Supporting Information for

Tandem Pd-Catalyzed Intermolecular Allylic Alkylation/Allylic Dearomatization Reaction of Benzoylmethyl Pyridines, Pyrazines and Quinolines

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General methods

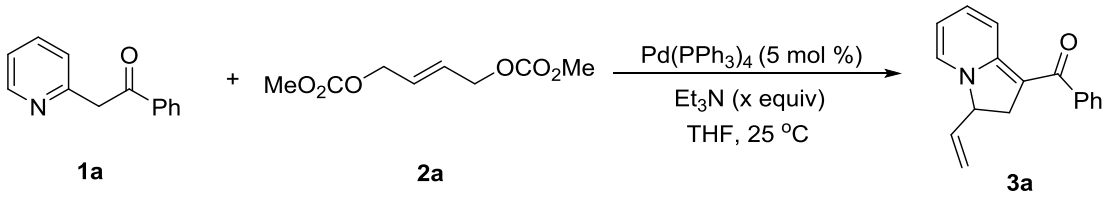
Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

^{1}H and ^{13}C NMR spectra were recorded on an Agilent instrument (400 MHz and 100 MHz, respectively) or an Agilent instrument (600 MHz and 150 MHz, respectively) or a Bruker instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{19}F NMR spectra were recorded on an Agilent instrument (376 MHz) or a Bruker instrument (376 MHz) and referenced relative to $CFCl_3$. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm).

Substrates **1a-1q**[1,2], **2a-2b**[3] were synthesized according to the literature procedure.

Optimization of the reaction conditions

Table S1. The effects of triethyl amine equivalents.[a]

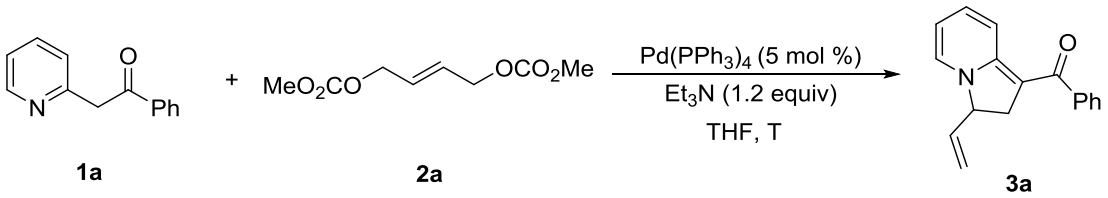


1a 2a 3a

Entry	x (equiv)	Time (h)	NMR yield (%)[b]
1	0.2	3	68 (64[c])
2	0.5	2.5	72 (65[c])
3	1.2	1.5	79 (74[c])

[a] Reaction conditions: 0.4 mmol of **1a**, 0.48 mmol of **2a**, 5 mol % of $Pd(PPh_3)_4$, x equiv of Et_3N in THF (4 mL) at 25 ℃. [b] Determined by ^1H NMR of the crude reaction mixture using dibromomethane as an internal standard. [c] Isolated yield.

Table S2. The effects of temperature.[a]

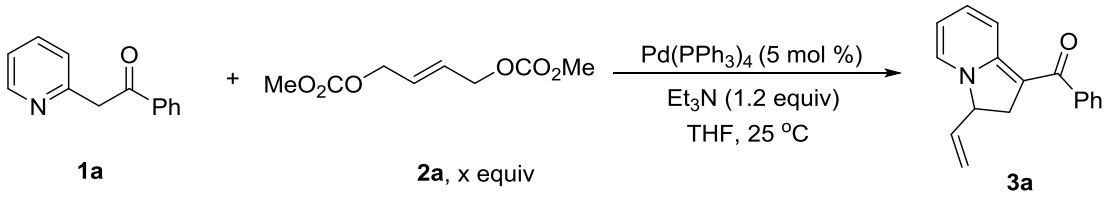


1a 2a 3a

Entry	T (°C)	Time (h)	NMR yield (%)[b]
1	0	24	14
2	10	24	54
3	20	1	68
4	25	1.5	79
5	50	24	<5

[a] Reaction conditions: 0.4 mmol of **1a**, 0.48 mmol of **2a**, 5 mol % of $Pd(PPh_3)_4$, 0.48 mmol of Et_3N in THF (4 mL) at T. [b] Determined by ^1H NMR of the crude reaction mixture using dibromomethane as an internal standard.

Table S3. The effects of **2a** equivalents.[a]



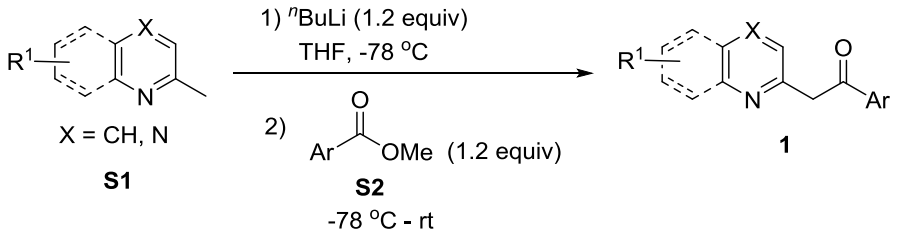
1a **2a**, x equiv **3a**

Entry	x (equiv)	Time (h)	NMR yield (%)[b]
1	1.2	1.5	79
2	1.5	2.5	57
3	2.0	24	17

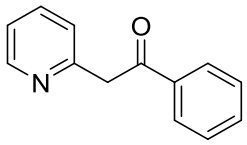
[a] Reaction conditions: 0.4 mmol of **1a**, x equiv of **2a**, 5 mol % of $Pd(PPh_3)_4$, 0.48 mmol of Et_3N in THF (4 mL) at 25 ℃. [b] Determined by ^1H NMR of the crude reaction mixture using dibromomethane as an internal standard.

Experimental details and characterization data

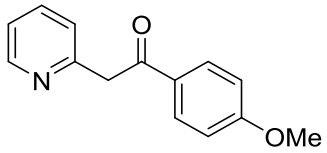
General procedure for the synthesis of substrate 1



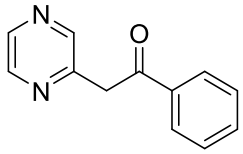
^{n}BuLi (2.5 M solution in hexanes, 1.2 equiv) was added dropwise to a stirred solution of **S1** (1.0 equiv) in THF (0.2 M) at -78 ℃ under Ar. After the resulting mixture was stirred at -78 ℃ for 2 h, **S2** (1.2 equiv) was added and stirred for another 1 h. Then, the solution was stirred for 12 h at room temperature. After the reaction was complete (monitored by TLC), the reaction was quenched by brine. The mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired products **1a**, **1d-1o**, **1t**. Both ketone and enol forms were observed by ^{1}H NMR, and the peaks of enol form were marked with asterisk*. The analytical data of the products are summarized below.



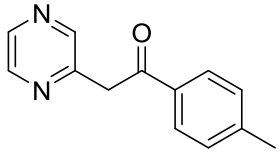
1a, orange solid, m.p. = 55.3-56.0 ℃ (Known compound, see: Muir, C. W.; Kennedy, A. R.; Redmond, J. M.; Watson, A. J. B. *Org. Biomol. Chem*. **2013**, *11*, 3337). 1.6 g, 50% yield (16 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1.4:1) δ 15.50* (br s, 1H), 8.60-8.52 (m, 1H), 8.29* (d, *J* = 4.8 Hz, 1H), 8.12-8.03 (m, 2H), 7.90-7.80* (m, 2H), 7.68-7.53* (m, 4H), 7.51-7.35 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.21-7.14 (m, 1H), 7.07* (d, *J* = 8.0 Hz, 1H), 6.98* (ddd, *J* = 7.2, 5.2, 1.2 Hz, 1H), 6.08* (s, 1H), 4.50 (s, 2H).



1b, yellow solid, m.p. = 69.7-70.4 ℃ (Known compound, see: Muir, C. W.; Kennedy, A. R.; Redmond, J. M.; Watson, A. J. B. *Org. Biomol. Chem*. **2013**, *11*, 3337). 1.6 g, 44% yield (16 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 5:1) δ 15.55* (br s, 1H), 8.54 (d, *J* = 4.8 Hz, 1H), 8.20* (d, *J* = 5.2 Hz, 1H), 8.09-7.98 (m, 2H), 7.82-7.77* (m, 2H), 7.60 (td, *J* = 7.6, 1.6 Hz, 1H), 7.56-7.51* (m, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.13 (dd, *J* = 6.8, 5.2 Hz, 1H), 7.00* (d, *J* = 8.4 Hz, 1H), 6.95-6.87 (m, 2H), 6.95-6.87* (m, 3H), 5.97* (s, 1H), 4.43 (s, 2H), 3.81, 3.81* (s, 3H).

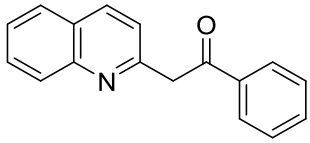


1f, orange solid, m.p. = 87.6-88.6 ℃ (Known compound, see: Carver, D. R.; Komin, A. P.; Hubbard, J. S.; Wolfe, J. F. *J. Org. Chem*. **1981**, *46*, 294). 1.8 g, 57% yield (16 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 2.8:1) δ 13.88* (br s, 1H), 8.61 (d, *J* = 1.2 Hz, 1H), 8.56-8.49 (m, 1H), 8.50-8.42 (m, 1H), 8.50-8.42* (m, 1H), 8.29-8.22* (m, 2H), 8.12-7.98 (m, 2H), 7.88-7.79* (m, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.48* (t, *J* = 7.6 Hz, 3H), 7.44-7.36 (m, 1H), 6.14* (s, 1H), 4.53 (s, 2H).

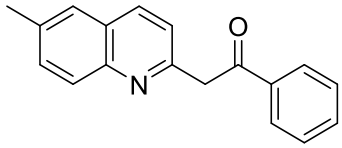


1g, orange solid, m.p. = 73.8-74.2 ℃. 1.7 g, 50% yield (16 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 5:1) δ 13.89* (br s, 1H), 8.61 (d, *J* = 1.6 Hz, 1H), 8.53 (t, *J* = 2.0 Hz, 1H), 8.47 (d, *J* = 2.4 Hz, 1H), 8.44* (d, *J* = 0.8 Hz, 1H), 8.29-8.22* (m, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.74* (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.24* (d, *J* = 8.4 Hz, 2H), 6.12* (s, 1H), 4.51 (s, 2H), 2.42 (s, 3H), 2.40* (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 164.9, 154.5, 151.5, 146.0, 144.7, 144.3, 144.3, 143.0, 140.4, 139.6, 139.1, 133.9, 132.5, 129.6, 129.3, 128.9, 125.6, 91.6, 45.5, 21.8,

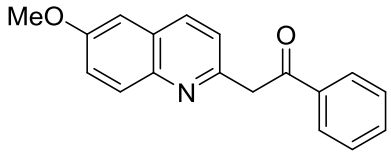
21.5. IR (thin film): $\nu_{max}(cm^{-1})$ = 3332, 3053, 2950, 2915, 2378, 2325, 2300, 2120, 1994, 1918, 1827, 1669, 1599, 1505, 1474, 1449, 1403, 1323, 1285, 1246, 1192, 1121, 1052, 1011, 988, 867, 842, 814, 780, 742, 713, 648, 570, 471. HRMS-ESI calcd for $C_{13}H_{13}N_2O$ $[M+H]^+$: 213.1022. Found: 213.1021.



1i, yellow solid, m.p. = 115.4-115.9 ℃ (Known compound, see: Wang, T.-L.; Ouyang, G..; He, Y.-M.; Fan, Q.-H. *Synlett* **2011**, *7*, 939). 1.3 g, 42% yield (12.5 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:20) δ 15.70* (br s, 1H), 8.11 (d, *J* = 8.0 Hz, 3H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.96* (dd, *J* = 5.6, 1.6 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.64* (d, *J* = 8.8 Hz, 1H), 7.59-7.37* (m, 6H), 7.25* (dd, *J* = 7.2, 4.8 Hz, 1H), 6.86* (d, *J* = 9.2 Hz, 1H), 6.08* (s, 1H), 4.70 (s, 2H).

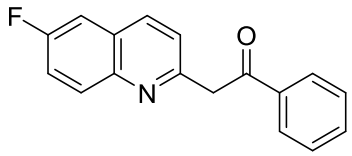


1l, yellow solid, m.p. = 117.5-118.3 ℃ (Known compound, see: Wang, T.-L.; Ouyang, G.; He, Y.-M.; Fan, Q.-H. *Synlett* **2011**, *7*, 939). 1.8 g, 49% yield (14 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:20) δ 15.71* (br s, 1H), 7.98-7.90* (m, 2H), 7.59* (d, *J* = 8.8 Hz, 1H), 7.45-7.32* (m, 5H), 7.29* (s, 1H), 6.82* (d, *J* = 9.2 Hz, 1H), 6.02* (s, 1H), 4.67 (s, 2H), 2.50 (s, 3H), 2.41* (s, 3H).

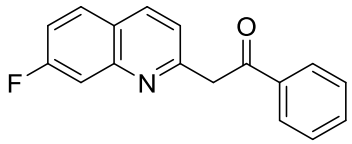


1m, yellow solid, m.p. = 145.8-146.4 ℃ (Known compound, see: Wang, T.-L.; Ouyang, G.; He, Y.-M.; Fan, Q.-H. *Synlett* **2011**, *7*, 939). 2.0 g, 61% yield (12 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:5) δ 16.07* (br s, 1H), 8.14-8.08 (m, 2H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.98-7.90* (m, 2H), 7.68* (d, *J* = 9.2 Hz, 1H), 7.52* (d, *J* = 8.8 Hz, 1H), 7.49-7.39* (m, 3H), 7.38-7.35 (m, 1H), 7.22* (dd, *J* = 9.2,

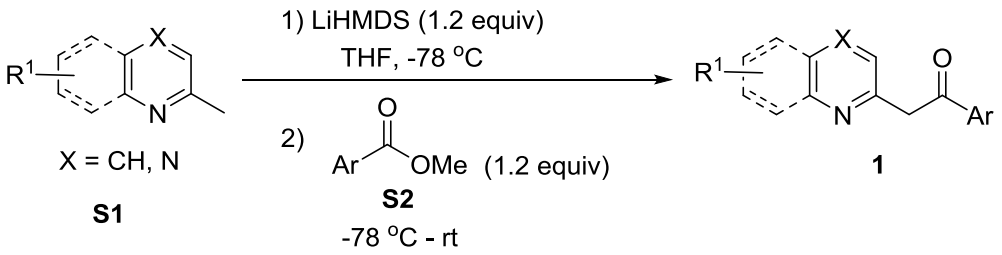
2.8 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.97-6.91* (m, 2H), 6.08* (s, 1H), 4.65 (s, 2H), 3.91 (s, 3H), 3.87* (s, 3H).



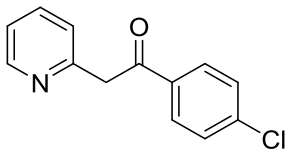
1n, yellow solid, m.p. = 127.9-128.5 ℃ (Known compound, see: Wang, T.-L.; Ouyang, G.; He, Y.-M.; Fan, Q.-H. *Synlett* **2011**, *7*, 939). 1.2 g, 36% yield (13 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:6.2) δ 15.86* (br s, 1H), 8.13-8.08 (m, 2H), 8.08-8.01 (m, 2H), 7.98-7.90* (m, 2H), 7.64* (d, *J* = 8.8 Hz, 1H), 7.59-7.49* (m, 1H), 7.59-7.49 (m, 2H), 7.49-7.38* (m, 3H), 7.49-7.38 (m, 4H), 7.30* (td, *J* = 8.8, 2.8 Hz, 1H), 7.21* (dd, *J* = 8.4, 2.8 Hz, 1H), 6.94* (d, *J* = 9.2 Hz, 1H), 6.09* (s, 1H), 4.68 (s, 2H).



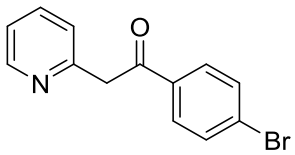
1p, yellow solid, m.p. = 108.2-109.1 ℃. 1.4 g, 42% yield (13 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:14.3) δ 15.71* (br s, 1H), 8.12-8.03 (m, 3H), 7.97-7.88* (m, 2H), 7.75 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.66 (dd, *J* = 10.4, 2.4 Hz, 1H), 7.57* (d, *J* = 9.2 Hz, 1H), 7.50-7.39* (m, 4H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.29 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.13* (dd, *J* = 9.6, 2.4 Hz, 1H), 6.96* (td, *J* = 8.4, 2.4 Hz, 1H), 6.78* (d, *J* = 9.2 Hz, 1H), 6.06* (s, 1H), 4.66 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.9(m), -113.2(m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 164.0 (d, *J* = 249.5 Hz), 157.0, 154.8, 139.8 (d, *J* = 123.0 Hz), 139.3, 136.5 (d, *J* = 185.0 Hz), 135.7, 133.5, 130.6, 129.6 (d, *J* = 101.0 Hz), 128.8 (d, *J* = 79.0 Hz), 128.4, 126.7, 121.6 (d, *J* = 27.0 Hz), 121.5 (d, *J* = 27.0 Hz), 120.3 (d, *J* = 17.0 Hz) 117.0, 116.7, 112.8 (d, *J* = 20.3 Hz), 112.7 (d, *J* = 23.7 Hz), 104.6 (d, *J* = 24.4 Hz) 90.7, 49.3. IR (thin film): ν_{max}(cm^{-1}) = 3076, 3053, 2954, 2920, 2853, 2387, 2304, 2116, 1994, 1877, 1817, 1626, 1584, 1534, 1510, 1447, 1404, 1322, 1300, 1274, 1207, 1177, 1147, 1105, 1062, 1023, 985, 942, 868, 835, 756, 726, 686, 656. HRMS-ESI calcd for $C_{17}H_{13}FNO$ $[M+H]^+$: 266.0976. Found: 266.0973.



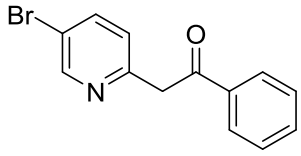
LiHMDS (1.0 M solution in THF, 1.2 equiv) was added dropwise to a stirred solution of **S1** (1.0 equiv) in THF (0.2 M) at -78 ℃ under Ar. After the resulting mixture was stirred at -78 ℃ for 2 h, **S2** (1.2 equiv) was added and stirred for another 1 h. Then, the solution was stirred for 12 h at room temperature. After the reaction was complete (monitored by TLC), the reaction was quenched by brine. The mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (PE/EtOAc = 10/1) to afford the desired products **1c**-**1e**, **1h**, **1j**-**1k**, **1o**, **1q**. Both ketone and enol forms were observed by ^{1}H NMR, and the peaks of enol form were marked with asterisk*. The analytical data of the products are summarized below.



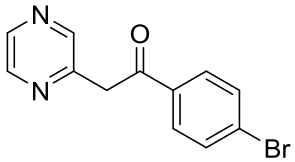
1c, yellow solid, m.p. = 88.2-89.1 ℃ (Known compound, see: Muir, C. W.; Kennedy, A. R.; Redmond, J. M.; Watson, A. J. B. *Org. Biomol. Chem*. **2013**, *11*, 3337). 1.1 g, 37% yield (13 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:1.2) δ 15.57* (br s, 1H), 8.58-8.51 (m, 1H), 8.27* (d, *J* = 5.2 Hz, 1H), 8.05-7.97 (m, 2H), 7.81-7.72* (m, 2H), 7.68-7.56 (m, 1H), 7.68-7.56* (m, 1H), 7.46-7.39 (m, 2H), 7.39-7.32* (m, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 6.8, 5.2 Hz, 1H), 7.05* (d, *J* = 8.0 Hz, 1H), 7.01-6.93* (m, 1H), 6.03* (s, 1H), 4.45 (s, 2H).



1d, orange soild, m.p. = 81.5-82.1 ℃ (Known compound, see: Muir, C. W.; Kennedy, A. R.; Redmond, J. M.; Watson, A. J. B. *Org. Biomol. Chem*. **2013**, *11*, 3337). 445 mg, 54% yield (3 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:1.3) δ 15.57* (br s, 1H), 8.55 (d, *J* = 4.0 Hz, 1H), 8.28* (d, *J* = 5.2 Hz, 1H), 7.98-7.89 (m, 2H), 7.71* (d, *J* = 8.8 Hz, 2H), 7.67-7.57 (m, 3H), 7.67-7.57* (m, 1H), 7.53* (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 6.8, 5.2 Hz, 1H), 7.06* (d, *J* = 8.0 Hz, 1H), 6.99* (dd, *J* = 6.4, 6.0 Hz, 1H), 6.05* (s, 1H), 4.45 (s, 2H).

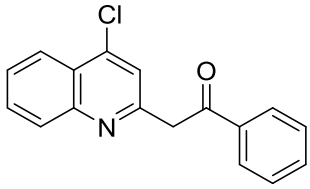


1e, yellow solid, m.p. = 91.2-92.0 ℃. 2.1 g, 33% yield (23 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 2:1) δ 14.35* (br s, 1H), 8.62 (d, *J* = 2.4 Hz, 1H), 8.43* (d, *J* = 2.4 Hz, 1H), 8.09-7.99 (m, 2H), 7.86-7.80* (m, 2H), 7.77 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.72* (dd, *J* = 8.8, 2.4 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.44-7.36* (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.99* (d, *J* = 8.4 Hz, 1H), 6.06* (s, 1H), 4.46 (s, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ 196.5, 162.8, 157.3, 153.9, 150.7, 146.7, 139.8, 139.3, 136.4, 135.8, 133.6, 129.7, 128.8, 128.5, 125.7, 125.6, 123.0, 119.3, 114.4, 94.5, 47.7. IR (thin film): ν_{max}(cm^{-1}) = 3053, 2669, 2348, 2124, 2089, 1990, 1895, 1846, 1723, 1617, 1577, 1533, 1491, 1464, 1448, 1428, 1372, 1349, 1268, 1200, 1182, 1147, 1128, 1078, 1057, 1028, 1005, 924, 856, 837, 762, 730, 685, 644. HRMS-ESI calcd for $C_{13}H_{11}BrNO$ $[M+H]^+$: 276.0019. Found: 276.0015.

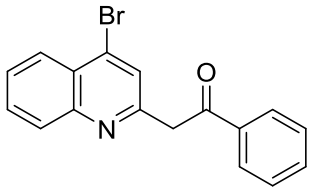


1h, orange solid, m.p. = 107.0-108.1 ℃. 1.8 g, 47% yield (14 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:9.1) δ 13.87* (br s, 1H), 8.61 (s, 1H), 8.54-8.51 (m, 1H), 8.49 (d, *J* = 2.4 Hz, 1H), 8.45* (s, 1H), 8.34-8.23* (m, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.69* (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.54* (d, *J* = 8.4 Hz, 2H), 6.11* (s, 1H), 4.48 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 163.5, 154.1, 151.0, 145.9, 144.4, 144.3, 143.2, 139.8, 139.6, 135.0, 134.2, 132.3, 131.84, 131.79,

131.6, 130.3, 129.1, 127.2, 124.4, 92.5, 45.5. IR (thin film): $\nu_{max}(cm^{-1})$ = 3076, 3042, 2678, 2645, 2378, 2327, 2298, 2247, 2200, 2115, 1998, 1916, 1859, 1806, 1767, 1680, 1629, 1584, 1504, 1482, 1445, 1406, 1370, 1316, 1280, 1232, 1182, 1163, 1138, 1073, 1046, 1009, 930, 881, 826, 782, 743, 716, 654, 627. HRMS-ESI calcd for $C_{12}H_{10}BrN_2O$ $[M+H]^+$: 276.9971. Found: 276.9973.

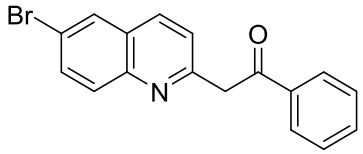


1j, orange solid, m.p. = 78.9-80.1 ℃. 2.2 g, 34% yield (23 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:11.1) δ 15.60* (br s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.08 (dd, *J* = 8.8, 7.6 Hz, 3H), 7.99-7.85* (m, 3H), 7.77-7.70 (m, 1H), 7.57* (td, *J* = 8.0, 1.2 Hz, 1H), 7.54-7.39* (m, 4H), 7.31* (td, *J* = 7.6, 1.2 Hz, 1H), 6.97* (d, *J* = 2.0 Hz, 1H), 6.01* (s, 1H), 4.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 154.0, 141.7, 139.5, 139.1, 133.7, 132.0, 130.7, 130.6, 129.4, 128.8, 128.5, 127.4, 126.7, 124.7, 124.4, 124.1, 122.4, 122.0, 121.6, 119.3, 90.3, 48.9. IR (thin film): $\nu_{max}(cm^{-1})$ = 3086, 3061, 3024, 2295, 2116, 2078, 1998, 1928, 1893, 1807, 1714, 1622, 1584, 1542, 1448, 1416, 1374, 1350, 1323, 1277, 1211, 1183, 1155, 1101, 1063, 1028, 1002, 985, 947, 851, 799, 755, 726, 682, 655, 635. HRMS-ESI calcd for $C_{17}H_{13}ClNO$ $[M+H]^+$: 282.0680. Found: 282.0676.

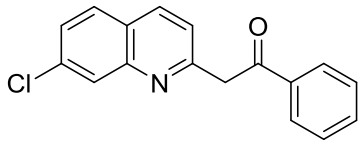


1k, orange solid, m.p. = 87.1-87.6 ℃. 861 mg, 53% yield (5 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:10) δ 15.59* (br s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.98-7.85* (m, 3H), 7.78-7.73 (m, 2H), 7.63-7.54* (m, 1H), 7.52-7.40* (m, 4H), 7.37-7.28* (m, 1H), 7.24* (d, *J* = 6.0 Hz, 1H), 6.02* (d, *J* = 3.6 Hz, 1H), 4.67 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.8, 154.0, 139.2, 139.1, 133.1, 132.1, 130.8, 128.9, 128.5, 127.5, 126.7, 125.6, 124.6, 123.1, 119.4, 90.1. IR (thin film): $\nu_{max}(cm^{-1})$ = 3740, 3670, 3058, 3024, 2672, 2355,

2321, 2119, 1998, 1891, 1837, 1801, 1767, 1619, 1583, 1538, 1450, 1416, 1363, 1317, 1279, 1208, 1155, 1091, 1065, 1029, 979, 930, 854, 806, 750, 723, 680, 655, 627, 579, 518, 486, 442. HRMS-ESI calcd for $C_{17}H_{13}BrNO$ $[M+H]^+$: 326.0175. Found: 326.0170.



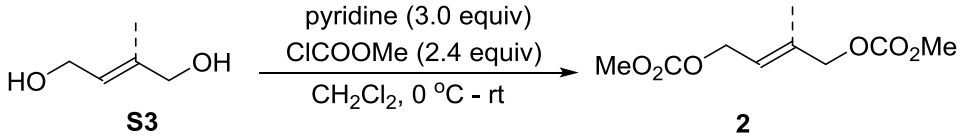
1o, yellow solid, m.p. = 141.9-142.8 ℃. 1.9 g, 59% yield (10 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:1.4) δ 15.65* (br s, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.96-7.89* (m, 2H), 7.73 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.60* (d, *J* = 2.0 Hz, 1H), 7.56* (dd, *J* = 8.8, 2.0 Hz, 1H), 7.50* (d, *J* = 9.2 Hz, 1H), 7.46-7.39* (m, 3H), 7.32* (d, *J* = 8.8 Hz, 1H), 6.84* (d, *J* = 9.2 Hz, 1H), 6.05* (s, 1H), 4.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 156.3, 154.4, 146.6, 139.1, 137.4, 135.5, 134.9, 133.9, 133.6, 133.1, 130.8, 130.7, 129.8, 129.7, 128.8, 128.8, 128.5, 126.7, 124.9, 123.5, 123.1, 120.5, 116.6, 90.9, 49.3. IR (thin film): ν_{max}(cm^{-1}) = 3081, 3054, 3032, 2959, 2921, 2851, 2626, 2376, 2312, 2175, 2120, 1993, 1891, 1811, 1784, 1763, 1716, 1632, 1579, 1550, 1527, 1440, 1419, 1378, 1335, 1306, 1262, 1222, 1187, 1156, 1085, 1065, 1020, 950, 926, 882, 852, 814, 789, 759, 735, 709, 690, 658, 629. HRMS-ESI calcd for $C_{17}H_{13}BrNO$ $[M+H]^+$: 326.0175. Found: 326.0170.



1q, yellow solid, m.p. = 146.1-146.7 ℃. 2.0 g, 58% yield (12 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) (ketone : enol = 1:11.1) δ 15.63* (br s, 1H), 8.13-8.08 (m, 2H), 8.08-8.03 (m, 1H), 7.97-7.89* (m, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.59* (d, *J* = 9.2 Hz, 1H), 7.50-7.39* (m, 5H), 7.19* (dd, *J* = 8.4, 2.0 Hz, 1H), 6.84* (d, *J* = 9.2 Hz, 1H), 6.08* (s, 1H), 4.67 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 154.7, 139.3, 139.2, 136.8, 136.4, 135.5, 133.6, 130.7, 128.9, 128.8, 128.7, 128.5, 128.2, 127.5, 126.8, 124.5, 122.6, 122.5, 122.0, 118.5, 90.9, 49.4. IR (thin film): ν_{max}(cm^{-1}) = 3087, 3036, 2382, 2321, 2303, 2174, 2114, 1994, 1939, 1886, 1799, 1622, 1590, 1539, 1493, 1449, 1424, 1395, 1335, 1320, 1295, 1193, 1175, 1148, 1130, 1096, 1072, 1025, 974, 934,

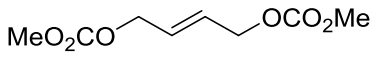
914, 856, 833, 788, 755, 719, 679, 650. HRMS-ESI calcd for $C_{17}H_{13}ClNO$ $[M+H]^+$: 282.0680. Found: 282.0677.

General procedure for the synthesis of substrates 2

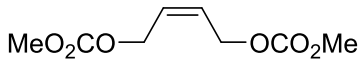


S3 **2**

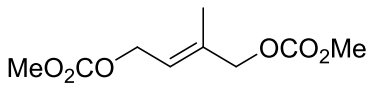
To a solution of **S3** (1.0 equiv) and pyridine (3.0 equiv) in CH_2Cl_2 (0.4 M) was added dropwisely methyl chloroformate (2.4 equiv) at 0 °C. After the addition was completed, the reaction mixture was slowly warmed to room temperature and stirred overnight. After the reaction was complete (monitored by TLC), the reaction was quenched with 2M HCl. The mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated by rotary evaporation. The residue was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford the desired product **2**.



2a, white solid, m.p. = 62.7-63.2 ℃ (Known compound, see: He, H.; Liu, W.-B.; Dai, L.-X.; You, S.-L. *Angew. Chem. Int. Ed.* **2010**, *49*, 1496). 2.3 g, 71% yield (16 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddd, *J* = 4.4, 3.2, 1.6 Hz, 2H), 4.68-4.63 (m, 4H), 3.80 (s, 6H).

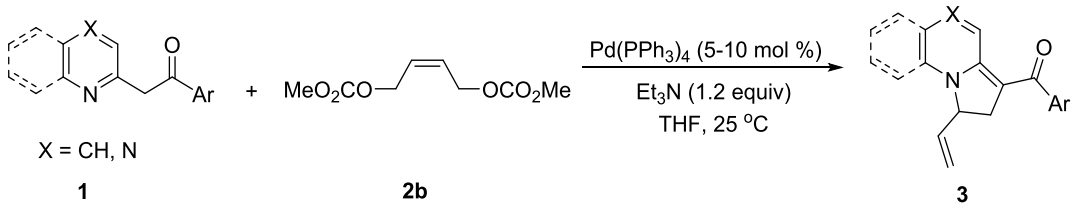


2b, colorless oil (Known compound, see: Wang, L.; Li, P.-F.; Menche, D. *Angew. Chem. Int. Ed.* **2010**, *49*, 9270). 2.5 g, 78% yield (16 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (t, *J* = 4.0 Hz, 2H), 4.76 (d, *J* = 5.2 Hz, 4H), 3.79 (s, 6H).

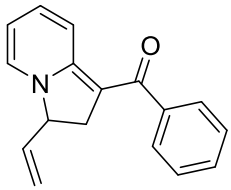


2c, white solid, m.p. = 37.7-37.9 ℃. 3.2 g, 93% yield (16 mmol scale). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77-5.61 (m, 1H), 4.70 (d, *J* = 6.4 Hz, 2H), 4.56 (s, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 155.6, 136.0, 121.7, 71.9, 63.9, 55.0, 54.9, 14.1. IR (thin film): $\nu_{max}(cm^{-1})$ = 3019, 2961, 2865, 1742, 1588, 1441, 1401, 1317, 1251, 1004, 932, 856, 784, 601, 567, 501, 443. HRMS-ESI calcd for $C_9H_{14}NaO_6$ $[M+Na]^+$: 241.0683. Found: 241.0683.

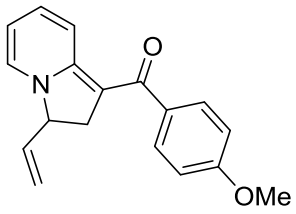
General procedure for Pd-catalyzed tandem allylic substitution reactions



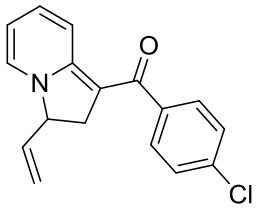
A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added **1** (0.4 mmol, 1.0 equiv), allylic carbonate **2b** (0.48 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (0.02 mmol, 5 mol %), Et_3N (0.48 mmol, 1.2 equiv) and THF (4 mL). The reaction mixture was stirred at room temperature. After the reaction was complete (monitored by TLC), brine (20 mL) was added to quench the reaction. This reaction mixture was extracted with EtOAc (3 x 15 mL). The extracts were combined, dried over Na_2SO_4, and evaporated under reduced pressure. The isomer ratio (**3f-3f'**, **3g-3g'** and **3h-3h'**) was determined by ^{1}H NMR of the crude reaction mixture. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH = 20/1) to afford the desired product **3**. The analytical data of the products are summarized below.



3a, red solid, m.p. = 78.4-79.3 ℃ (Known compound, see: Yang, Z.-P.; Wu, Q.-F.; You, S.-L. *Angew*. *Chem*. *Int*. *Ed*. **2014**, *53*, 6986). 73 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.65-7.03 (m, 7H), 6.20 (s, 1H), 5.98-5.82 (m, 1H), 5.35 (d, *J* = 9.6 Hz, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 4.77 (m, 1H), 3.42-3.26 (m, 1H), 2.92 (dd, *J* = 14.4, 8.4 Hz, 1H).

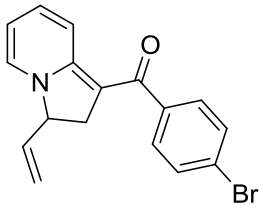


3b, red solid, m.p. = 108.6-110.3 ℃. 60.3 mg, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 3H), 7.47-6.91 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.14 (s, 1H), 5.92 (ddd, *J* = 17.2, 10.0, 8.8 Hz, 1H), 5.36 (d, *J* = 9.6 Hz, 1H), 5.34 (d, *J* = 16.8 Hz, 1H), 4.76 (m, 1H), 3.82 (s, 3H), 3.36 (dd, *J* = 14.4, 10.8 Hz, 1H), 2.96 (dd, *J* = 14.4, 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.0, 160.0, 154.8, 137.6, 136.1, 135.9, 134.2, 128.8, 120.2, 119.4, 113.2, 109.7, 96.9, 68.0, 55.2, 35.8. IR (thin film): ν_{max}(cm^{-1}) = 3063, 3008, 2945, 2920, 2844, 1622, 1602, 1578, 1523, 1472, 1442, 1420, 1404, 1331, 1294, 1243, 1182, 1163, 1128, 1106, 1090, 1018, 935, 868, 838, 802, 745, 690, 594, 527, 460. HRMS-ESI calcd for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1332. Found: 280.1327.

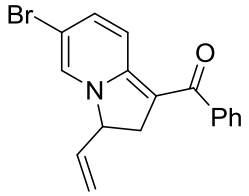


3c, red oil, 90.8 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.72-6.53 (m, 6H), 6.31 (s, 1H), 6.01-5.72 (m, 1H), 5.36 (d, *J* = 10.0 Hz, 1H), 5.34 (d, *J* = 17.6 Hz, 1H), 4.96-4.65 (m, 1H), 3.46-3.15 (m, 1H), 2.90 (dd, *J* = 14.0, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 155.3, 141.9, 138.6, 135.5, 134.1, 128.4, 127.8,

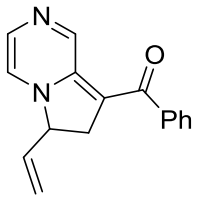
120.4, 119.8, 117.1, 111.0, 95.9, 68.5, 35.5. IR (thin film): $\nu_{max}(cm^{-1})$ = 3082, 2919, 2850, 1624, 1592, 1550, 1466, 1387, 1288, 1166, 1129, 1087, 1012, 836, 761, 522. HRMS-ESI calcd for $C_{17}H_{15}ClNO$ $[M+H]^+$: 284.0837. Found: 284.0834.



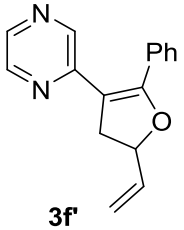
3d, red oil (Known compound, see: Yang, Z.-P.; Wu, Q.-F.; You, S.-L. *Angew*. *Chem*. *Int*. *Ed*. **2014**, *53*, 6986). 97.2 mg, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.65-7.03 (m, 6H), 6.30 (s, 1H), 6.04-5.80 (m, 1H), 5.39 (d, *J* = 9.6 Hz, 1H), 5.36 (d, *J* = 14.8 Hz, 1H), 4.93-4.68 (m, 1H), 3.44-3.19 (m, 1H), 2.92 (dd, *J* = 14.4, 8.4 Hz, 1H).



3e, red solid, m.p. = 113.5-114.7 ℃. 68.3 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05-6.58 (m, 8H), 6.01-5.82 (m, 1H), 5.41 (d, *J* = 8.8 Hz, 1H), 5.38 (d, *J* = 15.6 Hz, 1H), 4.86-4.70 (m, 1H), 3.40-3.17 (m, 1H), 2.94 (dd, *J* = 14.0, 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 185.7, 152.6, 143.1, 140.0, 135.4, 134.3, 129.1, 128.2, 126.9, 121.1, 120.2, 100.9, 68.3, 35.7. IR (thin film): $\nu_{max}(cm^{-1})$ = 3058, 3016, 2954, 2920, 2850, 1614, 1583, 1529, 1468, 1414, 1390, 1328, 1297, 1258, 1174, 1146, 1127, 1059, 1026, 998, 969, 950, 864, 838, 787, 724, 692, 657, 621, 528, 474, 417. HRMS-ESI calcd for $C_{17}H_{15}BrNO$ $[M+H]^+$: 328.0332. Found: 328.0326.



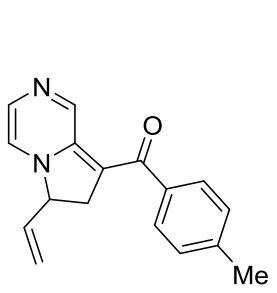
3f



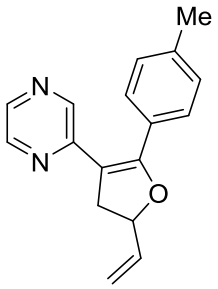
3f'

3f:**3f'** = 12.5:1

3f, dark solid, m.p. = 120.6-121.4 ℃ (Known compound, see: Yang, Z.-P.; Wu, Q.-F.; You, S.-L. *Angew*. *Chem*. *Int*. *Ed*. **2014**, *53*, 6986). 58.2 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.54 (d, *J* = 5.6 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.44-7.37 (m, 3H), 7.09 (d, *J* = 4.4 Hz, 1H), 6.82 (d, *J* = 4.0 Hz, 1H), 5.91 (ddd, *J* = 16.4, 9.6, 8.8 Hz, 1H), 5.42 (d, *J* = 9.6 Hz, 1H), 5.39 (d, *J* = 16.4 Hz, 1H), 4.82-4.67 (m, 1H), 3.35 (dd, *J* = 15.2, 11.6 Hz, 1H), 2.95 (dd, *J* = 15.6, 9.6 Hz, 1H).



