Supplementary Information for

Asymmetric Synthesis of (Aza)flavanones by the Evolution of CarOx Ligands

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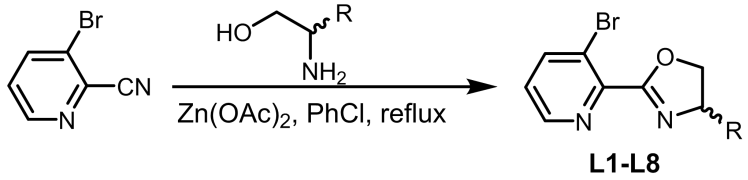
Content

1. General Information

All solvents and reagents were purchased from commercial sources (Energy or Meryer Chemicals etc.), they were analytically pure and used as received. Silica gel GF_{254} and column chromatography silica gel for isolation (200-300 mesh) were both purchased from Qingdao Broadchem Industrial Co., Ltd. Reaction progress was monitored by thin-layer chromatography (TLC) on silica gel GF_{254} with ultraviolet (UV_{254nm} and UV_{365nm}) detection. NMR spectra were measured either on a JMTC-500 (500 MHz) or a DPX Ascend 400 (400 MHz) spectrometer. The chemical shift values were corrected to 7.26 ppm (^{1}H NMR) and 77.16 ppm (^{13}C NMR) for $CHCl_3$. ^{1}H NMR splitting patterns are designated as singlet (s), double (d), triplet (t), quartet (q), doublet of doublets (dd), multiplets (m), etc. All first-order splitting patterns were assigned on the base of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). The identity of compounds was confirmed with HRMS using a Thermo Scientific Q Exactive. The melting point (m.p.) was corrected and recorded on the WRS-2A digital melting point instrument. The specific rotation ($[\alpha]_D^t$) was corrected and recorded on the SGWzz-3 polarimeter. The ee values were determined by HPLC LC-2030 Plus.

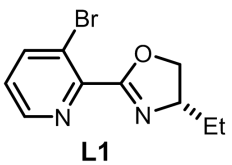
2. Synthesis and structural elucidation of new NHPyOx ligands

2.1 The synthesis of 3-bromo pyridine oxazolines

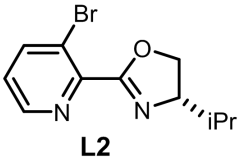


L1-L8

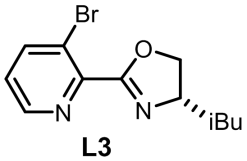
To a Schlenk flask charged with the compound 3-Bromo-2-cyanopyridine (3.0 mmol) and $Zn(OAc)_2$ (0.6 mmol, 0.2 equiv.) was added anhydrous PhCl (9 mL). Then chiral amino alcohol (3.6 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at 140 ℃ (heating mantle) until the full consumption of the starting material was detected by TLC. The mixture was quenched by the addition of a saturated aqueous solution of $NaHCO_3$ (5 mL) and separated, the water phase was extracted with EtOAc (5 mL × 3), and the combined organic phase was sequentially washed with water (5 mL × 2), dried over anhydrous sodium sulfate, and concentrated under vacuum. Purification by silica gel column chromatography on silica gel (200-300 m) with petroleum ether/EtOAc (3:1, v/v) as the eluent gave the compounds 3-Bromo-PyOx **L1-L8**.



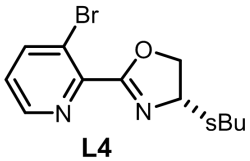
L1
Yellow oil, 52%



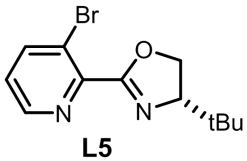
L2
Yellow oil, 55%



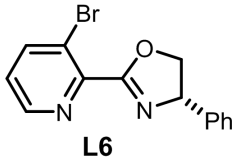
L3
Yellow oil, 65%



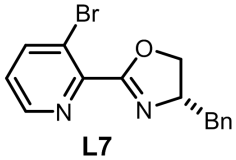
L4
Yellow oil, 75%



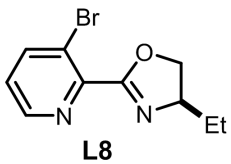
L5
Yellow oil, 72%



L6
Yellow oil, 55%

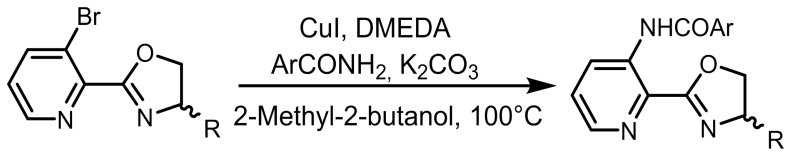


L7
Yellow oil, 68%



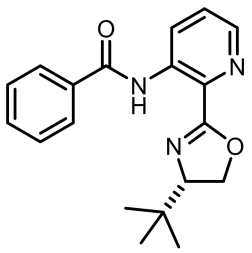
L8
Yellow oil, 55%

2.2 Synthesis and characteristic data of 3-arylamido-pyridine oxazolines



To a Schlenk tube charged with 3-Bromo-PyOx (0.2 mmol), K_2CO_3 (0.3 mmol, 1.5 equiv, 42 mg), CuI (0.05 mmol, 25 mol%, 9.5 mg), DMEDA (0.06 mmol, 30 mol%, 6.5 μL) and aryl formamide (0.4 mmol, 2.0 equiv) was added anhydrous 2-Methyl-2-butanol (0.8 mL, 0.25 M) under N_2 atmosphere. The reaction mixture was stirred at 100° C (heating mantle) until the full consumption of the starting material was detected by TLC. The mixture was quenched by the addition of H_2O (5 mL) and separated, the water phase was extracted with EtOAc (5 mL × 3), dried over anhydrous sodium sulfate, and concentrated under vacuum. Purification by silica gel column chromatography on silica gel (200-300 m) with petroleum ether/EtOAc (3:1, v/v) as the eluent gave the compounds 3-arylamido pyridine oxazolines.

(*S*)-N-(2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)pyridin-3-yl)benzamide (CL5)



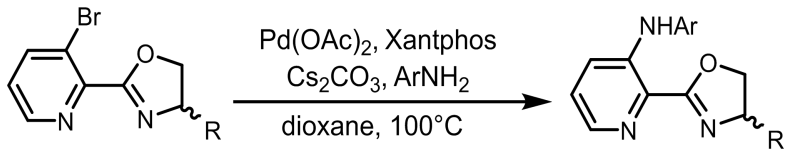
White solid, 31.0 mg, 48% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 13.01 (s, 1H), 9.33 (dd, J_1 = 8.6 Hz, J_2 = 1.5 Hz, 1H), 8.43 (dd, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H), 8.08 (dd, J_1 = 8.4 Hz, J_2 = 1.3 Hz, 2H), 7.61-7.53 (m, 1H), 7.51-7.43 (m, 3H), 4.53-4.43 (m, 1H), 4.36-4.26 (m, 2H), 0.97 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 163.9, 143.6, 138.2, 134.7, 132.3, 131.7, 128.8, 127.9, 127.6, 126.7, 76.7, 68.2, 34.1, 26.1.

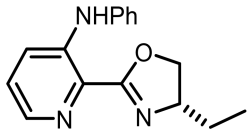
HRMS (ESI) $[M+H]^+$ calcd for $C_{19}H_{22}N_3O_2$: 324.1707, found: 324.1709.

2.3 Synthesis and characteristic data of 3-arylamino-pyridine oxazolines



To a Schlenk tube charged with 3-Bromo-PyOx (0.2 mmol), Cs_2CO_3 (0.4 mmol, 2.0 equiv, 130 mg), $Pd(OAc)_2$ (0.02 mmol, 10 mol%, 4.5 mg), Xantphos (0.024 mmol, 12 mol%, 13.9 mg) and arylamine (0.22 mmol, 1.2 equiv) was added anhydrous dioxane (1.0 mL, 0.2 M) under N_2 atmosphere. The reaction mixture was stirred at 100° C until the full consumption of the starting material was detected by TLC. The mixture was quenched by the addition of H_2O (5 mL) and separated, the water phase was extracted with EtOAc (5 mL × 3), dried over anhydrous sodium sulfate, and concentrated under vacuum. Purification by silica gel column chromatography on silica gel (200-300 m) with petroleum ether/EtOAc (5:1, v/v) as the eluent gave the compounds 3-arylamine pyridine oxazolines.

(*S*)-2-(4-ethyl-4,5-dihydrooxazol-2-yl)-N-phenylpyridin-3-amine (NL1)



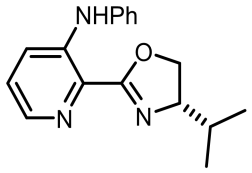
Yellow oil, 24.6 mg, 46% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.11 (dd, J_1 = 4.3 Hz, J_2 = 1.5 Hz, 1H), 7.65 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.42-7.33 (m, 2H), 7.27-7.22 (m, 2H), 7.18 (dd, J_1 = 8.6 Hz, J_2 = 4.4 Hz, 1H), 7.15-7.09 (m, 1H), 4.53 (dd, J_1 = 9.6 Hz, J_2 = 8.3 Hz, 1H), 4.42-4.34 (m, 1H), 4.09 (t, J = 8.1 Hz, 1H), 1.77-1.66 (m, 2H), 1.06 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 143.0, 140.3, 138.6, 129.6, 128.8, 126.0, 123.8, 122.3, 120.4, 71.3, 68.4, 29.1, 10.5.

HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{18}N_3O$: 268.1444, found: 268.1449.

(*S*)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)-N-phenylpyridin-3-amine (NL2)



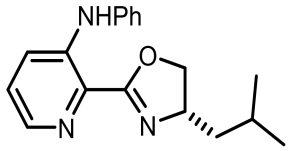
Yellow oil, 35.4 mg, 63% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.09 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 7.65 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.38-7.32 (m, 2H), 7.24-7.20 (m, 2H), 7.17-7.14 (m, 1H), 7.11-7.07 (m, 1H), 4.50-4.45 (m, 1H), 4.25-4.11 (m, 2H), 1.85-1.80 (m, 1H), 1.05 (d, J = 6.7 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 143.0, 140.4, 138.6, 129.6, 128.8, 125.9, 123.7, 122.0, 120.4, 73.1, 69.7, 33.4, 19.1, 18.9.

HRMS (ESI) $[M+H]^+$ calcd for $C_{17}H_{20}N_3O$: 282.1601, found: 282.1606.

(*S*)-2-(4-isobutyl-4,5-dihydrooxazol-2-yl)-N-phenylpyridin-3-amine (NL3)



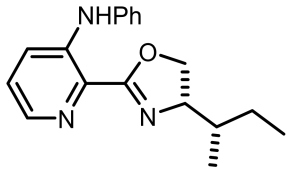
Yellow oil, 38.4 mg, 65% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 8.07 (dd, J_1 = 4.2 Hz, J_2 = 1.4 Hz, 1H), 7.61 (dd, J_1 = 8.8 Hz, J_2 = 1.5 Hz, 1H), 7.37-7.31 (m, 2H), 7.22-7.17 (m, 2H), 7.13 (dd, J_1 = 8.6 Hz, J_2 = 4.4 Hz, 1H), 7.11-7.04 (m, 1H), 4.52 (dd, J_1 = 9.5 Hz, J_2 = 7.8 Hz, 1H), 4.47-4.41 (m, 1H), 3.98 (t, J = 7.9 Hz, 1H), 1.91-1.79 (m, 1H), 1.69-1.64 (m, 1H), 1.46-1.41 (m, 1H), 0.98 (dd, J_1 = 6.6 Hz, J_2 = 4.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 142.9, 140.3, 138.6, 129.6, 128.8, 125.9, 123.7, 122.1, 120.4, 72.1, 65.4, 45.6, 25.9, 23.0, 22.7.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{22}N_3O$: 296.1757, found: 296.1749.

2-((*S*)-4-((*S*)-sec-butyl)-4,5-dihydrooxazol-2-yl)-N-phenylpyridin-3-amine (NL4)



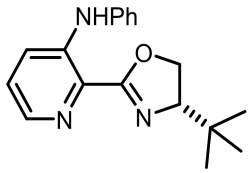
Yellow oil, 44.3 mg, 75% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.12 (dd, J_1 = 4.5 Hz, J_2 = 1.4 Hz, 1H), 7.67 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.41-7.37 (m, 2H), 7.25 (d, J = 7.9 Hz, 2H), 7.21-7.11 (m, 2H), 4.49 (t, J = 8.3 Hz, 1H), 4.35-4.30 (m, 1H), 4.17 (t, J = 8.1 Hz, 1H), 1.72-1.69 (m, 2H), 1.35-1.26 (m, 1H), 0.99 (t, J = 7.3 Hz, 3H), 0.94 (t, J = 5.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 142.9, 140.3, 138.6, 129.6, 128.8, 125.9, 123.7, 122.0, 120.3, 71.7, 69.3, 39.5, 26.1, 15.0, 11.4.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{22}N_3O$: 296.1757, found: 296.1760.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-N-phenylpyridin-3-amine (NL5)



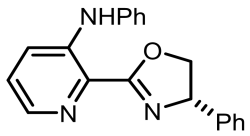
Yellow solid, 42.5 mg, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.12 (dd, J_1 = 4.3Hz, J_2 = 1.4 Hz, 1H), 7.71 (dd, J_1 = 8.6 Hz, J_2 =1.4 Hz, 1H), 7.40-7.36 (m, 2H), 7.26-7.24 (m, 2H), 7.22-7.18 (m, 1H), 7.14-7.09 (m, 1H), 4.43 (dd, J_1 = 9.7 Hz, J_2 = 8.2 Hz, 1H), 4.30-4.20 (m, 2H), 1.00 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 169.2, 143.9, 140.1, 137.2, 130.4, 129.6, 127.2, 123.9, 122.4, 121.9, 63.6, 60.0, 33.8, 27.1.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{22}N_3O$: 296.1757, found: 296.1750.

(*S*)-N-phenyl-2-(4-phenyl-4,5-dihydrooxazol-2-yl) pyridin-3-amine (NL6)



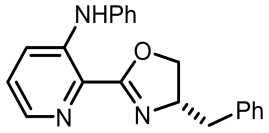
Yellow oil, 36.6 mg, 58% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 8.18 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 7.68 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.44-7.32 (m, 7H), 7.28-7.20 (m, 3H), 7.17-7.11 (m, 1H), 5.59 (dd, J_1 = 10.2 Hz, J_2 = 8.6 Hz, 1H), 4.88 (dd, J_1 = 10.2 Hz, J_2 = 8.5 Hz, 1H), 4.33 (t, J = 8.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 143.5, 142.1, 140.0, 138.7, 129.5, 128.9, 128.3, 127.8, 126.7, 126.3, 124.1, 122.7, 120.5, 73.7, 70.4.

HRMS (ESI) $[M+H]^+$ calcd for $C_{20}H_{18}N_3O$: 316.1444, found: 316.1449.

(*S*)-2-(4-benzyl-4,5-dihydrooxazol-2-yl)-N-phenylpyridin-3-amine (NL7)



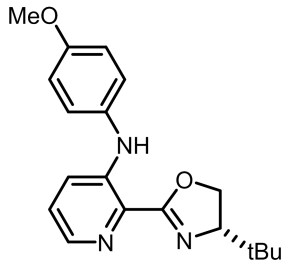
Yellow oil, 42.1 mg, 64% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H), 8.09 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 7.65 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.39-7.33 (m, 2H), 7.32-7.24 (m, 5H), 7.21-7.15 (m, 3H), 7.12-7.09 (m, 1H), 4.72-4.66 (m, 1H), 4.47 (dd, J_1 = 9.4 Hz, J_2 = 8.5 Hz, 1H), 4.18 (dd, J_1 = 8.5 Hz, J_2 = 7.6 Hz, 1H), 3.10 (dd, J_1 = 13.6 Hz, J_2 = 7.1 Hz, 1H), 2.86 (dd, J_1 = 13.6 Hz, J_2 = 7.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.0, 143.1, 140.3, 138.7, 138.1, 129.6, 129.3, 128.72, 128.67, 126.7, 126.1, 123.8, 122.1, 120.7, 71.1, 68.4, 42.3.

HRMS (ESI) $[M+H]^+$ calcd for $C_{21}H_{20}N_3O$: 330.1601, found: 330.1609.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-*N*-(4-methoxyphenyl)pyridin-3-amin e (NL8)



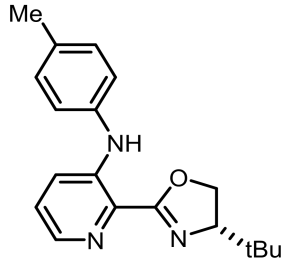
Yellow oil, 34.5 mg, 53% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.53 (s, 1H), 8.05 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 7.57 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.17-7.10 (m, 5H), 4.40-4.37 (m, 1H), 4.26-4.17 (m, 2H), 3.81 (s, 3H), 0.96 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 156.7, 144.4, 137.9, 133.1, 128.0, 126.0, 125.1, 119.7, 114.9, 76.5, 67.7, 55.6, 34.0, 26.0.

HRMS (ESI) $[M+H]^+$ calcd for $C_{19}H_{24}N_3O_2$: 326.1863, found: 326.1869.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-*N*-(p-tolyl)pyridin-3-amine (NL9)



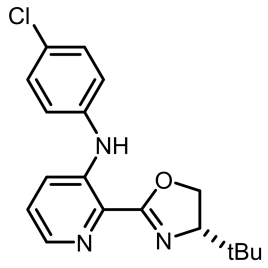
Yellow oil, 28.4 mg, 46% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.03 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 7.40 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.20-7.07 (m, 3H), 6.96-6.84 (m, 2H), 4.39 (dd, J_1 = 9.4 Hz, J_2 = 8.5 Hz, 1H), 4.28-4.14 (m, 2H), 2.34 (s, 3H), 0.95 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 143.5, 138.2, 137.6, 133.5, 130.2, 128.4, 126.0, 122.4, 120.1, 76.4, 67.7, 33.9, 26.0, 20.9.

HRMS (ESI) $[M+H]^+$ calcd for $C_{19}H_{24}N_3O$: 310.1914, found: 310.1918.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-*N*-(4-chlorophenyl)pyridin-3-amine (NL10)



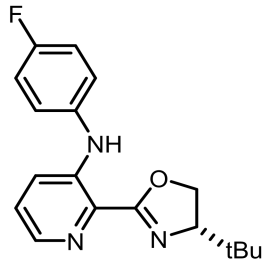
Yellow oil, 42.1 mg, 64% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.25 (s, 1H), 7.92 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 7.54 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.31-7.25 (m, 2H), 7.19 (dd, J_1 = 8.6 Hz, J_2 = 4.3 Hz, 1H), 7.16-7.10 (m, 2H), 3.98-3.90 (m, 2H), 3.69-3.63 (m, 1H), 1.03 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 143.6, 138.8, 137.6, 130.7, 129.6, 128.8, 127.3, 123.5, 121.8, 63.6, 60.1, 33.8, 27.1.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{21}ClN_3O$: 330.1368, found: 330.1370.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-*N*-(4-fluorophenyl)pyridin-3-amine (NL11)



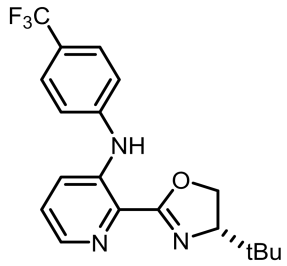
Yellow oil, 45.1 mg, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.07 (dd, J_1 = 4.4 Hz, J_2 = 1.4 Hz, 1H), 7.48 (dd, J_1 = 8.7 Hz, J_2 = 1.5 Hz, 1H), 7.36-7.29 (m, 1H), 7.19-7.12 (m, 2H), 7.05 (t, J = 8.6 Hz, 2H), 4.39 (dd, J_1 = 9.8 Hz, J_2 = 8.3 Hz, 1H), 4.27-4.16 (m, 2H), 0.96 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 159.5 (d, J = 242.7 Hz), 156.5, 145.7, 138.4, 136.0 (d, J = 2.6 Hz), 123.8 (d, J = 8.0 Hz), 116.3 (d, J = 22.5 Hz), 115.4, 109.2, 76.5, 69.3, 34.1, 26.0.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{21}FN_3O$: 314.1663, found: 314.1658.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-*N*-(4-(trifluoromethyl) phenyl) pyridin-3-amine (NL12)



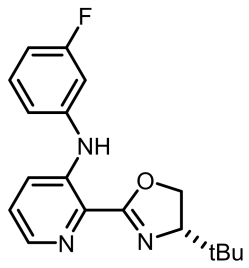
Yellow oil, 41.5 mg, 57% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 8.20 (dd, J_1 = 4.4 Hz, J_2 = 1.4 Hz, 1H), 7.79 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.32-7.24 (m, 3H), 4.43 (dd, J_1 = 9.8 Hz, J_2 = 8.3Hz, 1H), 4.33-4.20 (m, 2H), 0.98 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 144.0, 141.3, 139.9, 130.0, 126.9 (q, J = 3.7 Hz), 125.9, 124.6, 124.3 (d, J = 271.1 Hz), 124.2, 119.4, 76.4, 67.9, 33.9, 26.0.

HRMS (ESI) $[M+H]^+$ calcd for $C_{19}H_{21}F_3N_3O$: 364.1631, found: 364.1638.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-*N*-(3-fluorophenyl)pyridin-3-amine (NL13)



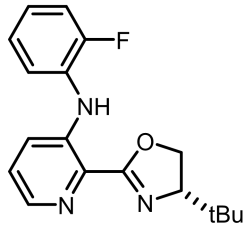
Yellow oil, 38.8 mg, 62% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.83 (s, 1H), 8.15 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 7.74 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 1H), 7.29 (td, J_1 = 8.3 Hz, J_2 = 6.6 Hz, 1H), 7.22 (dd, J_1 = 8.6 Hz, J_2 = 4.3 Hz, 1H), 7.01-6.91 (m, 2H), 6.76 (dd, J_1 = 8.3 Hz, J_2 = 2.4 Hz, 1H), 4.42 (dd, J_1 = 10.0 Hz, J_2 = 8.4 Hz, 1H), 4.29-4.19 (m, 2H), 0.98 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7 (d, J = 245.8 Hz), 163.5, 142.4 (d, J = 10.1 Hz), 142.1, 139.3, 130.7 (d, J = 9.8 Hz), 129.4, 126.0, 120.9, 116.5 (d, J = 2.9 Hz), 109.9 (d, J = 21.3 Hz), 107.7 (d, J = 23.7 Hz), 76.4, 67.8, 33.9, 26.0.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{21}FN_3O$: 314.1663, found: 314.1660.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-*N*-(2-fluorophenyl)pyridin-3-amine (NL14)



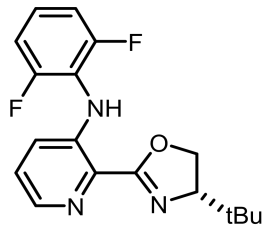
Yellow oil, 33.8 mg, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.11 (dd, J_1 = 4.3 Hz, J_2 = 1.4 Hz, 1H), 7.56-7.53 (m, 1H), 7.41-7.37 (m, 1H), 7.19-6.98 (m, 4H), 4.39 (dd, J_1 = 9.3 Hz, J_2 = 7.7 Hz, 1H), 4.26-4.17 (m, 2H), 0.95 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 155.5 (d, J = 245.9 Hz), 142.2, 139.0, 129.4, 128.5 (d, J = 11.8 Hz), 125.8, 124.3 (d, J = 3.8 Hz), 124.1 (d, J = 7.4 Hz), 122.2 (d, J = 1.8 Hz), 120.4 (d, J = 1.2 Hz), 116.3 (d, J = 19.6 Hz), 76.4, 67.8, 33.9, 25.9.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{21}FN_3O$: 314.1663, found: 314.1669.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-*N*-(2,6-difluorophenyl)pyridin-3-amine (NL15)



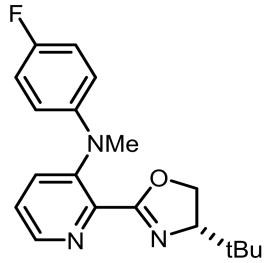
Yellow oil, 42.9 mg, 65% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.11 (d, *J* = 4.4 Hz, 1H), 7.19-7.07 (m, 2H), 6.98-6.94 (m, 3H), 4.41-4.37 (m, 1H), 4.27-4.18 (m, 2H), 0.94 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 157.78 (d, *J* = 249.2), 157.74 (d, *J* = 249.2),142.6, 139.0, 128.8, 125.2 (t, *J* = 9.6 Hz), 120.6 (d, *J* = 3.0 Hz), 117.2 (d, *J* = 15.7 Hz), 112.2 (d, *J* = 4.8 Hz), 112.0 (d, *J* = 4.7 Hz), 76.3, 67.8, 33.9, 25.8.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{20}F_2N_3O$: 331.1496, found: 331.1490.

(*S*)-2-(4-(tert-butyl)-4,5-dihydrooxazol-2-yl)-N-(4-fluorophenyl)-N-methylpyridin-3-amine (NMeNL11)



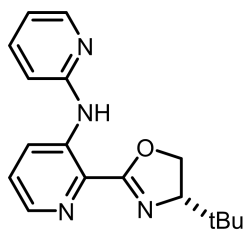
Yellow oil, 24.9 mg, 38% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55-8.53 (m, 1H), 7.62-7.60 (m, 1H), 7.43-7.40 (m, 1H), 6.88-6.84 (m, 2H), 6.58-6.55 (m, 2H), 4.16-4.12 (m, 1H), 3.95-3.91 (m, 1H), 3.89-3.84 (m, 1H), 3.26 (s, 3H), 0.79 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 156.7 (d, *J* = 237.1 Hz), 146.2, 145.3 (d, *J* = 8.8 Hz), 144.9, 136.6, 129.1 (d, *J* = 9.1 Hz), 126.3, 116.3 (d, *J* = 7.7 Hz), 115.5 (d, *J* = 22.4 Hz), 76.6, 68.8, 40.9, 33.6, 26.0.

HRMS (ESI) $[M+H]^+$ calcd for $C_{19}H_{23}FN_3O$: 328.1820 found: 328.1828.

(*S*)-*N*-(2-(4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)pyridin-3-yl)pyridin-2-amine (ZNL1)



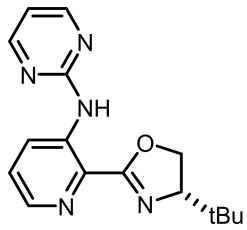
Yellow oil, 50.3 mg, 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 9.34 (dd, J_1 = 8.7, J_2 = 1.5 Hz, 1H), 8.30 – 8.28 (m, 1H), 8.22 (dd, J_1 = 4.4, J_2 = 1.5 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.35 (dd, J_1 = 8.7, J_2 = 4.4 Hz, 1H), 6.84 (dd, J_1 = 5.0, J_2 = 0.9 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 4.53 – 4.37 (m, 1H), 4.33 – 4.21 (m, 2H), 1.02 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 155.2, 147.7, 140.7, 140.3, 137.7, 129.7, 126.3, 125.3, 116.2, 113.1, 76.5, 67.9, 34.1, 26.1.

HRMS (ESI) $[M+H]^+$ calcd for $C_{17}H_{21}N_4O$: 297.1710 found: .297.1714

(*S*)-*N*-(2-(4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)pyridin-3-yl)pyrimidin-2-amine (ZNL2)



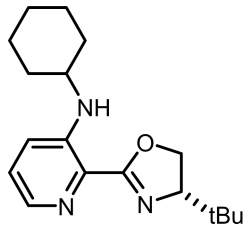
Yellow oil, 52.9 mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.28 (s, 1H), 9.30 (dd, J_1 = 8.7, J_2 = 1.5 Hz, 1H), 8.48 (d, J = 4.8 Hz, 2H), 8.28 (dd, J_1 = 4.4, J_2 =1.5 Hz, 1H), 7.38 (dd, J_1 = 8.7, J_2 = 4.4 Hz, 1H), 6.78 (t, J = 4.8 Hz, 1H), 4.43 – 4.39 (m, 1H), 4.31 – 4.28 (m, 2H), 1.02 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 160.3, 158.0, 141.1, 139.4, 130.6, 126.02, 125.98, 113.6, 76.5, 68.0, 34.2, 26.0.

HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{20}N_5O$: 298.1662 found: .298.1665

(*S*)-2-(4-(*tert*-butyl)-4,5-dihydrooxazol-2-yl)-*N*-cyclohexylpyridin-3-amine (ZNL3)



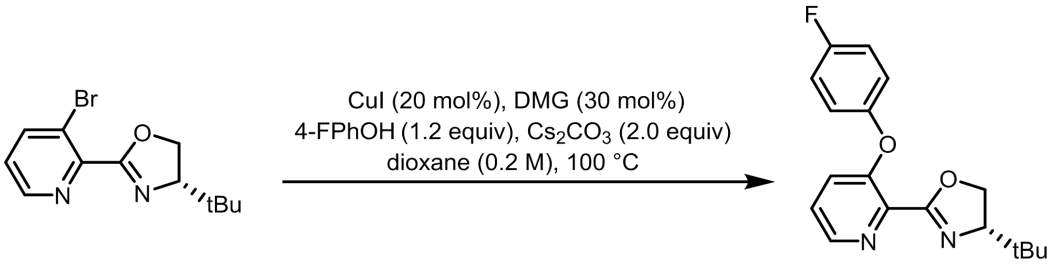
Yellow oil, 53.5 mg, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.91 (dd, J_1 = 4.3, J_2 =1.4 Hz, 1H), 7.14 (dd, J_1 = 8.6, J_2 = 4.3 Hz, 1H), 7.02 (dd, J_1 = 8.8, J_2 = 1.4 Hz, 1H), 4.37 – 4.30 (m, 1H), 4.20 – 4.13 (m, 2H), 3.38 – 3.21 (m, 1H), 2.20 – 1.94 (m, 2H), 1.79 – 1.74(m, 2H), 1.62– 1.57 (m, 1H), 1.43 – 1.27 (m, 5H), 0.94 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 145.3, 135.7, 127.2, 126.2, 118.1, 76.5, 67.4, 50.3, 34.0, 32.8, 32.7, 26.0, 25.9, 24.6, 24.4.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{28}N_3O$: 302.2227 found: 302.2235

(*S*)-4-(tert-butyl)-2-(3-(4-fluorophenoxy)pyridin-2-yl)-4,5-dihydrooxazole (OL11)



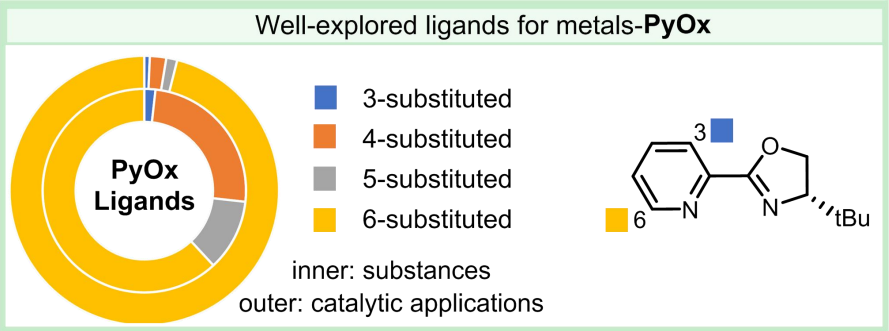
Yellow oil, 20.1 mg, 32% yield.

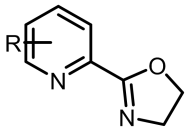
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43-8.42 (m, 1H), 7.32-7.26 (m, 2H), 6.99-6.84 (m, 4H), 4.29 (dd, J_1 = 10.1 Hz, J_2 = 8.5 Hz, 1H), 4.15-4.02 (m, 2H), 0.79 (s, 9H).

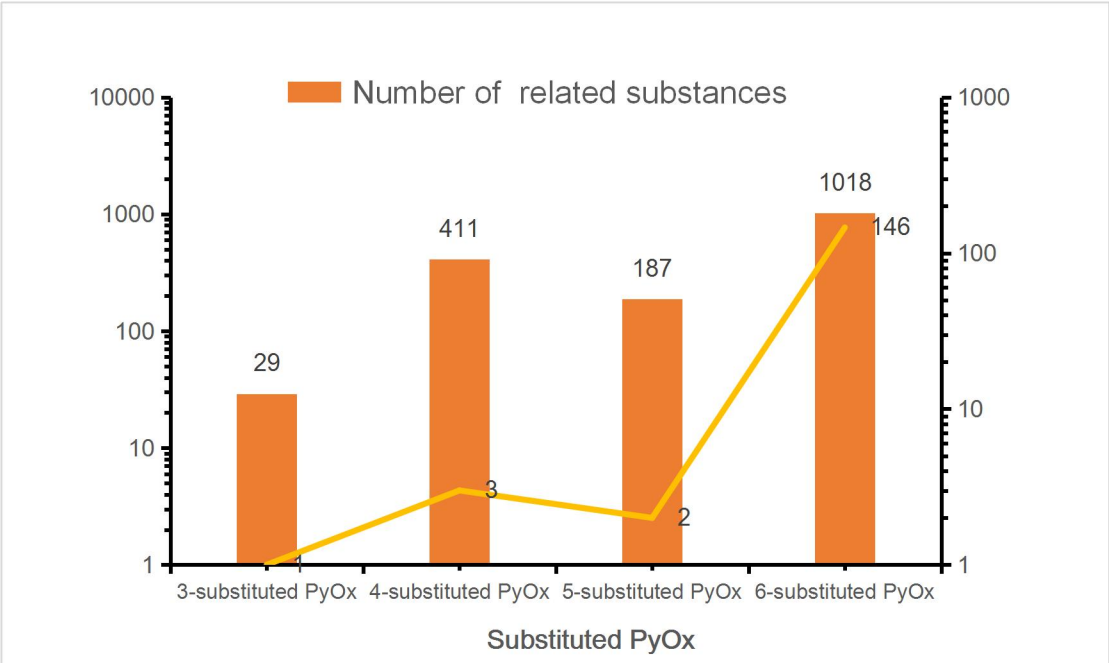
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 159.0 (d, J = 242.1 Hz), 153.0, 152.9 (d, J = 2.5 Hz), 144.9, 139.8, 128.2, 126.3, 119.7 (d, J = 8.4 Hz), 116.5 (d, J = 23.4 Hz),77.0,68.7, 34.0, 25.9.

HRMS (ESI) $[M+H]^+$ calcd for $C_{18}H_{20}FN_2O_2$: 315.1503, found: 315.1510.

2.4 Analysis of substituted PyOx ligands for asymmetric transformations

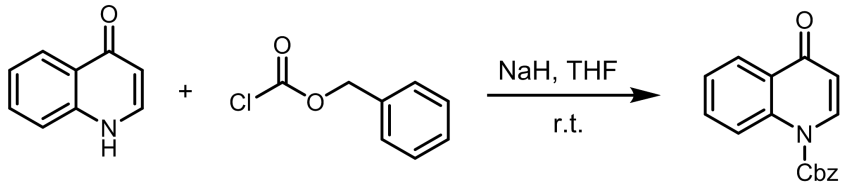


	Note
3-substituted PyOx	29 related substances 1 reference on asymmetric transformation
4-substituted PyOx	411 related substances 3 references on asymmetric transformation
5-substituted PyOx	187 related substances 2 references on asymmetric transformation
6-substituted PyOx	1018 related substances 146 references on asymmetric transformation



Scifinder search profiles of the non-ring fused PyOx ligands in asymmetric transformations were listed below (accessed on 08/29/2022)

3. Asymmetric addition of arylboronic acid to *N*-Cbz-4-quinolone

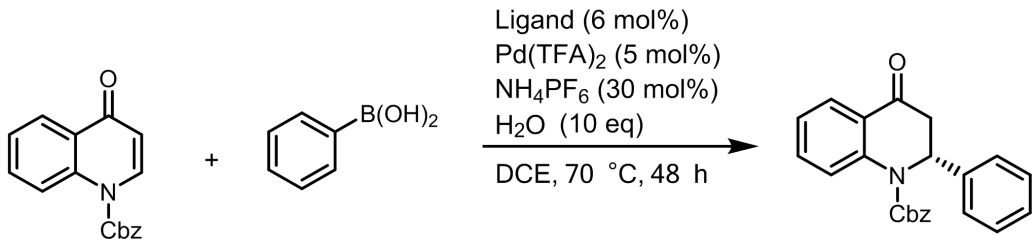


A solution of quinolin-4(1H)-ones (2.90 g, 20 mmol, 1 eq) in THF (20 mL) was added to a suspension of NaH (1.44 g, 60 mmol, 3 eq) in THF (15 mL) at room temperature, and the resulting mixture was stirred for 15 min at 55 °C. Benzyl chloroformate (3.73 mL, 30 mmol, 1.5 eq) was then added to it dropwise, and the mixture was stirred for 48 h at room temperature. The reaction was quenched with water and extracted with EtOAc. The organic layer was dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with petroleum ether/EtOAc (5:1, v/v) to afford compound as a white solid (1.65 g, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ δ 8.68 (d, J_1 = 9.0 Hz, 1H), 8.50 – 8.27 (m, 2H), 7.72 – 7.55 (m, 1H), 7.53 – 7.39 (m, 6H), 6.26 (d, J = 8.6 Hz, 1H), 5.47 (s, 2H).

The NMR data are in accordance with previously reported data (Org. Lett. 2022, 24, 5, 1228–1231.).

Unless otherwise mentioned, the other substituted *N*-Cbz-4-quinolone were synthesized according to this procedure.



1 **2** **3**

General procedure

Step 1: To a Schlenk tube charged $Pd(TFA)_2$ (1.7 mg, 5 mol%, 0.05 eq) and ligand (6 mol%, 0.06 eq) was added DCE (0.5 mL), The mixture was stirred at 70 ℃ (heating

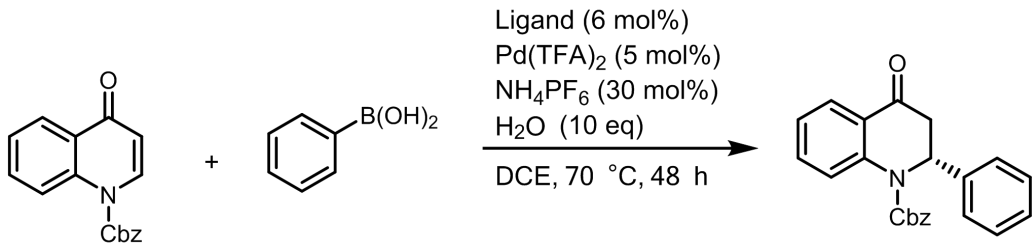
mantle) for 2 h to afford the catalyst solution.

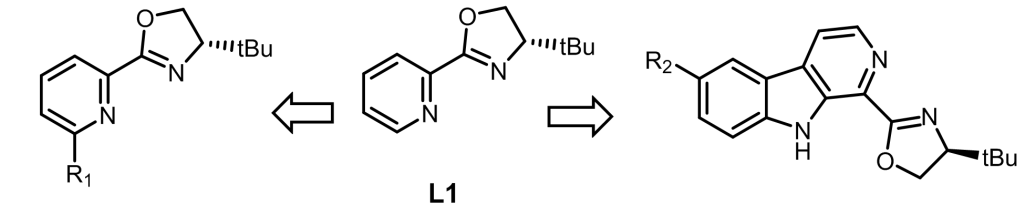
Step 2: To the above solution was added phenyl boronic acid (24.4 mg, 0.2 mmol, 2eq), NH_4PF_6 (4.9 mg, 30 mol%, 0.3 eq), **1** (27.9 mg, 0.1 mmol, 1 eq) and H_2O (18 μL, 10 eq). The wall of the tube was rinsed with DCE (0.5 mL) or some oil substrate was dissolved in DCE (0.5 mL) (The volume of solvent is 1.0 mL). The tube was placed in the modules of the reactor which was set at 70 ℃ (heating mantle) for 48 h, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography with petroleum ether/EtOAc (5/1, v/v) to give the product.

3.1 Establishement of the optimal condition

3.1.1 Initial chiral ligands screening

Table S1. Initial Ligand evaluation



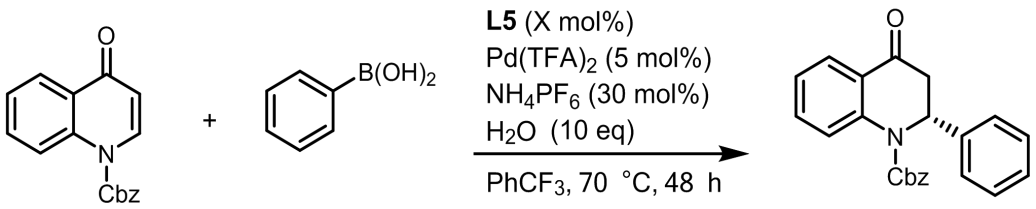


L2: R_1= CF_3, trace
L3: R_1=OMe, trace
L4: R_1= CH_3, trace

L1
53% yield, 72%ee

L5: R_2= H, 15% yield, 80%ee
L6: R_2=OMe, 8% yield, 66% ee
L7: R_2= Cl, trace

Table S2. Evaluation of Ligand loading

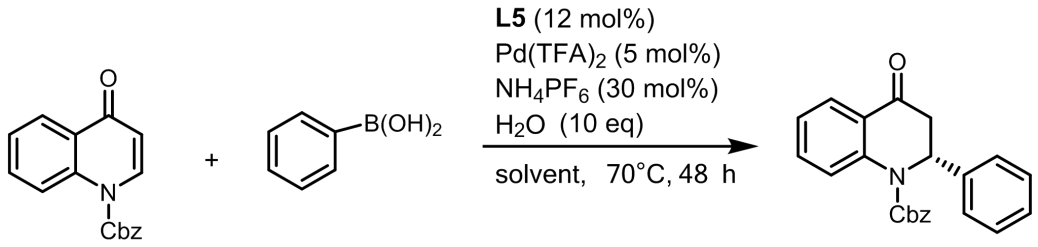


Entry	Ligand / mol%	Yield [a] / %	ee [b]/ %
1	5	28	0
2	6	15	80
3	7.5	15	46
4	10	22	64
5	12	42	77
6	15	48	77
7	20	28	87

a All reactions were run at 0.1 mmol scale. *b* Isolated yield and ee values were determined by HPLC on a chiral stationary phase.

3.1.2 Solvents screening

Table S3. Solvent effects



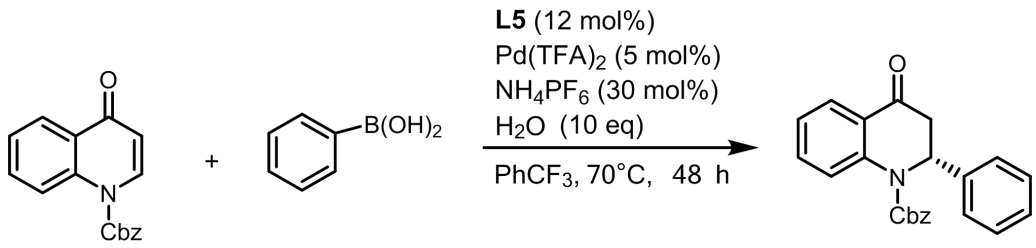
Entry	Solvent	Yield [a] / %	ee [b] / %
1	MeOH	56	87
2	EtOH	36	83
3	IPA	53	69
4	HFIP	trace	N.T.
5	Toluene	53	86
6	PhCl	46	84
7	DCB	28	27
.8.	$PhCF_3$	67	92
9	DMB	trace	trace
10	Benzene	47	80
11	DMF	28	89
12	DMSO	trace	N.T.
13	DCE	42	77
14	THF	trace	N.T.
15	MeOH: $PhCF_3$ (1:1)	31	86
16	H_2O	11	85

17	$PhNO_2$	39	65
18	DMPU	trace	N.T.
19	DCE: H_2O (1:1)	22.4	85

a All reactions were run at 0.1 mmol scale. *b* Isolated yield and ee values were determined by HPLC on a chiral stationary phase.

3.1.3 Arylboronic acid loading

Table S4. Stoichiometry of arylboronic acid

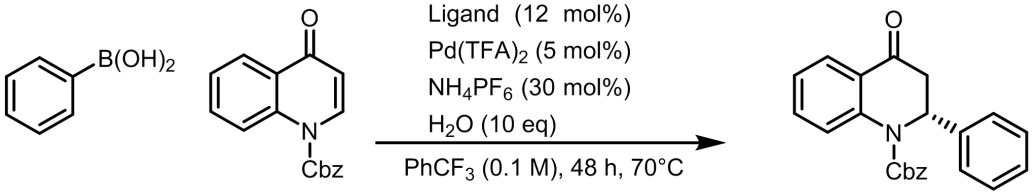


Entry	$PhB(OH)_2$ / eq	Yield [a] / %	ee [b] / %
1	1	34	80
2	2	67	92
3	3	63	77
4	4	43	85

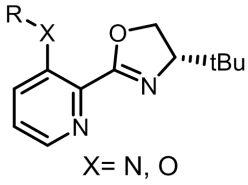
a All reactions were run at 0.1 mmol scale. *b* Isolated yield and ee values were determined by HPLC on a chiral stationary phase.

3.1.4 Ligands optimization based on L5

Table S5. Ligands optimization based on **L5**



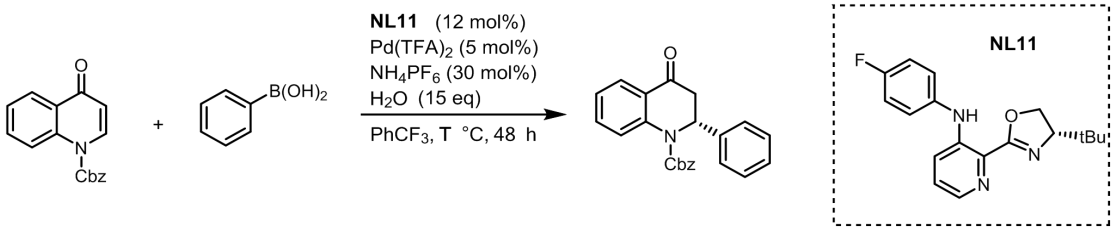
NL5:	45% yield,64% ee	**NL14:**	84% yield, 80% ee
NL8:	31% yield,92% ee	**NL15:**	56% yield, 84% ee
NL9:	53% yield,89% ee	**OL11:**	trace, N.T.
NL10:	78% yield,82% ee	**NMeNL11:**	trace, N.T.
NL11:	95% yield,73% ee	**ZNL1:**	trace, N.T.
NL12:	59% yield,59% ee	**ZNL3:**	trace, N.T.
NL13:	70% yield, 80% ee	**CL5:**	trace, N.T.



a All reactions were run at 0.1 mmol scale. *b* Isolated yield and ee values were determined by HPLC on a chiral stationary phase. on a chiral stationary phase.

3.1.5 Other parameters optimization

Table S6. Temperature influence

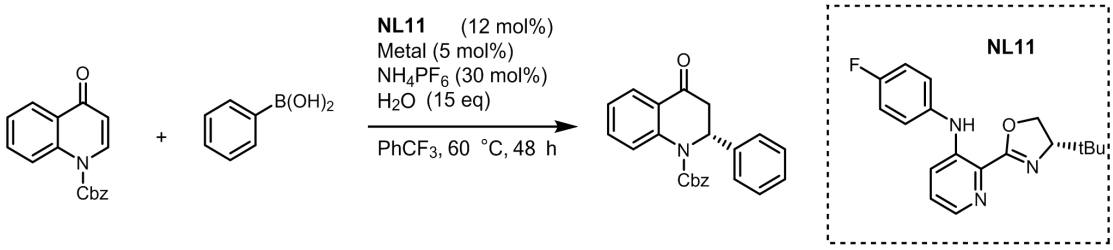


Entry	T / ℃	Yield [a] / %	ee [b] / %
1	70	95	73
2	60	95	91
3	50	90	95

a All reactions were run at 0.1 mmol scale. *b* Isolated yield and ee values were

determined by HPLC on a chiral stationary phase.

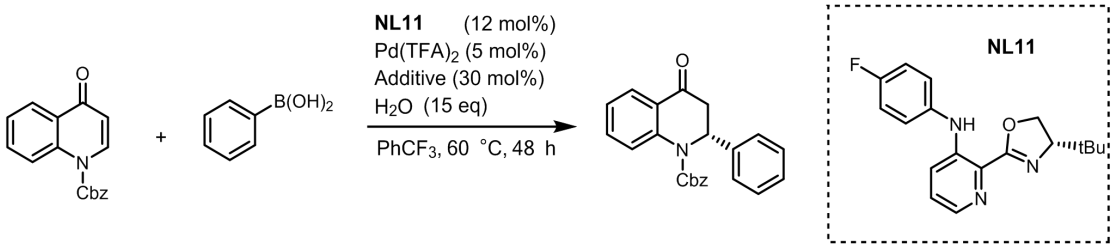
Table S7. Metal Screening



Entry	Metal	L2/mol%	Yield [a] / %	ee [b] / %
1	$Pd(OAc)_2$	12	78	87
2	$PdCl_2$	12	trace	--
3	$(Ph_3P)_2PdCl_2$	12	trace	--
4	$Cu(OAc)_2 \cdot H_2O$	12	trace	--
5	AgTFA	12	trace	--
6	$Pd(TFA)_2$	12	95	91
7	$Pd(TFA)_2$	6	70	87
8	$Pd(TFA)_2$	7.5	84	89
9	$Pd(TFA)_2$	10	89	86

a All reactions were run at 0.1 mmol scale. *b* Isolated yield and ee values were determined by HPLC on a chiral stationary phase.

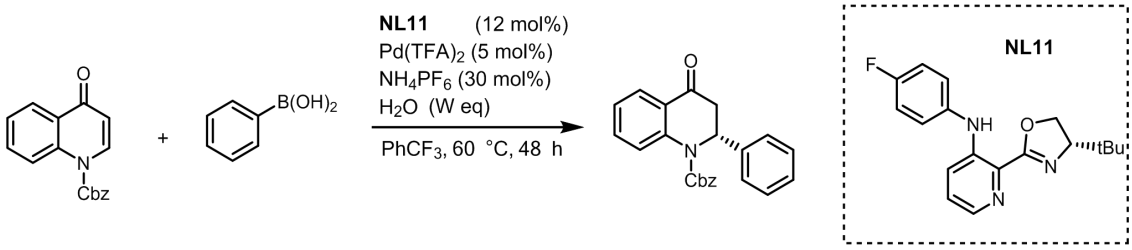
Table S8. Screening of additives



Entry	Additive	Additive/mol%	Yield [a] / %	ee [b] / %
1	NH_4BF_4	30	59	77
2	$NaSbF_6$	30	56	75
3	Ag_2CO_3	30	56	93
4	$B(C_6F_5)_3$	30	70	81
5	4-$FPhNH_2$	30	11	93
6	NH_4PF_6+4-$FPhNH_2$	30:12	78	89
7	NH_4PF_6	0	78	88
8	NH_4PF_6	10	84	95
9	NH_4PF_6	20	92	93
10	NH_4PF_6	30	95	91
11	NH_4PF_6	40	95	83
12	NH_4PF_6	50	78	90

a All reactions were run at 0.1 mmol scale. *b* Isolated yield and ee values were determined by HPLC on a chiral stationary phase.

Table S9. Stoichiometry of H_2O

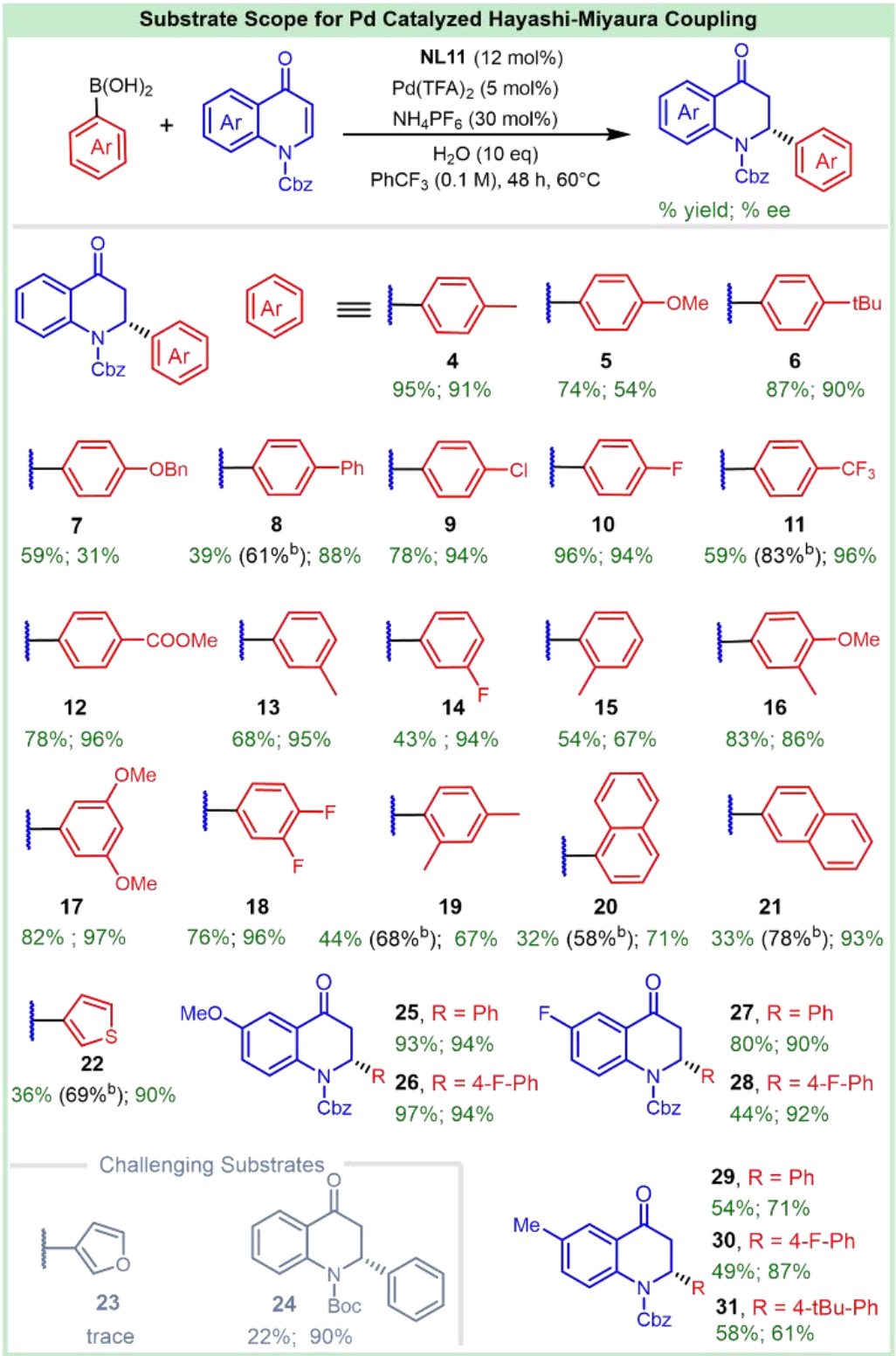


Entry	H_2O / eq	Yield [a] / %	ee [b] / %
1	0	84	92
2	5	95	89
3	10	95	91
5	20	95	92

a All reactions were run at 0.1 mmol scale. *b* Isolated yield and ee values were determined by HPLC on a chiral stationary phase.

3.2 Substrate scope

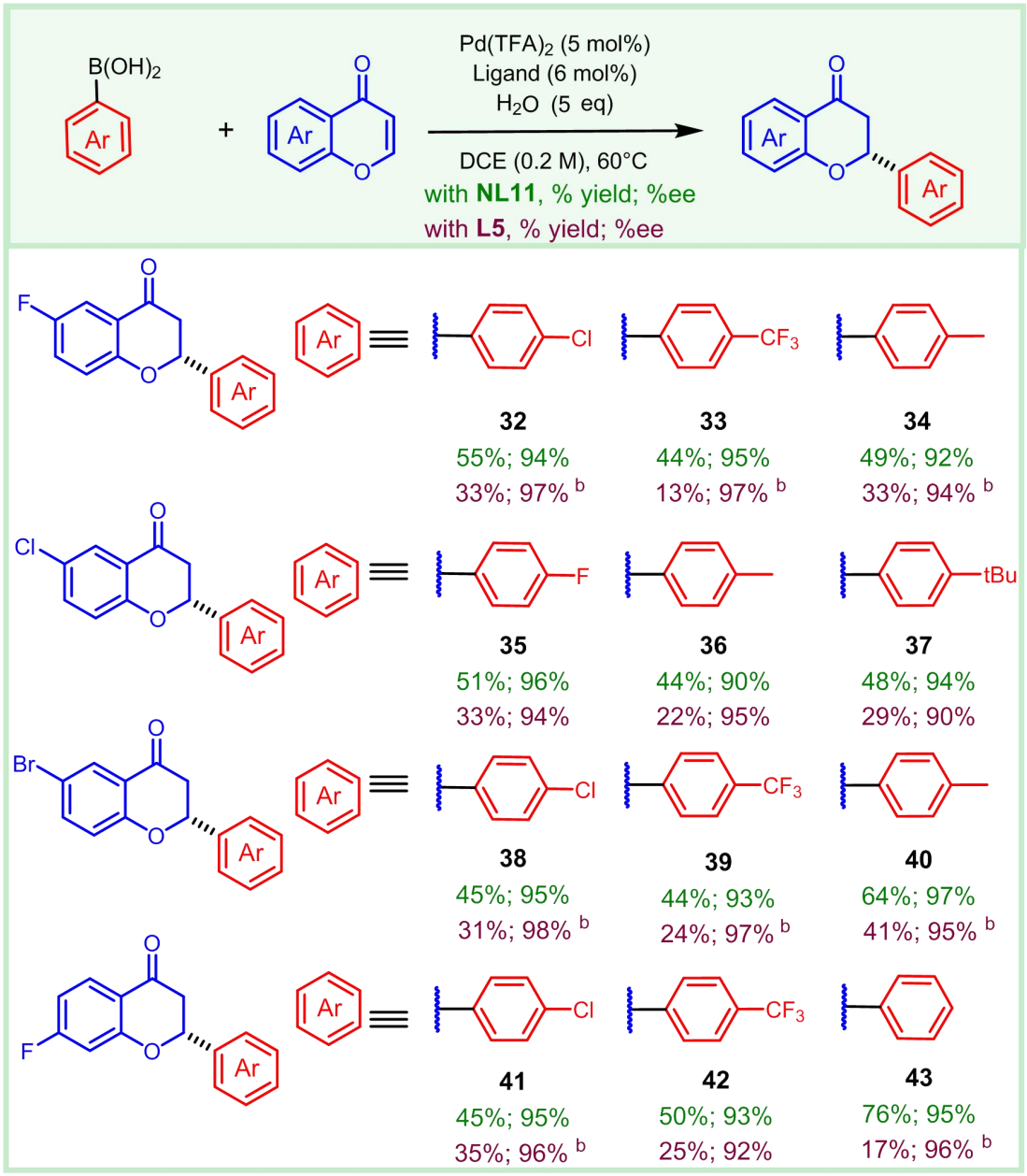
Table S10. Substrate scope for asymmetric addition of arylboronic acids to quinolones



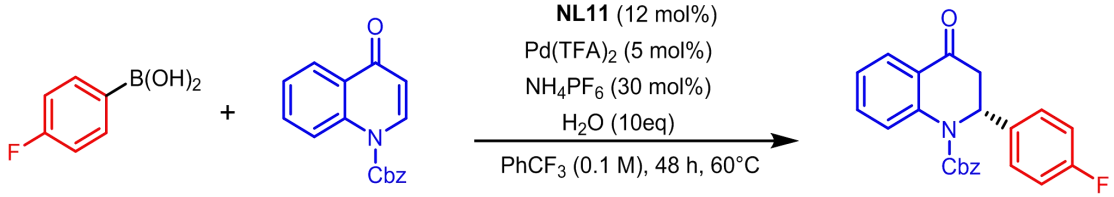
[a] Unless otherwise mentioned, the yields refer to the isolated yield, and the ee values were determined by HPLC on a chiral phase.

[b] Yield brsm.

3.3 Asymmetric addition of aryboronic acid to chromone by NL11



4. Procedure for the Synthesis of 10 on a 1-mmol-scale

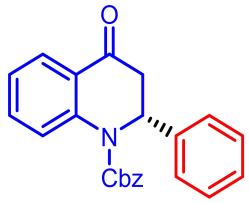


Step 1: To a Schlenk tube charged $Pd(TFA)_2$ (17 mg, 5 mol%) and NL11 (37 mg, 12 mol%) was added DCE (5.0 mL), The mixture was stirred at 60 ℃ (heating mantle) for 2 h to afford the catalyst solution.

Step 2: To the above solution was added 4F-phenyl boronic acid (280 mg, 2.0 mmol), NH_4PF_6 (49 mg, 30 mol%), **1** (279 mg, 1 mmol) and H_2O (180 μL, 10 eq). The wall of the tube was rinsed with DCE (5.0 mL) or some oil substrate was dissolved in DCE (0.5 mL) (The volume of solvent is 1.0 mL). The tube was placed in the modules of the reactor which was set at 60 ℃ (heating mantle) for 48 h, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography with petroleum ether/EtOAc (5/1, v/v) to give the product (325 mg, 87% yield).

5. Spectroscopic data for 2-phenyl-3,4-dihydroquinolines

(*R*)-benzyl 4-oxo-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate (3)



Yellow solid (95% isolated yield, 33.9 mg, 0.1 mmol), mp: 149.0-151.7 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J_1 = 7.8 Hz, J_2 =1.7 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.38-7.25 (m, 6H), 7.14-7.06 (m, 5H), 7.00-6.96 (m, 1H), 6.16 (dd, J_1 = 4.8 Hz, J_2 = 3.2 Hz, 1H), 5.32 (d, J = 12.2 Hz, 1H), 5.24 (d, J = 12.3 Hz, 1H), 3.22-3.21 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 154.4, 141.6, 138.2, 135.7, 134.7, 128.8, 128.7, 128.6, 128.3, 127.7, 127.0, 126.7, 125.2, 124.5, 124.3, 68.6, 56.2, 42.4.

$[\alpha]_D^{21}$= +78.6° (*c* 0.1, MeOH).

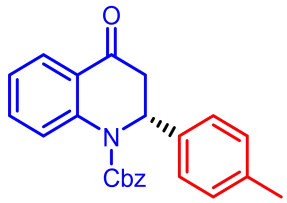
HRMS (ESI) $[M+H]^+$ calcd for $C_{23}H_{20}NO_3$: 358.1438, found: 358.1429.

HPLC Conditions: IPA/Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =13.0 min, major =16.2 min; ee =91%.

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	13.078	22606586	862042	M	50.163				50.163
2	16.499	22459396	736489	M	49.837				49.837
总计		45065982	1598531		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)- benzyl 4-oxo-2-(*p*-tolyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (4)



Yellow solid (95% isolated yield, 35.2 mg, 0.1 mmol), mp: 108.8-111.4 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

The NMR data and HRMS data are in accordance with that of previous publications (*Eur. J. Org. Chem*. 2011, 8, 1443–1446.)

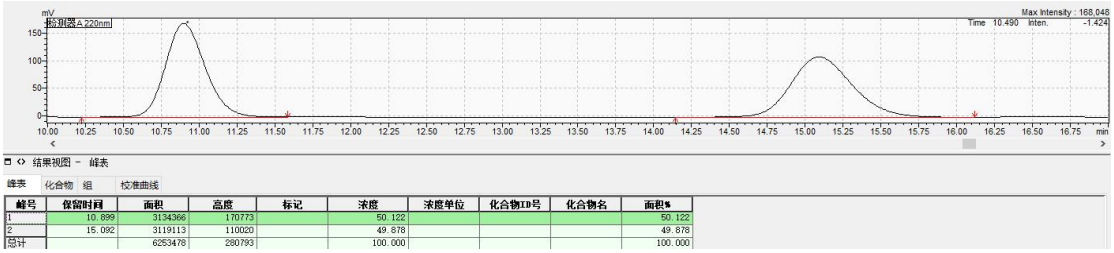
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.80 (d, J = 8.5 Hz, 1H), 7.46-7.33 (m, 7H), 7.09-7.06 (m, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.21 (t, J = 4.0 Hz, 1H), 5.40 (d, J = 12.4 Hz, 1H), 5.33 (d, J = 12.4 Hz, 1H), 3.32-3.24 (m, 2H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 154.1, 141.4, 139.8, 135.7, 134.7, 128.9, 128.7, 128.4, 127.1, 126.7, 126.6, 125.0, 124.4, 124.3, 122.7, 68.7, 53.8, 43.2, 29.8.

HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{22}NO_3$: 372.1594, found: 372.1588 .

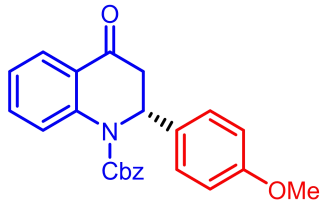
$[\alpha]_D^{21}$= +51.6° (*c* 0.1, MeOH).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =10.9 min, major =14.9 min; ee =91%.



Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(4-methoxyphenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (5)



Yellow solid (74% isolated yield, 28.6 mg, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.7 Hz, J_2 = 1.7 Hz, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.46-7.35 (m, 6H), 7.11-7.07 (m, 3H), 6.72 (d, J = 8.7 Hz, 2H), 6.19 (t, J = 4.0 Hz, 1H), 5.40 (*d*, J = 12.2 Hz, 1H), 5.32 (*d*, J = 12.3 Hz, 1H), 3.70 (s, 3H), 3.27 (d, J = 4.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 159.0, 154.4, 141.5, 135.7, 134.7, 130.1, 128.8, 128.6, 128.3, 127.9, 126.9, 125.2, 124.6, 124.3, 114.1, 68.6, 55.8, 55.3, 42.6.

HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{22}NO_4$: 388.1543, found: 388.1537 .

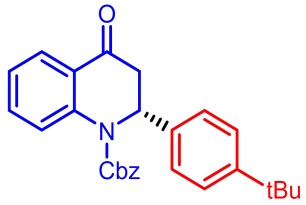
$[\alpha]_D^{28}$= + 60.3° (*c* 0.1, MeOH).

HPLC Conditions: IPA/ Hexanes (20:90), 1.0 mL/min, Daicel Chiralpak IC column, λ= 220 nm, t_R (min): minor =13.5 min, major =16.1 min; ee =54%.

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl

2-(4-(tert-butyl)phenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (6)



White solid (87% isolated yield, 35.9 mg, 0.1 mmol), mp: 106.9-108.2 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

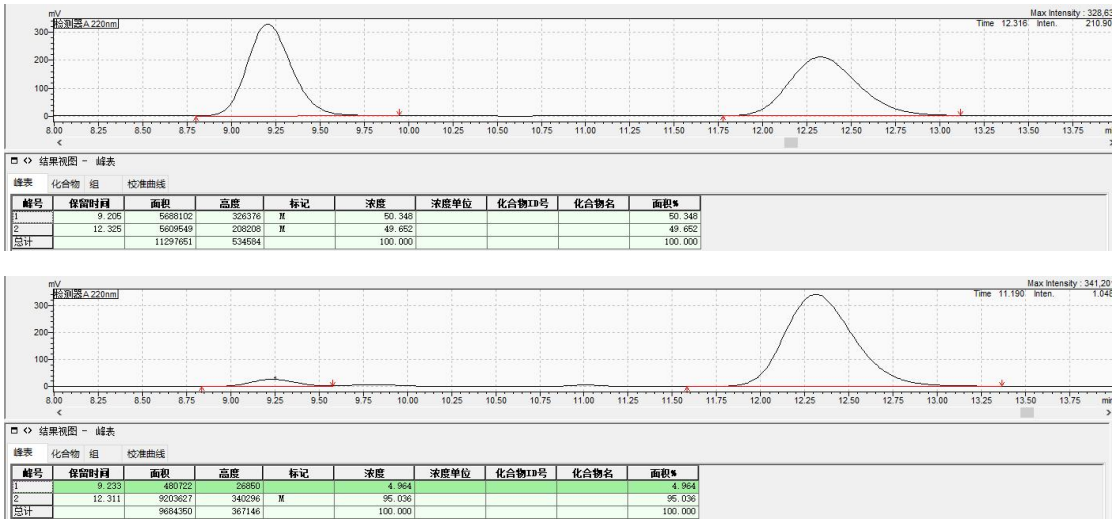
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J_1 = 7.8 Hz, J_2=1.8 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.50-7.44 (m, 1H), 7.41-7.35 (m, 5H), 7.23-7.21 (m, 2H), 7.11-7.07 (m, 3H), 6.21 (t, J = 4.1 Hz, 1H), 5.40 (d, J = 12.4 Hz, 1H), 5.32 (d, J = 12.4 Hz, 1H), 3.29 (d, J = 4.0 Hz, 2H), 1.22 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 154.5, 150.6, 141.8, 135.8, 135.1, 134.7, 128.8, 128.6, 128.3, 127.0, 126.4, 125.7, 125.2, 124.5, 124.2, 68.6, 56.1, 42.6, 34.5, 31.3.

HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{28}NO_3$: 414.2064, found: 414.2056.

$[\alpha]_D^{22}$= + 63.9° (*c* 0.1, $CHCl_3$).

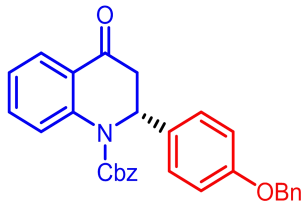
HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =9.2 min, major =12.3 min; ee = 90%.



Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(4-(benzyloxy)

phenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (7)



White solid (59% isolated yield, 27.3 mg, 0.1 mmol), mp: 148.8-151.7 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

Synthesized according to the general procedure and purified by flash chromatography (10:1 petroleum ether /EtOAc) to afford a white solid.

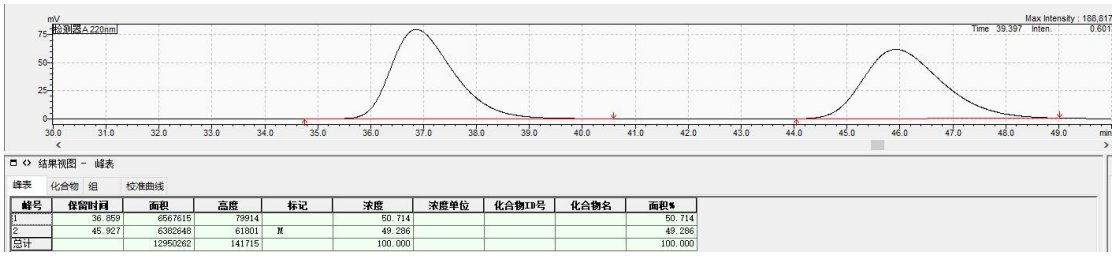
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.48-7.28 (m, 11H), 7.14-7.04 (m, 3H), 6.80 (d, J = 8.9 Hz, 2H), 6.19 (t, J = 4.0 Hz, 1H), 5.40 (d, J = 12.3 Hz, 1H), 5.32 (d, J = 12.4 Hz, 1H), 4.94 (s, 2H), 3.27 (d, J = 4.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 158.2, 154.4, 141.5, 136.8, 135.7, 134.7, 130.4, 128.8, 128.7, 128.6, 128.3, 128.2, 128.0, 127.6, 127.0, 125.2, 124.6, 124.3, 115.0, 70.0, 68.6, 55.8, 42.5.

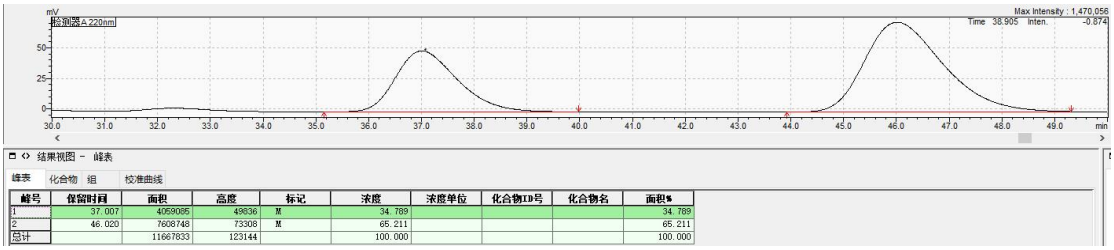
HRMS (ESI) $[M+H]^+$ calcd for $C_{30}H_{26}NO_4$: 464.1856, found: 464.1849 .

$[\alpha]_D^{23}$= + 47.2° (*c* 0.1, MeOH).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =36.0 min, major =46.0 min; ee = 31%.



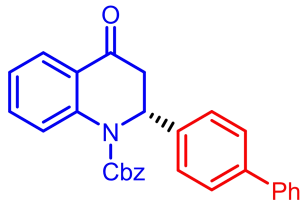
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	36.859	8567615	79914		50.714				50.714
2	45.927	8382648	61801	M	49.286				49.286
总计		12950262	141715		100.000				100.000



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	37.007	4059085	49836	M	34.789				34.789
2	46.020	7608748	73308	M	65.211				65.211
总计		11667833	123144		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-([1,1'-biphenyl]-4-yl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (8)



Yellow solid (39% isolated yield, 16.9 mg and 11.6 mg substrate, 0.1 mmol), mp: 167.5-169.6 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 7.9 Hz, 1.7 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.49-7.35 (m, 11H), 7.32-7.31 (m, 1H), 7.30-7.24 (m, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.28 (t, *J* = 4.0 Hz, 1H), 5.42 (d, *J* = 12.3 Hz, 1H), 5.34 (d, *J* = 12.3 Hz, 1H), 3.40-3.33 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 154.5, 141.7, 140.6, 140.4, 137.2, 135.7, 134.8, 128.9, 128.8, 128.7, 128.3, 127.6, 127.5, 127.2, 127.1, 125.2, 124.6, 124.4, 68.7, 56.2, 42.5.

HRMS (ESI) $[M+H]^+$ calcd for $C_{29}H_{24}NO_3$: 434.1751, found: 434.1724.

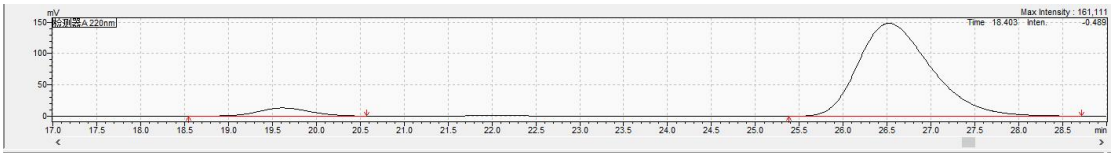
$[\alpha]_D^{20}$= +63.8° (*c* 0.1, MeOH).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =19.6 min, major =26.5 min; ee = 88%.

结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	19.509	2650314	61701		50.305				50.305
2	26.587	2519382	44022	M	49.695				49.695
总计		5069696	105724		100.000				100.000



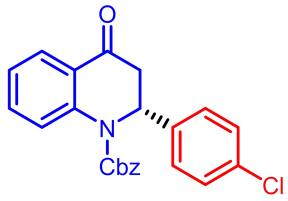
结果视图 - 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	19.615	550831	13173	M	6.044				6.044
2	26.520	8562797	149326	M	93.956				93.956
总计		9113628	162499		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-2 benzyl -(4-chlorophenyl)-4-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (9)



Colorless oil (78% isolated yield, 30.4 mg, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.48-7.44 (m, 1H), 7.41-7.36 (m, 5H), 7.18-7.07 (m, 5H), 6.23-6.17 (m, 1H), 5.39 (d, J = 12.2 Hz, 1H), 5.32 (d, J = 12.2 Hz, 1H), 3.29-3.27 (m, 2H).

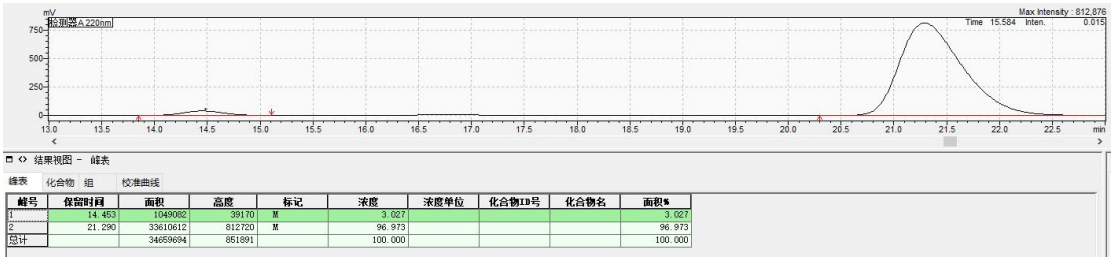
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 154.4, 141.4, 136.8, 135.6, 134.9, 133.7, 129.0, 128.9, 128.7, 128.4, 128.2, 127.1, 125.1, 124.6, 68.8, 55.9, 42.4.

$[\alpha]_D^{19}$= + 95.3° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M+H]^+$ calcd for $C_{23}H_{19}ClNO_3$: 392.1048, found: 392.1044 .

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =14.3 min, major =21.3 min; ee = 94%.

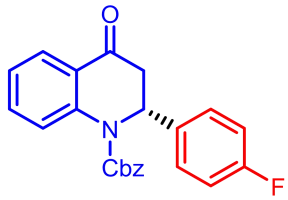
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.330	32930511	1225782	M	49.982				49.982
2	21.293	32954085	797470		50.018				50.018
总计		65884596	2023251		100.000				100.000



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.453	1049082	39170	M	3.027				3.027
2	21.290	33610612	812720	M	96.973				96.973
总计		34659694	851891		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-2 benzyl -(4-fluorophenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (10)



Colorless oil (96% isolated yield, 36.0 mg, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.48-7.44 (m, 1H), 7.41-7.35 (m, 5H),7.19-7.08 (m, 3H), 6.92-6.86 (m, 2H), 6.22– 6.20 (m, 1H), 5.40 (d, J = 12.2 Hz, 1H), 5.33 (d, J = 12.2 Hz, 1H), 3.34-3.23 (m, 2H).

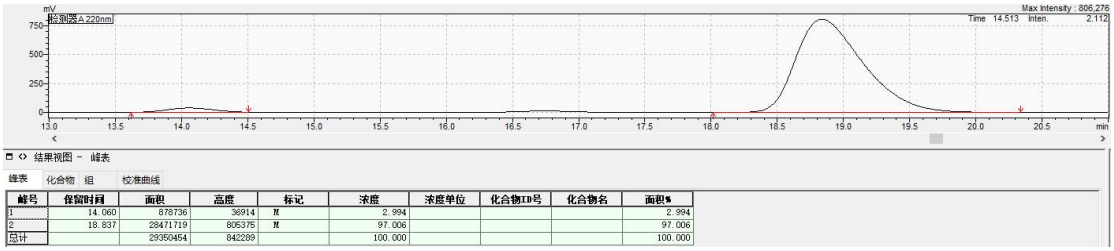
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.7, 162.2 (d, J = 247.0 Hz), 154.4, 141.4, 135.6, 134.8, 134.0 (d, J = 3.3 Hz), 128.9, 128.7, 128.5 (d, J = 8.2 Hz), 128.4, 127.1, 125.1, 124.6, 124.5, 115.7 (d, J = 21.6 Hz), 68.8, 55.8, 42.6.

HRMS (ESI) $[M+H]^+$ calcd for $C_{23}H_{19}FNO_3$: 376.1344, found: 376.1339.

$[\alpha]_D^{22}$= + 66.9° (*c* 0.1, MeOH).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =14.0 min, major =18.8 min; ee =94%.

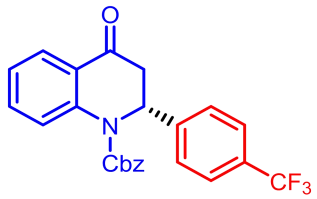
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	13.988	29934981	1160172	M	50.187				50.187
2	18.932	29712111	839574	M	49.813				49.813
总计		59647092	1999746		100.000				100.000



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.060	878736	36914	M	2.994				2.994
2	18.837	28471719	805375	M	97.006				97.006
总计		29350454	842289		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-4 benzyl-oxo-2-(3-(trifluoromethyl)phenyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (11)



Yellow oil (59% isolated yield, 25.1 mg and 8.1 mg substrate, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.9 Hz, J_2 =1.7 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.52-7.45(m, 3H), 7.40-7.36 (m, 5H), 7.34-7.29 (m, 2H), 7.13-7.08 (m, 1H), 6.27 (t, J = 4.4 Hz, 1H), 5.40 (d, J = 12.2 Hz, 1H), 5.33 (d, J = 12.2 Hz, 1H), 3.34-3.31 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.2, 154.4, 142.4, 141.4, 135.5, 135.0, 130.2 (d, J = 32.6 Hz), 128.9, 128.4, 128.0 (d, J = 197.5 Hz), 127.2, 127.1, 125.8 (q, J = 3.7 Hz), 125.0, 124.7, 124.5, 122.9, 68.9, 56.1, 42.4.

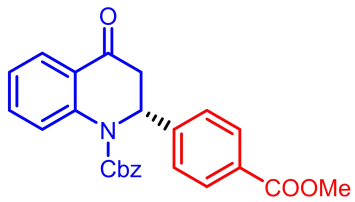
HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{19}F_3NO_3$: 426.1312 , found: 426.1321.

$[\alpha]_D^{25}$= + 119.4° (*c* 0.1, MeOH).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =13.2 min, major =21.3 min; ee =96%.

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(4-(methoxycarbonyl)phenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (12)



White solid (78% isolated yield, 32.4 mg, 0.1 mmol), mp: 163.0-165.2 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

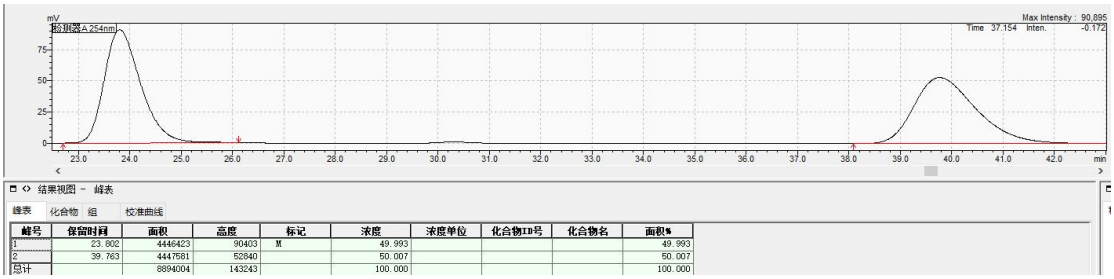
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 3H), 7.79 (d, J = 8.4 Hz, 1H), 7.48-7.43 (m, 1H), 7.41-7.32 (m, 5H), 7.27 (dd, J_1 = 7.2 Hz, J_2= 1.7 Hz, 2H), 7.11-7.06 (m, 1H), 6.27 (t, J = 4.0 Hz, 1H), 5.40 (d, J = 12.2 Hz, 1H), 5.33 (d, J = 12.2 Hz, 1H), 3.84 (s, 3H), 3.33 (d, J = 4.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.3, 166.6, 154.3, 143.3, 141.4, 135.5, 134.8, 130.0, 129.6, 128.9, 128.71, 128.66, 128.3, 127.1, 126.8, 125.0, 124.6, 124.5, 68.8, 56.2, 52.2, 42.3.

HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{22}NO_5$: 416.1493, found: 416.1489.

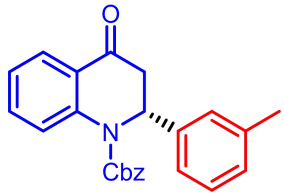
$[\alpha]_D^{26}$= + 48.3° (*c* 0.1, MeOH).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =23.8 min, major =39.7 min; ee = 96%.



Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)- benzyl 4-oxo-2-(*m*-tolyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (13)



Colorless oil (68% isolated yield, 25.2 mg, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

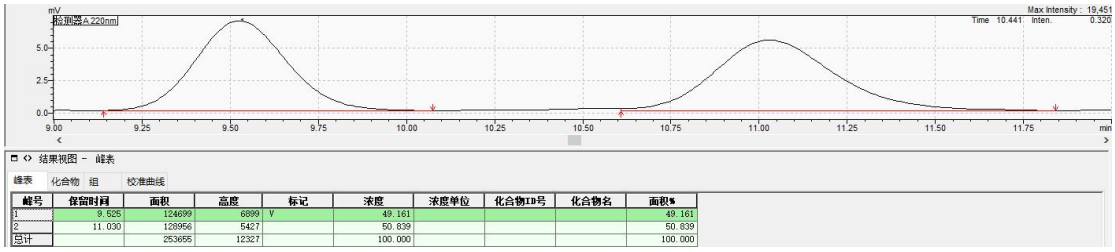
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.73-7.72 (m, 1H), 7.47-7.46 (m, 1H), 7.36-7.29 (m, 5H), 7.17-7.08(m, 3H), 6.93-6.89 (m, 2H), 6.26 (dd, J_1 = 6.4 Hz, J_2 = 1.9 Hz, 1H), 5.34 (d, J = 12.3 Hz, 1H), 5.22 (d, J = 12.3 Hz, 1H), 3.31 (dd, J_1 = 17.5 Hz, J_2 = 6.5 Hz, 1H), 3.11 (dd, J_1 = 17.5 Hz, J_2=1.9 Hz, 1H), 2.34 (s, 3H)

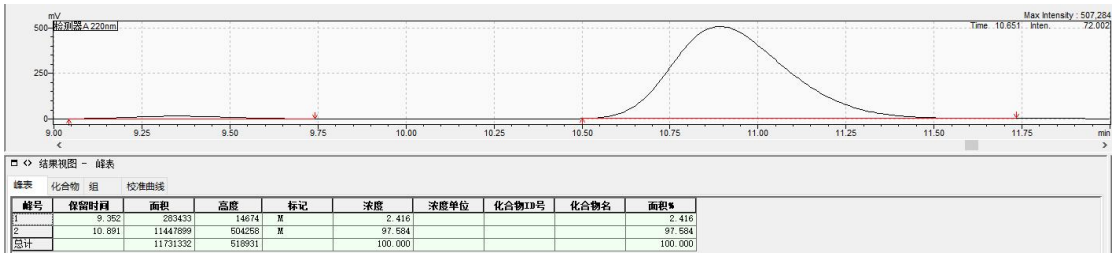
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 154.9, 142.8, 137.5, 137.2, 136.5, 135.4, 132.1, 129.5, 129.3, 128.9, 128.7, 127.6, 127.0, 126.8, 126.6, 125.5, 125.4, 69.3, 55.5, 43.5, 20.5.

HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{22}NO_3$: 372.1594, found: 372.1590.

$[\alpha]_D^{23}$= +53.6° (*c* 0.1, $CHCl_3$).

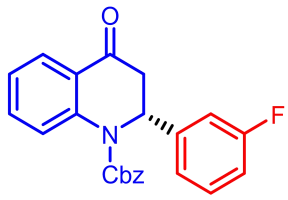
HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =9.3 min, major =10.9 min; ee = 95%.





Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-2 benzyl -(3-fluorophenyl)-4-oxo-3,4-dihydroquinoline-1(2*H*)-carboxylate (14)



Colorless oil (43% isolated yield, 16.1 mg 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.50-7.45 (m, 2H), 7.41-7.34 (m, 5H), 7.21-7.08 (m, 3H), 6.97-6.86 (m, 2H), 6.21 (t, J = 3.9 Hz, 1H), 5.40 (d, J = 12.2 Hz, 1H), 5.33 (d, J = 12.2 Hz, 1H), 3.30-3.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 163.1 (d, J = 246.9 Hz), 154.4, 141.4, 140.9 (d, J = 6.6 Hz), 135.6, 134.9, 130.4 (d, J = 8.2 Hz), 128.9, 128.7, 128.4, 127.1, 125.0, 124.6, 122.31, 122.28, 114.8 (d, J = 21.1 Hz), 114.1 (d, J = 22.6 Hz), 68.9, 56.0, 42.4.

HRMS (ESI) $[M+H]^+$ calcd for $C_{23}H_{19}FNO_3$: 376.1344, found: 376.1350.

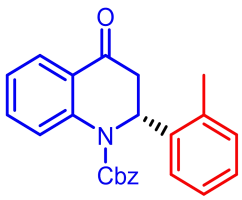
$[\alpha]_D^{26}$= + 65.2° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =14.0 min, major =17.8 min; ee =94%.

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	13.986	2740859	106229	M	50.211				50.211
2	17.832	2717801	86814	M	49.789				49.789
总计		5458661	193042		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)- benzyl 4-oxo-2-(*o*-tolyl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (15)



White solid (54% isolated yield, 20.0 mg, 0.1 mmol), mp: 105.4-117.9 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

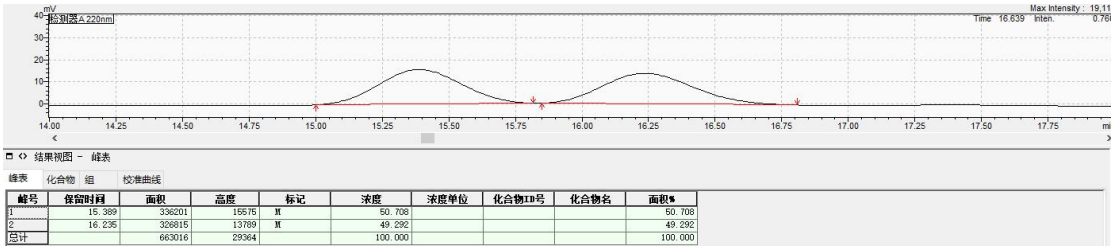
^{1}H NMR (400 MHz,$CDCl_3$) δ 7.95 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.73-7.72 (m, 1H), 7.47-7.46 (m, 1H), 7.36-7.29 (m, 5H), 7.17-7.08 (m, 3H), 6.93-6.89 (m, 2H), 6.26 (dd, J_1 = 6.4 Hz, J_2 = 1.9 Hz, 1H), 5.34 (d, J = 12.3 Hz, 1H), 5.22 (d, J = 12.3 Hz, 1H), 3.31 (dd, J_1 = 17.5 Hz, J_2 = 6.5 Hz, 1H), 3.11 (dd, J_1 = 17.5 Hz, J_2 = 1.9 Hz, 1H), 2.34 (s, 3H).

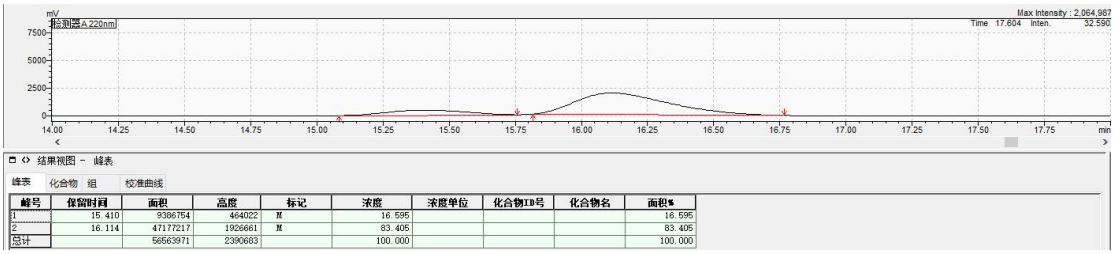
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 154.1, 142.0, 136.8, 136.4, 135.7, 134.7, 131.4, 128.8, 128.5, 128.2, 128.0, 126.9, 126.3, 126.1, 125.8, 124.8, 124.7, 68.6, 54.8, 42.8, 19.7.

HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{22}NO_3$: 372.1594, found: 372.1589

$[\alpha]_D^{24}$= +42.8° (*c* 0.1, $CHCl_3$).

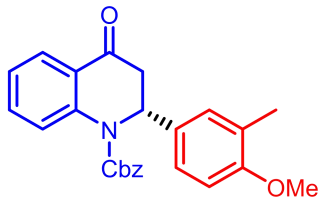
HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak IC column, λ= 220 nm, t_R (min): minor =15.4 min, major =16.1 min; ee = 67%.





Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(4-methoxy-3-methylphenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (16)



White solid (83% isolated yield, 33.3 mg, 0.1 mmol), mp: 184.3-186.7 ℃, column chromatography purification using petroleum ether/EtOAc (3:1, v/v) as eluents.

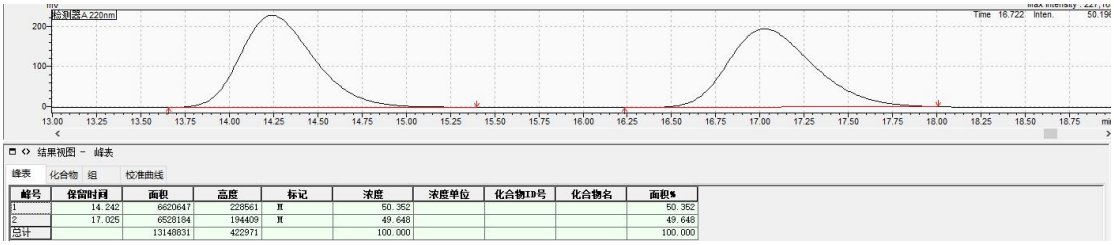
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.46-7.35 (m, 6H), 7.07 (dd, J_1 = 7.4 Hz, J_2 =1.1 Hz, 1H), 6.96-6.92 (m, 2H), 6.61 (d, J = 8.4 Hz, 1H), 6.16 (t, J = 4.0 Hz, 1H), 5.39 (d, J = 12.3 Hz, 1H), 5.34 (d, J = 12.2 Hz, 1H), 3.71 (s, 3H), 3.26-3.25 (m, 2H), 2.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 157.2, 154.4, 141.6, 135.8, 134.6, 129.6, 129.2, 128.8, 128.6, 128.3, 127.0, 126.9, 125.2, 125.0, 124.5, 124.2, 109.7, 68.5, 55.8, 55.3, 42.5, 16.4.

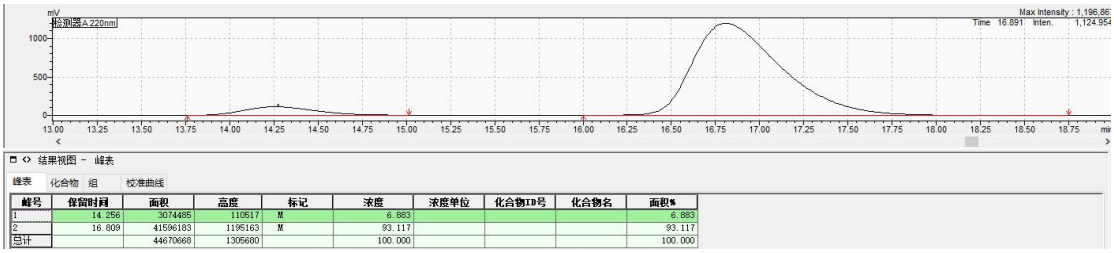
HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{24}NO_4$: 402.1700, found: 402.1689.

$[\alpha]_D^{26}$ = + 74.9° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =14.2 min, major =17.0 min; ee = 86%.



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.242	6620647	228561	M	50.352				50.352
2	17.025	6528184	194409	M	49.648				49.648
总计		13148831	422971		100.000				100.000

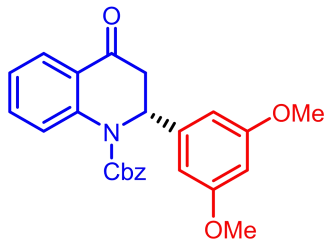


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.256	3074485	110517	M	6.883				6.883
2	16.809	41596183	1195163	M	93.117				93.117
总计		44670668	1305680		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl

2-(3,5-dimethoxyphenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (17)



White solid (82% isolated yield, 34.2 mg, 0.1 mmol), mp:157.1-159.0 ℃, column chromatography purification using petroleum ether/EtOAc (3:1, v/v) as eluents.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.49-7.45 (m, 1H), 7.42-7.35 (m, 5H), 7.11-7.08 (m, 1H), 6.30 (dd, J_1 = 2.2 Hz, J_2 =0.9 Hz, 2H), 6.24 (t, J = 2.3 Hz, 1H), 6.15 (t, J = 4.0 Hz, 1H), 5.38 (d, J = 12.3 Hz, 1H), 5.32 (d, J = 12.3 Hz, 1H), 3.64 (s, 6H), 3.27-3.26 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 161.0, 154.3, 141.7, 140.6, 135.7, 134.7, 128.8, 128.7, 128.6, 128.3, 127.1, 125.2, 124.45, 124.39, 105.2, 99.3, 68.6, 56.3, 55.3, 42.6.

HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{24}NO_5$: 418.1649, found: 418.1640.

$[\alpha]_D^{26}$= + 48.3° (*c* 0.1, $CHCl_3$).

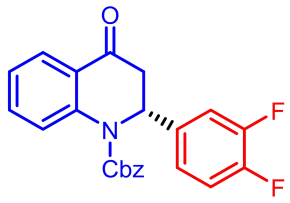
HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =25.6 min, major =37.8 min; ee = 97%.

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	25.626	2519111	44801	M	50.285				50.285
2	37.800	2490536	25018	M	49.715				49.715
总计		5009646	69819		100.000				100.000

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	25.125	11798626	203900	M	98.648				98.648
2	39.106	161668	2146	M	1.352				1.352
总计		11960294	206046		100.000				100.000

Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(3,4-difluorophenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (18)



Colorless oil (76% isolated yield, 29.9 mg and 5.3 mg substrate, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.9 Hz, J_2 =1.7 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.50-7.45 (m, 1H), 7.41-7.34 (m, 5H), 7.13-7.09 (m, 1H), 7.04-6.95 (m, 2H), 6.92-6.87 (m, 1H), 6.18-6.16 (m, 1H), 5.40 (d, J = 12.2 Hz, 1H), 5.33 (d, J = 12.2 Hz, 1H), 3.33-3.20 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 154.2, 151.3 (dd, J_1 = 71.2 Hz, J_2 = 12.7 Hz), 148.8 (dd, J_1 = 71.2 Hz, J_2 =12.6 Hz), 141.0, 135.3 (q, J = 16.0 Hz), 134.8, 128.8, 128.7, 128.3, 127.0, 124.8, 124.6, 124.4, 122.7 (dd, J_1 = 6.5 Hz, J_2 =3.6 Hz), 117.5 (d, J = 17.4 Hz), 116.1 (d, J = 18.2 Hz), 68.8, 55.5, 55.4, 42.2.

HRMS (ESI) $[M+H]^+$ calcd for $C_{23}H_{18}F_2NO_3$: 394.1249, found: 394.1241.

$[\alpha]_D^{29}$= + 73.0° (*c* 0.1, $CHCl_3$).

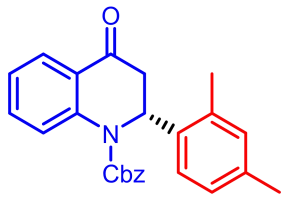
HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =14.6 min, major =21.6 min; ee = 96%.

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.607	5235089	198769		50.003				50.003
2	21.617	5234554	133026		49.997				49.997
总计		10469642	331795		100.000				100.000

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	14.686	44989	1921	M	2.292				2.292
2	21.704	1918249	48954		97.708				97.708
总计		1963238	50875		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(2,4-dimethylphenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (19)



White solid (44% isolated yield, 16.9 mg and 10.0 mg substrate, 0.1 mmol), mp: 67.6-68.7 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

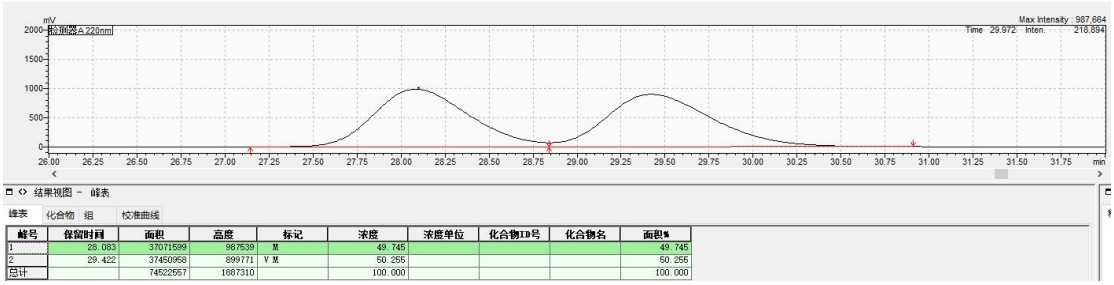
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.48-7.44 (m, 1H), 7.38-7.29 (m, 5H), 7.16-7.13 (m, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.88 (dd, J_1 = 7.6 Hz, J_2 =1.8 Hz, 1H), 6.67 (d, J = 1.8 Hz, 1H), 6.22 (dd, J_1 = 6.5 Hz, J_2= 1.9 Hz, 1H), 5.34 (d, J = 12.3 Hz, 1H), 5.22 (d, J = 12.3 Hz, 1H), 3.29 (dd, J_1 = 17.5 Hz, J_2 = 6.5 Hz, 1H), 3.11 (dd, J_1 = 17.5 Hz, J_2 =1.9 Hz, 1H), 2.29 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 154.1, 142.1, 136.6, 135.7, 135.4, 134.6, 133.2, 131.3, 128.7, 128.6, 128.5, 128.2, 127.1, 126.7, 125.9, 124.8, 124.7, 68.5, 54.7, 42.8, 21.2, 19.3.

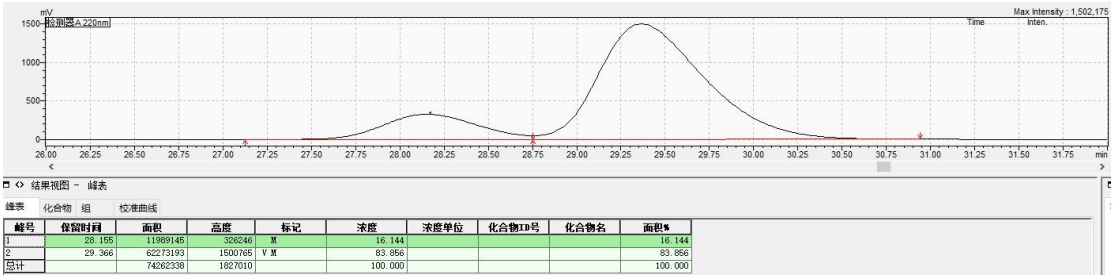
HRMS (ESI) $[M+H]^+$ calcd for $C_{25}H_{24}NO_3$: 386.1751, found: 386.1760.

$[\alpha]_D^{31}$= + 54.9° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =28.1min, major =29.4 min; ee = 67%.



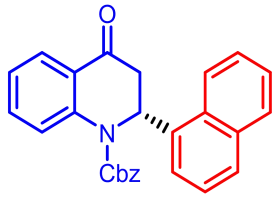
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	28.083	37071599	987539	M	49.745				49.745
2	29.422	37450958	899771	V M	50.255				50.255
总计		74522557	1887310		100.000				100.000



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	28.155	11989145	326246	M	16.144				16.144
2	29.366	62273193	1600765	V M	83.856				83.856
总计		74262338	1827010		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(naphthalen-1-yl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (20)



White solid (32% isolated yield, 13.0 mg and 12.6 mg substrate, 0.1 mmol), mp: 117.3-120.9 ℃, column chromatography purification using petroleum ether/EtOAc (5:1, v/v) as eluents.

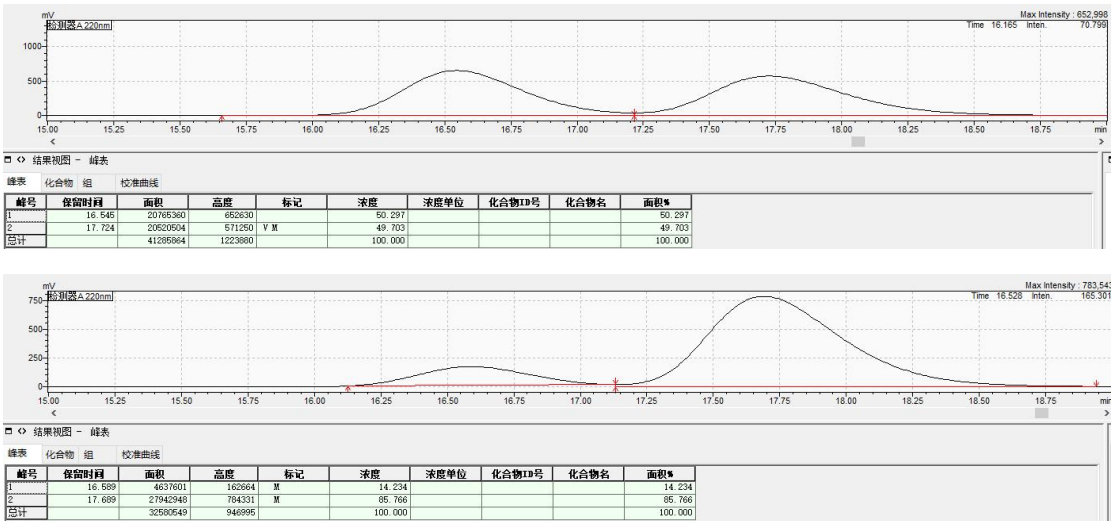
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23-8.21 (m, 1H), 7.97 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.83-7.80 (m, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.53-7.49 (m, 3H), 7.40-7.31 (m, 6H), 7.19-7.08 (m, 3H), 6.90-6.89 (m, 1H), 5.41 (d, J = 12.4 Hz, 1H), 5.29 (d, J = 12.4 Hz, 1H), 3.50-3.31 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6, 154.3, 141.7, 135.8, 134.5, 134.1, 134.0, 131.1, 129.2, 129.1, 128.8, 128.5, 128.1, 126.84, 126.81, 126.0, 125.5, 125.0, 124.9, 124.8, 123.4, 68.6, 54.3, 43.2.

HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{21}NO_3$: 407.1521 , found: 407.1529.

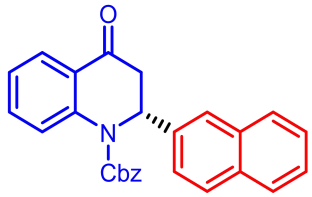
$[\alpha]_D^{25}$= + 76.5° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =16.5 min, major =17.7 min; ee = 71%.



Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(naphthalen-2-yl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (21)



White solid (33% isolated yield, 13.4 mg and 14.8 mg substrate, 0.1 mmol), mp: 140.8-143.8 ℃, column chromatography purification using petroleum ether/EtOAc (8:1, v/v) as eluents.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.48 -7.45 (m, 1H), 7.40-7.36 (m, 6H), 7.26 (s, 2H), 7.18-7.16 (m, 2H), 7.13-7.09 (m, 3H), 6.20 (dd, J_1 = 5.3 Hz, J_2 = 2.6 Hz, 1H), 5.39 (d, J = 12.1 Hz, 1H), 5.32 (d, J = 12.3 Hz, 1H), 3.29-3.27 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 154.5, 141.4, 135.7, 135.6, 134.7, 133.0, 132.6, 129.9, 128.7, 128.3, 128.2, 127.6, 127.0, 126.5, 125.7, 125.2, 124.8, 124.6, 124.5,123.3, 119.0, 68.7, 56.3, 42.3.

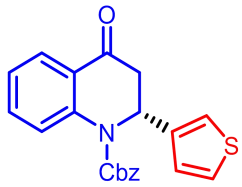
HRMS (ESI) $[M+H]^+$ calcd for $C_{27}H_{21}NO_3$: 407.1521, found: 407.1528.

$[\alpha]_D^{25}$= + 91.0° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =17.5 min, major =22.1 min; ee = 93%.

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl-4-oxo-2-(thiophen-3-yl)-3,4-dihydroquinoline-1(2H)-carboxylate (22)



White solid (36% isolated yield, 13.0 mg and 14.0 mg substrate, 0.1 mmol), mp: 91.1-91.5 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

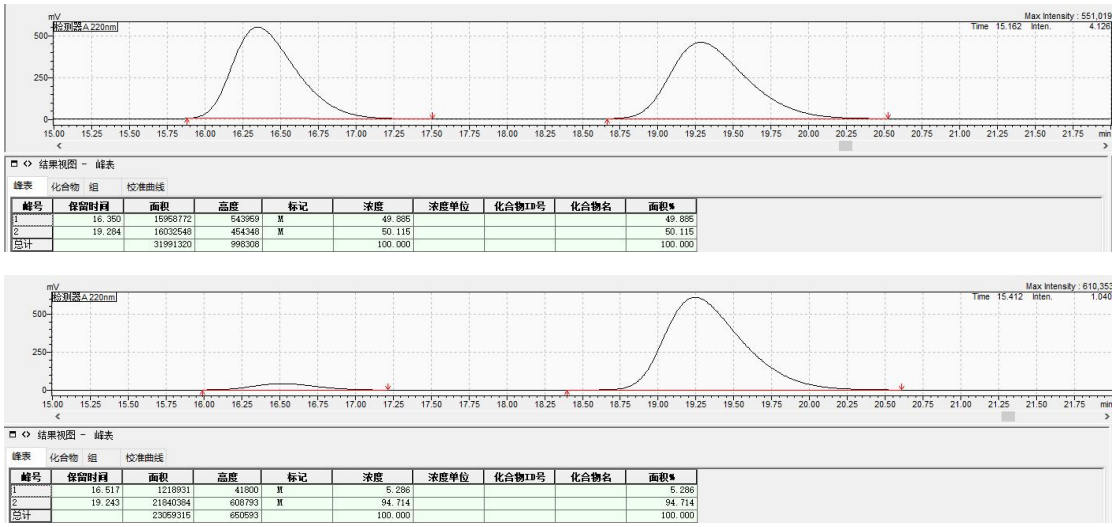
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.48-7.37 (m, 6H), 7.17 (dd, J = 5.0 Hz, 2.9 Hz, 1H), 7.12-7.08 (m, 1H), 6.95-6.93 (m, 1H), 6.89 (dd, J_1 = 5.1 Hz, J_2 =1.4 Hz, 1H), 6.22-6.19 (m, 1H), 5.39 (d, J = 12.3 Hz, 1H), 5.33 (d, J = 12.3 Hz, 1H), 3.26-3.20 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.9, 154.1, 141.4, 139.8, 135.7, 134.7, 128.9, 128.7, 128.4, 127.1, 126.71, 126.66, 124.9, 124.4, 124.3, 122.7, 68.7, 53.8, 43.2.

HRMS (ESI) $[M+H]^+$ calcd for $C_{21}H_{18}NO_3S$: 364.1002, found: 364.0920.

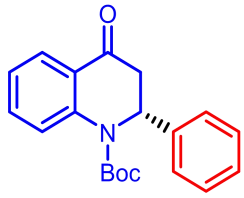
$[\alpha]_D^{26}$= + 50.5° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =16.4 min, major =19.3 min; ee = 90%.



Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-tert-butyl -4-oxo-2-phenyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (24)



Yellow solid (22% isolated yield, 7.1 mg and 20.0 mg substrate, 0.1 mmol), mp: 122.6-125.2 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

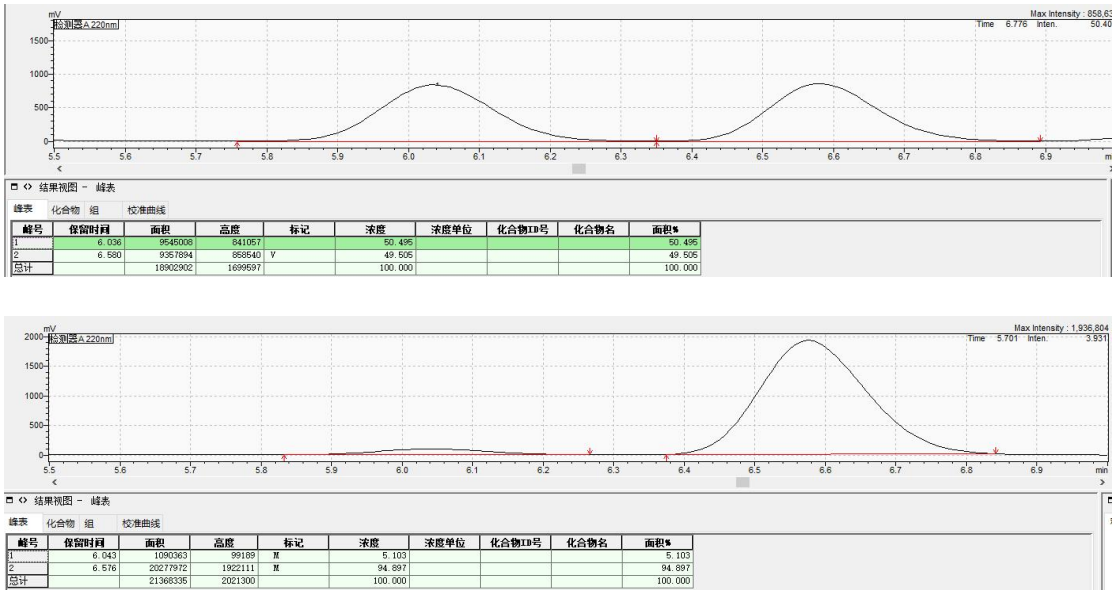
^{1}H NMR (500 MHz, $CHCl_3$) δ 7.88 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 7.77-7.75 (m, 1H), 7.46-7.42 (m, 1H), 7.23-7.14 (m, 5H), 7.06-7.03 (m, 1H), 6.16 (t, J = 4.0 Hz, 1H), 3.30-3.29 (m, 2H), 1.59 (s, 9H).

^{13}C NMR (126 MHz, $CHCl_3$) δ 193.3, 153.5, 142.2, 138.7, 134.4, 128.7, 127.6, 126.9, 126.7, 125.1, 124.7, 123.8, 82.7, 55.9, 42.5, 28.5.

HRMS (ESI) $[M+H]^+$ calcd for $C_{20}H_{22}NO_3$:324.1592 , found: 324.1588.

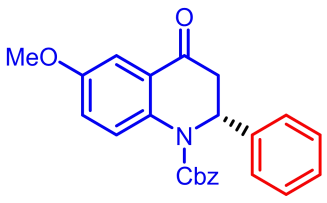
$[\alpha]_D^{24}$= + 79.4° (*c* 0.1, $CHCl_3$).

HPLC Conditions: 20% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak IC column, λ= 220 nm, t_R (min): minor =6.0 min, major =6.5 min; ee =90%.



Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(R)-benzyl-6-methoxy-4-oxo-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate (25)



Colorless oil (93% isolated yield, 36.0 mg, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, J_1 = 7.9 Hz, J_2 =1.7 Hz, 1H), 7.77 (d, J = 8.5 Hz, 1H), 7.46-7.35 (m, 6H), 7.11-7.06 (m, 3H), 6.73-6.71 (m, 2H), 6.19 (t, J = 4.0 Hz, 1H), 5.40 (d, J = 12.2 Hz, 1H), 5.32 (d, J = 12.3 Hz, 1H), 3.70 (s, 3H), 3.27 (d, J = 4.0 Hz, 2H).

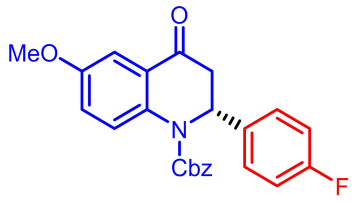
^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 159.0, 154.4, 141.5, 135.8, 134.7, 130.2, 128.9, 128.6, 128.3, 127.9, 126.9, 125.2, 124.6, 124.3, 114.1, 68.6, 55.8, 55.3, 42.5.

HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{22}NO_4$: 388.1543, found: 388.1550.

HPLC Conditions: 10% IPA/ Hexanes, 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =12.5 min, major =15.0 min; ee = 94%.

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(4-fluorophenyl)-6-methoxy-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (26)



Colorless oil (97% isolated yield, 39.2 mg, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc(10:1, v/v) as eluents.

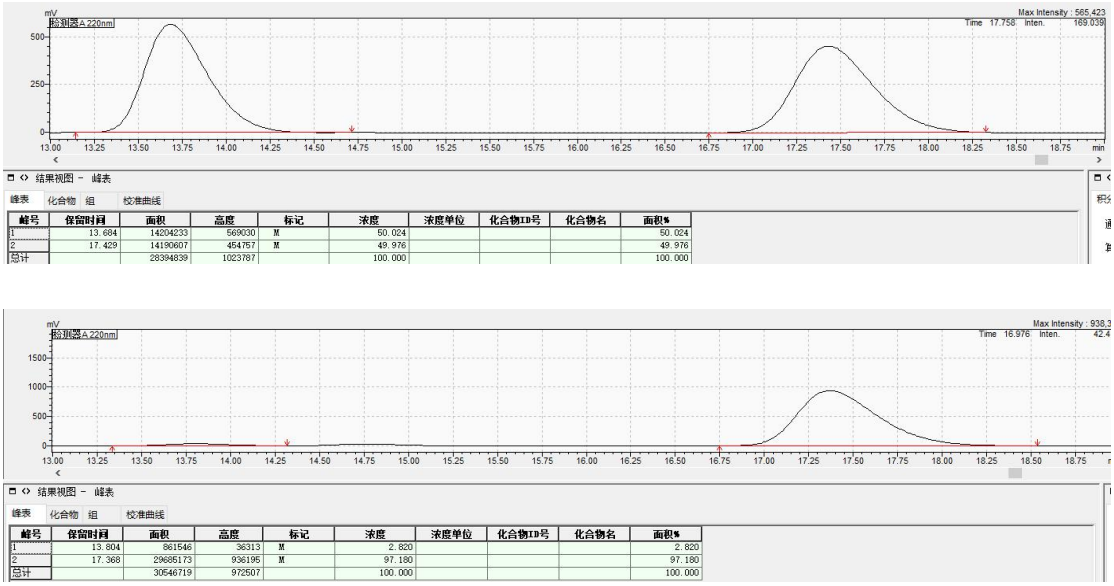
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 9.2 Hz, 1H), 7.39-7.32 (m, 6H), 7.15-7.12 (m, 2H), 7.03 (dd, J_1 = 9.2 Hz, J_2 =3.1 Hz, 1H), 6.90-6.86 (m, 2H), 6.18-6.17 (m, 1H), 5.38 (d, J = 12.3 Hz, 1H), 5.31 (d, J = 12.3 Hz, 1H), 3.76 (s, 3H), 3.27-3.25 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 162.2 (d, J = 247.0 Hz), 156.3, 154.5, 135.7, 134.9, 134.1 (d, J = 3.4 Hz), 128.9, 128.7, 128.5 (d, J = 8.3 Hz), 128.3, 126.3, 125.9, 122.9, 115.7 (d, J = 21.4 Hz), 108.4, 68.6, 55.8, 55.7, 42.5.

HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{21}FNO_4$: 406.1449, found: 406.1440.

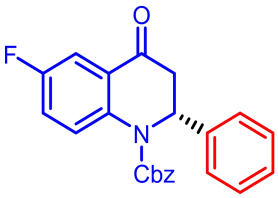
$[\alpha]_D^{30}$= + 78.1° (*c* 0.1, $CHCl_3$).

EIPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =14.1 min, major =17.9 min; ee = 94%.



Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 6-fluoro-4-oxo-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate (27)



White solid (80% isolated yield, 30.0 mg, 0.1 mmol), mp: 148.8-151.7 ℃, column chromatography purification using petroleum ether/EtOAc (5:1, v/v) as eluents.

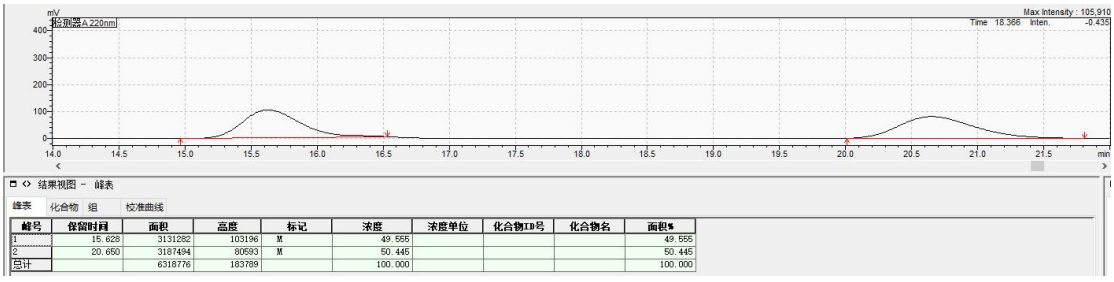
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J_1 = 9.4 Hz, J_2 = 4.5 Hz, 1H), 7.59 (dd, J_1 = 8.3 Hz, J_2 = 3.1 Hz, 1H), 7.44-7.41 (m, 5H), 7.30-7.18 (m, 6H), 6.29 (dd, J_1 = 5.5 Hz, J_2 = 2.2 Hz, 1H), 5.45 (d, J = 12.2 Hz, 1H), 5.38 (d, J = 12.3 Hz, 1H), 3.41-3.30 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.0, 159.1 (d, J = 246.3 Hz), 154.4, 137.8, 137.7 (d, J = 2.6 Hz), 135.6, 128.9 (d, J = 2.5 Hz), 128.7, 128.3, 127.9, 126.82, 126.76, 126.7, 126.6, 121.9 (d, J = 23.4 Hz), 112.6 (d, J = 23.2 Hz), 68.8, 56.2, 42.2.

HRMS (ESI) $[M+H]^+$ calcd for $C_{23}H_{19}FNO_3$: 376.1344, found: 376.1350.

$[\alpha]_D^{27}$= + 91.6° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =15.6 min, major =20.5 min; ee = 90 %.

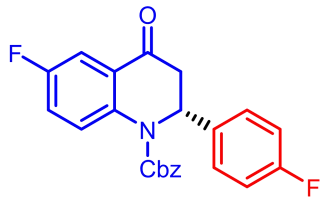


峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.628	3131282	103196	M	49.555				49.555
2	20.650	3187494	80593	M	50.445				50.445
总计		6318776	183789		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl

6-fluoro-2-(4-fluorophenyl)-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (28)



Colorless oil (44% isolated yield, 17.3 mg, 0.1 mmol), column chromatography purification using petroleum ethe r: EtOAc (5:1, v/v) as eluents.

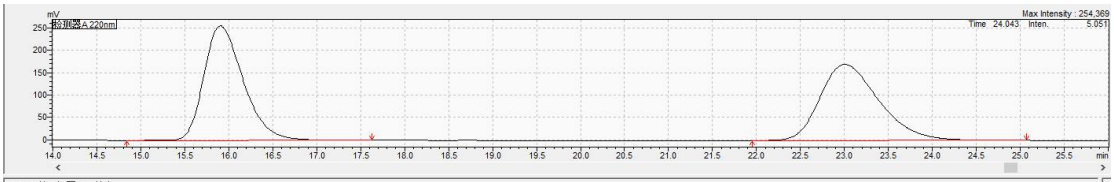
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, J_1 = 9.4 Hz, J_2 = 4.4 Hz, 1H), 7.55 (dd, J_1 = 8.3 Hz, J_2 =3.2 Hz, 1H), 7.42-7.36 (m, 5H), 7.18-7.09 (m, 3H), 6.93-6.87 (m, 2H), 6.21-6.20 (m, 1H), 5.39 (d, J = 12.3 Hz, 1H), 5.33 (d, J = 12.3 Hz, 1H), 3.29-2.28 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 162.3 (d, J = 247.2 Hz), 159.2 (d, J = 246.7 Hz), 154.3, 137.5, 135.5, 133.7 (d, J = 3.3 Hz), 128.9, 128.8, 128.5 (d, J = 8.4 Hz), 128.4, 126.8 (d, J = 7.2 Hz), 126.5 (d, J = 6.3 Hz), 122.1 (d, J = 23.5 Hz), 115.8 (d, J = 21.5 Hz), 112.7 (d, J = 23.1 Hz), 68.9, 55.7, 42.3.

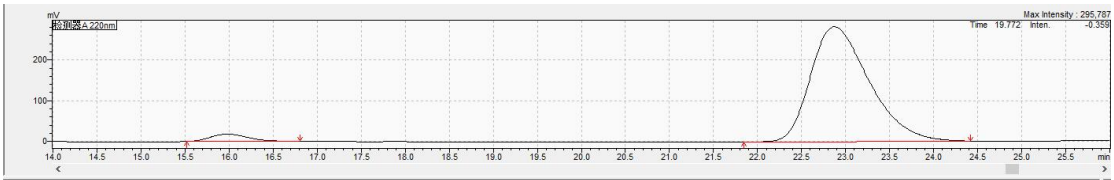
HRMS (ESI) $[M+H]^+$ calcd for $C_{23}H_{18}F_2NO_3$: 394.1249, found: 394.1240.

$[\alpha]_D^{31}$= + 93.1° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =15.9 min, major =22.8 min; ee = 92%.



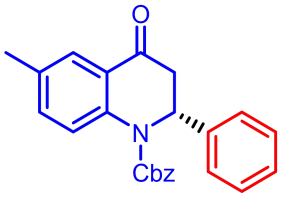
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.906	7961967	255661	M	50.191				50.191
2	23.005	7901322	169889	M	49.809				49.809
总计		15863289	425550		100.000				100.000



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.982	506224	17722	M	3.754				3.754
2	22.873	12979218	280977	M	96.246				96.246
总计		13485442	298699		100.000				100.000

Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%)

(*R*)-benzyl 6-methyl-4-oxo-2-phenyl-3,4-dihydroquinoline-1(2H)-carboxylate (29)



White solid (54% isolated yield, 20.0 mg, 0.1 mmol), mp: 165.0-167.3 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

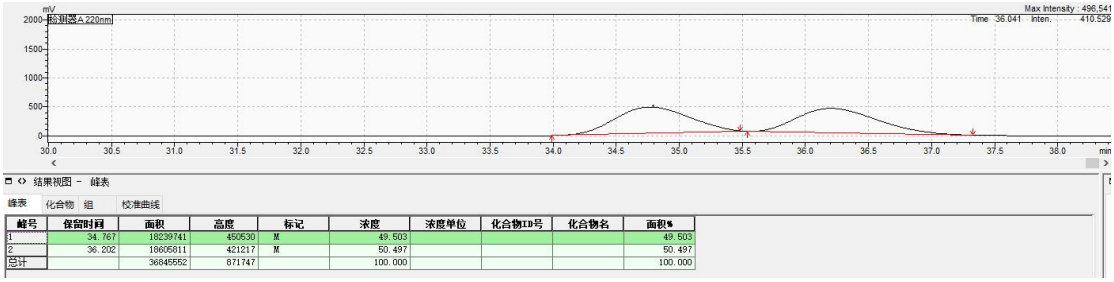
^{1}H NMR (500 MHz, $CHCl_3$) δ 7.68 (d, *J* = 2.4 Hz, 2H), 7.41-7.34 (m, 5H), 7.27-7.25 (m, 1H), 7.23-7.16 (m, 5H), 6.22 (t, *J* = 3.9 Hz, 1H), 5.39 (d, *J* = 12.3 Hz, 1H), 5.31 (d, *J* = 12.3 Hz, 1H), 3.29-3.28 (m, 2H), 2.26 (s, 3H).

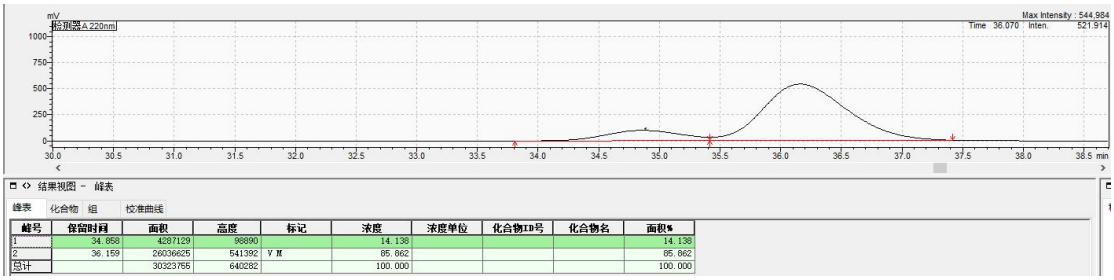
^{13}C NMR (126 MHz, $CHCl_3$) δ 193.2, 154.5, 139.2, 138.3, 135.8, 135.7, 134.1, 128.8, 128.7, 128.6, 128.3, 127.7, 126.9, 126.7, 124.9, 124.5, 68.6, 56.2, 42.5, 20.7.

HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{22}NO_3$: 372.1594, found: 372.1600.

$[\alpha]_D^{27}$= + 99.7° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak IC column, λ= 220 nm, t_R (min): minor =34.7 min, major =36.2 min; ee = 71%.

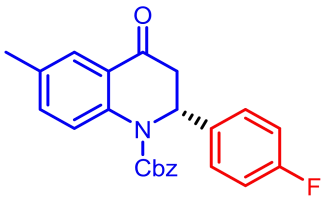




Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl

2-(4-fluorophenyl)-6-methyl-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (30)



White solid (49% isolated yield, 19.0 mg, 0.1 mmol), mp: 133.9-136.1 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

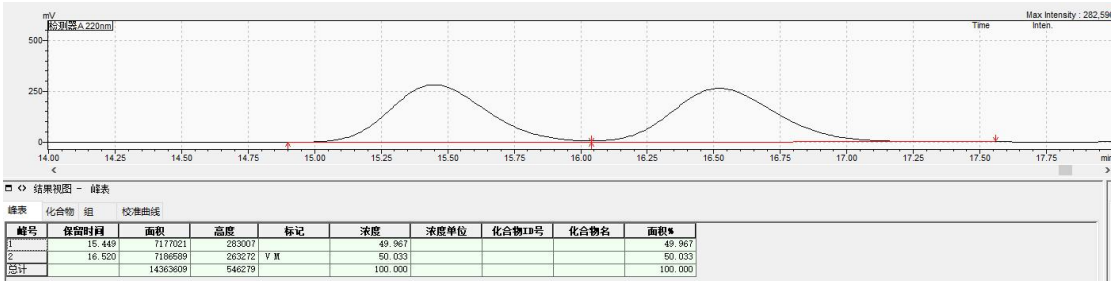
^{1}H NMR (400 MHz, $CHCl_3$) δ 7.69 (d, *J* = 2.3 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.40-7.35 (m, 5H), 7.28-7.25 (m, 1H), 7.17-7.13 (m, 2H), 6.90-6.87 (m, 2H), 6.20 –6.17 (m, 1H), 5.39 (d, *J* = 12.3 Hz, 1H), 5.31 (d, *J* = 12.3 Hz, 1H), 3.32-3.21 (m, 2H), 2.27 (s, 3H).

^{13}C NMR (101 MHz, $CHCl_3$) δ 192.9, 162.1 (d, J = 246.8 Hz), 154.4, 138.9, 135.8, 135.7, 134.3, 134.1 (d, J = 3.3 Hz), 128.8, 128.6, 128.5 (d, J = 8.2 Hz), 128.3, 126.9, 124.8, 124.5, 115.7 (d, J = 21.6 Hz), 68.7, 55.7, 42.5, 20.7.

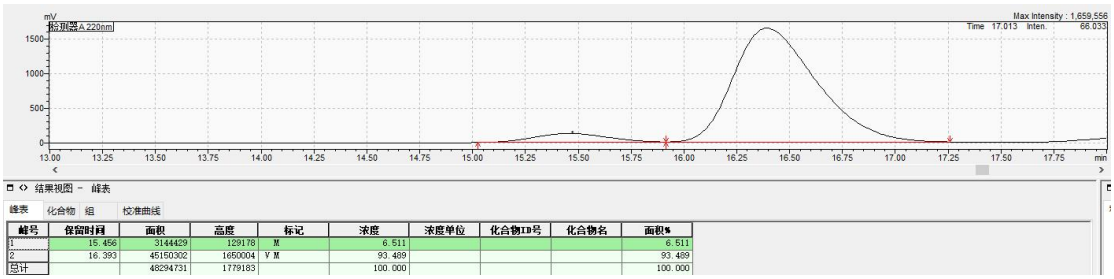
HRMS (ESI) $[M+H]^+$ calcd for $C_{24}H_{21}FNO_3$: 390.1500, found: 390.1509.

$[\alpha]_D^{30}$= +101.6° (*c* 0.1, $CHCl_3$).

HPLC Conditions: IPA/ Hexanes (20:80), 1.0 mL/min, Daicel Chiralpak IC column, λ= 220 nm, t_R (min): minor =15.4 min, major =16.5 min; ee = 87%.



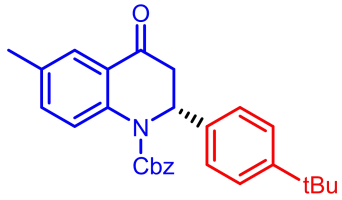
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.449	7177021	283007		49.967				49.967
2	16.520	7186589	263272	V M	50.033				50.033
总计		14363609	546279		100.000				100.000



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	15.456	3144429	129178	M	6.511				6.511
2	16.393	45150302	1650004	V M	93.489				93.489
总计		48294731	1779183		100.000				100.000

Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-benzyl 2-(4-(tert-butyl)phenyl)-6-methyl-4-oxo-3,4-dihydroquinoline-1(2H)-carboxylate (31)



Yellow oil (58% isolated yield, 25.0 mg, 0.1 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.73-7.70 (m, 2H), 7.41-7.34 (m, 6H), 7.22-7.20 (m, 2H), 7.11-7.09 (m, 2H), 6.18 (t, *J* = 4.0 Hz, 1H), 5.39 (d, *J* = 12.3 Hz, 1H), 5.29 (d, *J* = 12.3 Hz, 1H), 3.27 (d, *J* = 4.0 Hz, 2H), 2.28 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (101 MHz, $CHCl_3$) δ 193.3, 154.5, 150.5, 139.4, 135.8, 135.7, 135.3, 133.9, 128.8, 128.6, 128.3, 126.9, 126.4, 125.7, 124.9, 124.4, 68.5, 56.1, 42.6, 34.5, 31.3, 20.7.

HRMS (ESI) $[M+H]^+$ calcd for $C_{28}H_{30}NO_3$: 428.2220, found: 428.2214.

$[\alpha]_D^4$= +23.3° (*c* 0.1, $CHCl_3$).

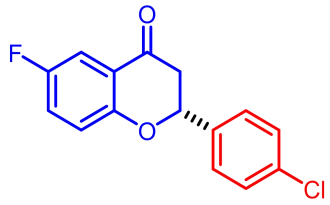
HPLC Conditions: IPA/ Hexanes (10:90), 1.0 mL/min, Daicel Chiralpak IC column, λ= 220 nm, t_R (min): minor =13.7 min, major =17.3 min; ee = 61%.

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	13.747	6424918	262577	H	50.333				50.333
2	17.360	6339795	205520	H	49.667				49.667
总计		12764713	468096		100.000				100.000

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	13.939	1332432	53293	H	19.192				19.192
2	17.527	5610230	181295	H	80.808				80.808
总计		6942662	234588		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-2-(4-chlorophenyl)-6-fluorochroman-4-one (32)



Yellow solid (55% isolated yield, 30.3 mg and 5.3 mg substrate, 0.2 mmol), column chromatography purification using petroleum ether/EtOAc (20:1, v/v) as eluents.

The NMR data and HRMS data are in accordance with that of previous publications (*J Agric Food Chem.* **2022,** *70*, 3409-3419.)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, J_1 = 8.1, J_2 = 3.3 Hz, 1H), 7.44 - 7.38 (m, 4H), 7.26 - 7.22 (m, 1H), 7.04 (dd, J_1 = 9.1, J_2 = 4.1 Hz, 1H), 5.45 (dd, J_1 = 13.2, J_2 = 3.0 Hz, 1H), 3.02 (dd, J_1 = 16.8, J_2 =13.1 Hz, 1H), 2.89 (dd, J_1 = 17.1, J_2 = 3.0 Hz, 1H).

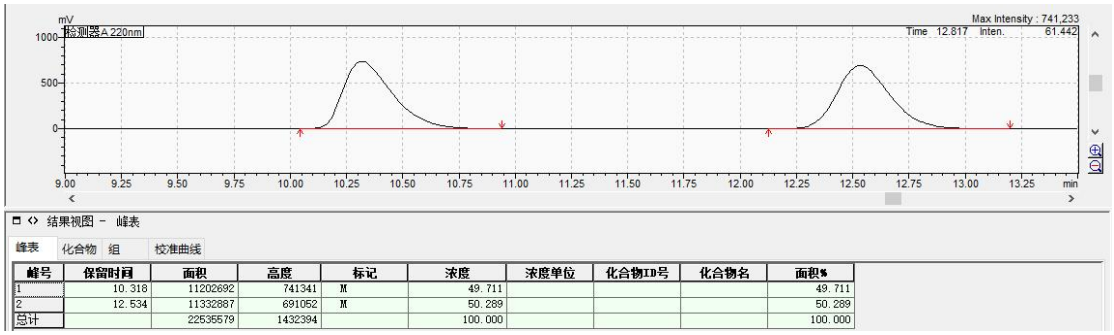
^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 157.7, 157.6 (d, J=243.1 Hz), 137.1, 134.9, 129.2, 127.6, 124.0 (d, J = 24.2 Hz), 121.5 (d, J = 7.0 Hz), 119.9 (d, J = 7.3 Hz), 112.2 (d, J = 23.2 Hz), 79.2, 44.4.

mp: 119.3.4 - 120.5 ℃.

$[\alpha]_D^{10}$= +46° (*c* 0.1, $CHCl_3$).

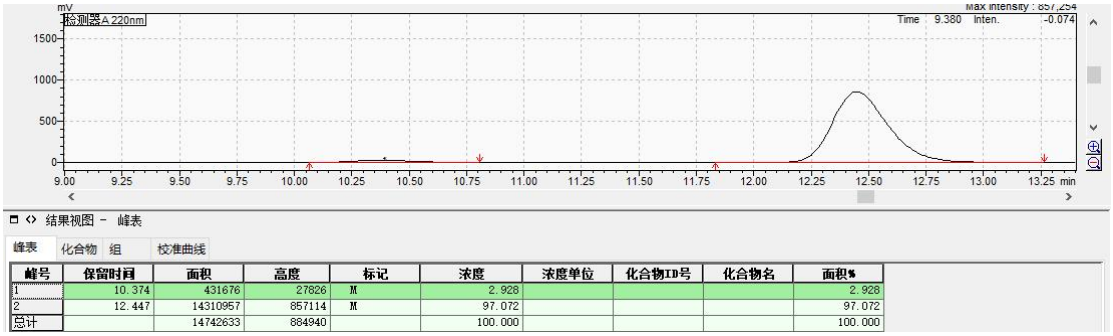
HRMS (ESI) $[M+H]^+$ calcd for $C_{15}H_{11}O_2FCl$: 277.0426, found: 277.0424.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =10.3 min, major=12.4min. ee = 94%.



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.318	11202692	741341	M	49.711				49.711
2	12.534	11332887	691052	M	50.289				50.289
总计		22535579	1432394		100.000				100.000

NL11:



结果视图 – 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.374	431676	27826	M	2.928				2.928
2	12.447	14310957	857114	M	97.072				97.072
总计		14742633	884940		100.000				100.000

L5:

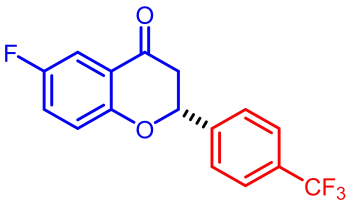
结果视图 – 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.429	224349	15717	M	1.472				1.472
2	12.536	15012298	909811	M	98.528				98.528
总计		15236647	925528		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-6-fluoro-2-(4-(trifluoromethyl)phenyl)chroman-4-one (33)



White solid (44% isolated yield, 27.3 mg, 0.2 mmol), mp: 121.4 - 125.7 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

The NMR data and HRMS data are in accordance with that of previous publications (*J Agric Food Chem.* **2022,** *70*, 3409-3419.)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.61 - 7.56 (m, 3H), 7.27 - 7.22 (m, 1H), 7.05 (dd, J_1 = 8.9, J_2 = 4.2 Hz, 1H), 5.53 (dd, J_1 = 13.1, J_2 = 3.2 Hz, 1H), 3.02 (dd, J_1 = 17.1, J_2 = 13.1 Hz, 1H), 2.92 (dd, J_1 = 17.0, J_2 = 3.3 Hz, 1H).

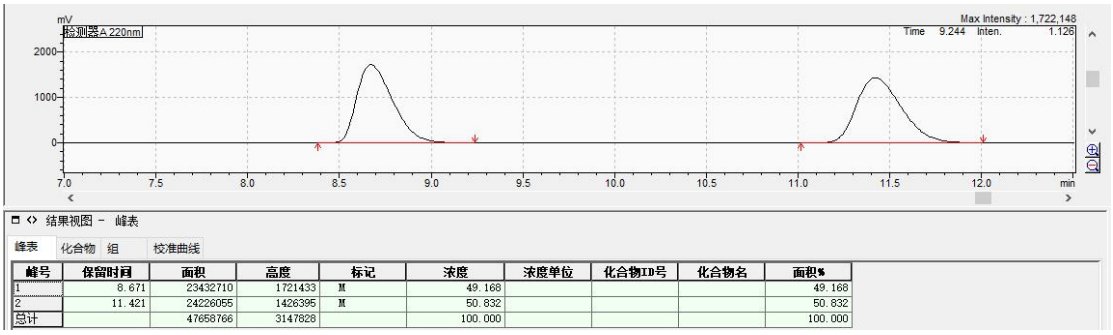
^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 157.7 (d, J = 242.7 Hz), 157.5, 142.5, 131.2 (d,

J = 32.5 Hz), 126.5, 126.1 (q, *J* = 4.0, 3.6 Hz), 124.1 (d, *J* = 24.3 Hz), 124.0 (d, *J* = 272.5 Hz), 121.5 (d, *J* = 7.0 Hz), 120.0 (d, *J* = 7.3 Hz), 112.3 (d, *J* = 23.1 Hz), 79.1, 44.5.

$[\alpha]_D^9$= +47° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{11}O_2F_4$: 311.0690, found: 311.0669.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =8.6 min, major=11.4 min. ee = 95%.

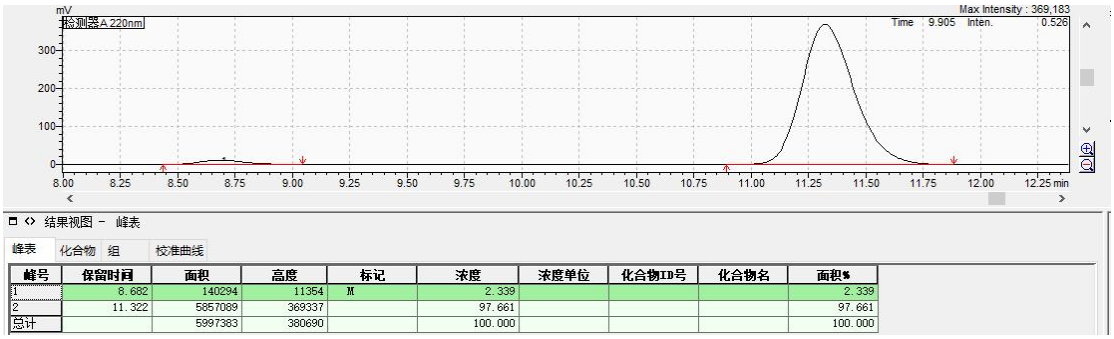


结果视图 - 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.671	23432710	1721433	M	49.168				49.168
2	11.421	24226055	1426395	M	50.832				50.832
总计		47658766	3147828		100.000				100.000

NL11:



结果视图 - 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.682	140294	11354	M	2.339				2.339
2	11.322	5857089	369337		97.661				97.661
总计		5997383	380690		100.000				100.000

L5:

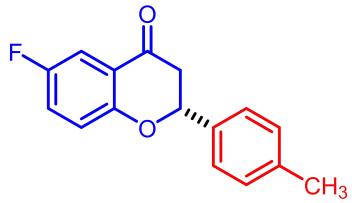
结果视图 - 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.750	30413	2436		1.596				1.596
2	11.474	1875588	119845	M	98.404				98.404
总计		1906001	122281		100.000				100.000

Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-6-fluoro-2-(*p*-tolyl)chroman-4-one (34)



White solid (49% isolated yield, 25.1 mg, 0.2 mmol), mp: 88.5 - 89.5 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

Synthesized according to the general procedure and purified by flash chromatography (10:1 petroleum ether /EtOAc) to afford a yellow solid. (25.1 mg, 49% yield)

The NMR data and HRMS data are in accordance with that of previous publications (*J Agric Food Chem.* **2022,** *70*, 3409-3419.)

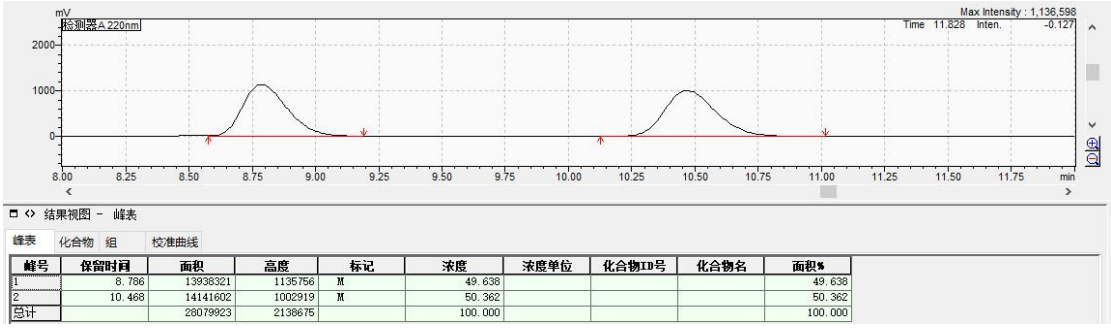
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J_1 = 8.3, J_2 = 3.2 Hz, 1H), 7.36 - 7.35 (m, 2H), 7.25 - 7.19 (m, 3H), 7.01 (dd, J_1 = 9.1, J_2 = 4.0 Hz, 1H), 5.42 (dd, J_1 = 13.6, J_2 = 2.8 Hz, 1H), 3.07 (dd, J_1 = 16.9, J_2 = 13.4 Hz, 1H), 2.87 (dd, J_1 = 17.1, J_2 = 2.9 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 158.0, 157.5 (d, J = 242.5 Hz), 139.0, 135.6, 129.7, 126.3, 123.8 (d, J = 24.3 Hz), 121.5 (d, J = 6.1 Hz), 120.0 (d, J = 7.3 Hz), 112.0 (d, J = 23.8 Hz), 79.9, 44.3, 21.3.

$[\alpha]_D^{11}$= +31° (*c* 0.1, $CHCl_3$).

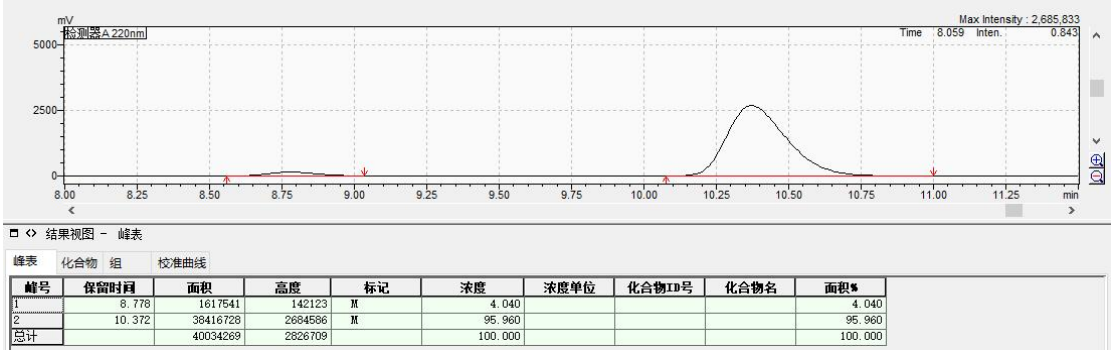
HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{14}O_2F$: 257.0972, found: 257.0970.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =8.7 min, major=10.4 min. ee = 92%.



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.786	13938321	1135756	M	49.638				49.638
2	10.468	14141602	1002919	M	50.362				50.362
总计		28079923	2138675		100.000				100.000

NL11:

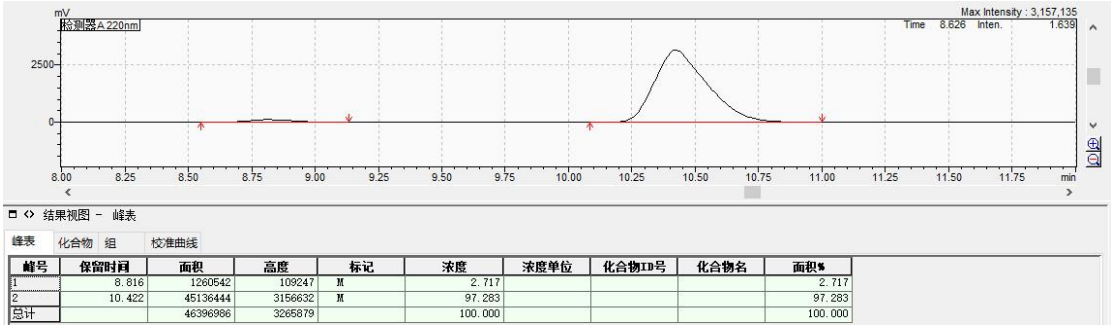


结果视图 – 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.778	1617541	142123	M	4.040				4.040
2	10.372	38416728	2684586	M	95.960				95.960
总计		40034269	2826709		100.000				100.000

L5:



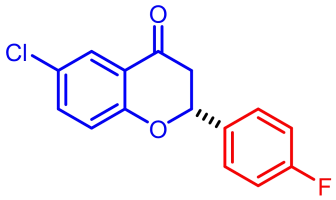
结果视图 – 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.816	1260542	109247	M	2.717				2.717
2	10.422	45136444	3156632	M	97.283				97.283
总计		46396986	3265879		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-6-chloro-2-(4-fluorophenyl)chroman-4-one (35)



Yellow solid (51% isolated yield, 28.2 mg, 0.2 mmol), mp: 91.3 – 93.4 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 2.7 Hz, 1H), 7.49 – 7.39 (m, 6H), 7.02 (d, J = 8.8 Hz, 1H), 5.47 (dd, J_1 = 13.3, J_2 = 3.0 Hz, 1H), 3.08 (dd, J_1 = 17.0, J_2 = 13.2 Hz, 1H), 2.91 (dd, J_1 = 17.0, J_2 = 3.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 160.1, 138.4, 136.1, 129.1, 129.0, 127.3, 126.5, 126.3, 121.8, 120.0, 79.9, 44.4.

$[\alpha]_D^{12}$= +53° (c 0.1, $CHCl_3$).

HRMS (ESI) $[M-H]^-$ calcd for $C_{15}H_9ClFO_2$: 275.0281, found: 275.0284.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =10.6 min, major=14.8 min. ee = 96%.

结果视图 – 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.684	4281839	305207		50.229				50.229
2	14.885	4242849	226153		49.771				49.771
总计		8524688	531360		100.000				100.000

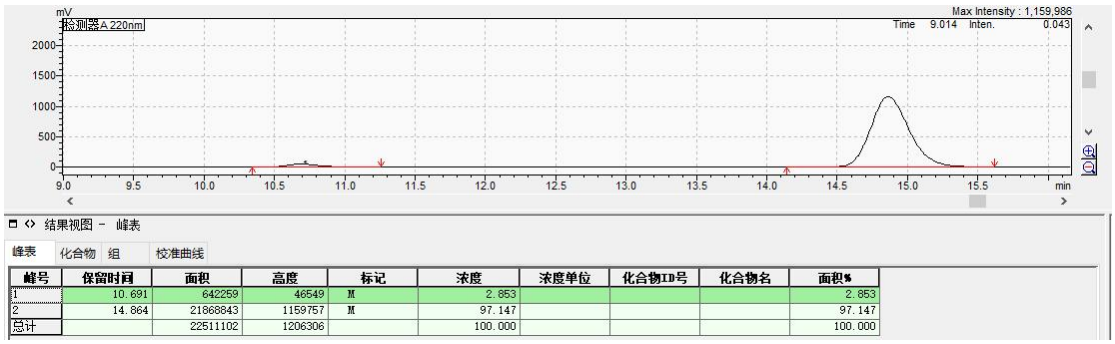
NL11:

结果视图 – 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.693	1122322	78290		1.890				1.890
2	14.863	58262781	3261778	M	98.110				98.110
总计		59385103	3340068		100.000				100.000

L5:



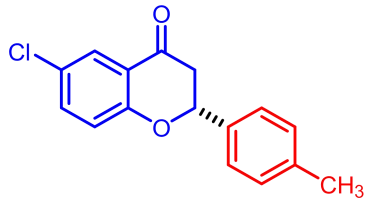
结果视图 – 峰表

峰表 | 化合物 | 组 | 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.691	642259	46549	M	2.853				2.853
2	14.864	21868843	1159757	M	97.147				97.147
总计		22511102	1206306		100.000				100.000

Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-6-chloro-2-(*p*-tolyl)chroman-4-one (36)



Yellow solid (44% isolated yield, 23.9 mg, 0.2 mmol), mp: 73.2 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

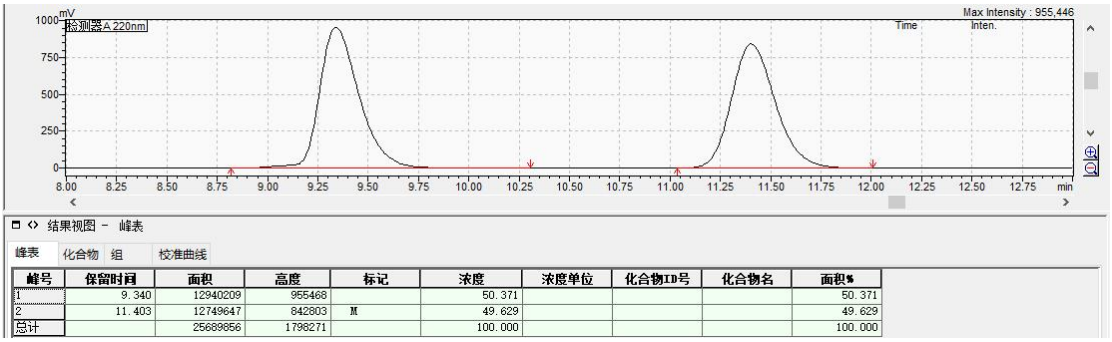
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 2.7 Hz, 1H), 7.40 – 7.30 (m, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.19 – 7.11 (m, 2H), 6.91 (d, J = 8.8 Hz, 1H), 5.35 (dd, J_1 = 13.2, J_2 = 2.9 Hz, 1H), 2.99 (dd, J_1 = 17.0, J_2 = 13.2 Hz, 1H), 2.79 (dd, J_1 = 17.0, J_2 = 2.9 Hz, 1H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 160.1, 139.0, 136.1, 135.4, 129.7, 127.2, 126.5, 126.3, 121.8, 120.0, 79.8, 44.2, 21.3.

$[\alpha]_D^{11}$= +59° (*c* 0.1, $CHCl_3$).

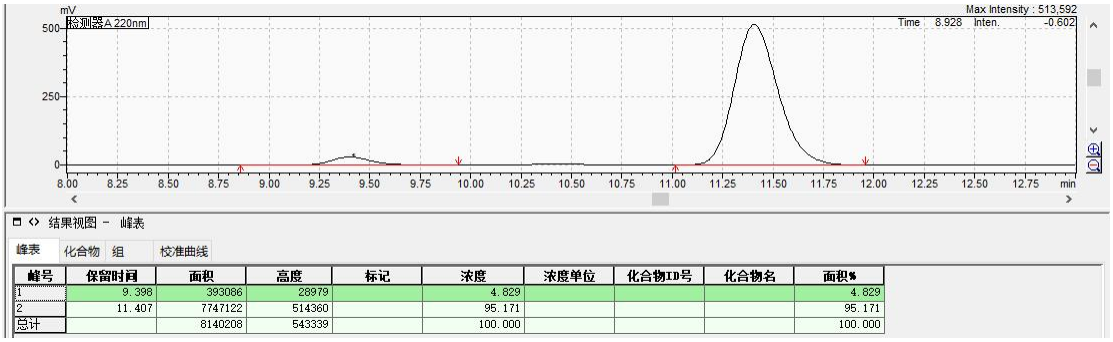
HRMS (ESI) $[M-H]^-$ calcd for $C_{16}H_{12}ClO_2$: 271.0531, found: 271.0526.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =9.3 min, major=11.4 min. ee = 90%.



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.340	12940209	955468		50.371				50.371
2	11.403	12749647	842803	M	49.629				49.629
总计		25689856	1798271		100.000				100.000

NL11:



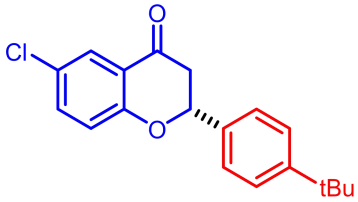
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.398	393086	28979		4.829				4.829
2	11.407	7747122	514360		95.171				95.171
总计		8140208	543339		100.000				100.000

L5:

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.402	50297	3756	M	2.450				2.450
2	11.410	2003011	133688	M	97.550				97.550
总计		2053308	137445		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-2-(4-(*tert*-butyl)phenyl)-6-chlorochroman-4-one (37)



Yellow solid (48% isolated yield, 30.1 mg, 0.2 mmol), mp: 102.2 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 2.7 Hz, 1H), 7.55 – 7.34 (m, 5H), 7.01 (d, J = 8.9 Hz, 1H), 5.45 (dd, J_1 = 13.3, J_2 = 2.9 Hz, 1H), 3.11 (dd, J_1 = 17.0, J_2 = 13.3 Hz, 1H), 2.90 (dd, J_1 = 17.0, J_2 = 2.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 160.2, 152.3, 136.1, 135.3, 127.2, 126.5, 126.2, 126.0, 121.8, 120.0, 79.9, 44.2, 31.4.

$[\alpha]_D^{14}$= +61° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M-H]^-$ calcd for $C_{19}H_{18}ClO_2$: 313.1001, found: 313.1001.

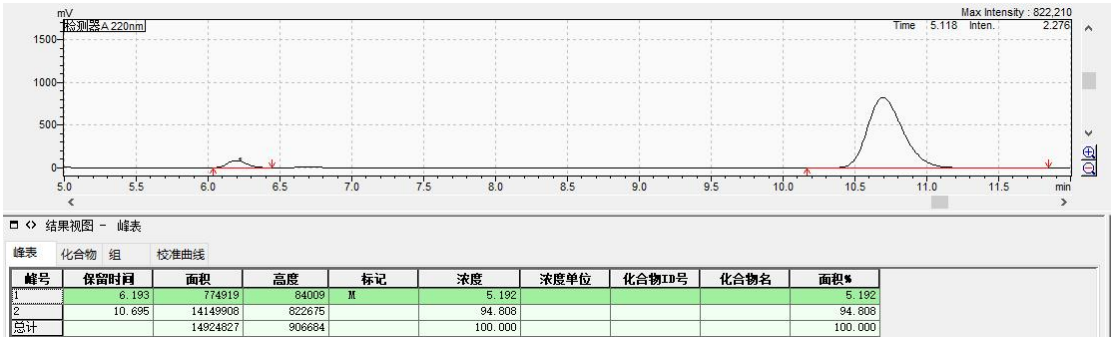
HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =6.1 min, major=10.7 min. ee = 94%.

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.178	11252466	1189417		49.950				49.950
2	10.705	11275044	661792	M	50.050				50.050
总计		22527510	1851209		100.000				100.000

NL11:

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.198	150622	16214	M	3.290				3.290
2	10.727	4427274	244736	M	96.710				96.710
总计		4577896	260950		100.000				100.000

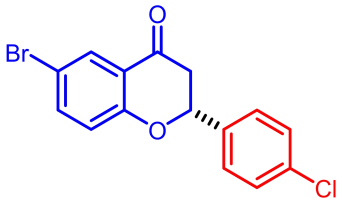
L5:



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	6.193	774919	84009	M	5.192				5.192
2	10.695	14149908	822675		94.808				94.808
总计		14924827	906684		100.000				100.000

Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-6-bromo-2-(4-chlorophenyl)chroman-4-one (38)



Yellow solid (45% isolated yield, 30.2 mg, 0.2 mmol), mp: 117.9 - 119.9 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

The NMR data and HRMS data are in accordance with that of previous publications (*J Agric Food Chem.* **2022,** *70*, 3409-3419.)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 2.5 Hz, 1H), 7.59 (dd, J_1 = 8.9, J_2 = 2.5 Hz, 1H), 7.44 -7.39 (m, 4H), 6.96 (d, J = 8.6 Hz, 1H), 5.45 (dd, J_1 = 13.1, J_2 = 2.9 Hz, 1H), 3.03 (dd, J_1 = 17.1, J_2 = 13.2 Hz, 1H), 2.91 - 2.87 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 160.3, 139.1, 136.9, 135.0, 129.7, 129.3, 127.7, 122.28, 120.3, 114.7, 79.2, 44.3.

$[\alpha]_D^{10}$= +35° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M+H]^+$ calcd for $C_{15}H_{11}O_2BrCl$: 336.9626, found: 336.9623.

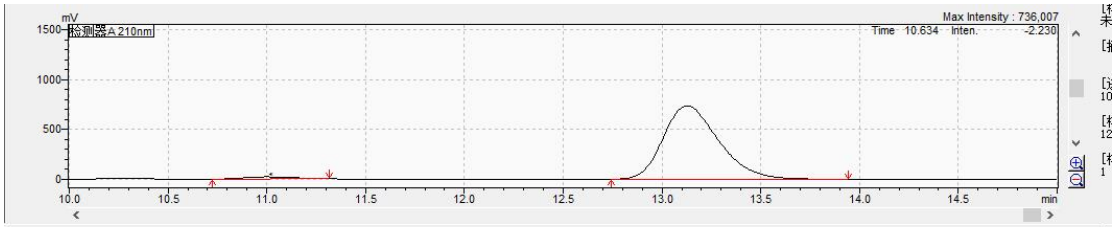
HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =12.0 min, major=14.4 min. ee = 95%.

结果视图 – 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.010	6230353	307657	M	50.044				50.044
2	14.479	6219492	325227	M	49.956				49.956
总计		12449845	632885		100.000				100.000

NL11:



结果视图 – 峰表

峰表 化合物 组 校准曲线

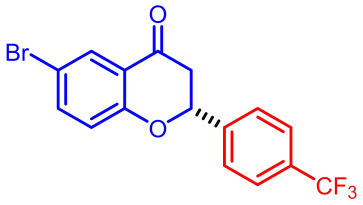
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.999	379676	21923	M	2.594				2.594
2	13.127	14259129	737357	M	97.406				97.406
总计		14638805	759280		100.000				100.000

L5:

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	12.188	84024	4785	M	0.992				0.992
2	14.460	8384896	438151	M	99.008				99.008
总计		8468920	442935		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-6-bromo-2-(4-(trifluoromethyl)phenyl)chroman-4-one (39)



Yellow solid (44% isolated yield, 32.5 mg, 0.2 mmol), mp: 117.8 - 118.2 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

The NMR data and HRMS data are in accordance with that of previous publications (*J Agric Food Chem.* **2022,** *70*, 3409-3419.)

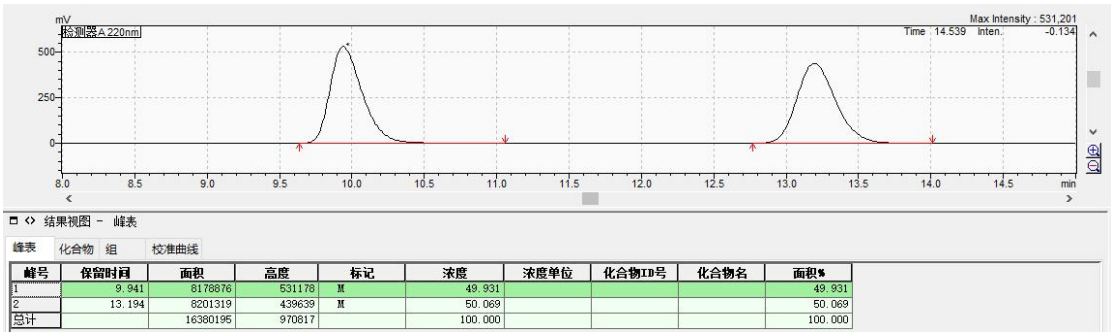
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 2.7 Hz, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.62 - 7.59 (m, 3H), 6.98 (d, J = 9.0 Hz, 1H), 5.55 (dd, J_1 = 12.9, J_2= 3.2 Hz, 1H), 3.04 (dd, J_1 = 16.9, J_2 = 12.9 Hz, 1H), 2.96 - 2.92 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1, 160.2, 142.3, 139.2, 131.1 (t, J = 33.1 Hz), 129.8, 126.5, 126.1 (q, J = 3.7 Hz), 124.0 (d, J = 271.9 Hz), 122.3, 120.3, 114.9, 79.1, 44.4.

$[\alpha]_D^{12}$= +65° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{11}O_2F_3$: 370.9889, found: 370.9888.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =10.2 min, major=13.5 min. ee = 93%.



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.941	8178876	531178	M	49.931				49.931
2	13.194	8201319	439639	M	50.069				50.069
总计		16380195	970817		100.000				100.000

NL11:

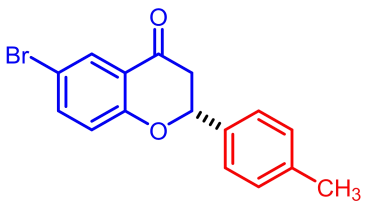
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.296	493435	29020		3.647				3.647
2	13.563	13037026	595082	M	96.353				96.353
总计		13530461	624103		100.000				100.000

L5:

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.008	159254	10356	M	1.551				1.551
2	13.193	10108921	541113	M	98.449				98.449
总计		10268175	551469		100.000				100.000

Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-6-bromo-2-(*p*-tolyl)chroman-4-one (40)



Yellow solid (64% isolated yield, 40.4 mg, 0.2 mmol), mp: 99.1 - 103.0 ℃, column

chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents. The NMR data and HRMS data are in accordance with that of previous publications (*J Agric Food Chem.* **2022,** *70*, 3409-3419.)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 - 8.01 (m, 1H), 7.57 - 7.54 (m, 1H), 7.34 (d, J = 7.6 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 6.93 (d, J = 8.9 Hz, 1H), 5.42 (dd, J_1 = 13.0, J_2 = 2.7 Hz, 1H), 3.07 (dd, J_1 = 17.0, J_2 = 13.2 Hz, 1H), 2.87 (dd, J_1 = 17.2, J_2 = 3.0 Hz, 1H), 2.37 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 160.6, 139.1, 138.9, 135.3, 129.7, 129.6, 126.3, 122.3, 120.4, 114.4, 79.8, 44.2, 21.3.

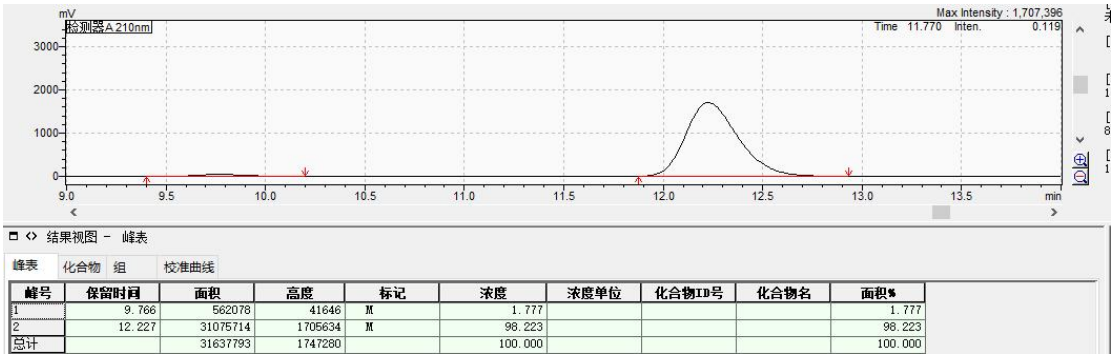
$[\alpha]_D^{12}$= +41° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{14}O_2Br$: 317.0172, found: 317.0171.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =9.7 min, major=12.2 min. ee = 97%.

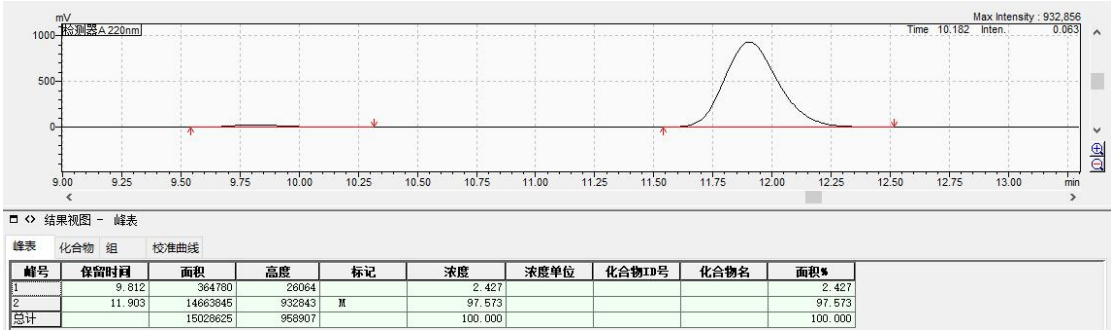
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.747	10779029	780768	M	49.887				49.887
2	11.908	10828061	691496	M	50.113				50.113
总计		21607090	1472264		100.000				100.000

NL11:



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.766	562078	41646	M	1.777				1.777
2	12.227	31075714	1705634	M	98.223				98.223
总计		31637793	1747280		100.000				100.000

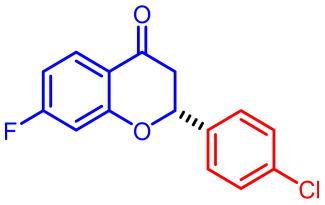
L5:



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.812	364780	26064		2.427				2.427
2	11.903	14663845	932843	M	97.573				97.573
总计		15028625	958907		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-2-(4-chlorophenyl)-7-fluorochroman-4-one (41)



Yellow solid (45% isolated yield, 24.8 mg, 0.2 mmol), mp: 86.8 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

The NMR data and HRMS data are in accordance with that of previous publications (*J Agric Food Chem.* **2022,** *70*, 3409-3419.)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, J_1 = 8.8, J_2 = 6.7 Hz, 1H), 7.44 - 7.38 (m, 4H), 6.80 - 6.72 (m, 2H), 5.48 (dd, J_1 = 13.2, J_2 = 2.9 Hz, 1H), 3.02 (dd, J_1 = 17.0, J_2 = 13.1 Hz, 1H), 2.87 (dd, J_1 = 17.1, J_2 = 2.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.2, 167.7 (d, J = 256.9 Hz), 163.0 (d, J = 13.4 Hz), 136.9, 134.9, 129.7 (d, J = 11.5 Hz), 129.2, 127.6, 117.9, 110.4 (d, J = 22.8 Hz), 105.1 (d, J = 25.0 Hz), 79.5, 44.3.

