

Supporting Information for

TfOH-Promoted Synthesis of 4,5-Dihydrooxazolo[5,4-c]isoquinolines via Formal [3+2] Cycloaddition of 4-Diazoisoquinolin-3-one and Benzonitriles

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General Information:

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Melting points were measured with a micro melting point apparatus. NMR spectra were obtained at 400 or 600 MHz for ^1H NMR, 100 or 150 MHz for ^{13}C NMR. ^1H NMR chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane (TMS). ^{13}C NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were reported in ppm referenced to the center line of a triplet at 77.00 ppm of CDCl_3 . The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants J were reported in hertz unit (Hz). All high-resolution mass spectra (HRMS) data were recorded on ESI mass spectrometer. Flash column chromatography was performed employing 300-400 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel HSGF254.

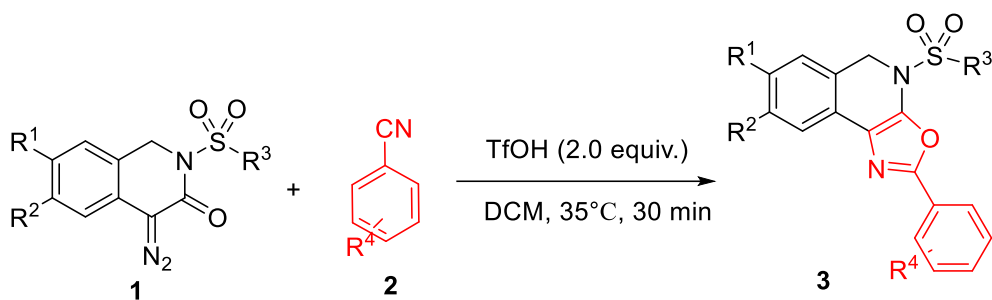
Substrates **1** were prepared according to the published procedures.^[1,2]

References:

[1] Ren, A.; Lu, P.; Wang, Y. *Chem. Commun.*, **2017**, 53, 3769.

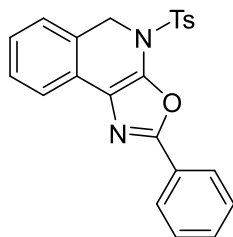
[2] Li, Z.; Chen, J.; Wu, L.; Ren, A.; Lu, P.; Wang, Y. *Org. Lett.*, **2020**, 22, 26-30.

Synthetic Procedure and Characterization Data for 3:



To an oven-dried Schlenk tube equipped with a magnetic stirring bar (parallel reactor) was added **2** (0.15 mmol) and TfOH (0.2 mmol). Then, a solution of **1** (0.1 mmol) in DCM (1 mL) was dripped slowly in 15-20 min. The reaction mixture was stirred at 35 °C for 0.5 h. After adding NaHCO₃ to quench reaction and cooling to room temperature, the resultant mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether /ethyl acetate = 15:1, v/v) to give pure product.

2-phenyl-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3a)



White solid; Yield: 33 mg, 81%; M.p.159-160°C

¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.14 (m, 2H), 7.52 – 7.48 (m, 3H), 7.40 – 7.35 (m, 3H), 7.17 – 7.13 (m, 1H), 7.09 – 7.05 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.00 (s, 2H), 2.19 (s, 3H).

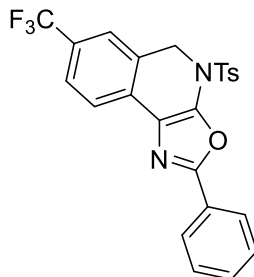
¹³C NMR (100 MHz, CDCl₃) δ 159.2, 144.6, 143.1, 133.1, 130.7, 129.1, 128.8, 128.3, 128.0, 127.5, 127.4, 127.4, 126.9, 126.8, 126.4, 125.7, 120.8, 53.2, 21.3.

HRMS (ESI) *m/z* calcd for C₂₃H₁₉N₂O₃S⁺ [M+H⁺]:403.1111; found:403.1112.

IR (film): 3055, 2915, 1922, 1636, 1595, 1492, 1451, 1363, 1292, 1245, 1170,

1154, 1088, 1014, 926, 851, 813, 781, 711, 676, 609, 545 cm^{-1} .

2-phenyl-4-tosyl-7-(trifluoromethyl)-4,5-dihydrooxazolo[5,4-c]isoquinoline (3b)



White solid; Yield: 28 mg, 60%; M.p.169-170 $^{\circ}\text{C}$

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17 – 8.15 (m, 2H), 7.53 – 7.49 (m, 4H), 7.42 – 7.37 (m, 3H), 7.14 (s, 1H), 6.94 (d, $J = 8.0$ Hz, 2H), 5.00 (s, 2H), 2.18 (s, 3H).

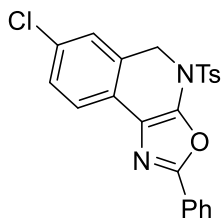
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.8, 145.2, 144.7, 133.0, 131.1, 130.2, 129.3, 129.0, 128.9, 127.8, 127.5, 127.2, 126.6, 125.0 (q, $J = 4.0$ Hz), 123.8 (q, $J = 270.3$ Hz), 122.8 (q, $J = 3.7$ Hz), 120.9, 52.8, 21.2.

$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.698.

HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_3\text{S}^+$ $[\text{M}+\text{H}^+]$: 471.0985; found: 471.0987

IR (film): 3065, 2925, 1710, 1634, 1551, 1481, 1424, 1371, 1326, 1246, 1170, 1123, 1073, 1022, 907, 841, 811, 711, 686, 666, 608, 550 cm^{-1} .

7-chloro-2-phenyl-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3c)



White solid; Yield: 29 mg, 66%; M.p.179-180 $^{\circ}\text{C}$.

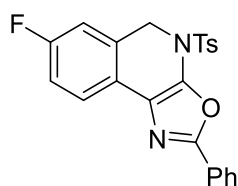
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17 – 8.12 (m, 2H), 7.53 – 7.49 (m, 3H), 7.39 – 7.37 (m, 2H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.13 (dd, $J = 8.0, 2.0$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.93 (d, $J = 2.0$ Hz, 1H), 4.94 (s, 2H), 2.24 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.5, 145.1, 143.3, 133.1, 133.0, 130.9, 129.3, 129.2, 128.9, 128.0, 127.6, 127.5, 126.7, 126.5, 126.1, 125.4, 122.0, 52.6, 21.4.

HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{18}\text{ClN}_2\text{O}_3\text{S}^+$ $[\text{M}+\text{H}^+]$: 437.0721; found:437.0725

IR (film): 3064, 2925, 1703, 1671, 1638, 1596,1545, 1494, 1449, 1368, 1187, 1171, 1085, 1023, 910, 813, 732, 710, 668 cm^{-1} .

7-fluoro-2-phenyl-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3d)



White solid; Yield: 30 mg, 71%; M.p.164-165 $^{\circ}\text{C}$.

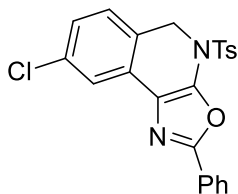
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.16 – 8.14 (m, 2H), 7.53 – 7.50 (m, 3H), 7.39 – 7.35 (m, 3H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.88 – 6.83 (m, 1H), 6.70 (dd, $J = 8.4, 2.4$ Hz, 1H), 4.96 (s, 2H), 2.22 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.0 (d, $J = 246.6$ Hz), 159.4, 144.9, 133.0, 130.9, 129.9 (d, $J = 7.5$ Hz), 129.2, 128.9, 127.8, 127.5, 126.7, 126.5, 123.1, 122.5 (d, $J = 8.3$ Hz), 114.7 (d, $J = 21.6$ Hz), 113.4 (d, $J = 23.1$ Hz), 52.8 (d, $J = 2.0$ Hz), 21.4.

HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{18}\text{FN}_2\text{O}_3\text{S}^+$ $[\text{M}+\text{H}^+]$: 421.1017; found: 421.1018

IR (film): 3066, 2925, 1705, 1661, 1592, 1489, 1448, 1359, 1287, 1234, 1187, 1032, 1008, 952, 845, 815, 709, 983 cm^{-1} .

8-chloro-2-phenyl-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3f)



White solid; Yield: 17 mg, 39%; M.p.143-144 $^{\circ}\text{C}$.

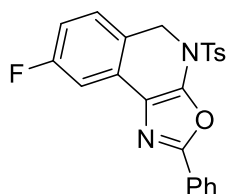
¹H NMR (400 MHz, CDCl₃) δ 8.16 – 8.13 (m, 2H), 7.53 – 7.50 (m, 3H), 7.38 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.34 (dd, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 2H), 2.25 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.5, 145.1, 143.9, 134.2, 132.9, 130.9, 129.3, 128.9, 128.5, 127.4, 127.1, 127.0, 126.7, 126.5, 125.7, 121.0, 52.7, 21.4.

HRMS (ESI) *m/z* calcd for C₂₃H₁₈ClN₂O₃S⁺ [M+H⁺]: 437.0721; found: 437.0719.

IR (film): 3065, 2924, 1705, 1634, 1596, 1493, 1369, 1265, 1187, 1171, 1115, 1087, 1022, 909, 814, 733, 691, 971, 600 cm⁻¹.

8-fluoro-2-phenyl-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3g)



White solid; Yield: 24 mg, 58%; M.p.129-130 °C.

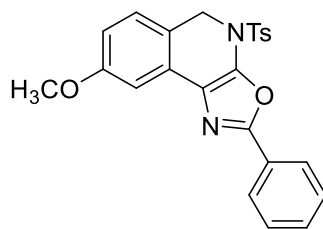
¹H NMR (400 MHz, CDCl₃) δ 8.16 – 8.13 (m, 2H), 7.53 – 7.50 (m, 3H), 7.38 – 7.36 (m, 2H), 7.11 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.98 – 6.92 (m, 3H), 6.79 – 6.74 (m, 1H), 4.98 (s, 2H), 2.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 162.6 (d, *J* = 245.2 Hz), 159.4, 144.9, 143.9, 133.1, 130.9, 129.2, 128.9, 127.6 (d, *J* = 3.0 Hz), 127.4, 127.3 (d, *J* = 8.5 Hz), 126.7, 126.5, 123.1 (d, *J* = 3.3 Hz), 113.7 (d, *J* = 22.1 Hz), 108.2 (d, *J* = 24.0 Hz), 52.6, 21.4.

HRMS (ESI) *m/z* calcd for C₂₃H₁₈FN₂O₃S⁺ [M+H⁺]: 421.1017; found: 421.1019.

IR (film): 3066, 2920, 1642, 1612, 1495, 1450, 1368, 1268, 1170, 1089, 1052, 891, 814, 773, 716, 670 cm⁻¹.

8-methoxy-2-phenyl-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3h)



White solid; Yield: 9 mg, 21%; M.p.78-79°C

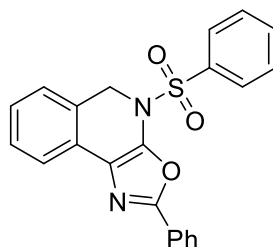
¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.14 (m, 2H), 7.51 – 7.50 (m, 3H), 7.40 – 7.37 (m, 2H), 6.97 – 6.95 (m, 3H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.62 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.96 (s, 2H), 3.78 (s, 3H), 2.22 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.6, 159.1, 144.6, 143.5, 133.3, 130.8, 129.2, 128.9, 128.1, 128.0, 127.4, 126.8, 126.5, 119.6, 113.4, 105.9, 55.5, 52.8, 21.4.

HRMS (ESI) *m/z* calcd for C₂₄H₂₁N₂O₄S⁺ [M+H⁺]: 433.1217; found: 433.1216.

IR (film): 3065, 2925, 2843, 1637, 1611, 1475, 1409, 1383, 1364, 1228, 1171, 1029, 1007, 910, 815, 776, 706, 681 cm⁻¹.

2-phenyl-4-(phenylsulfonyl)-4,5-dihydrooxazolo[5,4-c]isoquinoline (3j)



White solid; Yield: 29 mg, 75%; M.p. 157-158 °C

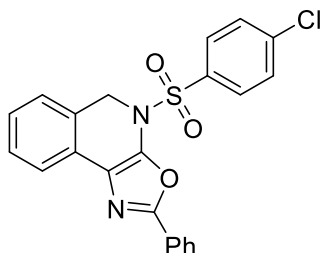
¹H NMR (400 MHz, CDCl₃) δ 8.18 – 8.15 (m, 2H), 7.53 – 7.49 (m, 5H), 7.40 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.17 – 7.11 (m, 3H), 7.09 – 7.05 (m, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.03 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 159.3, 142.9, 136.2, 133.6, 130.8, 128.9, 128.5, 128.33, 128.25, 127.6, 127.5, 127.3, 126.8, 126.6, 126.5, 120.9, 53.2.

HRMS (ESI) *m/z* calcd for C₂₂H₁₇N₂O₃S⁺ [M+H⁺]: 389.0954; found: 389.0951

IR (film): 3064, 2925, 2251, 1703, 1637, 1602, 1484, 1449, 1367, 1294, 1250, 1173, 1088, 1017, 911, 755, 719, 689, 609, 574 cm⁻¹.

4-((4-chlorophenyl)sulfonyl)-2-phenyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3k)



White solid; Yield: 29 mg, 69%; M.p.144-145 °C.

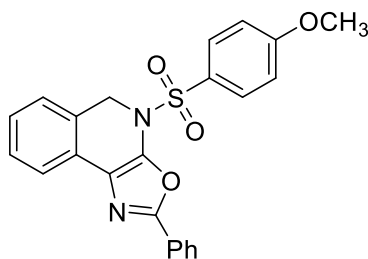
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17 – 8.15 (m, 2H), 7.53 – 7.50 (m, 3H), 7.44 – 7.38 (m, 3H), 7.23 – 7.19 (m, 1H), 7.14 – 7.08 (m, 3H), 6.98 (d, $J = 7.2$ Hz, 1H), 5.00 (s, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 159.6, 142.7, 140.3, 134.4, 130.9, 128.9, 128.80, 128.77, 128.4, 127.7, 127.2, 126.7, 126.6, 126.5, 125.7, 121.1, 53.4.

HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{16}\text{ClN}_2\text{O}_3\text{S}^+$ [$\text{M}+\text{H}^+$]: 423.0565; found: 423.0561.

IR (film): 3066, 2920, 1698, 1665, 1637, 1603, 1477, 1450, 1394, 1370, 1235, 1185, 1167, 1091, 1006, 830, 756, 707 cm^{-1} .

4-((4-methoxyphenyl)sulfonyl)-2-phenyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3l)



White solid; Yield: 29 mg, 70%; M.p.145-146 °C.

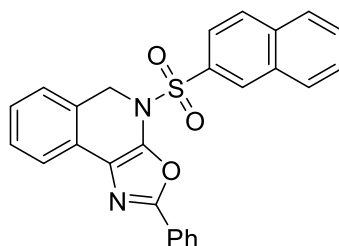
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.18 – 8.15 (m, 2H), 7.53 – 7.49 (m, 3H), 7.44 – 7.39 (m, 3H), 7.18 – 7.14 (m, 1H), 7.11 – 7.07 (m, 1H), 7.01 – 6.98 (m, 1H), 6.59 – 6.57 (m, 2H), 5.00 (s, 2H), 3.69 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 163.6, 159.3, 143.3, 130.8, 129.7, 128.9, 128.3, 128.1, 127.7, 127.6, 127.5, 126.8, 126.7, 126.5, 125.7, 120.9, 113.8, 55.5, 53.2.

HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{19}\text{N}_2\text{O}_4\text{S}^+$ $[\text{M}+\text{H}^+]$: 419.1060; found: 419.1060.

IR (film): 3061, 2841, 1703, 1595, 1573, 1497, 1450, 1363, 1300, 1258, 1188, 1165, 1090, 1024, 958, 920, 833, 806, 714, 674 cm^{-1} .

4-(naphthalen-2-ylsulfonyl)-2-phenyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3m)



White solid; Yield: 19 mg, 43%; M.p. 156-157 $^\circ\text{C}$.

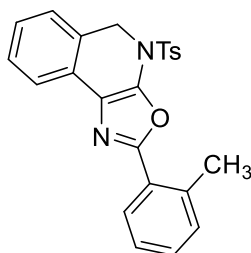
^1H NMR (400 MHz, CDCl_3) δ 8.18 – 8.15 (m, 2H), 8.12 (d, $J = 1.6$ Hz, 1H), 7.70 (t, $J = 7.6$ Hz, 2H), 7.58 – 7.43 (m, 7H), 7.24 – 7.21 (m, 1H), 6.93 – 6.85 (m, 3H), 5.06 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 143.1, 135.0, 133.4, 131.6, 130.8, 129.5, 129.1, 128.9, 128.7, 128.3, 128.2, 128.0, 127.6, 127.4, 127.3, 126.9, 126.53, 126.49, 125.5, 125.1, 122.1, 120.7, 53.3.

HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{19}\text{N}_2\text{O}_3\text{S}^+$ $[\text{M}+\text{H}^+]$: 439.1111; found: 439.1113.

IR (film): 3058, 2916, 2843, 2249, 1699, 1637, 1494, 1452, 1363, 1273, 1243, 1169, 1133, 1073, 1021, 908, 858, 774, 708, 667 cm^{-1} .

2-(*o*-Tolyl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3n)



White solid; Yield: 31mg, 75%; M.p. 128-129 $^\circ\text{C}$.

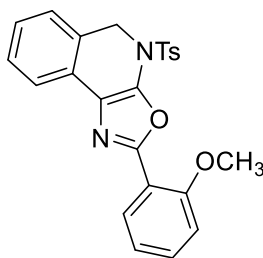
¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.10 (m, 1H), 7.41 – 7.31 (m, 6H), 7.17 – 7.13 (m, 1H), 7.09 – 7.05 (m, 1H), 6.98 – 6.96 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.01 (s, 2H), 2.78 (s, 3H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.6, 144.6, 142.9, 137.7, 133.2, 131.7, 130.3, 129.1, 129.0, 128.0, 127.8, 127.5, 127.4, 127.3, 126.9, 126.1, 125.9, 125.7, 120.8, 53.1, 22.1, 21.4.

HRMS (ESI) *m/z* calcd for C₂₄H₂₁N₂O₃S⁺ [M+H⁺]: 417.1267; found: 417.1267.

IR (film): 3062, 2925, 1701, 1639, 1599, 1493, 1454, 1365, 1293, 1241, 1187, 1170, 1088, 1032, 814, 773, 729, 672, 610, 552 cm⁻¹.

2-(2-Methoxyphenyl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3o)



White solid; Yield: 23 mg, 54%; M.p. 126-127 °C.

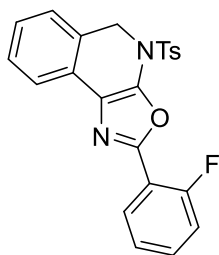
¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.40 – 7.38 (m, 2H), 7.16 – 7.05 (m, 4H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.00 (s, 2H), 4.03 (s, 3H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 157.83, 157.69, 144.5, 142.9, 133.2, 132.2, 130.4, 129.1, 127.9, 127.6, 127.5, 127.3, 126.8, 125.6, 121.1, 120.8, 116.0, 112.1, 56.2, 53.1, 21.4.

HRMS (ESI) *m/z* calcd for C₂₄H₂₀N₂O₄SNa⁺ [M+Na⁺]: 455.1036; found: 455.1037.

IR (film): 3069, 2925, 1704, 1660, 1483, 1362, 1293, 1241, 1165, 1034, 1010, 911, 816, 756, 682, 670, 568 cm⁻¹.

2-(2-fluorophenyl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3p)



White solid; Yield: 31 mg, 74%; M.p. 138-139 °C.

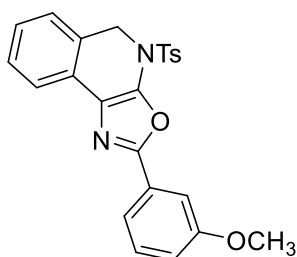
¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.11(m, 1H), 7.51 – 7.40 (m, 4H), 7.31 – 7.22 (m, 2H), 7.19 – 7.14 (m, 1H), 7.11 – 7.07 (m, 1H), 7.00 – 6.95 (m, 3H), 5.01 (s, 2H), 2.21 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 160.1 (d, *J* = 256.3 Hz), 155.3 (d, *J* = 5.1 Hz), 144.7, 143.4, 133.33, 132.28 (d, *J* = 8.4 Hz), 129.5, 129.2, 128.1, 127.8, 127.6, 127.52, 127.46, 126.6, 125.7, 124.5 (d, *J* = 3.7 Hz), 121.0, 116.9 (d, *J* = 21.1 Hz), 115.3 (*J* = 10.8 Hz), 53.1, 21.4.

HRMS (ESI) *m/z* calcd for C₂₃H₁₈FN₂O₃S⁺ [M+H⁺]: 421.1017; found: 421.1016.

IR (film): 3066, 2923, 1701, 1639, 1617, 1598, 1492, 1456, 1223, 1171, 1109, 1030, 958, 815, 767, 740, 671, 600, 552 cm⁻¹.

2-(3-Methoxyphenyl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3q)



White solid; Yield: 25 mg, 58%; M.p.101-102 °C.

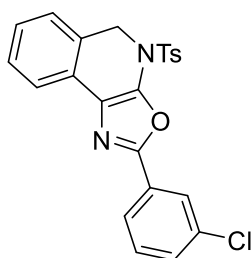
¹H NMR (400 MHz, CDCl₃) δ 7.76 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.67 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.17 – 7.13 (m, 1H), 7.10 – 7.04 (m, 2H), 6.98 – 6.95 (m, 1H), 6.94 – 6.91 (m, 2H), 5.00 (s, 2H), 3.92 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 159.2, 144.7, 143.2, 133.1, 130.0, 129.1, 128.2, 128.0, 127.9, 127.6, 127.5, 127.4, 126.6, 125.7, 120.9, 119.1, 117.5, 110.9, 55.5, 53.2, 21.4.

HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{21}\text{N}_2\text{O}_4\text{S}^+$ [$\text{M}+\text{H}^+$]: 433.1217; found: 433.1211.

IR (film): 3067, 2962, 2830, 1701, 1639, 1598, 1490, 1455, 1365, 1291, 1261, 1171, 1088, 1035, 958, 815, 730, 671, 599, 567, 552 cm^{-1} .

2-(3-chlorophenyl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3r)



White solid; Yield: 36 mg, 82%; M.p. 140-141 $^{\circ}\text{C}$.

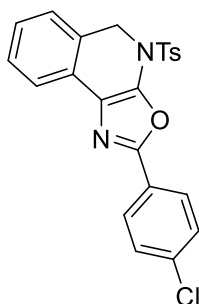
^1H NMR (400 MHz, CDCl_3) δ 8.14 – 8.13 (m, 1H), 8.02 (dt, $J = 6.4, 2.0$ Hz, 1H), 7.48 – 7.36 (m, 5H), 7.18 – 7.14 (m, 1H), 7.11 – 7.06 (m, 1H), 6.98 – 6.92 (m, 3H), 5.00 (s, 2H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 144.7, 143.5, 135.0, 133.1, 130.7, 130.2, 129.2, 128.5, 128.4, 128.1, 127.6, 127.4, 126.5, 126.4, 125.7, 124.5, 120.9, 53.1, 21.3.

HRMS (ESI) m/z calcd for $\text{C}_{23}\text{H}_{18}\text{ClN}_2\text{O}_3\text{S}^+$ [$\text{M}+\text{H}^+$]: 437.0721; found: 437.0719.

IR (film): 3065, 2923, 1702, 1636, 198, 1543, 1454, 1368, 1292, 1186, 1170, 1088, 1019, 813, 777, 725, 673, 609, 548 cm^{-1} .

2-(4-Chlorophenyl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3s)



White solid; Yield: 28 mg, 64%; M.p. 157-158 °C.

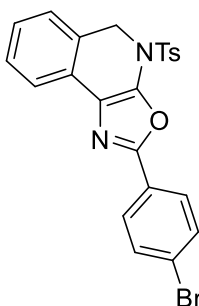
¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.48 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.39-7.36 (m, 3H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.06 (m, 1H), 7.00 – 6.91 (m, 3H), 4.99 (s, 2H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 158.3, 144.7, 143.3, 136.9, 133.1, 129.20, 129.17, 128.4, 128.0, 127.7, 127.6, 127.5, 127.4, 126.6, 125.7, 125.3, 120.9, 53.1, 21.4.

HRMS (ESI) *m/z* calcd for C₂₃H₁₈ClN₂O₃S⁺ [M+H⁺]: 437.0721; found: 437.0719.

IR (film): 3177, 3062, 2912, 2254, 1925, 1699, 1637, 1599, 1479, 1454, 1403, 1367, 1171, 1090, 1013, 909, 821, 731, 671, 611 cm⁻¹.

2-(4-Bromophenyl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3t)



White solid; Yield: 34 mg, 70%; M.p. 67-68 °C.

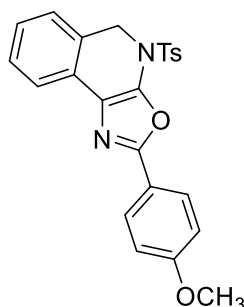
¹H NMR (400 MHz, CDCl₃) δ 8.03 – 8.00 (m, 2H), 7.66 – 7.62 (m, 2H), 7.39 – 7.35 (m, 3H), 7.17 – 7.13 (m, 1H), 7.10 – 7.06 m, 1H), 6.97 – 6.92 (m, 3H), 4.99 (s, 2H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 158.3, 144.7, 143.3, 133.1, 132.1, 129.2, 128.4, 128.0, 127.8, 127.57, 127.55, 127.4, 126.5, 125.8, 125.7, 125.2, 120.9, 53.1, 21.4.

HRMS (ESI) m/z calcd for $C_{23}H_{18}BrN_2O_3S^+$ $[M+H^+]$: 481.0216; found: 481.0216.

IR (film): 3064, 2916, 2249, 1914, 1703, 1637, 1599, 1493, 1477, 1454, 1399, 1367, 1293, 1170, 1088, 1071, 1009, 910, 832, 729, 672, 610, 546 cm^{-1} .

2-(4-Methoxyphenyl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3u)



White solid; Yield: 36 mg, 83%; M.p.126-127 °C.

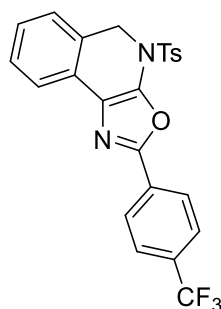
1H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 2H), 7.38 – 7.34 (m, 3H), 7.15 – 7.11 (m, 1H), 7.08 – 7.04 (m, 1H), 7.03 – 6.99 (m, 2H), 6.96 – 6.94 (m, 1H), 6.92 – 6.90 (m, 2H), 4.98 (s, 2H), 3.89 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 159.5, 144.6, 142.7, 133.1, 129.1, 128.2, 128.1, 127.9, 127.6, 127.5, 127.3, 126.8, 125.7, 120.8, 119.6, 114.3, 55.4, 53.2, 21.3.

HRMS (ESI) m/z calcd for $C_{24}H_{21}N_2O_4S^+$ $[M+H^+]$: 433.1217; found: 433.1219.

IR (film): 3062, 2941, 2839, 2253, 2052, 1916, 1703, 1638, 1611, 1500, 1455, 1366, 1255, 1170, 1088, 1024, 910, 839, 814, 767, 739, 673, 624, 602 cm^{-1} .

4-Tosyl-2-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazolo[5,4-c]isoquinoline (3v)



White solid; Yield: 30 mg, 63%; M.p.159-160 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.19 – 7.15 (m, 1H), 7.12 – 7.08 (m, 1H), 6.99 – 6.93 (m, 3H), 5.01 (s, 2H), 2.20 (s, 3H).

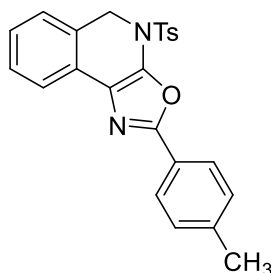
¹³C NMR (100 MHz, CDCl₃) δ 157.7, 144.8, 143.8, 133.2, 132.5 (q, *J* = 32.5 Hz), 130.0, 129.2, 128.5, 128.1, 127.7, 127.6, 127.4, 126.6, 126.5, 125.9 (q, *J* = 3.8 Hz), 125.8, 120.9, 53.1, 21.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.546.

HRMS (ESI) *m/z* calcd for C₂₄H₁₈F₃N₂O₃S⁺ [M+H⁺]: 471.0985; found: 471.0988.

IR (film): 3162, 2929, 1701, 1620, 1599, 1566, 1492, 1454, 1414, 1368, 1323, 1170, 1127, 1069, 1015, 849, 813, 768, 706, 671 cm⁻¹.

2-(*p*-Tolyl)-4-tosyl-4,5-dihydrooxazolo[5,4-*c*]isoquinoline (3w)



White solid; Yield: 31 mg, 74%; M.p.144-145 °C.

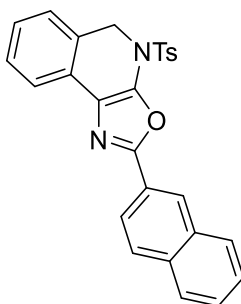
¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.03 (m, 2H), 7.39 – 7.30 (m, 5H), 7.16 – 7.12 (m, 1H), 7.08 – 7.04 (m, 1H), 6.96 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.99 (s, 2H), 2.43 (s, 3H), 2.18 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.5, 144.6, 142.9, 141.2, 133.1, 129.6, 129.1, 128.2, 128.0, 127.6, 127.4, 127.3, 126.8, 126.4, 125.7, 124.2, 120.8, 53.2, 21.6, 21.3.

HRMS (ESI) *m/z* calcd for C₂₄H₂₁N₂O₃S⁺ [M+H⁺]: 417.1267; found: 417.1269.

IR (film): 3030, 2922, 2249, 1916, 1702, 1637, 1598, 1500, 1455, 1404, 1367, 1294, 1169, 1088, 1018, 908, 824, 767, 729, 704, 673, 625, 601 cm⁻¹.

2-(Naphthalen-2-yl)-4-tosyl-4,5-dihydrooxazolo[5,4-*c*]isoquinoline (3x)



White solid; Yield: 31 mg, 68%; M.p. 143-144 °C.

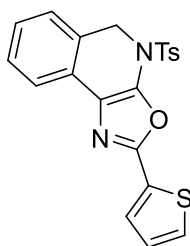
¹H NMR (400 MHz, CDCl₃) δ 8.66 (d, *J* = 1.6 Hz, 1H), 8.23 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.89 (dt, *J* = 6.4, 3.2 Hz, 1H), 7.58 – 7.55 (m, 2H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.11 – 7.07 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.03 (s, 2H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.5, 144.7, 143.3, 134.3, 133.1, 133.0, 129.2, 128.83, 128.75, 128.4, 128.0, 127.9, 127.6, 127.50, 127.47, 126.9, 126.7, 126.6, 125.7, 124.1, 123.2, 120.9, 53.2, 21.4.

HRMS (ESI) *m/z* calcd for C₂₇H₂₁N₂O₃S⁺[M+H⁺]: 453.1267; found: 453.1267.

IR (film): 3059, 2916, 2254, 1701, 1637, 1599, 1501, 1454, 1366, 1170, 1129, 1088, 953, 912, 863, 816, 753, 731, 672 cm⁻¹.

2-(Thiophen-2-yl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3y)



White solid; Yield: 33 mg, 82%; M.p.134-135.°C.

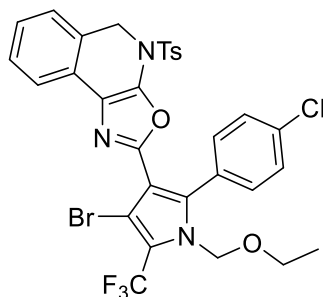
¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.48 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.17 – 7.11 (m, 2H), 7.09 – 7.04 (m, 1H), 6.96 – 6.92 (m, 3H), 4.98 (s, 2H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 155.5, 144.7, 142.6, 133.1, 129.4, 129.1, 128.7, 128.5, 128.3, 128.1, 128.0, 127.6, 127.5, 126.6, 125.7, 121.0, 53.2, 21.3.

HRMS (ESI) m/z calcd for $C_{21}H_{17}N_2O_3S_2^+$ $[M+H^+]$: 409.0675; found: 409.0673.

IR (film): 2925, 1636, 1596, 1497, 1455, 1364, 1202, 1170, 1087, 1050, 1014, 913, 853, 812, 722, 673, 607 cm^{-1} .

2-(4-Bromo-2-(4-chlorophenyl)-1-(ethoxymethyl)-5-(trifluoromethyl)-1H-pyrrol-3-yl)-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3z)



White solid; Yield: 33 mg, 47%; M.p. 119-120 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 4H), 7.23 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.13 – 7.03 (m, 4H), 6.96 – 6.94 (m, 1H), 6.82 (d, $J = 8.0$ Hz, 2H), 5.21 (s, 2H), 4.93 (s, 2H), 3.35 (q, $J = 7.2$ Hz, 2H), 2.18 (s, 3H), 1.14 (t, $J = 7.2$ Hz, 3H).

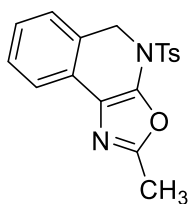
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 144.5, 143.3, 138.7 (q, $J = 1.4$ Hz), 136.1, 132.9, 132.5, 128.9, 128.8, 127.9, 127.5, 127.4, 127.3, 127.0, 126.5, 125.6, 122.0, 120.8, 112.8, 101.8 (q, $J = 2.8$ Hz), 75.1 (q, $J = 2.4$ Hz), 64.1, 53.1, 26.9, 21.3, 14.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -57.103.

HRMS (ESI) m/z calcd for $C_{31}H_{24}BrClF_3N_3NaO_4S^+$ $[M+Na^+]$: 728.0204; found: 728.0201.

IR (film): 3067, 2980, 2901, 1637, 1596, 1512, 1455, 1406, 1369, 1289, 1220, 1170, 1118, 1016, 910, 840, 813, 769, 731, 673, 612, 552 cm^{-1} .

2-Methyl-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3za)



White solid; Yield: 21 mg, 63%; M.p.142-143 °C.

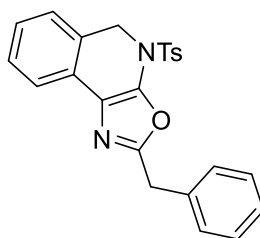
¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.31 (m, 2H), 7.24 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.12 – 7.08 (m, 1H), 7.05 – 7.01 (m, 1H), 6.93 – 6.90 (m, 3H), 4.92 (s, 2H), 2.59 (s, 3H), 2.19 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 159.5, 144.6, 142.8, 133.0, 129.6, 129.0, 128.4, 127.9, 127.4, 127.2, 126.7, 125.7, 120.5, 53.2, 21.3, 14.6.

HRMS (ESI) *m/z* calcd for C₁₈H₁₇N₂O₃S⁺ [M+H⁺]: 341.0954; found: 341.0953.

IR (film): 3064, 1698, 1599, 1494, 1453, 1363, 1295, 1233, 1171, 1122, 1033, 1009, 959, 911, 816, 785, 732, 670, 599 cm⁻¹.

2-Benzyl-4-tosyl-4,5-dihydrooxazolo[5,4-c]isoquinoline (3zb)



White solid; Yield: 30 mg, 72%; M.p.106-107 °C.

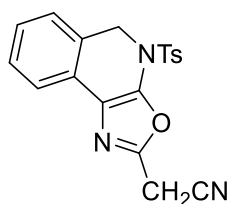
¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.35 (m, 4H), 7.32 – 7.24 (m, 2H), 7.22 – 7.20 (m, 2H), 7.12 – 7.08 (m, 1H), 7.07 – 7.02 (m, 1H), 6.95 – 6.93 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 2H), 4.93 (s, 2H), 4.20 (s, 2H), 2.17 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 160.8, 144.5, 143.2, 135.0, 132.9, 129.0, 128.8, 127.9, 127.4, 127.33, 127.26, 127.2, 126.9, 126.7, 125.6, 120.6, 53.2, 35.1, 21.3.

HRMS (ESI) *m/z* calcd for C₂₄H₂₁N₂O₃S⁺ [M+H⁺]: 417.1267; found: 417.1267.

IR (film): 3031, 2923, 1706, 1640, 1597, 1576, 1557, 1496, 1455, 1367, 1291, 1170, 1088, 1019, 949, 909, 813, 768, 738, 673, 605 cm⁻¹.

2-(4-Tosyl-4,5-dihydrooxazolo[5,4-c]isoquinolin-2-yl)acetonitrile (3zc)



White solid; Yield: 19 mg, 52%; M.p. 156-157 °C.

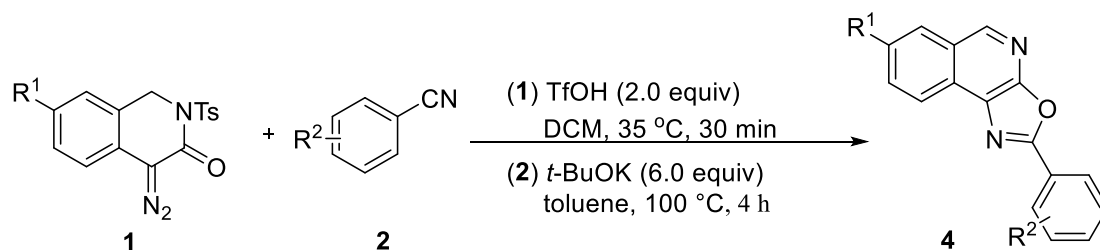
¹H NMR (600 MHz, CDCl₃) δ 7.38 – 7.36 (m, 2H), 7.31 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.17 – 7.14 (m, 1H), 7.11 – 7.08 (m, 1H), 6.98 – 6.95 (m, 3H), 4.96 (s, 2H), 4.04 (s, 2H), 2.22 (s, 3H).

¹³C NMR (150 MHz, CDCl₃) δ 150.6, 144.9, 144.2, 133.2, 129.3, 128.2, 127.9, 127.6, 127.5, 127.4, 126.0, 125.8, 120.9, 112.9, 53.1, 21.4, 18.8.

HRMS (ESI) *m/z* calcd for C₁₉H₁₆N₃O₃S⁺ [M+H⁺]: 366.0907; found: 366.0908.

IR (film): 2924, 2854, 1712, 1641, 1596, 1577, 1560, 1455, 1363, 1291, 1170, 1088, 1019, 911, 814, 773, 675, 607, 551 cm⁻¹.

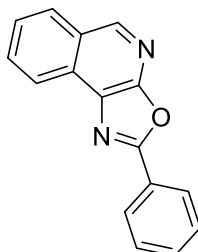
Synthetic Procedures and Characterization Data for 4



To a 25 ml round-bottom flask equipped with a magnetic stirring bar was added sequentially **2** (0.15 mmol) and TfOH (0.2 mmol). Then, a solution of **1** (0.1 mmol) in DCM (1 mL) was dripped slowly in 15-20 min. The reaction mixture was stirred at 35 °C (oil bath) for 0.5 h. After adding NaHCO₃ to quench reaction and cooling to room temperature, the resultant mixture was evaporated under reduced pressure. Then, *t*-BuOK (67 mg) and toluene (4 mL) were added. The mixture was stirred at 100 °C (oil bath) for 4 h. After cooling to room temperature, the resultant mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography

on silica gel (petroleum ether /ethyl acetate = 15:1, v/v) to give pure product.

2-Phenylloxazolo[5,4-c]isoquinoline (4a)



White solid; Yield: 17 mg, 68%; M.p.170-171°C.

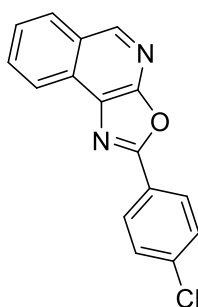
¹H NMR (400 MHz, CDCl₃) δ 9.00 (s, 1H), 8.53 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.38 – 8.34 (m, 2H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.67 – 7.63 (m, 1H), 7.58 – 7.54 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 161.7, 155.7, 148.4, 131.6, 131.3, 130.0, 129.0, 128.6, 128.0, 127.6, 127.5, 127.1, 126.3, 121.6.

