Supporting Information for:

Copper-mediated tandem reaction of β-ketoesters/ketones with tertiary amines for the synthesis of 2,3-dihydrofurans

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CONTENTS

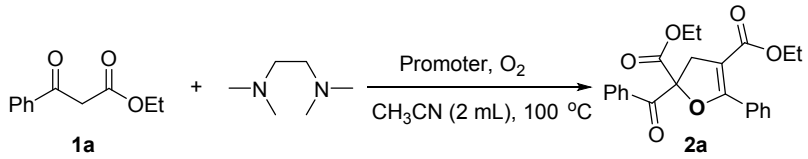
General experiment detail and metrials

Experimental: All non-aqueous reactions and manipulations were performed in air atmosphere using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on Agilent 400 spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. High resolution mass spectra (HRMS) Bruker Compass DataAnalysis 4.0 mass instrament (ESI). Single-crystal X-ray diffraction analysis was used on a Bruker Apex-II area-detector diffractometer at *ca* 293 K.

Optimization of the Reaction Conditions

A solution of CuX, ethyl 3-oxo-3-phenylpropanoate (96 mg, 0.5 mmol), TMEDA (70 mg, 1.2 equiv) in 2 mL of solvent was stirred 80-120 °C for 6 h under oxidative conditions. After warming to room temperature, the mixture was washed with water; then EA extract three times. Organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to leave a crude solid, which was purified by column chromatography on silica gel.

Table 1 Screen of CuX [a]

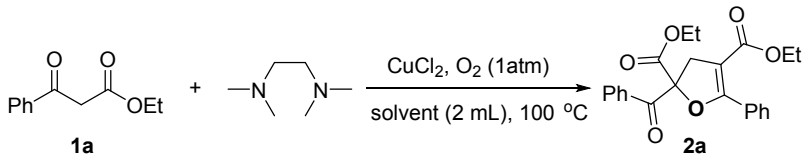


entry	CuX	yield (%)[b]
1	no	0
2	CuCl	trace
3	CuI	trace
4	CuBr	trace
5	CuF	trace
6	Cu_2O	trace
7	$CuCl_2$	63
8	$CuBr_2$	24
9	CuCN	trace
10	CuOAc	trace
11	$Cu(OAc)_2$	trace
12[c]	$Cu(acac)_2$	trace
13	$CuSO_4$	trace
14	I_2	0

[a] **1a** (0.5 mmol), TMEDA (0.6 mmol), copper (0.6 mmol), O_2 (1 atm), CH_3CN (2 mL), 100 °C, 6 h;

[b] Isolated yield;

Table 2 Screen of solvent[a]

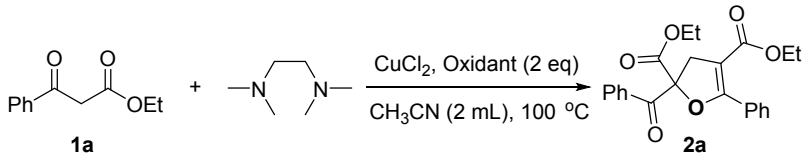


entry	Solvent(1mL)	Yield (%)[b]
1	DMSO	17
2	THF	trace
3	Dioxane	trace
4	CH_3CN	64
6	DMF	trace
7	hexane	trace
8	Xyl	trace
9	DMA	22
10	TBME	trace
11	DCM	trace
12[c]	EtOH	28
13	Toluene	trace
14	DME	trace
15	Mesitylene	trace

[a] **1a** (0.5 mmol), TMEDA (0.6 mmol), $CuCl_2$ (0.6 mmol), O_2 (1 atm), solvent (2 mL), 100 °C 6 h;

[b] Isolated yield;

Table 3 Screen of Oxidant [a]

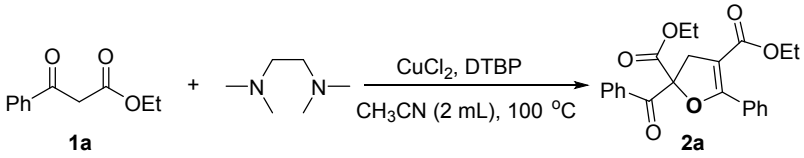


entry	Oxidant	Yield (%)[b]
1	TBHP(70% , aq)	trace
2	DTBP	81
3	Oxone	trace

4	m-CPBA	trace
5	$K_2S_2O_8$	trace
6	DDQ	38
7	O_2	64
8	Benzoyl Peroxide	trace

[a]**1a** (0.5 mmol), TMEDA (0.6 mmol), $CuCl_2$ (0.6 mmol), Oxidant (4 equiv), solvent (2 mL), 100 ^oC, 6 h; [b] isolated yield.

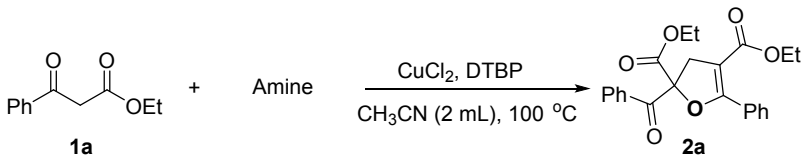
Table 4 Screen of other conditions [a]



entry	promoter	Yield (%)[b]
1	$CuCl_2$ (2 equiv)	trace
2	$CuCl_2$ (0.2 equiv)	trace
3	$CuCl_2$ (1.5 equiv)	70
4	$CuCl_2$ (1 equiv)	64
5	$CuCl_2$ (1.2 equiv)	81
6[c]	$CuCl_2$ (1.2 equiv)	79
7[d]	$CuCl_2$ (1.2 equiv)	68
8[e]	$CuCl_2$ (1.2 equiv)	82
9[f]	$CuCl_2$ (1.2 equiv)	70
10[g]	$CuCl_2$ (1.2 equiv)	66
11[h]	$CuCl_2$ (1.2 equiv)	74
12[i]	$CuCl_2$ (1.2 equiv)	80

[a]**1a** (0.5 mmol), TMEDA (0.6 mmol), $CuCl_2$ (0.6 mmol), DTBP (4 eq), CH_3CN (2 mL), 100 ^oC, 6 h; [b] isolated yield; [c]120 ^oC; [d] 80 ^oC ;[e] DTBP (2 eq); [f] DTBP (1.2 equiv); [g] DTBP (2 eq), 2 h; [h] DTBP (2 equiv), 4 h; [i] DTBP (1 equiv), 12 h.

Table 4 Screen of other condition [a]



1a 2a

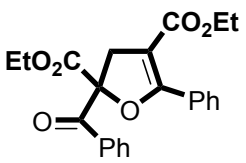
entry	Amine	Yield (%)[b]
1	Et_3N	trace
2	$PhNHCH_3$	46
3	$BnNHCH_3$	trace
4	$PhN(CH_3)_2$	trace

[a]1a (0.5 mmol), Amine (0.6 mmol), $CuCl_2$ (0.6 mmol), DTBP (4 eq), CH_3CN (2 mL), 100 °C, 6 h; [b] isolated yield;

General procedure Cu- promoter Tandem Reaction

$CuCl_2$ (80.7 mg, 0.6 mmol), β-ketoester derivatives (0.5 mmol, 1 eq) were added to a 50 mL Schleck tube under air. Then CH_3CN (2 mL), TMEDA (1.2 equiv) and DTBP (2 equiv) were added. The Schleck tube was sealed with a rubber septum and stirred for 6 h at 100 °C. The mixture was allowed to cool to room temperature, and washed with water, EA extract three times. The organic layer dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel and eluted with EtOAc/hexanes (1/20–1/10) to afford the desired product.

1. **Diethyl 2-benzoyl-5-phenyl-2,3-dihydrofuran-2,4-dicarboxylate** (**2a**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 2H), 7.81 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (dt, J = 14.4, 7.2 Hz, 3H), 4.19 (dq, J = 32, 6.8 Hz, 5H), 3.45 (d, J = 16.4 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 190.10, 169.27, 164.22, 162.65, 133.96, 133.64, 130.83, 129.95, 129.70, 128.88, 128.78, 127.78, 102.46, 90.15, 62.79, 60.33, 38.40, 14.32, 13.95. HRMS (ESI) calcd. for $C_{23}H_{22}NaO_6$ [M+23]: 417.1309, found: 417.1330



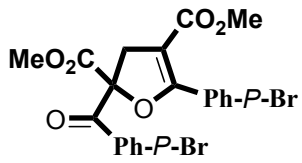
2. **Dimethyl 2-benzoyl-5-phenyl-2,3-dihydrofuran-2,4-dicarboxylate** (**2b**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 14.8 Hz, 1H), 7.47 (t, *J* = 14.8 Hz, 2H), 7.38 (dt, *J* = 14.8, 7.4 Hz, 3H), 4.20 (d, *J* = 16 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.50 (d, J = 16 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.03, 169.67, 164.53, 162.85, 134.03, 133.46, 130.93, 129.92, 129.61, 128.83, 128.67, 127.84, 102.08, 90.24, 53.61, 51.45, 38.48. HRMS (ESI) calcd. for $C_{21}H_{18}NaO_6$ [M+23]: 389.0996, found: 389.0995.

3. Diethyl2-(4-nitrobenzoyl)-5-(4-nitrophenyl)-2,3-dihydrofuran-2,4-dicarboxylate (**2c**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.30 – 8.20 (m, 4H), 8.00 (d, *J* = 8.8 Hz, 2H), 4.29 (td, *J* = 7.2, 4.0 Hz, 2H), 4.25 (dd, *J* = 9.2, 3.2 Hz, 1H), 4.22 – 4.15 (m, 2H), 3.49 (d, *J* = 17.2 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.46, 168.39, 163.37, 159.49, 150.88, 149.00, 137.99, 134.48, 131.01, 130.73, 124.05, 123.13, 105.70, 90.29, 63.51, 61.02, 38.52, 14.31, 14.03. HRMS (ESI) calcd. for $C_{21}H_{16}N_2NaO_{10}$ [M+23]: 479.0702, found: 479.0708.

4. Diethyl2-(2,3,4,5-tetrafluorobenzoyl)-5-(2,3,4,5-tetrafluorophenyl)-2,3-dihydrofuran-2,4-dicarboxylate (**2d**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 4.35 (dd, *J* = 11.2, 6.8 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.95 (d, *J* = 16.8 Hz, 1H), 3.55 (d, *J* = 16.8 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.39, 186.85, 166.86, 162.75, 154.17, 148.59, 148.00, 146.07, 145.45, 142.95, 142.40, 140.83, 139.71, 112.60, 107.49, 91.62, 62.88, 60.90, 38.12, 14.06. HRMS (ESI) calcd. for $C_{23}H_{14}F_8NaO_6$ [M+23]: 561.0555, found: 561.0552.

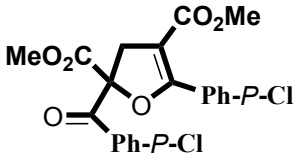
5. **Dimethyl2-(4-bromobenzoyl)-5-(4-bromophenyl)-2,3-dihydrofuran-2,4-dicarb-**

oxylate (**2e**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 87% yield. ^{1}H NMR



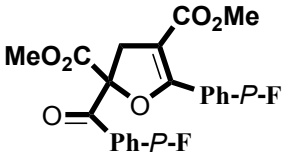
(400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 4.18 (d, *J* = 16.8 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.44 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.99, 169.44, 164.33, 161.55, 132.32, 132.15, 131.44, 131.27, 131.17, 129.75, 127.43, 125.64, 102.81, 90.20, 53.78, 51.67, 38.46. HRMS (ESI) calcd. for $C_{21}H_{16}Br_2NaO_6$ [M+23]: 544.9206, found: 544.9209.

6. Dimethyl 2-(4-chlorobenzoyl)-5-(4-chlorophenyl)-2,3-dihydrofuran- 2,4- dicarboxylate (**2f**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 99% yield. ^{1}H NMR

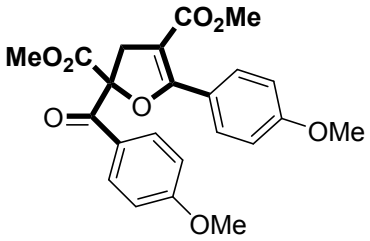


(400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 4.19 (d, *J* = 16.4 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.45 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.76, 169.45, 164.33, 161.47, 140.85, 137.13, 131.73, 131.38, 130.99, 129.30, 128.27, 126.97, 102.70, 90.19, 53.74, 51.58, 38.43. HRMS (ESI) calcd. for $C_{21}H_{16}Cl_2NaO_6$ [M+23]: 457.0216, found: 457.0195.

7. Dimethyl2-(4-fluorobenzoyl)-5-(4-fluorophenyl)-2,3-dihydrofuran-2,4- dicarboxylate (**2g**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.10 (m, 2H), 7.92 – 7.82 (m, 2H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 4.20 (d, J = 16.4 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.46 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.40, 169.60, 167.58, 165.47, 165.02, 164.47, 162.97, 161.69, 132.88, 131.99, 129.85, 124.69, 116.07, 114.99, 102.08, 90.20, 53.69, 51.52, 38.41. HRMS (ESI) calcd. for $C_{21}H_{16}F_2NaO_6$ [M+23]: 425.0807, found:425.0797.

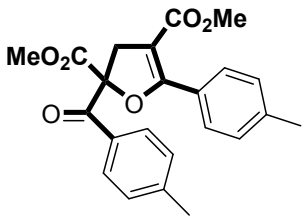


8. Dimethyl2-(4-methoxybenzoyl)-5-(4-methoxyphenyl)-2,3-dihydrofuran-2,4-dicarboxylate (**2h**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 6.95

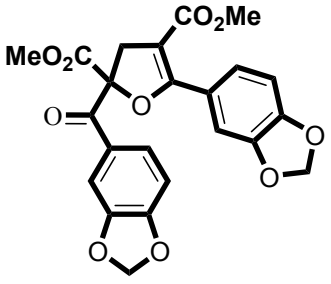


(d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.18 (d, *J* = 16.0 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H), 3.44 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.42, 169.95, 164.75, 164.08, 162.69, 161.53, 132.35, 131.34, 126.28, 120.97, 113.97, 113.13, 100.35, 90.00, 55.53, 55.32, 53.35, 51.25, 38.30. HRMS (ESI) calcd. for $C_{23}H_{22}NaO_8$ [M+23]: 449.1207, found: 449.1212.

9. Dimethyl 2-(4-methylbenzoyl)-5-(p-tolyl)-2,3-dihydrofuran-2,4-dicarboxylate (**2i**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.17 (d, *J* = 16.4 Hz, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.46 (d, *J* = 16.4 Hz, 1H), 2.41 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.63, 169.90, 164.72, 163.15, 145.11, 141.33, 130.94, 130.12, 129.57, 128.56, 125.87, 101.37, 90.18, 53.51, 51.36, 38.42, 29.81, 21.85, 14.24. HRMS (ESI) calcd. for $C_{23}H_{22}NaO_6$ [M+23]: 417.1309, found: 417.1312.

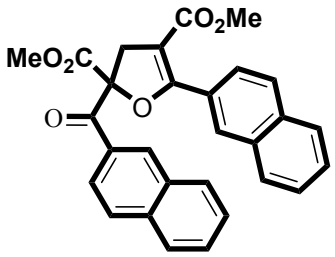


10. **Dimethyl5-(benzo[d][1,3]dioxol-5-yl)-2-(benzo[d][1,3]dioxole-5-carbonyl)-2,3-dihydrofuran-2,4-dicarboxylate** (**2j**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.06 (s, 2H), 5.99 (s, 2H), 4.17 (d, *J* = 16.4 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.42 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.03, 187.99, 169.93, 164.70, 162.29, 152.68, 149.83, 148.36, 147.17, 128.01, 126.84, 124.94, 122.32, 109.96, 109.54, 108.32, 107.87, 102.15, 101.56, 100.99, 90.00, 53.62, 51.43, 38.58. HRMS (ESI) calcd. for $C_{23}H_{18}NaO_{10}$ [M+23]: 477.0792, found: 477.0794.



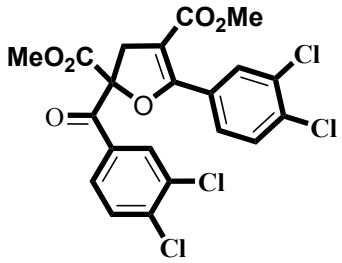
11. Dimethyl2-(2-naphthoyl)-5-(naphthalen-2-yl)-2,3-dihydrofuran-2,4-dicarboxylate (**2k**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 95% yield. ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.40 (s, 1H), 8.14 (d, J = 8.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz,



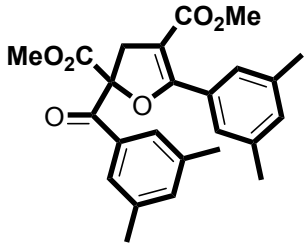
1H), 7.95 – 7.76 (m, 6H), 7.65 – 7.42 (m, 4H), 4.31 (d, *J* = 16.4 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.63 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.19, 169.82, 164.63, 162.91, 135.96, 134.44, 132.53, 132.47, 132.40, 130.81, 130.38, 130.18, 129.27, 129.04, 128.71, 127.86, 127.70, 127.59, 127.38, 127.07, 126.42, 126.08, 125.00, 102.45, 90.59, 53.65, 51.54, 38.80. HRMS (ESI) calcd. for $C_{29}H_{23}O_6$ [M+1]: 467.1489, found: 467.1502.

12. Dimethyl2-(3,4-dichlorobenzoyl)-5-(3,4-dichlorophenyl)-2,3-dihydrofuran-2,4-dicarboxylate (**2l**). The title compound was prepared according to the general



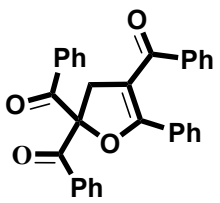
procedure and purified by column chromatography to give a white solid, 87% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.97 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 4.19 (d, *J* = 24.0 Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.49 (d, *J* = 16.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.02, 169.01, 164.07, 159.80, 139.21, 135.44, 133.94, 132.94, 132.52, 131.98, 131.51, 131.13, 130.69, 130.17, 128.83, 128.29, 103.80, 90.27, 53.95, 51.93, 38.49. HRMS (ESI) calcd. for $C_{21}H_{14}Cl_4NaO_6$ [M+23]: 524.9437, found: 524.9458.

