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Supplementary Information for:

*P-chiral 1,7-diphosphanorbornenes: from asymmetric phospha-Diels–Alder reactions towards applications in asymmetric catalysis**

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Table of contents

pages

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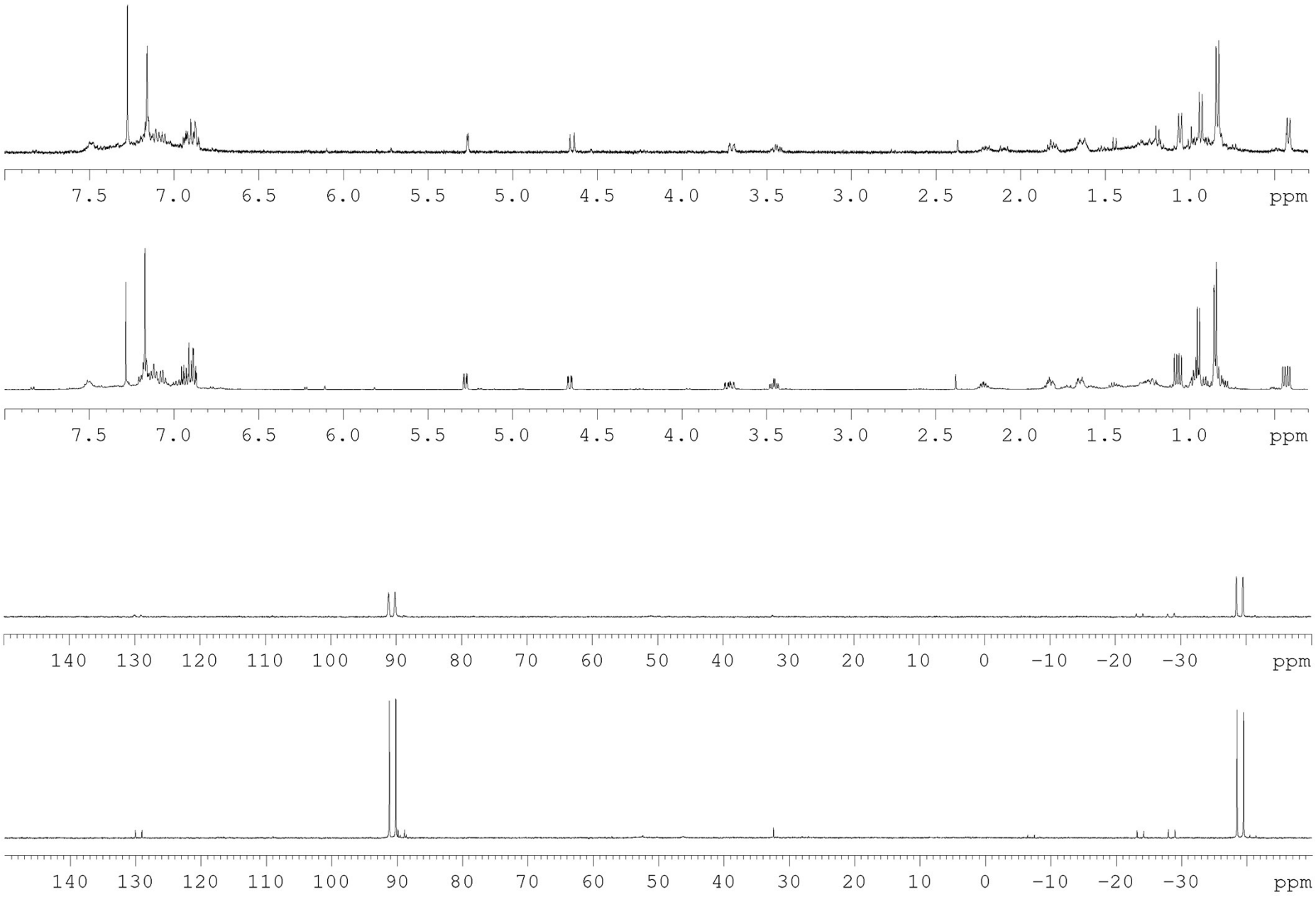
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140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm

Figure S1. 1D $^{31}P\{^{1}H\}$, ^{31}P, ^{1}H and $^{1}H\{^{31}P\}$ NMR spectra of **5a, 5b and 5c** in $CDCl_3$ at T = 303 K.

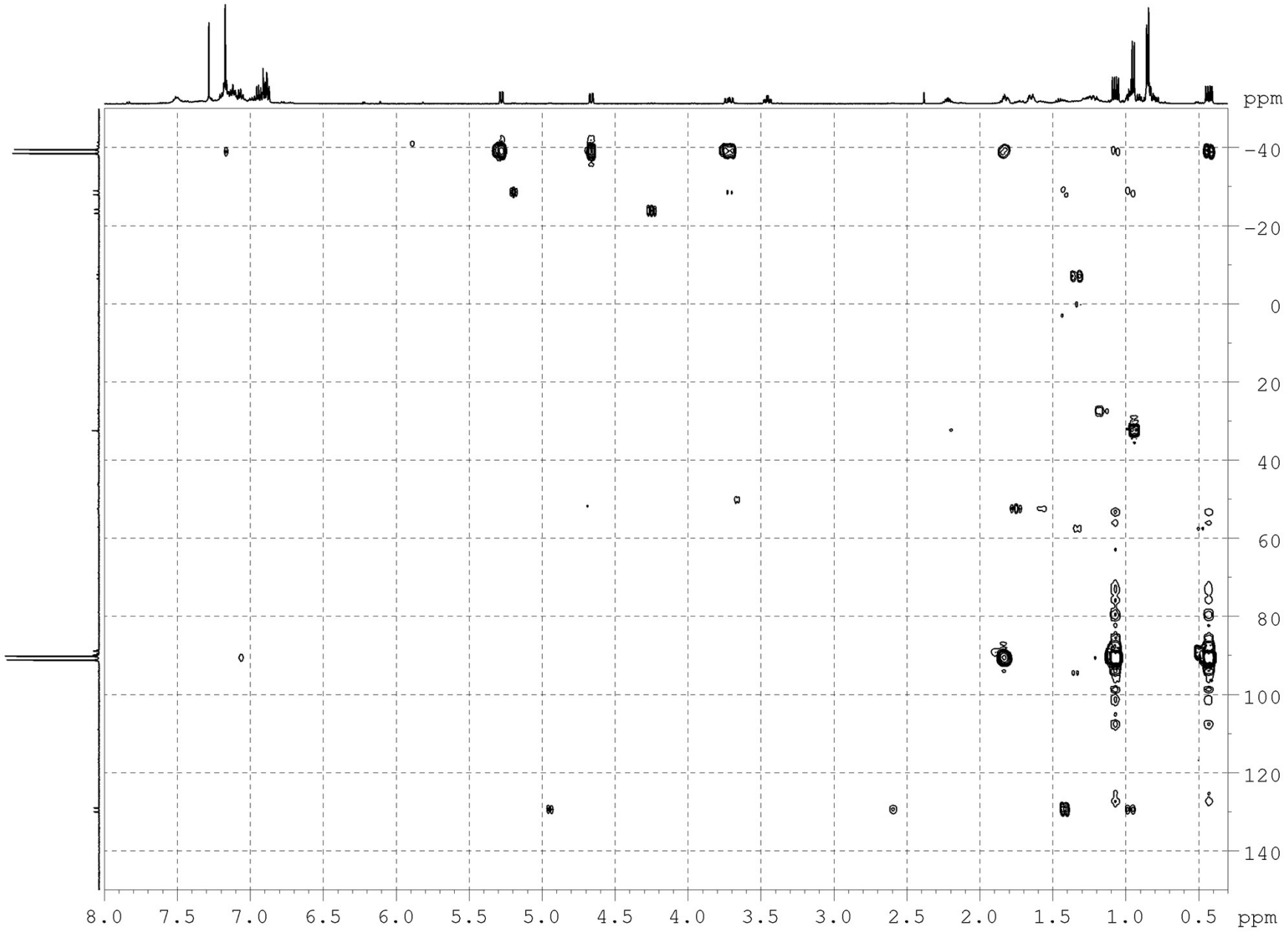

Figure S2. 2D ^{1}H-^{31}P HMBC NMR spectrum of **5a, 5b and 5c** in $CDCl_3$ at T = 303 K.

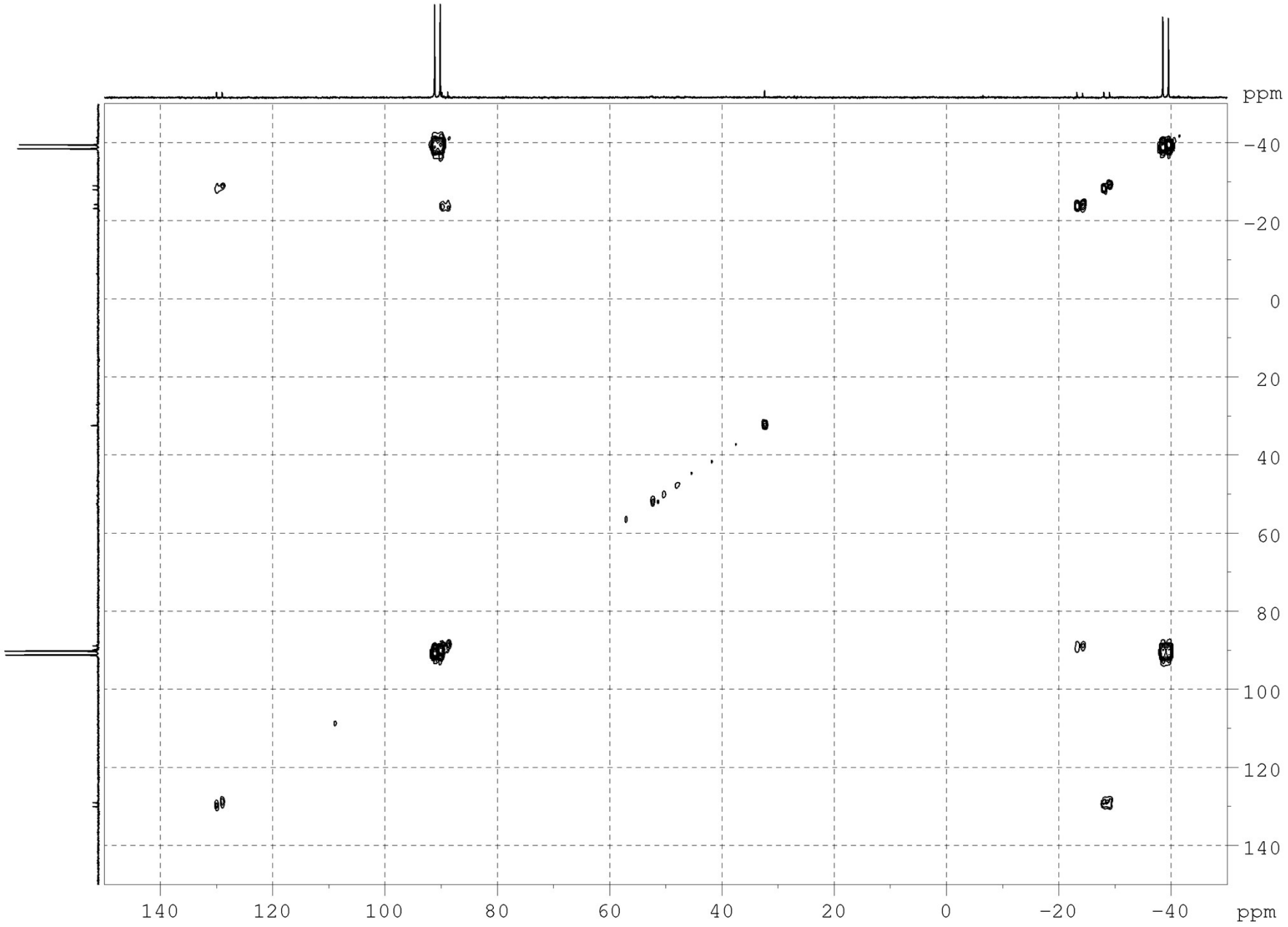

Figure S3. 2D ^{31}P-^{31}P COSY NMR spectrum of **5a, 5b and 5c** in $CDCl_3$ at T = 303 K.

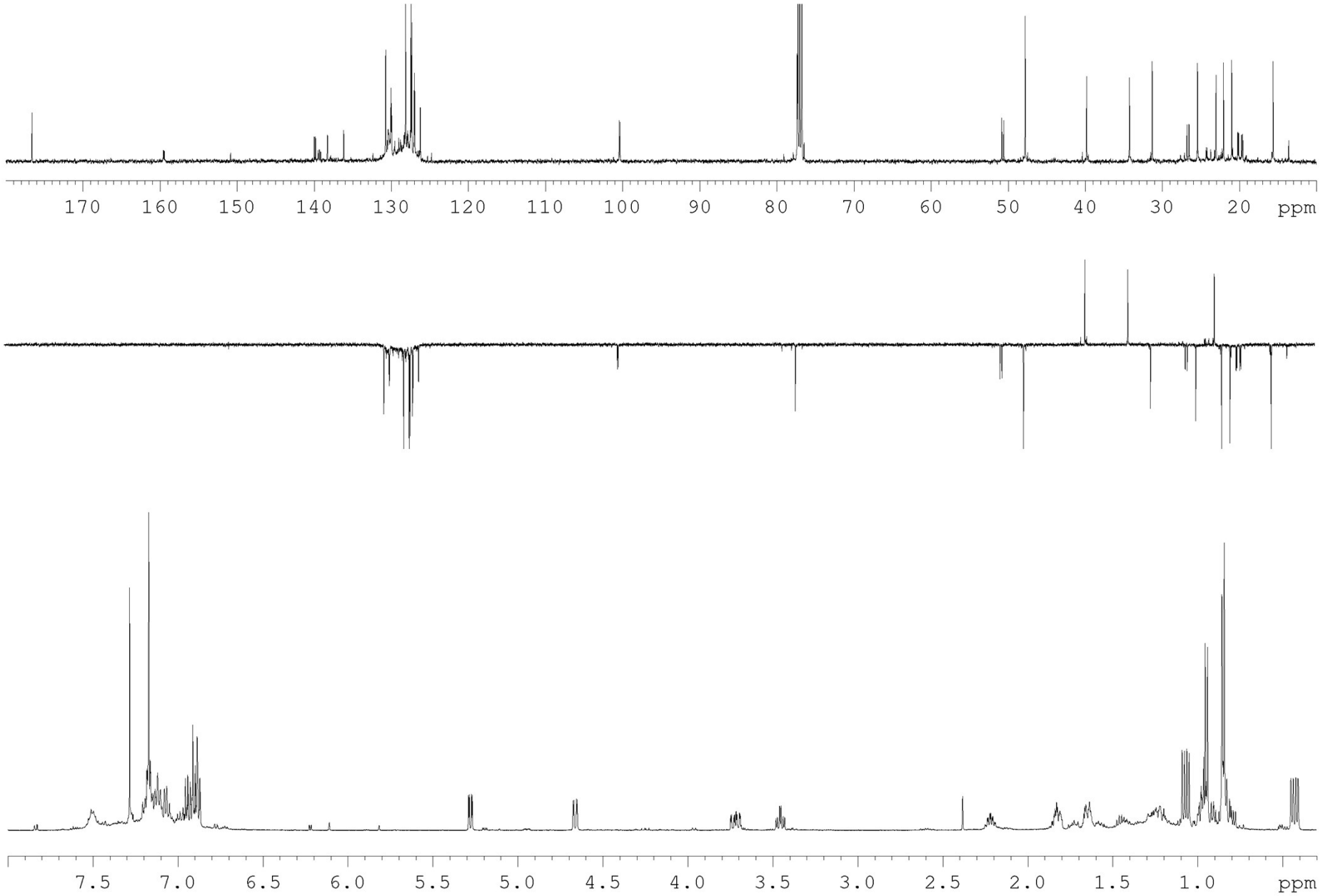

Figure S4. 1D ^{1}H, ^{13}C DEPT and $^{13}C\{^{1}H\}$ NMR spectra of **5a, 5b and 5c** in $CDCl_3$ at T = 303 K.

