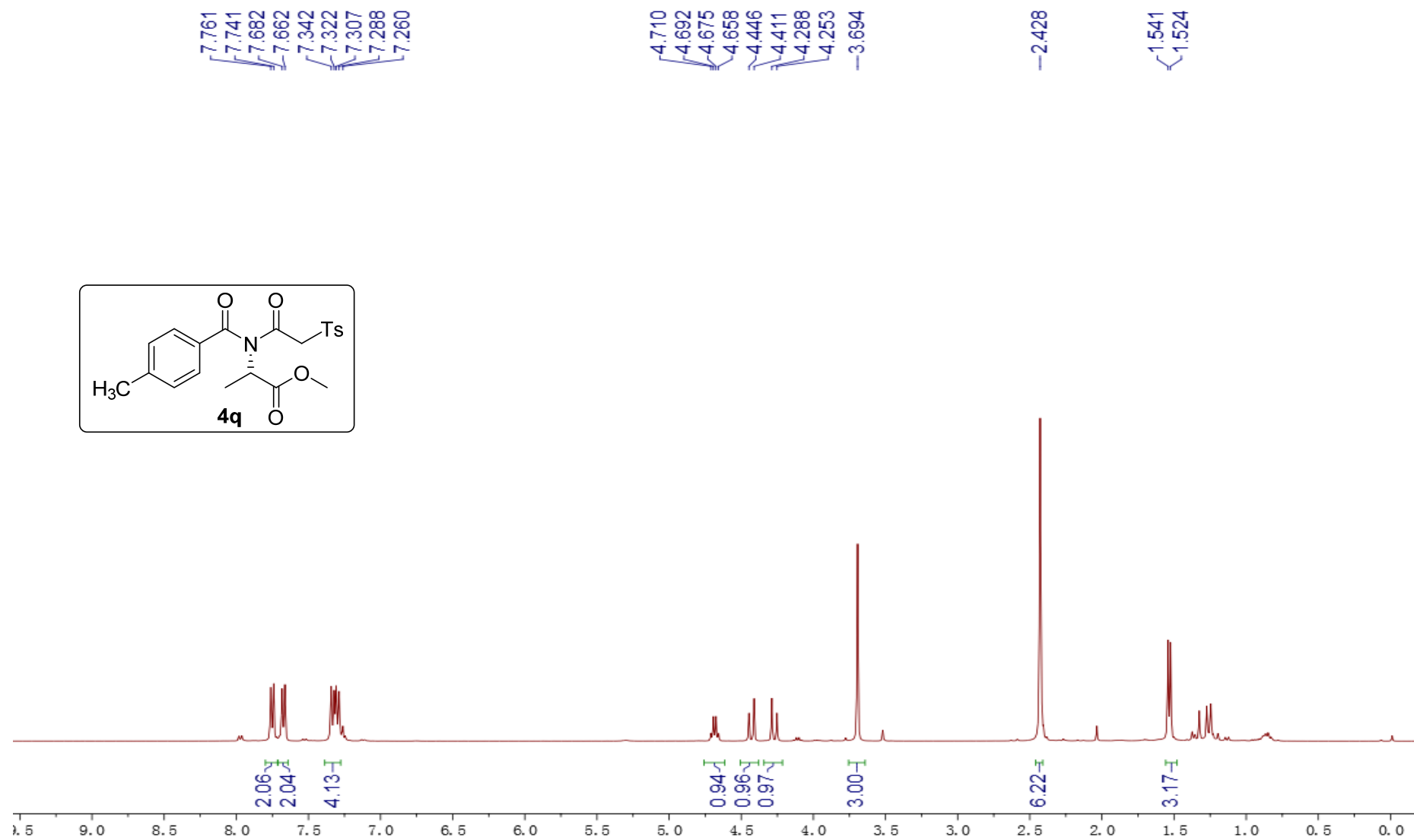
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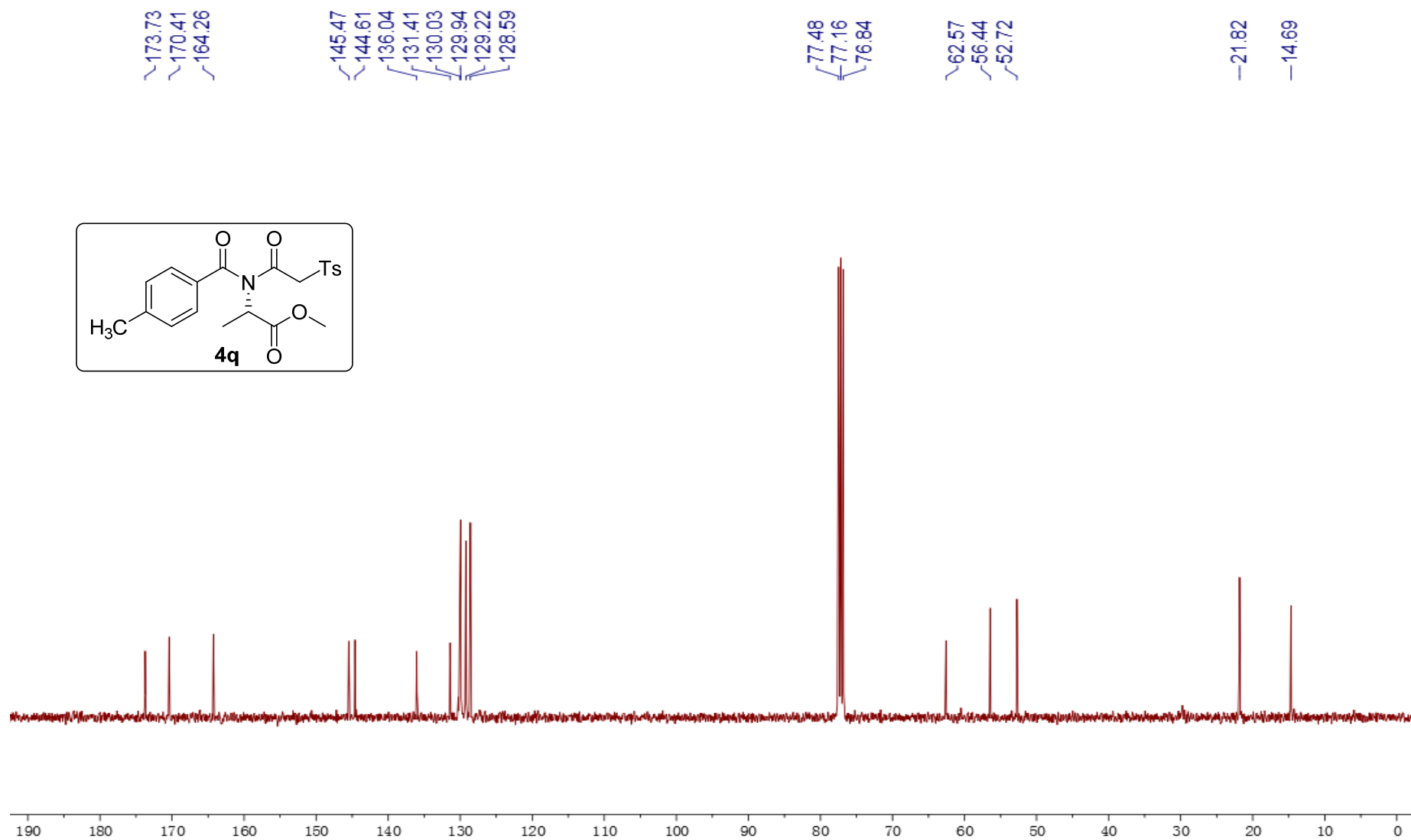
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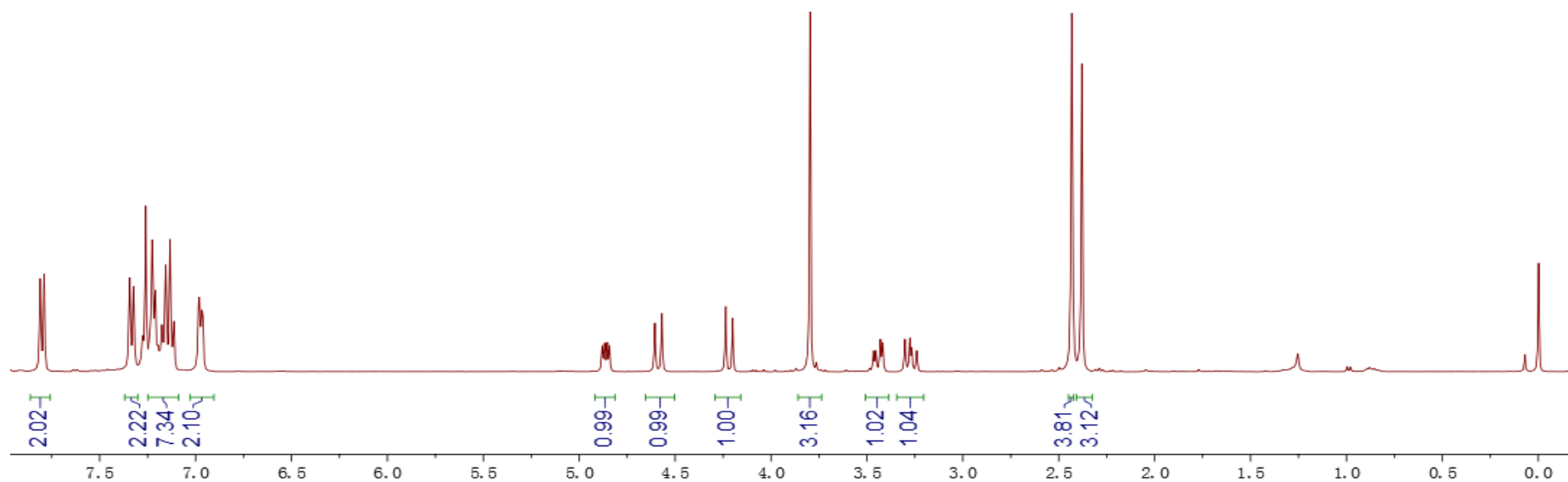
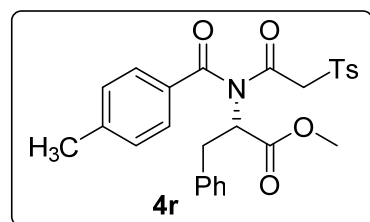


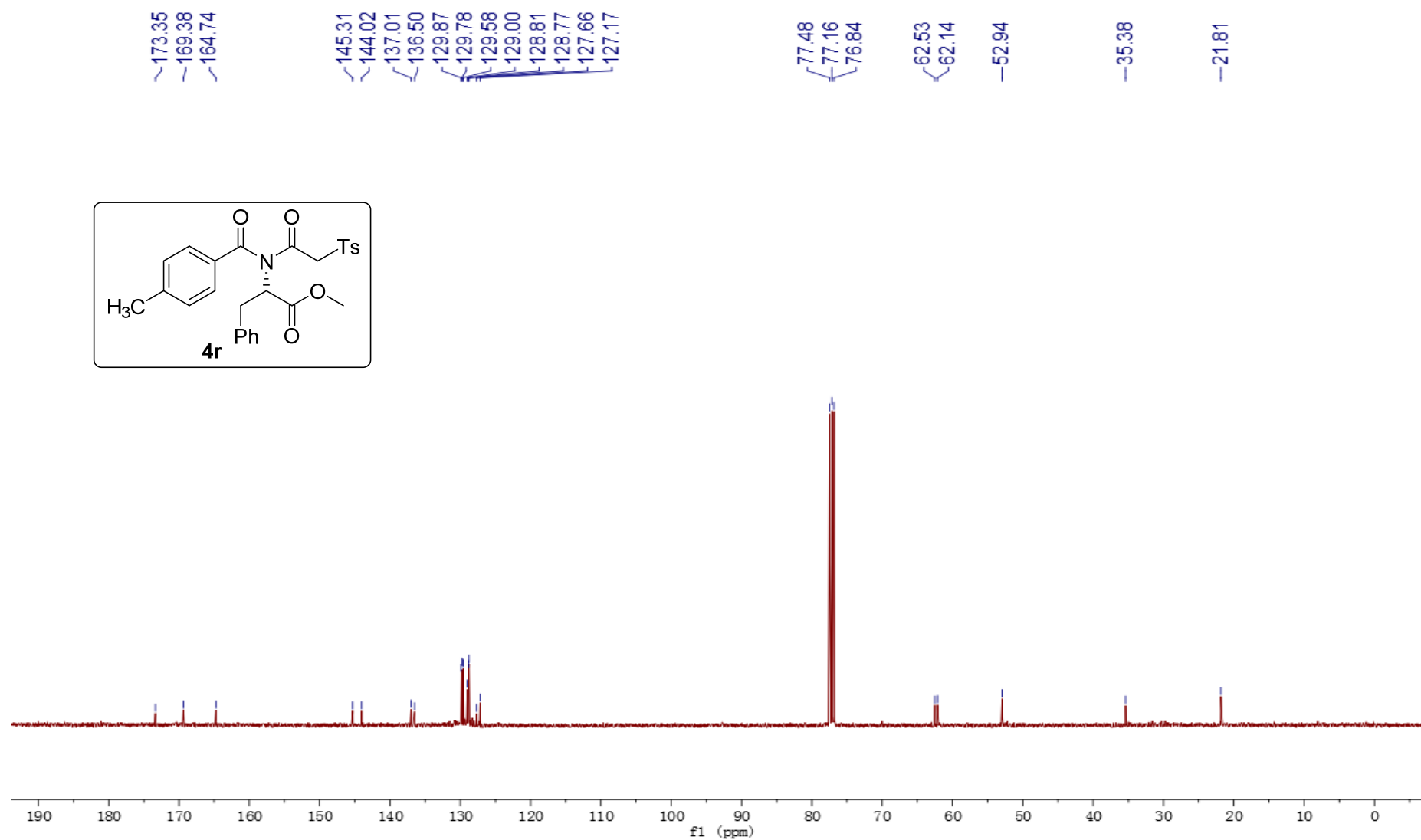
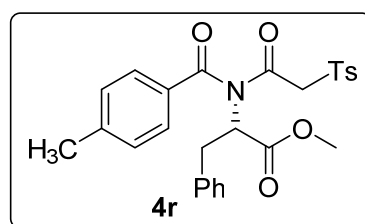