13. Dimethyl2-(3,4-dimethylbenzoyl)-5-(3,4-dimethylphenyl)-2,3-dihydrofuran-2,4-dicarboxylate (**2m**). The title compound was prepared according to the general



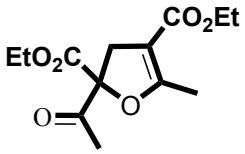
procedure and purified by column chromatography to give a white solid, 86% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.08 (s, 1H), 6.98 (d, *J* = 9.2 Hz, 3H), 4.07 (d, *J* = 16.0 Hz, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 3.47 (d, *J* = 16.0 Hz, 1H), 2.50 (s, 3H), 2.31 (d, *J* = 6.0 Hz, 6H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.81, 169.91, 164.68, 164.42, 143.04, 140.86, 140.19, 137.39, 133.16, 130.95, 130.84, 130.03, 126.35, 126.25, 126.03, 103.88, 91.45, 53.34, 51.25, 37.93, 21.88, 21.50, 19.54. HRMS (ESI) calcd. for $C_{25}H_{26}NaO_6$ [M+23]: 445.1622, found: 445.1619.

14. (5-phenyl-2,3-dihydrofuran-2,2,4-triyl)tris(phenylmethanone) (**2n**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 73% yield.^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 4H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.50 – 7.37 (m, 6H), 7.28 (s, 2H), 7.23 (s,

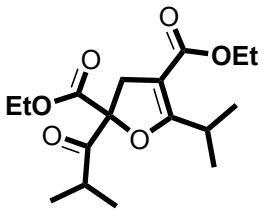


1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.08 (dt, *J* = 15.2, 7.7 Hz, 4H), 4.22 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.03, 192.76, 162.79, 138.47, 134.28, 133.63, 131.90, 130.61, 130.26, 129.78, 129.29, 129.24, 129.15, 129.04, 128.05, 127.99, 111.48, 96.31, 40.06. HRMS (ESI) calcd. for $C_{31}H_{22}NaO_4$ [M+23]: 481.1410 found: 481.1413.

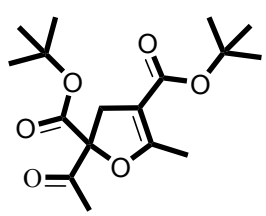
15. Diethyl 2-acetyl-5-methyl-2,3-dihydrofuran-2,4-dicarboxylate (**2o**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (qd, *J* = 7.2, 2.4 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.35 (dd, *J* = 40.0, 16.0 Hz, 2H), 2.29 (d, *J* = 5.6 Hz, 6H), 1.29 (dd, *J* = 17.2, 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.07, 167.80, 165.50, 164.88, 102.43, 92.01, 62.84, 60.07, 35.88, 25.37, 14.47, 14.10, 13.94. HRMS (ESI) calcd. for $C_{13}H_{18}NaO_6$ [M+23]: 293.0996, found: 293.1002.



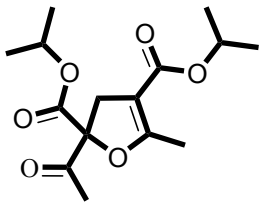
16. Diethyl 2,5-diisopropyl-2,3-dihydrofuran-2,4-dicarboxylate (**2p**). The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (dd, *J* = 12.4, 5.6Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.66 (dt, *J* = 13.6, 6.8 Hz, 1H), 3.37 (d, *J* = 15.6 Hz, 1H), 3.28 (d, *J* = 15.6 Hz, 1H), 3.09 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.28 (dd, *J* = 12.8, 6.4 Hz, 6H), 1.23 – 1.13 (m, 8H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.87 (dd, *J* = 15.2, 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.95, 173.36, 168.30, 164.95, 100.19, 91.79, 62.67, 60.06, 36.79, 36.73, 26.86, 19.73, 19.42, 19.05, 18.96, 14.55, 14.23. HRMS (ESI) calcd. for $C_{17}H_{26}NaO_6$ [M+23]: 349.1622, found: 349.1624.



17. Di-tert-butyl 2-acetyl-5-methyl-2,3-dihydrofuran-2,4-dicarboxylate (**2q**).The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (d, *J* = 16.1 Hz, 1H), 3.13 (d, *J* = 15.4 Hz, 1H), 2.27 (s, 3H), 2.23 (s, 3H), 1.48 (d, *J* = 2.8 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.22, 166.91, 164.48, 164.32, 103.67, 91.94, 84.05, 80.39, 35.76, 28.45, 27.89, 25.38, 13.92. HRMS (ESI) calcd. for $C_{17}H_{26}NaO_6$ [M+23]: 349.1622, found: 349.1615.

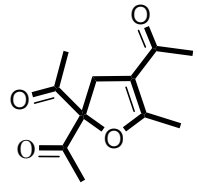


18. Diisopropyl 2-acetyl-5-methyl-2,3-dihydrofuran-2,4-dicarboxylate (**2r**). The



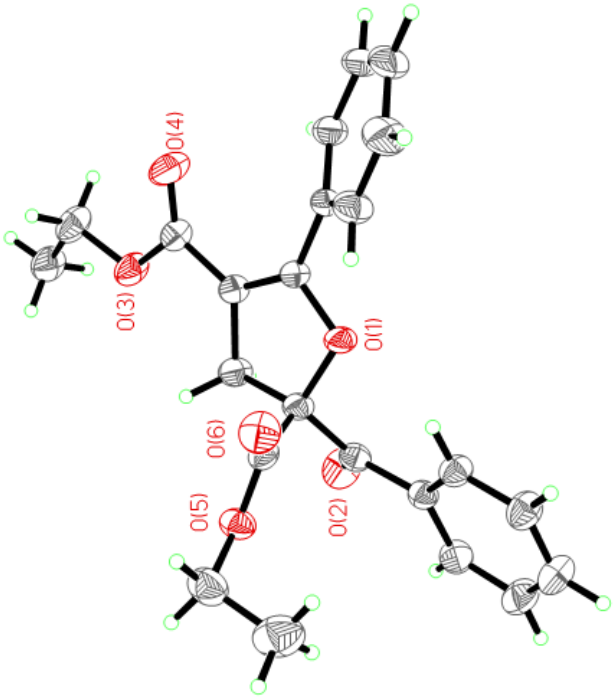
title compound was prepared according to the general procedure and purified by column chromatography to give a white solid, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (ddt, *J* = 27.2, 12.4, 6.2 Hz, 2H), 3.39 (d, *J* = 15.6 Hz, 1H), 3.23 (d, J = 15.6 Hz, 1H), 2.28 (d, *J* = 5.2 Hz, 6H), 1.27 (dd, *J* = 10.4, 6.2 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.94, 167.36, 165.17, 164.50, 102.70, 91.93, 70.86, 67.42, 35.72, 25.34, 22.14, 21.58, 13.93. HRMS (ESI) calcd. for $C_{15}H_{22}NaO_6$ [M+23]: 321.1309, found: 321.1311.

19. 1,1',1''-(5-methyl-2,3-dihydrofuran-2,2,4-triyl)tris(ethan-1-one) (**2s**). The title compound was prepared according to the general procedure and purified by column

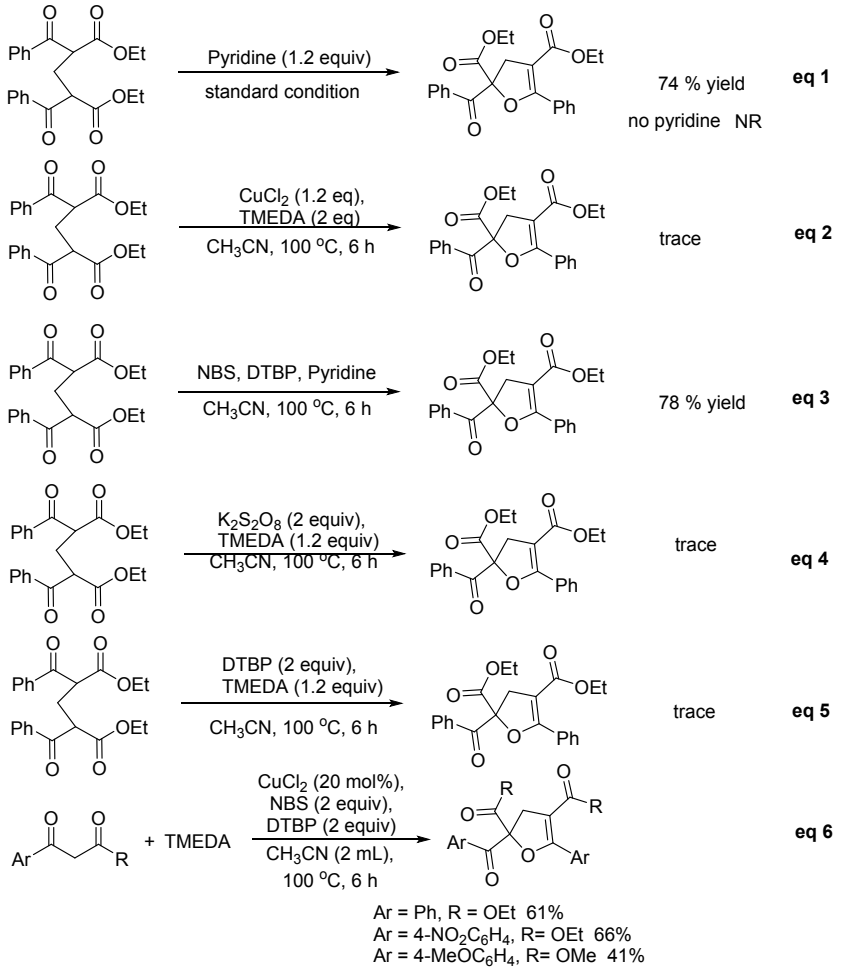


chromatography to give a white solid, 27% yield. ^{1}H NMR (400 MHz, CDCl3) δ 3.33 (s, 2H), 2.27 (t, *J* = 25.2 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.66, 193.71, 164.88, 111.50, 109.99, 97.81, 36.07, 29.58, 25.47, 14.6. HRMS (ESI) calcd. for $C_{11}H_{14}NaO_4$ [M+23]: 233.0784, found: 233.0797.

The X-ray of 2a

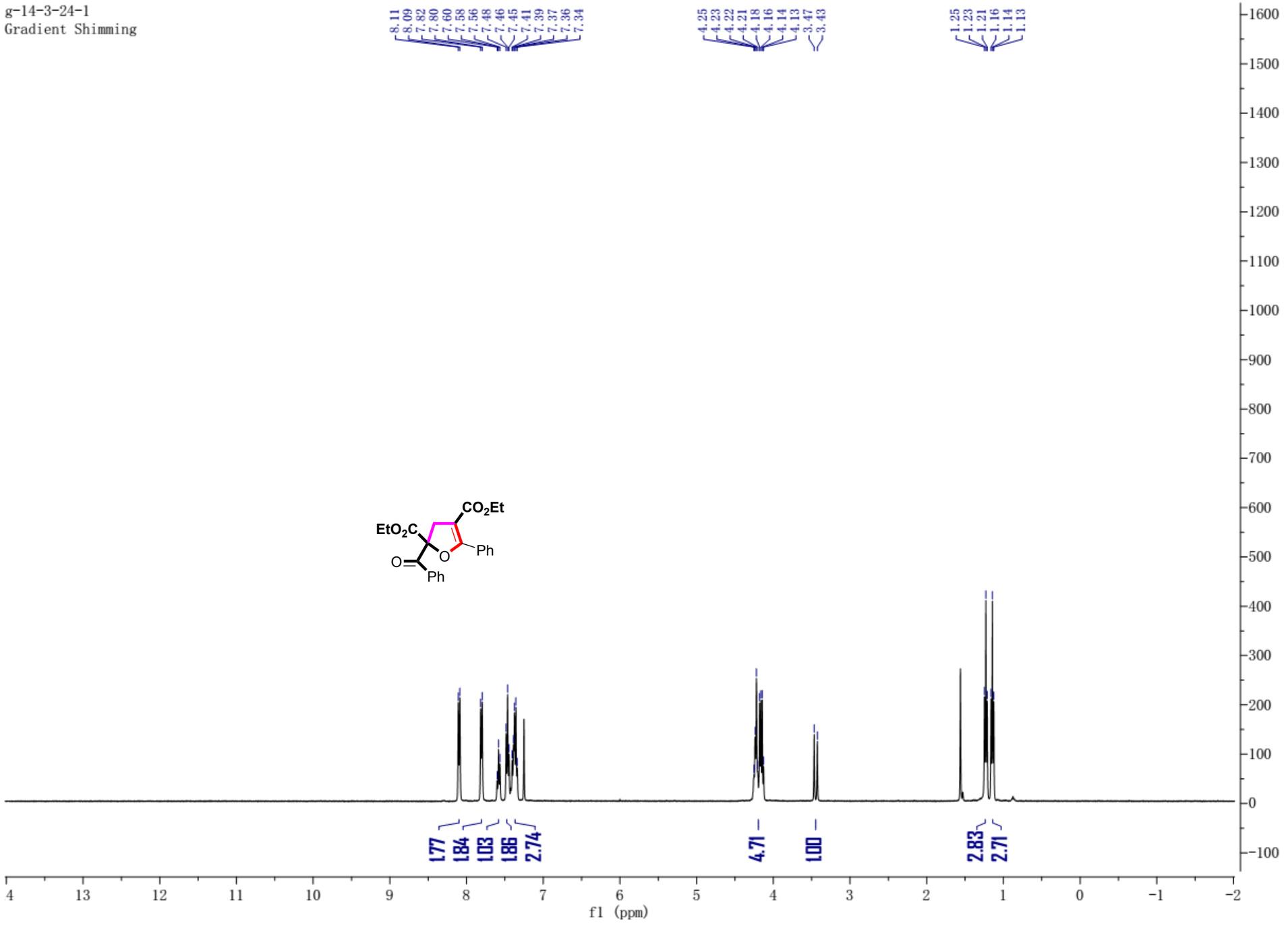


To study the reaction probably mechanism, we first employed methylene-bridged bis-1,3-dicarbonyl compounds as starting material, pyridine (2 equiv) instead of TMEDA was used under optical conditions, which afforded the target product in 74% yield (**eq 1**). $CuCl_2$ was used as promoter in the reaction without DTBP, we found there was trace of product exited (**eq 2**). When methylene-bridged bis-1,3-dicarbonyl compounds was used as starting material, NBS (2 eq) was used as halogen reagent in oxidant condition and pyridine as base, we found the reaction could also perform, which means the reaction might undergo a halogenation procedure (**eq 3**). In order to confirm the reaction undergo a carbocation process, the oxidant such $K_2S_2O_8$ and DTBP were used to oxidize the methylene-bridged bis-1,3-dicarbonyl compounds (**eq 4** and **5**). When $CuCl_2$ (20 mol %) instead stoichiometry copper, and NBS as additive were used, the reaction could carry on with middle yields (**eq 6**).