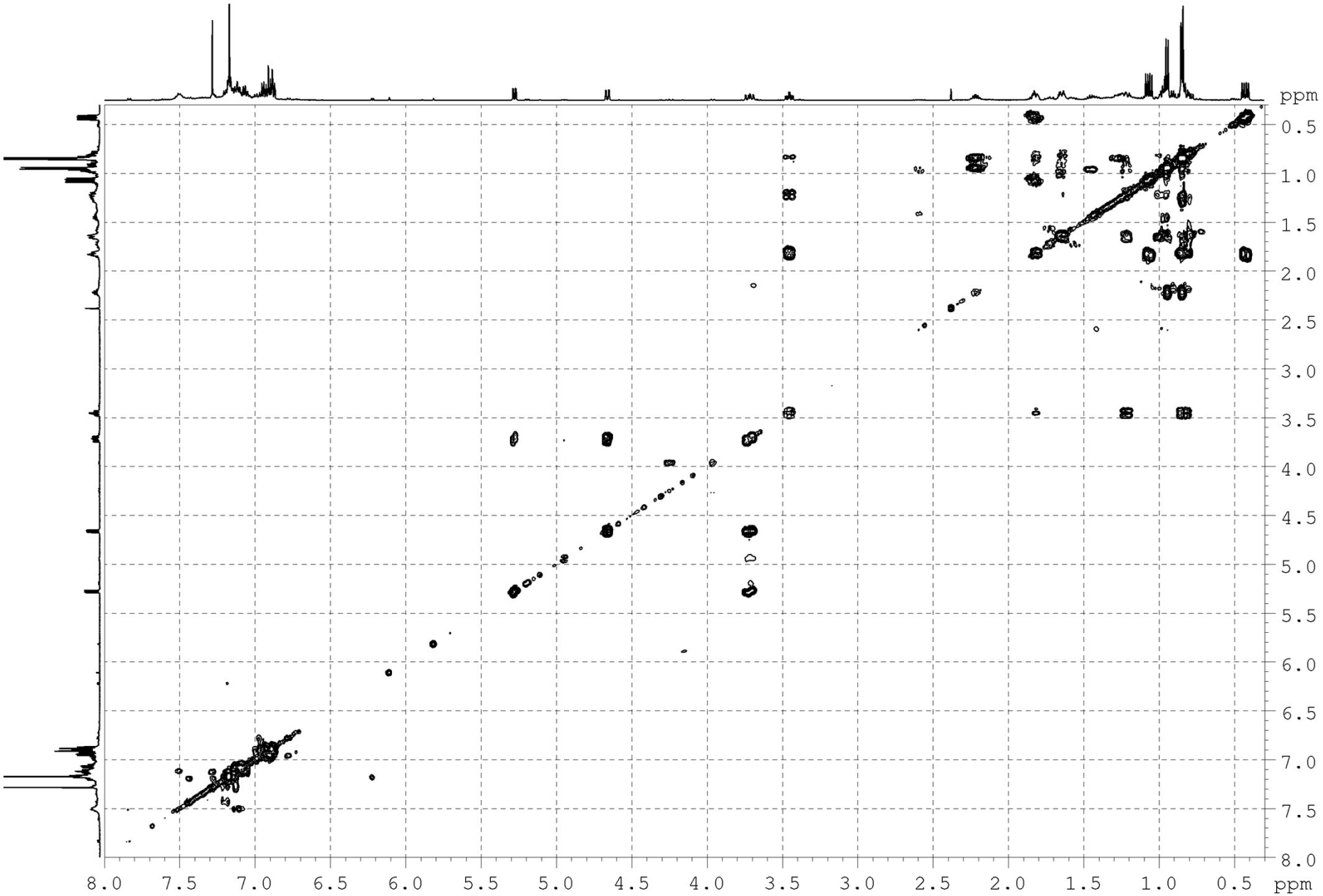

Figure S5. 2D ^{1}H-^{1}H COSY NMR spectrum of **5a, 5b and 5c** in $CDCl_3$ at T = 303 K.

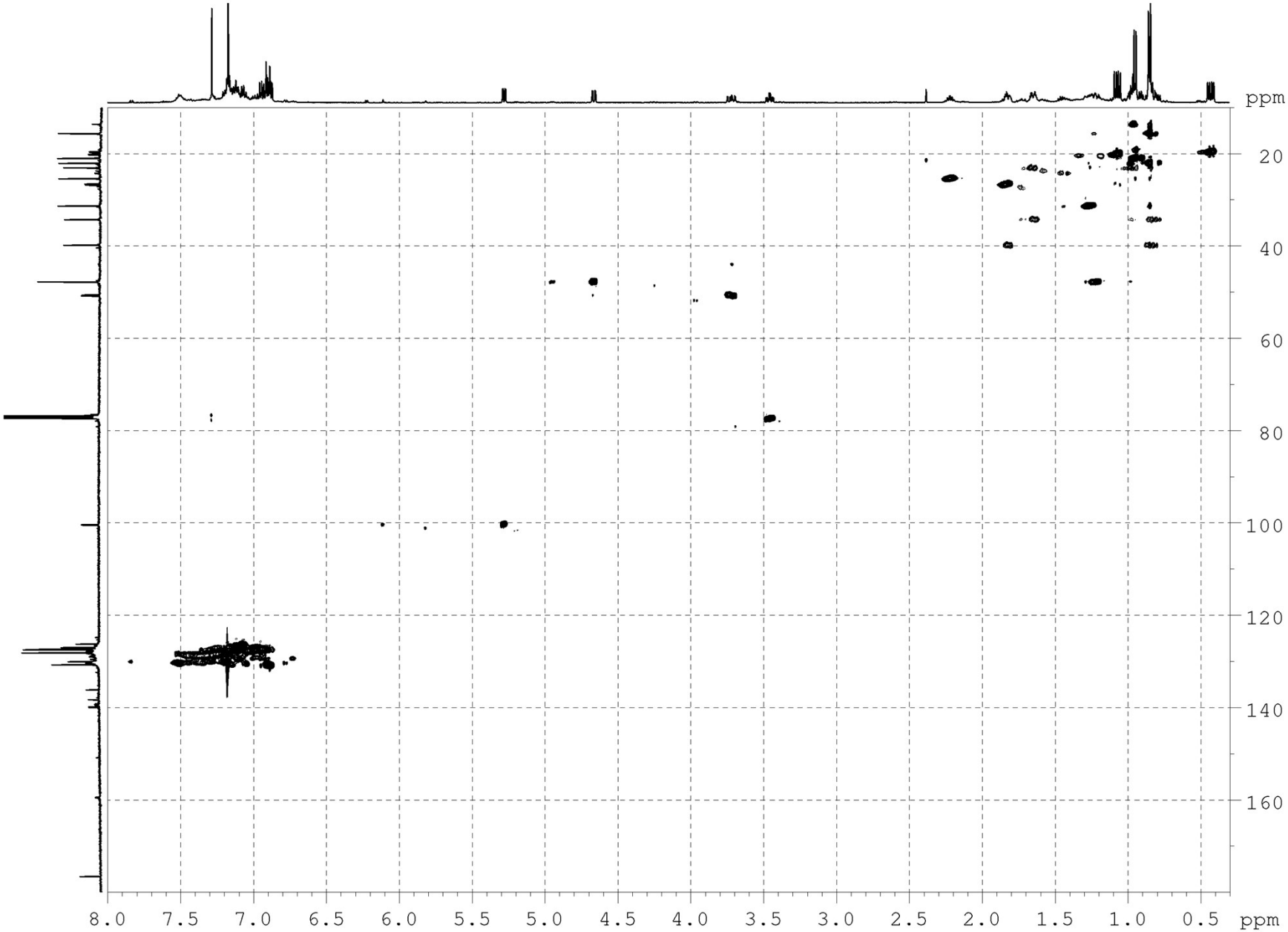

Figure S6. 2D ^{1}H-^{13}C HSQC NMR spectrum of **5a, 5b** and **5c** in $CDCl_3$ at T = 303 K.

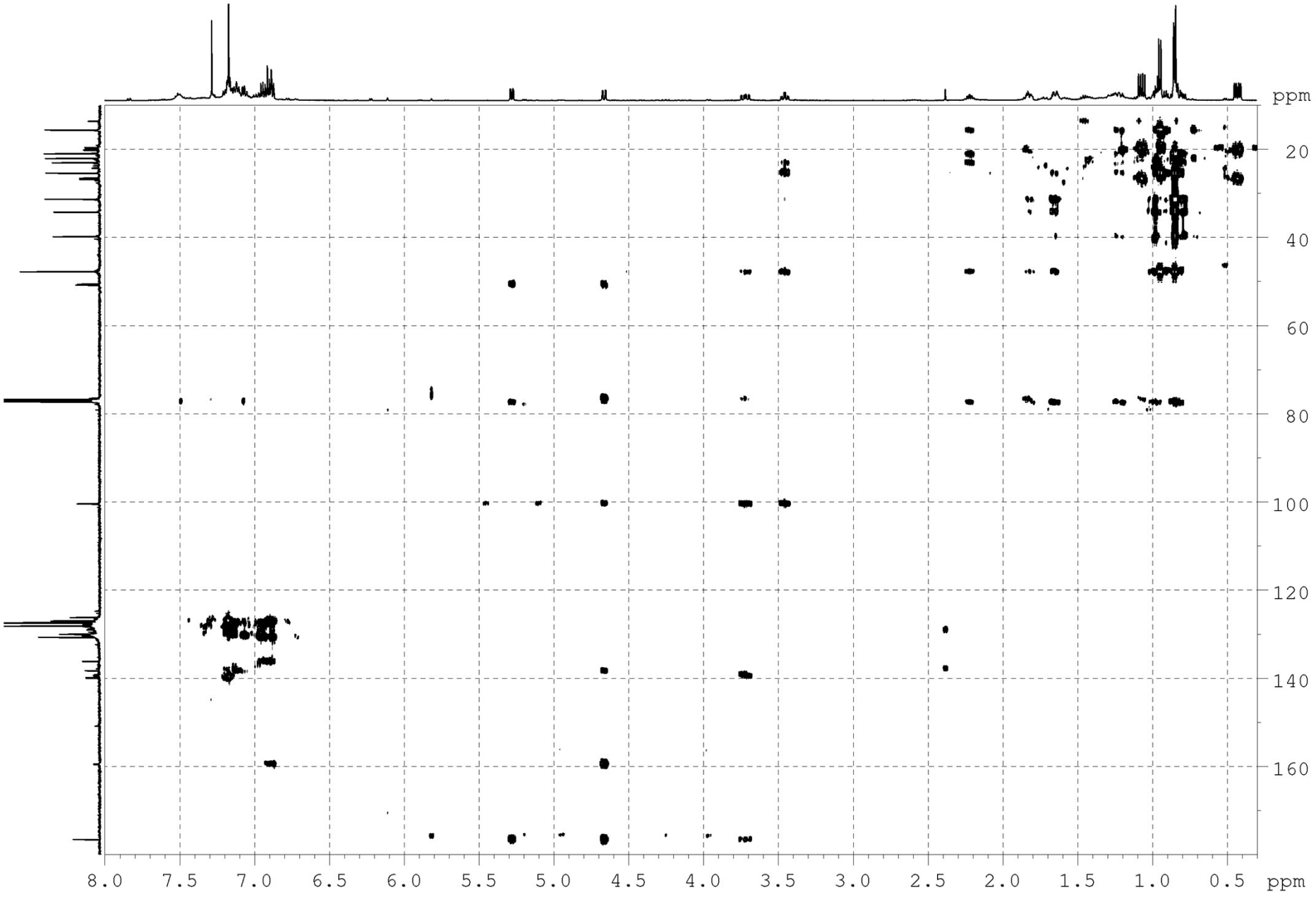

Figure S7. 2D ^{1}H-^{13}C HMBC NMR spectrum of **5a, 5b** and **5c** in $CDCl_3$ at T = 303 K.

