Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Gold-Catalyzed Oxidative Cyclization of Amide-Alkynes: Access to Functionalized γ-Lactams

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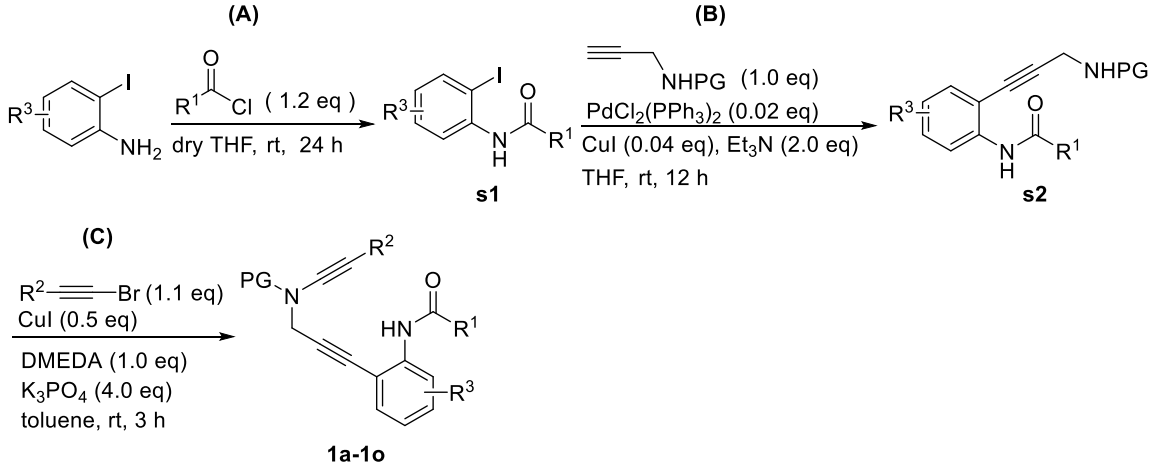
General Information. Ethyl acetate (ACS grade), hexanes (ACS grade) and anhydrous 1,2-dichloroethane (ACS grade) were obtained commercially and used without further purification. Methylene chloride, tetrahydrofuran and diethyl ether were purified according to standard methods unless otherwise noted. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Infrared spectra were recorded on a Nicolet iS 10 spectrometer as thin film and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass Q-Exactive Focus mass spectrometer using electron spray ionization.

^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration).

^{13}C NMR spectra were recorded on on a Bruker AV-400 spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

Representative synthetic procedures for the preparation of amide-tethered alkynes 1a-1o:

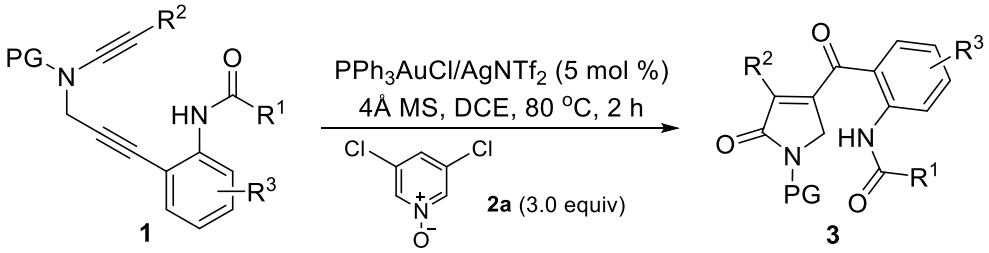


(A): Acyl chloride (12.0 mmol) was slowly added to a solution of 2-iodoaniline (10.0 mmol) in 20.0 mL dry THF at room temperature via dropping funnel. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 24 h. Upon completion, EtOAc (30 mL) was added, and the mixture was washed with 5% $NaHCO_3$, brine, dried over $MgSO_4$, and concentrated under reduced pressure to yield the crude iodobenzene **s1**, which was then used in the next step without purification.[1]

(B): Add $Pd(PPh_3)_2Cl_2$ (0.2 mmol, 140.4 mg), CuI (0.4 mmol, 76.0 mg) and triethylamine (20.0 mmol, 2020.0 mg) to a solution of the *N*-sulfonyl propargyl amine (10.0 mmol) and iodobenzene **s1** (10.0 mmol) in THF (30.0 mL) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 12 h. Upon completion, the reaction crude was filtered through a Celite plug and concentrated under vacuum, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired substrates **s2**.[2]

(C): To a mixture of **s2** (3.0 mmol), K_3PO_4 (12.0 mmol, 2544.0 mg), CuI (1.5 mmol, 285.0 mg), and DMEDA (3.0 mmol, 264.0 mg) in the reaction vial was added a solution of a respective brominated alkyne (3.3 mmol) in toluene. The reaction mixture was

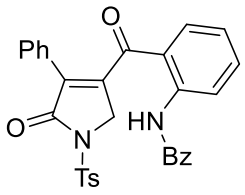
stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 3 h. Upon completion, the reaction crude was filtered through a Celite plug and concentrated under vacuum, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired enynamide substrates **1a-1o**.[2]



General procedure for the synthesis of γ-lactams 3:

3,5-Dichloropyridine *N*-oxide **2a** (0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) were added in this order to the amide-tethered alkynes **1** (0.2 mmol) in DCE (4.0 mL) at room temperature. The reaction mixture was stirred at 80 °C (80 °C, heating mantle temperature) and the progress of the reaction was monitored by TLC. The reaction typically took 2 h. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **3**.

***N*-(2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3a)**

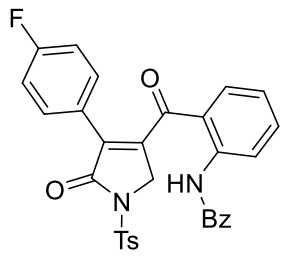


3a

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1a**, 0.2 mmol, 101.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3a** (83.3 mg, 77%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.22 (s, 1H), 8.93 (d, *J* = 8.5 Hz, 1H), 8.10 – 8.04 (m, 4H), 7.62 – 7.53 (m, 4H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.22 – 7.19 (m, 3H), 6.87 (t, *J* = 6.6 Hz, 1H), 4.82 (s, 2H), 2.46 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.3, 166.2, 166.1, 147.6, 145.7, 142.2, 137.1, 136.0, 134.7, 134.3, 133.3, 132.4, 129.9, 129.0, 128.9, 128.6, 128.4, 127.5, 122.7, 120.8, 119.7, 50.7, 21.7; IR (neat): 3284 (br), 2924, 1727, 1683, 1624, 1582, 1494, 1449, 1367, 1241, 1183, 1158, 1090, 965, 665; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{25}N_2O_5S$ 537.1479, found 537.1477.

_N_-(2-(4-(4-fluorophenyl)-5-oxo-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3b)

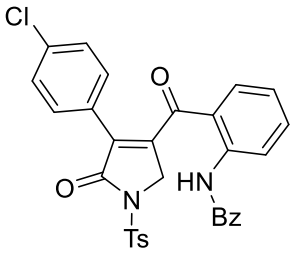


3b

The reaction was conducted with *N*-(2-(3-((*N*-((4-fluorophenyl)ethynyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1b**, 0.2 mmol, 104.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3b** (94.8 mg, 85%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.20 (s, 1H), 8.94 (d, *J* = 8.5 Hz, 1H), 8.10 – 8.03 (m, 4H), 7.63 – 7.55 (m, 4H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.32 (m, 4H), 6.93 – 6.88 (m, 3H), 4.82 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.1, 166.2, 166.0, 163.4 (d, *J* = 251.0 Hz), 147.5, 145.8, 142.3, 137.3, 134.8, 134.6, 134.3, 133.2, 132.4, 131.0 (d, *J* = 9.0 Hz), 129.9, 129.0, 128.3, 127.5, 124.5 (d, *J* = 3.0 Hz), 122.7, 120.9, 119.6, 115.9 (d, *J* = 22.0 Hz), 50.7, 21.7; IR (neat): 3284 (br), 2924, 1727, 1683, 1626, 1582, 1509, 1495, 1449, 1366, 1297, 1159, 1090, 966, 666; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{31}H_{24}FN_2O_5S$ 555.1384, found 555.1383.

_N_-(2-(4-(4-chlorophenyl)-5-oxo-1-tosyl-2,5-dihydro-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3c)

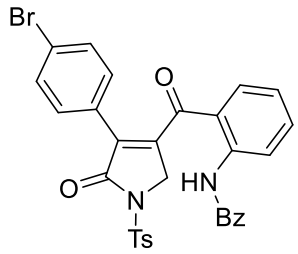


3c

The reaction was conducted with *N*-(2-(3-((*N*-((4-chlorophenyl)ethynyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1c**, 0.2 mmol, 107.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^{o}C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3c** (77.3 mg, 68%) as a pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.20 (s, 1H), 8.95 (d, *J* = 8.5 Hz, 1H), 8.09 – 8.02 (m, 4H), 7.61 – 7.54 (m, 4H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.19 (d, *J* = 6.9 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 4.81 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.0, 166.0(2), 165.9(7), 148.1, 145.8, 142.3, 137.4, 136.2, 134.6, 134.5, 134.2, 133.2, 132.4, 130.1, 130.0, 129.0, 128.3, 127.5, 126.8, 122.8, 121.0, 119.5, 50.8, 21.7; IR (neat): 3285 (br), 2925, 1728, 1682, 1626, 1581, 1529,

1494, 1449, 1367, 1297, 1138, 1090, 966, 665; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}ClN_2O_5S$ 571.1089, found 571.1088.

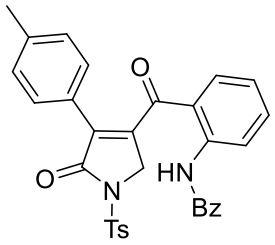
_N_-(2-(4-(4-bromophenyl)-5-oxo-1-tosyl-2,5-dihydro-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3d)



3d

The reaction was conducted with *N*-(2-(3-((*N*-((4-bromophenyl)ethynyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1d**, 0.2 mmol, 116.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3d** (82.4 mg, 67%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.19 (s, 1H), 8.95 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.54 (m, 4H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.34 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.91 (t, *J* = 7.6 Hz, 1H), 4.80 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.9, 166.0, 165.9, 148.1, 145.8, 142.3, 137.4, 134.6, 134.5, 134.2, 133.2, 132.4, 131.9, 130.3, 129.9, 129.0, 128.3, 127.5, 127.2, 124.6, 122.8, 121.0, 119.5, 50.8, 21.7; IR (neat): 3284 (br), 2923, 1727, 1660, 1605, 1582, 1527, 1464, 1449, 1362, 1298, 1172, 1089, 965, 664; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{23}BrN_2O_5SNa$ 637.0403, found 637.0399.

_N_-(2-(5-oxo-4-(_p_-tolyl)-1-tosyl-2,5-dihydro-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3e)

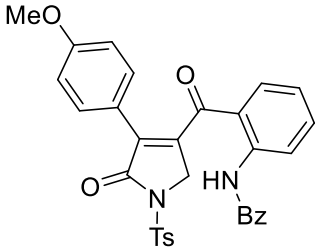


3e

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(*p*-tolylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1e**, 0.2 mmol, 103.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ºC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3e** (86.0 mg, 78%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.25 (s, 1H), 8.93 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 7.1 Hz, 2H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.61 – 7.56 (m, 4H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.88 (t, *J* = 7.6 Hz, 1H), 4.79 (s, 2H), 2.44 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.5, 166.4, 166.0, 146.8, 145.6, 142.2, 140.2, 137.0, 135.8, 134.8, 134.3, 133.3, 132.4, 129.9, 129.3, 128.9, 128.8, 128.3, 127.5, 125.5, 122.7, 120.8, 119.8, 50.6, 21.7, 21.3; IR (neat): 3282 (br), 2922, 1727, 1682, 1625, 1581, 1527, 1449, 1365, 1330, 1239, 1173, 1089, 965, 665; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{26}N_2O_5SNa$ 573.1455, found 573.1450.

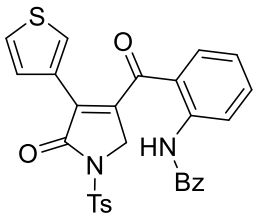
_N_-(2-(4-(4-methoxyphenyl)-5-oxo-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3f)



3f

The reaction was conducted with *N*-(2-(3-((*N*-((4-methoxyphenyl)ethynyl)-4-methylphenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1f**, 0.2 mmol, 107.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3f** (77.1 mg, 68%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.27 (s, 1H), 8.94 (d, *J* = 7.4 Hz, 1H), 8.10 (d, *J* = 6.7 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.62 – 7.55 (m, 4H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.30 (d, *J* = 6.9 Hz, 2H), 6.88 (t, *J* = 6.9 Hz, 1H), 6.72 (d, *J* = 6.9 Hz, 2H), 4.79 (s, 2H), 3.70 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.6, 166.6, 166.1, 160.8, 145.7, 145.6, 142.2, 137.0, 135.4, 134.8, 134.4, 133.3, 132.4, 130.5, 129.9, 129.0, 128.3, 127.5, 122.7, 120.8(3), 120.8(0), 119.7, 114.1, 55.2, 50.5, 21.7; IR (neat): 3282 (br), 2924, 1726, 1682, 1605, 1581, 1513, 1449, 1367, 1296, 1255, 1173, 1090, 966, 665; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{32}H_{26}N_2O_6SNa$ 589.1404, found 589.1397.

_N_-(2-(5-oxo-4-(thiophen-3-yl)-1-tosyl-2,5-dihydro-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3g)

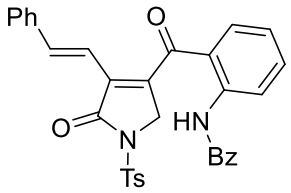


3g

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(thiophen-3-ylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1g**, 0.2 mmol, 102.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3g** (89.1 mg, 82%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.31 (s, 1H), 9.01 (d, *J* = 8.6 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 2H), 8.03 (d, *J* = 7.2 Hz, 2H), 7.95 – 7.90 (m, 1H), 7.66 – 7.54 (m, 5H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.13 – 7.11 (m, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 5.1 Hz, 1H), 4.77 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.7, 166.2, 166.1, 145.7, 144.9, 142.3, 137.5, 134.7, 134.3, 133.5, 132.4, 129.9, 129.8, 129.0, 128.5, 128.3, 127.5, 126.9, 126.2, 123.0, 121.0, 119.8, 50.7, 21.7; IR (neat): 3289 (br), 2920, 1727, 1628, 1581, 1527, 1449, 1368, 1298, 1243, 1173, 1089, 756, 666; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{29}H_{22}N_2O_5S_2Na$ 565.0862, found 565.0856.

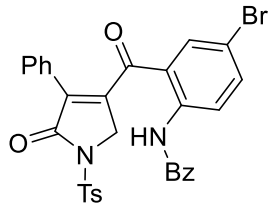
_N_-(2-(5-oxo-4-styryl-1-tosyl-2,5-dihydro-1_H_-pyrrole-3-carbonyl)phenyl)benzamide (3h)



3h

The reaction was conducted with *N*-(2-(3-((4-methyl-*N*-(4-phenylbut-3-en-1-yn-1-yl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1h**, 0.2 mmol, 106.2 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^{o}C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3h** (82.8 mg, 74%) as a pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.08 (s, 1H), 9.02 (d, *J* = 8.6 Hz, 1H), 8.08 – 8.03 (m, 5H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.62 – 7.53 (m, 4H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.26 – 7.23 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 16.2 Hz, 1H), 4.78 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.2, 166.3, 166.1, 145.7, 144.8, 141.8, 138.8, 137.1, 135.8, 134.9, 134.3, 133.6, 133.1, 132.4, 130.0, 129.4, 129.0, 128.7, 128.3, 127.5, 127.3, 123.0, 121.4(3), 121.3(8), 116.0, 50.2, 21.7; IR (neat): 3286 (br), 2922, 1724, 1682, 1621, 1580, 1525, 1448, 1369, 1239, 1171, 1127, 1088, 911, 666; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{33}H_{26}N_2O_5SNa$ 585.1455, found 585.1447.

***N*-(4-bromo-2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3i)**

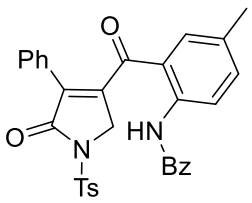


3i

The reaction was conducted with *N*-(4-bromo-2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1i**, 0.2 mmol, 116.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3i** (79.5 mg, 65%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.03 (s, 1H), 8.80 (d, *J* = 9.0 Hz, 1H), 8.10 – 8.02 (m, 4H), 7.63 – 7.53 (m, 4H), 7.52 – 7.46 (m, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.27 – 7.24 (m, 5H), 4.84 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.8, 166.1, 165.9, 146.4, 145.8, 140.8, 139.3, 138.1, 135.4, 134.6, 134.0, 132.6, 130.3, 130.0, 129.0(2), 128.9(8), 128.7, 128.4, 128.3, 127.4, 122.5, 121.1, 114.8, 50.4, 21.7; IR (neat): 3287 (br), 2922, 1729, 1684, 1627, 1598, 1573, 1492, 1370, 1288, 1239, 1171, 1089, 966, 666; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}BrN_2O_5S$ 615.0584, found 615.0580.

***N*-(4-methyl-2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3j)**

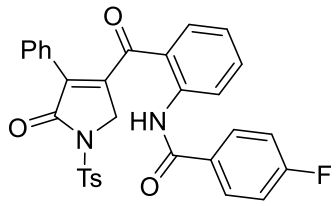


3j

The reaction was conducted with *N*-(4-methyl-2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1j**, 0.2 mmol, 103.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3j** (72.2 mg, 65%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.10 (s, 1H), 8.79 (d, *J* = 8.6 Hz, 1H), 8.08 – 8.04 (m, 4H), 7.60 – 7.53 (m, 3H), 7.38 – 7.20 (m, 9H), 4.83 (s, 2H), 2.45 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.0, 166.4, 165.9, 147.7, 145.7, 139.8, 137.8, 136.3, 134.7, 134.4, 133.4, 132.4, 132.3, 129.9(2), 129.8(8), 128.9(0), 128.8(5), 128.6, 128.4, 127.4, 120.8, 119.6, 50.7, 21.7, 20.3; IR (neat): 3289 (br), 2924, 1727, 1679, 1626, 1589, 1522, 1495, 1446, 1366, 1259, 1171, 1090, 969, 666; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{27}N_2O_5S$ 551.1635, found 551.1630.

4-fluoro-*N*-(2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3k)

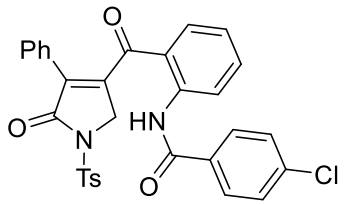


3k

The reaction was conducted with 4-fluoro-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1k**, 0.2 mmol, 104.6 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3k** (72.1 mg, 65%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.21 (s, 1H), 8.89 (d, *J* = 8.5 Hz, 1H), 8.12 – 8.09 (m, 2H), 8.05 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 6.3 Hz, 2H), 7.26 – 7.22 (m, 5H), 6.87 (t, *J* = 7.4 Hz, 1H), 4.82 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.4, 166.2, 165.3 (d, *J* = 251.0 Hz), 164.9, 147.5, 145.8, 142.2, 137.2, 136.1, 134.7, 133.4, 130.5 (d, *J* = 3.0 Hz), 129.9, 129.9 (d, *J* = 9.0 Hz), 128.9, 128.6, 128.4, 122.8, 120.8, 119.6, 116.1 (d, *J* = 22.0 Hz), 50.7, 21.7; IR (neat): 3283 (br), 2924, 1728, 1683, 1604, 1583, 1505, 1447, 1367, 1295, 1237, 1172, 1089, 964, 667; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}FN_2O_5S$ 555.1384, found 555.1382.

4-chloro-*N*-(2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3l)



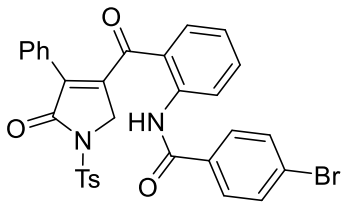
3l

The reaction was conducted with 4-chloro-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1l**, 0.2 mmol, 107.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3l** (85.5 mg, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.23 (s, 1H), 8.89 (d, *J* = 8.5 Hz, 1H), 8.03 (t, *J* = 7.5 Hz, 4H), 7.56 – 7.52 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 2H), 7.24 – 7.20 (m, 3H), 6.87 (t, *J* = 7.6 Hz, 1H), 4.81 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.4, 166.2, 164.9, 147.5, 145.8, 142.0, 138.8, 137.2, 136.1, 134.7, 133.4, 132.7, 129.9, 129.2, 128.9, 128.6, 128.4, 122.9, 120.8, 119.6, 50.7, 21.7; IR (neat): 3283 (br), 2924, 1728, 1685, 1624, 1584, 1530, 1490, 1448,

1367, 1239, 1172, 1093, 965, 666; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}ClN_2O_5S$ 571.1089, found 571.1083.

