Supporting Information

Difunctionalization of Alkenylpyridine *N*-Oxides by the Tandem Addition/Boekelheide Rearrangement

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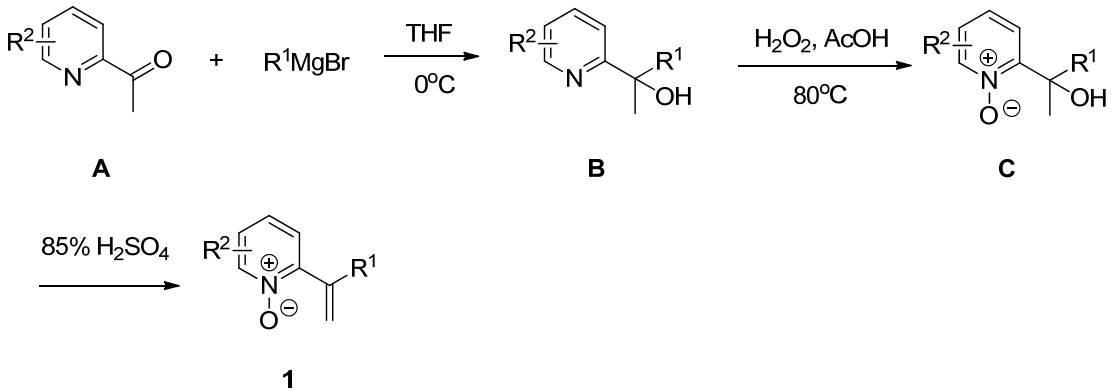
General methods:

Unless stated otherwise, all reactions were carried out in a flame dried glassware. All solvents were purified and dried according to standard methods prior to use. Alkenylpyridine *N*-Oxides **1**[1] and isothiocyanates **2**[2] were prepared according to literature. The solvents were distilled from indicated drying reagents: dichlormethane (CaH_2), tetrahydrofuran (Na), diethyl ether (Na), ethyl acetate ($CaCl_2$), 1,4-Dioxane (Na), toluene (Na). The reaction products were purified by chromatograph, using 200-300 mesh silica gel (Qingdao, China). ^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet or unresolved, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectra (HRMS) were obtained by the ESI ionization sources. IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm^{-1}.

General procedure and spectral data for the synthesis of 1[1]



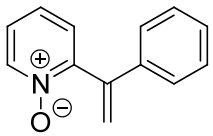
(1) To a solution of 2-acetylpyridine **A** (40 mmol) in THF (400 mL) was added PhMgBr (100 mmol) slowly at 0 °C, then the mixture was stirring overnight at room temperature. The reaction was monitored by TLC analysis. Upon completion, the reaction was quenched with water, extracted with EtOAc, the organic phase was washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by chromatography on silica gel to afford α-Phenyl-α-(2-pyridyl)ethanols **B**.

(2) 35% H_2O_2 (7 g) was added to α-Phenyl-α-(2-pyridyl)ethanol **B** (30 mmol) in glacial acetic acid (25 mL) under stirring, then the mixture was heated at 80 °C overnight. The reaction was monitored by TLC analysis. Upon completion, the mixture was concentrated, water was added and the product was extracted with DCM. The organic phase was washed with 5% aq $NaHCO_3$, dried over Na_2SO_4 and concentrated. The residue was purified by chromatography on silica gel affording α-Phenyl-α-(2-pyridyl-N-oxide)ethanols **C**.

(3) α-Phenyl-α-(2-pyridyl-N-oxide) ethanol **C** (2.15 g, 10 mmol) was dissolved in 85% H_2SO_4 (8 mL), the mixture was stirred for 20 min at 100 °C. Upon completion, the mixture was cooled to room temperature, then poured onto ice-water. The product was extracted with DCM, the organic phase was washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by chromatography on silica gel affording alkenylpyridine *N*-Oxides **1**.

Spectral data for the alkenylpyridine *N*-Oxides 1

2-(1-phenylvinyl)pyridine 1-oxide (**1a**)



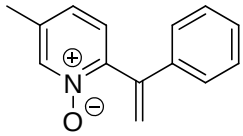
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30-8.17 (m, 1H), 7.39-7.35 (m, 1H), 7.34-7.21 (m, 7H), 5.94 (s, 1H), 5.63 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 142.8, 140.4, 137.7, 128.7, 128.3, 128.0, 126.0, 125.4, 125.3, 119.5;

IR: 3056, 1488, 1420, 1245, 1160, 911, 863, 778, 688 cm^{-1};

HRMS (ESI): $C_{13}H_{11}NO$+H, Calc: 198.0913, Found: 198.0910.

5-methyl-2-(1-phenylvinyl)pyridine 1-oxide (**1b**)



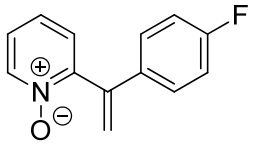
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.36 – 7.23 (m, 6H), 7.11 (s, 1H), 5.92 (s, 1H), 5.63 (s, 1H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 142.6, 140.2, 138.0, 135.9, 128.6, 128.2, 127.3, 126.7, 126.0, 119.3, 18.2;

IR: 2988, 1385, 1274, 1169, 938, 814, 754, 696 cm^{-1};

HRMS (ESI): $C_{14}H_{13}NO$+H, Calc: 212.1070, Found: 212.1065.

2-(1-(4-fluorophenyl)vinyl)pyridine 1-oxide (**1c**)



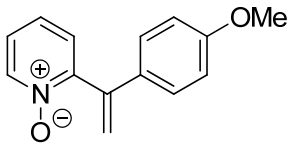
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.18 (m, 1H), 7.44 – 7.35 (m, 1H), 7.36 – 7.19 (m, 4H), 7.11 – 6.92 (m, 2H), 5.88 (s, 1H), 5.60 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 161.4, 150.2, 141.8, 140.3, 133.8, 133.7, 133.7, 127.8, 127.6, 127.5, 125.4, 125.4, 119.3, 115.6, 115.4;

IR: 3406, 1602, 1510, 1426, 1226, 1162, 837, 768 cm^{-1};

HRMS (ESI): $C_{13}H_{10}FNO$+H, Calc: 216.0819, Found: 216.0811.

2-(1-(4-methoxyphenyl)vinyl)pyridine 1-oxide (**1d**)



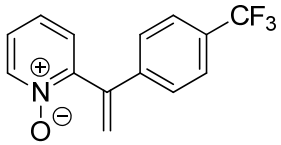
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (dd, *J* = 6.0, 1.7 Hz, 1H), 7.37 (dd, *J* = 6.8, 3.1 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.22 (d, *J* = 2.1 Hz, 1H), 7.20 (d, *J* = 2.2 Hz, 1H), 6.97 – 6.66 (m, 2H), 5.87 (s, 1H), 5.52 (s, 1H), 3.79 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 150.7, 142.0, 140.3, 130.1, 127.9, 127.1, 125.6, 125.1, 117.6, 114.0, 55.3;

IR: 3382, 1603, 1511, 1427, 1242, 1159, 1027, 838, 768 cm^{-1};

HRMS (ESI): $C_{14}H_{13}NO_2$+H, Calc: 228.1019, Found: 228.1027.

2-(1-(4-(trifluoromethyl)phenyl)vinyl)pyridine 1-oxide (**1e**)



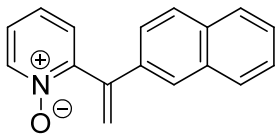
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 – 8.08 (m, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.27 (m, 2H), 5.98 (s, 1H), 5.71 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 142.0, 141.2, 140.2, 130.4, 130.1, 129.8, 129.5, 127.8, 126.1, 125.6, 125.6, 125.6, 125.5, 125.5, 122.8, 121.4, 100.0;

IR: 3048, 1614, 1425, 1324, 1253, 1101, 851, 764 cm^{-1};

HRMS(ESI): $C_{14}H_{10}F_3NO$+H, Calc: 266.0787, Found: 266.0787.

2-(1-(naphthalen-2-yl)vinyl)pyridine 1-oxide (**1f**)



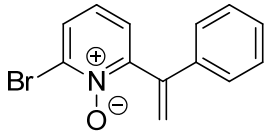
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 – 8.16 (m, 1H), 7.80 (dd, *J* = 8.9, 5.1 Hz, 2H), 7.74 (dt, *J* = 6.9, 3.6 Hz, 1H), 7.63 (s, 1H), 7.49 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.35 – 7.26 (m, 2H), 6.08 (s, 1H), 5.74 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 142.6, 140.4, 135.1, 133.4, 133.2, 128.3, 128.3, 128.0, 127.6, 126.2, 126.1, 125.4, 125.3, 125.0, 124.0, 119.9;

IR: 2987, 1483, 1417, 1260, 1246, 855, 821, 752 cm^{-1};

HRMS (ESI): $C_{17}H_{13}NO$+H, Calc: 248.1070, Found: 248.1068.

2-bromo-6-(1-phenylvinyl)pyridine 1-oxide (**1g**)



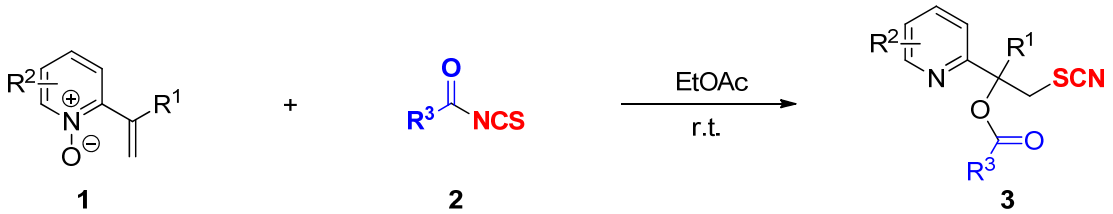
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.40 – 7.21 (m, 6H), 7.12 (t, *J* = 7.9 Hz, 1H), 5.89 (s, 1H), 5.63 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 143.0, 137.6, 130.0, 128.6, 128.2, 126.4, 125.9, 124.6, 124.5, 119.8;

IR: 2987, 1493, 1365, 1249, 915, 795, 750, 705cm^{-1};

HRMS (ESI): $C_{13}H_{10}BrNO$+H, Calc: 276.0019, Found: 276.0005.

General procedure and spectral data for the synthesis of 3



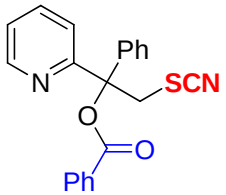
To a solution of alkenylpyridine *N*-Oxides **1** (0.10 mmol, 1.0 equiv) in dry EtOAc (1 mL) was added benzoyl isothiocyanates **2** (0.12 mmol, 1.2 equiv). Then the reaction mixture was stirred for 6 h at room temperature. The reaction was monitored by TLC analysis. Upon completion, the solvent was removed under vacuum and residue was purified by flash column chromatography (petroleum ether/ EtOAc 10:1) to give the pure desired products **3**.

1 mmol scale for the synthesis of 3a

To a solution of alkenylpyridine *N*-Oxides **1** (1.0 mmol, 1.0 equiv) in dry EtOAc (10 mL) was added benzoyl isothiocyanates **2** (1.2 mmol, 1.2 equiv). Then the reaction mixture was stirred for 6 h at room temperature. The reaction was monitored by TLC analysis. Upon completion, the solvent was removed under vacuum and residue was purified by flash column chromatography (petroleum ether/ EtOAc 10:1) to give the pure desired products **3a** (237.6 mg, 66.0% yield).

Spectral data for the 3

1-phenyl-1-(pyridin-2-yl)-2-thiocyanatoethyl benzoate (**3a**)



White solid (21 mg, 58% yield);

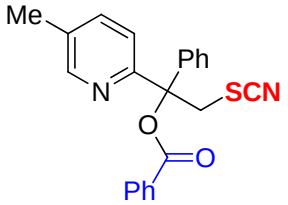
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 4.4 Hz, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.73 – 7.60 (m, 2H), 7.59 – 7.43 (m, 5H), 7.35 (dt, *J* = 24.0, 7.1 Hz, 3H), 7.28 – 7.19 (m, 1H), 4.77 (d, *J* = 13.7 Hz, 1H), 4.67 (d, *J* = 13.7 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 160.3, 148.5, 140.6, 137.2, 133.7, 130.0, 129.9, 128.8, 128.7, 128.4, 125.7, 123.0, 121.0, 112.2, 85.9, 41.8;

IR: 2154, 1723, 1586, 1277, 1232, 1093, 748, 707 cm^{-1};

HRMS (ESI): $C_{21}H_{16}N_2O_2S$+H, Calc: 361.1005, Found: 361.0995.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl benzoate (**3b**)



Yellow oil (36 mg, 60% yield);

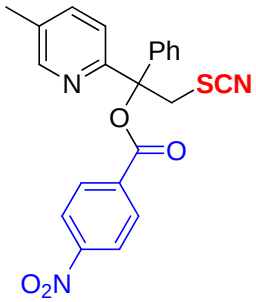
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.25 – 8.08 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.3 Hz, 3H), 7.36 (dd, *J* = 17.1, 7.0 Hz, 4H), 4.75 (d, *J* = 13.7 Hz, 1H), 4.66 (d, *J* = 13.6 Hz, 1H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 157.4, 148.7, 140.8, 137.8, 133.7, 132.7, 130.1, 130.0, 128.7, 128.7, 128.3, 125.7, 120.6, 112.3, 85.9, 41.9, 18.2;

IR: 2156, 1725, 1482, 1265, 1236, 1093, 734, 709 cm^{-1};

HRMS (ESI): $C_{22}H_{18}N_2O_2S$+H, Calc: 375.1162, Found: 375.1153.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl 4-nitrobenzoate (**3c**)



White solid (31 mg, 75% yield);

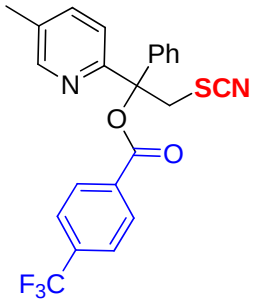
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.41 – 8.27 (m, 4H), 7.50 (s, 1H), 7.47 – 7.27 (m, 6H), 4.88 – 4.49 (m, 2H), 2.35 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 156.8, 150.9, 148.9, 140.2, 137.9, 135.5, 133.1, 131.1, 128.8, 128.6, 125.6, 123.8, 120.6, 112.3, 87.1, 41.5, 18.2;

IR: 2154, 1730, 1526, 1277, 1095, 836, 716, 697 cm^{-1};

HRMS (ESI): $C_{22}H_{17}N_3O_4S$+H, Calc: 420.1013, Found: 420.1005.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl 4-(trifluoromethyl)benzoate (**3d**)



Yellow oil (31 mg, 69% yield);

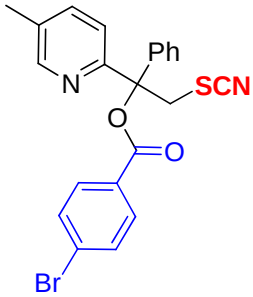
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.30 (m, 7H), 4.76 (d, *J* = 13.9 Hz, 1H), 4.62 (d, *J* = 13.9 Hz, 1H), 2.34 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 157.0, 148.9, 140.4, 137.9, 135.5, 135.2, 134.9, 134.6, 133.4, 132.9, 130.3, 128.8, 128.5, 125.8, 125.8, 125.7, 125.7, 125.6, 122.2, 120.6, 112.3, 86.7, 41.6, 18.2;

IR: 2156, 1731, 1324, 1278, 1129, 1093, 1064, 737, 699 cm^{-1};

HRMS (ESI): $C_{23}H_{17}F_3N_2O_2S$+H, Calc: 443.1036, Found: 443.1028.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl 4-bromobenzoate (**3e**)



Yellow oil (26 mg, 58% yield);

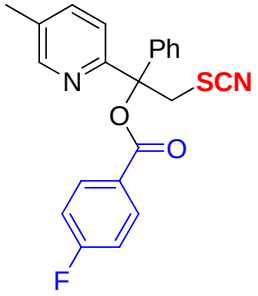
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.55 – 7.29 (m, 7H), 4.73 (d, *J* = 13.8 Hz, 1H), 4.61 (d, *J* = 13.8 Hz, 1H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3, 157.2, 148.8, 140.6, 137.9, 132.8, 132.1, 131.4, 129.0, 128.9, 128.7, 128.4, 125.6, 120.6, 112.3, 86.3, 41.8, 18.2;

IR: 2155, 1726, 1589, 1265, 1226, 1092, 1009, 736, 699 cm^{-1};

HRMS (ESI): $C_{28}H_{17}BrN_2O_2S$+H, Calc: 453.0267, Found: 453.0273.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl 4-fluorobenzoate (**3f**)



Yellow solid (24 mg, 61% yield);

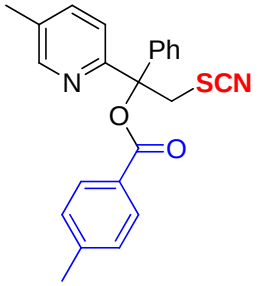
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.19 (ddd, *J* = 8.8, 5.1, 2.5 Hz, 2H), 7.59 – 7.27 (m, 7H), 7.25 – 7.12 (m, 2H), 4.93 – 4.27 (m, 2H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 164.9, 164.1, 157.3, 148.8, 140.7, 137.8, 132.8, 132.6, 132.5, 128.7, 128.4, 126.4, 125.7, 120.6, 116.0, 115.8, 112.4, 86.1, 41.8, 18.2;

IR: 2155, 1721, 1600, 1281, 1227, 1086, 766, 693 cm^{-1};

HRMS (ESI): $C_{22}H_{17}FN_2O_2S$+H, Calc: 393.1068, Found: 393.1072.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl 4-methylbenzoate (**3g**)



Yellow oil (20 mg, 51% yield);

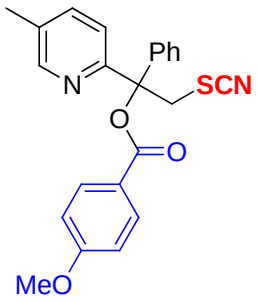
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.47 (dt, *J* = 8.4, 2.4 Hz, 3H), 7.43 – 7.27 (m, 6H), 4.94 – 4.48 (m, 2H), 2.45 (s, 3H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 157.6, 148.7, 144.5, 140.9, 137.8, 132.6, 130.0, 129.4, 128.7, 128.3, 127.4, 125.7, 120.5, 112.4, 85.6, 42.0, 21.8, 18.2;

IR: 2155, 1723, 1610, 1275, 1176, 1090, 749, 698 cm^{-1};

HRMS (ESI): $C_{23}H_{20}N_2O_2S$+H, Calc: 389.1318, Found: 389.1314.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl 4-methoxybenzoate (**3h**)



Yellow oil (14 mg, 35% yield);

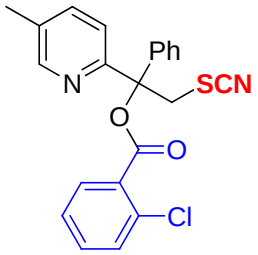
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 3H), 7.35 (dq, *J* = 14.9, 7.1 Hz, 4H), 7.00 (d, *J* = 8.8 Hz, 2H), 4.74 (d, *J* = 13.6 Hz, 1H), 4.64 (d, *J* = 13.6 Hz, 1H), 3.89 (s, 3H), 2.32 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 163.9, 157.6, 148.7, 141.0, 137.8, 132.6, 132.0, 128.7, 128.3, 125.7, 122.4, 120.5, 114.0, 112.4, 85.5, 55.6, 42.1, 18.2;

IR: 2154, 1717, 1604, 1257, 1165, 1089, 764, 696 cm^{-1};

HRMS (ESI): $C_{23}H_{20}N_2O_3S$+H, Calc: 405.1267, Found: 405.1271.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl 2-chlorobenzoate (**3i**)



Yellow oil (27 mg, 65% yield);

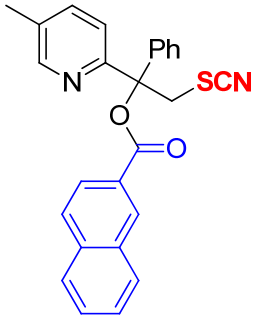
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.17 – 7.84 (m, 1H), 7.54 – 7.43 (m, 6H), 7.43 – 7.28 (m, 4H), 4.77 (d, *J* = 13.7 Hz, 1H), 4.67 (d, *J* = 13.7 Hz, 1H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 157.1, 148.8, 140.3, 137.8, 133.6, 133.1, 132.7, 132.0, 131.2, 130.1, 128.6, 128.4, 126.9, 125.9, 120.8, 112.3, 87.0, 41.8, 18.2;

IR: 2155, 1736, 1591, 1263, 1111, 1043, 748, 699 cm^{-1};

HRMS (ESI): $C_{22}H_{17}ClN_2O_2S$+H, Calc: 409.0772, Found: 409.0777.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl 2-naphthoate (**3j**)



Yellow oil (25 mg, 59% yield);

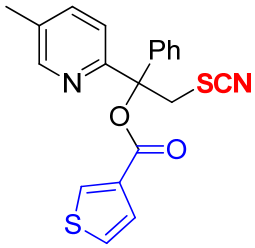
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.44 (s, 1H), 8.18 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.94 (dd, *J* = 15.4, 8.4 Hz, 2H), 7.71 – 7.55 (m, 2H), 7.56 – 7.45 (m, 3H), 7.46 – 7.38 (m, 3H), 7.38 – 7.31 (m, 1H), 4.85 – 4.62 (m, 2H), 2.34 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 157.4, 148.8, 140.8, 137.9, 135.9, 132.7, 132.5, 131.7, 129.6, 128.7, 128.7, 128.6, 128.4, 127.9, 127.3, 126.9, 125.8, 125.2, 120.7, 112.5, 86.1, 42.1, 18.2;

IR: 2156, 1723, 1480, 1264, 1192, 1085, 735, 701 cm^{-1};

HRMS (ESI): $C_{26}H_{20}N_2O_2S$+H, Calc: 425.1318, Found: 425.1314.

1-(5-methylpyridin-2-yl)-1-phenyl-2-thiocyanatoethyl thiophene-3-carboxylate (**3k**)



Yellow oil (21 mg, 55% yield);

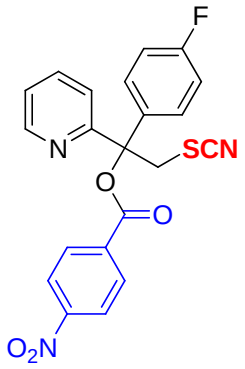
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 – 8.31 (m, 1H), 7.99 – 7.86 (m, 1H), 7.65 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.38 (dd, *J* = 8.0, 6.1 Hz, 3H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.17 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.78 – 4.53 (m, 2H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 157.2, 148.8, 140.6, 137.9, 134.6, 133.3, 133.3, 132.7, 128.7, 128.4, 128.2, 125.7, 120.6, 112.3, 86.2, 42.0, 18.2;

IR: 2156, 1715, 1412, 1263, 1221, 1072, 746, 702 cm^{-1};

HRMS (ESI): $C_{20}H_{16}N_2O_2S_2$+H, Calc: 381.0726, Found: 381.074.

1-(4-fluorophenyl)-1-(pyridin-2-yl)-2-thiocyanatoethyl 4-nitrobenzoate (**3l**)



White solid (28 mg, 66% yield);

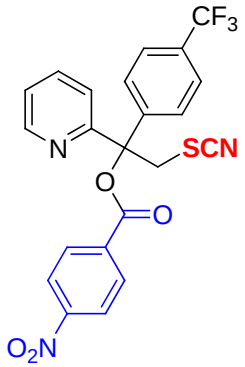
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 4.3 Hz, 1H), 8.34 (q, *J* = 8.9 Hz, 4H), 7.73 (td, *J* = 7.9, 1.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.42 (dd, *J* = 7.9, 6.0 Hz, 2H), 7.34 – 7.26 (m, 1H), 7.09 (t, *J* = 8.6 Hz, 2H), 4.71 (d, *J* = 14.1 Hz, 1H), 4.61 (d, *J* = 14.1 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 163.2, 161.3, 159.4, 151.0, 148.8, 137.5, 136.0, 135.2, 131.0, 127.7, 127.6, 123.9, 123.4, 120.9, 116.0, 115.8, 112.0, 86.8, 41.3;

IR: 2153, 1733, 1528, 1277, 1230, 1091, 751, 716 cm^{-1};

HRMS (ESI): $C_{21}H_{14}FN_3O_4S$+Na, Calc: 446.0581, Found: 446.0583.

1-(pyridin-2-yl)-2-thiocyanato-1-(4-(trifluoromethyl)phenyl)ethyl 4-nitrobenzoate (**3m**)



Yellow oil (28 mg, 60% yield);

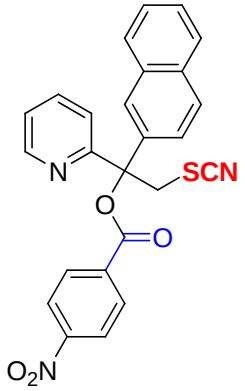
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 4.7 Hz, 1H), 8.44 – 8.26 (m, 4H), 7.75 (td, *J* = 7.8, 1.6 Hz, 1H), 7.71 – 7.55 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 7.4, 4.9 Hz, 1H), 4.82 (d, *J* = 14.2 Hz, 1H), 4.62 (d, *J* = 14.2 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.2, 158.9, 151.0, 149.0, 144.0, 137.6, 135.0, 131.1, 126.1, 126.0, 125.9, 125.0, 123.9, 123.6, 122.3, 120.8, 111.7, 86.7, 40.8;

IR: 2157, 1736, 1530, 1326, 1264, 1125, 1096, 746, 706 cm^{-1};

HRMS (ESI): $C_{22}H_{14}F_3N_3O_4S$+H, Calc: 474.0730, Found: 474.0712.

1-(naphthalen-2-yl)-1-(pyridin-2-yl)-2-thiocyanatoethyl 4-nitrobenzoate (**3n**)



Green solid (32 mg, 70% yield);

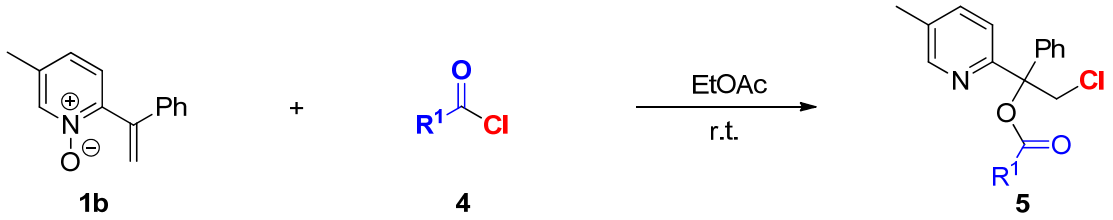
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 4.8 Hz, 1H), 8.39 (s, 4H), 8.02 – 7.93 (m, 1H), 7.85 (d, *J* = 8.7 Hz, 3H), 7.72 (td, *J* = 7.9, 1.7 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.47 (s, 1H), 7.30 – 7.26 (m, 1H), 4.92 (d, *J* = 14.1 Hz, 1H), 4.75 (d, *J* = 14.1 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 159.6, 150.9, 148.8, 137.4, 137.3, 135.4, 132.9, 132.8, 131.1, 129.0, 128.5, 127.7, 127.0, 126.9, 125.0, 123.9, 123.3, 122.7, 121.1, 112.2, 87.3, 41.1;

IR: 2156, 1734, 1529, 1349, 1264, 1095, 733, 704 cm^{-1};

HRMS (ESI): $C_{25}H_{17}N_3O_4S$+Na, Calc: 478.0832, Found: 478.0825.

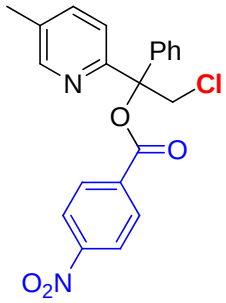
General procedure and spectral data for the synthesis of 5



To a solution of 5-methyl-2-(1-phenylvinyl)pyridine 1-oxide **1b** (0.10 mmol, 1.0 equiv) in dry EtOAc (1 mL) was added carbonyl chlorides **4** (0.12 mmol, 1.2 equiv). The reaction mixture was stirred for 0.5 h at room temperature. The reaction was monitored by TLC analysis. Upon completion, the solvent was removed under vacuum and residue was purified by flash column chromatography (petroleum ether/ EtOAc 40:1) to give the pure desired products **5**.

Spectral data of 5

2-chloro-1-(5-methylpyridin-2-yl)-1-phenylethyl 4-nitrobenzoate (**5a**)



Yellow oil (21 mg, 53% yield);

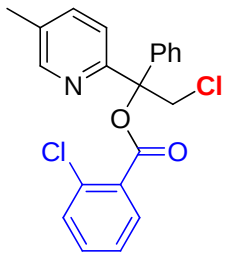
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.35 (d, *J* = 1.2 Hz, 4H), 7.53 – 7.45 (m, 3H), 7.42 – 7.27 (m, 4H), 5.12 (dd, *J* = 158.7, 11.9 Hz, 2H), 2.33 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 157.5, 150.8, 149.2, 140.8, 137.6, 135.9, 132.5, 130.9, 128.5, 128.1, 125.5, 123.8, 120.2, 86.8, 49.2, 18.2;

IR: 1738, 1527, 1348, 1280, 1233, 1099, 748, 720 cm^{-1};

HRMS (ESI): $C_{21}H_{17}ClN_2O_4$+H, Calc: 397.0950, Found: 397.0932.

2-chloro-1-(5-methylpyridin-2-yl)-1-phenylethyl 2-chlorobenzoate (**5b**)



Yellow oil (20 mg, 51% yield);

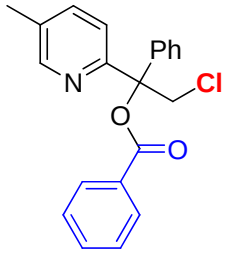
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.21 (m, 10H), 5.32 (d, *J* = 11.8 Hz, 1H), 4.96 (d, *J* = 11.8 Hz, 1H), 2.30 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 157.9, 149.0, 141.0, 137.5, 133.5, 132.7, 132.1, 131.6, 131.1, 130.8, 128.4, 127.8, 126.8, 125.6, 120.4, 86.7, 49.3, 18.2 .

IR: 1738, 1296, 1264, 1234, 1118, 1048, 735, 702 cm^{-1};

HRMS (ESI): $C_{21}H_{17}C_{l2}NO_2$+H, Calc: 386.0709, Found: 386.0698.

2-chloro-1-(5-methylpyridin-2-yl)-1-phenylethyl benzoate (**5c**)



White solid (14 mg, 40% yield);

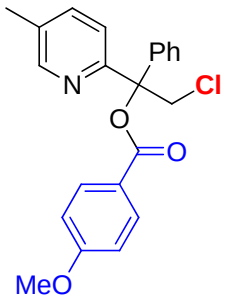
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 2.1 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.63 (tt, *J* = 6.8, 1.3 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.44 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.36 (dd, *J* = 8.1, 6.6 Hz, 3H), 7.32 – 7.26 (m, 1H), 5.32 (d, *J* = 11.8 Hz, 1H), 4.94 (d, *J* = 11.8 Hz, 1H), 2.31 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 158.3, 148.9, 141.4, 137.5, 133.4, 132.1, 130.6, 129.9, 128.6, 128.4, 127.8, 125.6, 120.2, 85.6, 49.5, 18.2;

IR: 1723, 1279, 1234, 1104, 1069, 1027, 748, 709 cm^{-1};

HRMS (ESI): $C_{21}H_{18}ClNO_2$+H, Calc: 352.1099, Found: 352.1090.

2-chloro-1-(5-methylpyridin-2-yl)-1-phenylethyl 4-methoxybenzoate (**5d**)



Yellow oil (16 mg, 42% yield);

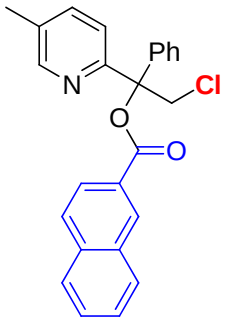
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.4 (s, 1H), 8.2 (d, J = 8.9 Hz, 2H), 7.6 – 7.5 (m, 2H), 7.5 – 7.4 (m, 1H), 7.4 (dq, J = 6.5, 3.5 Hz, 3H), 7.3 – 7.3 (m, 1H), 7.0 (d, J = 8.9 Hz, 2H), 5.3 (d, J = 11.7 Hz, 1H), 4.9 (d, J = 11.7 Hz, 1H), 3.9 (s, 3H), 2.3 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 163.7, 158.5, 148.9, 141.6, 137.5, 132.0, 132.0, 128.4, 127.7, 125.6, 122.9, 120.2, 113.9, 85.3, 55.5, 49.6, 18.2.

IR: 1716, 1605, 1257, 1165, 1096, 1028, 747, 696 cm^{-1};

HRMS (ESI): $C_{22}H_{20}ClNO_3$+H, Calc: 382.1204, Found: 382.1190.

2-chloro-1-(5-methylpyridin-2-yl)-1-phenylethyl 2-naphthoate (**5e**)



White solid (17 mg, 41% yield)

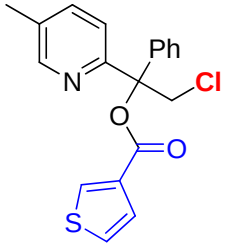
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 8.44 (s, 1H), 8.20 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.94 (dd, *J* = 13.8, 8.3 Hz, 2H), 7.67 – 7.53 (m, 4H), 7.50 – 7.34 (m, 4H), 7.31 (t, *J* = 7.3 Hz, 1H), 5.18 (dd, *J* = 158.5, 11.8 Hz, 2H), 2.32 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 158.3, 149.0, 141.5, 137.6, 135.8, 132.5, 132.1, 131.5, 129.5, 128.5, 128.4, 128.4, 127.8, 127.8, 126.8, 125.6, 125.6, 125.3, 120.3, 85.8, 49.6, 18.2.

IR: 1720, 1282, 1221, 1191, 1089, 747, 697 cm^{-1};

HRMS (ESI): $C_{25}H_{20}ClNO_2$+H, Calc: 402.1255, Found: 402.1247.

2-chloro-1-(5-methylpyridin-2-yl)-1-phenylethyl thiophene-3-carboxylate (**5f**)



Yellow oil (14 mg, 38% yield);

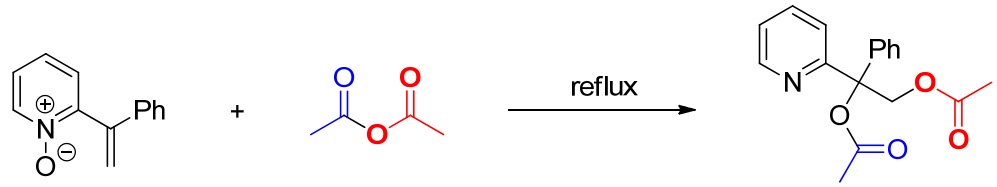
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.94 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.64 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.43 – 7.31 (m, 3H), 7.30 – 7.26 (m, 1H), 7.17 (dd, *J* = 4.8, 3.9 Hz, 1H), 5.11 (dd, *J* = 143.5, 11.8 Hz, 2H), 2.31 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 158.0, 148.9, 141.2, 137.6, 134.2, 133.8, 132.8, 132.2, 128.4, 128.0, 127.8, 125.5, 120.2, 86.0, 49.5, 18.2;

IR: 1714, 1415, 1264, 1221, 1088, 737, 700 cm^{-1};

HRMS (ESI):$C_{19}H_{16}ClNO_2S$+H, Calc: 358.0663, Found: 358.0650.

