Electronic Supplementary Information

Non-conventional coordination of cavity-confined metal centres

Rafael Gramage-Doria,[a] *Dominique Armspach,**[a] *Dominique Matt**[a] *and Loïc Toupet*[b]

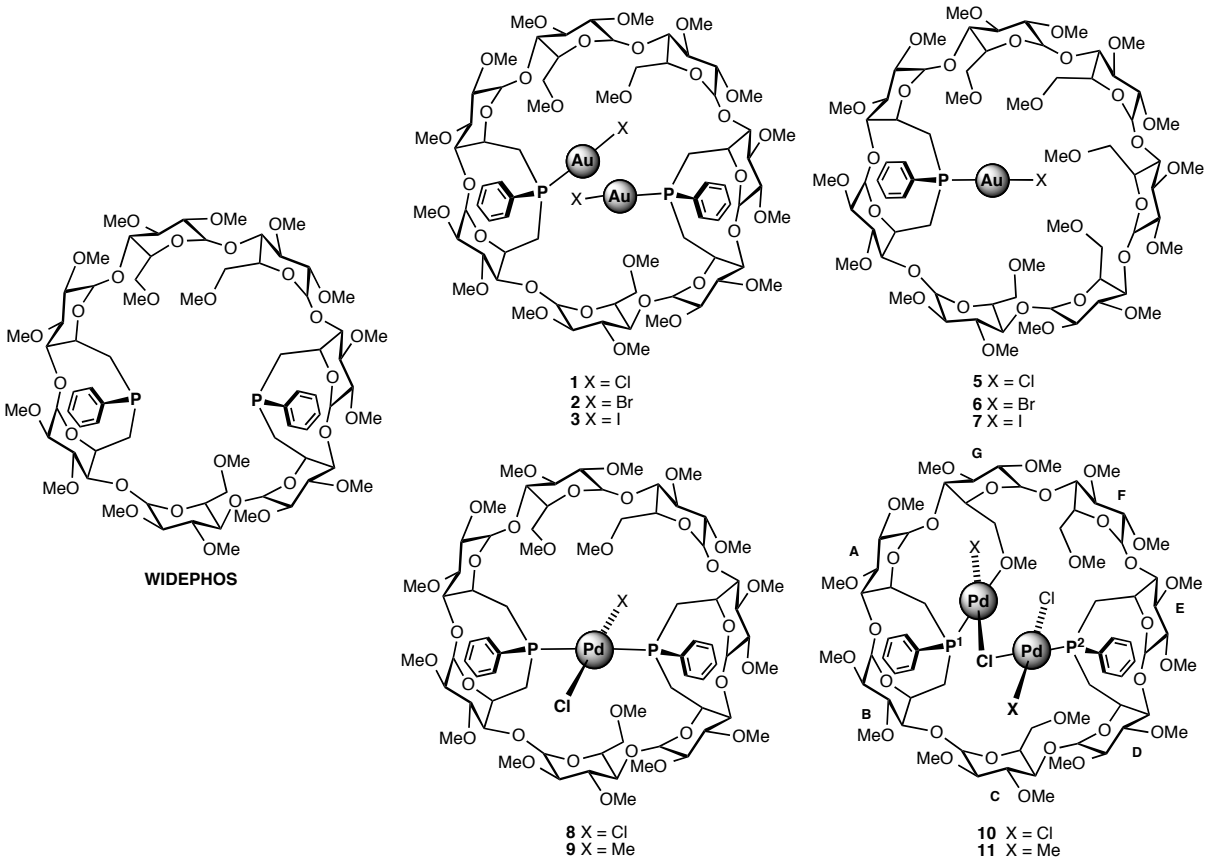
[a]*Laboratoire de Chimie Inorganique et Catalyse, Université de Strasbourg, Institut de Chimie de Strasbourg, UMR 7177 CNRS, 1, rue Blaise-Pascal, 67008 Strasbourg cedex, France. E-mail : d.armspach@unistra.fr or dmatt@unistra.fr*

[b]*Groupe Matière Condensée et Matériaux, UMR 6626, Université de Rennes 1, Campus de Beaulieu, 35042, Rennes cedex, France*

† Electronic supplementary information (ESI) available: Experimental details and CIF file for the reported complex. CCDC reference number 801259.

Content

- **Fig. SI-1**. Part of the ^{1}H NMR spectra of **WIDEPHOS** (top), complex **10** (middle) and complex **11** (bottom) recorded in $CDCl_3$ showing the methoxy signals.
- **Fig. SI-2**. Part of ^{1}H-^{1}H ROESY NMR spectrum of bridged dinuclear palladium(II) complex **11** recorded in $CDCl_3$ at 400.1 MHz.
- **NMR spectra of complexes 1-3, 5-11**
- **General procedure for full assignment of the ^{1}H NMR signals of the glucose units.**



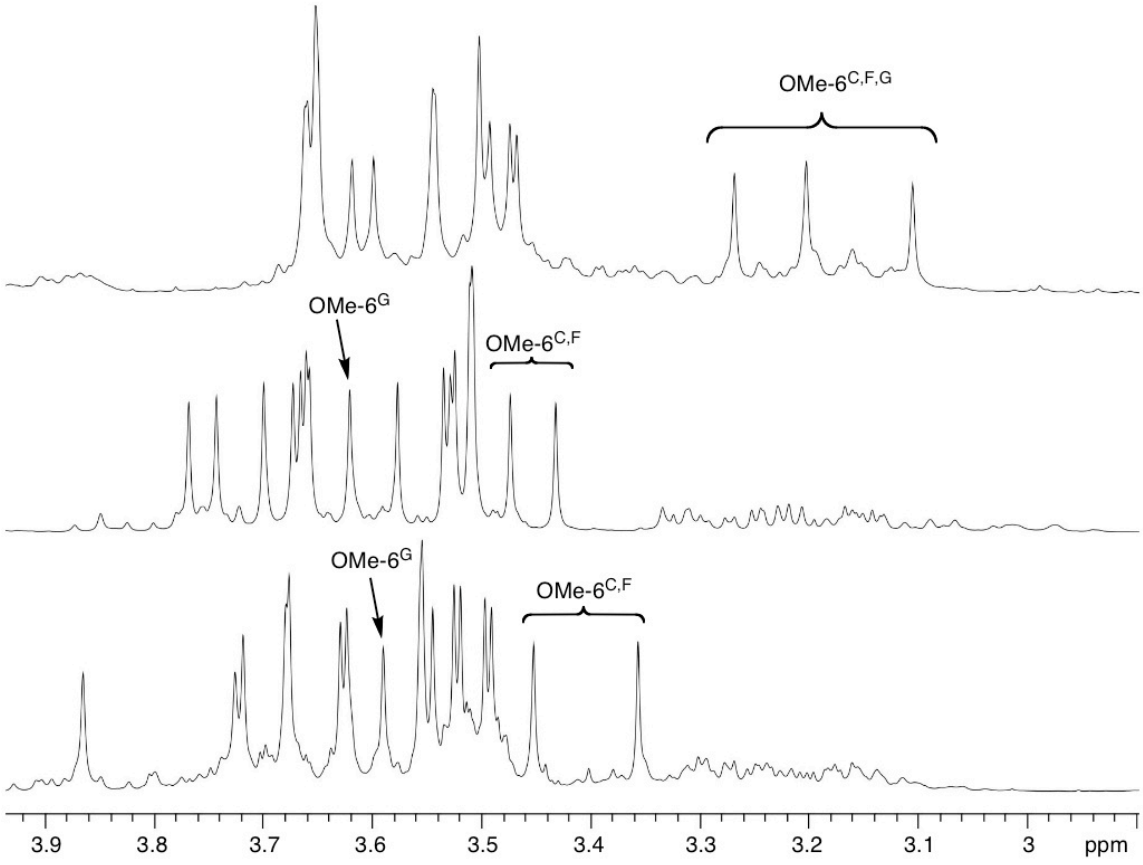


Fig. SI-1. Part of the ^{1}H NMR spectra of **WIDEPHOS** (top), complex **10** (middle) and complex **11** (bottom) recorded in $CDCl_3$ (298 K) showing the methoxy signals.

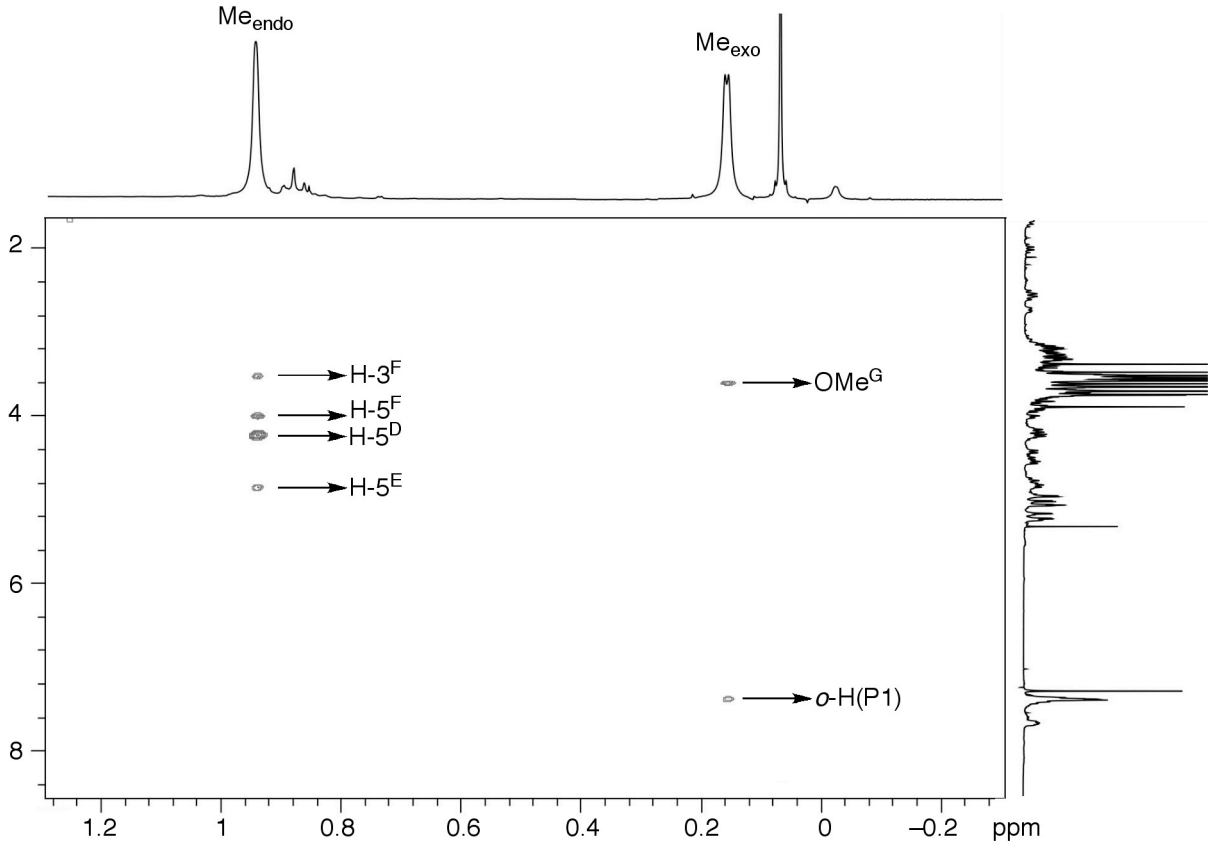
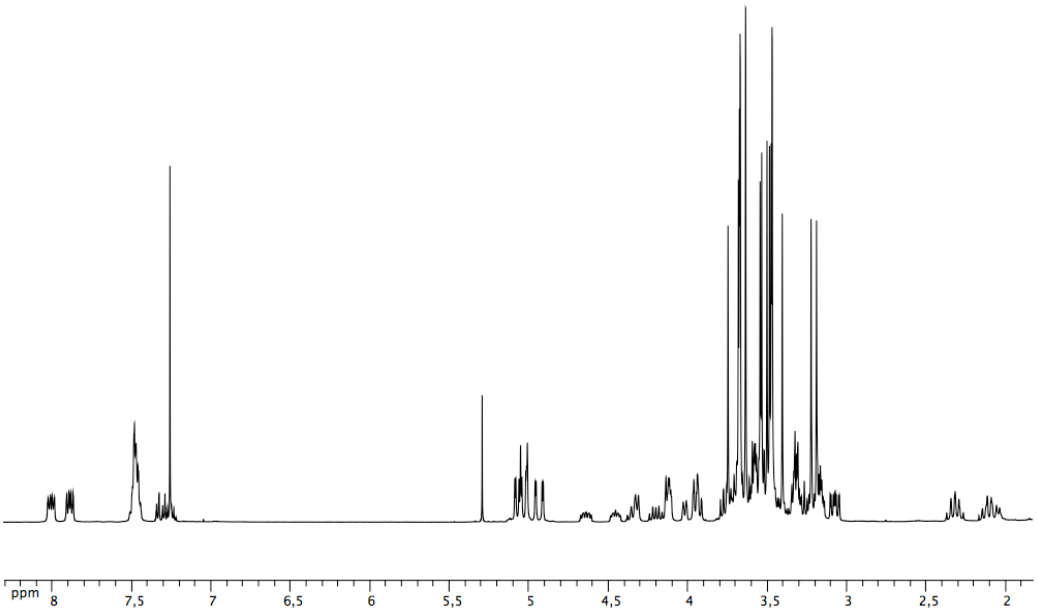
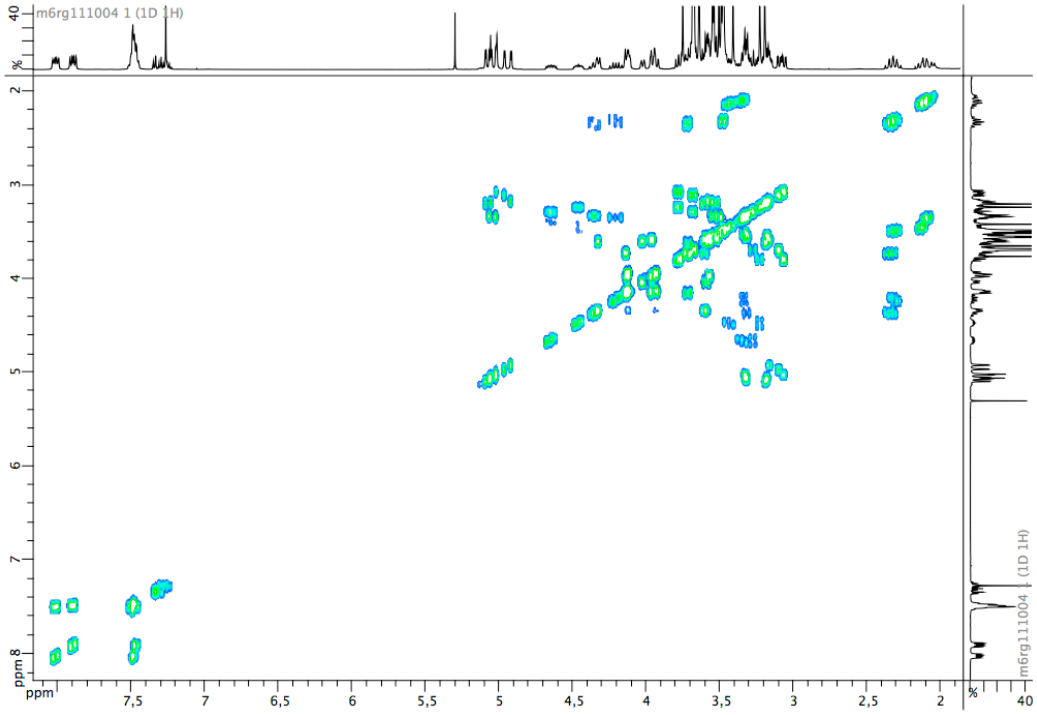


Fig. SI-2. Part of ^{1}H-^{1}H ROESY NMR spectrum of bridged dinuclear palladium(II) complex **11** recorded in $CDCl_3$ at 400.1 MHz.

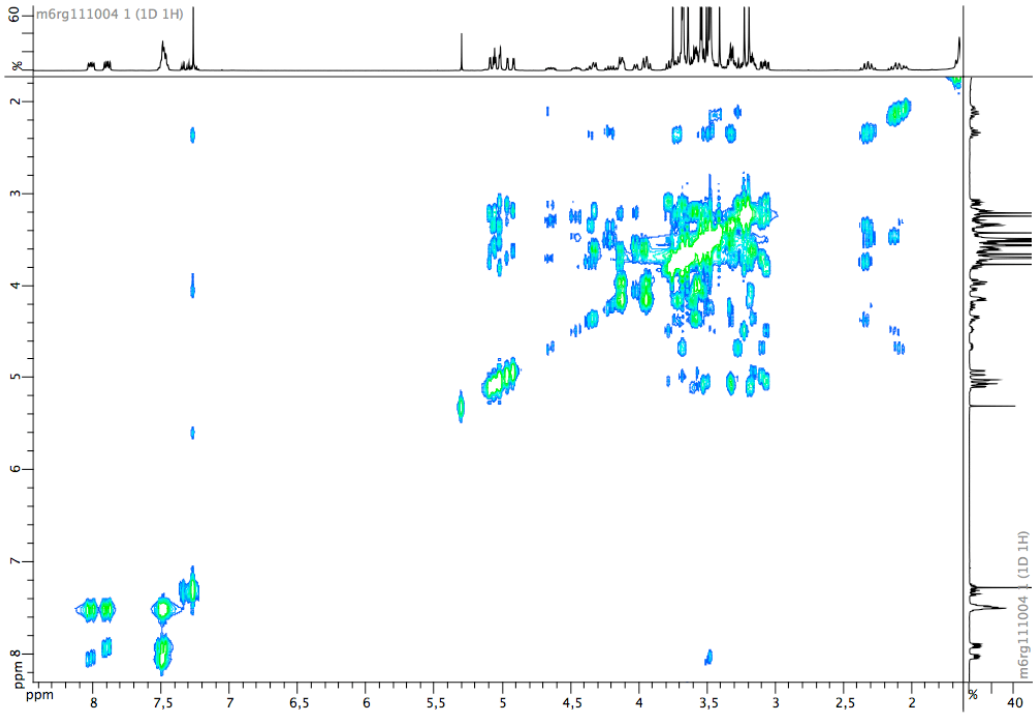
NMR spectra of complexes 1-3, 5-11



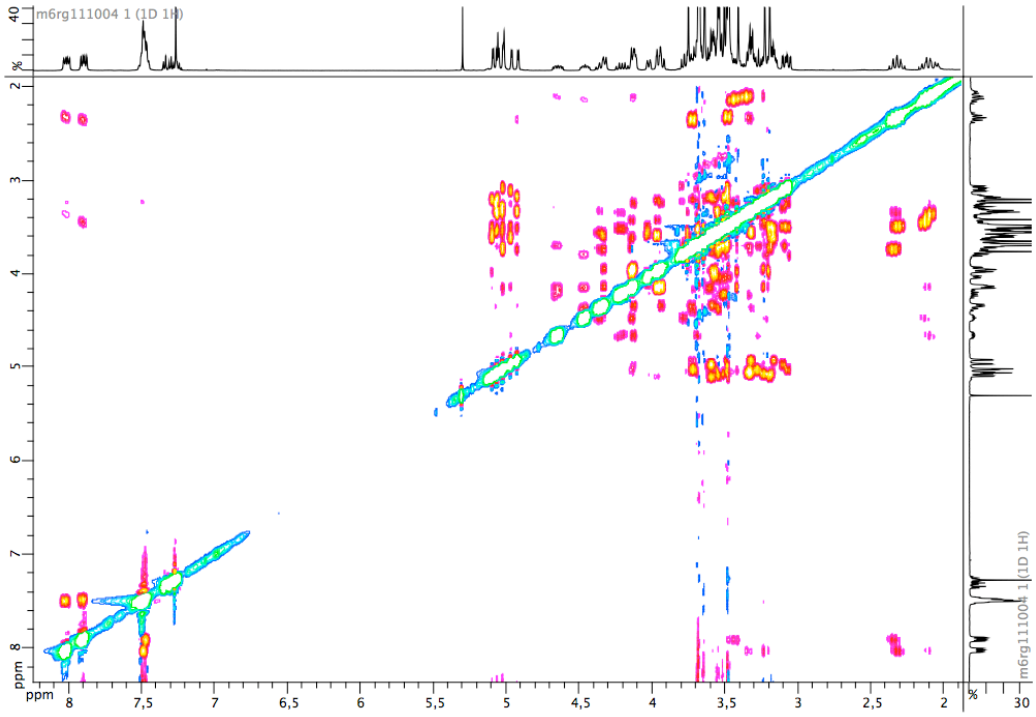
^{1}H NMR spectrum of **1** recorded in $CDCl_3$ at 500.1 MHz.



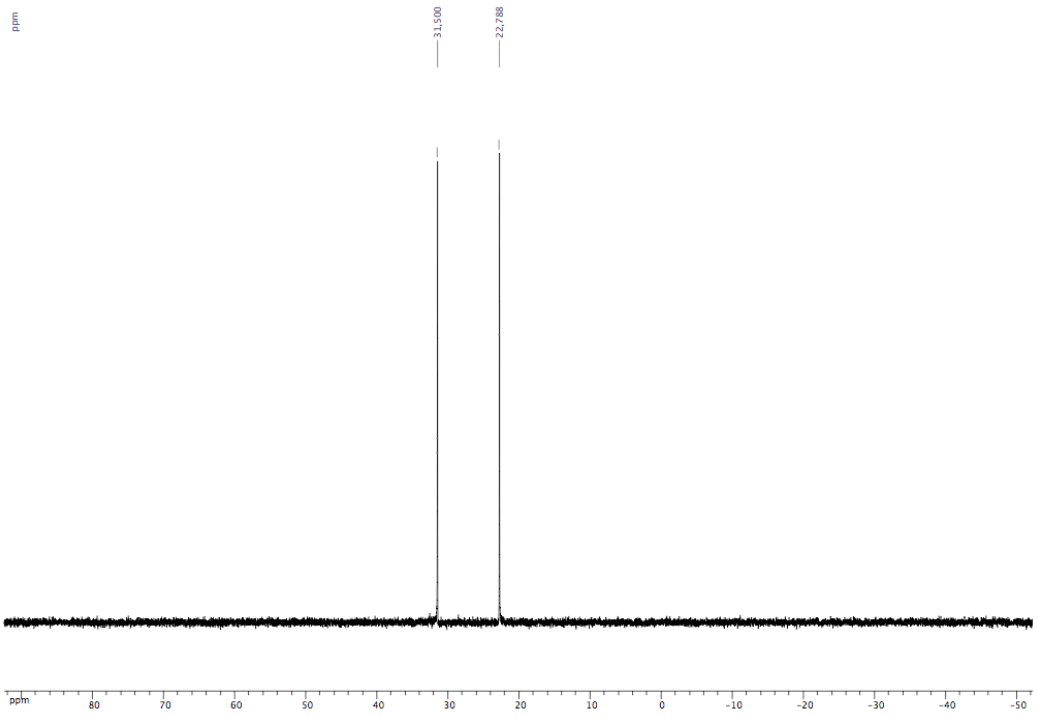
^{1}H-^{1}H COSY NMR spectrum of **1** recorded in $CDCl_3$ at 500.1 MHz.