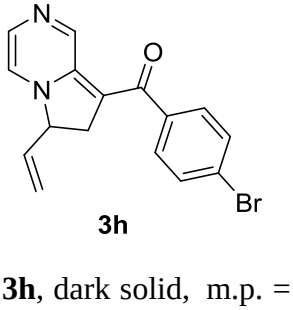
3g



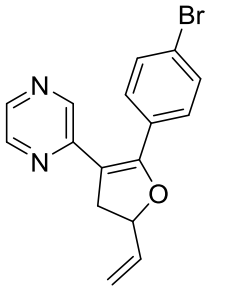
3g'

3g:**3g'** = 5.0:1

3g, dark solid, m.p. = 128.7-129.5 °C (Known compound, see: Yang, Z.-P.; Wu, Q.-F.; Shao, W.; You, S.-L. *J*. *Am*. *Chem*. *Soc*. **2015**, *137*, 15899). 54.3 mg, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 4.0 Hz, 1H), 6.85-6.70 (m, 1H), 5.99-5.82 (m, 1H), 5.42 (d, *J* = 9.6 Hz, 1H), 5.38 (d, *J* = 16.4 Hz, 1H), 4.78-4.66 (m, 1H), 3.36 (dd, *J* = 15.2, 12.0 Hz, 1H), 2.95 (dd, *J* = 15.6, 10.0 Hz, 1H), 2.38 (s, 3H).



3h

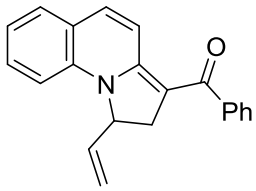


3h'

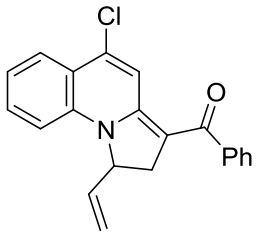
3h:**3h'** = 4.5:1

3h, dark solid, m.p. = 129.1-129.8 ℃ (Known compound, see: Yang, Z.-P.; Wu, Q.-F.; Shao, W.; You, S.-L. *J*. *Am*. *Chem*. *Soc*. **2015**, *137*, 15899). 48.7 mg, 37% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 4.0 Hz, 1H), 6.86 (d, *J* = 3.2 Hz, 1H), 5.92 (ddd, *J* = 17.2, 10.0, 8.8 Hz, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 5.41 (d, *J* = 18.0 Hz, 1H), 4.83-4.70 (m, 1H), 3.34 (dd, *J* = 15.2, 11.6 Hz, 1H), 2.94 (dd, *J* = 15.2, 9.6 Hz, 1H).

3h', brown solid, m.p. = 61.7-62.5 ℃. 10.5 mg, 8% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (t, *J* = 3.2, 1.6, 1.6 Hz, 1H), 8.38-8.33 (m, 1H), 8.22 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 6.09 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.0 Hz, 1H), 5.26-5.20 (m, 1H), 3.46 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.14 (dd, *J* = 15.2, 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 150.9, 143.8, 143.1, 140.6, 137.2, 131.9, 130.1, 130.0, 124.2, 117.1, 108.6, 81.5, 39.4. IR (thin film): ν_{max}(cm^{-1}) = 3645, 3357, 3063, 2993, 2920, 2853, 2383, 2322, 2289, 2237, 2180, 2101, 1992, 1913, 1719, 1633, 1583, 1512, 1482, 1403, 1356, 1233, 1150, 1099, 1067, 1003, 916, 829, 728, 650, 623, 528, 473. HRMS-ESI calcd for $C_{16}H_{14}BrN_2O$ $[M+H]^+$: 329.0284. Found: 329.0278.

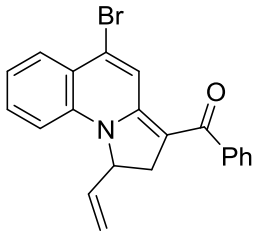


3i, yellow solid, m.p. = 132.5-133.2 ℃ (Known compound, see: Yang, Z.-P.; Wu, Q.-F.; Shao, W.; You, S.-L. *J. Am. Chem. Soc.* **2015**, *137*, 15899). 104.3 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.50 (m, 2H), 7.46-7.16 (m, 7H), 7.10-7.00 (m, 2H), 5.91 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 5.12 (d, *J* = 17.5 Hz, 1H), 5.13-5.04 (m, 1H), 3.54 (dd, *J* = 14.8, 11.6 Hz, 1H), 2.91 (dd, *J* = 15.2, 2.4 Hz, 1H).

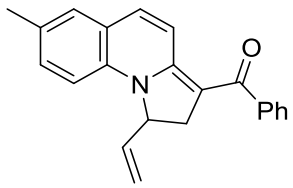


3j, red solid, m.p. = 96.2-97.1 ℃. 79.7 mg, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (s, 1H), 7.61-7.51 (m, 2H), 7.49-7.36 (m, 4H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 5.90 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 5.14 (d, *J* = 17.2 Hz, 1H), 5.11-5.06 (m, 1H), 3.55 (dd, *J* = 15.2, 11.6 Hz, 1H), 2.89 (dd, *J* = 15.2, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 151.4, 142.7, 142.1, 138.5, 135.8, 132.1, 129.8, 128.4, 127.2, 125.9, 122.3, 121.5,

118.8, 116.6, 114.3, 102.6, 62.9, 36.8. IR (thin film): $\nu_{max}(cm^{-1})$ = 3057, 2921, 2851, 2326, 2118, 2086, 1918, 1742, 1678, 1612, 1598, 1547, 1508, 1467, 1442, 1390, 1318, 1245, 1169, 1140, 1072, 998, 950, 925, 883, 844, 753, 717, 697. HRMS-ESI calcd for $C_{21}H_{17}ClNO$ $[M+H]^+$: 334.0993. Found: 334.0987.

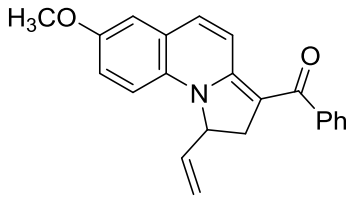


3k, red solid, m.p. = 85.8-86.1 ℃. 63.2 mg, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.61-7.51 (m, 2H), 7.49-7.36 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.89 (ddd, *J* = 17.2, 10.0, 7.6 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 5.14 (d, *J* = 18.0 Hz, 1H), 5.10-5.02 (m, 1H), 3.54 (dd, *J* = 14.8, 12.0 Hz, 1H), 2.93-2.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 151.4, 142.7, 138.3, 135.8, 133.8, 132.1, 129.8, 128.6, 128.3, 127.2, 122.8, 122.5, 122.4, 116.6, 114.2, 102.4, 62.9, 36.7. IR (thin film): $\nu_{max}(cm^{-1})$ = 3079, 3056, 2921, 2851, 2653, 2331, 2308, 2118, 2090, 2068, 1994, 1743, 1711, 1679, 1608, 1581, 1543, 1505, 1467, 1439, 1387, 1316, 1285, 1266, 1245, 1170, 1096, 1072, 1045, 1024, 998, 969, 949, 922, 903, 885, 845, 789, 748, 716, 699, 656, 614. HRMS-ESI calcd for $C_{21}H_{17}BrNO$ $[M+H]^+$: 378.0488. Found: 378.0477.

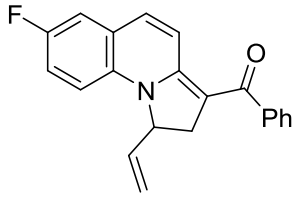


3l, red oil, 98.6 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.51 (m, 2H), 7.50-7.25 (m, 4H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.15 (s, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.89 (ddd, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.15 (d, *J* = 10.4 Hz, 1H), 5.10 (d, *J* = 17.6 Hz, 1H), 5.11-5.04 (m, 1H), 3.53 (dd, *J* = 14.8, 11.6 Hz, 1H), 2.90 (dd, *J* = 15.2, 2.8 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 152.7, 143.2, 136.1, 136.0, 132.2, 131.6, 129.7, 129.2, 128.2, 128.1, 127.1, 123.3, 118.8, 116.1, 113.9, 102.1, 62.7, 36.4, 20.6. IR (thin film): $\nu_{max}(cm^{-1})$ = 3667, 3055, 3023, 2920, 2854, 2220, 1614, 1581, 1565, 1505, 1476, 1414, 1369, 1343, 1293, 1266, 1235, 1170, 1118, 1070,

1055, 1026, 997, 945, 921, 884, 826, 805, 787, 753, 718, 696, 664, 643. HRMS-ESI calcd for $C_{22}H_{20}NO$ $[M+H]^+$: 314.1539. Found: 314.1531.

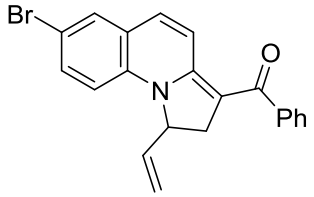


3m, red solid, m.p. = 118.3-118.9 ℃. 112.9 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.52 (m, 2H), 7.51-7.26 (m, 4H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.08-6.98 (m, 2H), 6.84 (s, 1H), 5.88 (ddd, *J* = 17.6, 10.4, 7.2 Hz, 1H), δ 5.14 (d, *J* = 10.4 Hz, 1H), 5.09 (d, *J* = 17.2 Hz, 1H), 5.10-5.03 (m, 1H), 3.78 (s, 3H), 3.53 (dd, *J* = 14.8, 11.6 Hz, 1H), 2.89 (dd, *J* = 14.8, 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 154.7, 152.5, 143.3, 136.1, 136.0, 132.6, 129.1, 128.1, 127.1, 124.1, 119.6, 119.5, 116.1, 115.3, 110.1, 101.5, 63.0, 55.6, 36.4. IR (thin film): ν_{max}(cm^{-1}) = 3360, 3055, 3008, 2921, 2851, 2325, 2117, 2088, 1997, 1892, 1864, 1708, 1612, 1563, 1505, 1476, 1442, 1412, 1340, 1284, 1239, 1190, 1172, 1127, 1070, 1053, 1026, 997, 947, 922, 865, 800, 788, 751, 717, 697, 665. HRMS-ESI calcd for $C_{22}H_{20}NO_2$ $[M+H]^+$: 330.1489. Found: 330.1482.

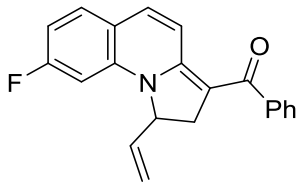


3n, red solid, m.p. = 67.2-67.9 ℃. 92.3 mg, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 5.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.51-7.22 (m, 4H), 7.16 (d, *J* = 9.6 Hz, 1H), 7.10 (td, *J* = 8.6, 2.8 Hz, 1H), 7.07-6.97 (m, 2H), 5.90 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 5.09-5.03 (m, 1H), 3.55 (dd, *J* = 15.2, 11.6 Hz, 1H), 2.91 (dd, *J* = 15.2, 3.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.5 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 157.6 (d, *J* = 242.6 Hz) 152.3, 143.0, 135.9, 135.2 (d, *J* = 1.9 Hz), 134.8 (d, *J* = 1.2 Hz), 129.6, 128.3, 127.2, 124.2 (d, *J* = 8.6 Hz), 120.4, 118.6 (d, *J* = 24.0 Hz), 116.4, 115.4 (d, *J* = 8.0 Hz), 113.4 (d, *J* = 22.6 Hz), 102.9, 63.0, 36.6. IR (thin film): ν_{max}(cm^{-1}) = 3057, 2920,

2853, 2120, 2080, 1706, 1622, 1566, 1510, 1478, 1421, 1370, 1342, 1287, 1239, 1155, 1127, 1071, 1055, 1025, 998, 937, 872, 845, 805, 787, 750, 713, 666, 623. HRMS-ESI calcd for $C_{21}H_{17}FNO$ $[M+H]^+$: 318.1289. Found: 318.1281.

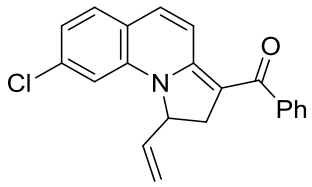


3o, red solid, m.p. = 83.1-83.6 ℃. 125.9 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.49 (m, 2H), 7.46-7.34 (m, 5H), 7.29 (s, 1H), 7.06 (d, *J* = 10.0 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 5.87 (ddd, *J* = 17.2, 10.4, 6.8 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 5.10 (d, *J* = 17.2 Hz, 1H), 5.02 (ddd, *J* = 10.4, 6.8, 3.2 Hz, 1H), 3.52 (dd, *J* = 15.2, 11.6 Hz, 1H), 2.88 (dd, *J* = 15.2, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 151.8, 142.7, 137.1, 135.6, 134.5, 133.5, 130.2, 129.6, 128.2, 127.1, 124.7, 120.1, 116.4, 115.4, 114.2, 103.5, 62.6, 36.6. IR (thin film): ν_{max}(cm^{-1}) = 3054, 2919, 2850, 2100, 1678, 1620, 1582, 1503, 1469, 1410, 1366, 1287, 1259, 1202, 1175, 1157, 1133, 1075, 1055, 1024, 997, 943, 879, 804, 787, 749, 698, 664. HRMS-ESI calcd for $C_{21}H_{17}BrNO$ $[M+H]^+$: 378.0488. Found: 378.0479.

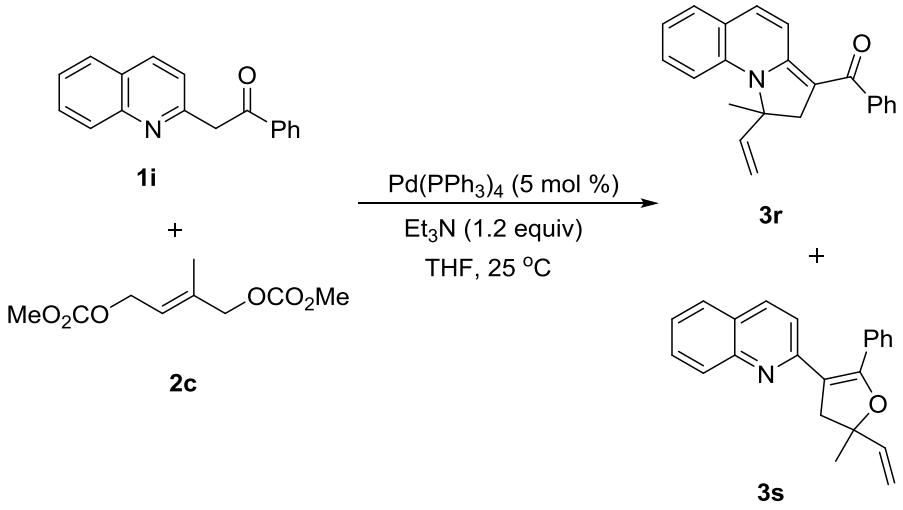


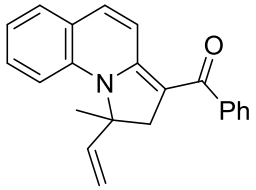
3p, red solid, m.p. = 115.9-116.4 ℃. 101.6 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.48 (m, 2H), 7.47-7.31 (m, 3H), 7.31-7.20 (m, 2H), 7.15 (d, *J* = 9.6 Hz, 1H), 6.80-6.67 (m, 2H), 5.89 (ddd, *J* = 17.6, 10.4, 7.2 Hz, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 5.15 (d, *J* = 17.2 Hz, 1H), 4.99 (ddd, *J* = 10.8, 6.8, 3.2 Hz, 1H), 3.54 (dd, *J* = 15.2, 11.6 Hz, 1H), 2.89 (dd, *J* = 15.2, 3.2 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.2 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 164.1 (d, *J* = 250.1 Hz), 152.2, 142.8, 139.7 (d, *J* = 12.0 Hz), 135.5, 135.3, 130.0 (d, *J* = 10.4 Hz), 129.6, 128.2, 127.2, 119.8 (d, *J* = 2 Hz), 117.9 (d, *J* = 2.6 Hz), 116.6, 109.7 (d, *J* = 23.1 Hz), 103.3, 100.8 (d, *J* = 27.0 Hz), 62.8, 36.6. IR (thin film): ν_{max}(cm^{-1}) = 3082, 3058, 3038, 2956, 2910, 2851, 2324, 2267, 2219, 2114, 2088, 1996, 1951, 1906, 1861, 1828, 1810, 1715,

1624, 1570, 1518, 1472, 1411, 1373, 1332, 1293, 1251, 1219, 1192, 1164, 1140, 1123, 1089, 1057, 1024, 990, 922, 897, 857, 830, 784, 718, 698, 669, 645. HRMS-ESI calcd for $C_{21}H_{17}FNO$ $[M+H]^+$: 318.1289. Found: 318.1281.

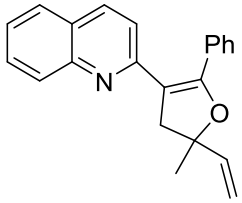


3q, red solid, m.p. = 98.5-99.7 ℃. 110.8 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.50 (m, 2H), 7.44-7.34 (m, 3H), 7.32-7.17 (m, 2H), 7.12 (d, *J* = 10.0 Hz, 1H), 6.97 (d, *J* = 10.4 Hz, 2H), 5.88 (ddd, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 5.14 (d, *J* = 17.2 Hz, 1H), 5.00 (ddd, *J* = 10.8, 6.8, 3.2 Hz, 1H), 3.53 (dd, *J* = 15.2, 11.6 Hz, 1H), 2.88 (dd, *J* = 15.2, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 151.9, 142.8, 139.0, 136.7, 135.5, 135.1, 129.7, 129.1, 128.3, 127.2, 122.0, 121.7, 119.1, 116.6, 113.7, 103.5, 62.5, 36.6. IR (thin film): ν_{max}(cm^{-1}) = 3668, 3058, 2921, 2852, 2225, 2122, 2093, 1708, 1620, 1581, 1508, 1466, 1404, 1373, 1320, 1277, 1250, 1213, 1175, 1158, 1131, 1092, 1057, 1025, 999, 965, 921, 877, 833, 785, 749, 701, 669, 644, 619. HRMS-ESI calcd for $C_{21}H_{17}ClNO$ $[M+H]^+$: 334.0993. Found: 334.0987.



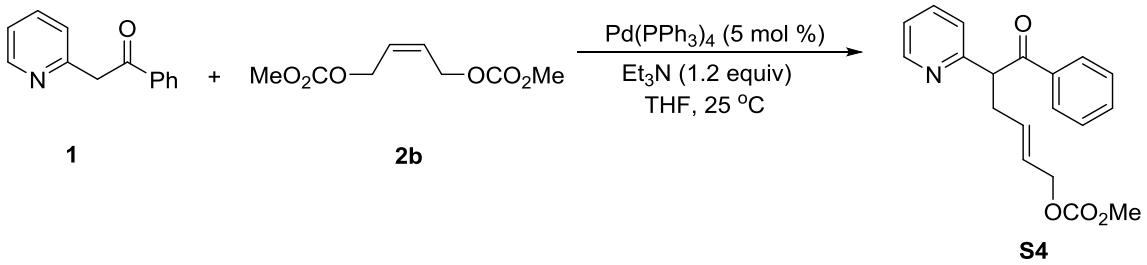


3r, red oil. 55.2 mg, 44% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.46 (m, 4H), 7.43-7.35 (m, 3H), 7.31 (m, 2H), 7.21 (d, *J* = 9.2 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.37 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.32 (d, *J* = 14.4 Hz, 1H), 5.29 (d, *J* = 7.6 Hz, 1H), 3.25 (d, *J* = 14.8 Hz, 1H), 2.97 (d, *J* = 15.2 Hz, 1H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 152.6, 143.3, 143.2, 137.9, 136.2, 130.3, 129.3, 128.6, 128.1, 127.1, 124.1, 121.8, 119.1, 114.4, 113.6, 101.4, 70.1, 46.9, 22.1. IR (thin film): $\nu_{max}(cm^{-1})$ = 3393, 3189, 3058, 2920, 2851, 2437, 2383, 2321, 2120, 1997, 1912, 1703, 1617, 1512, 1466, 1415, 1372, 1249, 1221, 1126, 1068, 1024, 992, 919, 872, 828, 784, 755, 711, 658, 613, 511, 434. HRMS-ESI calcd for $C_{22}H_{20}NO$ $[M+H]^+$: 314.1539. Found: 314.1532.



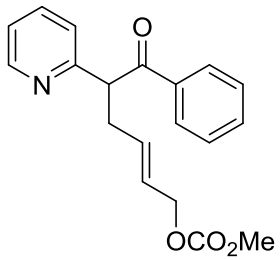
3s, yellow solid, m.p. = 67.6-68.1 ℃. 38.9 mg, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.66-7.55 (m, 4H), 7.42-7.30 (m, 4H), 7.17 (d, *J* = 8.8 Hz, 1H), 6.15 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.40 (d, *J* = 18.0 Hz, 1H), 5.14 (d, *J* = 10.8 Hz, 1H), 3.48 (d, *J* = 15.2 Hz, 1H), 3.39 (d, *J* = 15.2 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 155.0, 148.3, 142.2, 134.6, 132.0, 129.7, 129.3, 128.90, 128.88, 128.5, 127.4, 126.3, 125.5, 120.8, 112.6, 111.5, 85.2, 46.1, 26.5. IR (thin film): $\nu_{max}(cm^{-1})$ = 3875, 3772, 3734, 3695, 3657, 3447, 3388, 3052, 2973, 2909, 2850, 2652, 2435, 2386, 2342, 2246, 2212, 2098, 1994, 1946, 1914, 1885, 1840, 1811, 1768, 1722, 1631, 1597, 1549, 1496, 1448, 1417, 1363, 1330, 1295, 1234, 1180, 1110, 1067, 1027, 981, 926, 876, 826, 796, 756, 692, 648, 597, 517, 470. HRMS-ESI calcd for $C_{22}H_{20}NO$ $[M+H]^+$: 314.1539. Found: 314.1531.

Procedure for the synthesis of intermediate S4



1 **2b** **S4**

A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added **1** (0.4 mmol, 1.0 equiv), allylic carbonate **2b** (0.48 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (0.02 mmol, 5 mol %), Et_3N (0.48 mmol, 1.2 equiv) and THF (4 mL). The reaction mixture was stirred at room temperature for 2 h. After the generation of intermediate (monitored by TLC), brine (20 mL) was added to quench the reaction. This mixture was extracted with EtOAc (3 x 15 mL). The extracts were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EtOAc = 5/1) to afford **S4**.



S4, yellow oil (Known compound, see: Yang, Z.-P.; Wu, Q.-F.; You, S.-L. *Angew. Chem. Int. Ed.* **2014**, *53*, 6986). 75.5 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 2H), 7.60 (td, *J* = 8.0, 1.6 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.12 (dd, *J* = 7.2, 5.2 Hz, 1H), 5.84-5.72 (m, 1H), 5.69-5.54 (m, 1H), 4.91 (t, *J* = 7.2 Hz, 1H), 4.49 (d, *J* = 6.4 Hz, 2H), 3.74 (s, 3H), 3.01 (dt, *J* = 14.4, 7.2 Hz, 1H), 2.70 (dt, *J* = 14.0, 7.2, 6.8 Hz, 1H).

X-Ray crystal structure of 3r

CCDC 1890277

The crystal was obtained by slow evaporation of solution (DCM/PE = 10/1) of **3r**

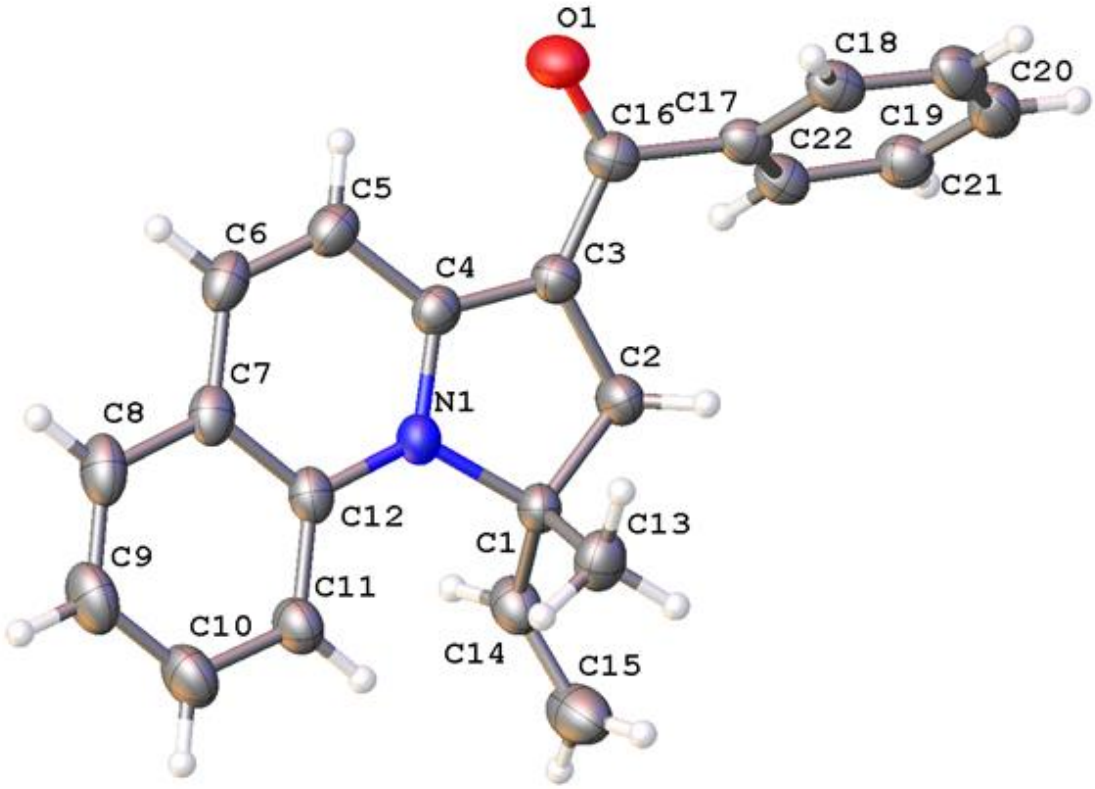


Table S4. Crystal data and structure refinement for mjl18654_0m.

Identification code	mjl18654_0m	
Empirical formula	C22 H19 N O	
Formula weight	313.38	
Temperature	297.89 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 23.4482(7) Å	α= 90 °.
	b = 10.6406(3) Å	β=129.2630(10) °.
	c = 17.9022(5) Å	γ = 90 °.
Volume	3458.30(18) $Å^3$	
Z	8	
Density (calculated)	1.204 Mg/m^3	

Absorption coefficient	0.367 mm^{-1}
F(000)	1328
Crystal size	0.2 x 0.18 x 0.15 mm^3
Theta range for data collection	4.190 to 54.927 °.
Index ranges	-28<=h<=28, -11<=k<=12, -21<=l<=21
Reflections collected	12776
Independent reflections	3271 [R(int) = 0.0540]
Completeness to theta = 53.594 °	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5759
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3271 / 0 / 218
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0570, wR2 = 0.1588
R indices (all data)	R1 = 0.0713, wR2 = 0.1716
Extinction coefficient	n/a
Largest diff. peak and hole	0.475 and -0.238 e.$Å^{-3}$

X-Ray crystal structure of 3s·HCl

CCDC 1905118

The crystal was obtained by slow evaporation of solution (DCM/n-pentane = 10/1) of **3s**·HCl

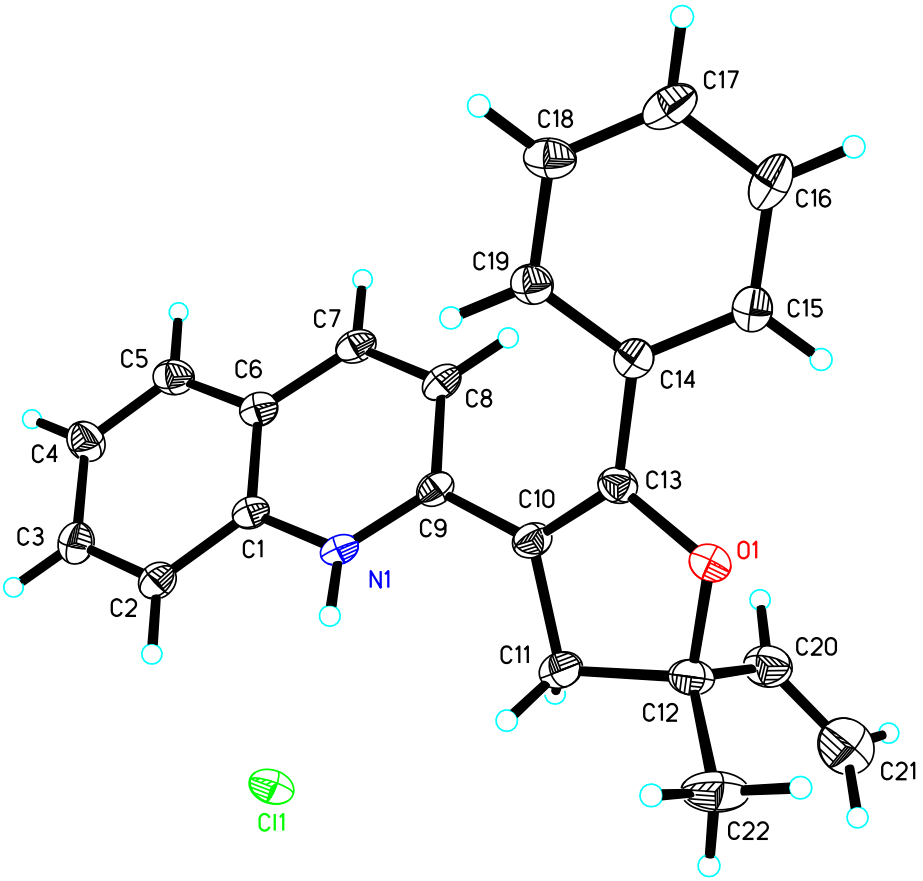


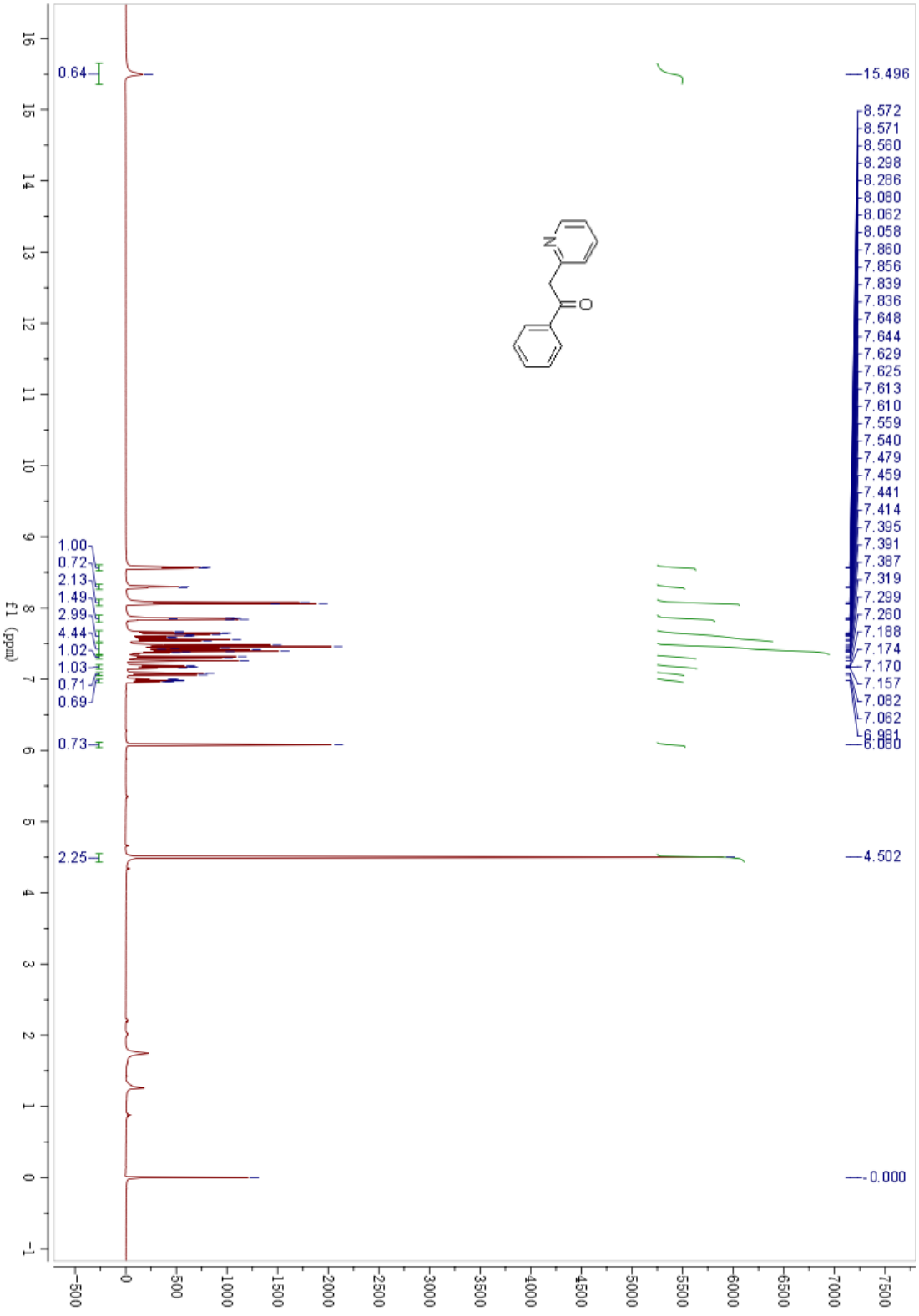
Table S5. Crystal data and structure refinement for d8v19161.

Identification code	d8v19161
Empirical formula	C22 H20 Cl N O
Formula weight	349.84
Temperature	193(2) K
Wavelength	0.71073 Å

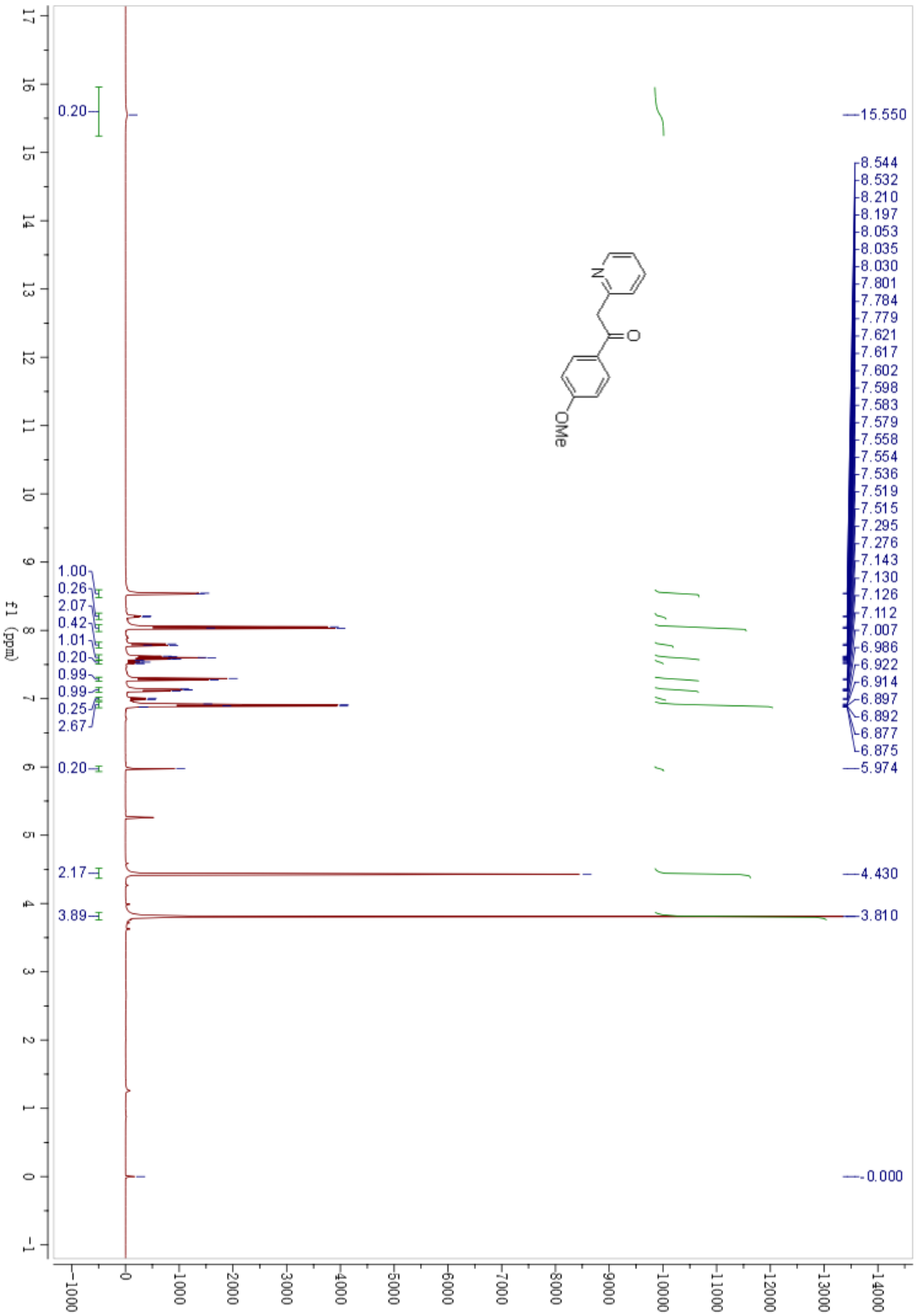
Crystal system	Orthorhombic	
Space group	I b a 2	
Unit cell dimensions	a = 18.4720(5) Å	α= 90 °.
	b = 29.1767(10) Å	β= 90 °.
	c = 6.8903(2) Å	γ = 90 °.
Volume	3713.54(19) $Å^3$	
Z	8	
Density (calculated)	1.251 Mg/m^3	
Absorption coefficient	0.214 mm^{-1}	
F(000)	1472	
Crystal size	0.200 x 0.130 x 0.090 mm^3	
Theta range for data collection	3.451 to 25.497 °.	
Index ranges	-22<=h<=20, -35<=k<=35, -8<=l<=8	
Reflections collected	17889	
Independent reflections	3440 [R(int) = 0.0376]	
Completeness to theta = 25.242 °	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6700	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3440 / 34 / 258	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.1058	
R indices (all data)	R1 = 0.0422, wR2 = 0.1089	
Absolute structure parameter	-0.02(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.602 and -0.220 $e.Å^{-3}$	

