Isonitrile ruthenium and iron PNP complexes: Synthesis, characterization and catalytic assessment for base-free dehydrogenative coupling of alcohols.

Duc Hanh Nguyen,[a] Delphine Merel,[a] Nicolas Merle,[a] Xavier Trivelli,[b] Frédéric Capet[a] and Régis M. Gauvin*[,c].

[a] Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

[b] Université de Lille, CNRS, INRA, Centrale Lille Institute, Univ. Artois, FR 2638 - IMEC - Institut Michel-Eugène Chevreul, F-59000 Lille, France

[c] Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France.

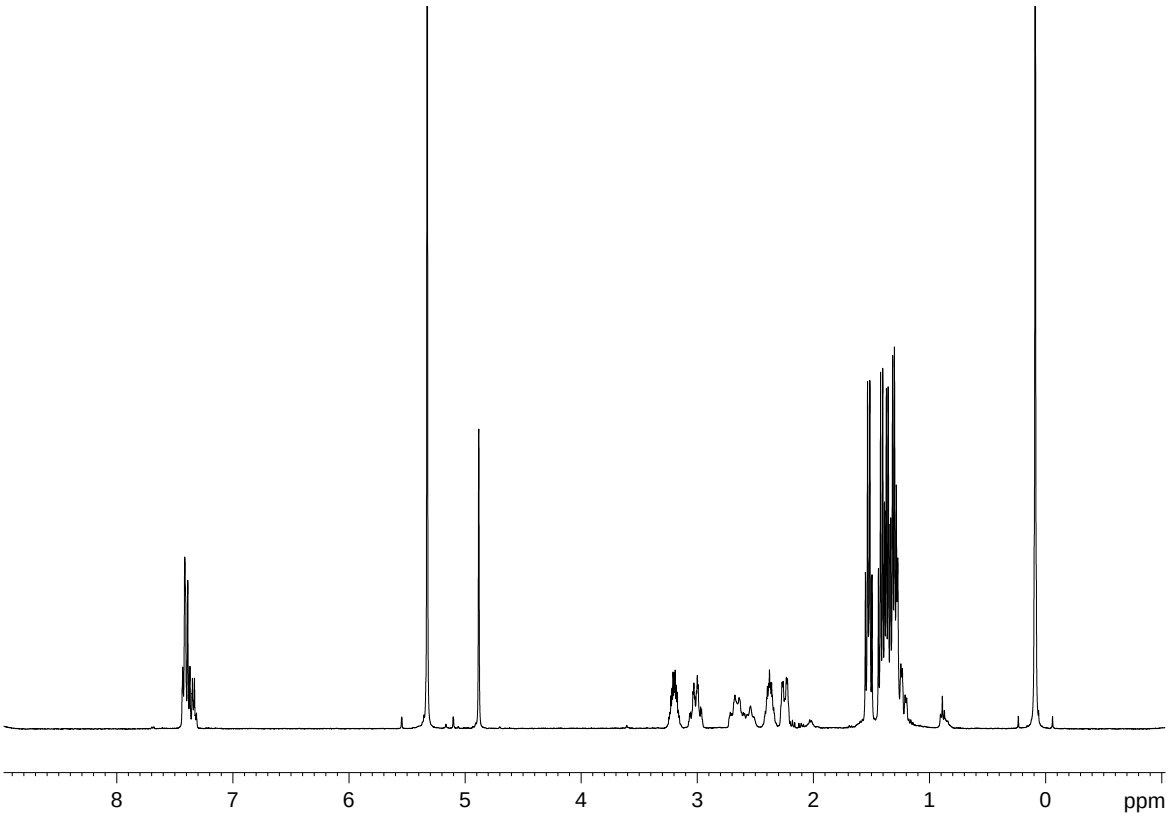
E-mail : regis.gauvin@chimieparistech.psl.eu

Electronic Supplementary Information

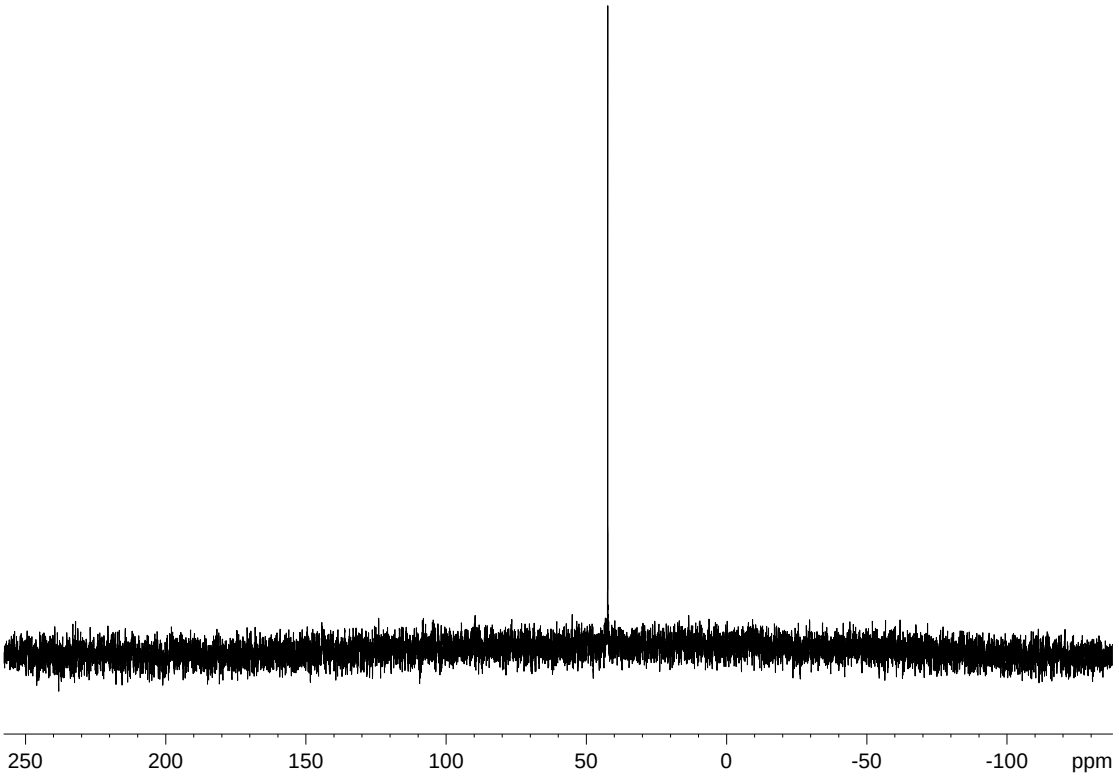
Table of contents

SI. NMR spectra of [Ru(Cl)$_2$(CN-CH$_2$Ph)(NH(CH$_2$CH$_2$P(*i*Pr)$_2$)$_2$)] 1a

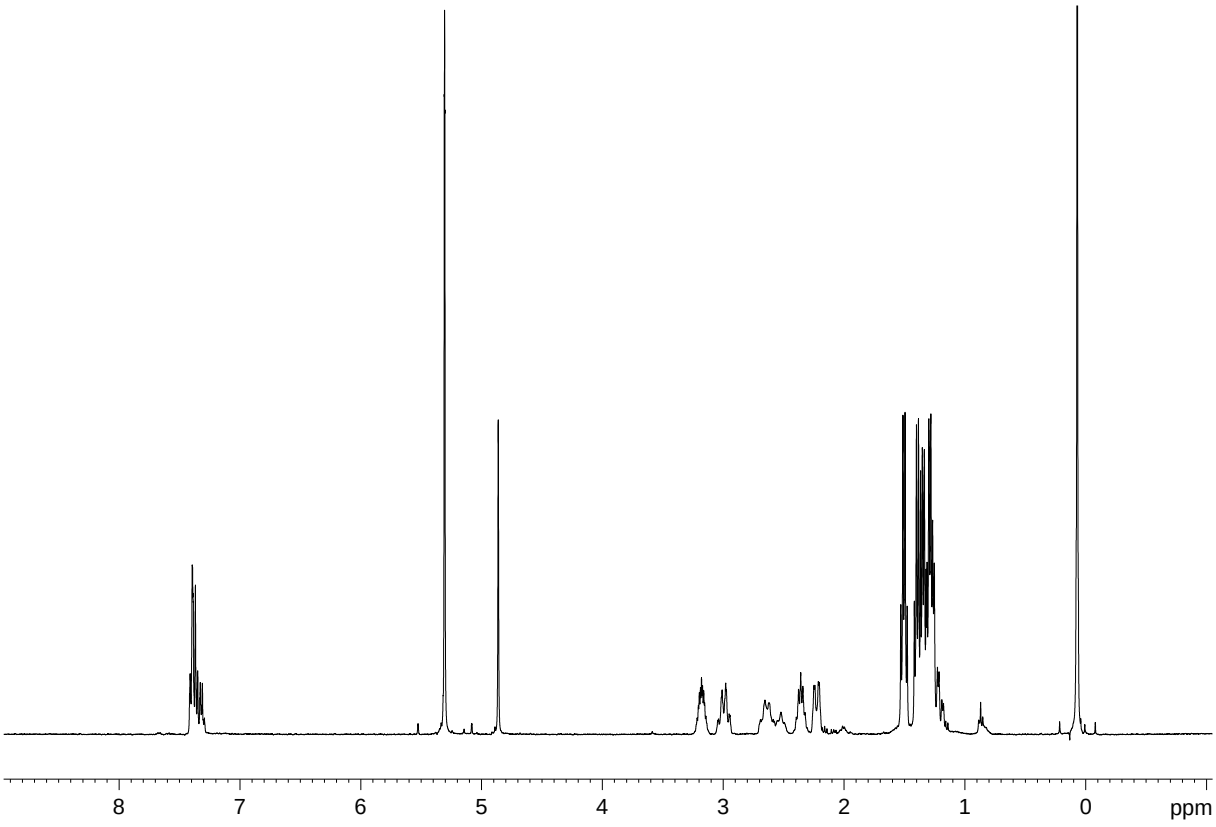
^{1}H NMR spectrum (CD_2Cl_2, 298 K).



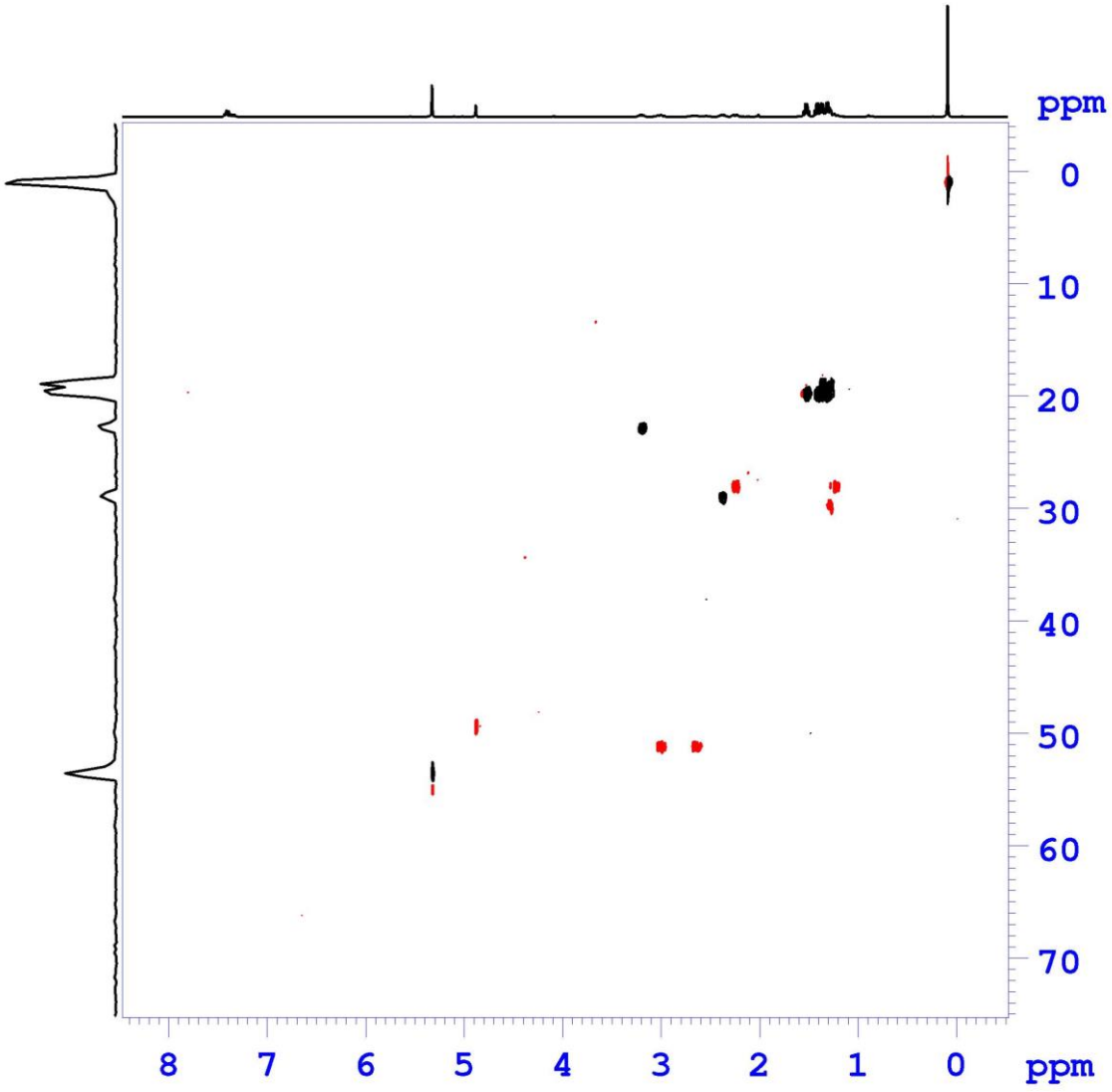
^{31}P{^{1}H} NMR spectrum (CD_2Cl_2, 298 K).

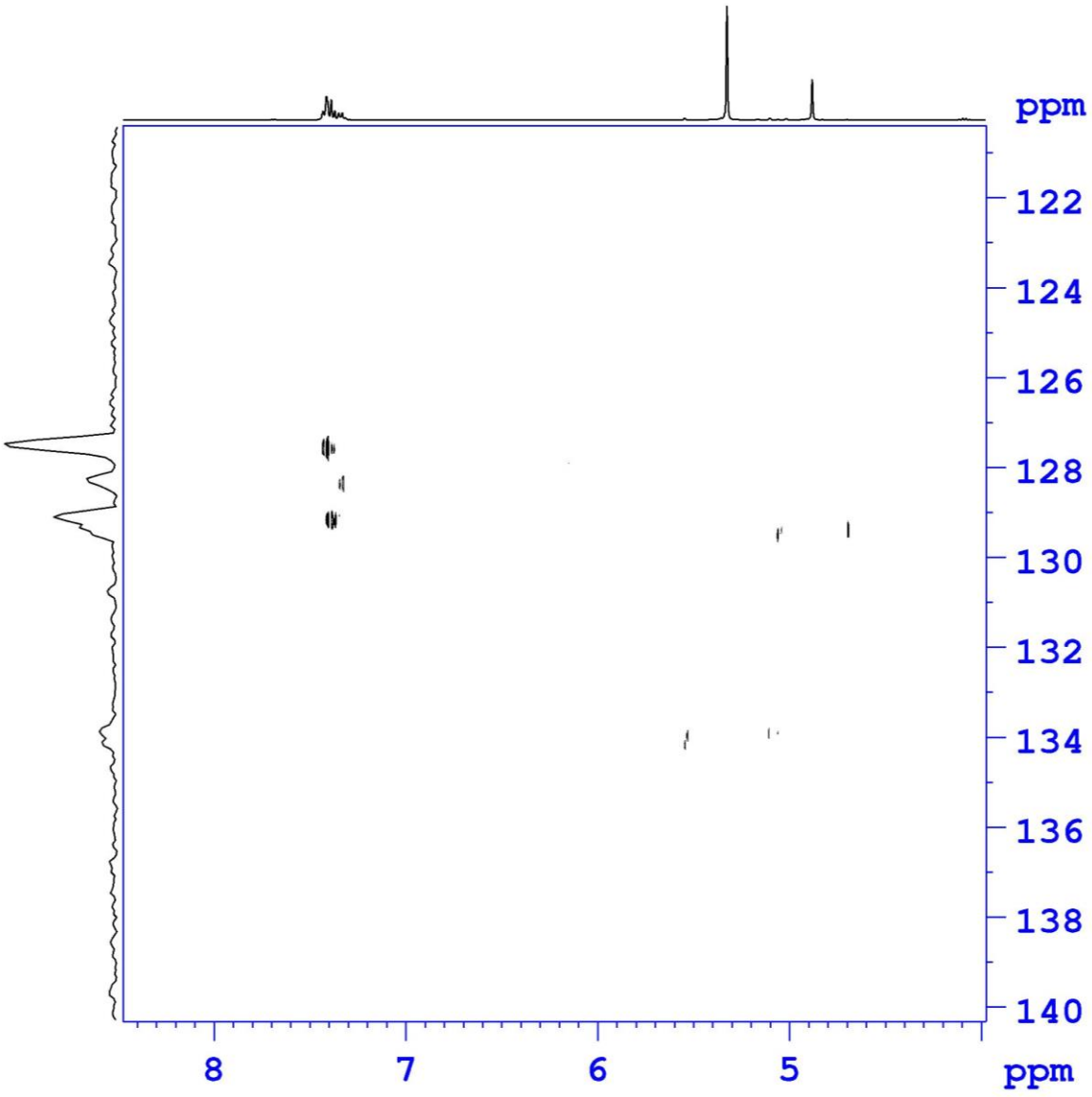


$^{1}H\{^{31}P\}$ NMR spectrum (CD_2Cl_2, 298 K).

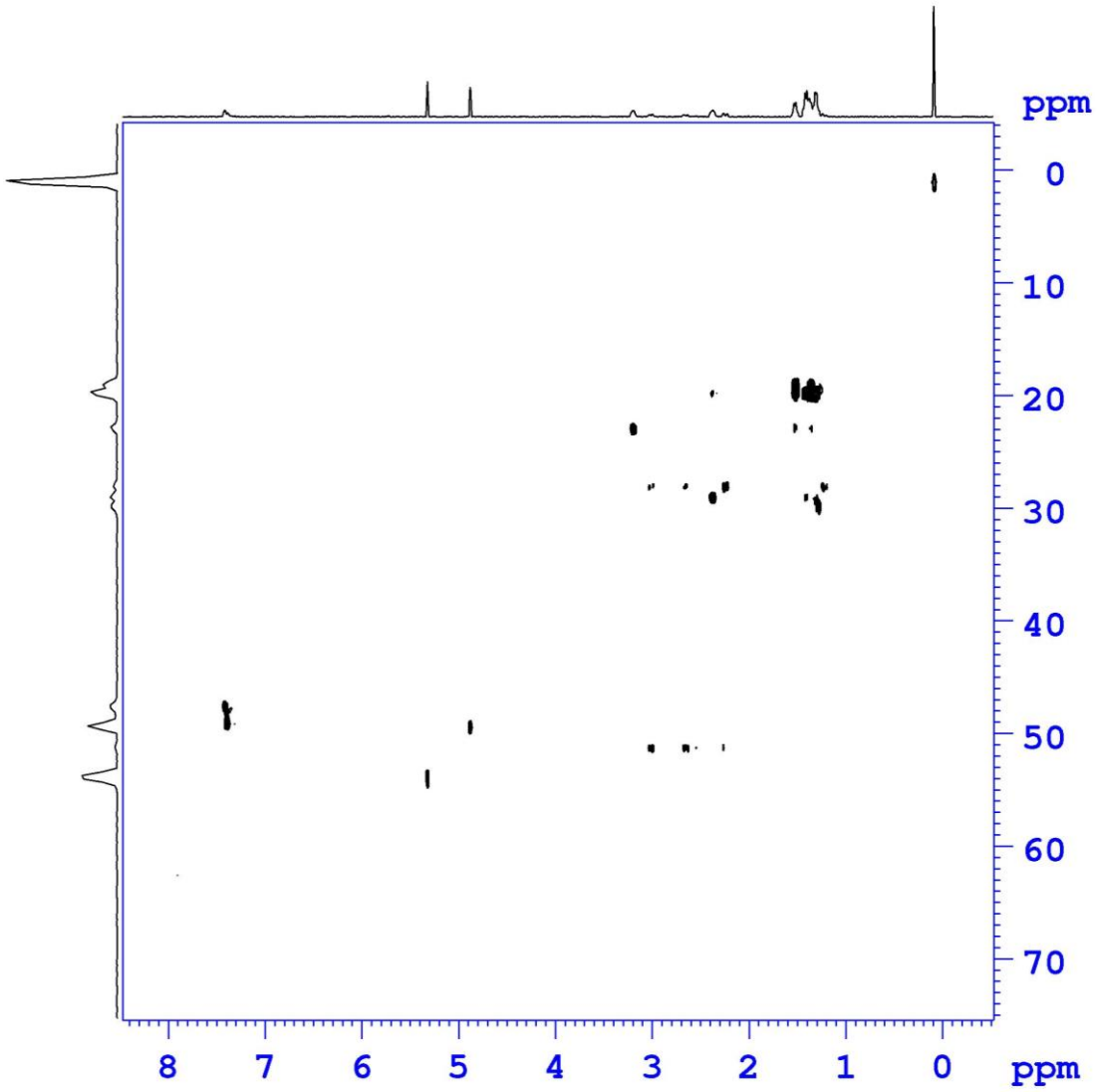


^{1}H-^{13}C 2D HSQC NMR spectrum (CD_2Cl_2, 298 K).

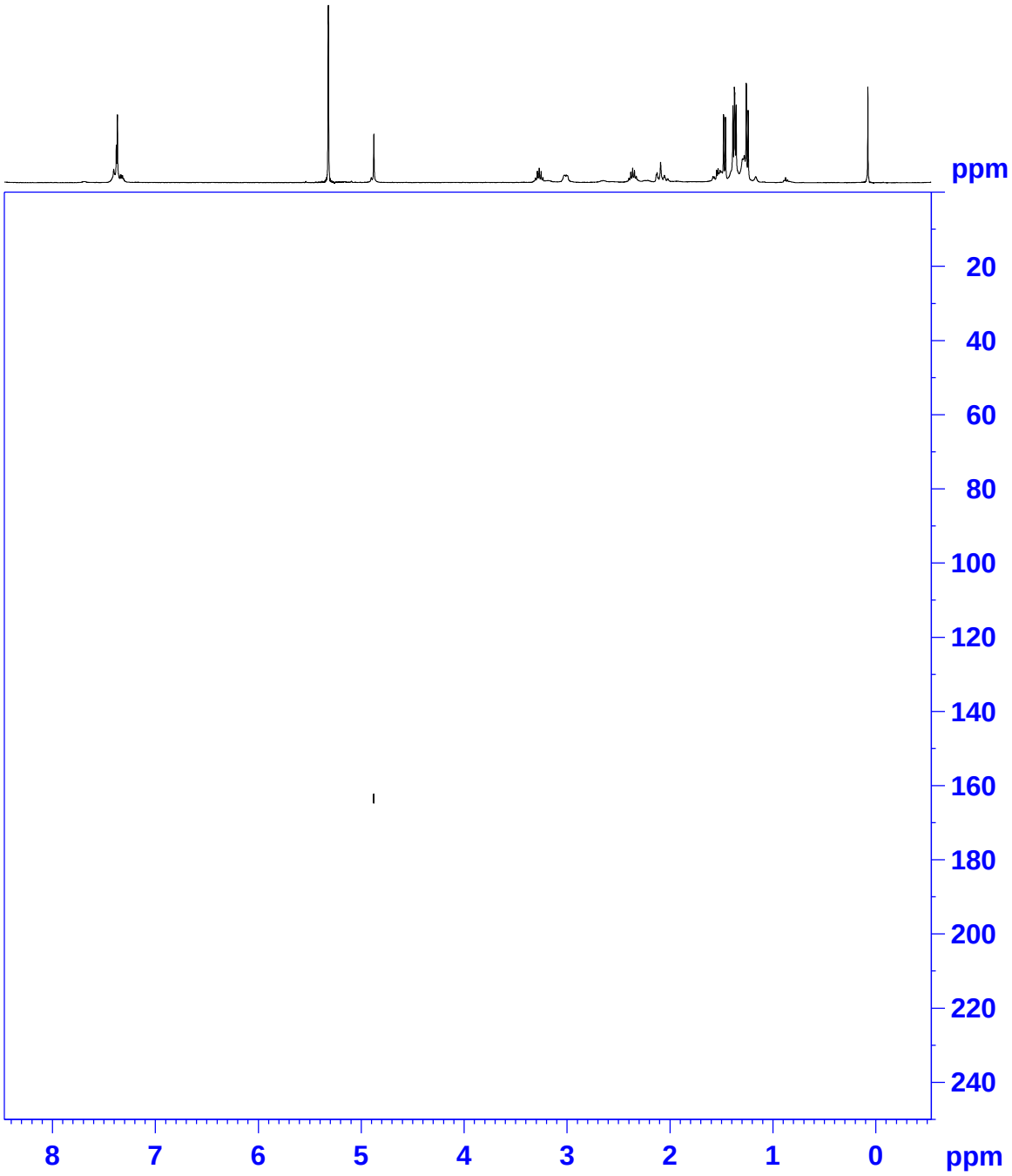



ppm
122
124
126
128
130
132
134
136
138
140
8
7
6
5
ppm

^{1}H-^{13}C 2D HSQC-TOCSY NMR spectrum (CD_2Cl_2, 293K).

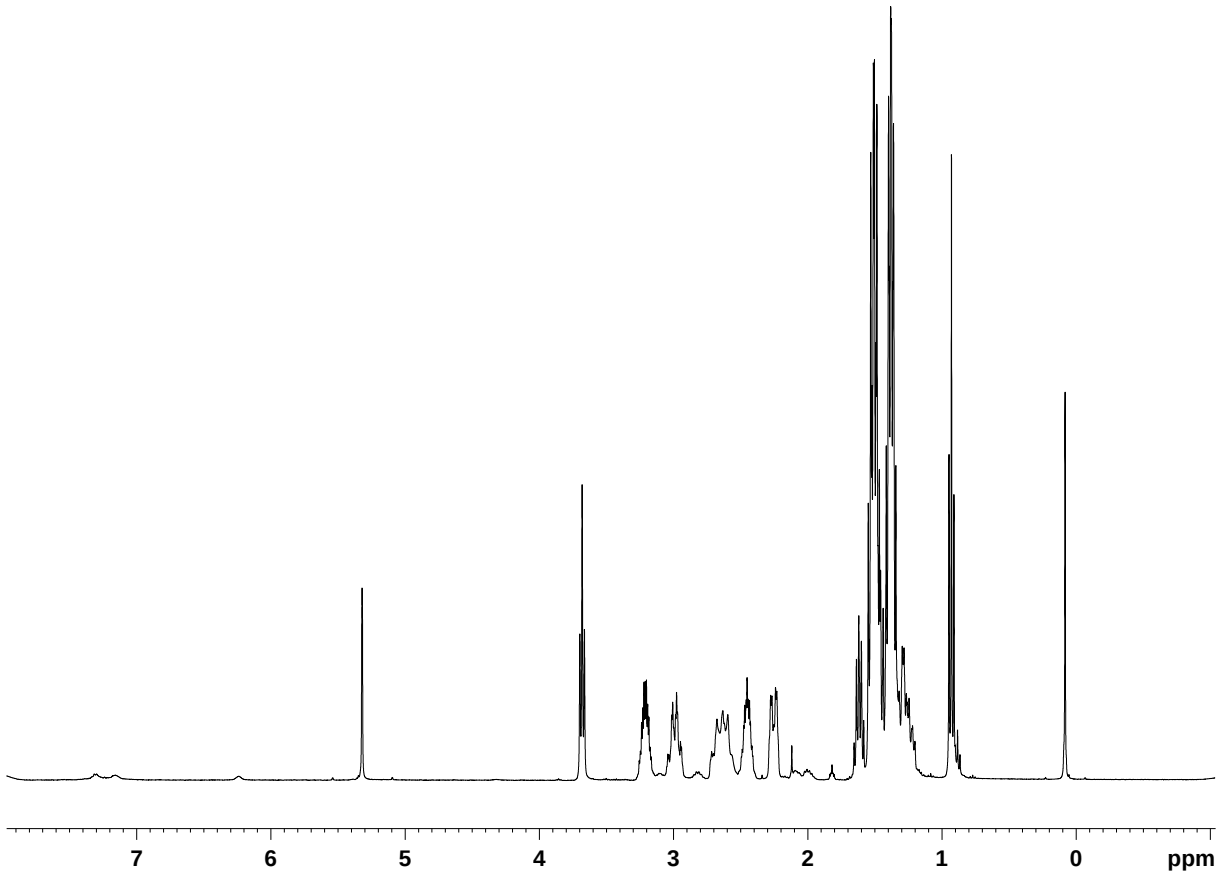


^{1}H-^{15}N 2D NMR HMBC spectrum (CD_2Cl_2, 298 K).

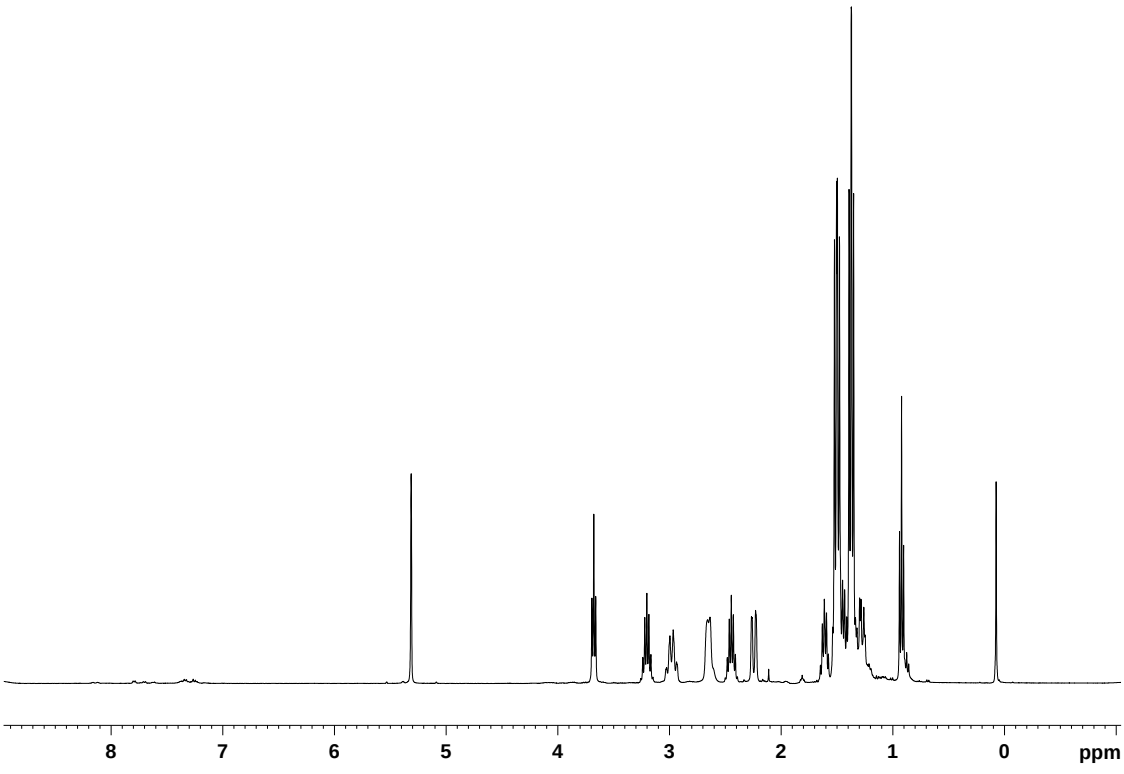


SII. NMR spectra of $[Ru(Cl)_2(CN\text{-}n\text{Bu})\{NH(CH_2CH_2P(iPr)_2)_2\}]$ 1b

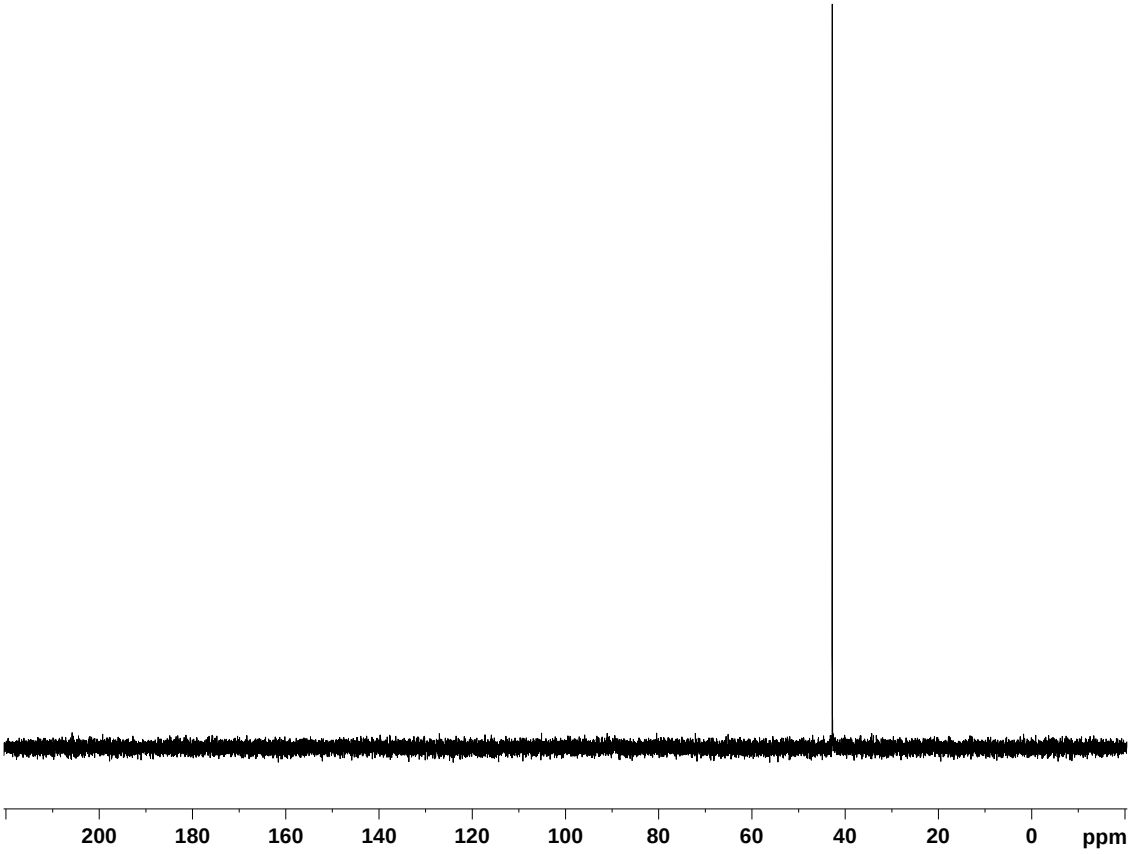
^1H NMR spectrum (CD_2Cl_2, 300 K).