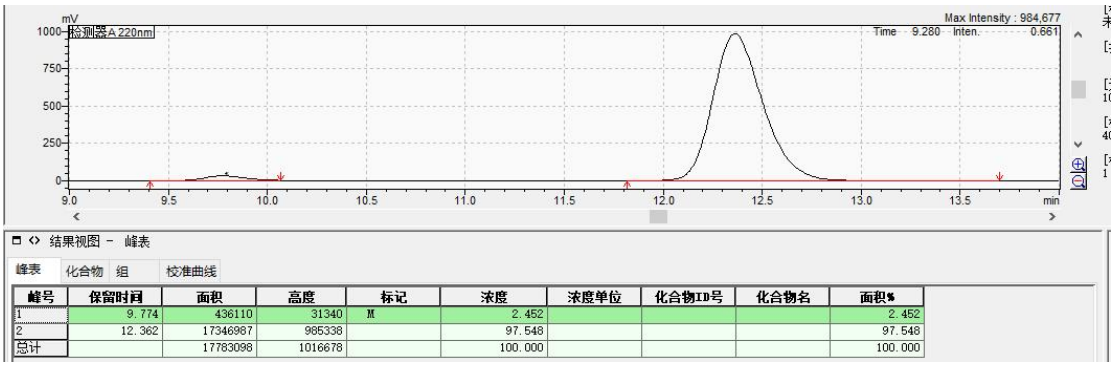
$[\alpha]_D^{11}$= +35° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M+H]^+$ calcd for $C_{15}H_{11}O_2FCl$: 277.0426, found: 277.0424.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =10.0 min, major=12.5 min. ee = 95%.

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.047	17585151	1285852		50.214				50.214
2	12.508	17435241	1095577		49.786				49.786
总计		35020391	2381429		100.000				100.000

NL11:



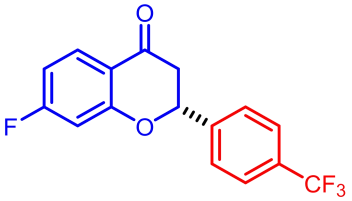
峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.774	436110	31340	M	2.452				2.452
2	12.362	17346987	985338		97.548				97.548
总计		17783098	1016678		100.000				100.000

L5:

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	10.107	588538	41288		1.822				1.822
2	12.493	31710440	1991279		98.178				98.178
总计		32298978	2032567		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-7-fluoro-2-(4-(trifluoromethyl)phenyl)chroman-4-one (42)



Yellow solid (50% isolated yield, 31.0 mg, 0.2 mmol), mp: 128.5 – 131.4 ℃, column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

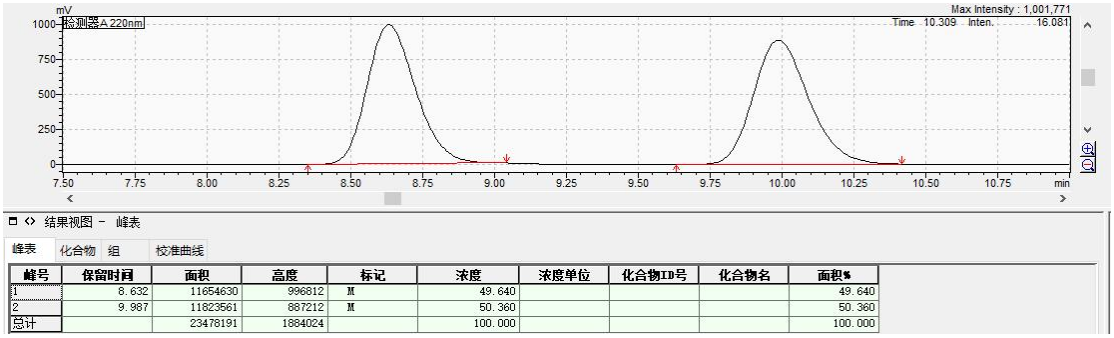
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J_1 = 8.8, J_2 = 6.6 Hz, 1H), 7.45 (dd, J_1 = 8.7, J_2 = 5.2 Hz, 2H), 7.13 (t, J = 8.6 Hz, 2H), 6.81 – 6.72 (m, 2H), 5.48 (dd, J_1 = 13.1, J_2 = 3.0 Hz, 1H), 3.05 (dd, J_1 = 16.9, J_2 = 13.1 Hz, 1H), 2.87 (dd, J_1 = 16.9, J_2 = 3.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 169.0, 166.5, 163.1 (d, J = 13.5 Hz), 163.0 (d, J = 248.1 Hz), 134.3 (d, J = 3.3 Hz), 129.8 (d, J = 11.4 Hz), 128.2 (d, J = 8.3 Hz), 118.0 (d, J = 2.5 Hz), 116.0 (d, J = 21.6 Hz), 110.4 (d, J = 22.6 Hz), 105.0 (d, J = 24.5 Hz), 79.6, 44.4.

$[\alpha]_D^{9}$= +49° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M+H]^+$ calcd for $C_{16}H_{12}F_4O_2$: 311.0690, found: 311.0693.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =8.6 min, major=9.9 min. ee = 93%.

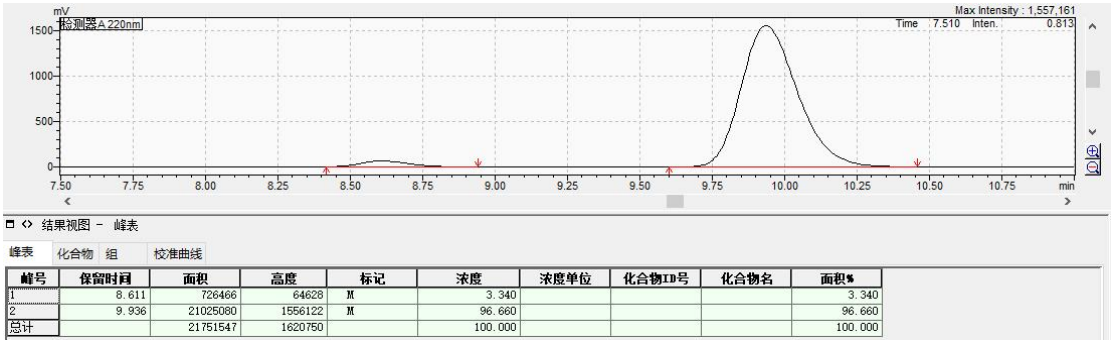


结果视图 - 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.632	11654630	996812	M	49.640				49.640
2	9.987	11823561	887212	M	50.360				50.360
总计		23478191	1884024		100.000				100.000

NL11:

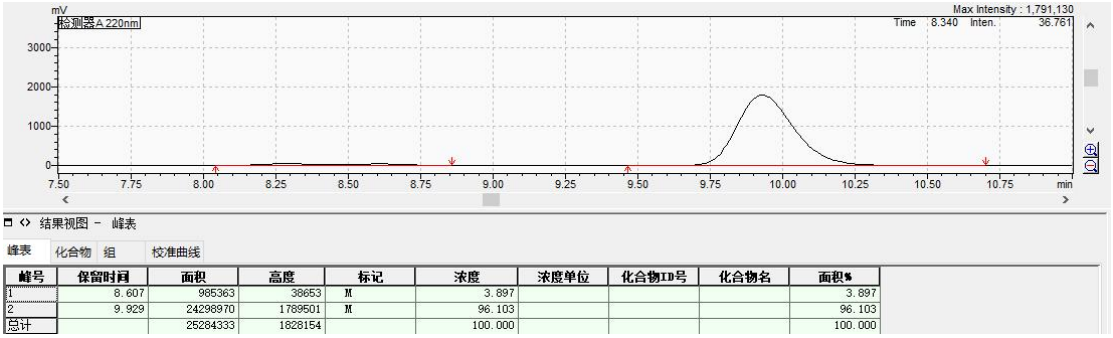


结果视图 - 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.611	726466	64628	M	3.340				3.340
2	9.936	21025080	1556122	M	96.660				96.660
总计		21751547	1620750		100.000				100.000

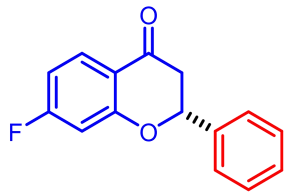
L5:



峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	8.607	985363	38653	M	3.897				3.897
2	9.929	24298970	1789501	M	96.103				96.103
总计		25284333	1828154		100.000				100.000

Annotation：Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

(*R*)-7-fluoro-2-phenylchroman-4-one (43)



Yellow oil (76% isolated yield, 36.8 mg, 0.2 mmol), column chromatography purification using petroleum ether/EtOAc (10:1, v/v) as eluents.

The NMR data and HRMS data are in accordance with that of previous publications (*J Agric Food Chem.* **2022,** *70*, 3409-3419.)

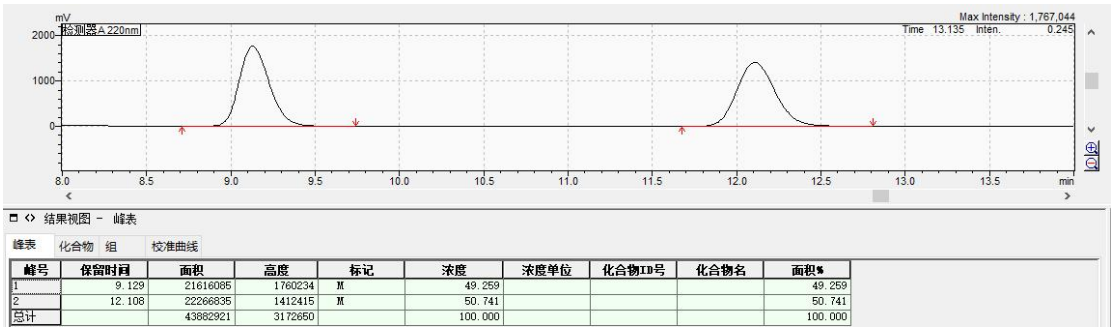
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 - 7.94 (m, 1H), 7.48 - 7.40 (m, 5H), 6.80 - 6.73 (m, 2H), 5.50 (dd, J_1 = 13.3, J_2 = 3.0 Hz, 1H), 3.11 - 3.05 (m, 1H), 2.89 (dd, J_1 = 16.9, J_2 = 3.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 167.7 (d, J = 256.0 Hz), 163.4, 163.3, 138.4, 129.7 (d, J = 11.8 Hz), 129.1 (d, J = 5.8 Hz), 126.3, 118.0, 110.2 (d, J = 22.9 Hz), 105.1 (d, J = 24.3 Hz), 80.3, 44.4.

$[\alpha]_D^{10}$= +41° (*c* 0.1, $CHCl_3$).

HRMS (ESI) $[M+H]^+$ calcd for $C_{15}H_{12}O_2F$: 243.0816, found: 243.0818.

HPLC Conditions: 10% IPA/ Hexanes, 0.9 mL/min, Daicel Chiralpak OD-H column, λ= 220 nm, t_R (min): minor =9.1 min, major=12.1 min. ee = 95%.

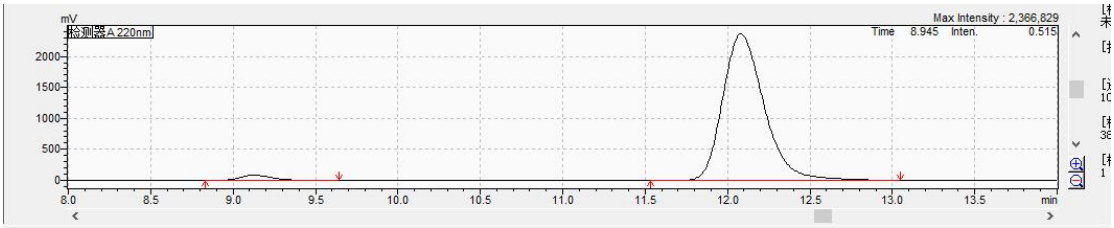


结果视图 – 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.129	21616085	1760234	M	49.259				49.259
2	12.108	22266835	1412415	M	50.741				50.741
总计		43882921	3172650		100.000				100.000

NL11:

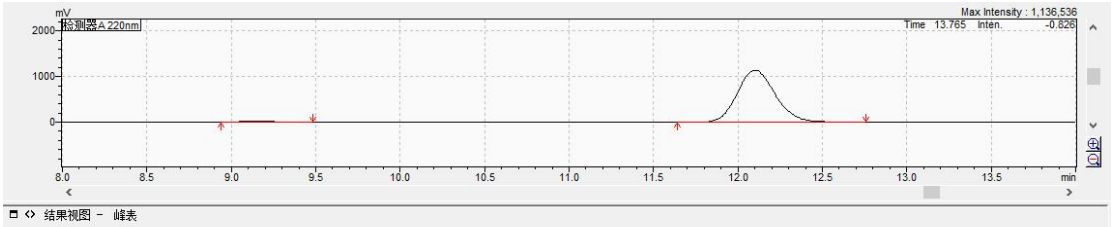


结果视图 – 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.127	1084267	84486	V	2.578				2.578
2	12.082	40966522	2367434	M	97.422				97.422
总计		42050789	2451920		100.000				100.000

L5:



结果视图 – 峰表

峰表 化合物 组 校准曲线

峰号	保留时间	面积	高度	标记	浓度	浓度单位	化合物ID号	化合物名	面积%
1	9.144	327407	28618	M	1.814				1.814
2	12.101	17719722	1136593	M	98.186				98.186
总计		18047130	1165211		100.000				100.000

Annotation： Peak number (峰号), Retention Time (min) (保留时间), Area (mV*min) (面积), Height (mV) (高度), Labeled peak (标记), Concentration (浓度) and Relative Area (%) (面积%).

6. Density functional theory (DFT) of NL11

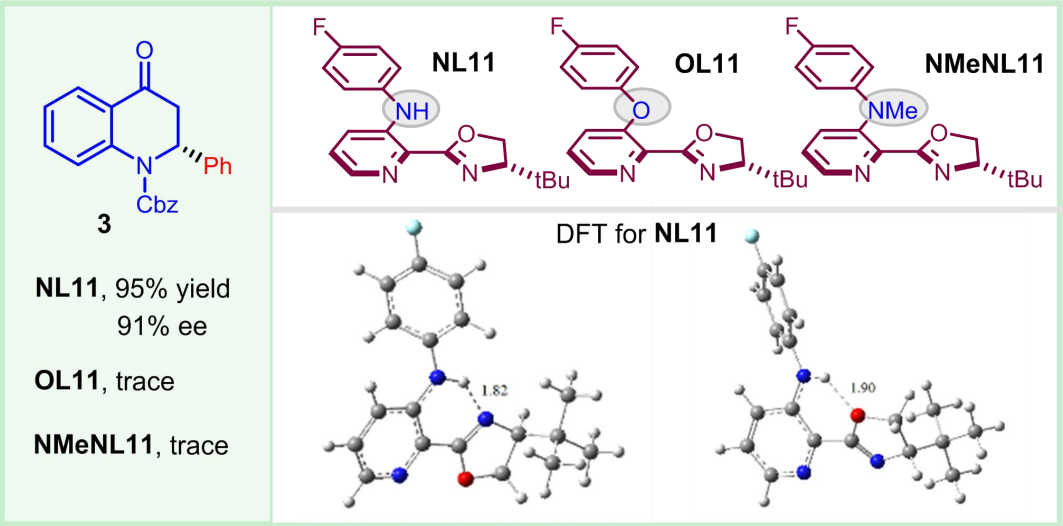
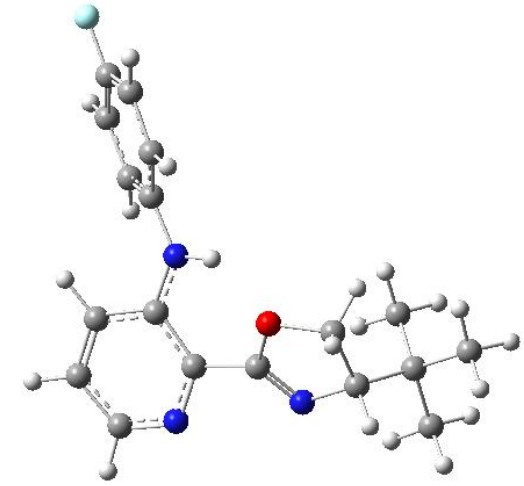


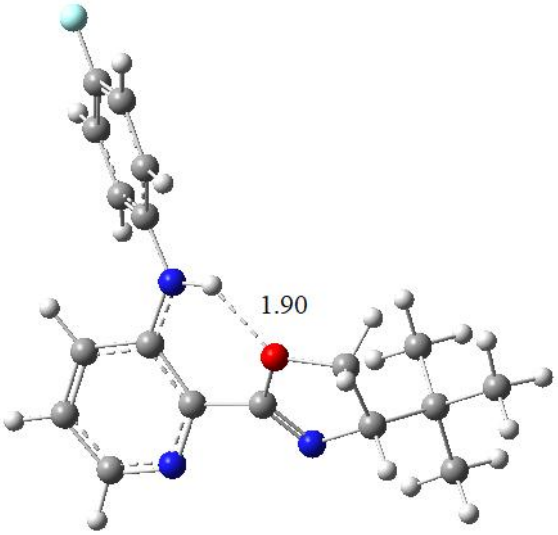
Figure 1 Control Experiments, X-ray, and DFT for Ligand **NL11**

Consistent with our previous observation, these modifications were detrimental, showing the indispensability of the NH segment for the current transformation. This may be due to the flexibility from the ring-opening of the carboline ring. The presence of NH-functionality could counterbalance this by forming an intramolecular H-bonding with oxazoline to further rigidify the ligand structure for improving catalytic performance. Density functional theory (DFT) calculation (Gaussian 16 software at the B3LYP-D3 level.) was carried out to show the potential hydrogen bonding between NH and oxazoline segment (**Figure 3**). The appended aromatic unit of **NHPyOx** may also possess a π-π stacking interaction with the substrates.

All calculations were performed using Gaussian 16 software with the density functional theory (DFT). Structure optimization was carried out at the B3LYP-D3 level of theory with the 6-311G(d,p) basis set for C, N, O, F and H. The vibrational frequencies were also computed at the same level.

# 1 NL11_1_opt
G = -1037.325473





C	-1.10890000	3.77969800	0.23881700
C	0.27546000	3.95716600	0.22330200
N	1.11418600	2.96566600	-0.04556200
C	0.63141500	1.74358800	-0.29337300
C	-0.75961600	1.44831900	-0.27850300
C	-1.62648200	2.52421200	-0.01583500
C	1.66458600	0.71692300	-0.55977100
O	1.27575800	-0.34997700	-1.34982500
C	2.43617700	-1.21166900	-1.46701300
C	3.51865700	-0.49830100	-0.61419300
N	2.85732200	0.72331200	-0.13489700
N	-1.23444300	0.17474300	-0.52691200
H	-0.58703200	-0.44294500	-0.99610800
C	-2.50562800	-0.33879900	-0.23145300
C	-3.07333600	-1.27413100	-1.10661000

C	-4.30176700	-1.86076800	-0.82565900
C	-4.97440400	-1.48936500	0.32712500
C	-4.44050500	-0.56581100	1.21190500
C	-3.20026300	-0.00085800	0.93807200
F	-6.17889000	-2.04358300	0.59762300
C	4.09639700	-1.32616600	0.56437000
C	5.14918500	-0.46775000	1.28237700
C	4.76508000	-2.59177400	0.00579500
C	2.98665100	-1.70544300	1.55602500
H	-1.76894100	4.61640500	0.43473000
H	0.71983800	4.92644700	0.42509100
H	-2.69561600	2.36376800	-0.03215600
H	2.69559000	-1.28044300	-2.52348900
H	2.15911600	-2.19931700	-1.09819800
H	4.36297100	-0.20172200	-1.24582900
H	-2.54591400	-1.53523500	-2.01675600
H	-4.74625000	-2.58586800	-1.49525700
H	-4.98515400	-0.31256800	2.11254000
H	-2.76014400	0.68895300	1.64562400
H	5.57235700	-1.01249600	2.13104400
H	4.70549400	0.46052900	1.64315000
H	5.96916200	-0.20975400	0.60513500
H	5.23607600	-3.15957800	0.81249400
H	4.04695800	-3.25592300	-0.48403200
H	5.54244700	-2.33751200	-0.72134200
H	2.20995200	-2.32057000	1.09202900
H	3.40421000	-2.28005700	2.38682400
H	2.51312500	-0.81052800	1.96380900

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2 NL11_2_opt

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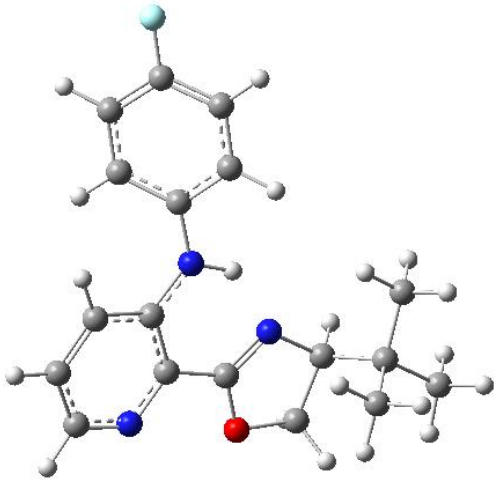
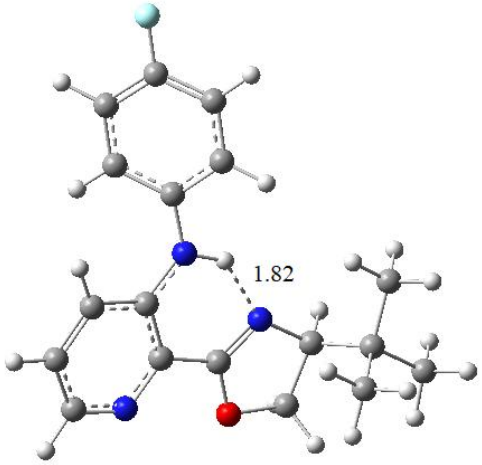
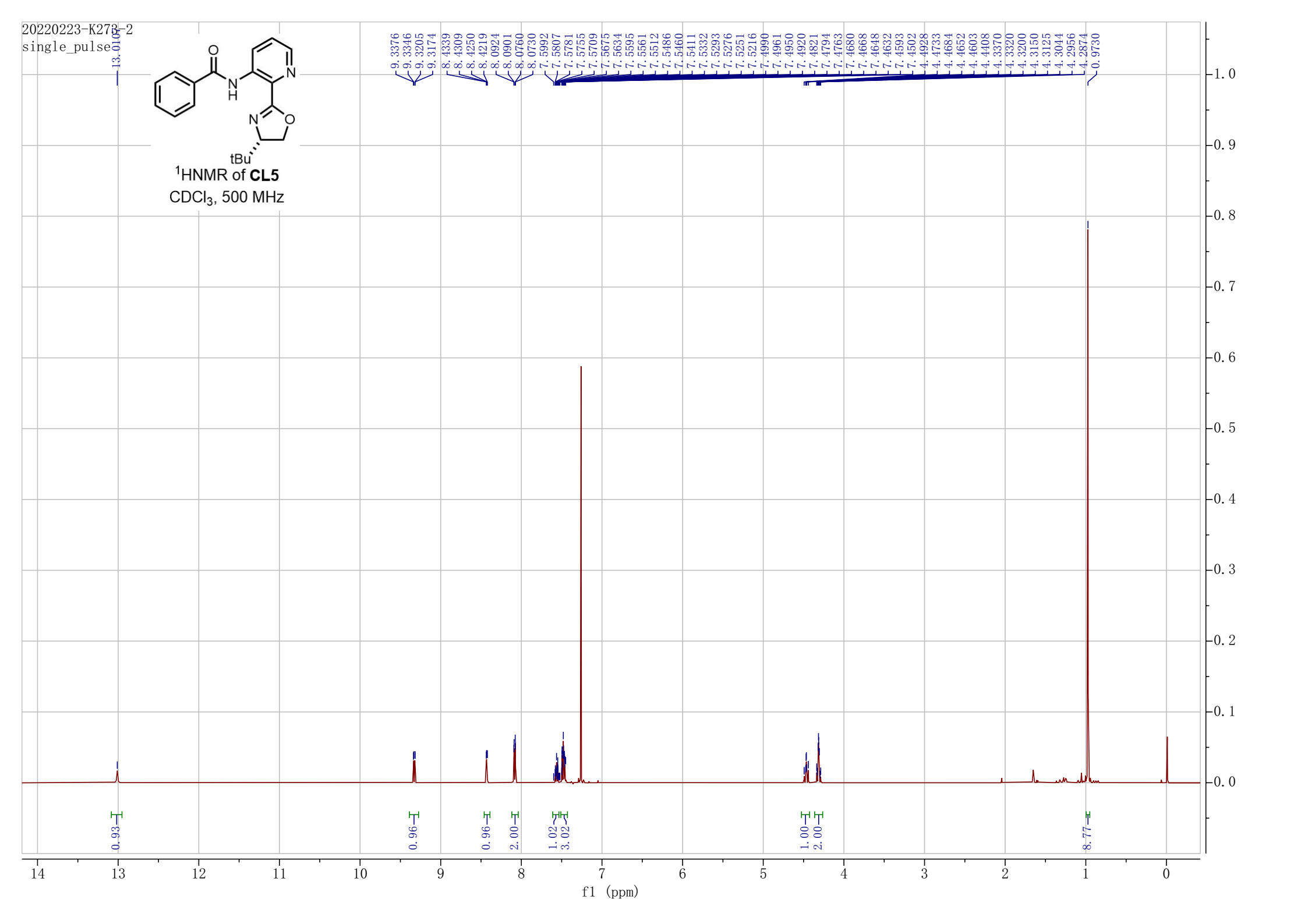


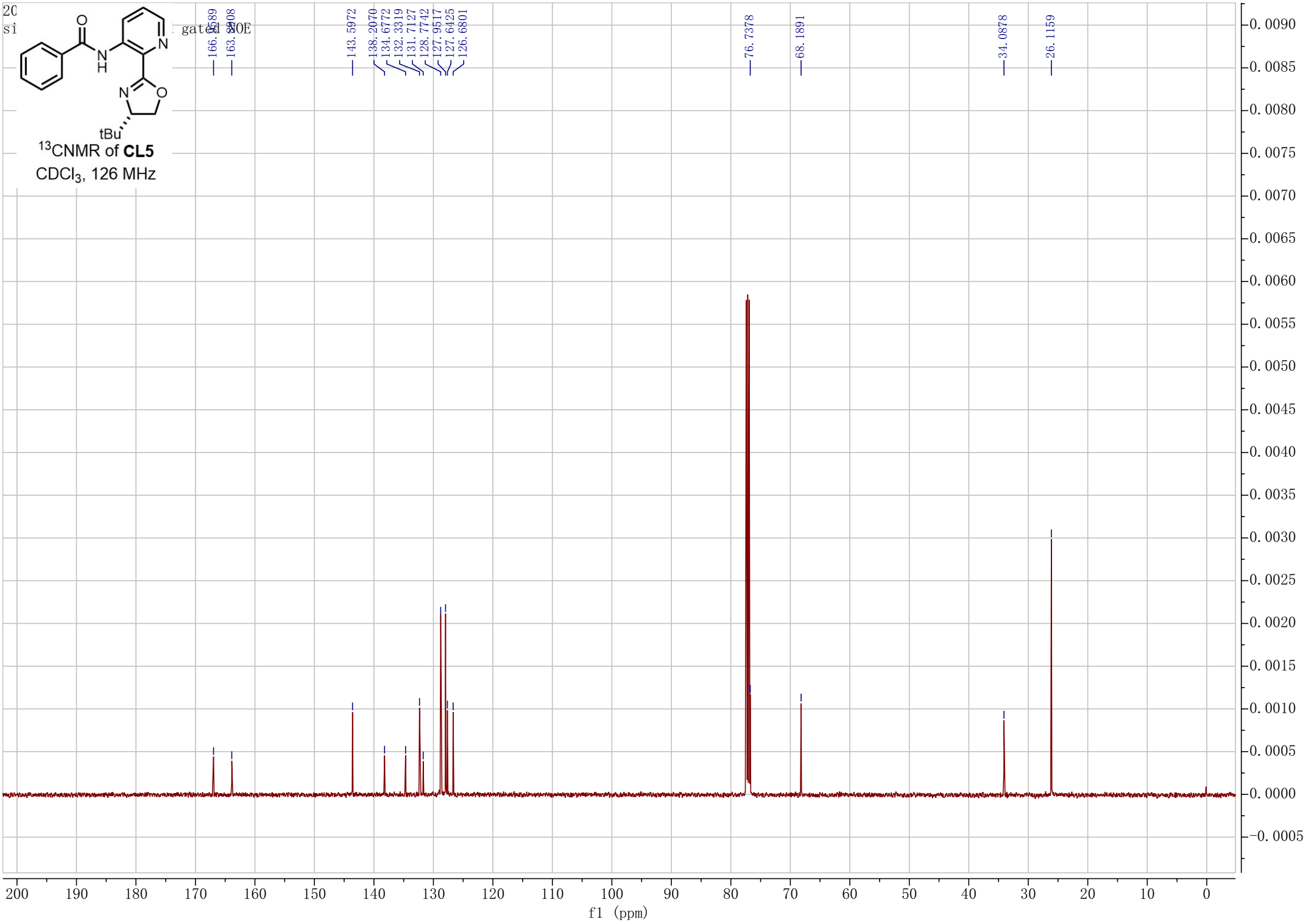


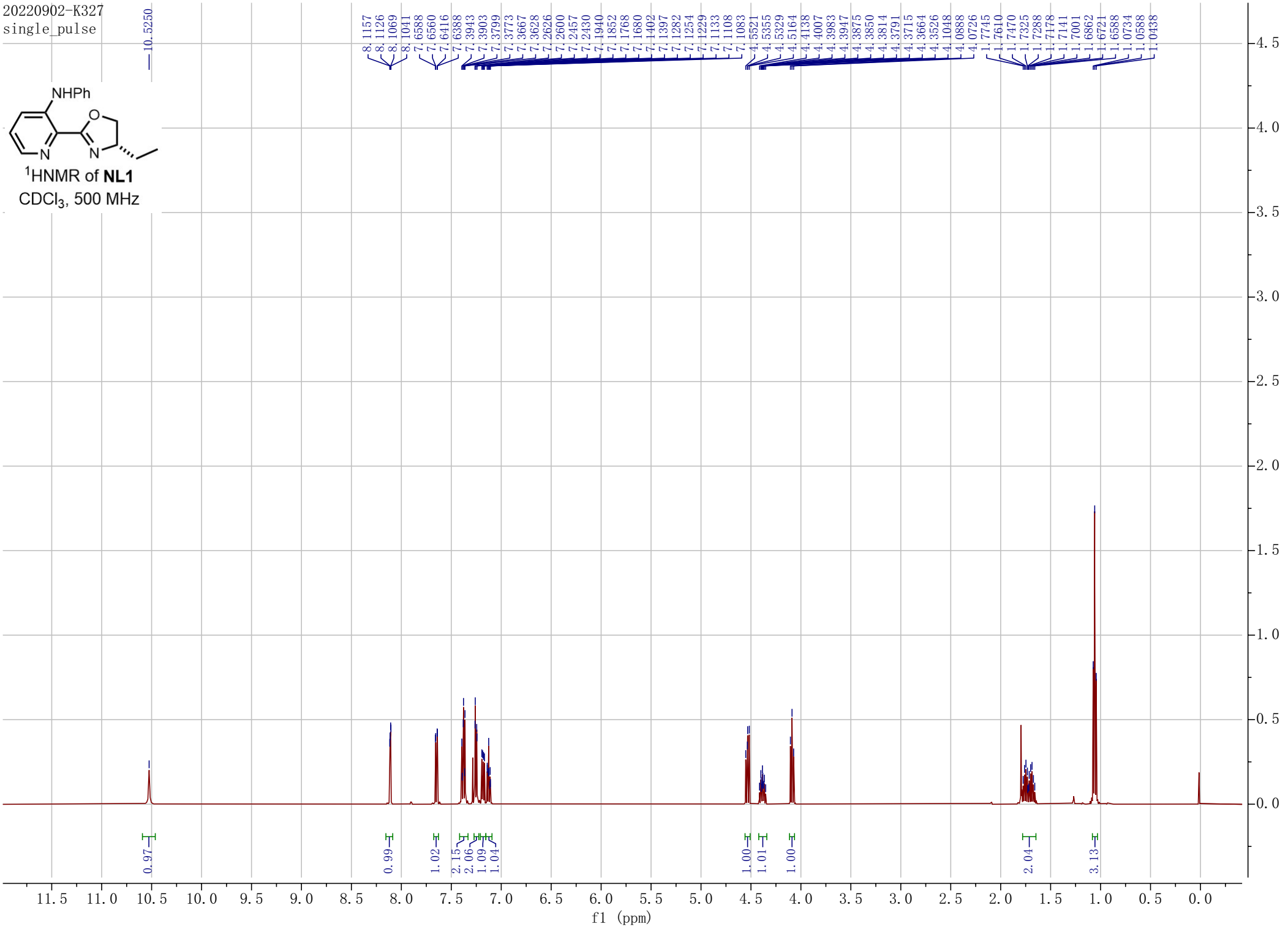
C	1.02677400	3.84073400	0.70828300
C	-0.31138700	4.13105200	0.42624800
N	-1.17426000	3.19580400	0.05714900
C	-0.75479700	1.93190900	-0.07781400
C	0.59787300	1.53324400	0.14560300
C	1.48192600	2.54445400	0.57140000
C	-1.78324400	0.94764500	-0.44104100
O	-3.03546700	1.41042700	-0.64880000
C	-3.83164100	0.26349400	-1.03412500
C	-2.88553600	-0.94963500	-0.84476800
N	-1.59113600	-0.31729200	-0.55626700
N	0.97510300	0.22519400	-0.00685800
H	0.19371500	-0.40992900	-0.19535200
C	2.27603600	-0.30221600	-0.03626500
C	2.49333000	-1.56441800	0.53161300
C	3.74492500	-2.16589800	0.47664300

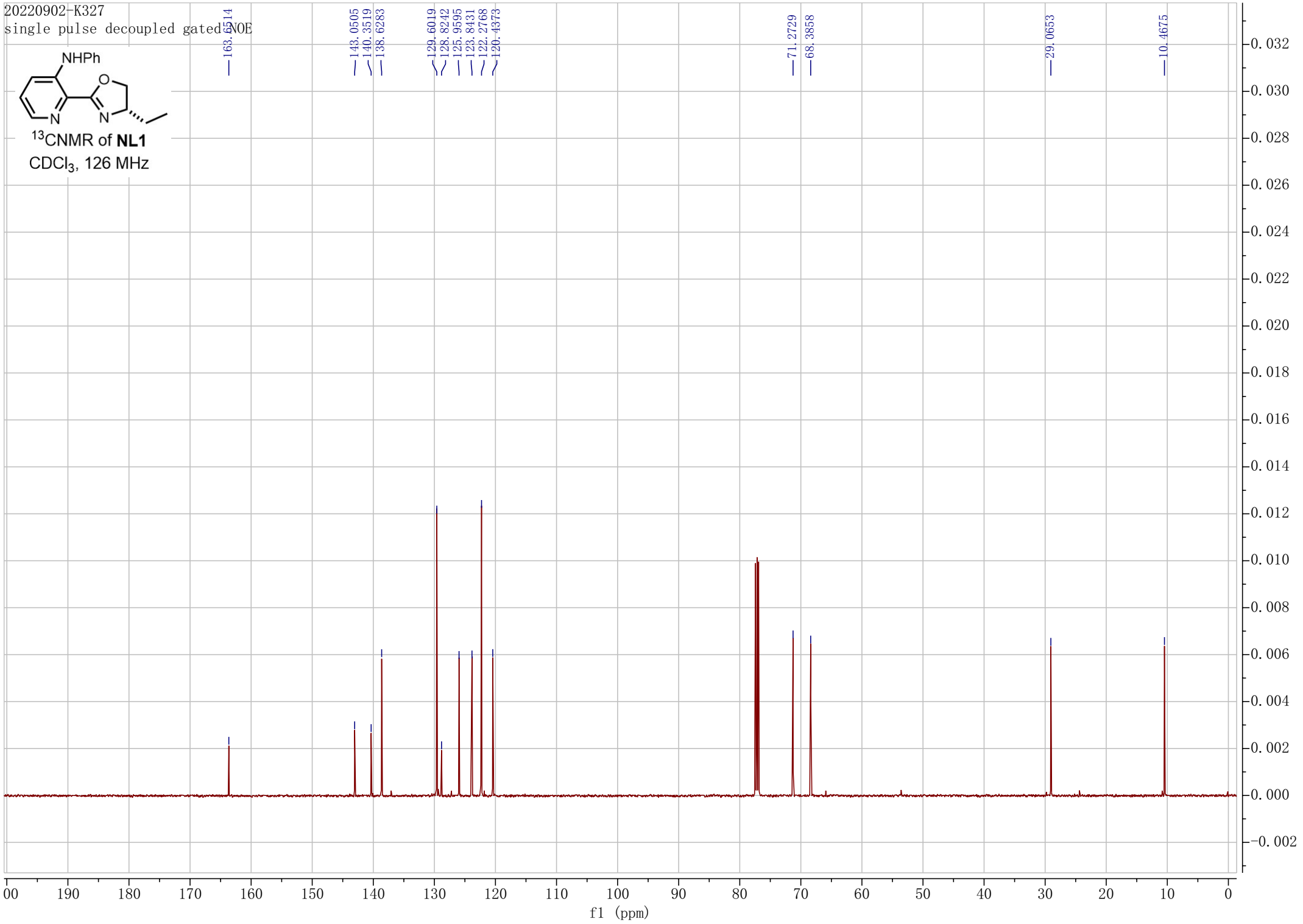
C	4.78803900	-1.48738700	-0.13316600
C	4.60568000	-0.23876900	-0.70566100
C	3.34506600	0.34710600	-0.66765700
F	6.01337400	-2.05988000	-0.17494500
C	-3.29056100	-1.95395300	0.26865600
C	-2.22444000	-3.05840500	0.33932100
C	-4.64320800	-2.58301400	-0.10002300
C	-3.38557700	-1.25135000	1.63079700
H	1.69810200	4.62378200	1.04093300
H	-0.69591100	5.14220300	0.51170200
H	2.50629200	2.29504700	0.80965800
H	-4.13864000	0.40259800	-2.07185500
H	-4.71575400	0.24743700	-0.39838400
H	-2.79889200	-1.51775100	-1.77659800
H	1.67029200	-2.06881200	1.02367100
H	3.92186600	-3.14143000	0.91108400
H	5.43891100	0.25276600	-1.19152200
H	3.18552400	1.30050500	-1.15304400
H	-2.49260400	-3.80043800	1.09640900
H	-1.24969500	-2.64083300	0.59609500
H	-2.12922700	-3.57525400	-0.62042300
H	-4.92503800	-3.33786400	0.63866700
H	-5.44597500	-1.84134900	-0.13152100
H	-4.59612700	-3.07294600	-1.07746500
H	-4.13493100	-0.45542900	1.63262500
H	-3.66655300	-1.96886200	2.40613700
H	-2.42546900	-0.81144300	1.90765800

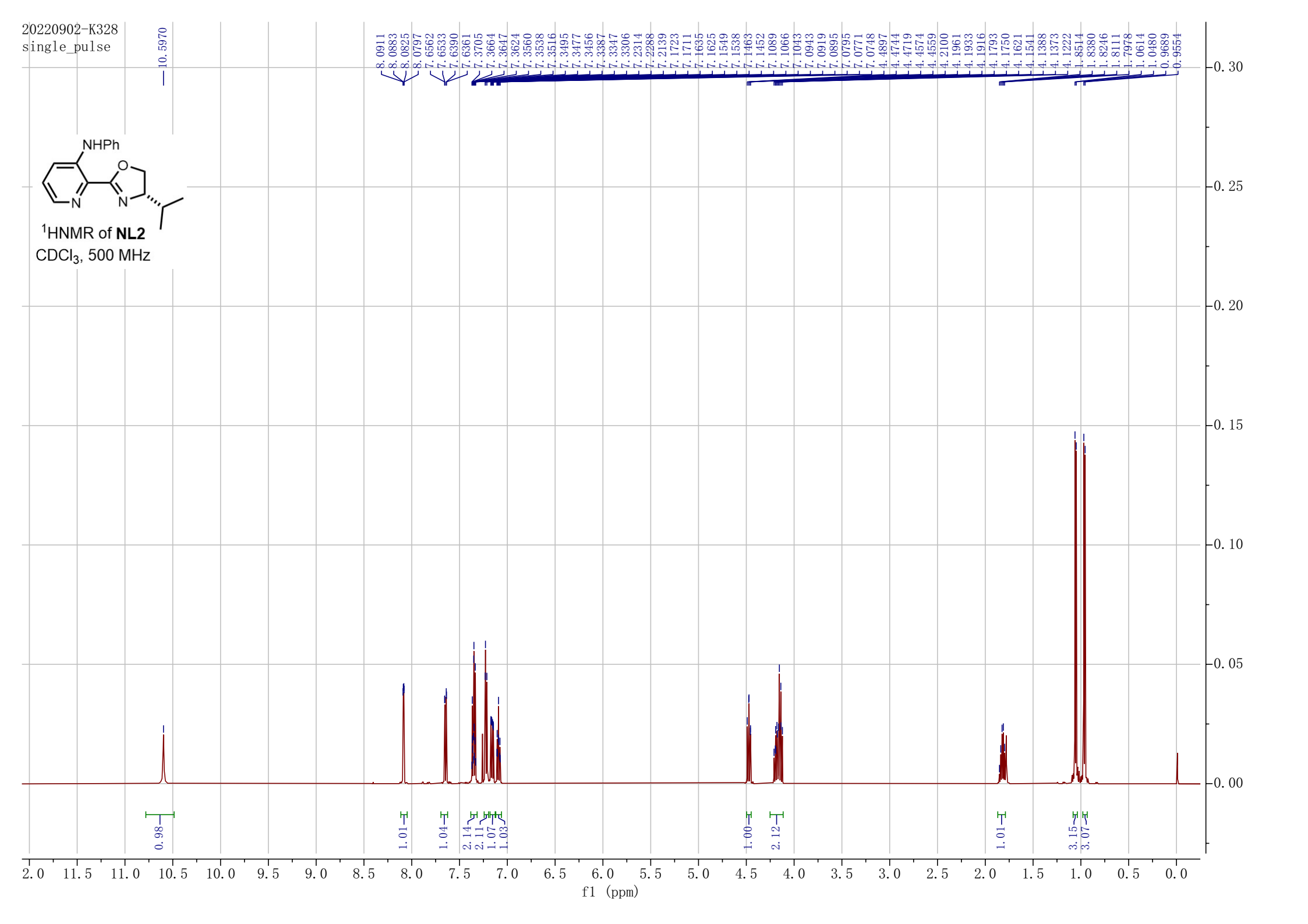
7. NMR spectra


20220223-K273-2
single_pulse
tBu
^{1}HNMR of **CL5**
$CDCl_3$, 500 MHz
f1 (ppm)

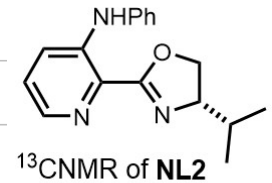

166.4589
163.4008
143.5972
138.2070
134.6772
132.3319
131.7127
128.7742
127.9517
127.6425
126.6801
76.7378
68.1891
34.0878
26.1159
tBu
13CNMR of CL5
CDCl3, 126 MHz
f1 (ppm)


20220902-K327
single_pulse
NHPh
O
N
N
^{1}HNMR of **NL1**
$CDCl_3$, 500 MHz
f1 (ppm)


20220902-K327
single pulse decoupled gated NOE
NHPh
O
N
N
13CNMR of NL1
CDCl3, 126 MHz
163.6514
143.0505
140.3519
138.6283
129.6019
128.8242
125.9595
123.8431
122.2768
120.4373
71.2729
68.3858
29.0653
10.4675
0.032
0.030
0.028
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
-0.002
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


20220902-K328
single_pulse
NHPh
N
O
N
^{1}HNMR of **NL2**
$CDCl_3$, 500 MHz
f1 (ppm)

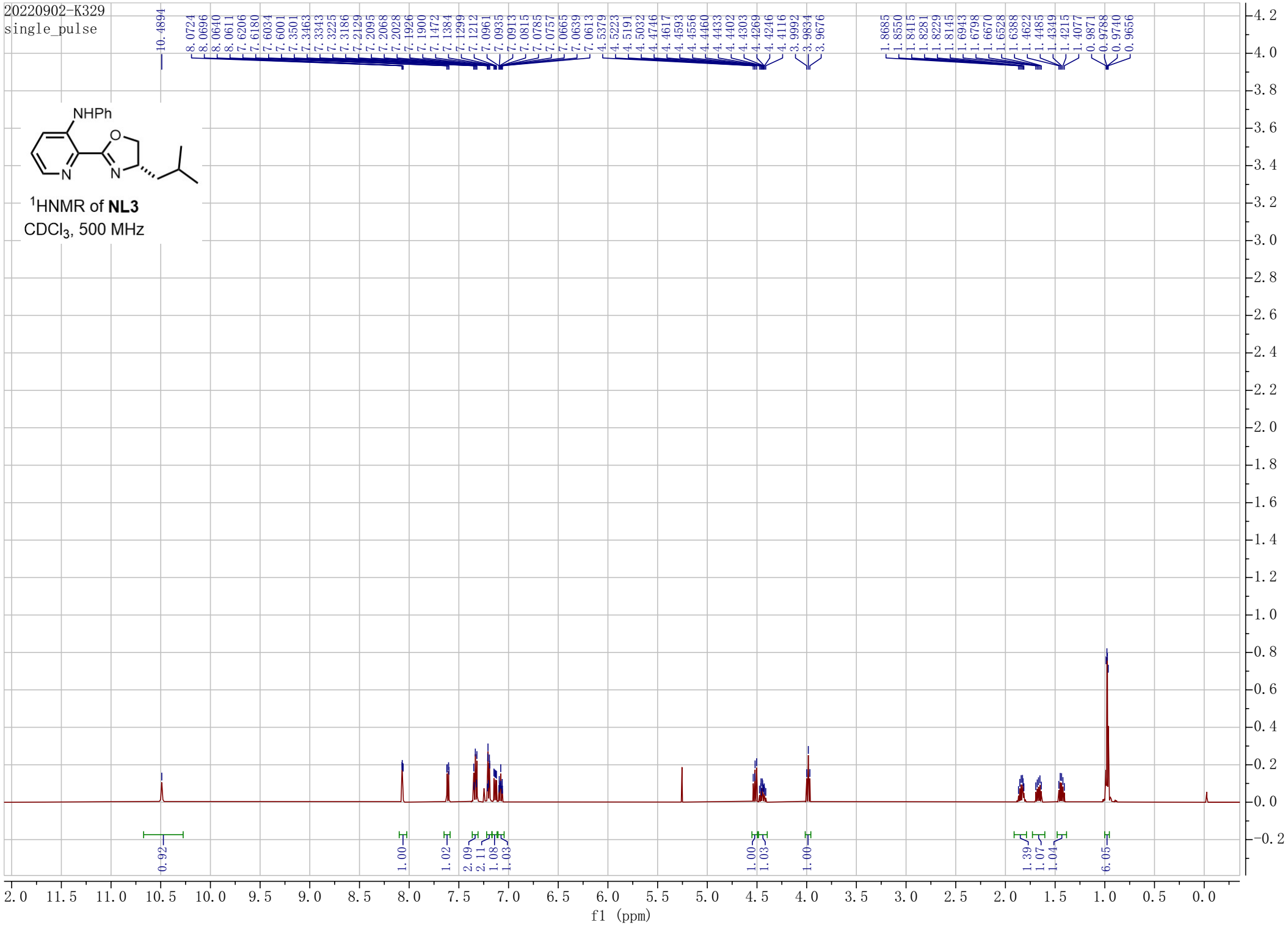
20220902-K328
single pulse decoupled gated NOE

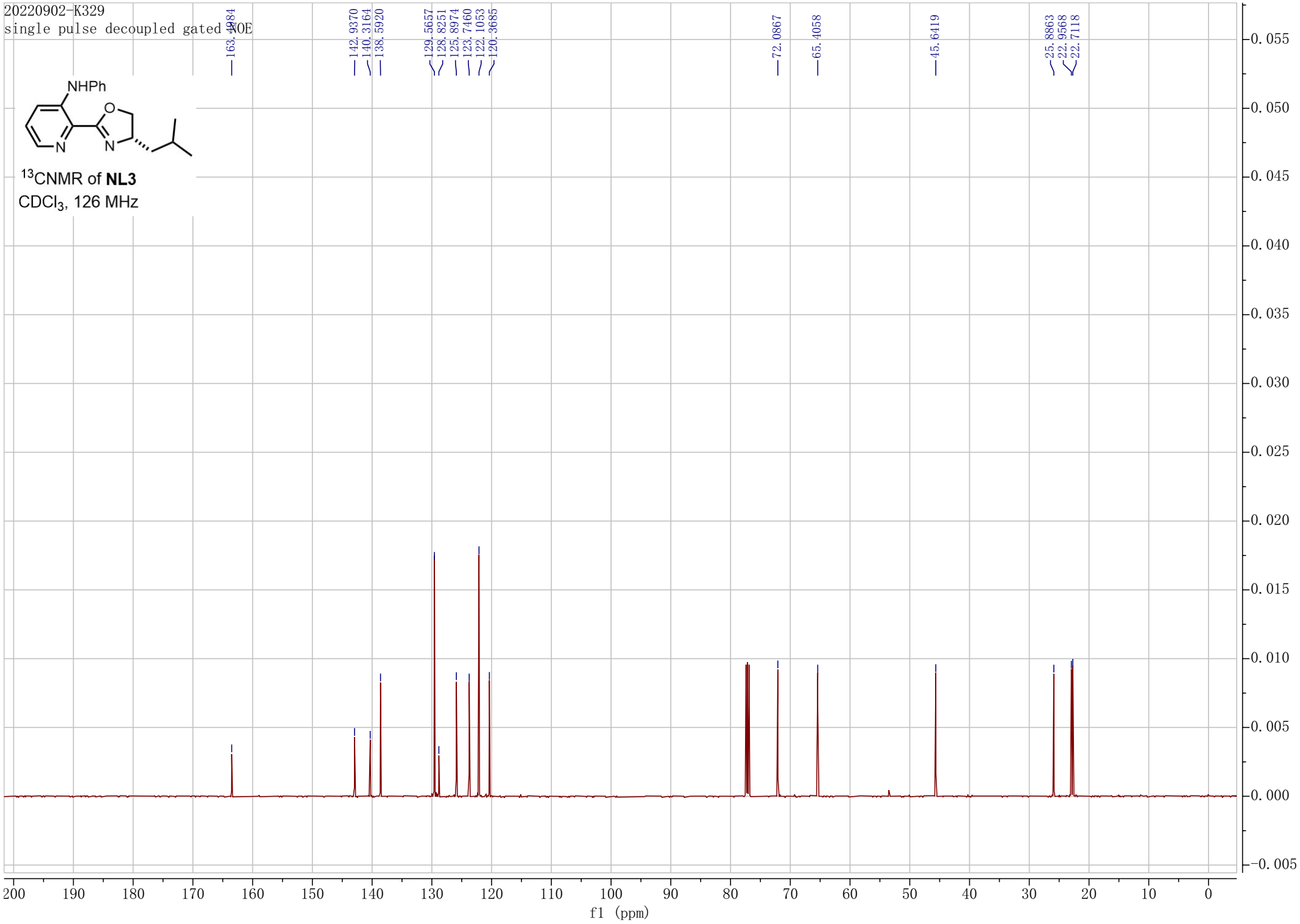


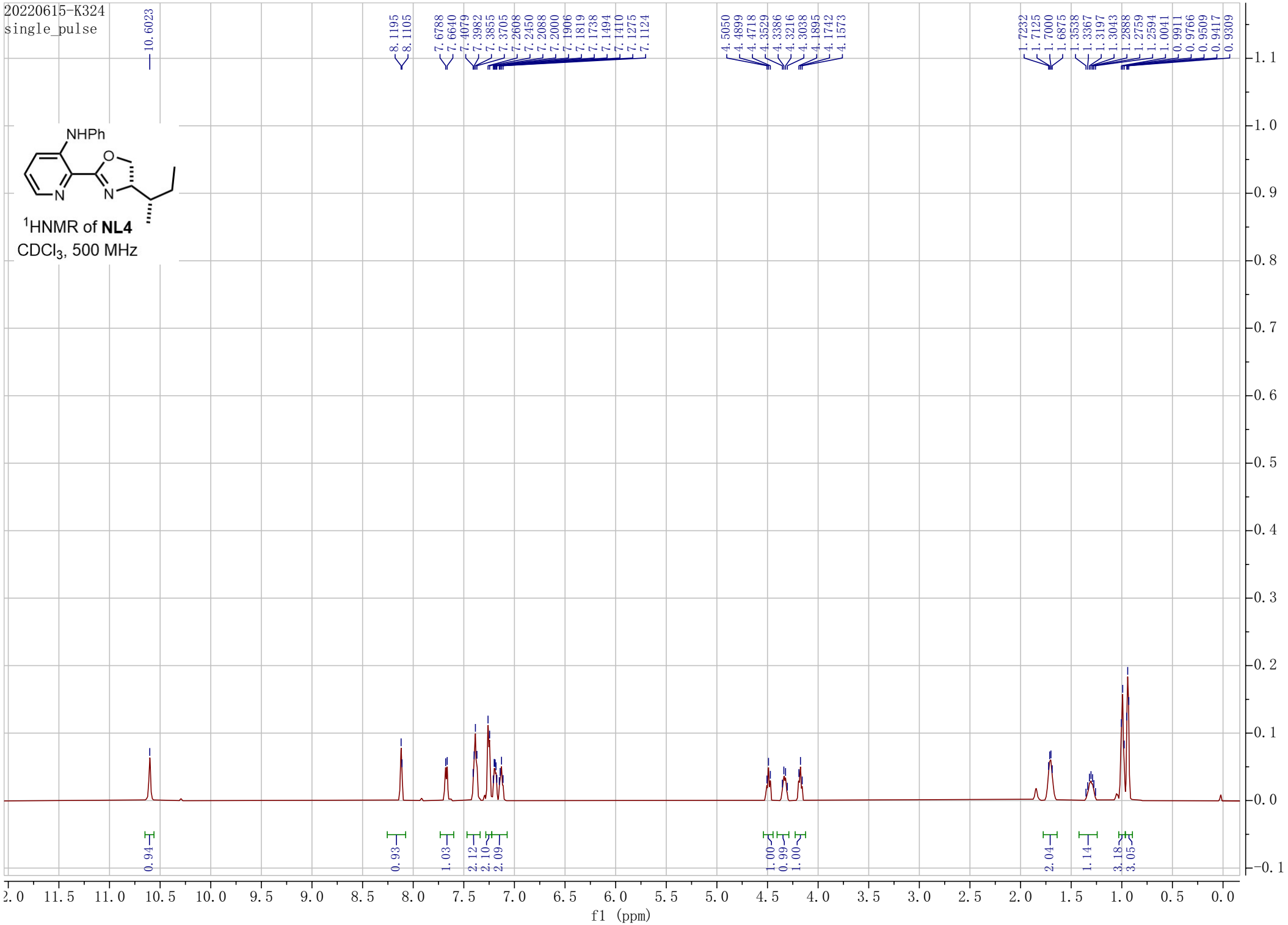
^{13}CNMR of **NL2**
$CDCl_3$, 126 MHz

163.9005
142.9667
140.3765
138.6191
129.5983
128.8030
125.9383
123.6999
121.9640
120.3798
73.1135
69.6853
33.3575
19.1082
18.8706

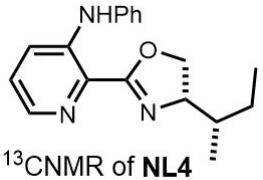
f1 (ppm)


20220902-K329
single_pulse
NHPh
O
N
N
^{1}HNMR of **NL3**
$CDCl_3$, 500 MHz
f1 (ppm)


20220902-K329
single pulse decoupled gated NOE
163.4984
142.9370
140.3164
138.5920
129.5657
128.8251
125.8974
123.7460
122.1053
120.3685
72.0867
65.4058
45.6419
25.8863
22.9568
22.7118
NHPh
O
N
N
13CNMR of NL3
CDCl3, 126 MHz
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


20220615-K324
single_pulse
NHPh
O
N
N
^{1}HNMR of **NL4**
$CDCl_3$, 500 MHz
f1 (ppm)

20220621-K324
single pulse decoupled gated NOE



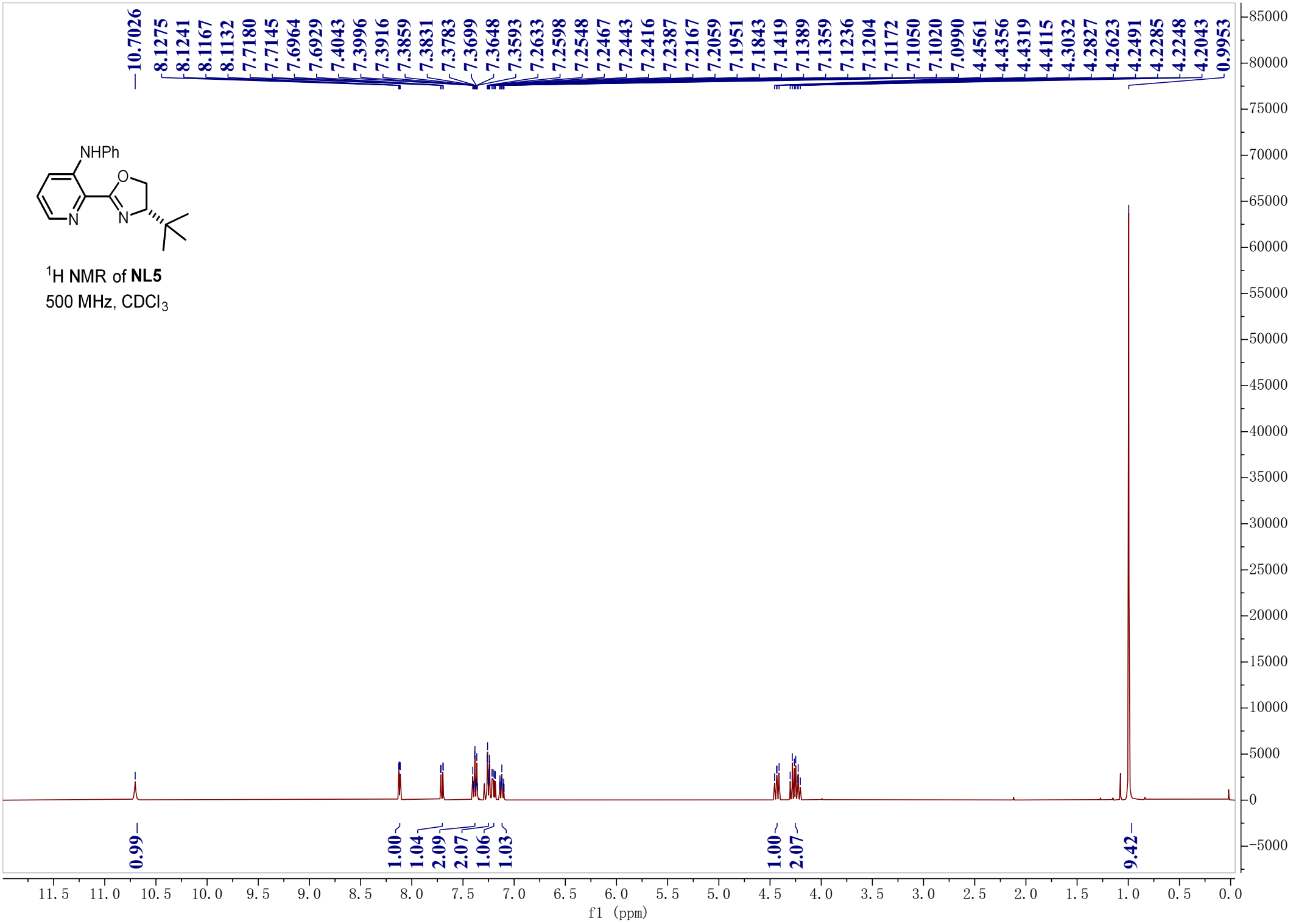
^{13}CNMR of **NL4**
$CDCl_3$, 126 MHz

163.3114
142.9471
140.3434
138.5725
129.5585
128.7881
125.8817
123.6879
122.0059
120.3155
71.7122
69.2622
39.5540
26.1357
14.9947
11.3951

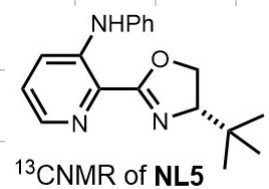
0.028
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
-0.002

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)


10.7026
8.1275
8.1241
8.1167
8.1132
7.7180
7.7145
7.6964
7.6929
7.4043
7.3996
7.3916
7.3859
7.3831
7.3783
7.3699
7.3648
7.3593
7.2633
7.2598
7.2548
7.2467
7.2443
7.2416
7.2387
7.2167
7.2059
7.1951
7.1843
7.1419
7.1389
7.1359
7.1236
7.1204
7.1172
7.1050
7.1020
7.0990
4.4561
4.4356
4.4319
4.4115
4.3032
4.2827
4.2623
4.2491
4.2285
4.2248
4.2043
0.9953
NHPh
O
N
N
1H NMR of NL5
500 MHz, CDCl3
0.99
1.00
1.04
2.09
2.07
1.06
1.03
1.00
2.07
9.42
f1 (ppm)

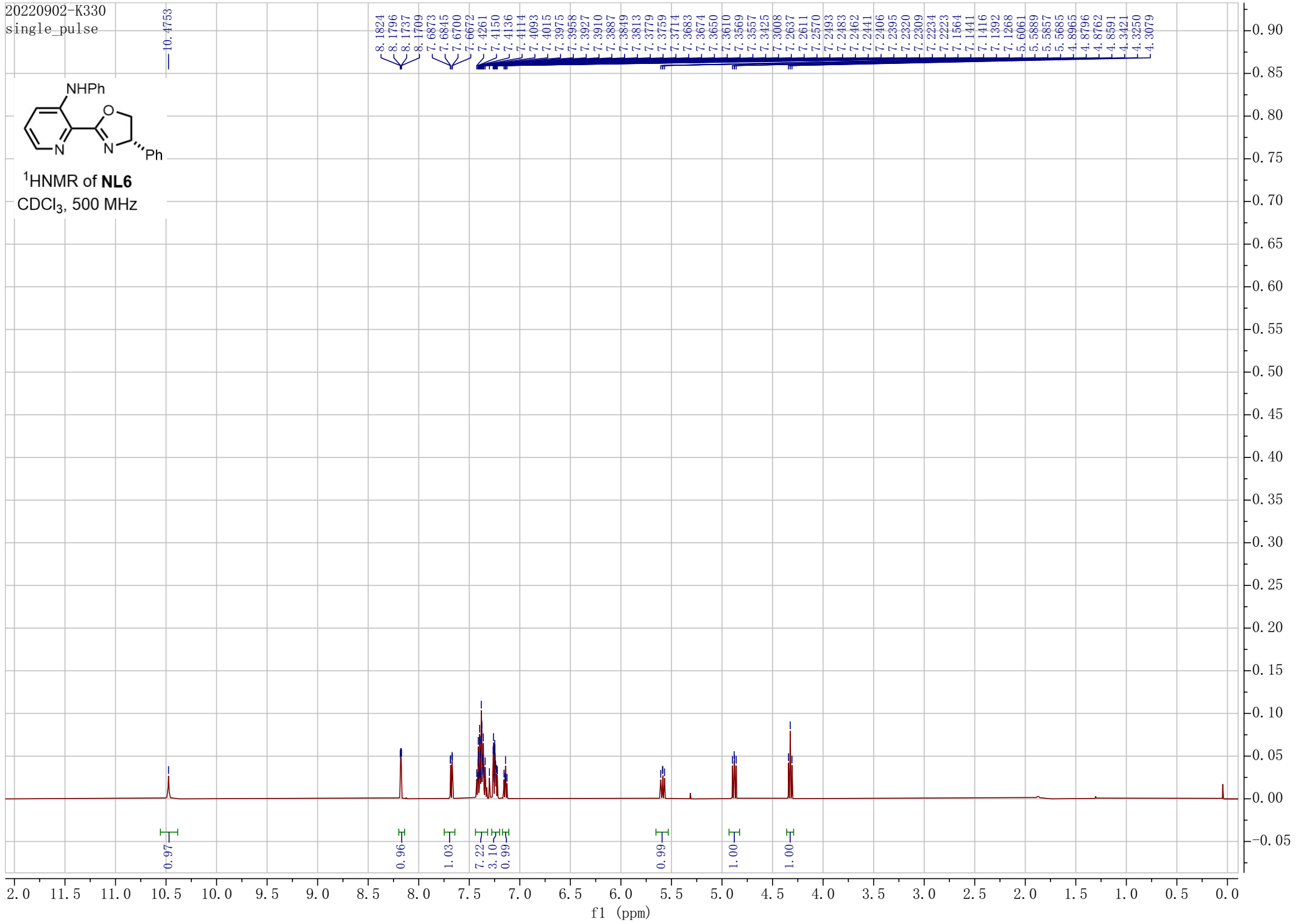
20220909-K412
single pulse decoupled gated NOE

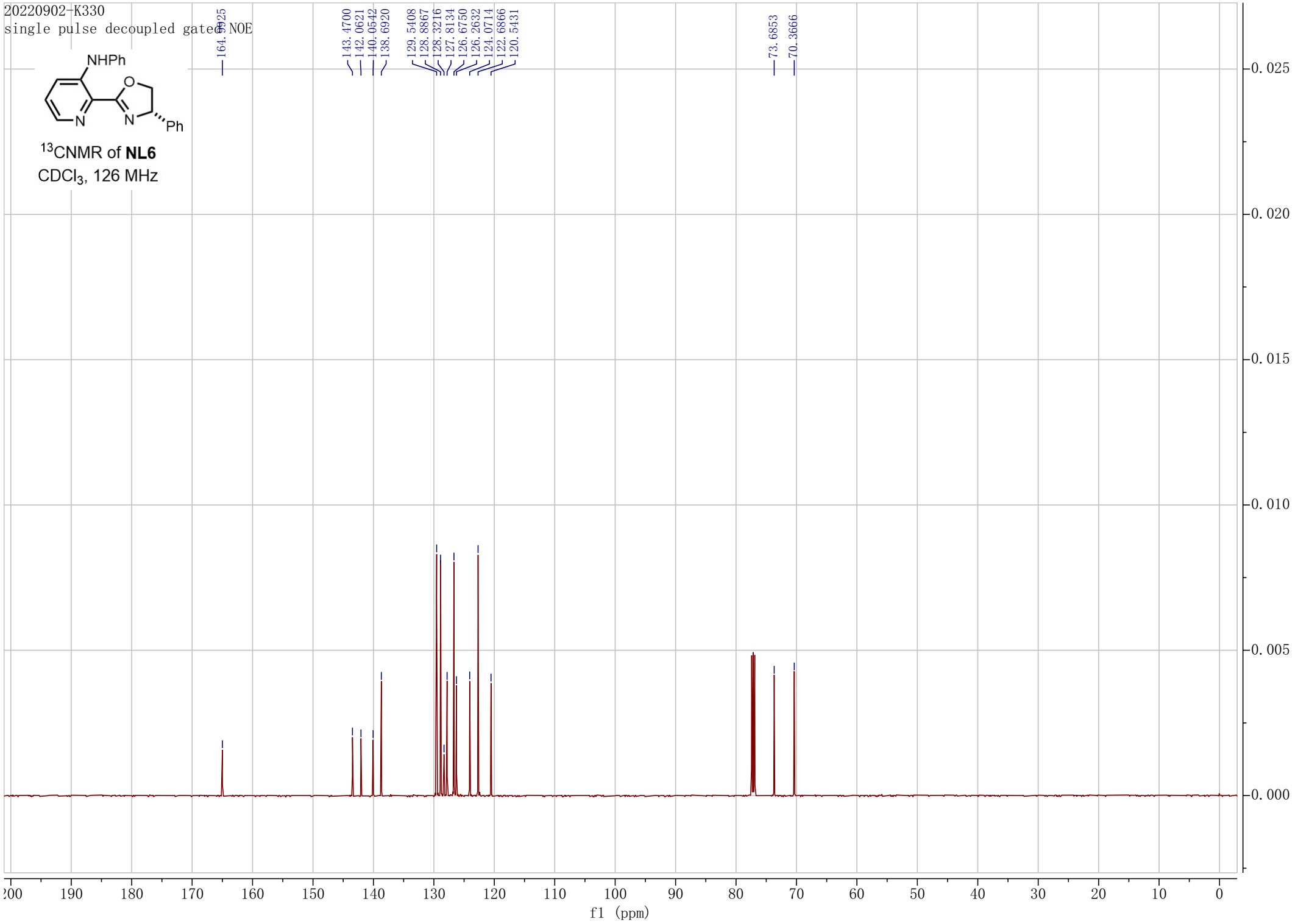


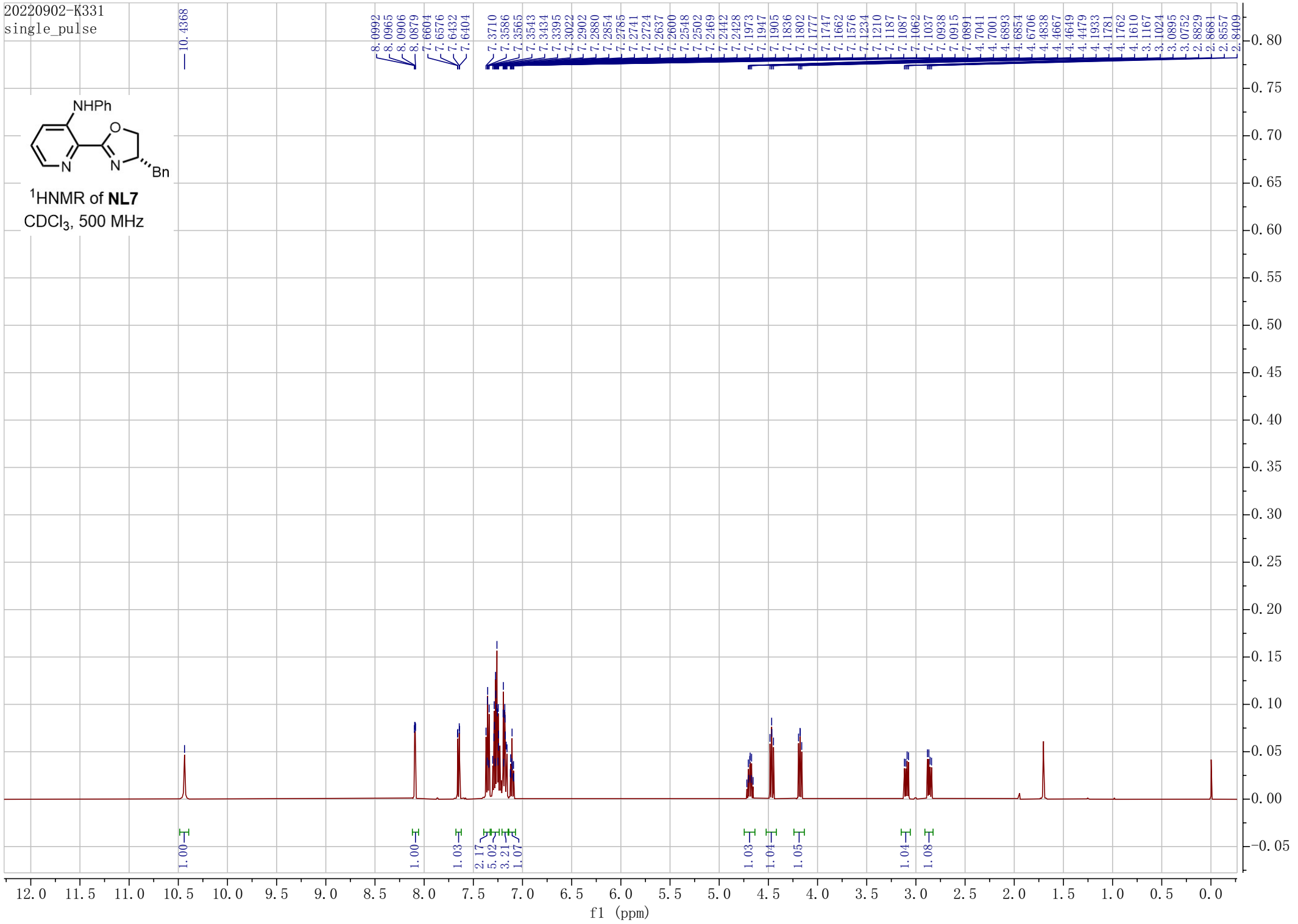
^{13}CNMR of **NL5**
$CDCl_3$, 126 MHz

169.1822
143.9302
140.1270
137.1721
130.4617
129.5630
127.2268
123.8994
122.3985
121.8798
63.5958
60.0293
33.8256
27.1298

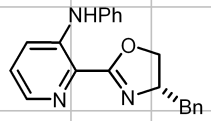
f1 (ppm)


20220902-K330
single_pulse
NHPh
N
O
N
Ph
^{1}HNMR of **NL6**
$CDCl_3$, 500 MHz
f1 (ppm)


20220902-K330
single pulse decoupled gated NOE
NHPh
O
N
N
Ph
13CNMR of NL6
CDCl3, 126 MHz
164.9925
143.4700
142.0621
140.0542
138.6920
129.5408
128.8867
128.3216
127.8134
126.6750
126.2632
124.0714
122.6866
120.5431
73.6853
70.3666
0.025
0.020
0.015
0.010
0.005
0.000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


20220902-K331
single_pulse
NHPh
O
N
N
Bn
^{1}HNMR of **NL7**
$CDCl_3$, 500 MHz
f1 (ppm)

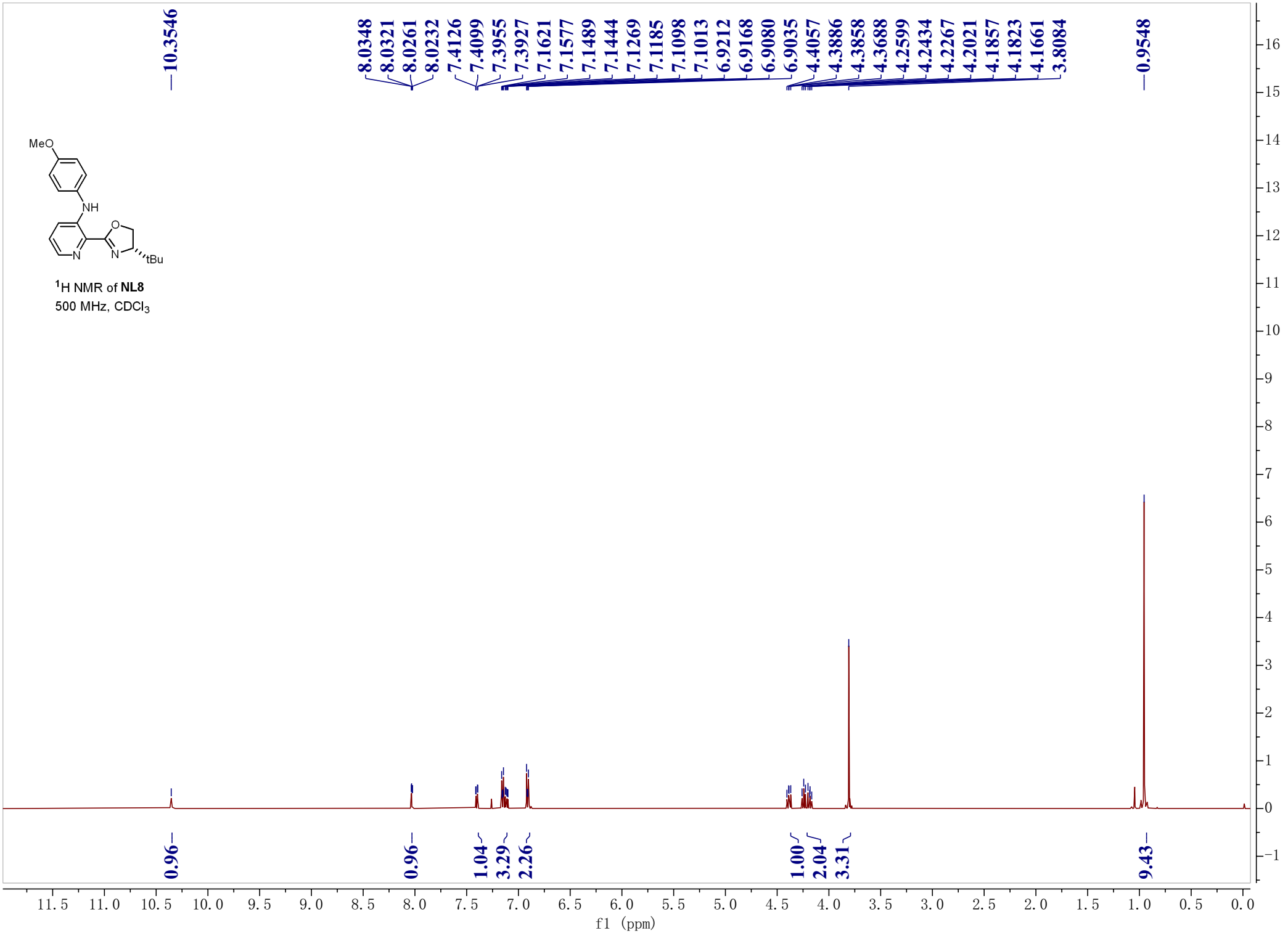
20220902-K331
single pulse decoupled gated NOE



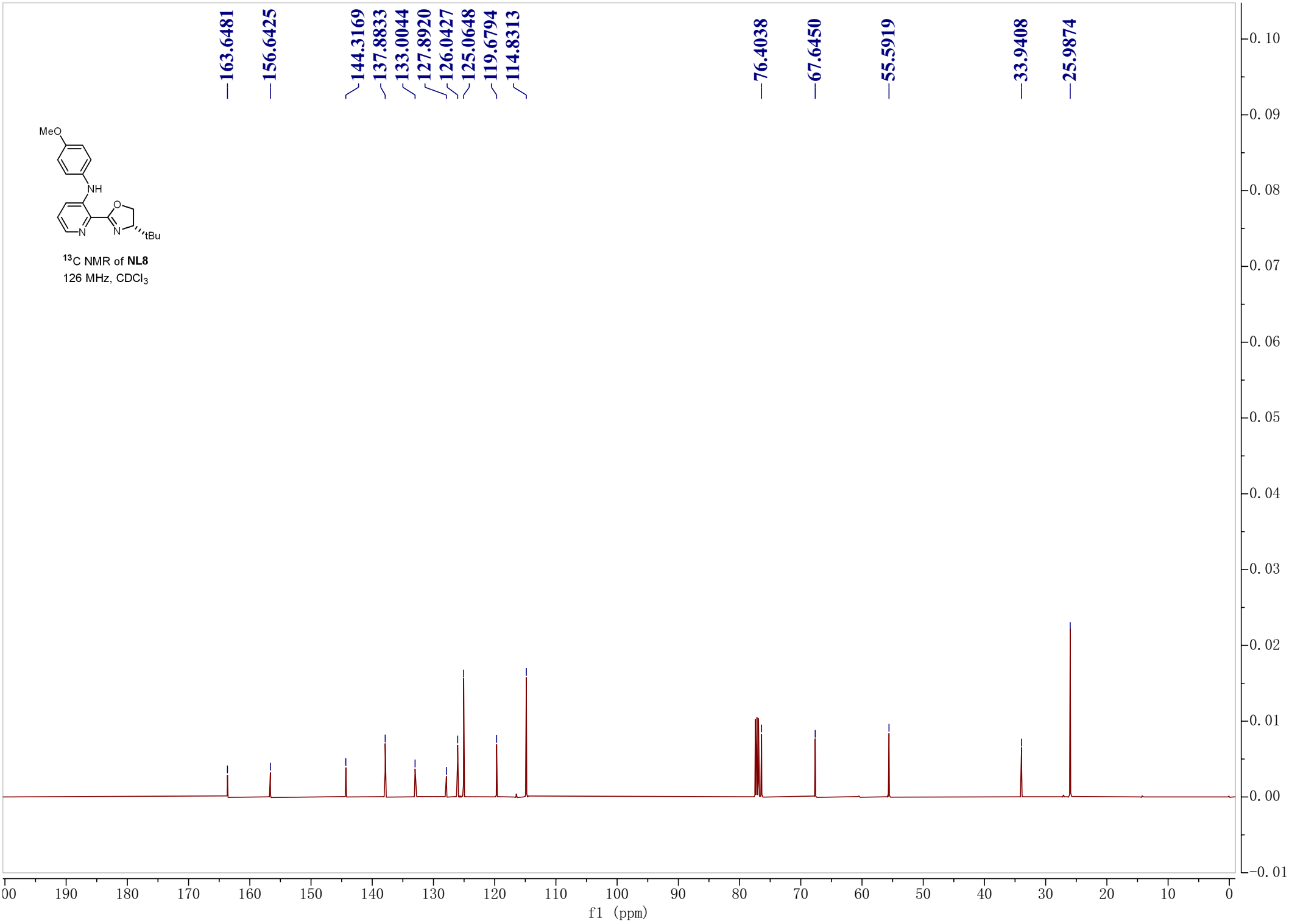
^{13}C NMR of **NL7**
126 MHz, $CDCl_3$

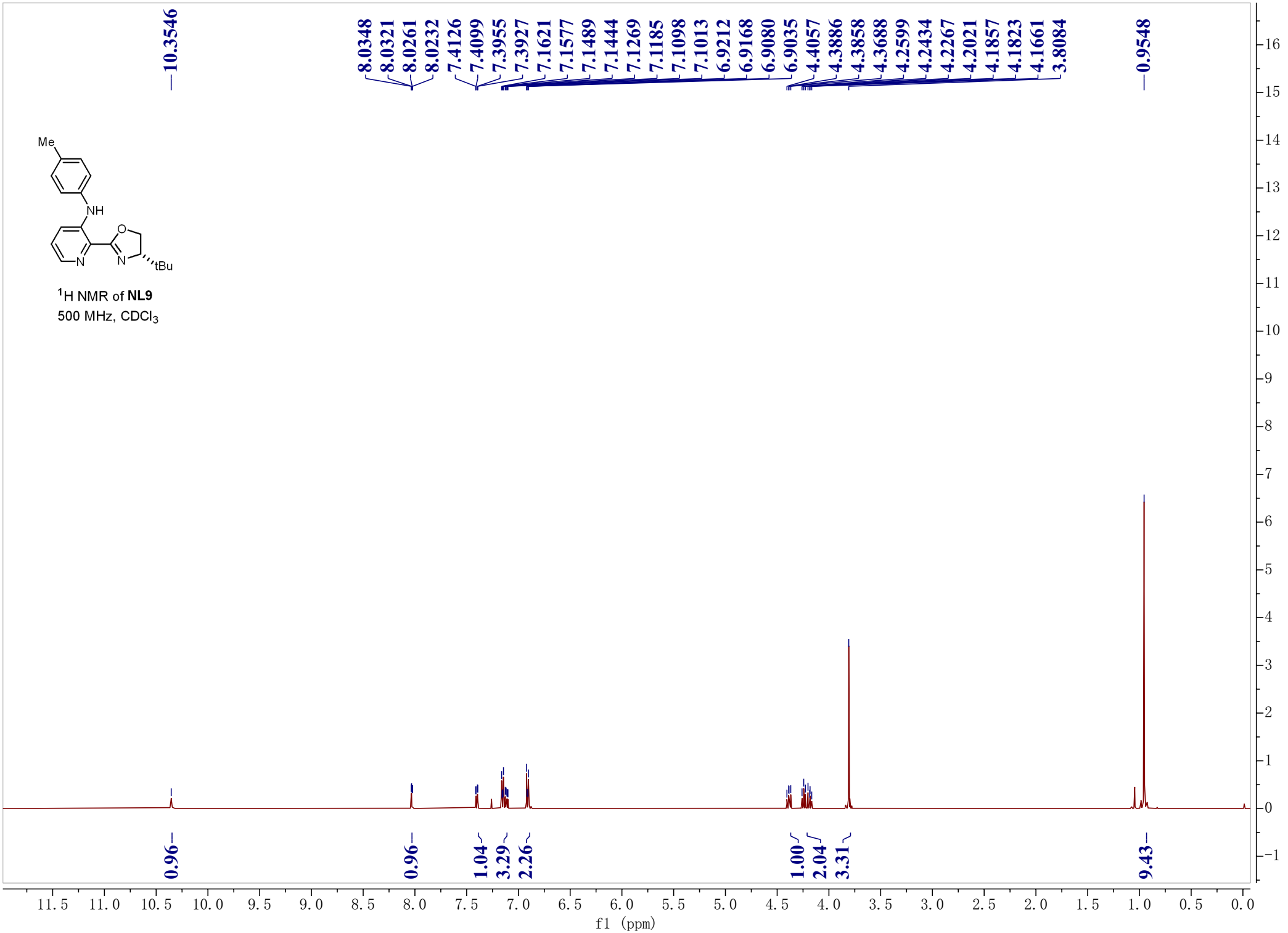
164.0333
143.0779
140.2949
138.7235
138.1531
129.5660
129.3413
128.7176
128.6655
126.6624
126.0982
123.8110
122.0832
120.6582
71.1266
68.3566
42.3414