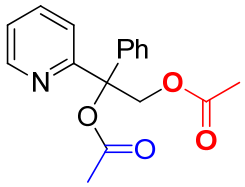
General procedure and spectral data for the synthesis of 7



1a **6** **7**, 80%

Alkenylpyridine *N*-Oxide **1a** (0.10 mmol, 1.0 equiv) was dissolved in 1 mL Ac_2O. Then the reaction mixture was stirred under reflux. After the reaction performed completely, the Ac_2O was removed under vacuum and residue was purified by flash column chromatography (petroleum ether/ EtOAc 20:1) to give the pure desired products **7**.

1-phenyl-1-(pyridin-2-yl)ethane-1,2-diyl diacetate (**7**)



Yellow solid (24 mg, 80% yield);

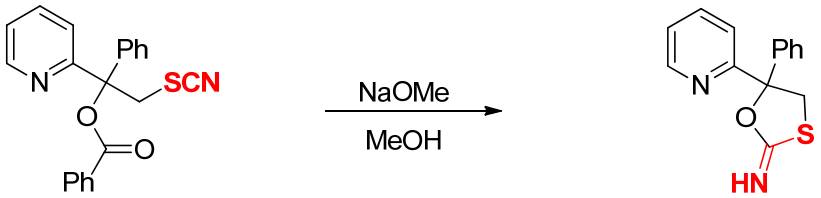
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 4.6 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 6.8 Hz, 3H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.18 – 7.14 (m, 1H), 7.10 (s, 1H), 5.40 (d, *J* = 11.8 Hz, 1H), 5.34 (d, *J* = 11.9 Hz, 1H), 2.14 (s, 3H), 1.82 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 169.2, 160.7, 148.6, 140.8, 136.6, 128.2, 127.6, 125.7, 122.4, 120.6, 85.0, 66.3, 22.0, 20.7;

IR: 1741, 1371, 1224, 1045, 750, 699 cm^{-1};

HRMS (ESI): $C_{17}H_{17}NO_4$+H, Calc: 300.1230, Found: 300.1221.

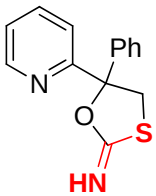
General procedure and spectral data for the synthesis of 8



3a **8**, 67%

NaOMe (1 equiv) was added slowly to a solution of **3a** (0.10 mmol, 1.0 equiv) in MeOH (1.0 mL), which was stirred for 2 h at room temperature. The reaction was monitored by TLC analysis. Upon completion, the solvent was removed under vacuum and residue was purified by flash column chromatography (petroleum ether/ EtOAc 10:1) to give the pure desired products **8**.

5-phenyl-5-(pyridin-2-yl)-1,3-oxathiolan-2-imine (**8**)



Yellow oil (17 mg, 67% yield);

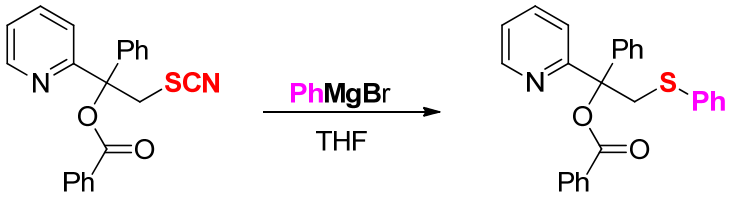
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (dt, *J* = 4.8, 1.2 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.61 – 7.52 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.25 (ddd, *J* = 6.6, 4.8, 1.6 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 3.92 (d, *J* = 10.8 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 159.5, 148.8, 140.9, 137.2, 128.6, 128.2, 125.1, 123.1, 121.2, 92.8, 42.7;

IR: 1650, 1565, 1380, 1264, 735, 702 cm^{-1};

HRMS (ESI): $C_{14}H_{12}N_2OS$+H, Calc: 257.0743, Found: 257.0736.

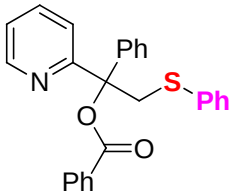
General procedure and spectral data for the synthesis of 9



3a **9**, 72%

PhMgBr (2.5 equiv) was added slowly to **3a** (0.1 mmol) in THF (1 mL) under stirring at 0 °C, then the mixture was stirring overnight at room temperature. The reaction was monitored by TLC analysis. Upon completion, the reaction was quenched with water, extracted with EtOAc, the organic phase was washed with brine, dried over Na_2SO_4 and evaporated. The residue was purified by chromatography on silica gel (petroleum ether/ EtOAc 20:1) affording the pure desired product **9**.

1-phenyl-2-(phenylthio)-1-(pyridin-2-yl)ethyl benzoate (**9**)



White solid (30 mg, 72% yield);

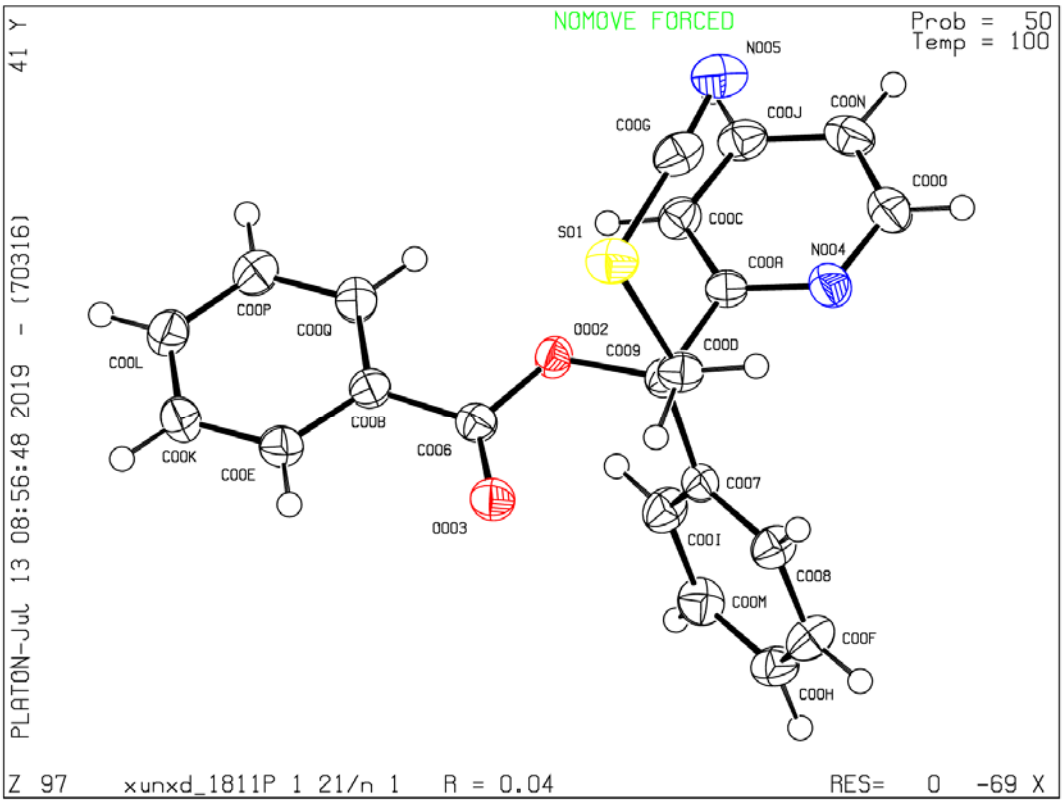
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 4.2 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.61 (ddd, *J* = 12.3, 9.1, 6.8 Hz, 2H), 7.53 (t, *J* = 8.3 Hz, 3H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.20 (m, 3H), 7.18 – 7.12 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 4.86 (d, *J* = 13.3 Hz, 1H), 4.59 (d, *J* = 13.3 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 162.0, 148.6, 142.5, 136.6, 135.9, 133.1, 130.7, 129.8, 128.5, 128.4, 128.3, 127.5, 126.5, 126.1, 125.6, 122.2, 120.6, 86.6, 42.5;

IR: 1722, 1585, 1432, 1277, 1233, 1096, 748, 707 cm^{-1};

HRMS (ESI): $C_{26}H_{21}NO_2S$+Na, Calc: 434.1185, Found: 434.1197.

X-ray Structure of 3a



Bond precision: C-C = 0.0026 A Wavelength=1.54184

Cell: a=14.2717(3) b=7.5736(1) c=17.5139(4)

alpha=90 beta=111.862(2) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	1756.90(6)	1756.90(6)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C21 H16 N2 O2 S	C21 H16 N2 O2 S
Sum formula	C21 H16 N2 O2 S	C21 H16 N2 O2 S
Mr	360.42	360.42

Dx,g cm-3	1.363	1.363
Z	4	4
Mu (mm-1)	1.781	1.781
F000	752.0	752.0
F000'	755.38	
h,k,lmax	18,9,22	17,9,22
Nref	3706	3522
Tmin,Tmax	0.685,0.837	0.329,1.000
Tmin'	0.558	

Correction method= # Reported T Limits: Tmin=0.329 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 0.950 Theta(max)= 76.750

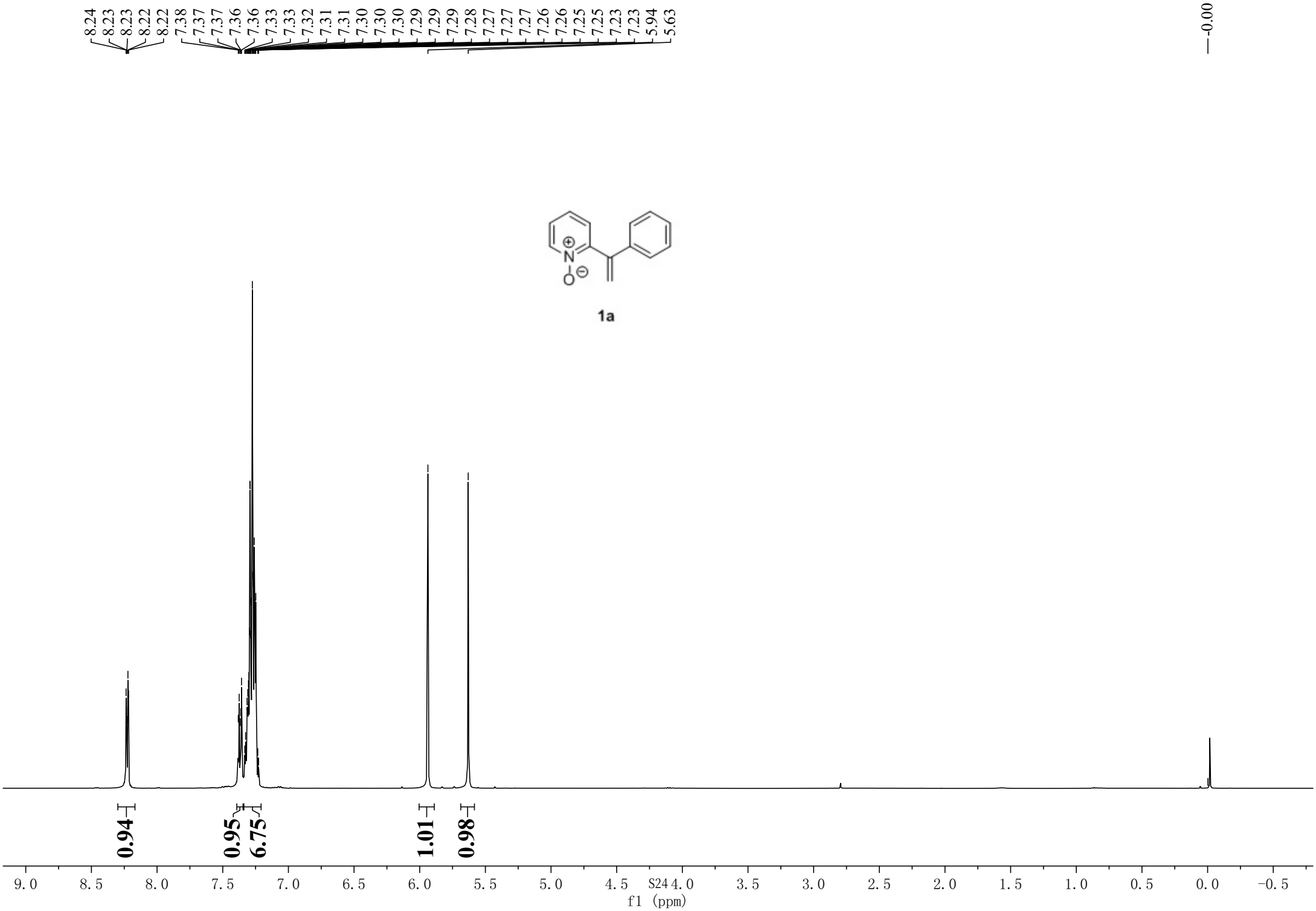
R(reflections)= 0.0448(3258) wR2(reflections)= 0.1286(3522)

S = 1.088 Npar= 235

References

[1] B. Modec, M. Stephan, *J. Chem. Crystal.* **2011**, *41*, 386-390;