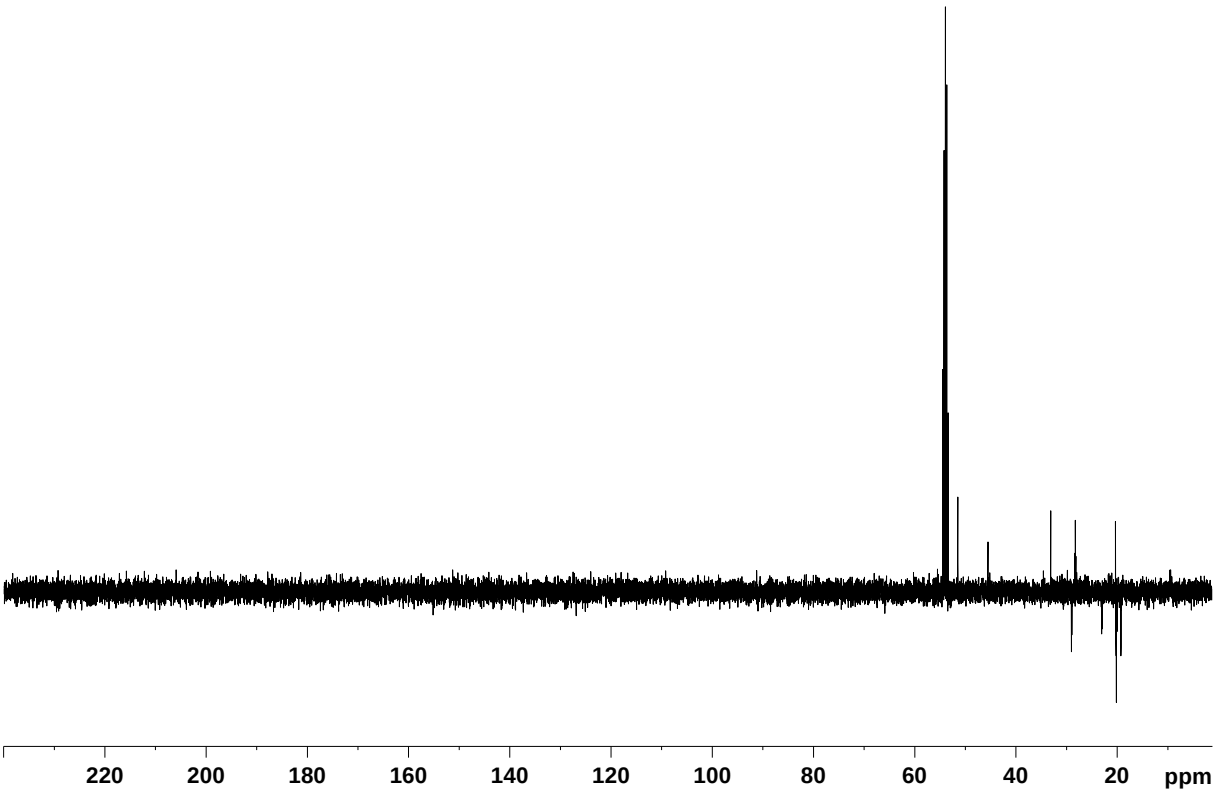
$^1H\{^{31}P\}$ NMR spectrum (CD_2Cl_2, 300 K).



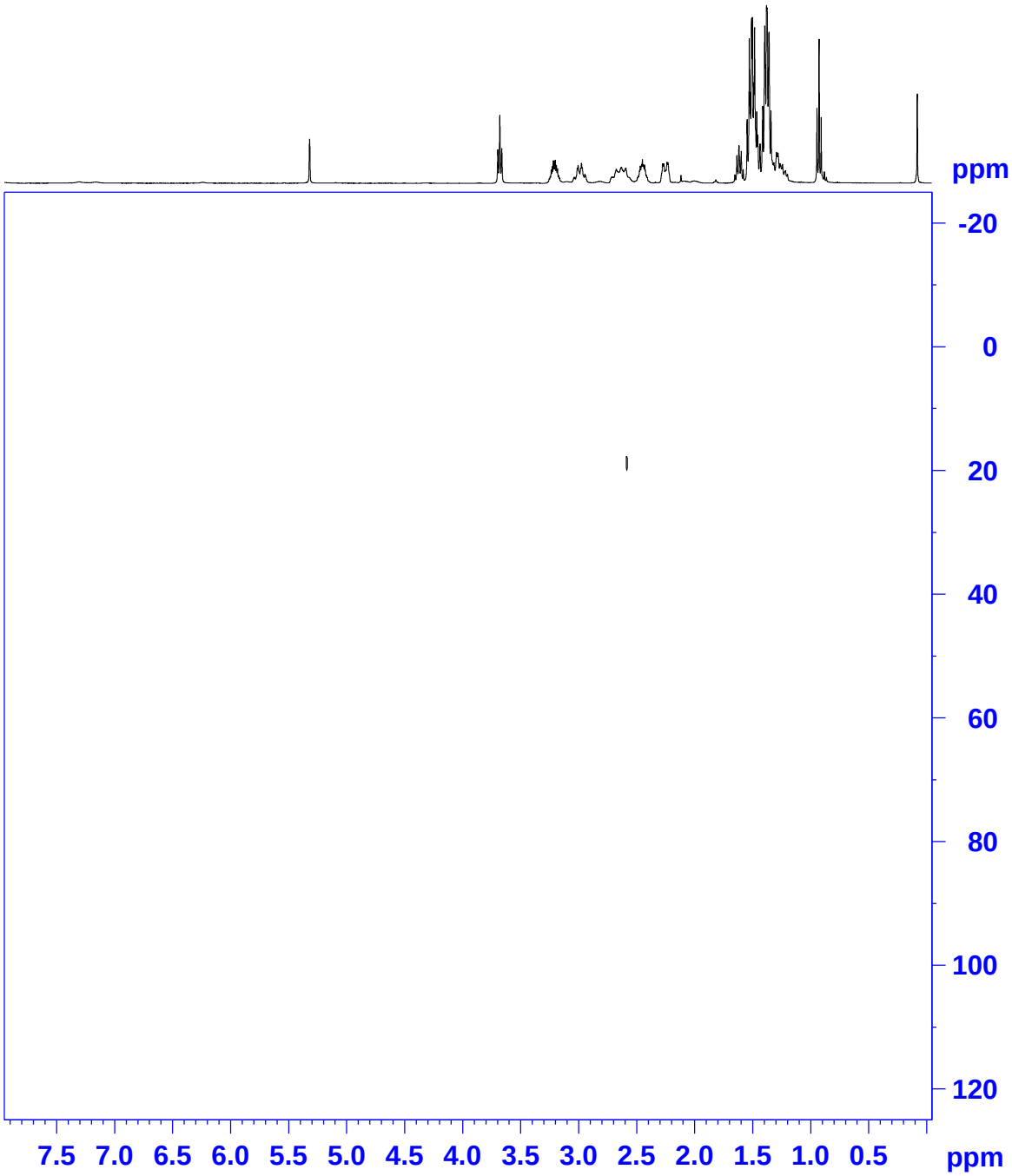
$^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 300 K).



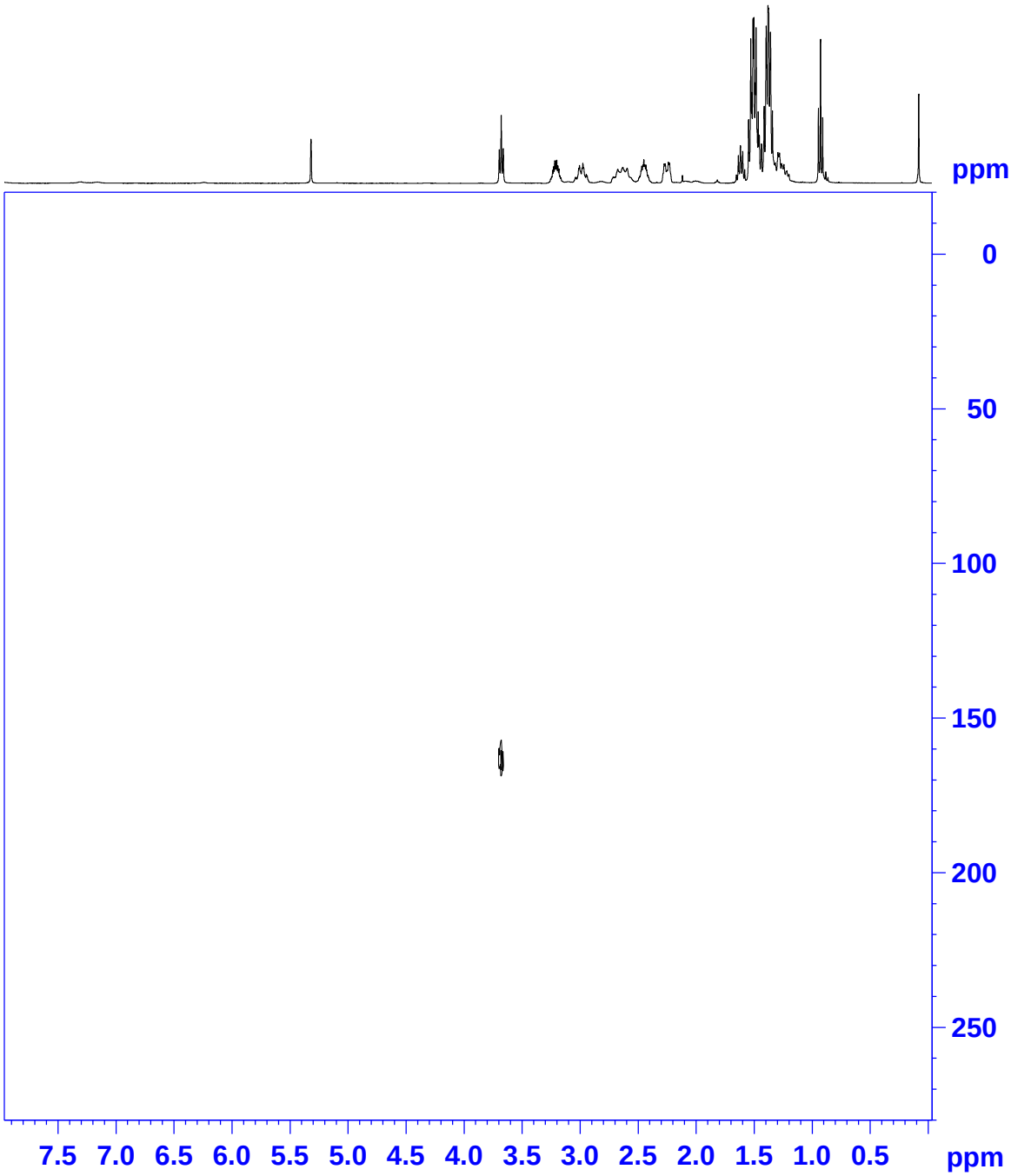
$^{13}C\{^{1}H\}$ JMOD NMR spectrum (CD_2Cl_2, 300 K).



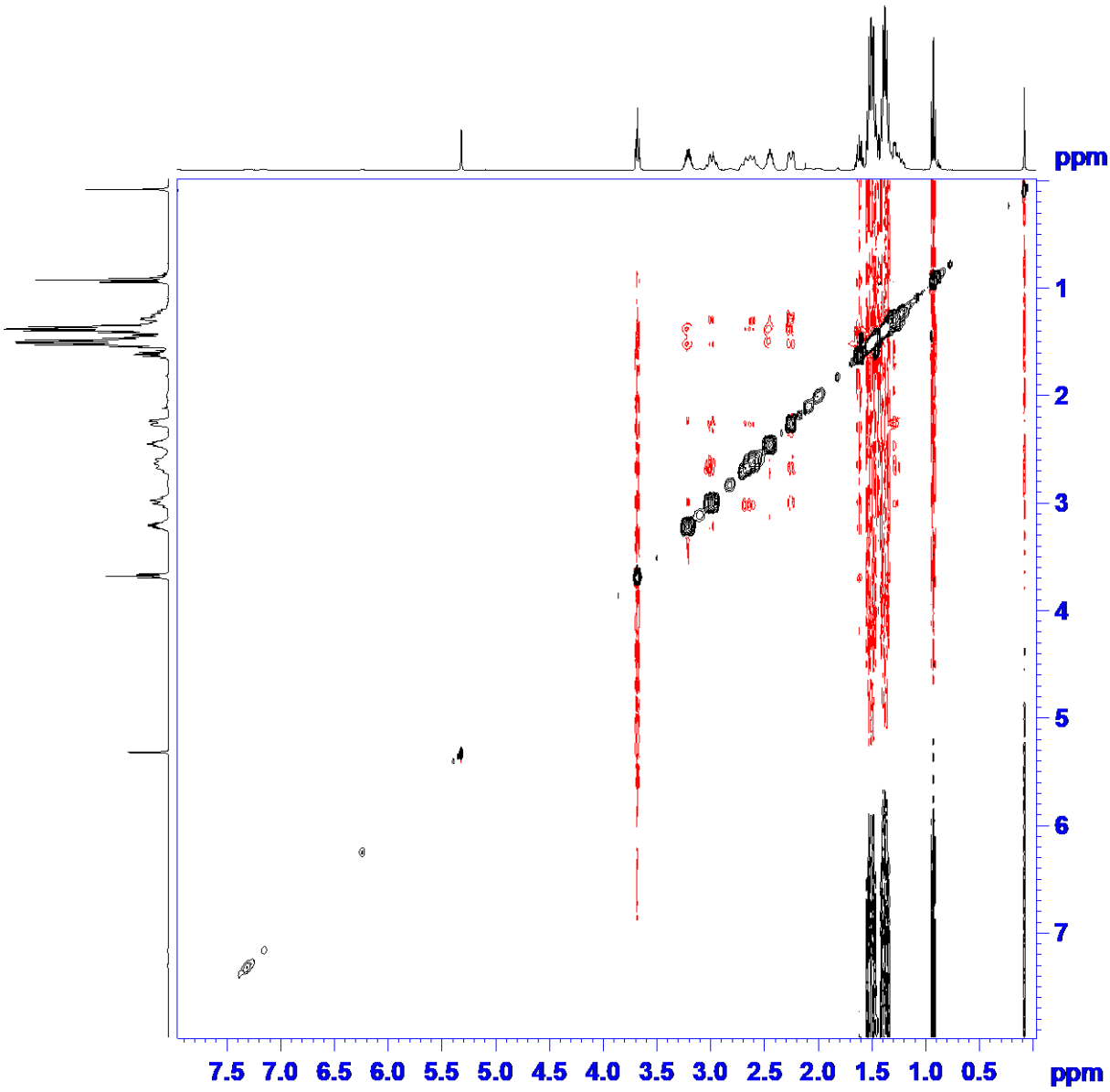
2D ^{1}H-^{15}N HSQC NMR spectrum (CD_2Cl_2, 300 K).



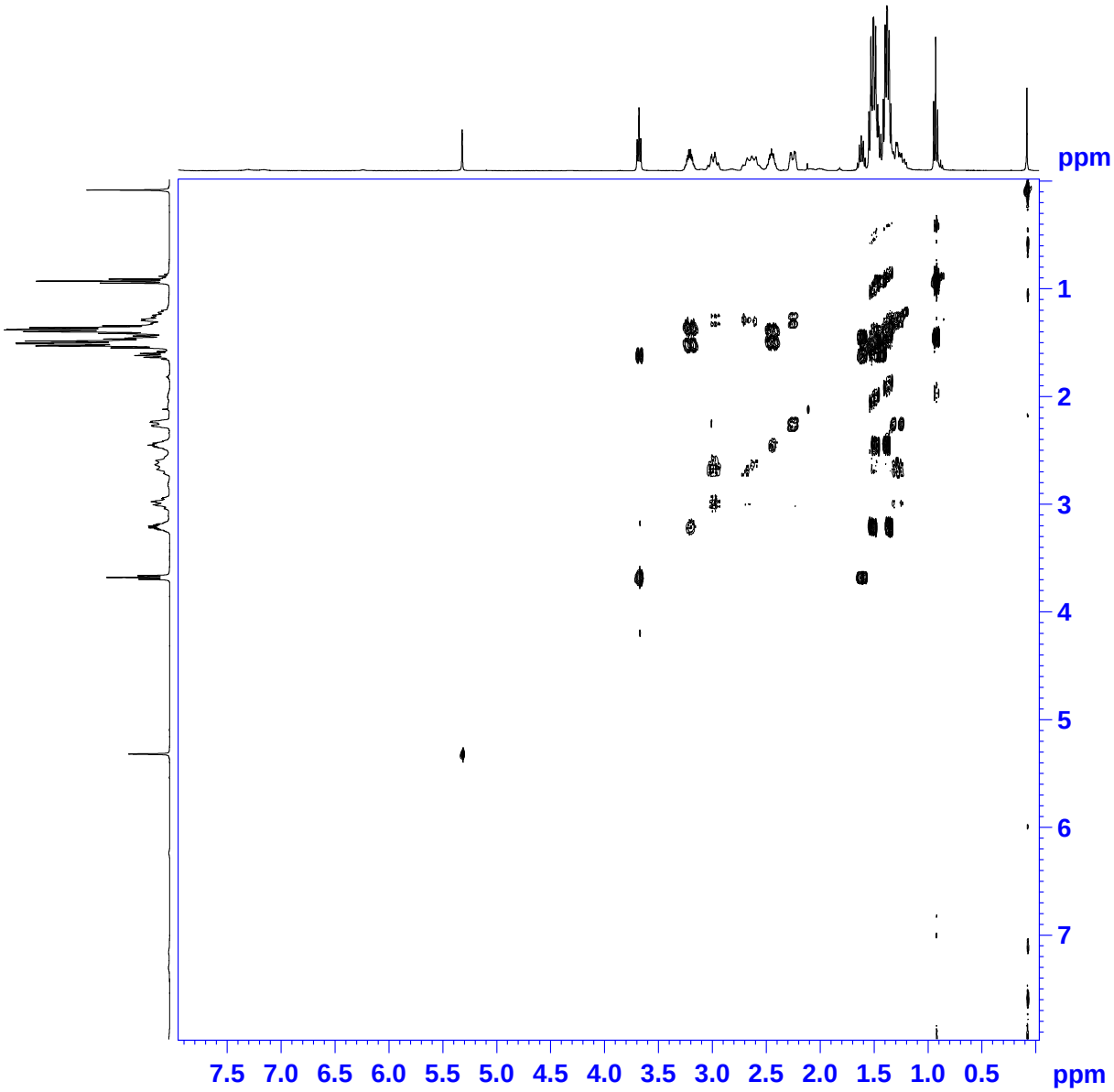
2D ^{1}H-^{15}N HMBC NMR (CD_2Cl_2, 300 K).



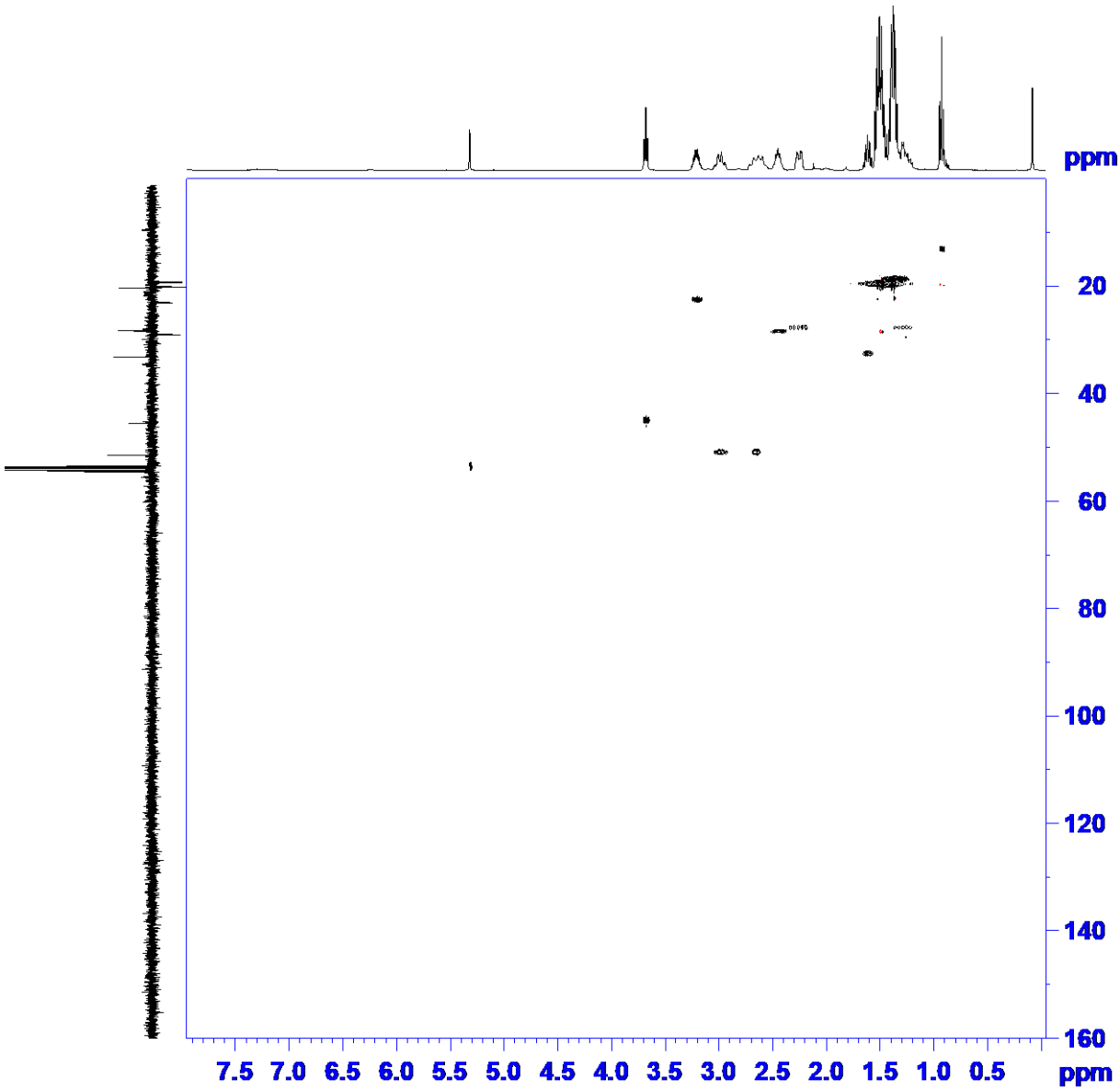
2D ^{1}H-^{1}H NOESY NMR (CD_2Cl_2, 300 K).



2D ^{1}H-^{1}H COSY NMR (CD_2Cl_2, 300 K).

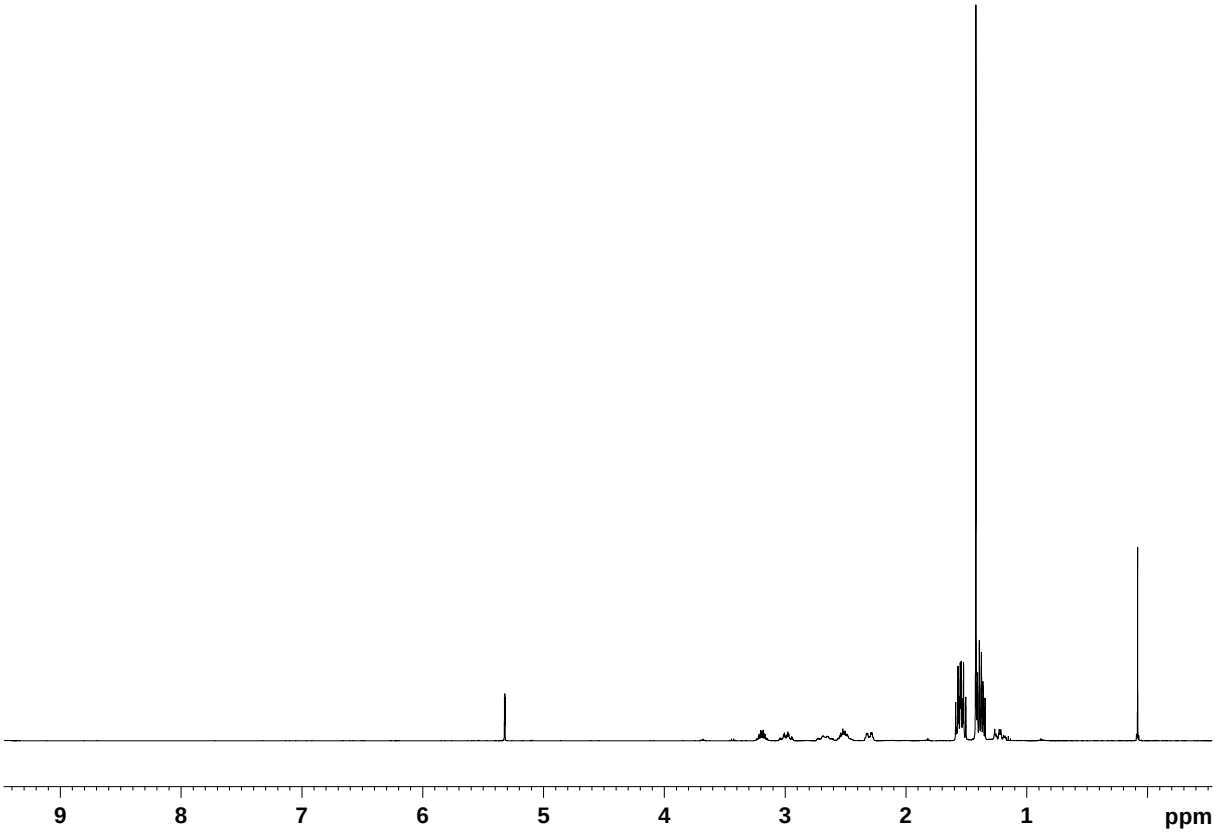


2D ^{1}H-^{13}C HSQC NMR (CD_2Cl_2, 300 K).

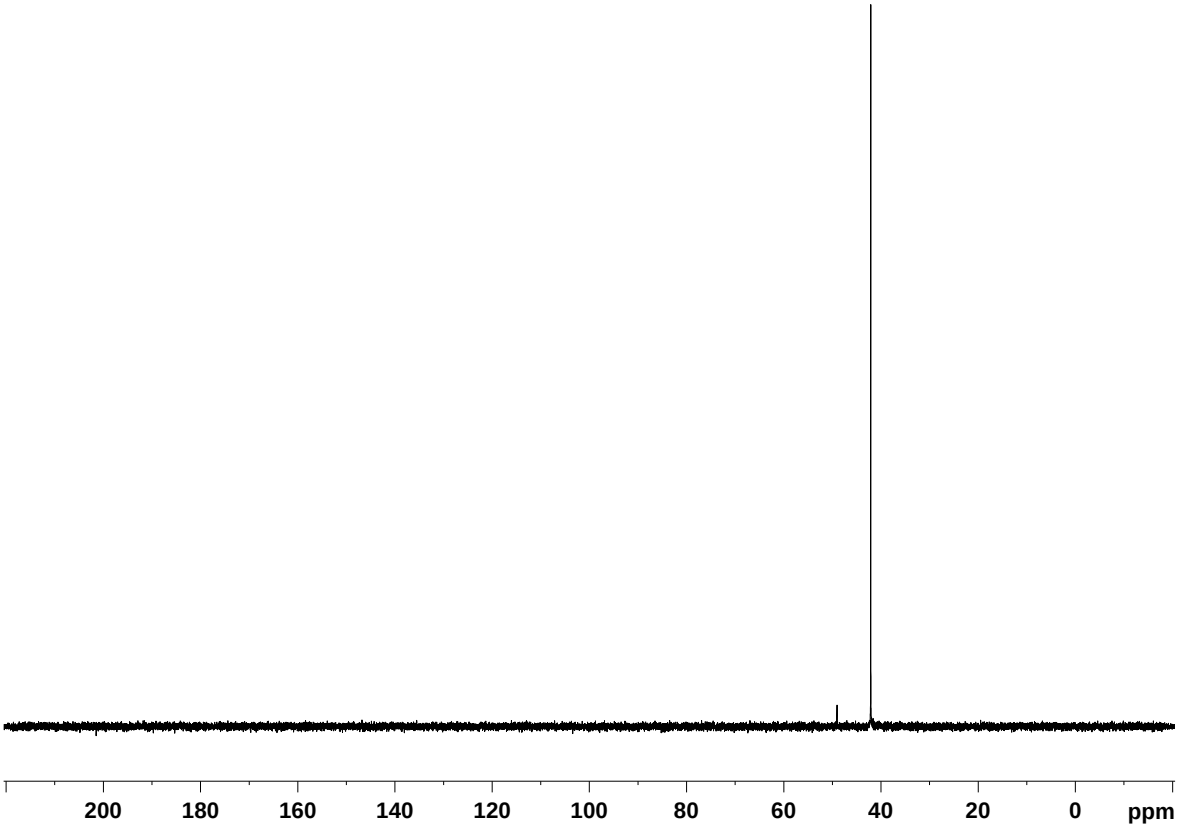


SIII. NMR spectra of [Ru(Cl)$_2$(CN-*t*Bu){NH(CH$_2$CH$_2$P(*i*Pr)$_2$)$_2$}] (1c)

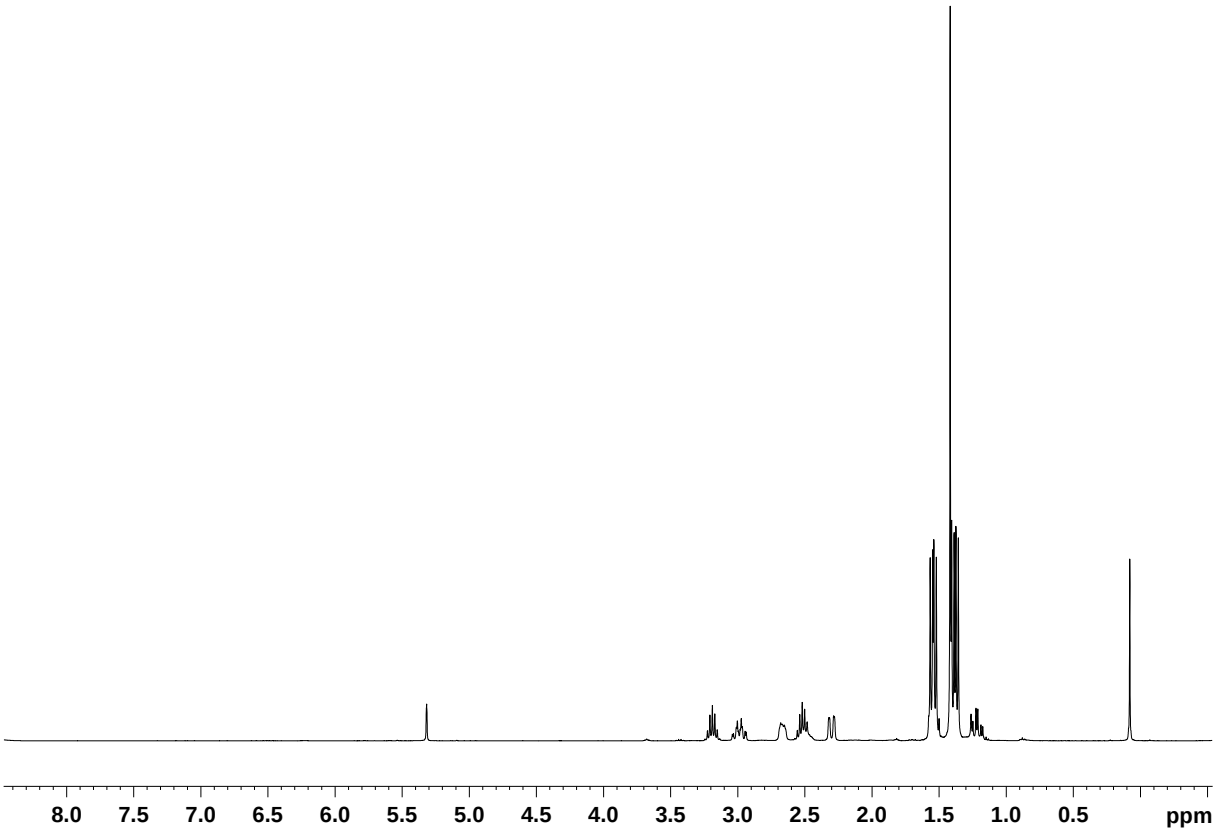
^{1}H NMR spectrum (C_6D_6, 300 K).