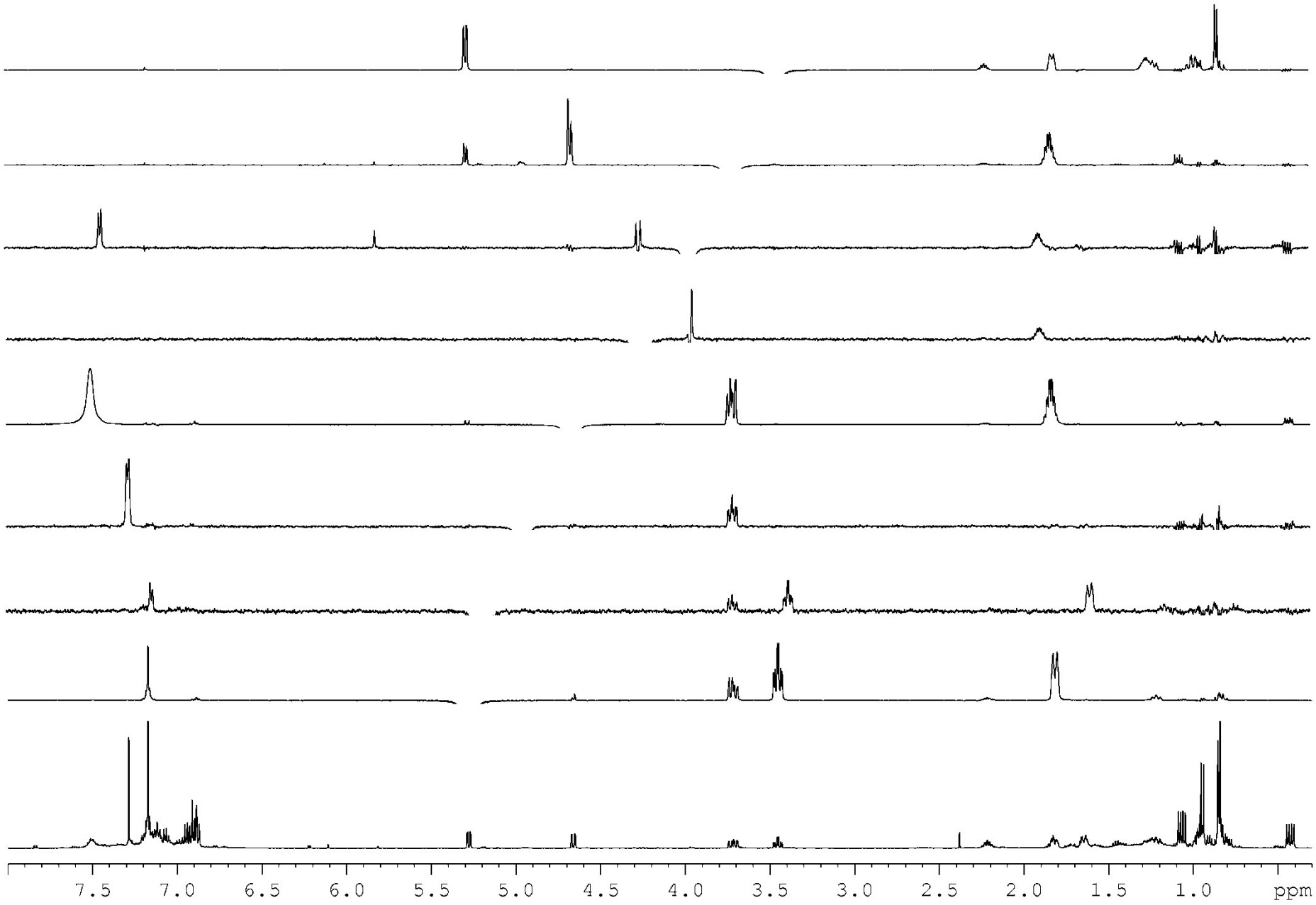

Figure S8.1. 1D ^{1}H and ^{1}H NOESY NMR spectra of **5a, 5b** and **5c** in $CDCl_3$ at T = 303 K.

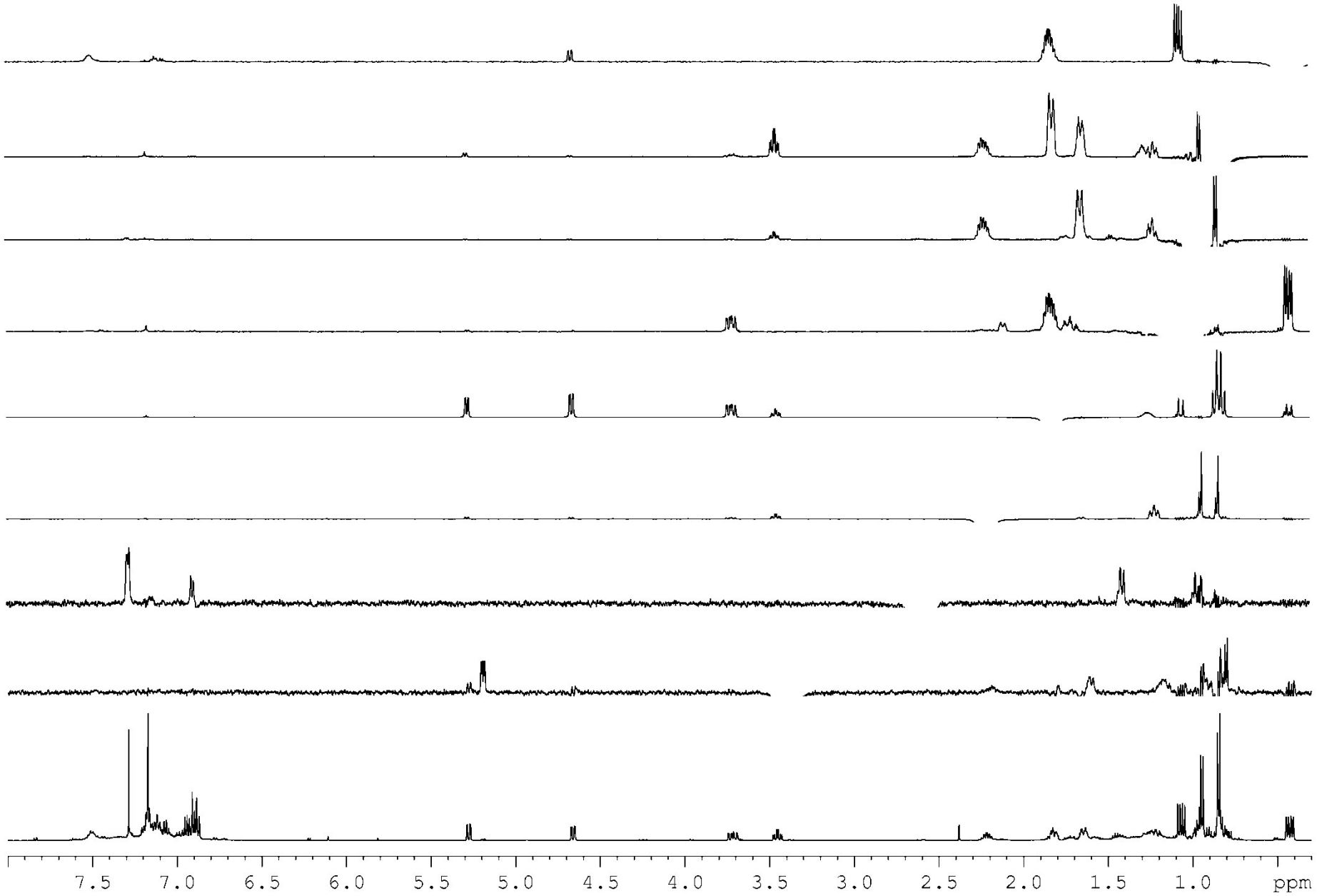

Figure S8.2. 1D ^{1}H and ^{1}H NOESY NMR spectra of **5a, 5b** and **5c** in $CDCl_3$ at T = 303 K.

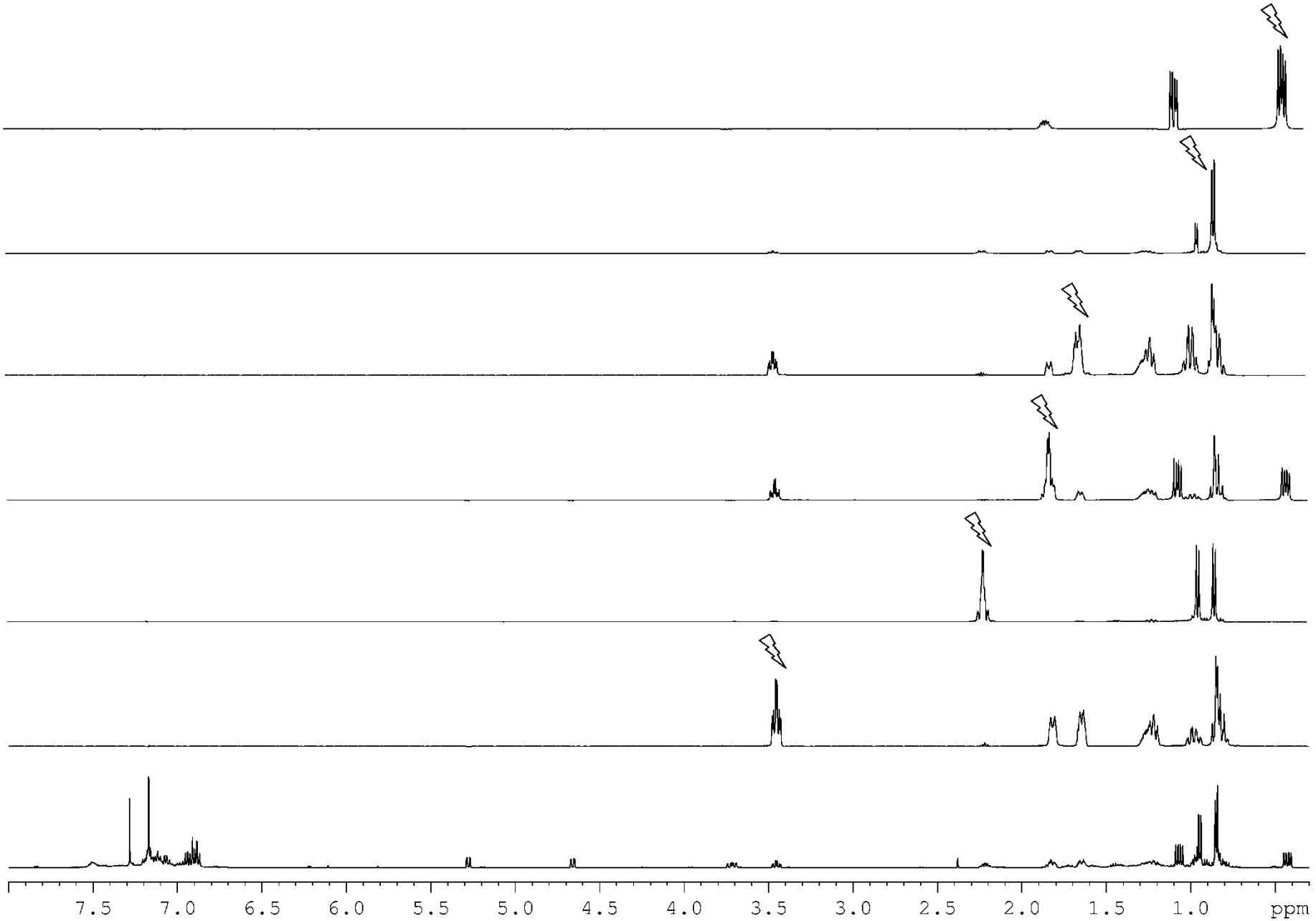

Figure S9. 1D ^{1}H and ^{1}H TOCSY NMR spectra of **5a, 5b** and **5c** in $CDCl_3$ at T = 303 K.

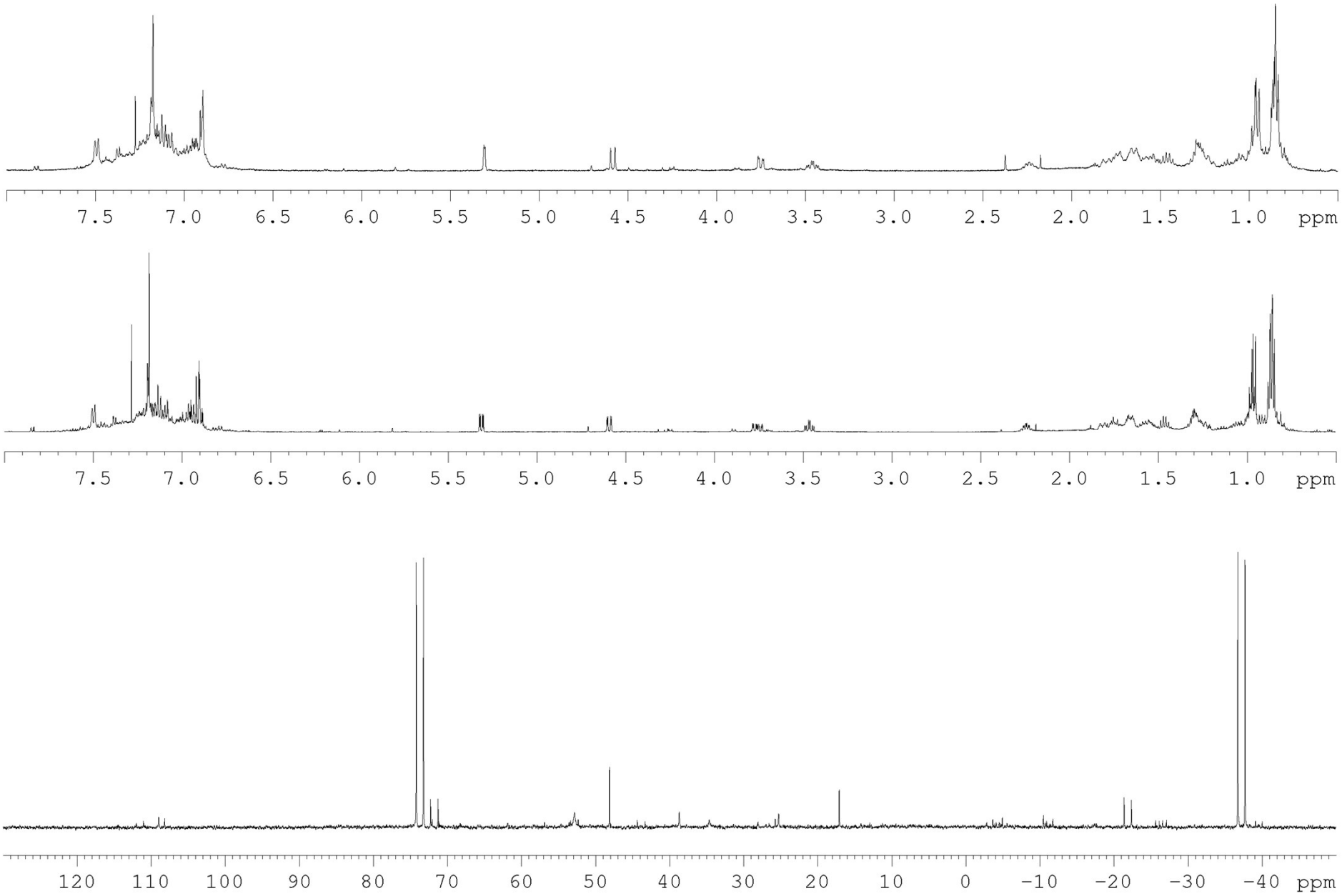

Figure S10. 1D $^{31}P\{^{1}H\}$, ^{1}H and $^{1}H\{^{31}P\}$ NMR spectra of **6a** and **6b** in $CDCl_3$ at T = 303 K.