[2] A. Dahiya, W. Ali, T. Alam, B. K. Patel, *Org. Biomol. Chem.* **2018**, *16*, 7787-7791.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7.27
7.27
7.26
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7.25
7.25
7.23
7.23
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5.63
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0.95
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1.01
0.98
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
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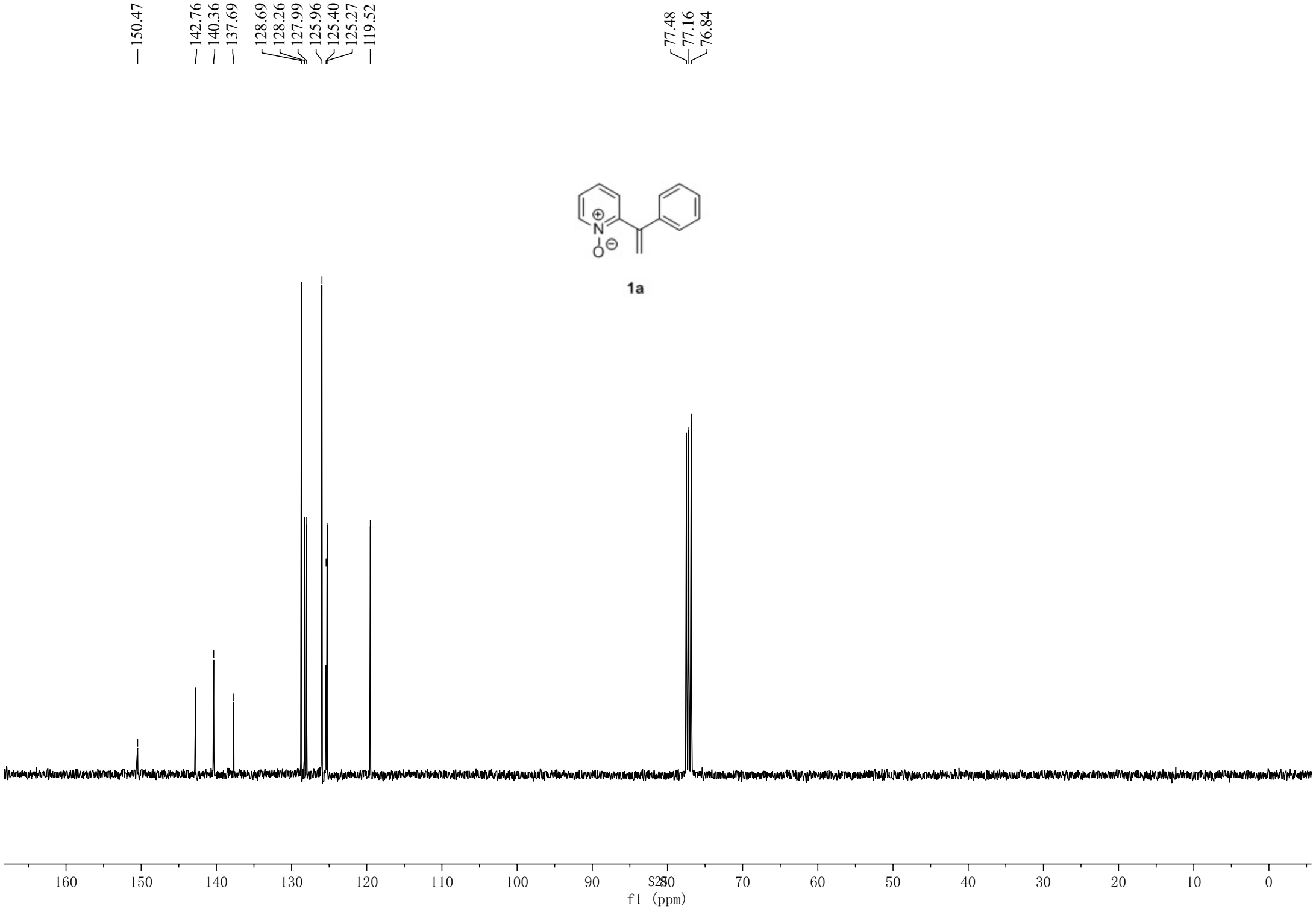
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77.16
76.84
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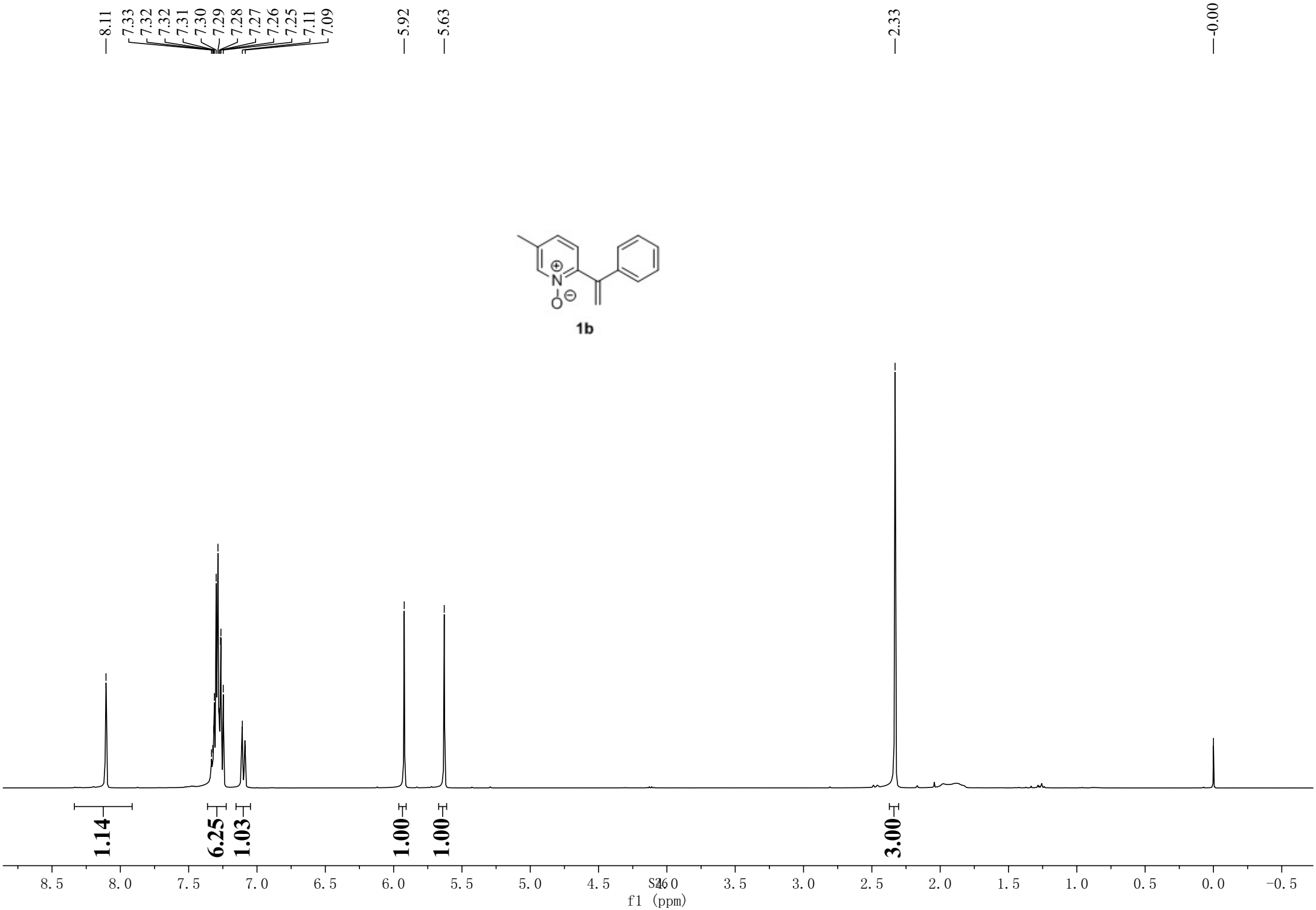
f1 (ppm)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7.09
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7.0
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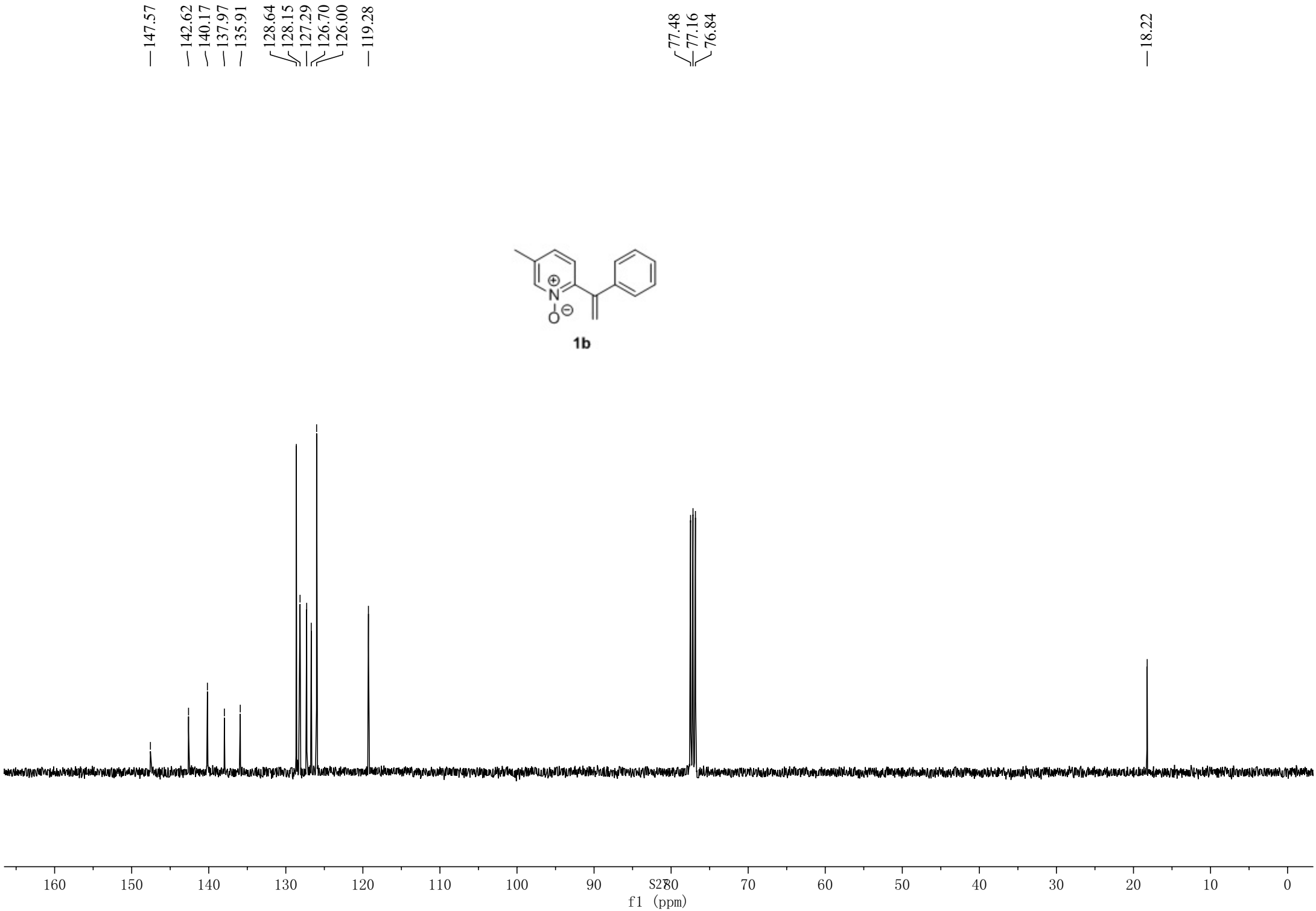
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18.22
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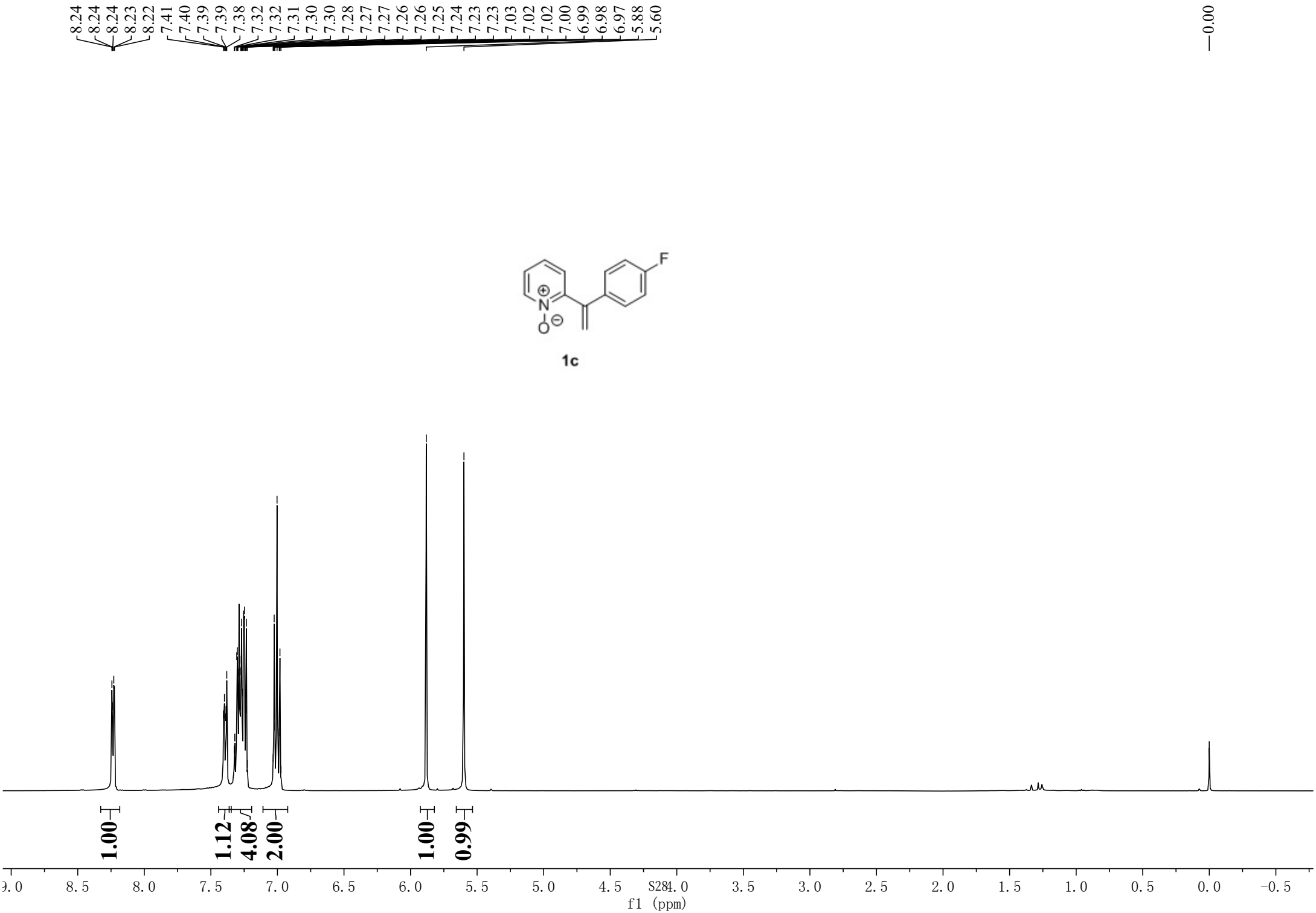
f1 (ppm)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6.97
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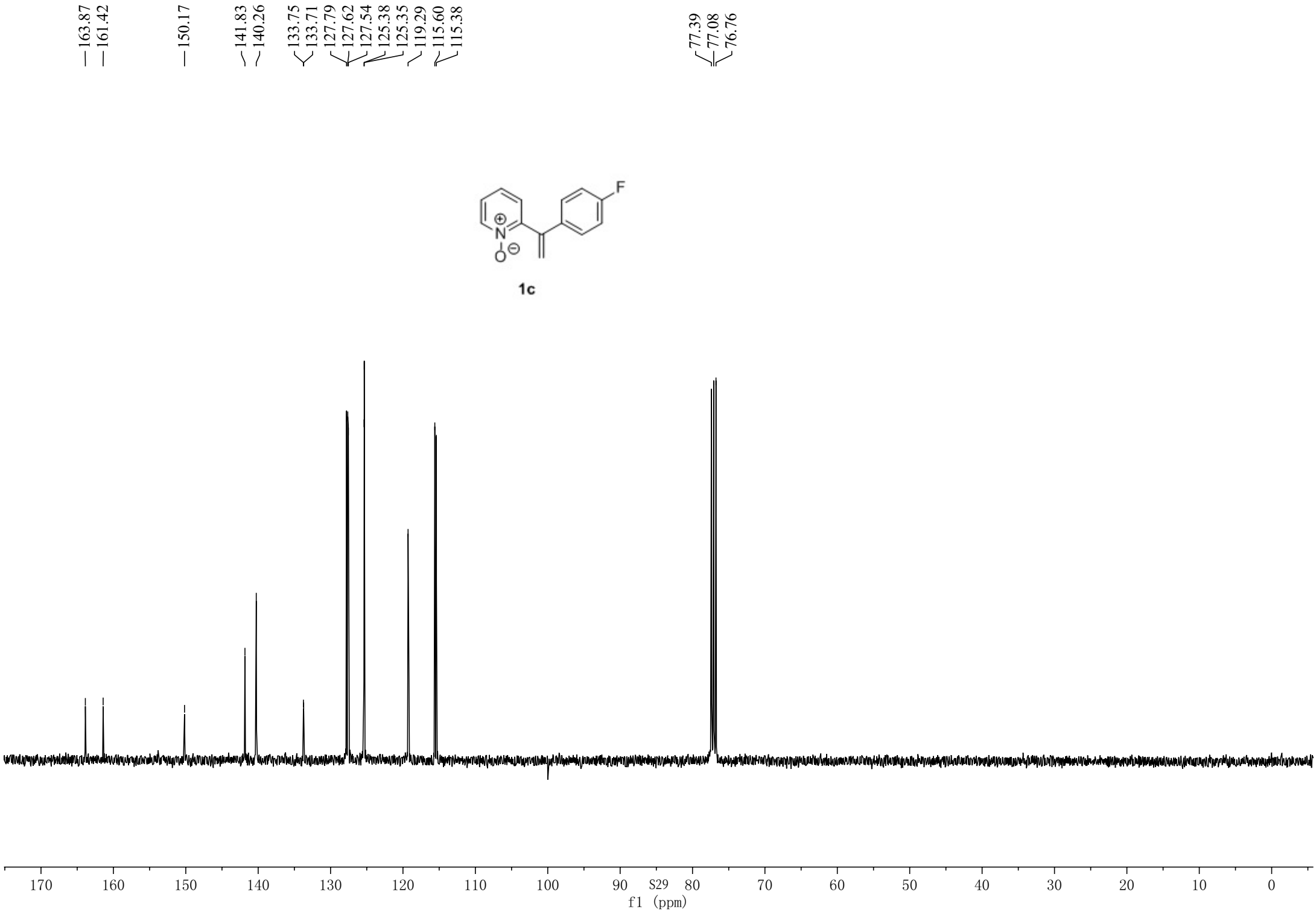
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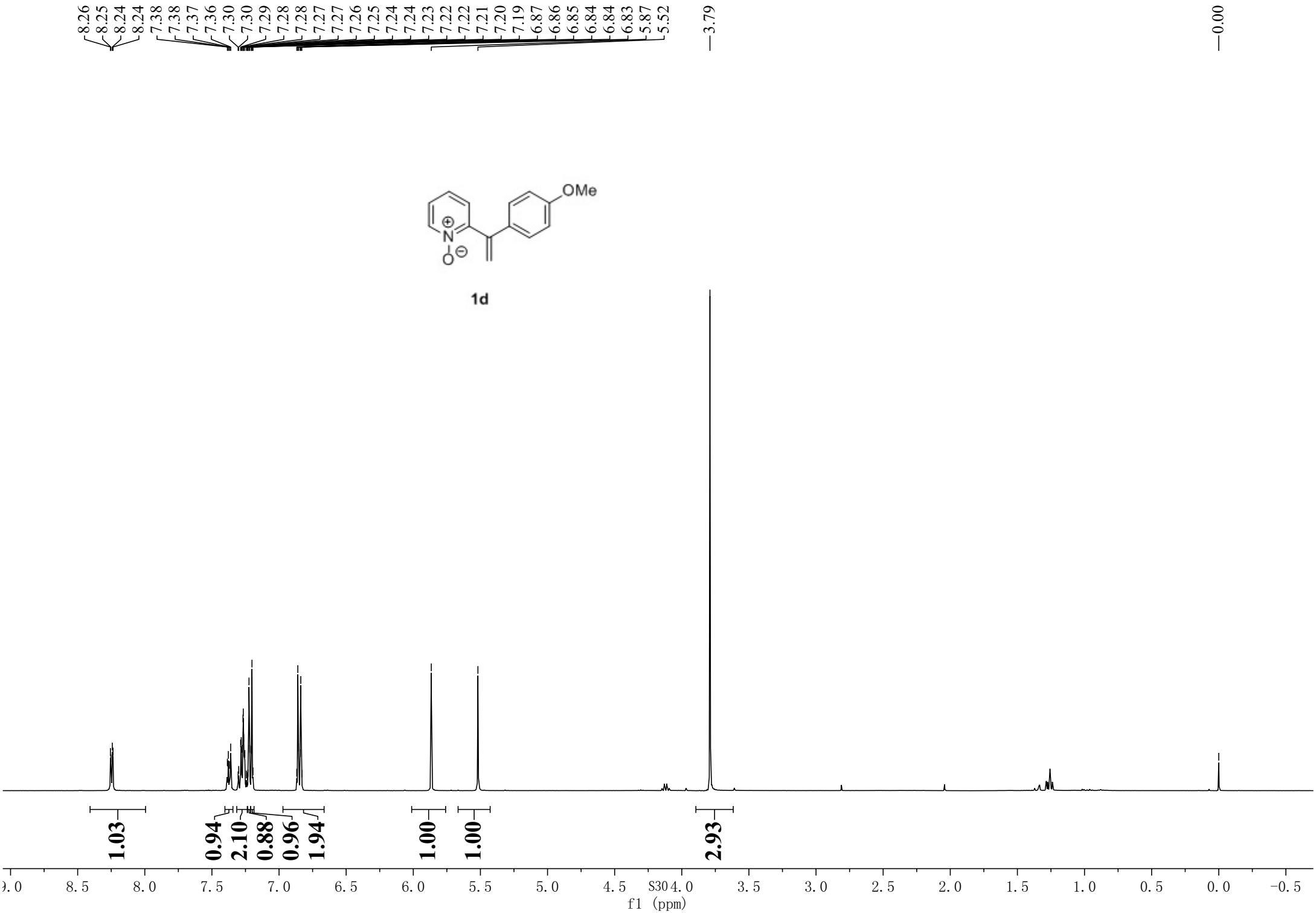
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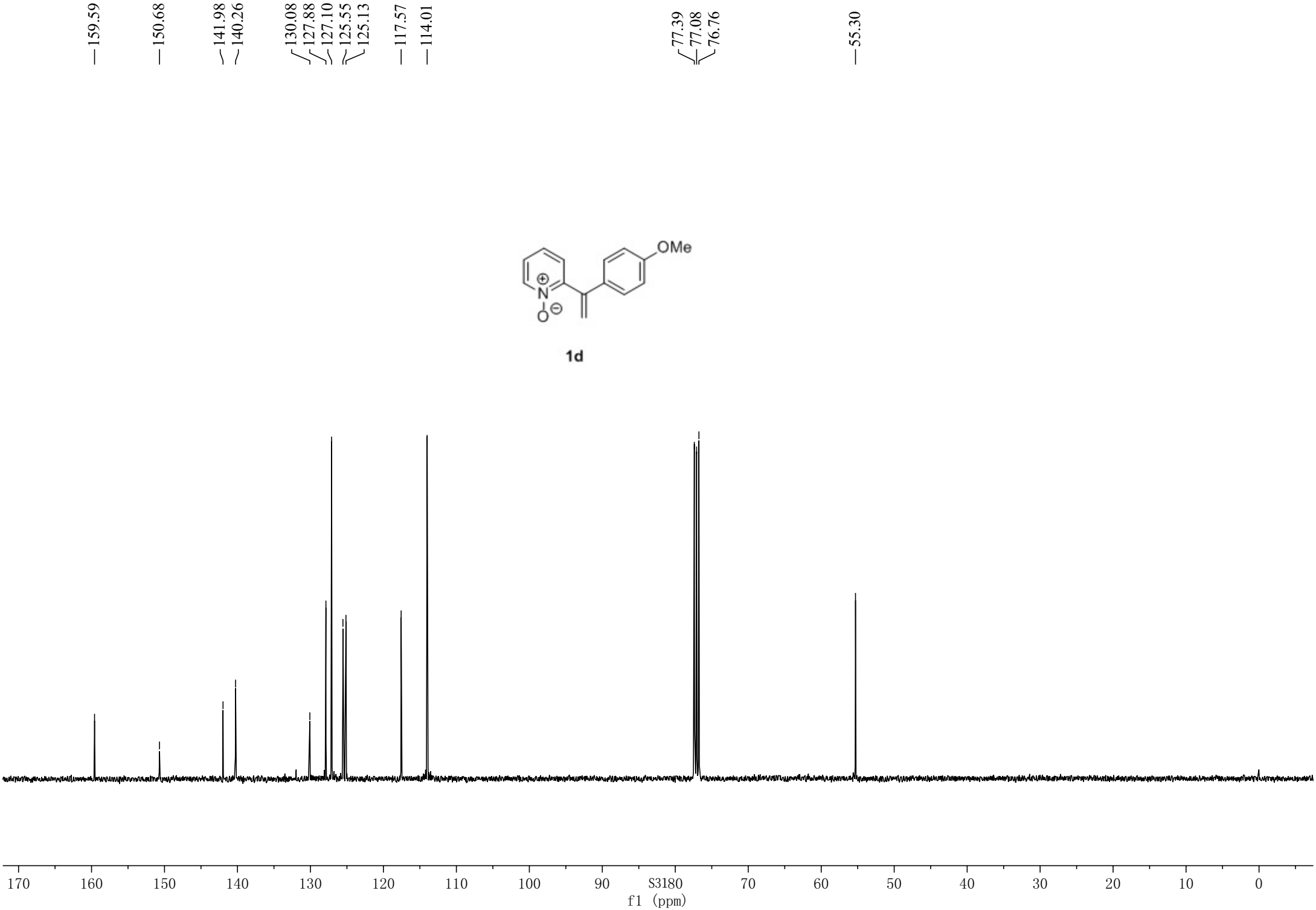
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O
1d
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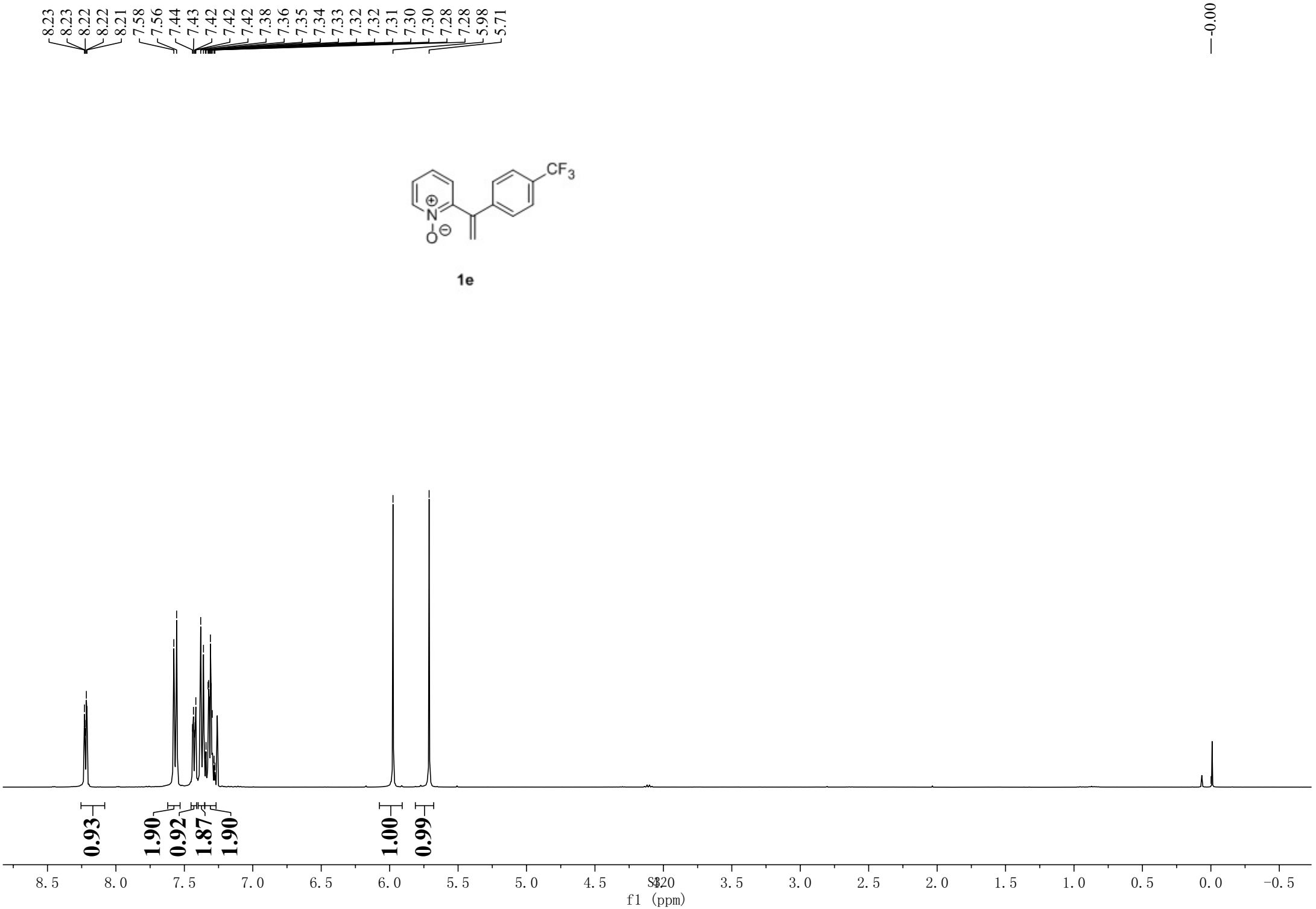
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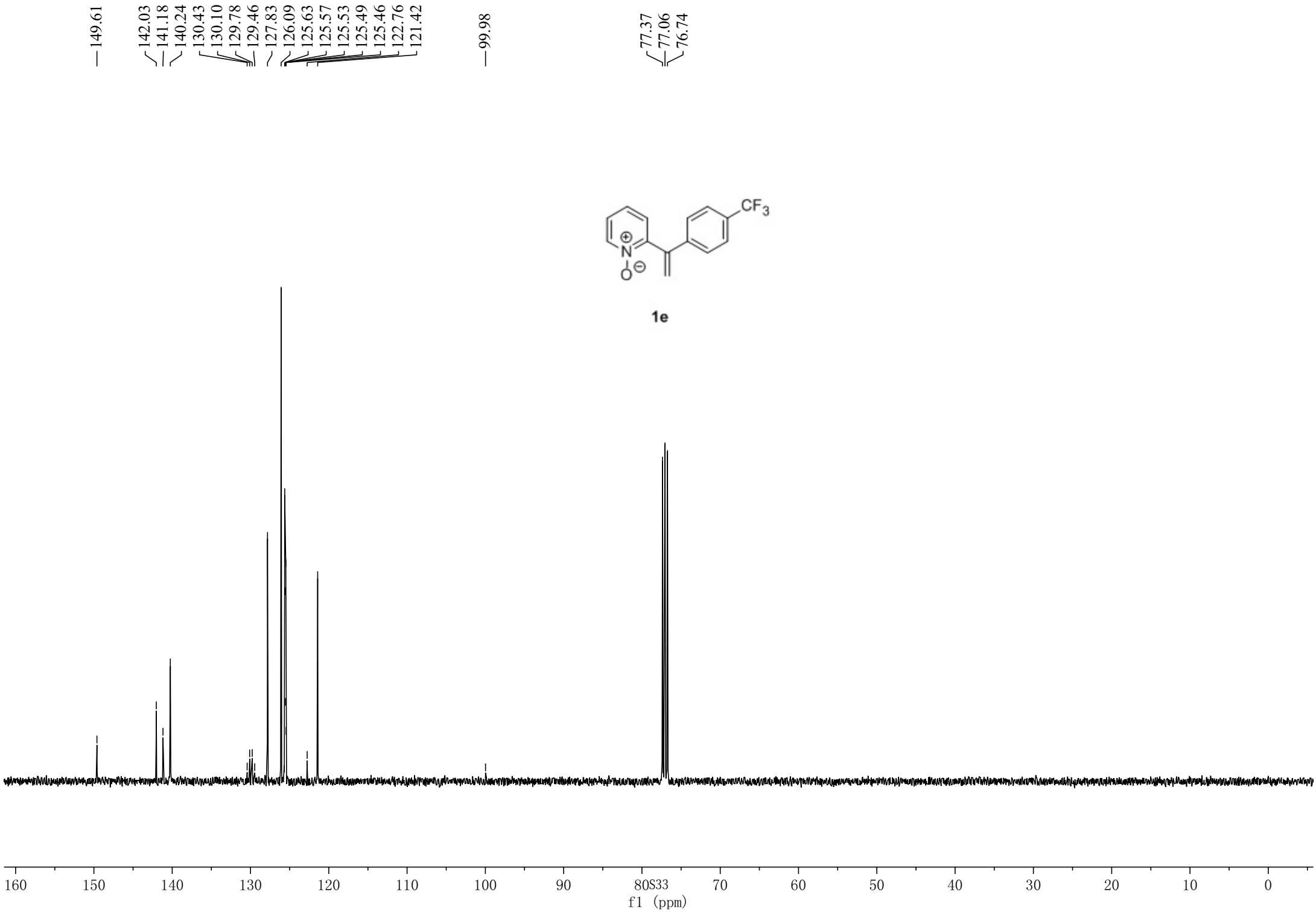
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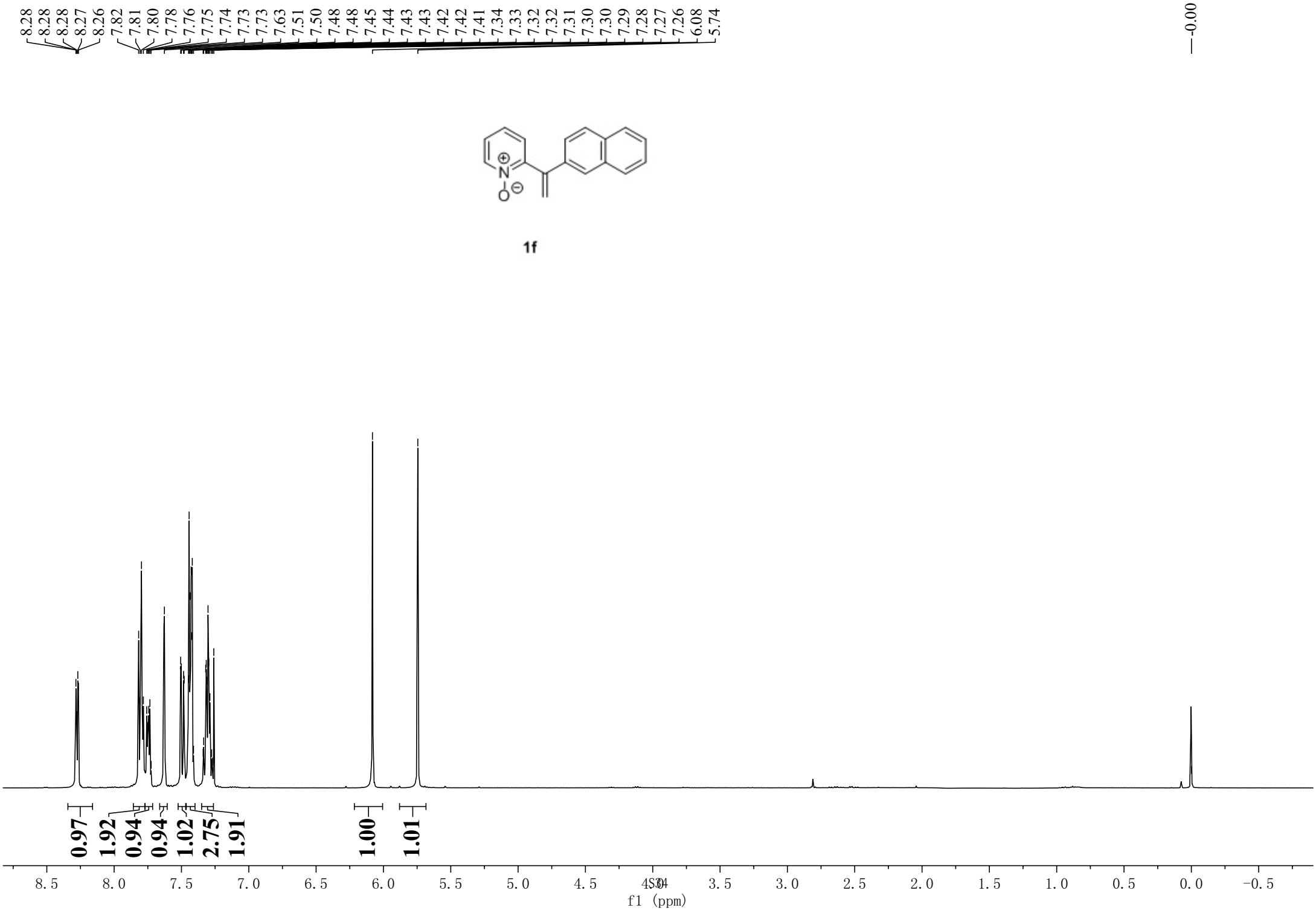
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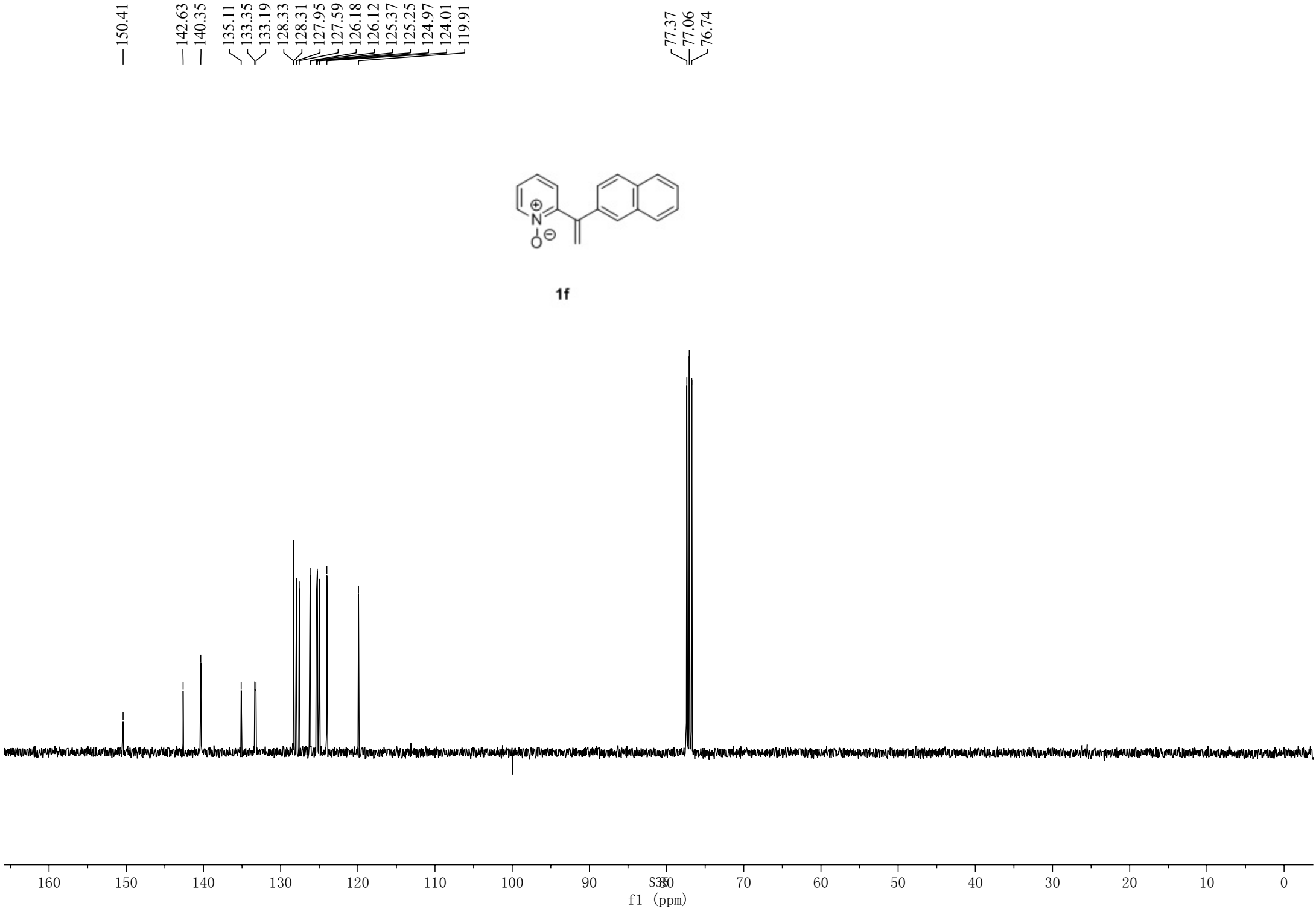
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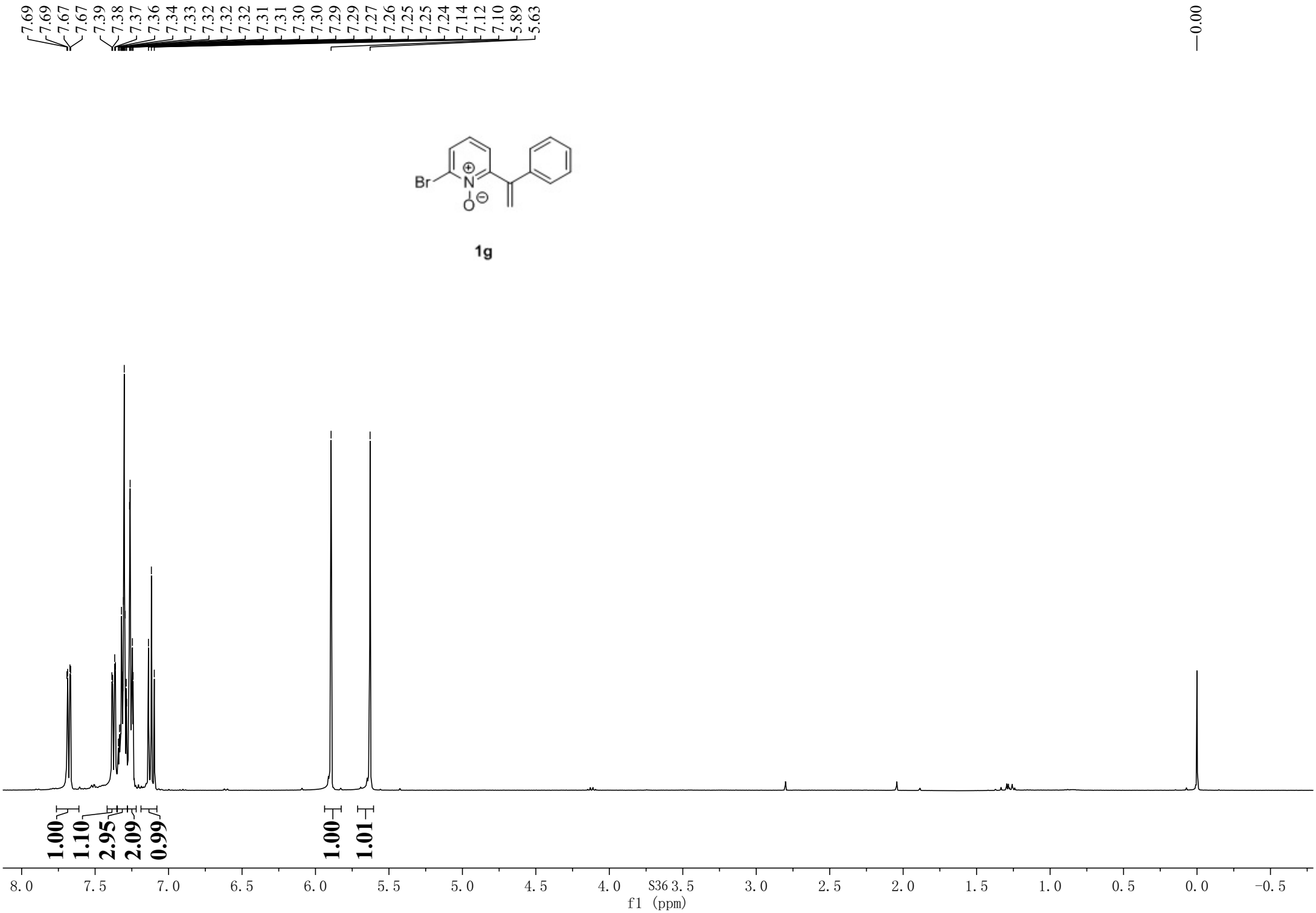
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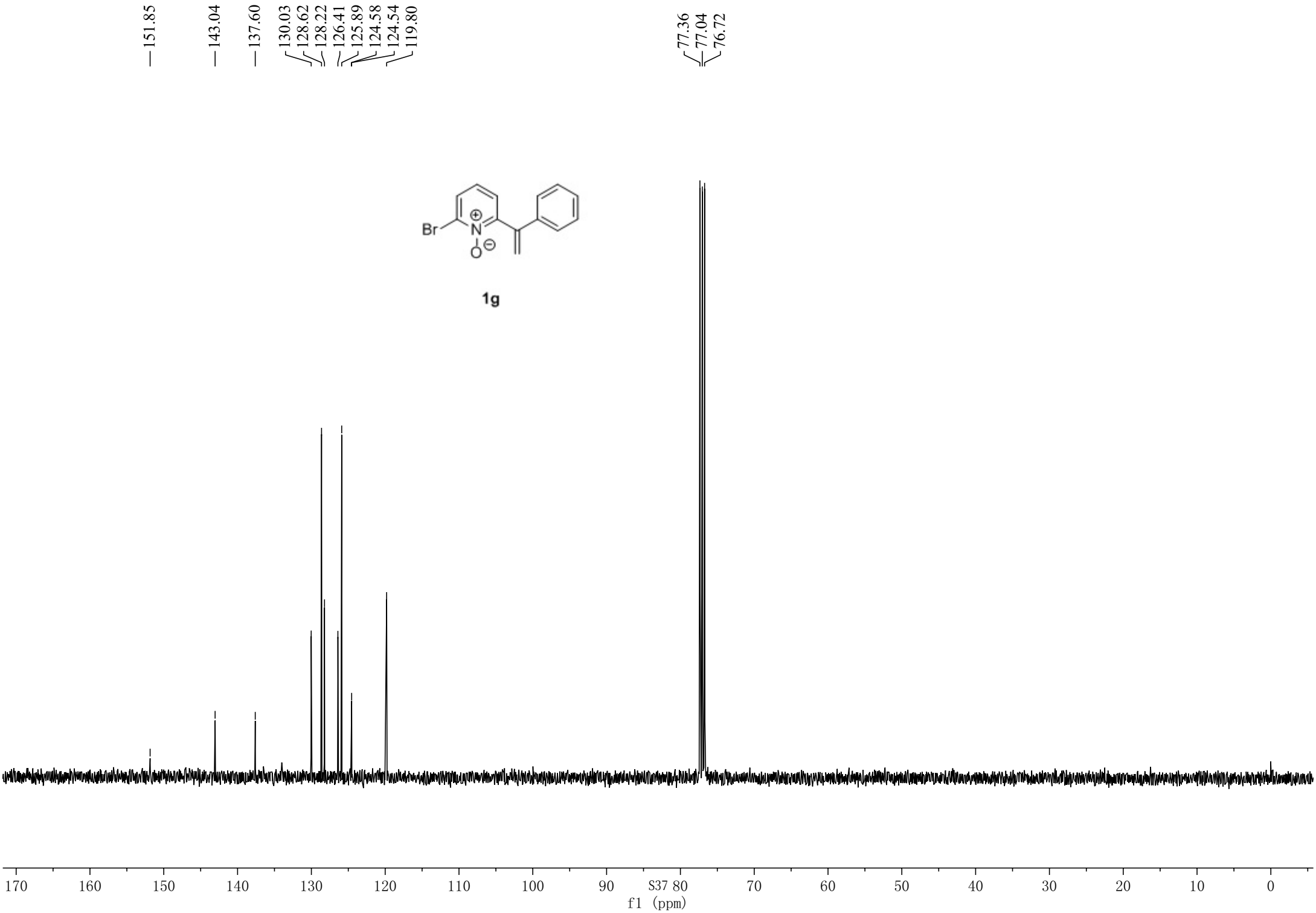
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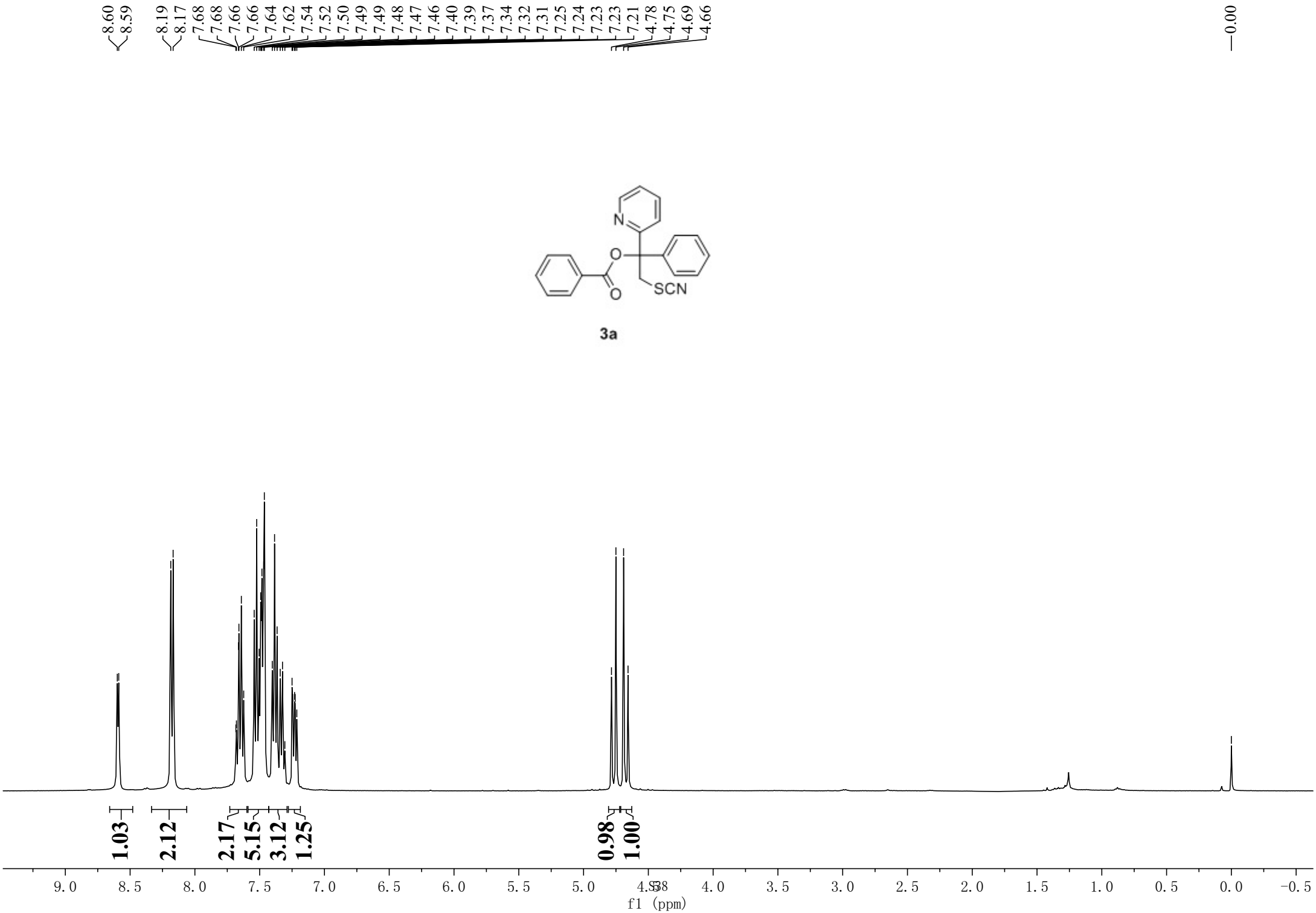
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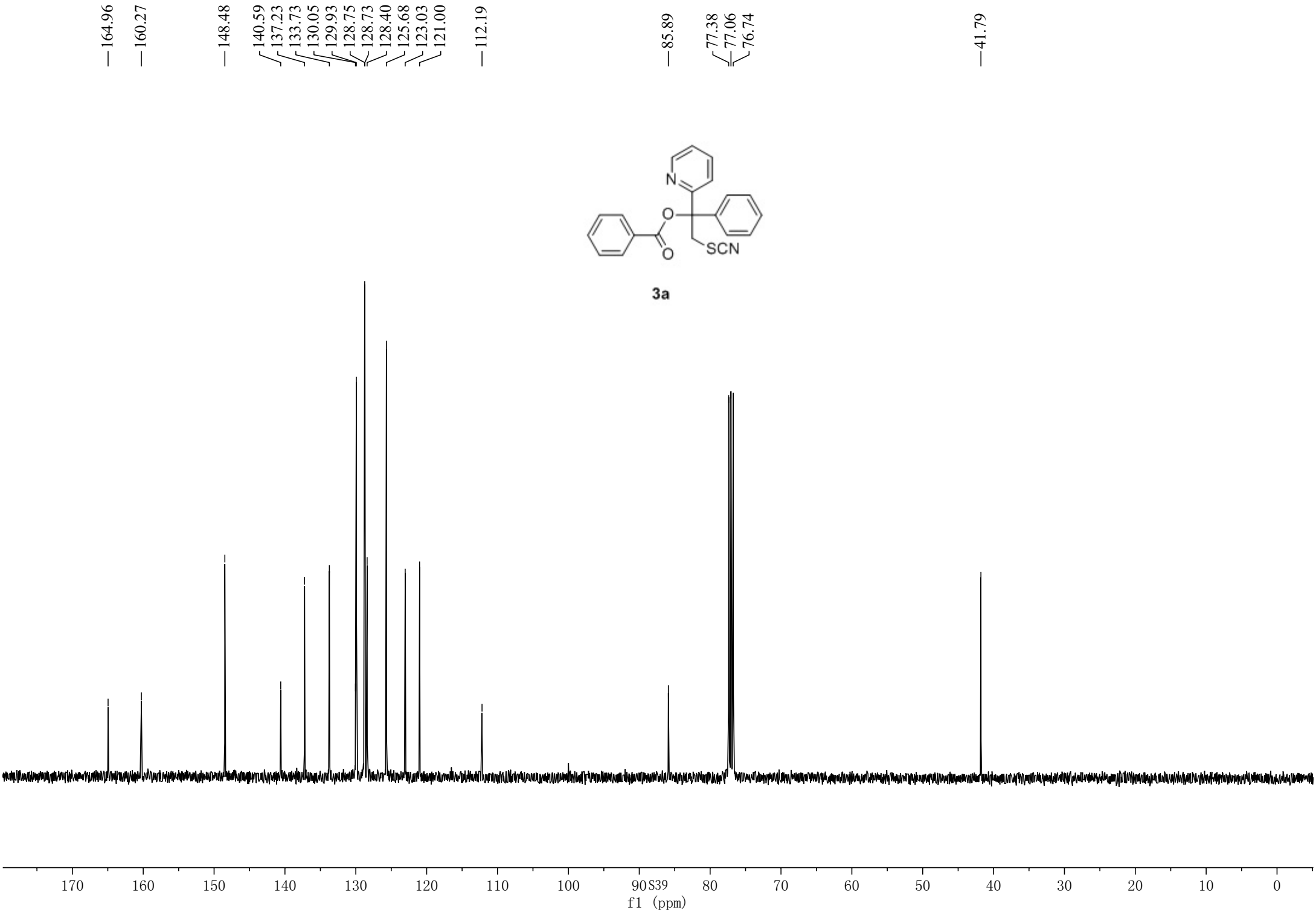
f1 (ppm)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20
10
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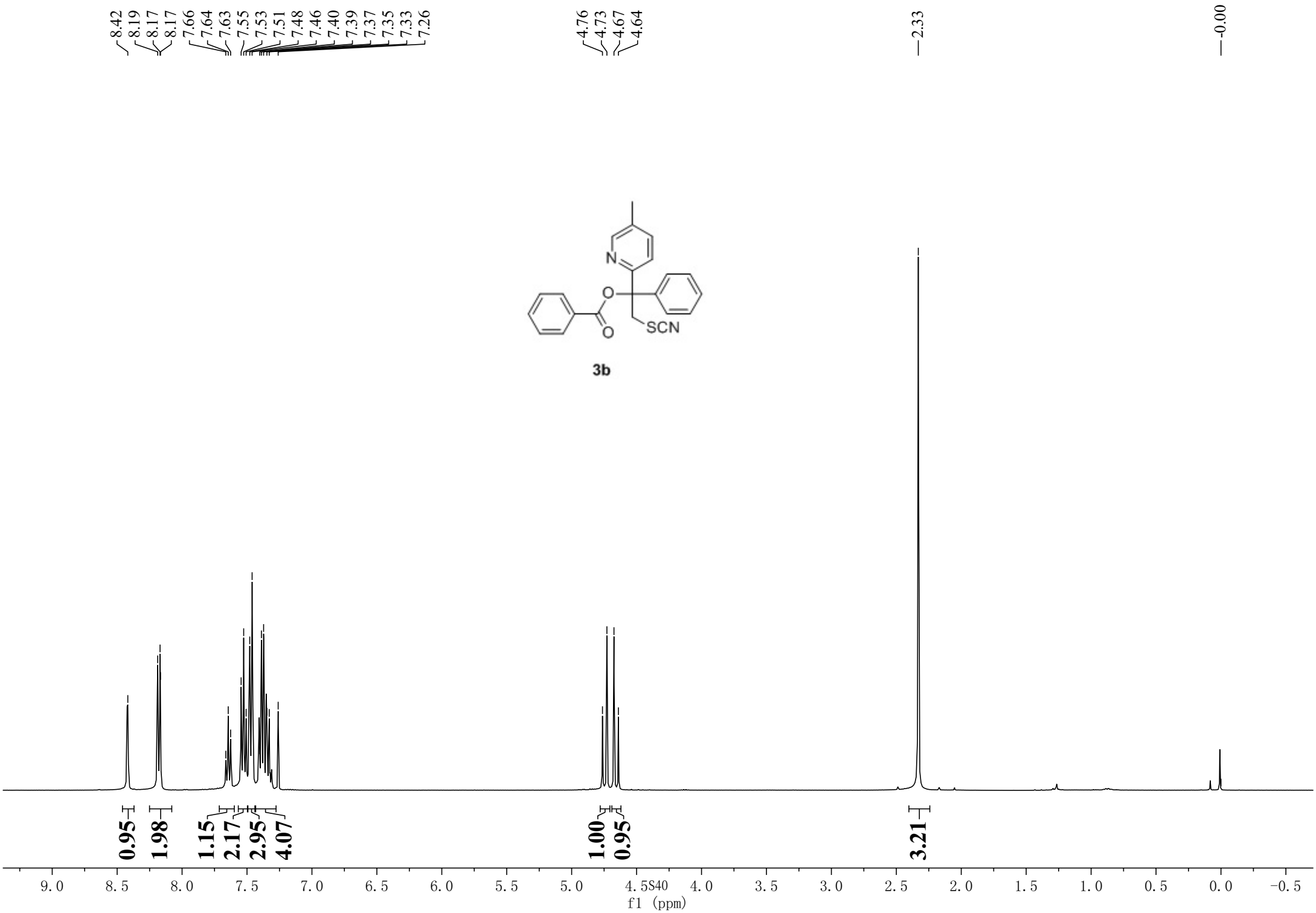
f1 (ppm)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7.39
7.37
7.35
7.33
7.26
4.76
4.73
4.67
4.64
2.33
-0.00
N
O
O
SCN
3b
0.95
1.98
1.15
2.17
2.95
4.07
1.00
0.95
3.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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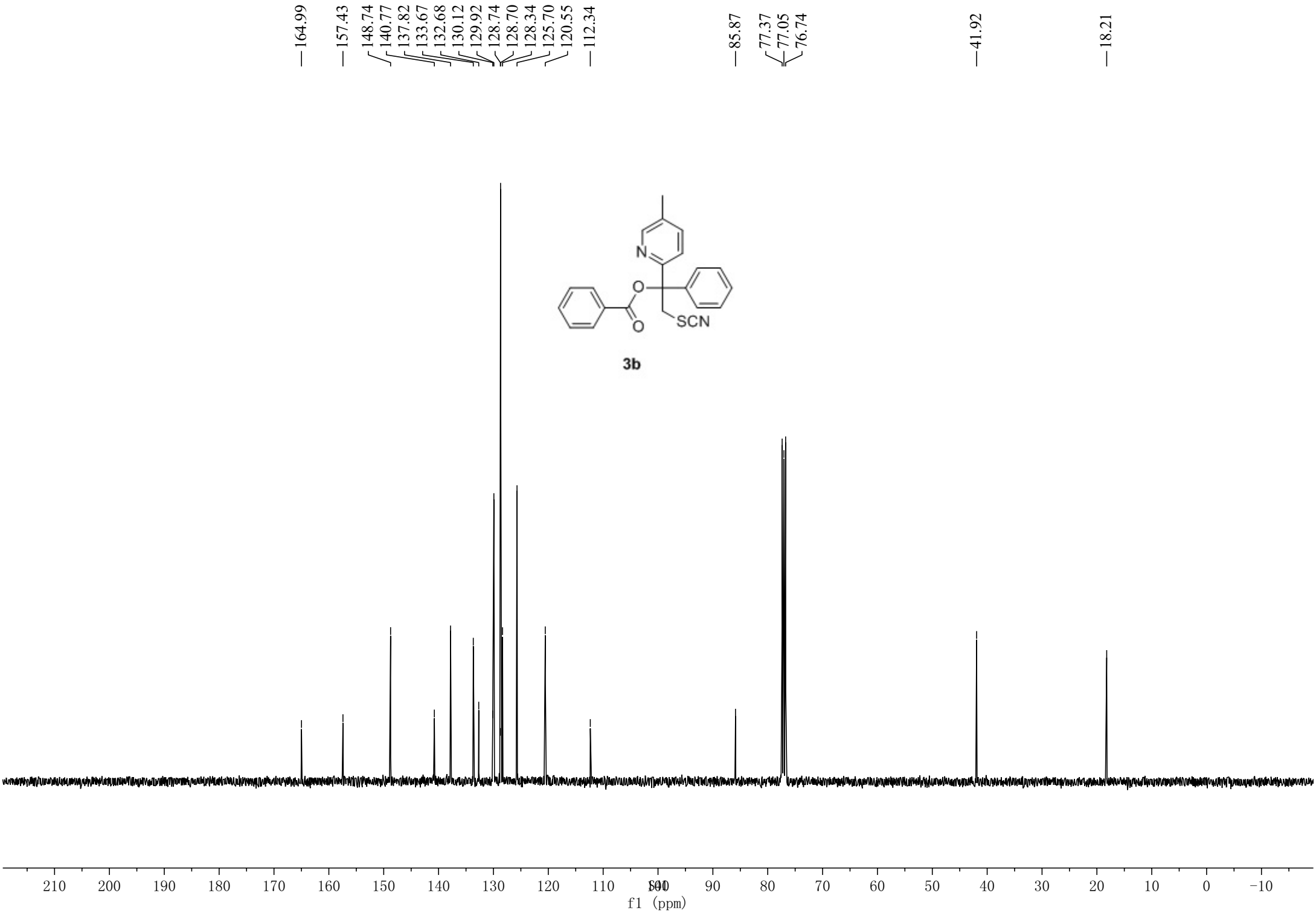
1.0
0.5
0.0
-0.5
f1 (ppm)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120.55
112.34
85.87
77.37
77.05
76.74
41.92
18.21
N
O
O
SCN
3b
210
200
190
180
170
160
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140
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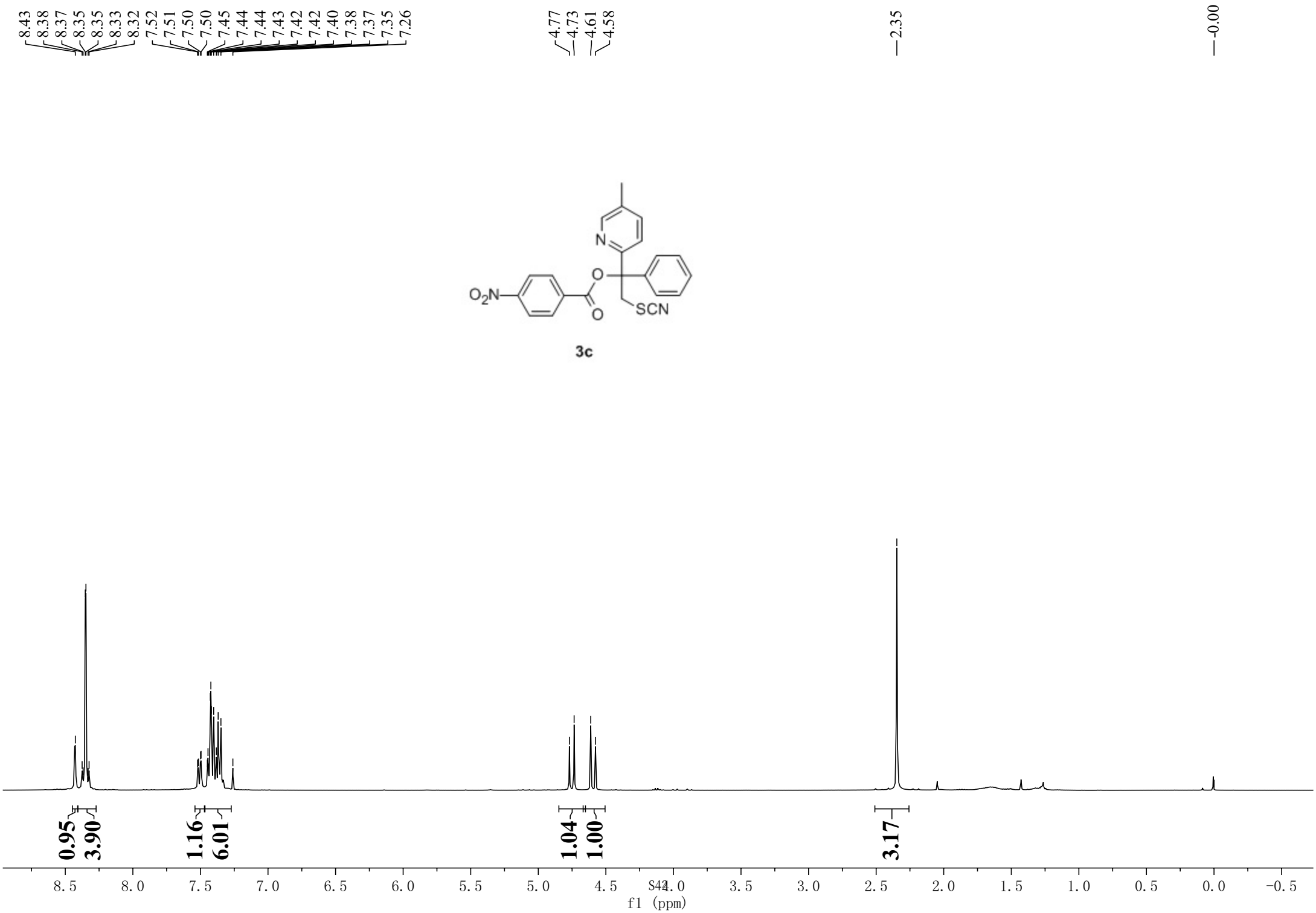
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.44
7.43
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7.42
7.40
7.38
7.37
7.35
7.26
4.77
4.73
4.61
4.58
2.35
-0.00
N
O
O_2N
O
SCN
3c
0.95
3.90
1.16
6.01
1.04
1.00
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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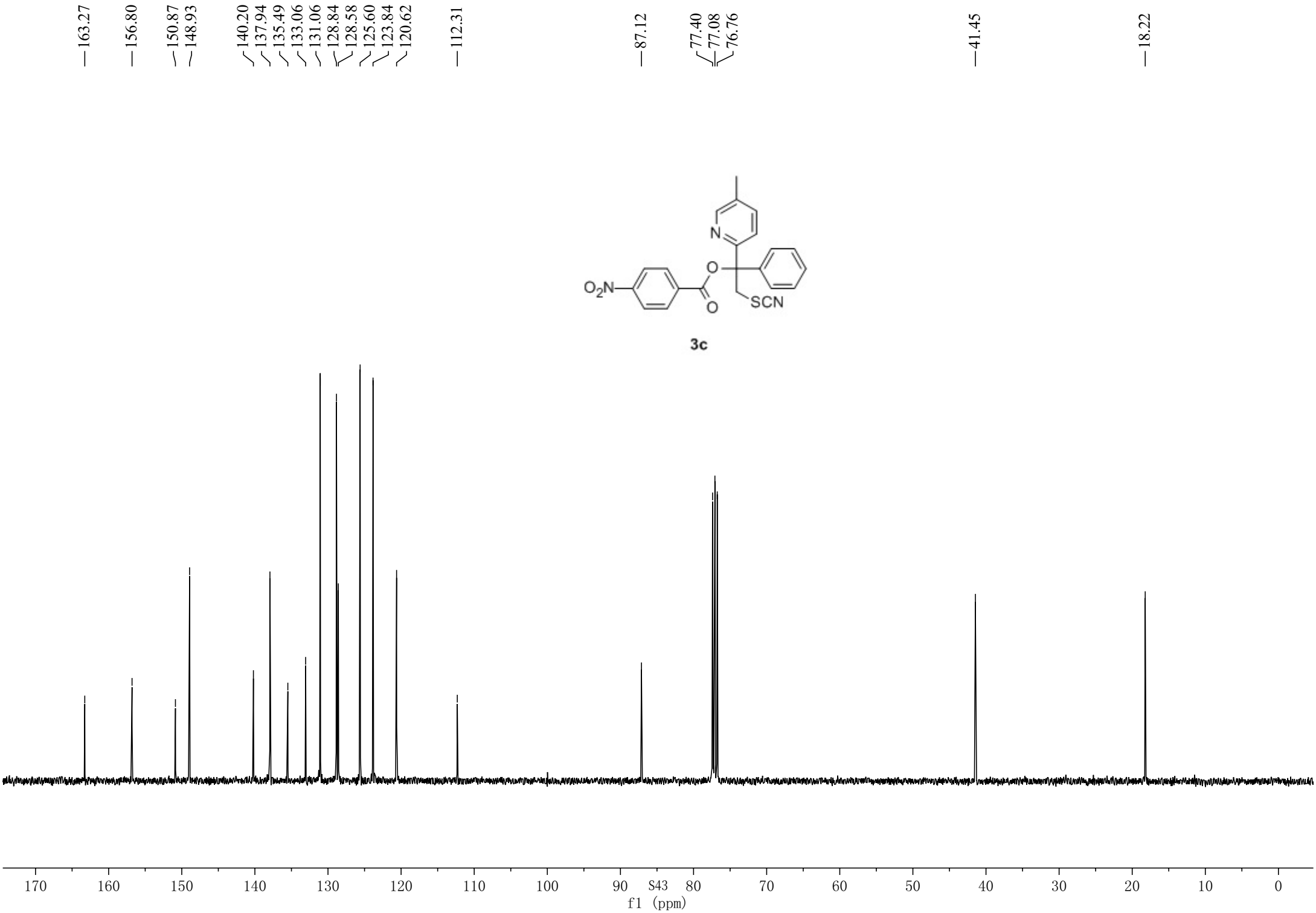
0.0
-0.5
f1 (ppm)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120.62
112.31
87.12
77.40
77.08
76.76
41.45
18.22
N
O
O_2N
O
SCN
3c
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130
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70
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50
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10
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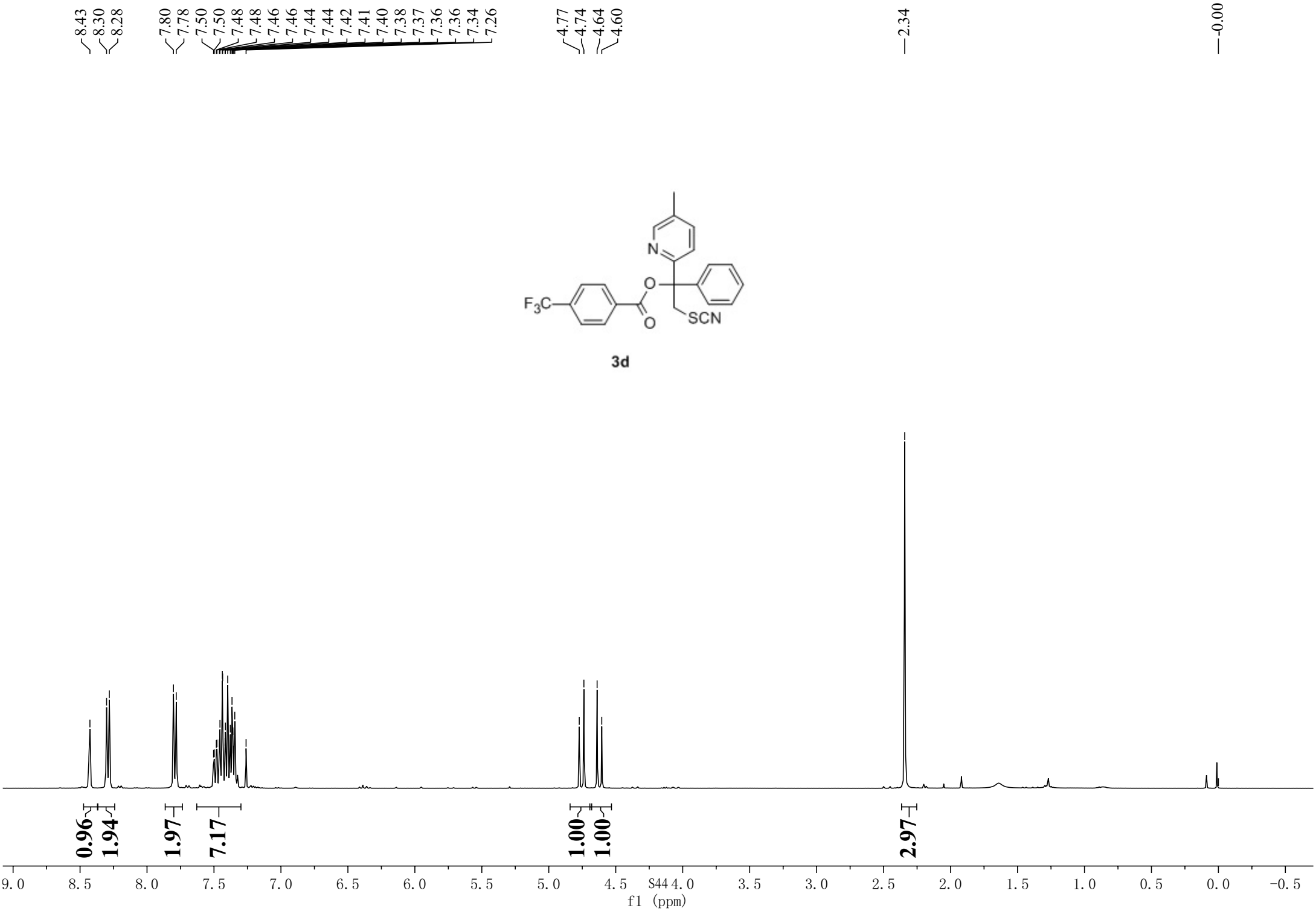
f1 (ppm)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7.44
7.42
7.41
7.40
7.38
7.37
7.36
7.36
7.34
7.26
4.77
4.74
4.64
4.60
2.34
-0.00
N
O
F3C
O
SCN
3d
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1.94
1.97
7.17
1.00
1.00
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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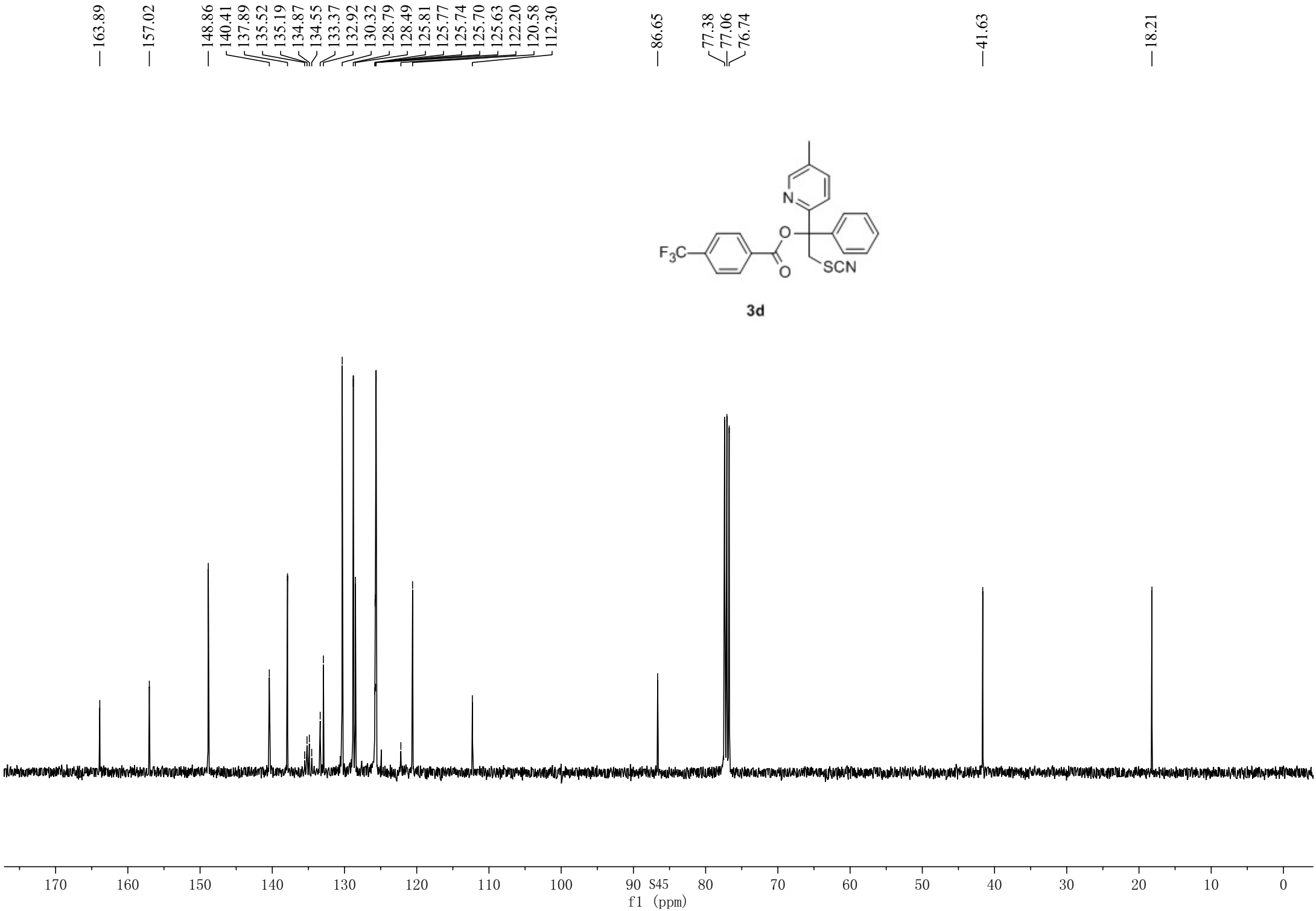
0.5
0.0
-0.5
f1 (ppm)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134.87
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130.32
128.79
128.49
125.81
125.77
125.74
125.70
125.63
122.20
120.58
112.30
86.65
77.38
77.06
76.74
41.63
18.21