Copies of NMR spectra

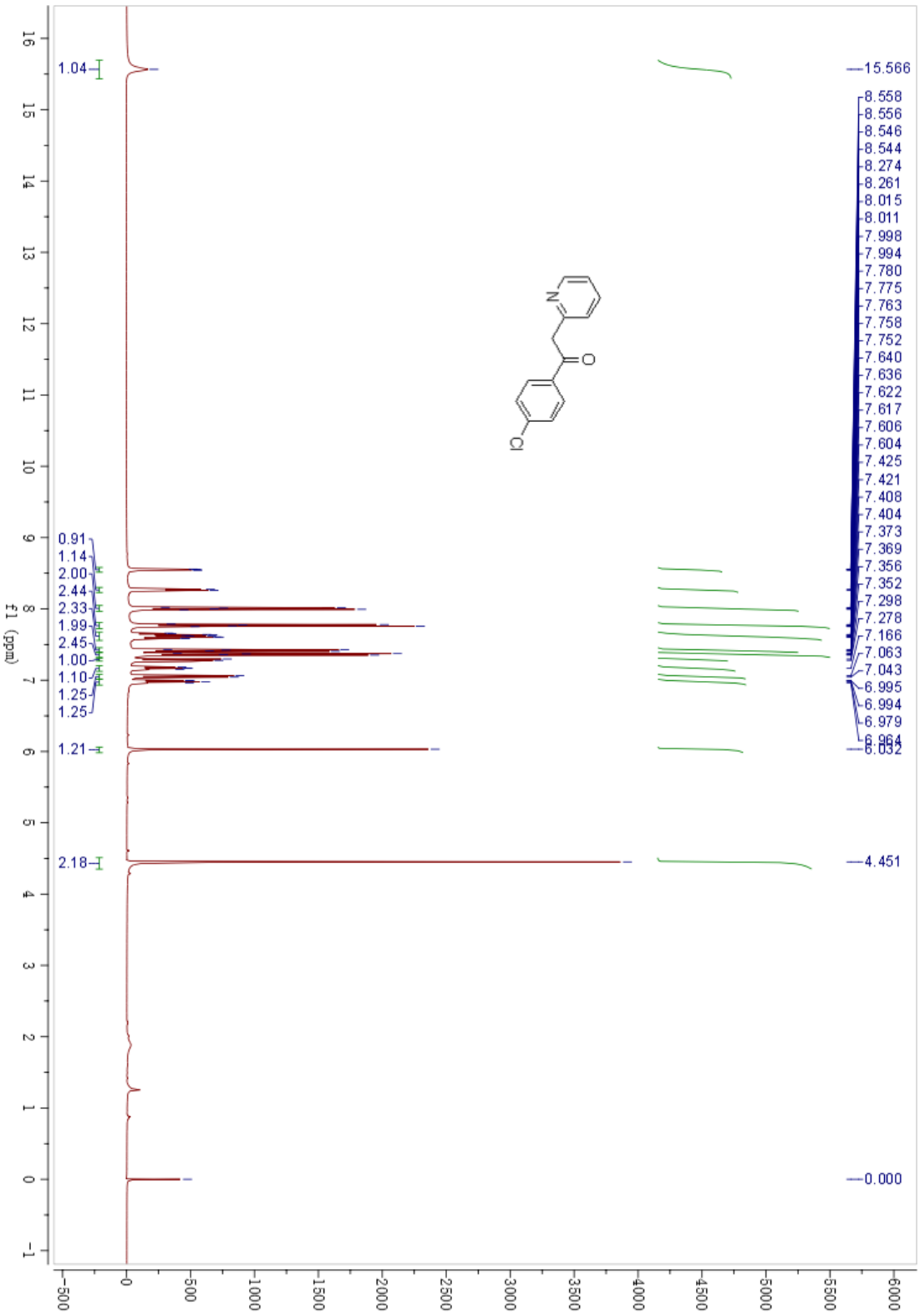
^{1}H NMR spectra of **1a**



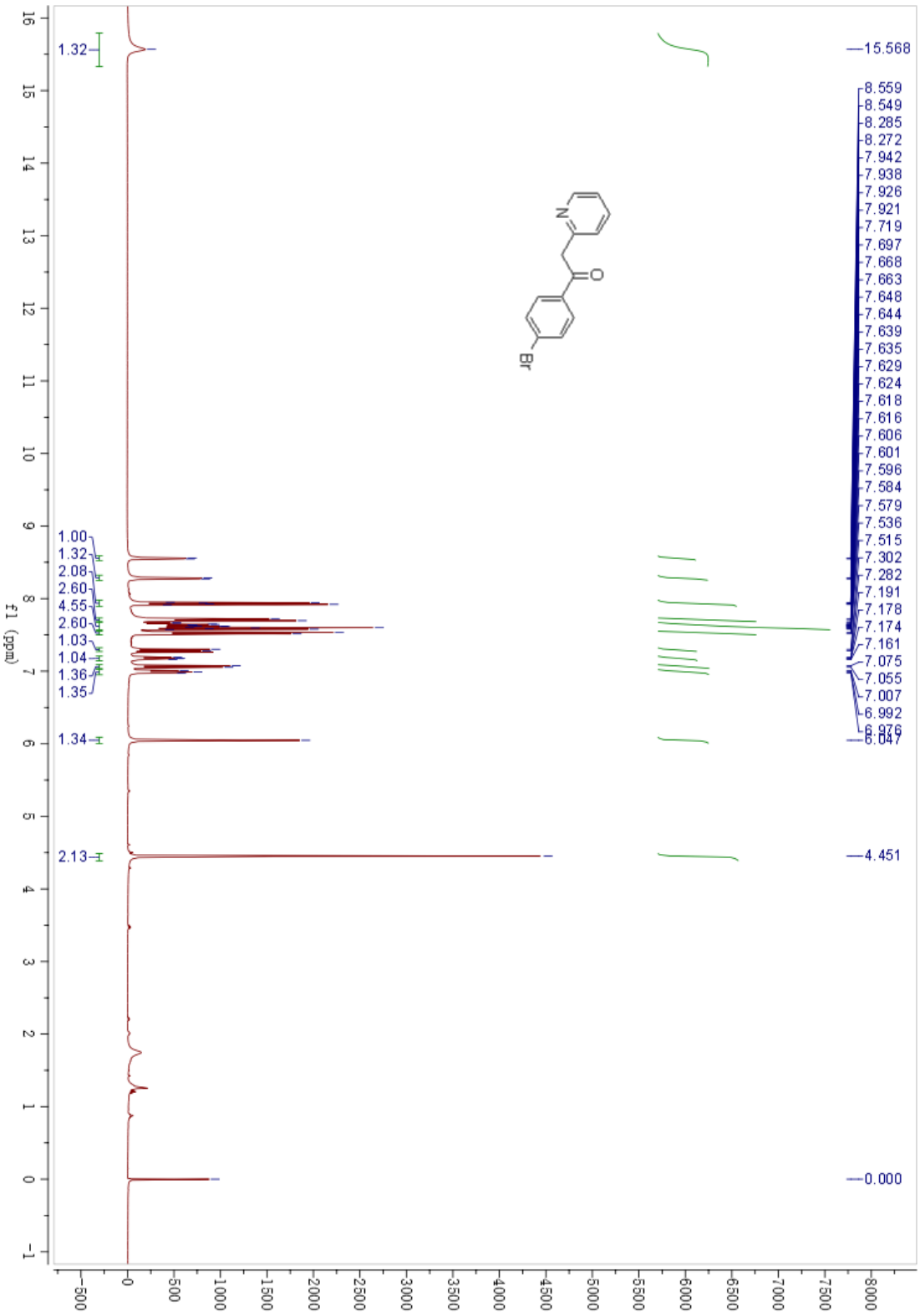
^{1}H NMR spectra of **1b**



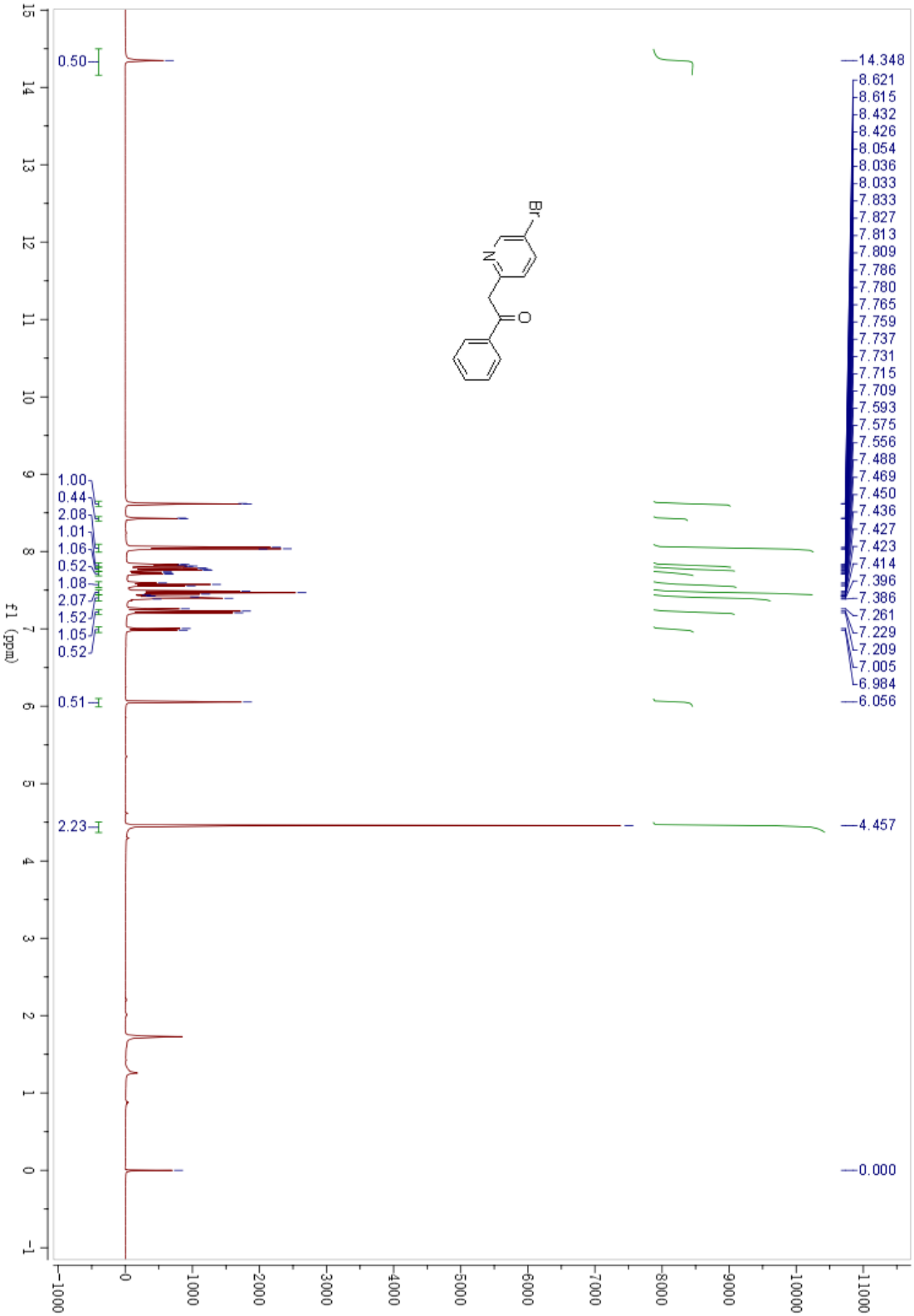
^{1}H NMR spectra of **1c**



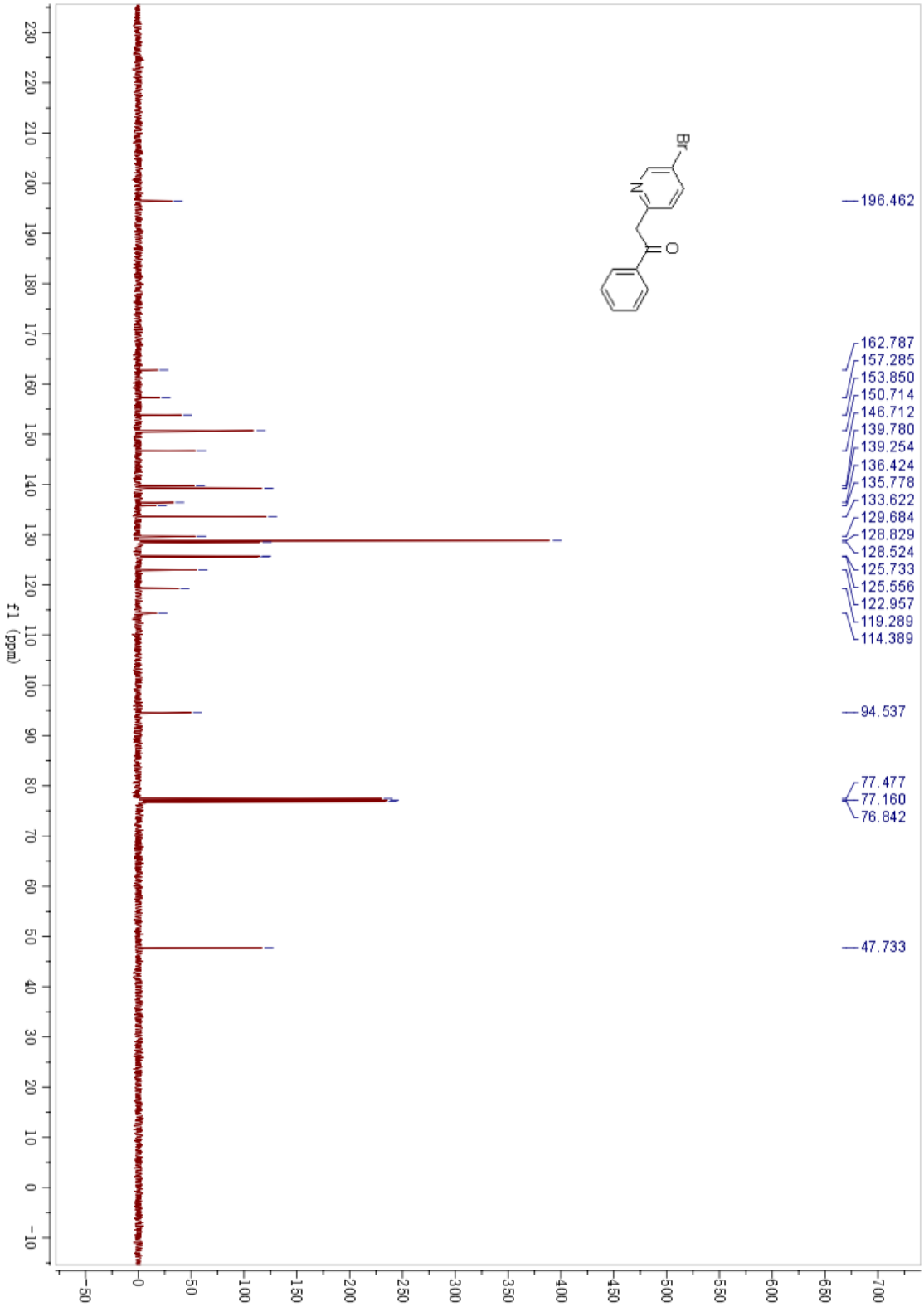
^{1}H NMR spectra of **1d**



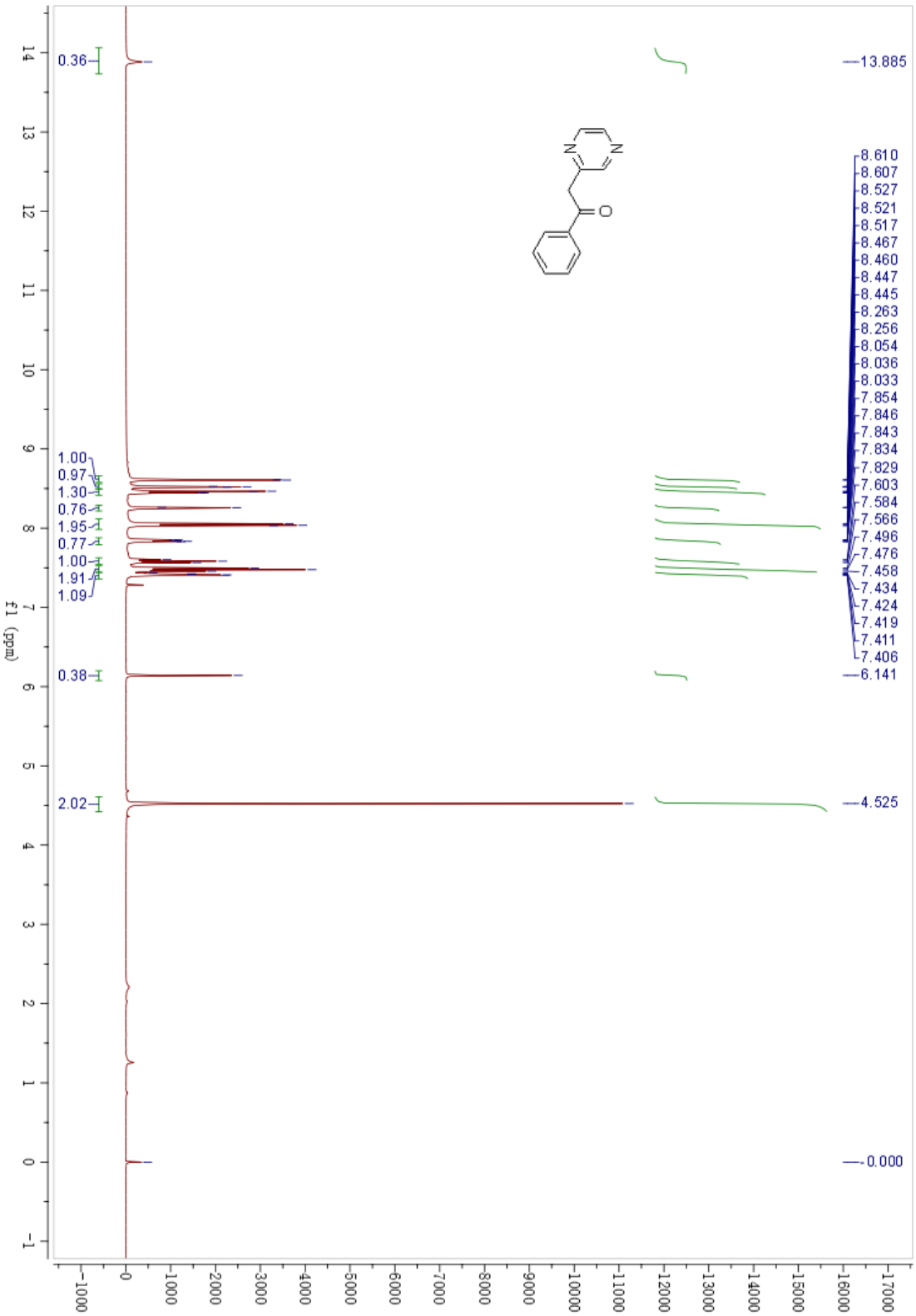
^{1}H NMR spectra of **1e**



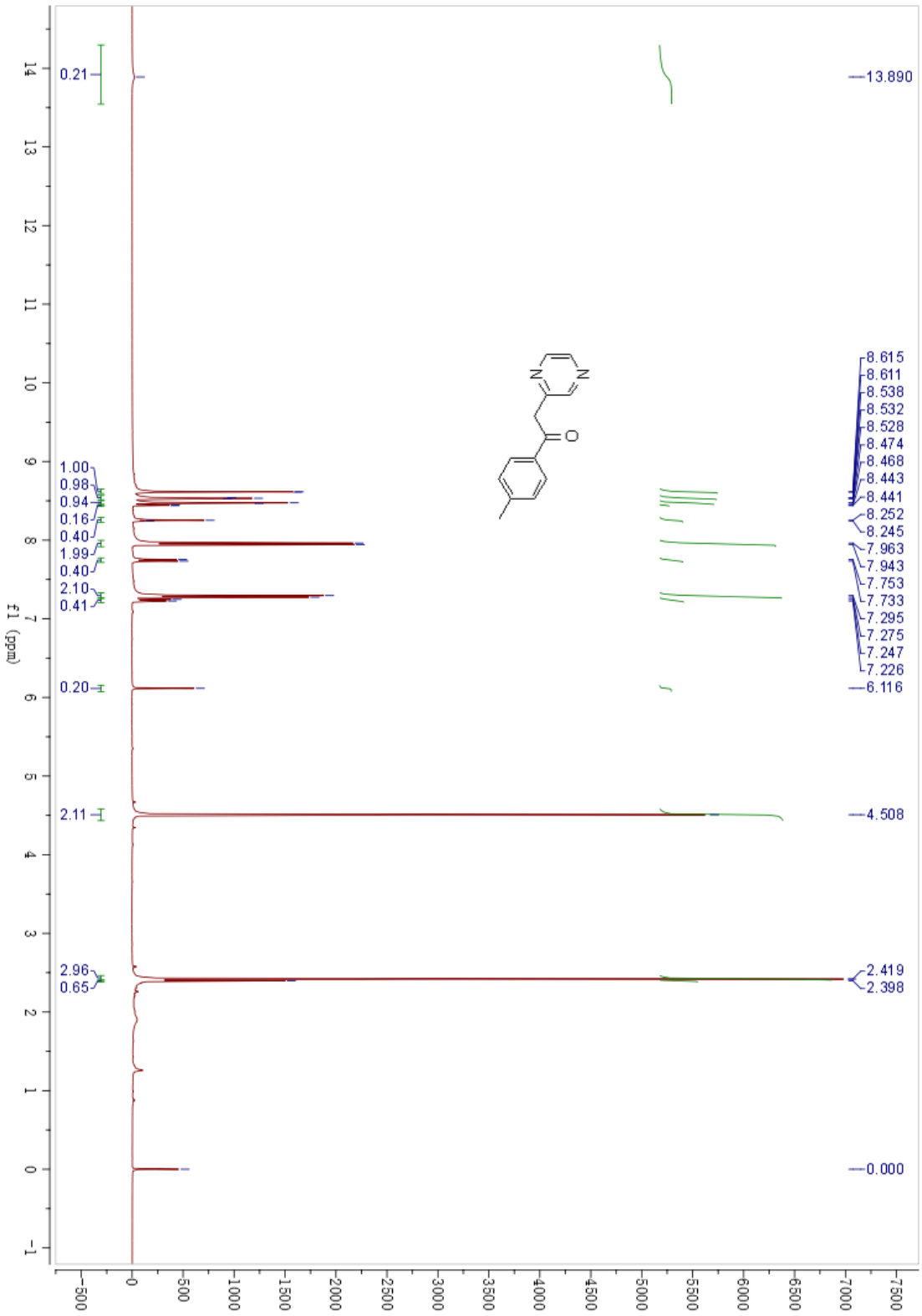
^{13}C NMR spectra of **1e**



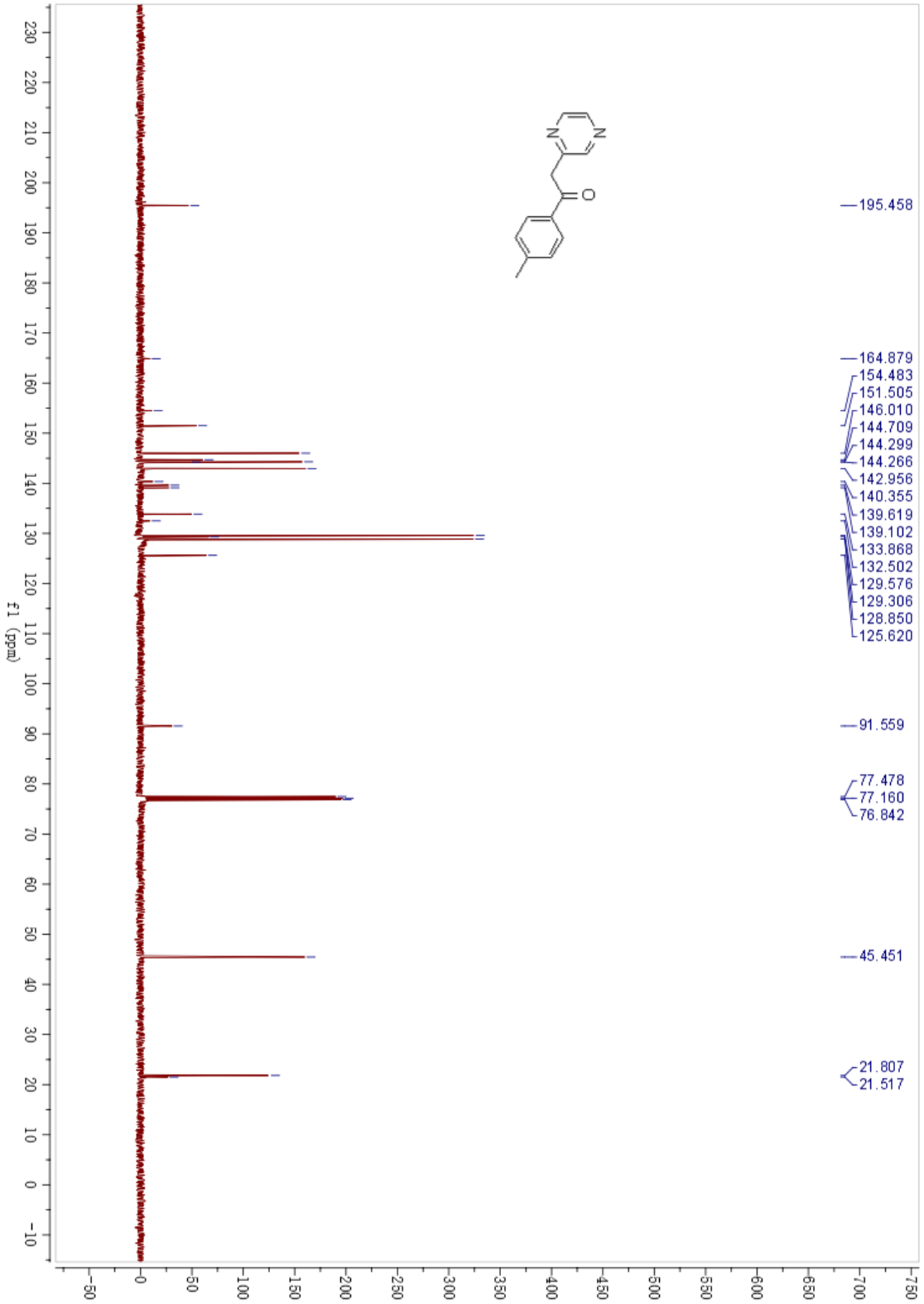
^{1}H NMR spectra of **1f**



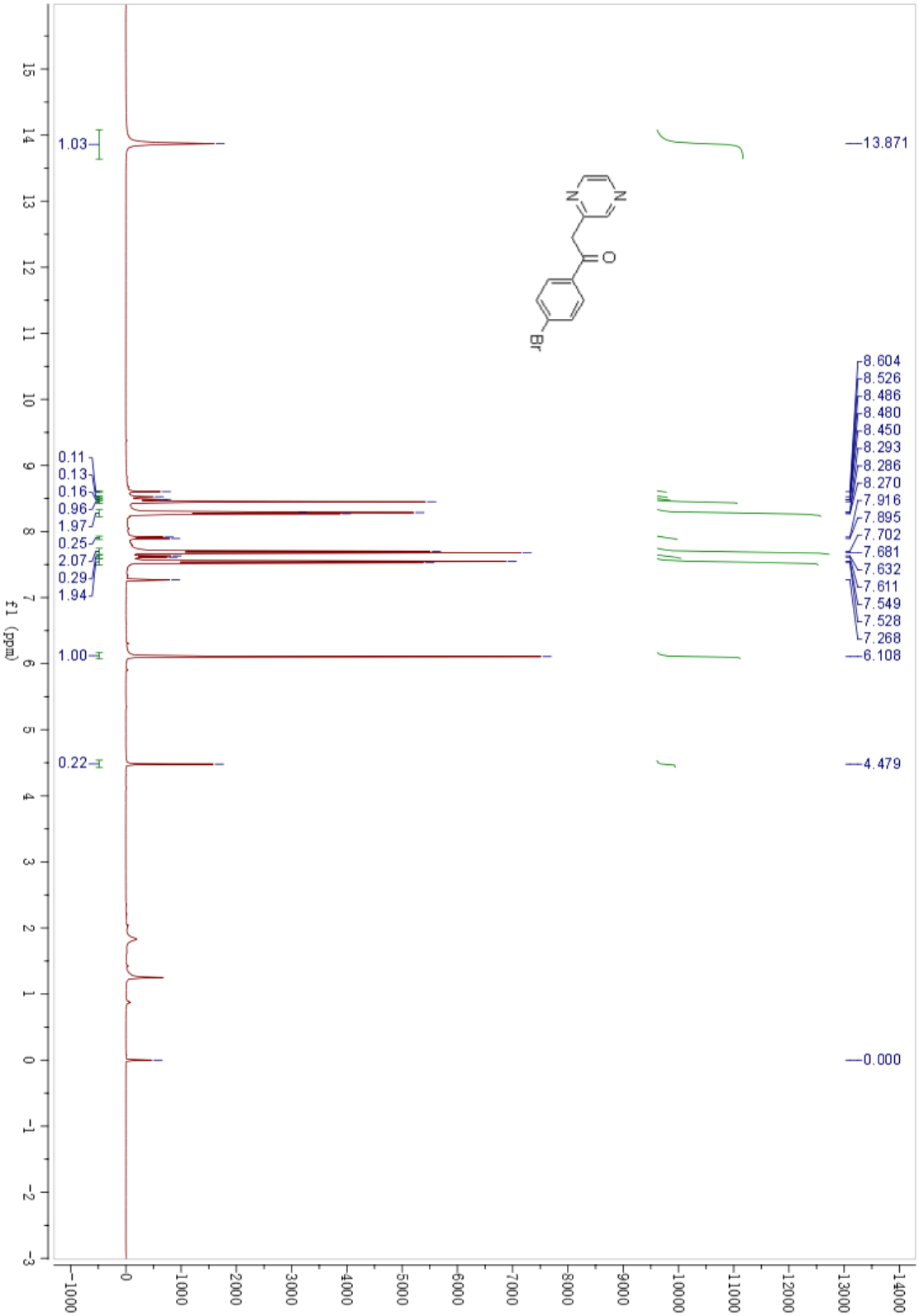
^{1}H NMR spectra of **1g**



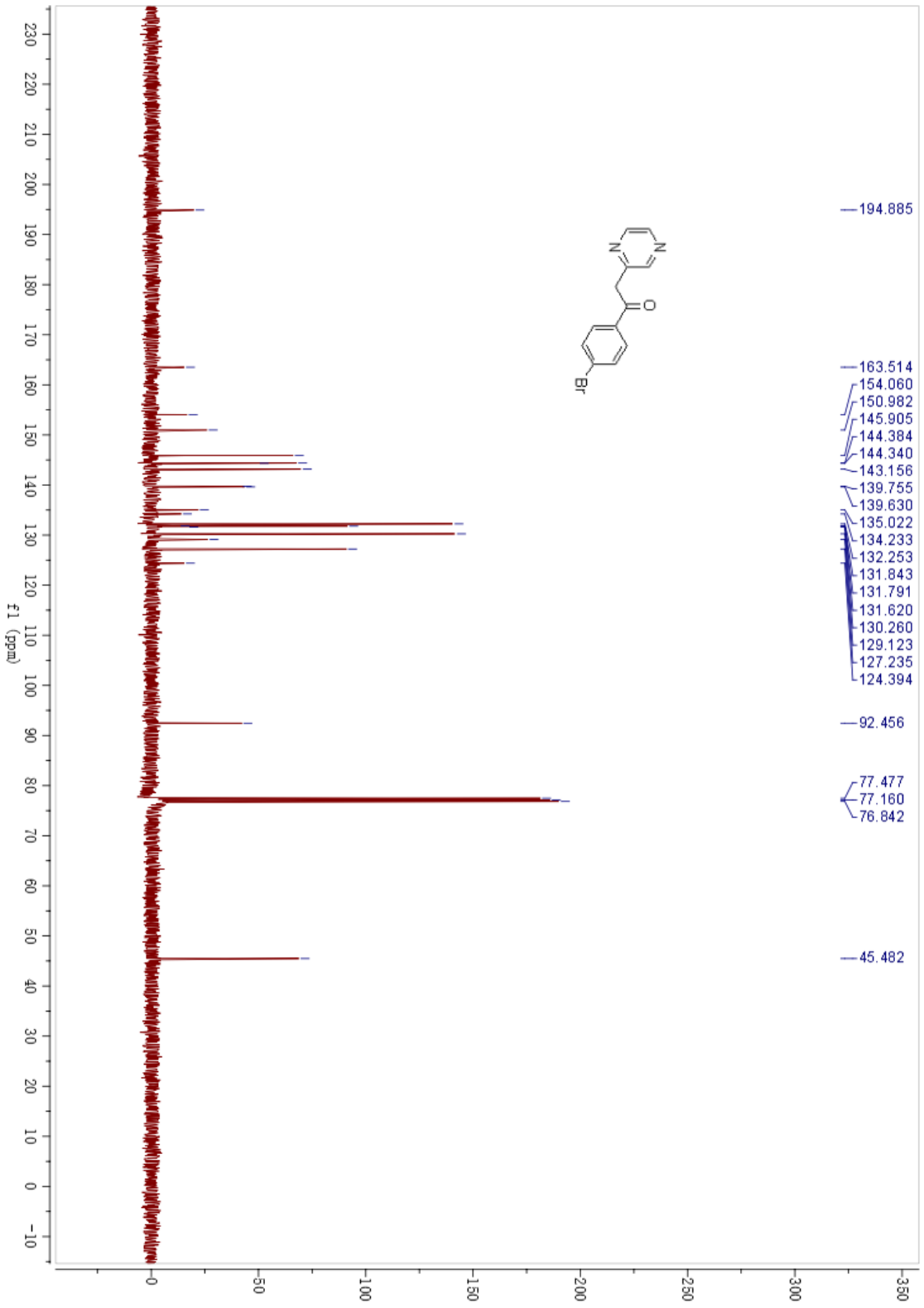
^{13}C NMR spectra of **1g**



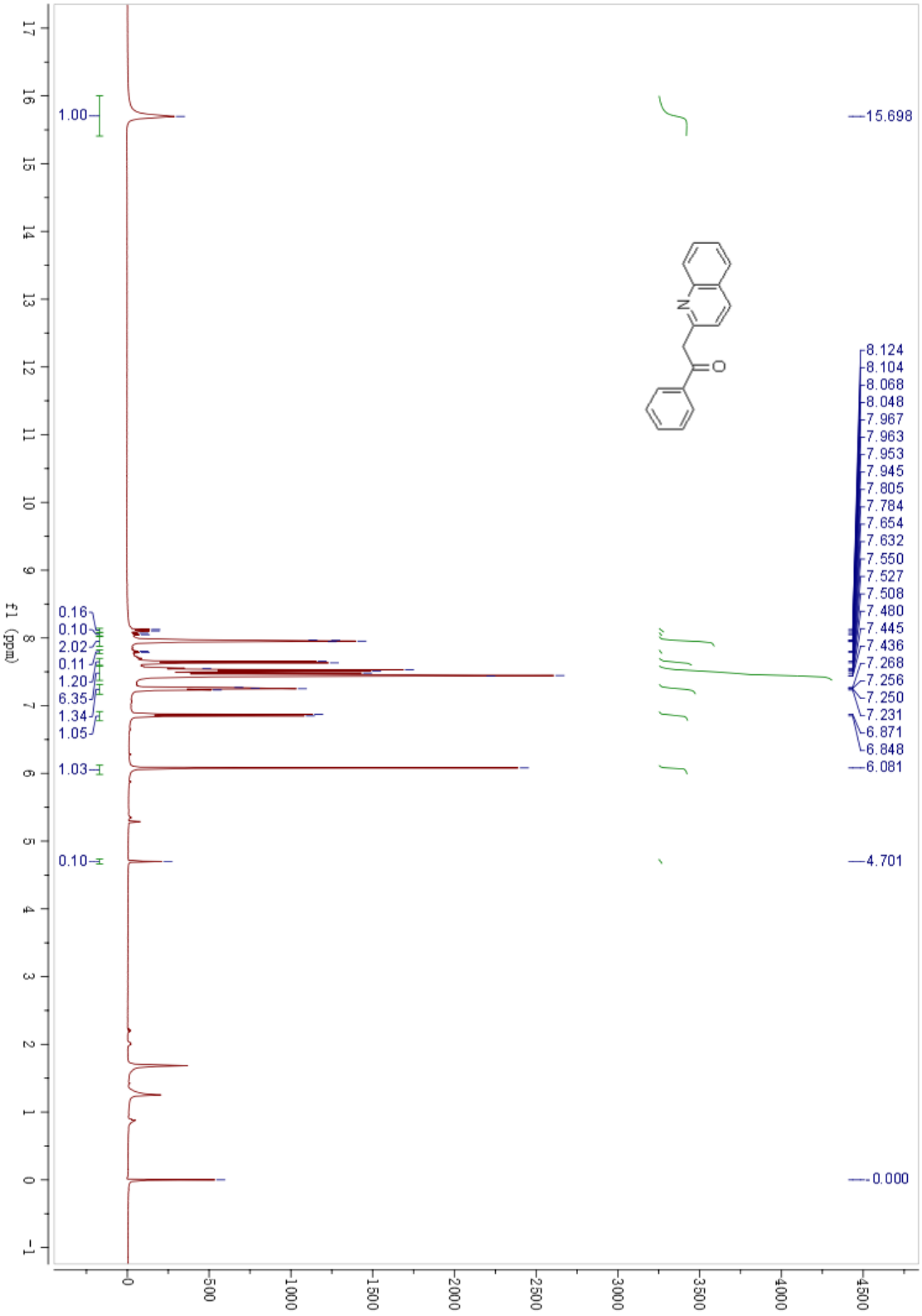