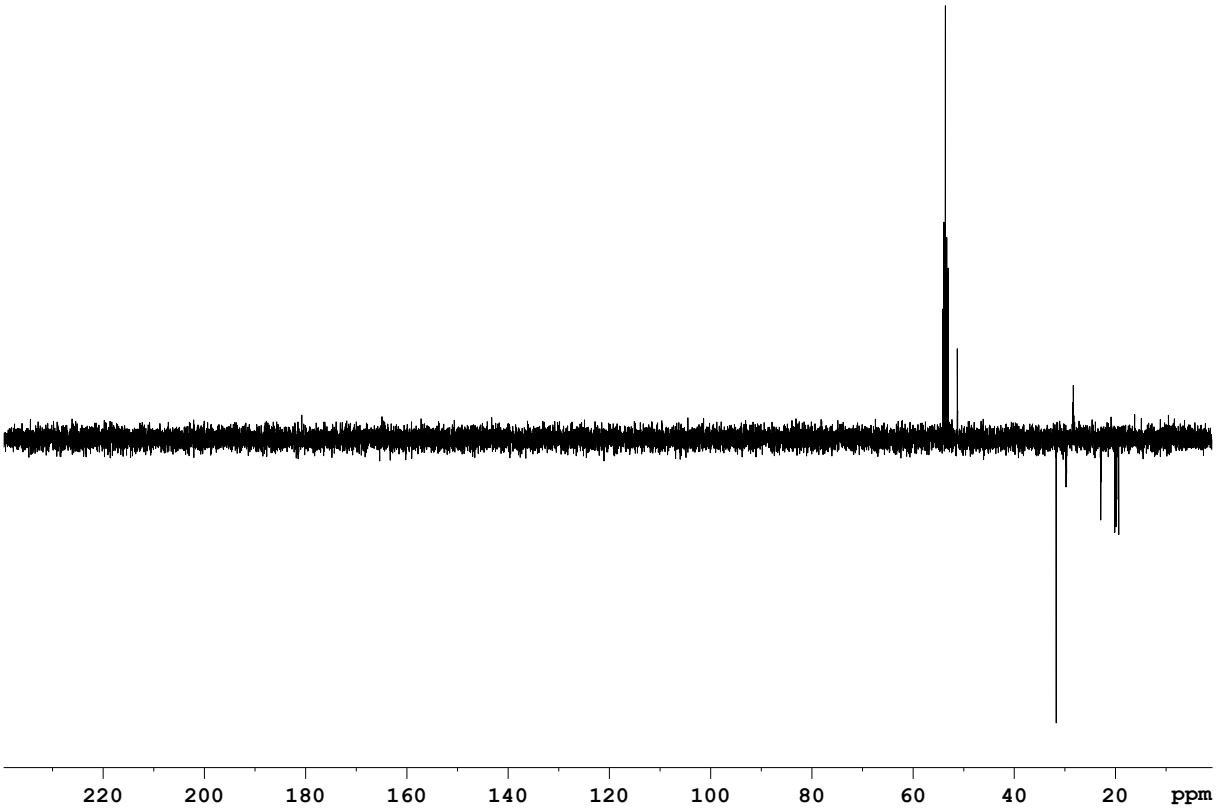
^{31}P{^{1}H} NMR spectrum (C_6D_6, 300 K).



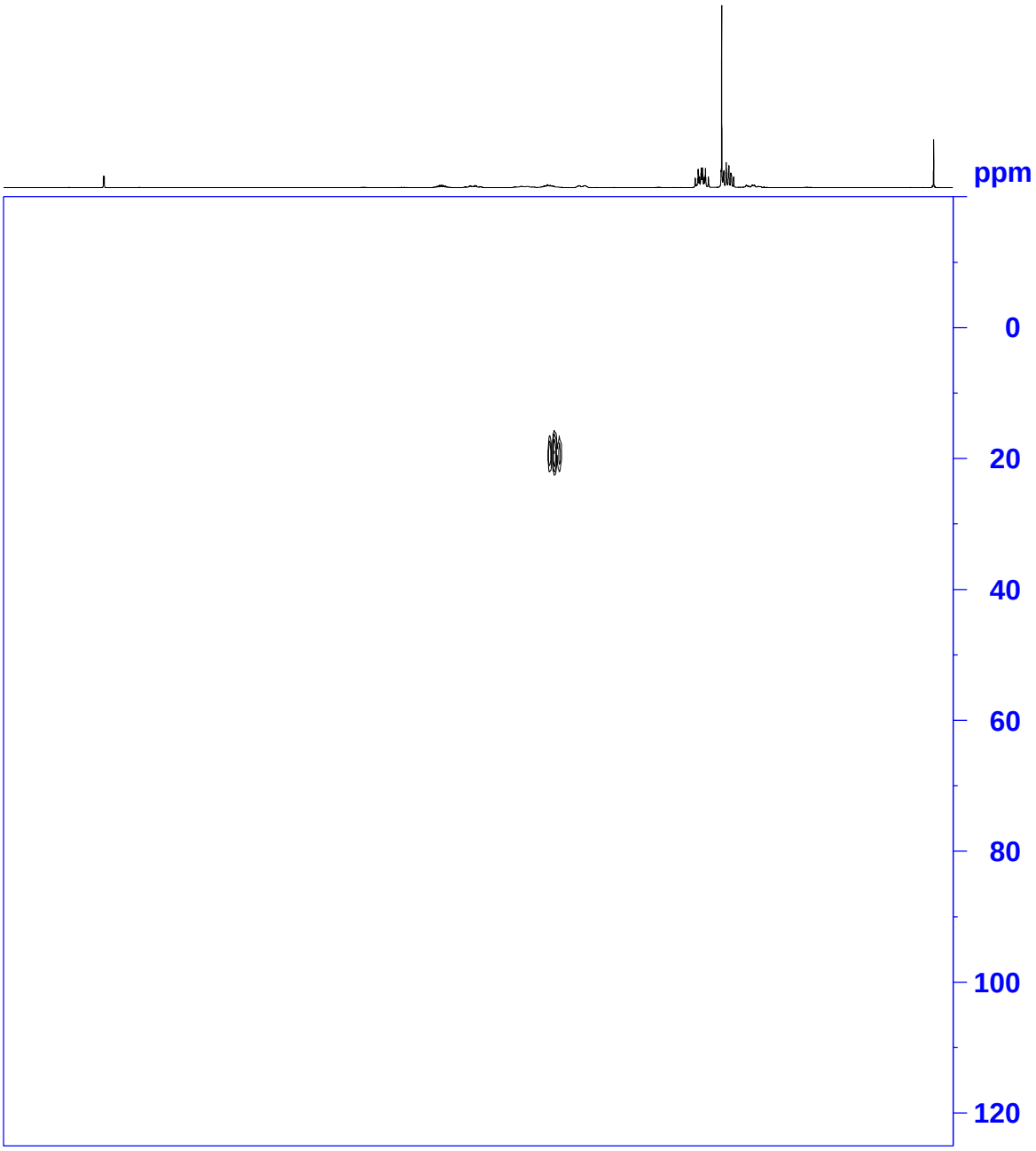
$^{1}H\{^{31}P\}$ NMR spectrum (C_6D_6, 300 K).



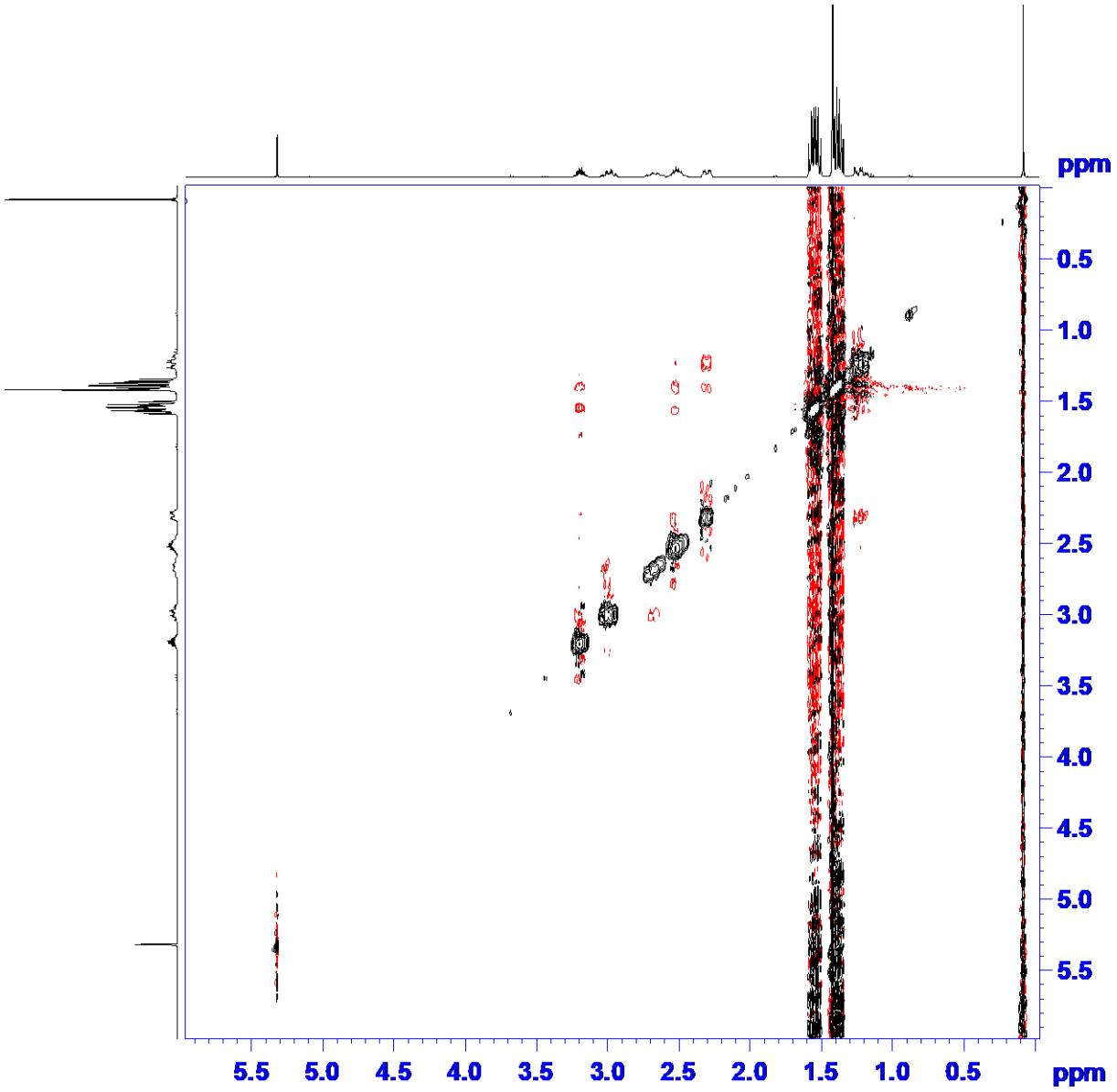
$^{13}C\{^{1}H\}$ JMOD NMR spectrum (C_6D_6, 300 K).



2D ^{1}H-^{15}N HSQC NMR spectrum (C_6D_6, 300 K).

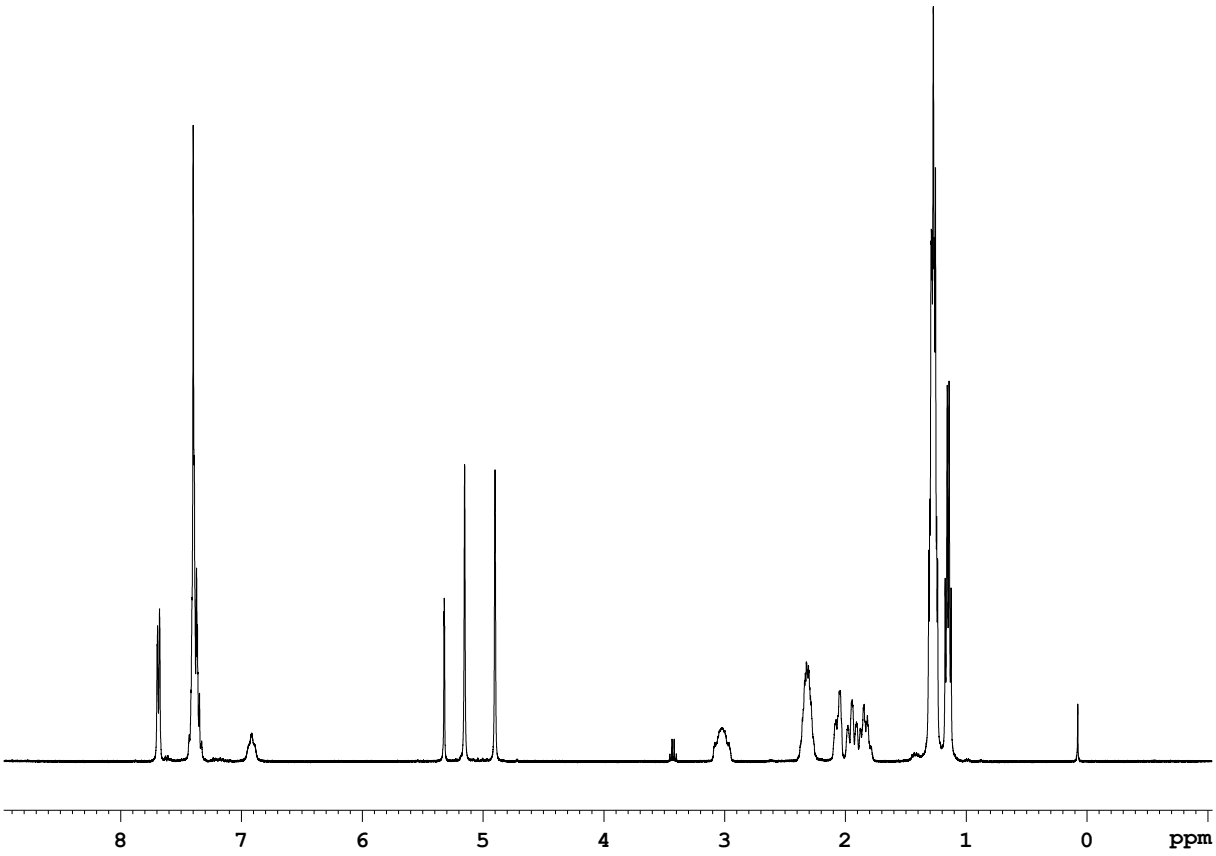


2D ^{1}H-^{1}H NOESY NMR spectrum (C_6D_6, 300 K).

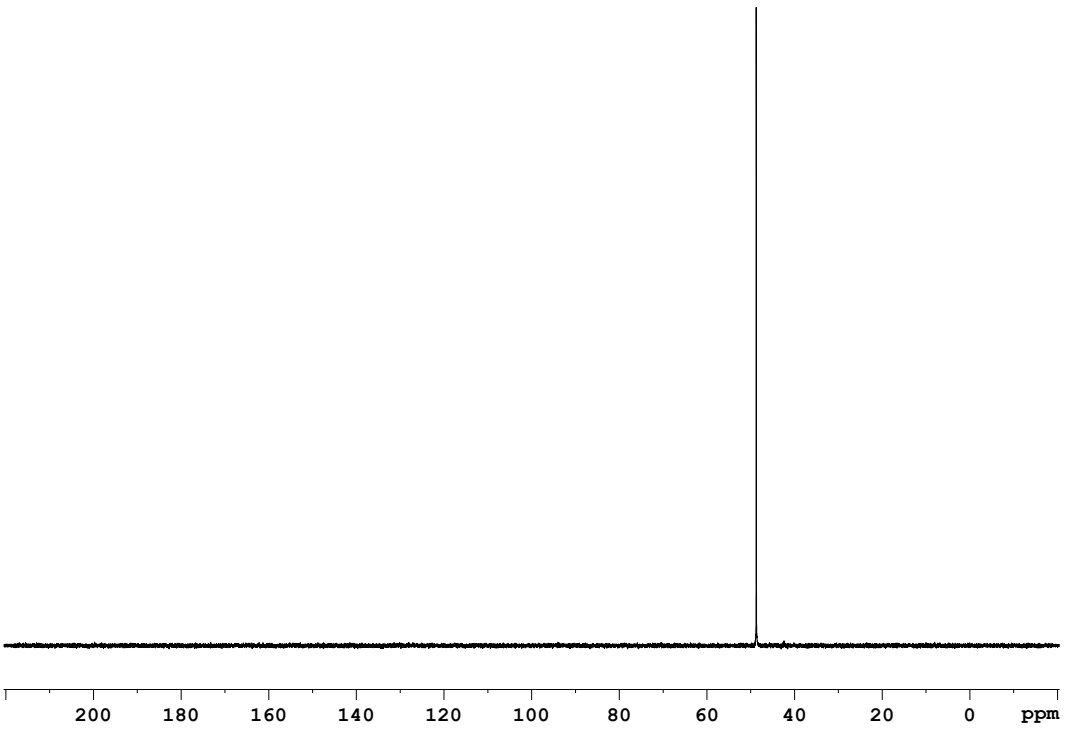


SIV. NMR spectra of [Ru(Cl)(CN-$CH_2Ph)_2$($NH(CH_2CH_2P(iPr)_2)_2$)](Cl) (2a)

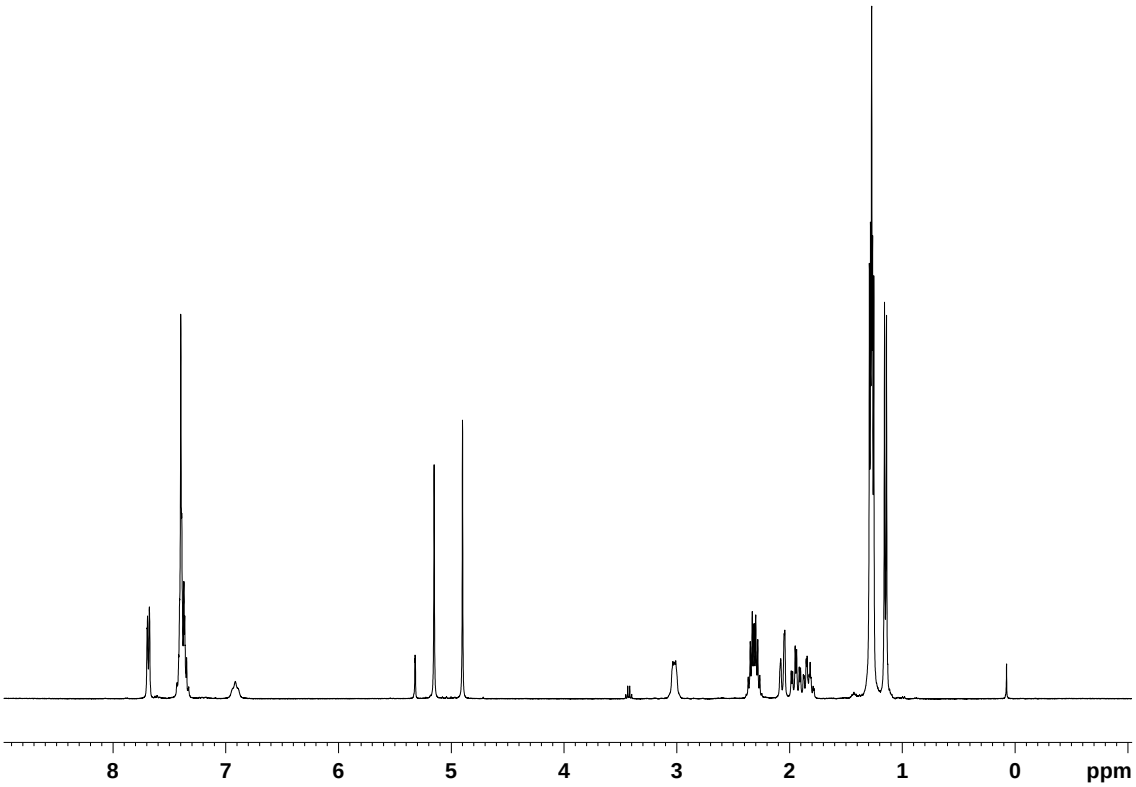
^1H NMR spectrum (CD_2Cl_2, 298 K).



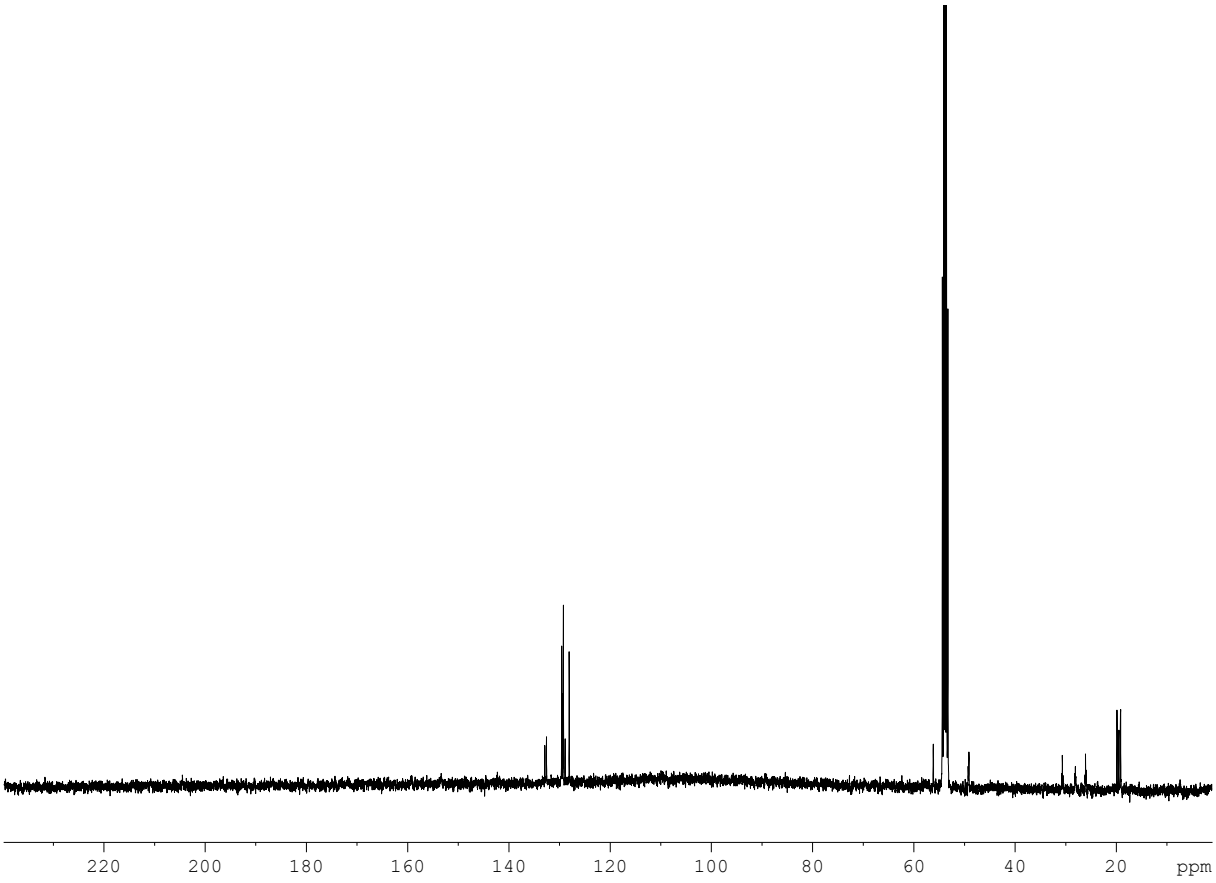
$^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 298 K).



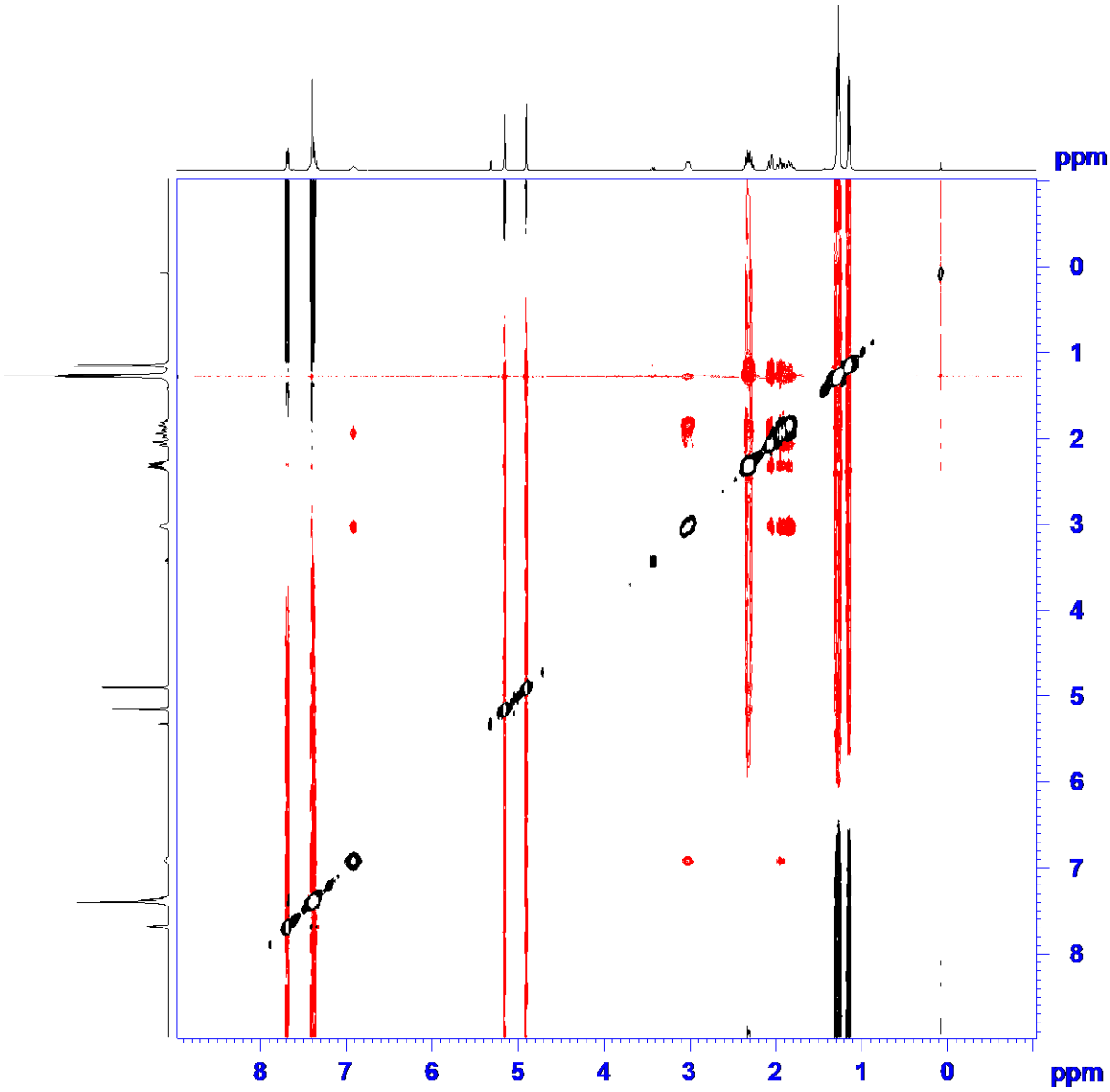
$^{1}H\{^{31}P\}$ NMR spectrum (CD_2Cl_2, 298 K).



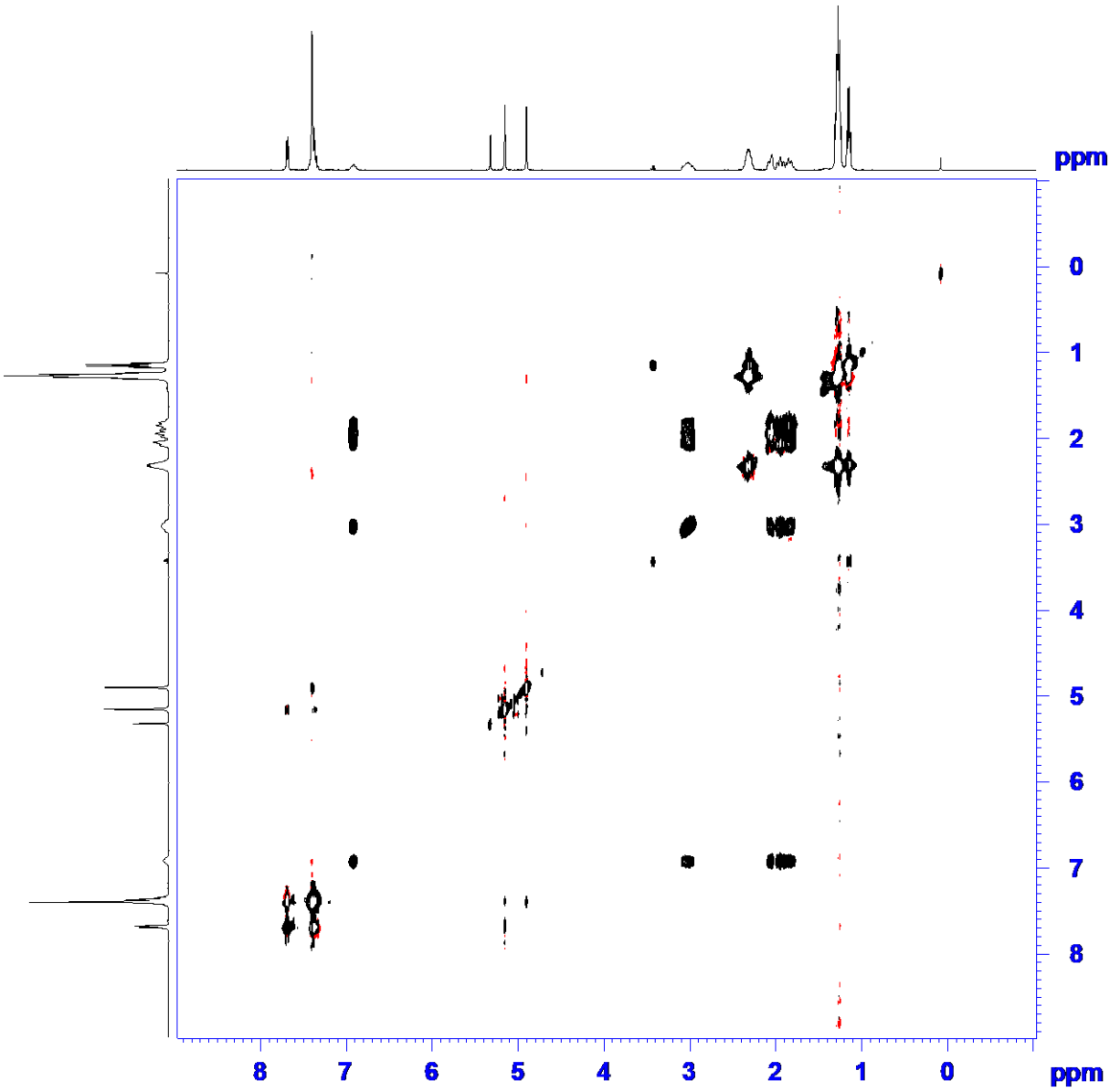
$^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K).