N
O
F3C
O
SCN
3d
170
160
150
140
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120
110
100
90
S45
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70
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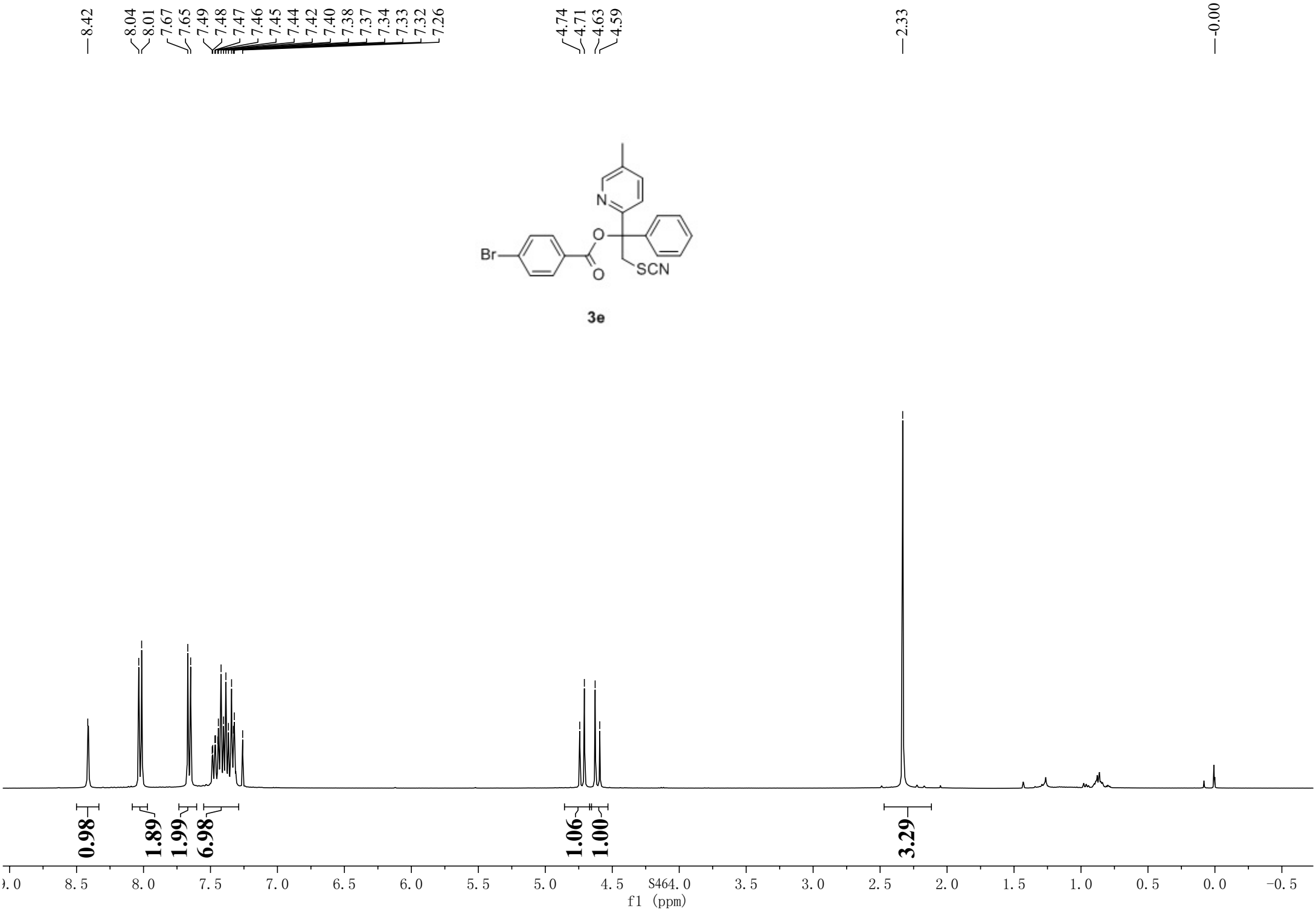
50
40
30
20
10
0
f1 (ppm)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7.47
7.46
7.45
7.44
7.42
7.40
7.38
7.37
7.34
7.33
7.32
7.26
4.74
4.71
4.63
4.59
2.33
-0.00
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O
Br
O
SCN
3e
0.98
1.89
1.99
6.98
1.06
1.00
3.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
1.5
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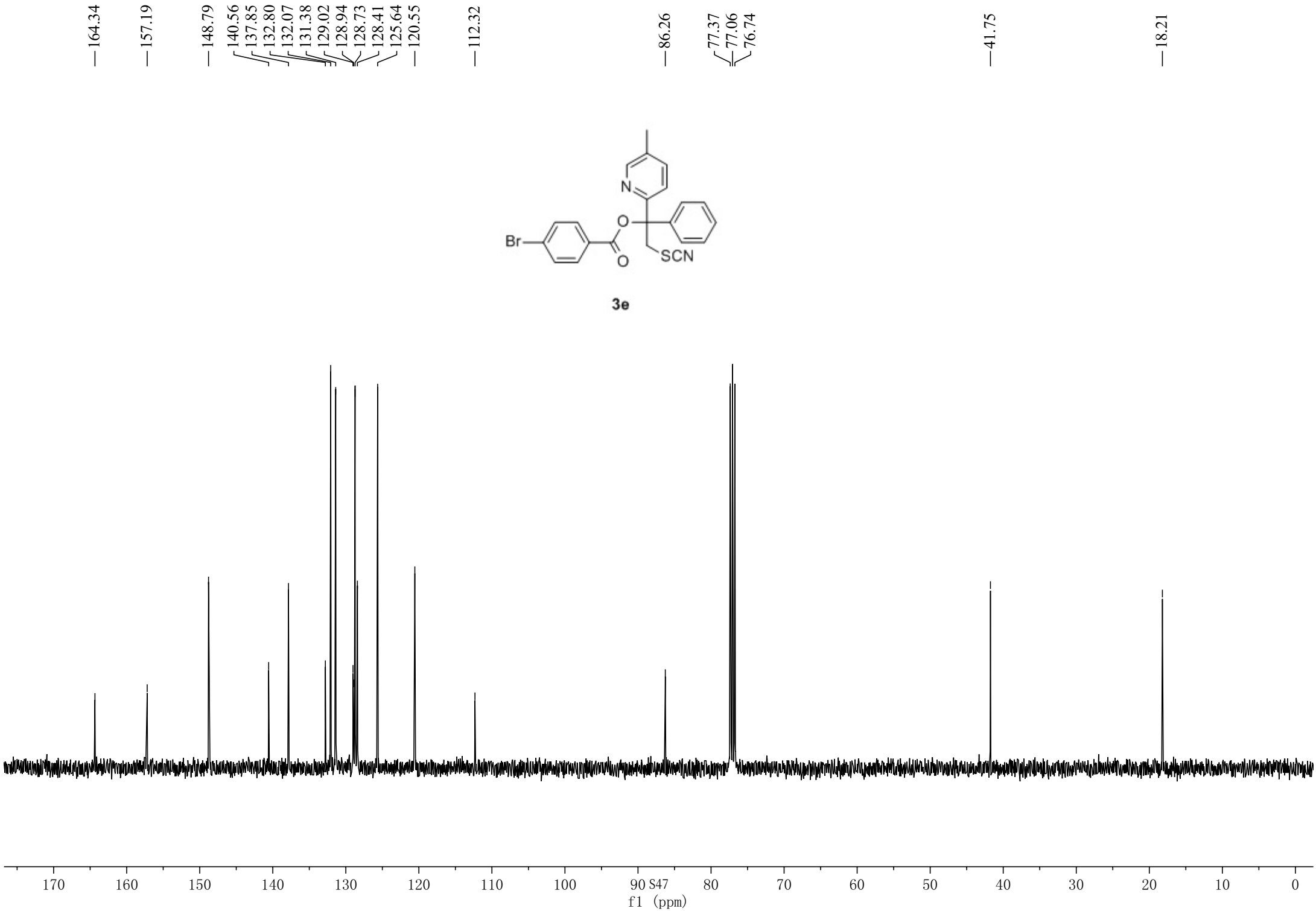
0.5
0.0
-0.5
f1 (ppm)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128.41
125.64
120.55
112.32
86.26
77.37
77.06
76.74
41.75
18.21
N
O
Br
O
SCN
3e
170
160
150
140
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120
110
100
90
S47
80
70
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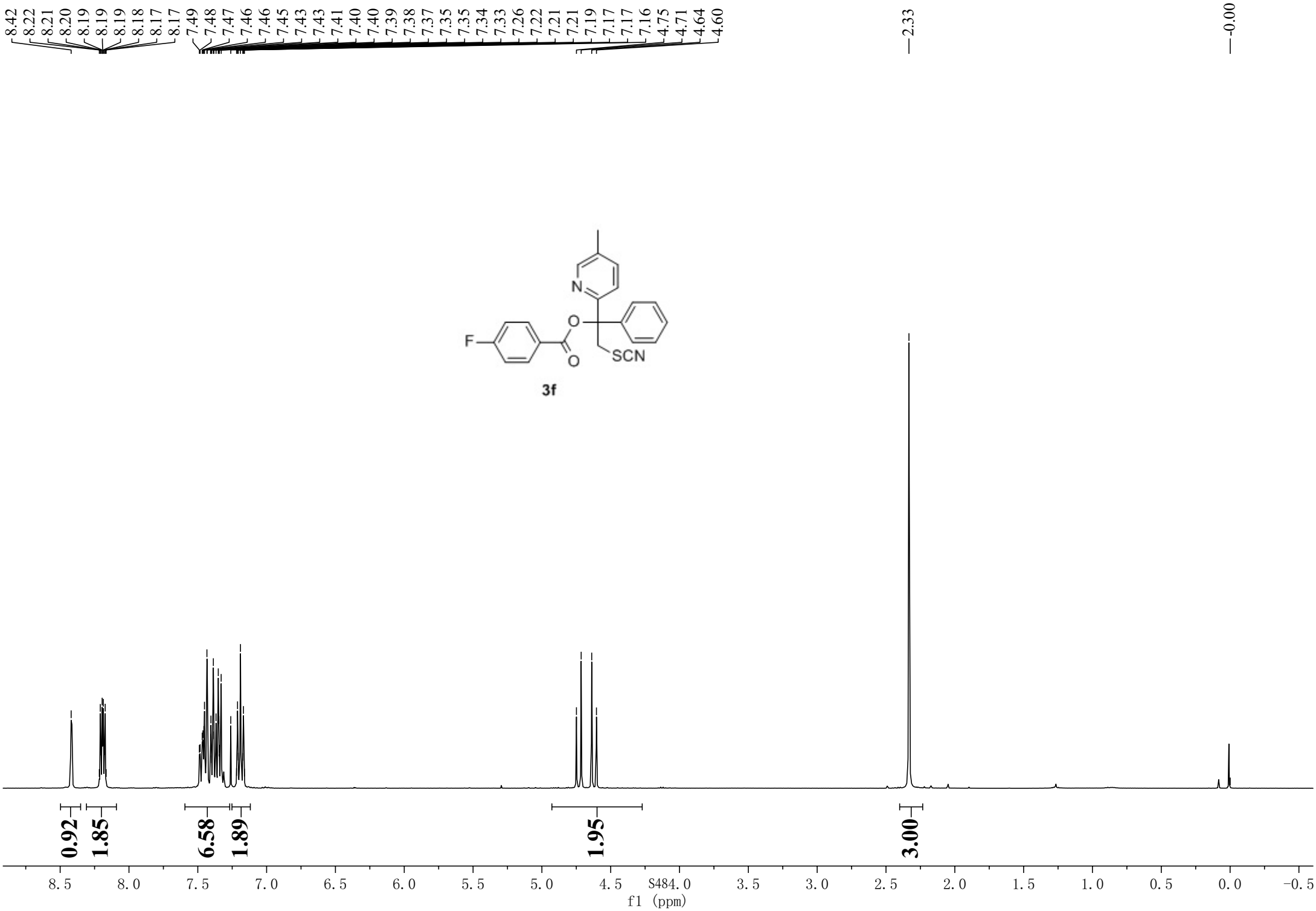
50
40
30
20
10
0
f1 (ppm)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7.46
7.45
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7.40
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7.38
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7.35
7.34
7.33
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7.19
7.17
7.17
7.16
4.75
4.71
4.64
4.60
2.33
-0.00
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O
F
O
SCN
3f
0.92
1.85
6.58
1.89
1.95
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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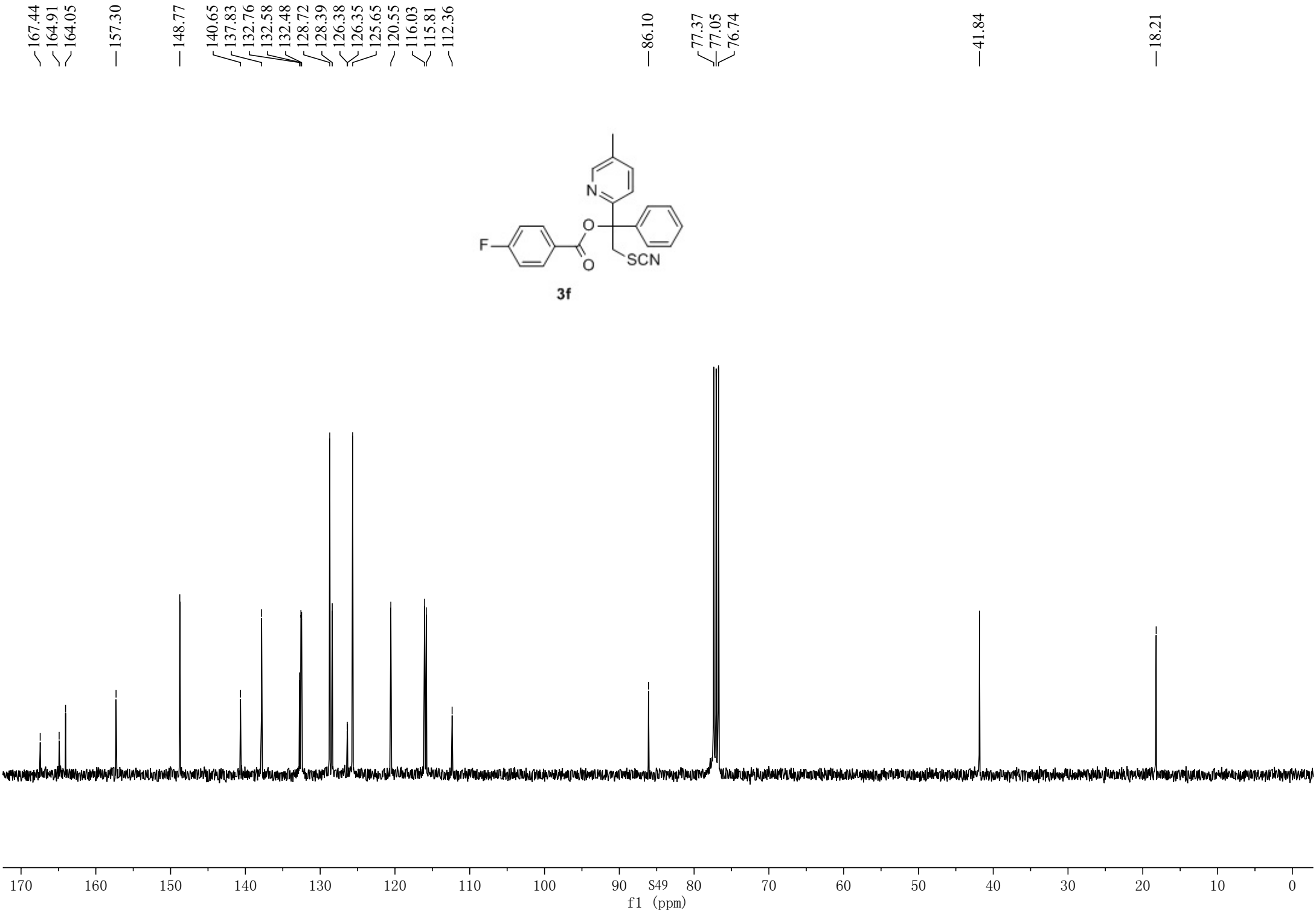
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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126.38
126.35
125.65
120.55
116.03
115.81
112.36
86.10
77.37
77.05
76.74
41.84
18.21
N
O
F
O
SCN
3f
170
160
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140
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120
110
100
90
S49
80
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50
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10
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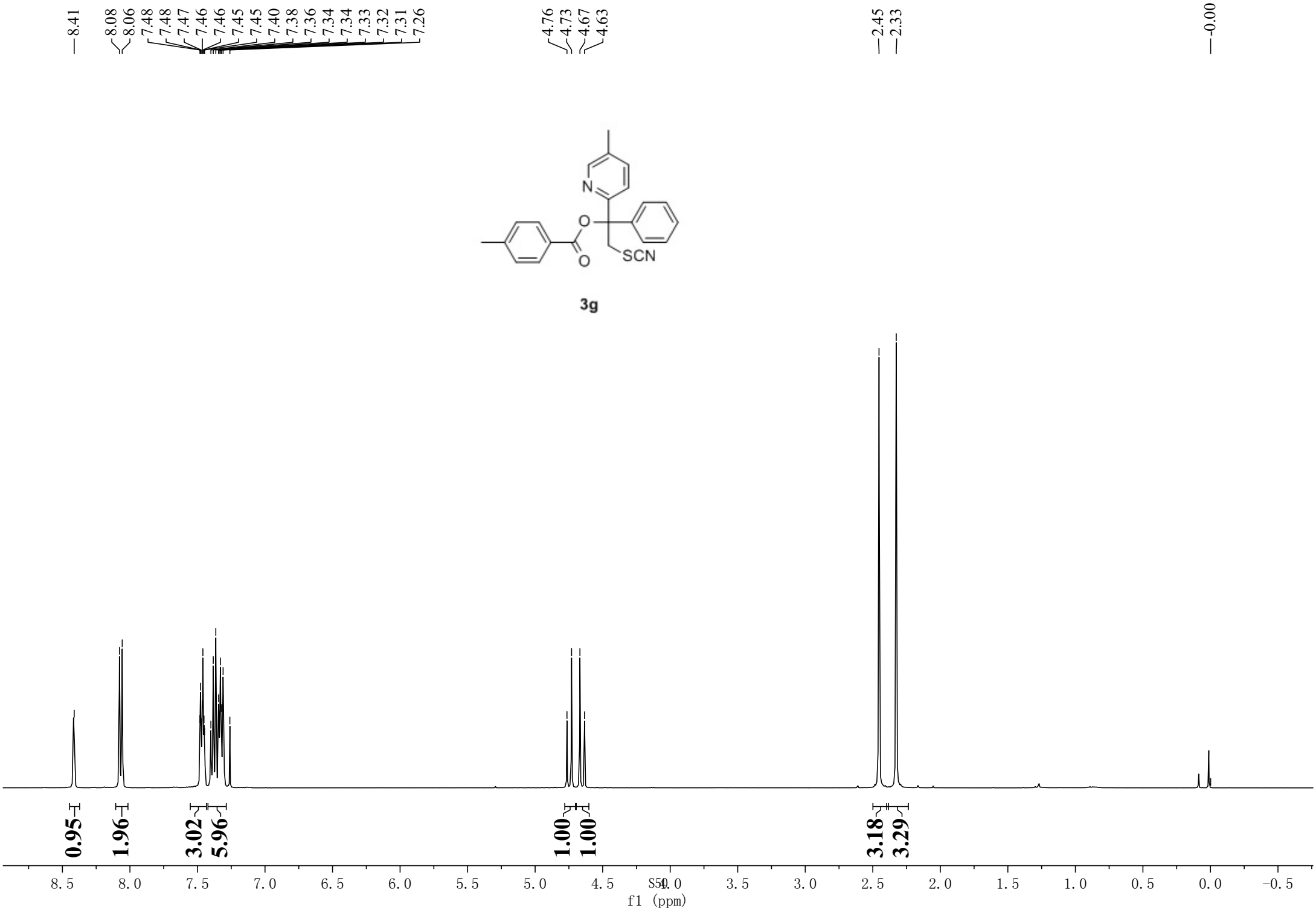
f1 (ppm)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7.45
7.45
7.40
7.38
7.36
7.34
7.34
7.33
7.32
7.31
7.26
4.76
4.73
4.67
4.63
2.45
2.33
-0.00
N
O
O
SCN
3g
0.95
1.96
3.02
5.96
1.00
1.00
3.18
3.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
1.5
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0.5
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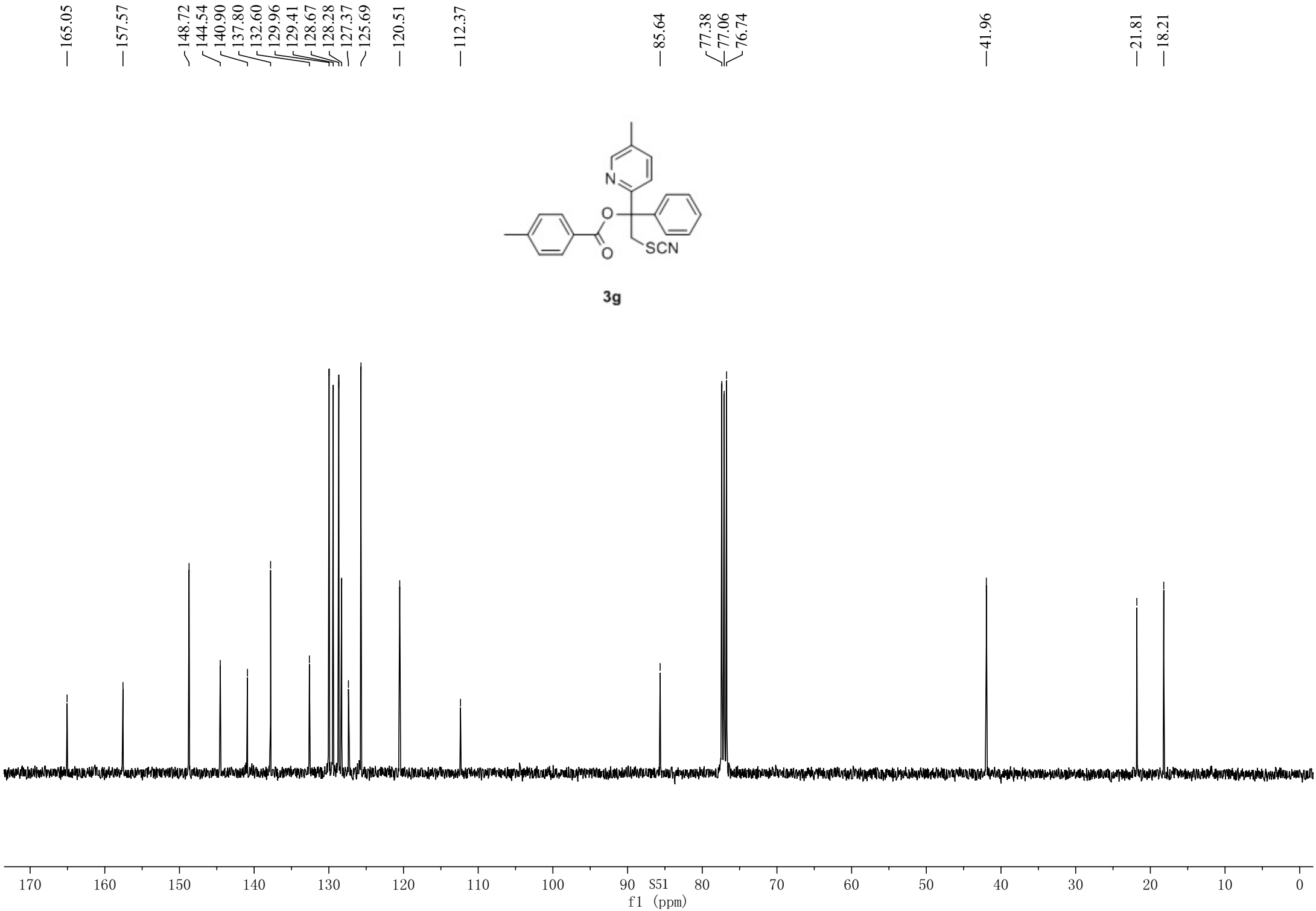
-0.5
f1 (ppm)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128.28
127.37
125.69
120.51
112.37
85.64
77.38
77.06
76.74
41.96
21.81
18.21
N
O
O
SCN
3g
170
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120
110
100
90
S51
80
70
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50
40
30
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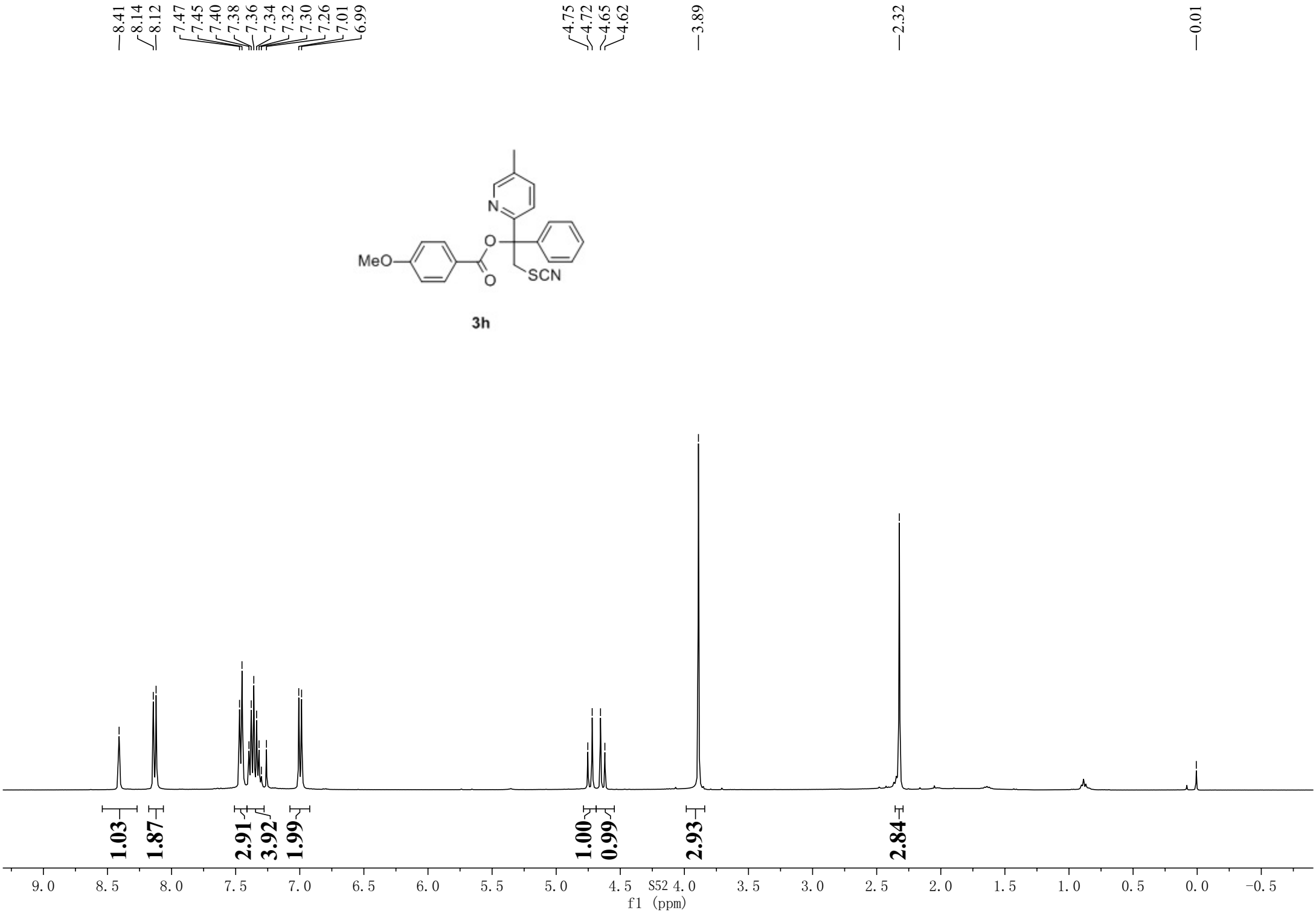
10
0
f1 (ppm)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7.32
7.30
7.26
7.01
6.99
4.75
4.72
4.65
4.62
3.89
2.32
0.01
N
O
MeO
O
SCN
3h
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2.91
3.92
1.99
1.00
0.99
2.93
2.84
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8.0
7.5
7.0
6.5
6.0
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5.0
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2.5
2.0
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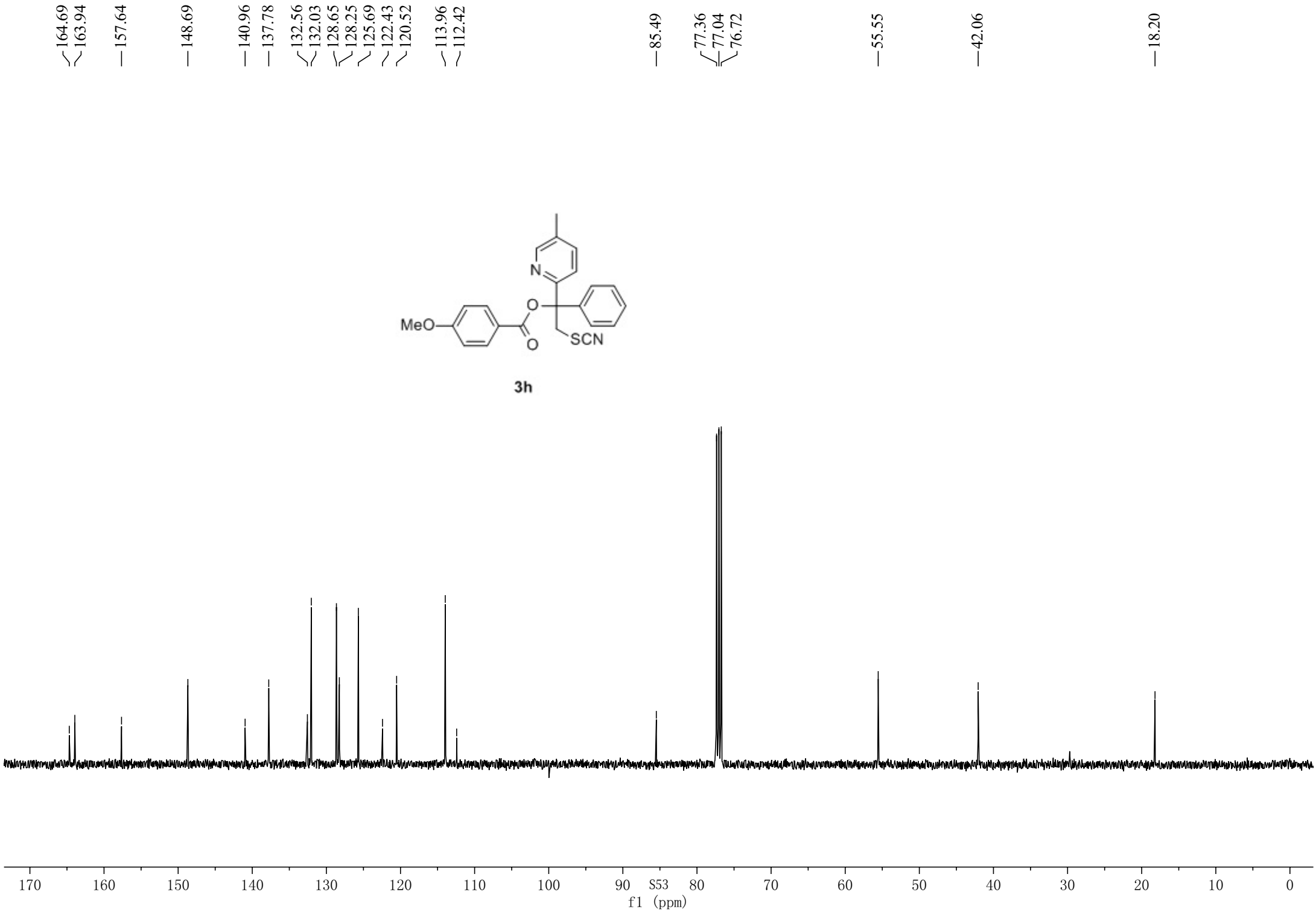
-0.5
f1 (ppm)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122.43
120.52
113.96
112.42
85.49
77.36
77.04
76.72
55.55
42.06
18.20
MeO
O
O
N
SCN
3h
170
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100
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S53
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70
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50
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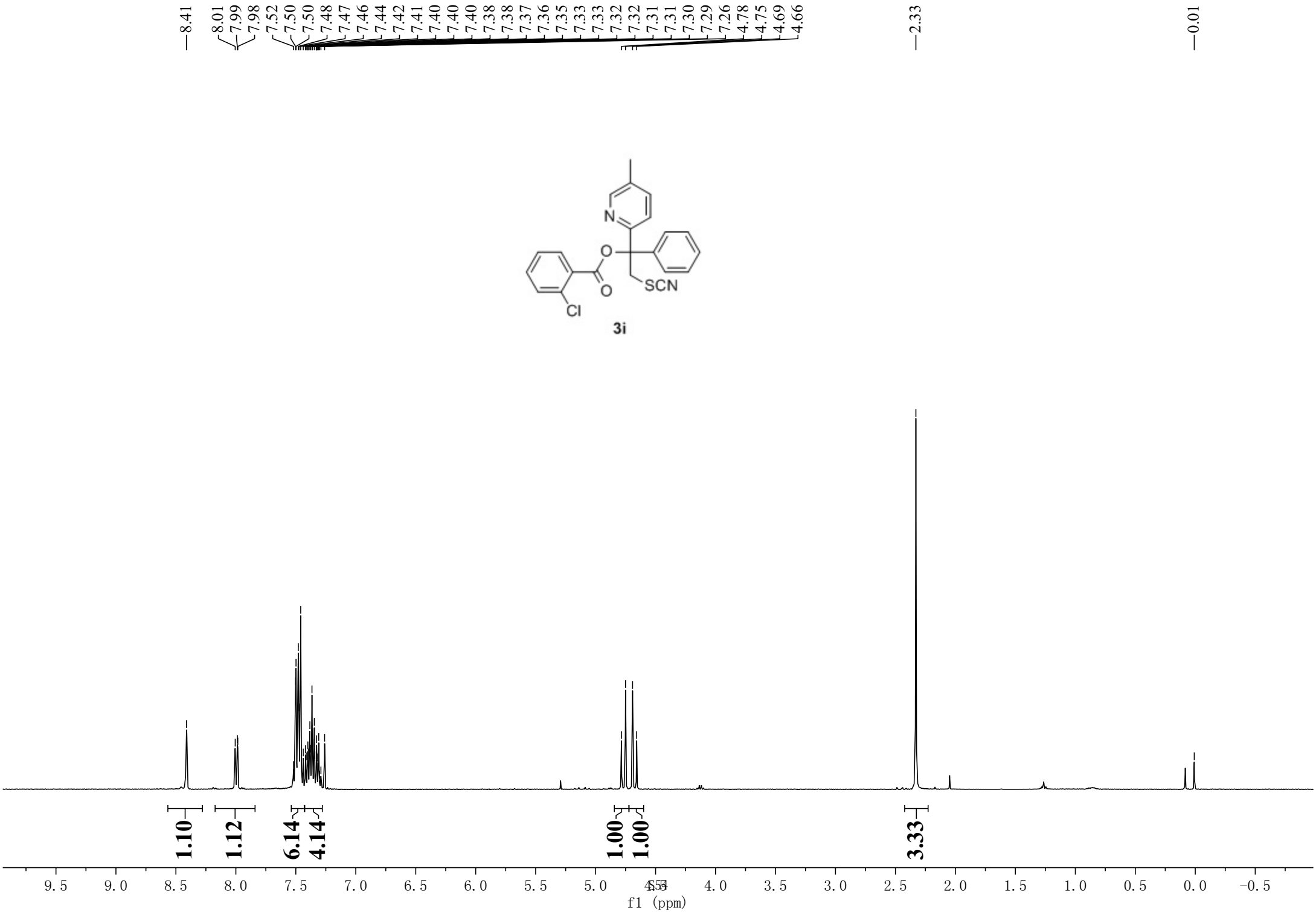
10
0
f1 (ppm)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7.40
7.40
7.40
7.38
7.38
7.37
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7.35
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.26
4.78
4.75
4.69
4.66
2.33
0.01
N
O
O
SCN
Cl
3i
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1.12
6.14
4.14
1.00
1.00
3.33
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8.5
8.0
7.5
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6.5
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5.0
