Total syntheses of gerberinol I and the pterophyllins 2 and 4 using the Casnati-Skattebøl reaction under different conditions

Jorgelina L. Pergomet,[a] Andrea B. J. Bracca[a] and Teodoro S. Kaufman[a,*]

[a]Instituto de Química Rosario (CONICET-UNR), Suipacha 531, S2002LRK, Rosario, Santa Fe, Argentina.

Tel/Fax: +54-341-4370477, ext. 105; E-mail: kaufman@iquir-conicet.gov.ar

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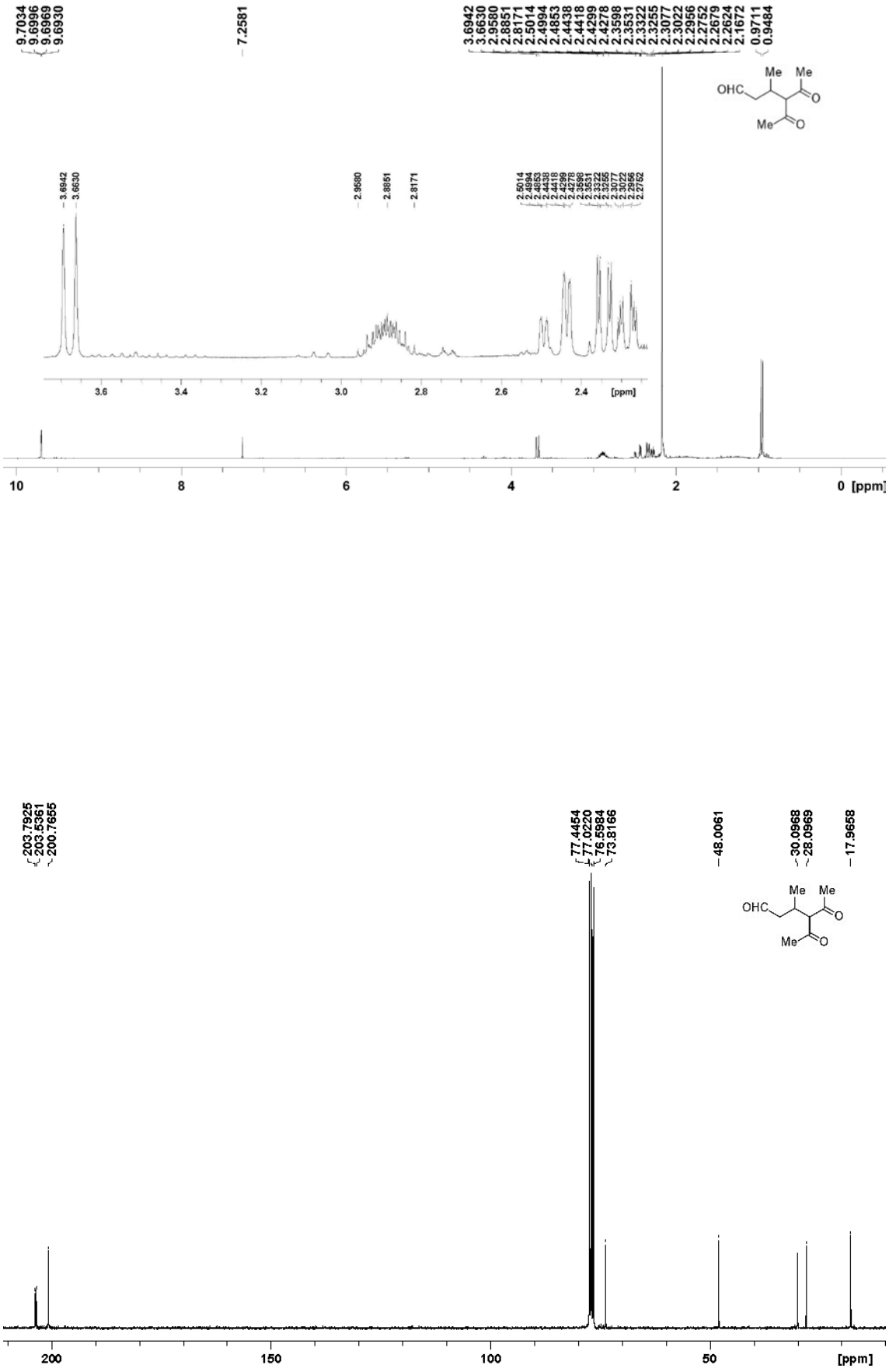


Figure S1. ^{1}H and ^{13}C NMR spectra of compound **13** in $CDCl_3$.

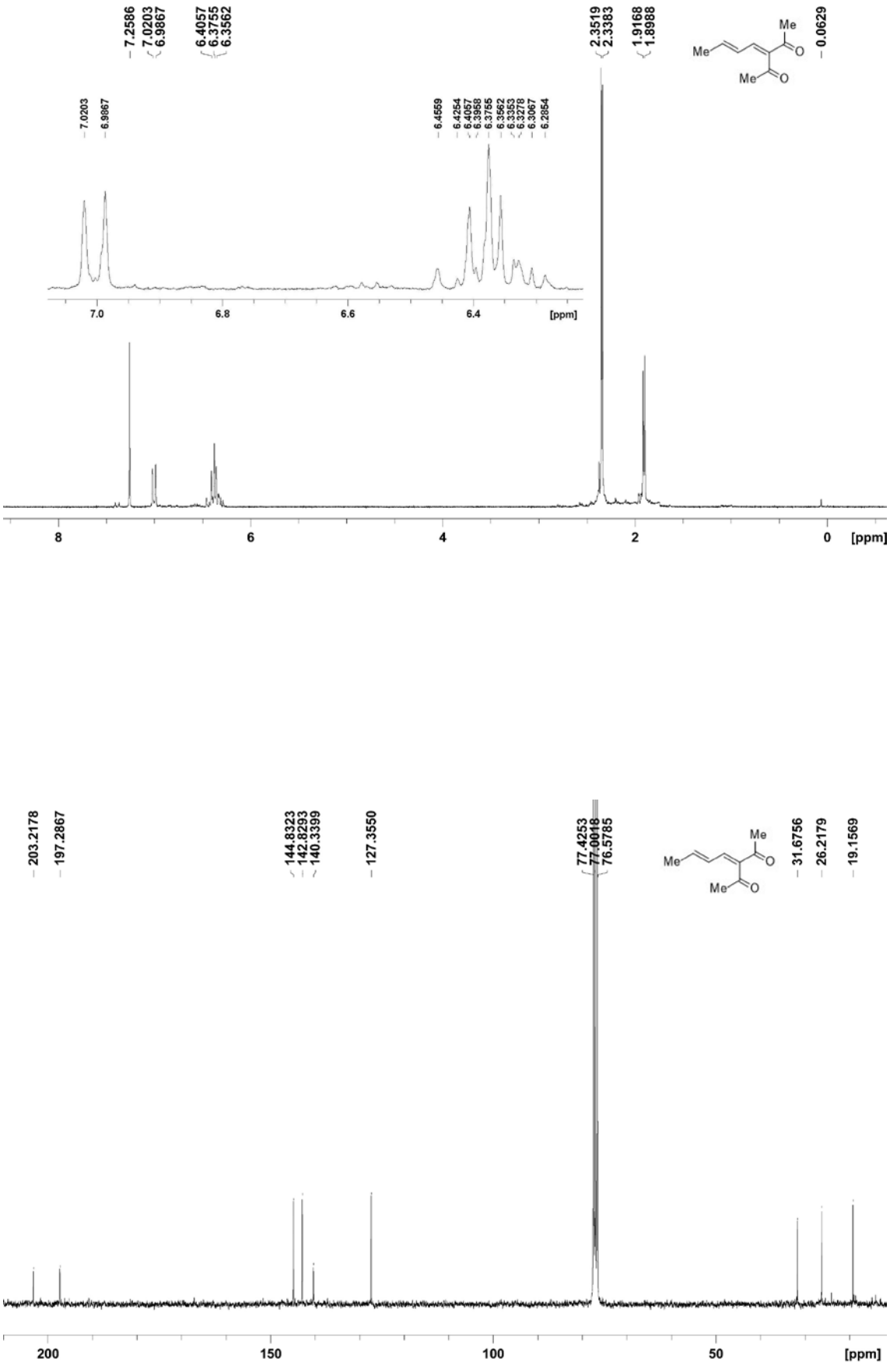


Figure S2. ^{1}H and ^{13}C NMR spectra of compound **13a** in $CDCl_3$.

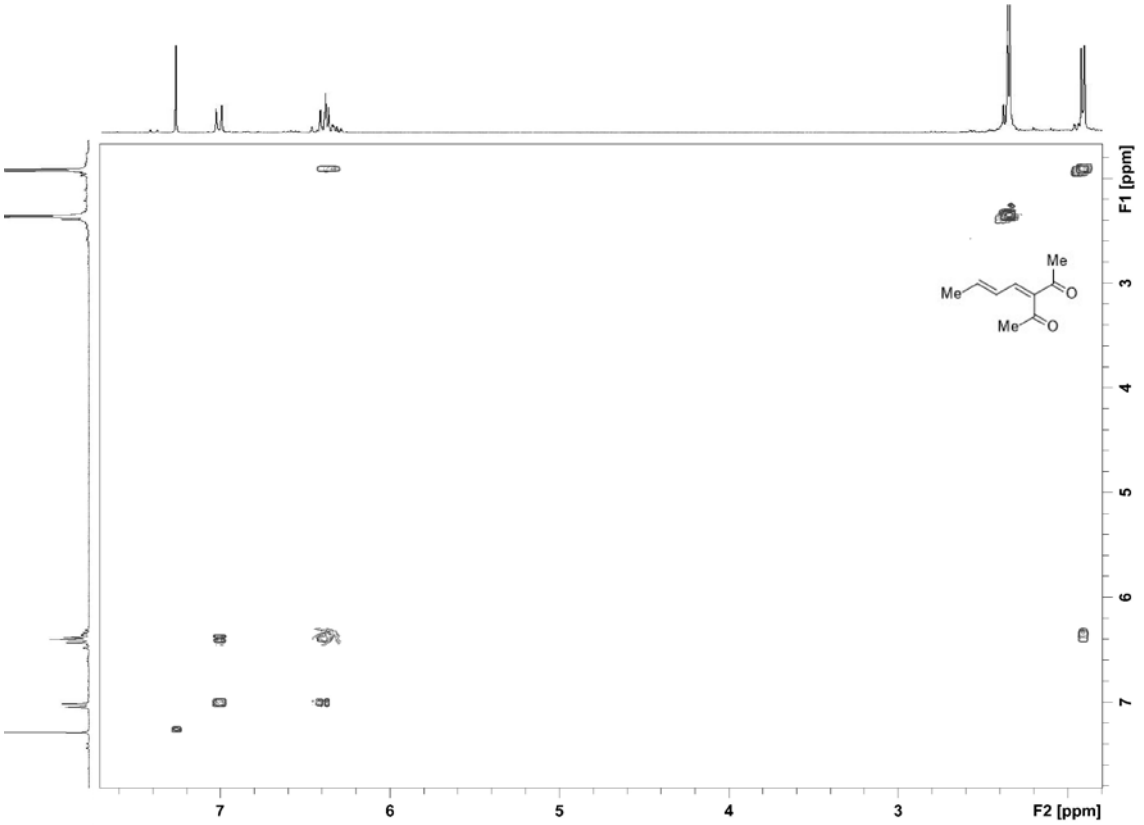
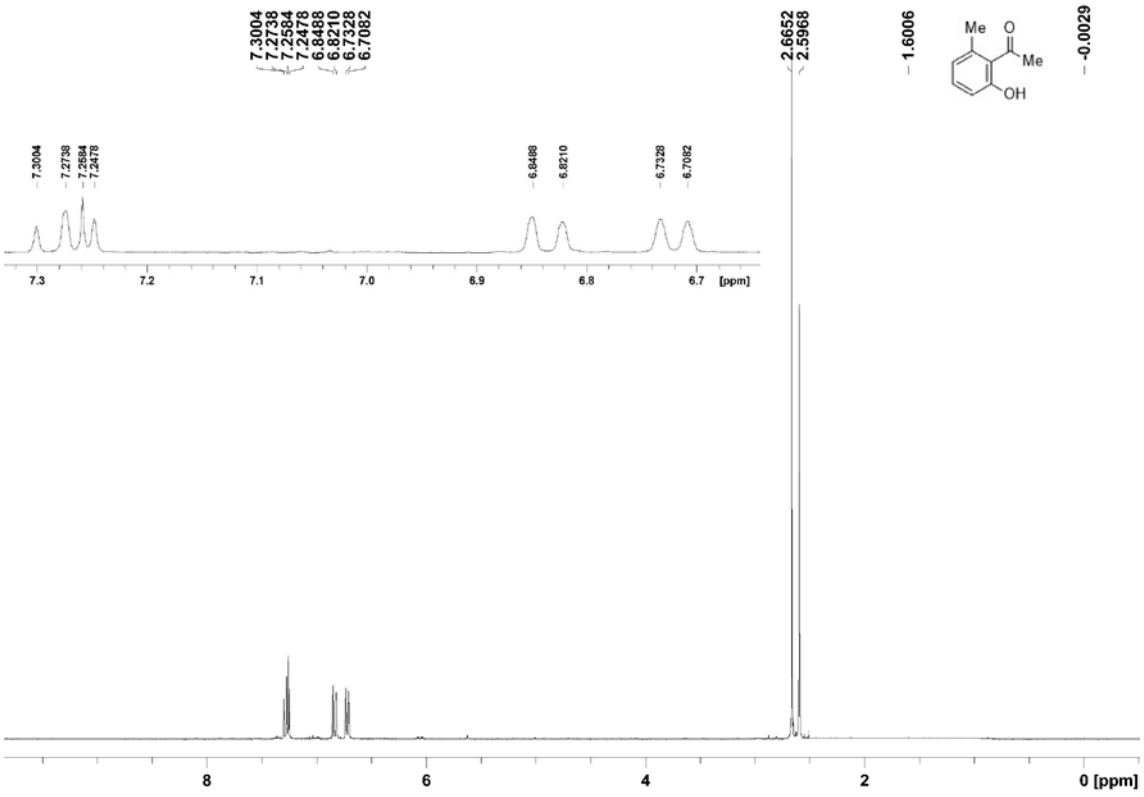