HRMS (ESI) *m/z* calcd for C₁₆H₁₁N₂O⁺ [M+H⁺]: 247.0866; found: 247.0867.

IR (film): 3451, 3058, 2923, 1637, 1568, 1484, 1450, 1379, 1363, 1275, 1258, 1150, 1073, 999, 920, 793, 777, 713, 704, 686, 645, 571, 481 cm⁻¹.

2-(4-Chlorophenyl)oxazolo[5,4-c]isoquinoline (4b)



White solid; Yield: 17 mg, 60%; M.p. 216-217 °C.

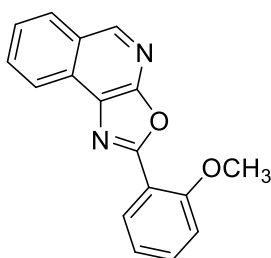
¹H NMR (400 MHz, CDCl₃) δ 9.00 (s, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.27 (dt, *J* = 8.4, 1.2 Hz, 2H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.63 – 7.67 (m, 1H), 7.54 – 7.2 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 155.7, 148.6, 137.8, 131.4, 130.0, 129.3, 128.7, 128.6, 127.9, 127.6, 126.4, 125.6, 121.5.

HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{10}\text{ClN}_2\text{O}^+$ [$\text{M}+\text{H}^+$]: 281.0476; found: 281.0475.

IR (film): 3450, 3083, 1801, 1640, 1603, 1561, 1479, 1448, 1431, 1358, 1216, 1179, 1110, 1054, 1010, 921, 861, 752, 730, 691, 570, 495 cm^{-1} .

2-(2-Methoxyphenyl)oxazolo[5,4-c]isoquinoline (4c)



White solid; Yield: 10 mg, 36%; M.p. 154-155 $^{\circ}\text{C}$.

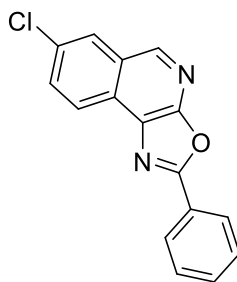
^1H NMR (400 MHz, CDCl_3) δ 9.02 (s, 1H), 8.58 (dt, $J = 8.0, 0.8$ Hz, 1H), 8.26 (dd, $J = 8.0, 1.6$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.84 – 7.89 (m, 1H), 7.62 – 7.66 (m, 1H), 7.51 – 7.56 (m, 1H), 7.17 – 7.11 (m, 2H), 4.06 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 160.5, 158.5, 155.4, 148.3, 132.9, 131.3, 131.1, 130.0, 128.5, 127.7, 127.5, 126.1, 121.8, 120.8, 116.0, 112.1, 56.1.

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_2^+$ [$\text{M}+\text{H}^+$]: 277.0972; found: 277.0970.

IR (film): 3454, 2924, 2853, 1724, 1637, 1600, 1584, 1467, 1360, 1255, 1171, 1088, 1010, 925, 815, 745, 665, 587, 545 cm^{-1} .

7-Chloro-2-phenyloxazolo[5,4-c]isoquinoline (4d)



White solid; Yield: 10 mg, 35%; M.p. 196-197 $^{\circ}\text{C}$.

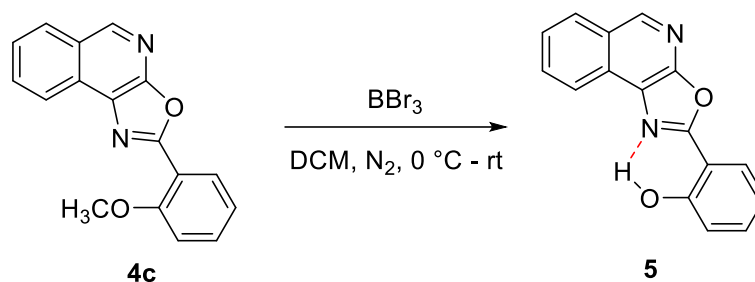
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.92 (s, 1H), 8.48 (d, $J = 8.8$ Hz, 1H), 8.36 – 8.33 (m, 2H), 8.11 (d, $J = 2.0$ Hz, 1H), 7.80 (dd, $J = 8.8, 2.0$ Hz, 1H), 7.59 – 7.55 (m, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.2, 155.8, 147.1, 132.2, 132.1, 131.9, 129.0, 128.24, 128.19, 128.10, 127.6, 127.3, 126.8, 123.5.

HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{10}\text{ClN}_2\text{O}^+ [\text{M}+\text{H}^+]$: 281.0476; found: 281.0477.

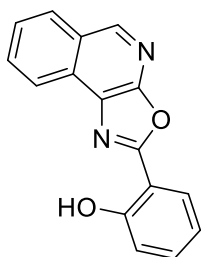
IR (film): 3451, 2923, 1637, 1603, 1560, 1475, 1447, 1389, 1359, 1343, 1272, 1076, 1013, 919, 808, 782, 710, 686, 594, 527, 485 cm^{-1} .

Synthetic procedures and Characterization Data for 5



To an oven-dried Schlenk tube equipped with a magnetic stirring bar was added **4c** (12 mg) and anhydrous CH_2Cl_2 (4 mL) under N_2 . The flask was cooled at 0 $^\circ\text{C}$. Then, BBr_3 (0.5 mL) was injected by a syringe. After the addition of BBr_3 was finished, the reaction mixture was stirred at room temperature for 19 h, water (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether /ethyl acetate = 6:1, v/v) to give pure product.

2-(Oxazolo[5,4-c]isoquinolin-2-yl)phenol (**5**)



White solid; Yield: 8 mg, 70%; M.p. 210-211°C.

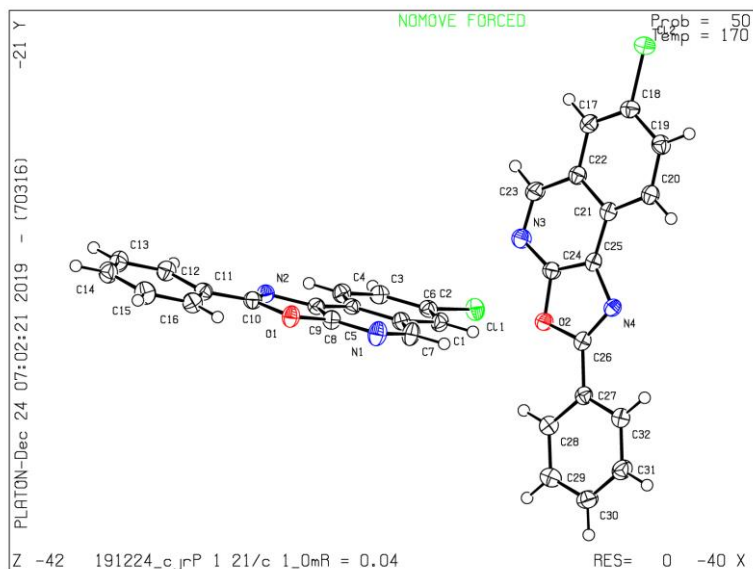
¹H NMR (400 MHz, CDCl₃) δ 11.39 (s, 1H), 9.04 (s, 1H), 8.45 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.17 – 8.13 (m, 2H), 7.90 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.69 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.48 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.16 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.09 – 7.05 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 161.7, 158.6, 154.2, 148.7, 133.7, 131.6, 129.1, 128.7, 127.7, 127.3, 126.7, 125.9, 121.5, 119.9, 117.5, 110.4.

HRMS (ESI) *m/z* calcd for C₁₆H₁₁N₂O₂⁺ [M+H⁺]: 263.0815; found: 263.0818.

IR (film): 3448, 3131, 1957, 1813, 1735, 1640, 1624, 1536, 1486, 1367, 1253, 1233, 1159, 1053, 996, 933, 837, 751, 672, 571 cm⁻¹.

Crystal Structures of 4d



Bond precision: C-C = 0.0030 Å Wavelength=0.71073

Cell: a=22.757(10) b=4.748(2) c=23.677(10)
 alpha=90 beta=104.854(16) gamma=90

Temperature: 170 K

	Calculated	Reported
Volume	2472.8(18)	2472.8(19)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C16 H9 Cl N2 O	C16 H9 Cl N2 O
Sum formula	C16 H9 Cl N2 O	C16 H9 Cl N2 O
Mr	280.70	280.70
Dx, g cm ⁻³	1.508	1.508
Z	8	8
Mu (mm ⁻¹)	0.304	0.304
F000	1152.0	1152.0
F000'	1153.60	
h, k, lmax	29, 6, 30	29, 6, 30
Nref	5415	5370
Tmin, Tmax	0.930, 0.985	0.701, 0.746
Tmin'	0.864	

Correction method= # Reported T Limits: Tmin=0.701 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.992 Theta(max)= 27.058

R(reflections)= 0.0439(4372) wR2(reflections)= 0.1108(5370)

S = 1.035 Npar= 361

Table S1. Photophysical Properties of Compounds 4c and 5

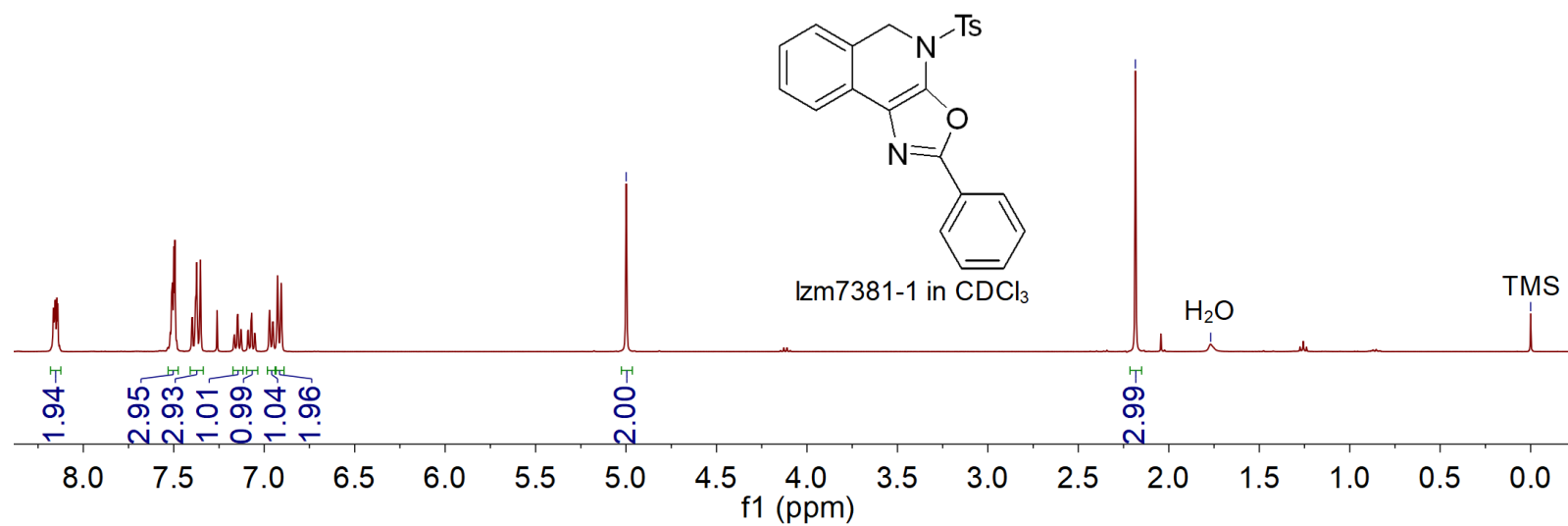
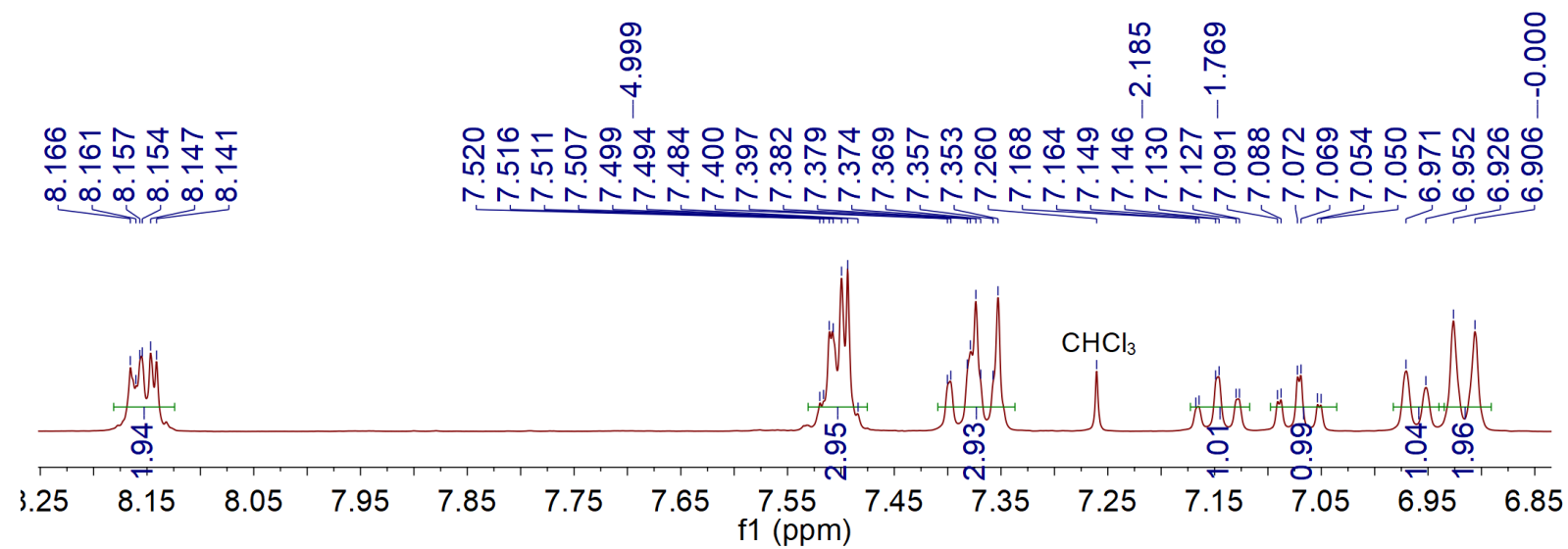
Compound	$\lambda_{\text{max}}^{\text{abs}}$ ($\epsilon/10^4$) ^[a]	$\lambda_{\text{sol}}^{\text{em}}$ Φ (%) ^[a]	Stokes	$\lambda_{\text{solid}}^{\text{em}}$
4c	348 (8.32)	372, 389, 409	41	418
	360 (6.42)	(41) ^[b]		
5	348 (13.13)	498	133	505
	365 (14.92)	(3) ^[c]		

[a] Measured in solution, $c=1 \times 10^{-5}$ M, excited at its maximum absorption wavelength

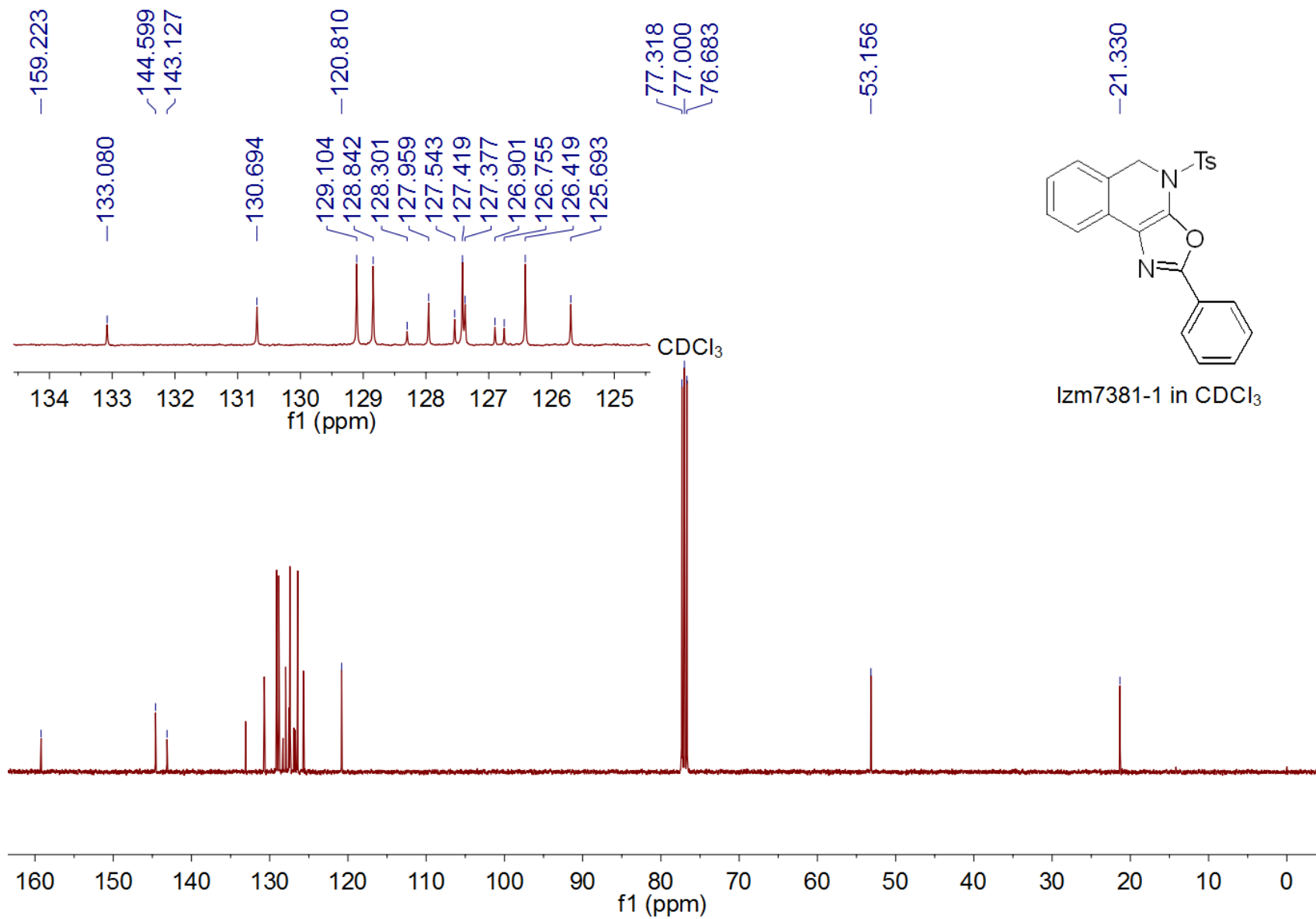
[b] Quantum yield (Φ) were calculated based on Quinine sulfate ($\Phi = 0.54$ in 0.1M H_2SO_4)

[c] Quantum yield (Φ) were calculated based on Anthracene ($\Phi = 0.27$ in ethanol)

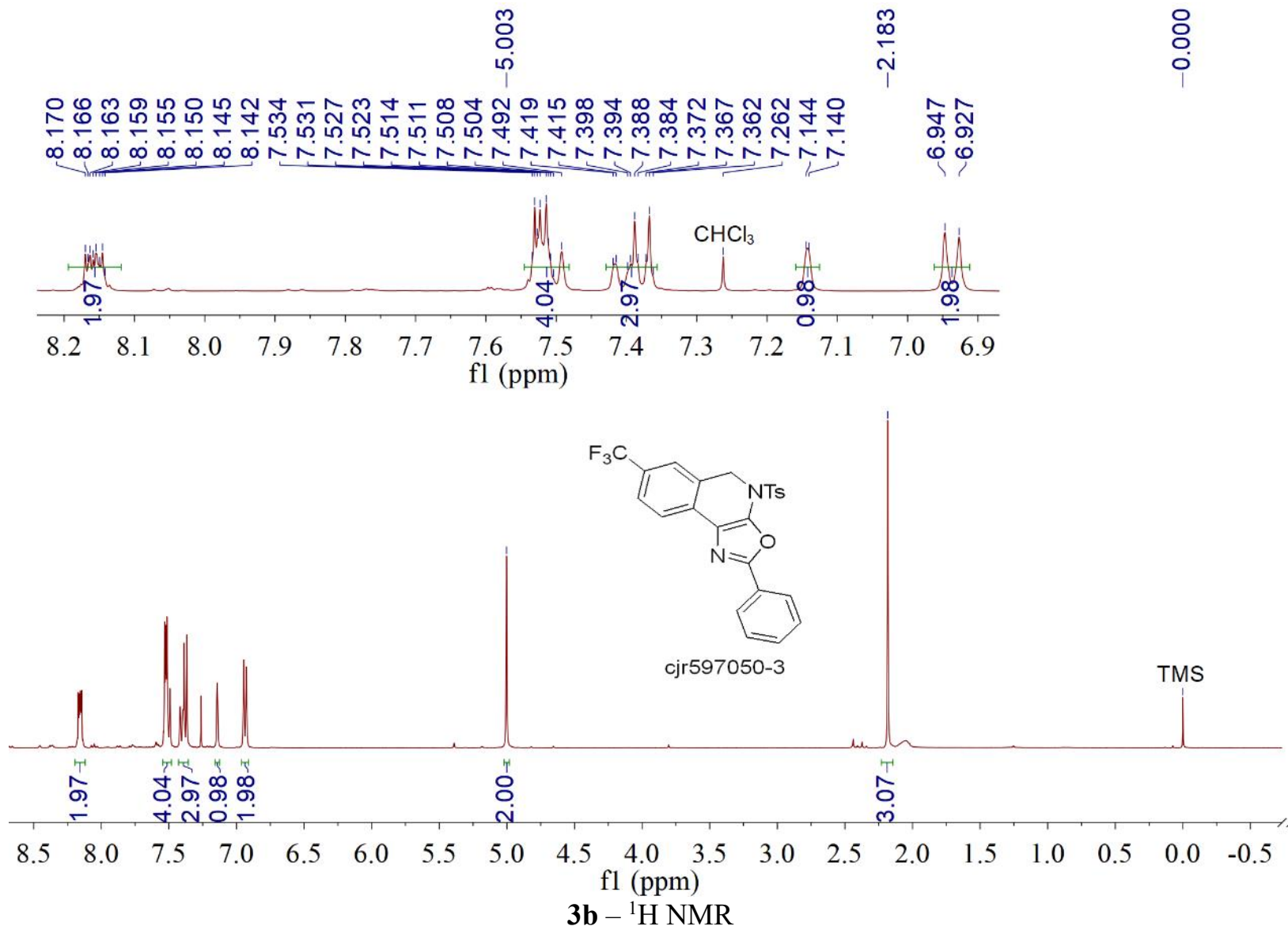
Copies of NMR Spectra:

