Copper-Catalyzed Intramolecular Direct Amination of sp^2 C-H Bond for the Synthesis of N-Aryl Acridones

Supporting Information

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General Remarks

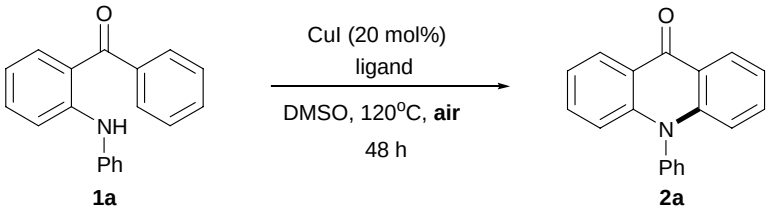
All manipulations were conducted with a standard Schlenk technique. ^{1}H-NMR spectra were recorded on a Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and calibrated with $CDCl_3$. Mass spectra were recorded using an Agilent 5975 GC-MS. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Experimental Procedures

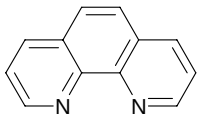
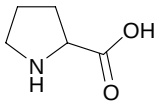
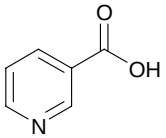
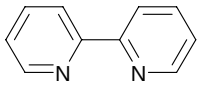
A Schlenk tube was charged with substrate **1** (0.3 mmol), CuI (0.06 mmol) and DMSO 1.6 mL. The mixture was stirred at 120 ^{o}C under air for 48 hours and monitored by TLC. The reaction was cooled down to room temperature, diluted with ethyl acetate, washed with brine (3×20 mL), dried over anhydrous Na_2SO_4, filtered, and dried under vaccum. The crude product was purified by column chromatography on silica gel to obtain the desired products **2**.

Table S1

Table *S1*. The Effect of Ligands[a]



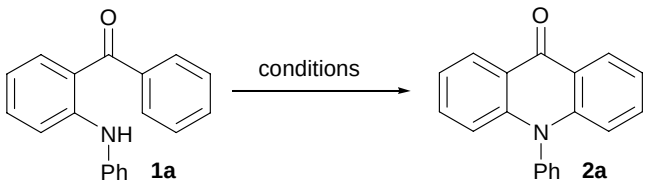
1a **2a**

entry	ligand (40 mol%)	yield (%)[b]
1	----------	78
2		74
3		23
4		4
5		74

[a] Reaction conditions: substrate **1a** (0.30 mmol), CuI (20 mol%), ligand (40 mol%), in DMSO (1.6 mL) stirred at 120 ^{o}C under air for 48 h. [b] Isolated yield.

Table *S2*

Table *S2.* Mechanism probing experiments[a]

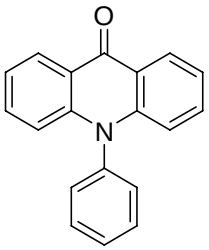


Entry	Cat. (20 mol%)	Yield (%)[b]
1	CuI	78
2[c]	CuI	0
3	$Cu(OAc)_2$	42
4[c]	$Cu((OAc)_2$	trace

[a] Reaction conditions: substrate **1a** (0.30 mmol), catalyst (20 mol%) in DMSO (1.6 mL) stirred at 120 ^{o}C under air for 48 h. [b] Isolated yield. [c] The reaction was carried out under N_2.

Analytical Data of Compounds 2

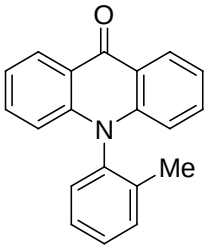
1) 10-Phenyl-9(10*H*)-acridinon (2a)[1]



2a

The reaction of phenyl(2-(phenylamino)phenyl)methanone (**1a**, 0.3 mmol, 82.0 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 63.4 mg (78%) of **2a** as solid. m.p.: 286-288 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, *J* = 7.6 Hz, 2H), 7.80-7.43 (m, 5H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.32-7.20 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.2, 143.2, 139.1, 133.3, 131.1, 130.1, 129.6, 127.4, 121.9, 121.6, 116.8 ppm; MS (70 eV): m/z (%) 271.1 (M^+, 100).

2) 10-(2-Methylphenyl)-9(10*H*)-acridinon (2b)

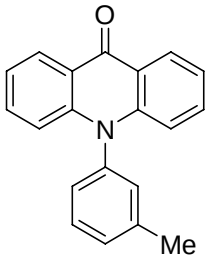


2b

The reaction of phenyl(2-((2-methylphenyl)amino)phenyl)methanone (**1b**, 0.3 mmol, 86.1 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 62 mg (73%) of **2b** as solid. m.p.: 208-209 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.61 (d, *J* = 7.6 Hz, 2H), 7.58-7.48 (m, 6H), 7.32-7.28 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 1.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.2, 142.4, 137.8, 137.5, 133.6, 132.4, 130.1, 129.9, 128.6, 127.5, 122.0, 121.7, 116.2, 17.0 ppm; MS (70 eV): m/z (%) 285.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{20}H_{16}NO$ $(M + H)^+$: 286.1226, found

286.1227.

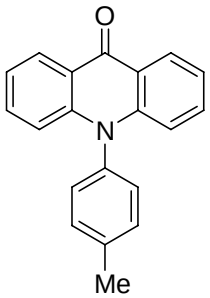
3) 10-(3-Methylphenyl)-9(10*H*)-acridinon (2c)



2c

The reaction of phenyl(2-((3-methylphenyl)amino)phenyl)methanone (**1c**, 0.3 mmol, 86.2 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 45 mg (53%) of **2c** as solid. m.p.: 205-207 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, J = 6.4 Hz, 2H), 7.61-7.42 (m, 4H), 7.30-7.10 (m, 4H), 6.79 (d, J = 10 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.2, 143.2, 141.4, 139.0, 133.2, 130.8, 130.5, 130.3, 127.3, 126.9, 121.9, 121.5, 116.9, 21.4 ppm; HRMS m/z (ESI) calcd for $C_{20}H_{16}NO$ $(M + H)^+$: 286.1226, found 286.1227.

4) 10-(4-Methylphenyl)-9(10*H*)-acridinon (2d)

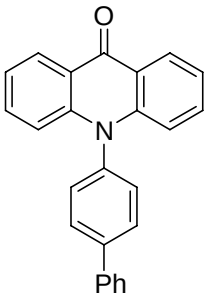


2d

The reaction of phenyl(2-((4-methylphenyl)amino)phenyl)methanone (**1d**, 0.3 mmol, 86.2 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 80 mg (93%) of **2d** as solid. m.p.: 281-283 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, J = 8.4 Hz, 2H), 7.53-7.48 (m, 4H), 7.29-7.22 (m, 4H), 6.80 (d, J = 8.4 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.3, 143.3, 140.0, 136.4, 133.1,

131.7, 129.7, 127.3, 121.9, 121.4, 116.9, 21.0 ppm; MS (70 eV): m/z (%) 285.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{20}H_{16}NO$ $(M + H)^+$: 286.1226, found 286.1226.

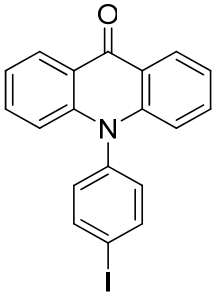
5) 10-(4-Phenylphenyl)-9(10*H*)-acridinon (2e)



2e

The reaction of phenyl(2-((4-phenylphenyl)amino)phenyl)methanone (**1e**, 0.3 mmol, 104.8 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 76 mg (73%) of **2e** as solid. m.p.: 268-269 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.61 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 6.8 Hz, 2H), 7.56-7.50 (m, 5H), 7.45 (d, J = 8.0 Hz, 2H), 7.32-7.24 (m, 2H), 6.87 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.1, 143.3, 142.7,139.7, 138.1, 133.4, 130.4, 129.7, 129.1, 128.2, 127.4, 127.3, 121.9, 121.6, 116.9 ppm; MS (70 eV): m/z (%) 347.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{25}H_{18}NO$ $(M + H)^+$: 348.1383, found 348.1381.

6) 10-(4-Iodophenyl)-9(10*H*)-acridinon (2f)

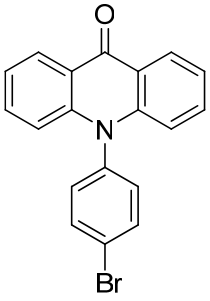


2f

The reaction of phenyl(2-((4-iodophenyl)amino)phenyl)methanone (**1f**, 0.3 mmol, 119.8 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure**

afforded 95 mg (80 %) of **2f** as solid. m.p.: 286-287 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, *J* = 8.0 Hz, 2H), δ = 8.06 (d, *J* = 8.0 Hz, 2H), 7.56-7.49 (m, 2H), 7.34-7.22 (m, 4H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.0, 142.9, 140.5, 138.8, 133.4, 132.2, 127.5, 122.0, 121.8, 116.5, 95.3 ppm; MS (70 eV): m/z (%) 397.0 (M^+, 100). HRMS m/z (ESI) calcd for $C_{19}H_{13}INO$ $(M + H)^+$: 398.0036, found 398.0039.

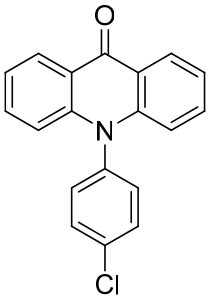
7) 10-(4-Bromophenyl)-9(10*H*)-acridinon (2g)



2g

The reaction of phenyl(2-((4-bromophenyl)amino)phenyl)methanone (**1g**, 0.3 mmol, 105.7 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 85 mg (81 %) of **2g** as solid. m.p.: 259-260 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, *J* = 7.6 Hz, 2H), δ = 7.85 (d, *J* = 8.4 Hz, 2H), 7.59-7.51 (m, 2H), 7.40-7.25 (m, 4H), 6.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.1, 143.0, 140.5, 138.1, 134.5, 133.4, 132.0, 127.5, 123.8, 121.8, 116.5 ppm; MS (70 eV): m/z (%) 349.0 (M^+, ^{80}Br , 100), 351.0 (M^+, ^{82}Br, 100). HRMS m/z (ESI) calcd for $C_{19}H_{13}BrNO$ $(M + H)^+$: 350.0175, found 350.0172.

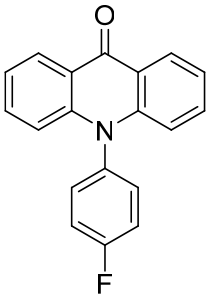
8) 10-(4-Chlorophenyl)-9(10*H*)-acridinon (2h)



2h

The reaction of phenyl(2-((4-chlorophenyl)amino)phenyl)methanone (**1h**, 0.3 mmol, 92.3 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 78 mg (85 %) of **2h** as solid. m.p.: 233-234 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.55-7.49 (m, 2H), 7.35-7.27 (m, 4H), 6.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.1, 143.0, 137.6, 135.8, 133.4, 131.6, 131.5, 127.5, 122.0, 121.8, 116.5 ppm; MS (70 eV): m/z (%) 305.1 (M^+, ^{35}Cl , 100) , 307.0 (M^+, ^{37}Cl, 35). HRMS m/z (ESI) calcd for $C_{19}H_{14}ClNO$ $(M + H)^+$: 306.0680, found 306.0679.

9) 10-(4-Fluorophenyl)-9(10*H*)-acridinon (2i)

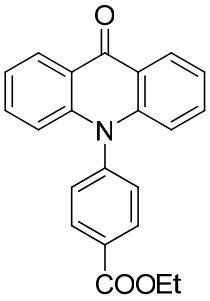


2i

The reaction of phenyl(2-((4-fluorophenyl)amino)phenyl)methanone (**1i**, 0.3 mmol, 87.4 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 62 mg (71 %) of **2i** as solid. m.p.: 271-272 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, *J* = 7.6 Hz, 2H), 7.55-7.49 (m, 2H), 7.47-7.35 (m, 4H), 7.31-7.25 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.1, 162.9 (d, *J* = 250 Hz), 143.2, 134.9 (d, *J* = 3.2 Hz), 133.4, 132.0 (d, *J* = 8.7 Hz), 127.4, 121.9, 121.7, 118.2 (d, *J* = 22.6 Hz), 116.6 ppm; ^{19}F NMR: (376 MHz, $CDCl_3$): δ = -109.4 ppm;

MS (70 eV): m/z (%) 289.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{19}H_{13}FNO$ $(M + H)^+$: 290.0976, found 290.0975.

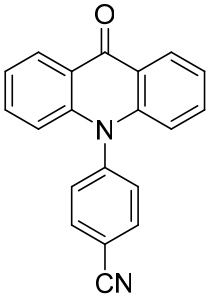
10) 10-(4-Ethoxycarbonylphenyl)-9(10*H*)-acridinon (2j)



2j

The reaction of phenyl(2-((4-ethoxycaronylphenyl)amino)phenyl)methanone (**1j**, 0.3 mmol, 103.6 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 57 mg (58 %) of **2j** as solid. m.p.: 219-220 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.61 (d, J = 8.4 Hz, 2H), 8.40 (d, J = 8.0 Hz, 2H), 7.56-7.46 (m, 4H), 7.33-7.25 (m, 2H), 6.72 (d, J = 8.4 Hz, 2H), 4.49 (q, J = 6.8 Hz, 2H), 1.47 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.1, 165.5, 143.1, 142.8, 133.4, 132.4, 132.0, 130.4, 127.5, 121.8, 116.5, 61.6, 14.3 ppm; MS (70 eV): m/z (%) 344.2 (100), 345.2 (M^+, 90). HRMS m/z (ESI) calcd for $C_{22}H_{18}NO_3$ $(M + H)^+$: 344.1281, found 344.1280.

11) 10-(4-Cyanophenyl)-9(10*H*)-acridinon (2k)

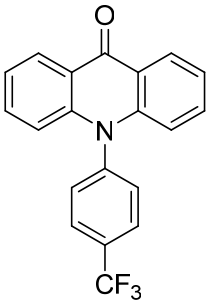


2k

The reaction of phenyl(2-((4-cyanophenyl)amino)phenyl)methanone (**1k**, 0.3 mmol, 89.5 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 27 mg (30 %) of **2k** as solid. m.p.: 330-332 ^oC; ^1H NMR ($CDCl_3$, 400 MHz):

δ = 8.6 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.60-7.50 (m, 4H), 7.36-7.30 (m, 2H), 6.64 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.9, 143.3, 142.5, 135.1, 133.6, 131.7, 127.7, 122.1, 122.0, 117.5, 116.0, 114.1 ppm; MS (70 eV): m/z (%) 297.1 (100), 298.1(M^+, 55). HRMS m/z (ESI) calcd for $C_{20}H_{13}N_2O$ $(M + H)^+$: 297.1023, found 297.1023.

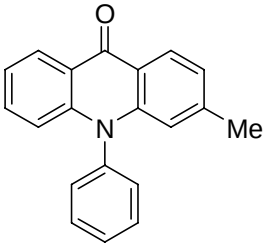
11) 10-(4-Trifluoromethylphenyl)-9(10*H*)-acridinon (2l)



2l

The reaction of phenyl(2-((4-trifluoromethylphenyl)amino)phenyl)methanone (**1l**, 0.3 mmol, 102.4 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 43 mg (42 %) of **2l** as solid. m.p.: 330-331 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.60 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.59-7.51 (m, 4H), 7.36-7.30 (m, 2H), 6.68 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.0, 142.7, 142.4, 133.5, 132.2, 131.9, 131.0, 128.4 (q, *J* = 3.6 HZ), 126.6 (q, *J* = 286 HZ), 125.0, 121.9, 116.3 ppm; ^{19}F NMR: (376 MHz, $CDCl_3$): δ = - 61.5 ppm; MS (70 eV): m/z (%) 339.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{20}H_{13}F_3NO$ $(M + H)^+$: 340.0944, found 340.0943.

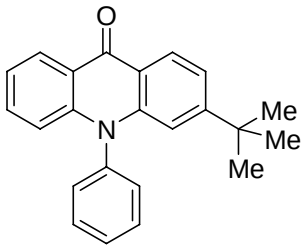
12) 3-Methyl-10- phenyl-9(10*H*)-acridinon (2m)



2m

The reaction of (2-(phenylamino)phenyl)(p-tolyl)methanone (**1m**, 0.24 mmol, 69 mg) and CuI (0.048 mmol, 9.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 46 mg (67 %) of **2m** as solid. m.p.: 263-264 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.58 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.8 Hz, 1H), 7.75-7.65 (m, 3H), 7.50-7.45 (m, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.34-7.25 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 6.51 (s, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.9, 144.3, 143.4, 143.2, 139.2, 133.0, 131.1, 130.1, 129.6, 127.3, 127.28, 123.4, 121.9, 121.4, 120.0, 116.8, 116.4, 22.3 ppm; MS (70 eV): m/z (%) 285.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{20}H_{16}NO$ $(M + H)^+$: 286.1226, found 286.1226.

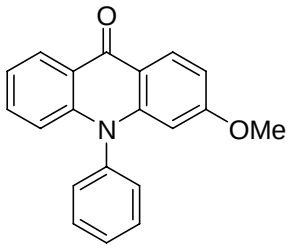
13) 3-*tert*-Butyl-10-phenyl-9(10H)-acridinon (2n)



2n

The reaction of (4-tert-butylphenyl)(2-(phenylamino)phenyl)methanone (**1n**, 0.3 mmol, 98.8 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 69 mg (70 %) of **2n** as solid. m.p.: 284-285 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (d, *J* = 7.6 Hz, 1H), 8.52 (d, *J* = 8.8 Hz, 1H), 7.78-7.62 (m, 3H), 7.50-7.45 (m, 1H), 7.40-7.22 (m, 4H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.71 (s, 1H), 1.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 157.1, 143.3, 143.2, 139.2, 132.9, 131.0, 130.1, 129.5, 127.2, 126.9, 121.3, 119.8, 116.7, 113.0, 35.3, 30.8 ppm; MS (70 eV): m/z (%) 327.2 (M^+, 100). HRMS m/z (ESI) calcd for $C_{23}H_{22}NO$ $(M + H)^+$: 328.1696, found 328.1698.

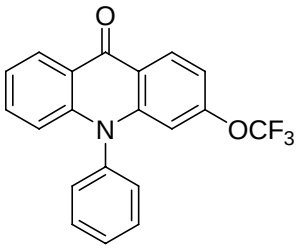
14) 3-Methoxy-10-phenyl-9(10H)-acridinon (2o)



2o

The reaction of (4-methoxyphenyl)(2-(phenylamino)phenyl)methanone (**1o**, 0.25 mmol, 76.0 mg) and CuI (0.05 mmol, 9.5 mg) in DMSO 1.6 mL under **typical procedure** afforded 22 mg (29 %) of **2o** as solid. m.p.: 202-203 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59-8.51 (m, 2H), 7.75-7.61 (m, 3H), 7.49-7.43 (m, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.28-7.24 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 6.1 (s, 1H), 3.7 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.3, 163.8, 145.2, 143.4, 139.2, 132.8, 131.1, 130.1, 129.61, 129.56, 127.3, 122.1, 121.5, 116.62, 116.58, 110.3, 99.7, 55.3 ppm; MS (70 eV): m/z (%) 301.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{20}H_{16}NO_2$ $(M + H)^+$: 302.1176, found 302.1174

15) 3-Trifluoromethoxy-10-phenyl-9(10H)-acridinon (2p)

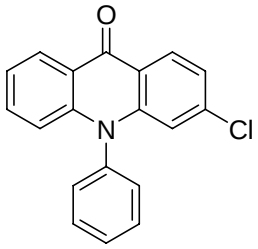


2p

The reaction of (4-trifluoromethoxy)(2-(phenylamino)phenyl)methanone (**1p**, 0.3 mmol, 107.2 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 49 mg (46 %) of **2p** as solid. m.p.: 223-224 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.64-8.55 (m, 2H), 7.76-7.67 (m, 3H), 7.55-7.49 (m, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.34-7.28 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.53 (s, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.2, 152.8, 144.3, 143.4, 140.8, 138.5, 133.6, 131.4, 130.0, 129.99, 129.8, 127.3, 122.1,, 120.3 (q, *J* = 257 HZ) 120.1

116.9, 113.8, 108.0 ppm; ^{19}F NMR: (376 MHz, $CDCl_3$): δ = -56.3 ppm; MS (70 eV): m/z (%) 355.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{20}H_{13}F_3NO_2$ $(M + H)^+$: 356.0893, found 356.0894

16) 3-Chloro-10-phenyl-9(10H)-acridinon (2q)

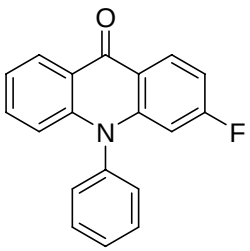


2q

The reaction of (4-chloro)(2-(phenylamino)phenyl)methanone (**1q**, 0.3 mmol, 92.3 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 70 mg (76 %) of **2q** as solid. m.p.: 261-262 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.58-8.49 (m, 2H), 7.76-7.64 (m, 3H), 7.55-7.48 (m, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.32-7.21 (m, 2H), 6.74-6.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.4, 143.8, 143.3, 139.8, 138.5, 133.5, 131.3, 129.97, 129.92, 129.1, 127.3, 122.3, 122.1, 120.3, 118.6, 116.9, 116.3 ppm; MS (70 eV): m/z (%) 305.1 (M^+, ^{35}Cl , 100) , 307.0 (M^+, ^{37}Cl, 35). HRMS m/z (ESI) calcd for $C_{19}H_{14}ClNO$ $(M + H)^+$: 306.0680, found 306.0680.

.

17) 3-Fluoro-10-phenyl-9(10H)-acridinon (2r)

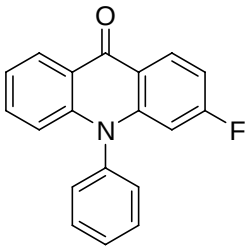


2r

The reaction of (4-fluoro)(2-(phenylamino)phenyl)methanone (**1r**, 0.3 mmol, 87.4 mg)

and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 29 mg (33 %) of **2r** as solid. m.p.: 275-276 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.62-8.55 (m, 2H), 7.75-7.61 (m, 3H), 7.53-7.47 (m, 3H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.32-7.21 (m, 1H), 7.01-6.95 (m, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 6.41-6.36 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.2, 165.9 (d, *J* = 250.9 Hz), 144.9 (d, *J* = 11.8 Hz), 143.4, 140.7, 138.7, 133.4, 131.3, 130.5 (d, *J* = 10.8 Hz), 129.93, 129.86, 127.3, 122.0, 118.7, 116.8, 110.4 (d, *J* = 23.1 Hz), 102.7 (d, *J* = 27.0 Hz) ppm; ^{19}F NMR: (376 MHz, $CDCl_3$): δ = -102.1 ppm; MS (70 eV): m/z (%) 289.1 (M^+, 100). HRMS m/z (ESI) calcd for $C_{19}H_{13}FNO$ $(M + H)^+$: 290.0976, found 290.0975.

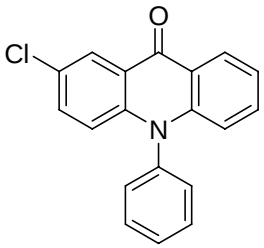
18) 3-Fluoro-10-phenyl-9(10H)-acridinon (2r)



2r

The reaction of (4-fluoro-2-(phenylamino)phenyl)(phenyl)methanone (**1s**, 0.3 mmol, 87.3 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 72 mg (83 %) of **2r** as solid.

19) 2-Chloro-10-phenyl-9(10H)-acridinon (2s)

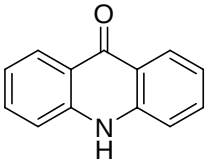


2s

The reaction of (5-chloro-2-(phenylamino)phenyl)(phenyl)methanone (**1t**, 0.3 mmol, 92.3 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure**

afforded 78 mg (85 %) of **2s** as solid. m.p.: 230-231^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.65-8.52 (m, 2H), 7.76-7.67 (m, 3H), 7.55-7.49 (m, 5H), 6.79-6.71 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 177.0, 143.1, 141.6, 138.8, 133.5, 133.4, 131.2, 129.9, 129.8, 127.6, 127.4, 126.4, 122.7, 121.9, 121.8, 118.6, 116.9 ppm; MS (70 eV): m/z (%) 305.1 (M^+, ^{35}Cl , 100) , 307.0 (M^+, ^{37}Cl, 35). HRMS m/z (ESI) calcd for $C_{19}H_{14}ClNO$ $(M + H)^+$: 306.0680, found 306.0681.

20) 10H-Acridin-9-one (5)[2]

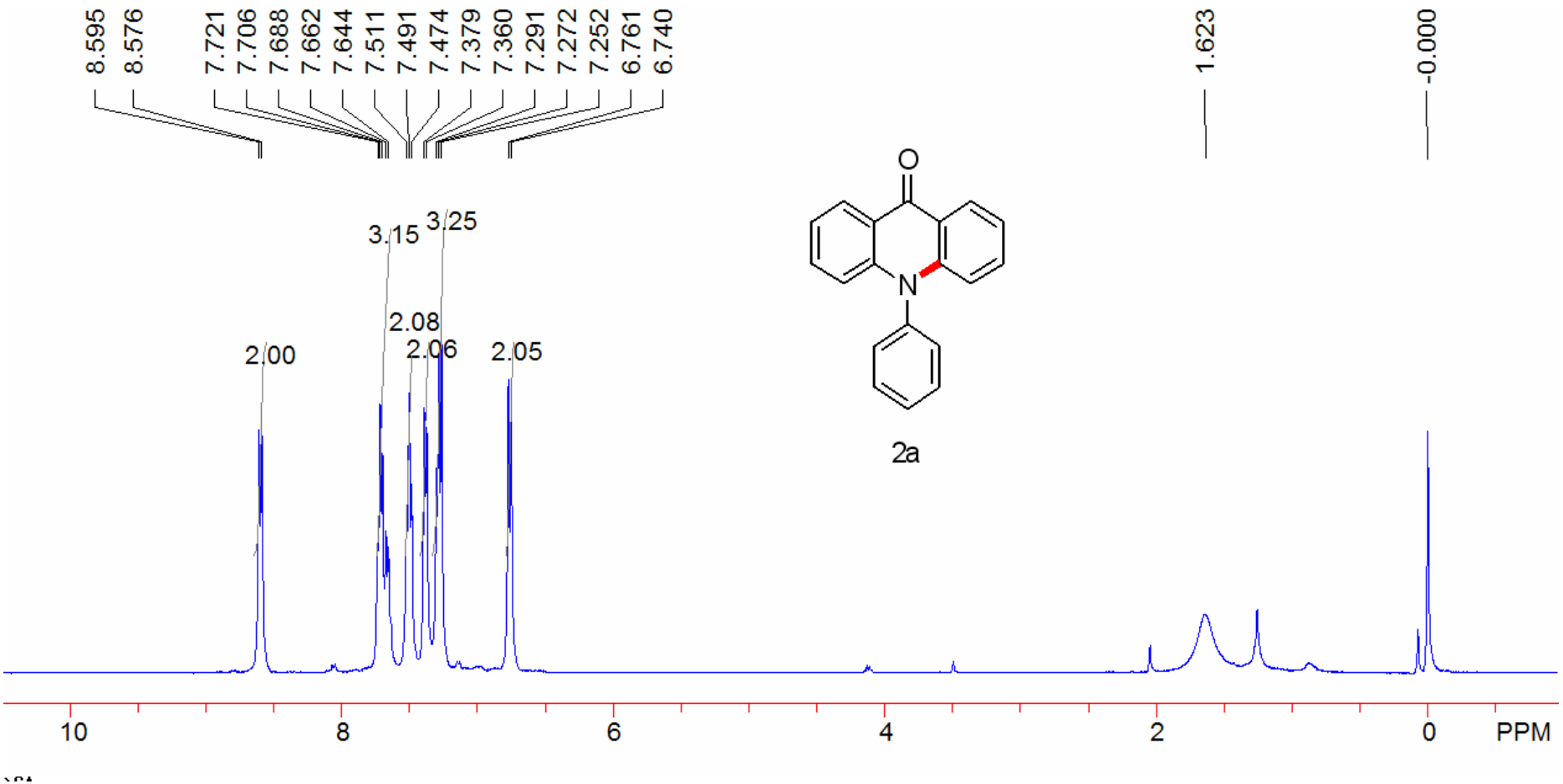


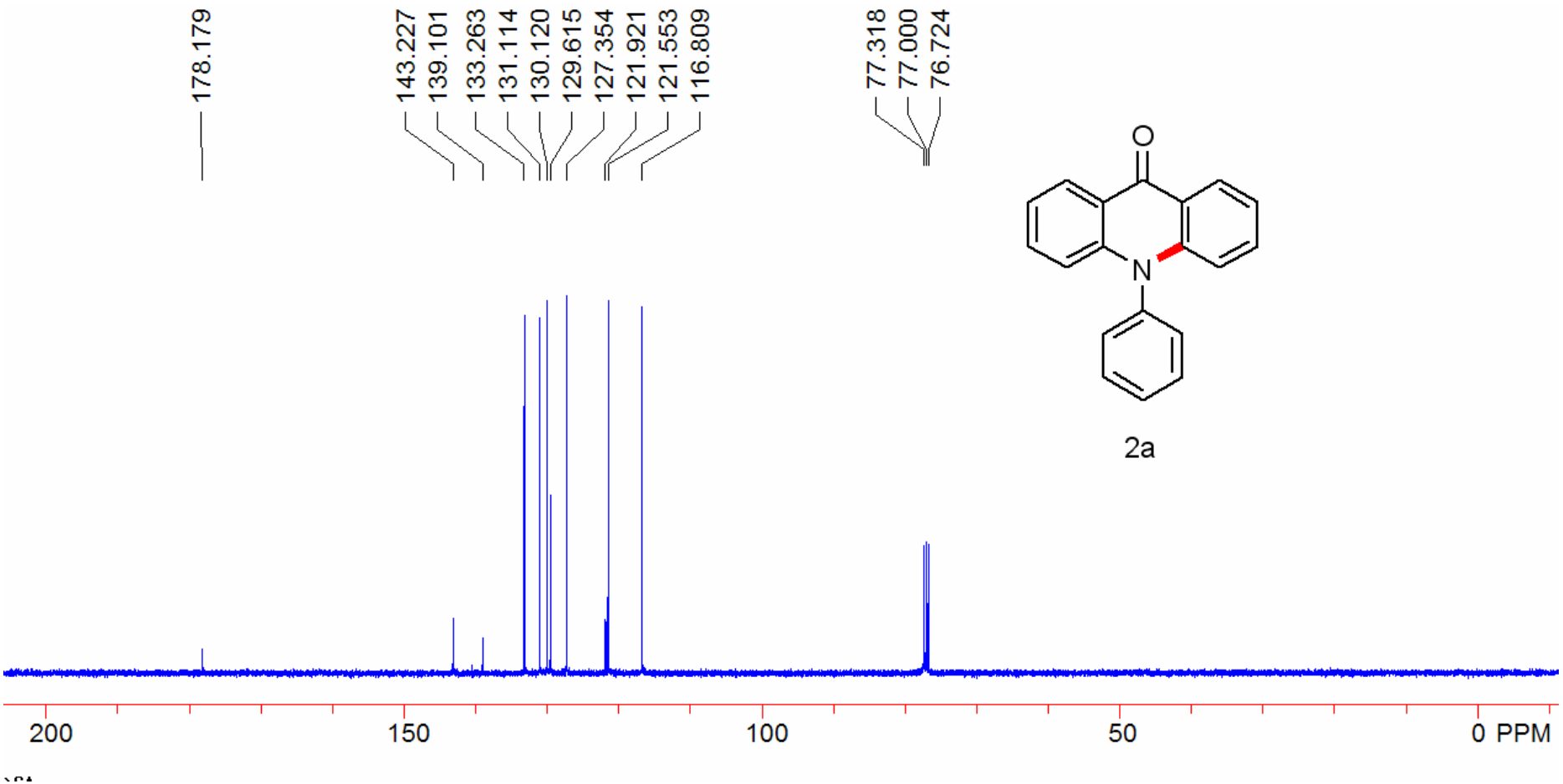
5

The reaction of **4** (0.3 mmol, 90 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under **typical procedure** afforded 30.5 mg (52 %) of **5** as solid. m.p. (acetic acid): 346-348 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 11.7 (br s, 1H), 8.23 (d, J = 8.0 Hz, 2H), 7.80-7.65 (m, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.30-7.20 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 176.8, 140.9, 133.4, 126.0, 121.0, 120.6, 117.3 ppm; MS (70 eV): m/z (%) 195.1 (M^+, 100).