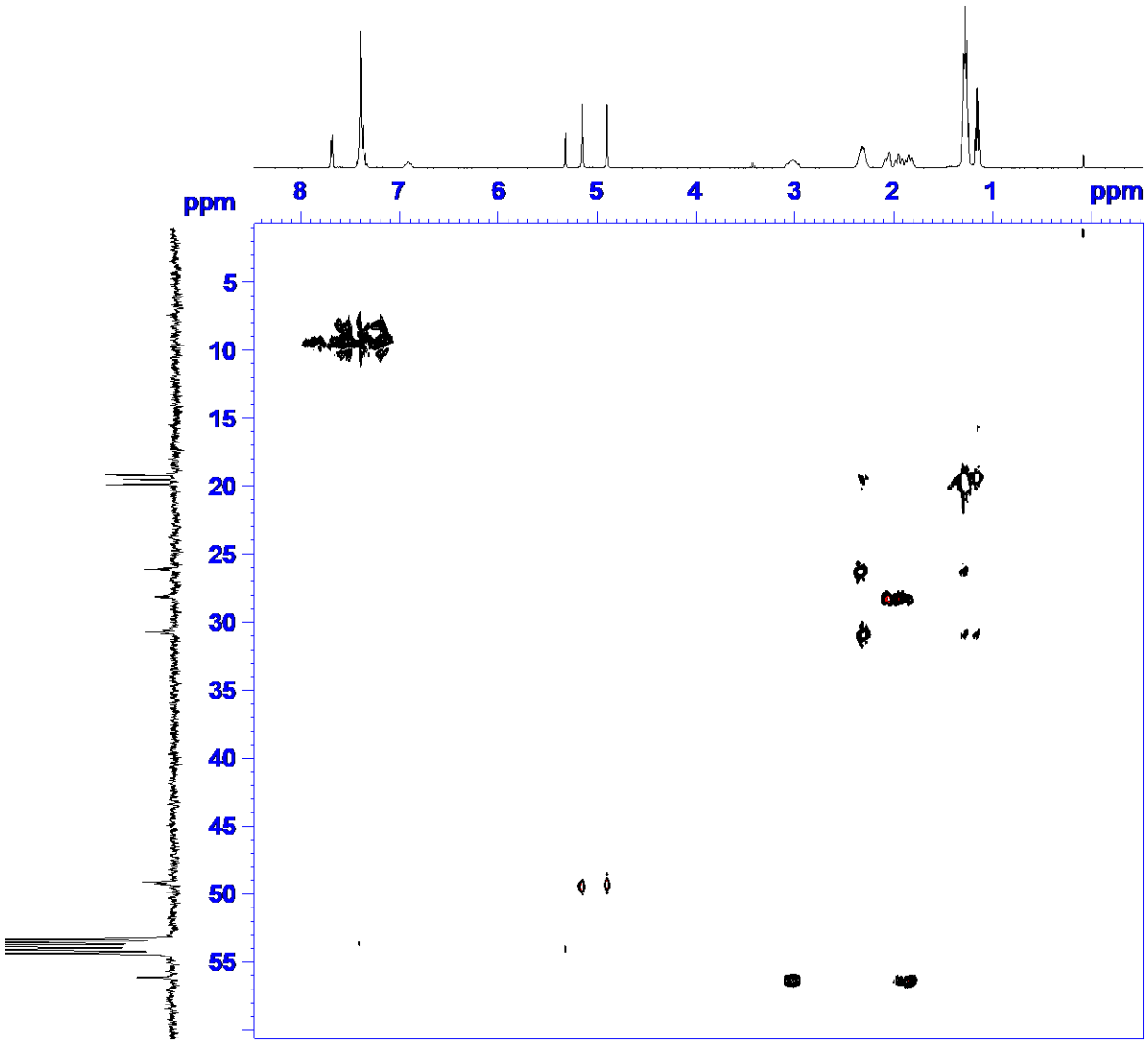
H-^{1}H 2D NOESY NMR spectrum (CD_2Cl_2, 298 K).



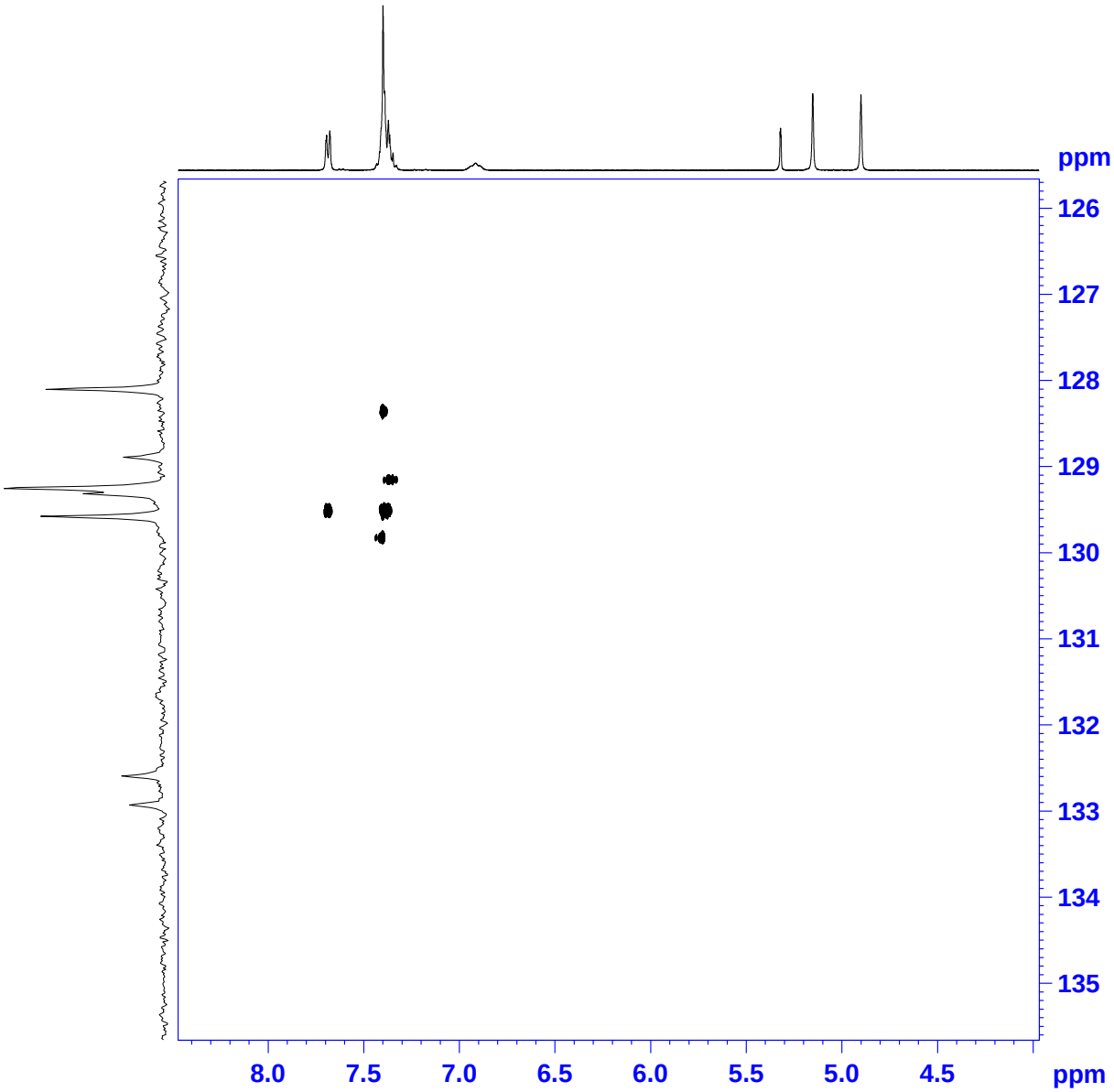
^{1}H-^{1}H 2D TOCSY NMR spectrum (CD_2Cl_2, 298 K).



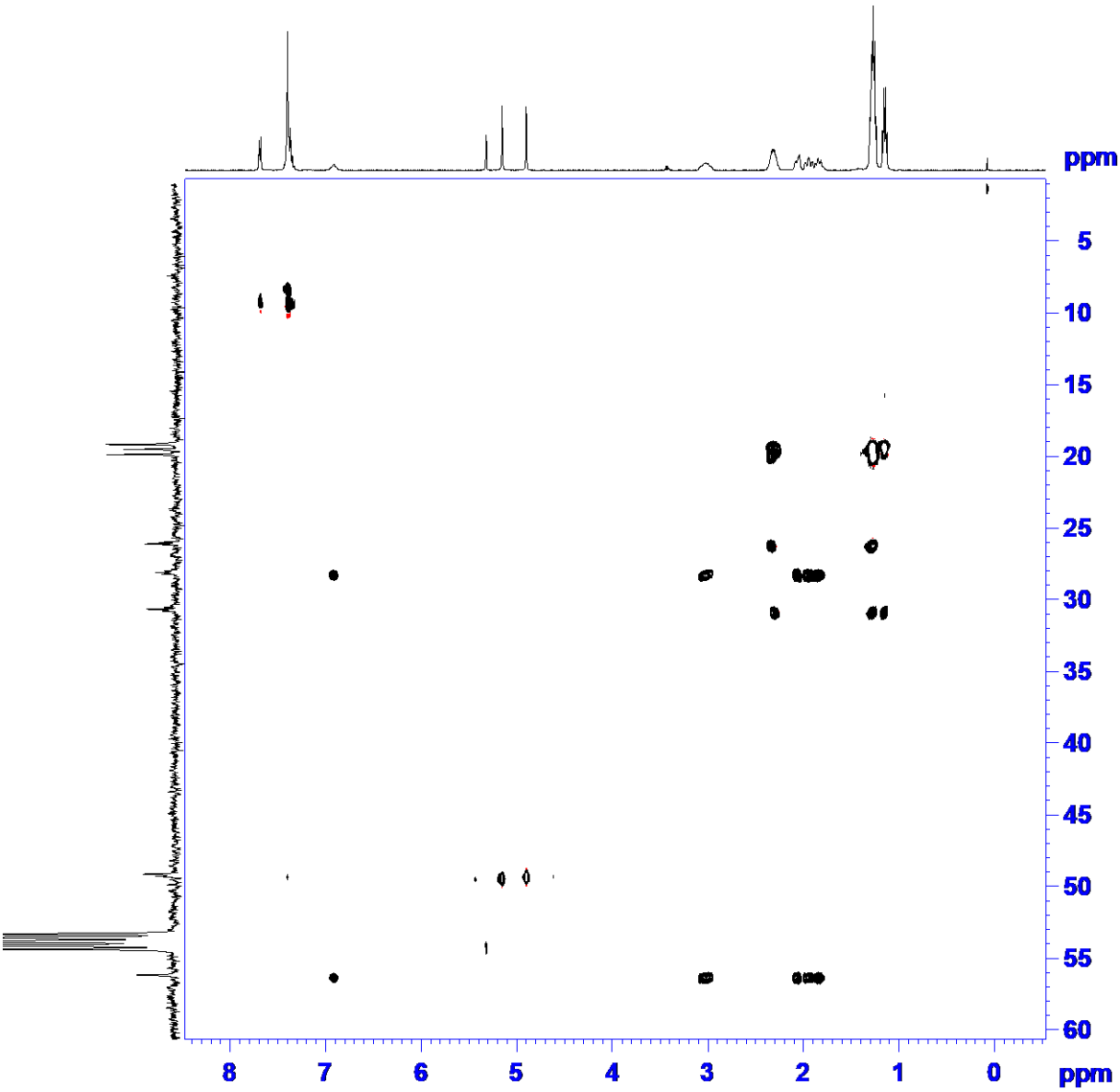
^{1}H-^{13}C 2D HSQC NMR spectrum (CD_2Cl_2, 298 K).



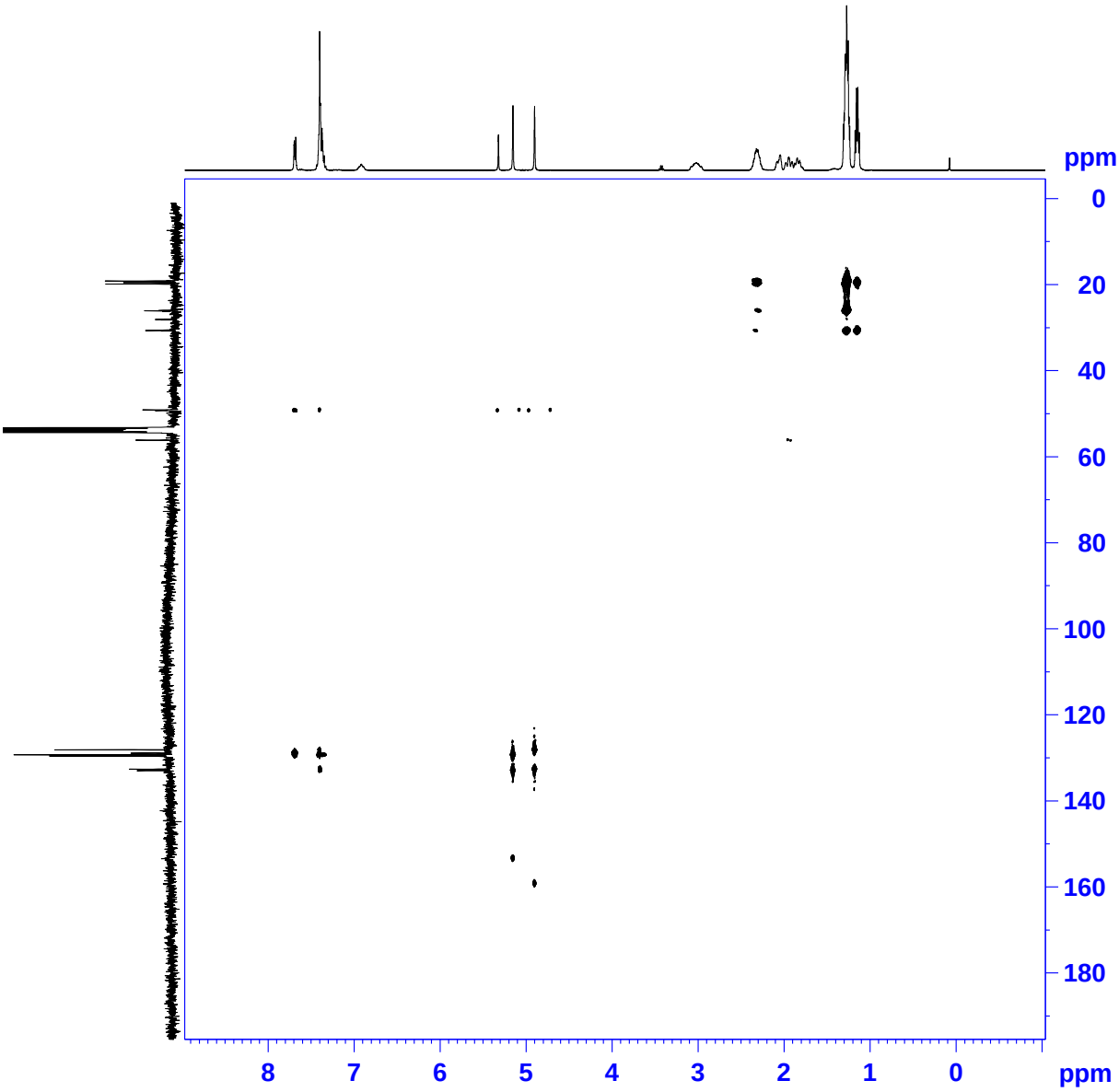
Zoomed ^{1}H-^{13}C 2D HSQC NMR spectrum (CD_2Cl_2, 298 K).



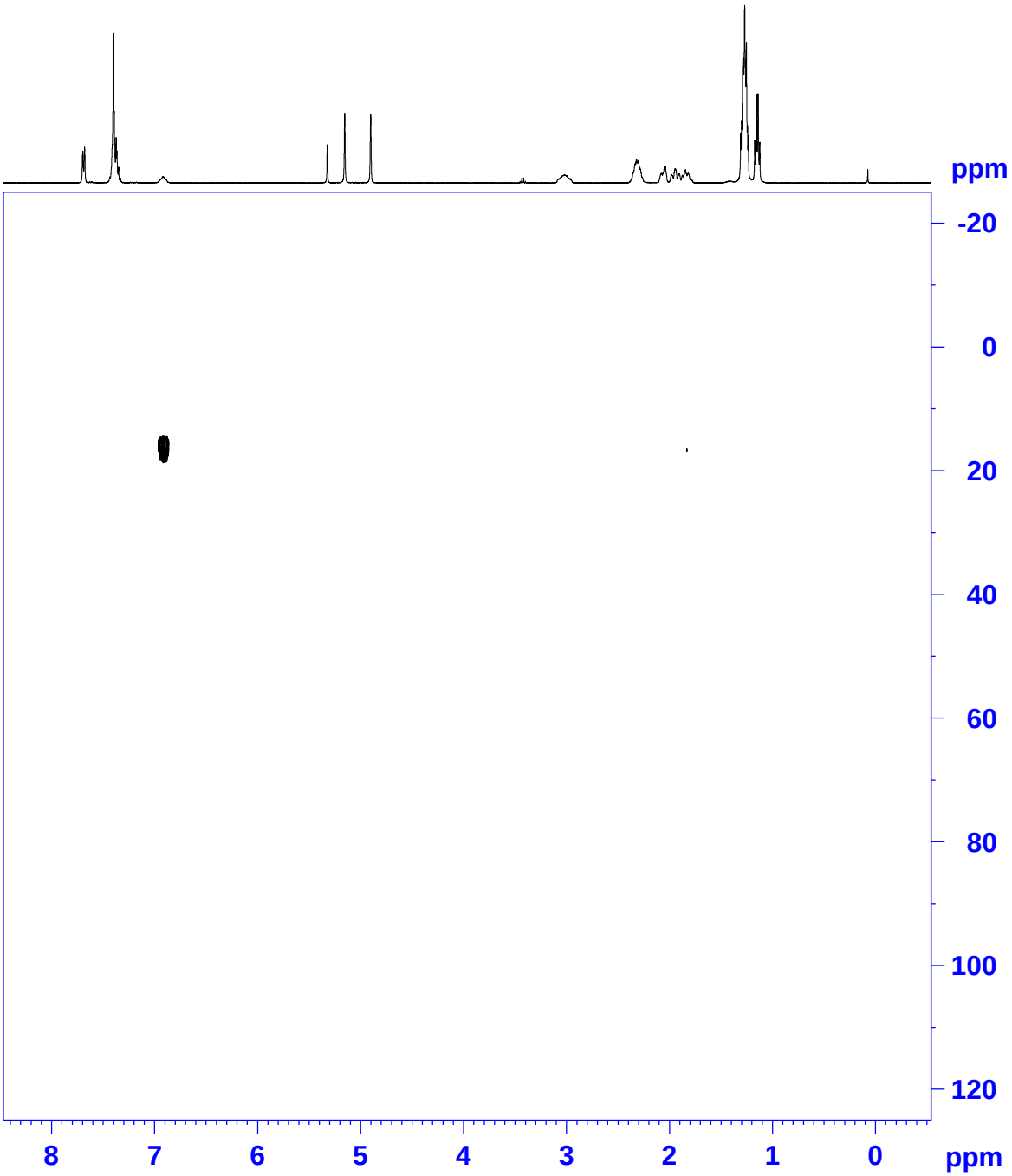
^{1}H-^{13}C 2D HSQC-TOCSY NMR spectrum (CD_2Cl_2, 298 K).



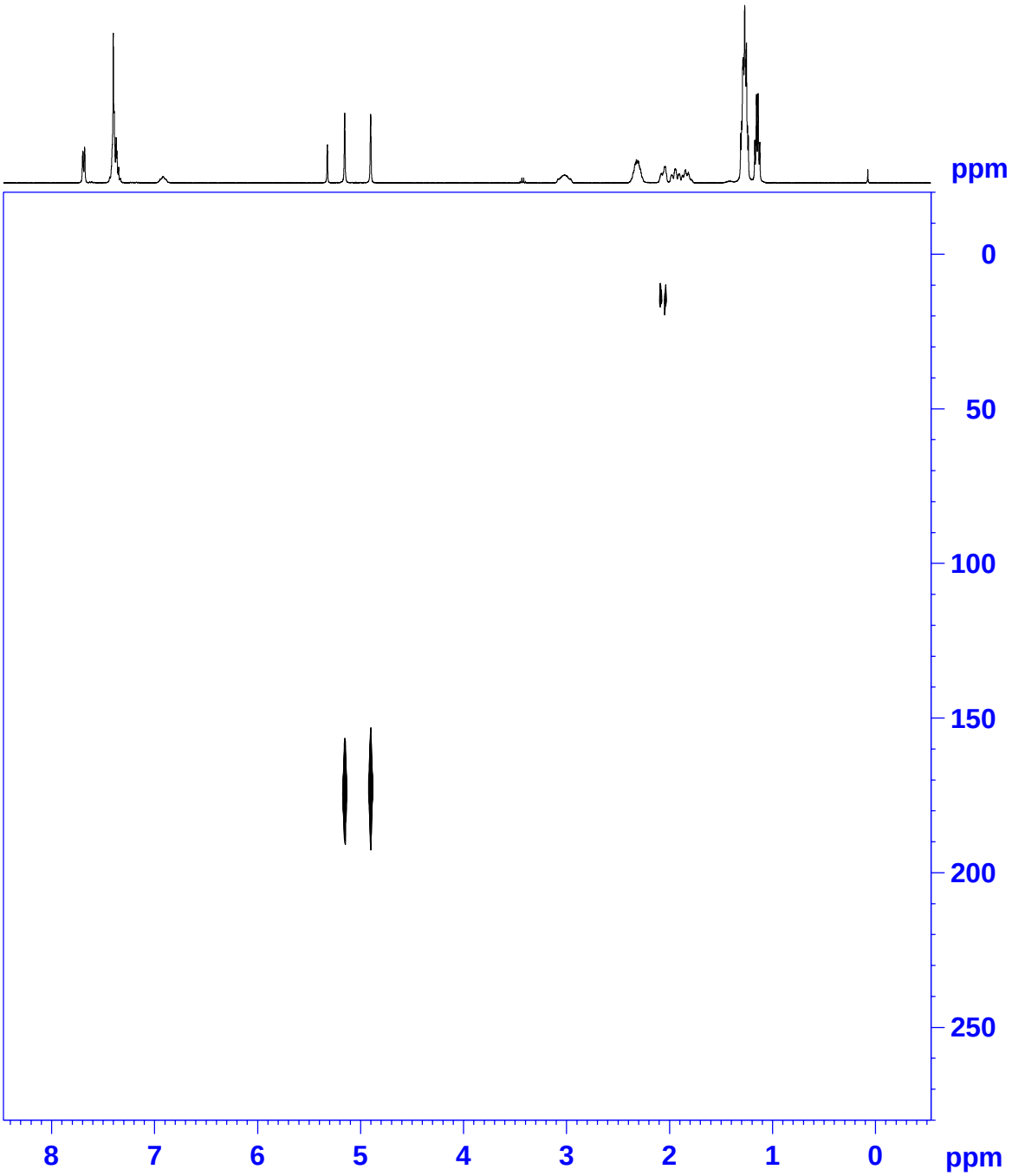
^{1}H-^{13}C 2D HMBC-TOCSY NMR spectrum (CD_2Cl_2, 298 K).



^{1}H-^{15}N 2D HSQC NMR spectrum (CD_2Cl_2, 298 K).

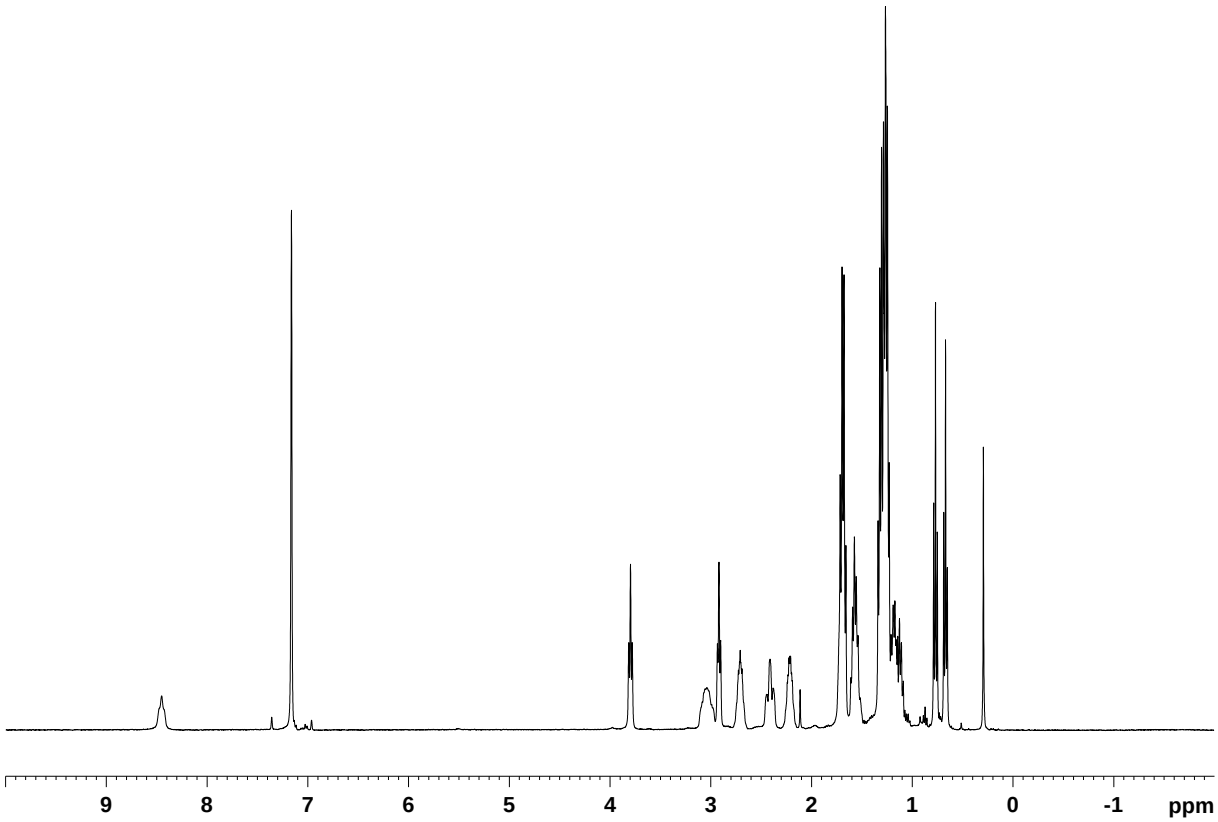


^{1}H-^{15}N 2D HMBC NMR spectrum (CD_2Cl_2, 298 K).

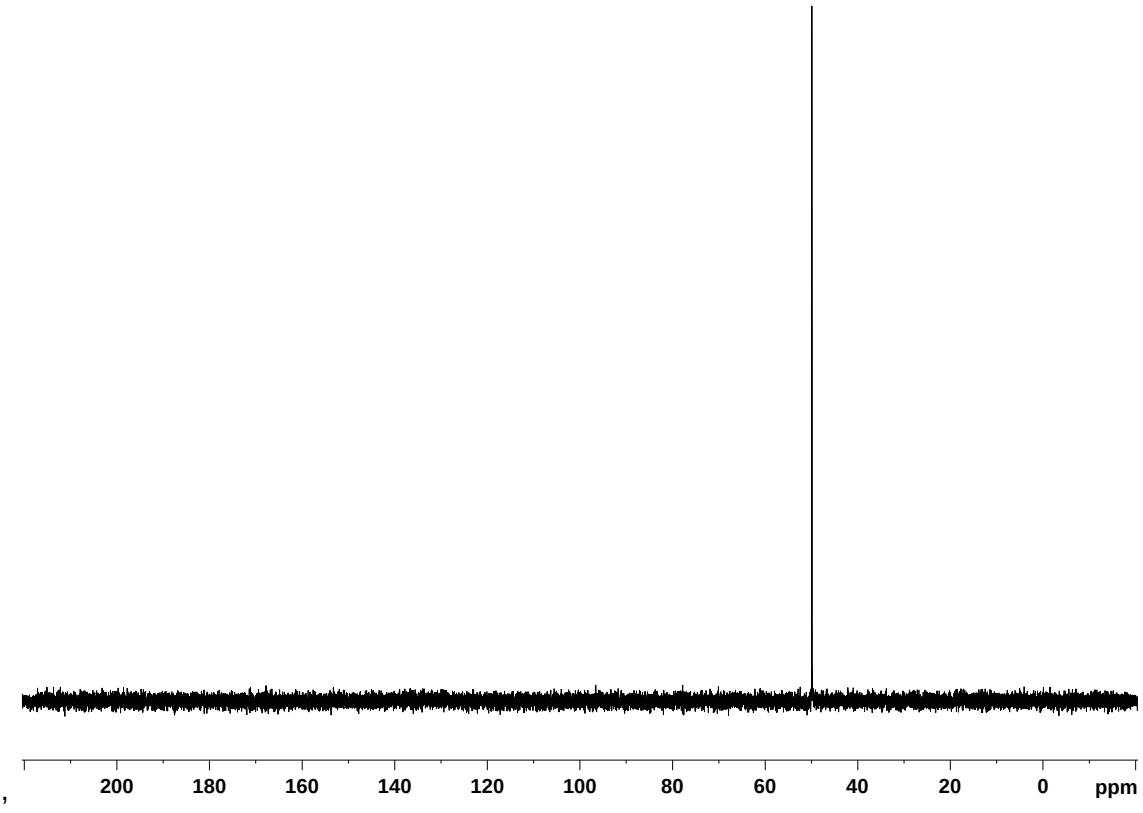


SV. NMR spectra of [Ru(Cl)(CN-*n*Bu)$_2${NH(CH$_2$CH$_2$P(*i*Pr)$_2$)$_2$}](Cl) (2b)

^{1}H NMR spectrum (C_6D_6, 300 K).

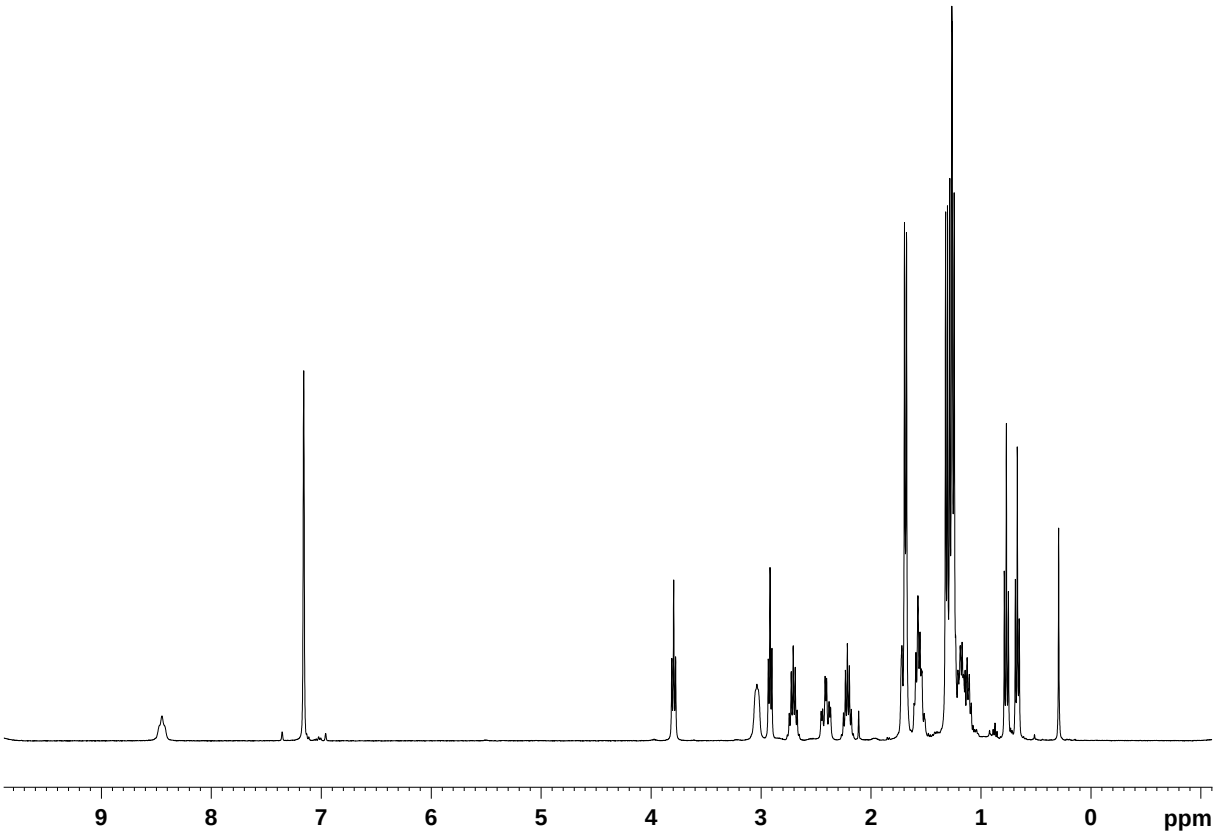


^{31}P{^{1}H} NMR spectrum (C_6D_6, 300 K).