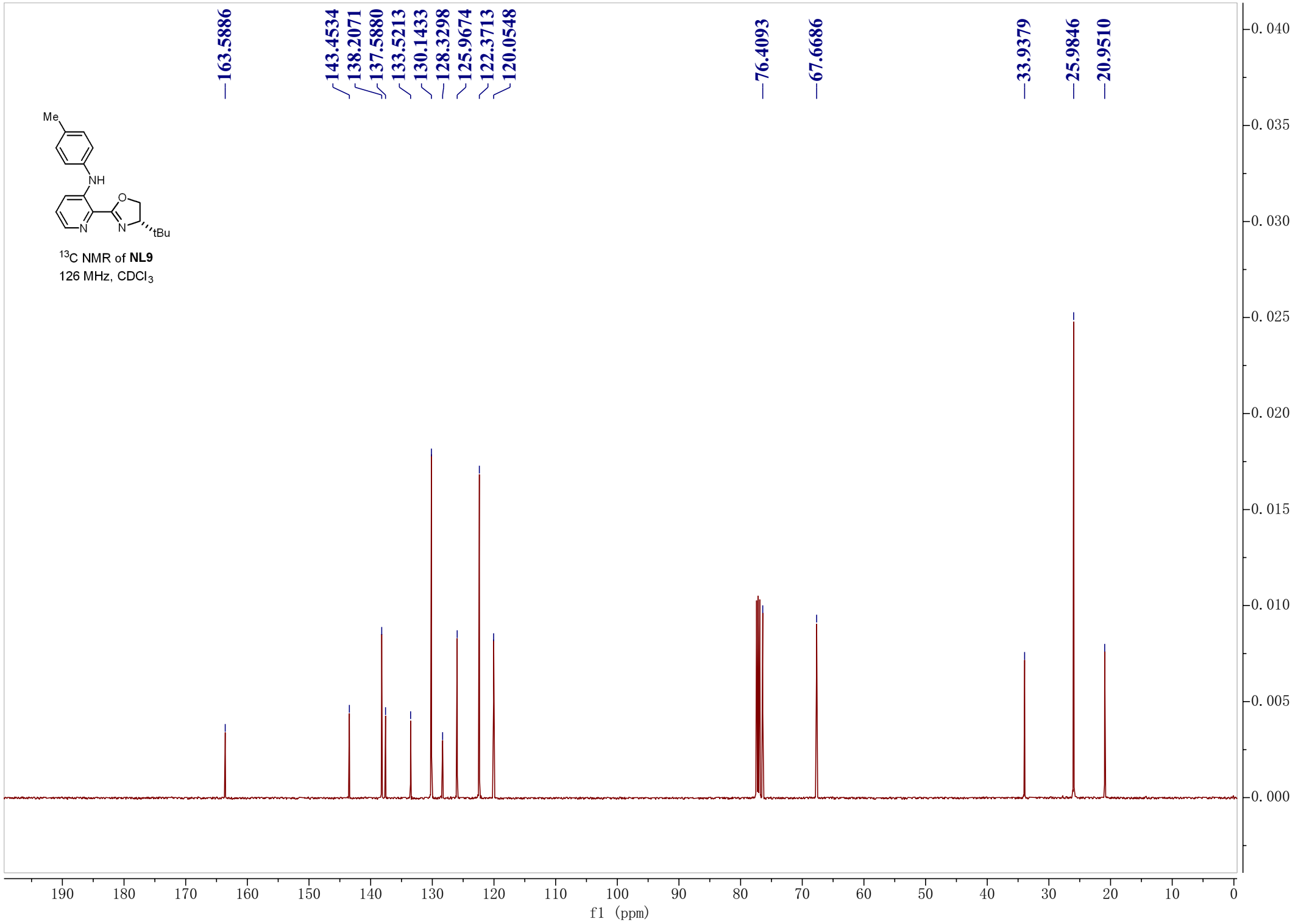
f1 (ppm)

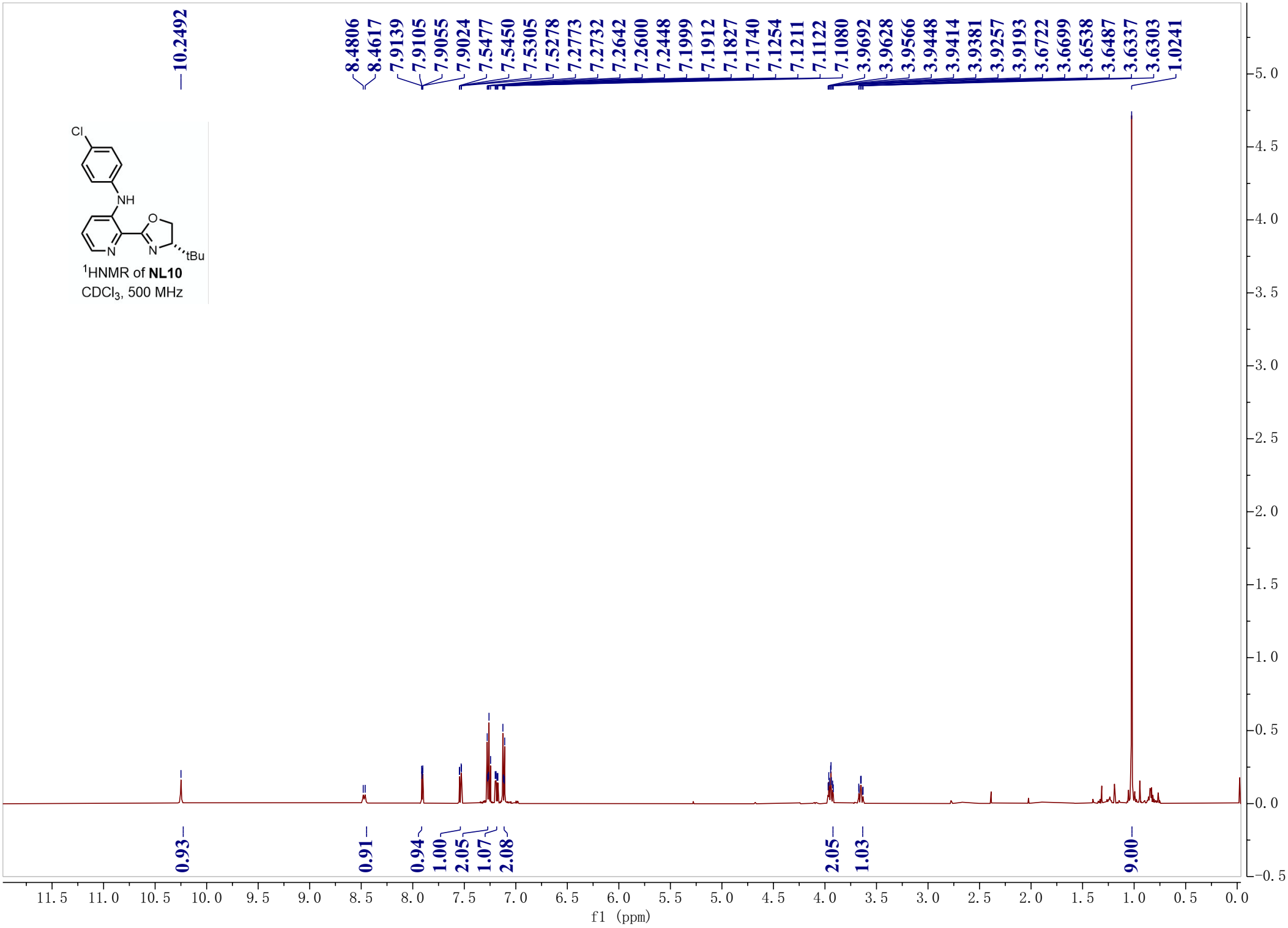


^{1}H NMR of **NL8**
500 MHz, $CDCl_3$

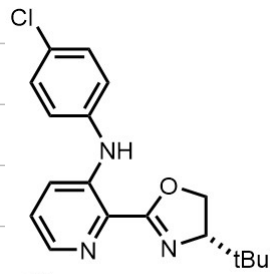

163.6481
156.6425
144.3169
137.8833
133.0044
127.8920
126.0427
125.0648
119.6794
114.8313
76.4038
67.6450
55.5919
33.9408
25.9874
MeO
NH
O
N
N
tBu
13C NMR of NL8
126 MHz, CDCl3
f1 (ppm)


10.3546
8.0348
8.0321
8.0261
8.0232
7.4126
7.4099
7.3955
7.3927
7.1621
7.1577
7.1489
7.1444
7.1269
7.1185
7.1098
7.1013
6.9212
6.9168
6.9080
6.9035
4.4057
4.3886
4.3858
4.3688
4.2599
4.2434
4.2267
4.2021
4.1857
4.1823
4.1661
3.8084
0.9548
Me
NH
O
N
N
tBu
1H NMR of NL9
500 MHz, CDCl3
0.96
0.96
1.04
3.29
2.26
1.00
2.04
3.31
9.43
f1 (ppm)


163.5886
143.4534
138.2071
137.5880
133.5213
130.1433
128.3298
125.9674
122.3713
120.0548
76.4093
67.6686
33.9379
25.9846
20.9510
Me
NH
O
N
N
tBu
^{13}C NMR of NL9
126 MHz, CDCl$_3$
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


10.2492
8.4806
8.4617
7.9139
7.9105
7.9055
7.9024
7.5477
7.5450
7.5305
7.5278
7.2773
7.2732
7.2642
7.2600
7.2448
7.1999
7.1912
7.1827
7.1740
7.1254
7.1211
7.1122
7.1080
3.9692
3.9628
3.9566
3.9448
3.9414
3.9381
3.9257
3.9193
3.6722
3.6699
3.6538
3.6487
3.6337
3.6303
1.0241
Cl
NH
O
N
N
tBu
1HNMR of NL10
CDCl3, 500 MHz
0.93
0.91
0.94
1.00
2.05
1.07
2.08
2.05
1.03
9.00
f1 (ppm)

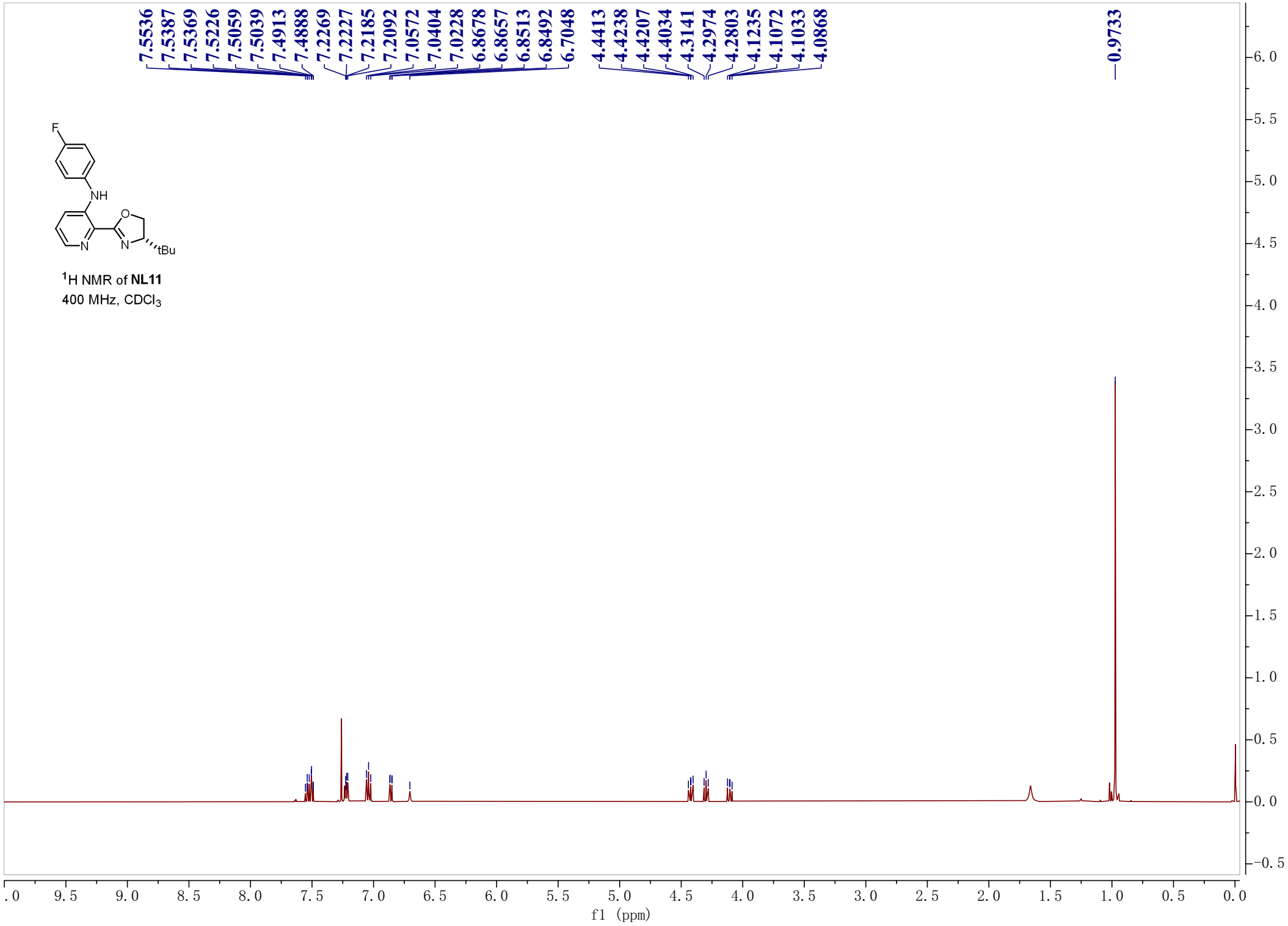
20220909-K413
single pulse decoupled gated NOE

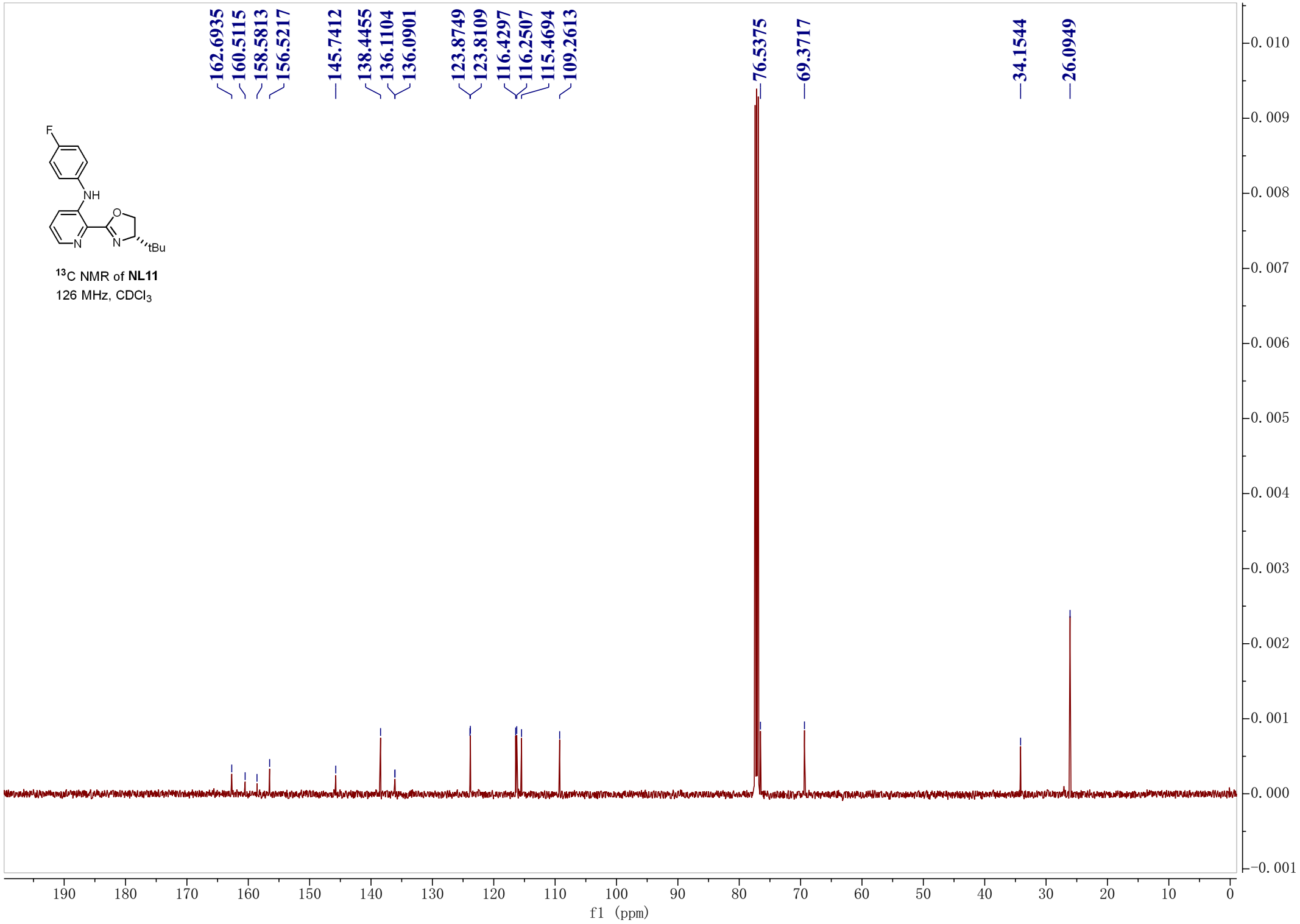


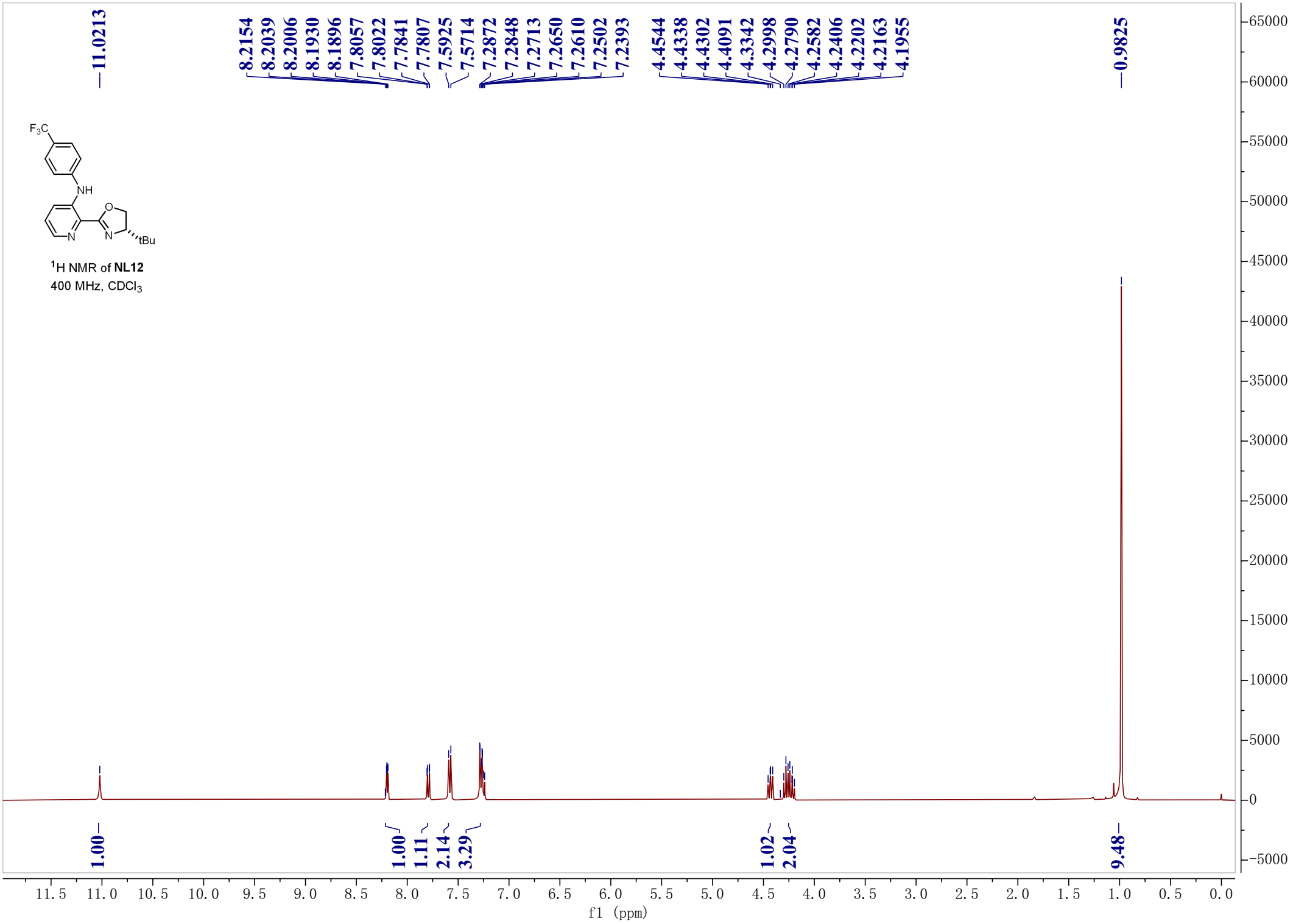
^{13}CNMR of **NL10**
$CDCl_3$, 126 MHz

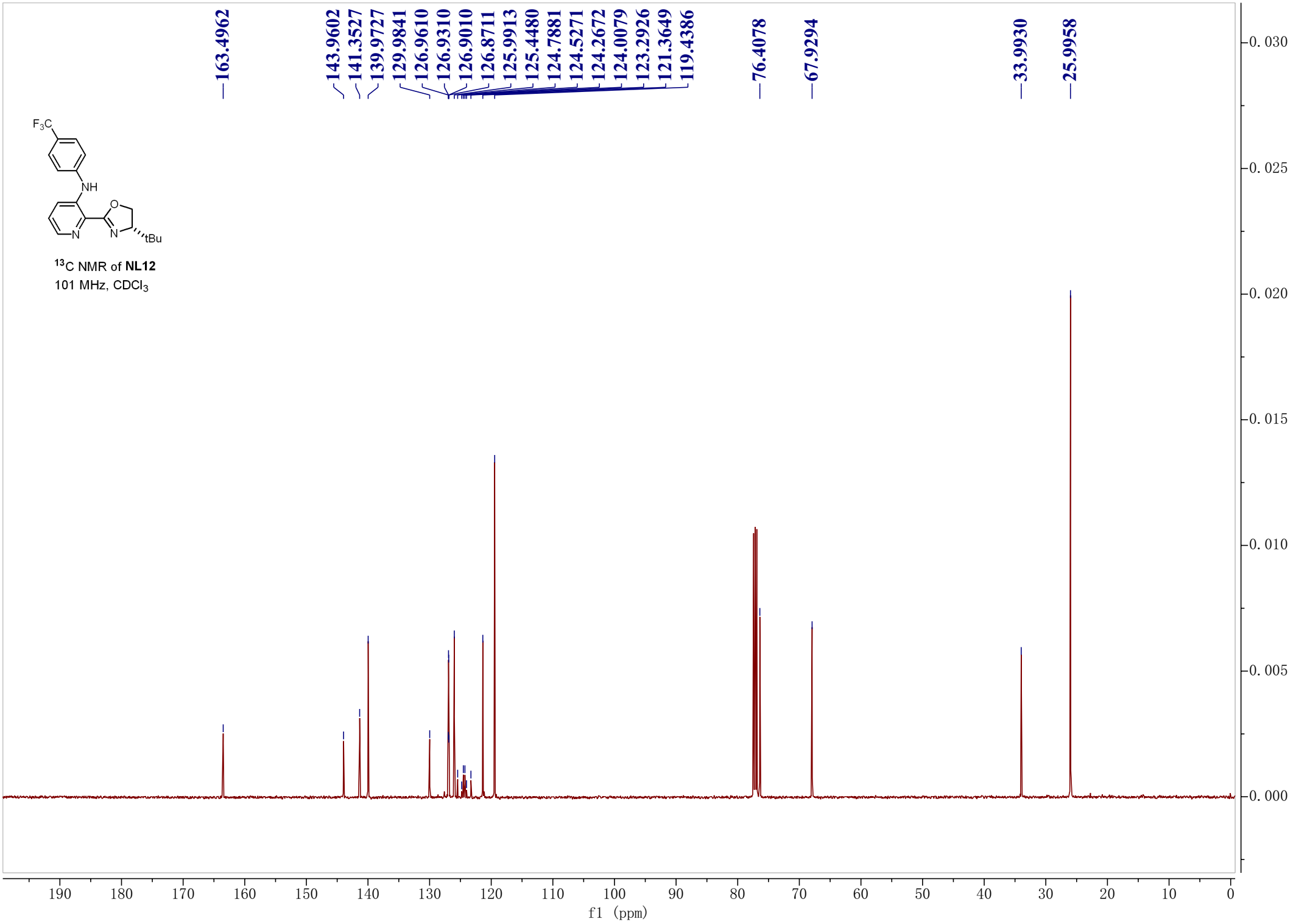
169.6972
143.5779
138.8165
137.5710
130.7016
129.6377
128.7804
127.3105
123.5235
121.8327
63.5912
60.0650
33.8346
27.1311

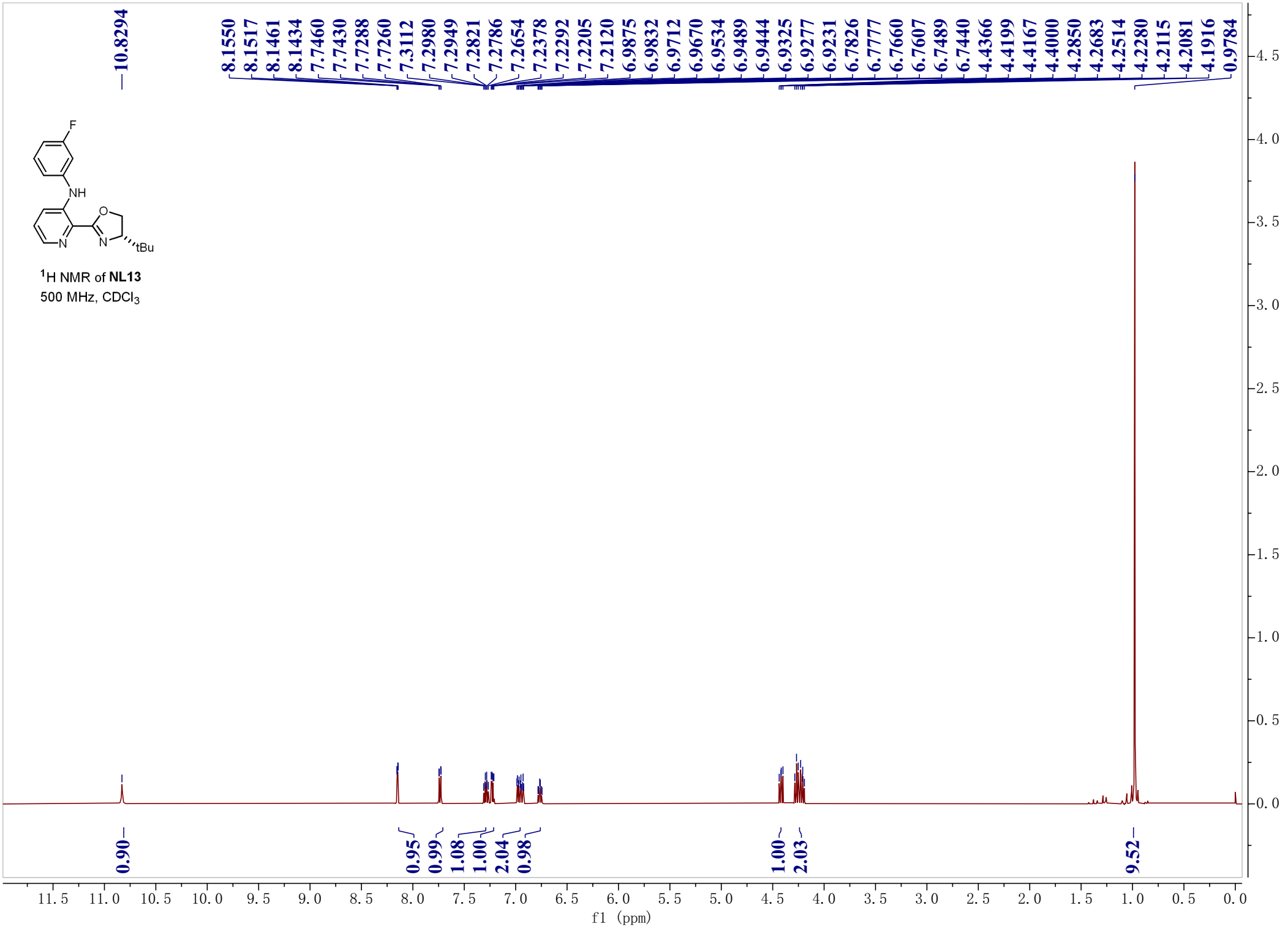
f1 (ppm)

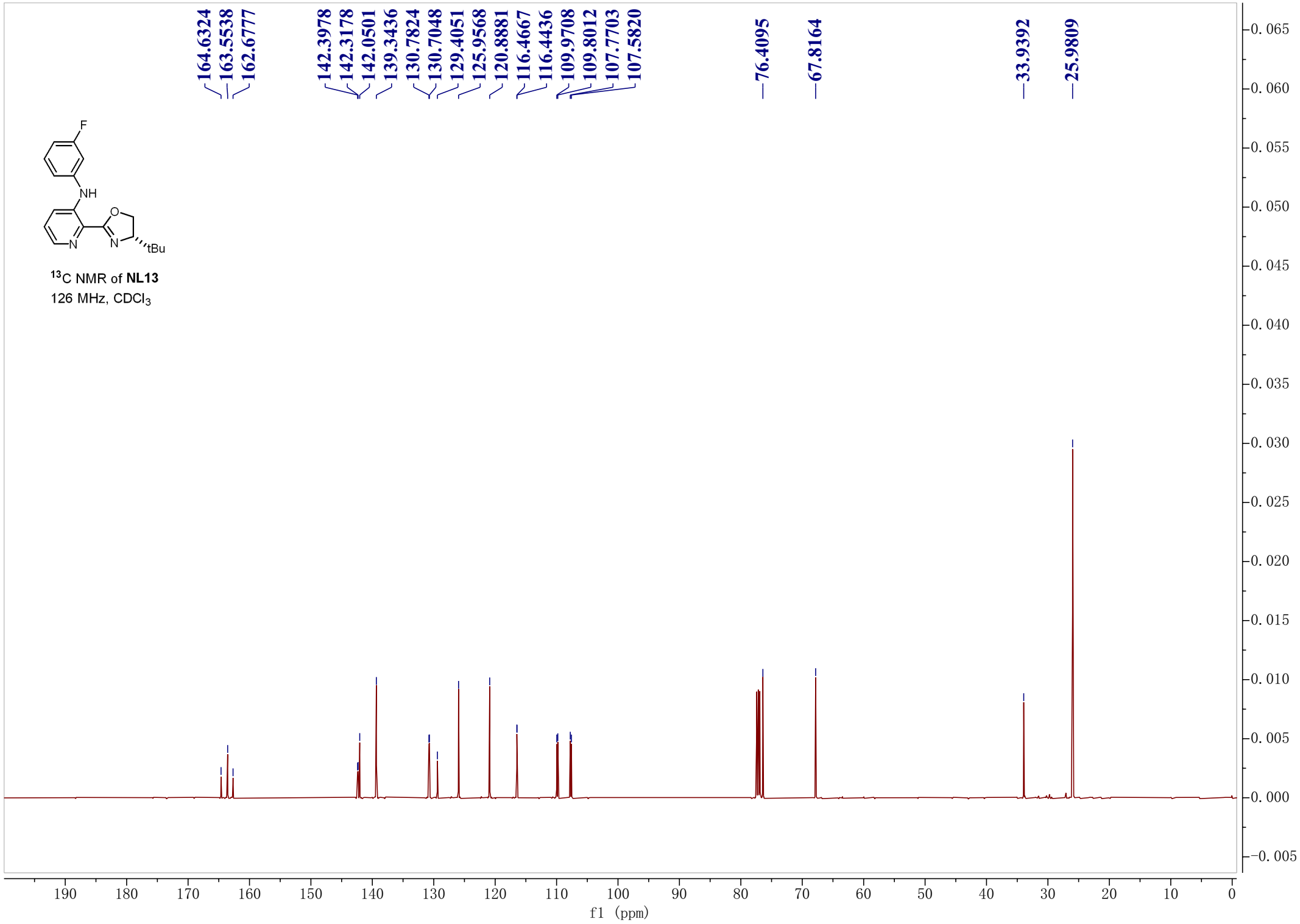

7.5536
7.5387
7.5369
7.5226
7.5059
7.5039
7.4913
7.4888
7.2269
7.2227
7.2185
7.2092
7.0572
7.0404
7.0228
6.8678
6.8657
6.8513
6.8492
6.7048
4.4413
4.4238
4.4207
4.4034
4.3141
4.2974
4.2803
4.1235
4.1072
4.1033
4.0868
0.9733
F
NH
O
N
N
tBu
1H NMR of NL11
400 MHz, CDCl3
f1 (ppm)

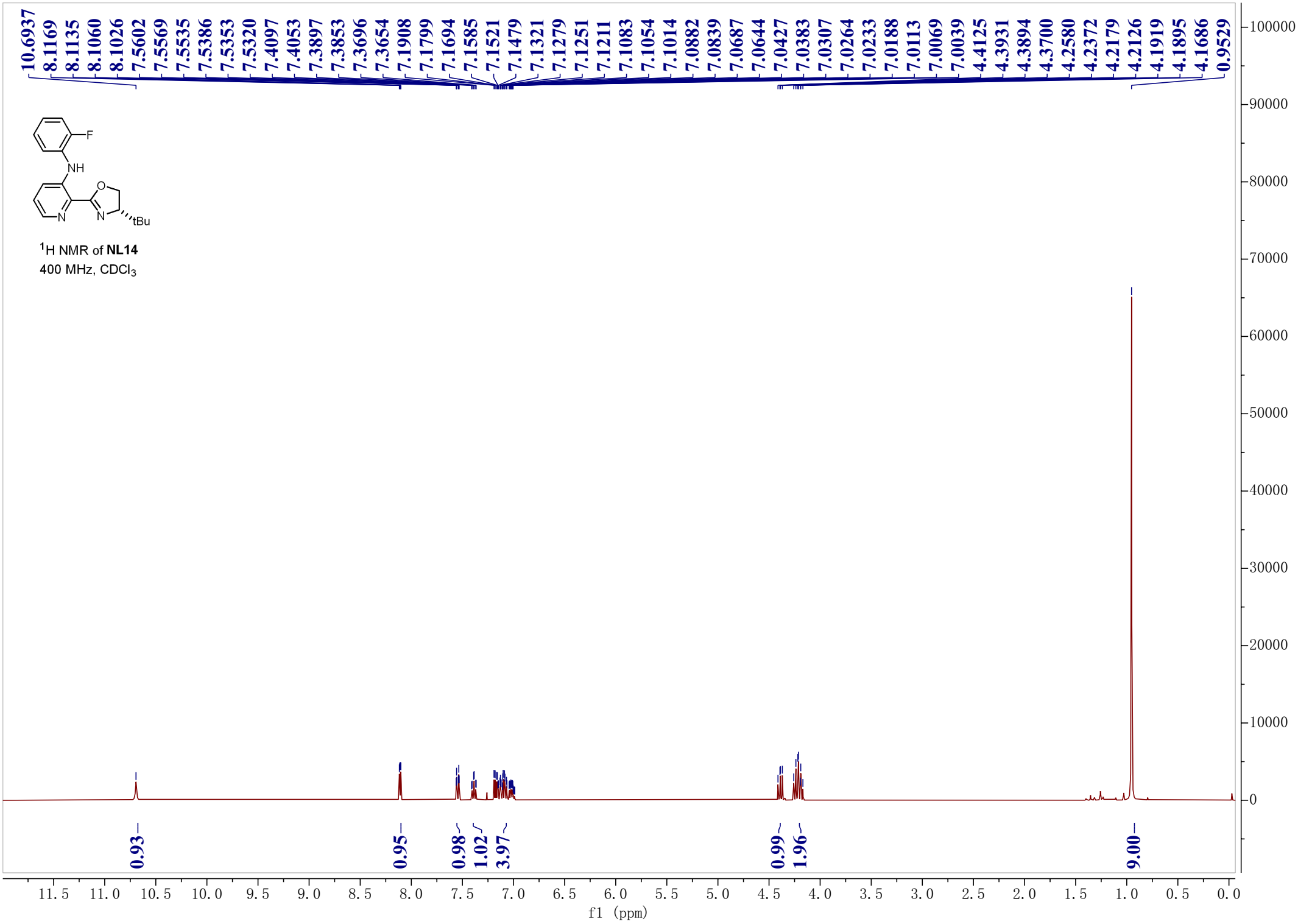

162.6935
160.5115
158.5813
156.5217
145.7412
138.4455
136.1104
136.0901
123.8749
123.8109
116.4297
116.2507
115.4694
109.2613
76.5375
69.3717
34.1544
26.0949
F
NH
O
N
N
tBu
13C NMR of NL11
126 MHz, CDCl3
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

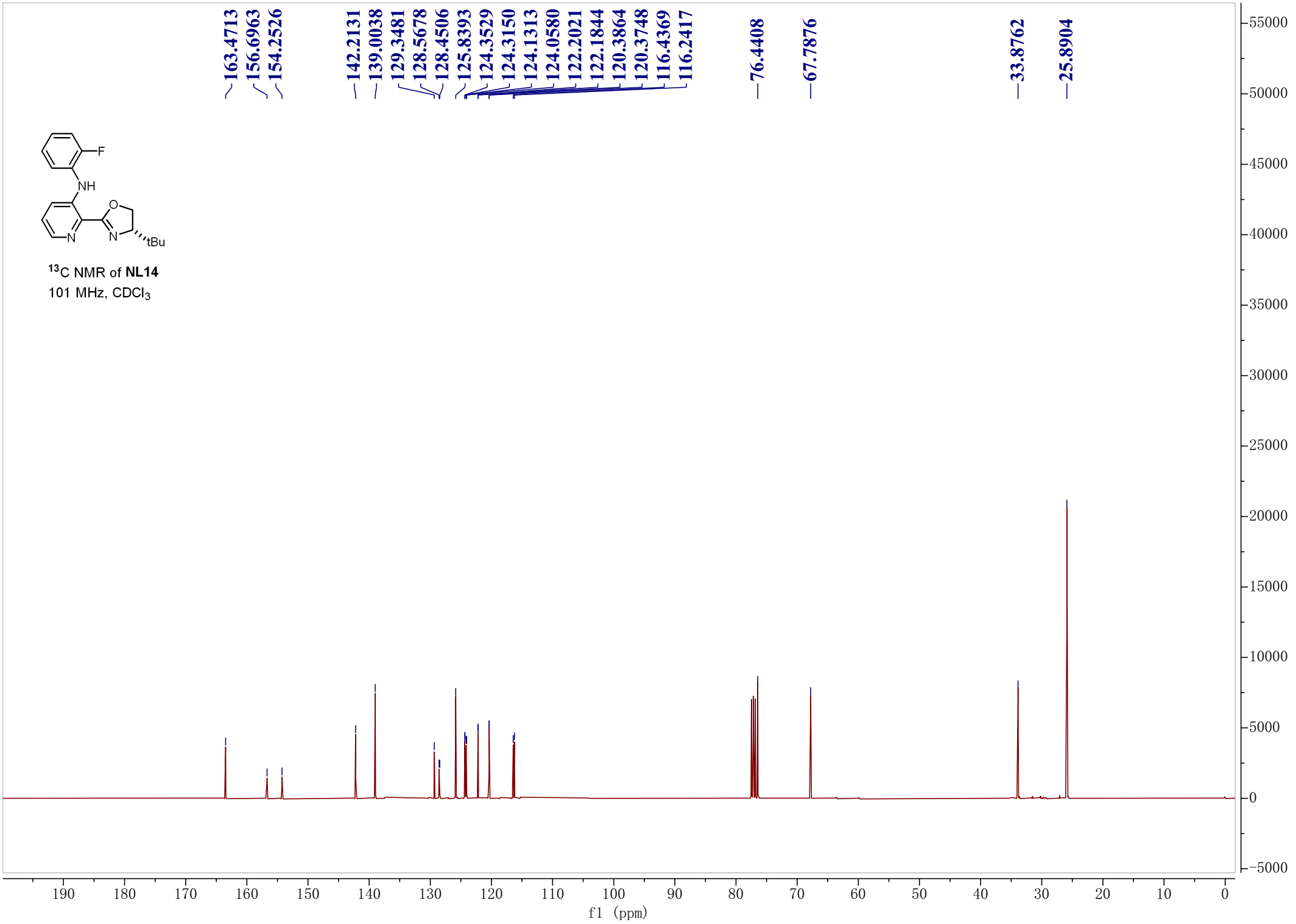

11.0213
8.2154
8.2039
8.2006
8.1930
8.1896
7.8057
7.8022
7.7841
7.7807
7.5925
7.5714
7.2872
7.2848
7.2713
7.2650
7.2610
7.2502
7.2393
4.4544
4.4338
4.4302
4.4091
4.3342
4.2998
4.2790
4.2582
4.2406
4.2202
4.2163
4.1955
0.9825
F3C
NH
O
N
N
tBu
1H NMR of NL12
400 MHz, CDCl3
1.00
1.00
1.11
2.14
3.29
1.02
2.04
9.48
f1 (ppm)


163.4962
143.9602
141.3527
139.9727
129.9841
126.9610
126.9310
126.9010
126.8711
125.9913
125.4480
124.7881
124.5271
124.2672
124.0079
123.2926
121.3649
119.4386
76.4078
67.9294
33.9930
25.9958
F3C
NH
O
N
N
tBu
13C NMR of NL12
101 MHz, CDCl3
0.030
0.025
0.020
0.015
0.010
0.005
0.000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

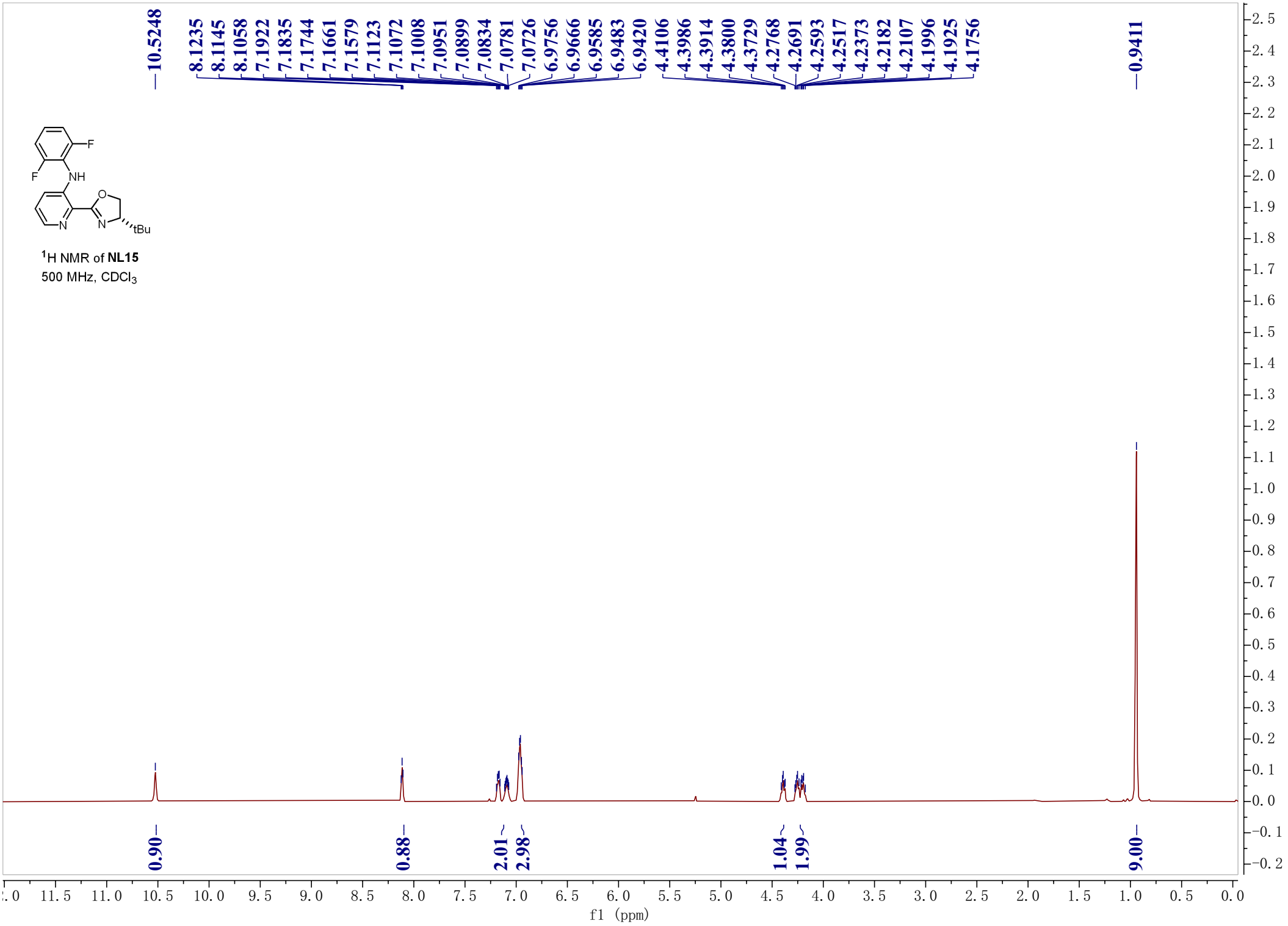

10.8294
8.1550
8.1517
8.1461
8.1434
7.7460
7.7430
7.7288
7.7260
7.3112
7.2980
7.2949
7.2821
7.2786
7.2654
7.2378
7.2292
7.2205
7.2120
6.9875
6.9832
6.9712
6.9670
6.9534
6.9489
6.9444
6.9325
6.9277
6.9231
6.7826
6.7777
6.7660
6.7607
6.7489
6.7440
4.4366
4.4199
4.4167
4.4000
4.2850
4.2683
4.2514
4.2280
4.2115
4.2081
4.1916
0.9784
F
NH
O
N
N
tBu
1H NMR of NL13
500 MHz, CDCl3
0.90
0.95
0.99
1.08
1.00
2.04
0.98
1.00
2.03
9.52
f1 (ppm)


164.6324
163.5538
162.6777
142.3978
142.3178
142.0501
139.3436
130.7824
130.7048
129.4051
125.9568
120.8881
116.4667
116.4436
109.9708
109.8012
107.7703
107.5820
76.4095
67.8164
33.9392
25.9809
F
NH
O
N
N
tBu
13C NMR of NL13
126 MHz, CDCl3
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

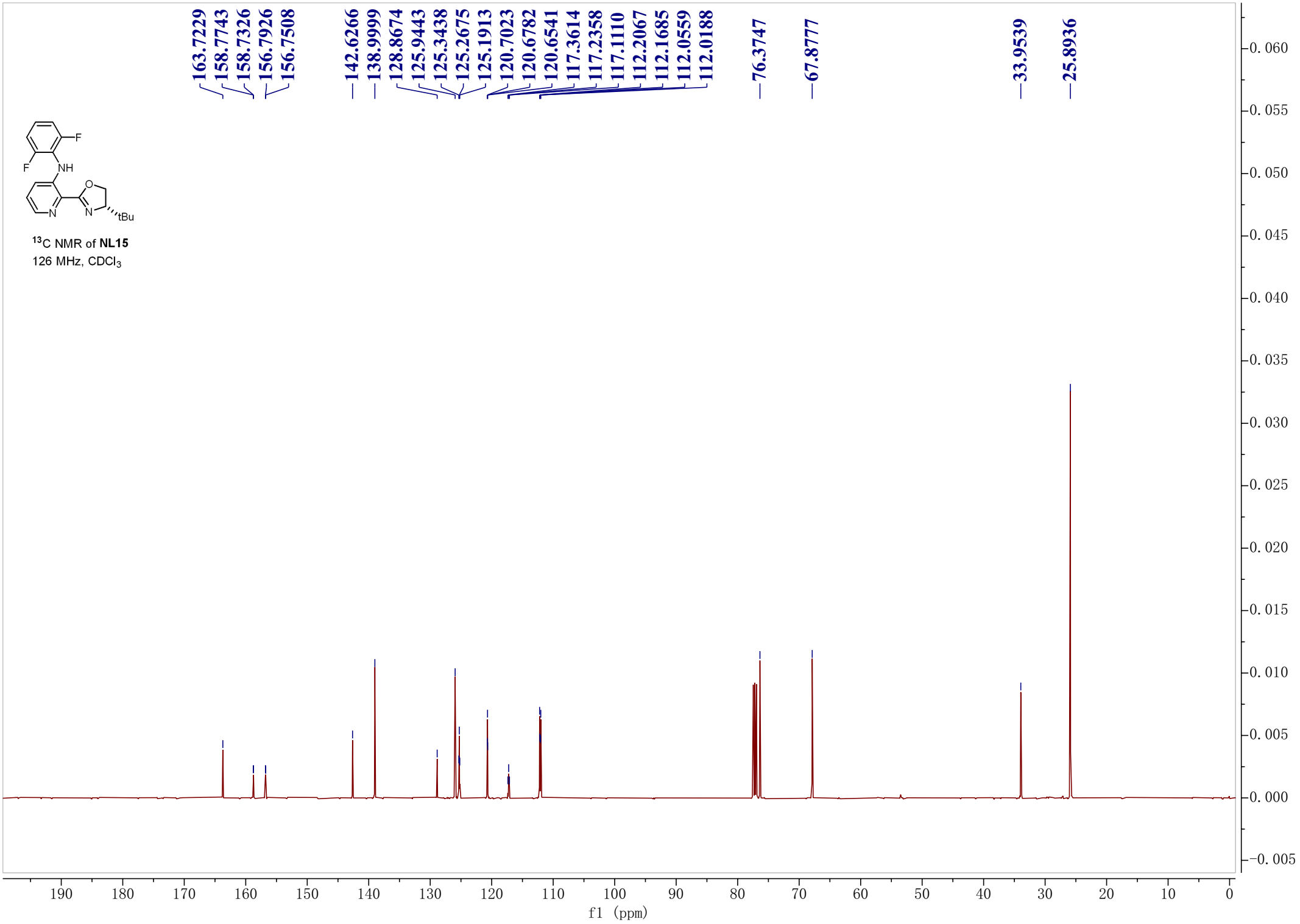

10.6937
8.1169
8.1135
8.1060
8.1026
7.5602
7.5569
7.5535
7.5386
7.5353
7.5320
7.4097
7.4053
7.3897
7.3853
7.3696
7.3654
7.1908
7.1799
7.1694
7.1585
7.1521
7.1479
7.1321
7.1279
7.1251
7.1211
7.1083
7.1054
7.1014
7.0882
7.0839
7.0687
7.0644
7.0427
7.0383
7.0307
7.0264
7.0233
7.0188
7.0113
7.0069
7.0039
4.4125
4.3931
4.3894
4.3700
4.2580
4.2372
4.2179
4.2126
4.1919
4.1895
4.1686
0.9529
F
NH
O
N
N
tBu
1H NMR of NL14
400 MHz, CDCl3
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0.93
0.95
0.98
1.02
3.97
0.99
1.96
9.00
11.5
11.0
10.5
10.0
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
f1 (ppm)

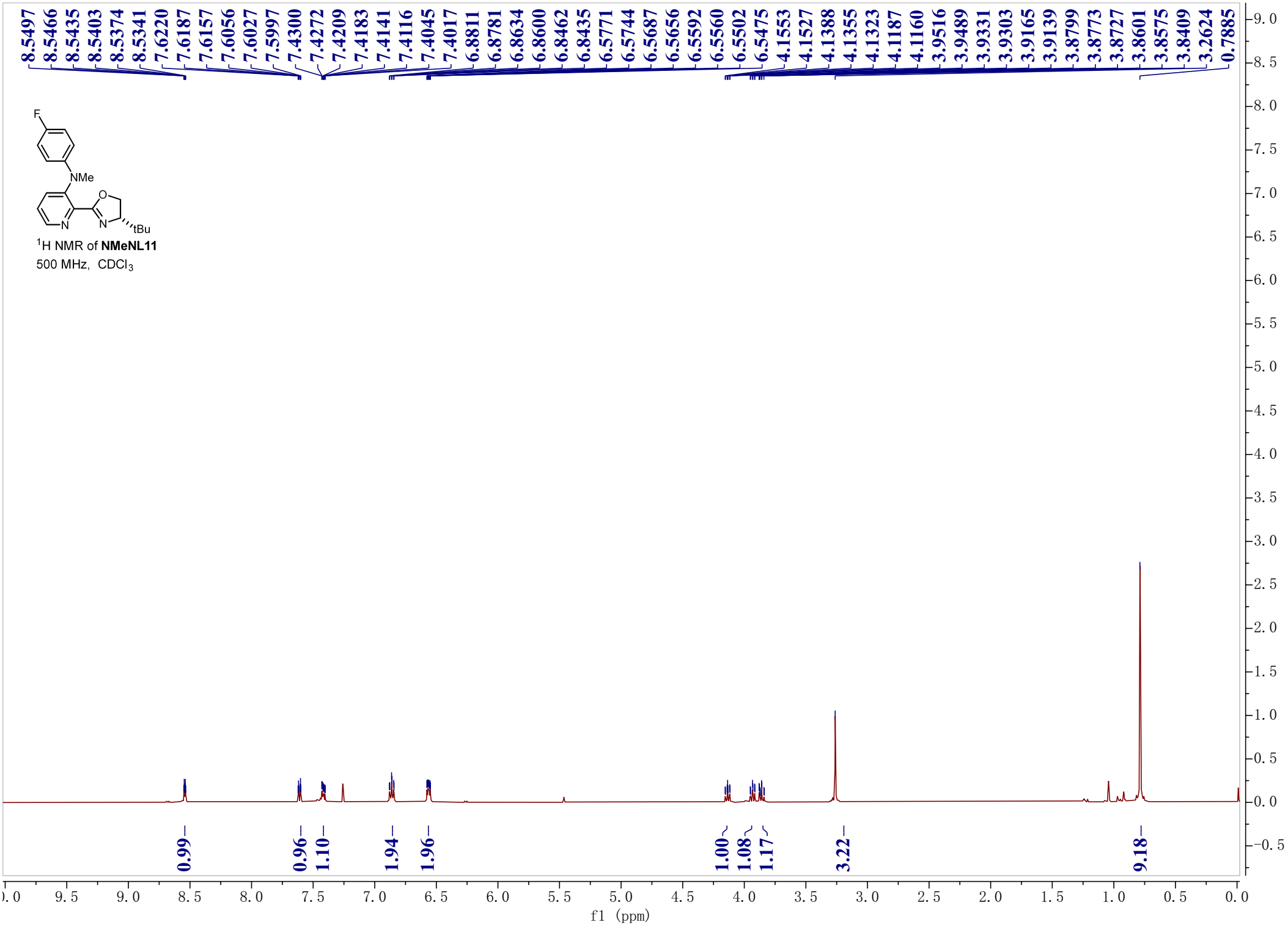


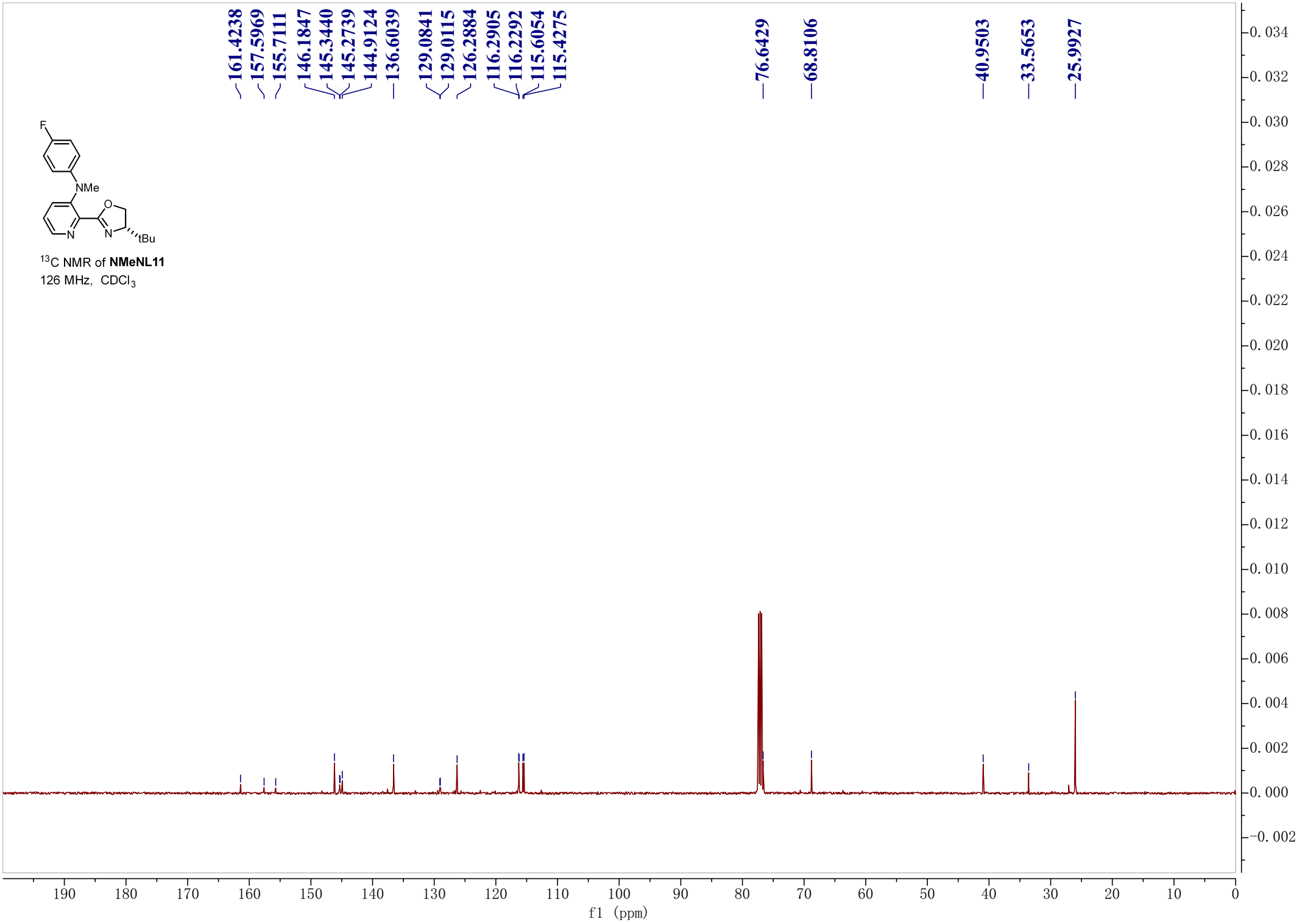
^{13}C NMR of **NL14**
101 MHz, $CDCl_3$



^{1}H NMR of **NL15**
500 MHz, $CDCl_3$

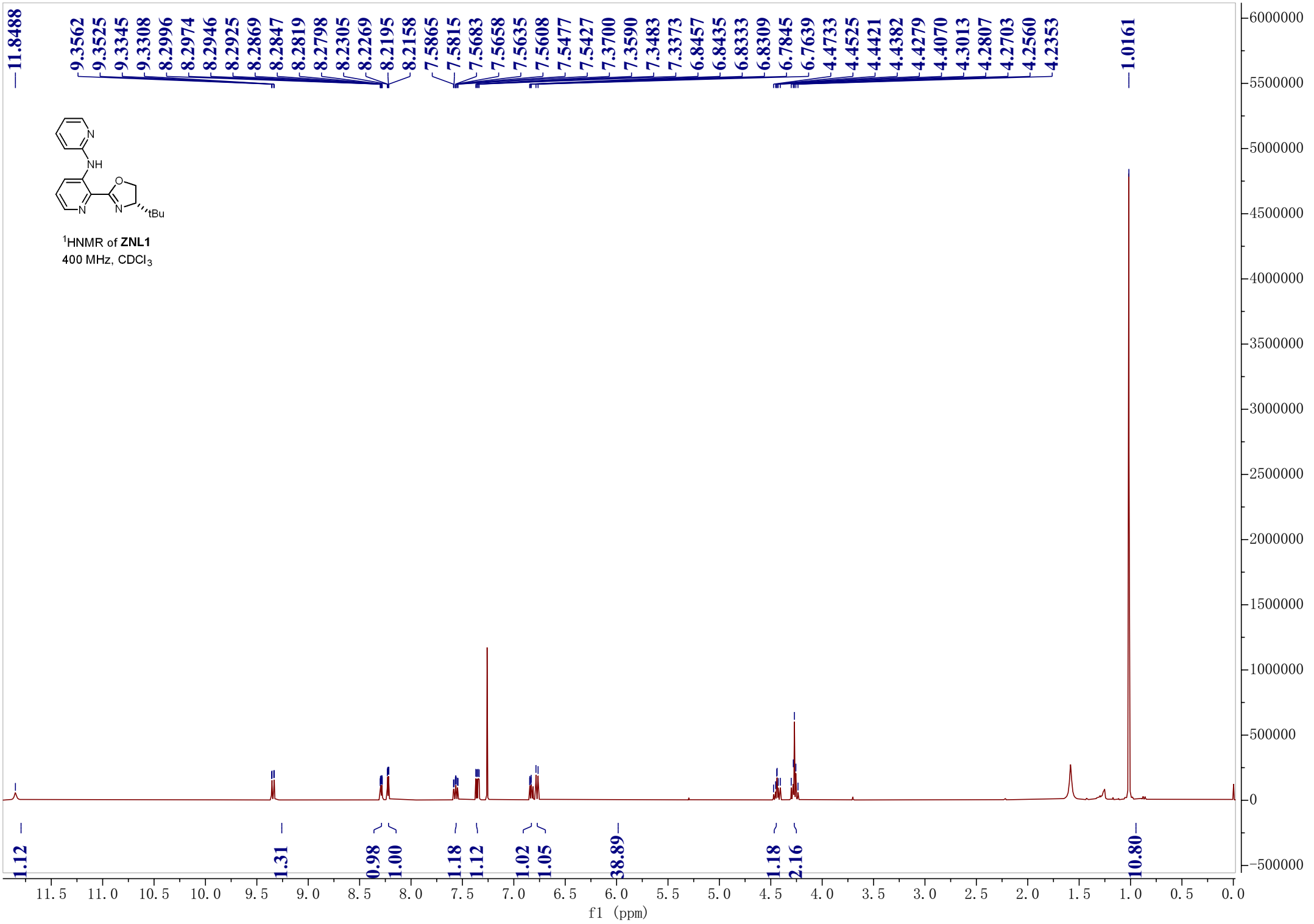

163.7229
158.7743
158.7326
156.7926
156.7508
142.6266
138.9999
128.8674
125.9443
125.3438
125.2675
125.1913
120.7023
120.6782
120.6541
117.3614
117.2358
117.1110
112.2067
112.1685
112.0559
112.0188
76.3747
67.8777
33.9539
25.8936
F
F
NH
O
N
N
tBu
13C NMR of NL15
126 MHz, CDCl3
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
−0.005
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

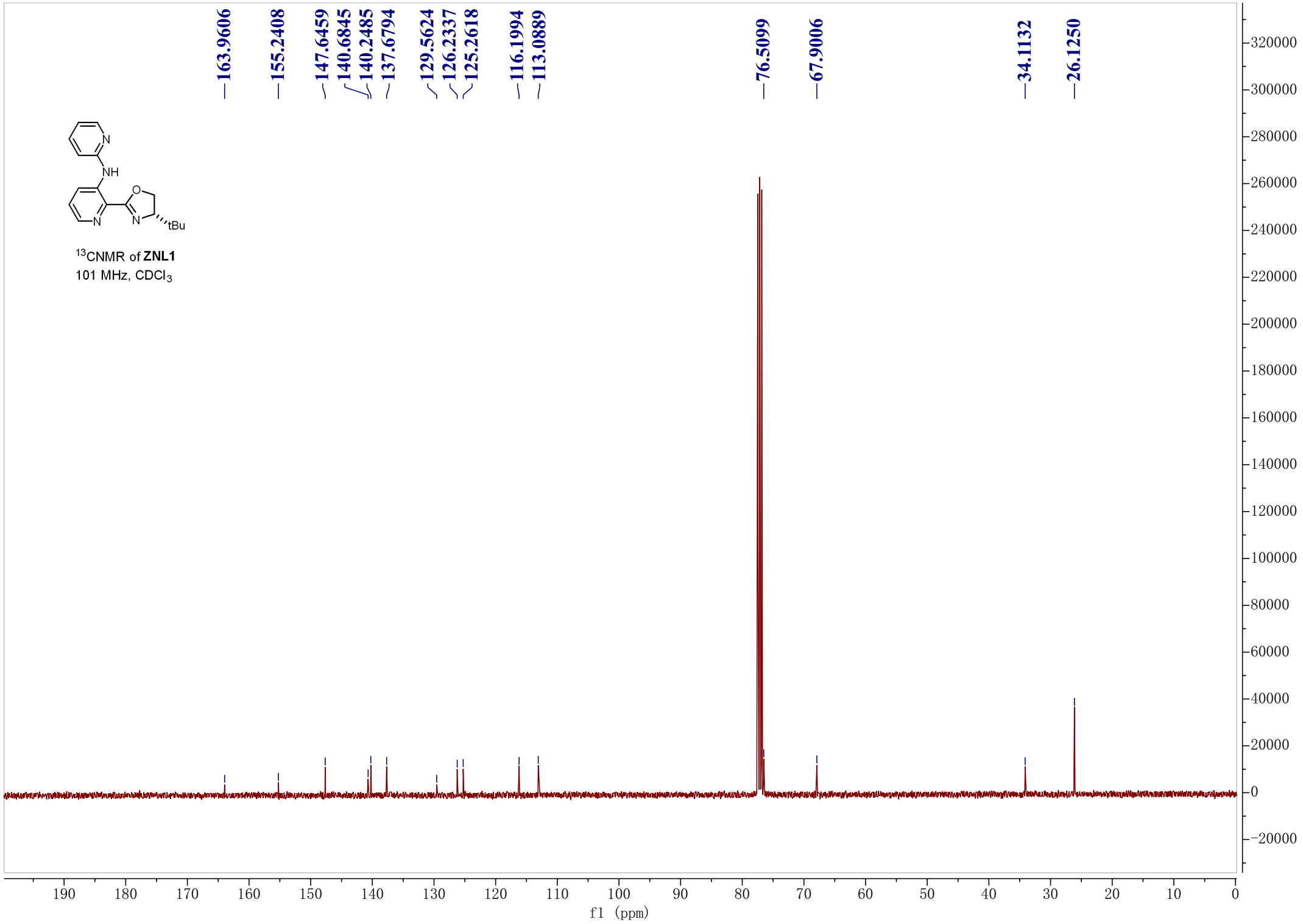

8.5497
8.5466
8.5435
8.5403
8.5374
8.5341
7.6220
7.6187
7.6157
7.6056
7.6027
7.5997
7.4300
7.4272
7.4209
7.4183
7.4141
7.4116
7.4045
7.4017
6.8811
6.8781
6.8634
6.8600
6.8462
6.8435
6.5771
6.5744
6.5687
6.5656
6.5592
6.5560
6.5502
6.5475
4.1553
4.1527
4.1388
4.1355
4.1323
4.1187
4.1160
3.9516
3.9489
3.9331
3.9303
3.9165
3.9139
3.8799
3.8773
3.8727
3.8601
3.8575
3.8409
3.2624
0.7885
F
NMe
O
N
N
tBu
1H NMR of NMeNL11
500 MHz, CDCl3
0.99
0.96
1.10
1.94
1.96
1.00
1.08
1.17
3.22
9.18
f1 (ppm)

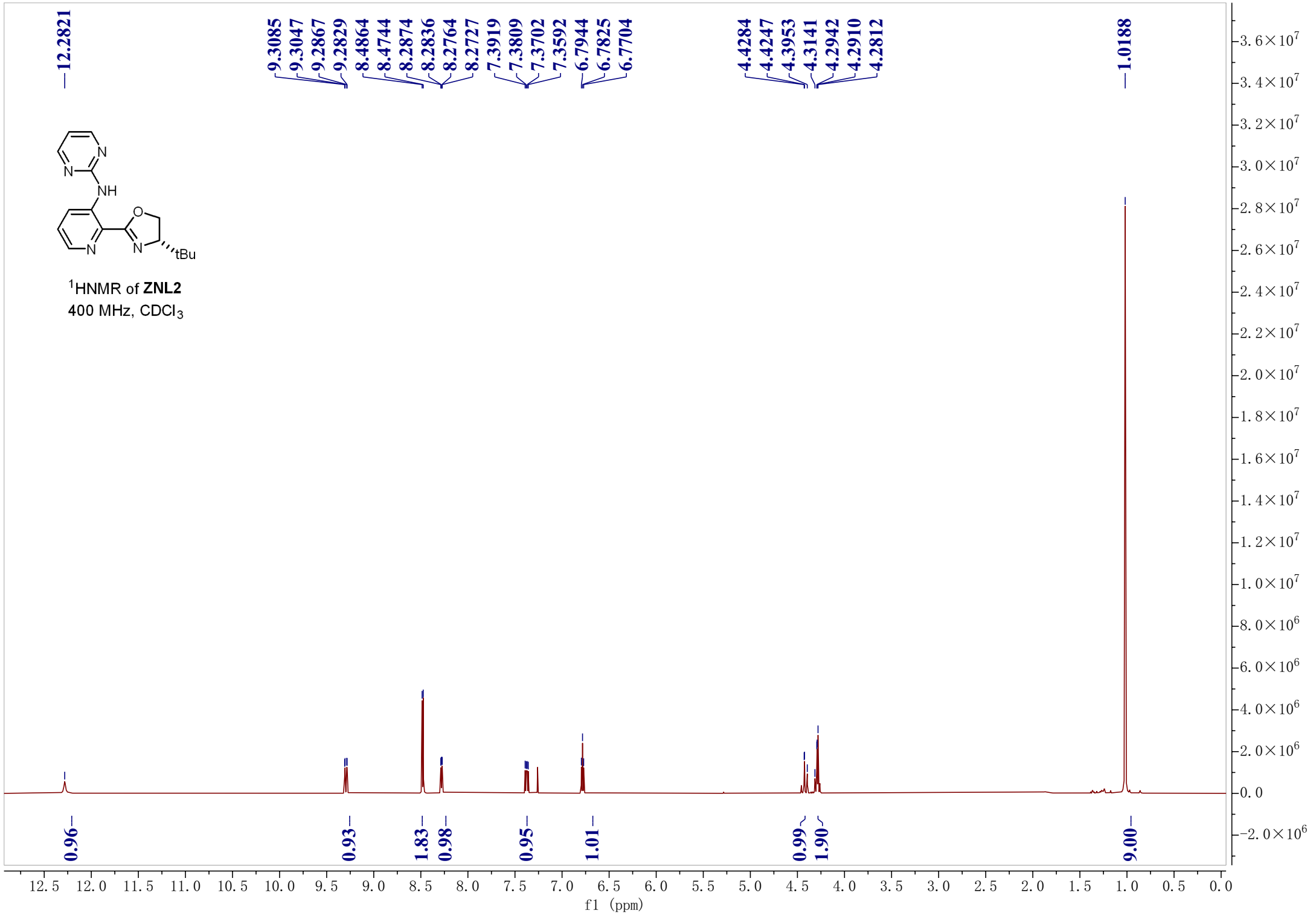


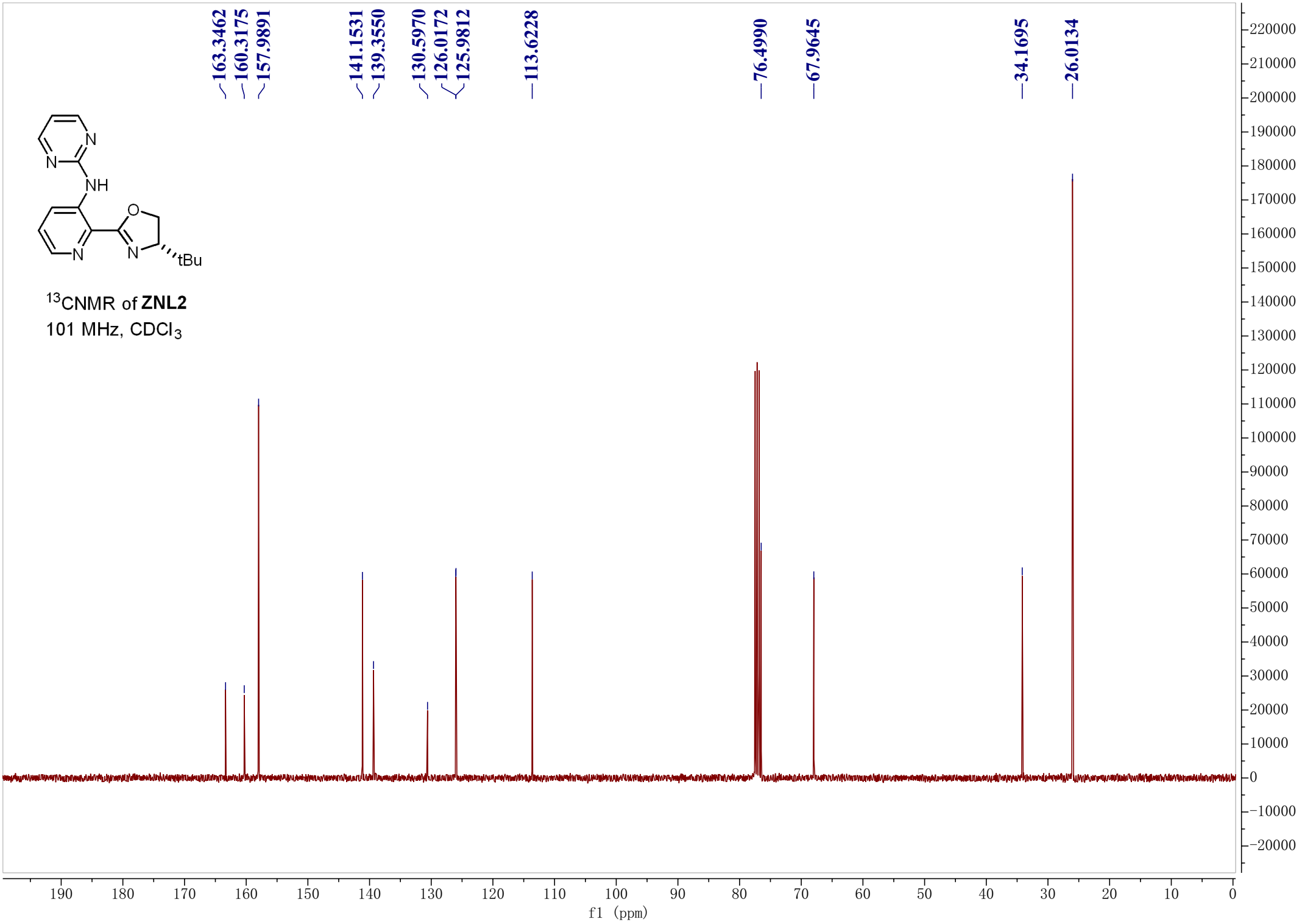
^{13}C NMR of **NMeNL11**

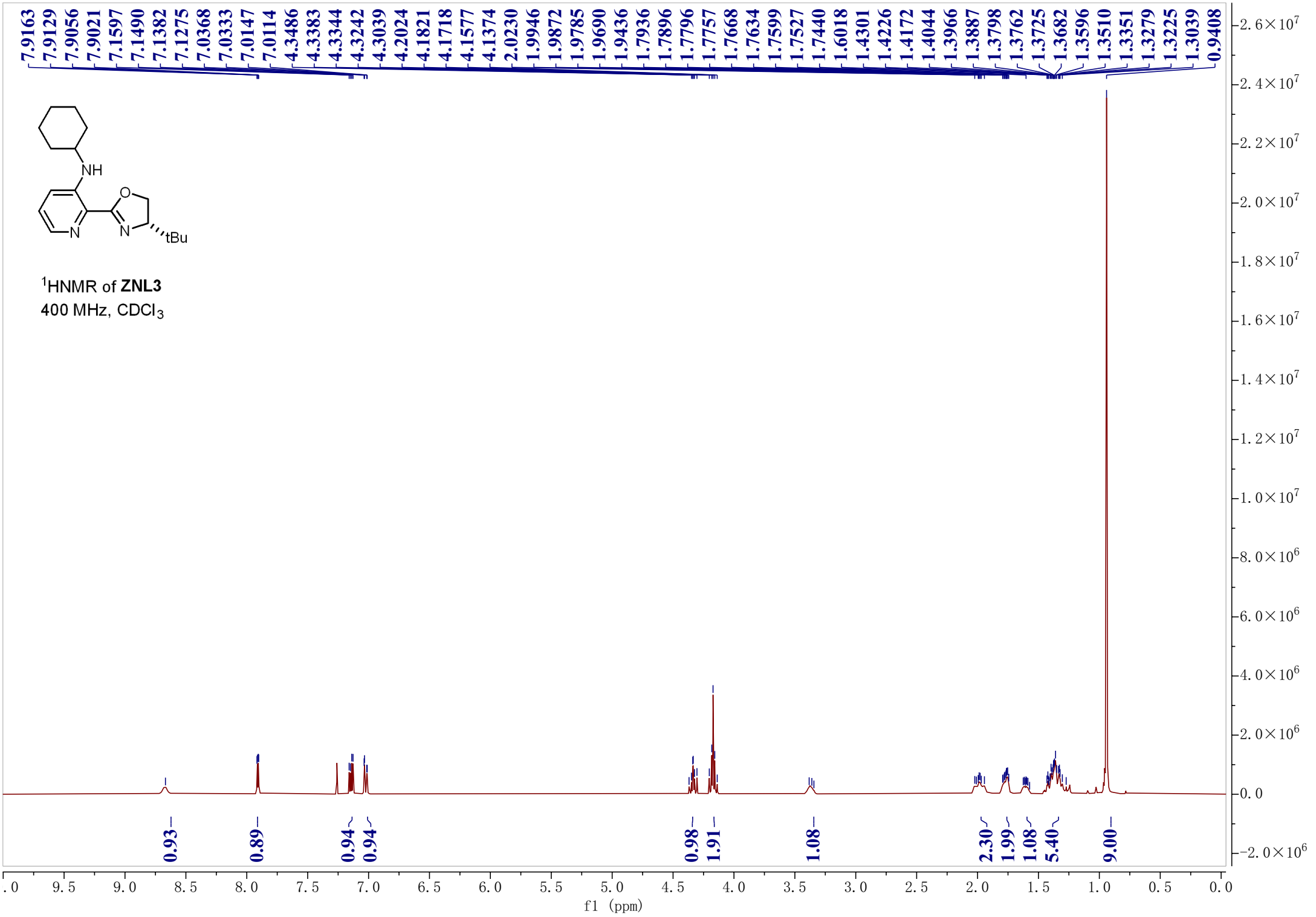
126 MHz, $CDCl_3$

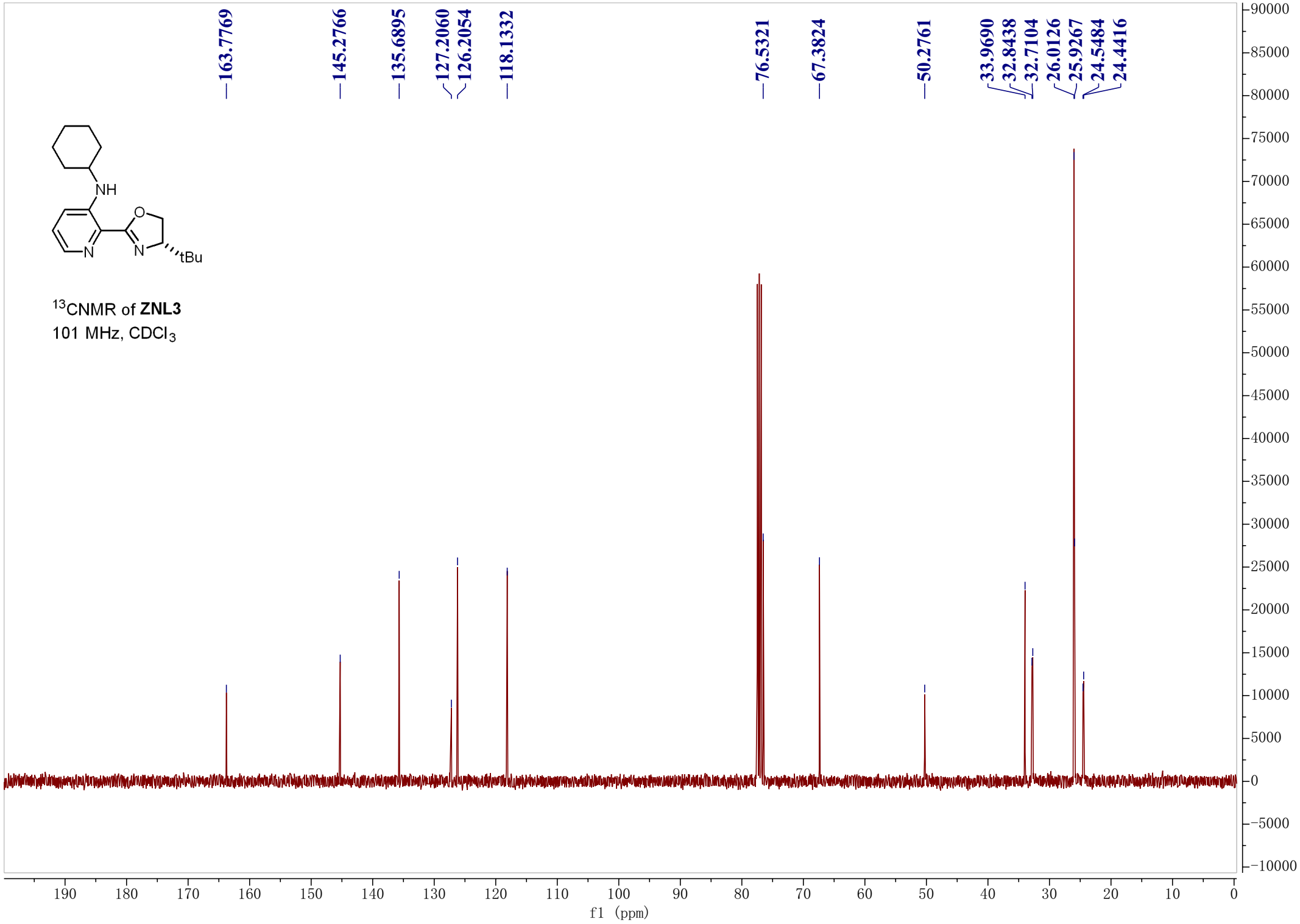

11.8488
9.3562
9.3525
9.3345
9.3308
8.2996
8.2974
8.2946
8.2925
8.2869
8.2847
8.2819
8.2798
8.2305
8.2269
8.2195
8.2158
7.5865
7.5815
7.5683
7.5658
7.5635
7.5608
7.5477
7.5427
7.3700
7.3590
7.3483
7.3373
6.8457
6.8435
6.8333
6.8309
6.7845
6.7639
4.4733
4.4525
4.4421
4.4382
4.4279
4.4070
4.3013
4.2807
4.2703
4.2560
4.2353
1.0161
NH
N
O
tBu
1HNMR of ZNL1
400 MHz, CDCl3
1.12
1.31
0.98
1.00
1.18
1.12
1.02
1.05
38.89
1.18
2.16
10.80
f1 (ppm)