^{1}H NMR spectra of **1h**



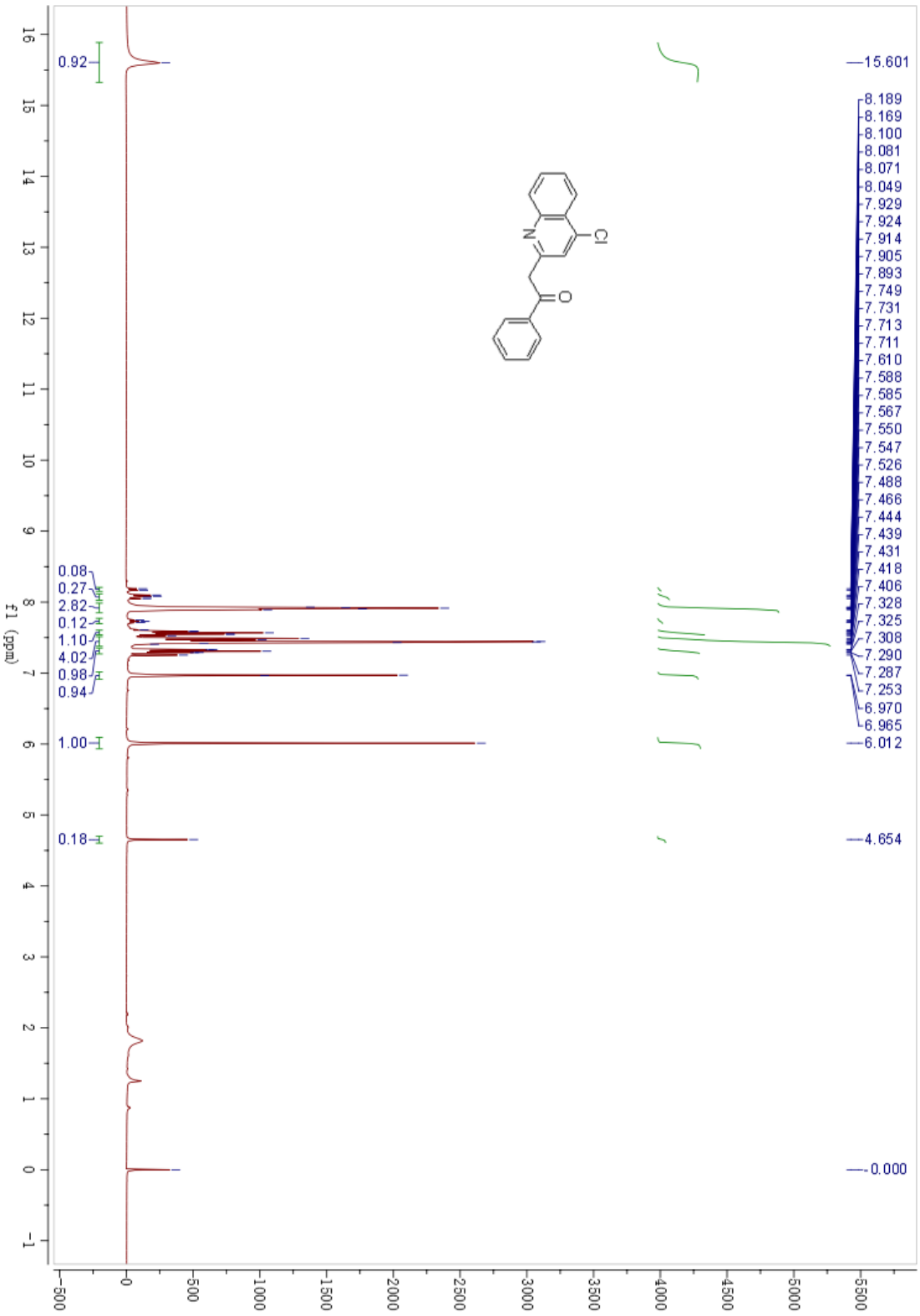
^{13}C NMR spectra of **1h**



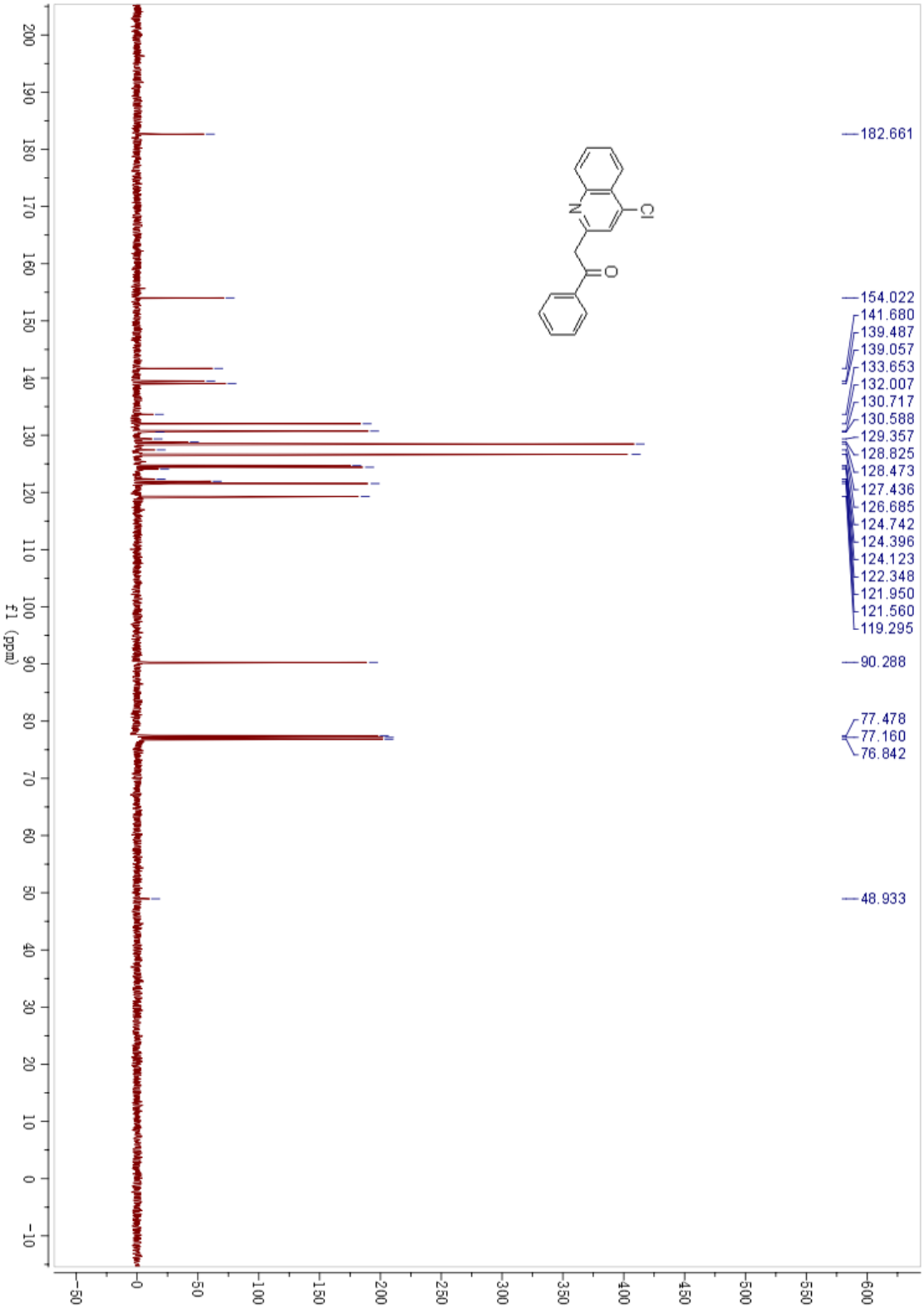
^{1}H NMR spectra of **1i**



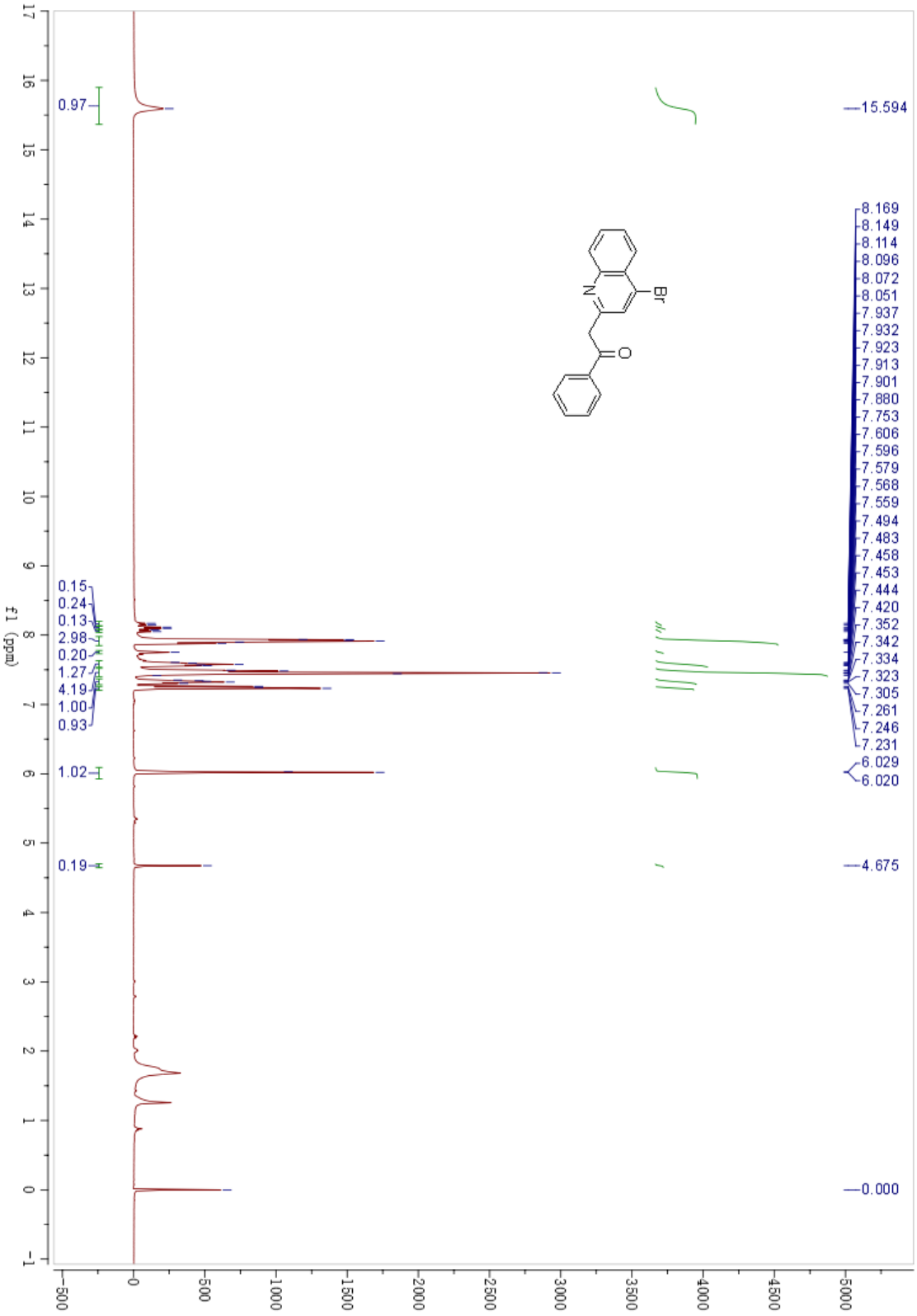
^{1}H NMR spectra of **1j**



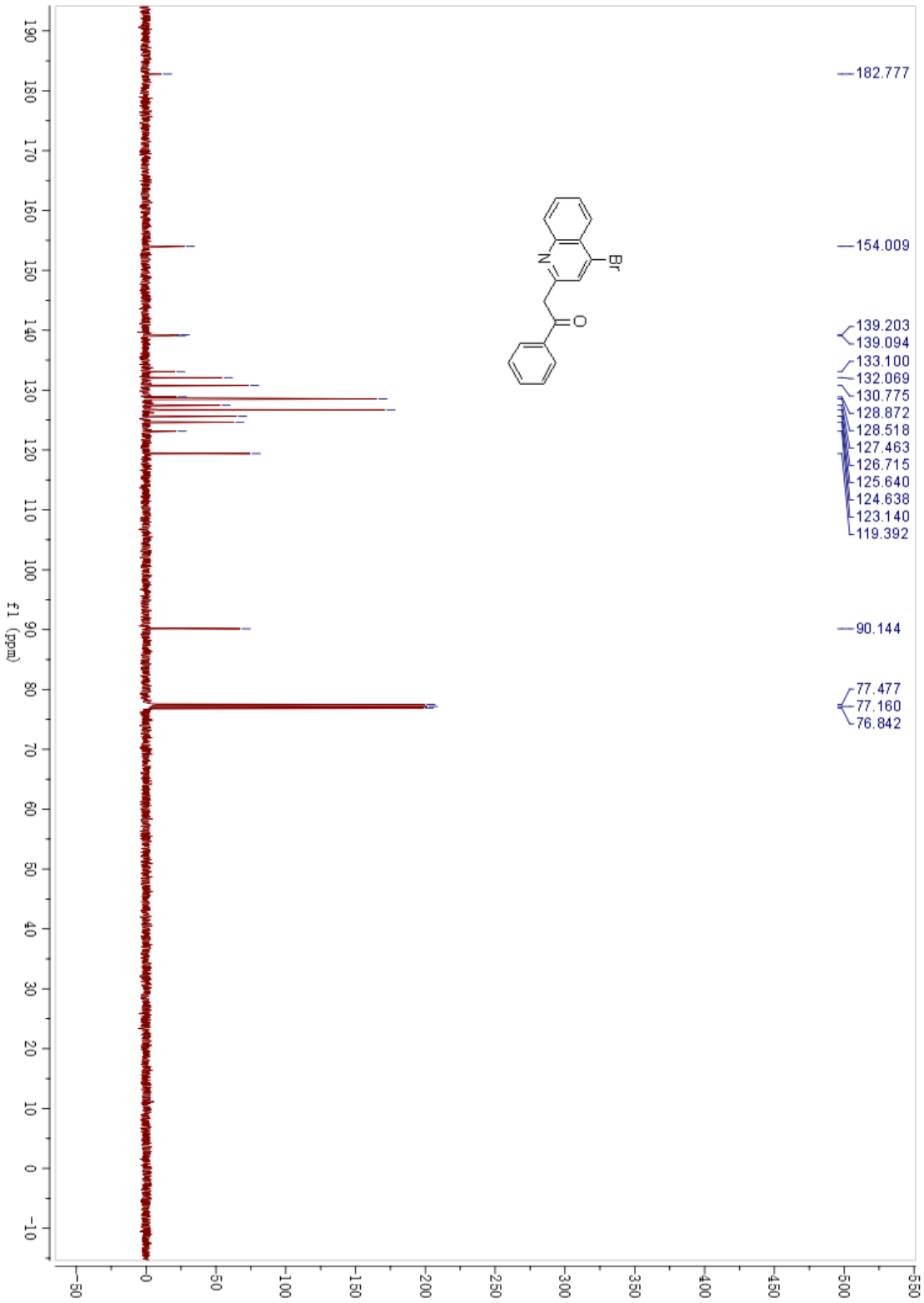
^{13}C NMR spectra of **1j**



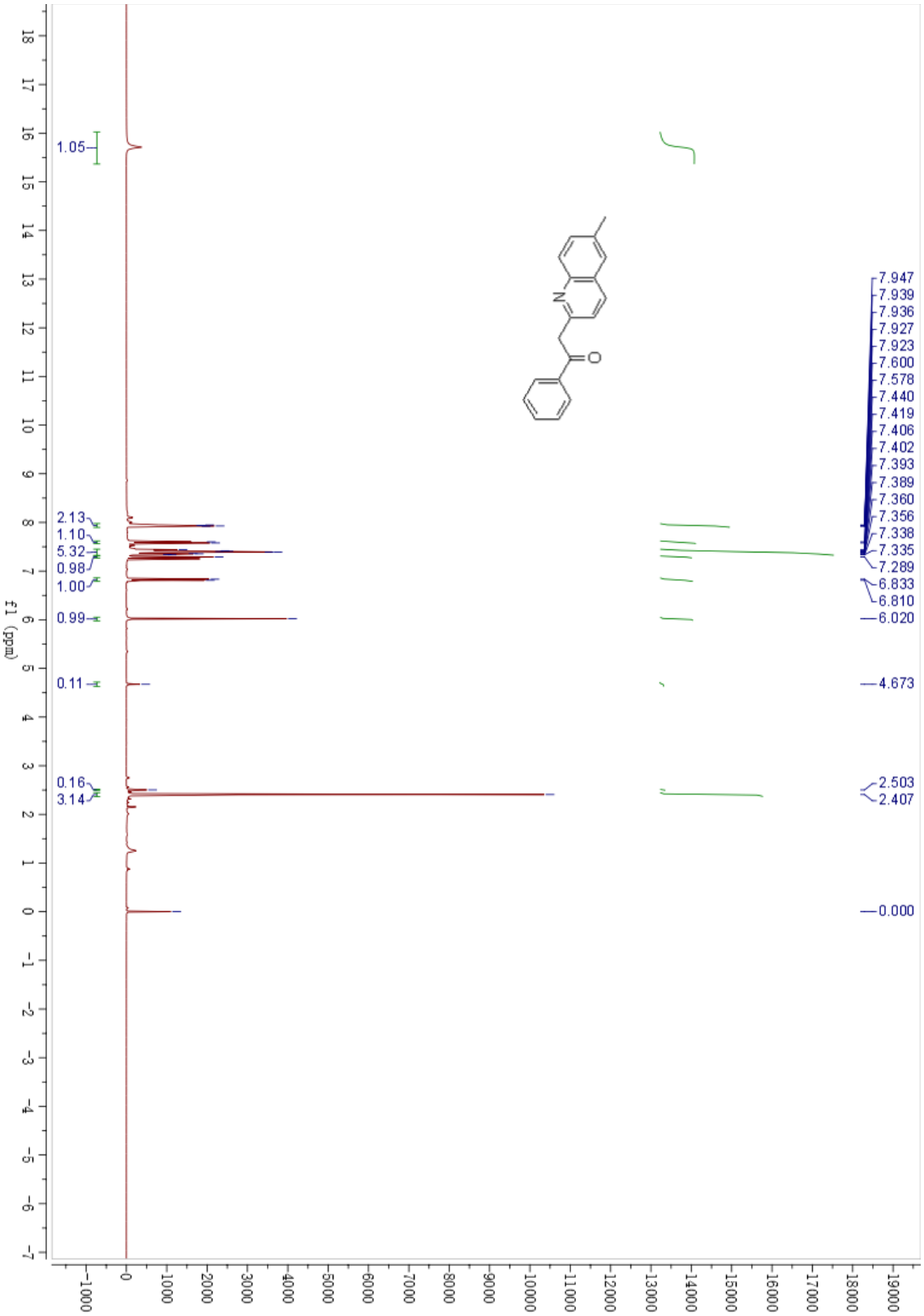
^{1}H NMR spectra of **1k**



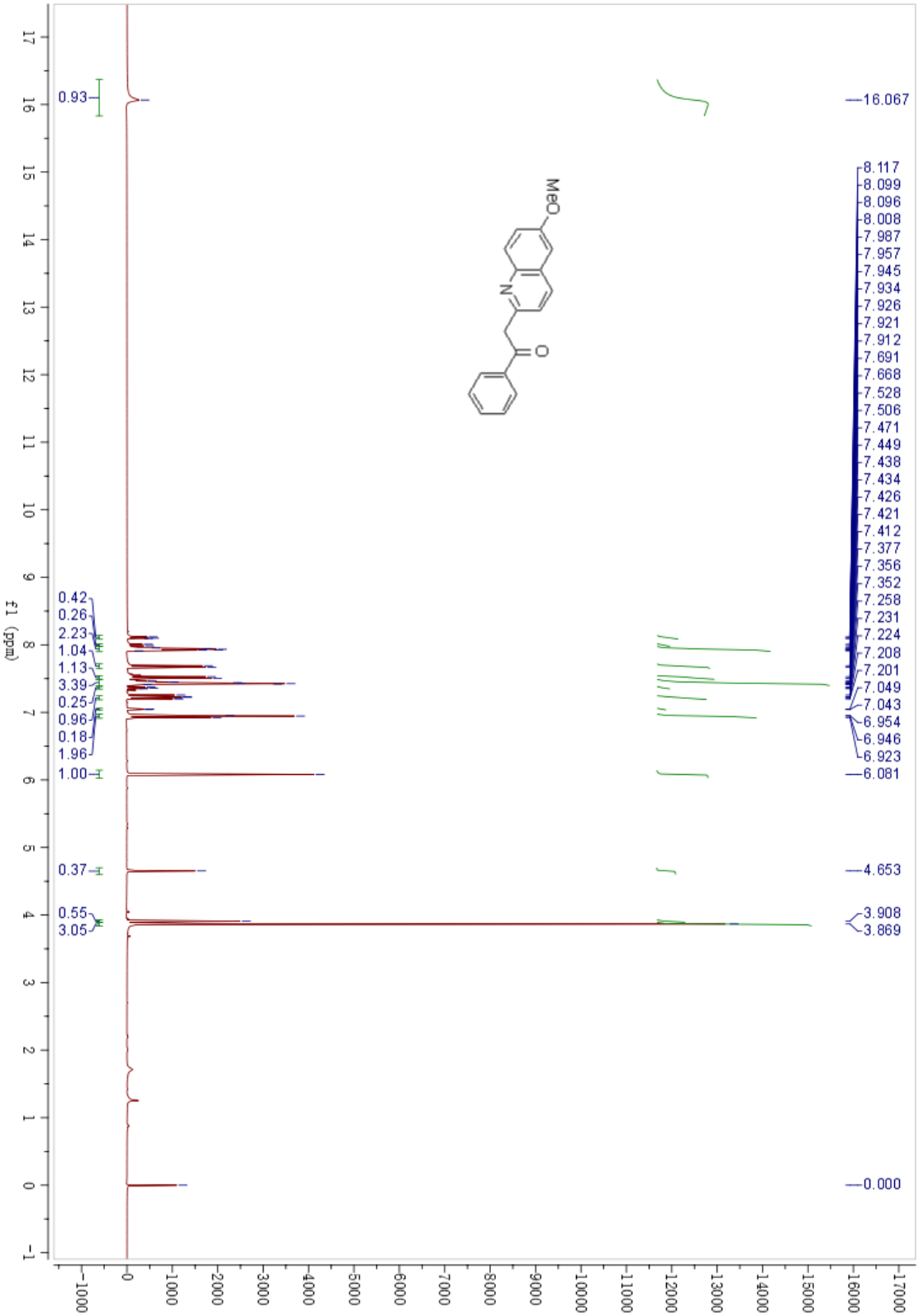
^{13}C NMR spectra of **1k**



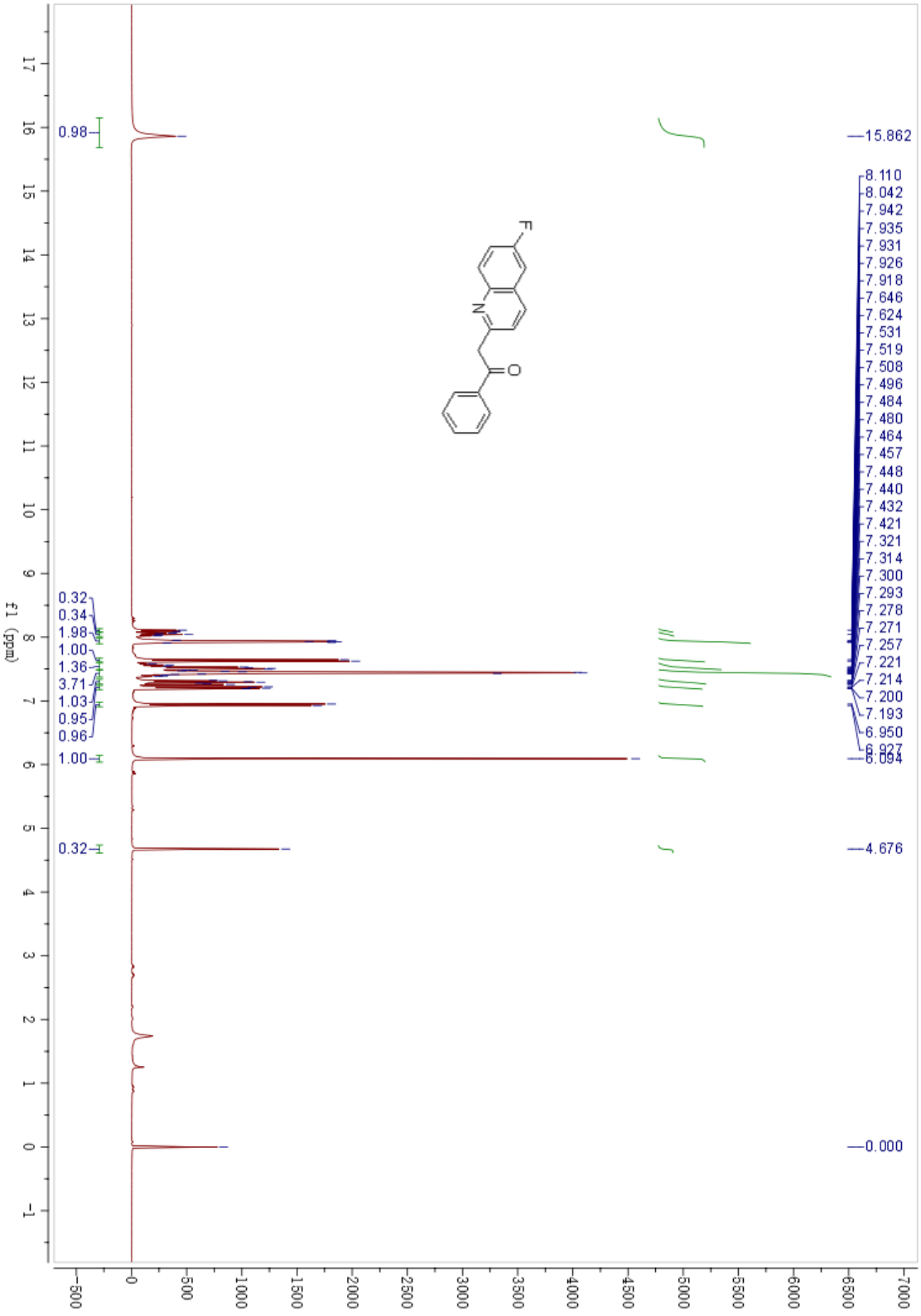
^{1}H NMR spectra of **1l**



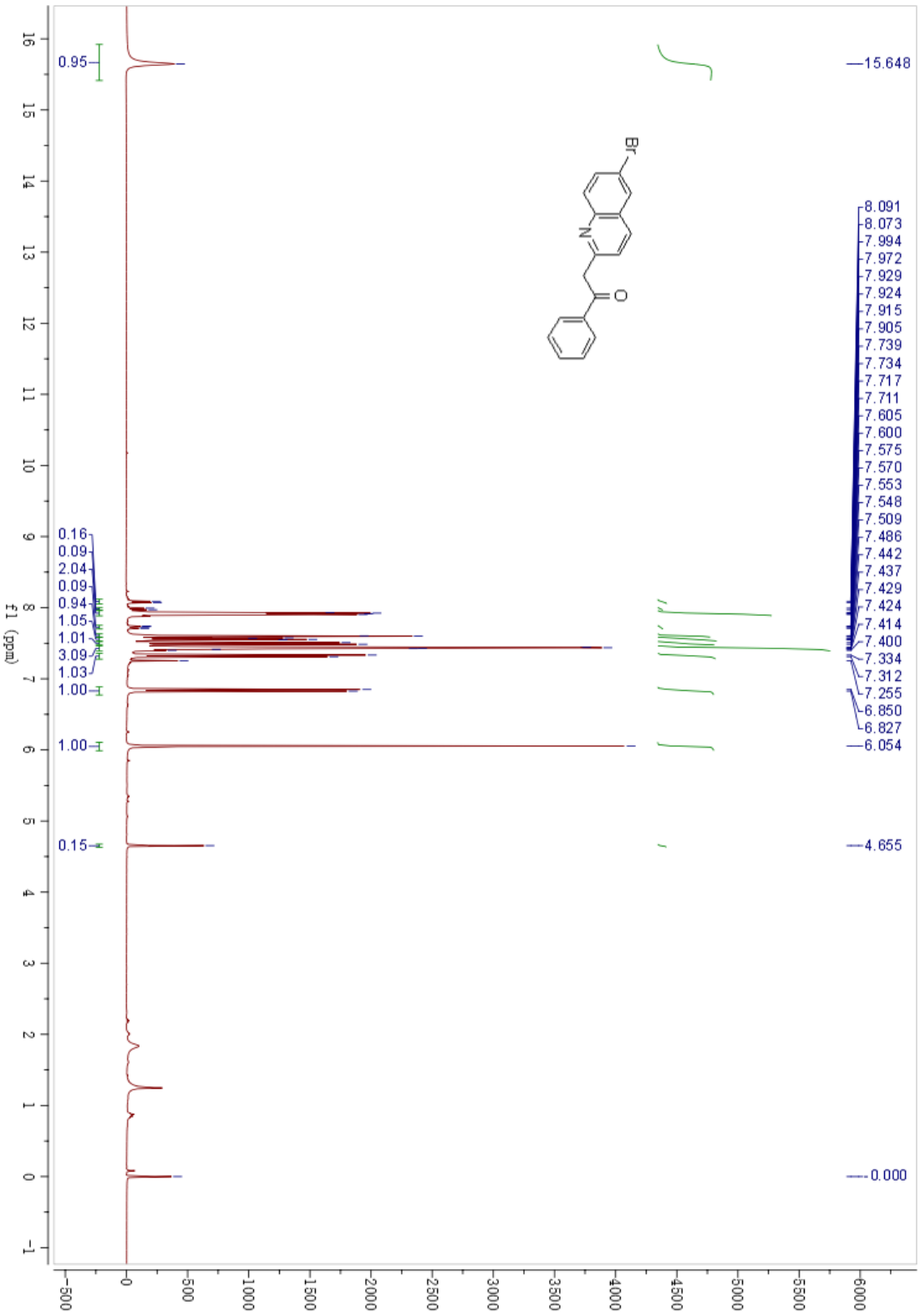
^{1}H NMR spectra of **1m**



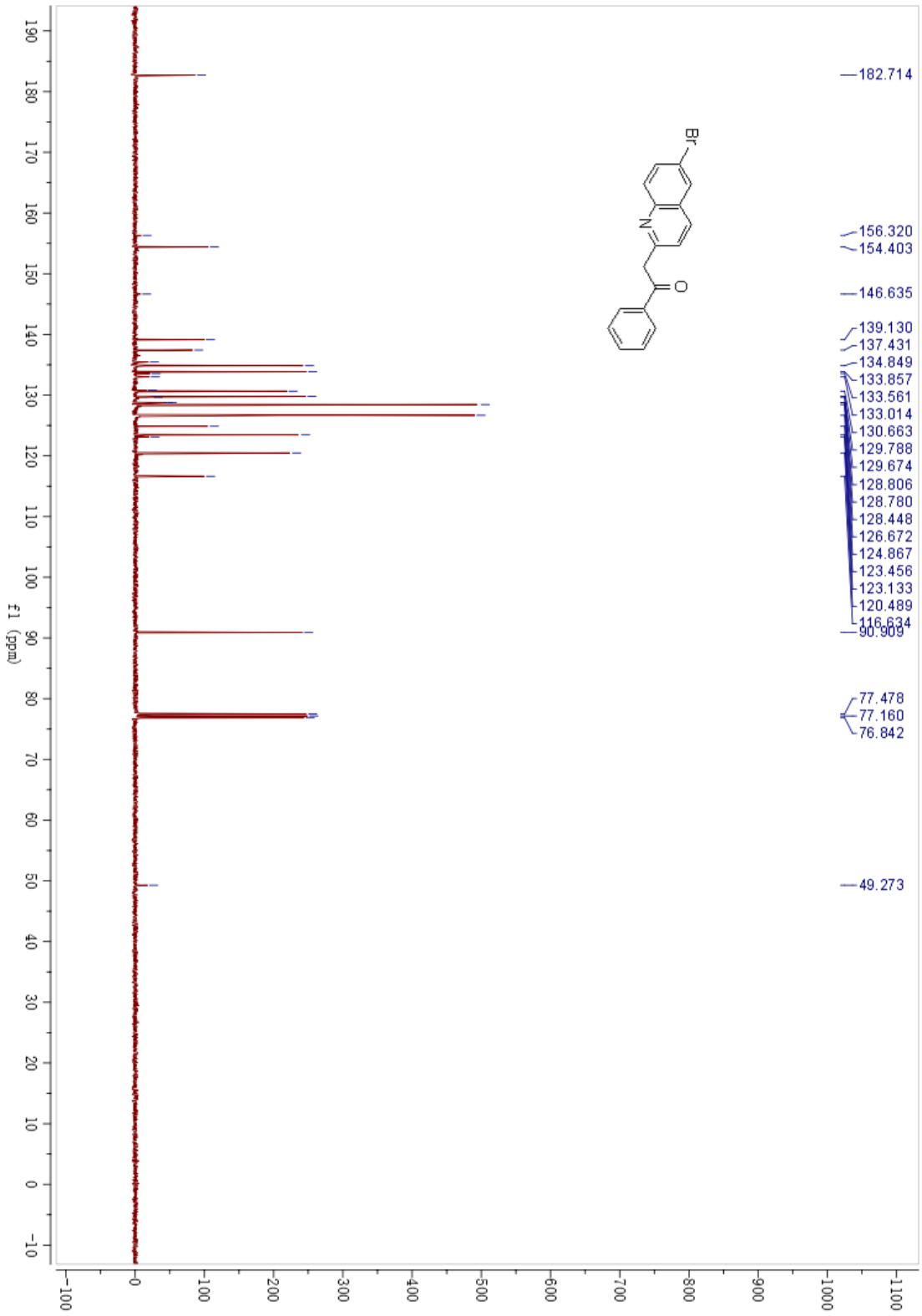
^{1}H NMR spectra of **1n**