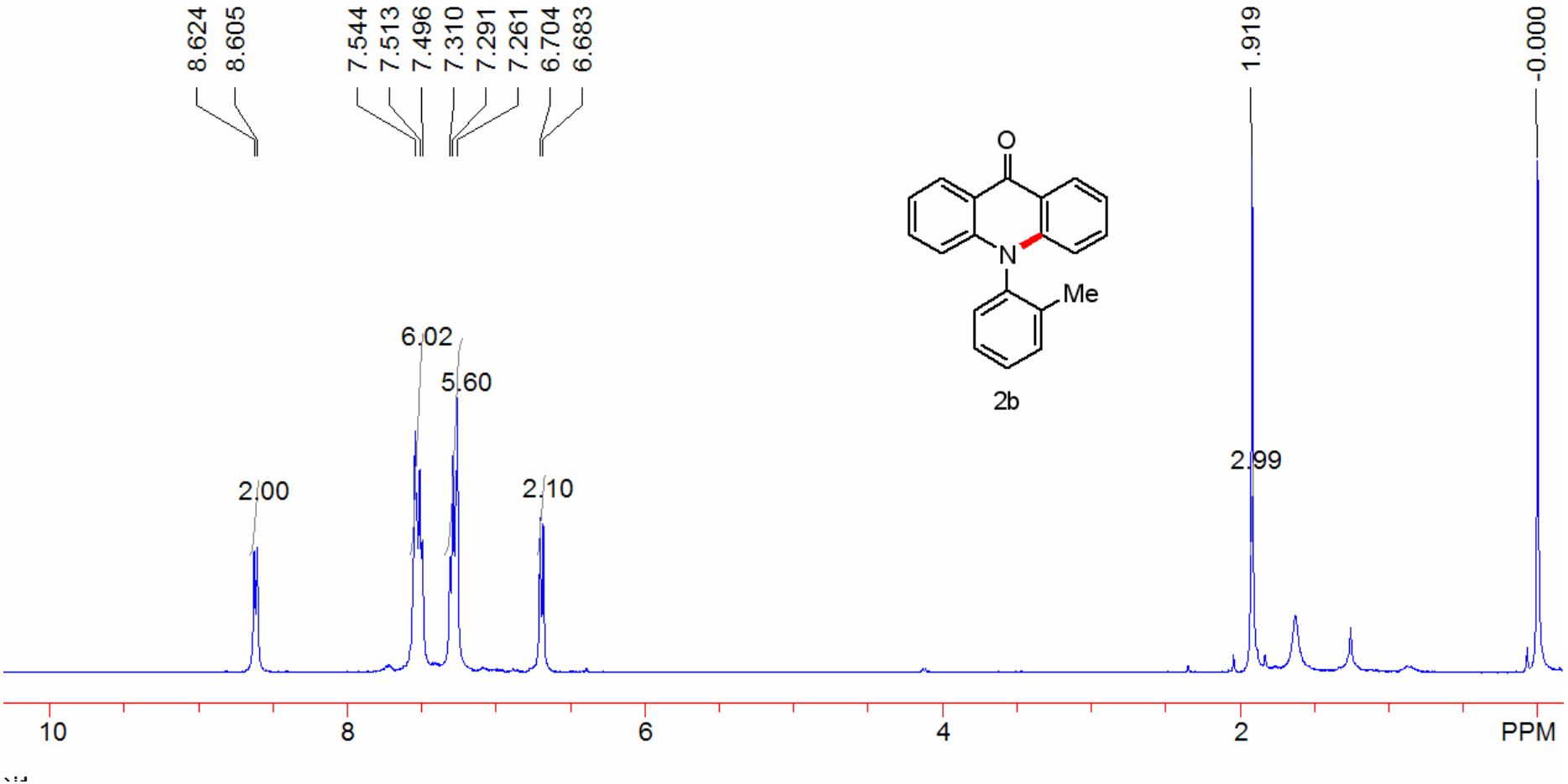
References

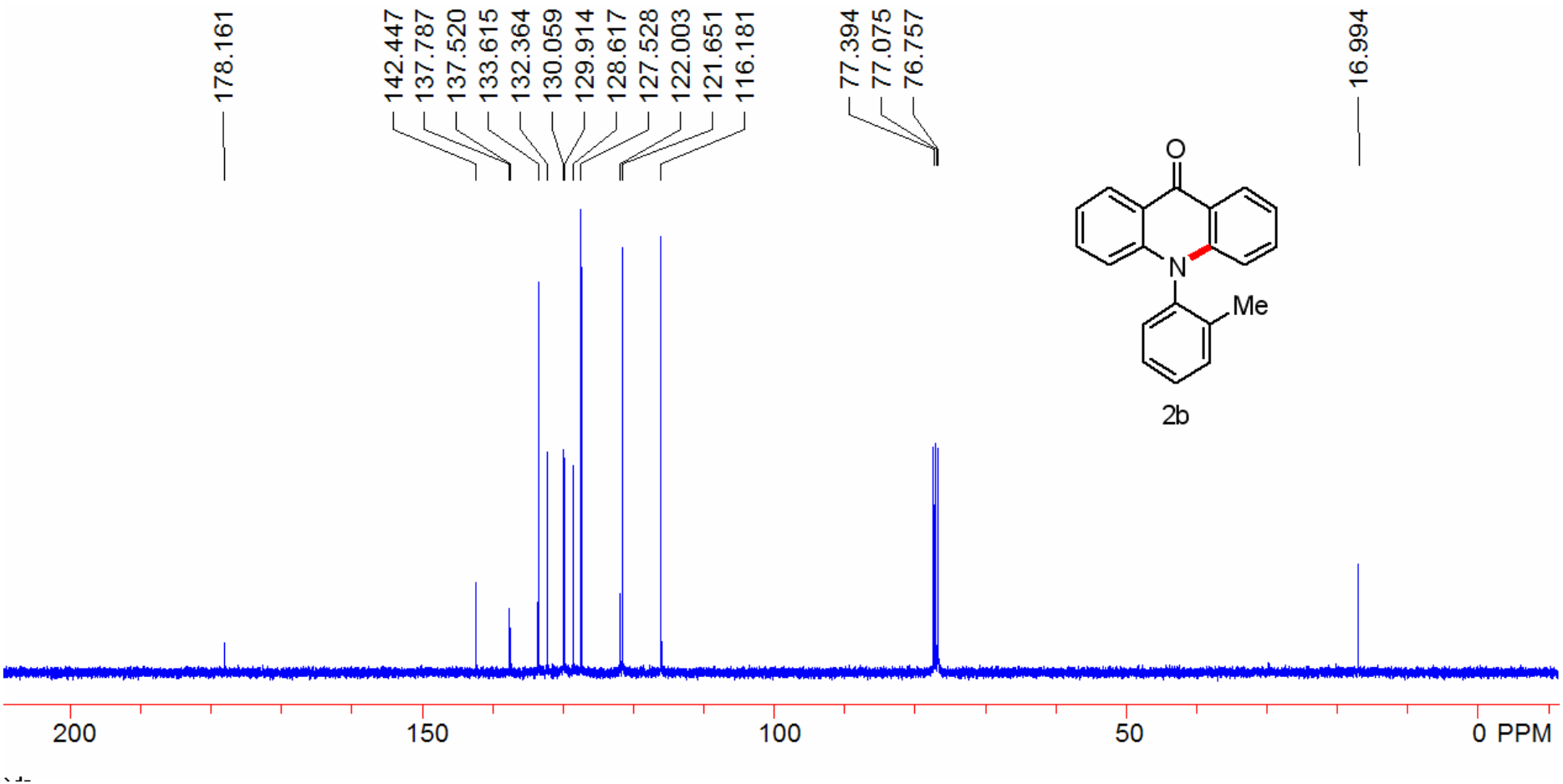
1. Y. Fang, D. C. Rogness, R. C. Larock, F. Shi, *J. Org. Chem.*, 2012, **77**, 6262.
2. A. Pintér, A. Sud, D. Sureshkumar, M. Klussmann, *Angew. Chem., Int. Ed.* 2010, **49**, 5004.





2a

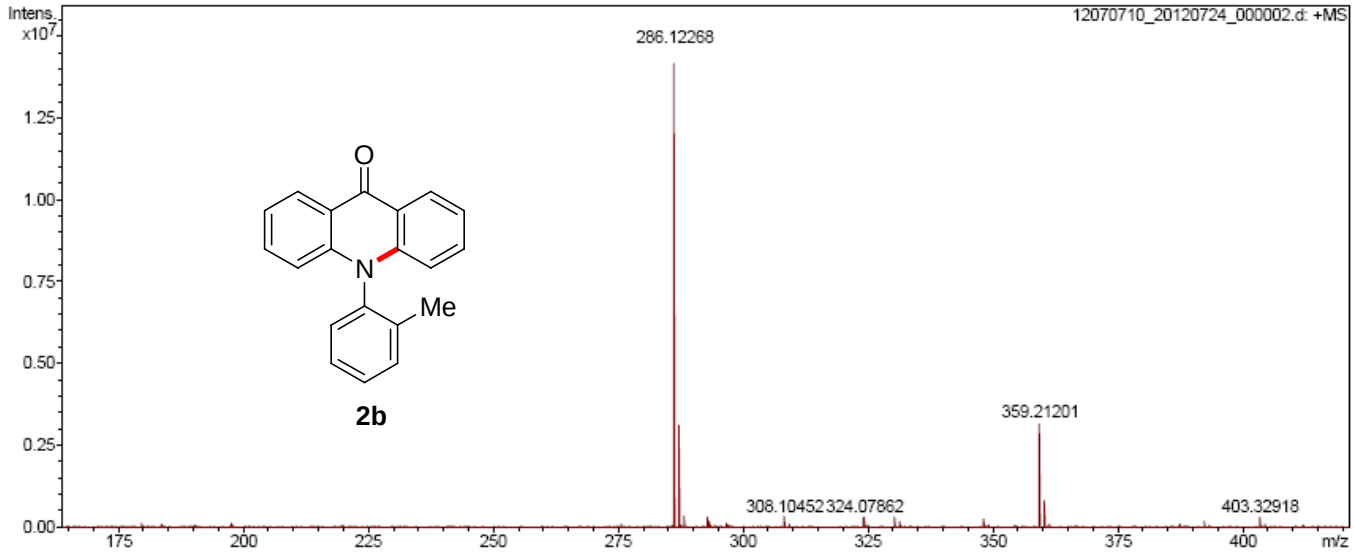




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000002.d	Acquisition Date	7/24/2012 1:28:54 PM
Sample	L132-3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



2b

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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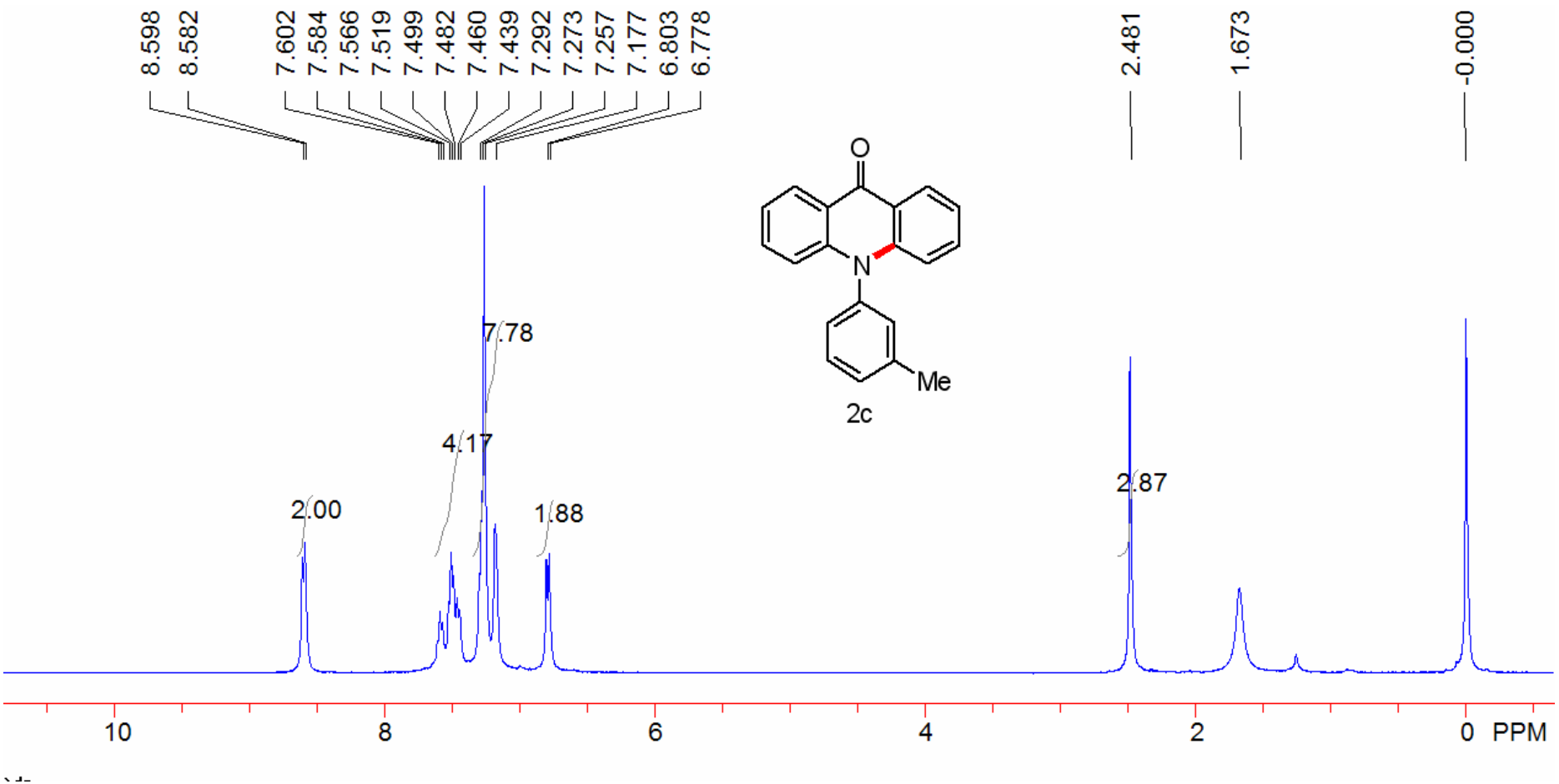
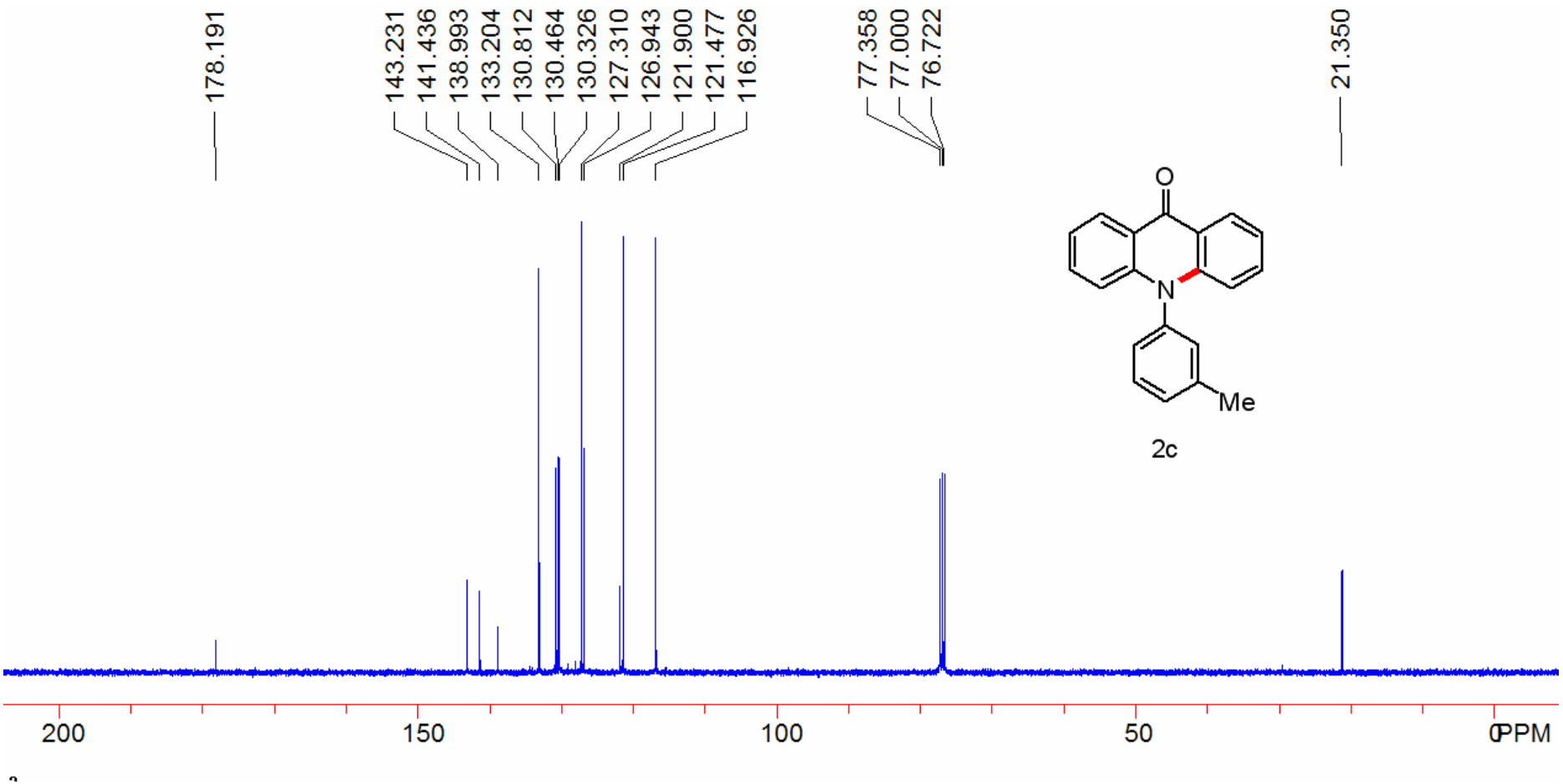
Bruker Compass DataAnalysis 4.0 printed: 7/24/2012 1:29:34 PM Page 1 of 1

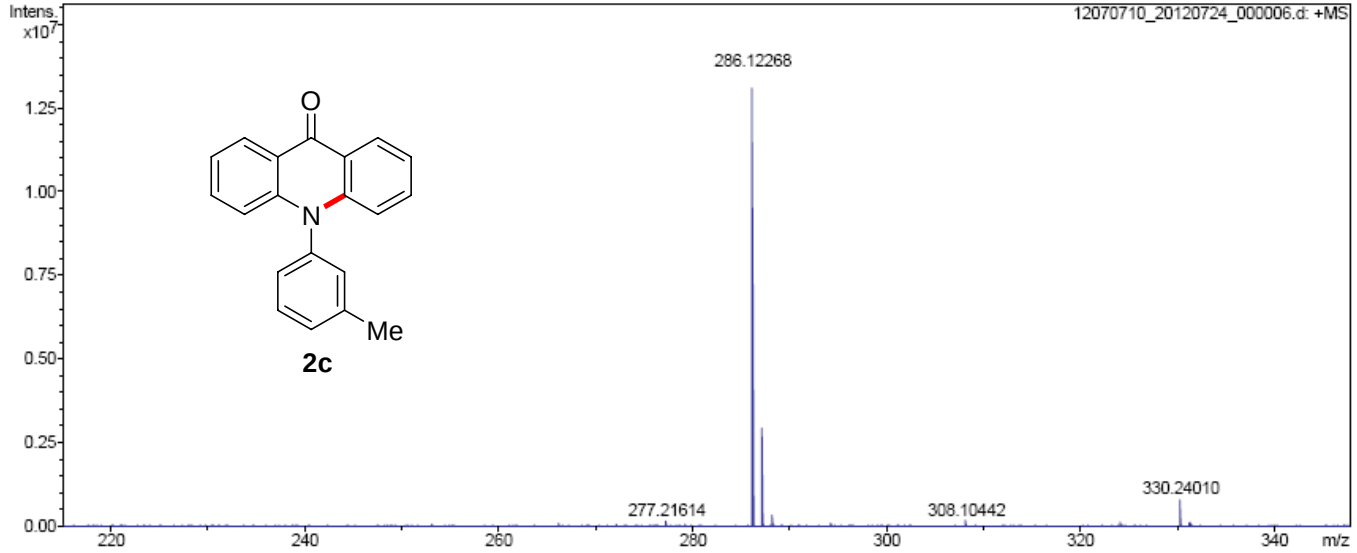




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000006.d	Acquisition Date	7/24/2012 1:32:37 PM
Sample	L144-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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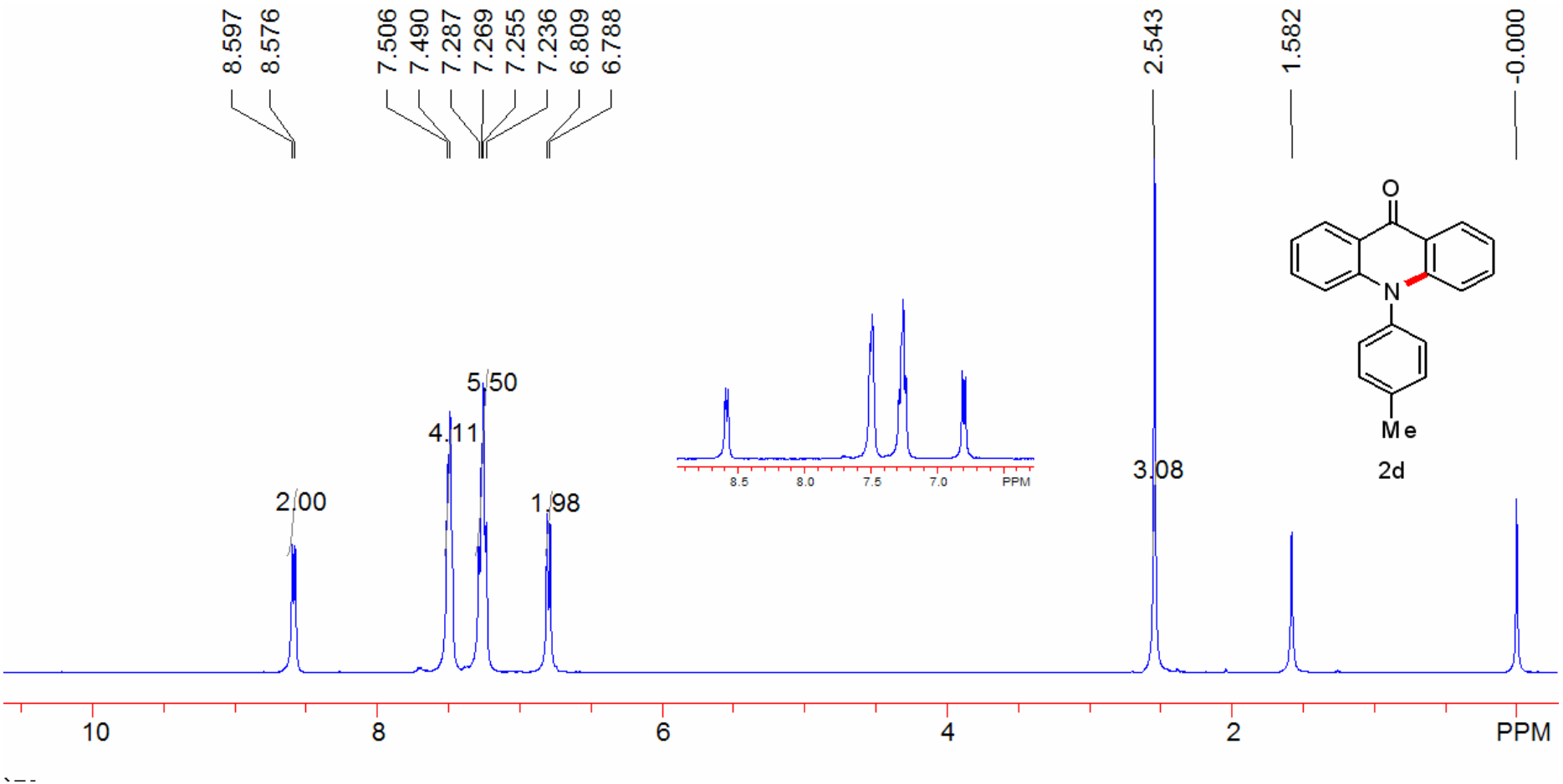
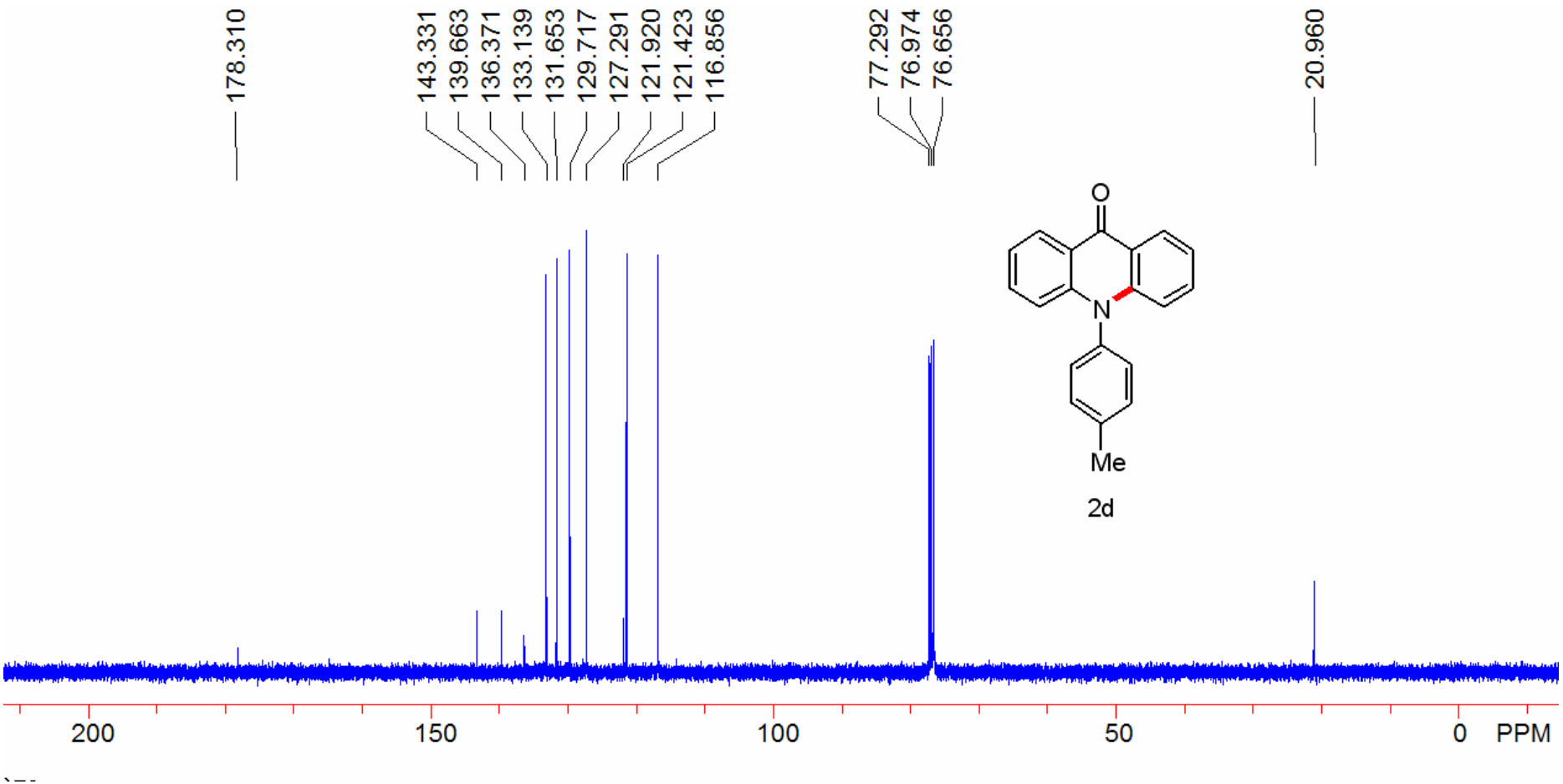
Bruker Compass DataAnalysis 4.0 printed: 7/24/2012 1:33:39 PM Page 1 of 1