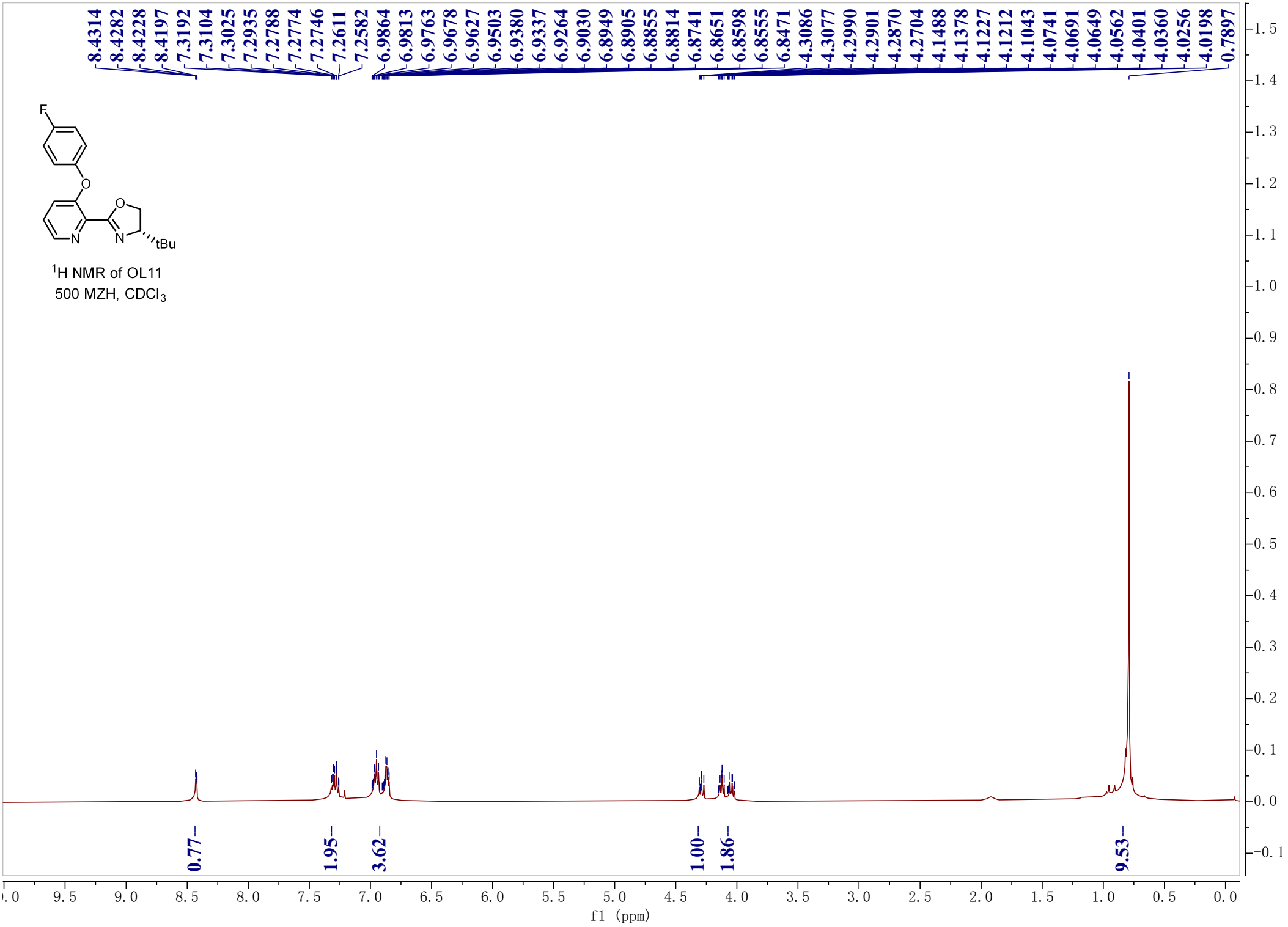

163.9606
155.2408
147.6459
140.6845
140.2485
137.6794
129.5624
126.2337
125.2618
116.1994
113.0889
76.5099
67.9006
34.1132
26.1250
NH
O
N
N
N
tBu
13CNMR of ZNL1
101 MHz, CDCl3
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
−20000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

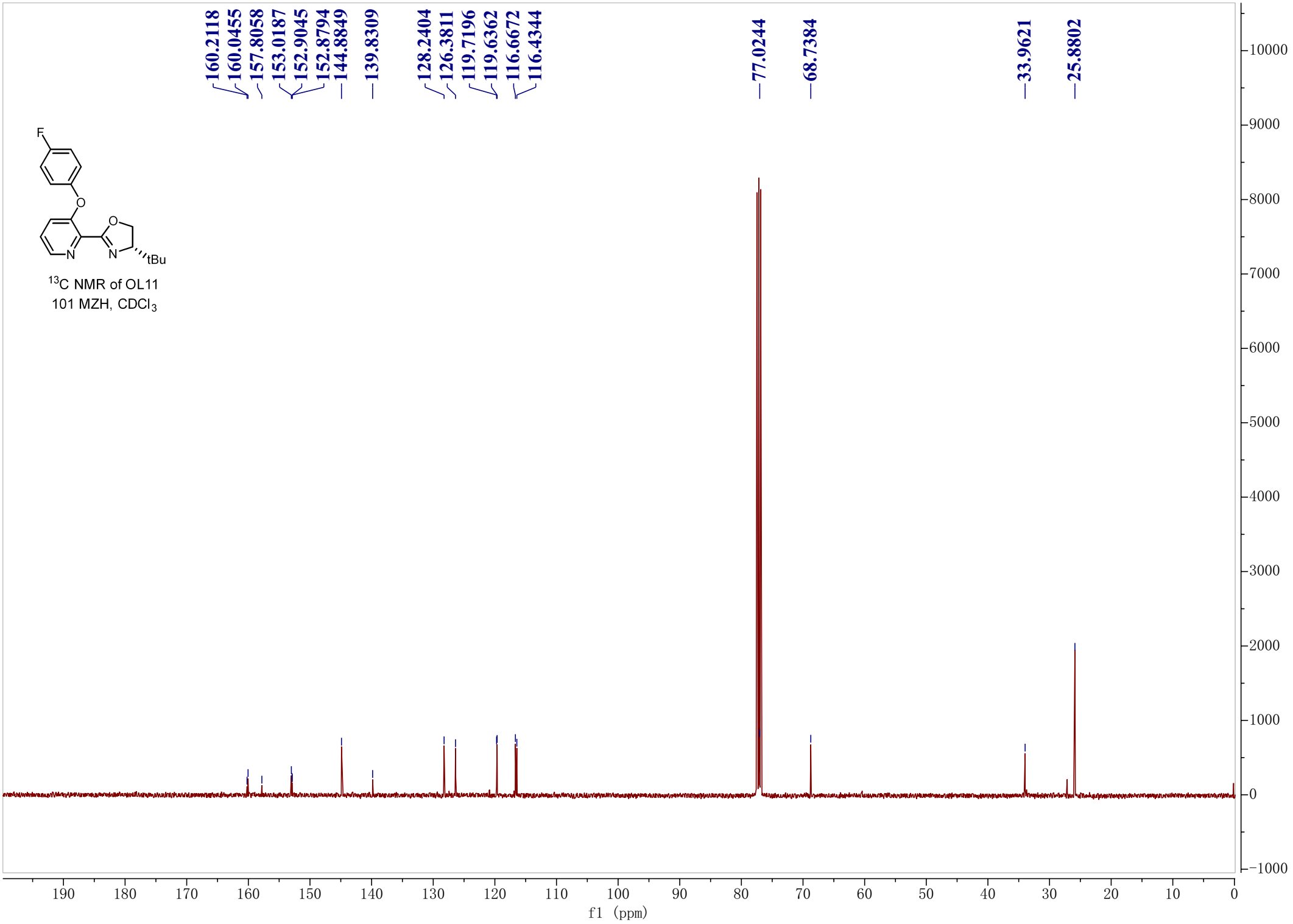

12.2821
9.3085
9.3047
9.2867
9.2829
8.4864
8.4744
8.2874
8.2836
8.2764
8.2727
7.3919
7.3809
7.3702
7.3592
6.7944
6.7825
6.7704
4.4284
4.4247
4.3953
4.3141
4.2942
4.2910
4.2812
1.0188
NH
O
N
tBu
1HNMR of ZNL2
400 MHz, CDCl3
0.96
0.93
1.83
0.98
0.95
1.01
0.99
1.90
9.00
f1 (ppm)

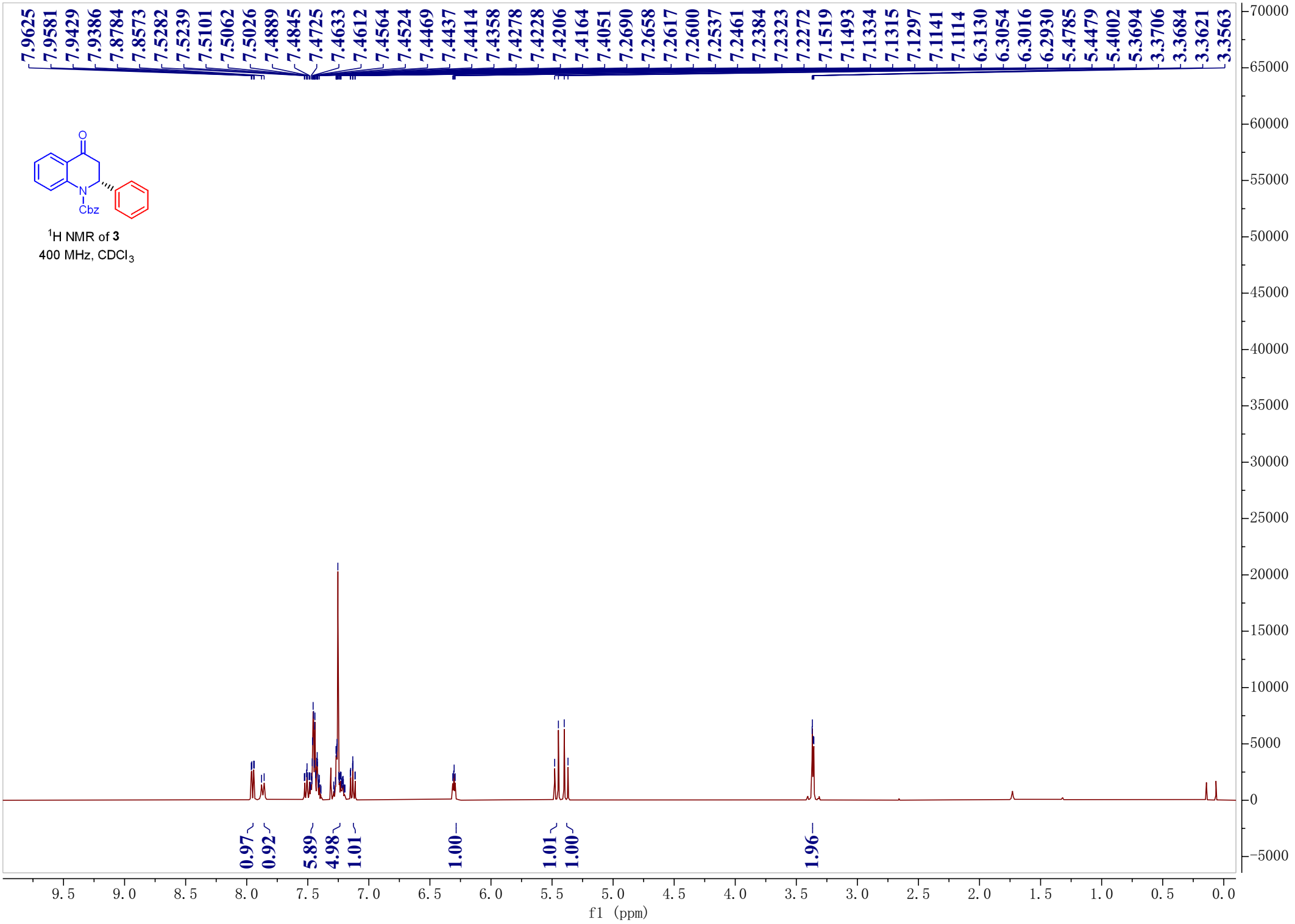

163.3462
160.3175
157.9891
141.1531
139.3550
130.5970
126.0172
125.9812
113.6228
76.4990
67.9645
34.1695
26.0134
NH
O
N
tBu
13CNMR of ZNL2
101 MHz, CDCl3
f1 (ppm)

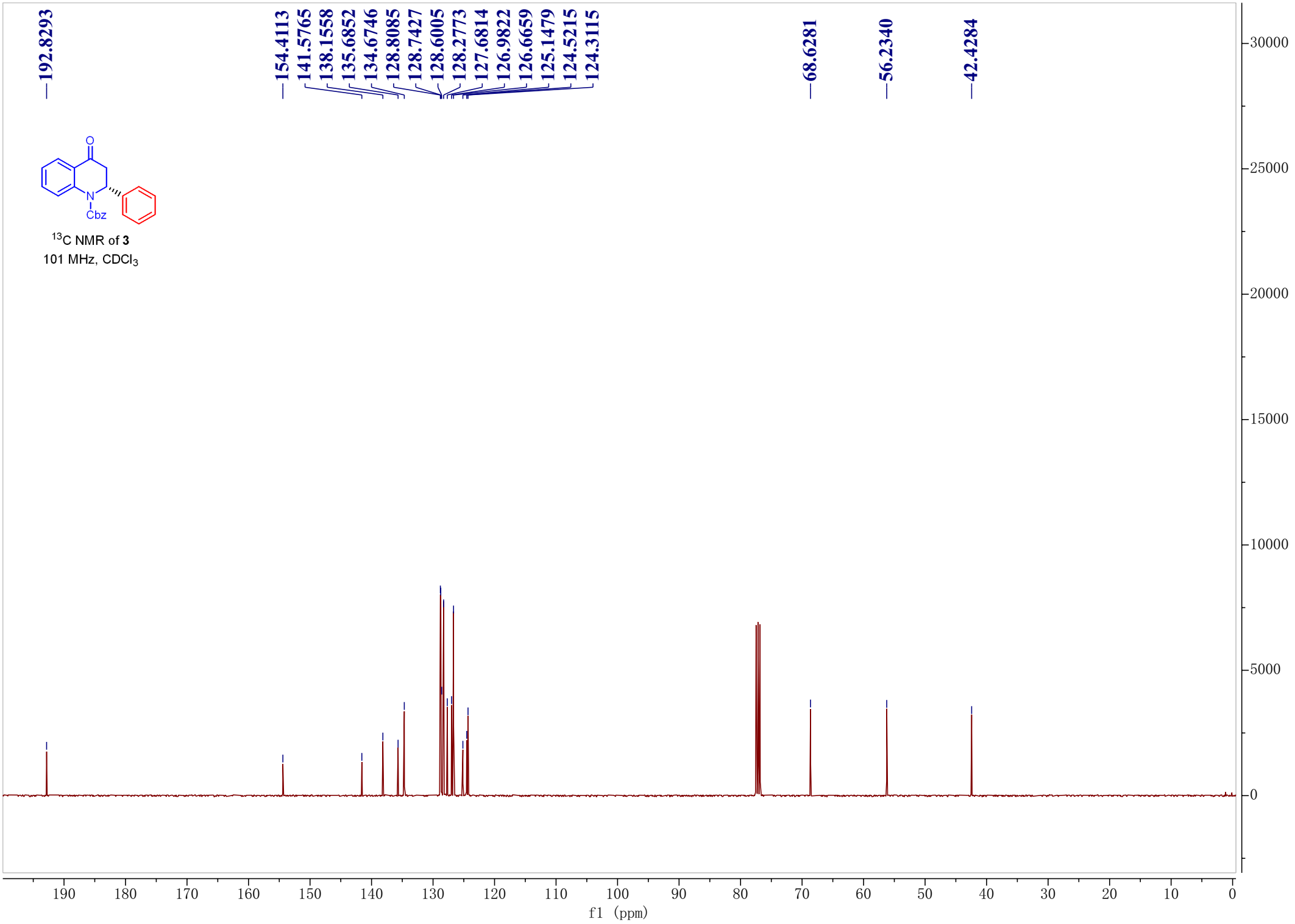

7.9163
7.9129
7.9056
7.9021
7.1597
7.1490
7.1382
7.1275
7.0368
7.0333
7.0147
7.0114
4.3486
4.3383
4.3344
4.3242
4.3039
4.2024
4.1821
4.1718
4.1577
4.1374
2.0230
1.9946
1.9872
1.9785
1.9690
1.9436
1.7936
1.7896
1.7796
1.7757
1.7668
1.7634
1.7599
1.7527
1.7440
1.6018
1.4301
1.4226
1.4172
1.4044
1.3966
1.3887
1.3798
1.3762
1.3725
1.3682
1.3596
1.3510
1.3351
1.3279
1.3225
1.3039
0.9408
NH
O
N
N
tBu
1HNMR of ZNL3
400 MHz, CDCl3
0.93
0.89
0.94
0.94
0.98
1.91
1.08
2.30
1.99
1.08
5.40
9.00
f1 (ppm)


163.7769
145.2766
135.6895
127.2060
126.2054
118.1332
76.5321
67.3824
50.2761
33.9690
32.8438
32.7104
26.0126
25.9267
24.5484
24.4416
NH
O
N
N
tBu
13CNMR of ZNL3
101 MHz, CDCl3
f1 (ppm)


8.4314
8.4282
8.4228
8.4197
7.3192
7.3104
7.3025
7.2935
7.2788
7.2774
7.2746
7.2611
7.2582
6.9864
6.9813
6.9763
6.9678
6.9627
6.9503
6.9380
6.9337
6.9264
6.9030
6.8949
6.8905
6.8855
6.8814
6.8741
6.8651
6.8598
6.8555
6.8471
4.3086
4.3077
4.2990
4.2901
4.2870
4.2704
4.1488
4.1378
4.1227
4.1212
4.1043
4.0741
4.0691
4.0649
4.0562
4.0401
4.0360
4.0256
4.0198
0.7897
F
O
O
N
N
tBu
1H NMR of OL11
500 MZH, CDCl3
0.77
1.95
3.62
1.00
1.86
9.53
f1 (ppm)

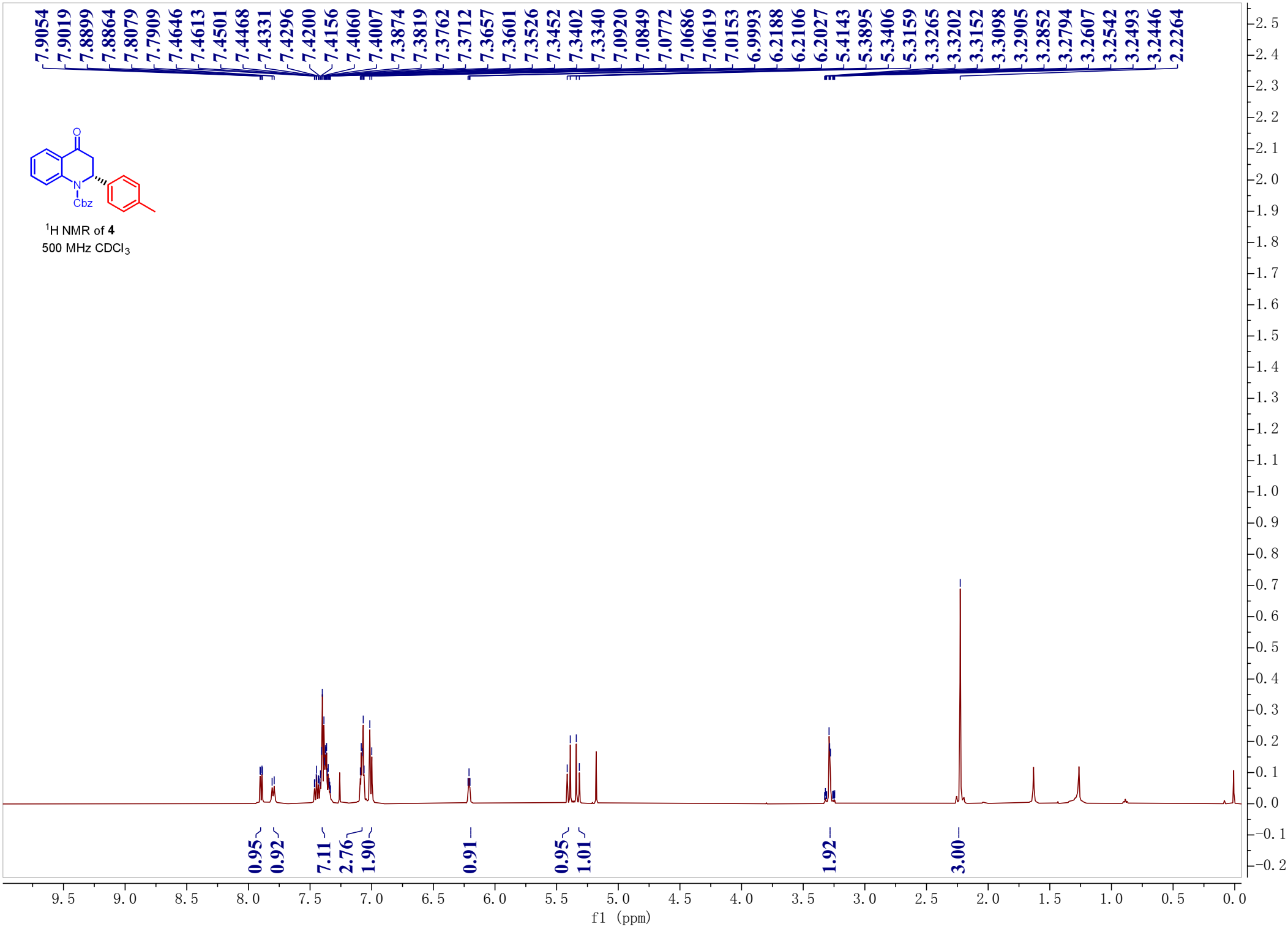

160.2118
160.0455
157.8058
153.0187
152.9045
152.8794
144.8849
139.8309
128.2404
126.3811
119.7196
119.6362
116.6672
116.4344
77.0244
68.7384
33.9621
25.8802
F
O
O
N
N
tBu
13C NMR of OL11
101 MZH, CDCl3
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9625
7.9581
7.9429
7.9386
7.8784
7.8573
7.5282
7.5239
7.5101
7.5062
7.5026
7.4889
7.4845
7.4725
7.4633
7.4612
7.4564
7.4524
7.4469
7.4437
7.4414
7.4358
7.4278
7.4228
7.4206
7.4164
7.4051
7.2690
7.2658
7.2617
7.2600
7.2537
7.2461
7.2384
7.2323
7.2272
7.1519
7.1493
7.1334
7.1315
7.1297
7.1141
7.1114
6.3130
6.3054
6.3016
6.2930
5.4785
5.4479
5.4002
5.3694
3.3706
3.3684
3.3621
3.3563
O
N
Cbz
1H NMR of 3
400 MHz, CDCl3
0.97
0.92
5.89
4.98
1.01
1.00
1.01
1.00
1.96
f1 (ppm)

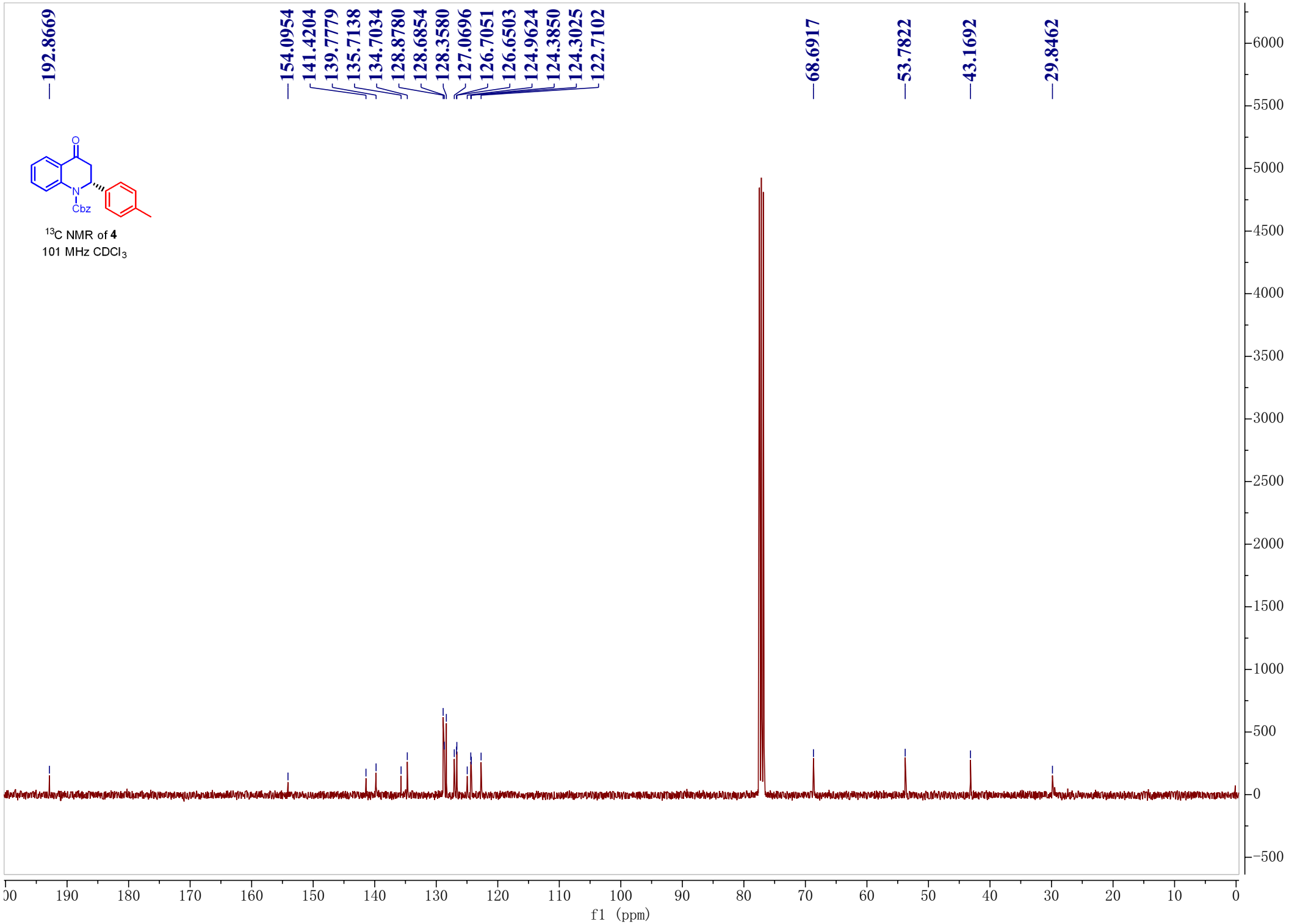


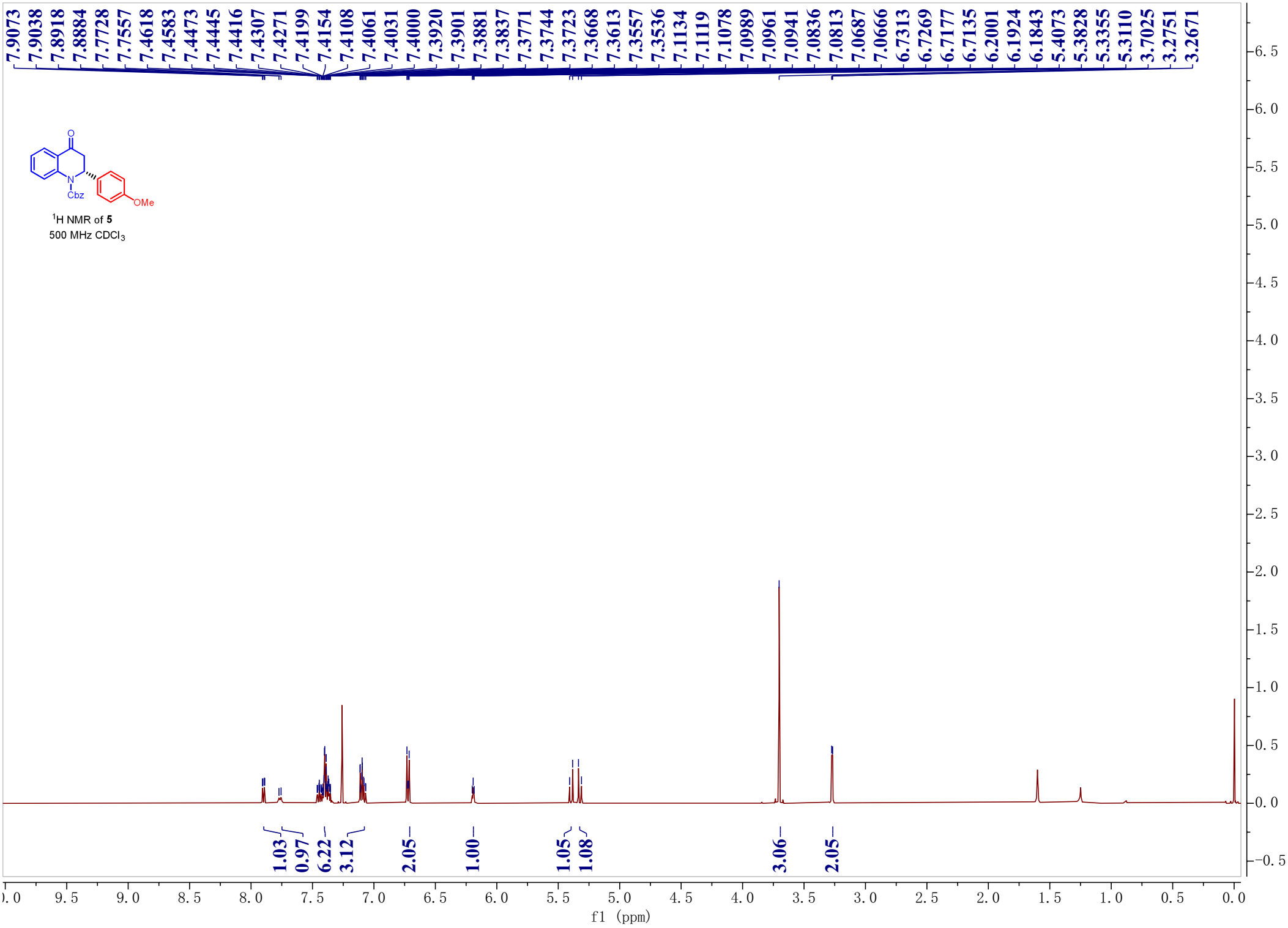
^{13}C NMR of **3**

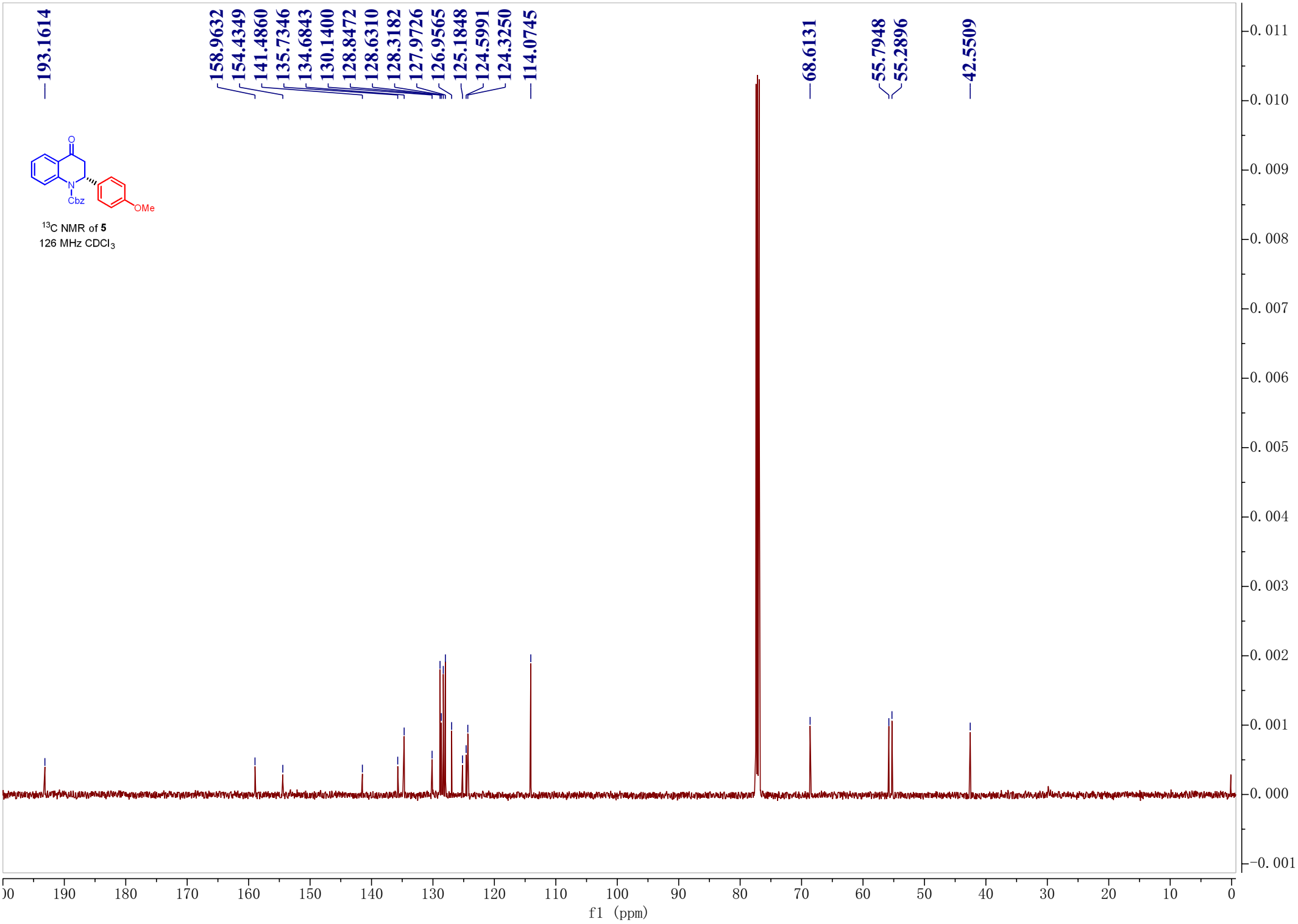
101 MHz, $CDCl_3$



^{1}H NMR of **4**
500 MHz $CDCl_3$


192.8669
154.0954
141.4204
139.7779
135.7138
134.7034
128.8780
128.6854
128.3580
127.0696
126.7051
126.6503
124.9624
124.3850
124.3025
122.7102
68.6917
53.7822
43.1692
29.8462
O
N
Cbz
13C NMR of 4
101 MHz CDCl3
f1 (ppm)


7.9073
7.9038
7.8918
7.8884
7.7728
7.7557
7.4618
7.4583
7.4473
7.4445
7.4416
7.4307
7.4271
7.4199
7.4154
7.4108
7.4061
7.4031
7.4000
7.3920
7.3901
7.3881
7.3837
7.3771
7.3744
7.3723
7.3668
7.3613
7.3557
7.3536
7.1134
7.1119
7.1078
7.0989
7.0961
7.0941
7.0836
7.0813
7.0687
7.0666
6.7313
6.7269
6.7177
6.7135
6.2001
6.1924
6.1843
5.4073
5.3828
5.3355
5.3110
3.7025
3.2751
3.2671
O
N
Cbz
OMe
1H NMR of 5
500 MHz CDCl3
1.03
0.97
6.22
3.12
2.05
1.00
1.05
1.08
3.06
2.05
f1 (ppm)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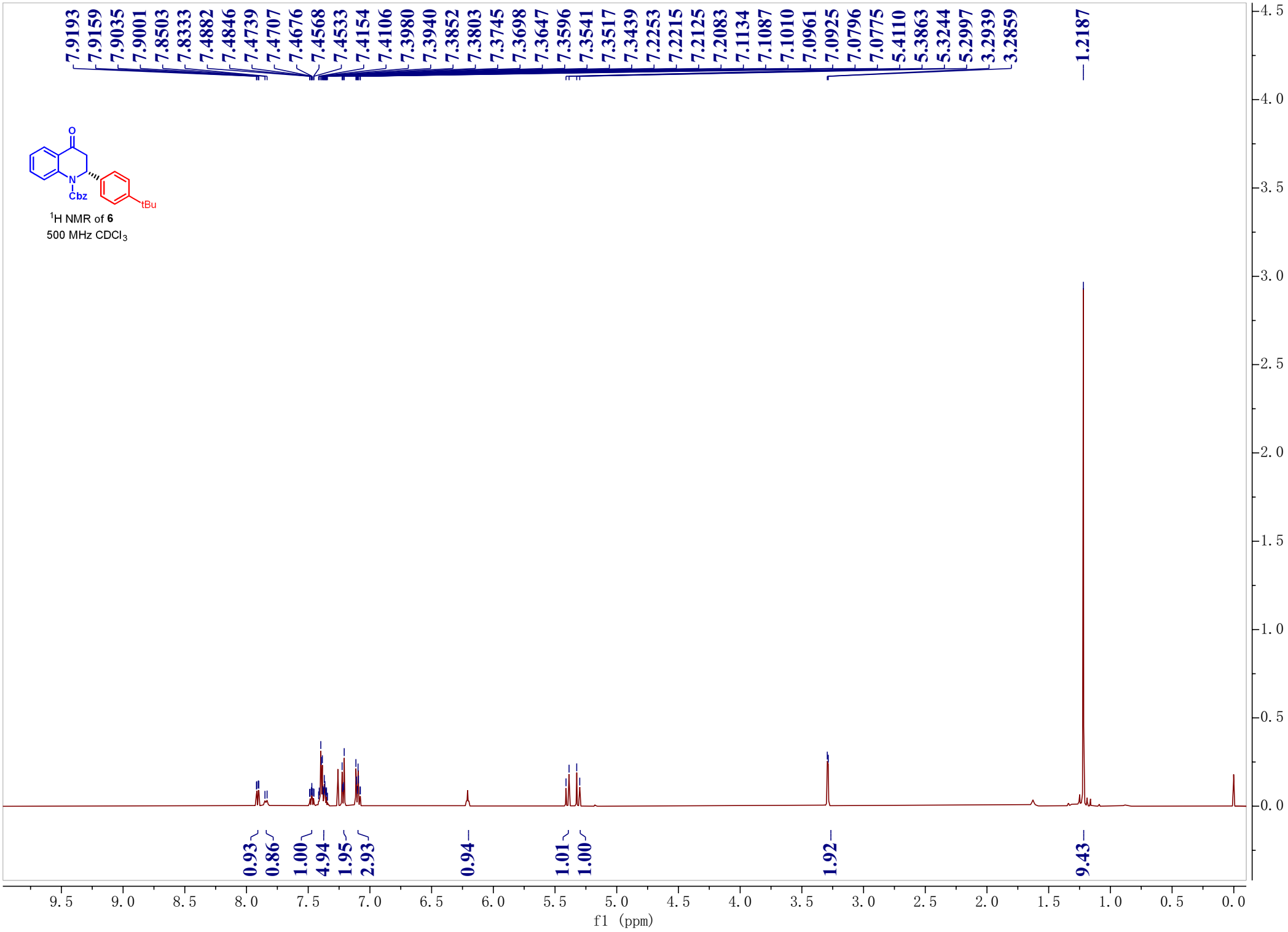
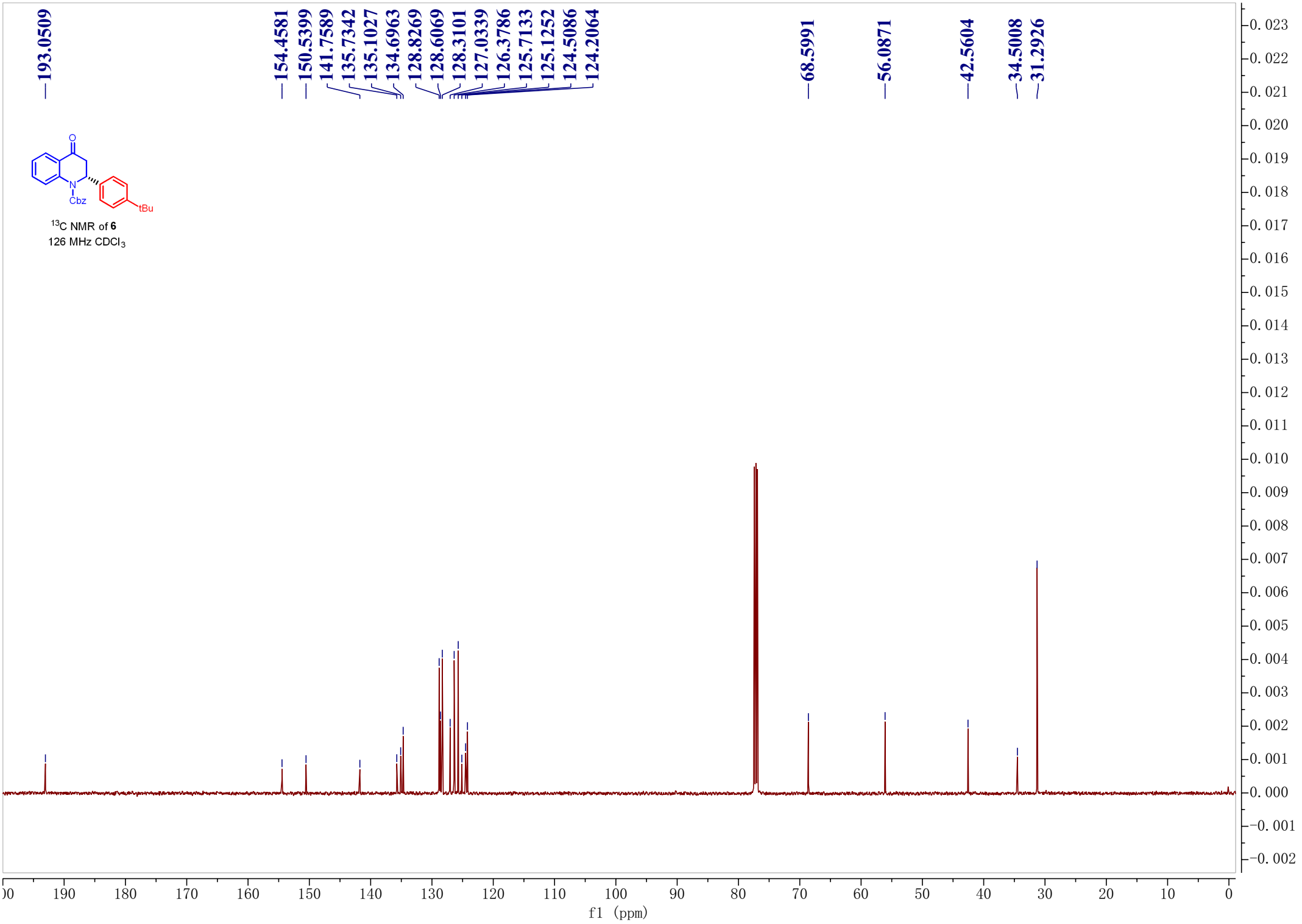
158.9632
154.4349
141.4860
135.7346
134.6843
130.1400
128.8472
128.6310
128.3182
127.9726
126.9565
125.1848
124.5991
124.3250
114.0745
68.6131
55.7948
55.2896
42.5509
O
N
Cbz
OMe
13C NMR of 5
126 MHz CDCl3
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
f1 (ppm)


7.9193
7.9159
7.9035
7.9001
7.8503
7.8333
7.4882
7.4846
7.4739
7.4707
7.4676
7.4568
7.4533
7.4154
7.4106
7.3980
7.3940
7.3852
7.3803
7.3745
7.3698
7.3647
7.3596
7.3541
7.3517
7.3439
7.2253
7.2215
7.2125
7.2083
7.1134
7.1087
7.1010
7.0961
7.0925
7.0796
7.0775
5.4110
5.3863
5.3244
5.2997
3.2939
3.2859
1.2187
O
N
Cbz
tBu
1H NMR of 6
500 MHz CDCl3
0.93
0.86
1.00
4.94
1.95
2.93
0.94
1.01
1.00
1.92
9.43
f1 (ppm)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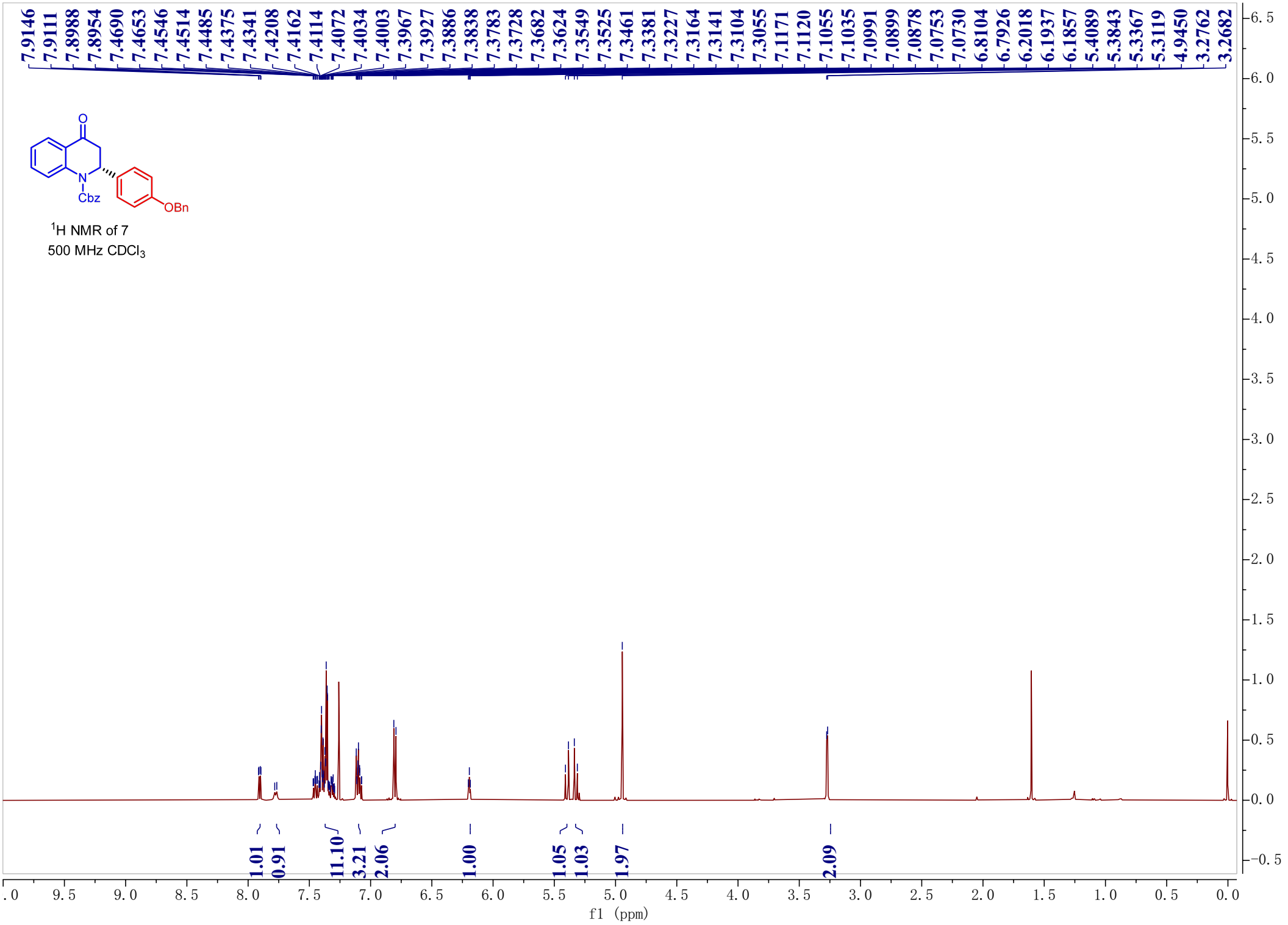
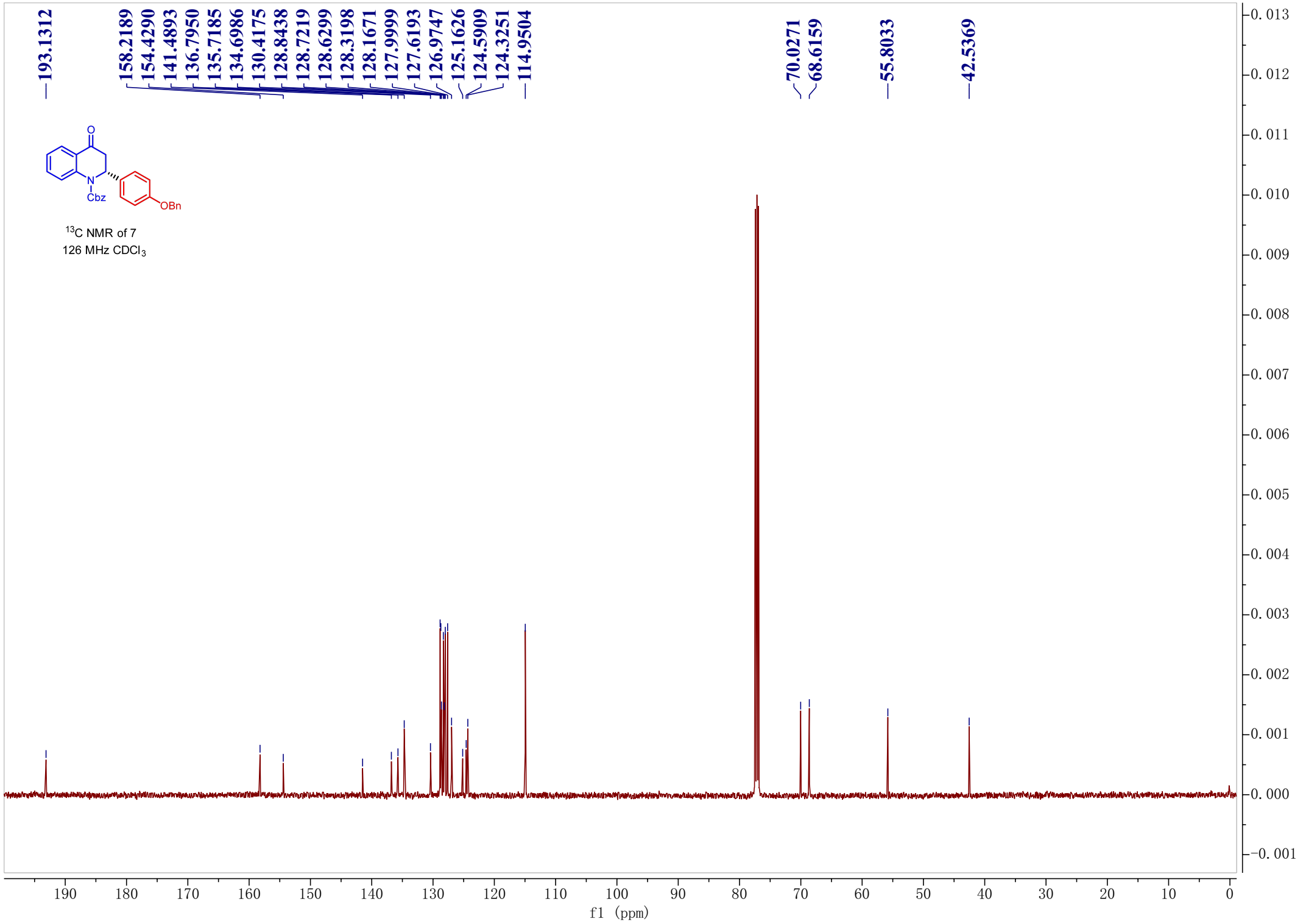
154.4581
150.5399
141.7589
135.7342
135.1027
134.6963
128.8269
128.6069
128.3101
127.0339
126.3786
125.7133
125.1252
124.5086
124.2064
68.5991
56.0871
42.5604
34.5008
31.2926
Cbz
tBu
13C NMR of 6
126 MHz CDCl3
f1 (ppm)


7.9146
7.9111
7.8988
7.8954
7.4690
7.4653
7.4546
7.4514
7.4485
7.4375
7.4341
7.4208
7.4162
7.4114
7.4072
7.4034
7.4003
7.3967
7.3927
7.3886
7.3838
7.3783
7.3728
7.3682
7.3624
7.3549
7.3525
7.3461
7.3381
7.3227
7.3164
7.3141
7.3104
7.3055
7.1171
7.1120
7.1055
7.1035
7.0991
7.0899
7.0878
7.0753
7.0730
6.8104
6.7926
6.2018
6.1937
6.1857
5.4089
5.3843
5.3367
5.3119
4.9450
3.2762
3.2682
O
N
Cbz
OBn
1H NMR of 7
500 MHz CDCl3
1.01
0.91
11.10
3.21
2.06
1.00
1.05
1.03
1.97
2.09
f1 (ppm)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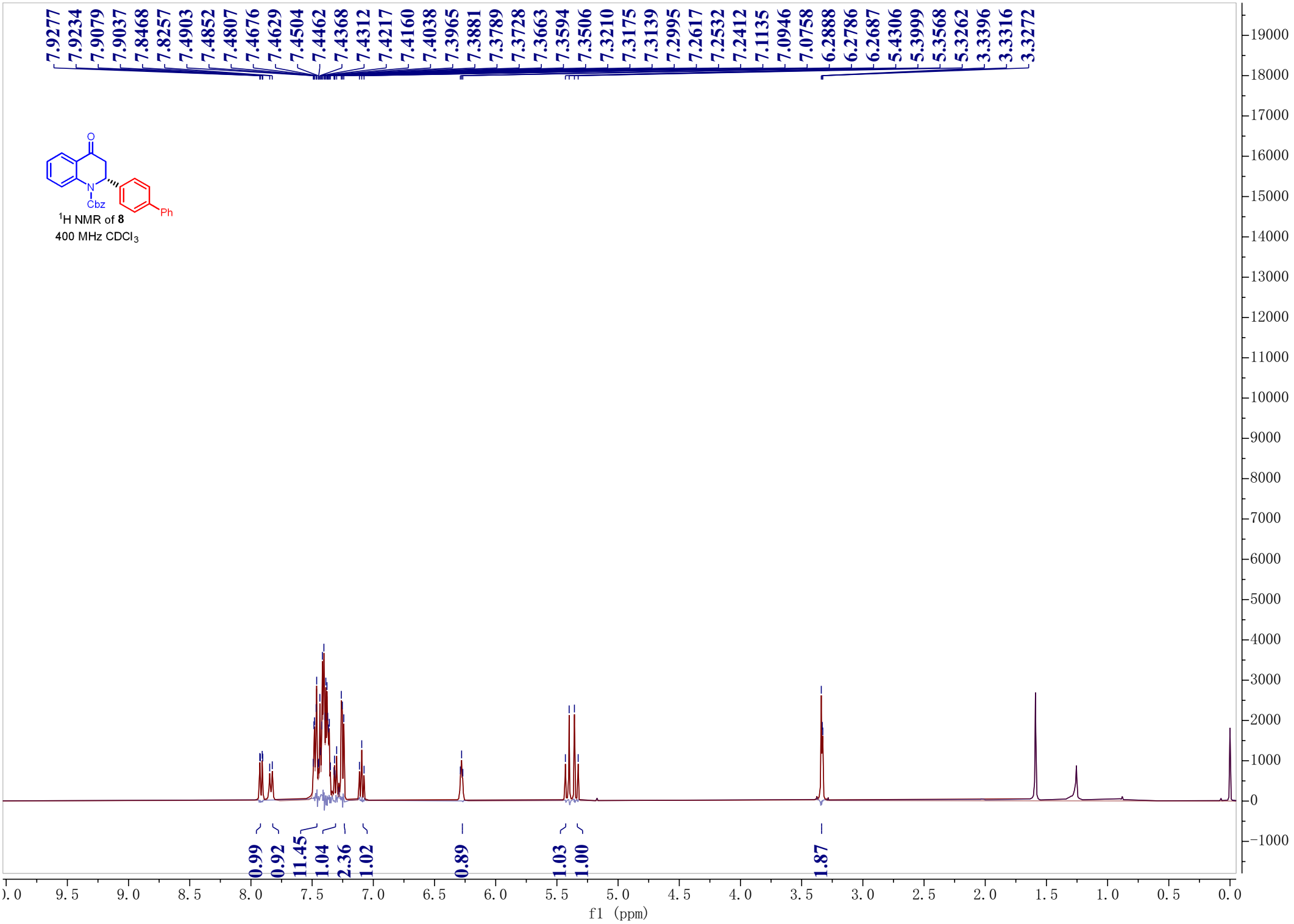
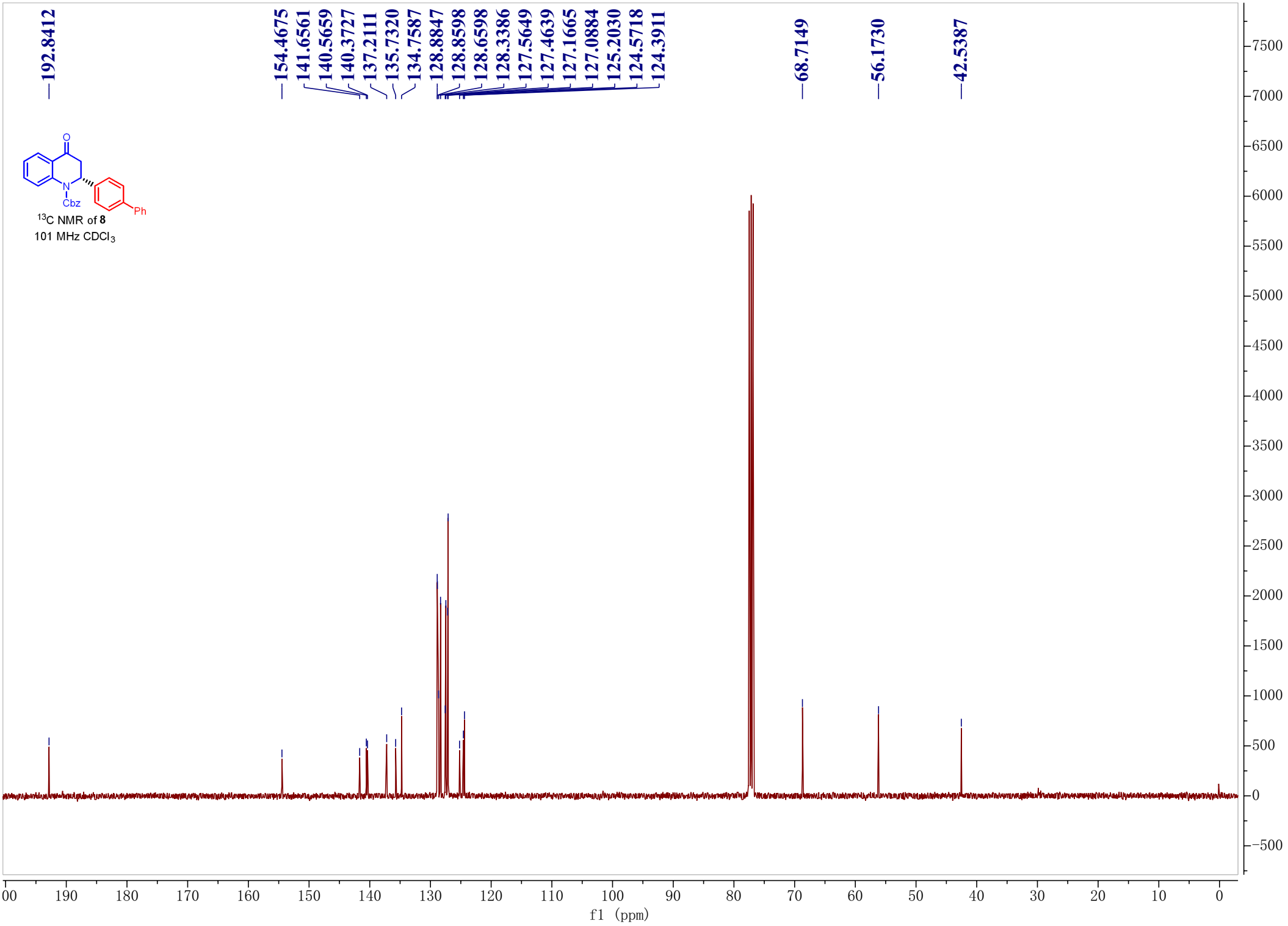
158.2189
154.4290
141.4893
136.7950
135.7185
134.6986
130.4175
128.8438
128.7219
128.6299
128.3198
128.1671
127.9999
127.6193
126.9747
125.1626
124.5909
124.3251
114.9504
70.0271
68.6159
55.8033
42.5369
O
N
Cbz
OBn
13C NMR of 7
126 MHz CDCl3
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9277
7.9234
7.9079
7.9037
7.8468
7.8257
7.4903
7.4852
7.4807
7.4676
7.4629
7.4504
7.4462
7.4368
7.4312
7.4217
7.4160
7.4038
7.3965
7.3881
7.3789
7.3728
7.3663
7.3594
7.3506
7.3210
7.3175
7.3139
7.2995
7.2617
7.2532
7.2412
7.1135
7.0946
7.0758
6.2888
6.2786
6.2687
5.4306
5.3999
5.3568
5.3262
3.3396
3.3316
3.3272
O
N
Cbz
Ph
1H NMR of 8
400 MHz CDCl3
0.99
0.92
11.45
1.04
2.36
1.02
0.89
1.03
1.00
1.87
f1 (ppm)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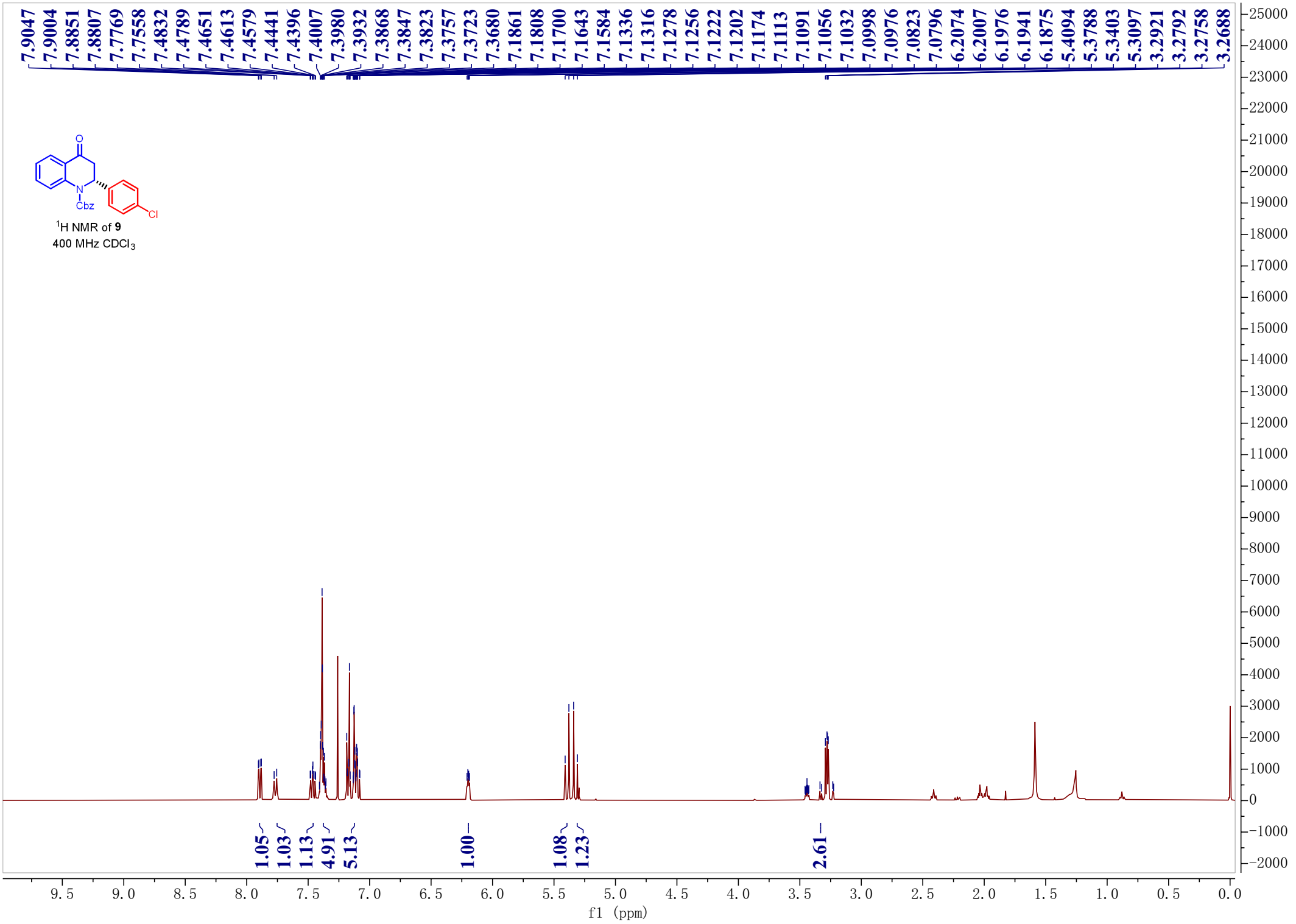
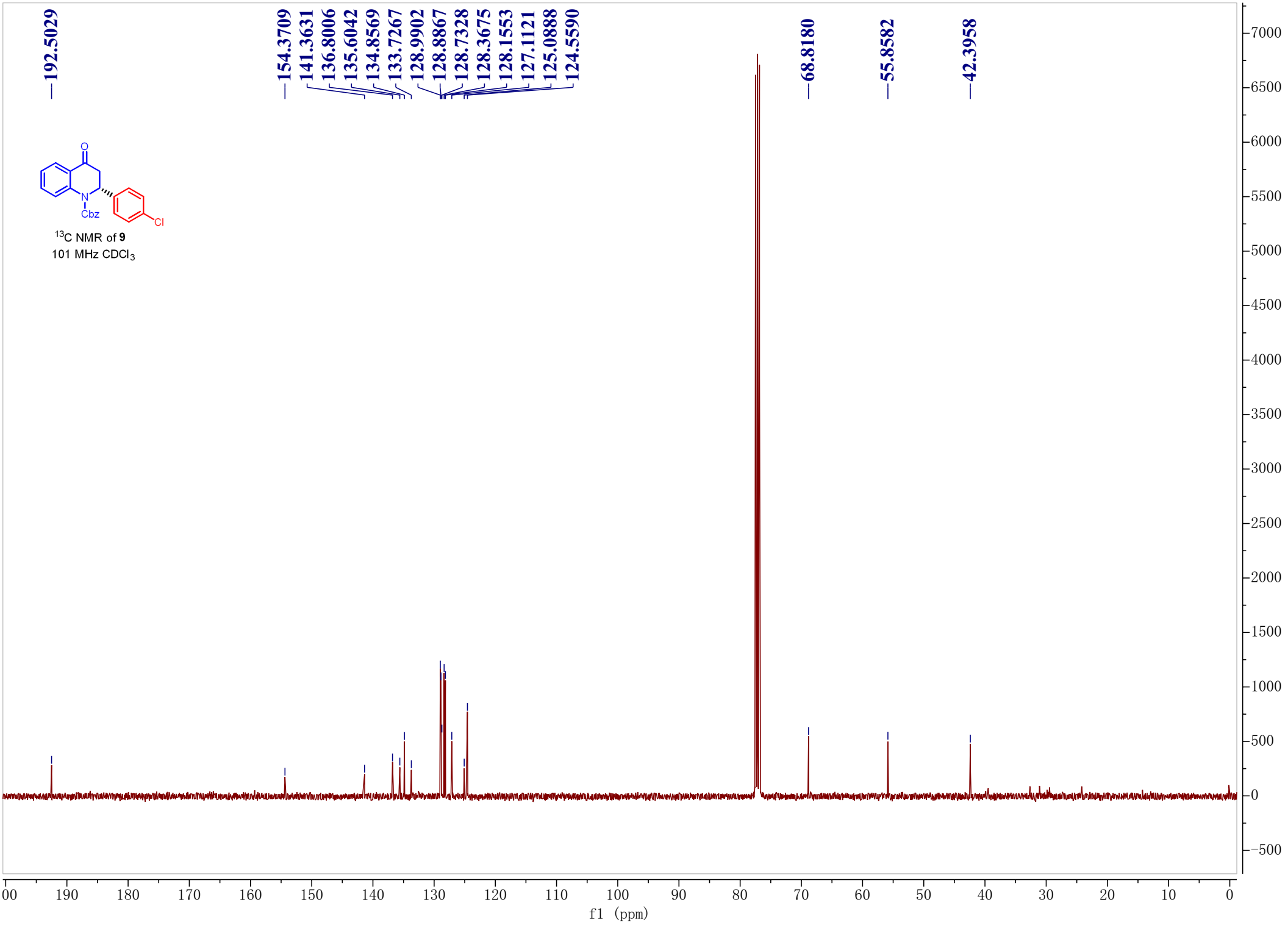
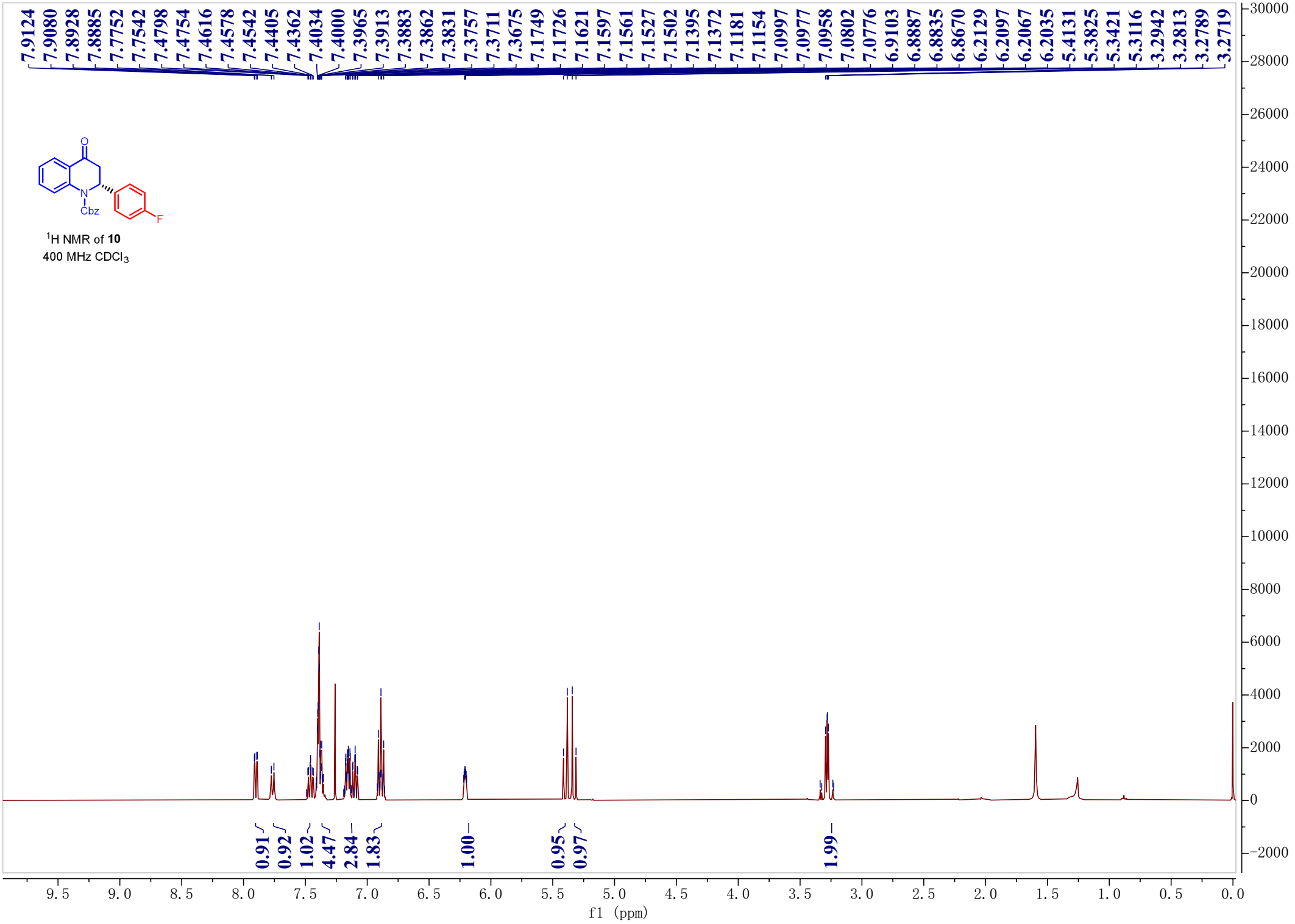
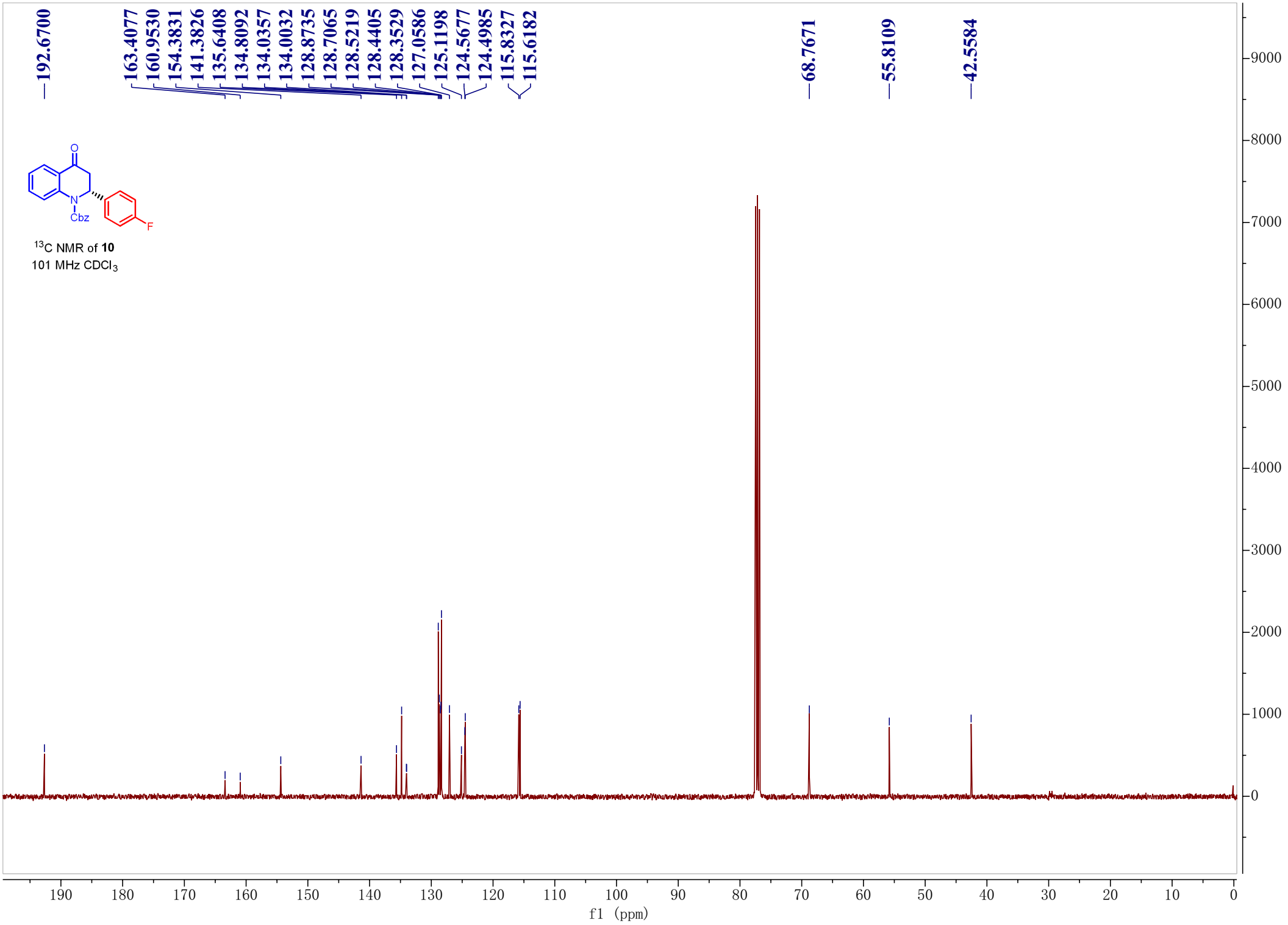
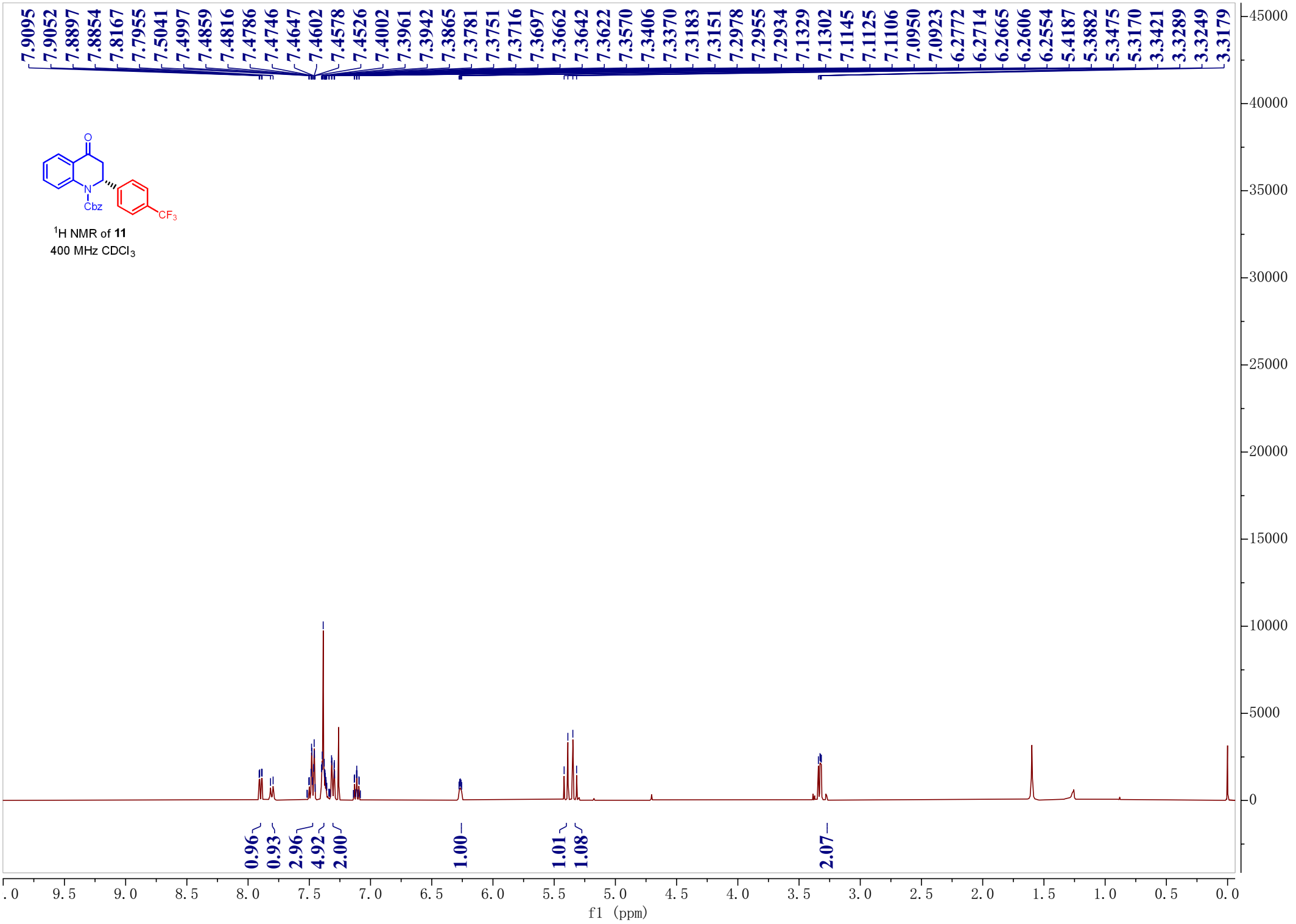
154.4675
141.6561
140.5659
140.3727
137.2111
135.7320
134.7587
128.8847
128.8598
128.6598
128.3386
127.5649
127.4639
127.1665
127.0884
125.2030
124.5718
124.3911
68.7149
56.1730
42.5387
O
N
Cbz
Ph
13C NMR of 8
101 MHz CDCl3
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

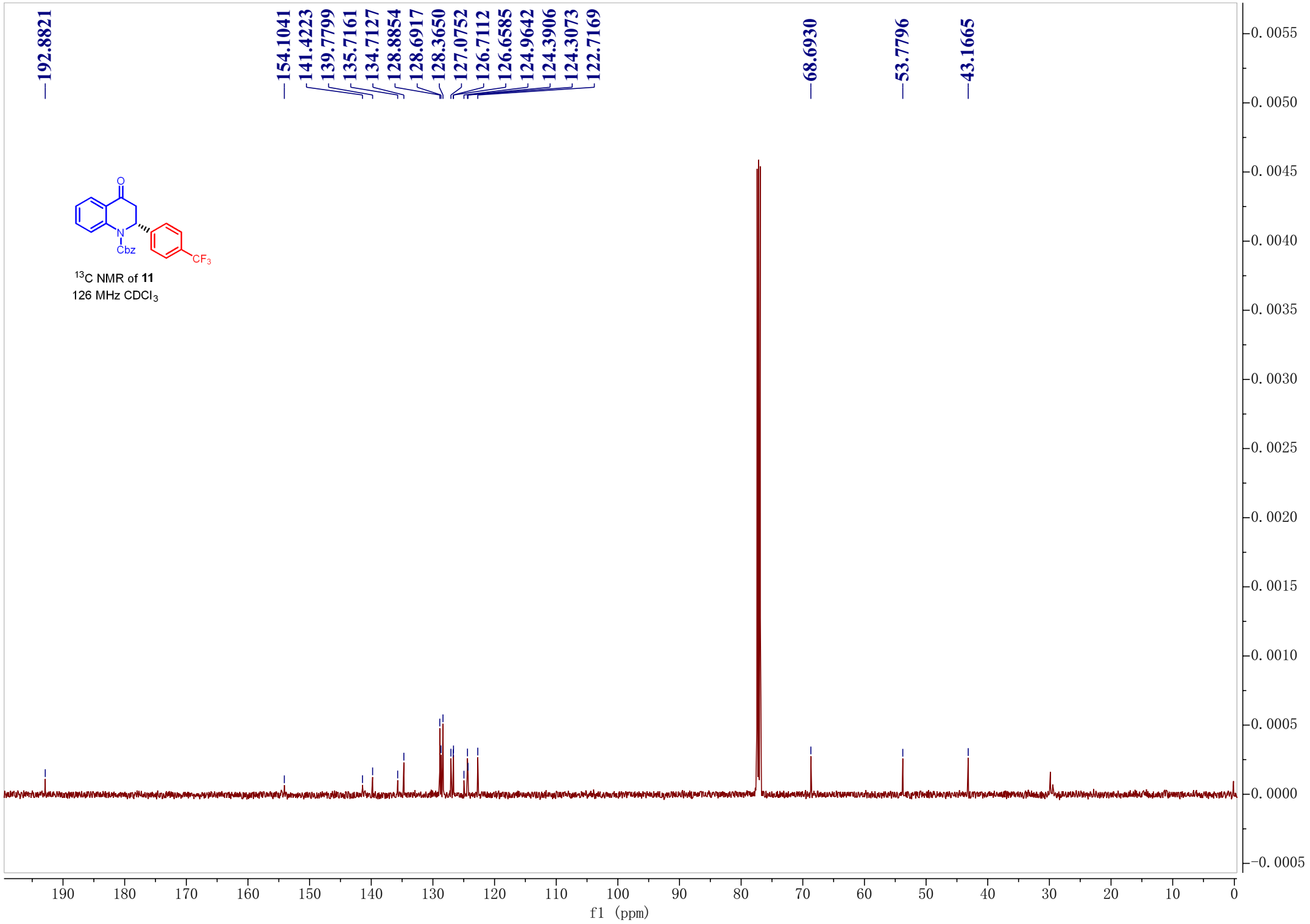

7.9047
7.9004
7.8851
7.8807
7.7769
7.7558
7.4832
7.4789
7.4651
7.4613
7.4579
7.4441
7.4396
7.4007
7.3980
7.3932
7.3868
7.3847
7.3823
7.3757
7.3723
7.3680
7.1861
7.1808
7.1700
7.1643
7.1584
7.1336
7.1316
7.1278
7.1256
7.1222
7.1202
7.1174
7.1113
7.1091
7.1056
7.1032
7.0998
7.0976
7.0823
7.0796
6.2074
6.2007
6.1976
6.1941
6.1875
5.4094
5.3788
5.3403
5.3097
3.2921
3.2792
3.2758
3.2688
O
N
Cbz
Cl
1H NMR of 9
400 MHz CDCl3
1.05
1.03
1.13
4.91
5.13
1.00
1.08
1.23
2.61
f1 (ppm)