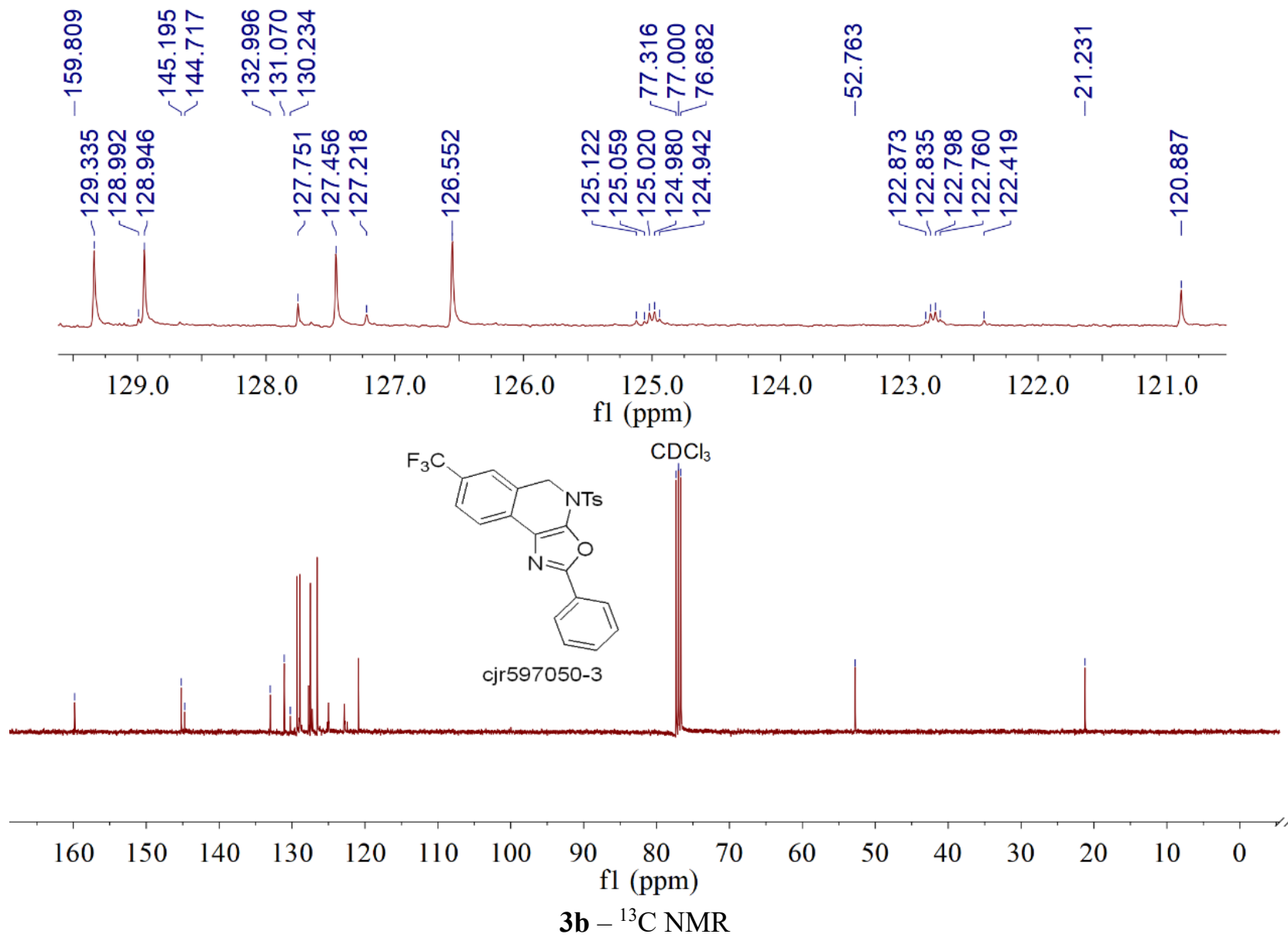


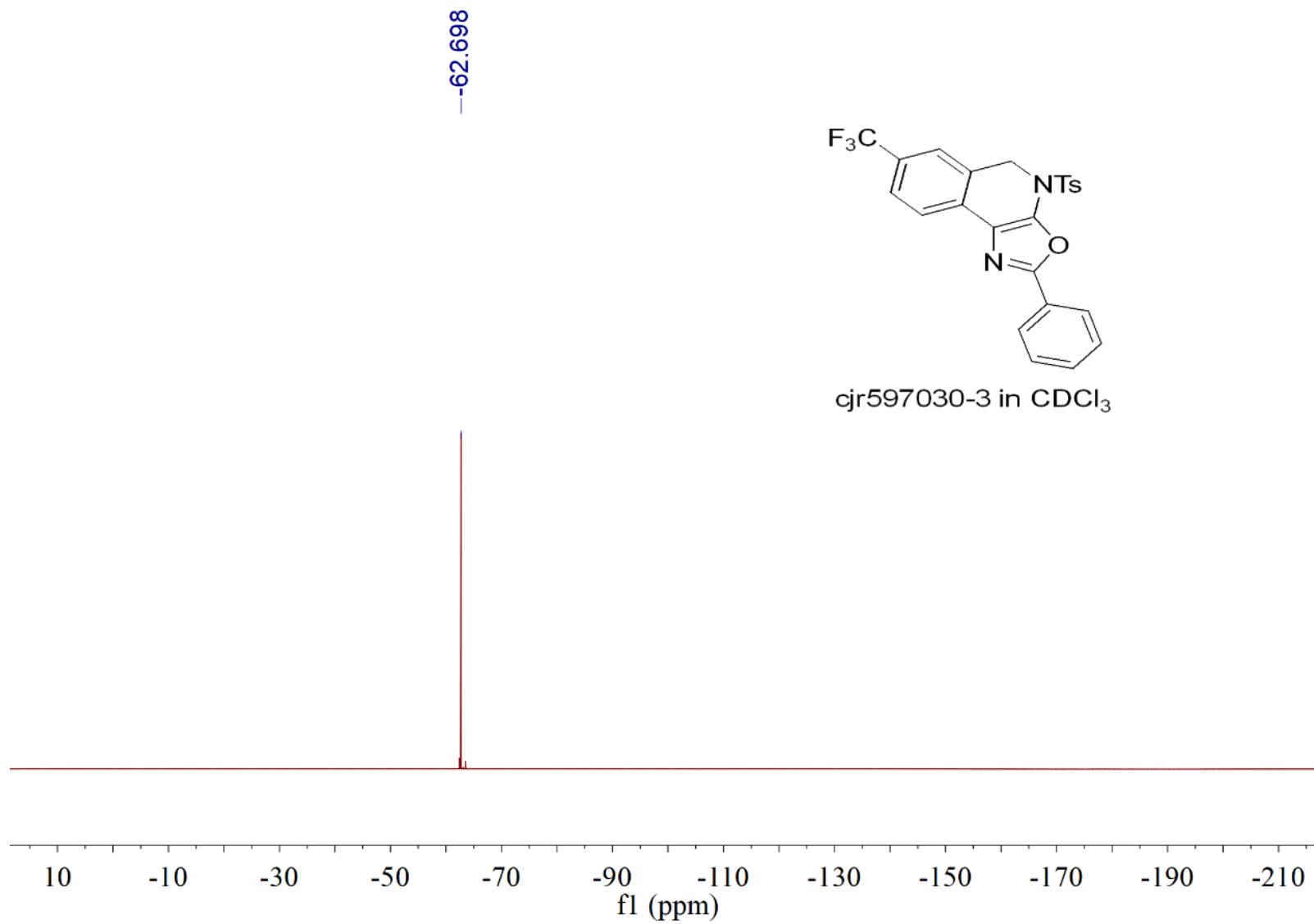
3a – ¹H NMR



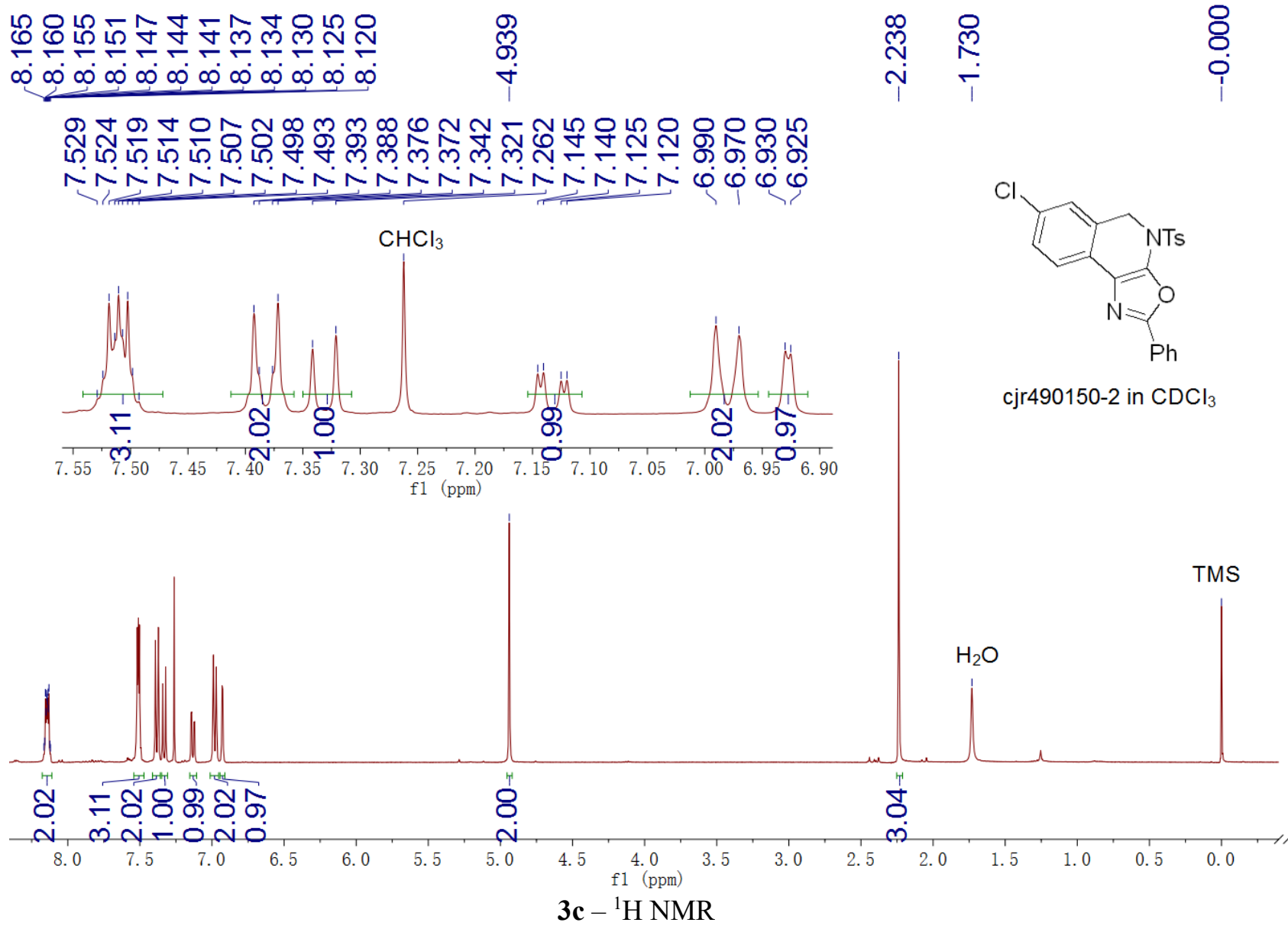
3a – ^{13}C NMR

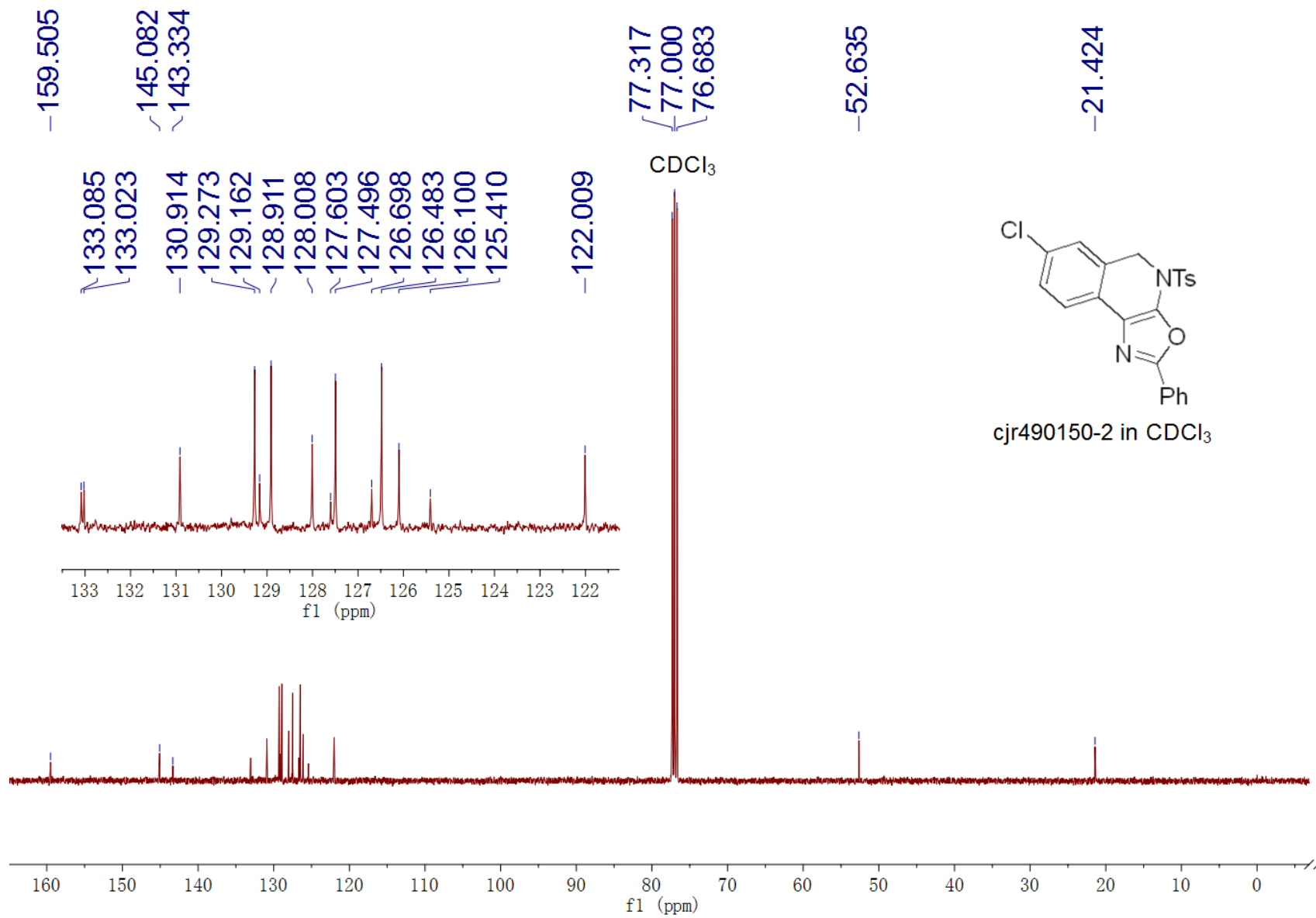


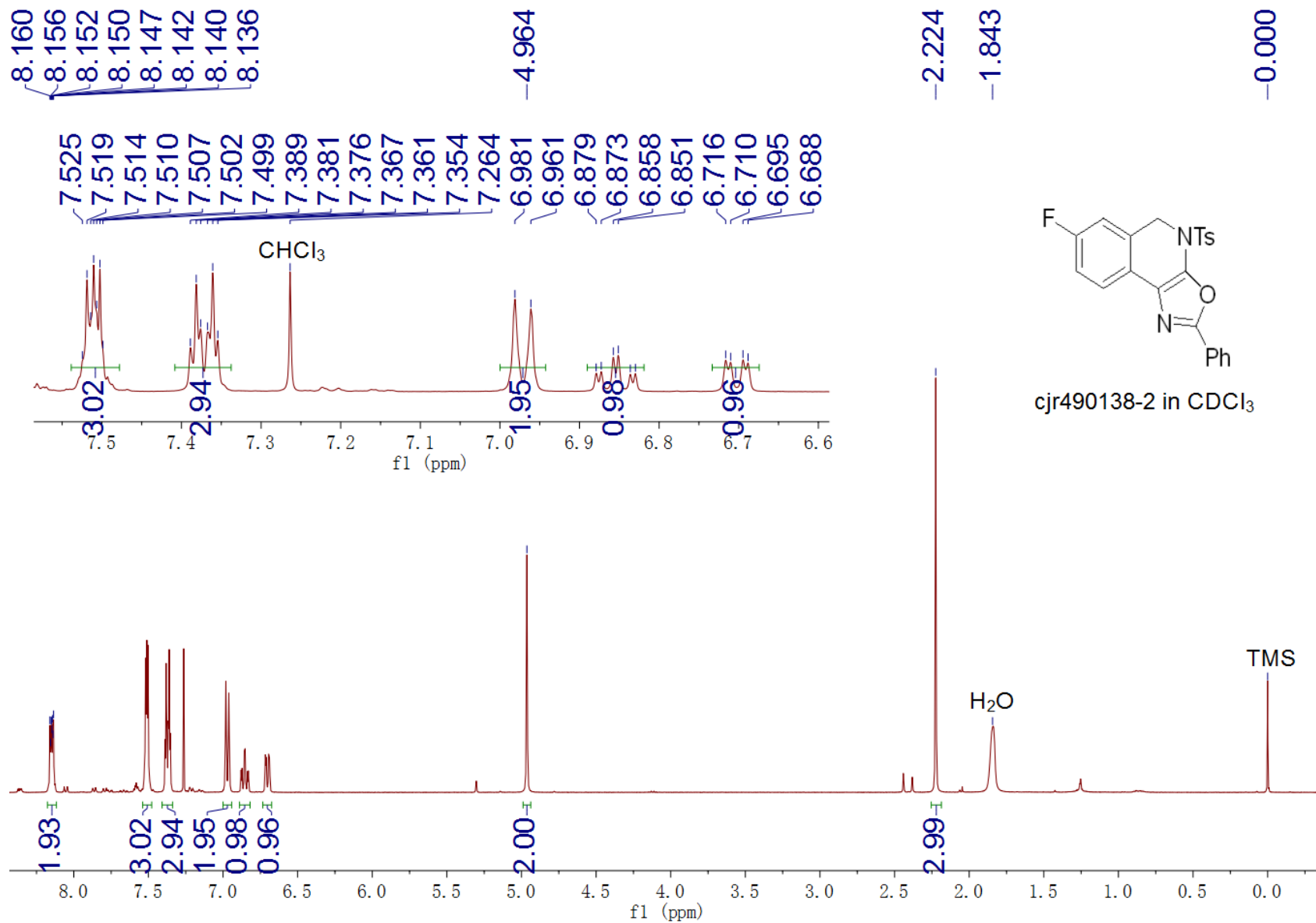


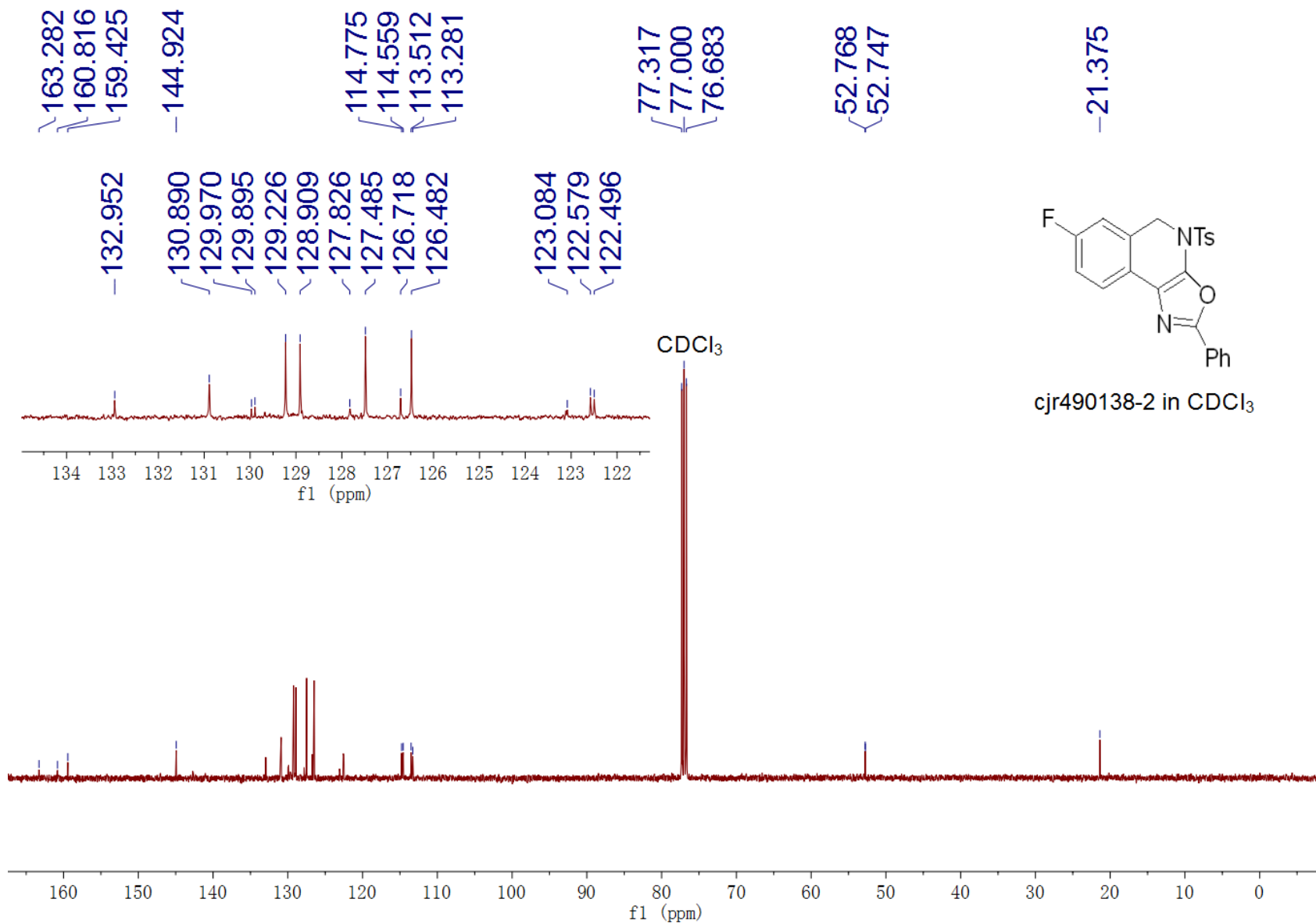


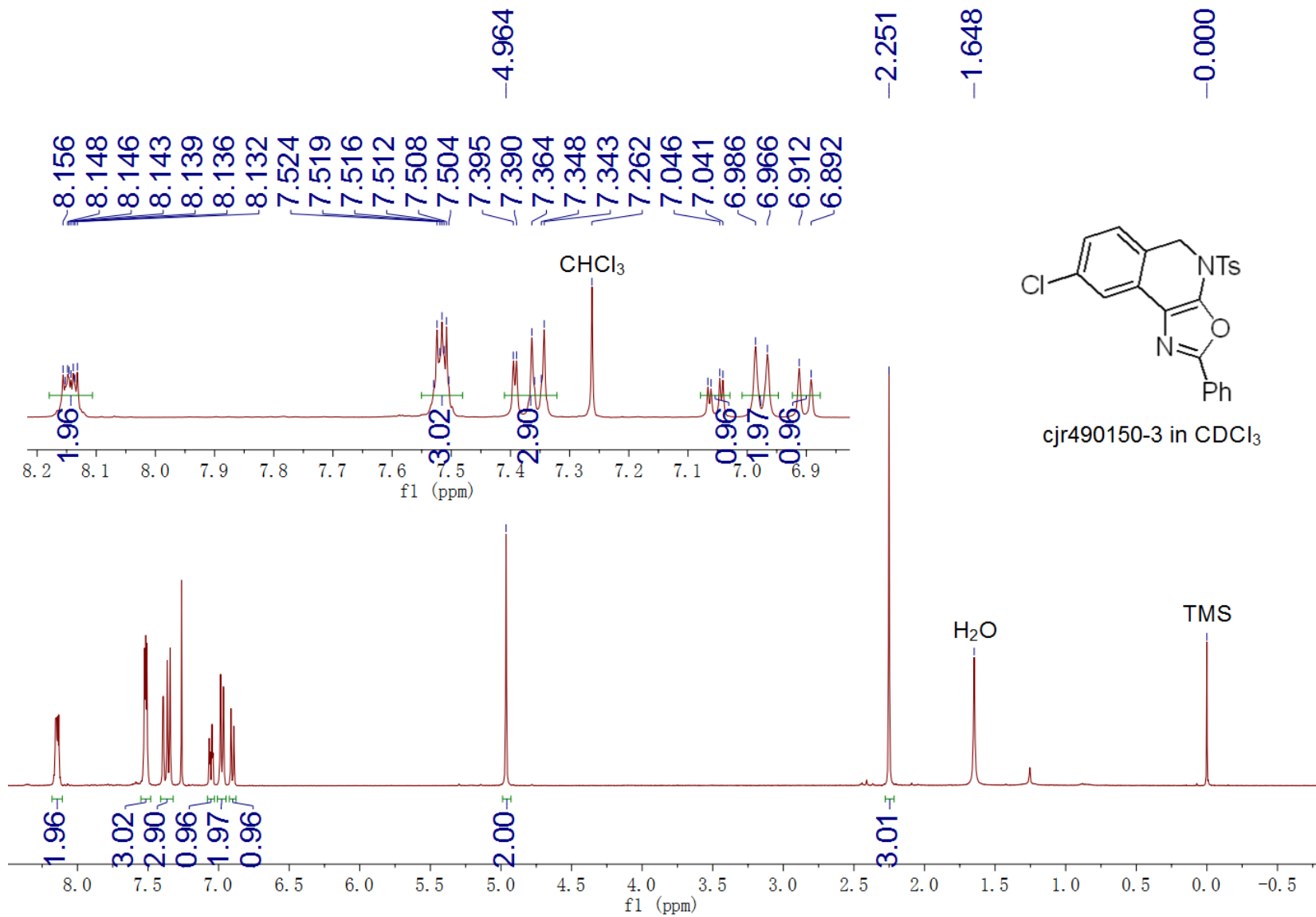
3b – ^{19}F NMR

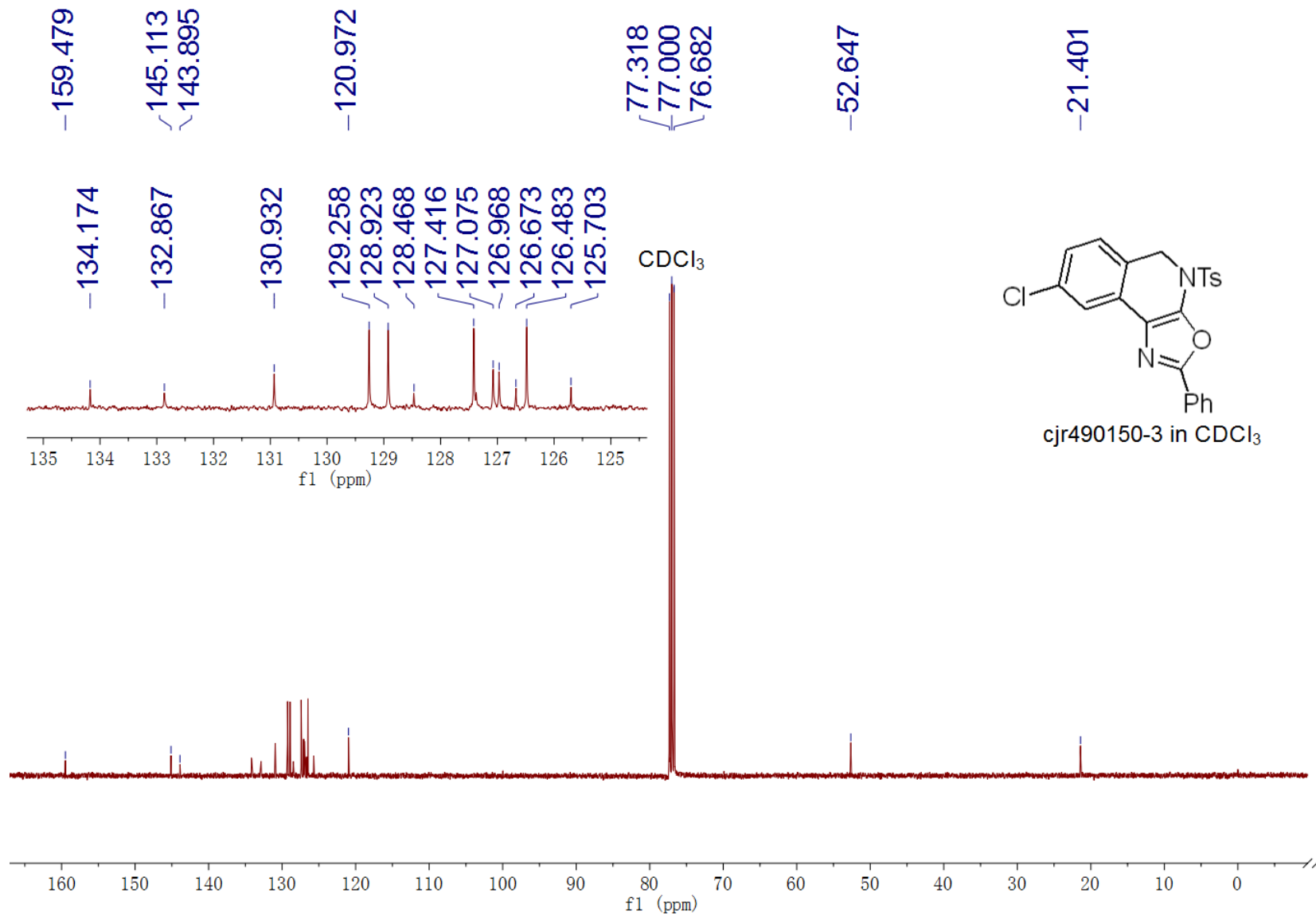




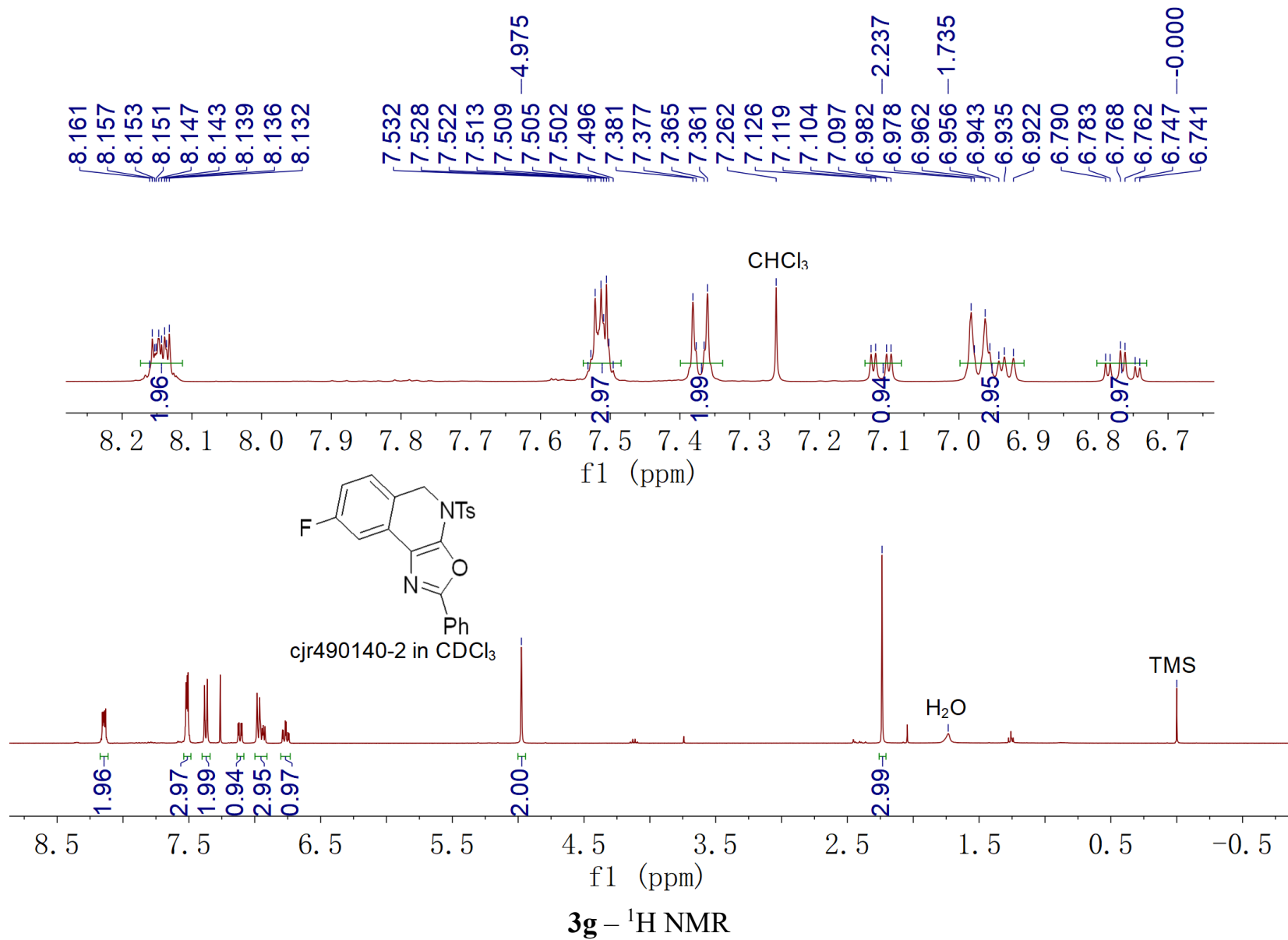


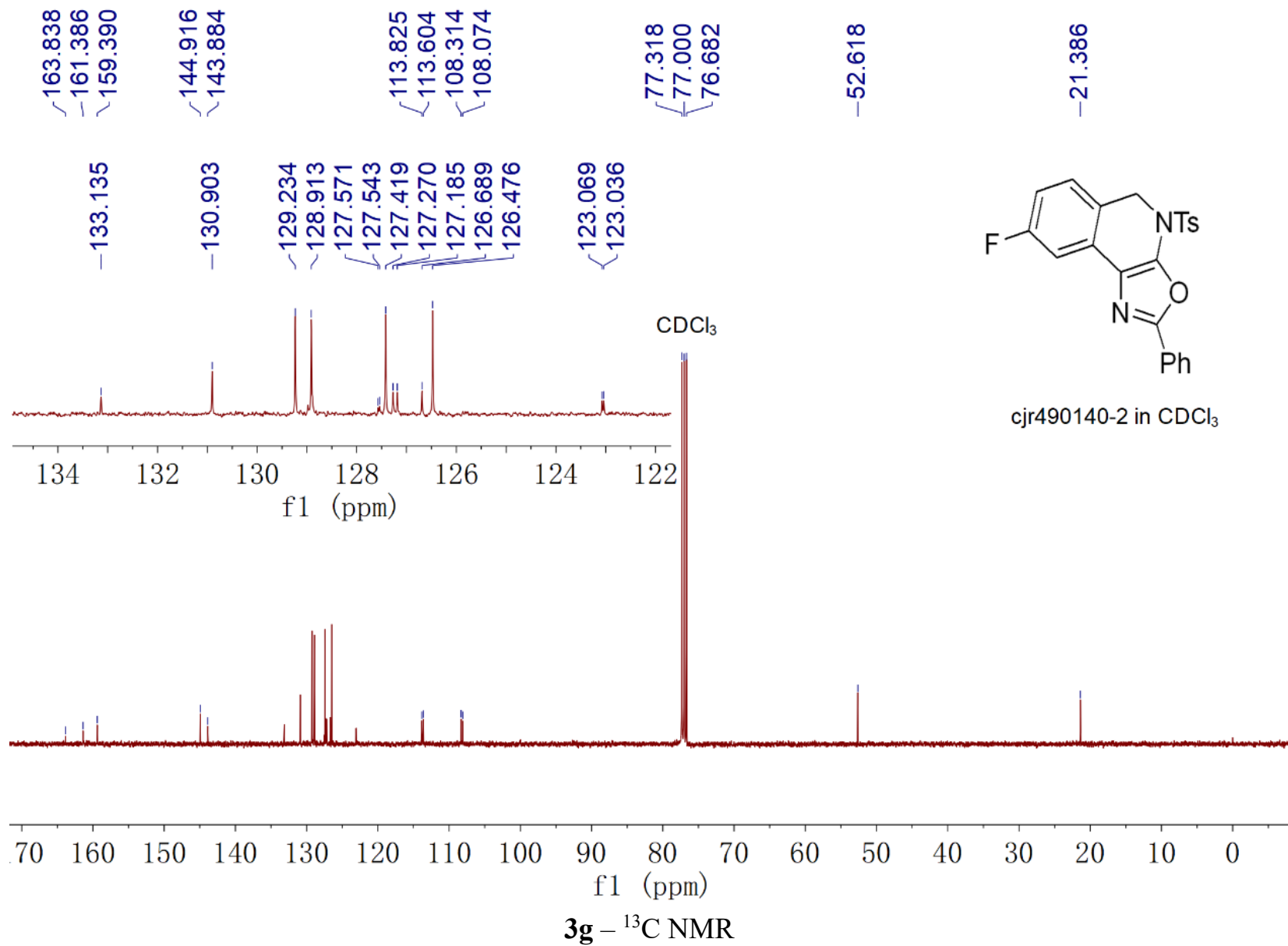


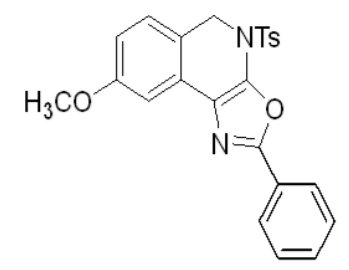
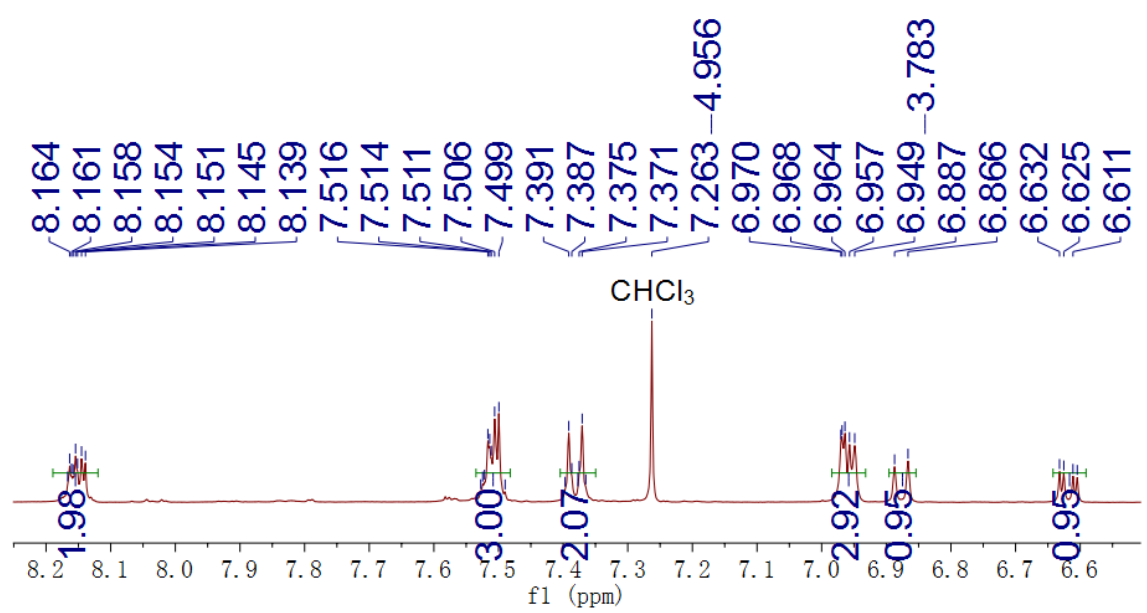




3f – ¹³C NMR

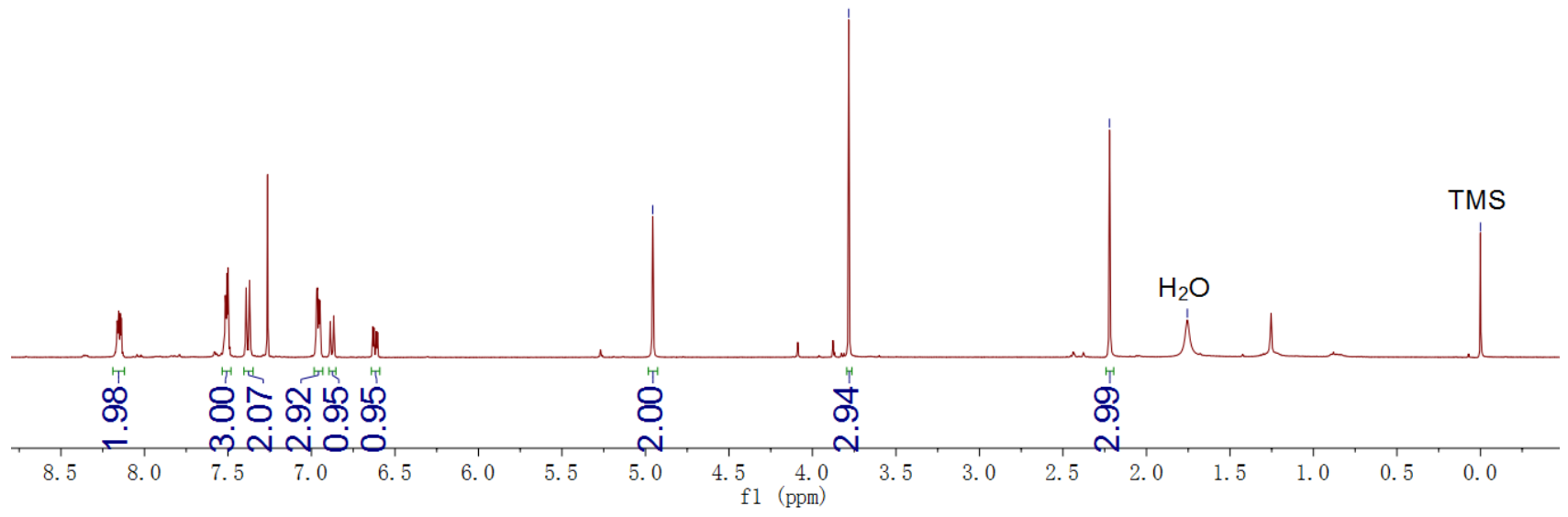




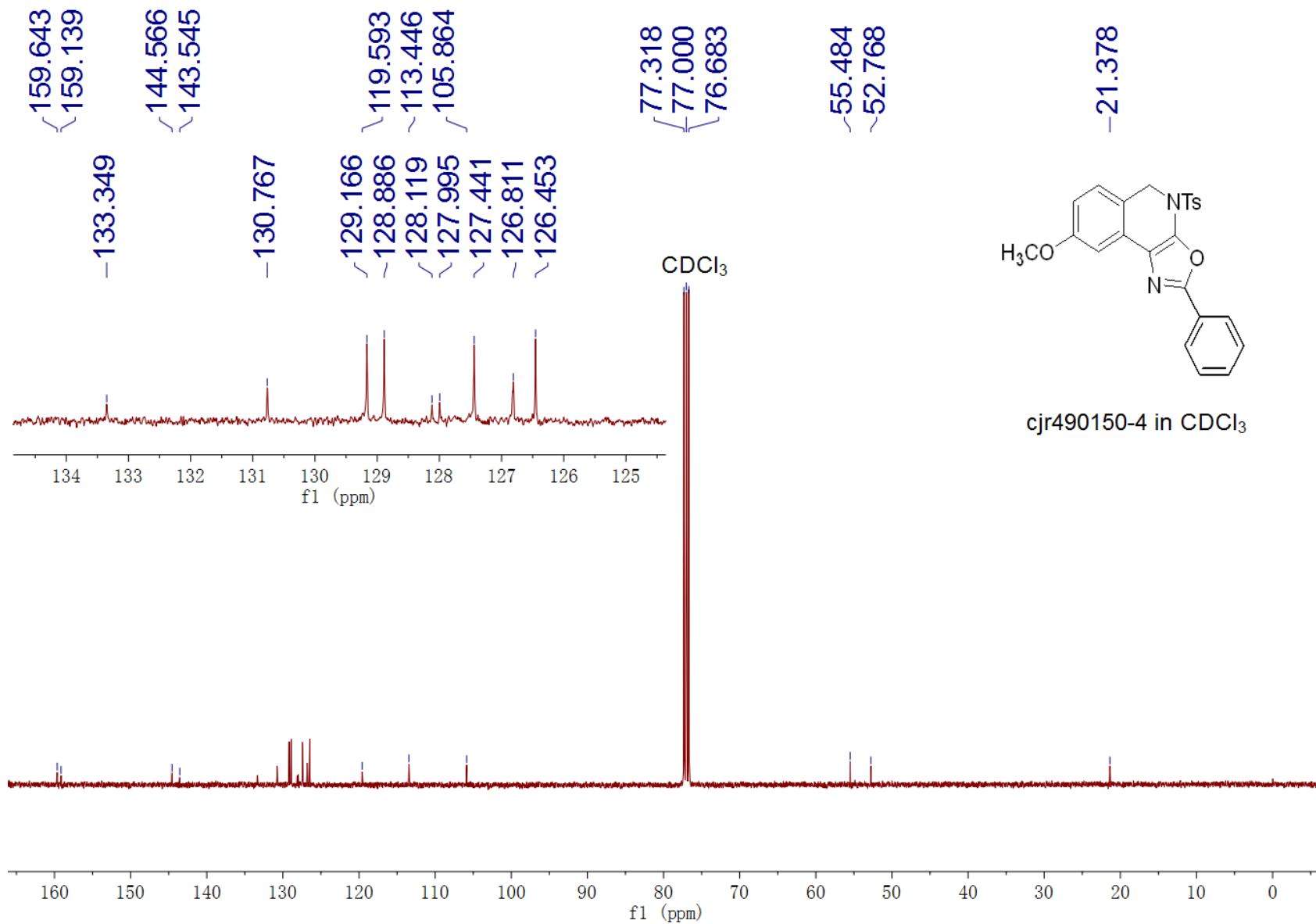


cjr490150-4 in CDCl₃

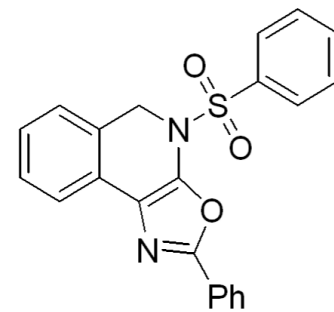
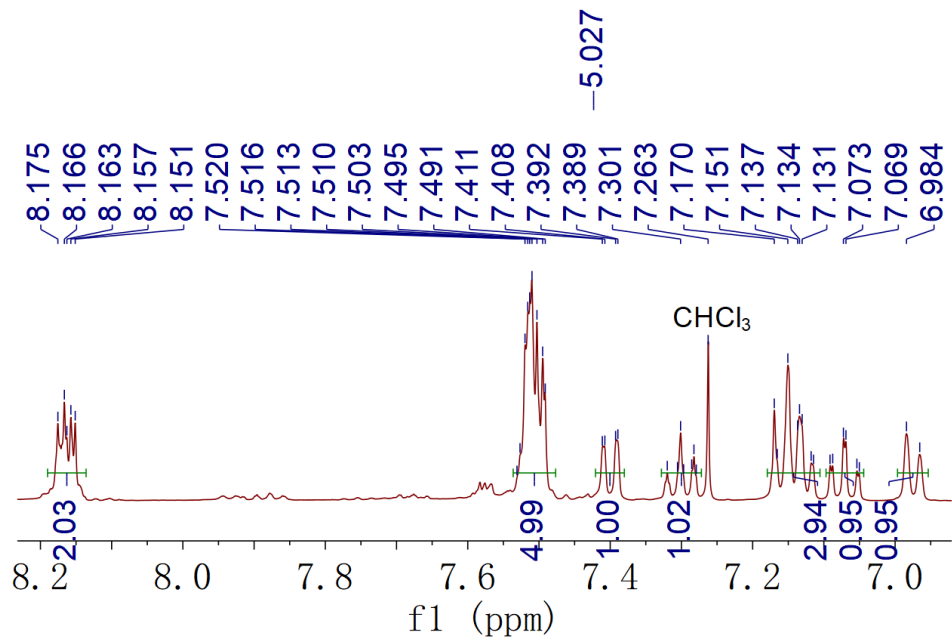
-2.221
-1.755
-0.000