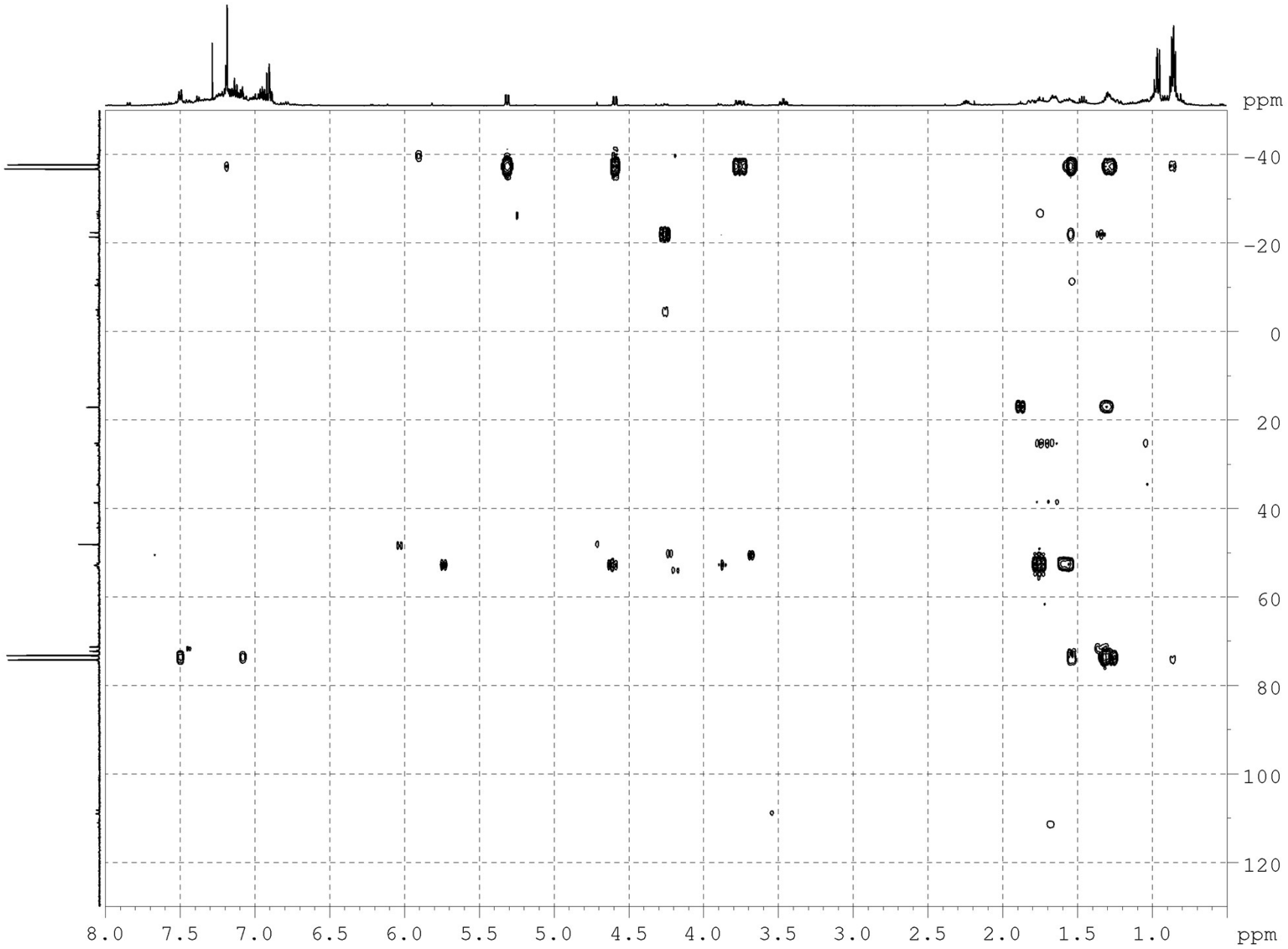

Figure S11. 2D ^{1}H-^{31}P HMBC NMR spectrum of **6a** and **6b** in $CDCl_3$ at T = 303 K.

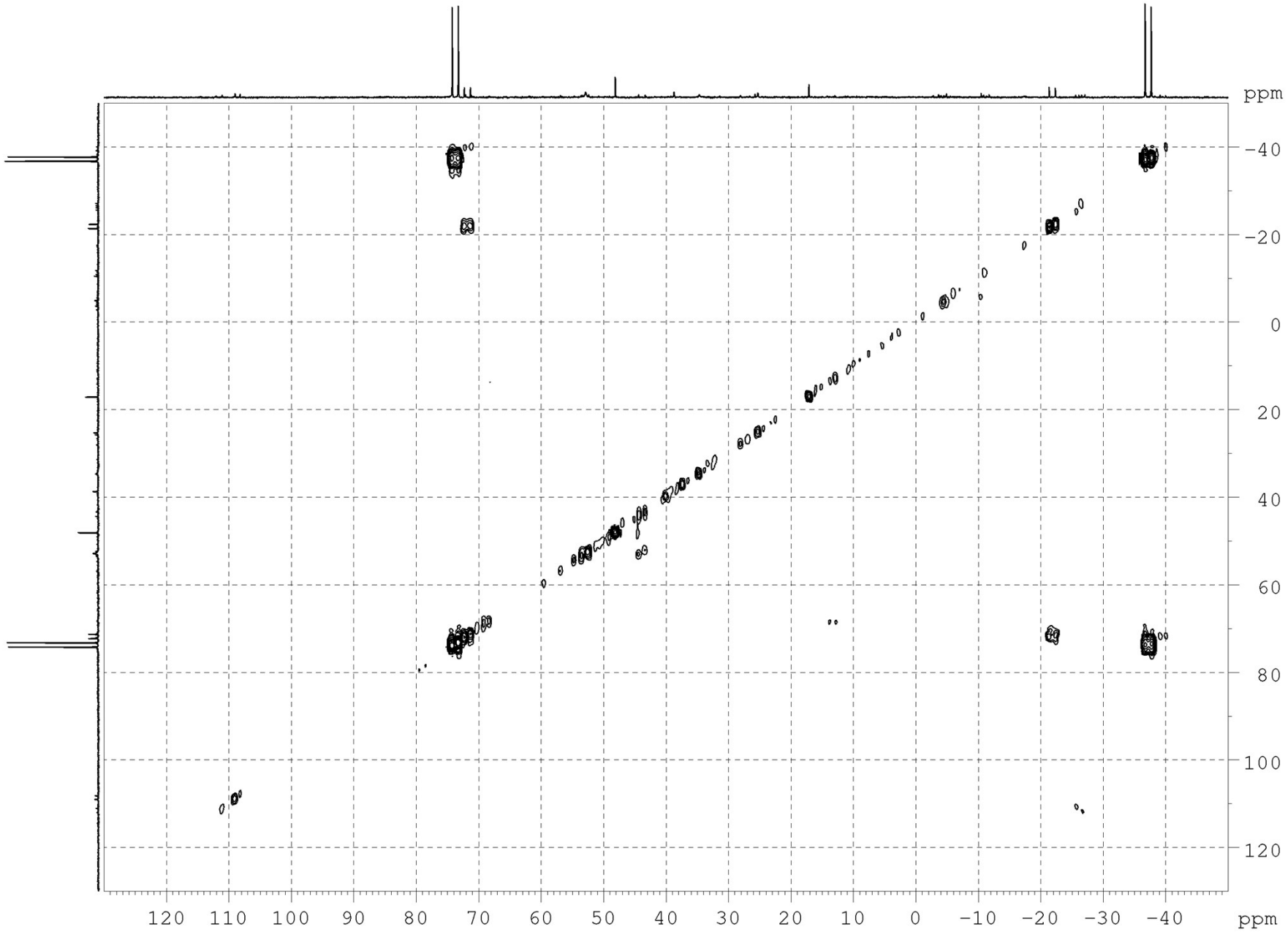

Figure S12. 2D ^{31}P-^{31}P COSY NMR spectrum of **6a** and **6b** in $CDCl_3$ at T = 303 K.

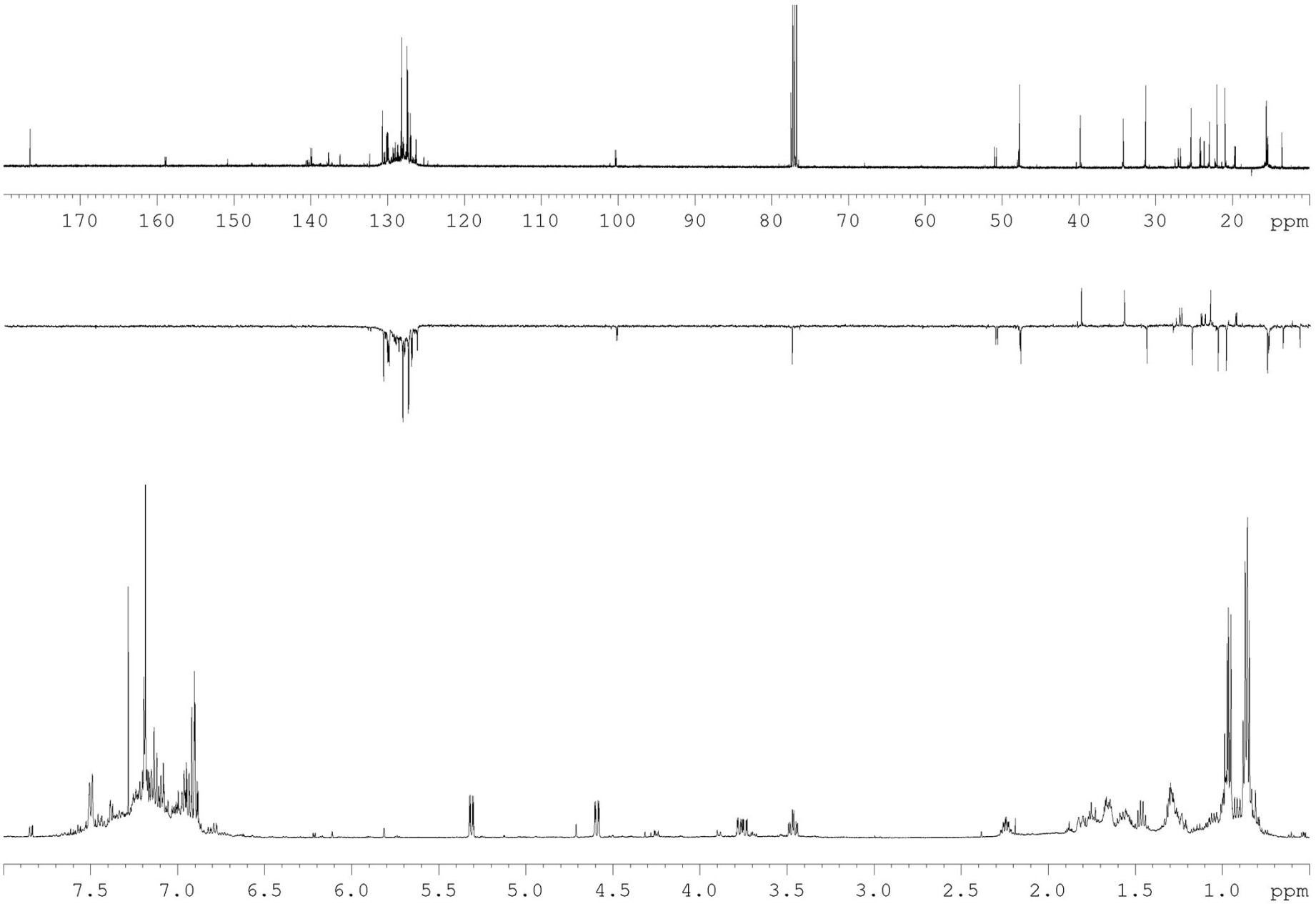

Figure S13. 1D ^{1}H, ^{13}C DEPT and $^{13}C\{^{1}H\}$ NMR spectra of **6a** and **6b** in $CDCl_3$ at T = 303 K.