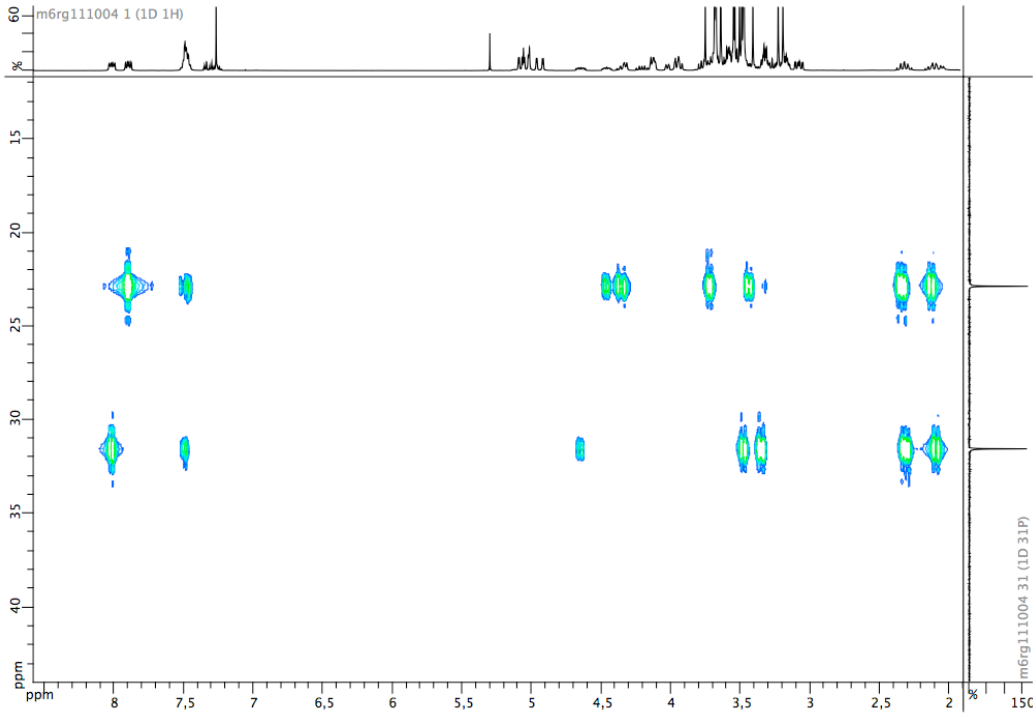
^{1}H-^{1}H TOCSY NMR spectrum of **1** recorded in $CDCl_3$ at 500.1 MHz.



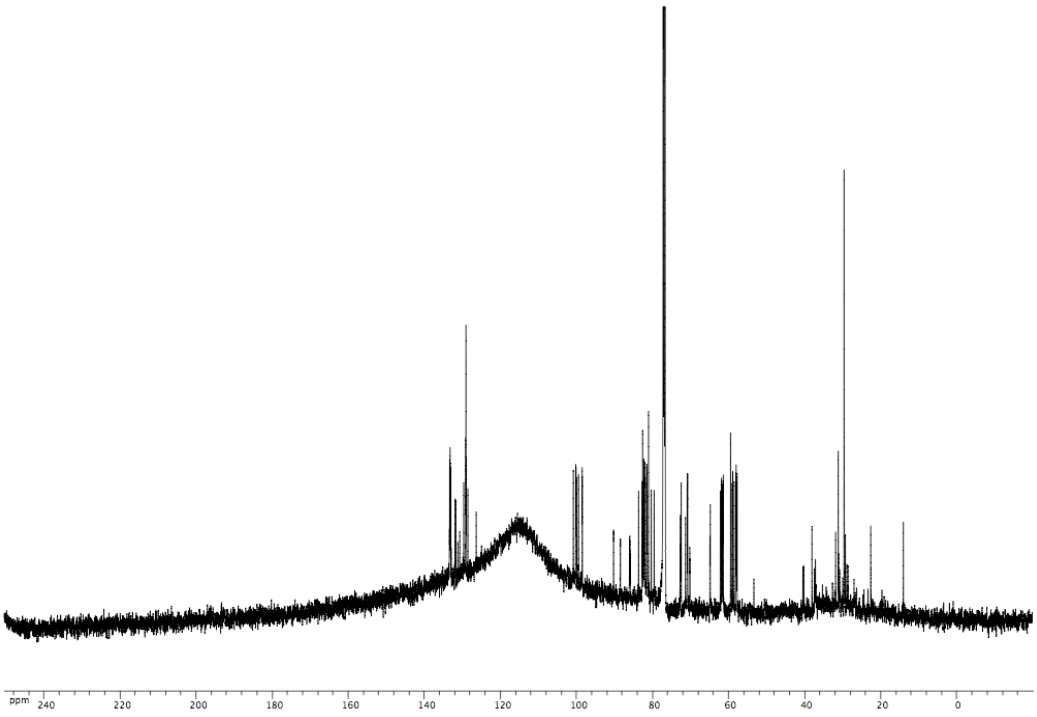
^{1}H-^{1}H ROESY NMR spectrum of **1** recorded in $CDCl_3$ at 500.1 MHz.



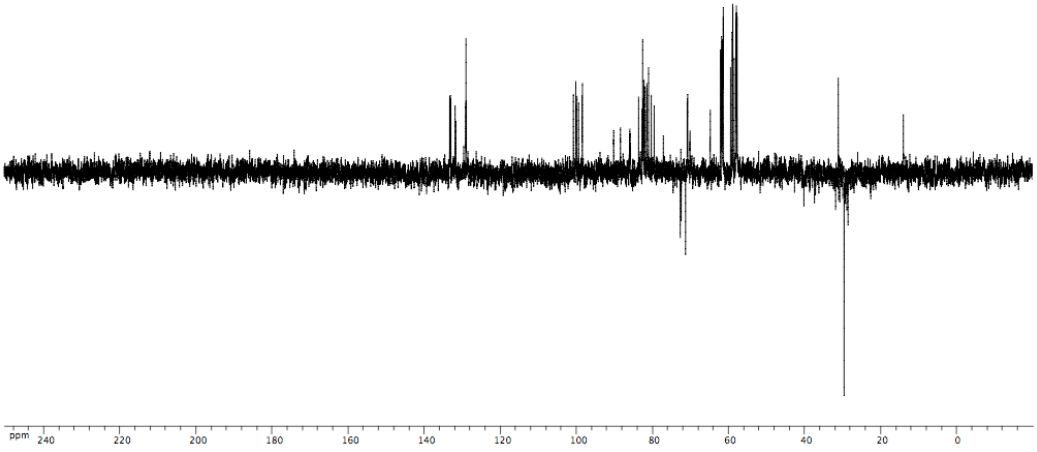
$^{31}P\{^{1}H\}$ NMR spectrum of **1** recorded in $CDCl_3$ at 121.5 MHz.



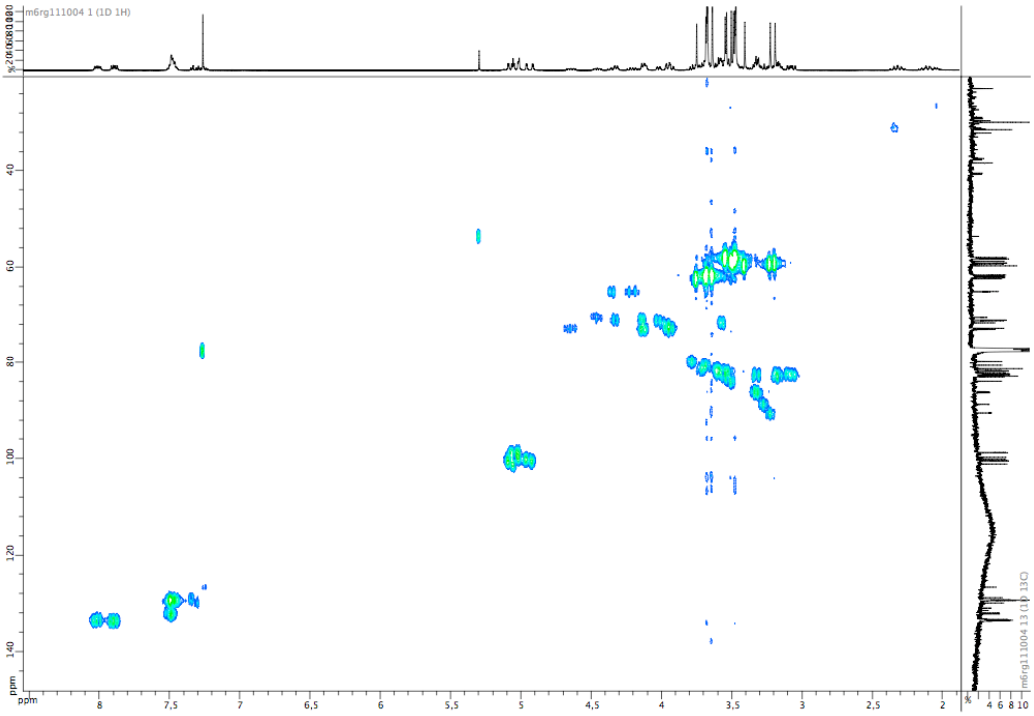
^{1}H-$^{31}P\{^{1}H\}$ NMR spectrum of **1** recorded in $CDCl_3$ at 500.1 MHz.



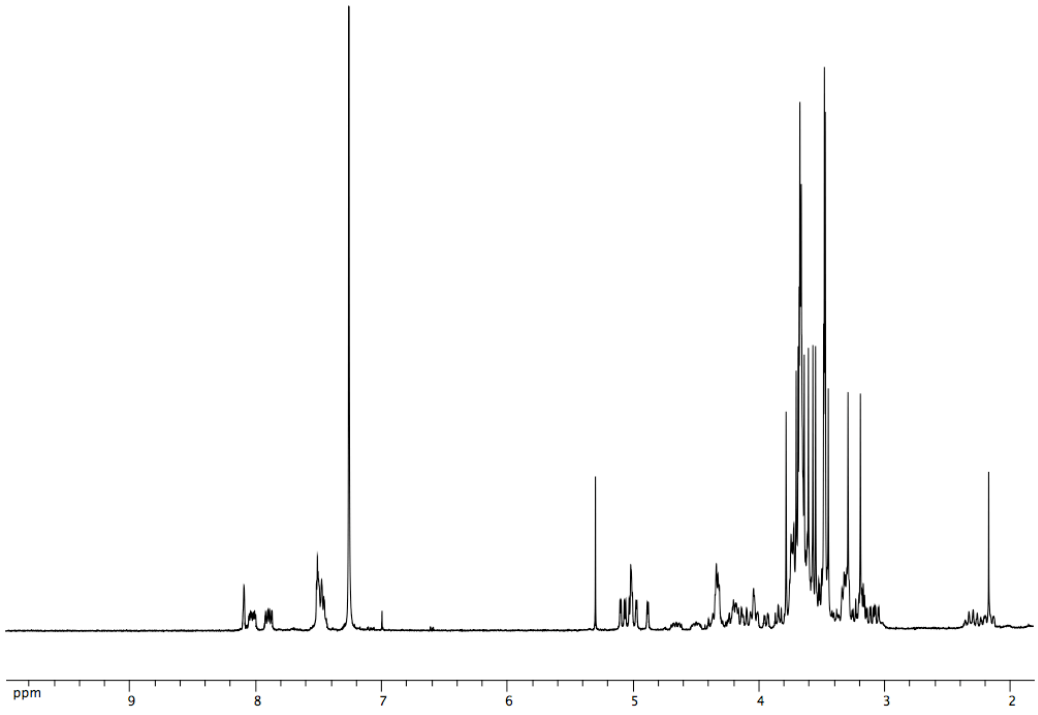
$^{13}C\{^{1}H\}$ NMR spectrum of **1** recorded in $CDCl_3$ at 125.8 MHz.



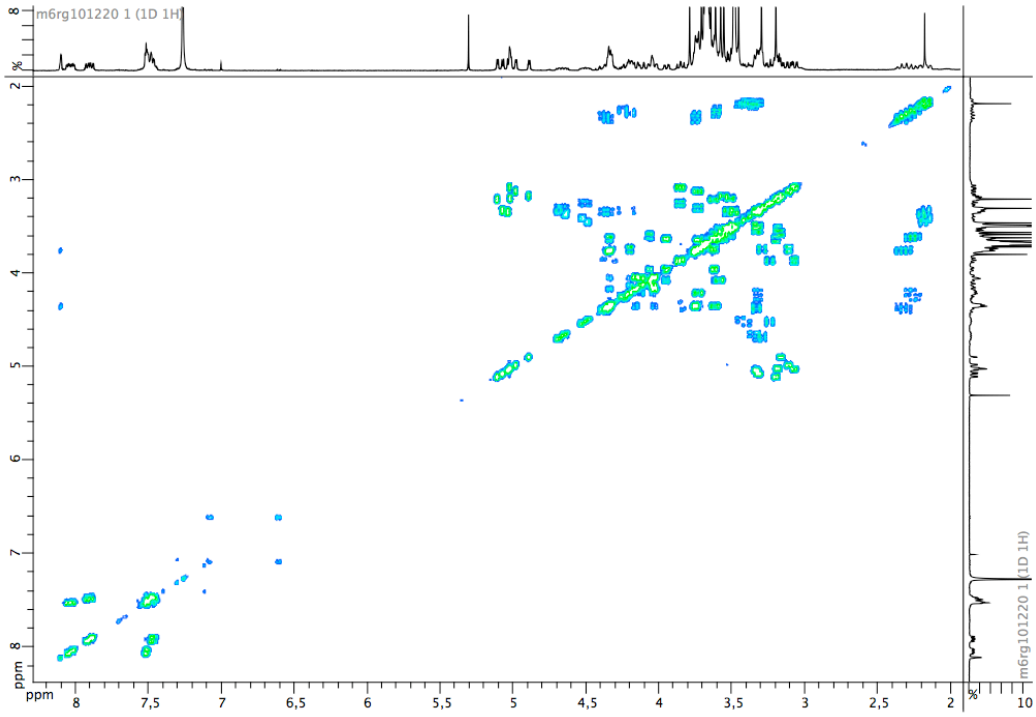
DEPT135 spectrum of **1** recorded in $CDCl_3$ at 125.8 MHz.



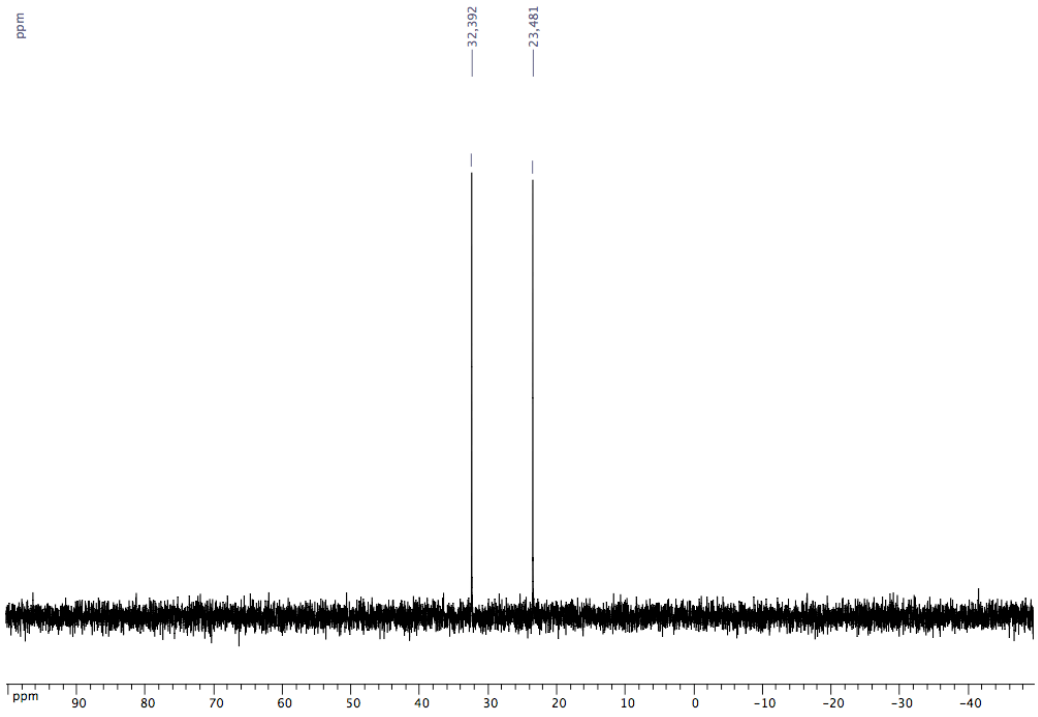
^{1}H-$^{13}C\{^{1}H\}$ HMQC spectrum of **1** recorded in $CDCl_3$ at 500.1 MHz.



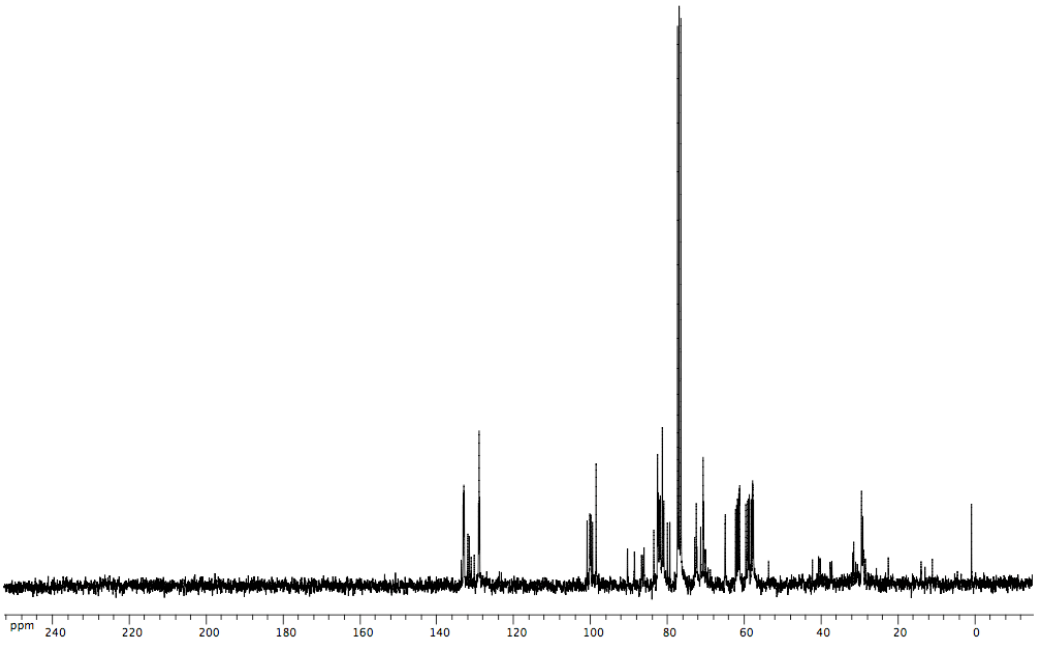
^{1}H NMR spectrum of **2** recorded in $CDCl_3$ at 400.1 MHz.



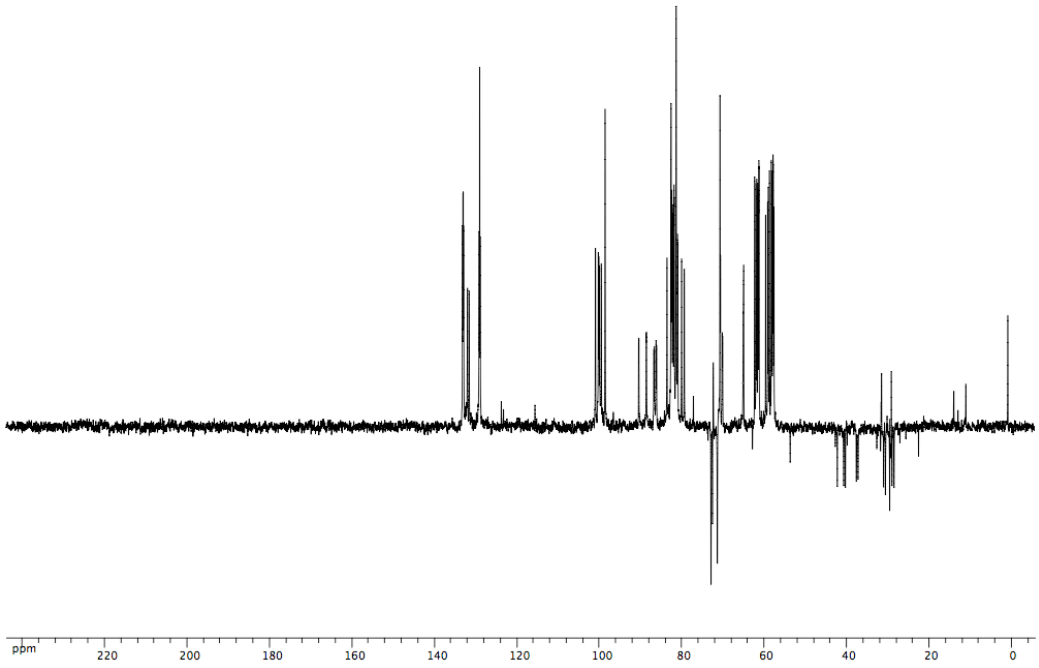
^{1}H-^{1}H COSY NMR spectrum of **2** recorded in $CDCl_3$ at 400.1 MHz.



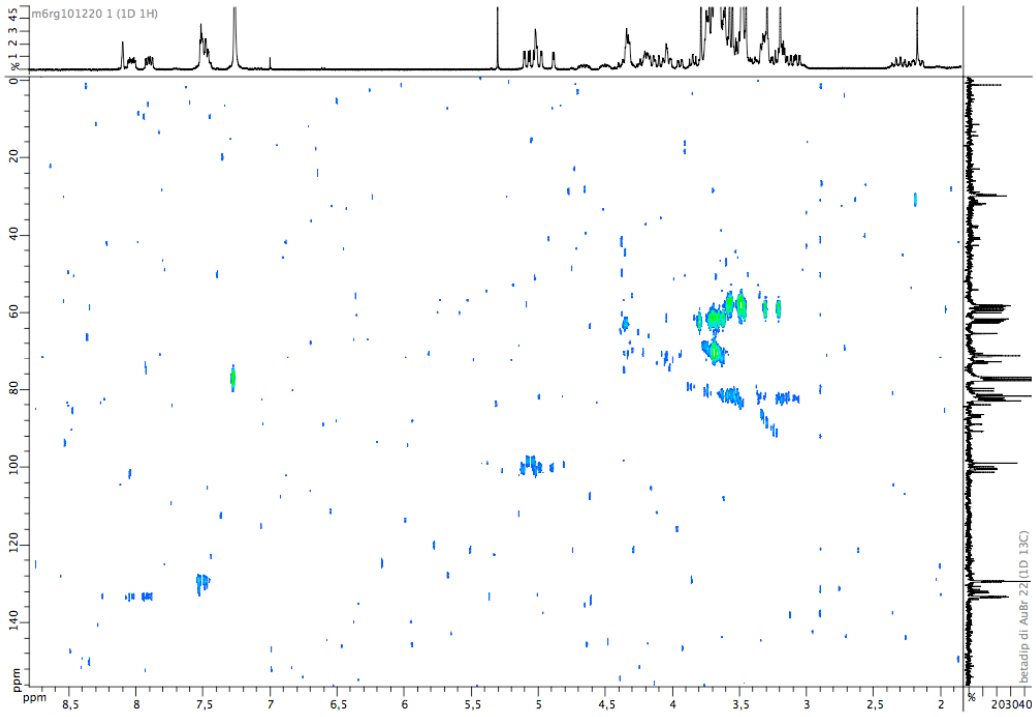
$^{31}P\{^{1}H\}$ NMR spectrum of **2** recorded in $CDCl_3$ at 121.5 MHz.



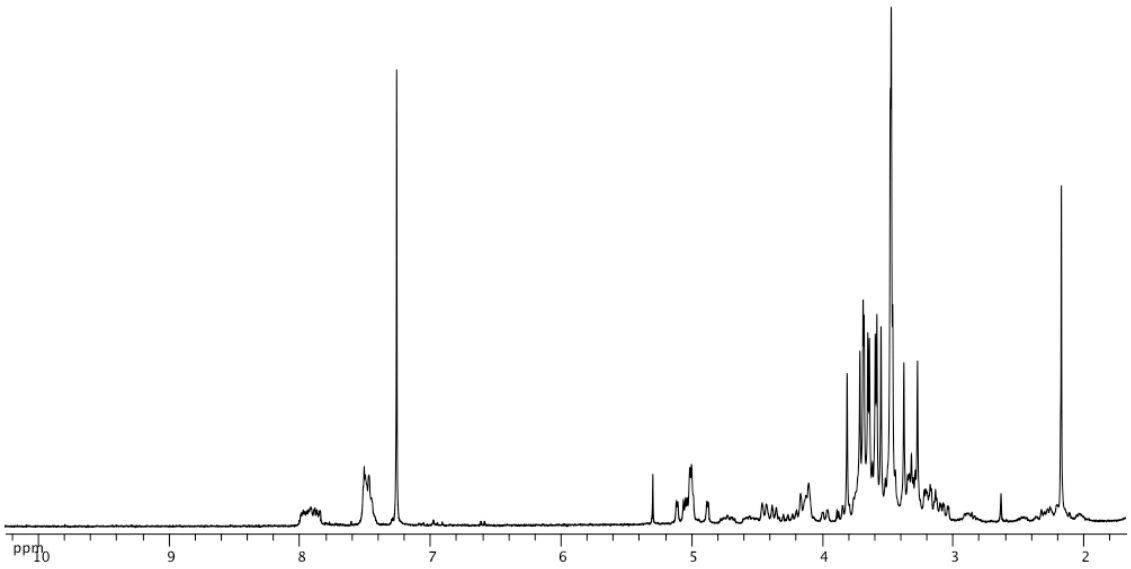
$^{13}C\{^{1}H\}$ NMR spectrum of **2** recorded in $CDCl_3$ at 75.5 MHz.