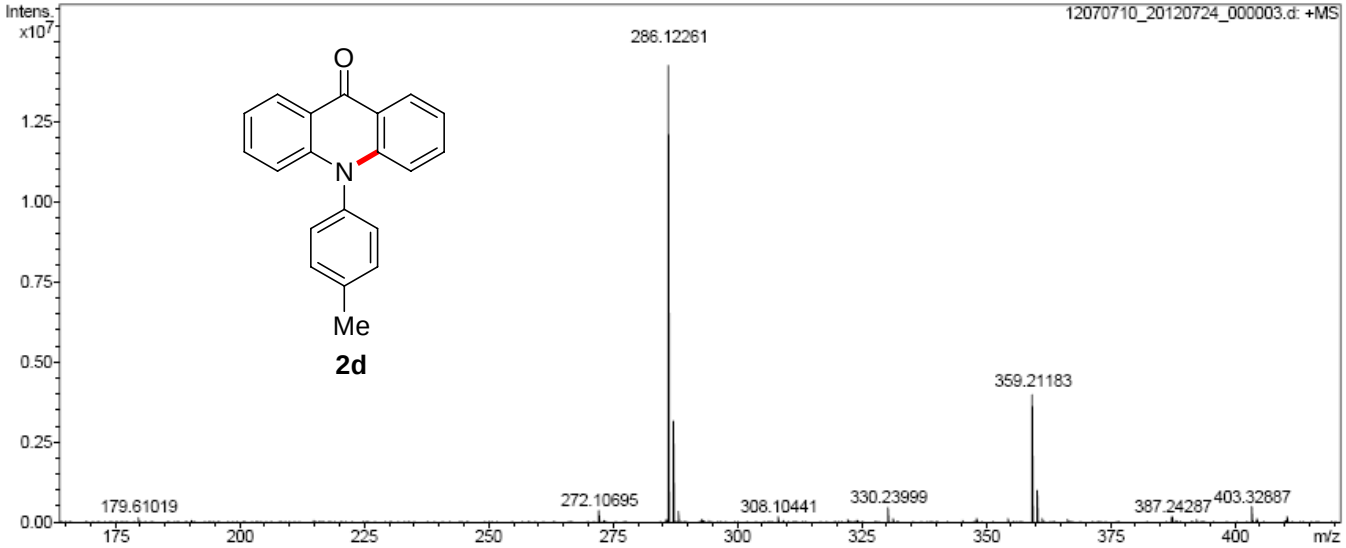




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000003.d	Acquisition Date	7/24/2012 1:29:50 PM
Sample	L130-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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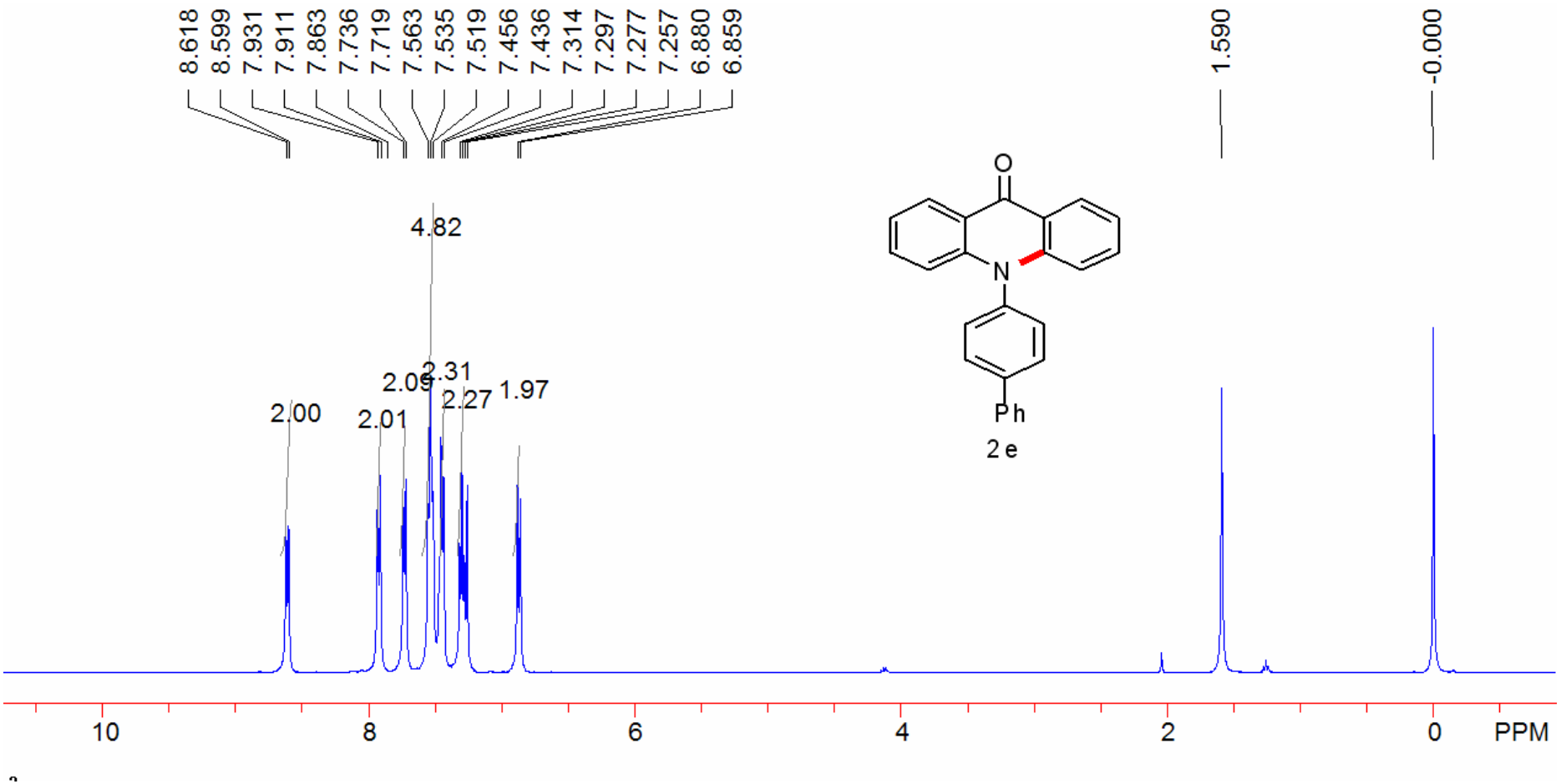
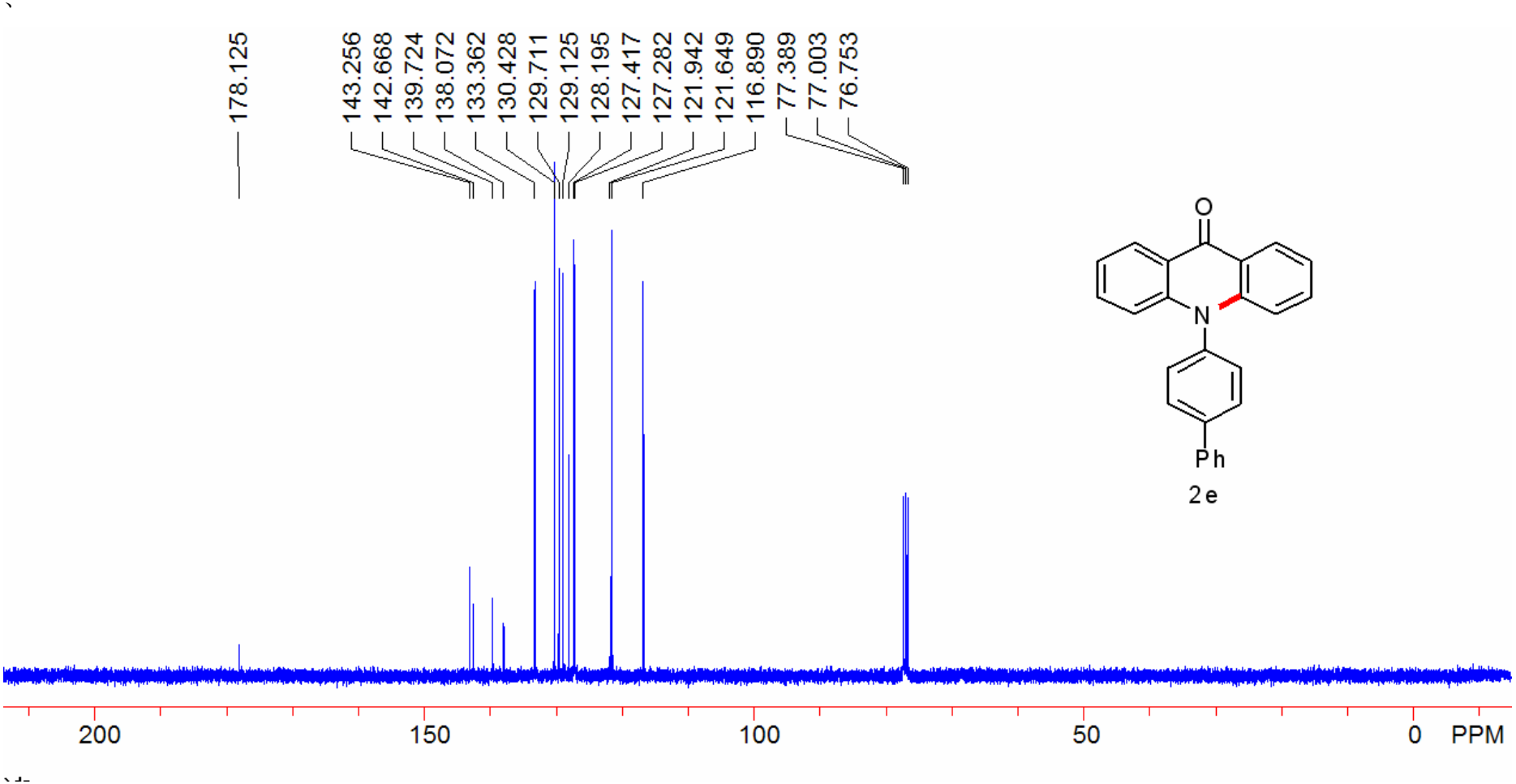
Bruker Compass DataAnalysis 4.0 printed: 7/24/2012 1:30:52 PM Page 1 of 1

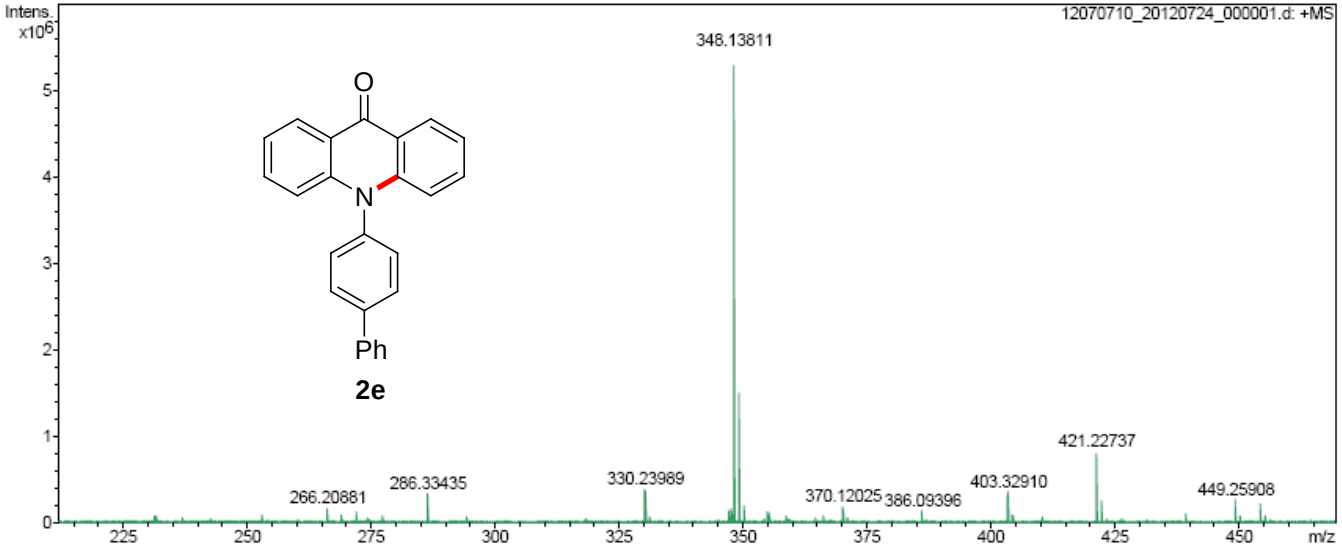




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000001.d	Acquisition Date	7/24/2012 1:27:46 PM
Sample	L131-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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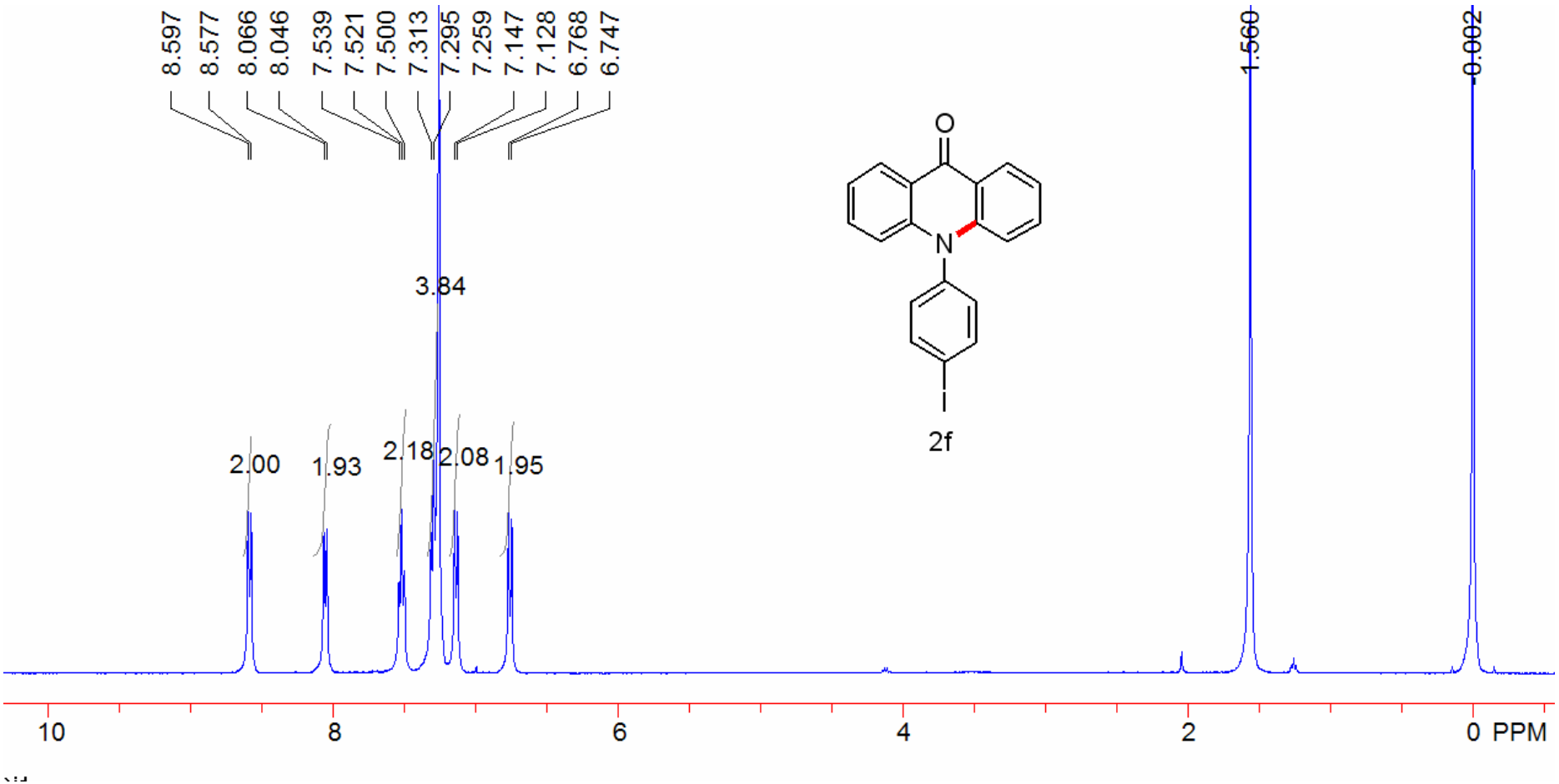
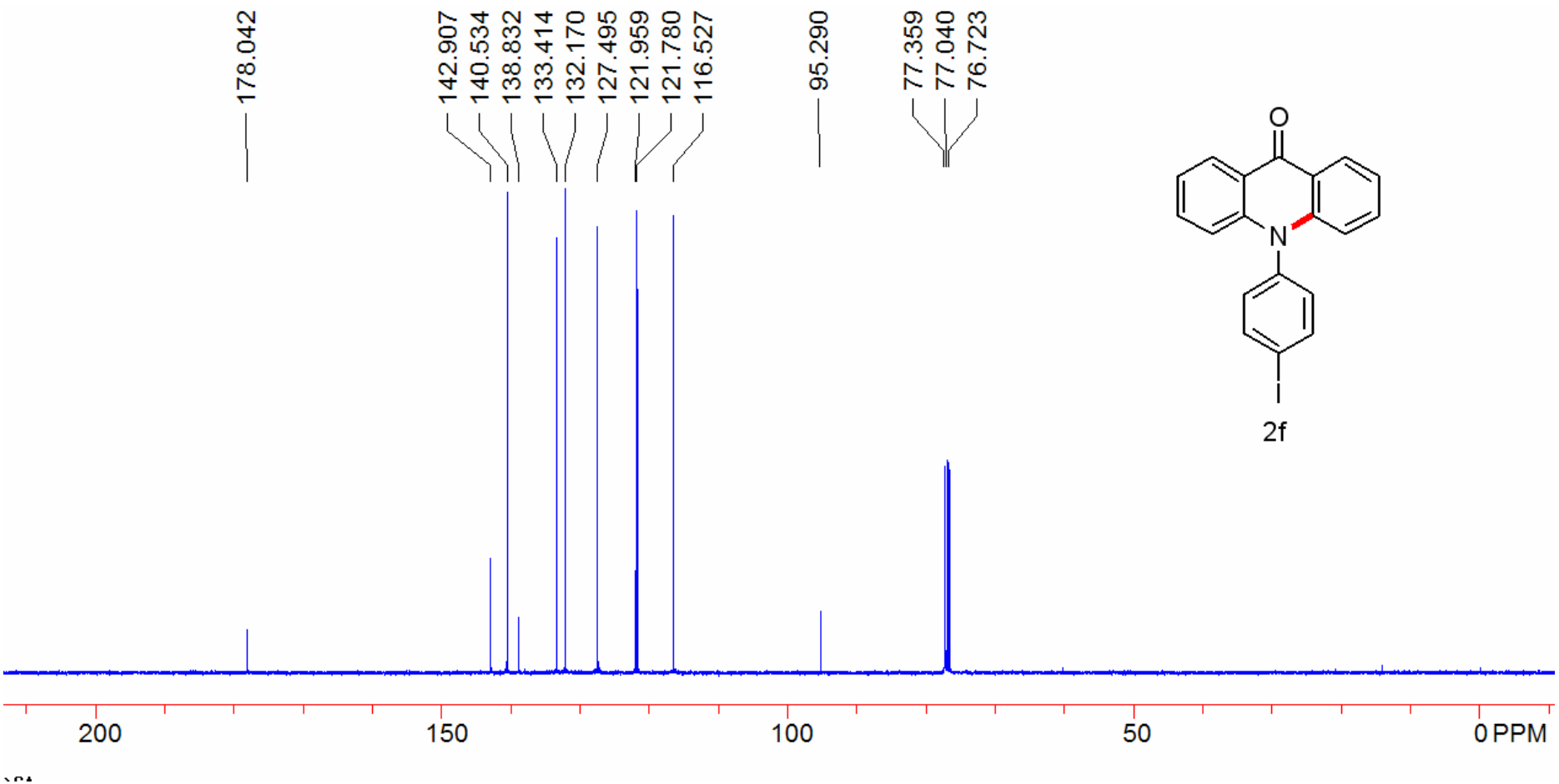
Bruker Compass DataAnalysis 4.0 printed: 7/24/2012 1:28:35 PM Page 1 of 1

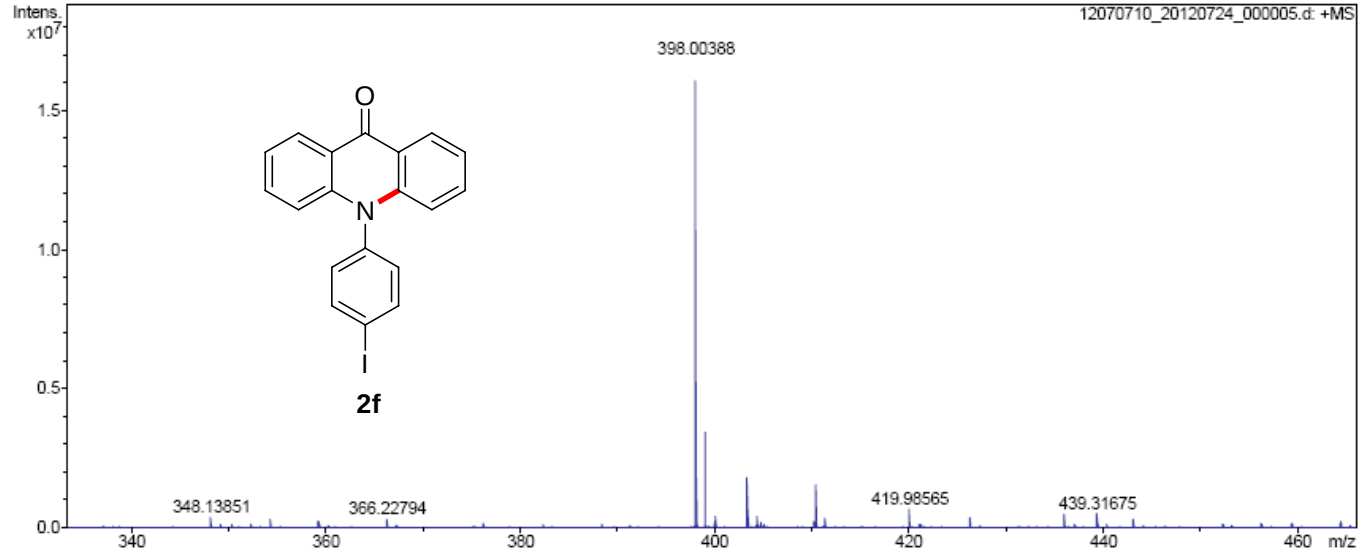




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000005.d	Acquisition Date	7/24/2012 1:31:31 PM
Sample	L141-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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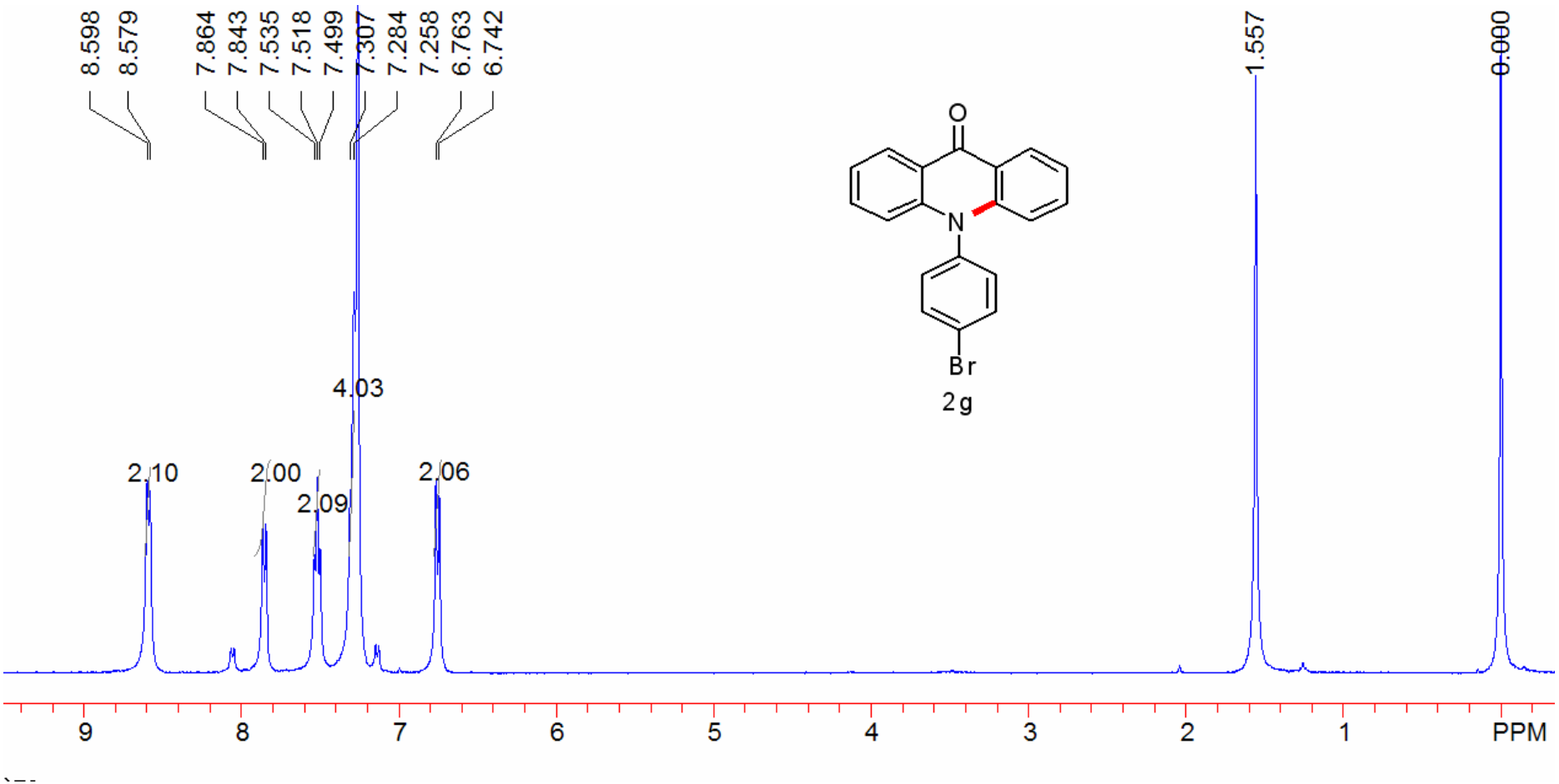
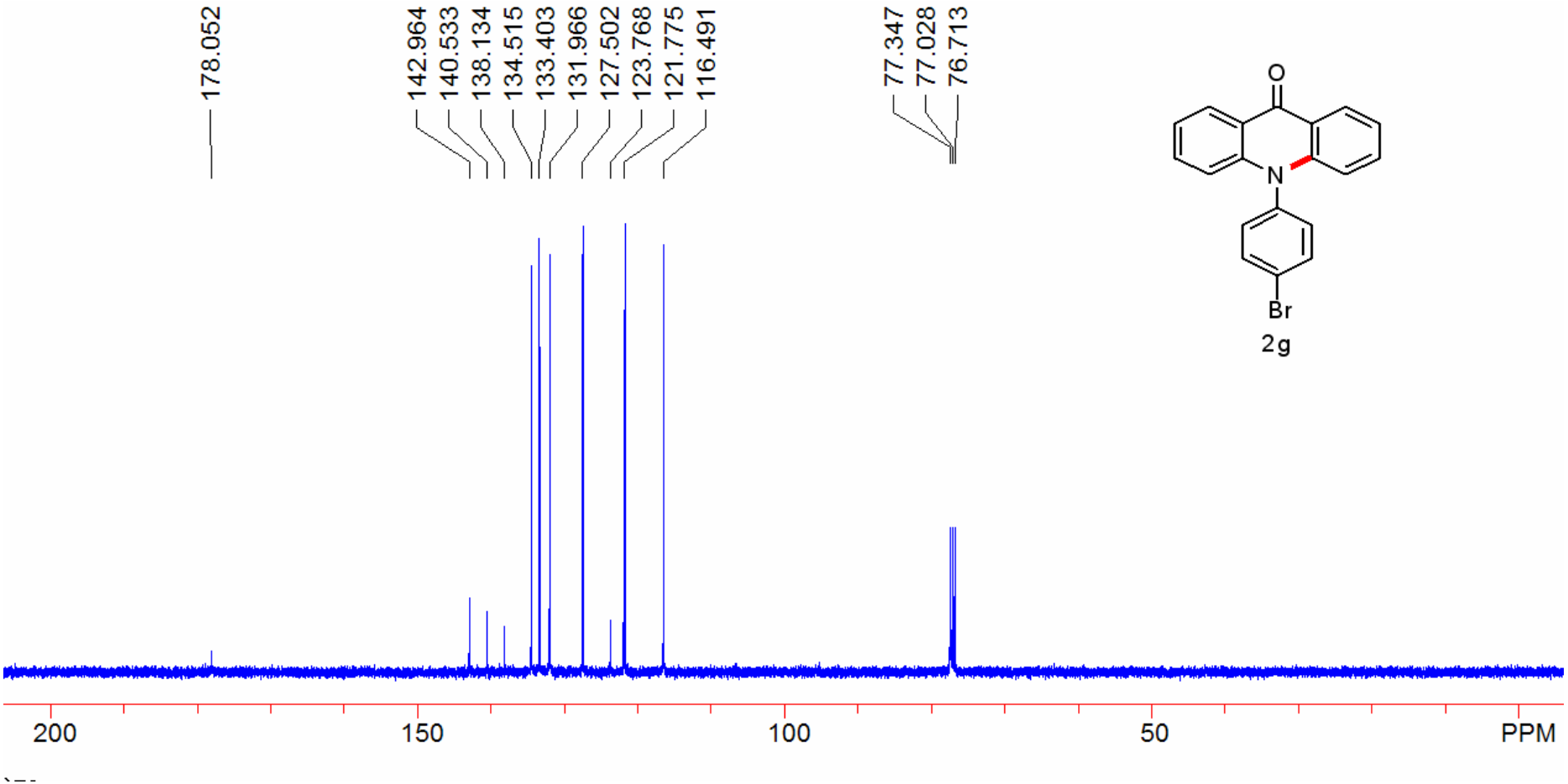
Bruker Compass DataAnalysis 4.0 printed: 7/24/2012 1:32:43 PM Page 1 of 1





Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000010.d	Acquisition Date	7/24/2012 1:36:39 PM
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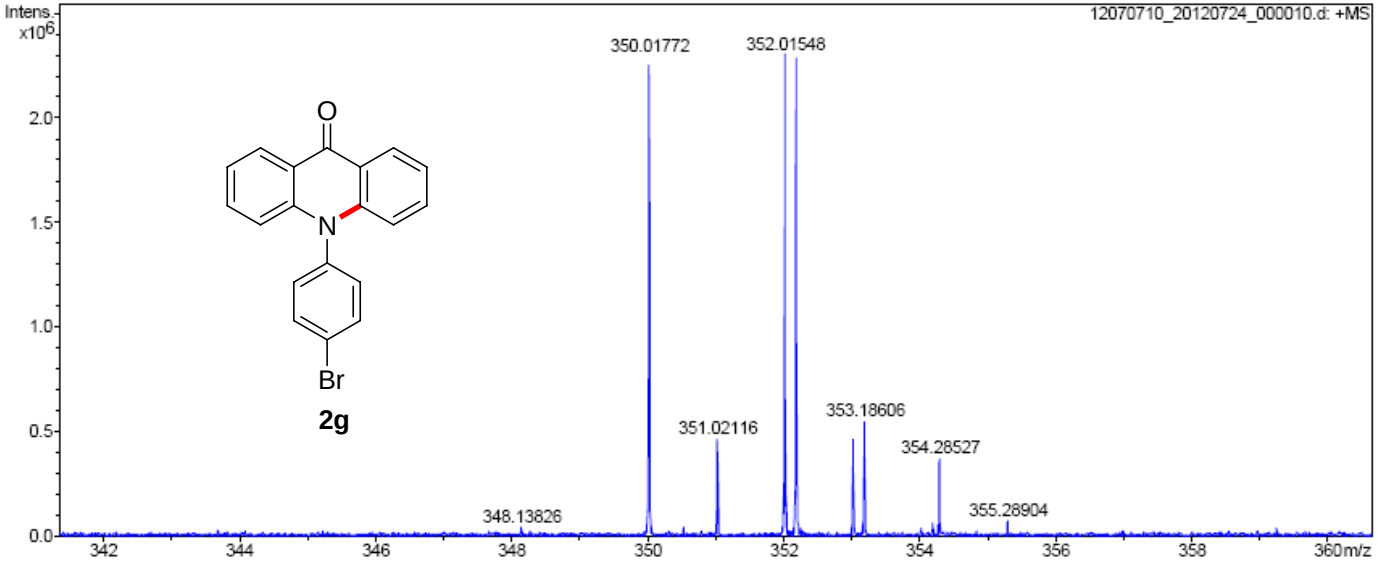
Comment	ESI Positive	Operator	Peking University



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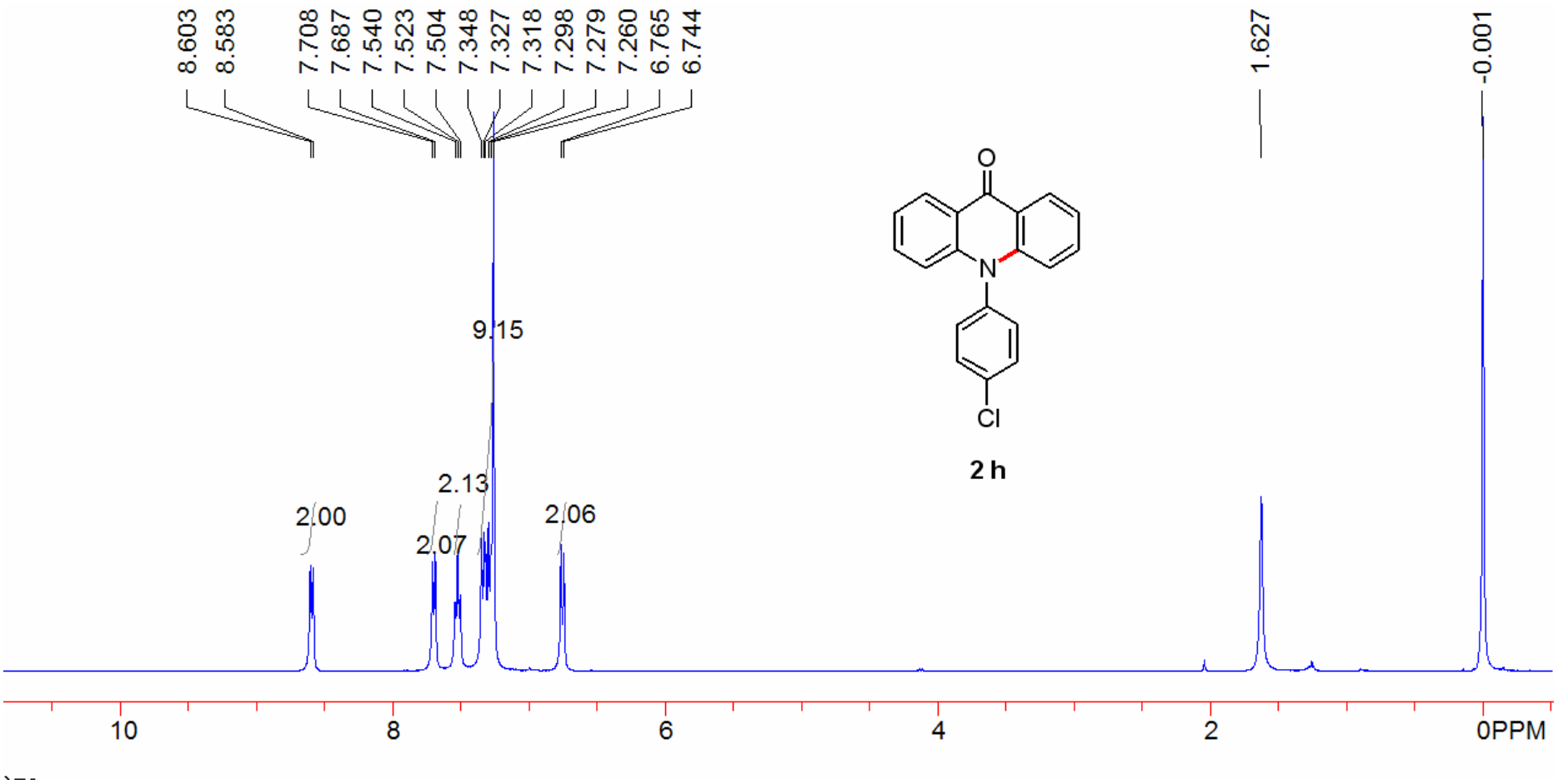
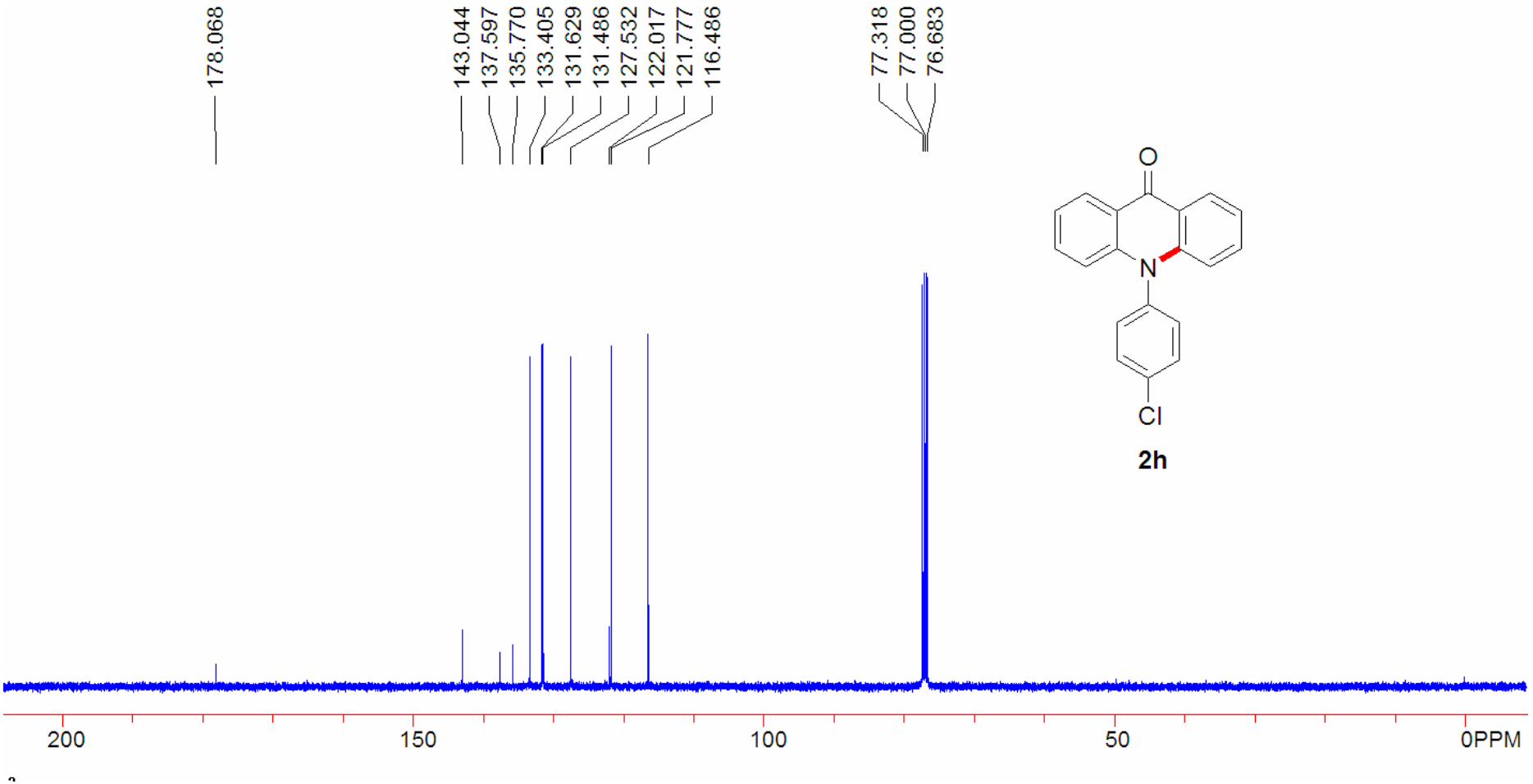
Bruker Compass DataAnalysis 4.0 printed: 7/24/2012 1:39:08 PM Page 1 of 1

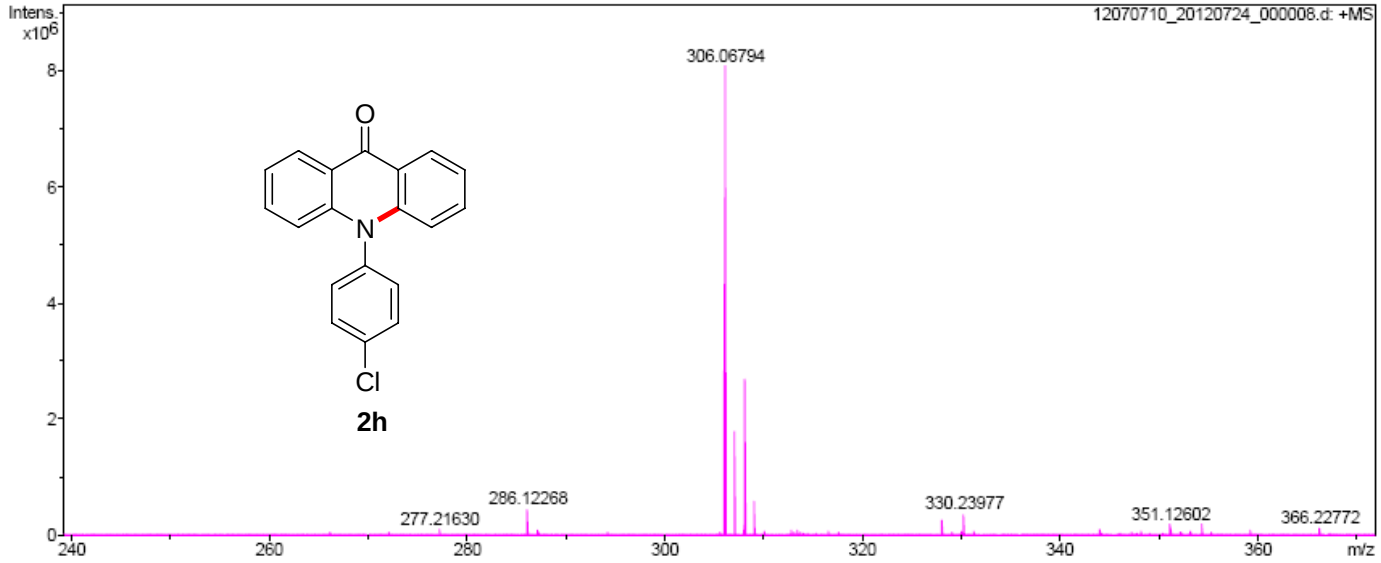




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000008.d	Acquisition Date	7/24/2012 1:34:30 PM
Sample	L130-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
306.06794	1	C 19 H 13 Cl N O	100.00	306.06802	0.1	0.2	7.1	13.5	even	ok

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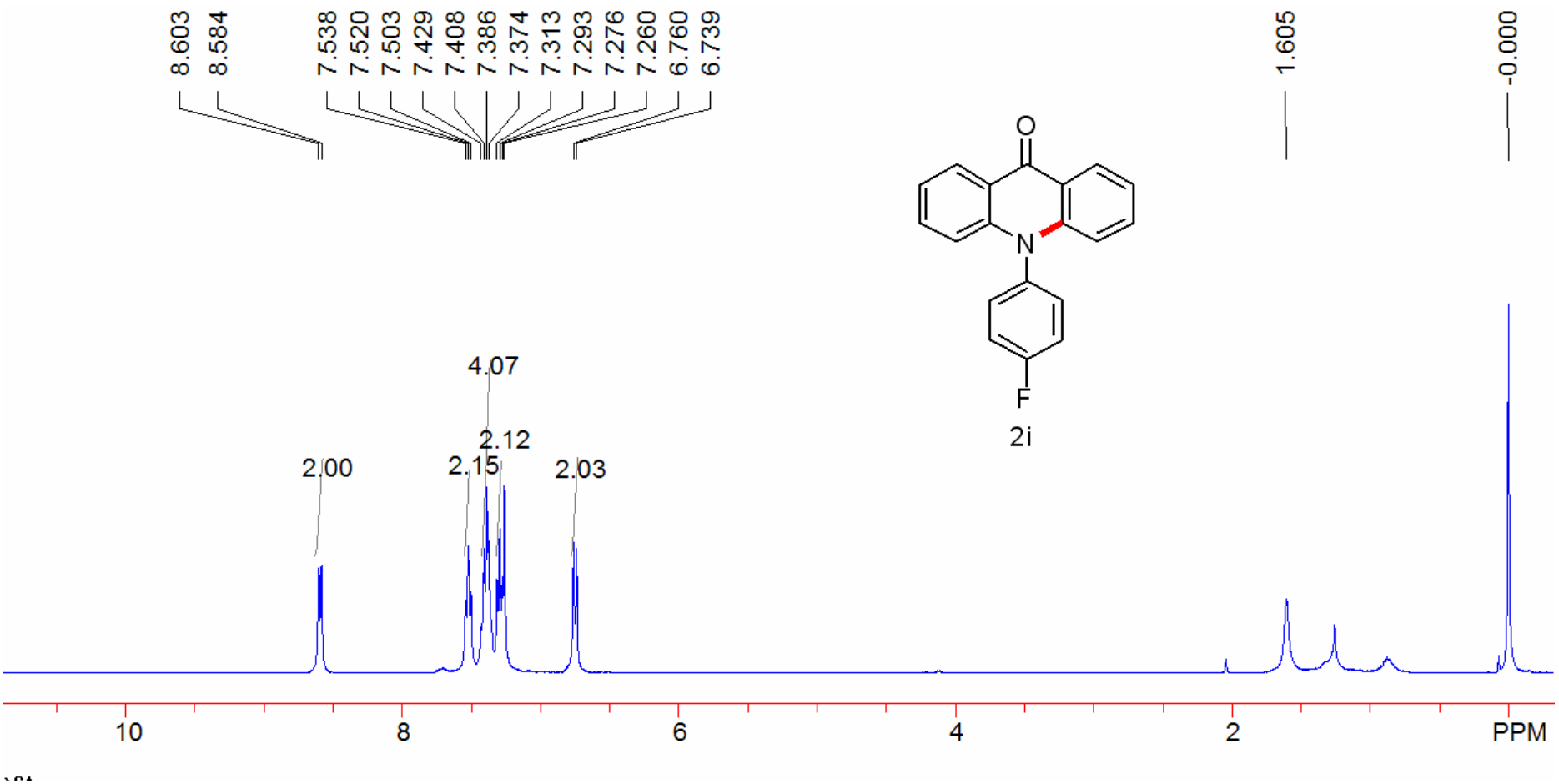
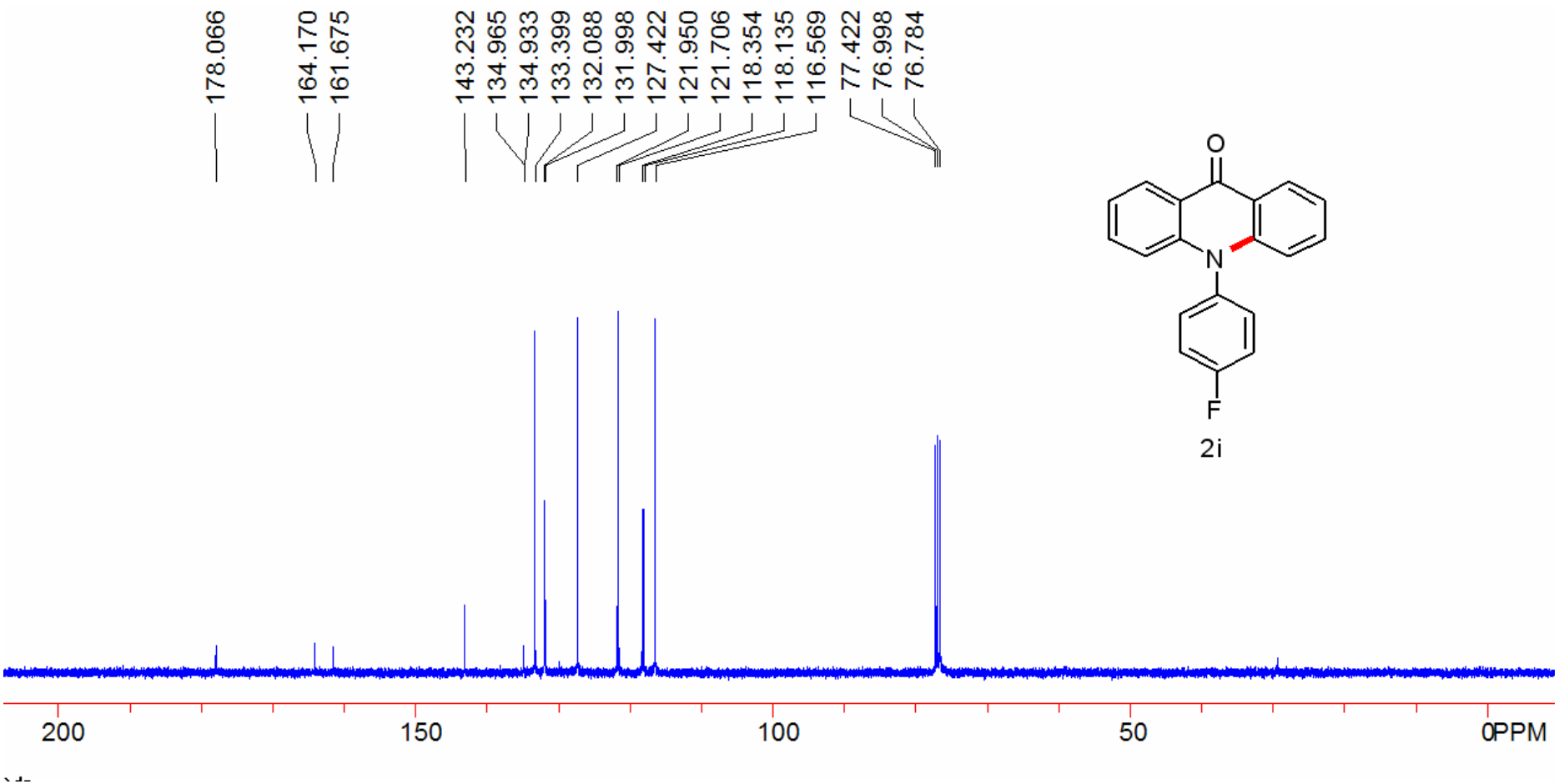
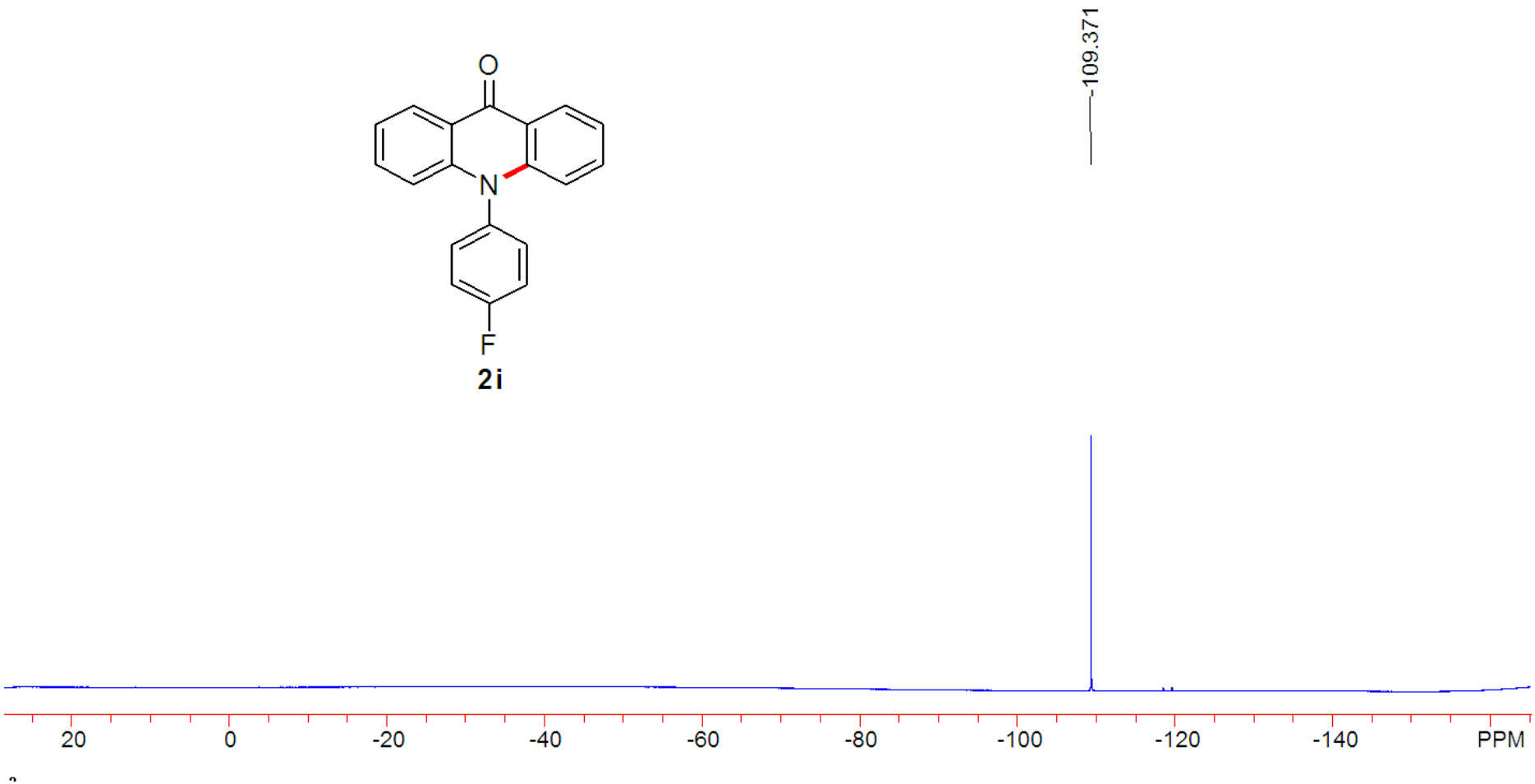




