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Supporting Information

Tetrasubstituted Allenes by Palladium-Catalyzed Three-Component Tandem Michael Addition / Cross-Coupling Reaction

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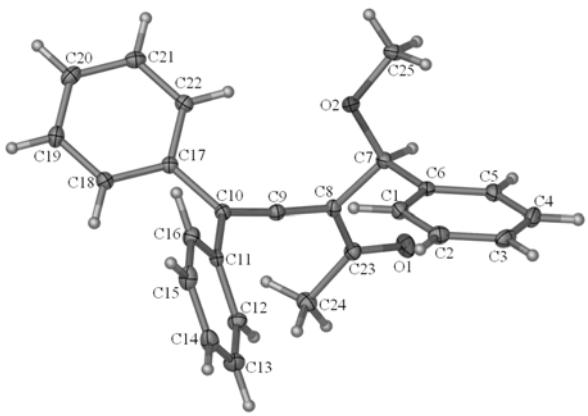
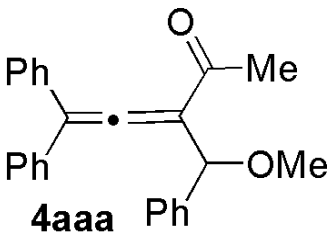
1.0 General procedure for synthesis of allene 4

A solution of electron deficient enyne **1** (0.25 mmol, 1.0 equiv), Nucleophiles (1.0 mmol, 4.0 equiv), aryl halides (0.5 mmol, 2.0 equiv), Ag_2O(0.15 mmol, 0.6 equiv) and $Pd(PPh_3)_4$ (0.0125 mmol, 5 mol%) in 1.0 mL of dioxane was stirred at 45～80^{0}C under N_2. After the reaction was complete which was determined by TLC analysis, the reaction was cooled down to room temperature, after filtration and evaporation, the residue was purified by column chromatography on silica gel (hexanes : Et_2O = 20:1～5:1) to afford allene **4**.

2.0 X-ray diffraction analysis data



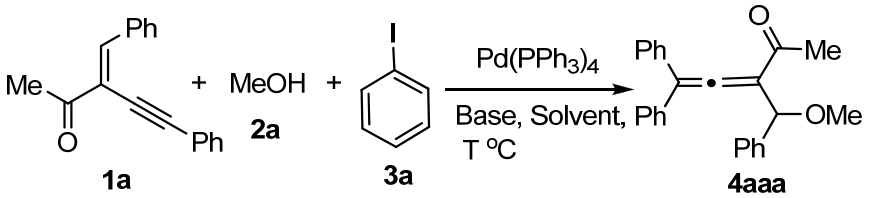


4aaa

Figure 1. ORTEP depiction of compound **4aaa**

X-ray data for compound **4aaa**(CH_2Cl_2 / hexanes)**:** $C_{25}H_{22}O_2$, Mw=354.43, orthorhombic, pbca space group, Mo-Kα(0.71073Å), R1(I > 2σ(I))= 0.0370, wR2 = 0.0973, a = 19.5589(7) Å, b = 8.1704(3) Å, c = 24.0587(9) Å, V = 3844.7(2) Å^3, T = 173(2) K, Z = 8, reflections collected /unique: 41565/3388 (Rint = 0.0295), number of observations [I > 2σ(I)] 3052, parameters 244. CCDC 741112(**4aaa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge form The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

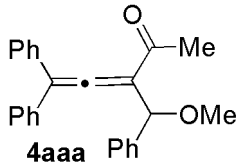
3.0 Optimization of the reaction conditions [a]



Entry	Base	solvent	T(^{0}C)	Time(h)	Tield(%)[b]
1[c,d]	K_2CO_3(4.0)	CH_3CN	80	18	15
2[c]	Ag_2CO_3(4.0)	CH_3CN	80	23	20
3[c,d]	Na_2CO_3(4.0)	CH_3CN	80	48	--[e]
4[c]	Ag_2O(1.5)	CH_3CN	80	8	47
5[c]	Ag_2O(0.6)	CH_3CN	80	4	73
6[c]	Ag_2O(0.6)	CH_3CN	70	7	64
7[f]	Et_3N(2.0)	dioxane	80	12	trace
8[f]	$[(CH_3)_2CH]_2NC_2H_5$(2.0)	dioxane	80	12	trace
9[f]	**Ag_2O(0.6)**	**dioxane**	**80**	**12**	**93**
10[f]	Ag_2O(0.6)	toluene	80	13	60
11[f]	Ag_2O(0.6)	THF	80	13	0
12[f]	Ag_2O(0.6)	DMSO	80	13	41
13[f]	Ag_2O(0.6)	$ClCH_2CH_2Cl$	80	12	58
14[f]	Ag_2O(0.6)	DMF	80	12	66
15[f,g]	Ag_2O(0.6)	dioxane	80	13	15[h]

[a] Reaction conditions: 0.25 mmol **1a**, 4.0 equiv of methanol **2a** , 2.0 equiv of iodobenzene **3a** employed, solvent (1.0 ml), N_2 atmosphere. [b] Yield of isolated product. [c] 10 mol% $Pd(PPh_3)_4$ was used. [d] 10 mol% Ag_2CO_3 was added. [e] an incomplete reaction, not isolated. [f] 5 mol% $Pd(PPh_3)_4$ was used. [g] Bromobenzene was used instead of iodobenzene. [h] based on recovery of material **1a**.

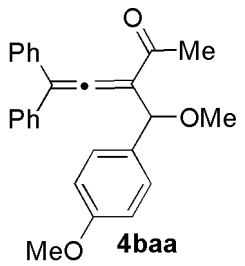
4.0 The characterization data for the newly synthesized compounds as well as the copies of the ^{1}H NMR、^{13}C NMR spectra of all products are given below.



4aaa

4aaa Flash column chromatography (hexanes / Et_2O = 10:1) in 93% yield.

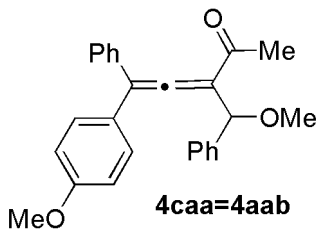
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.08 (m, 13 H), 6.90-6.80 (m, 2H), 5.30 (s, 1 H), 3.22 (s, 3 H), 2.24 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.6, 196.7, 140.2, 134.2, 133.9, 128.7, 128.5, 128.3, 128.2, 128.13, 128.11(2C), 127.6, 127.0, 116.0, 114.6, 78.8, 57.3, 27.7 ppm; MS (EI) *m/z* (%): 354 (M^+, 2.34), 121 (100); HRMS calcd for $C_{25}H_{22}O_2$: 354.1620, found: 354.1617.



4baa

4baa Flash column chromatography (hexanes / Et_2O = 10:1) in 81% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.21 (m, 10 H), 7.05 (d, *J* = 7.8 Hz, 2 H), 6.80 (d, *J* = 7.8 Hz, 2 H), 5.34 (s, 1 H), 3.77 (s, 3 H), 3.31 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 196.8, 159.2, 134.3, 134.2, 132.3, 128.7, 128.5, 128.4, 128.3(2C), 128.2, 128.1, 115.9, 114.8, 113.5, 78.6, 57.1, 55.2, 27.8 ppm; MS (EI) *m/z* (%): 384 (M^+, 0.18), 151 (100); HRMS calcd for $C_{26}H_{24}O_3$: 384.1725, found: 384.1721.



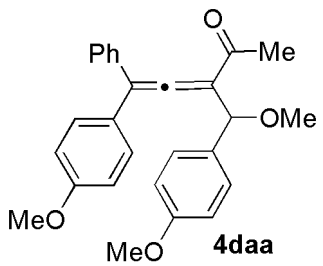
4caa=4aab

4caa (dr = 1.0/1.0) Flash column chromatography (hexanes / Et_2O = 10:1) in 70% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.11 (m, 10 H), 6.77 (d, *J* = 8.4 Hz, 2 H), 6.69 (d, *J* = 8.4 Hz, 2 H), 5.31 (s, 1 H), 3.71 (s, 3 H), 3.23 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 197.0, 159.6, 140.5, 134.5, 129.4, 128.7, 128.4, 128.19, 128.16, 127.6, 127.1, 126.1, 115.7, 114.5, 114.0, 78.8, 57.3, 55.3, 27.7 ppm; MS (EI) *m/z* (%): 384(M^+, 5.06), 121(100); HRMS calcd for $C_{26}H_{24}O_3$: 384.1725, found: 384.1725.

The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.11 (m, 10 H), 6.85(d, *J* = 8.1 Hz, 4 H), 5.31 (s, 1 H), 3.75 (s, 3 H), 3.24 (s, 3H), 2.26 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 197.0, 159.7, 140.4, 134.3, 129.6, 128.5, 128.19, 128.13, 128.06, 127.6, 127.1, 126.3, 115.7, 114.5, 114.2, 78.9, 57.4, 55.3, 27.7 ppm; MS (EI) *m/z* (%): 384 (M^+, 5.07), 121 (100); HRMS calcd for $C_{26}H_{24}O_3$: 384.1725, found: 384.1725.

The same structure **4aab** was obtained in 90% yield (dr = 1.2/1.0) by MCR of 2-pheny lethynyl-3-phenyl-2-butylene-1-one **1a**, methanol **2a** and 1-iodo-4-methoxy benzene **3b**.



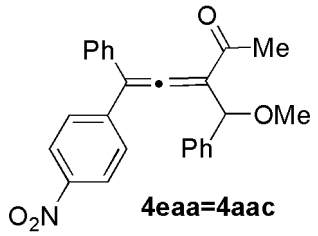
4daa

4daa (dr = 1.0/1.0) Flash column chromatography (hexanes / ethyl acetate = 10:1) in 81% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.23 (m, 5 H), 7.17 (d, *J* = 8.1 Hz, 2 H), 6.86 (d, *J* = 8.1 Hz, 2 H), 6.72 (d, *J* = 8.1 Hz, 2 H), 6.70 (d, *J* = 8.1 Hz, 2 H), 5.23 (s, 1 H), 3.71 (s, 3 H), 3.68 (s, 3 H), 3.20 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.4, 197.0, 159.6, 159.2, 134.6, 132.5, 129.4, 128.7, 128.38, 128.35, 128.2, 126.2, 115.6, 114.6, 114.0, 113.5, 78.5, 57.1, 55.3, 55.2, 27.7 ppm; MS

(EI) *m/z* (%): 414 (M^+,0.41), 151 (100); HRMS calcd for $C_{27}H_{26}O_4$: 414.1831, found: 414.1828.

The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 2 H),7.25-7.14 (m, 5 H), 6.98–6.90 (m, 2 H), 6.85 (d, *J* = 8.7 Hz, 2 H), 6.69 (d, *J* = 8.4 Hz, 2 H), 5.23 (s, 1 H), 3.76 (s, 3 H), 3.67 (s, 3 H), 3.21 (s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 197.0, 159.7, 159.2, 134.5, 132.4, 129.6, 128.5, 128.4, 128.2, 128.1, 126.4, 115.6, 114.7, 114.2, 113.5, 78.6, 57.1, 55.3, 55.2, 27.7 ppm; MS (EI) *m/z* (%): 414 (M^+, 0.38), 151 (100); HRMS calcd for $C_{27}H_{26}O_4$: 414.1819, found: 414.1831.

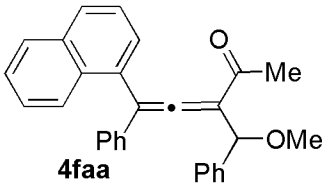


4eaa=4aac

4eaa (dr = 1.8/1.0) Flash column chromatography (hexanes / ethyl acetate = 10:1) in 71% yield. Two diastereoisomers are hard to be separated by column chromatography on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$): δ = [8.16 (d, *J* = 8.4 Hz, 0.7 H) , 7.99 (d, *J* = 8.4 Hz, 1.3 H)]; [7.50-7.16 (m, 10 H)]; [6.97 (d, *J* = 8.4 Hz, 1.3 H) , 6.85 (d, *J* = 7.2 Hz, 0.7 H)]; [5.34 (s, 0.65 H), 5.31 (s, 0.35 H)]; [3.24 (s, 3 H)]; [2.27(s, 3 H)]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = (215.2, 215.1), (195.72, 195.65), (147.5, 147.3), (141.3, 141.1), (140.1, 139.7), (133.1, 132.9), (129.1, 128.88), (128.85, 128.82), 128.7, 128.3, (128.2, 128.1), 128.0, (126.9, 126.7), (124.0, 123.7), (115.45, 115.40), (114.9, 114.8), (78.9, 78.7), (57.38, 57.36), 27.9 ppm; MS (70 eV): *m/z* (%): 399 (M^+, 0.12), 121 (100); HRMS calcd for $C_{25}H_{21}NO_4$: 399.1471, found: 399.1469.

The same structure **4aac** was obtained in 73% yield (dr = 1.2/1.0) by MCR of 2-phenylethynyl-3-phenyl-2-butylene-1-one **1a**, methanol **2a** and 1-iodo-4-nitro benzene **3c**

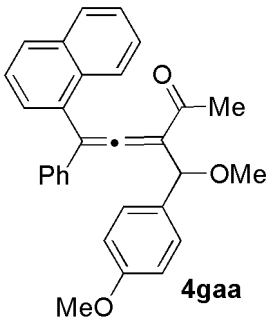


4faa

4faa (dr = 1.3/1.0) Flash column chromatography (hexanes / Et_2O = 10:1) in 73% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (t, *J* = 8.1 Hz, 2 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 7.65-7.15 (m, 12 H), 6.99-6.93 (m, 2 H), 5.38 (s, 1 H), 3.22 (s, 3 H), 2.43 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.6, 196.8, 140.6, 134.2, 133.9, 131.9, 131.7, 129.0, 128.7, 128.34, 128.28, 128.0, 127.9, 127.8, 127.0, 126.7, 126.4, 126.3, 126.1, 125.6, 114.4, 114.0, 78.9, 57.2, 28.0 ppm; MS (EI) *m/z* (%): 404 (M^+, 1.36), 121 (100); HRMS calcd for $C_{29}H_{24}O_2$: 404.1776, found: 404.1765.

The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.6 Hz, 2 H), 7.55 (d, *J* = 8.4 Hz, 1 H), 7.35 (t, *J* = 7.2 Hz, 1 H), 7.27-7.07 (m, 12H), 6.65 (d, *J* = 6.9 Hz, 1 H), 5.29 (s, 1 H), 3.30 (s, 3 H), 2.33 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.5, 196.8, 140.0, 134.2, 133.7, 131.7, 131.2, 128.8(2C), 128.3(2C), 128.2, 128.0, 127.8, 127.7, 127.3, 126.9, 126.4, 125.9, 125.4, 114.1, 113.7, 79.3, 57.6, 28.1 ppm; MS (EI) *m/z* (%): 404 (M^+, 4.65), 151 (100); HRMS calcd for $C_{29}H_{24}O_2$: 404.1776, found: 404.1763.



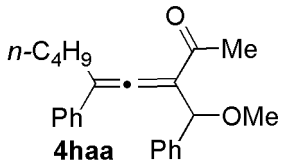
4gaa

4gaa (dr = 1.5/1.0) Flash column chromatography (hexanes / Et_2O = 10:1) in 65% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.82 (m, 3 H), 7.67-7.34 (m, 6 H), 7.26-7.18 (m, 3 H), 7.02 (d, *J* = 4.5 Hz, 2 H), 6.87 (d, *J* = 8.1 Hz, 2 H), 5.30 (s, 1 H), 3.82 (s, 3 H), 3.19 (s, 3 H), 2.42 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.4,

196.9, 159.3, 134.4, 133.9, 132.6, 131.9, 131.8, 129.0, 128.7, 128.4, 128.3, 128.0, 126.7, 126.4, 126.3, 126.1, 125.6, 114.6, 113.9, 113.7, 78.6, 57.0, 55.3, 28.1 ppm; MS (EI) *m/z* (%): 434 (M^+, 0.38),151 (100); HRMS calcd for $C_{30}H_{26}O_3$: 434.1882, found: 434.1886.

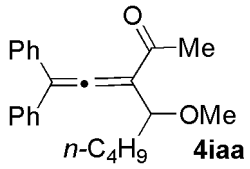
The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.49-7.21 (m, 8 H), 7.19 (d, *J* = 7.8 Hz, 2 H), 6.97 (d, *J* = 6.9 Hz, 1 H), 6.72 (d, *J* = 8.1 Hz, 2 H), 5.33 (s, 1 H), 3.76 (s, 3 H), 3.39 (s, 3 H), 2.44 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.3, 196.9, 159.2, 134.3, 133.8, 132.0, 131.7, 131.5, 128.84, 128.81, 128.5, 128.2, 128.0, 127.7, 126.9, 126.3, 126.0, 125.97, 125.4, 114.3, 113.6, 78.9, 57.4, 55.2, 28.2 ppm; MS (EI) *m/z* (%): 434 (M^+, 0.68), 151 (100); HRMS calcd for $C_{30}H_{26}O_3$: 434.1882, found: 434.1880.



4haa

4haa (dr = 1.2/1.0) Flash column chromatography (hexanes / Et_2O = 20:1) in 48% yield. Two diastereoisomers are hard to be separated by column chromatography on silica gel.

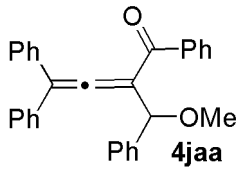
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.10 (m, 9 H), 6.89-6.87 (m, 1H), [5.33 (s, 0.55 H), 5.30 (s, 0.45 H)]; [3.26(s, 1.35 H), 3.24 (s, 1.65 H)], 2.49(dd, *J* = 7.5 Hz, *J* = 7.8 Hz, 1 H), 2.33-2.22 (m, 1 H), [2.16 (s, 1.65 H), 2.15 (s, 1.35 H)], 1.57-1.34 (m, 2 H), 1.14-0.94 (m, 2 H), [0.88 (t, *J* = 7.2 Hz, 1.65 H), 0.69 (t, *J* = 7.2 Hz, 1.35 H)]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = (214.3, 214.2), 197.3, (140.8, 140.7), (134.0, 133.8), (128.7, 128.4), (128.1, 128.0), (127.8, 127.6), (127.42, 127.38), (126.7, 126.67), (126.2, 126.0), (115.1, 115.0), (113.2, 113.1), (78.5, 78.3), (57.3, 57.2), (30.02, 29.96), (29.8, 29.4), (27.5, 27.4), (22.6, 22.5), (13.8, 13.7) ppm; MS (70 eV): *m/z* (%): 334 (M^+, 0.54), 121 (100); HRMS calcd for $C_{23}H_{26}O_2$: 334.1933, found: 334.1927.



4iaa

4iaa Flash column chromatography (hexanes / Et_2O = 20:1) in 81% yield.

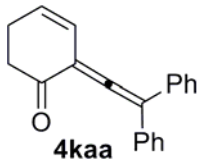
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.20 (m, 10 H), 4.24 (t, *J* = 6.3 Hz, 1 H), 3.15 (s, 3 H), 2.30 (s, 3 H), 1.68-1.52 (m, 2 H), 1.35-1.04 (m, 4 H), 0.71 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.0, 197.7, 134.41, 134.38, 128.7, 128.4, 128.3, 128.2, 115.8, 113.5, 77.0, 57.1, 35.2, 27.9, 27.8, 22.5, 13.9 ppm; MS (EI) *m/z* (%): 334 (M^+, 8.85), 234 (100); HRMS calcd for $C_{23}H_{26}O_2$: 334.1933, found: 334.1935.



4jaa

4jaa Flash column chromatography (hexanes / Et_2O = 10:1) in 96% yield.

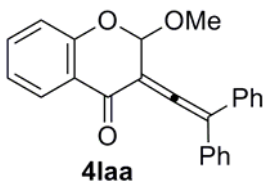
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.5 Hz, 2 H), 7.49-7.14 (m, 16 H), 6.92 (d, *J* = 6.6 Hz, 2 H), 5.64 (s, 1 H), 3.44 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.3, 193.2, 140.3, 137.8, 134.4, 134.3, 132.3, 128.8, 128.5, 128.4, 128.3, 128.2(2C), 128.1, 128.0, 127.8, 127.6, 126.9, 115.6, 112.5, 80.12, 57.6 ppm; MS (EI) *m/z* (%): 416 (M^+, 2.74), 121 (100); HRMS calcd for $C_{30}H_{24}O_2$: 416.1776, found: 416.1775.



4kaa

4kaa Flash column chromatography (hexanes / Et_2O = 10:1) in 97% yield.

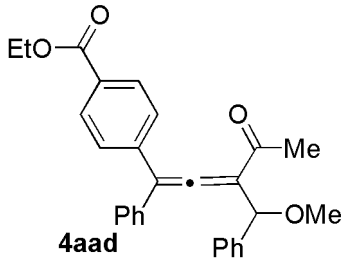
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.24 (m, 10 H), 6.37 (d, *J* = 9.9 Hz, 1 H), 6.06–5.93 (m, 1 H), 2.67 (t, *J* = 6.9 Hz, 2 H), 2.63-2.52 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.9, 198.2, 134.5, 128.8(2C), 128.6(2C), 128.5(2C), 128.1, 124.2, 116.2, 38.8, 24.6 ppm; MS (EI) *m/z* (%): 272 (M^+, 3.42), 84 (100) ; HRMS calcd for $C_{20}H_{16}O$: 272.1201, found: 272.1205.



4laa

4laa Flash column chromatography (hexanes / Et_2O = 10:1) in 45% yield.

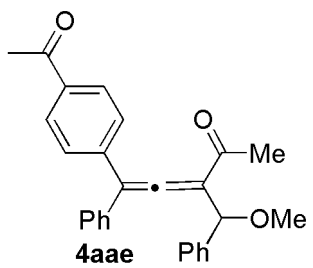
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 1 H), 7.58-7.43 (m, 2 H), 7.47 (d, *J* = 7.2 Hz, 1 H), 7.41-7.28 (m, 8H), 7.10 (d, *J* = 7.8 Hz, 1 H), 7.05 (d, *J* = 8.1 Hz, 1 H), 5.88 (s, 1 H), 3.50 (s, 3 H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.4, 180.2, 157.3, 136.0, 133.9, 133.6, 128.94, 128.89, 128.71(2C), 128.68, 128.6, 127.3, 122.4, 122.2, 118.5, 117.6, 104.8, 101.2, 56.0 ppm; MS (EI) *m/z* (%): 354 (M^+, 15.31), 323 (100) ; HRMS calcd for $C_{24}H_{18}O_3$: 354.1256, found: 354.1257.



4aad

4aad (dr = 1.5/1.0) Flash column chromatography (hexanes / ethyl acetate = 10:1) in 88% yield. Two diastereoisomers are hard to be separated by column chromatography on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$): δ = [7.98 (d, *J* = 8.4 Hz, 1.2 H, 7.83 (d, *J* = 8.4 Hz, 0.8 H]; 7.39-7.13 (m, 10 H), [6.91 (d, *J* = 8.4 Hz, 0.8 H, 6.84 (d, *J* = 9.3 Hz, 1.2 H]; [5.32 (s, 0.6 H), 5.30 (s, 0.4 H)]; 4.30 (q, *J* = 7.2 Hz, 2 H), 3.23 (s, 3 H), 2.26 (s, 3 H), [1.31 (t, *J* = 7.2 Hz, 1.8 H), 1.28 (t, *J* = 7.2 Hz, 1.2 H)]; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 214.9, 196.2, 166.05, (140.13, 140.05), (138.9, 138.7), (133.7, 133.4), 130.2, (130.04, 130.0), 129.7, 128.8, (128.6, 128.5), (128.3, 128.2), (128.1, 128.0), (127.8, 127.7), (127.0, 126.8), (115.5, 115.0), (78.9, 78.8), 61.0, 57.3, 27.8, 14.3 ppm; MS (70 eV): *m/z* (%): 426 (M^+, 0.84), 121 (100); HRMS calcd for $C_{28}H_{26}O_4$: 426.1831, found: 426.1828.

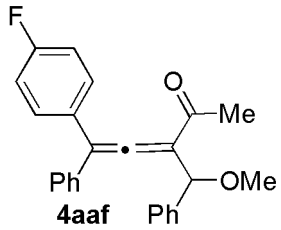


4aae

4aae (dr = 1.5/1.0) Flash column chromatography (hexanes / ethyl acetate = 10:1) in 87% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2 H), 7.40–7.10 (m, 10 H), 6.94 (d, *J* = 8.4 Hz, 2 H), 5.32 (s, 1 H), 3.24 (s, 3 H), 2.50 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 197.3, 196.2, 140.2, 139.0, 136.5, 133.6, 128.9, 128.5(2C), 128.4, 128.24, 128.2, 127.8, 126.9, 115.5, 115.1, 78.8, 57.4, 27.8, 26.5 ppm; MS (EI) *m/z* (%): 396 (M^+, 0.47), 121 (100); HRMS calcd for $C_{27}H_{24}O_3$: 396.1725, found: 396.1726.

The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 7.21-7.10 (m, 8 H), 6.88-6.80(m, 2 H), 5.31 (s, 1 H), 3.25 (s, 3 H), 2.55 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 197.4, 196.2, 140.0, 139.3, 136.7, 133.4, 128.8, 128.7, 128.42, 128.39, 128.21, 128.20, 127.8, 127.0, 115.5, 115.1, 78.9, 57.4, 27.9, 26.6 ppm; MS (EI) *m/z* (%): 396 (M^+, 0.50), 121 (100); HRMS calcd for $C_{27}H_{24}O_3$: 396.1725, found: 396.1724.



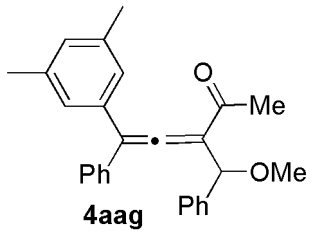
4aaf

4aaf(dr = 1.5/1.0) Flash column chromatography (hexanes / Et_2O = 10:1) in 87% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.10 (m, 10 H), 7.00 (t, *J* = 8.7 Hz, 2 H), 6.88–6.81 (m, 2 H), 5.30 (s, 1 H), 3.23(s, 3 H), 2.25 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 196.5, 162.7 (d, $^{1}J_{CF}$ = 246.8 Hz), 140.2, 133.9, 130.3, 130.2, 130.1 (d, $^{4}J_{CF}$ = 8.3 Hz), 128.6, 128.2, 128.0 (d, $^{2}J_{CF}$ = 40.5 Hz), 127.7, 127.0,

115.8 (d, $^3J_{CF}$ = 21.0 Hz), 115.2, 114.9, 78.9, 57.3, 27.7 ppm; MS (EI) *m/z* (%): 372 (M^+, 1.96), 121 (100); HRMS calcd for $C_{25}H_{21}O_2F$: 372.1526, found: 372.1528.

The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.10 (m, 10 H), 6.90-6.75 (m, 4 H), 5.32 (s, 1 H), 3.24 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.6, 196.6, 162.6 (d, $^1J_{CF}$ = 246.8 Hz), 140.4, 134.1, 130.0 (d, $^4J_{CF}$ = 7.5 Hz), 129.8, 128.8, 128.1 (d, $^2J_{CF}$ = 50.3 Hz), 128.3, 128.2, 127.0, 115.5 (d, $^3J_{CF}$ = 21.8 Hz), 115.2, 114.8, 78.8, 57.4, 27.8 ppm; MS (EI) *m/z* (%): 372 (M^+, 1.11), 121 (100); HRMS calcd for $C_{25}H_{21}O_2F$: 372.1526, found: 372.1526.

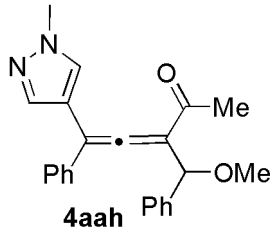


4aag

4aag (dr = 1.1/1.0) Flash column chromatography (hexanes / Et_2O = 10:1) in 93% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.08 (m, 8 H), 6.94–6.81 (m, 5 H), 5.30 (s, 1 H), 3.25 (s, 3 H), 2.26 (s, 3 H), 2.23 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 196.9, 140.5, 138.2, 134.3, 134.1, 130.0, 128.4, 128.2, 128.1, 128.0, 127.6, 127.0, 126.2, 116.1, 114.4, 78.9, 57.3, 27.7, 21.3 ppm; MS (EI) *m/z* (%): 382 (M^+, 1.59), 121 (100); HRMS calcd for $C_{27}H_{26}O_2$: 382.1933, found: 382.1932.

The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.17 (m, 10 H), 6.81 (s, 1 H), 6.39 (s, 2 H), 5.32 (s, 1 H), 3.23 (s, 3 H), 2.26 (s, 3 H), 2.11 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.8, 197.0, 140.6, 138.0, 134.4, 133.8, 129.8, 128.7, 128.3, 128.2, 128.1, 127.7, 127.1, 126.0, 116.1, 114.4, 78.8, 57.3, 27.7, 21.1 ppm; MS (EI) *m/z* (%): 382 (M^+, 1.48), 121 (100); HRMS calcd for $C_{27}H_{26}O_3$: 382.1933, found: 382.1934.

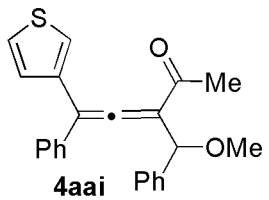


4aah

4aah (dr = 2.0/1.0) Flash column chromatography (hexanes / ethyl acetate = 2:1) in 52% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.10 (m, 10 H), 7.03 (s, 1 H), 6.67 (s, 1 H), 5.34 (s, 1 H), 3.71 (s, 3 H), 3.22 (s, 3 H), 2.22 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.9, 196.7, 140.8, 138.4, 134.0, 129.0, 128.8, 128.4, 128.2, 127.60, 127.57, 126.8, 114.5, 114.3, 108.0, 78.5, 57.2, 38.9, 27.6 ppm; MS (EI) *m/z* (%): 358 (M^+, 3.68), 121(100); HRMS calcd for $C_{23}H_{22}N_2O_2$: 358.1681, found: 358.1683.

The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (s, 1 H), 7.33 (s, 1 H), 7.30-7.10(m, 8 H), 6.96-6.88 (m, 2 H), 5.31 (s, 1 H), 3.86 (s, 3 H), 3.27 (s, 3 H), 2.23 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 196.8, 140.3, 138.7, 133.9, 129.3, 128.6, 128.3, 128.2, 127.7, 127.5, 127.0, 115.1, 114.3, 108.0, 78.9, 57.4, 39.2, 27.7 ppm; MS (EI) *m/z* (%): 358 (M^+, 3.83), 121(100); HRMS calcd for $C_{23}H_{22}N_2O_2$: 358.1681, found: 358.1685.

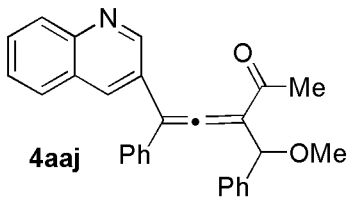


4aai

4aai (dr = 1.7/1.0) Flash column chromatography (hexanes / ethyl acetate = 10:1) in 72% yield. Two diastereoisomers are hard to be separated by column chromatography on silica gel.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39-7.09 (m, 11 H), [6.90 (dd, *J* = 4.5, 3.0 Hz, 1.26 H), 6.73 (dd, *J* = 0.9 Hz, 1.5 Hz, 0.37 H), 6.61(d, *J* = 5.1 Hz, 0.37 H)]; 5.31 (s, 1 H), [3.25 (s, 1.90 H), 3.22 (s, 1.1 H)]; 2.24 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = (215.2, 215.1), 196.6, (140.5, 140.3), (134.5, 134.2), (134.1, 134.0), 128.7, (128.5, 128.4), (128.22, 128.18), (128.1, 127.9), (127.7, 127.6), (127.3, 127.04), (126.98,

126.92), (126.2, 125.9), (123.9, 123.7), (114.44, 114.38), (111.71, 111.65), (78.8, 78.7), (57.4, 57.2), 27.7 ppm; MS (70 eV): *m/z* (%): 360 (M^+, 1.21), 121 (100); HRMS calcd for $C_{23}H_{20}O_2S$: 360.1184, found: 360.1184.

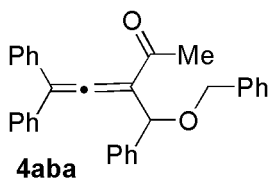


4aaj

4aaj(dr = 1.2/1.0) Flash column chromatography (hexanes / ethyl acetate = 5:1) in 62% yield.

The first fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (s, 1 H), 8.0 (d, *J* = 8.4 Hz, 1 H), 7.66–7.11 (m, 14 H), 5.37 (s, 1 H), 3.26 (s, 3 H), 2.30 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 196.1, 149.6, 147.2, 140.2, 134.9, 133.3, 129.9, 129.04, 128.99, 128.7, 128.3, 128.1, 127.9, 127.8, 127.7, 127.3, 127.1, 126.8, 115.2, 113.4, 78.7, 57.4, 27.9 ppm; MS (EI) *m/z* (%): 405 (M^+, 2.66), 121 (100); HRMS calcd for $C_{28}H_{23}NO_2$: 405.1729, found: 405.1729.

The second fraction: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (d, *J* = 1.8 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 8.01 (d, *J* = 1.5 Hz, 1 H), 7.75–7.62 (m, 2 H), 7.49 (dd, *J* = 7.2, 7.8 Hz, 1 H), 7.32-7.12 (m, 8 H), 6.98-6.90 (m, 2 H), 5.33 (s, 1 H), 3.26 (s, 3 H), 2.30 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.8, 196.1, 150.3, 147.5, 140.1, 134.9, 133.2, 130.0, 129.2, 128.9, 128.6, 128.2, 128.03, 128.0, 127.82, 127.79, 127.7, 127.2, 127.0, 115.5, 113.5, 78.8, 57.3, 27.9 ppm; MS (EI) *m/z* (%): 405 (M^+, 2.57), 121 (100); HRMS calcd for $C_{28}H_{23}NO_2$: 405.1729, found: 405.1731.

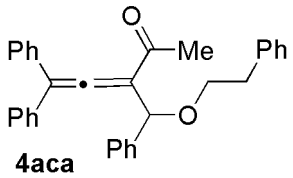


4aba

4aba Flash column chromatography (hexanes / Et_2O = 10:1) in 47% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.10 (m, 18 H), 6.94–6.88 (m, 2 H), 5.54 (s, 1 H), 4.39 (s, 2 H), 2.26 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.9, 196.7, 140.5, 138.2,

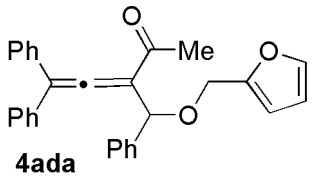
134.3, 134.0, 128.7, 128.53, 128.49, 128.2(3C), 128.19(2C), 128.15, 127.7, 127.4, 127.1, 116.1, 114.9, 76.6, 71.2, 27.8 ppm; MS (EI) *m/z* (%): 430 (M^+, 0.06), 339 (M^+-CH_2Ph, 1.86), 91 (100); HRMS calcd for $C_{31}H_{26}O_2$: 430.1933, found: 430.1931.



4aca

4aca Flash column chromatography (hexanes / Et_2O = 10:1) in 52% yield.

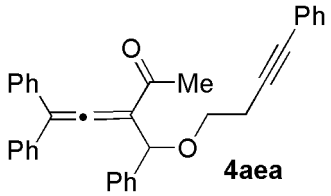
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 5 H), 7.33–6.95 (m, 15 H), 5.51 (s, 1 H), 3.71-3.49 (m, 2 H), 2.83 (t, *J* = 6.9 Hz, 2 H), 2.32 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 196.8, 140.7, 138.9, 134.4, 134.1, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1(3C), 127.5, 127.0, 126.0, 116.0, 115.0, 77.2, 70.2, 36.4, 27.8 ppm; MS (EI) *m/z* (%): 444 (M^+, 0.10), 105 (100); HRMS calcd for $C_{32}H_{28}O_2$: 444.2089, found: 444.2084.



4ada

4ada Flash column chromatography (hexanes / Et_2O = 10:1) in 52 % yield.

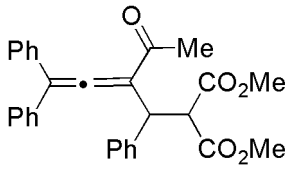
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42-7.30 (m, 8 H), 7.30-7.16 (m, 6 H), 7.02-6.92 (m, 2 H), 6.29 (s, 1 H), 6.21 (d, *J* = 2.4 Hz, 1 H), 5.60 (s, 1 H), 4.45 (d, *J* = 12.6 Hz, 1 H), 4.40 (d, *J* = 12.6 Hz, 1 H), 2.33 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 214.9, 196.6, 151.6, 142.6, 140.2, 134.3, 134.1, 128.7, 128.54, 128.51, 128.22, 128.15(2C), 128.1, 127.7, 127.2, 116.1, 114.7, 110.2, 109.3, 76.3, 63.2, 27.7 ppm; MS (70 eV): *m*/*z* (%): 420 (M^+, 0.97), 81 (100); HRMS calcd for $C_{29}H_{24}O_3$: 420.1725, found: 420.1725.



4aea

4aea Flash column chromatography (hexanes / Et_2O = 10:1) in 37 % yield.