Figure S3. COSY spectrum of compound **13a** in $CDCl_3$



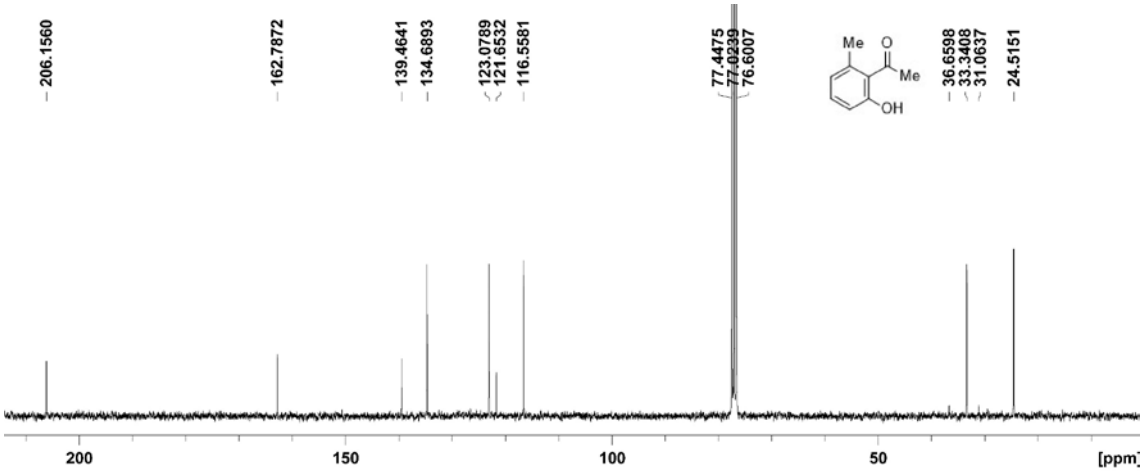


Figure S4. ^{1}H and ^{13}C NMR spectra of compound **10** in $CDCl_3$.

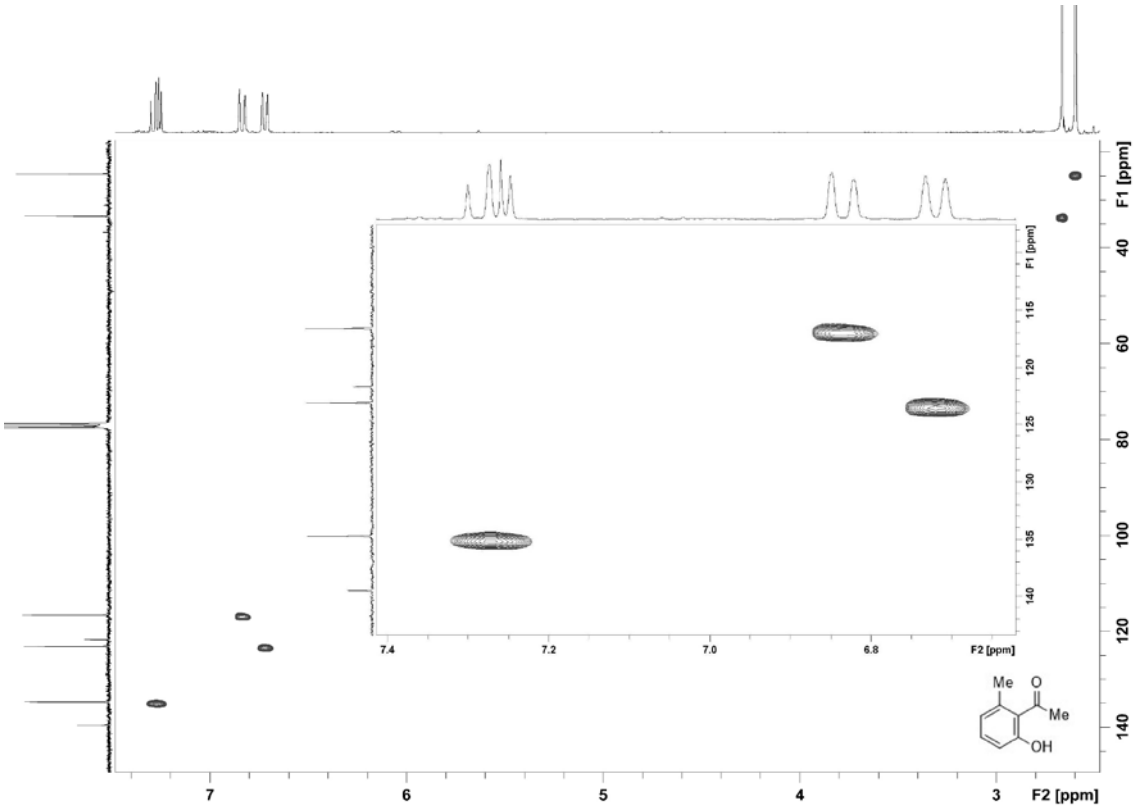


Figure S5. HSQC spectrum of compound **10** in $CDCl_3$

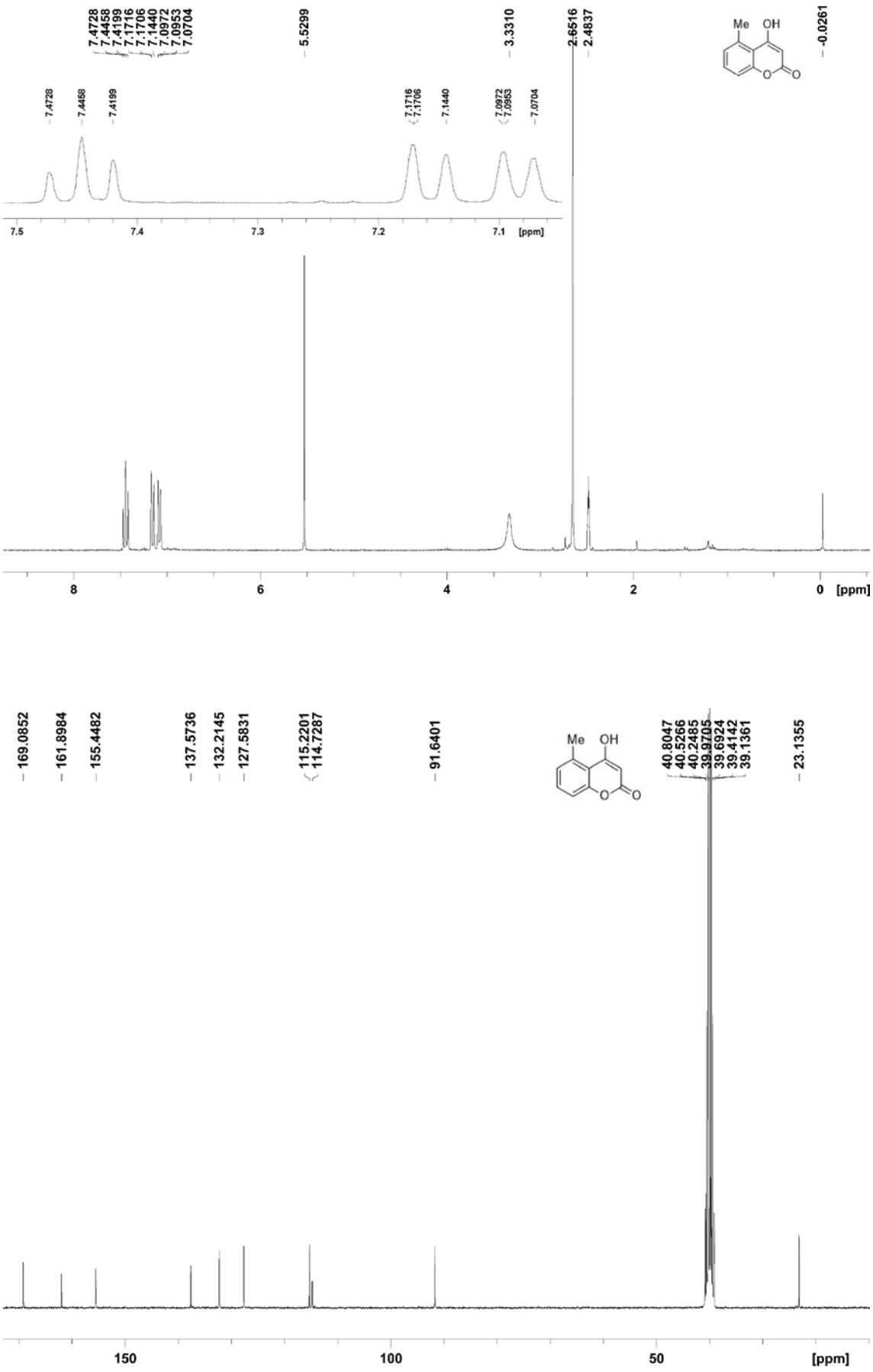


Figure S6. ^{1}H and ^{13}C NMR spectra of compound **9** in DMSO-d_6.