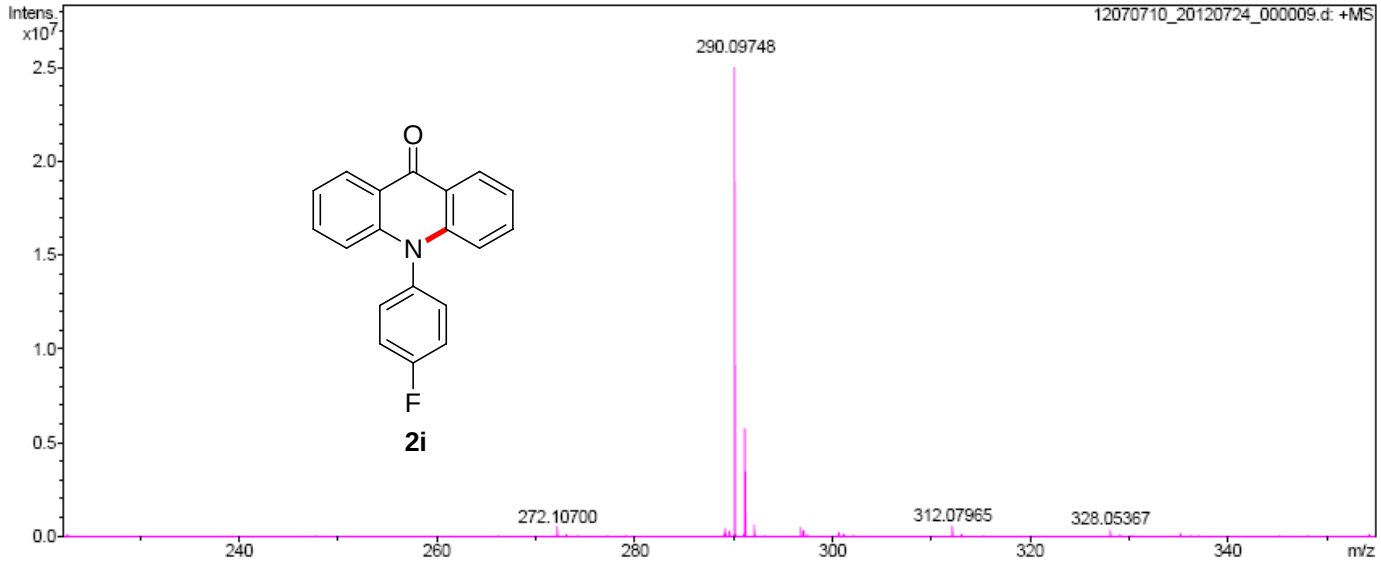


2i

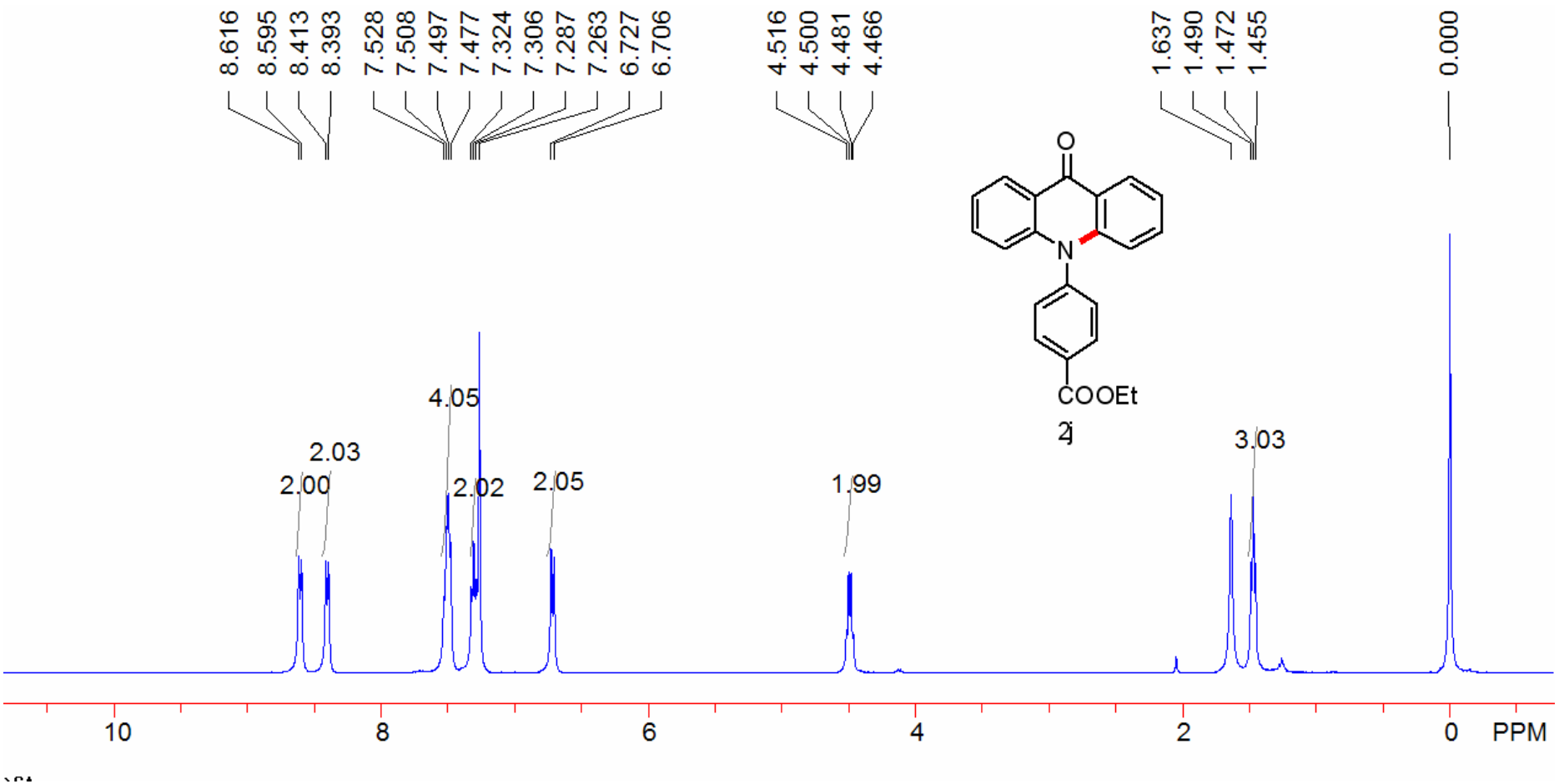
Peking University Mass Spectrometry Sample Analysis Report

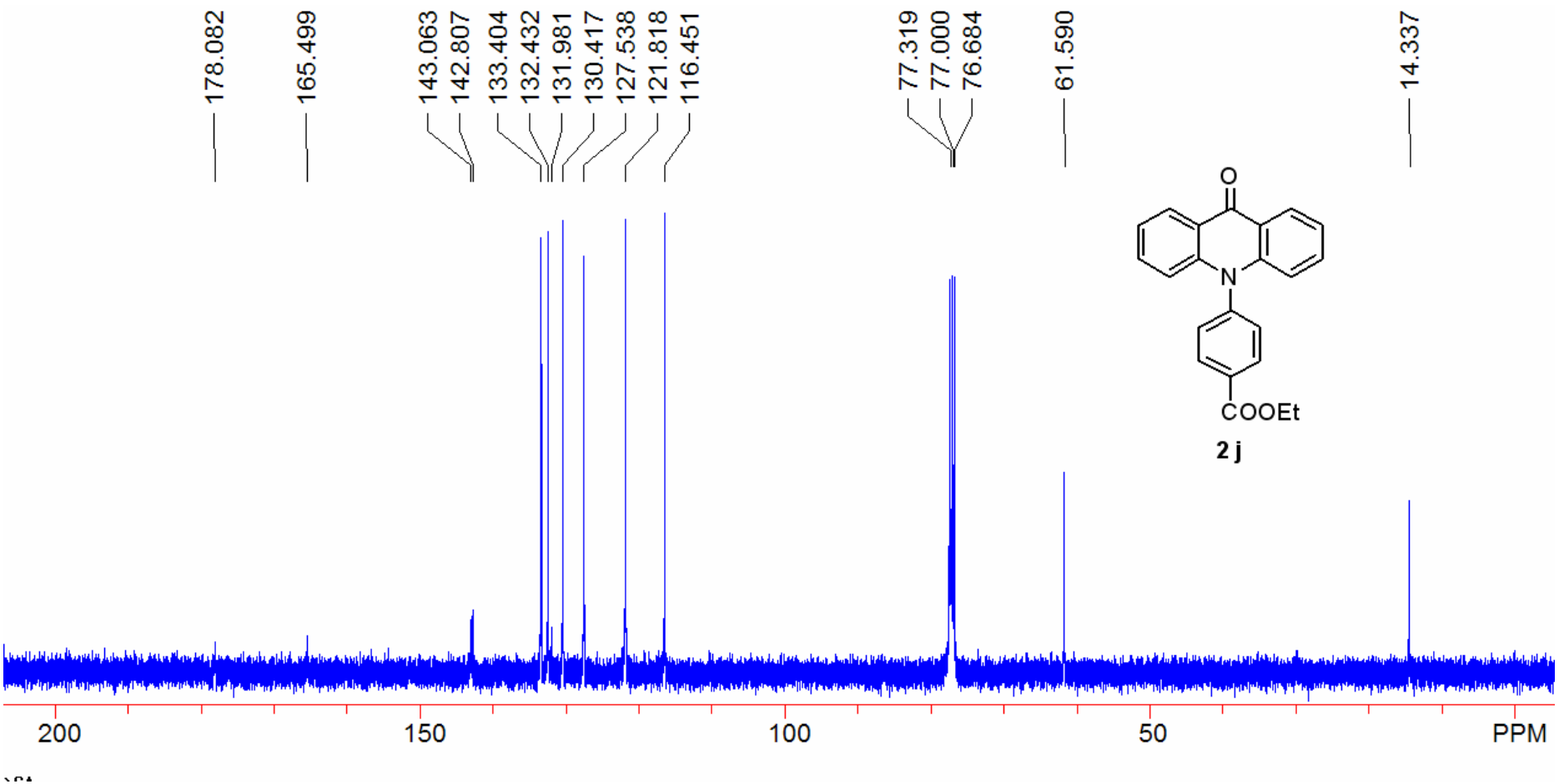
Analysis Info

Analysis Name	12070710_20120724_000009.d	Acquisition Date	7/24/2012 1:35:43 PM
Sample	L132-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
290.09748	1	C 19 H 13 F N O	100.00	290.09757	0.1	0.3	11.4	13.5	even	ok





Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000007.d	Acquisition Date	7/24/2012 1:33:38 PM
Sample	L137-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
344.12803	1	C 22 H 18 N O 3	100.00	344.12812	0.1	0.3	4.5	14.5	even	ok

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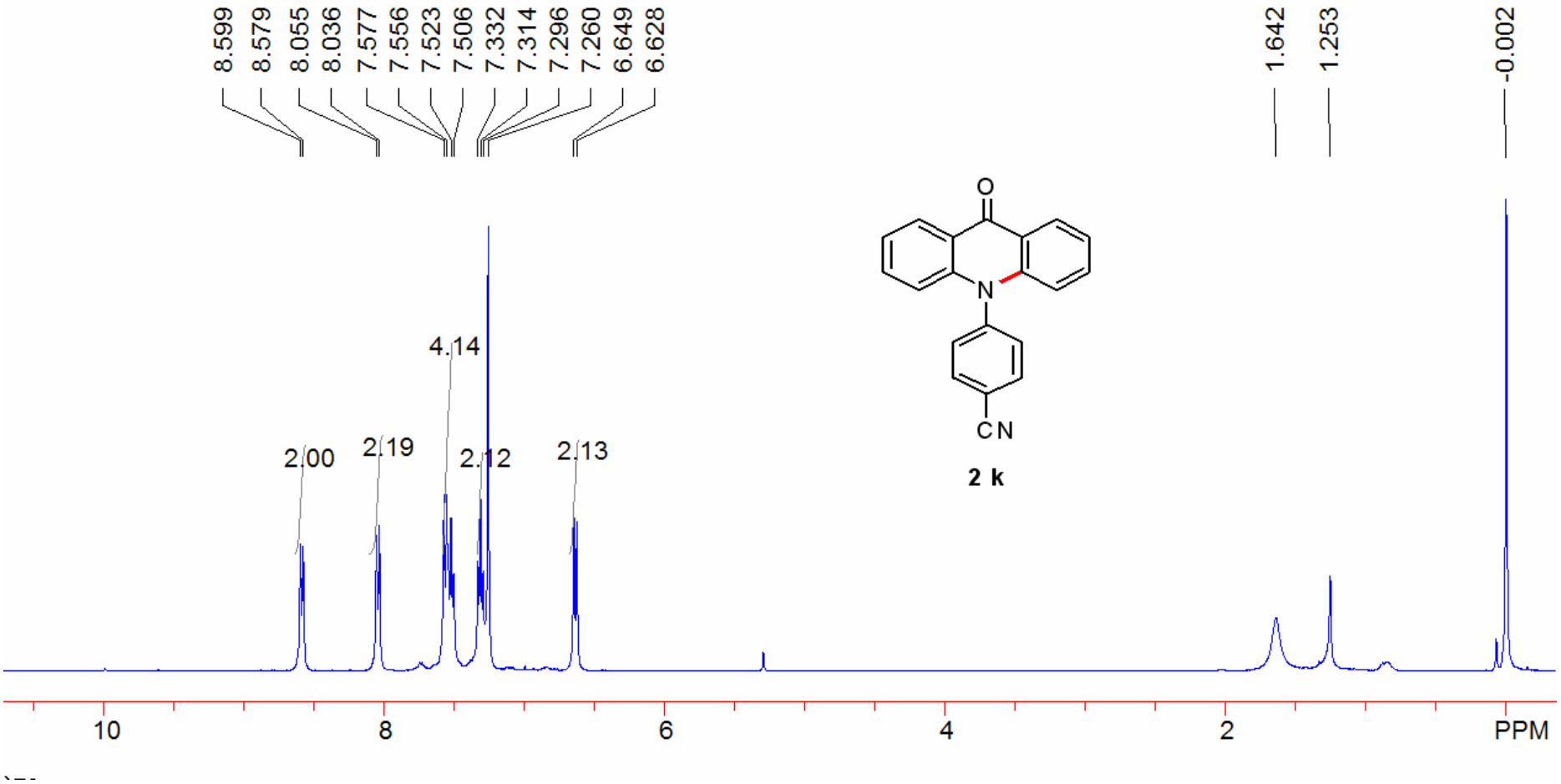
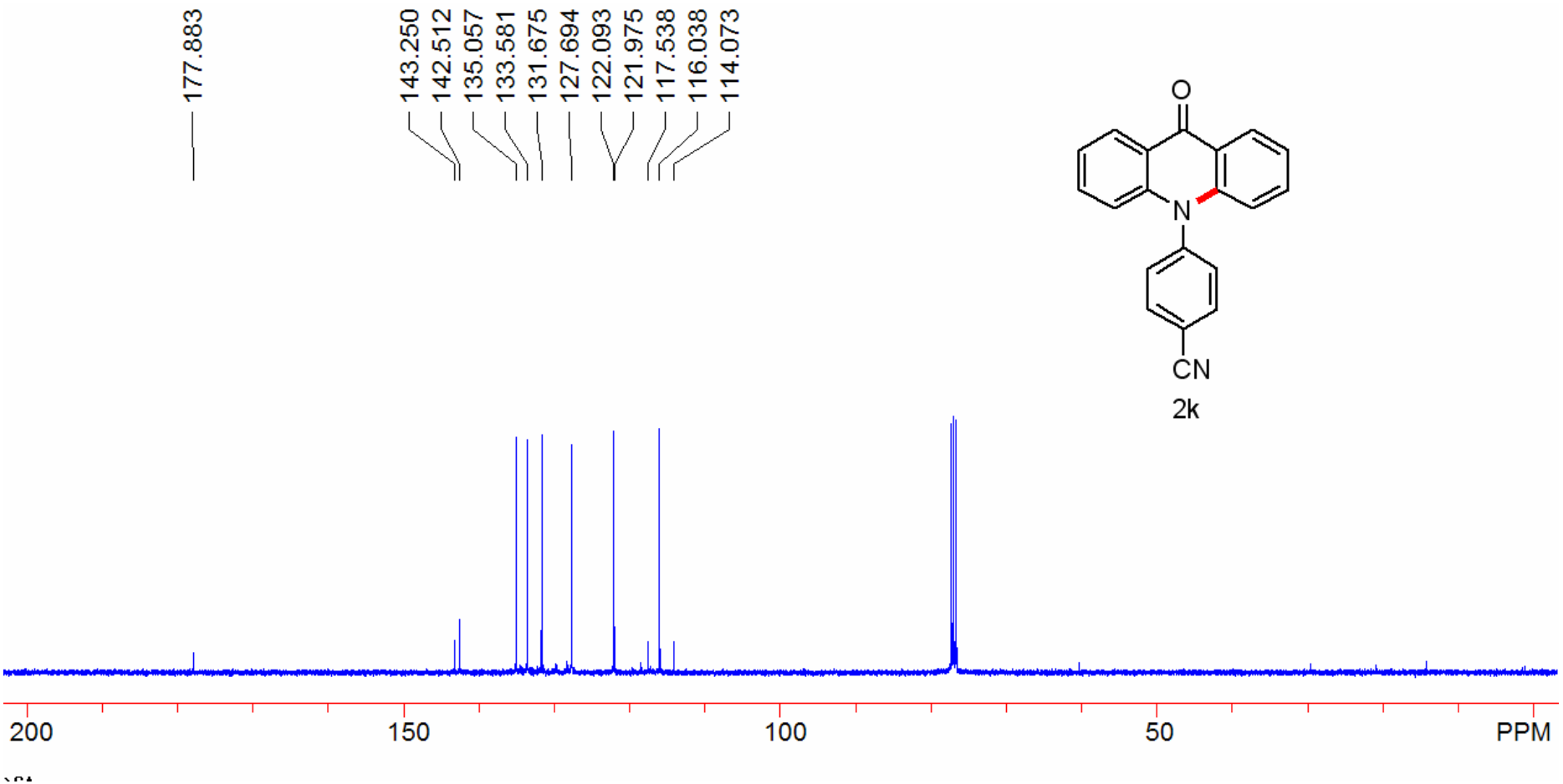
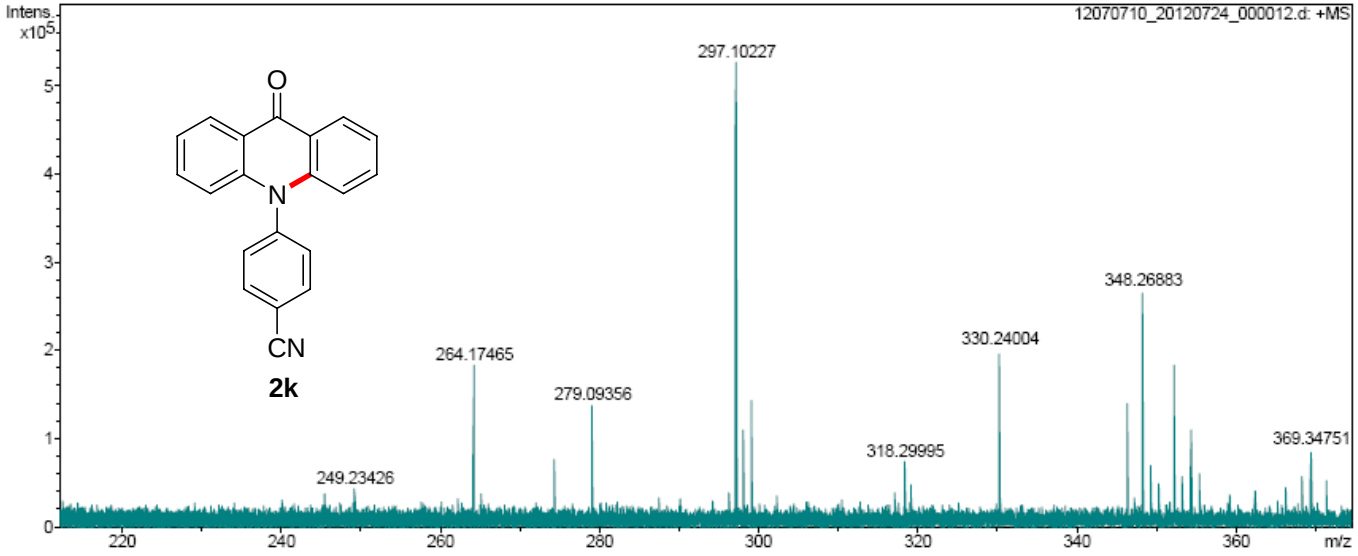




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000012.d	Acquisition Date	7/24/2012 1:39:32 PM
Sample	L139-3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
297.10227	1	C 20 H 13 N 2 O	100.00	297.10224	-0.0	-0.1	14.8	15.5	even	ok

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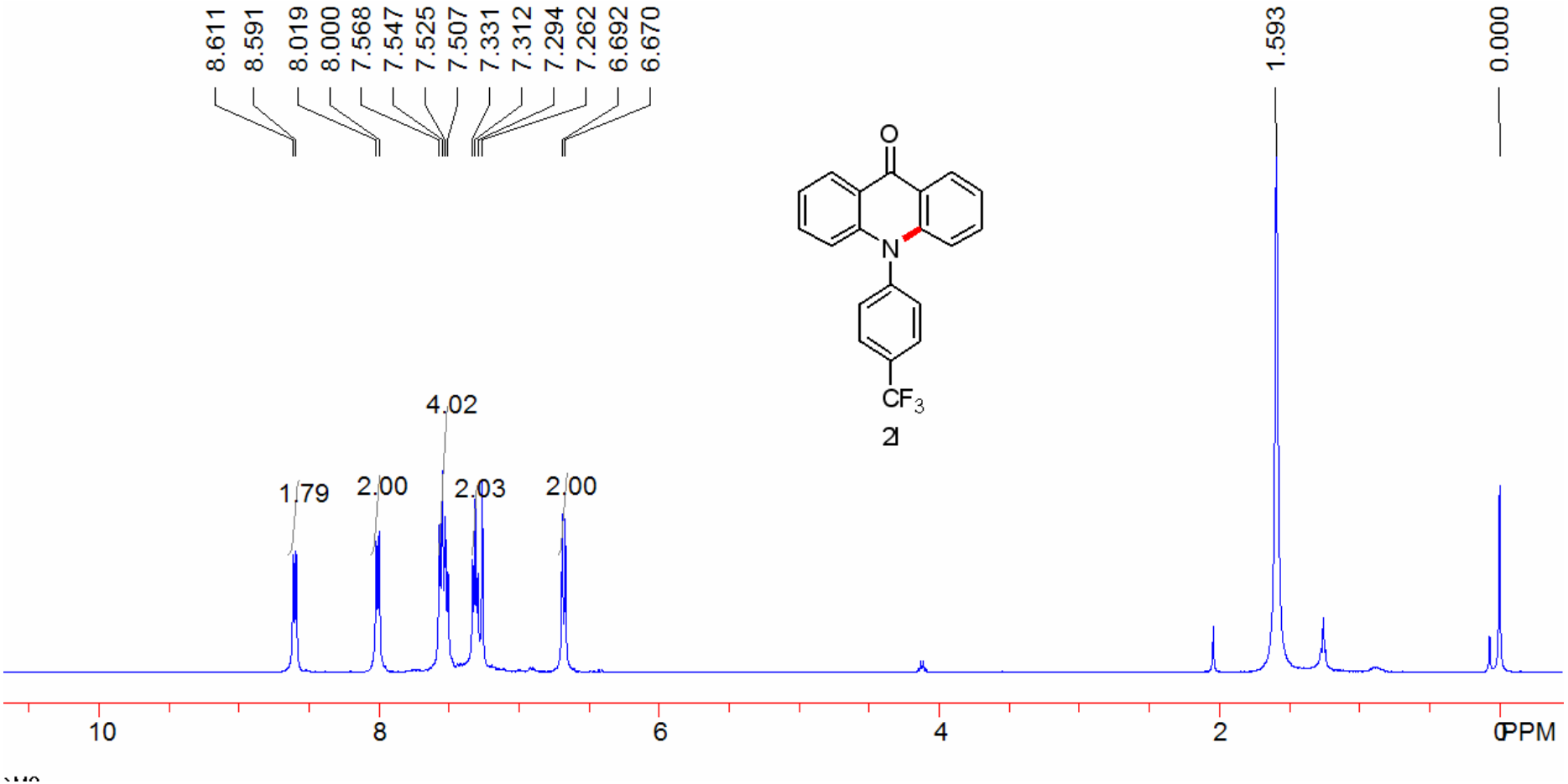
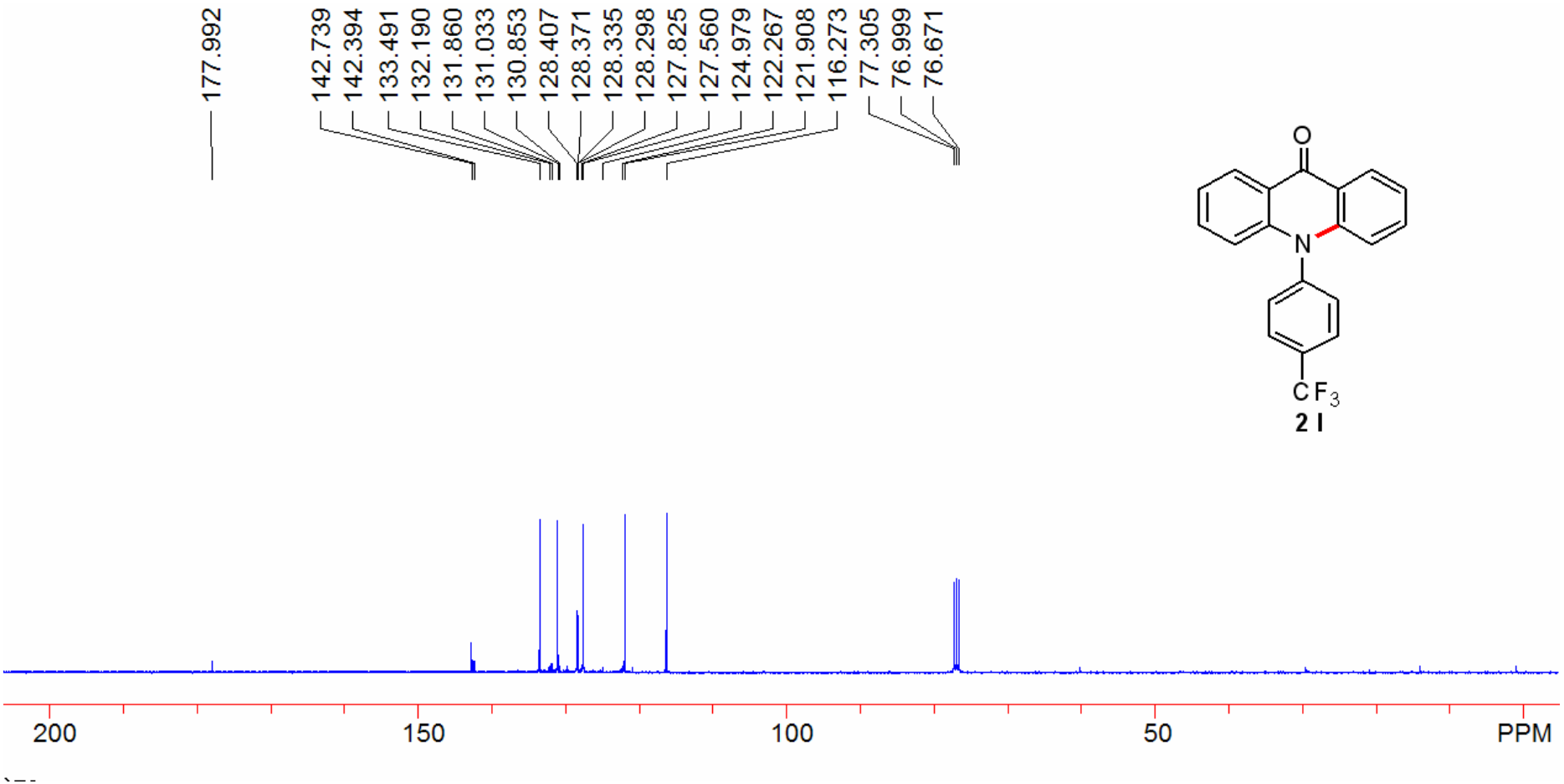
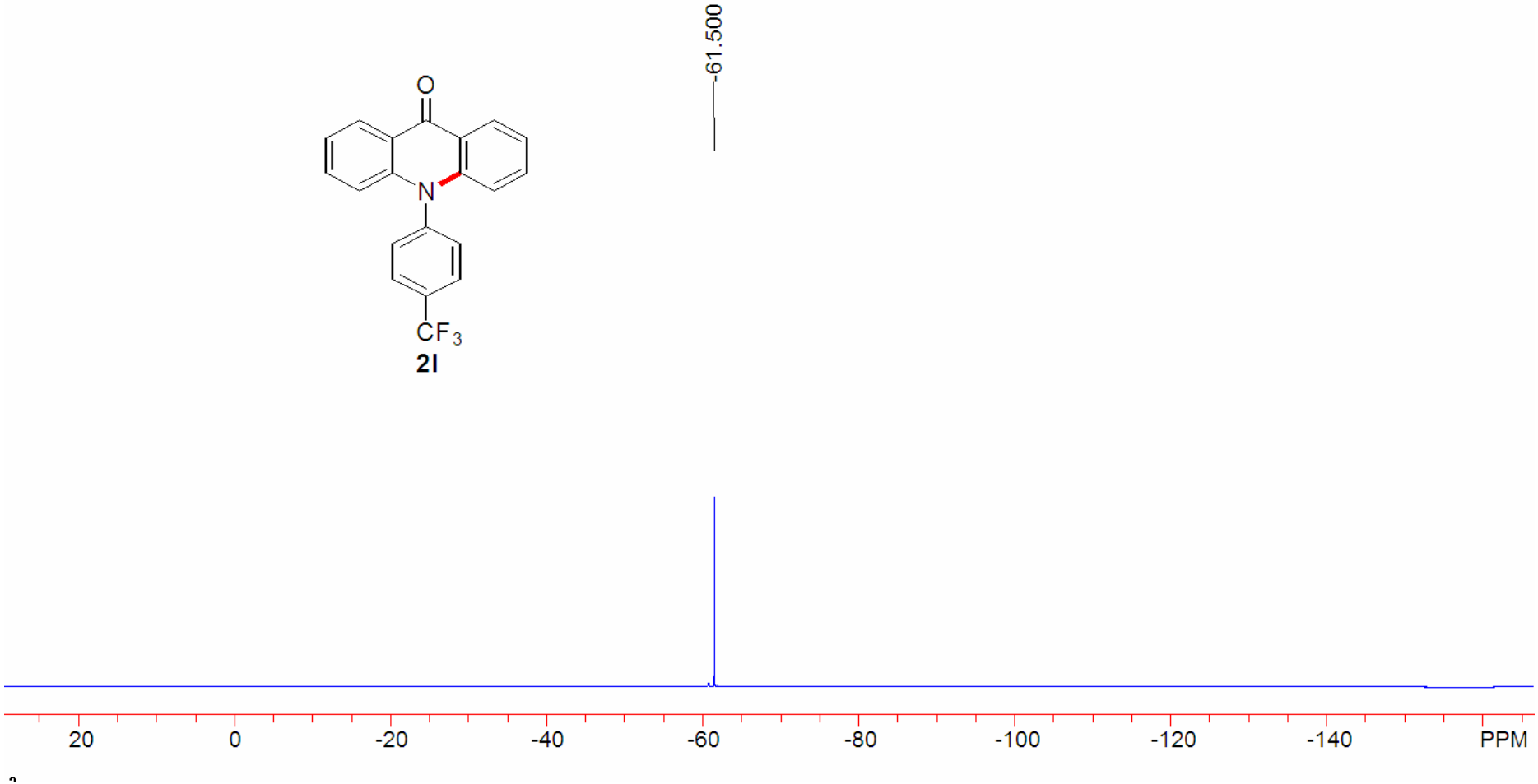