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3.0
2.5
2.0
1.5
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0.5
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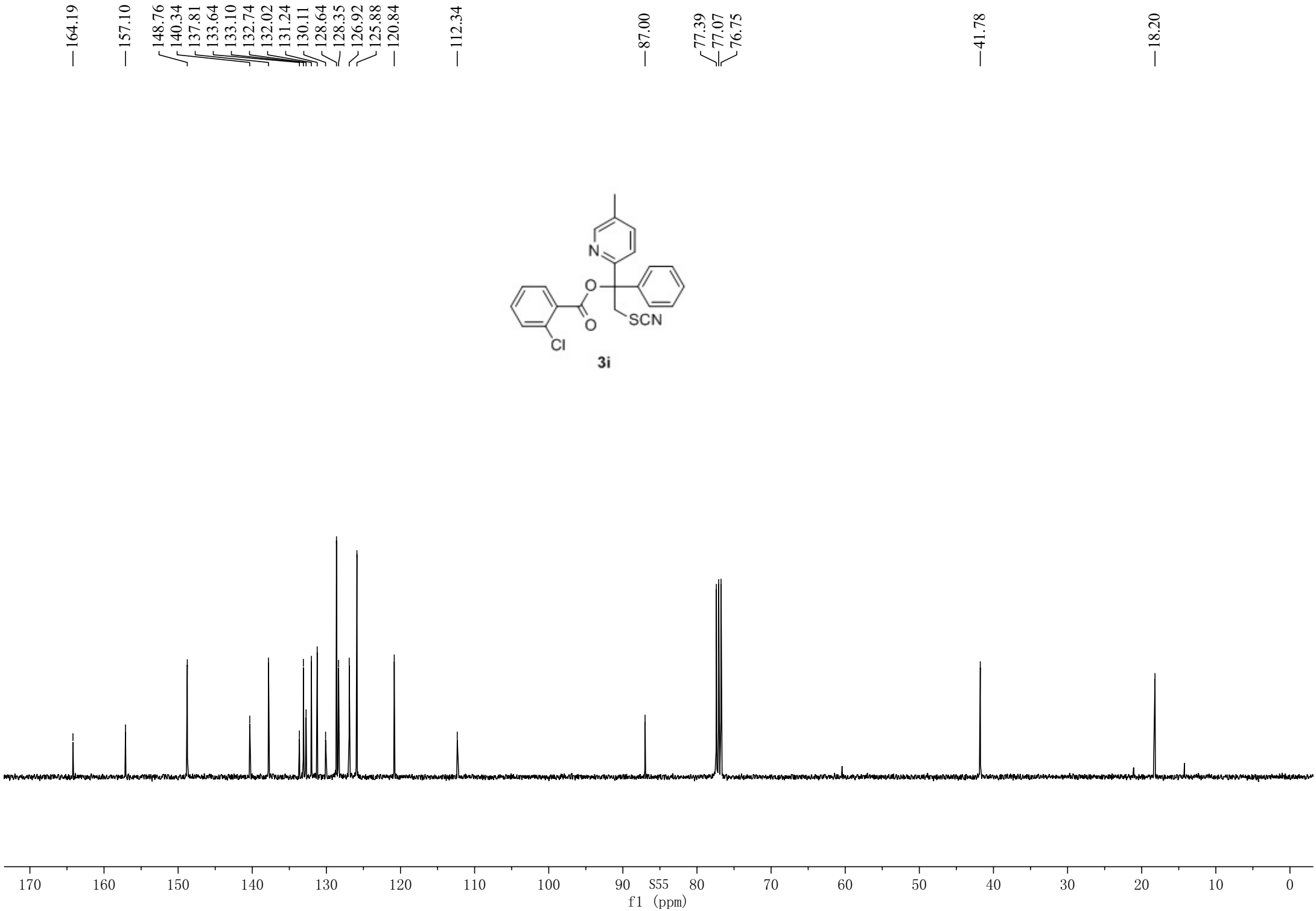
-0.5
f1 (ppm)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76.75
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O
O
SCN
Cl
3i
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50
40
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10
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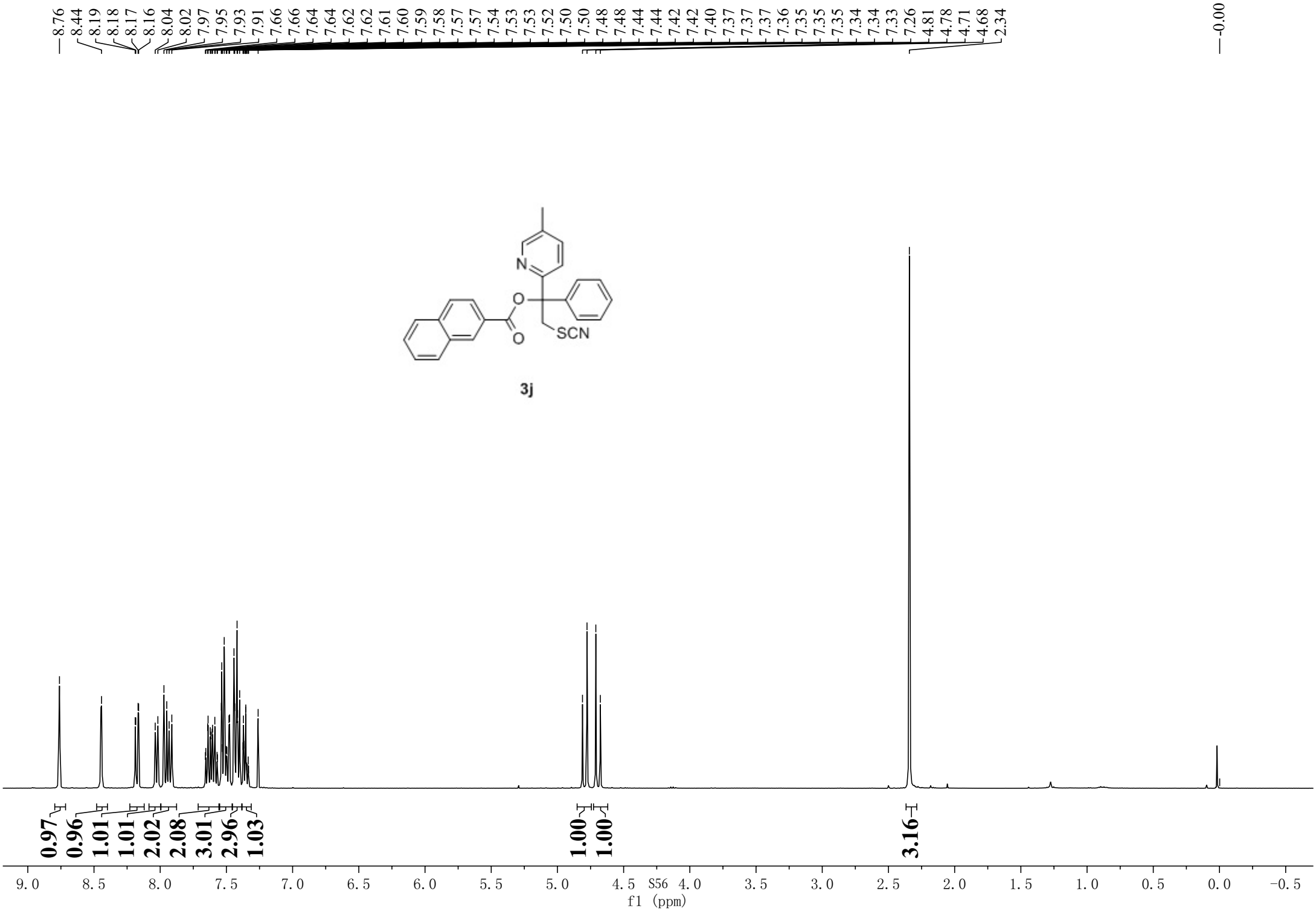
f1 (ppm)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7.40
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7.34
7.33
7.26
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4.78
4.71
4.68
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O
O
SCN
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0.96
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1.01
2.02
2.08
3.01
2.96
1.03
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1.00
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6.5
6.0
5.5
5.0
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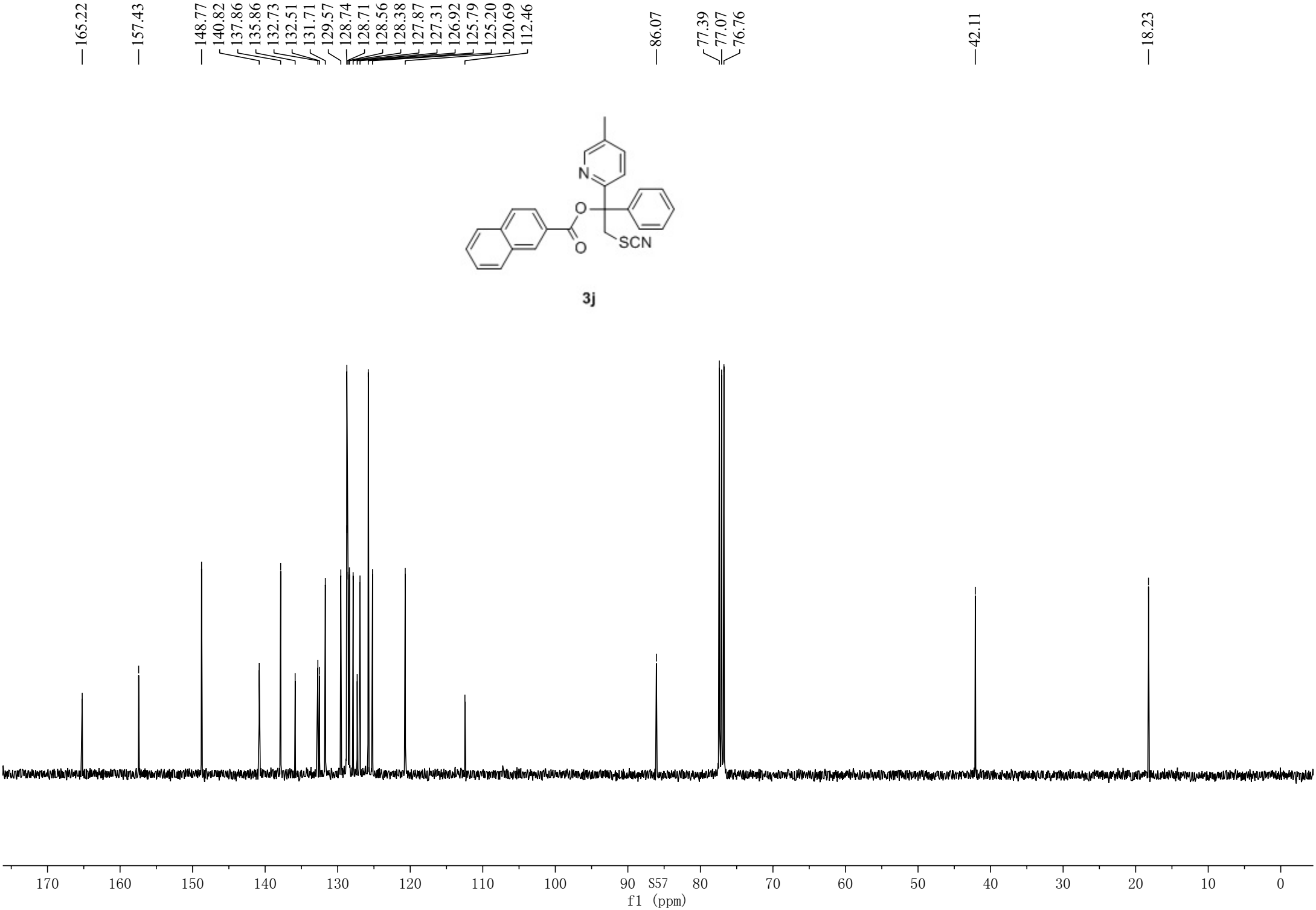
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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128.56
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127.31
126.92
125.79
125.20
120.69
112.46
86.07
77.39
77.07
76.76
42.11
18.23
N
O
O
SCN
3j
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120
110
100
90
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70
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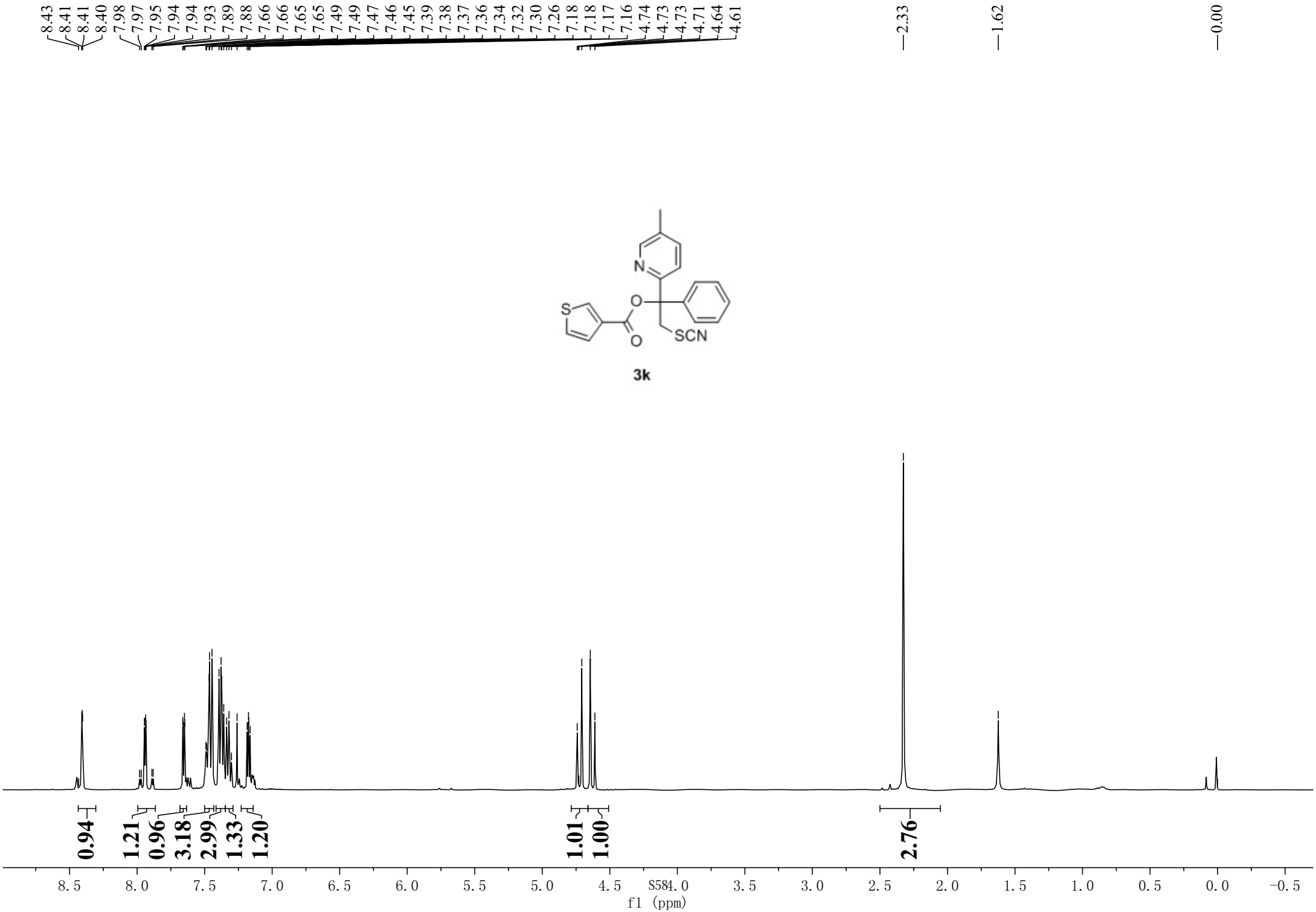
50
40
30
20
10
0
f1 (ppm)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7.49
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7.36
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2.33
1.62
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S
O
O
SCN
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0.96
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1.33
1.20
1.01
1.00
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7.5
7.0
6.5
6.0
5.5
5.0
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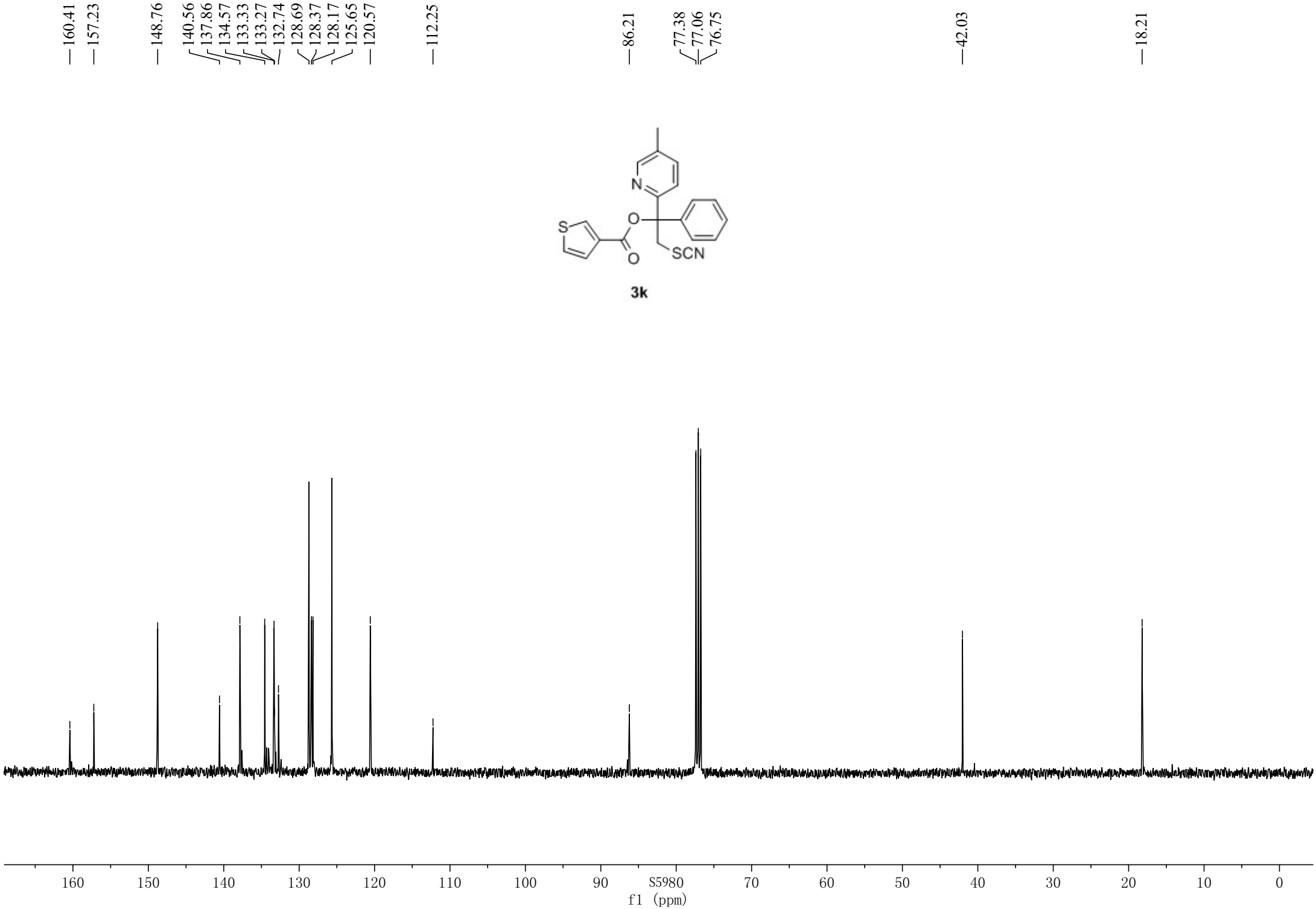
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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125.65
120.57
112.25
86.21
77.38
77.06
76.75
42.03
18.21
N
O
S
O
SCN
3k
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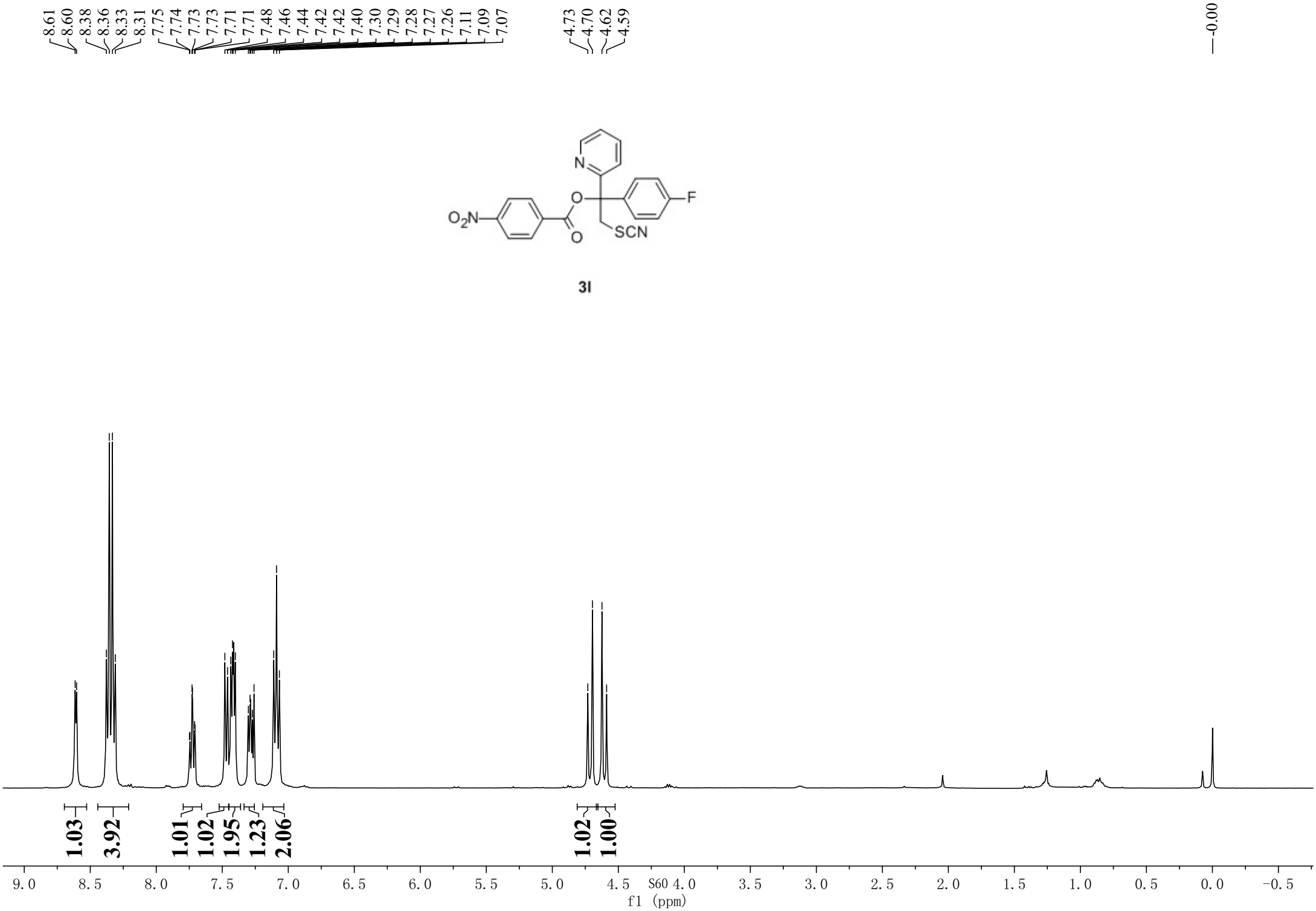
150
140
130
120
110
100
90
S5980
70
60
50
40
30
20
10
0
f1 (ppm)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8.38
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7.74
7.73
7.73
7.71
7.71
7.48
7.46
7.44
7.42
7.42
7.40
7.30
7.29
7.28
7.27
7.26
7.11
7.09
7.07
4.73
4.70
4.62
4.59
-0.00
N
O
F
O_2N
O
SCN
3l
1.03
3.92
1.01
1.02
1.95
1.23
2.06
1.02
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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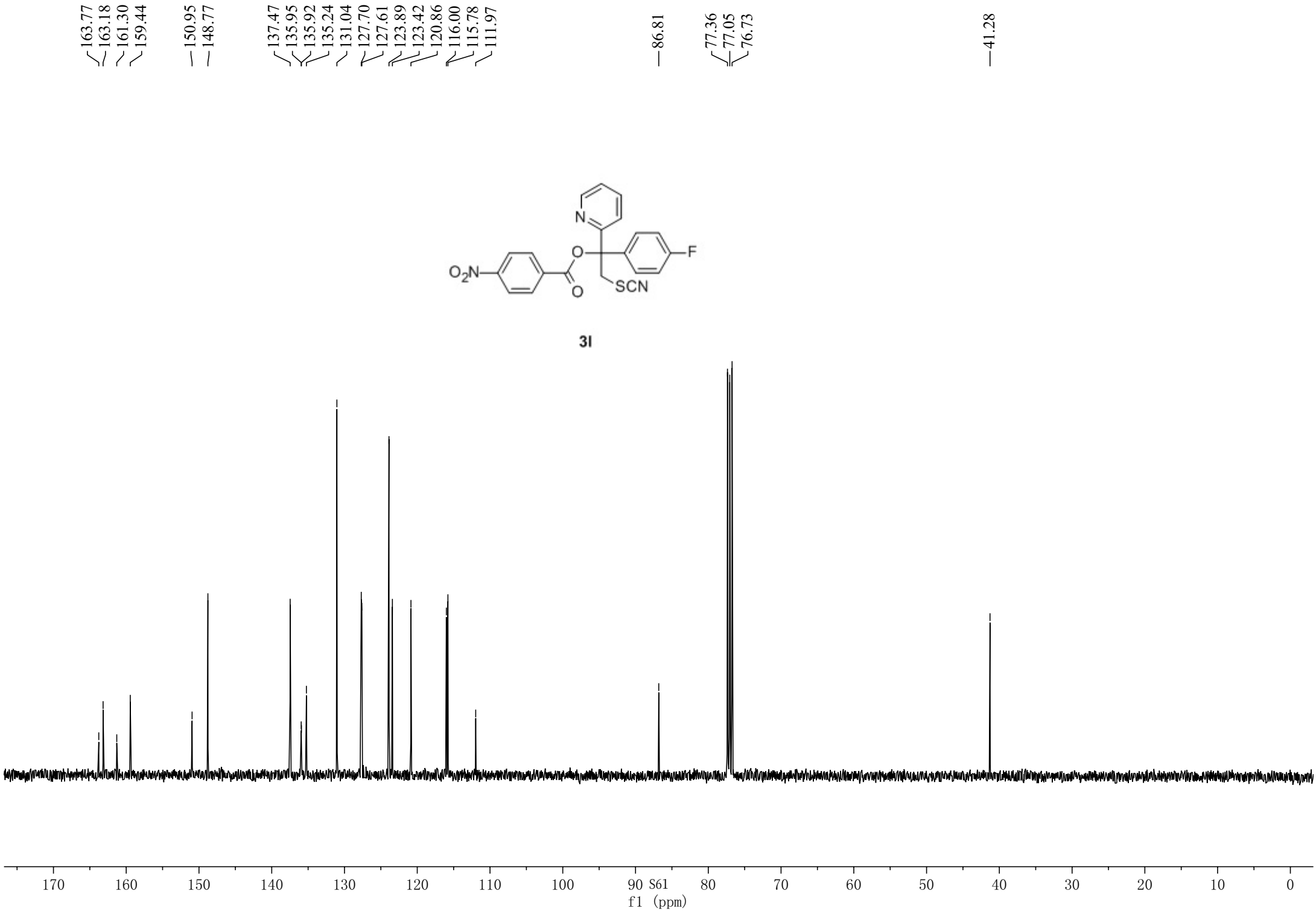
0.0
-0.5
f1 (ppm)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135.95
135.92
135.24
131.04
127.70
127.61
123.89
123.42
120.86
116.00
115.78
111.97
86.81
77.36
77.05
76.73
41.28
N
O
F
O_2N
O
SCN
3l
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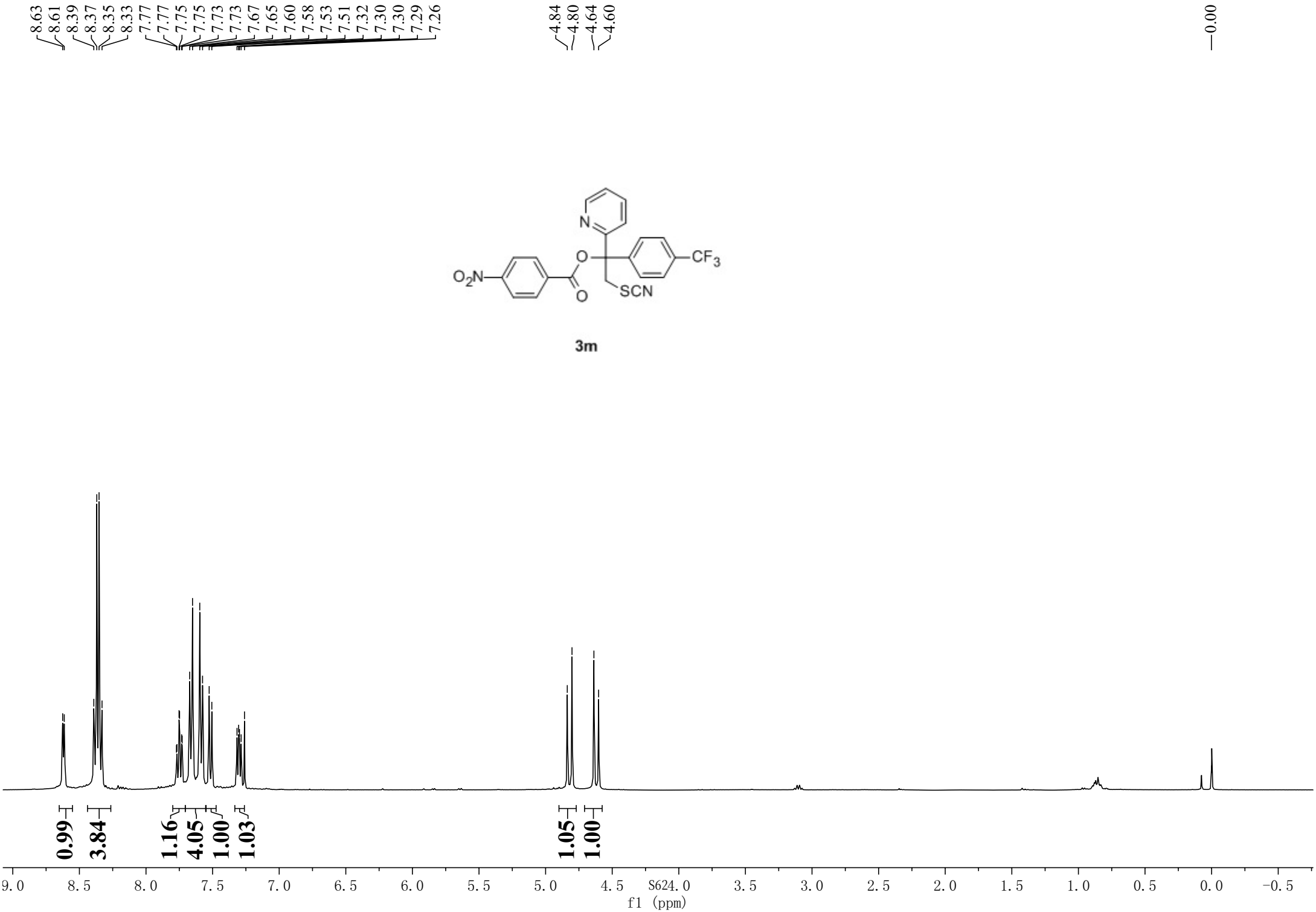
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.77
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7.75
7.73
7.73
7.67
7.65
7.60
7.58
7.53
7.51
7.32
7.30
7.30
7.29
7.26
4.84
4.80
4.64
4.60
0.00
N
O
CF3
O2N
O
SCN
3m
0.99
3.84
1.16
4.05
1.00
1.03
1.05
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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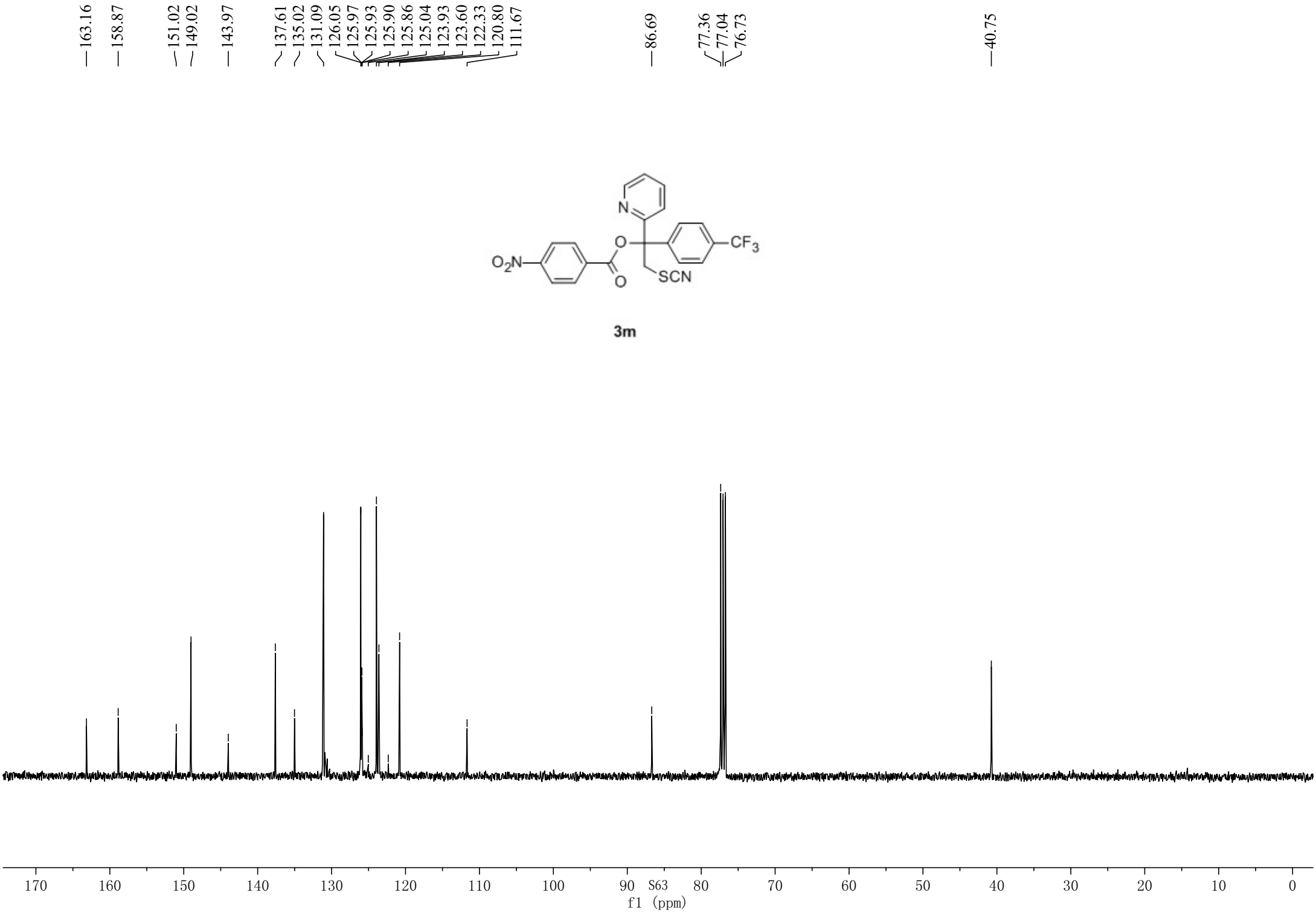
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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131.09
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125.93
125.90
125.86
125.04
123.93
123.60
122.33
120.80
111.67
86.69
77.36
77.04
76.73
40.75
N
O
CF3
O2N
O
SCN
3m
170
160
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140
130
120
110
100
90
80
70
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50
40
30
20
10
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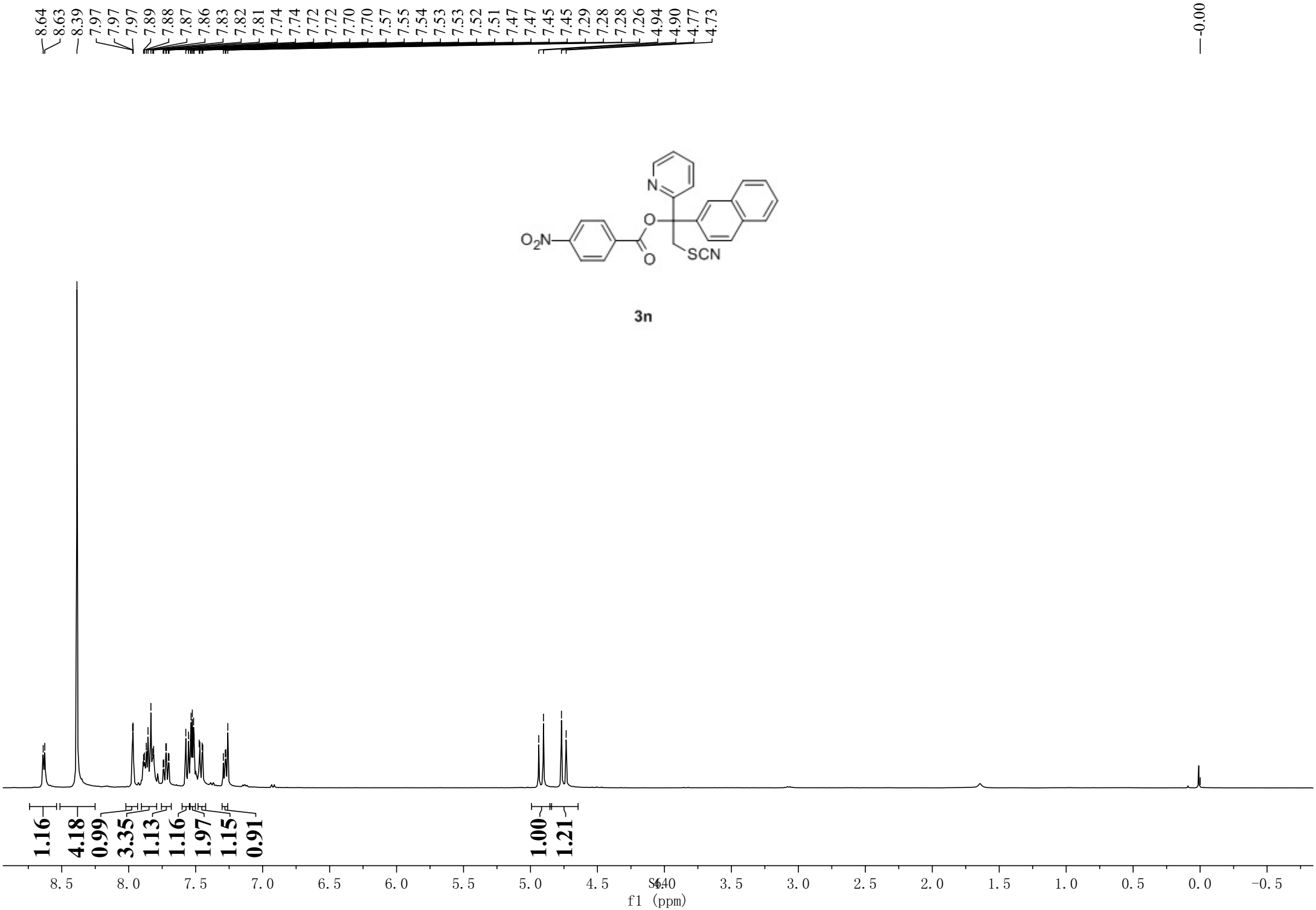
f1 (ppm)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7.88
7.87
7.86
7.83
7.82
7.81
7.74
7.74
7.72
7.72
7.70
7.70
7.57
7.55
7.54
7.53
7.53
7.52
7.51
7.47
7.47
7.45
7.45
7.29
7.28
7.28
7.26
4.94
4.90
4.77
4.73
-0.00
N
O
O_2N
O
SCN
3n
1.16