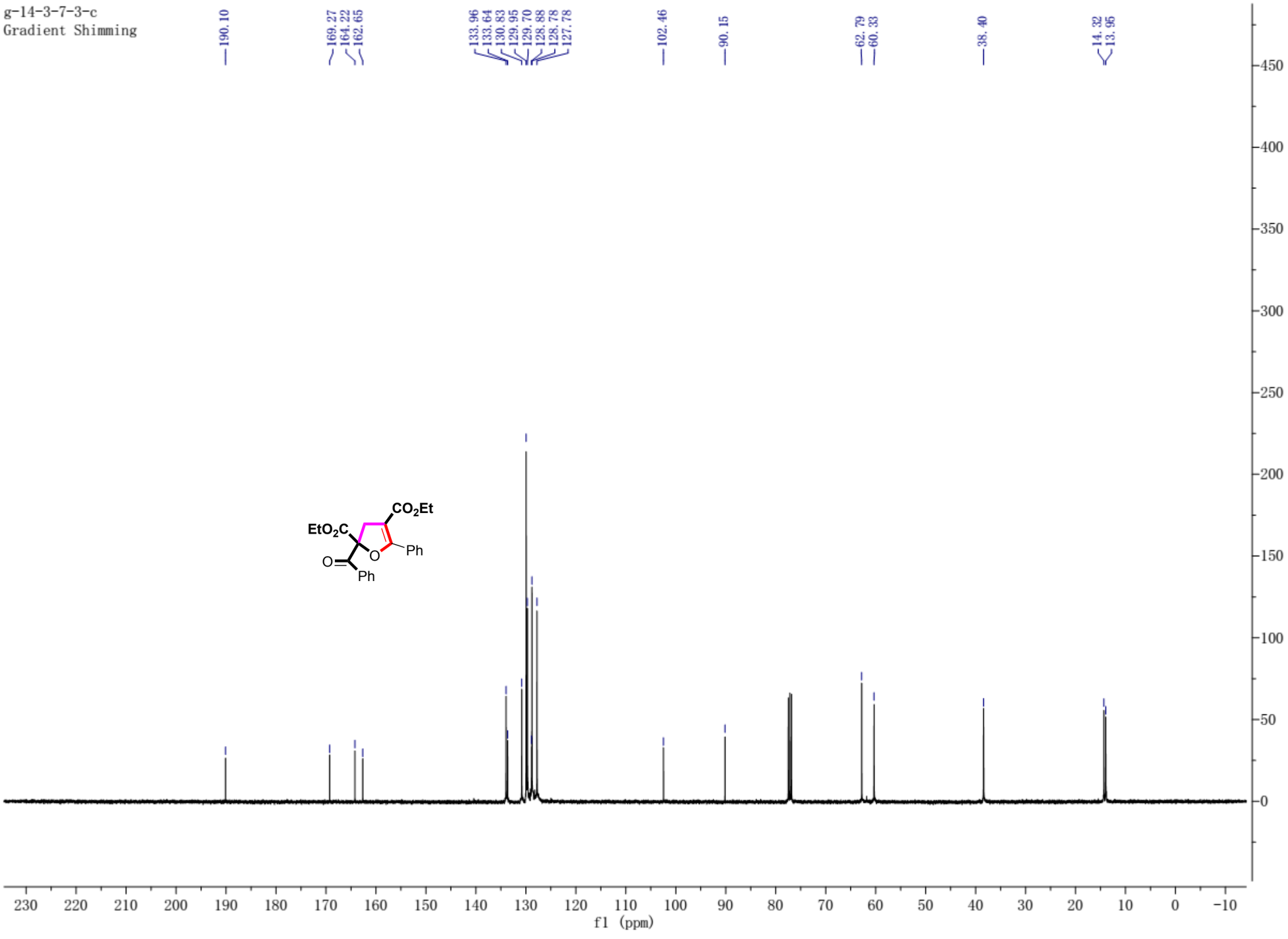


Copies of product ^{1}H NMR and ^{13}C NMR

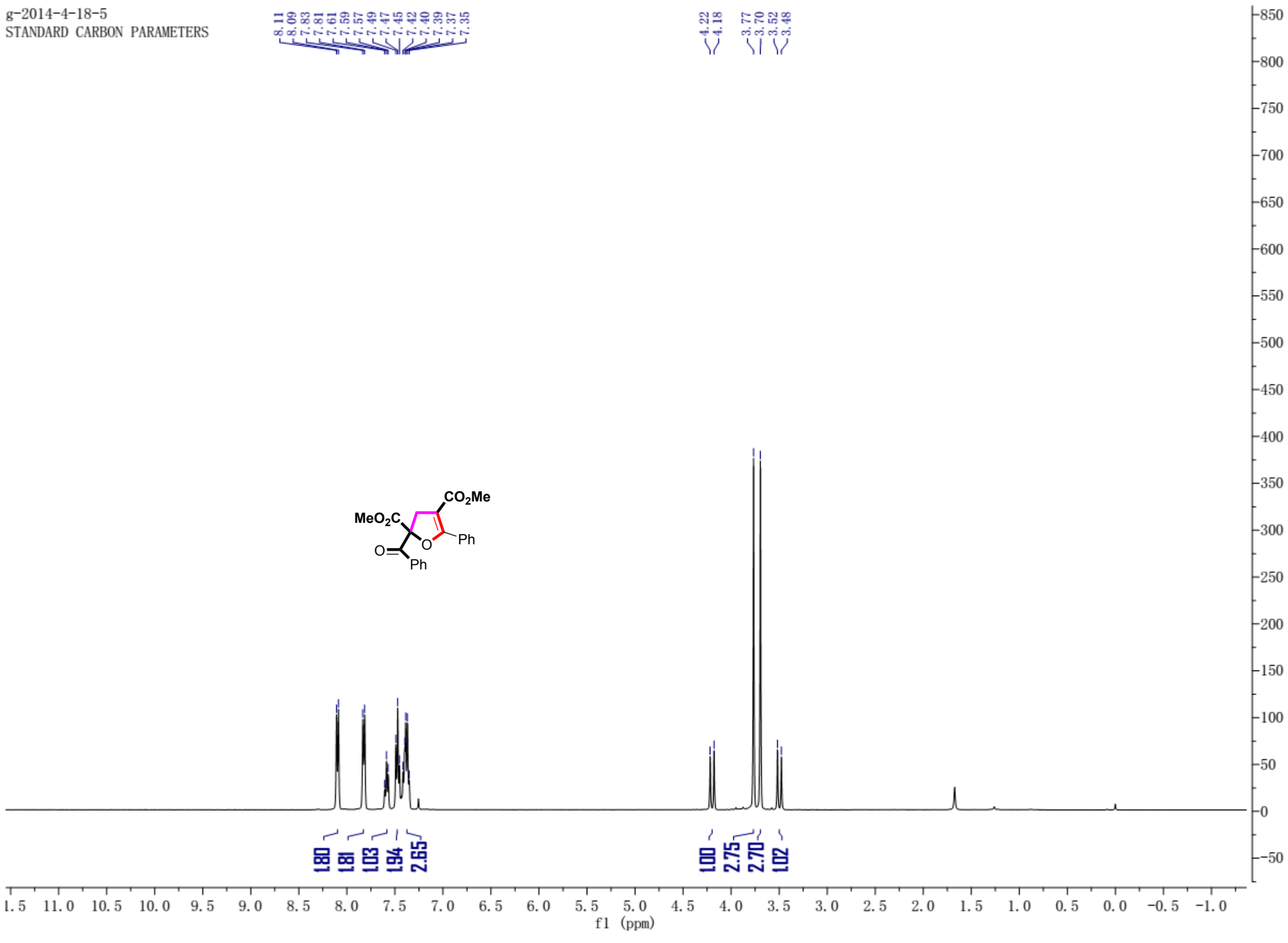
g-14-3-24-1
Gradient Shimming



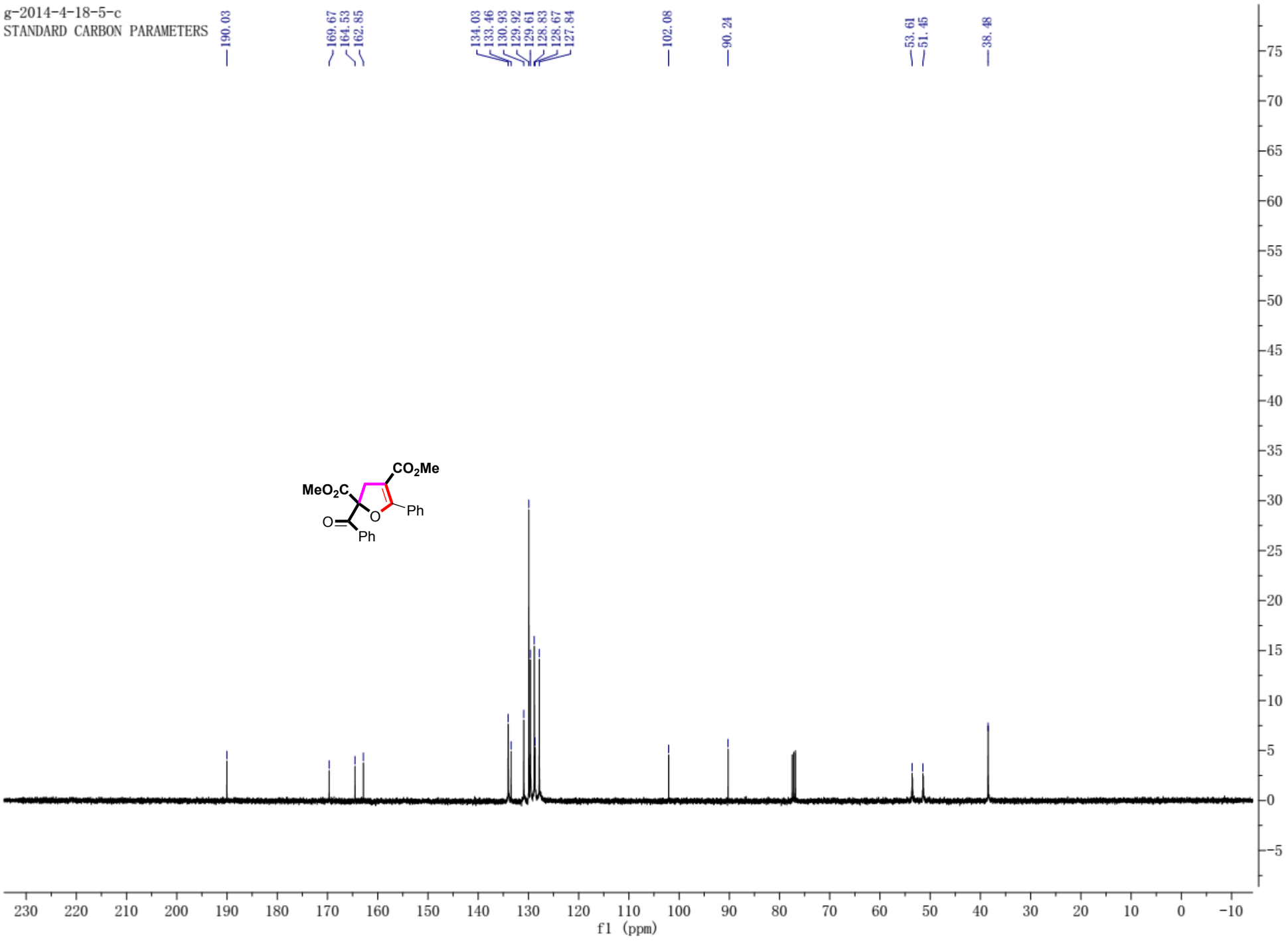
g-14-3-7-3-c
Gradient Shimming



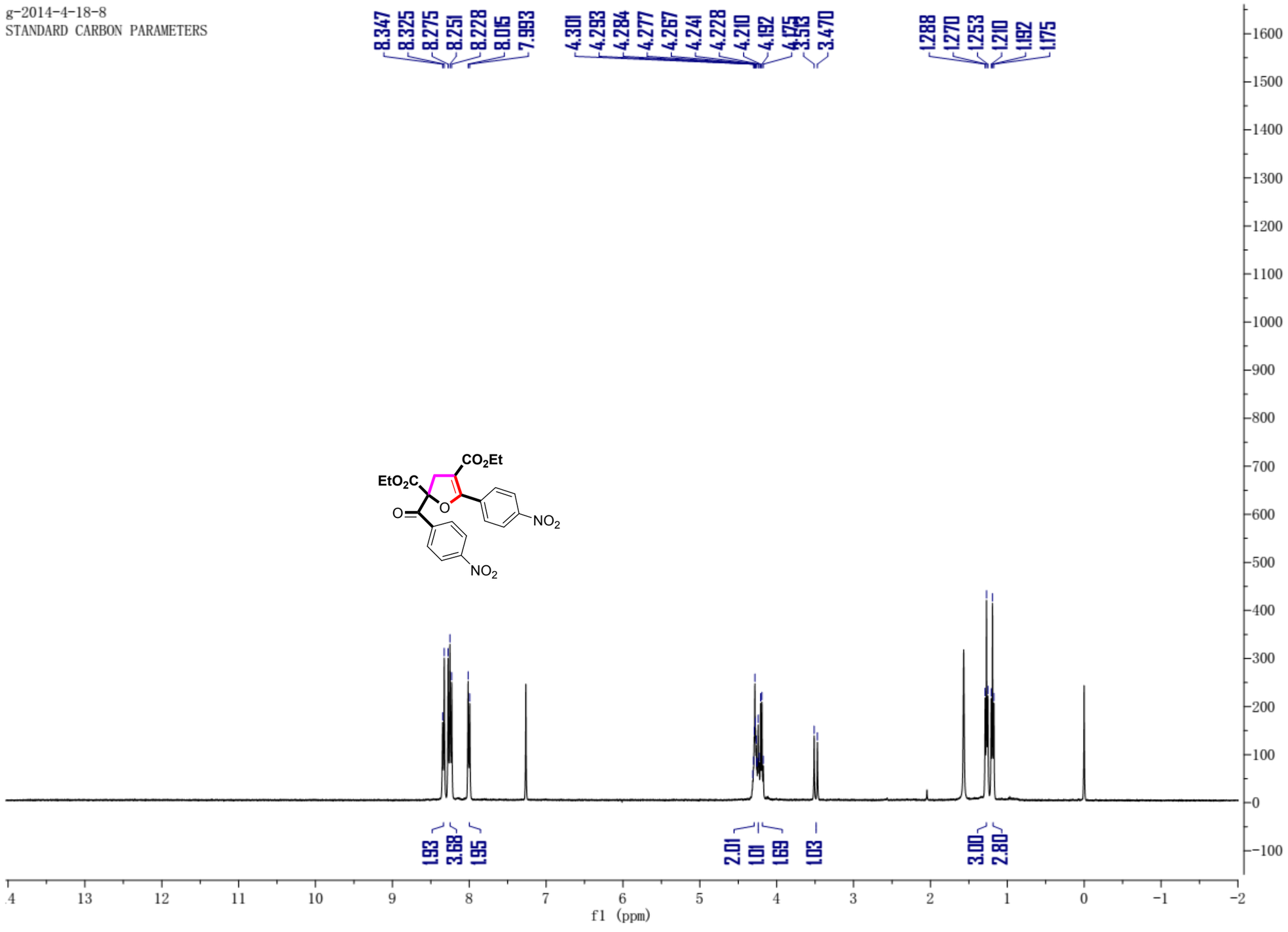
g-2014-4-18-5
STANDARD CARBON PARAMETERS



g-2014-4-18-5-c
STANDARD CARBON PARAMETERS

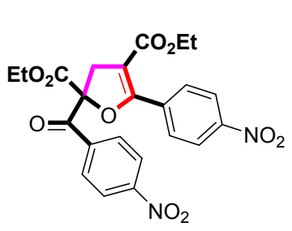


g-2014-4-18-8
STANDARD CARBON PARAMETERS



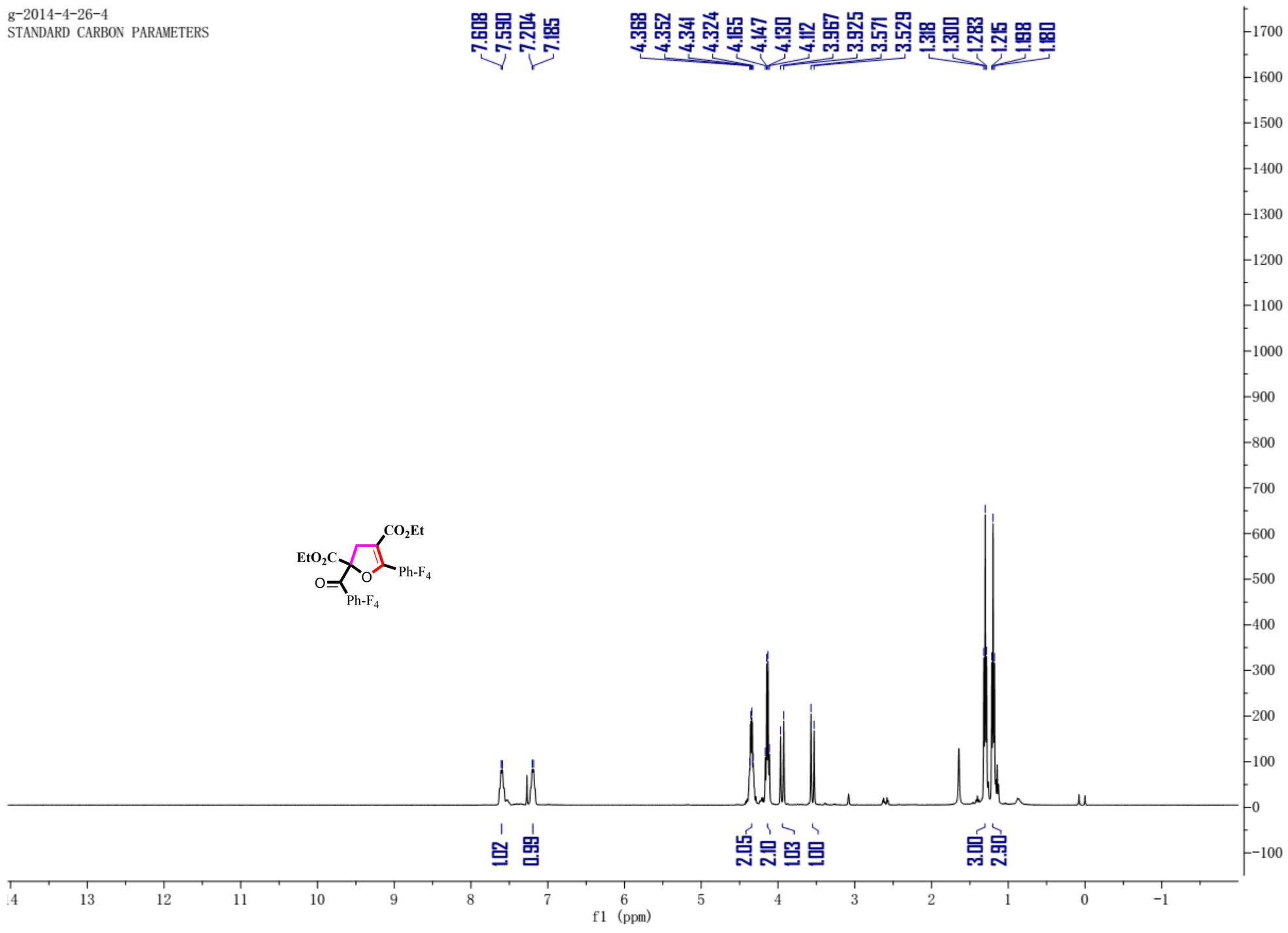
g-2014-4-18-8-c
STANDARD CARBON PARAMETERS

188.46
168.39
163.37
159.49
150.88
149.00
137.99
134.48
131.01
130.73
124.05
123.13
105.70
90.29
63.51
61.02
38.52
14.31
14.03