4-bromo-*N*-(2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3m)

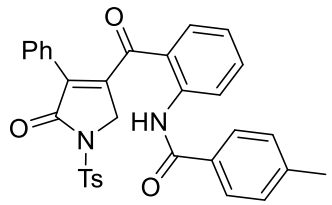


3m

The reaction was conducted with 4-bromo-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1m**, 0.2 mmol, 116.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3m** (97.3 mg, 79%) as a yellow solid (mp 165-167 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.23 (s, 1H), 8.88 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.22 – 7.19 (m, 3H), 6.87 (t, *J* = 7.6 Hz, 1H), 4.81 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.4, 166.2, 165.0, 147.5, 145.8, 142.0, 137.2, 136.1, 134.7, 133.4, 133.2, 132.2, 129.9, 129.0, 128.9, 128.6, 128.4, 127.3, 122.9, 120.8, 119.6, 50.7, 21.7; IR (neat): 3282 (br), 2924, 1728, 1684, 1606, 1585, 1529, 1487, 1448, 1328, 1296, 1172, 1090, 965, 666; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{24}BrN_2O_5S$ 615.0584, found 615.0583.

4-methyl-*N*-(2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3n)

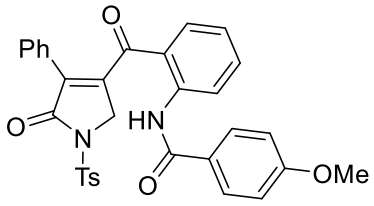


3n

The reaction was conducted with 4-methyl-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1n**, 0.2 mmol, 103.8 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 ^oC (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3n** (75.5 mg, 69%) as a pale yellow oil.

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.19 (s, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 3.1 Hz, 2H), 7.98 (d, *J* = 2.8 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.37 – 7.32 (m, 6H), 7.26 – 7.21 (m, 3H), 6.88 – 6.83 (m, 1H), 4.82 (s, 2H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.2, 166.3, 166.1, 147.7, 145.7, 143.1, 142.4, 137.1, 135.9, 134.8, 133.3, 131.5, 129.9, 129.6, 128.9, 128.6, 128.4, 127.5, 122.5, 120.8, 119.6, 50.7, 29.7, 21.7, 21.6; IR (neat): 3286 (br), 2922, 1728, 1683, 1610, 1581, 1507, 1447, 1367, 1297, 1240, 1172, 1089, 965, 667; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{27}N_2O_5S$ 551.1635, found 551.1631.

4-methoxy-*N*-(2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3o)



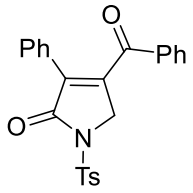
3o

The reaction was conducted with 4-methoxy-*N*-(2-(3-((4-methyl-*N*-(phenylethynyl)phenyl)sulfonamido)prop-1-yn-1-yl)phenyl)benzamide (**1o**, 0.2 mmol,

107.0 mg), 3,5-dichloropyridine *N*-oxide (**2a**, 0.6 mmol, 98.4 mg), PPh_3AuCl (0.01 mmol, 5.0 mg), $AgNTf_2$ (0.01 mmol, 3.9 mg), and 4Å molecular sieves (40 mg) in DCE (4.0 mL) at 80 °C (80 °C, heating mantle temperature). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) yielded **3o** (81.4 mg, 72%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.16 (s, 1H), 8.91 (d, *J* = 8.5 Hz, 1H), 8.07 – 8.03 (m, 4H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.23 – 7.20 (m, 3H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.84 (t, *J* = 7.6 Hz, 1H), 4.81 (s, 2H), 3.90 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.2, 166.3, 165.6, 162.9, 147.8, 145.7, 142.6, 137.1, 135.8, 134.8, 133.3, 129.9, 129.5, 128.9, 128.6, 128.4(0), 128.3(6), 126.6, 122.4, 120.7, 119.5, 114.2, 55.5, 50.7, 21.7; IR (neat): 3286 (br), 2923, 1727, 1680, 1606, 1581, 1531, 1447, 1367, 1296, 1251, 1173, 1090, 965 ,667; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{32}H_{27}N_2O_6S$ 567.1584, found 567.1580.

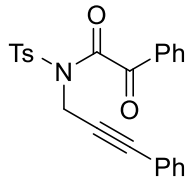
4-benzoyl-3-phenyl-1-tosyl-1,5-dihydro-2*H*-pyrrol-2-one (3p)



3p

This compound is known and the spectroscopic data match those reported.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.9 Hz, 2H), 7.67 (d, *J* = 6.8 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.19 – 7.13 (m, 3H), 4.80 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 166.6, 147.7, 145.6, 136.4, 134.8, 134.4, 134.2, 129.9, 129.7, 129.4, 129.2, 128.7, 128.6, 128.4, 128.3, 50.6, 21.7.

2-oxo-2-phenyl-*N*-(3-phenylprop-2-yn-1-yl)-*N*-tosylacetamide (3pa)

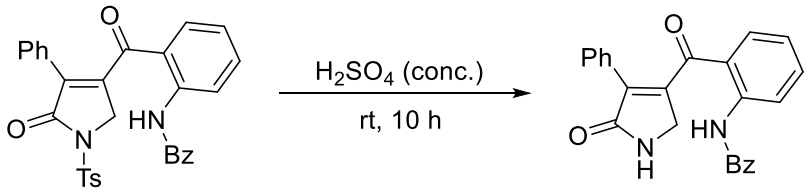


3pa

This compound is known and the spectroscopic data match those reported.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 4H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.34 – 7.26 (m, 5H), 7.15 (d, *J* = 7.1 Hz, 2H), 4.86 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 166.3, 145.9, 134.5(3), 134.4(9), 132.8, 131.7, 129.9, 129.7, 128.9, 128.8, 128.6, 128.1, 121.9, 84.6, 81.6, 34.9, 21.6.

Synthetic Applications

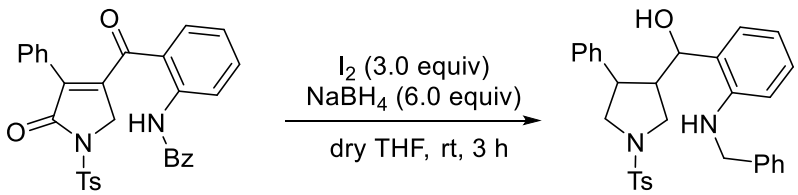
N-(2-(5-oxo-4-phenyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (4)



3a **4**, 61%

H_2SO_4 (98%, 8.0 mL) was added to a flame dried *Schlenk*-flask containing **3a** (0.2 mmol, 107.4 mg) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction took 10 h. Upon completion, the solution was diluted with 20 mL EtOAc and neutralized with saturated Na_2CO_3 at 0 ^oC. The aqueous phase was extracted with EtOAc three times and the combined organic phase was dried with Mg_2SO_4. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **4** (46.6 mg, 61% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.31 (s, 1H), 8.91 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 7.1 Hz, 2H), 7.85 (s, 1H), 7.61 – 7.49 (m, 6H), 7.42 (d, *J* = 3.4 Hz, 2H), 7.26 – 7.24 (m, 2H), 6.84 (t, *J* = 7.5 Hz, 1H), 4.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.4, 166.1, 148.2, 141.9, 136.4, 134.5, 133.5, 132.3, 129.8, 129.3, 129.0, 128.9, 128.5, 127.5, 122.5, 120.7, 120.4, 47.6; IR (neat): 3277 (br), 2921, 1693, 1621, 1605, 1581, 1526, 1494, 1448, 1384, 1296, 1163, 1088, 911, 697; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{19}N_2O_3$ 383.1390, found 383.1387.

(2-(benzylamino)phenyl)(4-phenyl-1-tosylpyrrolidin-3-yl)methanol (5)



3a **5**, 99%

To a mixture of I_2 (0.6 mmol, 152.4 mg), and $NaBH_4$ (1.2 mmol, 45.6 mg) was added to a solution of compound **3a** (0.2 mmol, 107.4 mg) in DCE (4.0 mL) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. Upon completion, the mixture was then concentrated and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product **5** (101.4 mg, 99% yield, yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.08 (m, 14H), 6.83 (d, *J* = 7.4 Hz, 1H), 6.66 – 6.62 (m, 2H), 4.52 (d, *J* = 8.5 Hz, 1H), 4.31 – 4.18 (m, 2H), 3.77 – 3.72 (m, 1H), 3.37 – 3.32 (m, 1H), 3.23 – 3.18 (m, 3H), 3.03 – 2.97 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 143.6, 141.4, 139.2, 133.4, 129.7, 129.5, 128.8, 128.6, 128.4, 127.7, 127.4, 127.3, 127.1, 127.0, 124.2, 116.7, 111.8, 78.8, 55.4, 50.6, 48.2, 48.0, 47.9, 21.6; IR (neat): 3373 (br), 2921, 1653, 1603, 1515, 1494, 1452, 1384, 1161, 1088, 1042, 1021, 751, 667; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{31}H_{33}N_2O_3S$ 513.2206, found 513.2203.

Reference

(1) Evindar, G.; Batey, R. A. Parallel synthesis of a library of benzoxazoles and benzothiazoles using ligand-accelerated copper-catalyzed cyclizations of ortho-halobenzanilides. *J. Org. Chem.* **2006**, *71*, 1802-1808.

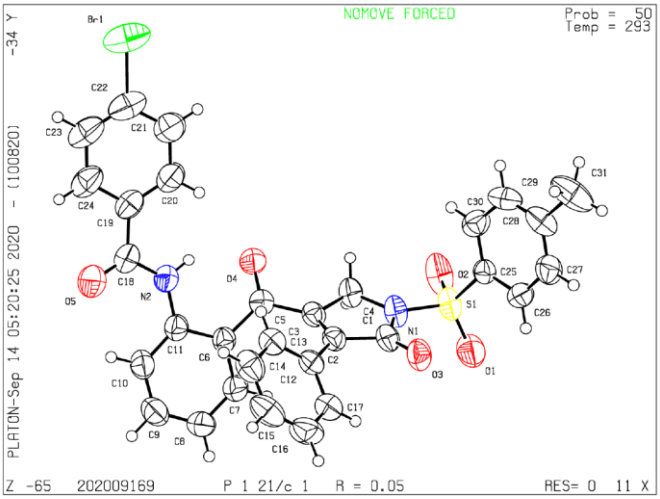
(2) Shen, W.-B.; Tang, X.-T.; Zhang, T.-T.; Liu, S.-Y.; He, J.-M.; Su, T.-F. Cu(I)-catalyzed oxidative cyclization of enynamides: regioselective access to cyclopentadiene frameworks and 2-aminofurans. *Org. Lett.* **2020**, *22*, 6799-6804.

(3) Liu, R.; Winston-McPherson, G. N.; Yang, Z.-Y.; Zhou, X.; Song, W.; Guzei, I. A.; Xu, X.; Tang, W. Generation of rhodium(I) carbenes from ynamides and their reactions with alkynes and alkenes. *J. Am. Chem. Soc.* **2013**, *135*, 8201-8204.

(4) Zhu, G.; Gao, W.-C.; Jiang, X. Rh(I)-catalyzed carbene migration/carbonylation/cyclization: straightforward construction of fully substituted aryne precursors. *J. Am. Chem. Soc.* **2021**, *143*, 1334-1340.

4-bromo-*N*-(2-(5-oxo-4-phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole-3-carbonyl)phenyl)benzamide (3m). CCDC Number = 2049244

Crystal of **3m** was grown by slow evaporation of hexane/dichloromethane solution of **3m** at room temperature (25 °C). X-ray diffraction data was collected at 293 K on a Rigaku Gemini E diffractometer with graded-multilayer focused CuK(alpha) X-rays.



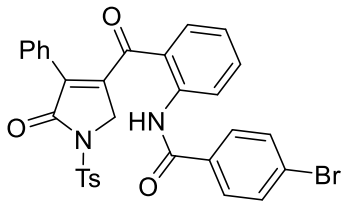


Figure S2. Crystal structure of **3m** with thermal ellipsoids at 50% probability

---

```
Bond precision:  C-C = 0.0053 A          Wavelength=1.54184

Cell:            a=10.9570(4)     b=29.1941(10)       c=8.9667(3)
                 alpha=90         beta=101.076(3)     gamma=90
Temperature:     293 K

                 Calculated                Reported
Volume           2814.84(17)               2814.84(18)
Space group      P 21/c                    P 1 21/c 1
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C31 H23 Br N2 O5 S        C31 H23 Br N2 O5 S
Sum formula      C31 H23 Br N2 O5 S        C31 H23 Br N2 O5 S
Mr               615.47                    615.48
Dx,g cm-3        1.452                     1.452
Z                4                         4
Mu (mm-1)        3.046                     3.046
F000             1256.0                    1256.0
F000'            1257.95
h,k,lmax         13,34,10                  13,34,10
Nref             5029                      5010
Tmin,Tmax        0.756,0.885               0.664,1.000
Tmin'            0.518

Correction method= # Reported T Limits: Tmin=0.664 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996          Theta(max)= 67.068

R(reflections)= 0.0485( 3531)     wR2(reflections)= 0.1328( 5010)

S = 1.038                 Npar= 366
```

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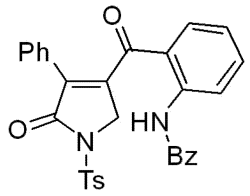
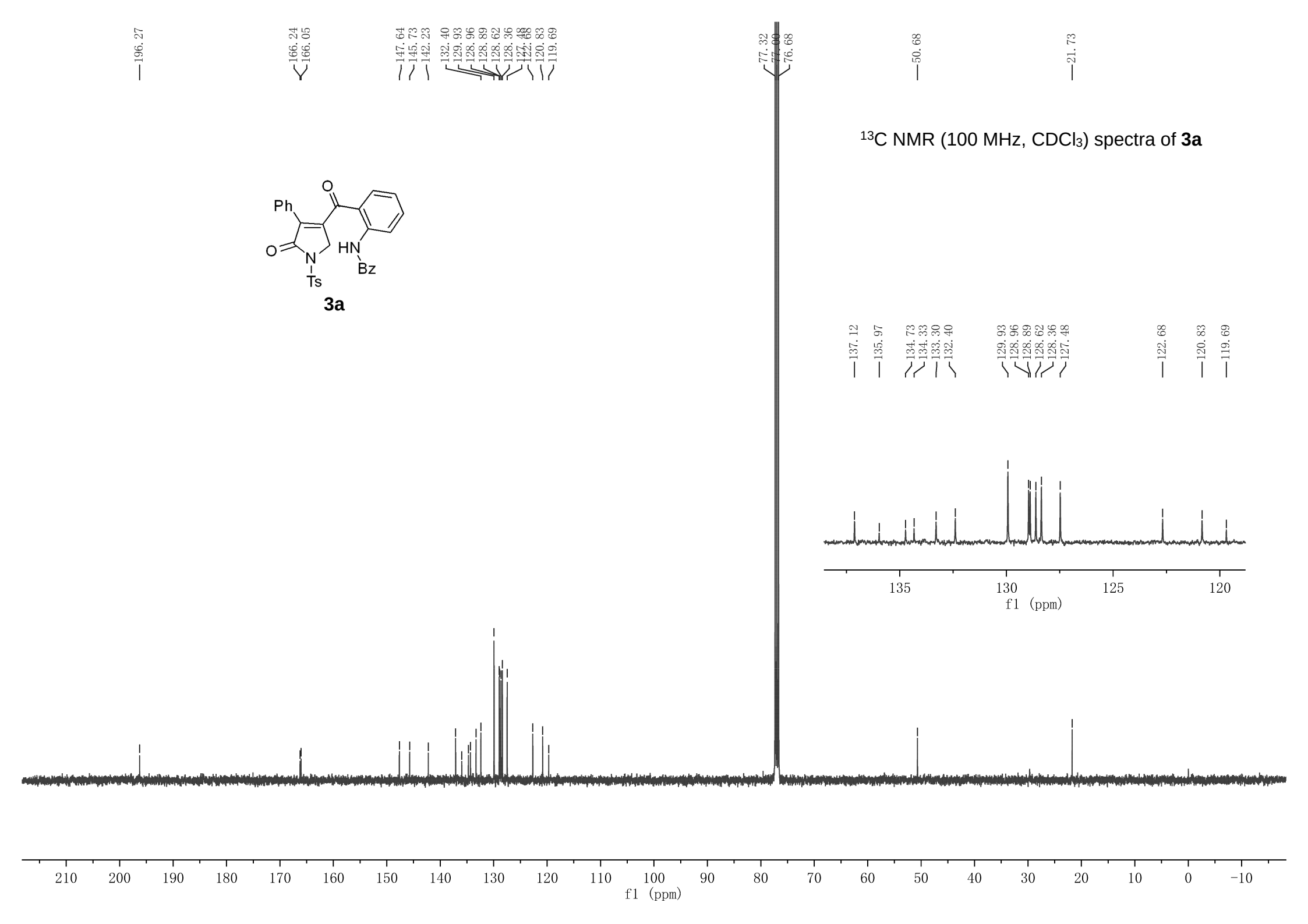
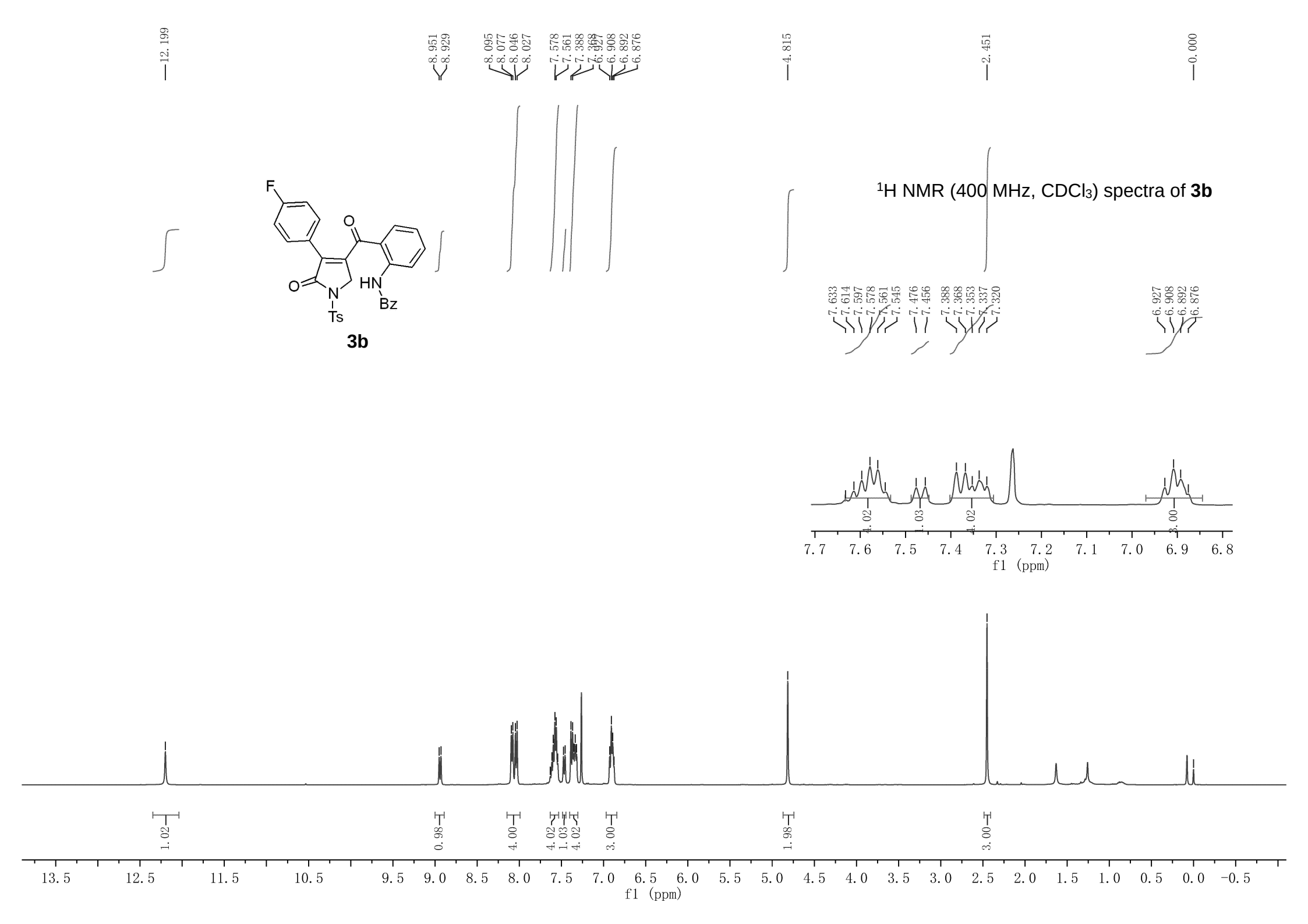
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3a**