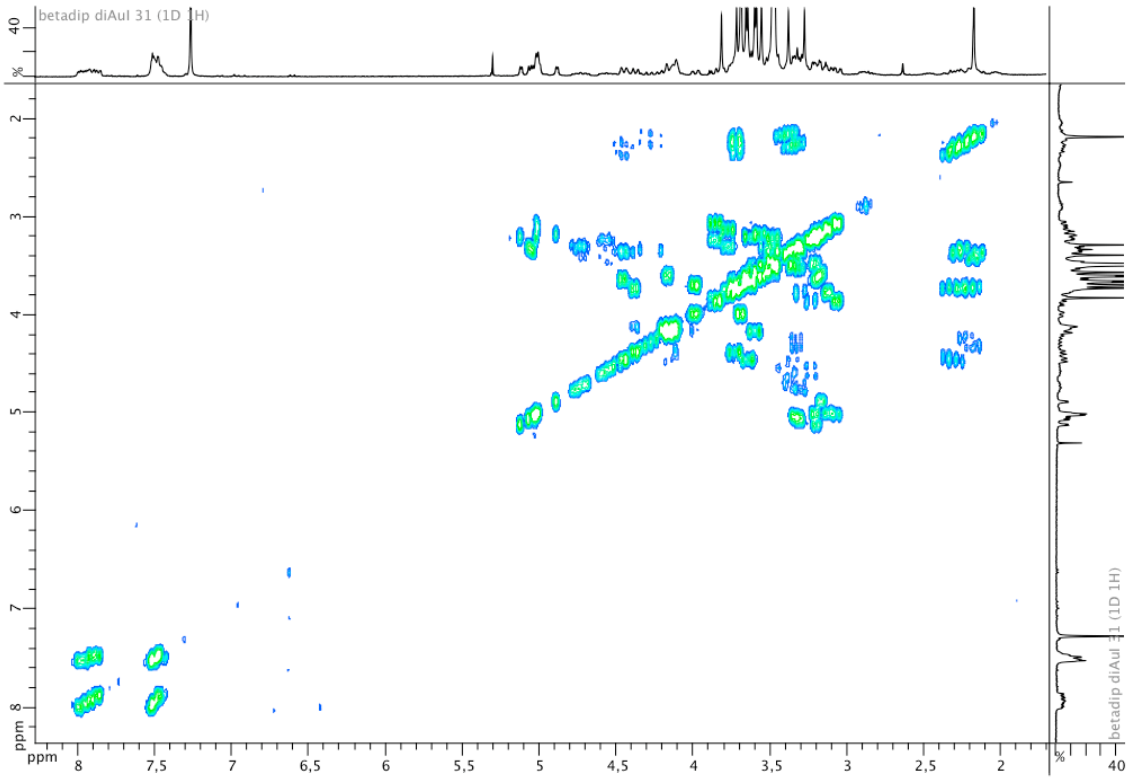
DEPT135 spectrum of **2** recorded in $CDCl_3$ at 75.5 MHz.



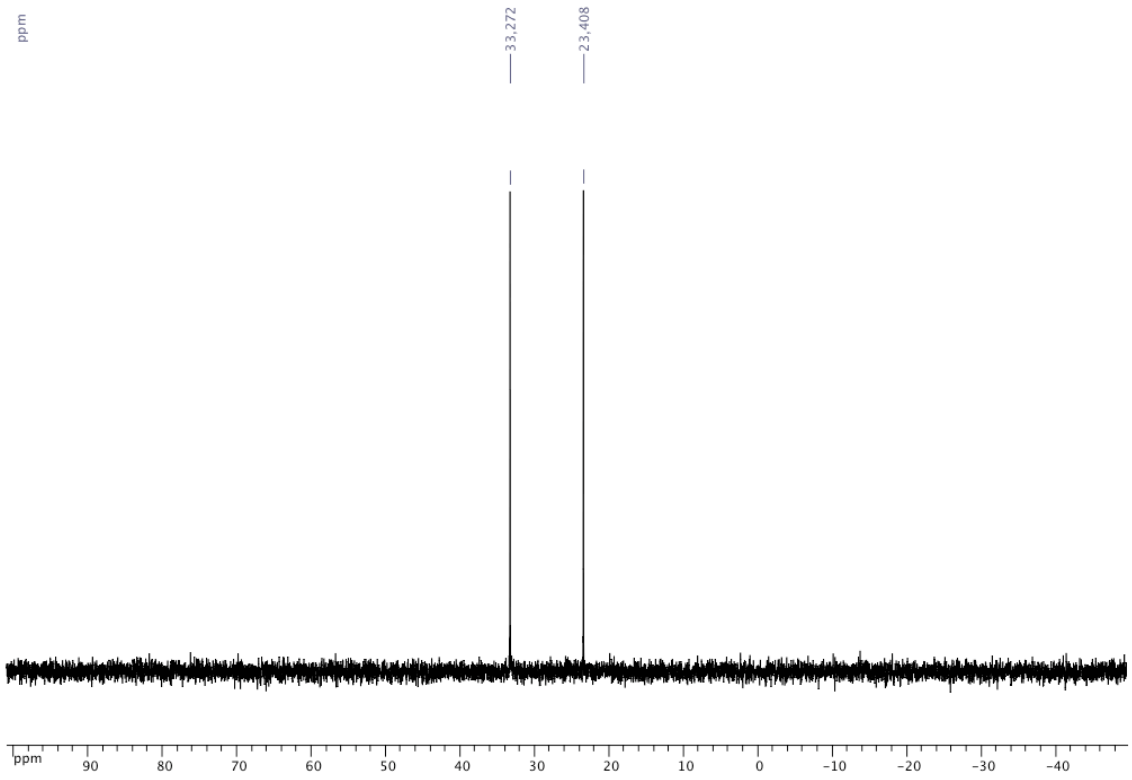
^{1}H-^{13}C{^{1}H} HMQC spectrum of **2** recorded in $CDCl_3$ at 400.1 MHz.



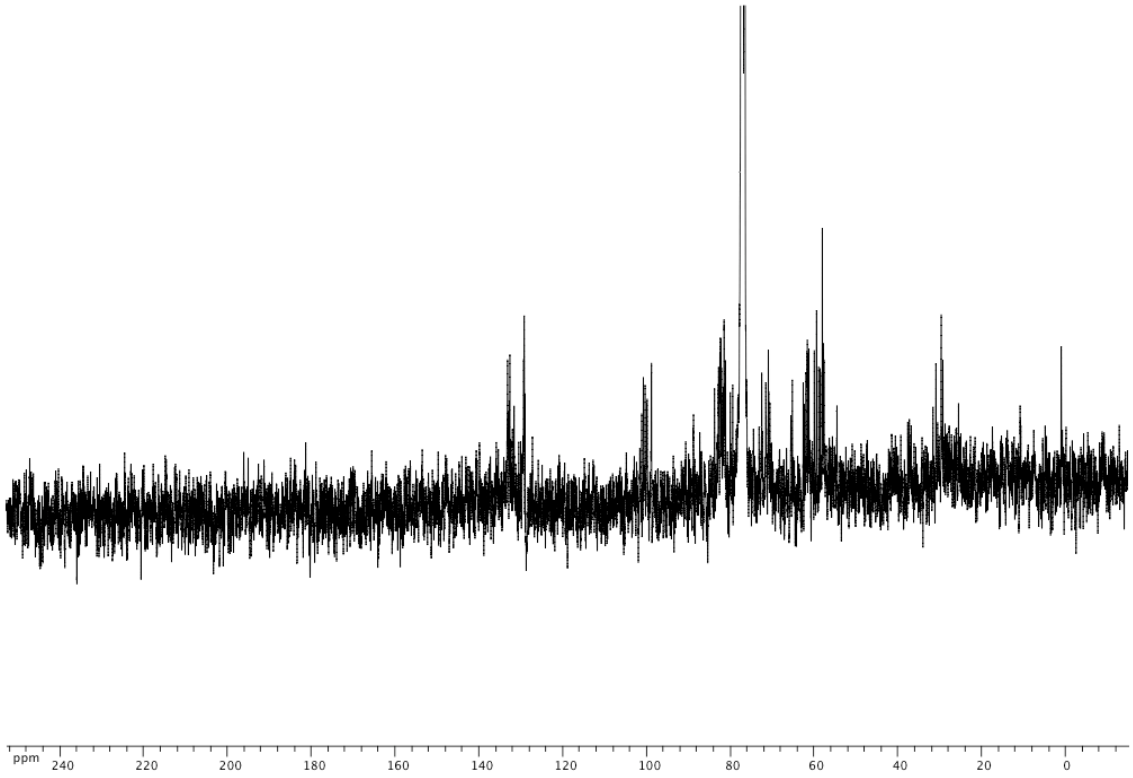
^{1}H NMR spectrum of **3** recorded in $CDCl_3$ at 300.1 MHz.



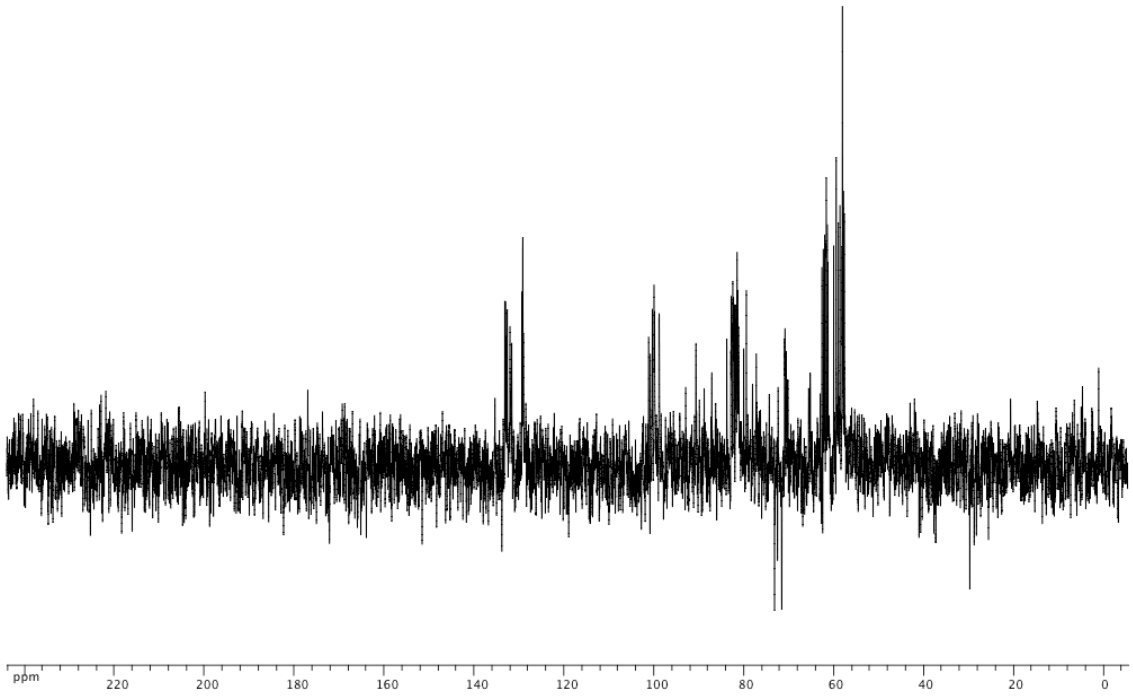
^{1}H-^{1}H COSY NMR spectrum of **3** recorded in $CDCl_3$ at 300.1 MHz.



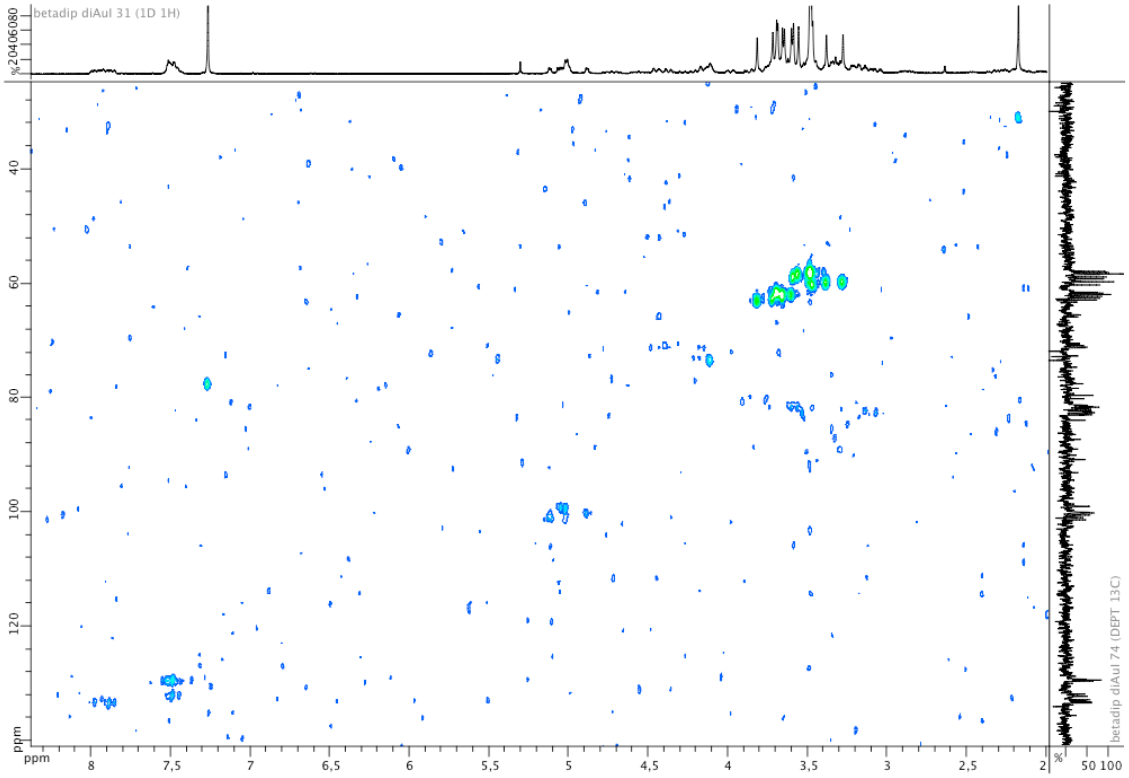
$^{31}P\{^{1}H\}$ NMR spectrum of **3** recorded in $CDCl_3$ at 121.5 MHz.



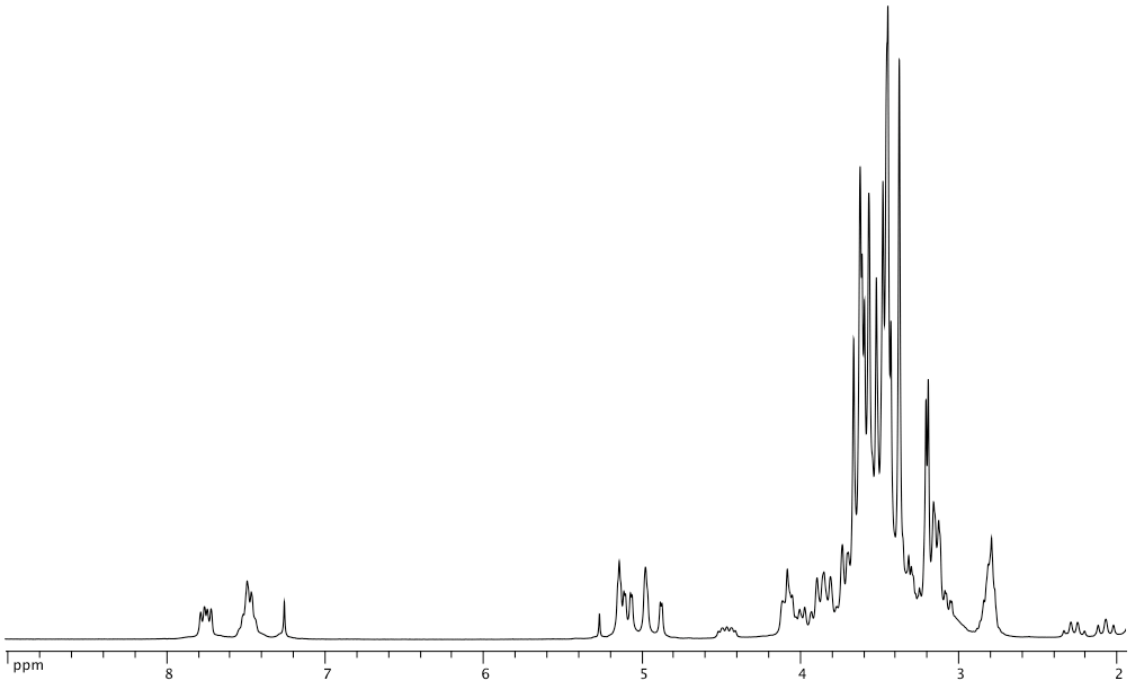
$^{13}C\{^{1}H\}$ NMR spectrum of **3** recorded in $CDCl_3$ at 75.5 MHz.



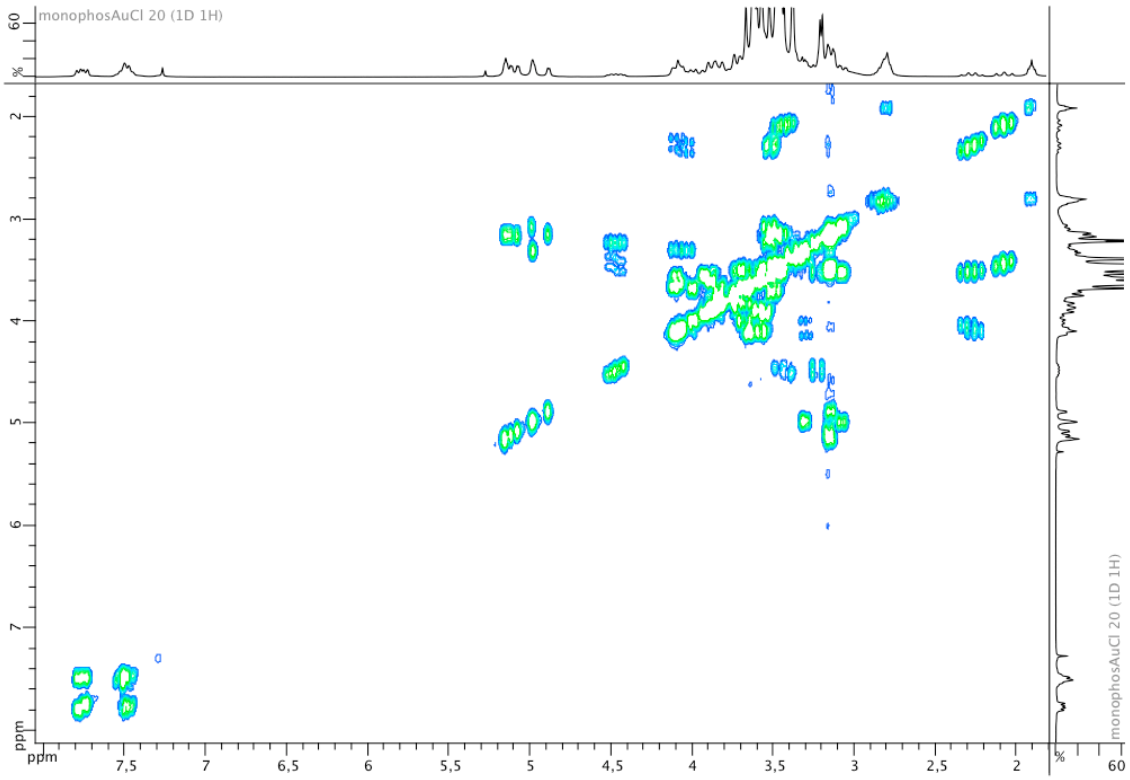
DEPT135 spectrum of **3** recorded in $CDCl_3$ at 75.5 MHz.



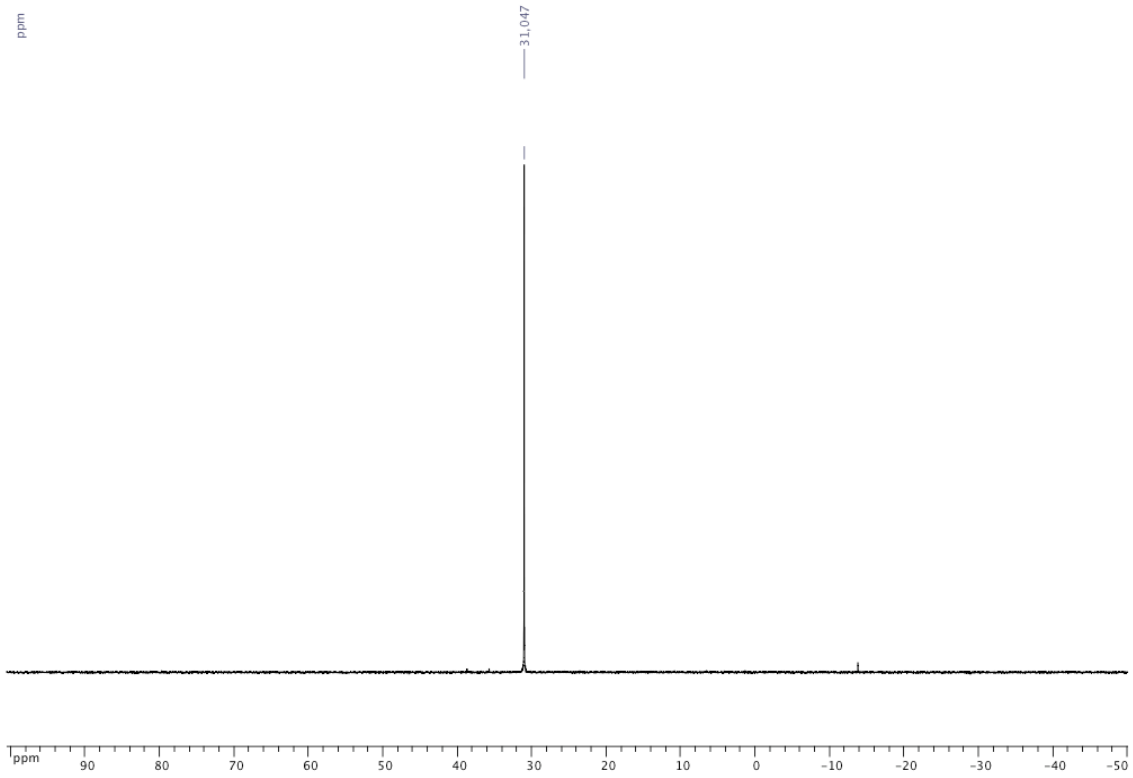
^{1}H-^{13}C{^{1}H} HMQC spectrum of **3** recorded in $CDCl_3$ at 300.1 MHz.