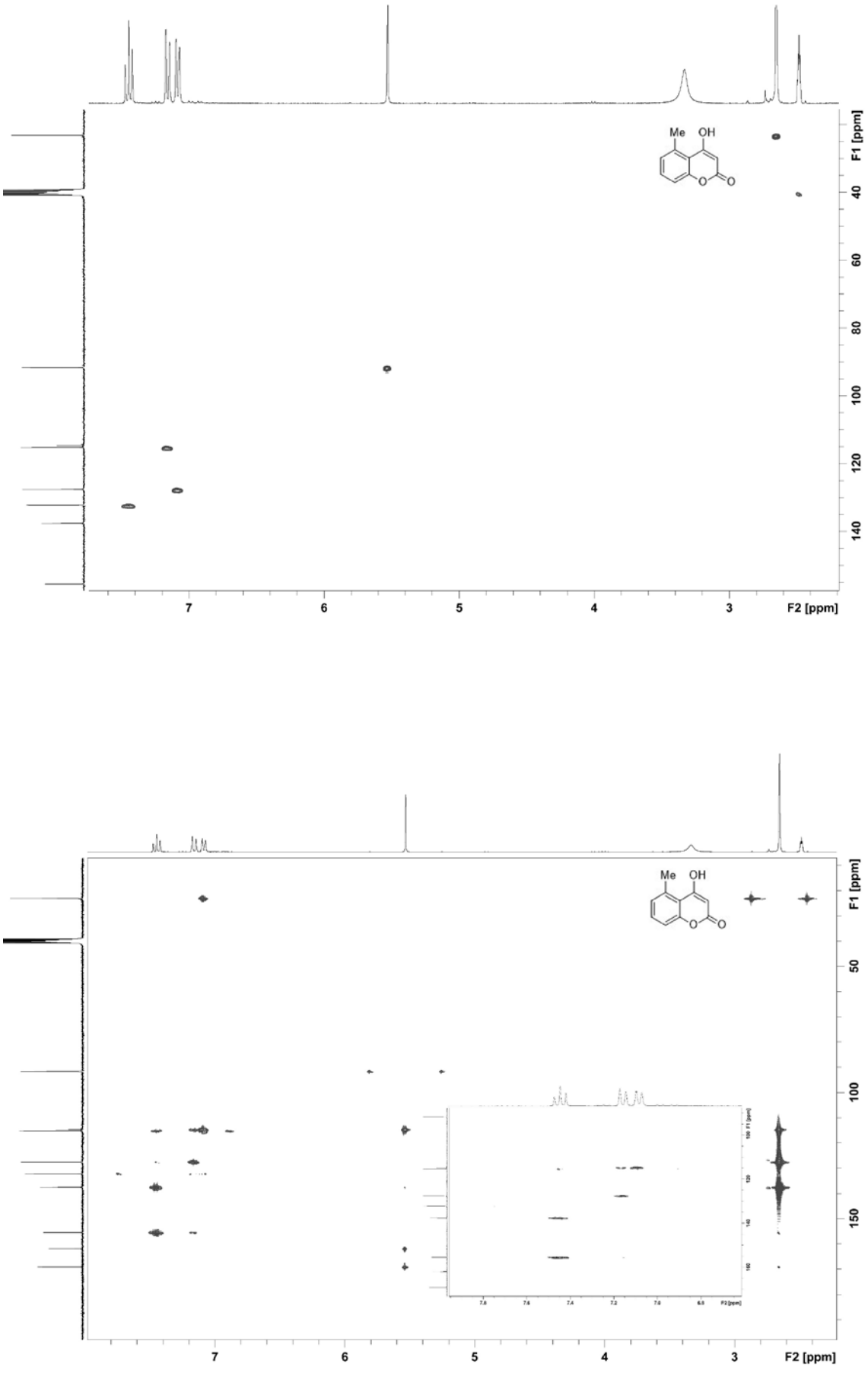


Figure S7. HSQC (top) and HMBC (bottom) spectra of compound **9** in DMSO-d_6.

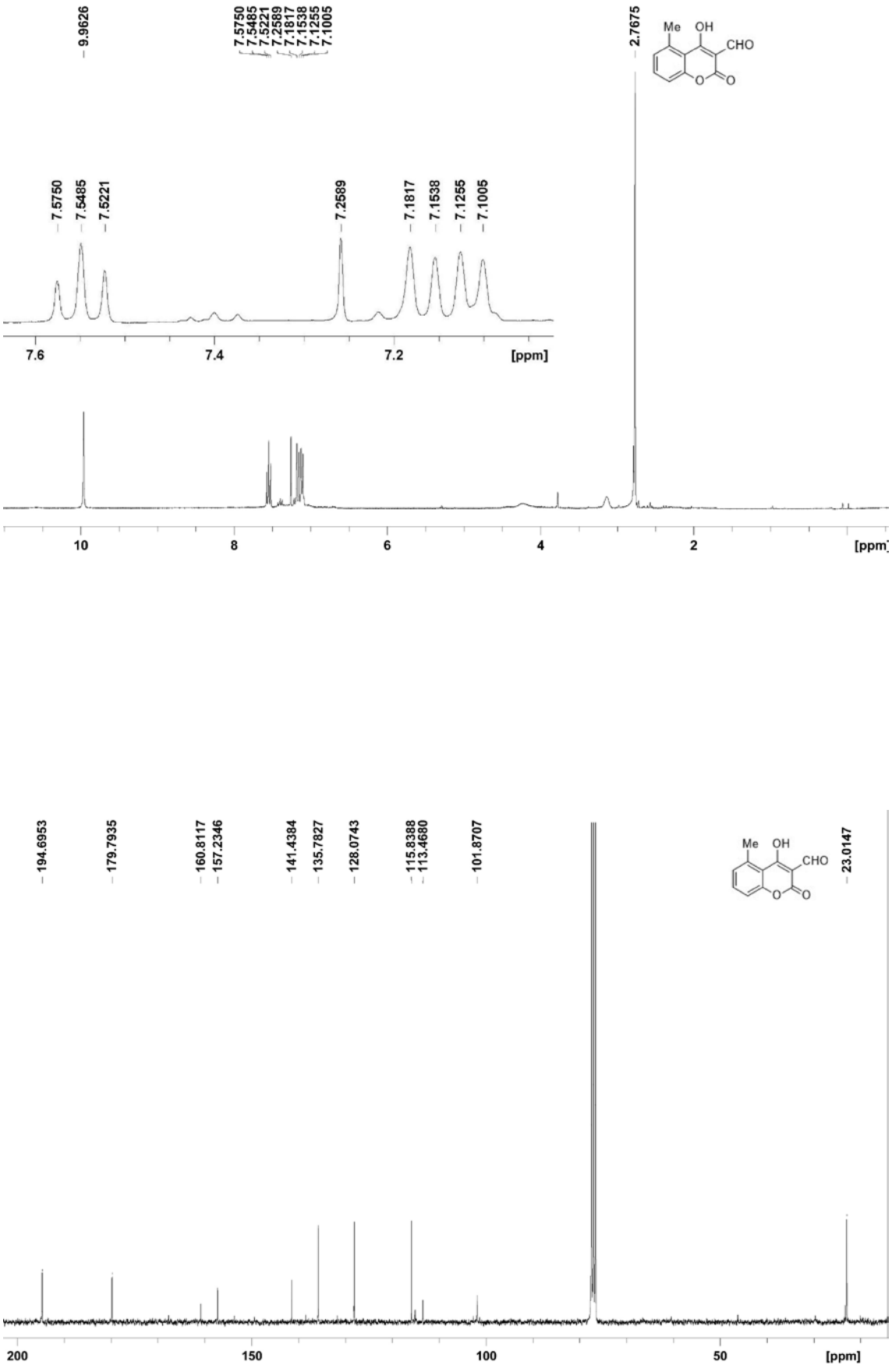


Figure S8. ^{1}H and ^{13}C NMR spectra of compound **8** in $CDCl_3$.

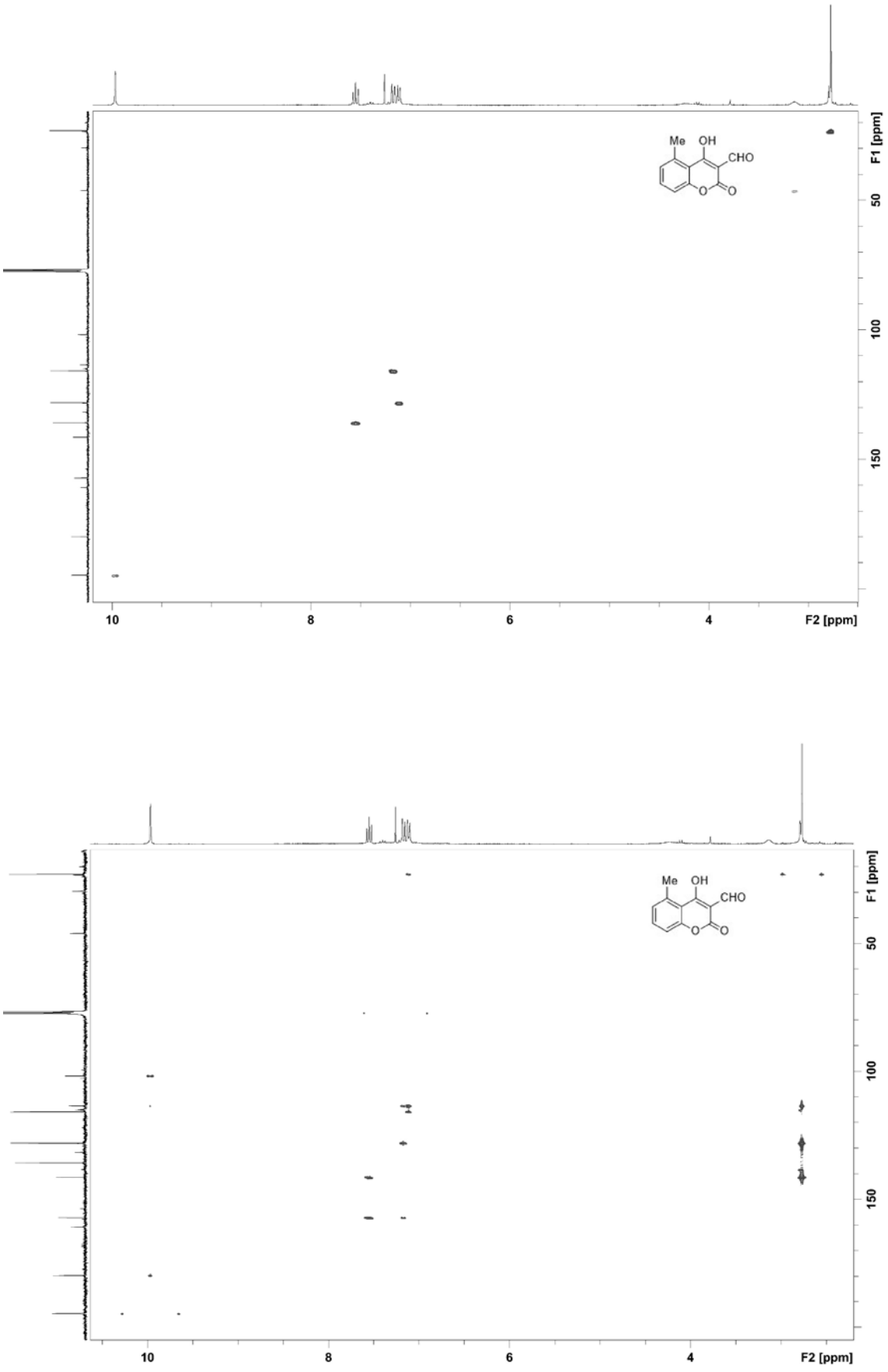


Figure S9. HSQC (top) and HMBC (bottom) spectra of compound **8** in $CDCl_3$

Figure S10. ^{1}H and ^{13}C NMR spectra of compound **17** in $CDCl_3$.