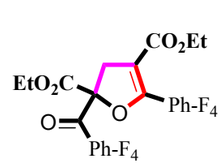
f1 (ppm)

g-2014-4-26-4
STANDARD CARBON PARAMETERS



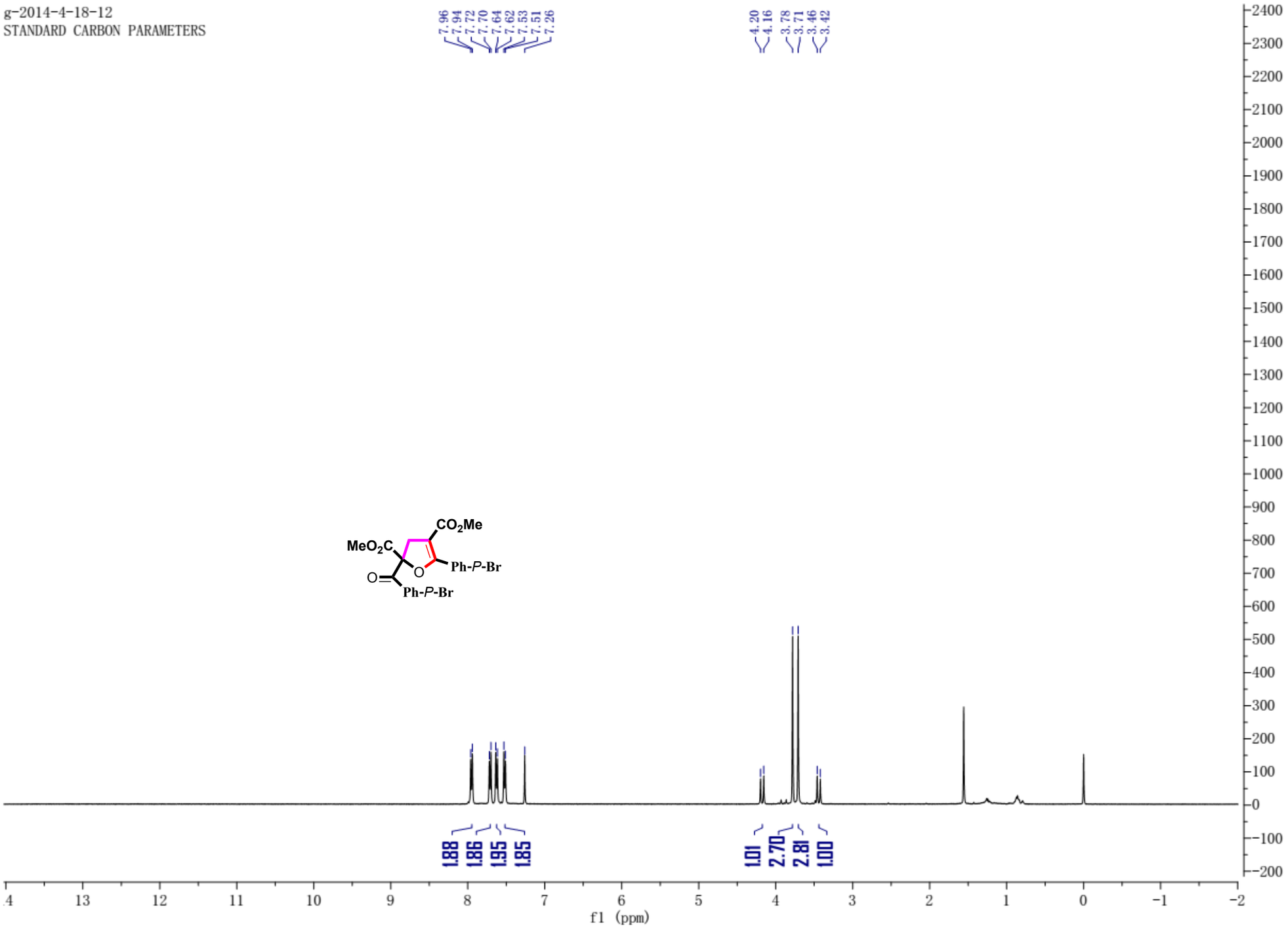
g-2014-4-26-4-c
STANDARD CARBON PARAMETERS

187.39
186.85
166.86
162.75
154.17
148.59
148.00
146.07
145.45
142.95
142.40
140.83
139.71
112.60
107.49
91.62
62.88
60.90
38.12
14.06



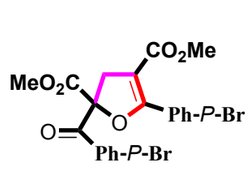
f1 (ppm)

g-2014-4-18-12
STANDARD CARBON PARAMETERS



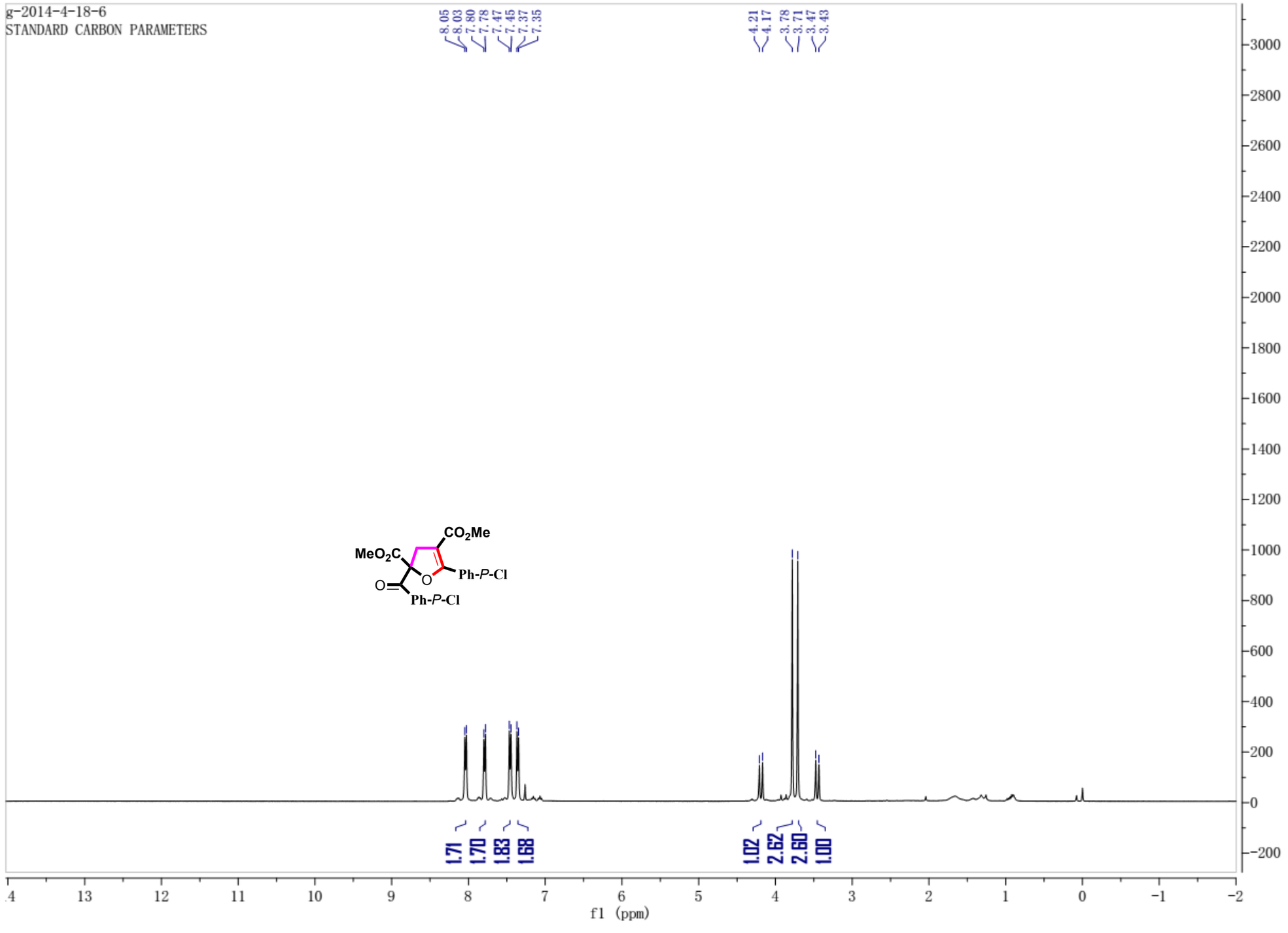
g-2014-4-18-12-c
STANDARD CARBON PARAMETERS

188.99
169.44
164.33
161.55
132.32
132.15
131.44
131.27
131.17
129.75
127.43
125.64
102.81
90.20
53.78
51.67
38.46

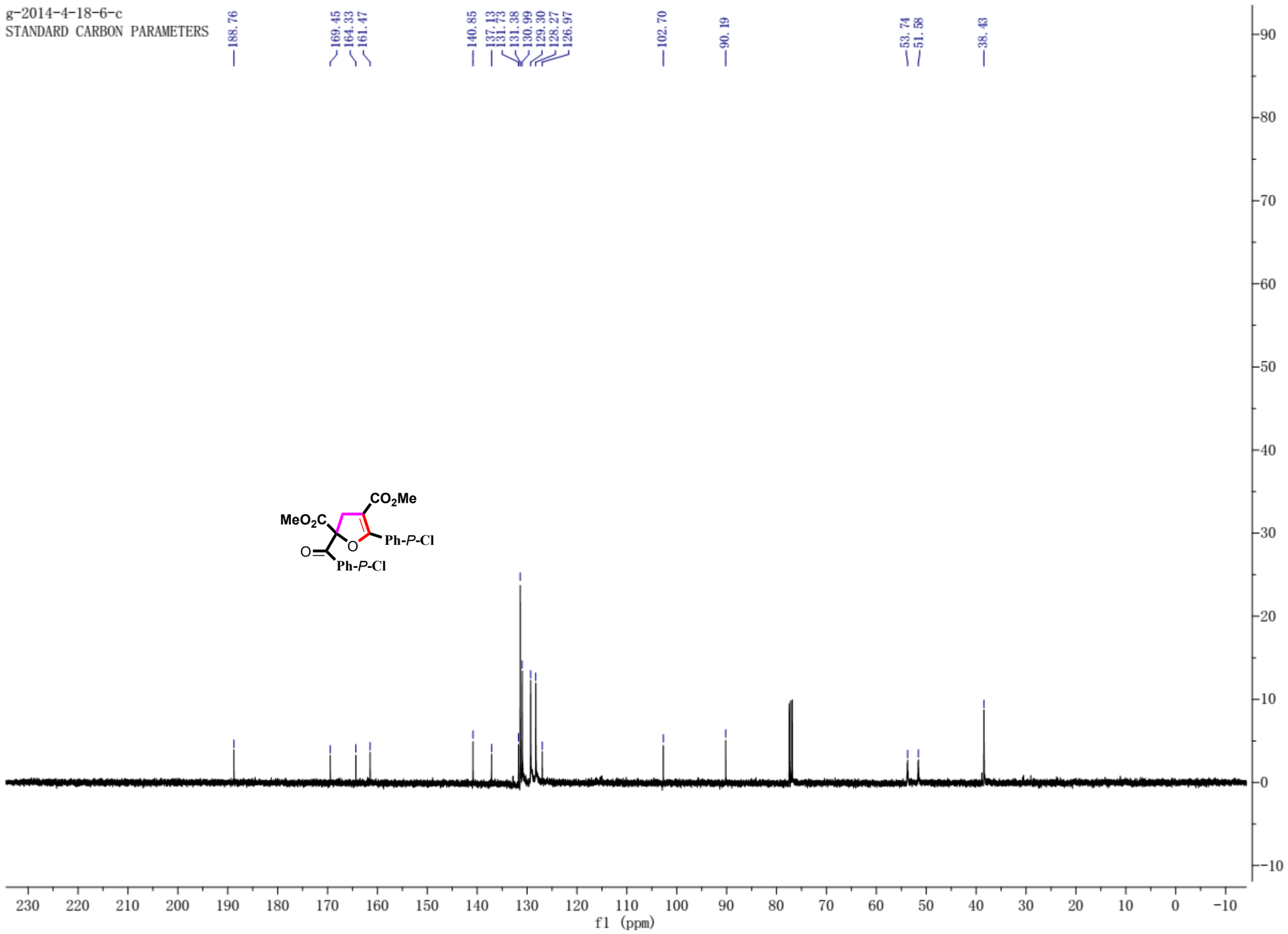


f1 (ppm)

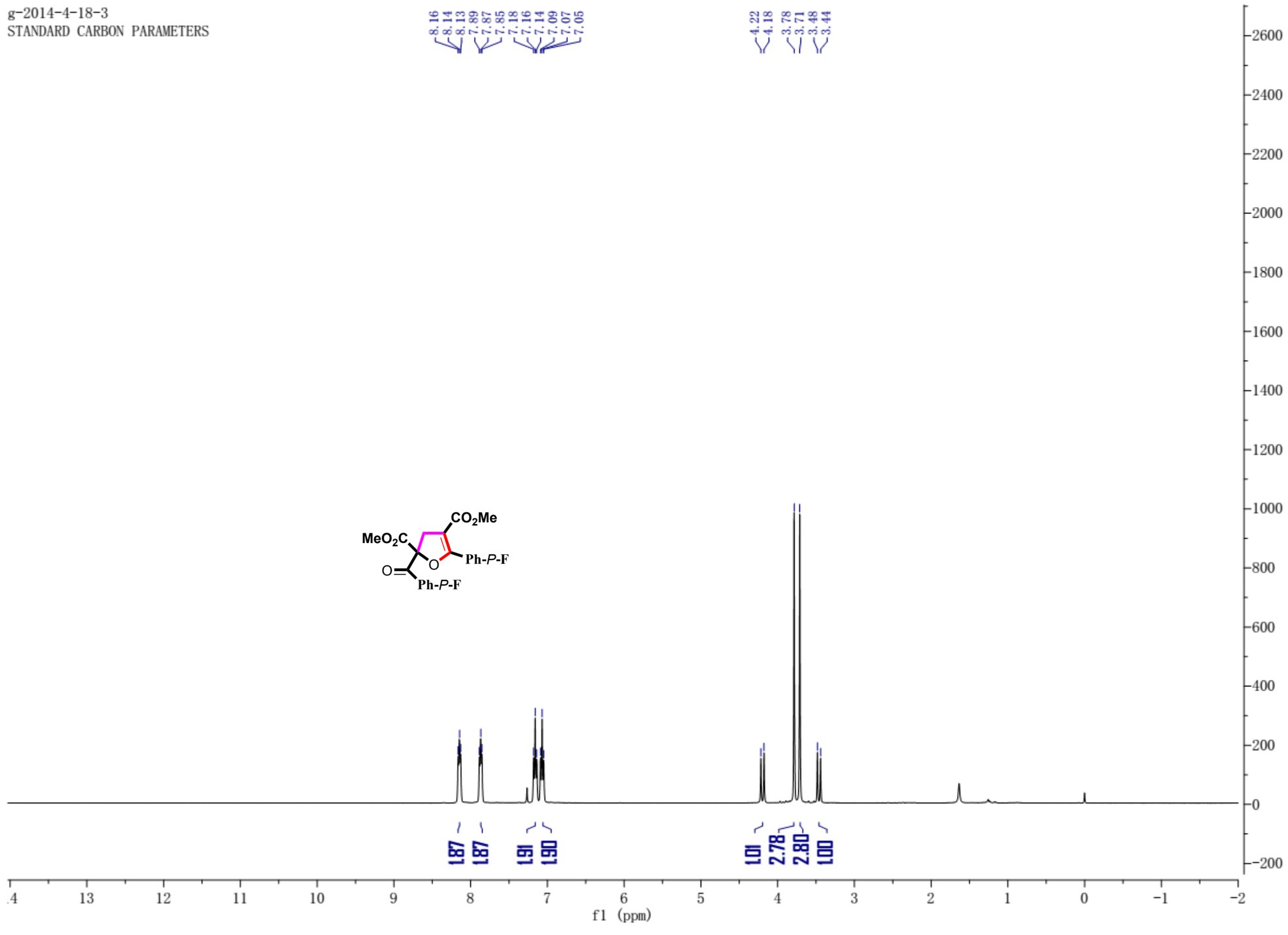
g-2014-4-18-6
STANDARD CARBON PARAMETERS



