

SUPPLEMENTARY INFORMATION

New approach to synthesis of functional derivatives of *nido*-carborane: Alkylation of [9-MeS-*nido*-7,8-C₂B₉H₁₁]

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Figure S1. ¹¹B{¹H} NMR spectrum of [9-Et(Me)S-*nido*-7,8-C₂B₉H₁₁] (**2**) in CDCl₃.

Figure S2. ¹¹B NMR spectrum of [9-Et(Me)S-*nido*-7,8-C₂B₉H₁₁] (**2**) in CDCl₃.

Figure S3. ¹H NMR spectrum of [9-Pr(Me)S-*nido*-7,8-C₂B₉H₁₁] (**3**) in CDCl₃.

Figure S4. ¹¹B{¹H} NMR spectrum of [9-Pr(Me)S-*nido*-7,8-C₂B₉H₁₁] (**3**) in CDCl₃.

Figure S5. ¹¹B NMR spectrum of [9-Pr(Me)S-*nido*-7,8-C₂B₉H₁₁] (**3**) in CDCl₃.

Figure S6. ¹H NMR spectrum of [9-Bu(Me)S-*nido*-7,8-C₂B₉H₁₁] (**4**) in CDCl₃.

Figure S7. ¹¹B{¹H} NMR spectrum of [9-Bu(Me)S-*nido*-7,8-C₂B₉H₁₁] (**4**) in CDCl₃.

Figure S8. ¹¹B NMR spectrum of [9-Bu(Me)S-*nido*-7,8-C₂B₉H₁₁] (**4**) in CDCl₃.

Figure S9. ¹H NMR spectrum of [9-Bn(Me)S-*nido*-7,8-C₂B₉H₁₁] (**5**) in CDCl₃.

Figure S10. ¹³C NMR spectrum of [9-Bn(Me)S-*nido*-7,8-C₂B₉H₁₁] (**5**) in CDCl₃.

Figure S11. ¹¹B{¹H} NMR spectrum of [9-Bn(Me)S-*nido*-7,8-C₂B₉H₁₁] (**5**) in CDCl₃.

Figure S12. ¹¹B NMR spectrum of [9-Bn(Me)S-*nido*-7,8-C₂B₉H₁₁] (**5**) in CDCl₃.

Figure S13. ¹H NMR spectrum of [9-BrCH₂CH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**6**) in CDCl₃.

Figure S14. ¹¹B{¹H} NMR spectrum of [9-BrCH₂CH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**6**) in CDCl₃.

Figure S15. ^{11}B NMR spectrum of [9-BrCH₂CH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**6**) in CDCl₃.

Figure S16. ^1H NMR spectrum of [9-EtOCH₂CH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**7**) in CDCl₃.

Figure S17. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of [9-EtOrCH₂CH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**7**) in CDCl₃.

Figure S18. ^{11}B NMR spectrum of [9-EtOCH₂CH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**7**) in CDCl₃.

Figure S19. ^1H NMR spectrum of [9-H₂C=CH(Me)S-*nido*-7,8-C₂B₉H₁₁] (**8**) in CDCl₃.

Figure S20. ^{13}C NMR spectrum of [9-H₂C=CH(Me)S-*nido*-7,8-C₂B₉H₁₁] (**8**) in CDCl₃.

Figure S21. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of [9-H₂C=CH(Me)S-*nido*-7,8-C₂B₉H₁₁] (**8**) in CDCl₃.

Figure S22. ^{11}B NMR spectrum of [9-H₂C=CH(Me)S-*nido*-7,8-C₂B₉H₁₁] (**8**) in CDCl₃.

Figure S23. ^1H NMR spectrum of [9-H₂C=CHCH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**9**) in CDCl₃.

Figure S24. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of [9-H₂C=CHCH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**9**) in CDCl₃.

Figure S25. ^{11}B NMR spectrum of [9-H₂C=CHCH₂(Me)S-*nido*-7,8-C₂B₉H₁₁] (**9**) in CDCl₃.

Figure S26. ^1H NMR spectrum of [9-HC≡C(Me)S-*nido*-7,8-C₂B₉H₁₁] (**10**) in CDCl₃.

Figure S27. ^{13}C NMR spectrum of [9-HC≡C(Me)S-*nido*-7,8-C₂B₉H₁₁] (**10**) in CDCl₃.

Figure S28. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of [9-HC≡C(Me)S-*nido*-7,8-C₂B₉H₁₁] (**10**) in CDCl₃.

Figure S29. ^{11}B NMR spectrum of [9-HC≡C(Me)S-*nido*-7,8-C₂B₉H₁₁] (**10**) in CDCl₃.

Figure S30. ^1H NMR spectrum of [9-H₂C=C=CH(Me)S-*nido*-7,8-C₂B₉H₁₁] (**11**) in CDCl₃.

Figure S31. ^{13}C NMR spectrum of [9-H₂C=C=CH(Me)S-*nido*-7,8-C₂B₉H₁₁] (**11**) in CDCl₃.

Figure S32. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of [9-H₂C=C=CH(Me)S-*nido*-7,8-C₂B₉H₁₁] (**11**) in CDCl₃.

Figure S33. ^{11}B NMR spectrum of [9-H₂C=C=CH(Me)S-*nido*-7,8-C₂B₉H₁₁] (**11**) in CDCl₃.

Table S1. Bond lengths distribution in [9-RMeS-*nido*-7,8-C₂B₉H₁₁] derivatives in comparison with [*nido*-7,8-C₂B₉H₁₂]⁻ anion.

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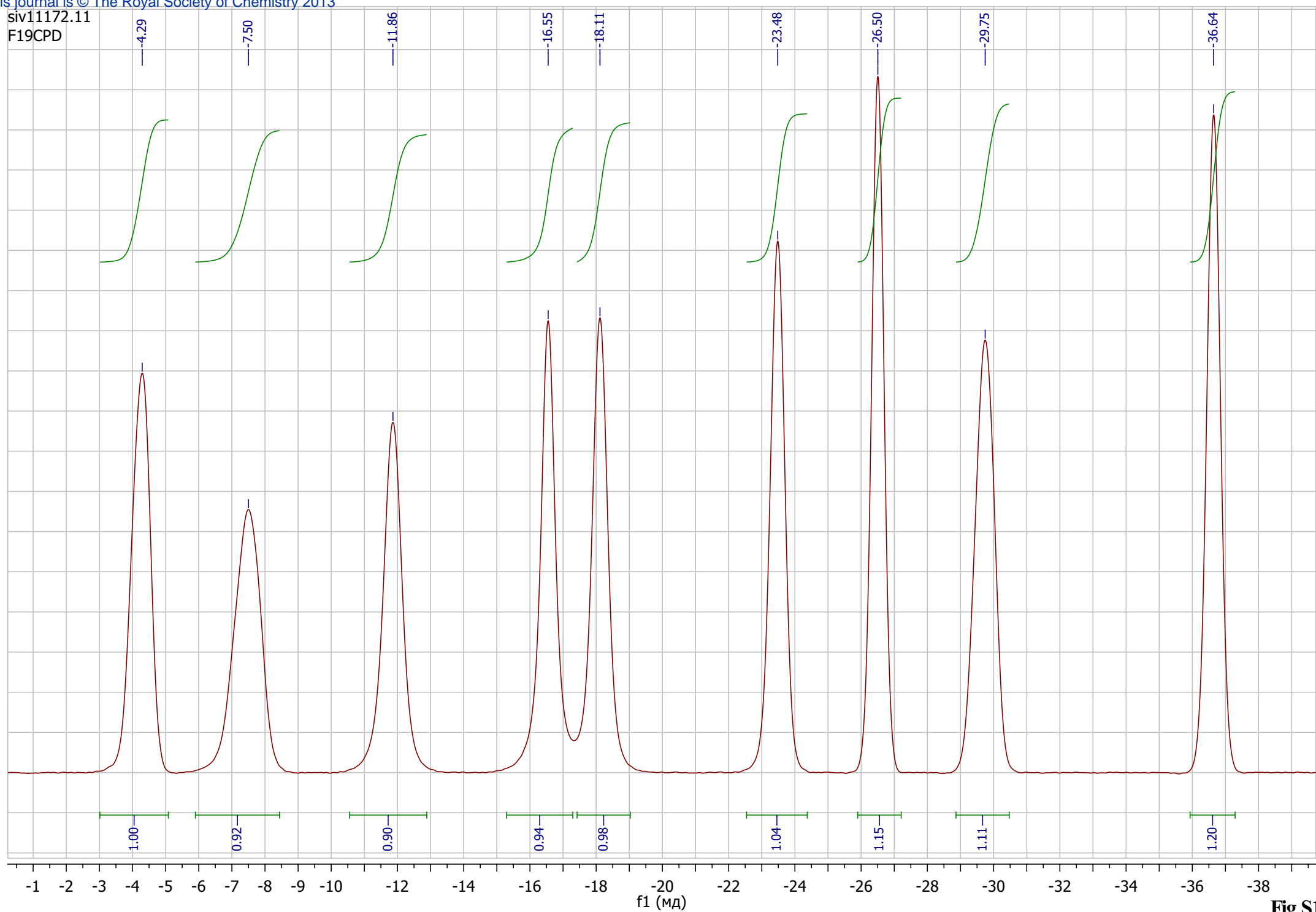


Fig S1

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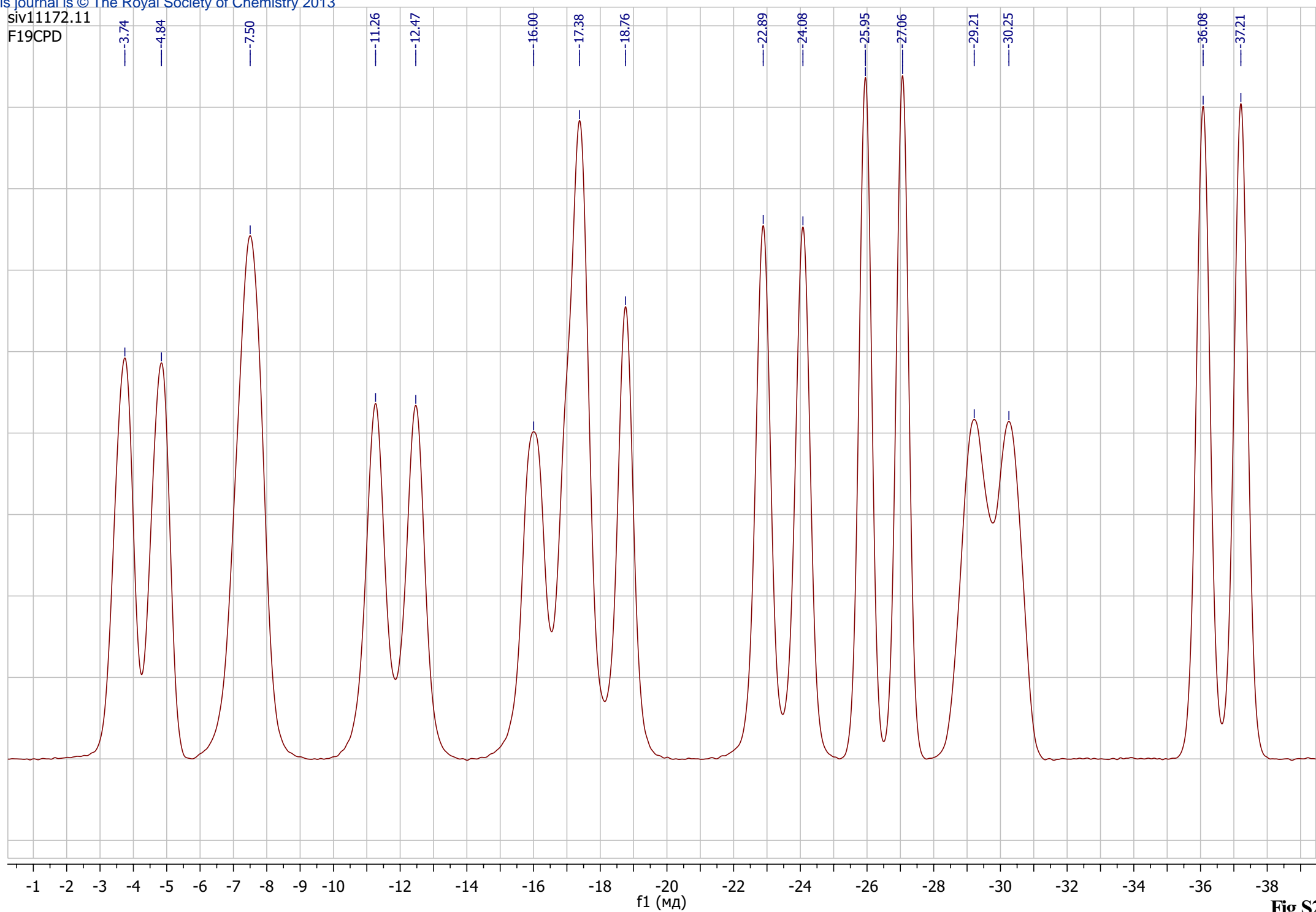


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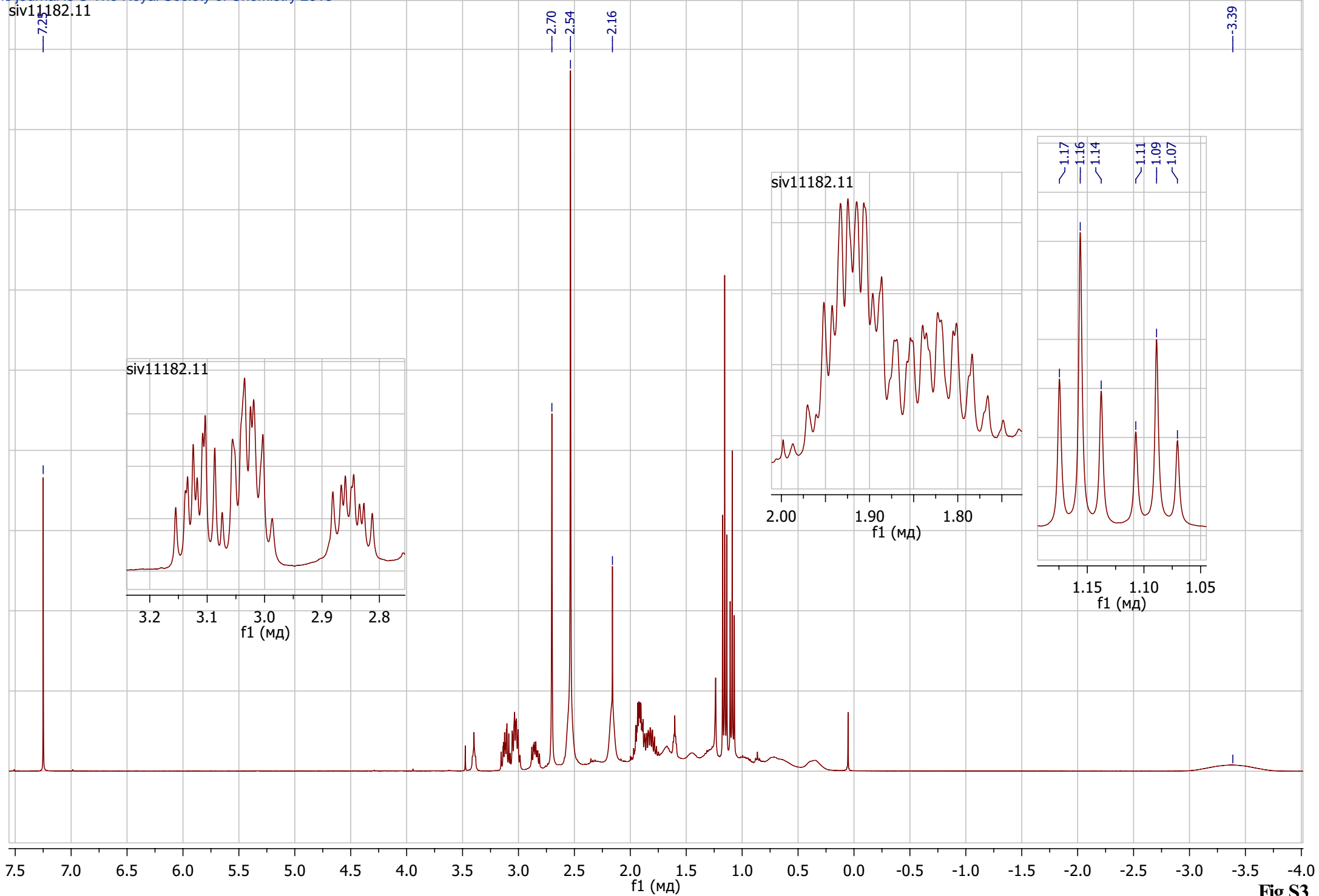