4.18
0.99
3.35
1.13
1.16
1.97
1.15
0.91
1.00
1.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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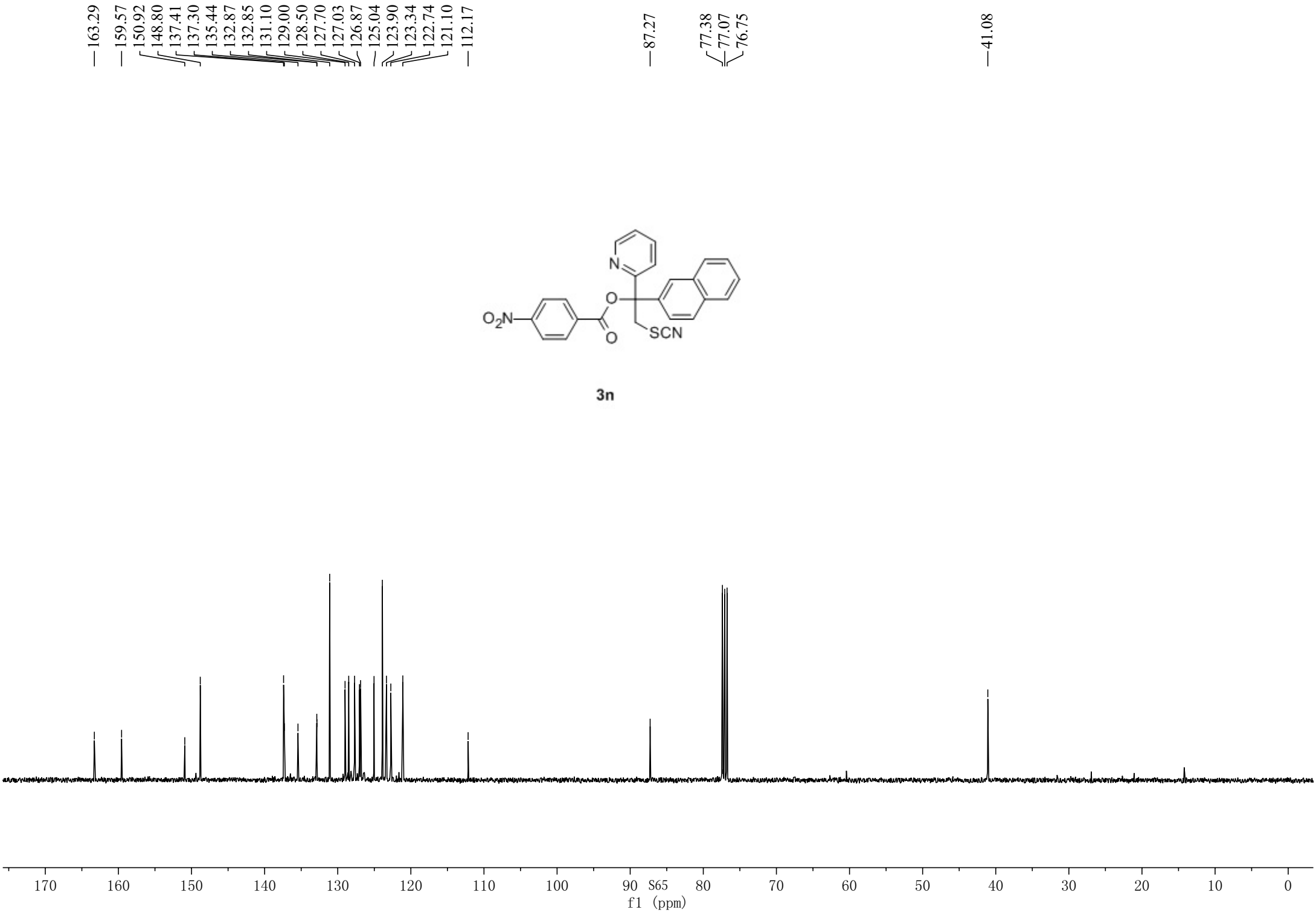
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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137.30
135.44
132.87
132.85
131.10
129.00
128.50
127.70
127.03
126.87
125.04
123.90
123.34
122.74
121.10
112.17
87.27
77.38
77.07
76.75
41.08
N
O
O_2N
O
SCN
3n
170
160
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140
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120
110
100
90
S65
80
70
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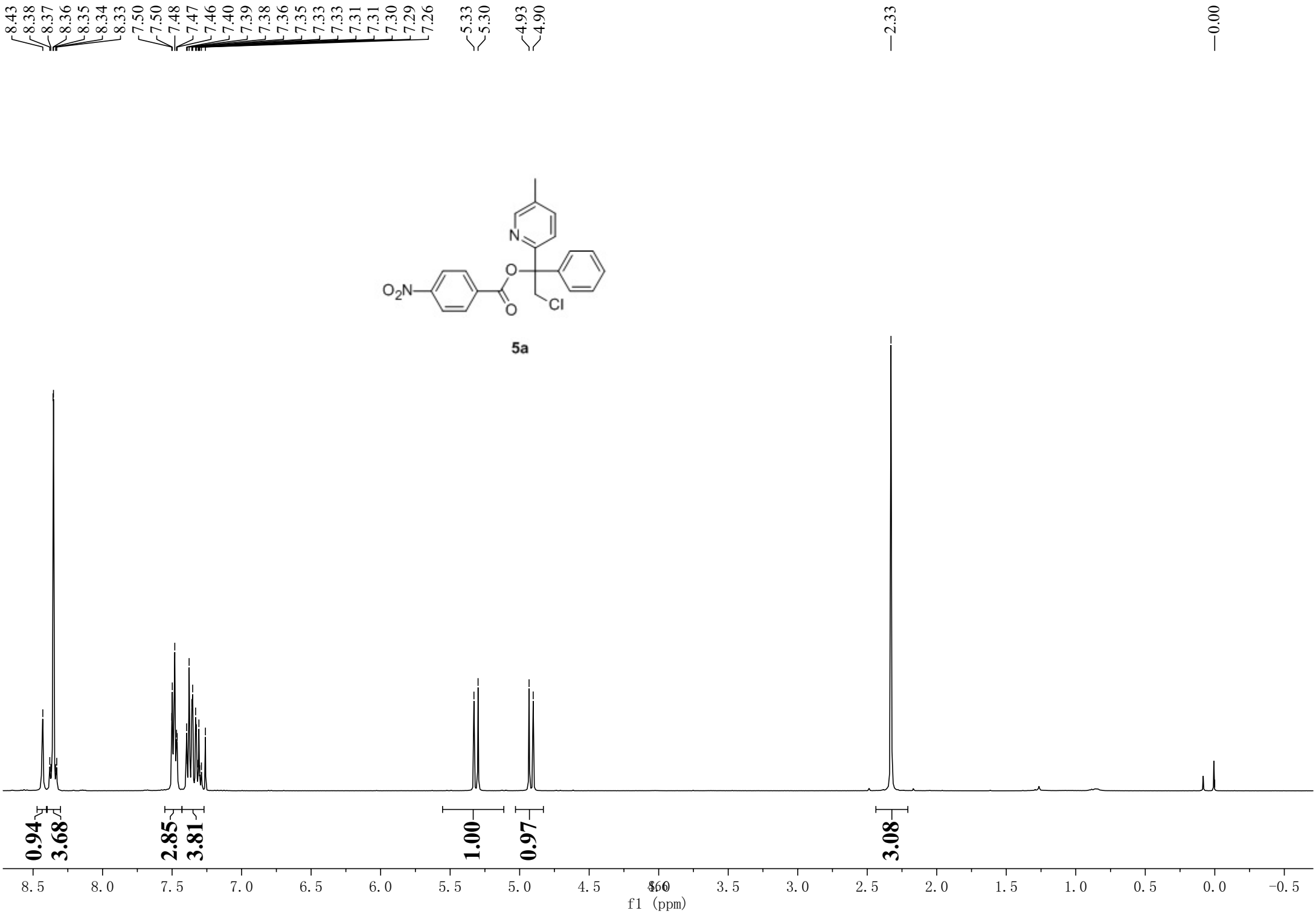
50
40
30
20
10
0
f1 (ppm)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8.37
8.36
8.35
8.34
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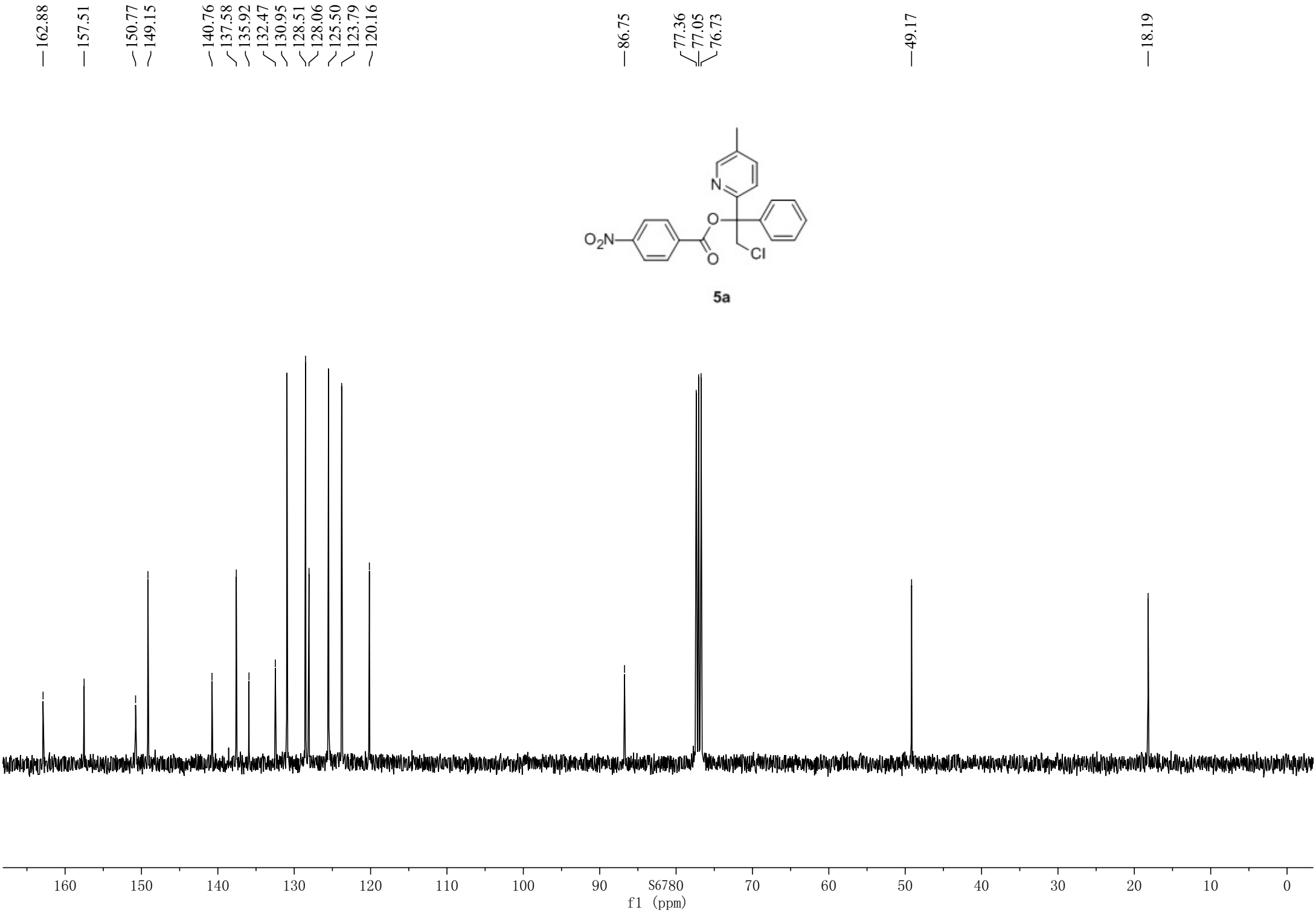
7.50
7.50
7.48
7.47
7.46
7.40
7.39
7.38
7.36
7.35
7.33
7.33
7.31
7.31
7.30
7.29
7.26
5.33
5.30
4.93
4.90
2.33
0.00
N
O
O2N
O
Cl
5a
0.94
3.68
2.85
3.81
1.00
0.97
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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137.58
135.92
132.47
130.95
128.51
128.06
125.50
123.79
120.16
86.75
77.36
77.05
76.73
49.17
18.19
N
O
O_2N
O
Cl
5a
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150
140
130
120
110
100
90
S6780
70
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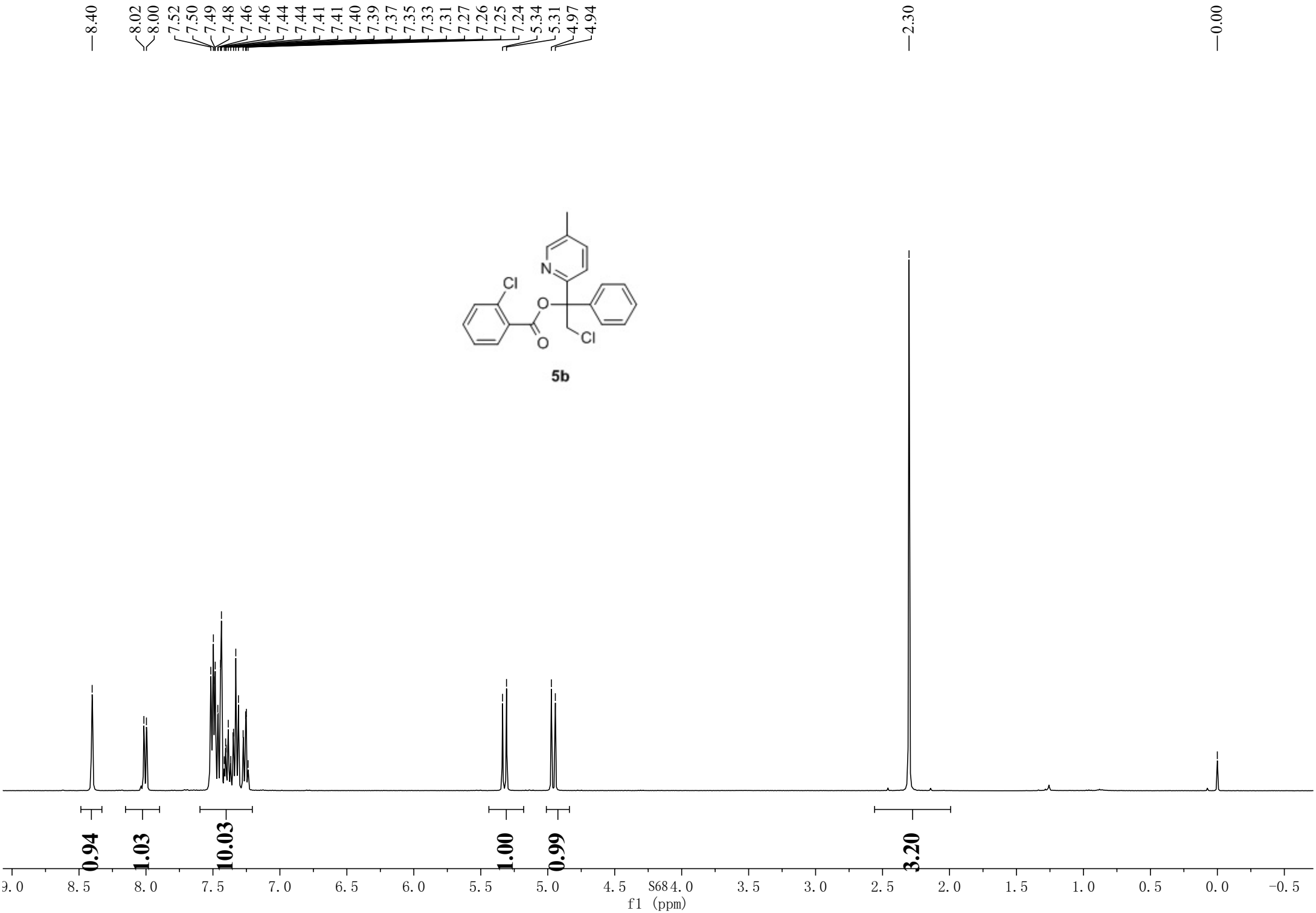
50
40
30
20
10
0
f1 (ppm)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7.49
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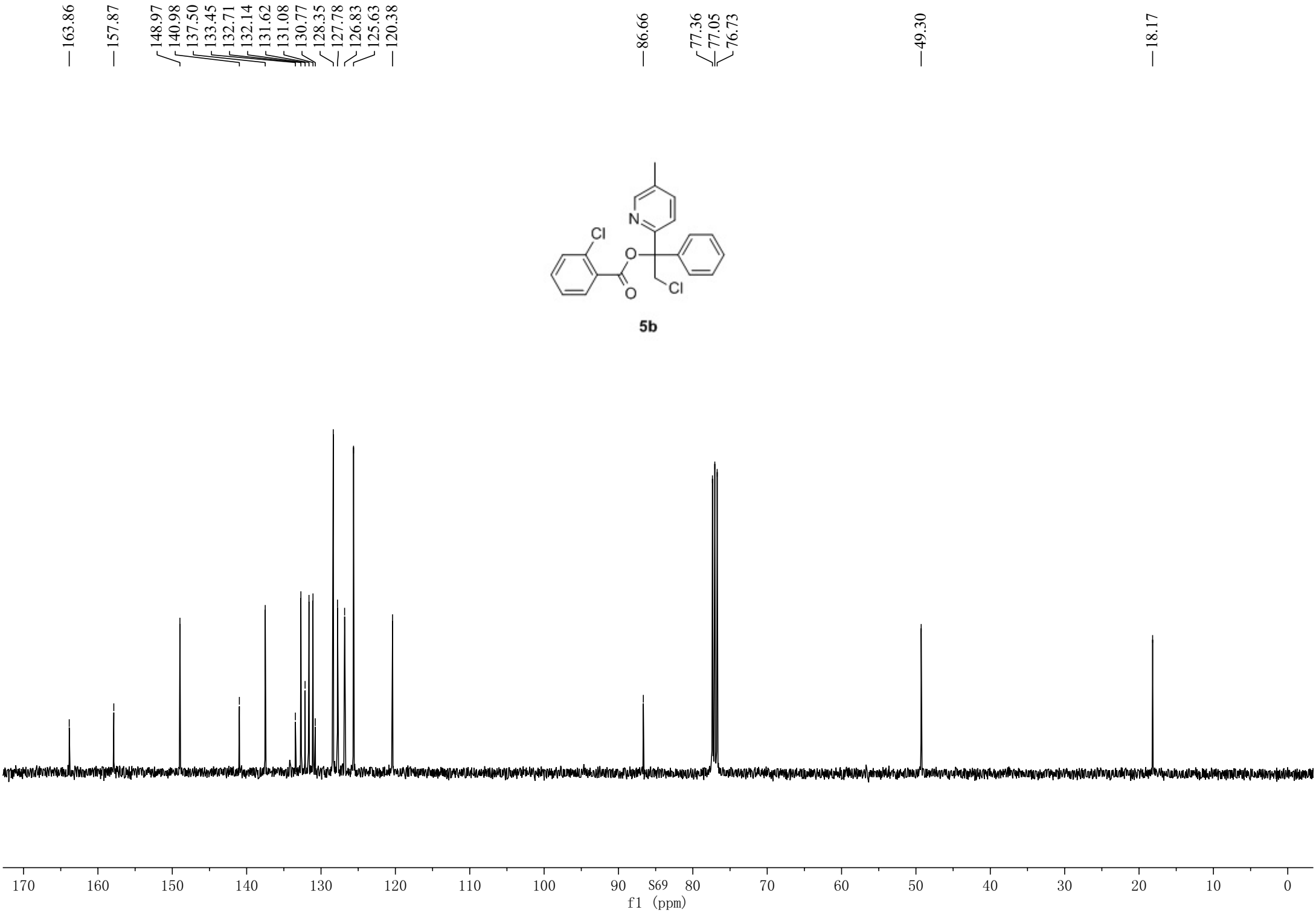
7.46
7.46
7.44
7.44
7.41
7.41
7.40
7.39
7.37
7.35
7.33
7.31
7.27
7.26
7.25
7.24
5.34
5.31
4.97
4.94
2.30
0.00
N
Cl
O
O
Cl
5b
0.94
1.03
10.03
1.00
0.99
3.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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131.08
130.77
128.35
127.78
126.83
125.63
120.38
86.66
77.36
77.05
76.73
49.30
18.17
N
Cl
O
O
Cl
5b
170
160
150
140
130
120
110
100
90
80
70
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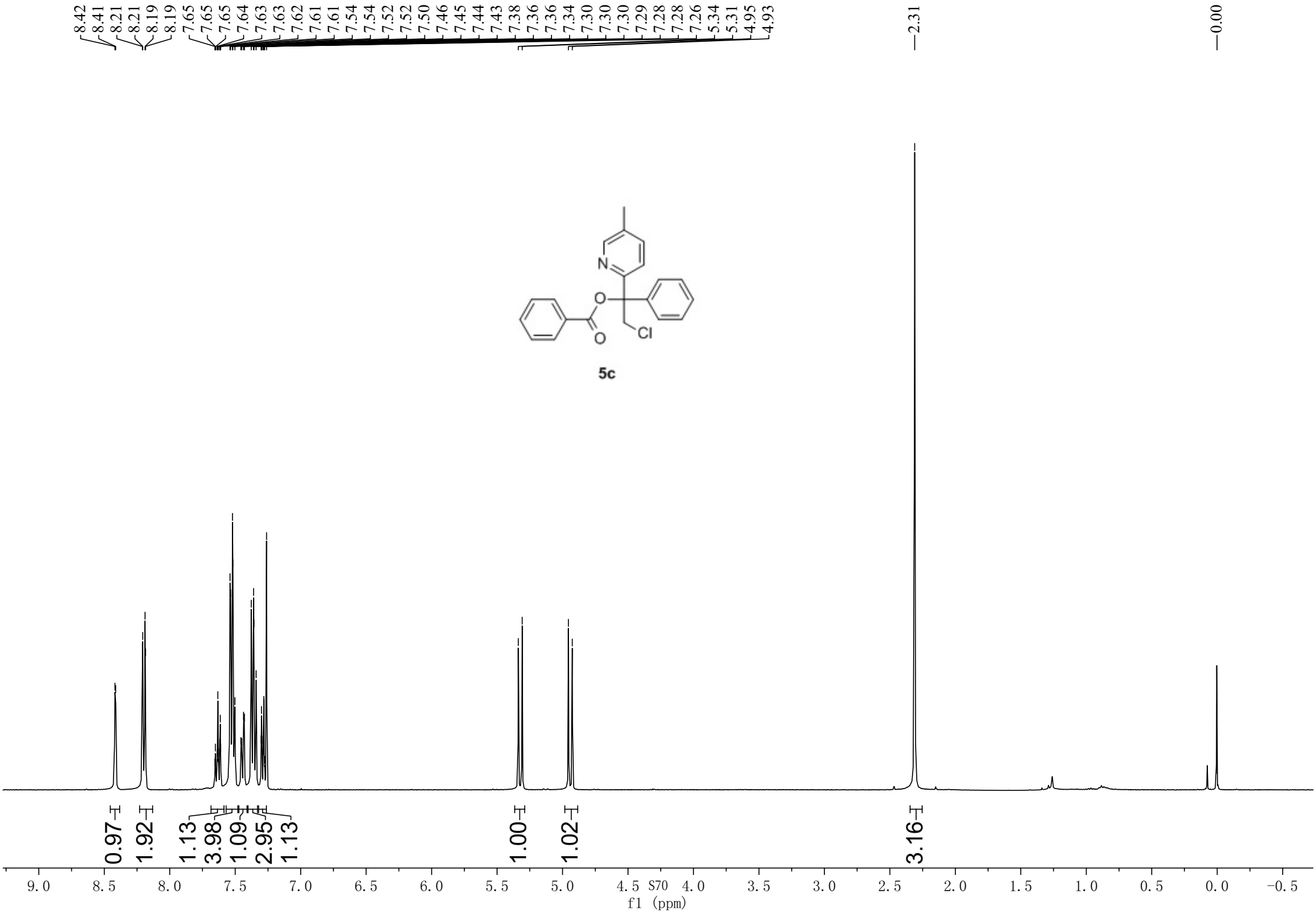
50
40
30
20
10
0
f1 (ppm)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7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.54
7.54
7.52
7.52
7.50
7.46
7.45
7.44
7.43
7.38
7.36
7.36
7.34
7.30
7.30
7.30
7.29
7.28
7.28
7.26
5.34
5.31
4.95
4.93
2.31
0.00
N
O
O
Cl
5c
0.97
1.92
1.13
3.98
1.09
2.95
1.13
1.00
1.02
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
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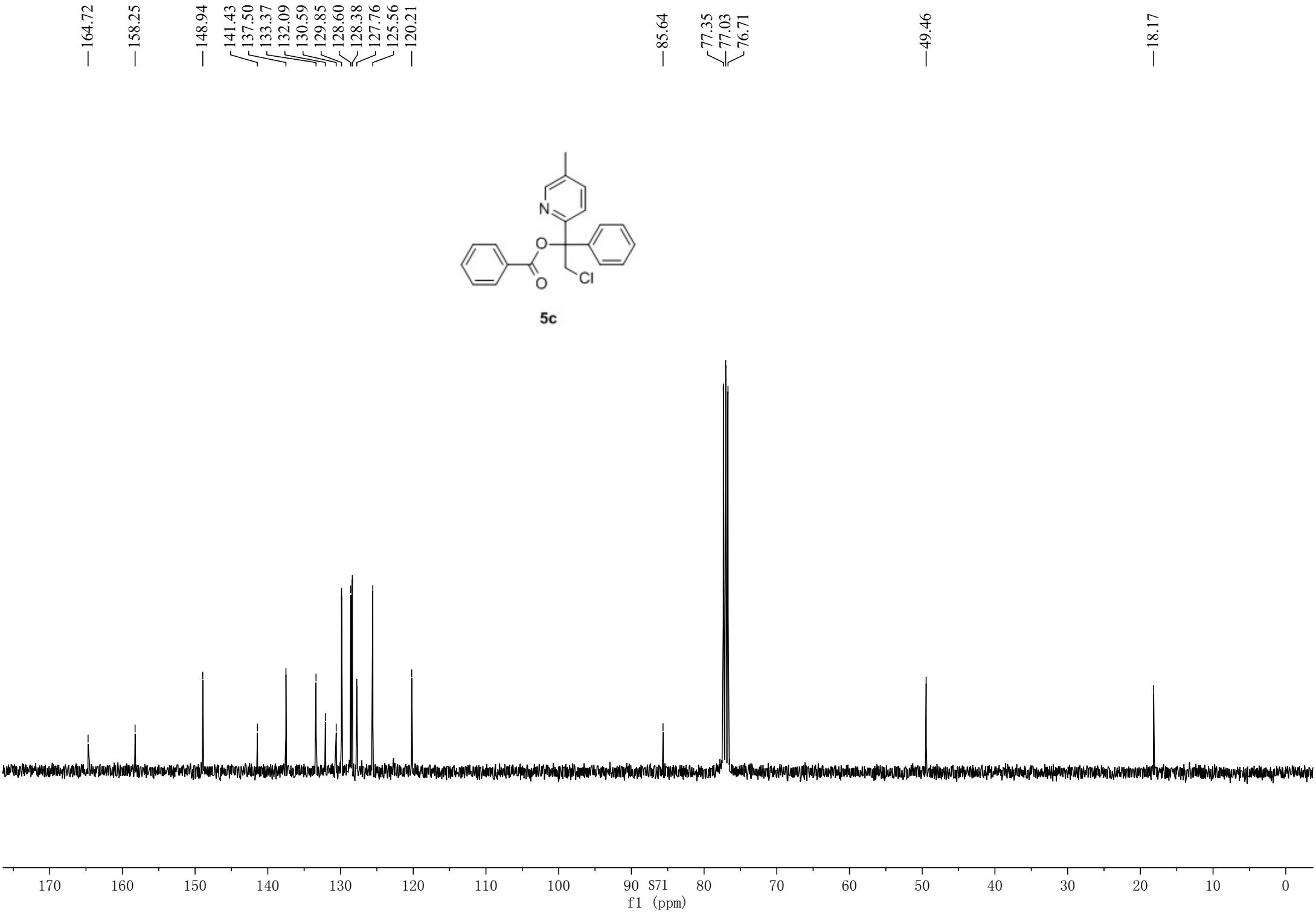
0.5
0.0
-0.5
f1 (ppm)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128.38
127.76
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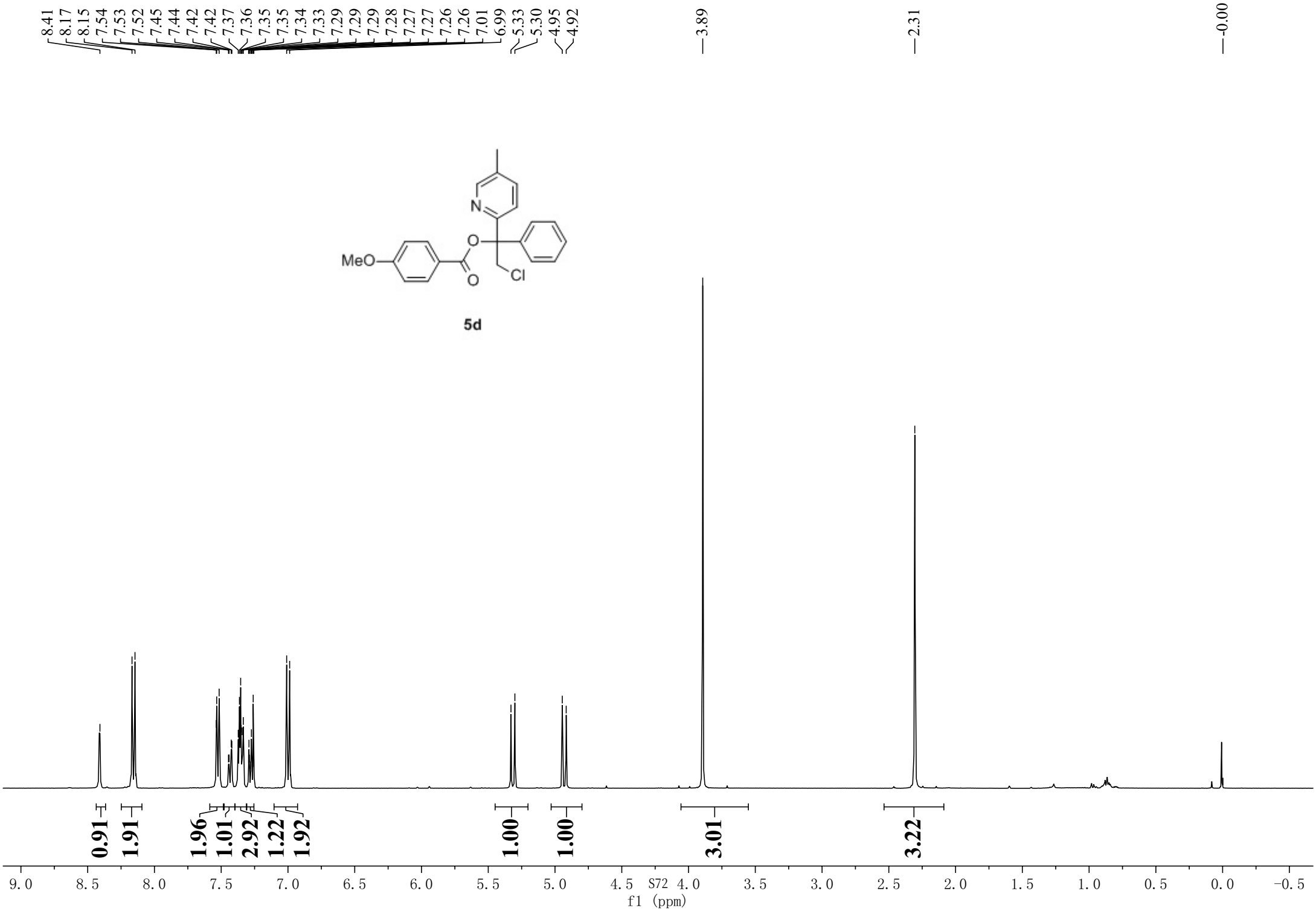
120.21
85.64
77.35
77.03
76.71
49.46
18.17
N
O
O
Cl
5c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.44
7.42
7.42
7.37
7.36
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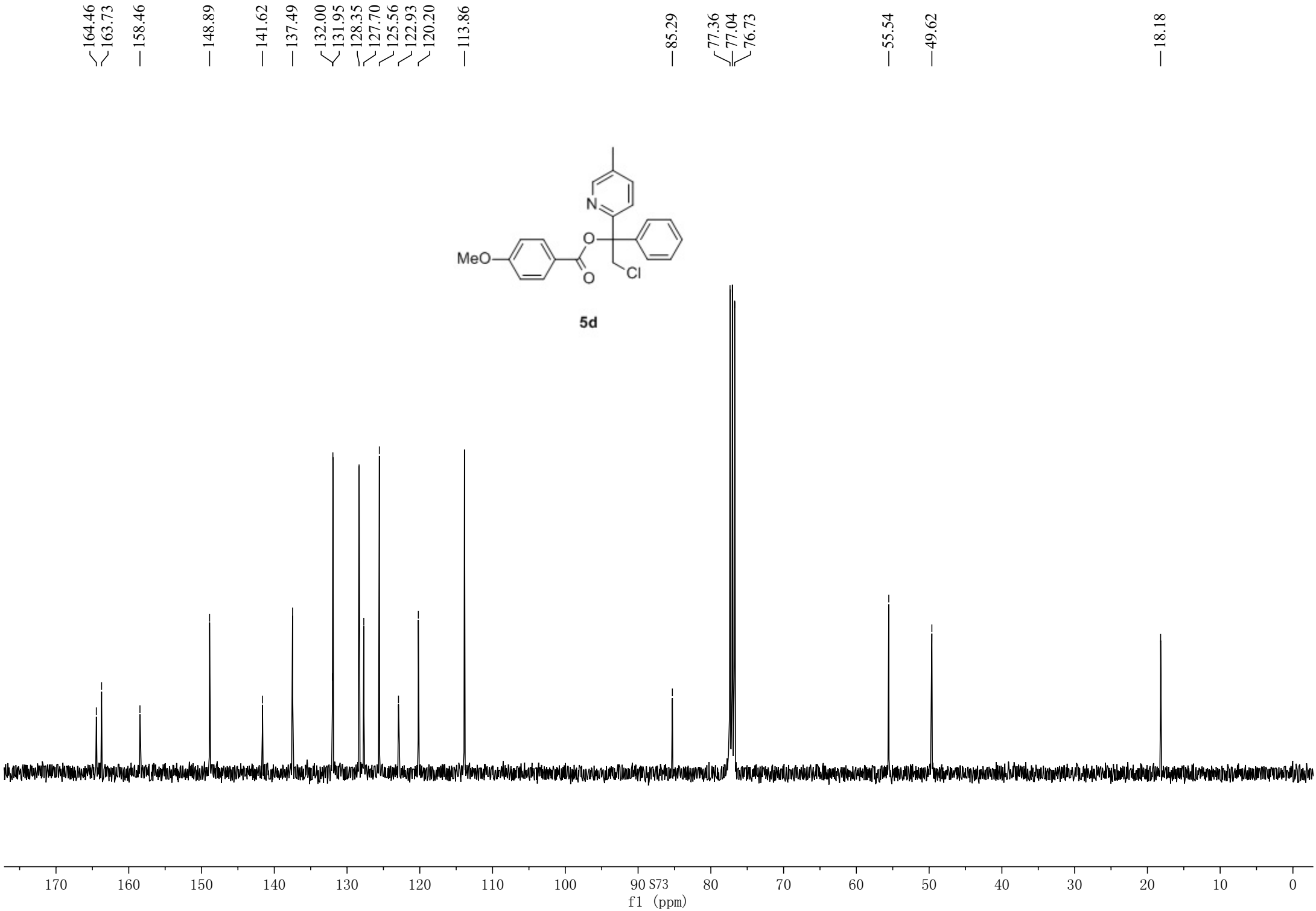
7.35
7.34
7.33
7.29
7.29
7.29
7.28
7.27
7.27
7.26
7.26
7.01
6.99
5.33
5.30
4.95
4.92
3.89
2.31
-0.00
MeO
O
O
N
Cl
5d
0.91
1.91
1.96
1.01
2.92
1.22
1.92
1.00
1.00
3.01
3.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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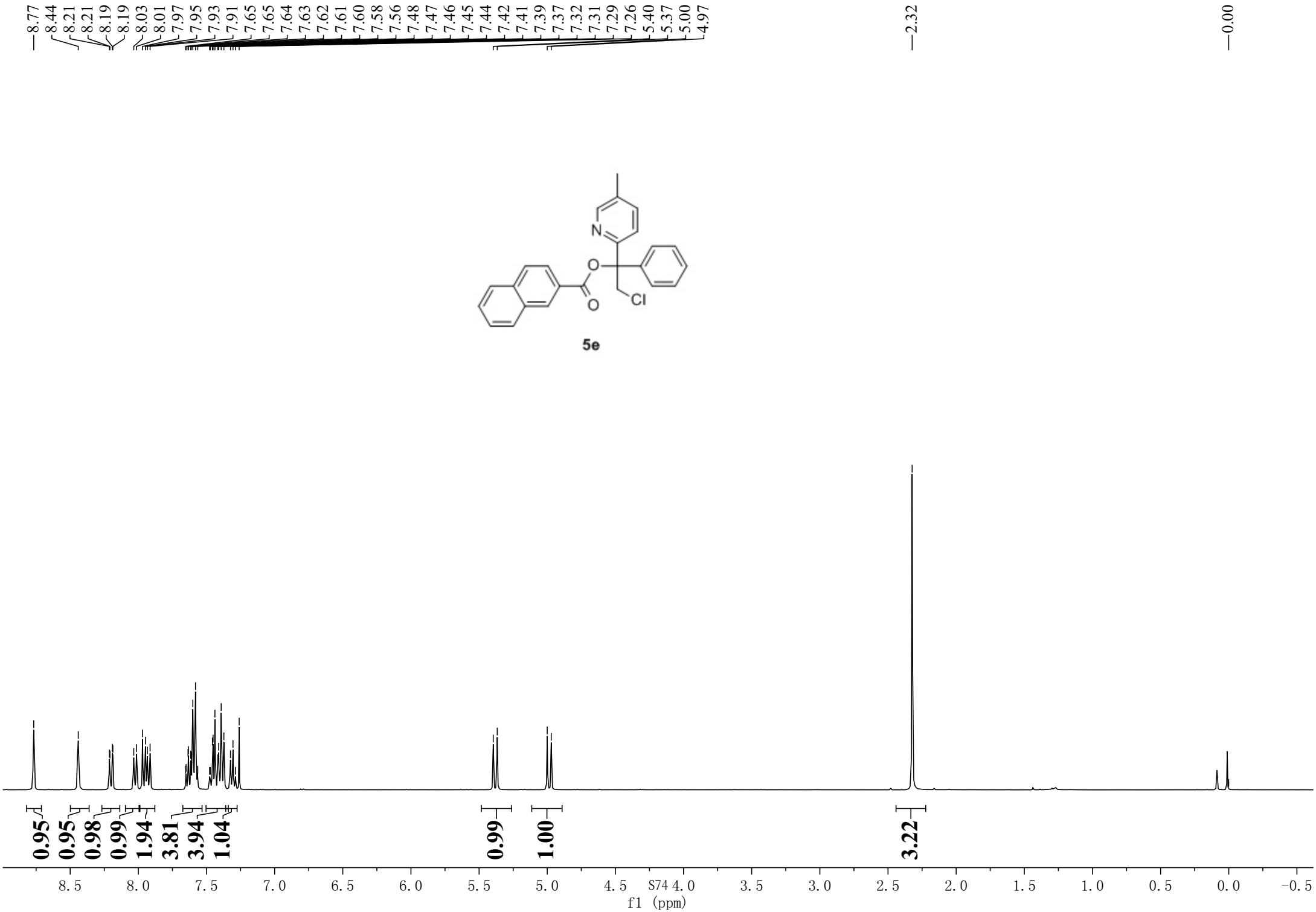
122.93
120.20
113.86
85.29
77.36
77.04
76.73
55.54
49.62
18.18
N
O
MeO
O
Cl
5d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.19
8.03
8.01
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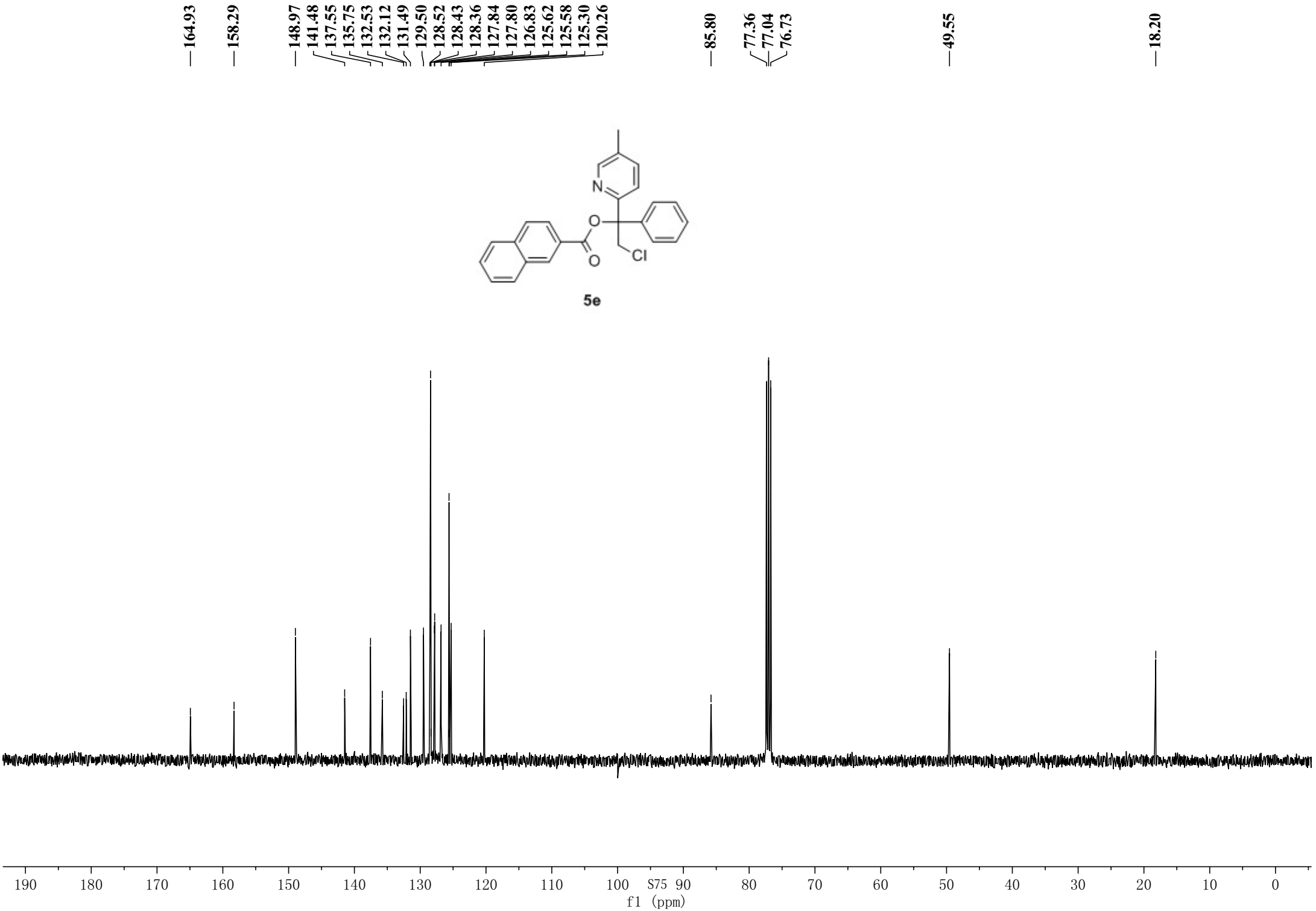
7.95
7.93
7.91
7.65
7.65
7.64
7.63
7.62
7.61
7.60
7.58
7.56
7.48
7.47
7.46
7.45
7.44
7.42
7.41
7.39
7.37
7.32
7.31
7.29
7.26
5.40
5.37
5.00
4.97
2.32
0.00
N
O
O
Cl
5e
0.95
0.95
0.98
0.99
1.94
3.81
3.94
1.04
0.99
1.00
3.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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127.80
126.83
125.62
125.58
125.30
120.26
85.80
77.36
77.04
76.73
49.55
18.20
N
O
O
Cl
5e
190
180
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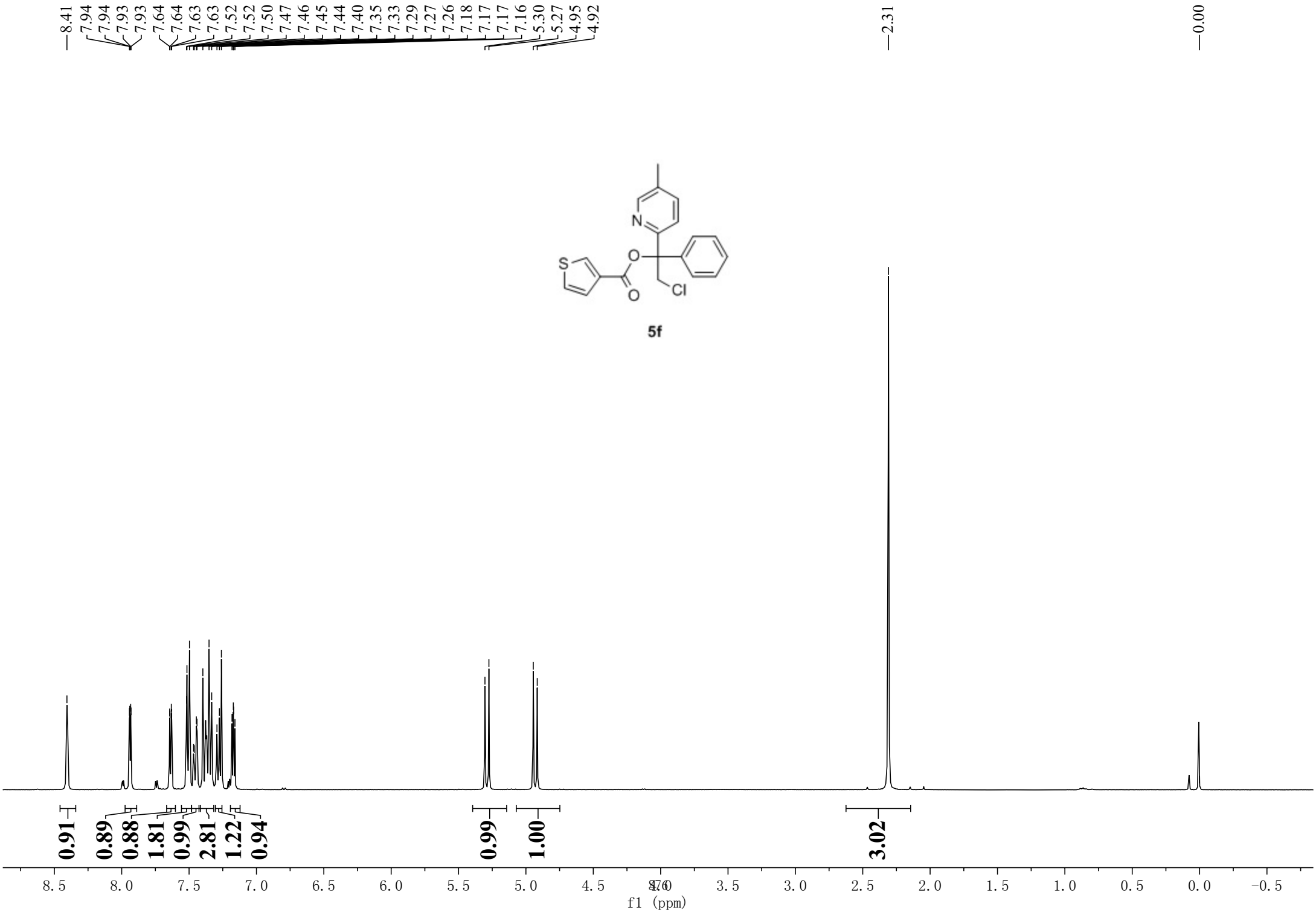
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.52
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7.47
7.46
7.45
7.44
7.40
7.35
7.33
7.29
7.27
7.26
7.18
7.17
7.17
7.16
5.30
5.27
4.95
4.92
2.31
0.00
N
S
O
O
Cl
5f
0.91
0.89
0.88
1.81
0.99
2.81
1.22
0.94
0.99
1.00
3.02
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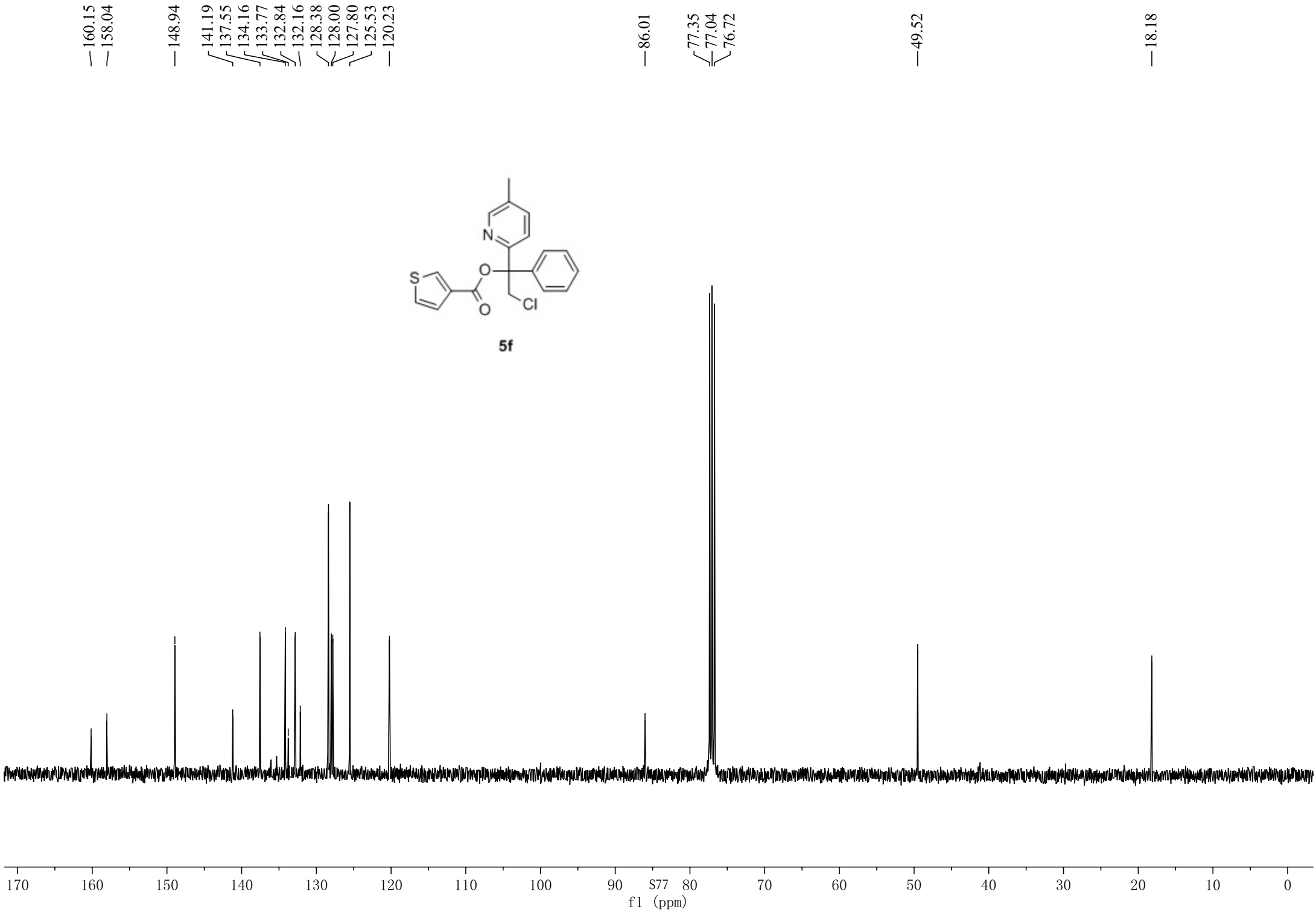
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