2 l



2l

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000013.d	Acquisition Date	7/24/2012 1:40:45 PM
Sample	L140-3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

2l

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
340.09434	1	C 20 H 13 F 3 N O	100.00	340.09438	0.0	0.1	2.8	13.5	even	ok

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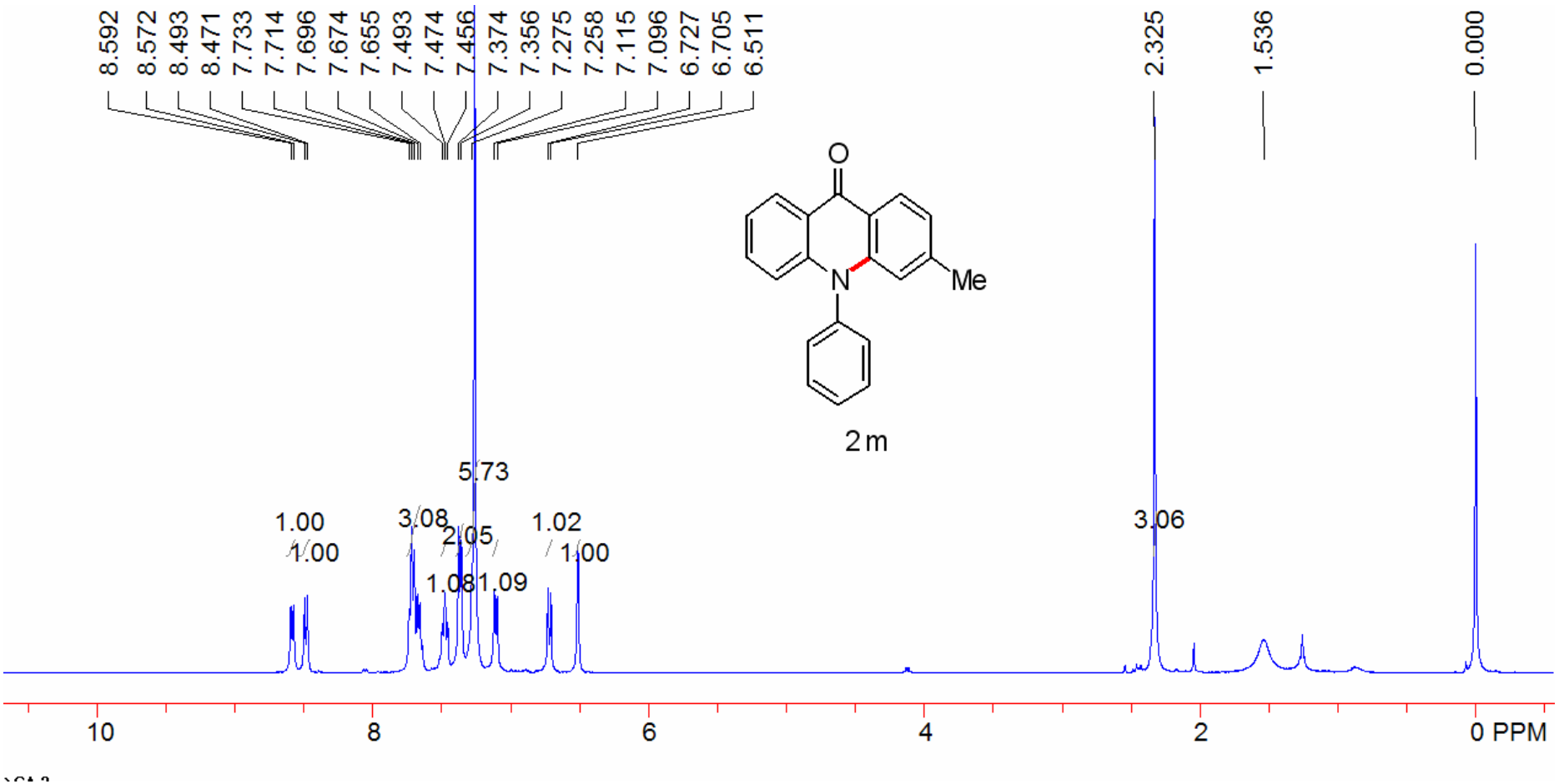
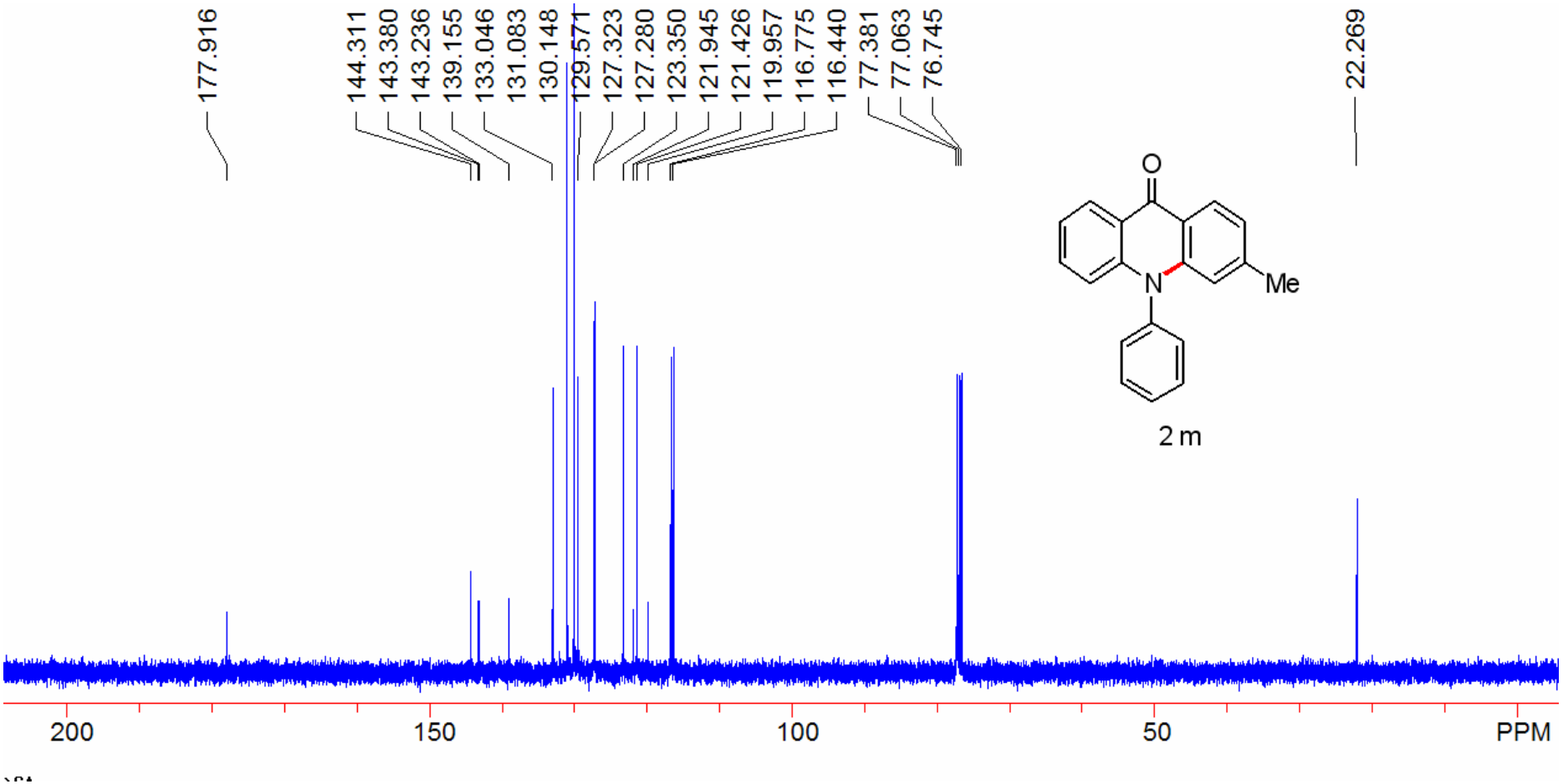
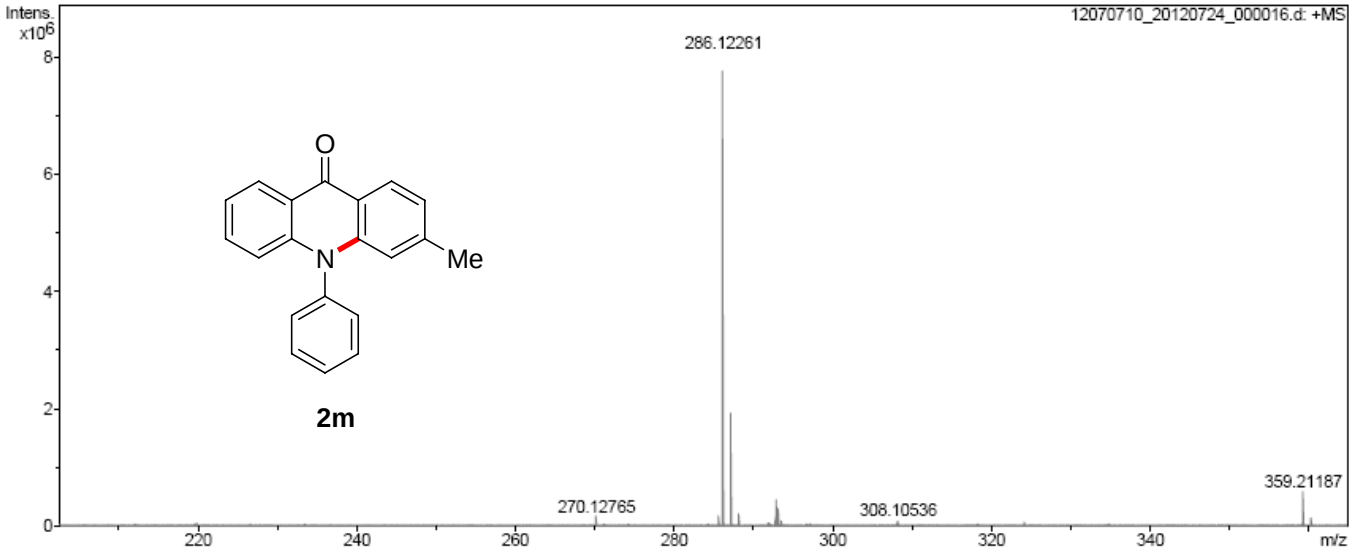




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000016.d	Acquisition Date	7/24/2012 1:43:40 PM
Sample	L142-4	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



2m

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
286.12261	1	C 20 H 16 N O	100.00	286.12264	0.0	0.1	15.9	13.5	even	ok

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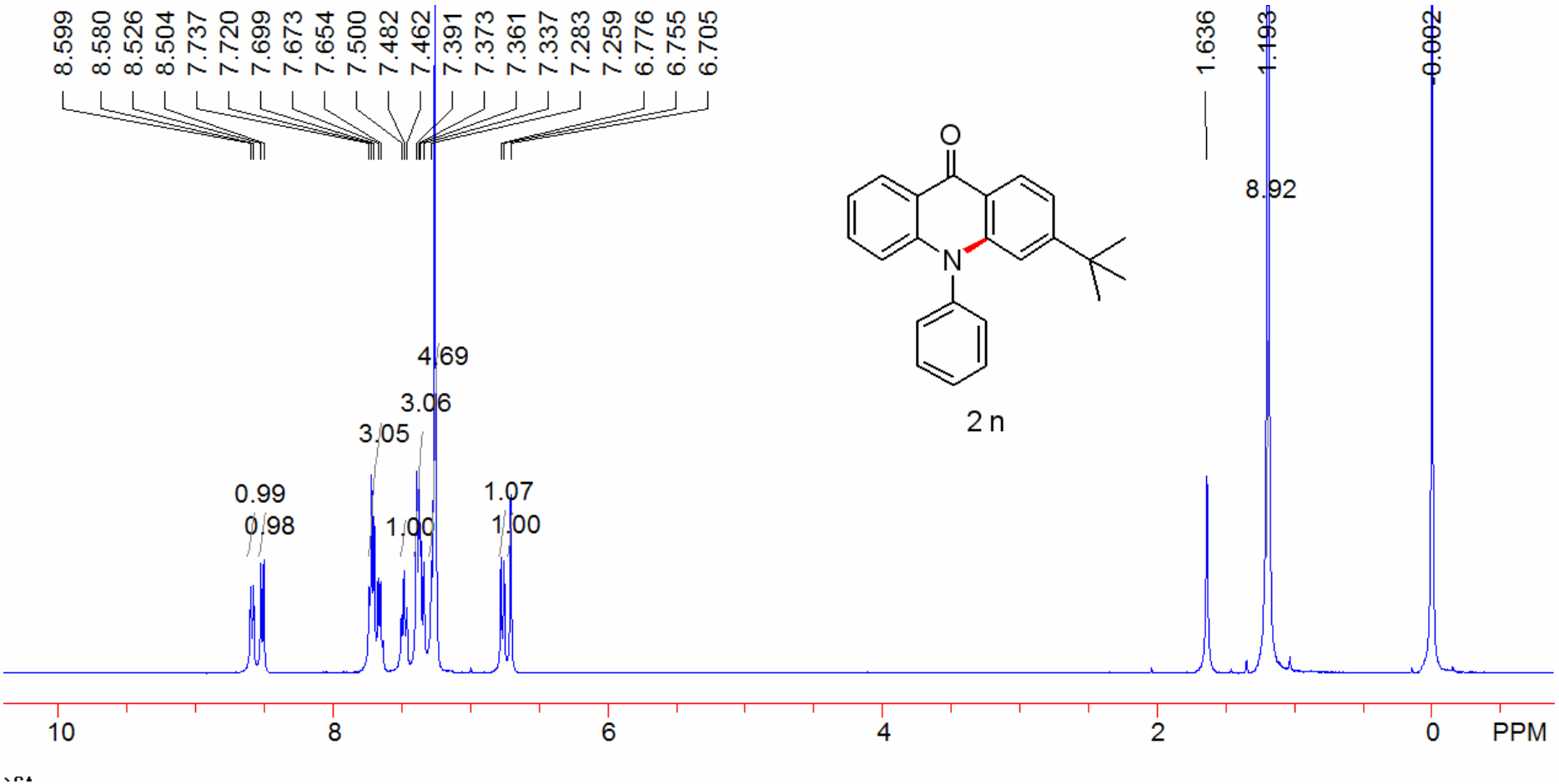
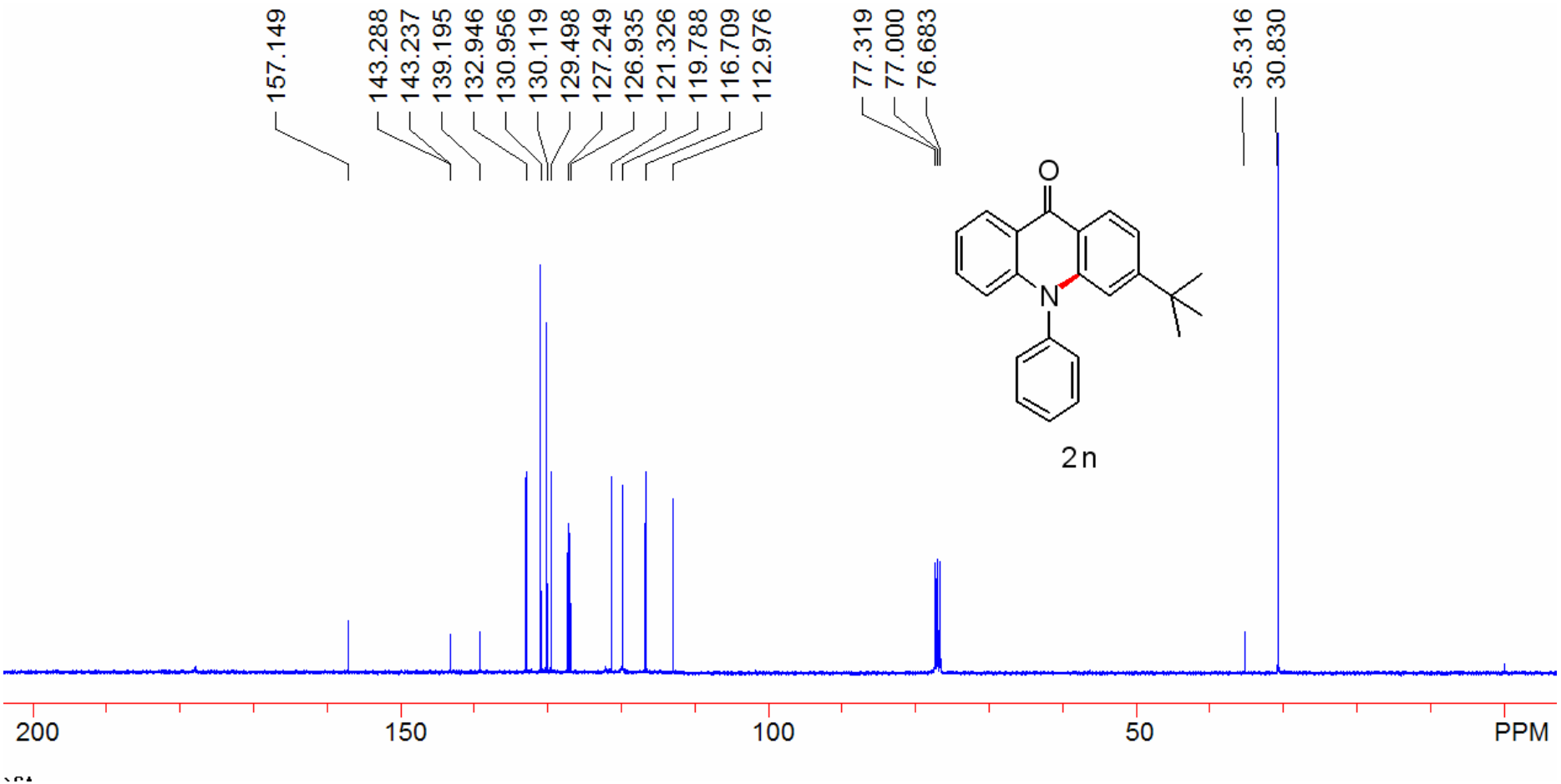
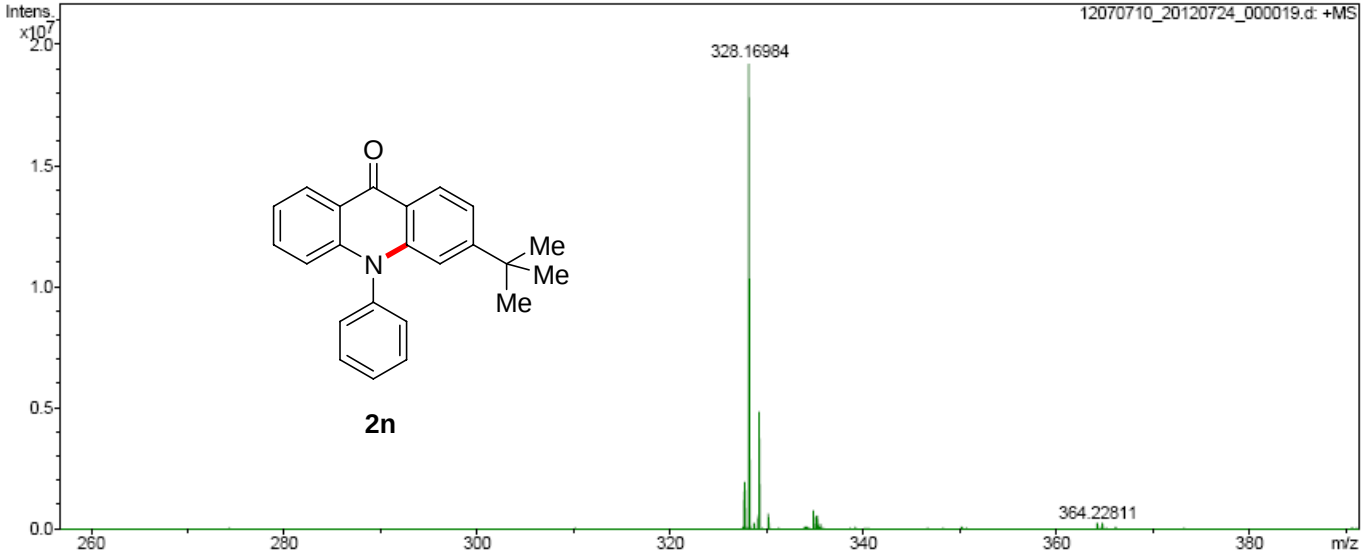




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000019.d	Acquisition Date	7/24/2012 1:46:45 PM
Sample	L142-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



2n

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
328.16984	1	C 23 H 22 N O	100.00	328.16959	-0.3	-0.8	7.0	13.5	even	ok

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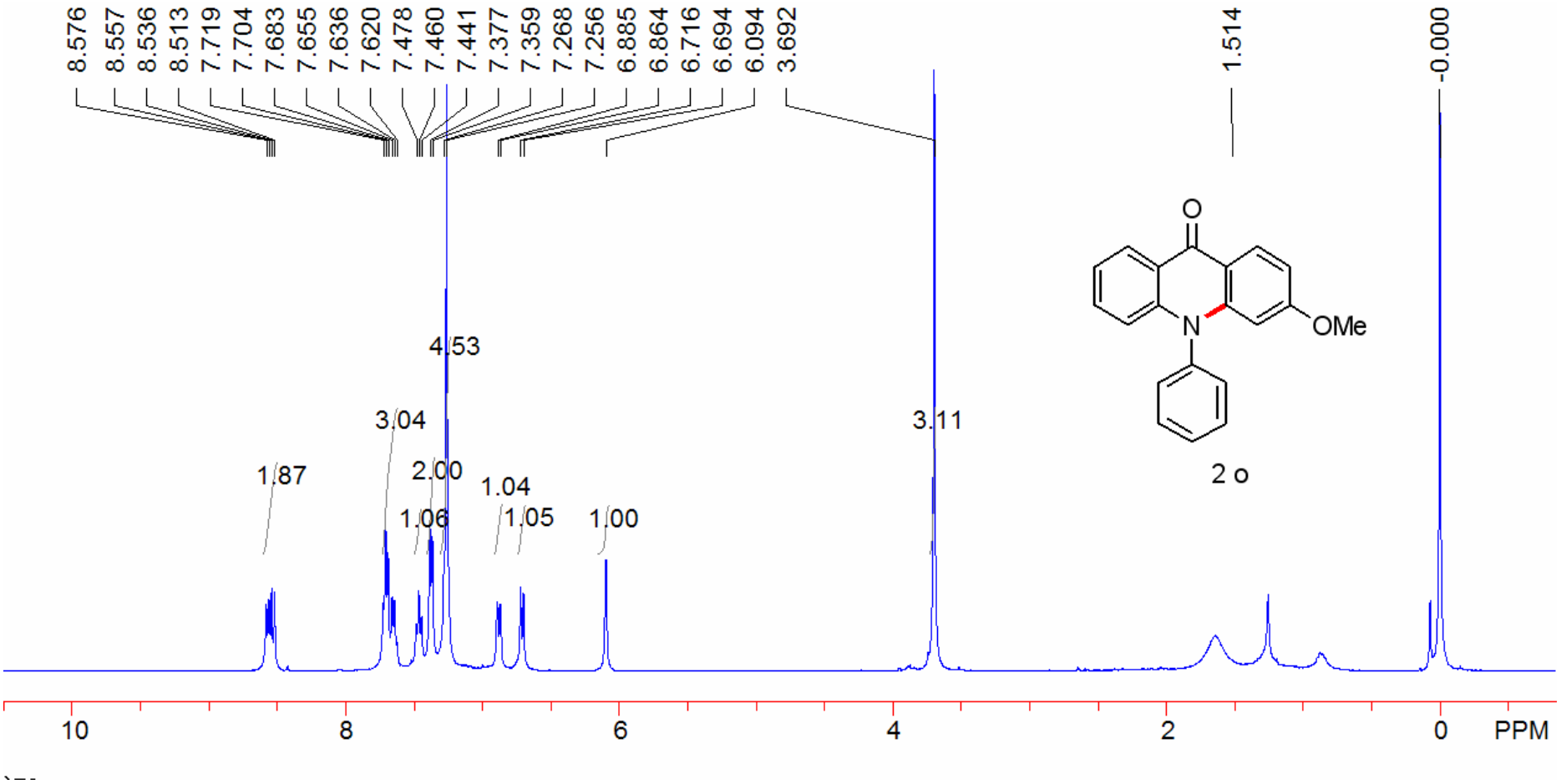
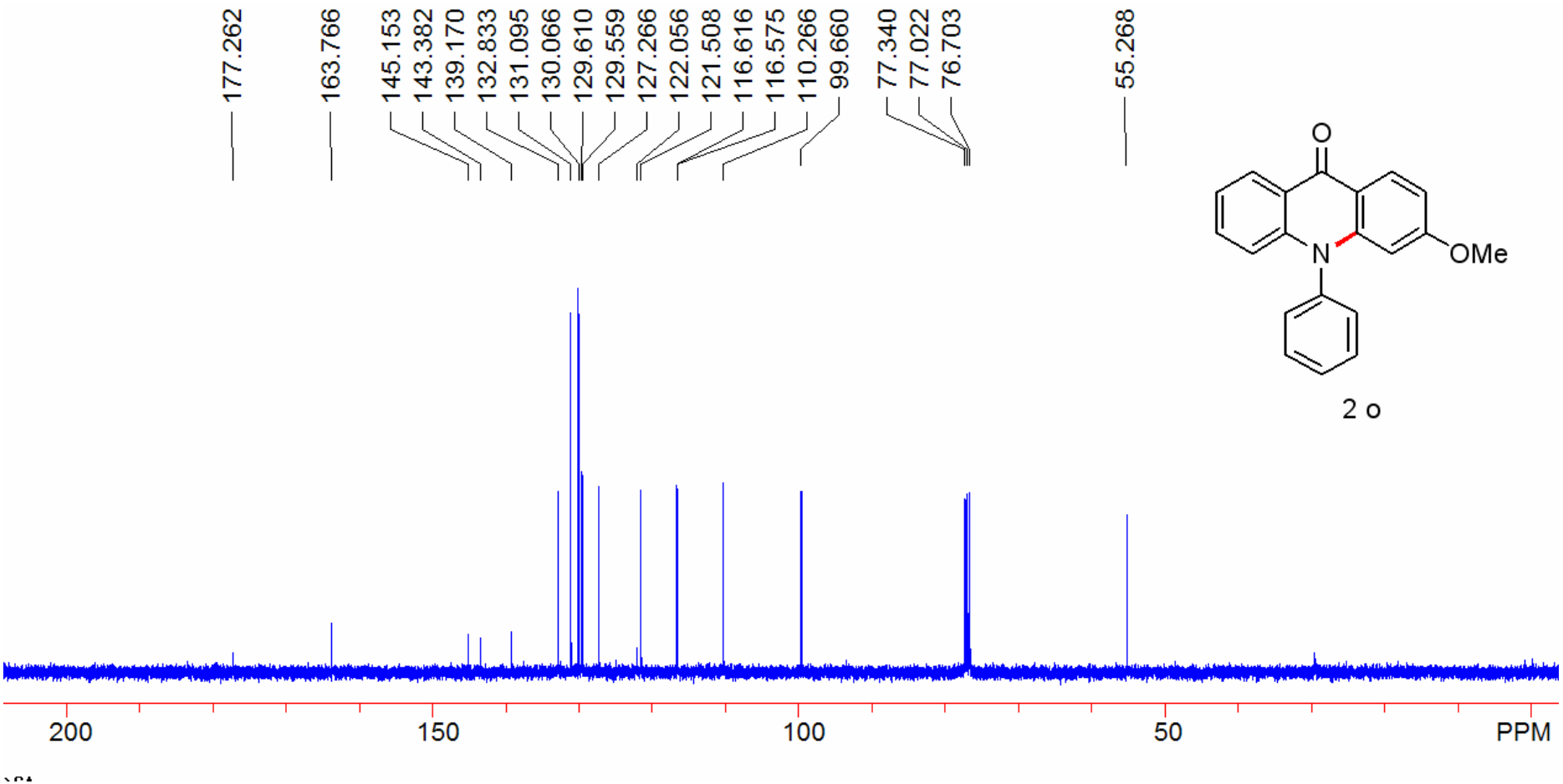
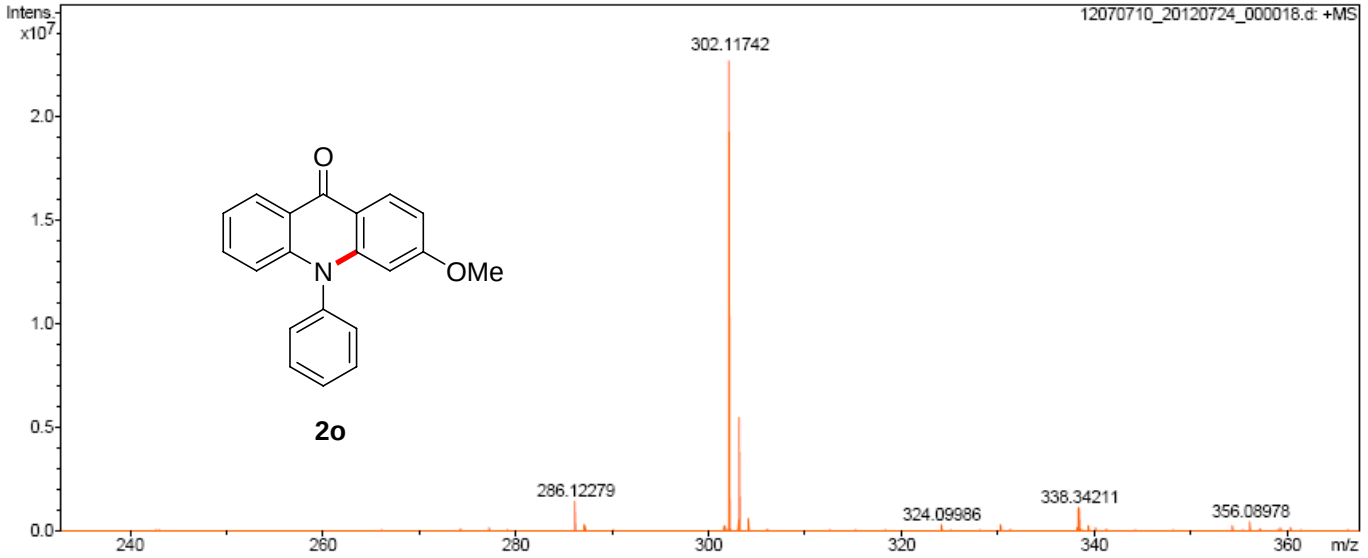