g-2014-4-18-6-c
STANDARD CARBON PARAMETERS

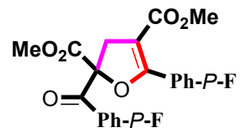


g-2014-4-18-3
STANDARD CARBON PARAMETERS

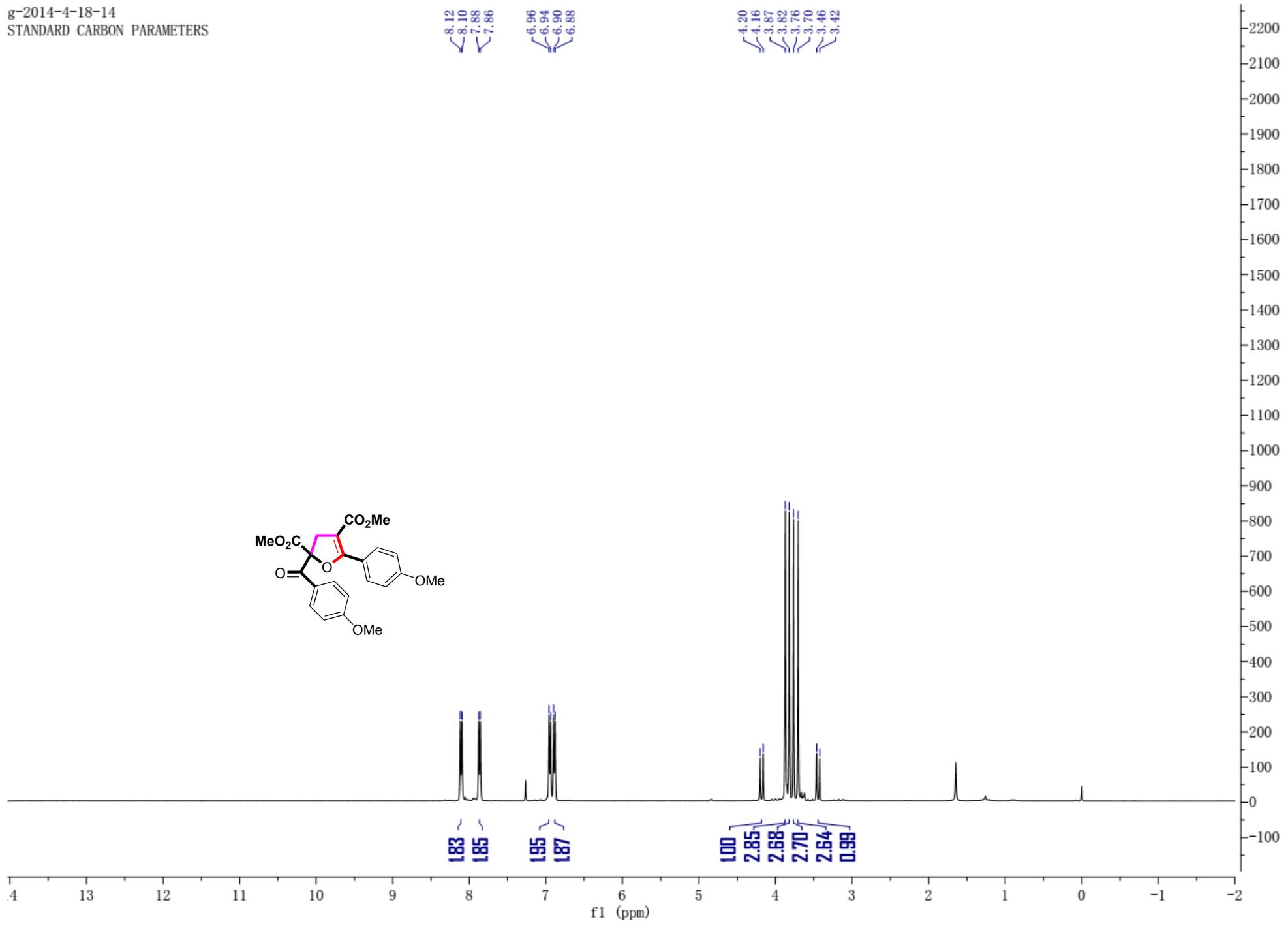


g-2014-4-18-3-c
STANDARD CARBON PARAMETERS

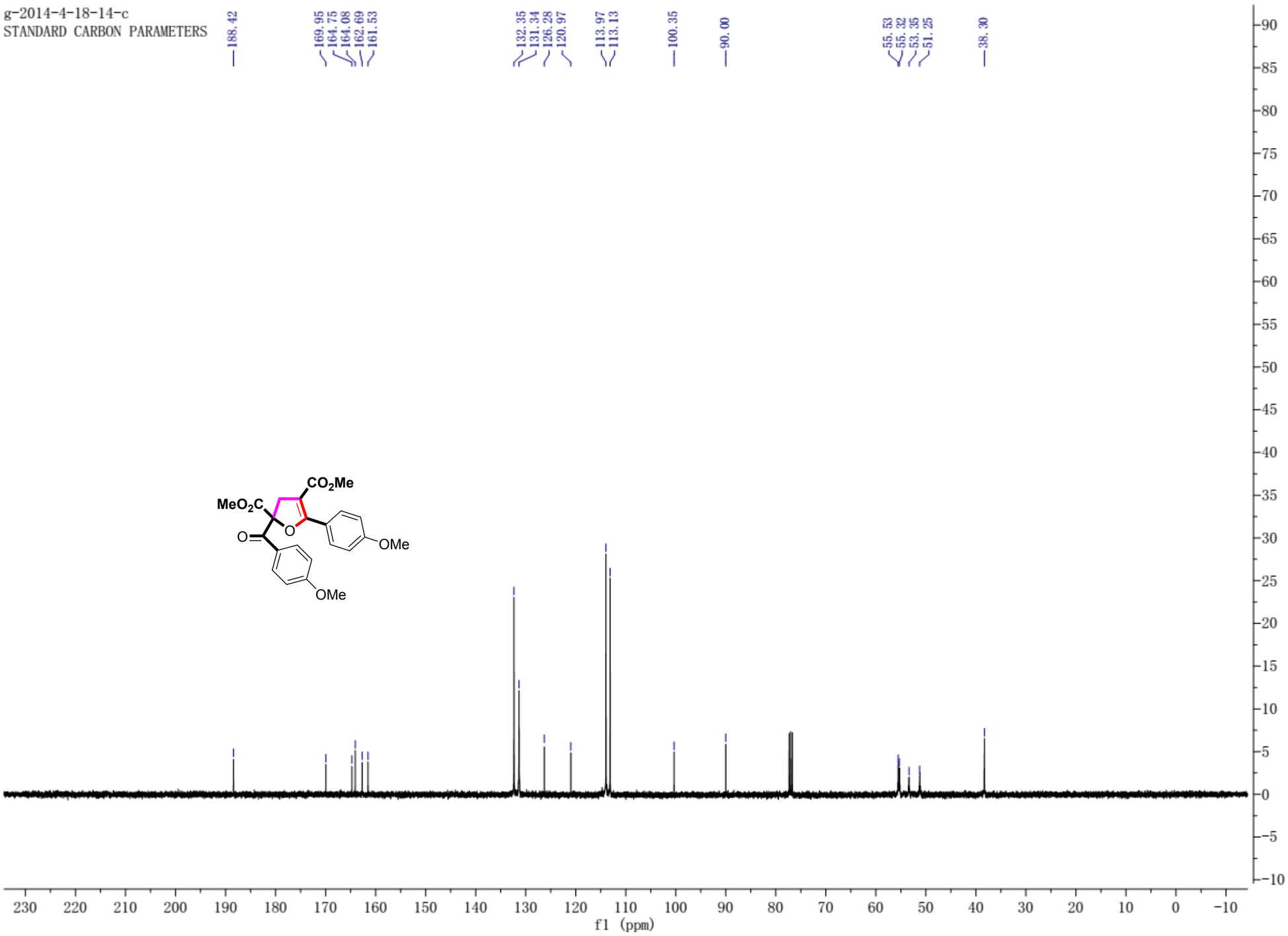
188.40
169.60
167.58
165.47
165.02
164.47
162.97
161.69
132.88
131.99
129.85
124.69
116.07
114.99
102.08
90.20
53.69
51.52
38.41



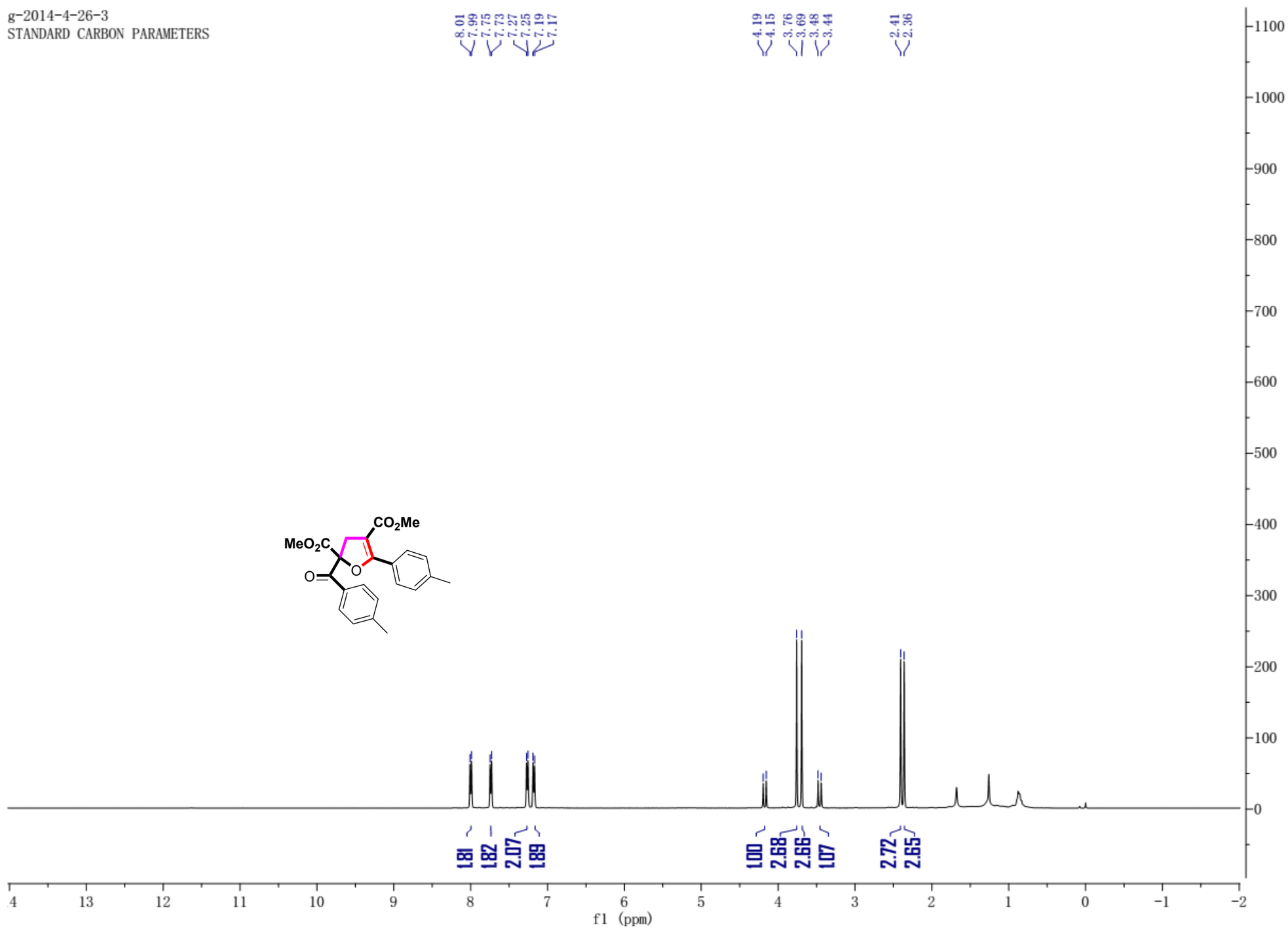
g-2014-4-18-14
STANDARD CARBON PARAMETERS



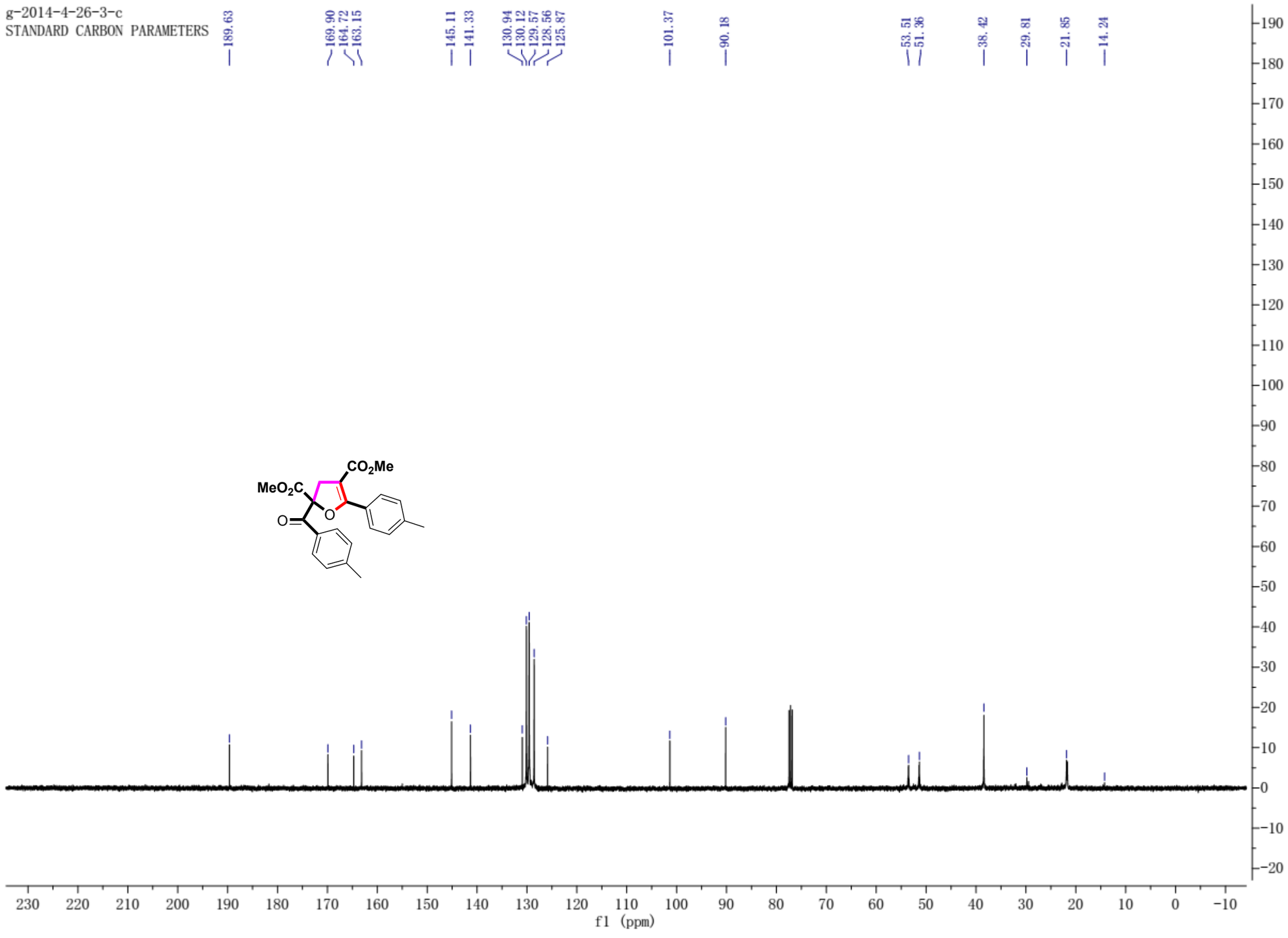
g-2014-4-18-14-c
STANDARD CARBON PARAMETERS



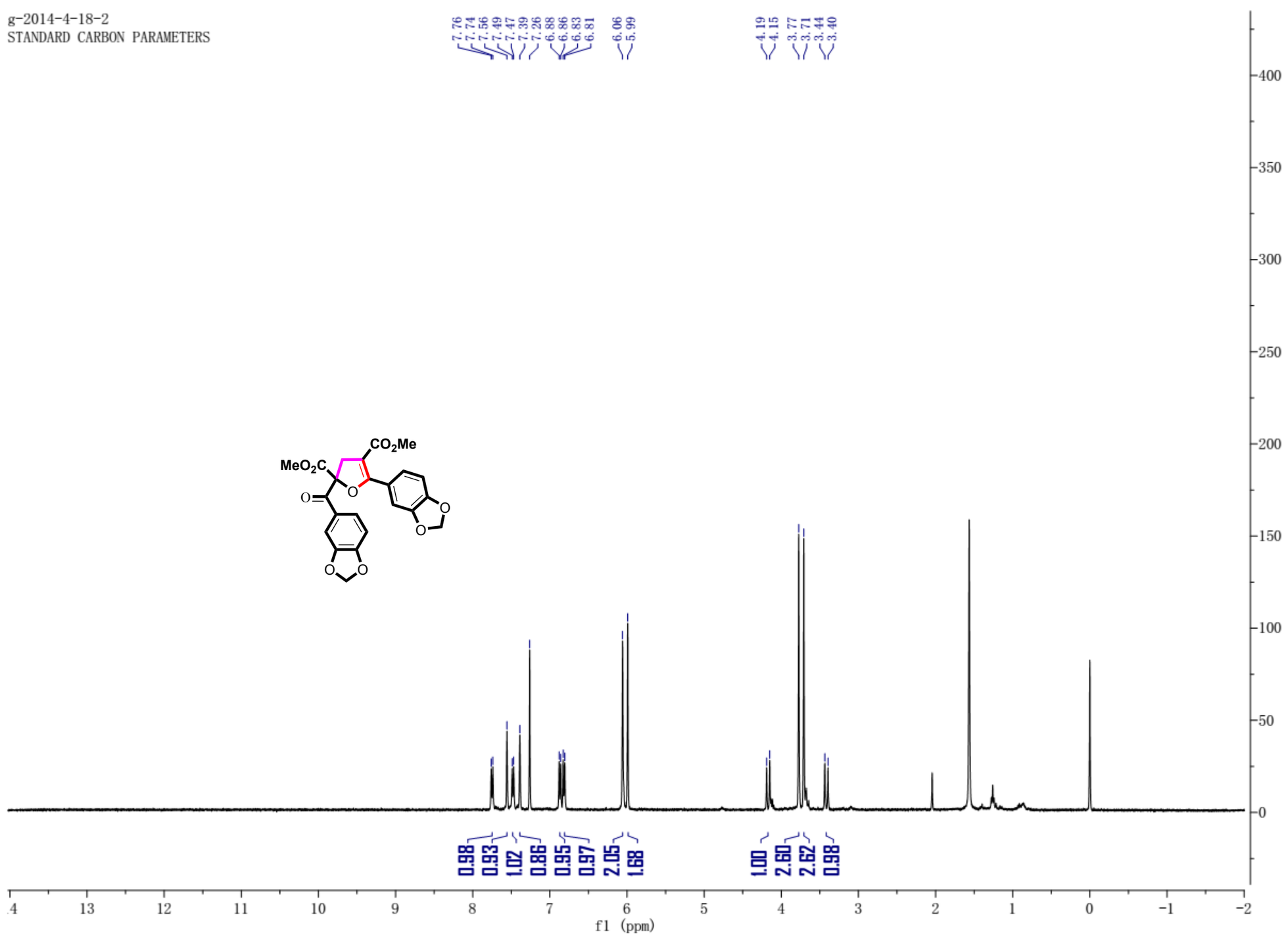
g-2014-4-26-3
STANDARD CARBON PARAMETERS