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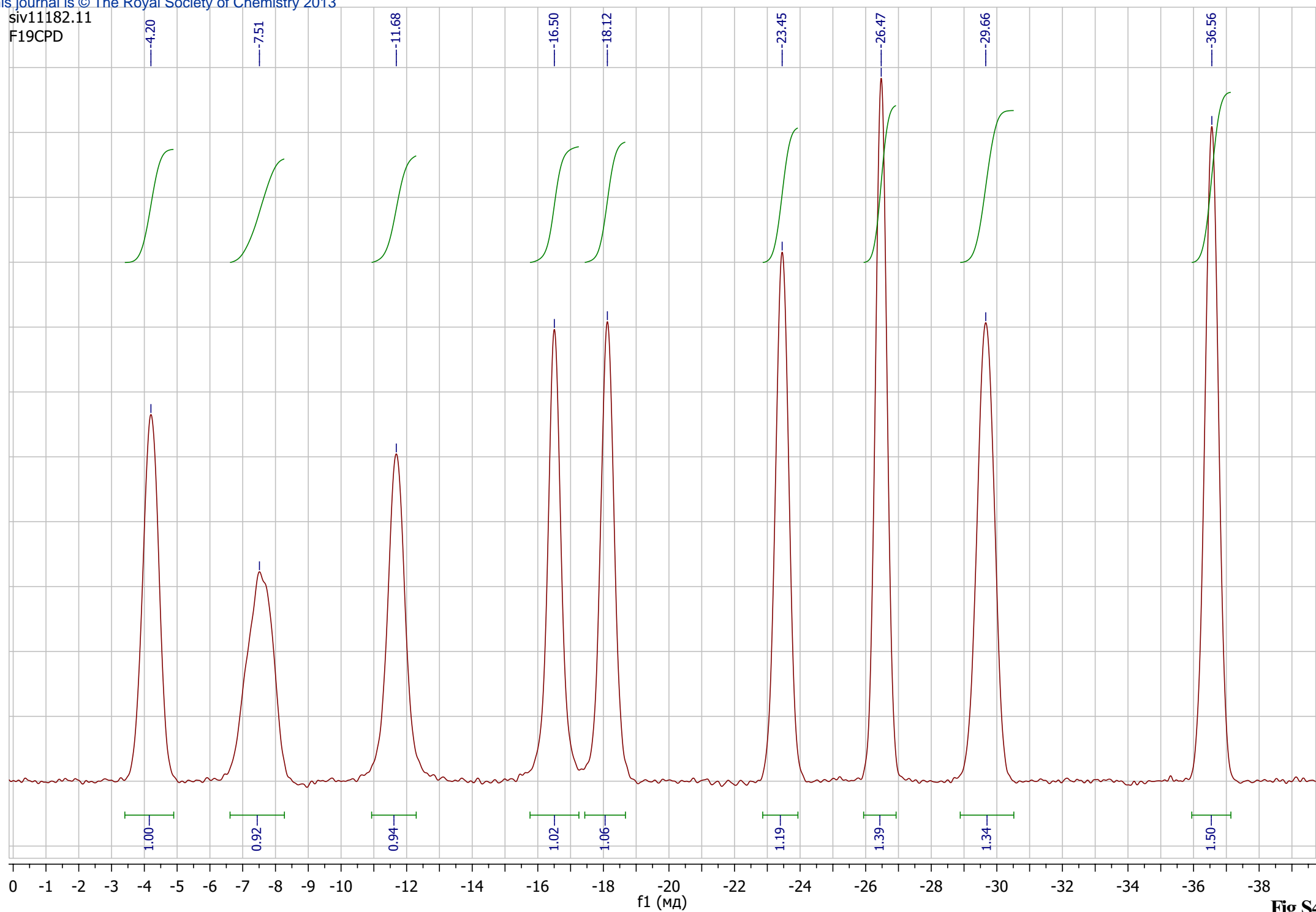


Fig S4

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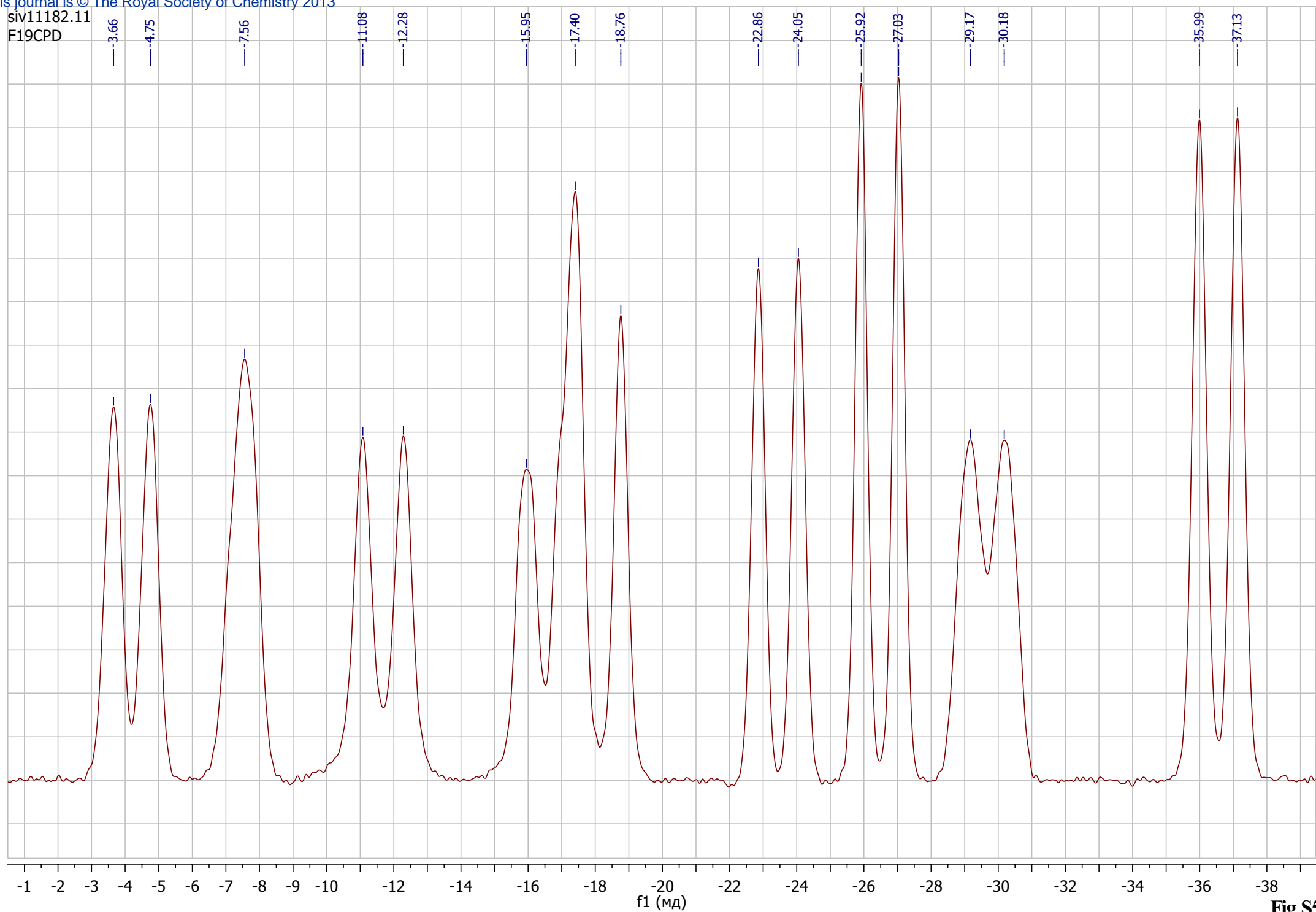


Fig S5

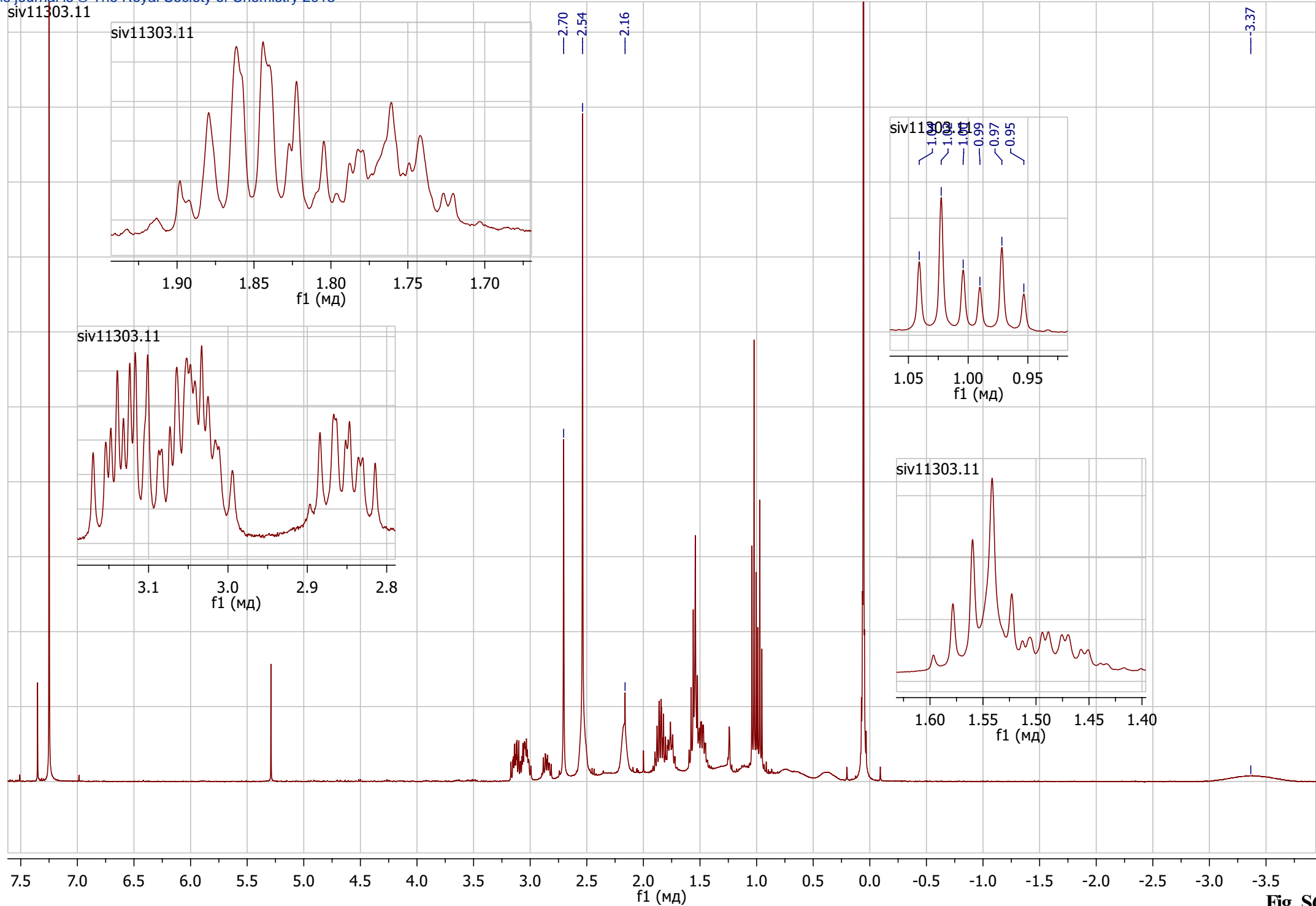


Fig. S6

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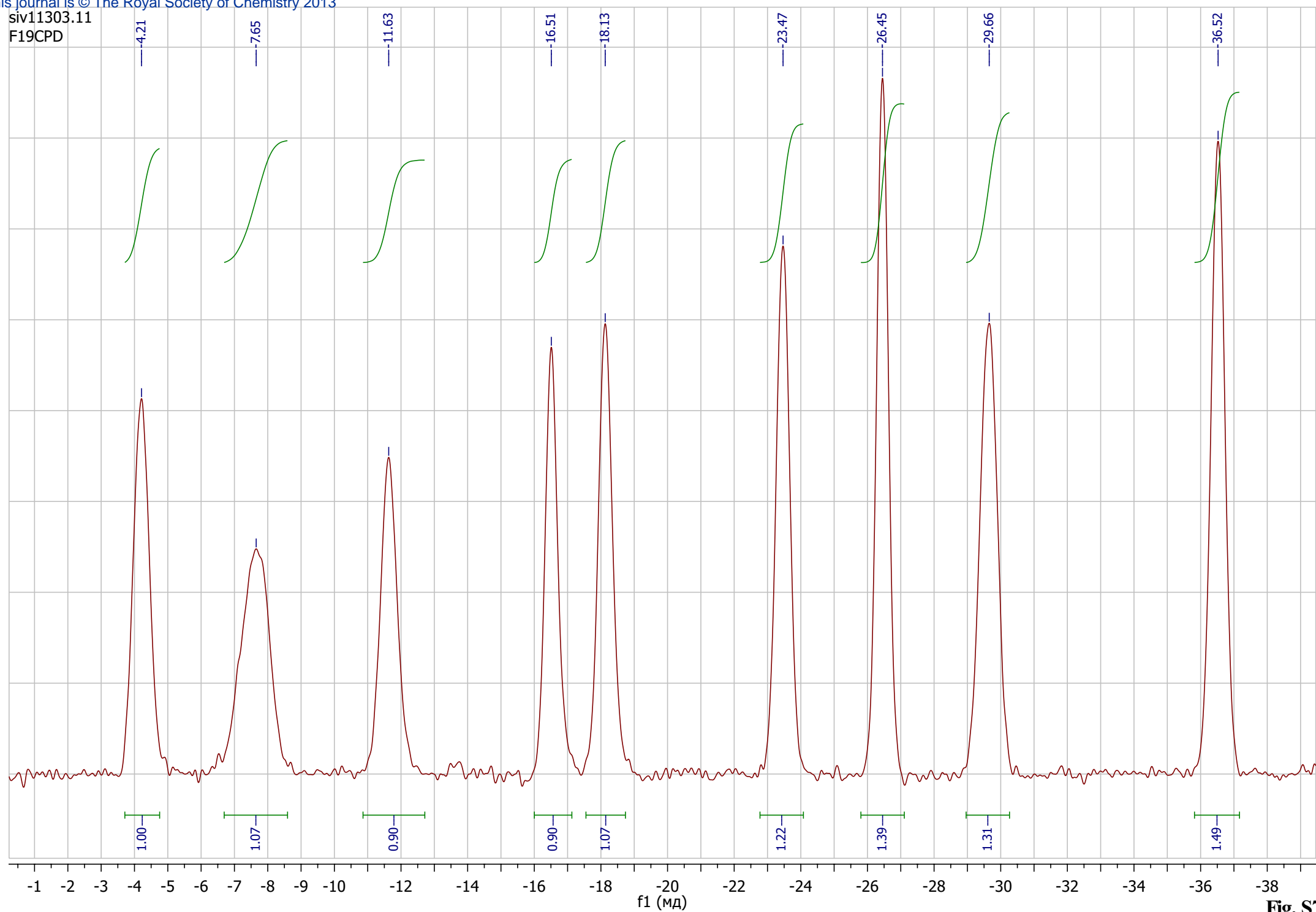


