Enantioselective synthesis of benzoindolizidine derivatives using chiral phase-transfer catalytic intramolecular domino aza-Michael addition/ alkylation

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Supplementary Information

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1. General information.

Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715), Optical rotations were recorded on a A212000-T APIV/IW. Column chromatography was performed on Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Bruker AVANCE Ⅲ–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; Infrared (IR) spectra were recorded on a Nicolet iS10 spectrophotometer and are reported as wavenumber (cm^{-1}). HRMS was measured by Agilent G 6500. Optical rotations were recorded on a A212000-T APIV/IW.

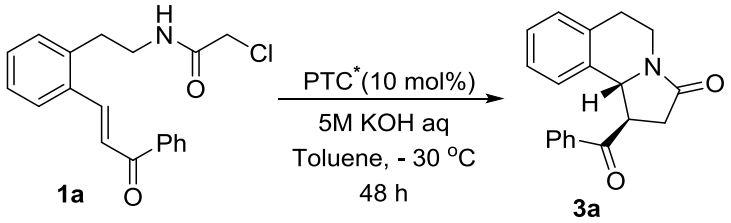
1[1] was prepared according to published literature procedures. 1-(triphenylphosphoranylidene) propan-2-one, 2-(triphenylphosphoranylidene)-acetophenon, 2-chloroacetyl chloride, KOH (85% w/w) were commercially available. Other Wittig reagents[2] and all the chiral PTC[3] were prepared according to the published literature procedures.

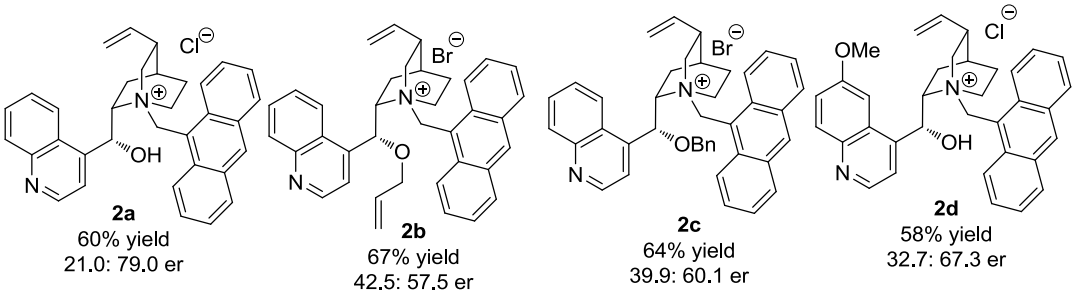
1 Y. Chen, R. D. Crockett, X. Wang, R. D. Larsen, S. Cui and M. M. Faul, *Synlett*, 2013, **24**, 301-304.
(b) J. Guo, X. Sun and S. Yu, *Org. Biomol. Chem.*, 2014, **12**, 265-268.

2 J. Yang, G. A. Felton, M. J. Krische, *J. Am. Chem. Soc*., 2004, **126**, 1634-1635.

3 (a) T. Ooi, M. Kameda and K. Maruoka, *J. Am. Chem. Soc.*, 2003, **125**, 5139-5151
(b) E. J. Corey, F. Xu and M. C. Noe, *J. Am. Chem. Soc*., 1997, **119**, 12414-12415.

2. Catalyst screening[a,b]



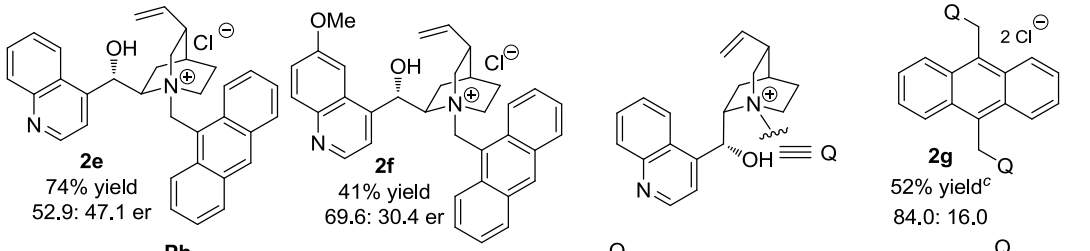


2a 60% yield 21.0: 79.0 er

2b 67% yield 42.5: 57.5 er

2c 64% yield 39.9: 60.1 er

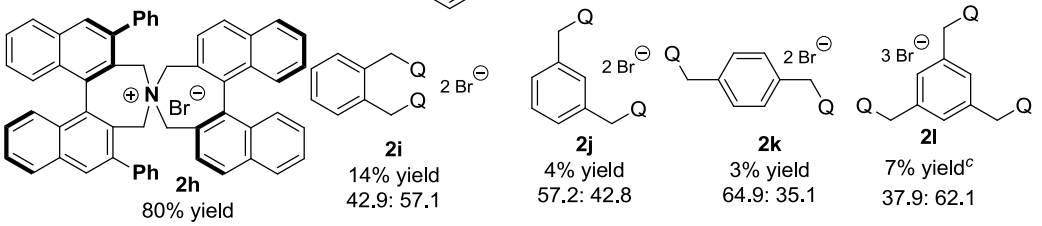
2d 58% yield 32.7: 67.3 er



2e 74% yield 52.9: 47.1 er

2f 41% yield 69.6: 30.4 er

2g 52% yield[c] 84.0: 16.0



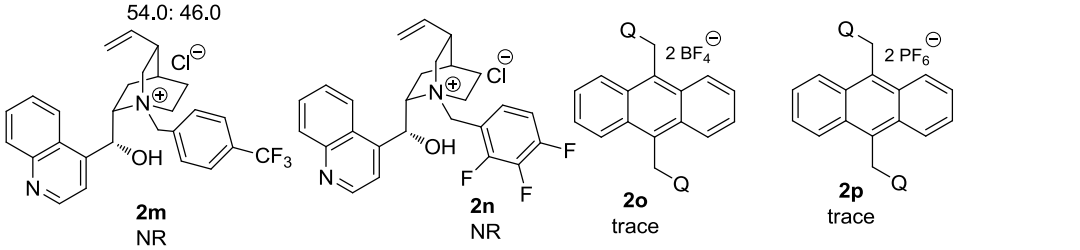
2h 80% yield 54.0: 46.0

2i 14% yield 42.9: 57.1

2j 4% yield 57.2: 42.8

2k 3% yield 64.9: 35.1

2l 7% yield[c] 37.9: 62.1

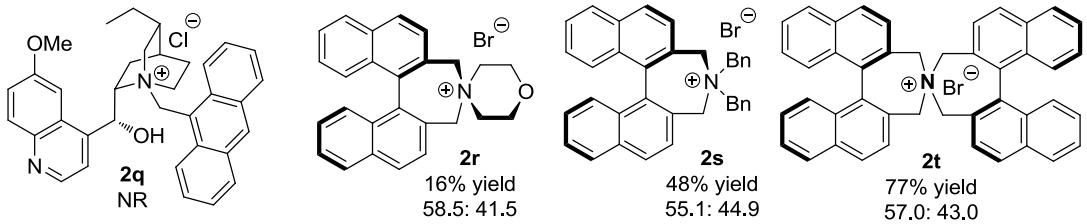


2m NR

2n NR

2o trace

2p trace



2q NR

2r 16% yield 58.5: 41.5

2s 48% yield 55.1: 44.9

2t 77% yield 57.0: 43.0

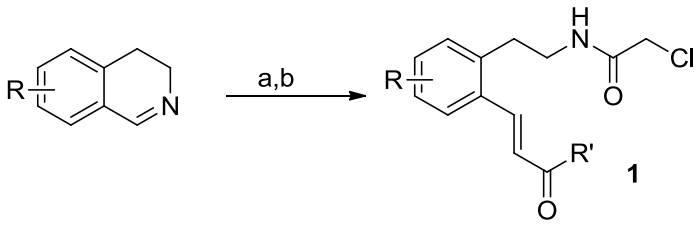
[a]A solution of **1** (0.10 mmol), **2** (0.01 mmol), and 5M KOH (0.2 mL, 1.0 mmol) in toluene (2 mL) at -30 °C was stirred for 48 h. [b] ^{1}H NMR yield with CH_2Br_2 as internal standard. [c]The reaction carried out at -20 ℃.

3. Optimization of reaction conditions

Entry	Base	Cat.2g [equiv.].	Toluene [mL]	Temp. [℃]	Yield [%[a]]	Er
1	5M KOH 0.2mL	0.1	2.0	-20	52	84.0/16.0
2	5M KOH 0.1mL	0.1	2.0	-20	27	67.5/32.5
3	5M KOH 0.4mL	0.1	2.0	-20	68	83.6/16.4
4	5M KOH 0.8mL	0.1	2.0	-20	75	84.0/16.0
5	5M KOH 2.0mL	0.1	2.0	-20	19	83.7/16.3
6	5M KOH 0.8mL	0.1	2.0	-30	51	88.7/11.3
7	5M KOH 0.8mL	0.1	2.0	-40	10	74.6/25.4
8	6M KOH 0.8mL	0.1	2.0	-30	trace	--
9	3M KOH 0.8mL	0.1	2.0	-30	33	84.0/16.0
10	5M KOH 0.8mL	0.2	2.0	-30	20	78.2/21.8
11	5M KOH 0.8mL	0.05	2.0	-30	trace	--

[a] ^{1}H NMR yield with CH_2Br_2 as internal standard.

4. Representative procedures for the preparation and characterization of the starting materials

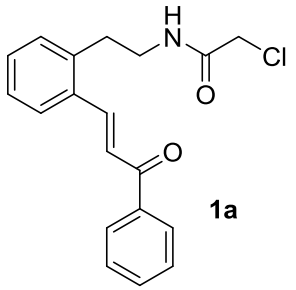


Reaction conditions : a). 2-chloroacetyl chloride, sat.$NaHCO_3$, CH_2Cl_2, 0 ^oC ; b). Wittig reagents, toluene, reflux, 6-12h.

1 was prepared according to General Procedure **A**: To a vigorously stirred mixture of 3,4-dihydroisoquinoline (1.0 mmol, 1.0 equiv), dichloromethane (10 mL), and saturated aqueous sodium hydrogen carbonate (10 ml) was added dropwise a solution of 2-chloroacetyl chloride (124.2 mg, 1.1 mmol, 1.1 equiv) in dichloromethane (2 mL) at 0 ℃, and the mixture was stirred vigorously at 0 ℃ until the reaction was completed (monitoring by TLC) . The organic phase was separated and the aqueous phase was extracted with dichloromethane (5.0 mL × 3). The combined organic phase was washed with brine, dried over Na_2SO_4. The solvent was removed under reduced

pressure to afford the crude product and the crude mixture purified by flash chromatography with hexanes / ethyl acetate to afford the intermediates.

Intermediate (0.5 mmol, 1.0 equiv) and the Wittig reagent (0.6 mmol, 1.2 equiv) were added to the flask, stirred vigorously at 110 ℃ until the reaction was completed, monitoring with TLC. The mixture was cool to room temperature, without removed the solvent under reduced pressure, the mixture was loaded on silica gel column and purified by flash chromatography (ethyl acetate /hexanes) to afford the pure product **1**.



1a

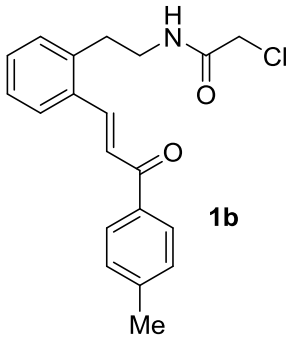
According to General Procedure A: **1a** was obtained as a white solid in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 15.6 Hz, 1H), 8.05 (s, 1H), 8.04 (t, *J* = 1.6 Hz, 1H), 7.75 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.61 - 7.57 (m, 1H), 7.55 - 7.49 (m, 3H), 7.38 (td, *J* = 7.2, 1.2 Hz, 1H), 7.32 (td, *J* = 7.4, 1.2 Hz, 1H), 7.27 - 7.25 (m, 1H), 6.73 (brs, 1H), 4.01 (s, 2H), 3.54 (dd, *J* = 13.2, 6.8 Hz, 2H), 3.06 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 190.00, 165.99, 141.35, 138.76, 138.01, 133.90, 133.02, 130.74, 130.61, 128.72, 128.55, 127.43, 126.90, 123.80, 42.65, 40.91, 32.78.

FTIR (film): ν_{max} 3303, 2920, 2849, 1656, 1605, 1594, 1571, 1556, 1481, 1447, 1331, 1214, 1016, 968, 749 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{18}ClNNaO_2$ $(M+Na)^+$: 350.0924, found: 350.0922.



1b

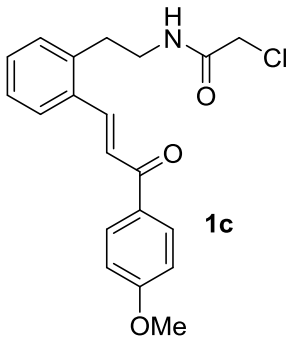
According to General Procedure A: **1b** was obtained as a yellow solid in 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.6 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 15.4 Hz, 1H), 7.40 – 7.28 (m, 4H), 7.25 (d, *J* = 7.5 Hz, 1H), 6.74 (brs, 1H), 4.00 (s, 2H), 3.53 (q, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.48, 165.99, 143.89, 140.92, 138.68, 135.44, 134.02, 130.70, 130.47, 129.42, 128.70, 127.39, 126.89, 123.88, 42.65, 40.89, 32.76, 21.73.

FTIR (film): ν_{max} 3309, 1664, 1642, 1609, 1593, 1541, 1479, 1409, 1325, 1292, 1175, 1026, 978, 753 cm^{-1}.

HRMS (ESI) calcd for $C_{20}H_{20}ClNNaO_2$ $(M+Na)^+$: 364.1080, found: 364.1076.



1c

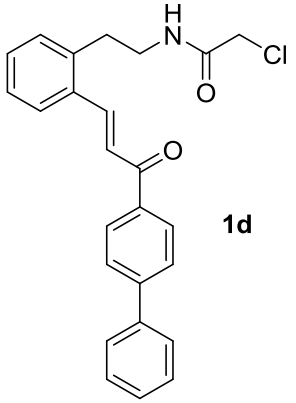
According to General Procedure A: **1c** was obtained as a yellow solid in 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.2 Hz, 1H), 8.08 – 8.03 (m, 2H), 7.74 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.52 (d, *J* = 15.2 Hz, 1H), 7.37 (td, *J* = 7.6, 1.5 Hz, 1H), 7.32 (td, *J* = 7.6, 1.3 Hz, 1H), 7.26 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.01 – 6.96 (m, 2H), 6.70 (brs, 1H), 4.01 (s, 2H), 3.89 (s, 3H), 3.54 (q, *J* = 6.8 Hz, 2H), 3.06 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.24, 165.96, 163.58, 140.54, 138.59, 134.13, 130.91, 130.89, 130.69, 130.38, 127.38, 126.87, 123.77, 113.93, 55.54, 42.65, 40.88, 32.78.

FTIR (film): ν_{max} 3277, 1653, 1604, 1586, 1553, 1338, 1305, 1257, 1219, 1167 cm^{-1}.

HRMS (ESI) calcd for $C_{20}H_{20}ClNNaO_3$ $(M+Na)^+$: 380.1029, found: 380.1029.



1d

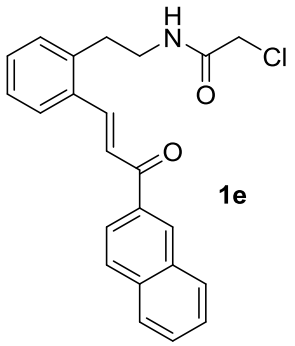
According to General Procedure A: **1d** was obtained as a yellow solid in 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 15.2 Hz, 1H), 8.14 (s, 1H), 8.12 (s, 1H), 7.78 (d, *J* = 6.8 Hz, 1H), 7.75 (s, 1H), 7.73 (s, 1H), 7.66 (t, *J* = 1.6 Hz, 1H), 7.64 (s, 1H), 7.57 (d, *J* = 15.2 Hz, 1H), 7.62 – 7.46 (m, 2H), 7.44 – 7.30 (m, 3H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.72 (brs, 1H), 4.02 (s, 2H), 3.55 (q, *J* = 6.8 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.45, 166.00, 145.74, 141.30, 139.88, 138.78, 136.71, 133.96, 130.77, 130.63, 129.18, 129.00, 128.30, 127.45, 127.37, 127.32, 126.92, 123.75, 42.66, 40.94, 32.82.

FTIR (film): ν_{max} 3324, 2938, 1647, 1590, 1539, 1485, 1405, 1338, 1318, 1219, 1194, 1032, 1005, 979, 835, 751, 693 cm^{-1}.

HRMS (ESI) calcd for $C_{25}H_{22}ClNNaO_2$ $(M+Na)^+$: 426.1237, found: 426.1236.



1e

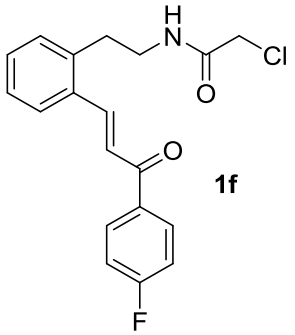
According to General Procedure A: **1e** was obtained as a yellow solid in 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.20 (d, *J* = 15.2 Hz, 1H), 8.12 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.68 (d, *J* = 15.2 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.39 (td, *J* = 7.6, 1.6 Hz, 1H), 7.35 (td, *J* = 7.6, 1.6 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.71 (brs, 1H), 4.01 (s, 2H), 3.56 (q, *J* = 6.8 Hz, 2H), 3.08 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.80, 165.99, 141.32, 138.77, 135.59, 135.37, 134.00, 132.58, 130.76, 130.62, 130.11, 129.58, 128.69, 128.54, 127.87, 127.46, 126.98, 126.88, 124.45, 123.87, 42.66, 40.93, 32.82.

FTIR (film): ν_{max} 3312, 3067, 1652, 1590, 1549, 1325, 1277, 1185, 1122, 1015, 968, 828, 761 cm^{-1}.

HRMS (ESI) calcd for $C_{23}H_{20}ClNNaO_2$ $(M+Na)^+$: 400.1080, found: 400.1081.



1f

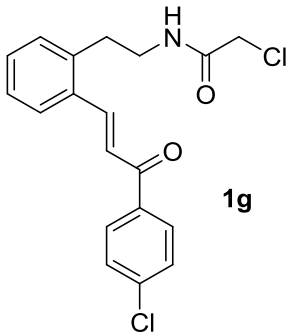
According to General Procedure A: **1f** was obtained as a yellow solid in 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 15.2 Hz, 1H), 8.12 – 8.05 (m, 2H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.50 (d, *J* = 15.6 Hz, 1H), 7.39 (td, *J* = 7.4, 1.2 Hz, 1H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.22 – 7.13 (m, 2H), 6.69 (brs, 1H), 4.02 (s, 2H), 3.54 (dd, *J* = 13.6, 6.8 Hz, 2H), 3.07 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.32, 165.97, 165.73 (d, *J* = 254.8 Hz), 141.60, 138.79, 134.36 (d, *J* = 2.7 Hz), 133.81, 131.21, 131.12, 130.77, 130.70, 127.45, 126.89, 123.33, 115.96, 115.74, 42.64, 40.93, 32.80.

FTIR (film): ν_{max} 3310, 1664, 1638, 1597, 1502, 1409, 1327, 1296, 1028, 1154, 1024, 980, 832, 752 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{17}ClFNNaO_2$ $(M+Na)^+$: 368.0830, found: 368.0833.



1g

According to General Procedure A: **1g** was obtained as a yellow solid in 71% yield.

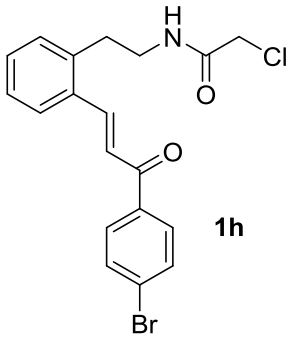
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 15.6 Hz, 1H), 8.01 (s, 1H), 7.98 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 6.67 (brs, 1H), 4.02 (s, 2H), 3.54 (q, *J* = 6.8 Hz, 2H), 3.07 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.65, 165.96, 141.87, 139.44, 138.85, 136.32, 133.74, 130.78, 129.96, 129.03, 127.46, 126.91, 123.21, 42.64, 40.94, 32.80.

FTIR (film): ν_{max} 3312, 1665, 1642, 1595, 1537, 1409, 1291, 1209, 1087, 1027, 1010, 981, 830, 756

cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{17}Cl_2NNaO_2$ $(M+Na)^+$: 384.0534, found: 384.0530.



1h

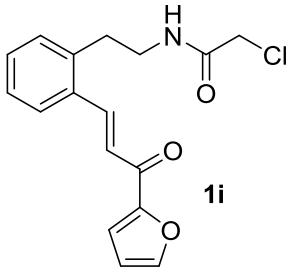
According to General Procedure A: **1h** was obtained as a yellow solid in 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 15.4 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.78 – 7.71 (m, 1H), 7.69 – 7.61 (m, 2H), 7.47 (d, *J* = 15.4 Hz, 1H), 7.40 (td, *J* = 7.4, 1.2 Hz, 1H), 7.33 (t, *J* = 7.0 Hz, 1H), 7.29 – 7.26 (m, 1H), 6.68 (brs, 1H), 4.02 (s, 2H), 3.54 (dd, *J* = 13.6, 6.8 Hz, 2H), 3.06 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.86, 165.96, 141.93, 138.85, 136.74, 133.73, 132.02, 130.80, 130.79, 130.06, 128.16, 127.47, 126.91, 123.17, 42.64, 40.94, 32.81.

FTIR (film): ν_{max} 3315, 1665, 1642, 1594, 1536, 1476, 1409, 1322, 1290, 1208, 1067, 1024, 1007, 975, 826, 787, 756 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{17}BrClNNaO_2$ $(M+Na)^+$: 428.0029, found: 428.0026.



1i

According to General Procedure A: **1i** was obtained as a light green solid in 60% yield.

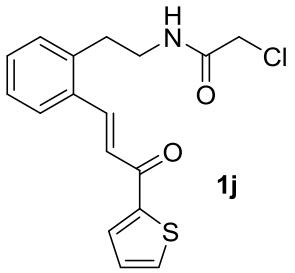
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 15.6 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 1.2 Hz, 1H), 7.46 – 7.22 (m, 5H), 6.72 (brs, 1H), 6.61 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.02 (s, 2H), 3.54 (q, *J* = 6.8 Hz, 2H), 3.07 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.78, 165.97, 153.62, 146.73, 140.52, 138.83, 133.71, 130.73, 130.65, 127.39, 126.96, 123.20, 117.81, 112.66, 42.64, 40.90, 32.75.

FTIR (film): ν_{max} 3290, 2947, 2880, 1649, 1603, 1590, 1558, 1461, 1392, 1330, 1306, 1241, 1215,

1190, 1152, 1039, 1010, 965, 881, 758 cm^{-1}.

HRMS (ESI) calcd for $C_{17}H_{16}ClNNaO_3$ $(M+Na)^+$: 340.0716, found: 340.0714.



1j

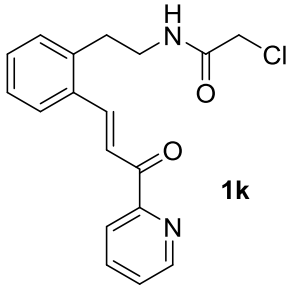
According to General Procedure A: **1j** was obtained as a brown solid in 63% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 15.2 Hz, 1H), 7.88 (d, *J* = 3.2 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.43 – 7.36 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 6.0 Hz, 1H), 7.20 (dd, *J* = 4.8, 4.0 Hz, 1H), 6.69 (brs, 1H), 4.02 (s, 2H), 3.54 (q, *J* = 6.8 Hz, 2H), 3.07 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 181.78, 165.96, 145.39, 140.70, 138.78, 134.19, 133.74, 132.02, 130.76, 130.65, 128.36, 127.43, 126.93, 123.65, 42.65, 40.90, 32.80.

FTIR (film): ν_{max} 3295, 1654, 1646, 1589, 1558, 1515, 1410, 1351, 1327, 1233, 1219, 1061, 966, 858, 749 cm^{-1}.

HRMS (ESI) calcd for $C_{17}H_{16}ClNNaO_2S$ $(M+Na)^+$: 356.0488, found: 356.0491.



1k

According to General Procedure A: **1k** was obtained as a brown solid in 50% yield.

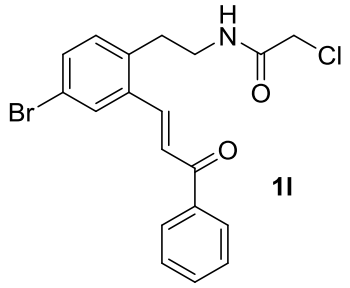
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.0 Hz, 1H), 8.26 (s, 2H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.89 (td, *J* = 7.6, 1.6 Hz, 2H), 7.50 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.37 (td, *J* = 7.6, 1.6 Hz, 1H), 7.32 (td, *J* = 7.6, 1.6 Hz, 1H), 7.26 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.71 (brs, 1H), 4.03 (s, 2H), 3.56 (q, *J* = 6.8 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.35, 166.00, 154.09, 148.90, 141.19, 138.86, 137.08, 134.02, 130.67, 130.62, 127.38, 127.35, 127.01, 123.02, 122.78, 42.65, 41.00, 32.80.

FTIR (film): ν_{max} 3285, 3087, 1656, 1594, 1558, 1427, 1406, 1329, 1269, 1220, 1190, 1024, 979,

752 cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{17}ClN_2NaO_2$ $(M+Na)^+$: 351.0876, found: 351.0875.



1l

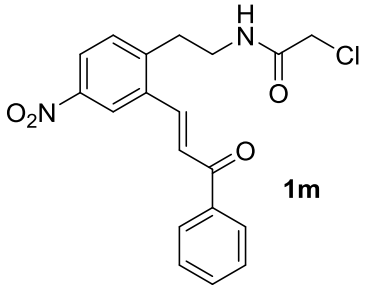
According to General Procedure A: **1l** was obtained as a yellow solid in 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.02 (m, 3H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.56 – 7.45 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.73 (brs, 1H), 4.02 (s, 2H), 3.51 (q, *J* = 6.8 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.51, 166.06, 139.74, 137.69, 137.59, 135.97, 133.27, 133.23, 132.31, 129.59, 128.79, 128.60, 124.71, 121.22, 42.62, 40.67, 32.39.

FTIR (film): ν_{max} 3318, 1658, 1643, 1603, 1544, 1480, 1446, 1406, 1320, 1263, 1215, 1174, 1117, 1019, 910, 857, 824, 786, 725, 692 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{17}BrClNNaO_2$ $(M+Na)^+$: 428.0029, found: 428.0026.



1m

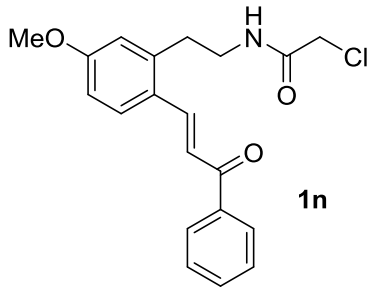
According to General Procedure A: **1m** was obtained as a yellow solid in 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.0 Hz, 1H), 8.20 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.15 – 8.05 (m, 3H), 7.71 – 7.60 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 1H), 6.81 (brs, 1H), 4.03 (s, 2H), 3.59 (q, *J* = 6.8 Hz, 2H), 3.17 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.14, 166.22, 147.24, 145.67, 138.74, 137.40, 135.53, 133.53, 131.77, 128.88, 128.66, 126.06, 124.44, 121.71, 42.57, 40.33, 33.01.

FTIR (film): ν_{max} 3332, 2927, 1652, 1600, 1542, 1515, 1434, 1343, 1265, 1221, 1076, 976, 836, 803, 762, 729, 690 cm^{-1}.

HRMS (ESI) calcd for $C_{19}H_{17}ClN_2NaO_4$ $(M+Na)^+$: 395.0775, found: 395.0774.



1n

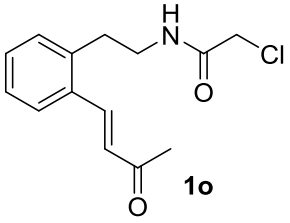
According to General Procedure A: **1n** was obtained as a yellow solid in 73% yield;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 15.6 Hz, 1H), 8.04 (s, 1H), 8.02 (d, *J* = 1.2 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 15.6 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.78 (d, *J* = 2.8 Hz, 1H), 6.77 (brs, 1H),4.02 (s, 2H), 3.84 (s, 3H), 3.54 (dd, *J* = 13.6, 6.8 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.07, 166.02, 161.56, 141.02, 140.95, 138.32, 132.79, 128.64, 128.49, 128.44, 126.24, 121.22, 115.45, 113.60, 55.44, 42.66, 40.89, 32.98.

FTIR (film): ν_{max} 3335, 2938, 2834, 1650, 1586, 1575, 1539, 1444, 1412, 1343, 1315, 1266, 1246, 1216, 1184, 1163, 1103, 1019, 974, 810, 779, 688 cm^{-1}.

HRMS (ESI) calcd for $C_{20}H_{20}ClNNaO_3$ $(M+Na)^+$: 380.1029, found: 380.1029.



1o

According to General Procedure A: **1o** was obtained as a white solid in 56 % yield.

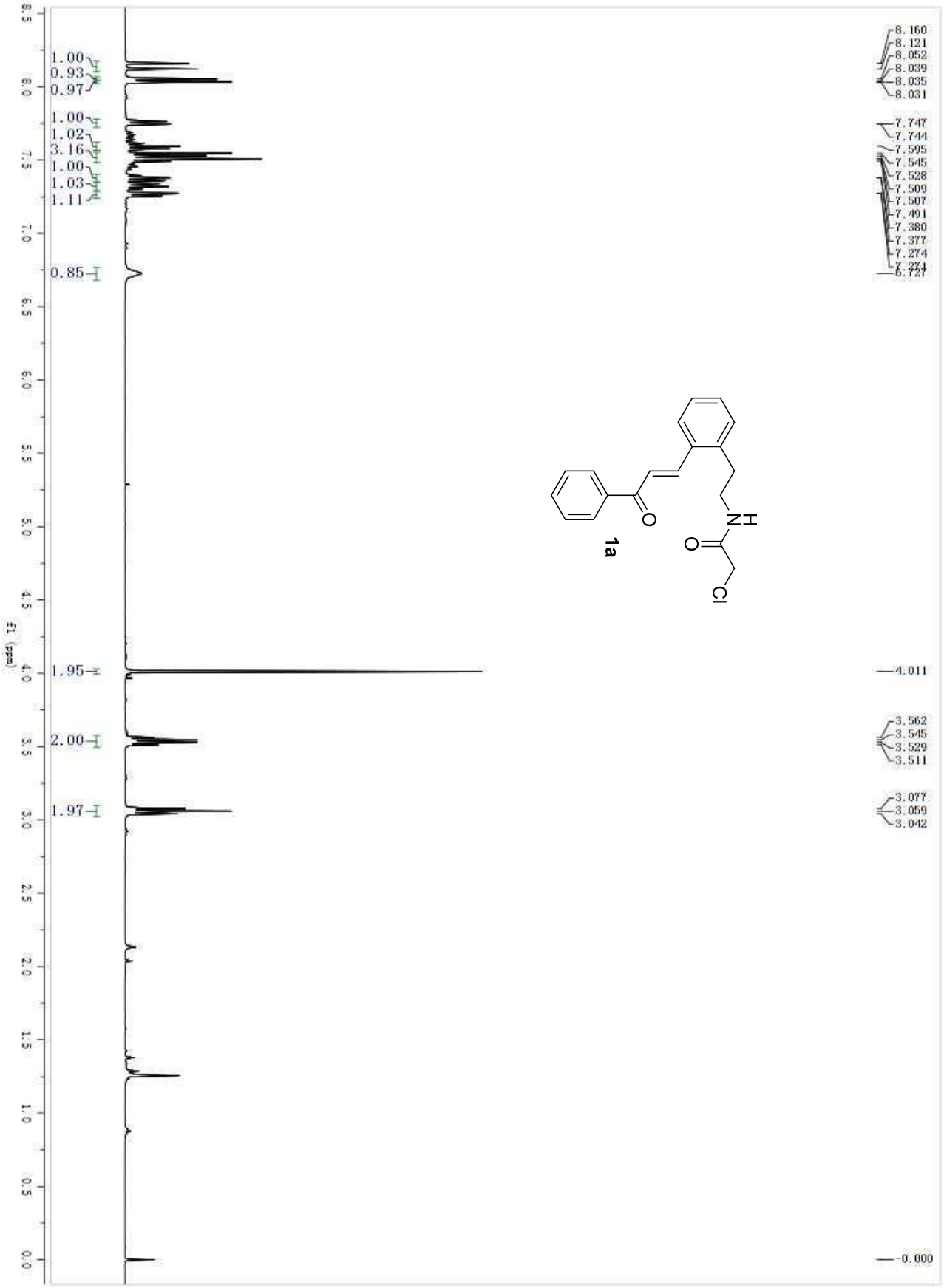
^{1}H NMR (400 MHz, CDCl3): δ 7.93 (d, *J* = 16.0 Hz, 1H), 7.63 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.36 (td, *J* = 7.2, 1.2 Hz, 1H), 7.31-7.29 (m, 1H), 7.24 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.77 (brs, 1H), 6.68(d, *J* = 16.0 Hz, 1H), 4.03 (s, 2H), 3.53-3.47 (m, 2H), 3.04(t, *J* = 7.4, 2H), 2.44 (s, 3H).

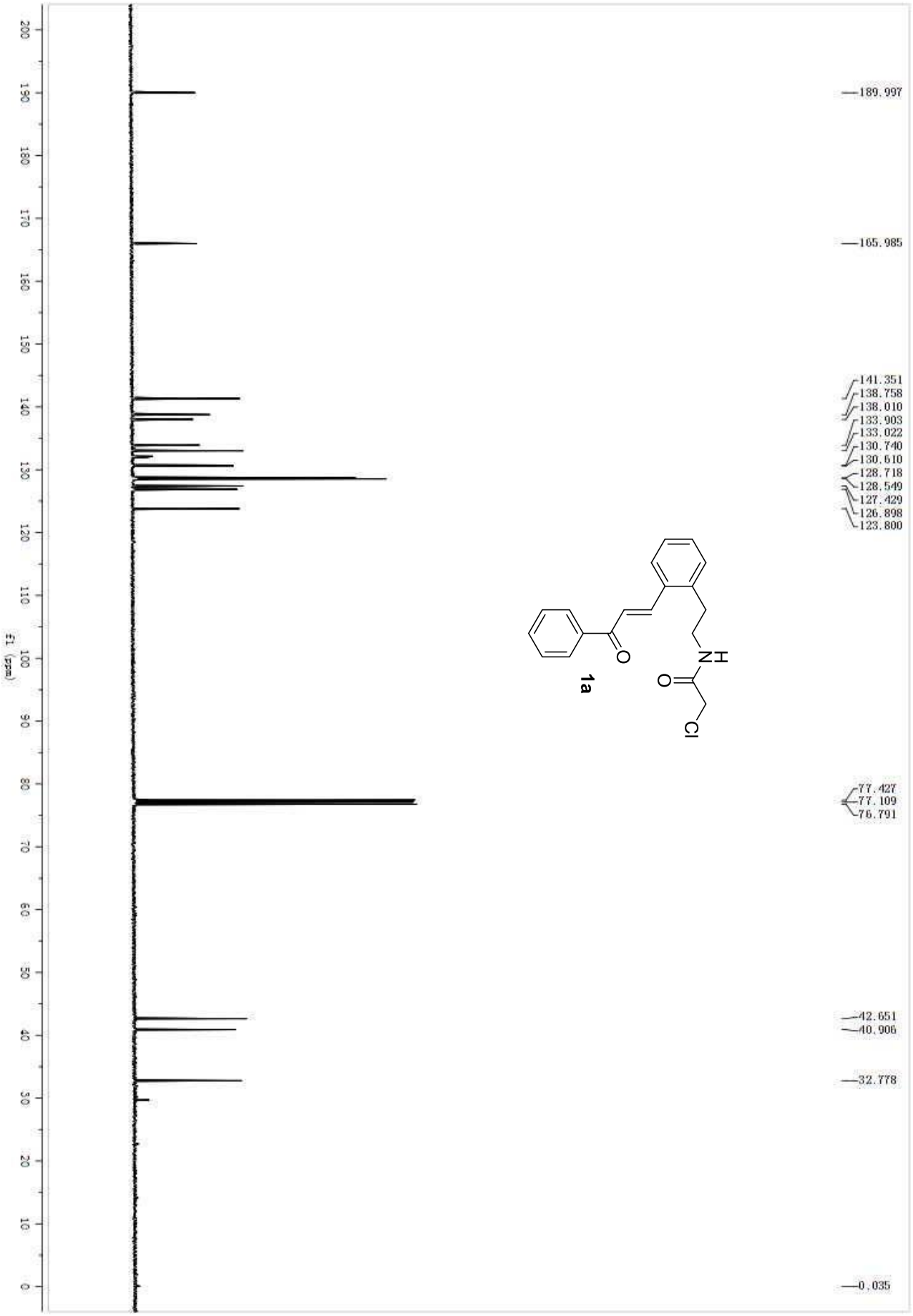
^{13}C NMR (100 MHz, CDCl3): δ = 198.64, 166.14, 140.12, 138.20, 133.57, 130.57, 130.51, 129.07, 127.50, 126.86, 42.60, 41.12, 32.92, 27.77.

FTIR (film): v max 3351, 3065, 2994, 2925, 1657, 1633, 1523, 1482, 1463, 1433, 1359, 974, 759, 675 cm-1.

HRMS (ESI) calcd for $C_{14}H_{16}ClNO_2$ Na (M+Na)+: 288.0767, found: 288.0765.