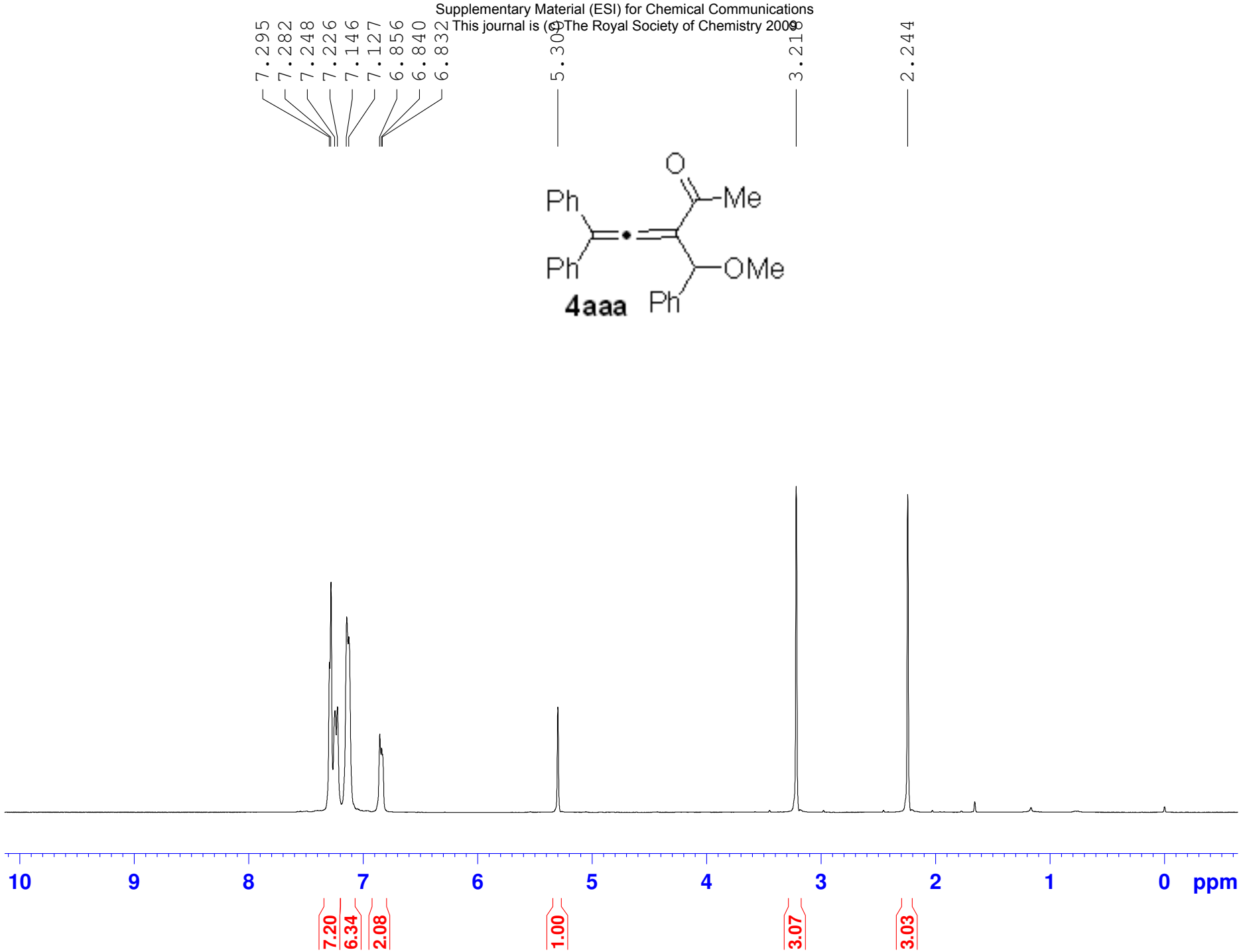
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.08 (m, 18 H), 6.94-6.84 (m, 2 H), 5.49 (s, 1 H), 3.58-3.51 (m, 2 H), 2.57 (t, *J* = 7.2 Hz, 2 H), 2.26 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 214.7, 196.7, 140.4, 134.3, 134.0, 131.5, 128.7, 128.5, 128.4, 128.23, 128.18, 128.15, 128.1(2C), 127.7, 127.6, 127.1, 123.7, 116.1, 114.9, 86.9, 81.4, 77.3, 67.7, 27.8, 20.8 ppm; MS (70 eV): *m*/*z* (%): 468 (M^+, 1.10), 129 (100); HRMS calcd for $C_{34}H_{28}O_2$: 468.2089, found: 468.2090.



4afa

4afa Flash column chromatography (hexanes / Et_2O = 5:1) in 70 % yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40-7.05 (m, 15 H), 4.75 (d, *J* = 12.3 Hz, 1 H), 3.96 (d, *J* = 12.3 Hz, 1 H), 3.31 (s, 3 H), 3.23 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.3, 195.8, 167.7, 167.6, 139.0, 134.1, 134.0, 128.8, 128.7, 128.43, 128.36, 128.32, 128.27(2C), 128.2, 127.2, 116.7, 114.0, 56.6, 52.30, 52.28, 42.8, 27.4 ppm; MS (70 eV): *m*/*z* (%): 454 (M^+, 1.07), 279 (100); HRMS calcd for $C_{29}H_{26}O_5$: 454.1780, found: 454.1781.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7.226
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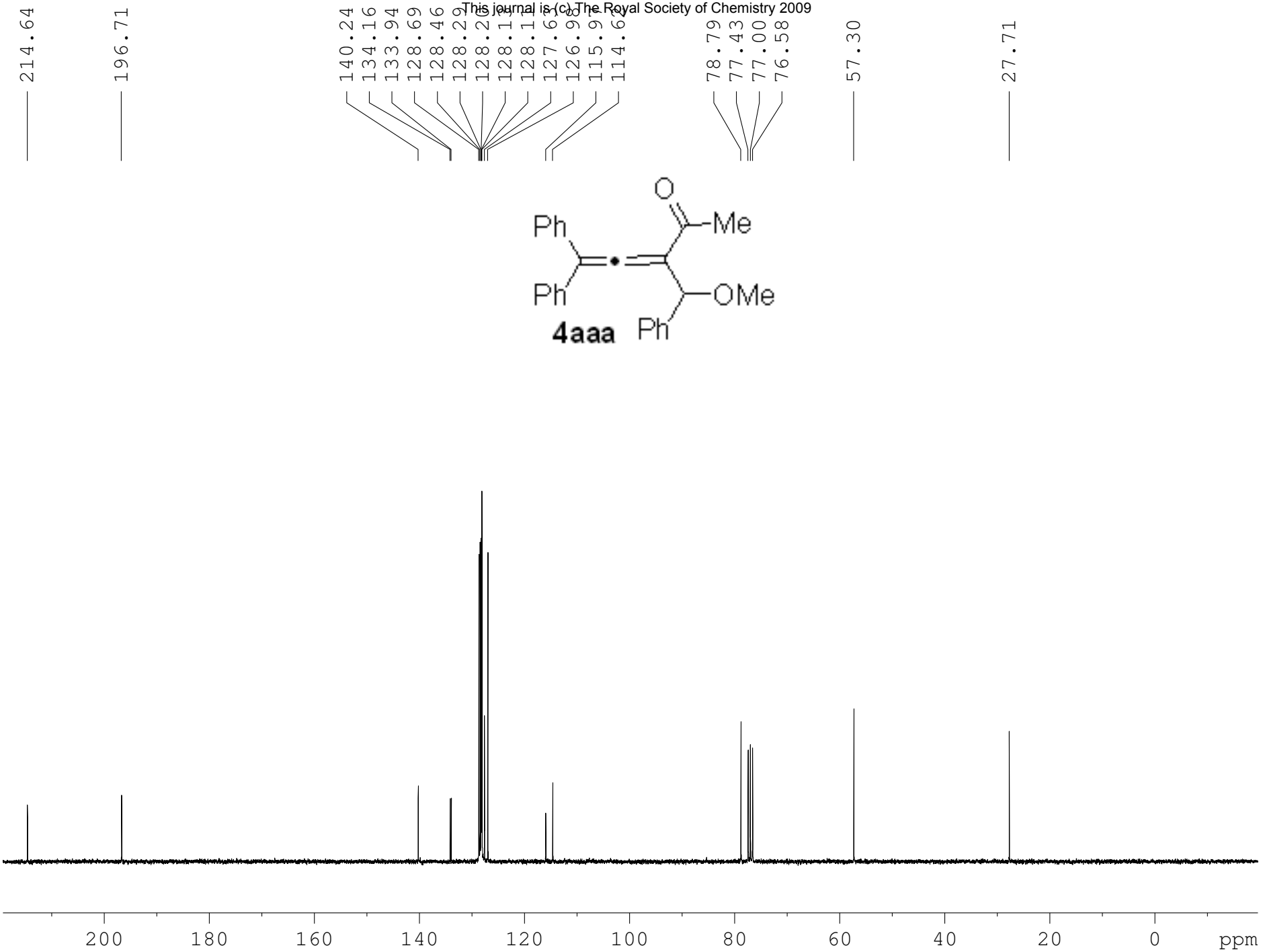
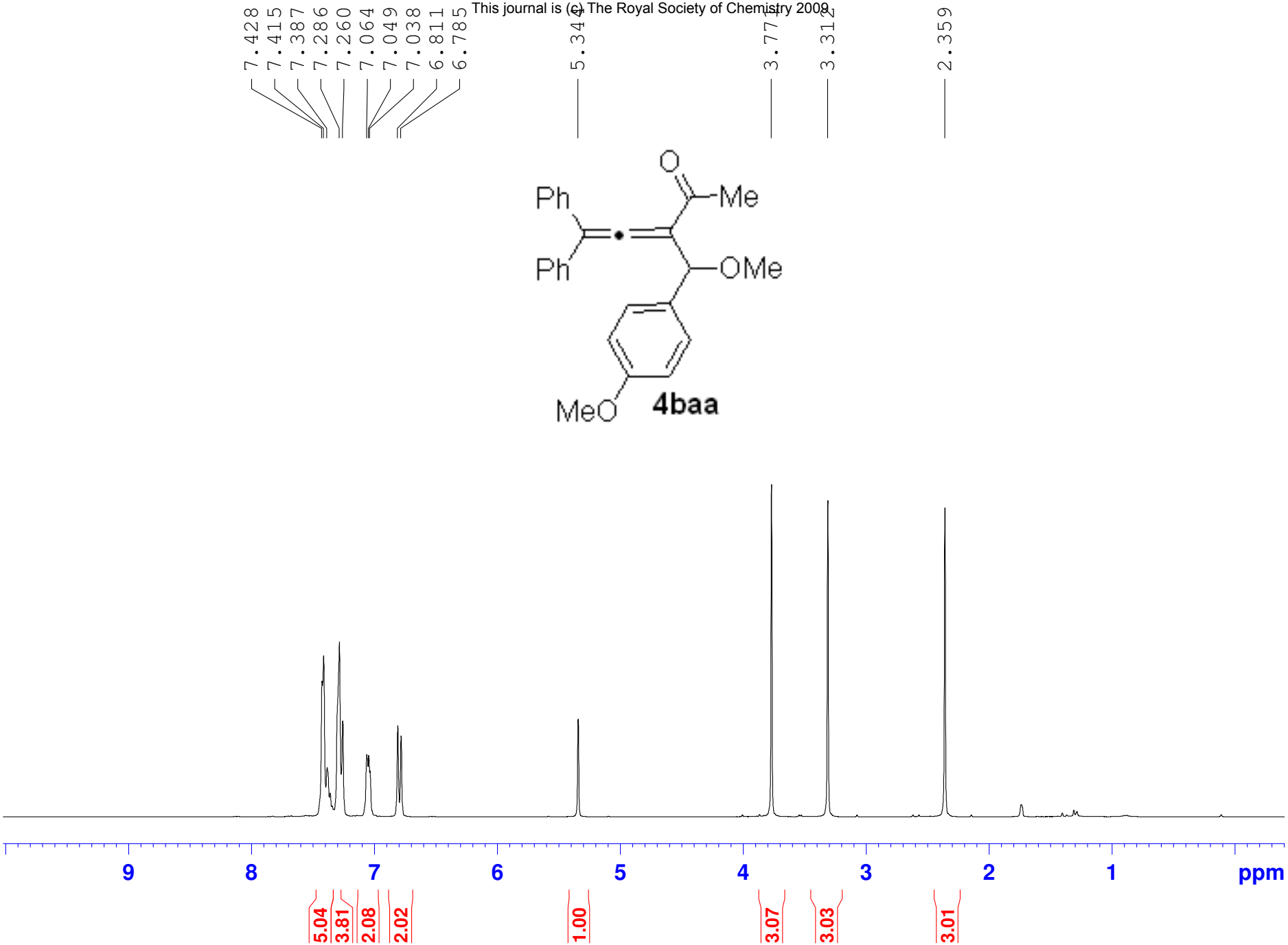
6.840
6.832
5.309
3.218
2.244
Ph
Ph
O
Me
OMe
Ph
4aaa
10
9
8
7
6
5
4
3
2
1
0
ppm
7.20
6.34
2.08
1.00
3.07
3.03


214.64
196.71
140.24
134.16
133.94
128.69
128.46
128.29
128.20
128.19
128.11
127.63
126.98
115.97
114.63
78.79
77.43
77.00
76.58
57.30
27.71
Ph
Ph
O
Me
OMe
Ph
4aaa
200
180
160
140
120
100
80
60
40
20
0
ppm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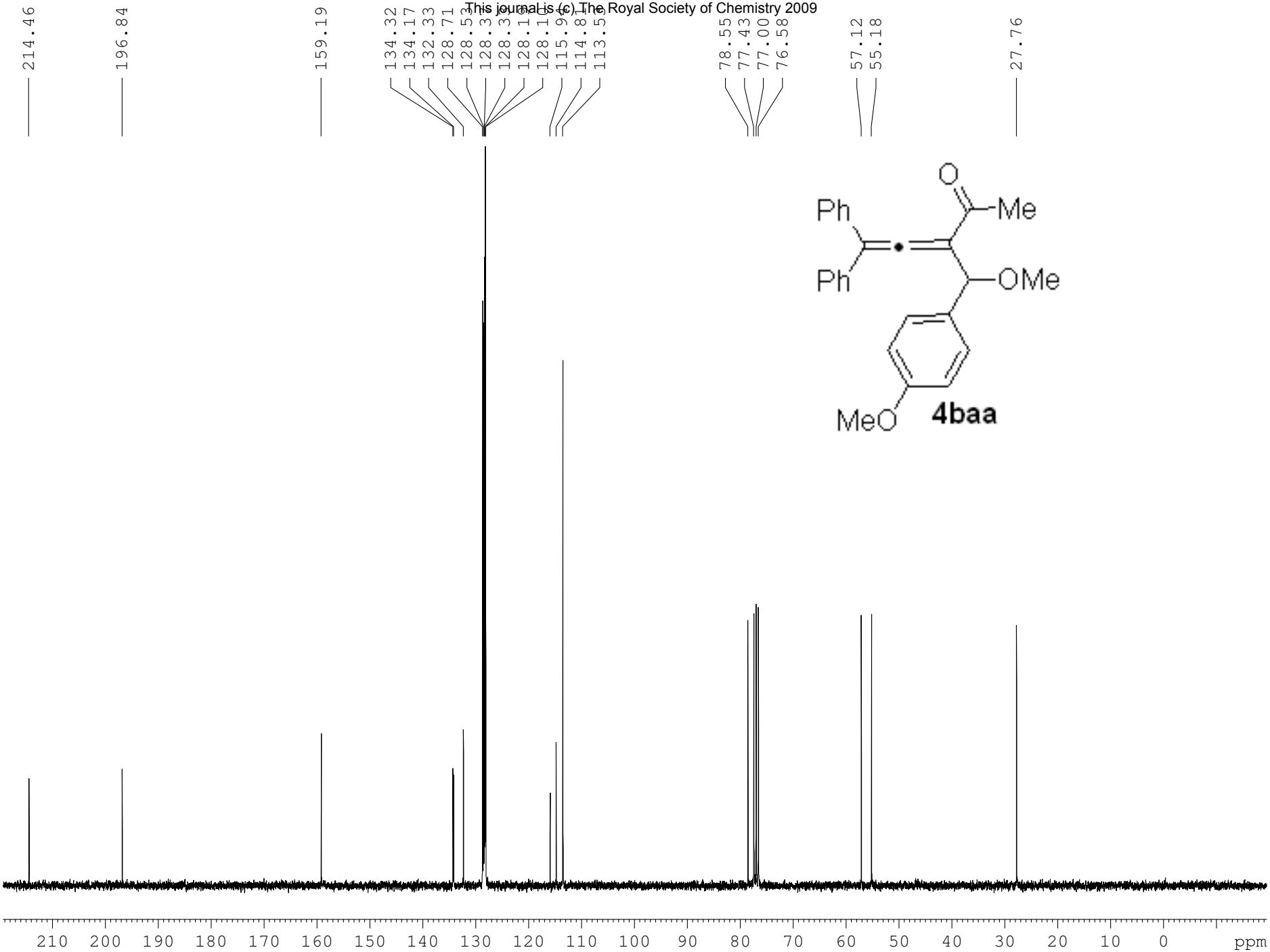
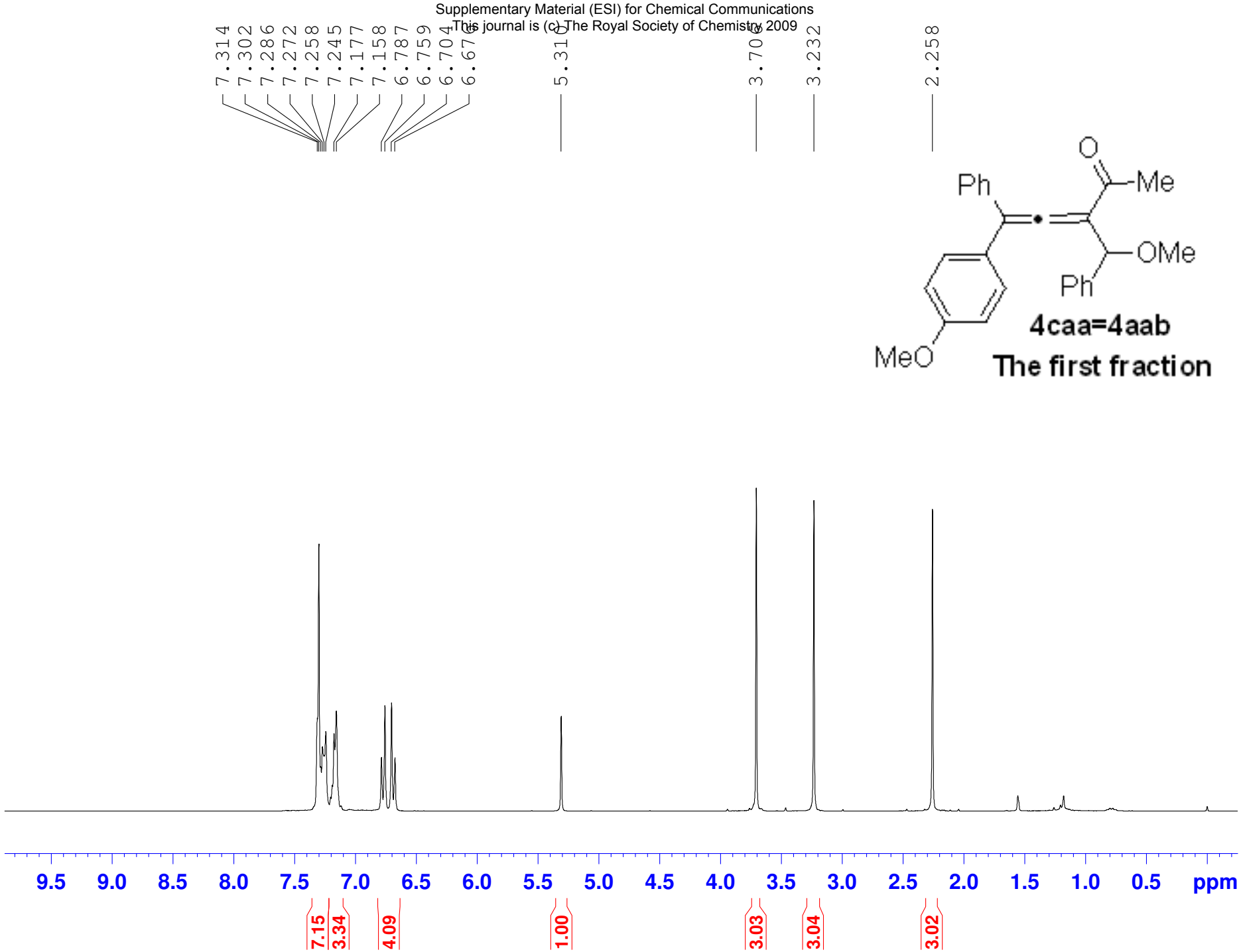
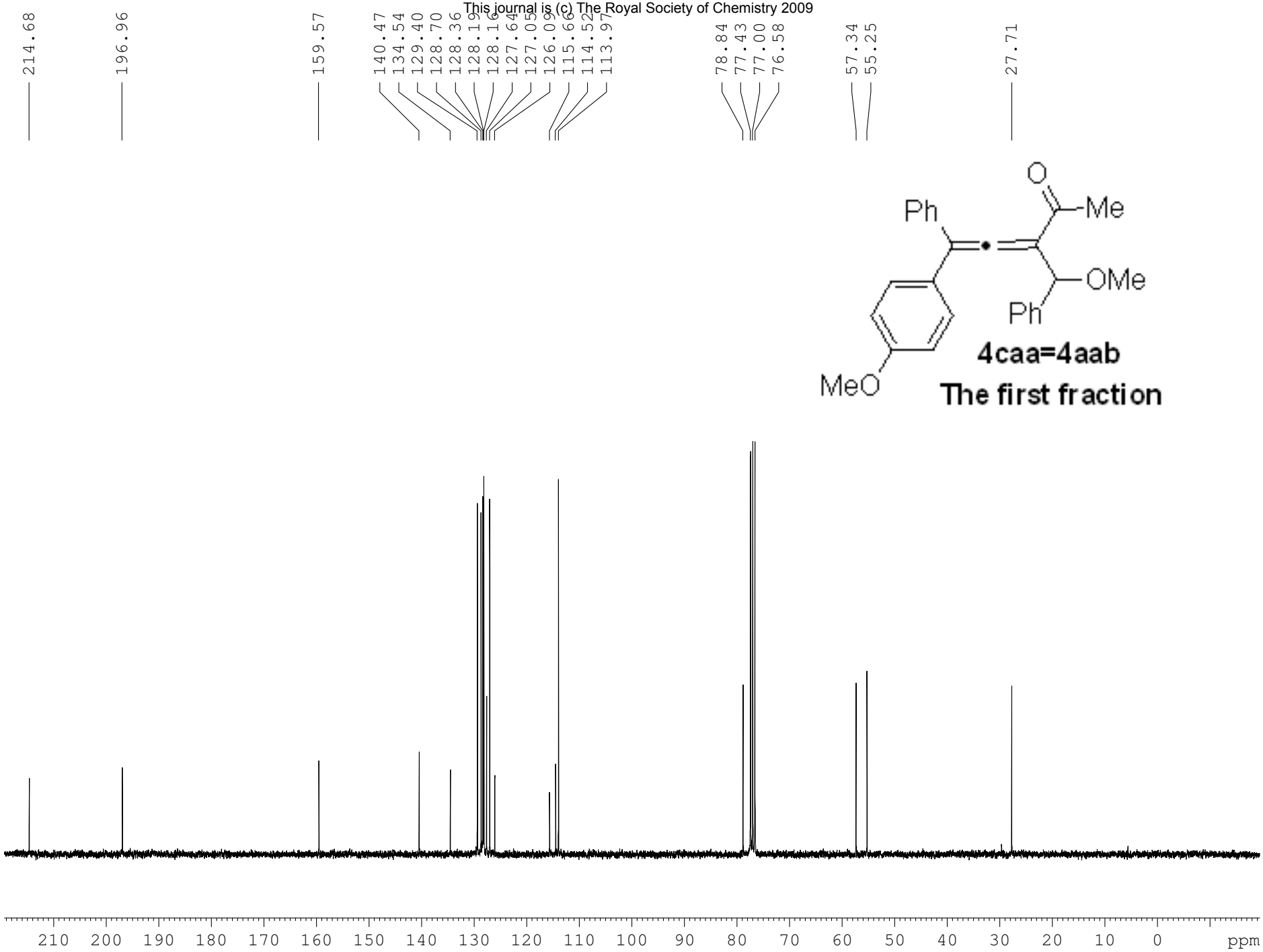
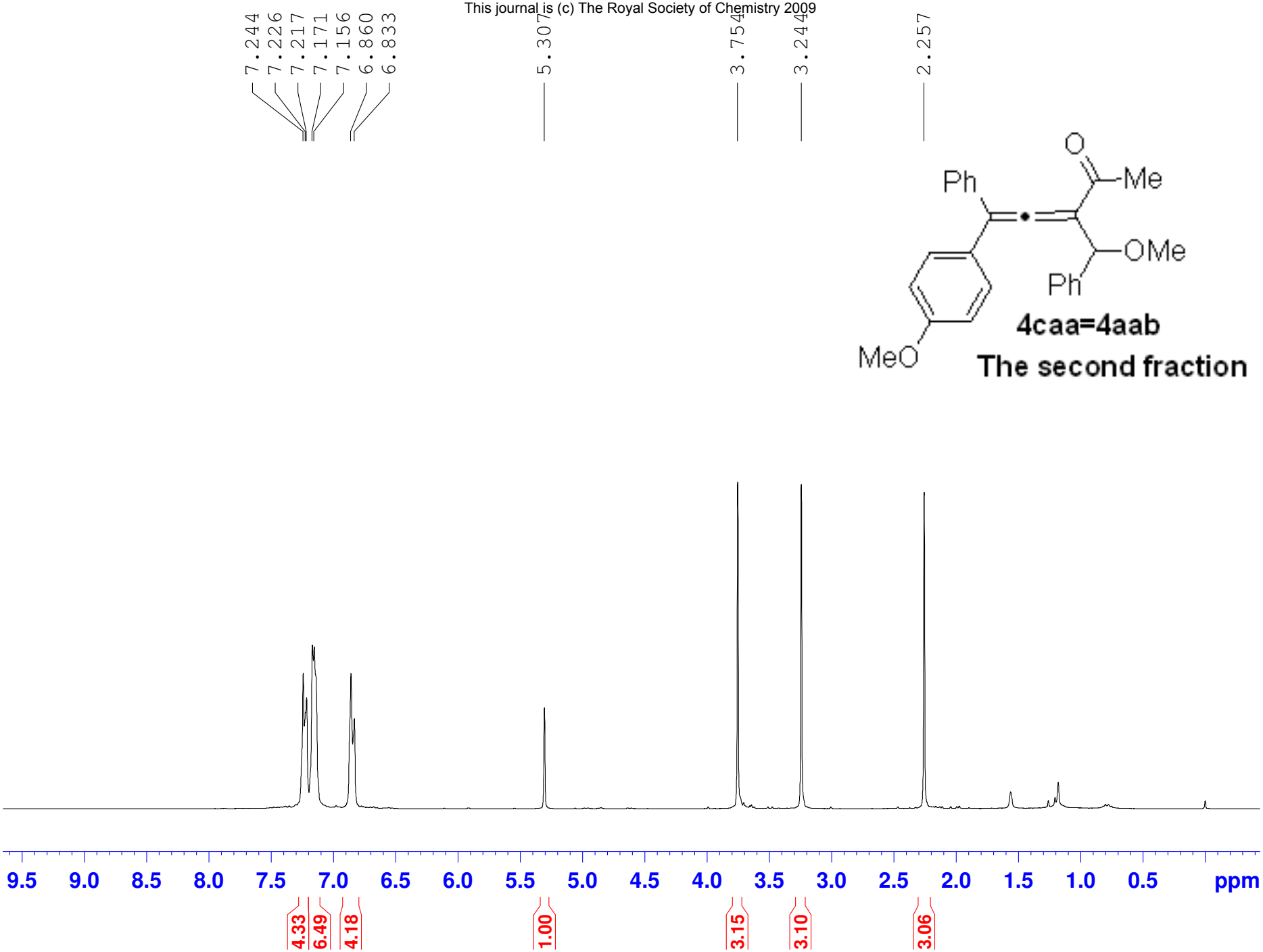
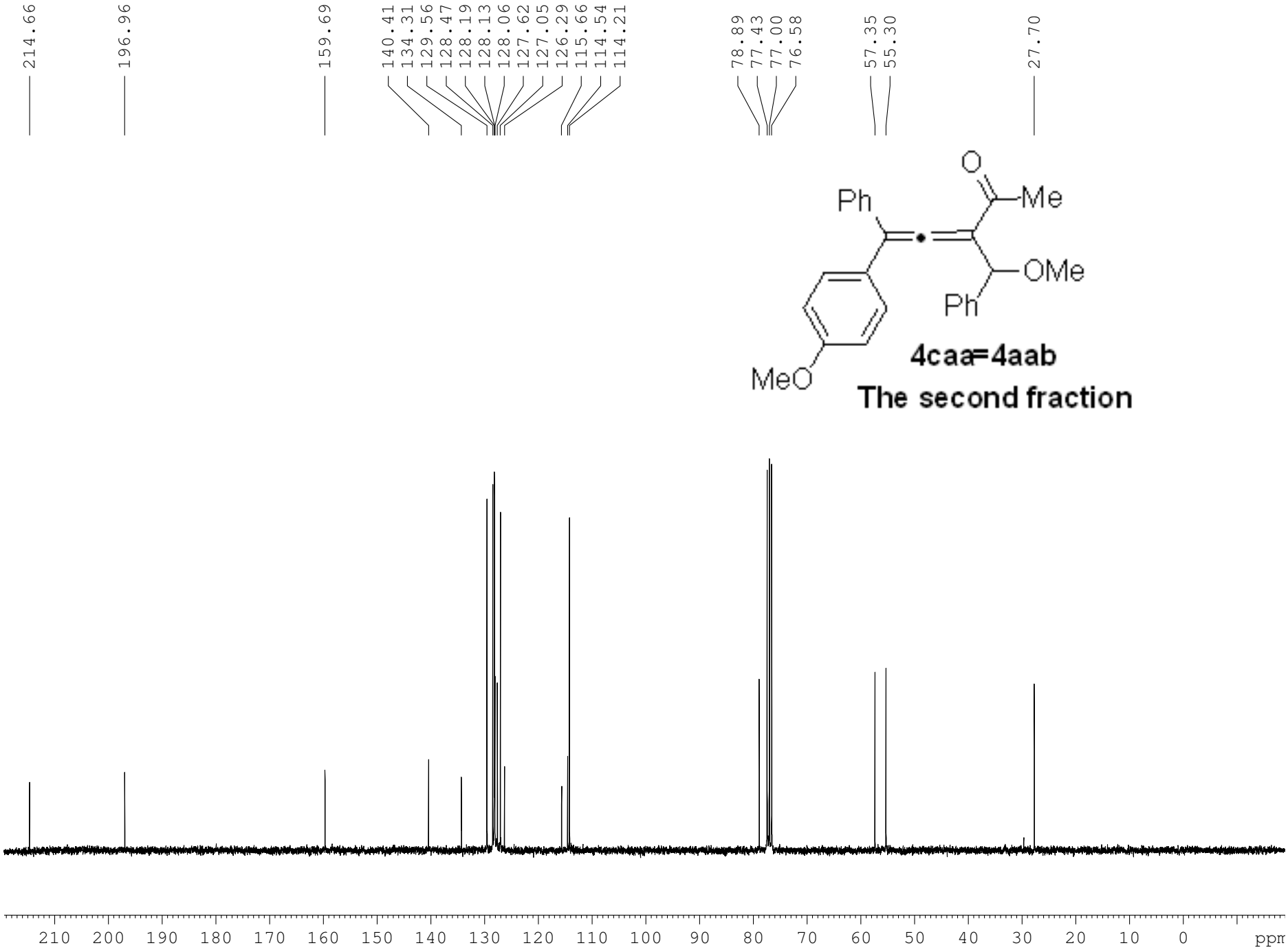
7.415
7.387
7.286
7.260
7.064
7.049
7.038
6.811
6.785
5.344
3.771
3.312
2.359
Ph
Ph
O
Me
OMe
MeO
4baa
9
8
7
6
5
4
3
2
1
ppm
5.04
3.81
2.08
2.02
1.00
3.07
3.03
3.01

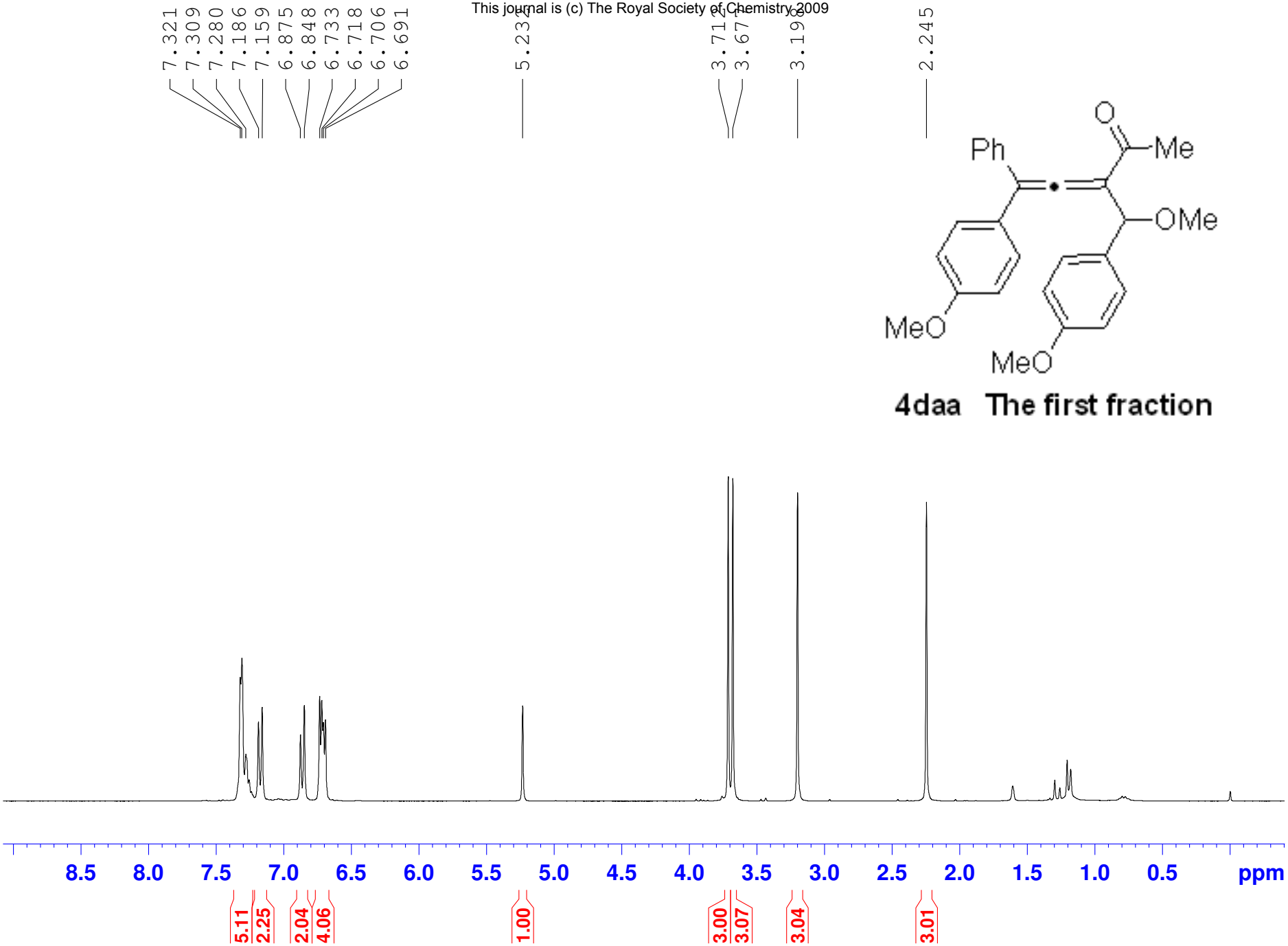

214.46
196.84
159.19
134.32
134.17
132.33
128.71
128.53
128.33
128.30
128.15
128.11
115.96
114.81
113.56
78.55
77.43
77.00
76.58
57.12
55.18
27.76
Ph
Ph
O
Me
OMe
MeO
4baa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.314
7.302
7.286
7.272
7.258
7.245
7.177
7.158
6.787
6.759
6.704
6.676
5.310
3.706
3.232
2.258
Ph
O
Me
OMe
Ph
MeO
4caa=4aab
The first fraction
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
7.15
3.34
4.09
1.00
3.03
3.04
3.02