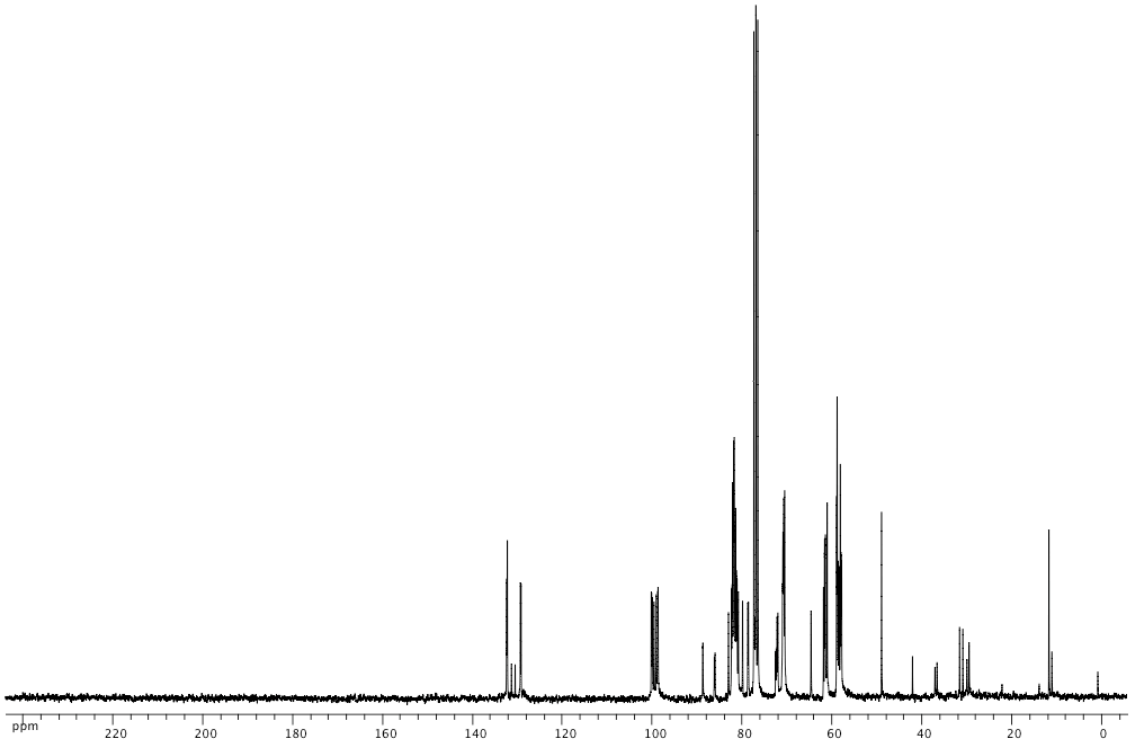
^{1}H NMR spectrum of **5** recorded in $CDCl_3$ at 300.1 MHz.



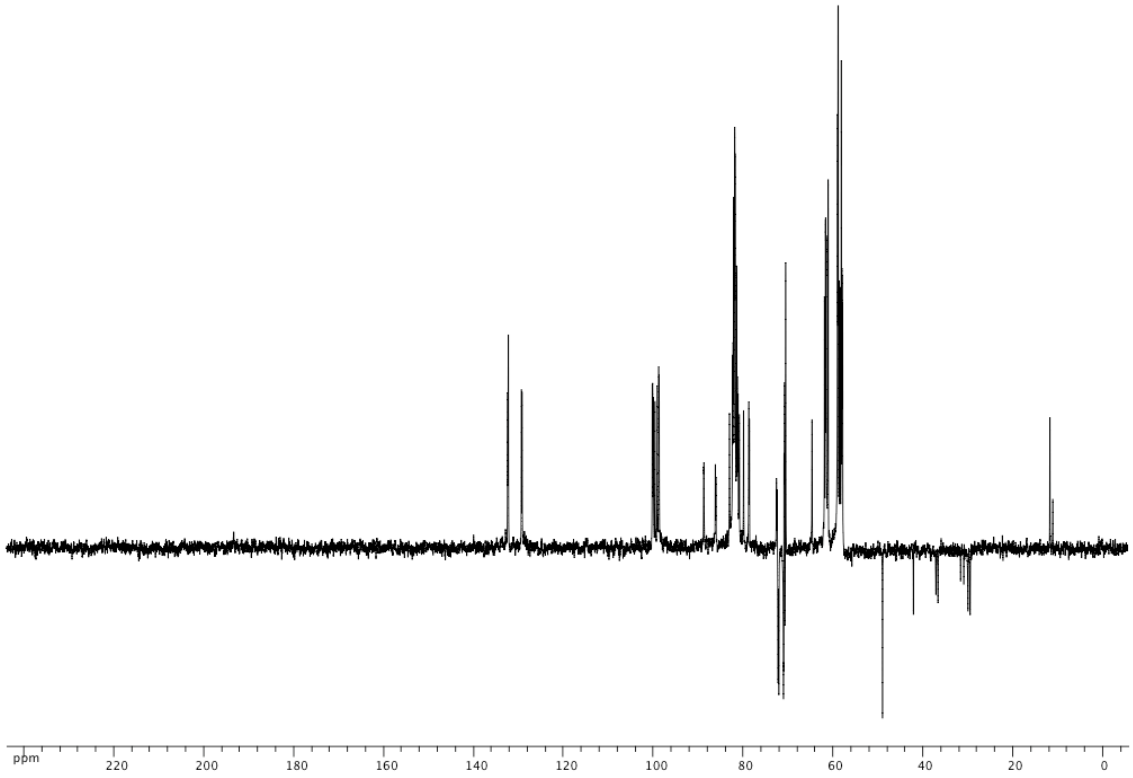
^{1}H-^{1}H COSY NMR spectrum of **5** recorded in $CDCl_3$ at 300.1 MHz.



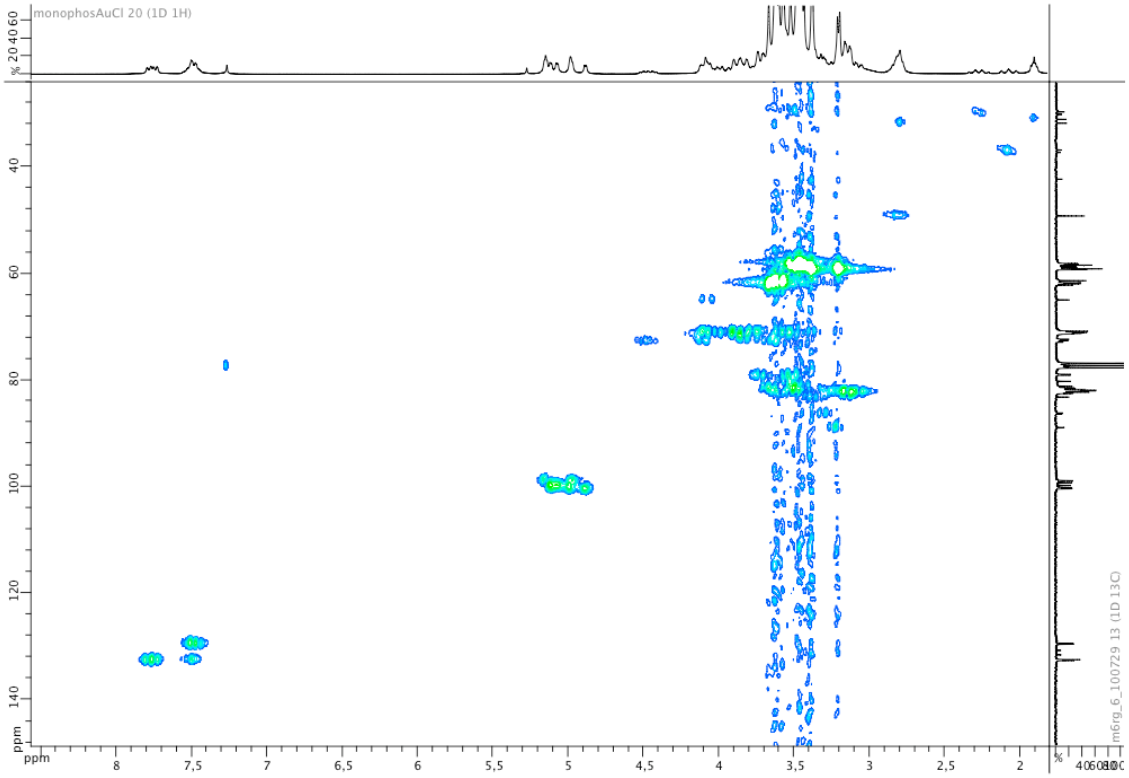
$^{31}P\{^{1}H\}$ NMR spectrum of **5** recorded in $CDCl_3$ at 121.5 MHz.



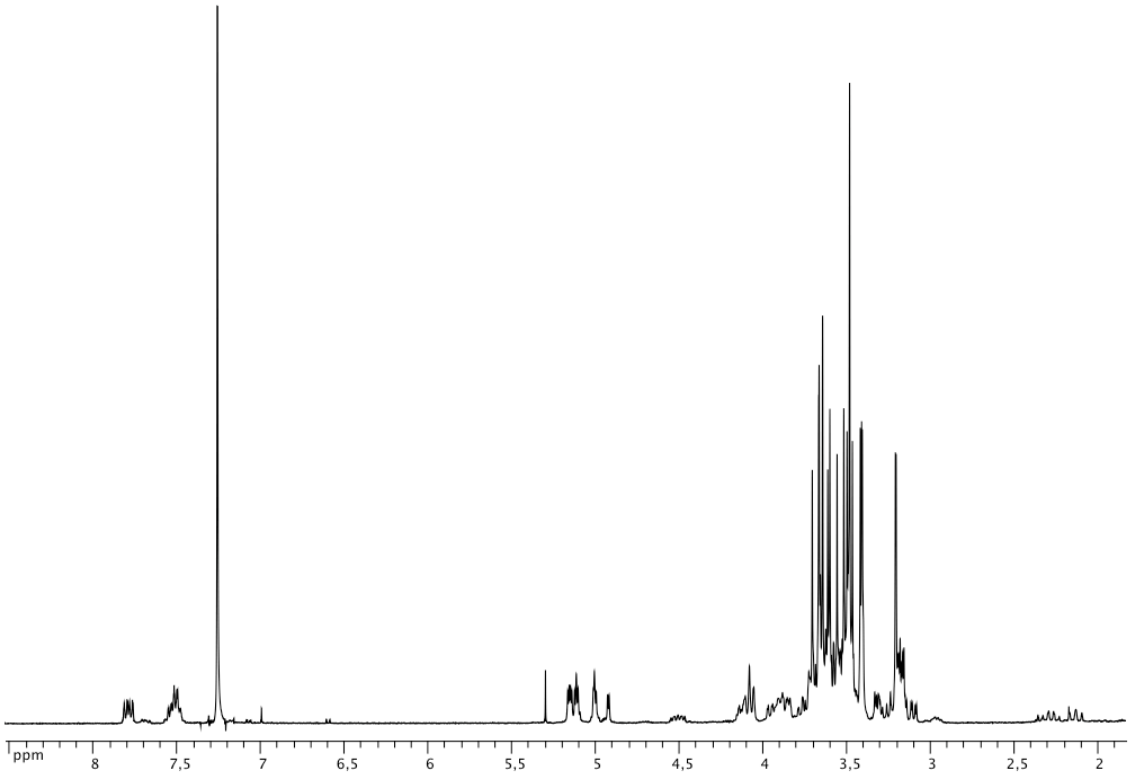
$^{13}C\{^{1}H\}$ NMR spectrum of **5** recorded in $CDCl_3$ at 75.5 MHz.



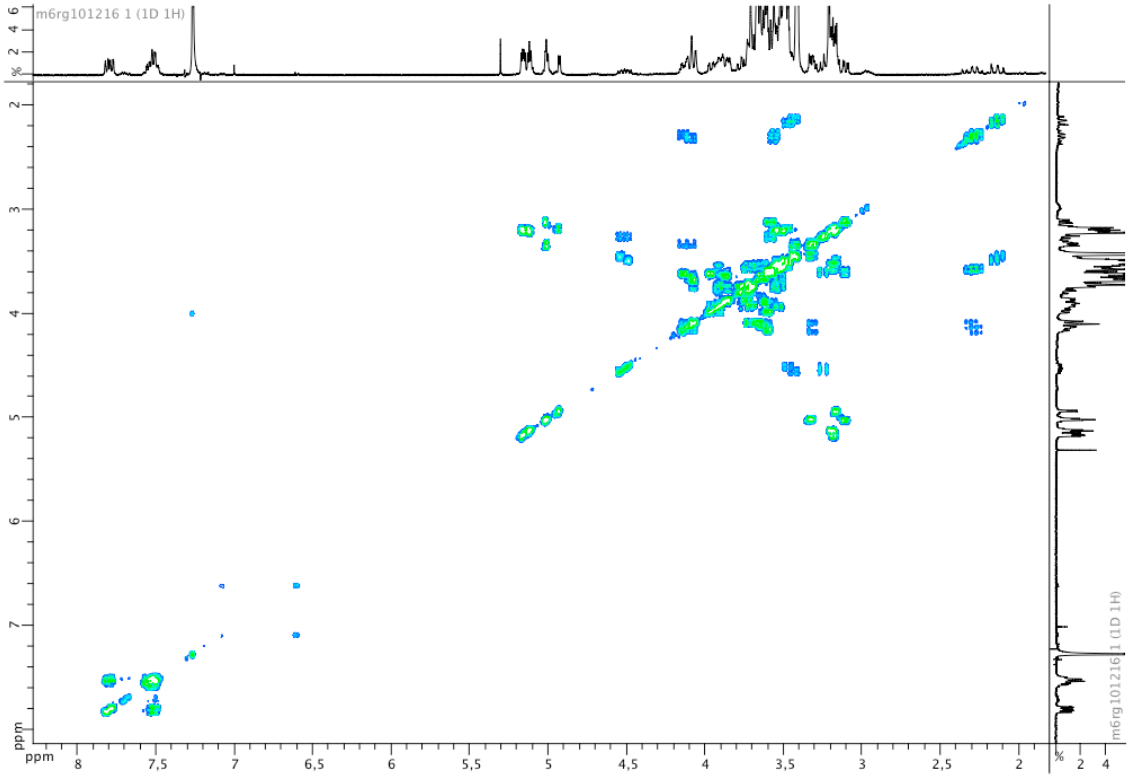
DEPT135 spectrum of **5** recorded in $CDCl_3$ at 75.5 MHz.



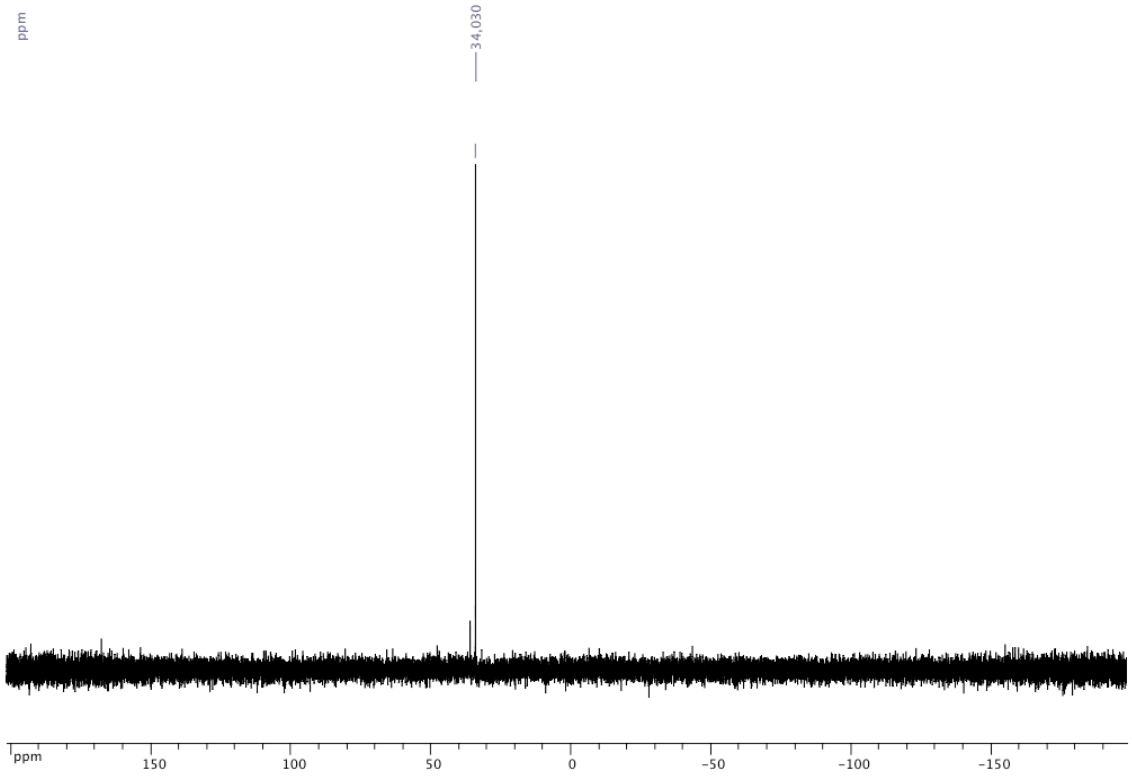
^{1}H-$^{13}C\{^{1}H\}$ HMQC spectrum of **5** recorded in $CDCl_3$ at 300.1 MHz.



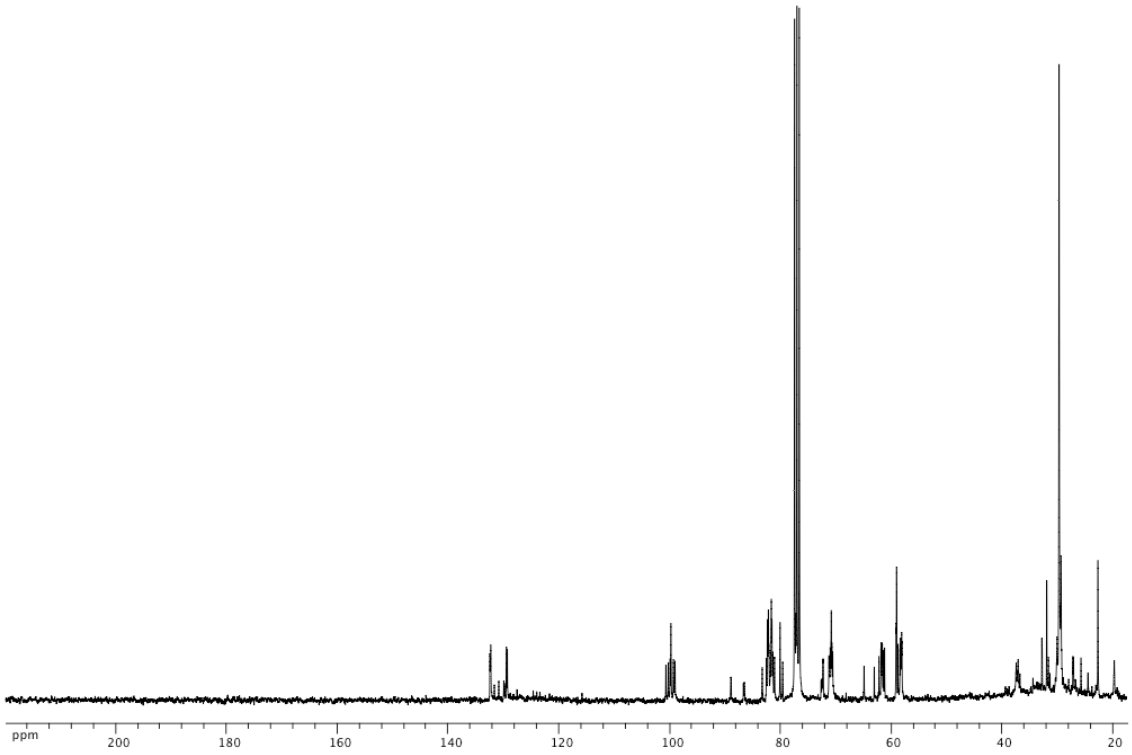
^{1}H NMR spectrum of **6** recorded in $CDCl_3$ at 400.1 MHz.



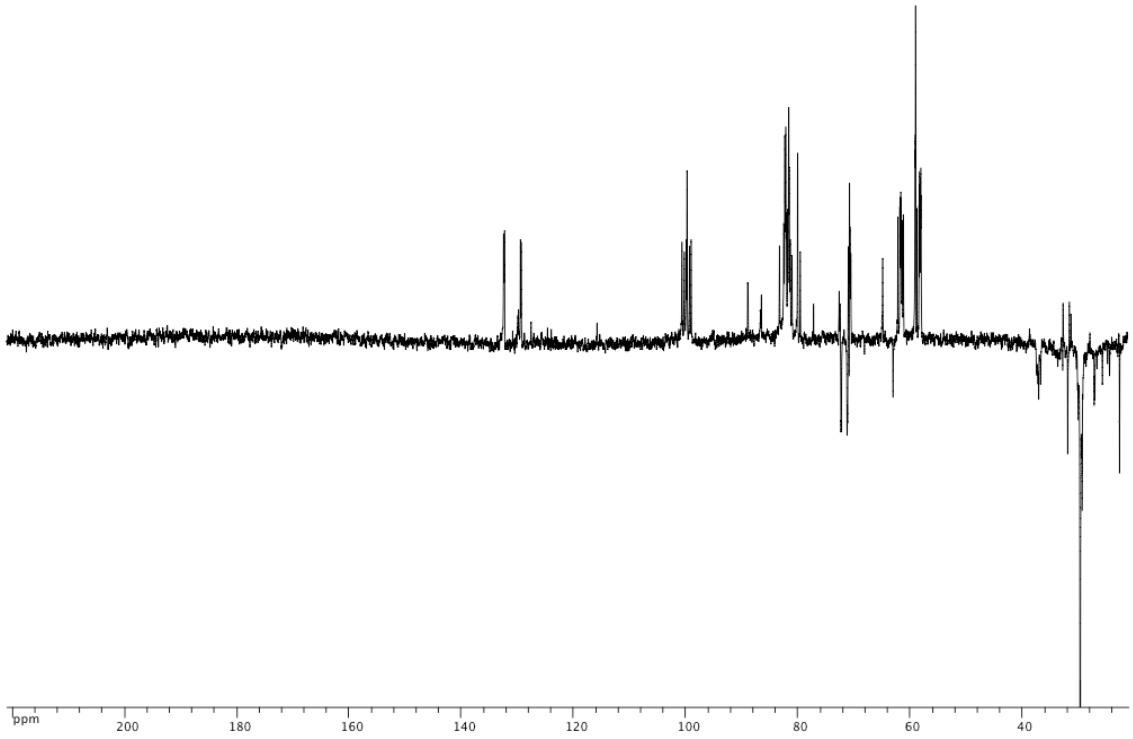
^{1}H-^{1}H COSY NMR spectrum of **6** recorded in $CDCl_3$ at 400.1 MHz.



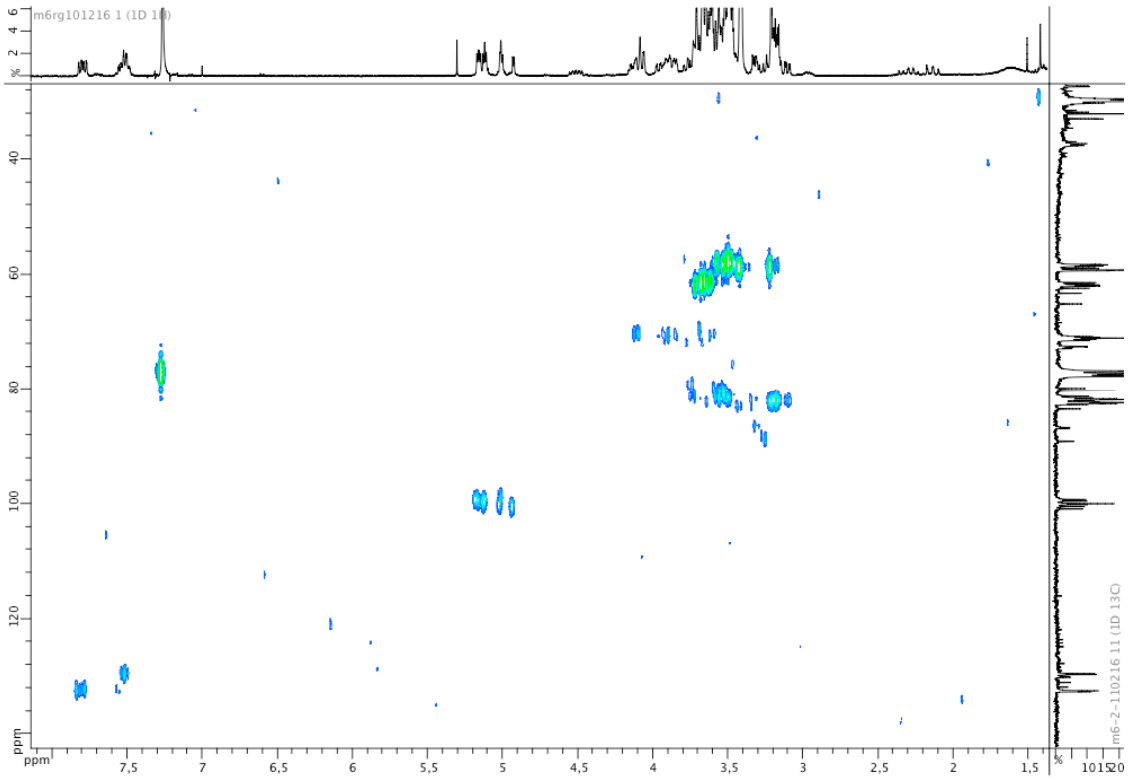
$^{31}P\{^{1}H\}$ NMR spectrum of **6** recorded in $CDCl_3$ at 121.5 MHz.