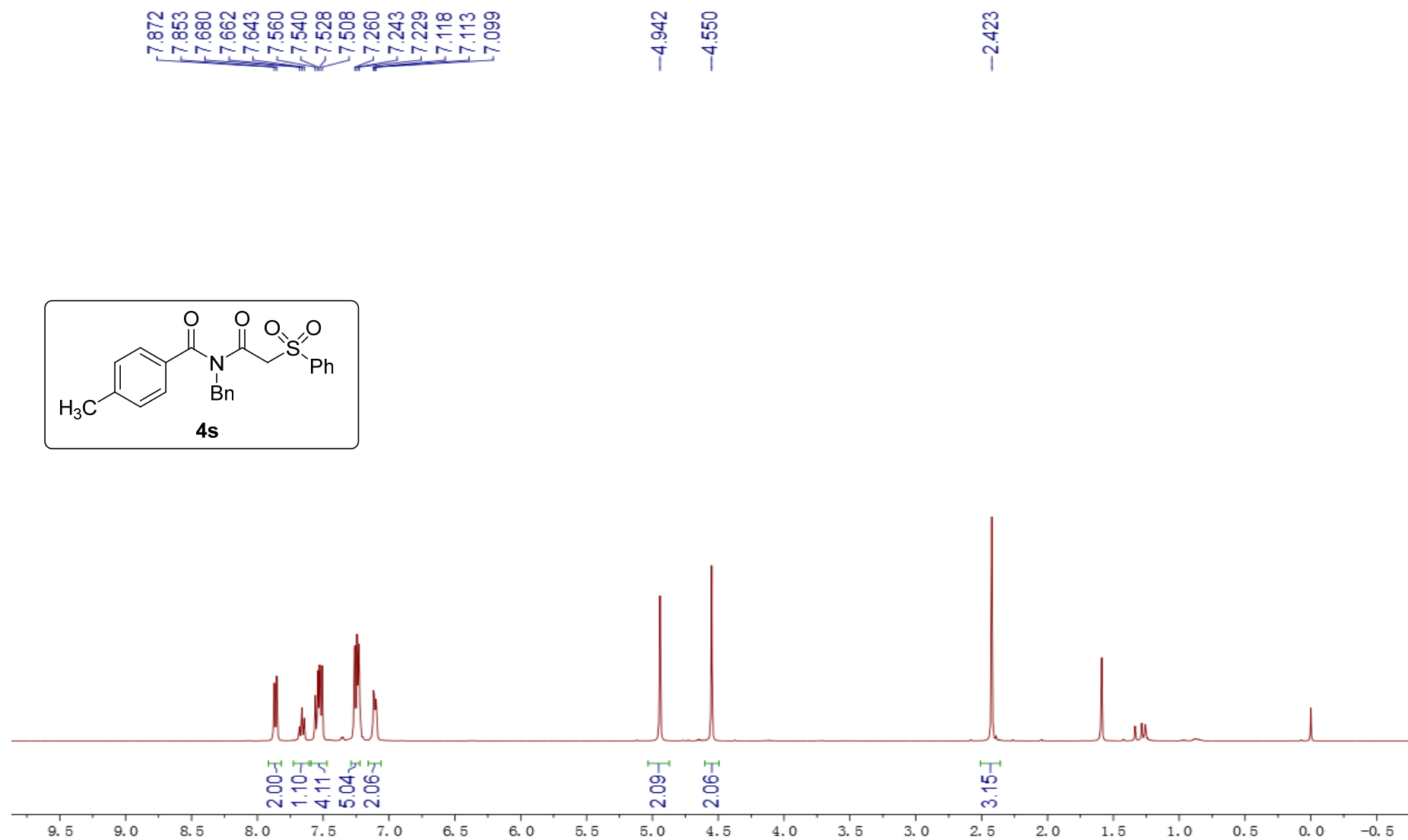
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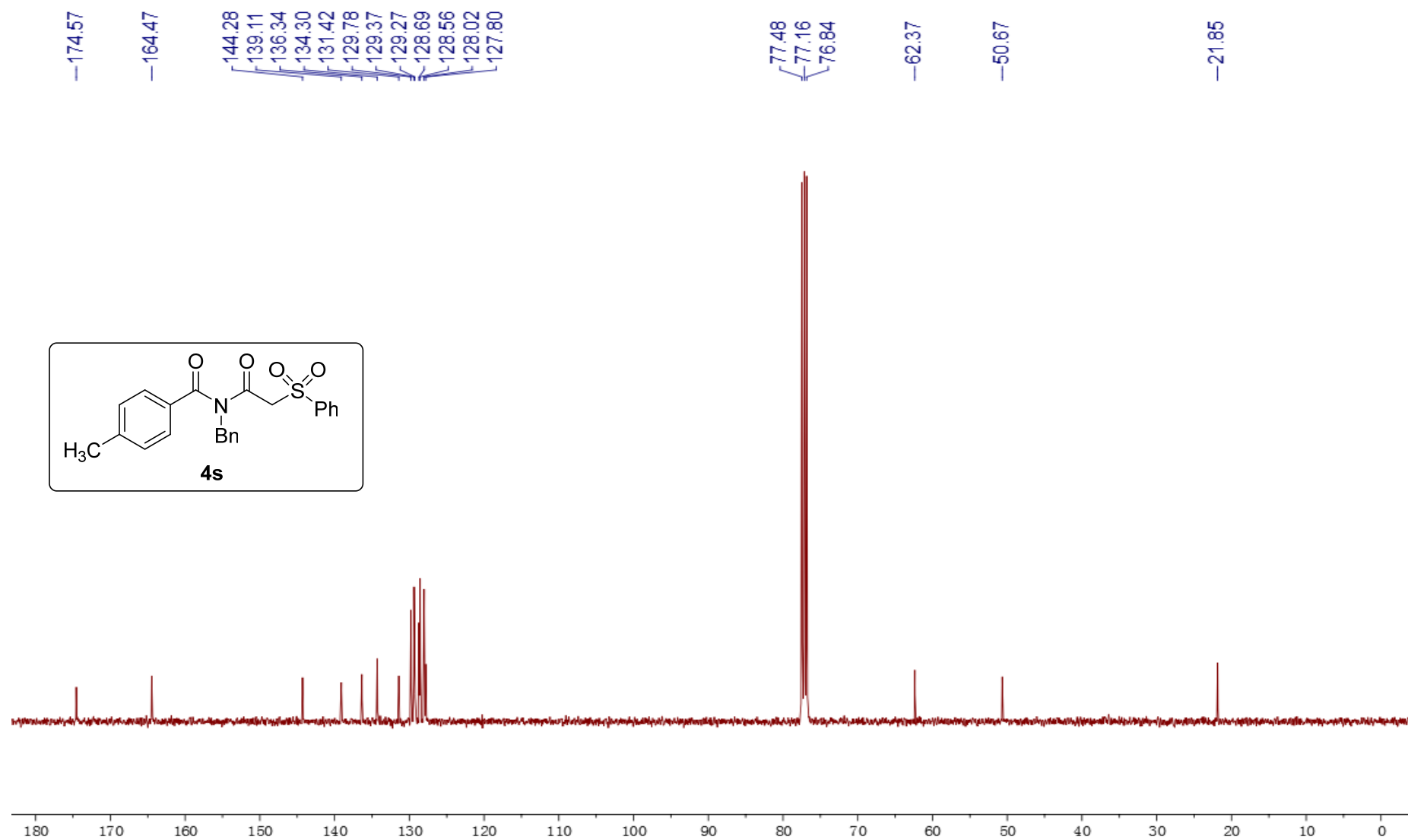
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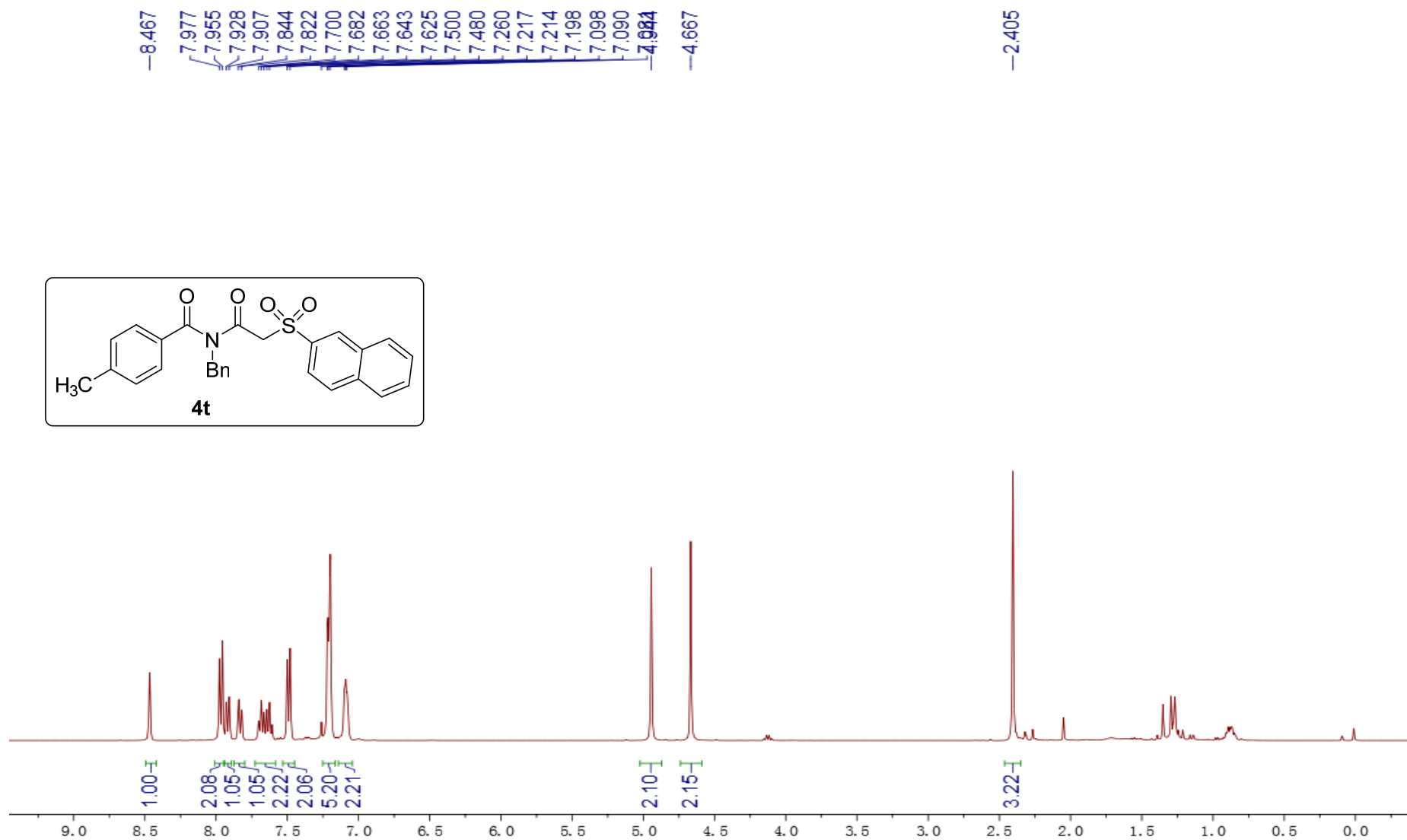
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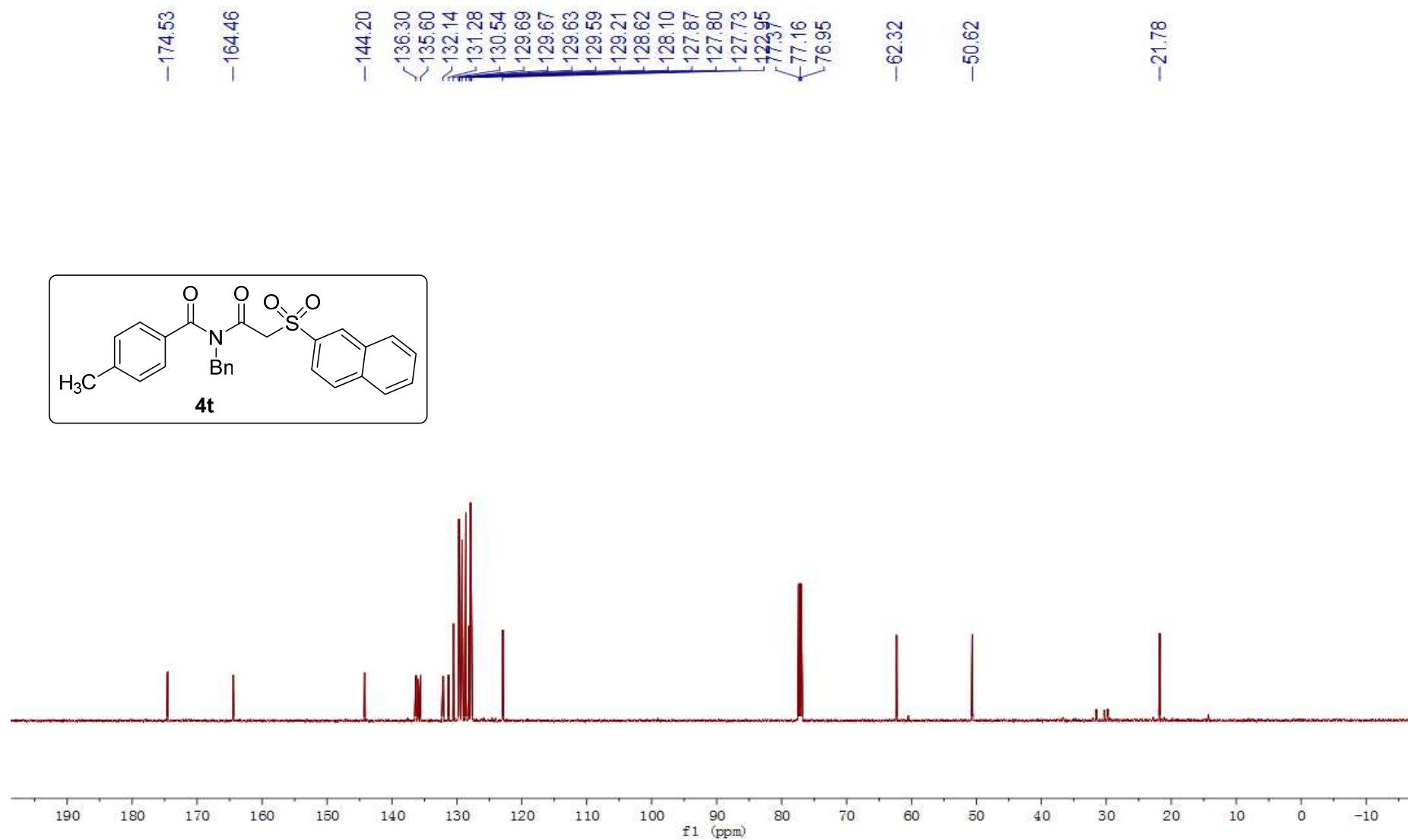
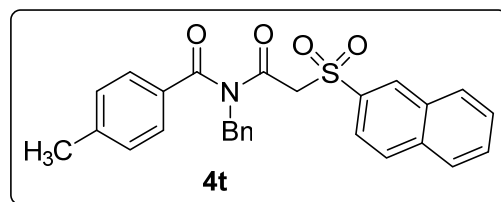










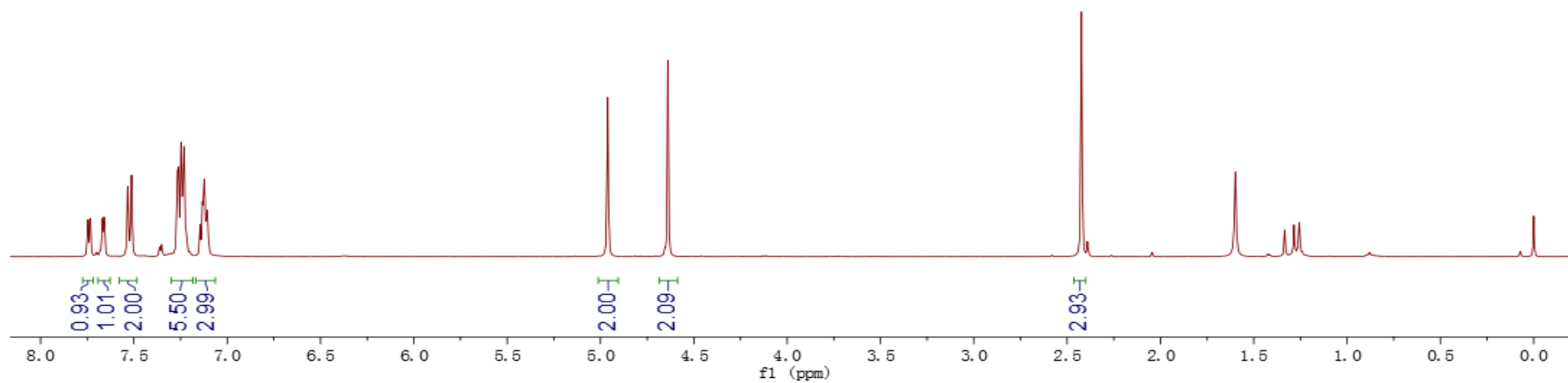
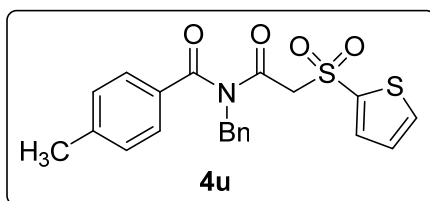