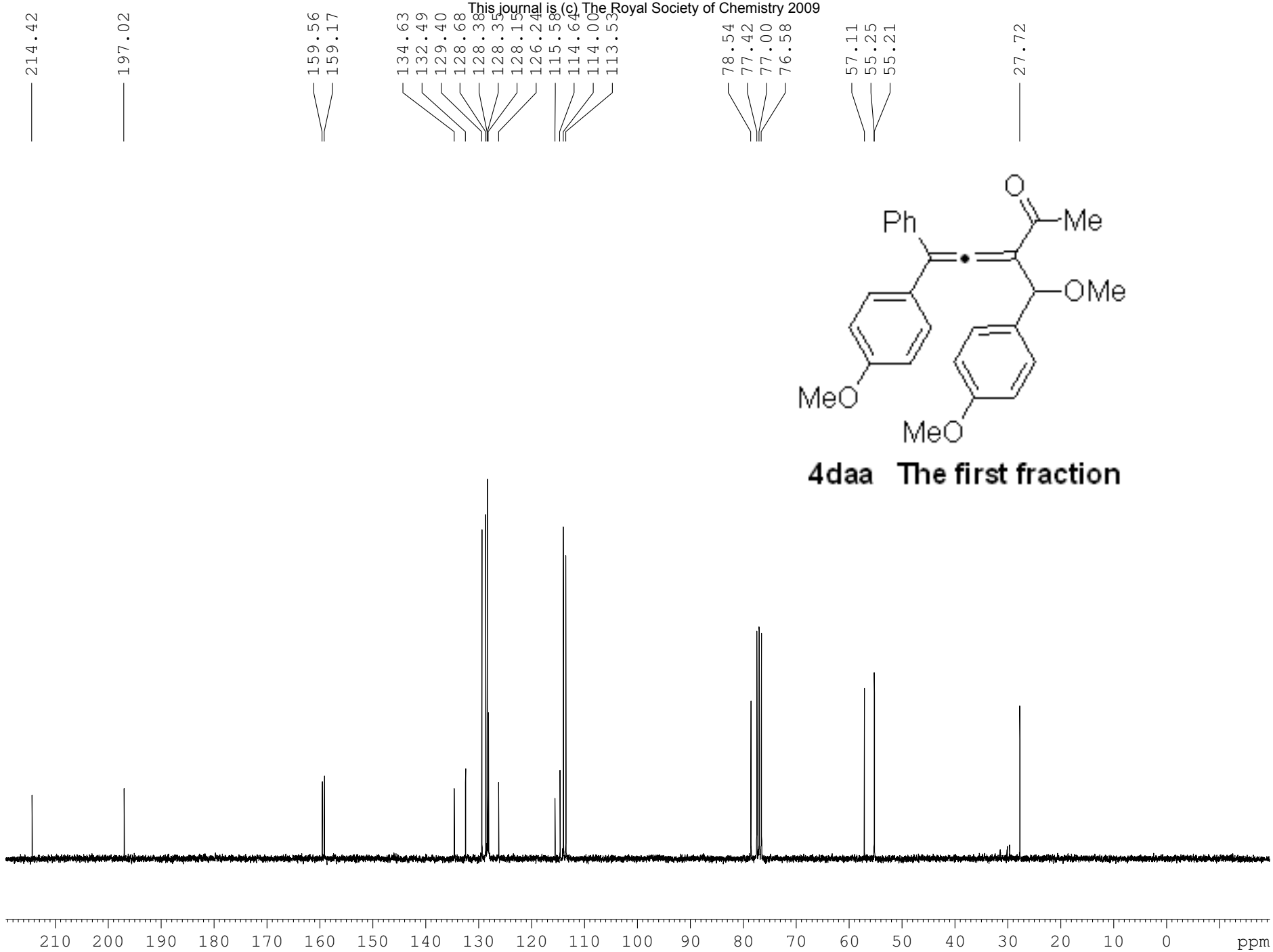

214.68
196.96
159.57
140.47
134.54
129.40
128.70
128.36
128.19
128.16
127.64
127.05
126.09
115.66
114.52
113.97
78.84
77.43
77.00
76.58
57.34
55.25
27.71
Ph
O
Me
OMe
Ph
MeO
4caa=4aab
The first fraction
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

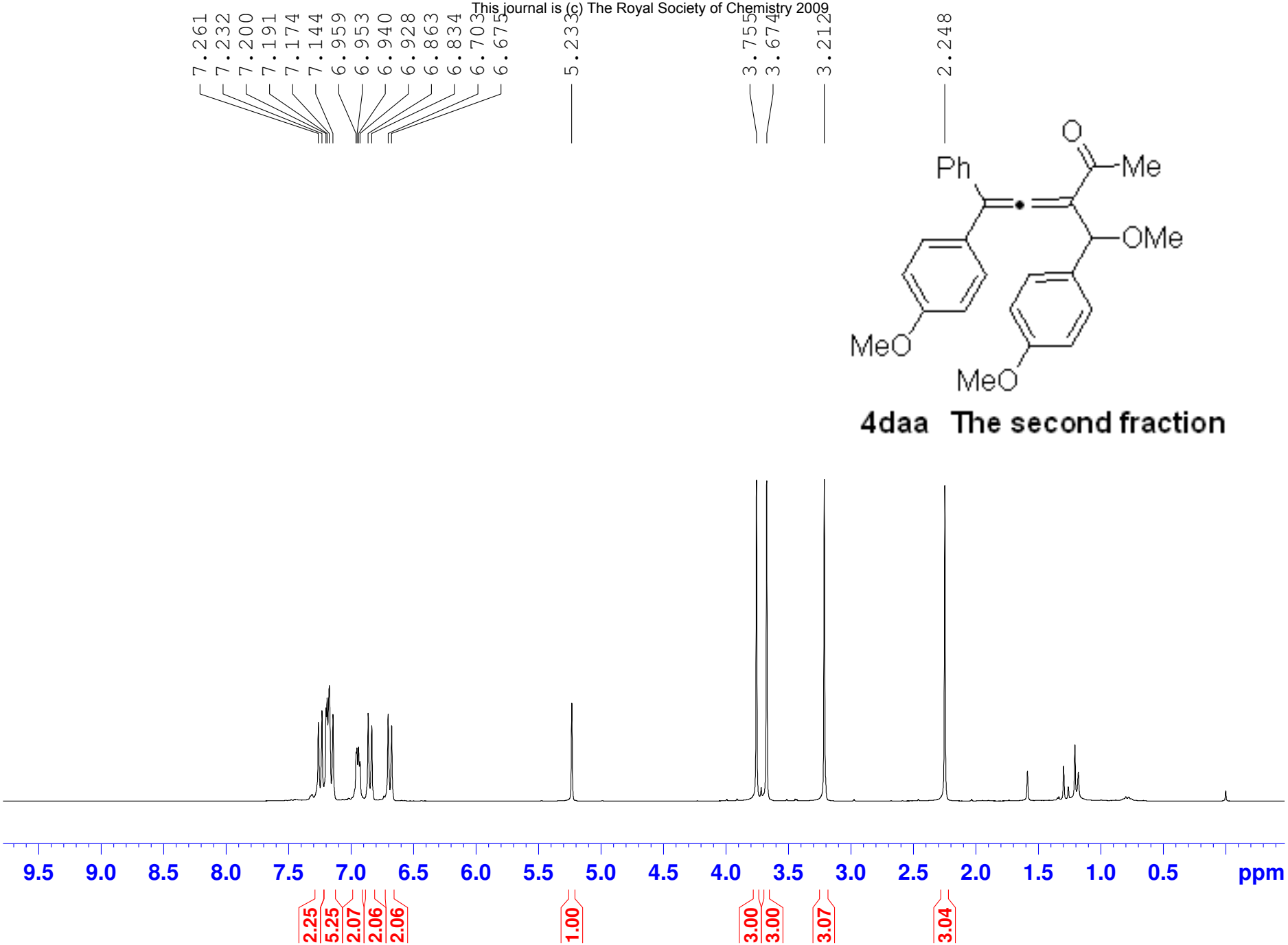

7.244
7.226
7.217
7.171
7.156
6.860
6.833
5.307
3.754
3.244
2.257
Ph
O
Me
OMe
Ph
MeO
4caa=4aab
The second fraction
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.33
6.49
4.18
1.00
3.15
3.10
3.06


214.66
196.96
159.69
140.41
134.31
129.56
128.47
128.19
128.13
128.06
127.62
127.05
126.29
115.66
114.54
114.21
78.89
77.43
77.00
76.58
57.35
55.30
27.70
Ph
O
Me
OMe
Ph
MeO
4caa=4aab
The second fraction
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

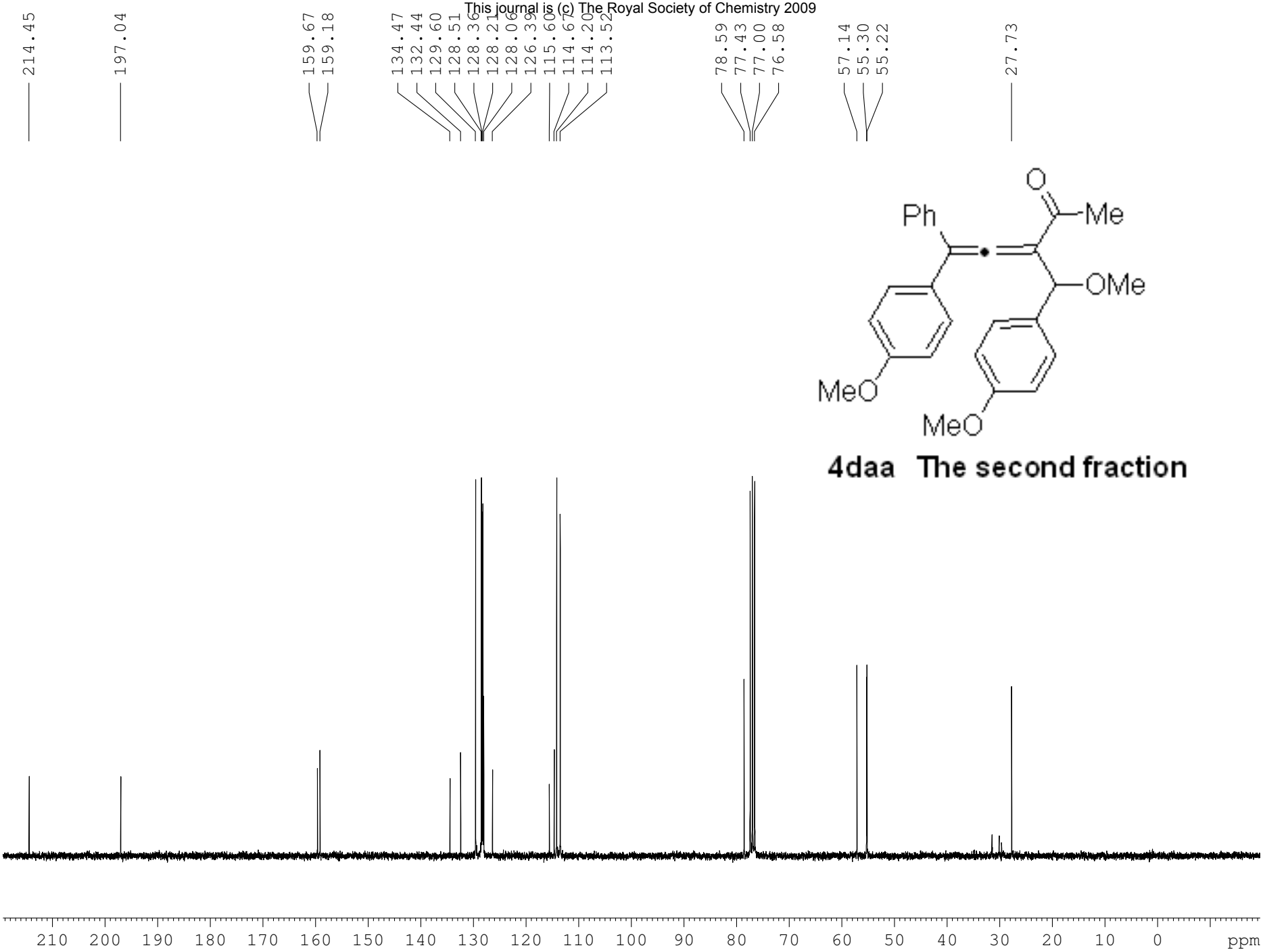


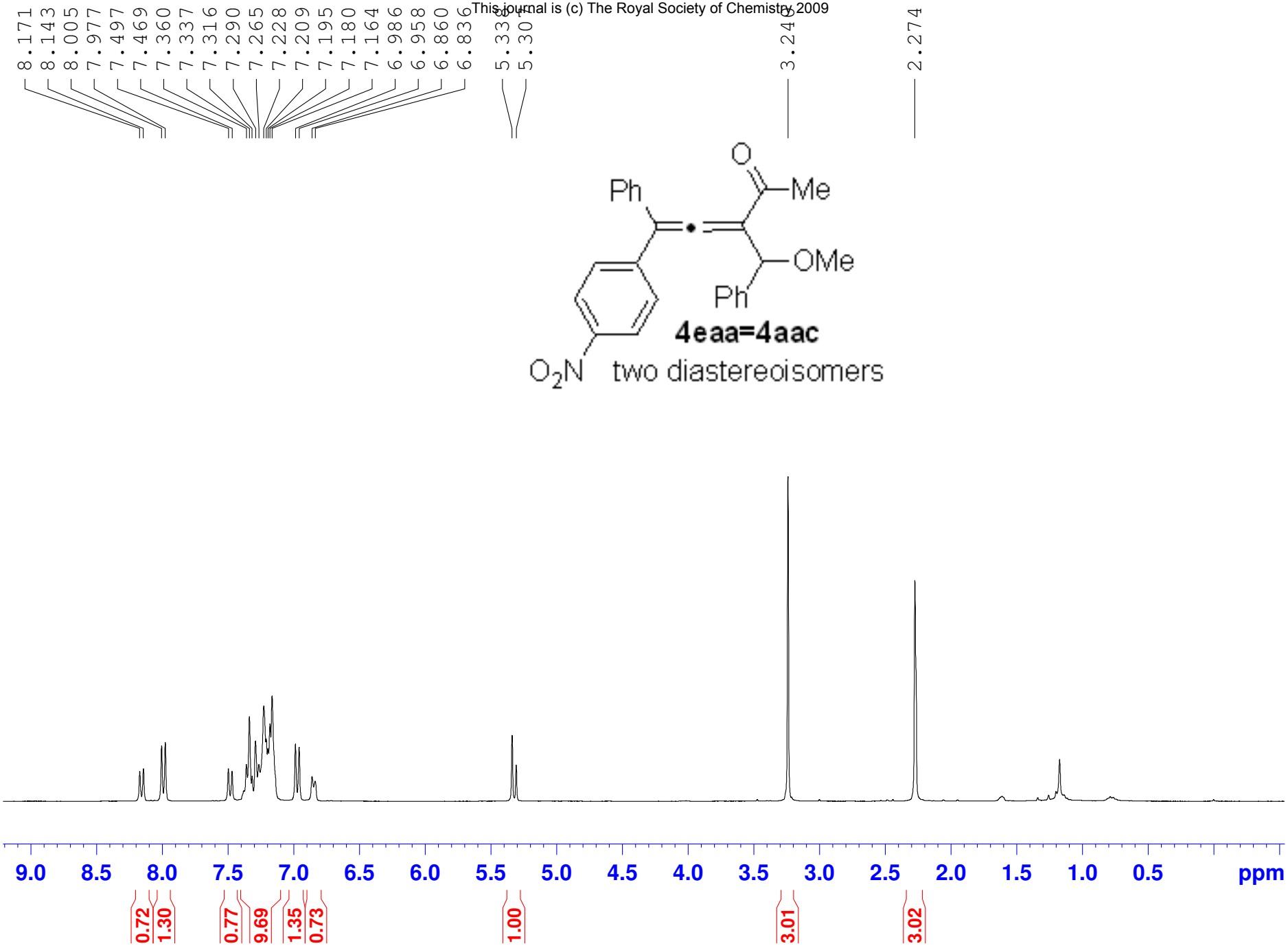
4daa The first fraction

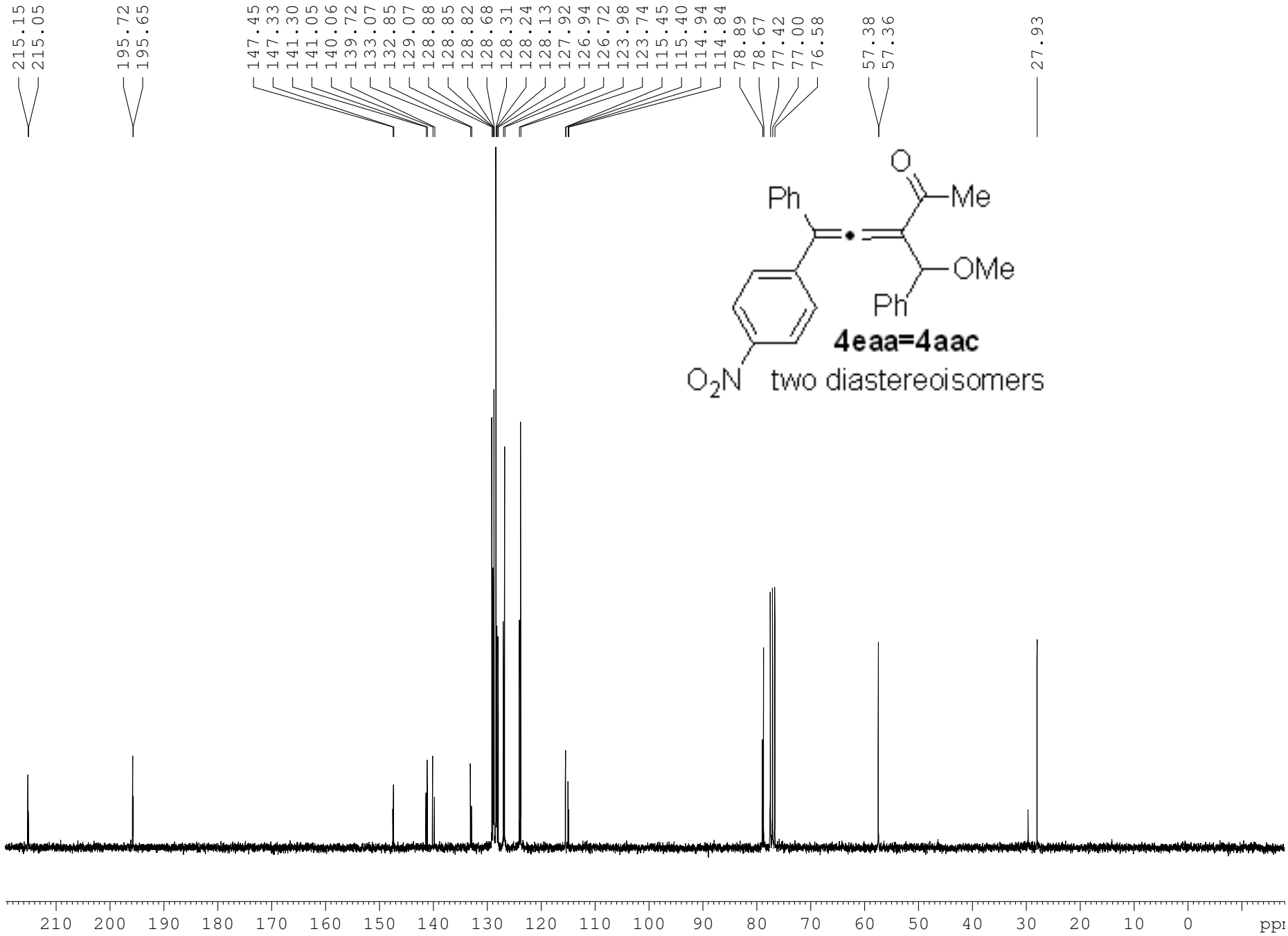

214.42
197.02
159.56
159.17
134.63
132.49
129.40
128.68
128.38
128.35
128.15
126.24
115.58
114.64
114.00
113.53
78.54
77.42
77.00
76.58
57.11
55.25
55.21
27.72
O
Ph
Me
OMe
MeO
MeO
4daa The first fraction
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

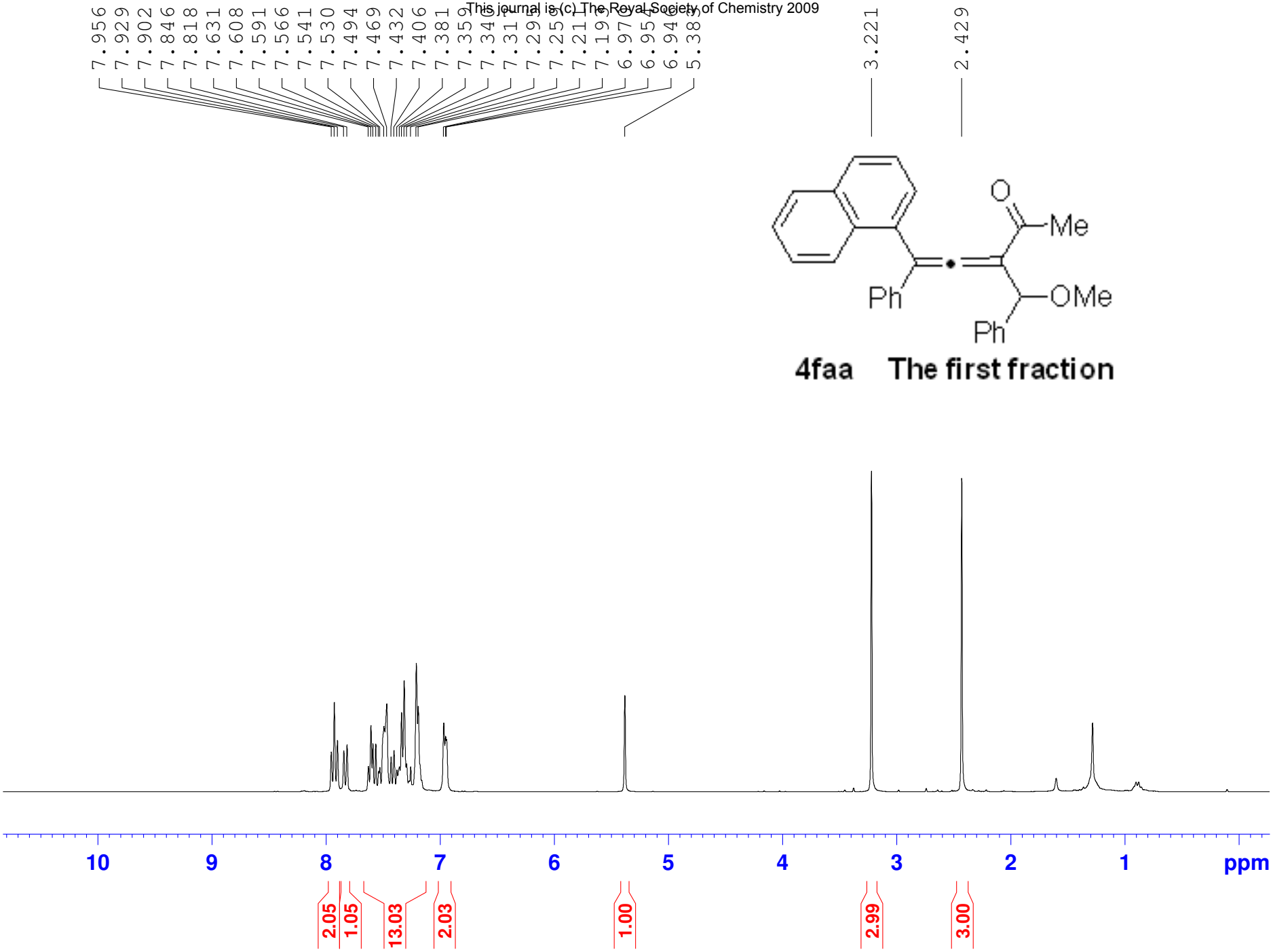


4daa The second fraction


214.45
197.04
159.67
159.18
134.47
132.44
129.60
128.51
128.36
128.21
128.06
126.39
115.60
114.67
114.20
113.52
78.59
77.43
77.00
76.58
57.14
55.30
55.22
27.73
Ph
O
Me
OMe
MeO
MeO
4daa The second fraction
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


8.171
8.143
8.005
7.977
7.497
7.469
7.360
7.337
7.316
7.290
7.265
7.228
7.209
7.195
7.180
7.164
6.986
6.958
6.860
6.836
5.331
5.301
3.240
2.274
Ph
O
Me
OMe
Ph
O2N
4eaa=4aac
two diastereoisomers
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.72
1.30
0.77
9.69
1.35
0.73
1.00
3.01
3.02


215.15
215.05
195.72
195.65
147.45
147.33
141.30
141.05
140.06
139.72
133.07
132.85
129.07
128.88
128.85
128.82
128.68
128.31
128.24
128.13
127.92
126.94
126.72
123.98
123.74
115.45
115.40
114.94
114.84
78.89
78.67
77.42
77.00
76.58
57.38
57.36
27.93
Ph
O
Me
OMe
Ph
O_2N
4eaa=4aac
two diastereoisomers
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



4faa The first fraction

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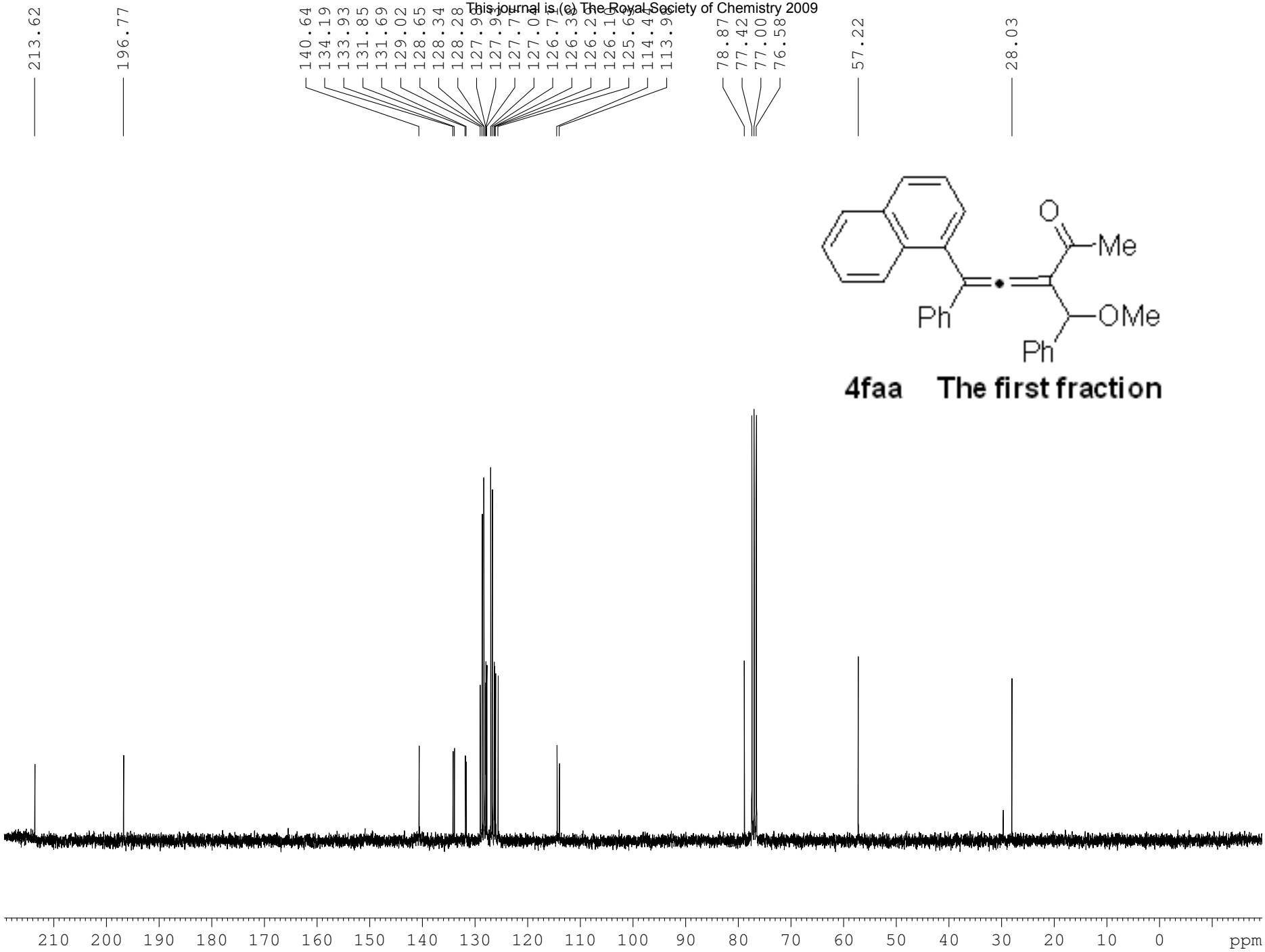
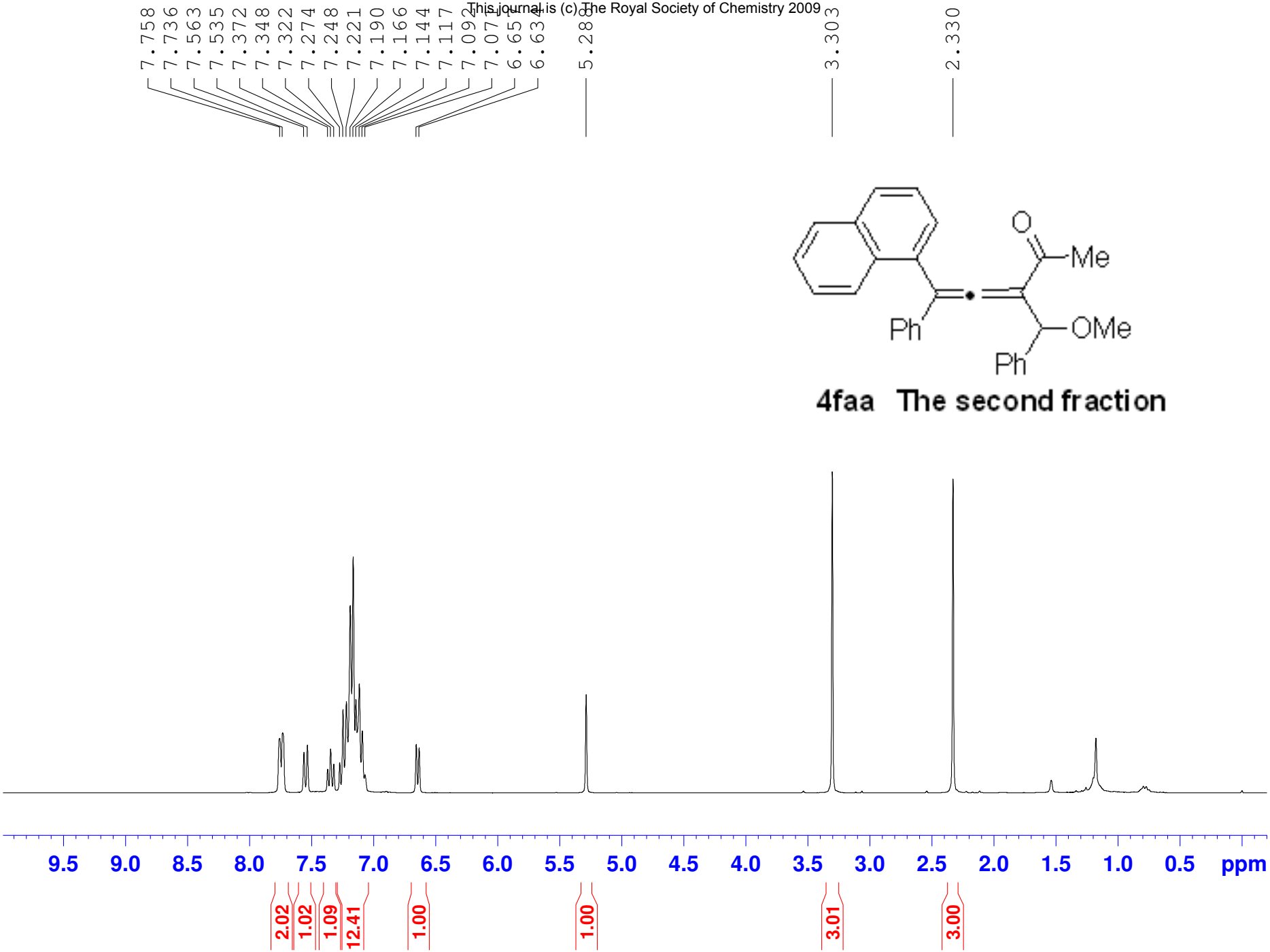


4faa The first fraction


7.758
7.736
7.563
7.535
7.372
7.348
7.322
7.274
7.248
7.221
7.190
7.166
7.144
7.117
7.092
7.071
6.654
6.634
5.280
3.303
2.330
O
Me
Ph
OMe
Ph
4faa The second fraction
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.02
1.02
1.09
12.41
1.00
1.00
3.01
3.00

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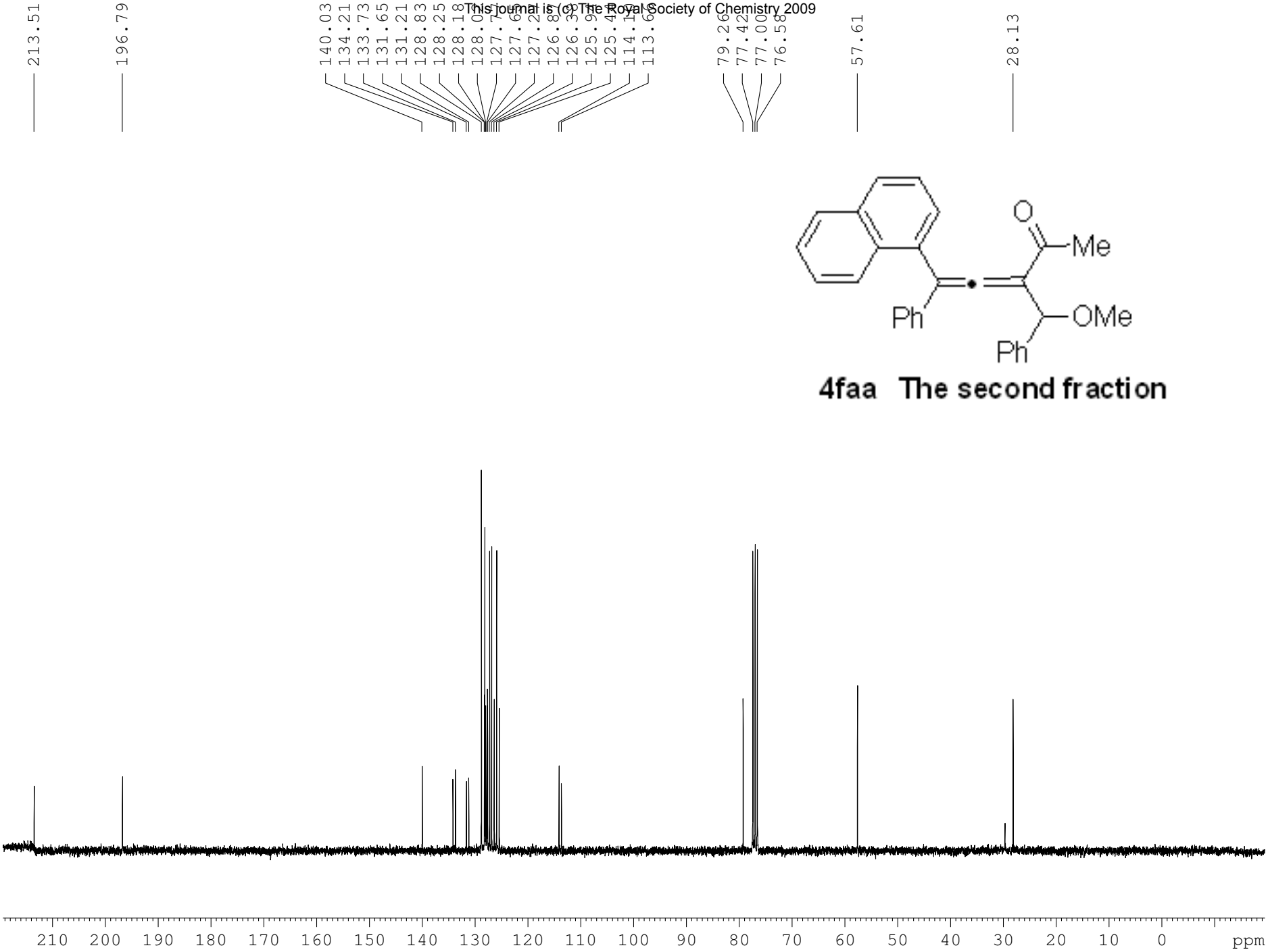
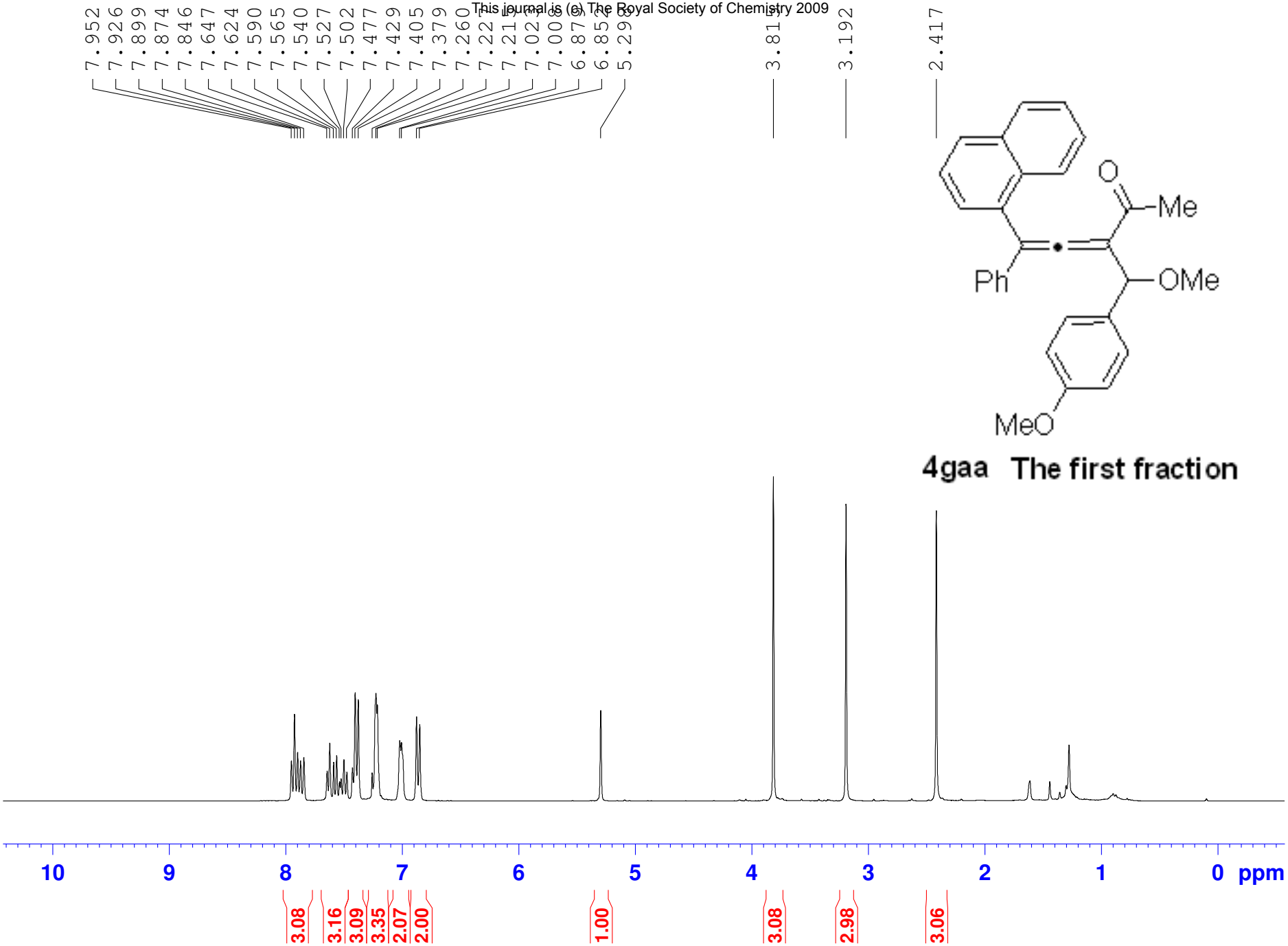