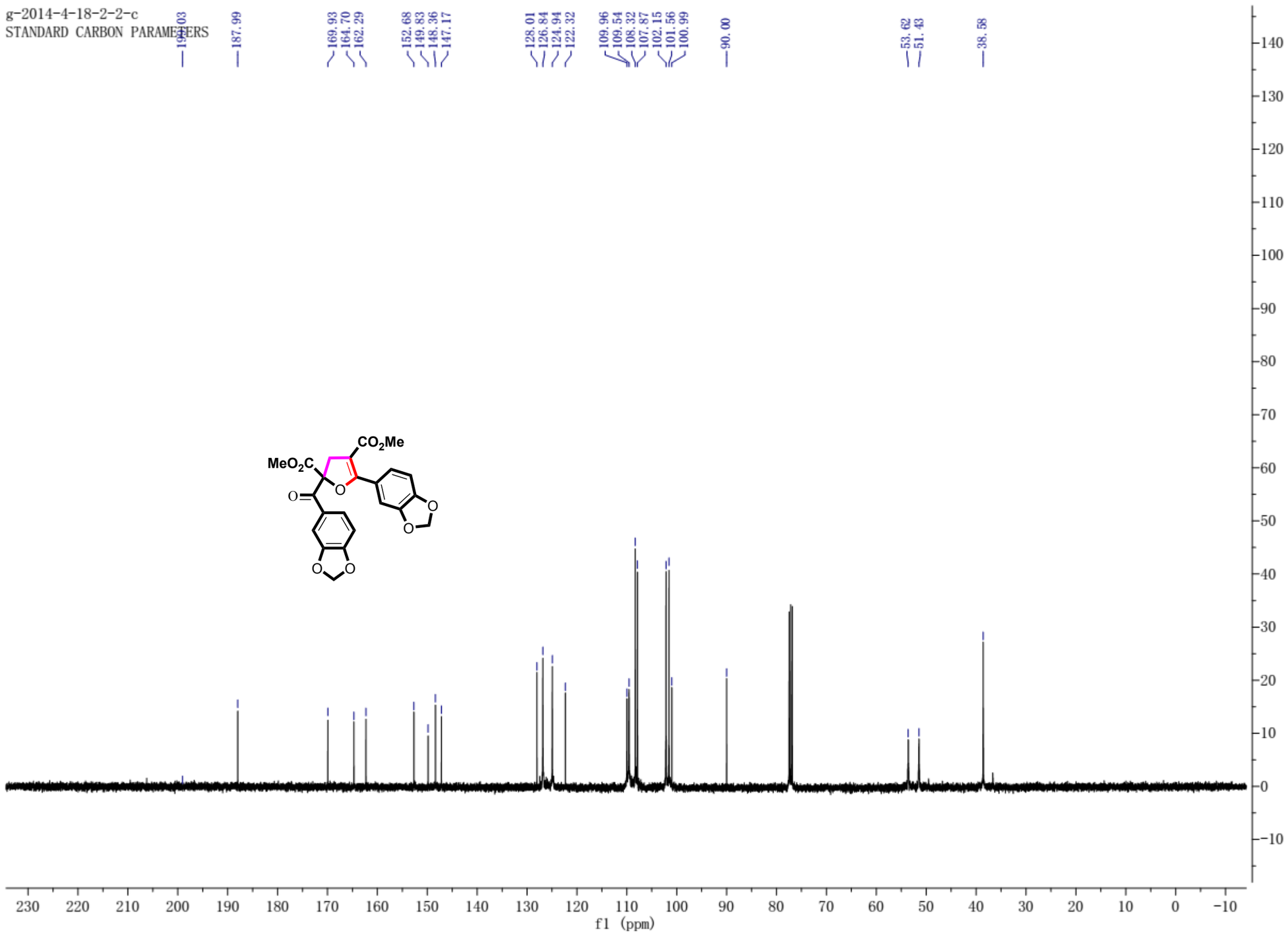
g-2014-4-26-3-c
STANDARD CARBON PARAMETERS



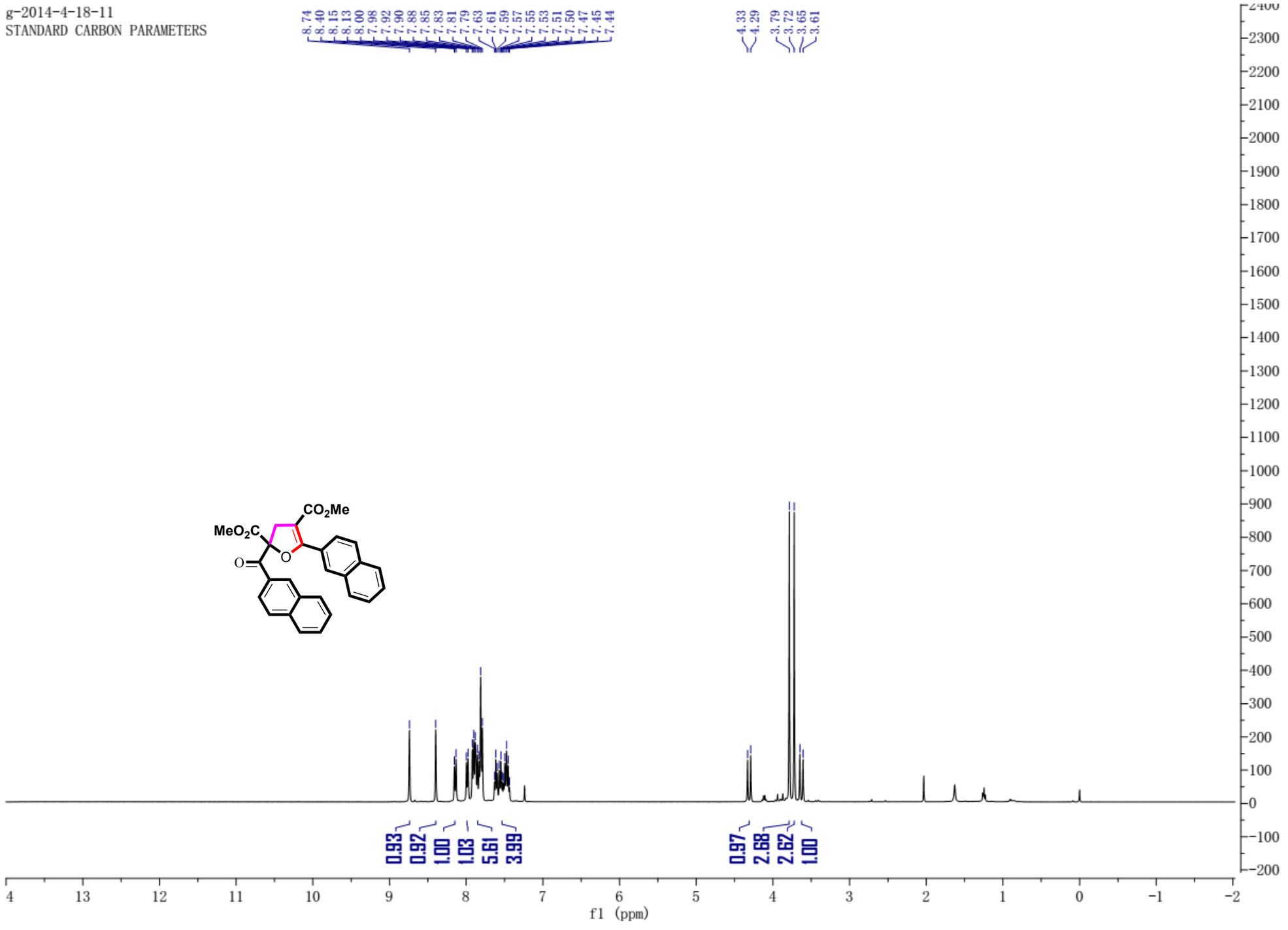
g-2014-4-18-2
STANDARD CARBON PARAMETERS



g-2014-4-18-2-2-c
STANDARD CARBON PARAMETERS



g-2014-4-18-11
STANDARD CARBON PARAMETERS



g-2014-4-18-11-c
STANDARD CARBON PARAMETERS

190.19
169.82
164.63
162.91
135.96
134.44
132.53
132.47
132.40
130.81
130.38
130.18
129.27
129.04
128.71
127.86
127.70
127.59
127.38
127.07
126.42
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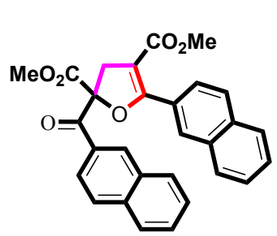
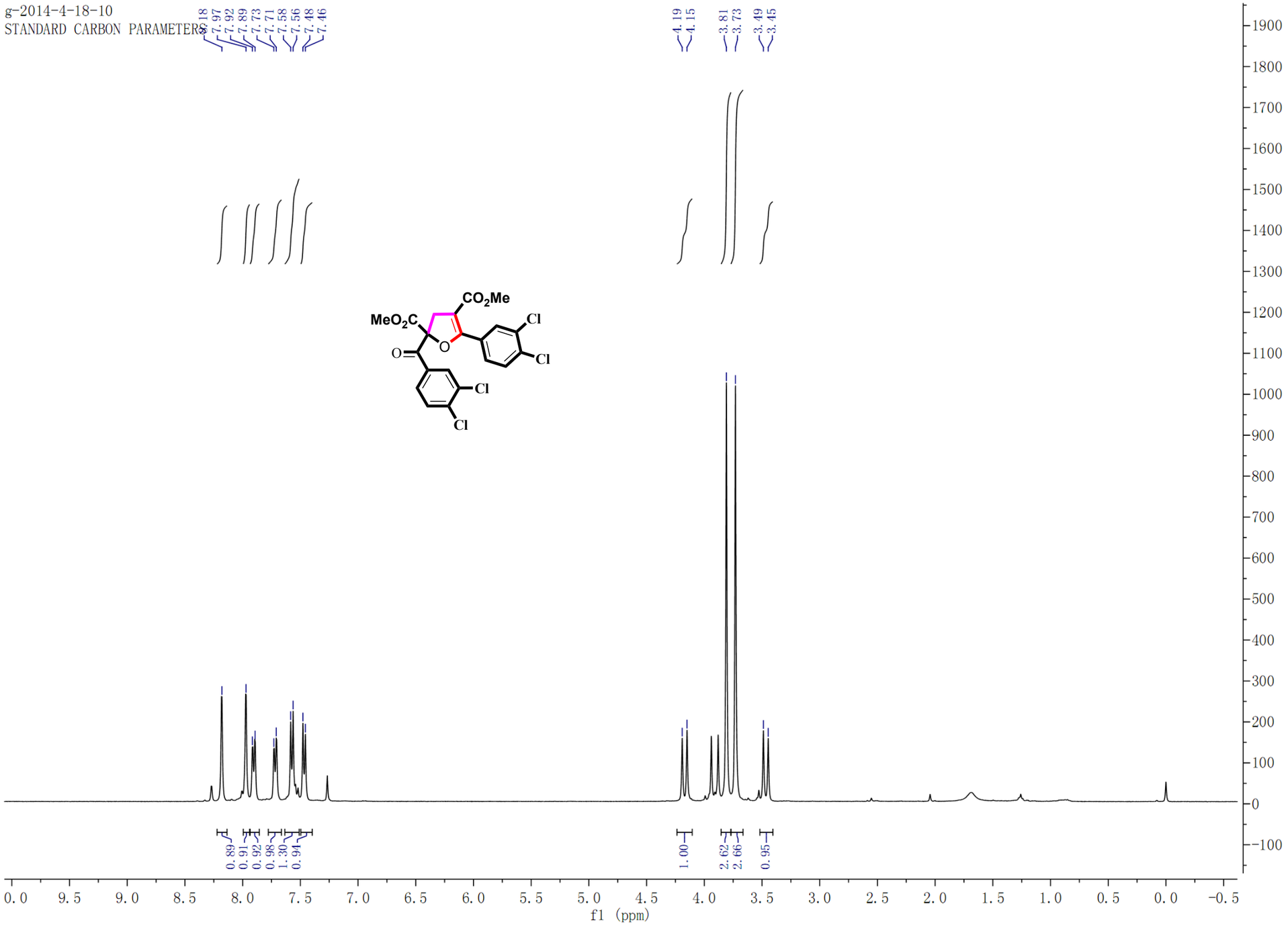
125.00
102.45
90.59
53.65
51.54
38.80

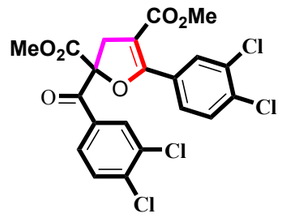


g-2014-4-18-10
STANDARD CARBON PARAMETERS



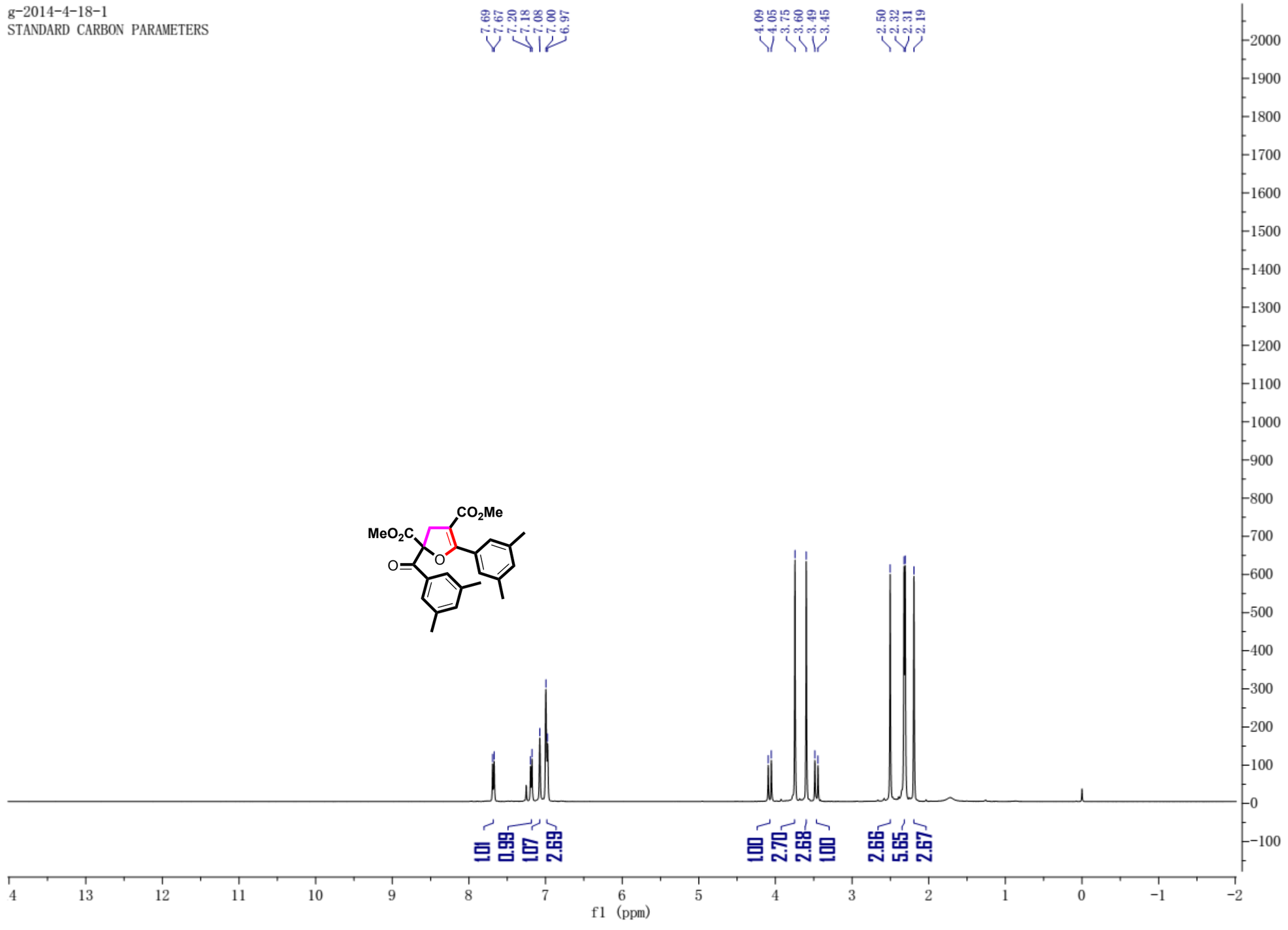
g-2014-4-18-10-c
STANDARD CARBON PARAMETERS

188.0
169.0
164.1
159.8
139.2
135.4
133.9
132.9
132.5
132.0
131.5
131.1
130.7
130.2
128.8
128.3
103.8
90.3
54.0
51.9
38.5

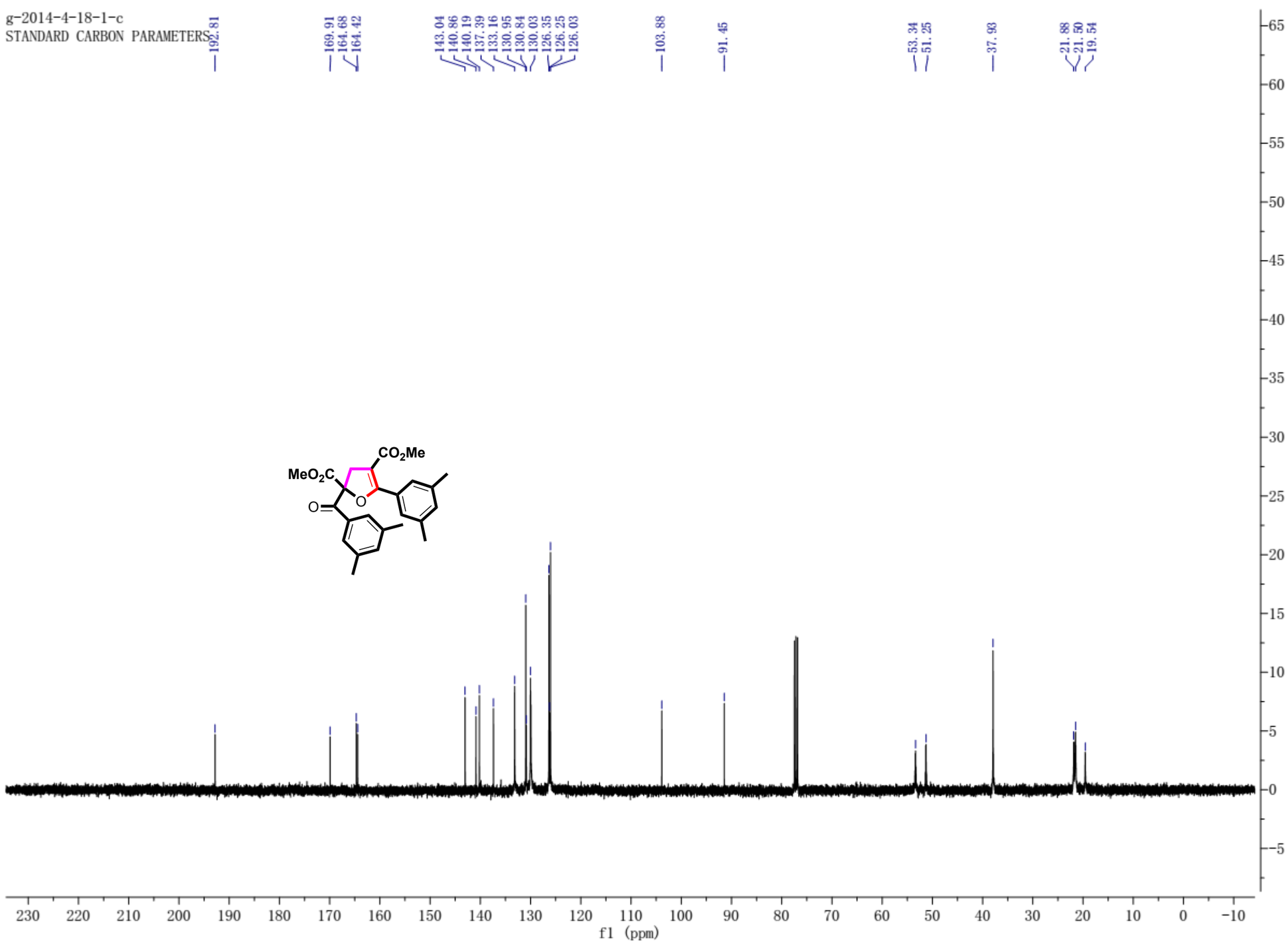


f1 (ppm)