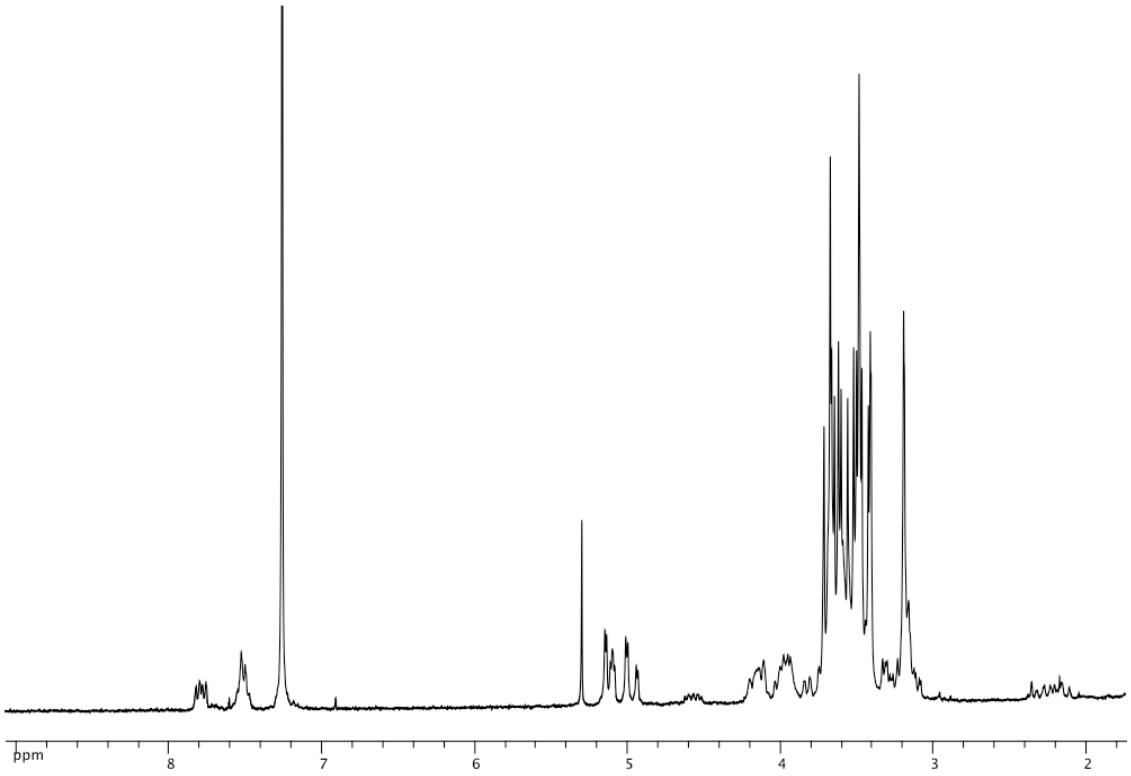
$^{13}C\{^{1}H\}$ NMR spectrum of **6** recorded in $CDCl_3$ at 75.5 MHz.



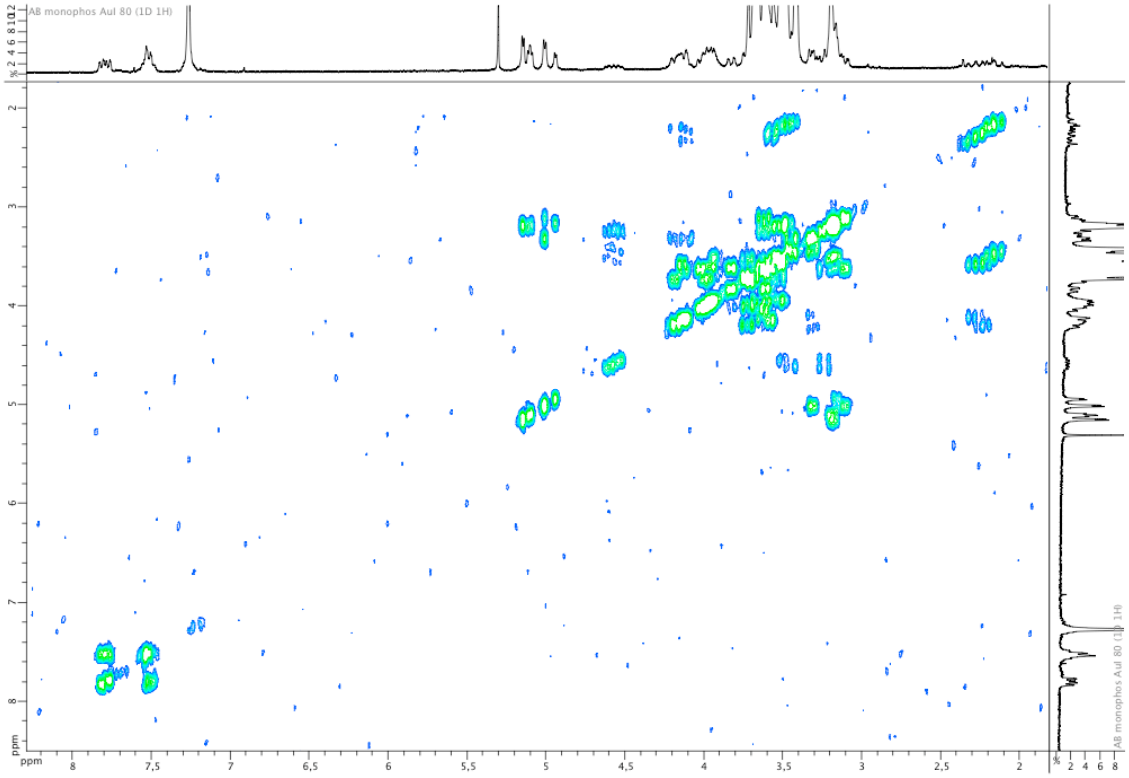
DEPT135 spectrum of **6** recorded in $CDCl_3$ at 75.5 MHz.



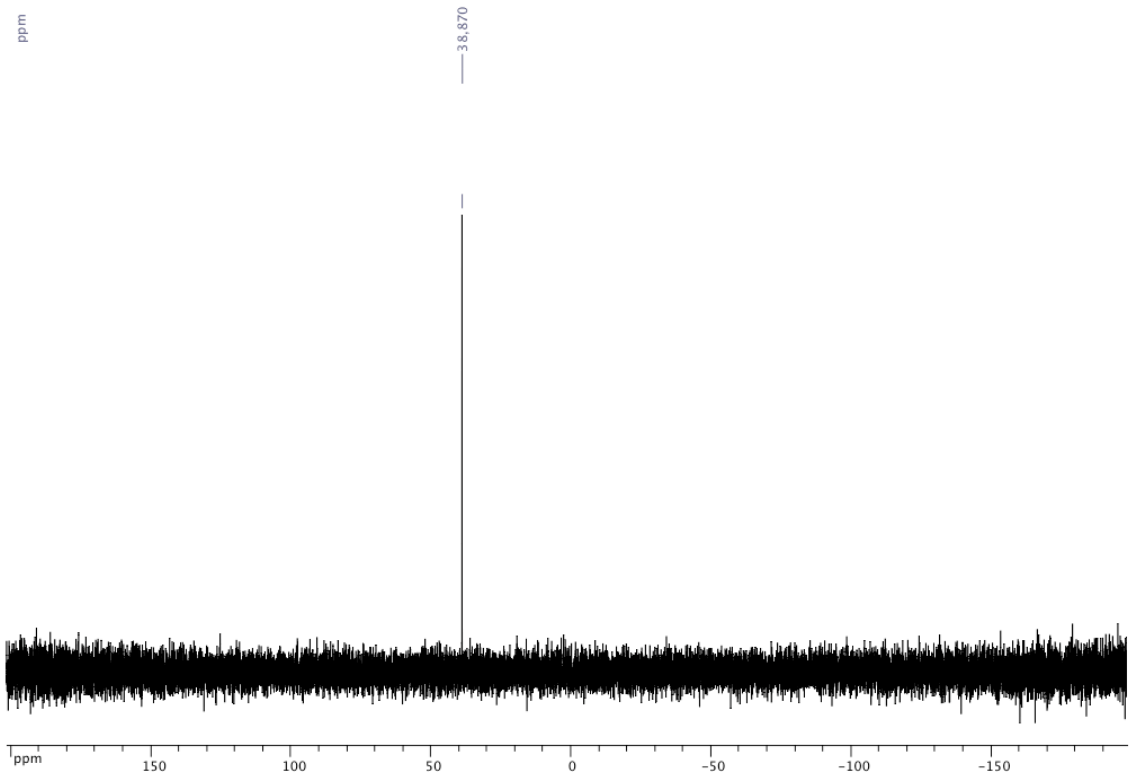
^{1}H-$^{13}C\{^{1}H\}$ HMQC spectrum of **6** recorded in $CDCl_3$ at 400.1 MHz.



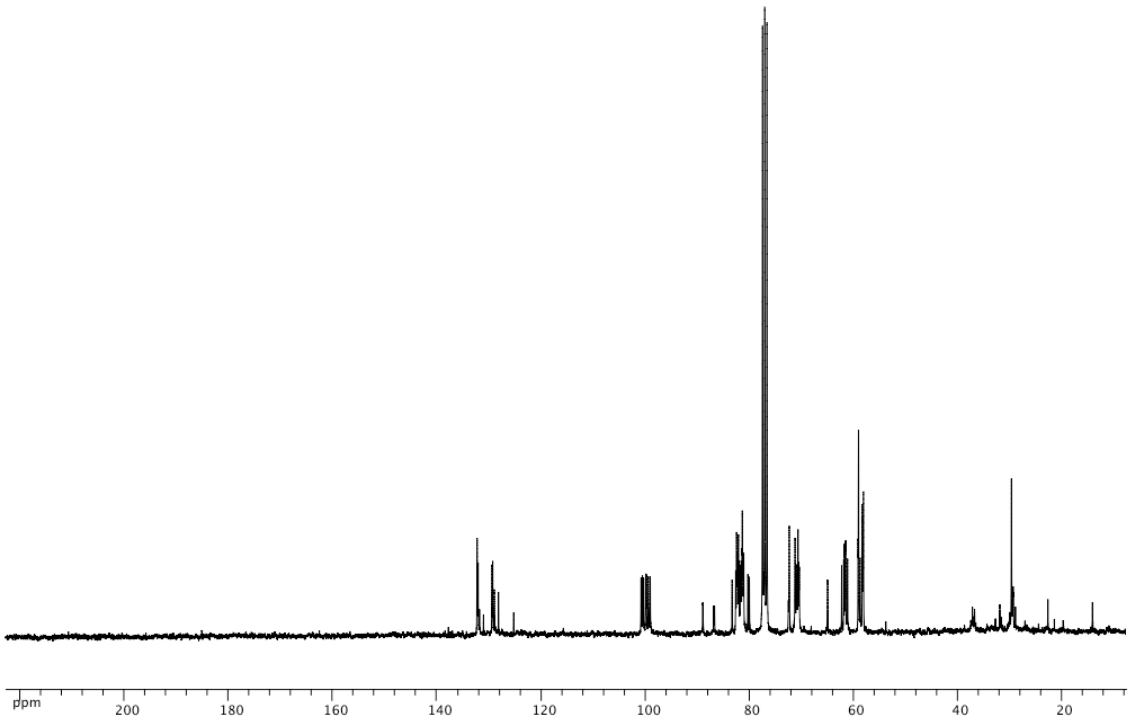
^{1}H NMR spectrum of **7** recorded in $CDCl_3$ at 300.1 MHz.



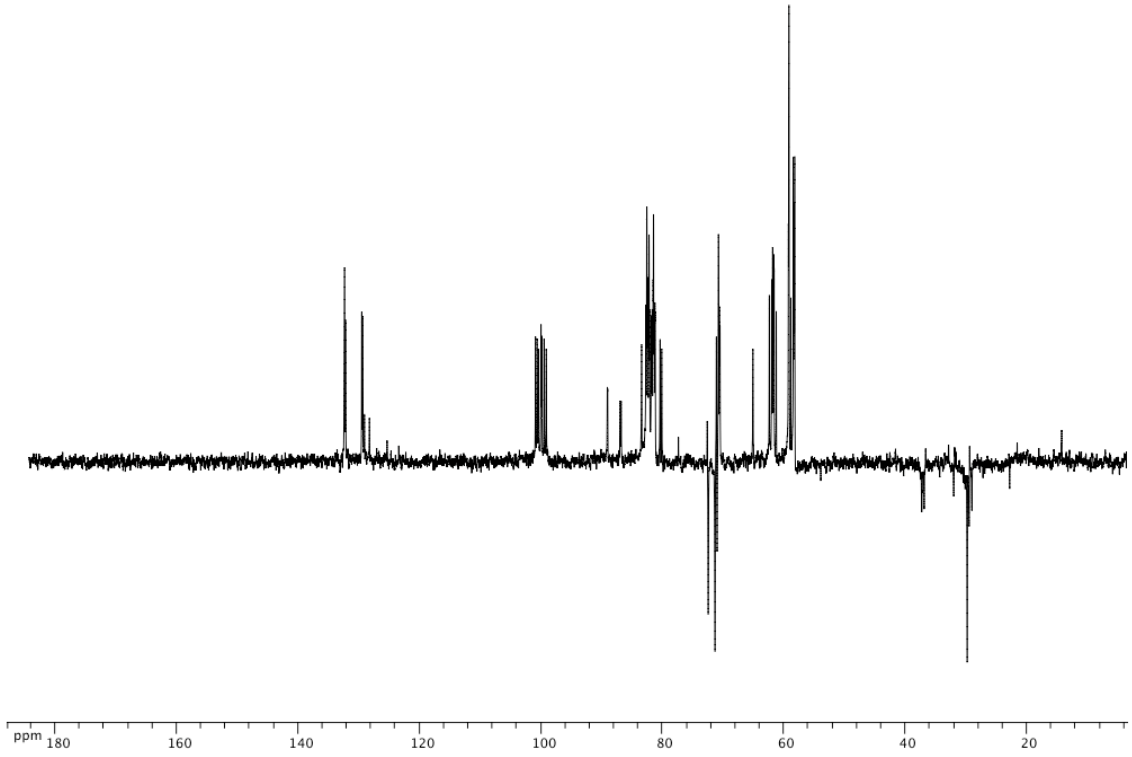
^{1}H-^{1}H COSY NMR spectrum of **7** recorded in $CDCl_3$ at 300.1 MHz.



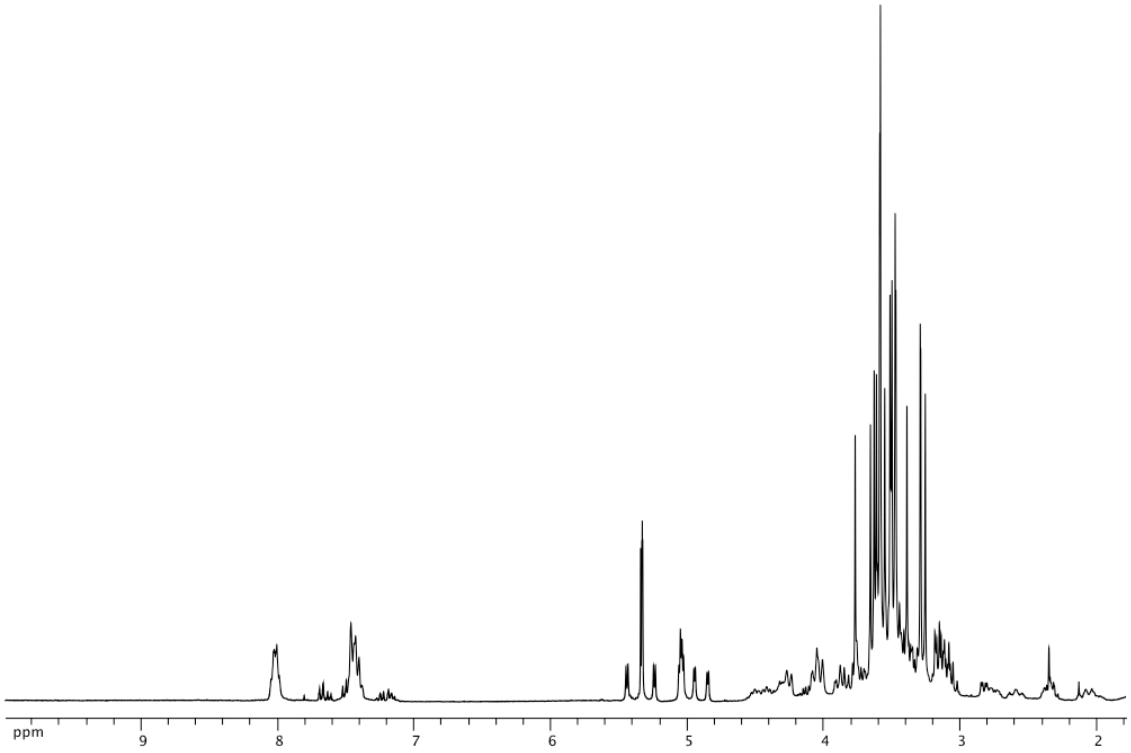
$^{31}P\{^{1}H\}$ NMR spectrum of **7** recorded in $CDCl_3$ at 121.5 MHz.



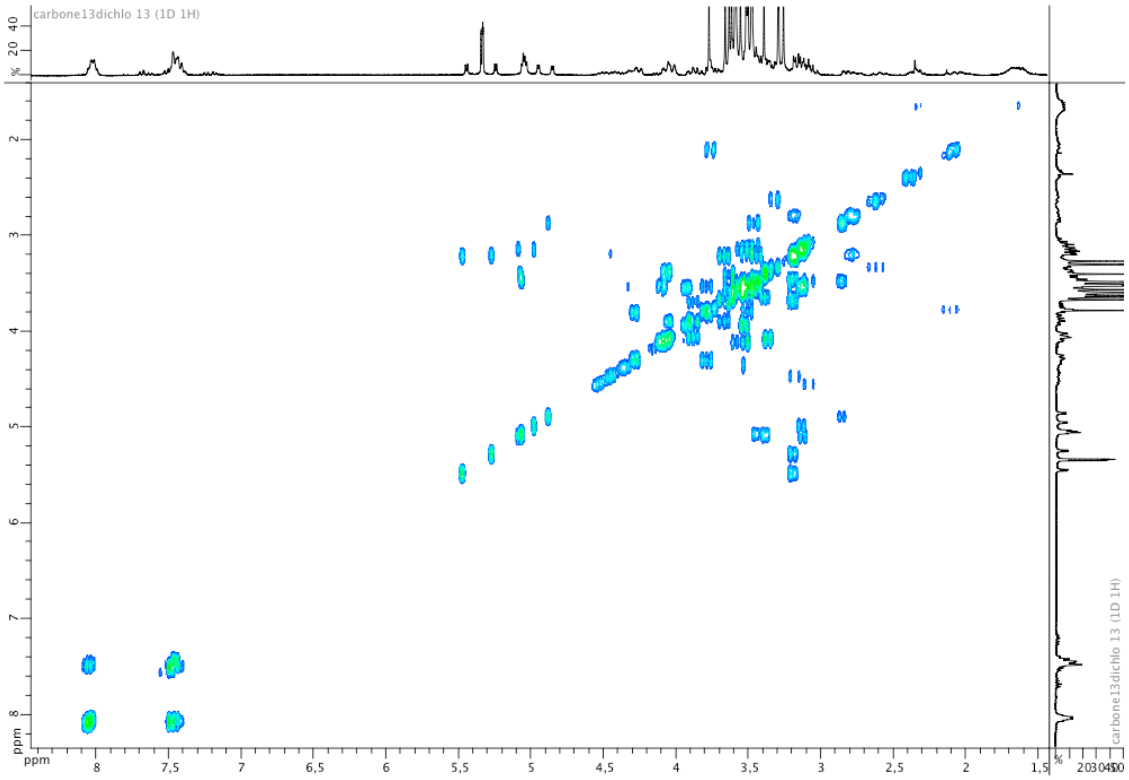
$^{13}C\{^{1}H\}$ NMR spectrum of **7** recorded in $CDCl_3$ at 75.5 MHz.



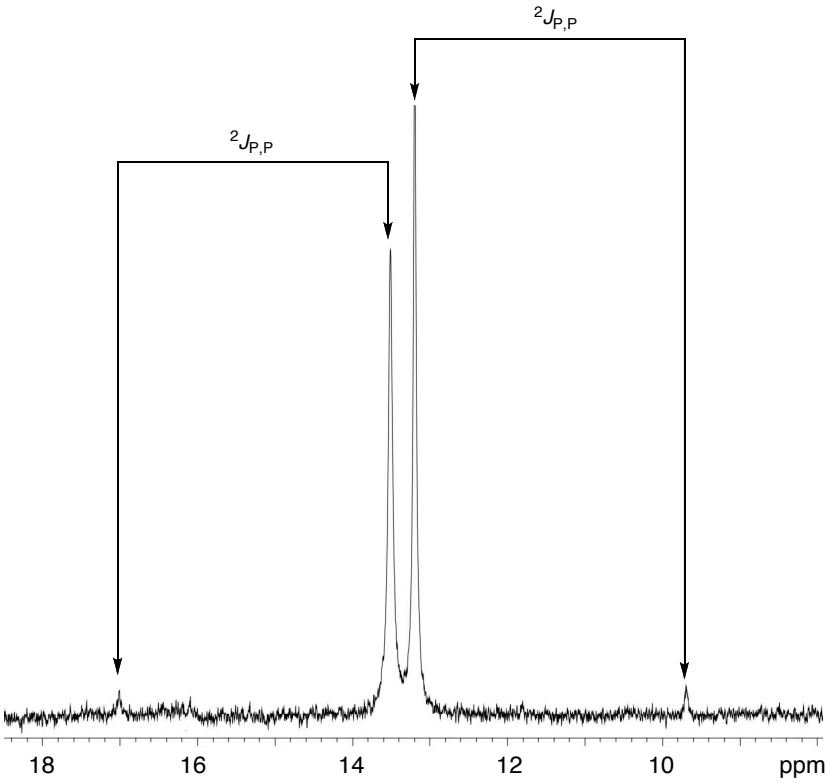
DEPT135 spectrum of **7** recorded in $CDCl_3$ at 75.5 MHz.