4faa The second fraction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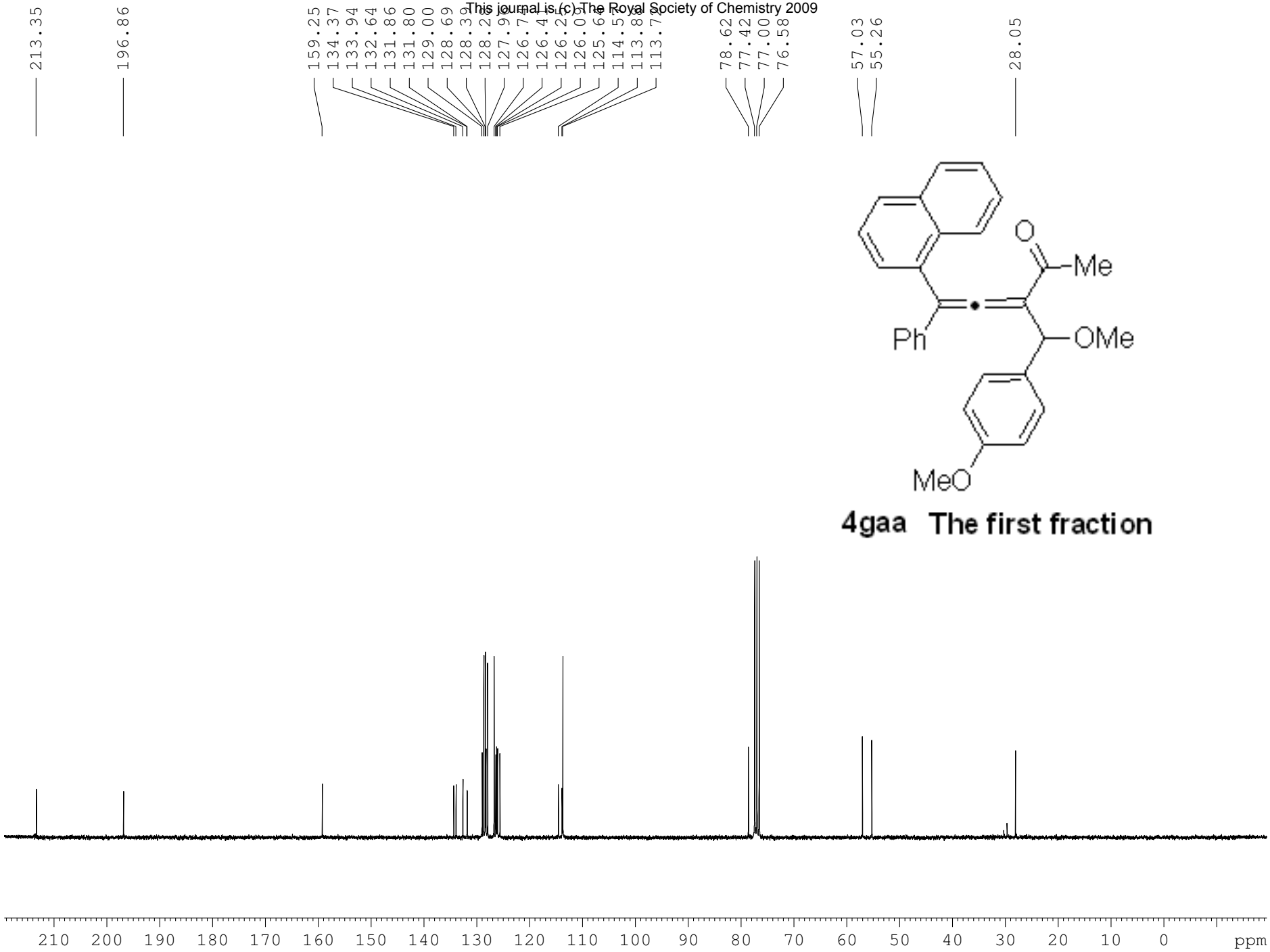
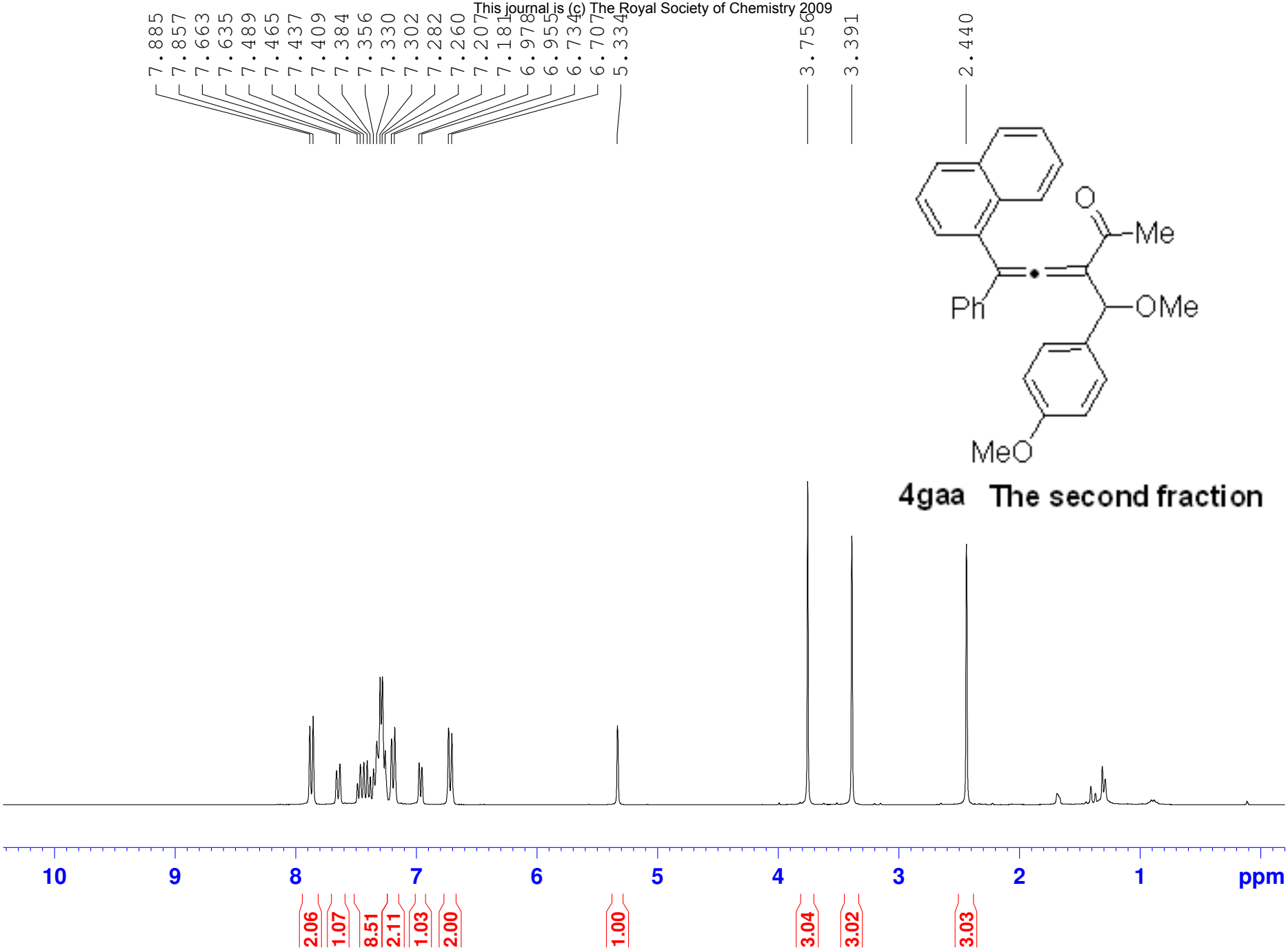
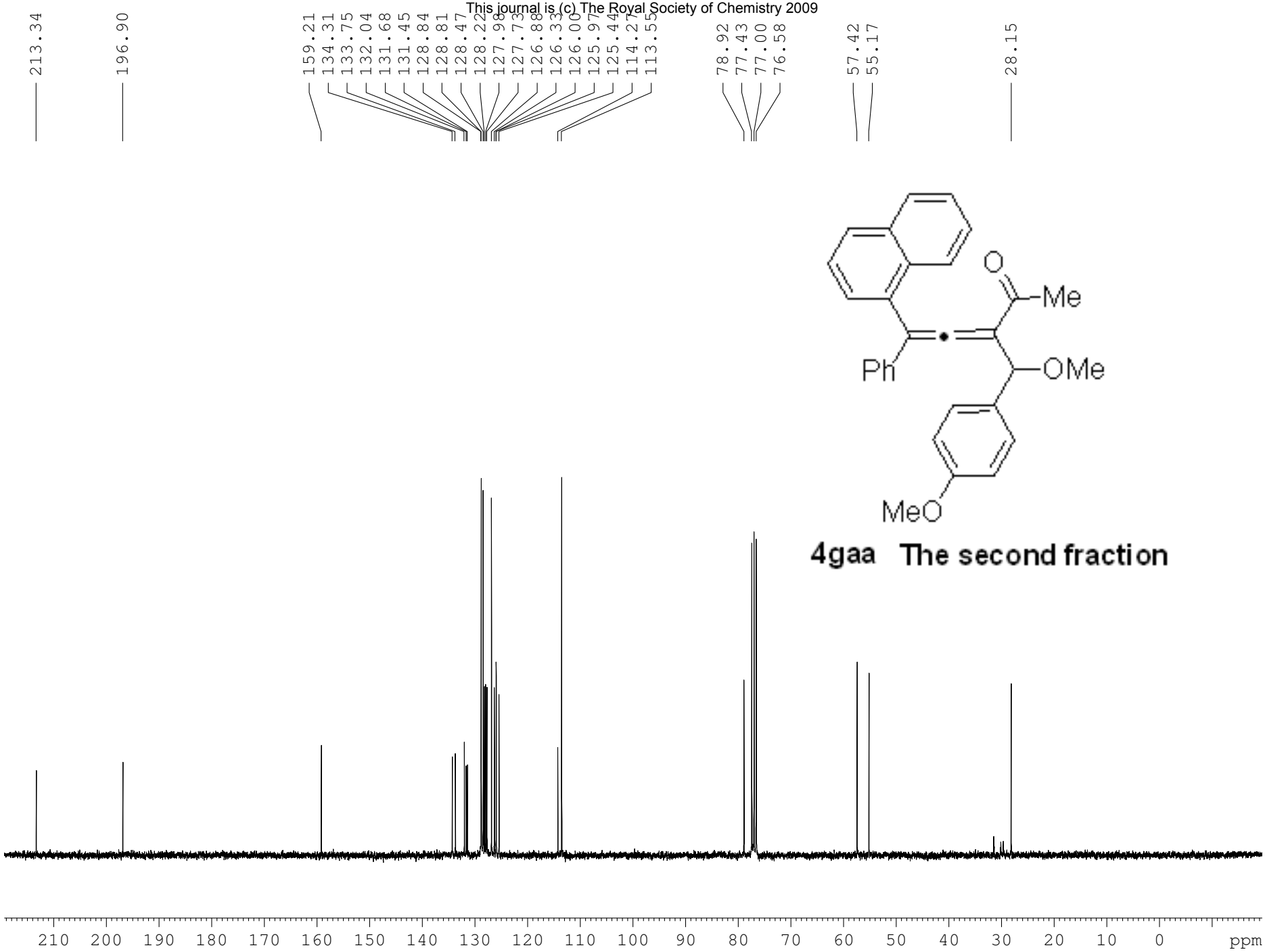
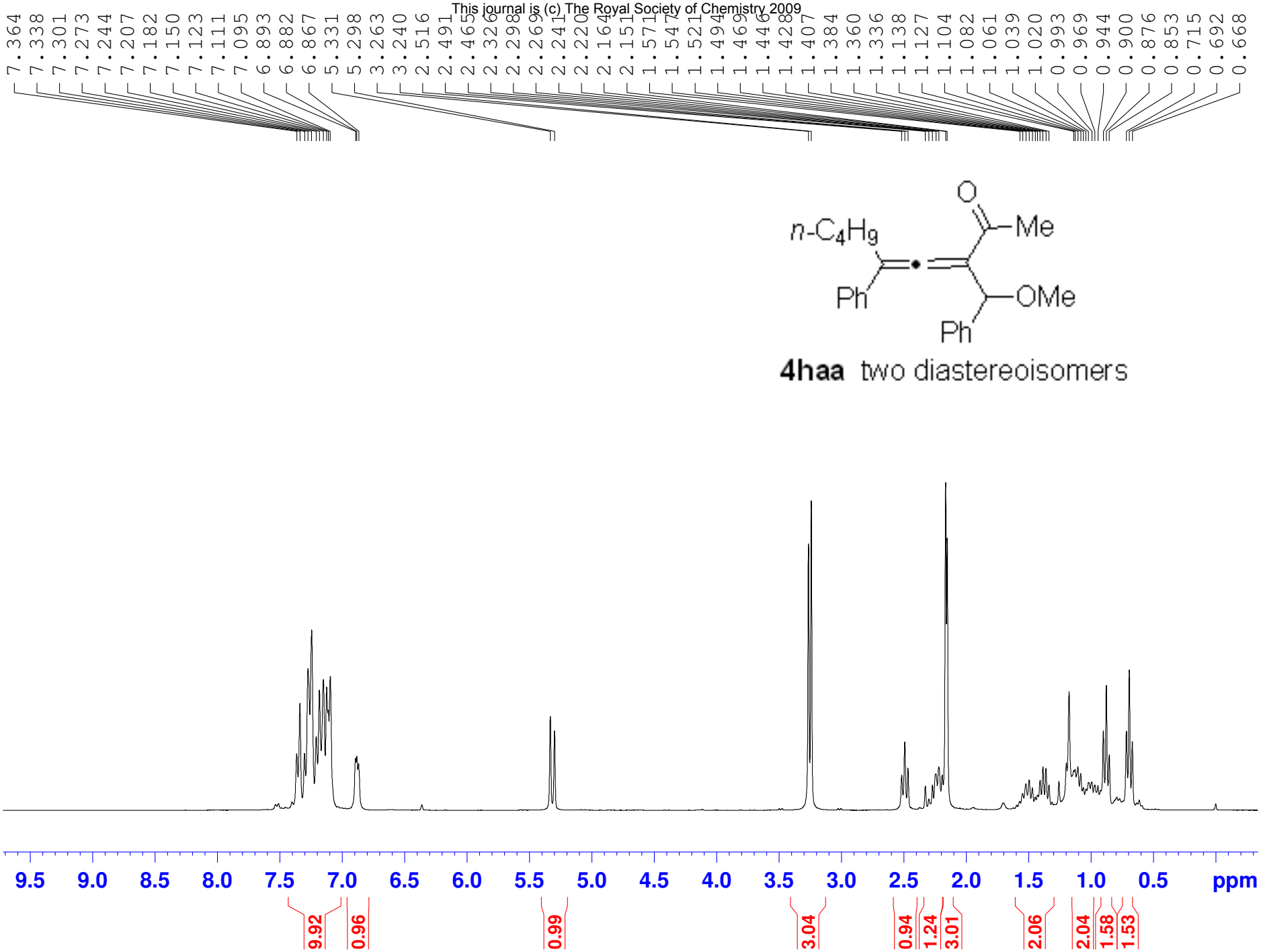
7.926
7.899
7.874
7.846
7.647
7.624
7.590
7.565
7.540
7.527
7.502
7.477
7.429
7.405
7.379
7.260
7.22
7.21
7.02
7.00
6.87
6.85
5.29
3.81
3.192
2.417
O
Me
Ph
OMe
MeO
4gaa The first fraction
10
9
8
7
6
5
4
3
2
1
0 ppm
3.08
3.16
3.09
3.35
2.07
2.00
1.00
3.08
2.98
3.06



4gaa The first fraction


7.885
7.857
7.663
7.635
7.489
7.465
7.437
7.409
7.384
7.356
7.330
7.302
7.282
7.260
7.207
7.181
6.978
6.955
6.734
6.707
5.334
3.756
3.391
2.440
O
Me
Ph
OMe
MeO
4gaa The second fraction
10
9
8
7
6
5
4
3
2
1
ppm
2.06
1.07
8.51
2.11
1.03
2.00
1.00
3.04
3.02
3.03


213.34
196.90
159.21
134.31
133.75
132.04
131.68
131.45
128.84
128.81
128.47
128.22
127.98
127.73
126.88
126.33
126.00
125.97
125.44
114.27
113.55
78.92
77.43
77.00
76.58
57.42
55.17
28.15
O
Me
Ph
OMe
MeO
4gaa The second fraction
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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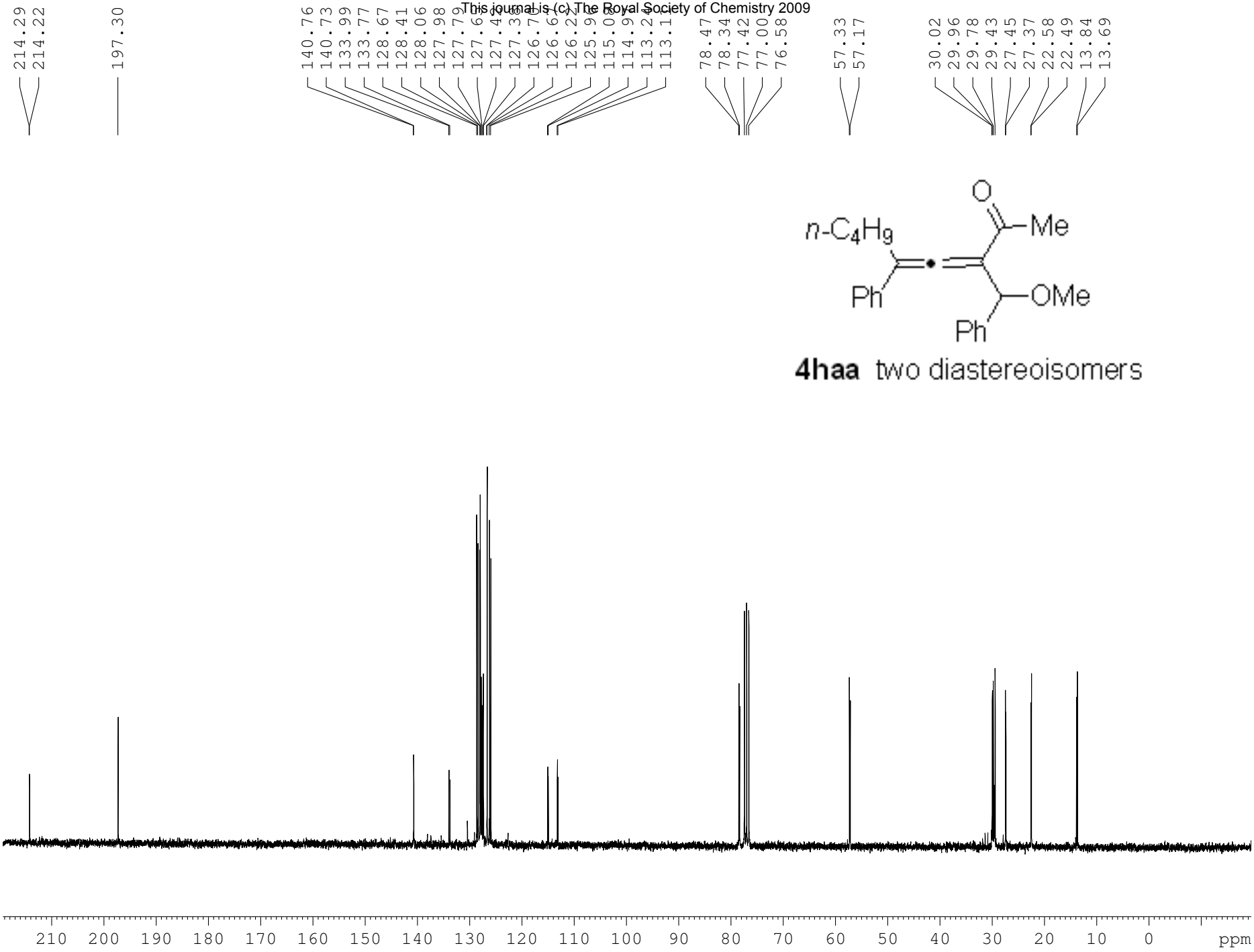
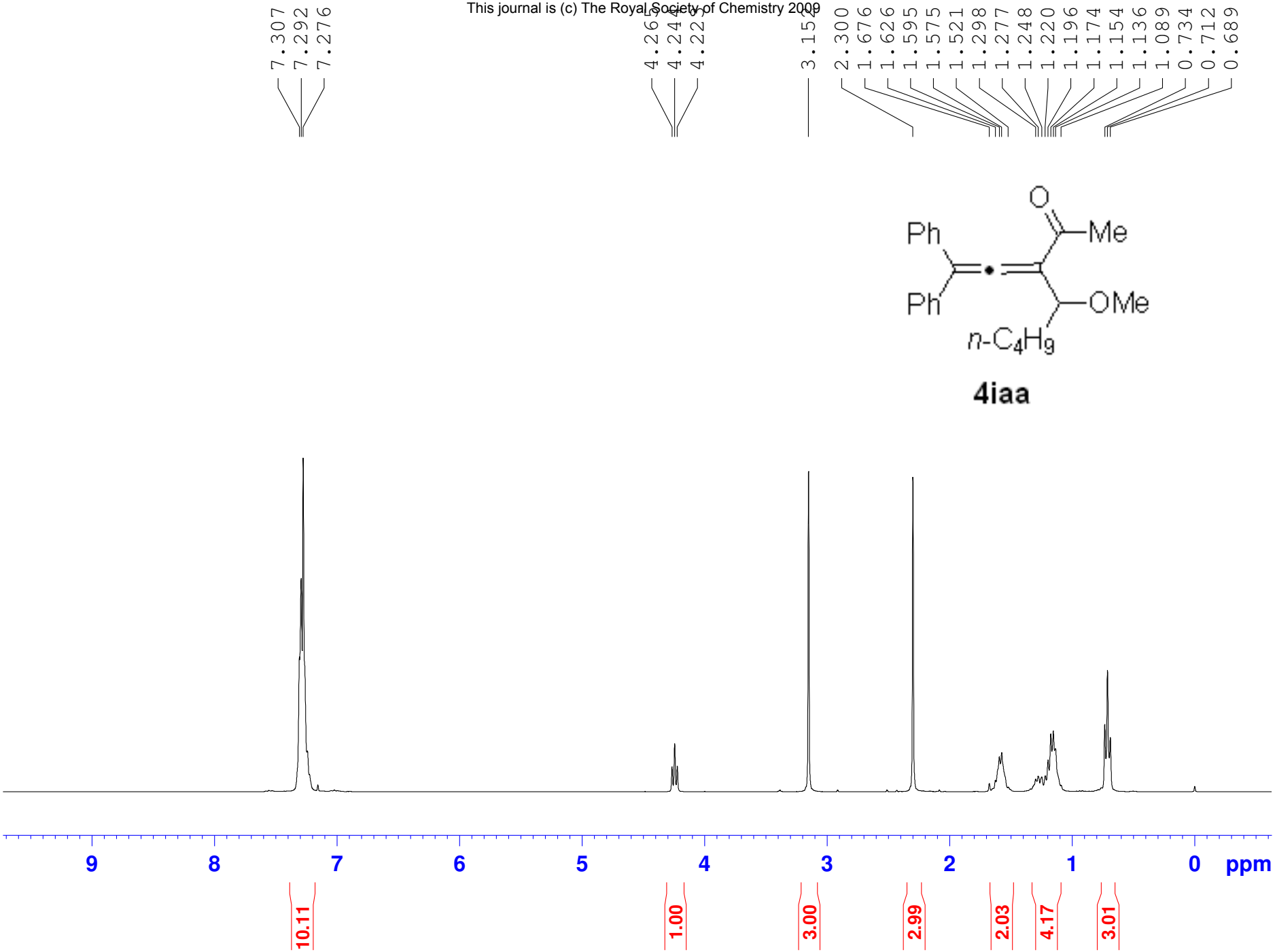
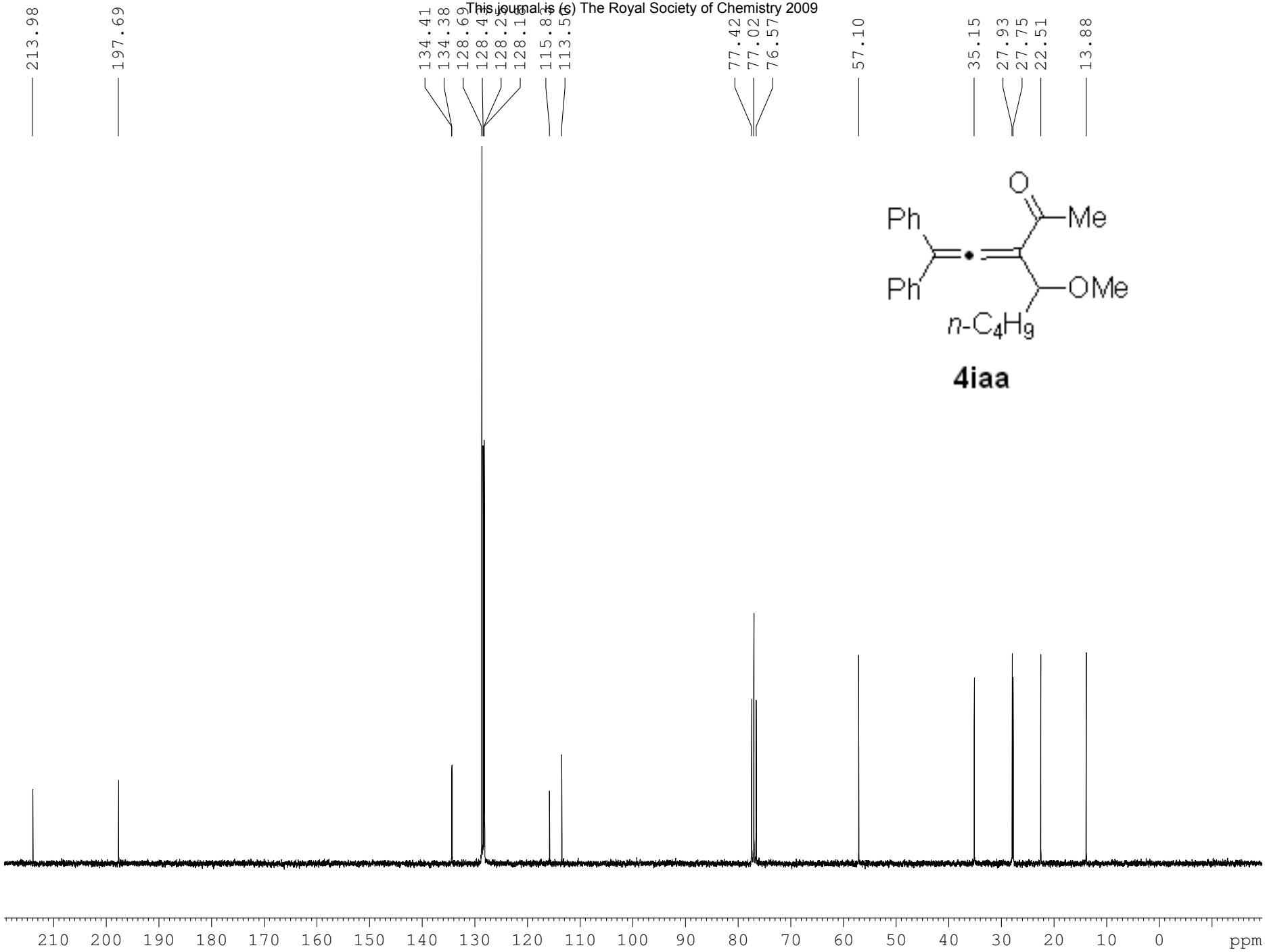
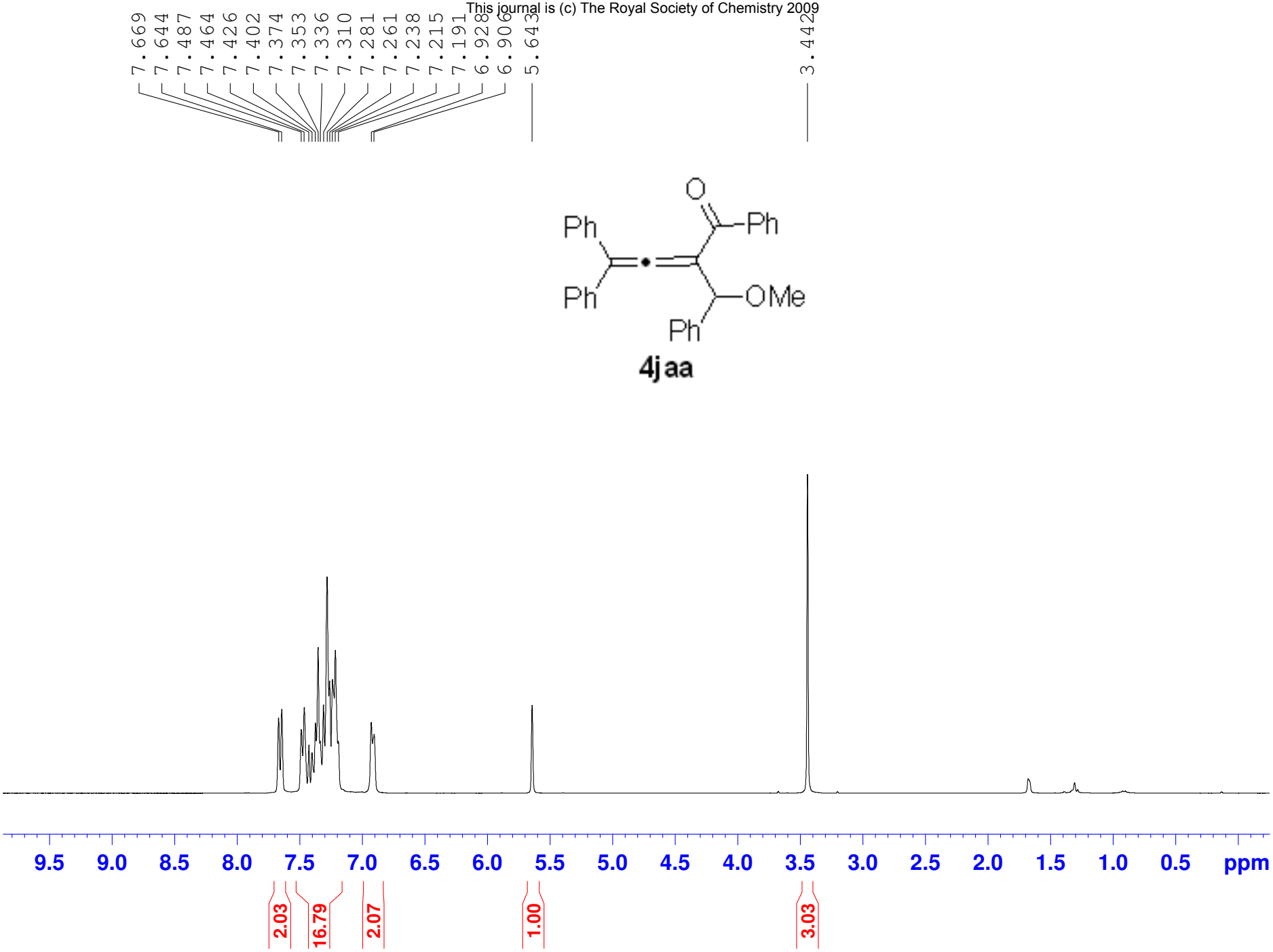
7.338
7.301
7.273
7.244
7.207
7.182
7.150
7.123
7.111
7.095
6.893
6.882
6.867
5.331
5.298
3.263
3.240
2.516
2.491
2.465
2.326
2.298
2.269
2.241
2.220
2.164
2.151
1.571
1.547
1.521
1.494
1.469
1.446
1.428
1.407
1.384
1.360
1.336
1.138
1.127
1.104
1.082
1.061
1.039
1.020
0.993
0.969
0.944
0.900
0.876
0.853
0.715
0.692
0.668
O
n-C4H9
Me
Ph
OMe
Ph
4haa two diastereoisomers
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
9.92
0.96
0.99
3.04
0.94
1.24
3.01
2.06
2.04
1.58
1.53


214.29
214.22
197.30
140.76
140.73
133.99
133.77
128.67
128.41
128.06
127.98
127.79
127.6
127.4
127.3
126.7
126.6
126.2
125.9
115.0
114.9
113.2
113.1
78.47
78.34
77.42
77.00
76.58
57.33
57.17
30.02
29.96
29.78
29.43
27.45
27.37
22.58
22.49
13.84
13.69
O
n-C4H9
Me
Ph
OMe
Ph
4haa two diastereoisomers
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.307
7.292
7.276
4.26
4.24
4.22
3.15
2.300
1.676
1.626
1.595
1.575
1.521
1.298
1.277
1.248
1.220
1.196
1.174
1.154
1.136
1.089
0.734
0.712
0.689
Ph
Ph
O
Me
OMe
n-C4H9
4iaa
9
8
7
6
5
4
3
2
1
0
ppm
10.11
1.00
3.00
2.99
2.03
4.17
3.01


213.98
197.69
134.41
134.38
128.69
128.41
128.26
128.16
115.85
113.50
77.42
77.02
76.57
57.10
35.15
27.93
27.75
22.51
13.88
Ph
Ph
O
Me
OMe
n-C4H9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

4iaa


7.669
7.644
7.487
7.464
7.426
7.402
7.374
7.353
7.336
7.310
7.281
7.261
7.238
7.215
7.191
6.928
6.906
5.643
3.442
Ph
Ph
O
Ph
OMe
Ph
4jaa
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
16.79
2.07
1.00
3.03

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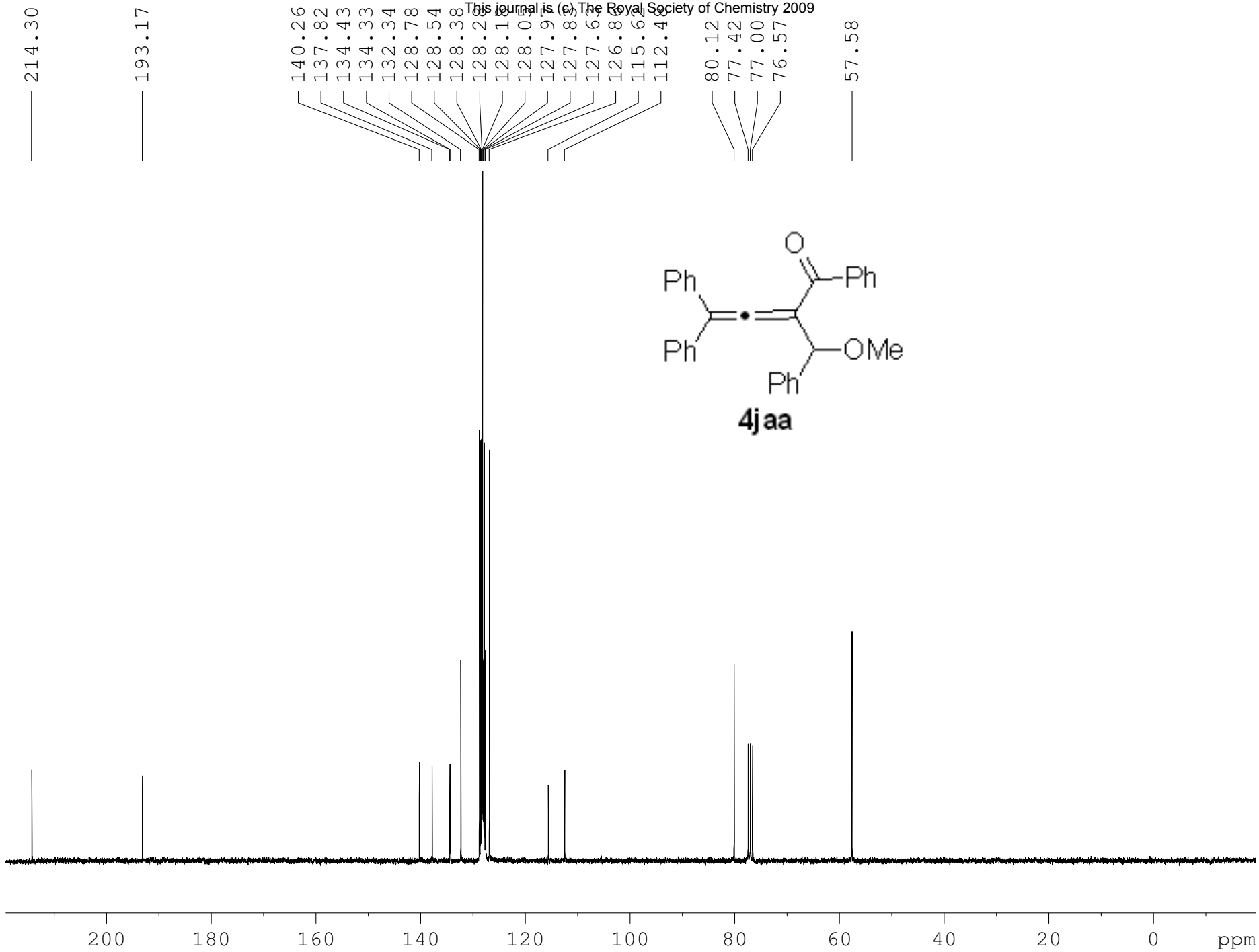