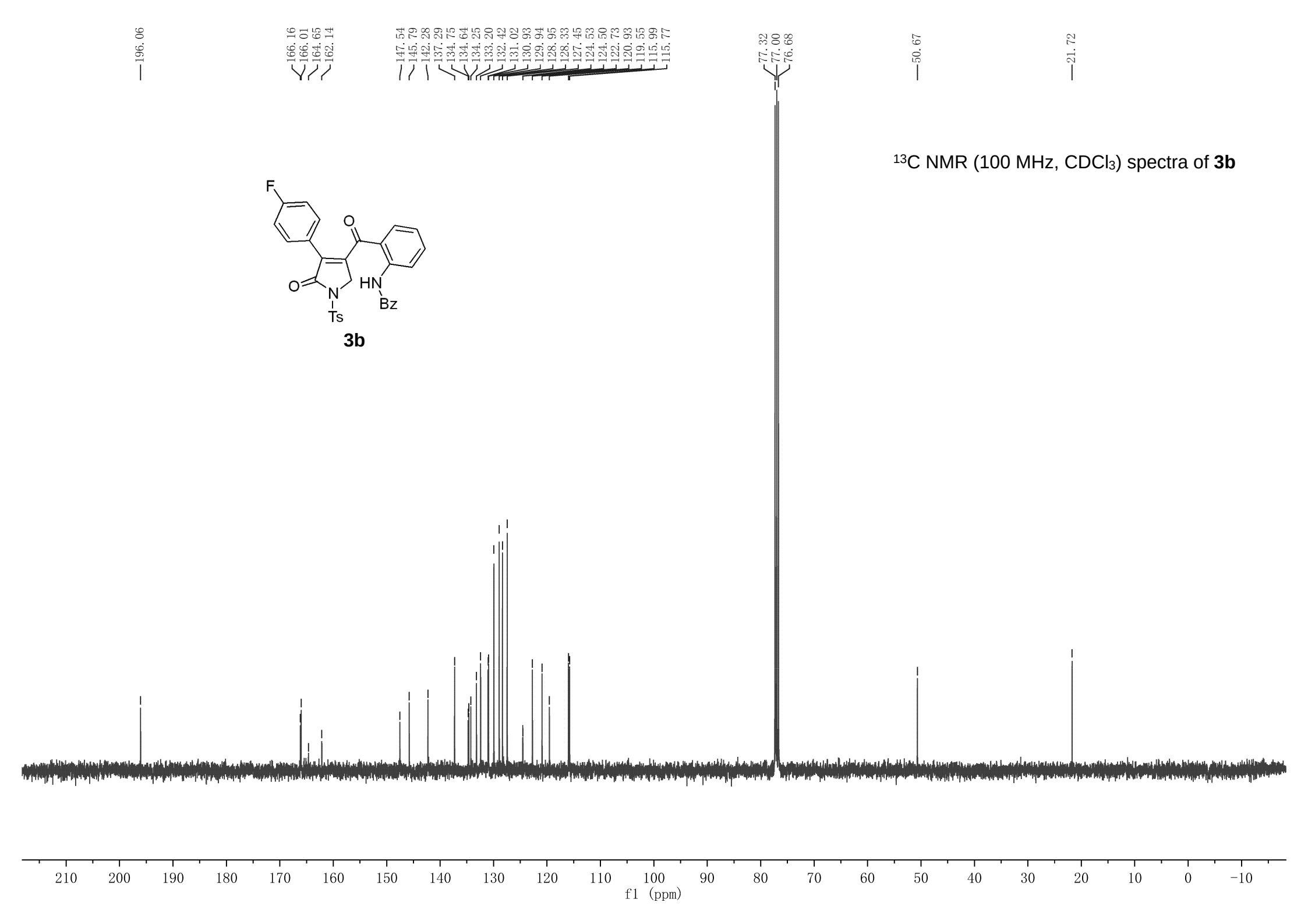


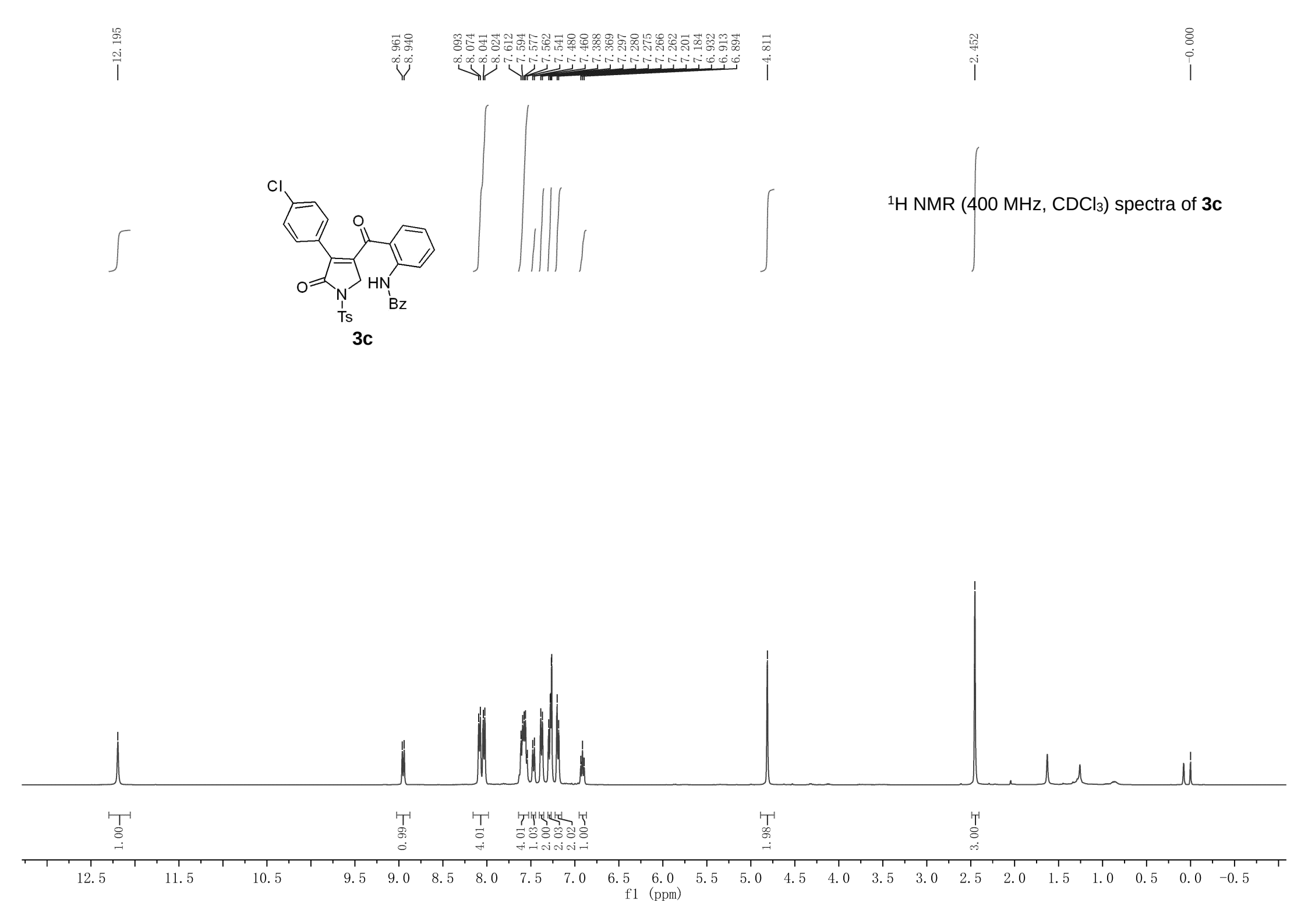
3a



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


12.199
8.951
8.929
8.095
8.077
8.046
8.027
7.578
7.561
7.388
6.908
6.892
6.876
4.815
2.451
0.000
7.633
7.614
7.597
7.578
7.561
7.545
7.476
7.456
7.388
7.368
7.353
7.337
7.320
6.927
6.908
6.892
6.876
F
O
O
N
Ts
HN
Bz
3b
1H NMR (400 MHz, CDCl3) spectra of 3b
4.02
1.03
4.02
3.00
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
1.02
0.98
4.00
4.02
1.03
4.02
3.00
1.98
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

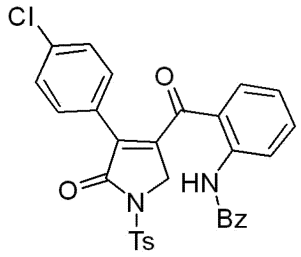

196.06
166.16
166.01
164.65
162.14
147.54
145.79
142.28
137.29
134.75
134.64
134.25
133.20
132.42
131.02
130.93
129.94
128.95
128.33
127.45
124.53
124.50
122.73
120.93
119.55
115.99
115.77
77.32
77.00
76.68
50.67
21.72
F
O
O
N
Ts
HN
Bz
3b
13C NMR (100 MHz, CDCl3) spectra of 3b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



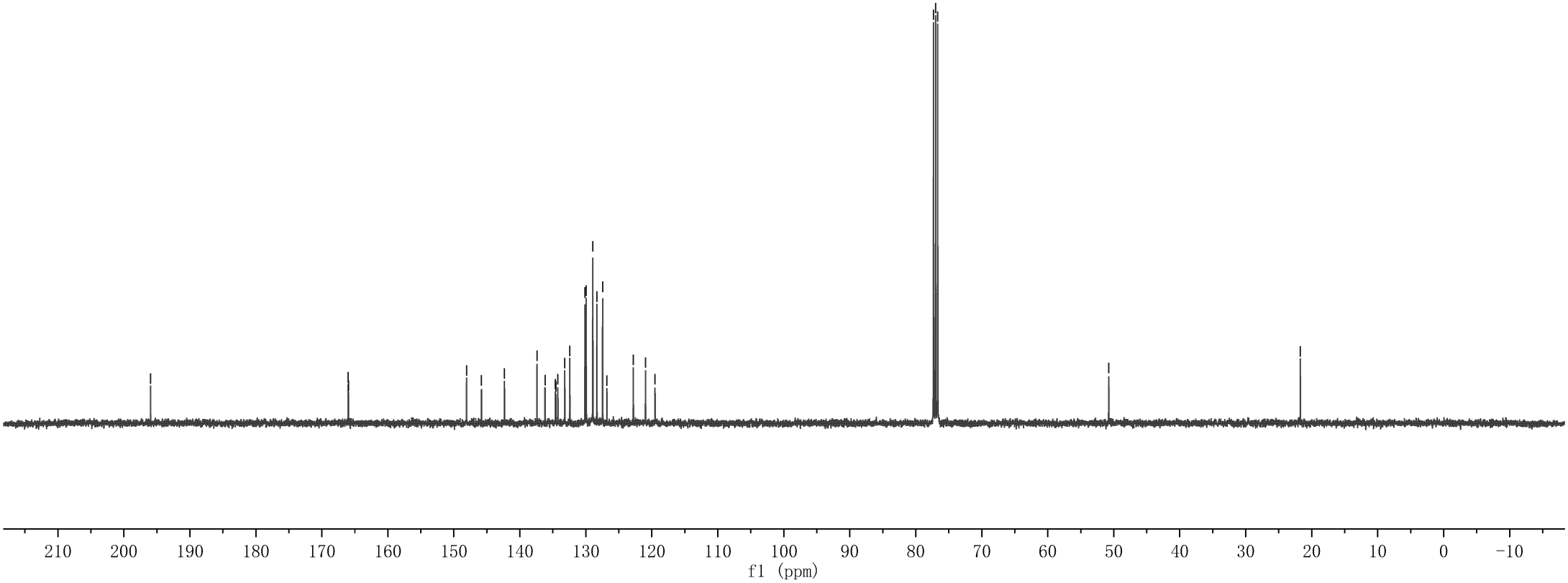
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3c**

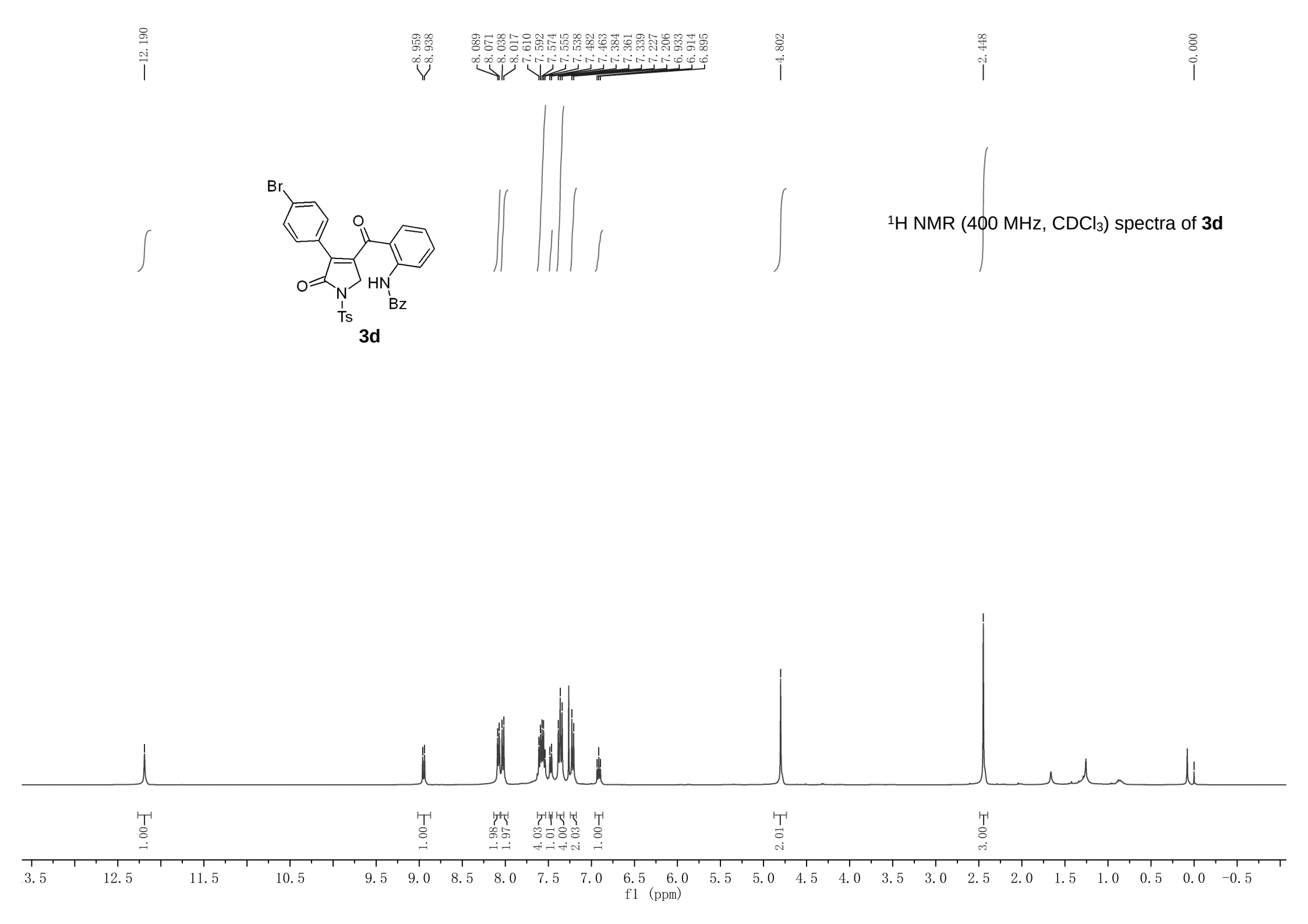
195.96
166.02
165.97
148.08
145.81
142.33
137.40
136.18
134.61
134.53
134.24
133.19
132.43
130.14
129.95
128.95
128.33
127.45
126.80
122.80
120.95
119.51
77.32
77.00
76.68
50.75
21.72

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



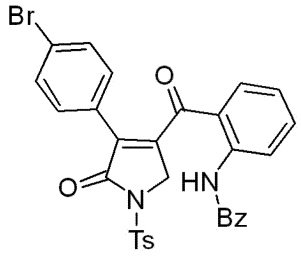
3c





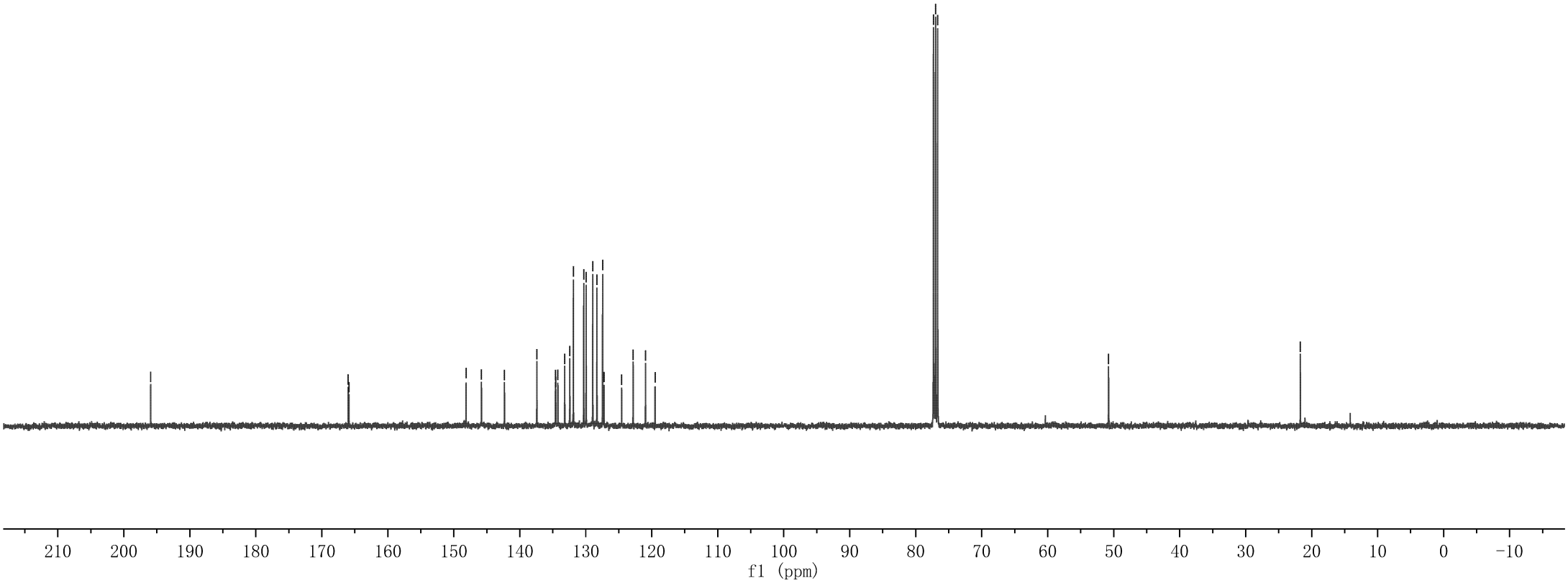
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3d**

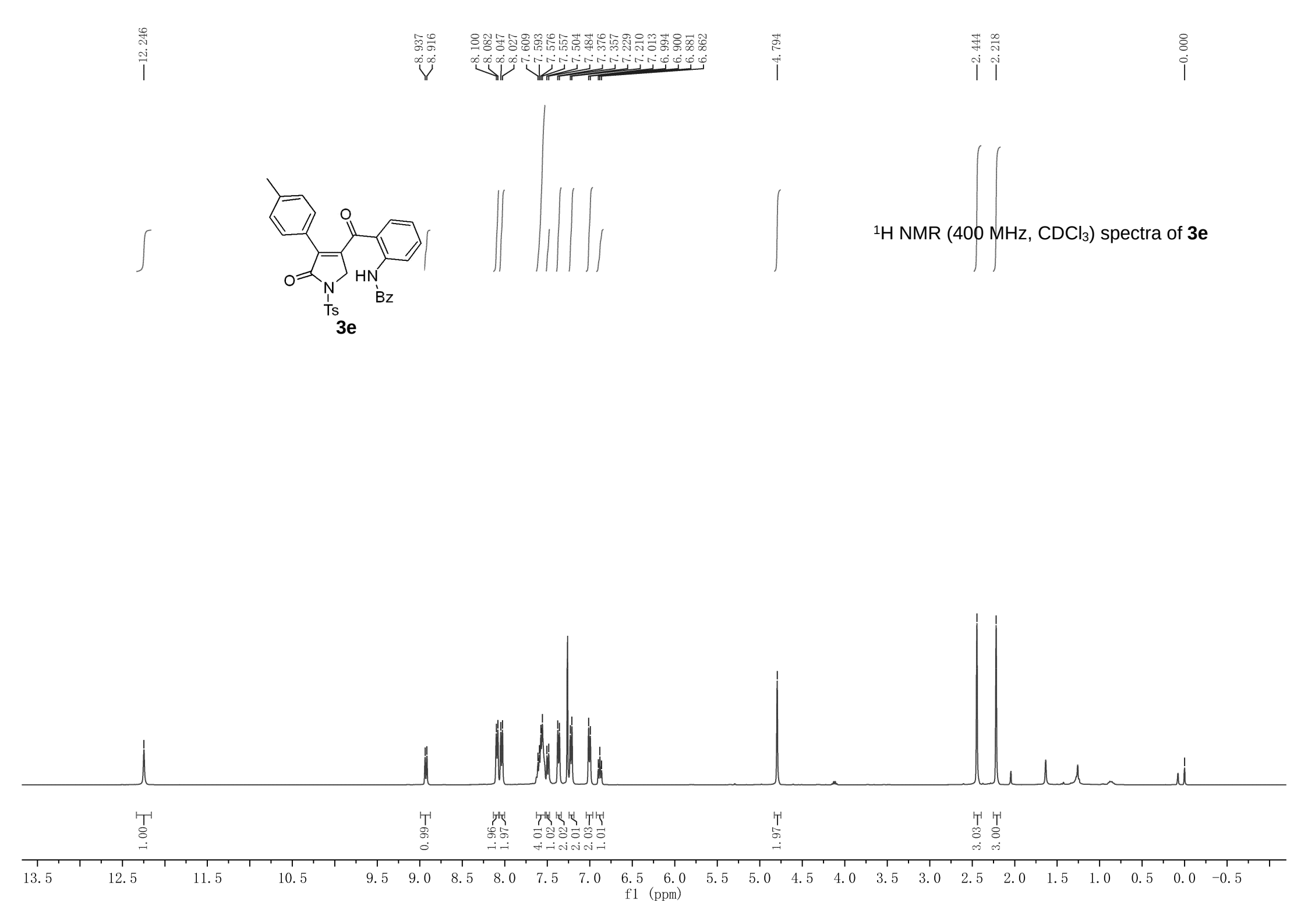
195.94
166.01
165.89
148.14
145.81
142.32
137.41
134.60
134.54
134.22
133.19
132.42
131.88
130.31
129.94
128.95
128.31
127.45
127.24
124.56
122.82
120.95
119.50
77.32
77.00
76.68
50.78
21.72