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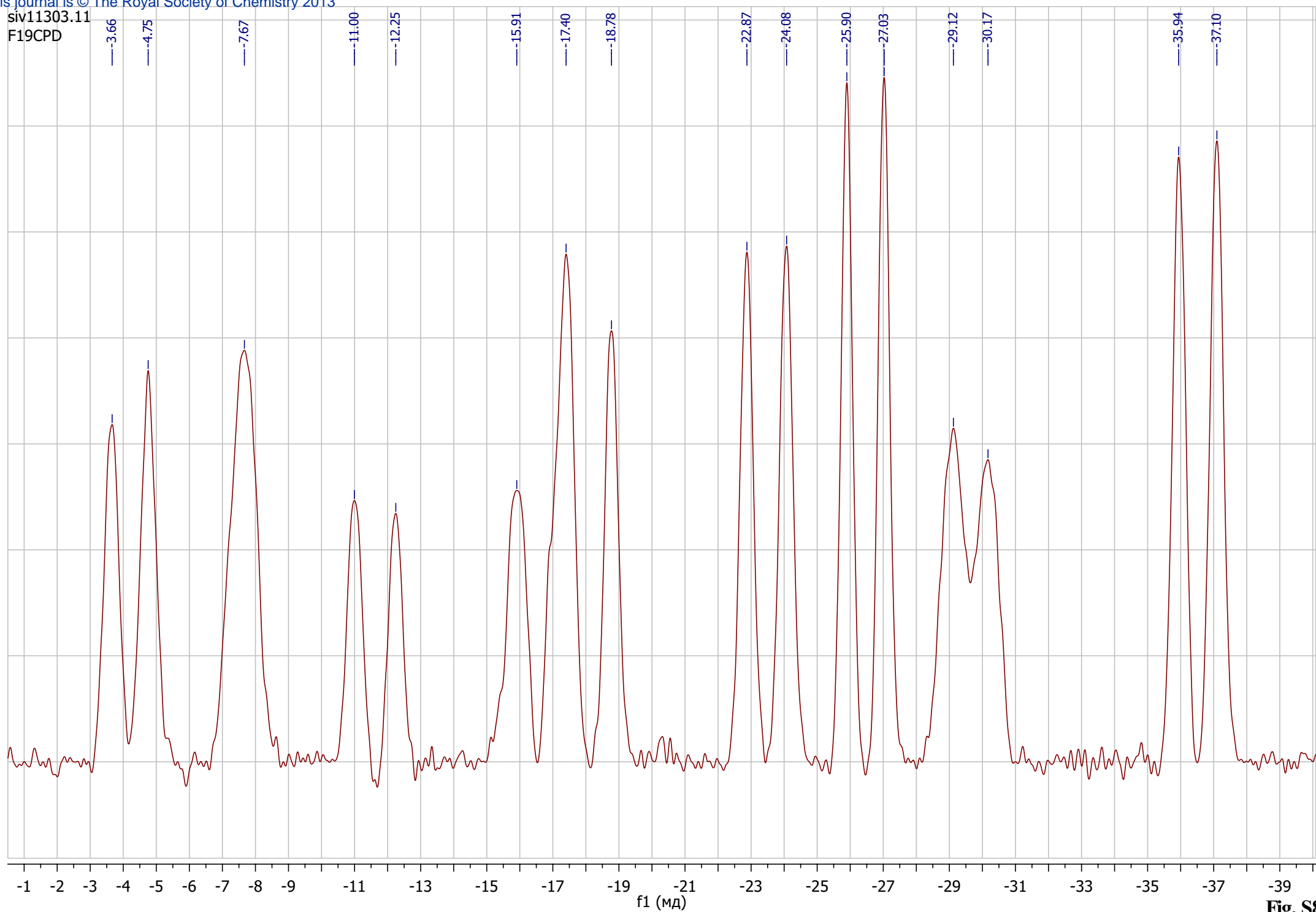


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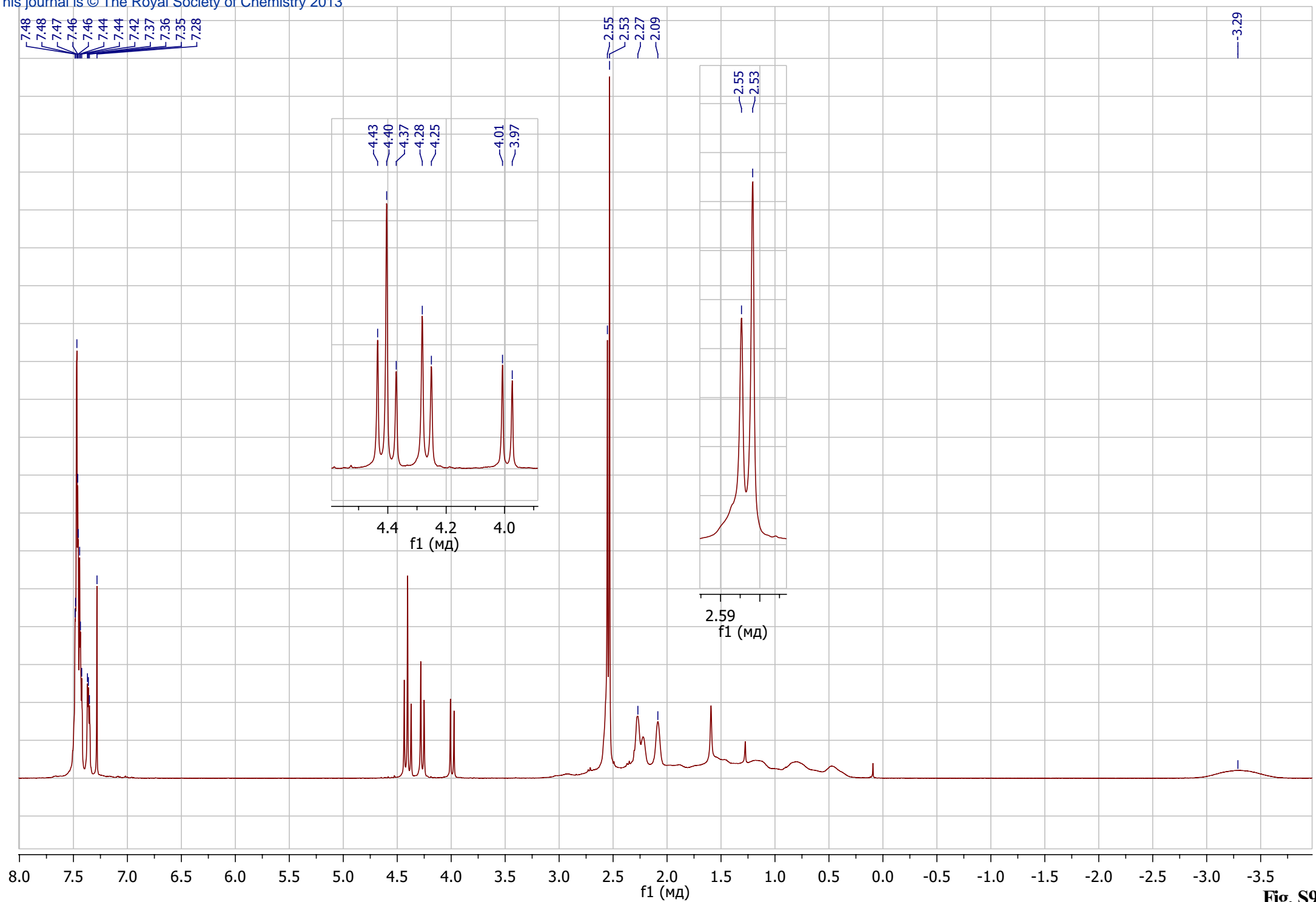


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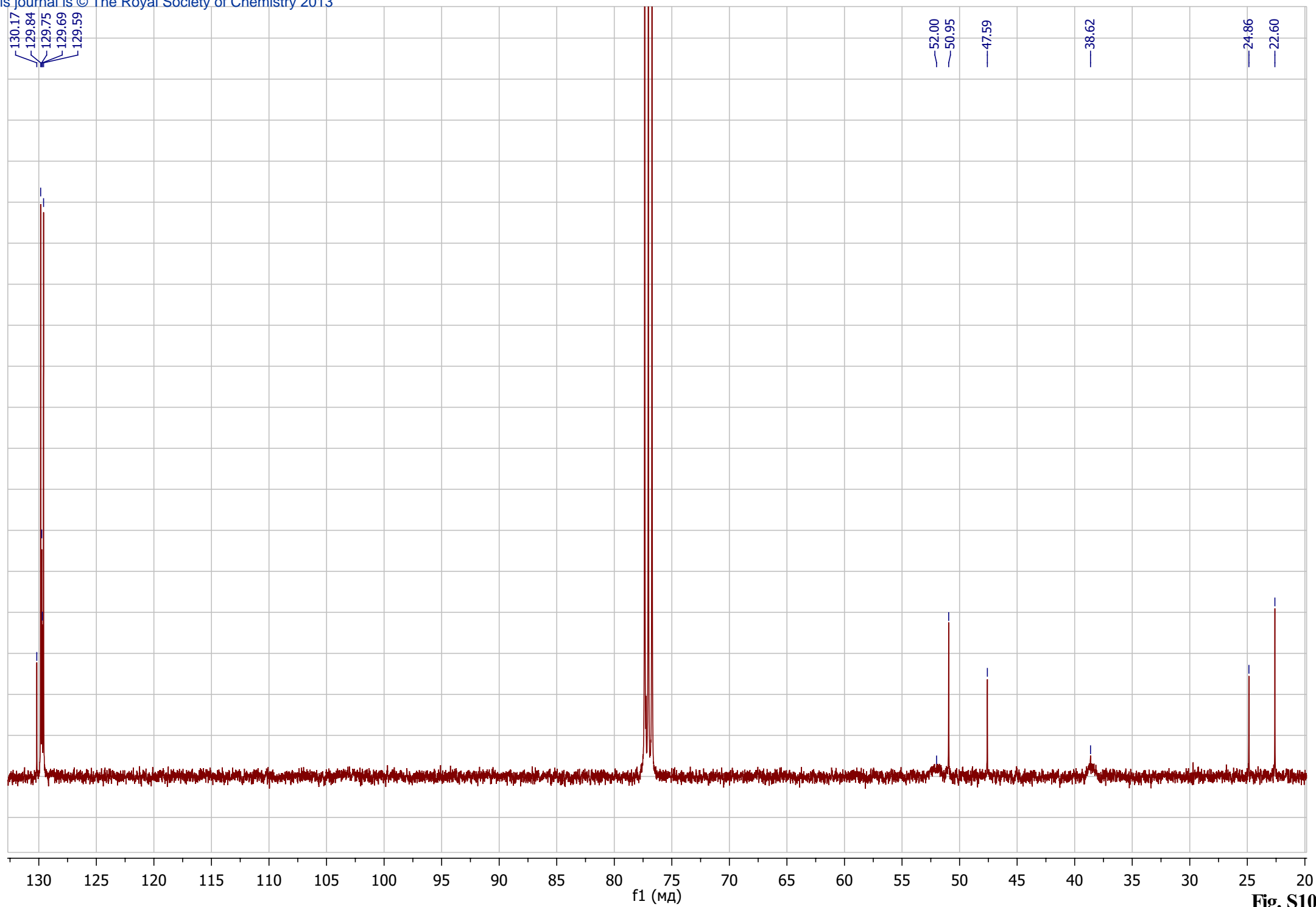


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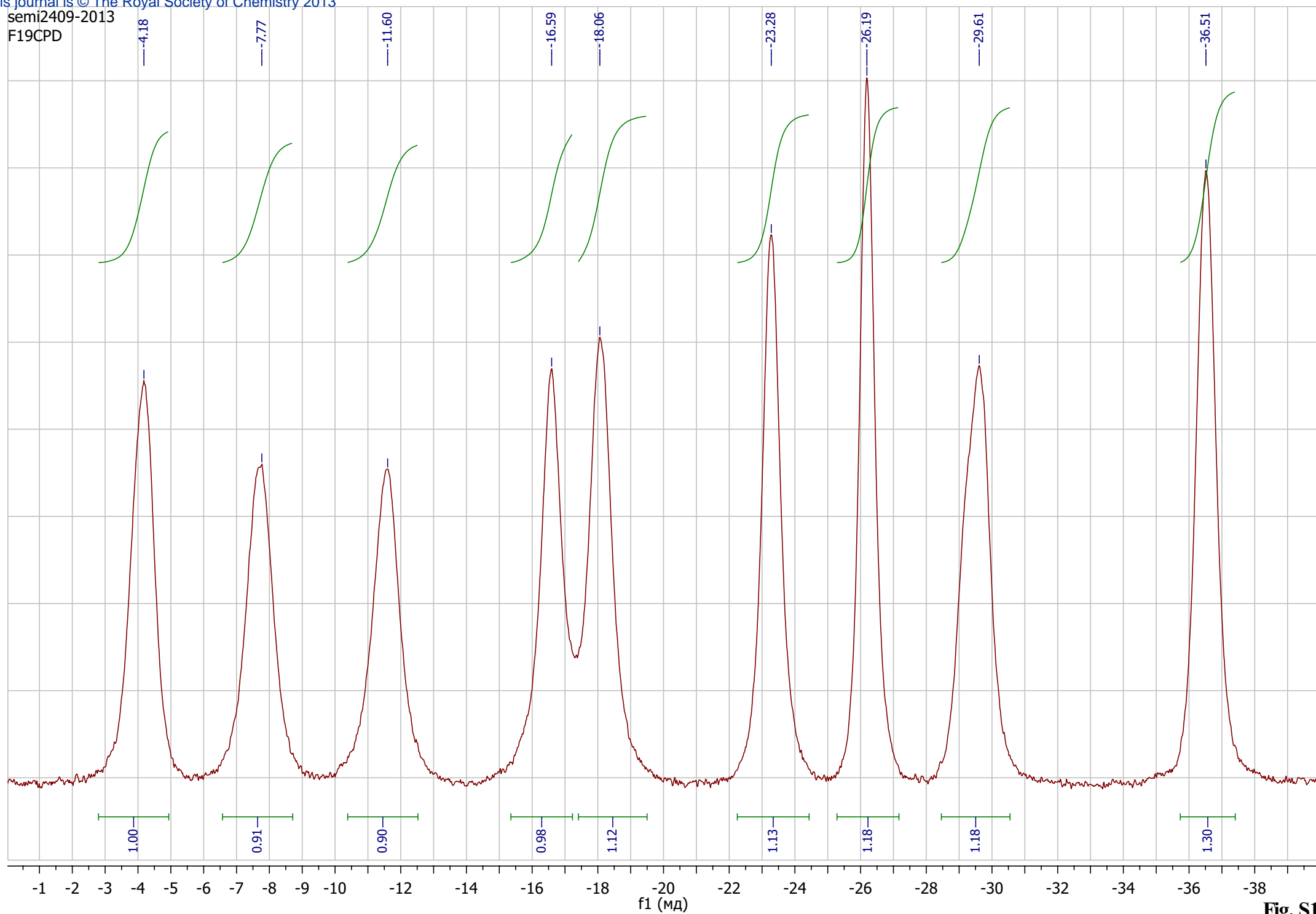


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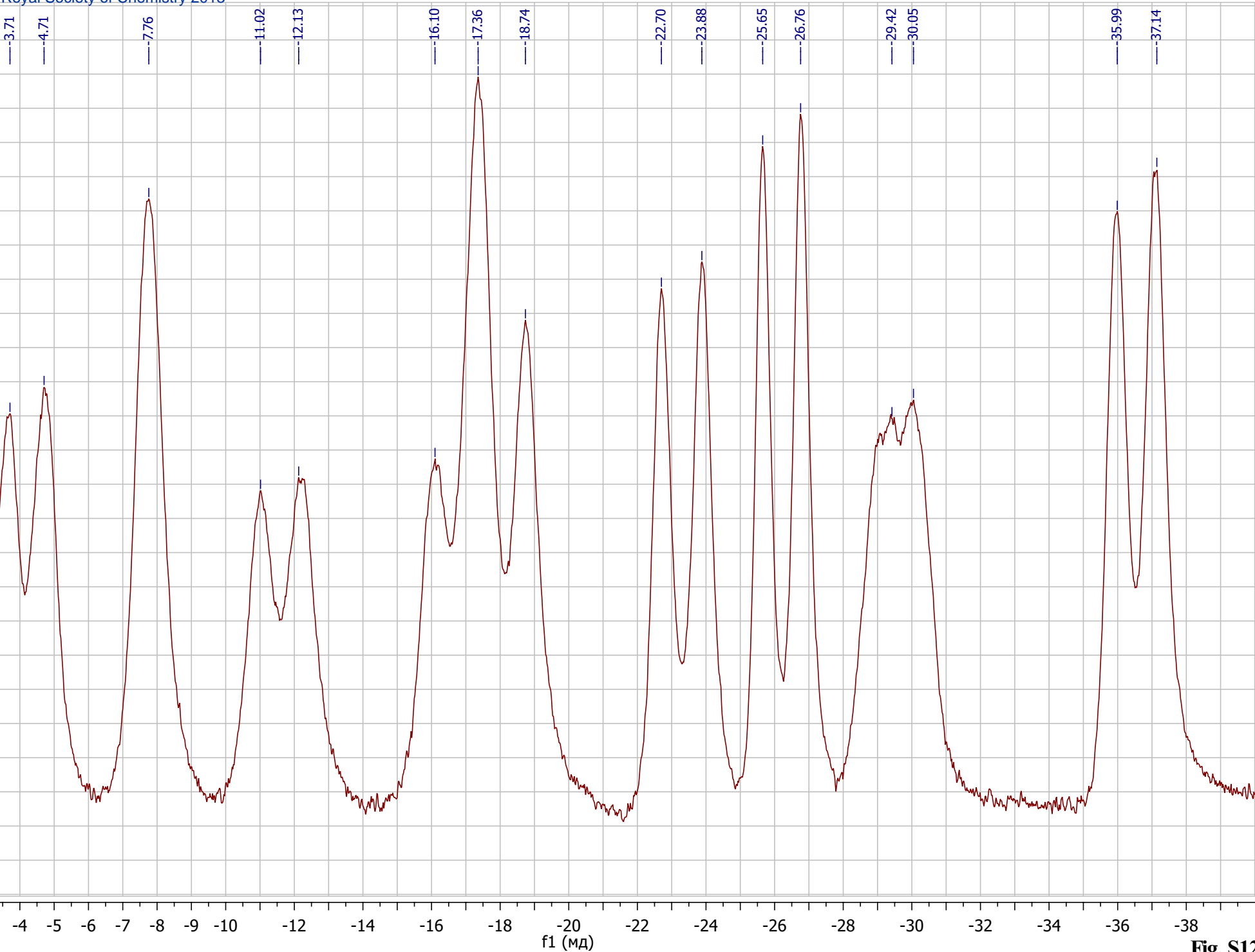