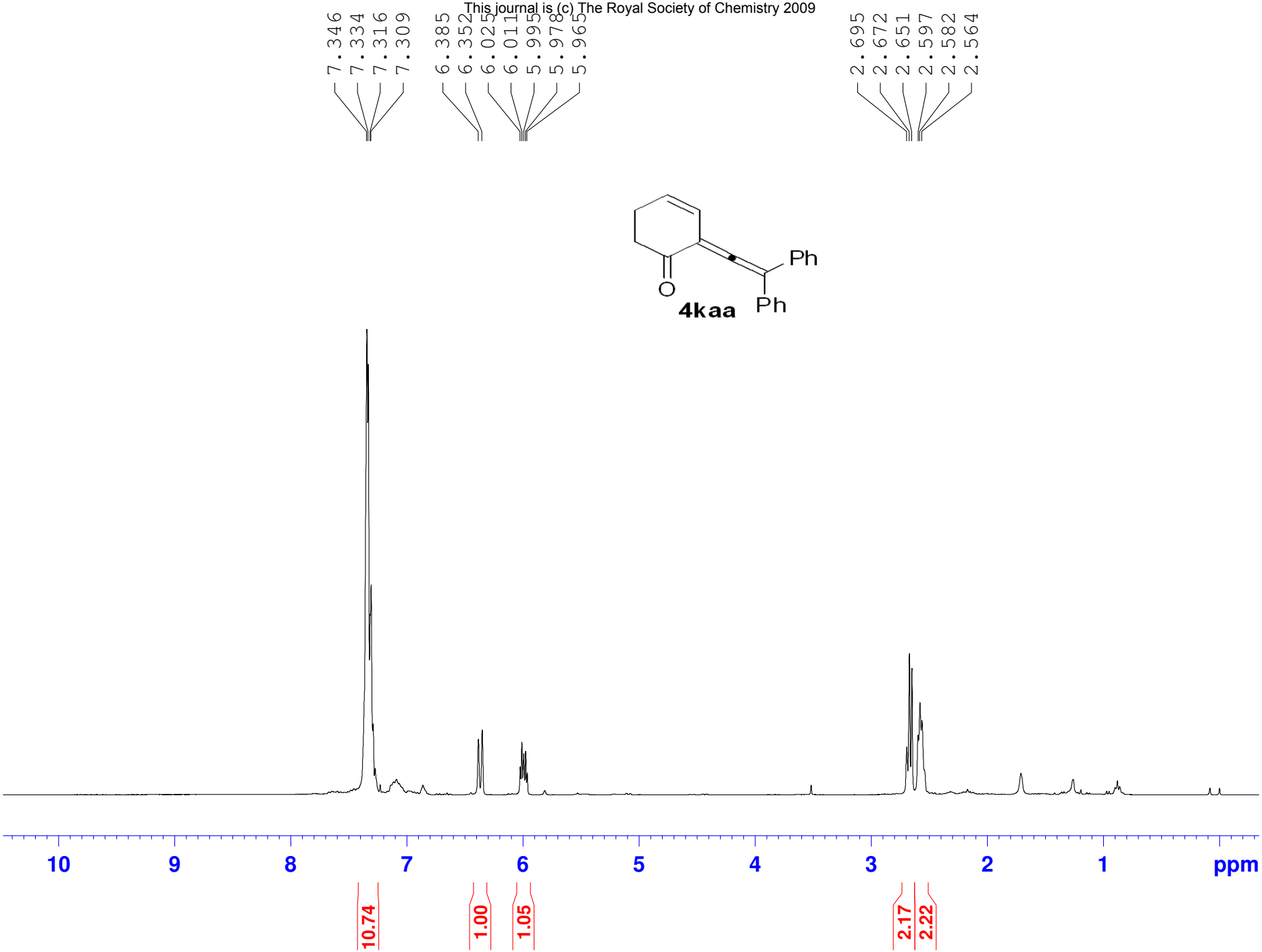
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2.672
2.651
2.597
2.582
2.564
Ph
O
Ph
4kaa
10
9
8
7
6
5
4
3
2
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ppm
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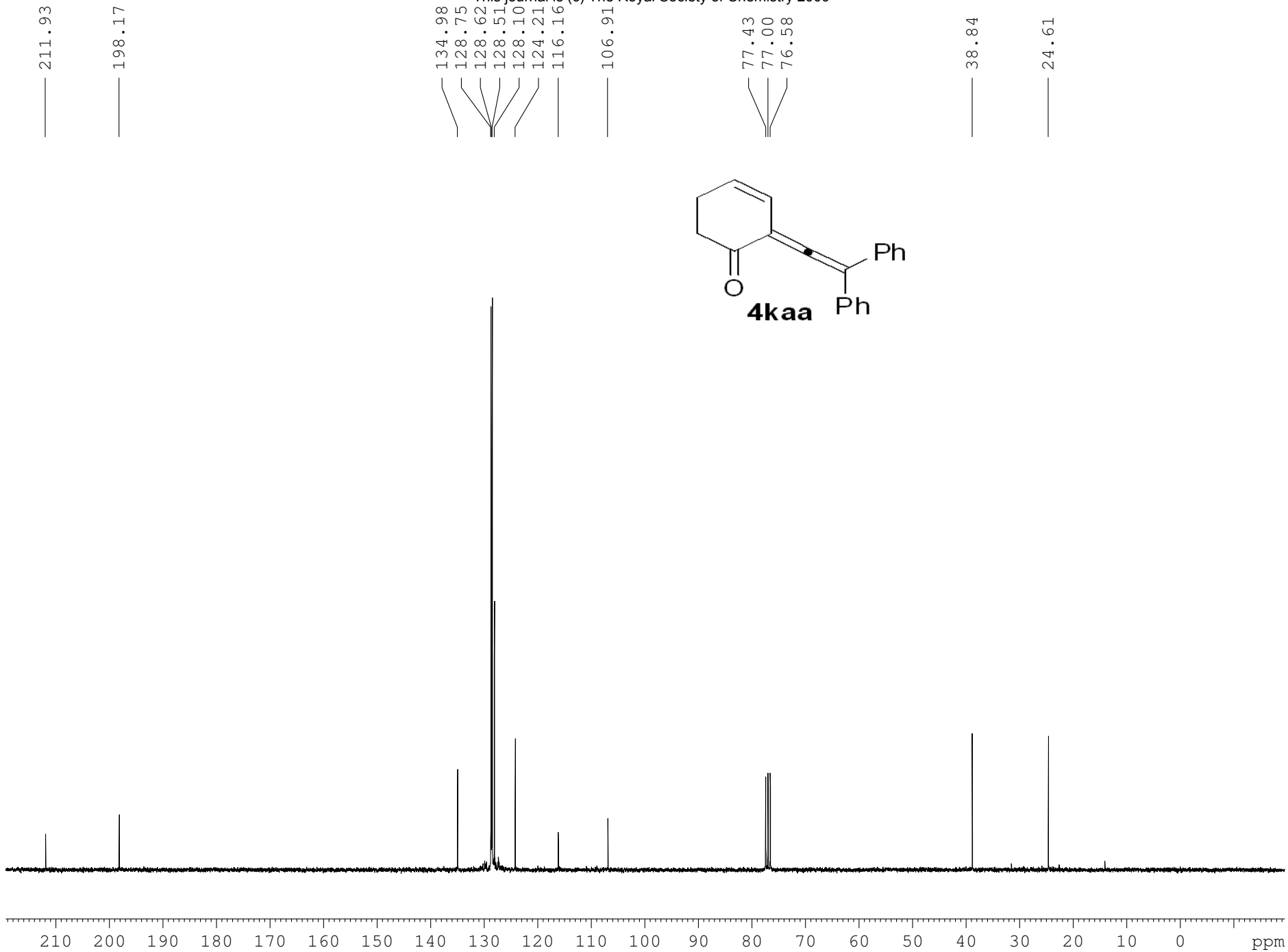
1.05
2.17
2.22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198.17
134.98
128.75
128.62
128.51
128.10
124.21
116.16
106.91
77.43
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76.58
38.84
24.61
Ph
O
Ph
4kaa
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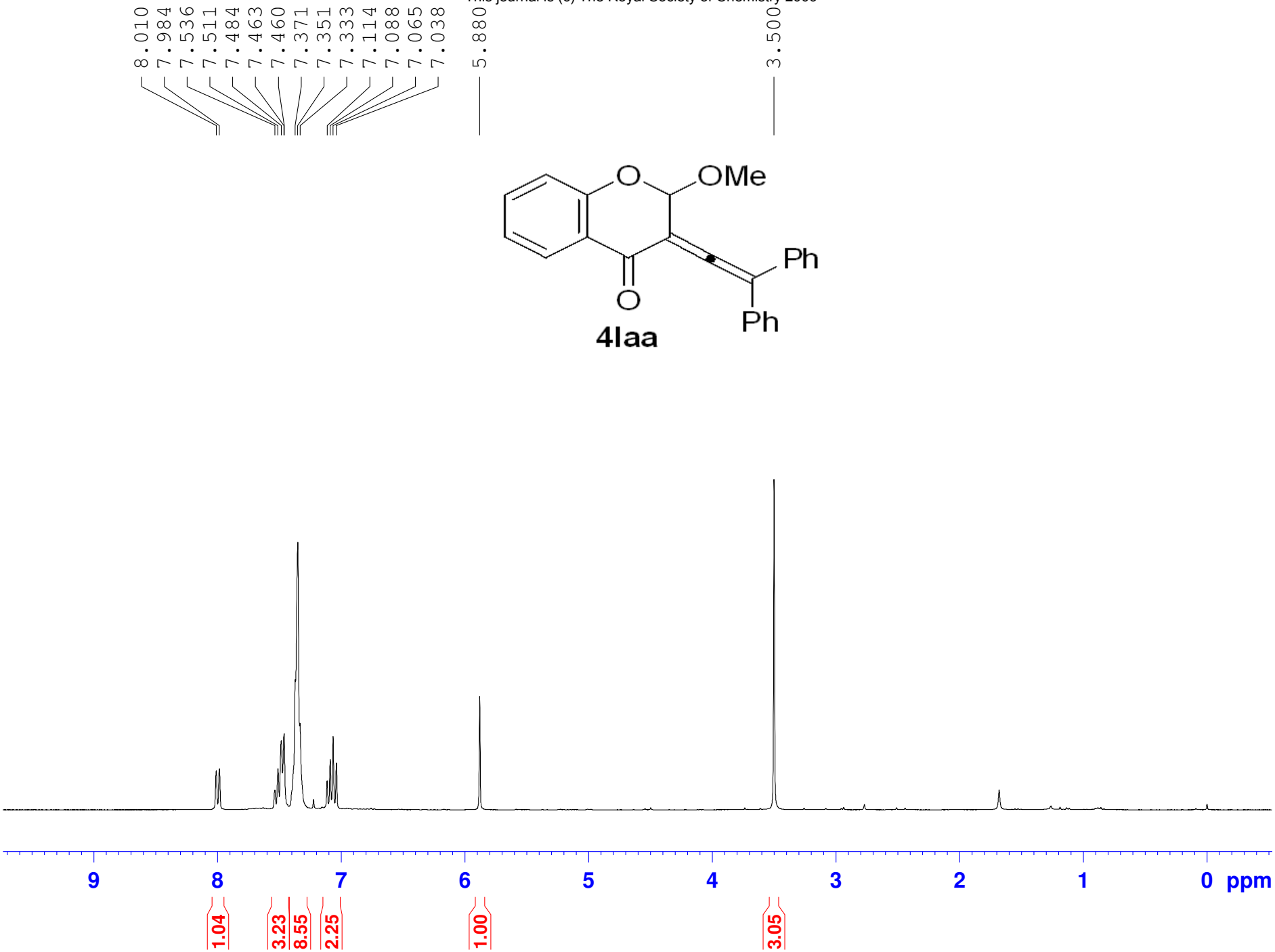
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7.371
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7.333
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7.088
7.065
7.038
5.880
3.500
O
OMe
Ph
Ph
O
4Iaa
9
8
7
6
5
4
3
2
1
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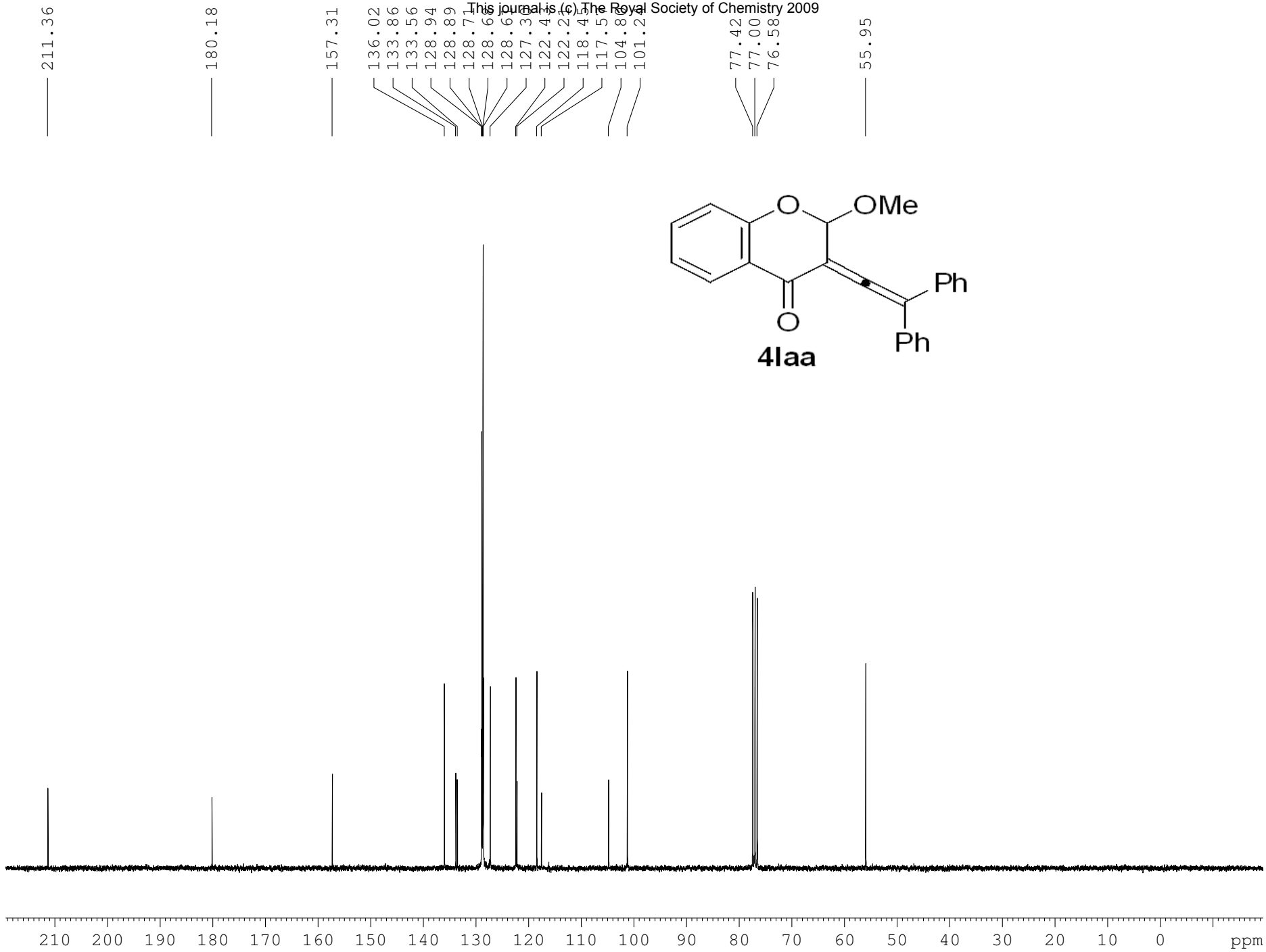
1.04
3.23
8.55
2.25
1.00
3.05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128.61
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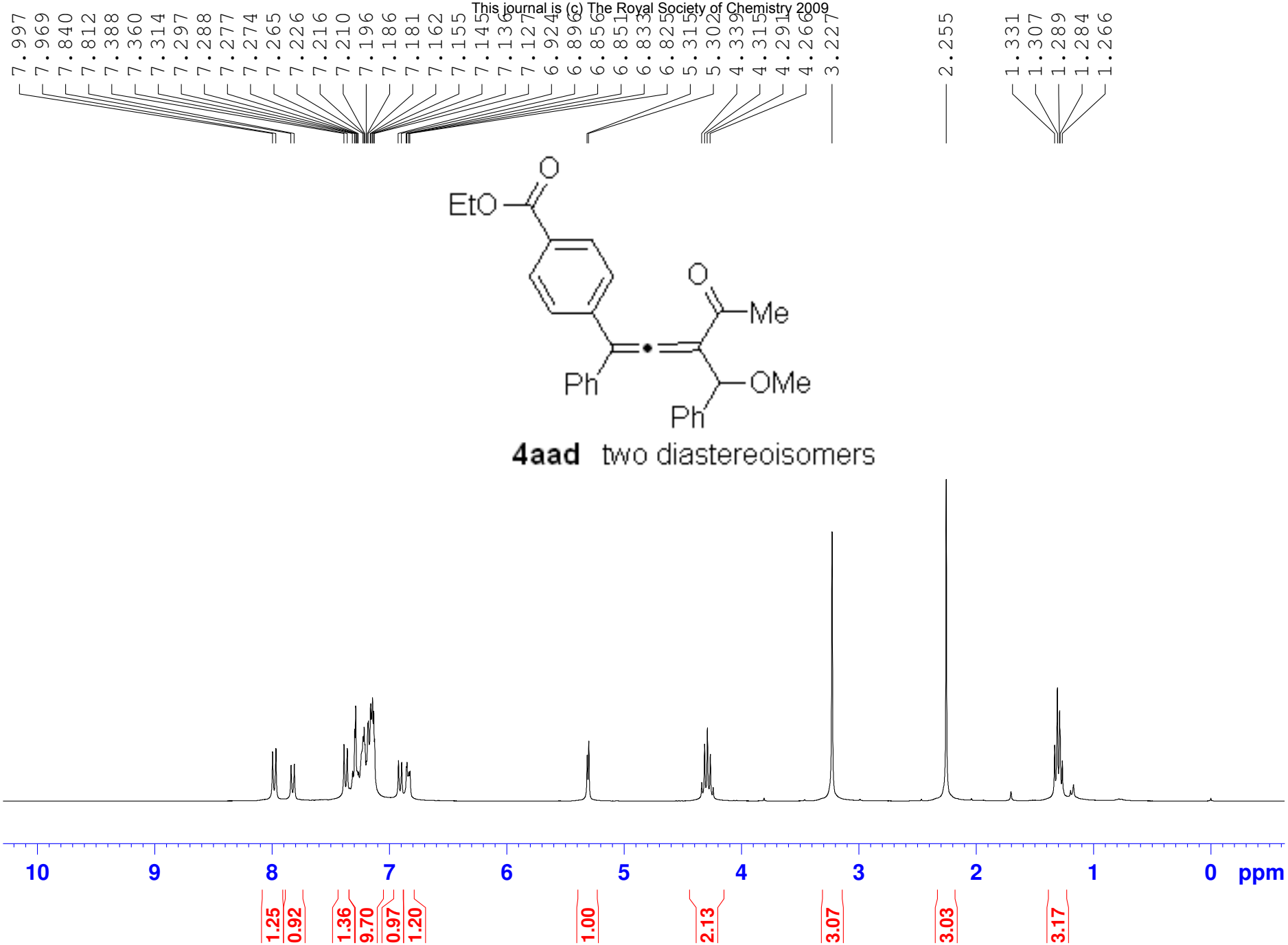
122.41
122.21
118.41
117.51
104.81
101.24
77.42
77.00
76.58
55.95
O
OMe
Ph
O
Ph
4Iaa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.277
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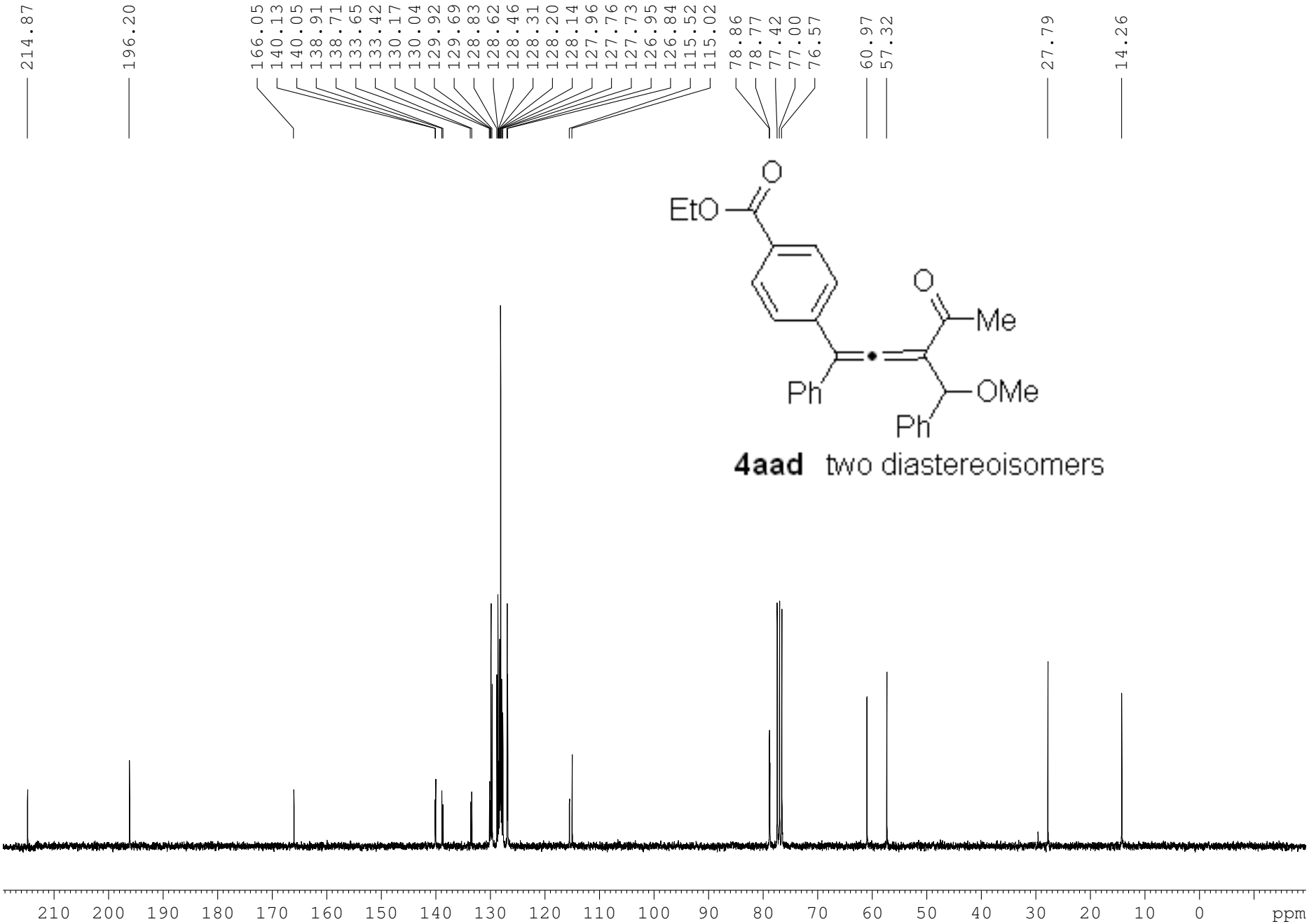
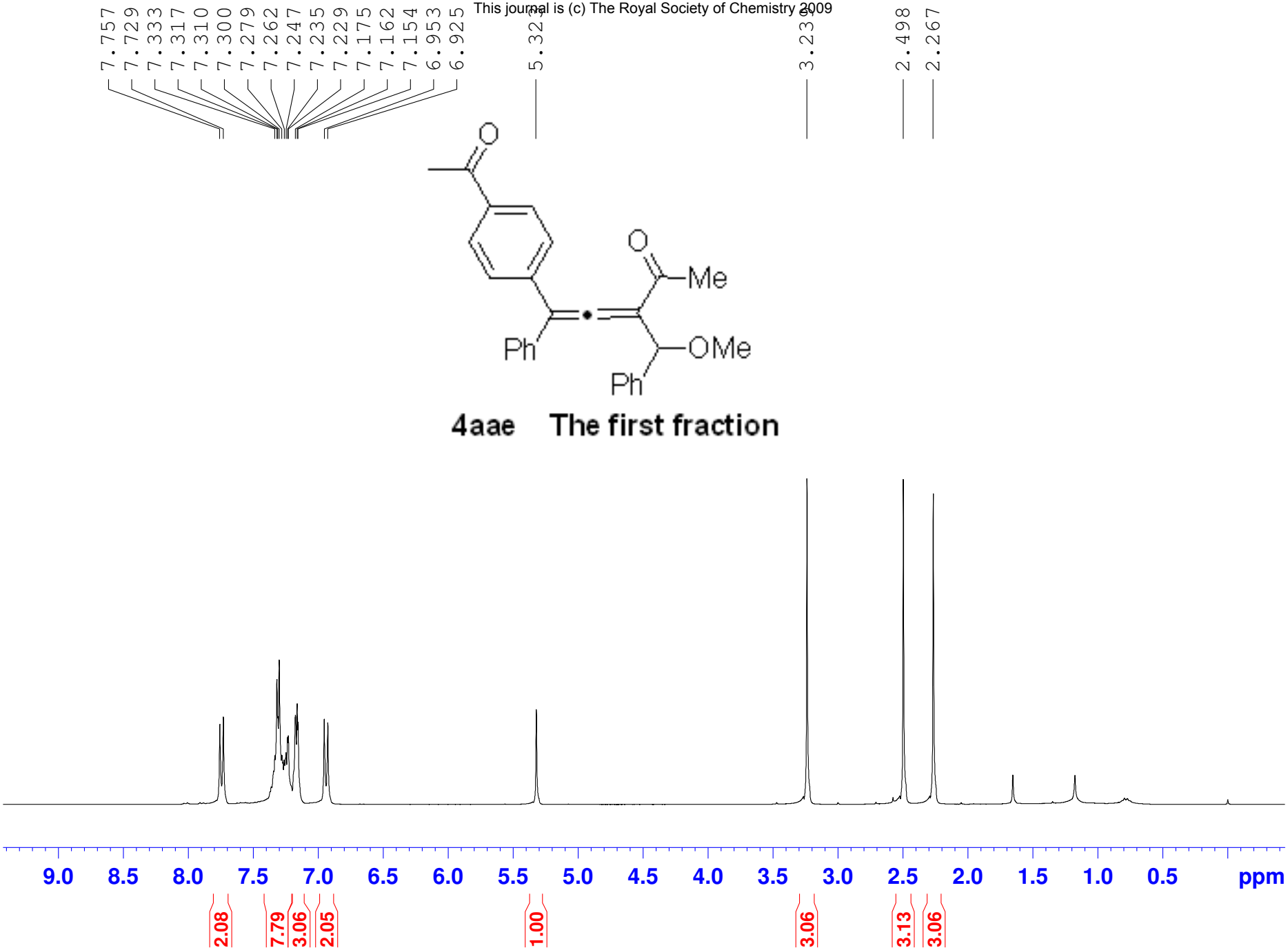
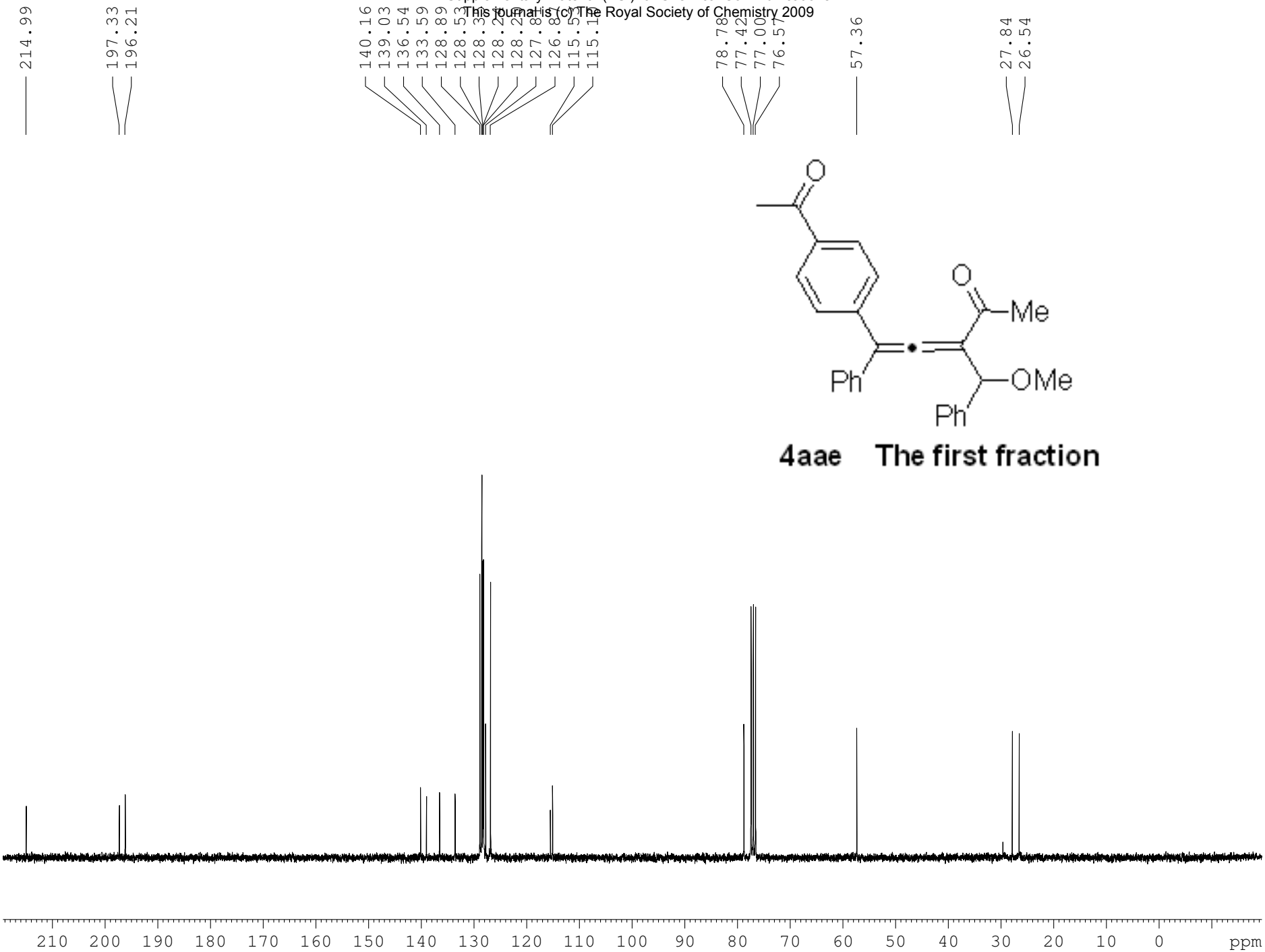
7.265
7.226
7.216
7.210
7.196
7.186
7.181
7.162
7.155
7.145
7.136
7.127
6.924
6.896
6.856
6.851
6.833
6.825
5.315
5.302
4.339
4.315
4.291
4.266
3.227
2.255
1.331
1.307
1.289
1.284
1.266
EtO
O
O
Me
Ph
OMe
Ph
4aad two diastereoisomers
10
9
8
7
6
5
4
3
2
1
0
ppm
1.25
0.92
1.36
9.70
0.97
1.20
1.00
2.13
3.07
3.03
3.17



4aad two diastereoisomers



4aae The first fraction



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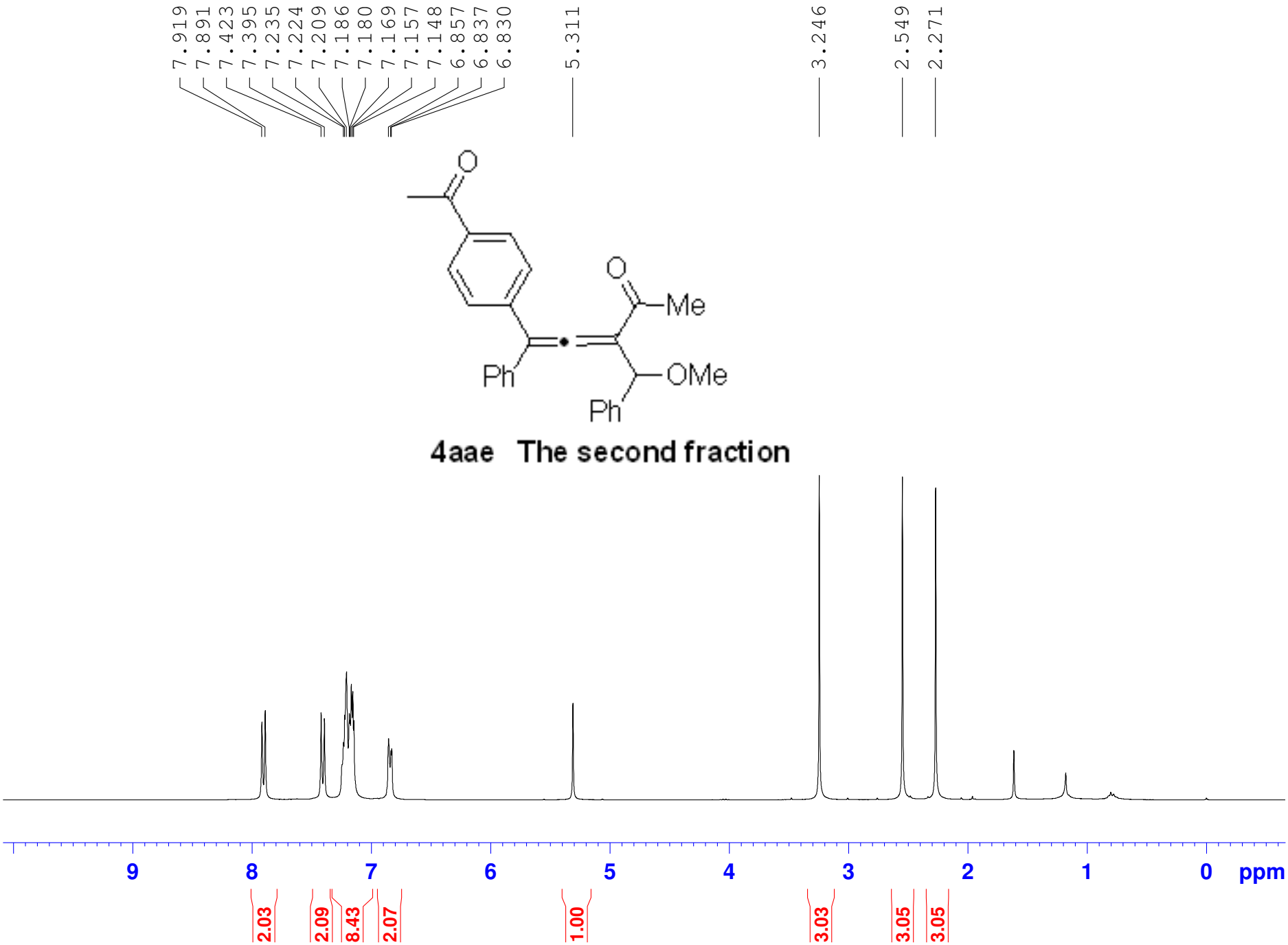