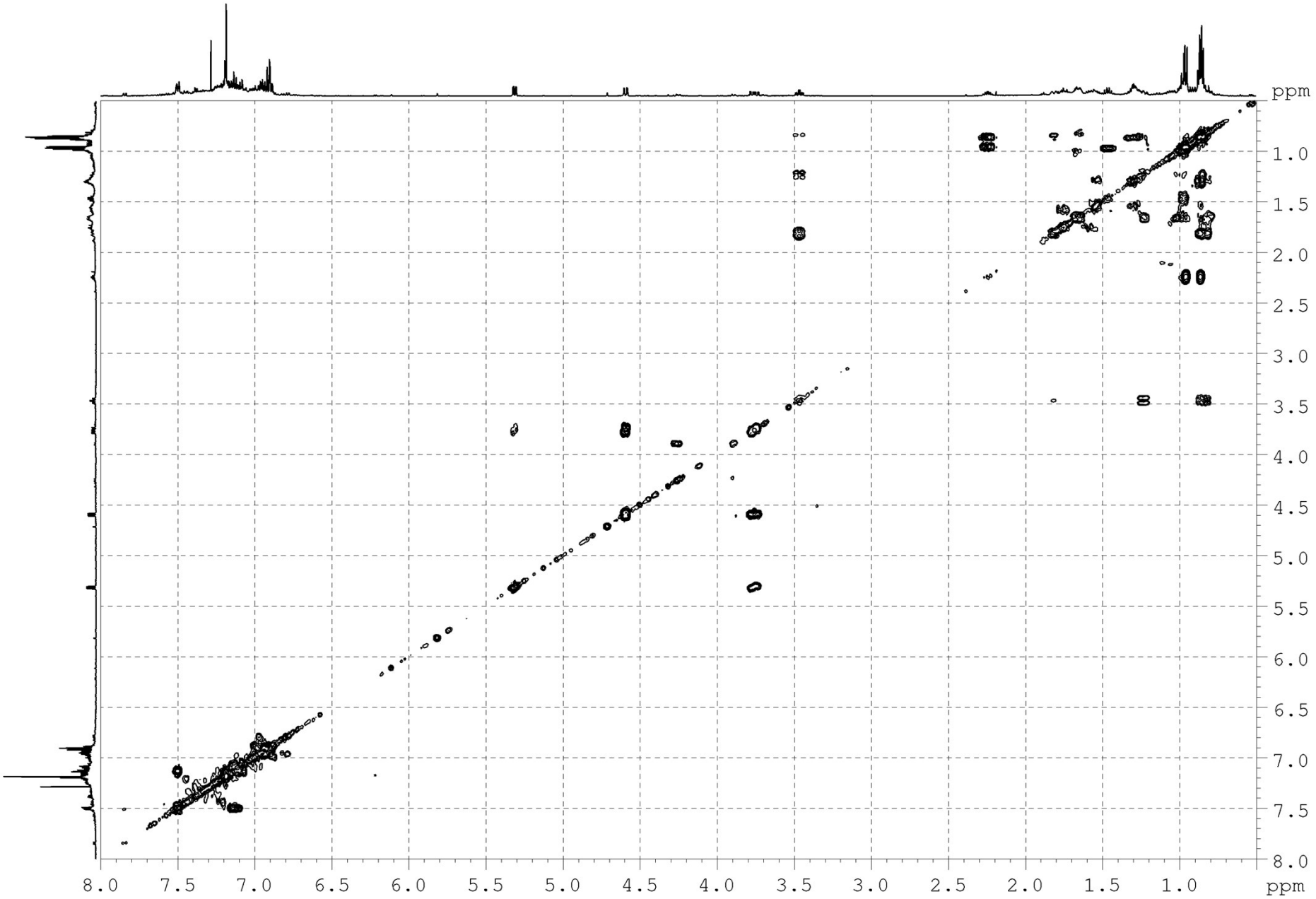

Figure S14. 2D ^{1}H-^{1}H COSY NMR spectrum of **6a** and **6b** in $CDCl_3$ at T = 303 K.

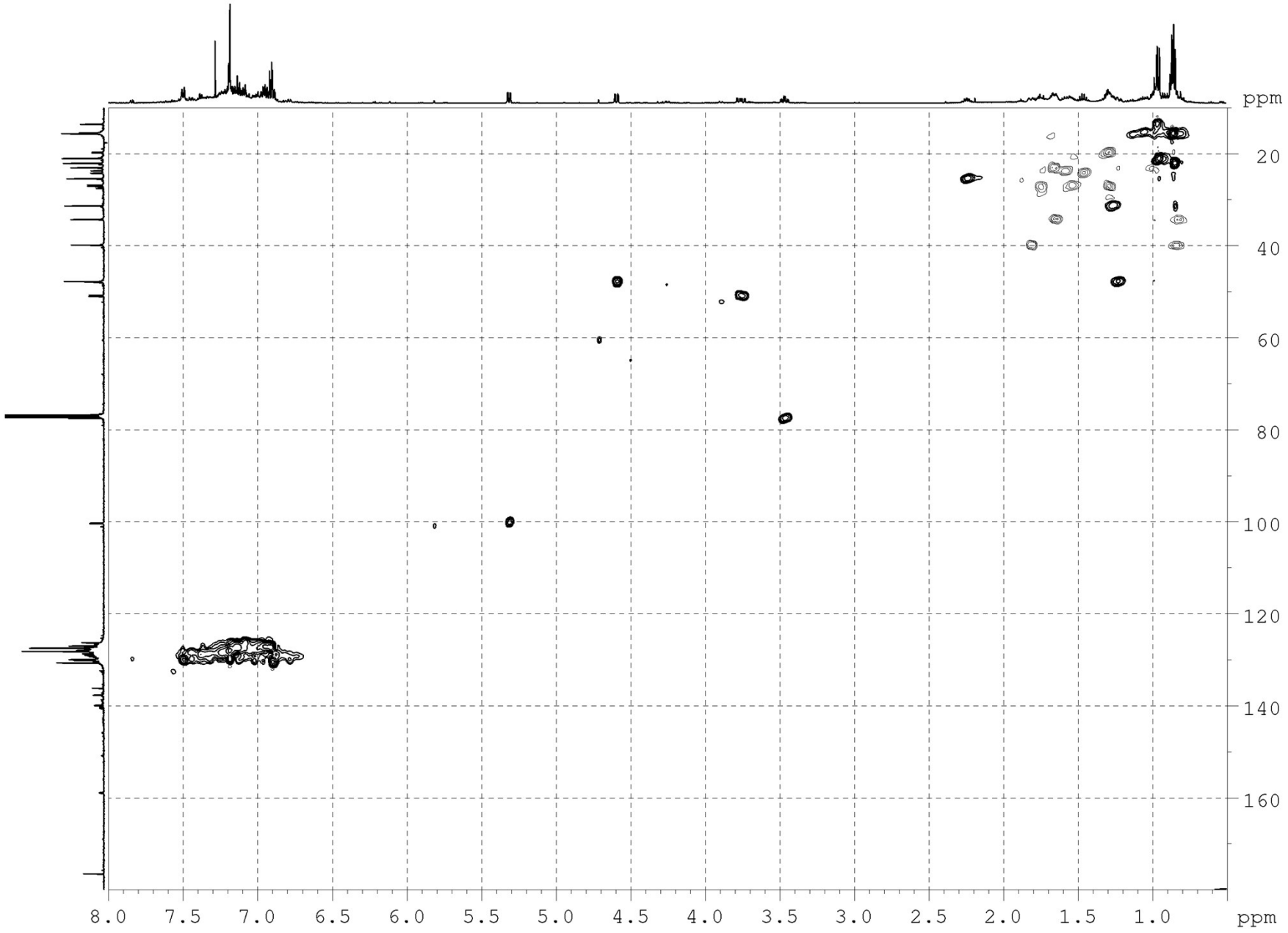

Figure S15. 2D ^{1}H-^{13}C HSQC NMR spectrum of **6a** and **6b** in $CDCl_3$ at T = 303 K.

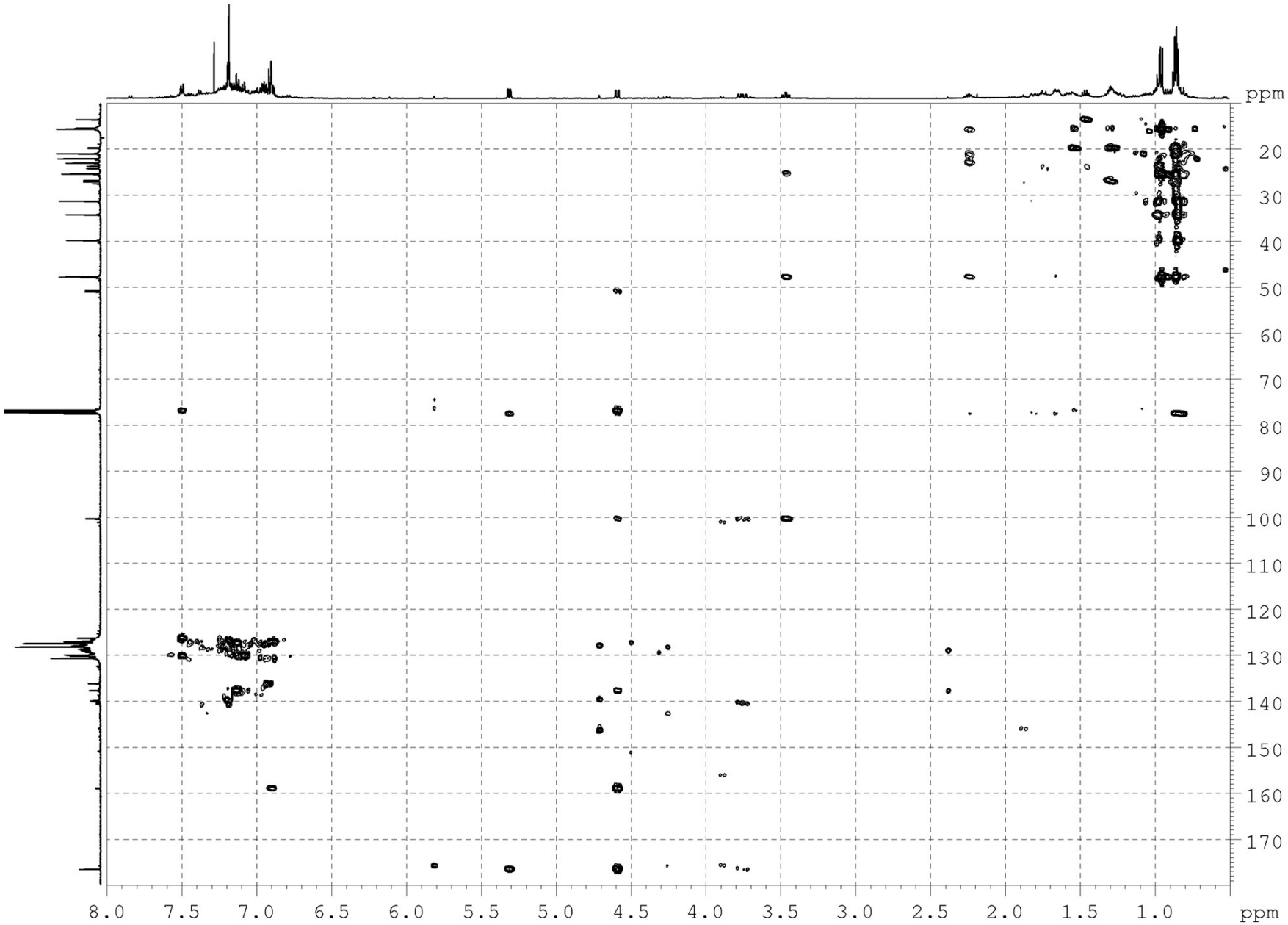

Figure S16. 2D ^{1}H-^{13}C HMBC NMR spectrum of **6a** and **6b** in $CDCl_3$ at T = 303 K.

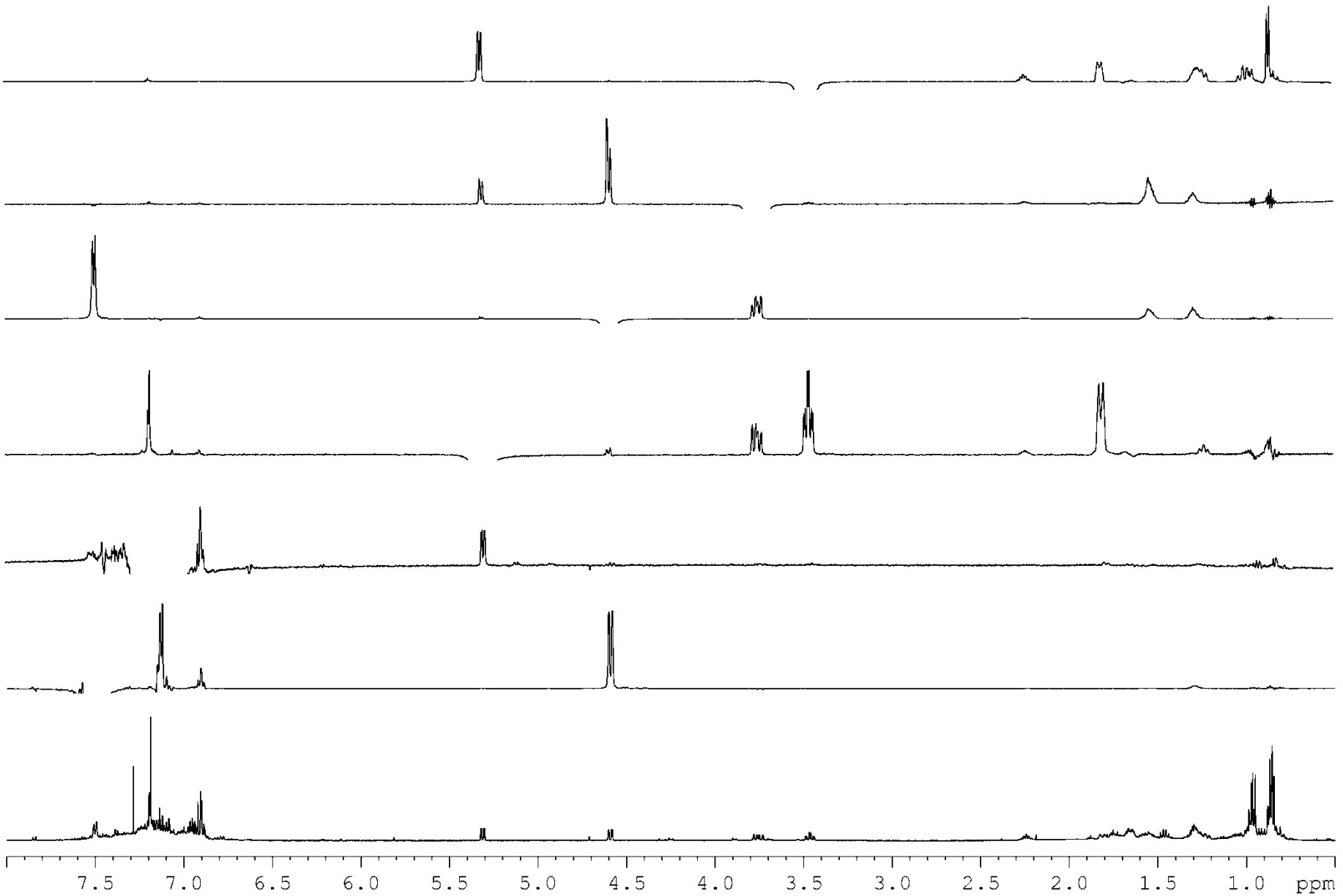

Figure S17.1. 1D ^{1}H and ^{1}H NOESY NMR spectra of **6a** and **6b** in $CDCl_3$ at T = 303 K.