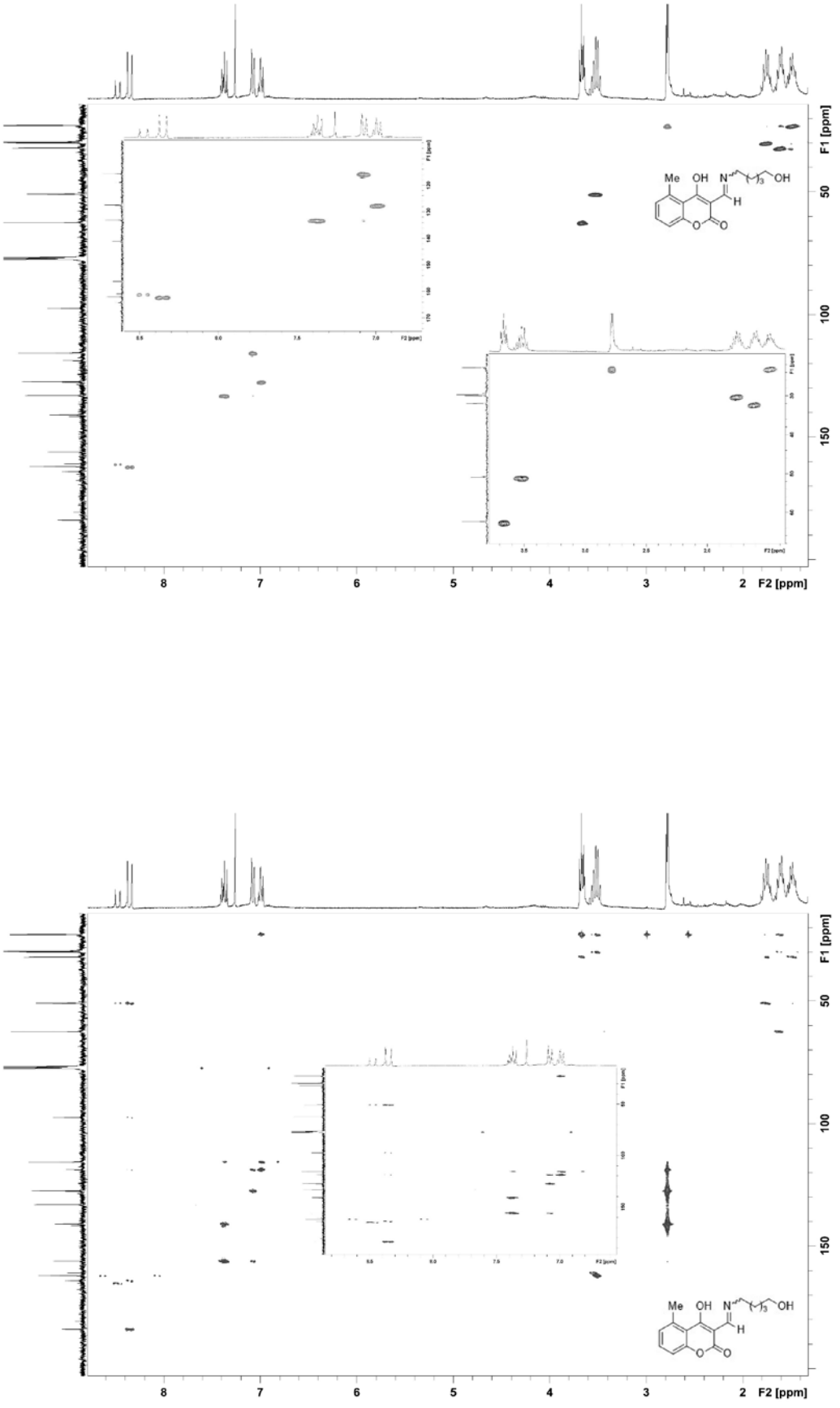


Figure S11. HSQC (top) and HMBC (bottom) spectra of compound **17** in $CDCl_3$

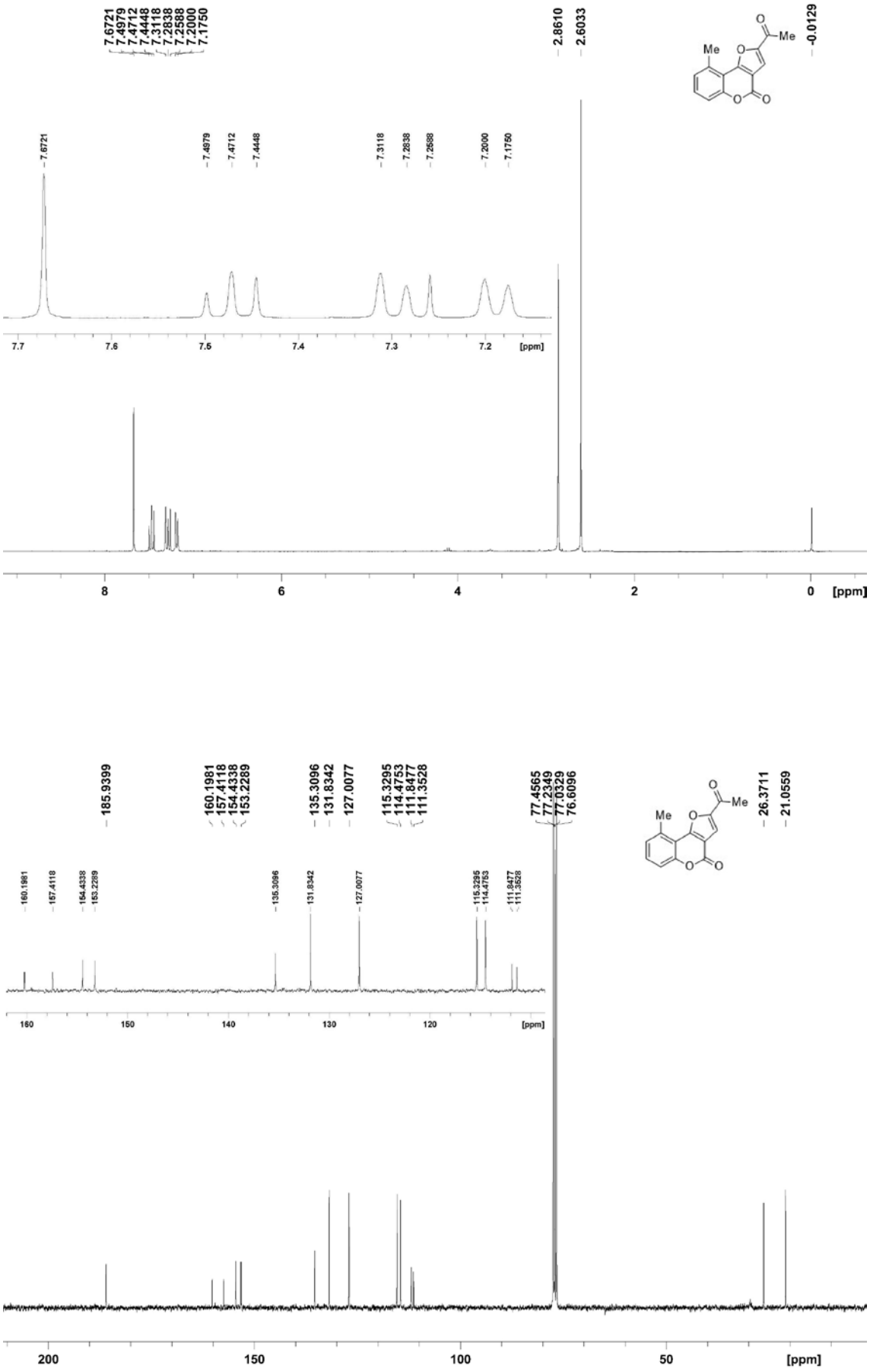


Figure S12. ^{1}H and ^{13}C NMR spectra of compound **4b** in $CDCl_3$.