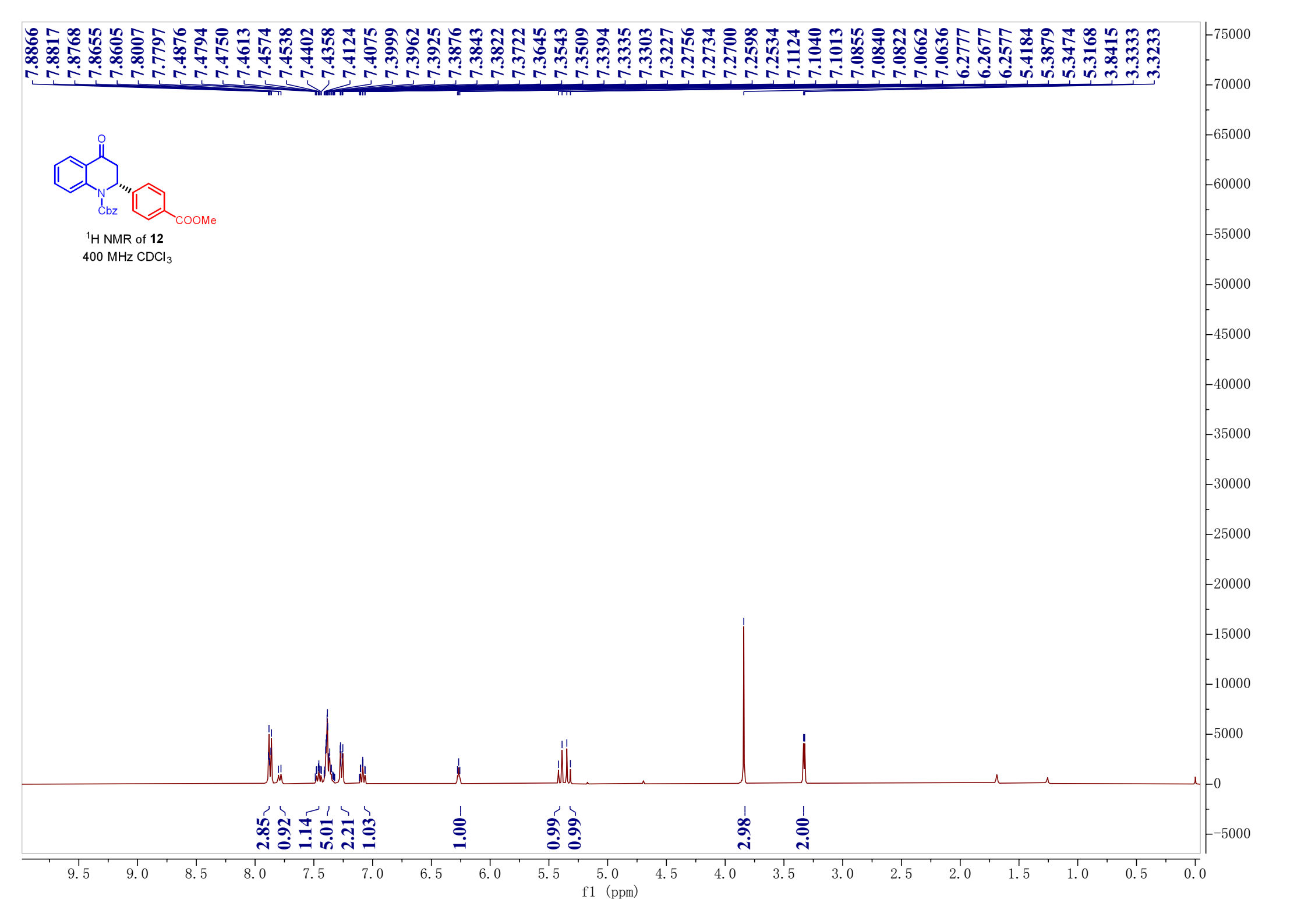

192.5029
154.3709
141.3631
136.8006
135.6042
134.8569
133.7267
128.9902
128.8867
128.7328
128.3675
128.1553
127.1121
125.0888
124.5590
68.8180
55.8582
42.3958
O
N
Cbz
Cl
13C NMR of 9
101 MHz CDCl3
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

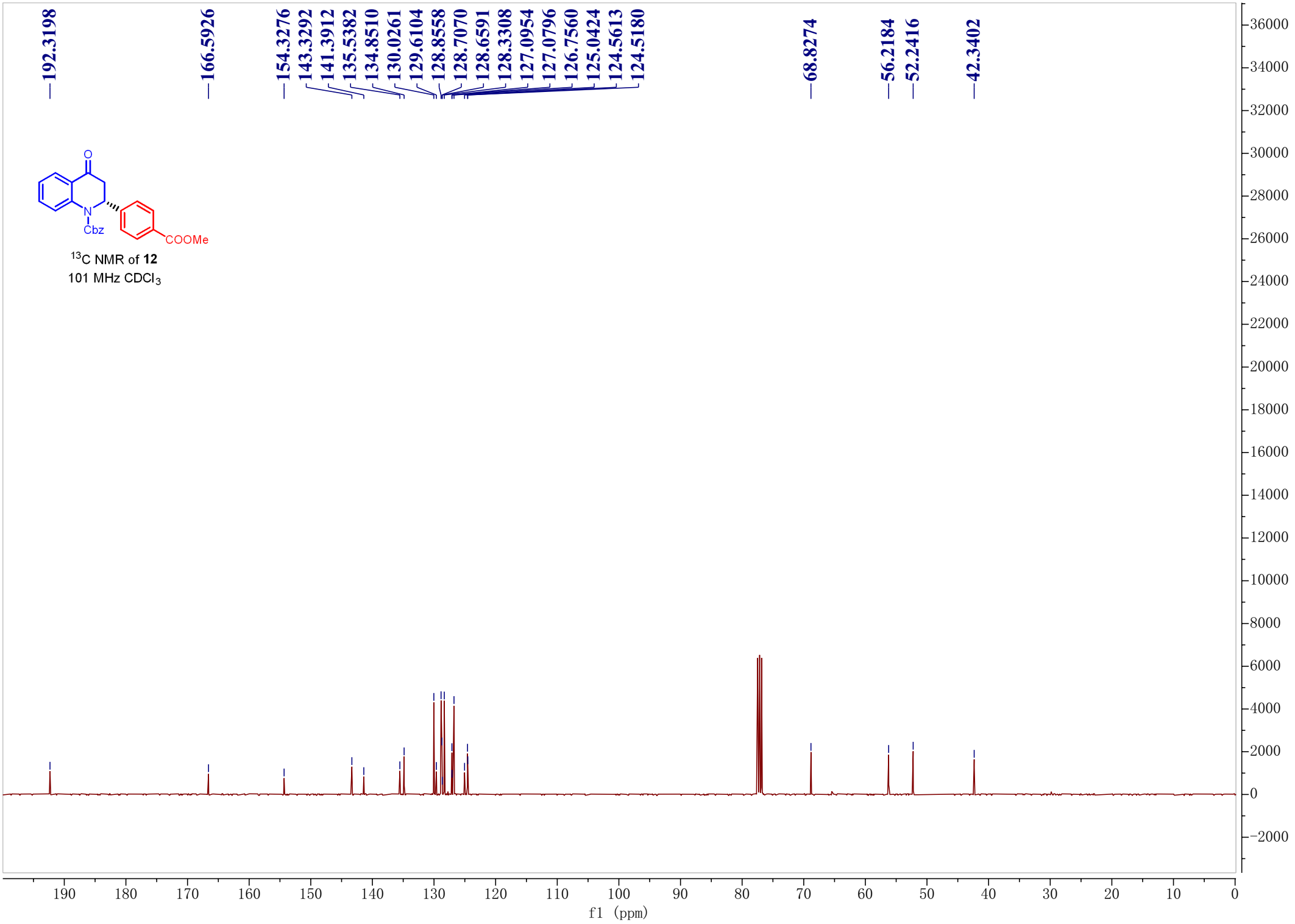

7.9124
7.9080
7.8928
7.8885
7.7752
7.7542
7.4798
7.4754
7.4616
7.4578
7.4542
7.4405
7.4362
7.4034
7.4000
7.3965
7.3913
7.3883
7.3862
7.3831
7.3757
7.3711
7.3675
7.1749
7.1726
7.1621
7.1597
7.1561
7.1527
7.1502
7.1395
7.1372
7.1181
7.1154
7.0997
7.0977
7.0958
7.0802
7.0776
6.9103
6.8887
6.8835
6.8670
6.2129
6.2097
6.2067
6.2035
5.4131
5.3825
5.3421
5.3116
3.2942
3.2813
3.2789
3.2719
O
N
Cbz
F
1H NMR of 10
400 MHz CDCl3
0.91
0.92
1.02
4.47
2.84
1.83
1.00
0.95
0.97
1.99
f1 (ppm)

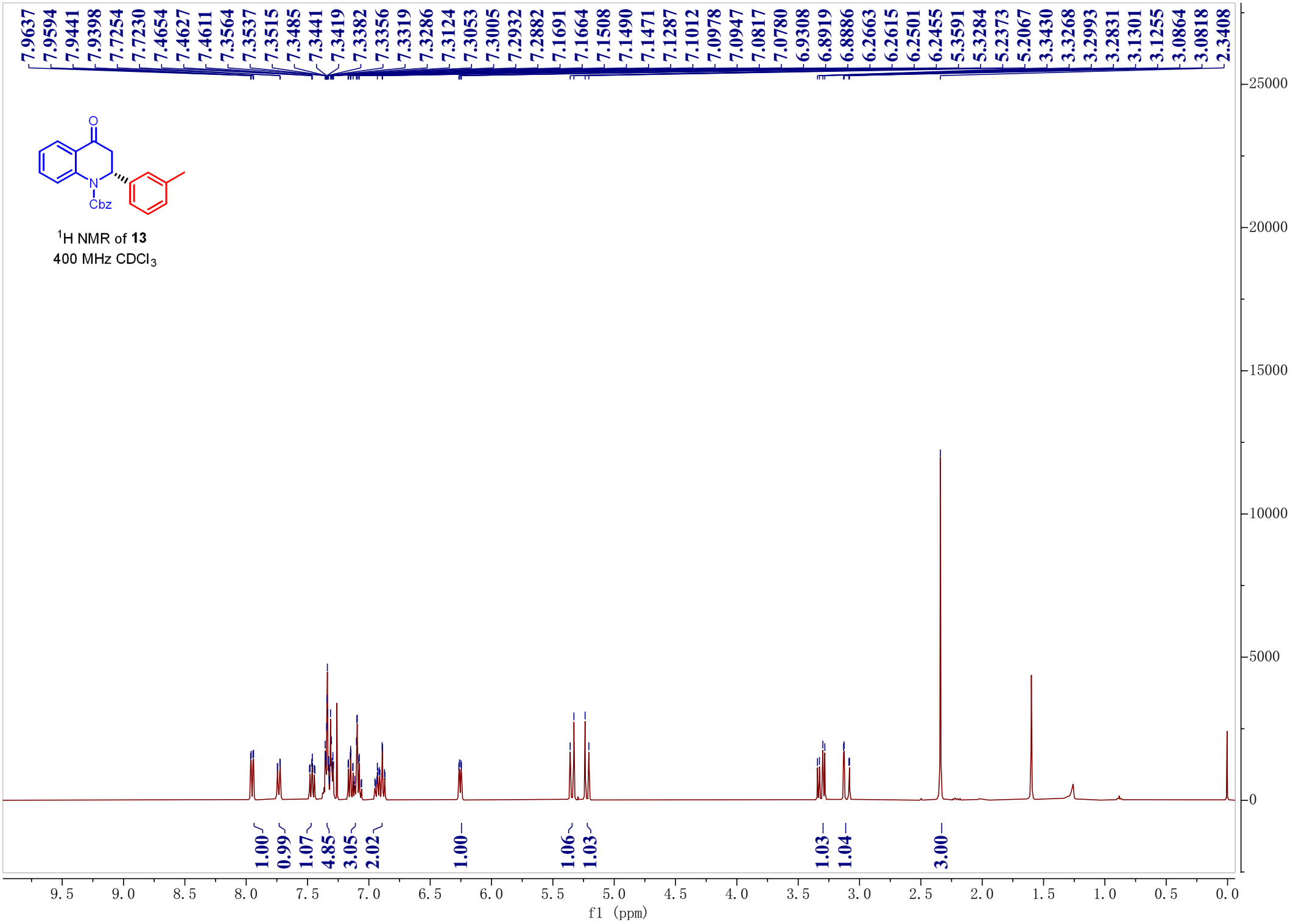

192.6700
163.4077
160.9530
154.3831
141.3826
135.6408
134.8092
134.0357
134.0032
128.8735
128.7065
128.5219
128.4405
128.3529
127.0586
125.1198
124.5677
124.4985
115.8327
115.6182
68.7671
55.8109
42.5584
O
N
Cbz
F
13C NMR of 10
101 MHz CDCl3
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9095
7.9052
7.8897
7.8854
7.8167
7.7955
7.5041
7.4997
7.4859
7.4816
7.4786
7.4746
7.4647
7.4602
7.4578
7.4526
7.4002
7.3961
7.3942
7.3865
7.3781
7.3751
7.3716
7.3697
7.3662
7.3642
7.3622
7.3570
7.3406
7.3370
7.3183
7.3151
7.2978
7.2955
7.2934
7.1329
7.1302
7.1145
7.1125
7.1106
7.0950
7.0923
6.2772
6.2714
6.2665
6.2606
6.2554
5.4187
5.3882
5.3475
5.3170
3.3421
3.3289
3.3249
3.3179
O
N
Cbz
CF3
1H NMR of 11
400 MHz CDCl3
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0.96
0.93
2.96
4.92
2.00
1.00
1.01
1.08
2.07
.0
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
f1 (ppm)

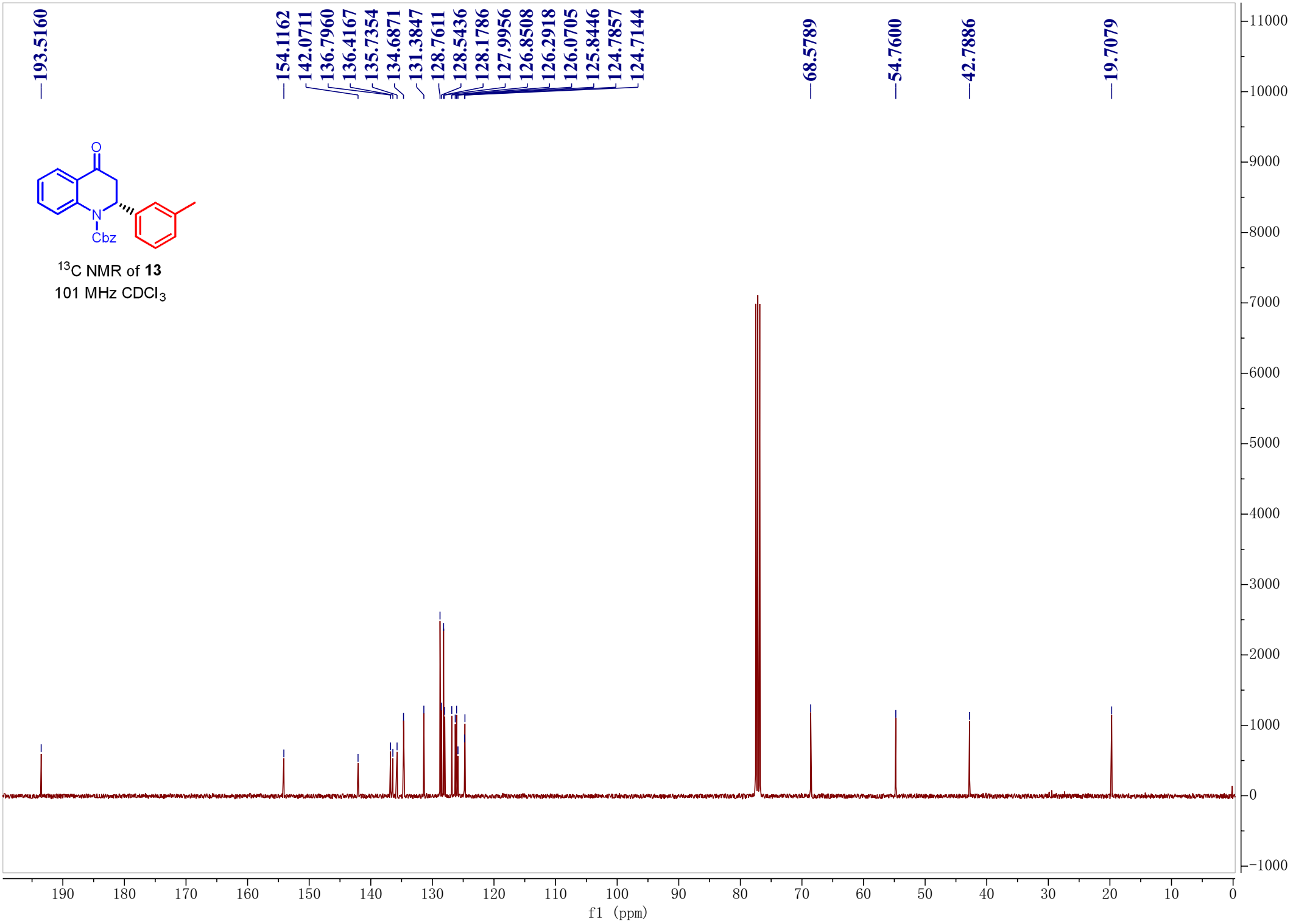

192.8821
154.1041
141.4223
139.7799
135.7161
134.7127
128.8854
128.6917
128.3650
127.0752
126.7112
126.6585
124.9642
124.3906
124.3073
122.7169
68.6930
53.7796
43.1665
O
N
Cbz
CF3
13C NMR of 11
126 MHz CDCl3
0.0055
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
−0.0005
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

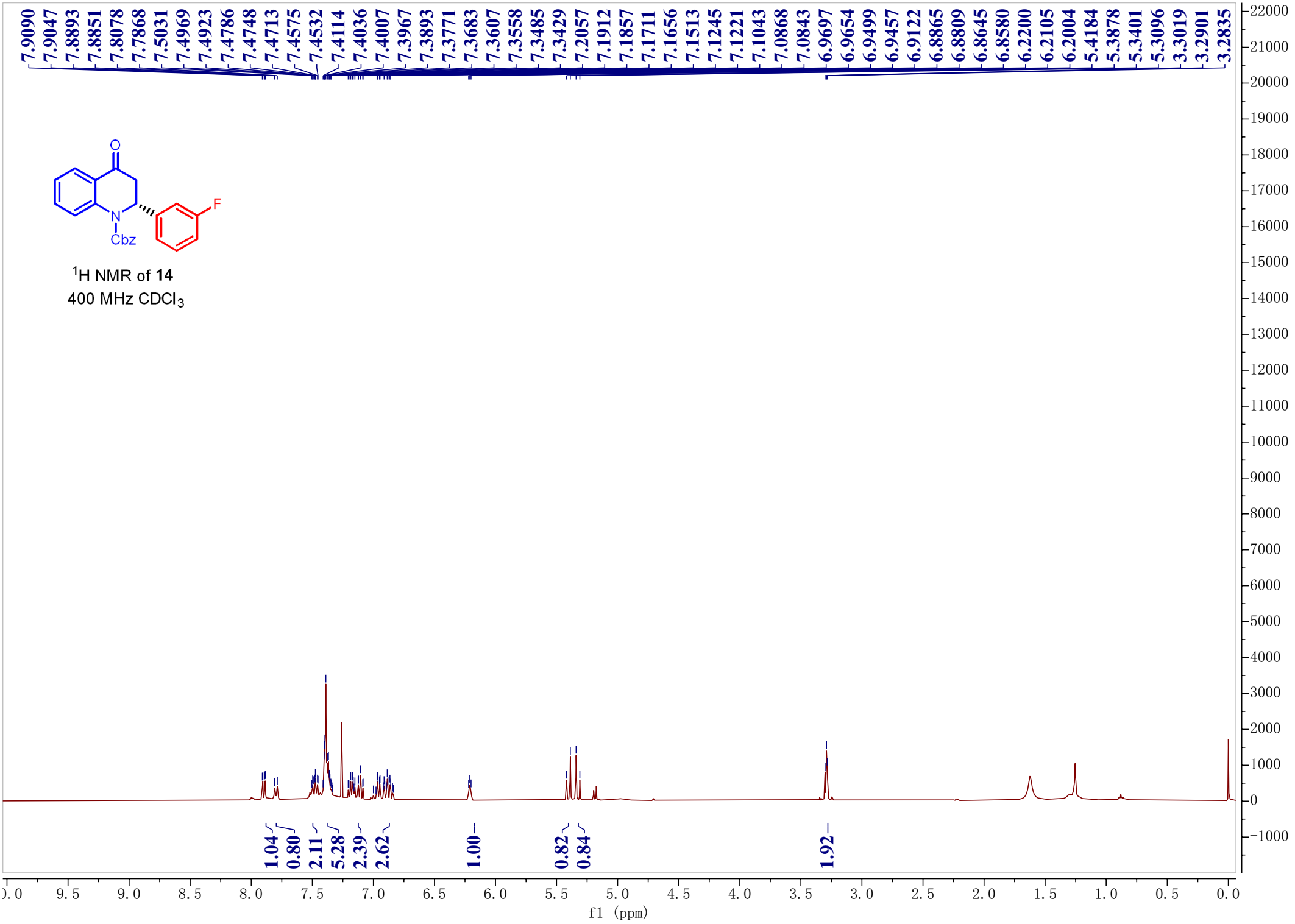

7.8866
7.8817
7.8768
7.8655
7.8605
7.8007
7.7797
7.4876
7.4794
7.4750
7.4613
7.4574
7.4538
7.4402
7.4358
7.4124
7.4075
7.3999
7.3962
7.3925
7.3876
7.3843
7.3822
7.3722
7.3645
7.3543
7.3509
7.3394
7.3335
7.3303
7.3227
7.2756
7.2734
7.2700
7.2598
7.2534
7.1124
7.1040
7.1013
7.0855
7.0840
7.0822
7.0662
7.0636
6.2777
6.2677
6.2577
5.4184
5.3879
5.3474
5.3168
3.8415
3.3333
3.3233
O
N
Cbz
COOMe
1H NMR of 12
400 MHz CDCl3
2.85
0.92
1.14
5.01
2.21
1.03
1.00
0.99
0.99
2.98
2.00
f1 (ppm)

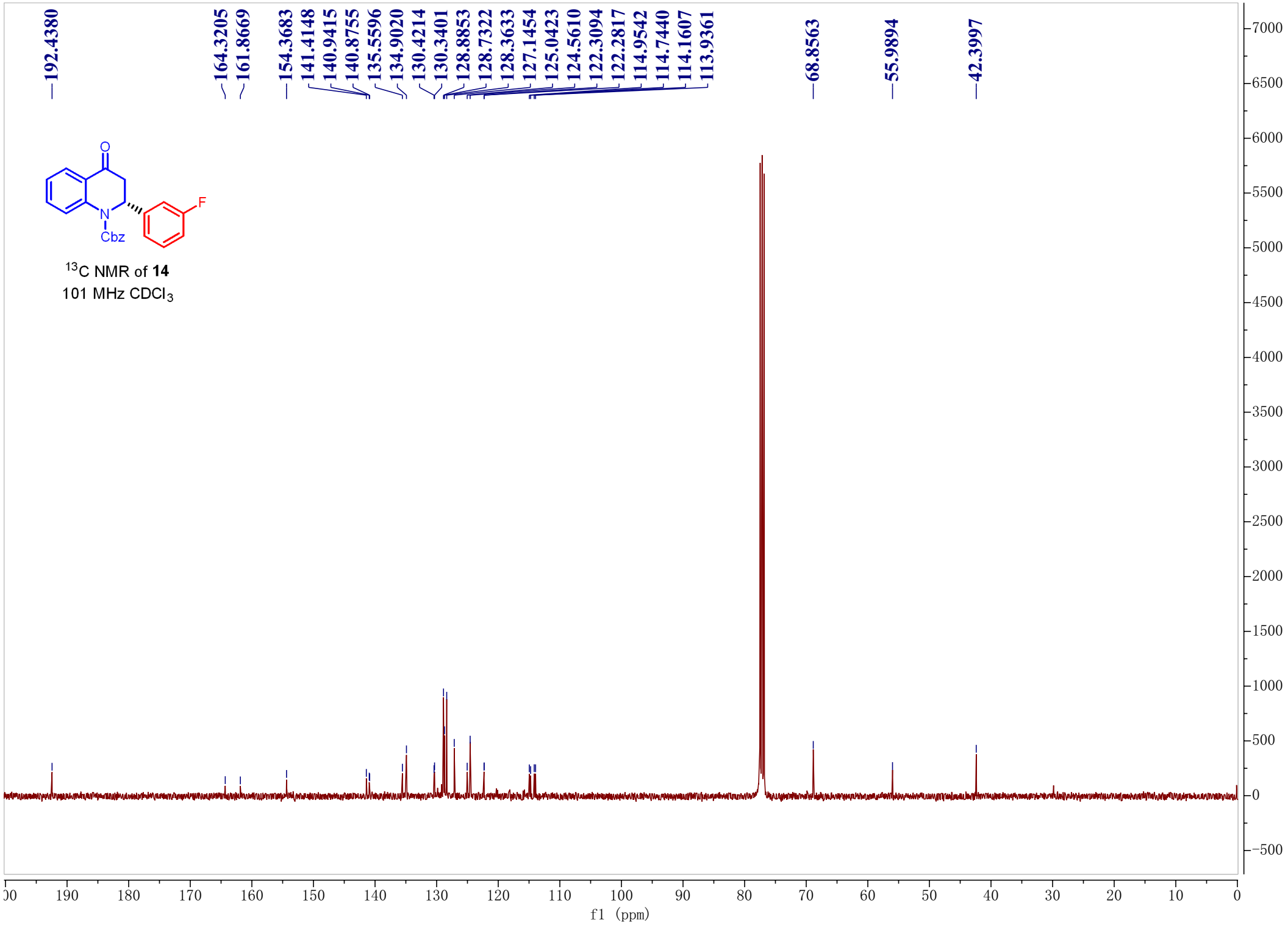

192.3198
166.5926
154.3276
143.3292
141.3912
135.5382
134.8510
130.0261
129.6104
128.8558
128.7070
128.6591
128.3308
127.0954
127.0796
126.7560
125.0424
124.5613
124.5180
68.8274
56.2184
52.2416
42.3402
O
N
Cbz
COOMe
13C NMR of 12
101 MHz CDCl3
f1 (ppm)

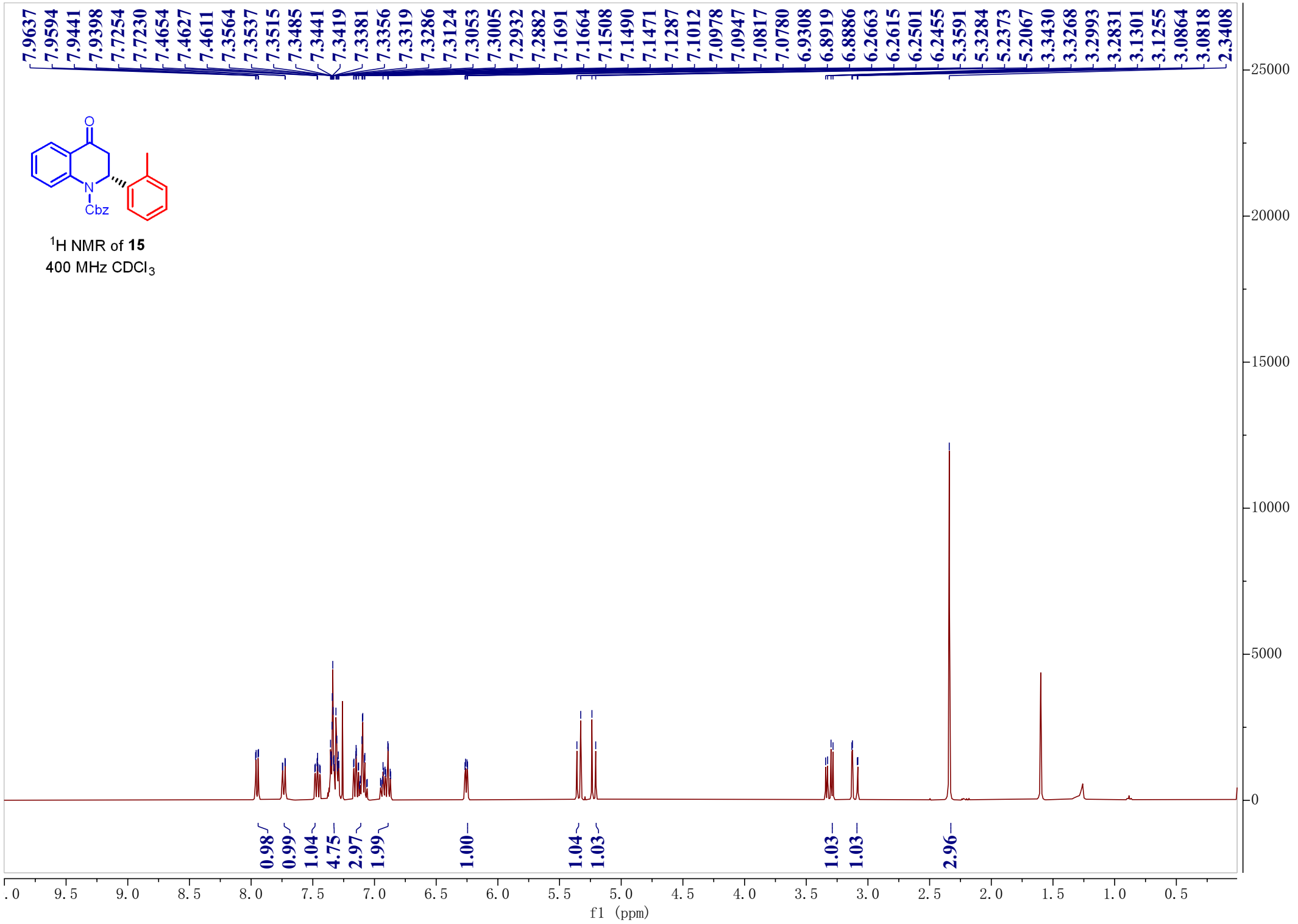


^{1}H NMR of **13**
400 MHz $CDCl_3$

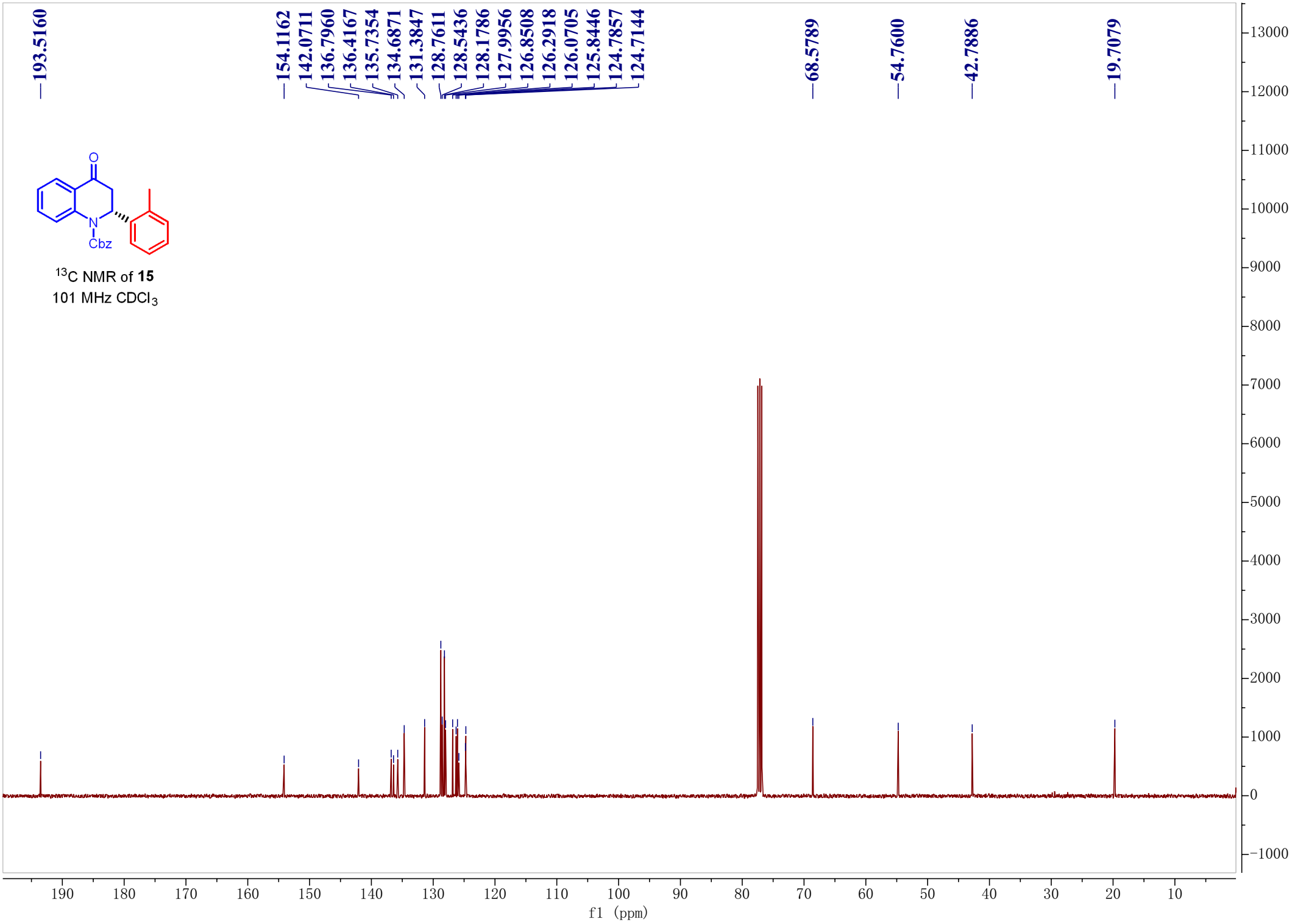

193.5160
154.1162
142.0711
136.7960
136.4167
135.7354
134.6871
131.3847
128.7611
128.5436
128.1786
127.9956
126.8508
126.2918
126.0705
125.8446
124.7857
124.7144
68.5789
54.7600
42.7886
19.7079
O
N
Cbz
13C NMR of 13
101 MHz CDCl3
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9090
7.9047
7.8893
7.8851
7.8078
7.7868
7.5031
7.4969
7.4923
7.4786
7.4748
7.4713
7.4575
7.4532
7.4114
7.4036
7.4007
7.3967
7.3893
7.3771
7.3683
7.3607
7.3558
7.3485
7.3429
7.2057
7.1912
7.1857
7.1711
7.1656
7.1513
7.1245
7.1221
7.1043
7.0868
7.0843
6.9697
6.9654
6.9499
6.9457
6.9122
6.8865
6.8809
6.8645
6.8580
6.2200
6.2105
6.2004
5.4184
5.3878
5.3401
5.3096
3.3019
3.2901
3.2835
O
N
Cbz
F
1H NMR of 14
400 MHz CDCl3
1.04
0.80
2.11
5.28
2.39
2.62
1.00
0.82
0.84
1.92
f1 (ppm)

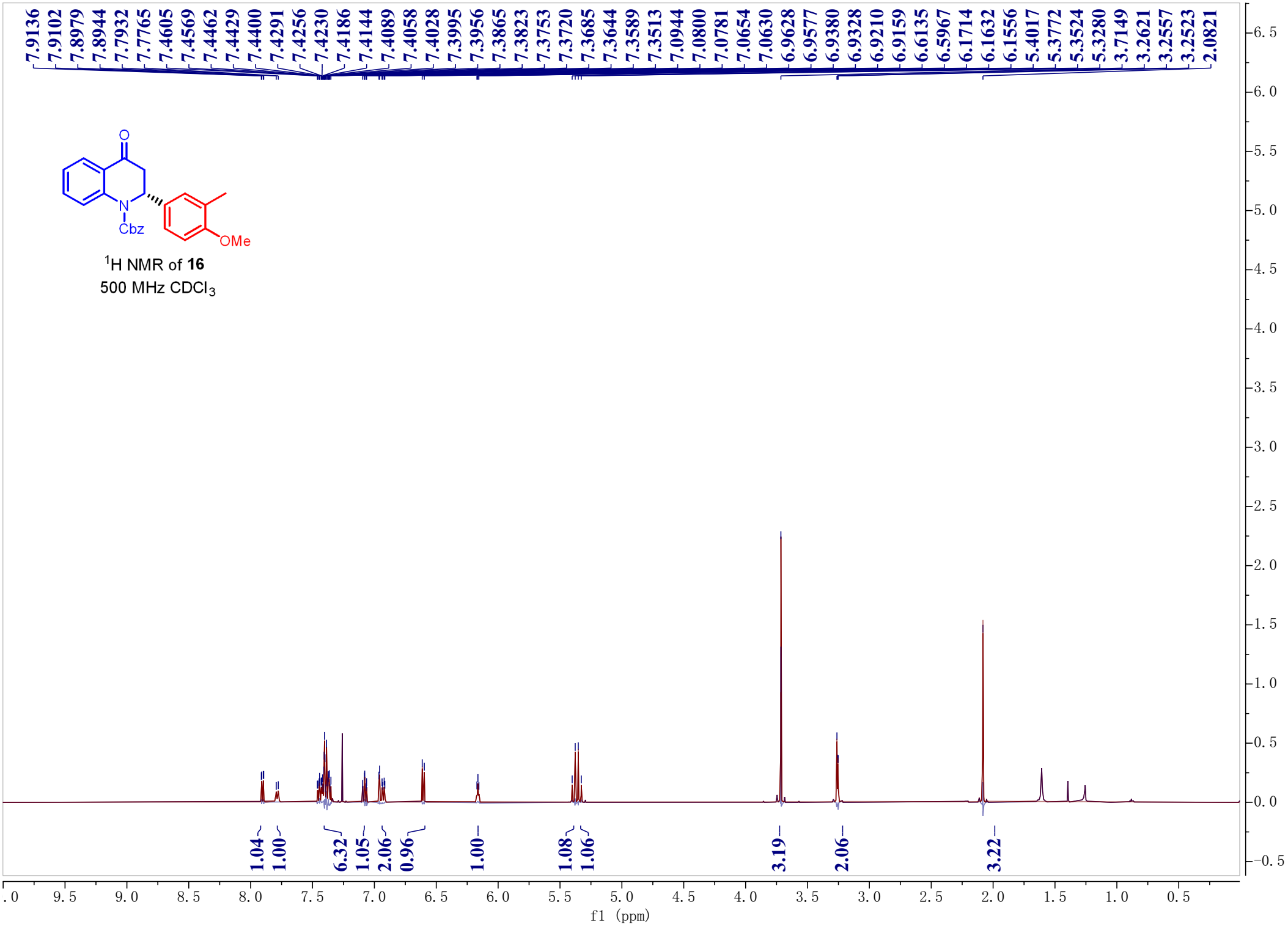

192.4380
164.3205
161.8669
154.3683
141.4148
140.9415
140.8755
135.5596
134.9020
130.4214
130.3401
128.8853
128.7322
128.3633
127.1454
125.0423
124.5610
122.3094
122.2817
114.9542
114.7440
114.1607
113.9361
68.8563
55.9894
42.3997
O
N
Cbz
F
13C NMR of 14
101 MHz CDCl3
f1 (ppm)



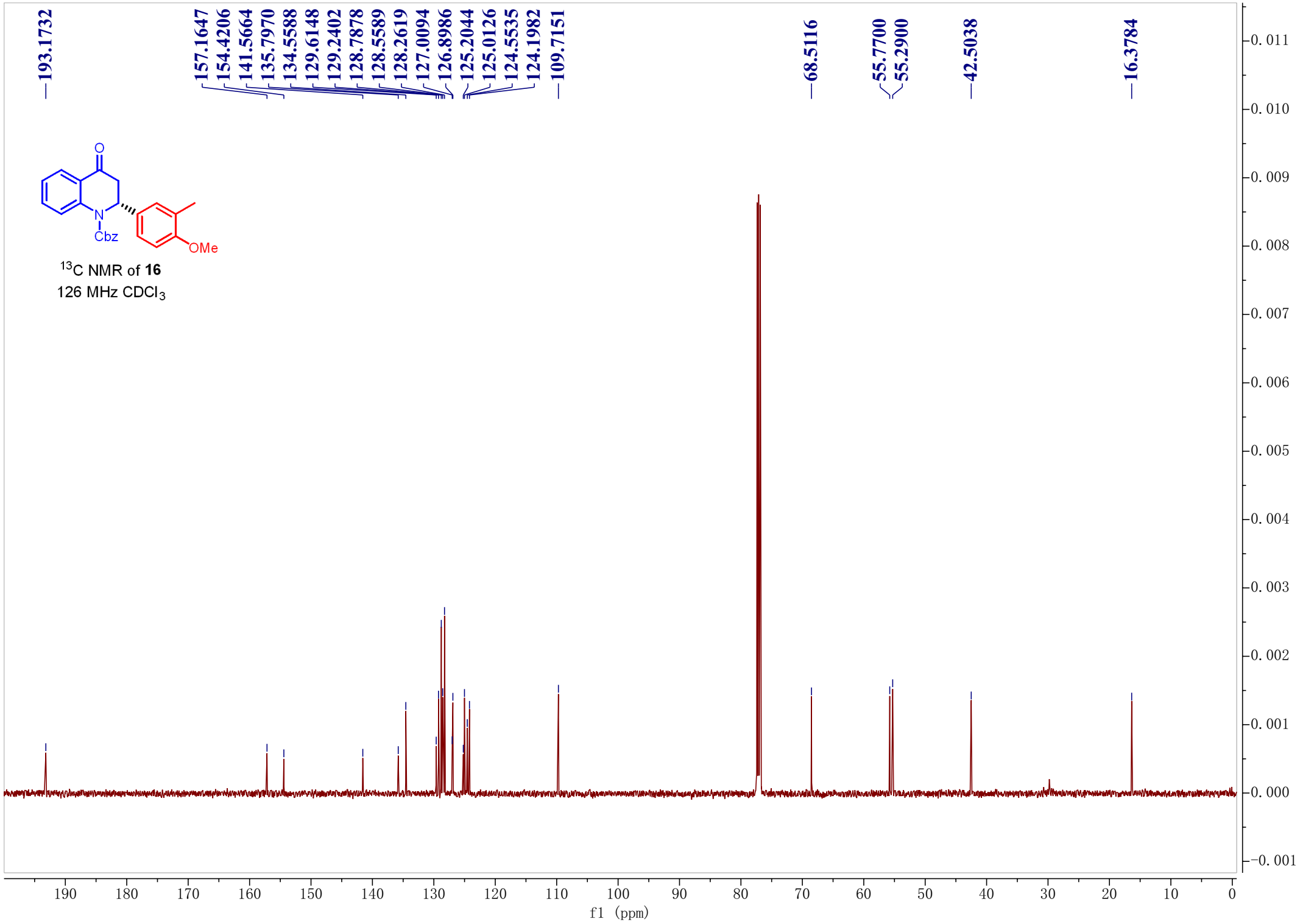
^{1}H NMR of **15**
400 MHz $CDCl_3$

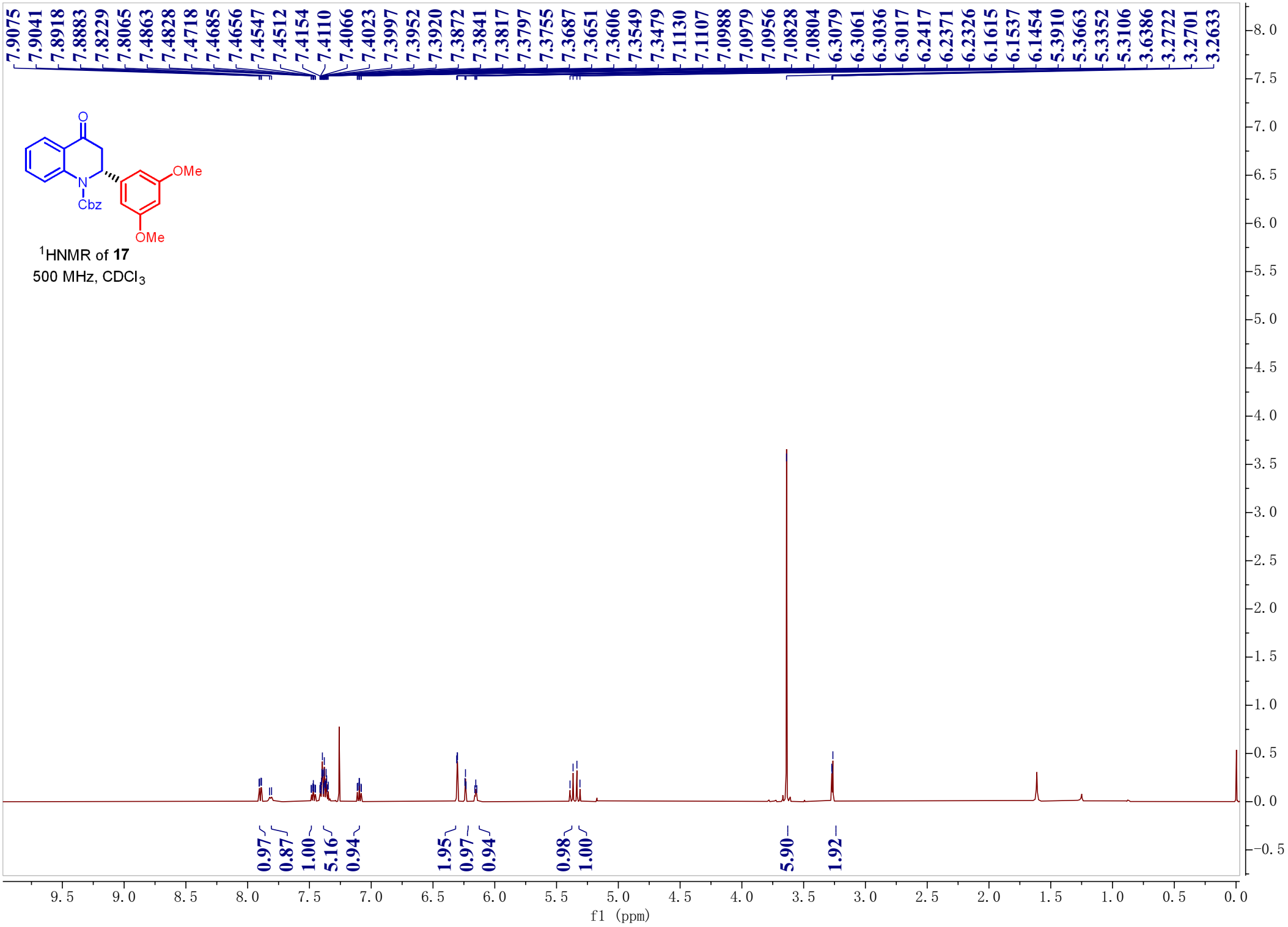


^{13}C NMR of **15**
101 MHz $CDCl_3$



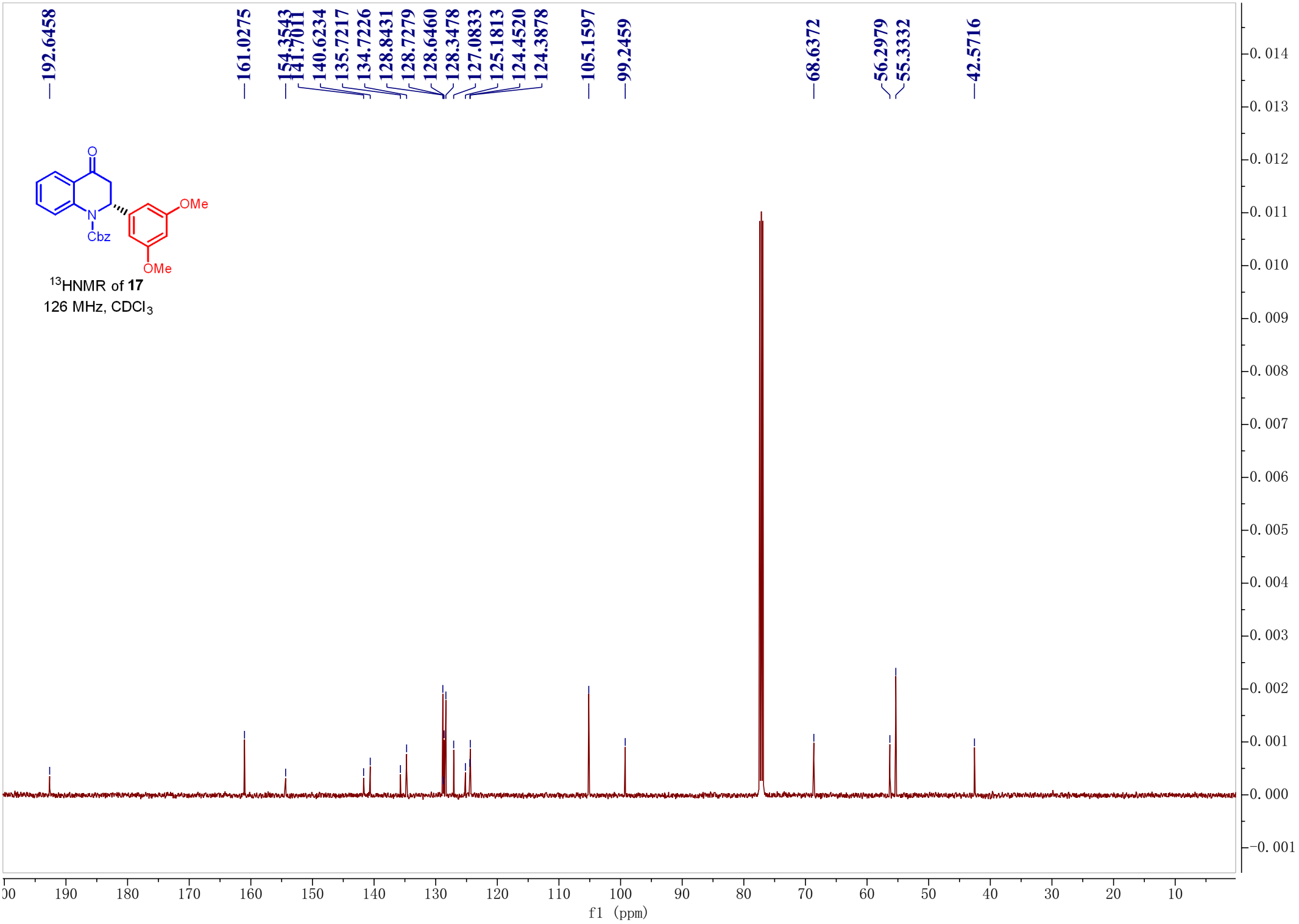
^{1}H NMR of **16**
500 MHz $CDCl_3$

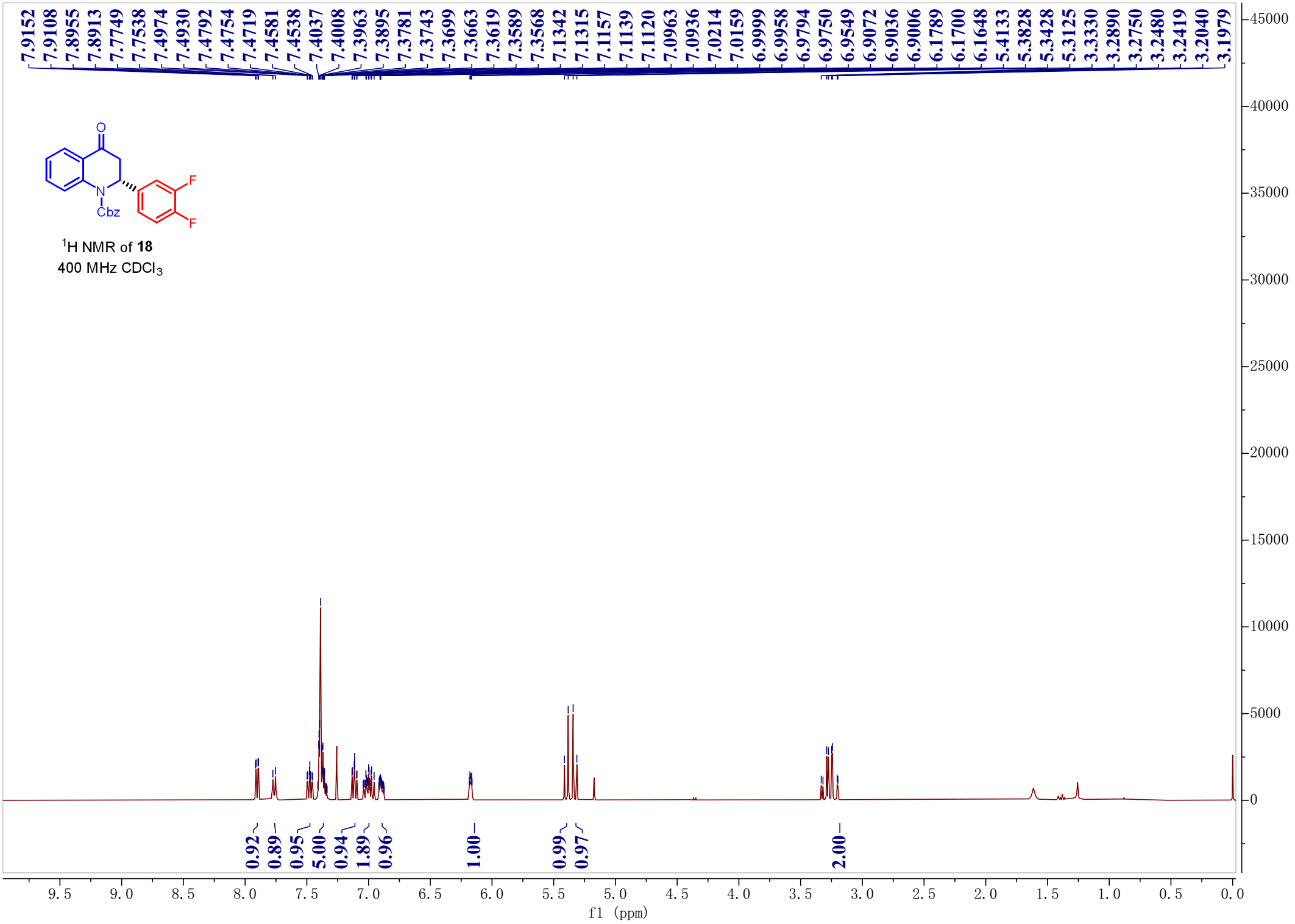

193.1732
157.1647
154.4206
141.5664
135.7970
134.5588
129.6148
129.2402
128.7878
128.5589
128.2619
127.0094
126.8986
125.2044
125.0126
124.5535
124.1982
109.7151
68.5116
55.7700
55.2900
42.5038
16.3784
O
N
Cbz
OMe
13C NMR of 16
126 MHz CDCl3
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

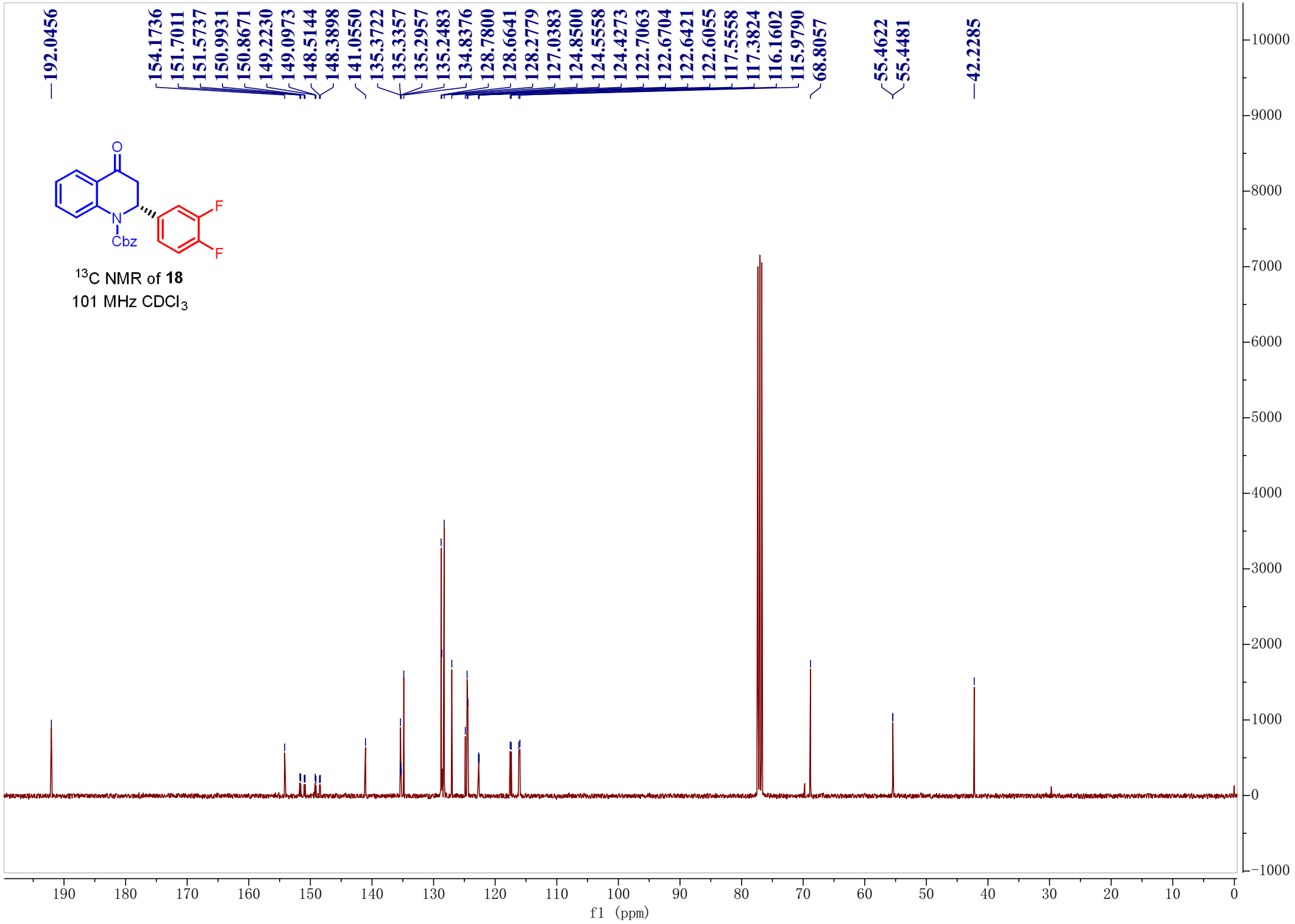


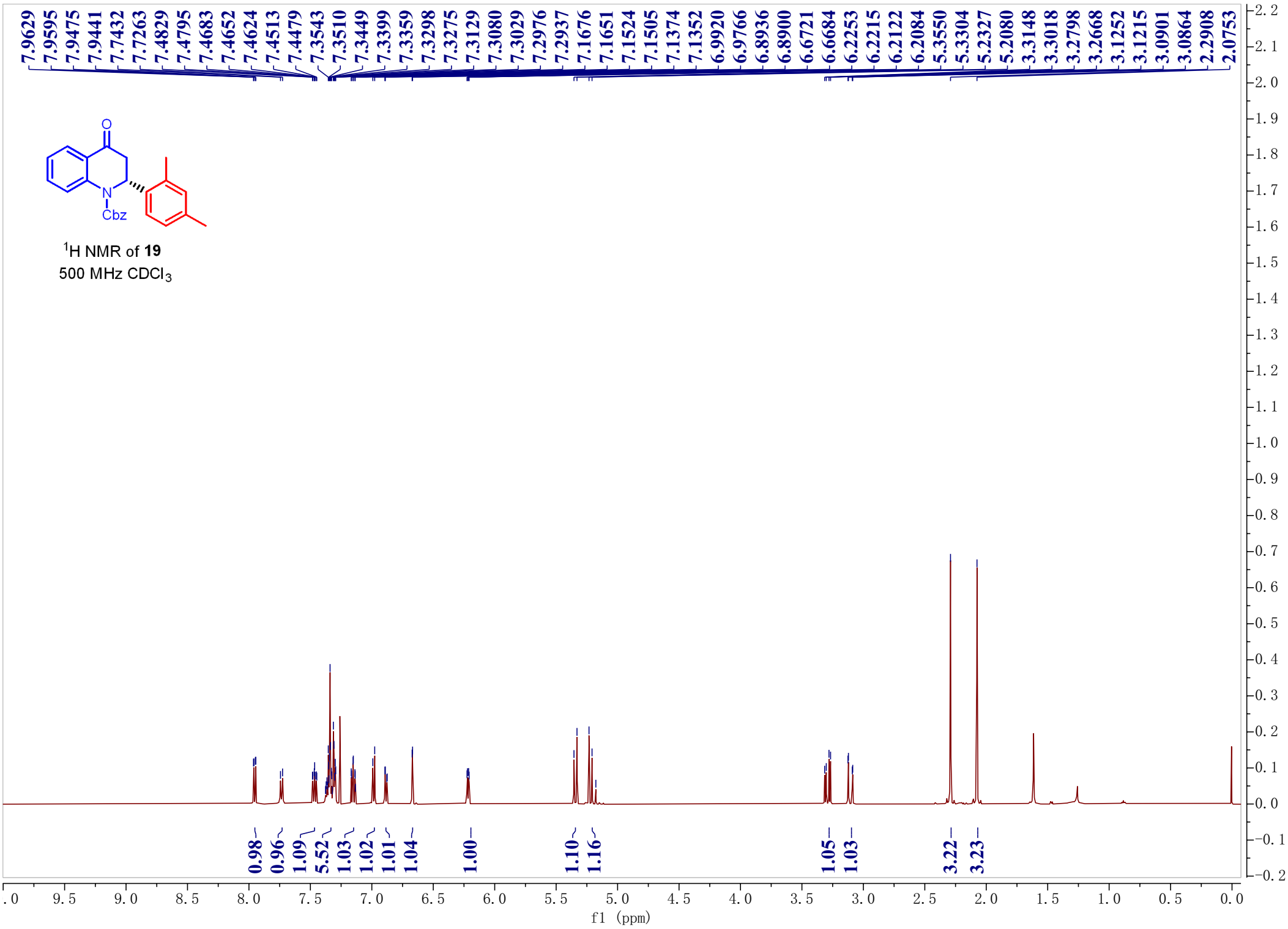
^{1}HNMR of **17**

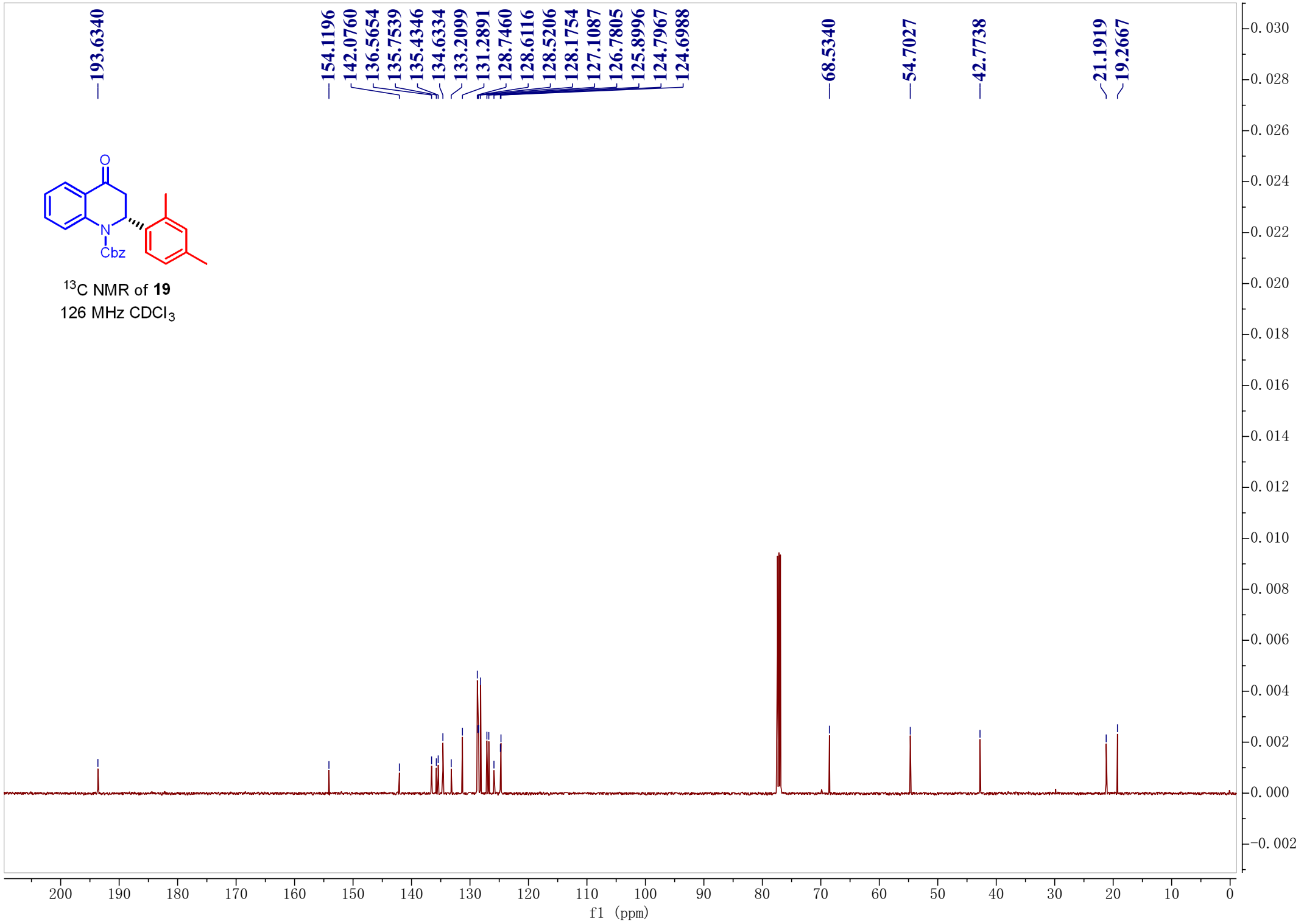
500 MHz, $CDCl_3$


192.6458
161.0275
154.3543
141.7011
140.6234
135.7217
134.7226
128.8431
128.7279
128.6460
128.3478
127.0833
125.1813
124.4520
124.3878
105.1597
99.2459
68.6372
56.2979
55.3332
42.5716
O
N
Cbz
OMe
OMe
13HNMR of 17
126 MHz, CDCl3
0.014
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
−0.001
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

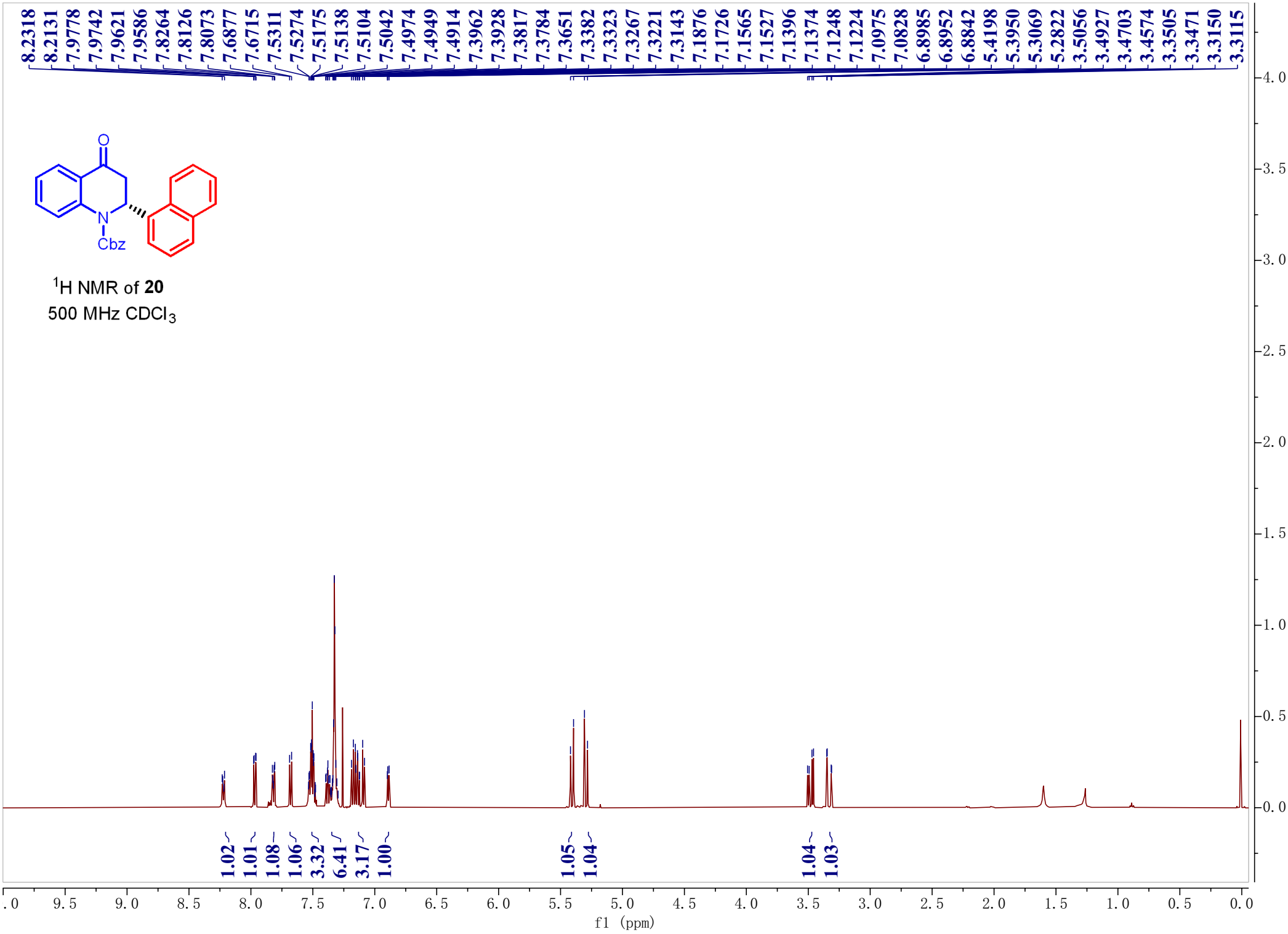

7.9152
7.9108
7.8955
7.8913
7.7749
7.7538
7.4974
7.4930
7.4792
7.4754
7.4719
7.4581
7.4538
7.4037
7.4008
7.3963
7.3895
7.3781
7.3743
7.3699
7.3663
7.3619
7.3589
7.3568
7.1342
7.1315
7.1157
7.1139
7.1120
7.0963
7.0936
7.0214
7.0159
6.9999
6.9958
6.9794
6.9750
6.9549
6.9072
6.9036
6.9006
6.1789
6.1700
6.1648
5.4133
5.3828
5.3428
5.3125
3.3330
3.2890
3.2750
3.2480
3.2419
3.2040
3.1979
O
N
Cbz
F
F
1H NMR of 18
400 MHz CDCl3
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
0.92
0.89
0.95
5.00
0.94
1.89
0.96
1.00
0.99
0.97
2.00
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
f1 (ppm)


192.0456
154.1736
151.7011
151.5737
150.9931
150.8671
149.2230
149.0973
148.5144
148.3898
141.0550
135.3722
135.3357
135.2957
135.2483
134.8376
128.7800
128.6641
128.2779
127.0383
124.8500
124.5558
124.4273
122.7063
122.6704
122.6421
122.6055
117.5558
117.3824
116.1602
115.9790
68.8057
55.4622
55.4481
42.2285
O
N
Cbz
F
F
13C NMR of 18
101 MHz CDCl3
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9629
7.9595
7.9475
7.9441
7.7432
7.7263
7.4829
7.4795
7.4683
7.4652
7.4624
7.4513
7.4479
7.3543
7.3510
7.3449
7.3399
7.3359
7.3298
7.3275
7.3129
7.3080
7.3029
7.2976
7.2937
7.1676
7.1651
7.1524
7.1505
7.1374
7.1352
6.9920
6.9766
6.8936
6.8900
6.6721
6.6684
6.2253
6.2215
6.2122
6.2084
5.3550
5.3304
5.2327
5.2080
3.3148
3.3018
3.2798
3.2668
3.1252
3.1215
3.0901
3.0864
2.2908
2.0753
O
N
Cbz
1H NMR of 19
500 MHz CDCl3
0.98
0.96
1.09
5.52
1.03
1.02
1.01
1.04
1.00
1.10
1.16
1.05
1.03
3.22
3.23
f1 (ppm)

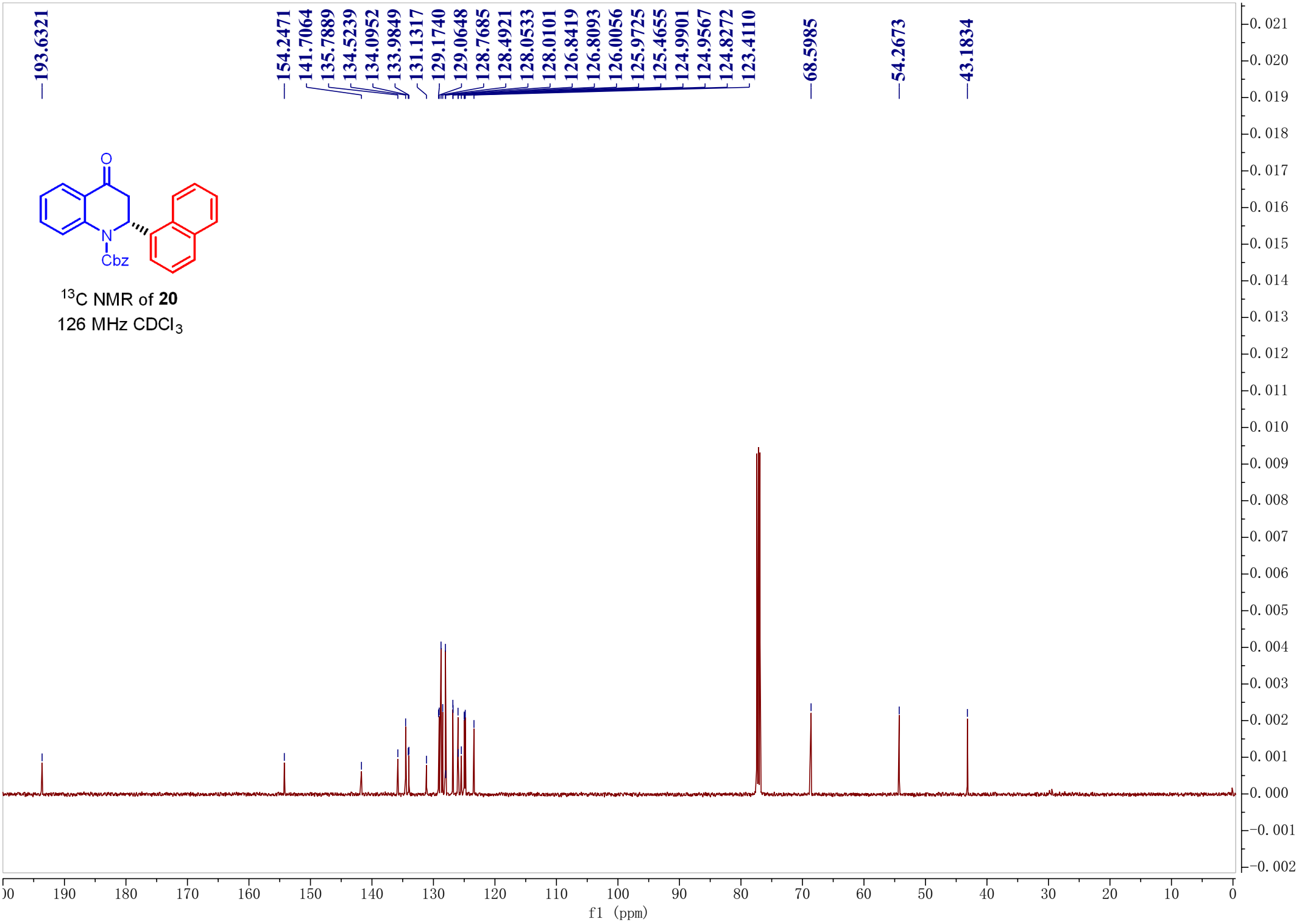


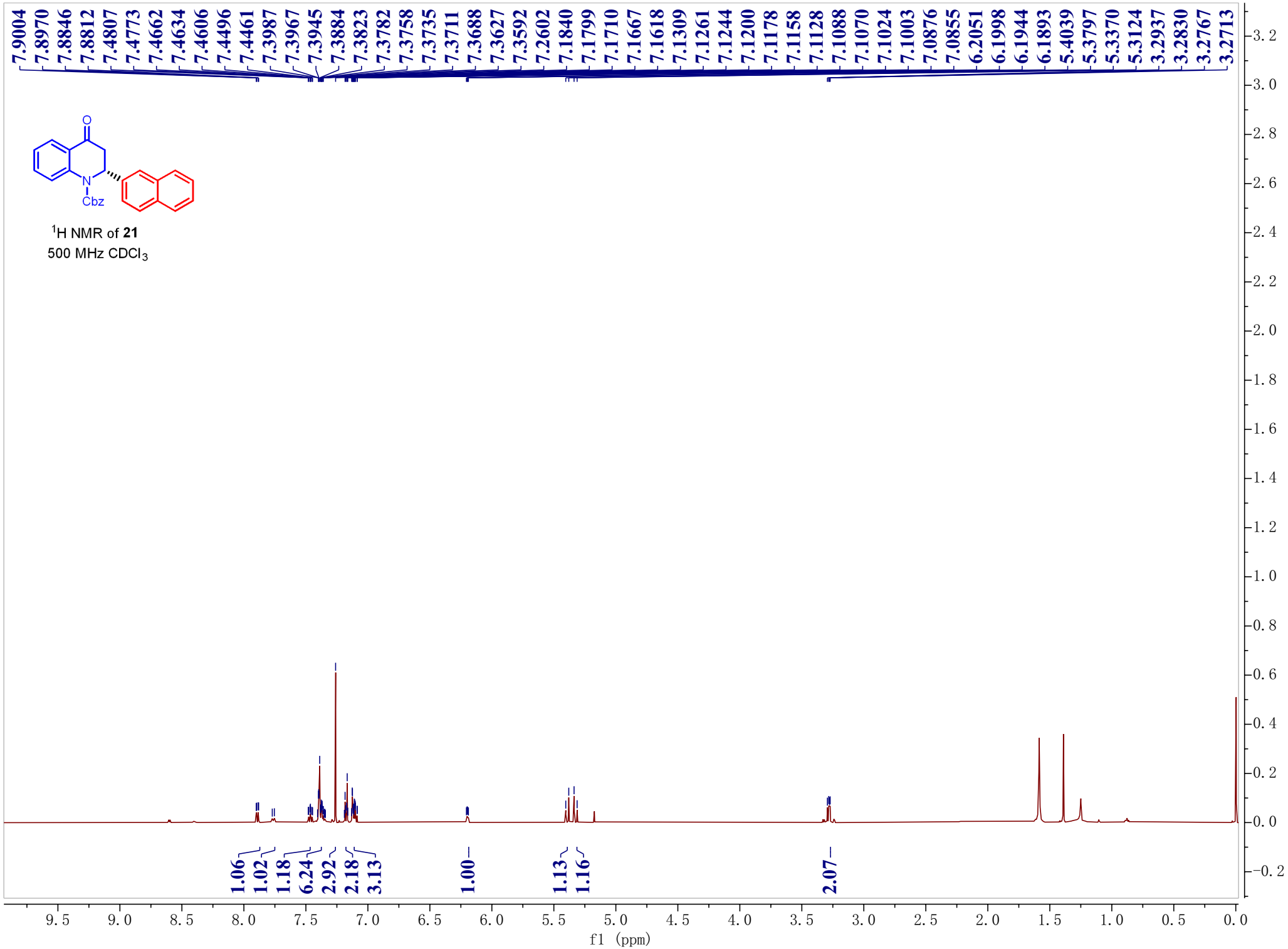
^{13}C NMR of **19**
126 MHz $CDCl_3$



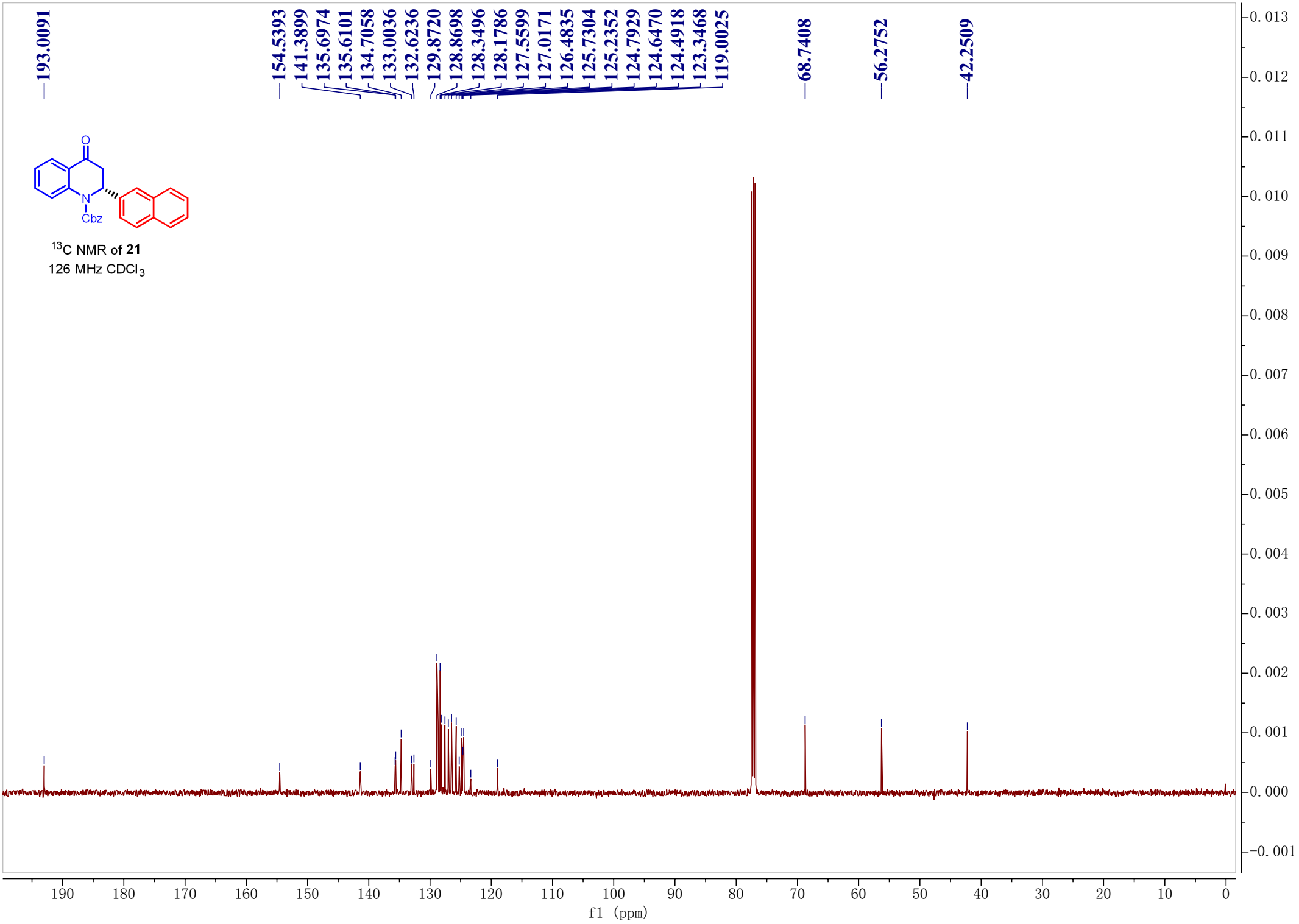
^{1}H NMR of **20**

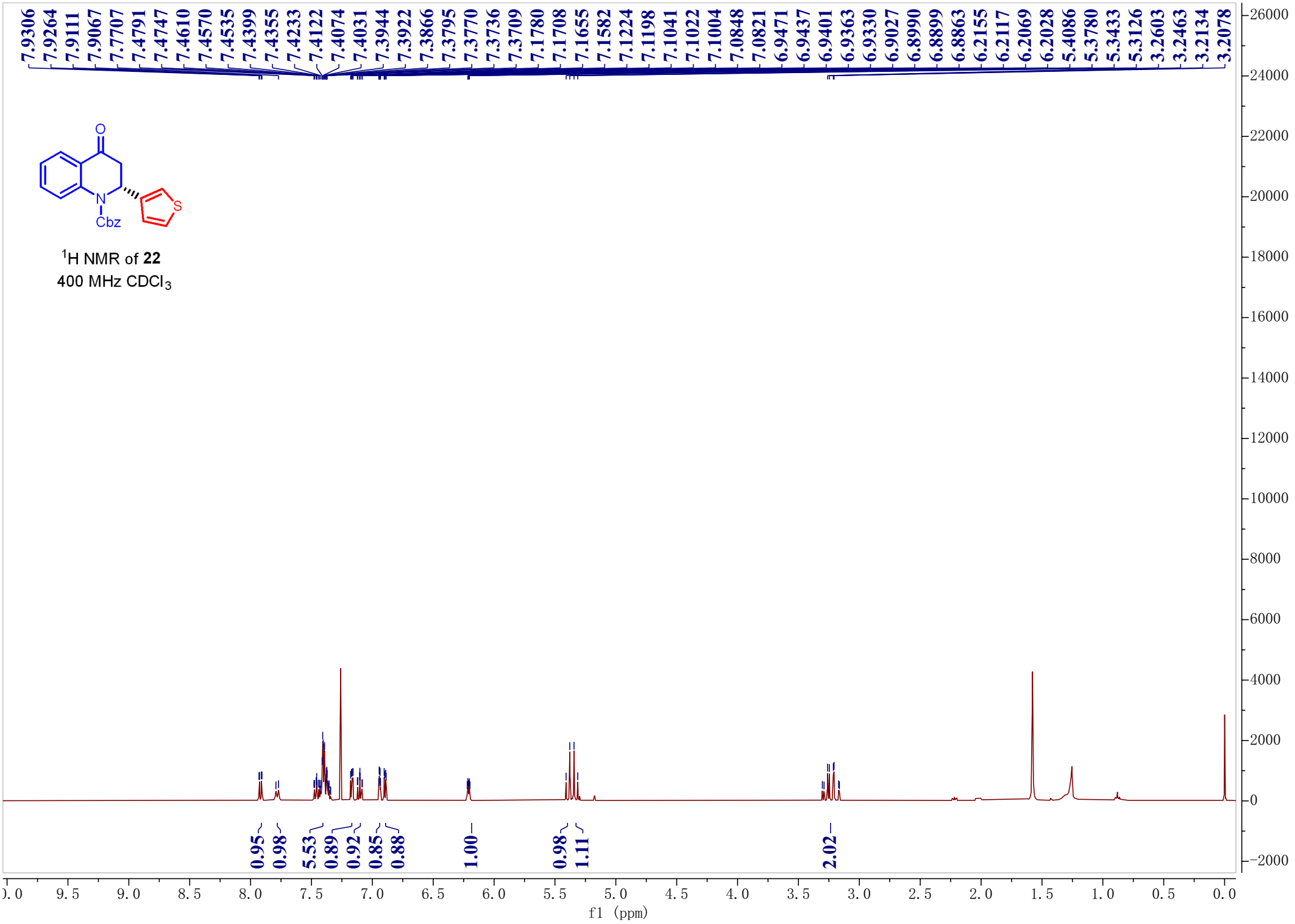
500 MHz $CDCl_3$


193.6321
154.2471
141.7064
135.7889
134.5239
134.0952
133.9849
131.1317
129.1740
129.0648
128.7685
128.4921
128.0533
128.0101
126.8419
126.8093
126.0056
125.9725
125.4655
124.9901
124.9567
124.8272
123.4110
68.5985
54.2673
43.1834
O
N
Cbz
13C NMR of 20
126 MHz CDCl3
f1 (ppm)