5. ^{1}H NMR and ^{13}C NMR spectra

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130.740
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127.429
126.898
123.800
77.427
77.109
76.791
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40.906
32.778
0.035
f1 (ppm)
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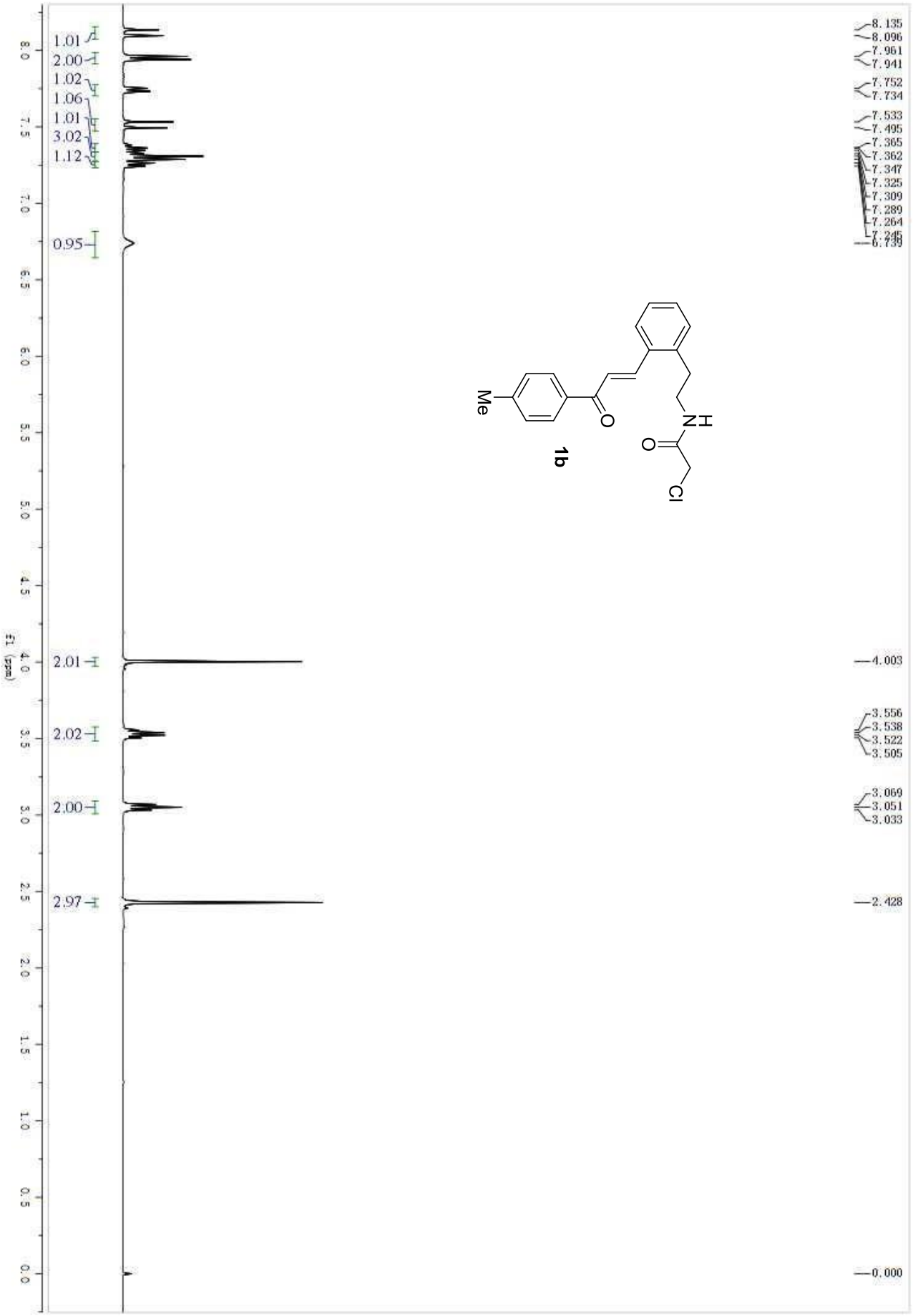
N
H
O
Cl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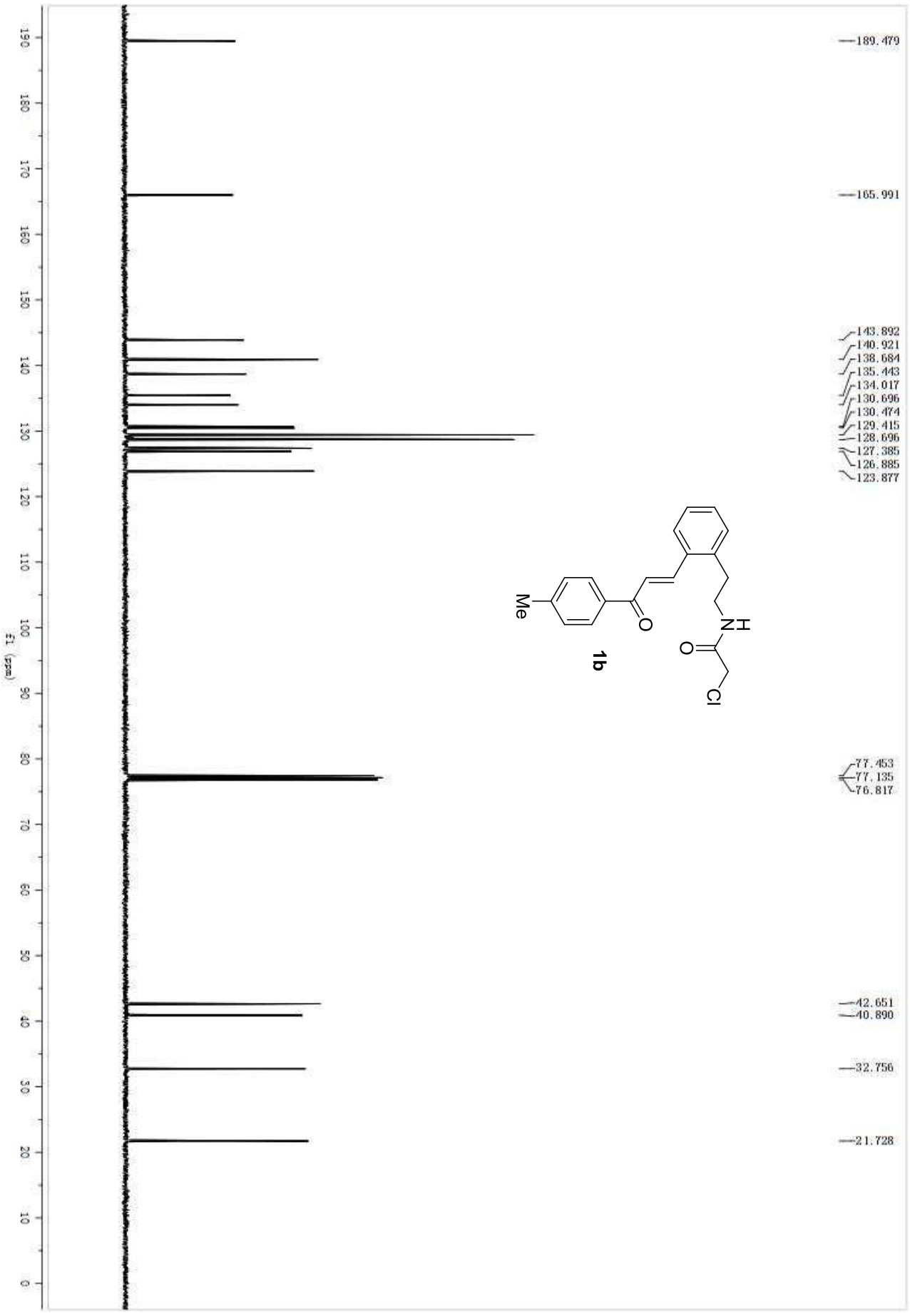
7.309
7.289
7.264
7.246
6.739
1.01
2.00
1.02
1.06
1.01
3.02
1.12
0.95
2.01
2.02
2.00
2.97
4.003
3.556
3.538
3.522
3.505
3.069
3.051
3.033
2.428
0.000
f1 (ppm)
Me
O
N
H
O
Cl
1b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130.696
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128.696
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123.877
77.453
77.135
76.817
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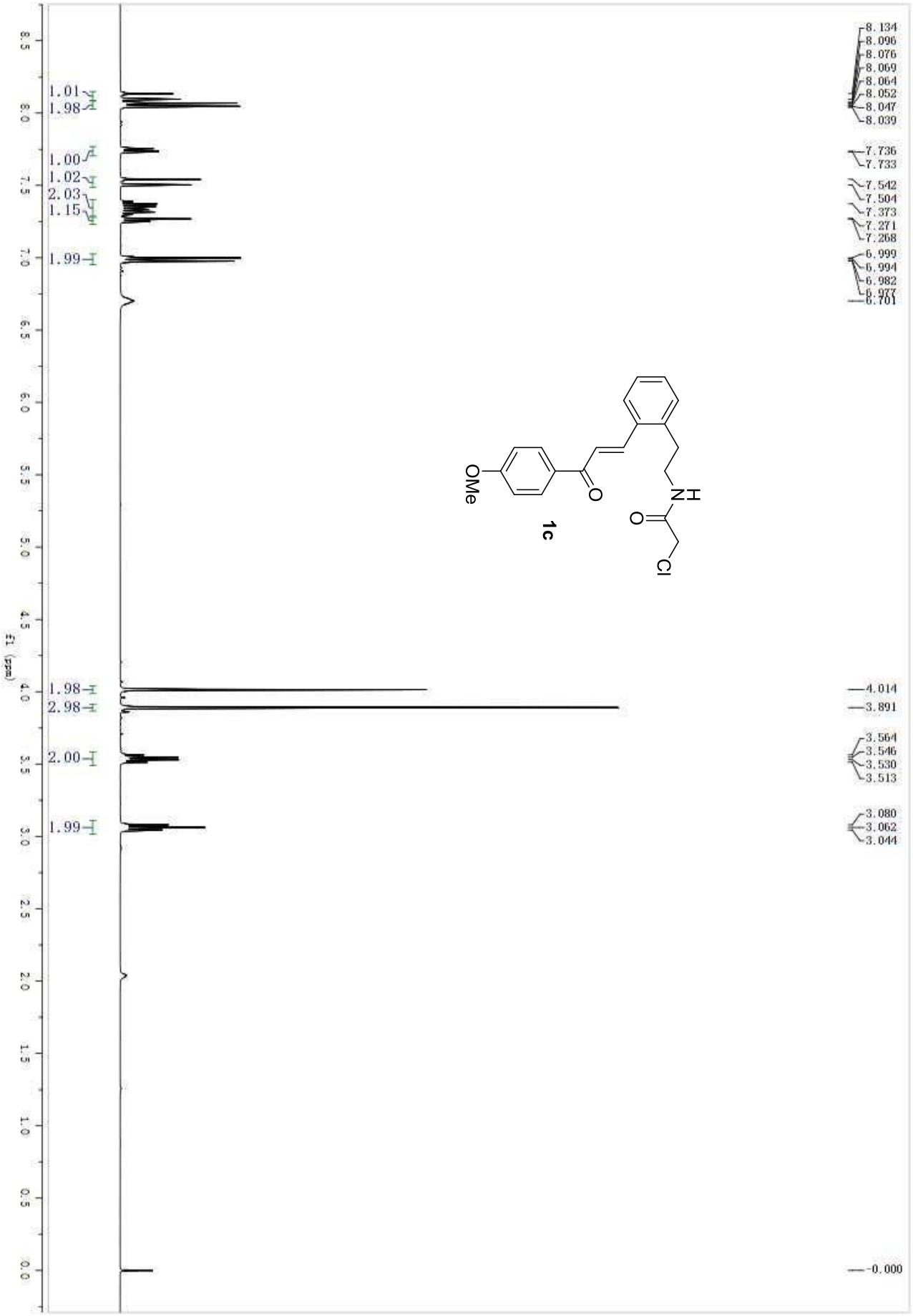
40.890
32.756
21.728
f1 (ppm)
Me
O
N
H
O
Cl
1b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8.069
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8.047
8.039
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7.733
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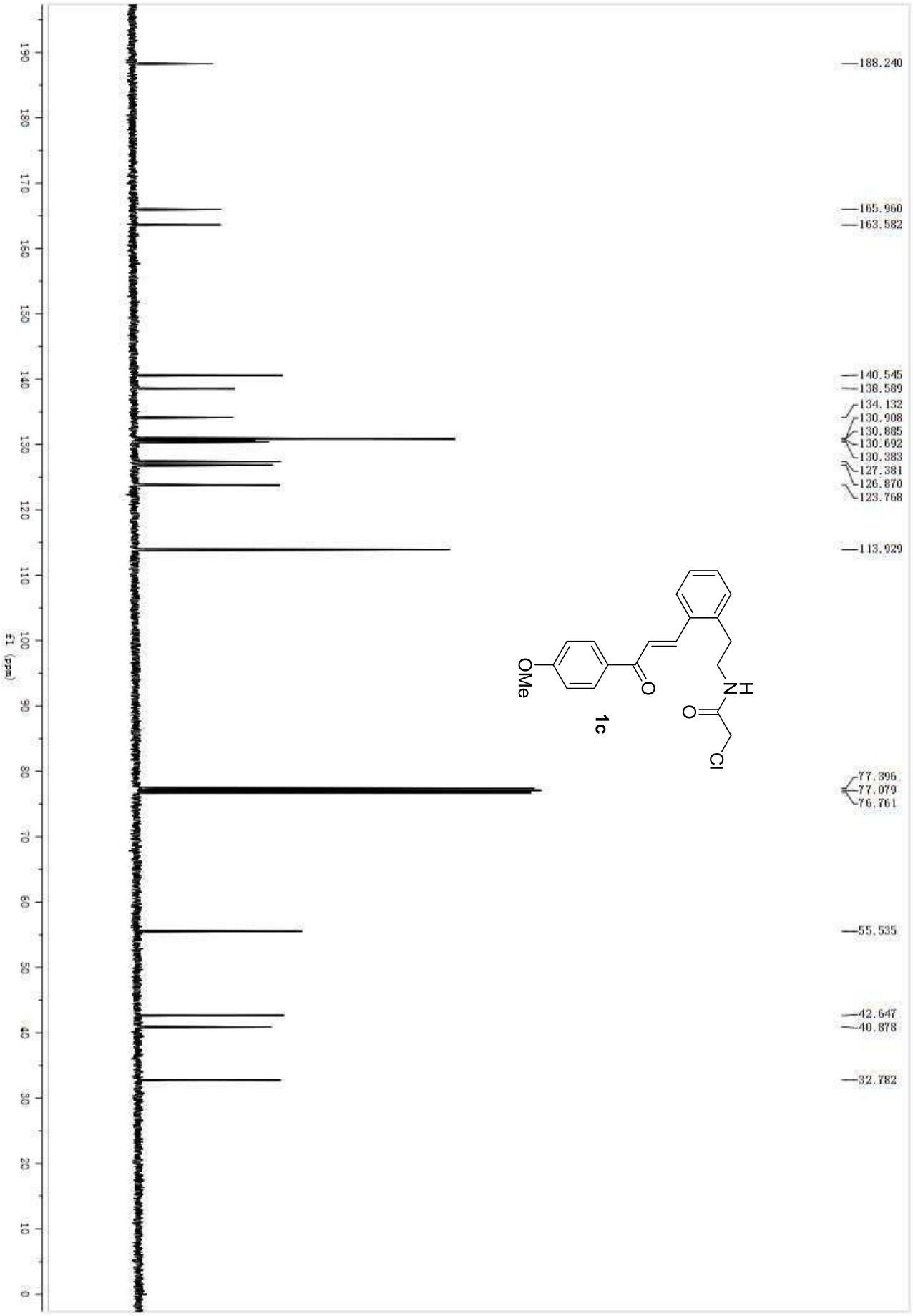
7.373
7.271
7.268
6.999
6.994
6.982
6.977
6.701
4.014
3.891
3.564
3.546
3.530
3.513
3.080
3.062
3.044
0.000
1.01
1.98
1.00
1.02
2.03
1.15
1.99
1.98
2.98
2.00
1.99
f1 (ppm)
OMe
O
N
H
O
Cl
1c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123.768
113.929
77.396
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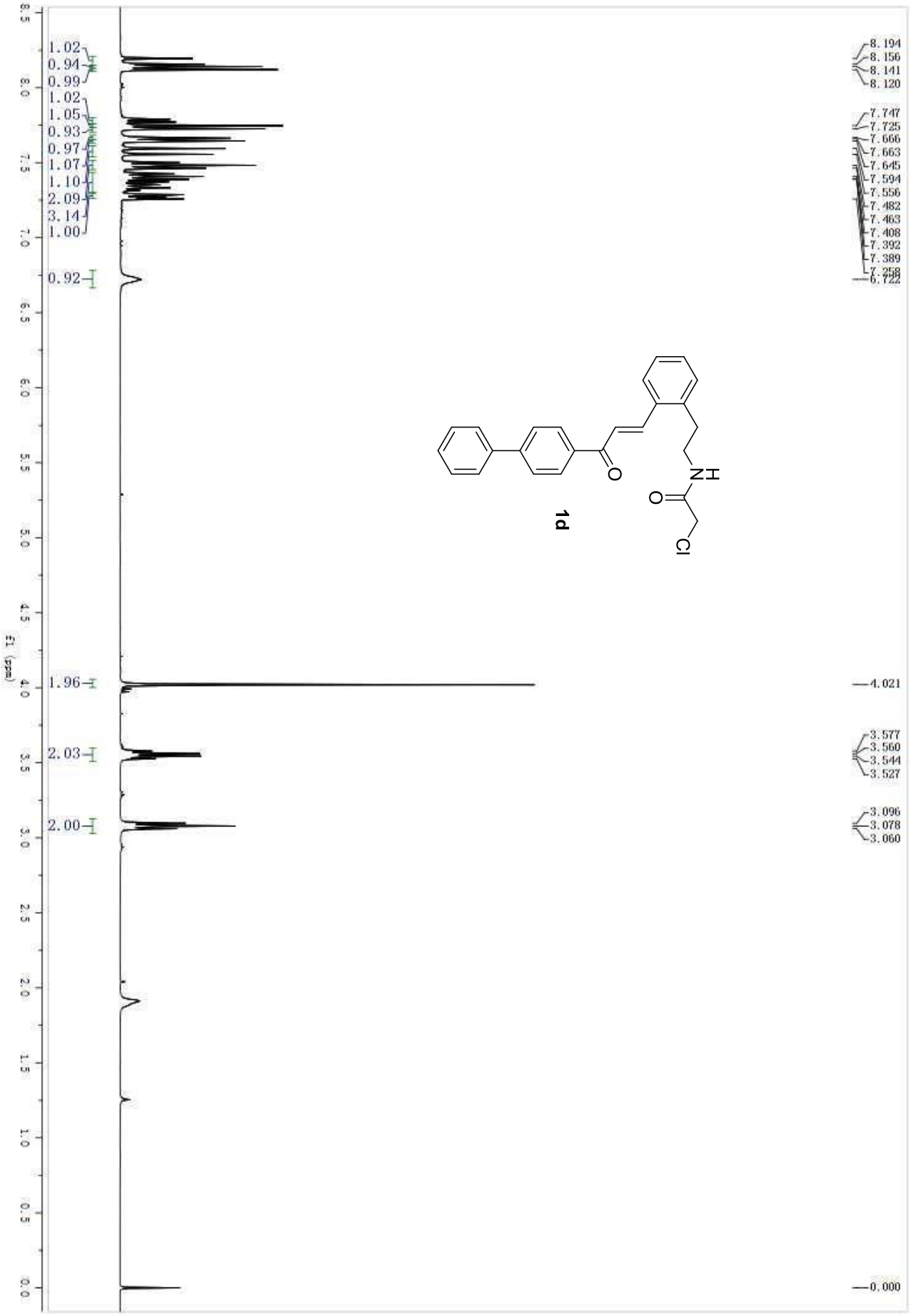
76.761
55.535
42.647
40.878
32.782
OMe
O
N
H
O
Cl
1c
f1 (ppm)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0.93
0.97
1.07
1.10
2.09
3.14
1.00
0.92
1.96
2.03
2.00
8.194
8.156
8.141
8.120
7.747
7.725
7.666
7.663
7.645
7.594
7.556
7.482
7.463
7.408
7.392
7.389
7.258
6.722
4.021
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3.560
3.544
3.527
3.096
3.078
3.060
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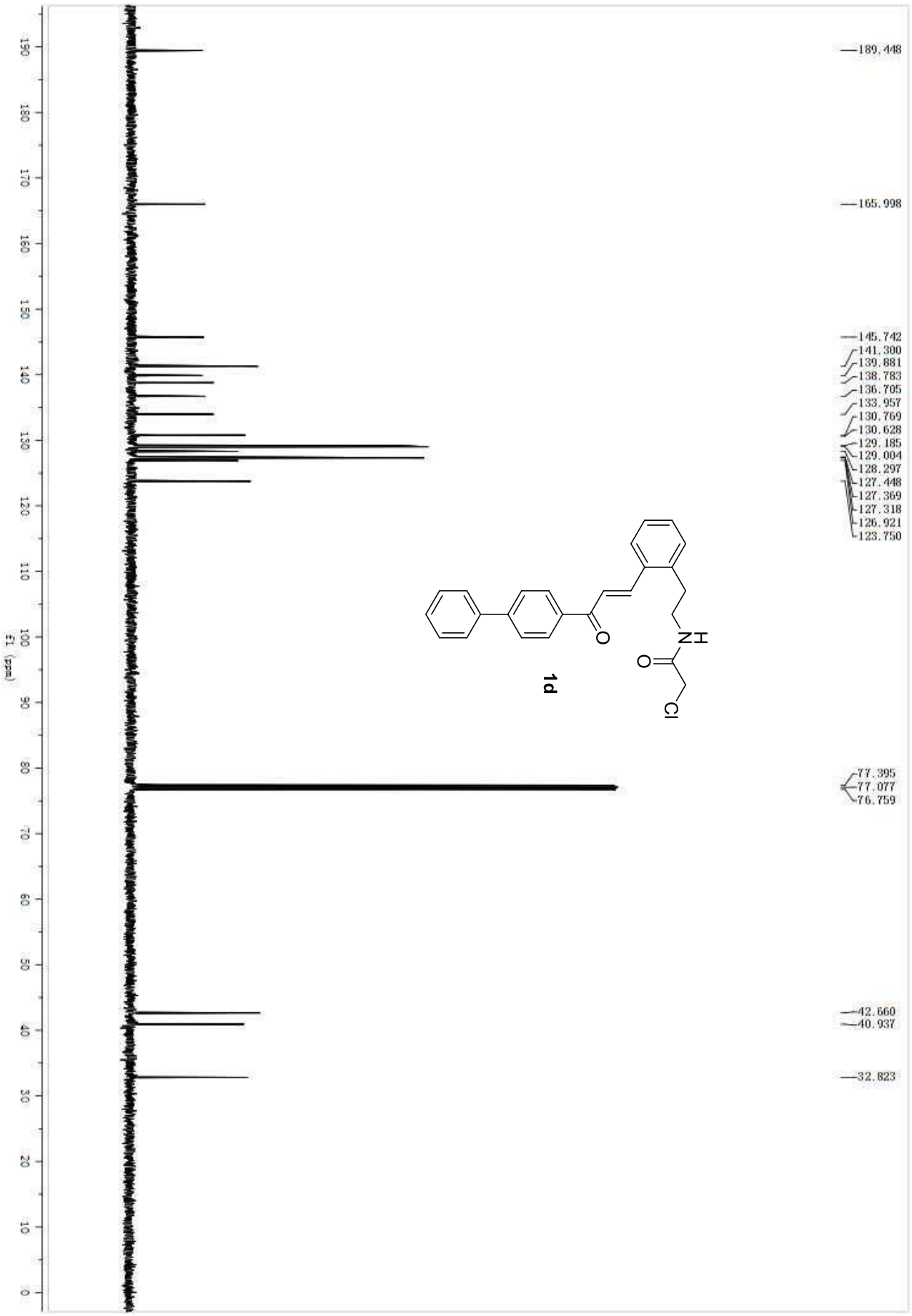
f1 (ppm)
1d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139.881
138.783
136.705
133.957
130.769
130.628
129.185
129.004
128.297
127.448
127.369
127.318
126.921
123.750
77.395
77.077
76.759
42.660
40.937
32.823
f1 (ppm)
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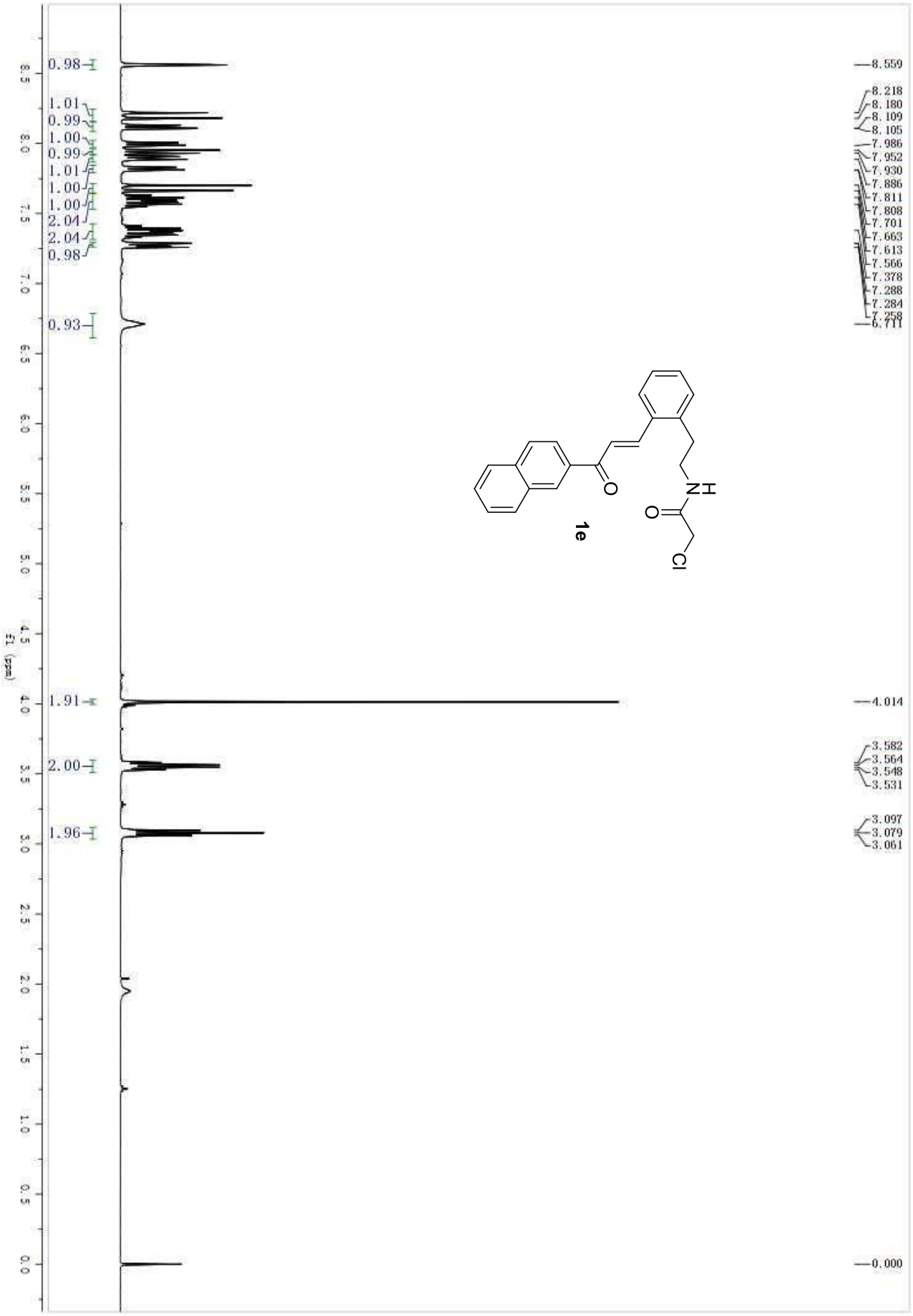
N
H
O
Cl
1d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1.00
0.99
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1.00
1.00
2.04
2.04
0.98
0.93
1.91
2.00
1.96
8.559
8.218
8.180
8.109
8.105
7.986
7.952
7.930
7.886
7.811
7.808
7.701
7.663
7.613
7.566
7.378
7.288
7.284
7.258
6.711
4.014
3.582
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f1 (ppm)
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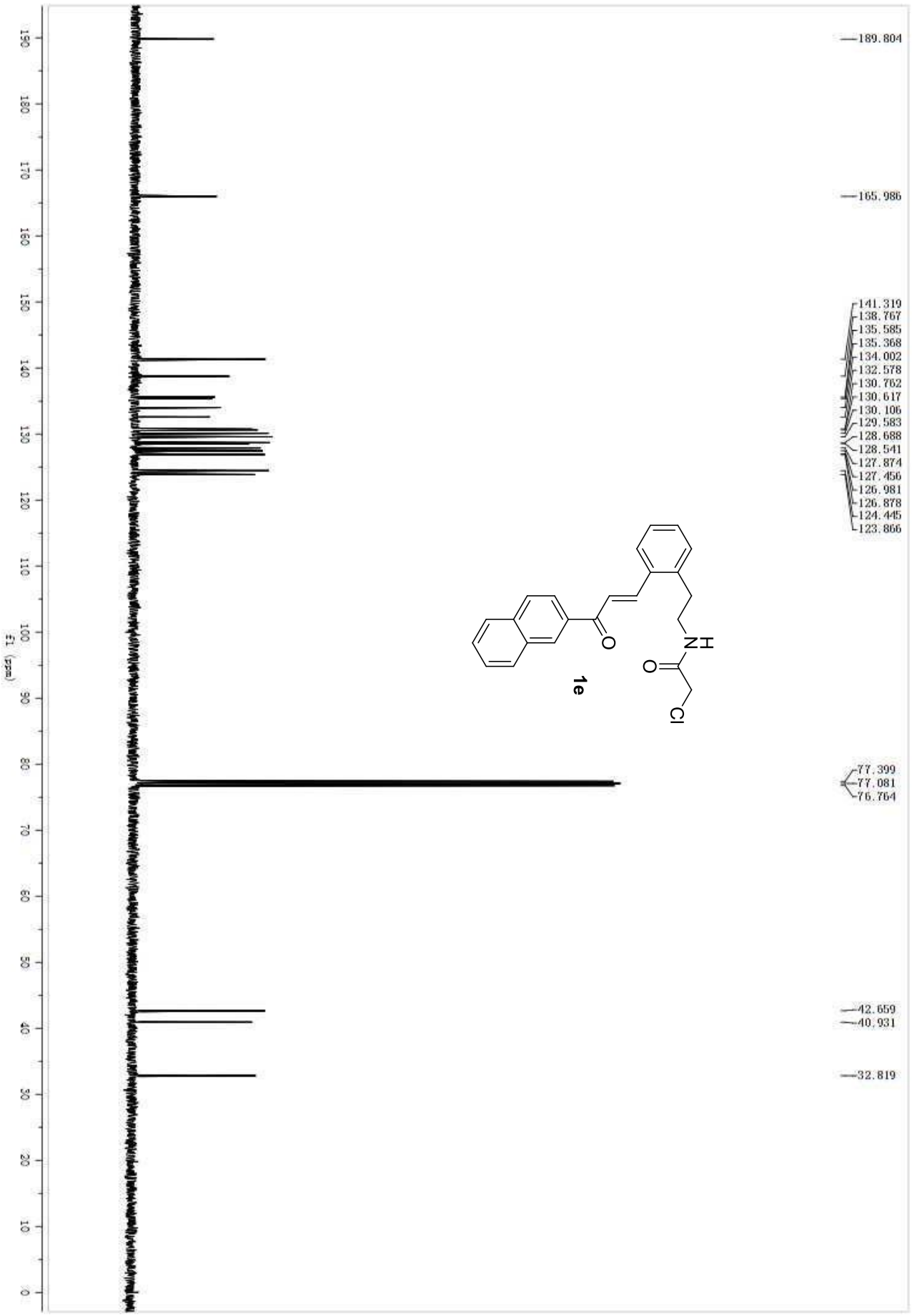
H
O
Cl
1e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128.688
128.541
127.874
127.456
126.981
126.878
124.445
123.866
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76.764
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40.931
32.819
f1 (ppm)
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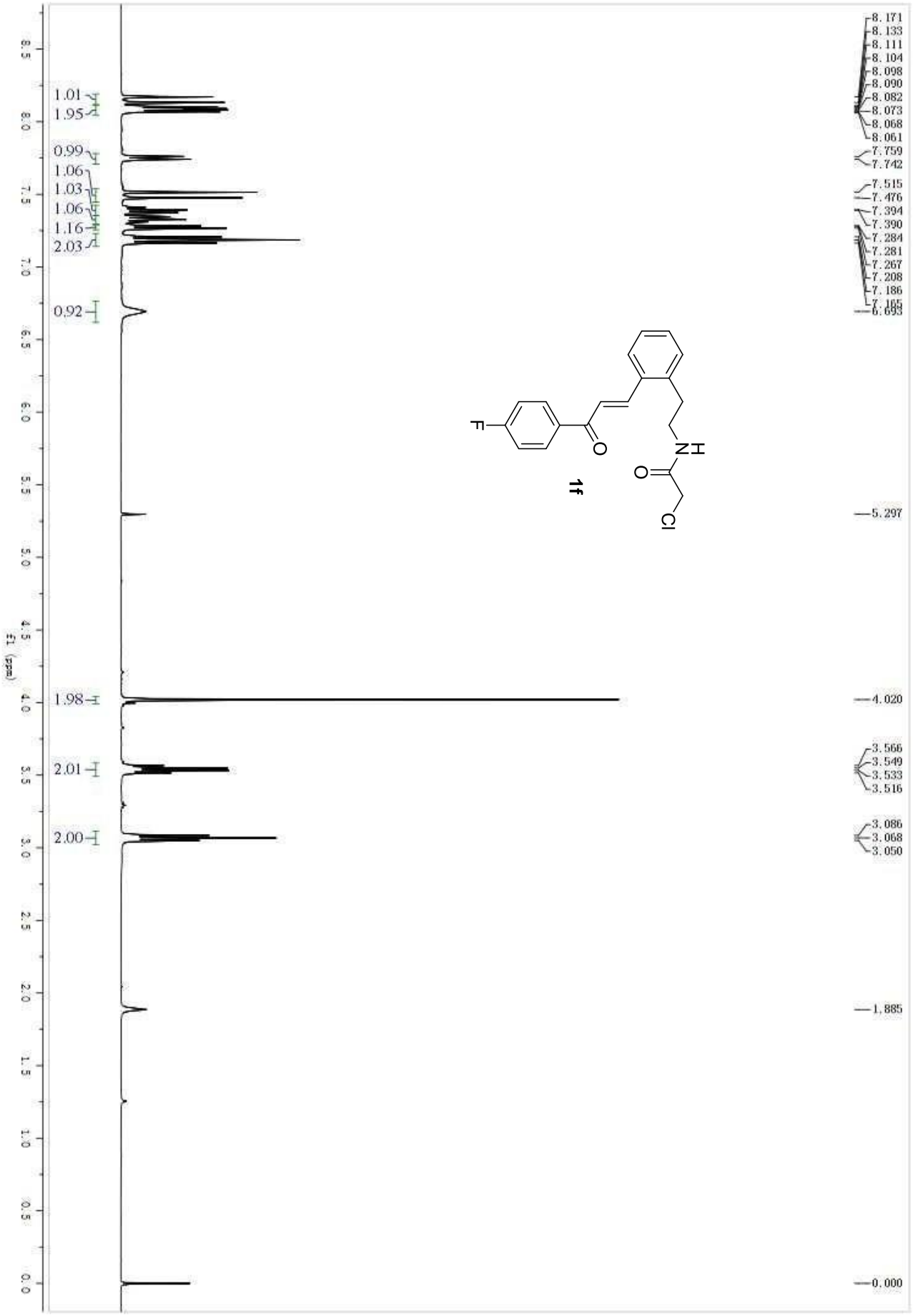
N
H
O
Cl
1e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8.061
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7.515
7.476
7.394
7.390
7.284
7.281
7.267
7.208
7.186
7.165
6.693
5.297
4.020
3.566
3.549
3.533
3.516
3.086
3.068
3.050
1.885
0.000
1.01
1.95
0.99
1.06
1.03
1.06
1.16
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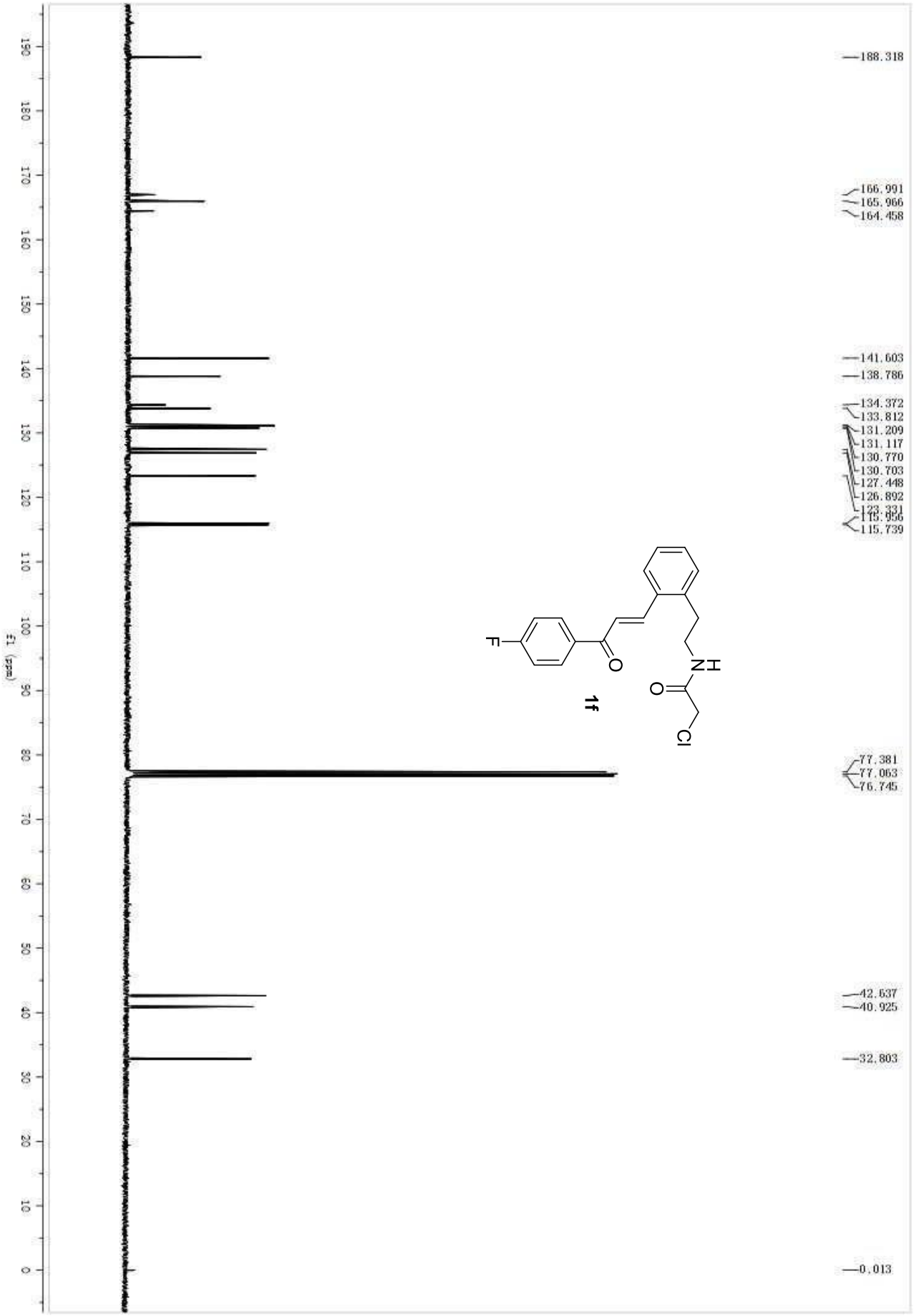
0.92
1.98
2.01
2.00
F
O
H
N
O
Cl
1f
f1 (ppm)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126.892
123.331
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115.739
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42.637
40.925
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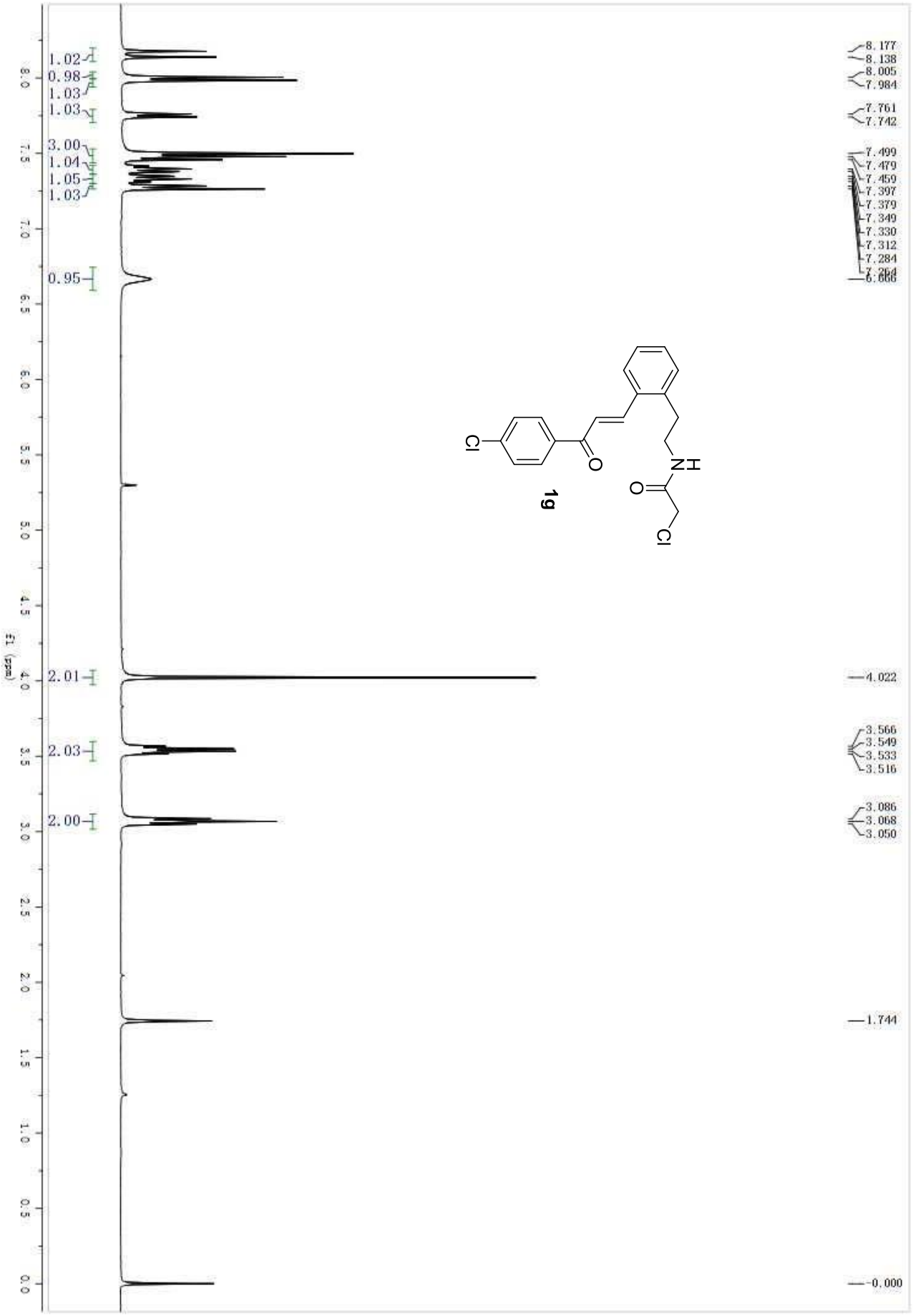
F
O
N
H
O
Cl
1f
f1 (ppm)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7.312
7.284
7.264
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0.98
1.03
1.03
3.00
1.04
1.05
1.03
0.95
2.01
2.03
2.00
4.022
3.566
3.549
3.533
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3.050
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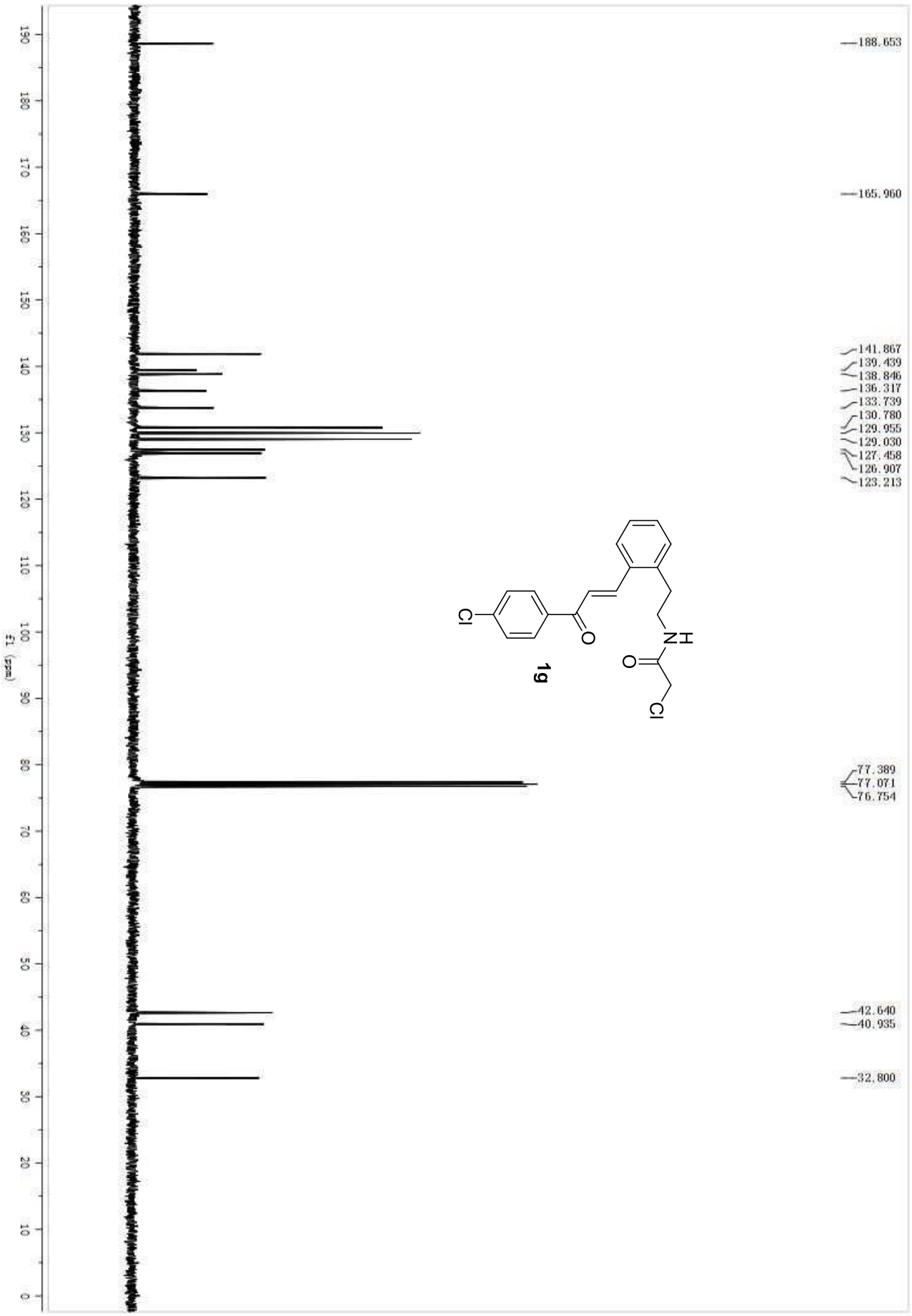
N
H
O
Cl
1g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123.213
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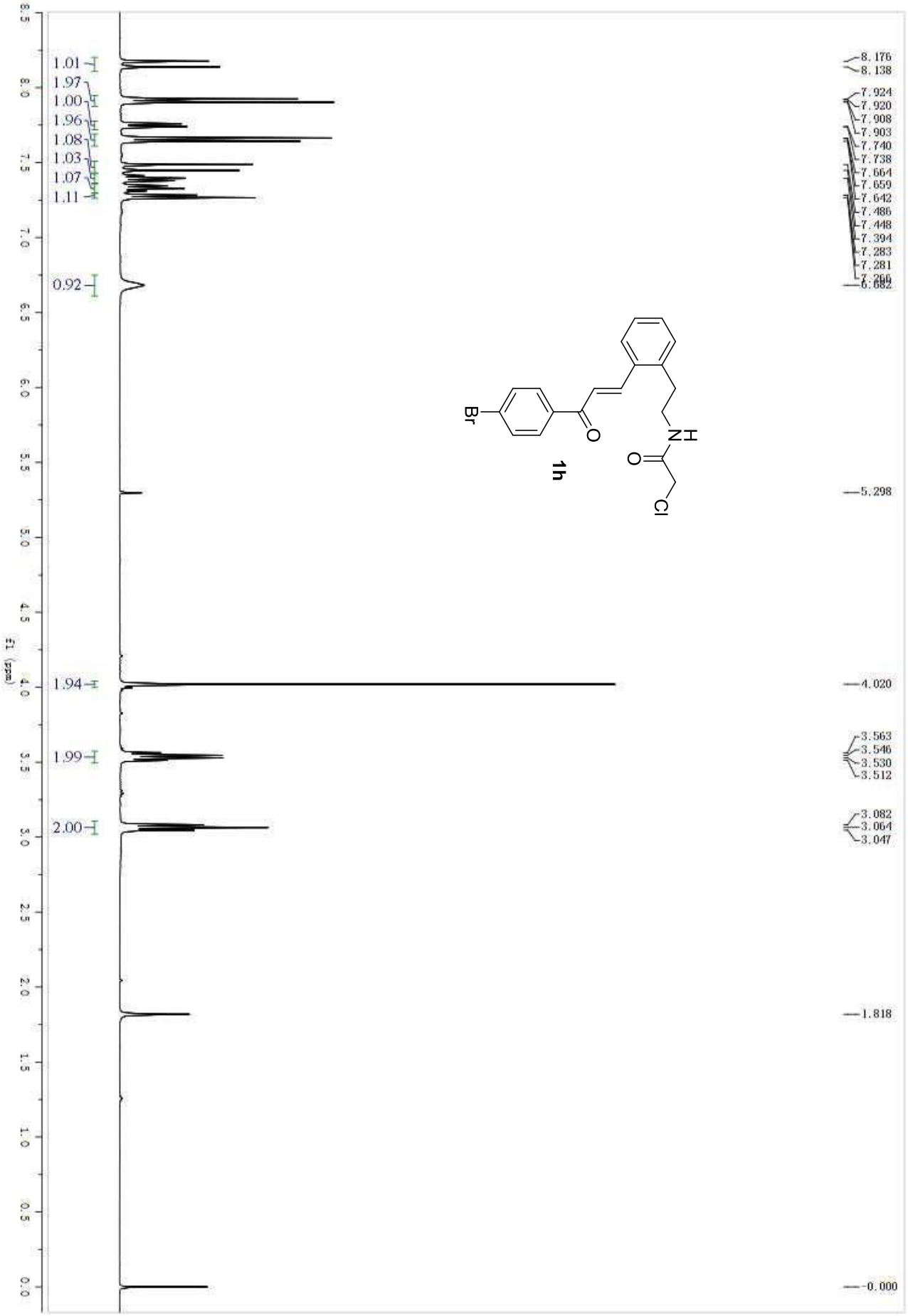
f1 (ppm)
Cl
O
N
H
O
Cl
1g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1.96
1.08
1.03
1.07
1.11
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1.94
1.99
2.00
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8.138
7.924
7.920
7.908
7.903
7.740
7.738
7.664
7.659
7.642
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7.448
7.394
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7.281
7.266
6.682
5.298
4.020
3.563
3.546
3.530
3.512
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3.064
3.047
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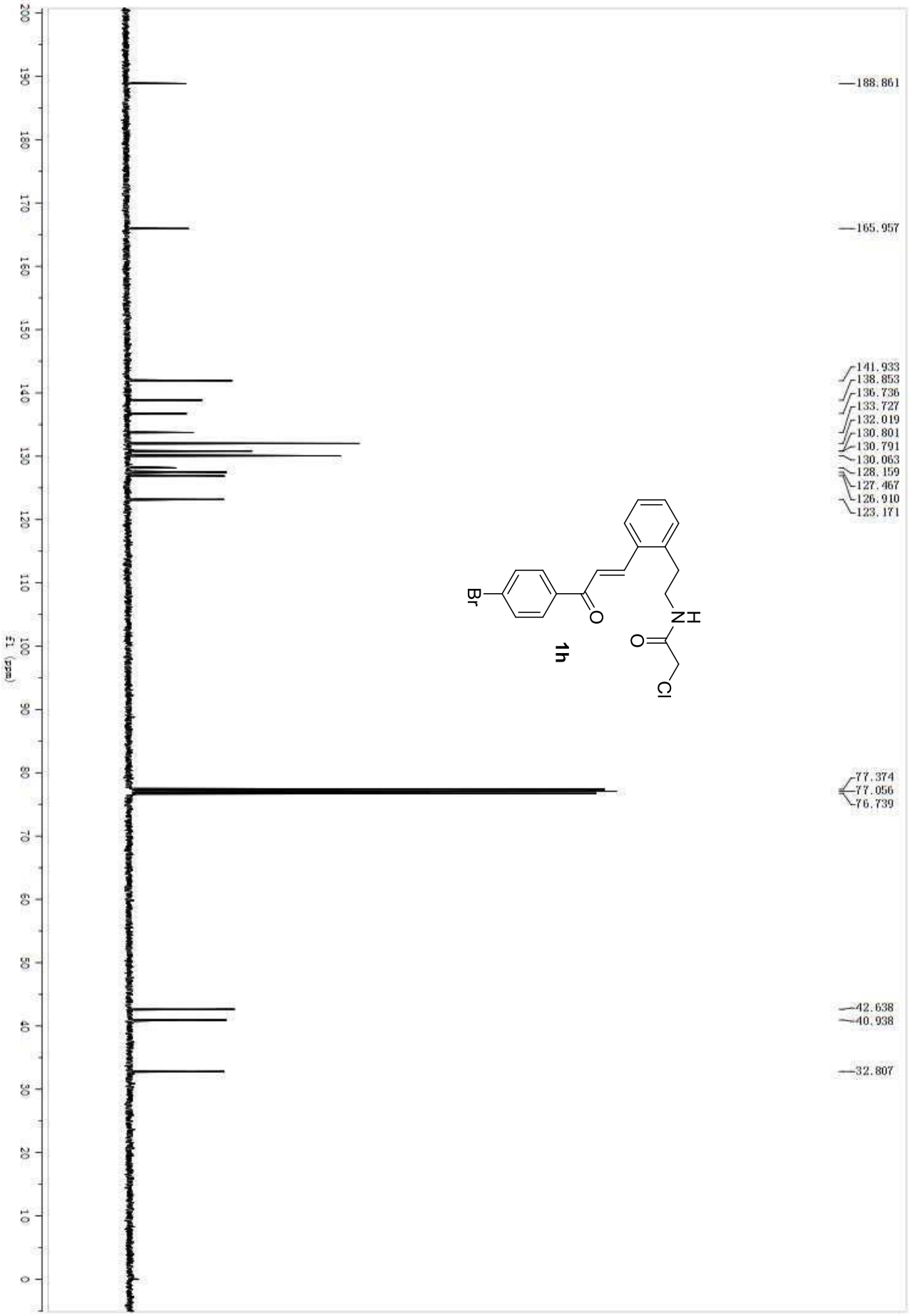
0.000
f1 (ppm)
Br
O
N
H
O
Cl
1h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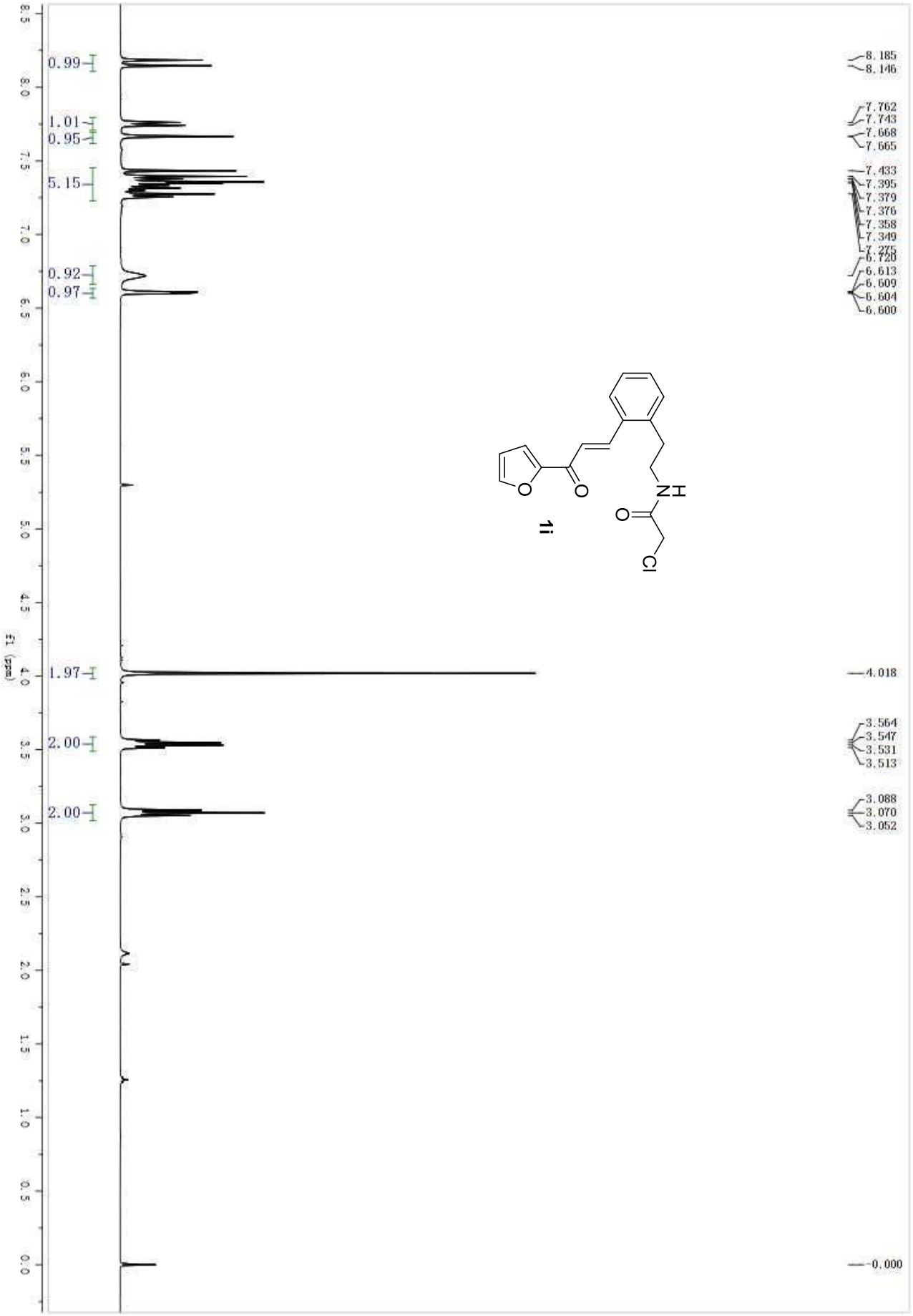
130.791
130.063
128.159
127.467
126.910
123.171
77.374
77.056
76.739
42.638
40.938
32.807
f1 (ppm)
Br
O
N
H
O
Cl
1h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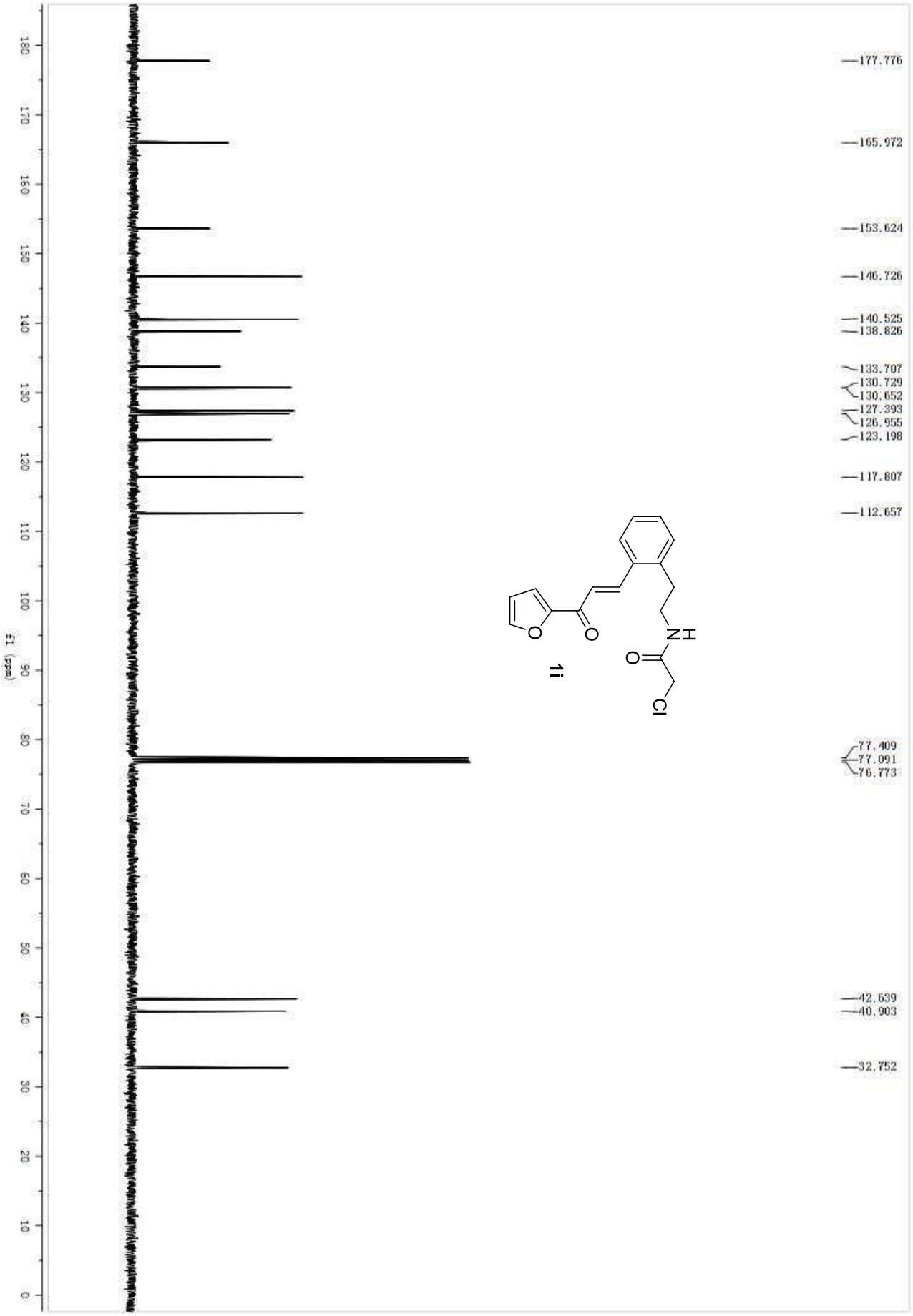
8.146
7.762
7.743
7.668
7.665
7.433
7.395
7.379
7.376
7.358
7.349
7.275
6.720
6.613
6.609
6.604
6.600
4.018
3.564
3.547
3.531
3.513
3.088
3.070
3.052
0.000
0.99
1.01
0.95
5.15
0.92
0.97
1.97
2.00
2.00
f1 (ppm)
O
O
N
H
O
Cl
1i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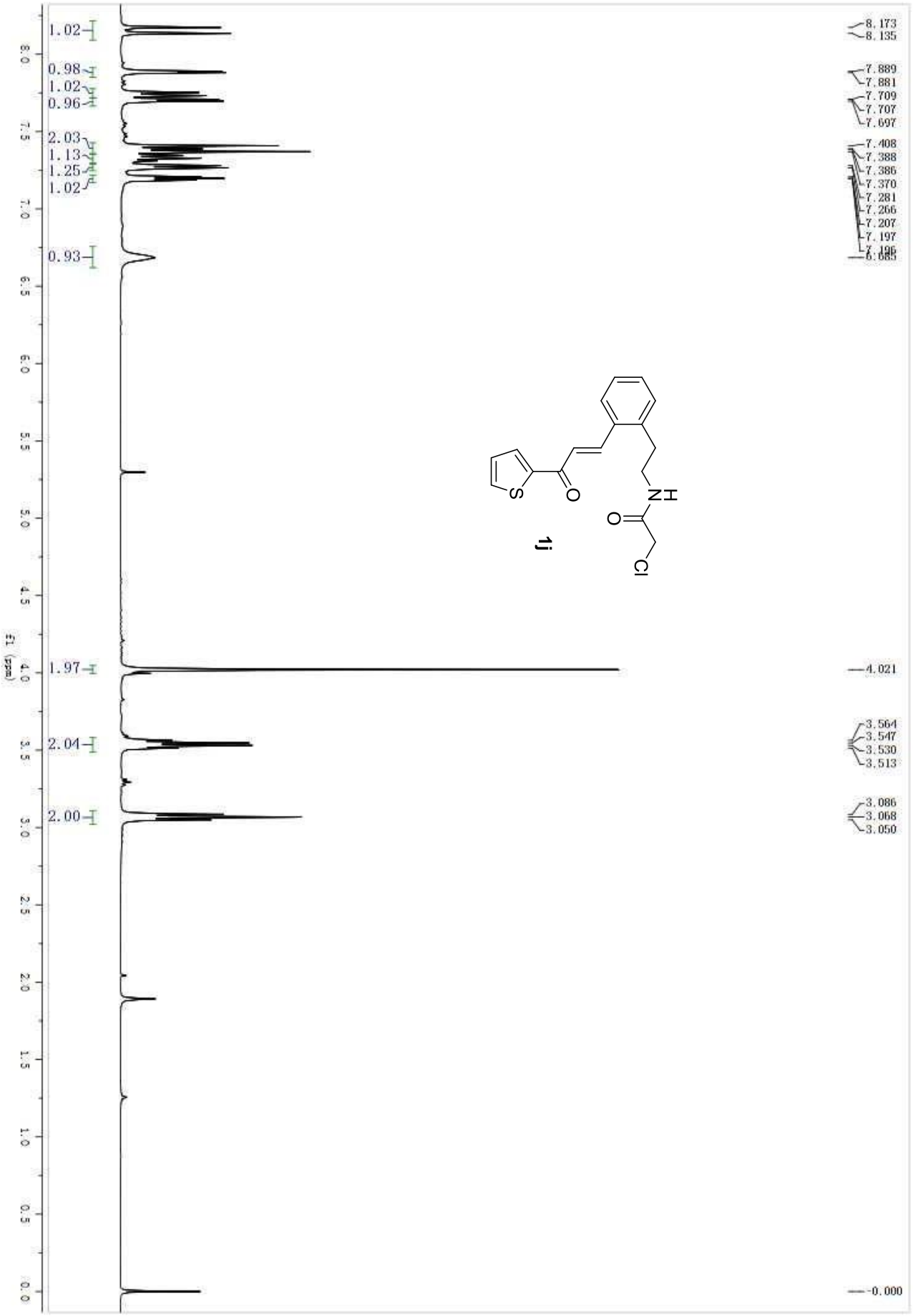
165.972
153.624
146.726
140.525
138.826
133.707
130.729
130.652
127.393
126.955
123.198
117.807
112.657
77.409
77.091
76.773
42.639
40.903
32.752
O
O
H
N
O
Cl
1i
f1 (ppm)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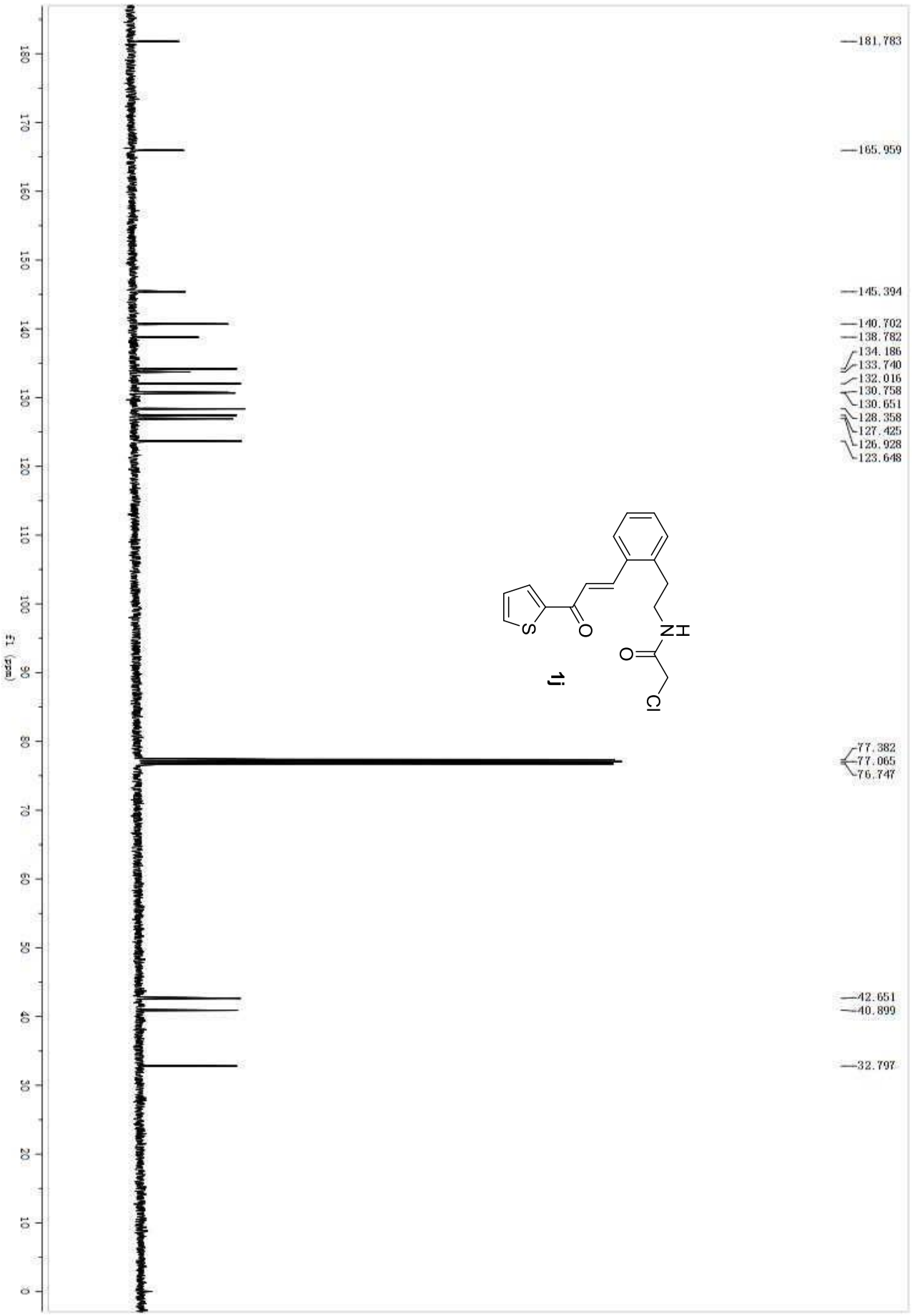
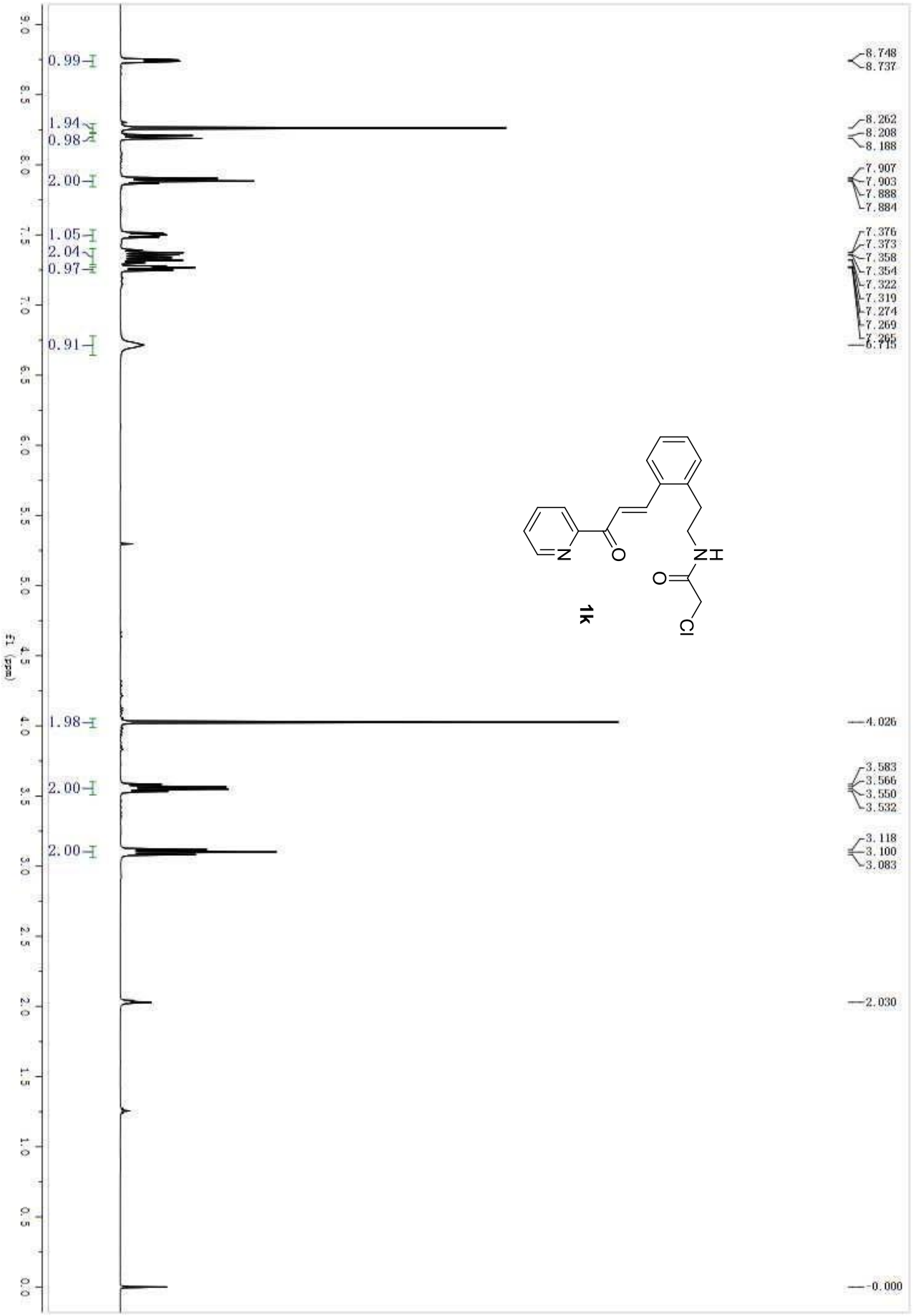
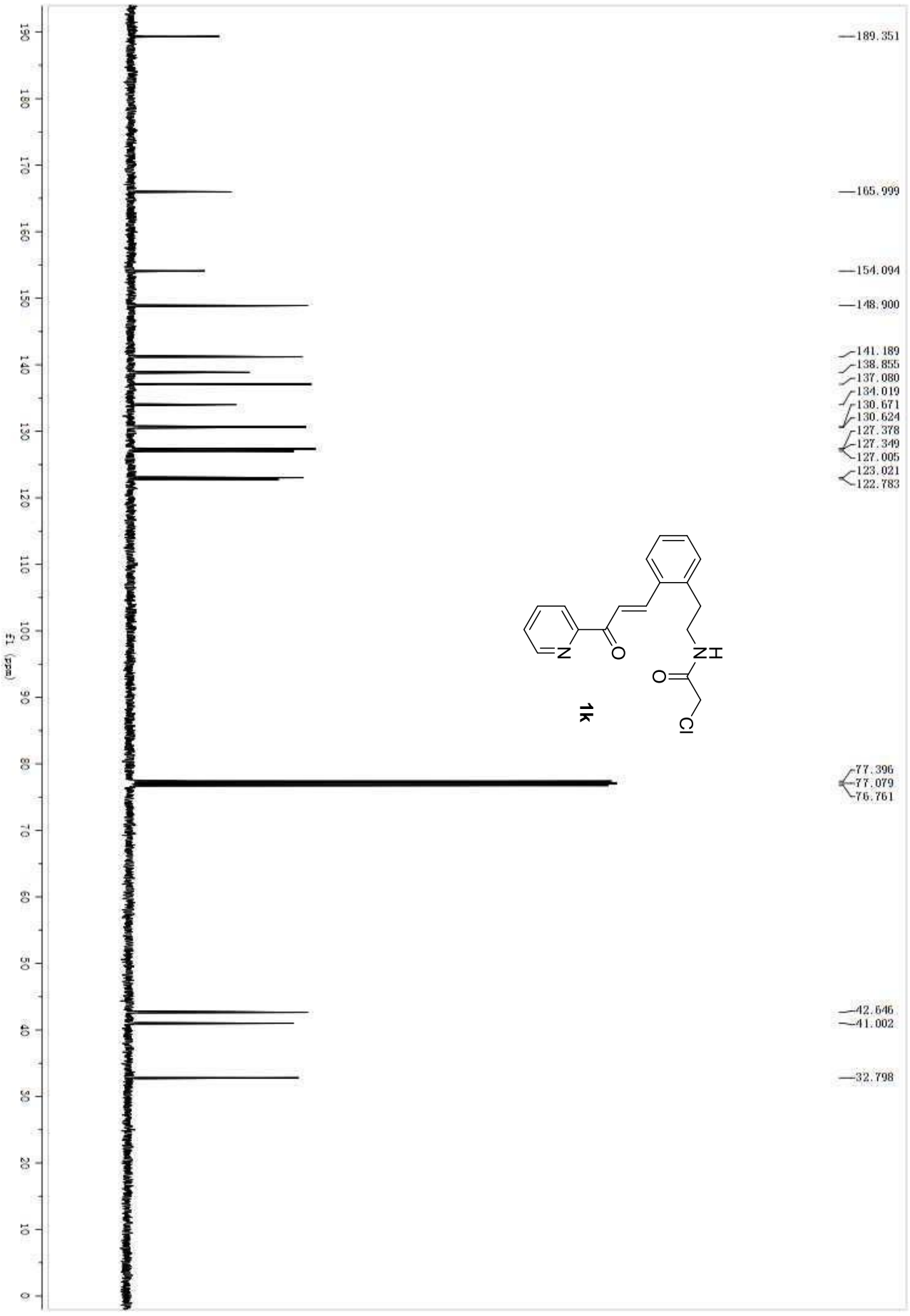
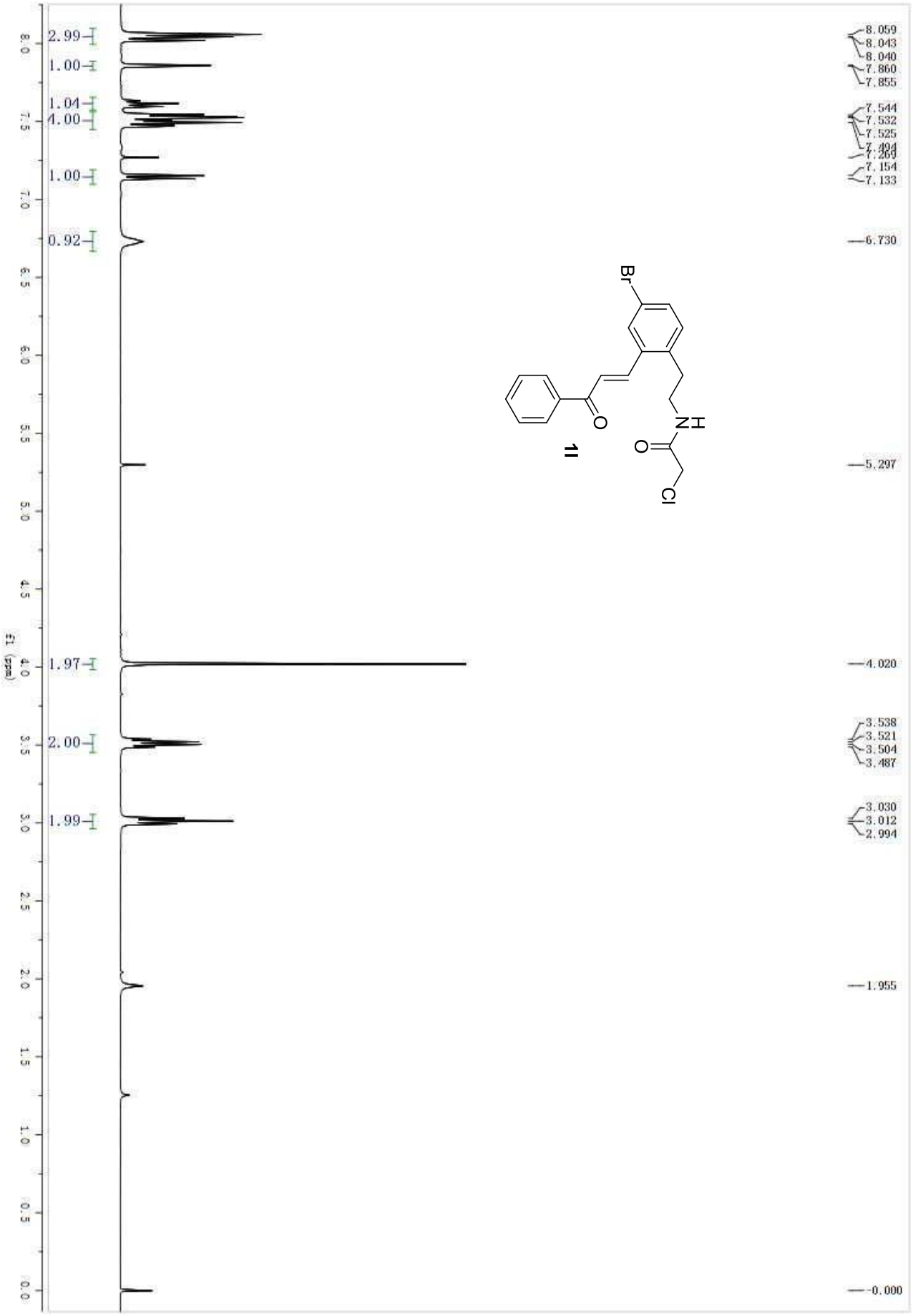
1.02
0.96
2.03
1.13
1.25
1.02
0.93
1.97
2.04
2.00
8.173
8.135
7.889
7.881
7.709
7.707
7.697
7.408
7.388
7.386
7.370
7.281
7.266
7.207
7.197
7.196
6.685
4.021
3.564
3.547
3.530
3.513
3.086
3.068
3.050
-0.000
f1 (ppm)
S
O
NH
O
Cl