160.15
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141.19
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134.16
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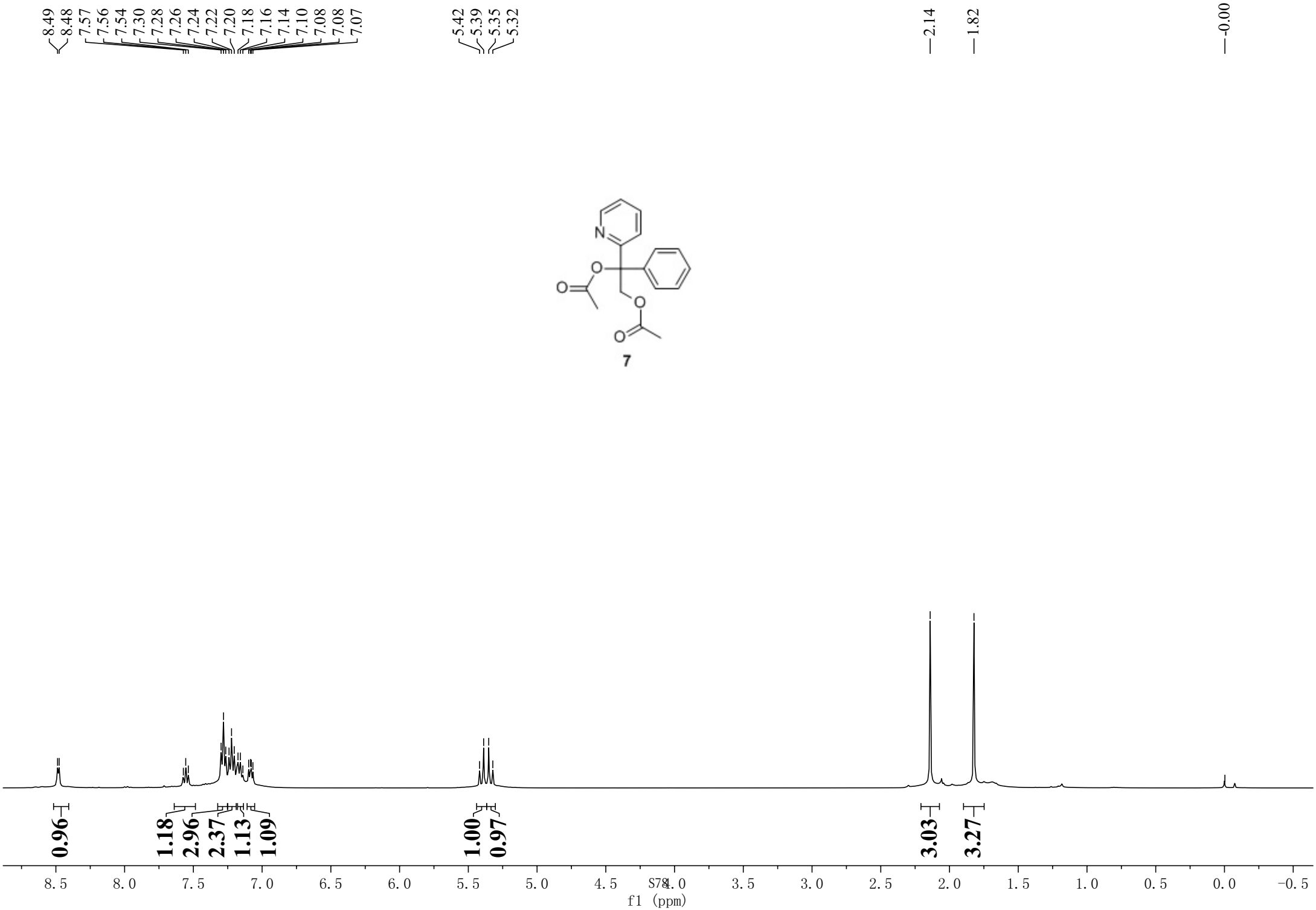
132.84
132.16
128.38
128.00
127.80
125.53
120.23
86.01
77.35
77.04
76.72
49.52
18.18
N
O
S
O
Cl
5f
170
160
150
140
130
120
110
100
90
S77
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.24
7.22
7.20
7.18
7.16
7.14
7.10
7.08
7.08
7.07
5.42
5.39
5.35
5.32
2.14
1.82
-0.00
N
O
O
O
O
7
0.96
1.18
2.96
2.37
1.13
1.09
1.00
0.97
3.03
3.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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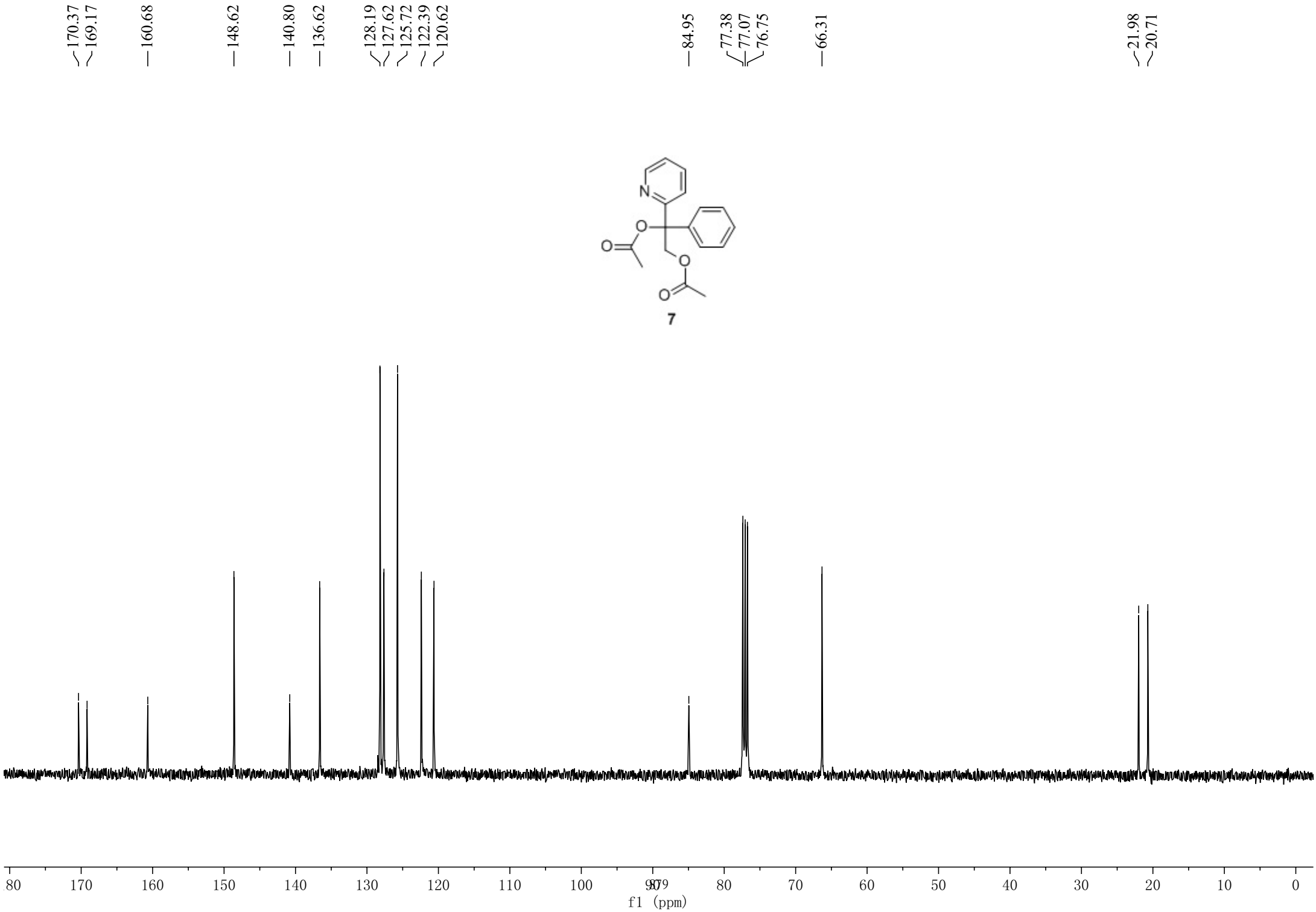
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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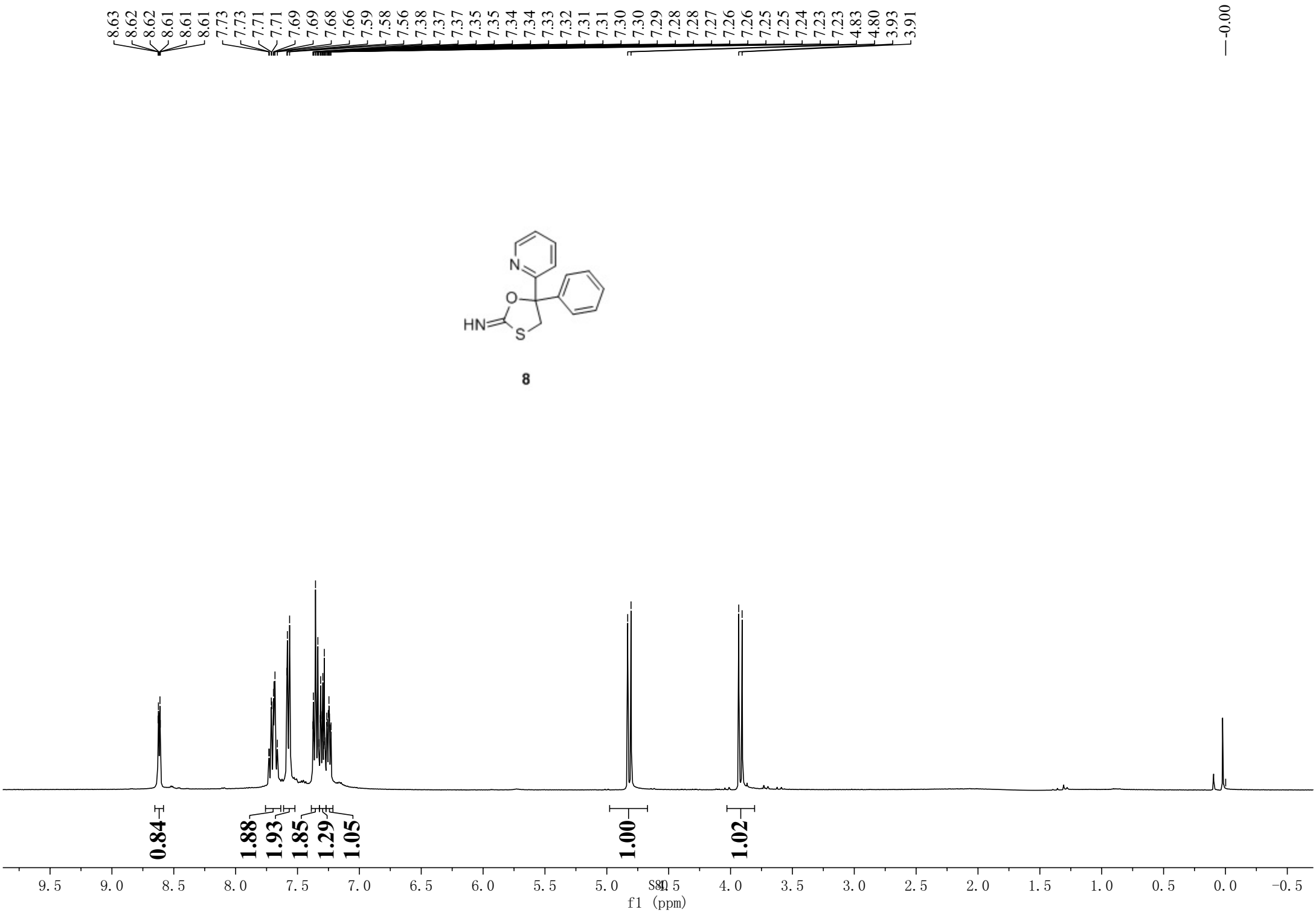
140.80
136.62
128.19
127.62
125.72
122.39
120.62
84.95
77.38
77.07
76.75
66.31
21.98
20.71
N
O
O
O
O
7
f1 (ppm)