Fig. S12

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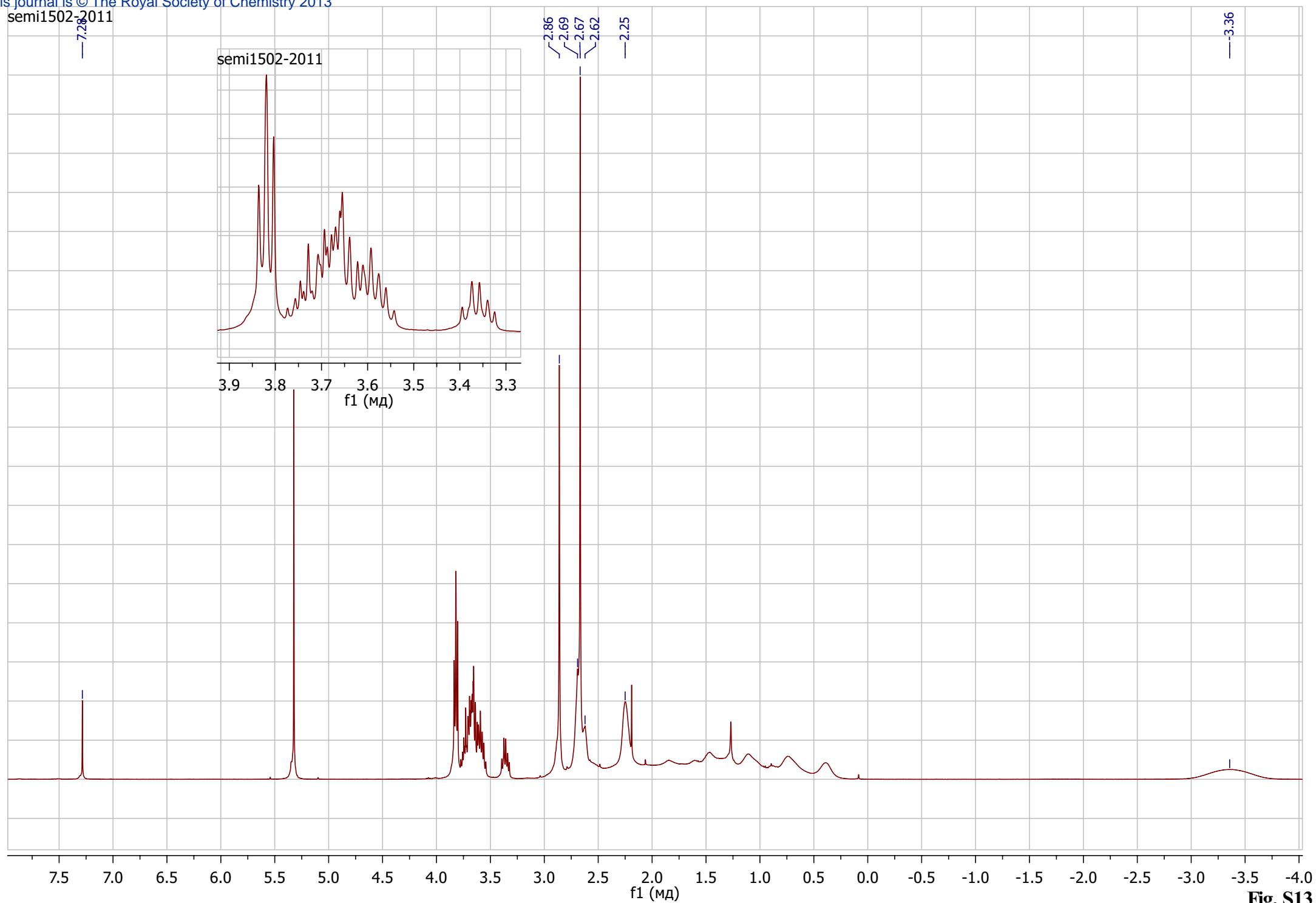


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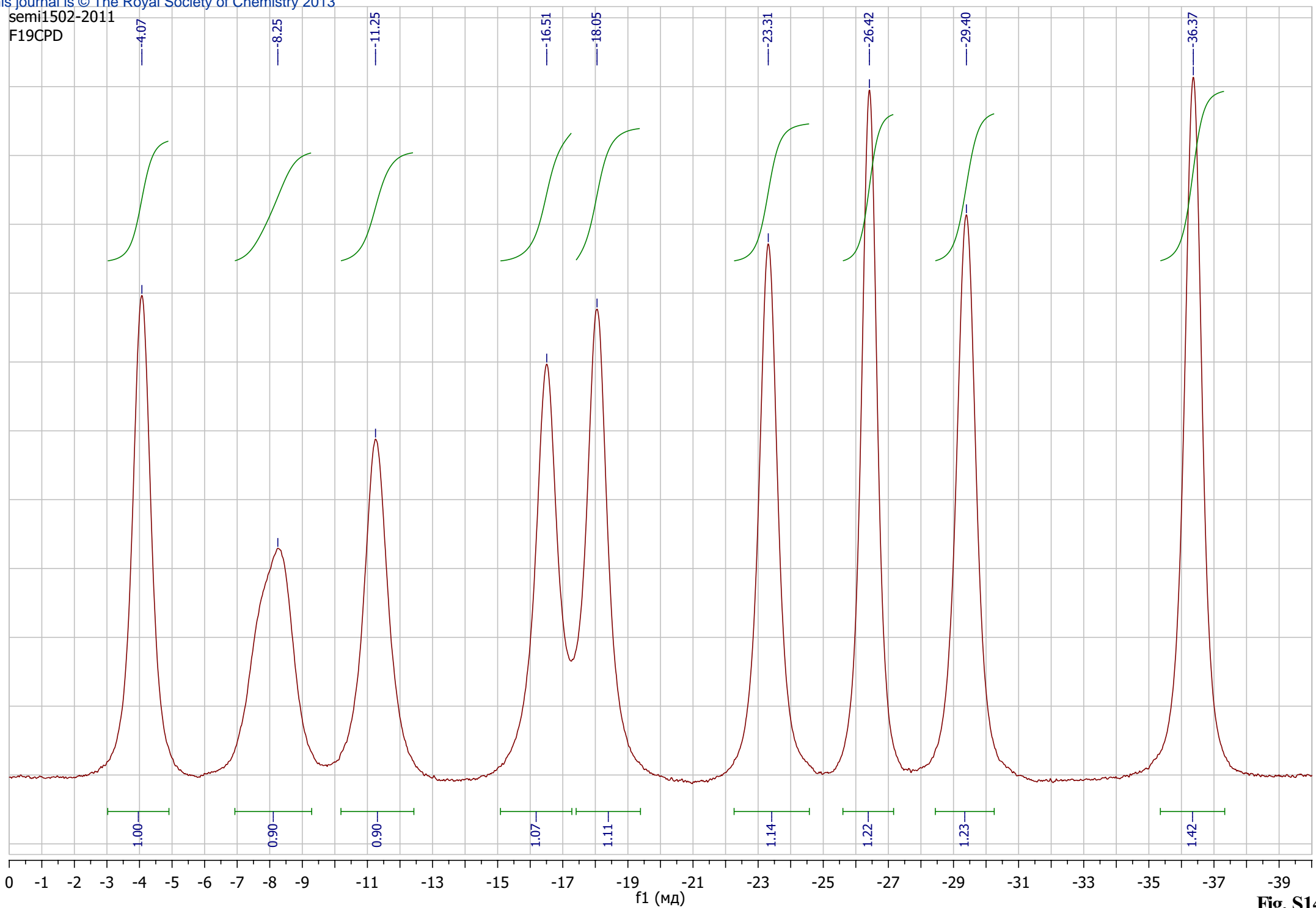


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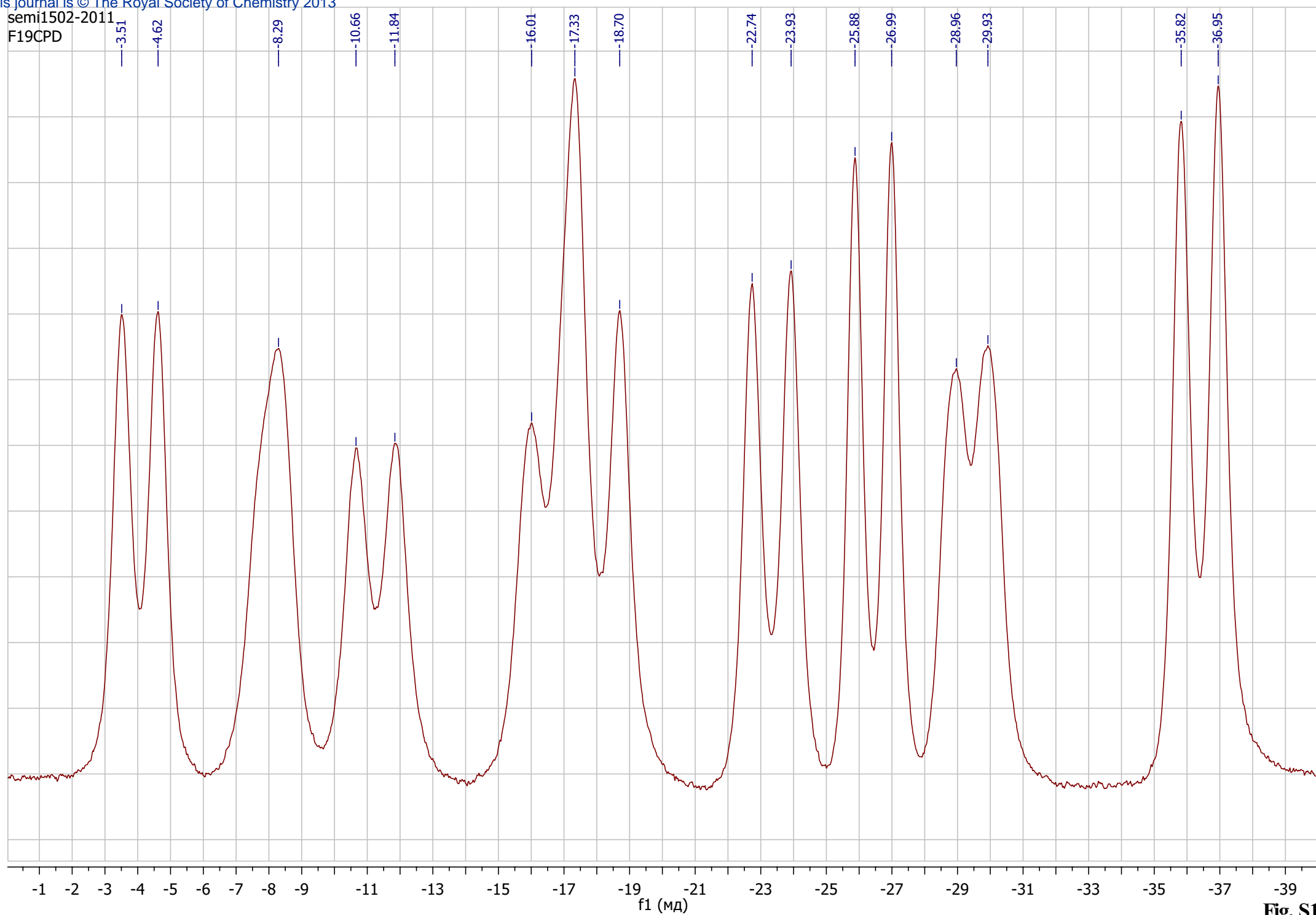


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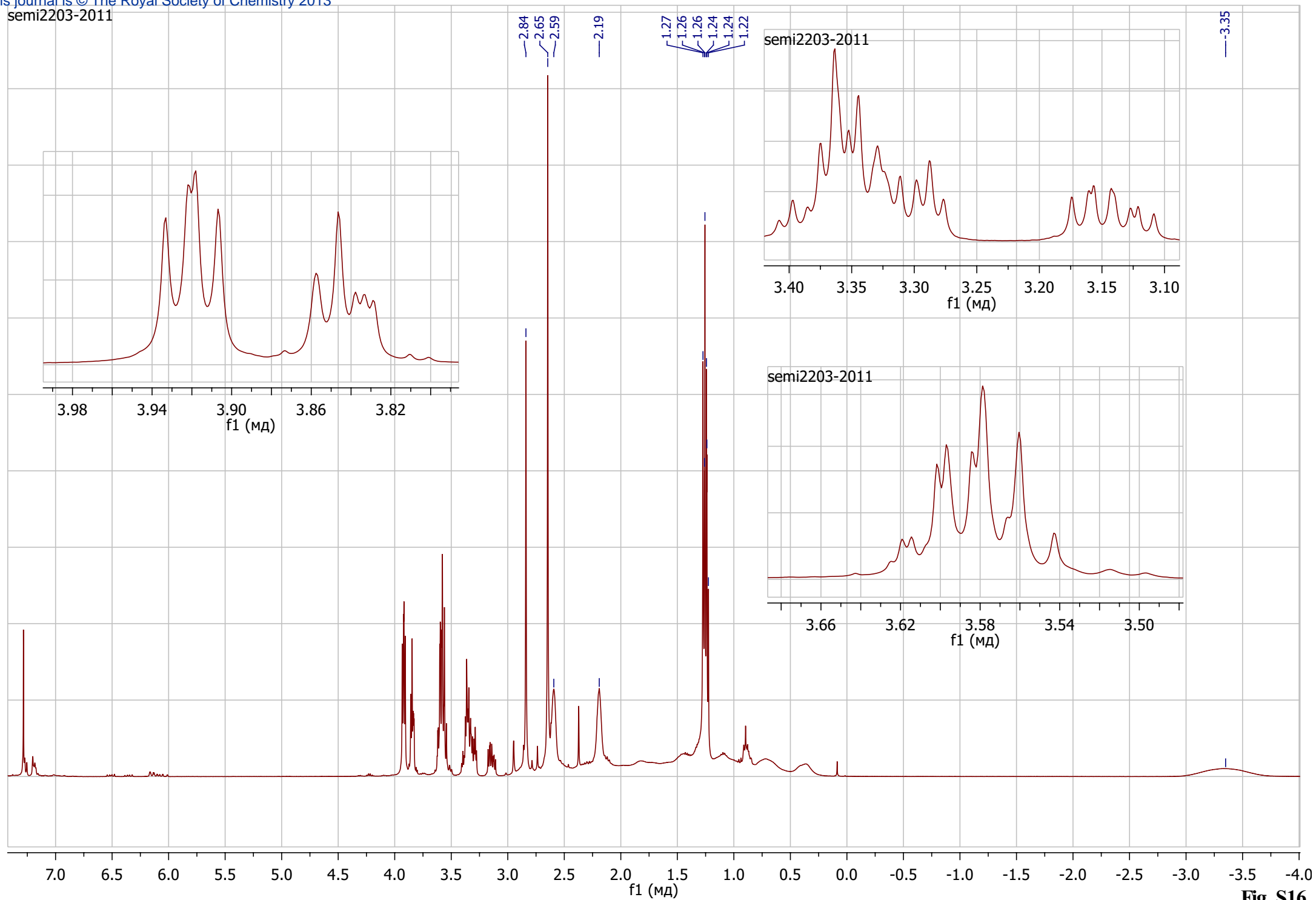