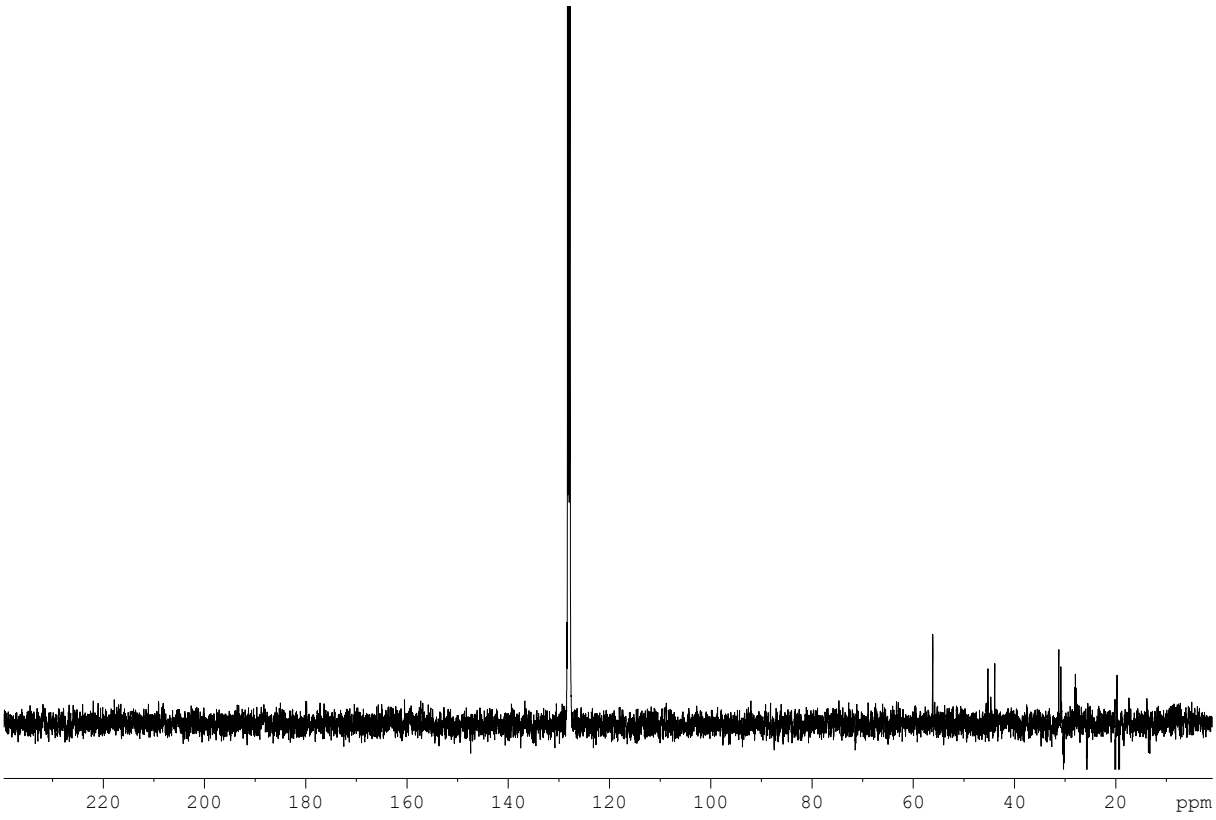


,

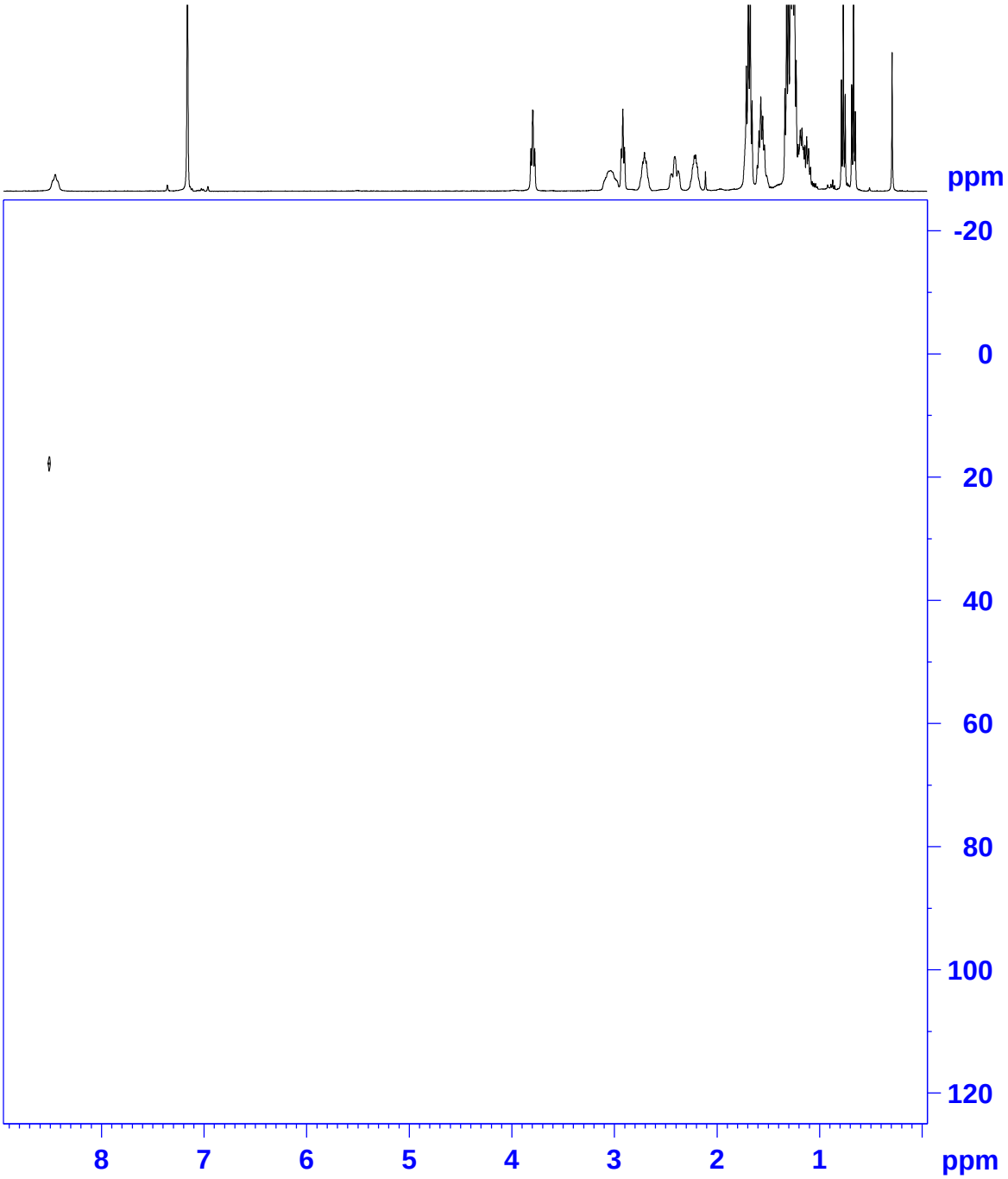
$^{1}H\{^{31}P\}$ NMR spectrum (C_6D_6, 300 K).



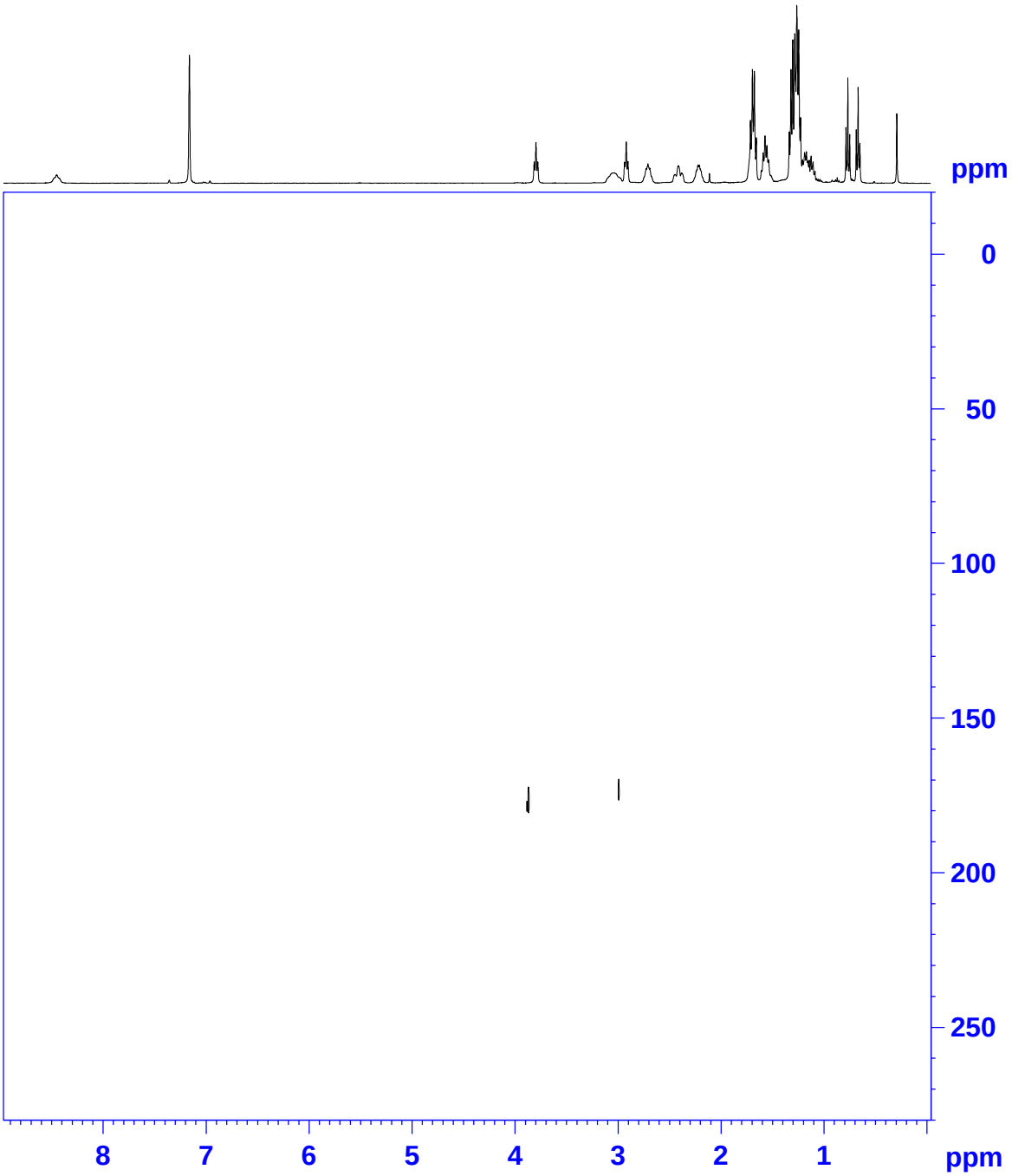
$^{13}C\{^{1}H\}$ JMOD NMR spectrum (C_6D_6, 300 K).



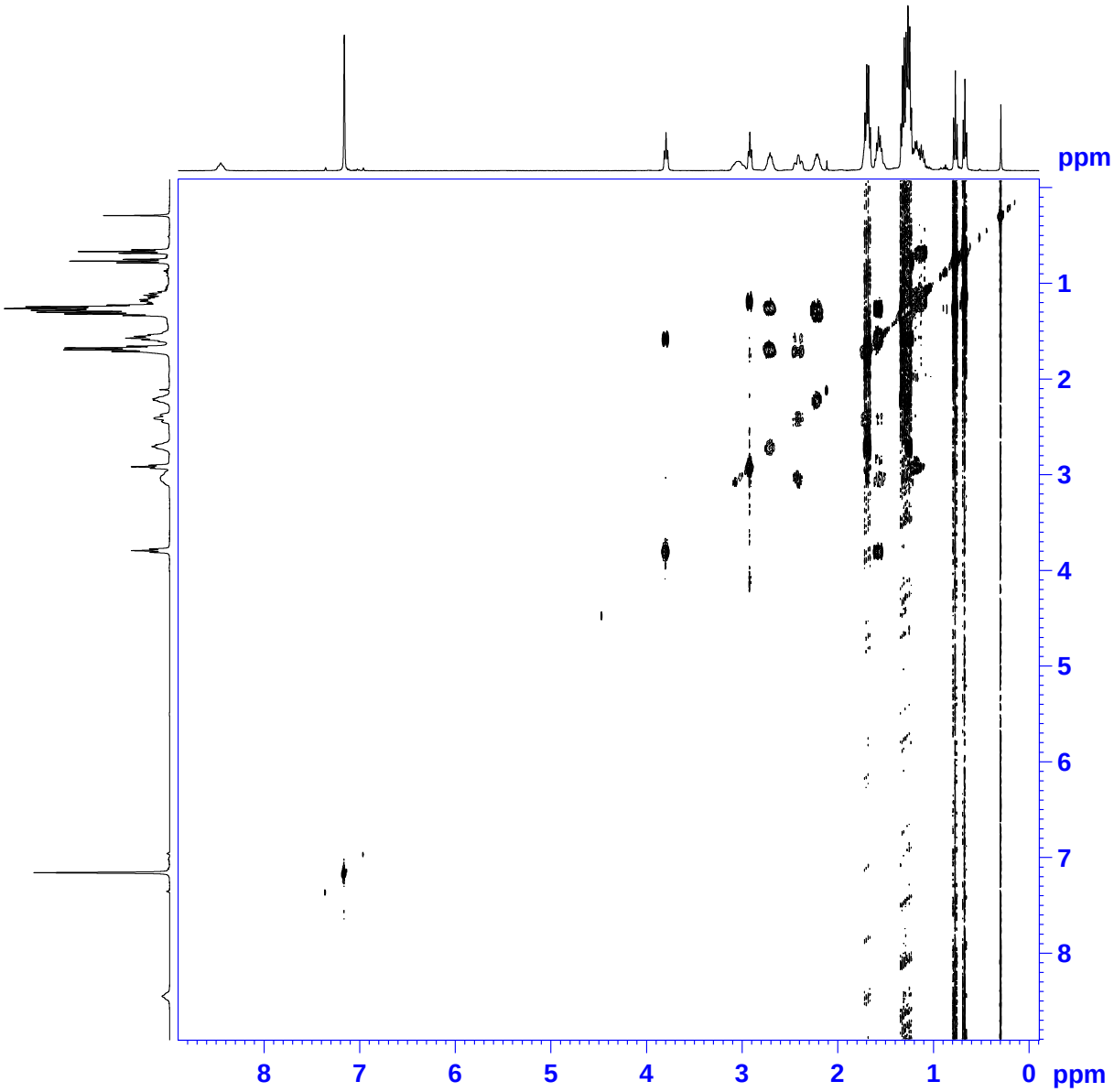
2D ^{1}H-^{15}N HSQC NMR spectrum (C_6D_6, 300 K).



2D ^{1}H-^{15}N HMBC NMR spectrum (C_6D_6, 300 K).

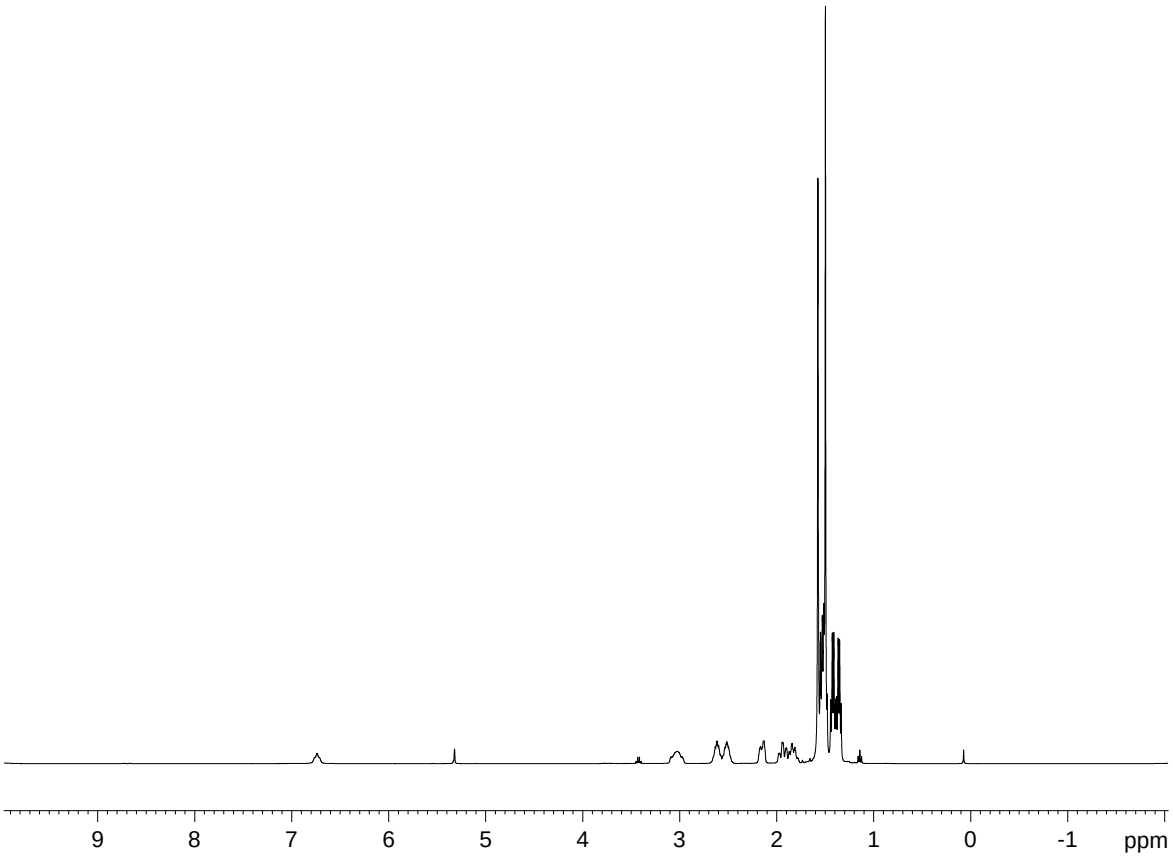


2D ^{1}H-^{1}H COSY NMR spectrum (C_6D_6, 300 K).

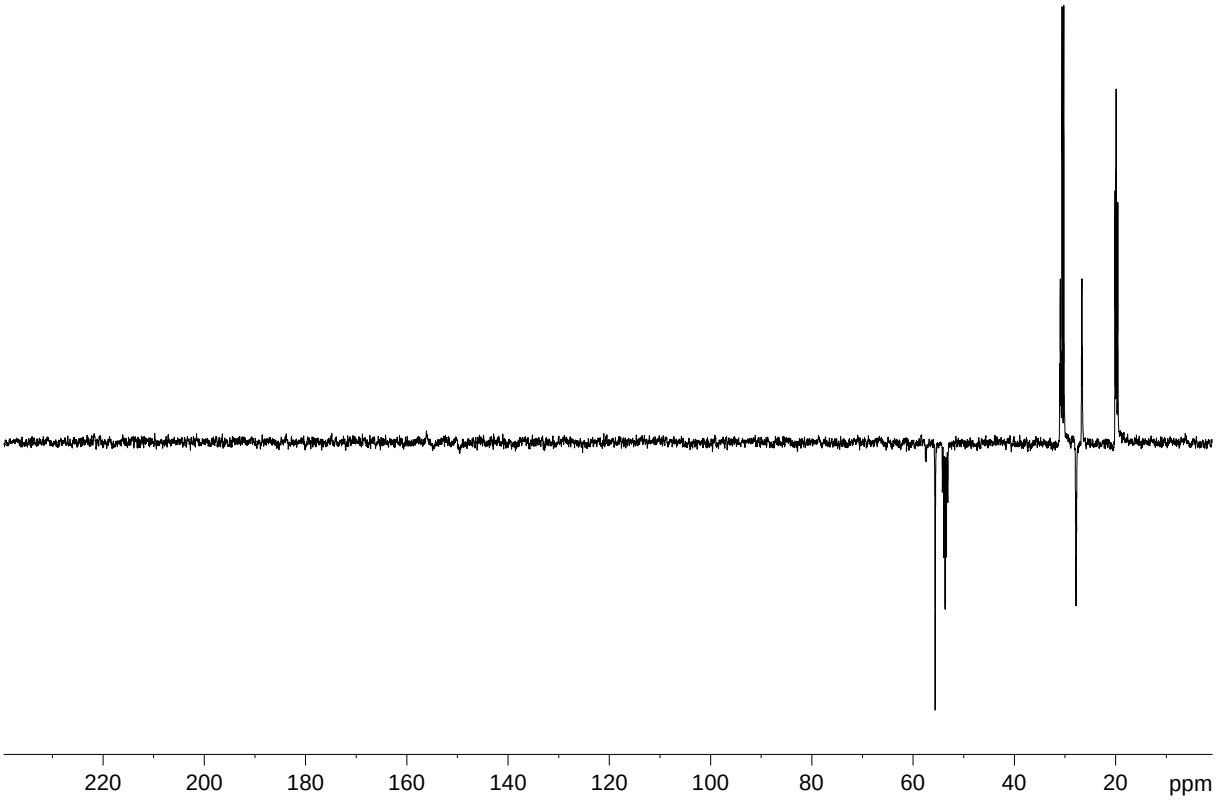


SVI. NMR spectra of [Ru(Cl)(CN-*t*Bu)$_2${NH(CH$_2$CH$_2$P(*i*Pr)$_2$)$_2$}](Cl) (2c)

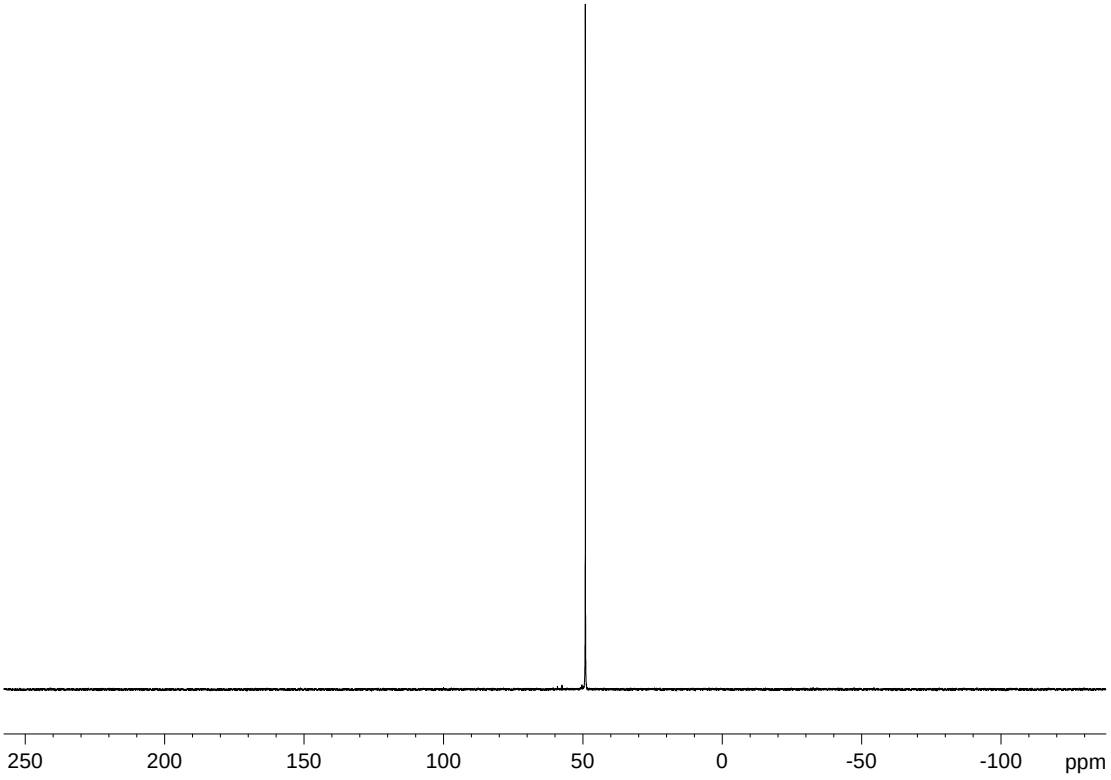
^{1}H NMR spectrum (300 K, CD_2Cl_2)



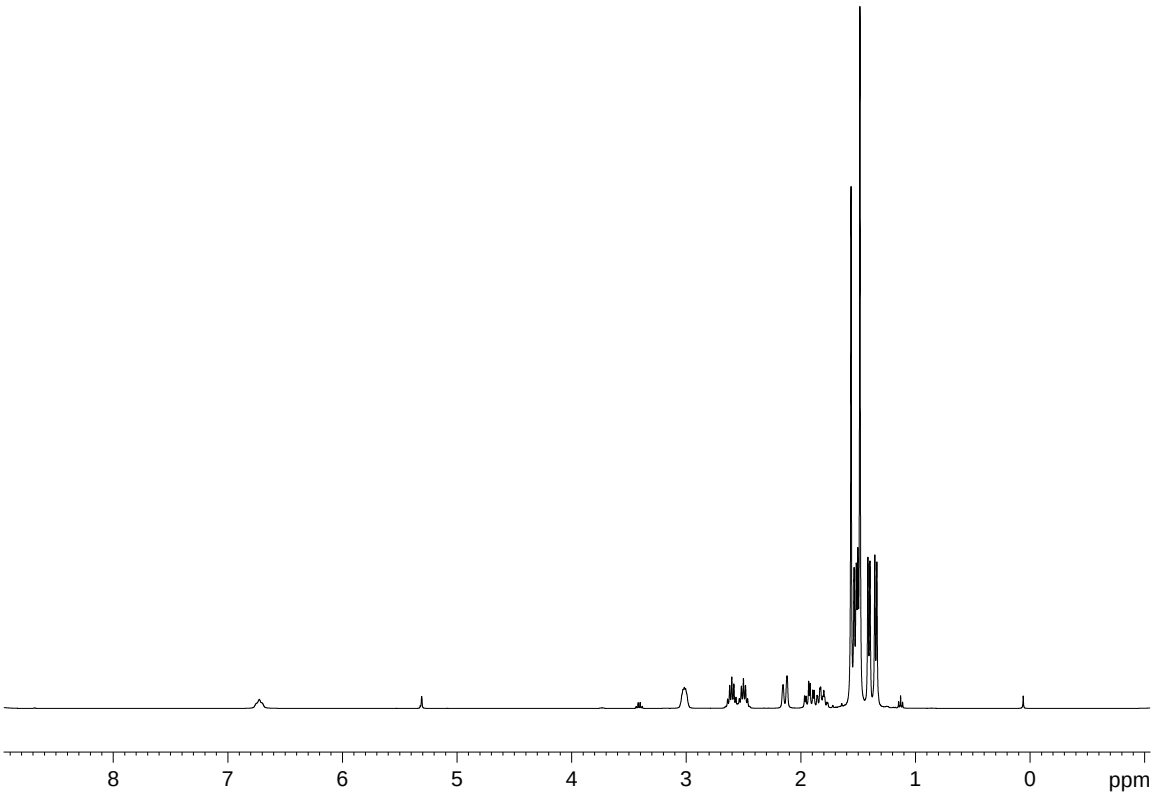
^{13}C{^{1}H} JMOD NMR spectrum (300 K, CD_2Cl_2).



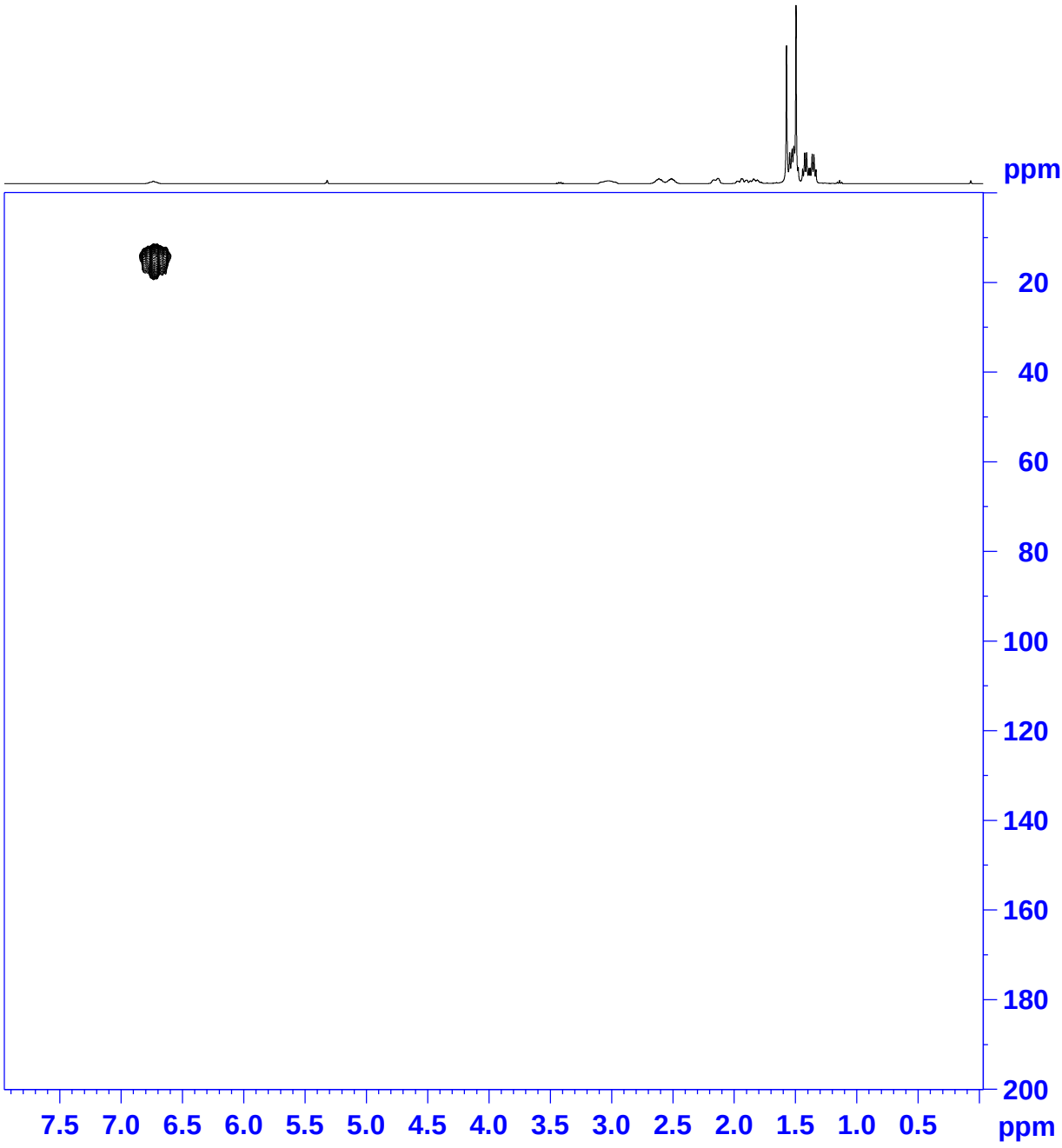
$^{31}P\{^{1}H\}$ NMR spectrum (300 K, CD_2Cl_2).



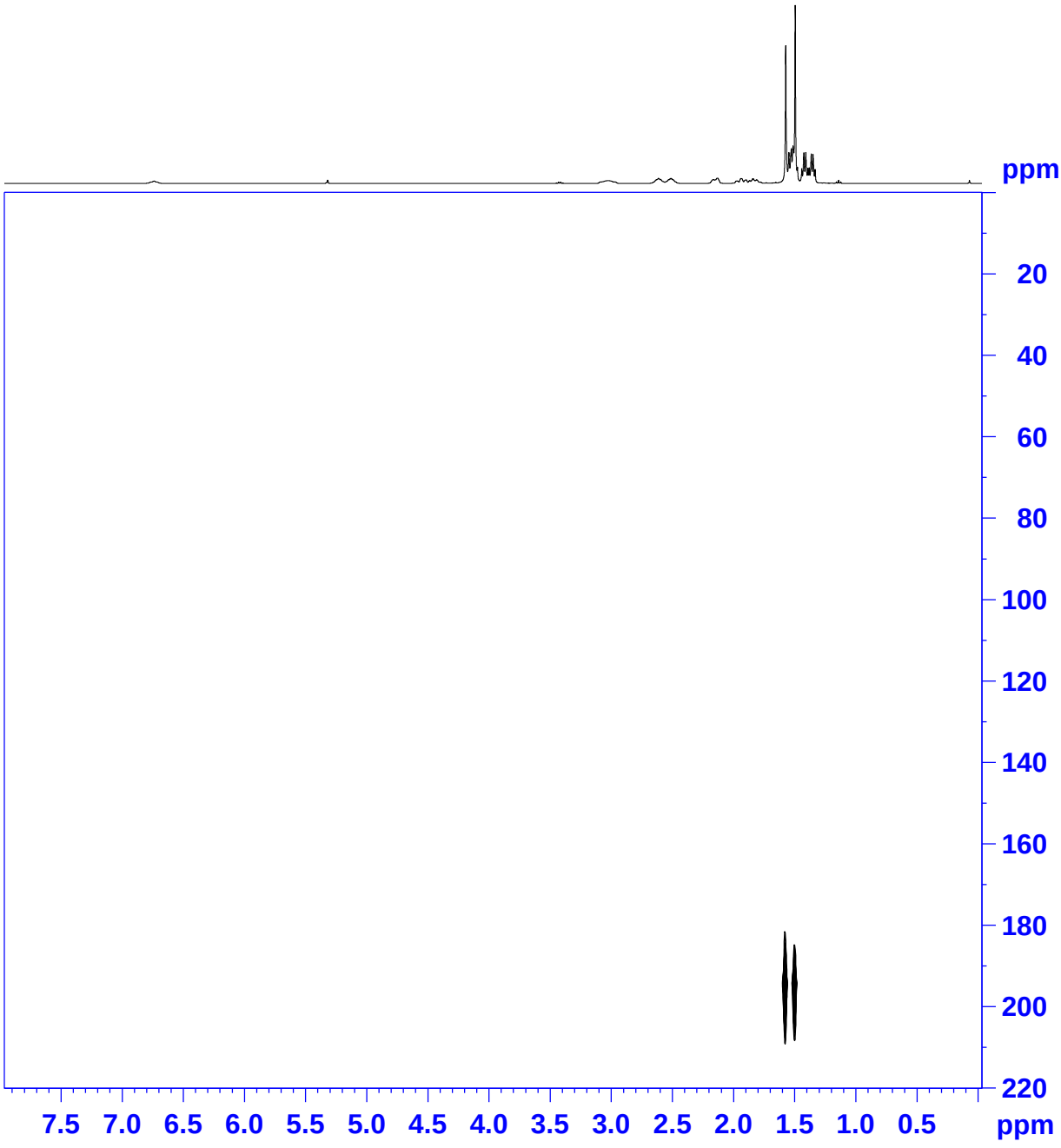
$^{1}H\{^{31}P\}$ NMR spectrum (300 K, CD_2Cl_2).