8.63
8.62
8.62
8.61
8.61
8.61
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7.73
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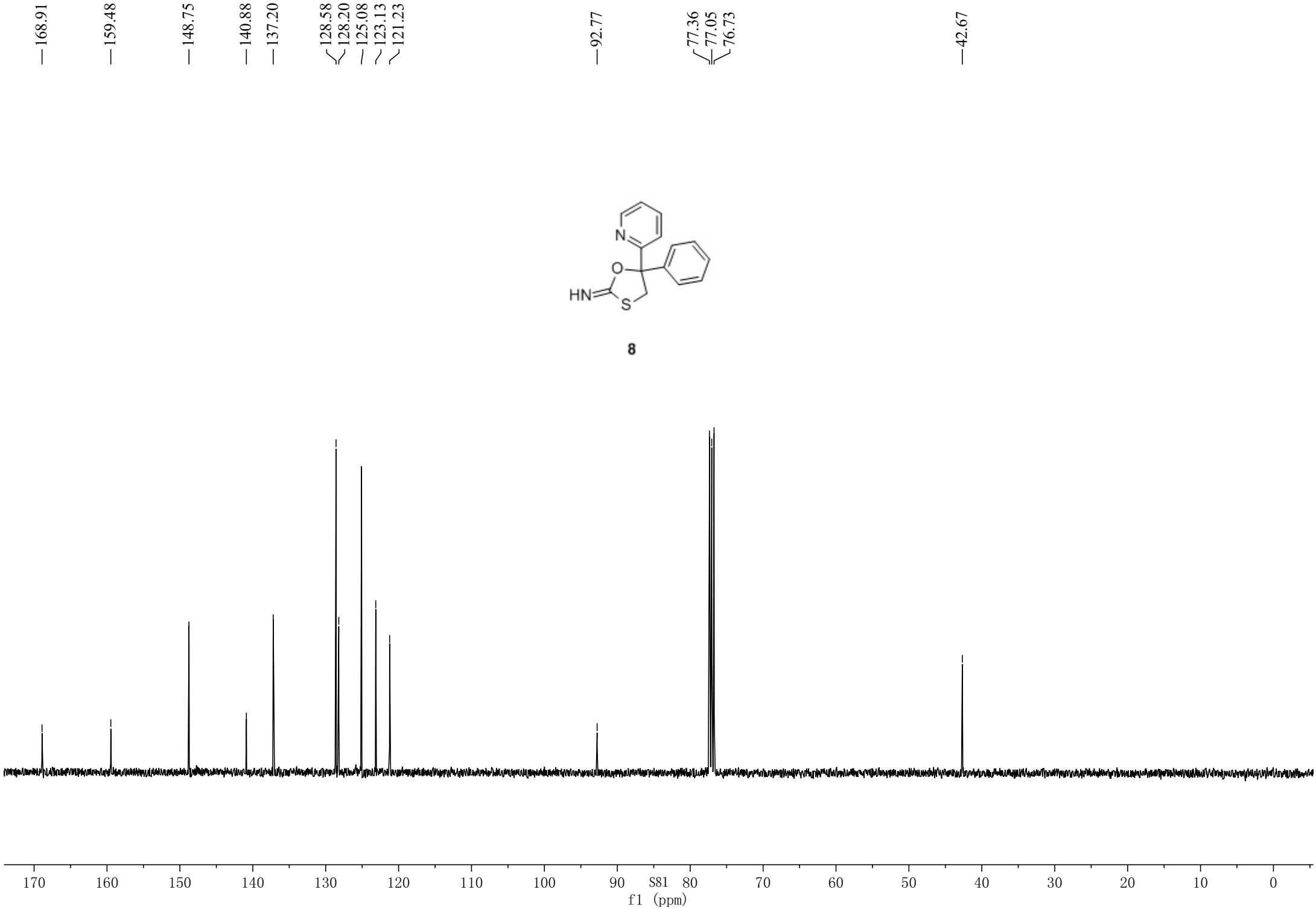
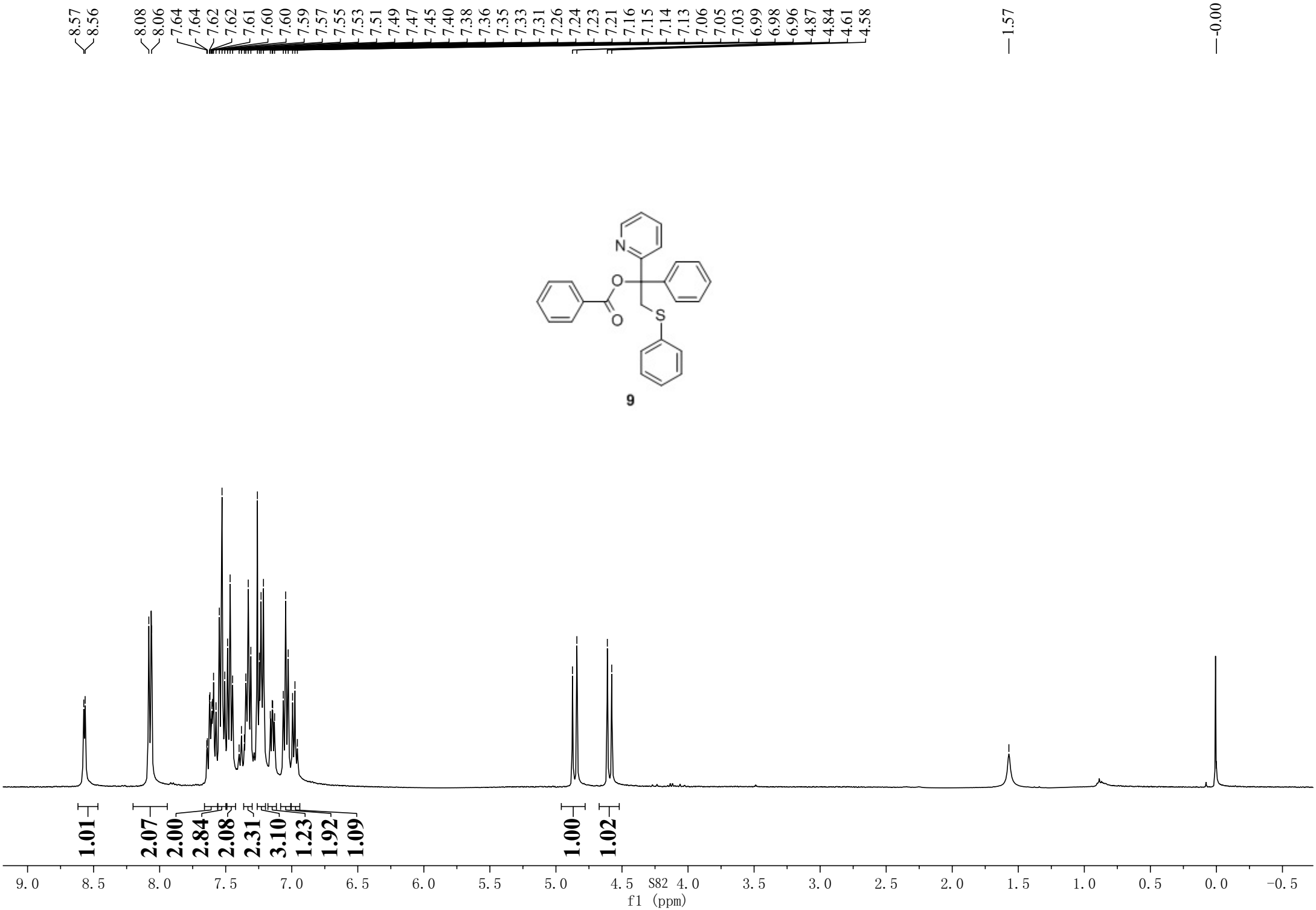
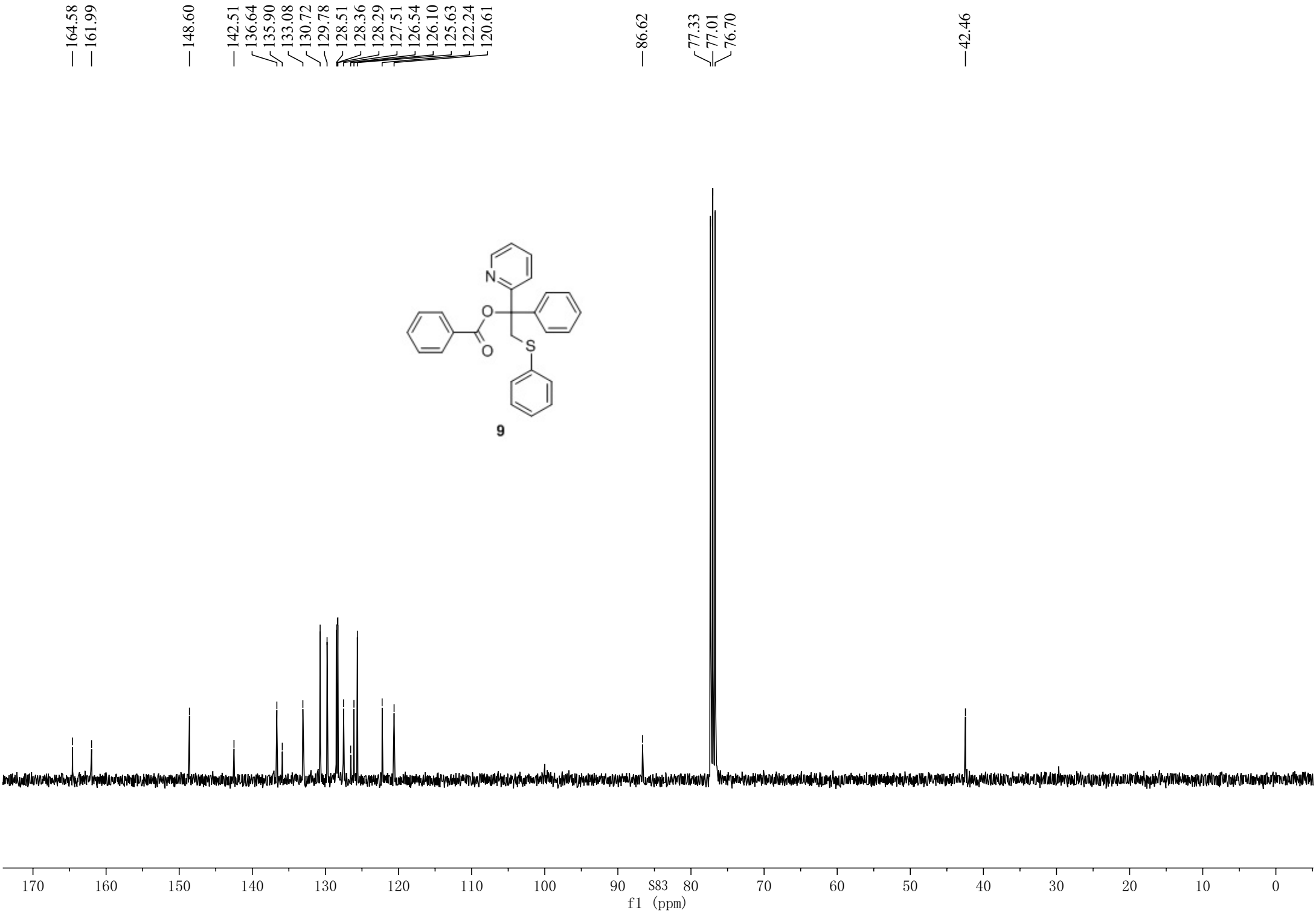
7.69
7.69
7.68
7.66
7.59
7.58
7.56
7.38
7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.23
4.83
4.80
3.93
3.91
0.00
N
O
HN
S
8
0.84
1.88
1.93
1.85
1.29
1.05
1.00
1.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


168.91
159.48
148.75
140.88
137.20
128.58
128.20
125.08
123.13
121.23
92.77
77.36
77.05
76.73
42.67
N
O
HN
S
8
170
160
150
140
130
120
110
100
90
S81
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.57
8.56
8.08
8.06
7.64
7.64
7.62
7.62
7.61
7.60
7.60
7.59
7.57
7.55
7.53
7.51
7.49
7.47
7.45
7.40
7.38
7.36
7.35
7.33
7.31
7.26
7.24
7.23
7.21
7.16
7.15
7.14
7.13
7.06
7.05
7.03
6.99
6.98
6.96
4.87
4.84
4.61
4.58
1.57
-0.00
N
O
O
S
9
1.01
2.07
2.00
2.84
2.08
2.31
3.10
1.23
1.92
1.09
1.00
1.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


164.58
161.99
148.60
142.51
136.64
135.90
133.08
130.72
129.78
128.51
128.36
128.29
127.51
126.54
126.10
125.63
122.24
120.61
86.62
77.33
77.01
76.70
42.46
N
O
O
S
9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)