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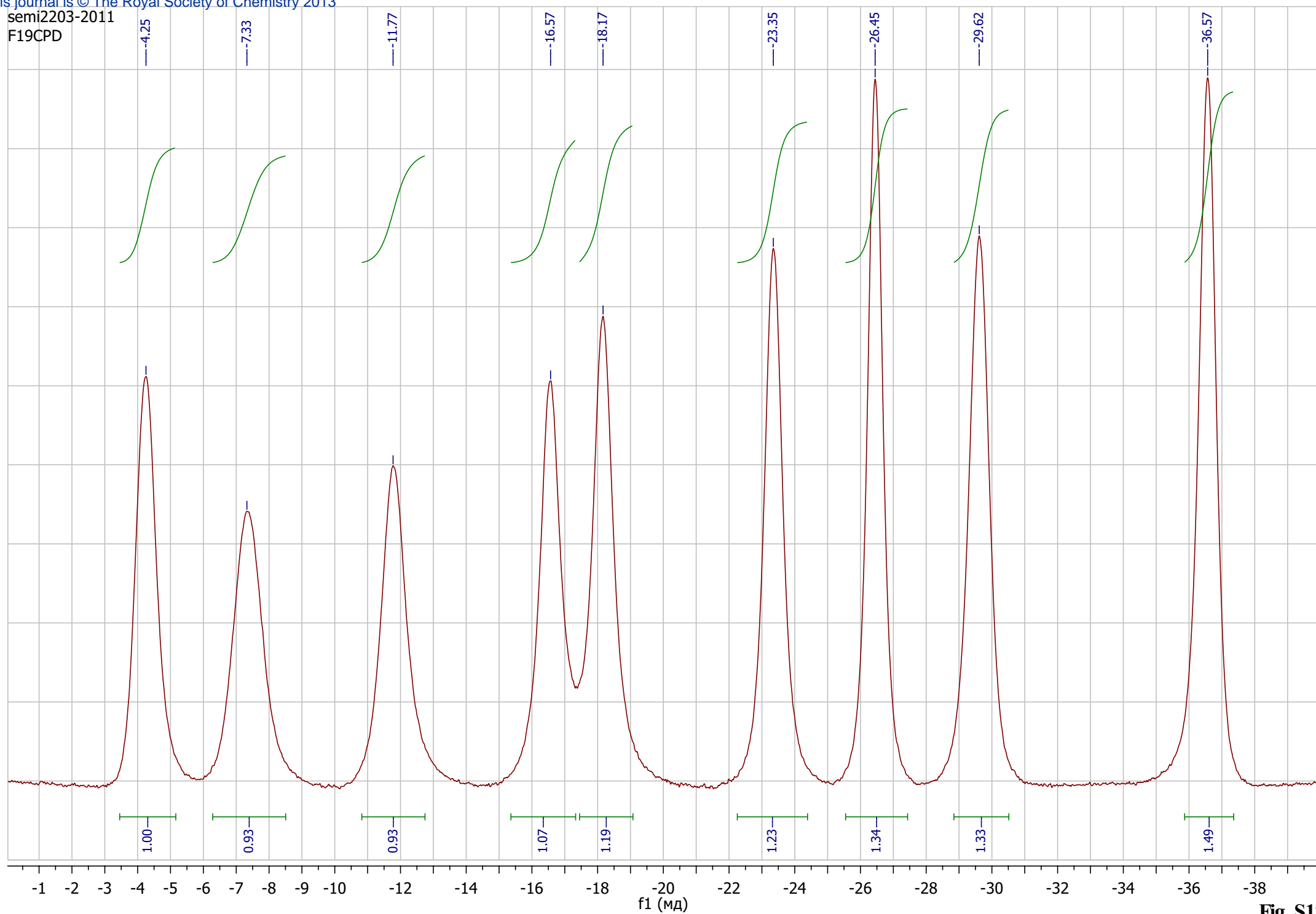


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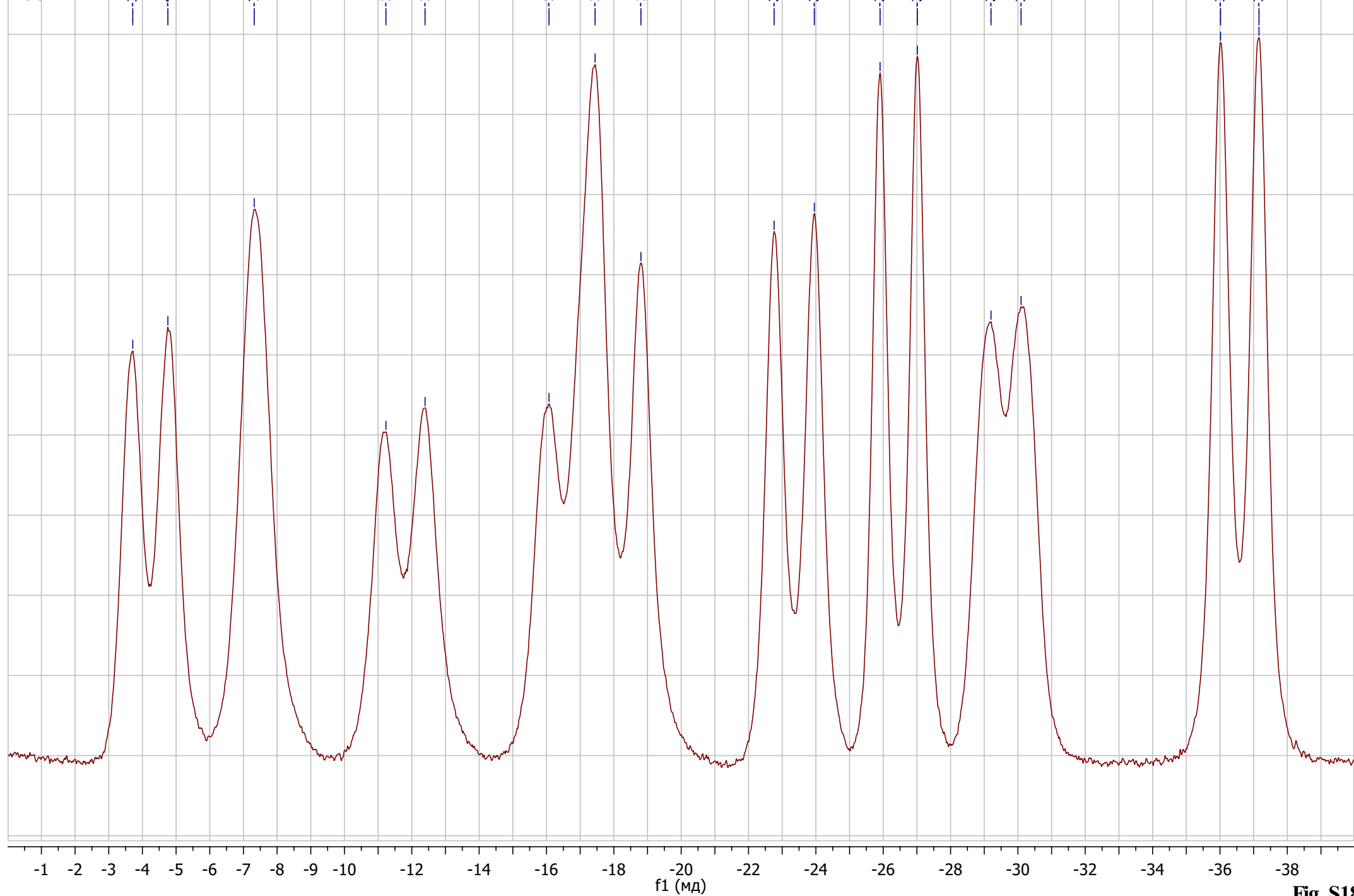


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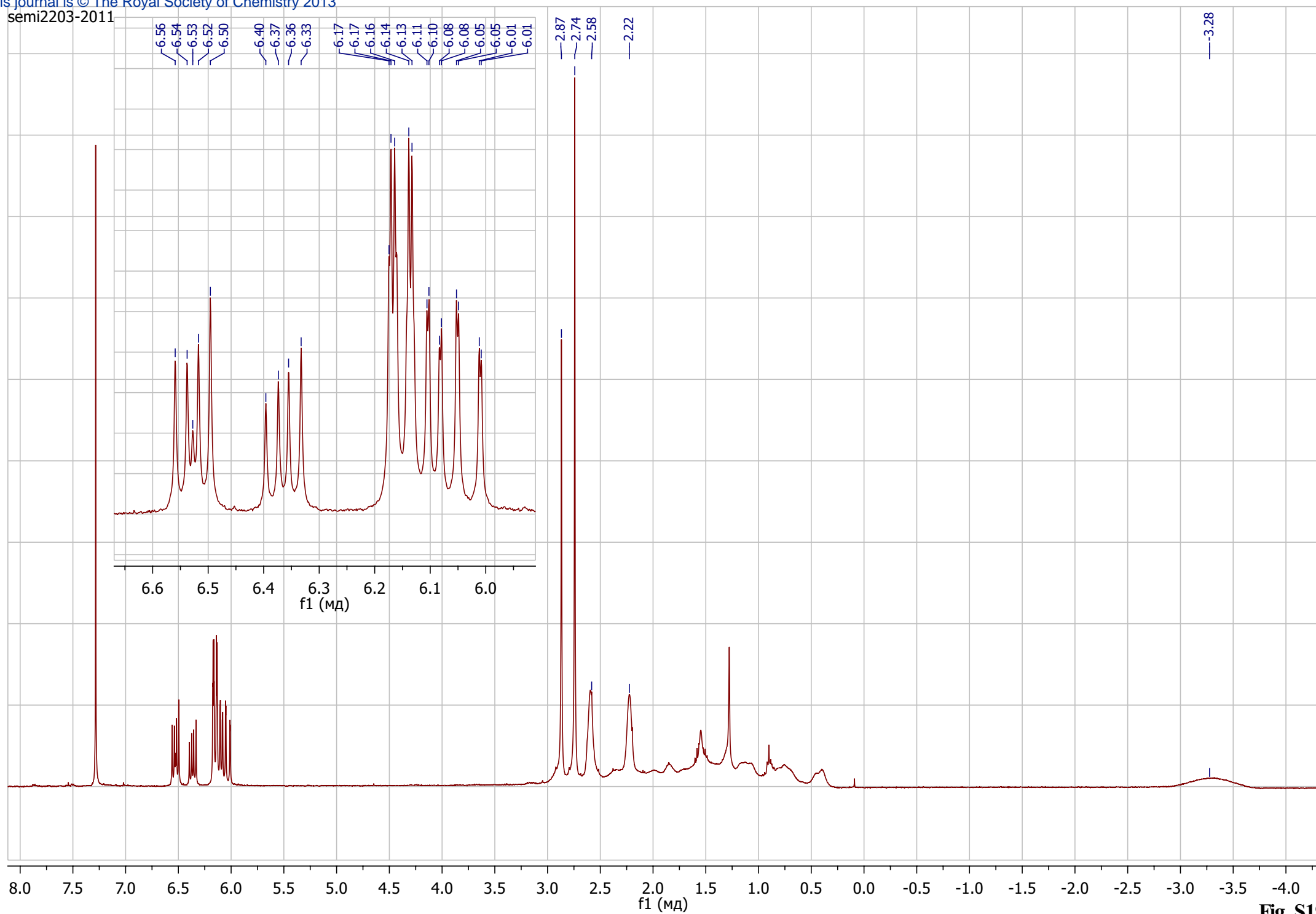


Fig. S19

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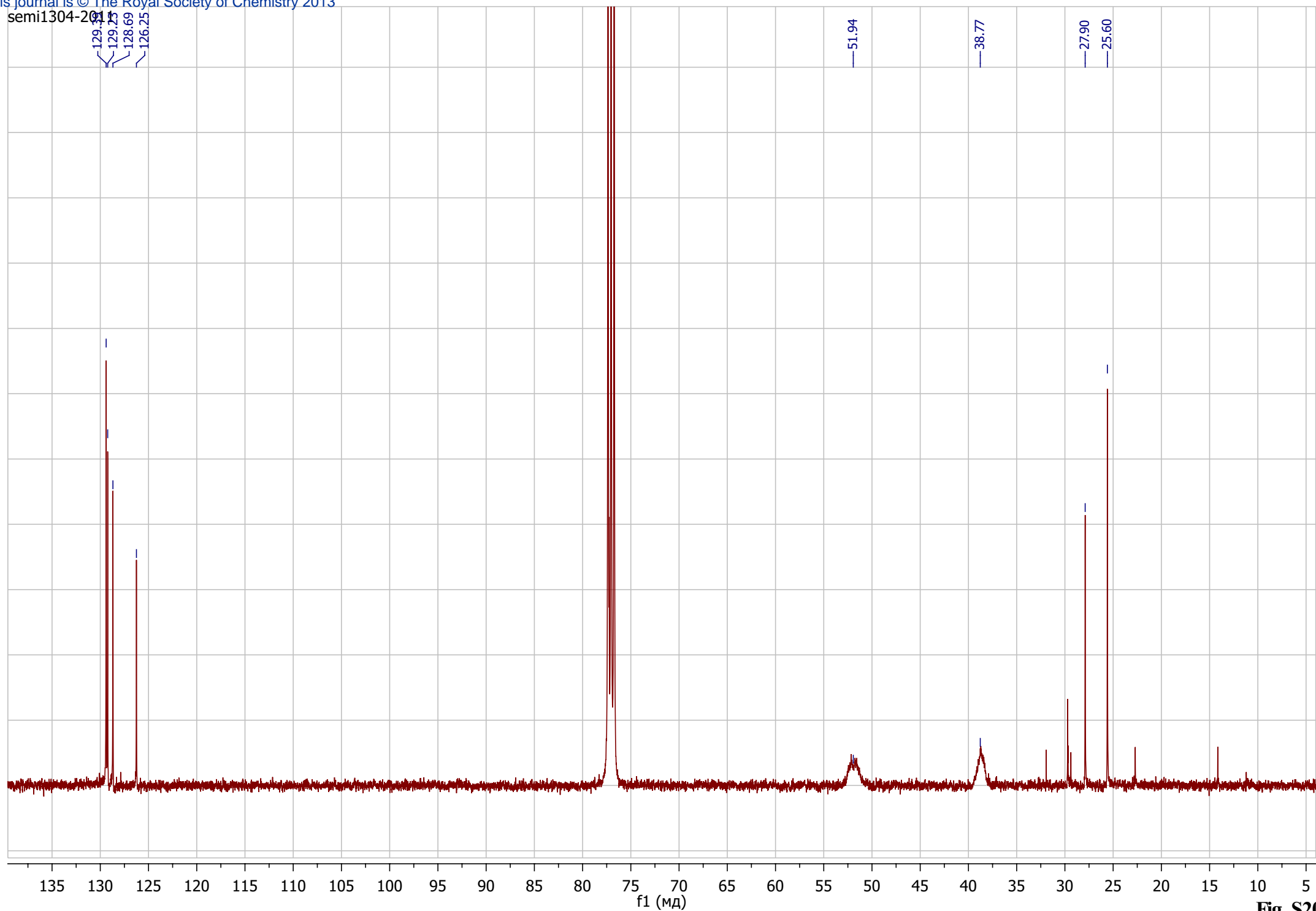


Fig. S20

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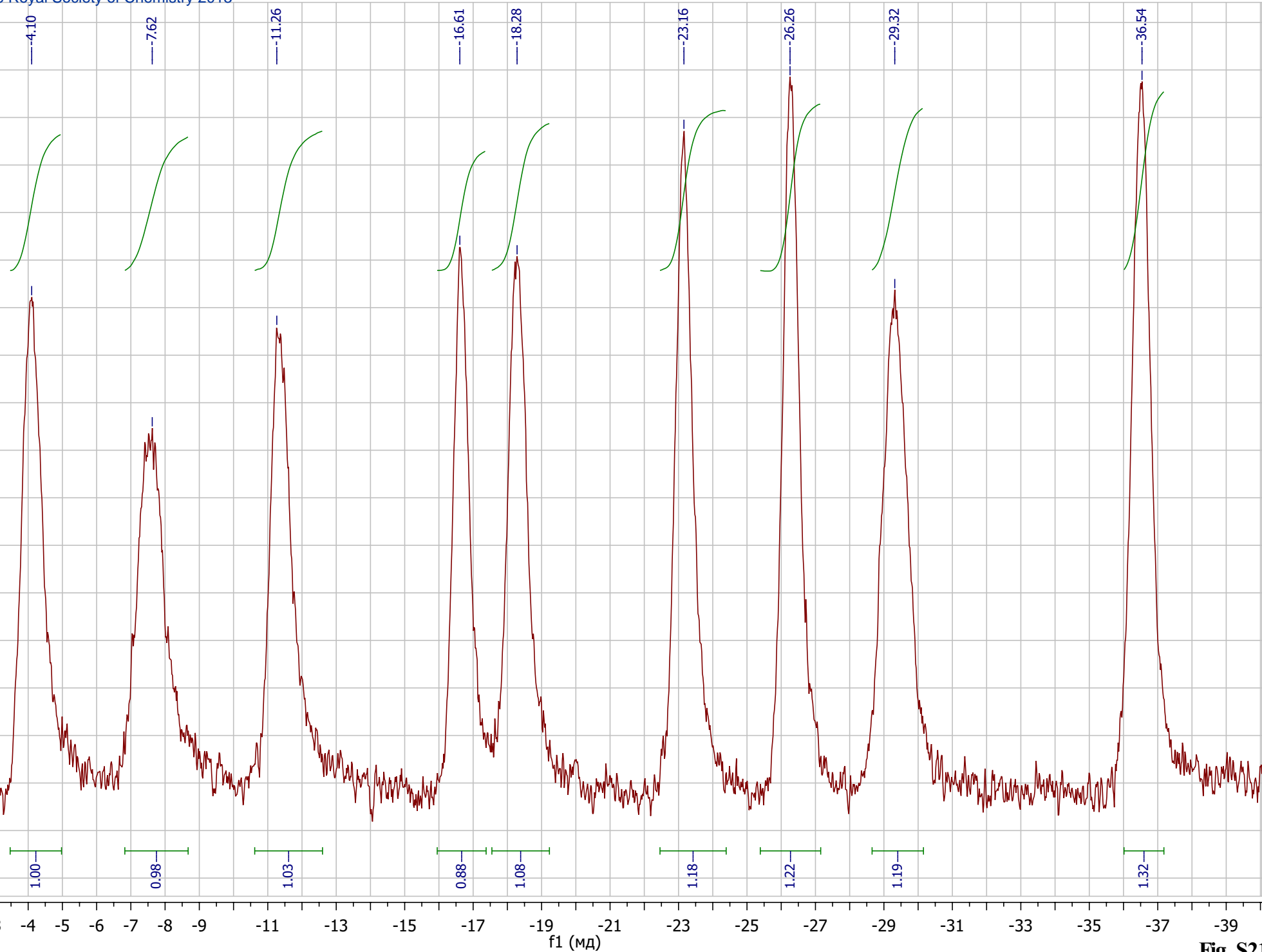