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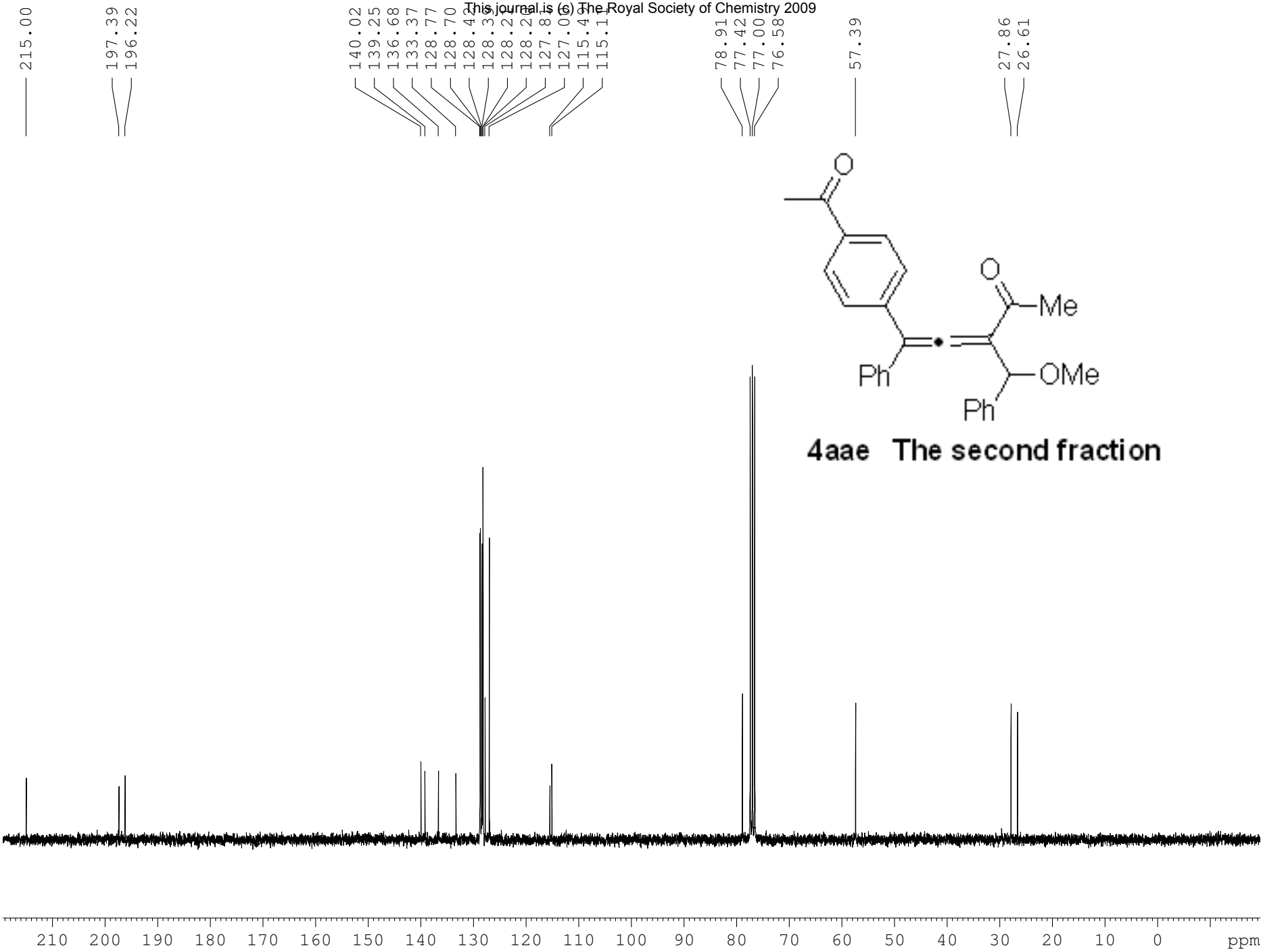

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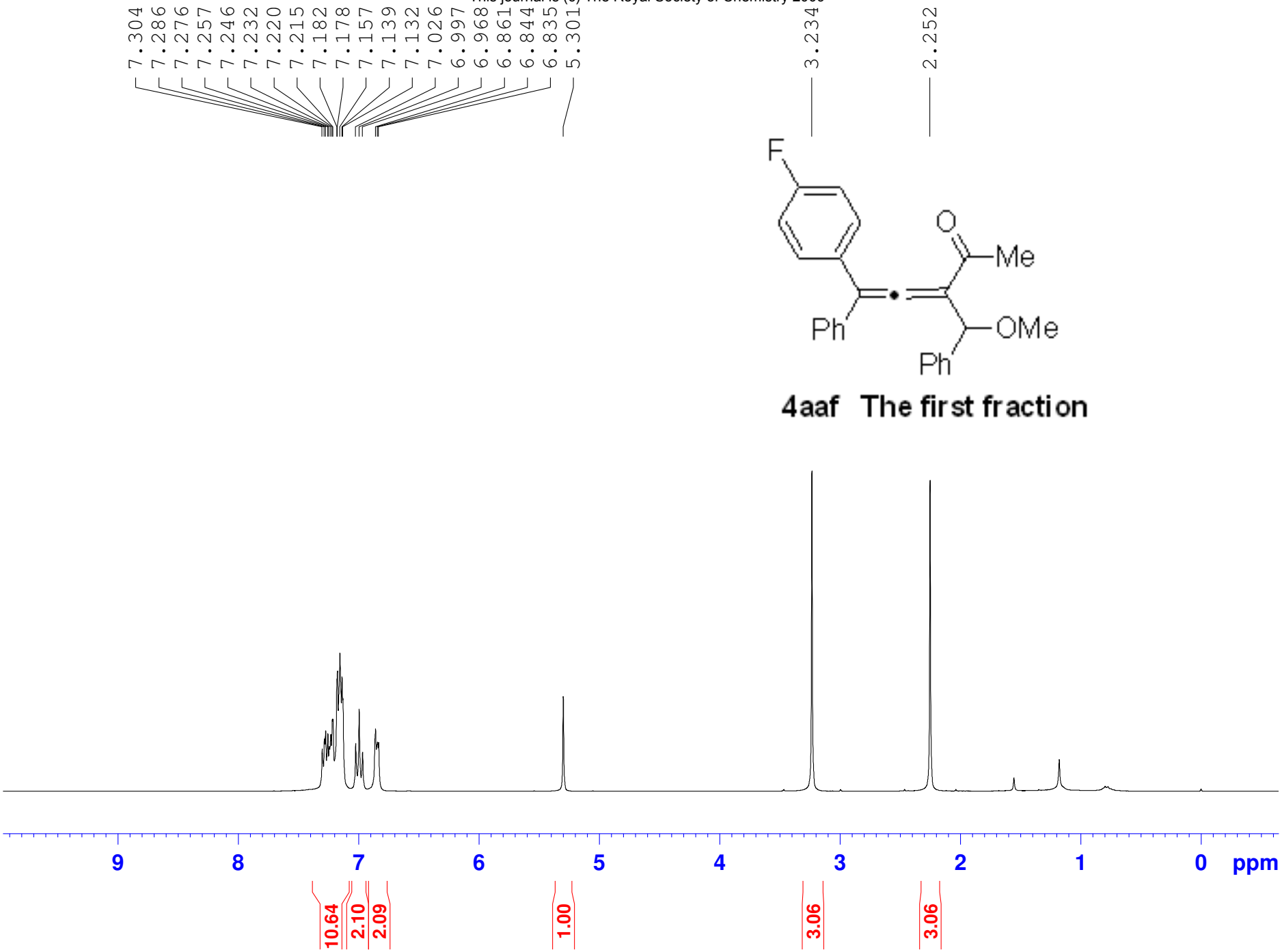
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7.286
7.276
7.257
7.246
7.232
7.220
7.215
7.182
7.178
7.157
7.139
7.132
7.026
6.997
6.968
6.861
6.844
6.835
5.301
3.234
2.252
F
O
Me
Ph
OMe
Ph
4aaf The first fraction
9
8
7
6
5
4
3
2
1
0
ppm
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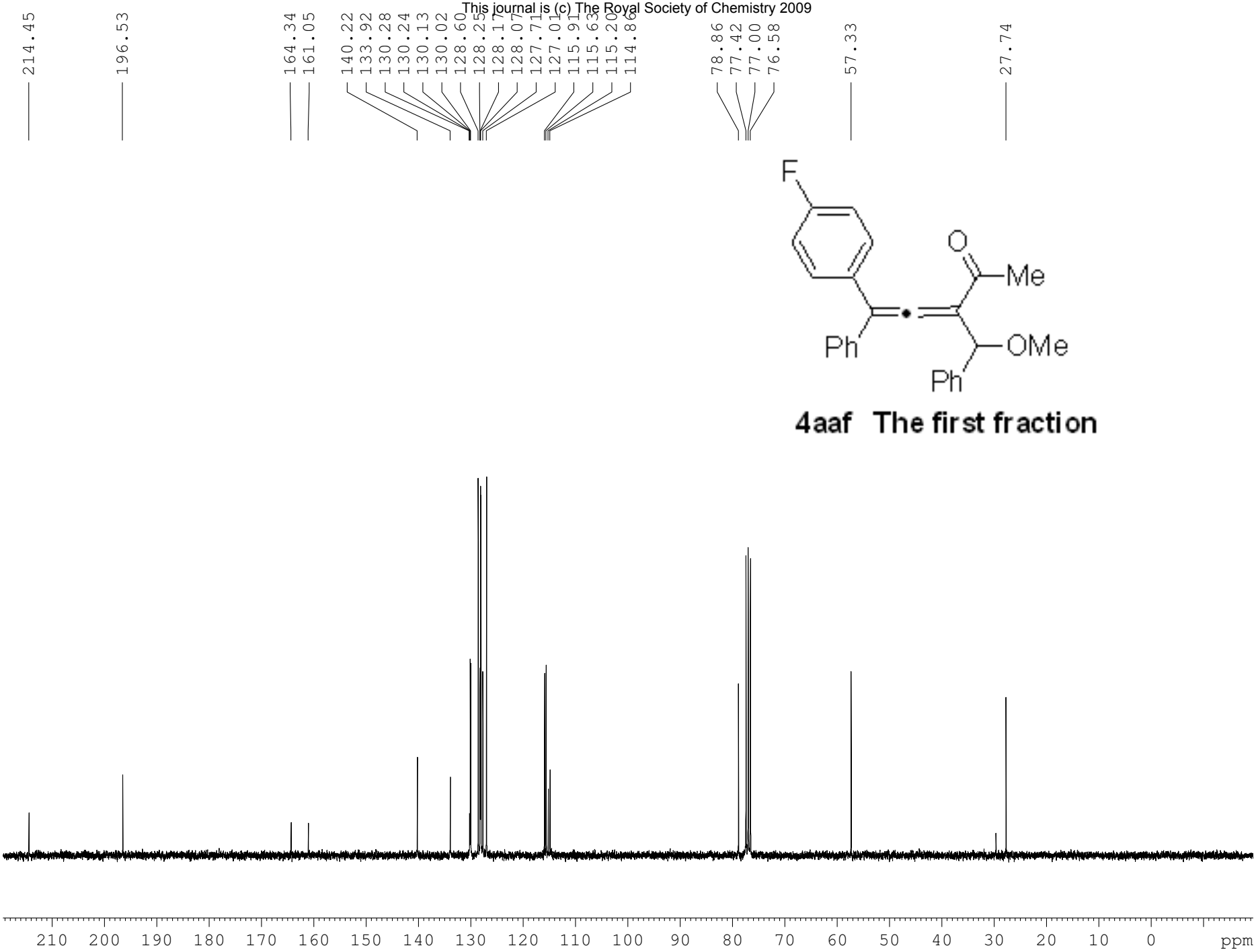
2.09
1.00
3.06
3.06



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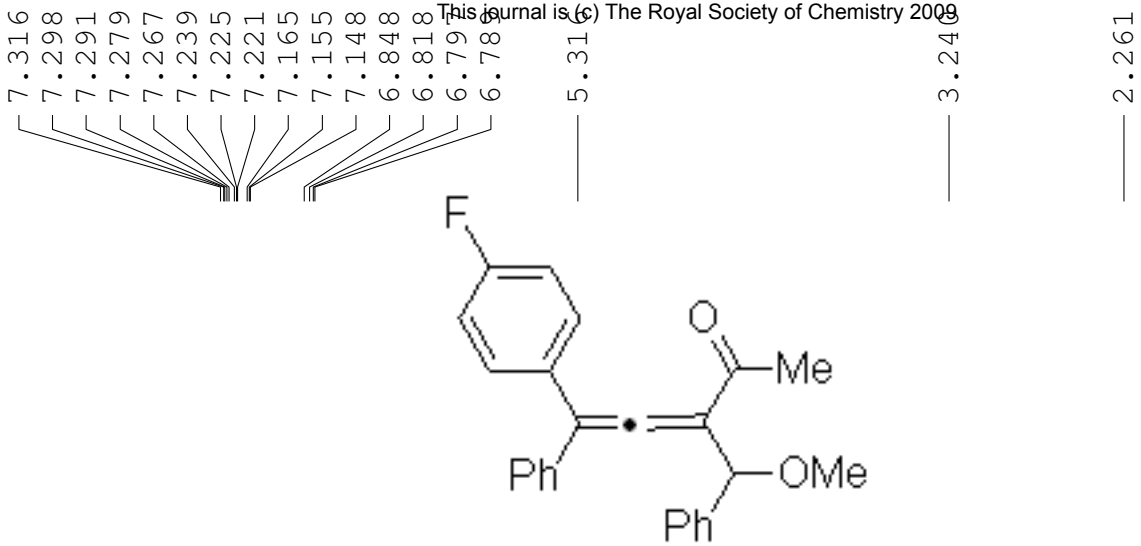

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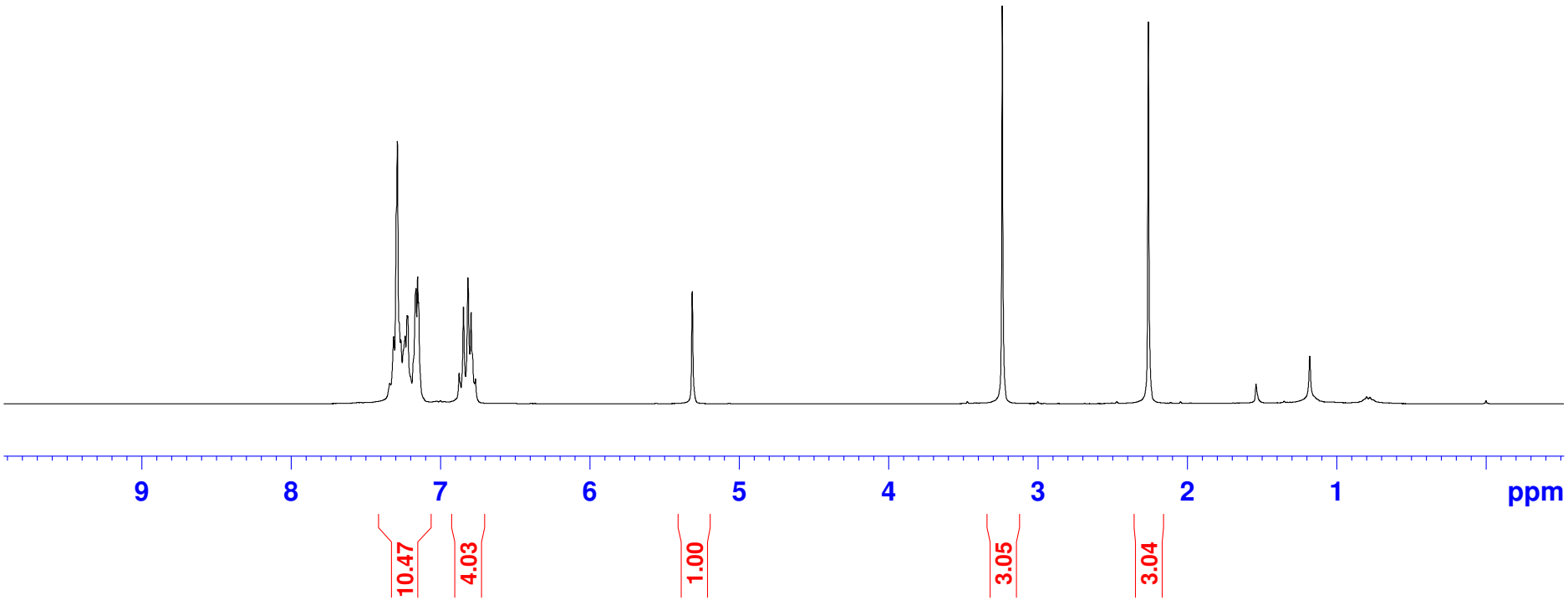

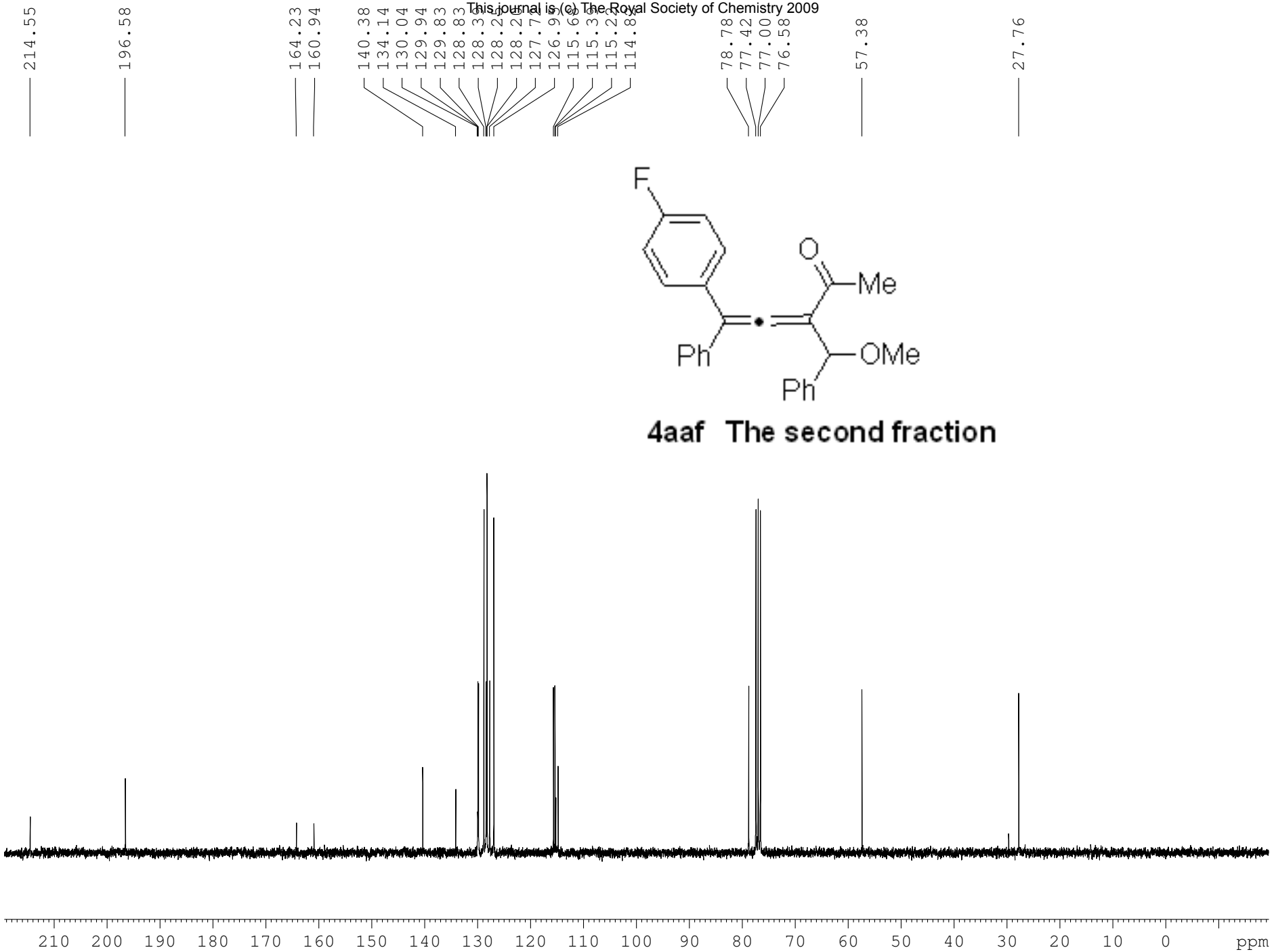

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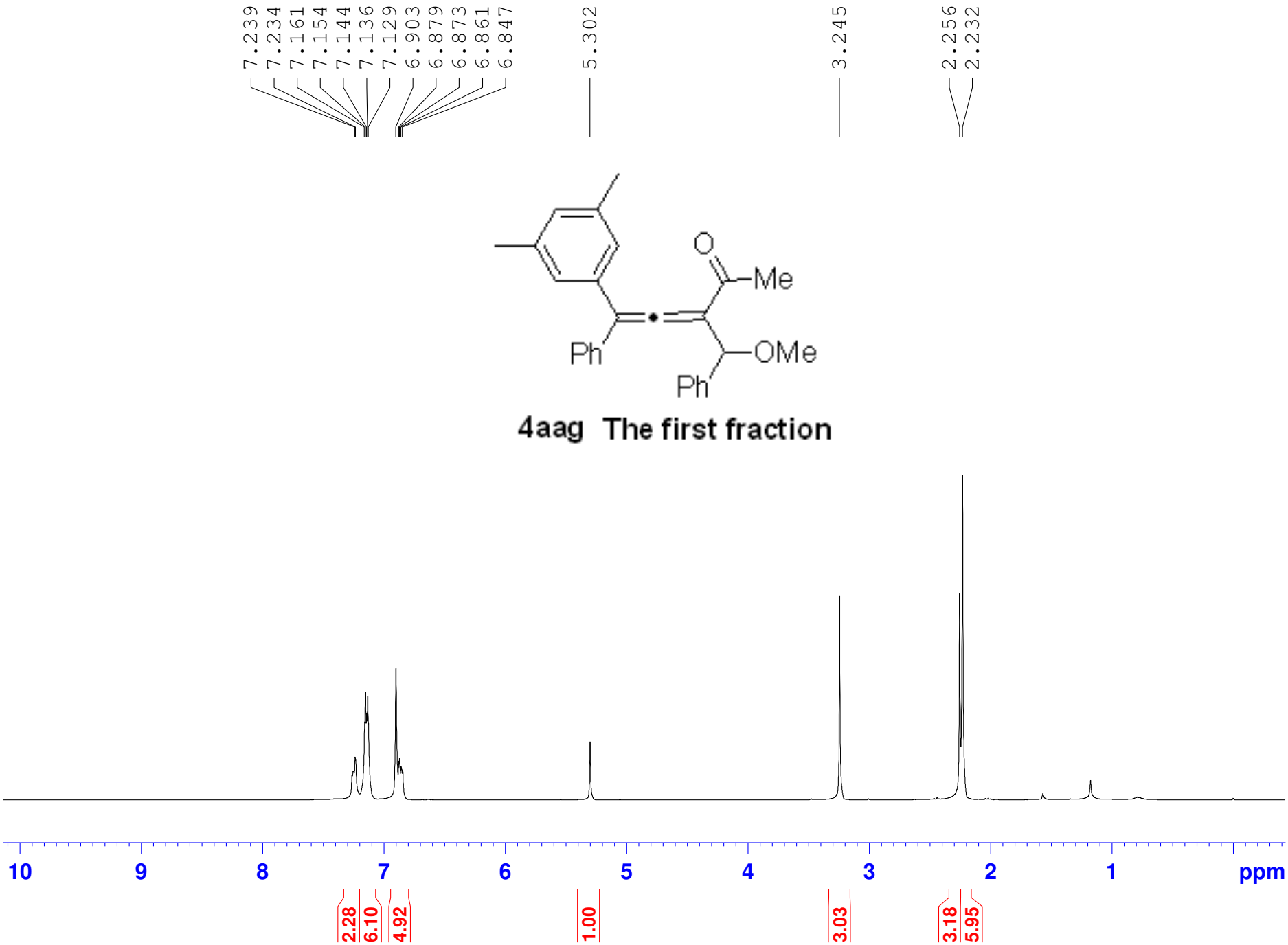

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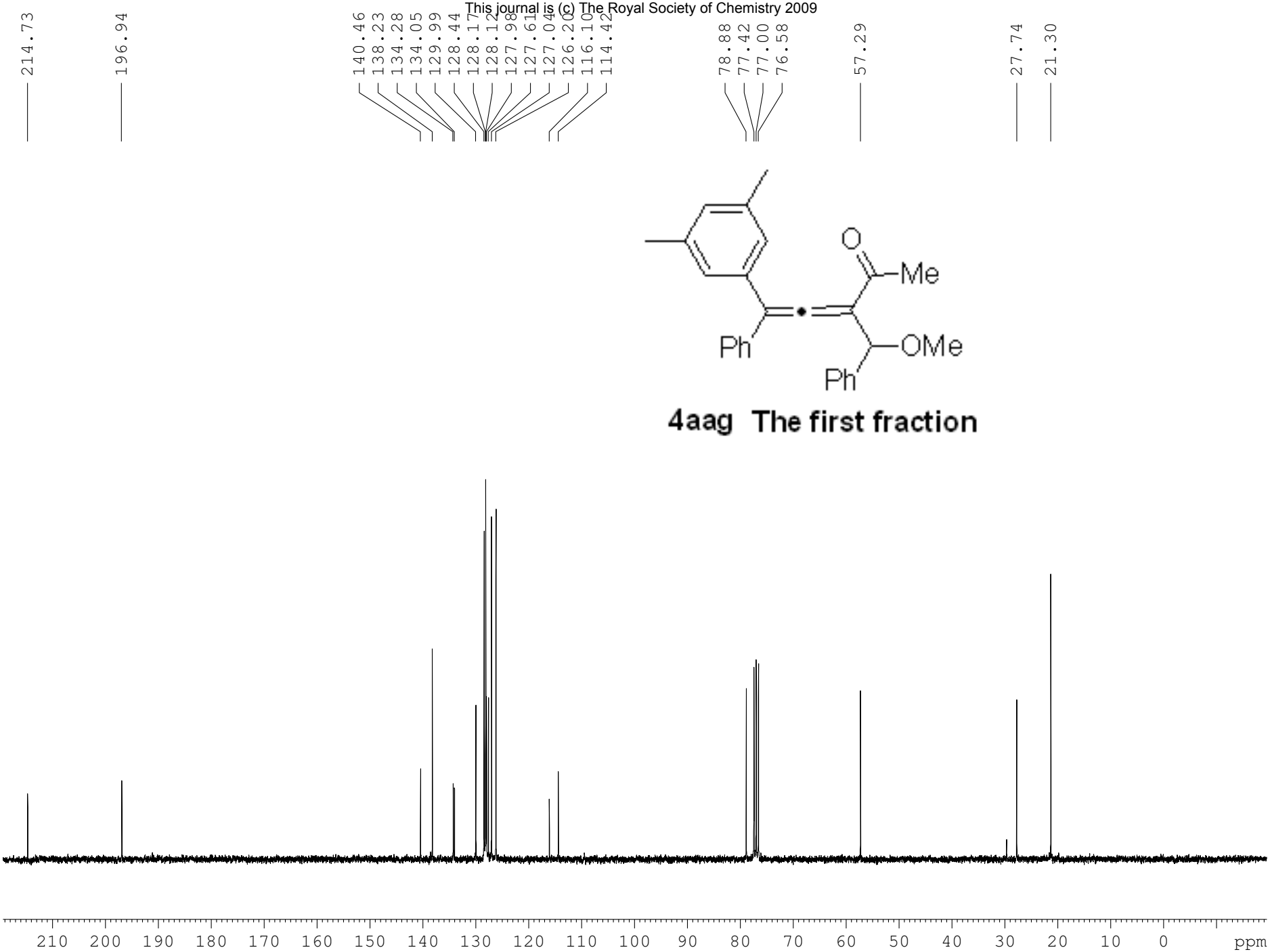

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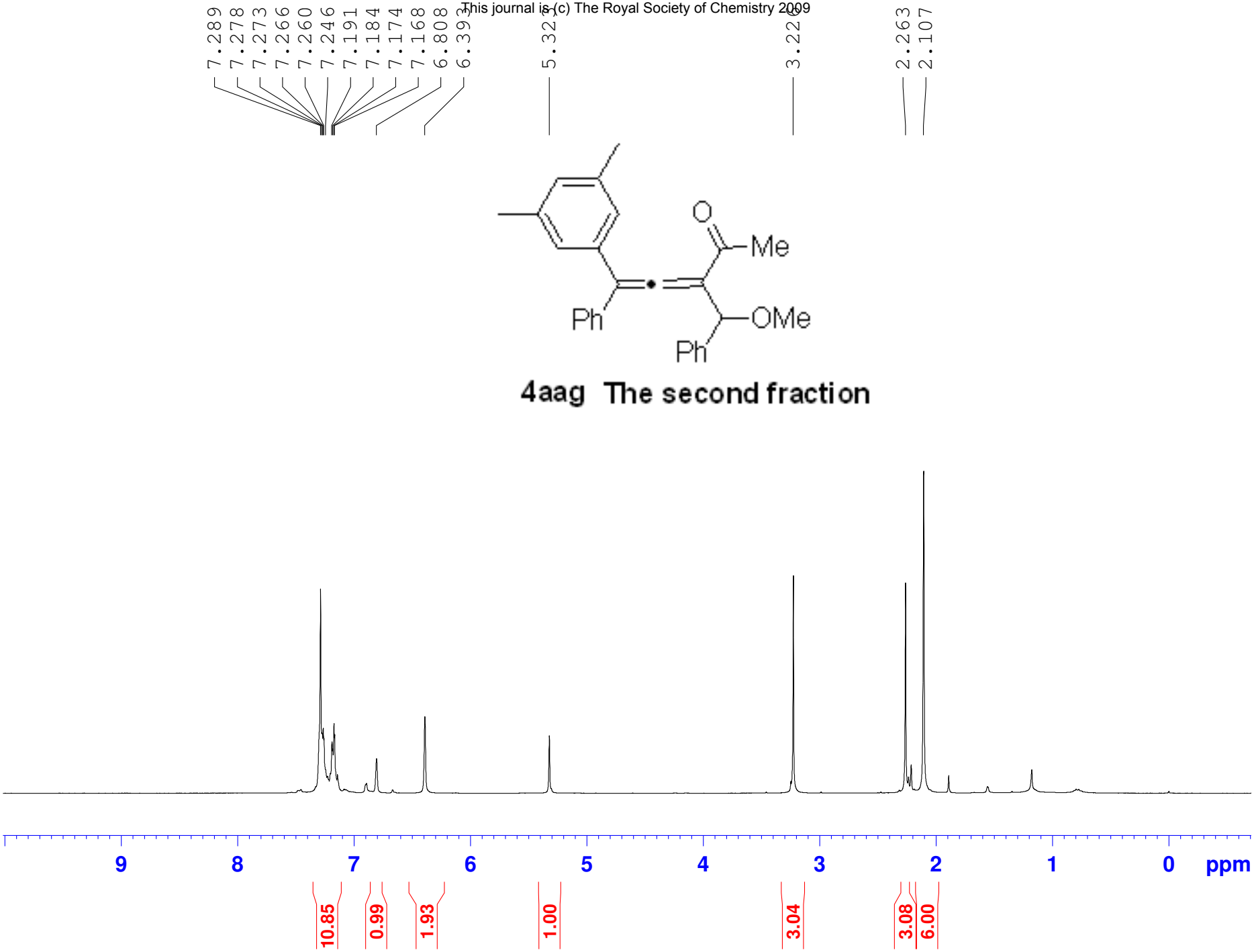
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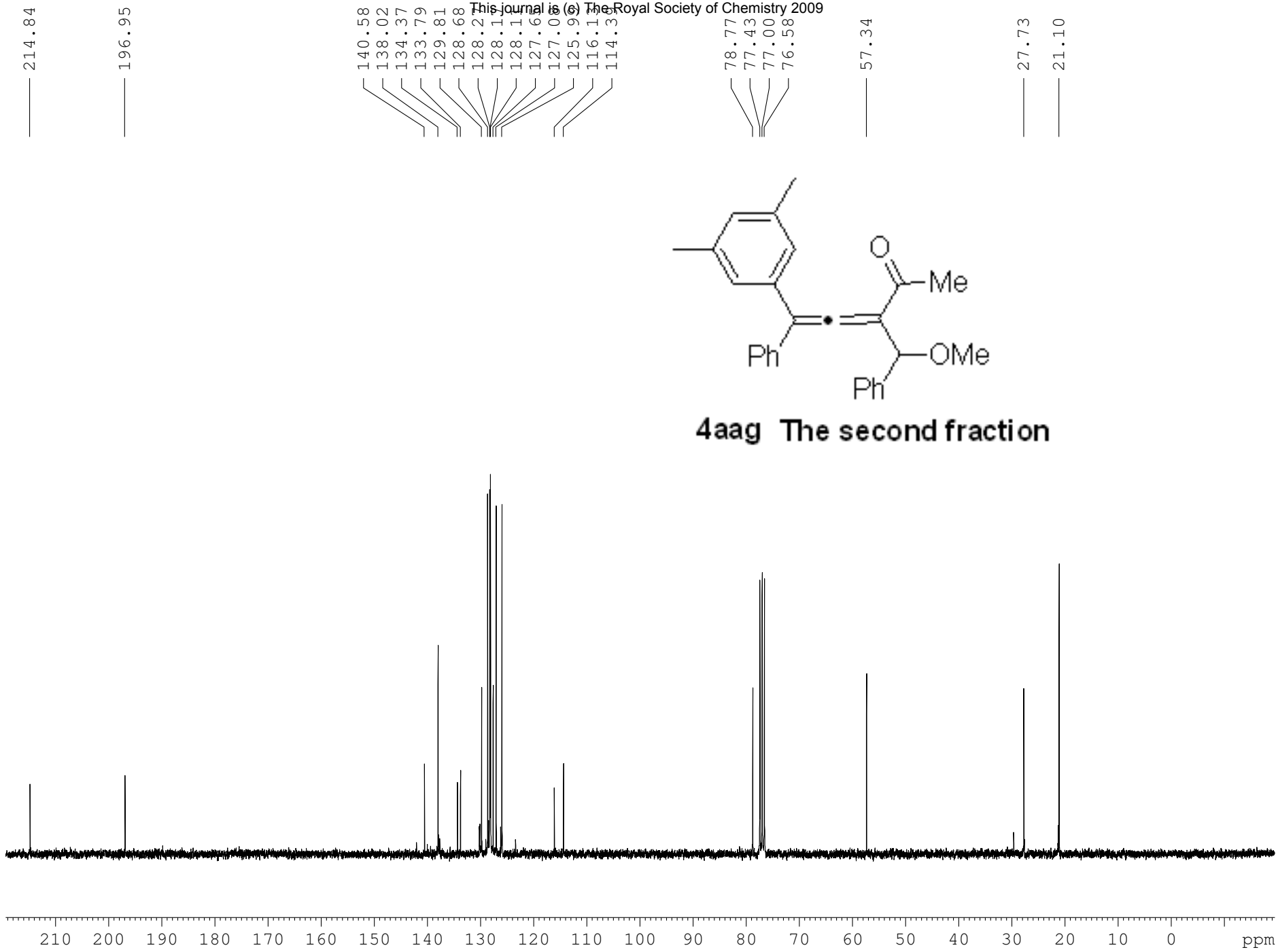
7.278
7.273
7.266
7.260
7.246
7.191
7.184
7.174
7.168
6.808
6.393
5.321
3.220
2.263
2.107
O
Me
Ph
OMe
Ph
4aag The second fraction
9
8
7
6
5
4
3
2
1
0
ppm
10.85
0.99
1.93
1.00
3.04
3.08
6.00



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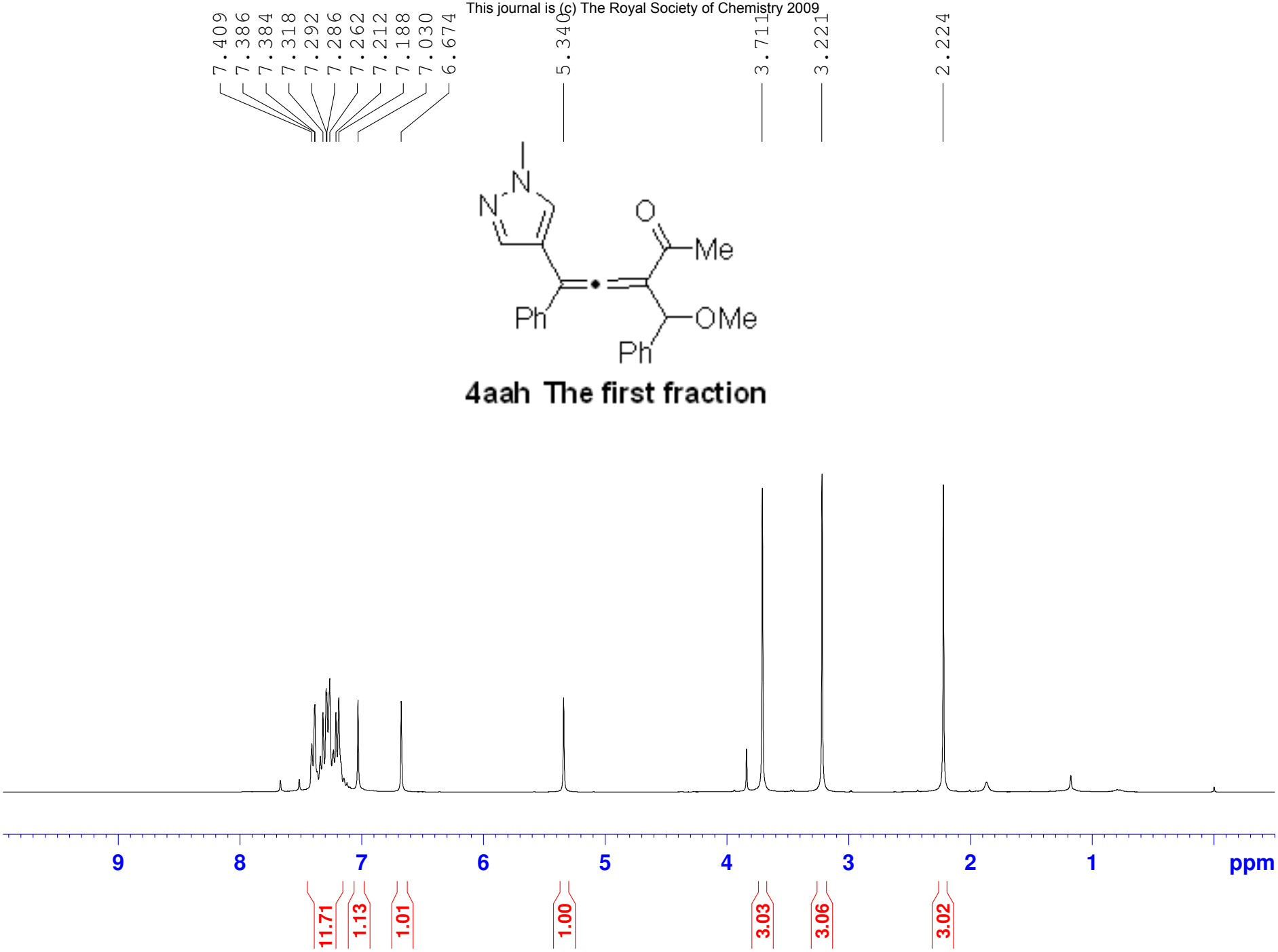