3d

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

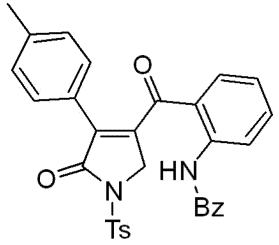




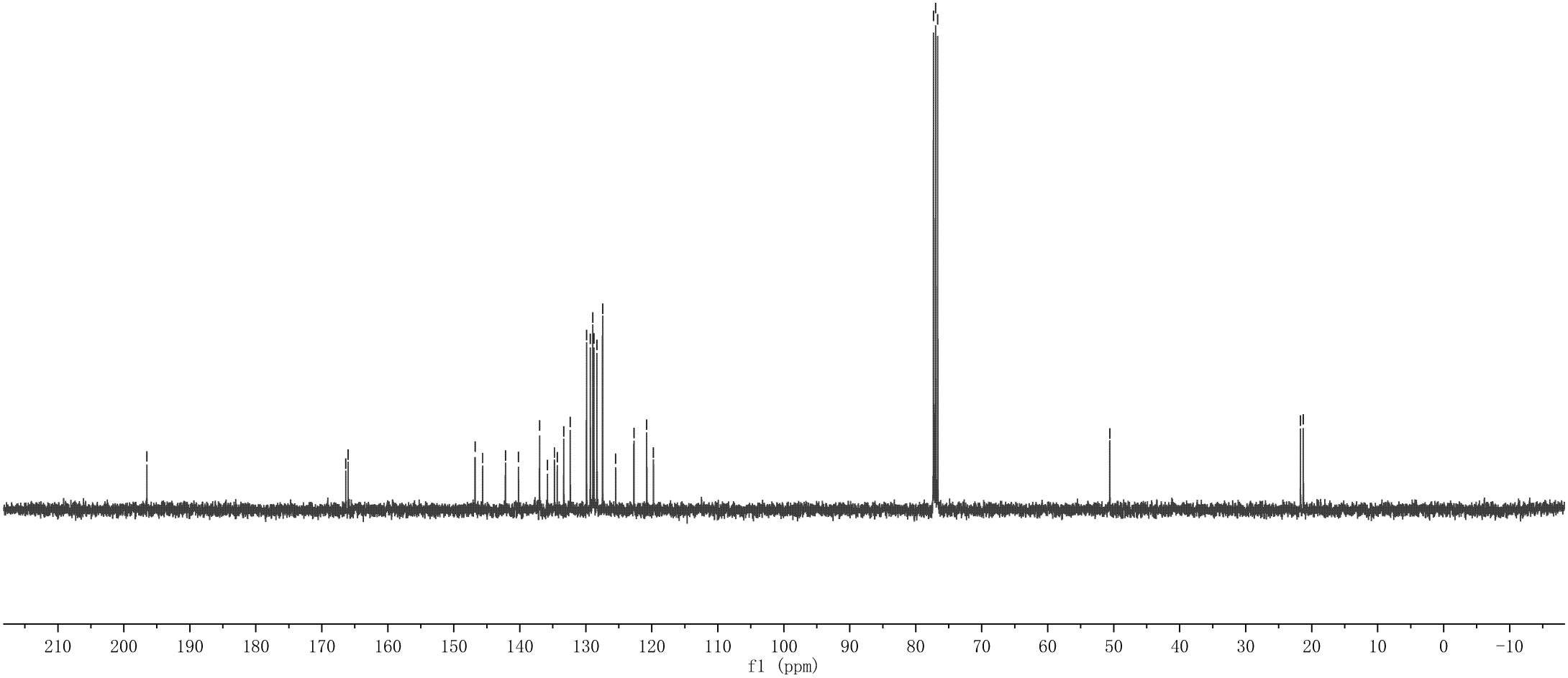
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3e**

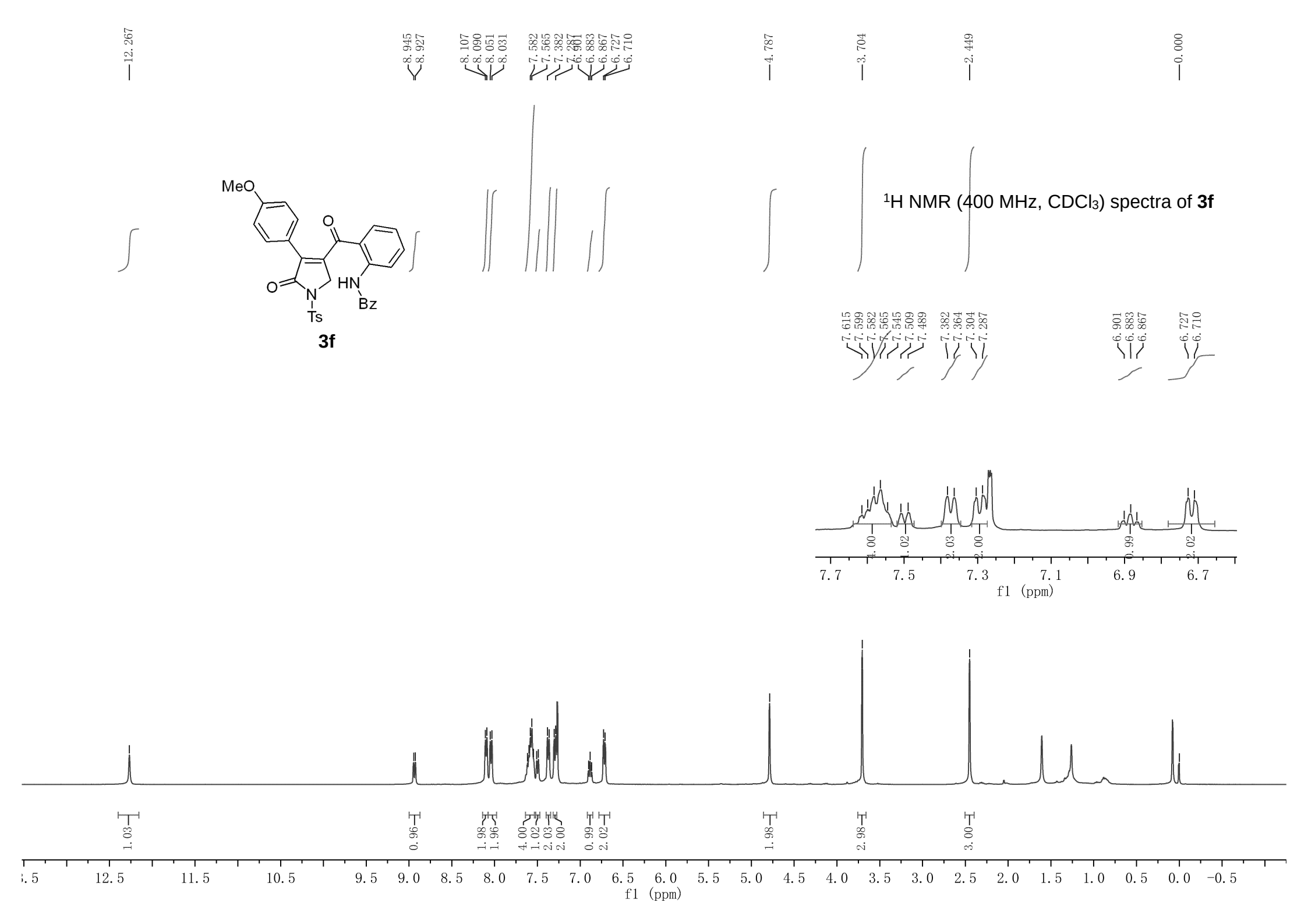
196.52
166.37
166.03
146.79
145.63
142.18
140.20
137.01
135.82
134.75
134.33
133.34
132.36
129.89
129.32
128.93
128.76
128.31
127.46
125.47
122.71
120.77
119.75
77.32
77.00
76.68
50.60
21.70
21.28

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



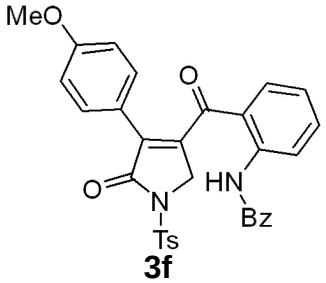
3e



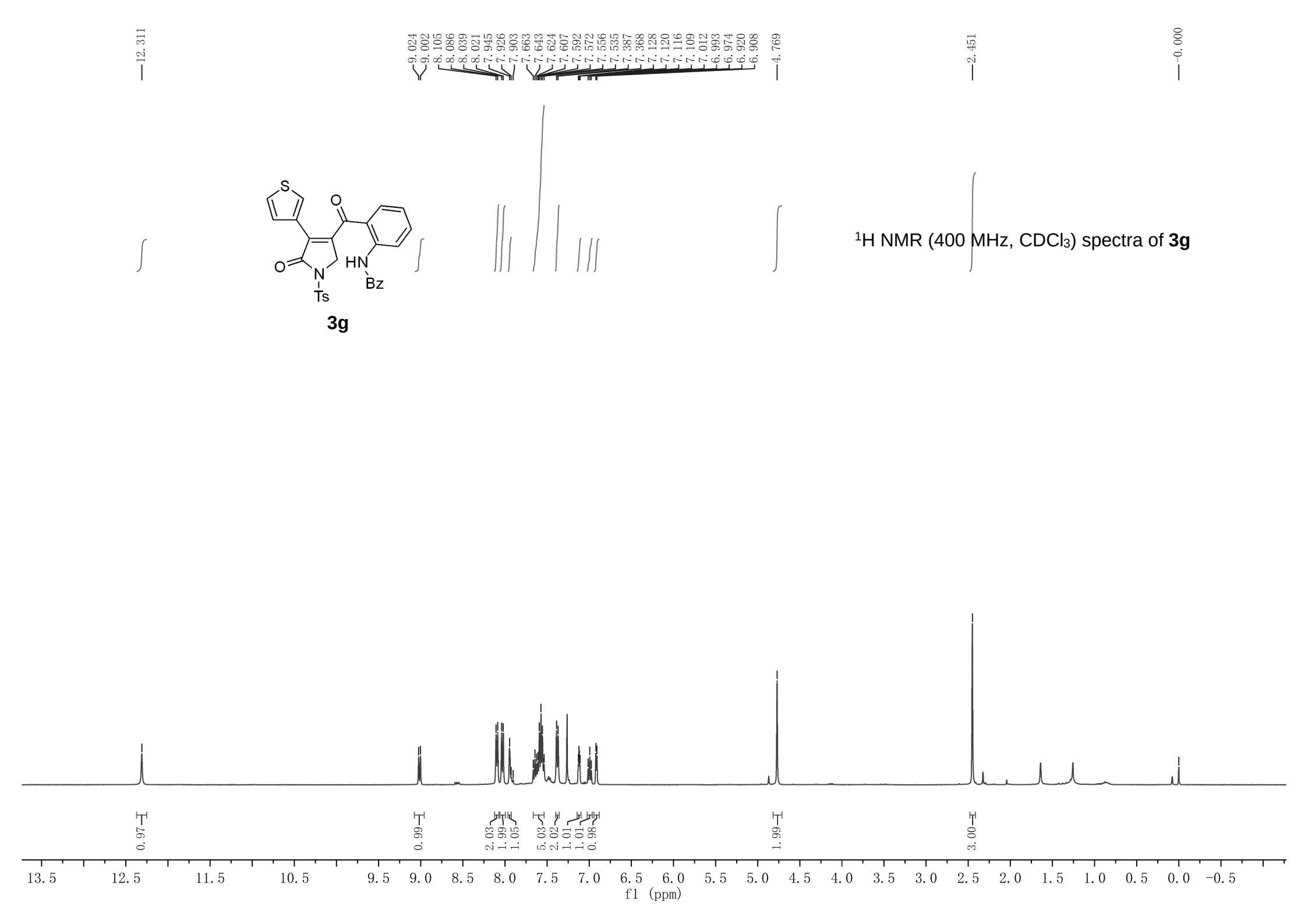


^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3f**

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



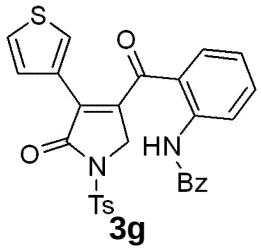
3f



3g

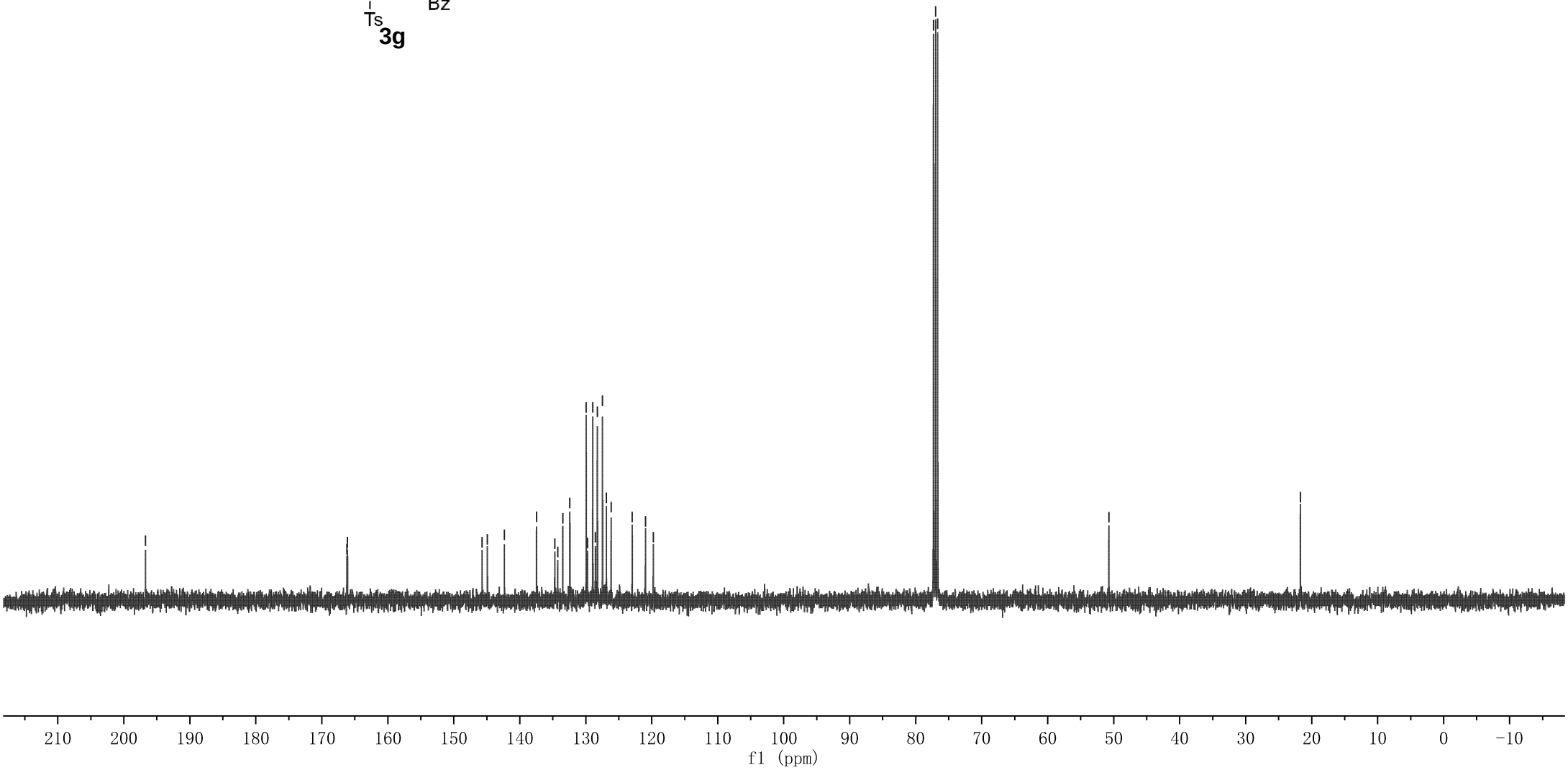
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3g**

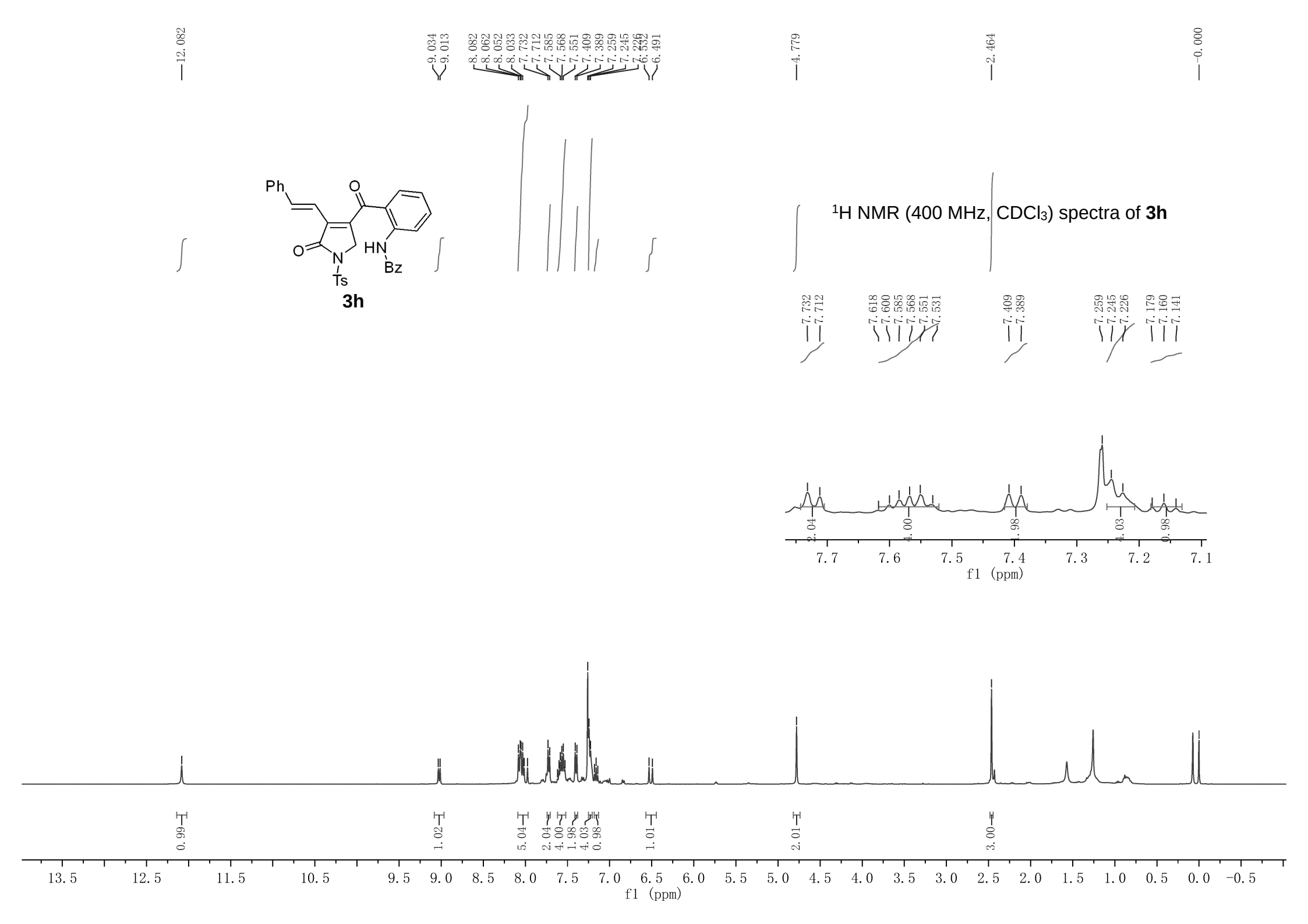
196.72
166.20
166.11
145.71
144.91
142.33
137.46
134.70
134.25
133.49
132.41
129.94
129.75
128.95
128.54
128.25
127.46
126.88
126.16
122.96
120.95
119.77
77.32
77.00
76.68
50.73
21.71