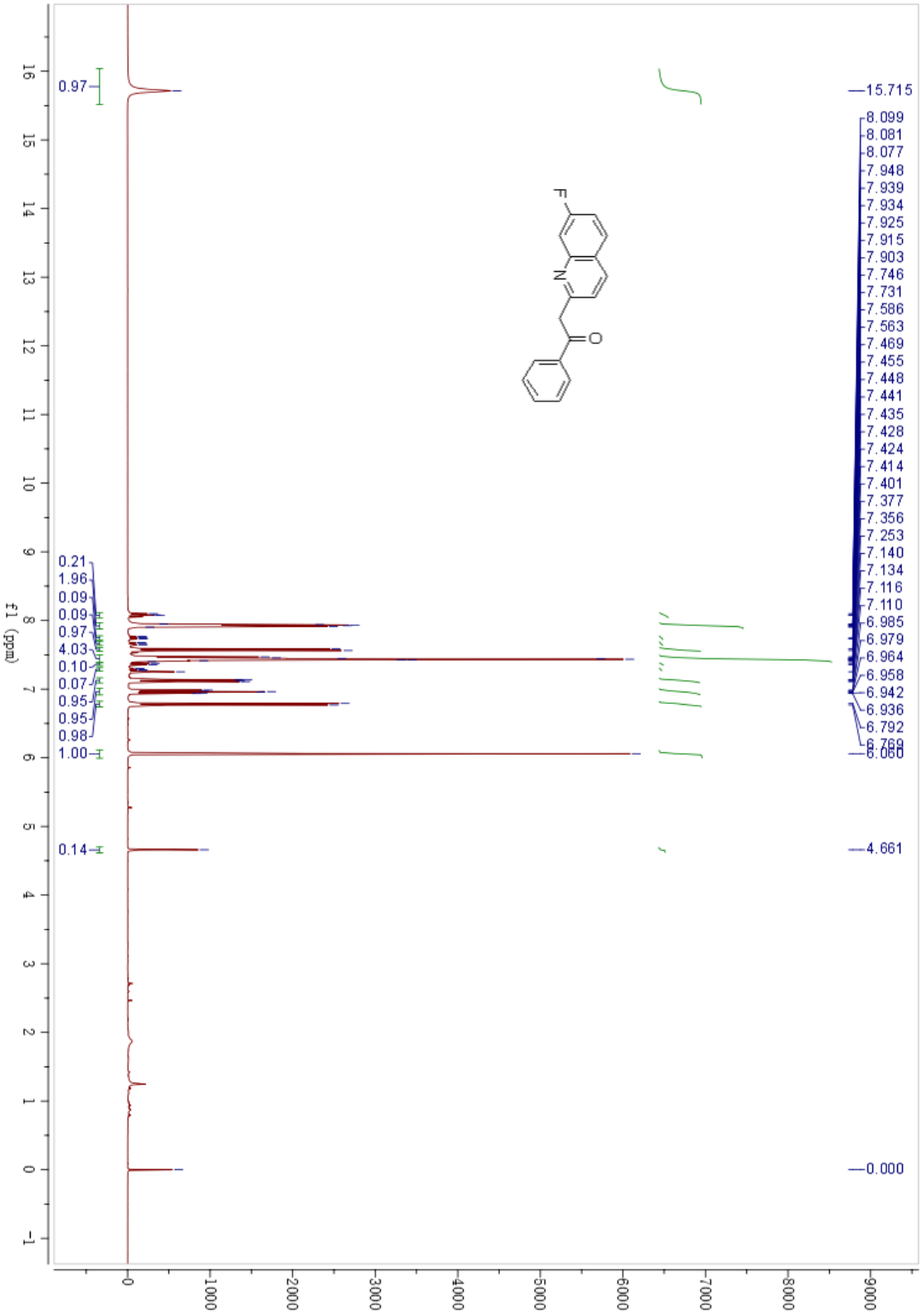
^{1}H NMR spectra of **1o**



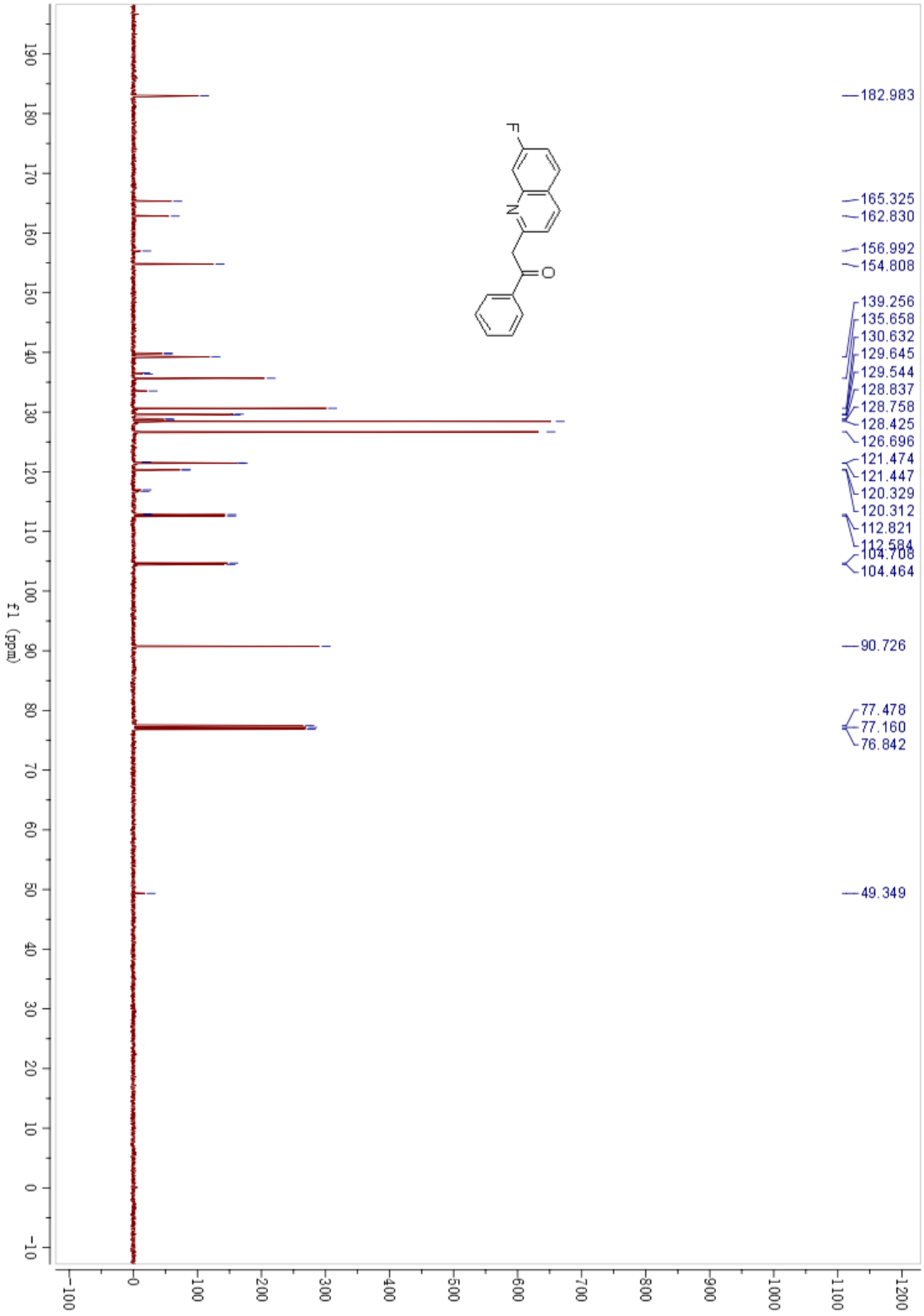
^{13}C NMR spectra of **1o**



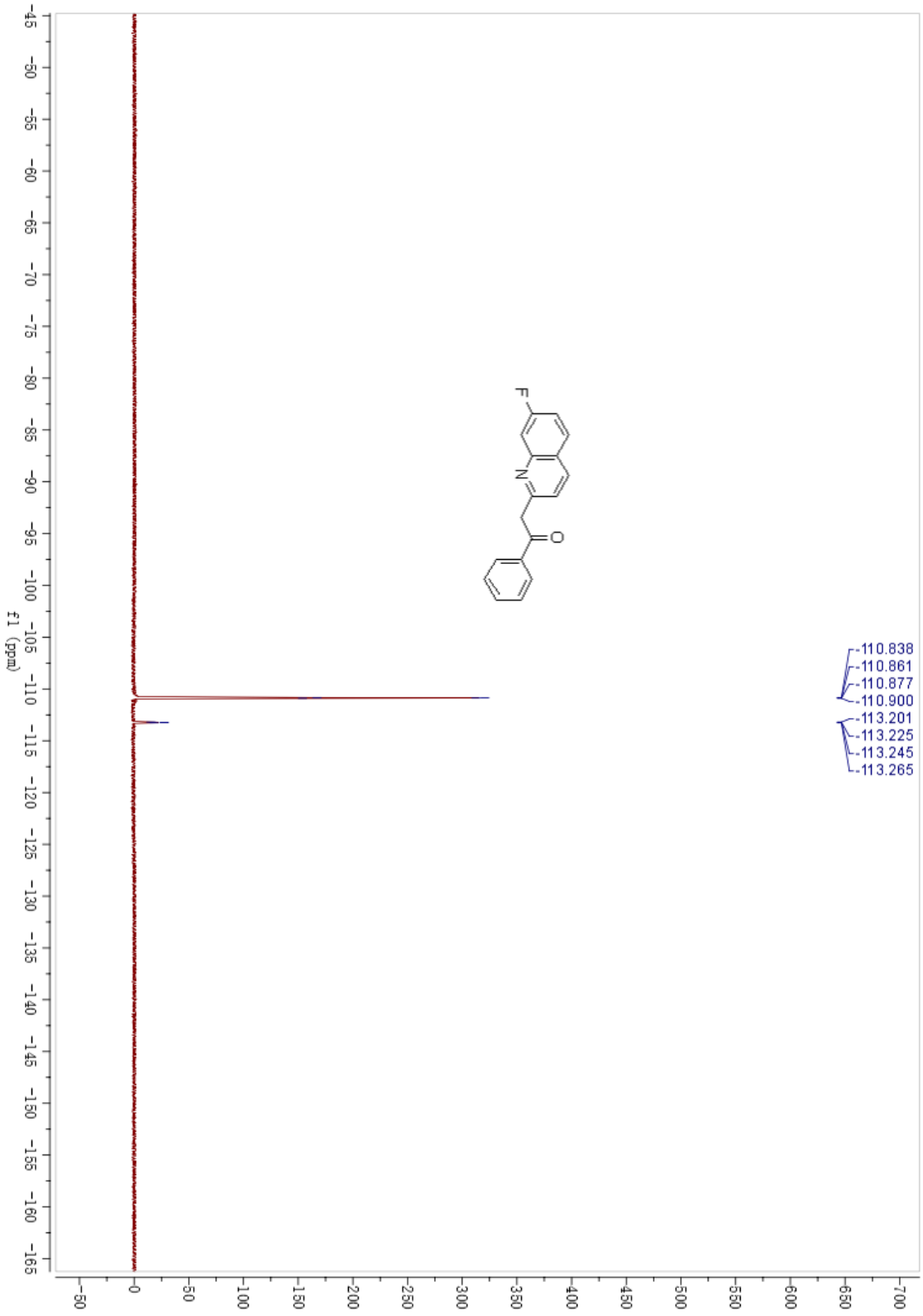
^{1}H NMR spectra of **1p**



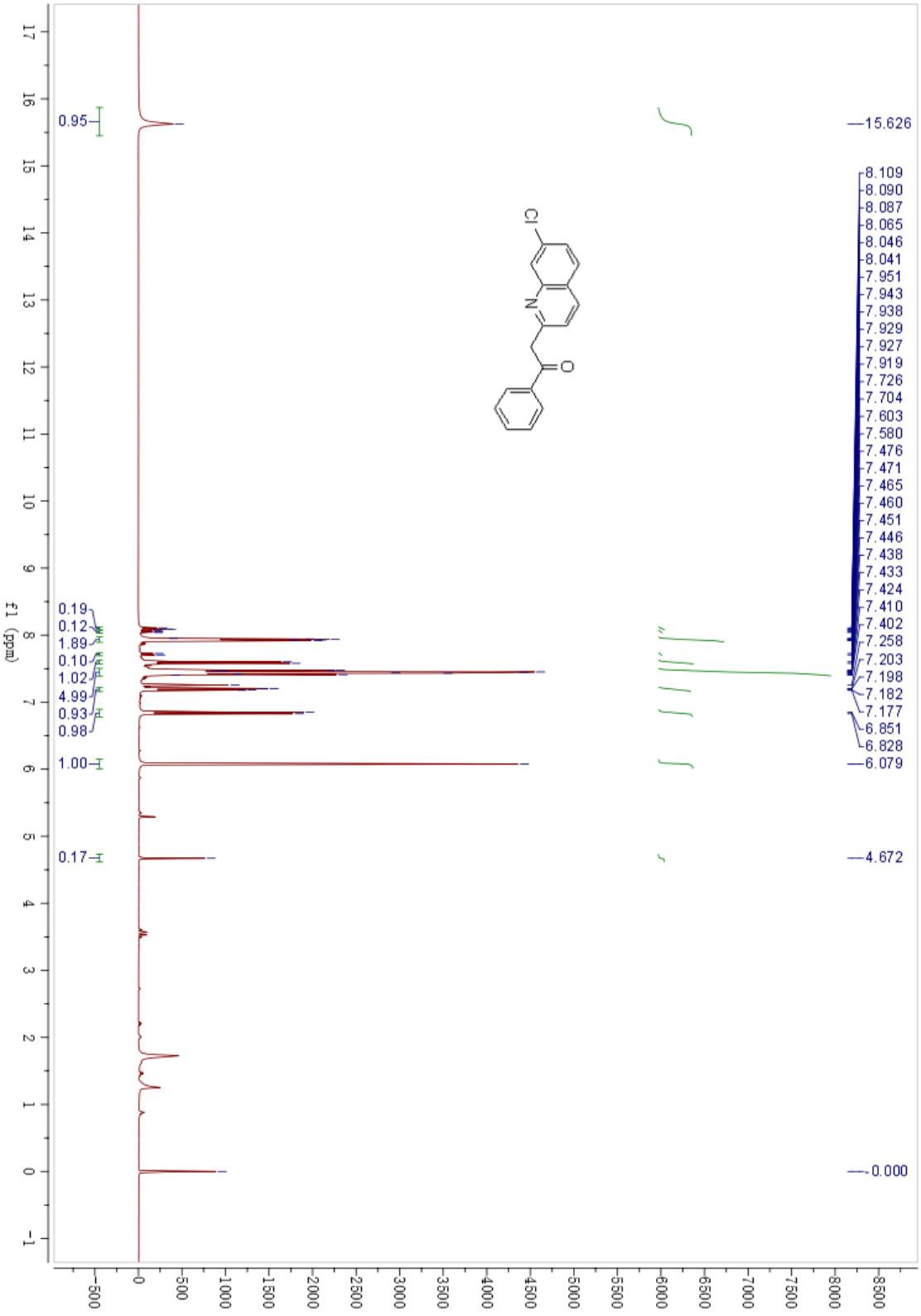
^{13}C NMR spectra of **1p**



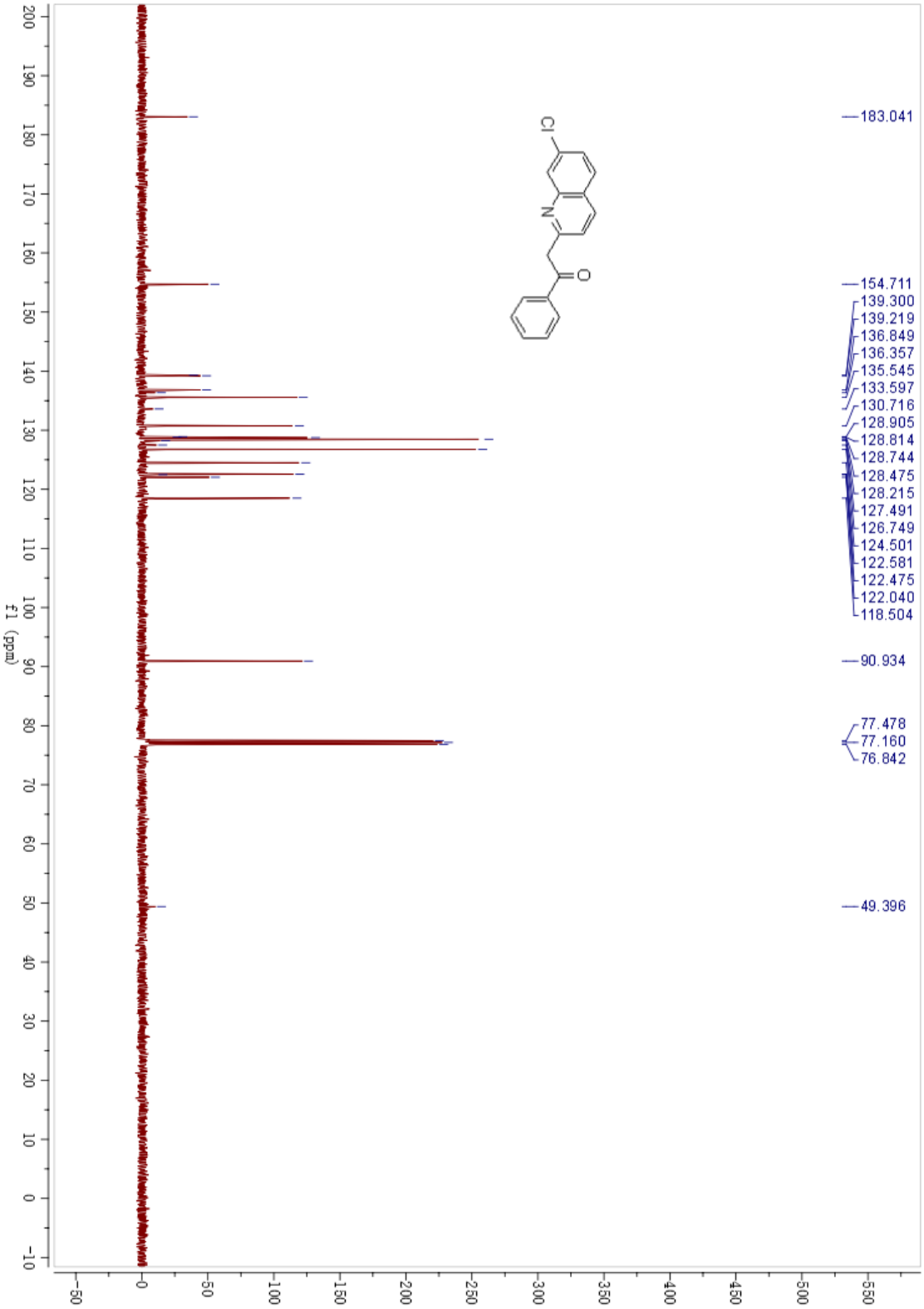
^{19}F NMR spectra of **1p**



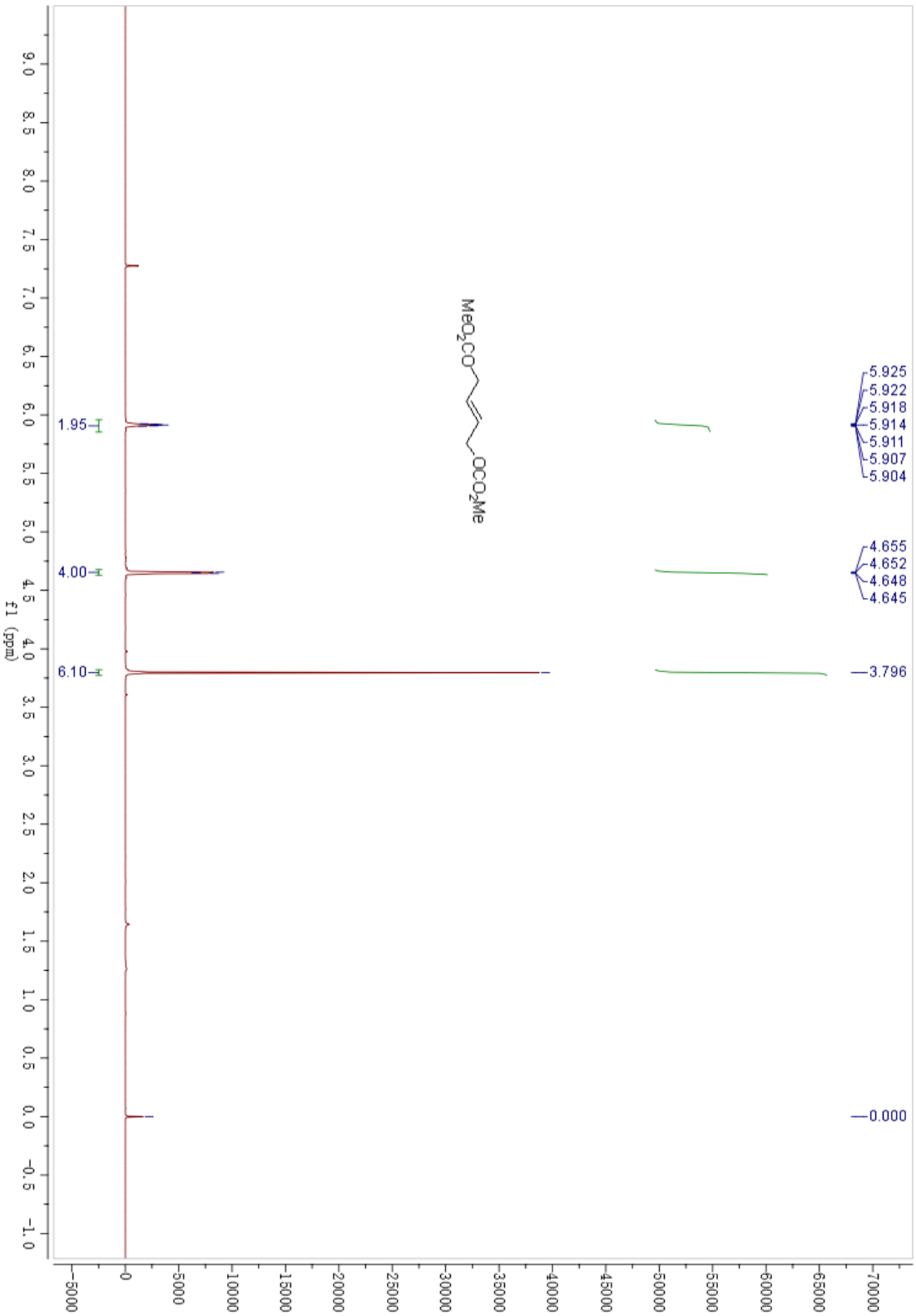
^{1}H NMR spectra of **1q**



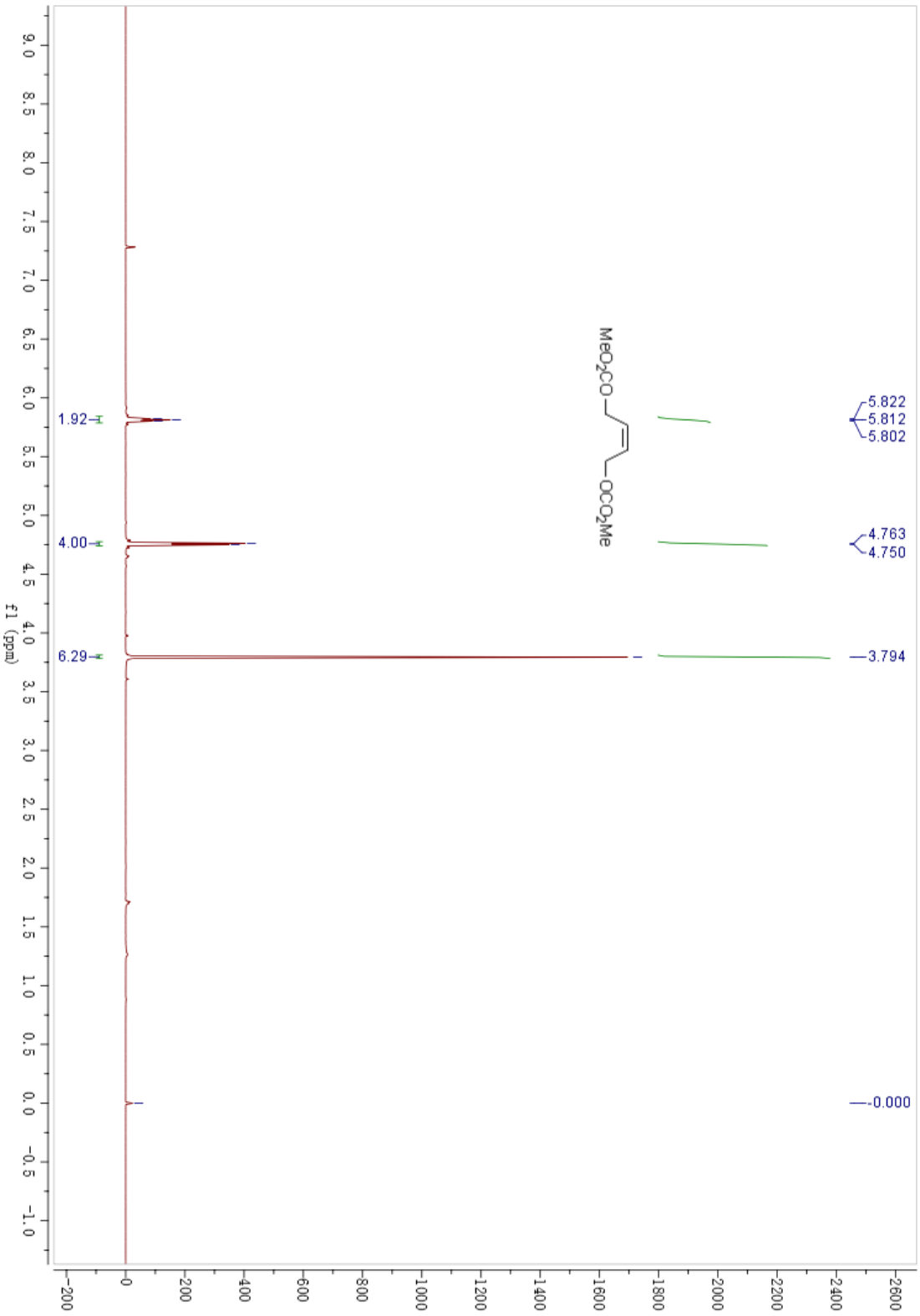
^{13}C NMR spectra of **1q**



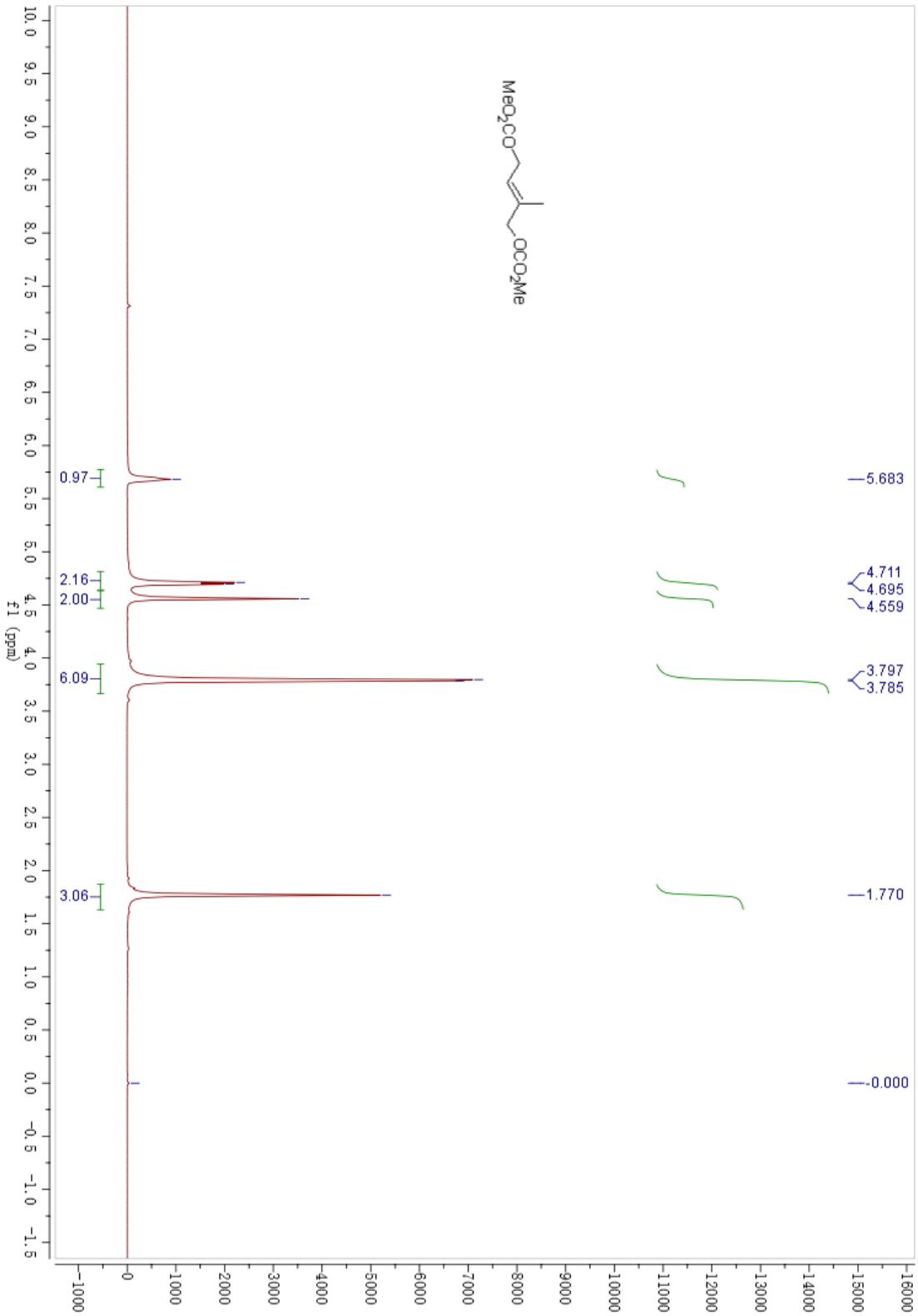
^{1}H NMR spectra of **2a**



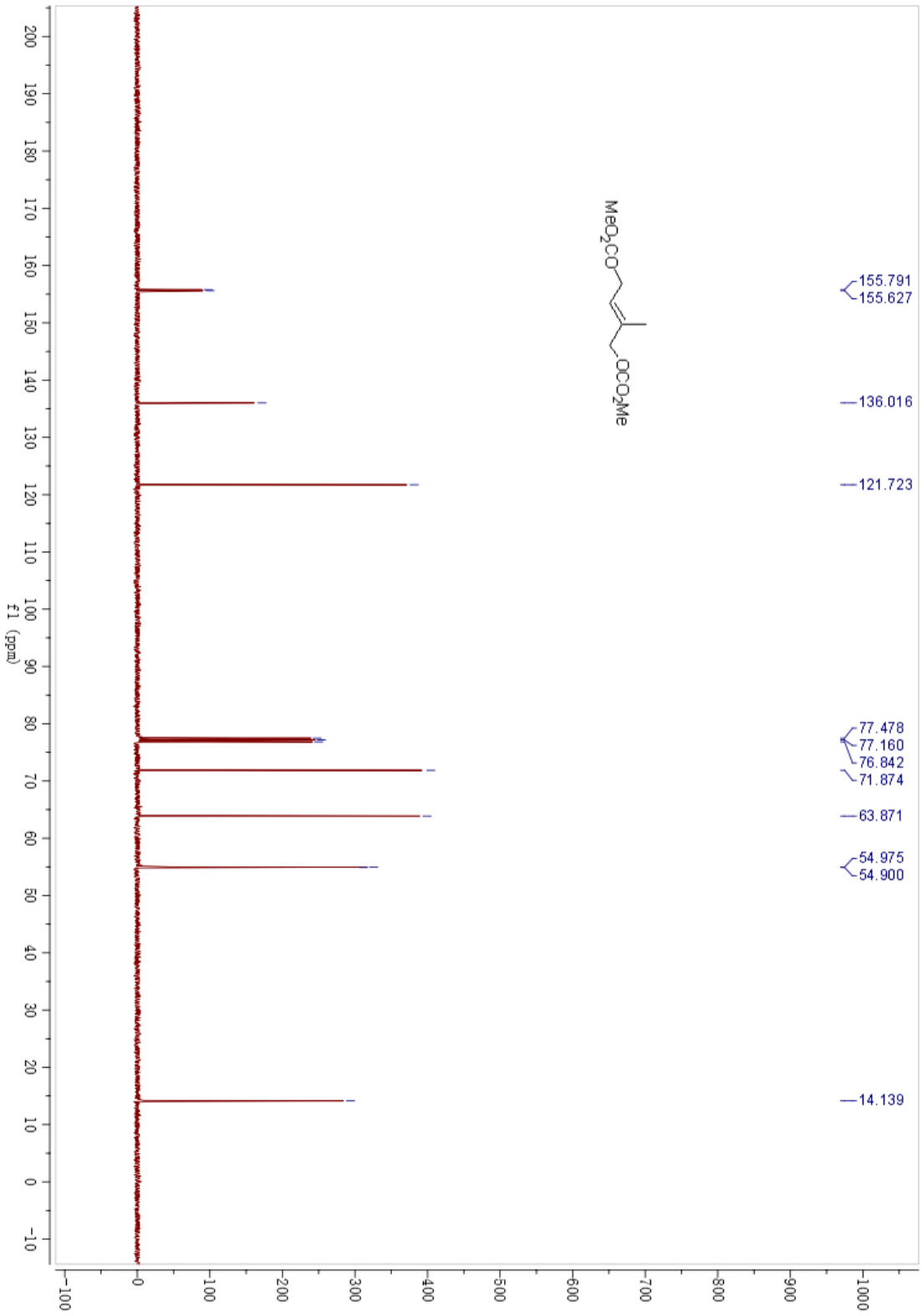
^{1}H NMR spectra of **2b**



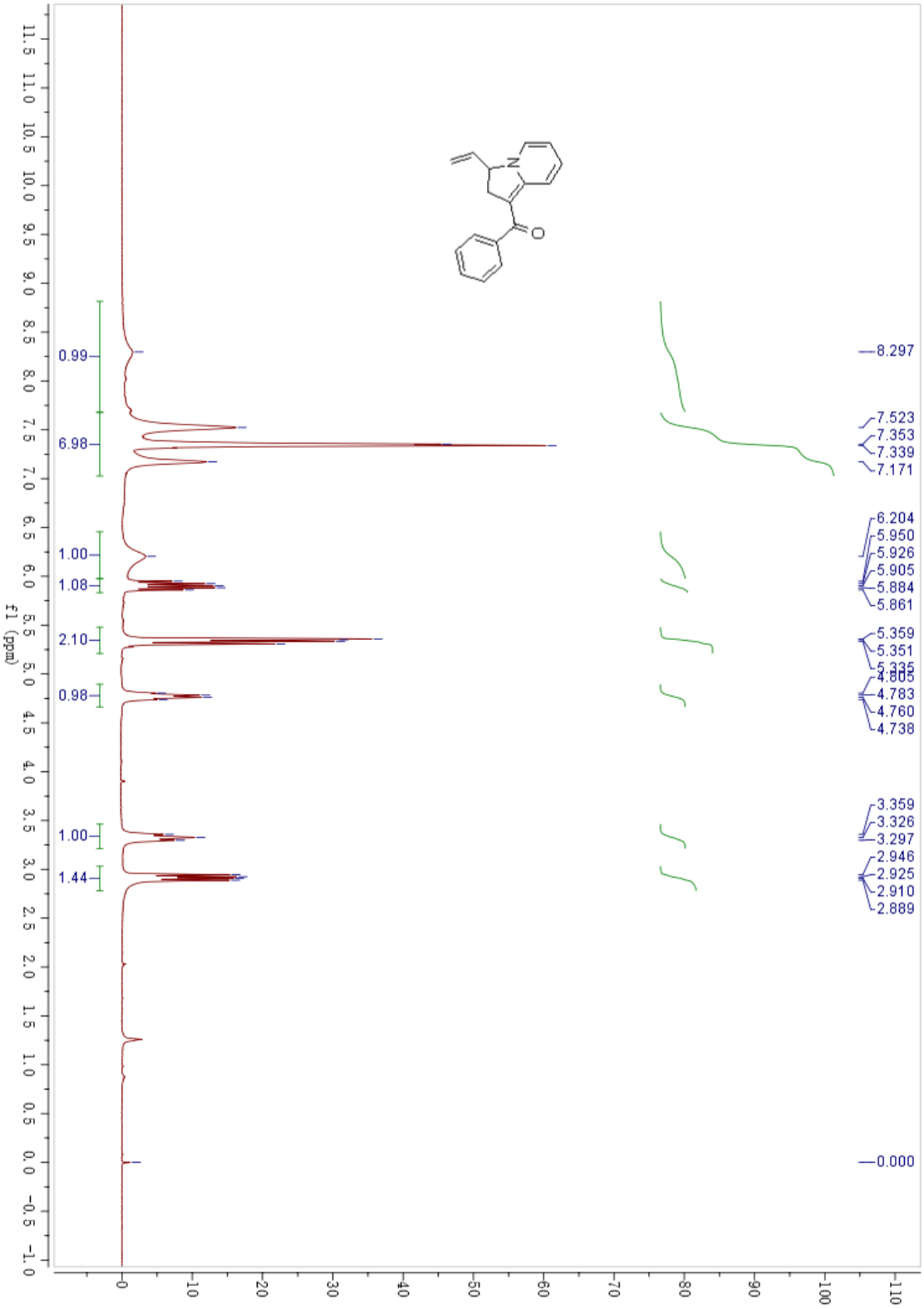