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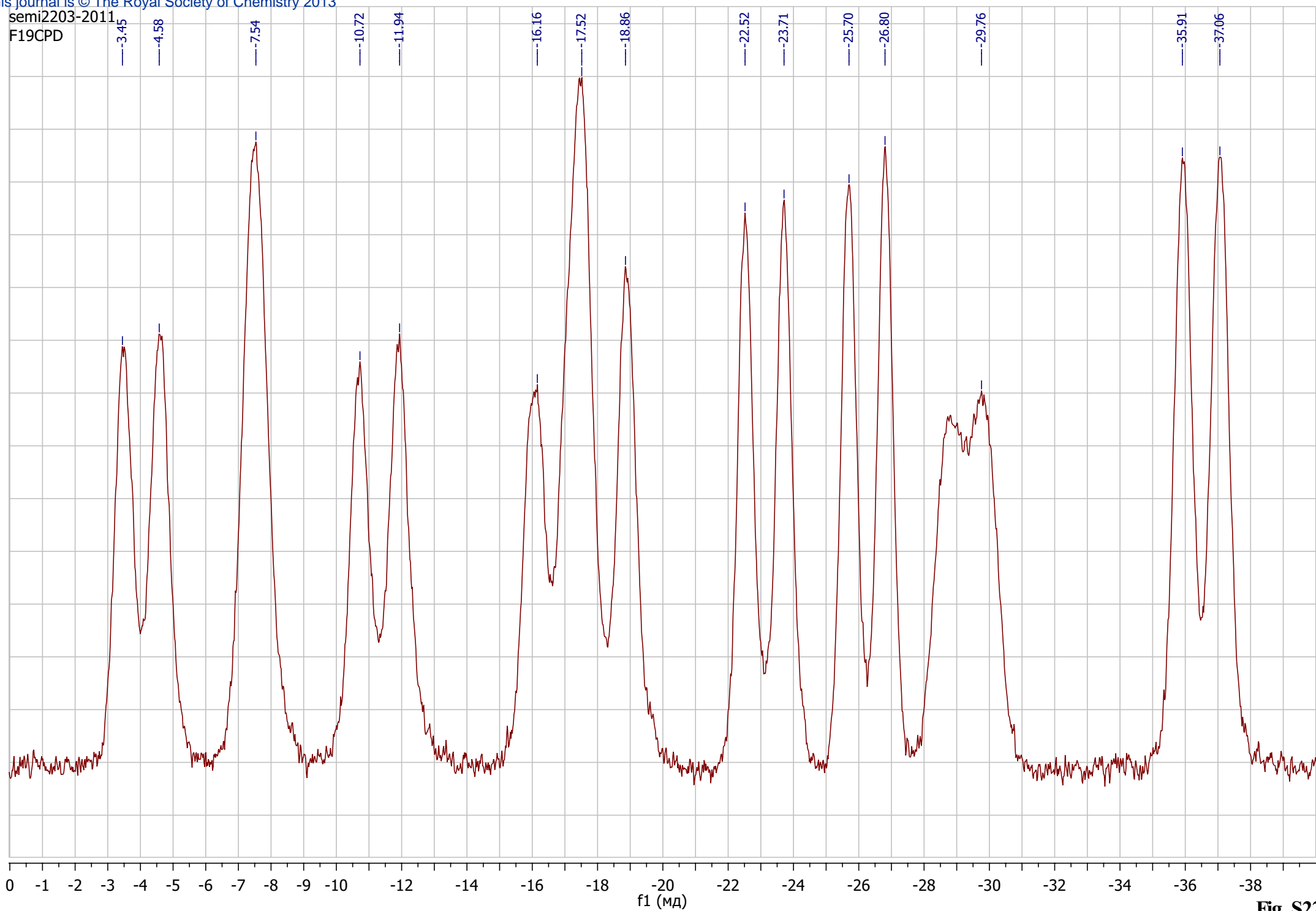
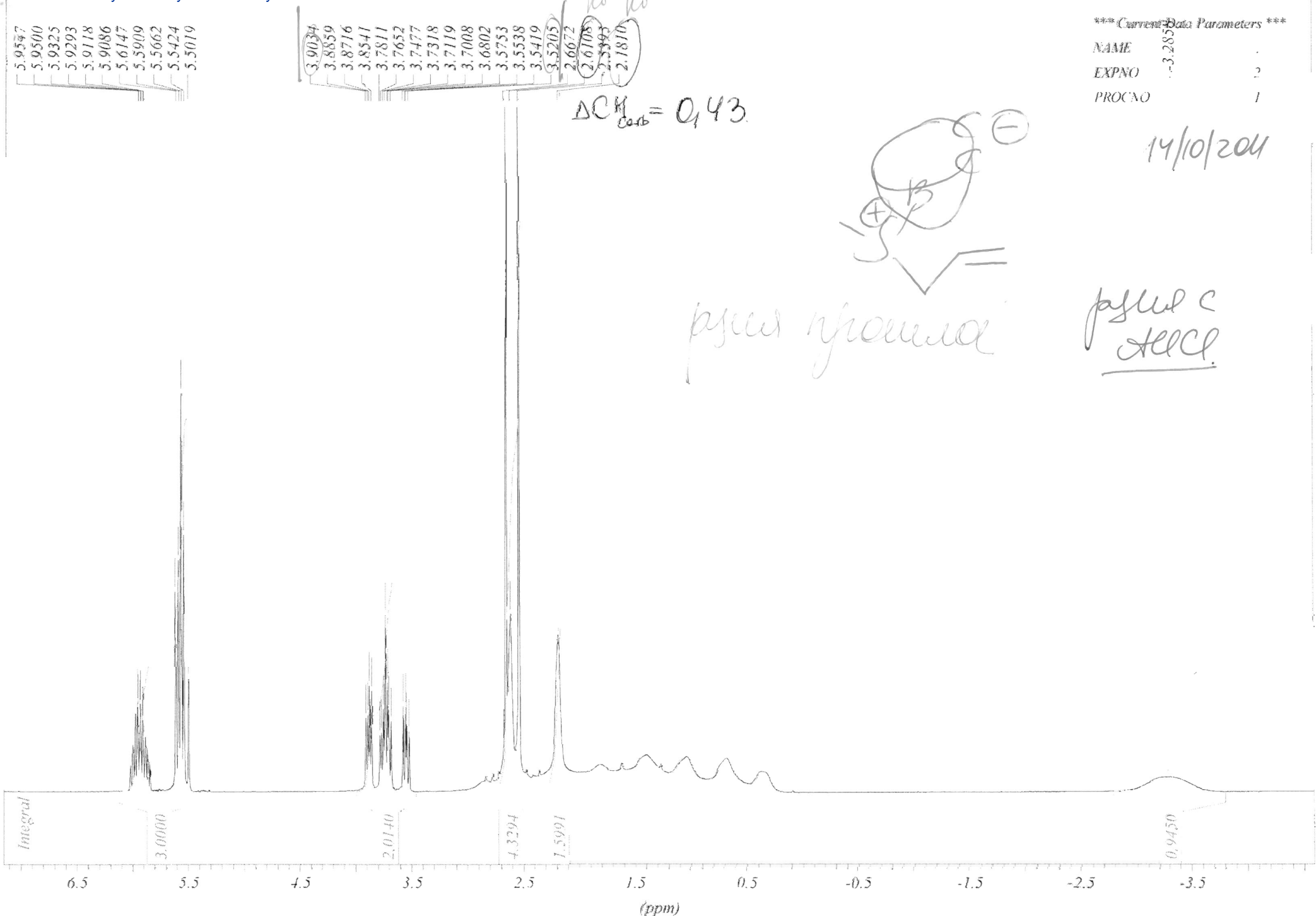
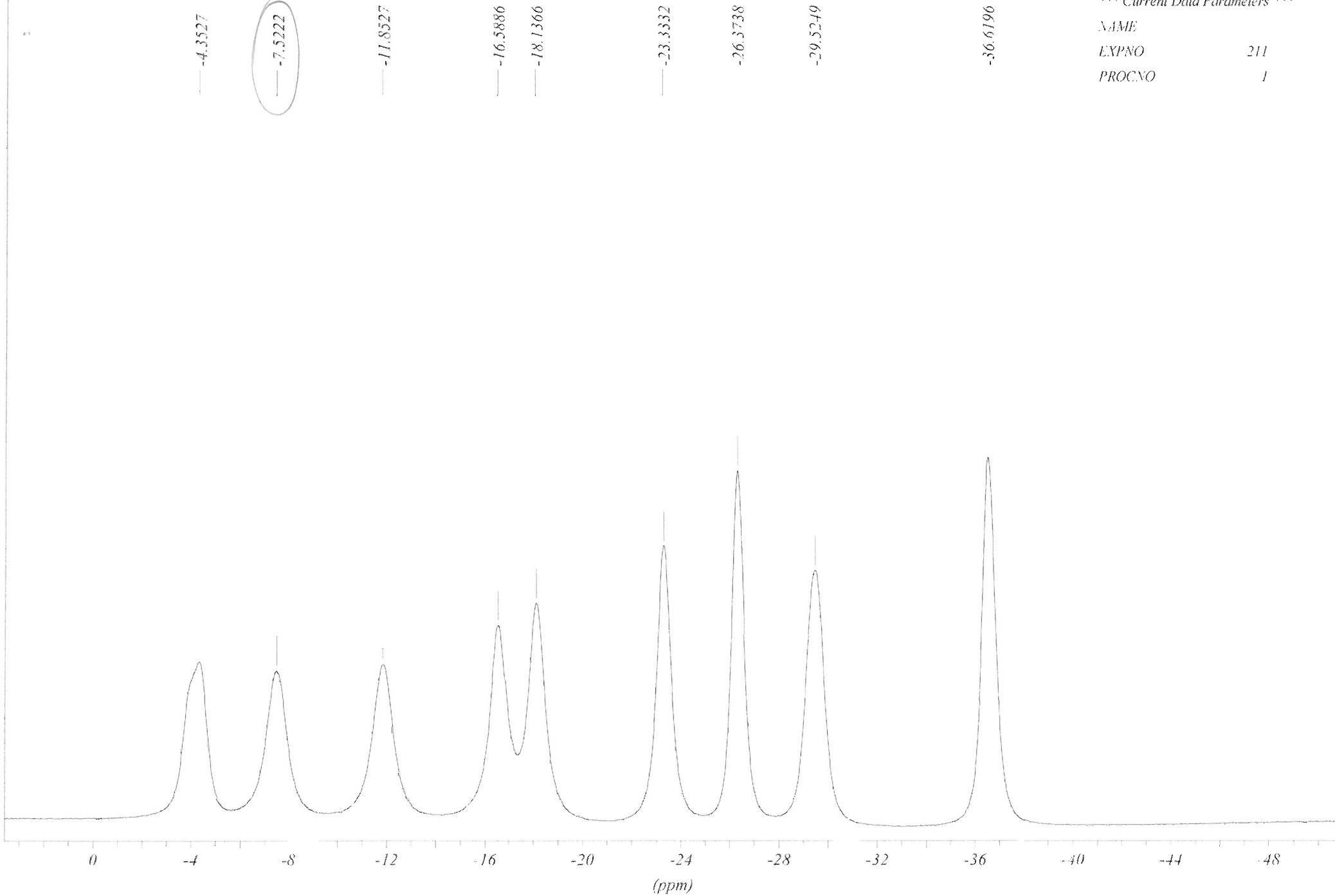