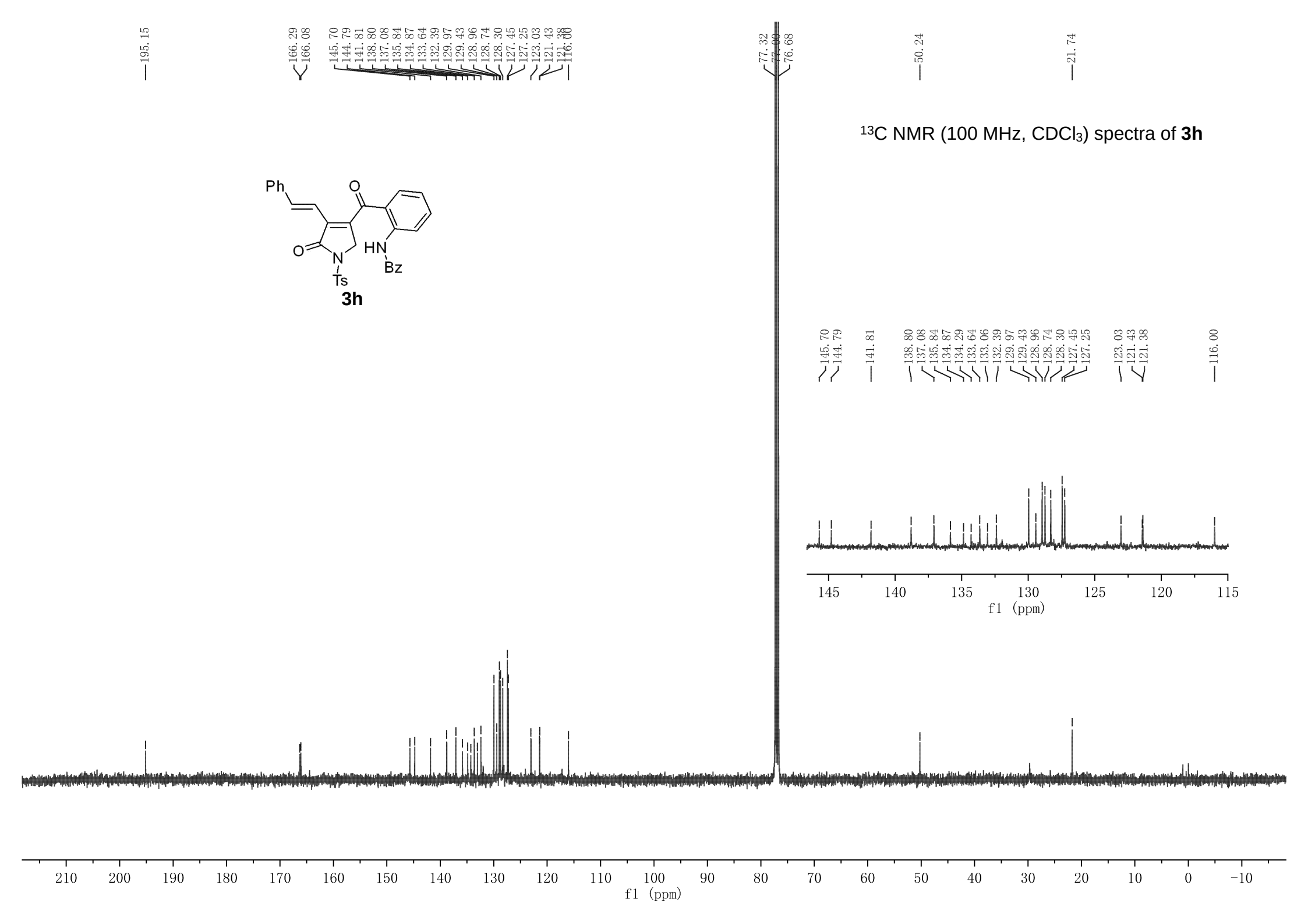


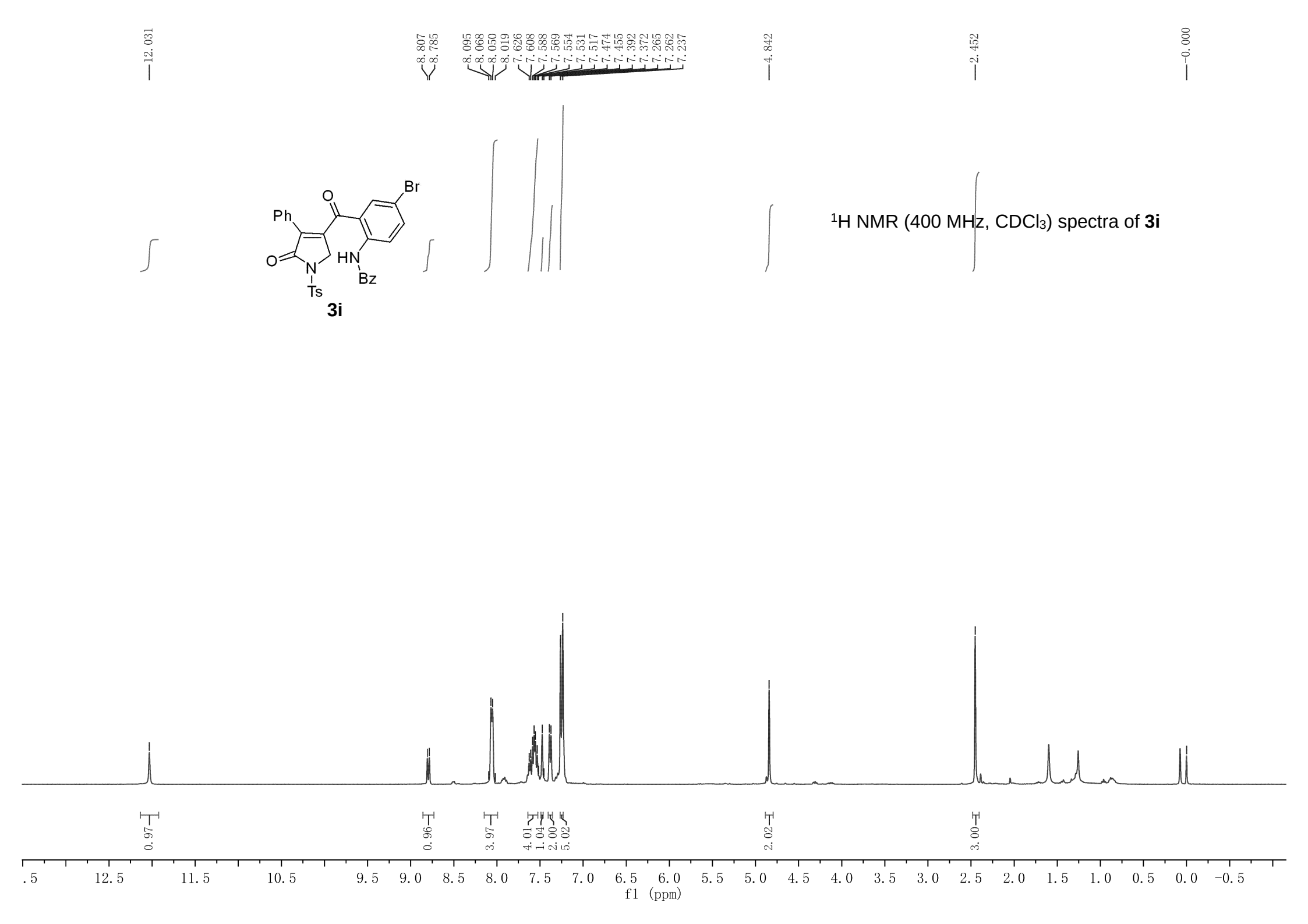
3g

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




12.082
9.034
9.013
8.082
8.062
8.052
8.033
7.732
7.712
7.585
7.568
7.551
7.409
7.389
7.259
7.245
7.226
6.532
6.491
4.779
2.464
0.000
Ph
O
O
N
Ts
HN
Bz
3h
1H NMR (400 MHz, CDCl3) spectra of 3h
7.732
7.712
7.618
7.600
7.585
7.568
7.551
7.531
7.409
7.389
7.259
7.245
7.226
7.179
7.160
7.141
2.04
4.00
1.98
4.03
0.98
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)
0.99
1.02
5.04
2.04
4.00
1.98
4.03
0.98
1.01
2.01
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

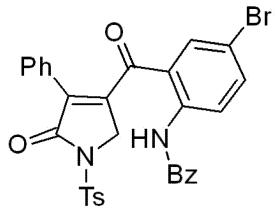

195.15
166.29
166.08
145.70
144.79
141.81
138.80
137.08
135.84
134.87
133.64
132.39
129.97
129.43
128.96
128.74
128.30
127.45
127.25
123.03
121.43
121.38
116.00
77.32
77.00
76.68
50.24
21.74
Ph
O
O
N
Ts
HN
Bz
3h
13C NMR (100 MHz, CDCl3) spectra of 3h
f1 (ppm)
f1 (ppm)



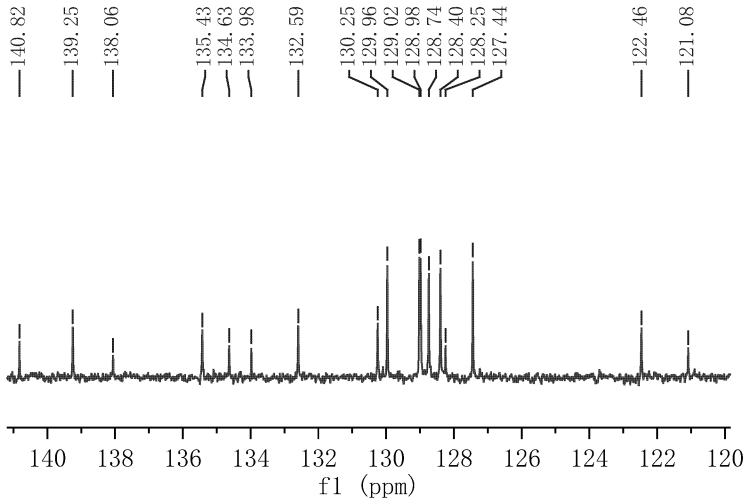
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3i**

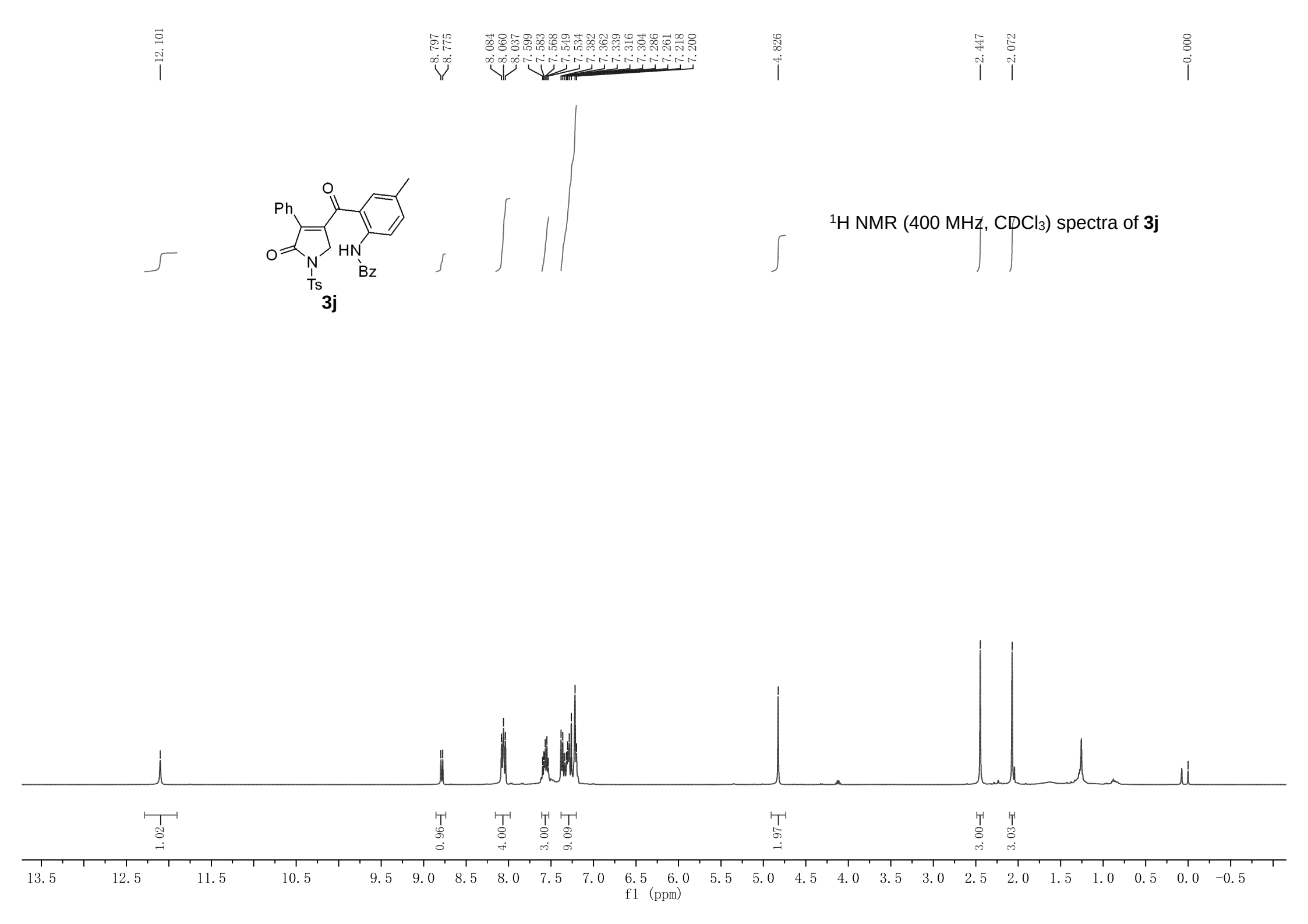
194.84
166.05
165.89
146.42
145.81
132.59
130.25
129.96
129.02
128.98
128.74
128.40
121.08
114.79
77.32
77.00
76.68
50.43
21.74