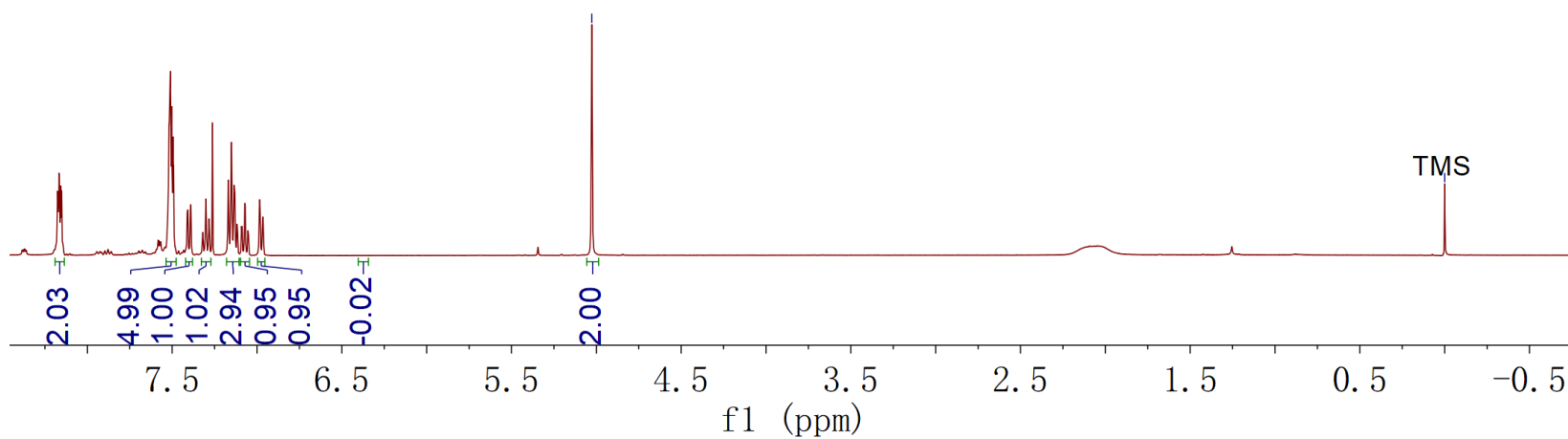
3h - ¹H NMR



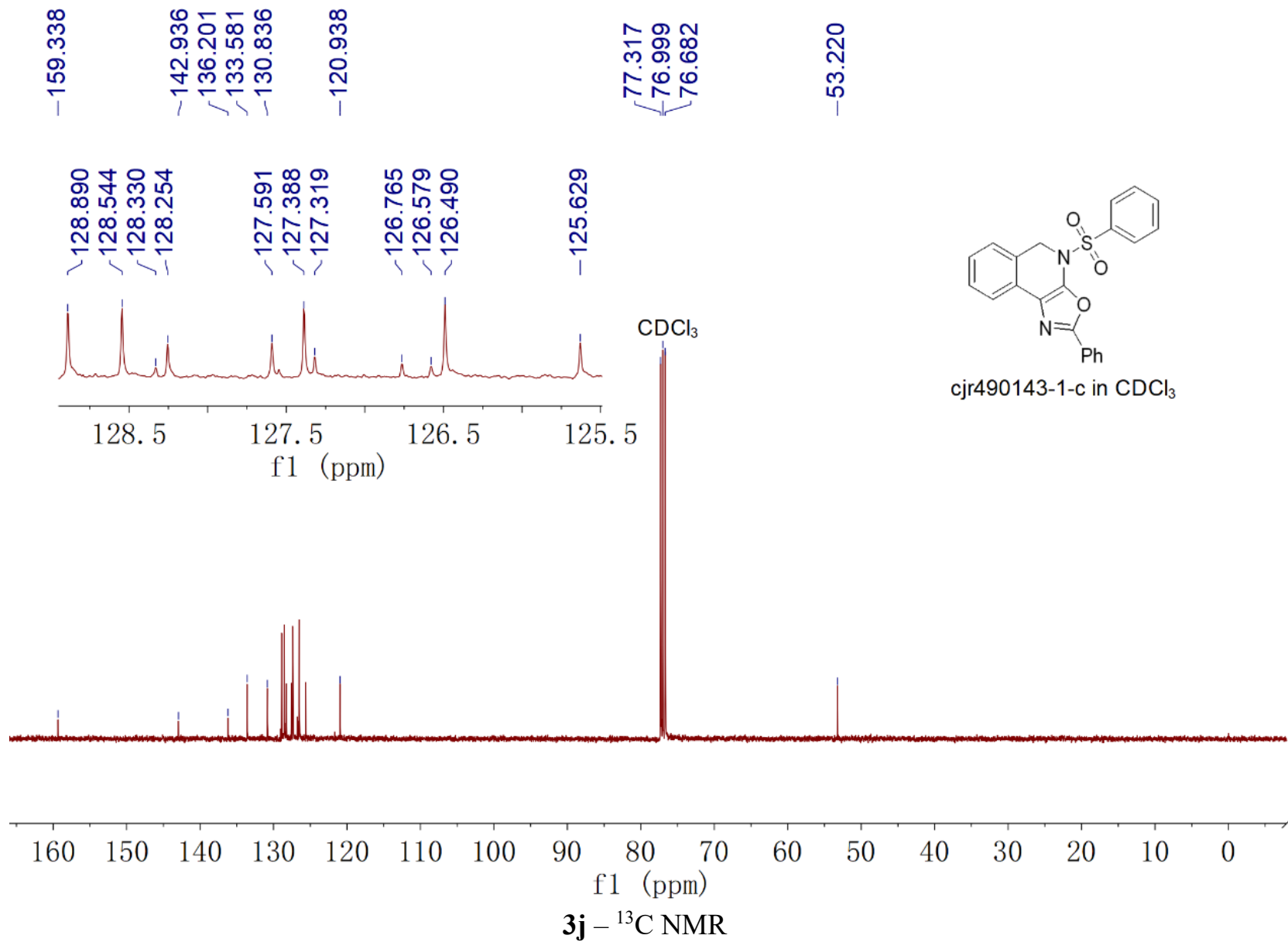
3h – ¹³C NMR

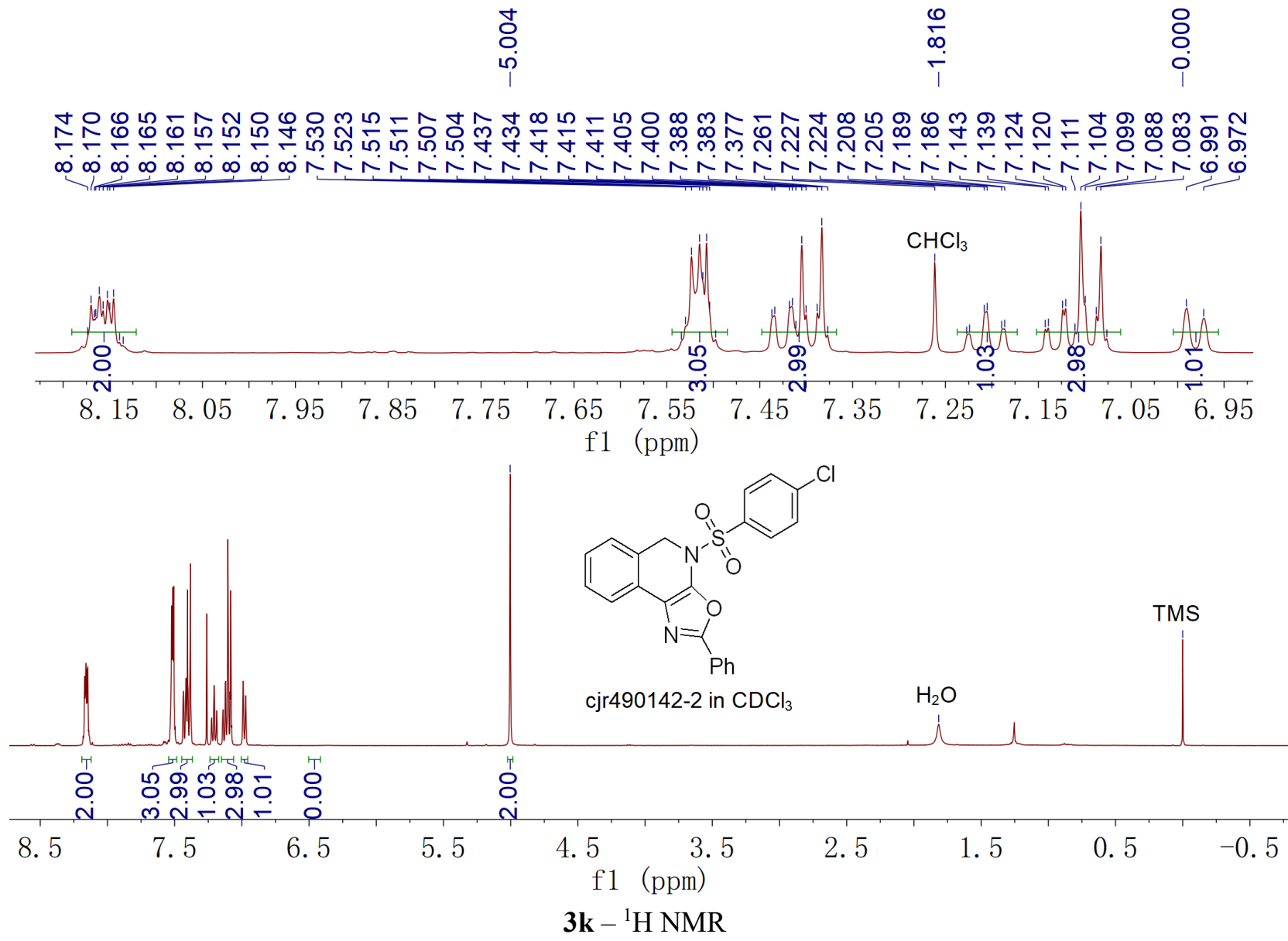


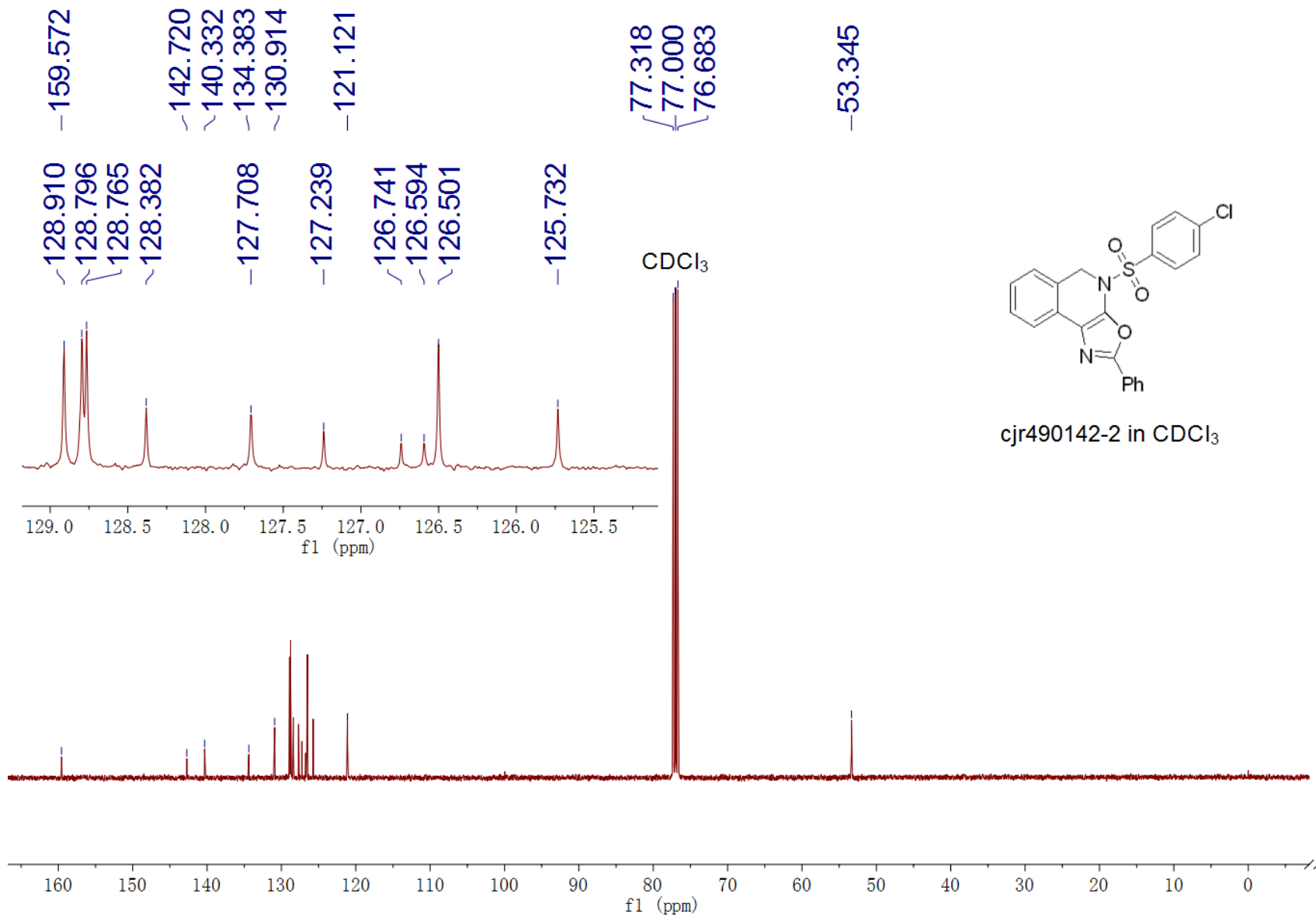
cjr490143-1-c in CDCl₃



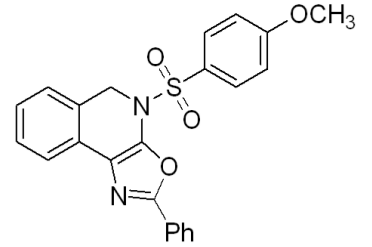
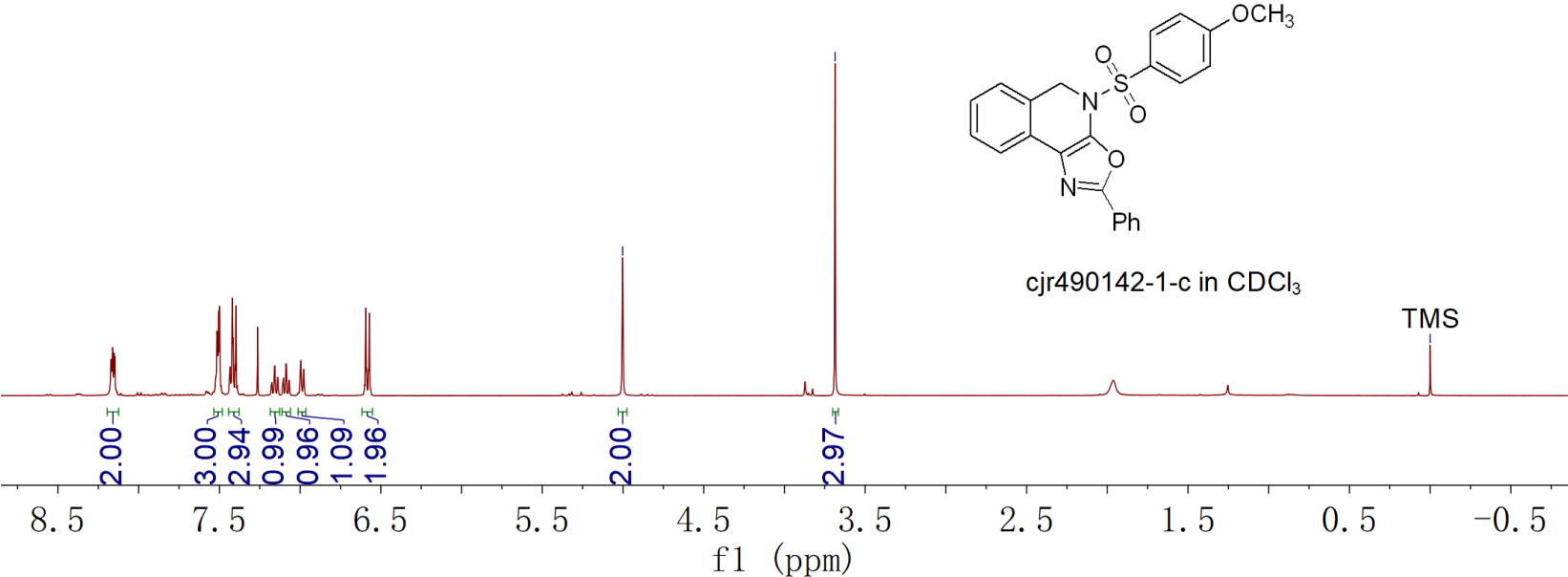
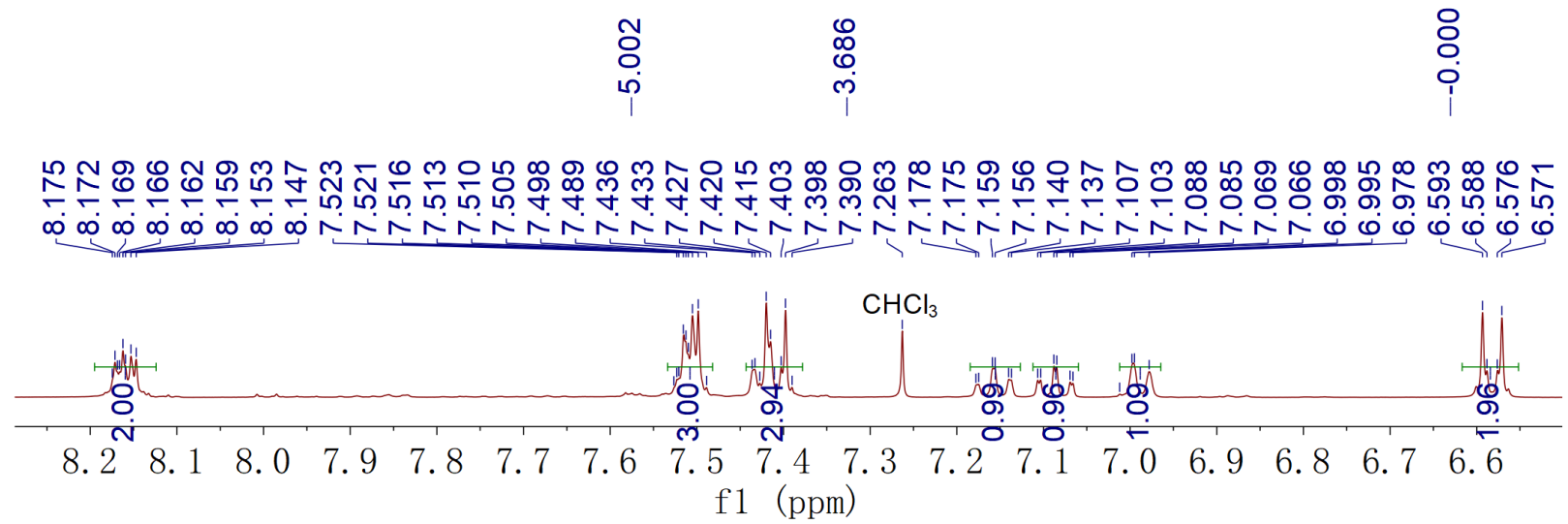
3j – ¹H NMR





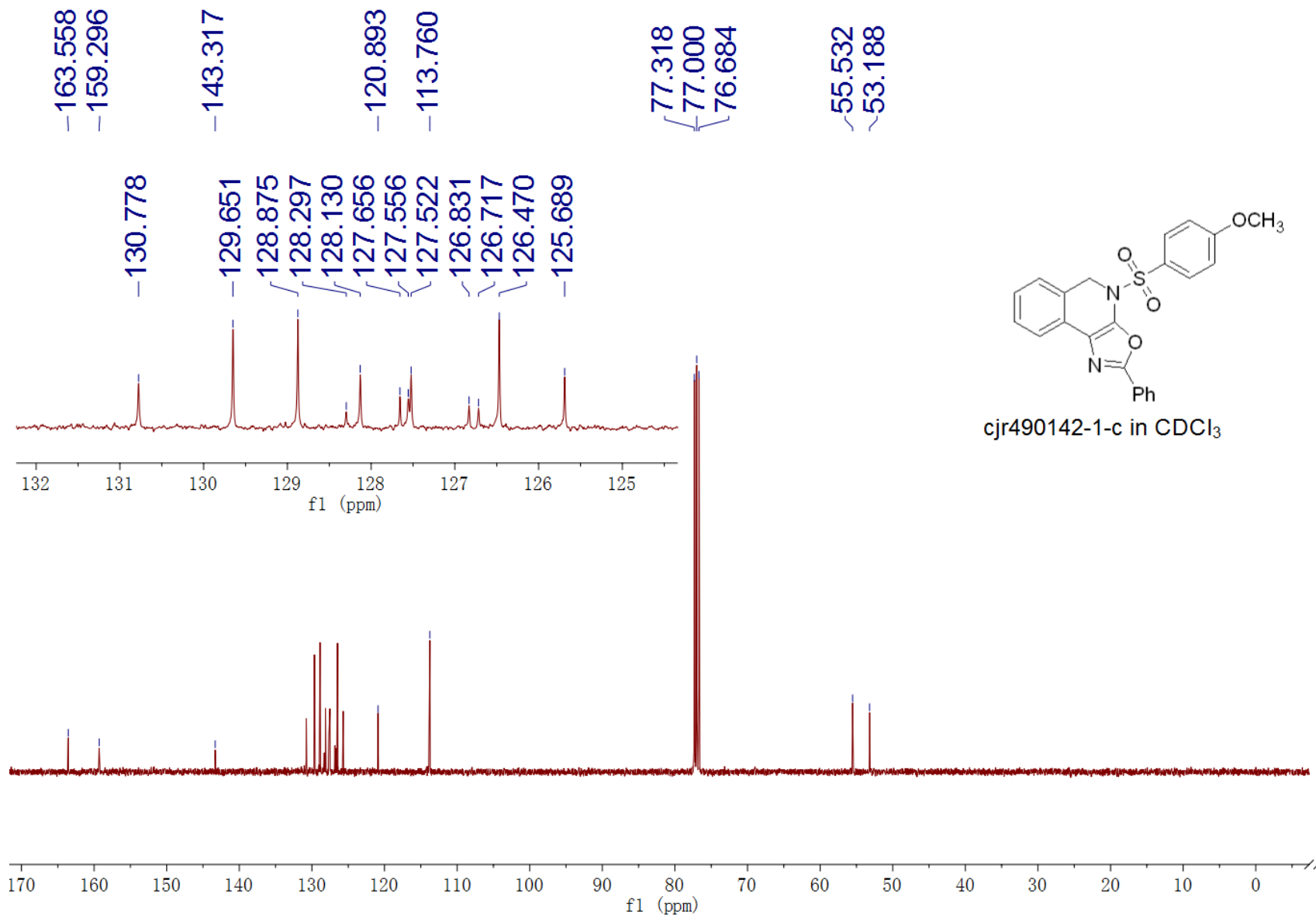


3k – ¹³C NMR

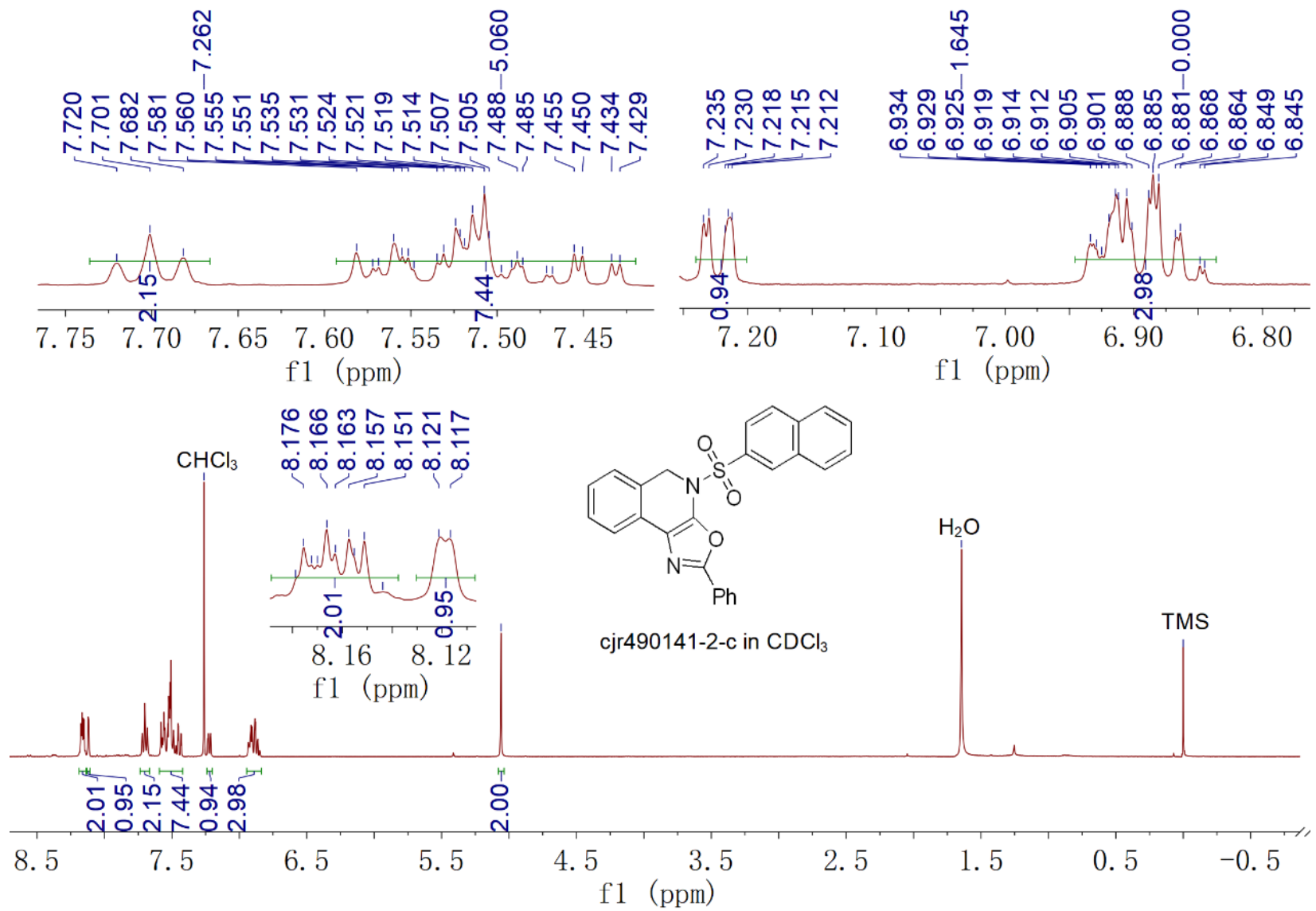


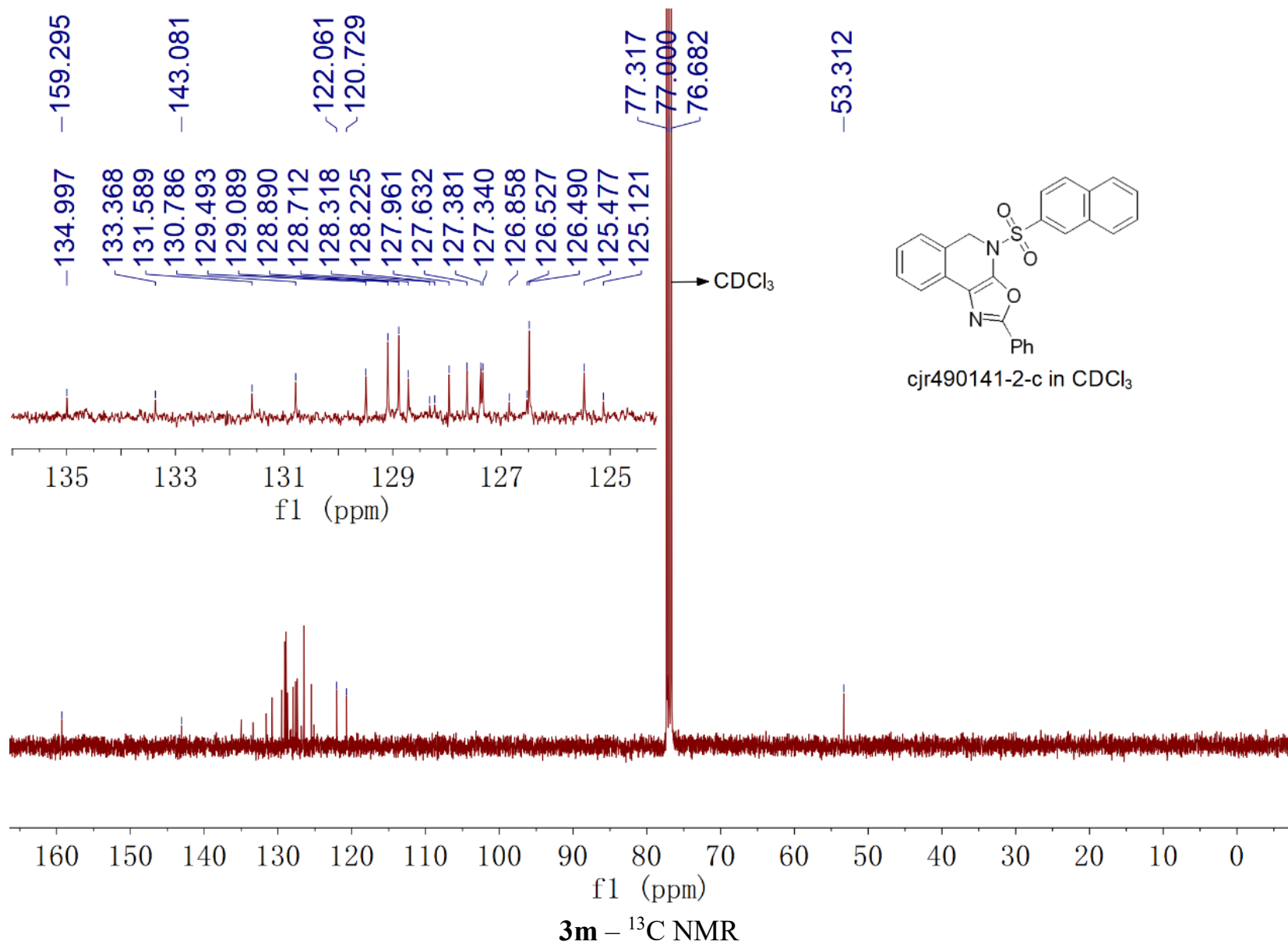
cjr490142-1-c in CDCl₃

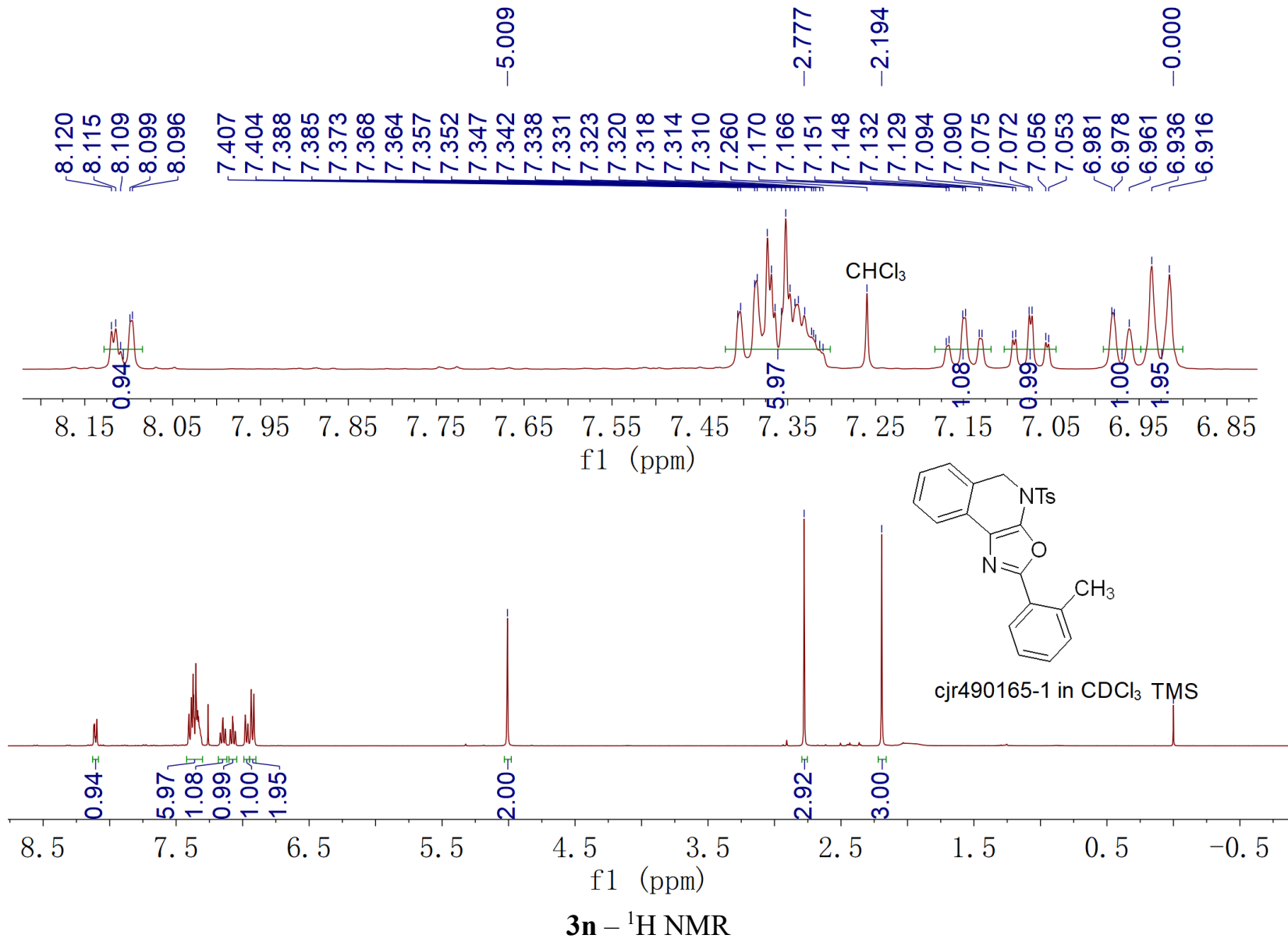
31 – ¹H NMR

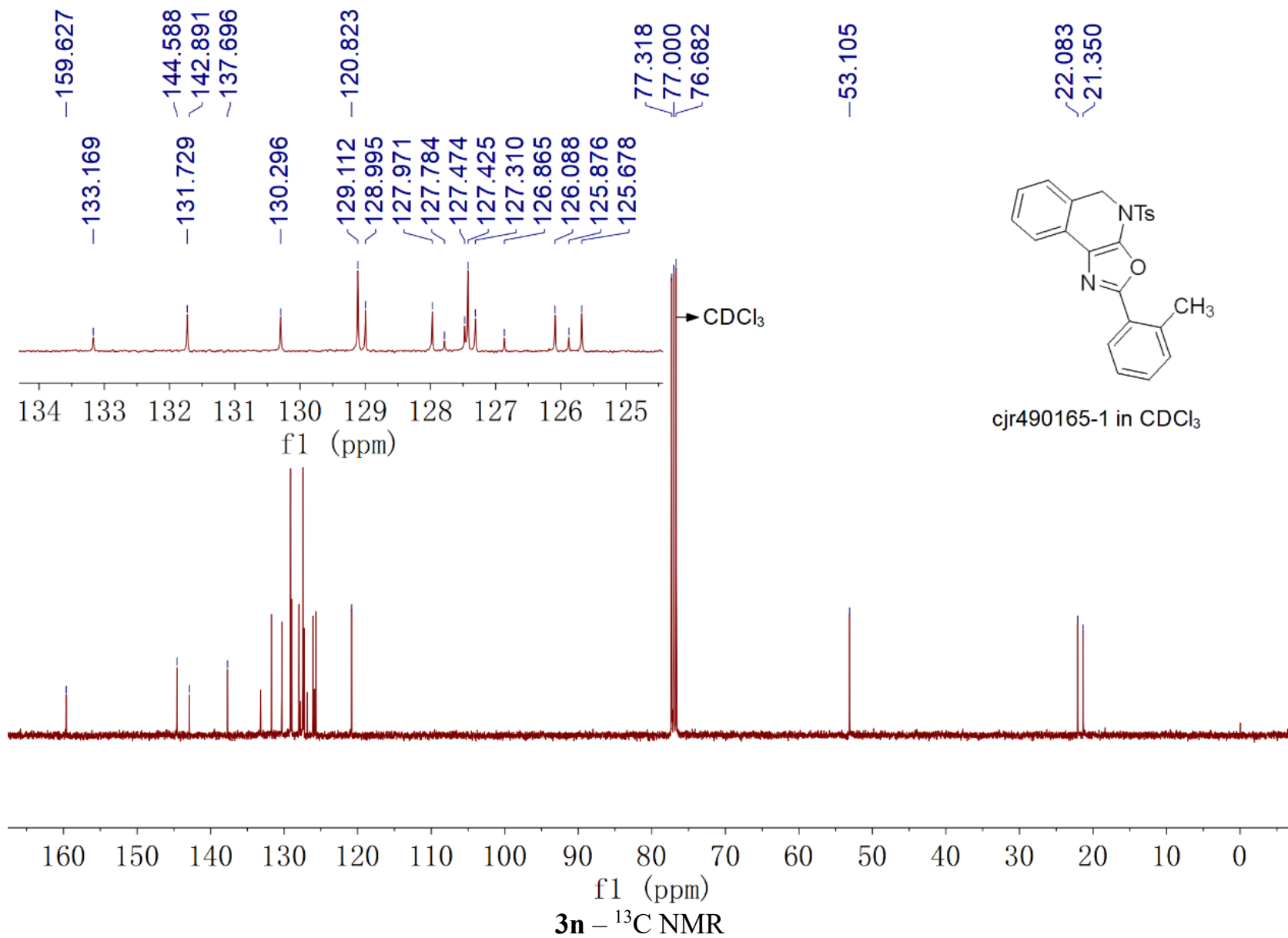


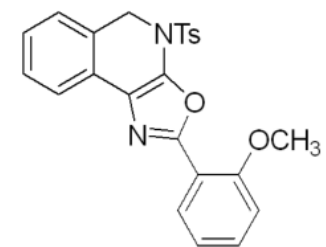
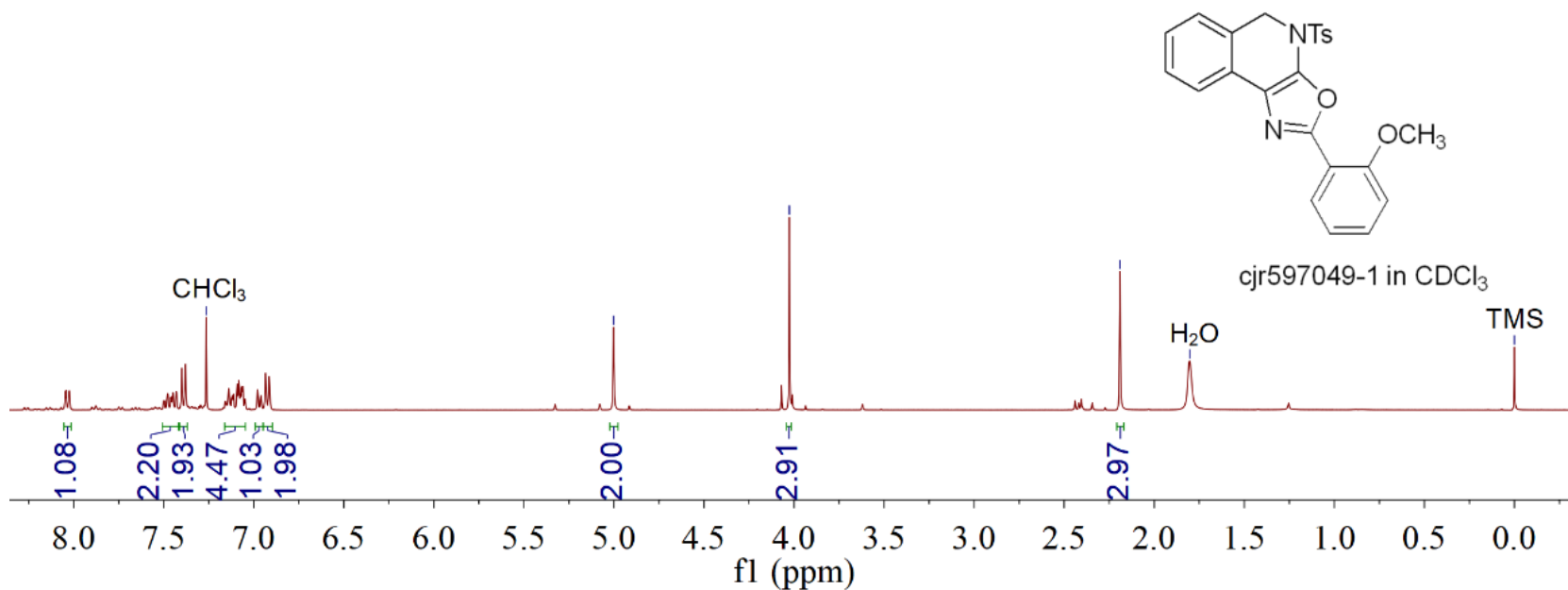
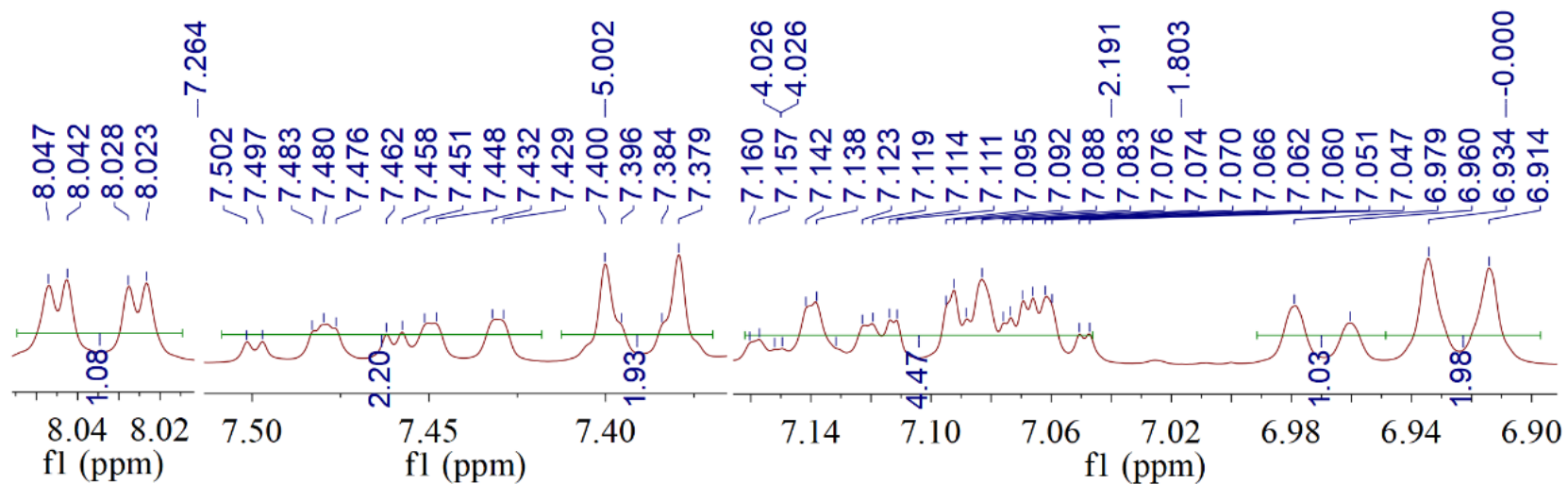
3I – ¹³C NMR