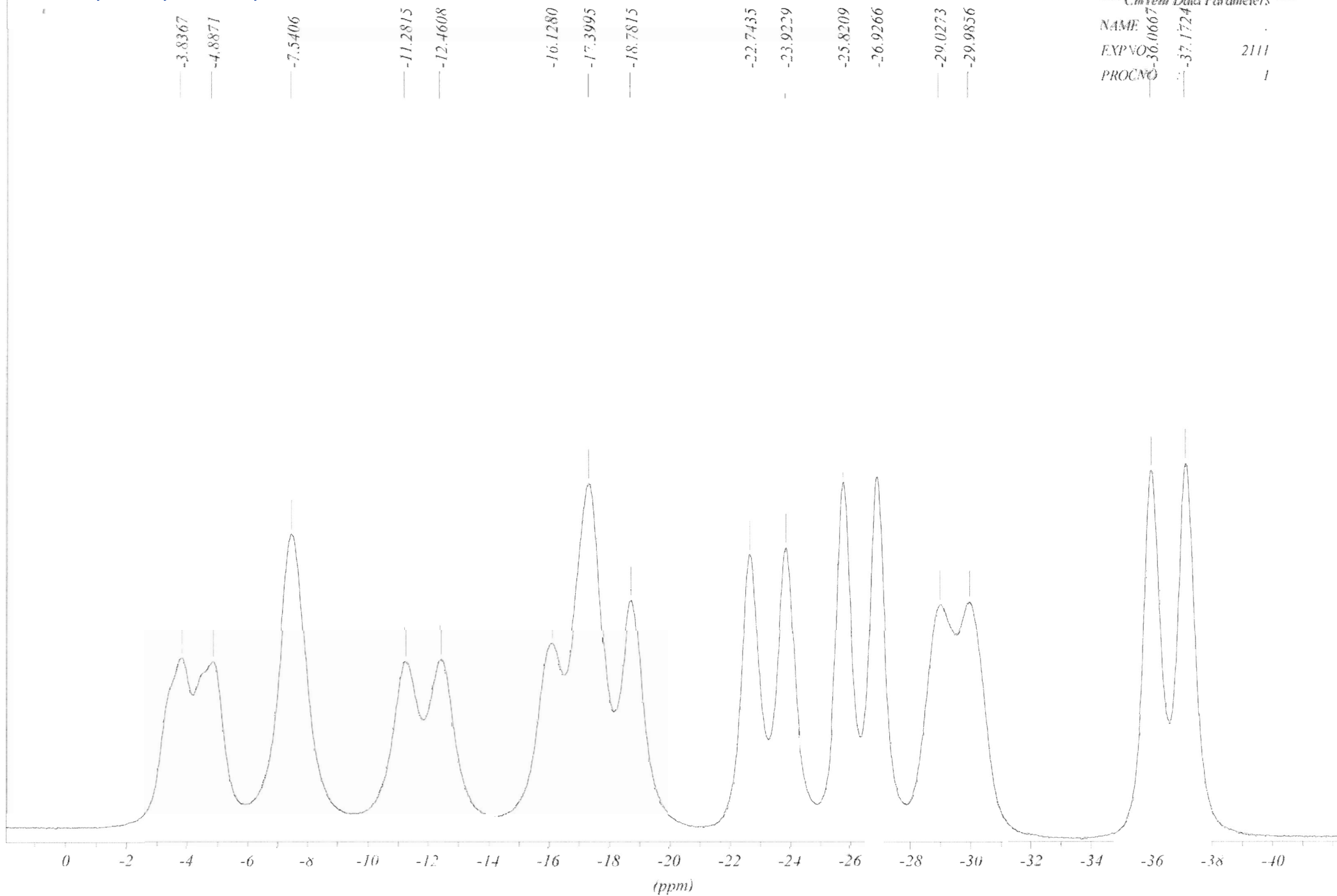
Fig. S22



*** Current Data Parameters ***

NAME
EXPNO 211
PROCNO 1





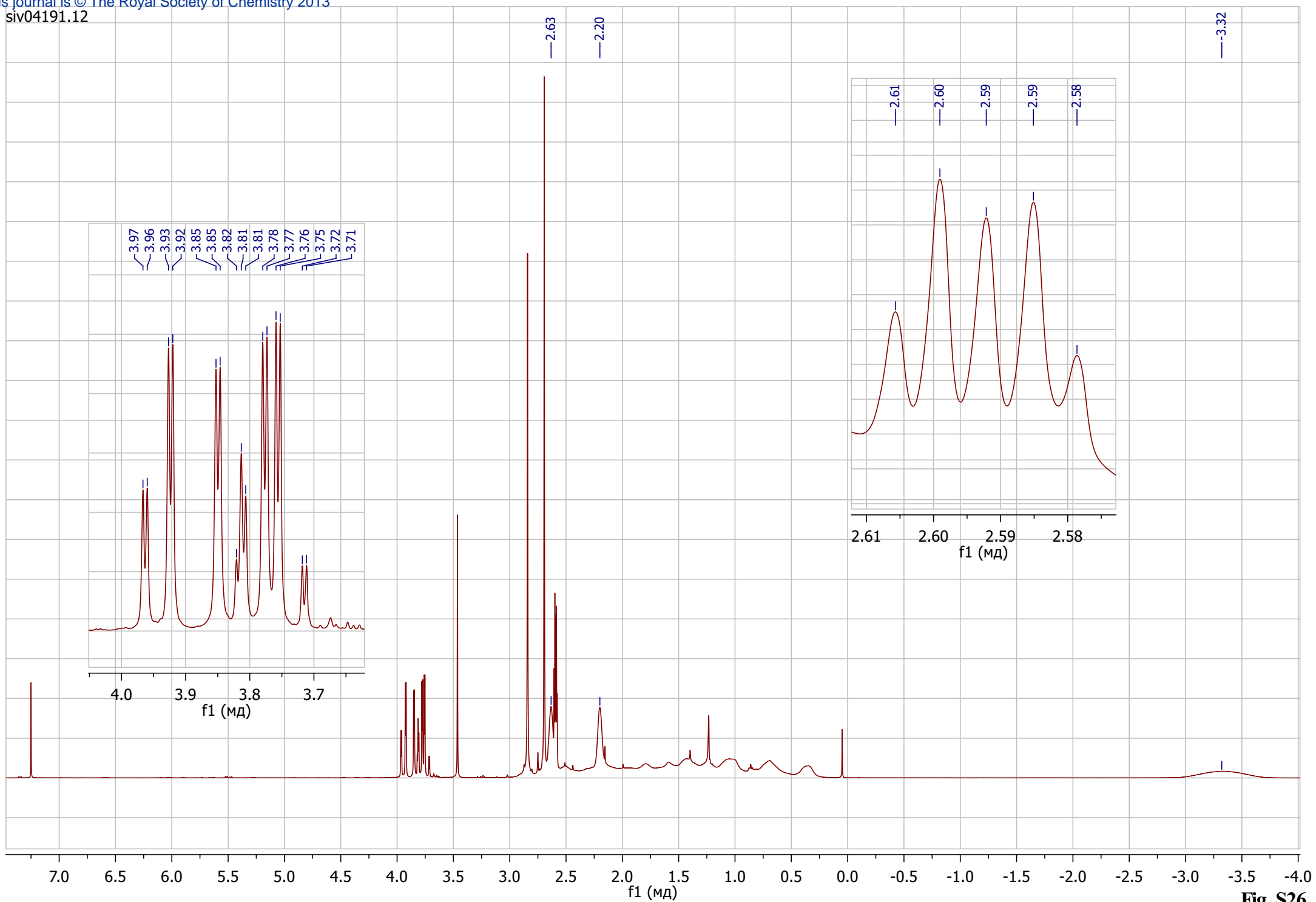


Fig. S26

siv03162.12

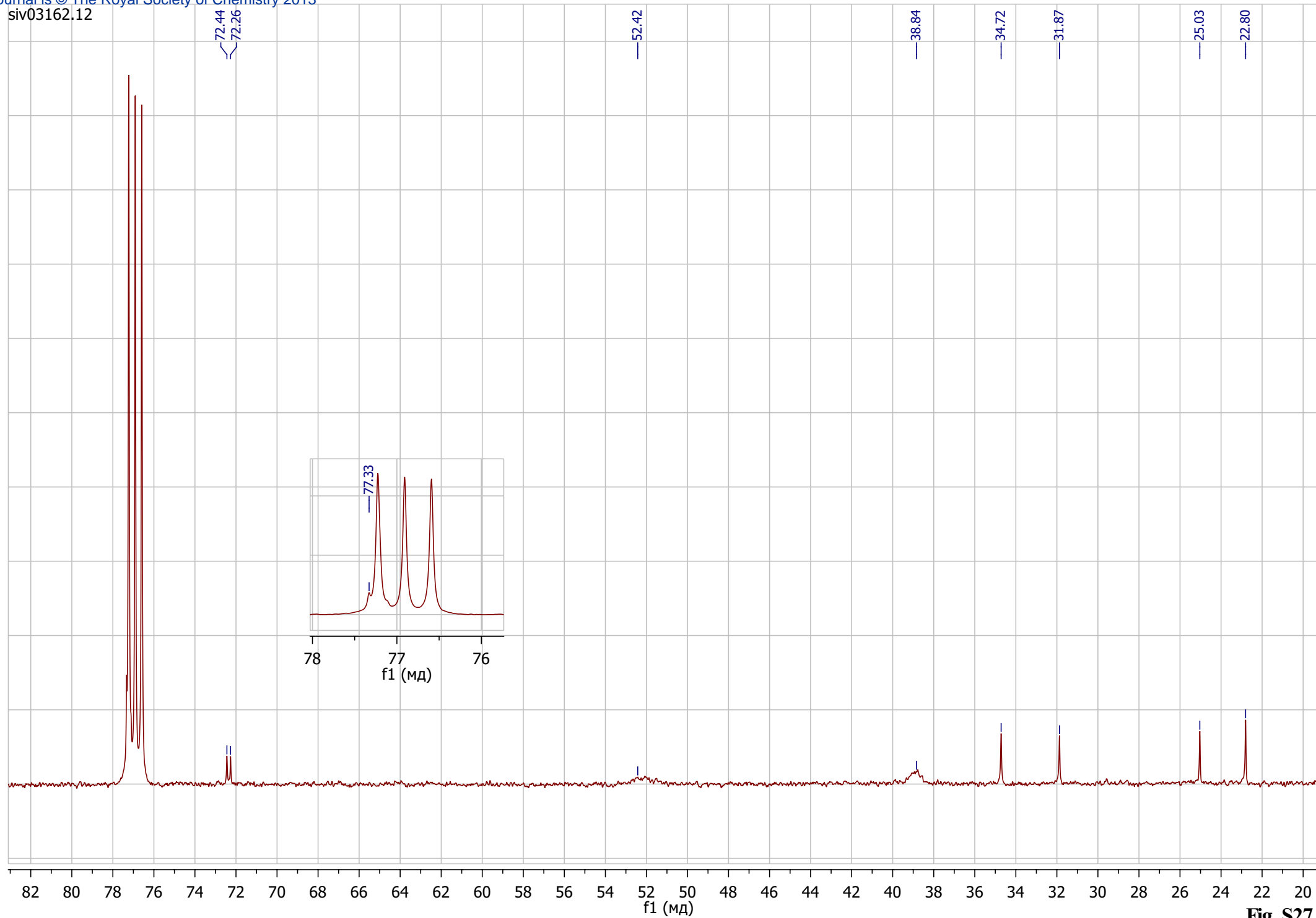


Fig. S27

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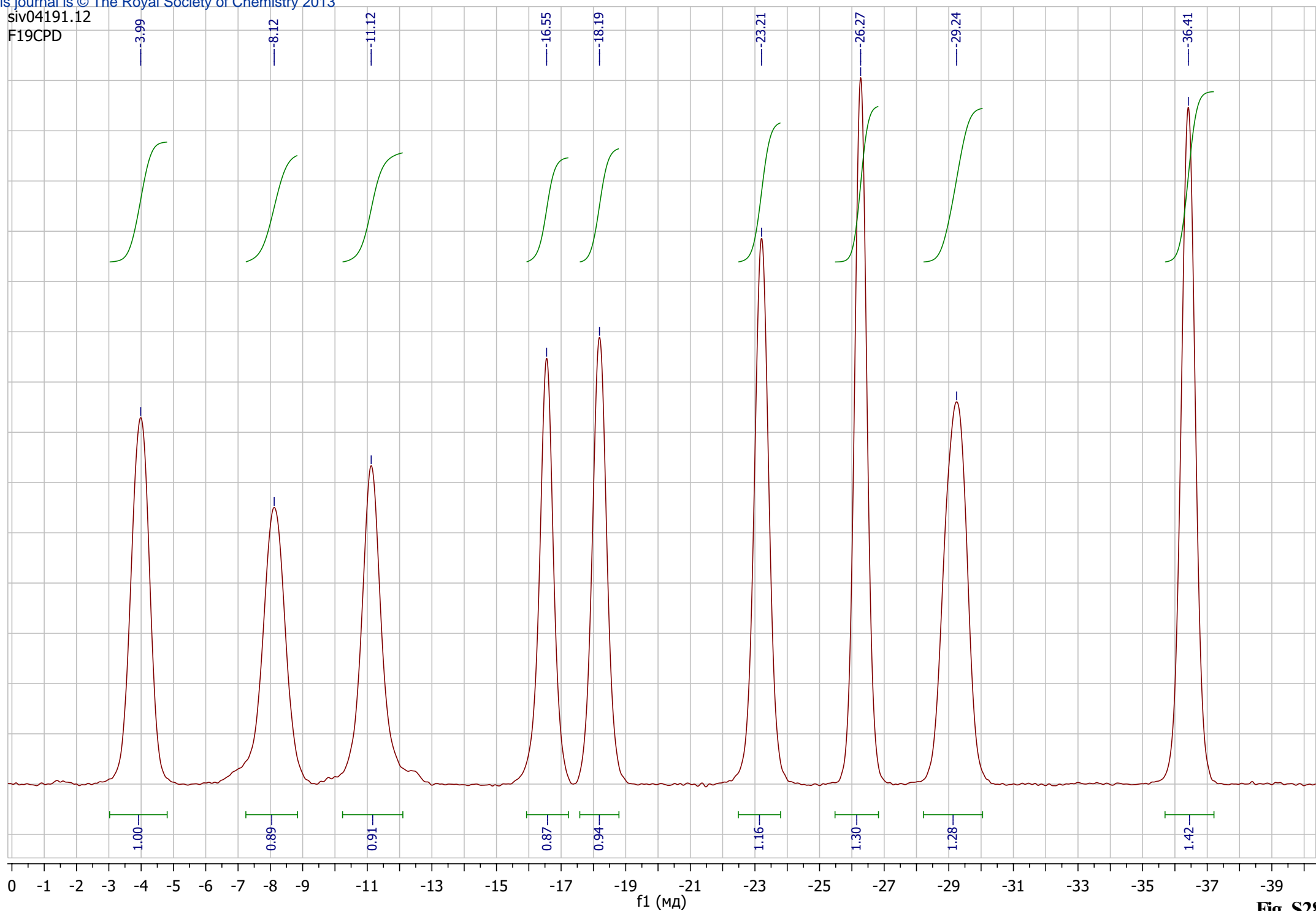


Fig. S28

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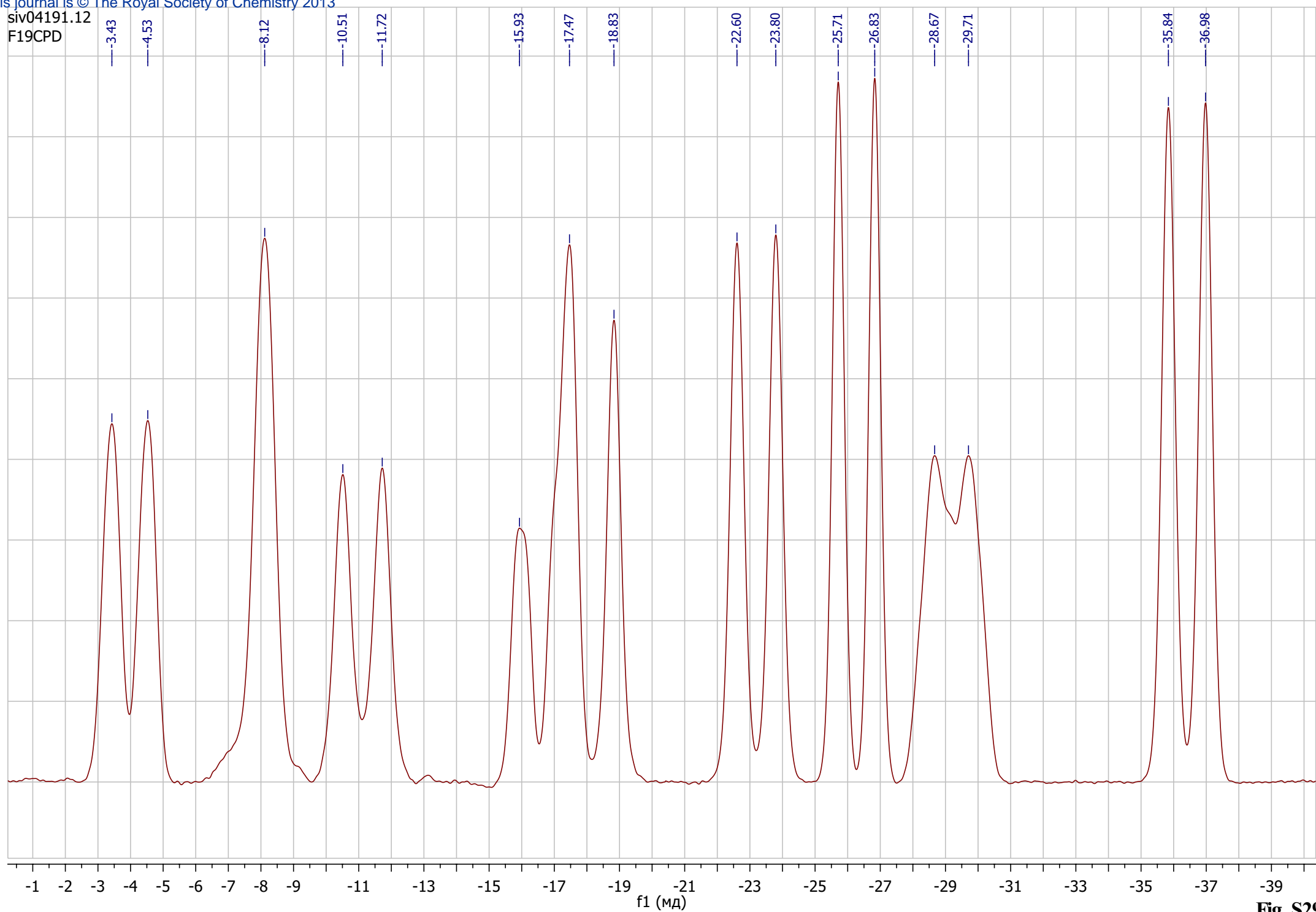


Fig. S29

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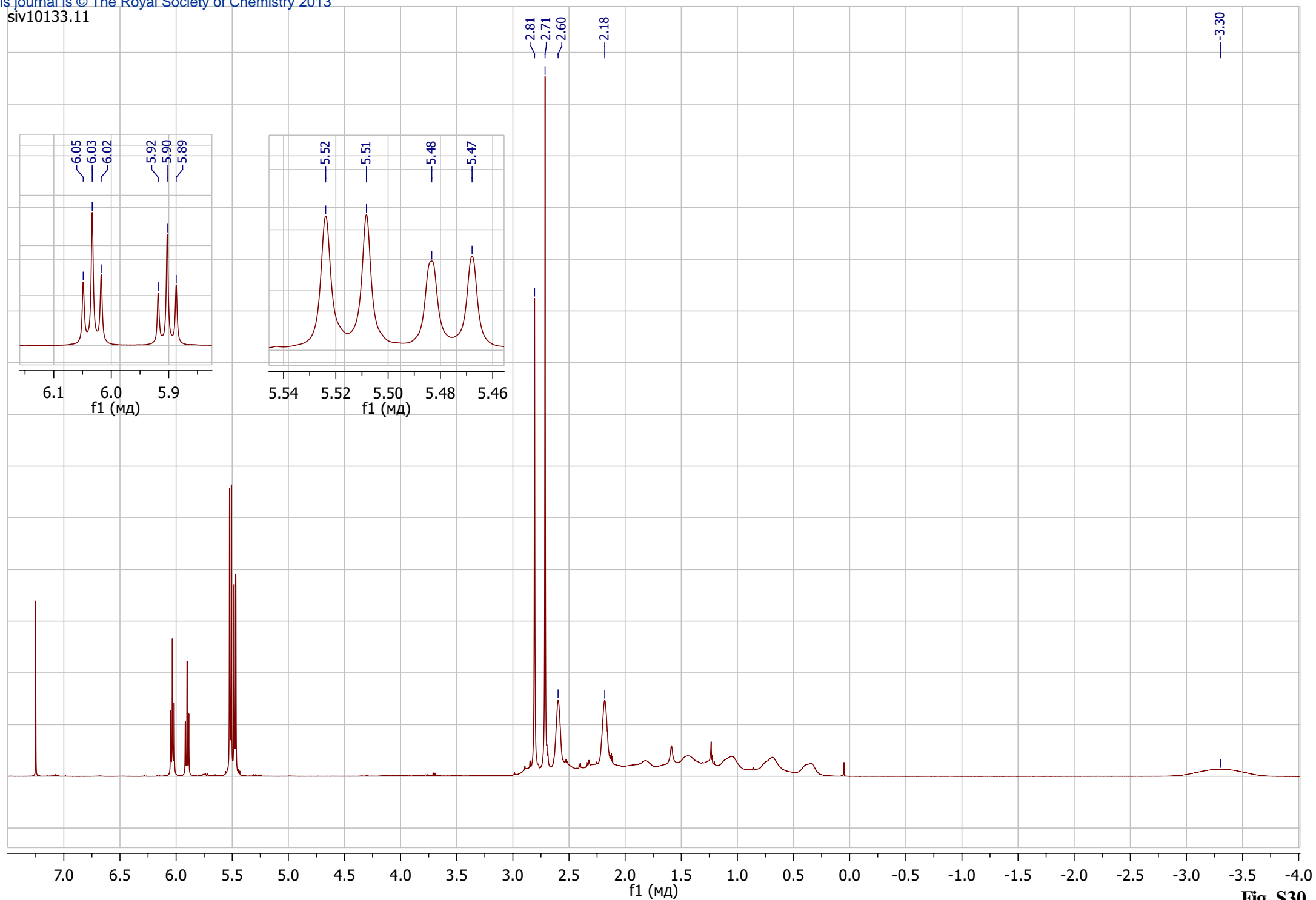