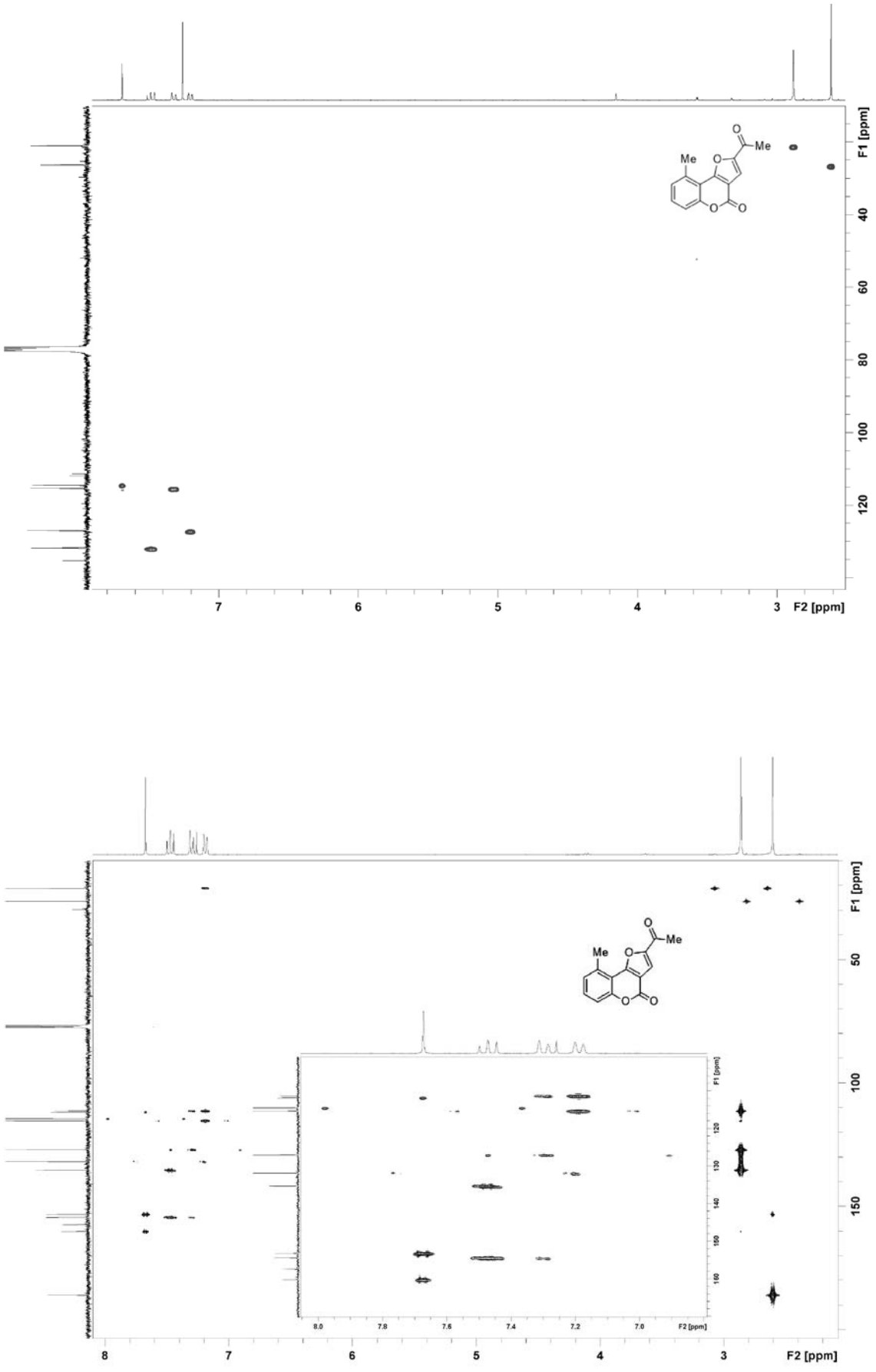


Figure S13. HSQC (top) and HMBC (bottom) spectra of compound **4b** in $CDCl_3$

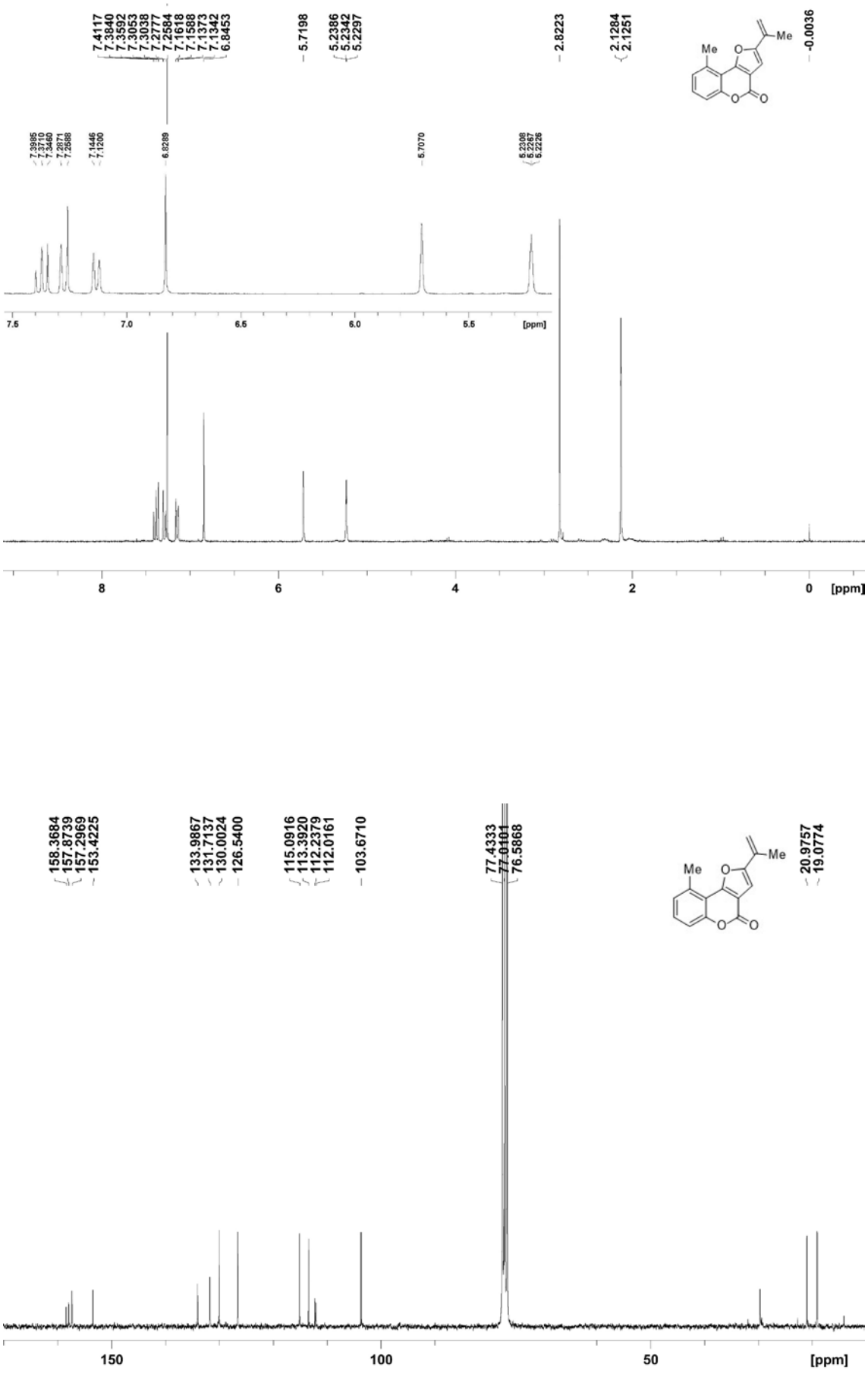


Figure S14. ^{1}H and ^{13}C NMR spectra of compound **4a** in $CDCl_3$.

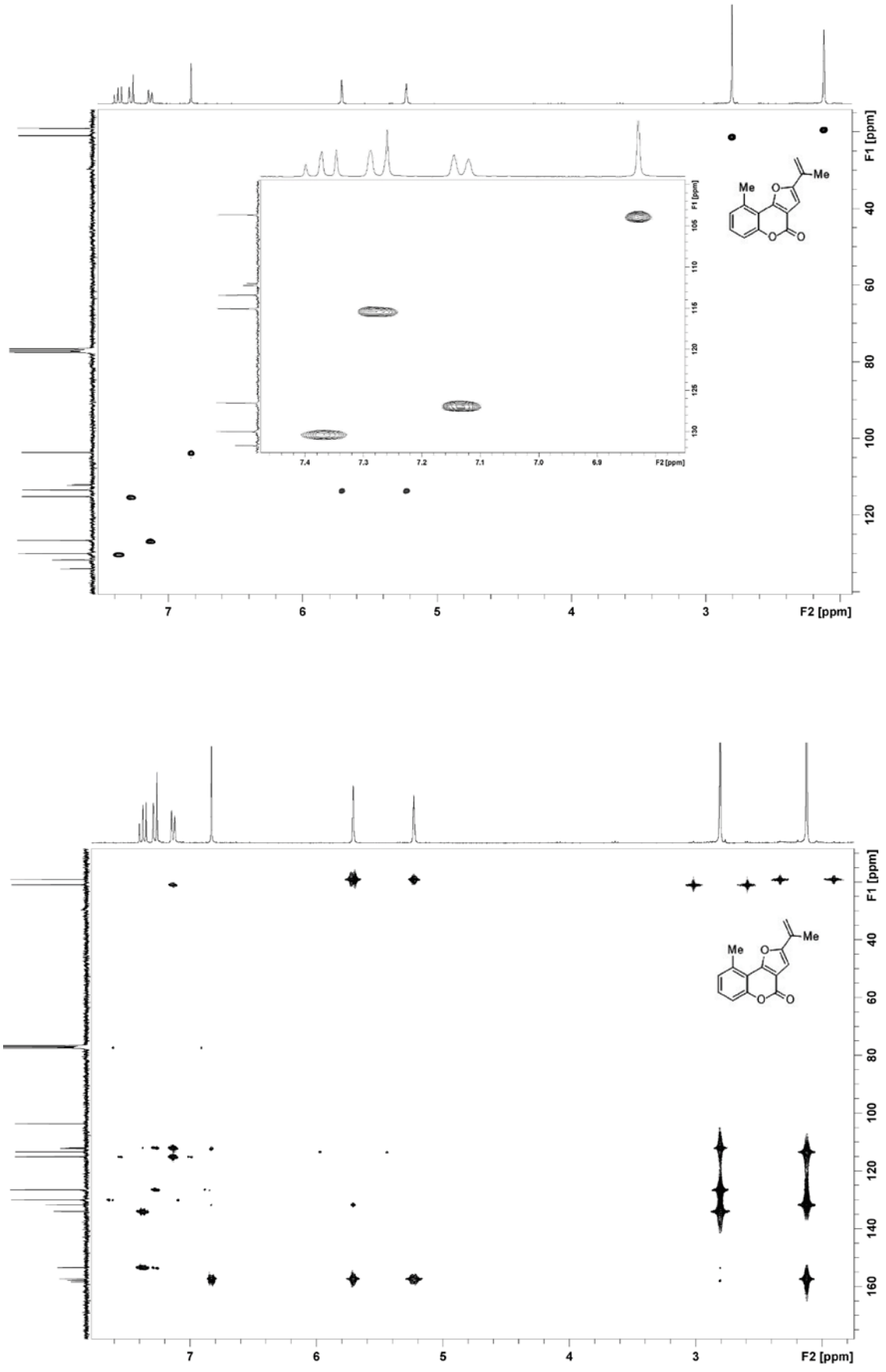


Figure S15. HSQC (top) and HMBC (bottom) spectra of compound **4a** in $CDCl_3$.

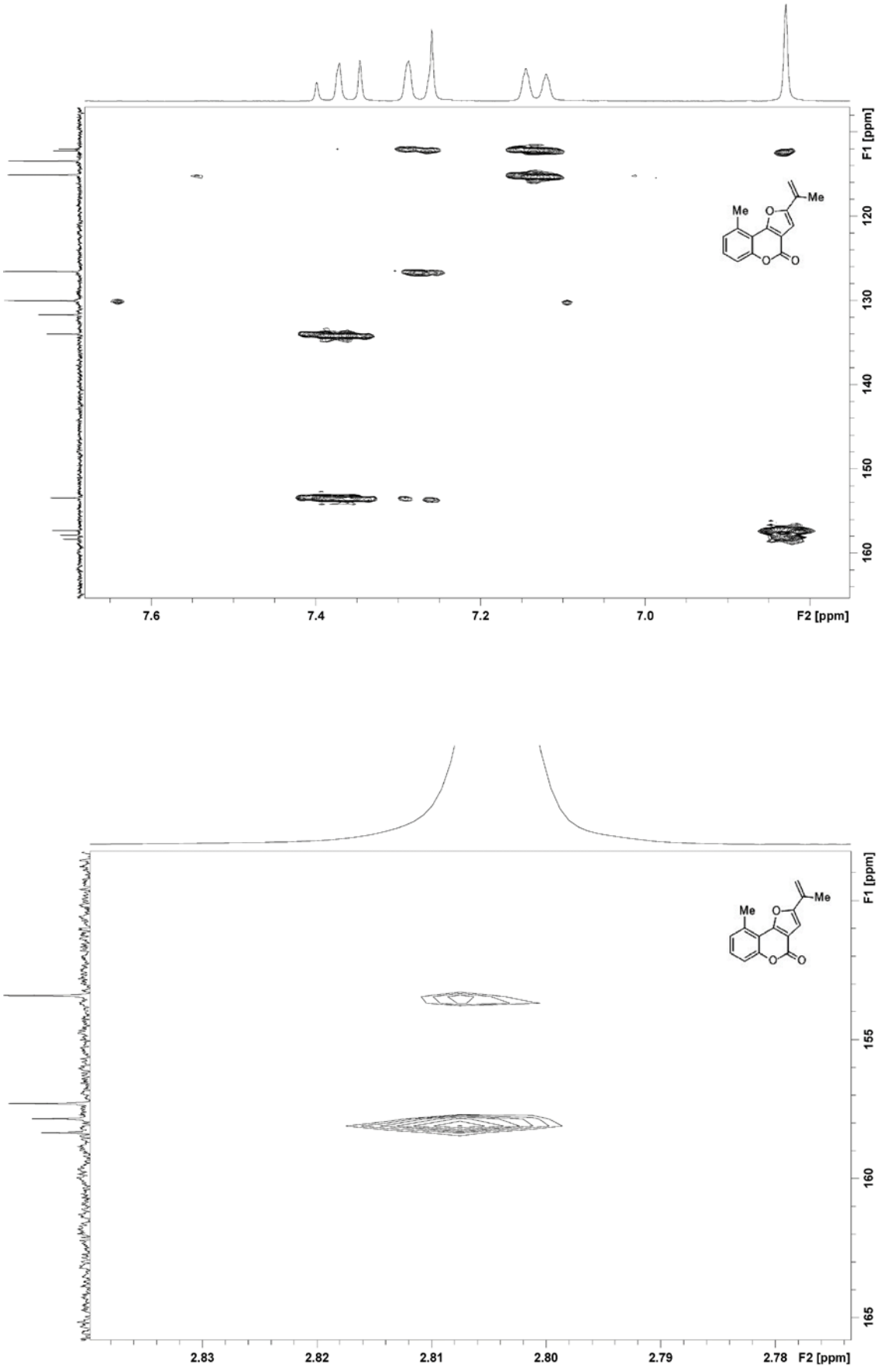


Figure S16. Expansion plots of the HMBC spectrum of compound **4a** in $CDCl_3$.