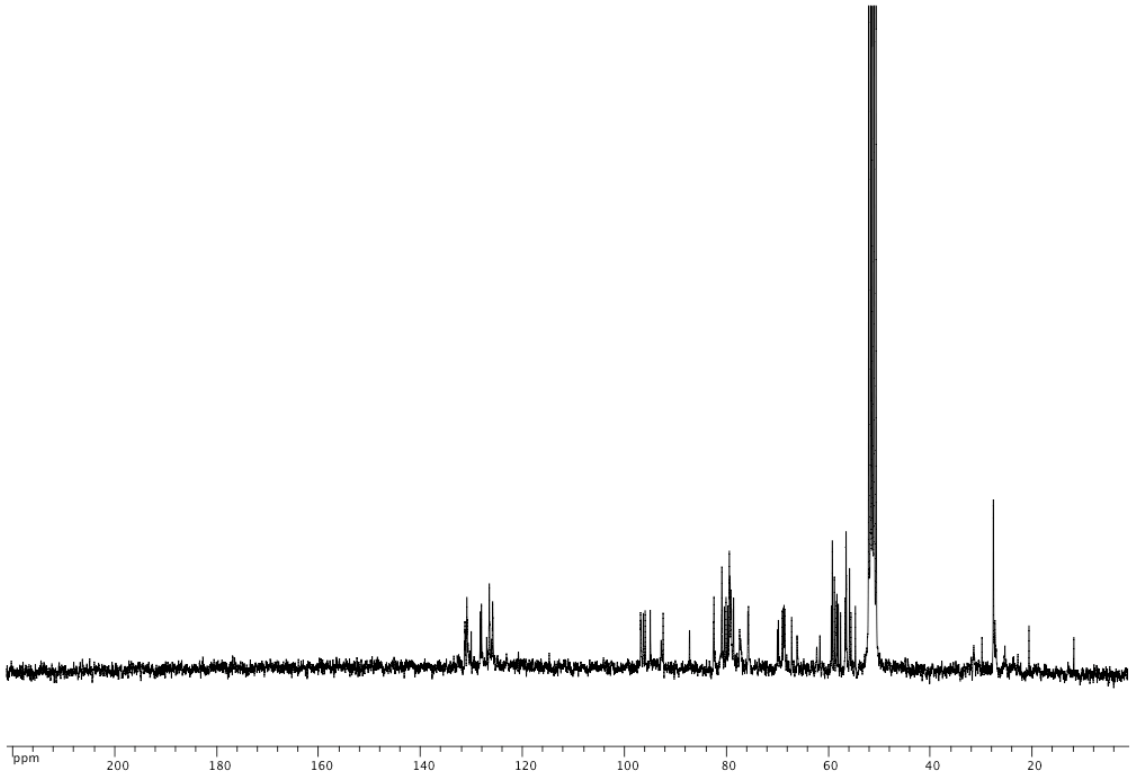
^{1}H NMR spectrum of **8** recorded in CD_2Cl_2 at 300.1 MHz.



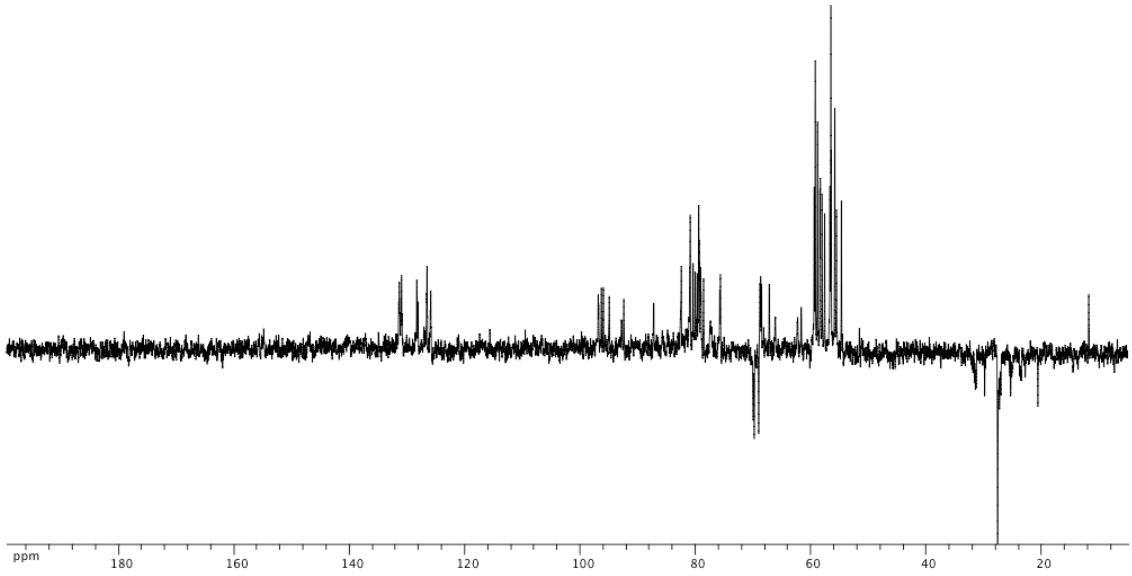
^{1}H-^{1}H COSY NMR spectrum of **8** recorded in $CDCl_3$ at 300.1 MHz.



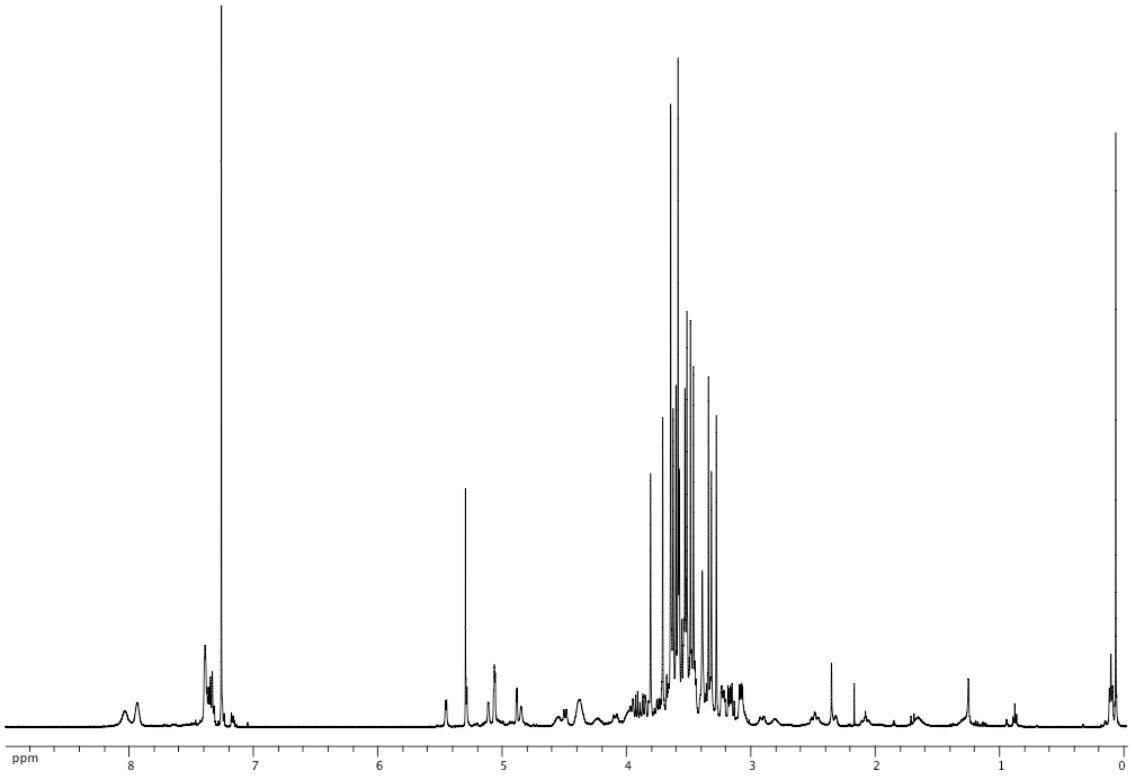
$^{31}P\{^1H\}$ NMR spectrum of **8** recorded in $C_2D_2Cl_4$ at 162.0 MHz.



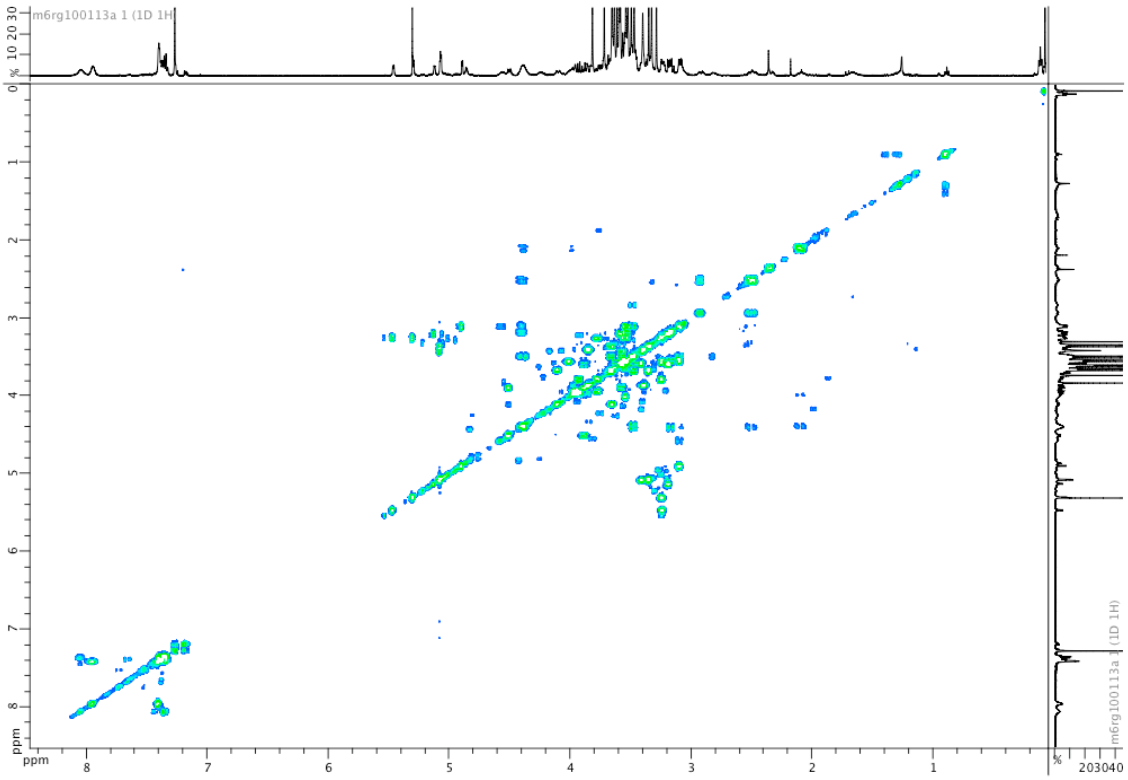
$^{13}C\{^{1}H\}$ NMR spectrum of **8** recorded in CD_2Cl_2 at 75.5 MHz.



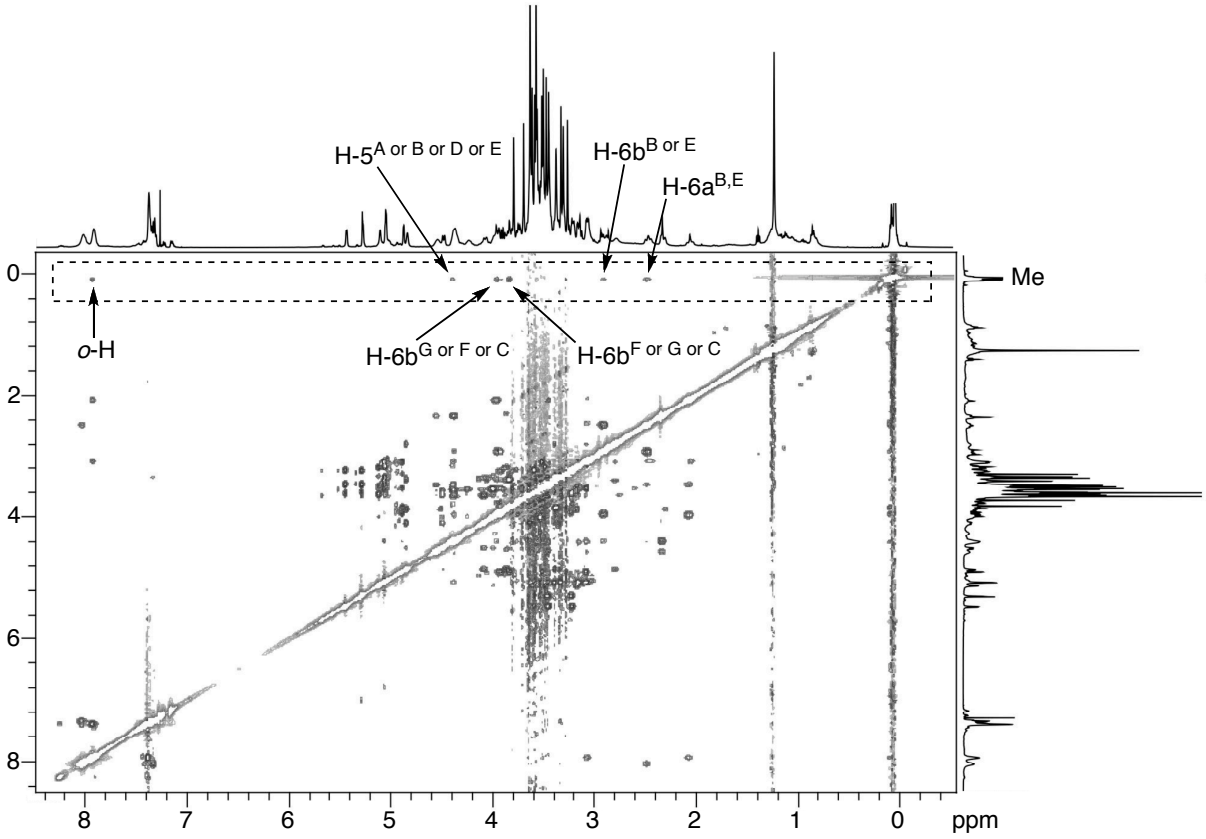
DEPT135 spectrum of **8** recorded in CD_2Cl_2 at 75.5 MHz.



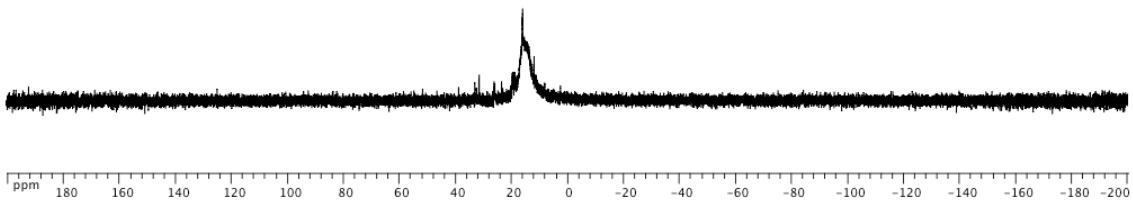
^{1}H NMR spectrum of **9** recorded in $CDCl_3$ at 500.1 MHz.



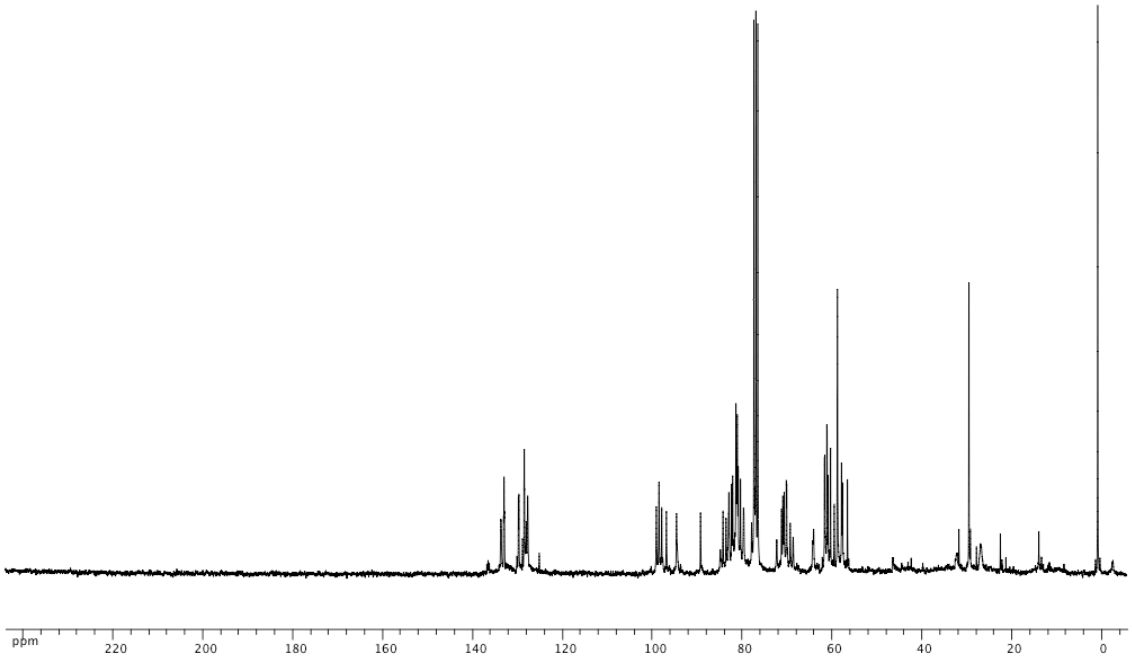
^{1}H-^{1}H COSY NMR spectrum of **9** recorded in $CDCl_3$ at 500.1 MHz.



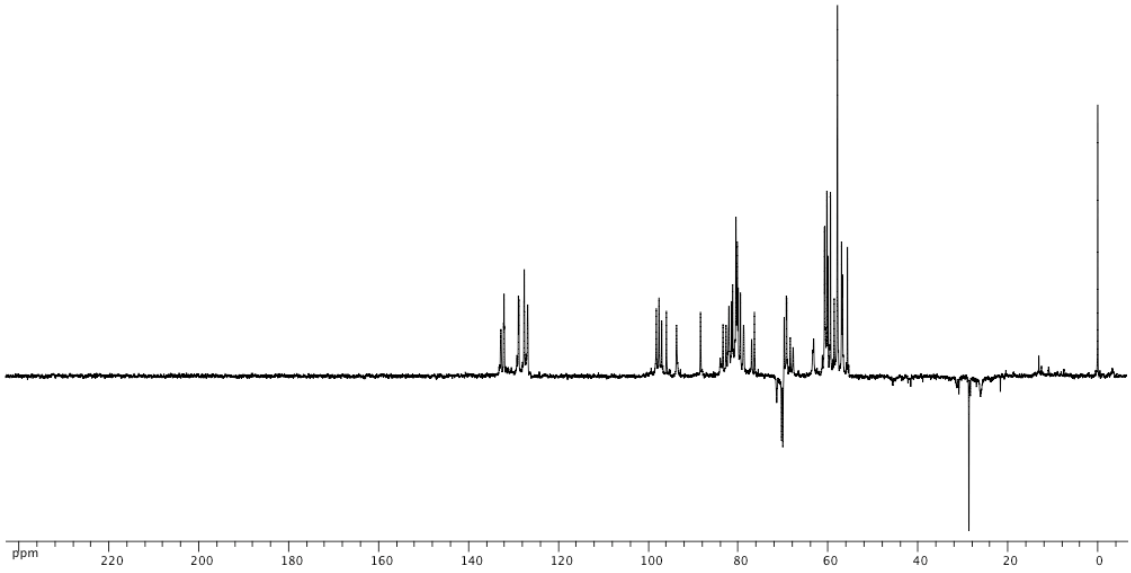
^{1}H-^{1}H ROESY NMR spectrum of **9** recorded in $CDCl_3$ at 500.1 MHz.



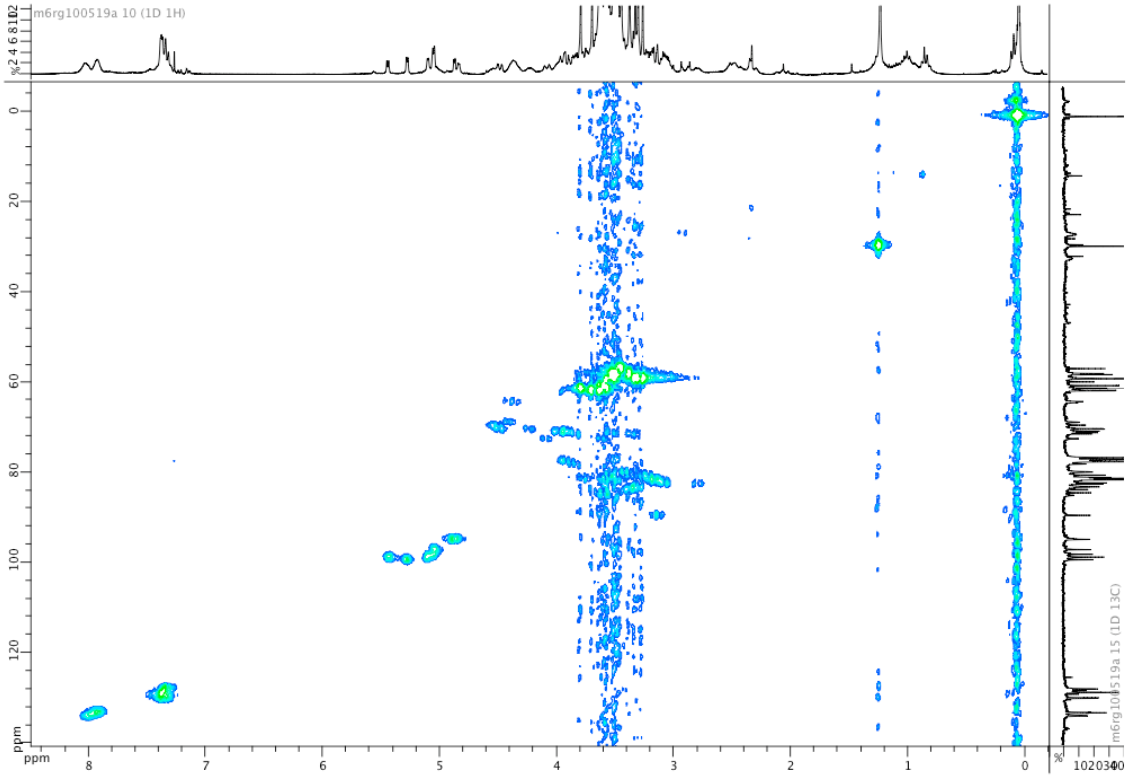
$^{31}P\{^{1}H\}$ NMR spectrum of **9** recorded in $CDCl_3$ at 121.5 MHz (298 K).



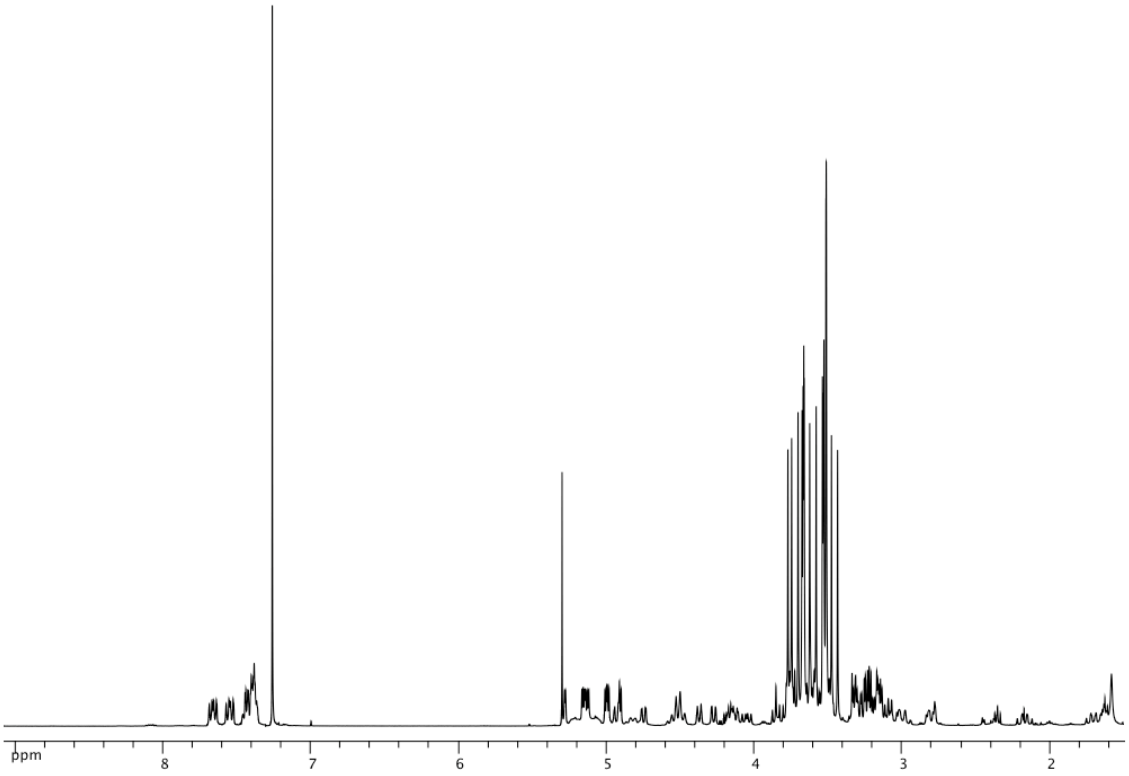
$^{13}C\{^{1}H\}$ NMR spectrum of **9** recorded in $CDCl_3$ at 75.5 MHz.