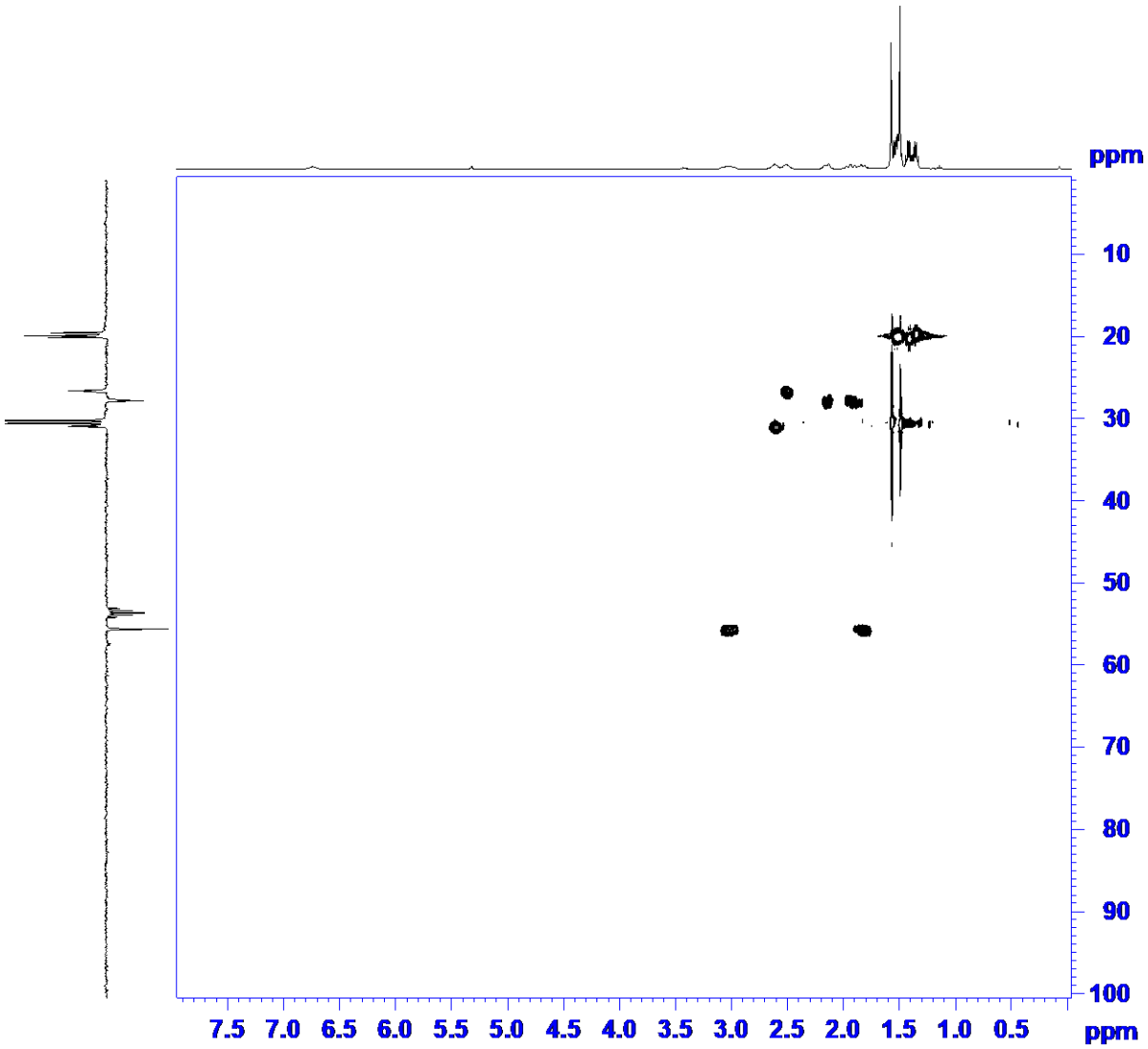
2D ^{1}H-^{15}N HSQC spectrum (300 K, CD_2Cl_2).



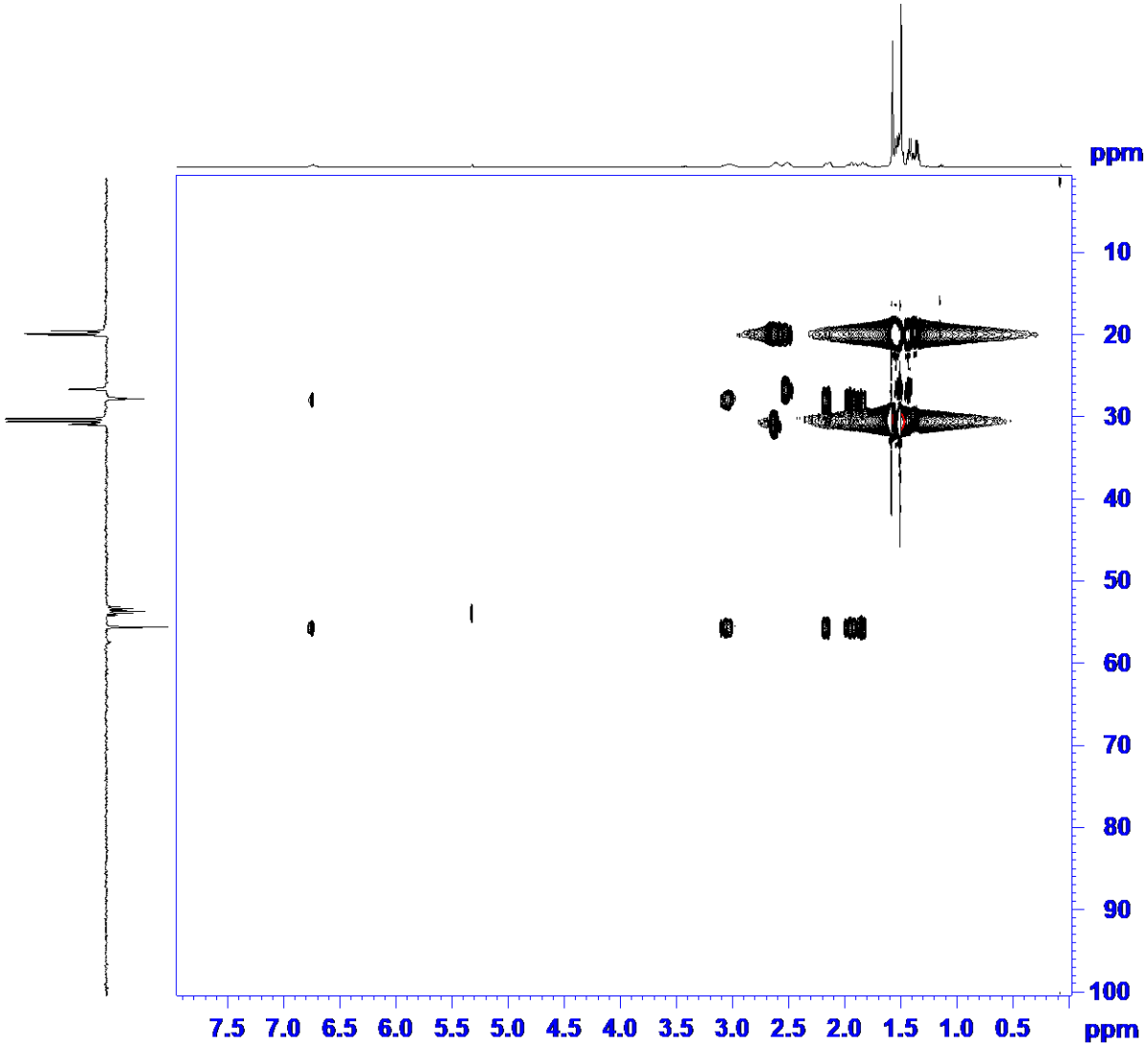
2D ^{1}H-^{15}N HMBC spectrum (300 K, CD_2Cl_2).



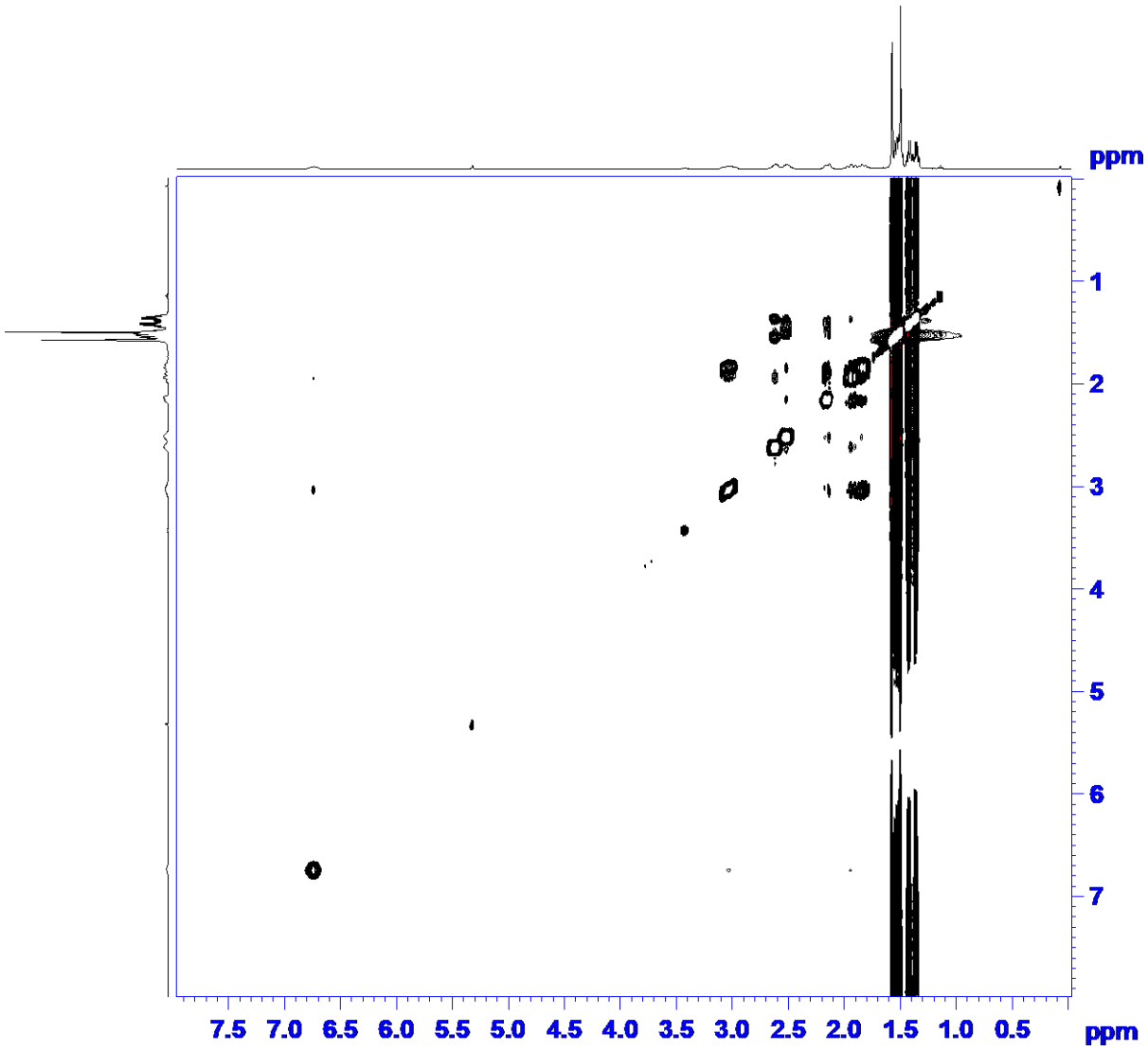
2D ^{1}H-^{13}C HSQC NMR spectrum (300 K, CD_2Cl_2).



2D ^{1}H-^{13}C TOCSY HSQC NMR spectrum (300 K, CD_2Cl_2).

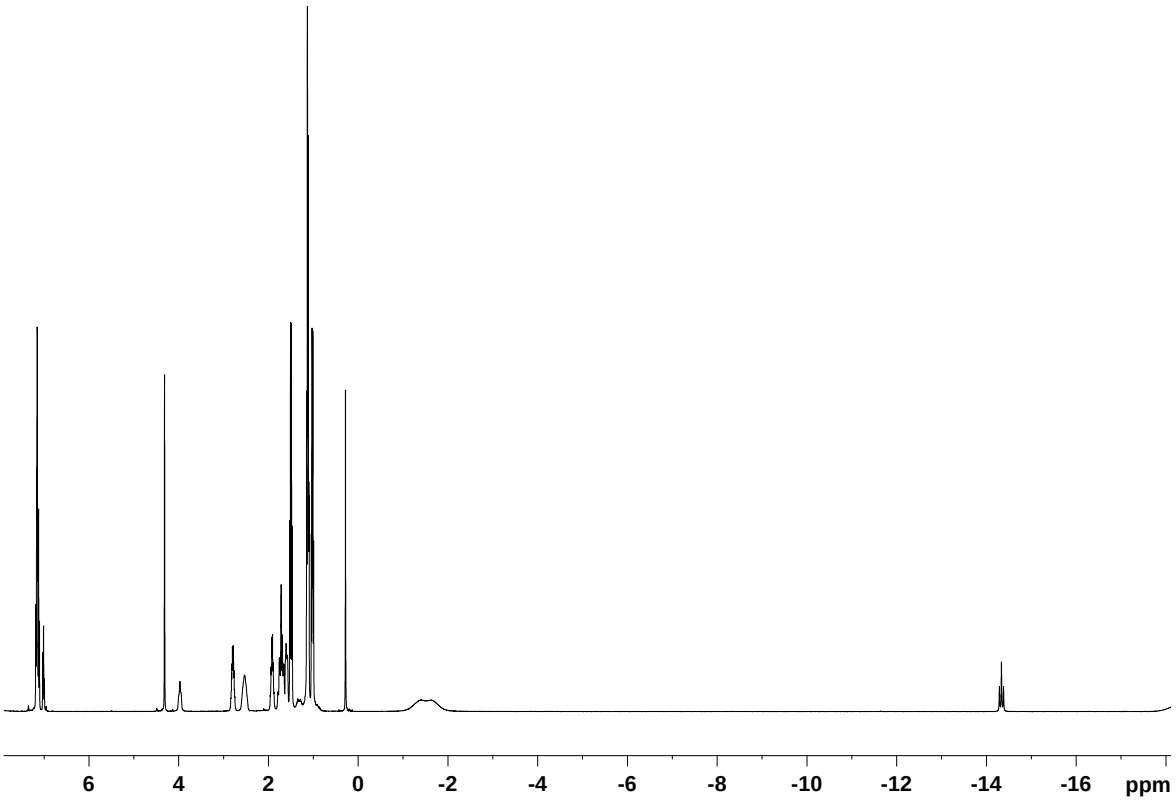


2D ^{1}H-^{1}H NOESY NMR spectrum (300 K, CD_2Cl_2).

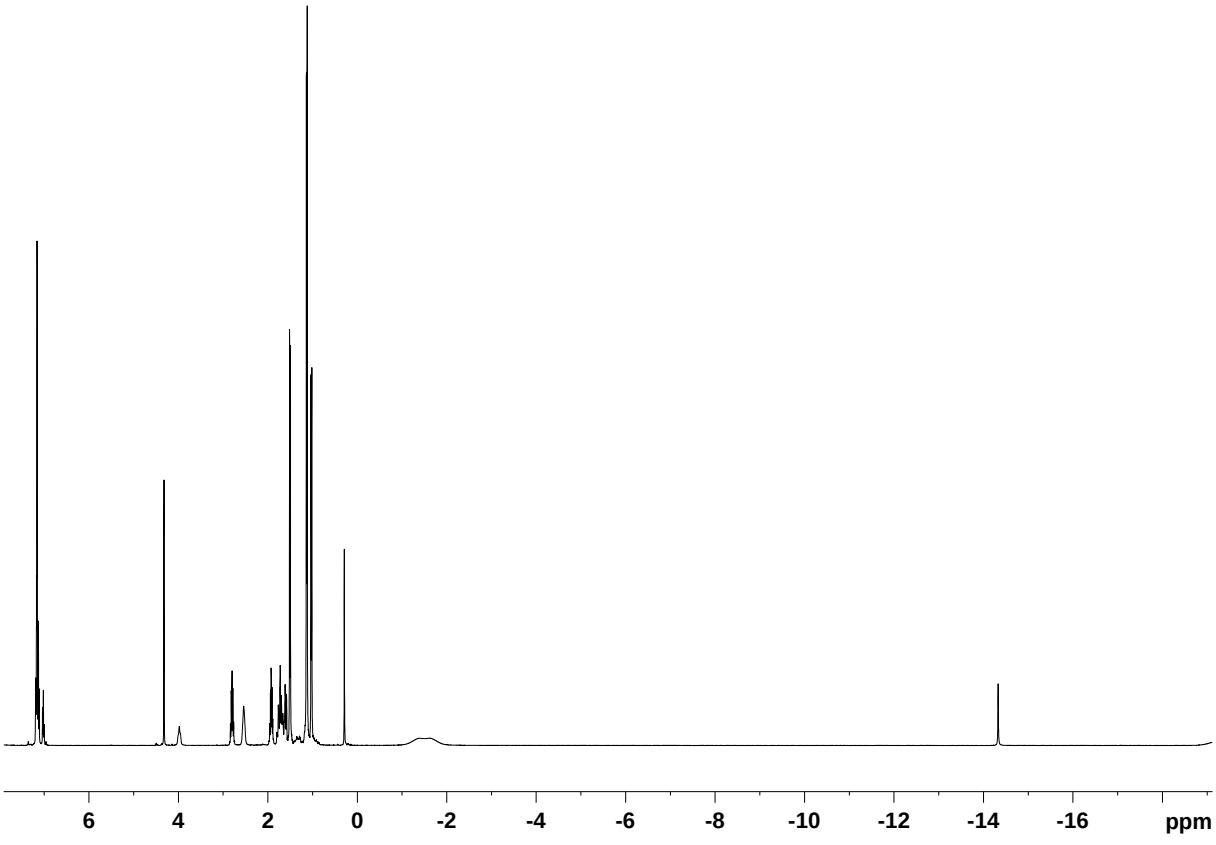


SVII. NMR spectra of [Ru(H)(BH_4)(CN-CH_2Ph){NH($CH_2CH_2P(iPr)_2)_2$}] (3a)

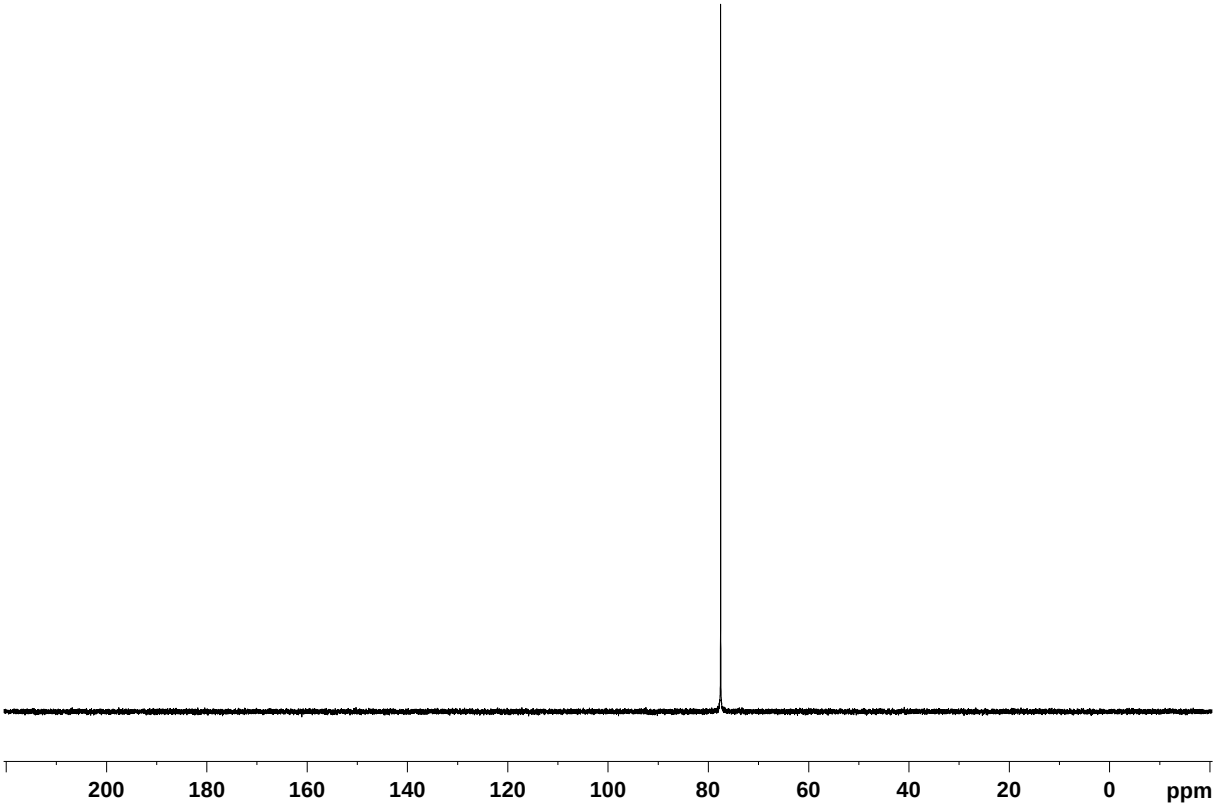
^{1}H NMR spectrum (C_6D_6, 298 K).



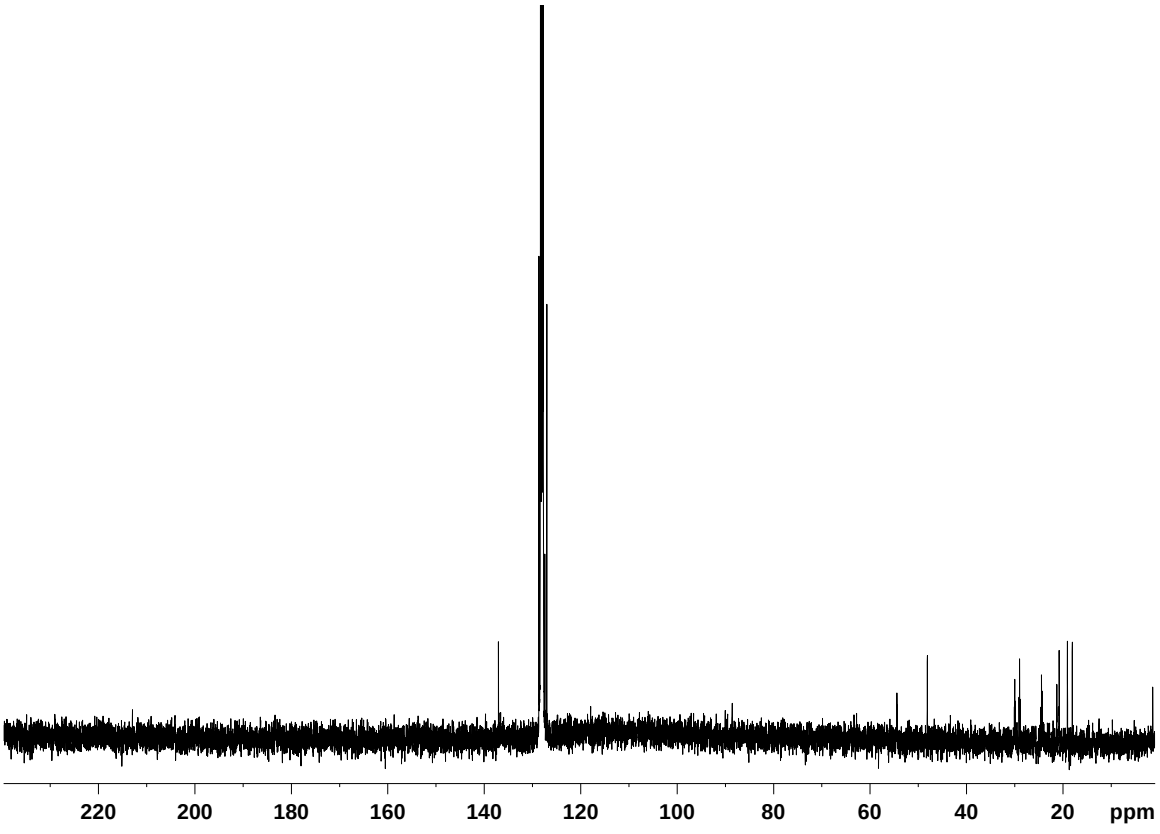
^{1}H{^{31}P} NMR spectrum (C_6D_6, 298 K).



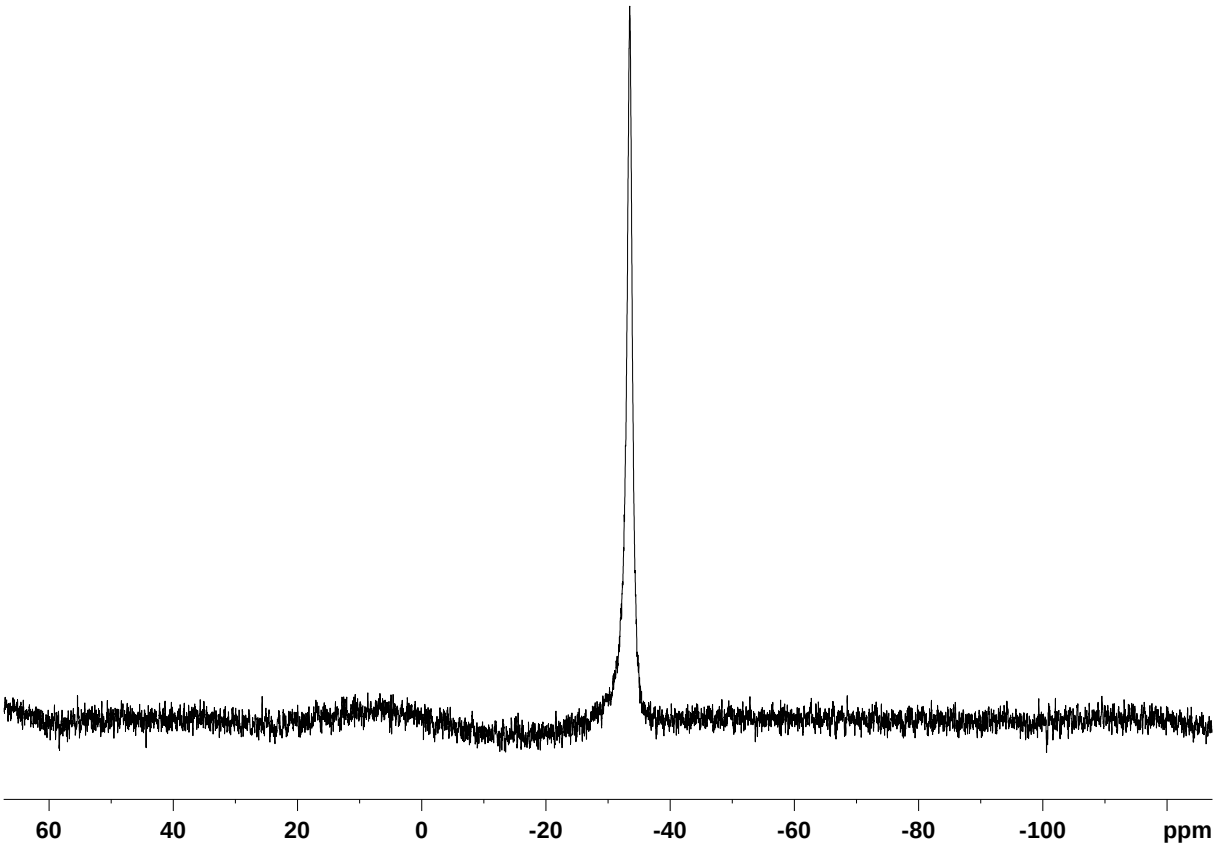
$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K).



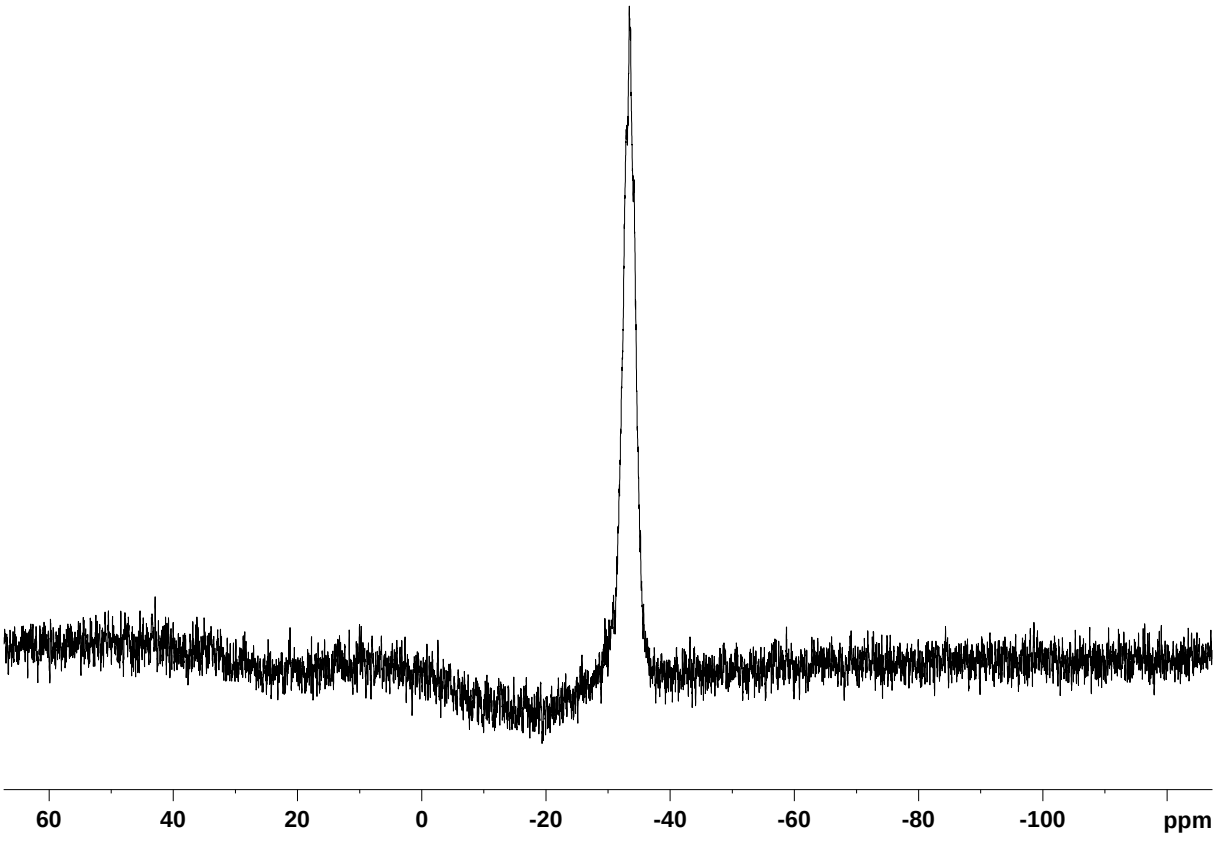
$^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K).