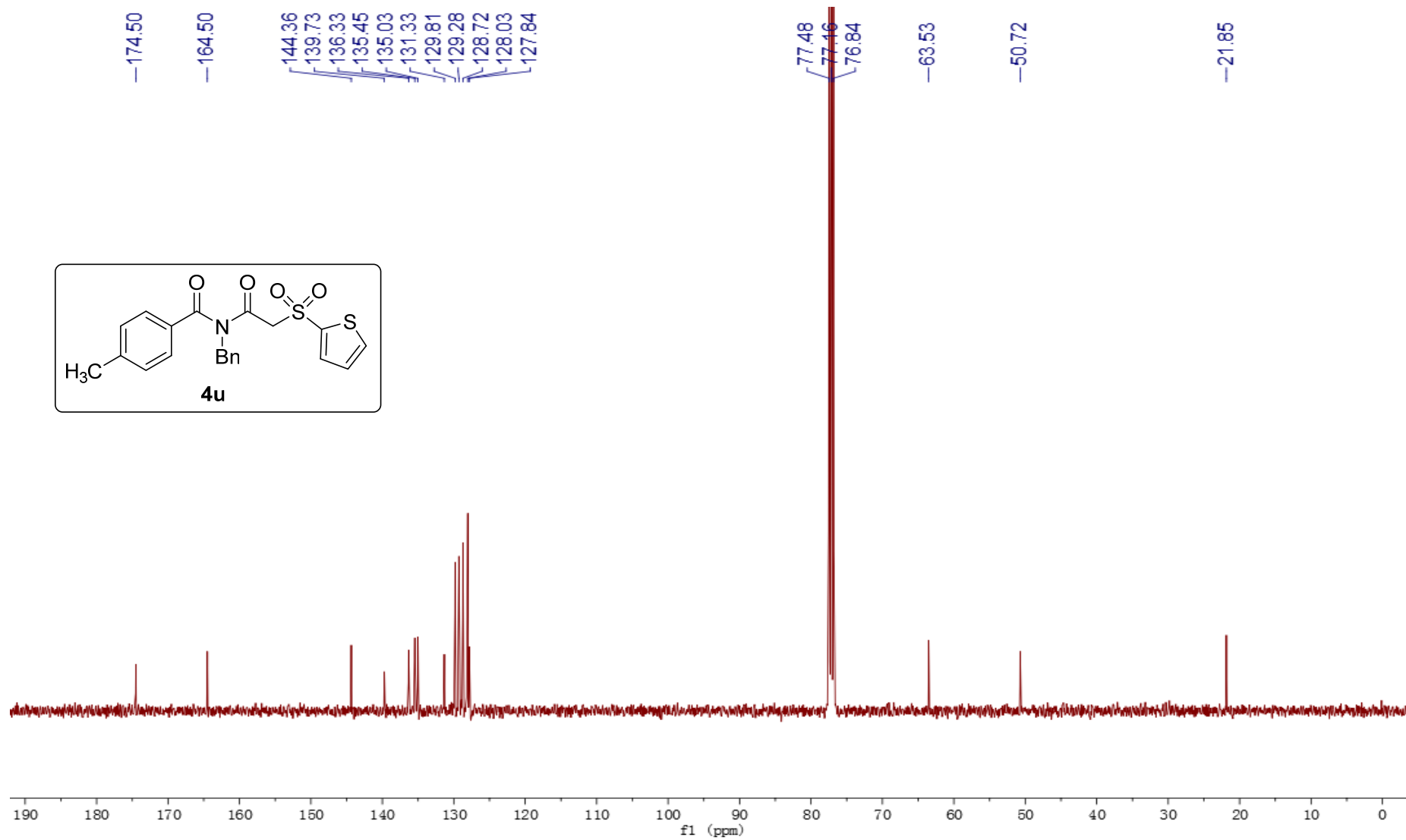
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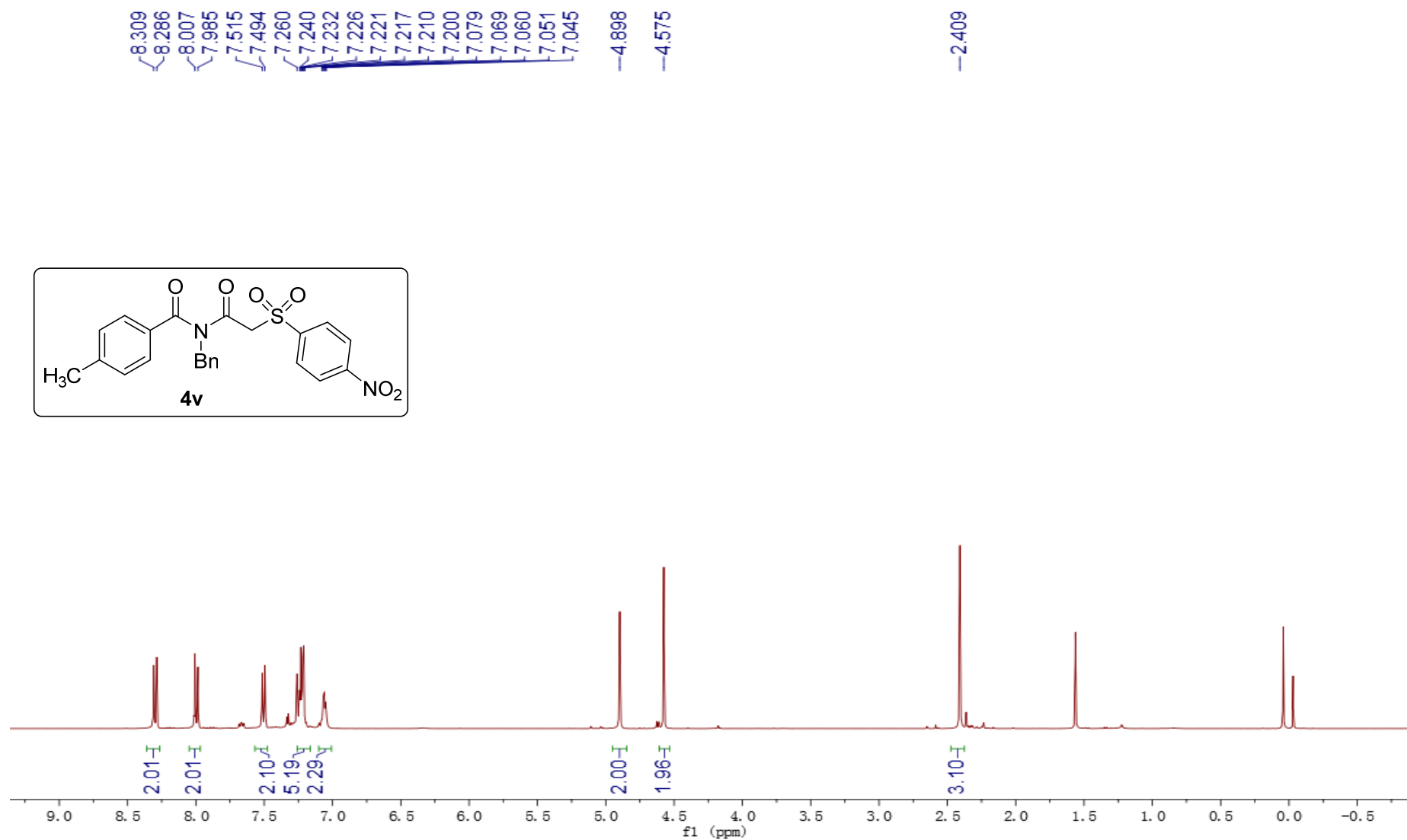
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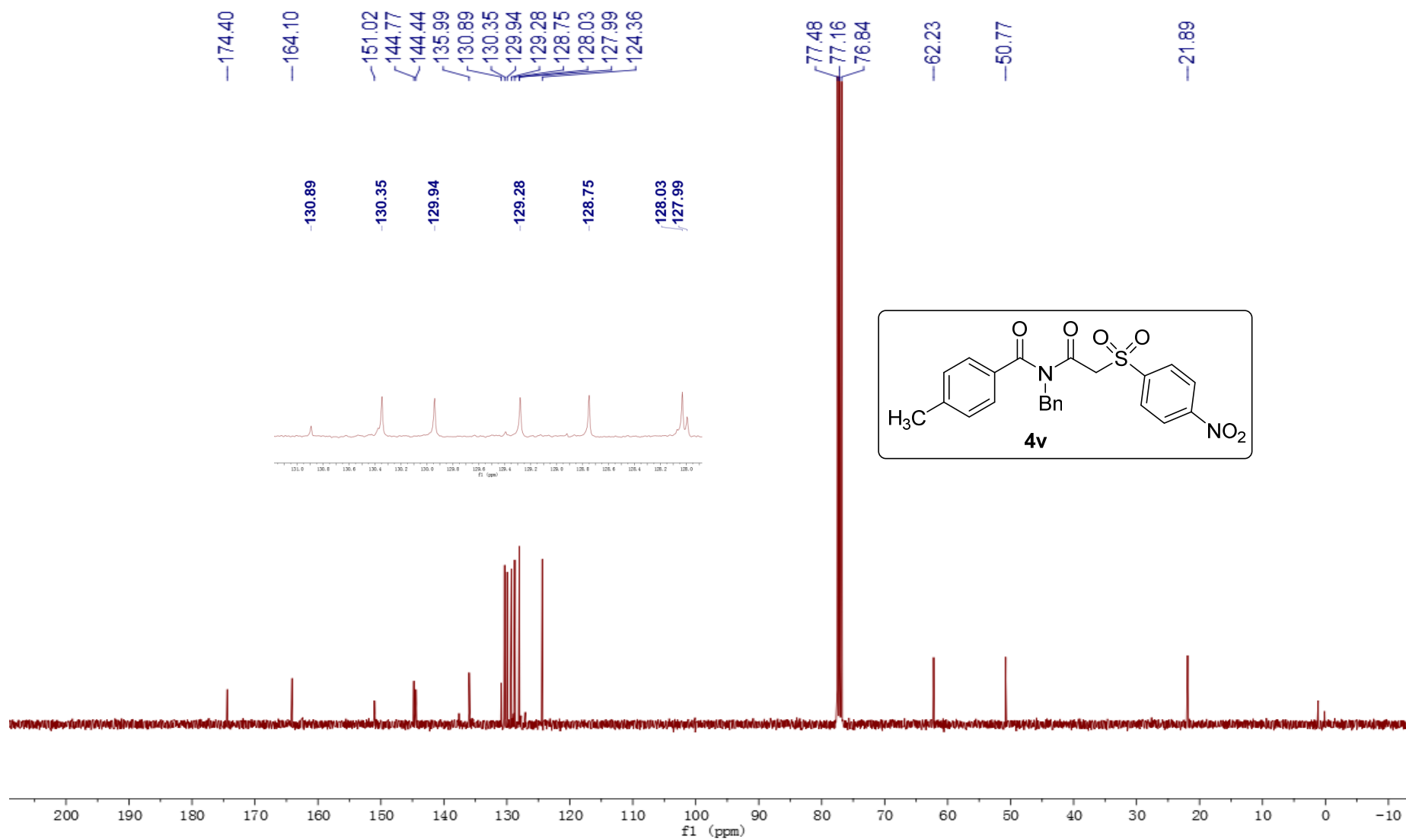
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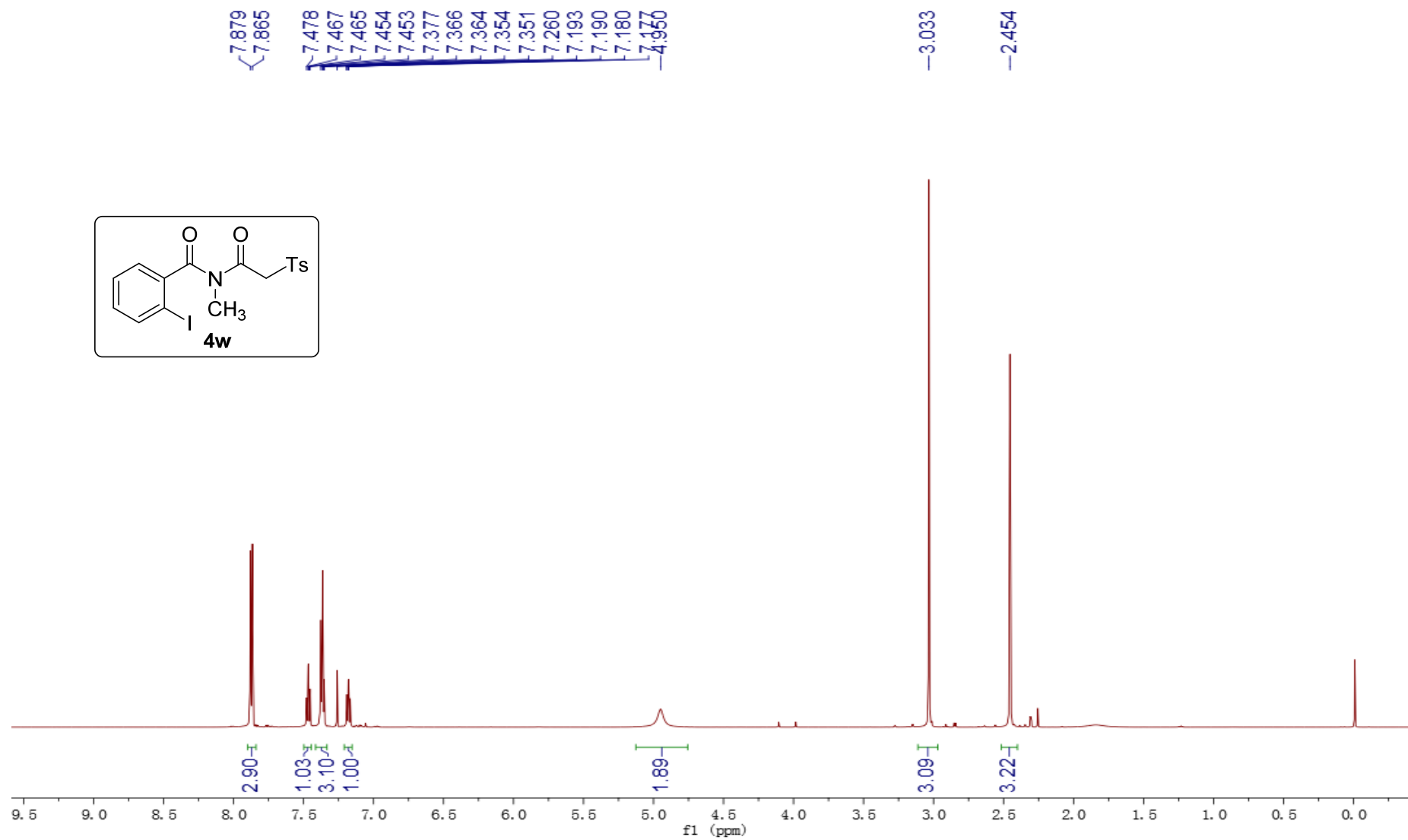
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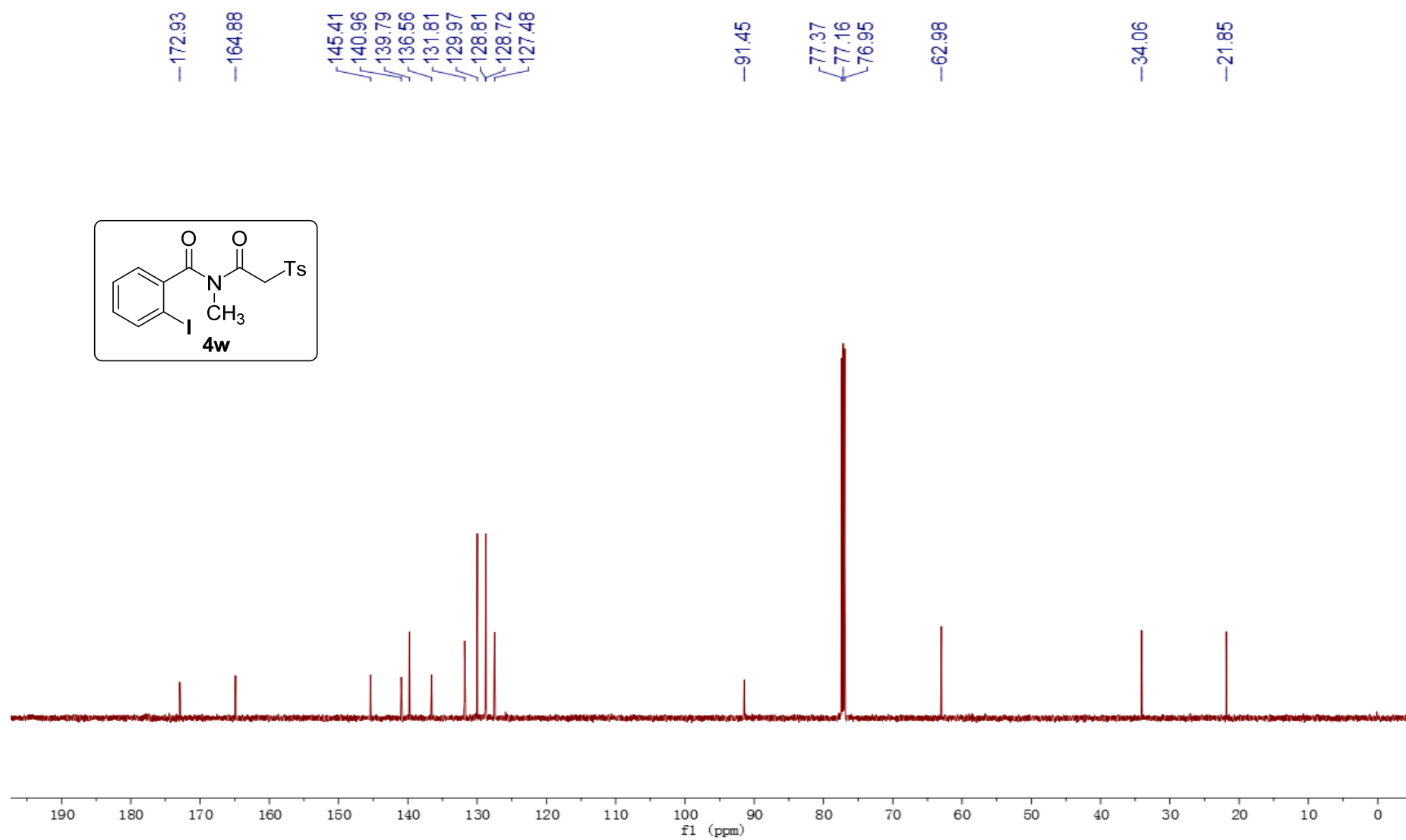