^{1}H NMR spectra of **2c**



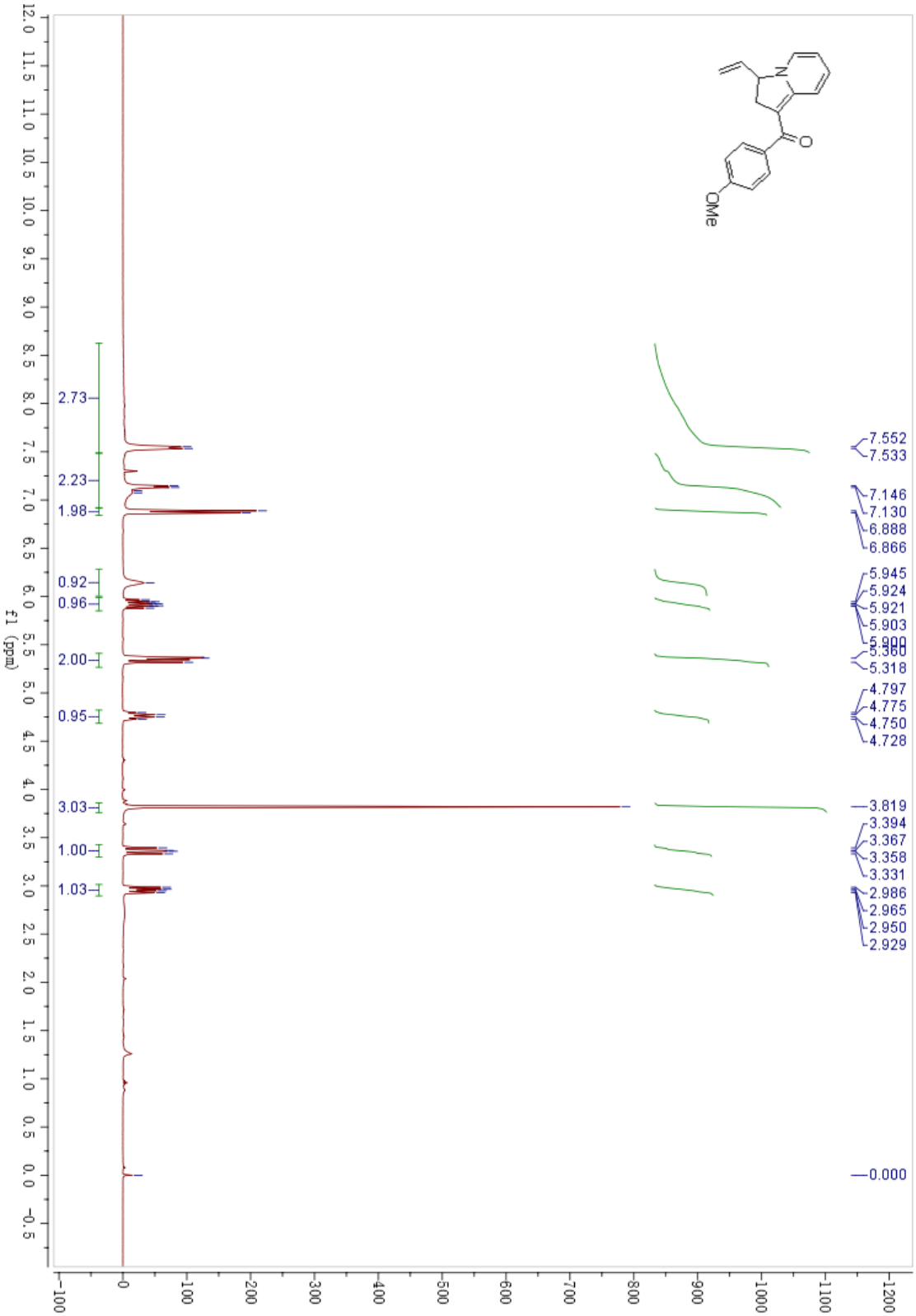
^{13}C NMR spectra of **2c**



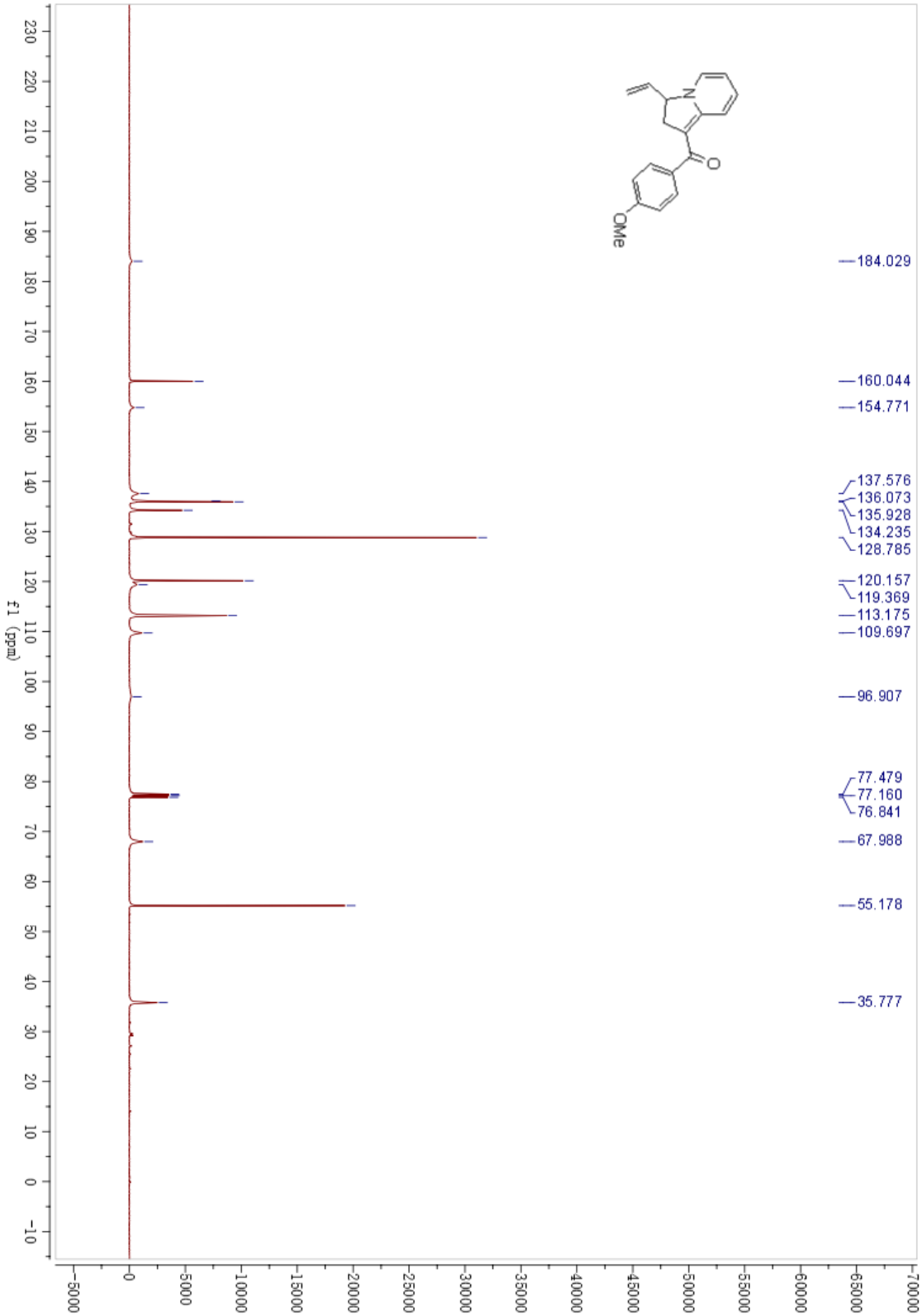
^{1}H NMR spectra of **3a**



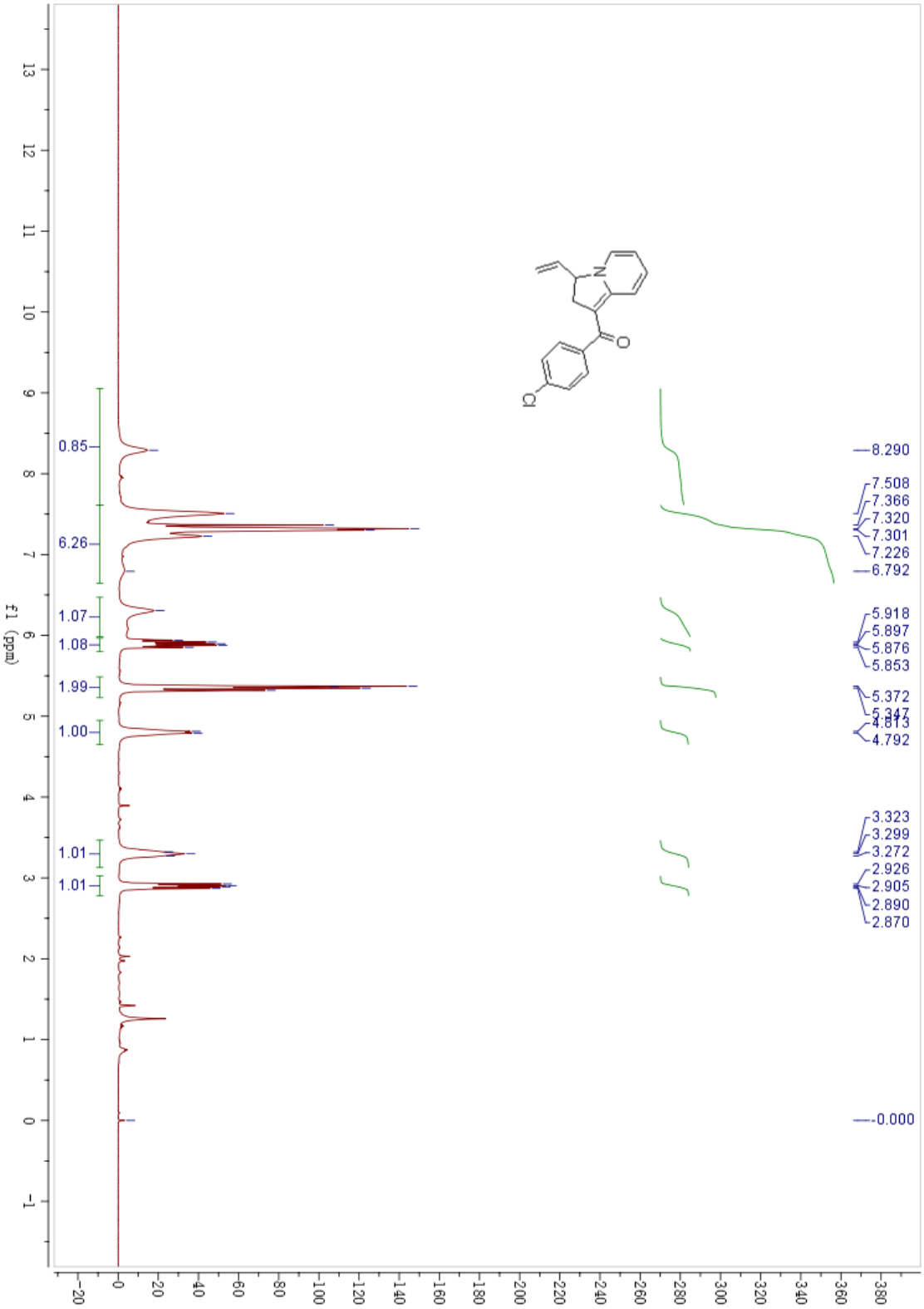
^{1}H NMR spectra of **3b**



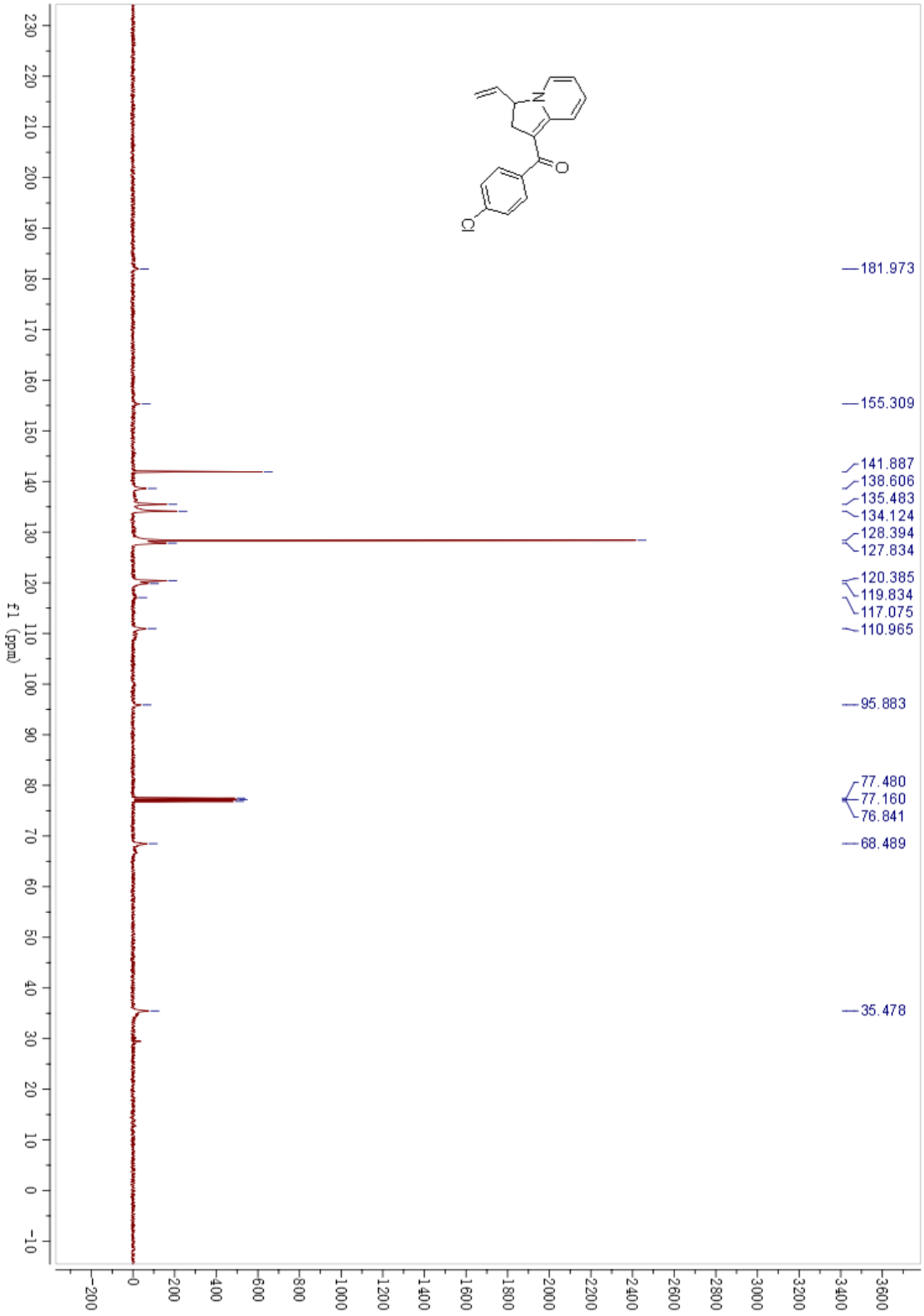
^{13}C NMR spectra of **3b**



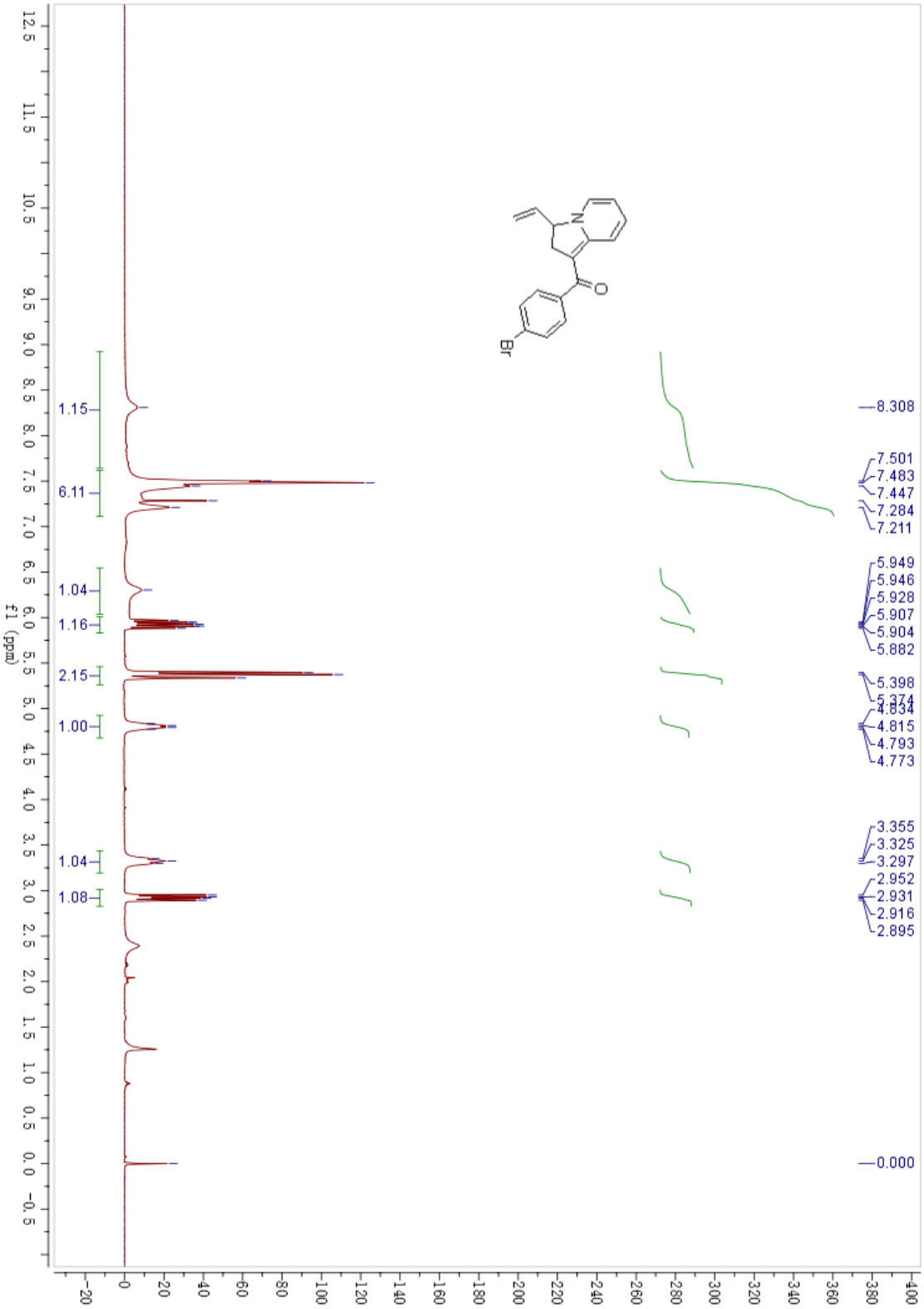
^{1}H NMR spectra of **3c**



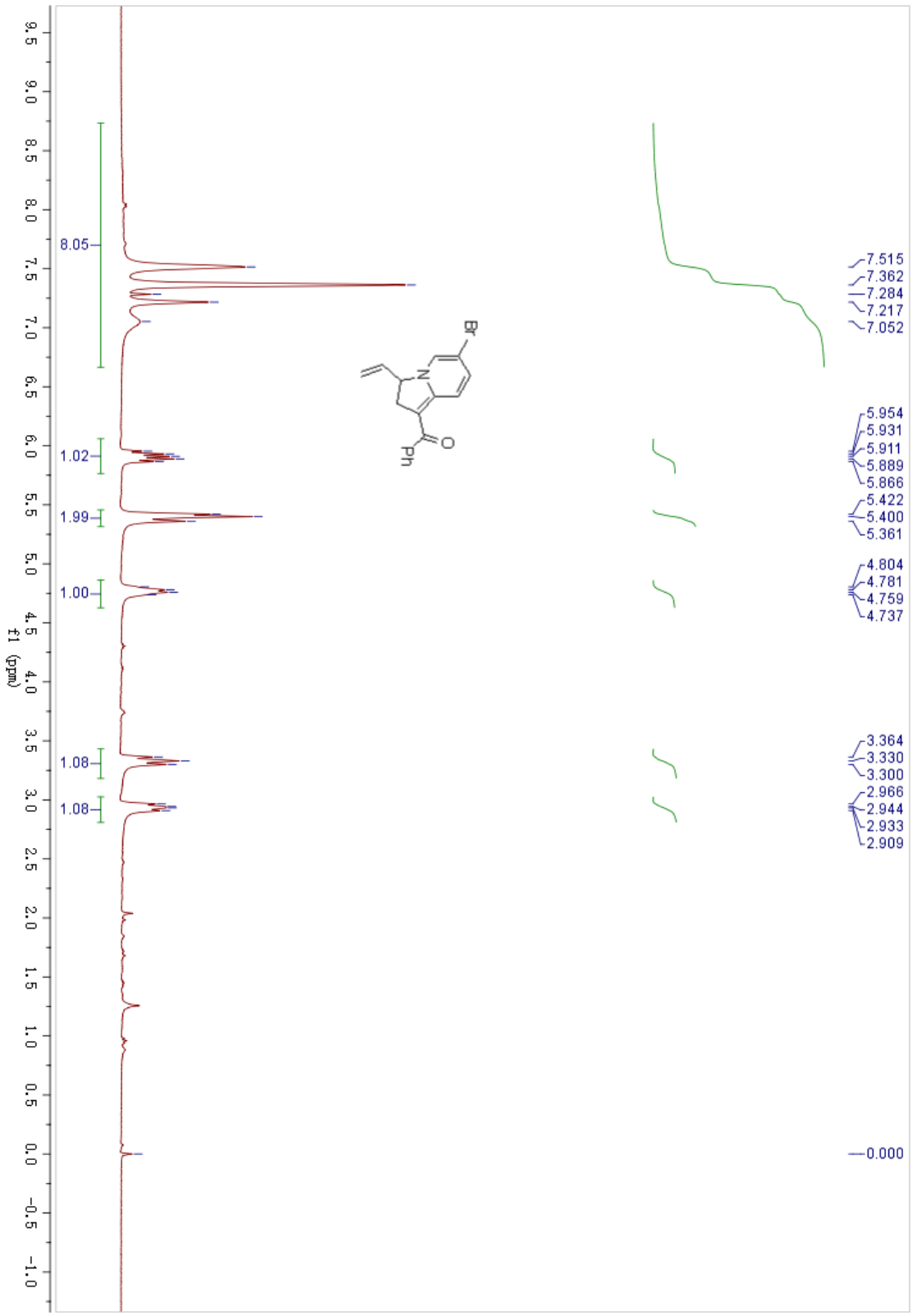
^{13}C NMR spectra of **3c**



^{1}H NMR spectra of **3d**



^{1}H NMR spectra of **3e**



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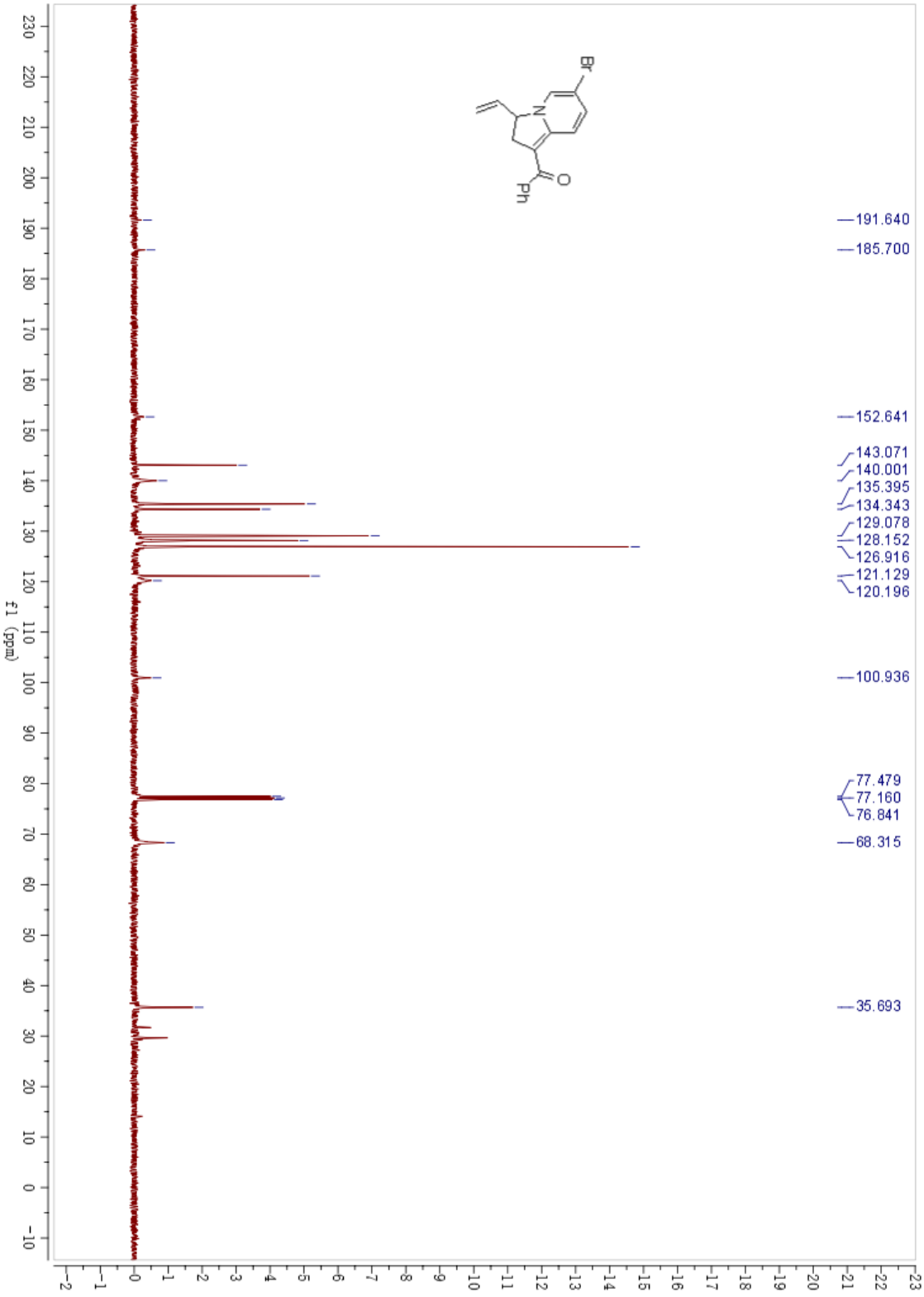
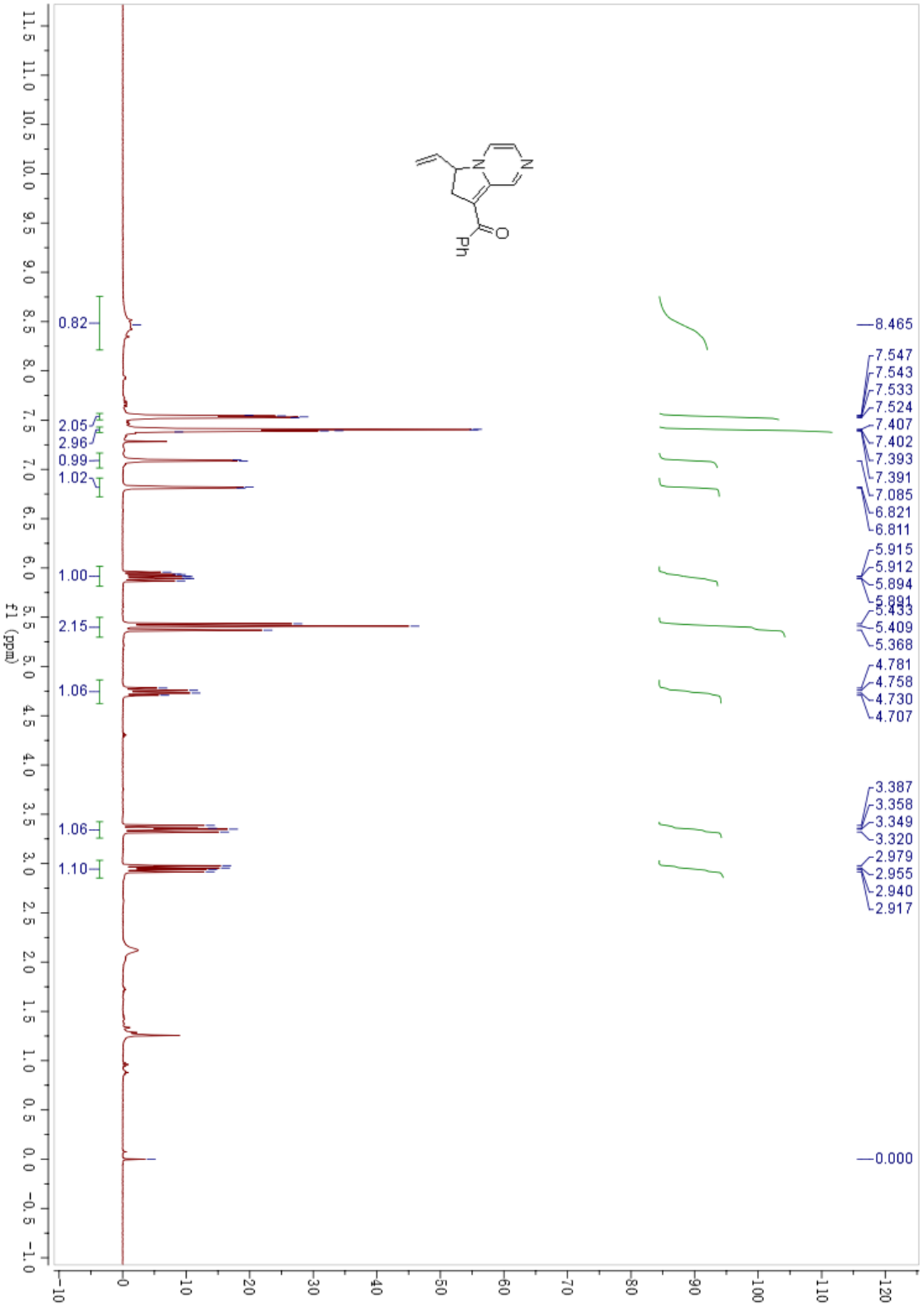
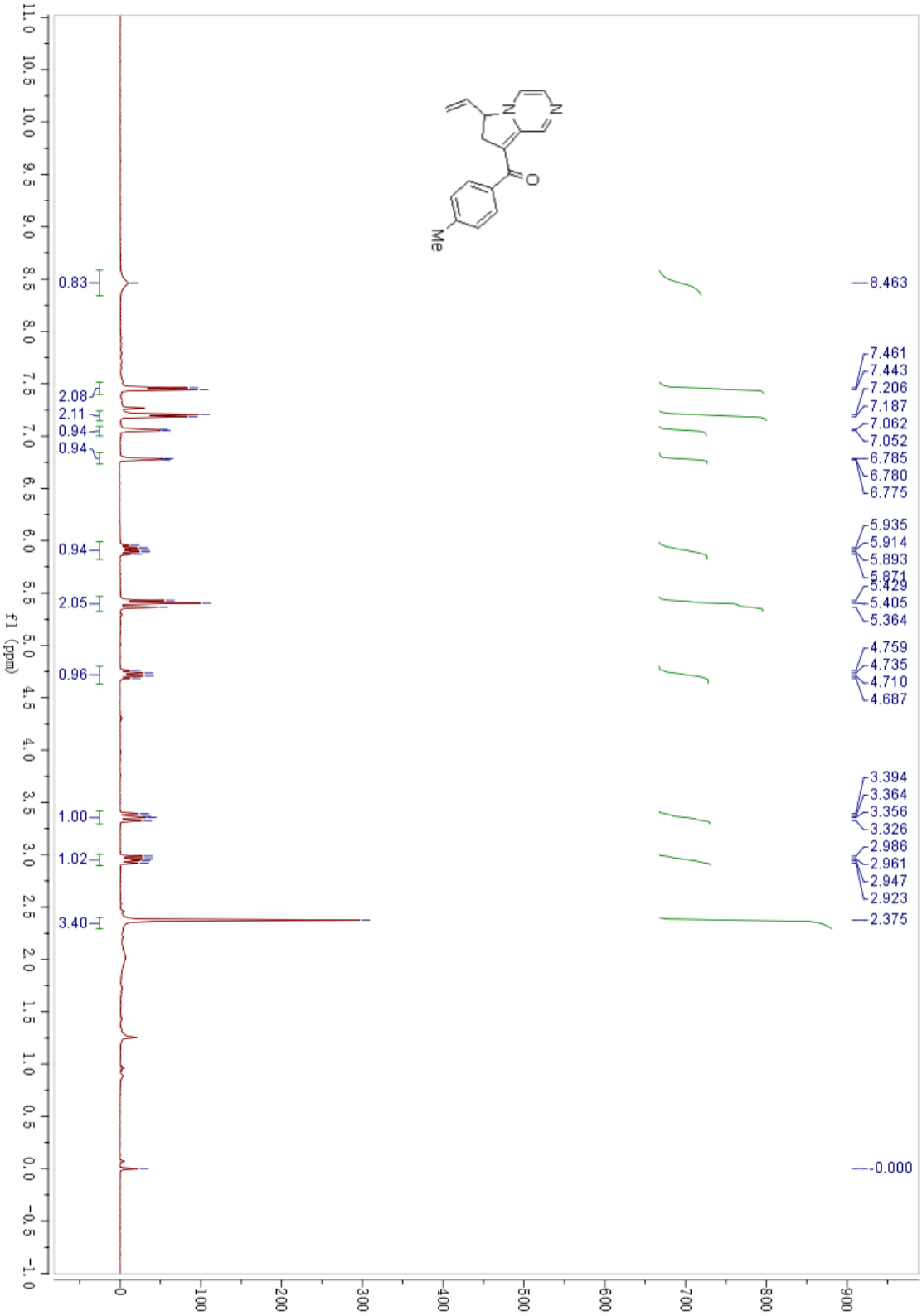