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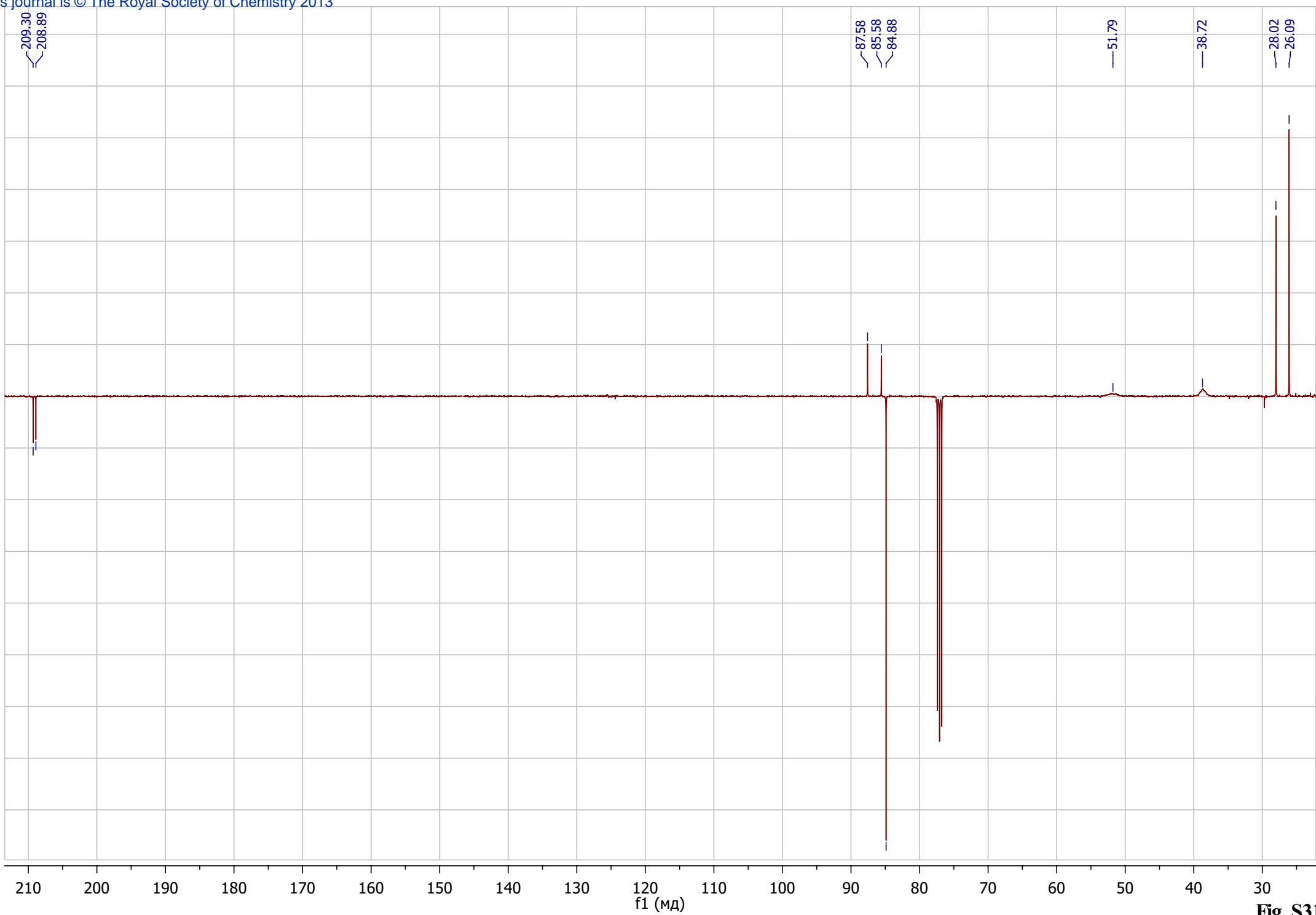


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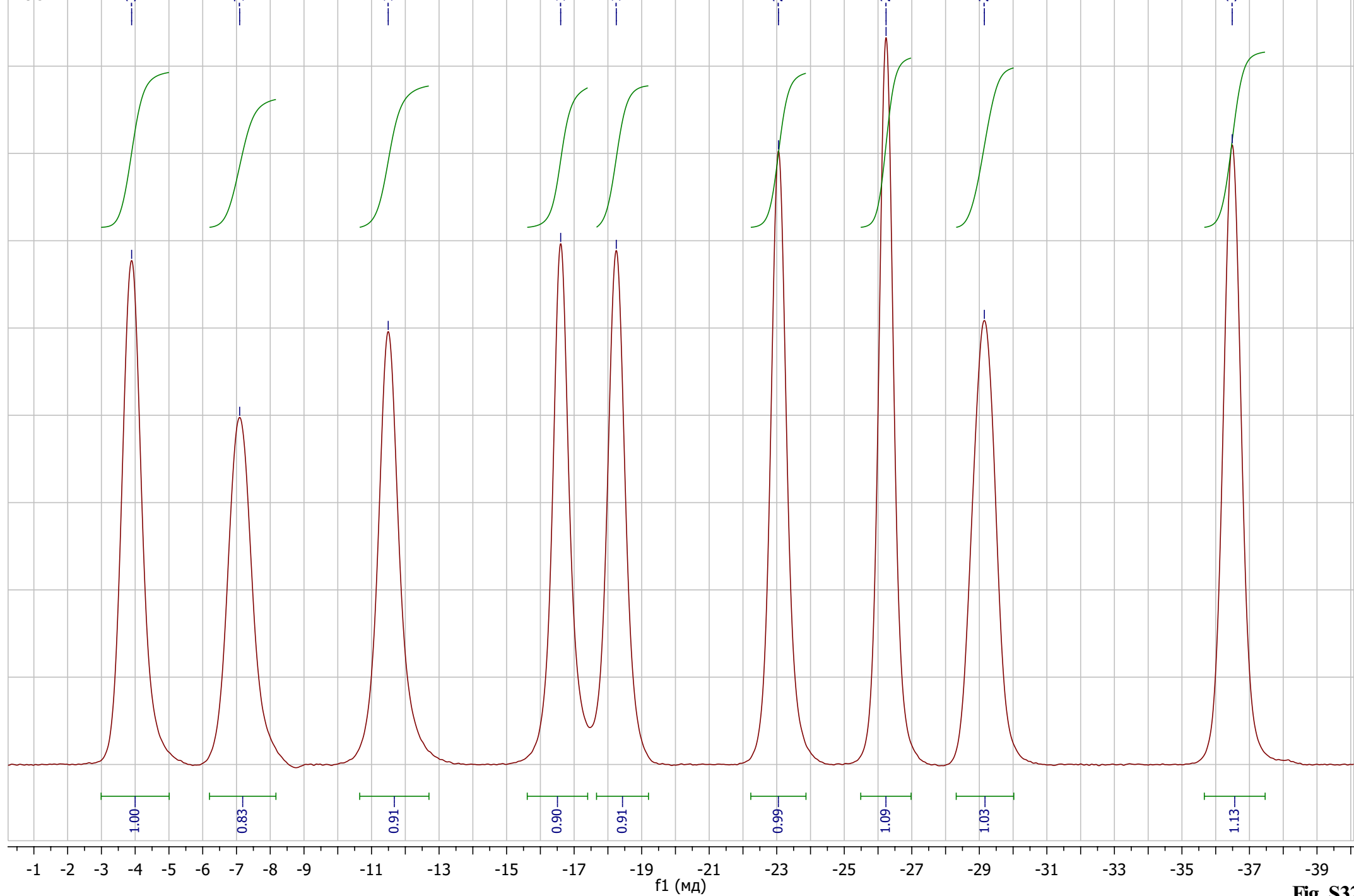


Fig. S32

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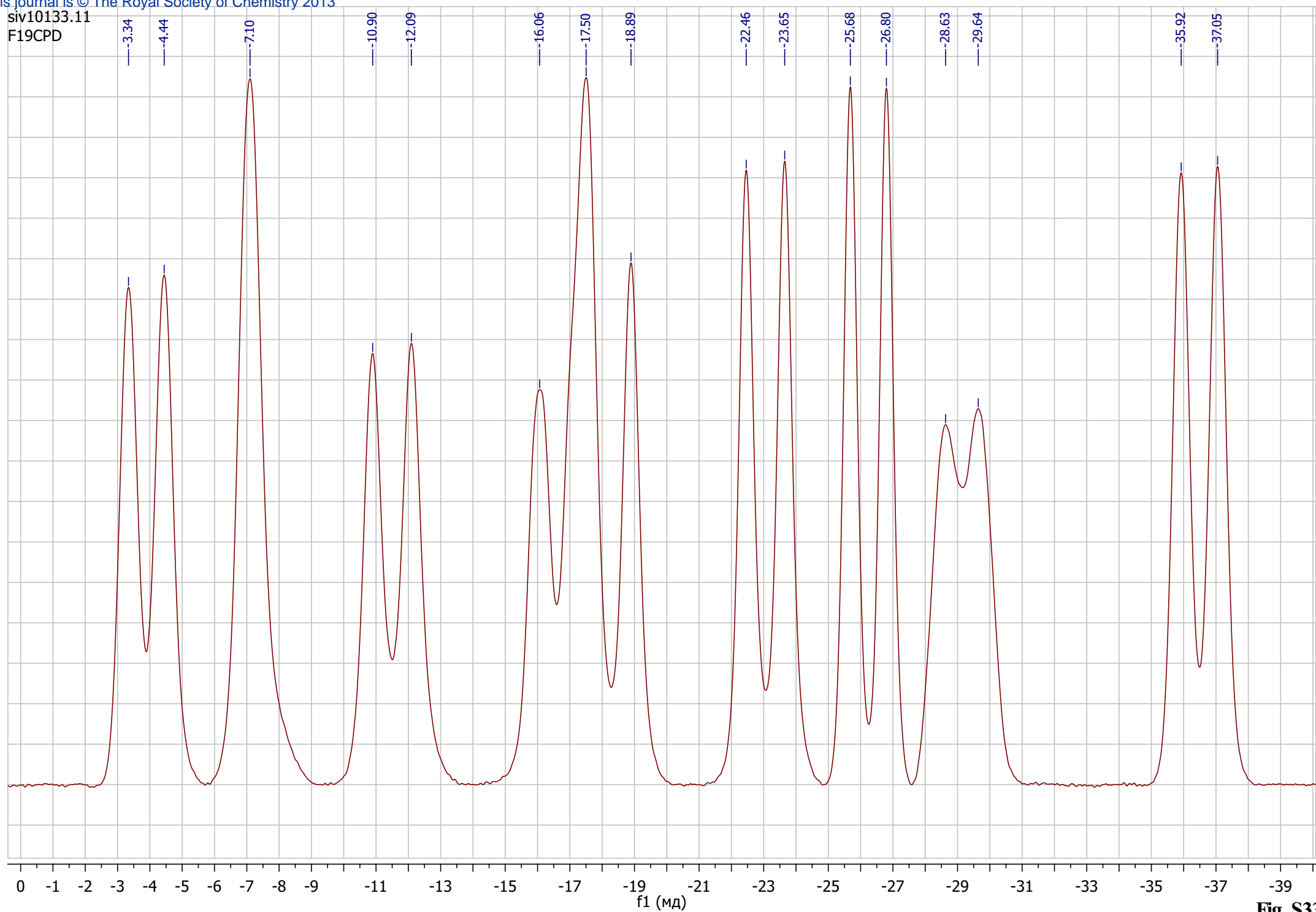


Fig. S33

Table S1. Bond lengths distribution in [9-RMeS-*nido*-7,8-C₂B₉H₁₁] derivatives in comparison with [nido-7,8-C₂B₉H₁₂]⁻ anion

Bond	anion ^a	anion ^b	SMe ₂ -derivative ^c first molecule	SMe ₂ -derivative ^c second molecule	Compound 7	Compound 5
B1-B2	1.761	1.757	1.740(5)	1.724(5)	1.755(3)	1.759(2)
B1-B3	1.773	1.777	1.778(5)	1.769(5)	1.774(3)	1.782(2)
B1-B4	1.767	1.775	1.774(4)	1.777(5)	1.774(3)	1.769(2)
B1-B5	1.793	1.795	1.777(4)	1.768(5)	1.787(3)	1.782(2)
B1-B6	1.799	1.798	1.795(4)	1.793(5)	1.811(3)	1.809(2)
B2-B3	1.755	1.758	1.740(5)	1.728(6)	1.756(3)	1.757(2)
B3-B4	1.762	1.770	1.769(5)	1.768(5)	1.778(3)	1.775(2)
B4-B5	1.756	1.747	1.767(4)	1.771(5)	1.763(2)	1.771(2)
B5-B6	1.823	1.820	1.797(4)	1.790(5)	1.811(3)	1.811(2)
B6-B2	1.758	1.763	1.762(5)	1.757(5)	1.775(3)	1.773(2)
B2-C7	1.716	1.715	1.690(5)	1.679(5)	1.698(2)	1.699(2)
B3-C7	1.712	1.715	1.712(5)	1.704(5)	1.704(2)	1.707(2)
B3-C8	1.718	1.731	1.740(5)	1.738(5)	1.725(2)	1.737(2)
B4-C8	1.719	1.738	1.752(4)	1.744(5)	1.735(2)	1.736(2)
B4-B9	1.795	1.796	1.749(4)	1.757(4)	1.759(3)	1.769(2)
B5-B9	1.764	1.764	1.736(4)	1.736(4)	1.748(3)	1.741(2)
B5-B10	1.782	1.781	1.779(4)	1.776(4)	1.796(3)	1.801(2)
B6-B10	1.779	1.782	1.785(4)	1.788(5)	1.791(3)	1.795(2)
B6-B11	1.779	1.768	1.775(5)	1.777(5)	1.800(3)	1.795(2)
B2-B11	1.803	1.804	1.800(5)	1.796(5)	1.808(3)	1.812(2)
C7-C8	1.555	1.564	1.525(4)	1.531(4)	1.550(2)	1.549(2)
C8-B9	1.607	1.622	1.571(4)	1.582(4)	1.594(2)	1.591(2)
B9-B10	1.831	1.813	1.775(4)	1.773(4)	1.780(3)	1.788(2)
B10-B11	1.853	1.841	1.843(5)	1.851(5)	1.861(3)	1.863(2)
B11-C7	1.614	1.621	1.623(5)	1.613(5)	1.637(2)	1.637(2)

^a [nido-7,8-C₂B₉H₁₂]⁻ anion, refcode CENBUS¹; ^b [nido-7,8-C₂B₉H₁₂]⁻ anion, refcode GUNHUS01¹; ^c [9-Me₂S-*nido*-7,8-C₂B₉H₁₁], refcode VYUHIG¹, there are two independent molecules in the asymmetric unit cell

References

1. F.H. Allen, *Acta Crystallogr.*, **2002**, B58, 380; (b) *Cambridge Structural Database*, **2012**, Version 5.34