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

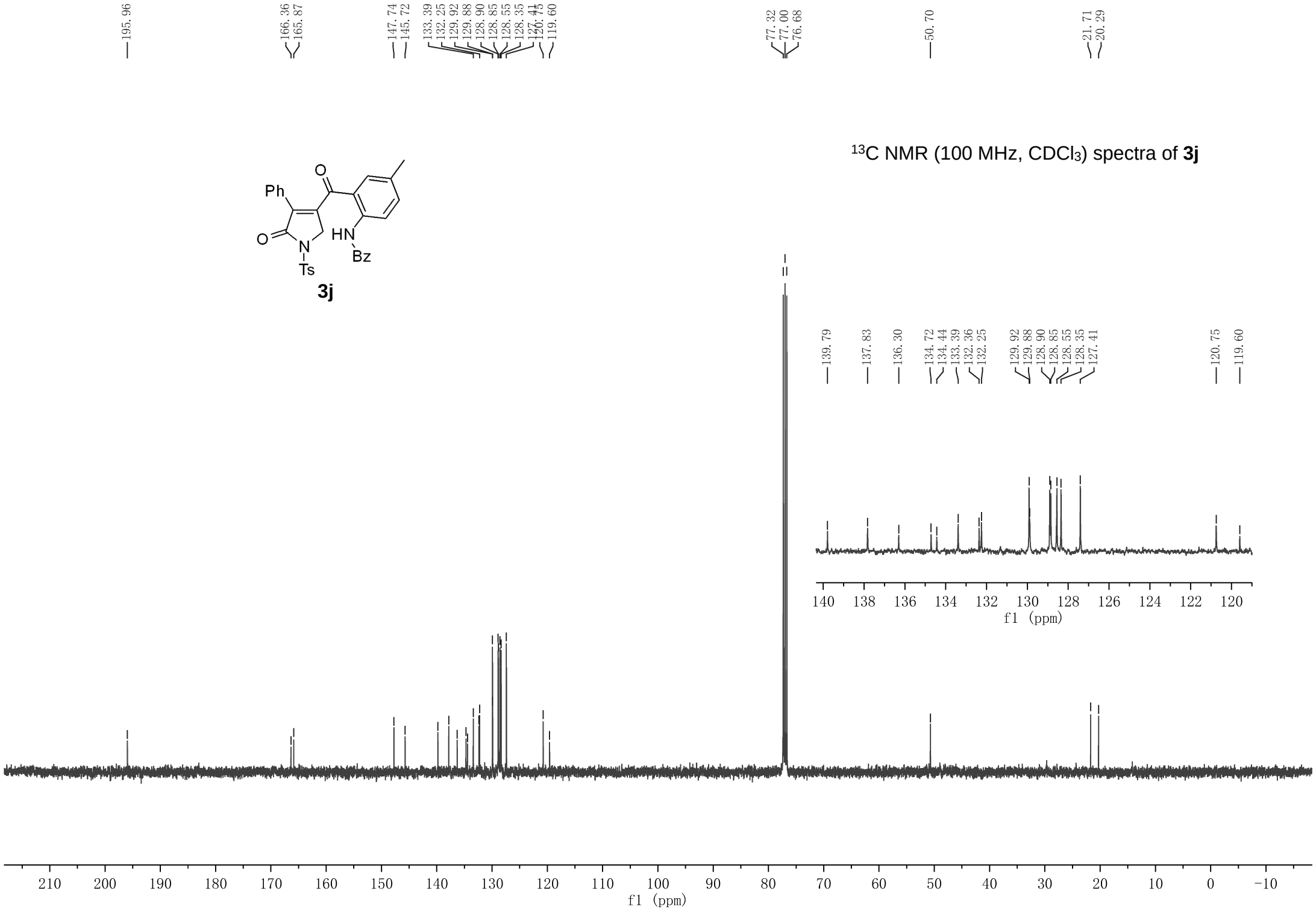


3i

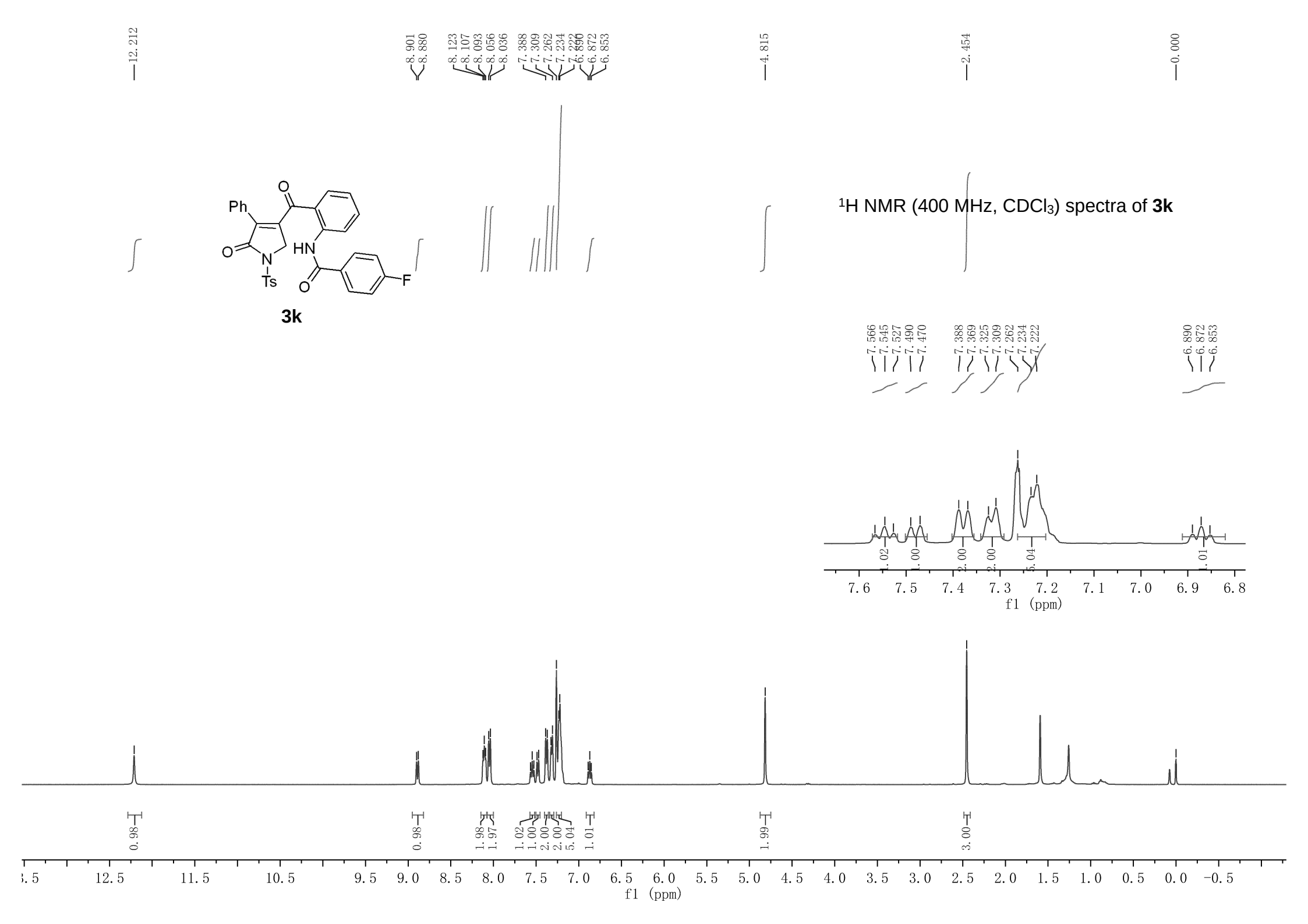


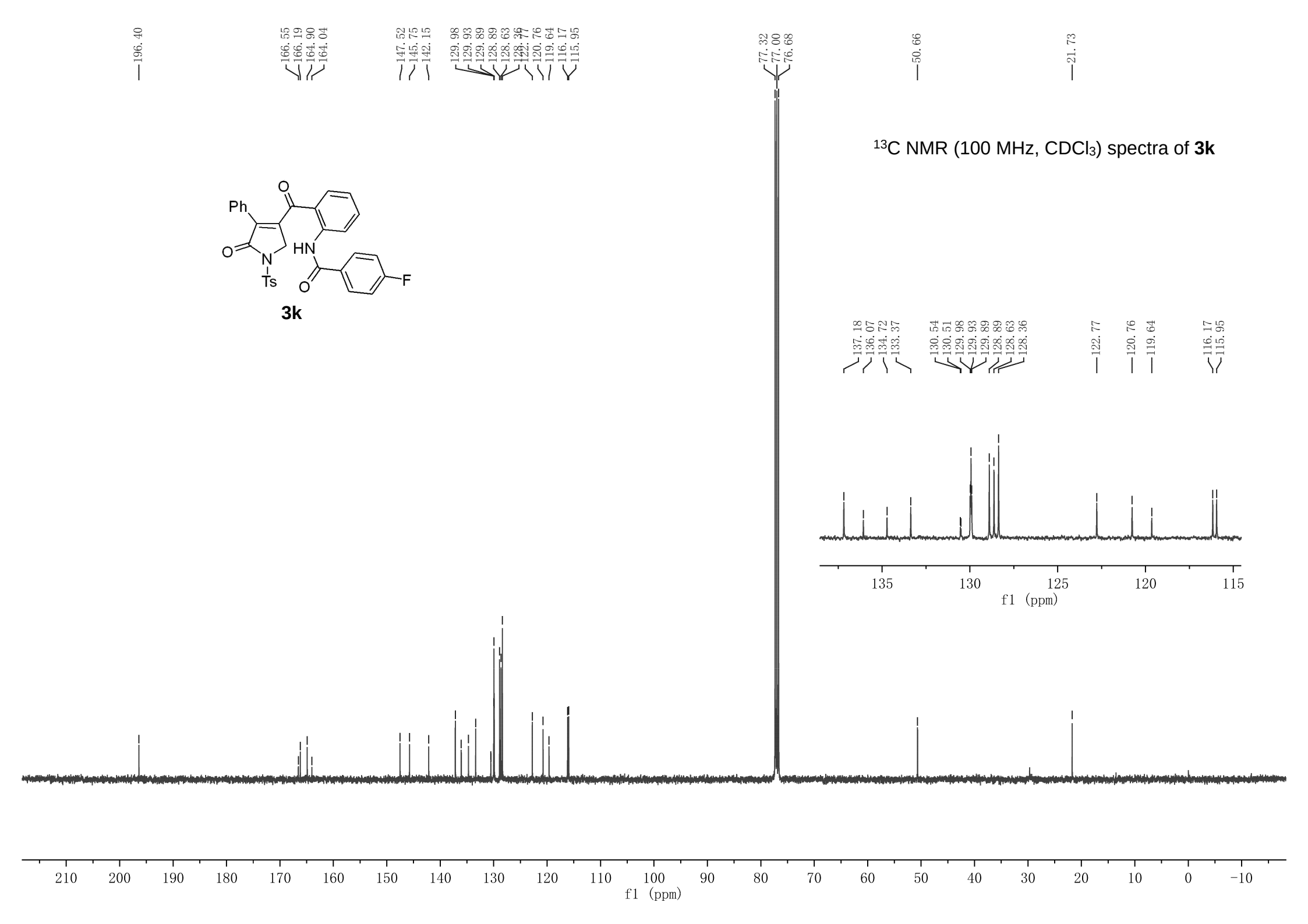


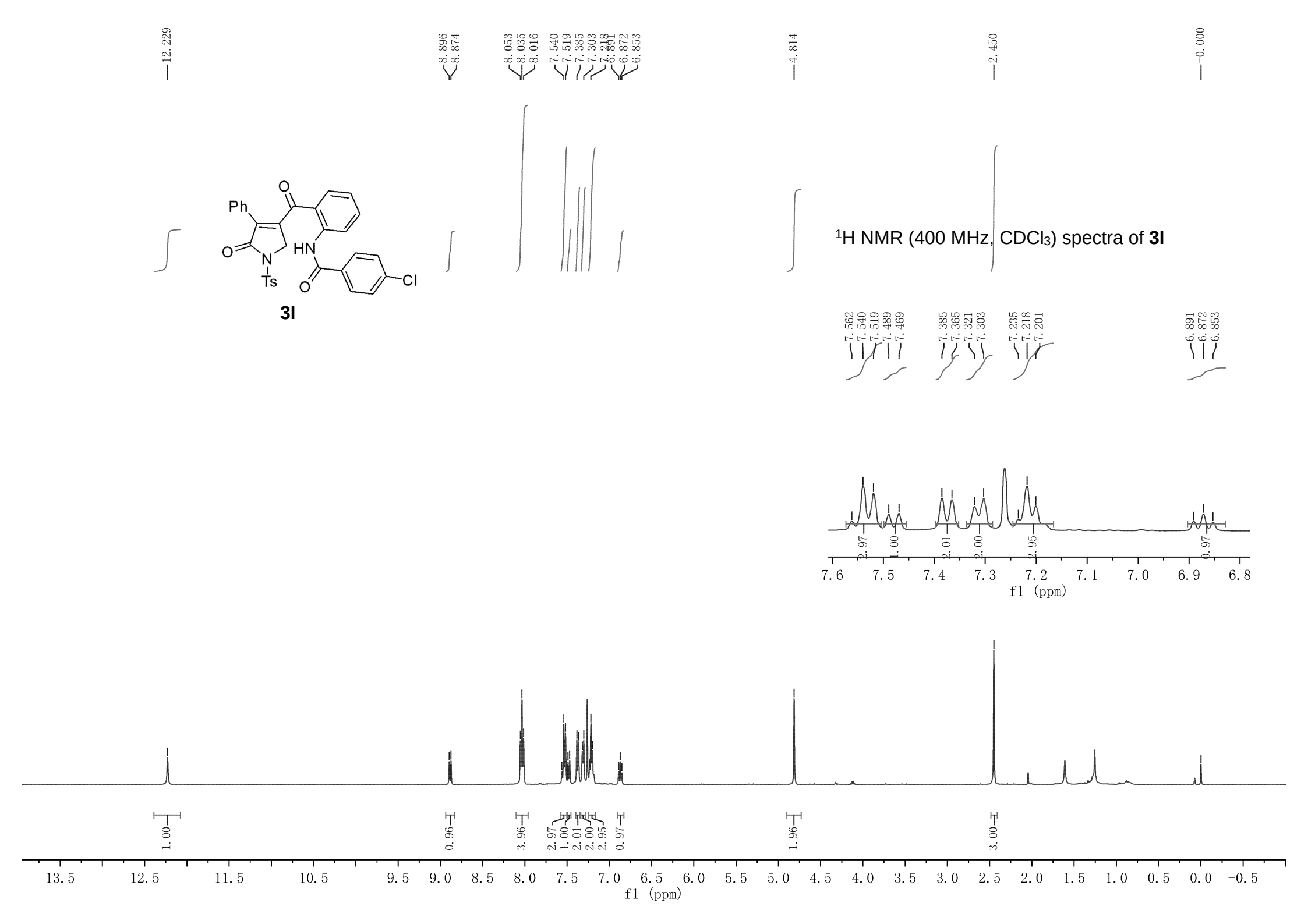
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3j**



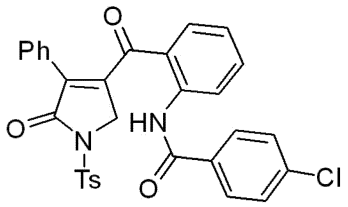
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3j**


12.212
8.901
8.880
8.123
8.107
8.093
8.056
8.036
7.388
7.309
7.262
7.234
6.890
6.872
6.853
4.815
2.454
0.000
Ph
O
HN
N
Ts
F
3k
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3k**
7.566
7.545
7.527
7.490
7.470
7.388
7.369
7.325
7.309
7.262
7.234
7.222
6.890
6.872
6.853
1.02
1.00
2.00
2.00
5.04
1.01
f1 (ppm)
0.98
0.98
1.98
1.97
1.02
1.00
2.00
2.00
5.04
1.01
1.99
3.00
f1 (ppm)


196.40
166.55
166.19
164.90
164.04
147.52
145.75
142.15
129.98
129.93
129.89
128.89
128.63
128.36
122.77
120.76
119.64
116.17
115.95
77.32
77.00
76.68
50.66
21.73
^{13}C NMR (100 MHz, CDCl$_3$) spectra of **3k**
Ph
O
HN
N
Ts
F
3k
137.18
136.07
134.72
133.37
130.54
130.51
129.98
129.93
129.89
128.89
128.63
128.36
122.77
120.76
119.64
116.17
115.95
135
130
125
120
115
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

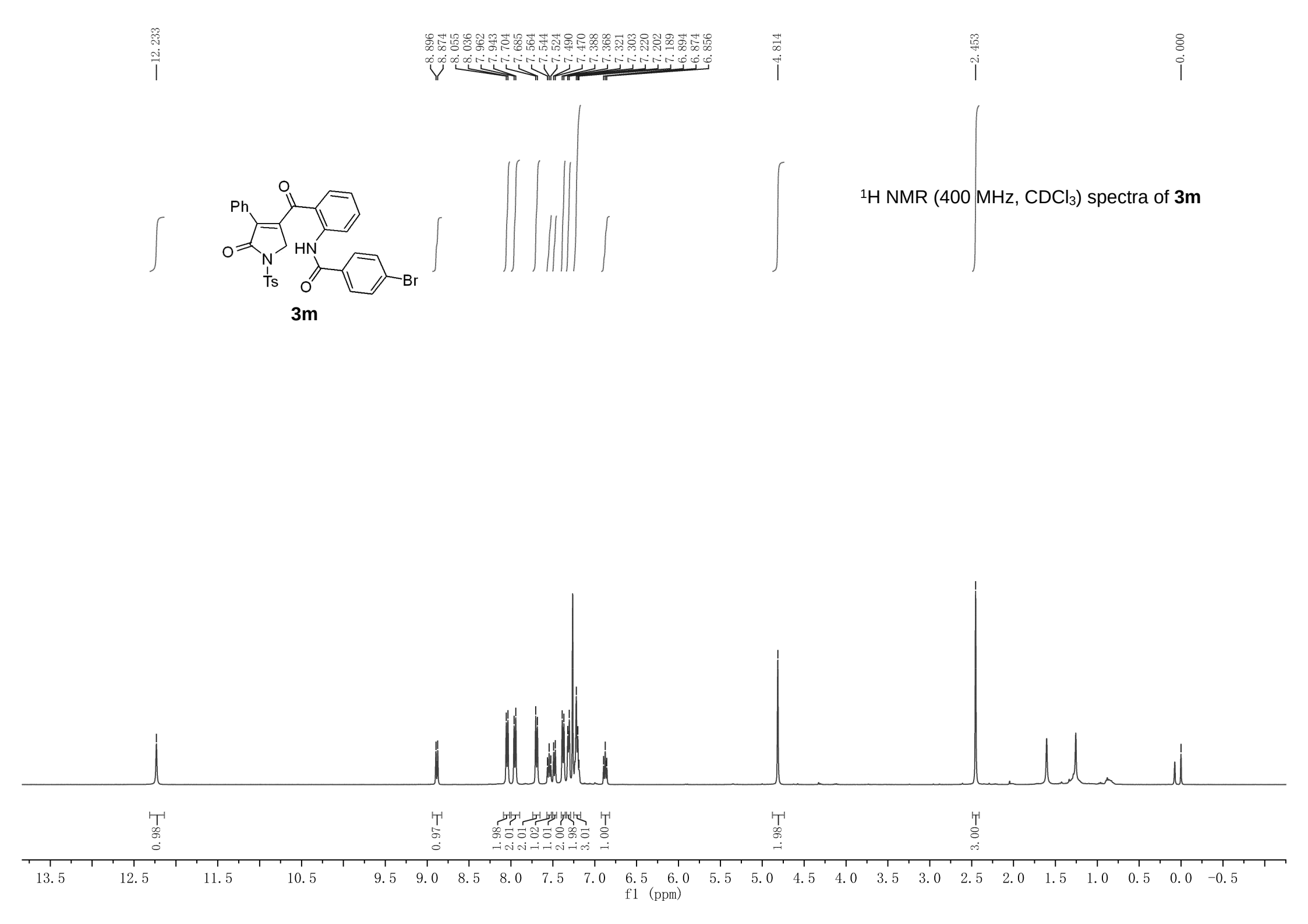

12.229
8.896
8.874
8.053
8.035
8.016
7.540
7.519
7.385
7.303
7.218
6.891
6.872
6.853
4.814
2.450
0.000
Ph
O
N
Ts
HN
Cl
3l
1H NMR (400 MHz, CDCl3) spectra of 3l
7.562
7.540
7.519
7.489
7.469
7.385
7.365
7.321
7.303
7.235
7.218
7.201
6.891
6.872
6.853
2.97
1.00
2.01
2.00
2.95
0.97
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
1.00
0.96
3.96
2.97
1.00
2.01
2.00
2.95
0.97
1.96
3.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

196.39
166.18
164.91
147.48
145.75
142.02
138.77
137.17
136.09
134.69
133.38
132.71
129.93
129.22
128.89
128.62
128.35
122.86
120.77
119.64
77.32
77.00
76.68
50.65
21.73



3l

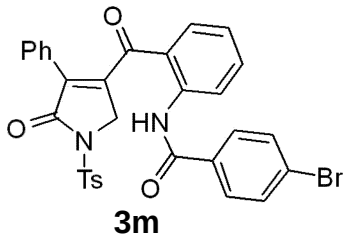
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3l**



3m

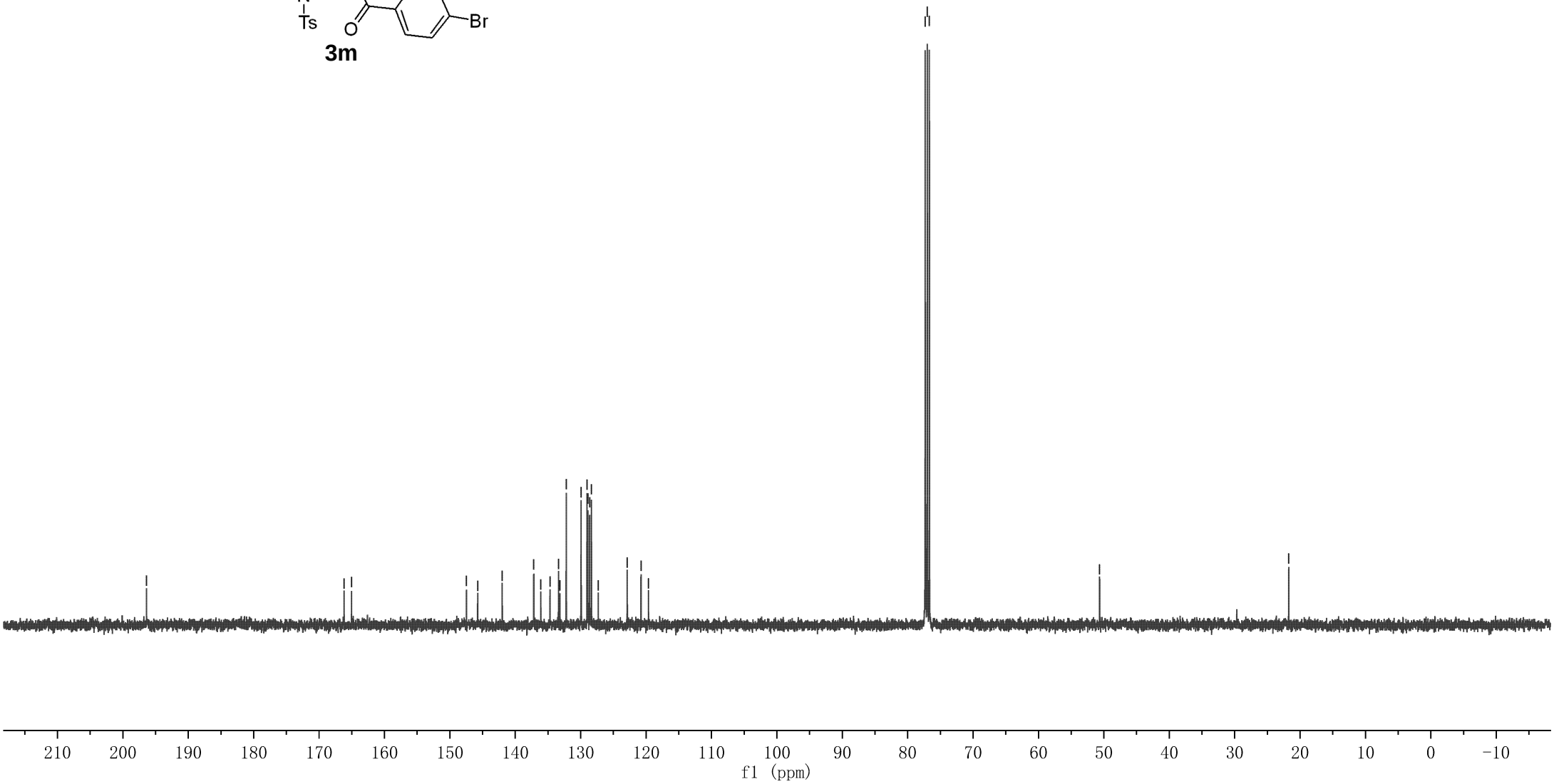
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **3m**

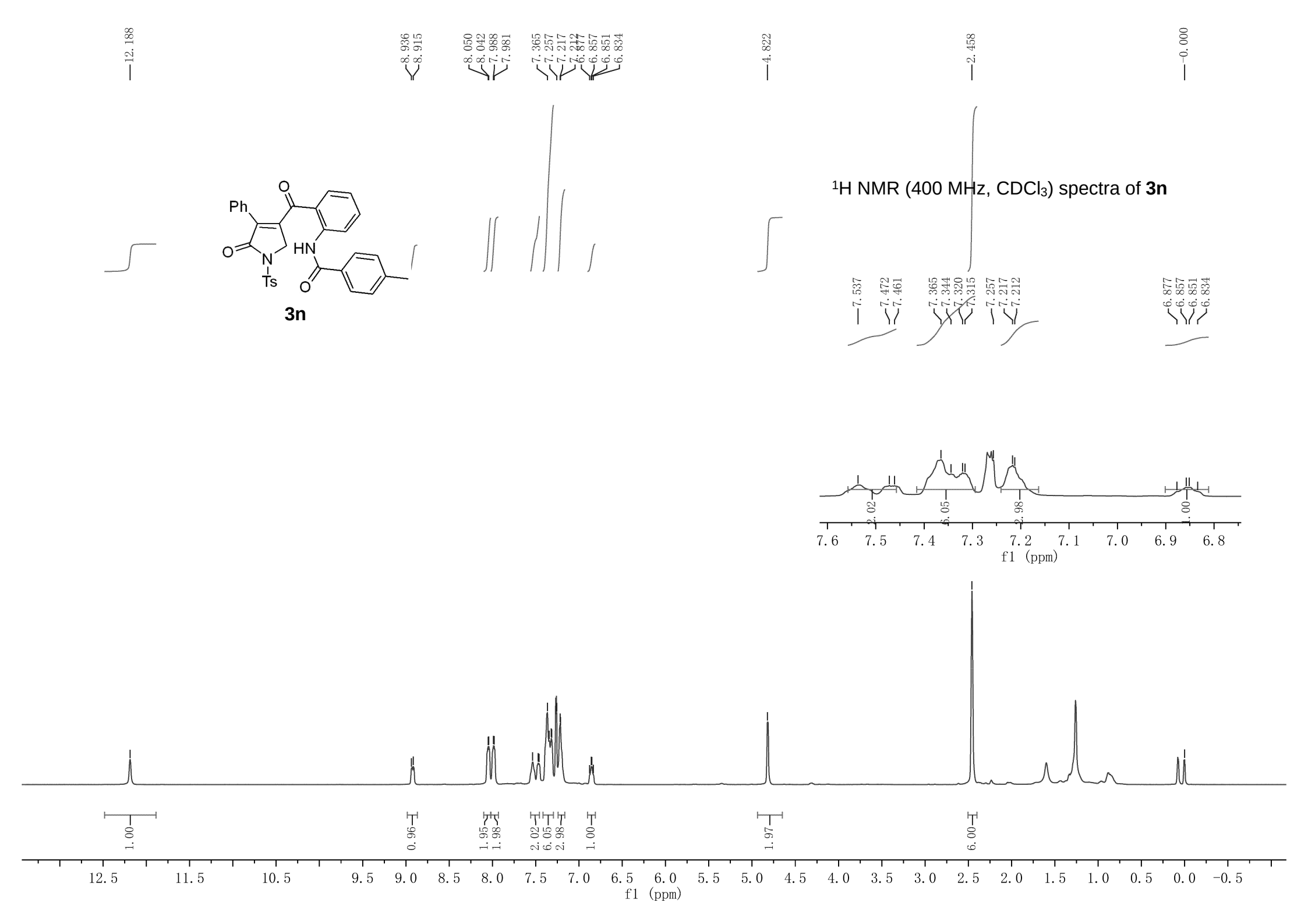
196.39
166.17
165.03
147.46
145.75
141.99
137.17
136.10
134.69
133.39
133.17
132.21
129.93
129.04
128.89
128.62
128.36
127.31
122.88
120.77
119.64
77.32
77.00
76.68
50.65
21.73