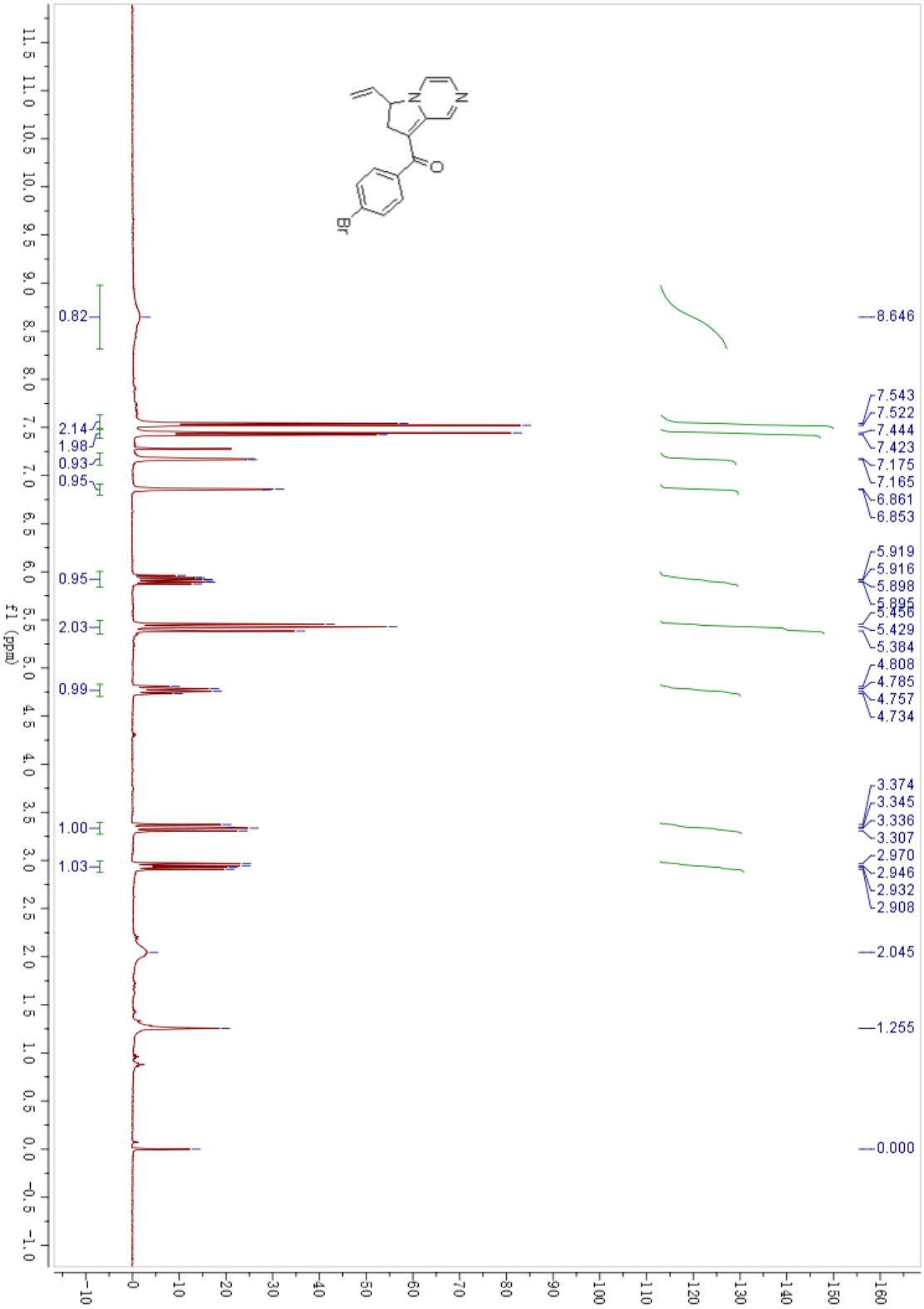
^{1}H NMR spectra of **3f**



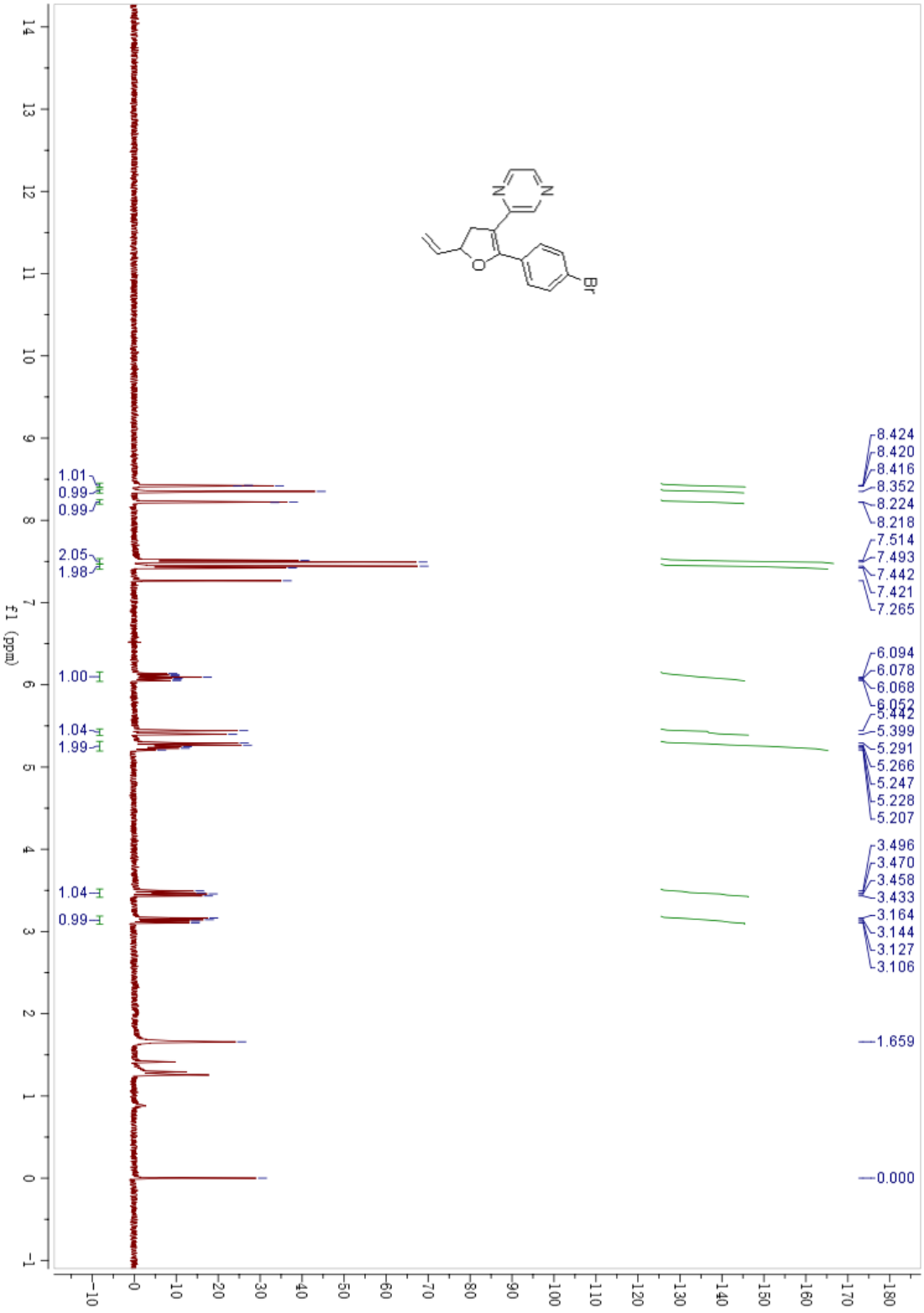
^{1}H NMR spectra of **3g**



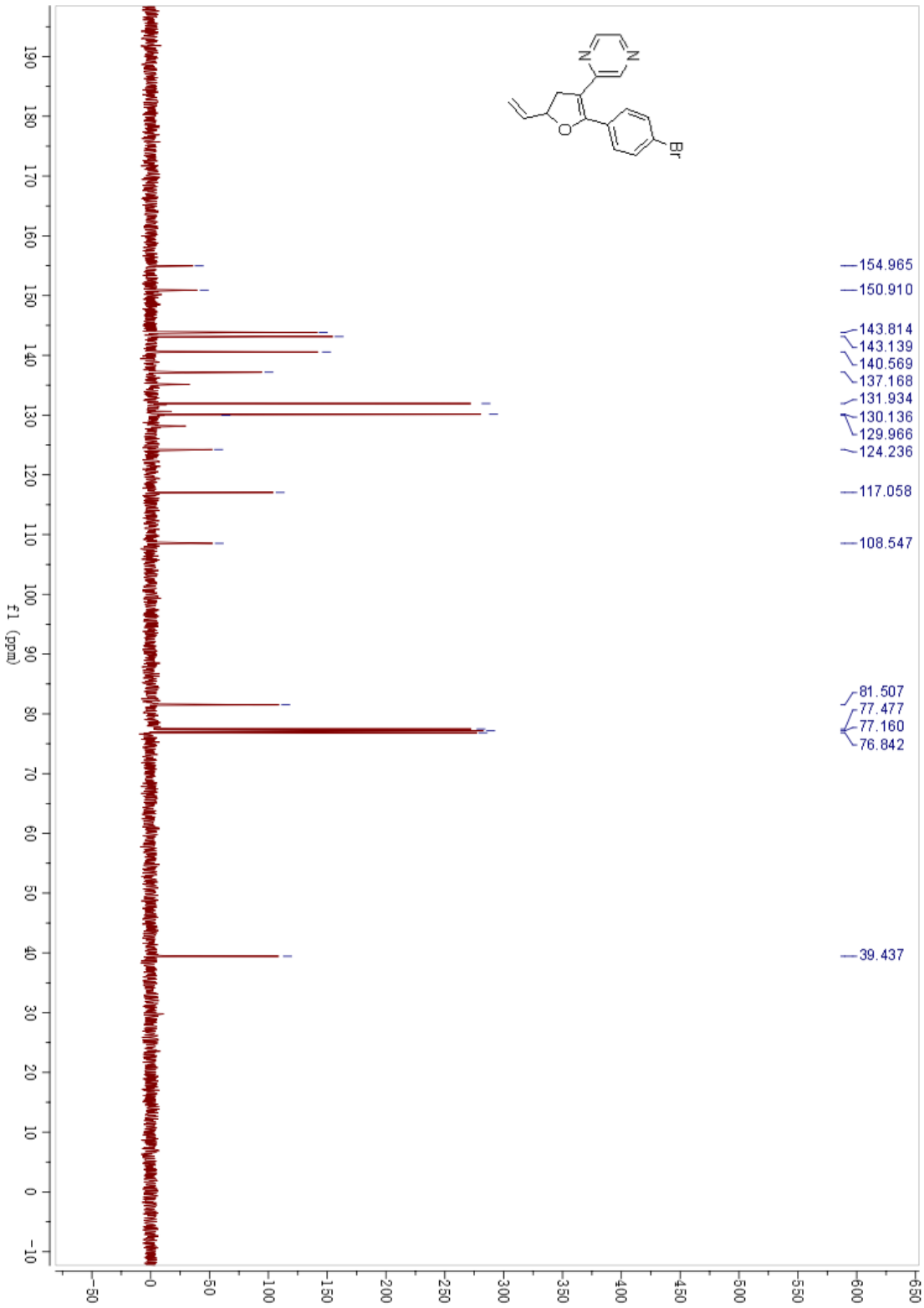
^{1}H NMR spectra of **3h**



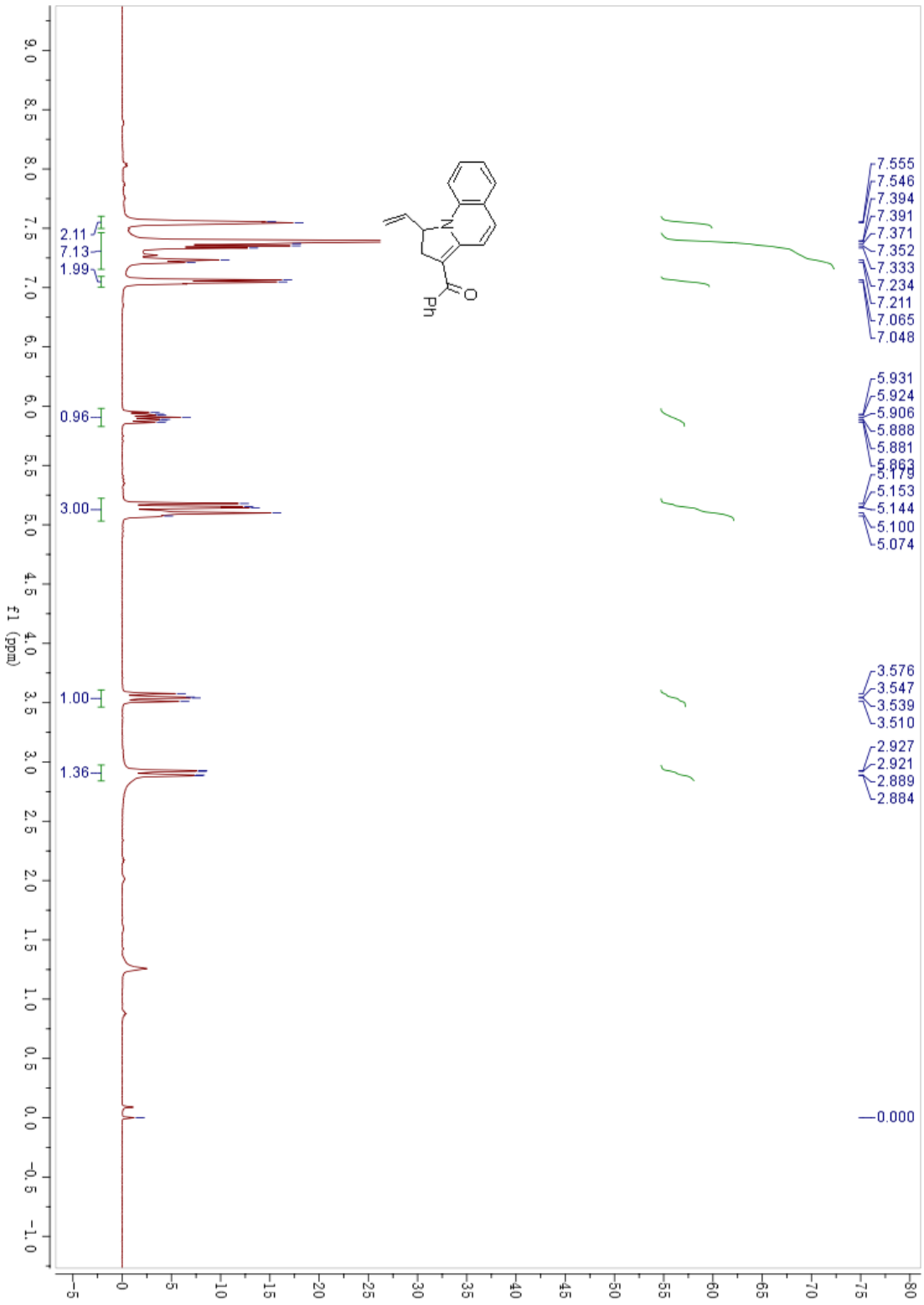
^{1}H NMR spectra of **3h'**



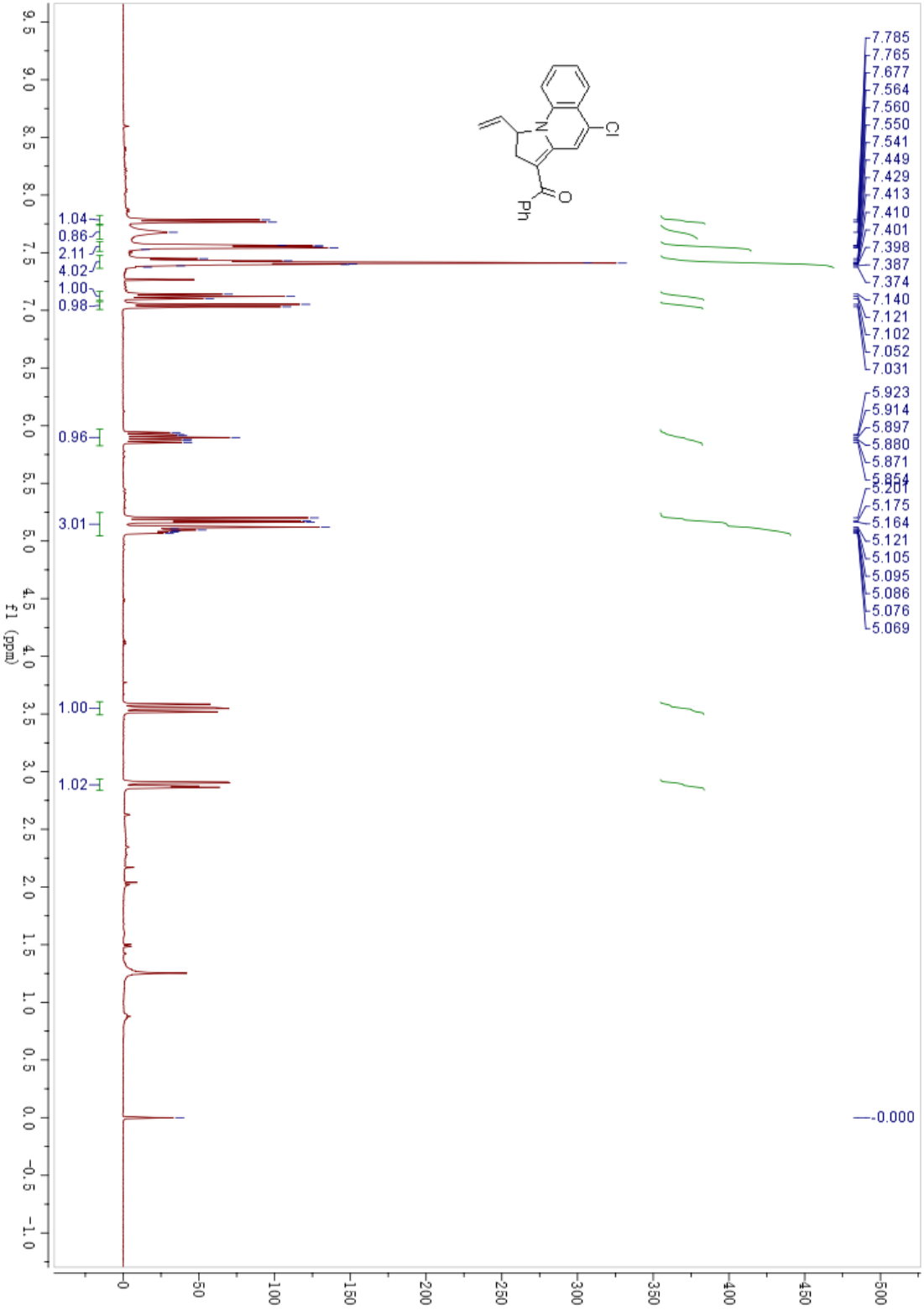
^{13}C NMR spectra of **3h'**



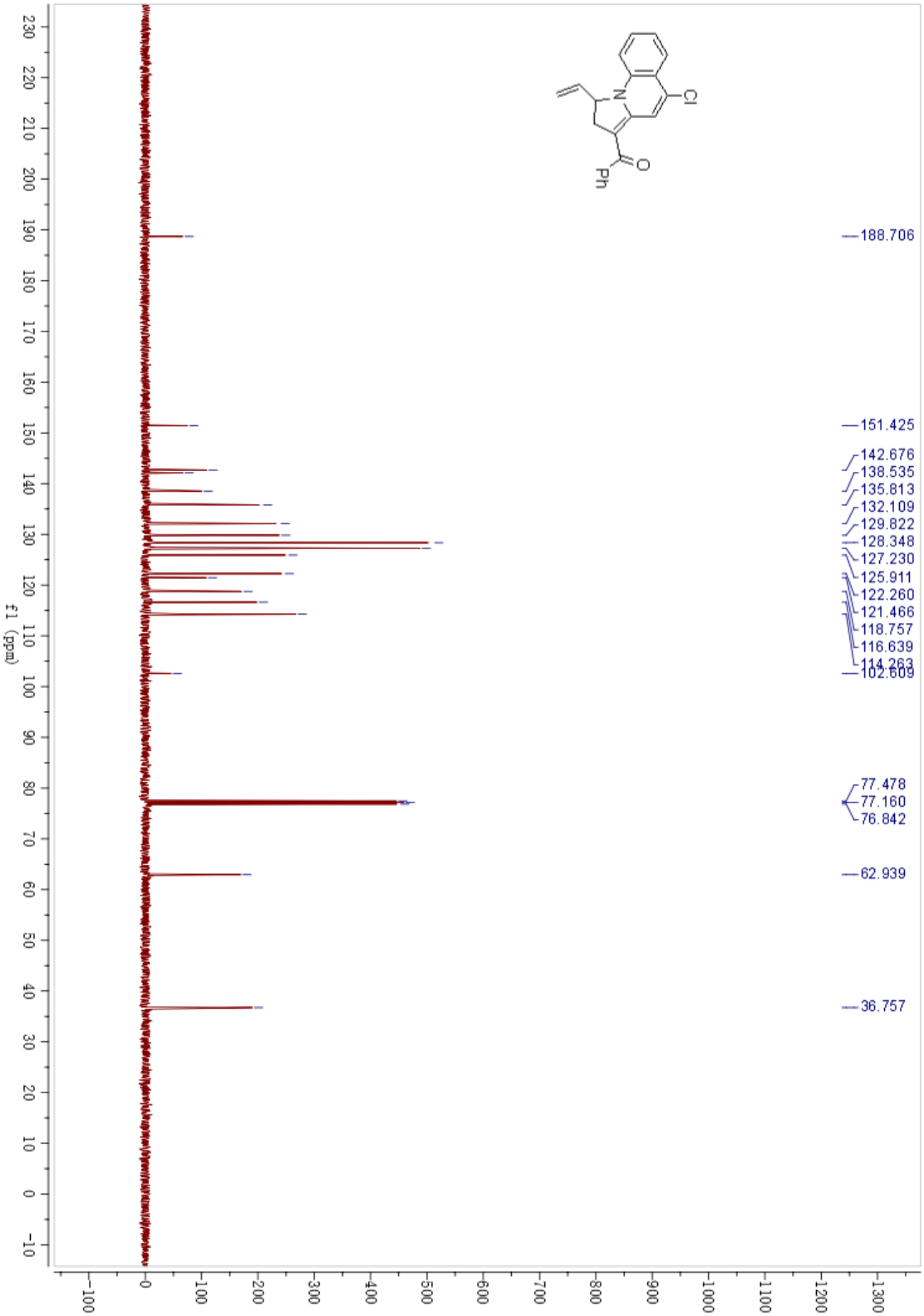
^{1}H NMR spectra of **3i**



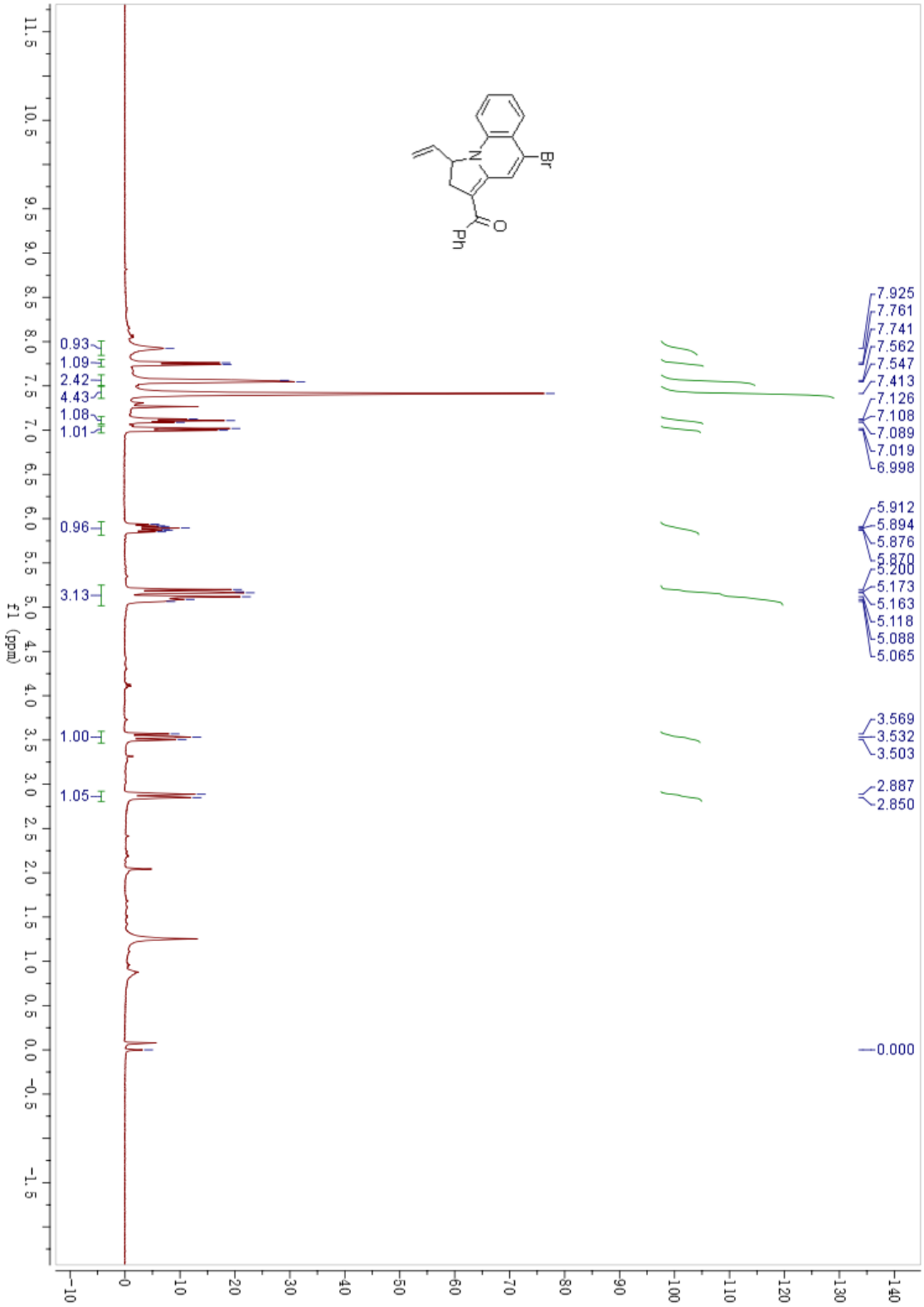
^{1}H NMR spectra of **3j**



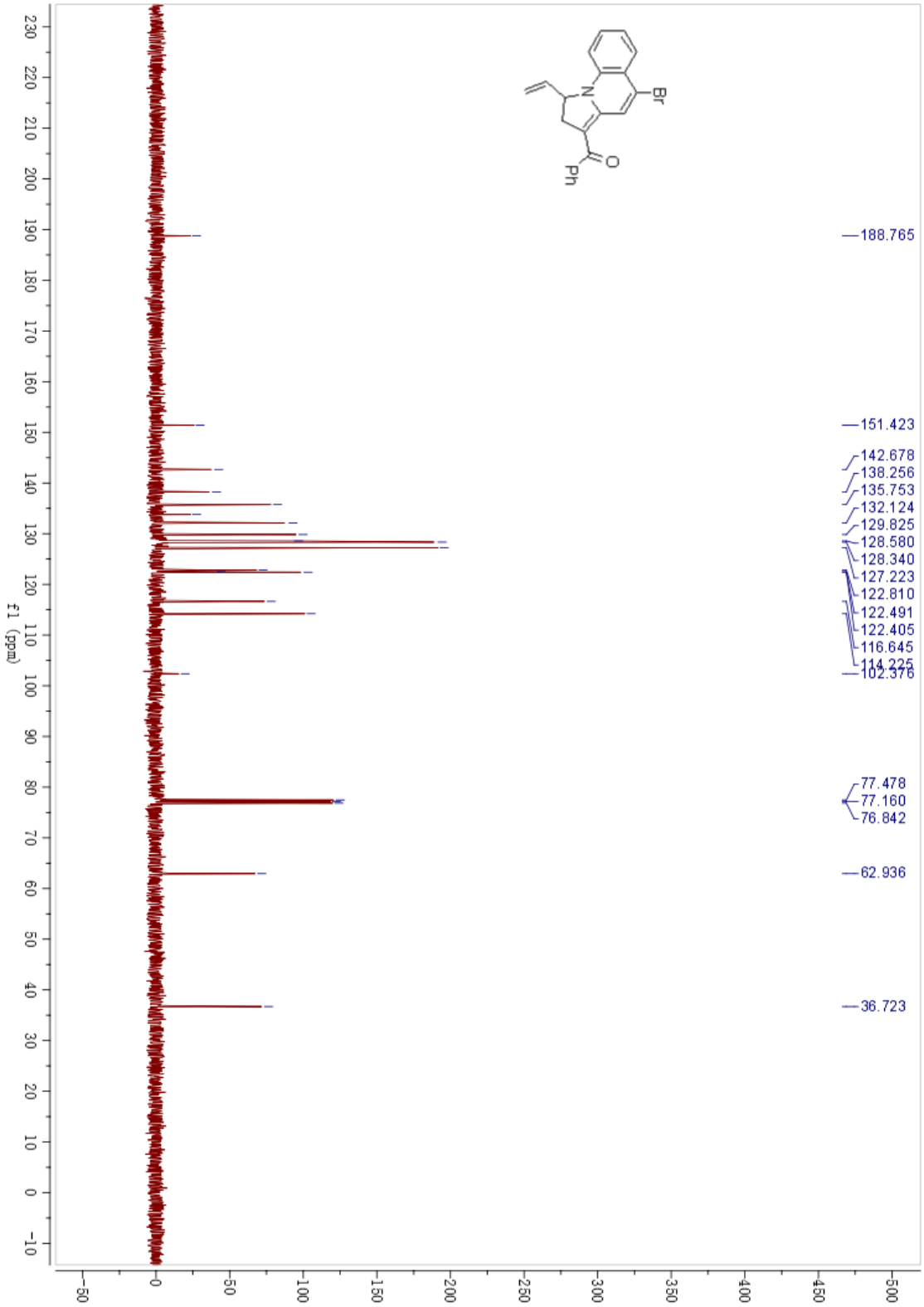
^{13}C NMR spectra of **3j**



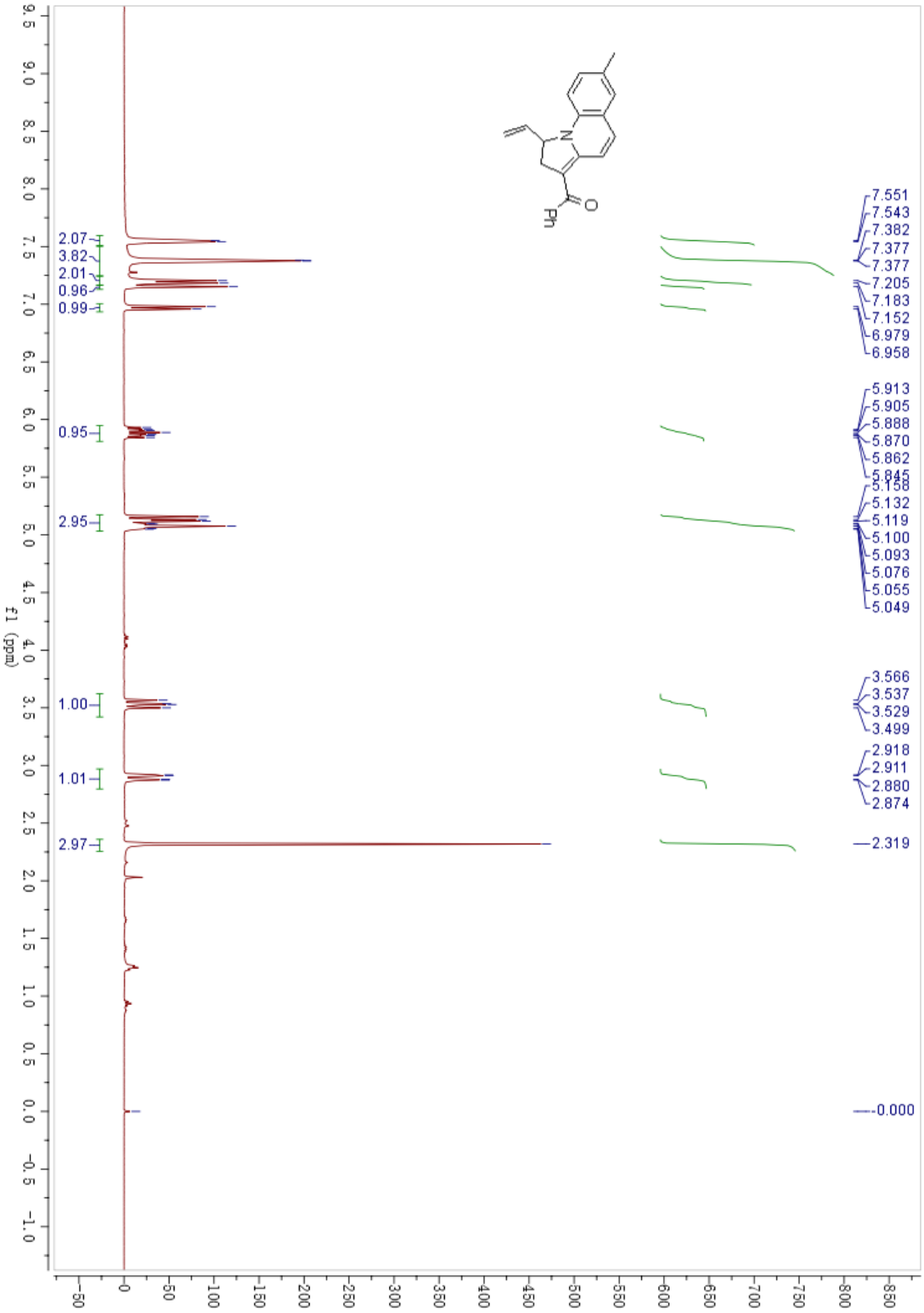
^{1}H NMR spectra of **3k**



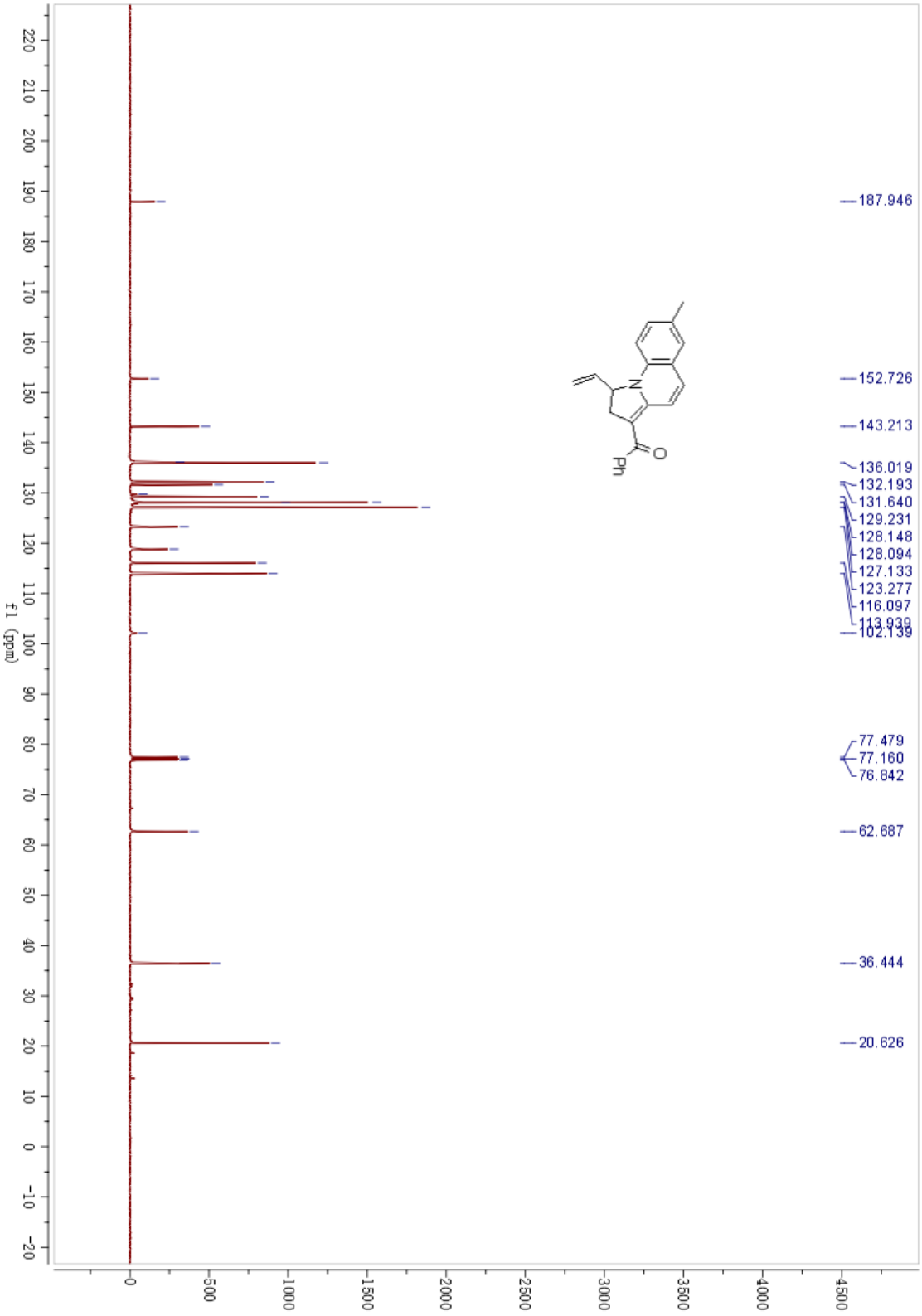
^{13}C NMR spectra of **3k**



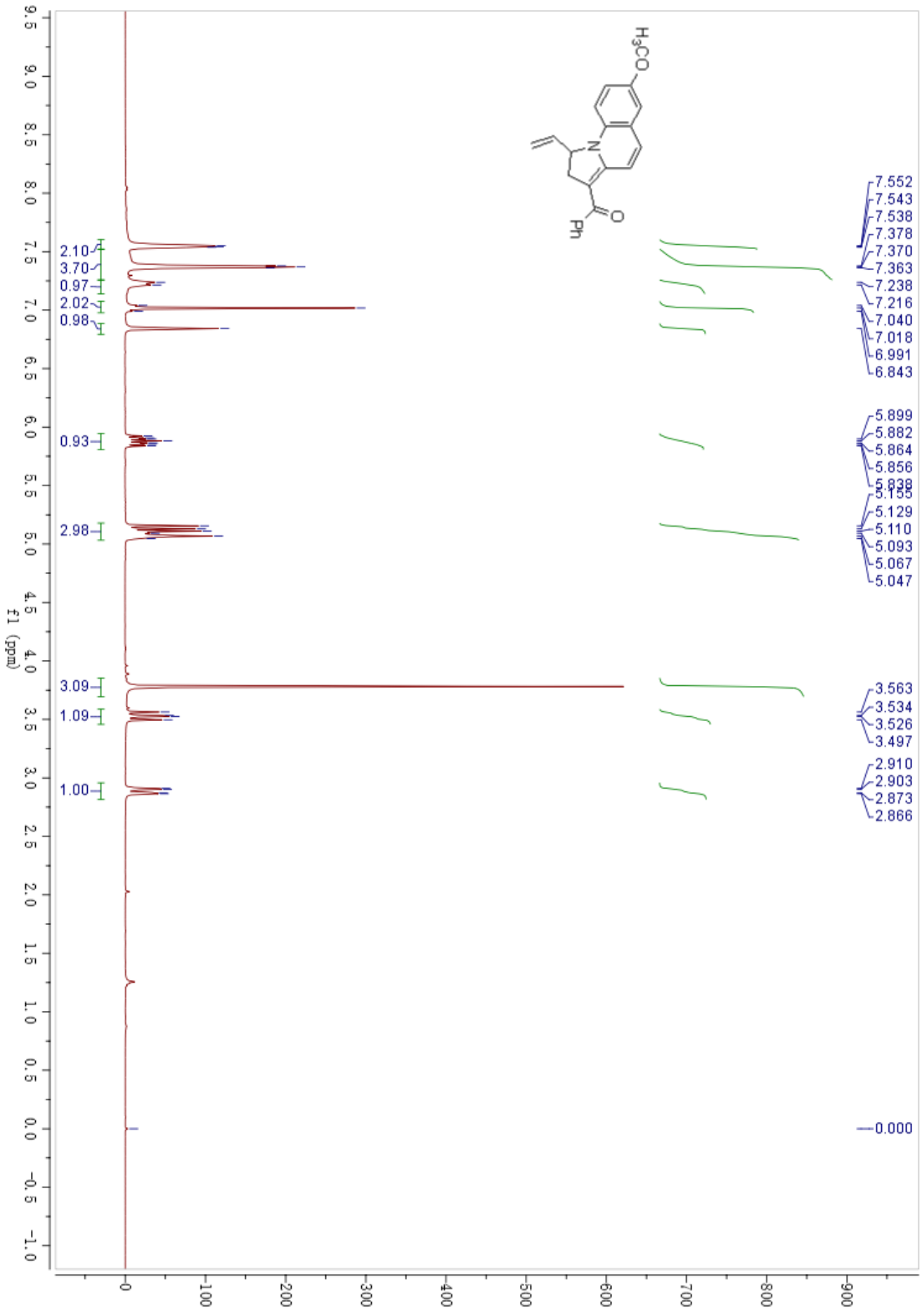
^{1}H NMR spectra of **3l**



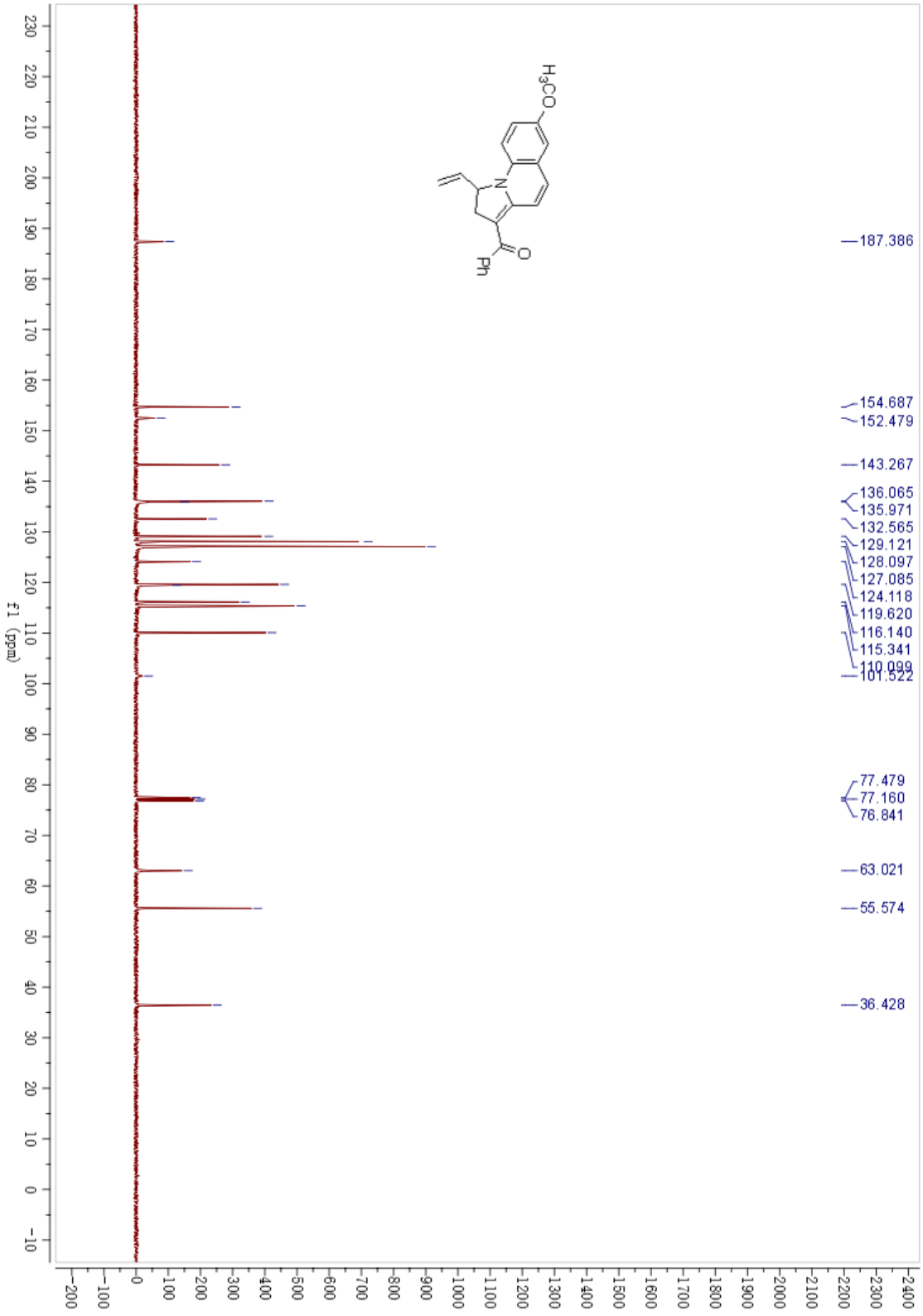
^{13}C NMR spectra of **3l**



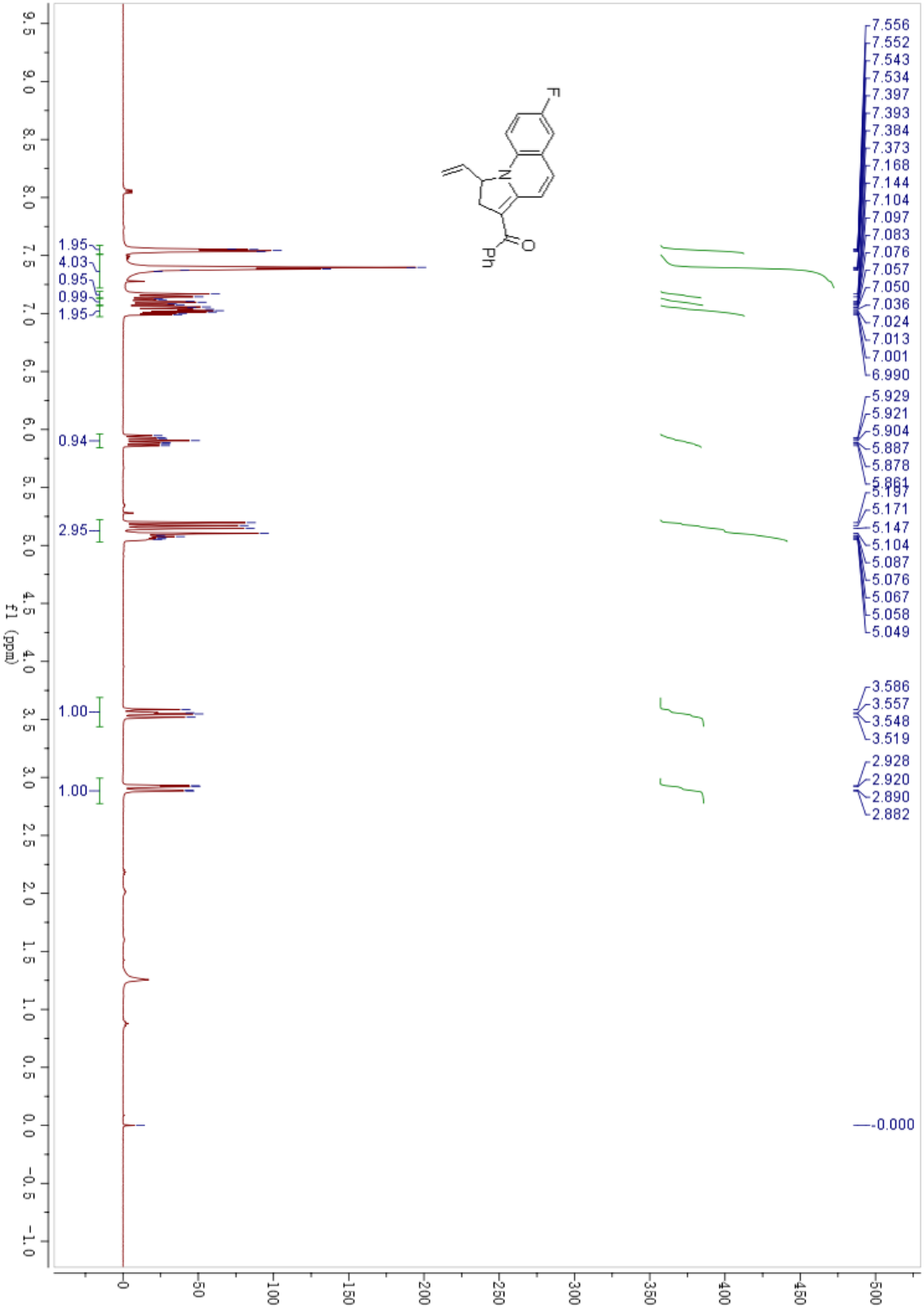
^{1}H NMR spectra of **3m**



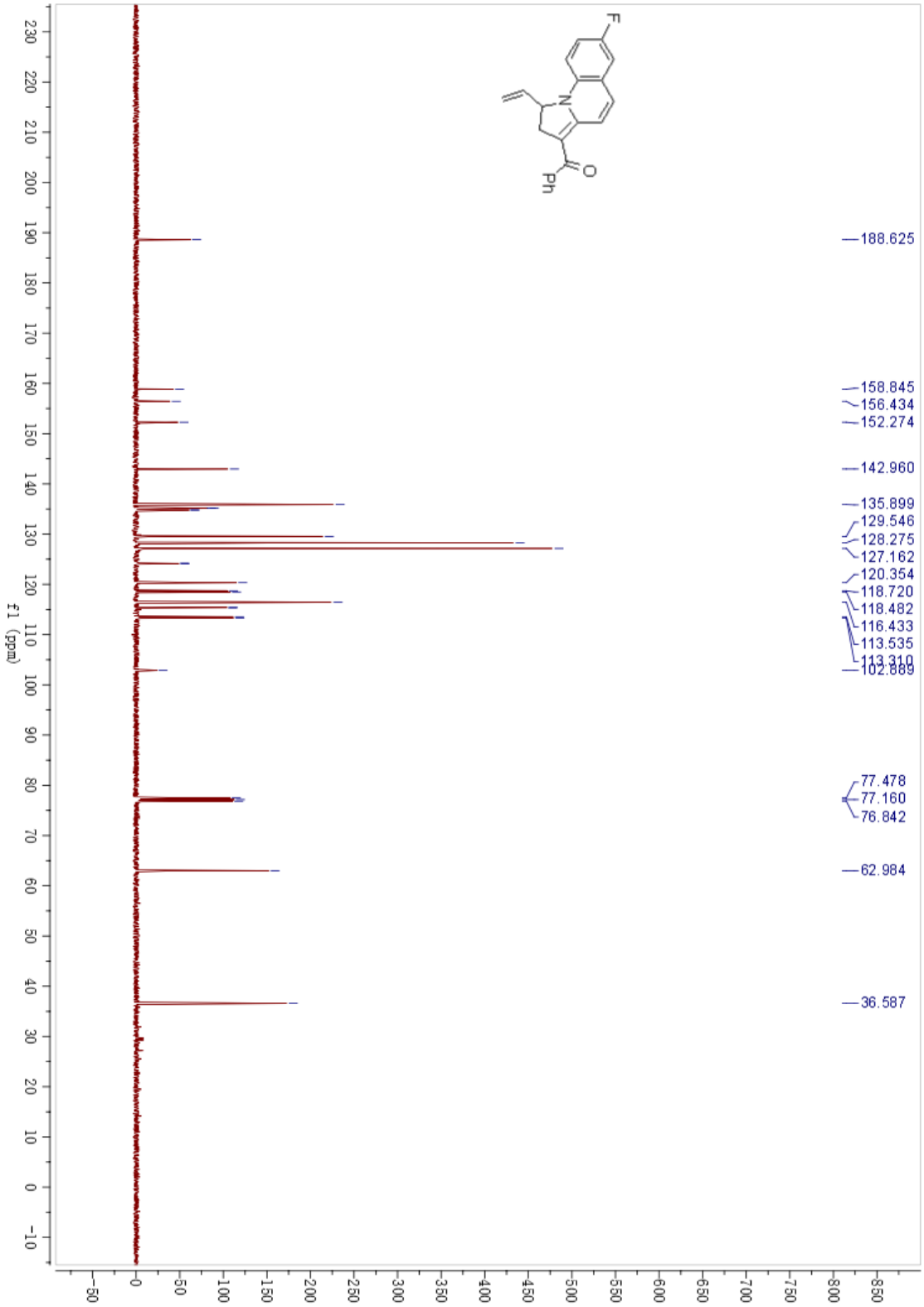
^{13}C NMR spectra of **3m**



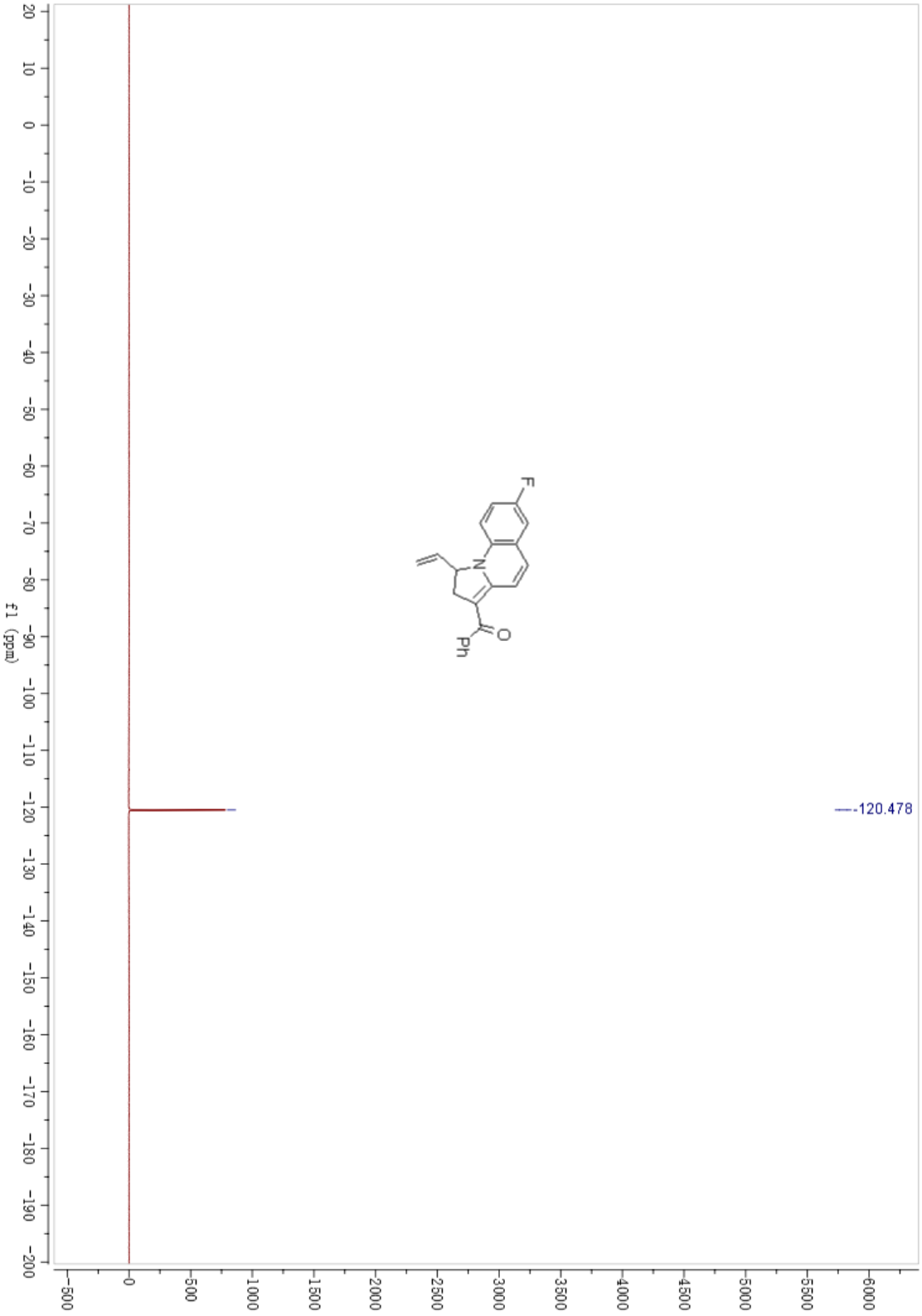
^{1}H NMR spectra of **3n**



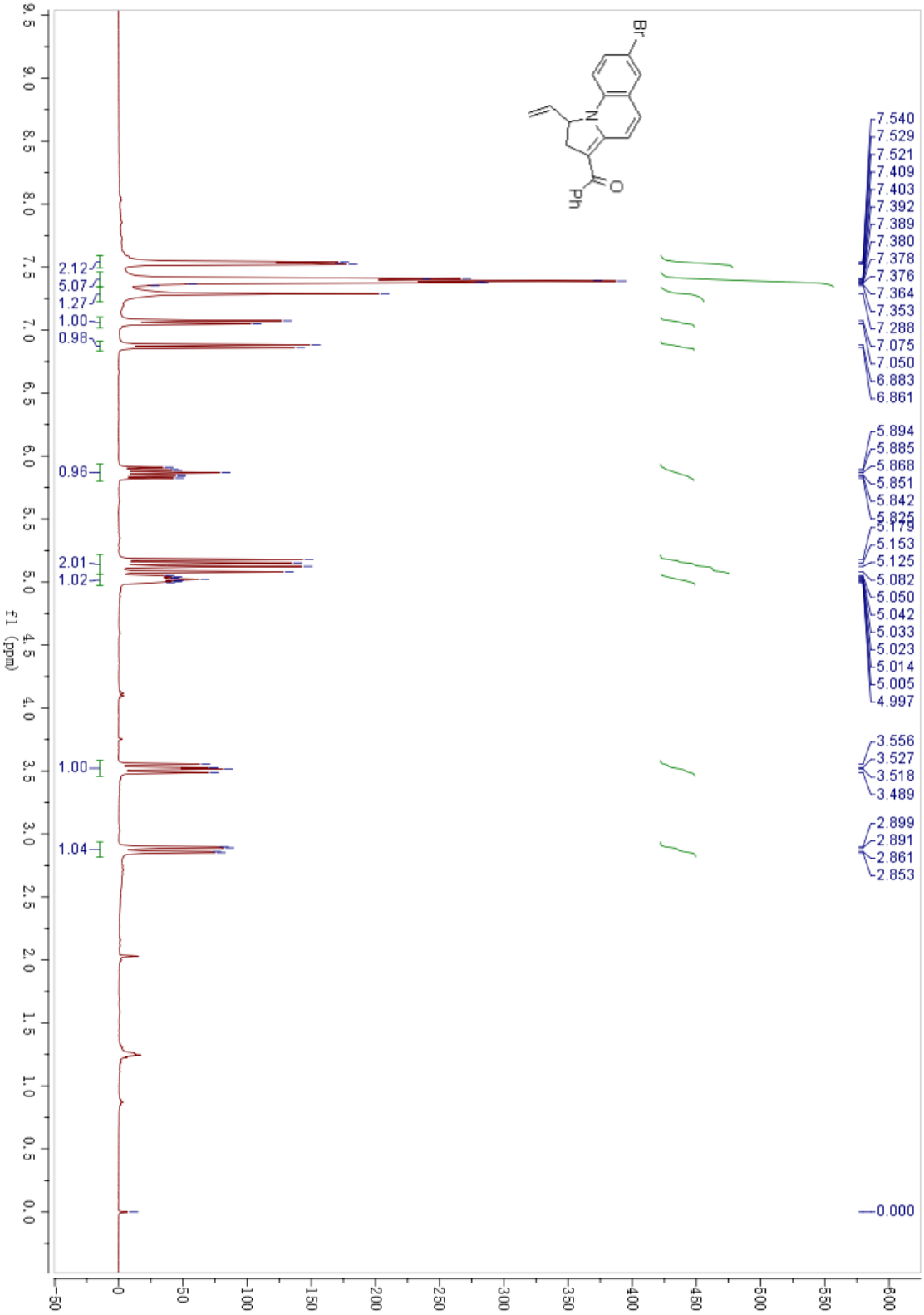
^{13}C NMR spectra of **3n**



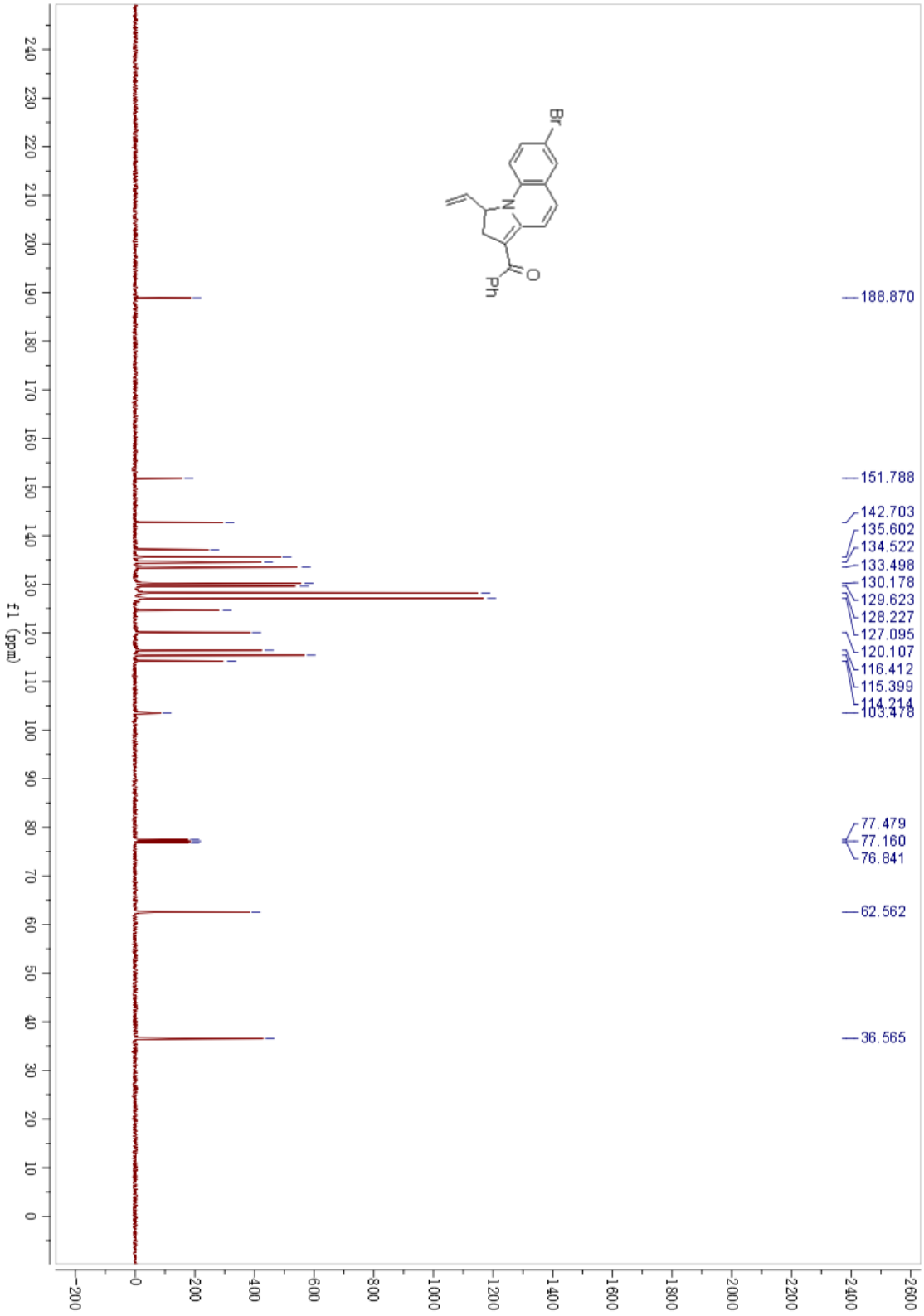