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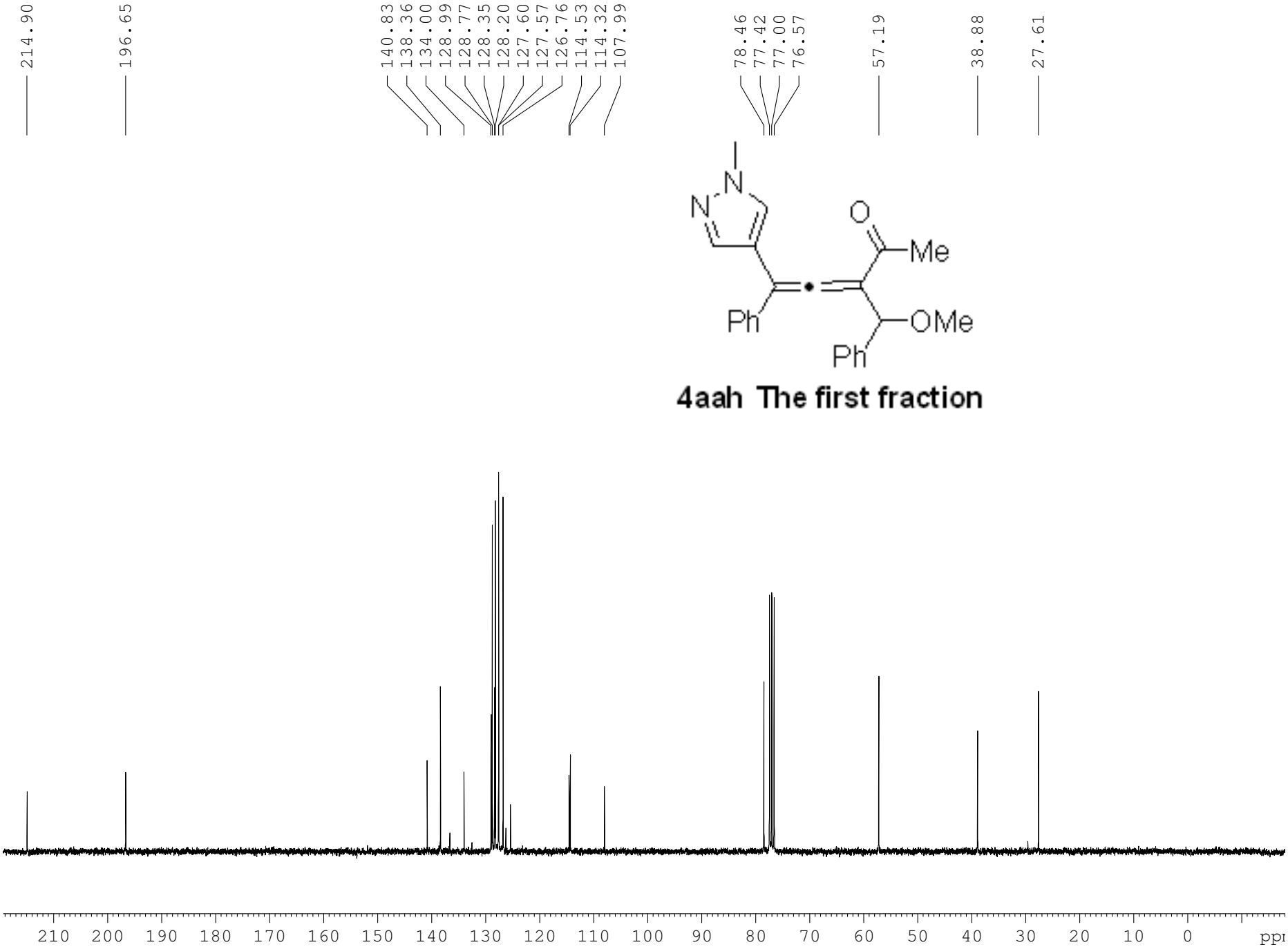

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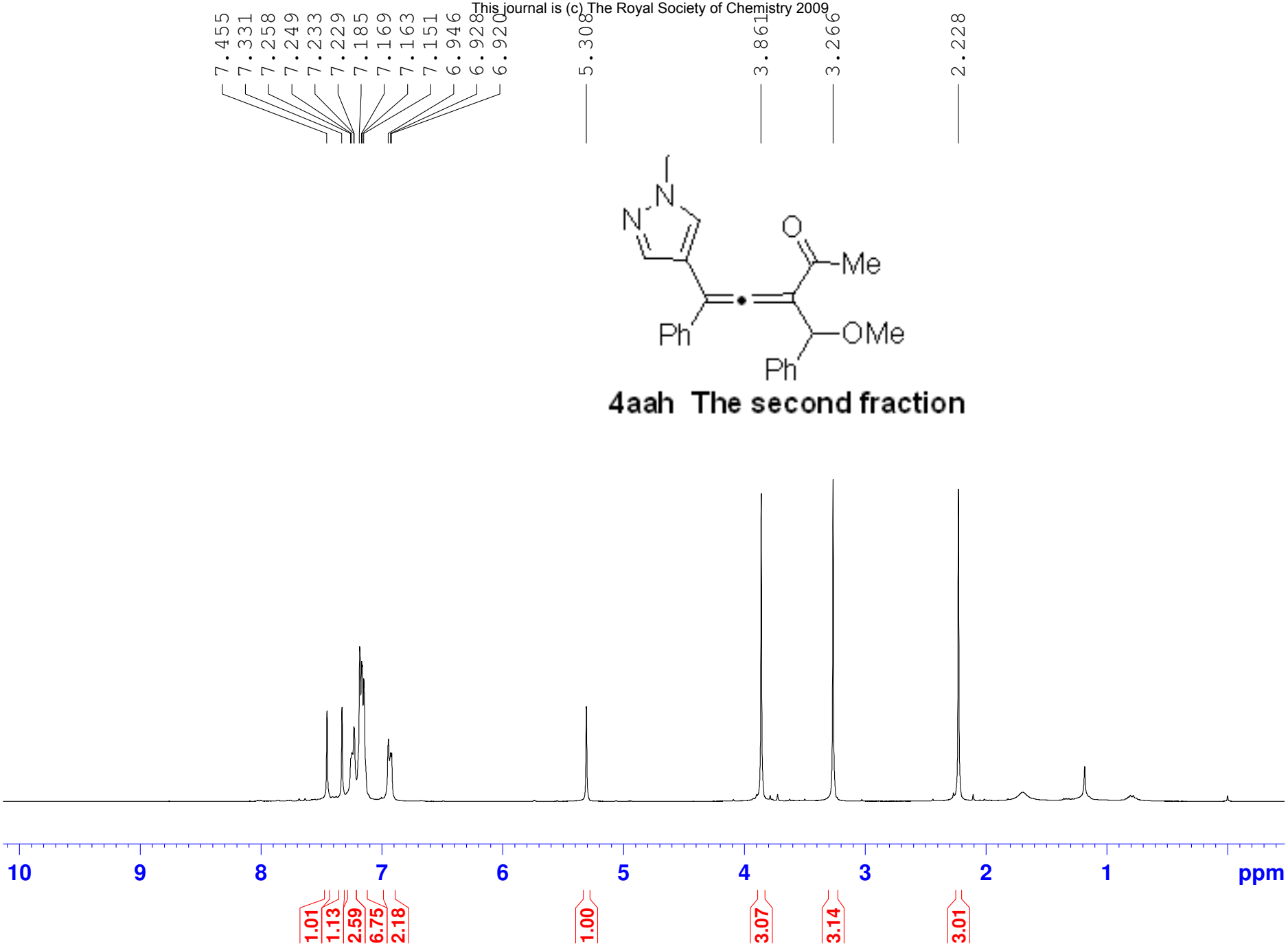

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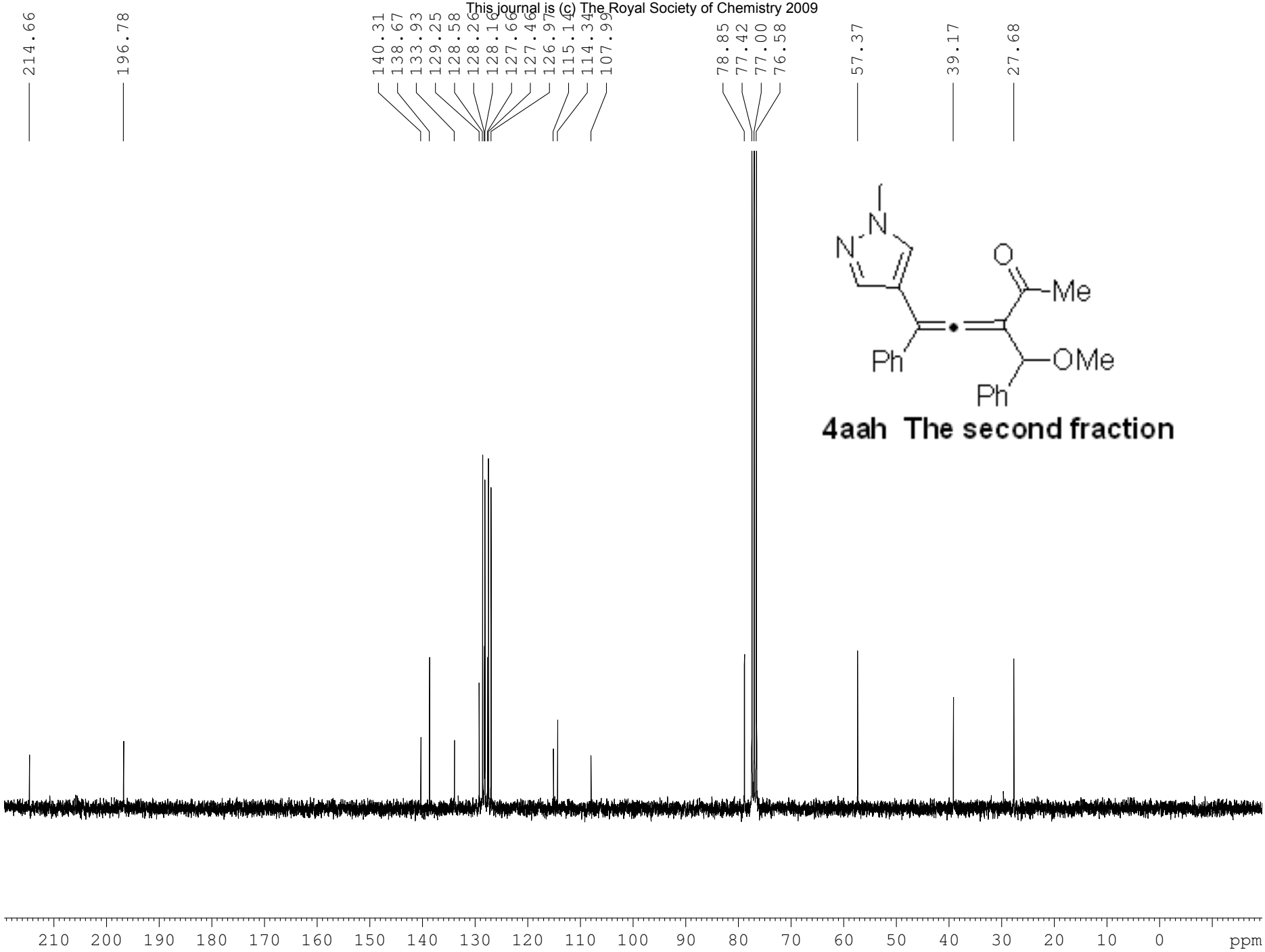

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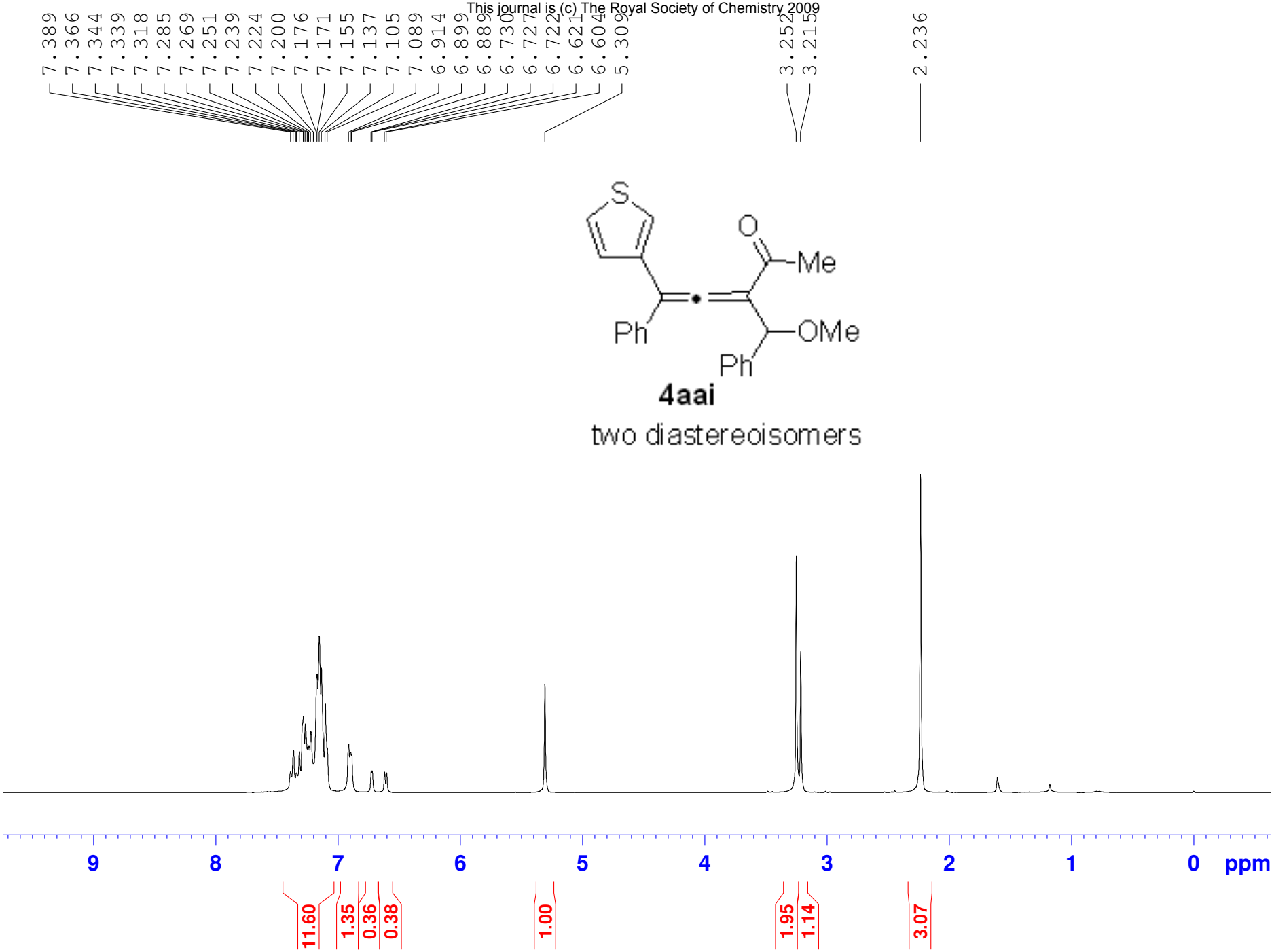
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7.285
7.269
7.251
7.239
7.224
7.200
7.176
7.171
7.155
7.137
7.105
7.089
6.914
6.899
6.889
6.730
6.727
6.722
6.621
6.604
5.309
3.252
3.215
2.236
S
O
Me
Ph
OMe
Ph
4aai
two diastereoisomers
9
8
7
6
5
4
3
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1
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ppm
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0.38
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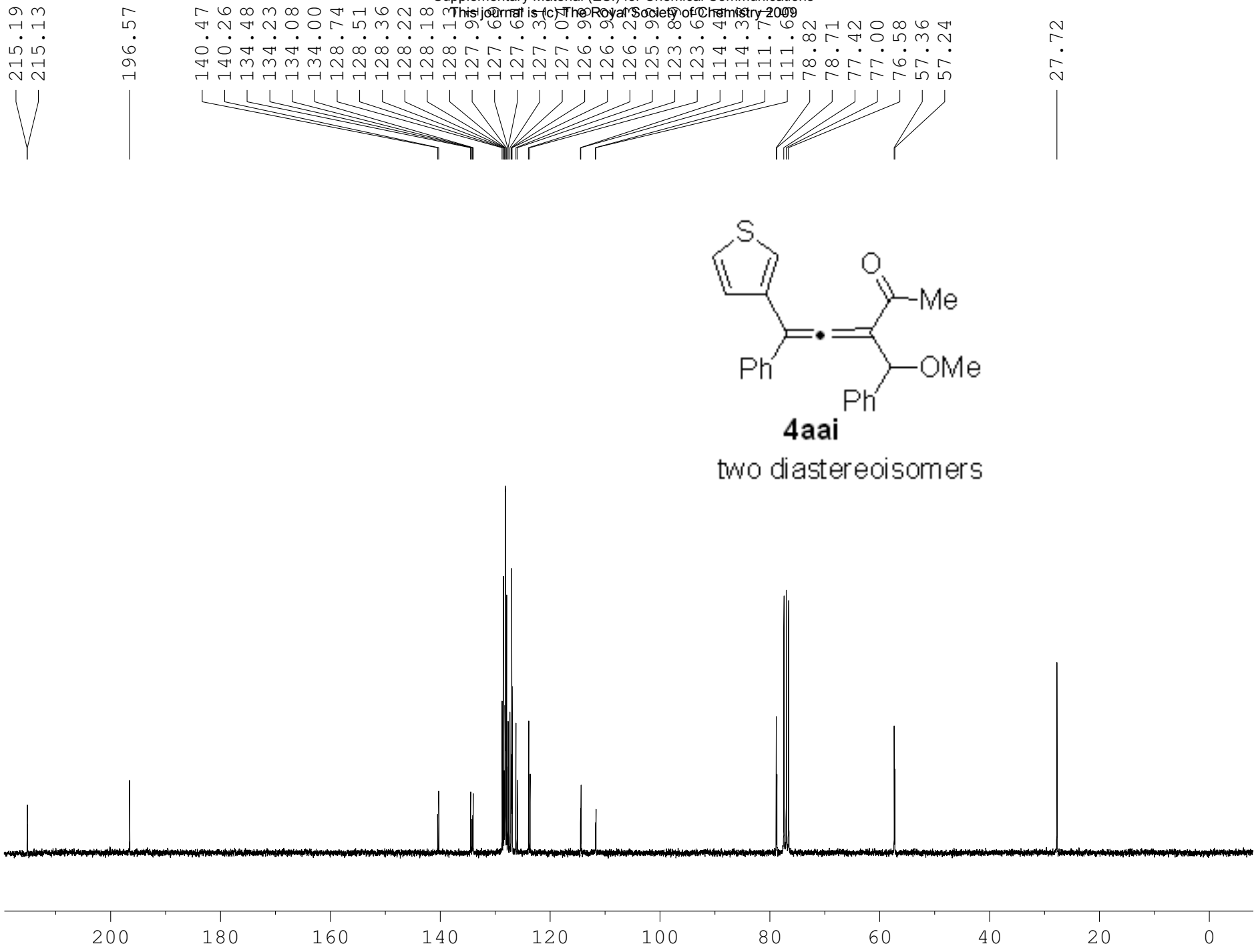
1.14
3.07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128.51
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128.22
128.18
127.92
127.60
127.60
127.31
127.07
126.92
126.92
126.22
125.92
123.89
123.60
114.44
114.33
111.77
111.60
78.82
78.71
77.42
77.00
76.58
57.36
57.24
27.72
S
O
Me
Ph
OMe
Ph
4aai
two diastereoisomers
200
180
160
140
120
100
80
60
40
20
0

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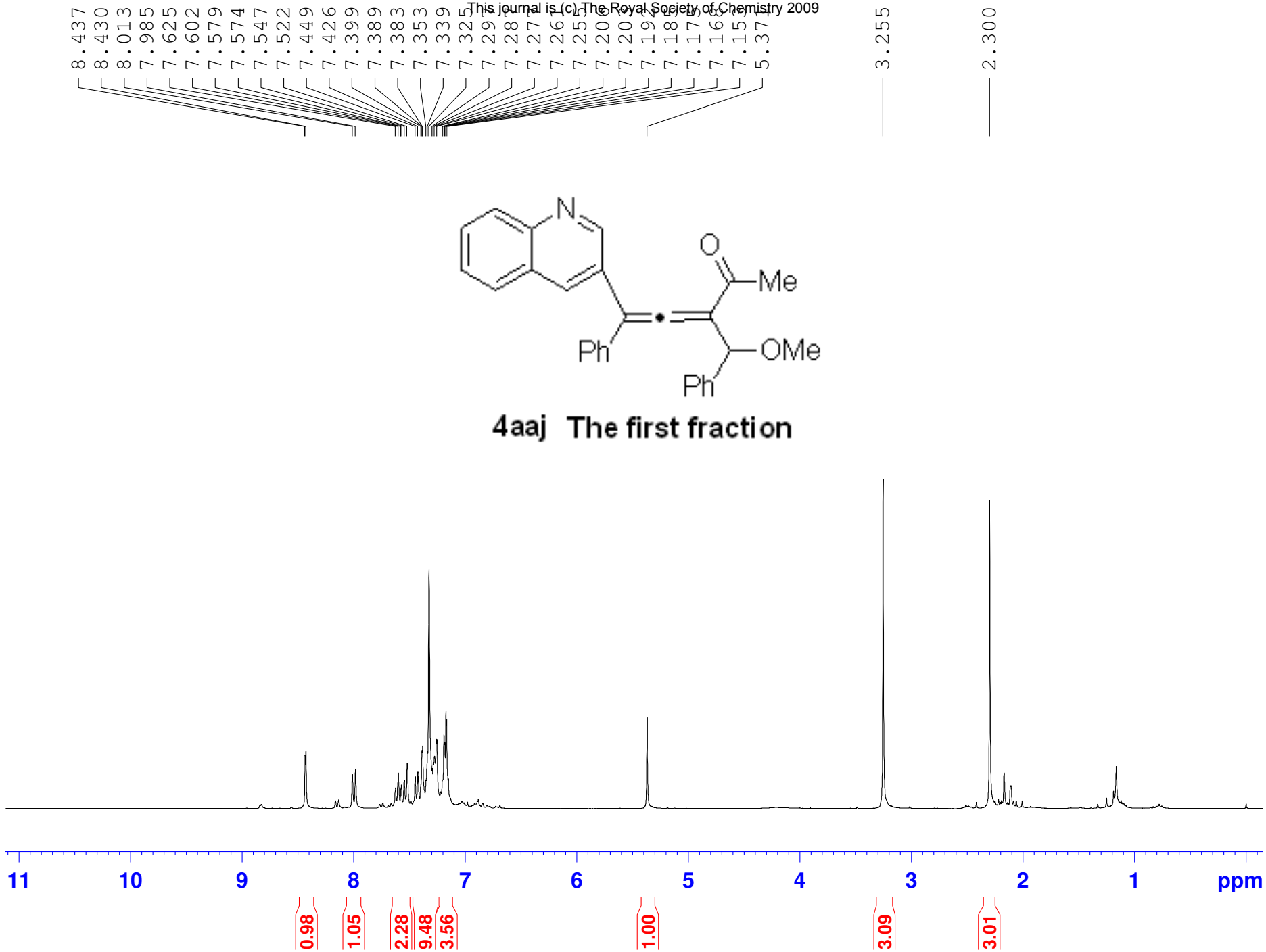

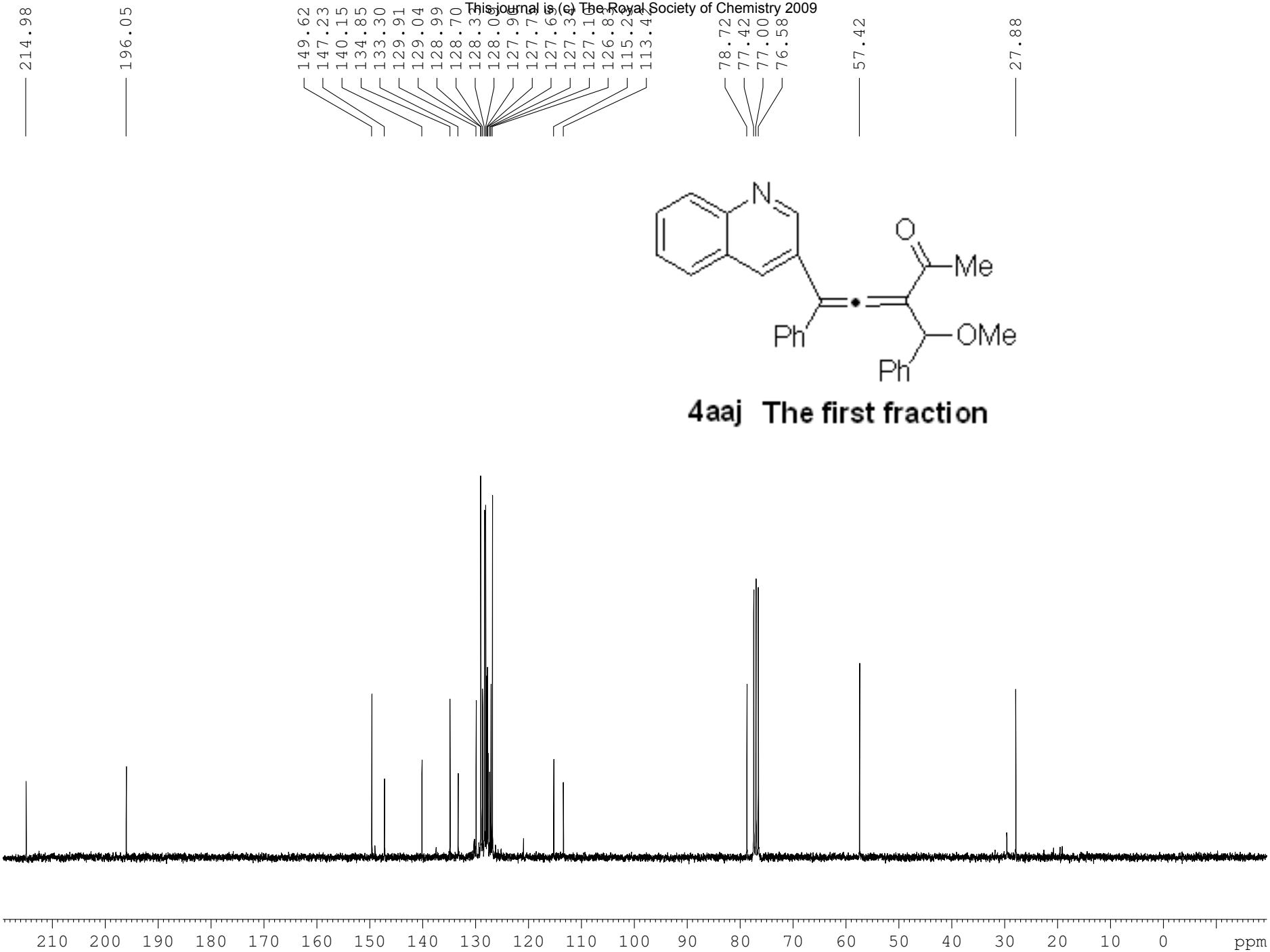

4aaj The first fraction

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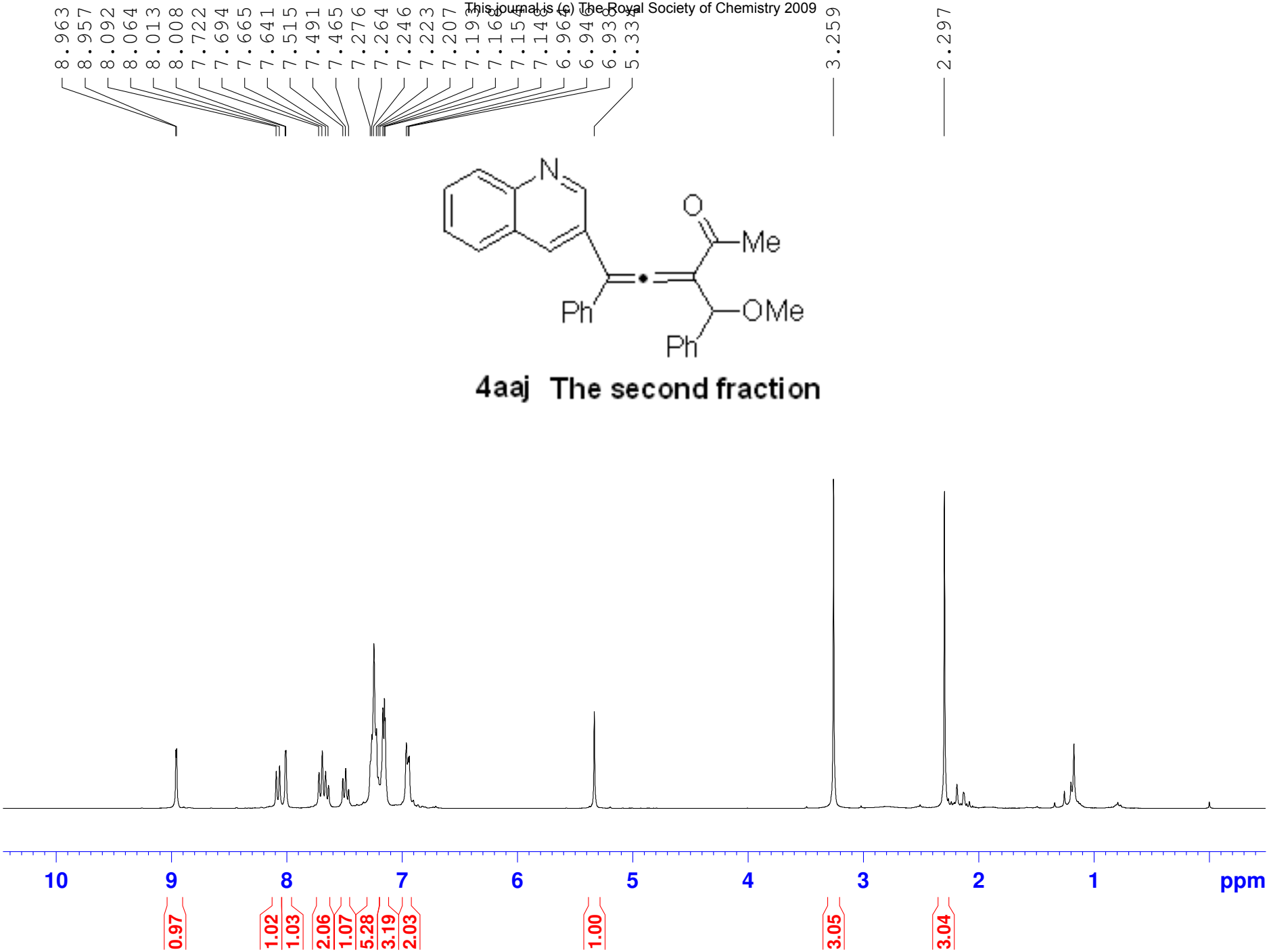