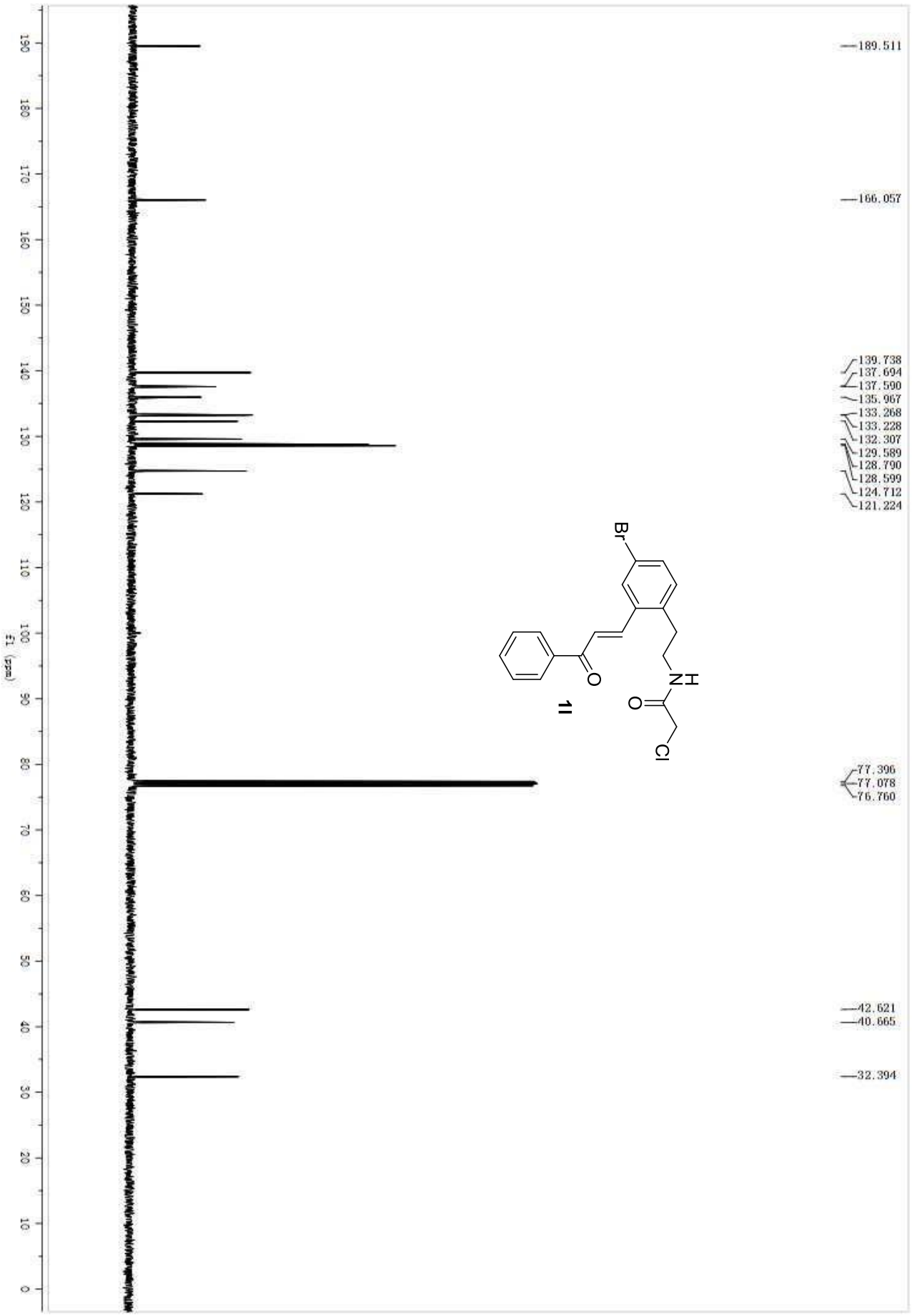
1j

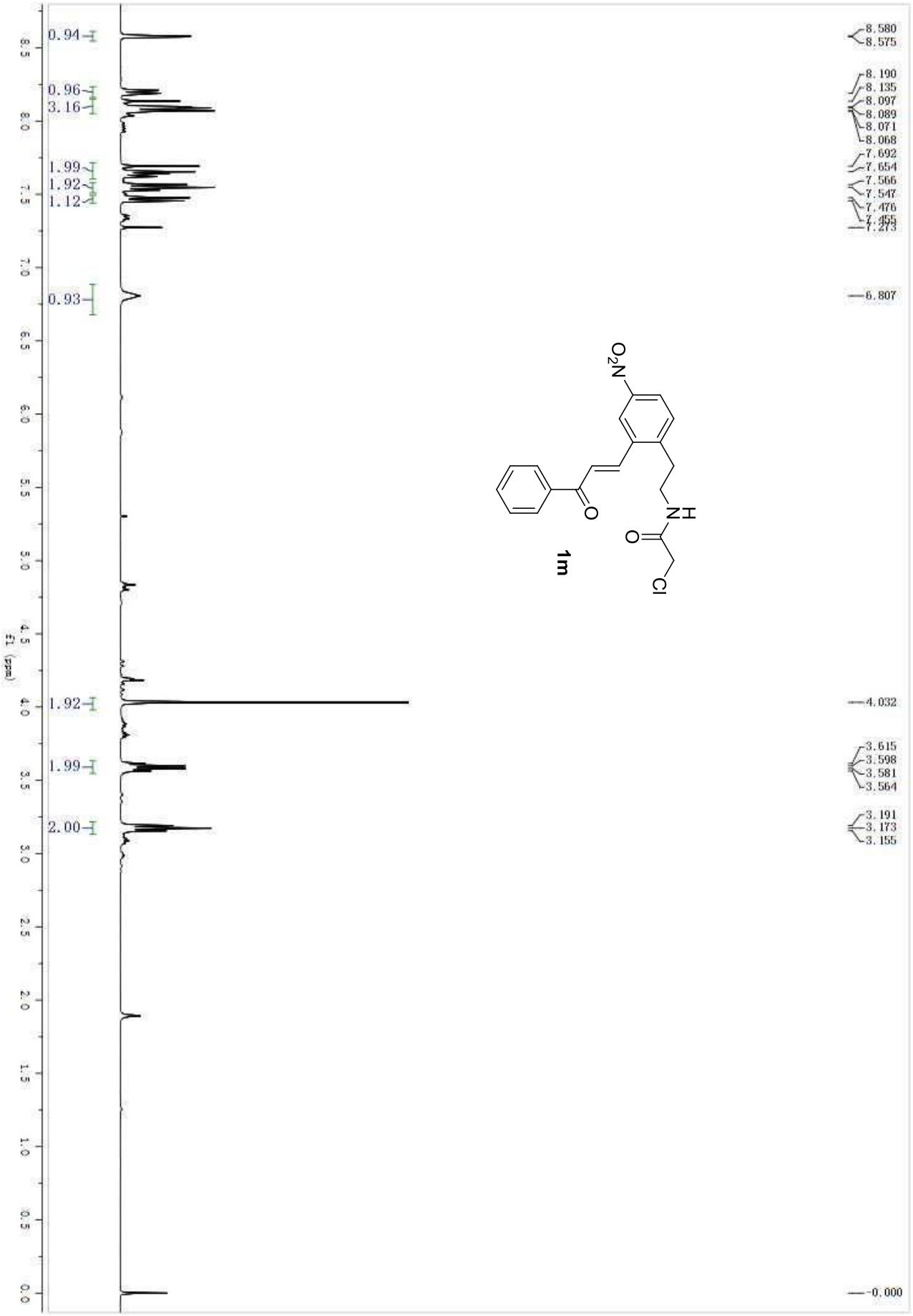

181.783
165.959
145.394
140.702
138.782
134.186
133.740
132.016
130.758
130.651
128.358
127.425
126.928
123.648
77.382
77.065
76.747
42.651
40.899
32.797
f1 (ppm)
1j