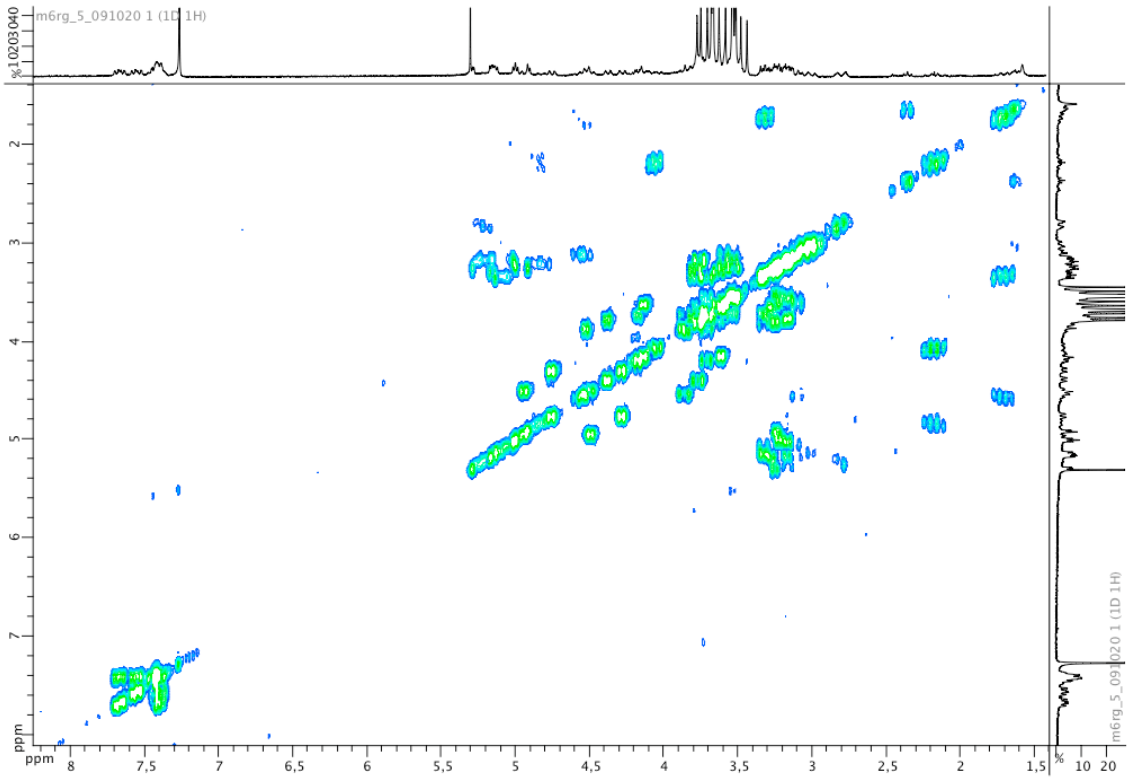
DEPT135 spectrum of **9** recorded in $CDCl_3$ at 75.5 MHz.



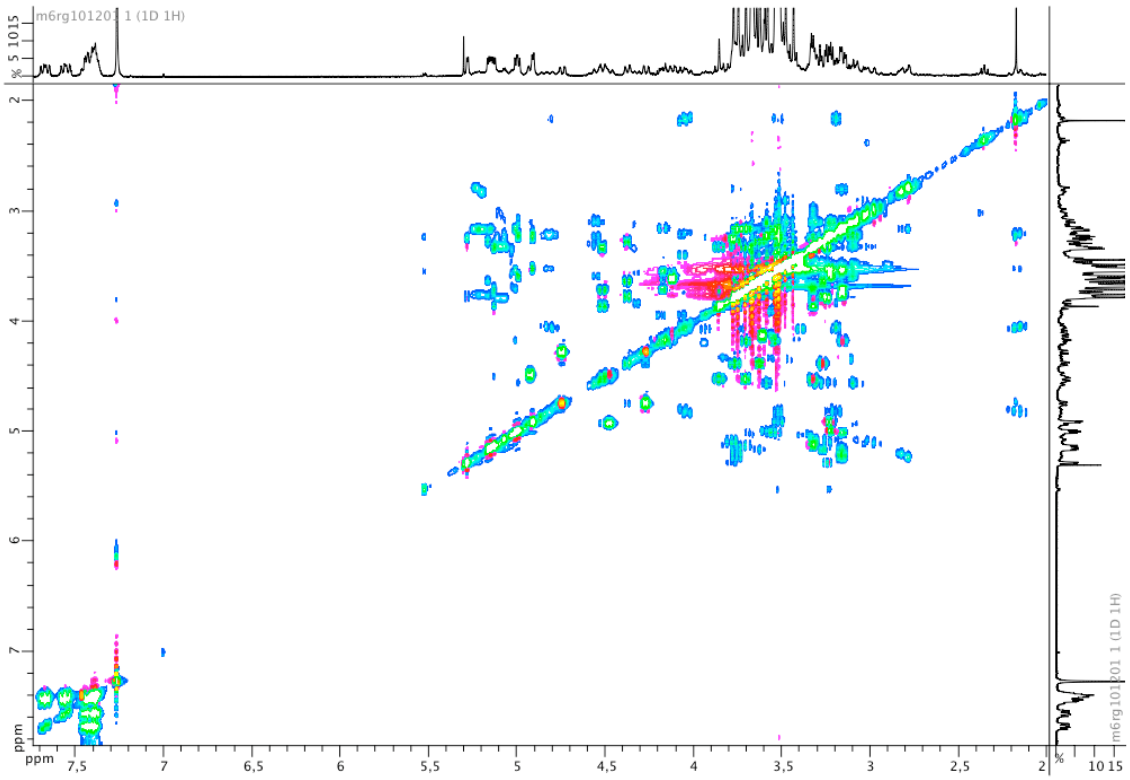
^{1}H-^{13}C{^{1}H} HMQC spectrum of **9** recorded in $CDCl_3$ at 300.1 MHz.



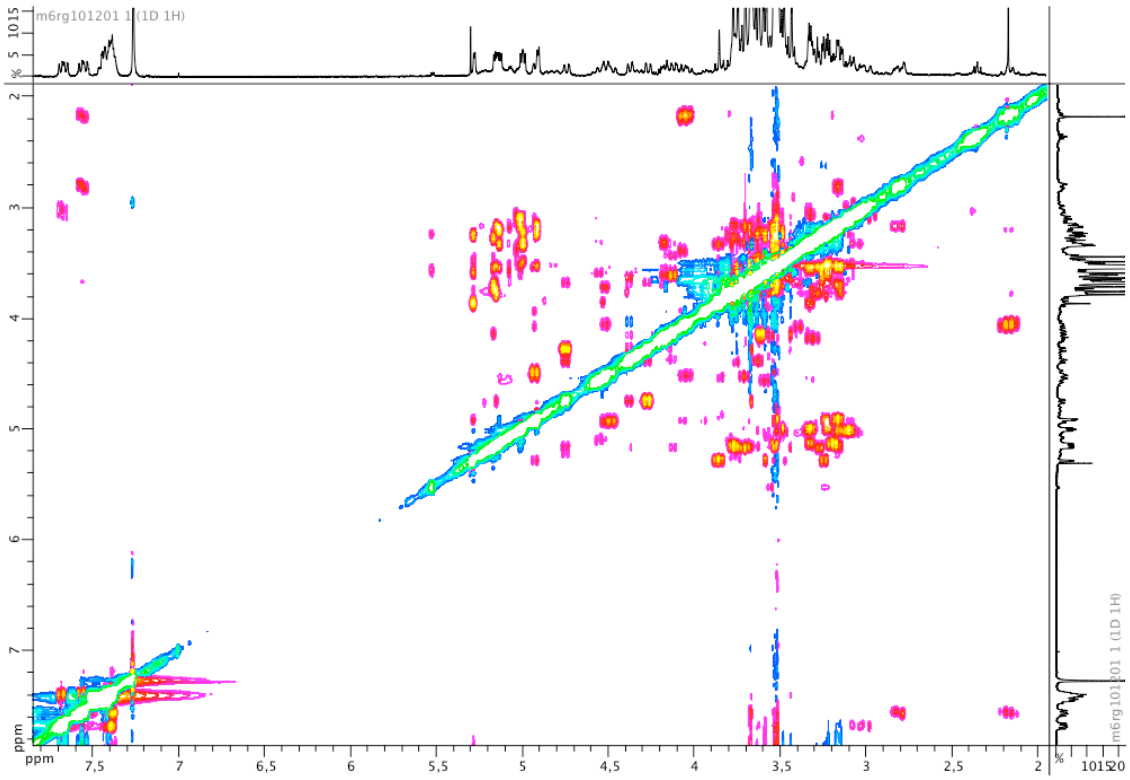
^{1}H NMR spectrum of **10** recorded in $CDCl_3$ at 400.1 MHz.



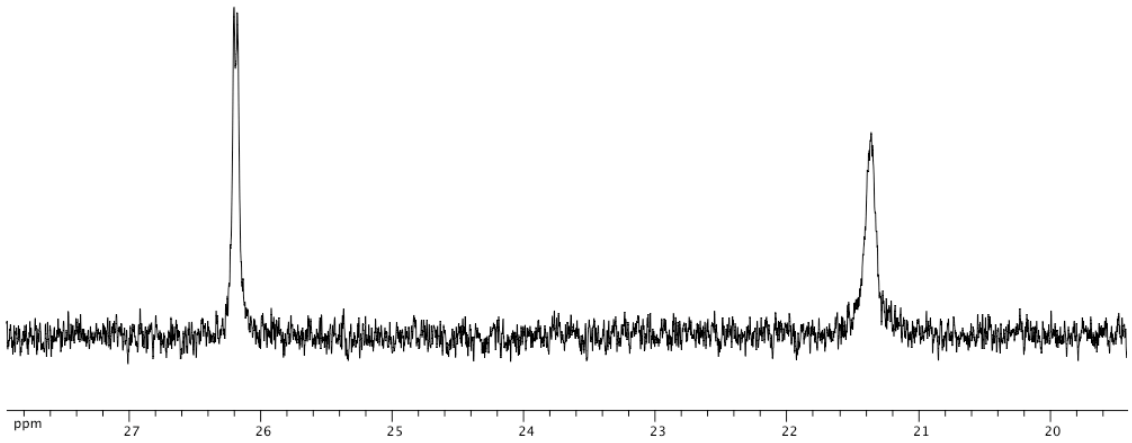
^{1}H-^{1}H COSY NMR spectrum of **10** recorded in $CDCl_3$ at 400.1 MHz.



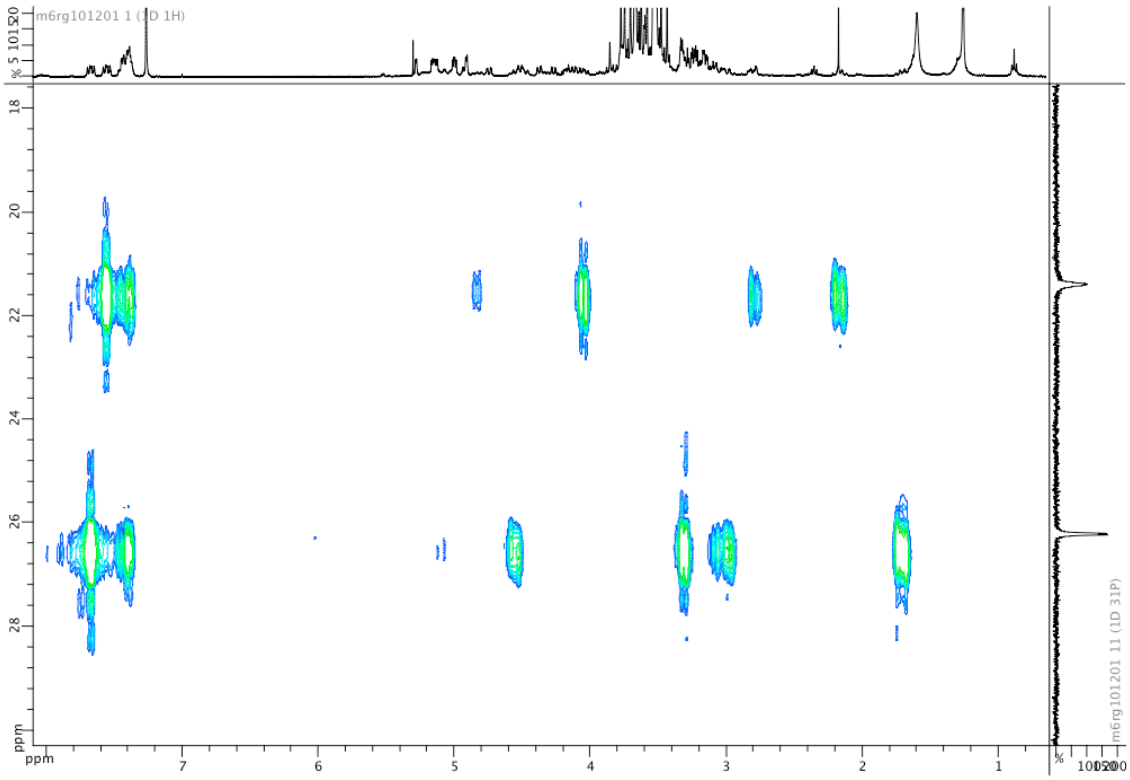
^{1}H-^{1}H TOCSY NMR spectrum of **10** recorded in $CDCl_3$ at 400.1 MHz.



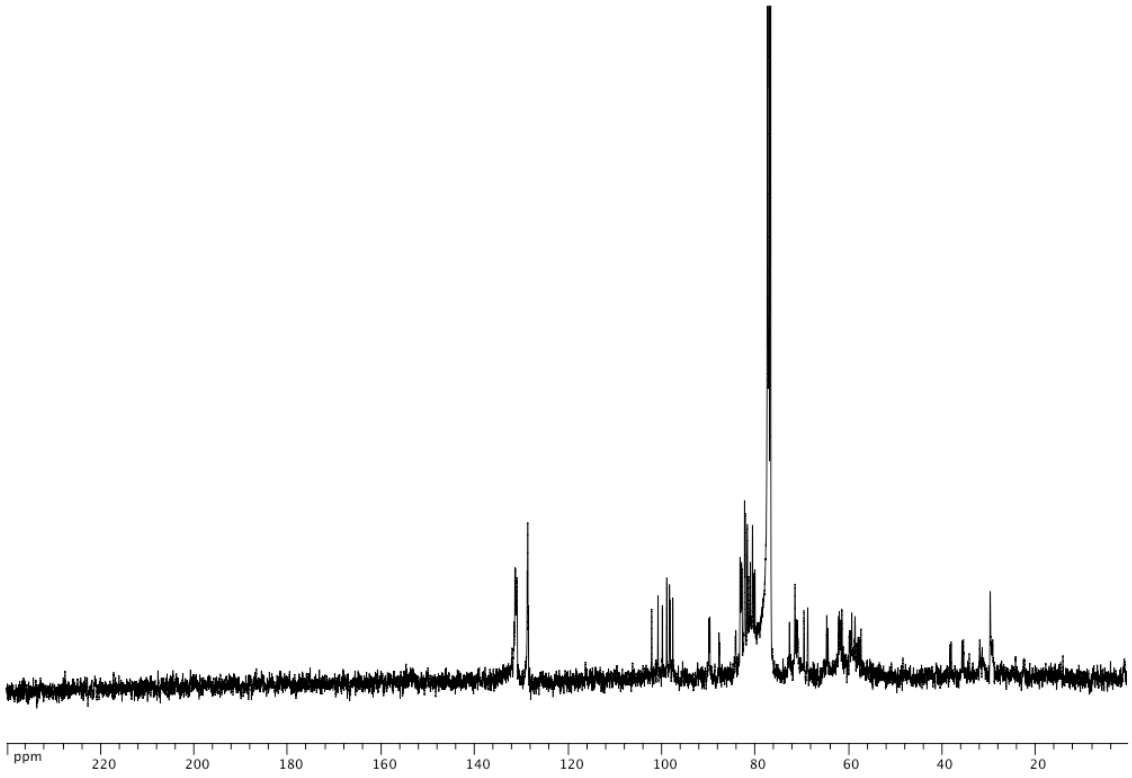
^{1}H-^{1}H ROESY NMR spectrum of **10** recorded in $CDCl_3$ at 400.1 MHz.



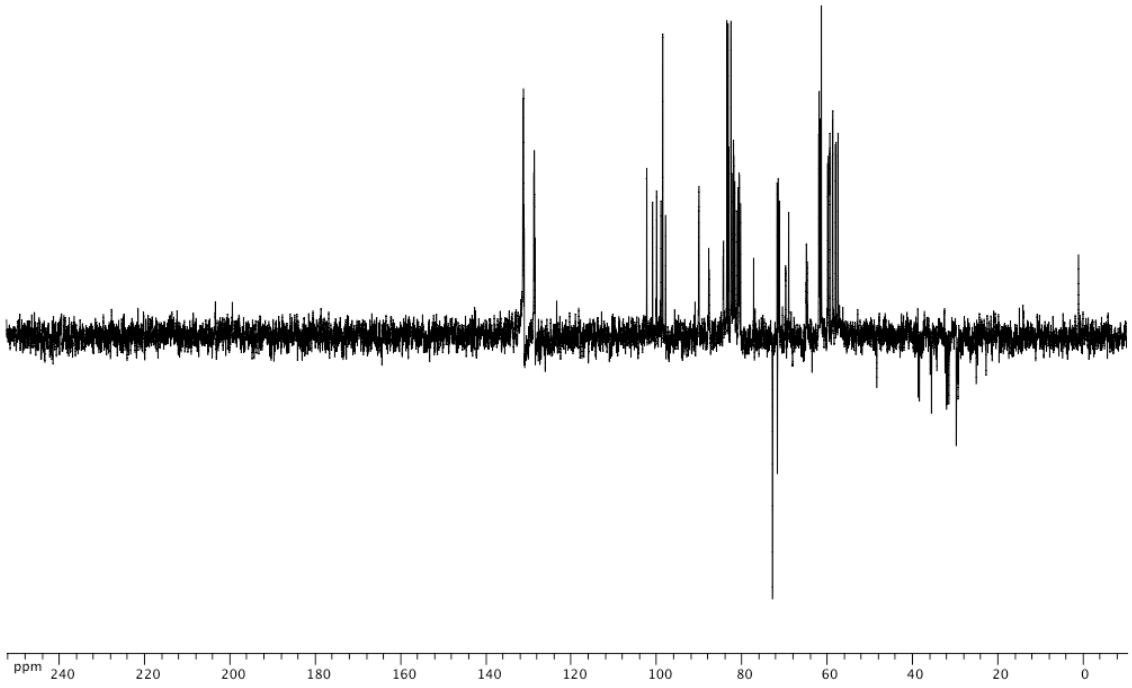
$^{31}P\{^{1}H\}$ NMR spectrum of **10** recorded in $CDCl_3$ at 162.0 MHz (298 K).



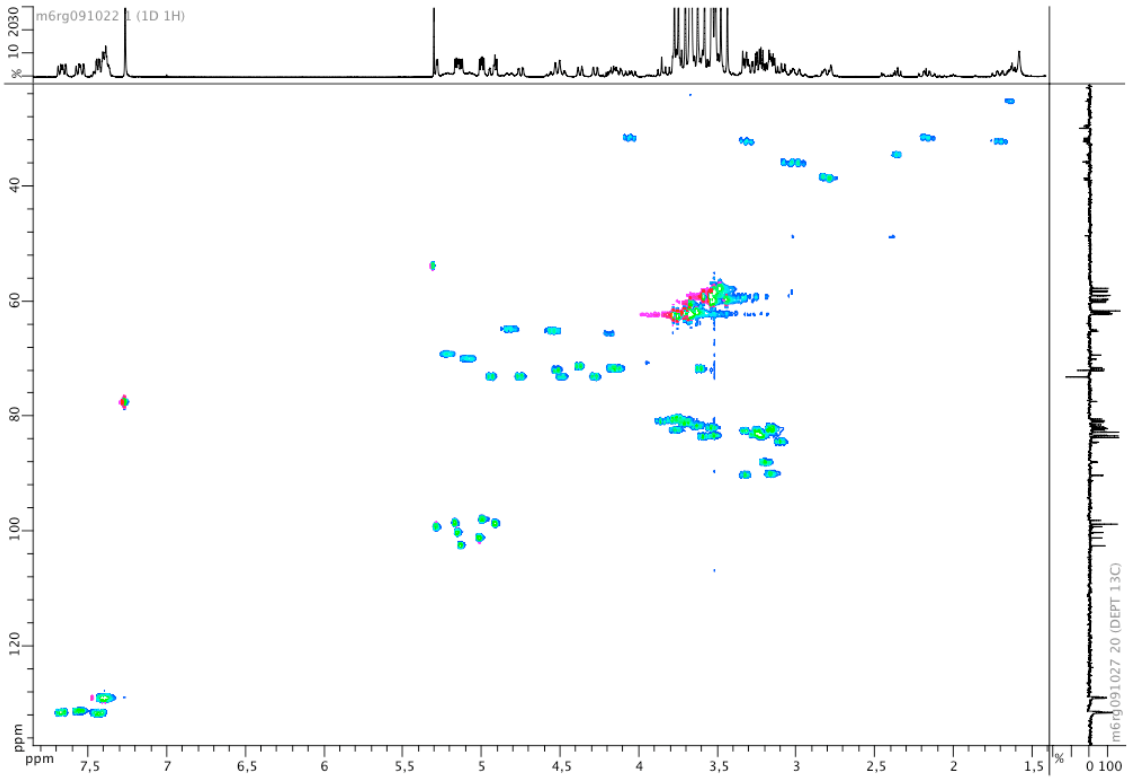
^{1}H-^{31}P{^{1}H} NMR spectrum of **10** recorded in $CDCl_3$ at 400.1 MHz.



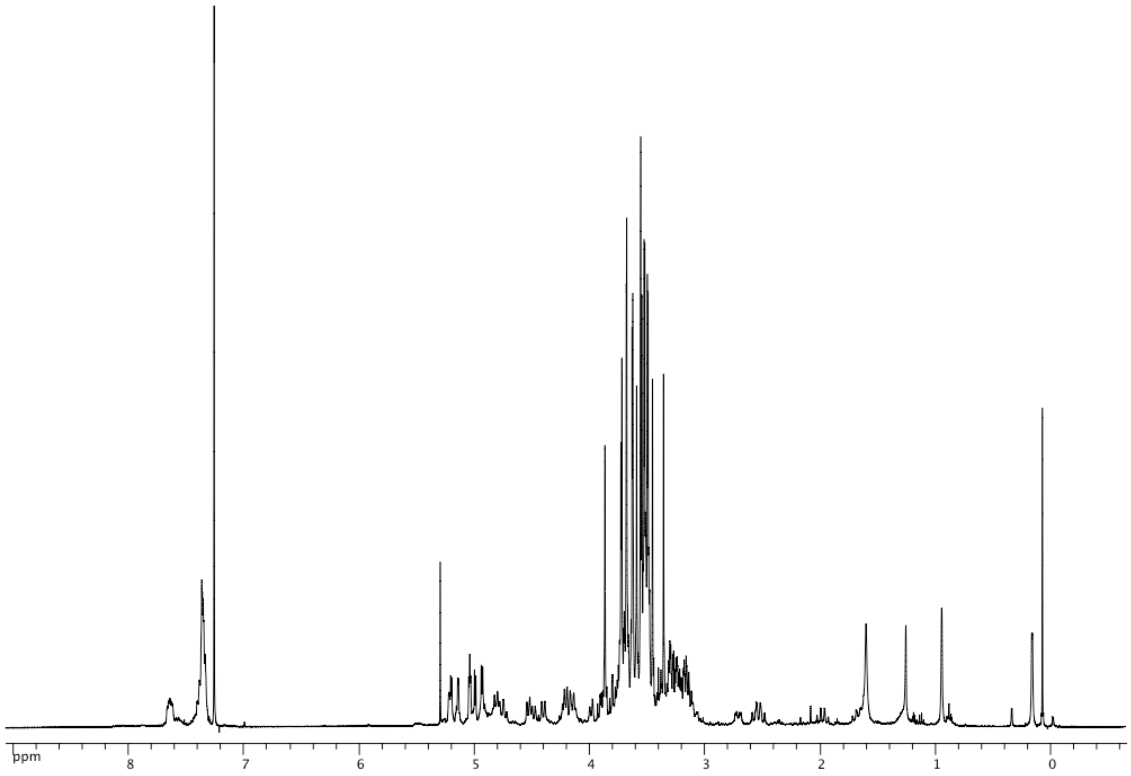
$^{13}C\{^{1}H\}$ NMR spectrum of **10** recorded in $CDCl_3$ at 100.6 MHz.