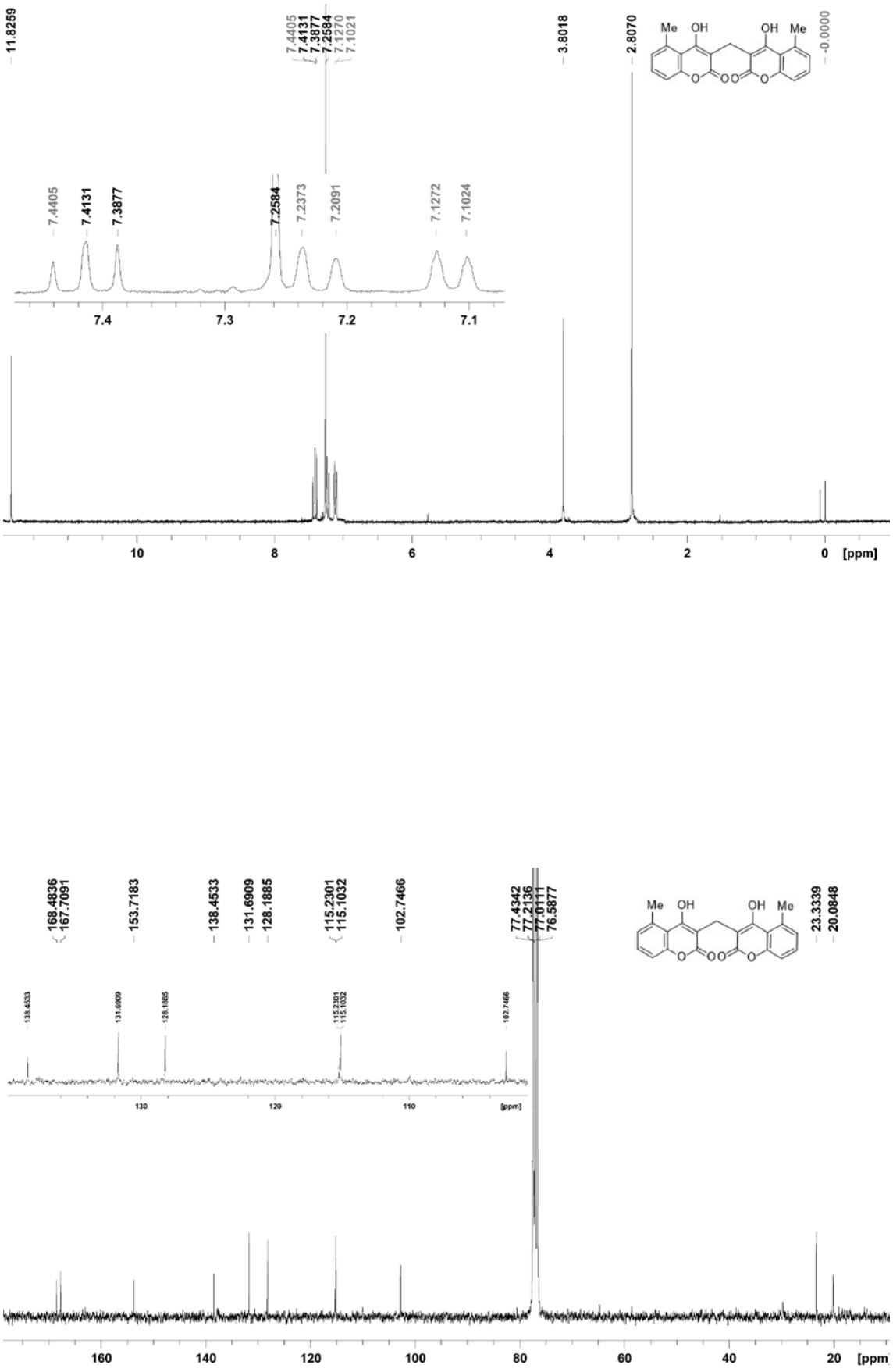


Figure S17. ^{1}H and ^{13}C NMR spectra of compound **6a** in $CDCl_3$.

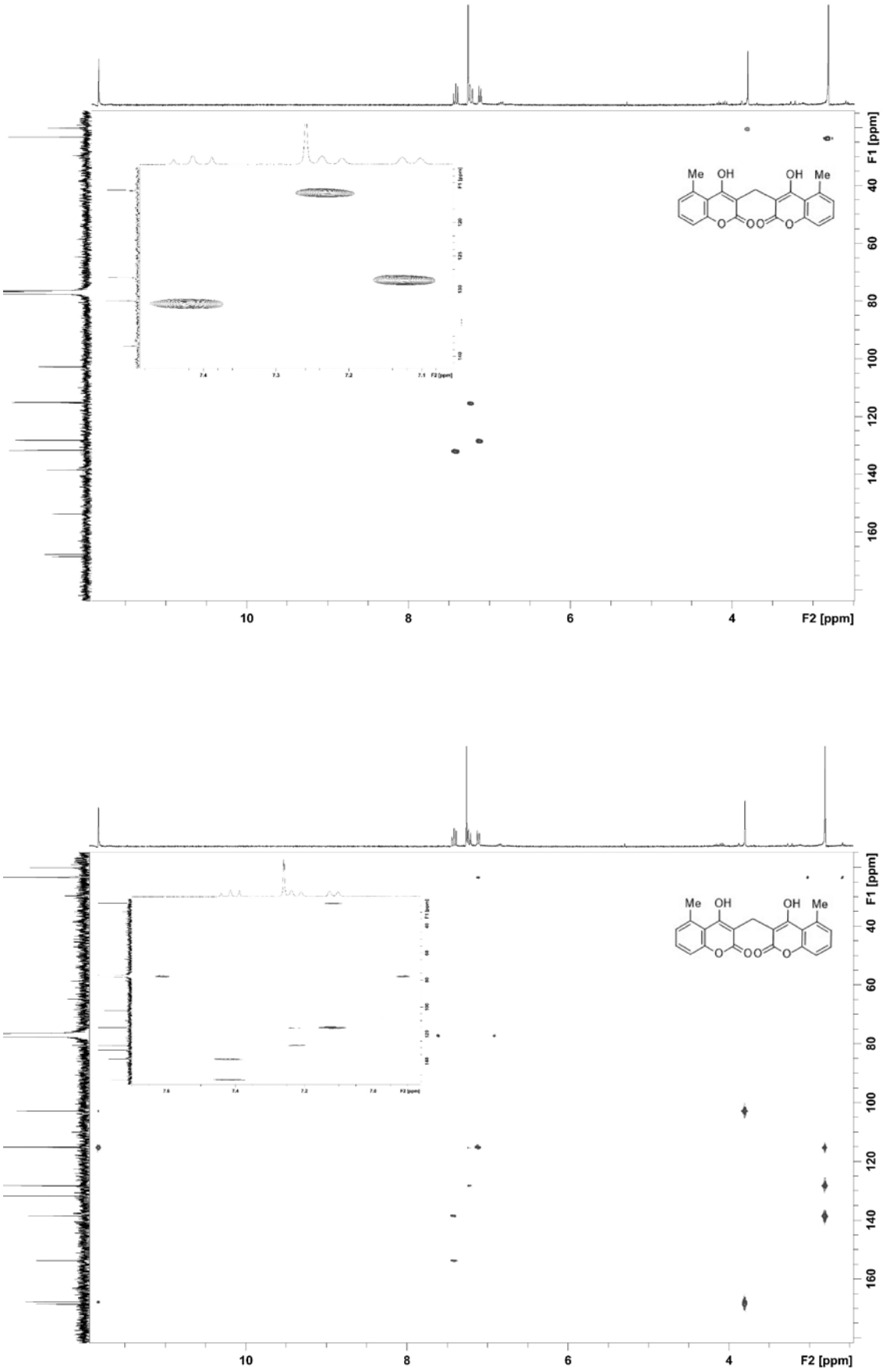


Figure S18. HSQC (top) and HMBC (bottom) spectra of compound **6a** in $CDCl_3$

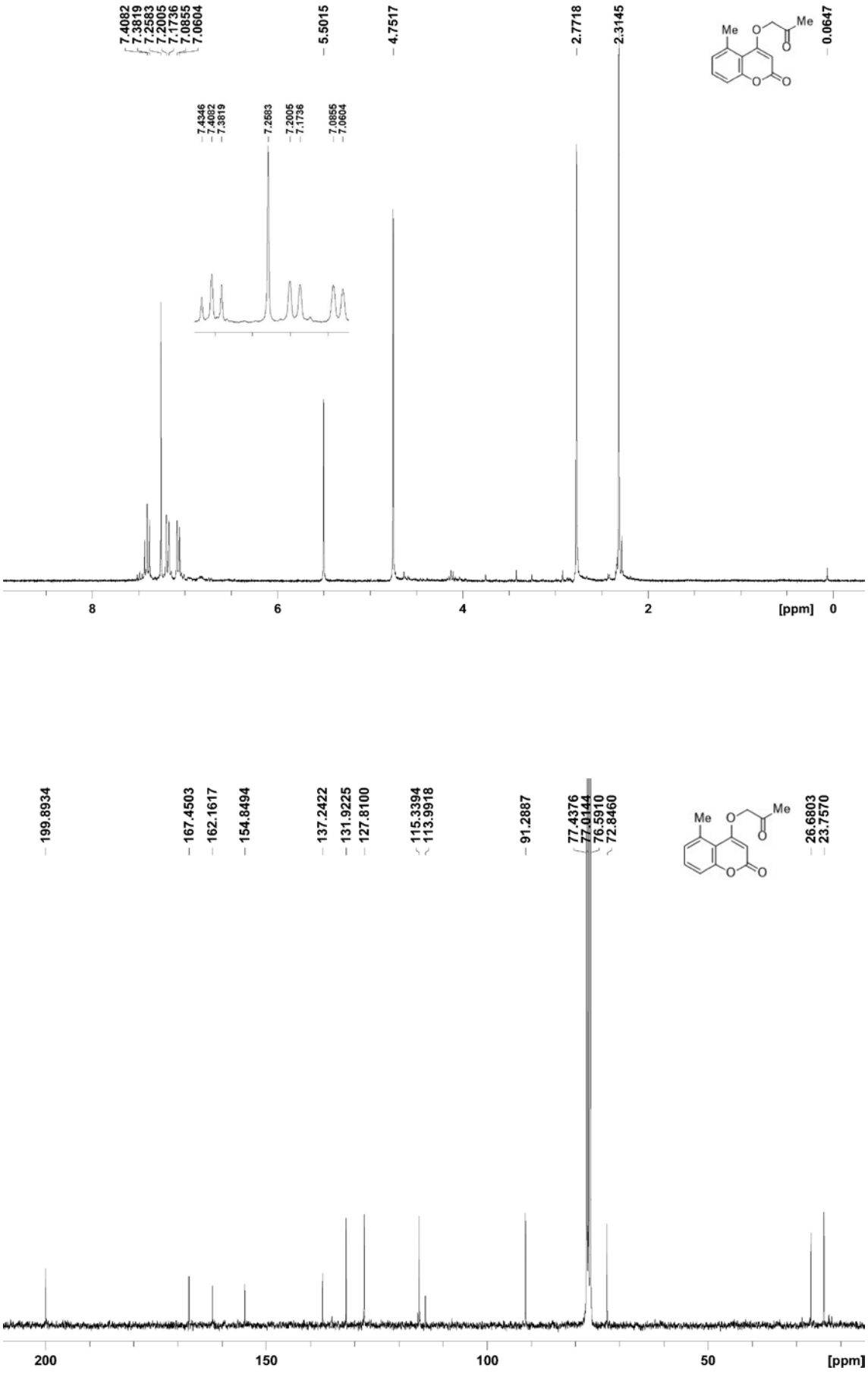


Figure S19. ^{1}H and ^{13}C NMR spectra of compound **9a** in $CDCl_3$.