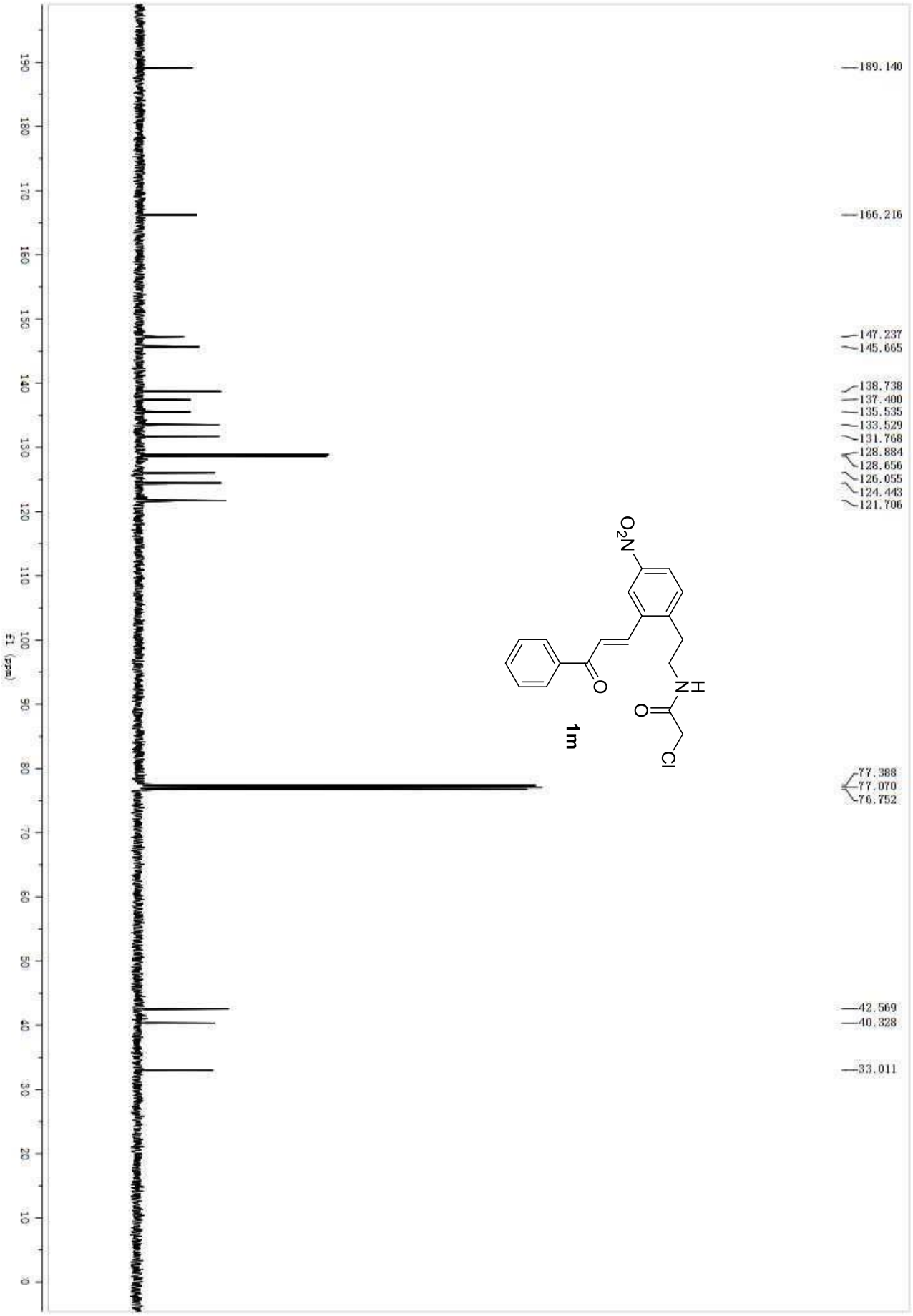

8.748
8.737
8.262
8.208
8.188
7.907
7.903
7.888
7.884
7.376
7.373
7.358
7.354
7.322
7.319
7.274
7.269
7.265
6.715
4.026
3.583
3.566
3.550
3.532
3.118
3.100
3.083
2.030
0.000
0.99
1.94
0.98
2.00
1.05
2.04
0.97
0.91
1.98
2.00
2.00
f1 (ppm)
1k

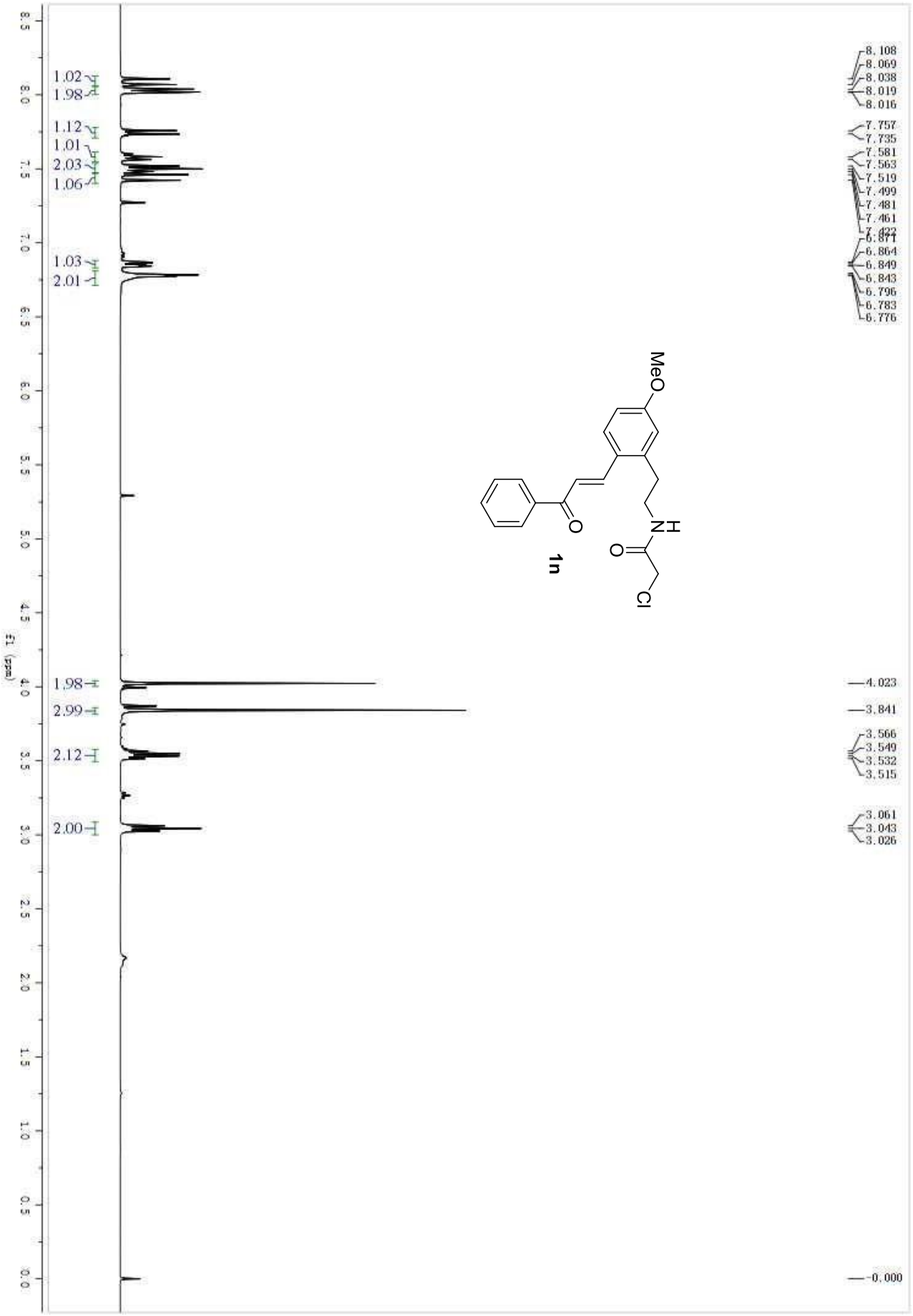

189.351
165.999
154.094
148.900
141.189
138.855
137.080
134.019
130.671
130.624
127.378
127.349
127.005
123.021
122.783
77.396
77.079
76.761
42.646
41.002
32.798
f1 (ppm)
1k

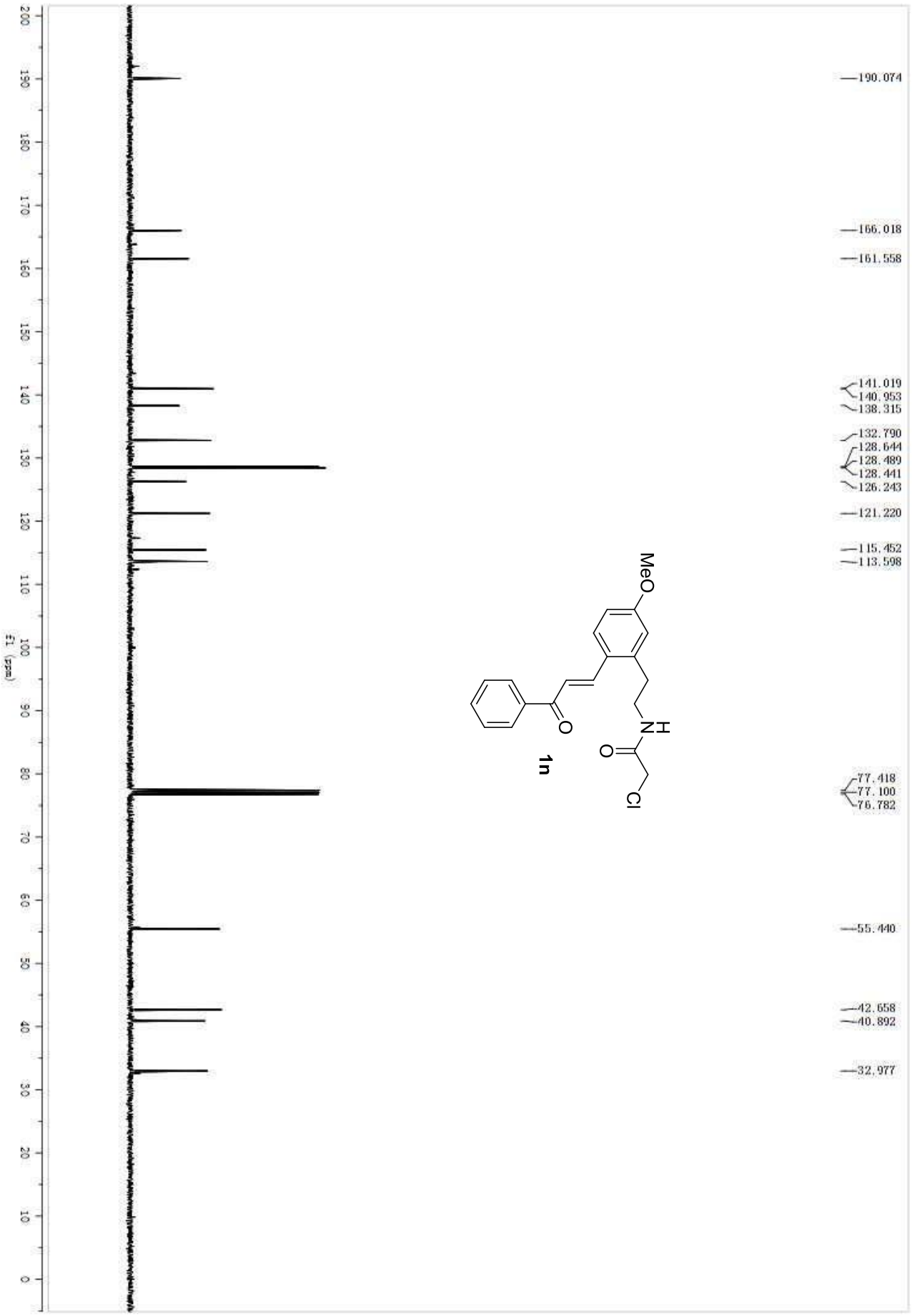

2.99
1.00
1.04
4.00
1.00
0.92
1.97
2.00
1.99
8.059
8.043
8.040
7.860
7.855
7.544
7.532
7.525
7.494
7.269
7.154
7.133
6.730
5.297
4.020
3.538
3.521
3.504
3.487
3.030
3.012
2.994
1.955
0.000
F1 (ppm)
Br
O
N
H
O
Cl
11

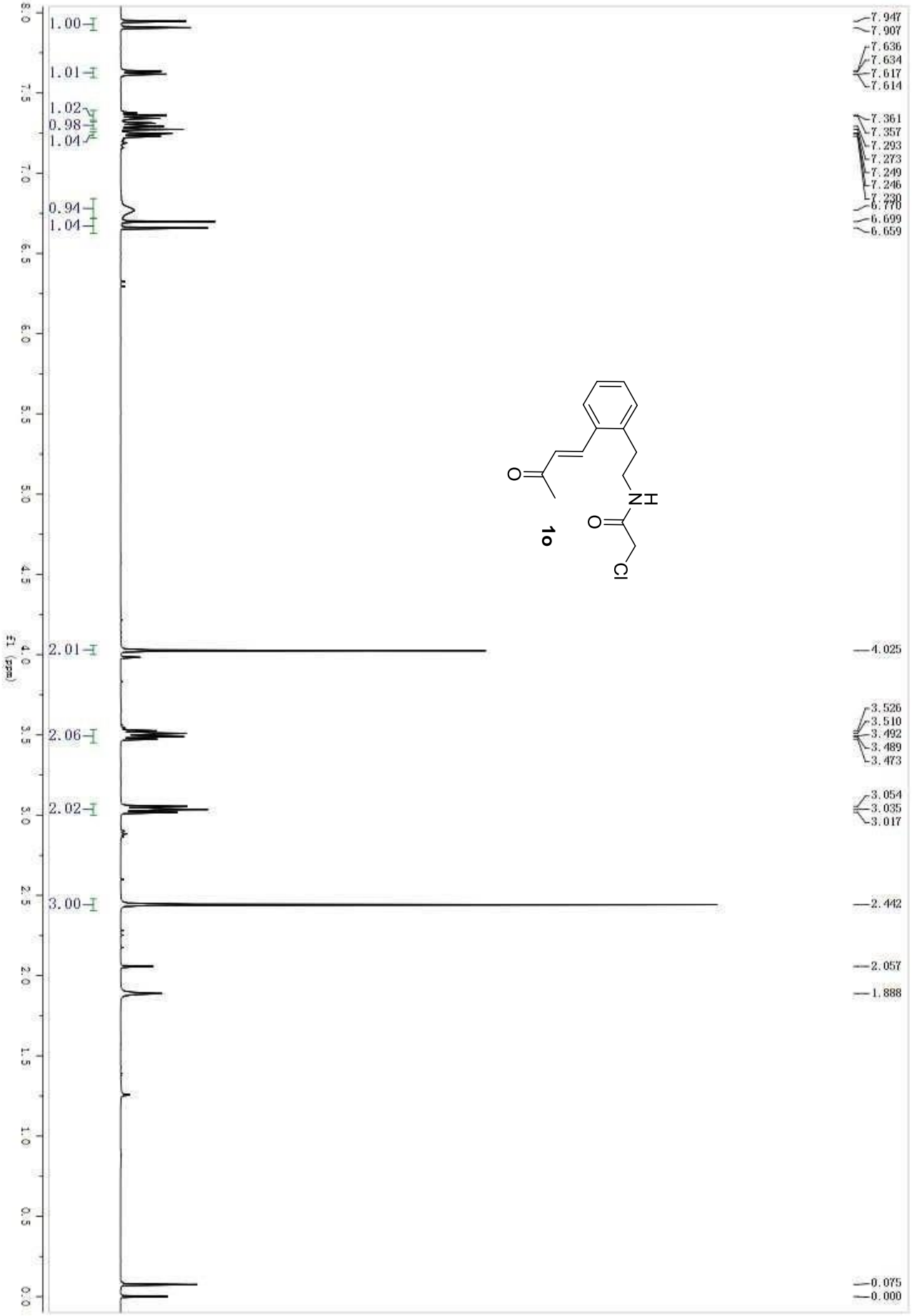

189.511
166.057
139.738
137.694
137.590
135.967
133.268
133.228
132.307
129.589
128.790
128.599
124.712
121.224
77.396
77.078
76.760
42.621
40.665
32.394
f1 (ppm)
Br
O
N
H
O
Cl
11

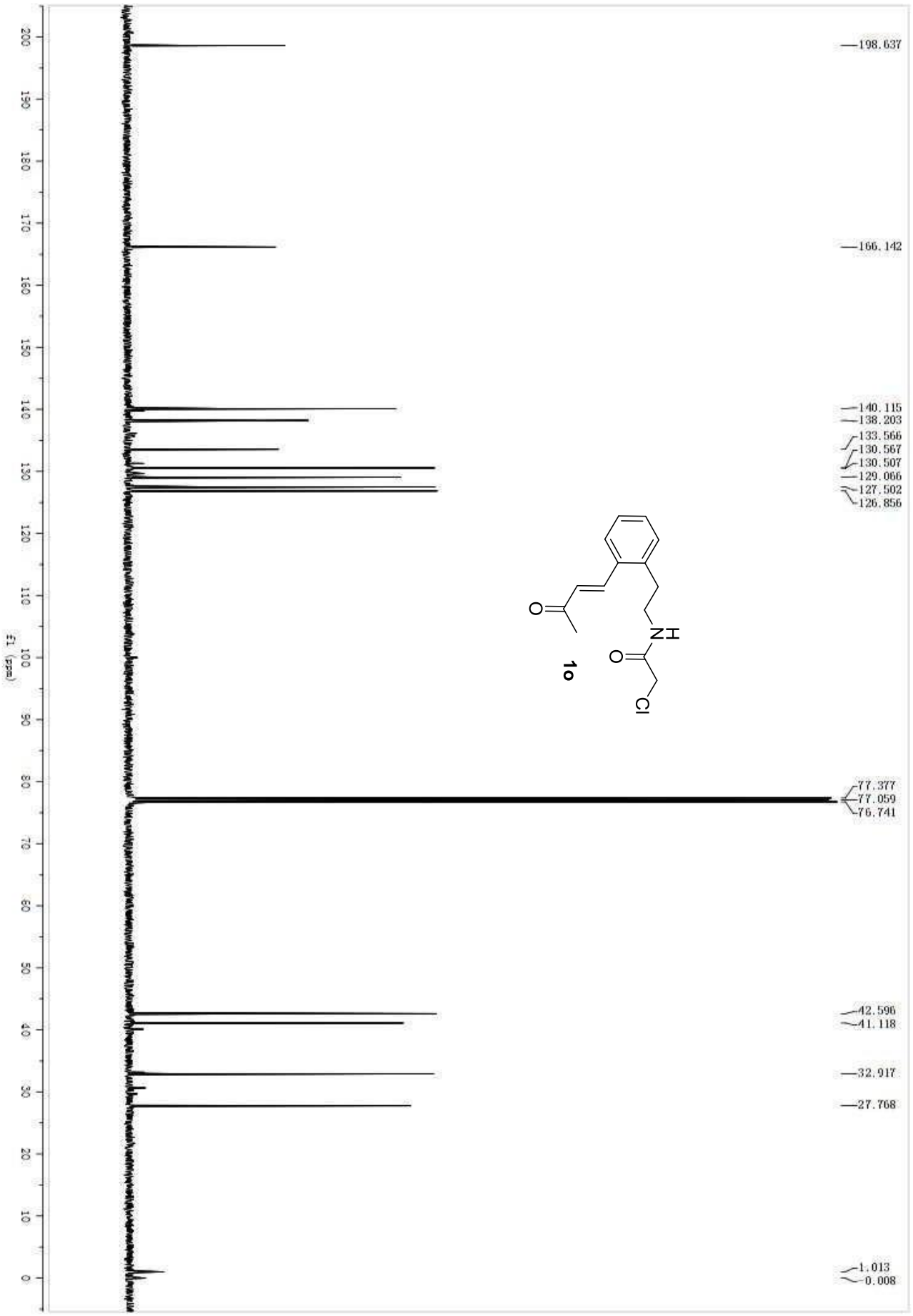

8.580
8.575
8.190
8.135
8.097
8.089
8.071
8.068
7.692
7.654
7.566
7.547
7.476
7.455
7.273
6.807
4.032
3.615
3.598
3.581
3.564
3.191
3.173
3.155
0.000
0.94
0.96
3.16
1.99
1.92
1.12
0.93
1.92
1.99
2.00
f1 (ppm)
O2N
O
N
H
O
Cl
1m

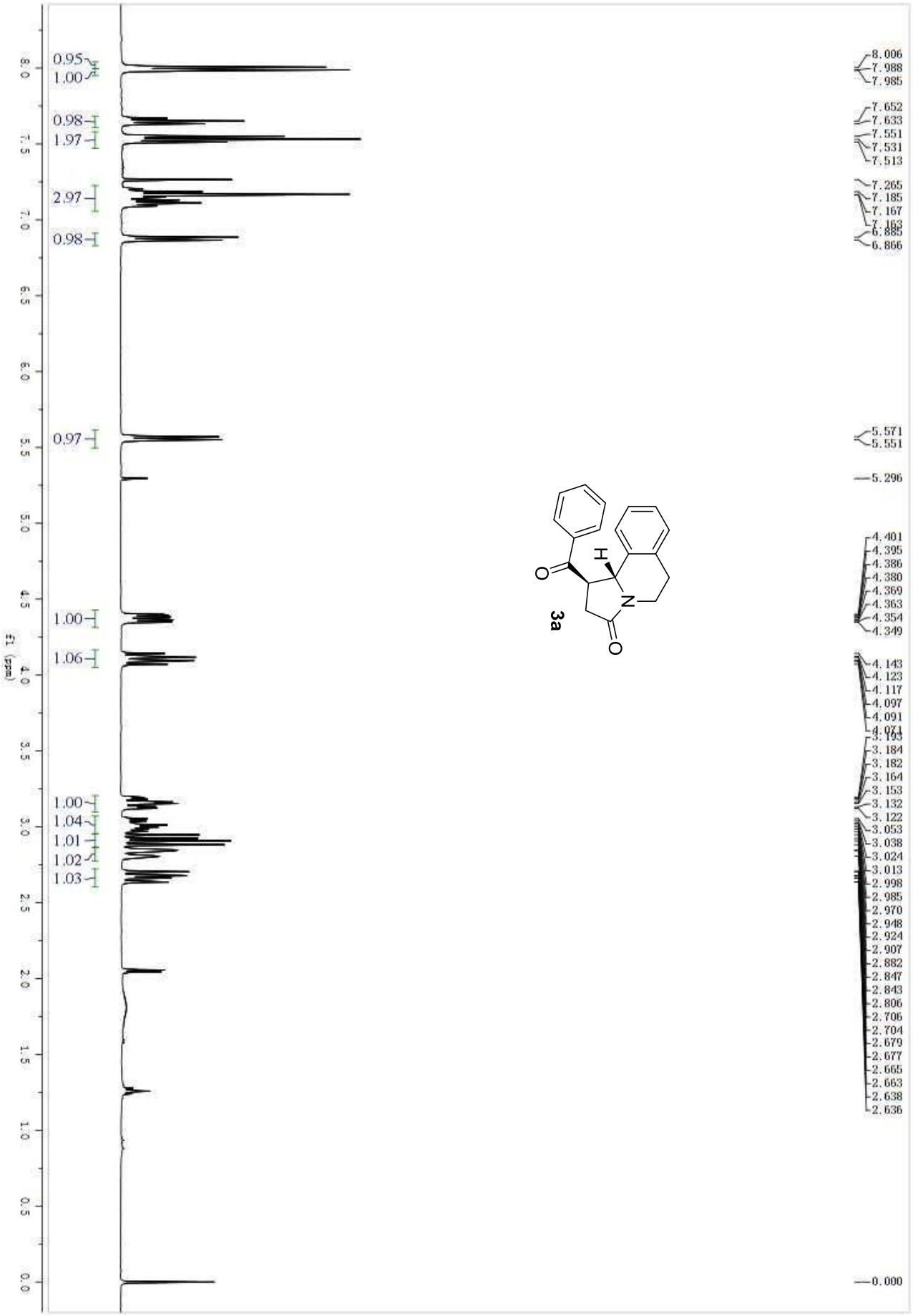

189.140
166.216
147.237
145.665
138.738
137.400
135.535
133.529
131.768
128.884
128.656
126.055
124.443
121.706
77.388
77.070
76.752
42.569
40.328
33.011
f1 (ppm)
O2N
O
N
H
O
Cl
1m

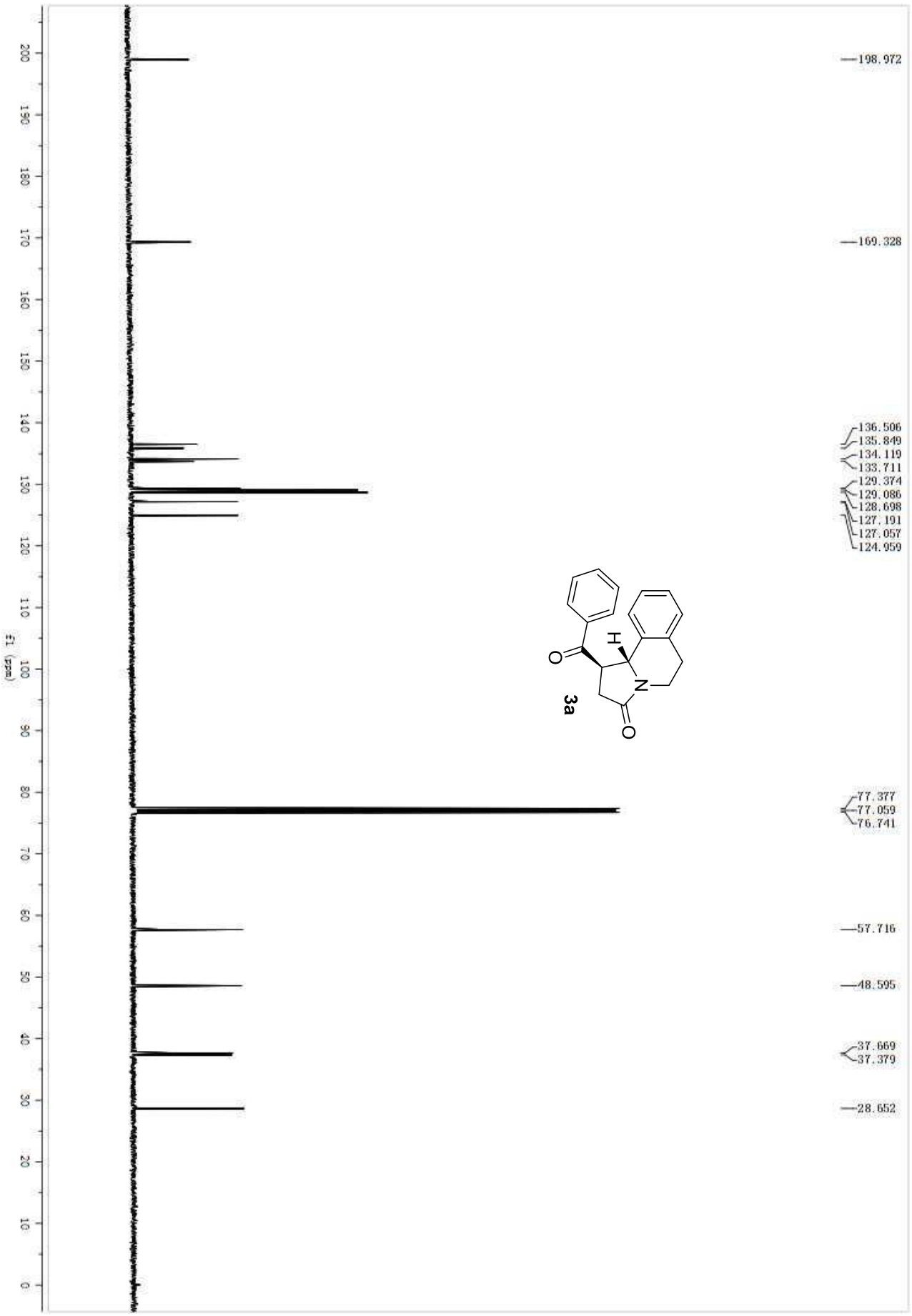

8.108
8.069
8.038
8.019
8.016
7.757
7.735
7.581
7.563
7.519
7.499
7.481
7.461
7.422
6.871
6.864
6.849
6.843
6.796
6.783
6.776
4.023
3.841
3.566
3.549
3.532
3.515
3.061
3.043
3.026
0.000
1.02
1.98
1.12
1.01
2.03
1.06
1.03
2.01
1.98
2.99
2.12
2.00
MeO
O
N
H
O
Cl
1n
f1 (ppm)

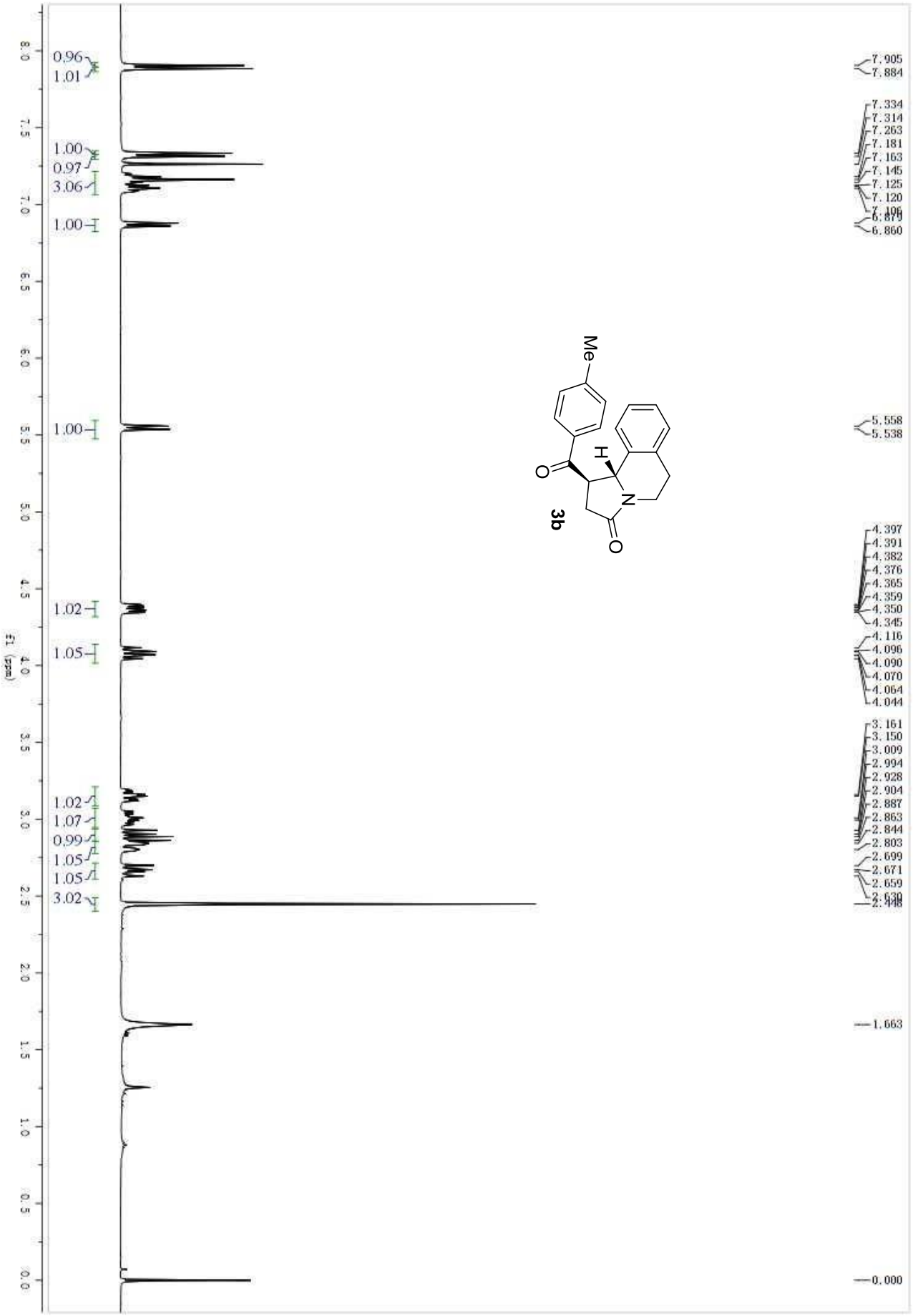

190.074
166.018
161.558
141.019
140.953
138.315
132.790
128.644
128.489
128.441
126.243
121.220
115.452
113.598
77.418
77.100
76.782
55.440
42.658
40.892
32.977
MeO
O
N
H
O
Cl
1n
f1 (ppm)


1.00
1.01
1.02
0.98
1.04
0.94
1.04
2.01
2.06
2.02
3.00
7.947
7.907
7.636
7.634
7.617
7.614
7.361
7.357
7.293
7.273
7.249
7.246
7.230
6.770
6.699
6.659
4.025
3.526
3.510
3.492
3.489
3.473
3.054
3.035
3.017
2.442
2.057
1.888
0.075
0.000
F1 (ppm)
O
N
H
O
Cl
1o


198.637
166.142
140.115
138.203
133.566
130.567
130.507
129.066
127.502
126.856
77.377
77.059
76.741
42.596
41.118
32.917
27.768
1.013
0.008
O
N
H
O
Cl
1o
f1 (ppm)


8.006
7.988
7.985
7.652
7.633
7.551
7.531
7.513
7.265
7.185
7.167
6.885
6.866
5.571
5.551
5.296
4.401
4.395
4.386
4.380
4.369
4.363
4.354
4.349
4.143
4.123
4.117
4.097
4.091
3.193
3.184
3.182
3.164
3.153
3.132
3.122
3.053
3.038
3.024
3.013
2.998
2.985
2.970
2.948
2.924
2.907
2.882
2.847
2.843
2.806
2.706
2.704
2.679
2.677
2.665
2.663
2.638
2.636
0.000
0.95
1.00
0.98
1.97
2.97
0.98
0.97
1.00
1.06
1.00
1.04
1.01
1.02
1.03
f1 (ppm)
H
O
N
O
3a


198.972
169.328
136.506
135.849
134.119
133.711
129.374
129.086
128.698
127.191
127.057
124.959
77.377
77.059
76.741
57.716
48.595
37.669
37.379
28.652
f1 (ppm)
3a