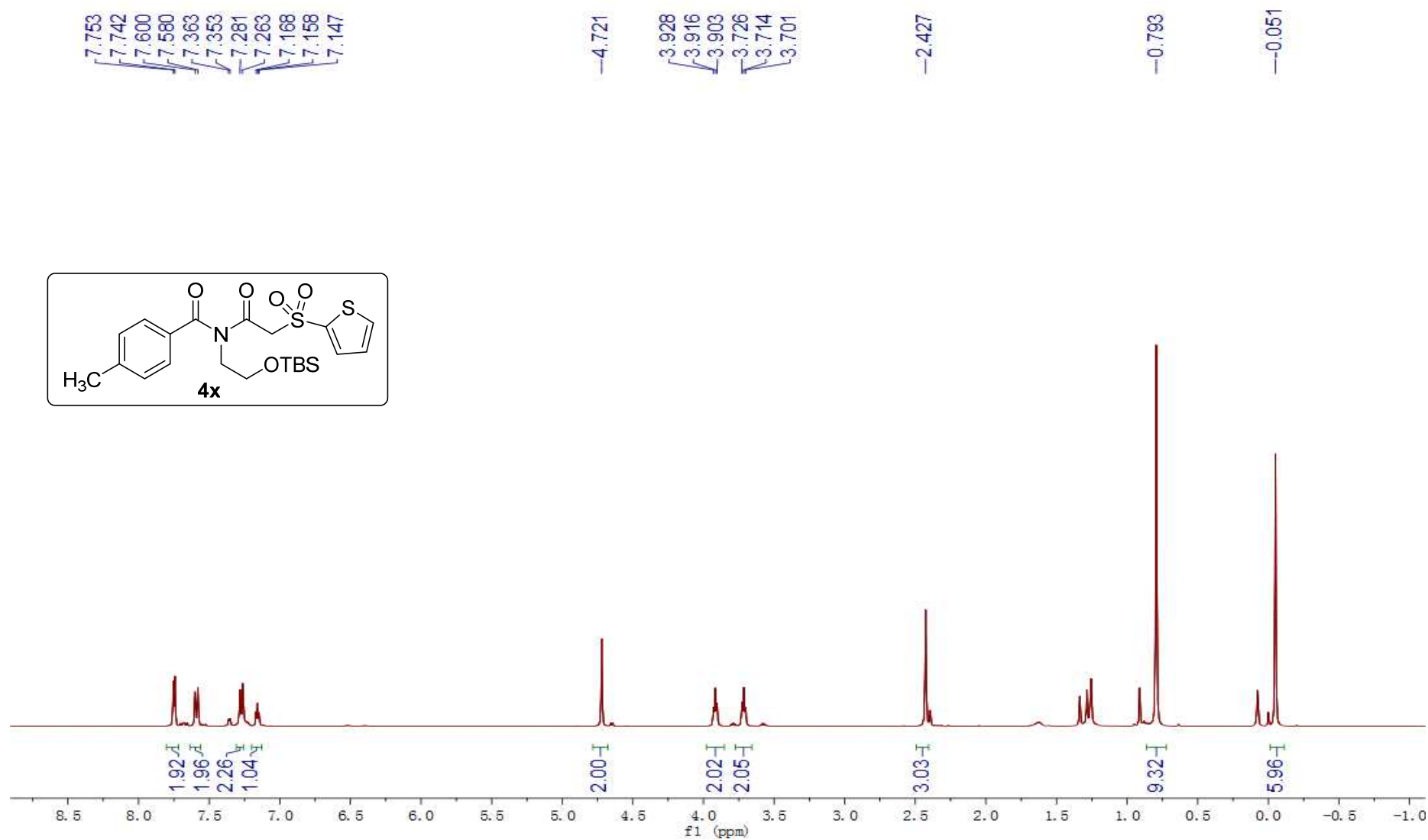


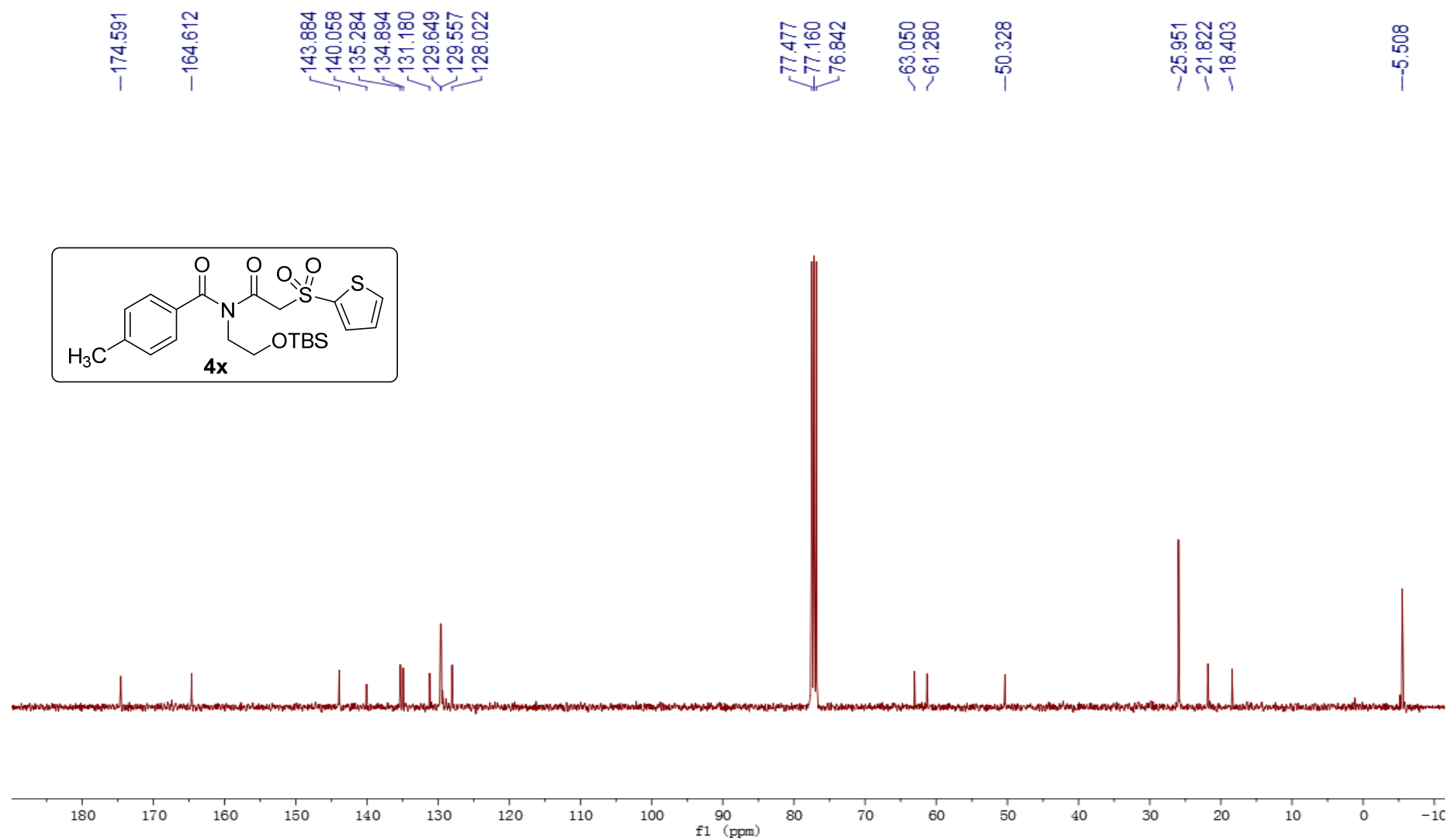


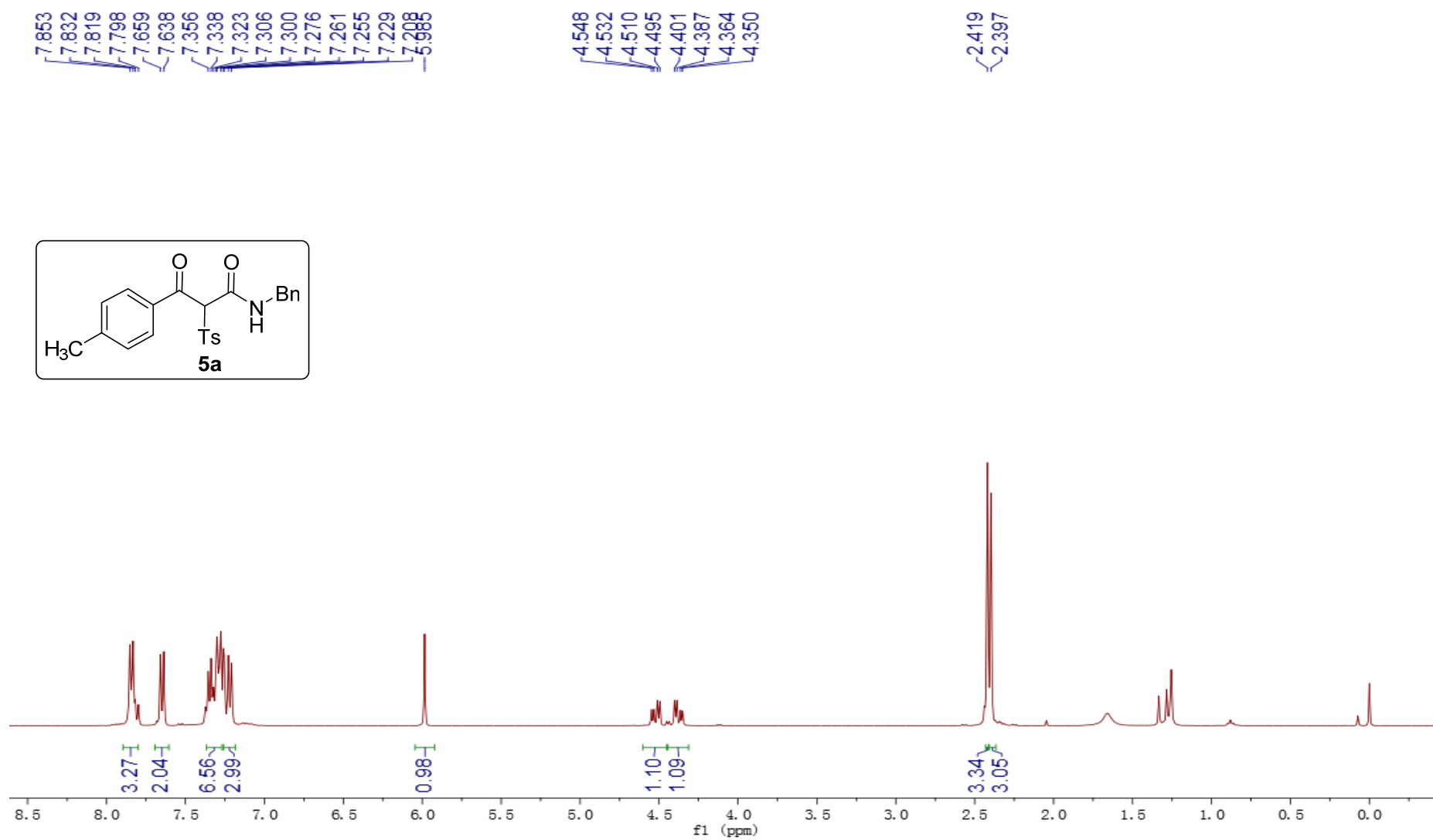


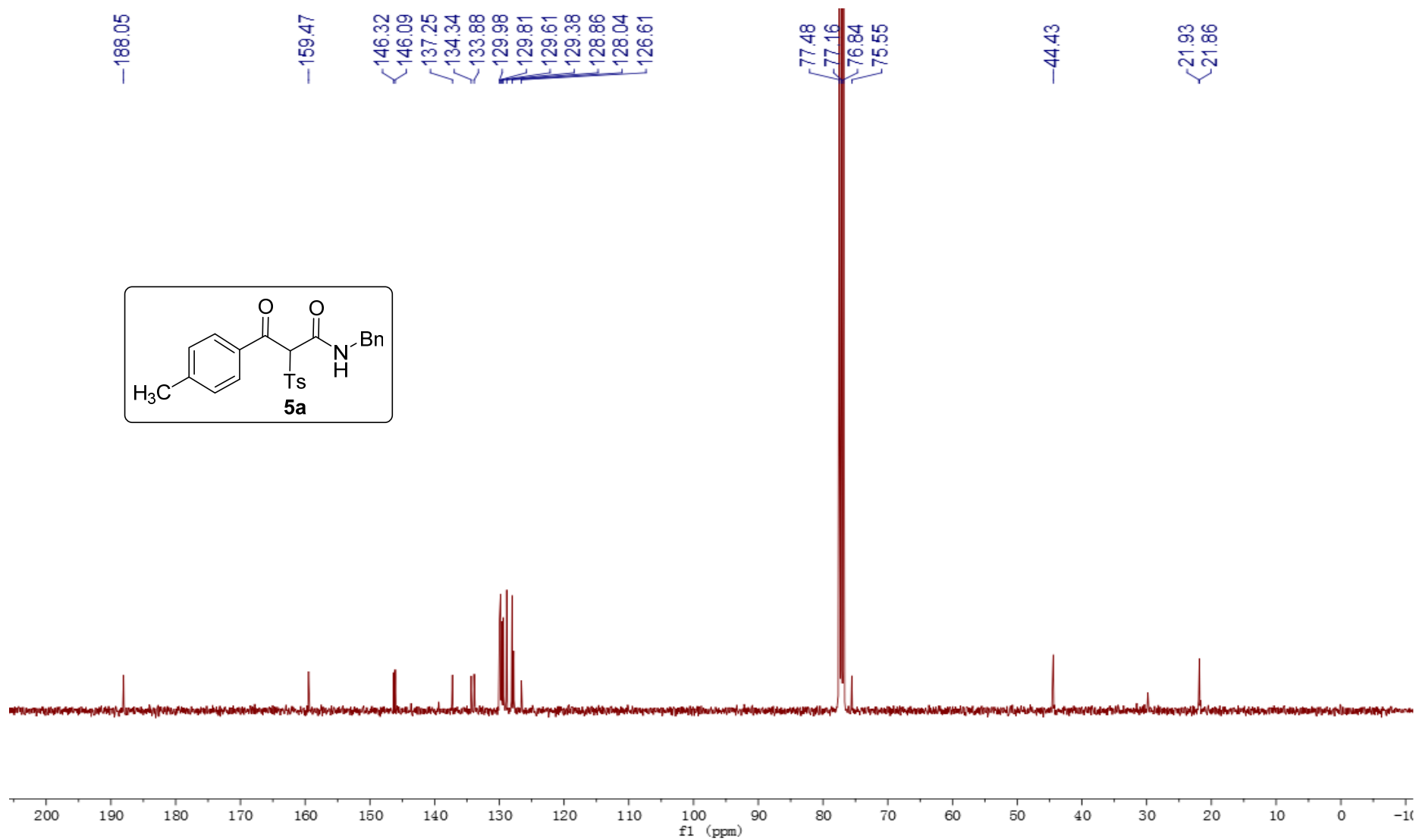










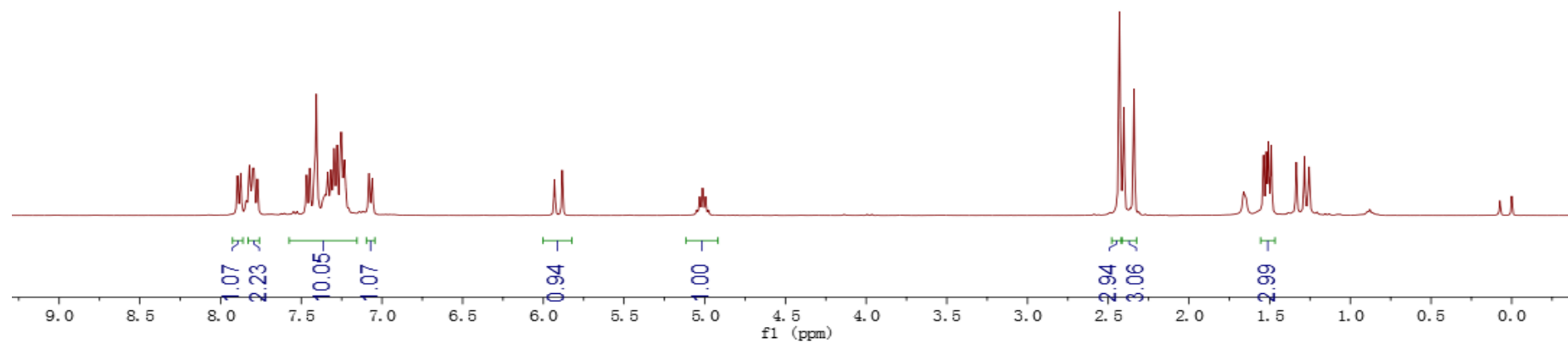
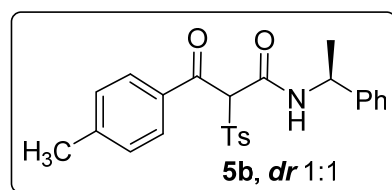


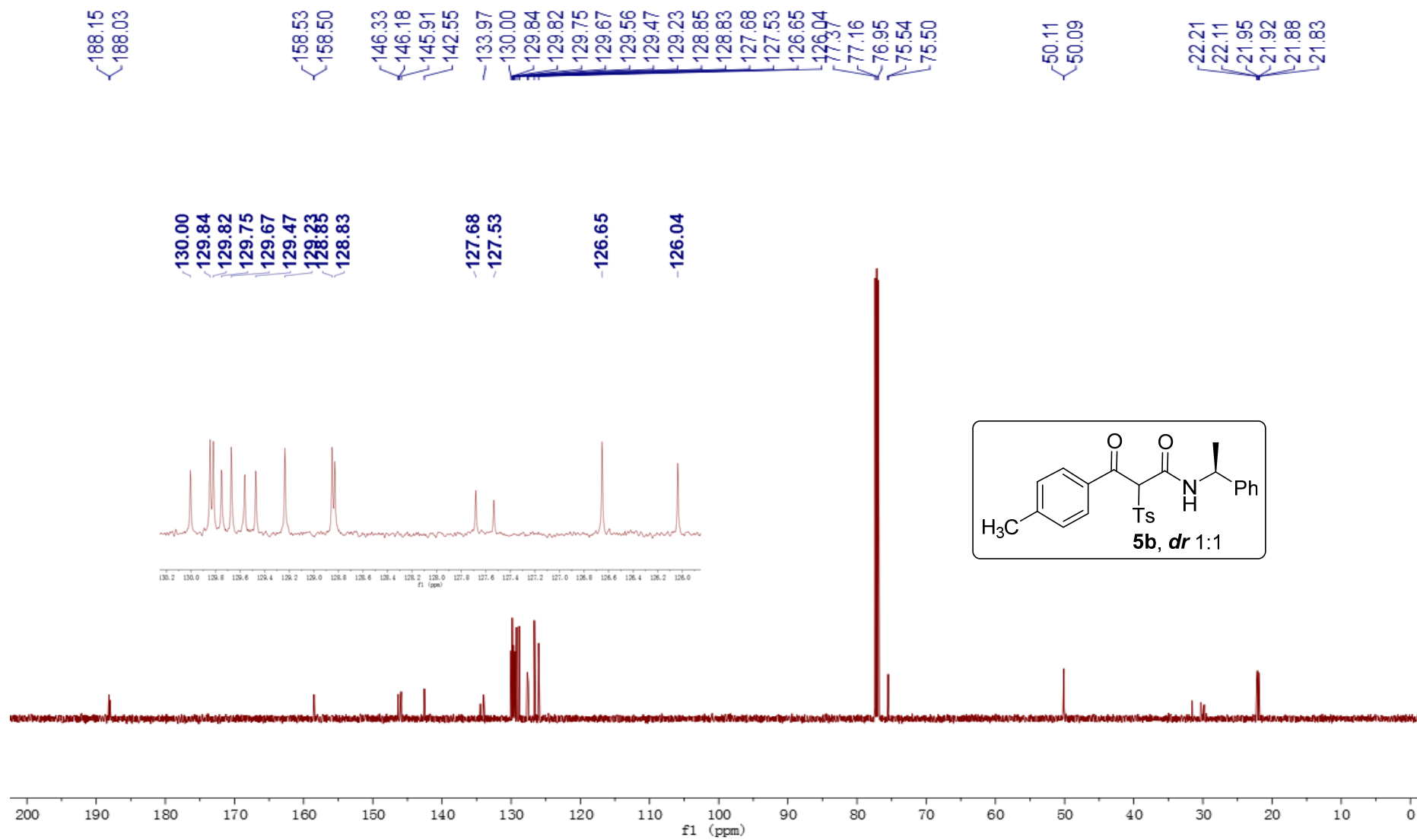