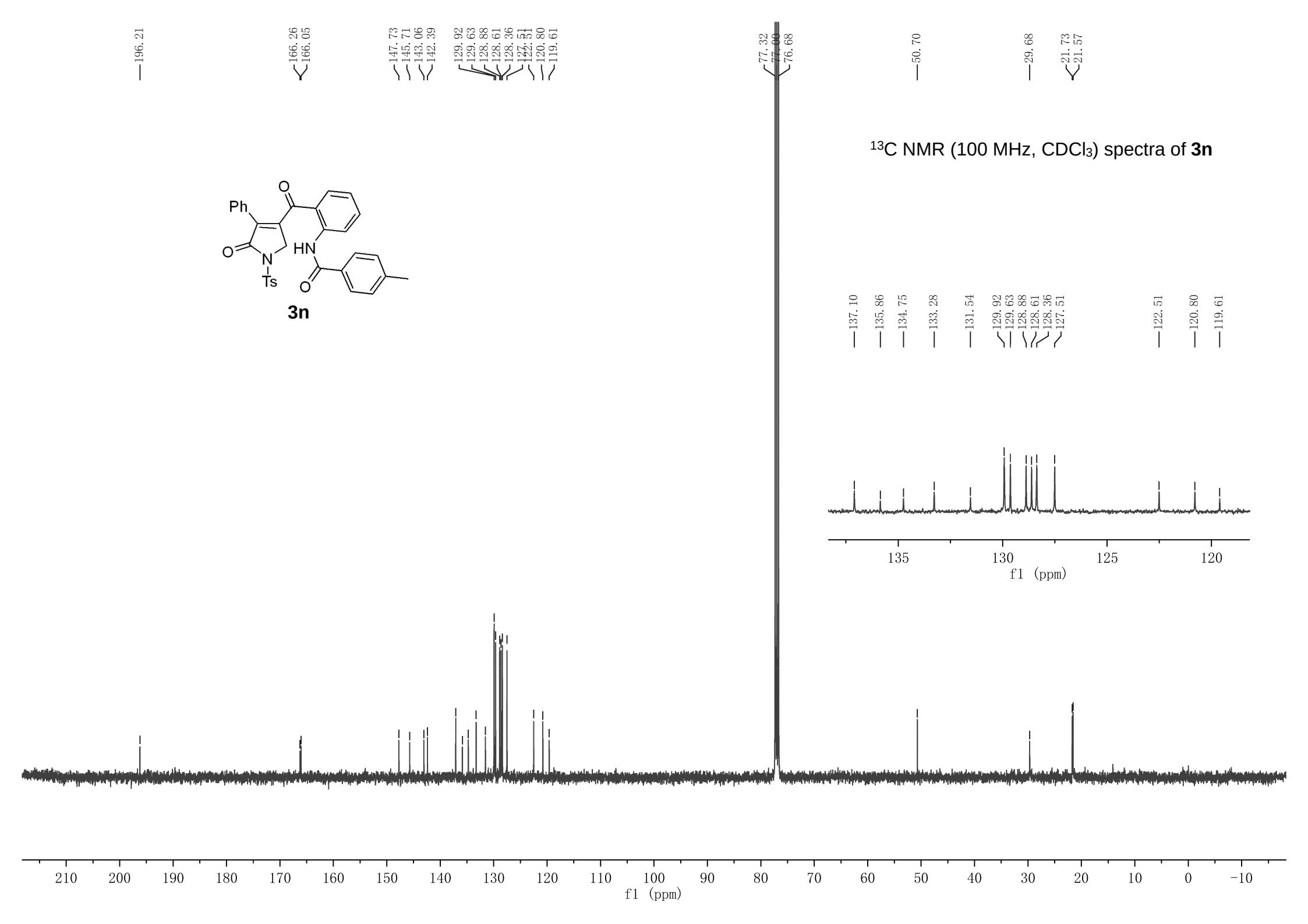


3m

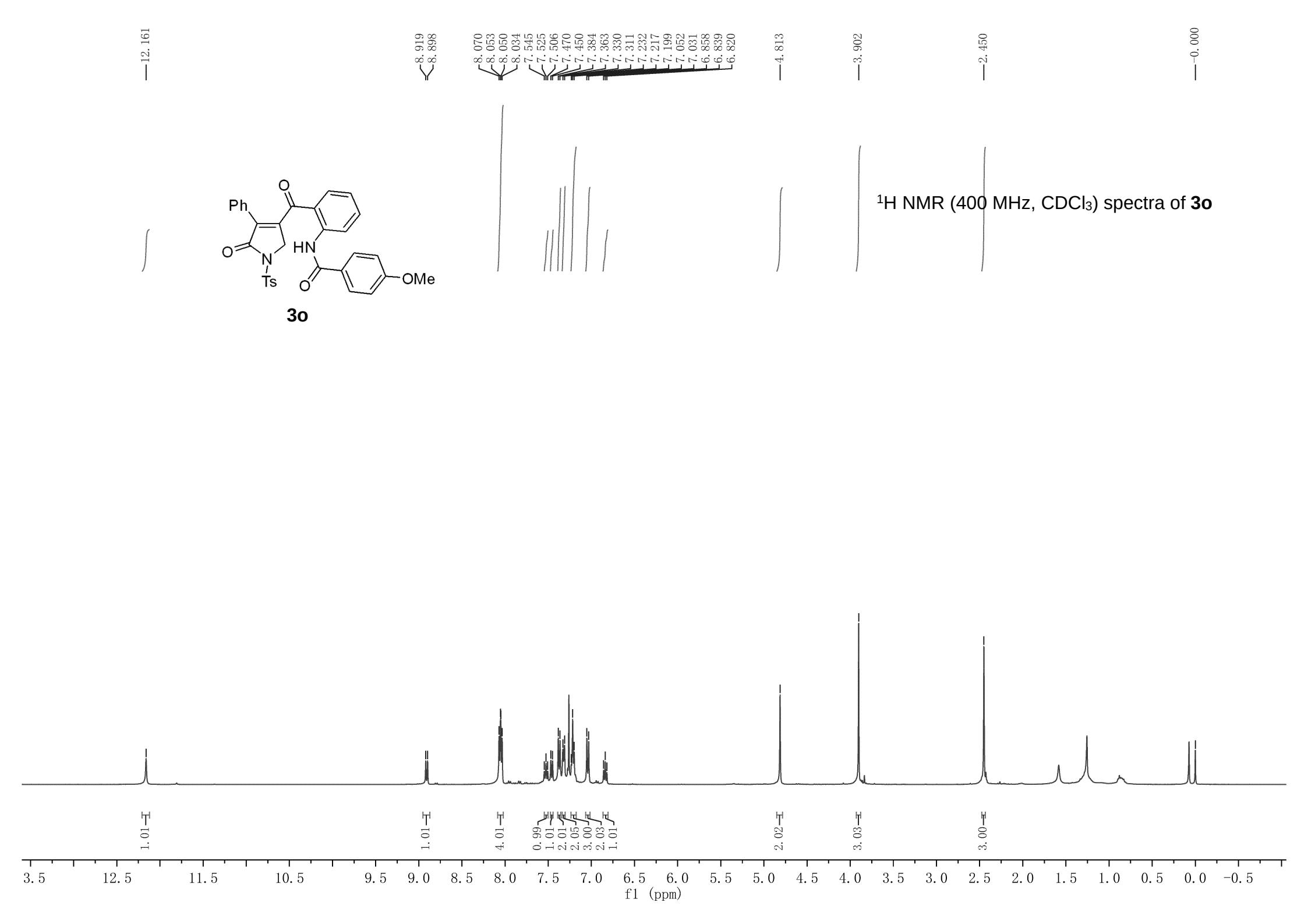
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3m**




12.188
8.936
8.915
8.050
8.042
7.988
7.981
7.365
7.257
7.217
6.877
6.857
6.851
6.834
4.822
2.458
0.000
Ph
O
O
N
Ts
HN
O
3n
1H NMR (400 MHz, CDCl3) spectra of 3n
7.537
7.472
7.461
7.365
7.344
7.320
7.315
7.257
7.217
7.212
6.877
6.857
6.851
6.834
2.02
6.05
2.98
1.00
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00
0.96
1.95
1.98
2.02
6.05
2.98
1.00
1.97
6.00
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



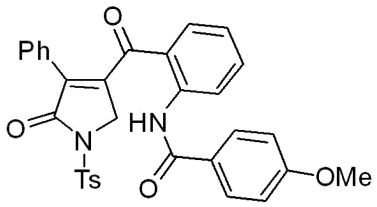
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3n**