0.96
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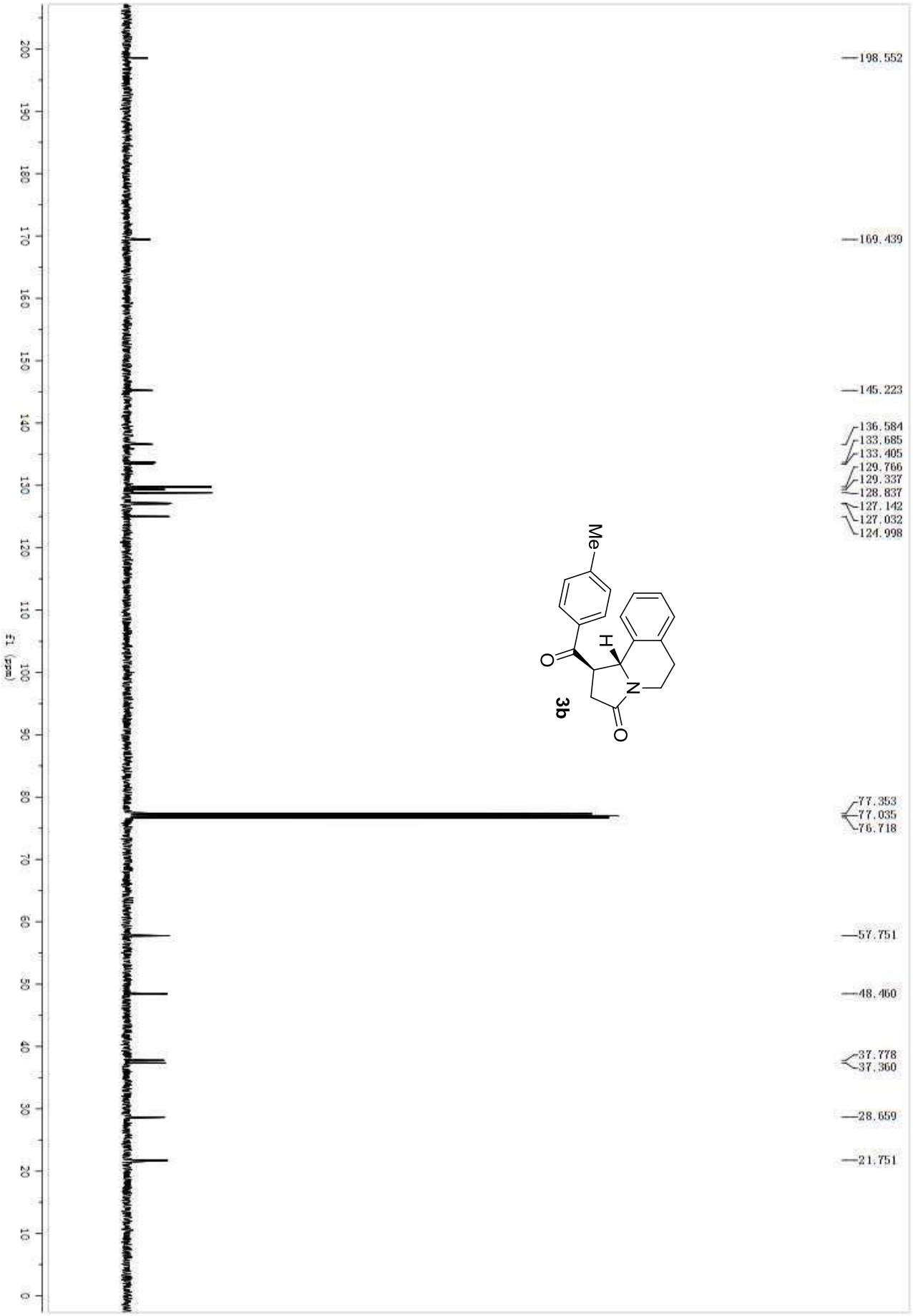
1.00
0.97
3.06
1.00
1.00
1.02
1.05
1.02
1.07
0.99
1.05
1.05
3.02
7.905
7.884
7.334
7.314
7.263
7.181
7.163
7.145
7.125
7.120
6.879
6.860
5.558
5.538
4.397
4.391
4.382
4.376
4.365
4.359
4.350
4.345
4.116
4.096
4.090
4.070
4.064
4.044
3.161
3.150
3.009
2.994
2.928
2.904
2.887
2.863
2.844
2.803
2.699
2.671
2.659
1.663
0.000
Me
H
O
N
O
3b
f1 (ppm)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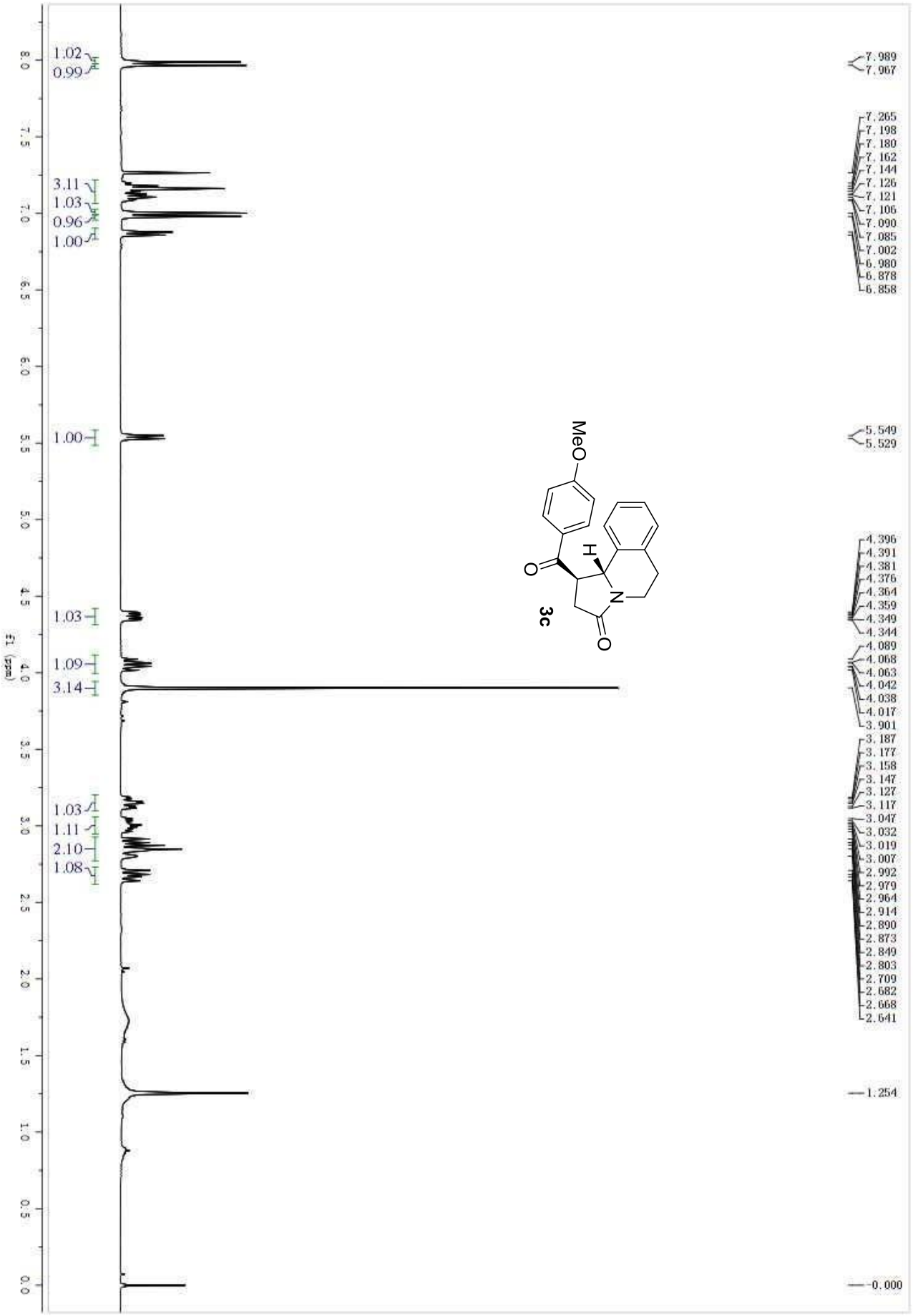
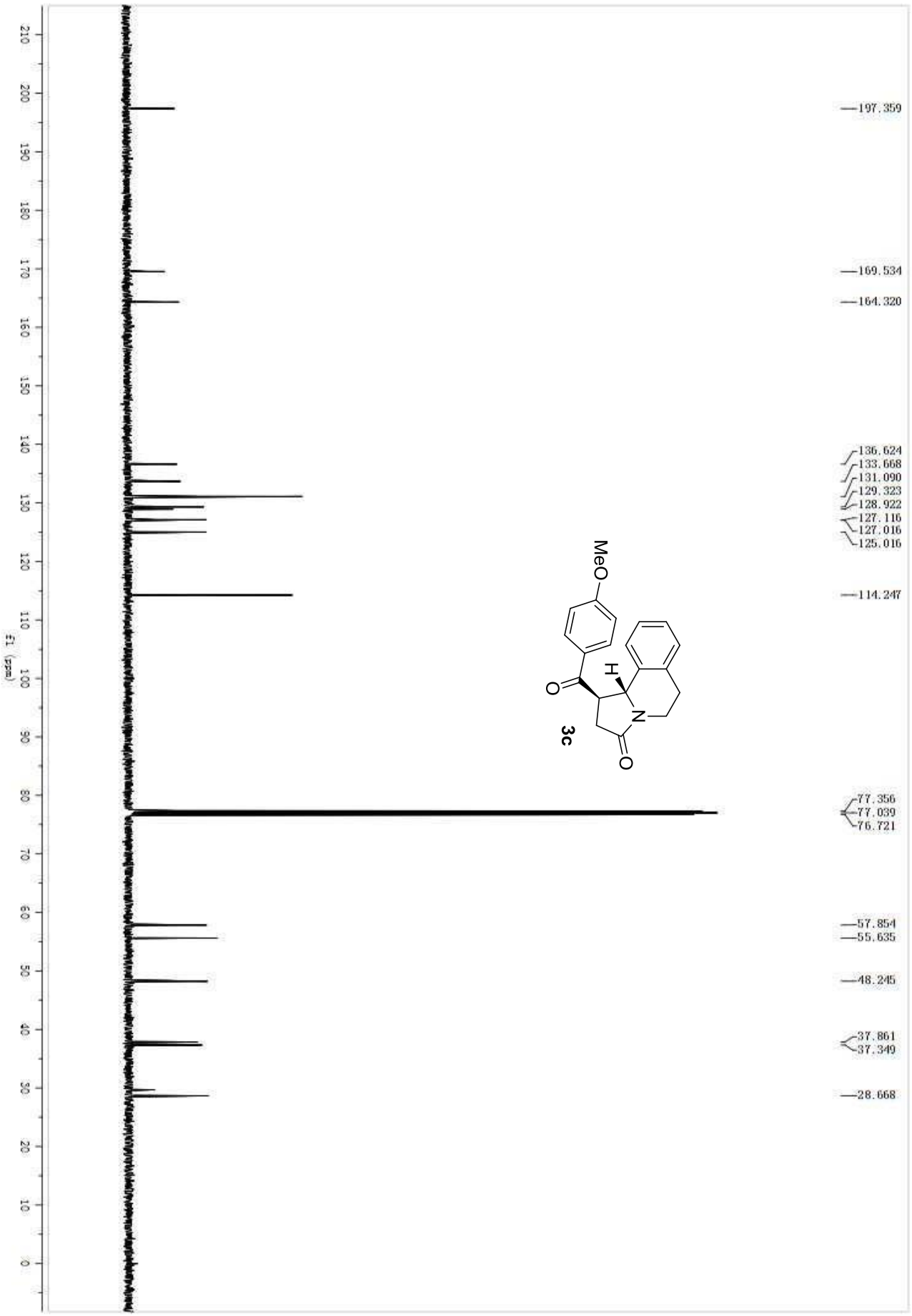
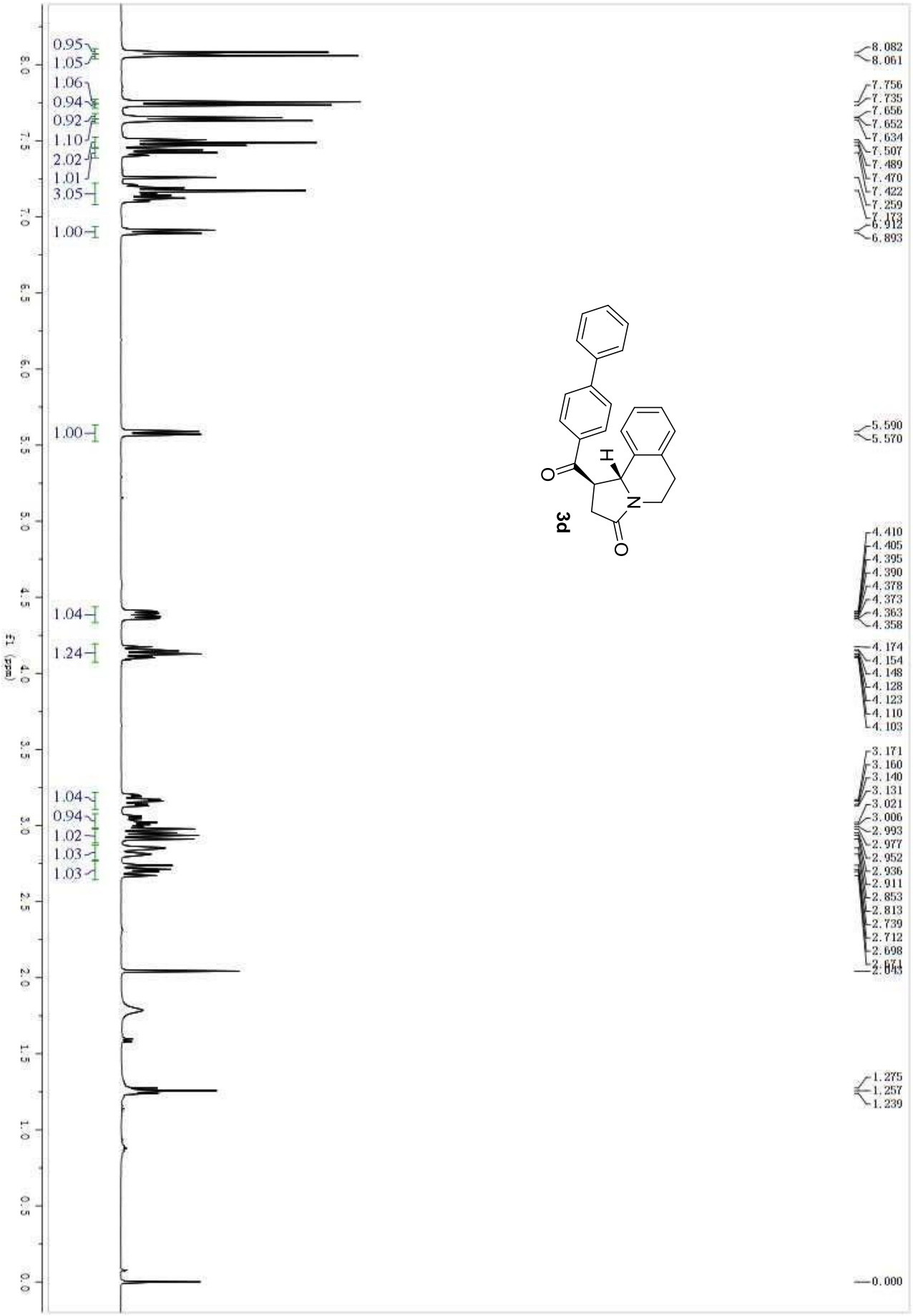
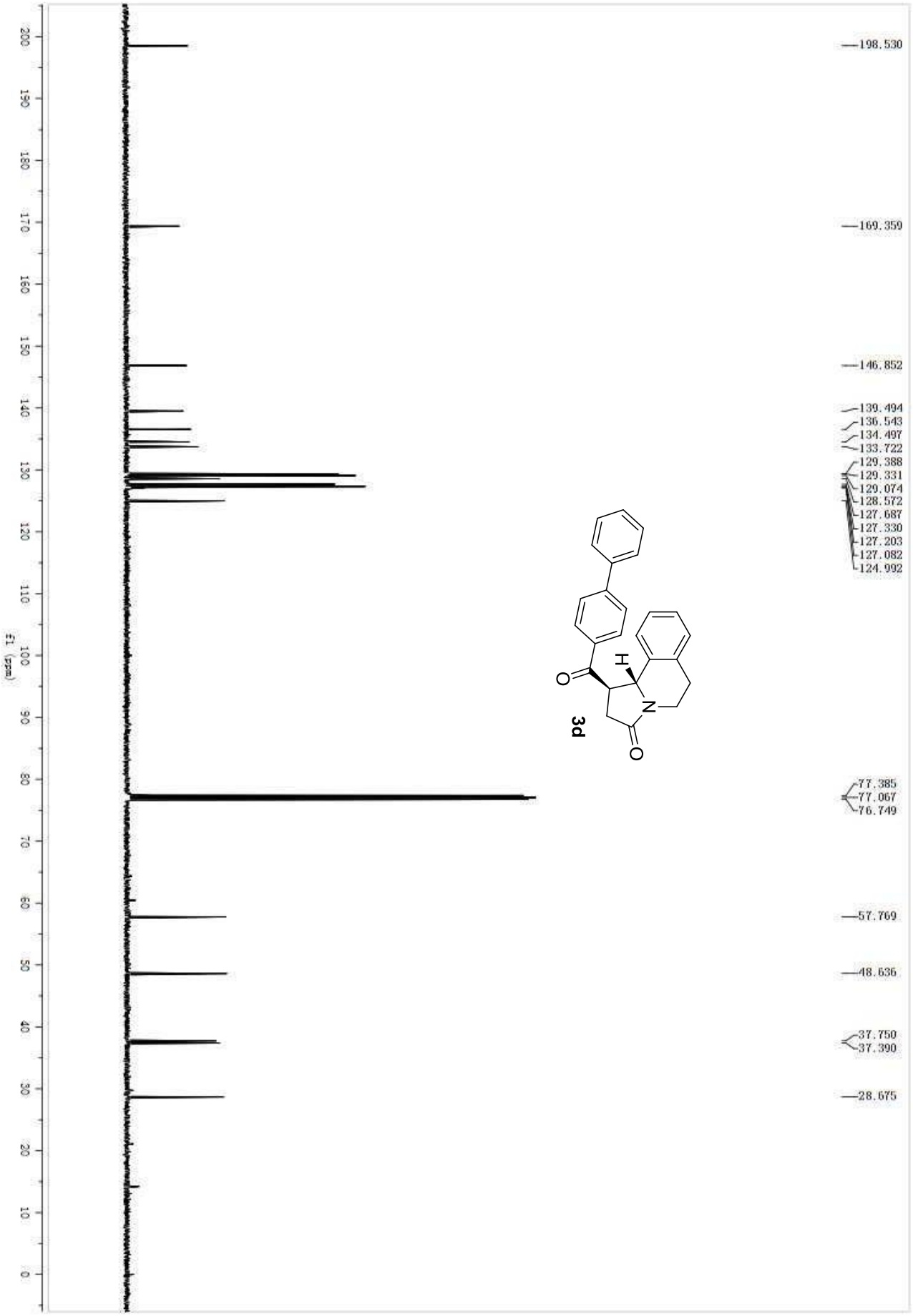
136.584
133.685
133.405
129.766
129.337
128.837
127.142
127.032
124.998
77.353
77.035
76.718
57.751
48.460
37.778
37.360
28.659
21.751
Me
H
O
N
O
3b
F1 (ppm)


1.02
0.99
3.11
1.03
0.96
1.00
1.00
1.03
1.09
3.14
1.03
1.11
2.10
1.08
7.989
7.967
7.265
7.198
7.180
7.162
7.144
7.126
7.121
7.106
7.090
7.085
7.002
6.980
6.878
6.858
5.549
5.529
4.396
4.391
4.381
4.376
4.364
4.359
4.349
4.344
4.089
4.068
4.063
4.042
4.038
4.017
3.901
3.187
3.177
3.158
3.147
3.127
3.117
3.047
3.032
3.019
3.007
2.992
2.979
2.964
2.914
2.890
2.873
2.849
2.803
2.709
2.682
2.668
2.641
1.254
0.000
MeO
O
H
N
O
3c
f1 (ppm)


197.359
169.534
164.320
136.624
133.668
131.090
129.323
128.922
127.116
127.016
125.016
114.247
77.356
77.039
76.721
57.854
55.635
48.245
37.861
37.349
28.668
MeO
O
H
N
O
3c
f1 (ppm)


0.95
1.05
1.06
0.94
0.92
1.10
2.02
1.01
3.05
1.00
1.00
1.04
1.24
1.04
0.94
1.02
1.03
1.03
8.082
8.061
7.756
7.735
7.656
7.652
7.634
7.507
7.489
7.470
7.422
7.259
7.173
6.912
6.893
5.590
5.570
4.410
4.405
4.395
4.390
4.378
4.373
4.363
4.358
4.174
4.154
4.148
4.128
4.123
4.110
4.103
3.171
3.160
3.140
3.131
3.021
3.006
2.993
2.977
2.952
2.936
2.911
2.853
2.813
2.739
2.712
2.698
1.275
1.257
1.239
0.000
f1 (ppm)
3d


198.530
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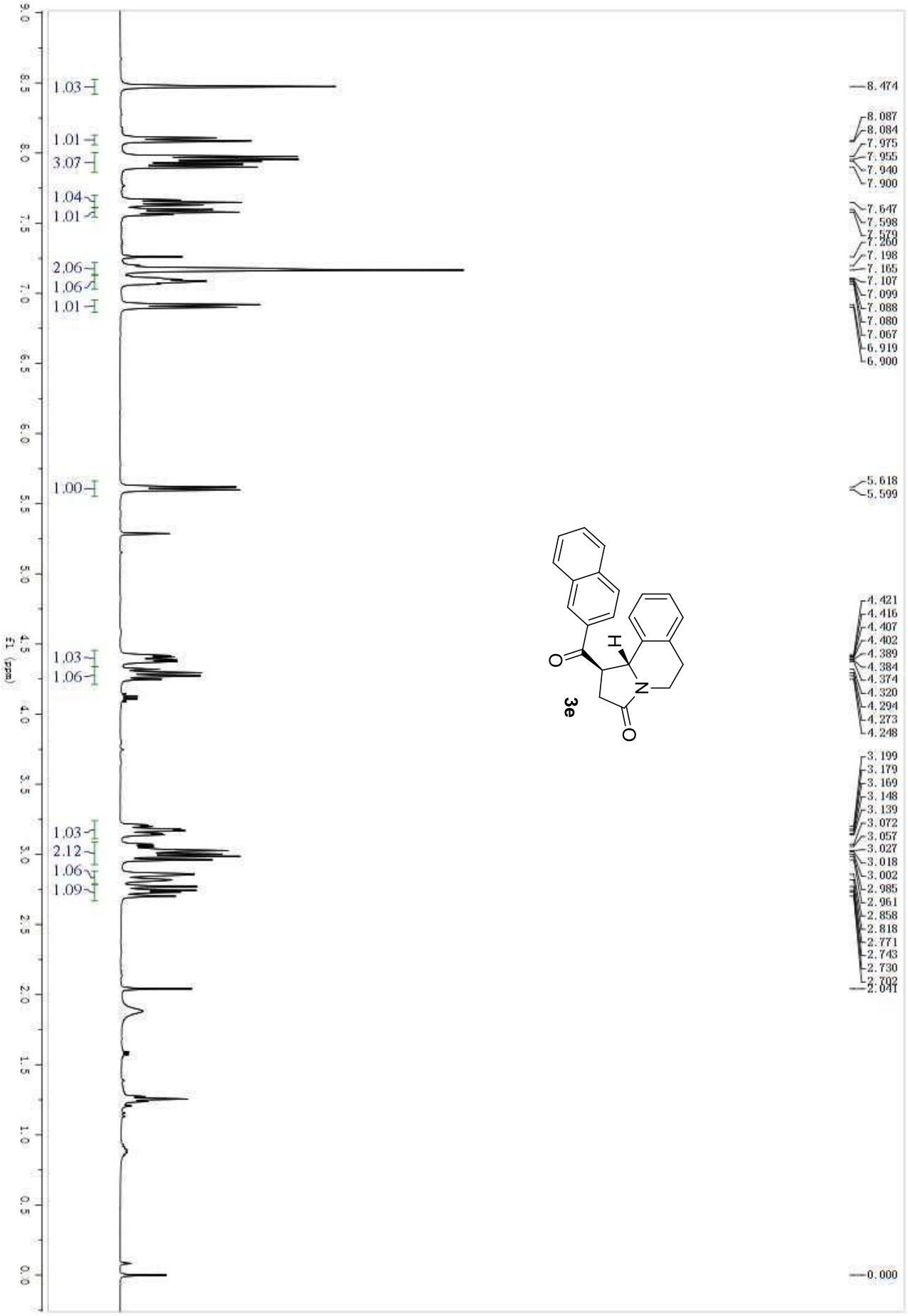
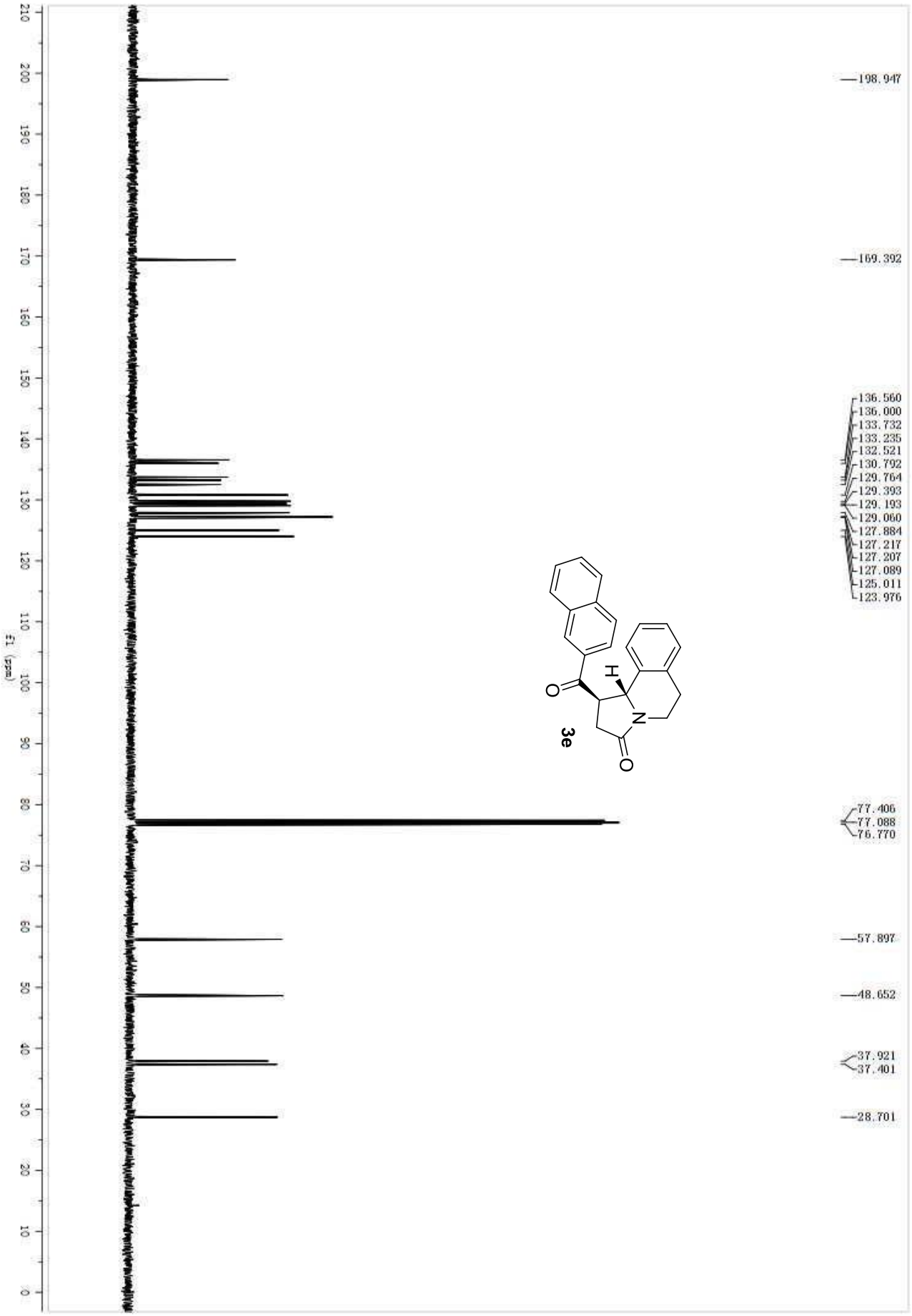
136.543
134.497
133.722
129.388
129.331
129.074
128.572
127.687
127.330
127.203
127.082
124.992
77.385
77.067
76.749
57.769
48.636
37.750
37.390
28.675
f1 (ppm)
3d


1.03
1.01
3.07
1.04
1.01
2.06
1.06
1.01
1.00
1.03
1.06
1.03
2.12
1.06
1.09
8.474
8.087
8.084
7.975
7.955
7.940
7.900
7.647
7.598
7.579
7.260
7.198
7.165
7.107
7.099
7.088
7.080
7.067
6.919
6.900
5.618
5.599
4.421
4.416
4.407
4.402
4.389
4.384
4.374
4.320
4.294
4.273
4.248
3.199
3.179
3.169
3.148
3.139
3.072
3.057
3.027
3.018
3.002
2.985
2.961
2.858
2.818
2.771
2.743
2.730
2.702
2.041
0.000
f1 (ppm)
H
O
N
O
3e


198.947
169.392
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136.000
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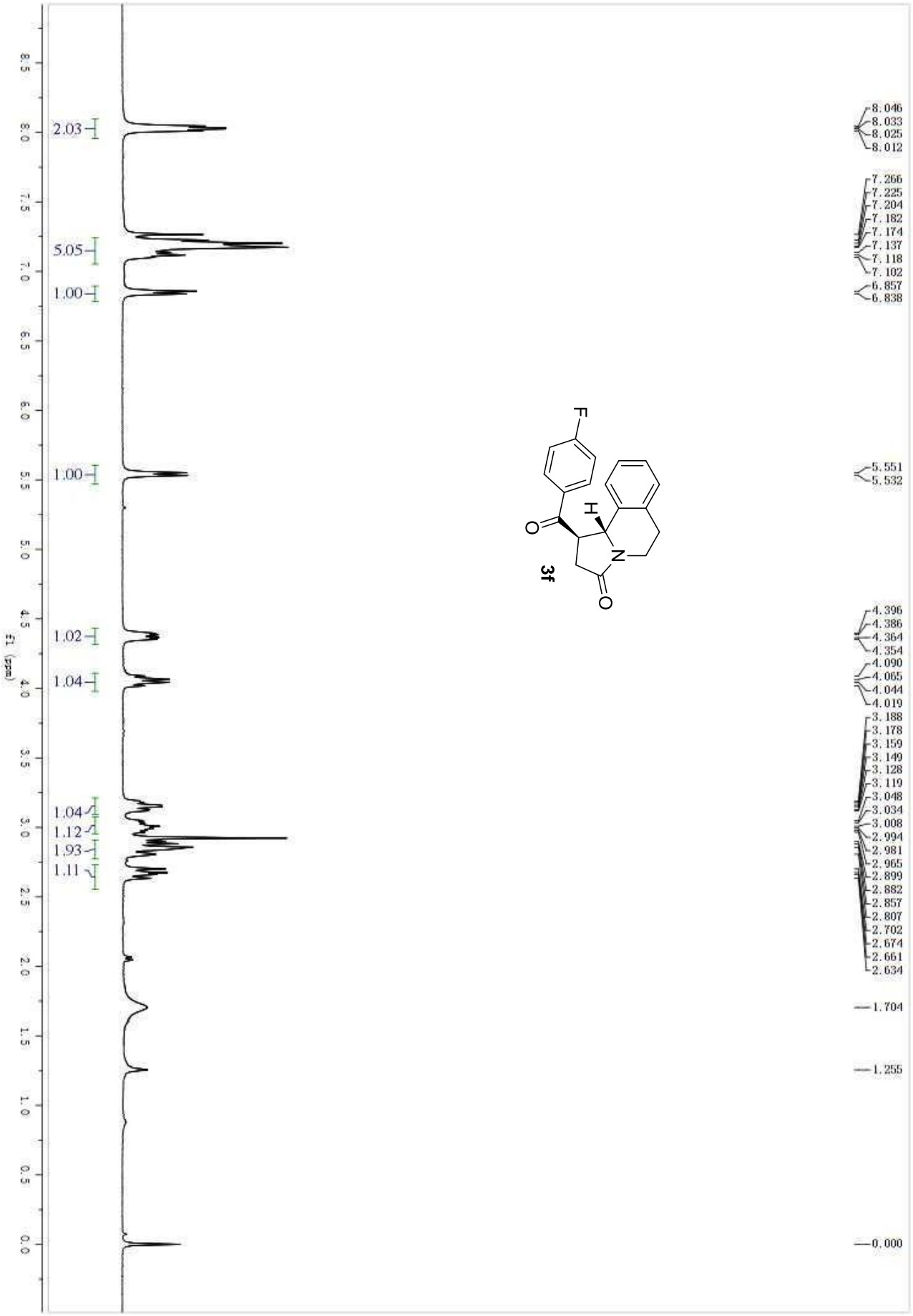
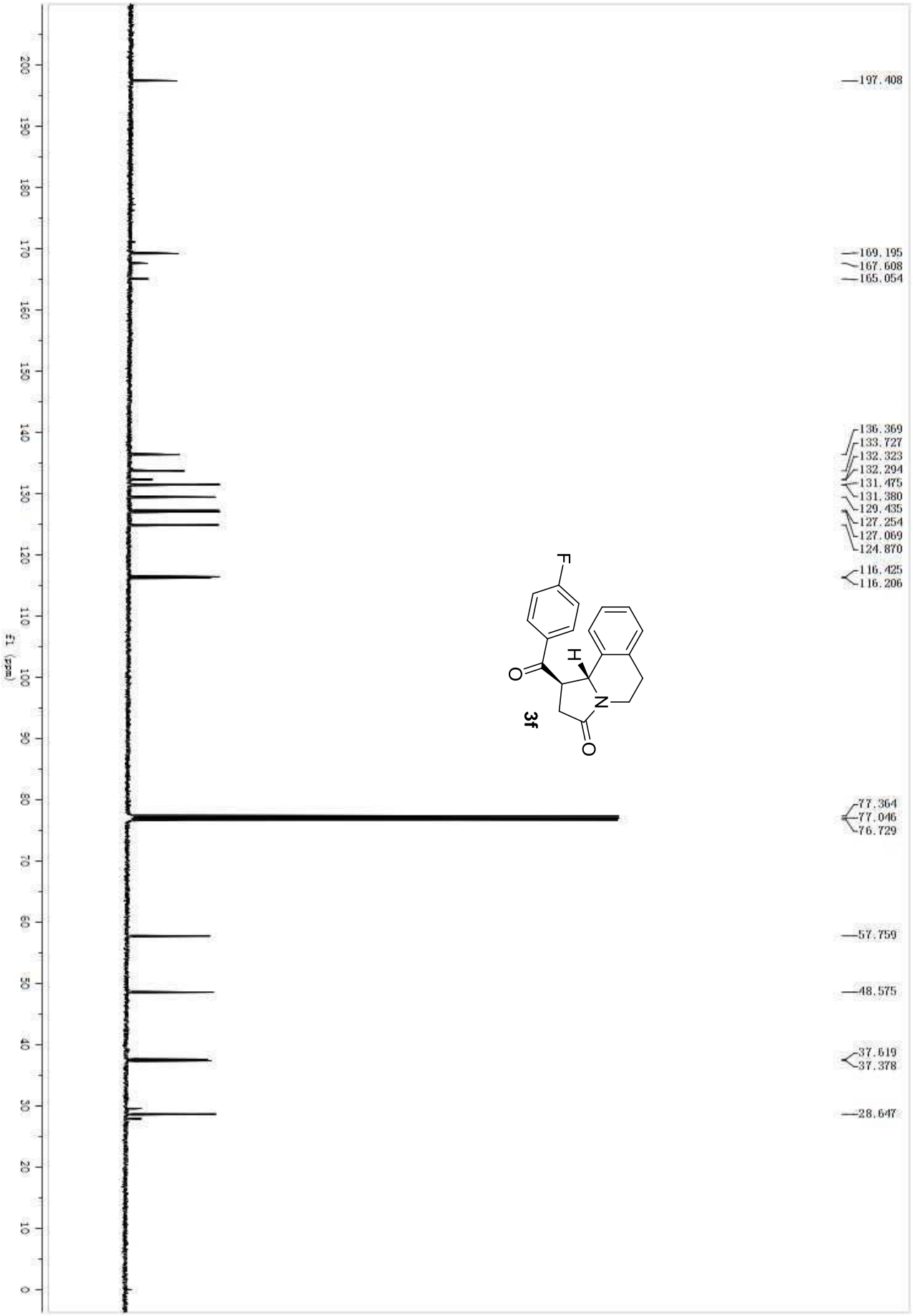
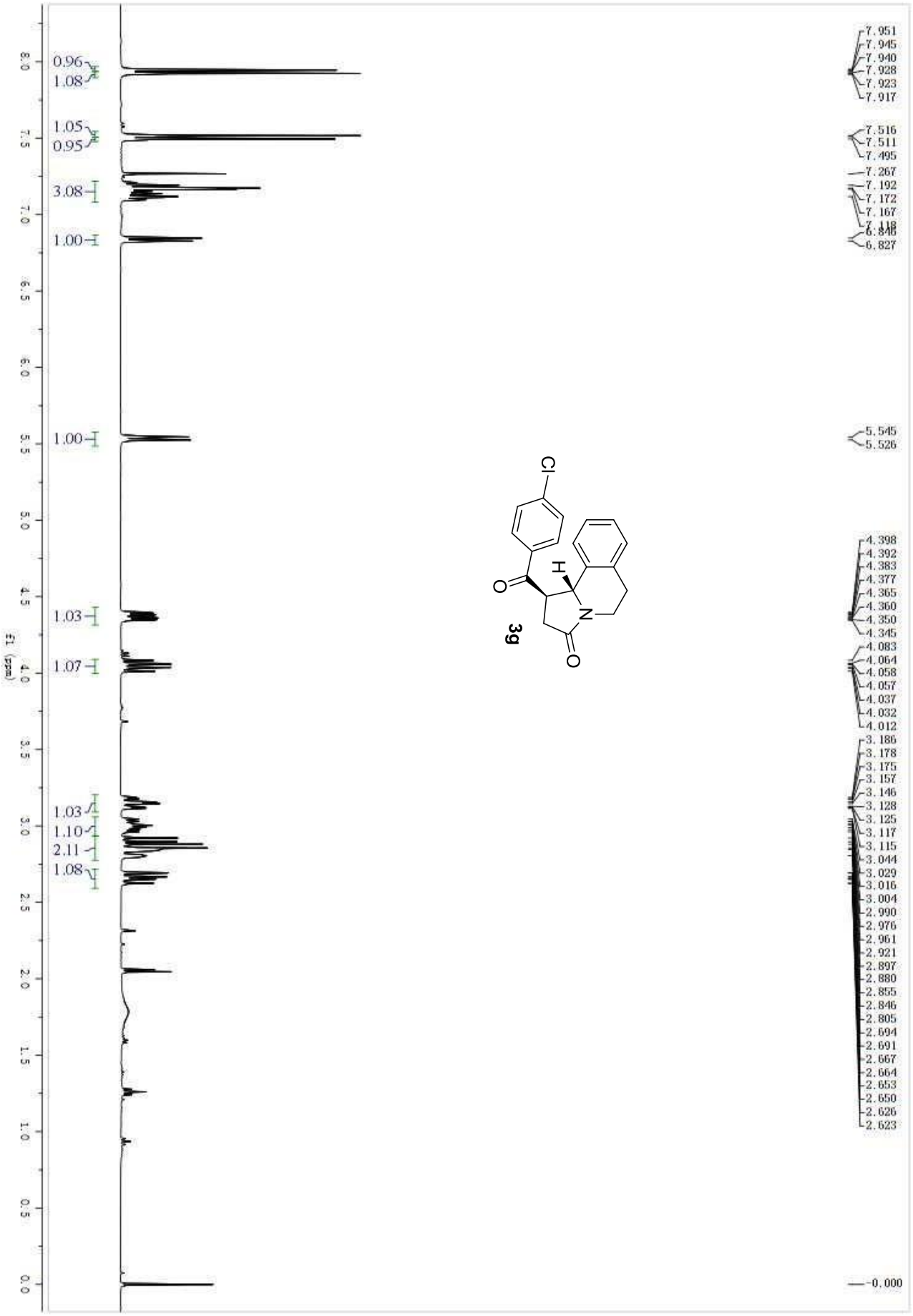
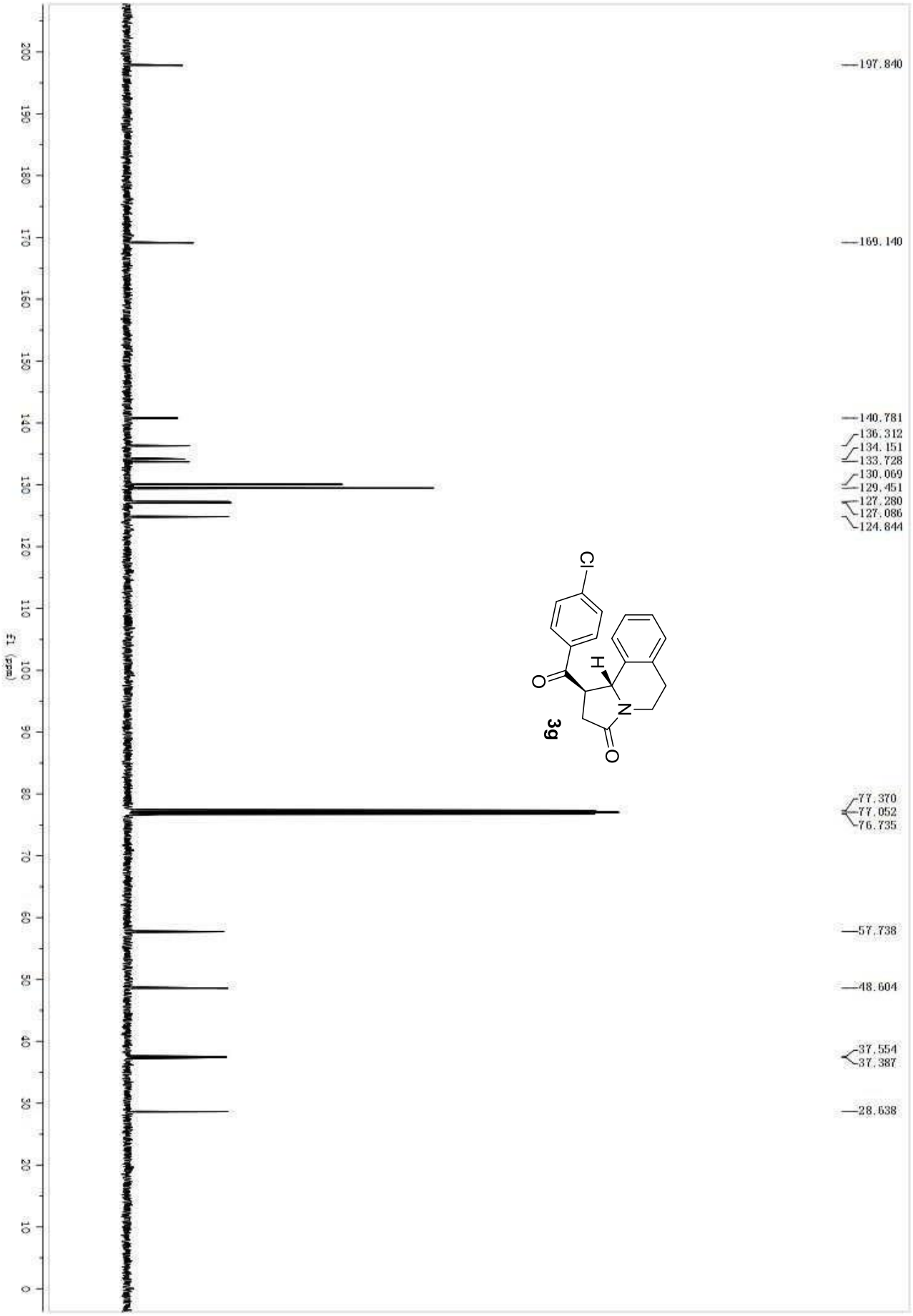
133.235
132.521
130.792
129.764
129.393
129.193
129.060
127.884
127.217
127.207
127.089
125.011
123.976
77.406
77.088
76.770
57.897
48.652
37.921
37.401
28.701
f1 (ppm)
3e