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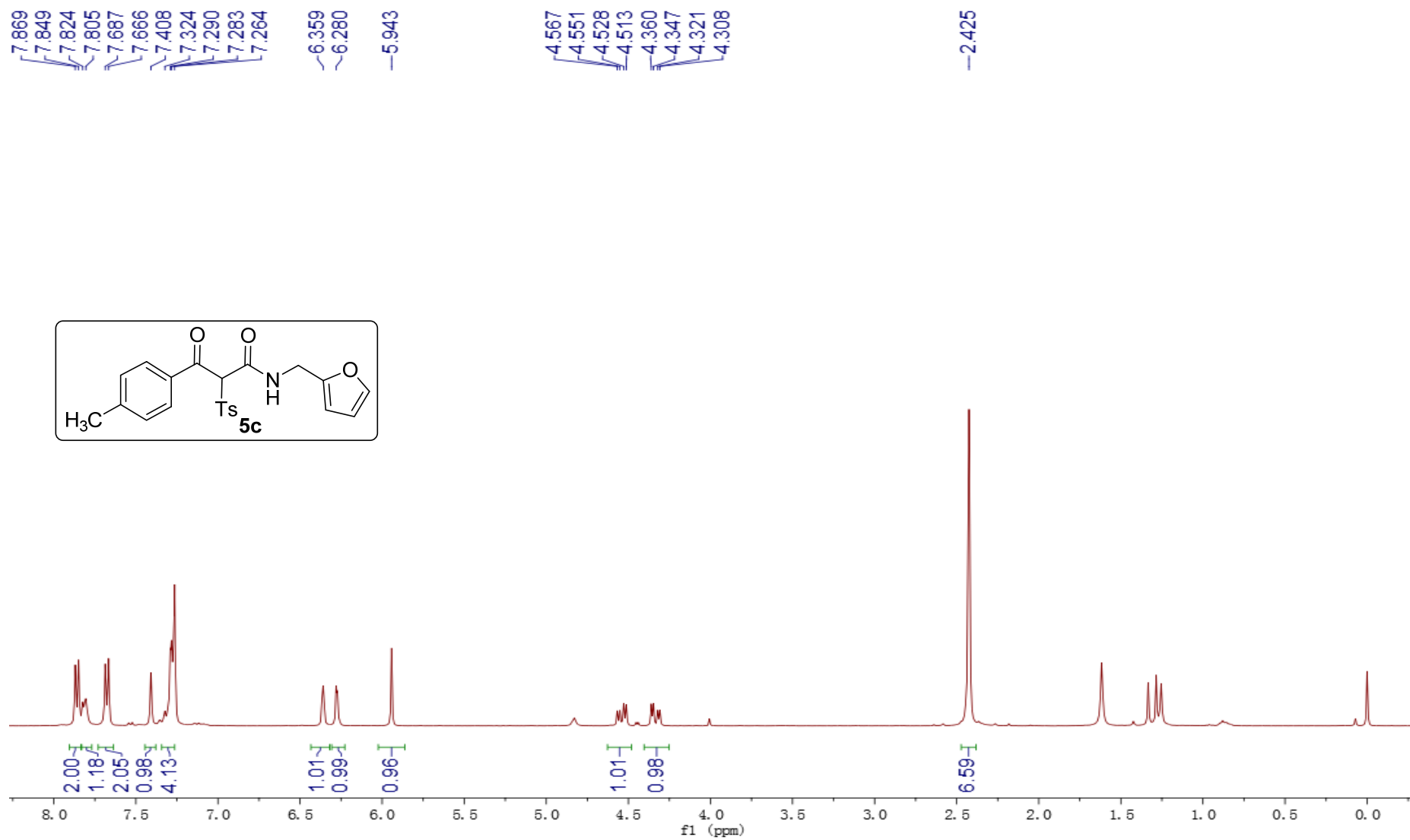
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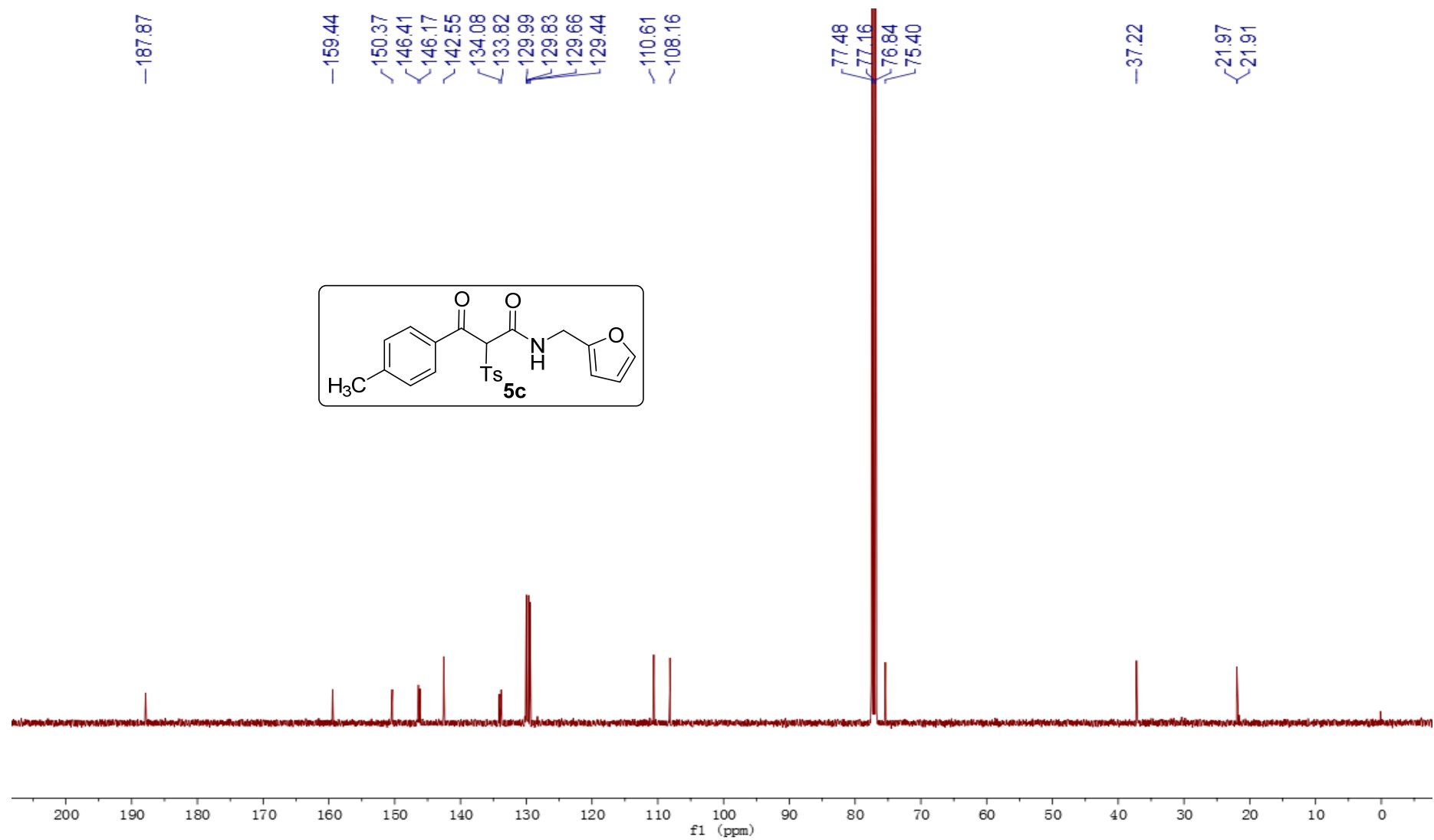
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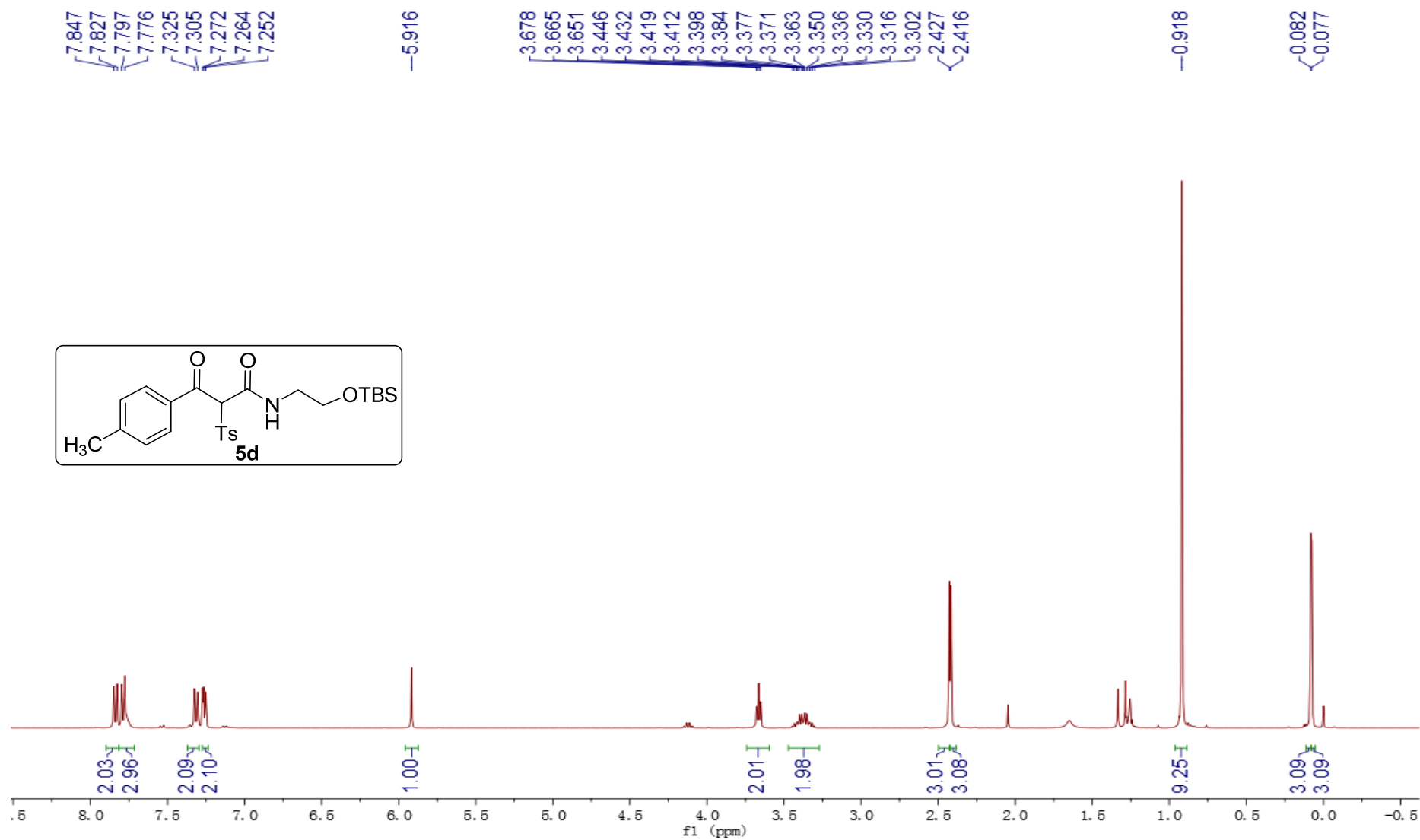
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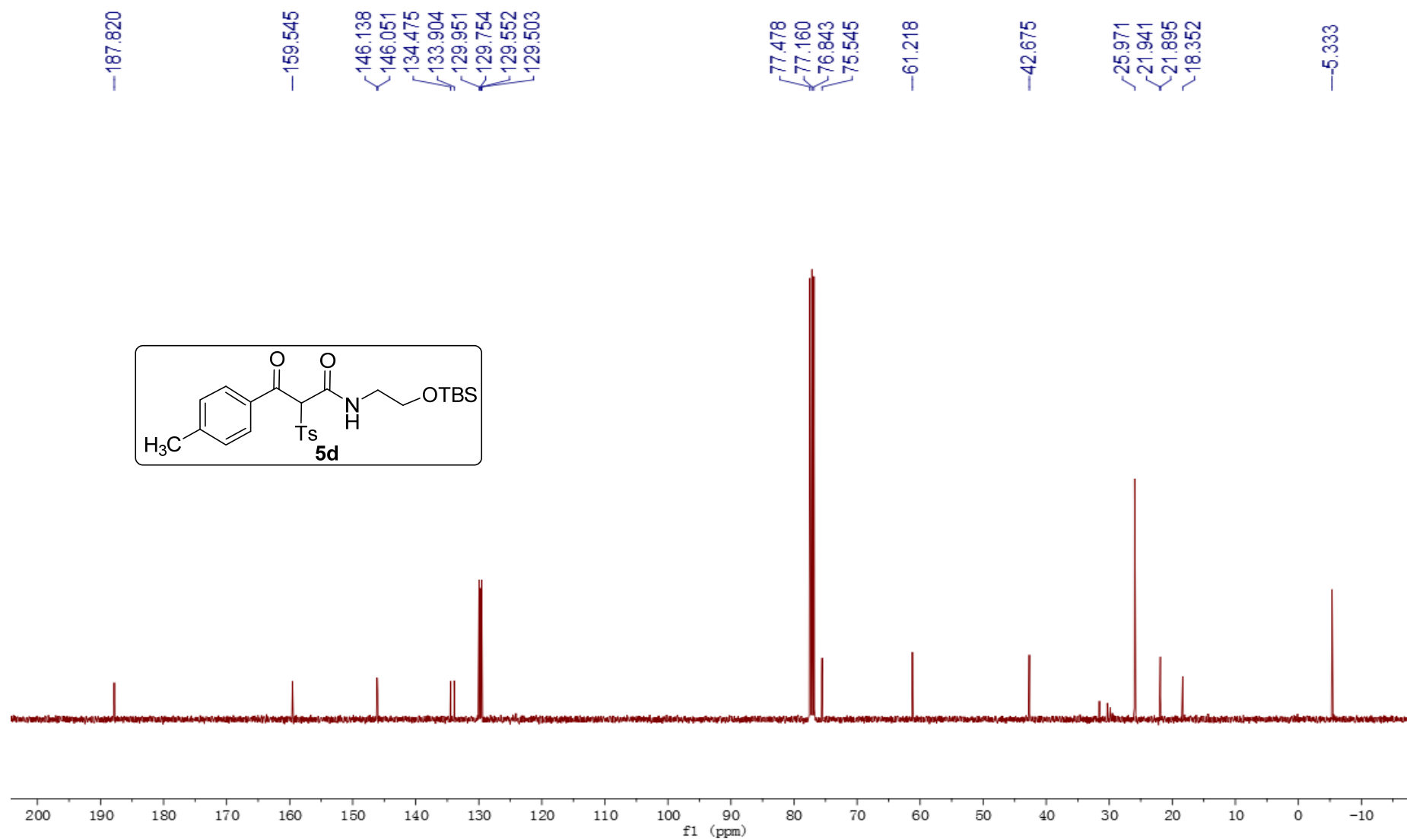