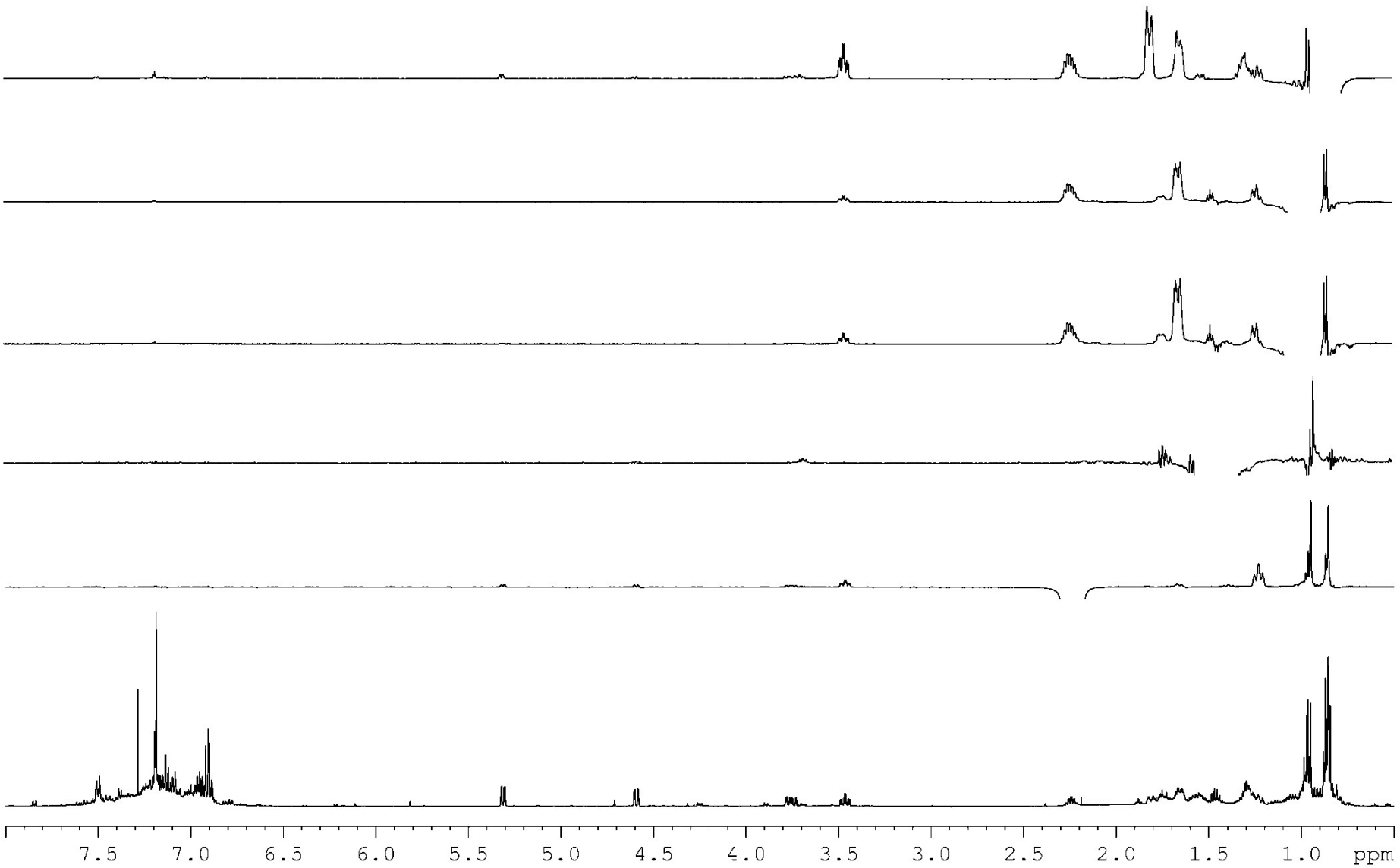

Figure S17.2. 1D ^{1}H and ^{1}H NOESY NMR spectra of **6a** and **6b** in $CDCl_3$ at T = 303 K.

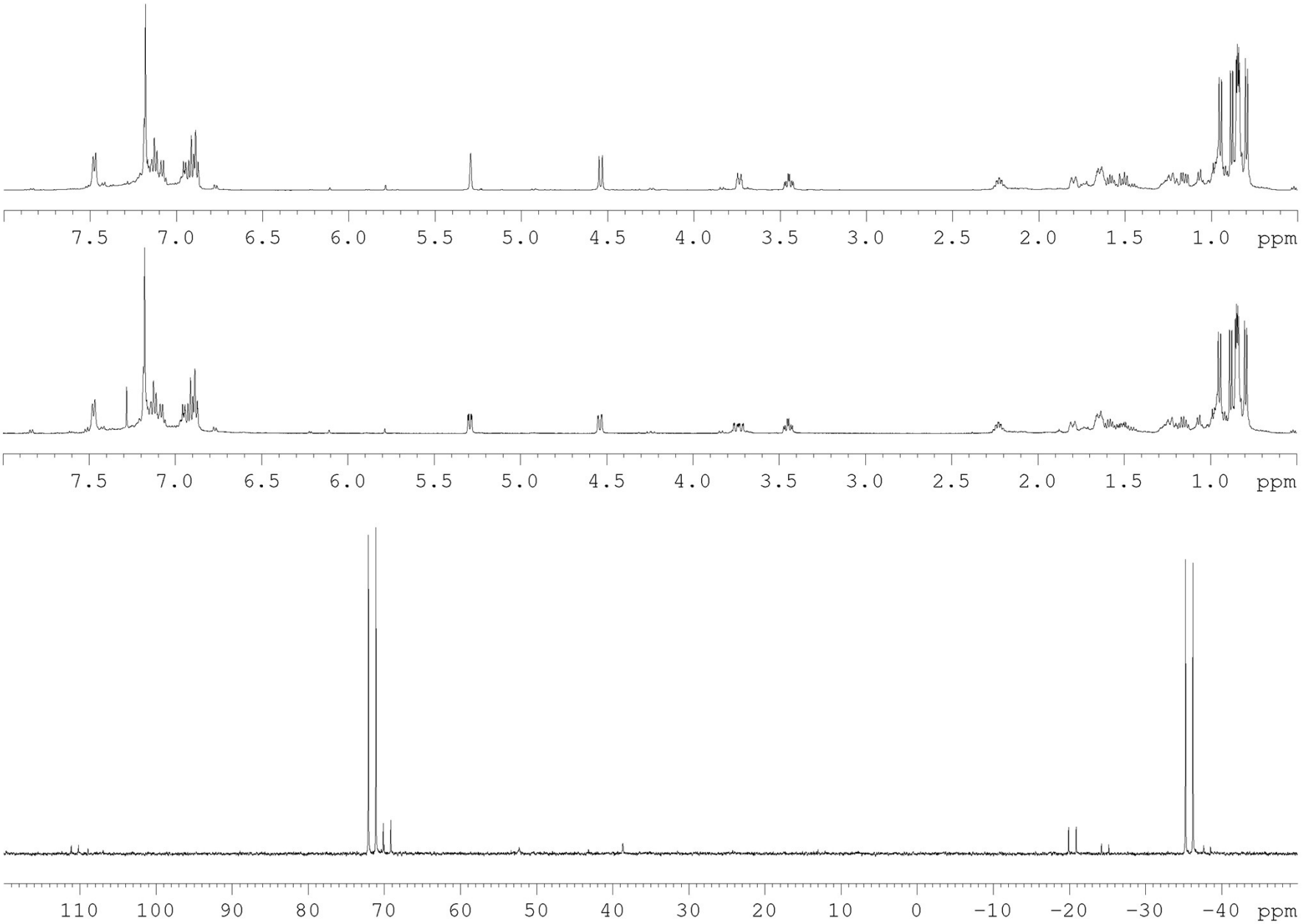

Figure S18. 1D $^{31}P\{^{1}H\}$, ^{1}H and $^{1}H\{^{31}P\}$ NMR spectra of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

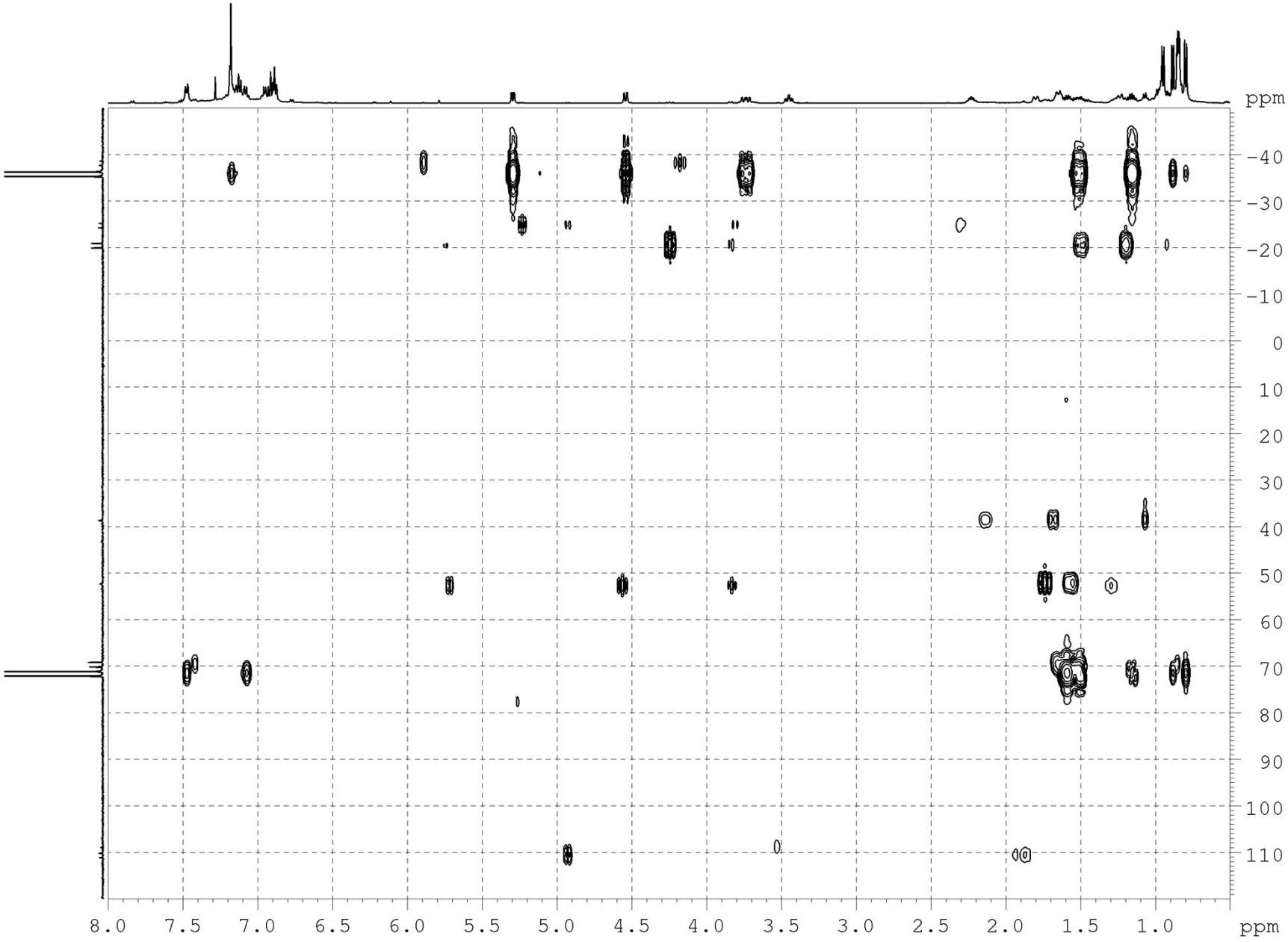

Figure S19. 2D ^{1}H-^{31}P HMBC NMR spectrum of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

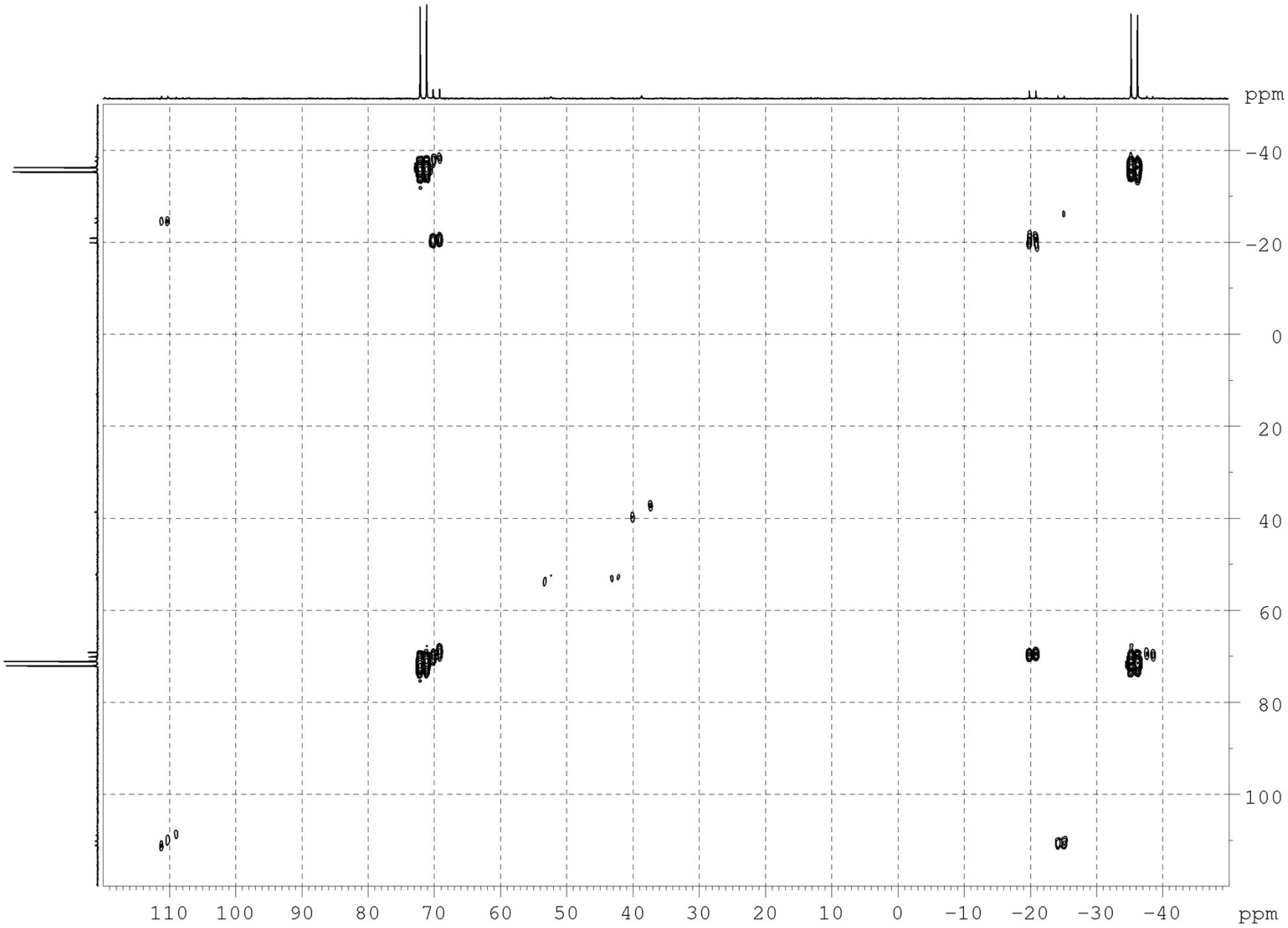

Figure S20. 2D ^{31}P-^{31}P COSY NMR spectrum of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