2.03
5.05
1.00
1.00
1.02
1.04
1.04
1.12
1.93
1.11
f1 (ppm)
8.046
8.033
8.025
8.012
7.266
7.225
7.204
7.182
7.174
7.137
7.118
7.102
6.857
6.838
5.551
5.532
4.396
4.386
4.364
4.354
4.090
4.065
4.044
4.019
3.188
3.178
3.159
3.149
3.128
3.119
3.048
3.034
3.008
2.994
2.981
2.965
2.899
2.882
2.857
2.807
2.702
2.674
2.661
2.634
1.704
1.255
0.000
F
O
H
N
O
3f


197.408
169.195
167.608
165.054
136.369
133.727
132.323
132.294
131.475
131.380
129.435
127.254
127.069
124.870
116.425
116.206
77.364
77.046
76.729
57.759
48.575
37.619
37.378
28.647
F
H
O
N
O
3f
f1 (ppm)


7.951
7.945
7.940
7.928
7.923
7.917
7.516
7.511
7.495
7.267
7.192
7.172
7.167
6.846
6.827
5.545
5.526
4.398
4.392
4.383
4.377
4.365
4.360
4.350
4.345
4.083
4.064
4.058
4.057
4.037
4.032
4.012
3.186
3.178
3.175
3.157
3.146
3.128
3.125
3.117
3.115
3.044
3.029
3.016
3.004
2.990
2.976
2.961
2.921
2.897
2.880
2.855
2.846
2.805
2.694
2.691
2.667
2.664
2.653
2.650
2.626
2.623
0.96
1.08
1.05
0.95
3.08
1.00
1.00
1.03
1.07
1.03
1.10
2.11
1.08
-0.000
f1 (ppm)
Cl
O
H
N
O
3g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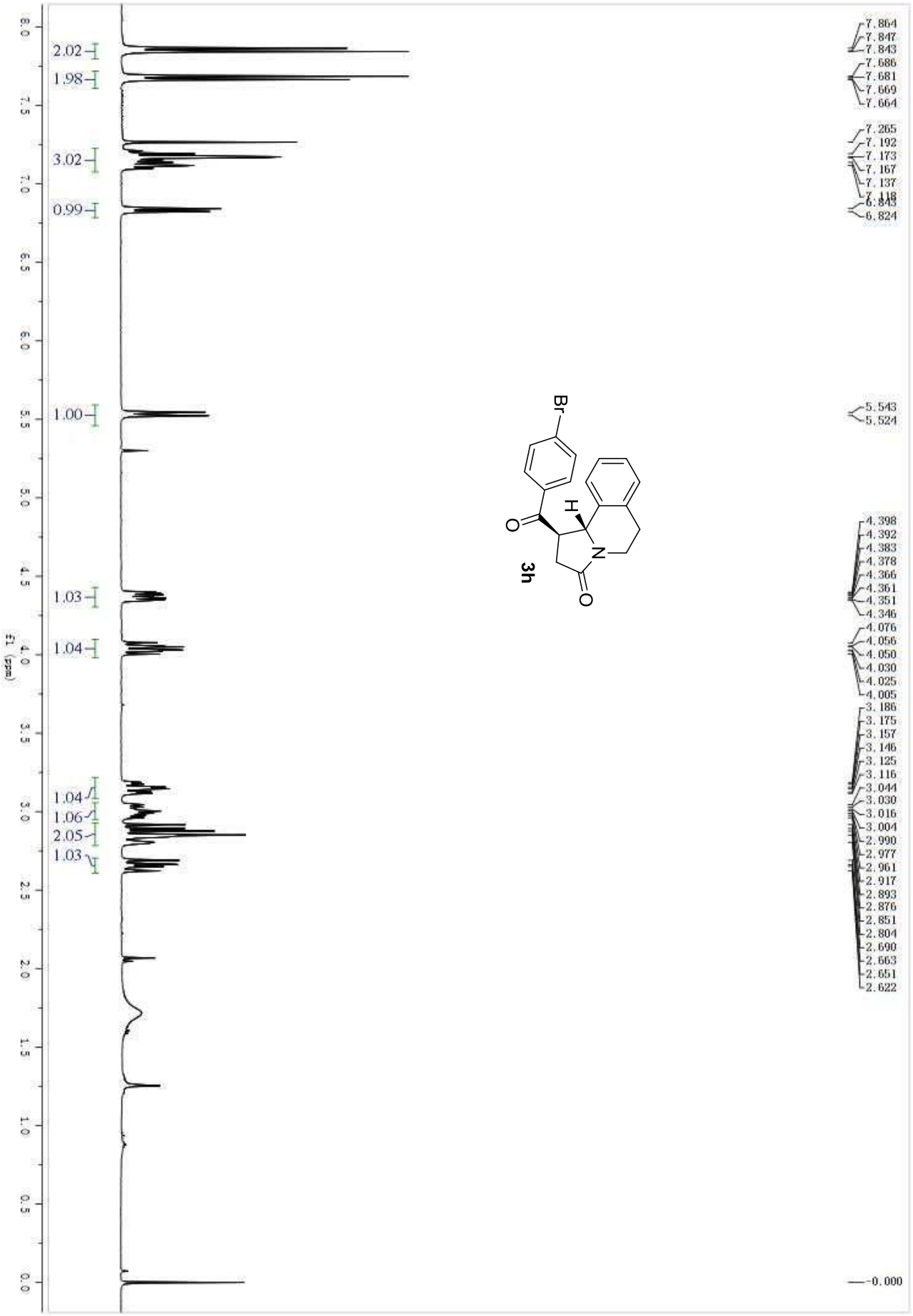
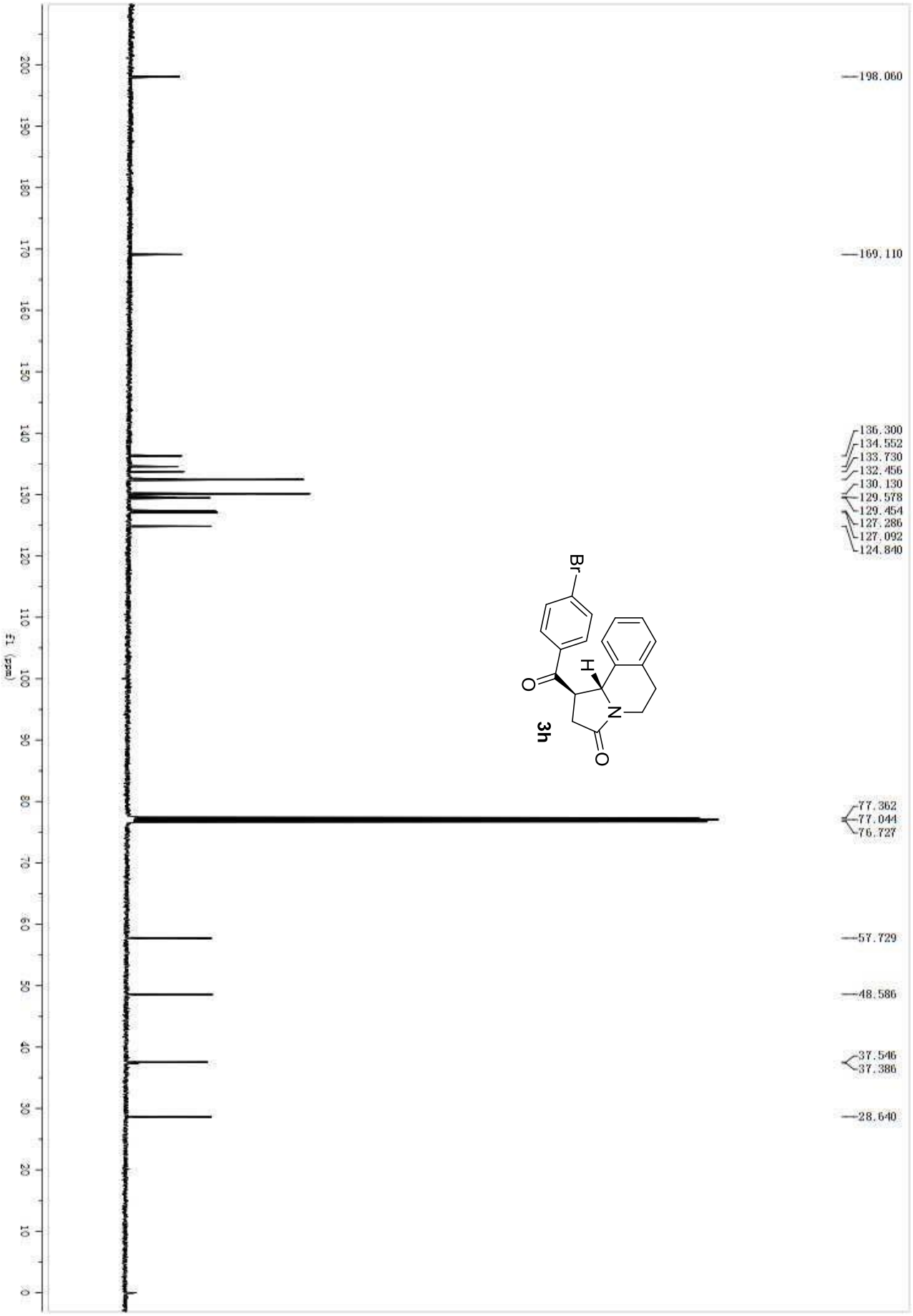
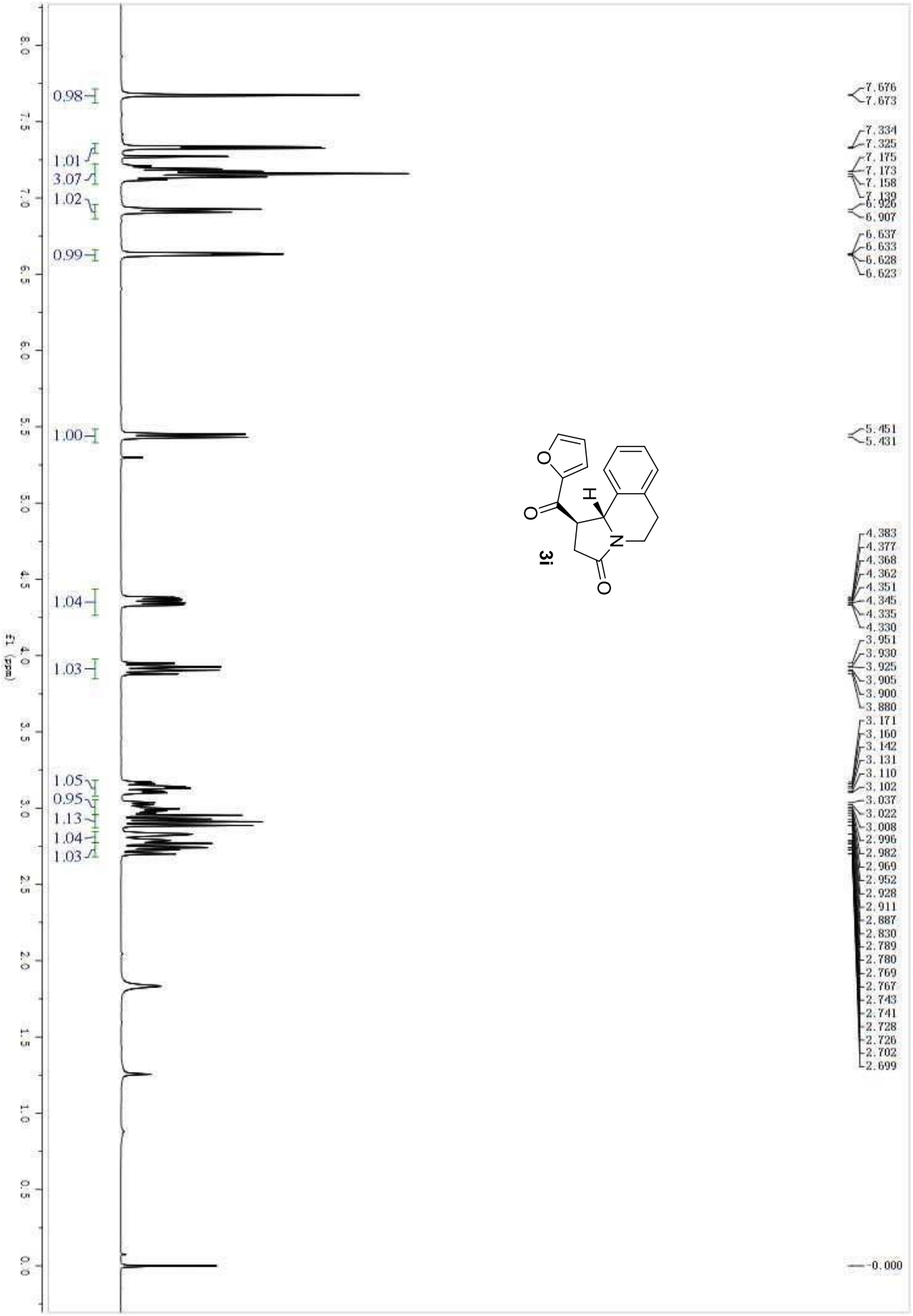
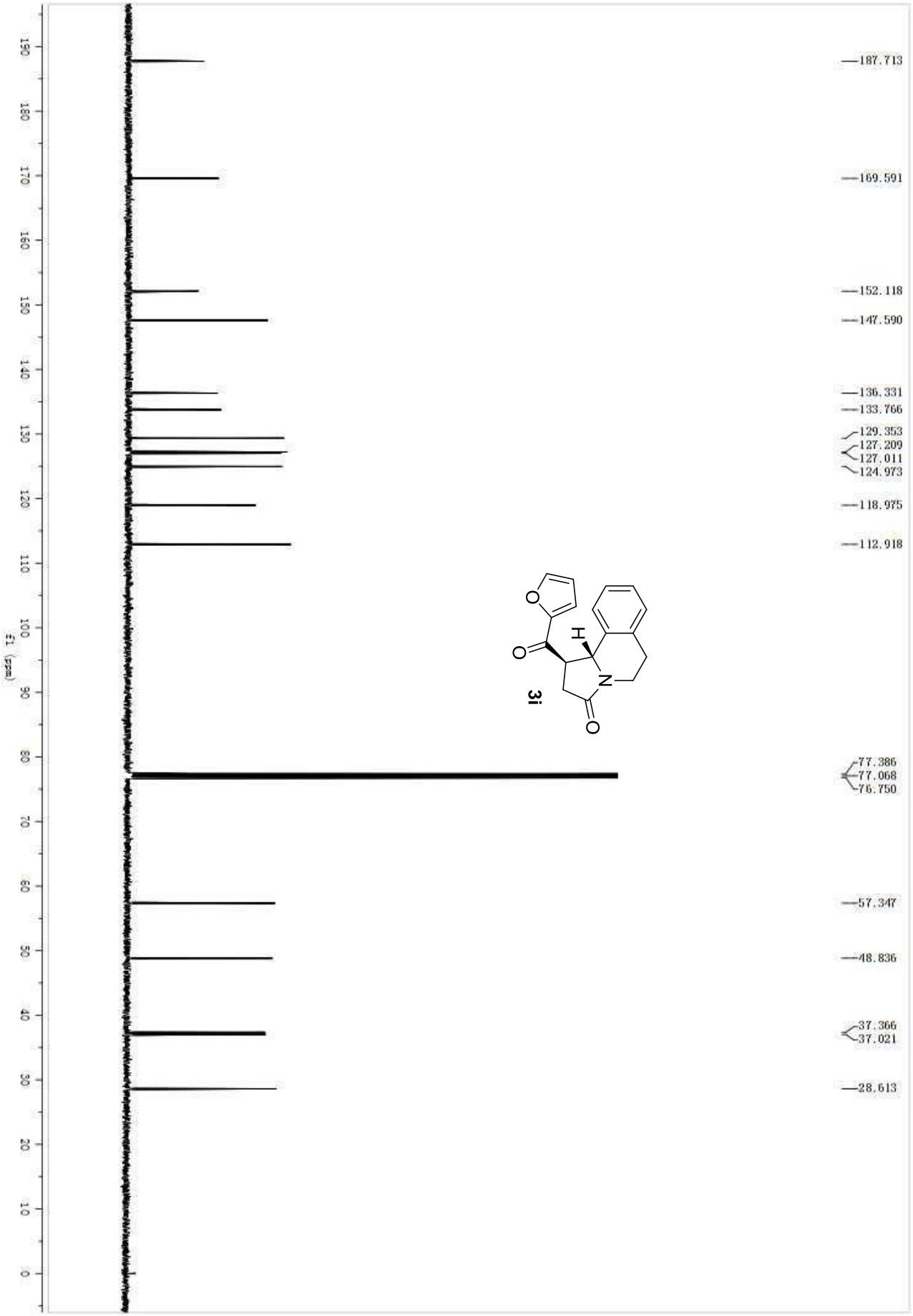
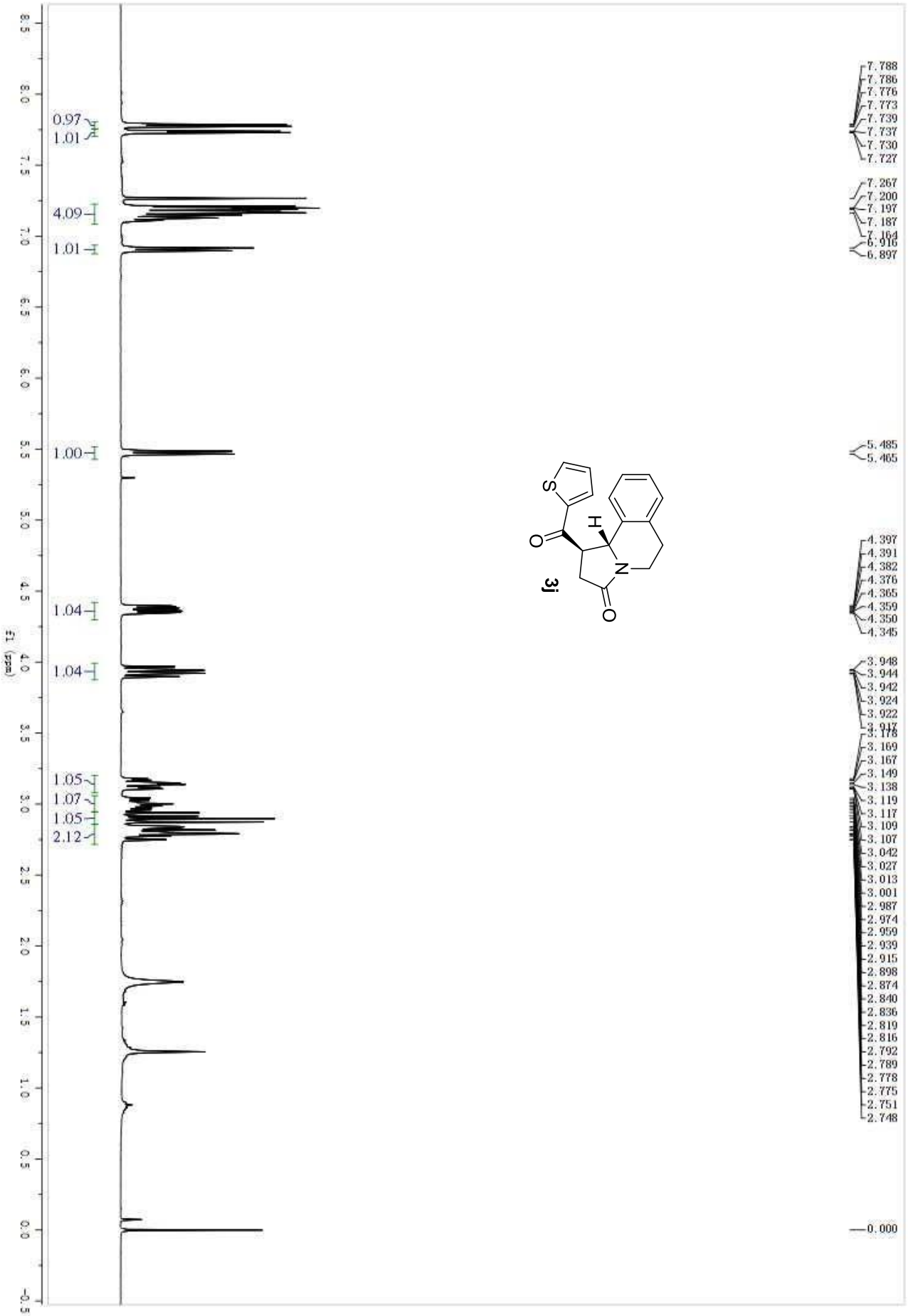
169.140
140.781
136.312
134.151
133.728
130.069
129.451
127.280
127.086
124.844
77.370
77.052
76.735
57.738
48.604
37.554
37.387
28.638
f1 (ppm)
Cl
O
H
N
O
3g

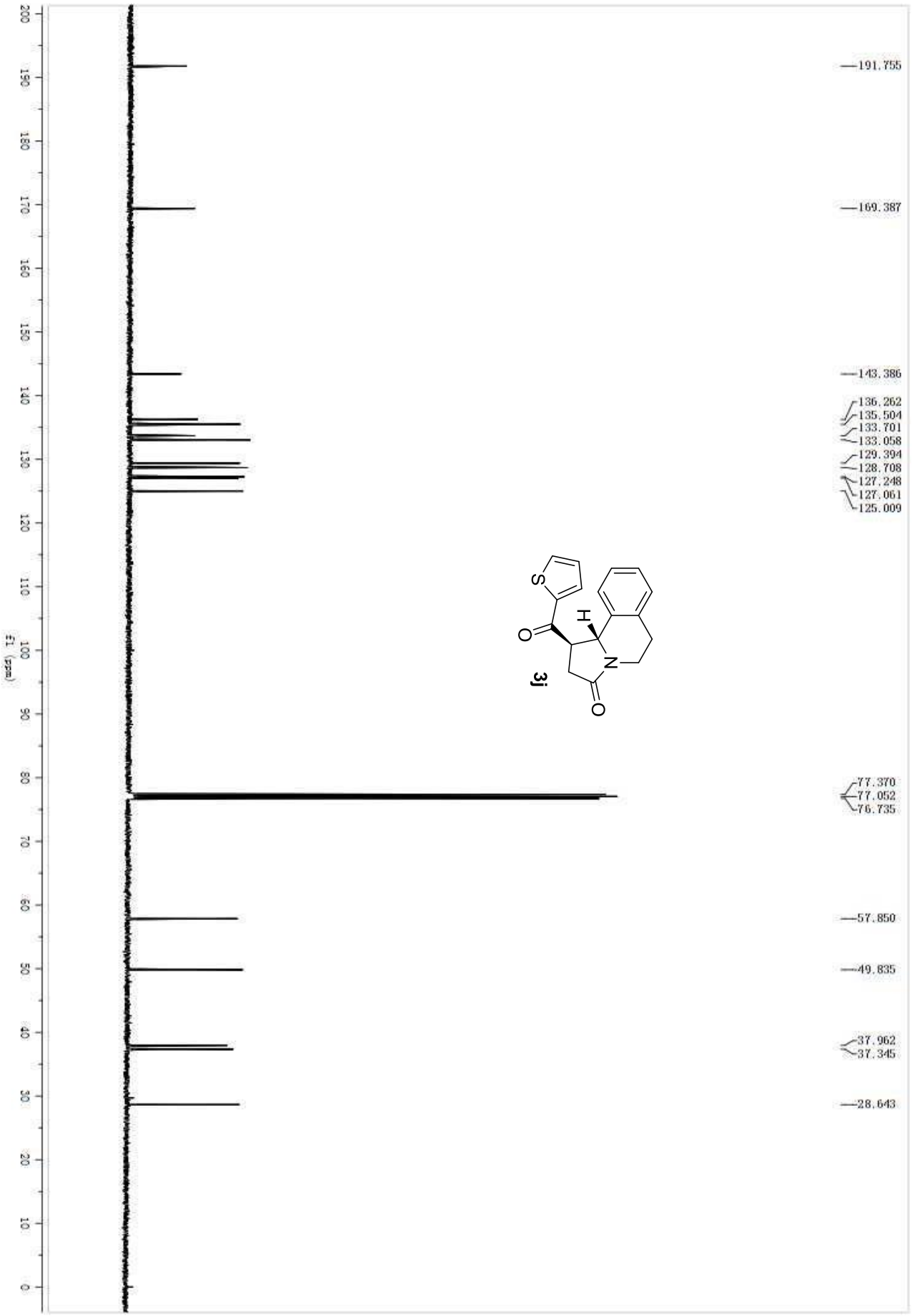

7.864
7.847
7.843
7.686
7.681
7.669
7.664
7.265
7.192
7.173
7.167
7.137
7.118
6.843
6.824
5.543
5.524
4.398
4.392
4.383
4.378
4.366
4.361
4.351
4.346
4.076
4.056
4.050
4.030
4.025
4.005
3.186
3.175
3.157
3.146
3.125
3.116
3.044
3.030
3.016
3.004
2.990
2.977
2.961
2.917
2.893
2.876
2.851
2.804
2.690
2.663
2.651
2.622
-0.000
2.02
1.98
3.02
0.99
1.00
1.03
1.04
1.04
1.06
2.05
1.03
f1 (ppm)
Br
O
H
N
O
3h

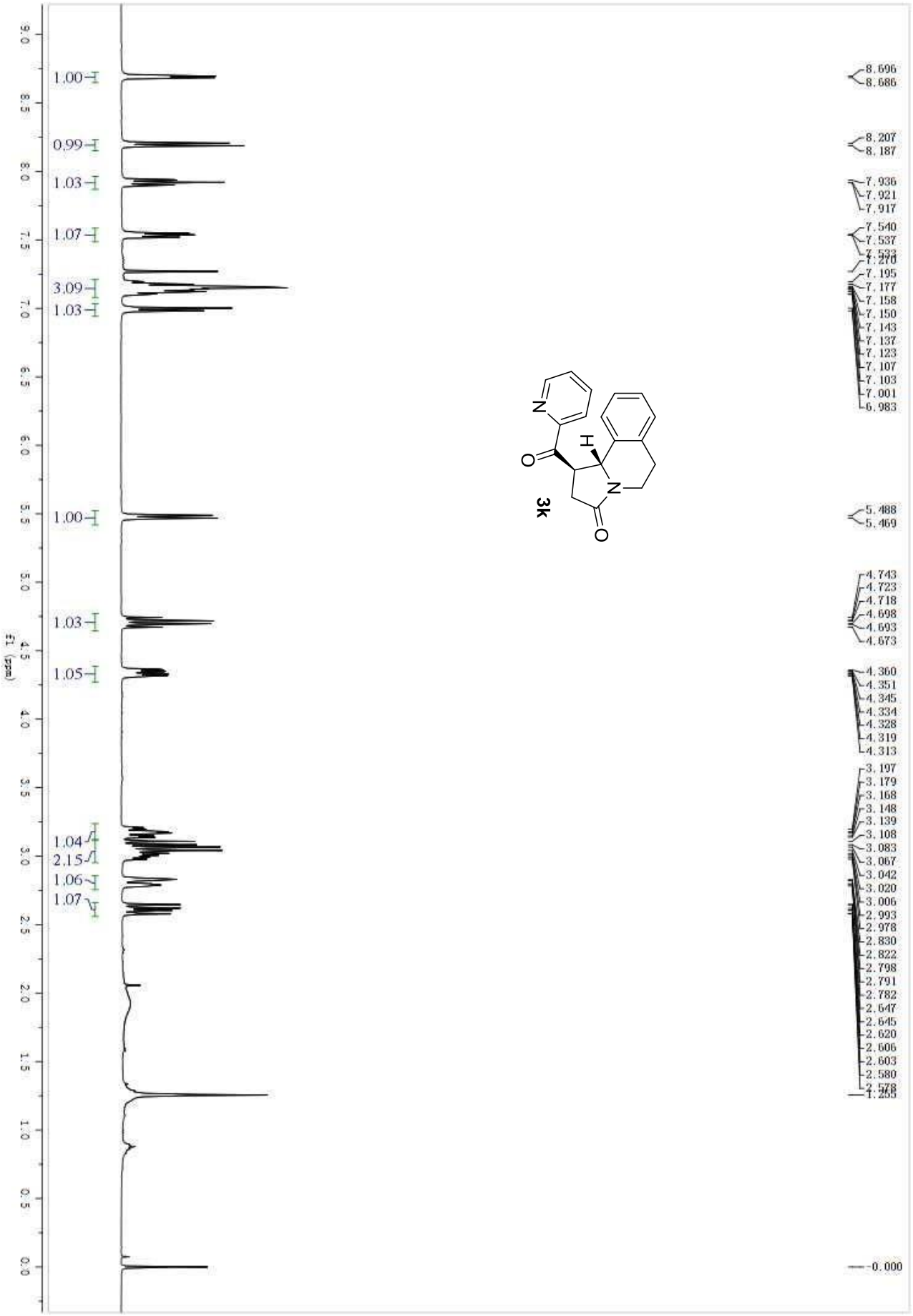

198.060
169.110
136.300
134.552
133.730
132.456
130.130
129.578
129.454
127.286
127.092
124.840
77.362
77.044
76.727
57.729
48.586
37.546
37.386
28.640
f1 (ppm)
Br
O
H
N
O
3h

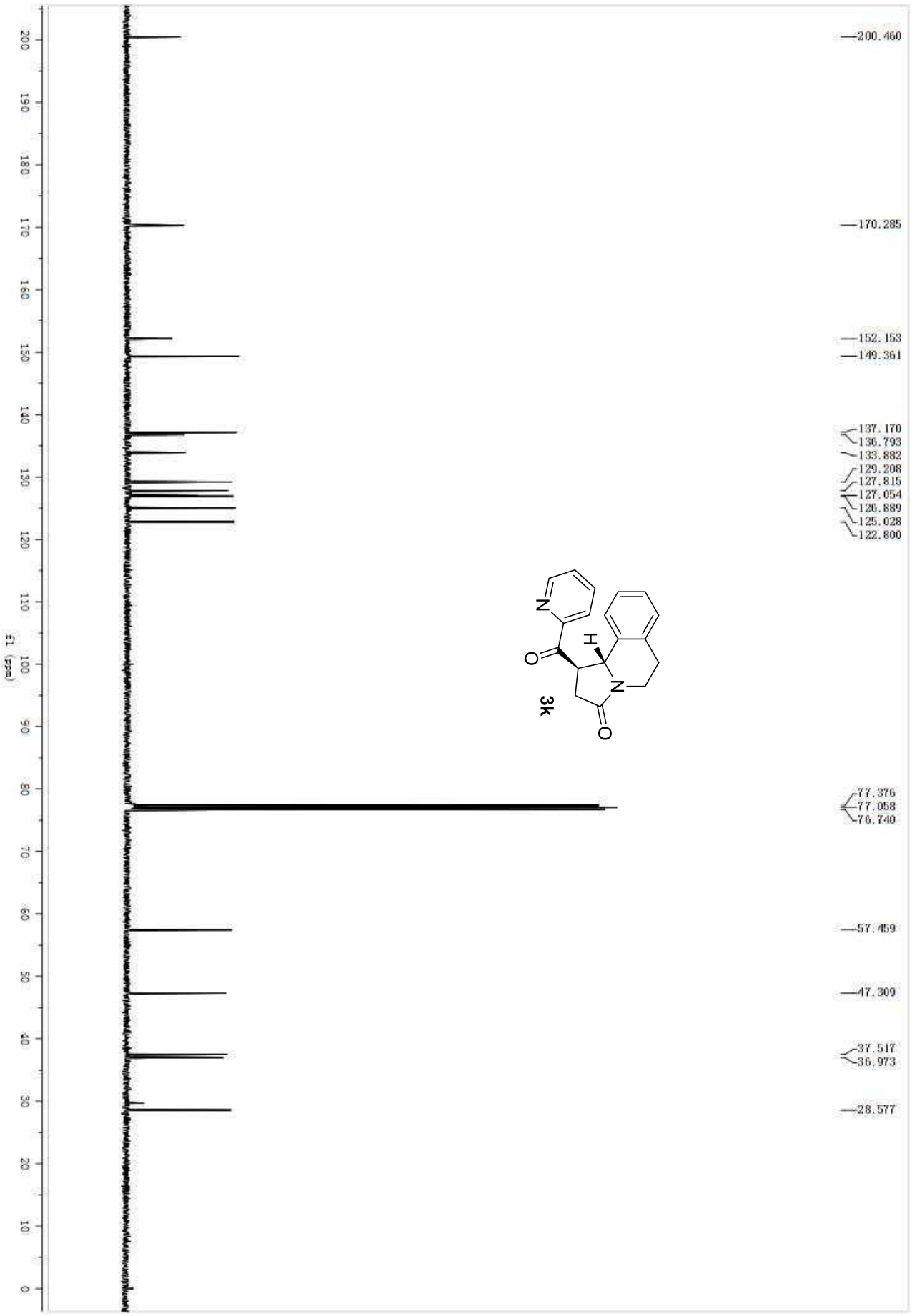

0.98
1.01
3.07
1.02
0.99
1.00
1.04
1.03
1.05
0.95
1.13
1.04
1.03
f1 (ppm)
7.676
7.673
7.334
7.325
7.175
7.173
7.158
7.139
6.926
6.907
6.637
6.633
6.628
6.623
5.451
5.431
4.383
4.377
4.368
4.362
4.351
4.345
4.335
4.330
3.951
3.930
3.925
3.905
3.900
3.880
3.171
3.160
3.142
3.131
3.110
3.102
3.037
3.022
3.008
2.996
2.982
2.969
2.952
2.928
2.911
2.887
2.830
2.789
2.780
2.769
2.767
2.743
2.741
2.728
2.726
2.702
2.699
0.000
O
O
H
N
O
3i

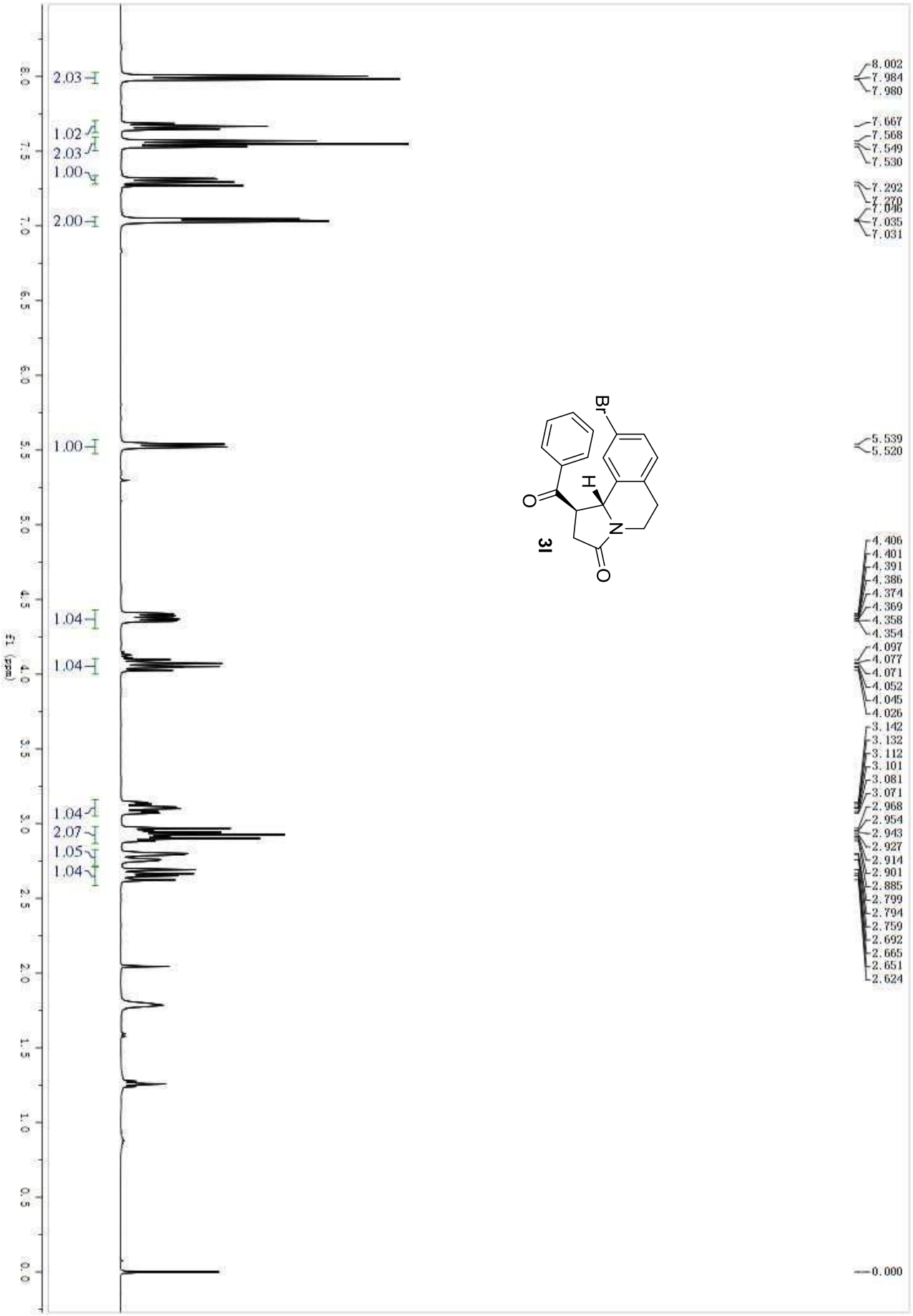

187.713
169.591
152.118
147.590
136.331
133.766
129.353
127.209
127.011
124.973
118.975
112.918
77.386
77.068
76.750
57.347
48.836
37.366
37.021
28.613
f1 (ppm)
3i