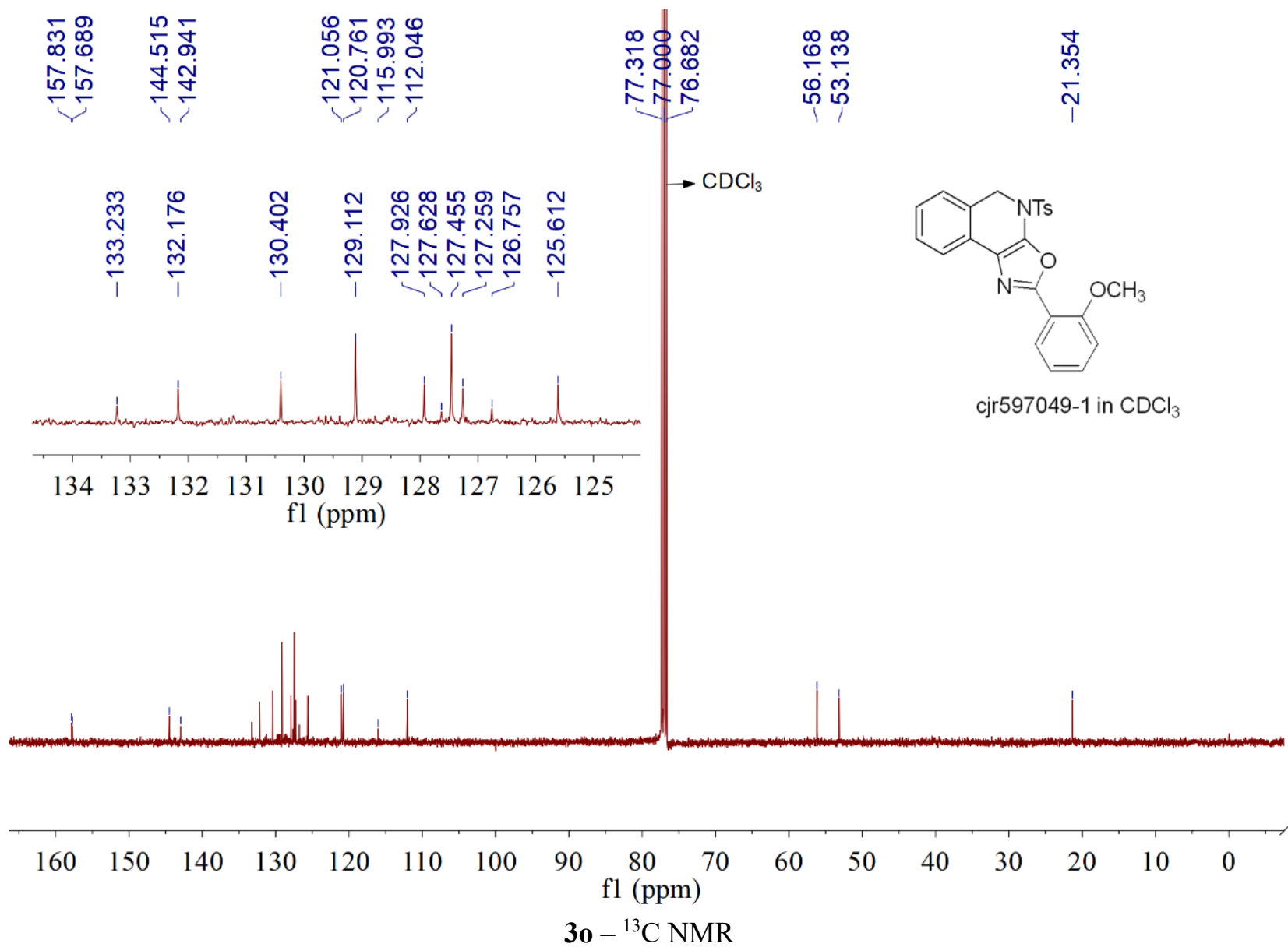


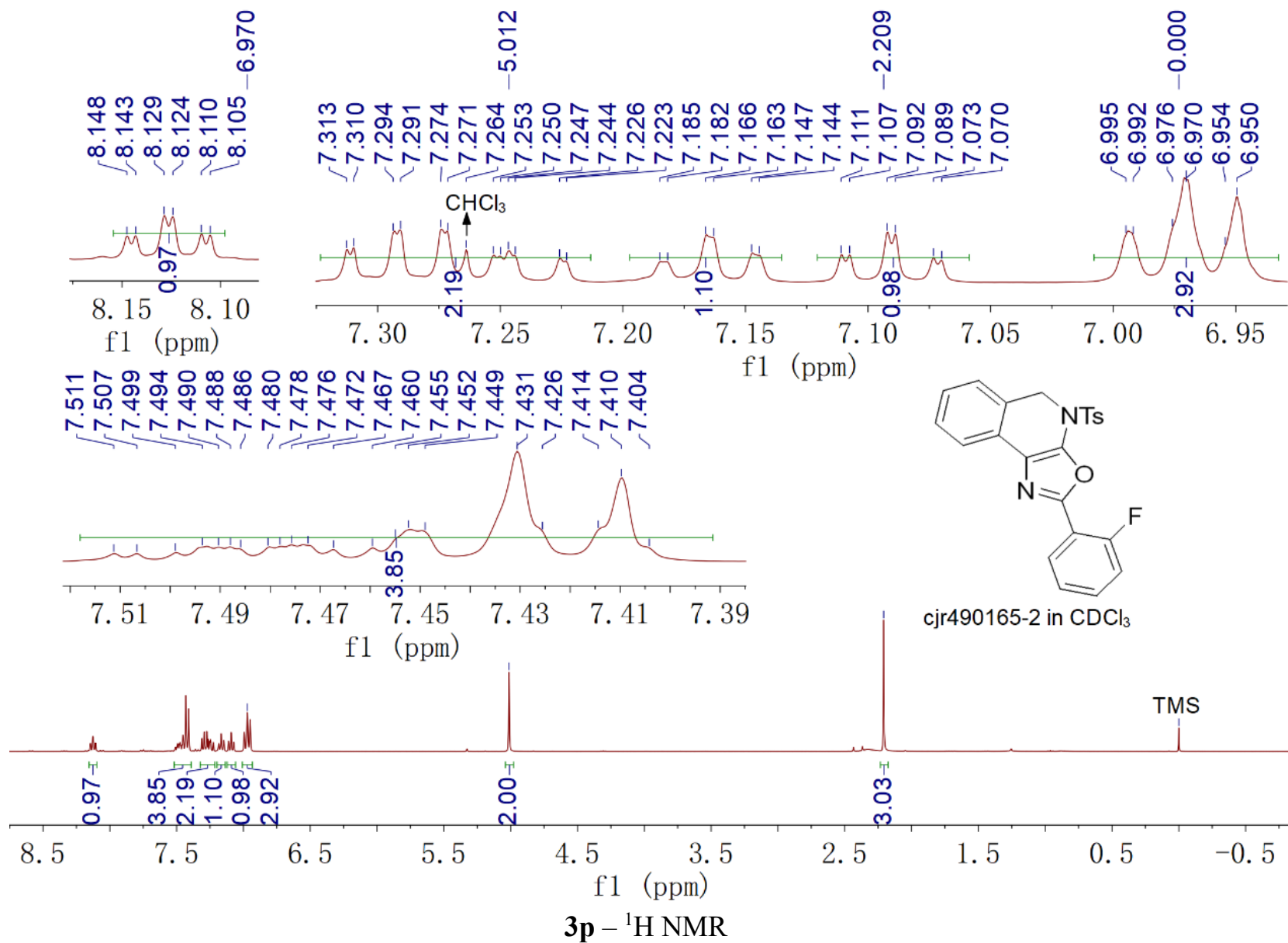


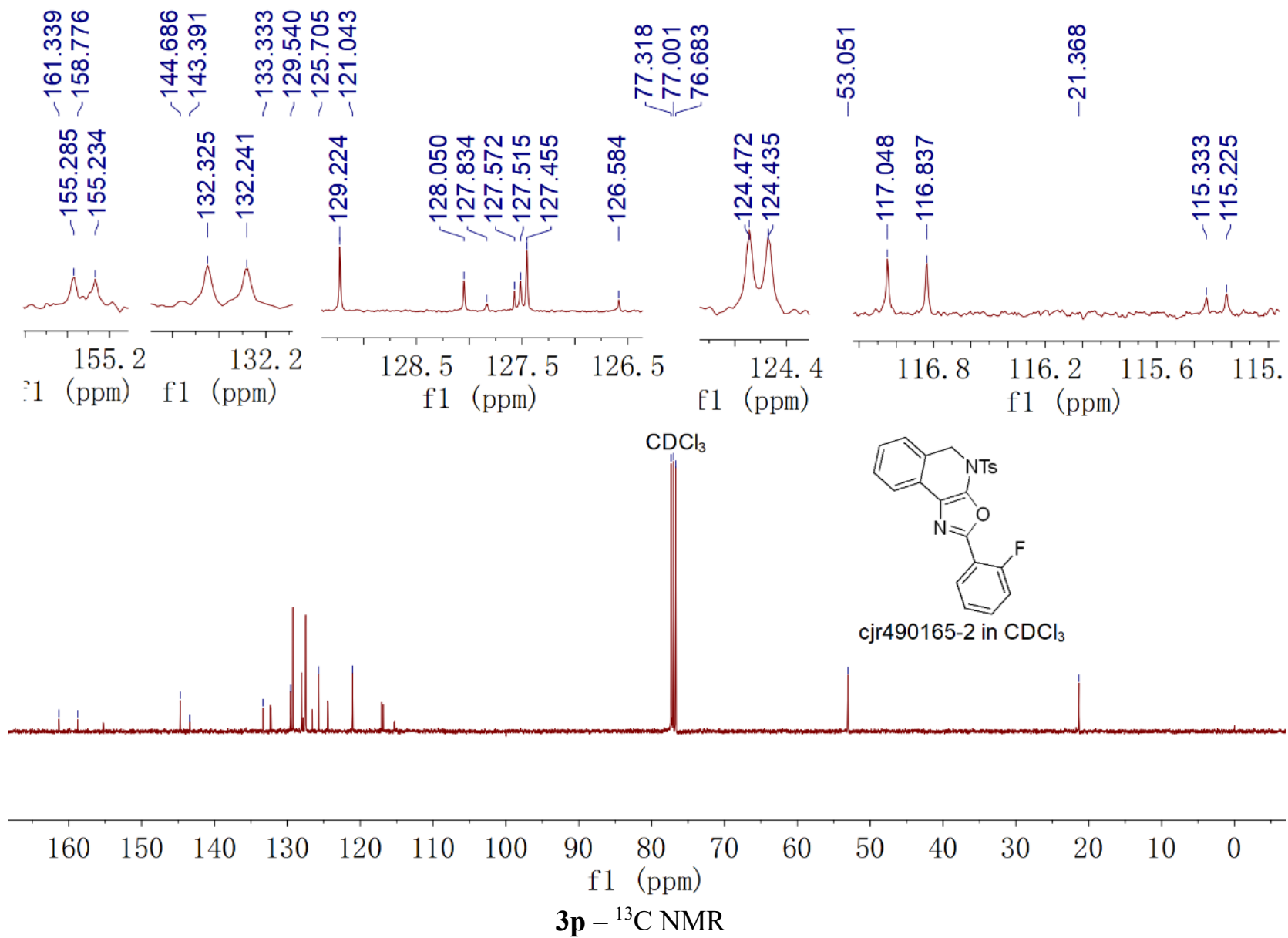


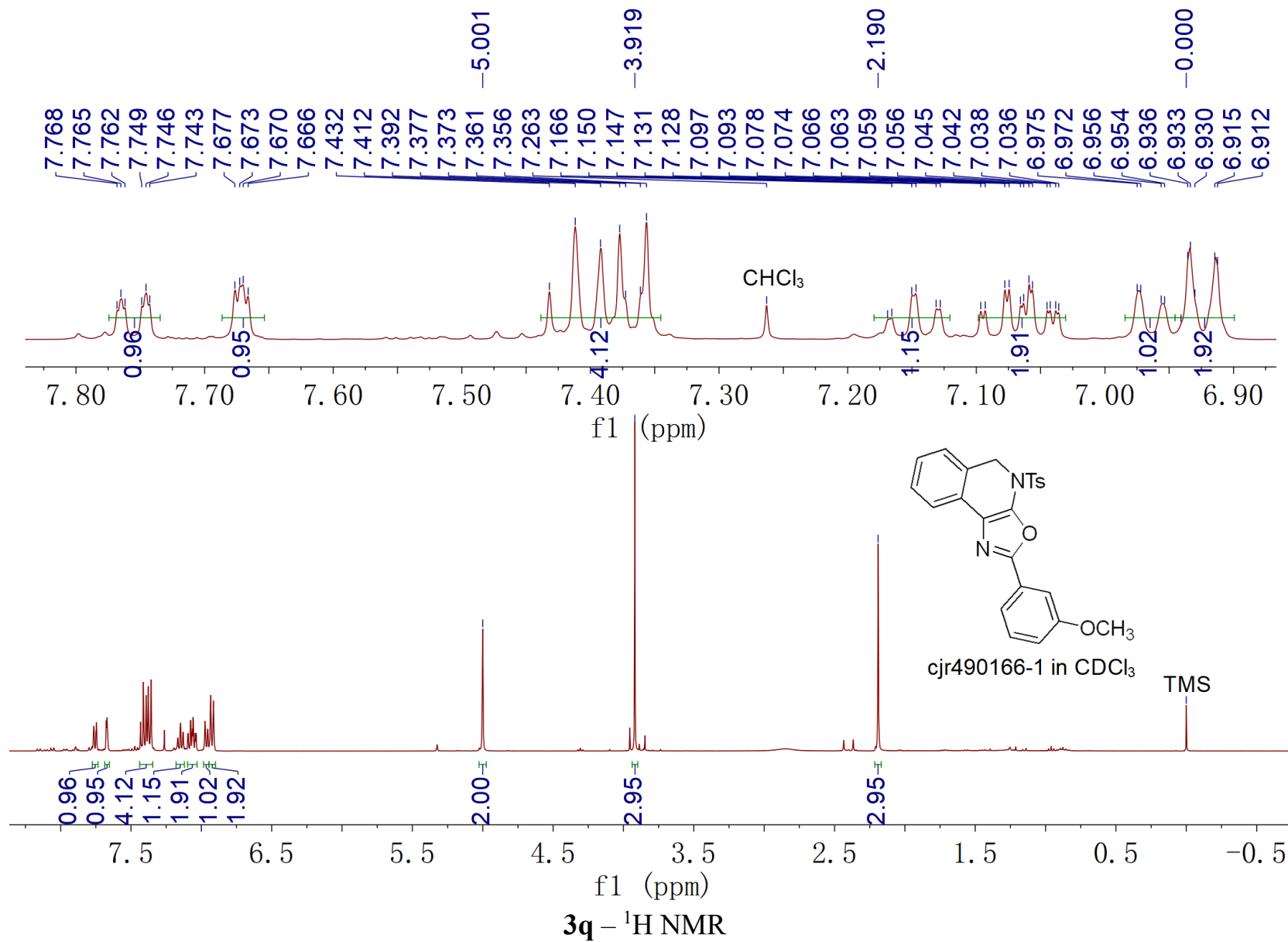
cjr597049-1 in CDCl₃

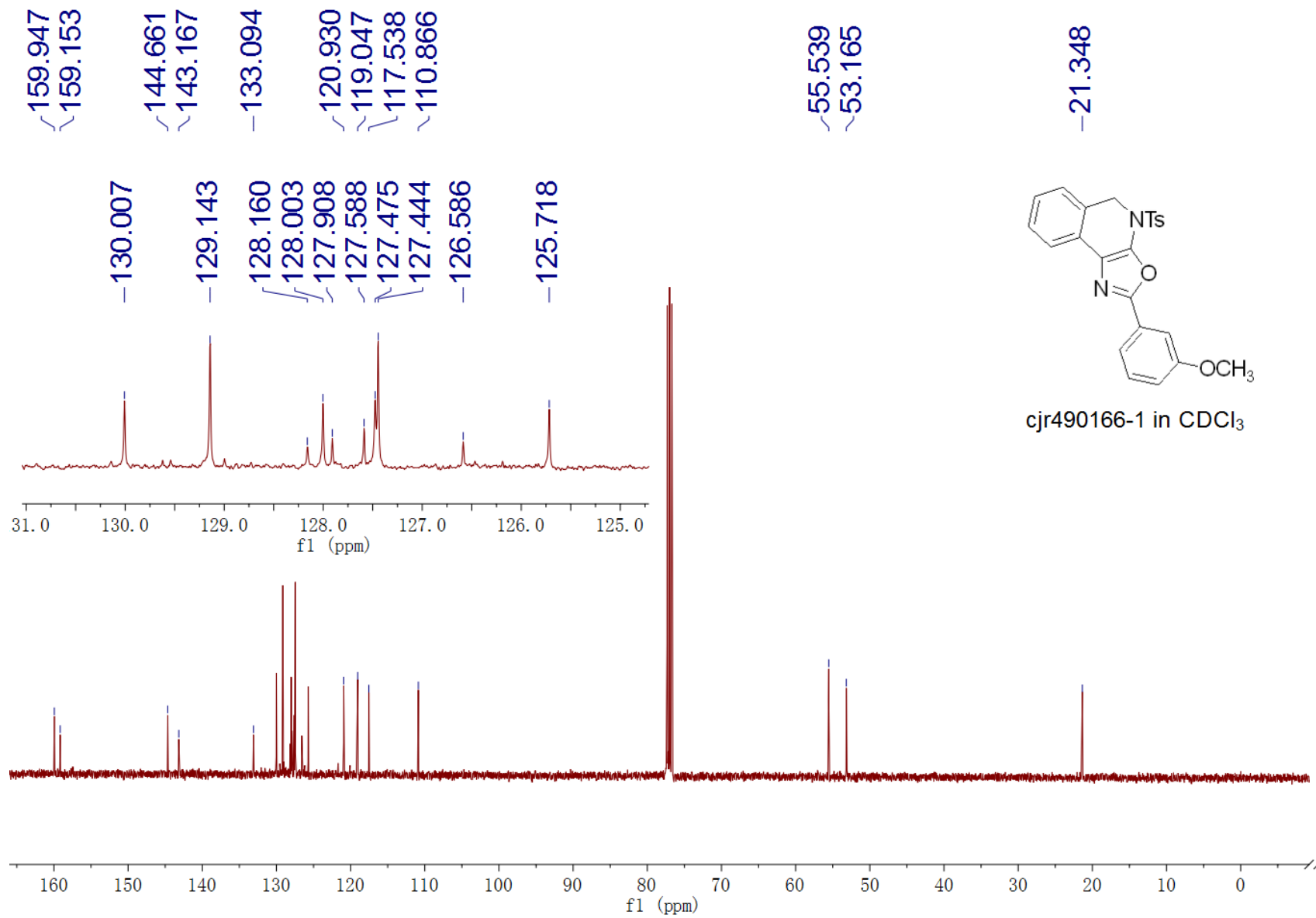
30 – ¹H NMR



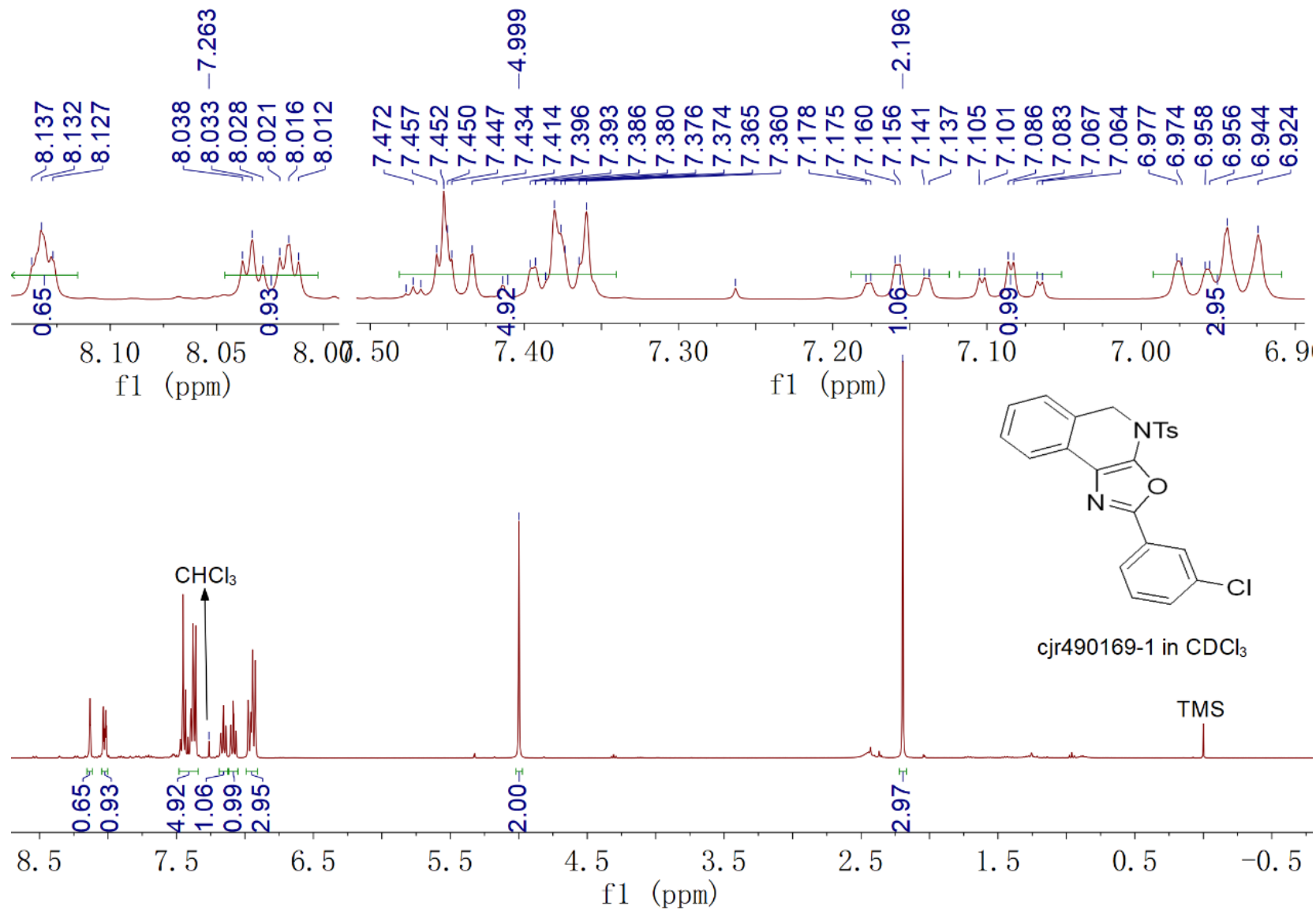


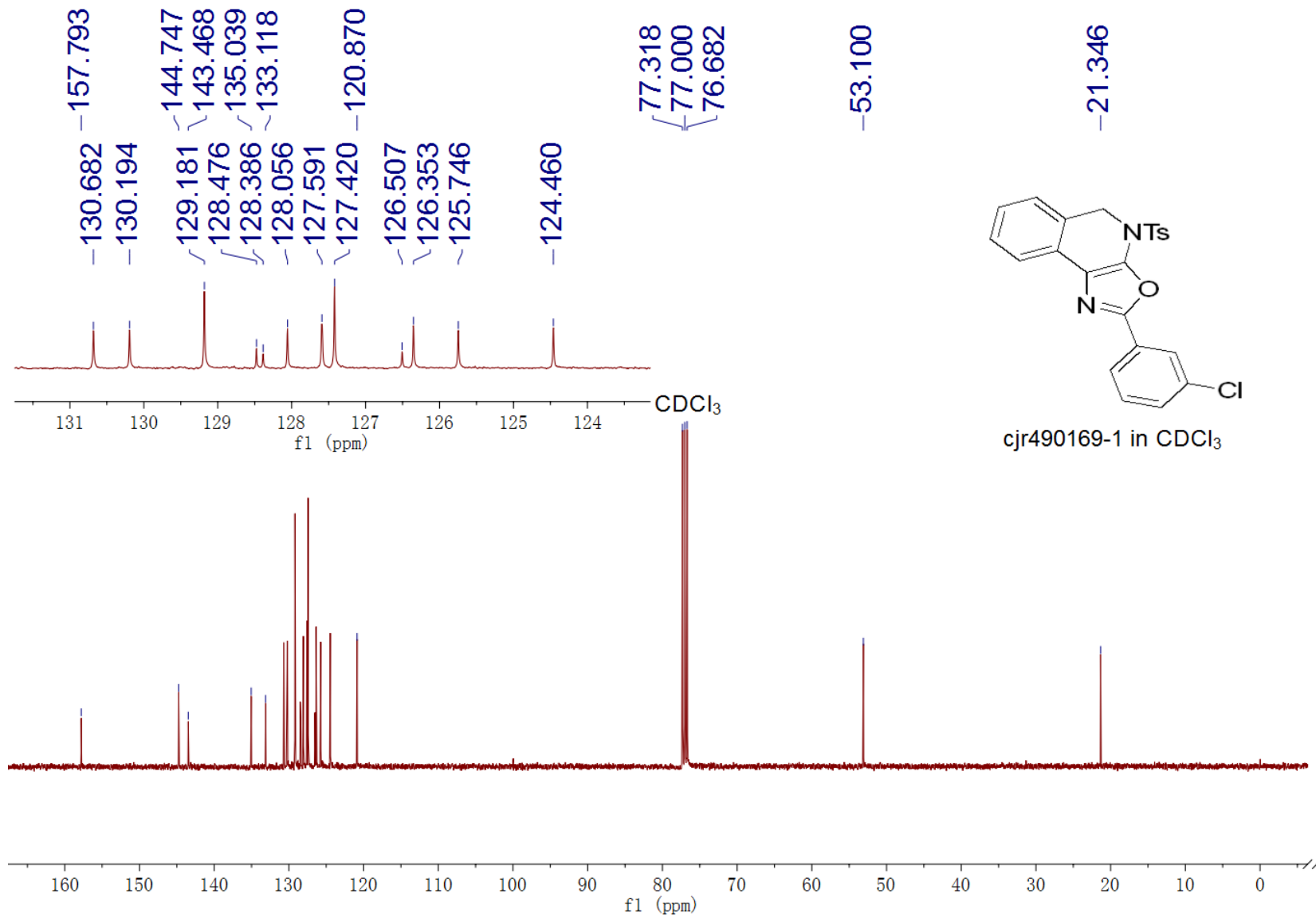




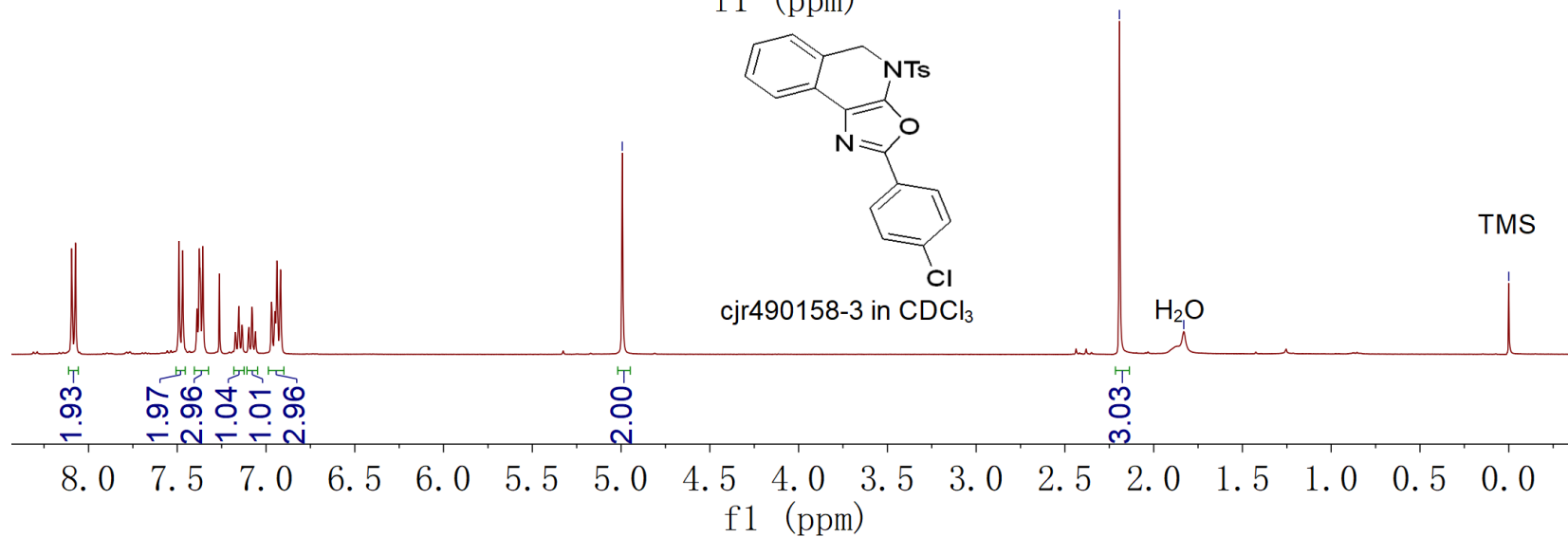
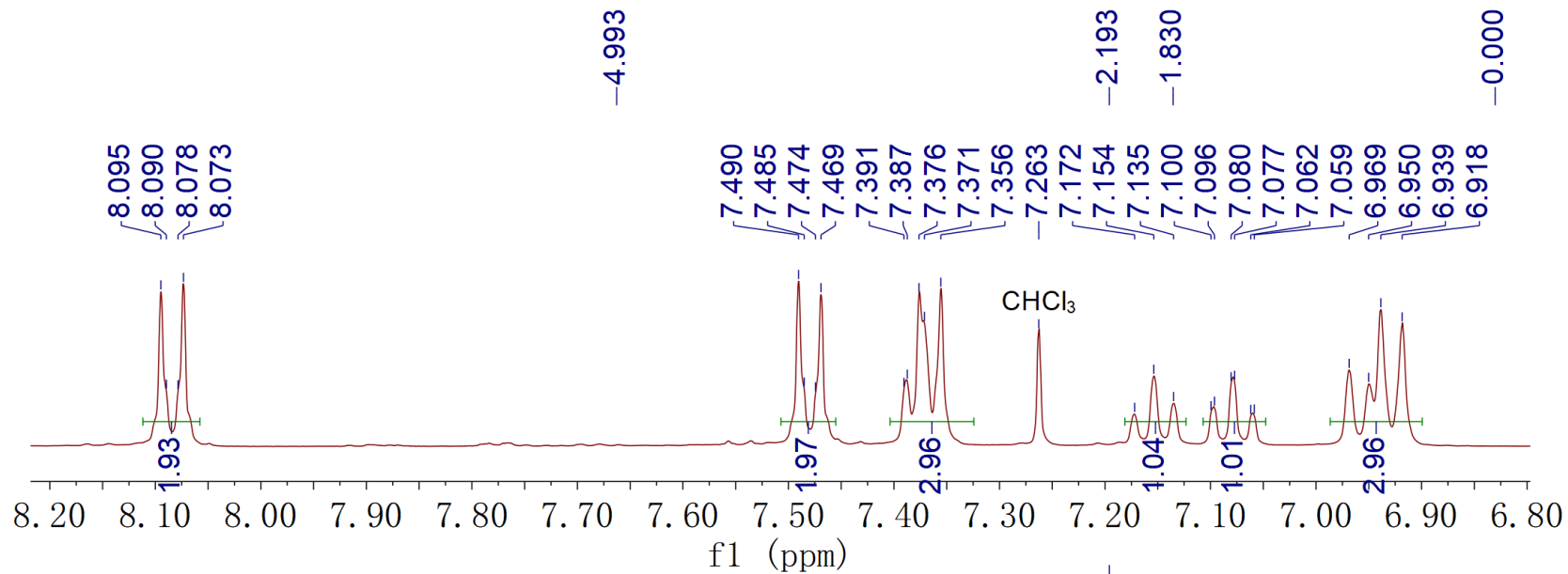


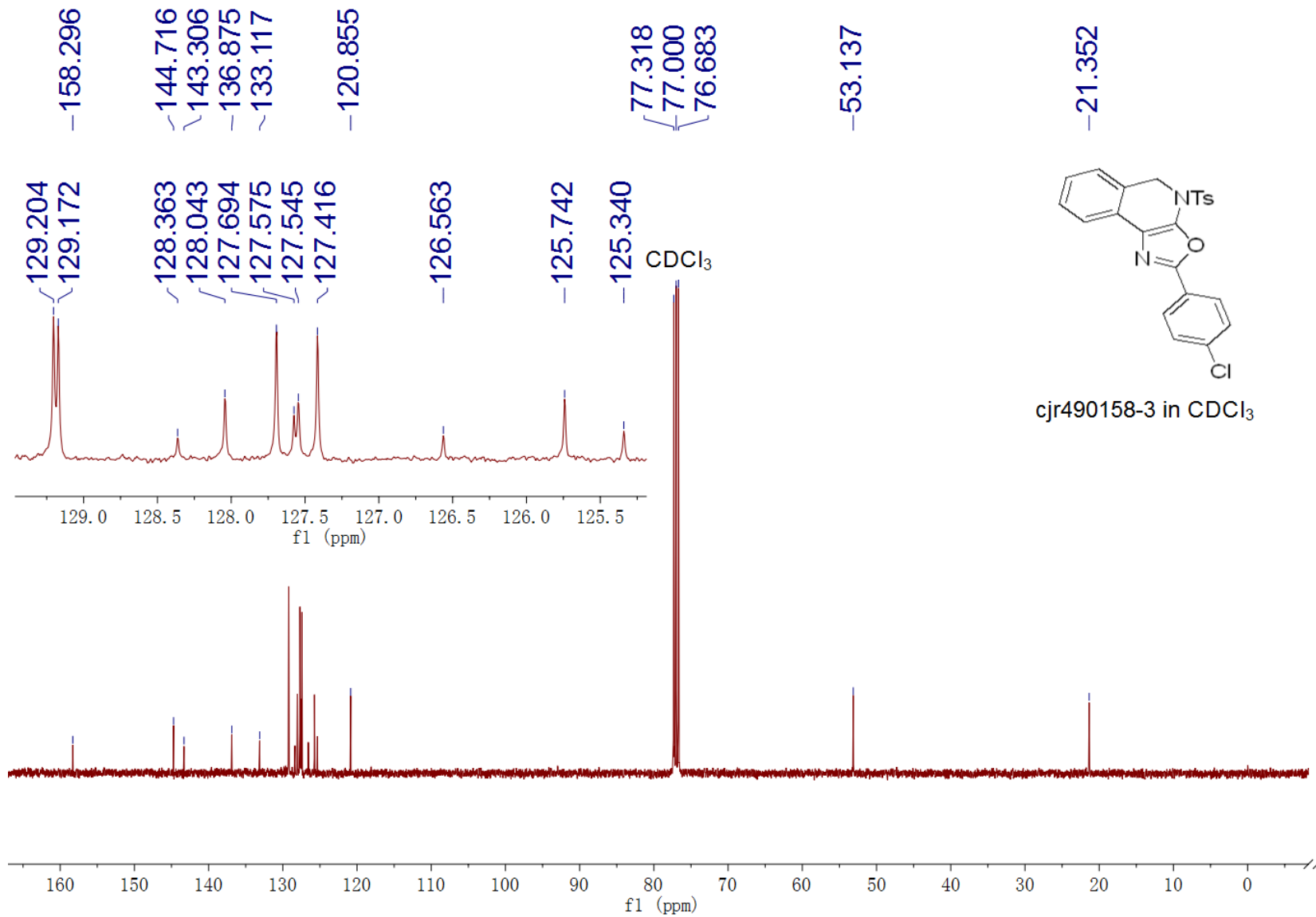
3q – ¹³C NMR



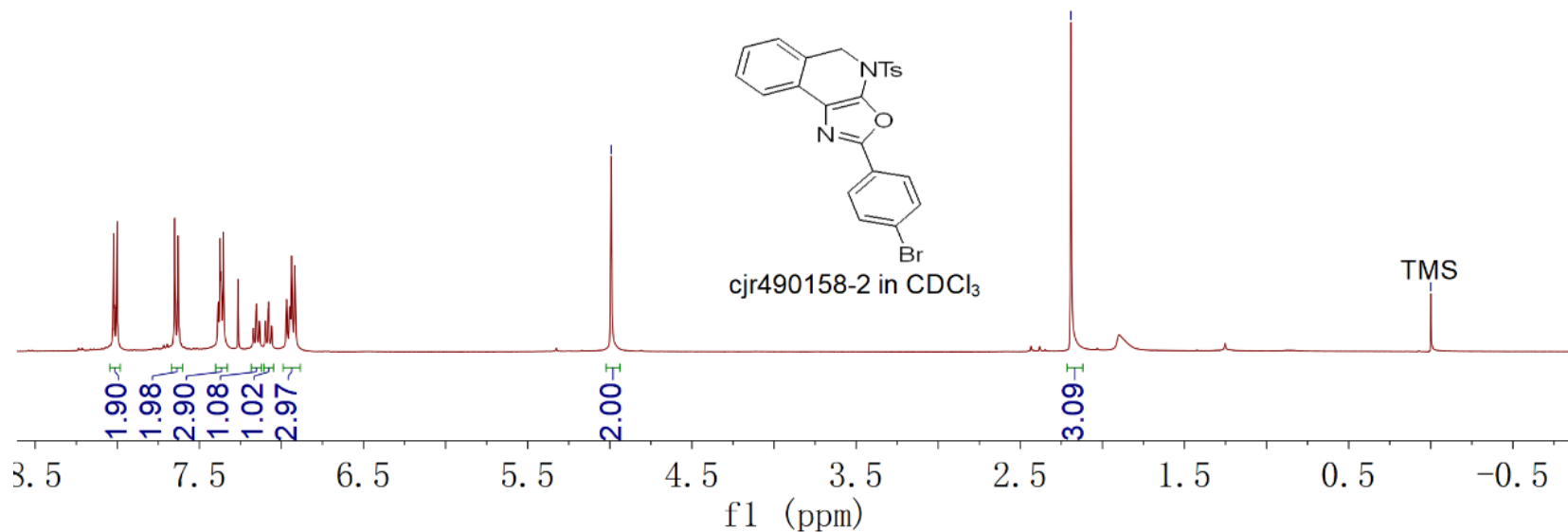
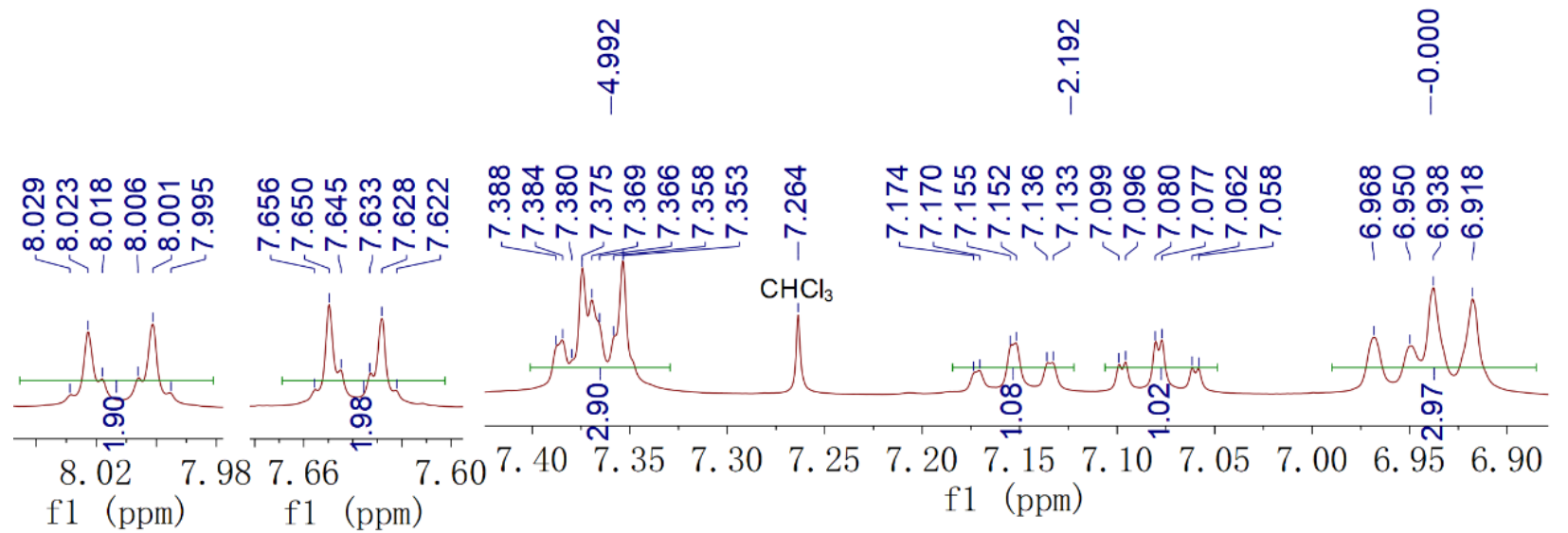