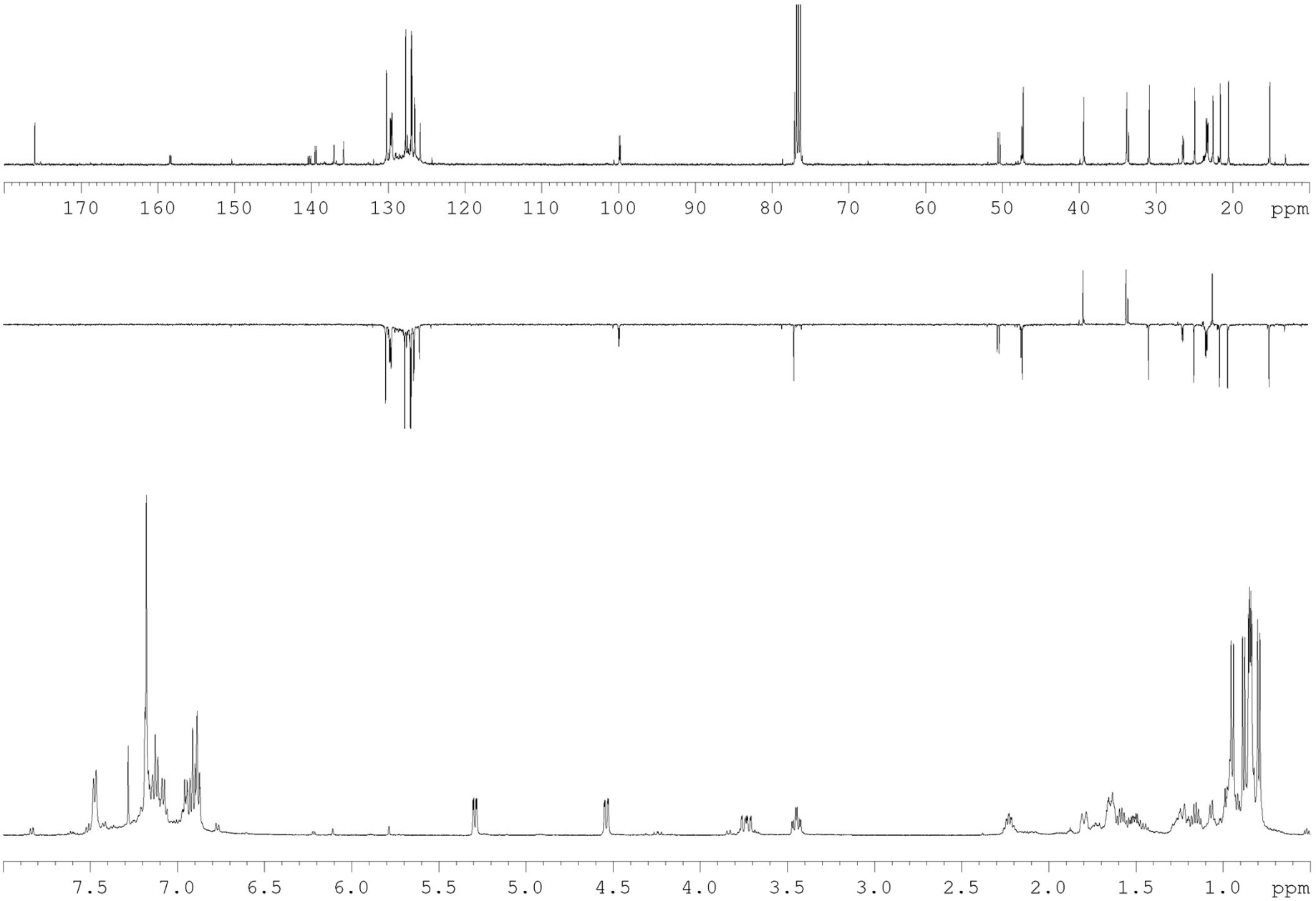

Figure S21. 1D ^{1}H, ^{13}C DEPT and $^{13}C\{^{1}H\}$ NMR spectra of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

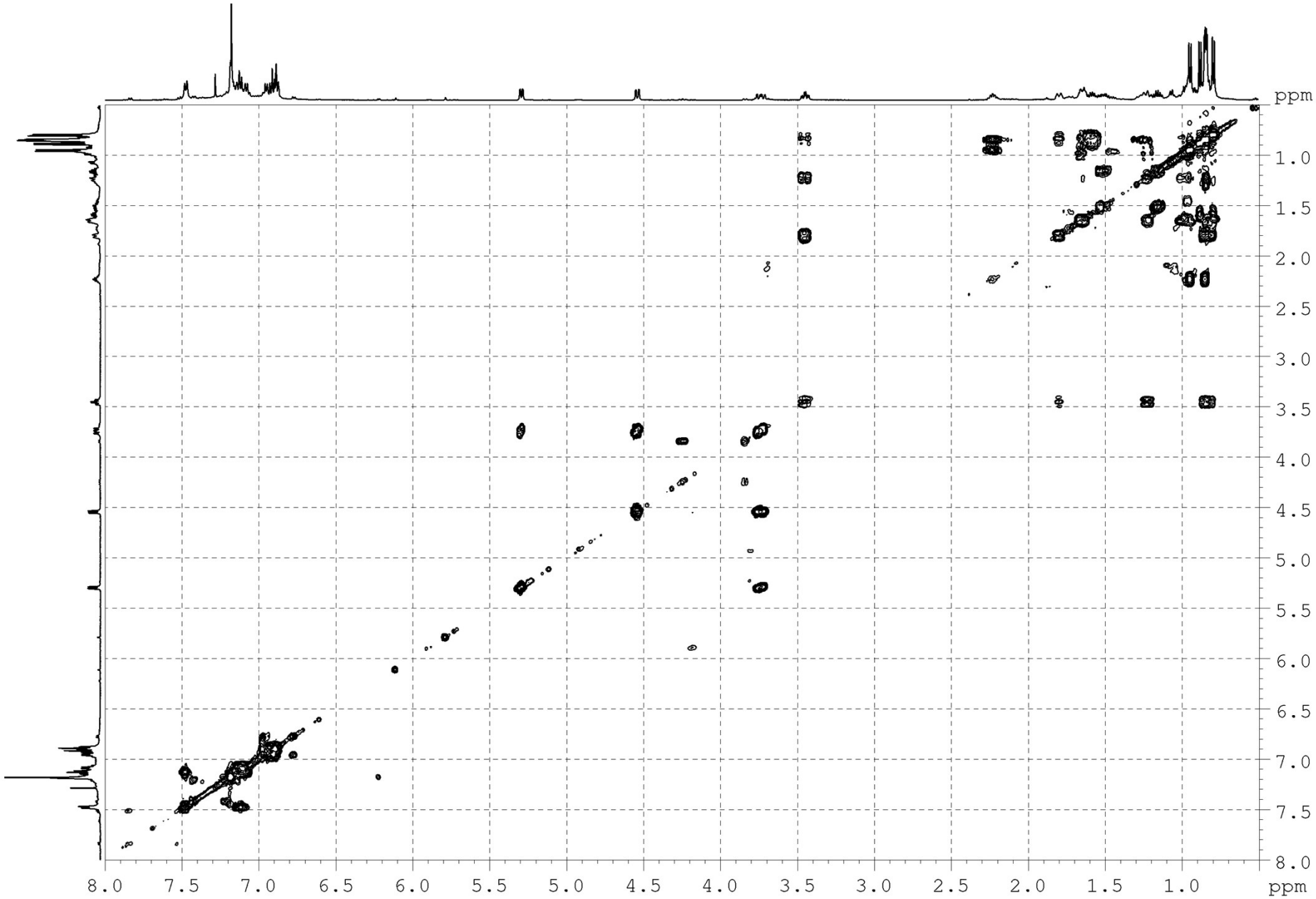

Figure S22. 2D ^{1}H-^{1}H COSY NMR spectrum of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

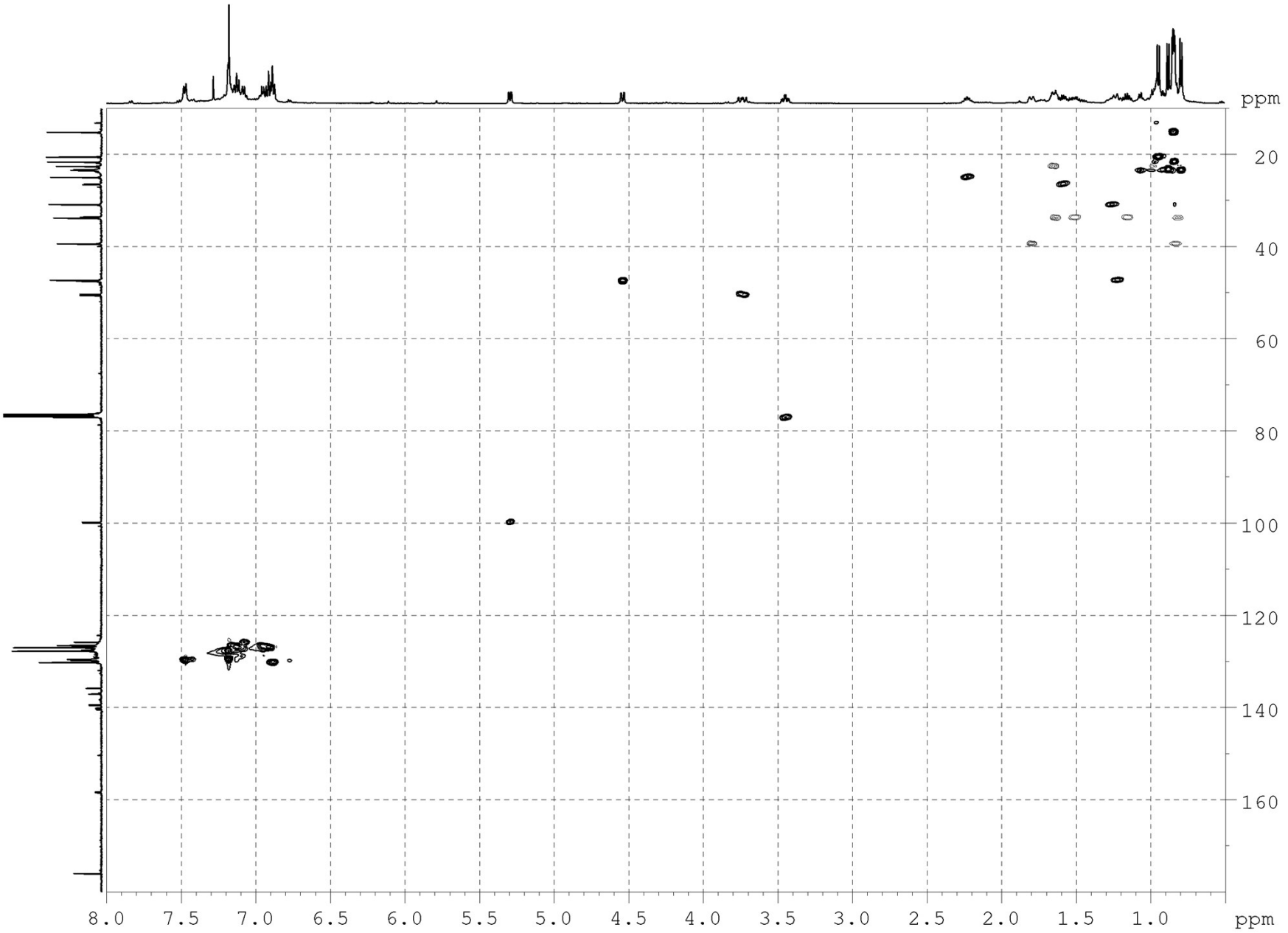

Figure S23. 2D ^{1}H-^{13}C HSQC NMR spectrum of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