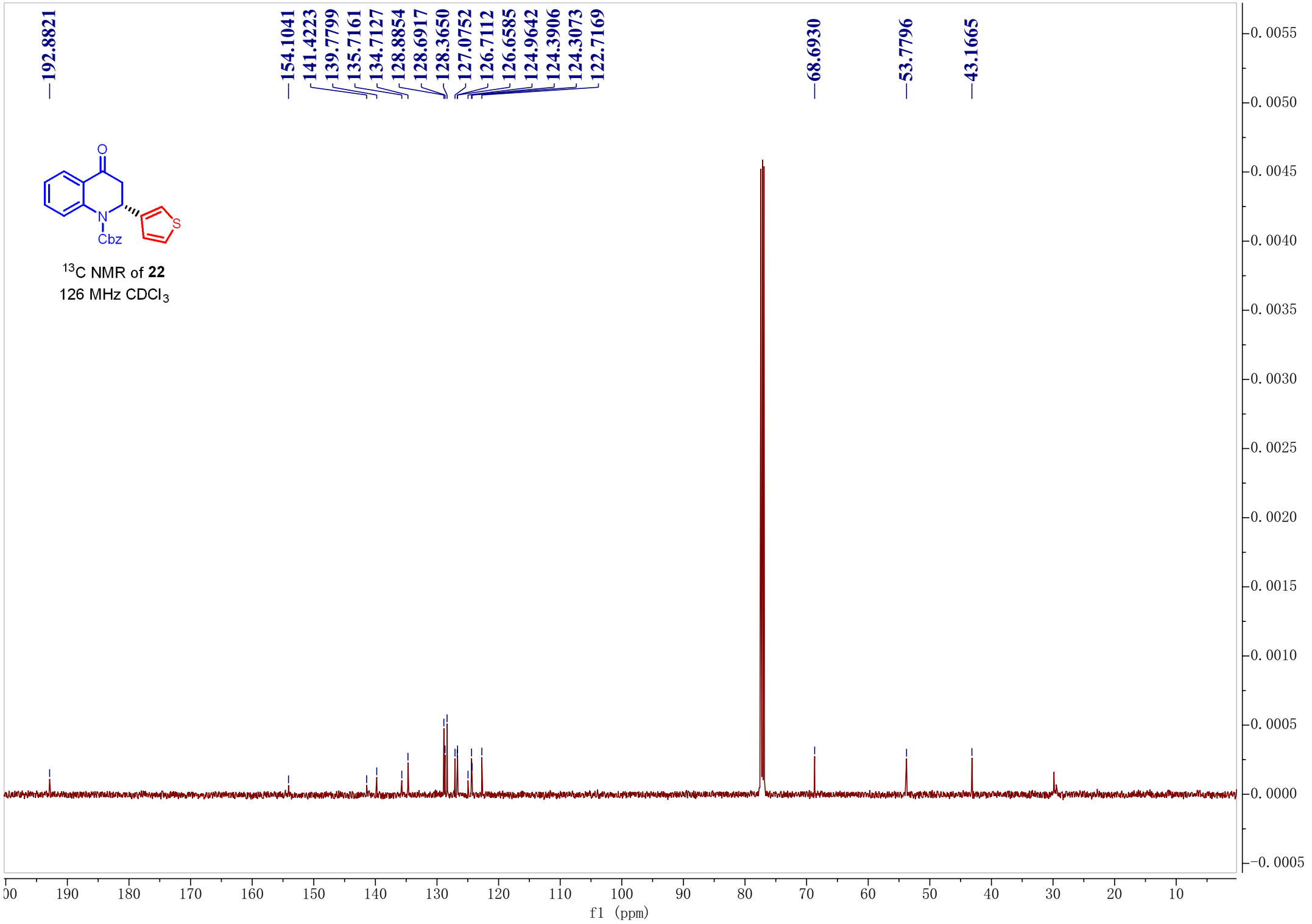


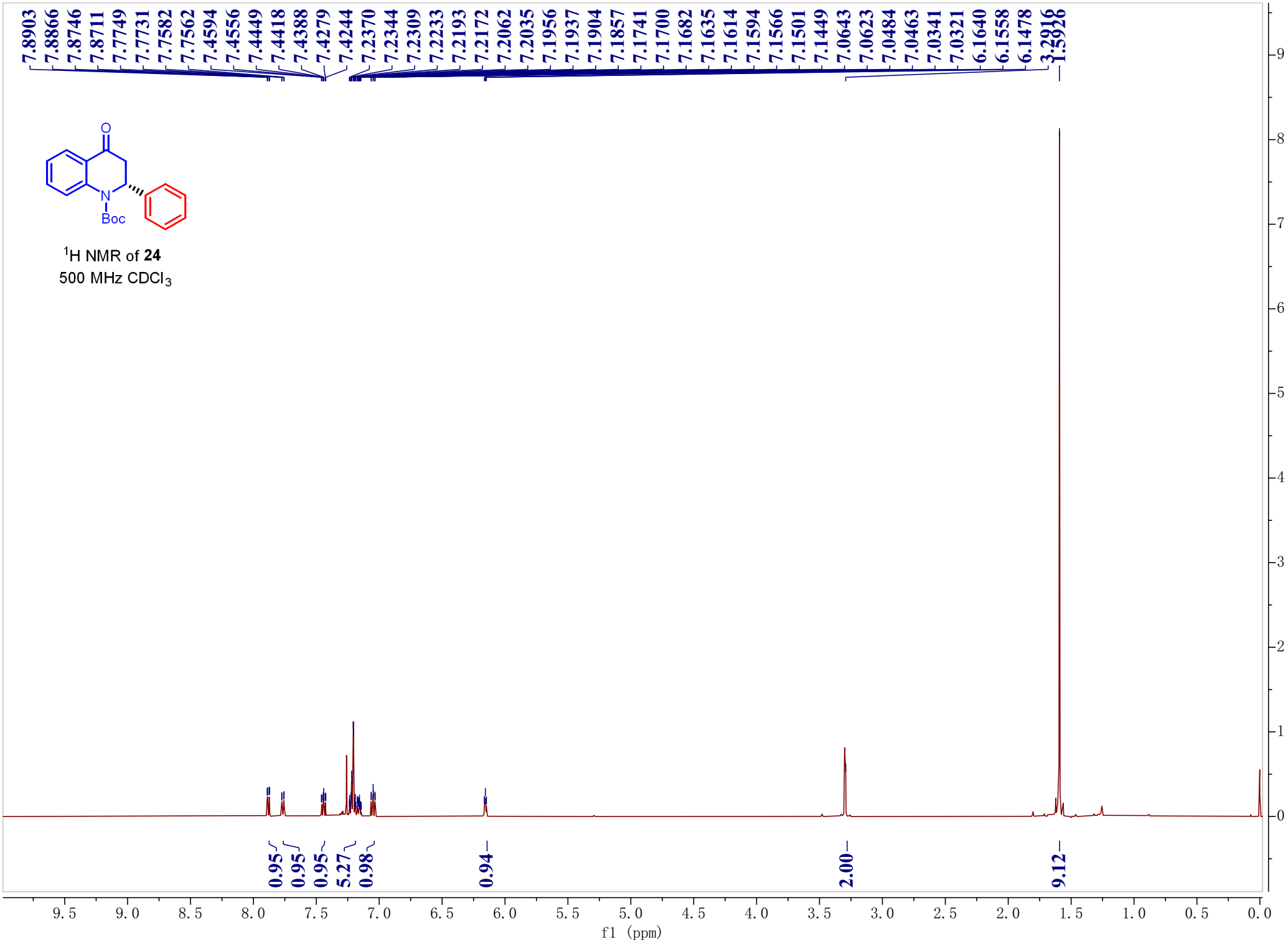
^{1}H NMR of **21**
500 MHz $CDCl_3$


193.0091
154.5393
141.3899
135.6974
135.6101
134.7058
133.0036
132.6236
129.8720
128.8698
128.3496
128.1786
127.5599
127.0171
126.4835
125.7304
125.2352
124.7929
124.6470
124.4918
123.3468
119.0025
68.7408
56.2752
42.2509
O
N
Cbz
13C NMR of 21
126 MHz CDCl3
0.013
0.012
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
-0.001
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

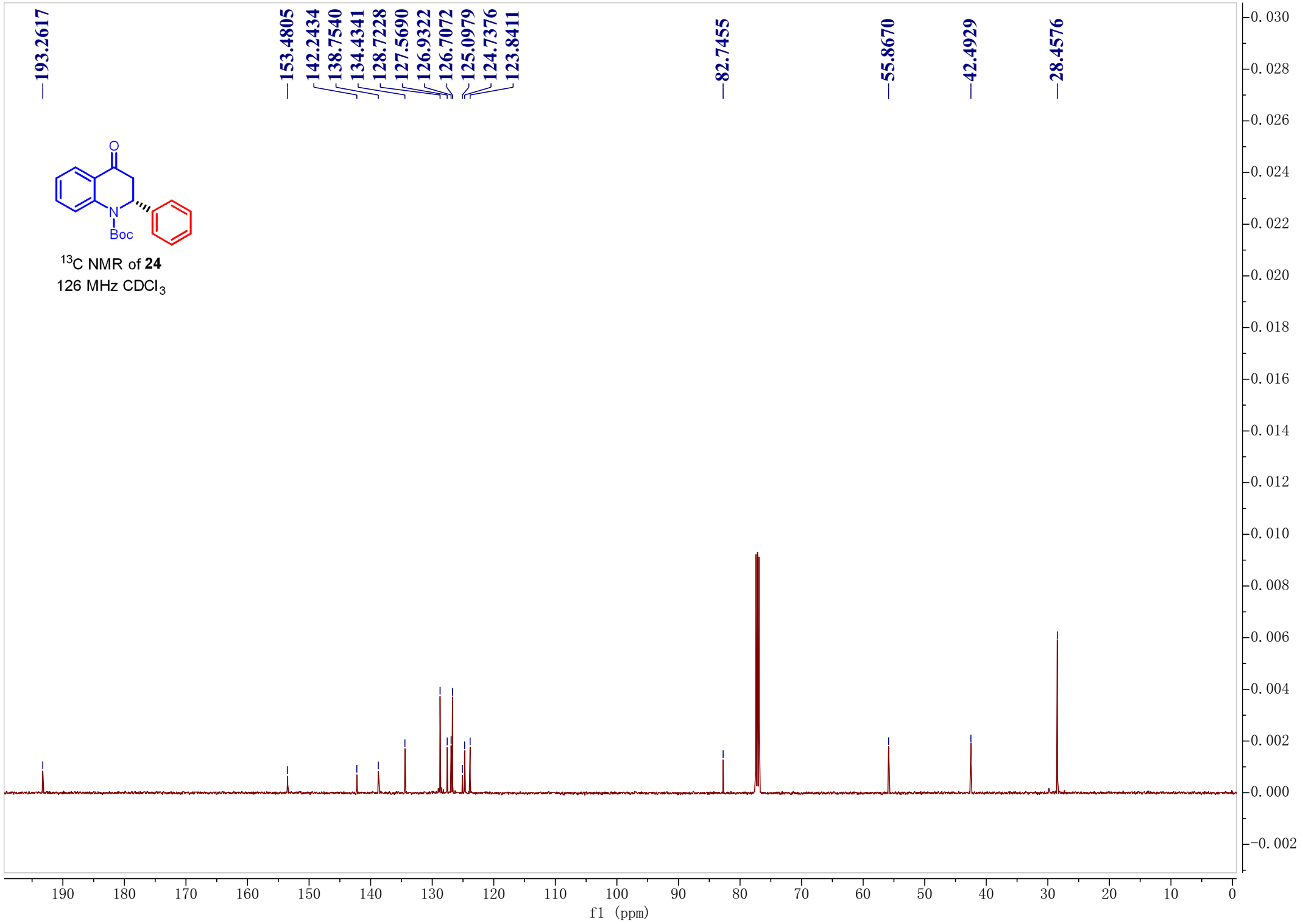


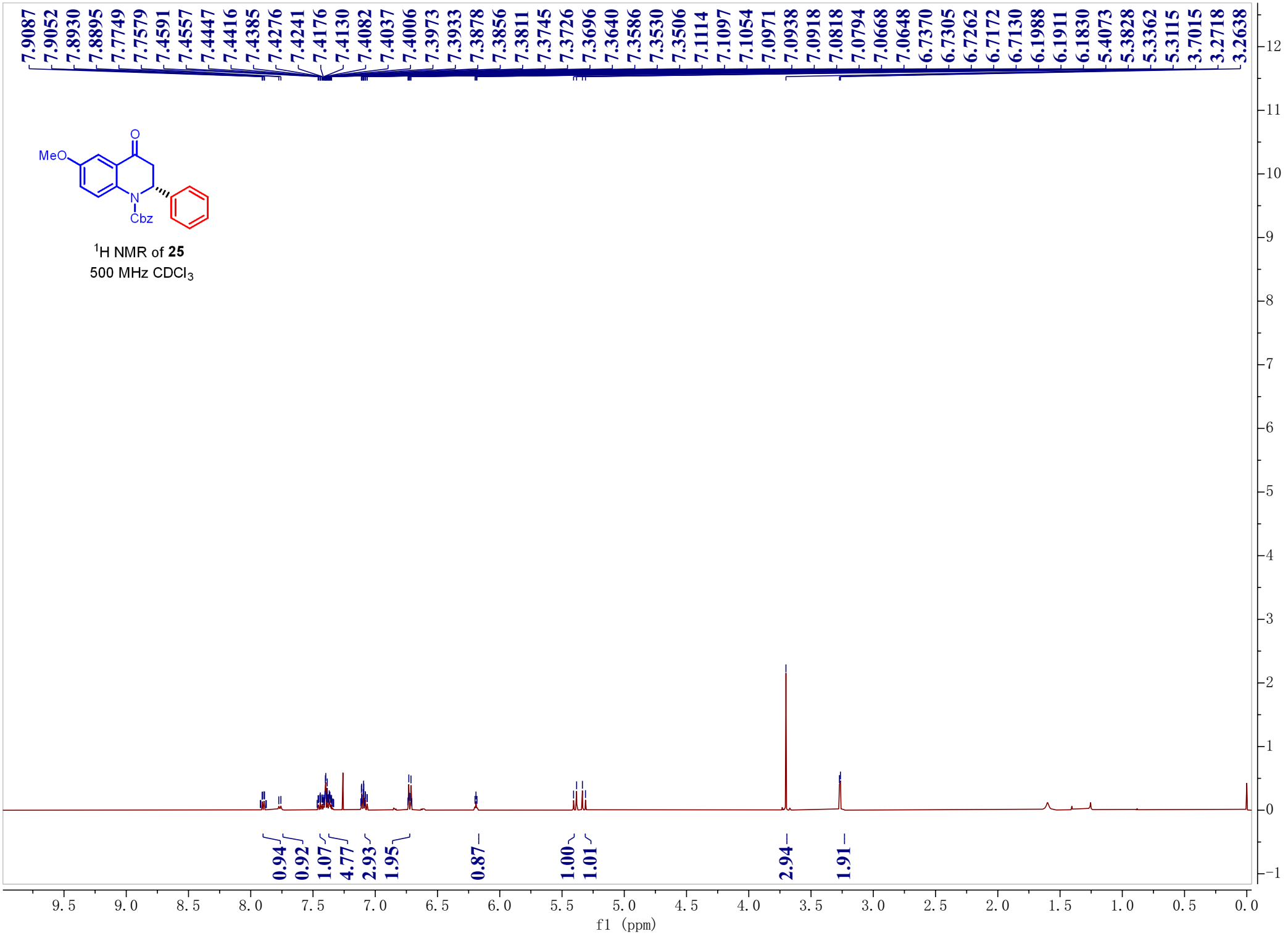
^{1}H NMR of **22**
400 MHz $CDCl_3$


192.8821
154.1041
141.4223
139.7799
135.7161
134.7127
128.8854
128.6917
128.3650
127.0752
126.7112
126.6585
124.9642
124.3906
124.3073
122.7169
68.6930
53.7796
43.1665
O
N
Cbz
S
13C NMR of 22
126 MHz CDCl3
0.0055
0.0050
0.0045
0.0040
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
−0.0005
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

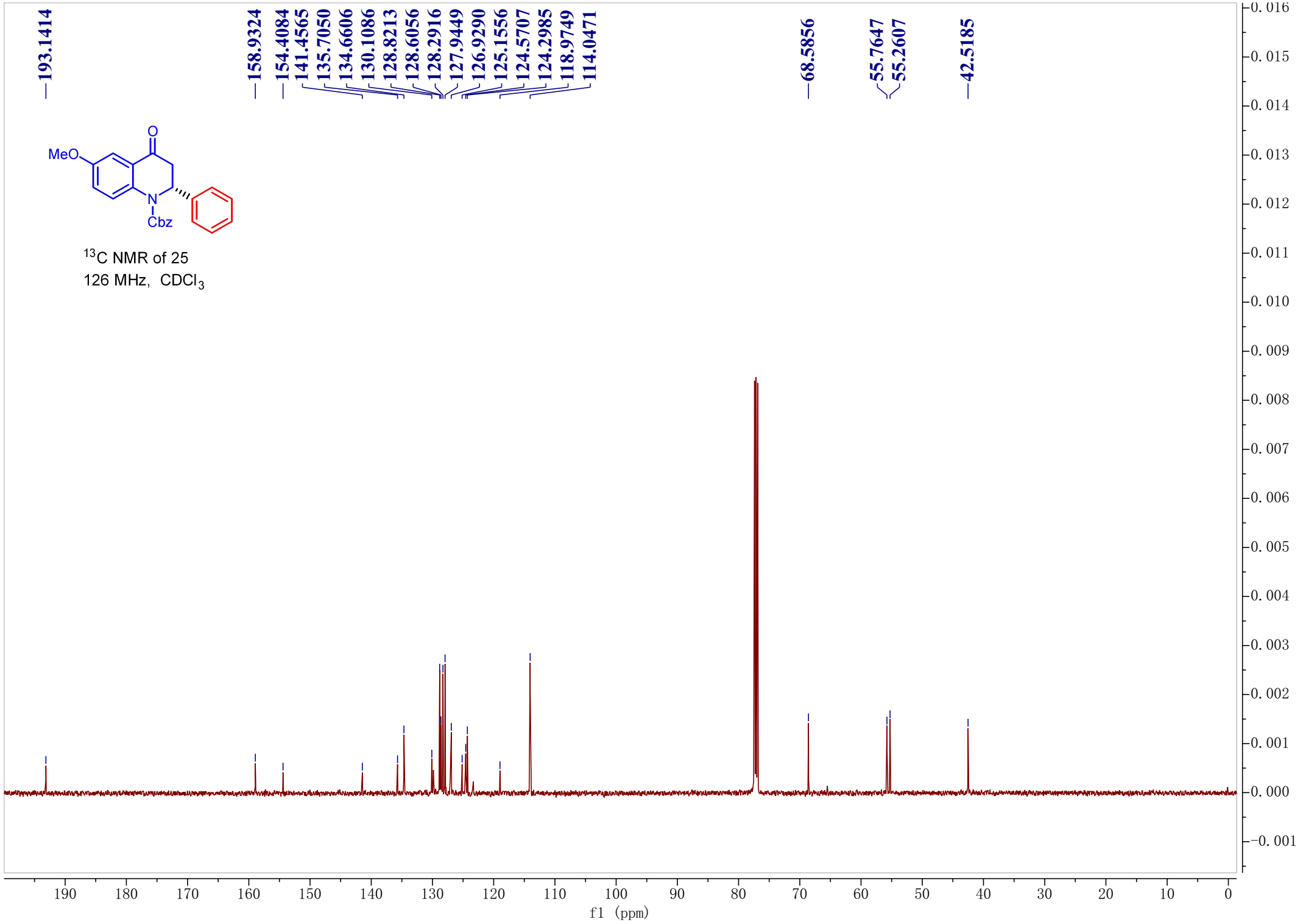


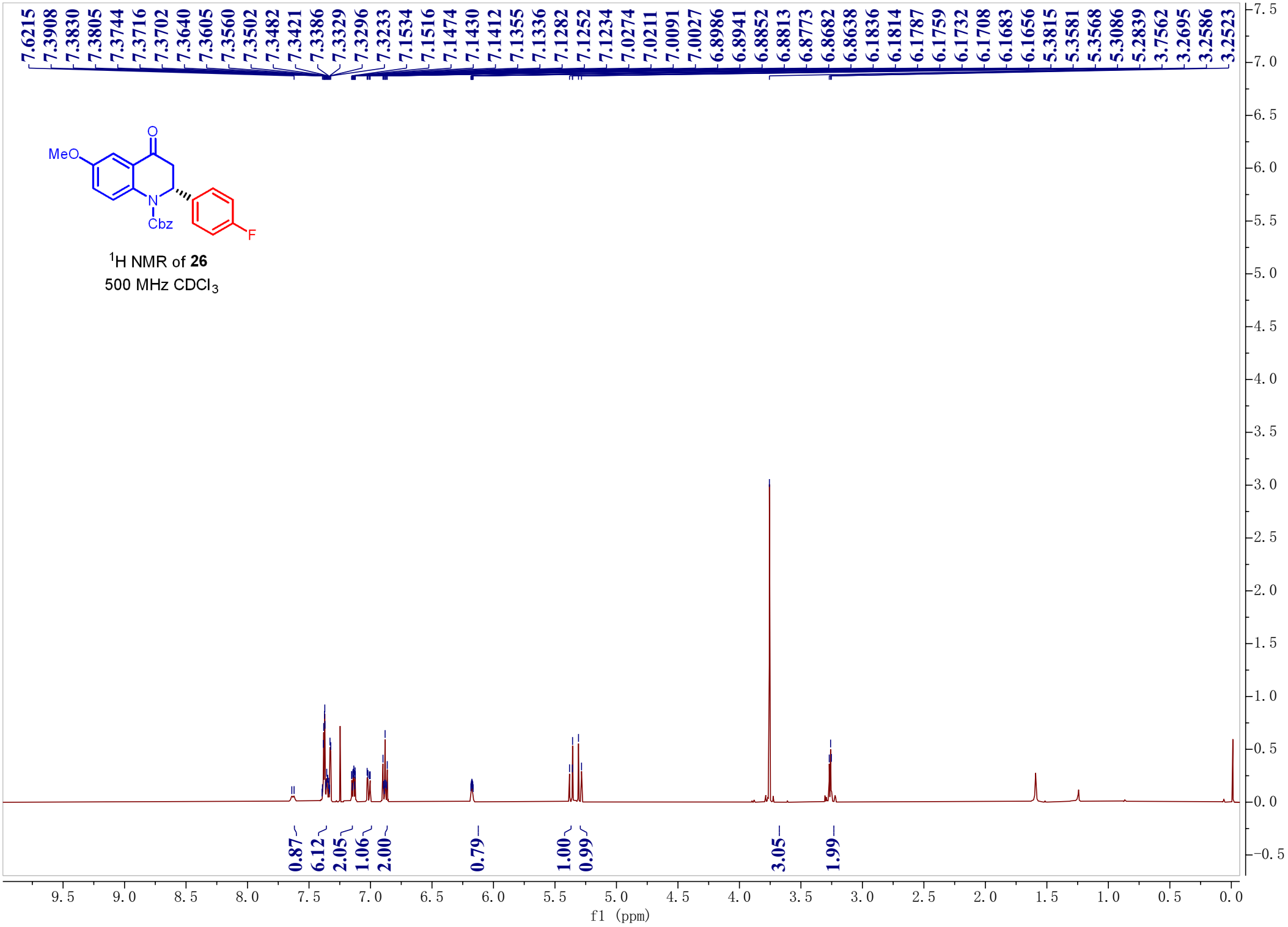
^{1}H NMR of **24**
500 MHz $CDCl_3$


193.2617
153.4805
142.2434
138.7540
134.4341
128.7228
127.5690
126.9322
126.7072
125.0979
124.7376
123.8411
82.7455
55.8670
42.4929
28.4576
O
N
Boc
13C NMR of 24
126 MHz CDCl3
0.030
0.028
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
−0.002
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

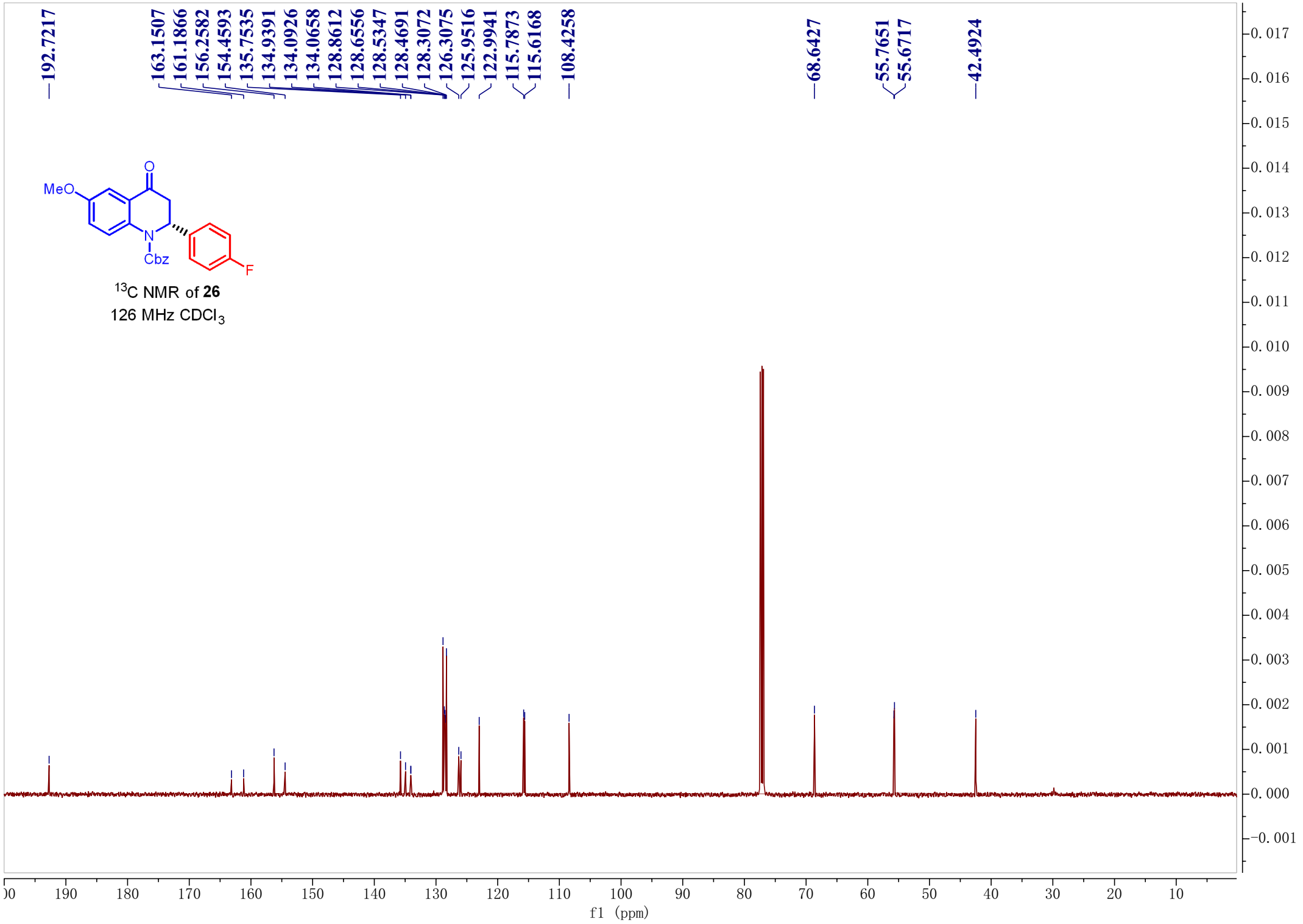


^{1}H NMR of **25**
500 MHz $CDCl_3$

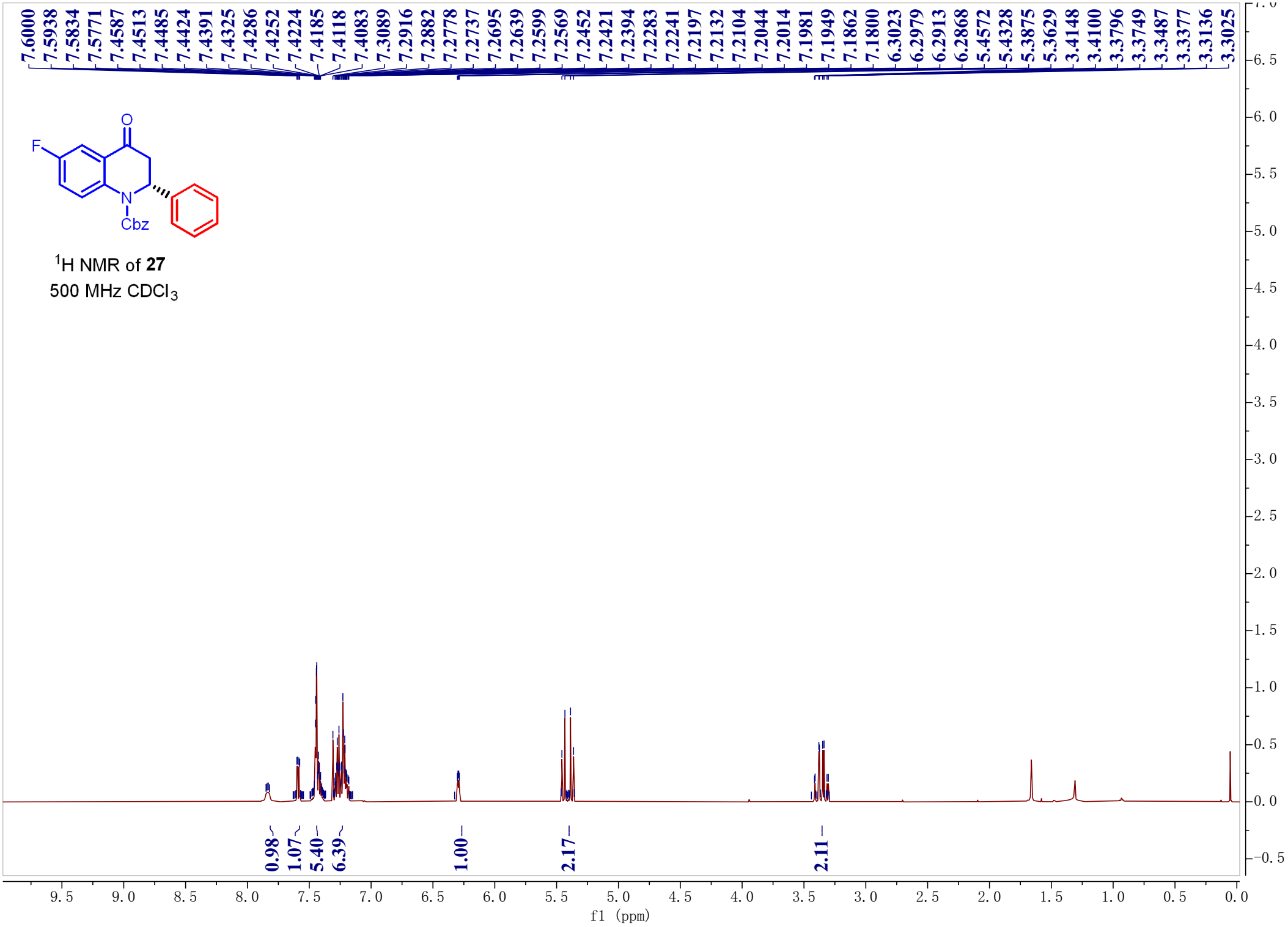

193.1414
158.9324
154.4084
141.4565
135.7050
134.6606
130.1086
128.8213
128.6056
128.2916
127.9449
126.9290
125.1556
124.5707
124.2985
118.9749
114.0471
68.5856
55.7647
55.2607
42.5185
MeO
O
N
Cbz
13C NMR of 25
126 MHz, CDCl3
f1 (ppm)

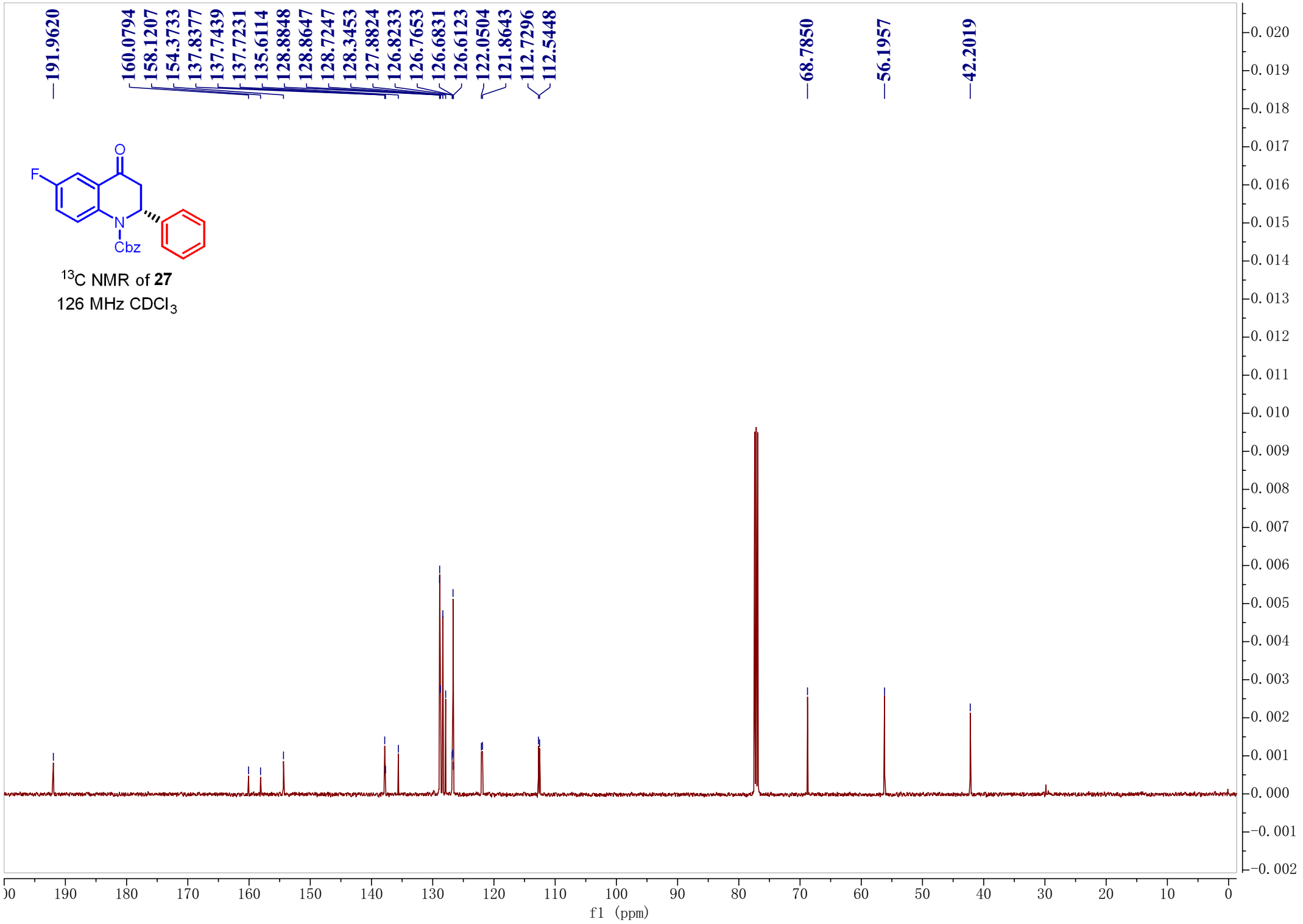


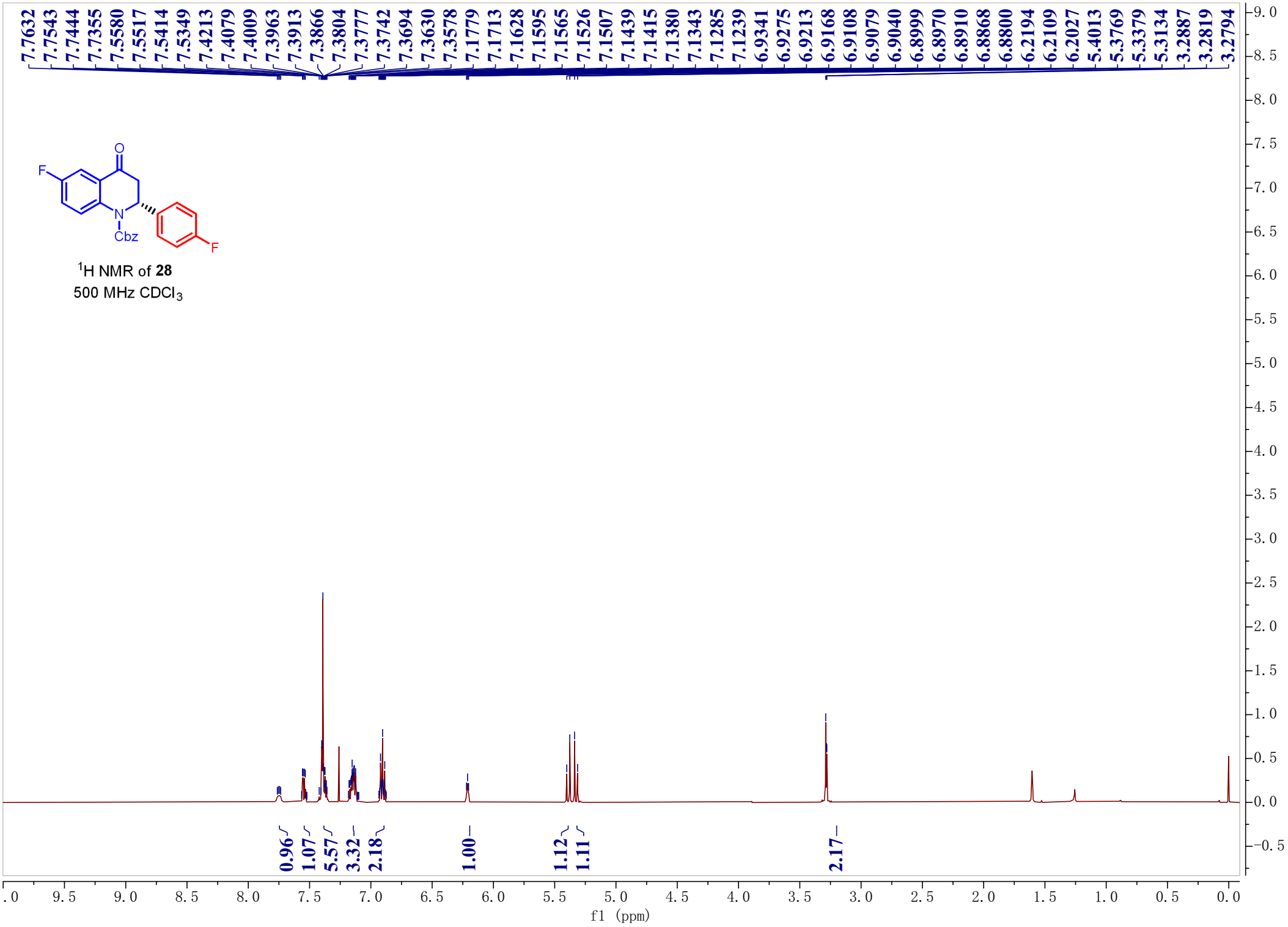
^{1}H NMR of **26**
500 MHz $CDCl_3$



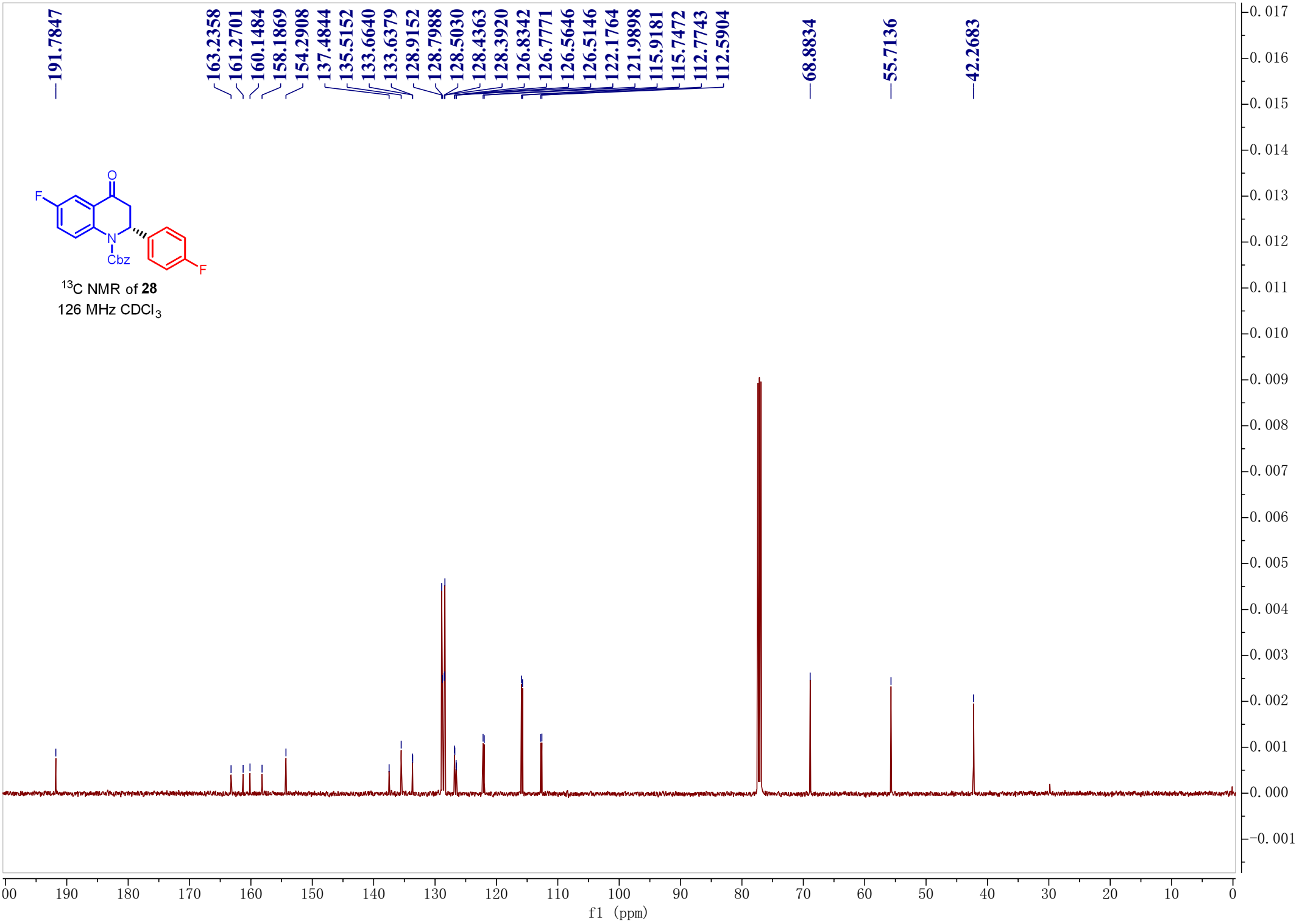
^{13}C NMR of **26**
126 MHz $CDCl_3$


7.6000
7.5938
7.5834
7.5771
7.4587
7.4513
7.4485
7.4424
7.4391
7.4325
7.4286
7.4252
7.4224
7.4185
7.4118
7.4083
7.3089
7.2916
7.2882
7.2778
7.2737
7.2695
7.2639
7.2599
7.2569
7.2452
7.2421
7.2394
7.2283
7.2241
7.2197
7.2132
7.2104
7.2044
7.2014
7.1981
7.1949
7.1862
7.1800
6.3023
6.2979
6.2913
6.2868
5.4572
5.4328
5.3875
5.3629
3.4148
3.4100
3.3796
3.3749
3.3487
3.3377
3.3136
3.3025
O
F
N
Cbz
1H NMR of 27
500 MHz CDCl3
0.98
1.07
5.40
6.39
1.00
2.17
2.11
f1 (ppm)

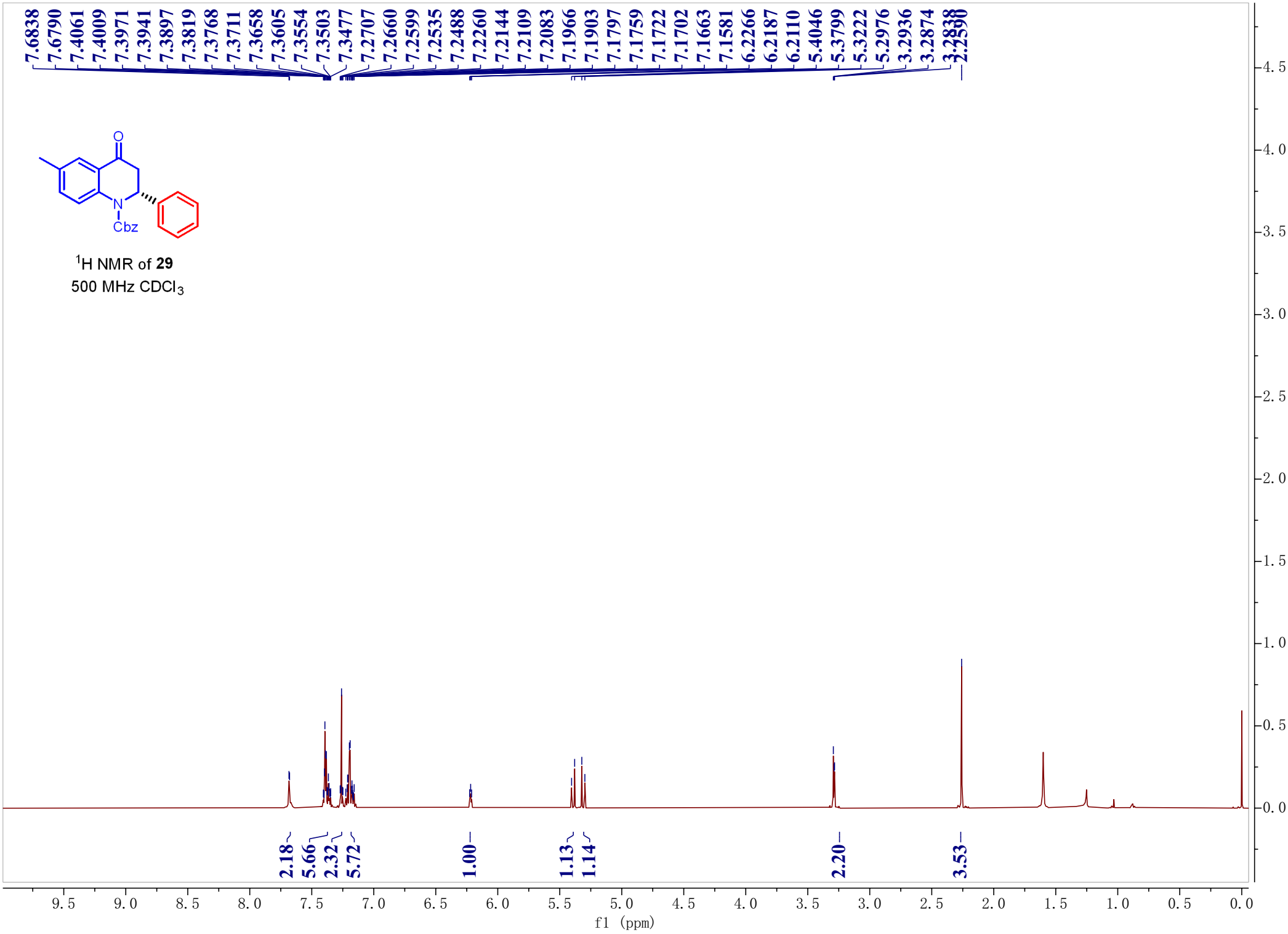

191.9620
160.0794
158.1207
154.3733
137.8377
137.7439
137.7231
135.6114
128.8848
128.8647
128.7247
128.3453
127.8824
126.8233
126.7653
126.6831
126.6123
122.0504
121.8643
112.7296
112.5448
68.7850
56.1957
42.2019
F
O
N
Cbz
13C NMR of 27
126 MHz CDCl3
f1 (ppm)

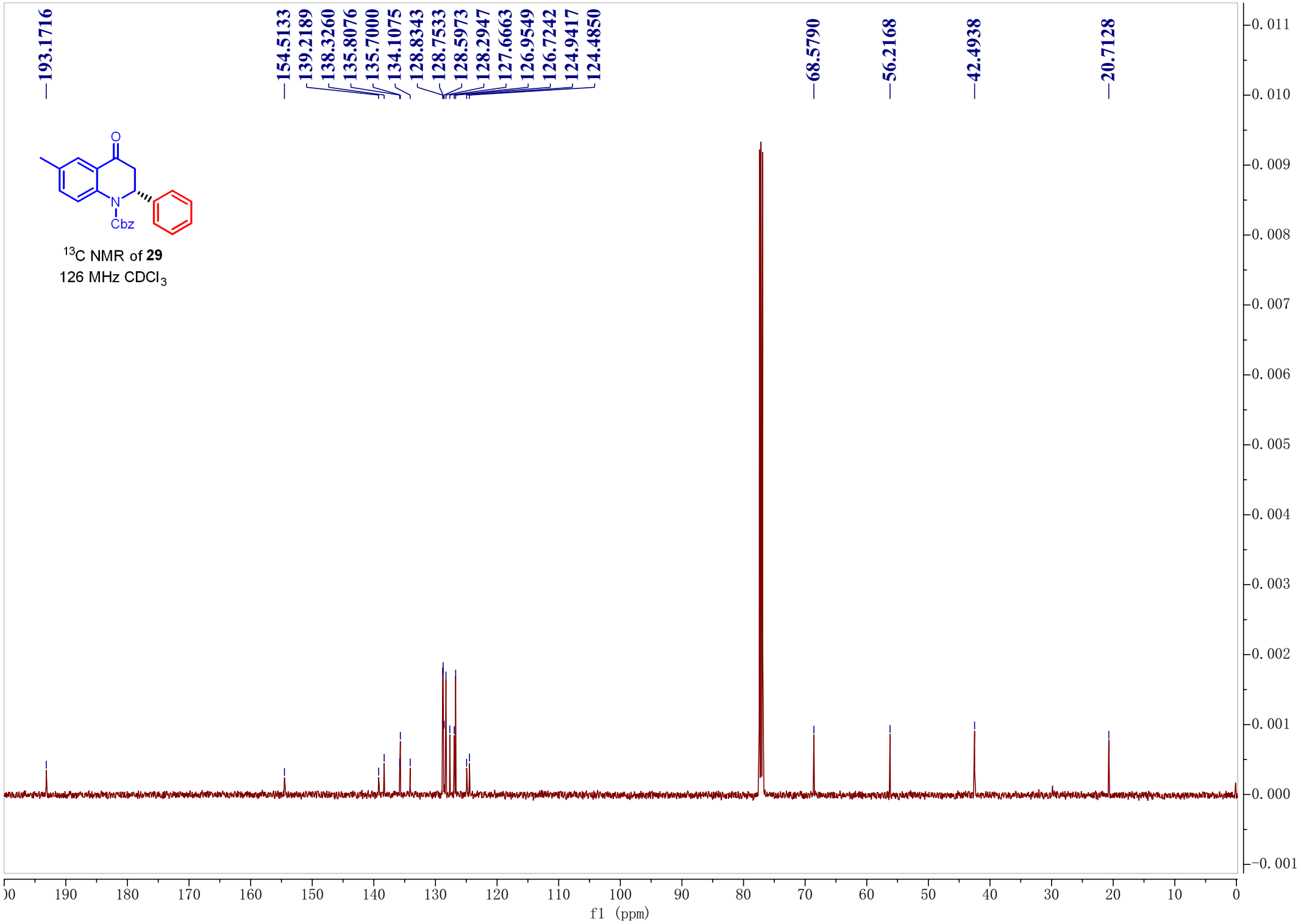


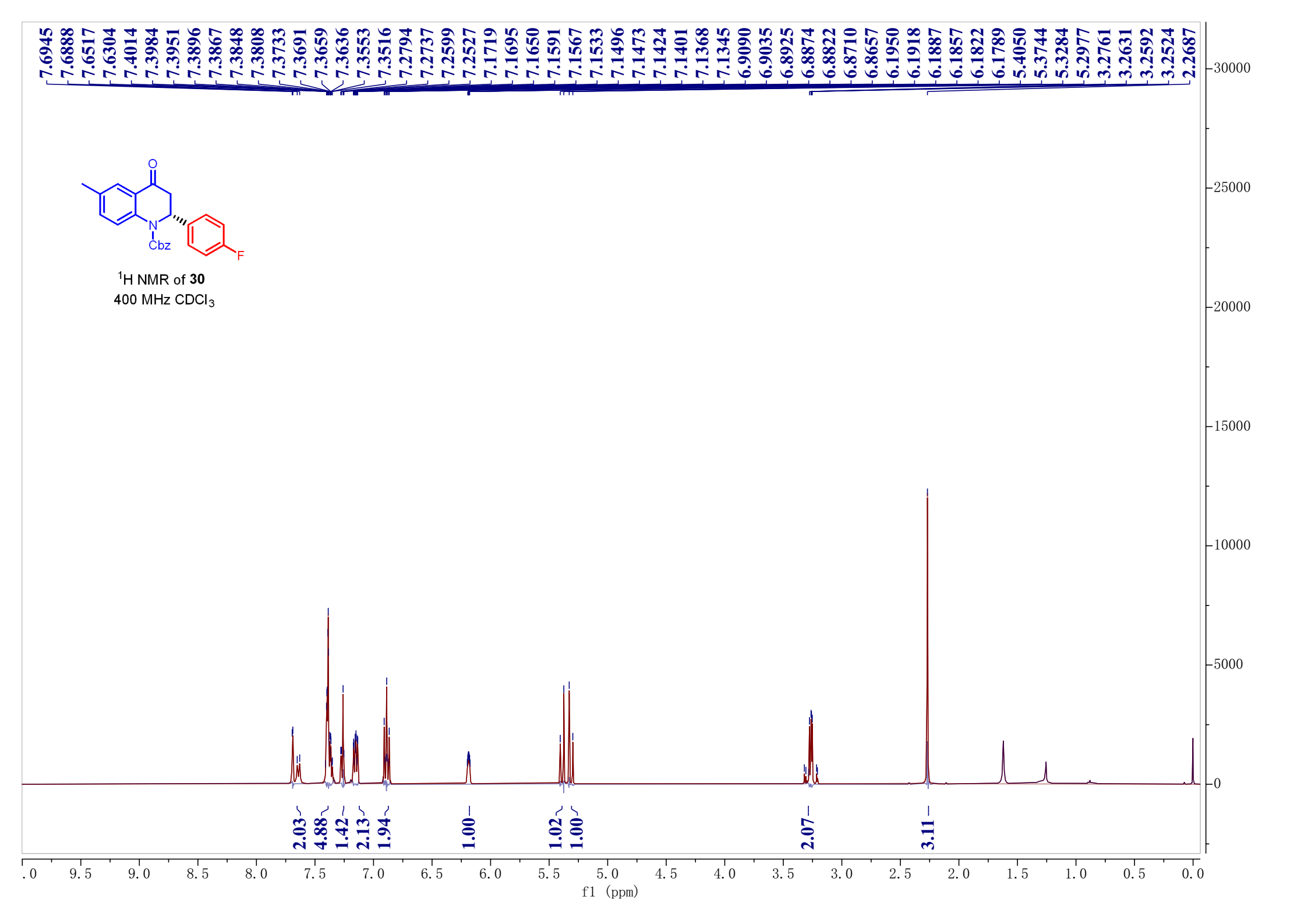
^{1}H NMR of **28**
500 MHz $CDCl_3$

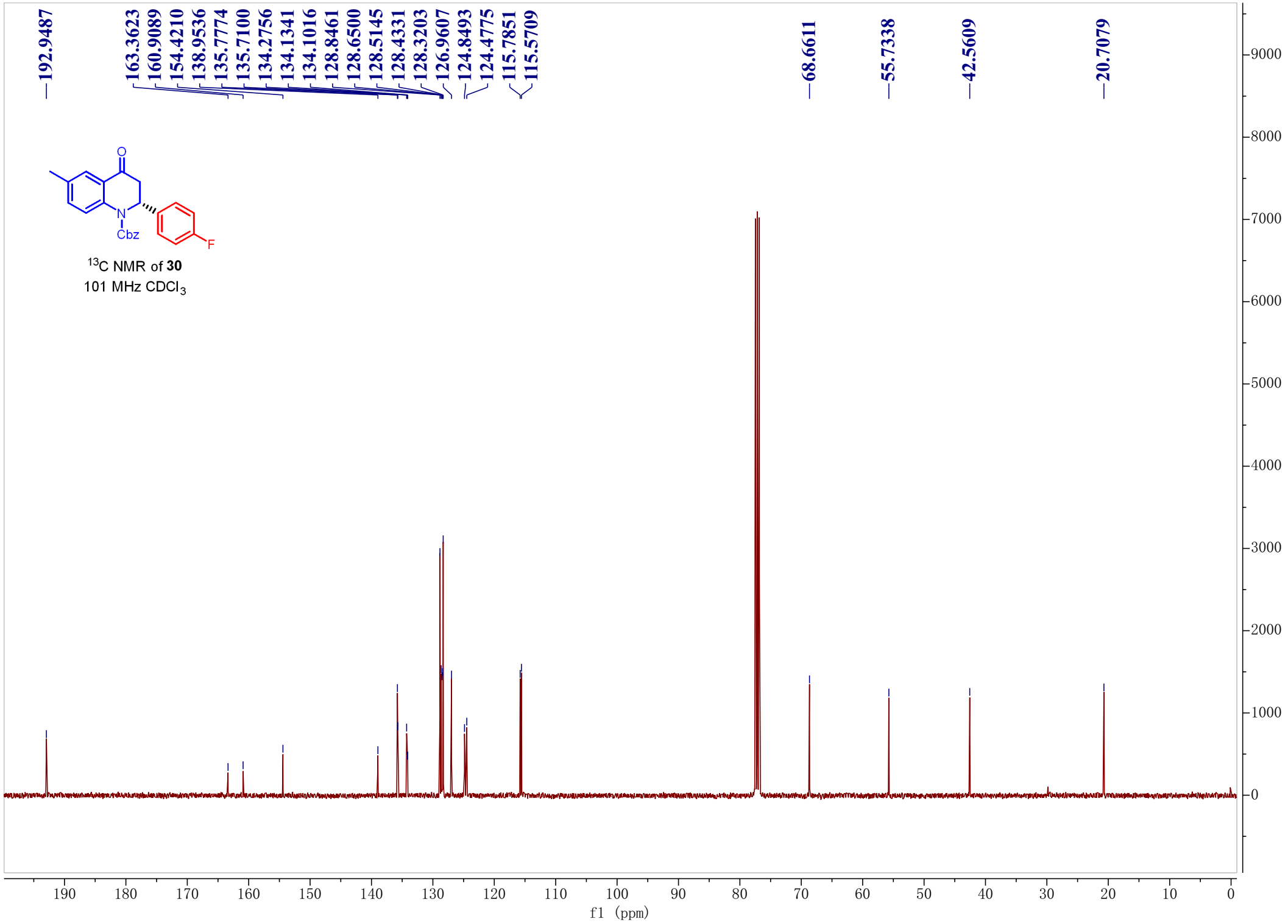


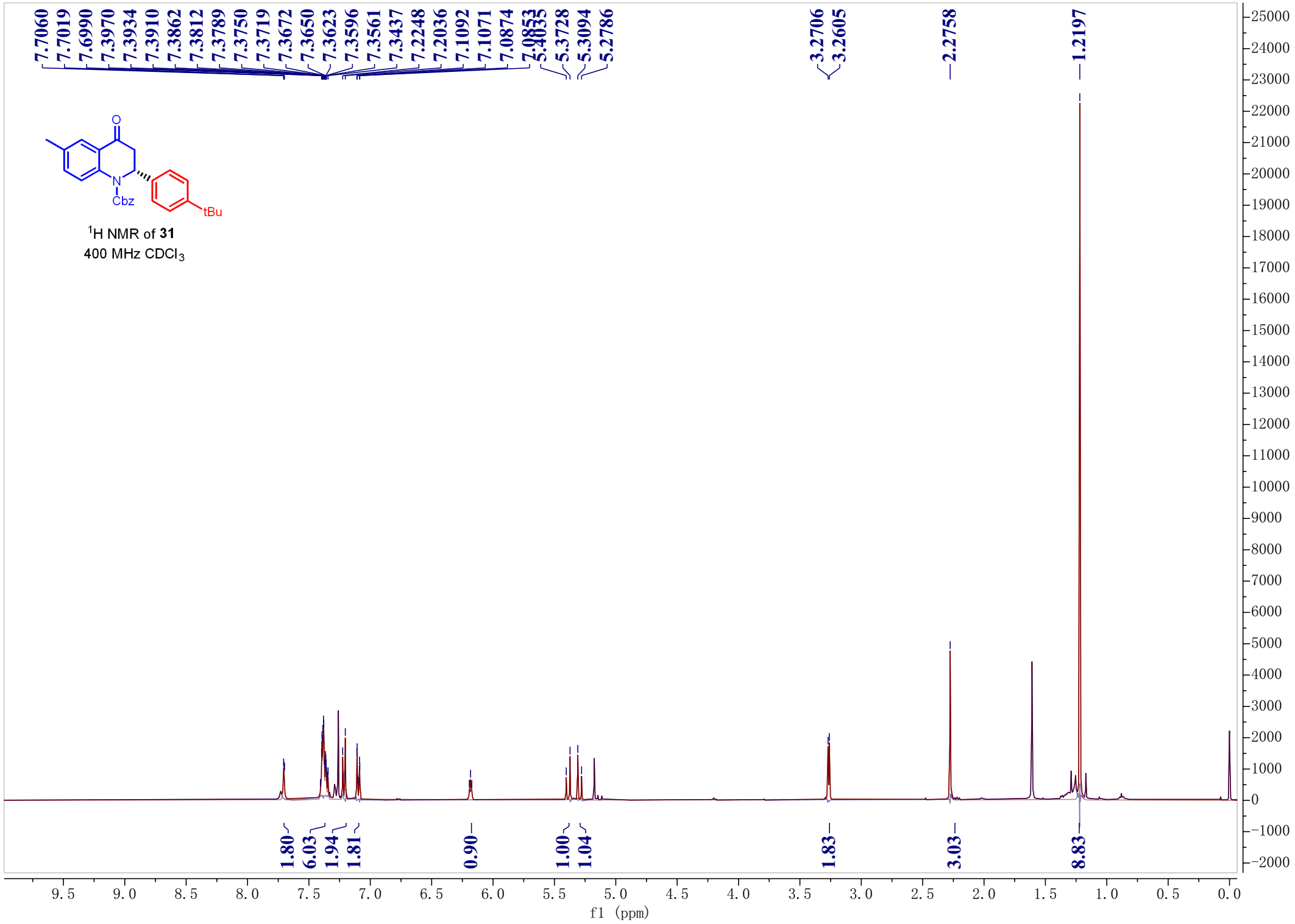
^{13}C NMR of **28**
126 MHz $CDCl_3$


7.6838
7.6790
7.4061
7.4009
7.3971
7.3941
7.3897
7.3819
7.3768
7.3711
7.3658
7.3605
7.3554
7.3503
7.3477
7.2707
7.2660
7.2599
7.2535
7.2488
7.2260
7.2144
7.2109
7.2083
7.1966
7.1903
7.1797
7.1759
7.1722
7.1702
7.1663
7.1581
6.2266
6.2187
6.2110
5.4046
5.3799
5.3222
5.2976
3.2936
3.2874
3.2838
3.2590
O
N
Cbz
1H NMR of 29
500 MHz CDCl3
2.18
5.66
2.32
5.72
1.00
1.13
1.14
2.20
3.53
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
f1 (ppm)

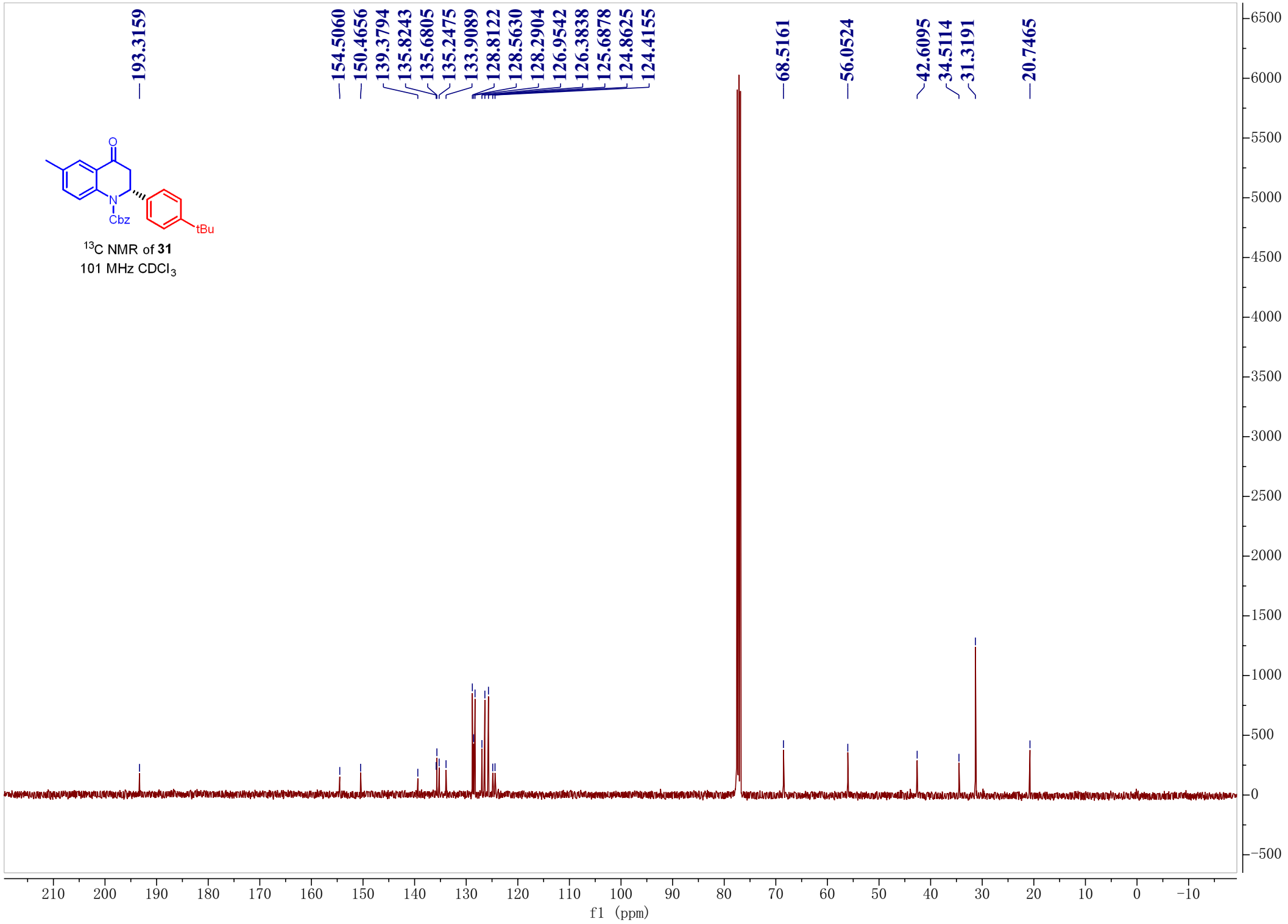

193.1716
154.5133
139.2189
138.3260
135.8076
135.7000
134.1075
128.8343
128.7533
128.5973
128.2947
127.6663
126.9549
126.7242
124.9417
124.4850
68.5790
56.2168
42.4938
20.7128
O
N
Cbz
13C NMR of 29
126 MHz CDCl3
0.011
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
−0.001
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

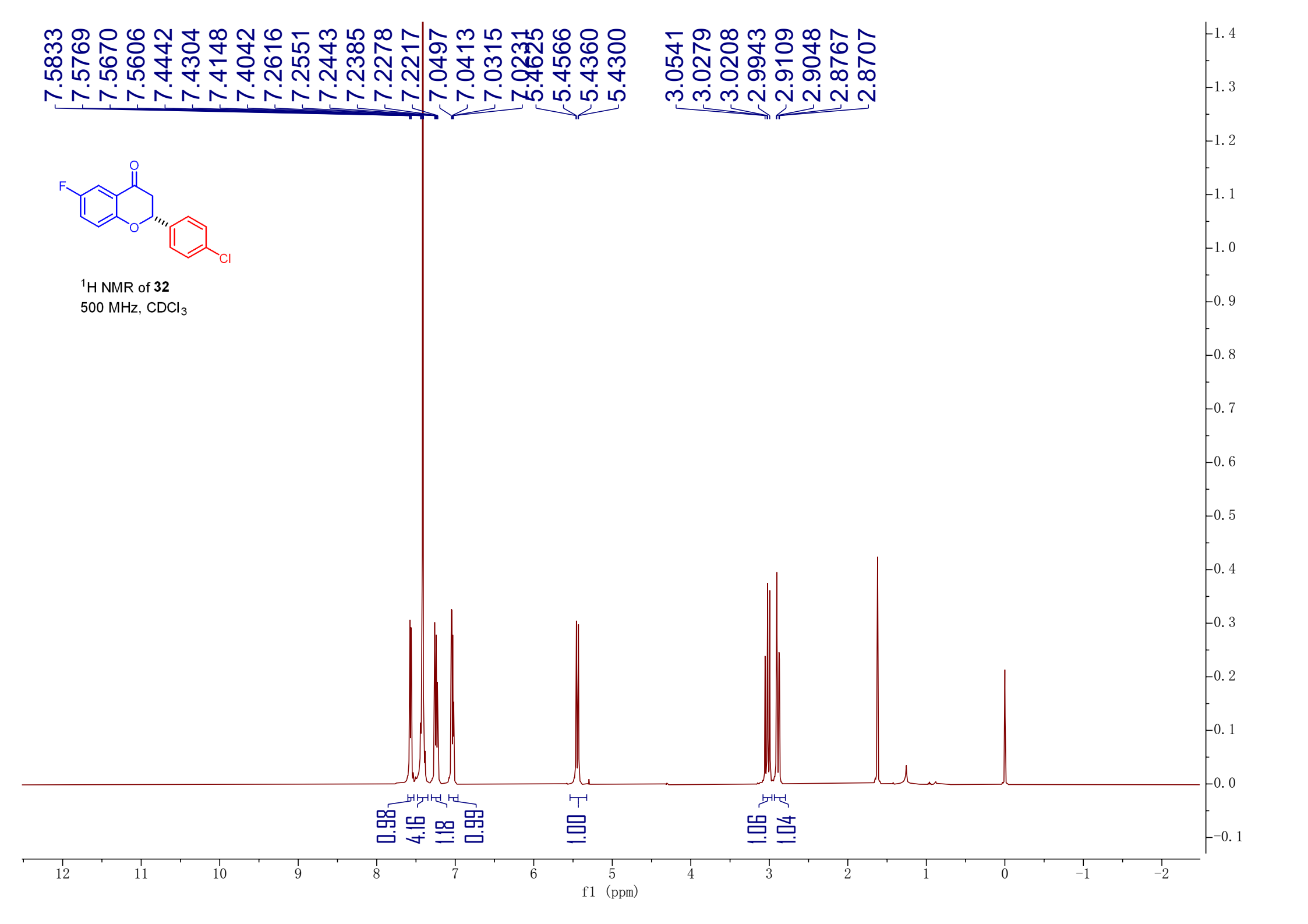

7.6945
7.6888
7.6517
7.6304
7.4014
7.3984
7.3951
7.3896
7.3867
7.3848
7.3808
7.3733
7.3691
7.3659
7.3636
7.3553
7.3516
7.2794
7.2737
7.2599
7.2527
7.1719
7.1695
7.1650
7.1591
7.1567
7.1533
7.1496
7.1473
7.1424
7.1401
7.1368
7.1345
6.9090
6.9035
6.8925
6.8874
6.8822
6.8710
6.8657
6.1950
6.1918
6.1887
6.1857
6.1822
6.1789
5.4050
5.3744
5.3284
5.2977
3.2761
3.2631
3.2592
3.2524
2.2687
O
N
Cbz
F
1H NMR of 30
400 MHz CDCl3
30000
25000
20000
15000
10000
5000
0
2.03
4.88
1.42
2.13
1.94
1.00
1.02
1.00
2.07
3.11
.0
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
f1 (ppm)


192.9487
163.3623
160.9089
154.4210
138.9536
135.7774
135.7100
134.2756
134.1341
134.1016
128.8461
128.6500
128.5145
128.4331
128.3203
126.9607
124.8493
124.4775
115.7851
115.5709
68.6611
55.7338
42.5609
20.7079
O
N
Cbz
F
13C NMR of 30
101 MHz CDCl3
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

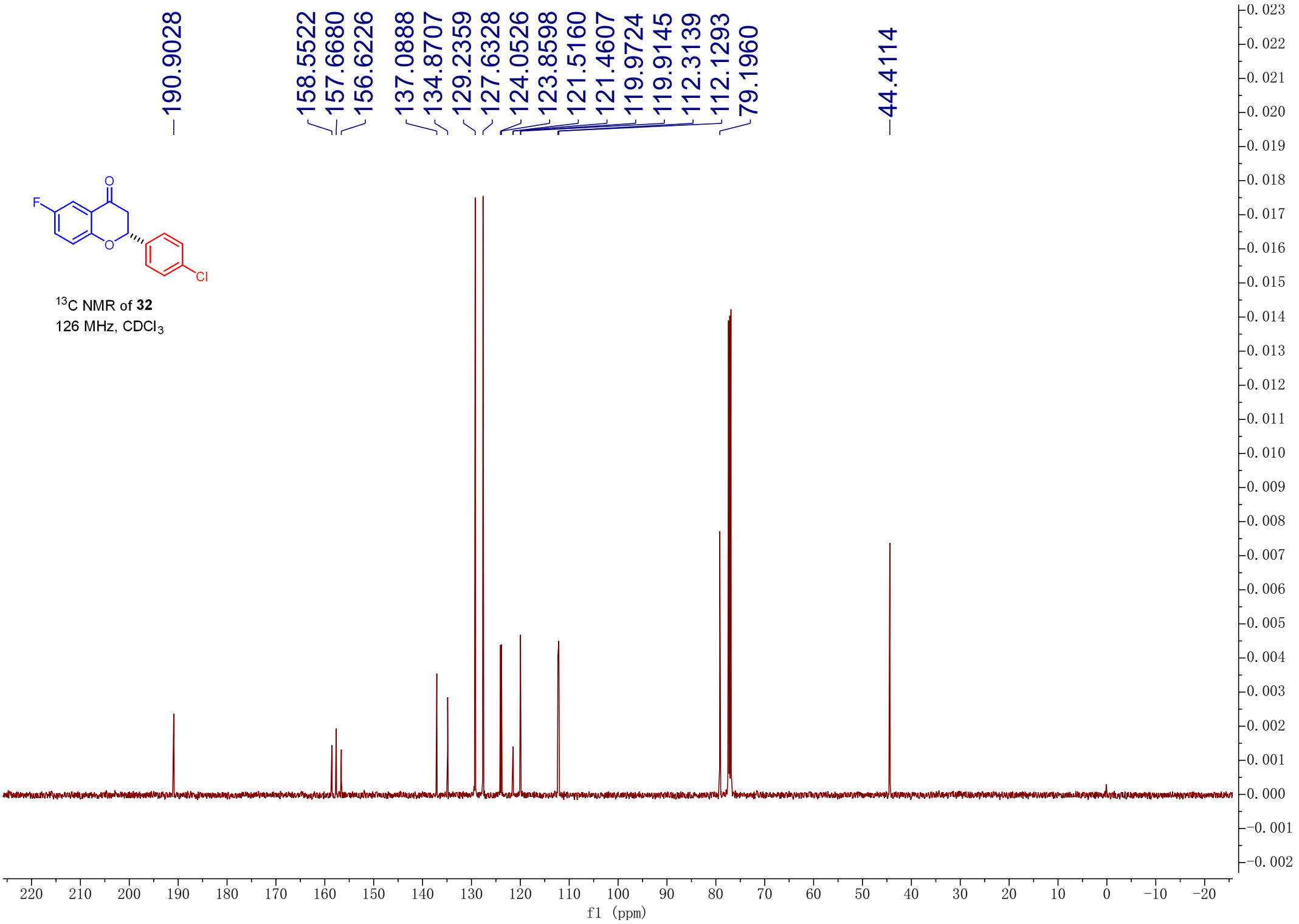


^{1}H NMR of **31**
400 MHz $CDCl_3$


193.3159
154.5060
150.4656
139.3794
135.8243
135.6805
135.2475
133.9089
128.8122
128.5630
128.2904
126.9542
126.3838
125.6878
124.8625
124.4155
68.5161
56.0524
42.6095
34.5114
31.3191
20.7465
O
N
Cbz
tBu
13C NMR of 31
101 MHz CDCl3
f1 (ppm)