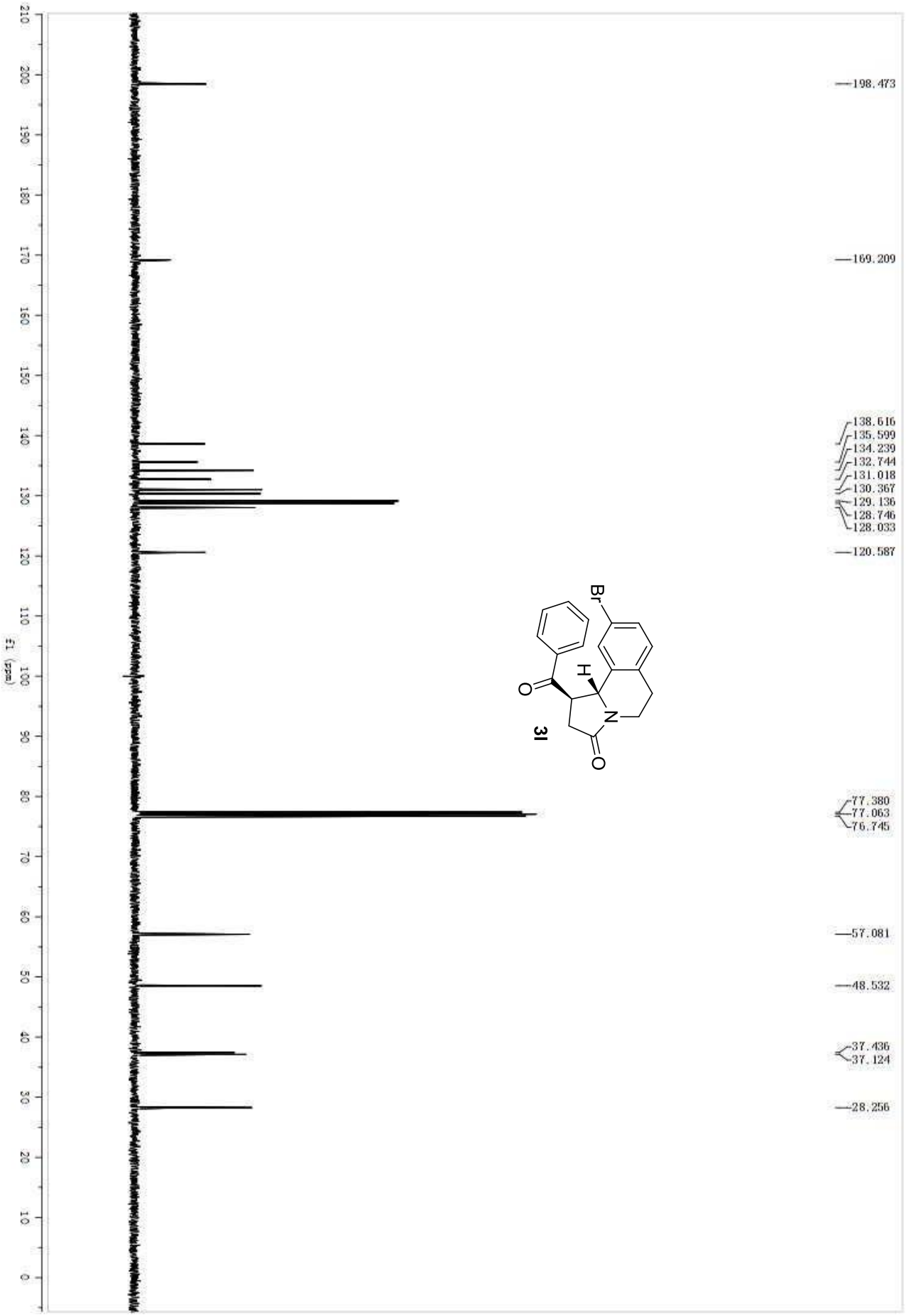

7.788
7.786
7.776
7.773
7.739
7.737
7.730
7.727
7.267
7.200
7.197
7.187
7.164
6.916
6.897
5.485
5.465
4.397
4.391
4.382
4.376
4.365
4.359
4.350
4.345
3.948
3.944
3.942
3.924
3.922
3.178
3.169
3.167
3.149
3.138
3.119
3.117
3.109
3.107
3.042
3.027
3.013
3.001
2.987
2.974
2.959
2.939
2.915
2.898
2.874
2.840
2.836
2.819
2.816
2.792
2.789
2.778
2.775
2.751
2.748
0.000
0.97
1.01
4.09
1.01
1.00
1.04
1.04
1.05
1.07
1.05
2.12
f1 (ppm)
3j

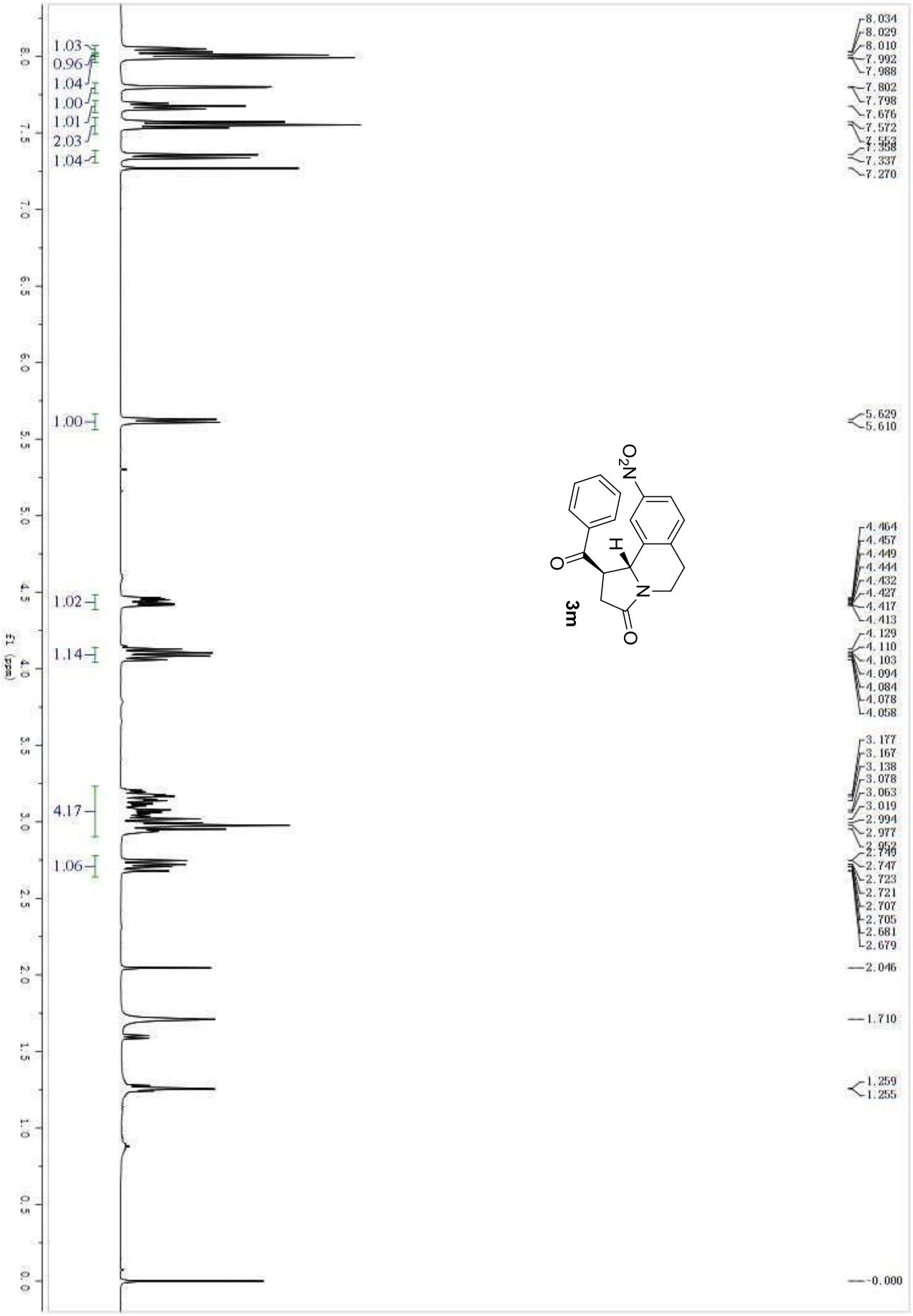

191.755
169.387
143.386
136.262
135.504
133.701
133.058
129.394
128.708
127.248
127.061
125.009
77.370
77.052
76.735
57.850
49.835
37.962
37.345
28.643
f1 (ppm)
S
H
O
N
O
3j

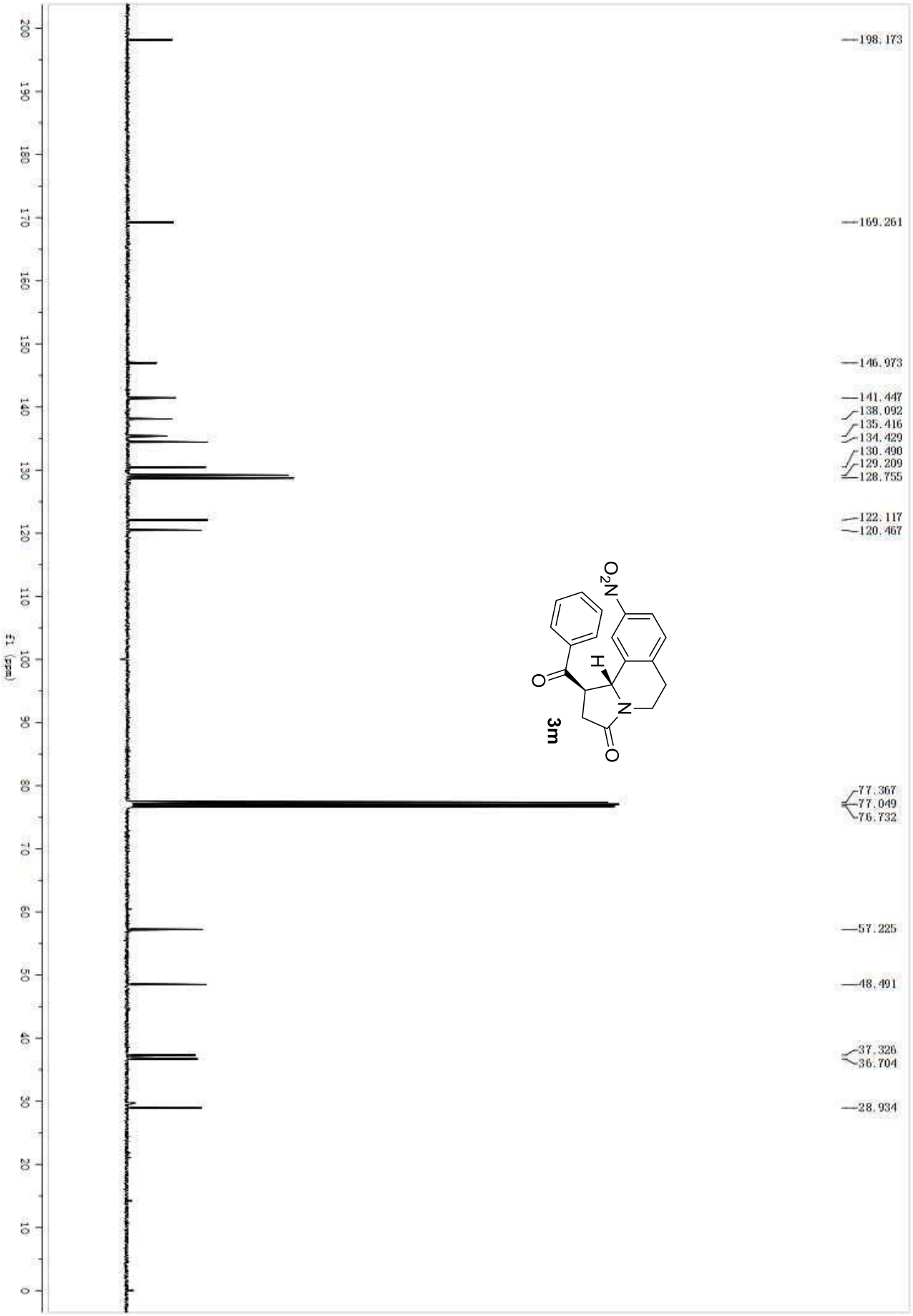

1.00
0.99
1.03
1.07
3.09
1.03
1.00
1.03
1.05
1.04
2.15
1.06
1.07
f1 (ppm)
8.696
8.686
8.207
8.187
7.936
7.921
7.917
7.540
7.537
7.270
7.195
7.177
7.158
7.150
7.143
7.137
7.123
7.107
7.103
7.001
6.983
5.488
5.469
4.743
4.723
4.718
4.698
4.693
4.673
4.360
4.351
4.345
4.334
4.328
4.319
4.313
3.197
3.179
3.168
3.148
3.139
3.108
3.083
3.067
3.042
3.020
3.006
2.993
2.978
2.830
2.822
2.798
2.791
2.782
2.647
2.645
2.620
2.606
2.603
2.580
2.578
1.255
0.000
3k

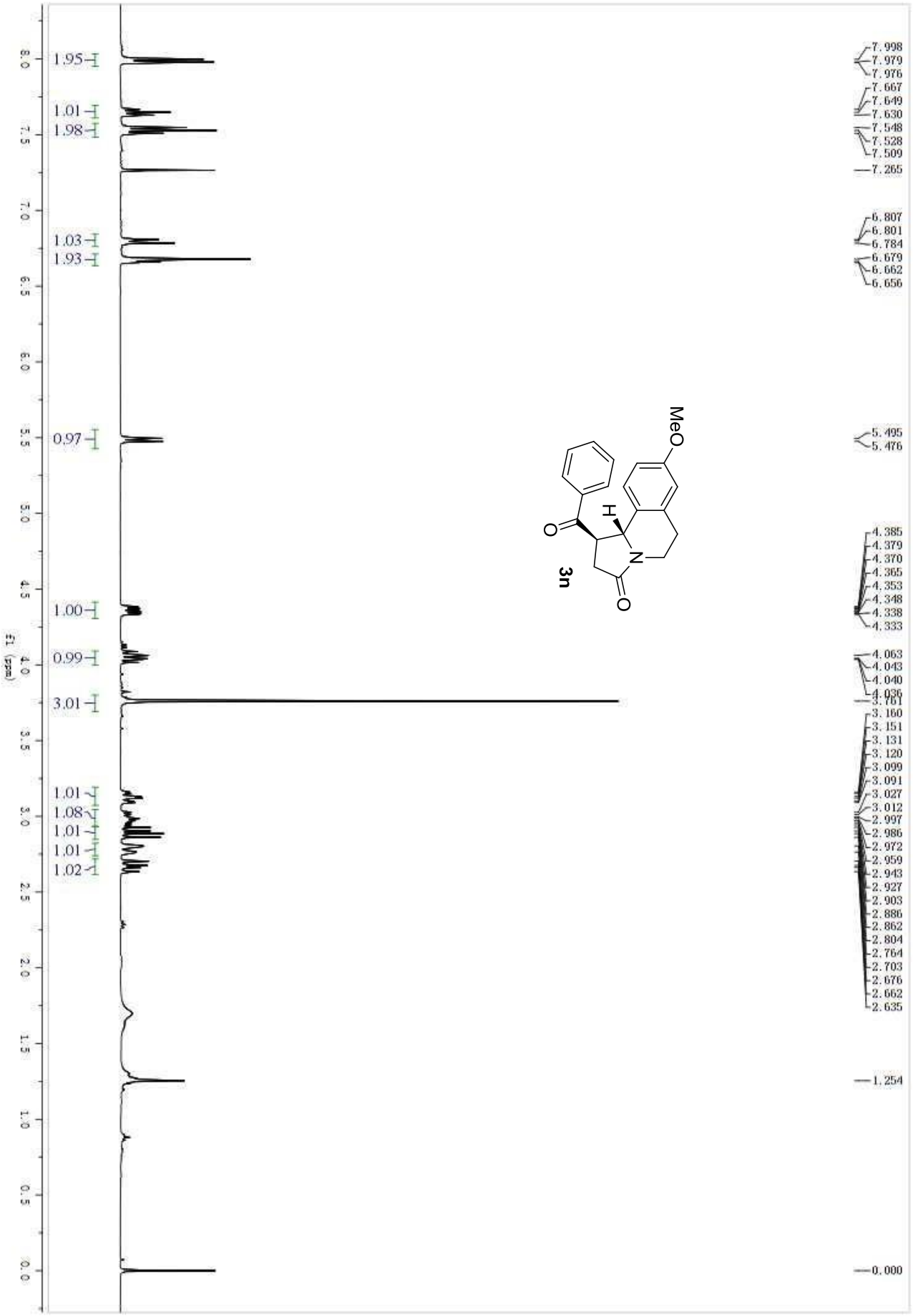

200.460
170.285
152.153
149.361
137.170
136.793
133.882
129.208
127.815
127.054
126.889
125.028
122.800
77.376
77.058
76.740
57.459
47.309
37.517
36.973
28.577
f1 (ppm)
3k

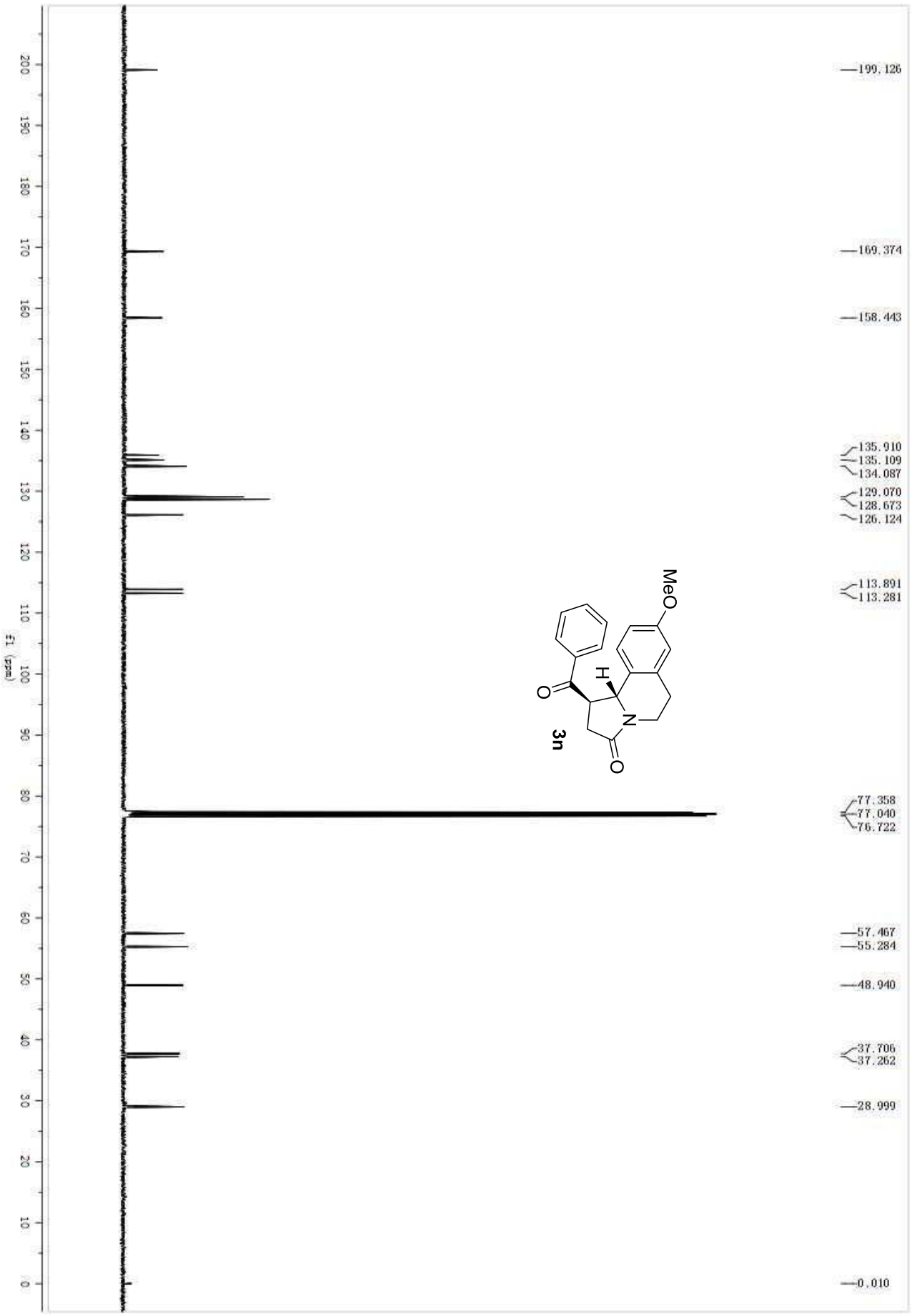

2.03
1.02
2.03
1.00
2.00
1.00
1.04
1.04
1.04
2.07
1.05
1.04
f1 (ppm)
8.002
7.984
7.980
7.667
7.568
7.549
7.530
7.292
7.270
7.046
7.035
7.031
5.539
5.520
4.406
4.401
4.391
4.386
4.374
4.369
4.358
4.354
4.097
4.077
4.071
4.052
4.045
4.026
3.142
3.132
3.112
3.101
3.081
3.071
2.968
2.954
2.943
2.927
2.914
2.901
2.885
2.799
2.794
2.759
2.692
2.665
2.651
2.624
0.000
Br
H
O
N
O
3l


198.473
169.209
138.616
135.599
134.239
132.744
131.018
130.367
129.136
128.746
128.033
120.587
77.380
77.063
76.745
57.081
48.532
37.436
37.124
28.256
f1 (ppm)
Br
H
O
N
O
3l

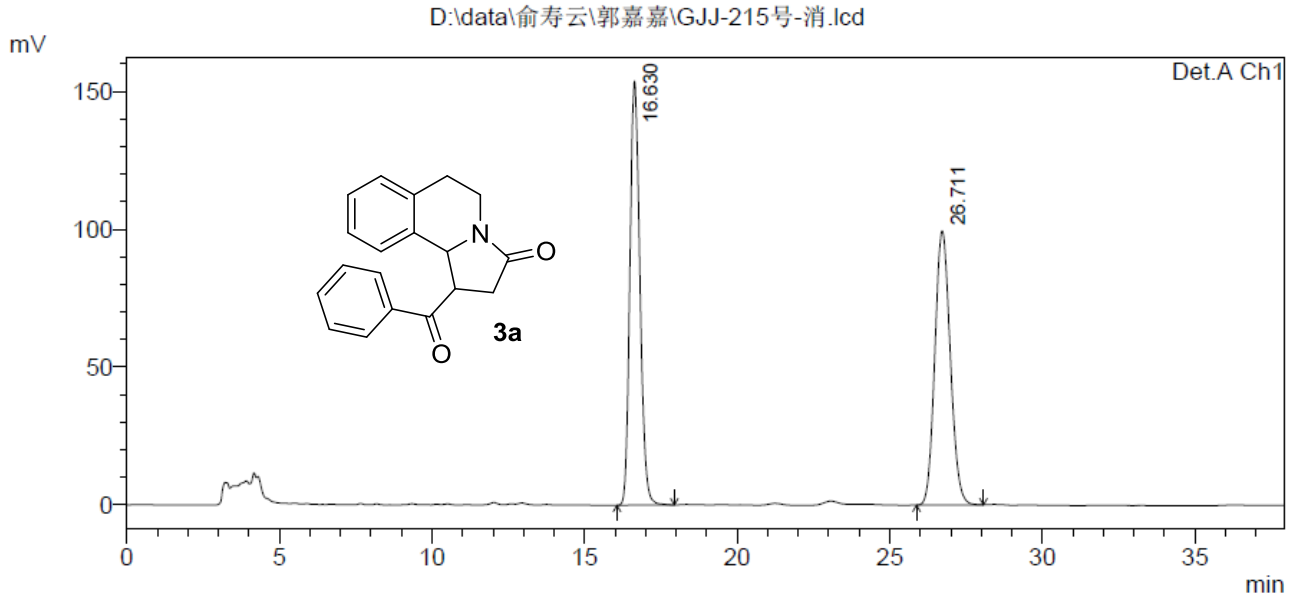

8.034
8.029
8.010
7.992
7.988
7.802
7.798
7.676
7.572
7.553
7.337
7.270
5.629
5.610
4.464
4.457
4.449
4.444
4.432
4.427
4.417
4.413
4.129
4.110
4.103
4.094
4.084
4.078
4.058
3.177
3.167
3.138
3.078
3.063
3.019
2.994
2.977
2.747
2.723
2.721
2.707
2.705
2.681
2.679
2.046
1.710
1.259
1.255
0.000
1.03
0.96
1.04
1.00
1.01
2.03
1.04
1.00
1.02
1.14
4.17
1.06
O2N
H
O
N
O
3m
f1 (ppm)


198.173
169.261
146.973
141.447
138.092
135.416
134.429
130.490
129.209
128.755
122.117
120.467
77.367
77.049
76.732
57.225
48.491
37.326
36.704
28.934
f1 (ppm)
O2N
H
O
N
O
3m


7.998
7.979
7.976
7.667
7.649
7.630
7.548
7.528
7.509
7.265
6.807
6.801
6.784
6.679
6.662
6.656
5.495
5.476
4.385
4.379
4.370
4.365
4.353
4.348
4.338
4.333
4.063
4.043
4.040
4.036
3.761
3.160
3.151
3.131
3.120
3.099
3.091
3.027
3.012
2.997
2.986
2.972
2.959
2.943
2.927
2.903
2.886
2.862
2.804
2.764
2.703
2.676
2.662
2.635
1.254
0.000
1.95
1.01
1.98
1.03
1.93
0.97
1.00
0.99
3.01
1.01
1.08
1.01
1.01
1.02
f1 (ppm)
MeO
H
O
N
O
3n


199.126
169.374
158.443
135.910
135.109
134.087
129.070
128.673
126.124
113.891
113.281
77.358
77.040
76.722
57.467
55.284
48.940
37.706
37.262
28.999
0.010
MeO
H
O
N
O
3n
f1 (ppm)

6. HPLC of the products

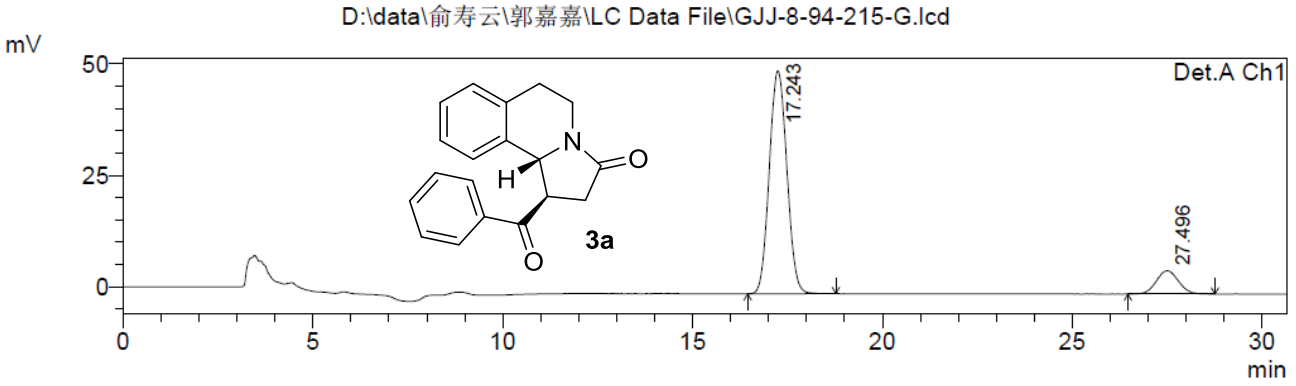


1 Det.A Ch1/254nm

PeakTable

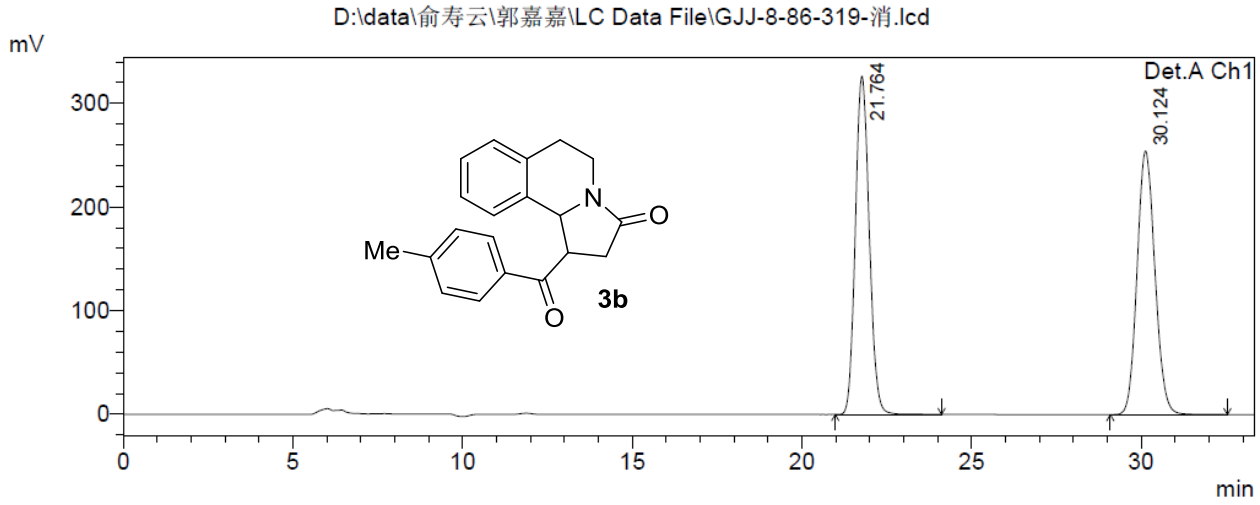
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.630	3514008	153847	50.094	60.734
2	26.711	3500876	99464	49.906	39.266
Total		7014884	253311	100.000	100.000



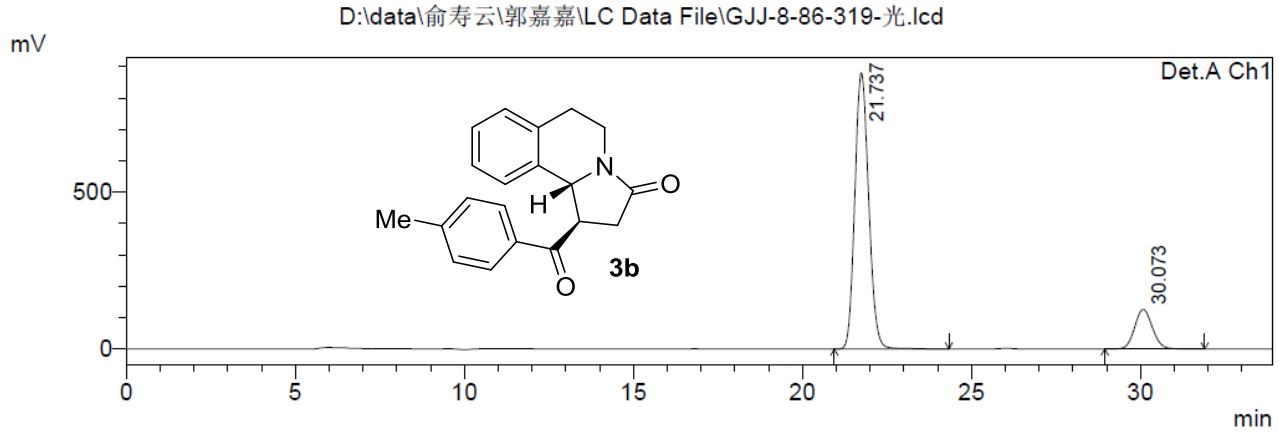
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.243	1612278	49992	88.358	90.542
2	27.496	212441	5222	11.642	9.458
Total		1824720	55214	100.000	100.000



Detector A Ch1 254nm

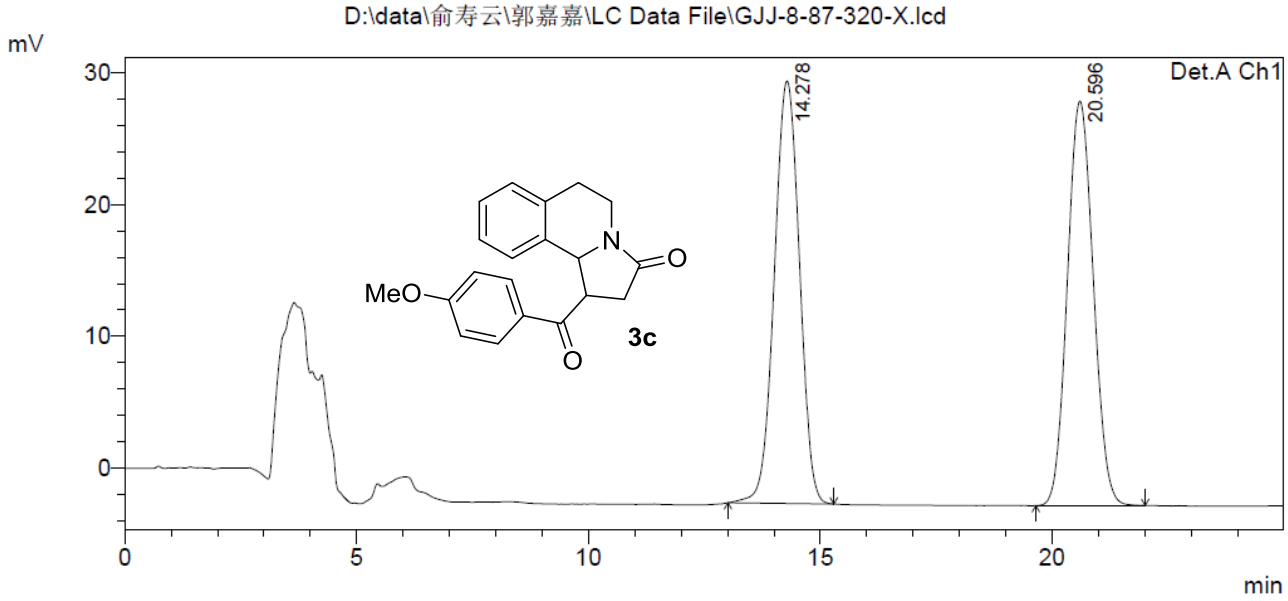
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.764	9300636	326300	49.976	56.209
2	30.124	9309648	254209	50.024	43.791
Total		18610283	580509	100.000	100.000



PeakTable

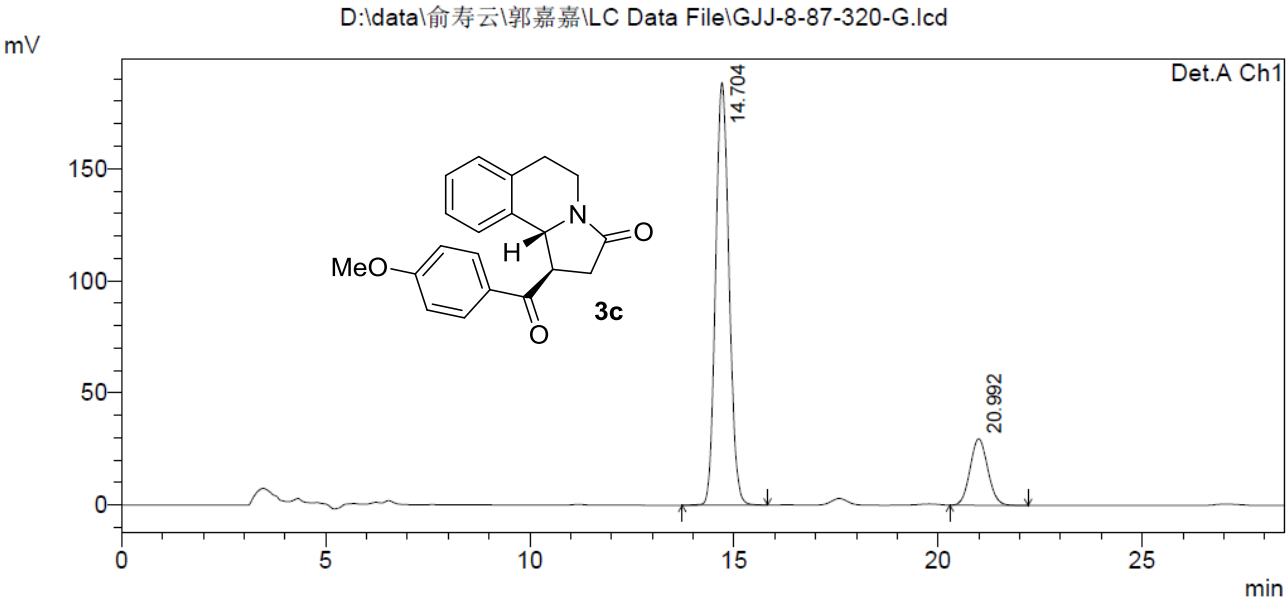
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.737	25101631	881318	84.586	87.472
2	30.073	4574064	126230	15.414	12.528
Total		29675695	1007548	100.000	100.000



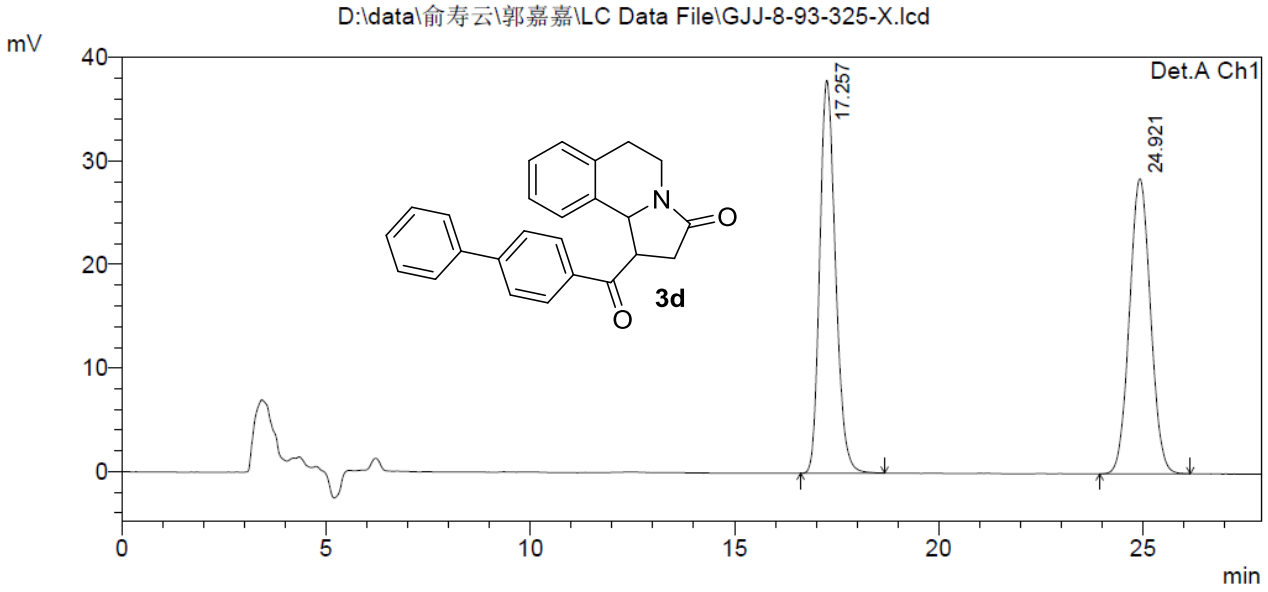
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.278	1208219	32023	50.329	51.089
2	20.596	1192441	30657	49.671	48.911
Total		2400660	62680	100.000	100.000



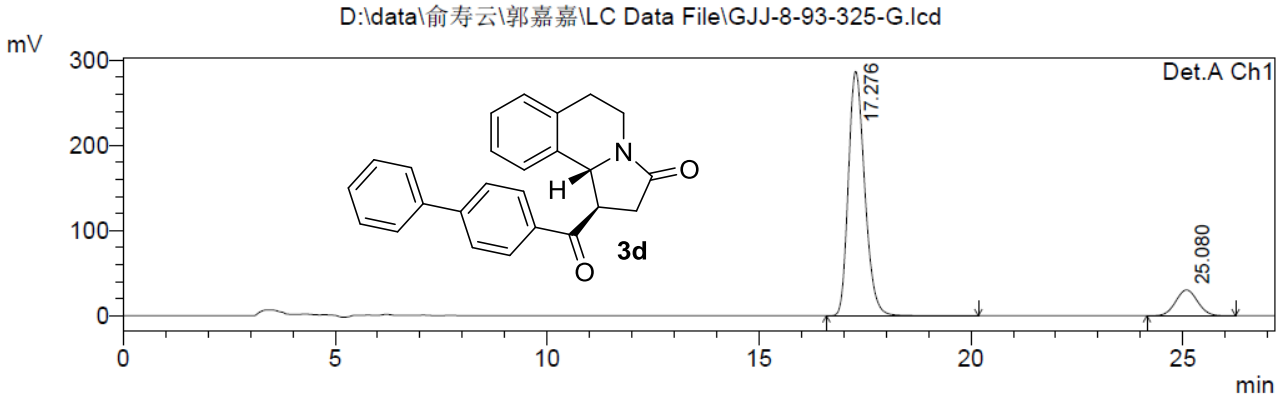
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.704	4317996	188343	82.916	86.422
2	20.992	889654	29591	17.084	13.578
Total		5207650	217934	100.000	100.000



Detector A Ch1 254nm

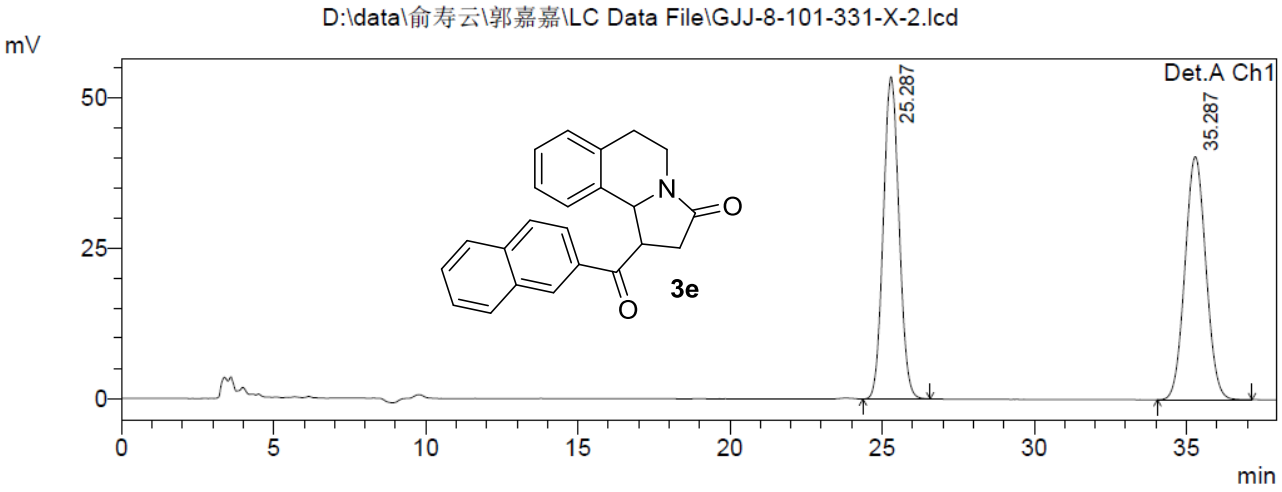
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.257	1018364	37932	49.941	57.104
2	24.921	1020783	28494	50.059	42.896
Total		2039147	66426	100.000	100.000