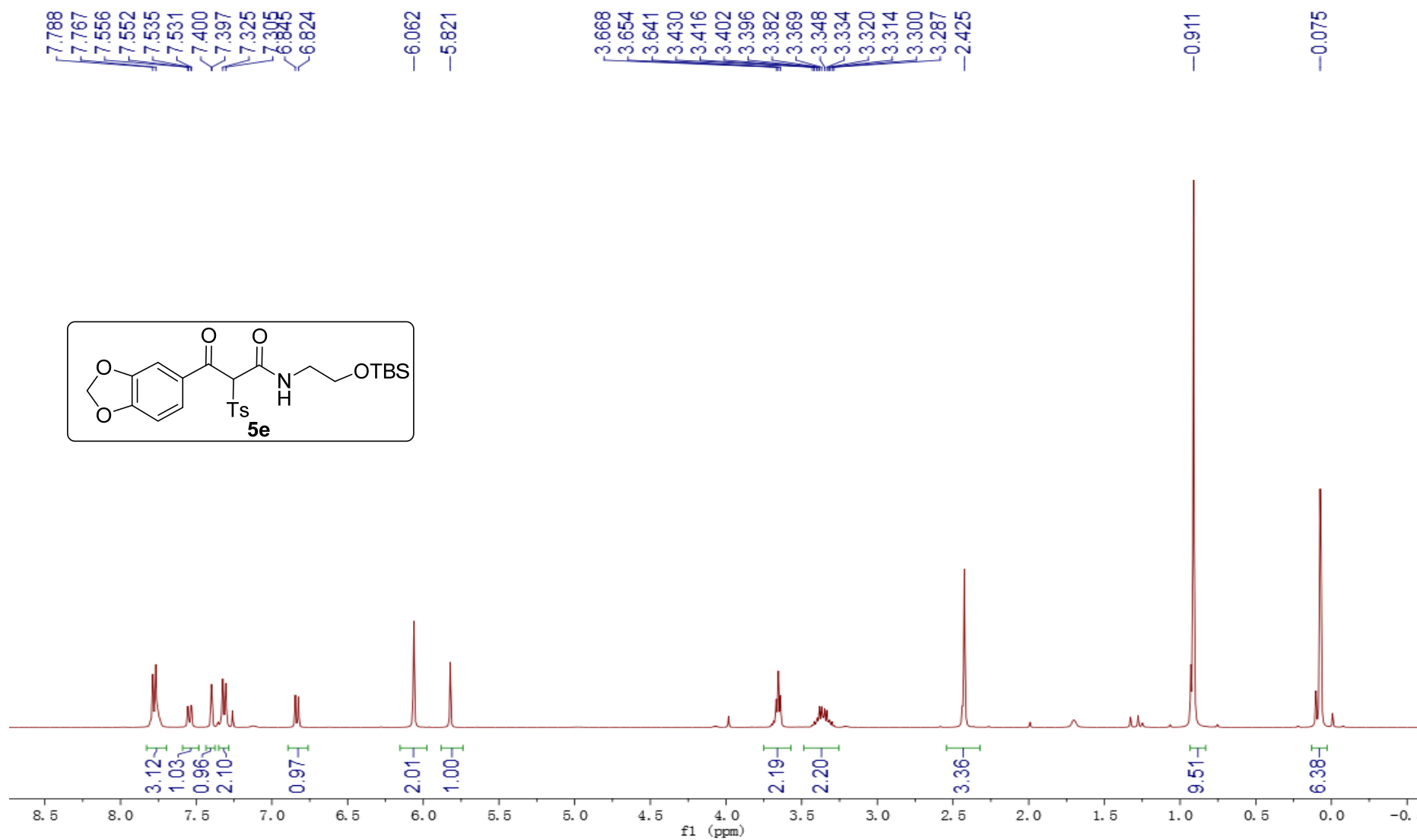


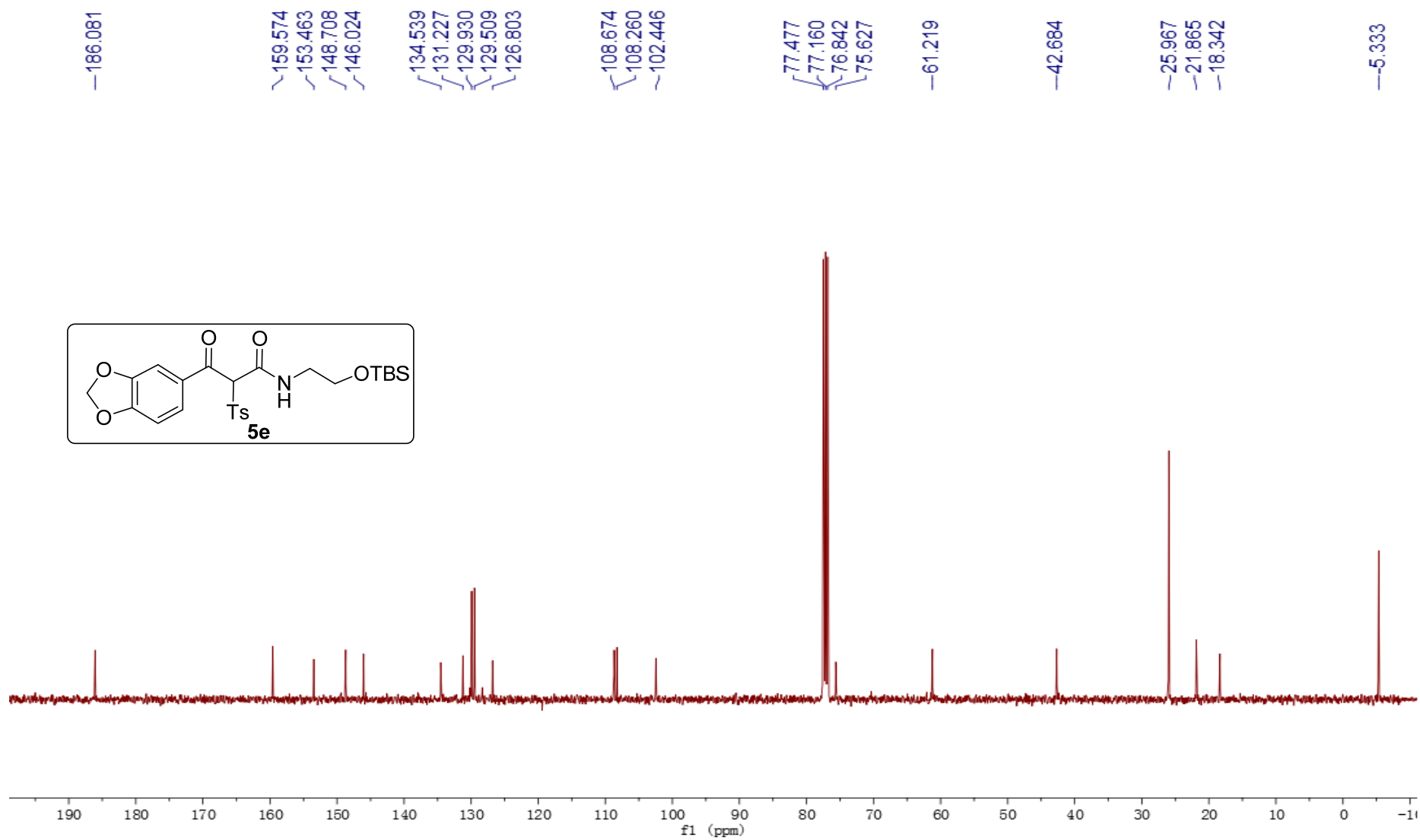


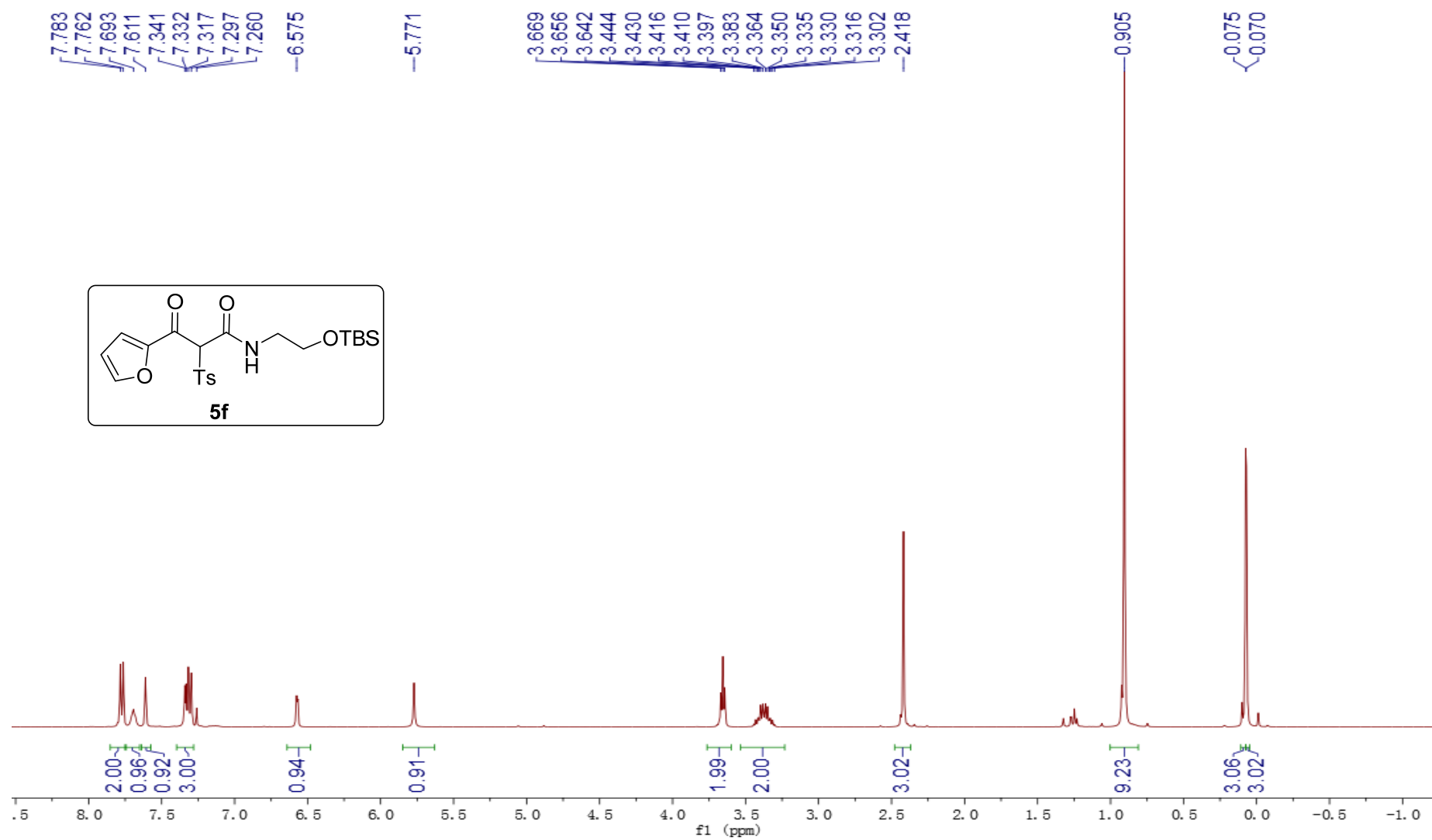


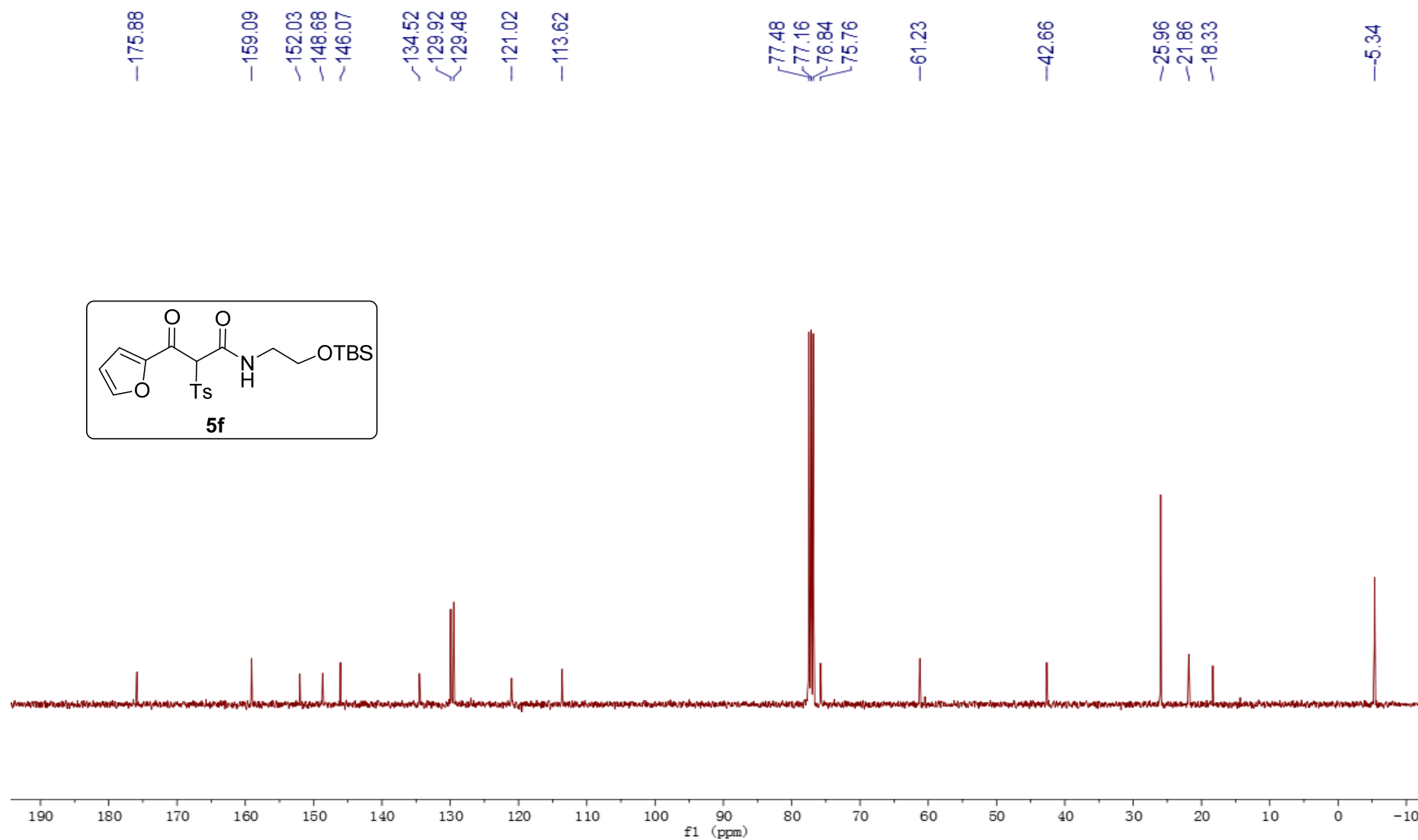
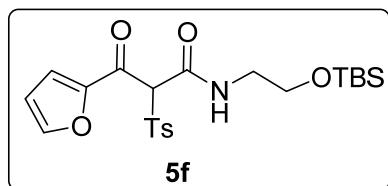