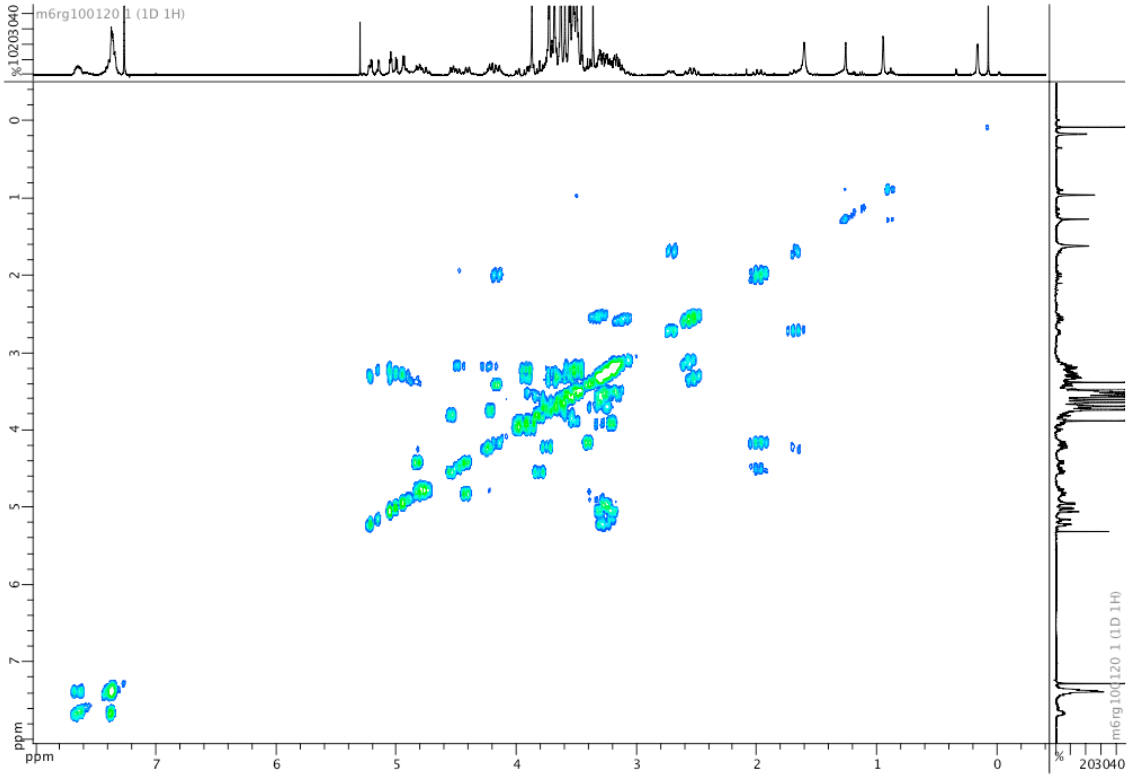
DEPT135 spectrum of **10** recorded in $CDCl_3$ at 100.6 MHz.



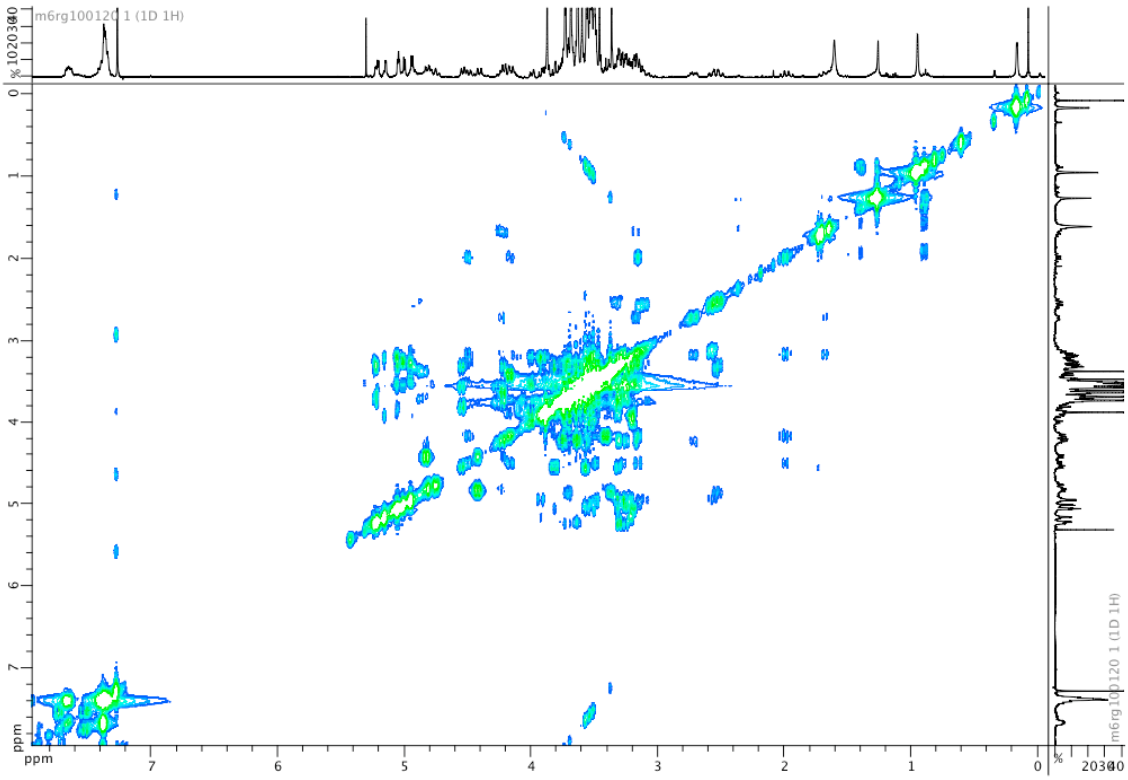
^{1}H-$^{13}C\{^{1}H\}$ HMQC spectrum of **10** recorded in $CDCl_3$ at 400.1 MHz.



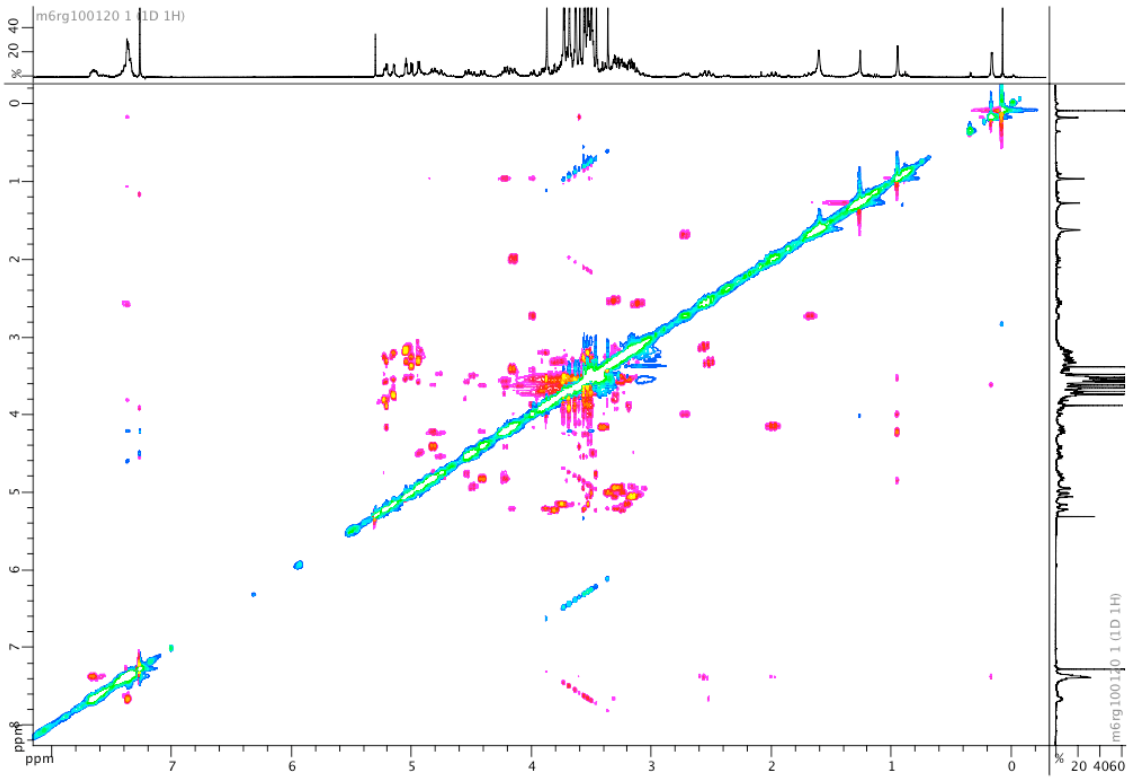
^{1}H NMR spectrum of **11** recorded in $CDCl_3$ at 400.1 MHz.



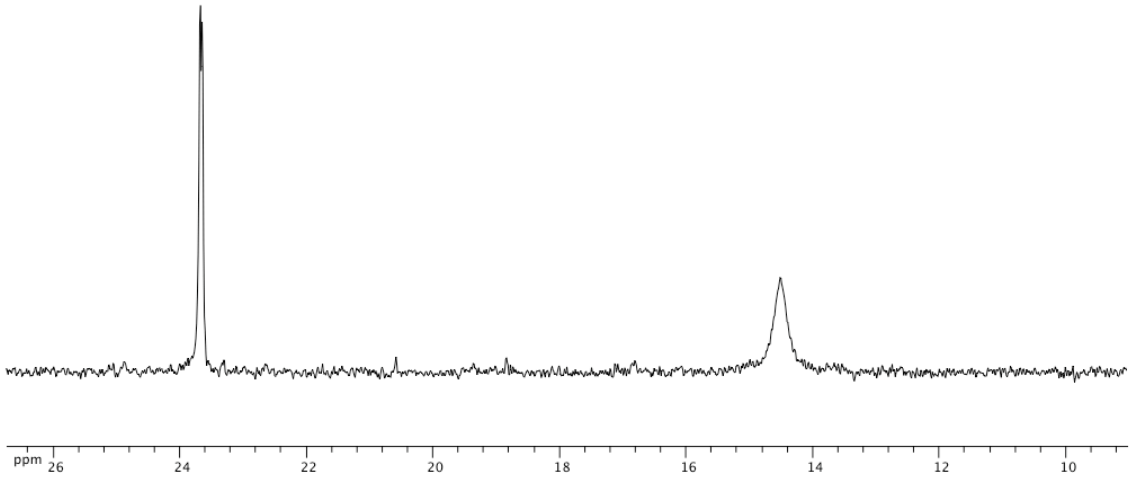
^{1}H-^{1}H COSY NMR spectrum of **11** recorded in $CDCl_3$ at 400.1 MHz.



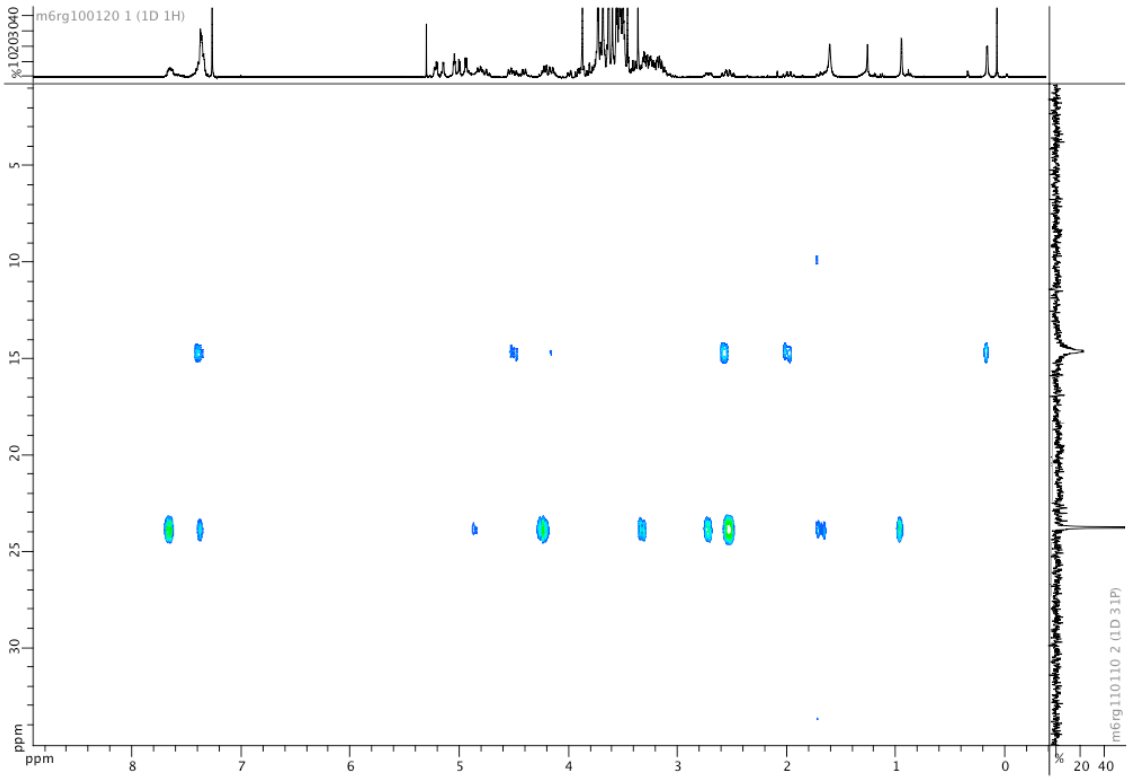
^{1}H-^{1}H TOCSY NMR spectrum of **11** recorded in $CDCl_3$ at 400.1 MHz.



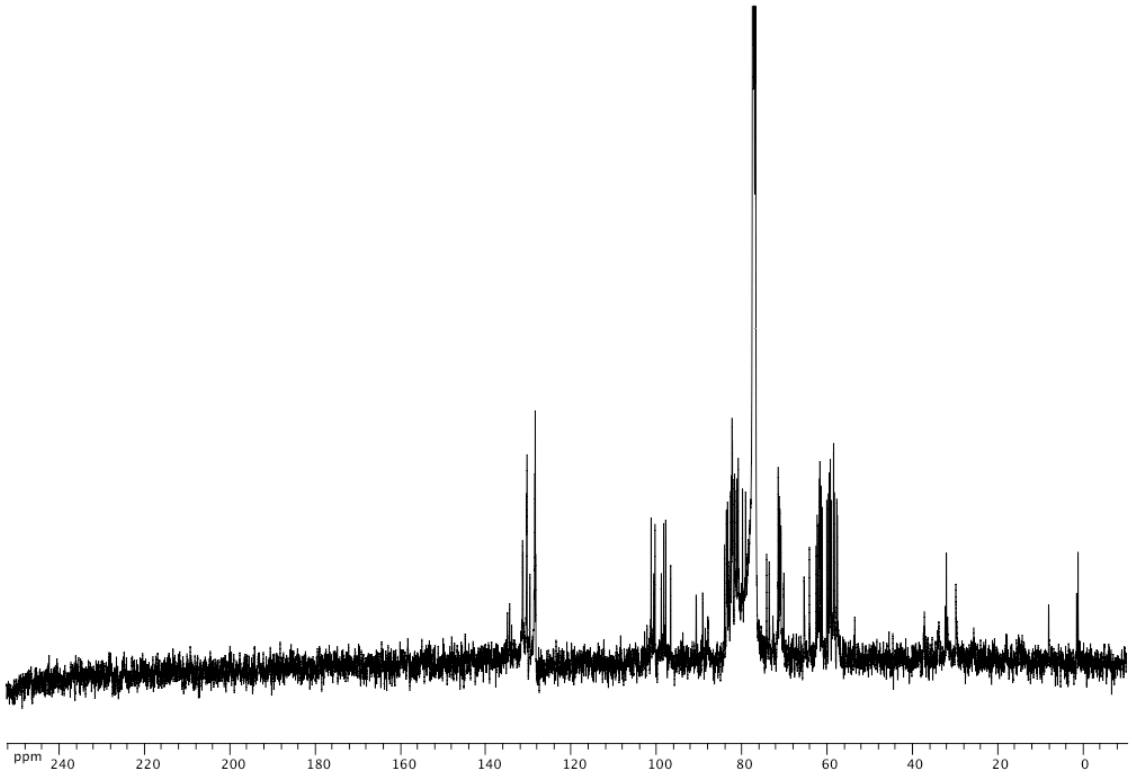
^{1}H-^{1}H ROESY NMR spectrum of **11** recorded in $CDCl_3$ at 400.1 MHz.



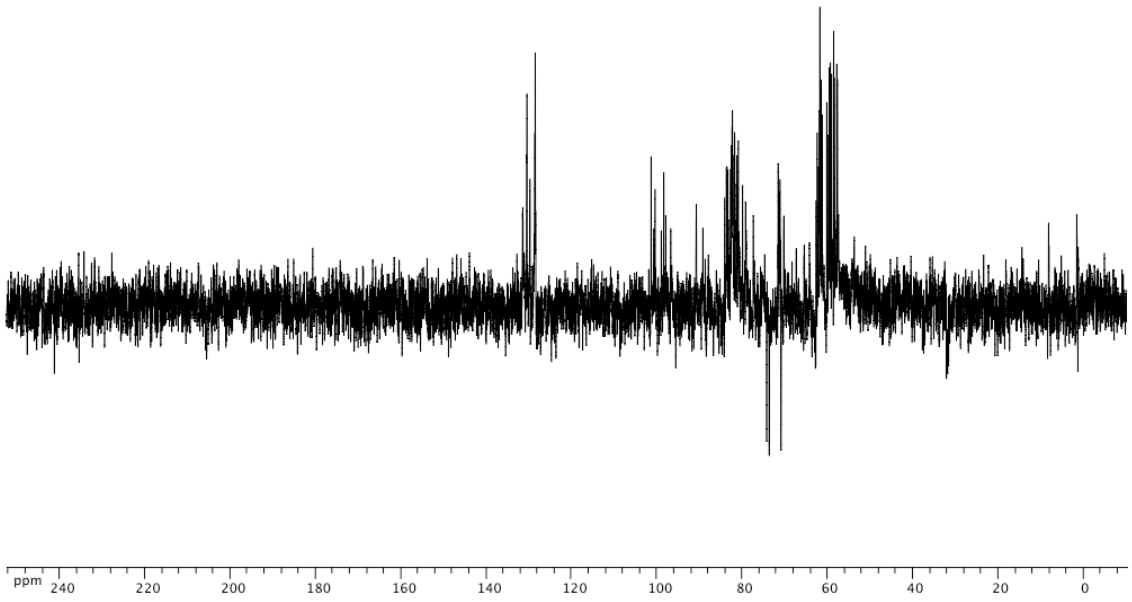
$^{31}P\{^{1}H\}$ NMR spectrum of **11** recorded in $CDCl_3$ at 162.0 MHz (298 K).



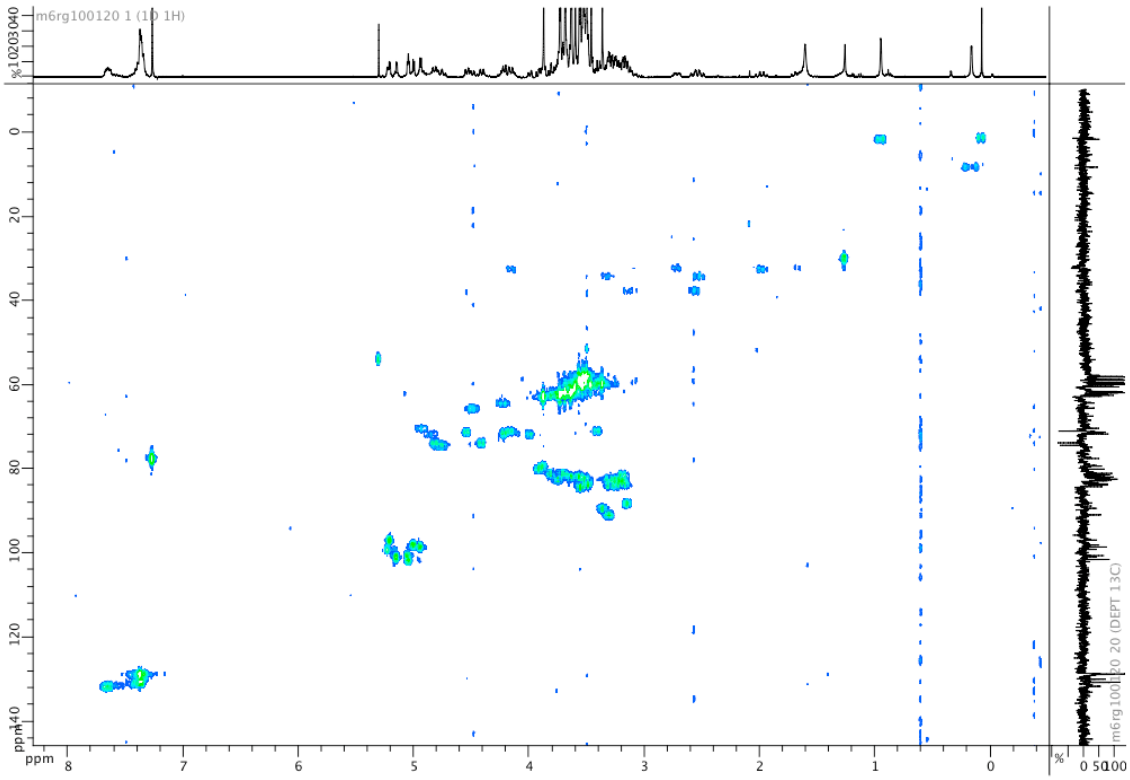
^{1}H-$^{31}P\{^{1}H\}$ NMR spectrum of **11** recorded in $CDCl_3$ at 400.1 MHz.



$^{13}C\{^{1}H\}$ NMR spectrum of **11** recorded in $CDCl_3$ at 100.6 MHz.



DEPT135 spectrum of **11** recorded in $CDCl_3$ at 100.6 MHz.



^{1}H-^{13}C{^{1}H} HMQC spectrum of **11** recorded in $CDCl_3$ at 400.1 MHz.

General procedure for full assignment of the ^{1}H NMR signals of the glucose units.

The strategy applied for full structural assignment began with the differentiation between capped and non-capped C-6 carbon atoms by DEPT 135. These appear as two distinct sets of signals. The H-6 protons could then be identified using ^{1}H-^{13}C HMQC (Heteronuclear Multiple Quantum Coherence spectroscopy). By using TOCSY (TOtal Correlation SpectroscopY) and COSY (COrrelated SpectroscopY), each H-6 proton was correlated to the set of protons belonging to the same glucose residue. The connectivity between individual glucose units was then established via a ROESY (Rotating frame Overhauser Effect SpectroscopY) experiment showing the proximity between H-4$_N$ and H-1$_{N+1}$ protons (N and N+1 standing for neighbouring glucose moieties labeled in the alphabetical order).