^{19}F NMR spectra of **3n**



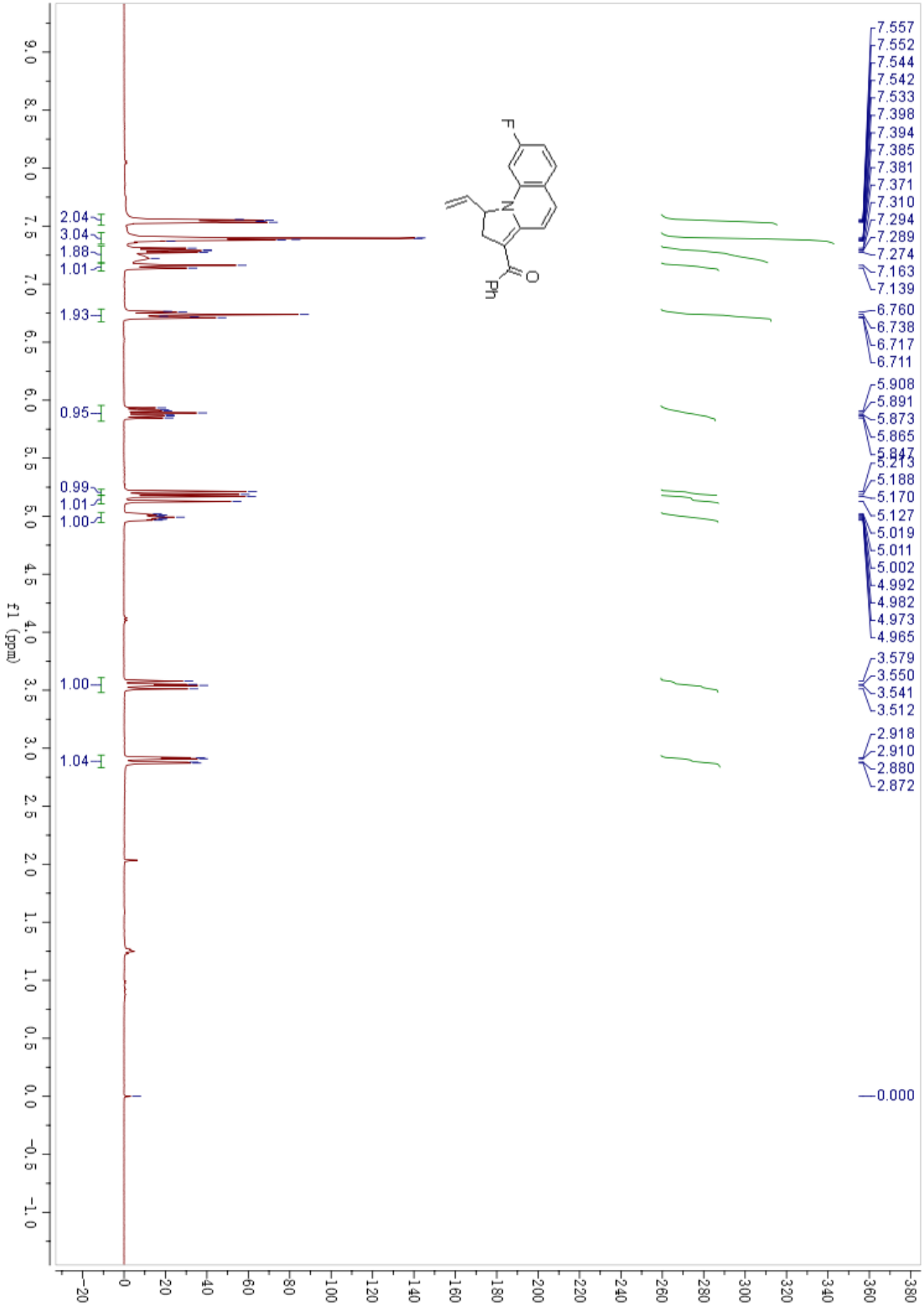
^{1}H NMR spectra of **3o**



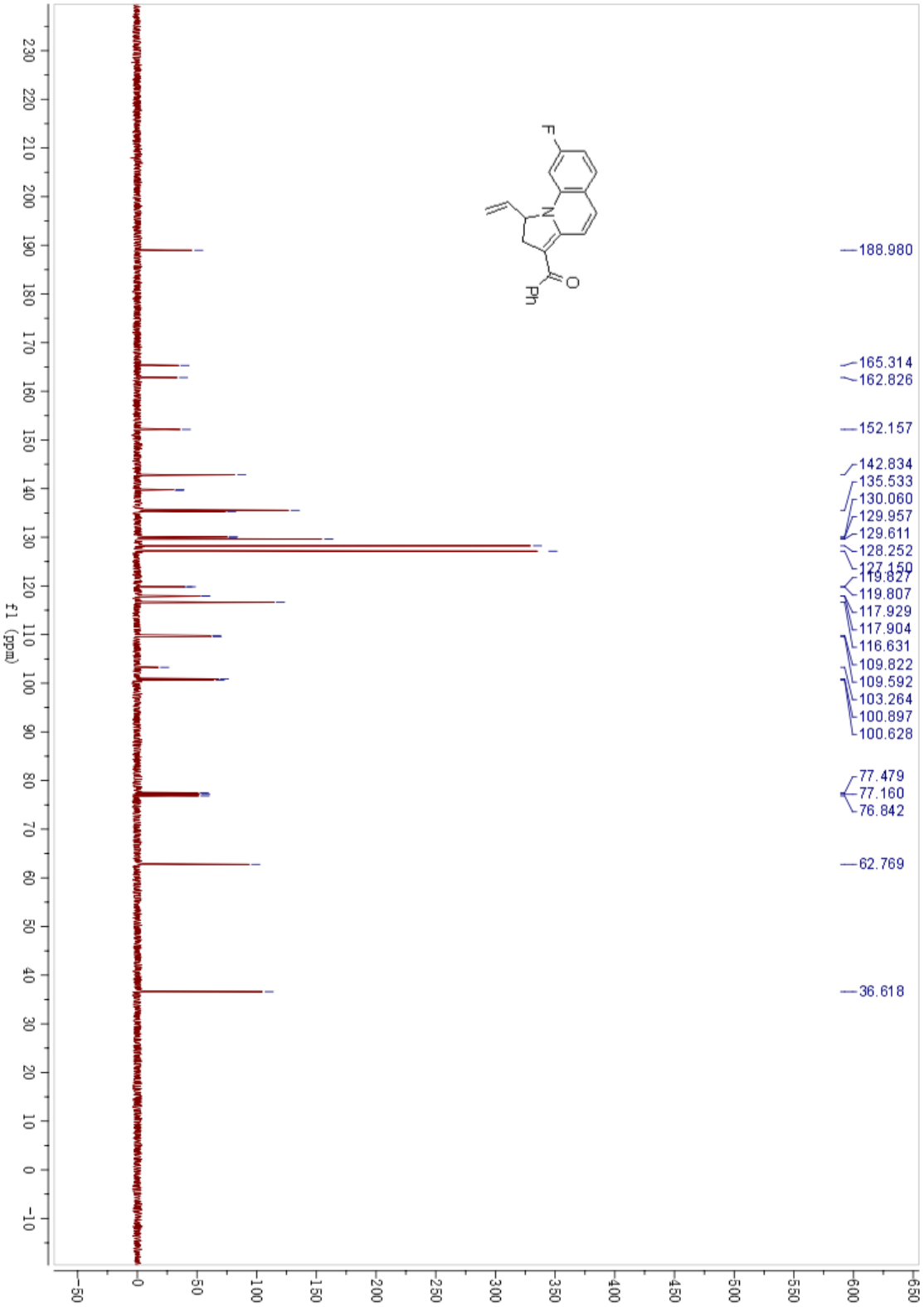
^{13}C NMR spectra of **3o**



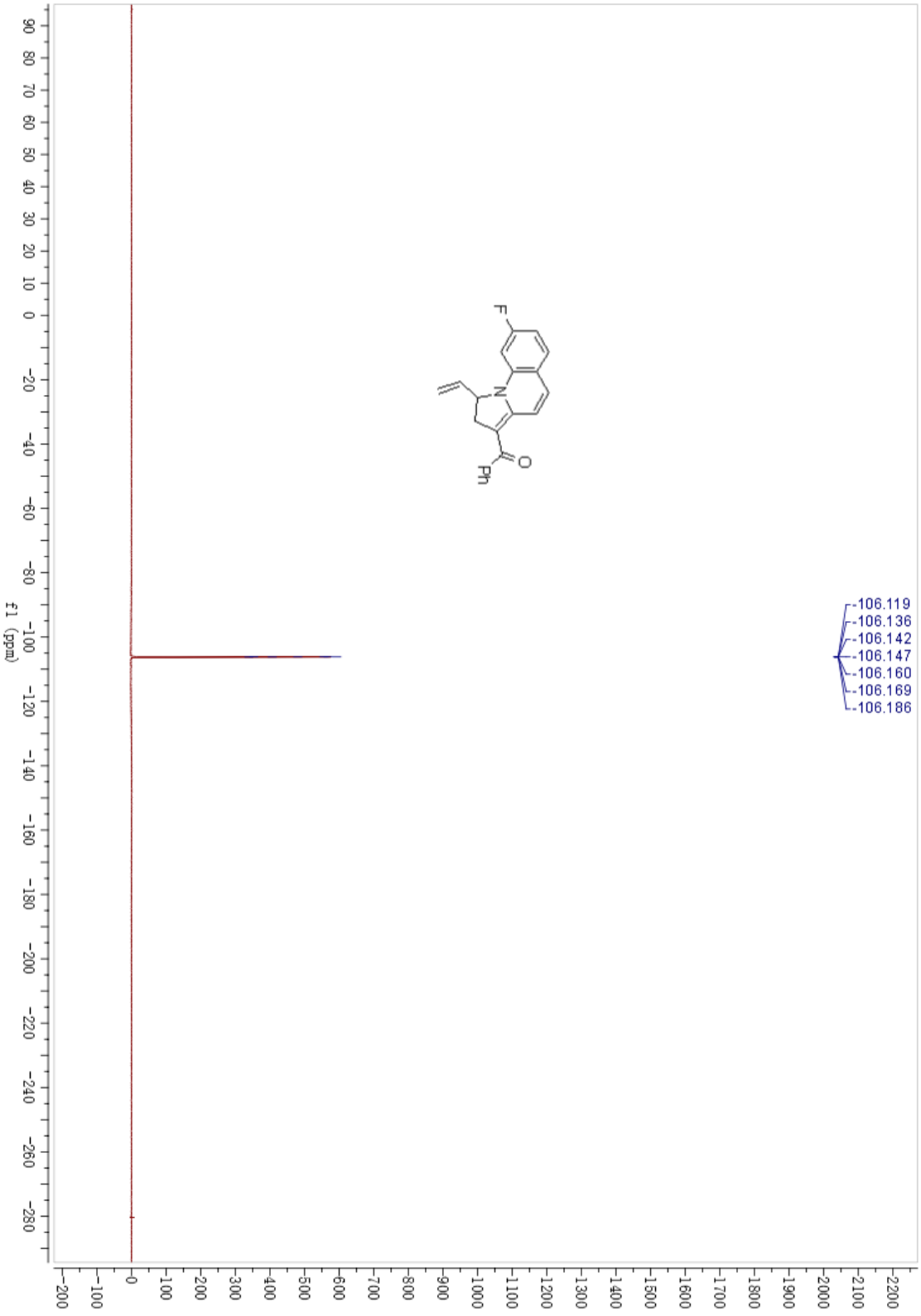
^{1}H NMR spectra of **3p**



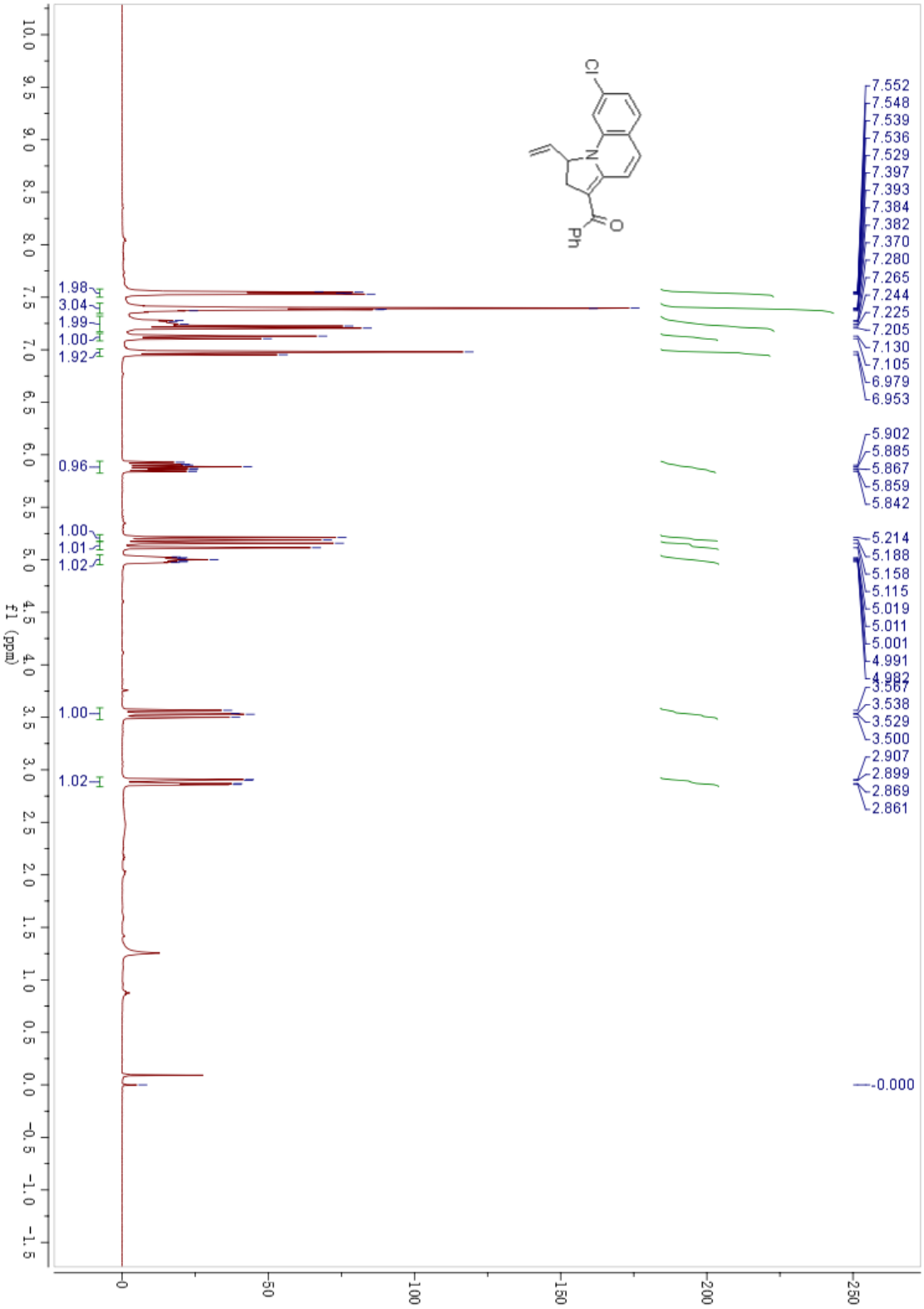
^{13}C NMR spectra of **3p**



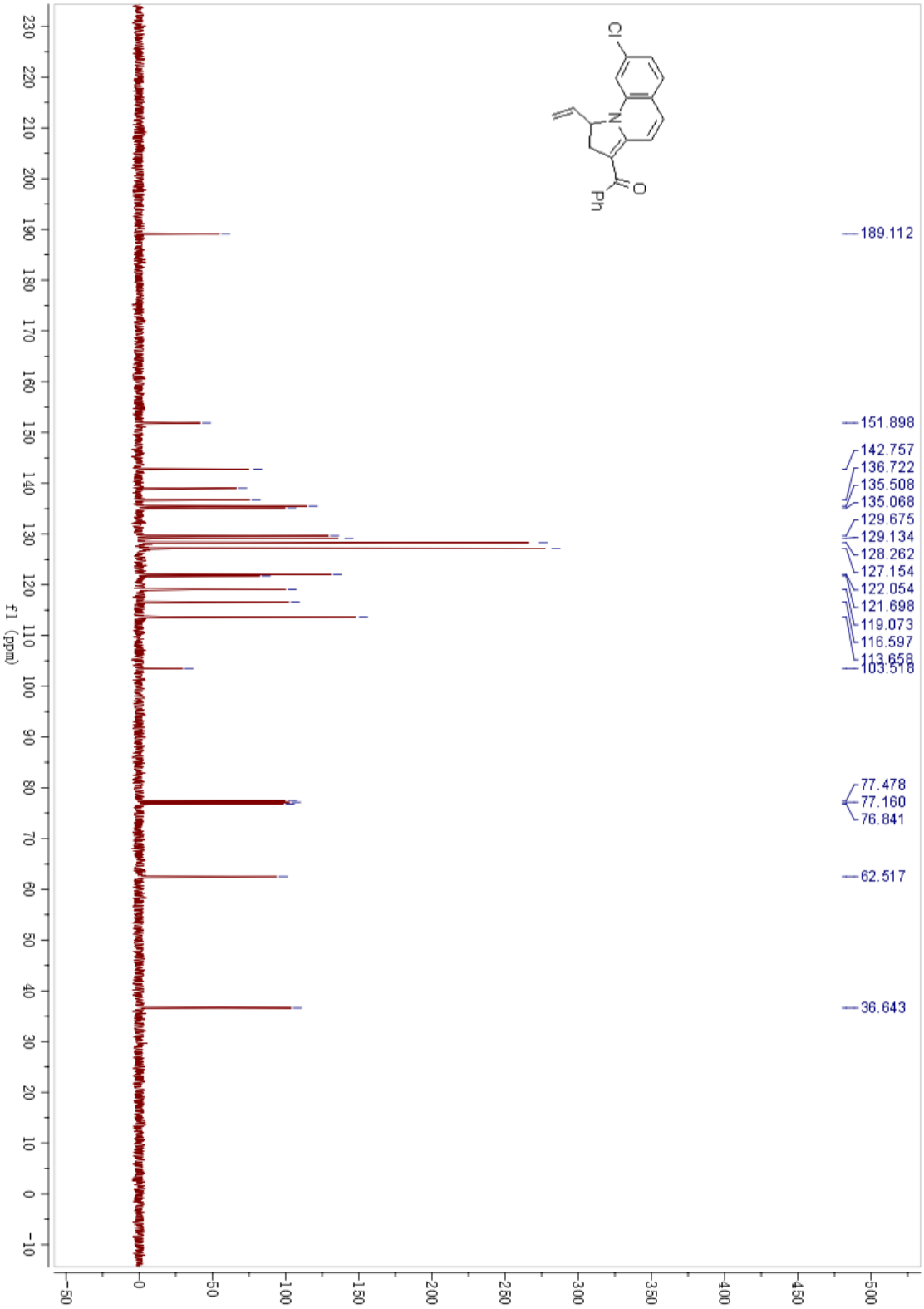
^{19}F NMR spectra of **3p**



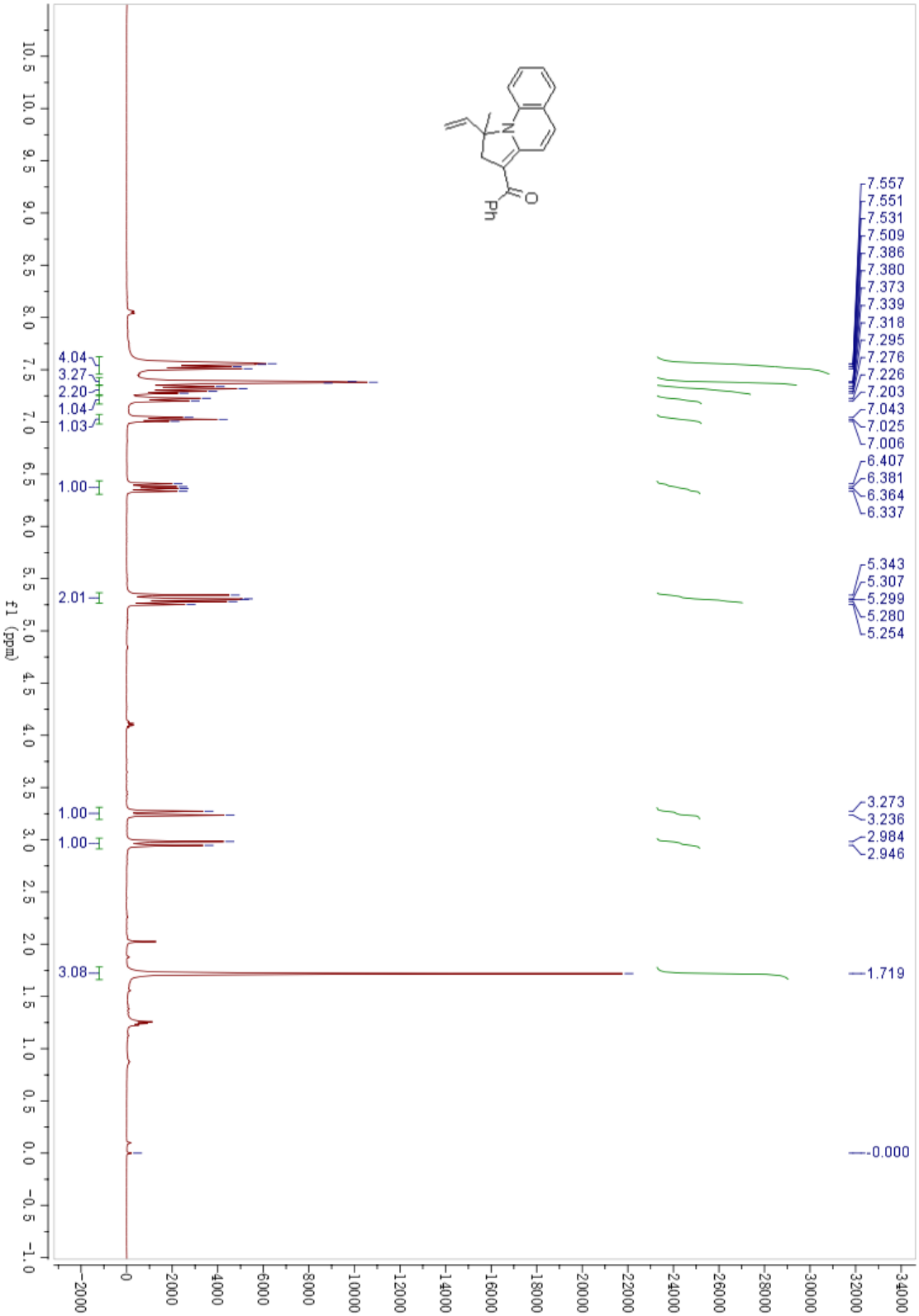
^{1}H NMR spectra of **3q**



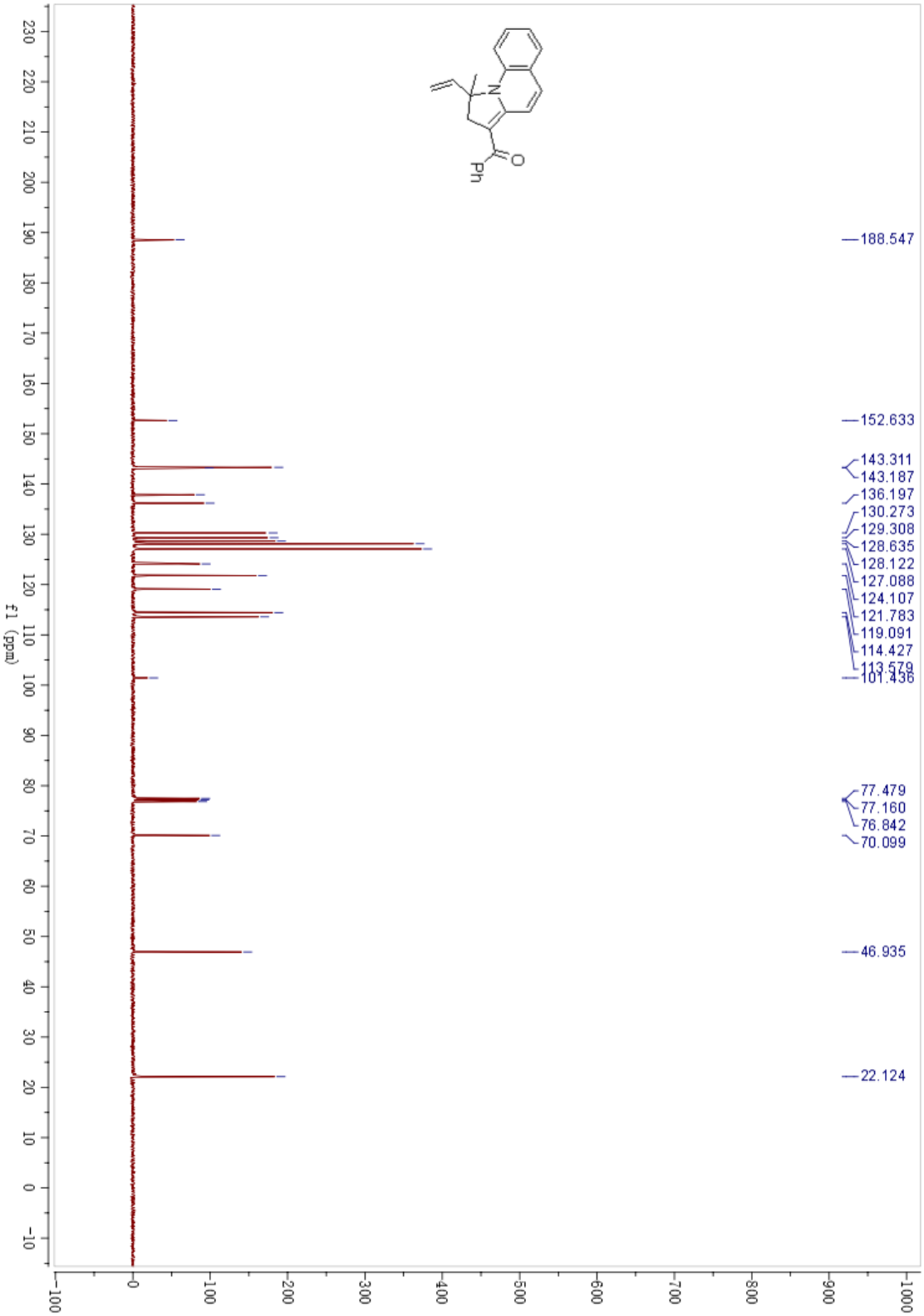
^{13}C NMR spectra of **3q**



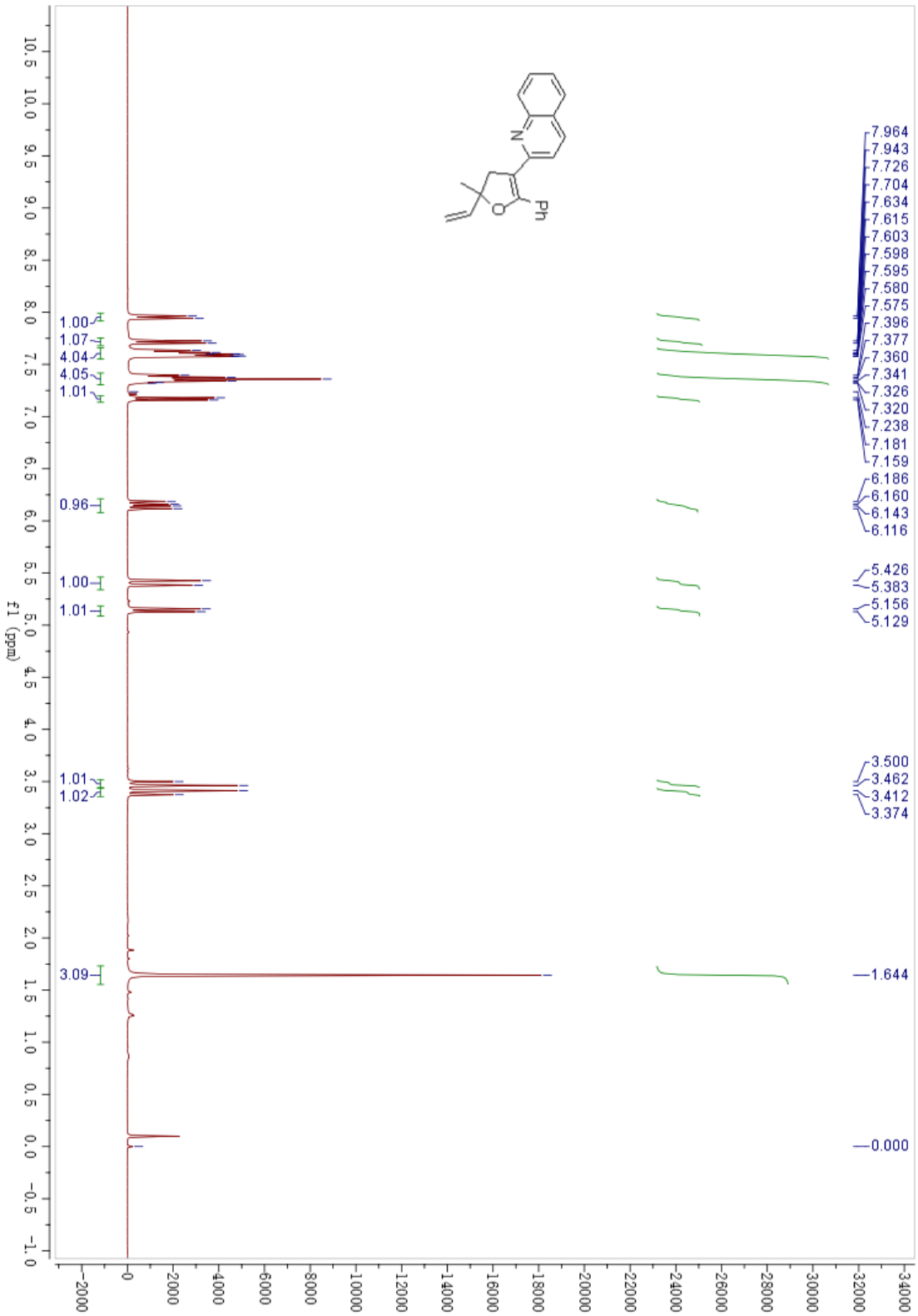
^{1}H NMR spectra of **3r**



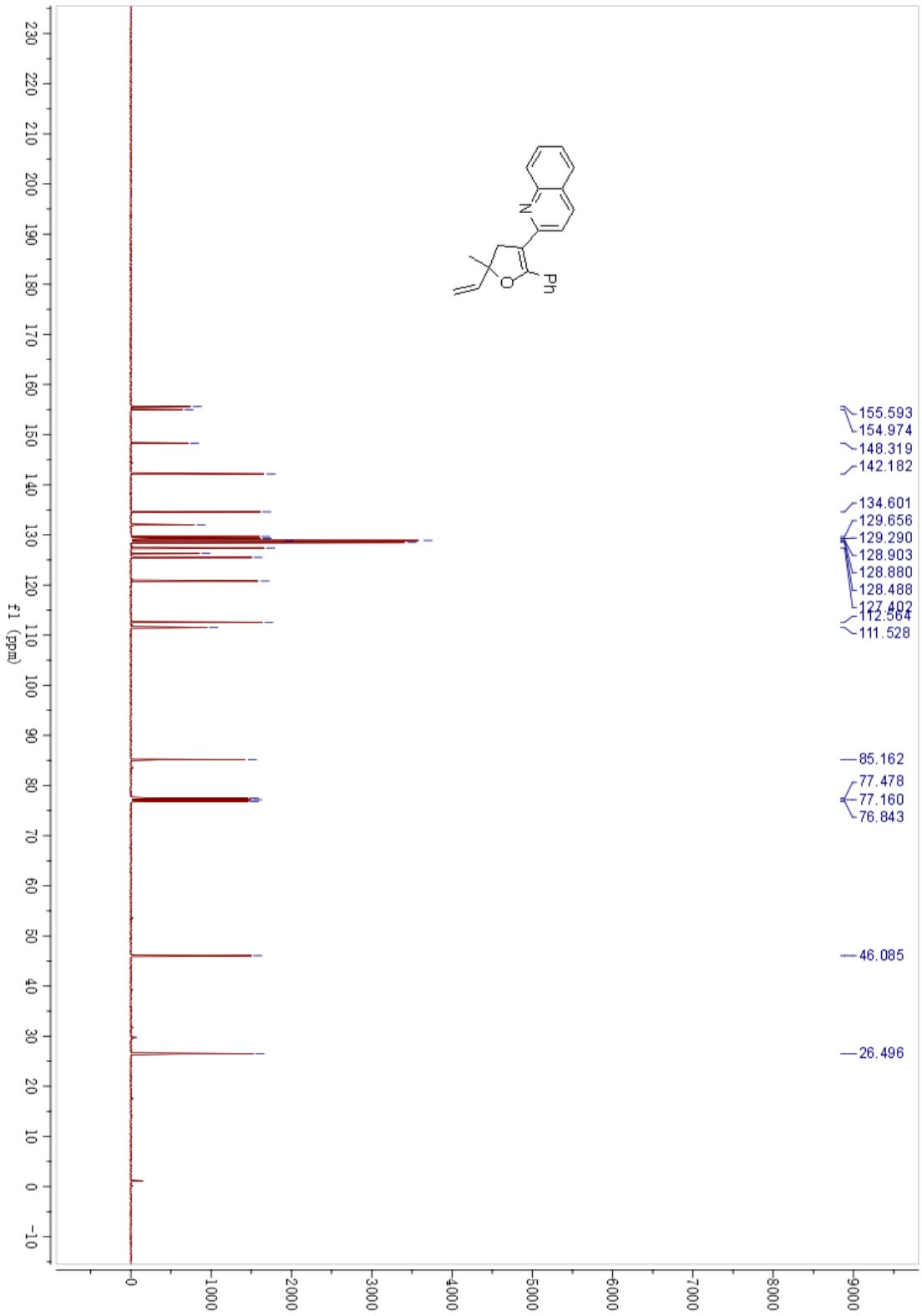
^{13}C NMR spectra of **3r**



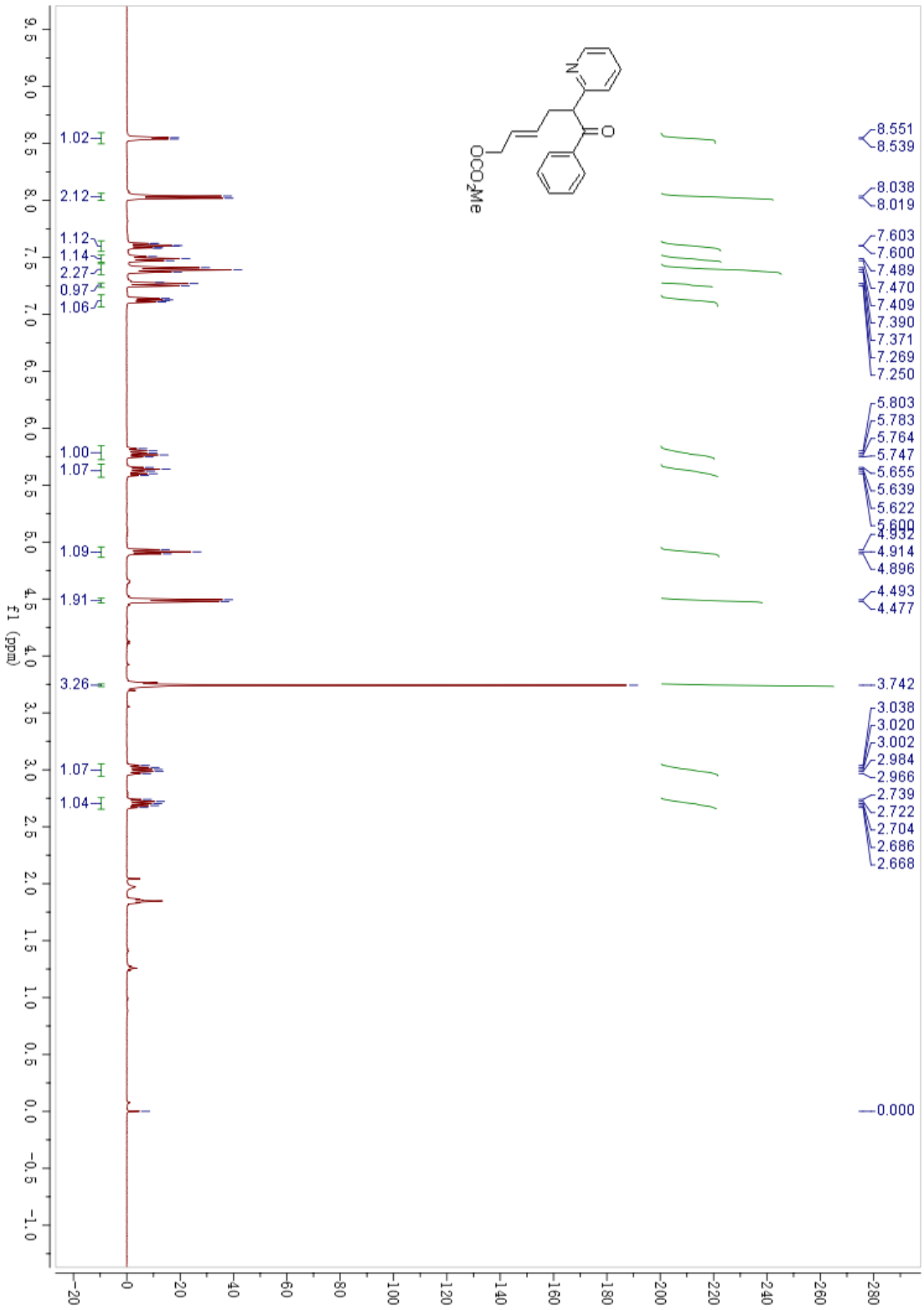
^{1}H NMR spectra of **3s**



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



^{1}H NMR spectra of **S4**



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[1] Muir, C. W.; Kennedy, A. R.; Redmond, J. M.; Watson, A. J. B. *Org. Biomol. Chem*. **2013**, *11*, 3337.

[2] Wang, T.-L.; Ouyang, G.; He, Y.-M.; Fan, Q.-H. *Synlett* **2011**, *7*, 939.

[3] Wuts, P. G. M.; Ashford, S. W.; Anderson, A. M.; Atkins, J. R. *Org. Lett.* **2003**, *5*, 1483.