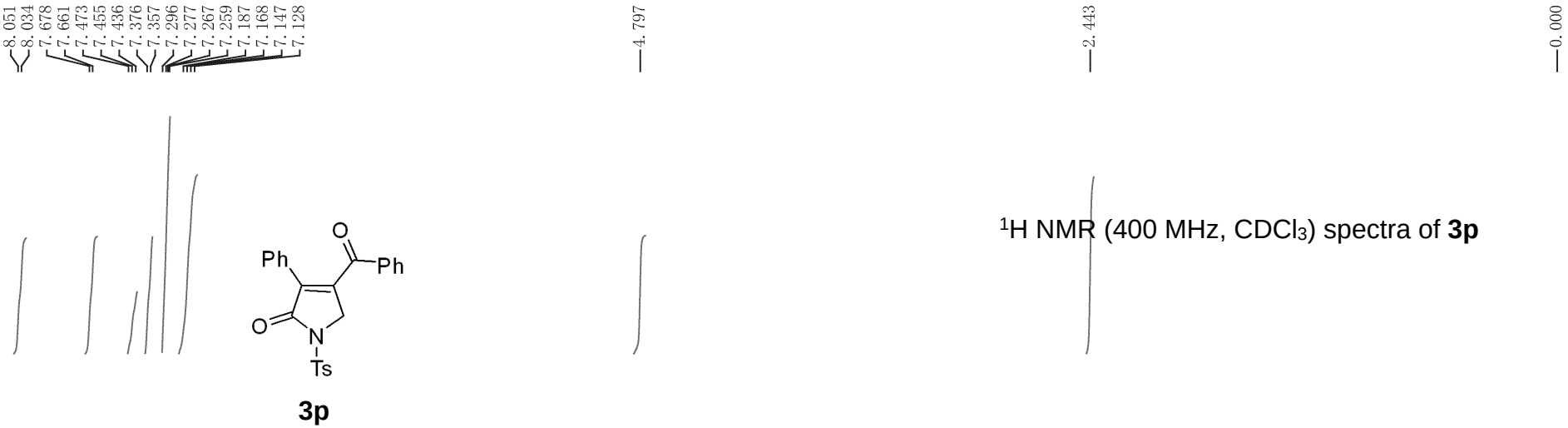
3o

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

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

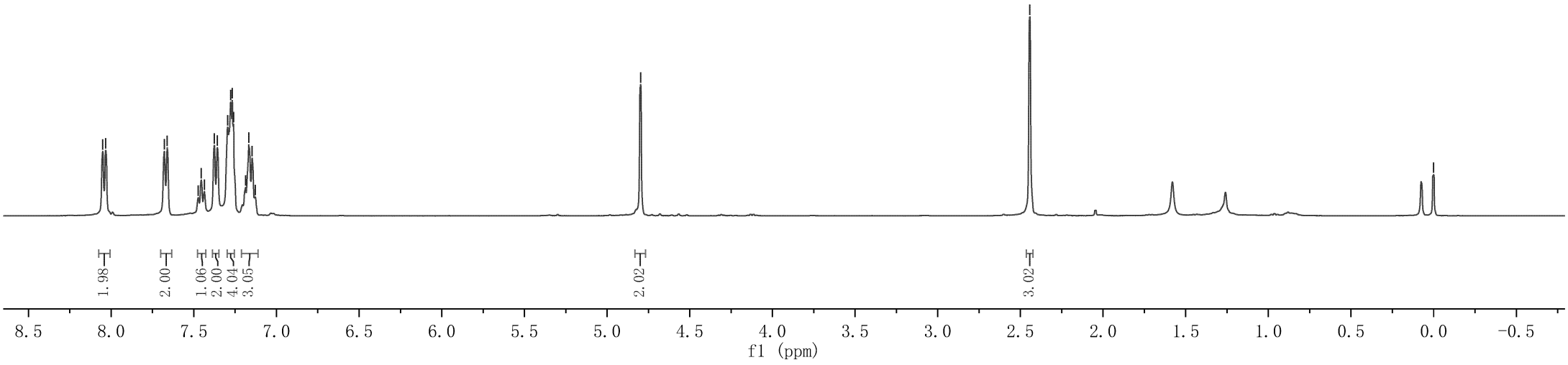


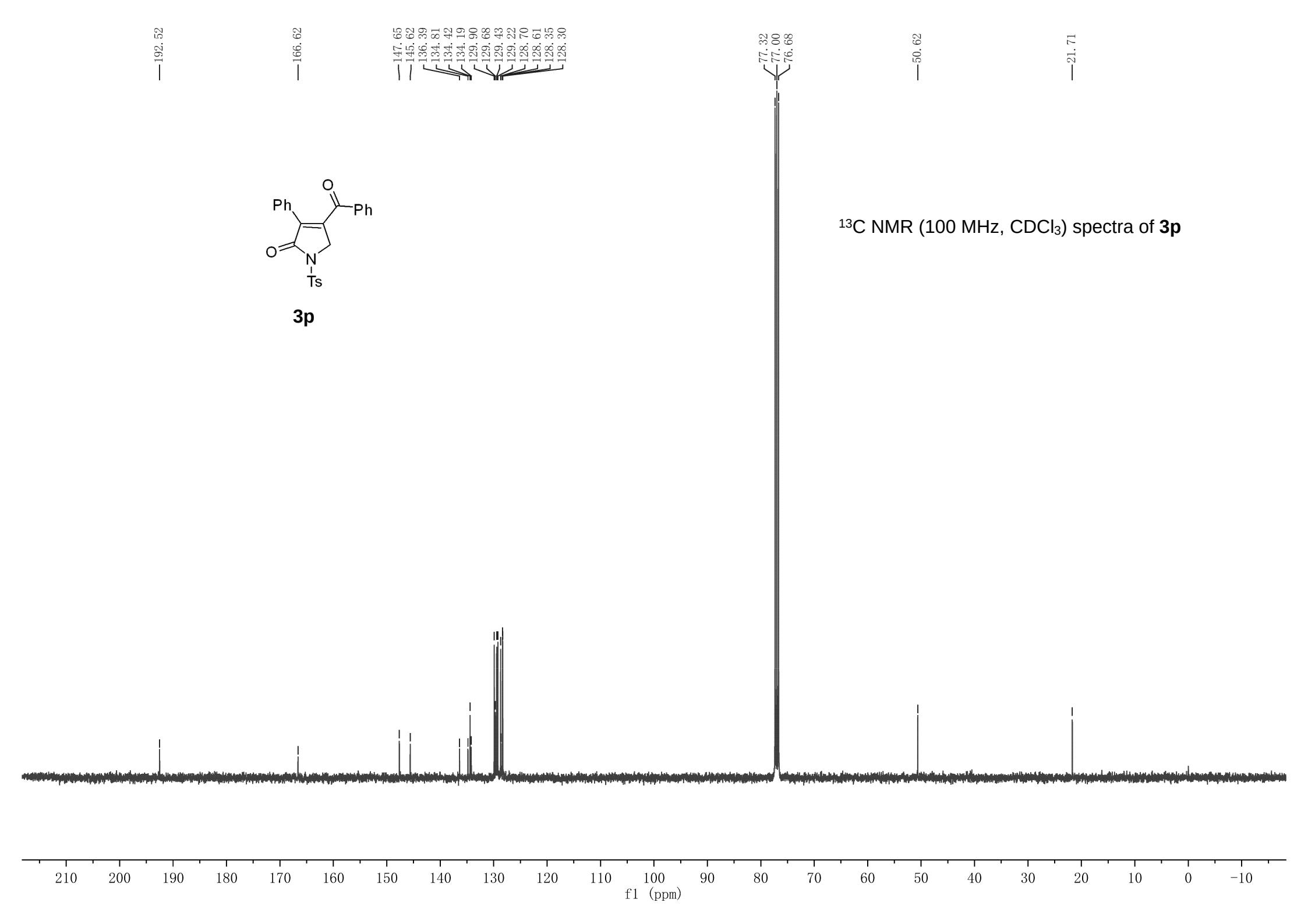
3o

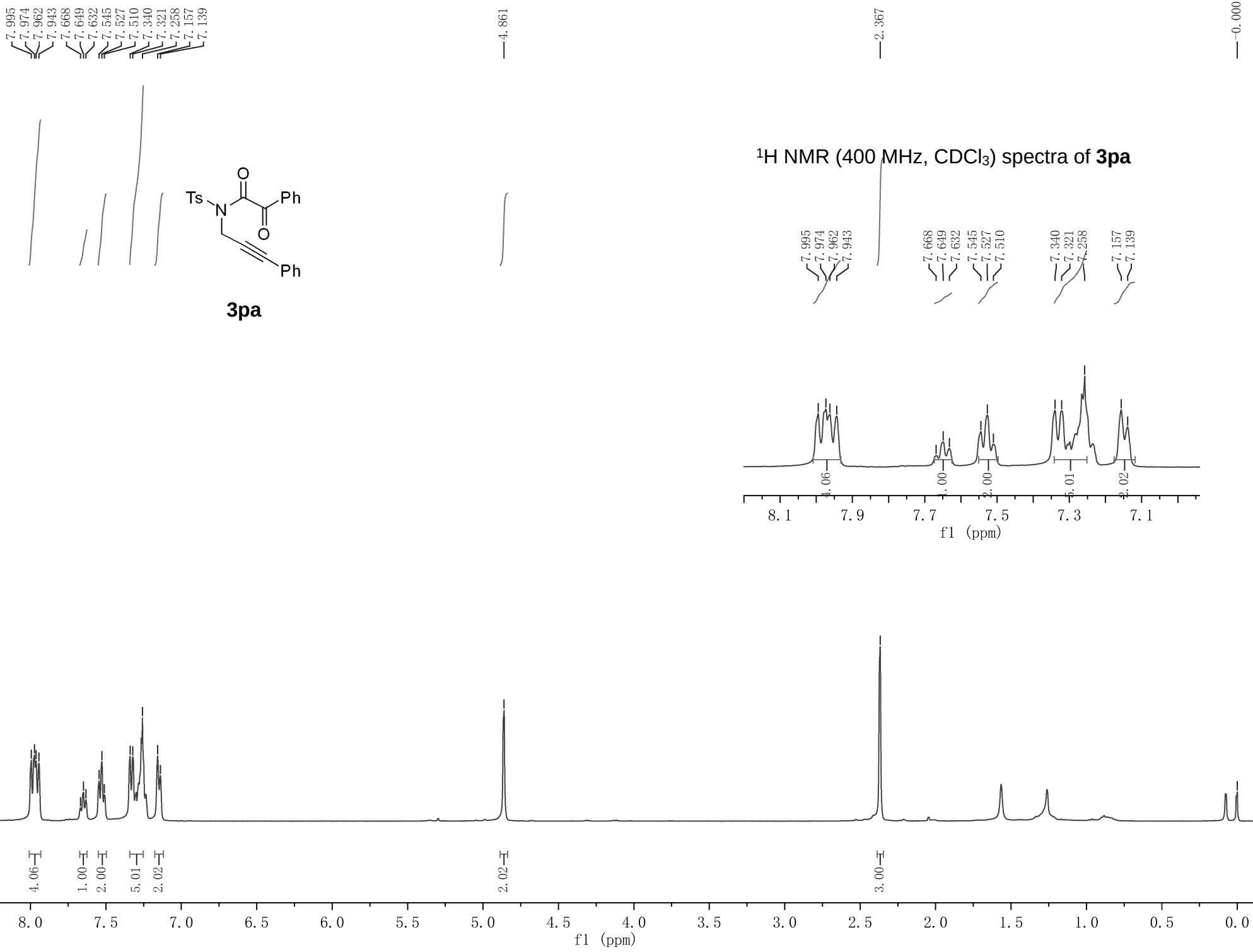


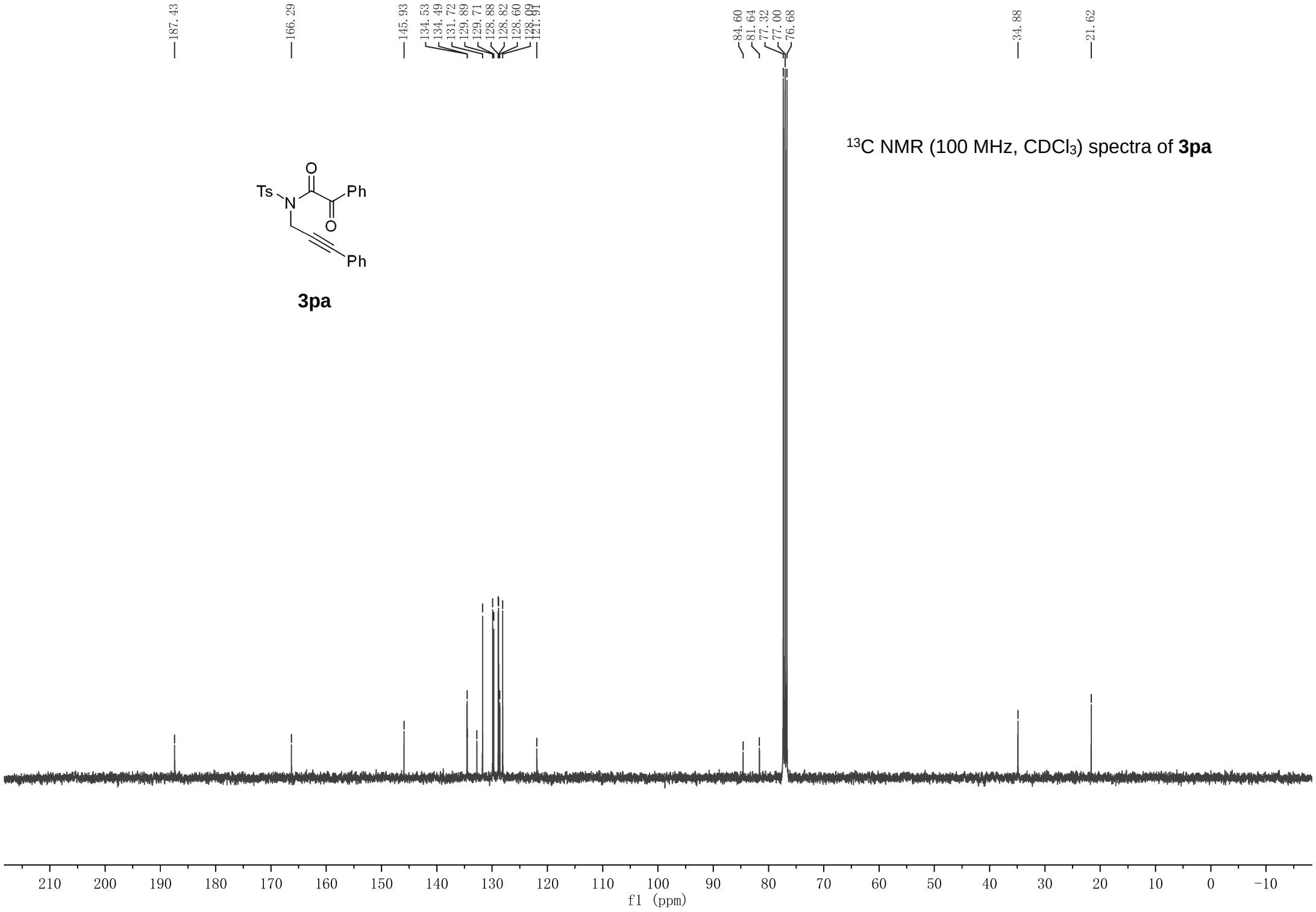
3p

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



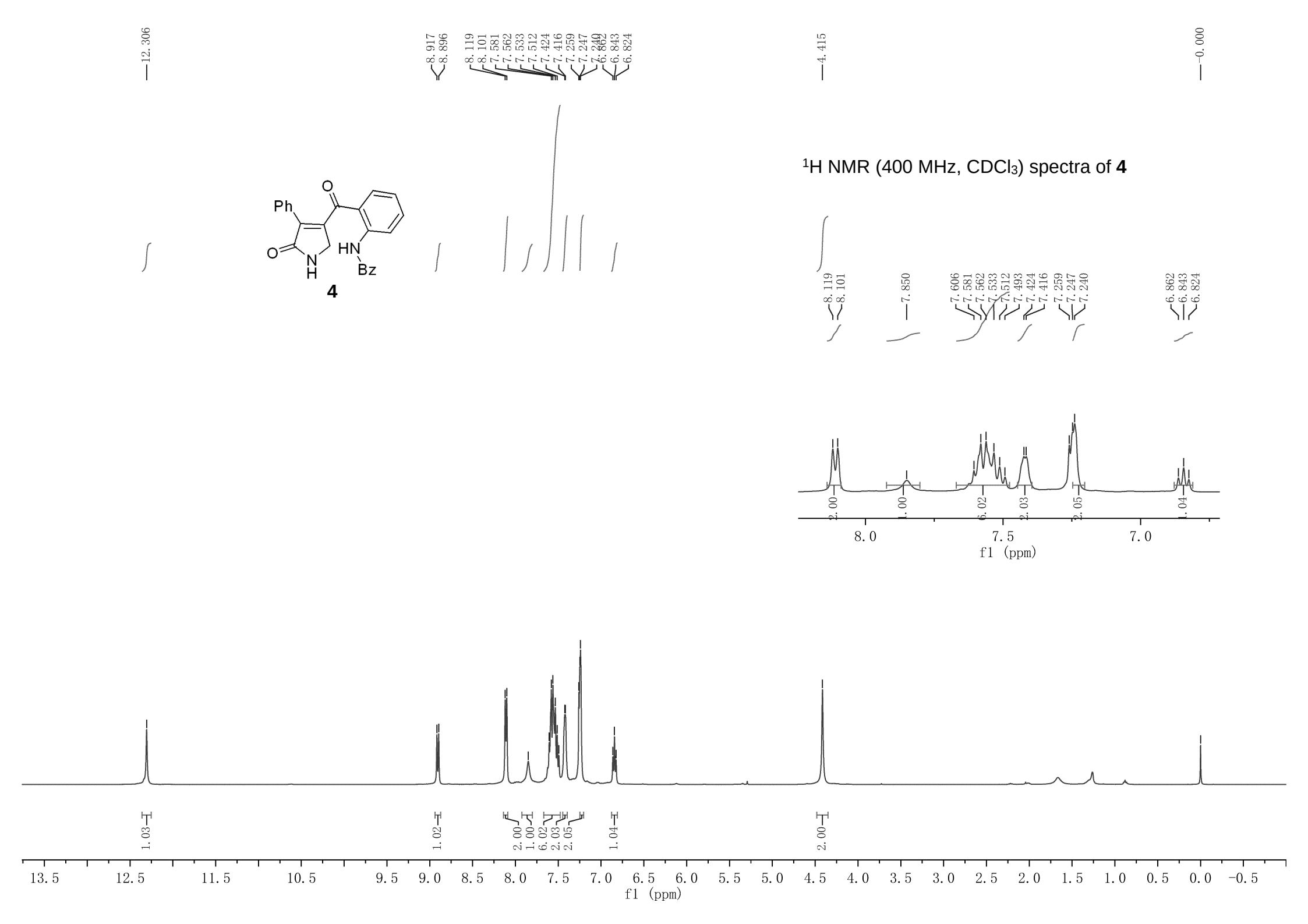

192.52
166.62
147.65
145.62
136.39
134.81
134.42
134.19
129.90
129.68
129.43
129.22
128.70
128.61
128.35
128.30
77.32
77.00
76.68
50.62
21.71
Ph
O
Ph
O
N
Ts
3p
13C NMR (100 MHz, CDCl3) spectra of 3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

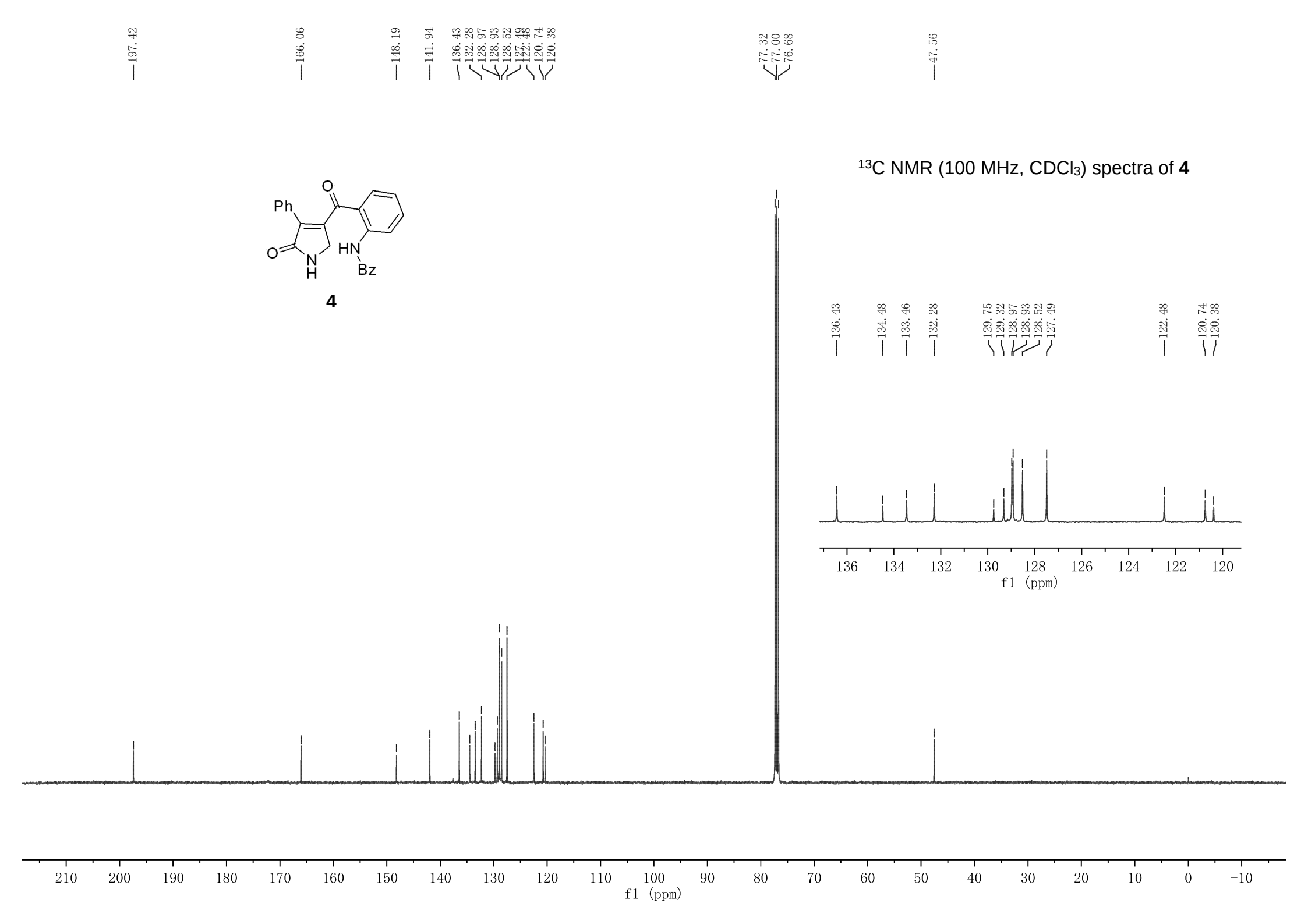

7.995
7.974
7.962
7.943
7.668
7.649
7.632
7.545
7.527
7.510
7.340
7.321
7.258
7.157
7.139
4.861
2.367
0.000
Ts
N
O
O
Ph
Ph
3pa
1H NMR (400 MHz, CDCl3) spectra of 3pa
4.06
1.00
2.00
5.01
2.02
3.00
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

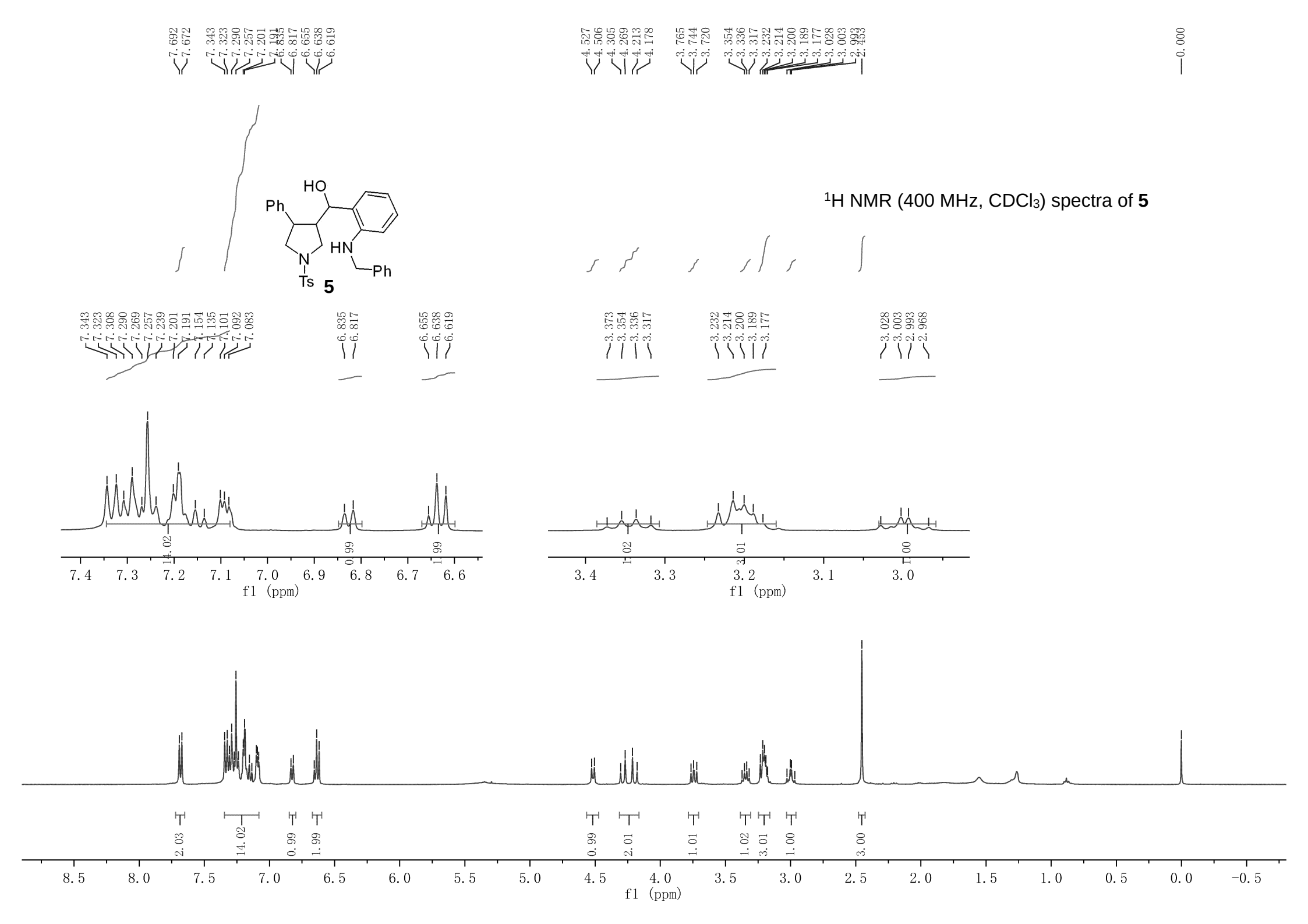


3pa

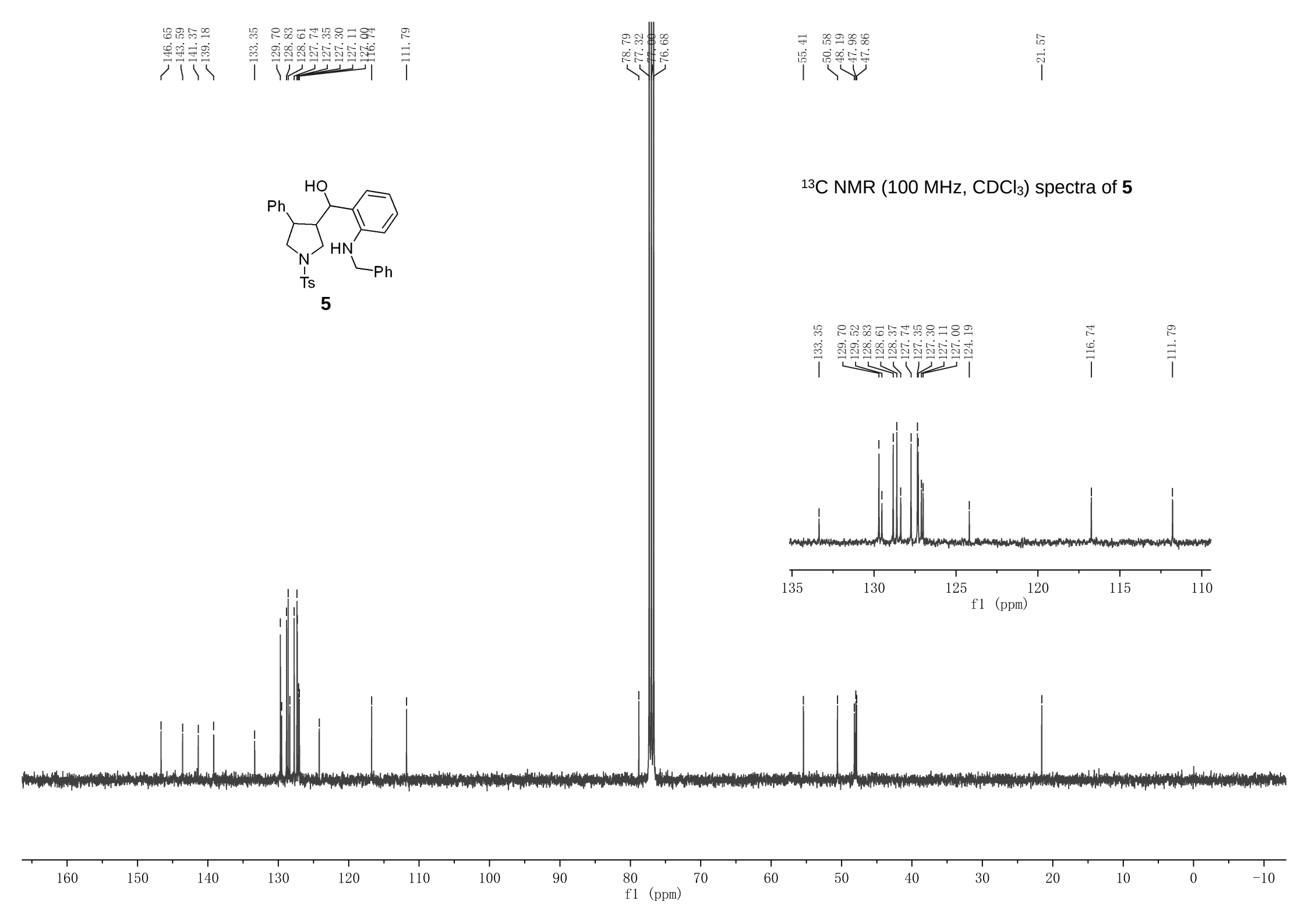
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3pa**


12.306
8.917
8.896
8.119
8.101
7.581
7.562
7.533
7.512
7.424
7.416
7.259
7.247
7.240
6.862
6.843
6.824
4.415
0.000
Ph
O
O
N
H
HN
Bz
4
1H NMR (400 MHz, CDCl3) spectra of 4
8.119
8.101
7.850
7.606
7.581
7.562
7.533
7.512
7.493
7.424
7.416
7.259
7.247
7.240
6.862
6.843
6.824
2.00
1.00
6.02
2.03
2.05
1.04
8.0
7.5
7.0
f1 (ppm)
1.03
1.02
2.00
1.00
6.02
2.03
2.05
1.04
2.00
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


197.42
166.06
148.19
141.94
136.43
132.28
128.97
128.93
128.52
127.49
120.74
120.38
77.32
77.00
76.68
47.56
Ph
O
O
N
H
HN
Bz
4
13C NMR (100 MHz, CDCl3) spectra of 4
136.43
134.48
133.46
132.28
129.75
129.32
128.97
128.93
128.52
127.49
122.48
120.74
120.38
136
134
132
130
128
126
124
122
120
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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


146.65
143.59
141.37
139.18
133.35
129.70
128.83
128.61
127.74
127.35
127.30
127.11
127.00
116.74
111.79
78.79
77.32
77.00
76.68
55.41
50.58
48.19
47.98
47.86
21.57
HO
Ph
HN
N
Ts
Ph
5
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **5**
133.35
129.70
129.52
128.83
128.61
128.37
127.74
127.35
127.30
127.11
127.00
124.19
116.74
111.79
135
130
125
120
115
110
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)