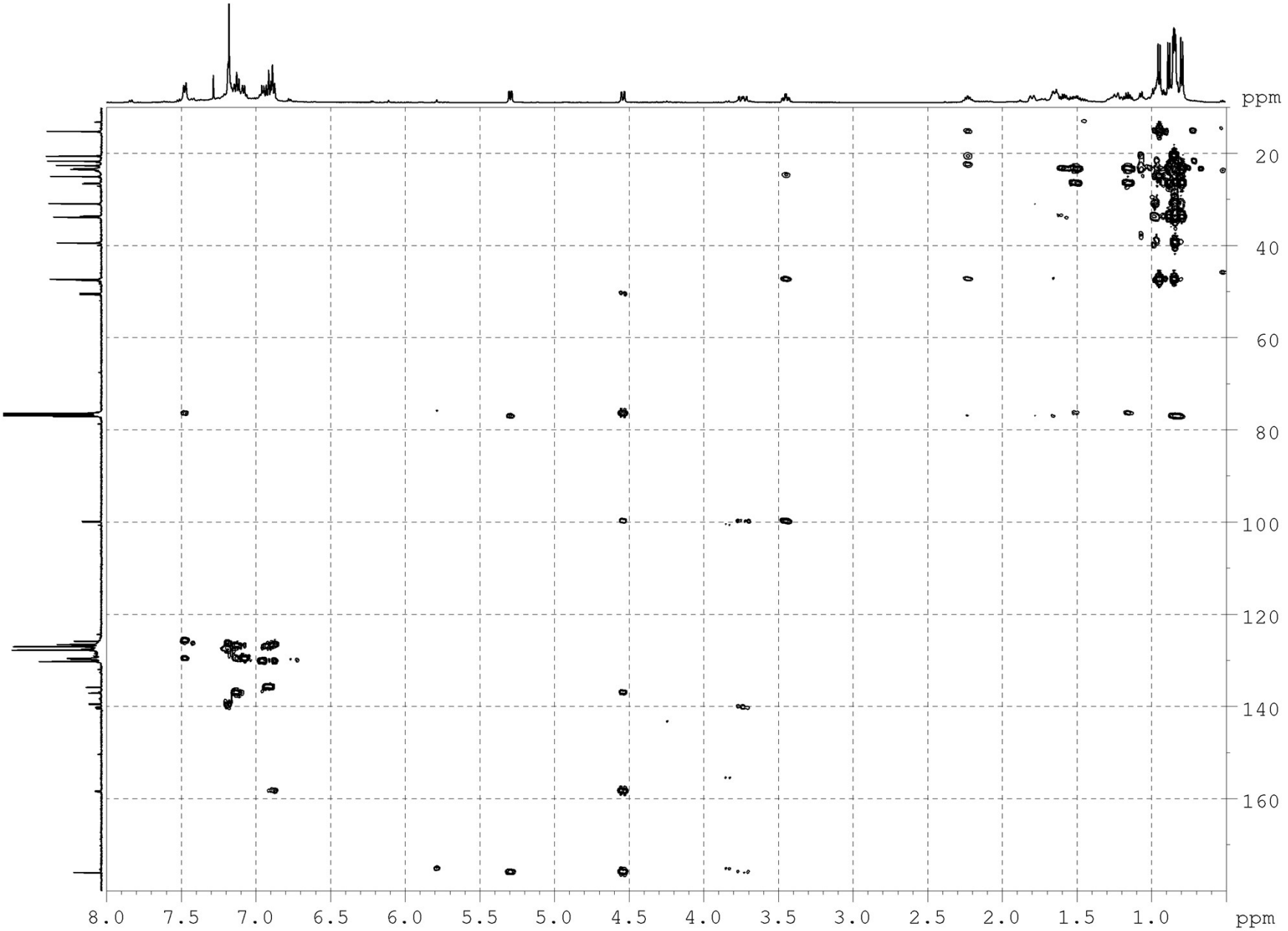

Figure S24. 2D ^{1}H-^{13}C HMBC NMR spectrum of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

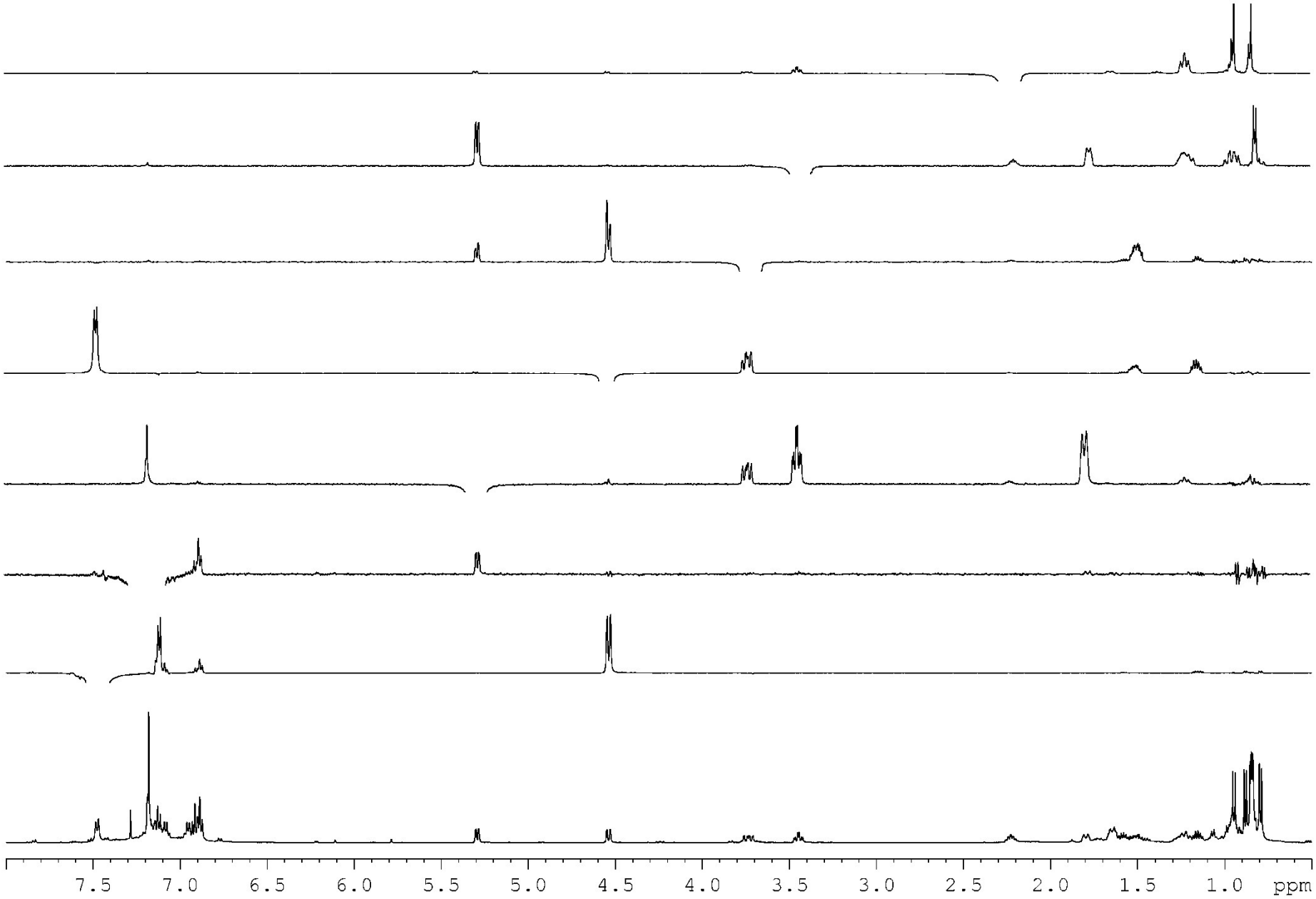

Figure S25.1. 1D ^{1}H and ^{1}H NOESY NMR spectra of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

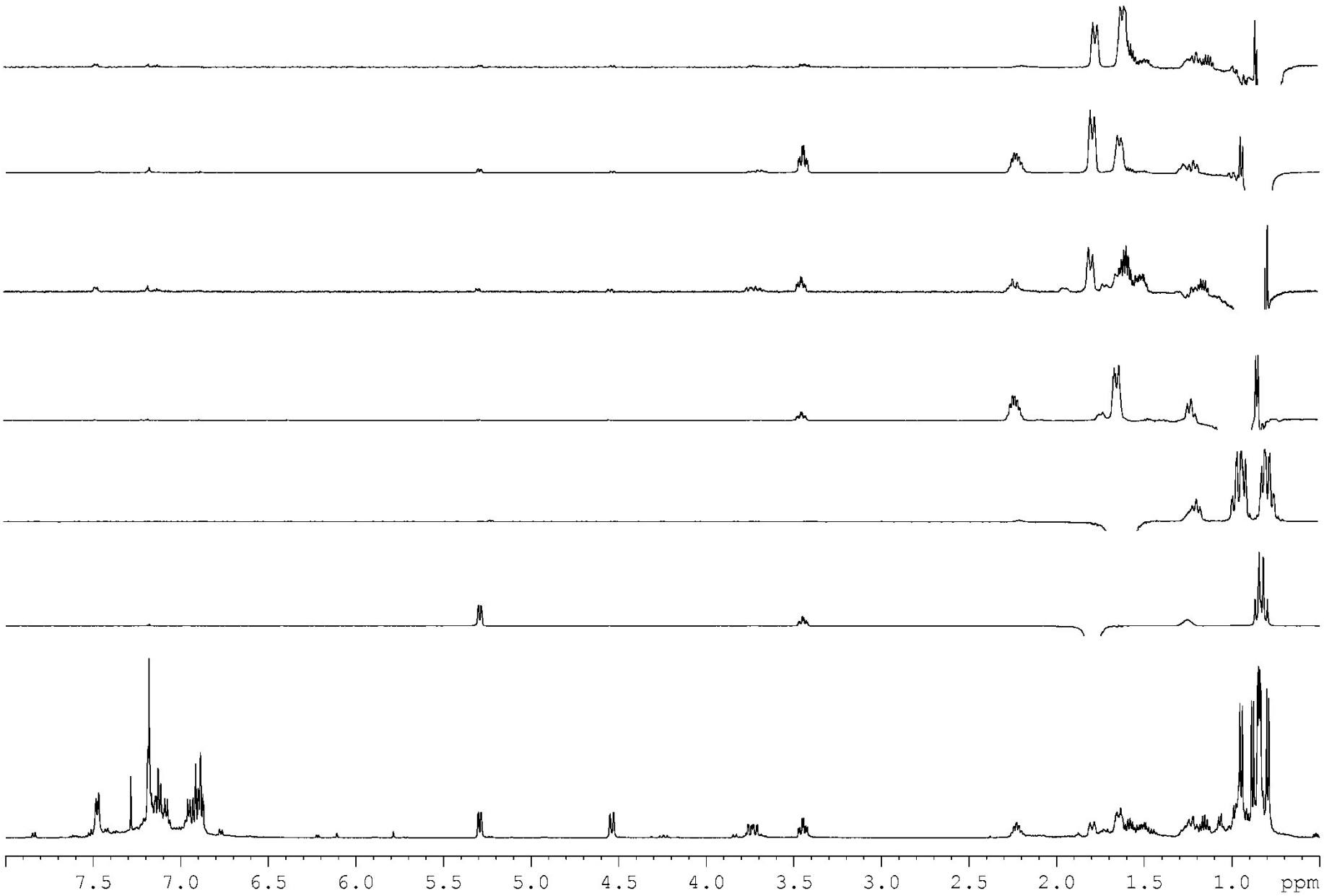

Figure S25.2. 1D ^{1}H and ^{1}H NOESY NMR spectra of **7a, 7b** and **7c** in $CDCl_3$ at T = 303 K.

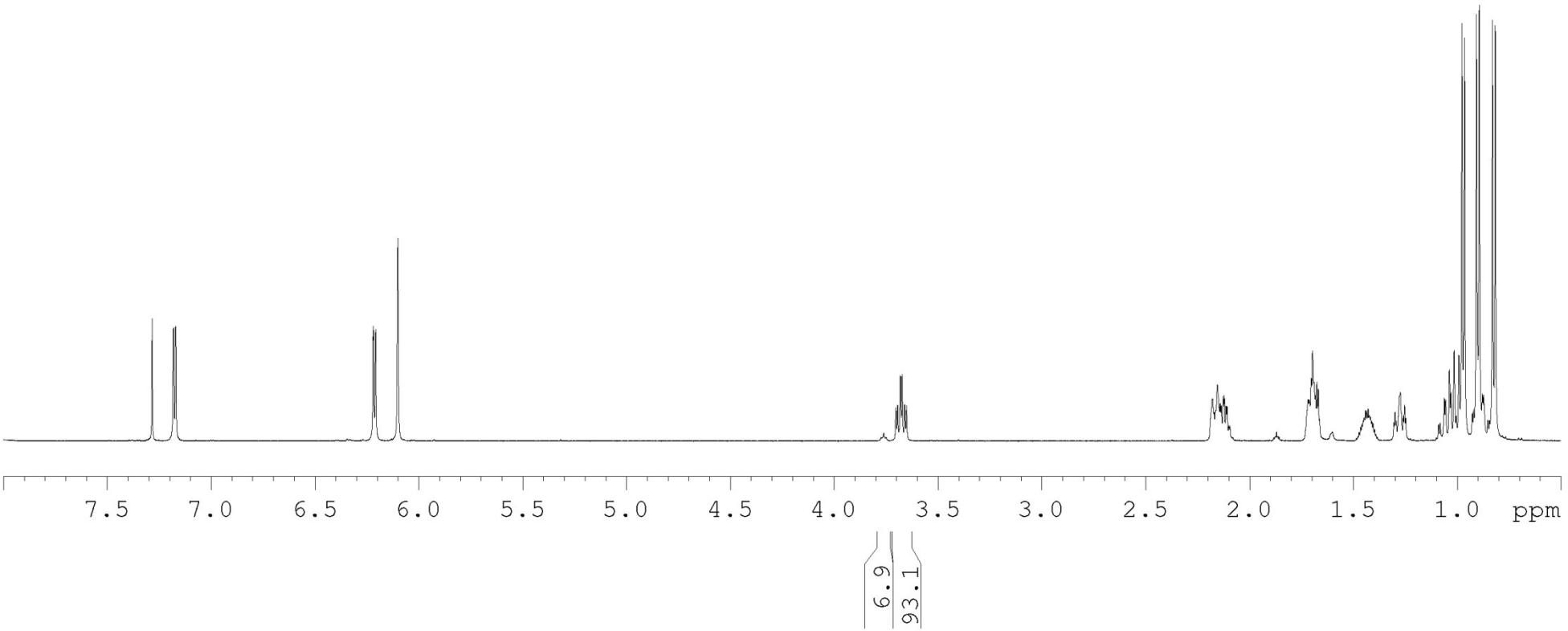

Figure S26. 1D ^{1}H NMR spectra of **4** (MOxF) in $CDCl_3$ at T = 303 K.

Table S1. Results of calculations (PBE1PBE/6-31+G(d)) for **5*** (model of **5a-c**, with *i*-Pr instead of menthyl).

isomer	Energy, Hartree	Energy, kcal/mol
anti_endo_exo	**-2107.068256**	**0**
anti_endo_endo	-2107.0647414	2.2
anti_exo_endo	-2107.0583059	6.2
anti_exo_exo	-2107.0565838	7.3
syn_endo_exo	**-2107.0626099**	**3.5**
syn_endo_endo	-2107.0592958	5.6
syn_exo_endo	-2107.0510919	10.8
syn_exo_exo	-2107.0478526	12.8