3r – ¹³C NMR

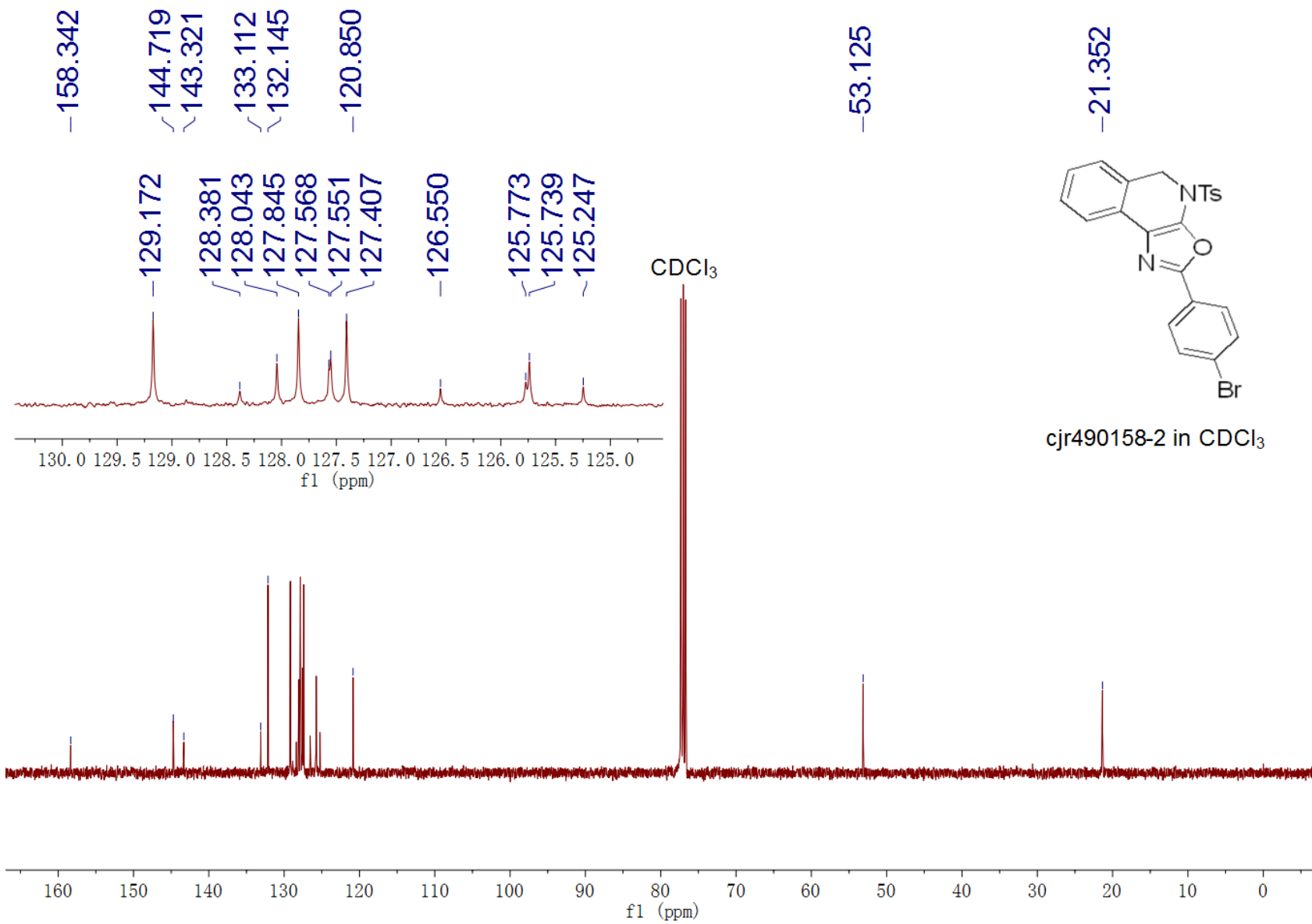


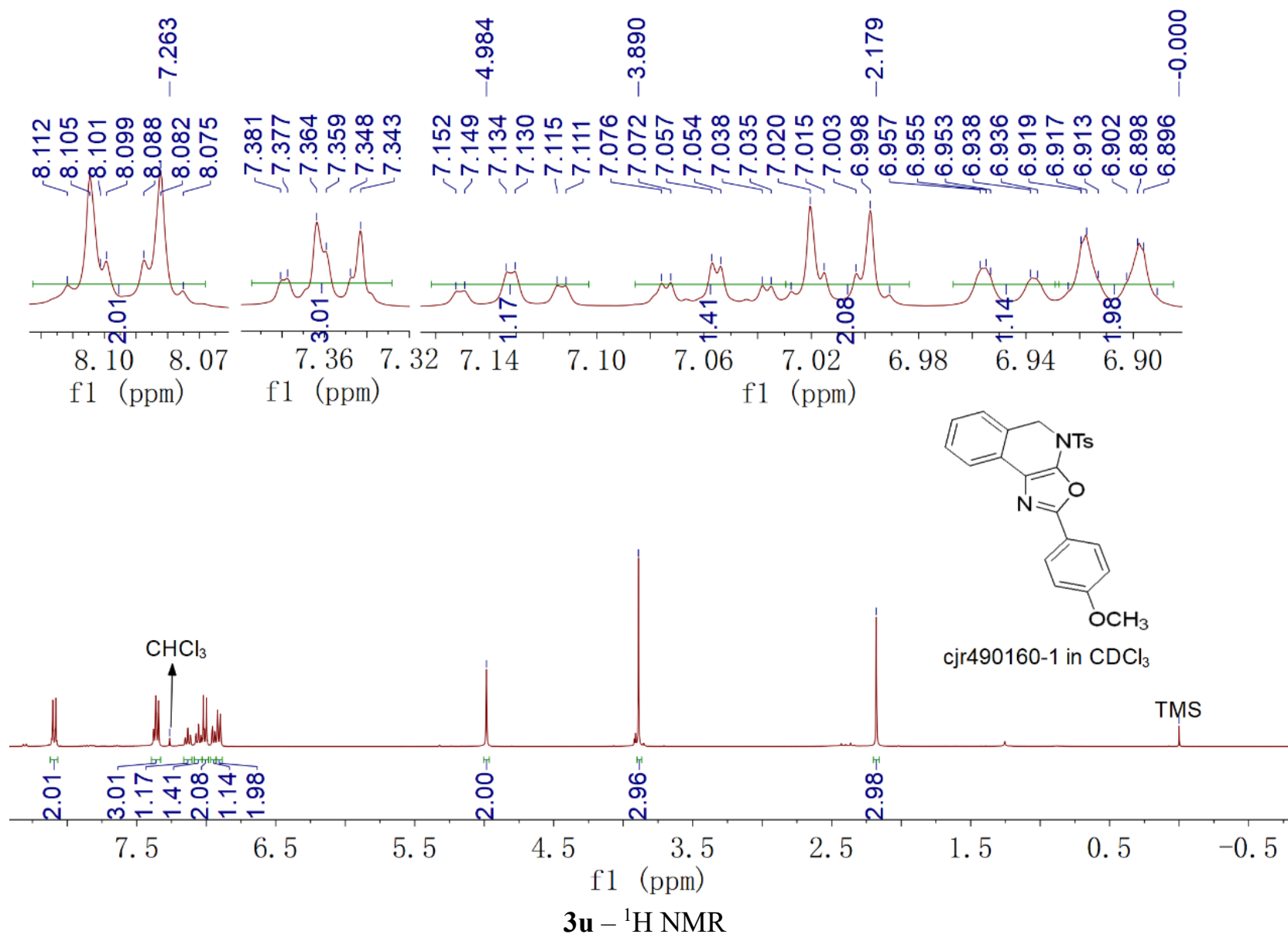


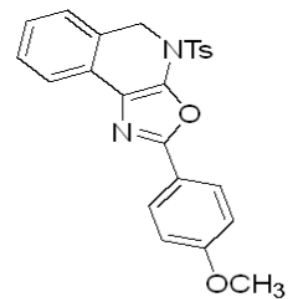
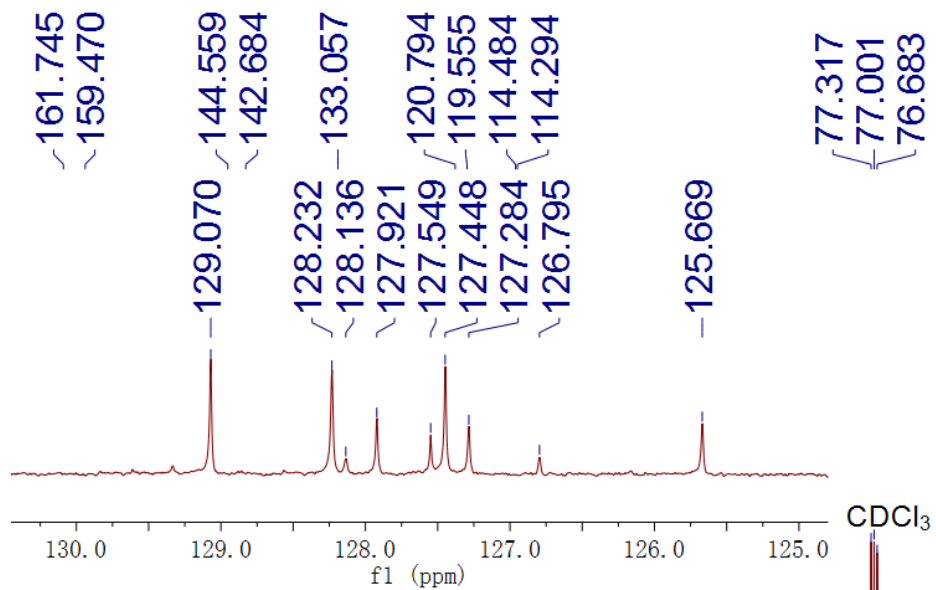
3s – ^{13}C NMR



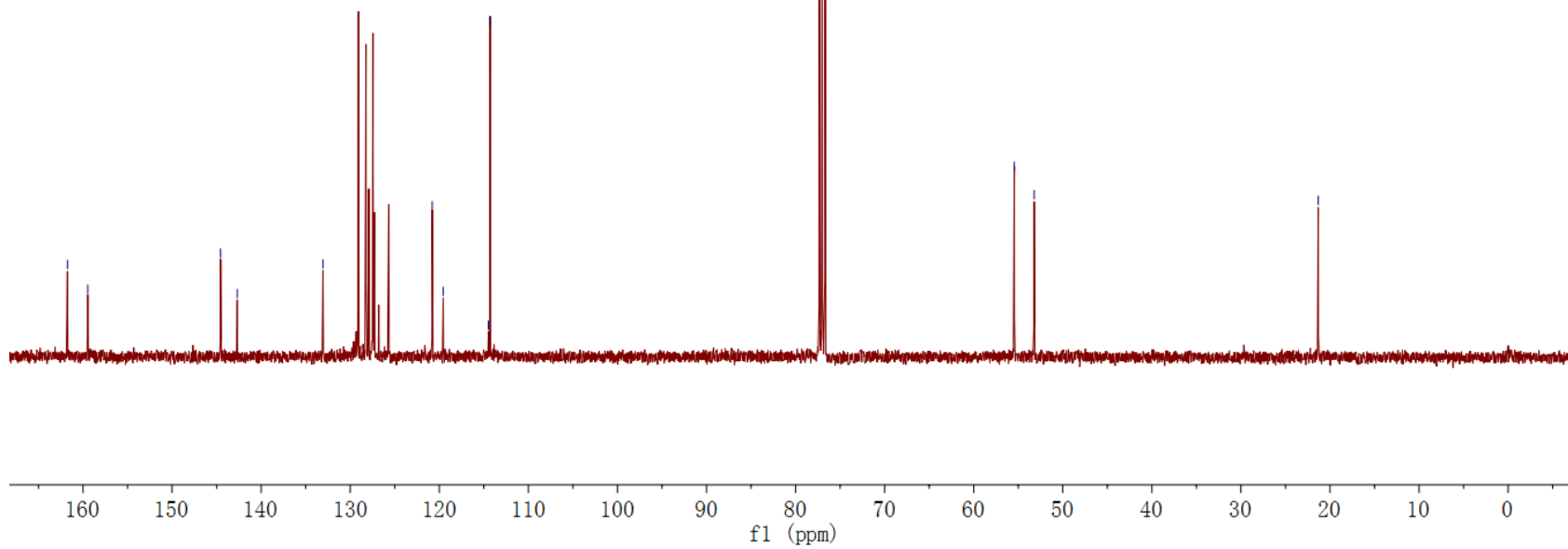
3t – ¹H NMR



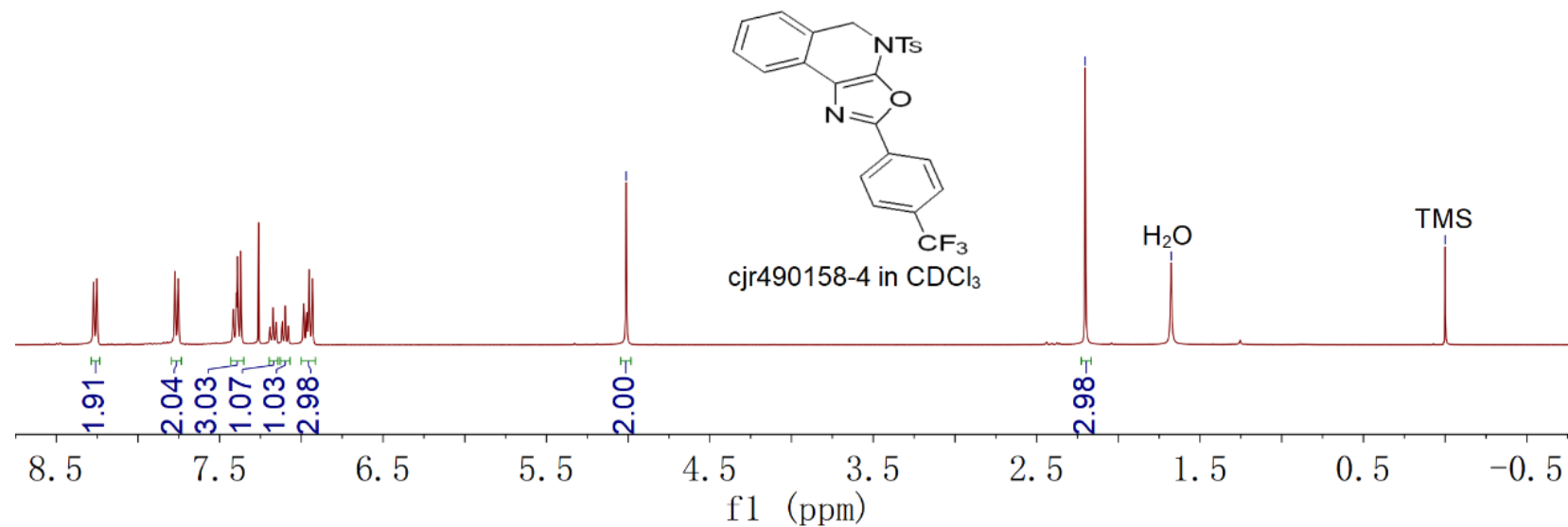
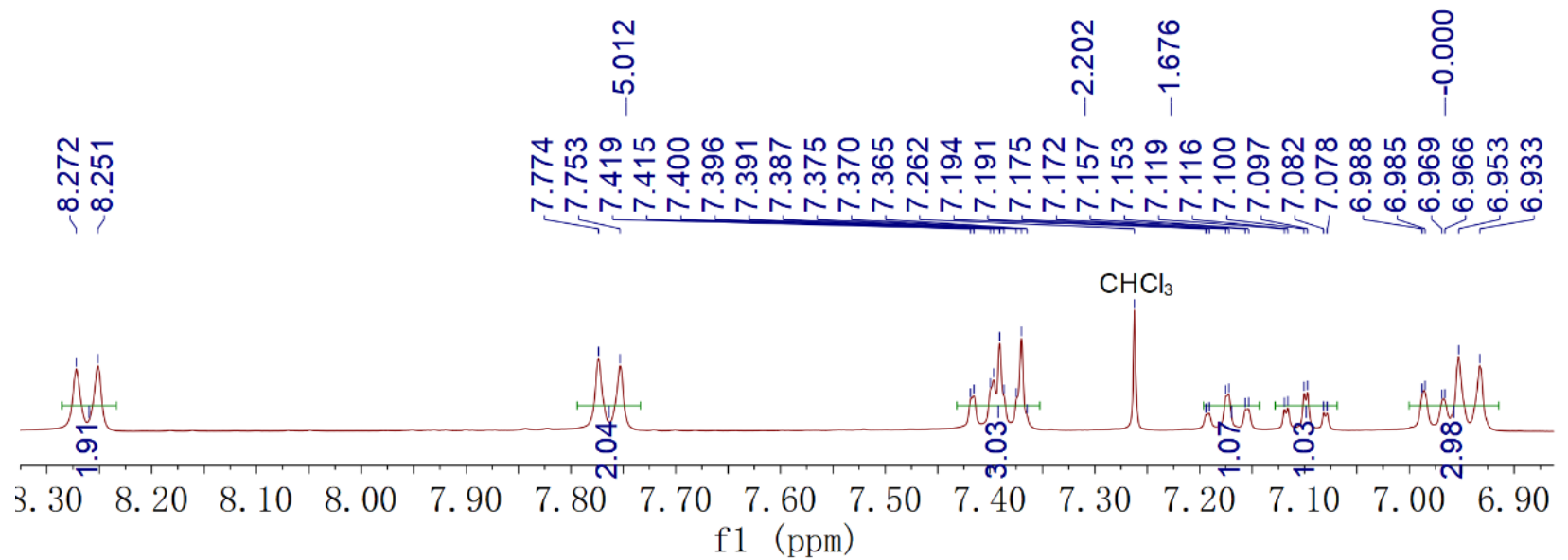


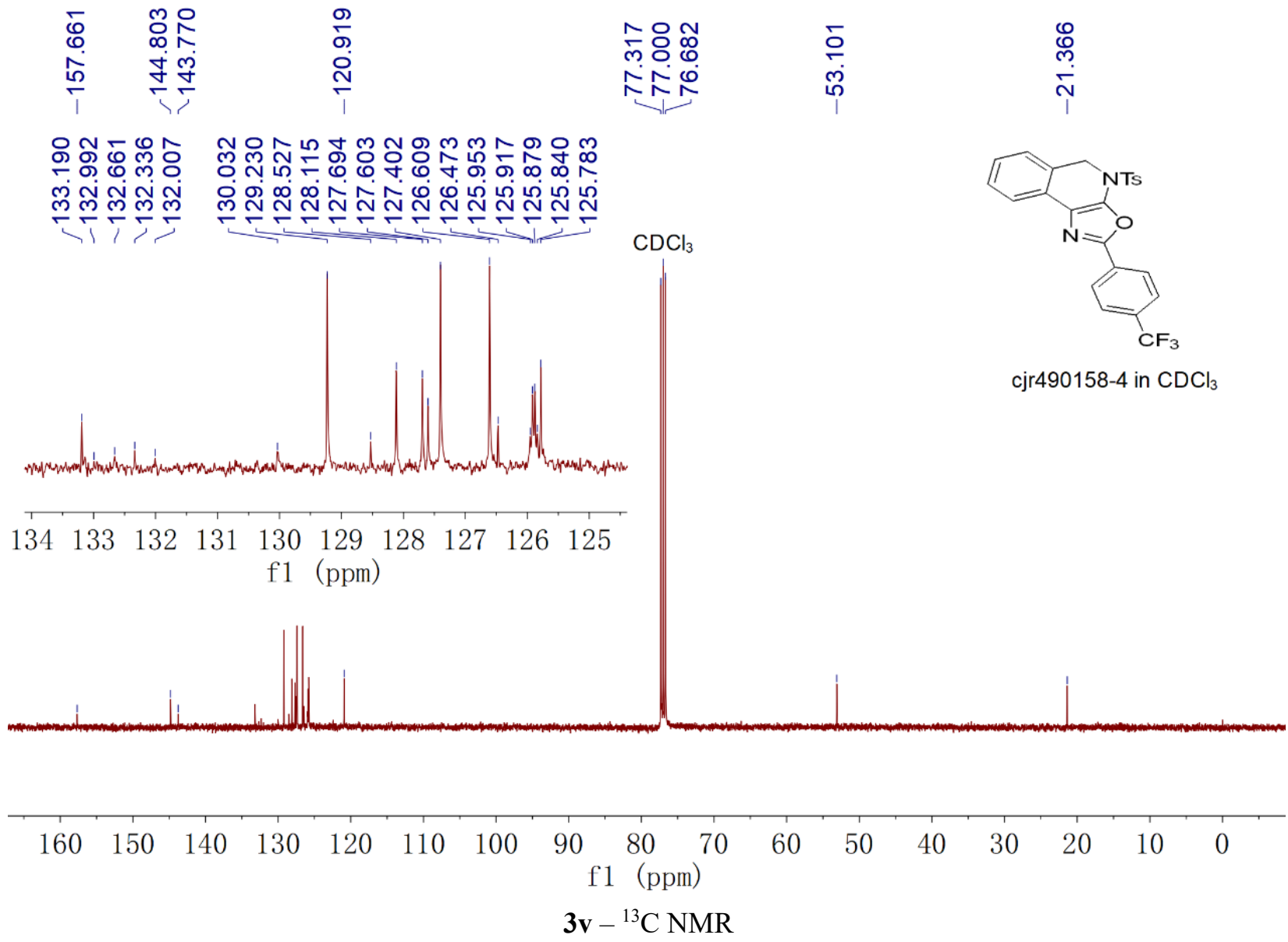


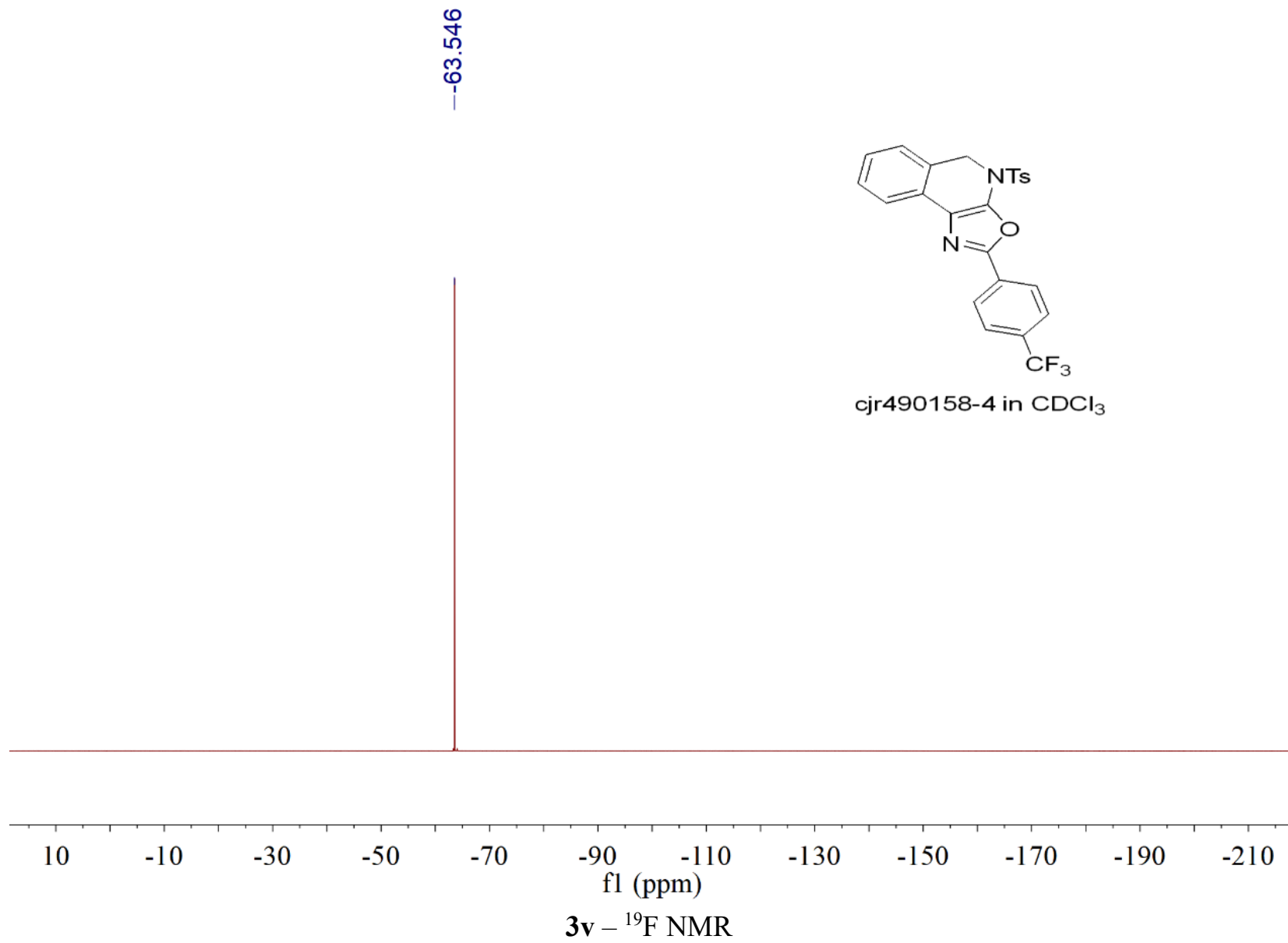
cjr490160-1 in CDCl₃

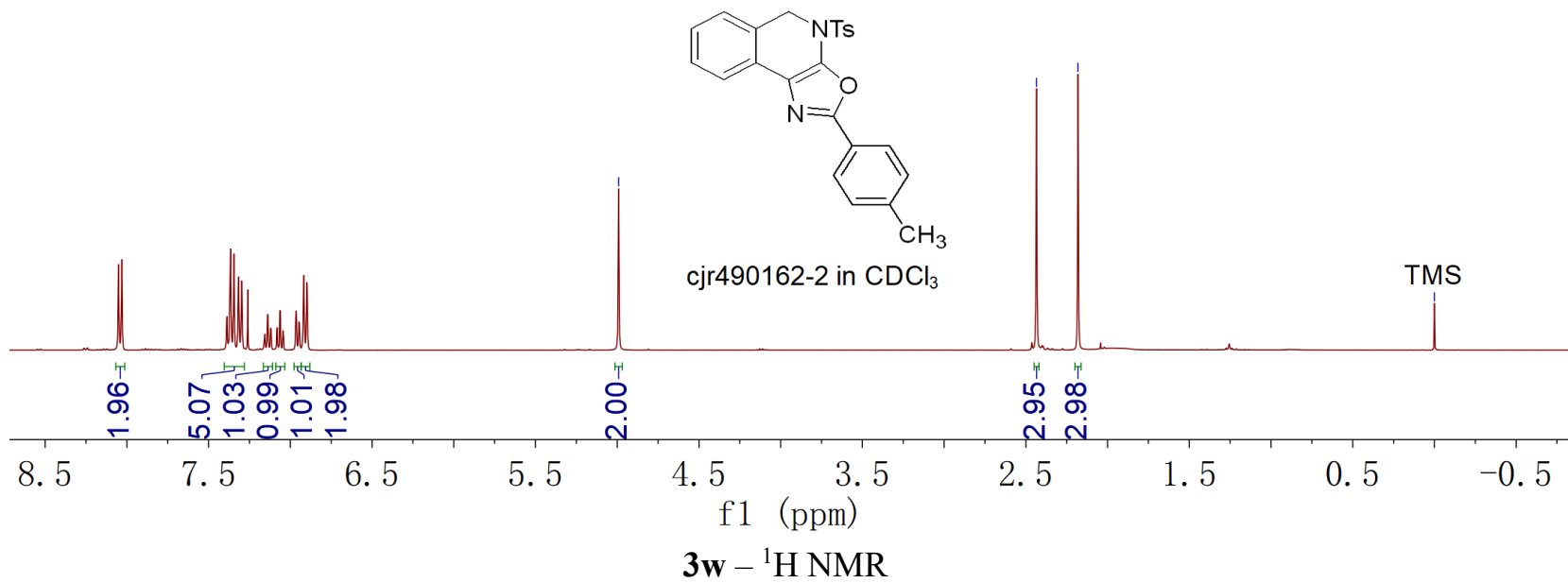
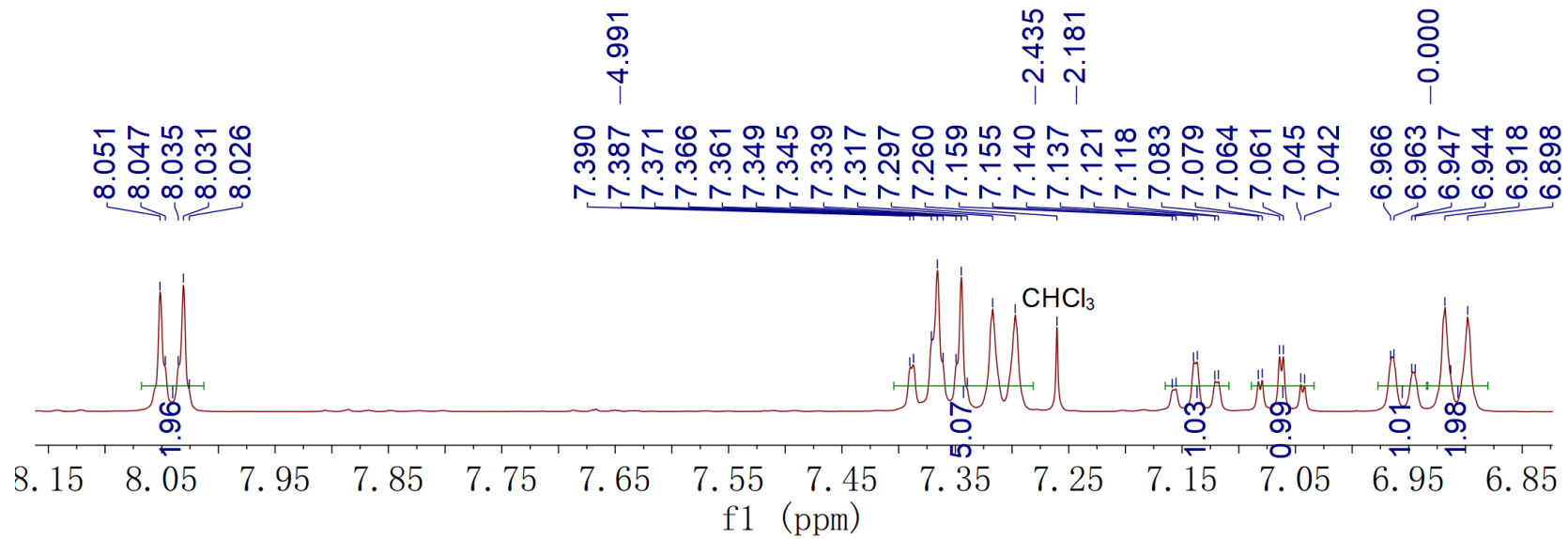


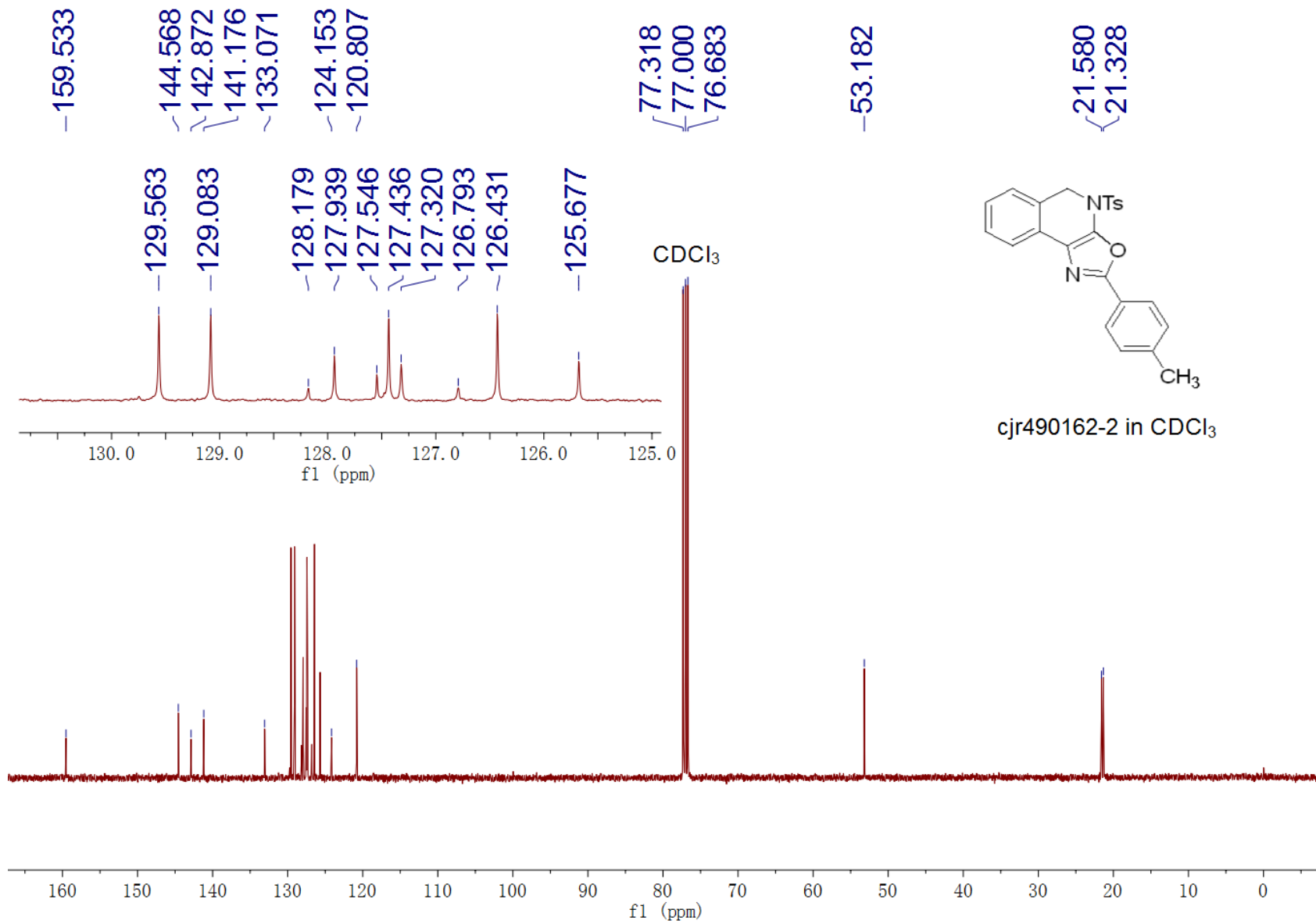
3u – ¹³C NMR



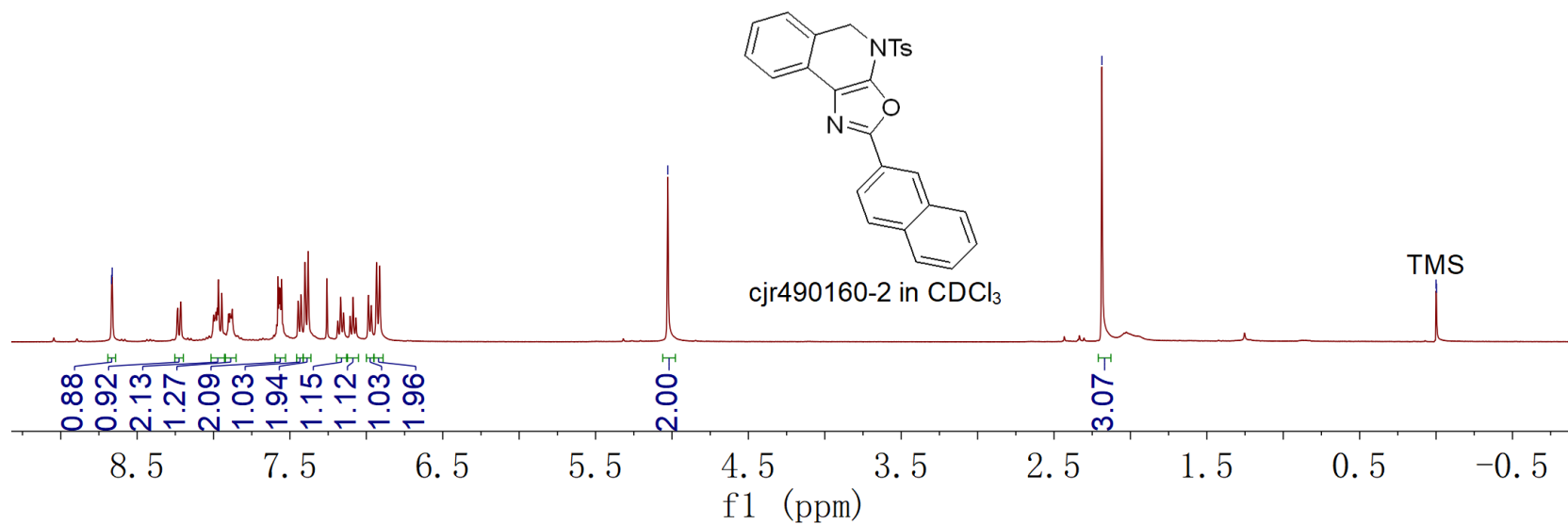
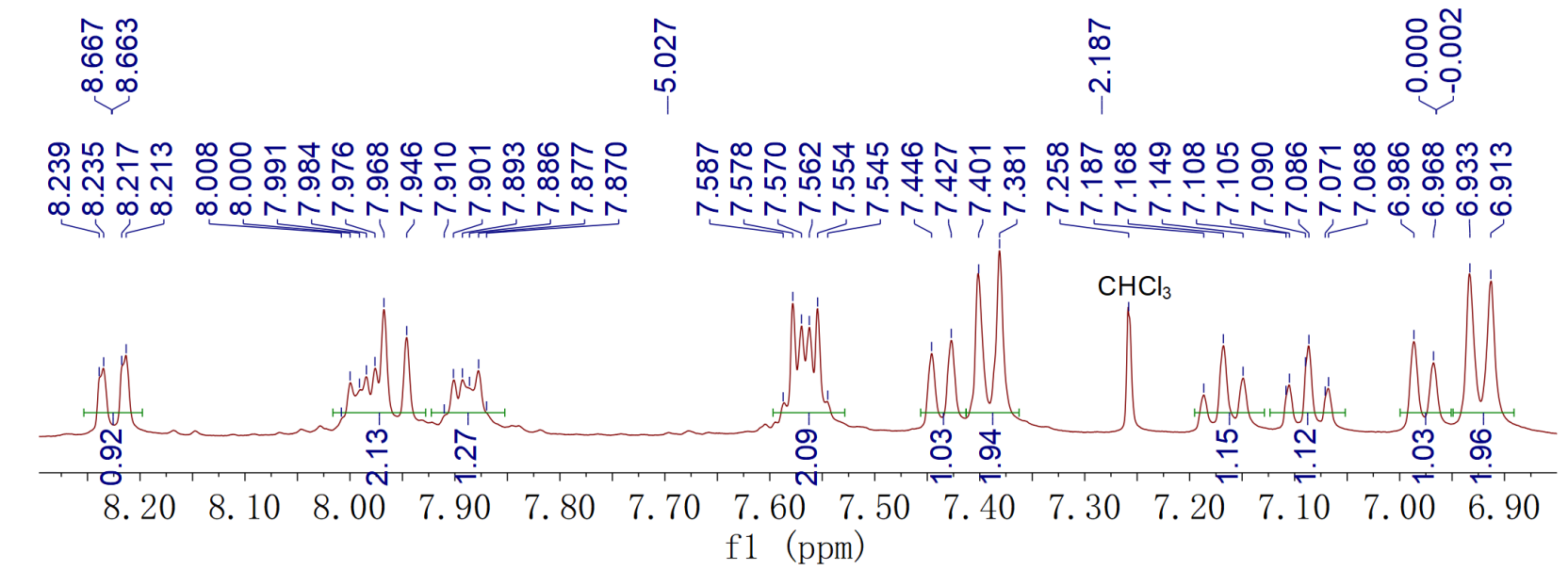