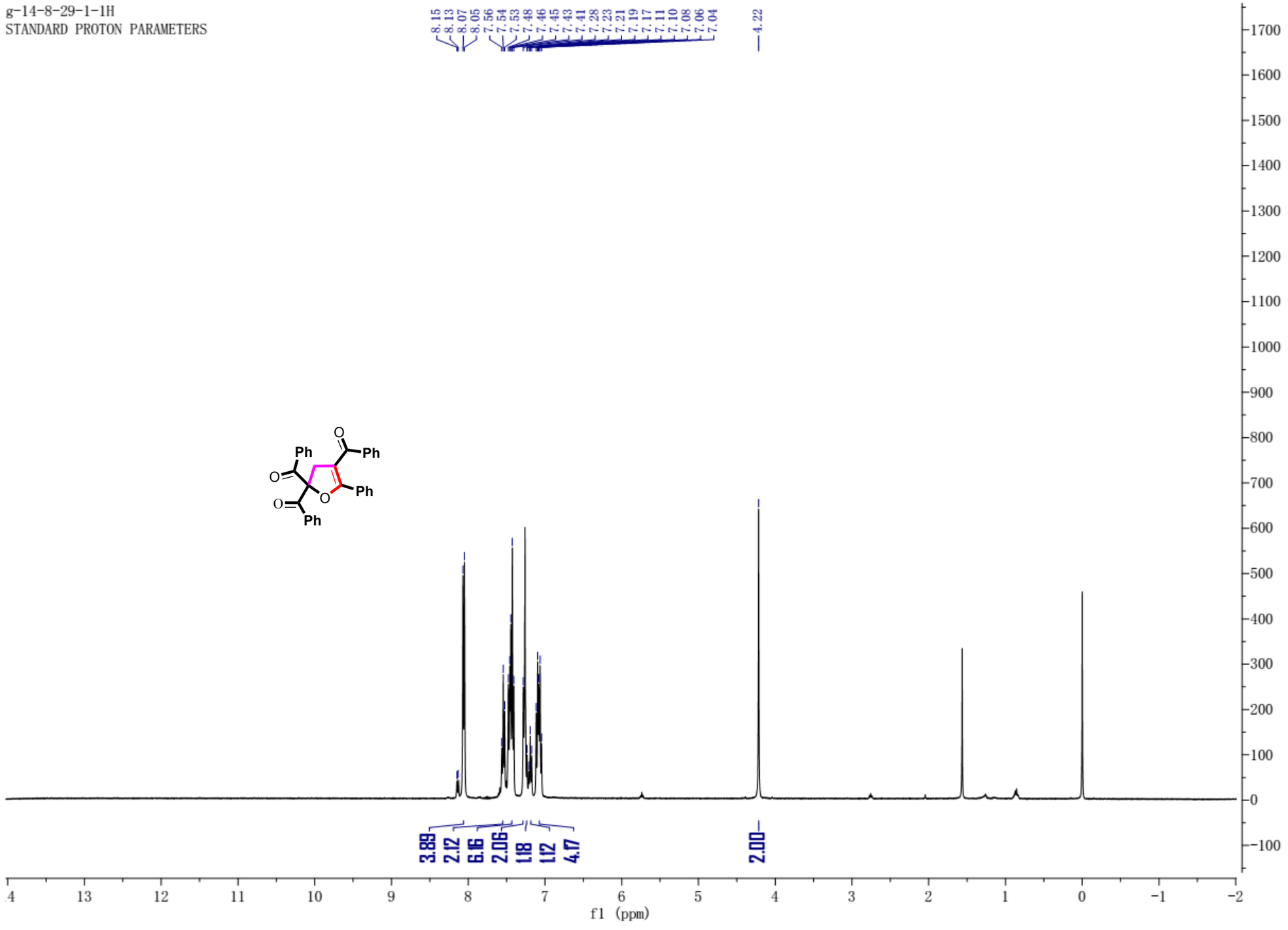
g-2014-4-18-1
STANDARD CARBON PARAMETERS



g-2014-4-18-1-c
STANDARD CARBON PARAMETERS



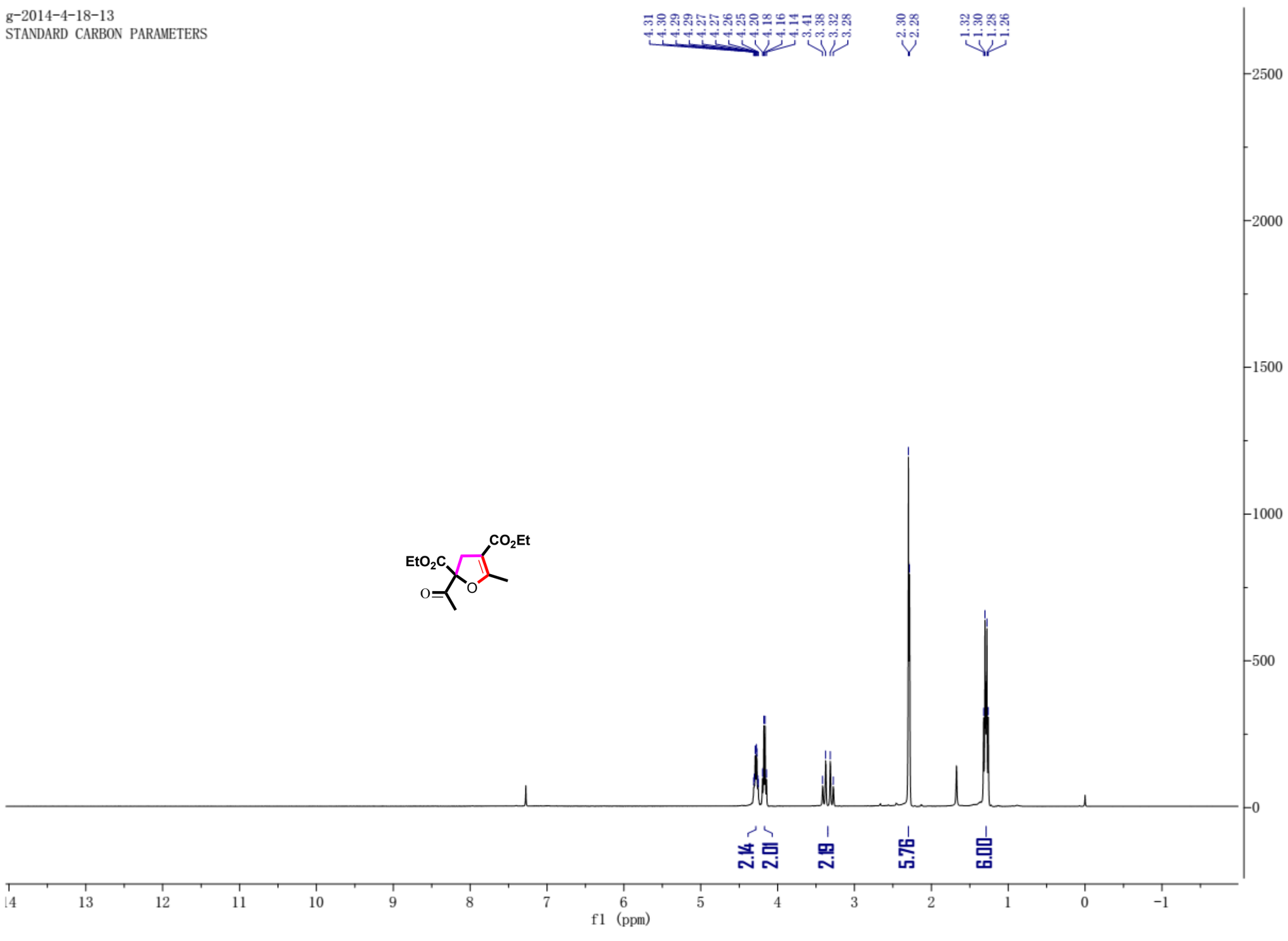
g-14-8-29-1-1H
STANDARD PROTON PARAMETERS



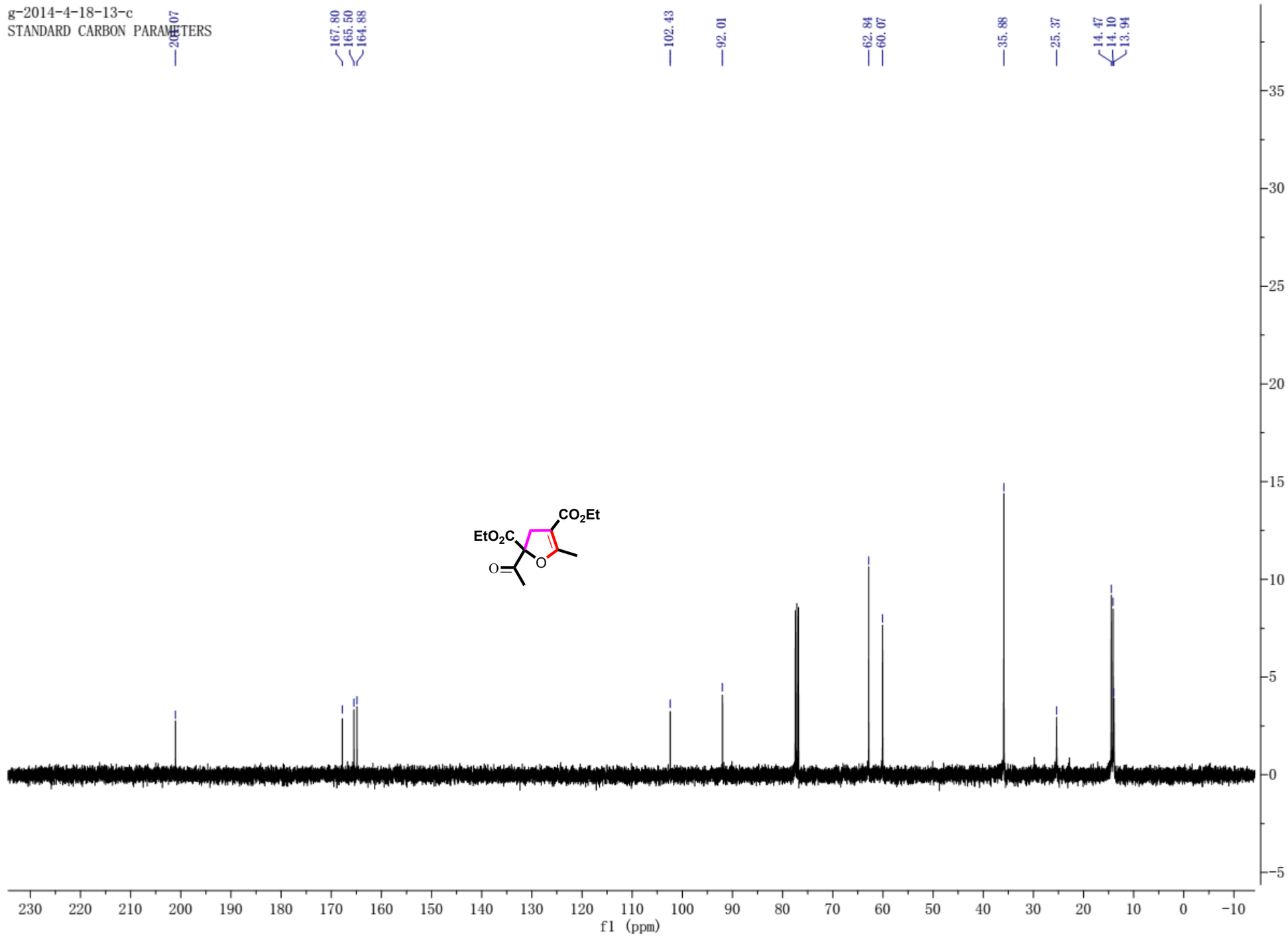
g-14-8-29-1-13C
STANDARD PROTON PARAMETER

f1 (ppm)

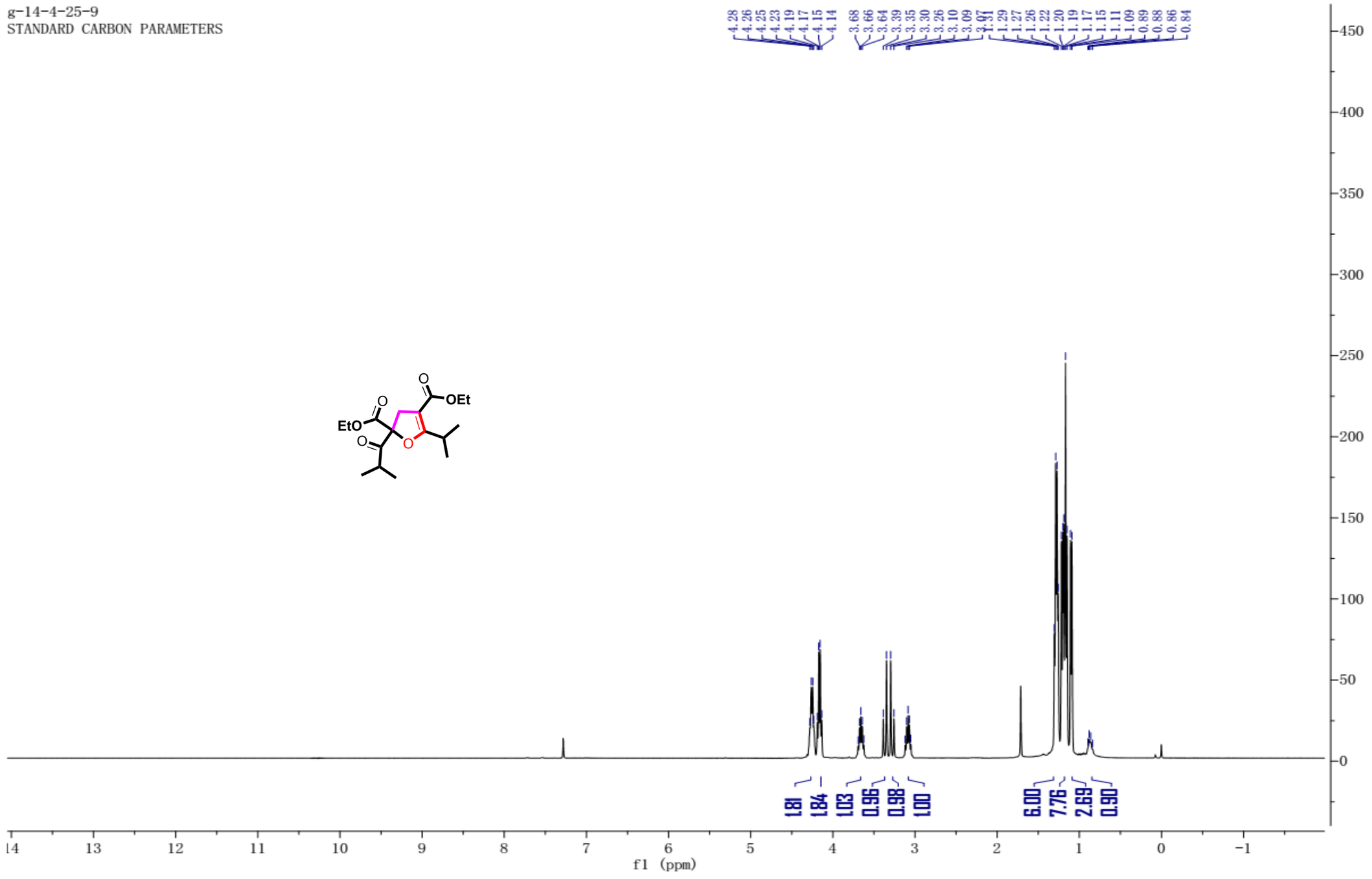
g-2014-4-18-13
STANDARD CARBON PARAMETERS



g-2014-4-18-13-c
STANDARD CARBON PARAMETERS

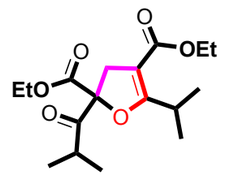


g-14-4-25-9
STANDARD CARBON PARAMETERS



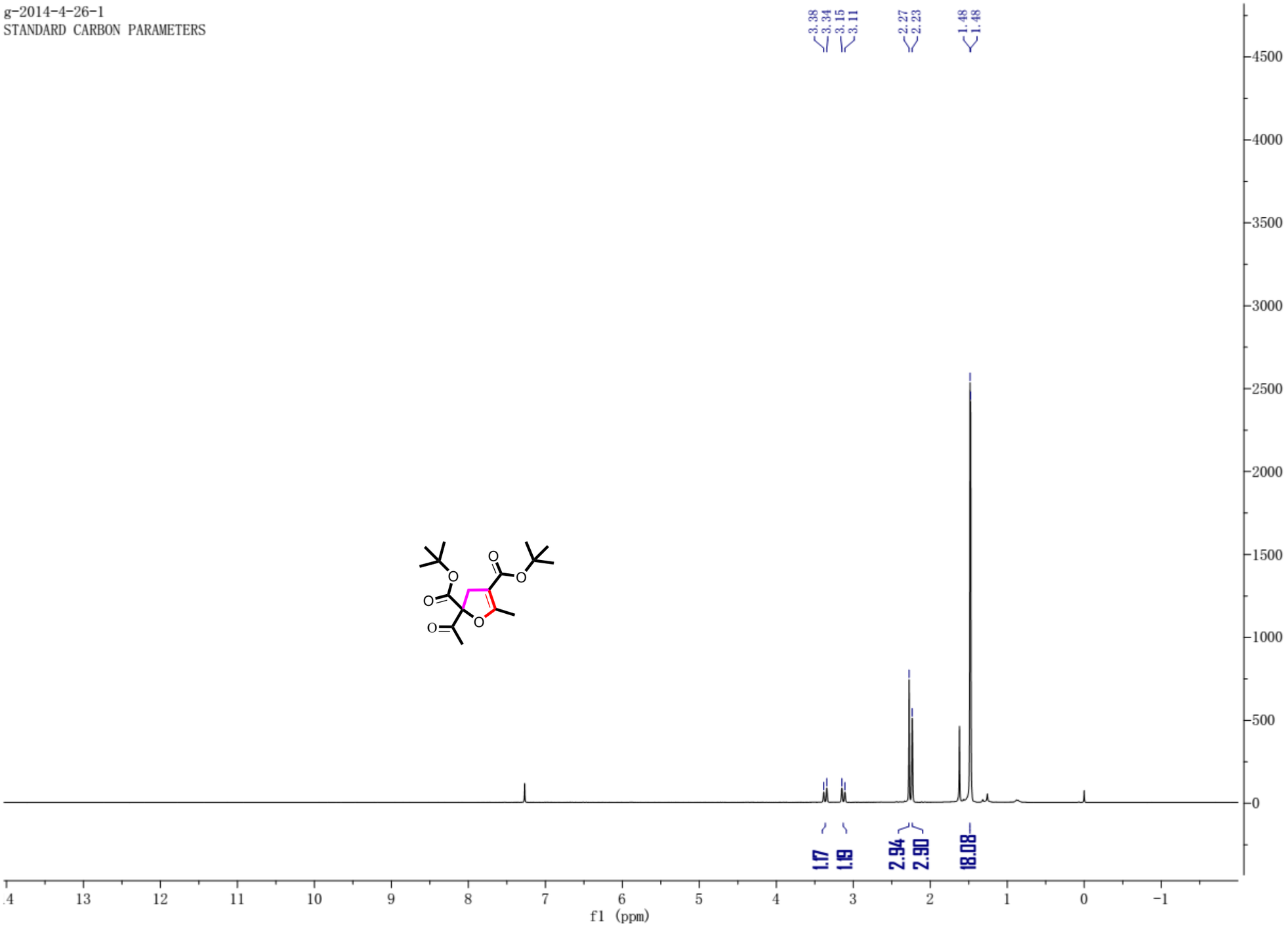
LULIN-13C-1
Gradient Shimming

207.95
173.36
168.30
164.95
100.19
91.79
62.67
60.06
36.79
36.73
26.86
19.73
19.42
19.05
18.96
14.55
14.23