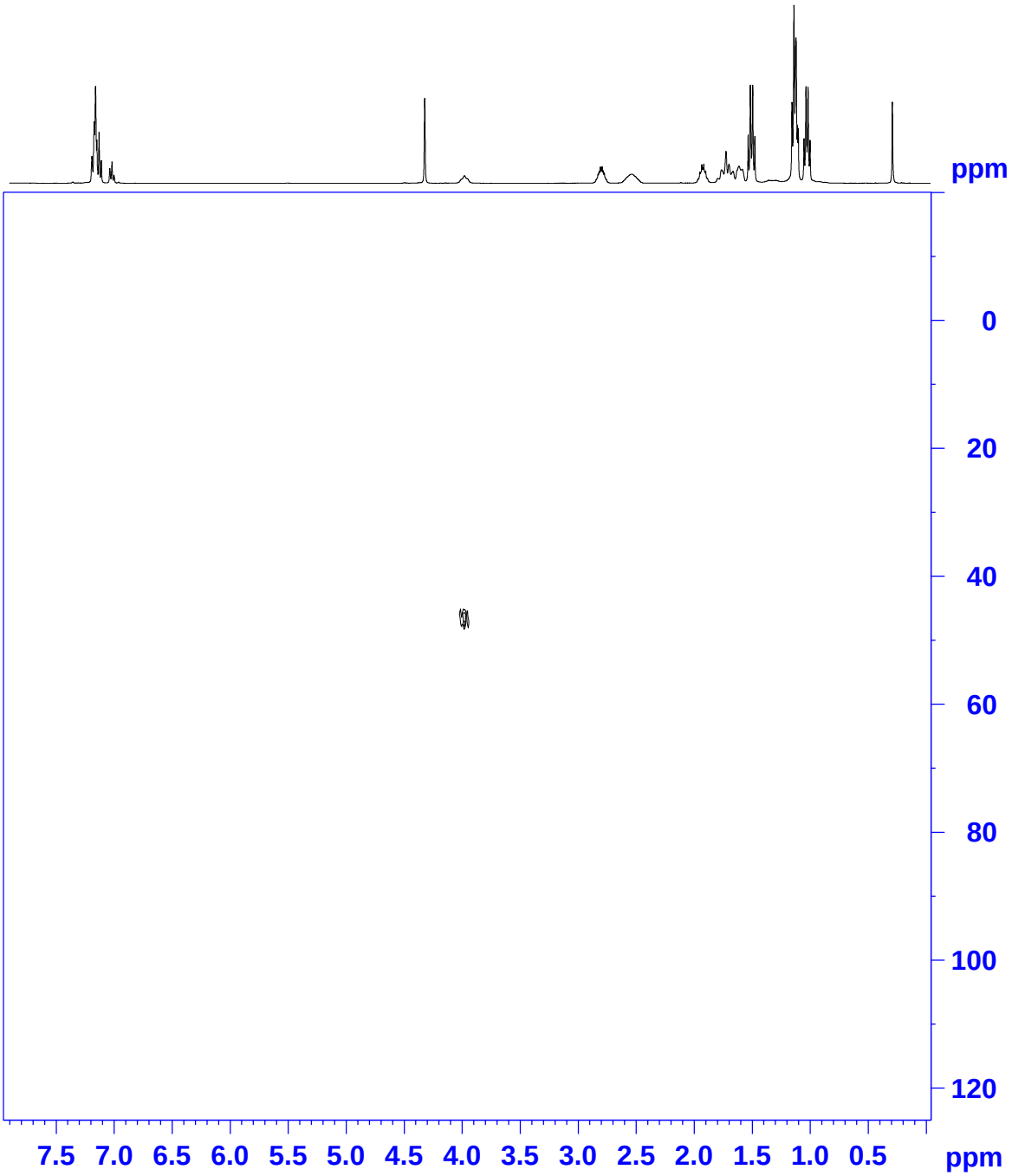
$^{11}B\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K).



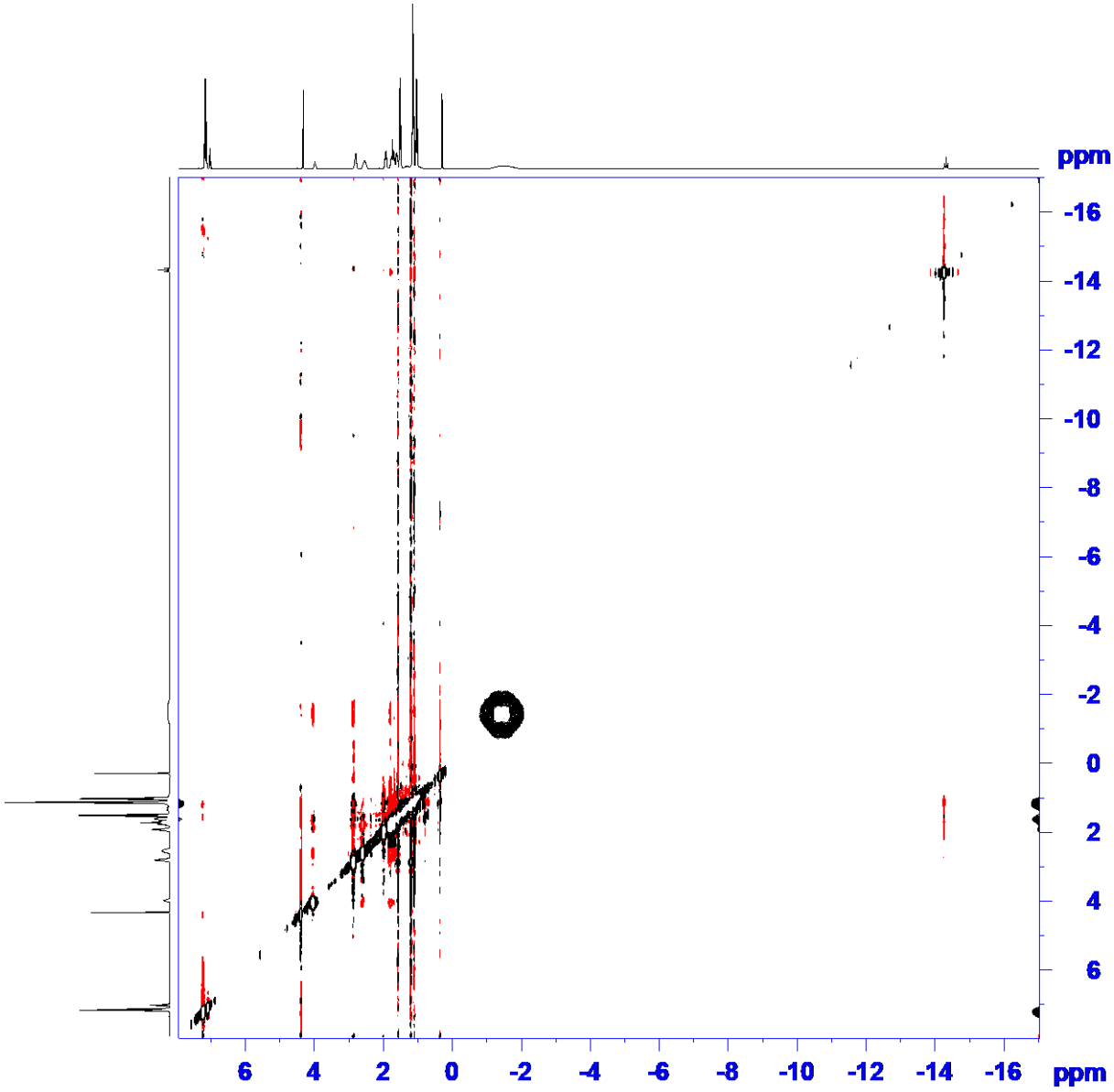
^{11}B NMR spectrum (C_6D_6, 298 K).



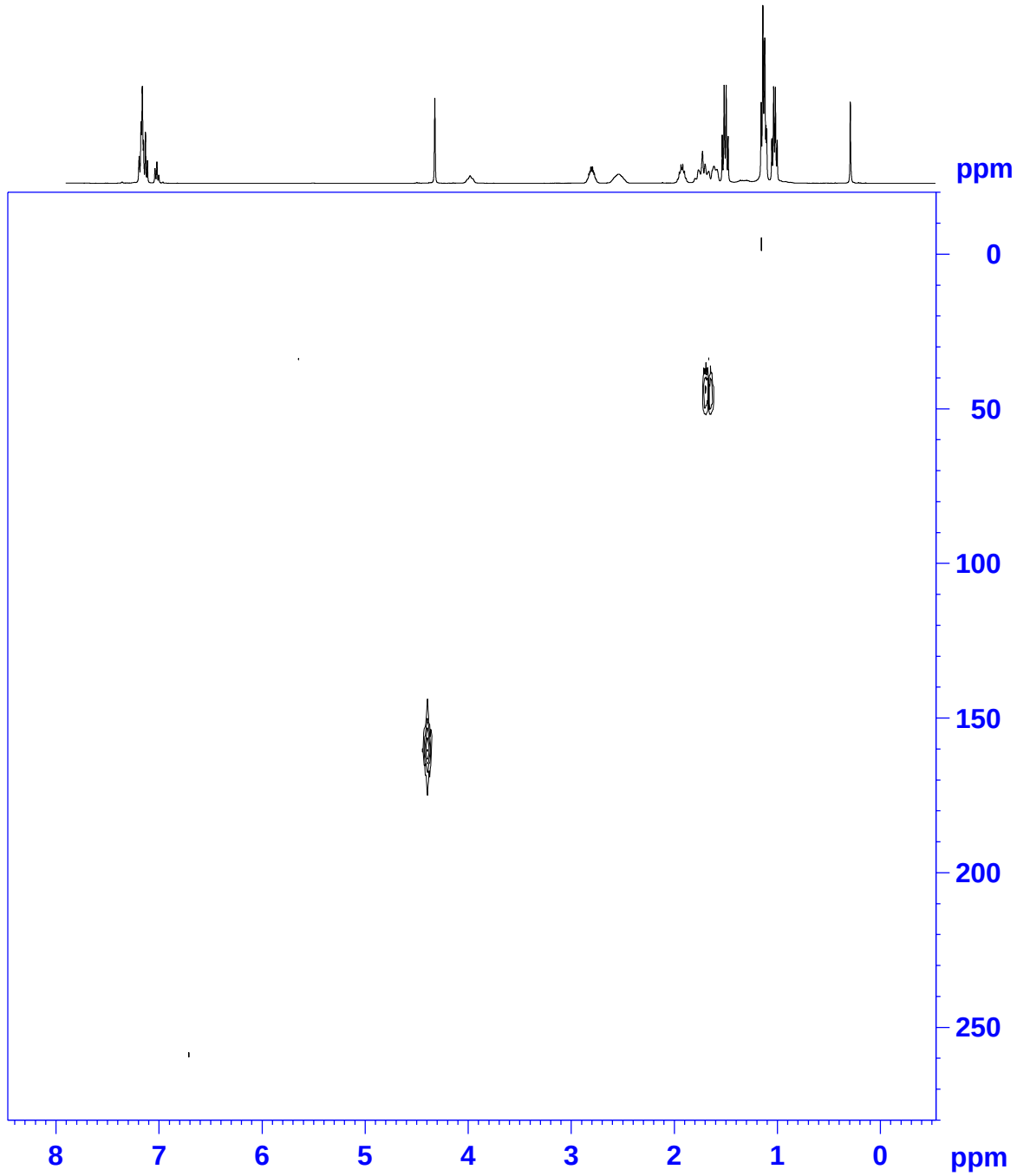
2D ^{1}H-^{15}N HSQC NMR (C_6D_6, 298 K).



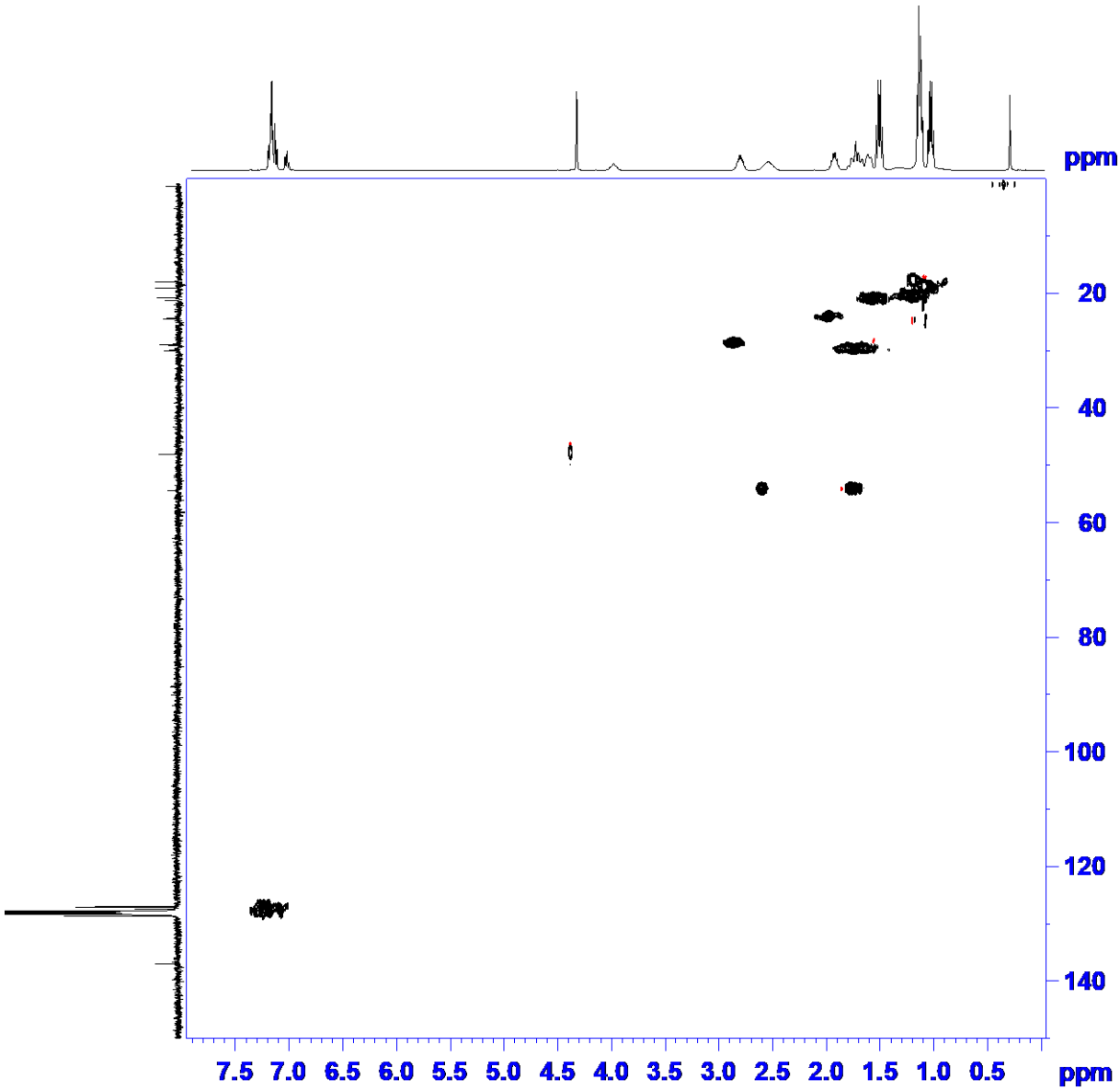
2D ^{1}H-^{1}H NOESY NMR (C_6D_6, 298 K).



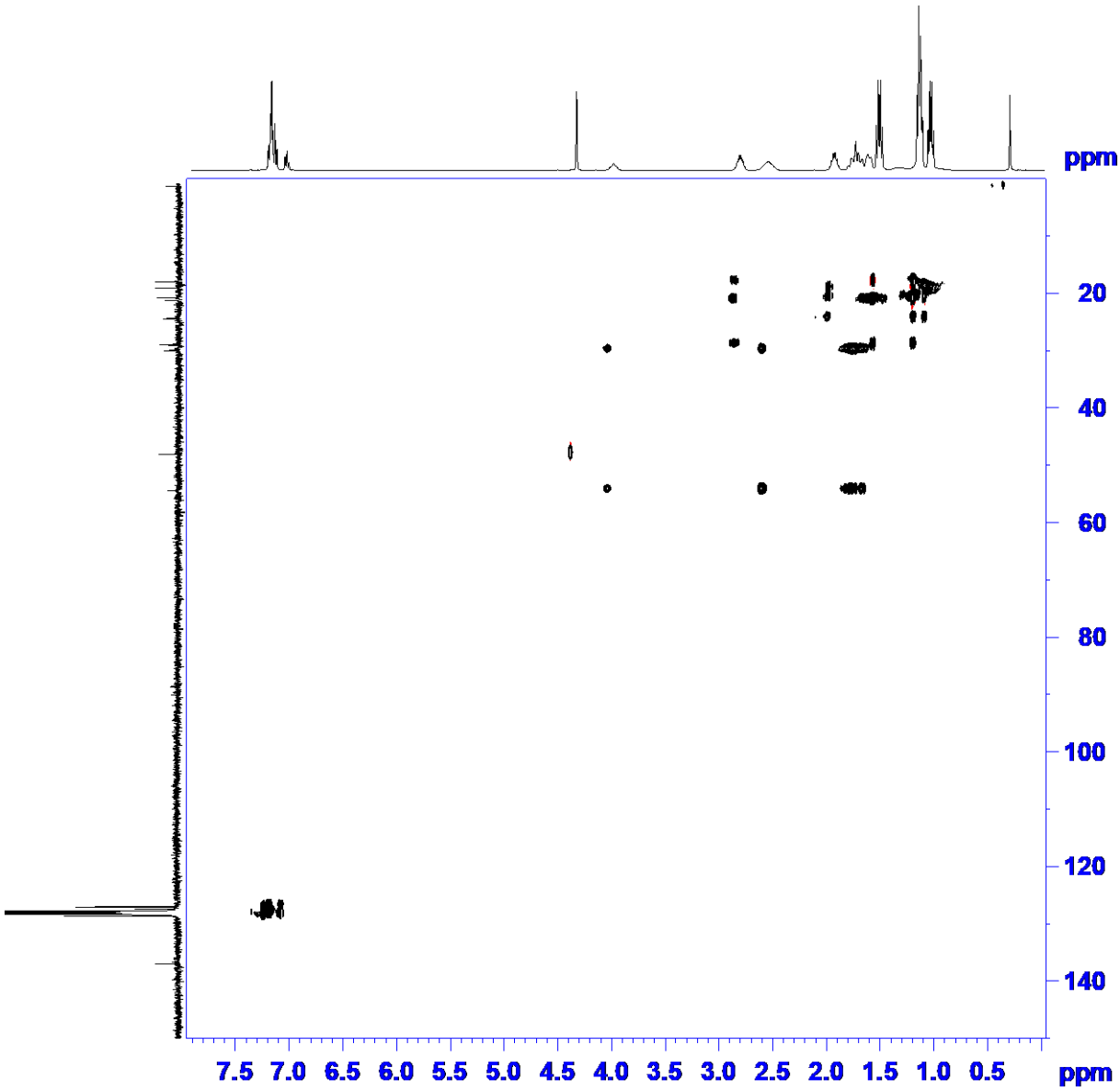
2D ^{1}H-^{15}N HMBC NMR (C_6D_6, 298 K).



2D ^{1}H-^{13}C HSQC NMR (C_6D_6, 298 K).

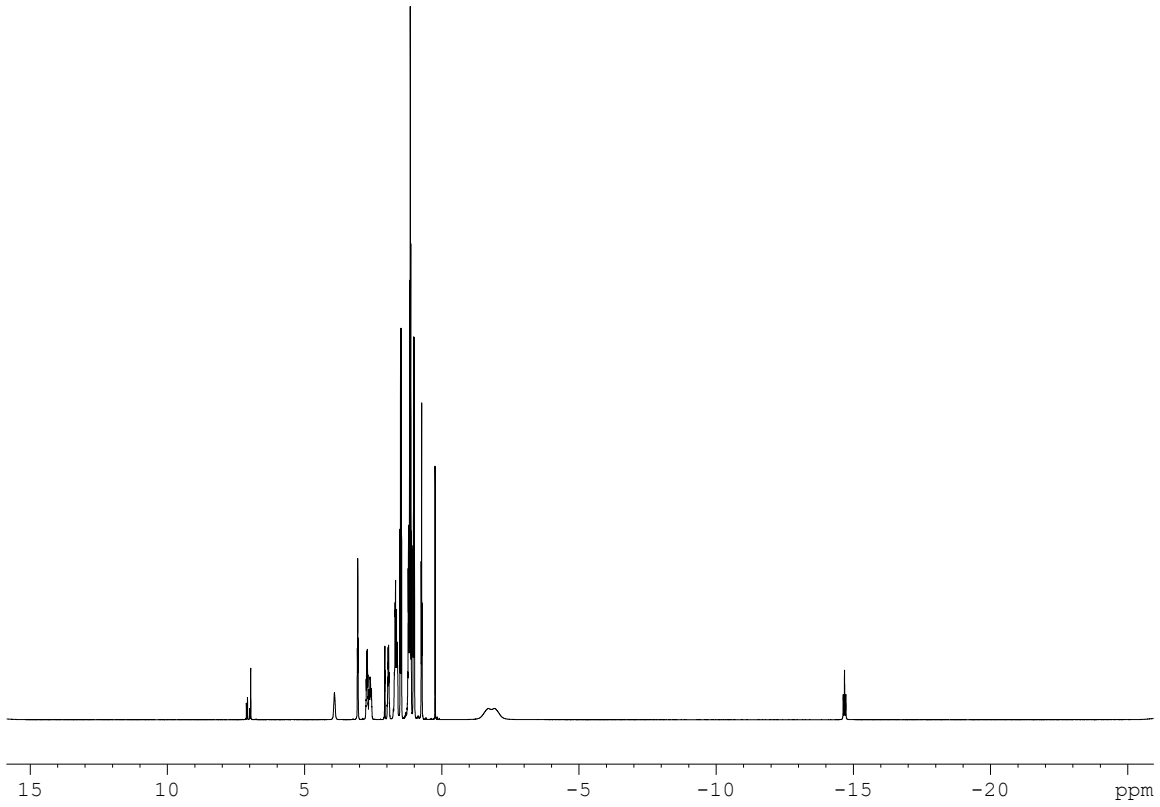


2D ^{1}H-^{13}C HSQC-TOCSY NMR (C_6D_6, 298 K).

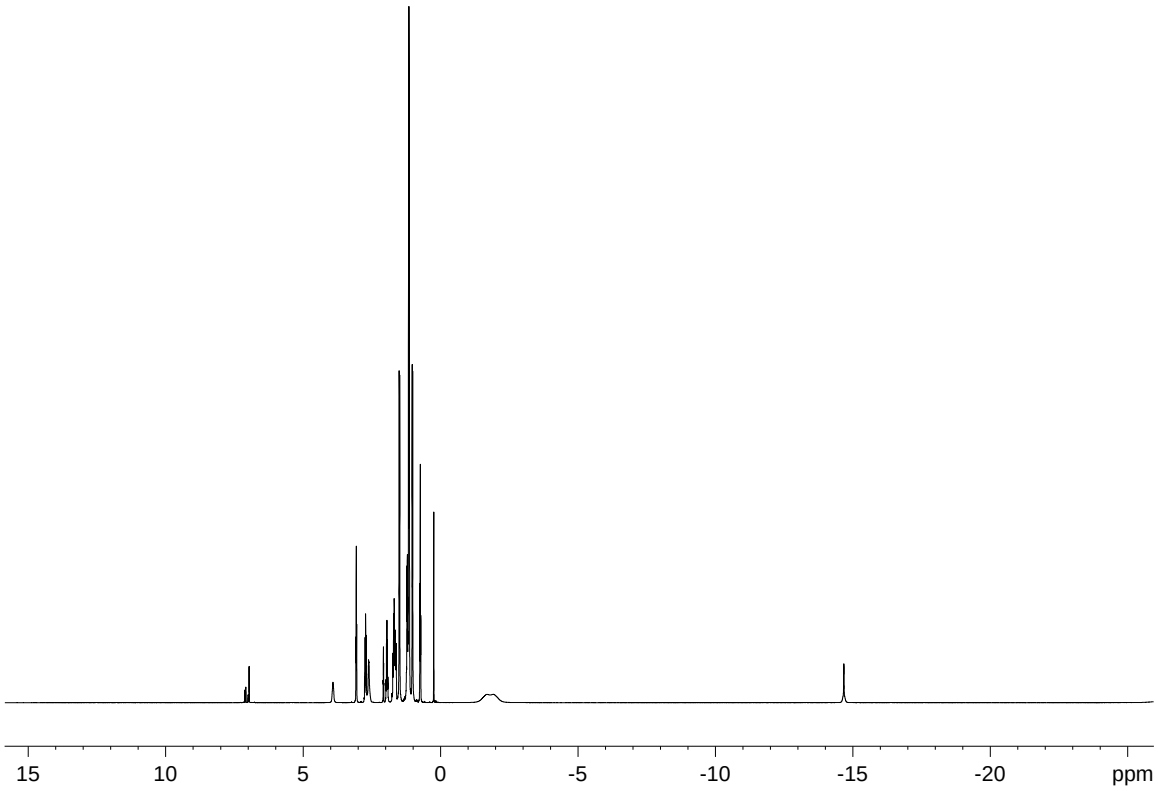


SVIII. NMR spectra of [Ru(H)(BH_4)(CN-*n*Bu)$_2${NH(CH_2CH_2P(*i*Pr)$_2$)$_2$}] (3b)

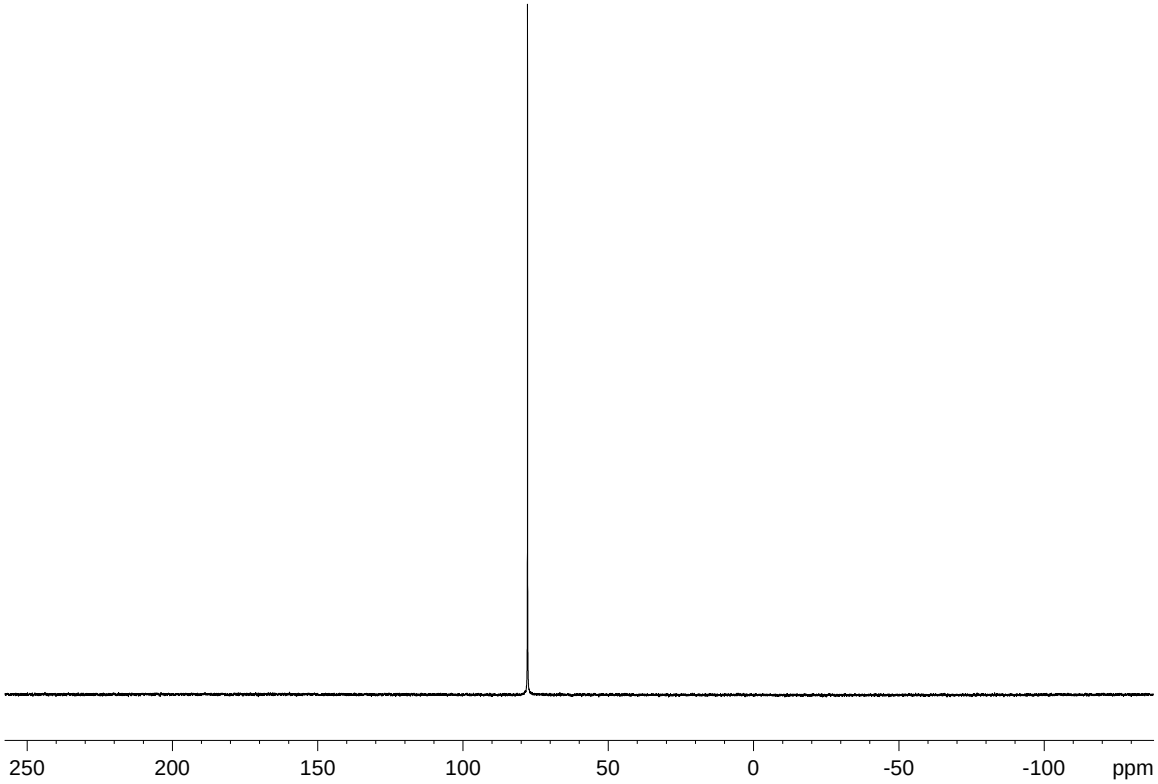
^{1}H NMR spectrum (300 K, C_7D_8).



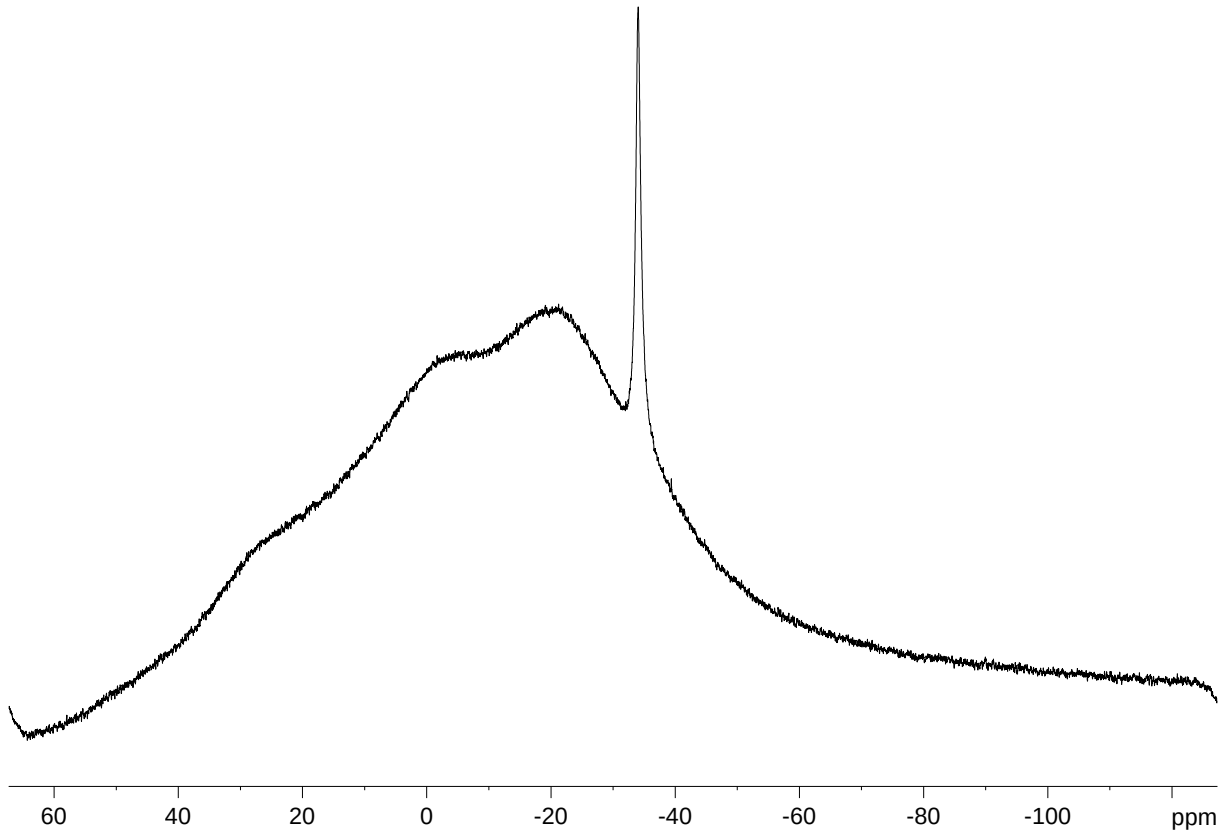
^{1}H{^{31}P} NMR spectrum (300 K, C_7D_8).



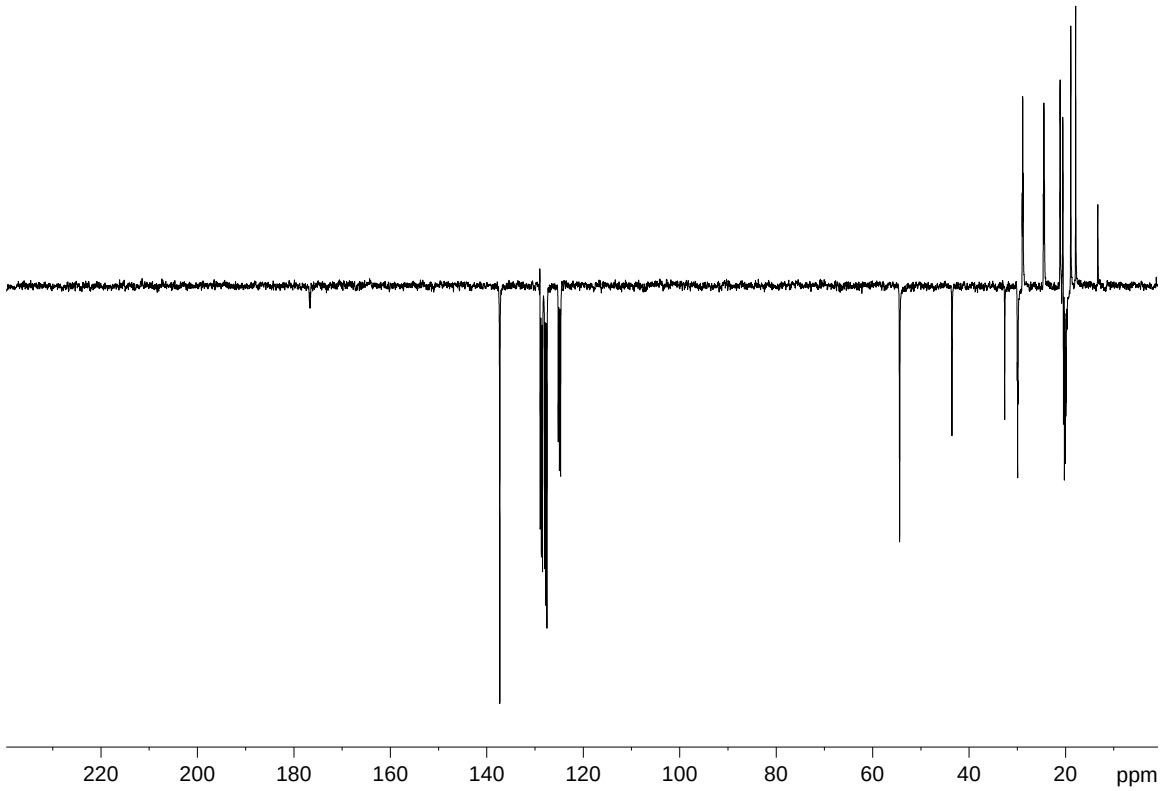
$^{31}P\{^{1}H\}$ NMR spectrum (300 K, C_7D_8).