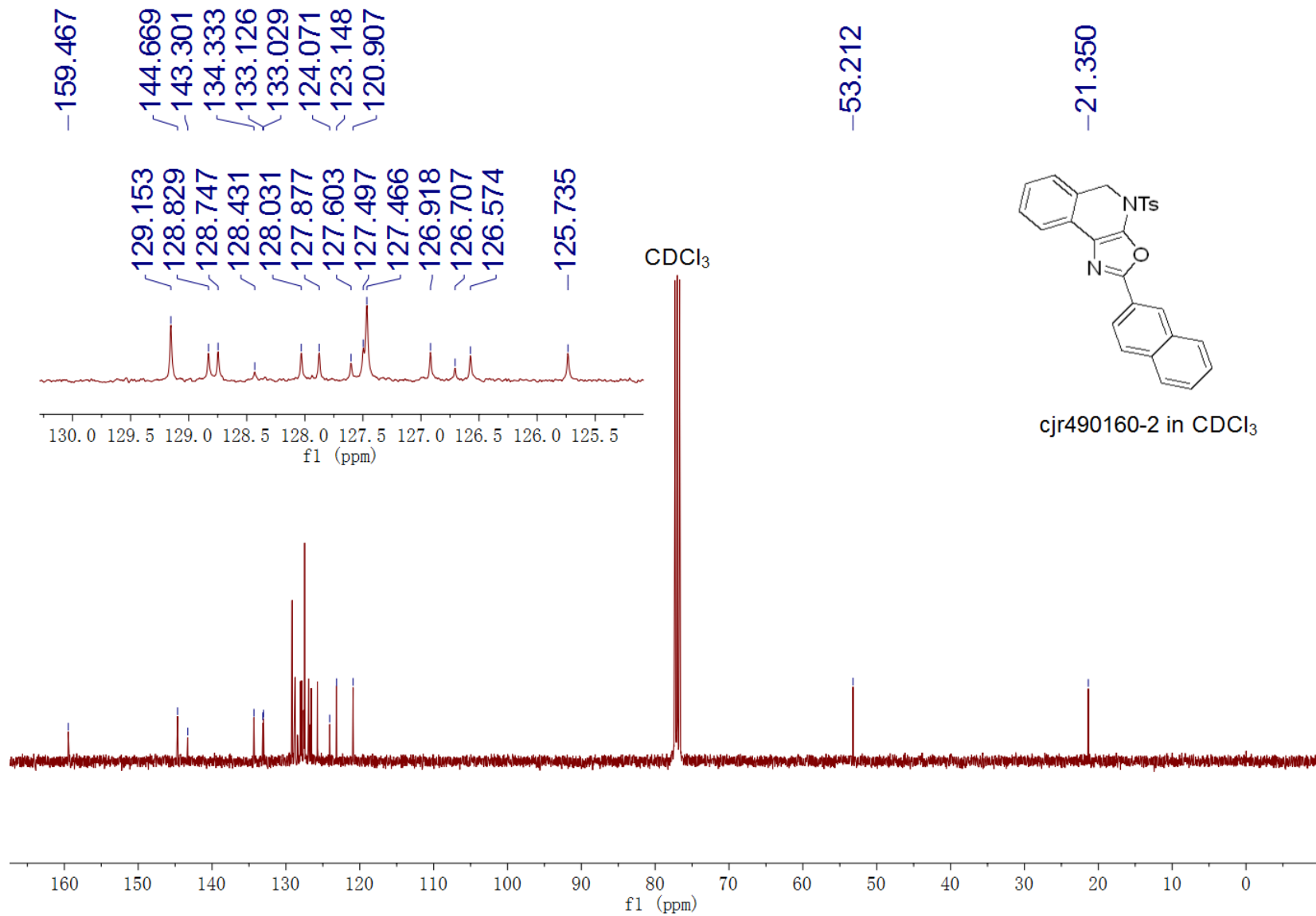




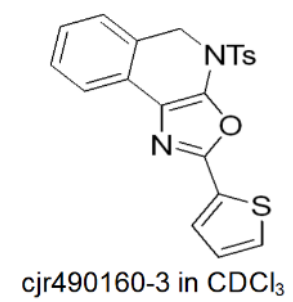
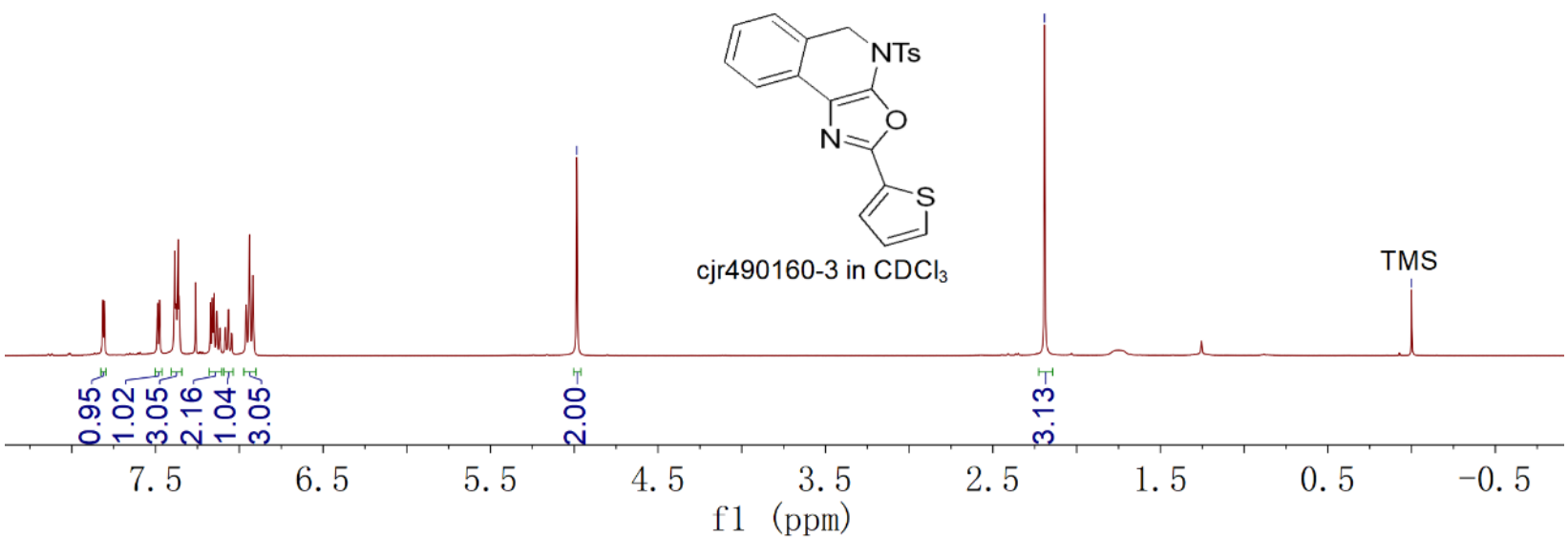
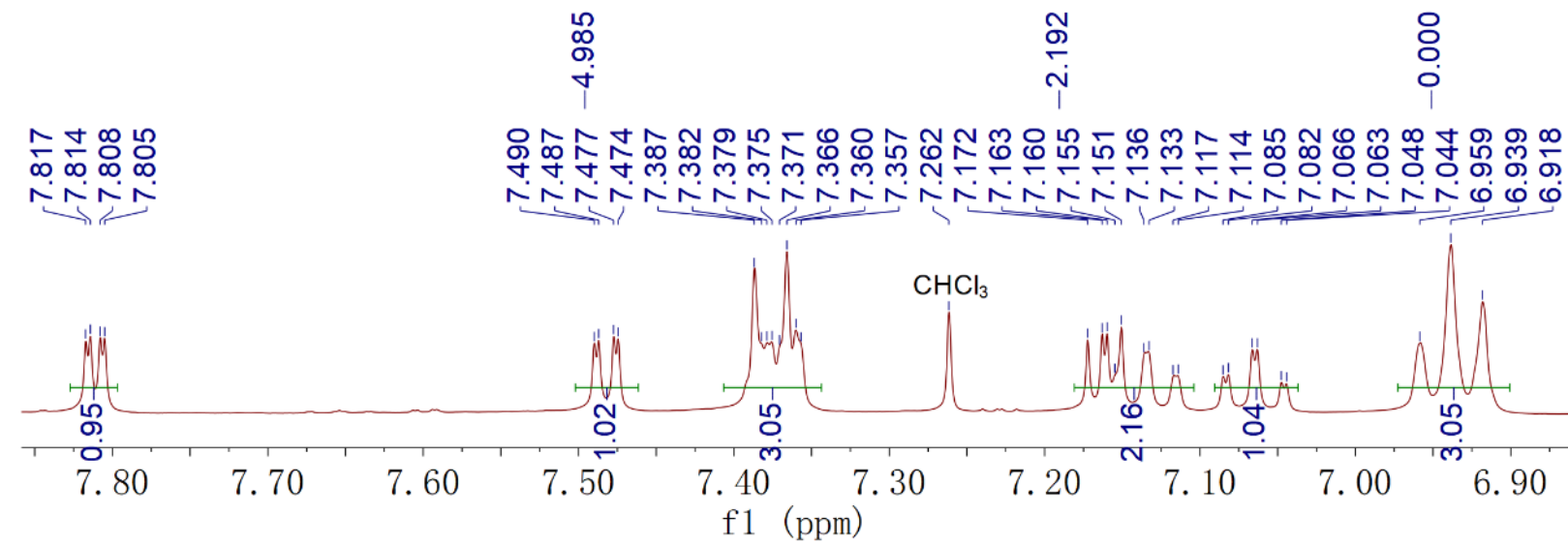
3w - ¹³C NMR



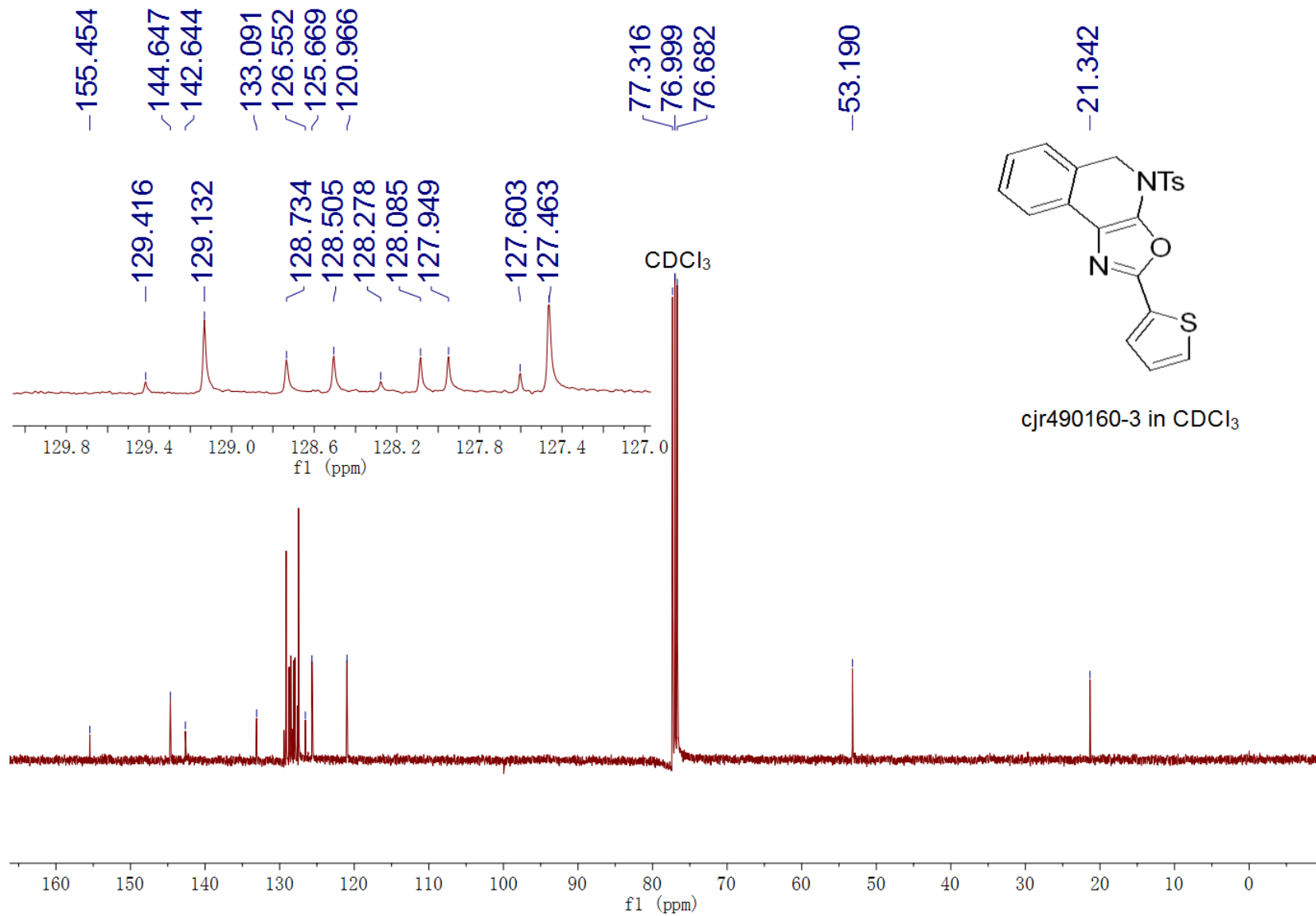
3x - ¹H NMR



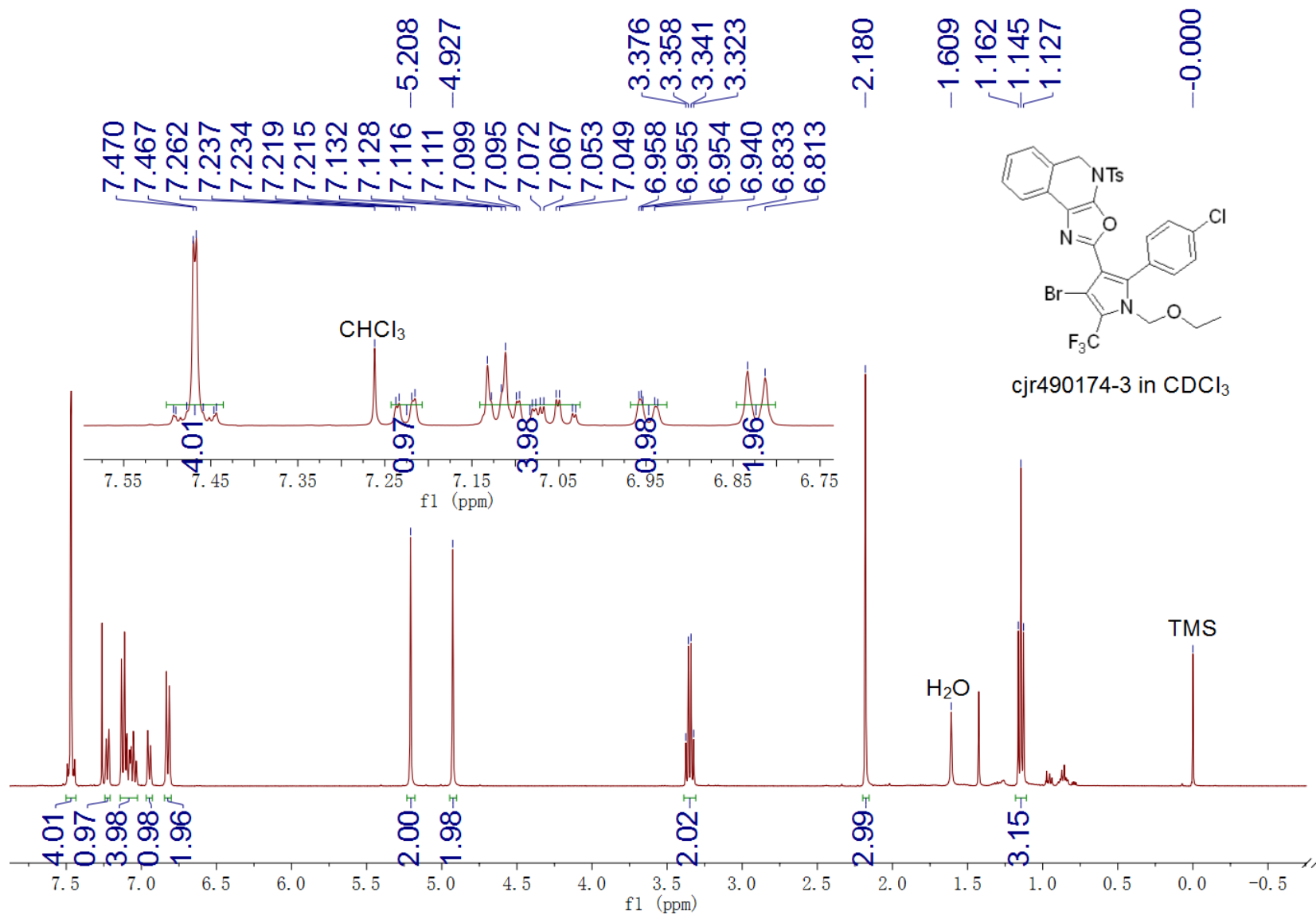
3x - ^{13}C NMR

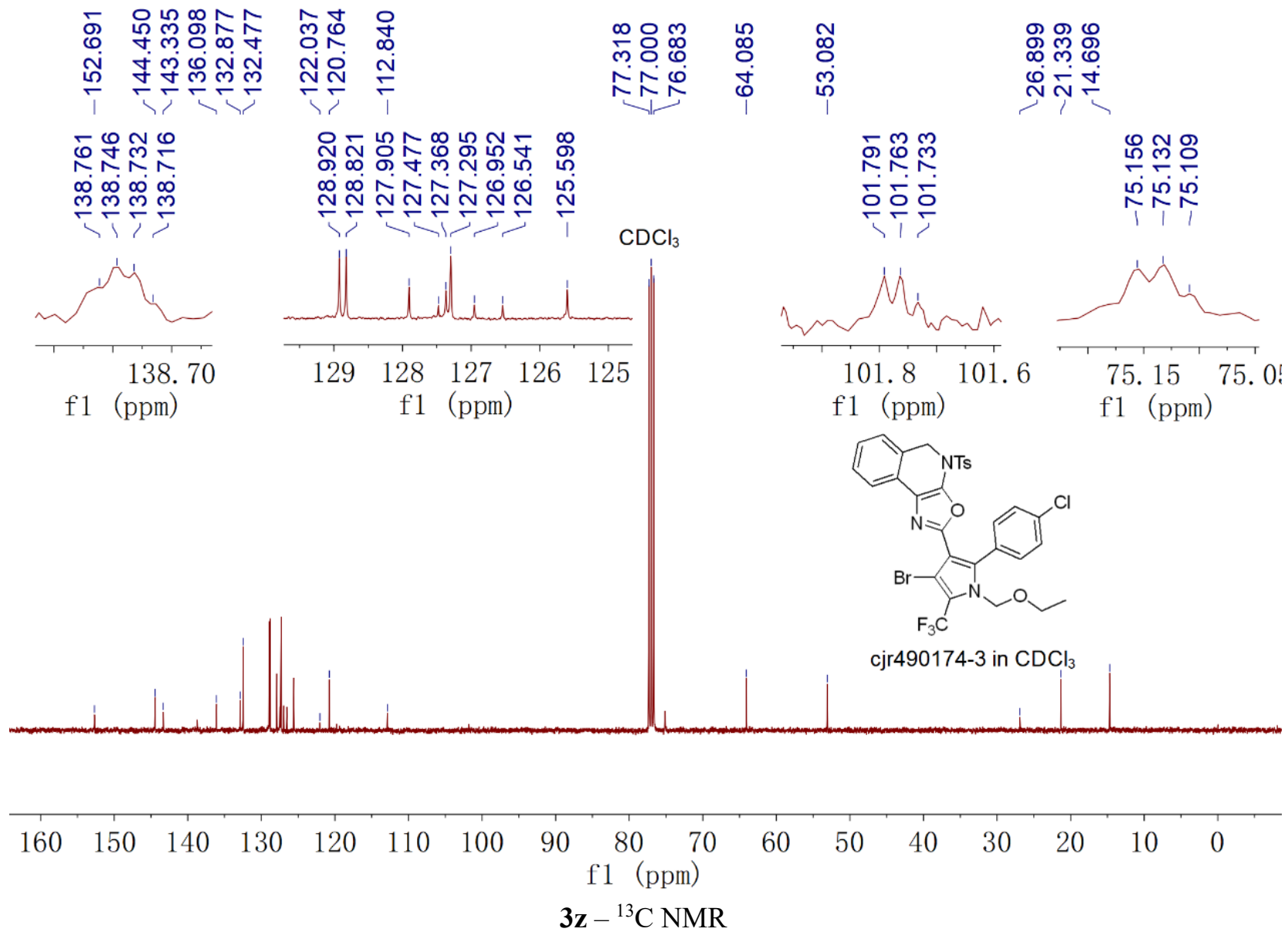


3y – ¹H NMR

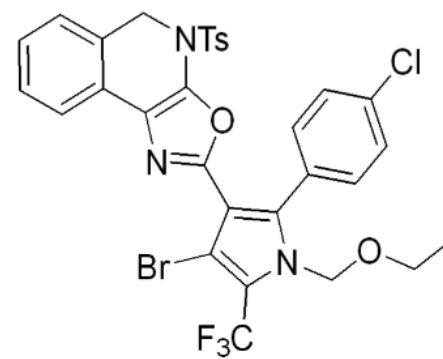


3y – ¹³C NMR





--57.103

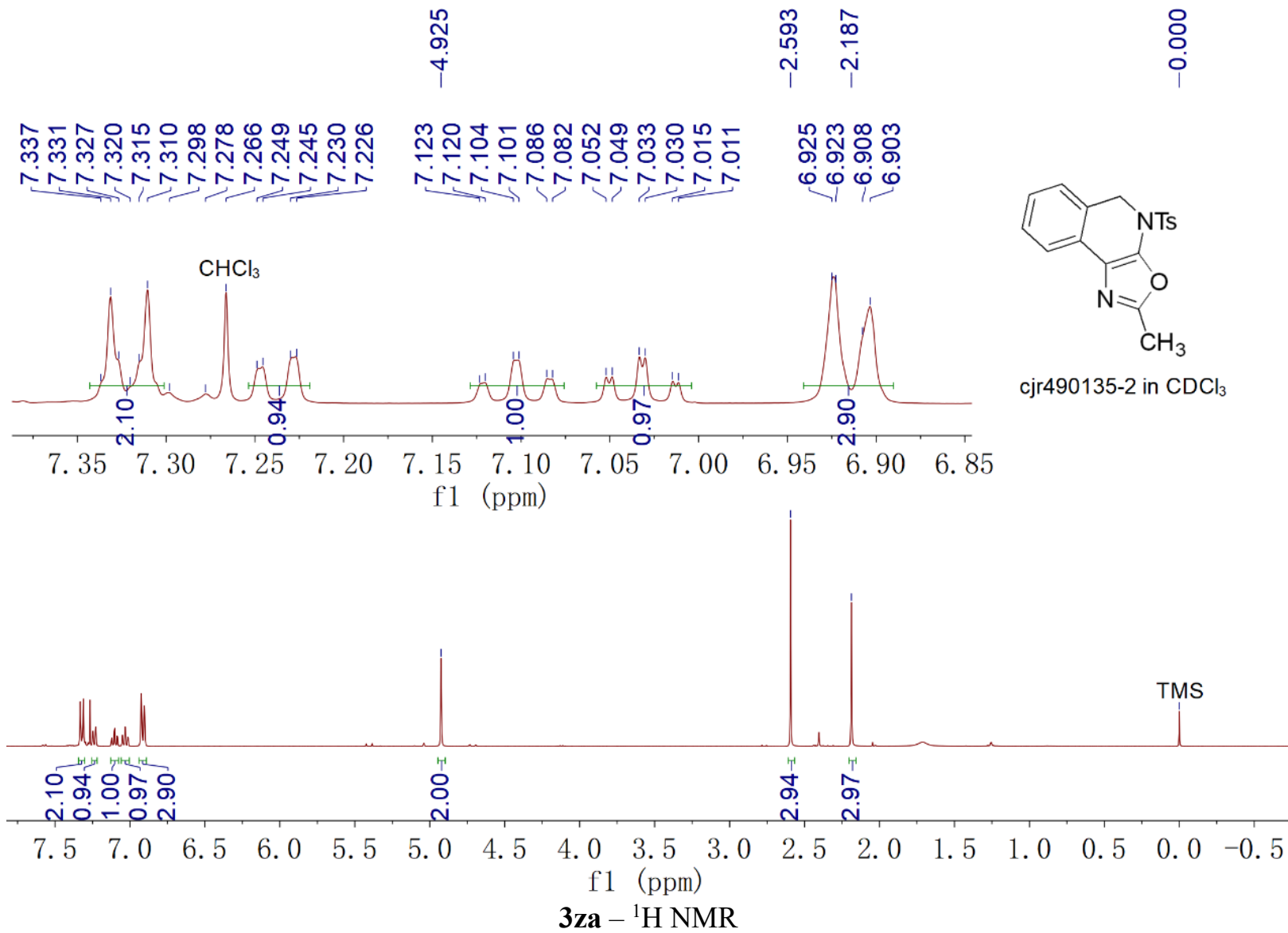


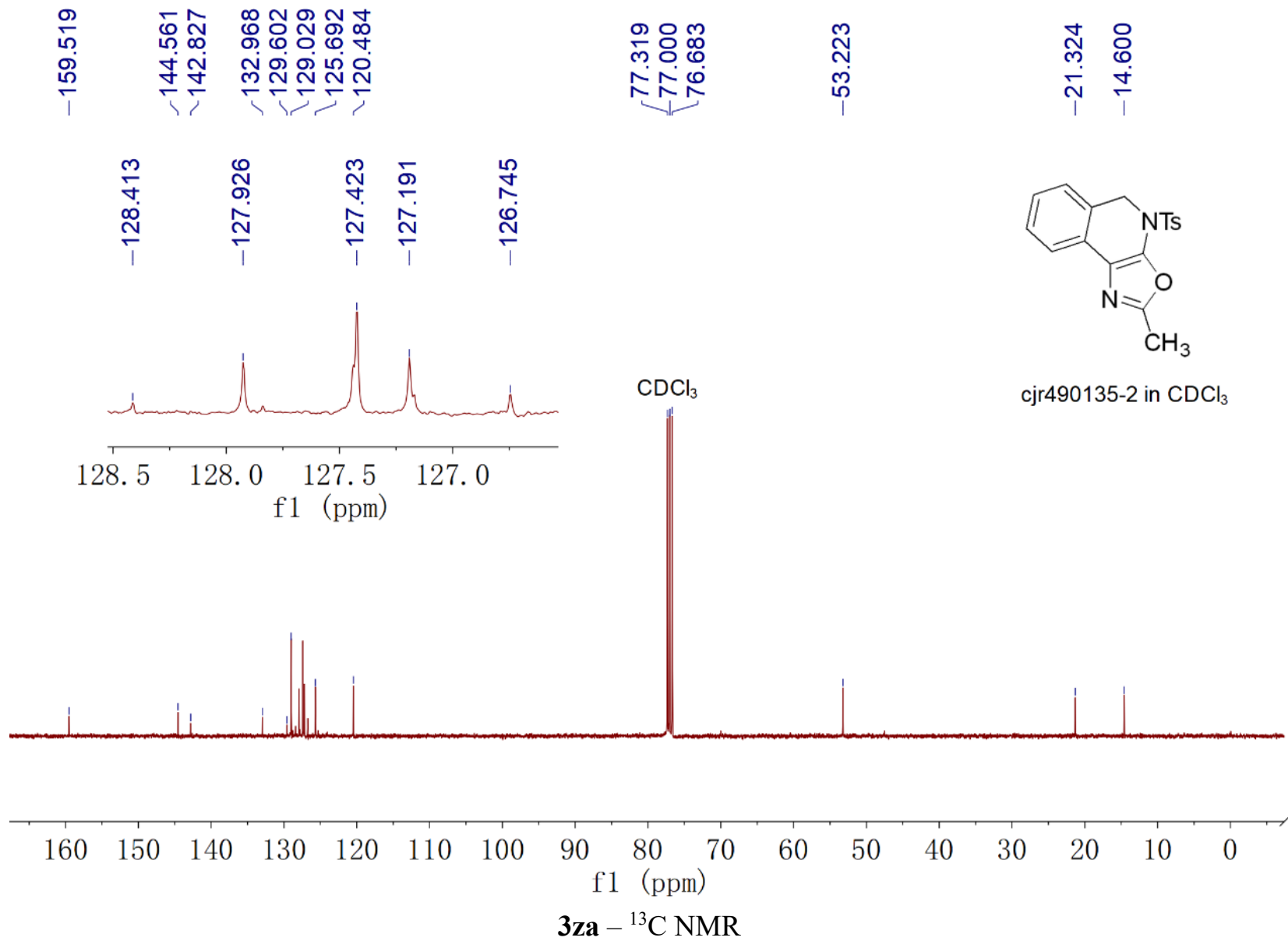
cjrcmj in CDCl₃

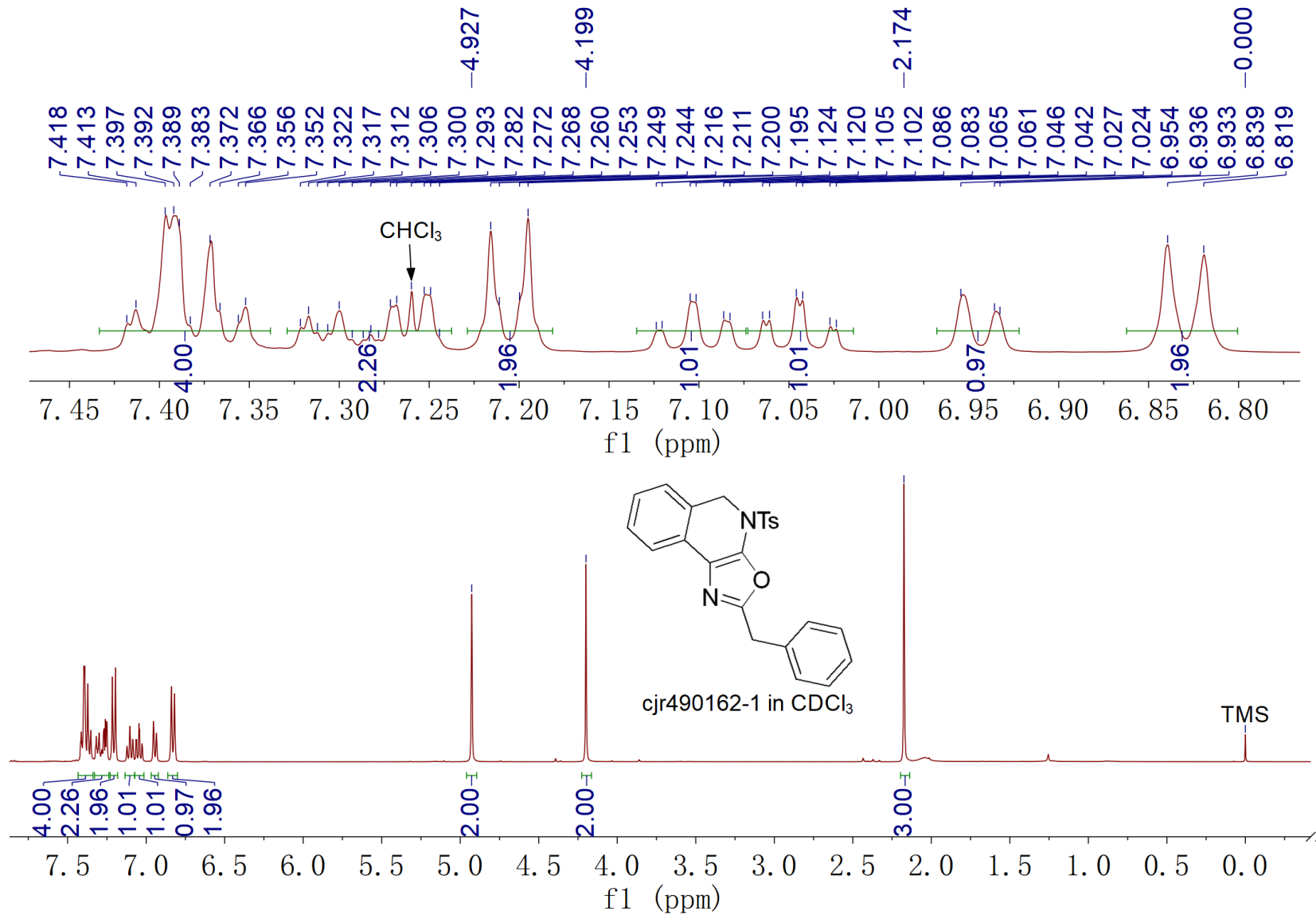


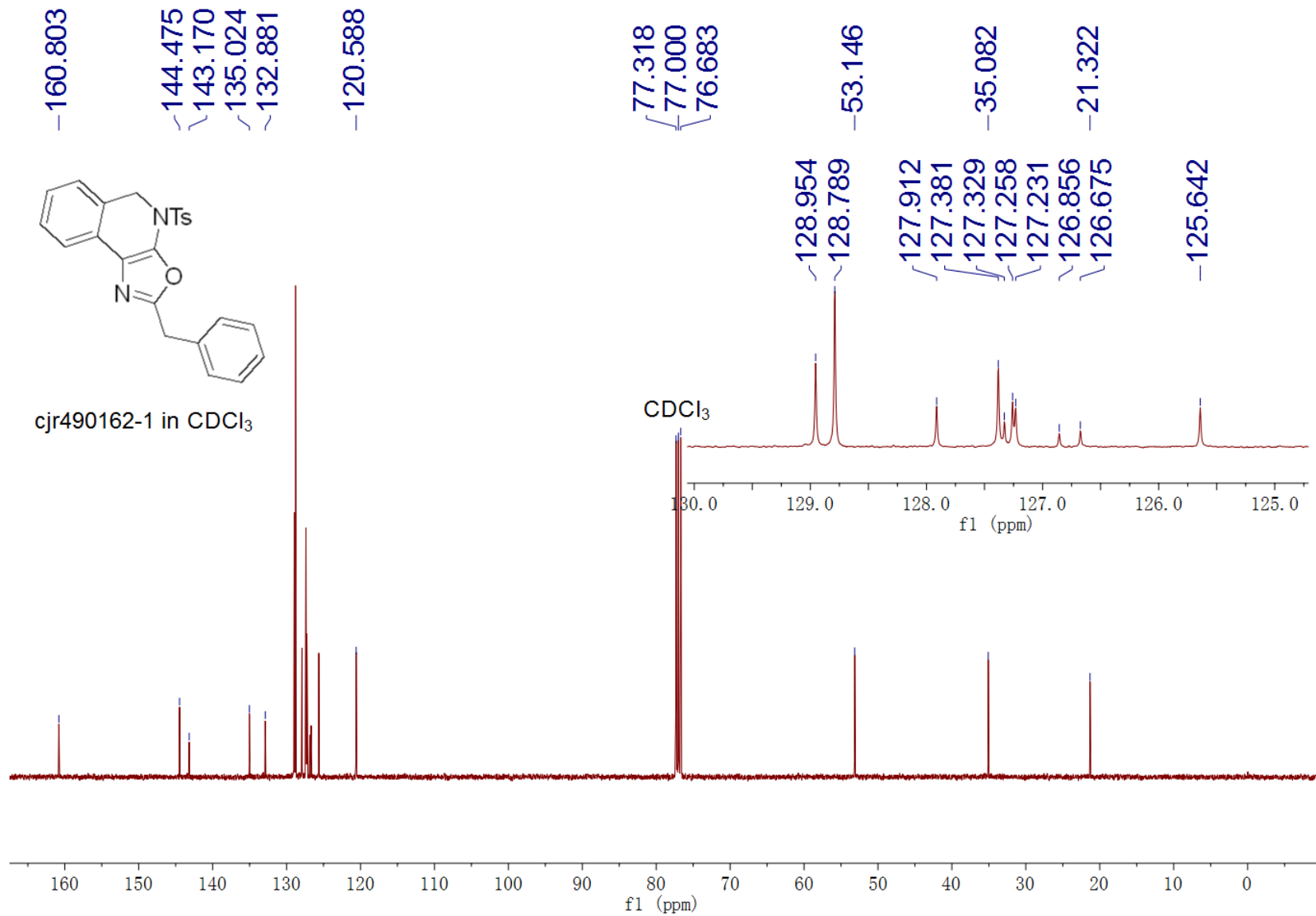
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

3z - ¹⁹F NMR

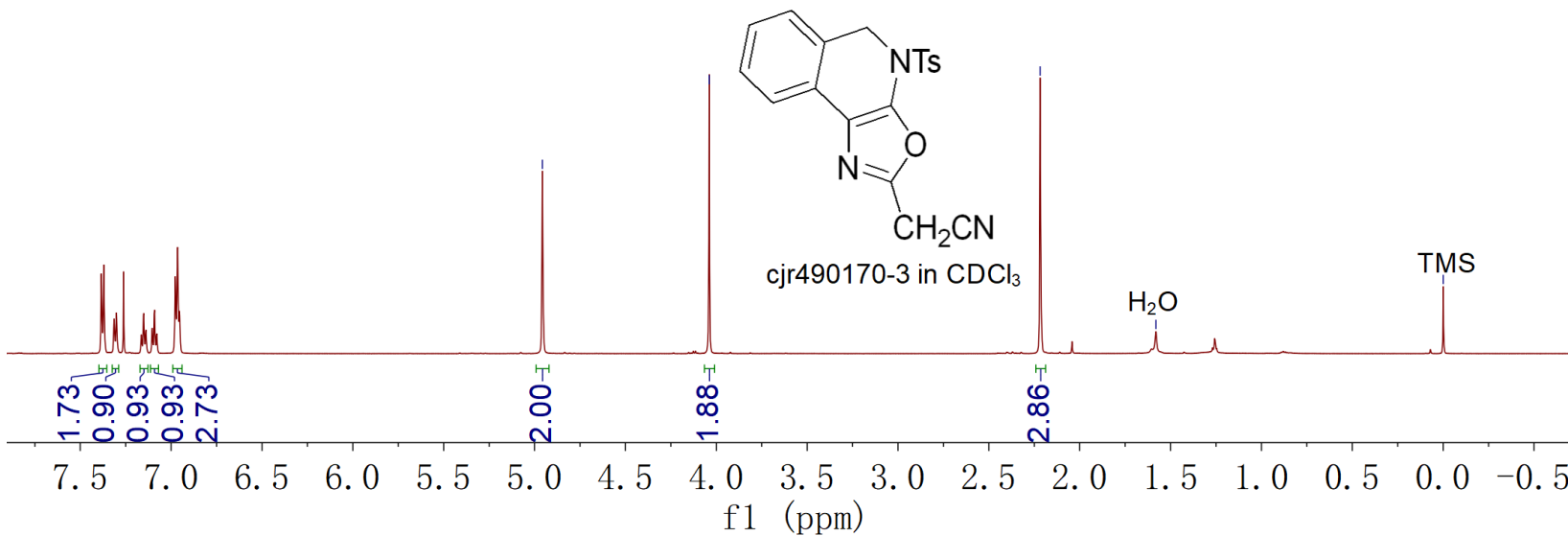
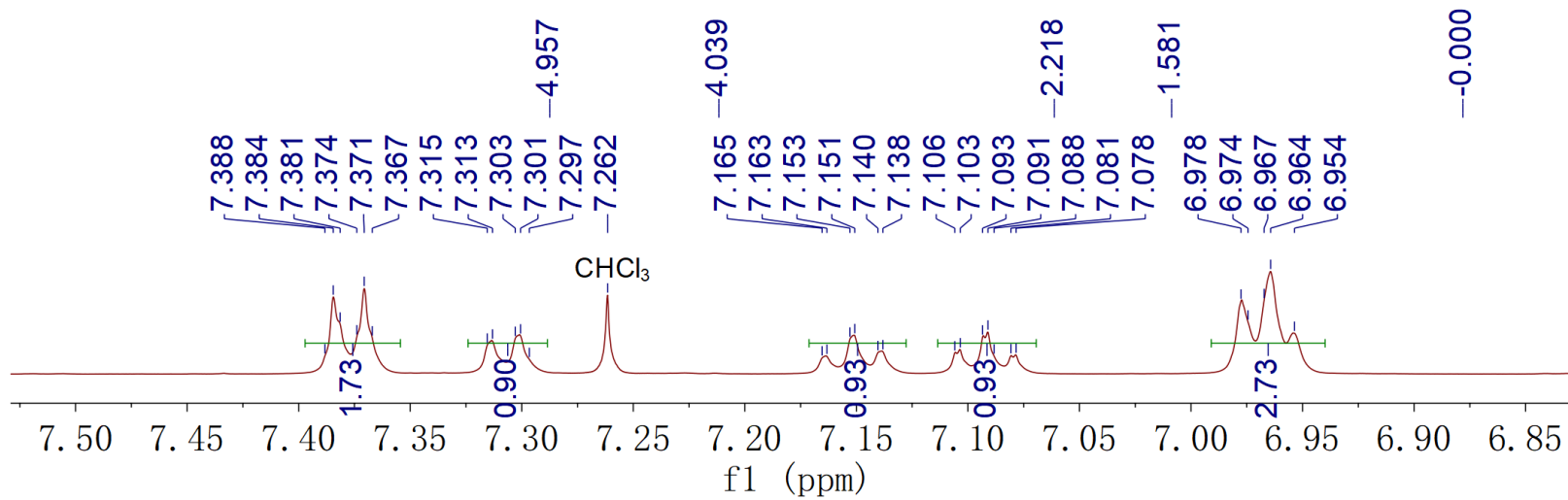