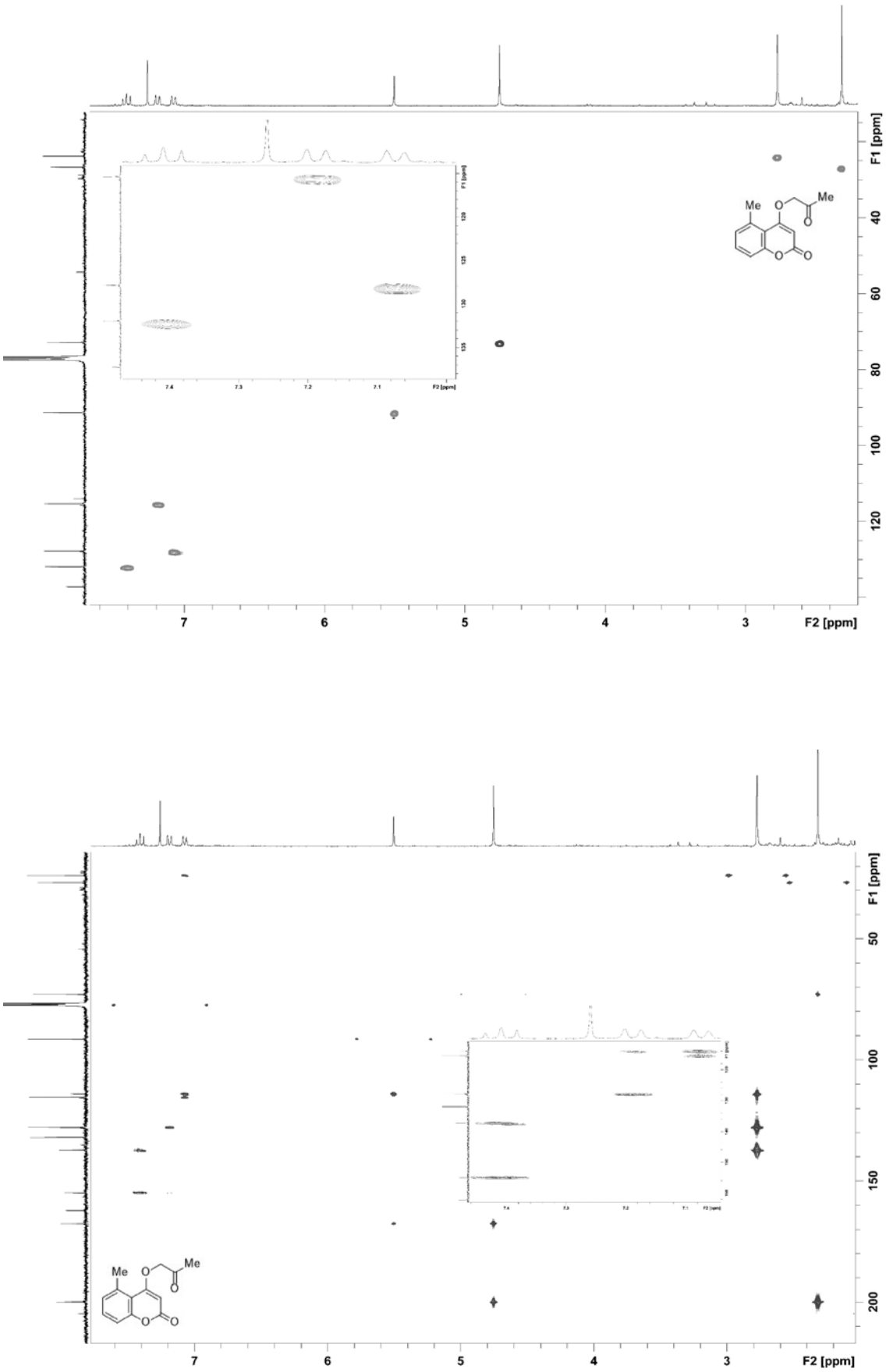


Figure S20. HSQC (top) and HMBC (bottom) spectra of compound **9a** in $CDCl_3$

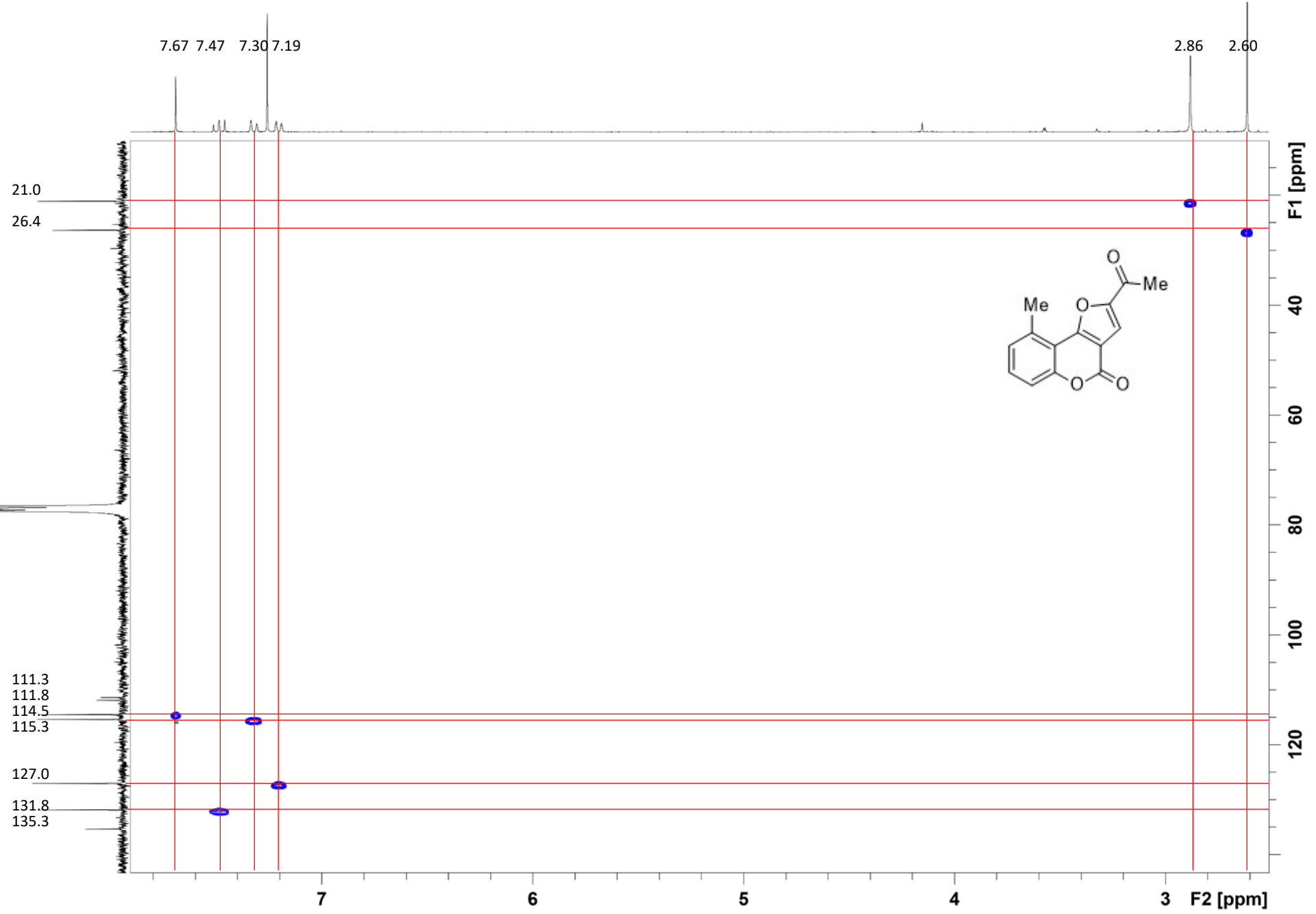


Figure S21. Spectral correlations. HSQC spectrum of compound **4b** in $CDCl_3$

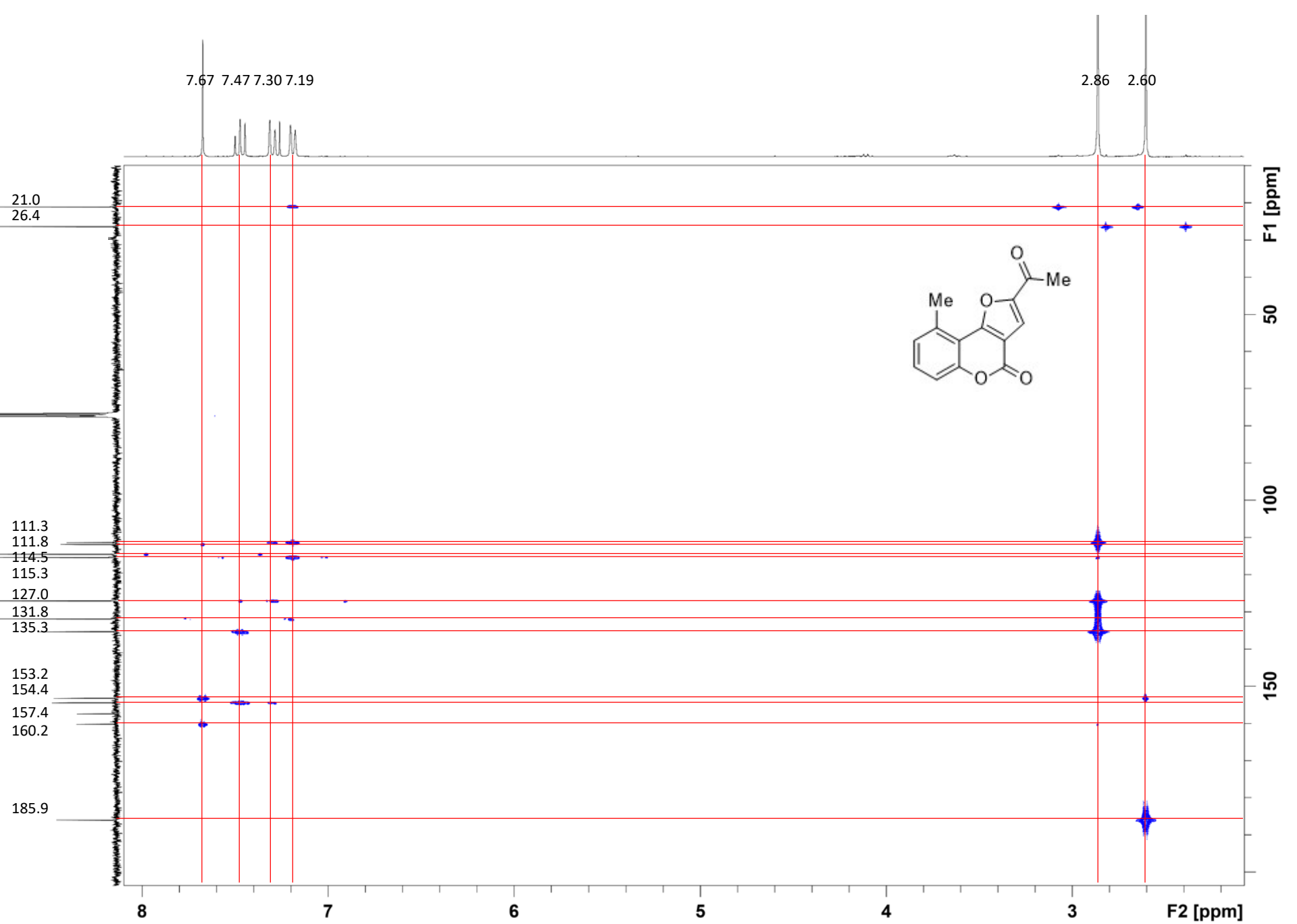


Figure S22. Spectral correlations. HMBC spectrum of compound **4b** in $CDCl_3$

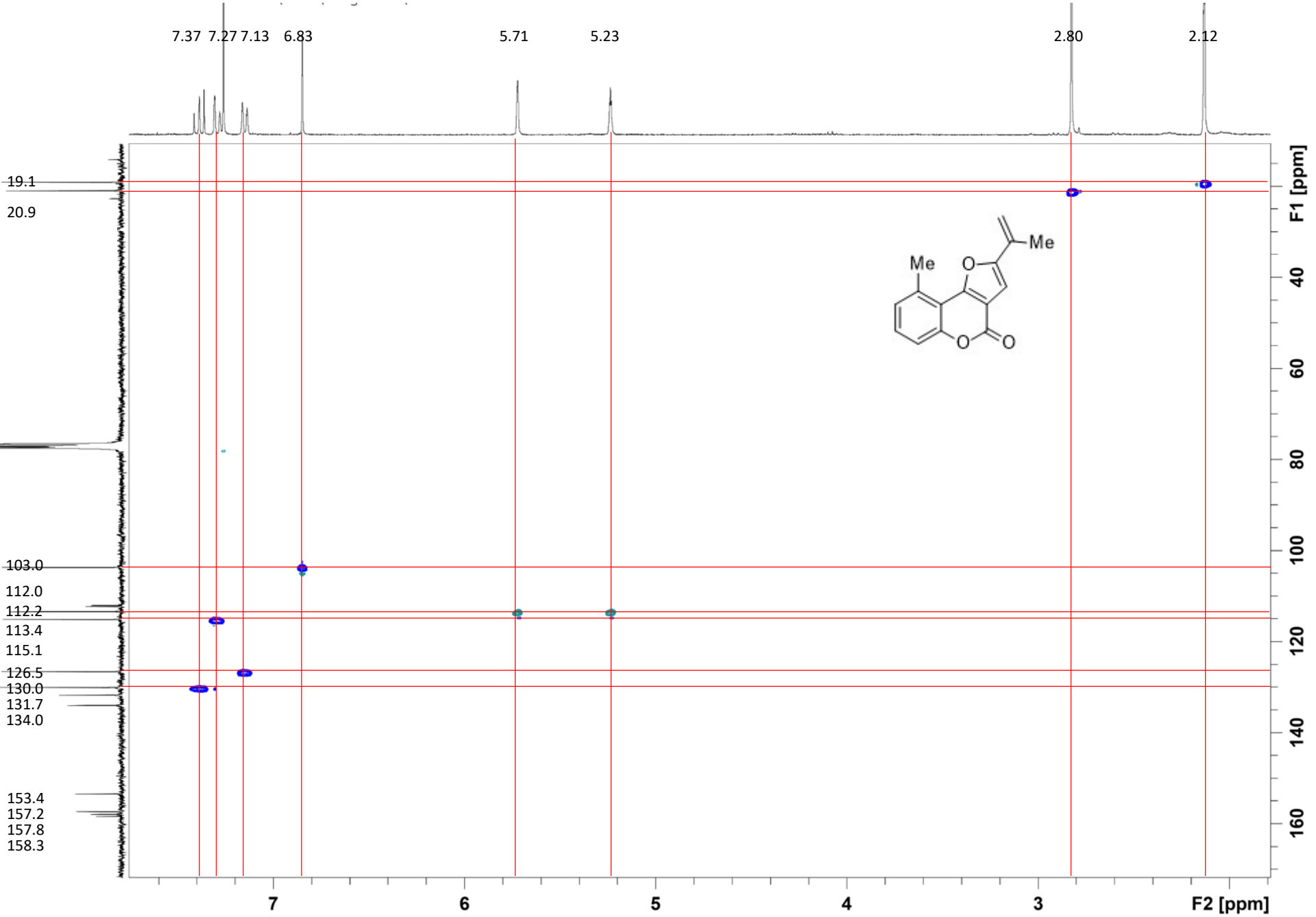


Figure S23. Spectral correlations. HSQC spectrum of compound **4a** in $CDCl_3$

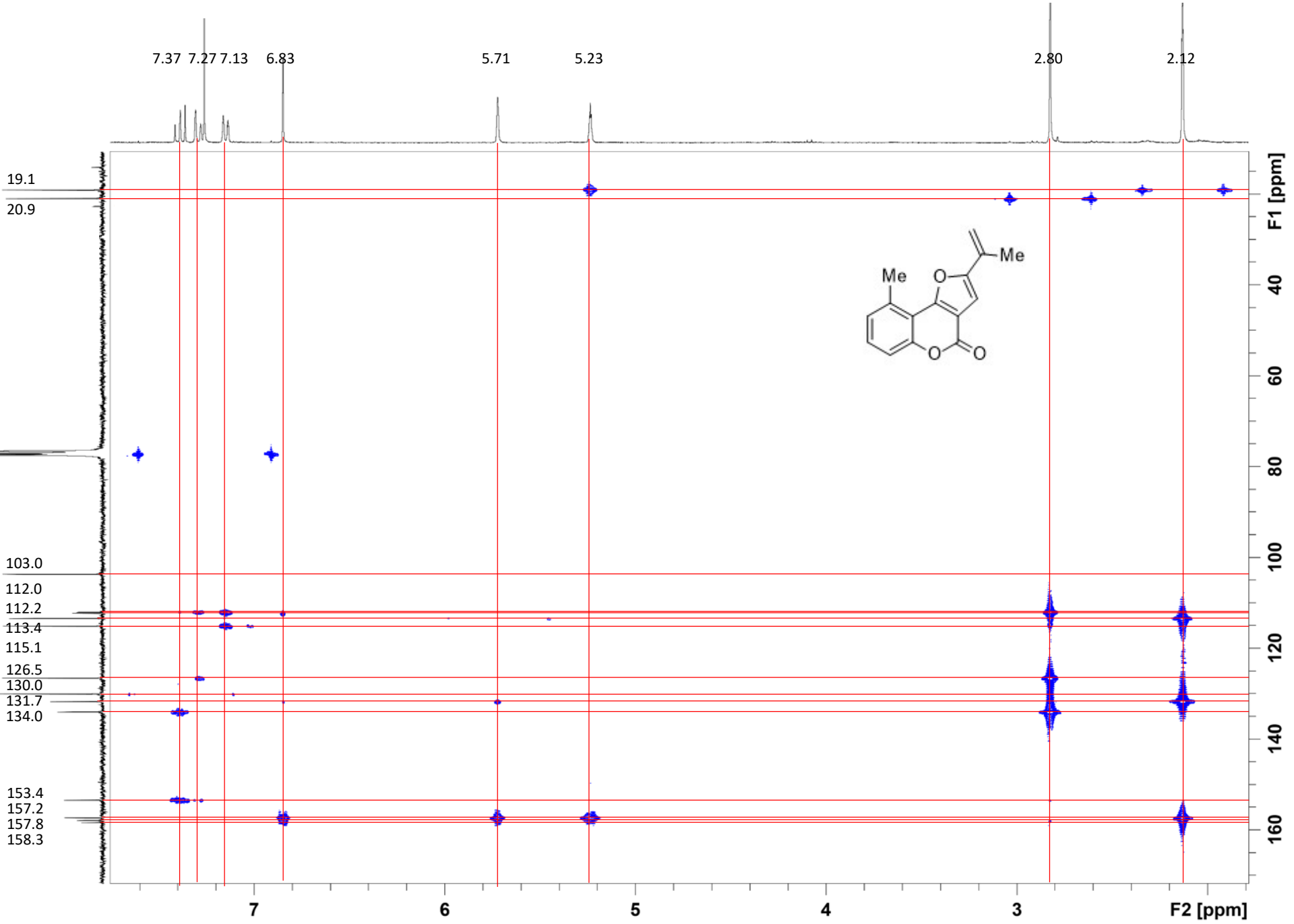


Figure S24. Spectral correlations. HMBC spectrum of compound **4a** in $CDCl_3$

Table S1. Summary of ^{1}H and ^{13}C NMR spectral data of compounds 4a and 4b

Pterophyllin 4

Position	Original assignment		Proposed assignment		HSQC	HMBC
	^{1}H NMR (300 MHz)	^{13}C NMR	^{1}H NMR (300 MHz)	^{13}C NMR	(H→C)	(H→C)
2	-	*	-	157.4	-	-
3	-	**125.9**	-	**111.8**	-	-
4	-	**157.8**	-	**160.2**	-	-
4a	-	112.0	-	111.3	-	-
5	-	135.1	-	135.3	-	-
6	7.18 (d, 1H, *J* = 7.7)	127.1	7.19 (d, 1H, *J* = 8.0)	127.0	C-6	4a, 7, 8
7	7.47 (dd, 1H, *J* = 7.7, 8.8)	131.9	7.47 (t, 1H, *J* = 8.0)	131.8	C-7	5, 6, 8a
8	7.31 (d, 1H, *J* = 8.8)	115.2	7.30 (d, 1H, *J* = 8.0)	115.3	C-8	4a, 6, 8a