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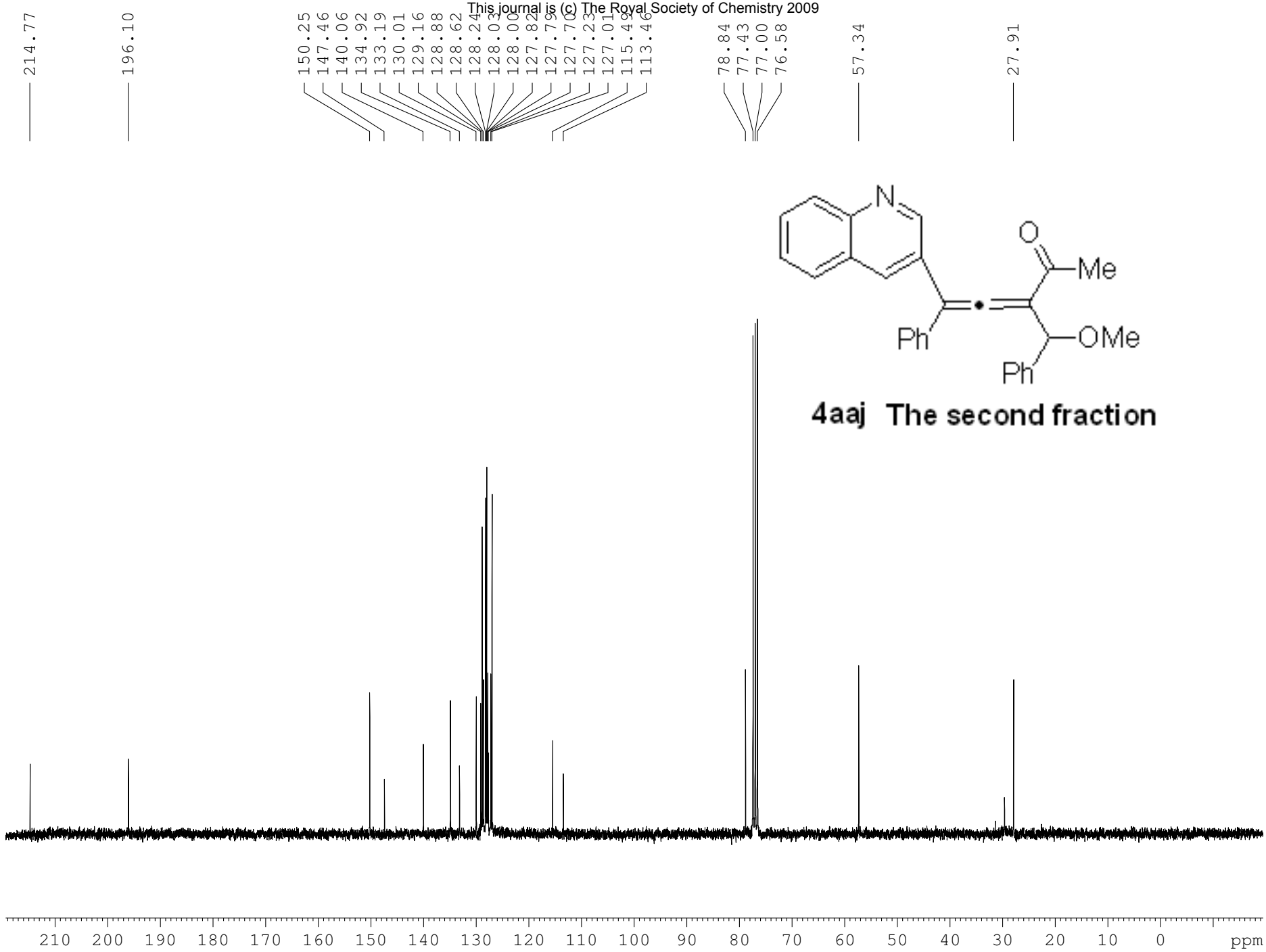
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134.92
133.19
130.01
129.16
128.88
128.62
128.24
128.03
128.00
127.82
127.79
127.70
127.23
127.01
115.49
113.46
78.84
77.43
77.00
76.58
57.34
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N
O
Me
Ph
OMe
Ph
4aaj The second fraction
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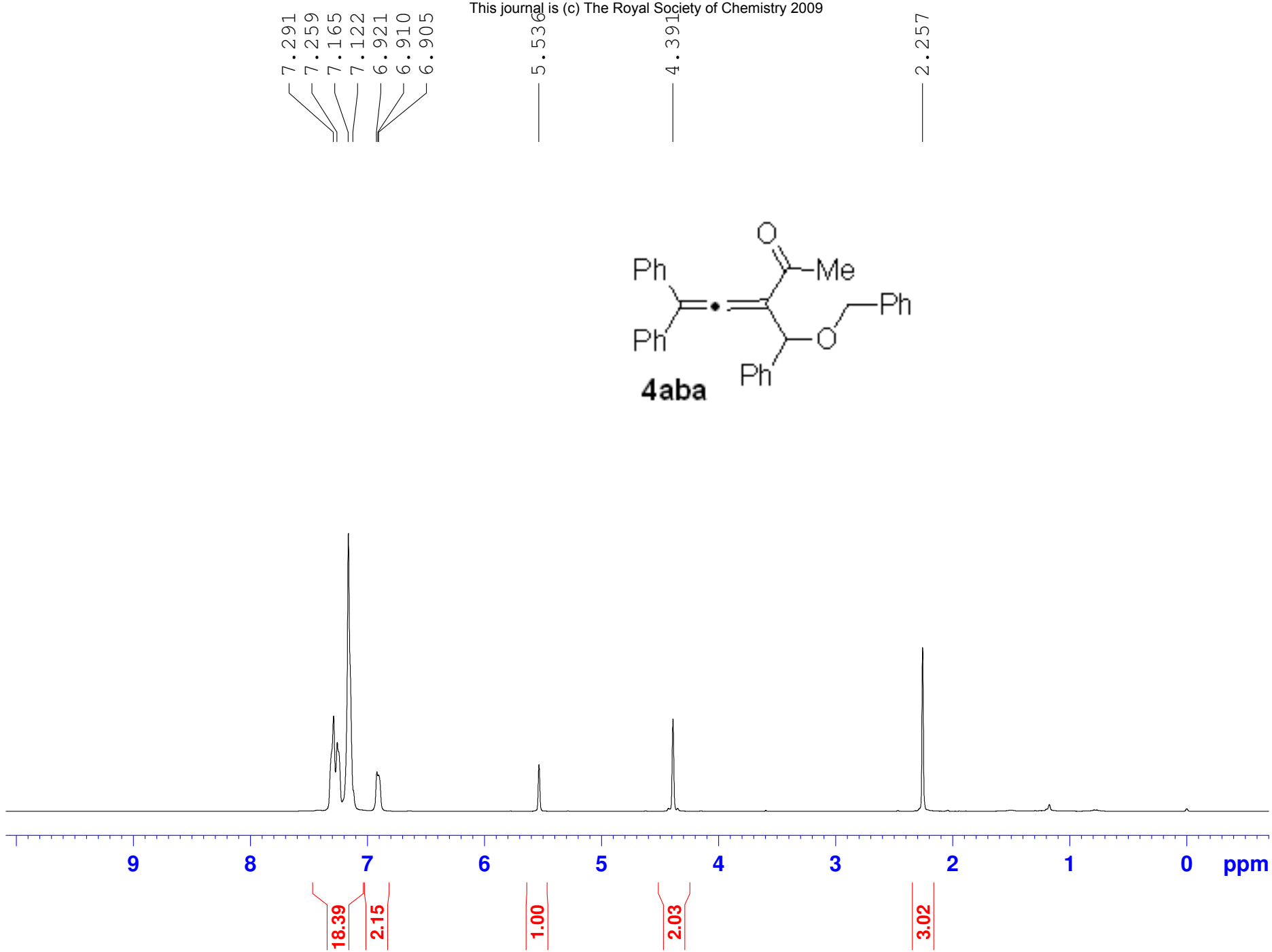
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6.910
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5.536
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Ph
O
Me
Ph
O
Ph
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ppm
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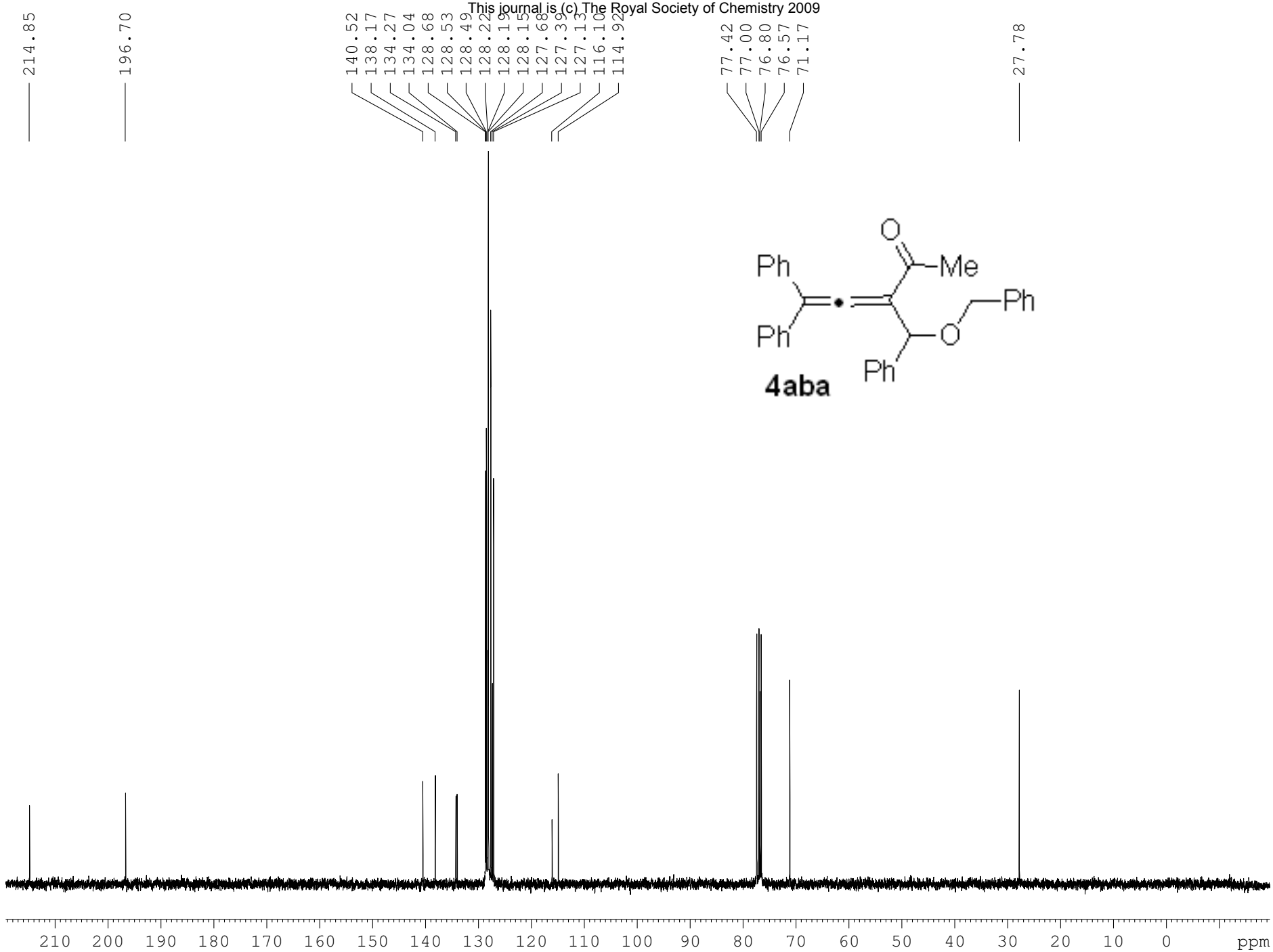
1.00
2.03
3.02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128.53
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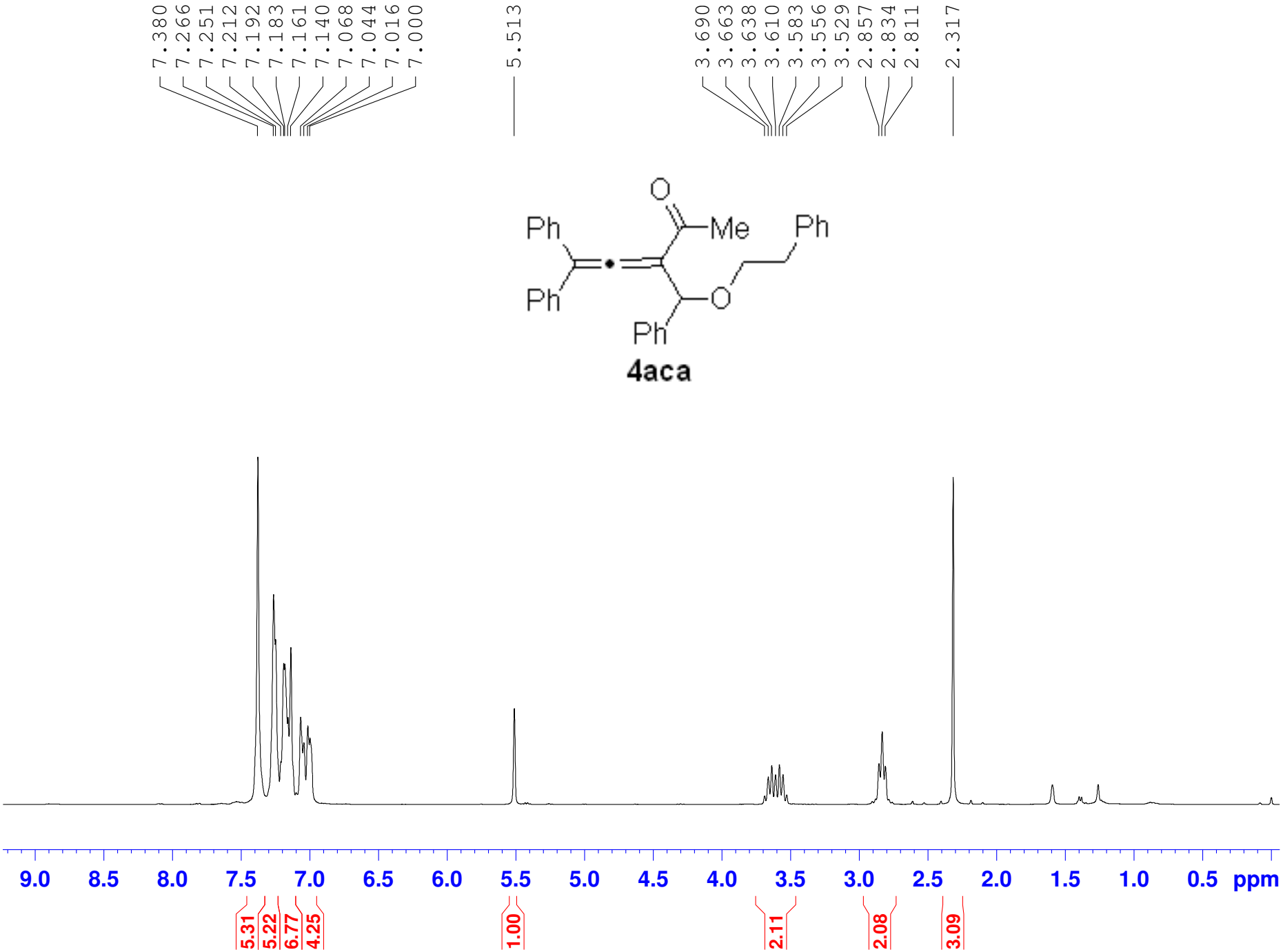
127.39
127.13
116.10
114.92
77.42
77.00
76.80
76.57
71.17
27.78
Ph
Ph
O
Me
Ph
O
Ph
4aba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.192
7.183
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7.140
7.068
7.044
7.016
7.000
5.513
3.690
3.663
3.638
3.610
3.583
3.556
3.529
2.857
2.834
2.811
2.317
Ph
Ph
O
Me
Ph
O
Ph
4aca
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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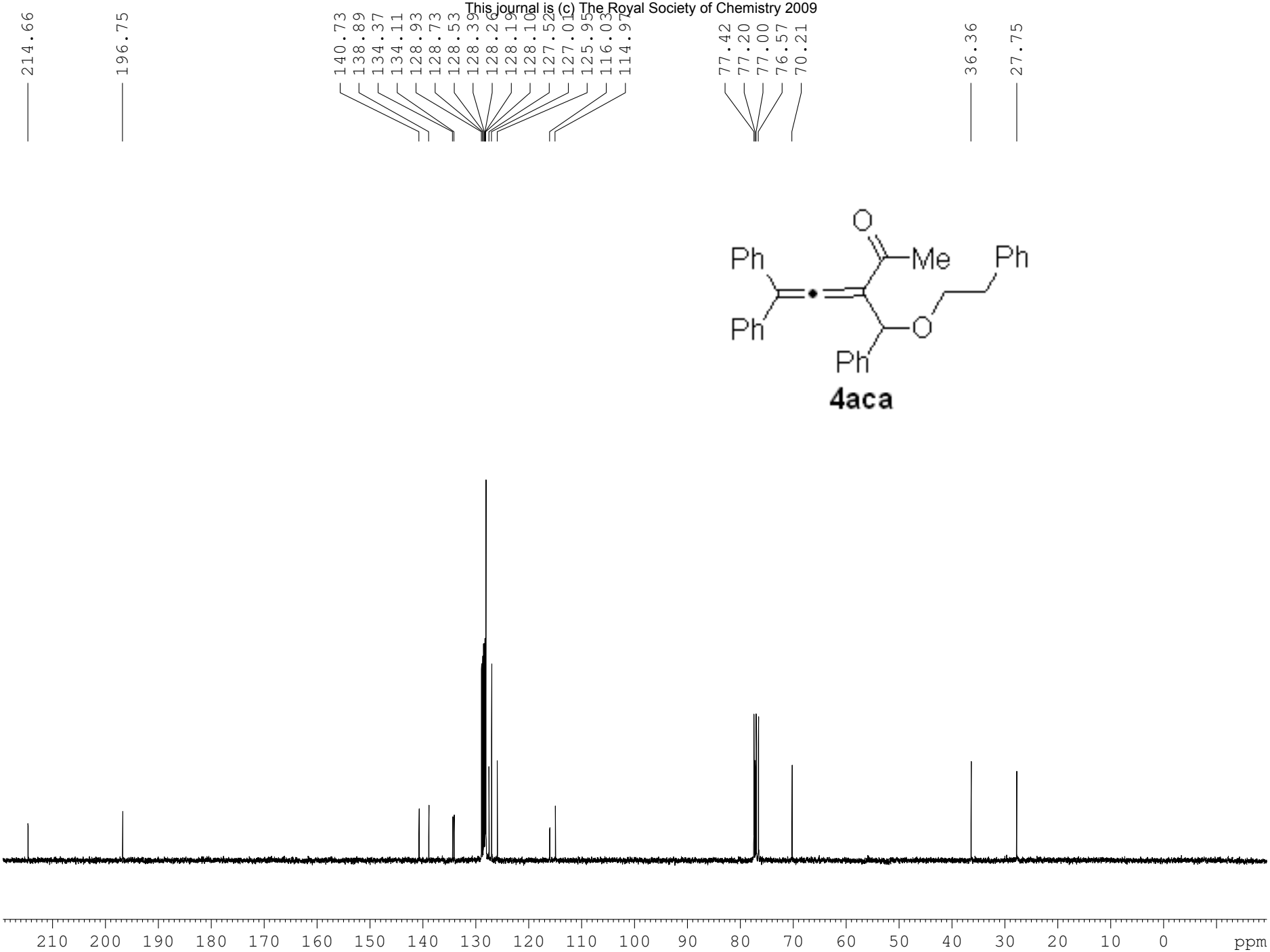
2.08
3.09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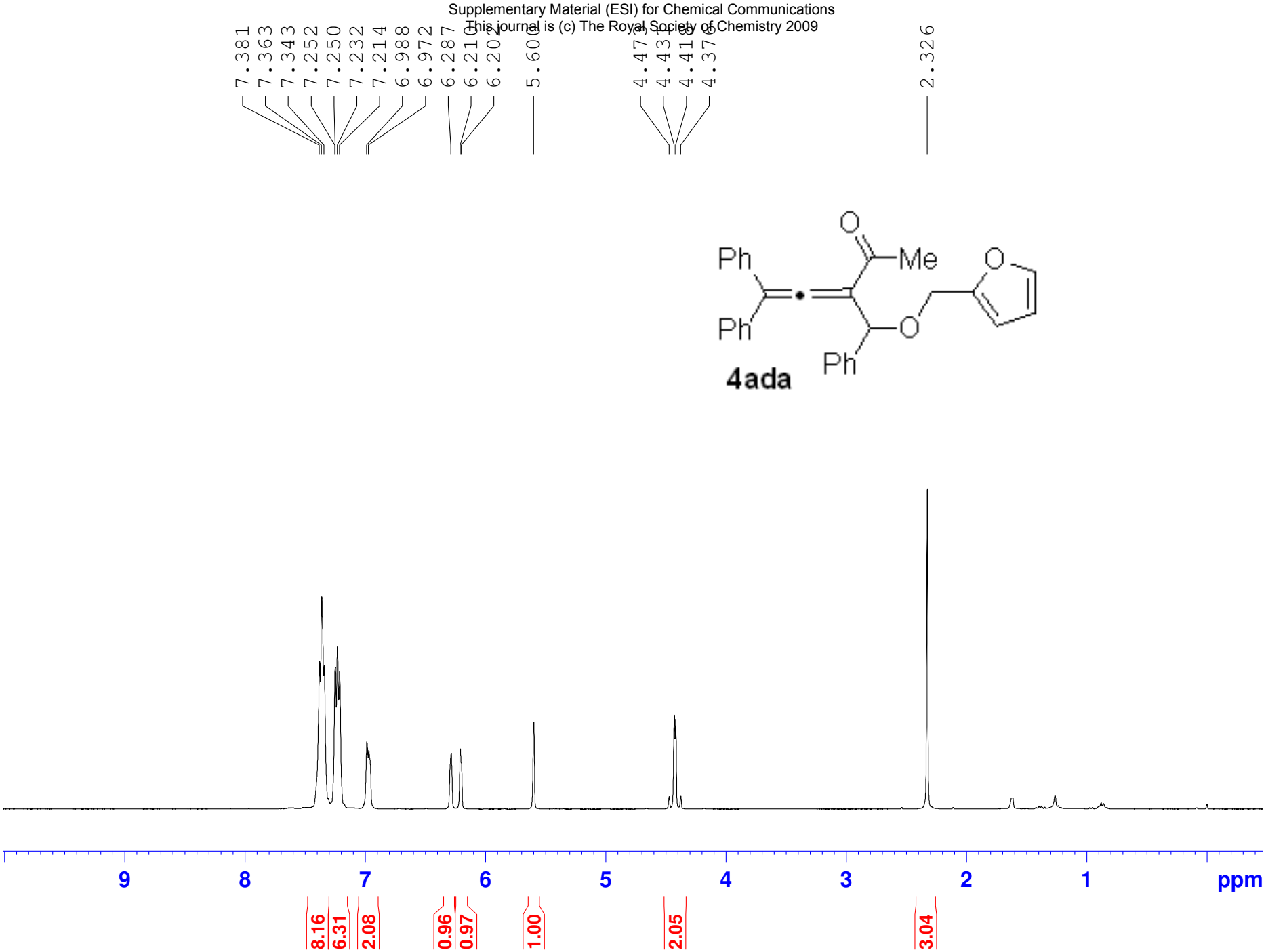
128.39
128.26
128.19
128.10
127.52
127.01
125.95
116.03
114.97
77.42
77.20
77.00
76.57
70.21
36.36
27.75
O
Ph
Me
Ph
Ph
O
Ph
4aca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.232
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6.972
6.287
6.210
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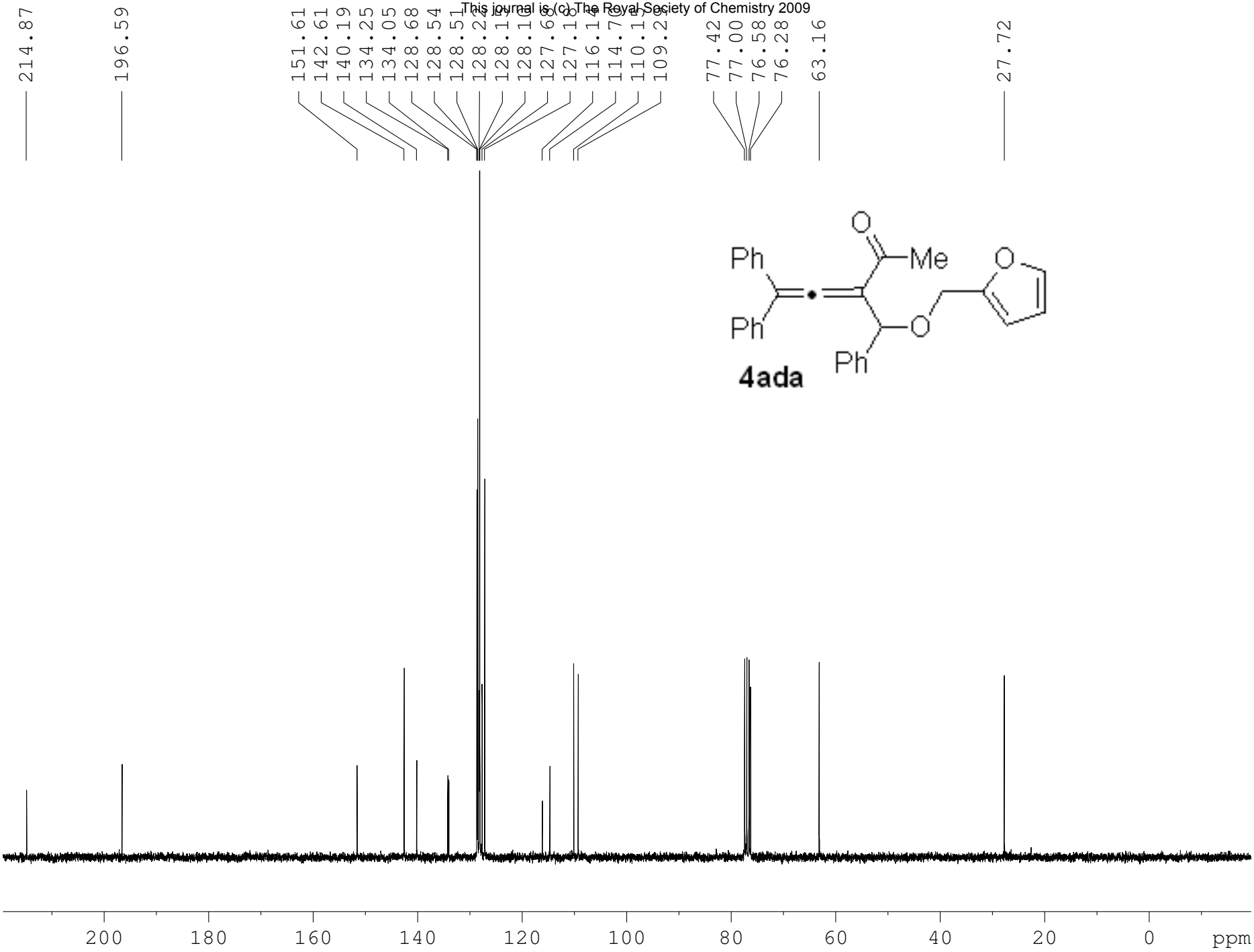
5.600
4.473
4.431
4.416
4.376
2.326
Ph
Ph
Me
O
O
O
Ph
4ada
9
8
7
6
5
4
3
2
1
ppm
8.16
6.31
2.08
0.96
0.97
1.00
2.05
3.04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151.61
142.61
140.19
134.25
134.05
128.68
128.54
128.51
128.24
128.19
128.16
127.68
127.18
116.14
114.76
110.15
109.25
77.42
77.00
76.58
76.28
63.16
27.72
Ph
Ph
O
Me
O
O
Ph
4ada
200
180
160
140
120
100
80
60
40
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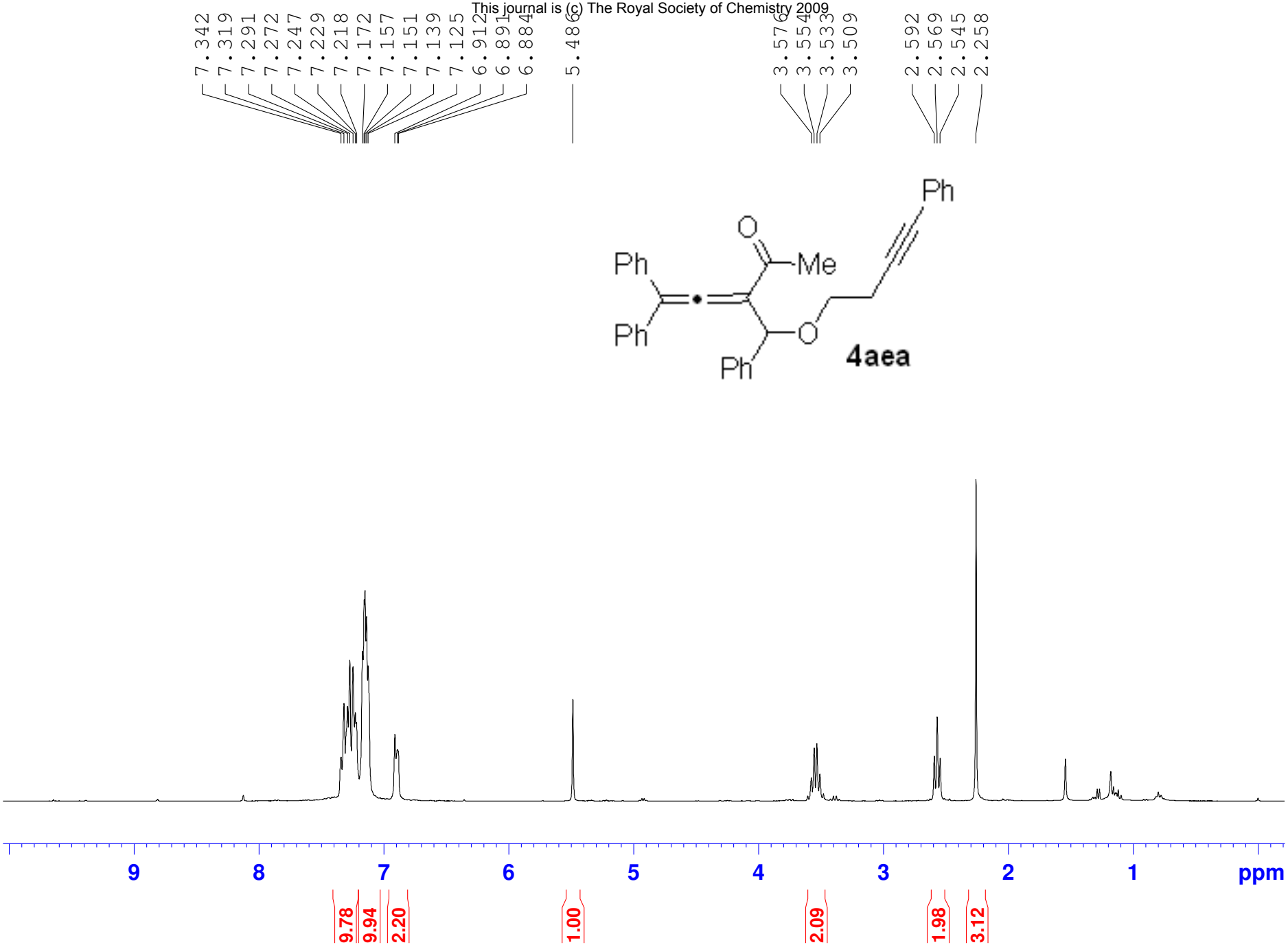
0
ppm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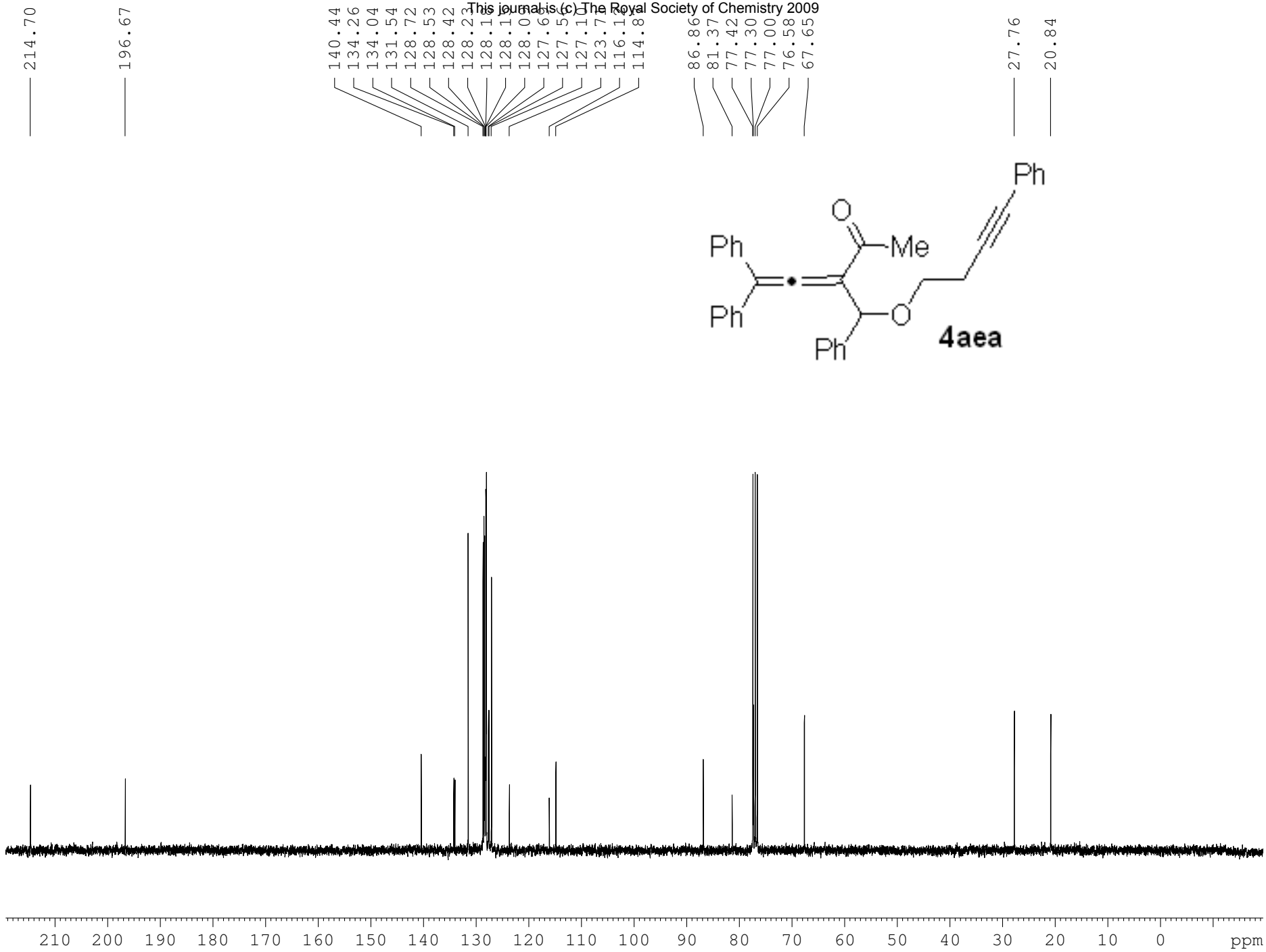
7.172
7.157
7.151
7.139
7.125
6.912
6.891
6.884
5.486
3.576
3.554
3.533
3.509
2.592
2.569
2.545
2.258
Ph
O
Me
Ph
Ph
O
Ph
4aea
9
8
7
6
5
4
3
2
1
ppm
9.78
9.94
2.20
1.00
2.09
1.98
3.12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134.26
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131.54
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128.53
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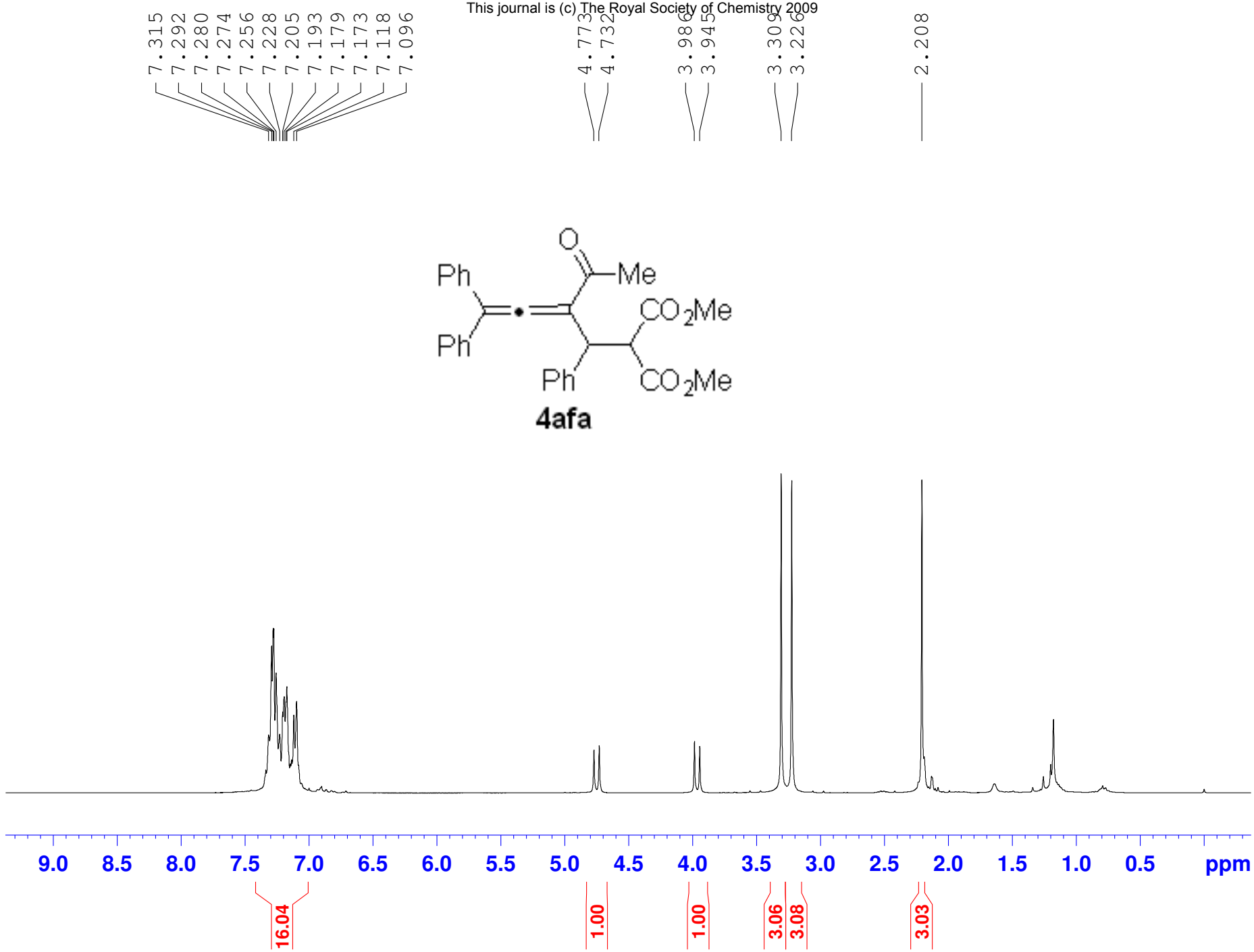
128.23
128.15
128.11
128.01
127.65
127.55
127.11
123.71
116.11
114.87
86.86
81.37
77.42
77.30
77.00
76.58
67.65
27.76
20.84
Ph
O
Me
Ph
Ph
O
Ph
4aea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.280
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7.228
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7.173
7.118
7.096
4.773
4.732
3.986
3.945
3.309
3.226
2.208
Ph
Ph
O
Me
CO2Me
Ph
CO2Me
4afa
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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ppm
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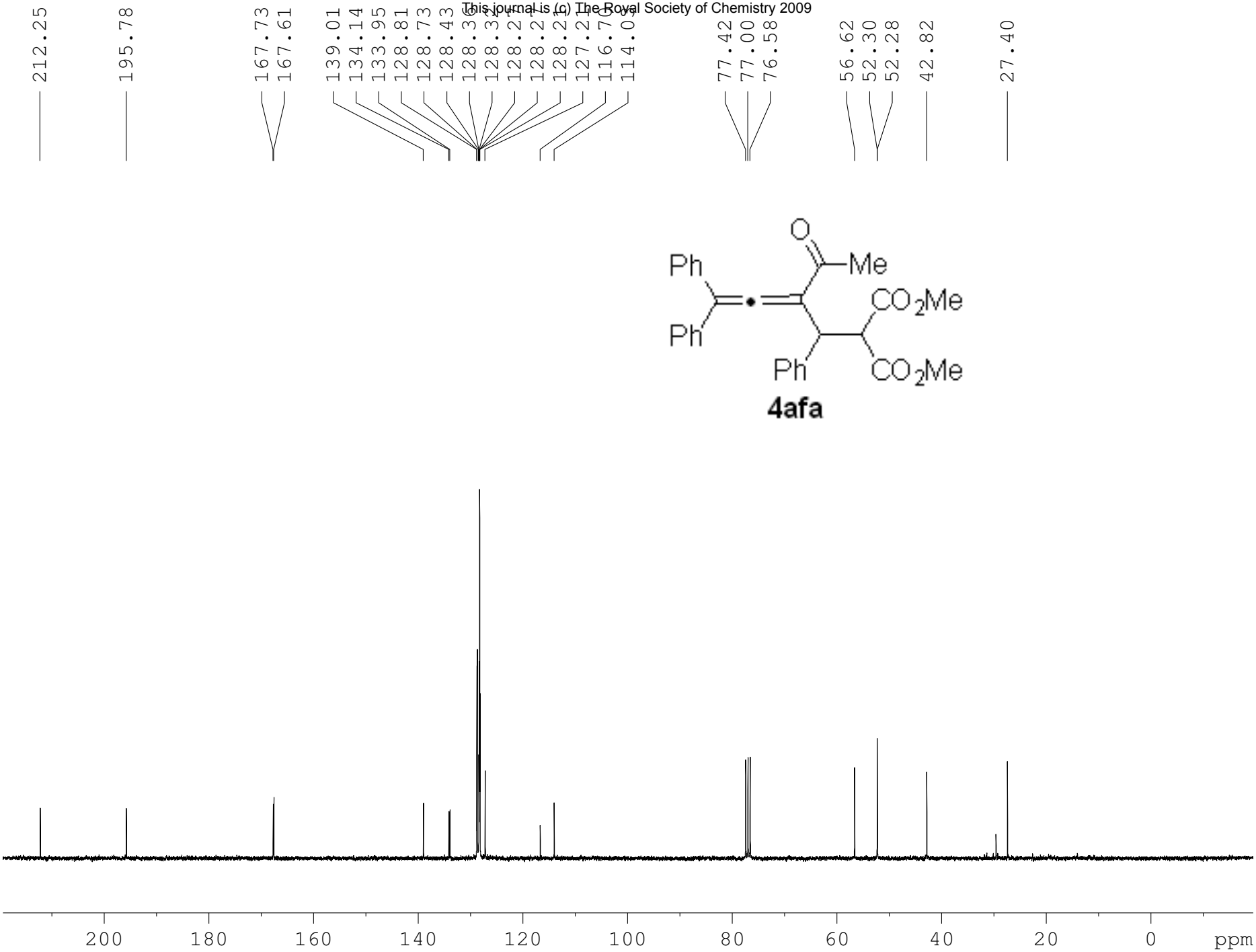
3.06
3.08
3.03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128.21
128.21
128.21
127.21
116.75
114.09
77.42
77.00
76.58
56.62
52.30
52.28
42.82
27.40
Ph
Ph
O
Me
CO2Me
Ph
CO2Me
4afa
200
180
160
140
120
100
80
60
40
20
0
ppm