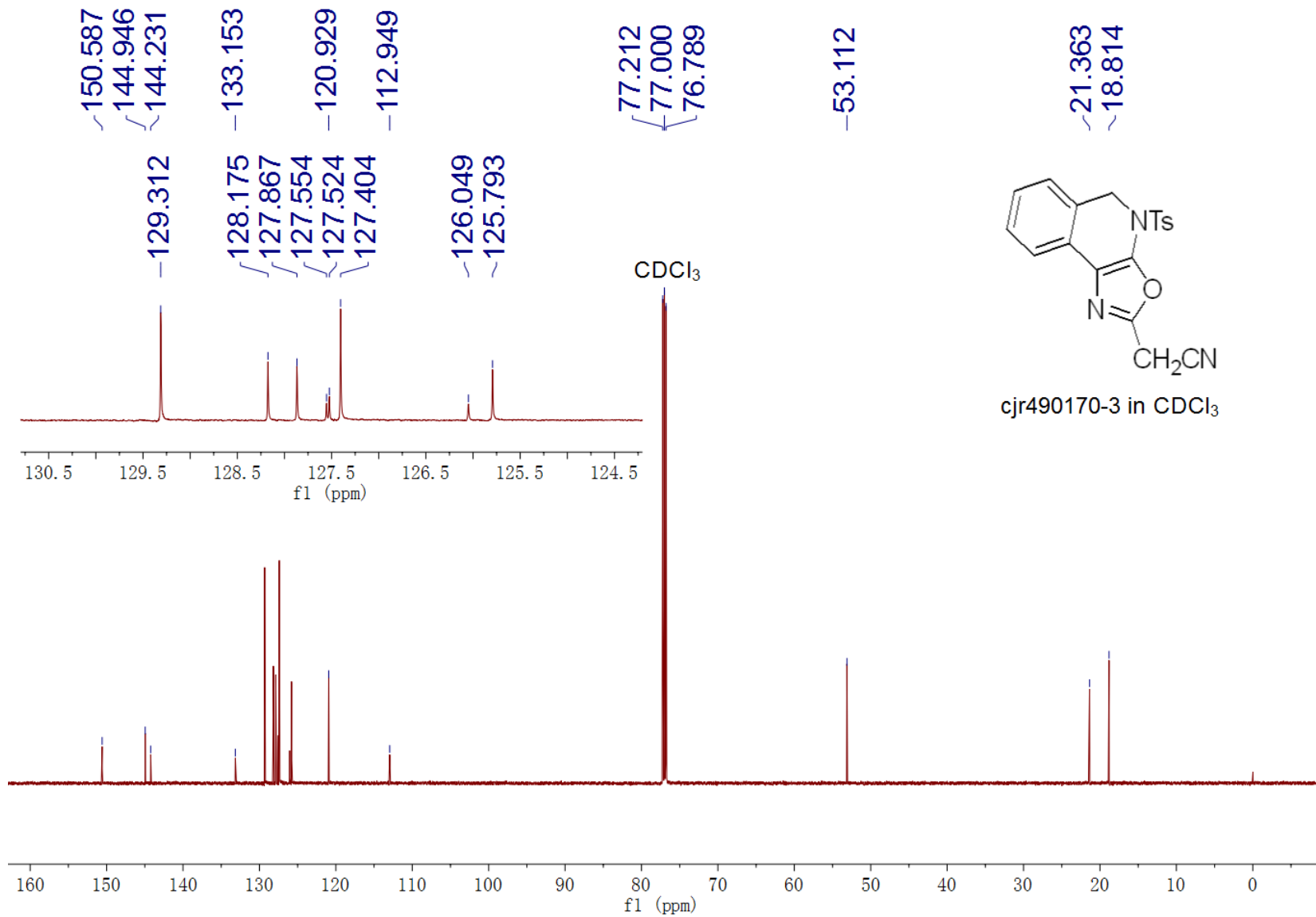




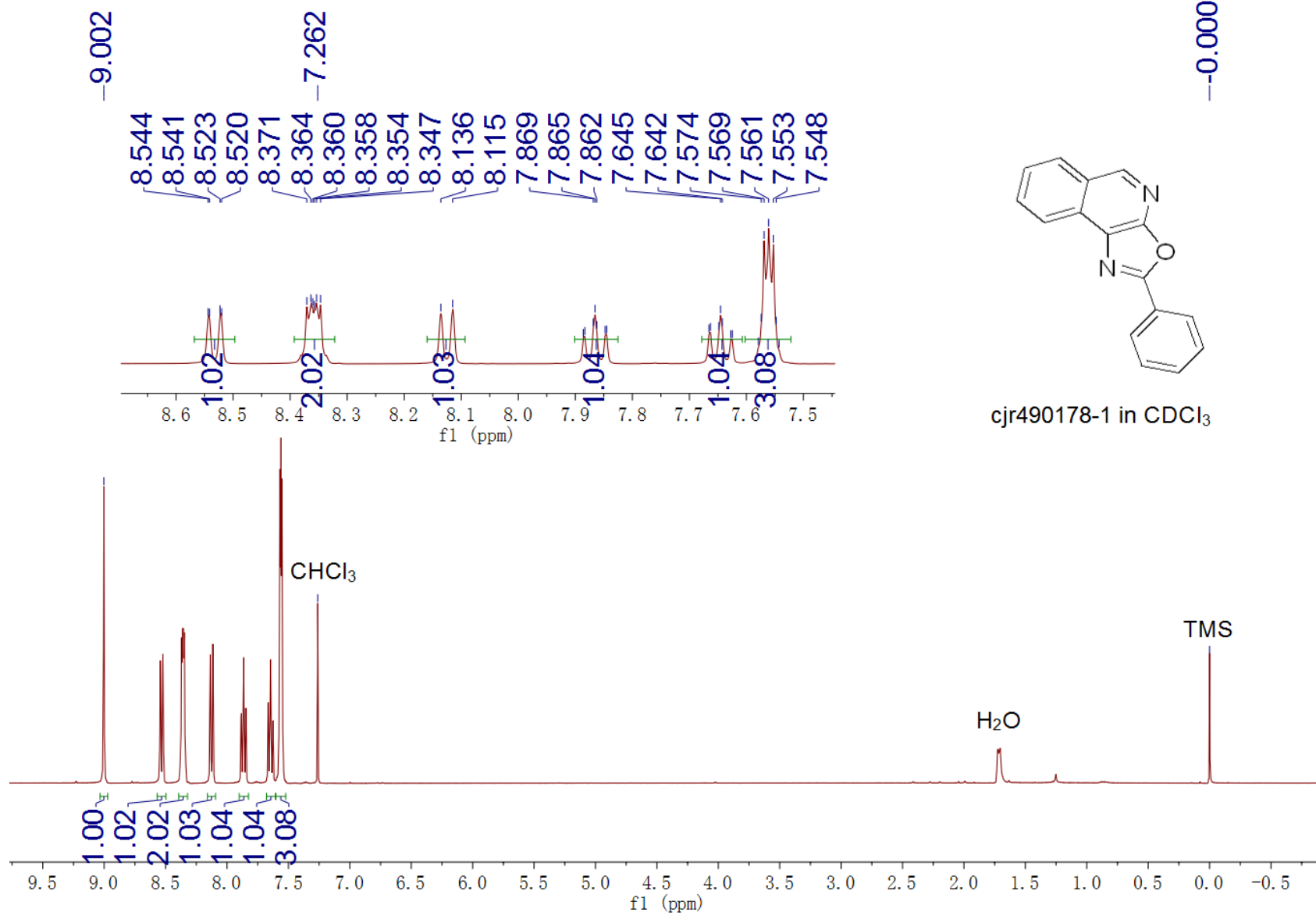
3zb – ¹³C NMR



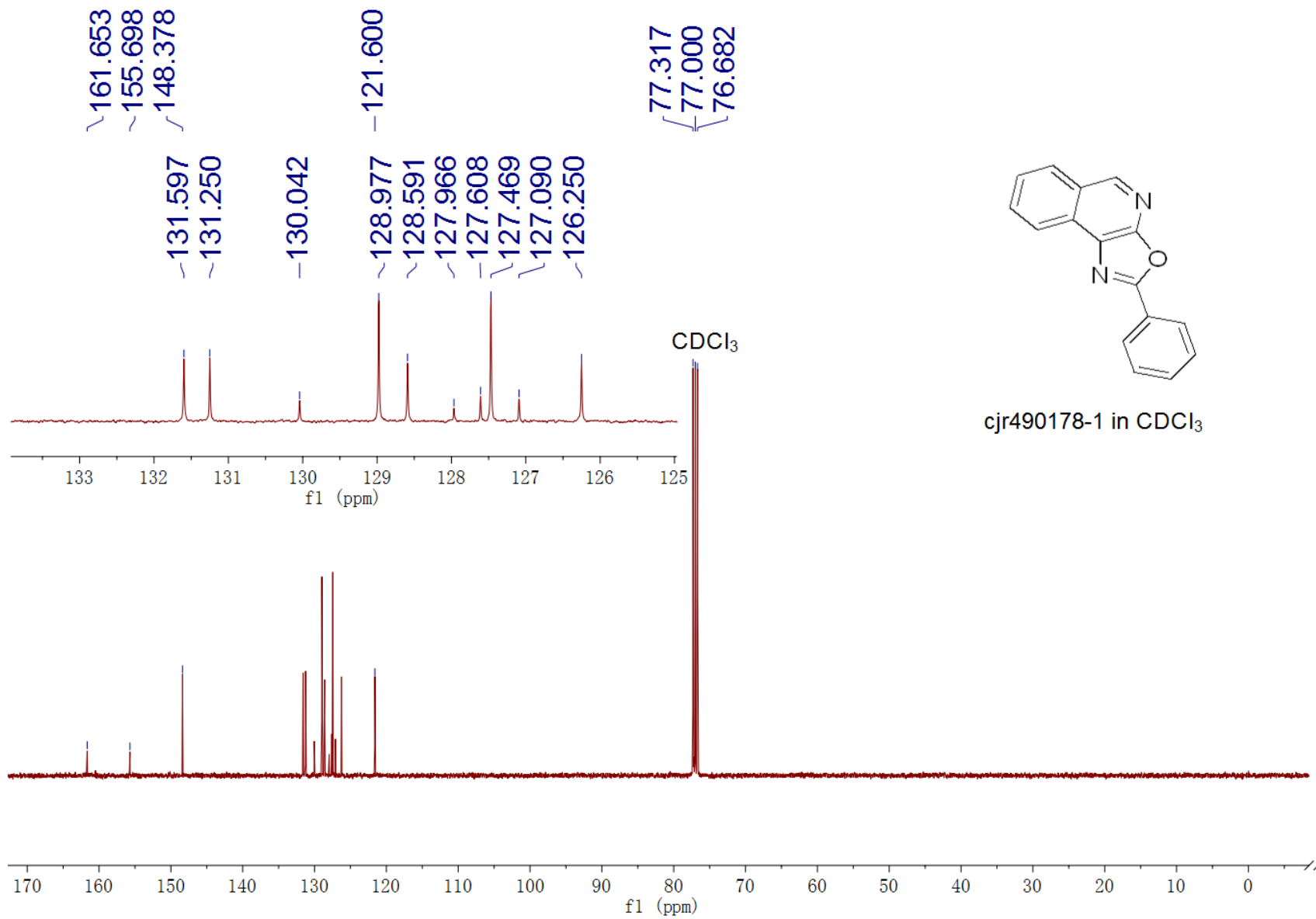
3zc – ¹H NMR

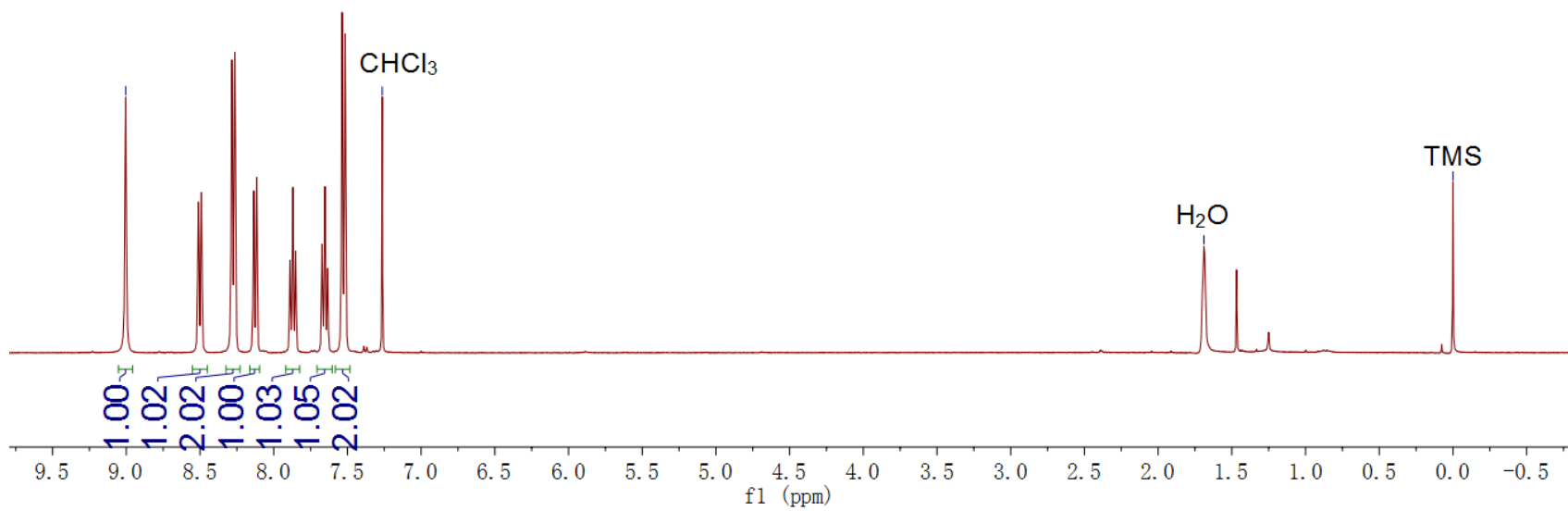
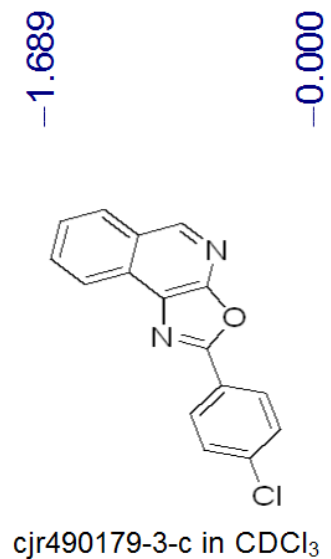
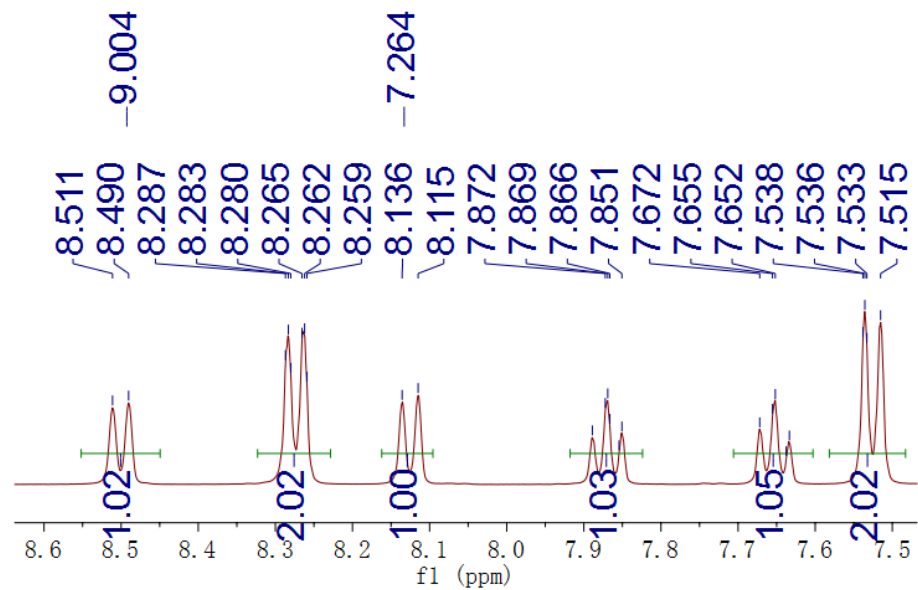


3zc – ¹³C NMR

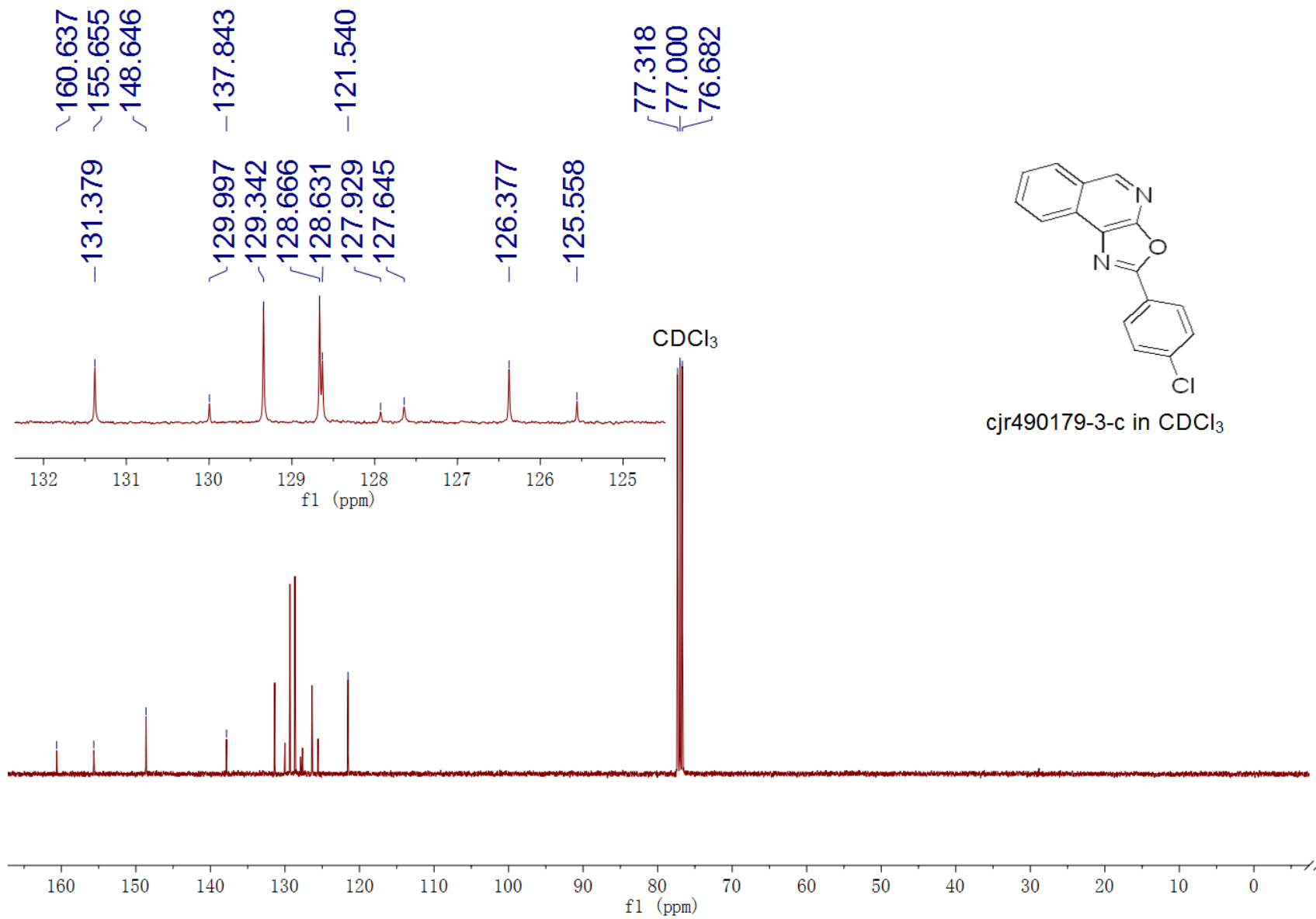


4a – ^1H NMR

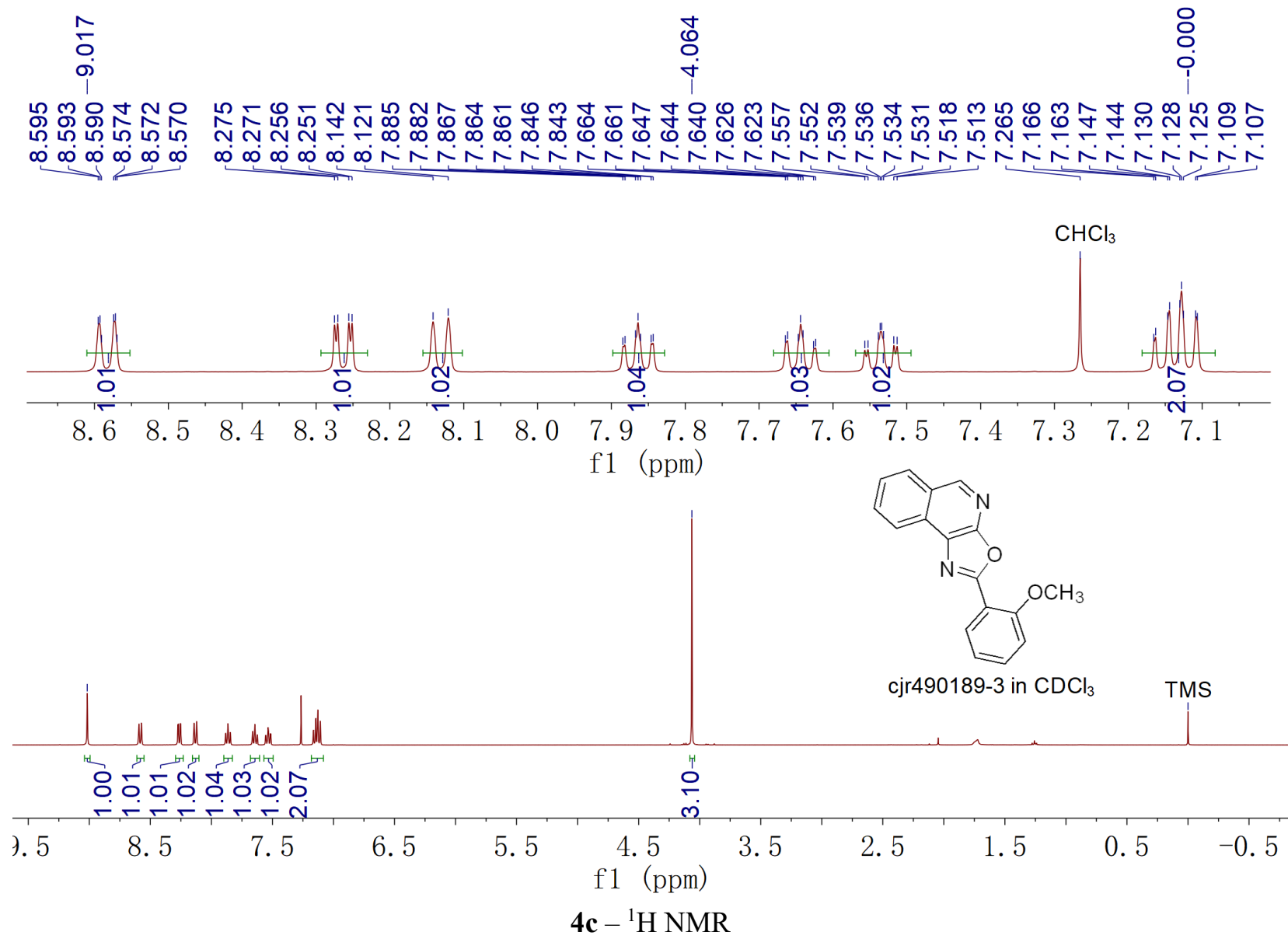


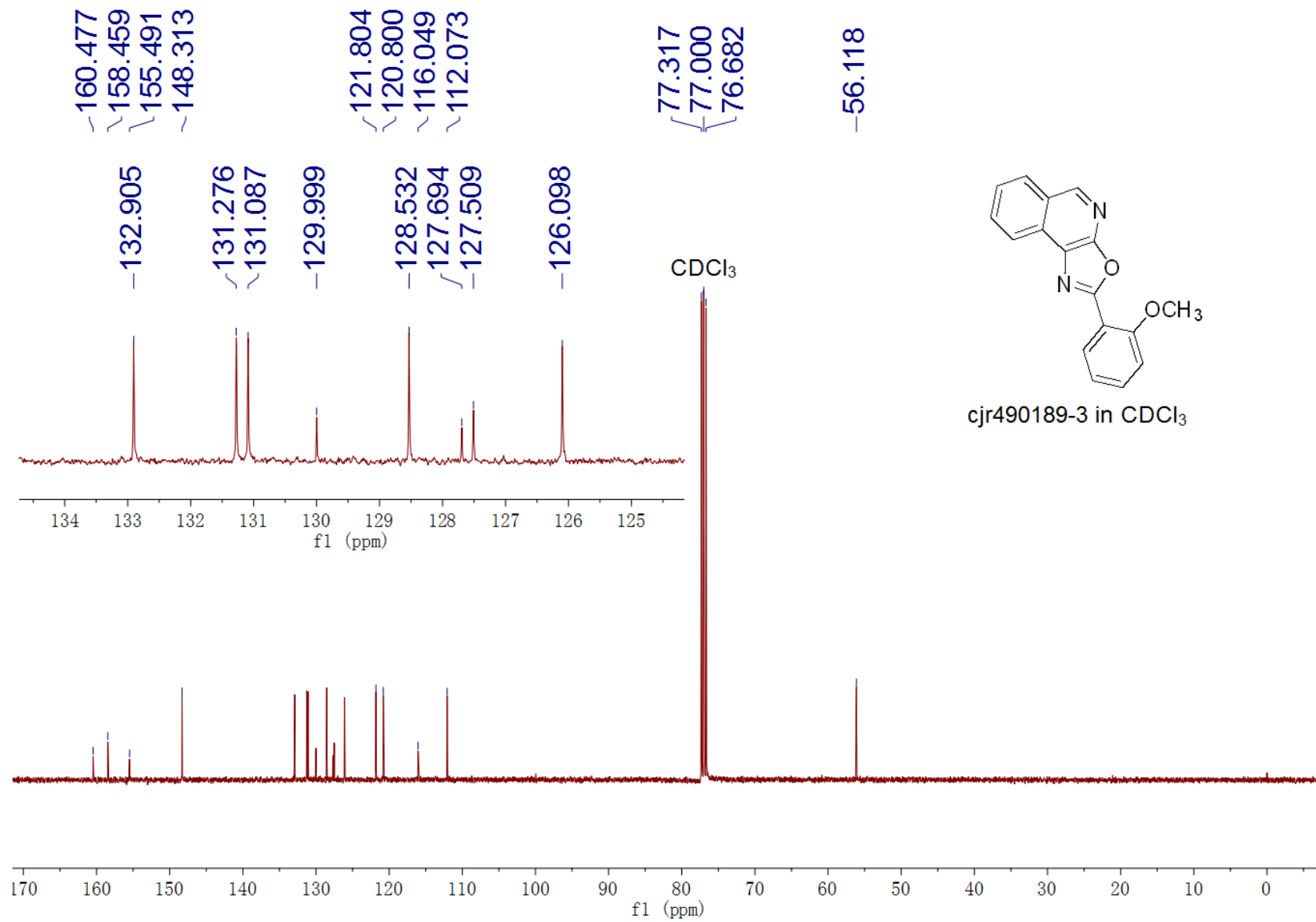


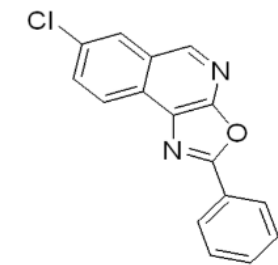
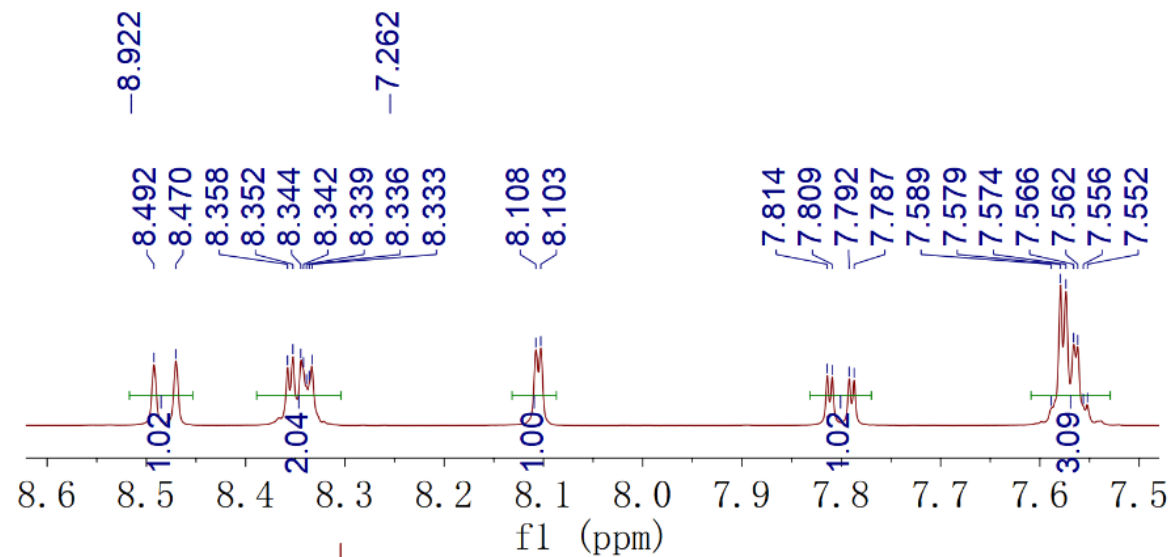
4b – ¹H NMR



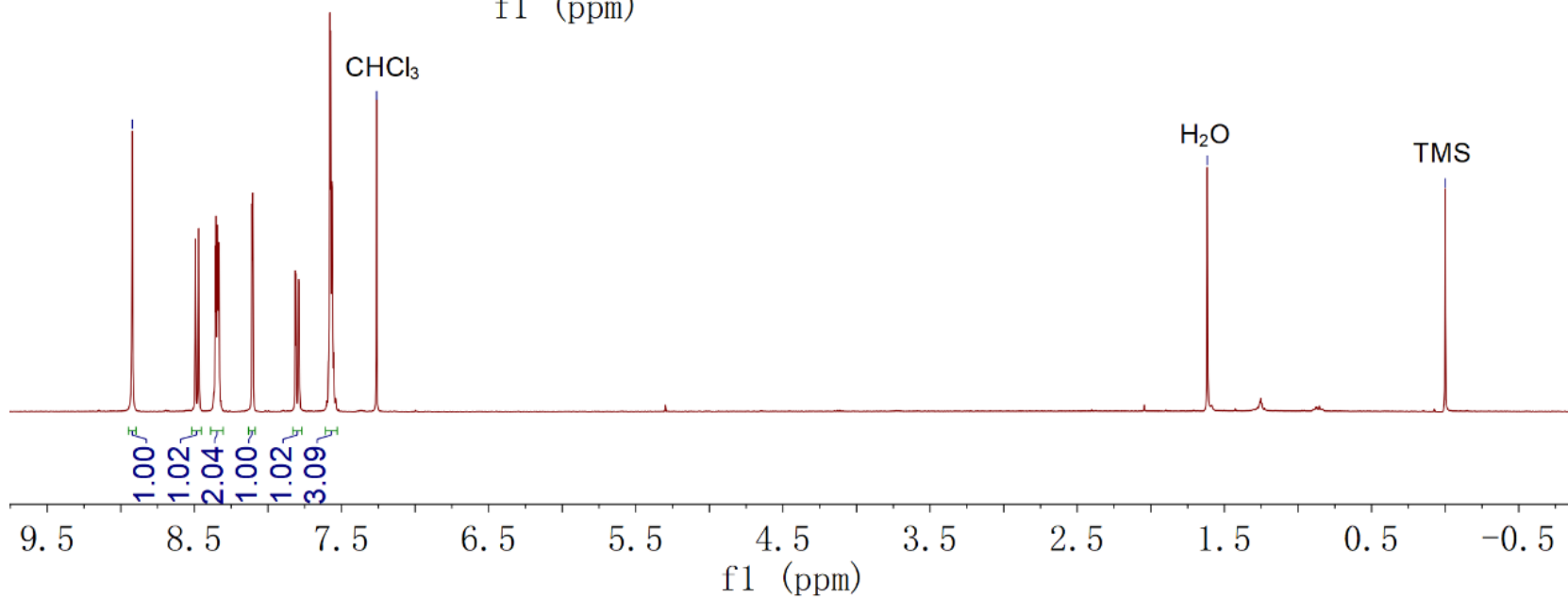
4b – ¹³C NMR



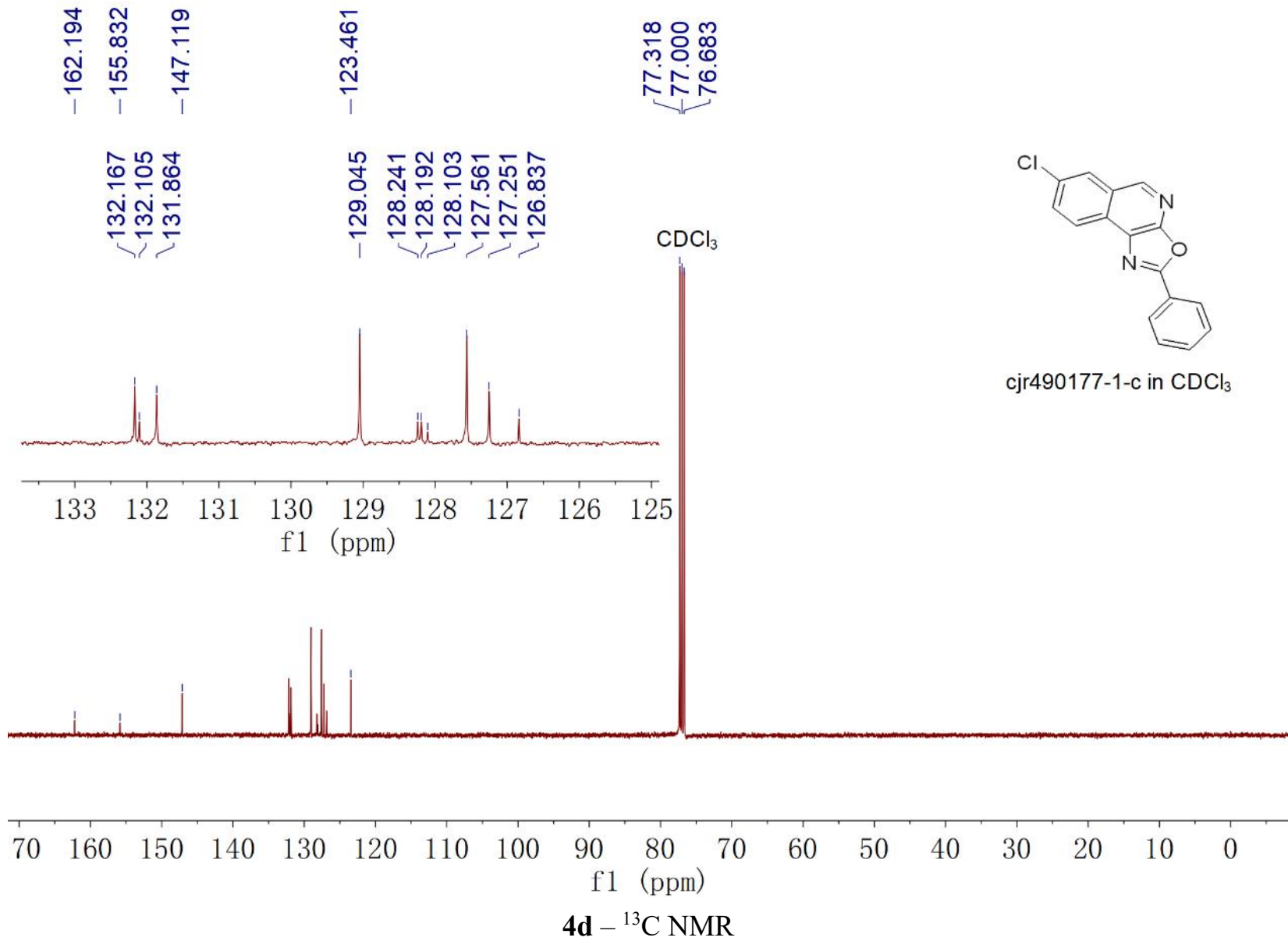


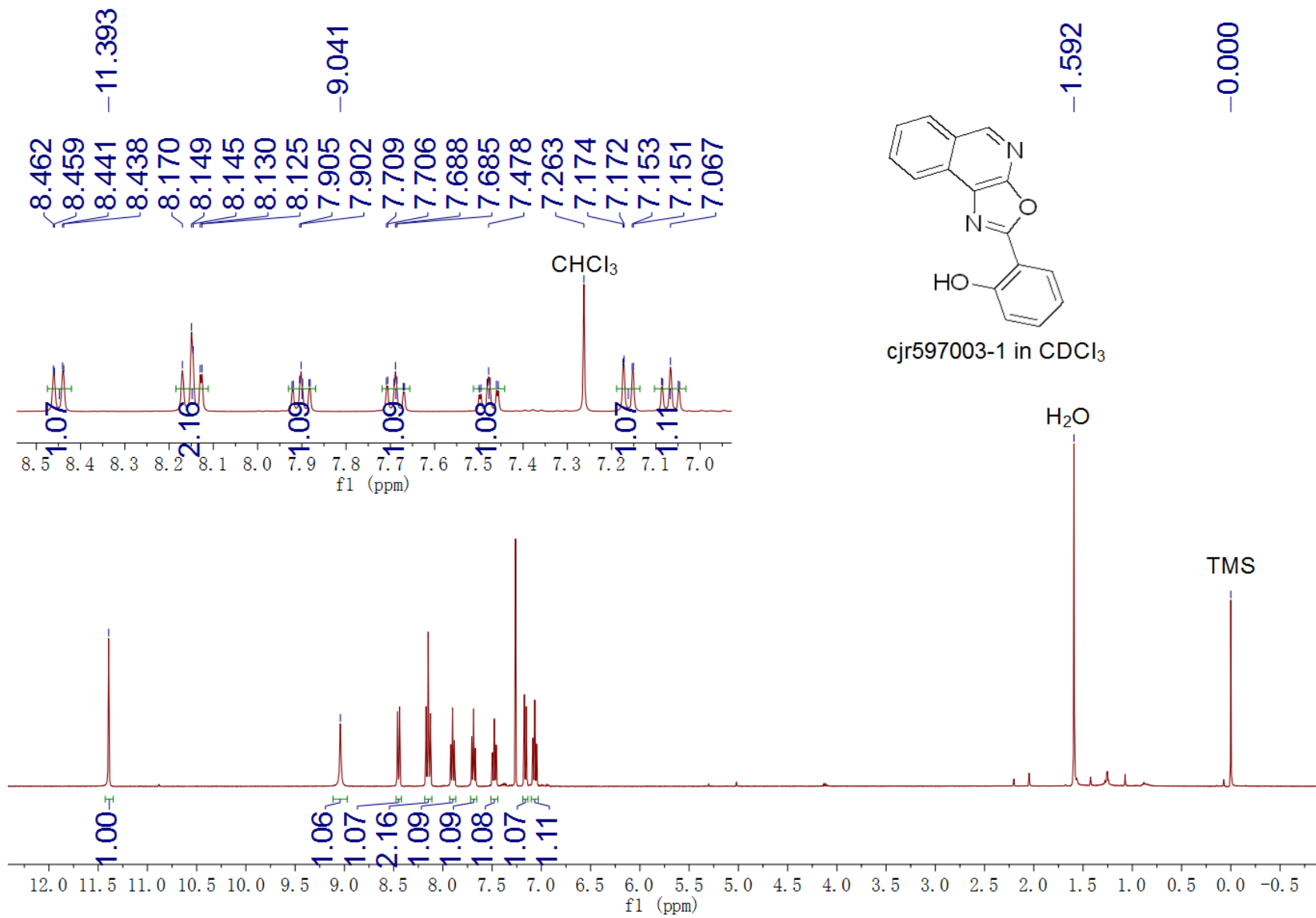


cjr490177-1-c in CDCl₃



4d - ¹H NMR





5 – ¹H NMR