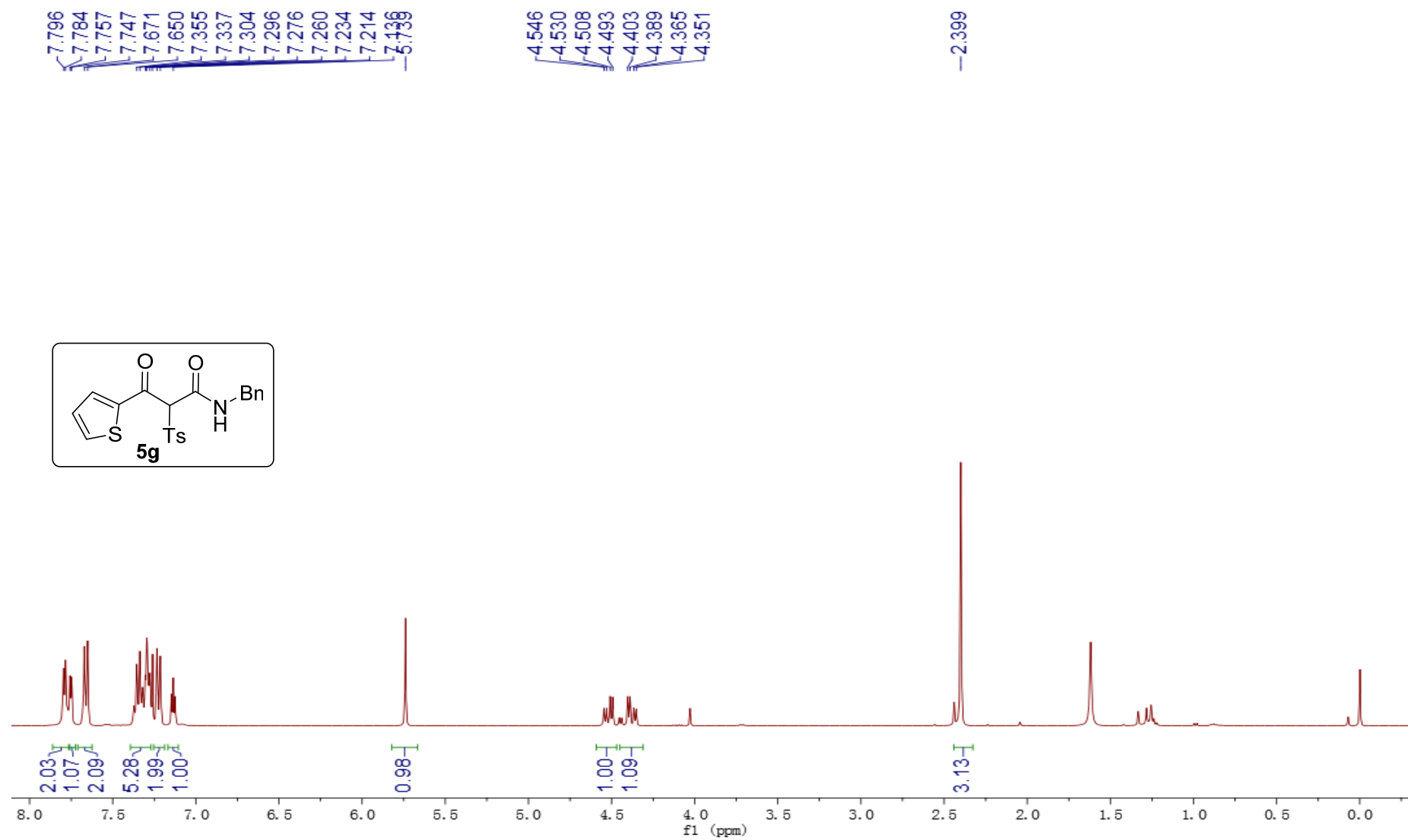


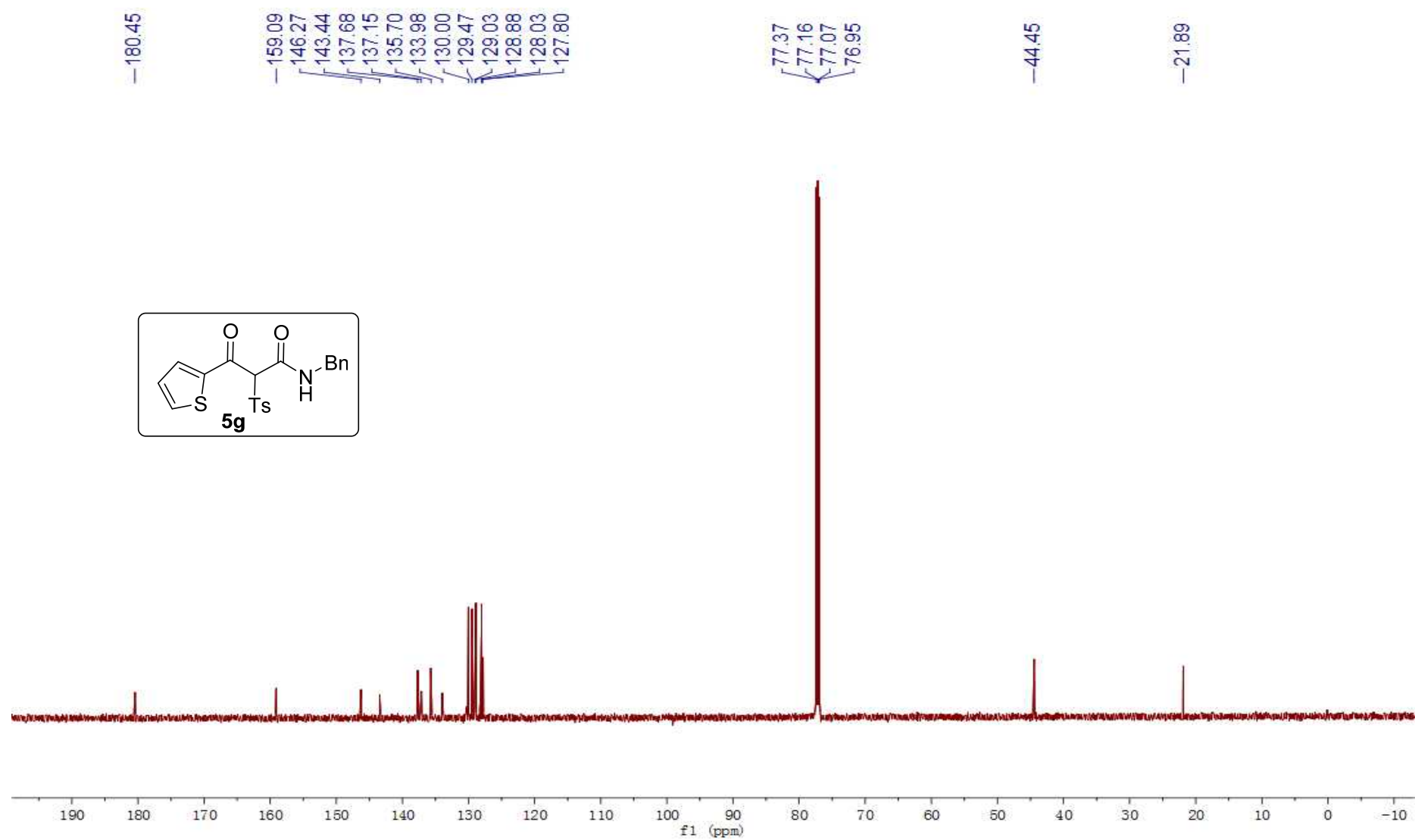


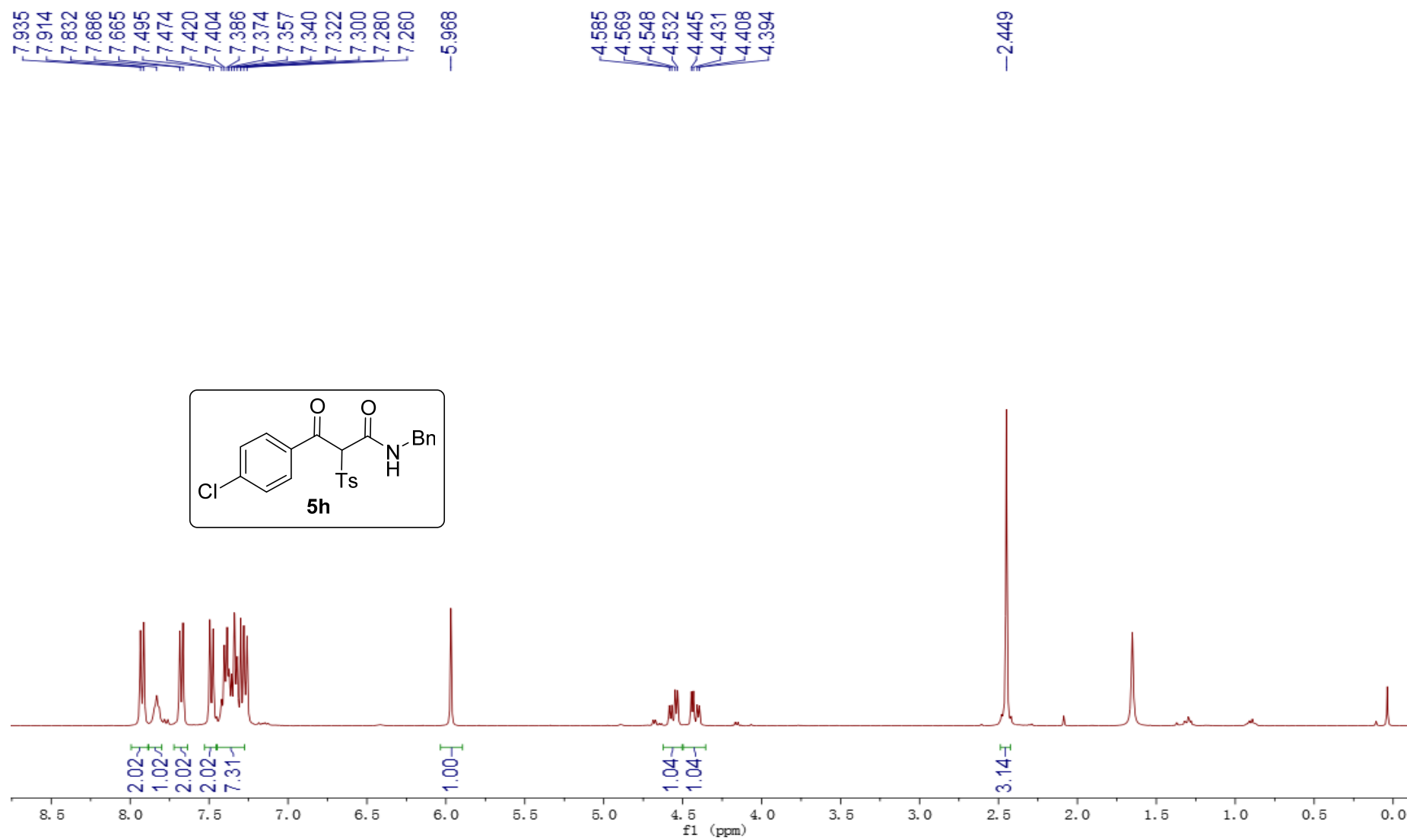


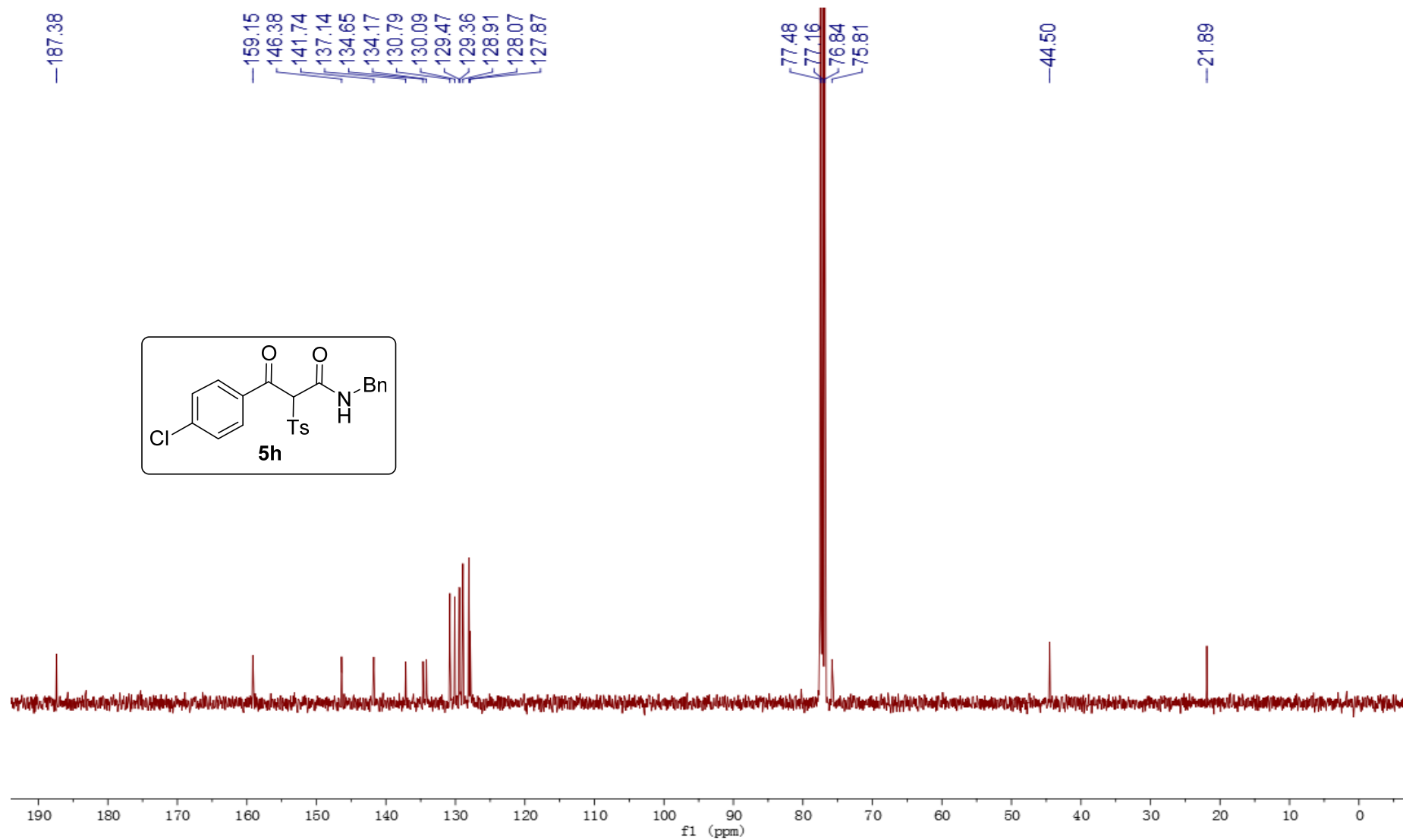


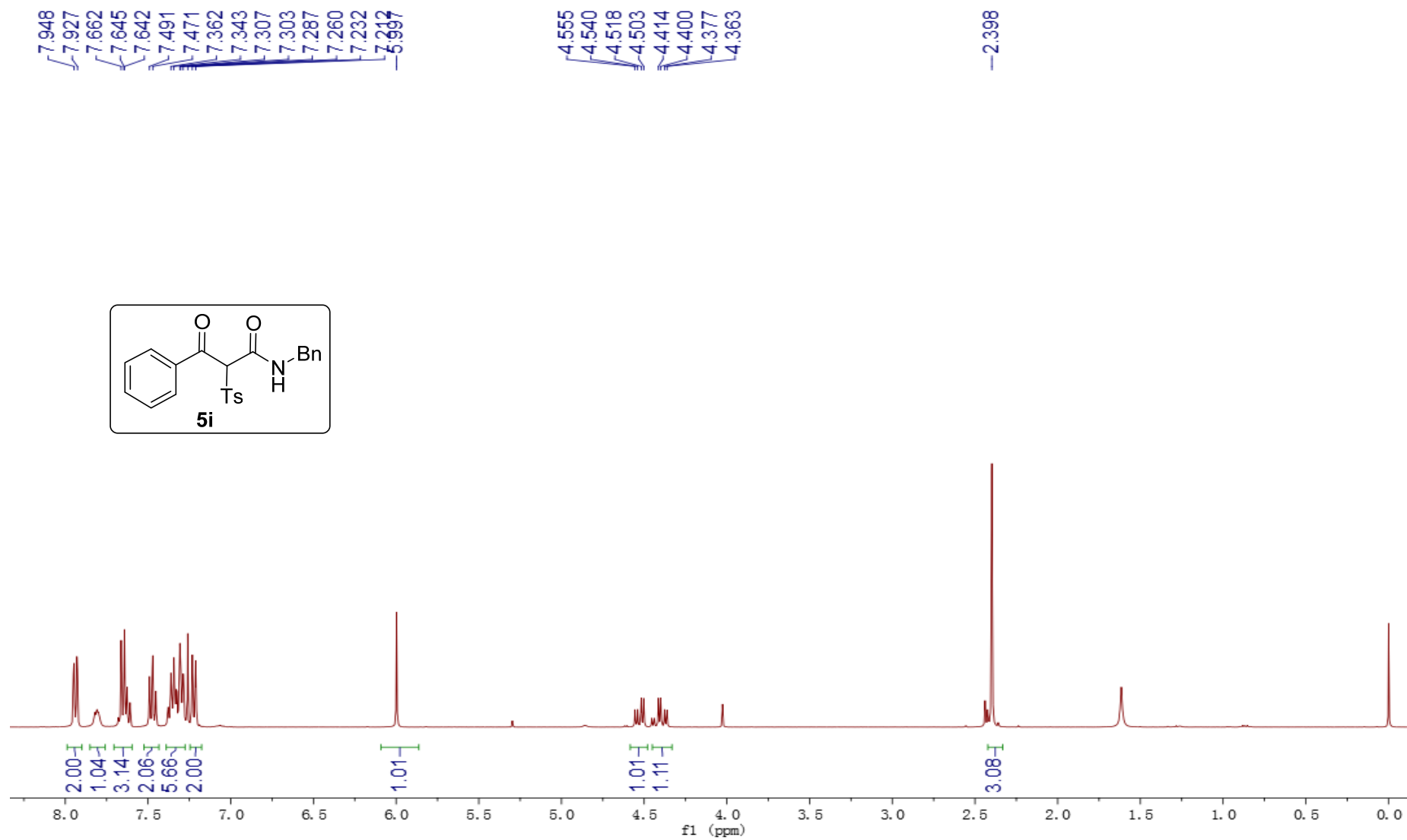


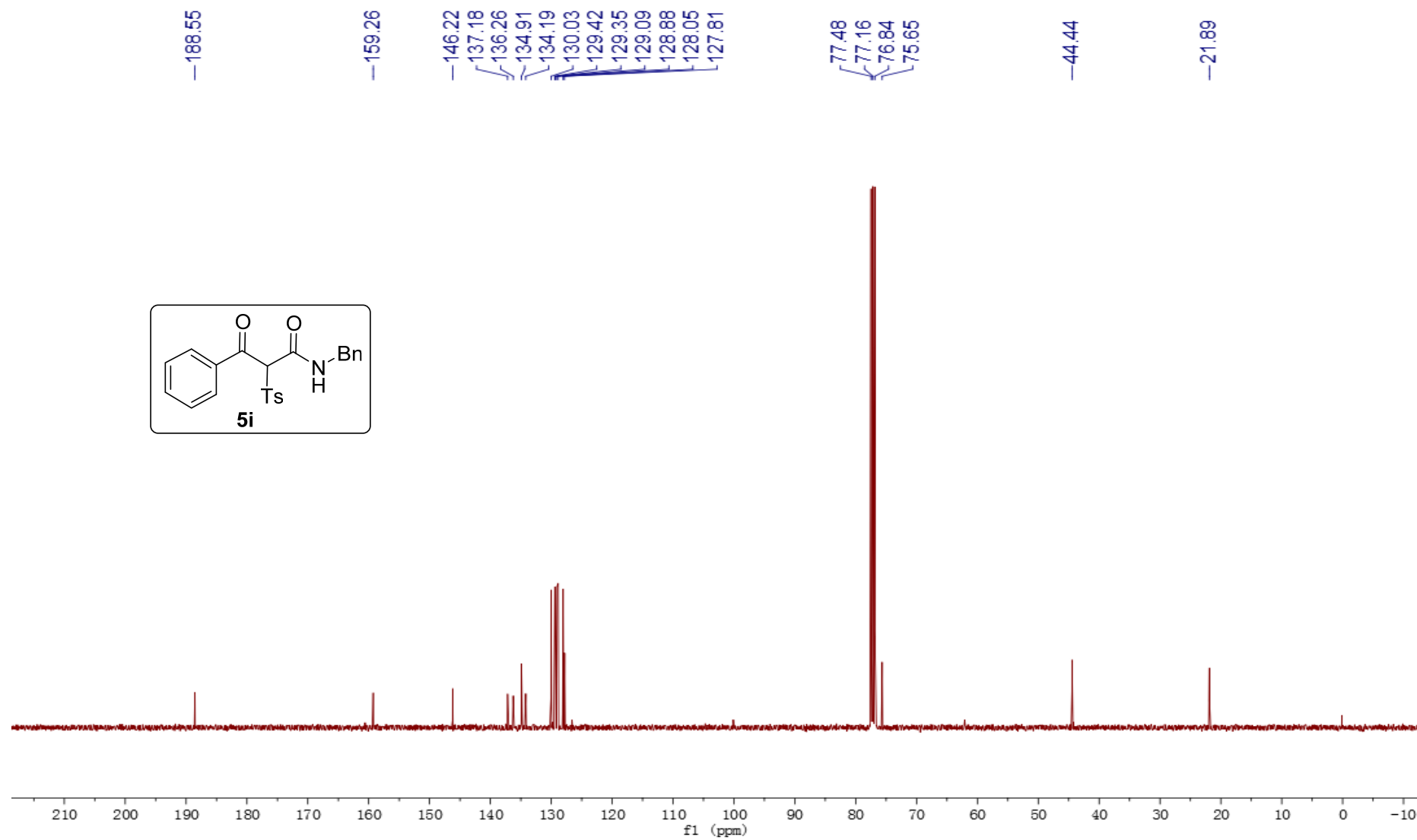
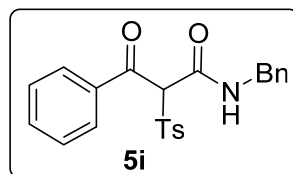