8a	-	**153.1**	-	**154.4**	-	-
9	2.86 (s, 3H)	21.1	2.86 (s, 3H)	21.0	C-9	4, 4a, 5, 6
1’	7.68 (s, 1H)	114.4	7.67 (s, 1H)	114.5	C-1’	2’, 3, 4
2’	-	**154.2**	-	**153.2**	-	-
3’	-	186.1	-	185.9	-	-
4’	-	-	-	-	-	-
5’	2.59 (s, 3H)	26.4	2.60 (s, 3H)	26.4	C-5’	2’, 3’

Pterophyllin 2

Position	Original assignment		Proposed assignment		HSQC	HMBC
	^{1}H NMR (300 MHz)	^{13}C NMR	^{1}H NMR (300 MHz)	^{13}C NMR	(H→C)	(H→C)
2	-	*	-	158.3	-	-
3	-	**122.1**	-	**112.2**	-	-
4	-	**162.7**	-	**157.8**	-	-
4a	-	**108.9**	-	**112.0**	-	-
5	-	134.0	-	134.0	-	-
6	7.13 (d, 1H, *J* = 7.2)	126.5	7.13 (d, 1H, *J* = 7.4)	126.5	C-6	4a, 8
7	7.37 (dd, 1H, *J* = 7.2, 7.5)	130.0	7.37 (t, 1H, *J* = 8.0, 7.4)	130.0	C-7	5, 8a
8	7.28 (d, 1H, *J* = 7.5)	115.1	7.27 (d, 1H, *J* = 8.0)	115.1	C-8	4a, 6, 8a
8a	-	153.8	-	153.4	-	-
9	2.81 (s, 3H)	**22.7**	2.80 (s, 3H)	**20.9**	C-9	4, 4a, 6, 8a
1’	6.83 (s, 1H)	103.7	6.83 (s, 1H)	103.0	C-1’	2’, 3, 3’
2’	-	*	-	157.2	-	-
3’	-	*	-	131.7	-	-
4’	5.22 (d, 1H, *J* = 1.0) 5.70 (d, 1H, *J* = 1.0)	113.4	5.23 (bq, 1H, *J* = 1.1) 5.71 (bs, 1H)	113.4	C-4’	2’, 3’, 5’
5’	2.11 (s, 3H)	19.1	2.12 (bt, 3H, *J* = 1.1)	19.1	C-5’	2’, 3’, 4’

* The authors informed that these signals were not observable in their spectra.