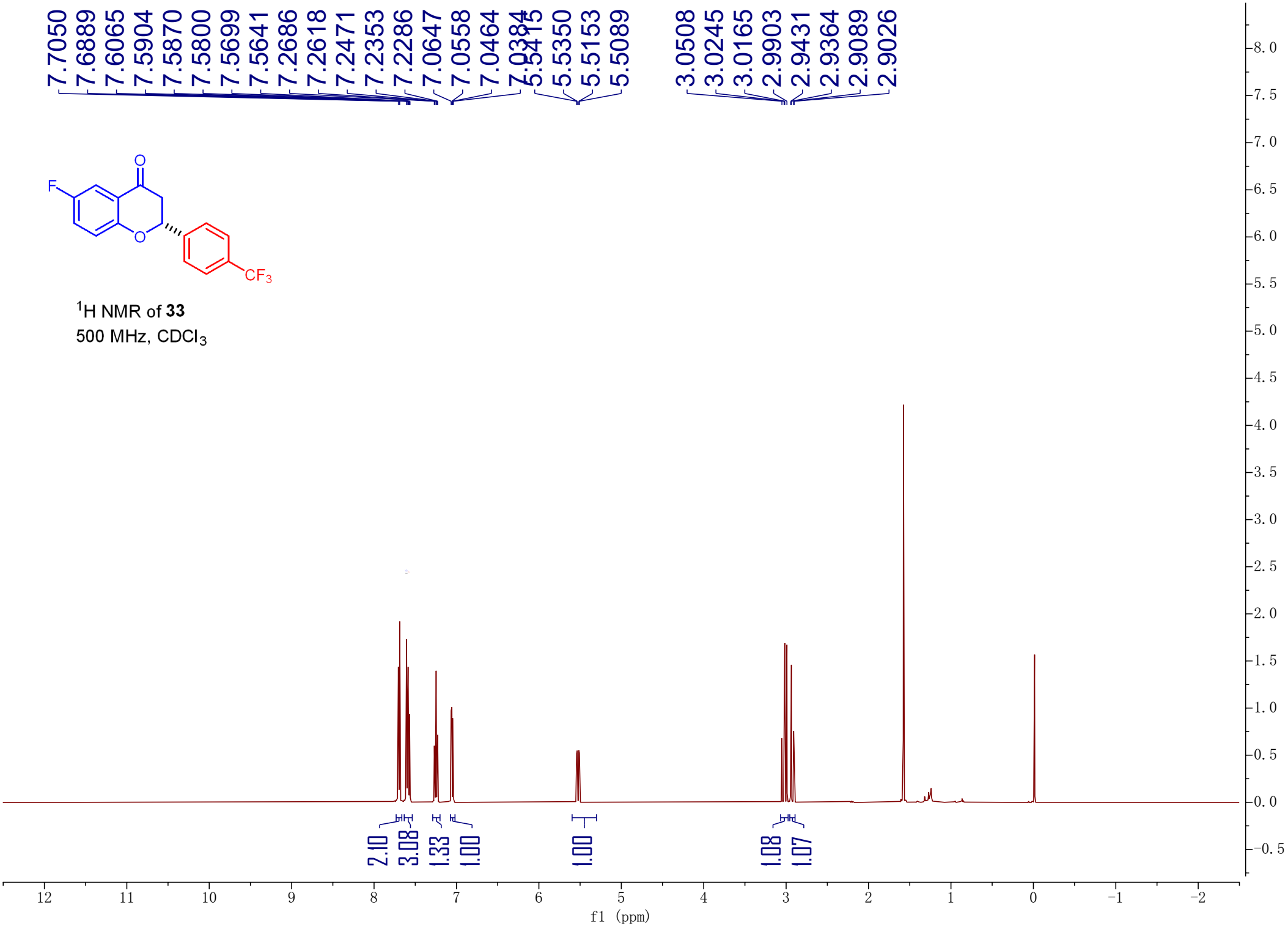


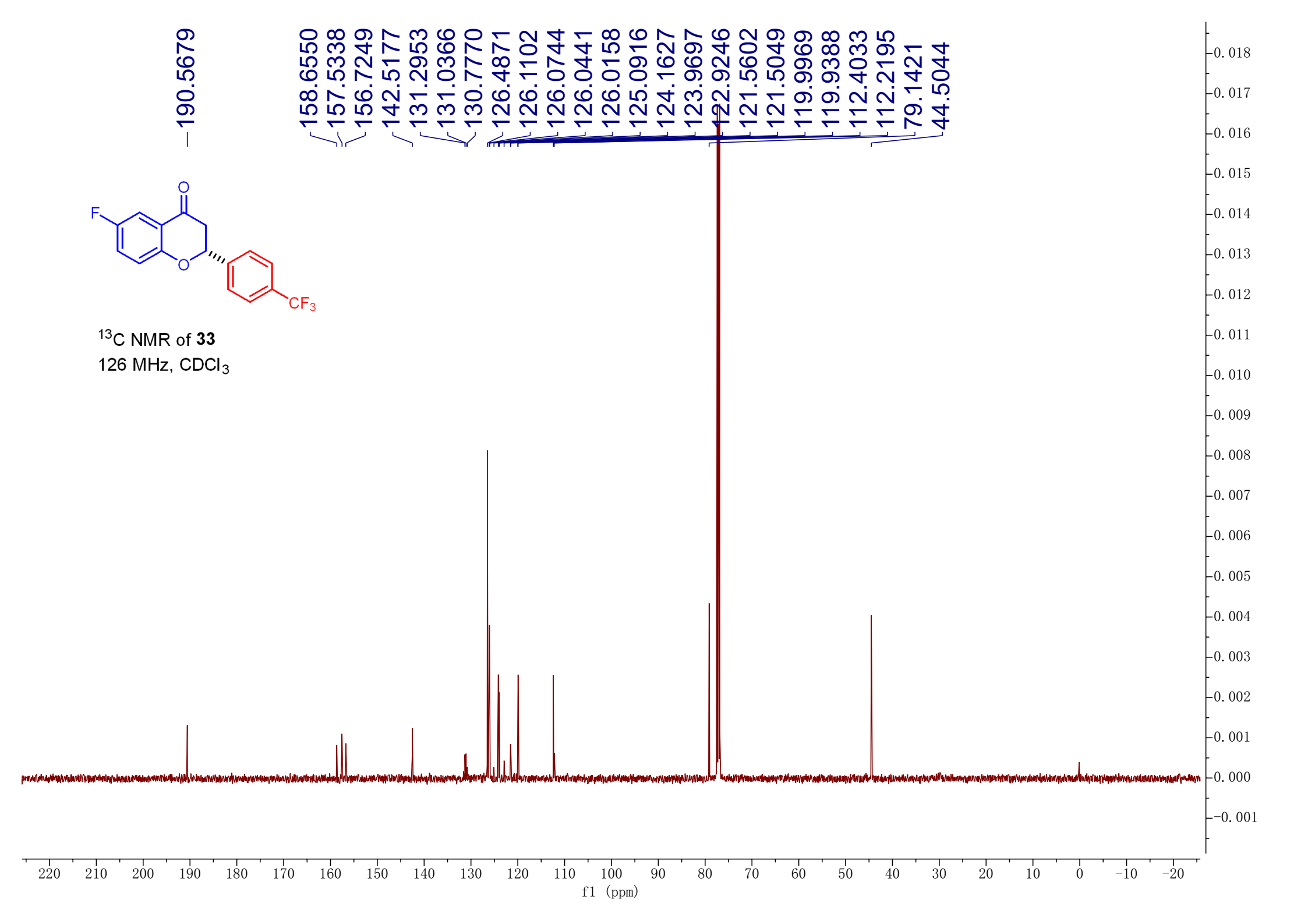
^{1}H NMR of **32**
500 MHz, $CDCl_3$

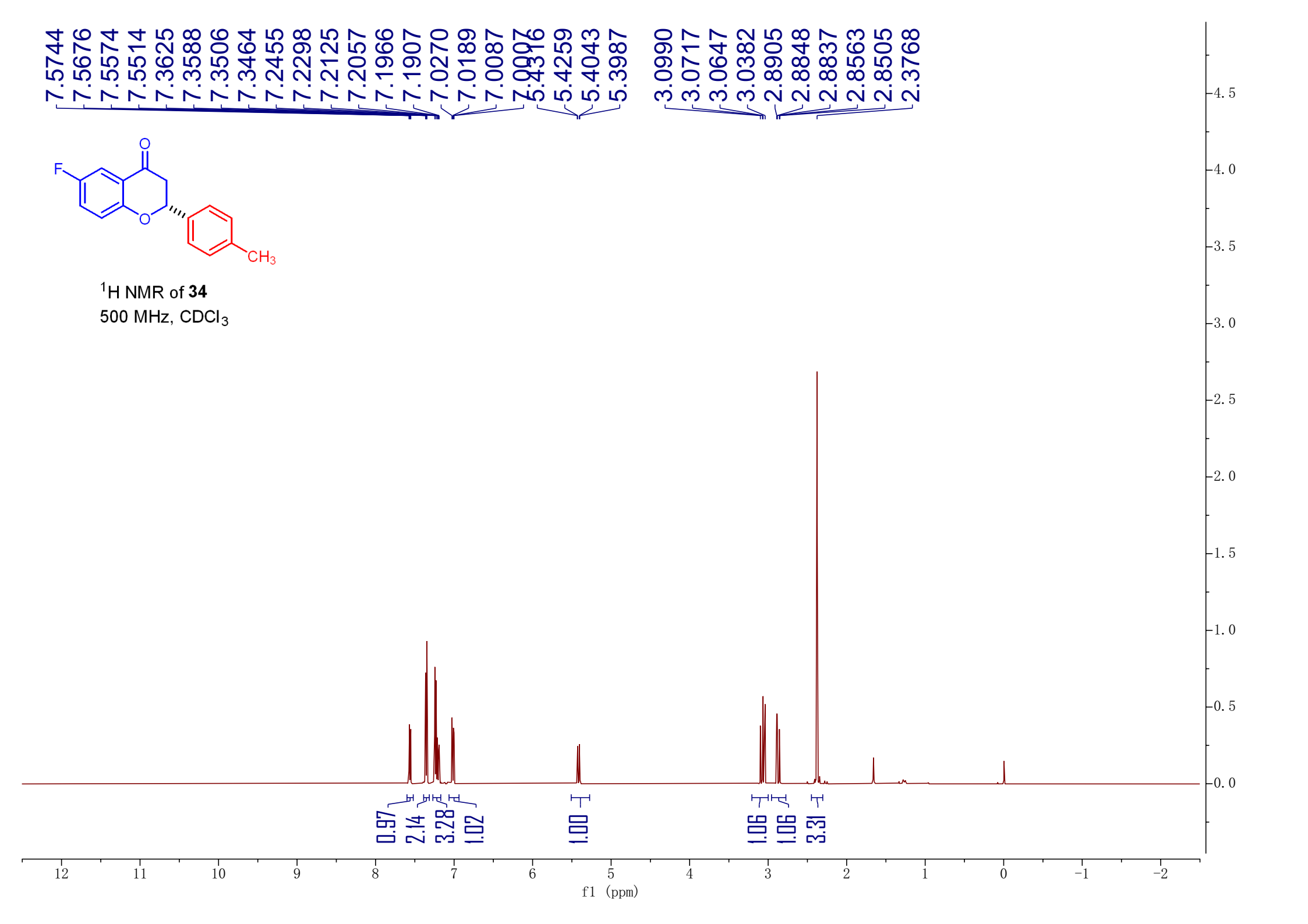

190.9028
158.5522
157.6680
156.6226
137.0888
134.8707
129.2359
127.6328
124.0526
123.8598
121.5160
121.4607
119.9724
119.9145
112.3139
112.1293
79.1960
44.4114
F
O
O
Cl
^{13}C NMR of **32**
126 MHz, $CDCl_3$
f1 (ppm)

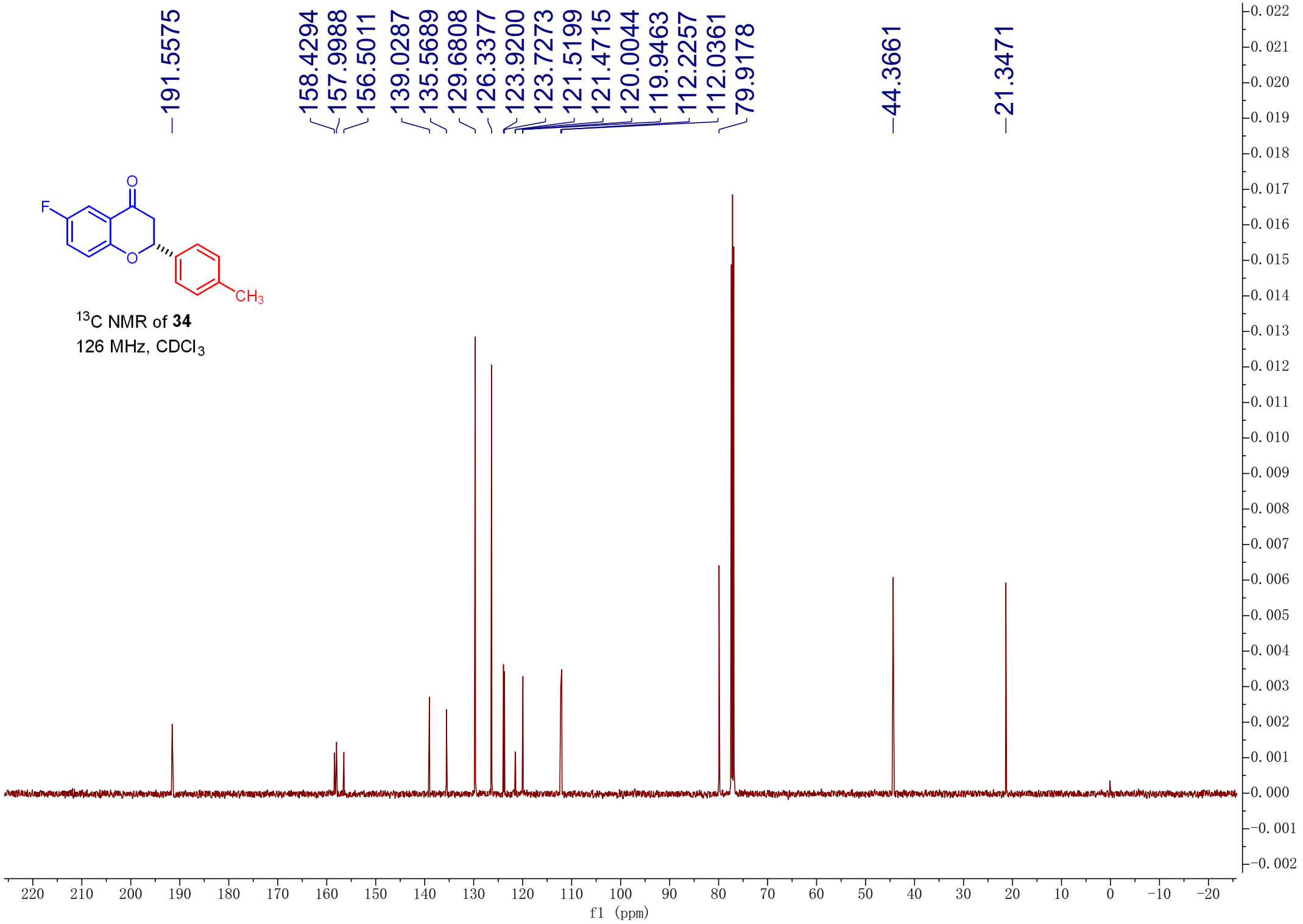
^{1}H NMR of **33**

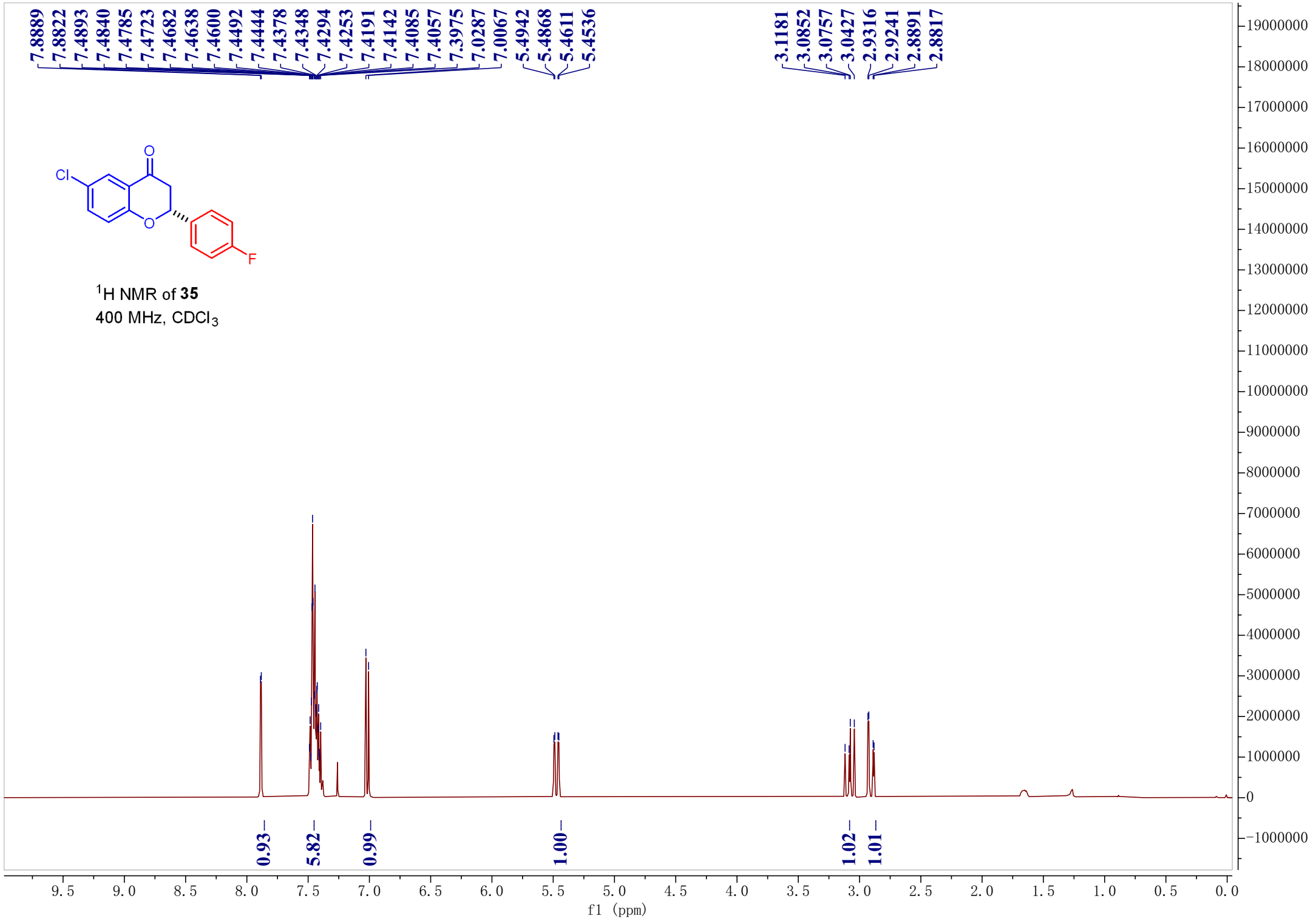
500 MHz, $CDCl_3$

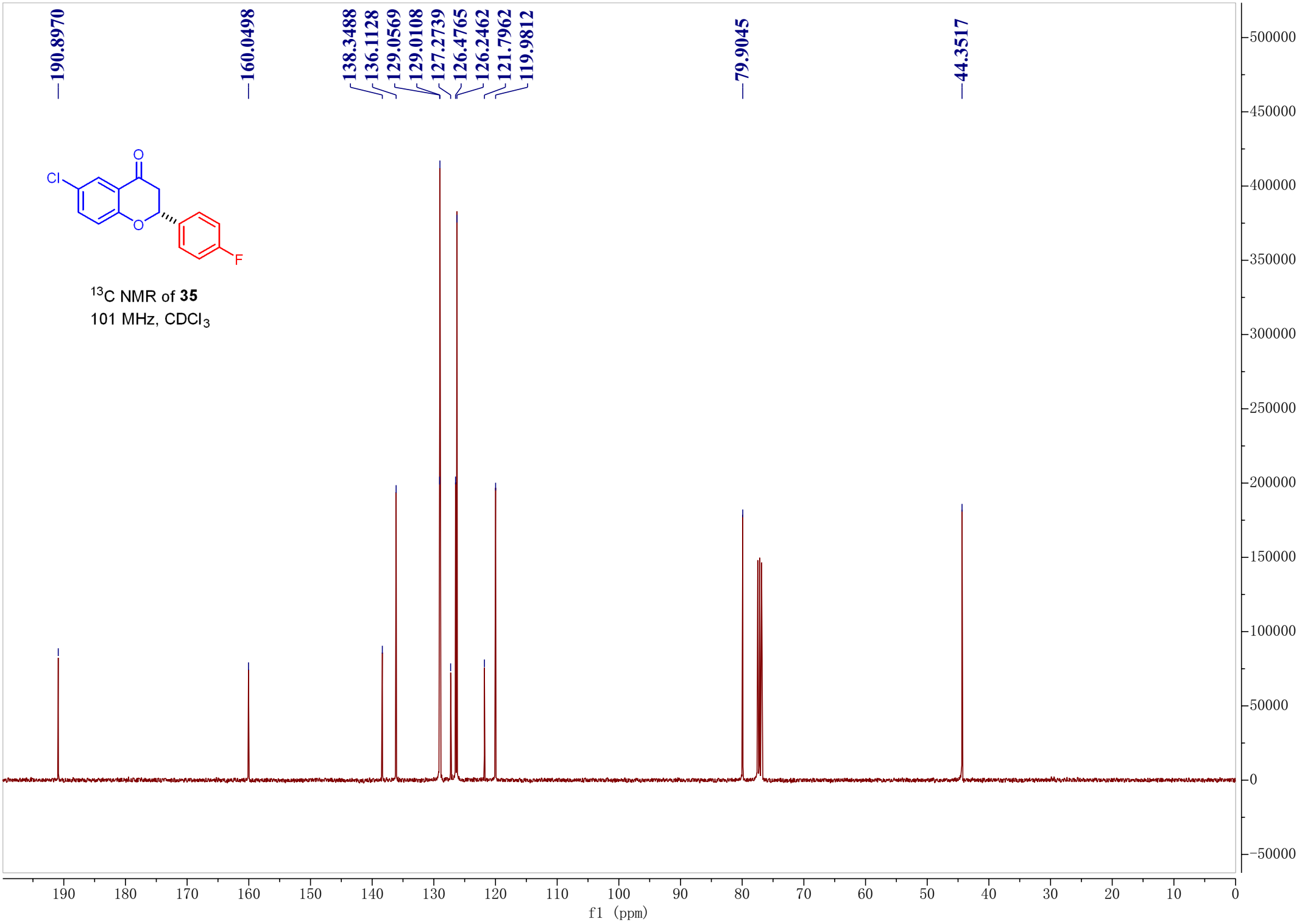


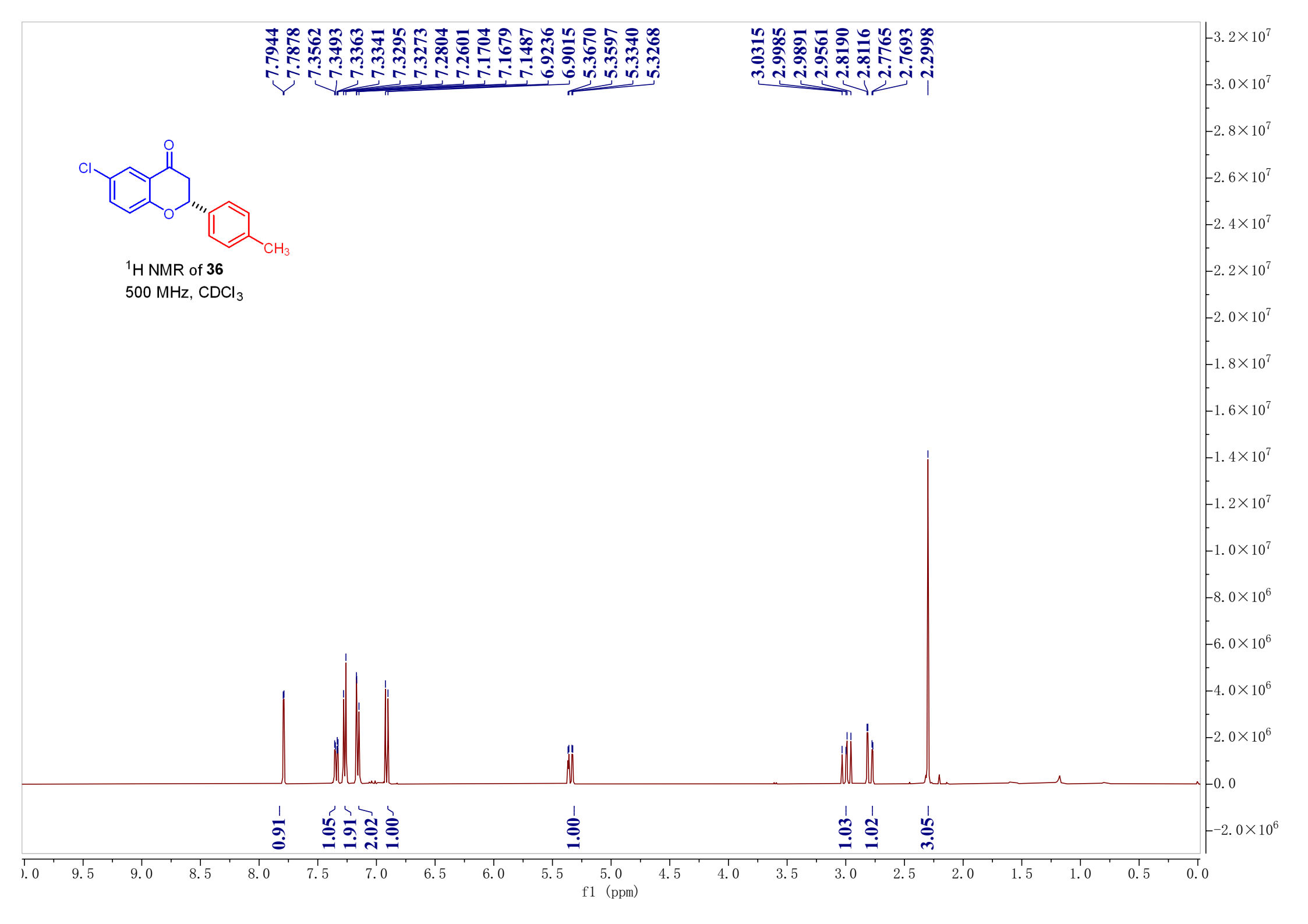

190.5679
158.6550
157.5338
156.7249
142.5177
131.2953
131.0366
130.7770
126.4871
126.1102
126.0744
126.0441
126.0158
125.0916
124.1627
123.9697
122.9246
121.5602
121.5049
119.9969
119.9388
112.4033
112.2195
79.1421
44.5044
F
O
O
CF3
13C NMR of 33
126 MHz, CDCl3
f1 (ppm)

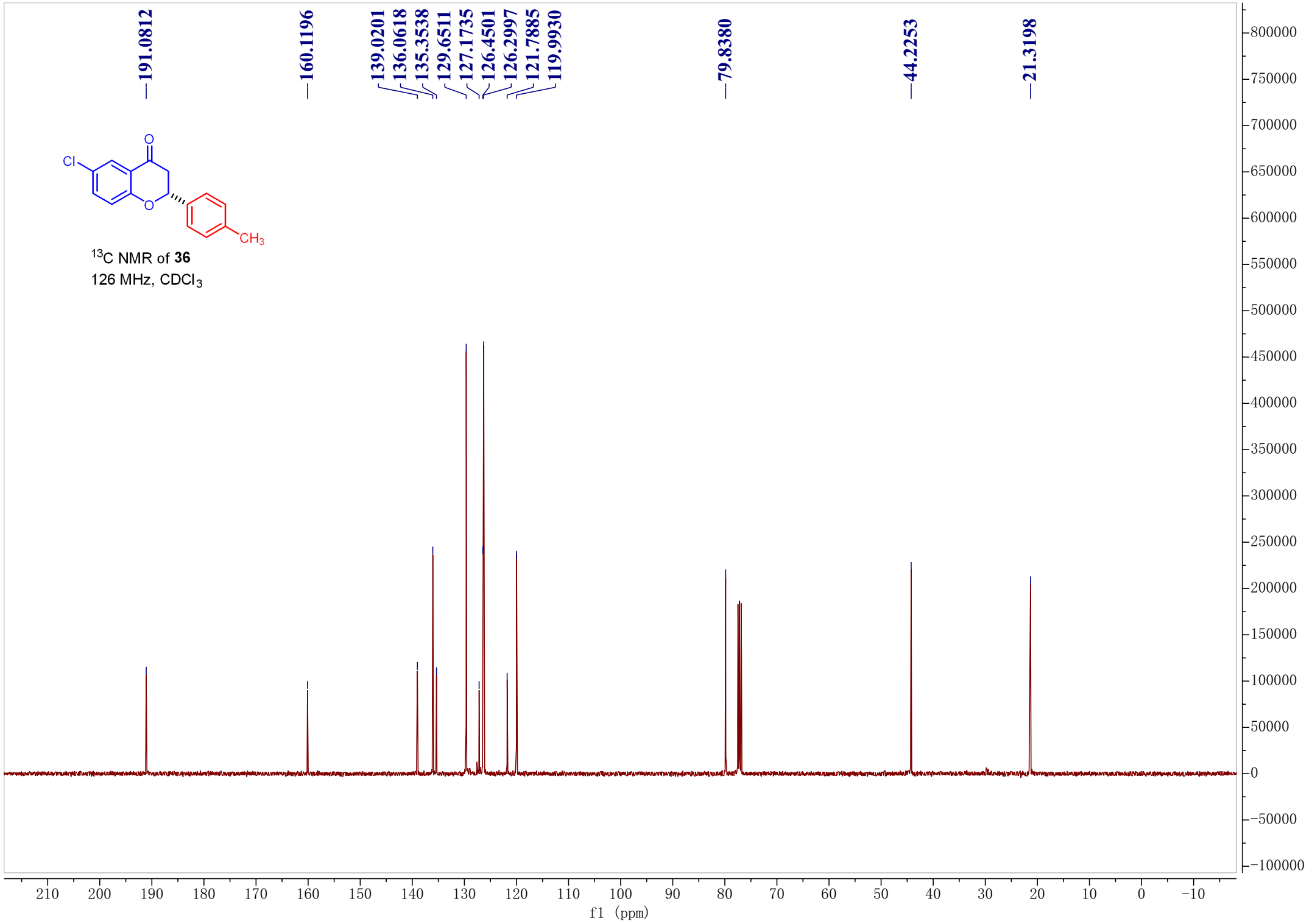

7.5744
7.5676
7.5574
7.5514
7.3625
7.3588
7.3506
7.3464
7.2455
7.2298
7.2125
7.2057
7.1966
7.1907
7.0270
7.0189
7.0087
5.4316
5.4259
5.4043
5.3987
3.0990
3.0717
3.0647
3.0382
2.8905
2.8848
2.8837
2.8563
2.8505
2.3768
F
O
O
CH3
1H NMR of 34
500 MHz, CDCl3
0.97
2.14
3.28
1.02
1.00
1.06
1.06
3.31
f1 (ppm)

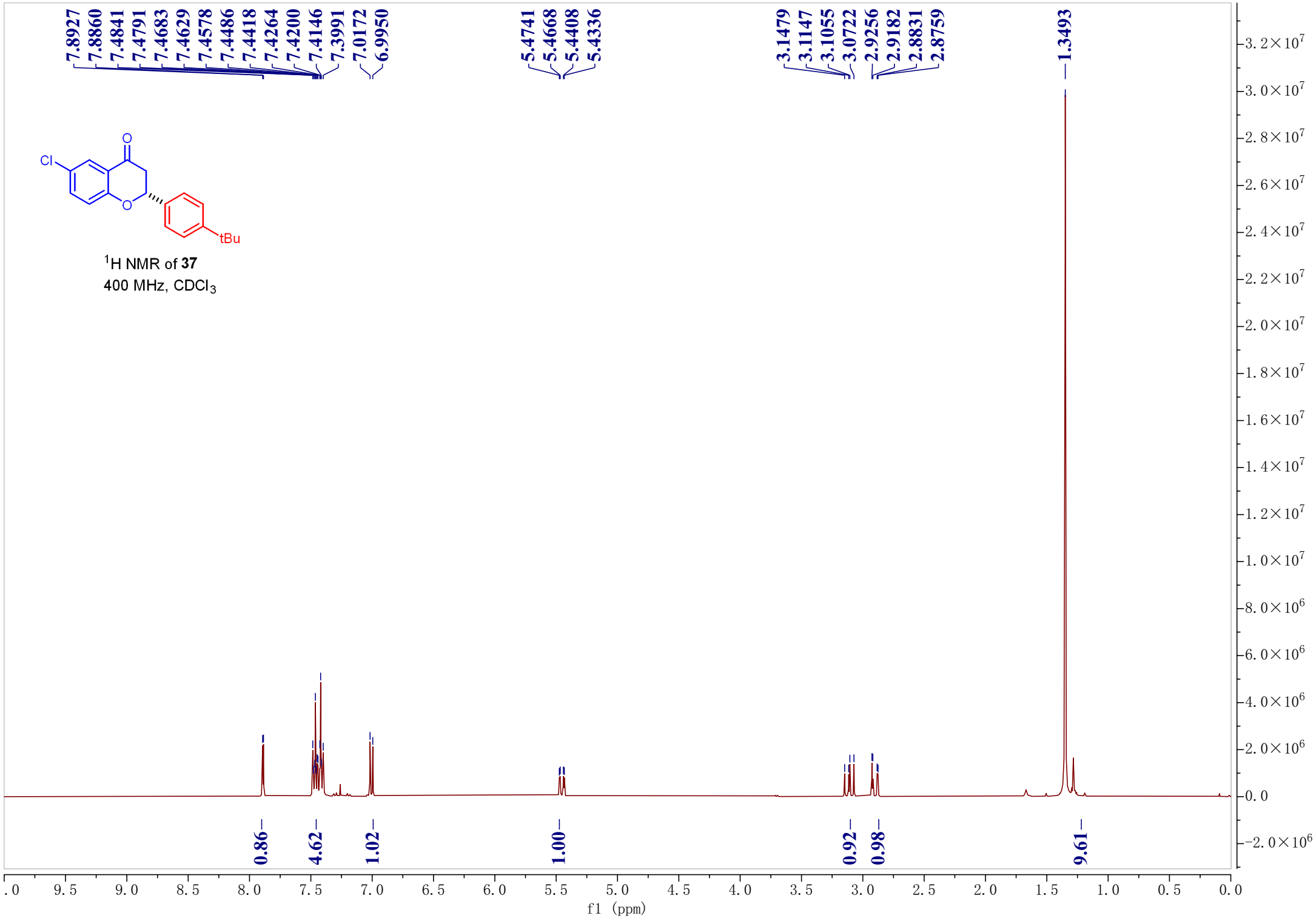

191.5575
158.4294
157.9988
156.5011
139.0287
135.5689
129.6808
126.3377
123.9200
123.7273
121.5199
121.4715
120.0044
119.9463
112.2257
112.0361
79.9178
44.3661
21.3471
F
O
O
CH3
13C NMR of 34
126 MHz, CDCl3
f1 (ppm)

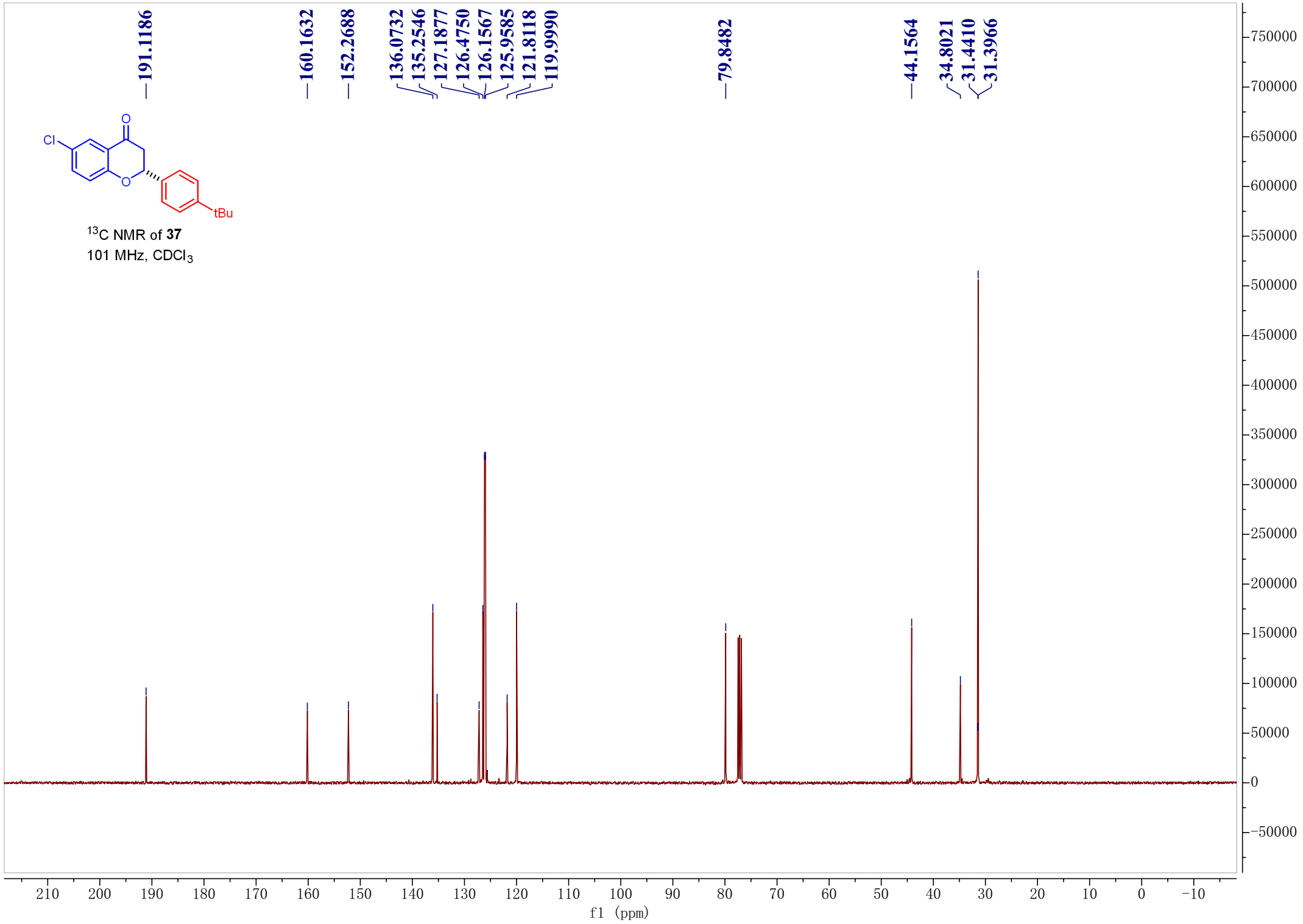

7.8889
7.8822
7.4893
7.4840
7.4785
7.4723
7.4682
7.4638
7.4600
7.4492
7.4444
7.4378
7.4348
7.4294
7.4253
7.4191
7.4142
7.4085
7.4057
7.3975
7.0287
7.0067
5.4942
5.4868
5.4611
5.4536
3.1181
3.0852
3.0757
3.0427
2.9316
2.9241
2.8891
2.8817
Cl
O
O
F
1H NMR of 35
400 MHz, CDCl3
0.93
5.82
0.99
1.00
1.02
1.01
f1 (ppm)

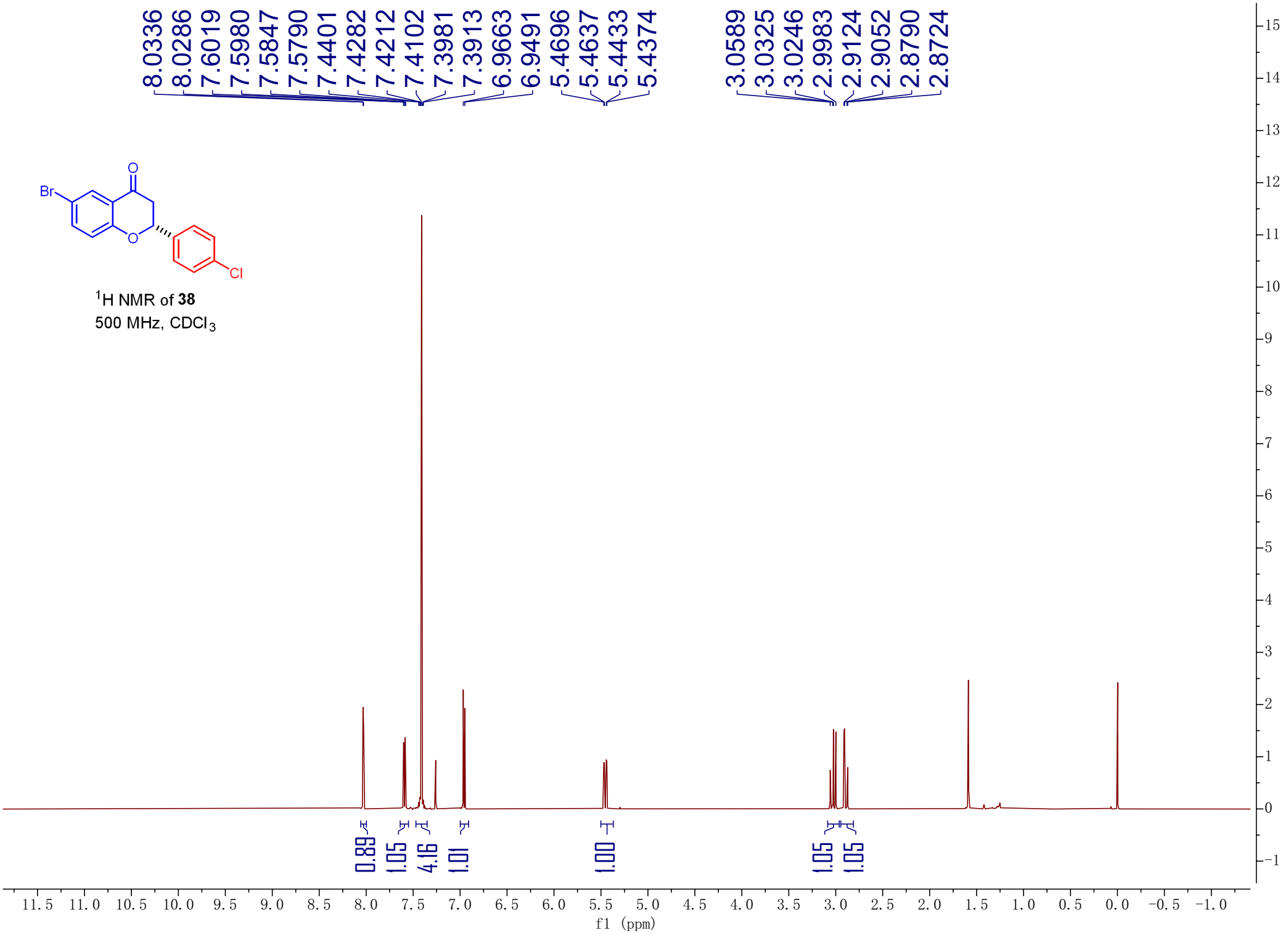

190.8970
160.0498
138.3488
136.1128
129.0569
129.0108
127.2739
126.4765
126.2462
121.7962
119.9812
79.9045
44.3517
Cl
O
O
F
^{13}C NMR of **35**
101 MHz, $CDCl_3$
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.7944
7.7878
7.3562
7.3493
7.3363
7.3341
7.3295
7.3273
7.2804
7.2601
7.1704
7.1679
7.1487
6.9236
6.9015
5.3670
5.3597
5.3340
5.3268
3.0315
2.9985
2.9891
2.9561
2.8190
2.8116
2.7765
2.7693
2.2998
Cl
O
O
CH3
1H NMR of 36
500 MHz, CDCl3
0.91
1.05
1.91
2.02
1.00
1.00
1.03
1.02
3.05
f1 (ppm)

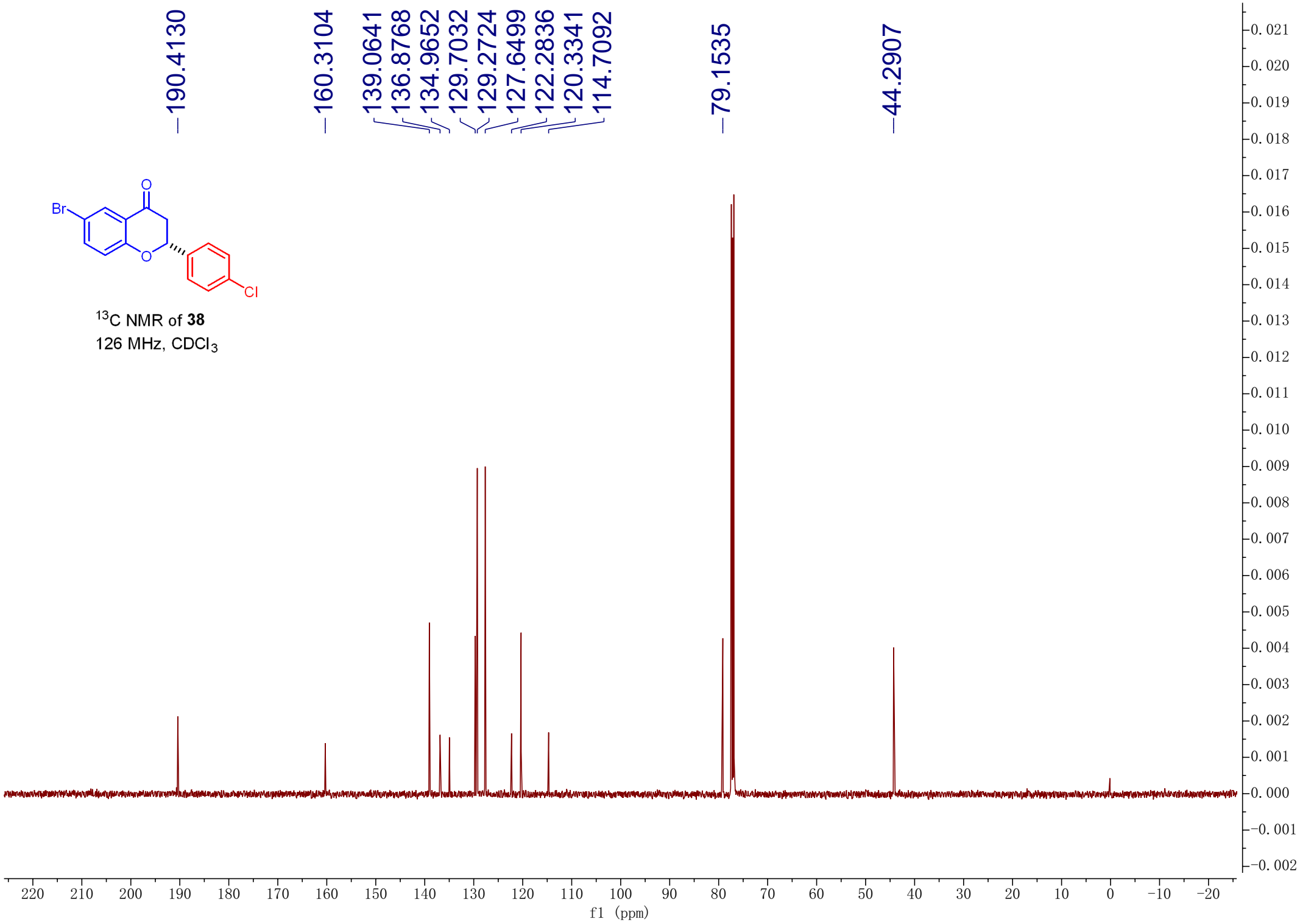

191.0812
160.1196
139.0201
136.0618
135.3538
129.6511
127.1735
126.4501
126.2997
121.7885
119.9930
79.8380
44.2253
21.3198
Cl
O
O
CH3
13C NMR of 36
126 MHz, CDCl3
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
−100000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

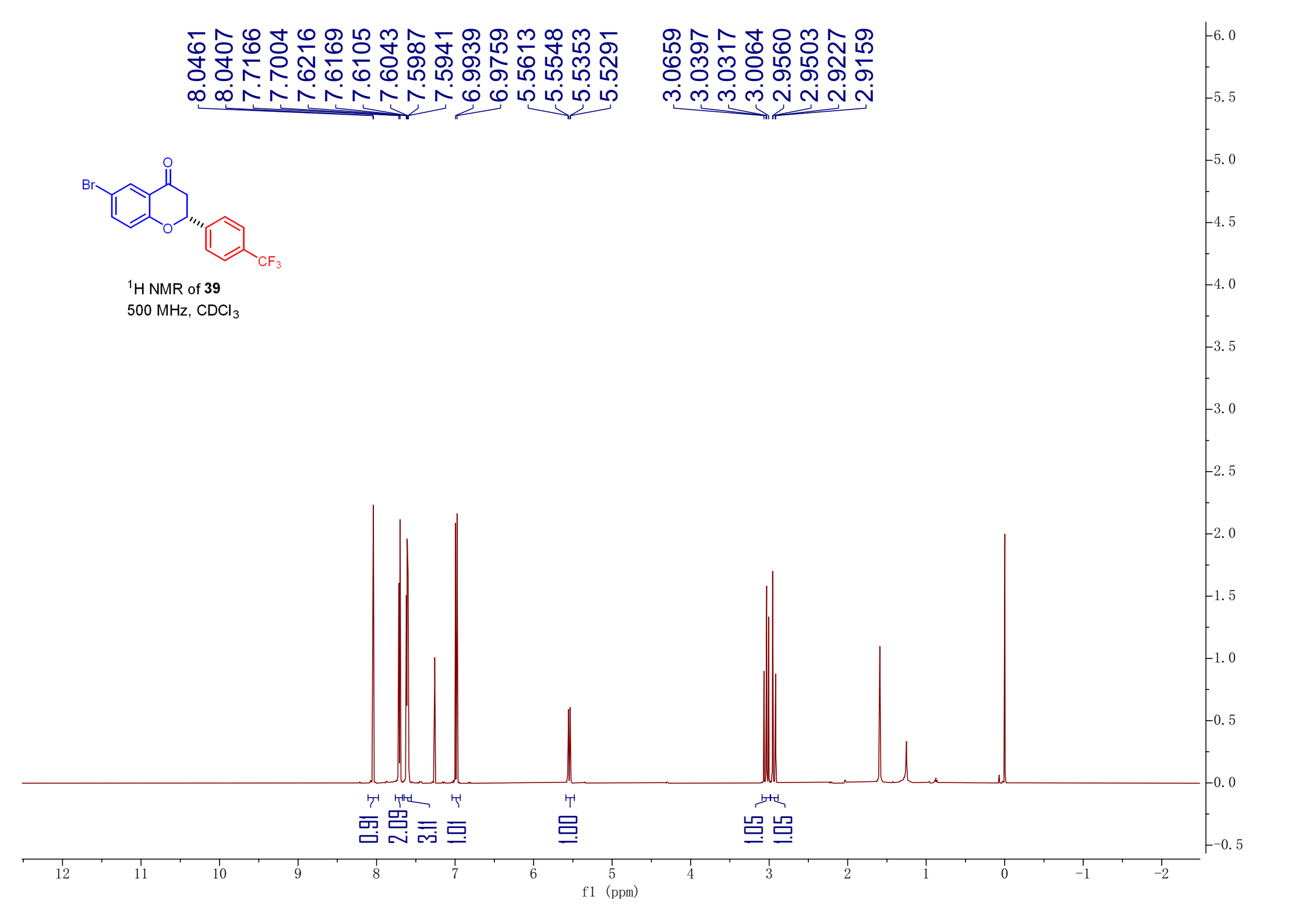

7.8927
7.8860
7.4841
7.4791
7.4683
7.4629
7.4578
7.4486
7.4418
7.4264
7.4200
7.4146
7.3991
7.0172
6.9950
5.4741
5.4668
5.4408
5.4336
3.1479
3.1147
3.1055
3.0722
2.9256
2.9182
2.8831
2.8759
1.3493
Cl
O
O
tBu
1H NMR of 37
400 MHz, CDCl3
0.86
4.62
1.02
1.00
0.92
0.98
9.61
f1 (ppm)


191.1186
160.1632
152.2688
136.0732
135.2546
127.1877
126.4750
126.1567
125.9585
121.8118
119.9990
79.8482
44.1564
34.8021
31.4410
31.3966
Cl
O
O
tBu
13C NMR of 37
101 MHz, CDCl3
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
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)

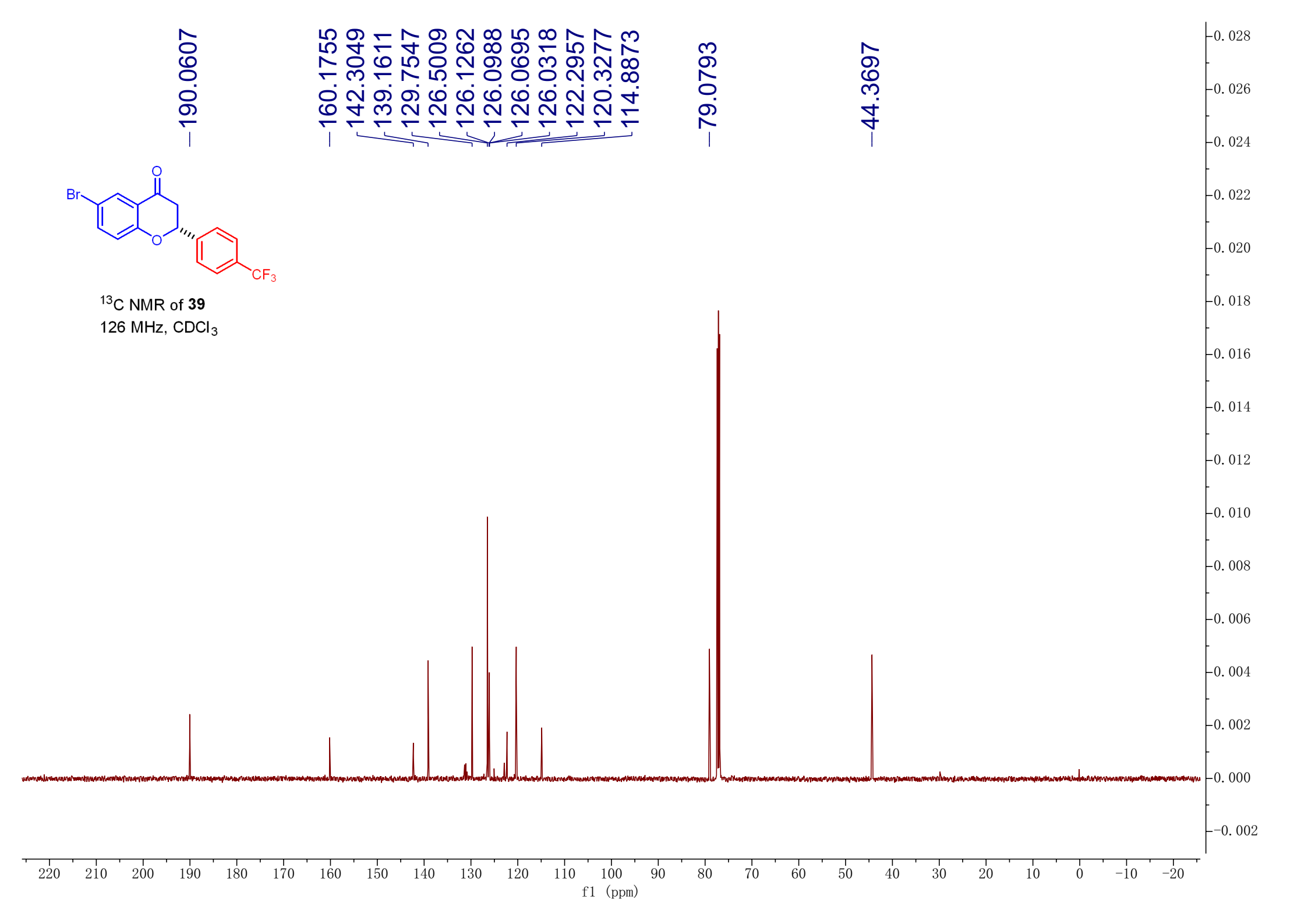


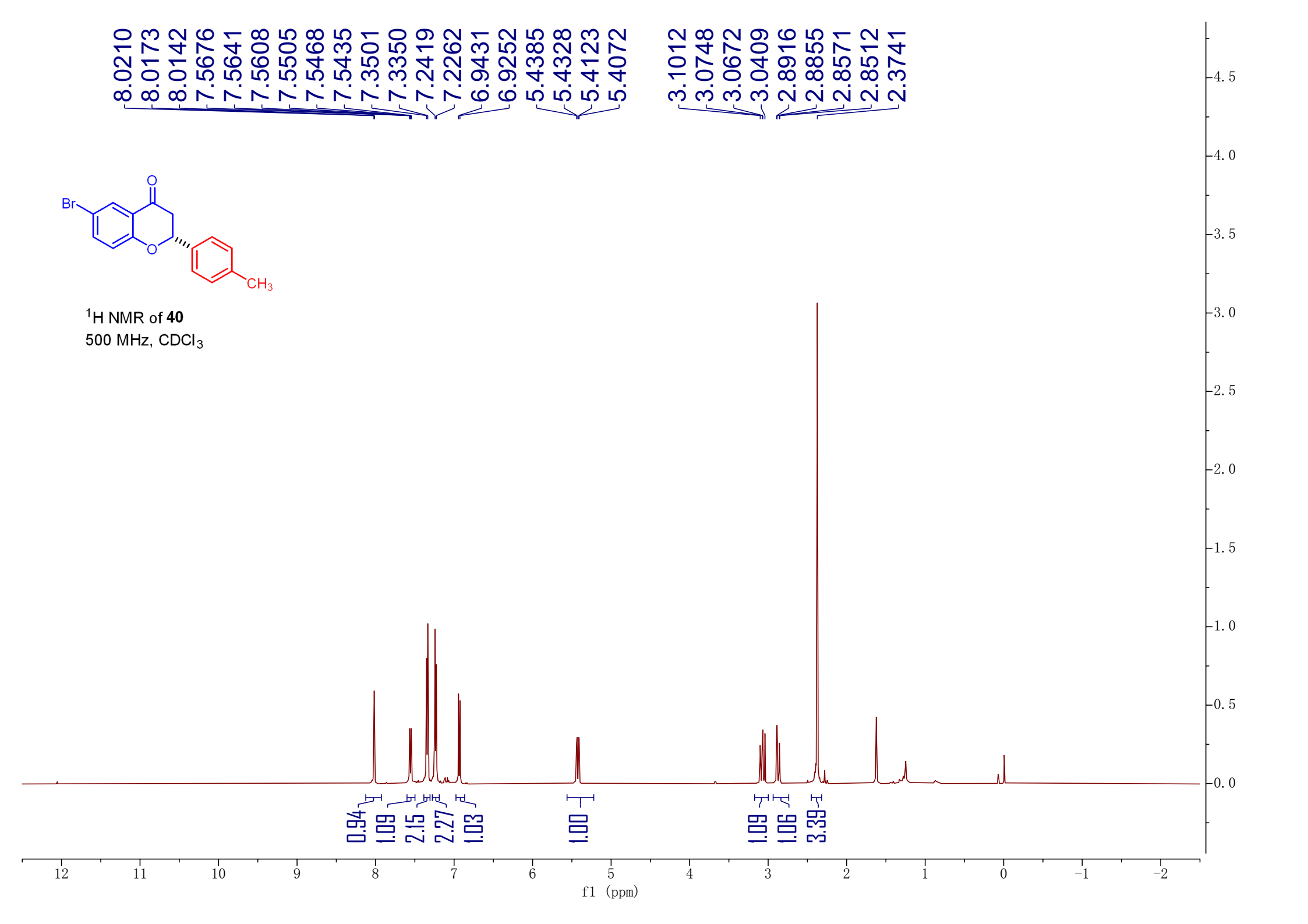
^{1}H NMR of **38**
500 MHz, $CDCl_3$

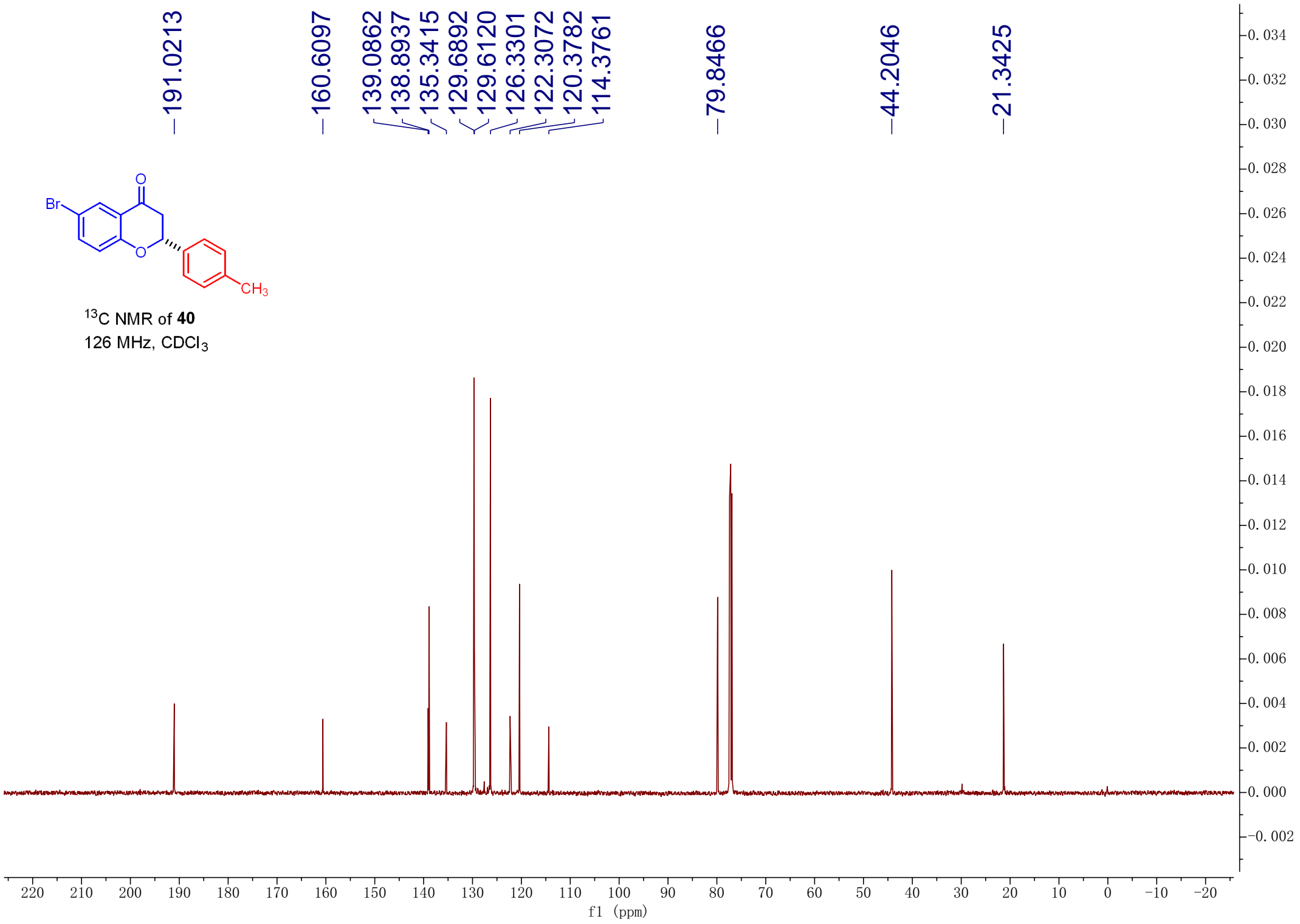

190.4130
160.3104
139.0641
136.8768
134.9652
129.7032
129.2724
127.6499
122.2836
120.3341
114.7092
79.1535
44.2907
Br
O
O
Cl
^{13}C NMR of **38**
126 MHz, $CDCl_3$
f1 (ppm)

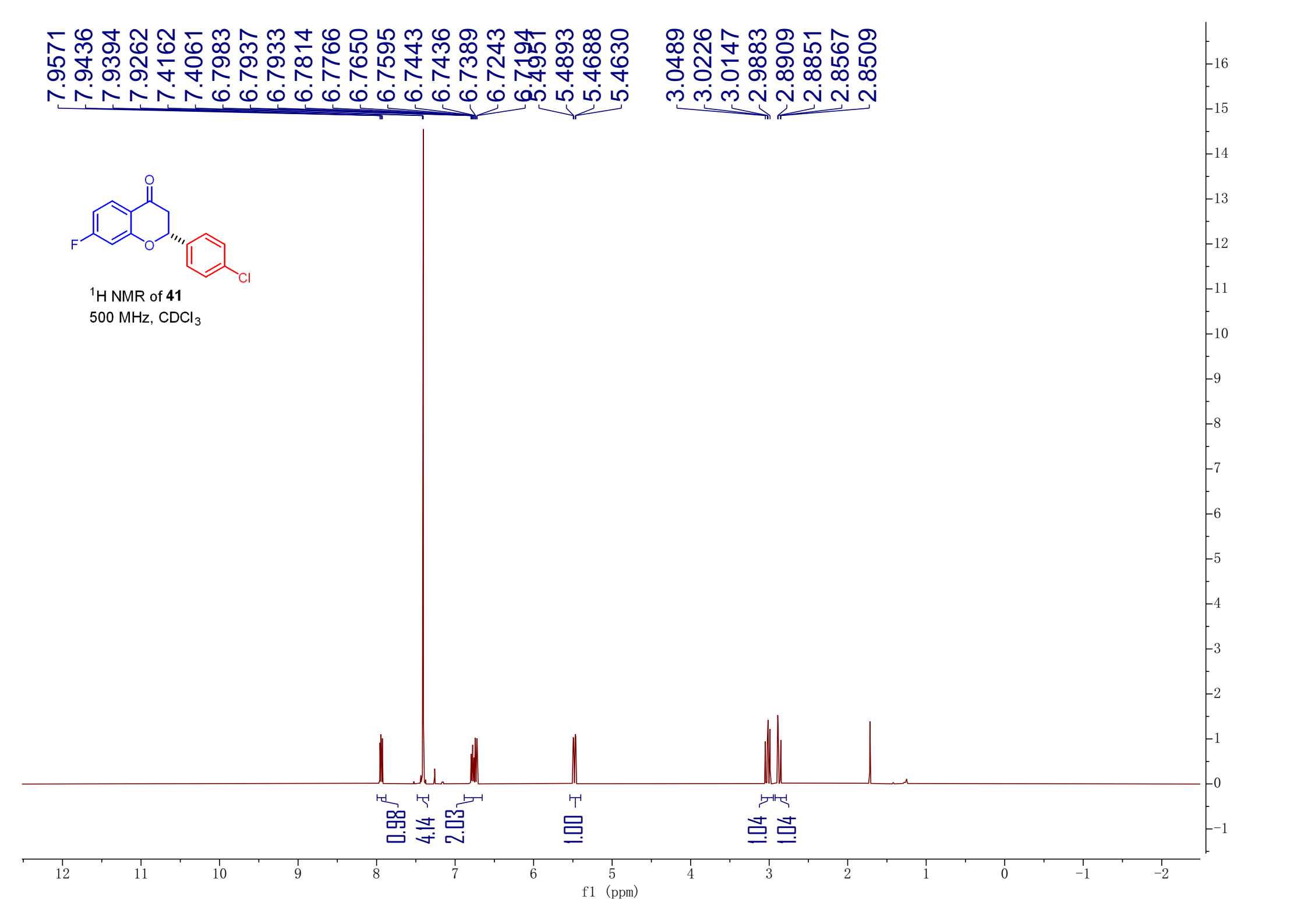


^{1}H NMR of **39**
500 MHz, $CDCl_3$

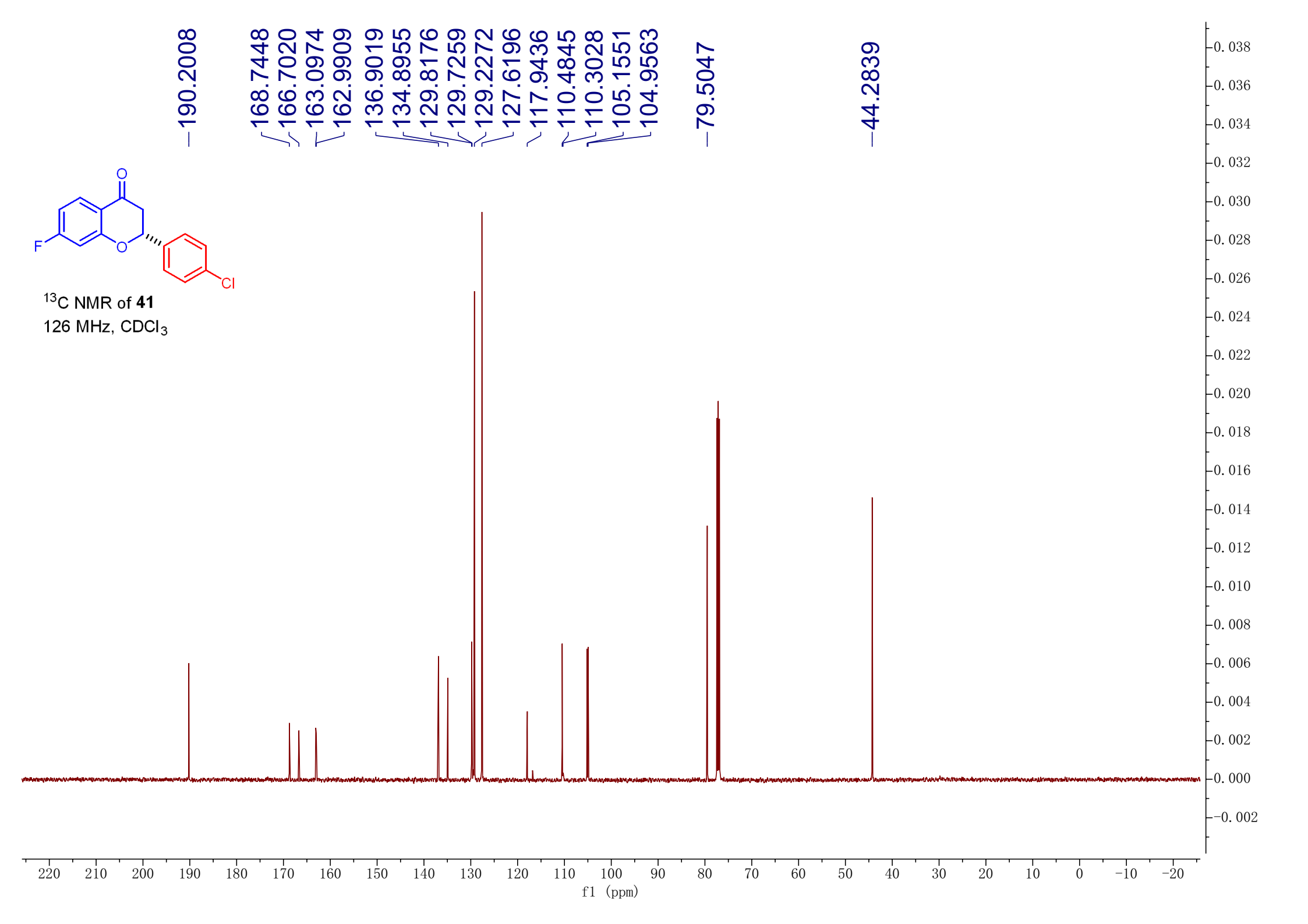

190.0607
160.1755
142.3049
139.1611
129.7547
126.5009
126.1262
126.0988
126.0695
126.0318
122.2957
120.3277
114.8873
79.0793
44.3697
Br
O
O
CF3
13C NMR of 39
126 MHz, CDCl3
0.028
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
-0.002
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

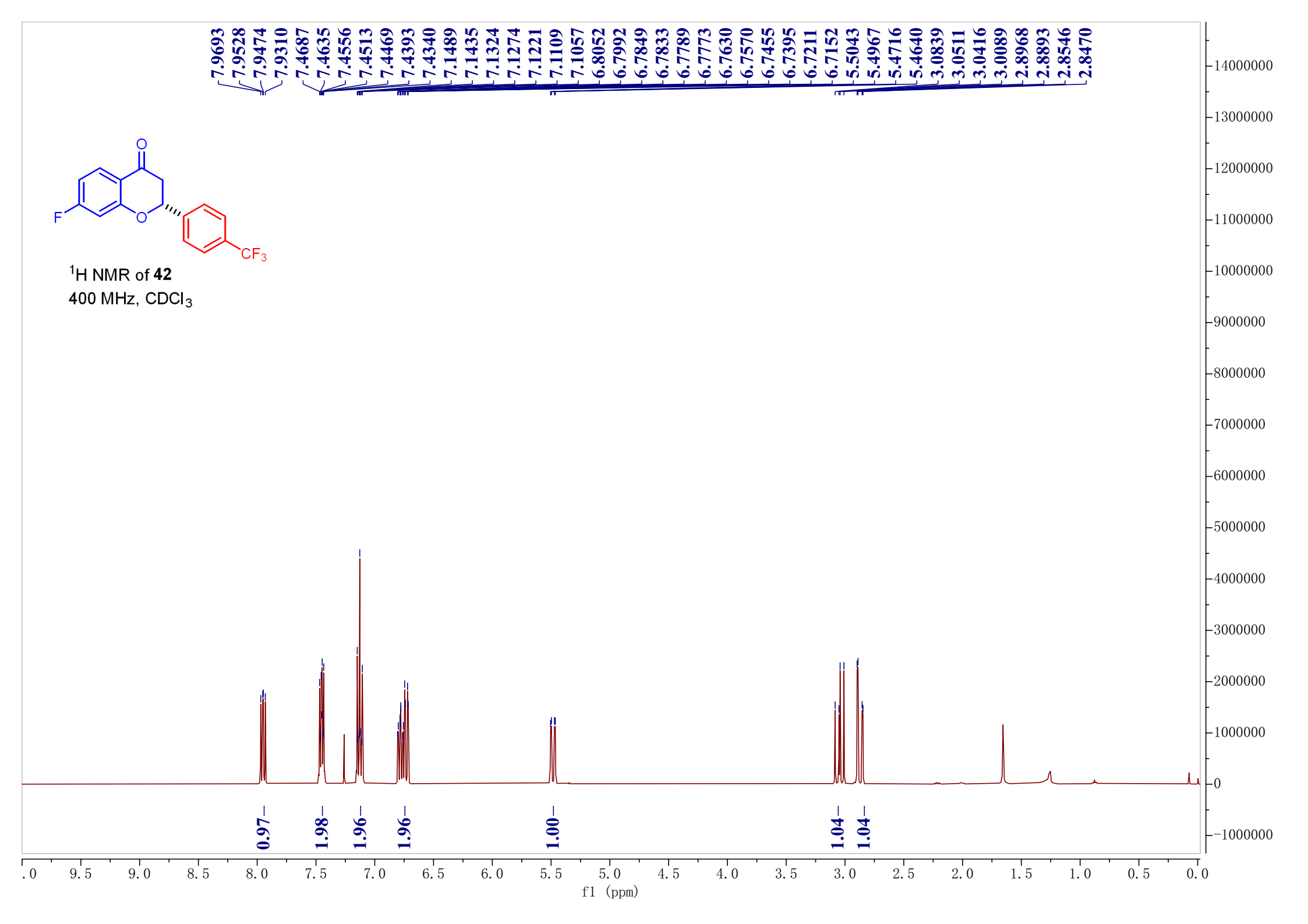

8.0210
8.0173
8.0142
7.5676
7.5641
7.5608
7.5505
7.5468
7.5435
7.3501
7.3350
7.2419
7.2262
6.9431
6.9252
5.4385
5.4328
5.4123
5.4072
3.1012
3.0748
3.0672
3.0409
2.8916
2.8855
2.8571
2.8512
2.3741
Br
O
O
CH3
1H NMR of 40
500 MHz, CDCl3
0.94
1.09
2.15
2.27
1.03
1.00
1.09
1.06
3.39
f1 (ppm)

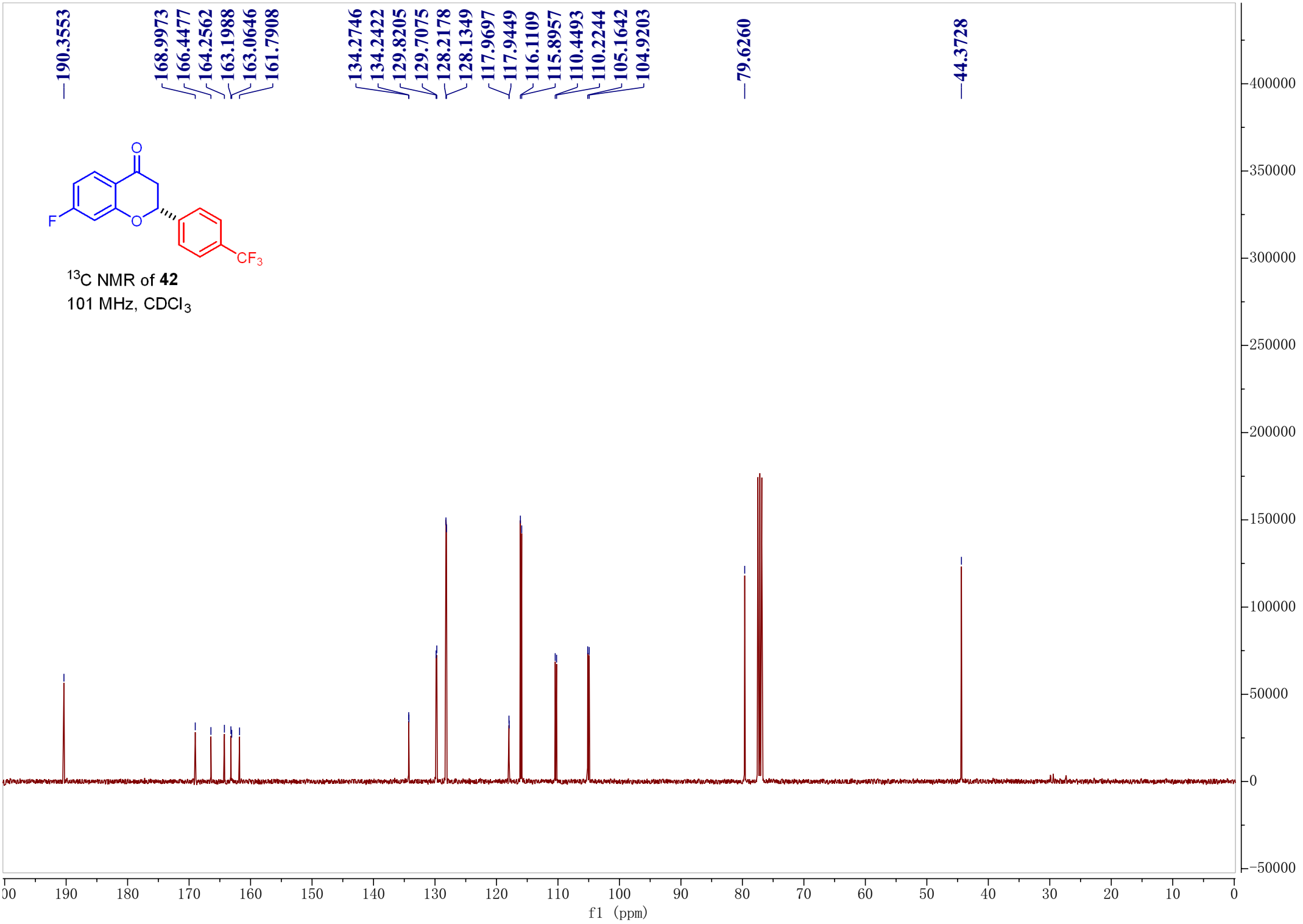

191.0213
160.6097
139.0862
138.8937
135.3415
129.6892
129.6120
126.3301
122.3072
120.3782
114.3761
79.8466
44.2046
21.3425
Br
O
O
CH3
13C NMR of 40
126 MHz, CDCl3
f1 (ppm)

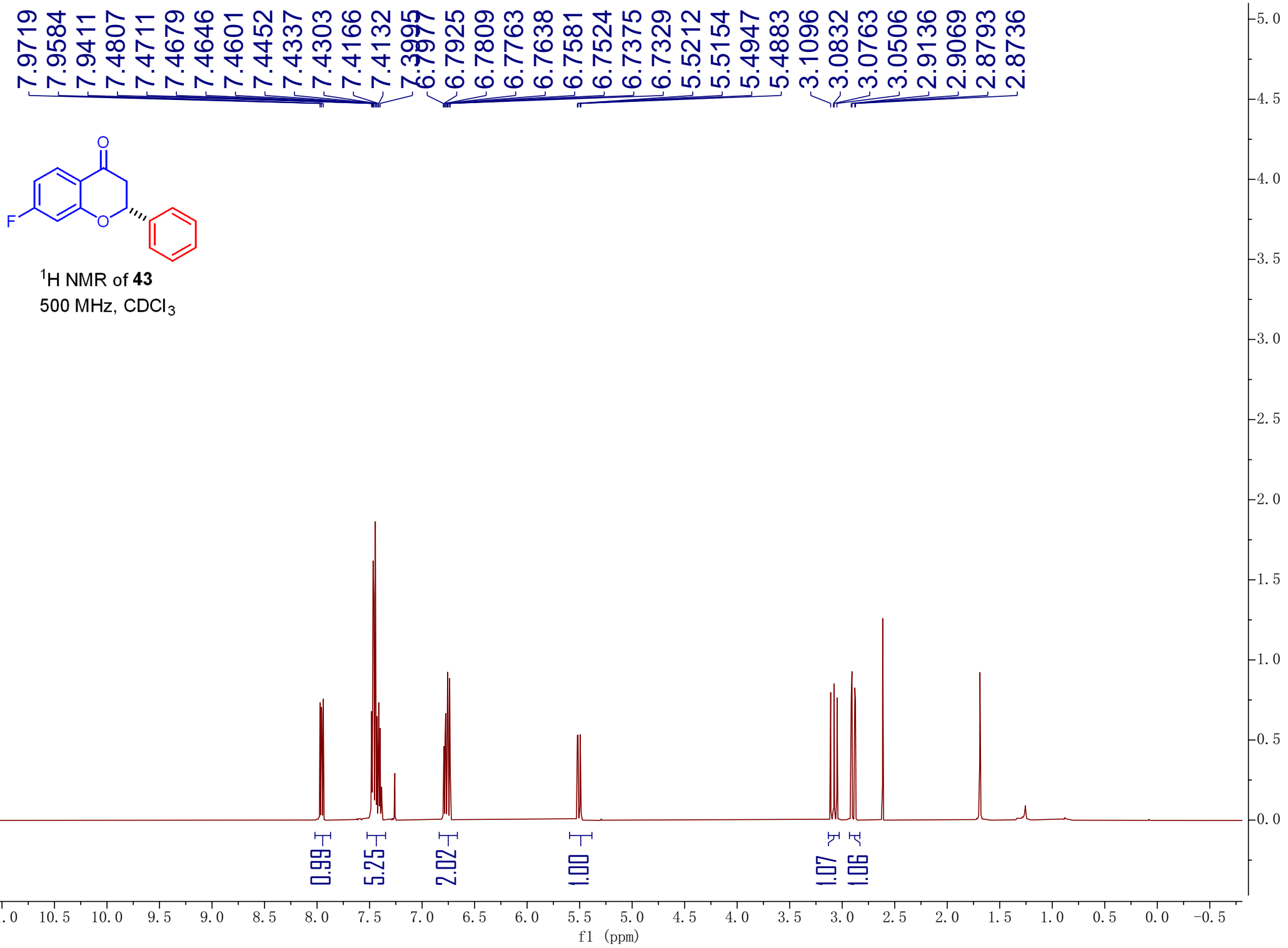


^{1}H NMR of **41**
500 MHz, $CDCl_3$


190.2008
168.7448
166.7020
163.0974
162.9909
136.9019
134.8955
129.8176
129.7259
129.2272
127.6196
117.9436
110.4845
110.3028
105.1551
104.9563
79.5047
44.2839
O
F
O
Cl
13C NMR of 41
126 MHz, CDCl3
f1 (ppm)

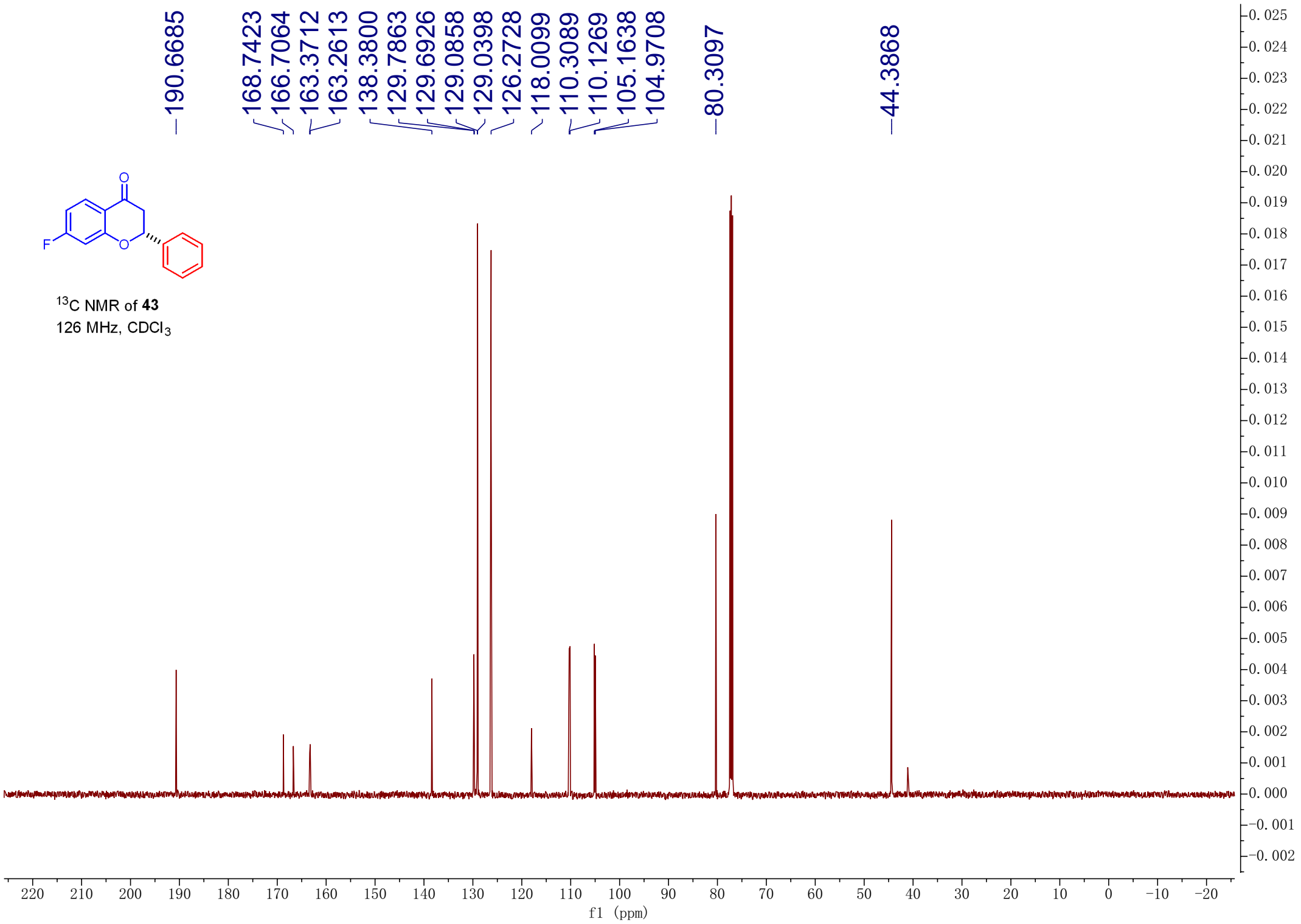

7.9693
7.9528
7.9474
7.9310
7.4687
7.4635
7.4556
7.4513
7.4469
7.4393
7.4340
7.1489
7.1435
7.1324
7.1274
7.1221
7.1109
7.1057
6.8052
6.7992
6.7849
6.7833
6.7789
6.7773
6.7630
6.7570
6.7455
6.7395
6.7211
6.7152
5.5043
5.4967
5.4716
5.4640
3.0839
3.0511
3.0416
3.0089
2.8968
2.8893
2.8546
2.8470
O
F
O
CF3
1H NMR of 42
400 MHz, CDCl3
0.97
1.98
1.96
1.96
1.00
1.04
1.04
f1 (ppm)


190.3553
168.9973
166.4477
164.2562
163.1988
163.0646
161.7908
134.2746
134.2422
129.8205
129.7075
128.2178
128.1349
117.9697
117.9449
116.1109
115.8957
110.4493
110.2244
105.1642
104.9203
79.6260
44.3728
O
F
O
CF3
13C NMR of 42
101 MHz, CDCl3
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



^{1}H NMR of **43**

500 MHz, $CDCl_3$


190.6685
168.7423
166.7064
163.3712
163.2613
138.3800
129.7863
129.6926
129.0858
129.0398
126.2728
118.0099
110.3089
110.1269
105.1638
104.9708
80.3097
44.3868
O
F
O
^{13}C NMR of **43**
126 MHz, $CDCl_3$
f1 (ppm)