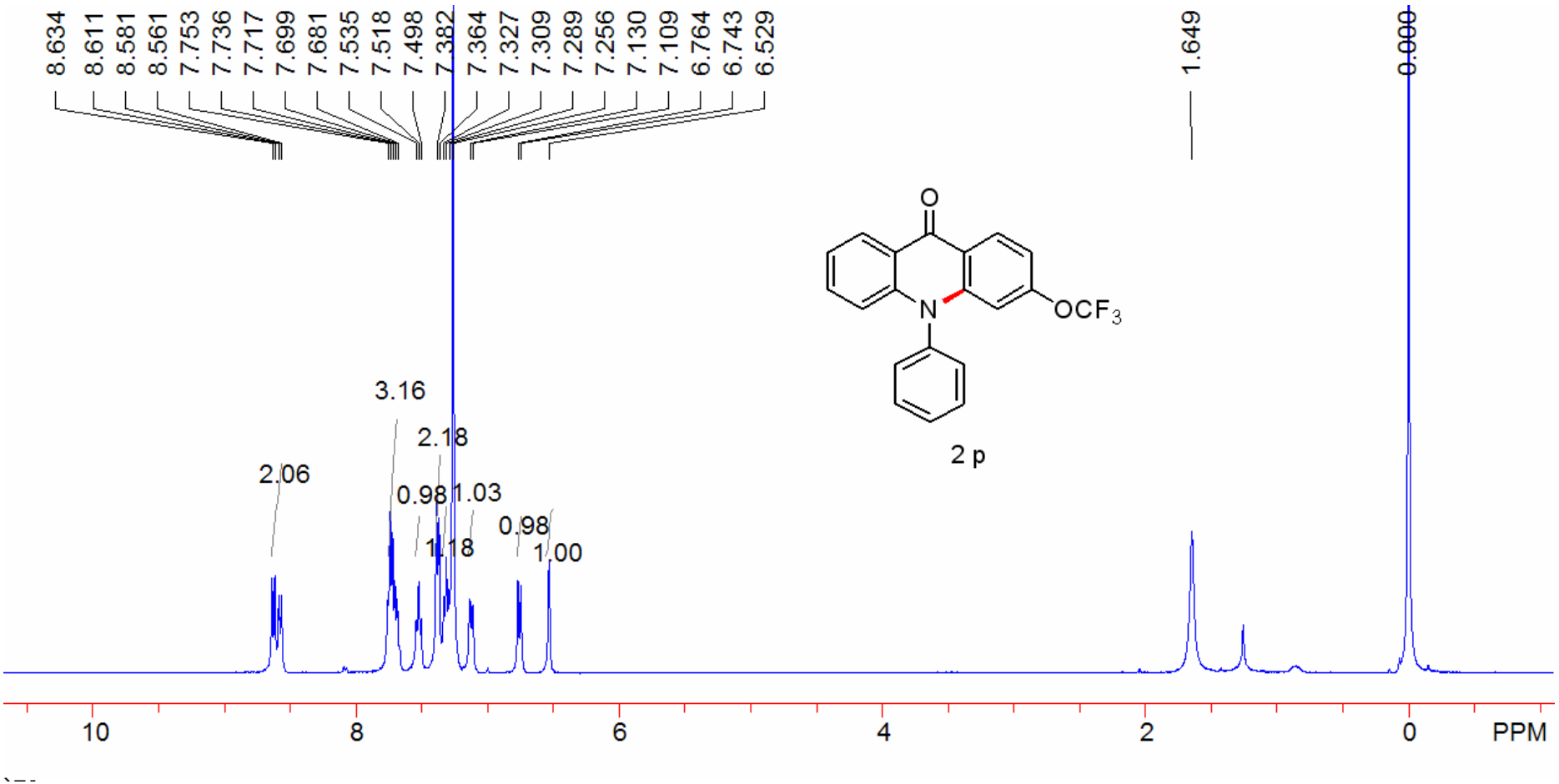
Peking University Mass Spectrometry Sample Analysis Report

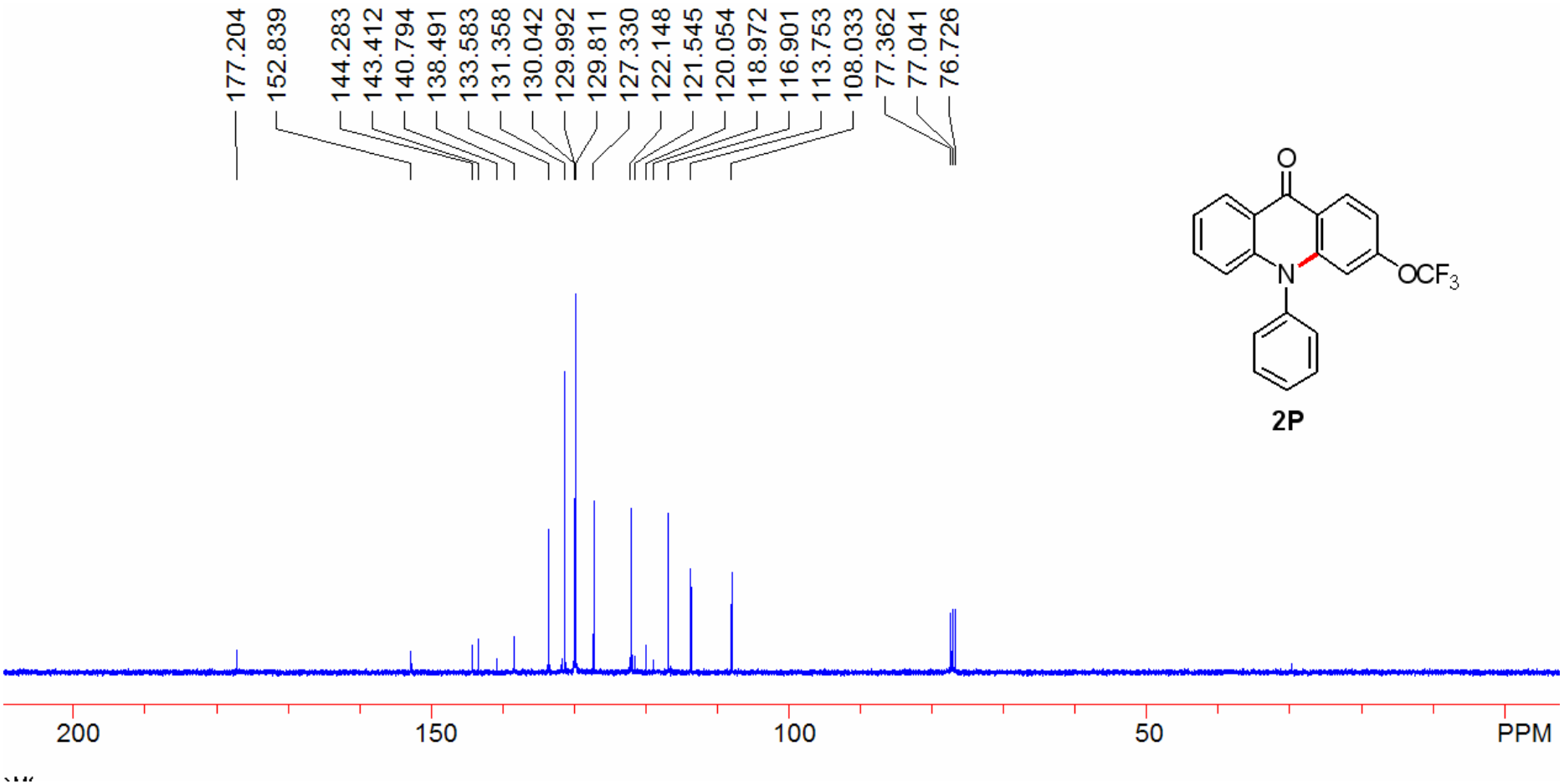
Analysis Info

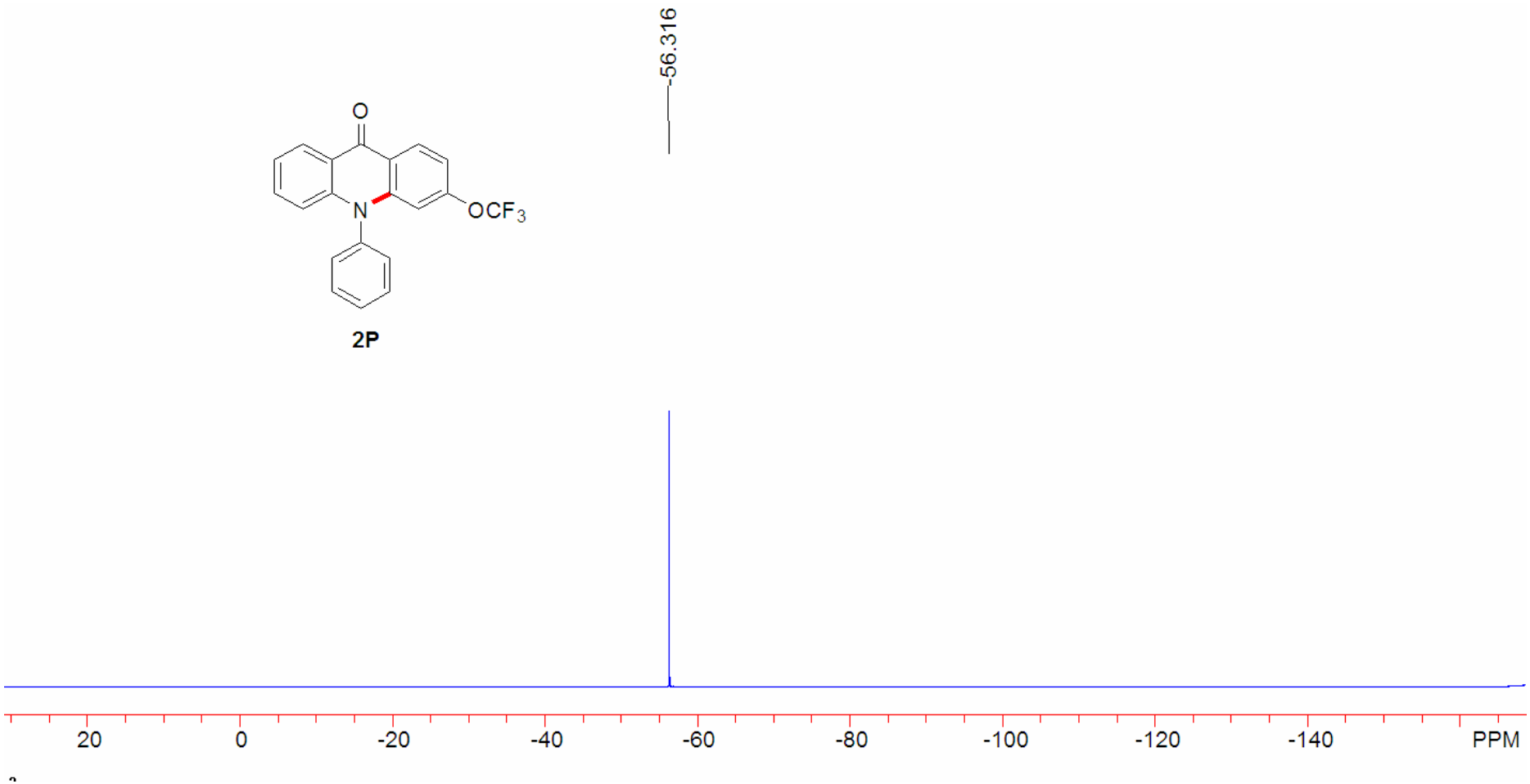
Analysis Name	12070710_20120724_000018.d	Acquisition Date	7/24/2012 1:45:42 PM
Sample	L142-3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
302.11742	1	C 20 H 16 N O 2	100.00	302.11756	0.1	0.4	11.8	13.5	even	ok





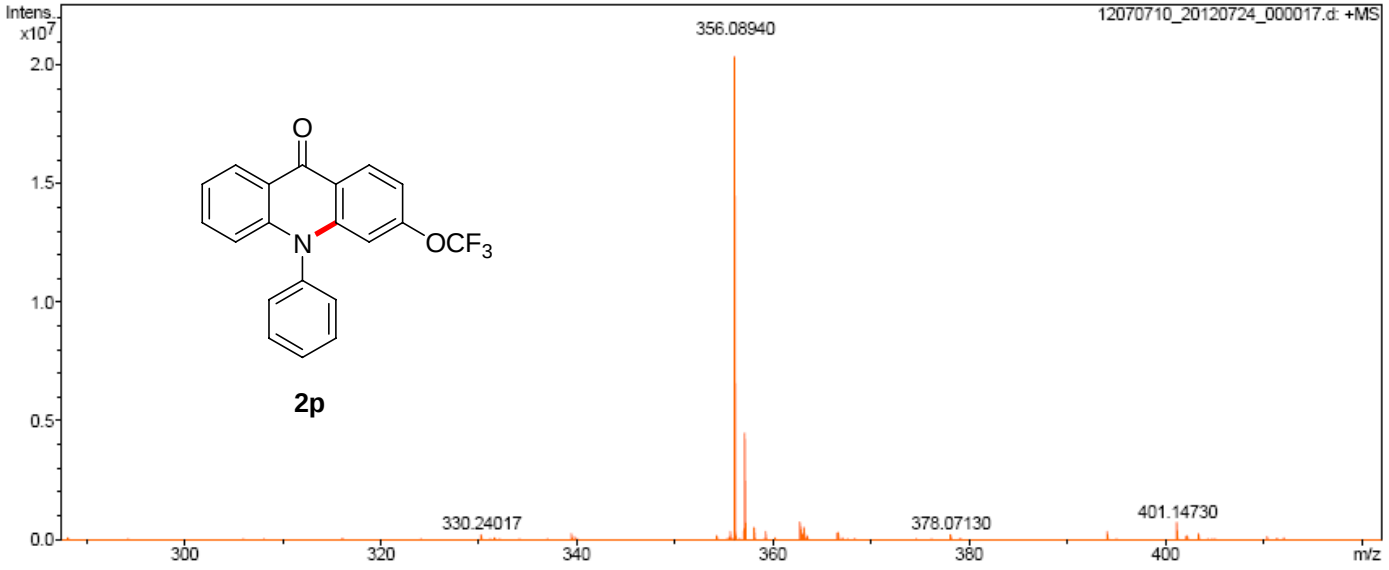


2P

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000017.d	Acquisition Date	7/24/2012 1:44:44 PM
Sample	L145-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



2p

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
356.08940	1	C 20 H 13 F 3 N O 2	100.00	356.08929	-0.1	-0.3	0.4	13.5	even	ok

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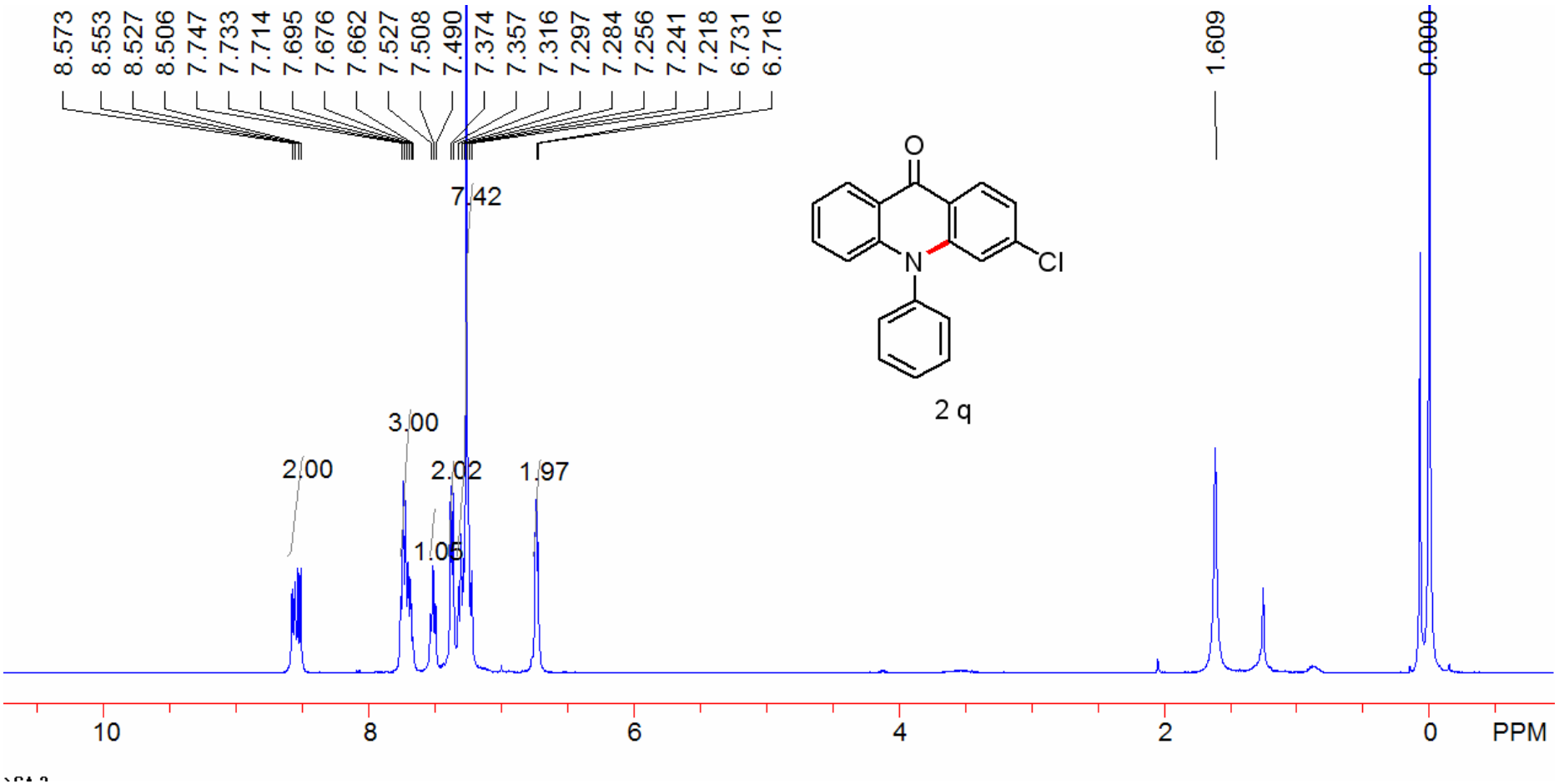
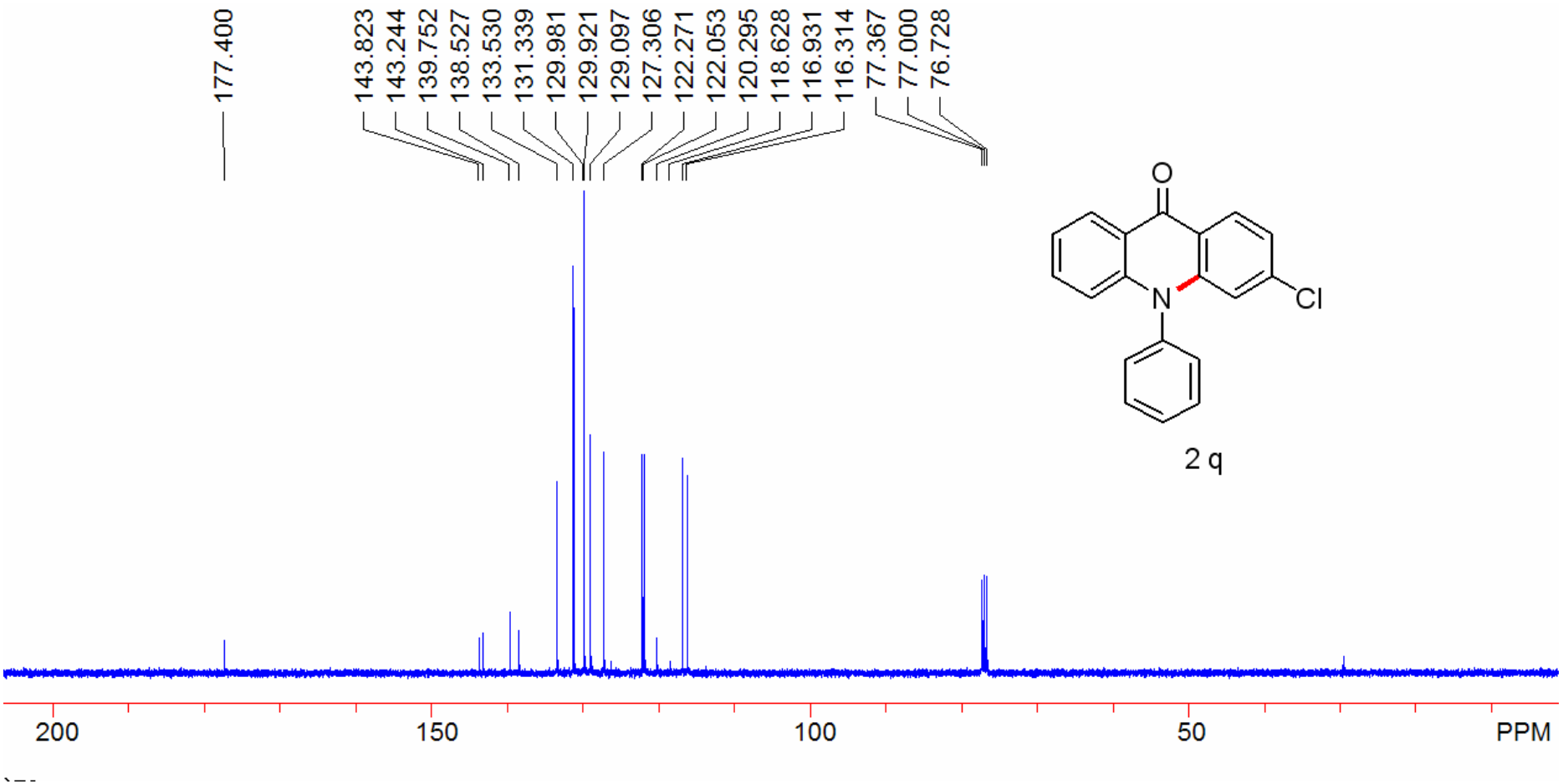
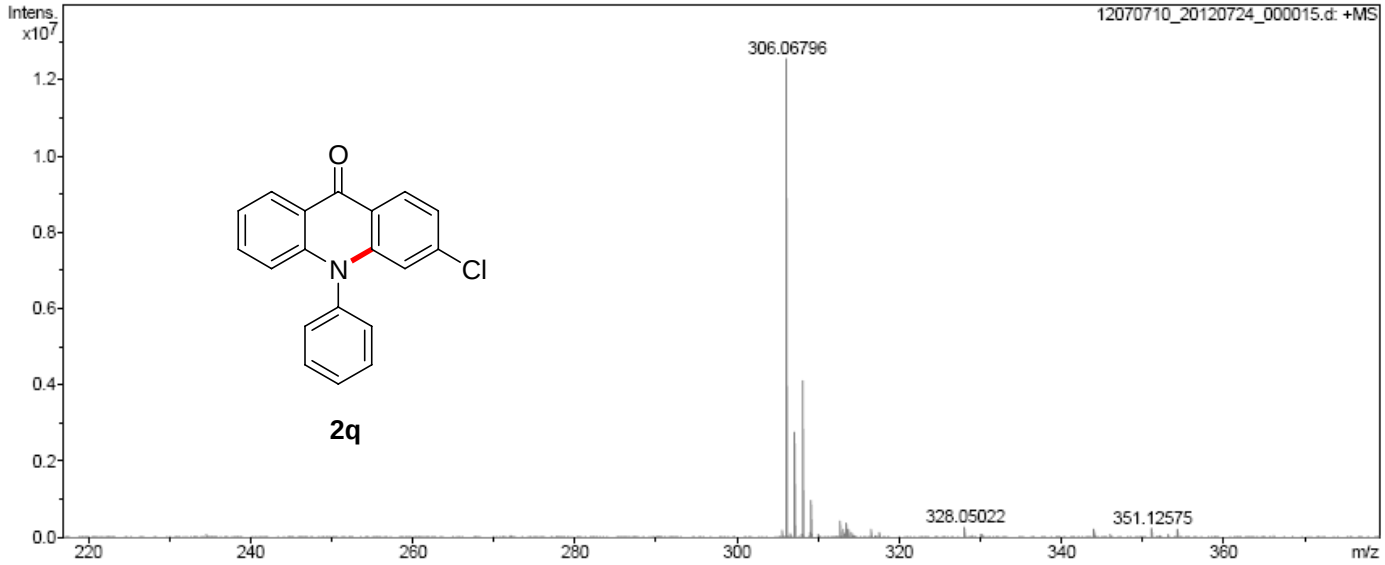




Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000015.d	Acquisition Date	7/24/2012 1:42:45 PM
Sample	L142-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



2q

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
306.06796	1	C 19 H 13 Cl N O	100.00	306.06802	0.1	0.2	8.3	13.5	even	ok