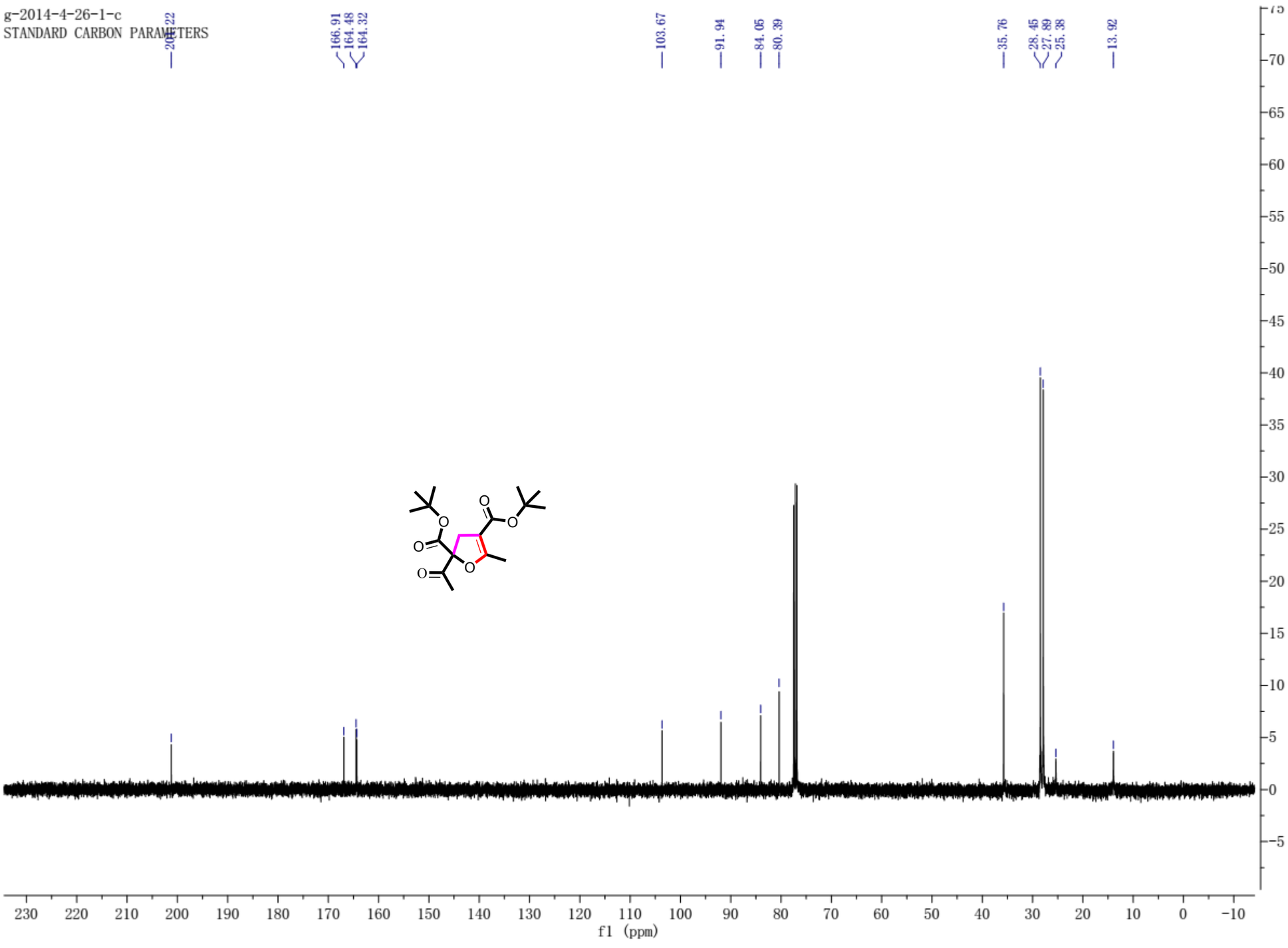


f1 (ppm)

g-2014-4-26-1
STANDARD CARBON PARAMETERS



g-2014-4-26-1-c
STANDARD CARBON PARAMETERS



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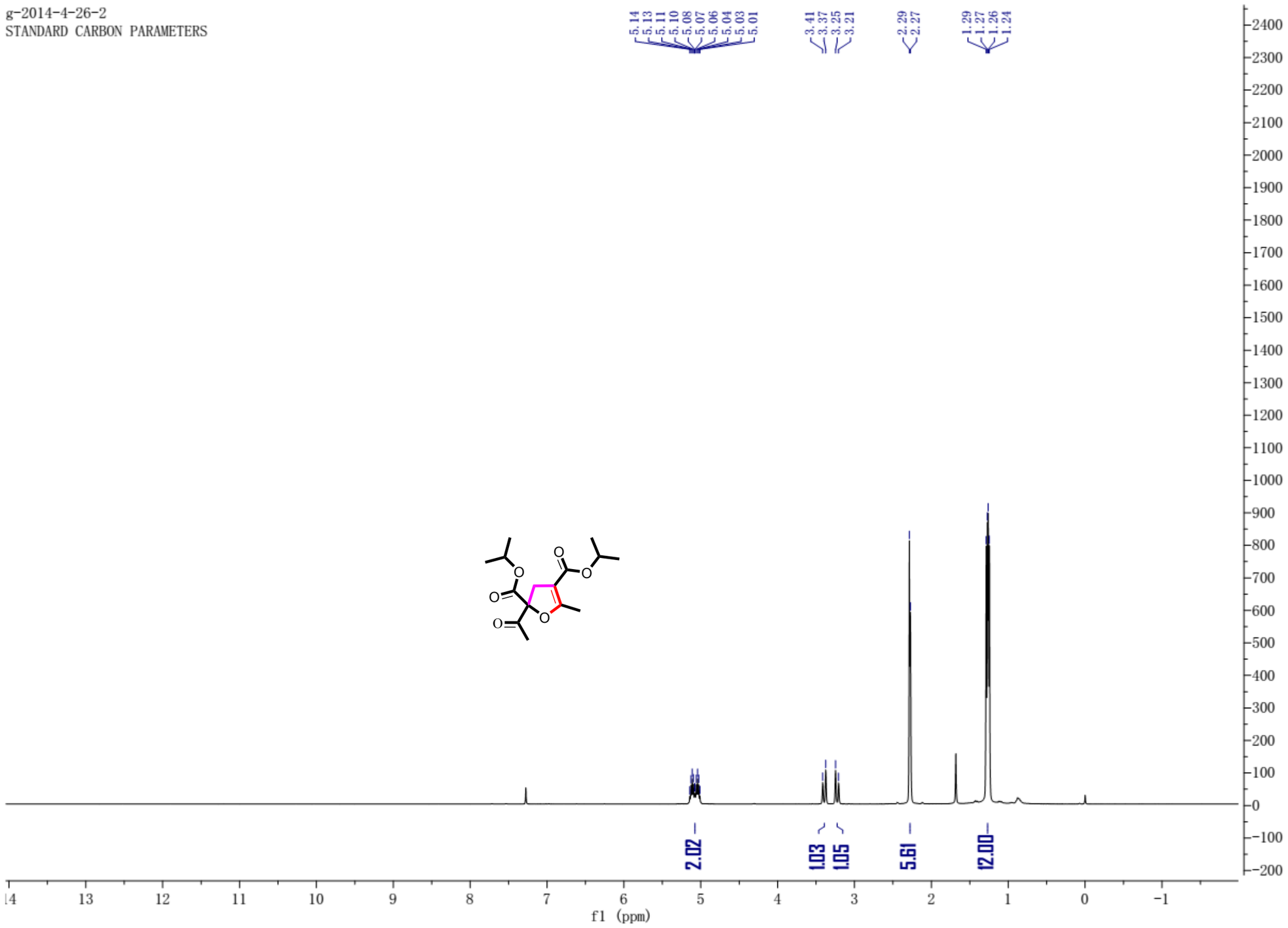
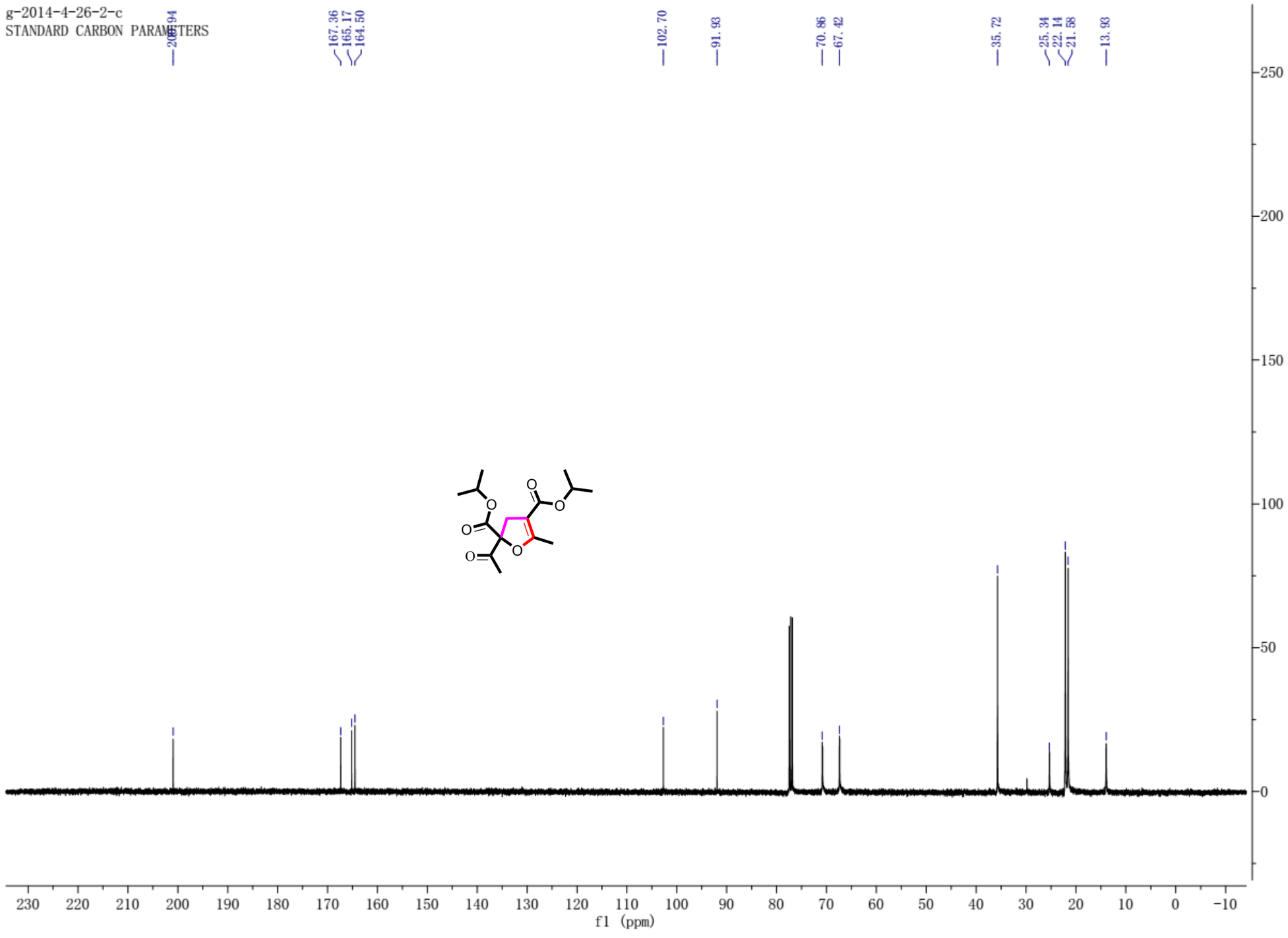
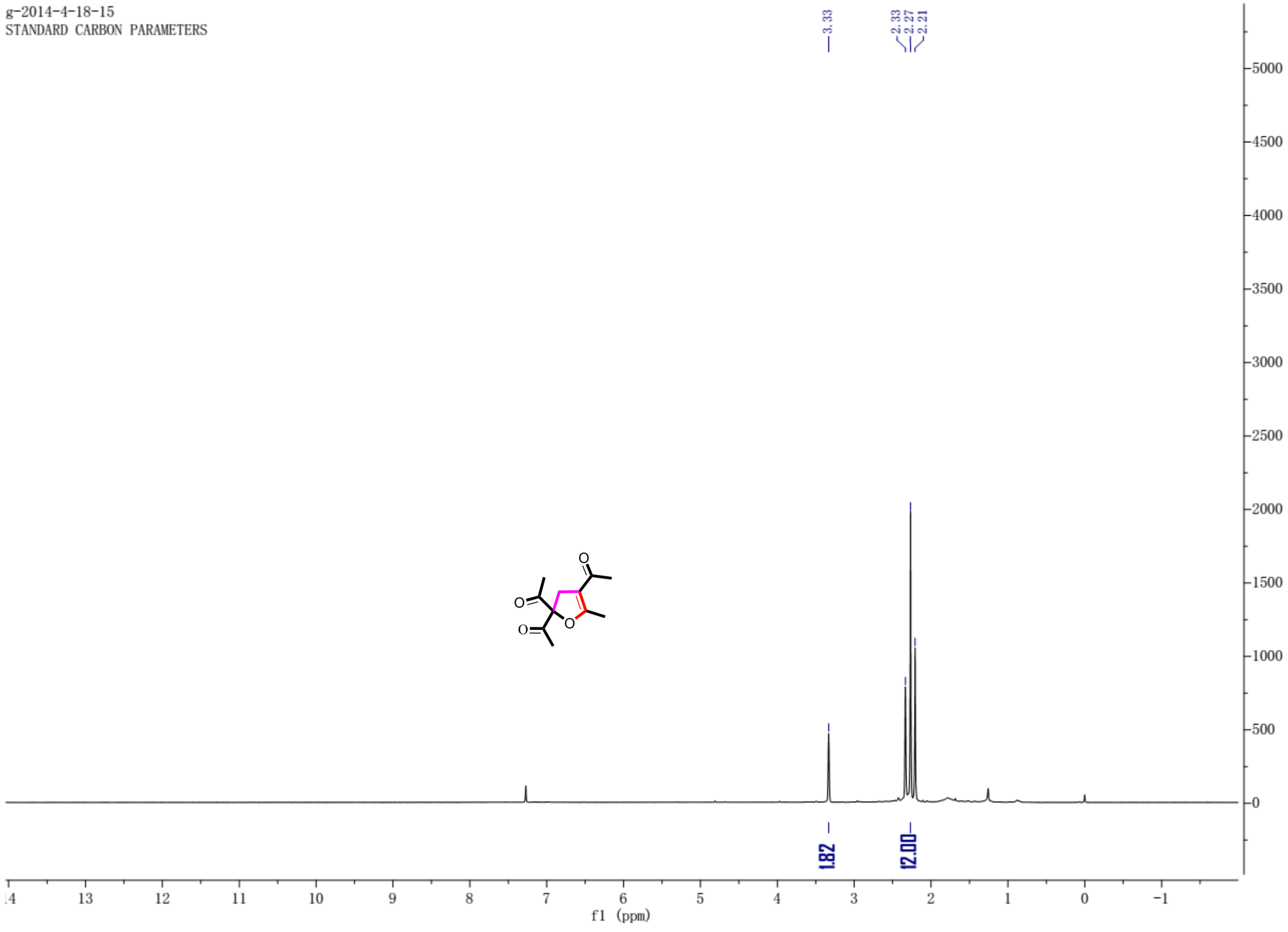
STANDARD CARBON PARAMETERS



g-2014-4-26-2-c
STANDARD CARBON PARAMETERS



g-2014-4-18-15
STANDARD CARBON PARAMETERS



g-2014-4-18-15-c
STANDARD CARBON PARAMETER