PeakTable

Detector A Ch1 254nm

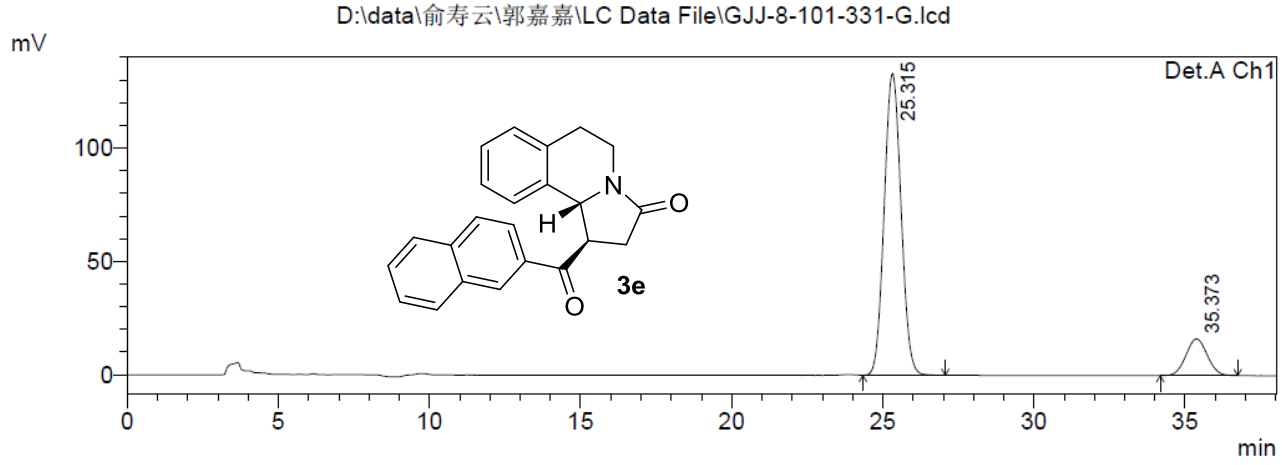
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.276	7699351	287053	87.585	90.444
2	25.080	1091412	30328	12.415	9.556
Total		8790763	317381	100.000	100.000



PeakTable

Detector A Ch1 254nm

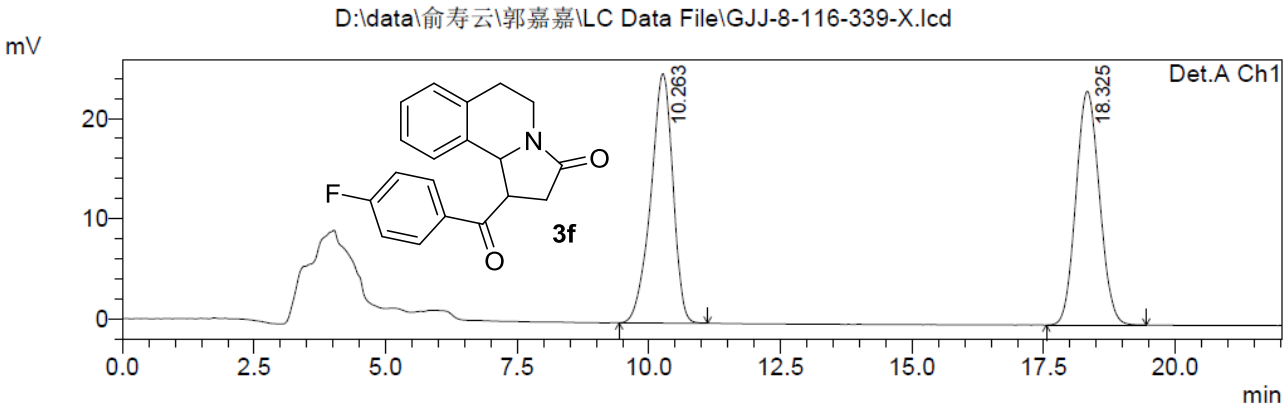
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.287	1928200	53542	49.911	56.992
2	35.287	1935078	40403	50.089	43.008
Total		3863278	93945	100.000	100.000



PeakTable

Detector A Ch1 254nm

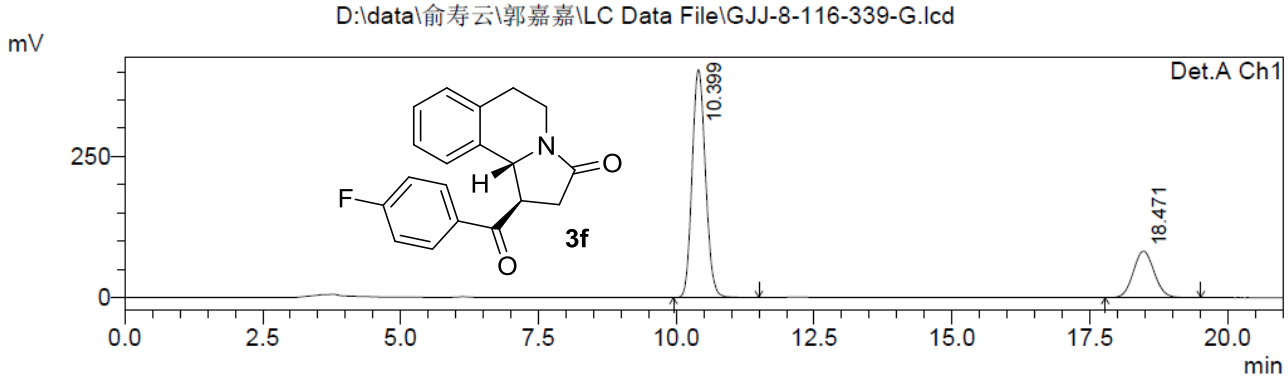
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.315	5164886	133112	86.607	89.148
2	35.373	798735	16205	13.393	10.852
Total		5963621	149317	100.000	100.000



PeakTable

Detector A Ch1 254nm

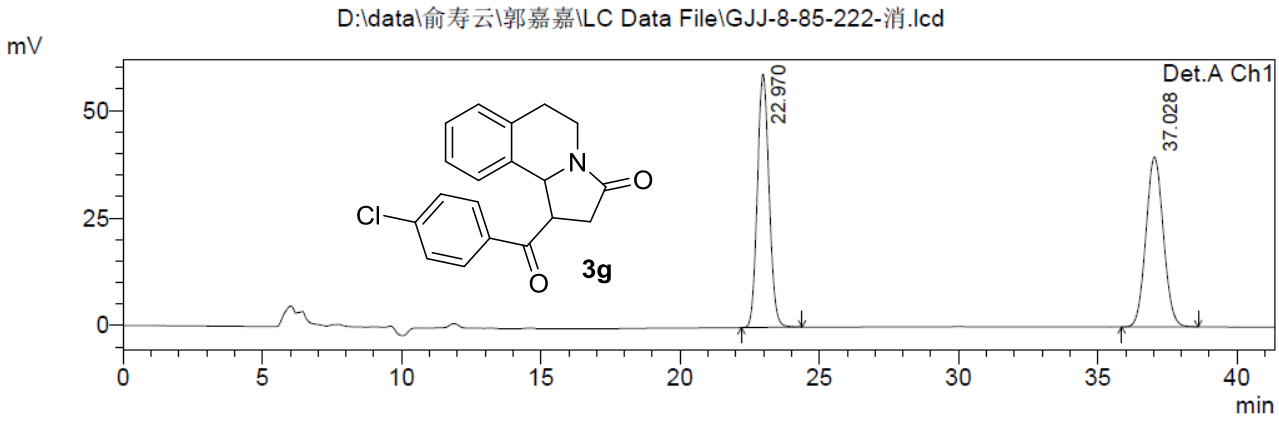
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.263	728024	24931	49.970	51.632
2	18.325	728893	23355	50.030	48.368
Total		1456917	48285	100.000	100.000



PeakTable

Detector A Ch1 254nm

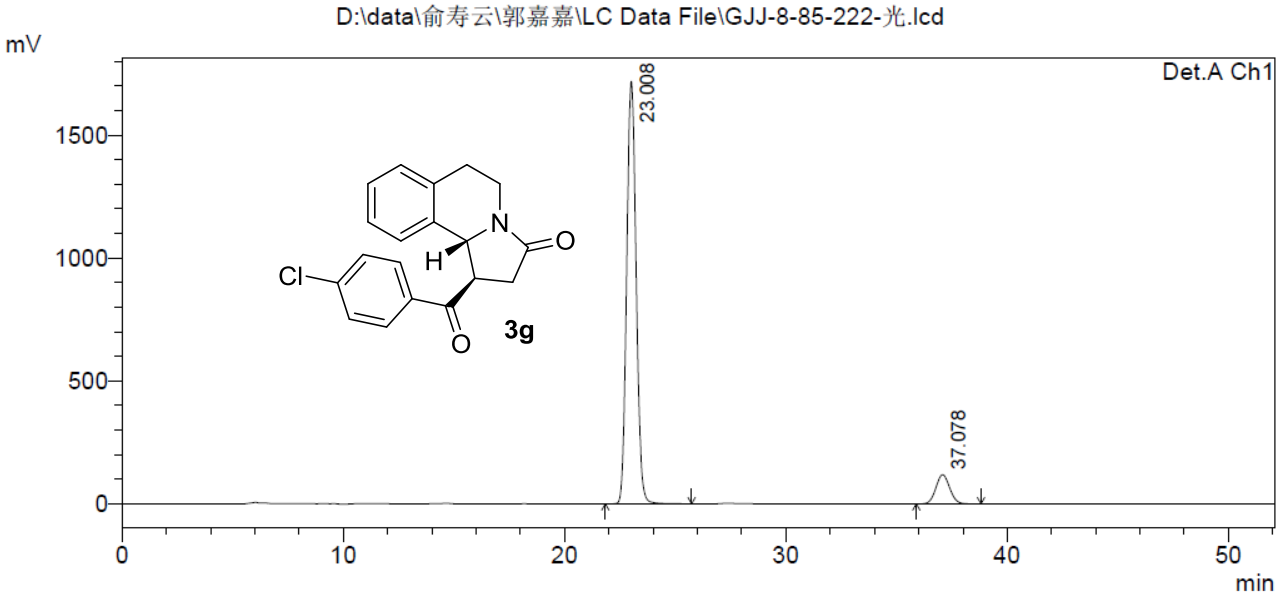
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.399	6809592	403880	75.852	83.028
2	18.471	2167898	82561	24.148	16.972
Total		8977490	486442	100.000	100.000



PeakTable

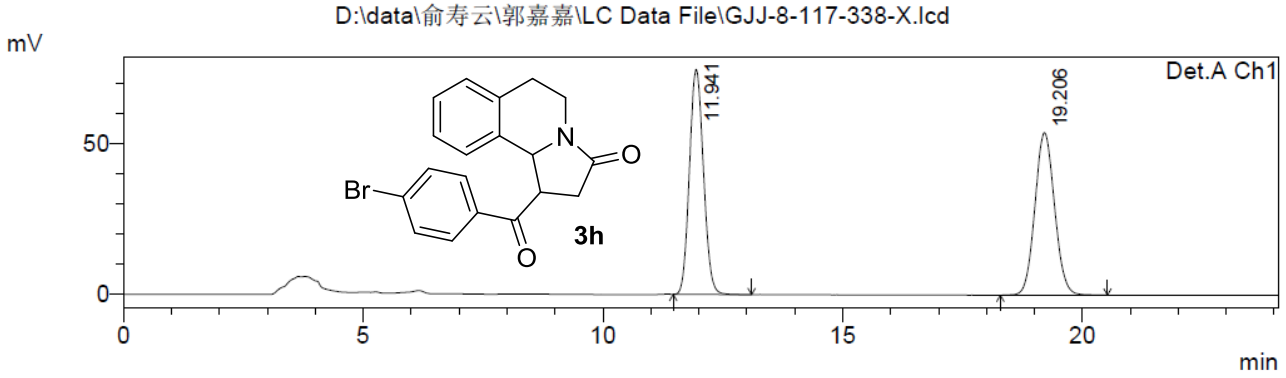
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.970	1724015	58952	49.970	59.834
2	37.028	1726074	39574	50.030	40.166
Total		3450089	98526	100.000	100.000



Detector A Ch1 254nm

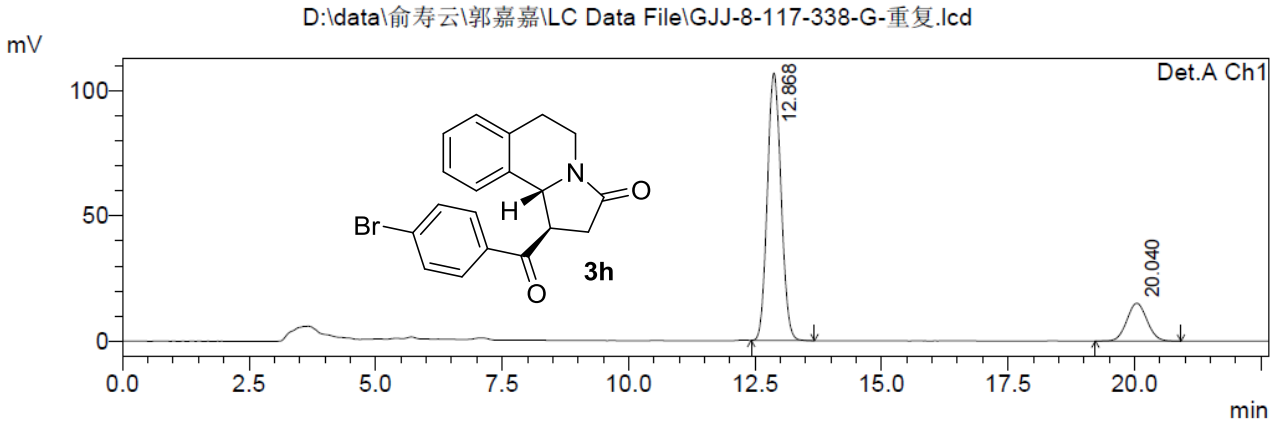
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.008	51112677	1719829	90.863	93.551
2	37.078	5140057	118562	9.137	6.449
Total		56252734	1838391	100.000	100.000



PeakTable

Detector A Ch1 254nm

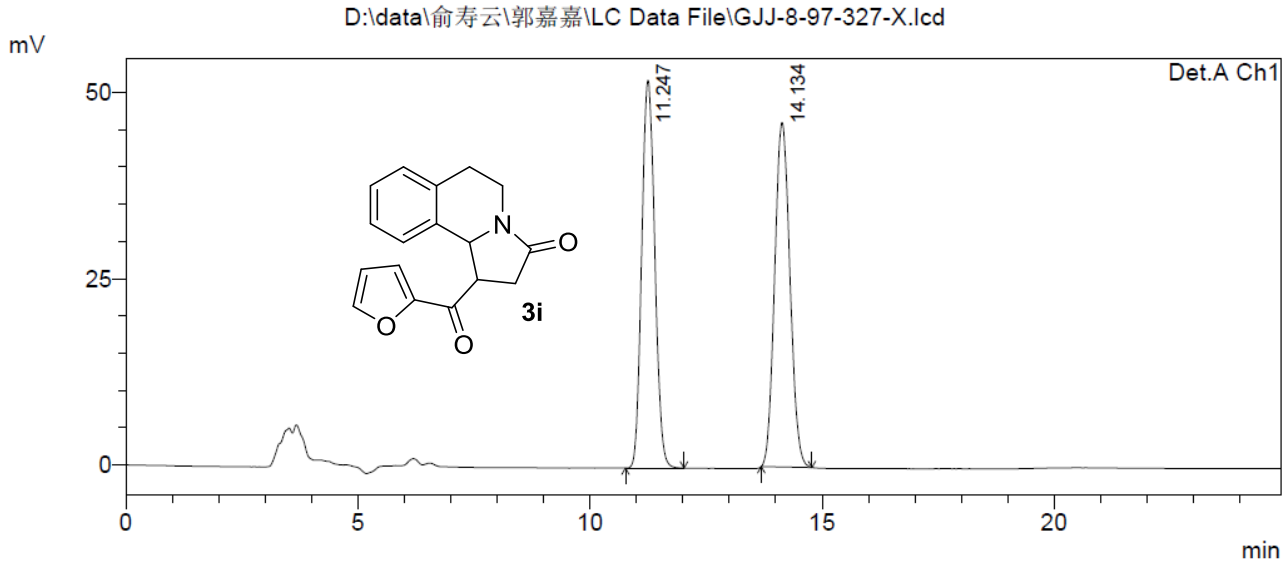
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.941	1523521	74702	49.809	58.084
2	19.206	1535190	53908	50.191	41.916
Total		3058711	128610	100.000	100.000



PeakTable

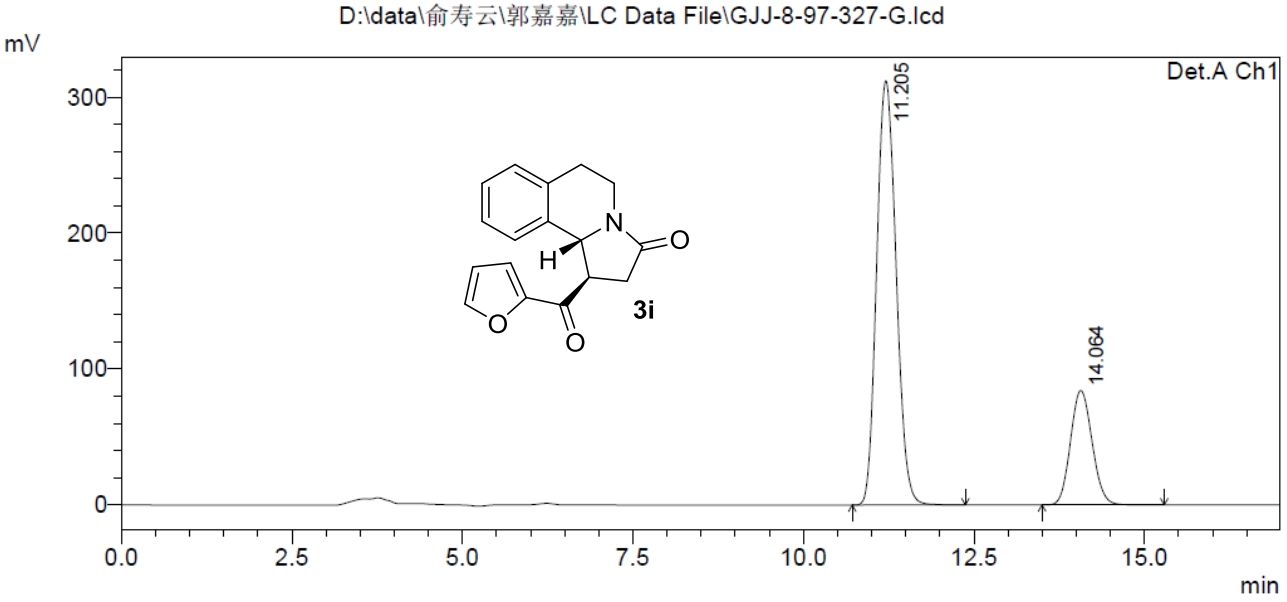
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.868	2016142	106730	82.816	87.592
2	20.040	418355	15120	17.184	12.408
Total		2434497	121850	100.000	100.000



Detector A Ch1 254nm

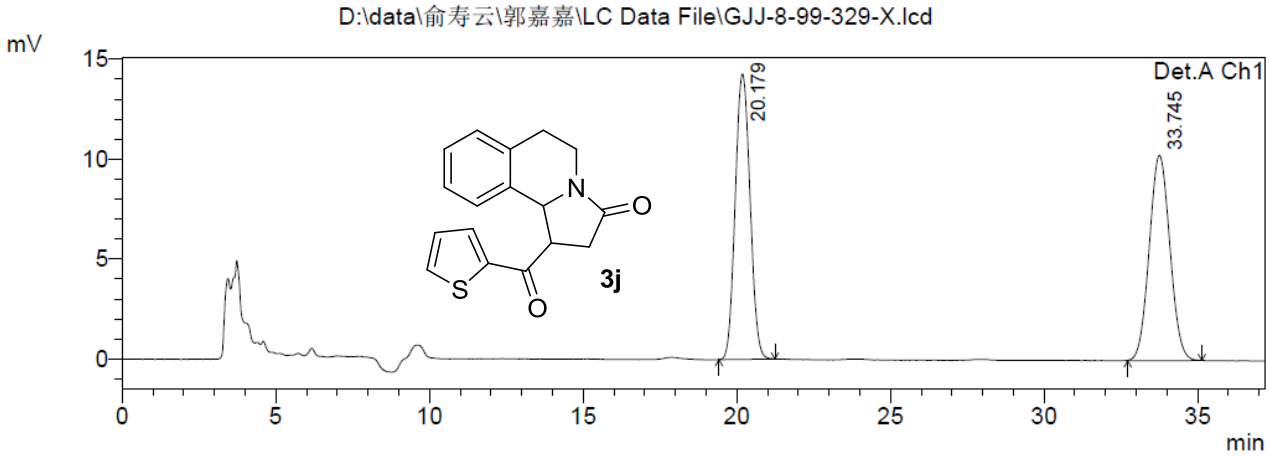
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.247	1020933	52059	49.080	52.954
2	14.134	1059209	46251	50.920	47.046
Total		2080142	98310	100.000	100.000



PeakTable

Detector A Ch1 254nm

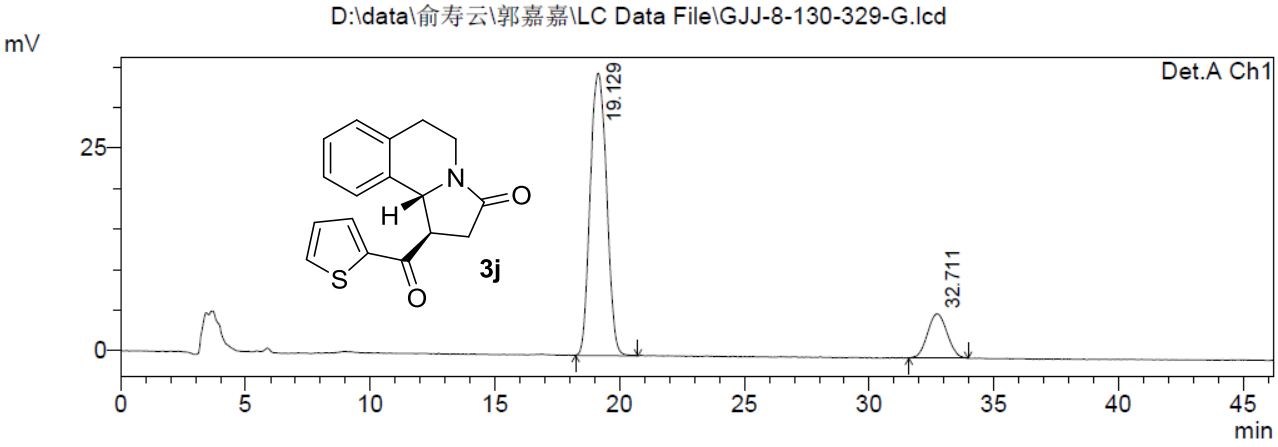
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.205	6196656	312131	76.965	78.748
2	14.064	1854570	84234	23.035	21.252
Total		8051226	396366	100.000	100.000



PeakTable

Detector A Ch1 254nm

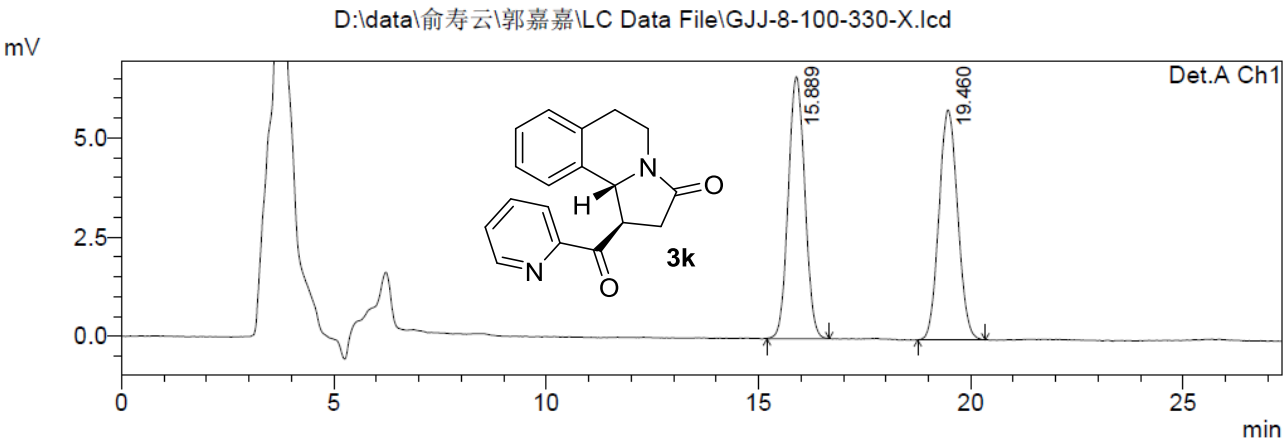
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.179	478467	14277	49.898	58.160
2	33.745	480431	10271	50.102	41.840
Total		958898	24547	100.000	100.000



PeakTable

Detector A Ch1 254nm

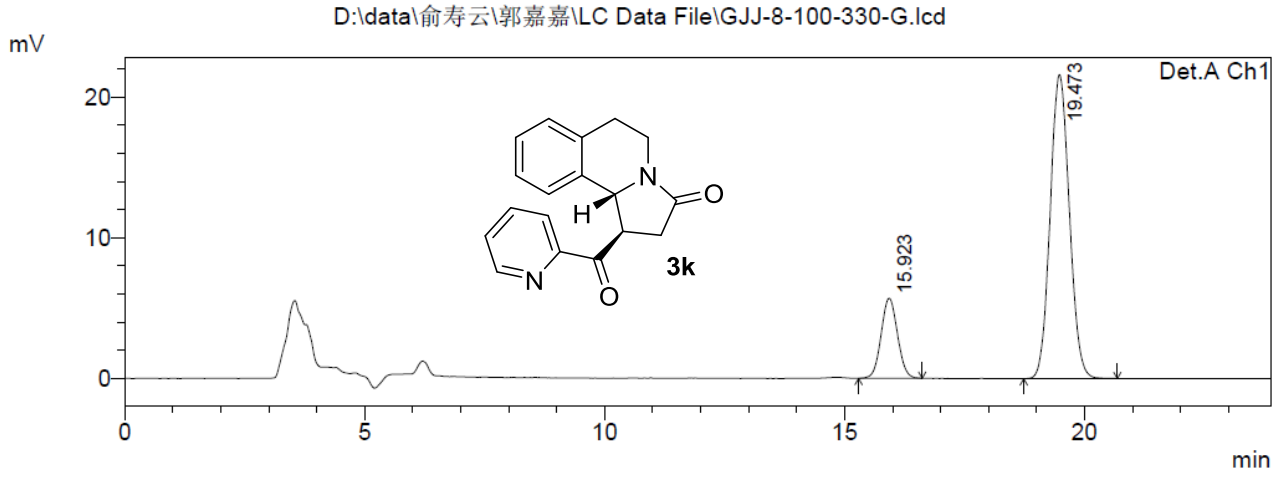
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.129	1601790	34867	84.153	86.383
2	32.711	301629	5496	15.847	13.617
Total		1903418	40364	100.000	100.000



PeakTable

Detector A Ch1 254nm

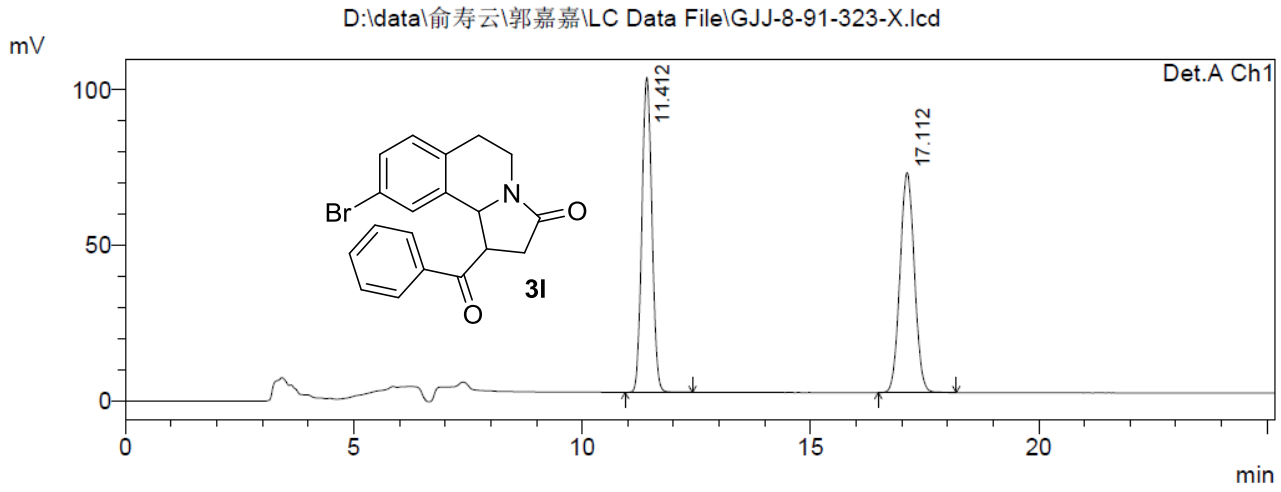
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.889	179471	6608	50.227	53.276
2	19.460	177849	5796	49.773	46.724
Total		357320	12404	100.000	100.000



PeakTable

Detector A Ch1 254nm

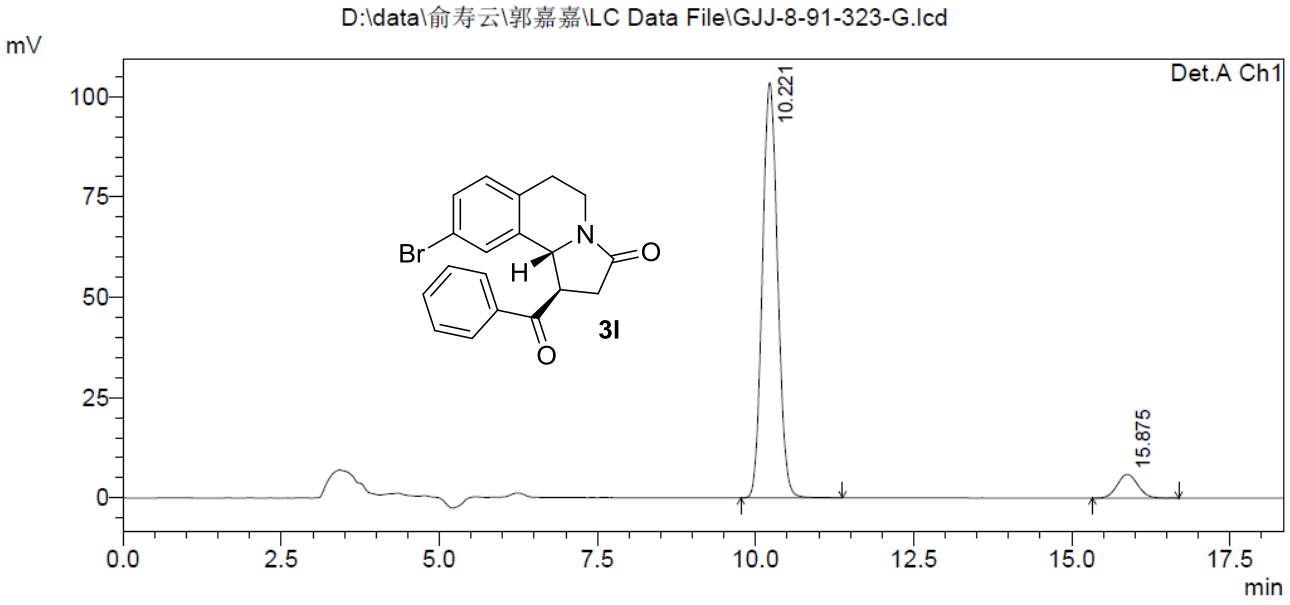
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.923	135286	5702	18.325	20.872
2	19.473	602978	21615	81.675	79.128
Total		738265	27316	100.000	100.000



PeakTable

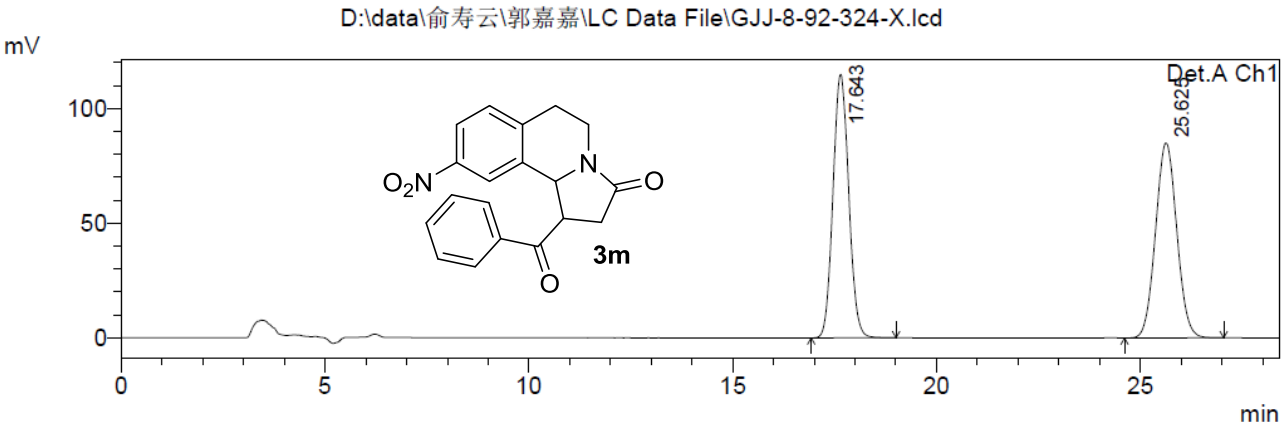
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.412	1547195	101226	49.944	58.881
2	17.112	1550647	70690	50.056	41.119
Total		3097842	171916	100.000	100.000



Detector A Ch1 254nm

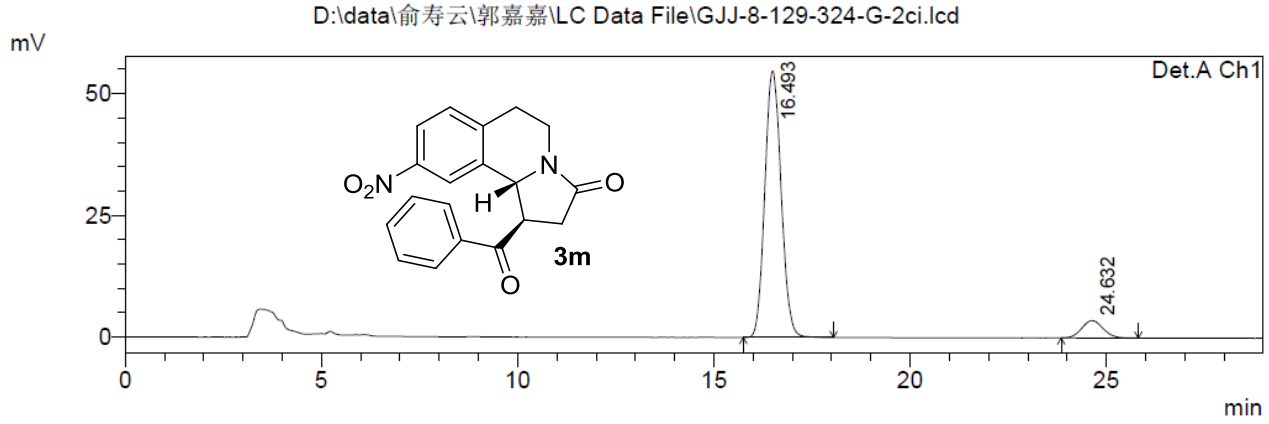
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.221	1734369	103460	92.775	94.593
2	15.875	135065	5913	7.225	5.407
Total		1869434	109374	100.000	100.000



PeakTable

Detector A Ch1 254nm

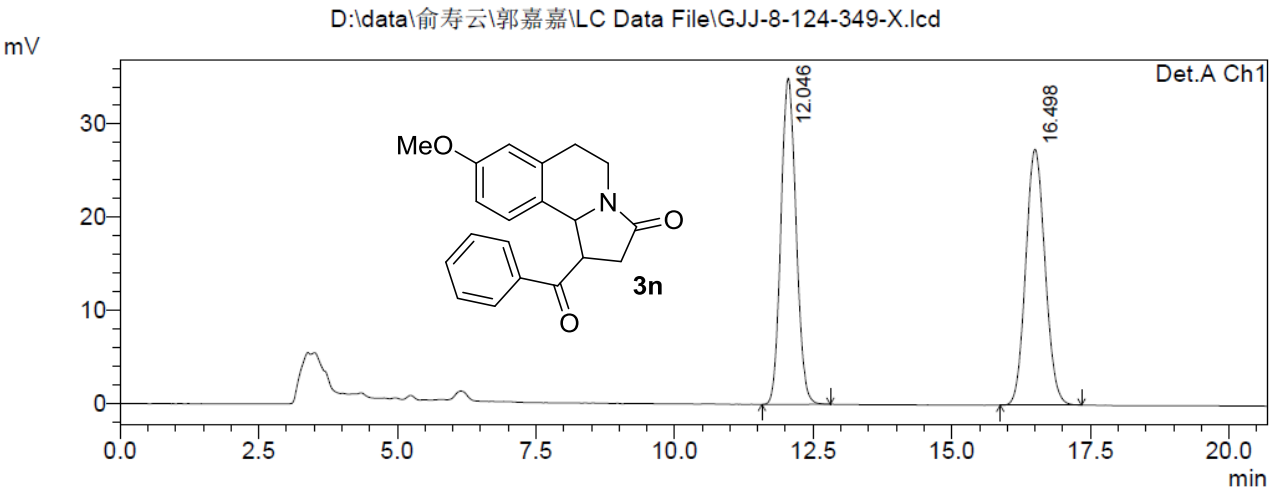
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.643	3091501	115009	50.078	57.473
2	25.625	3081843	85099	49.922	42.527
Total		6173344	200108	100.000	100.000



PeakTable

Detector A Ch1 254nm

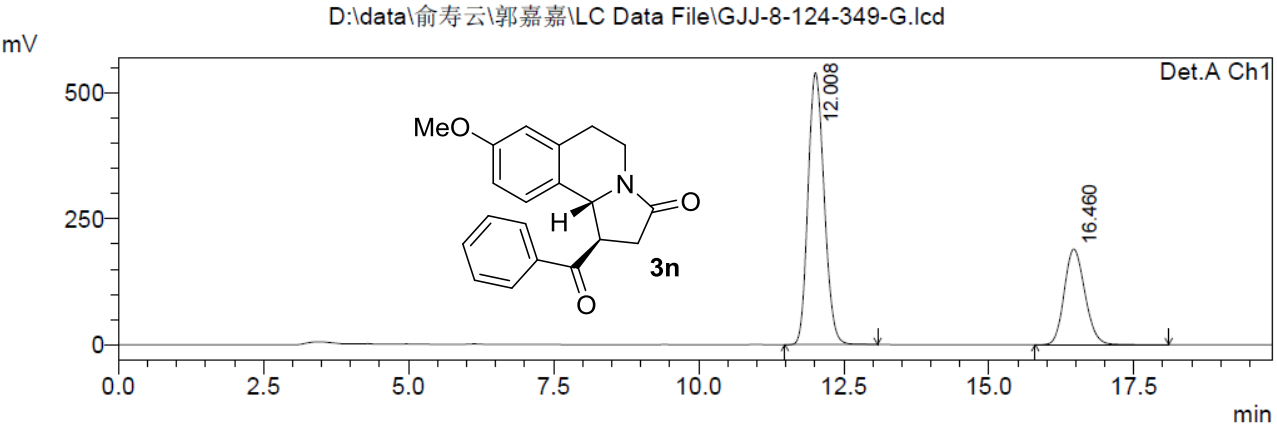
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.493	1589089	54797	92.133	93.878
2	24.632	135696	3574	7.867	6.122
Total		1724784	58370	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.046	666631	35035	49.922	56.044
2	16.498	668727	27478	50.078	43.956
Total		1335358	62513	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.008	10450030	540766	68.990	73.987
2	16.460	4697172	190124	31.010	26.013
Total		15147202	730890	100.000	100.000

7. X-ray spectra of 3l (CCDC 1029009)