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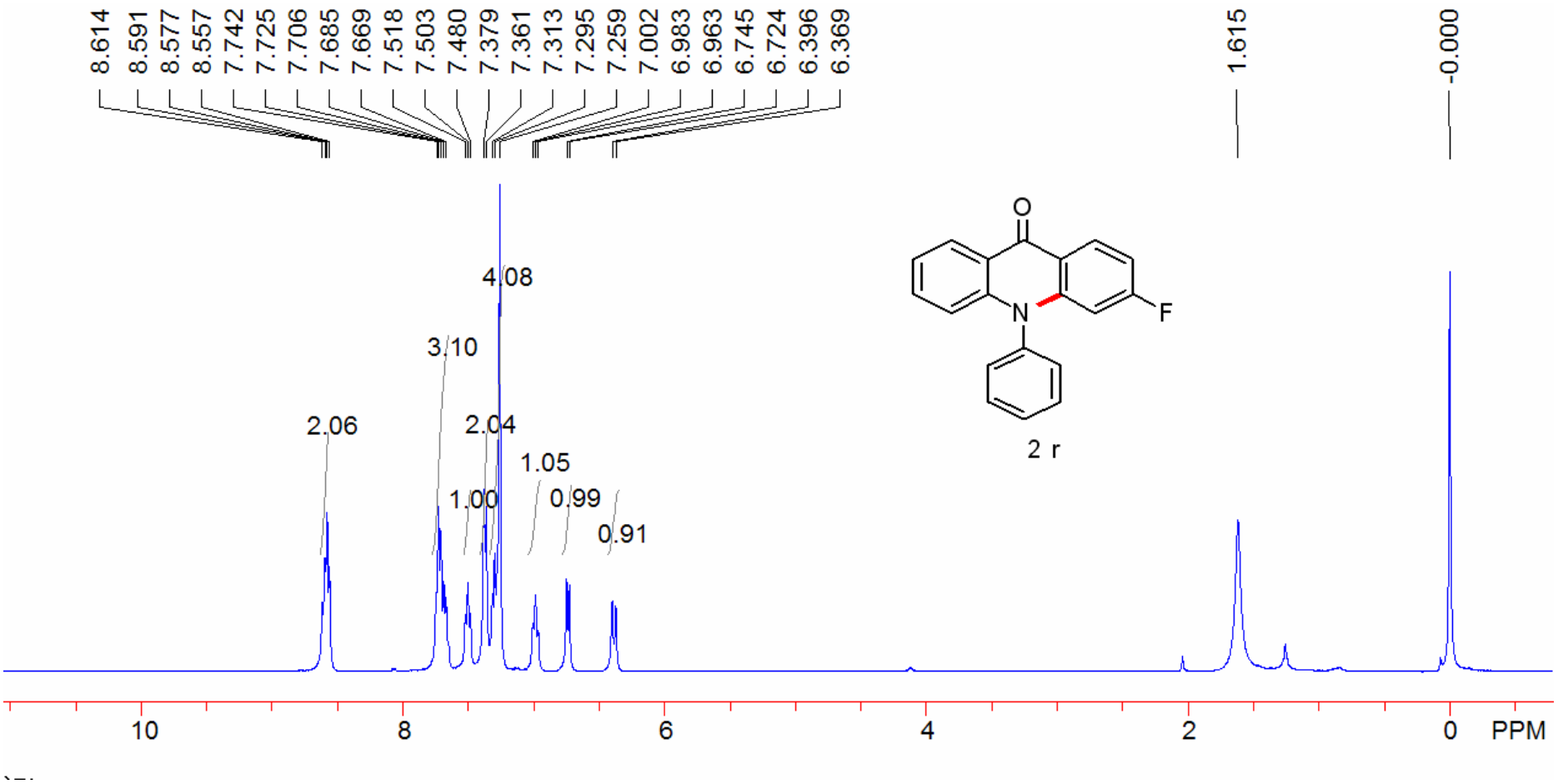
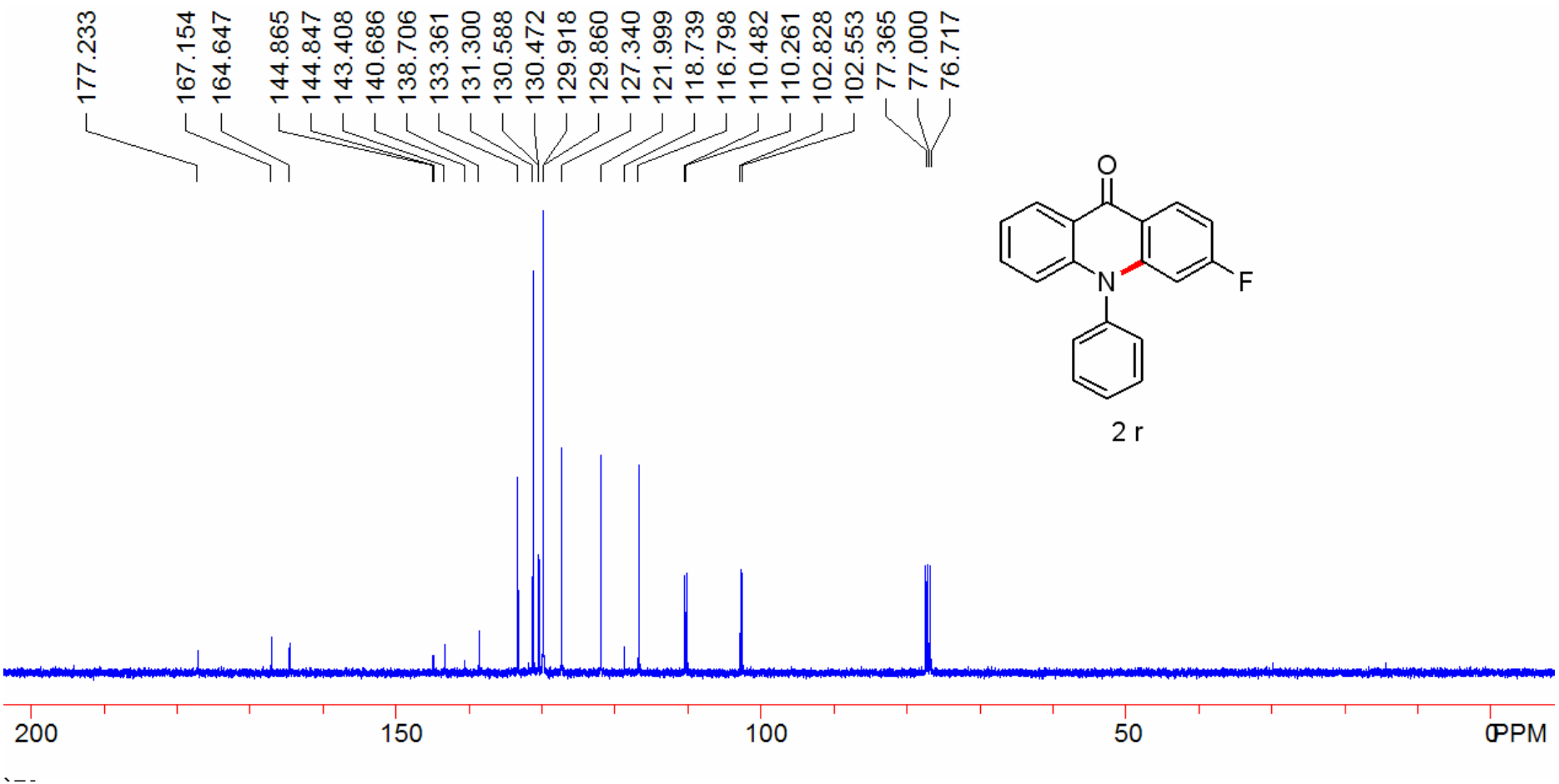
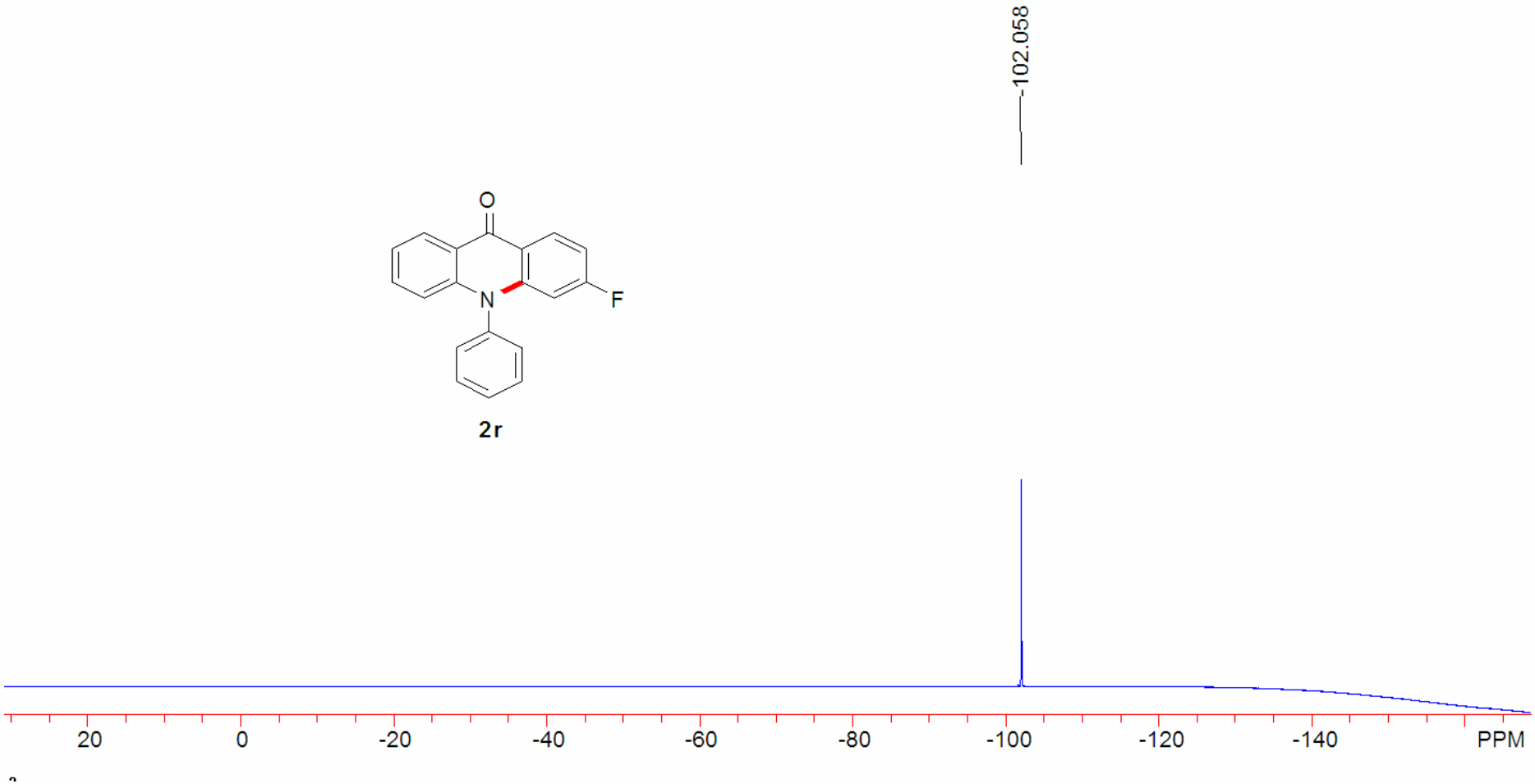




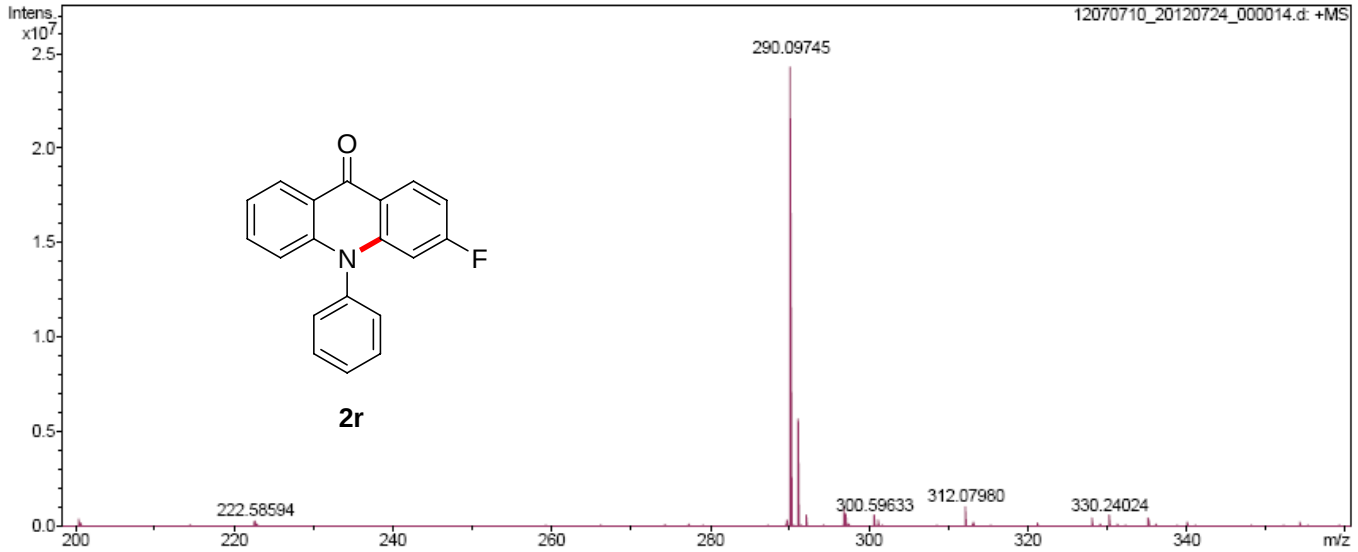


2r

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12070710_20120724_000014.d	Acquisition Date	7/24/2012 1:41:52 PM
Sample	L146-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



2r

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
290.09745	1	C 19 H 13 F N O	100.00	290.09757	0.1	0.4	13.3	13.5	even	ok

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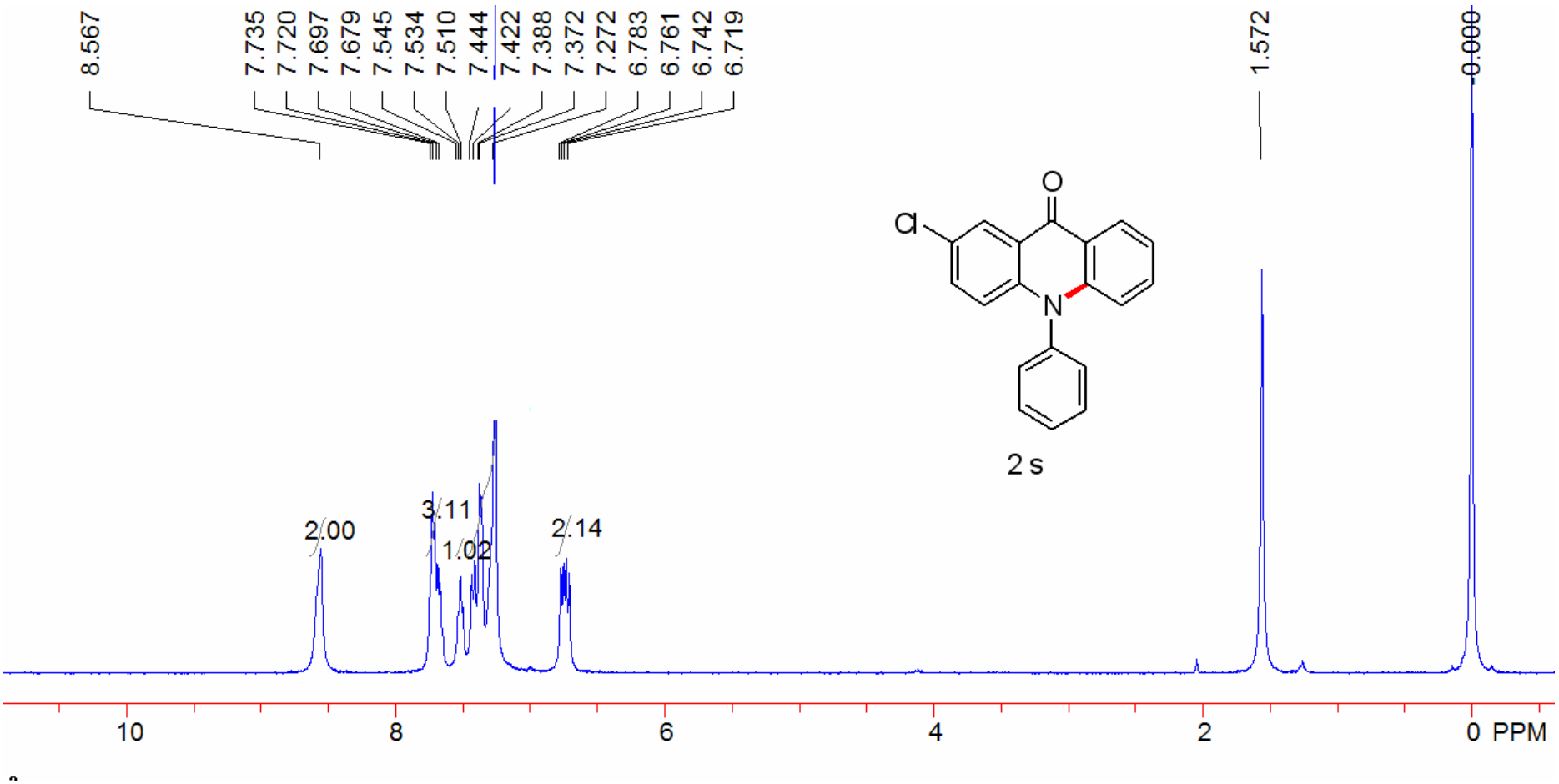
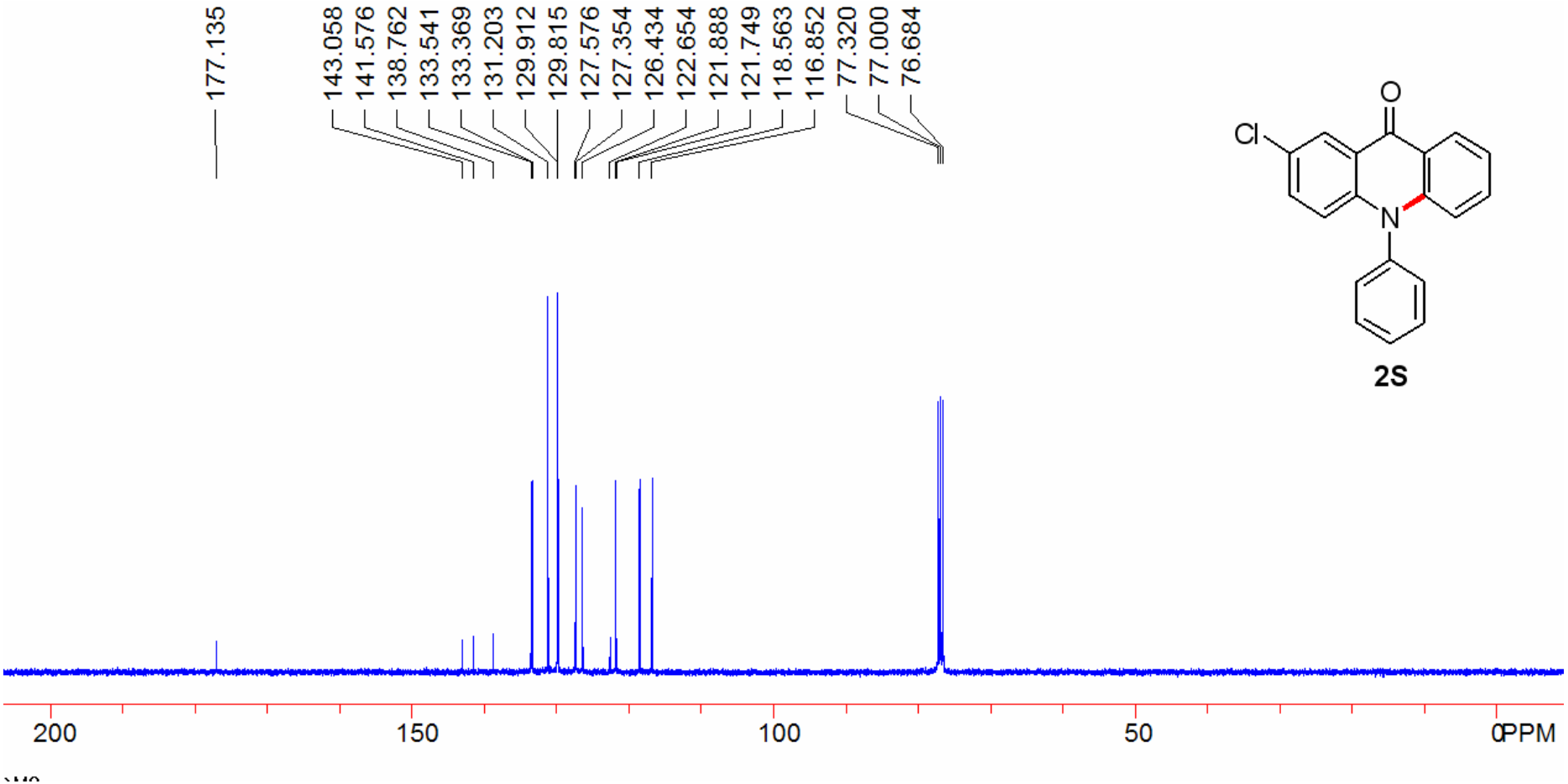


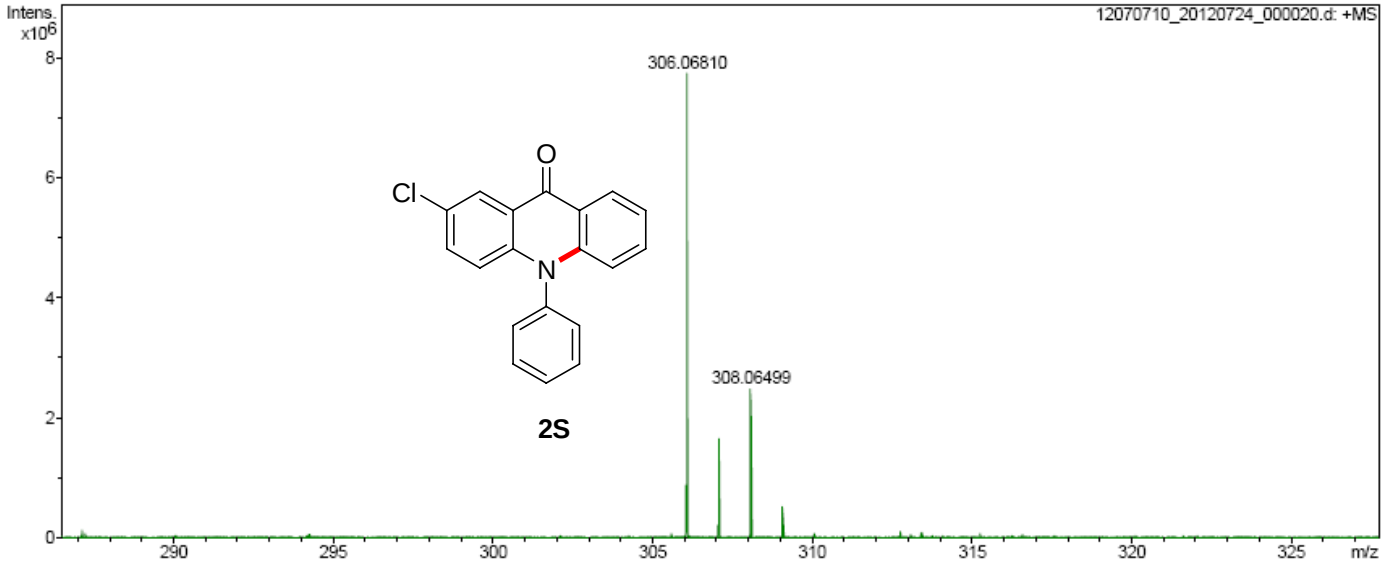


2S

Peking University Mass Spectrometry Sample Analysis Report

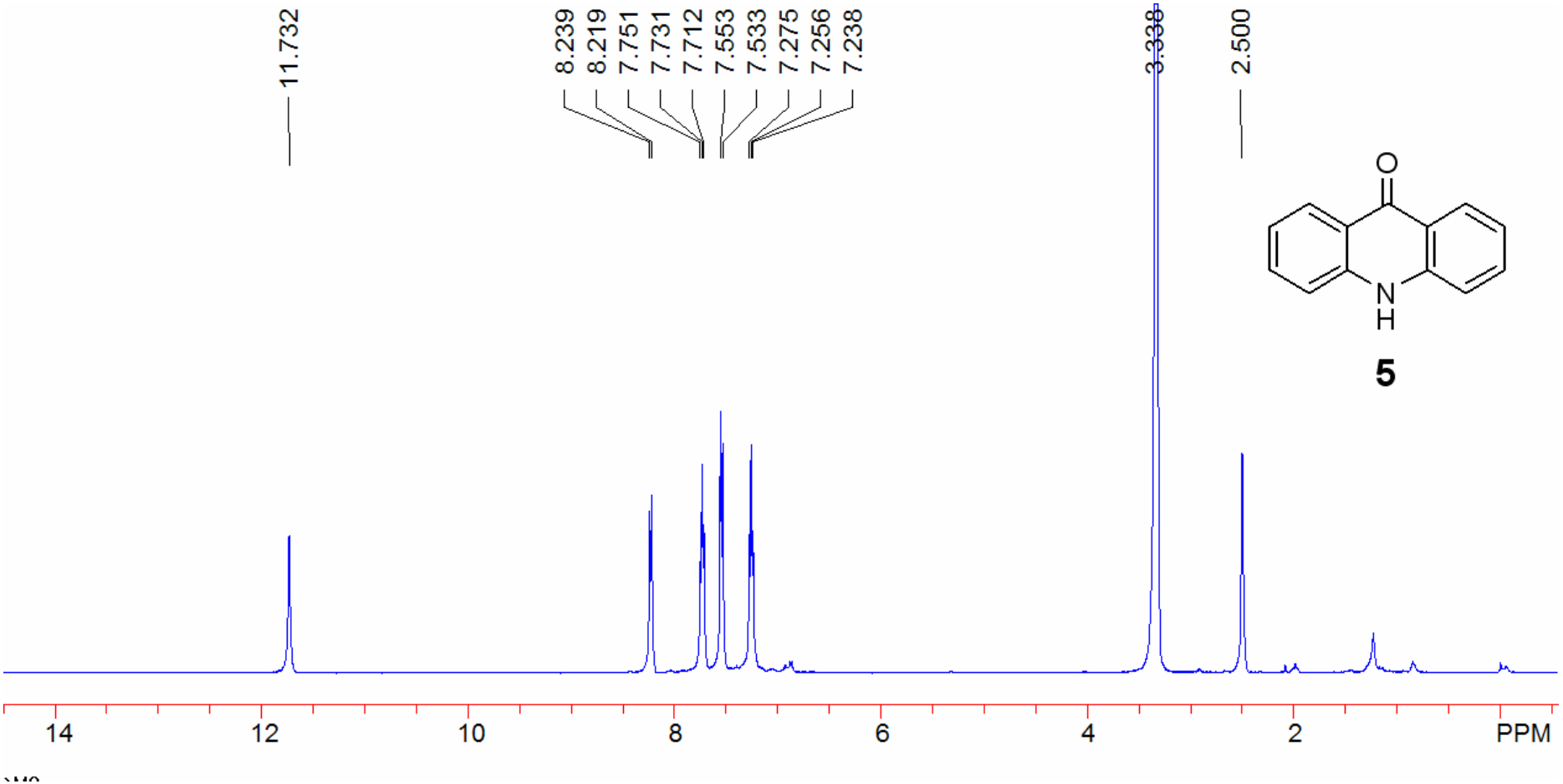
Analysis Info

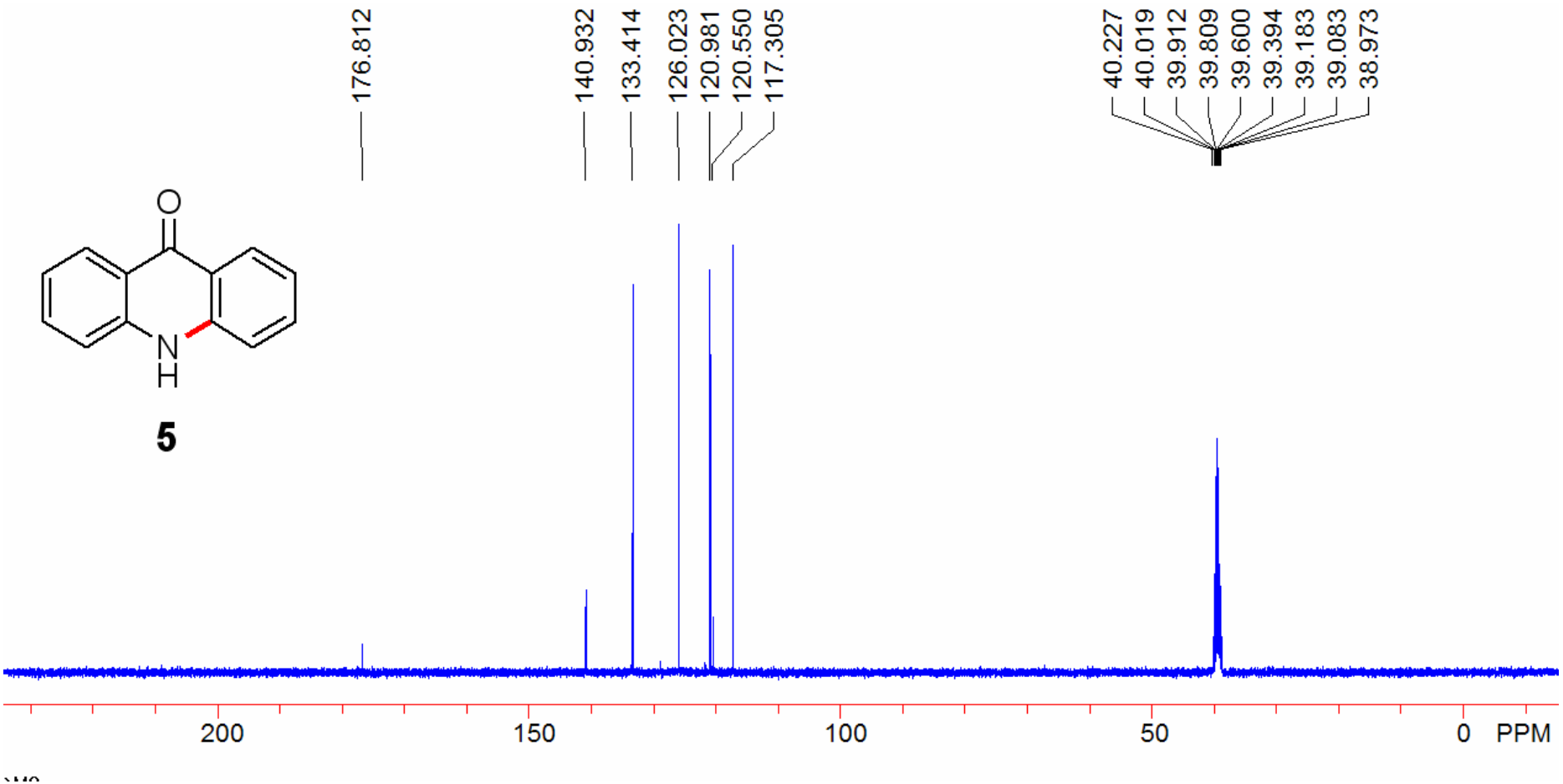
Analysis Name	12070710_20120724_000020.d	Acquisition Date	7/24/2012 1:47:37 PM
Sample	L139-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



2S

Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
306.06810	1	C 19 H 13 Cl N O	100.00	306.06802	-0.1	-0.3	7.6	13.5	even	ok





5