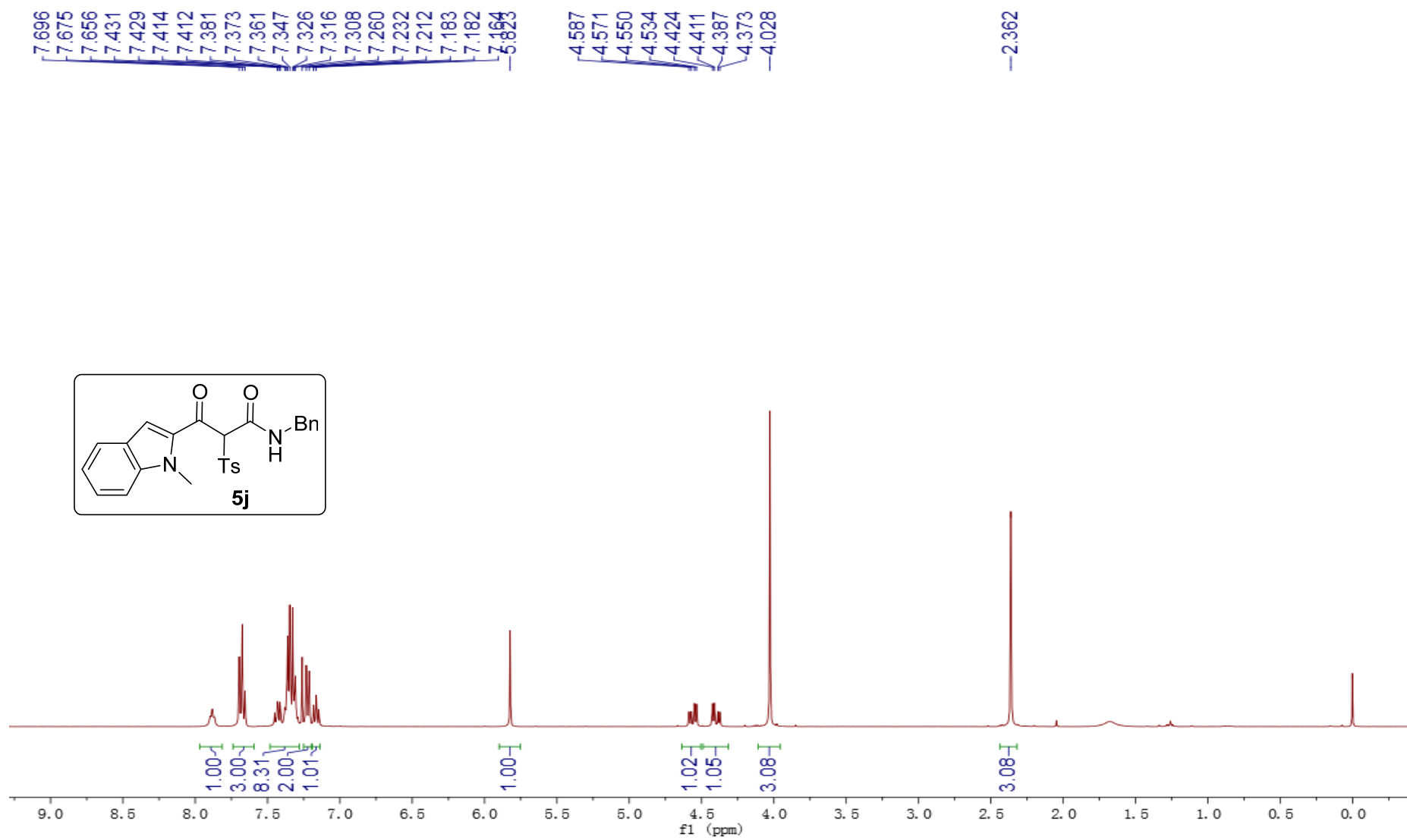




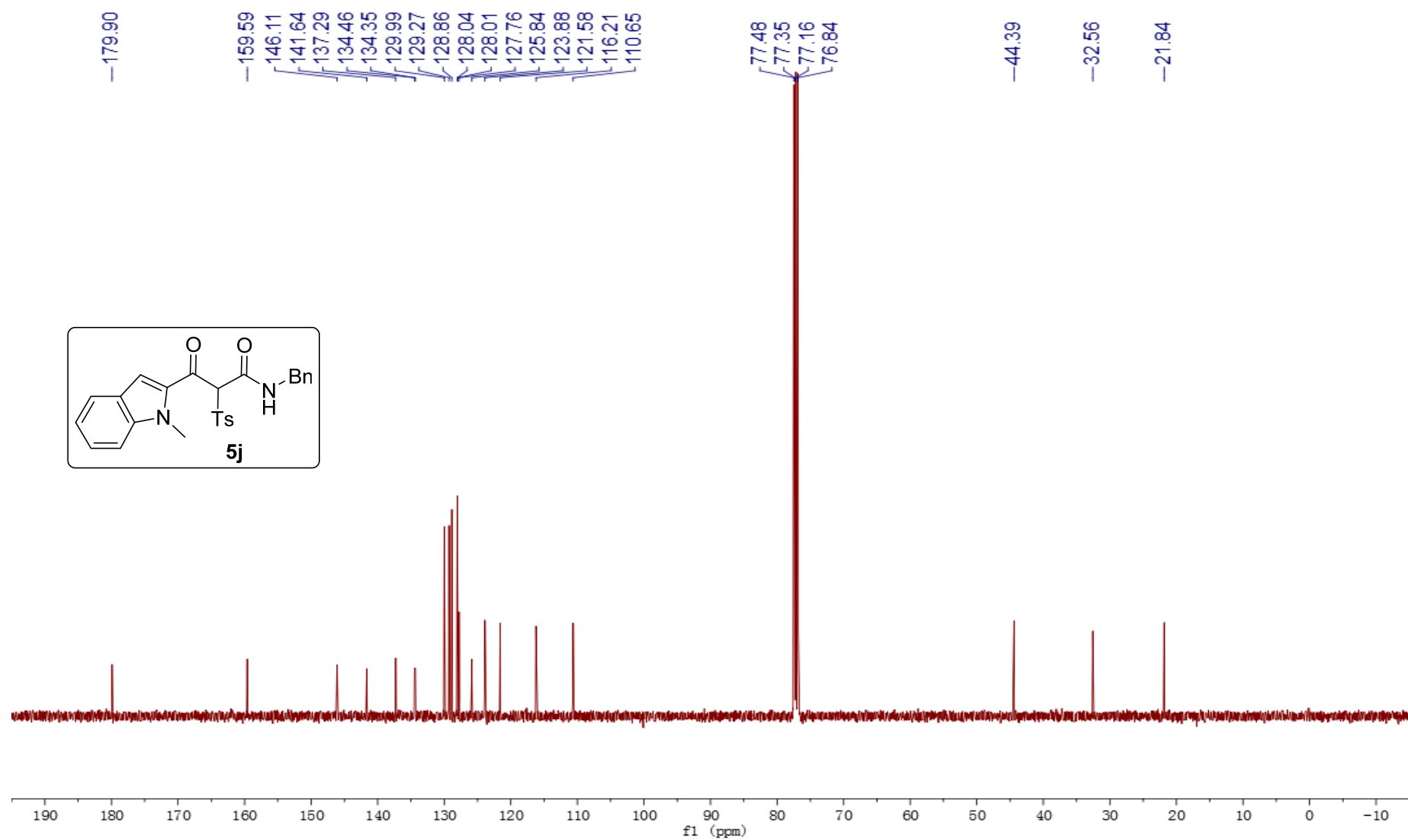




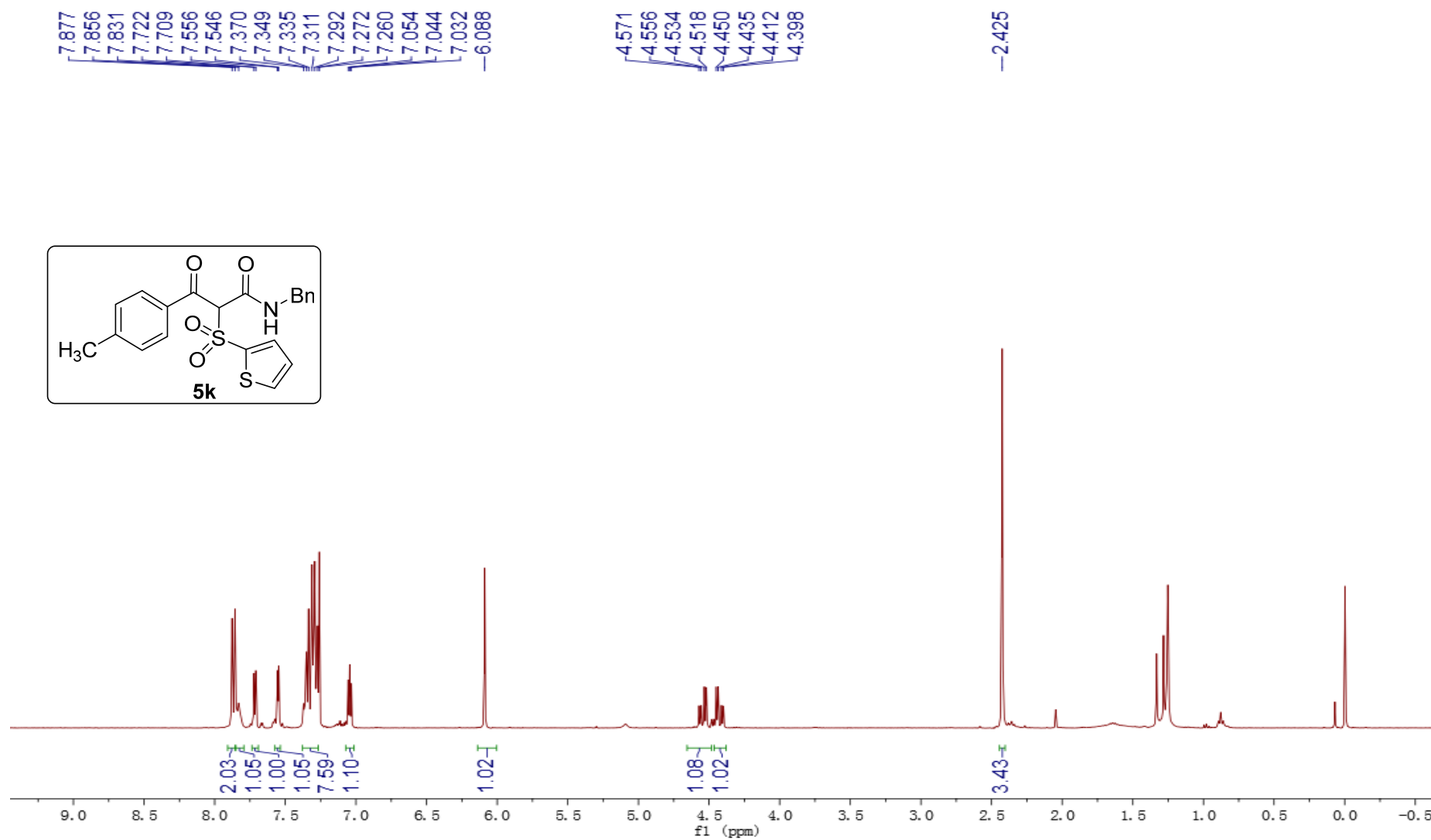


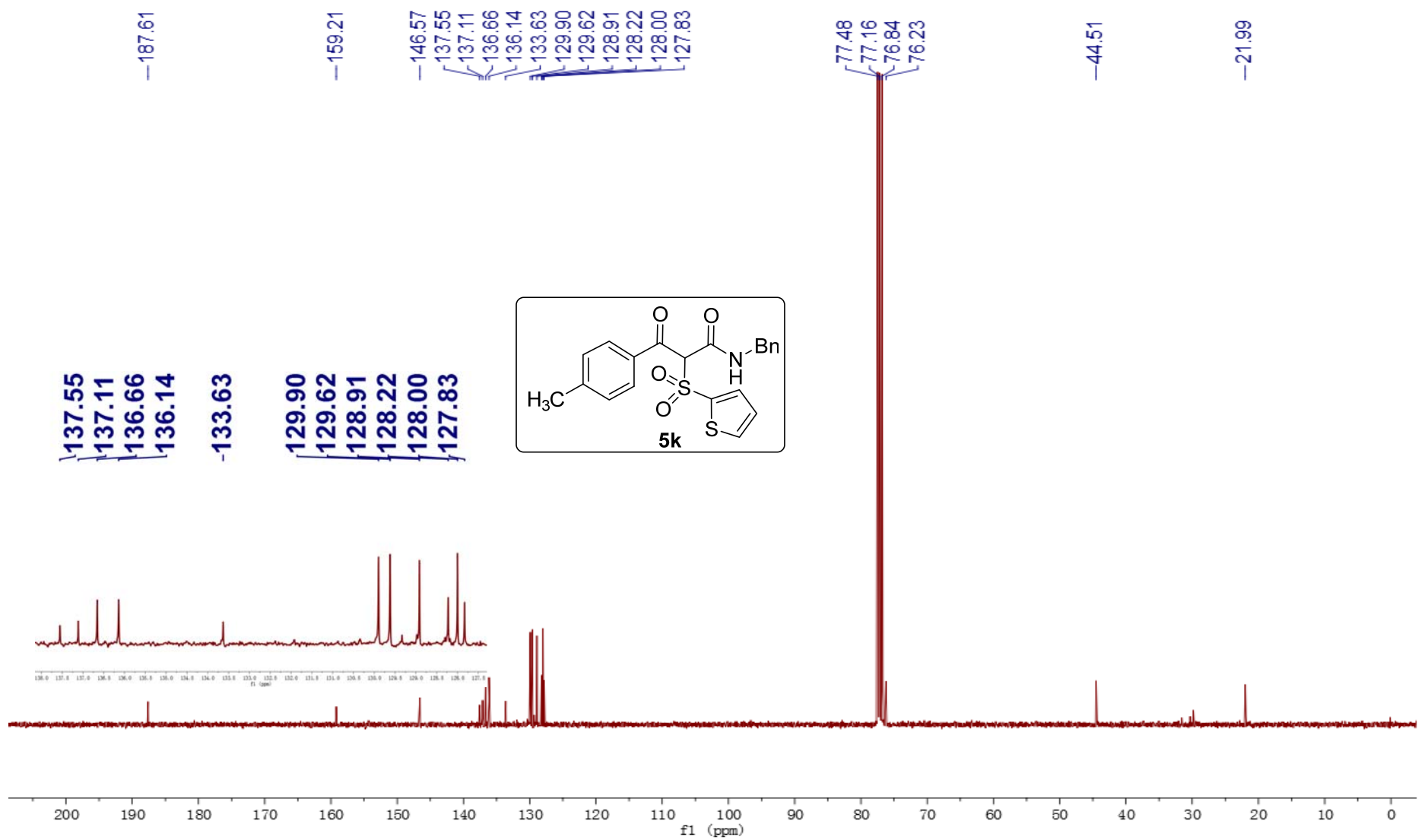


S100

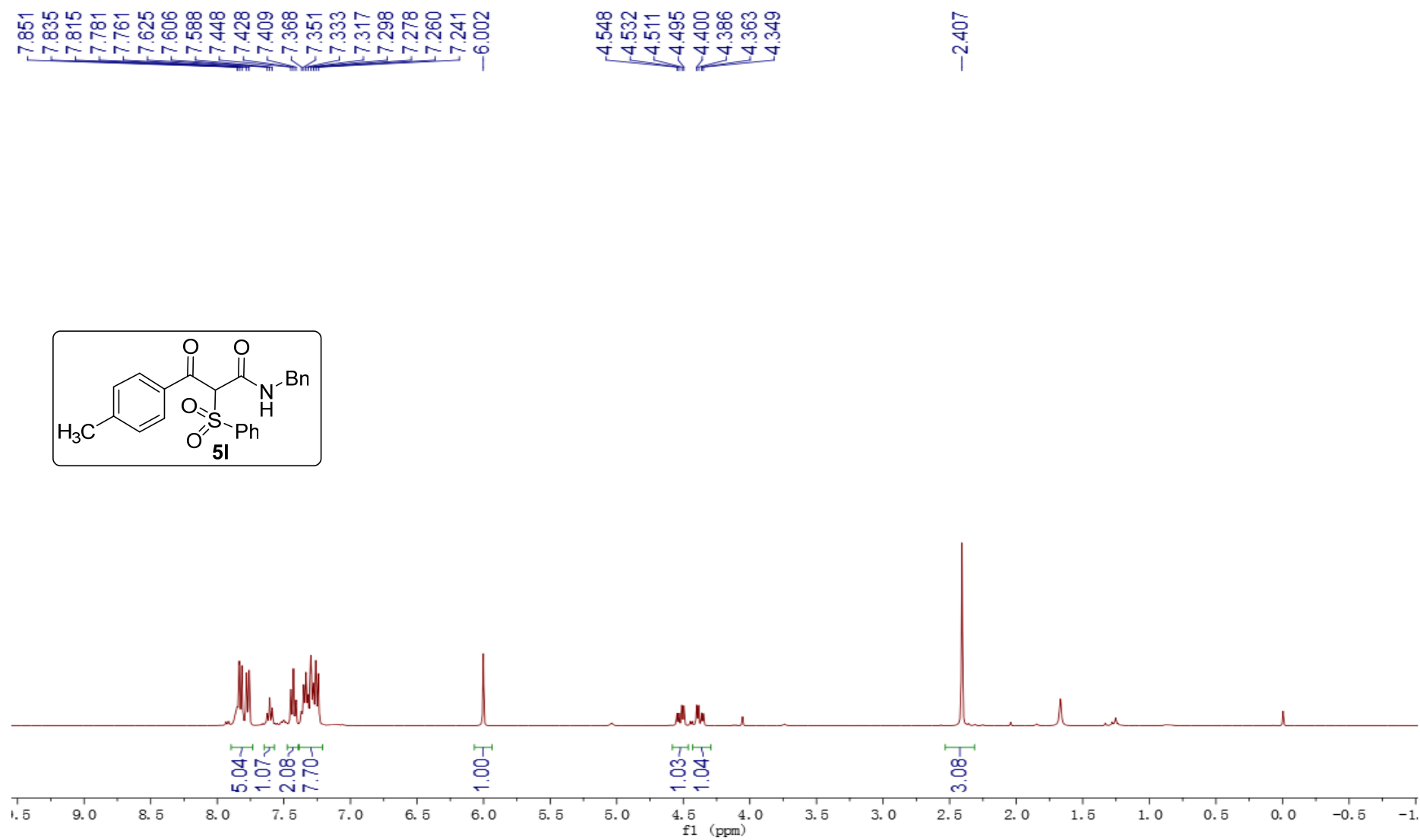


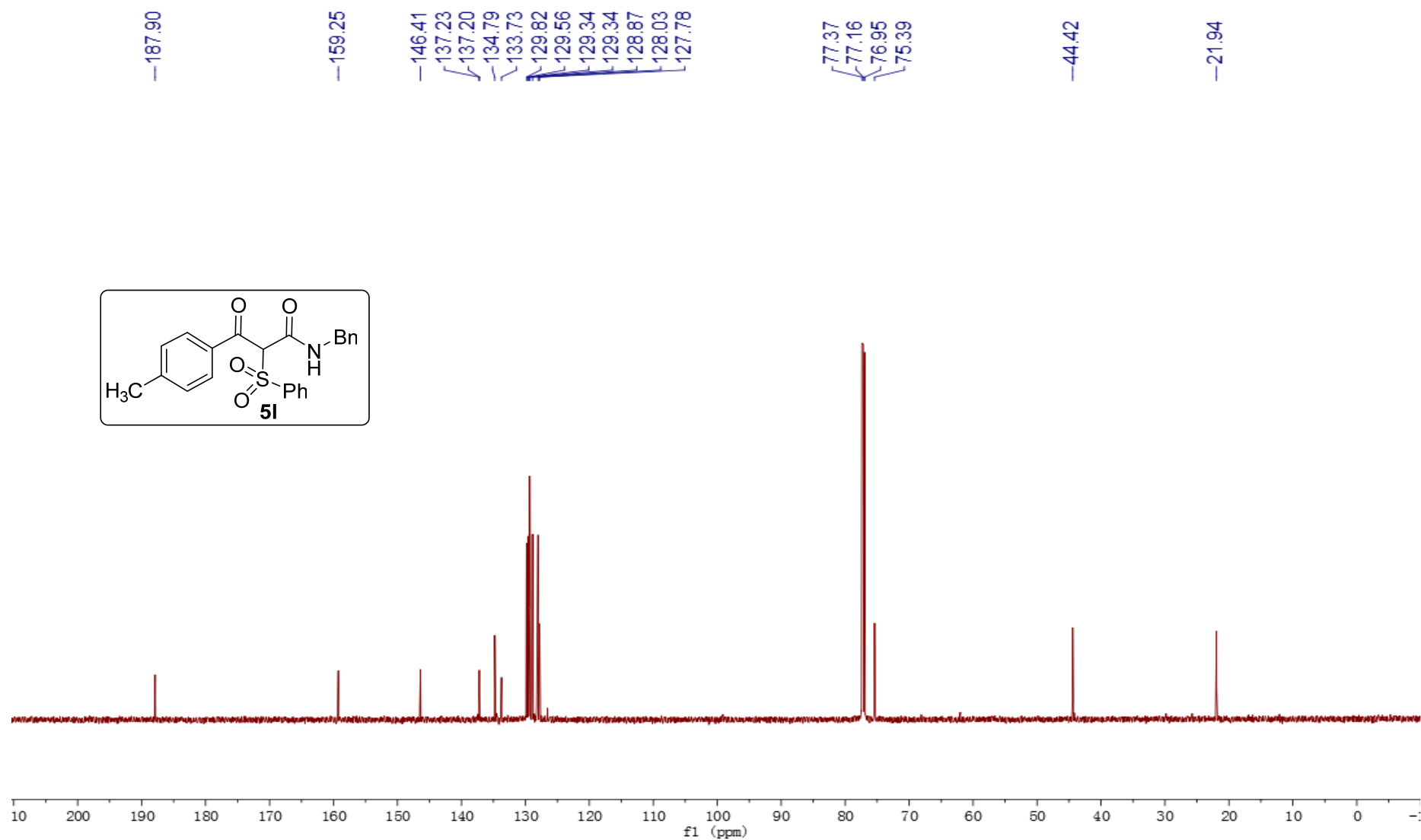
S101



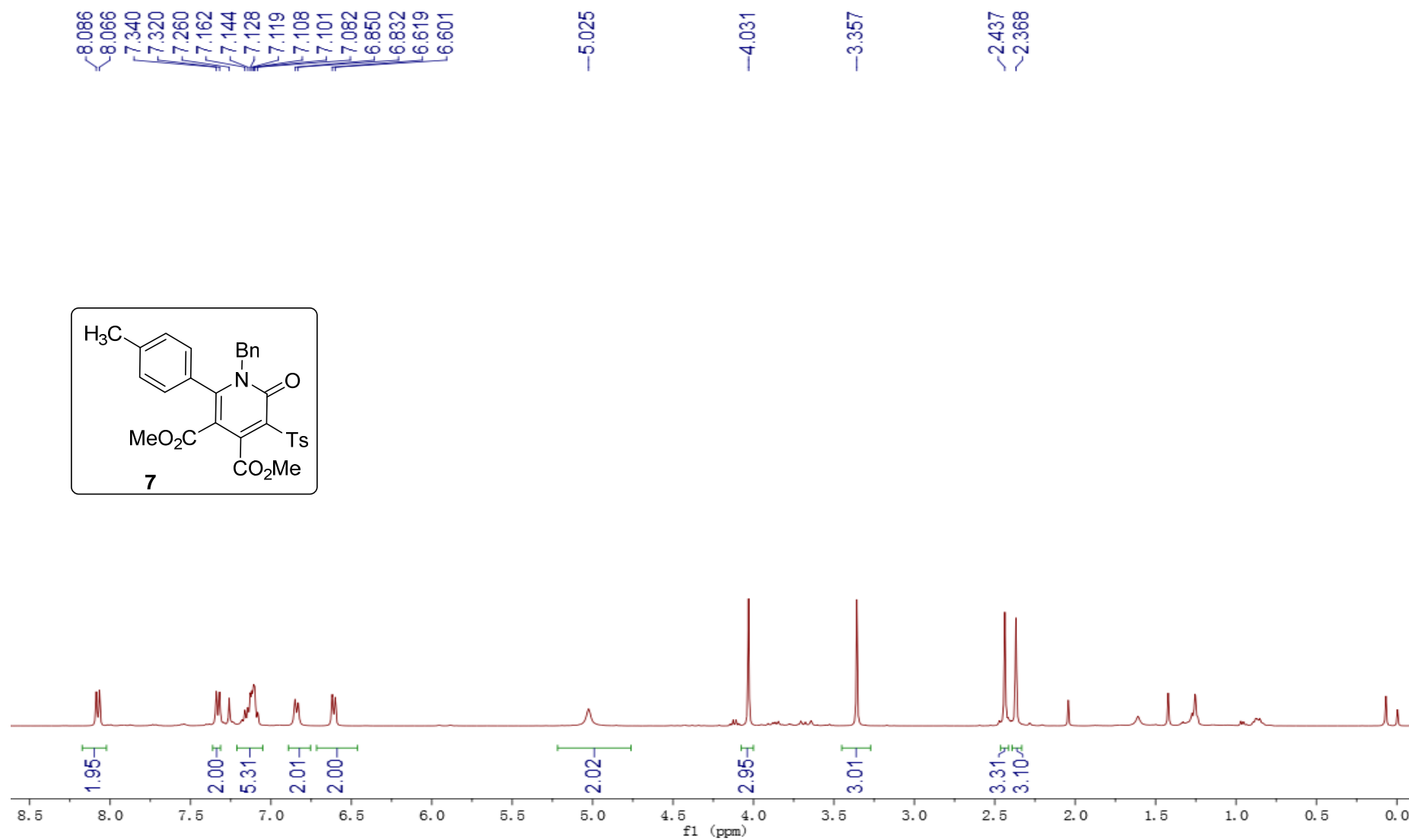


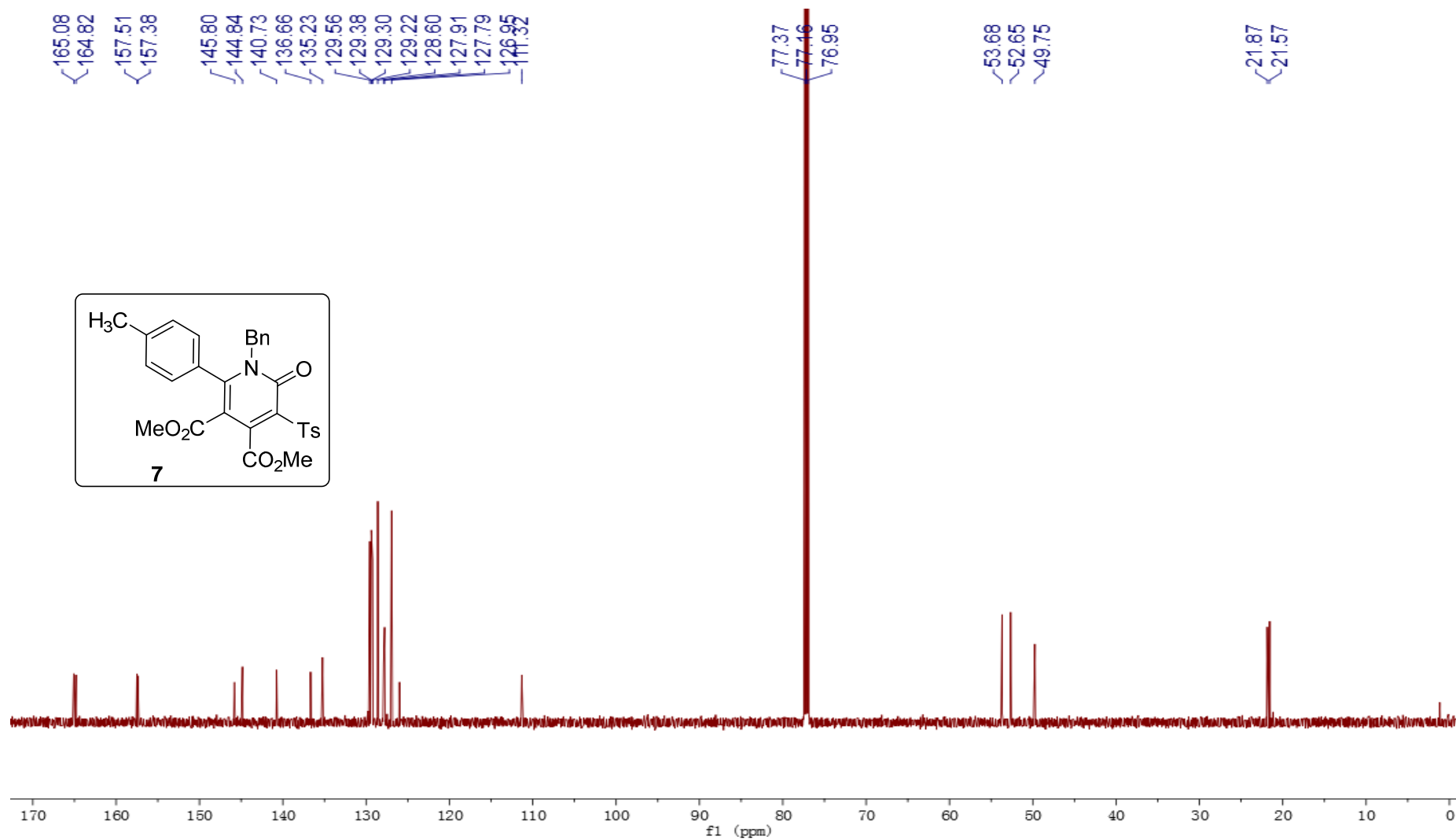
S103



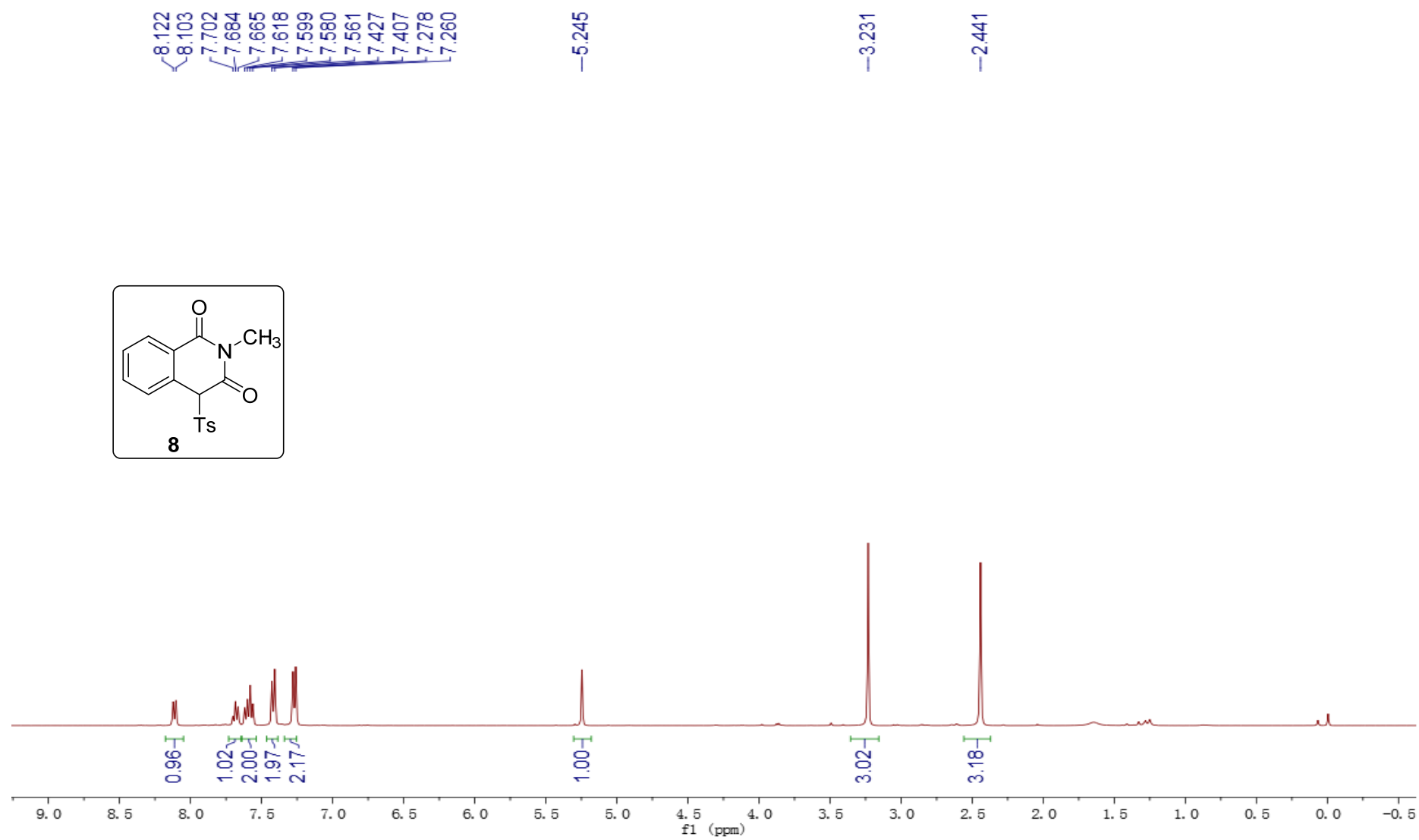


S105





S107



S108