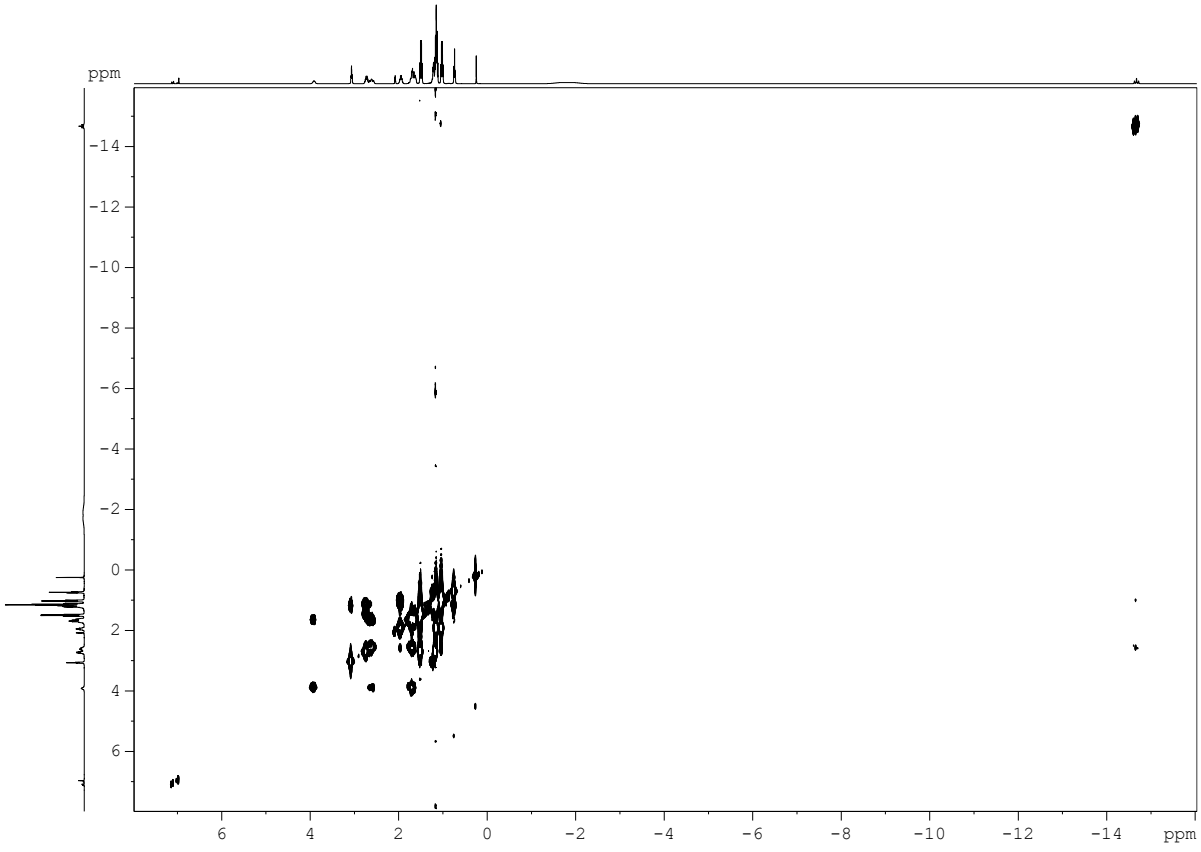
$^{11}B\{^{1}H\}$ NMR spectrum (300 K, C_7D_8).



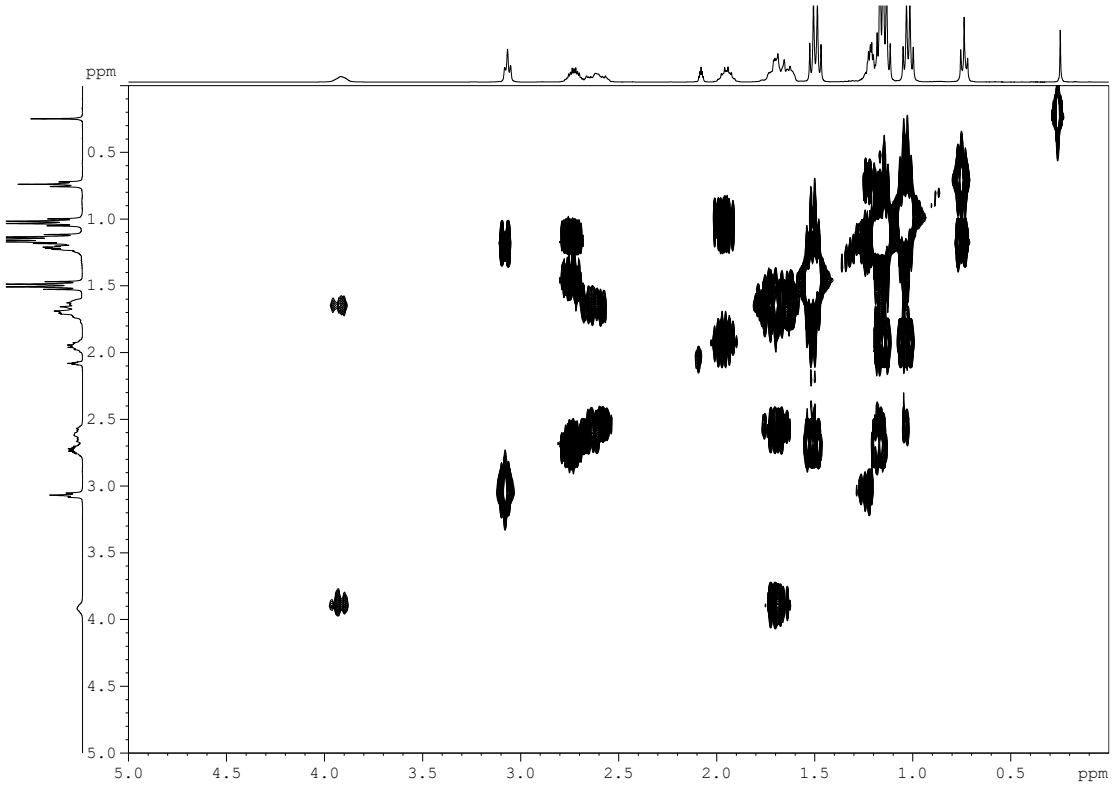
$^{13}C\{^{1}H\}$ JMOD NMR spectrum (300 K, C_7D_8).



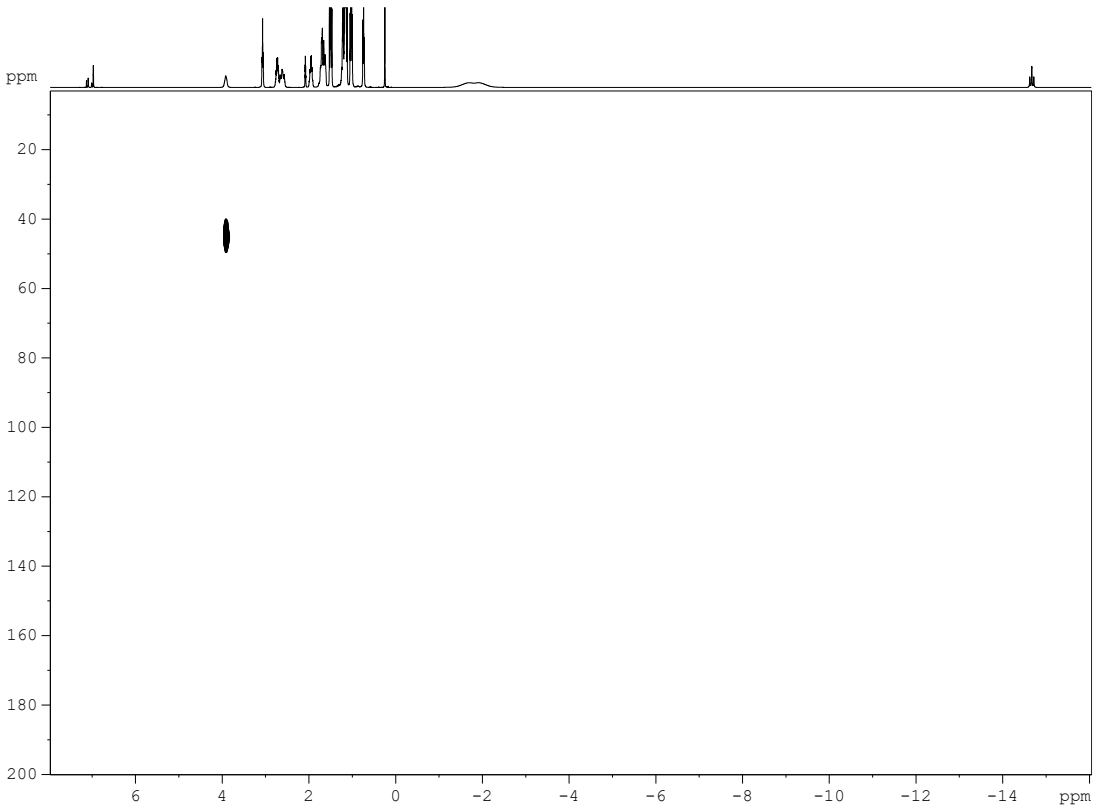
2D ^{1}H-^{1}H COSY NMR spectrum (300 K, C_7D_8).



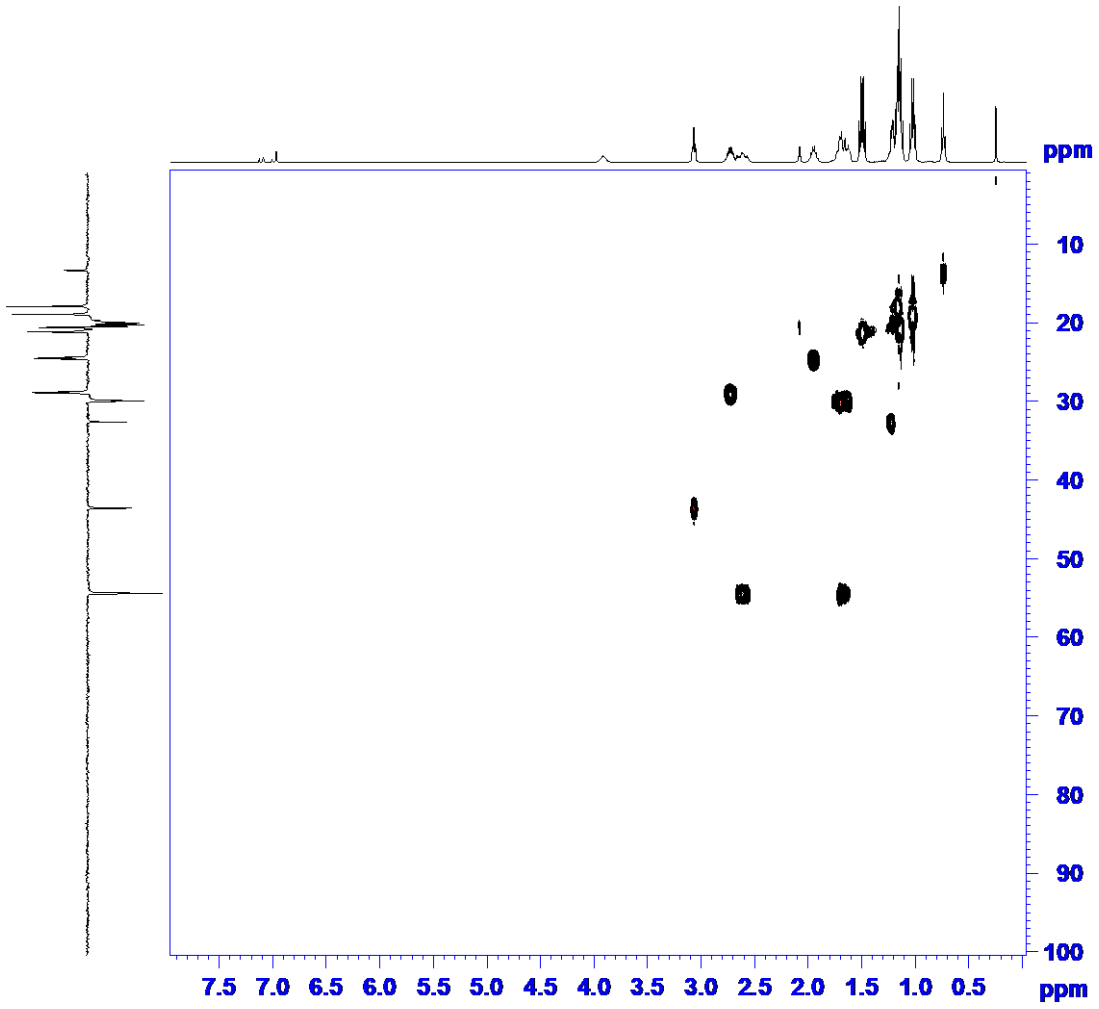
2D ^{1}H-^{1}H COSY NMR spectrum (300 K, C_7D_8).



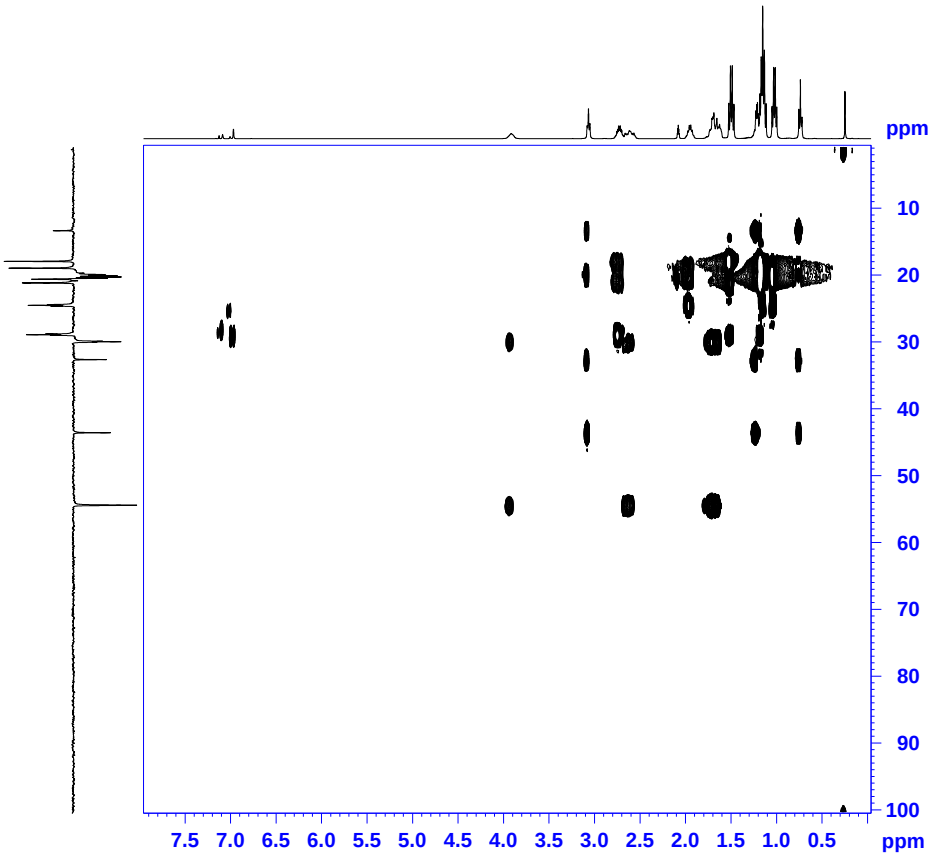
2D ^{1}H-^{15}N HSQC NMR spectrum (300 K, C_7D_8).



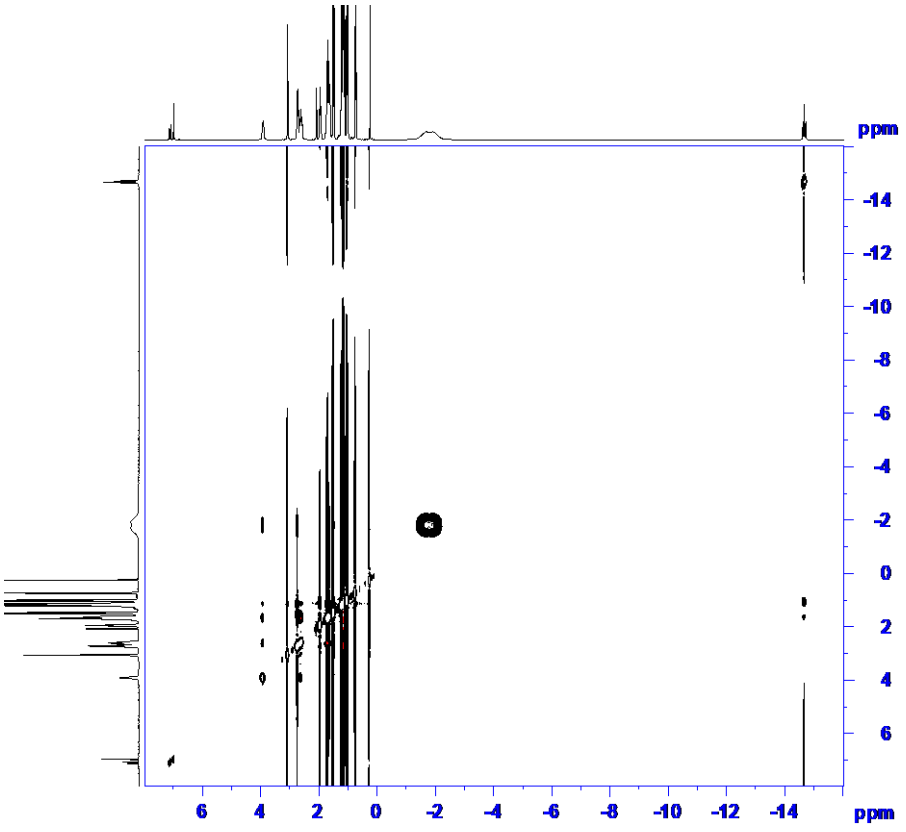
2D ^{1}H-^{13}C HSQC NMR spectrum (300 K, C_7D_8).



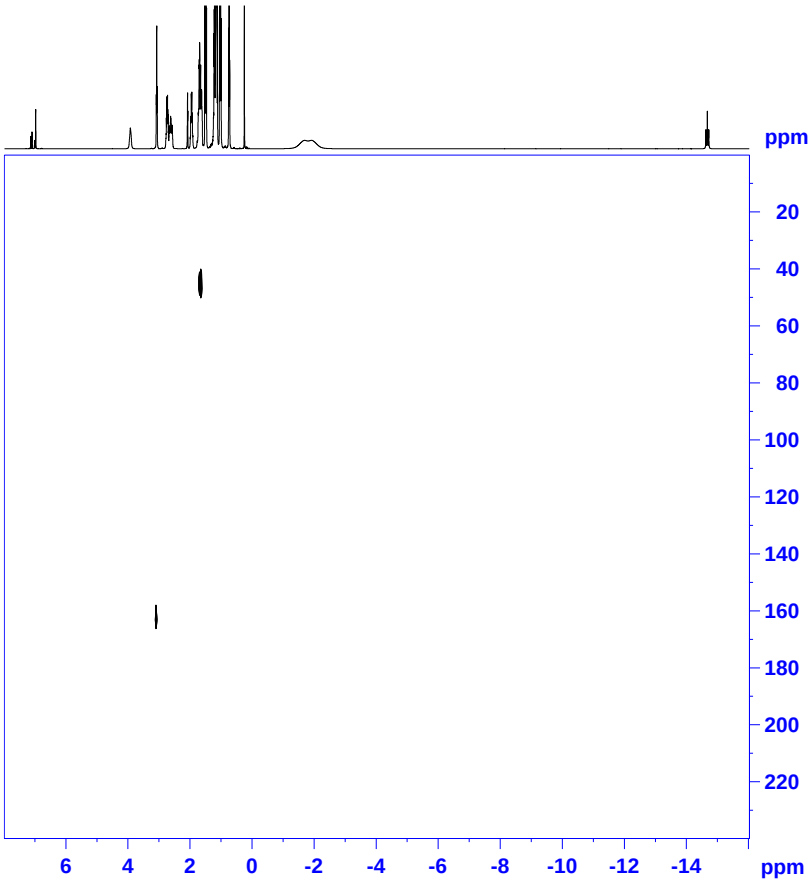
2D ^{1}H-^{13}C TOCSY HSQC NMR (300 K, C_7D_8).



2D ^{1}H-^{1}H NOESY NMR spectrum (300 K, C_7D_8).

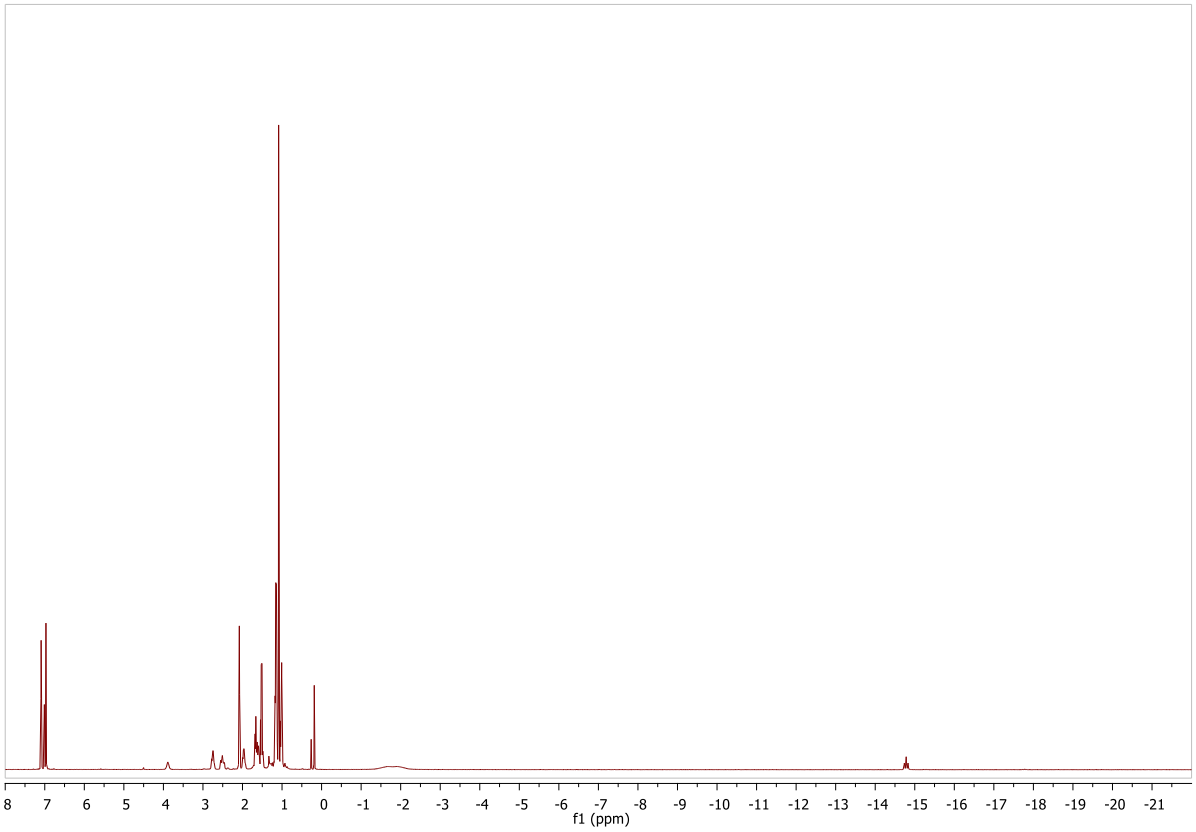


^{1}H-^{15}N HMBC NMR (300 K, C_7D_8).

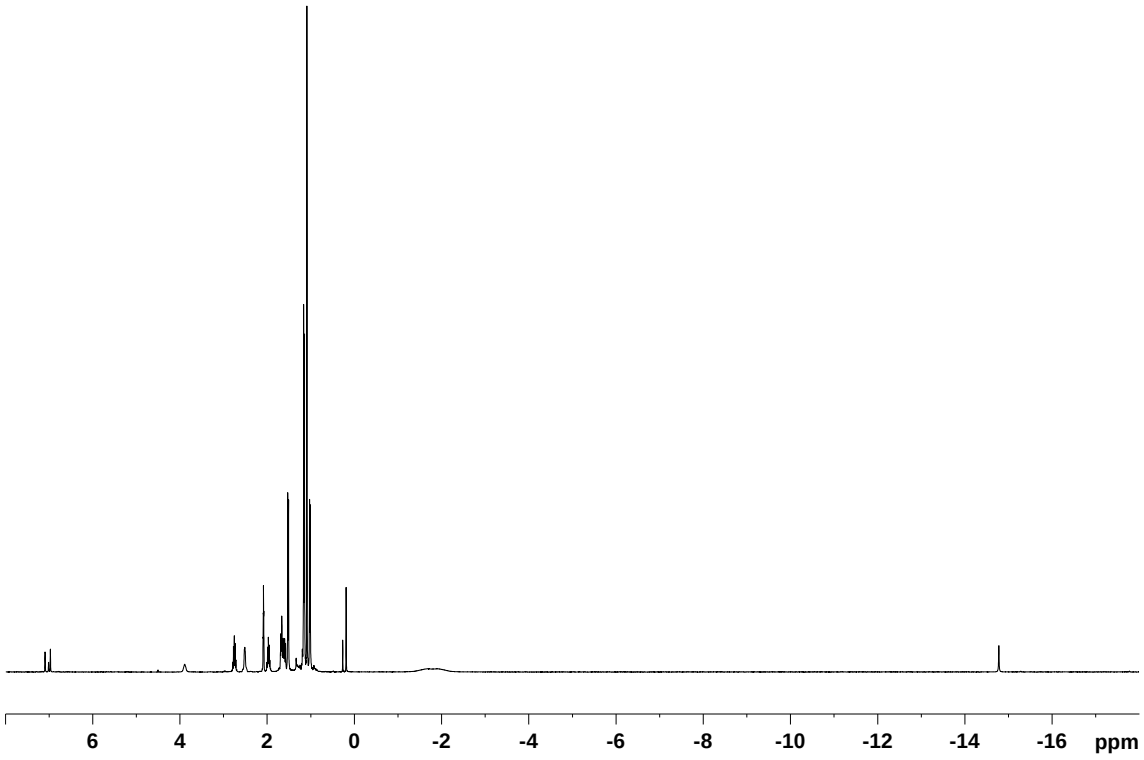


SIX. NMR spectra and X-ray structure of [Ru(H)(BH_4)(CN-*t*Bu){NH($CH_2CH_2P(iPr)_2)_2$}] (3c)

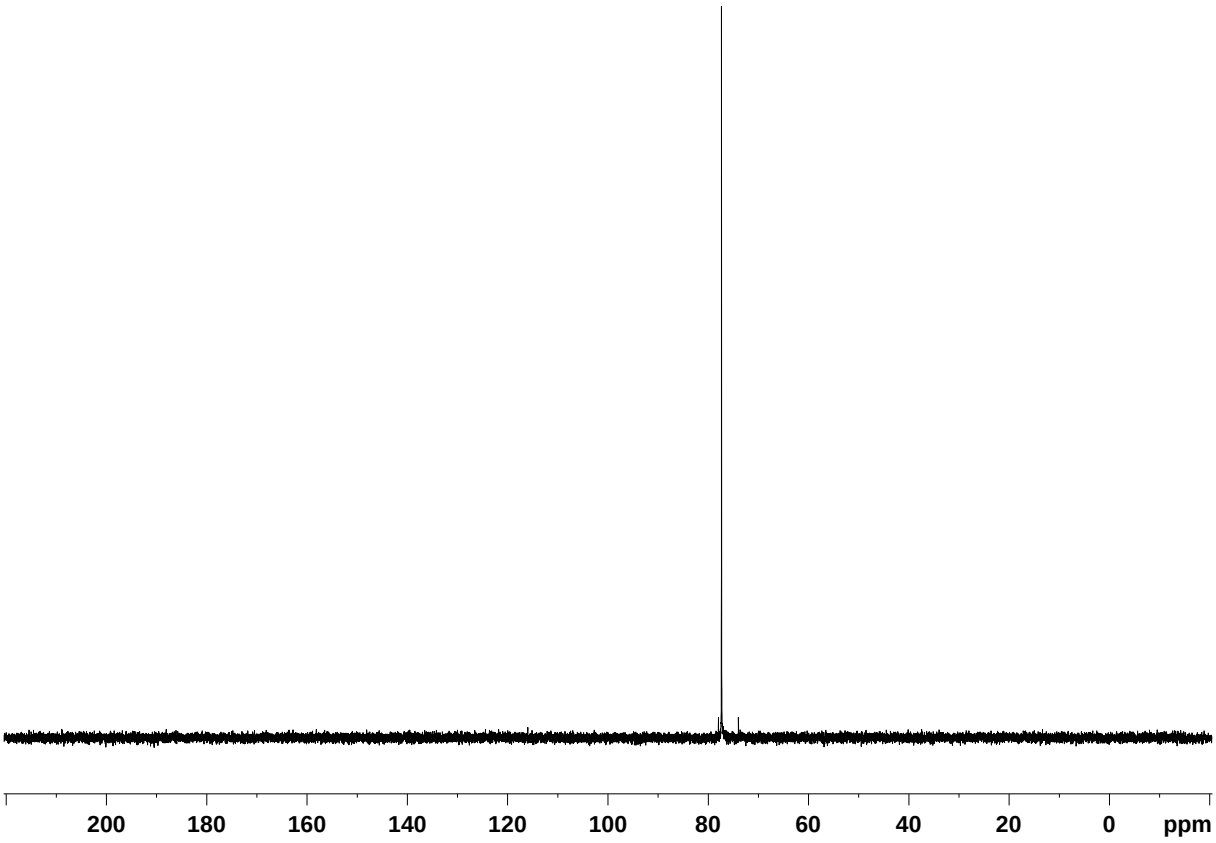
^{1}H NMR spectrum (Tol-d8, 293 K).



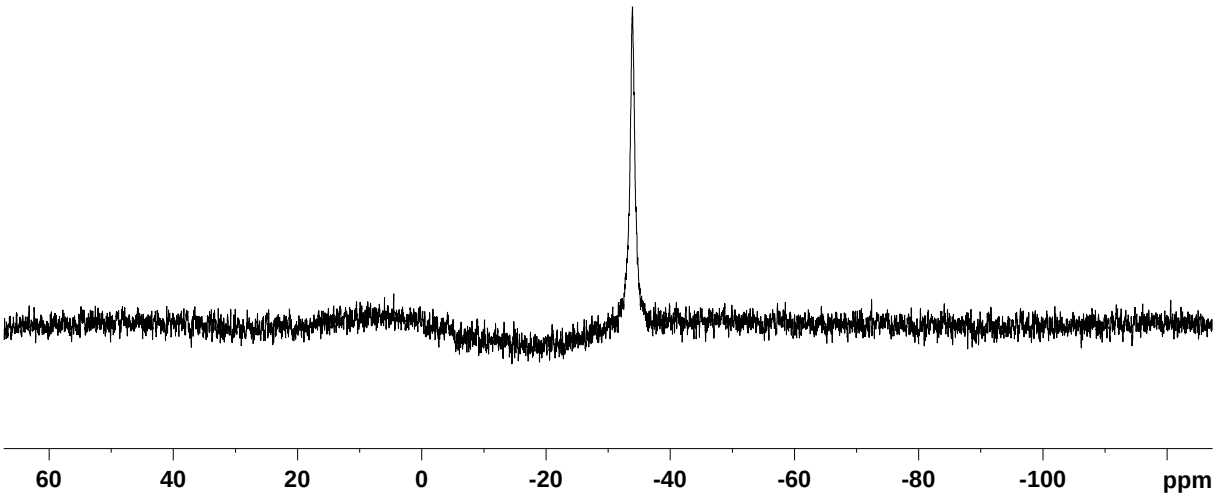
^{1}H{^{31}P} NMR spectrum (Tol-d8, 293K).



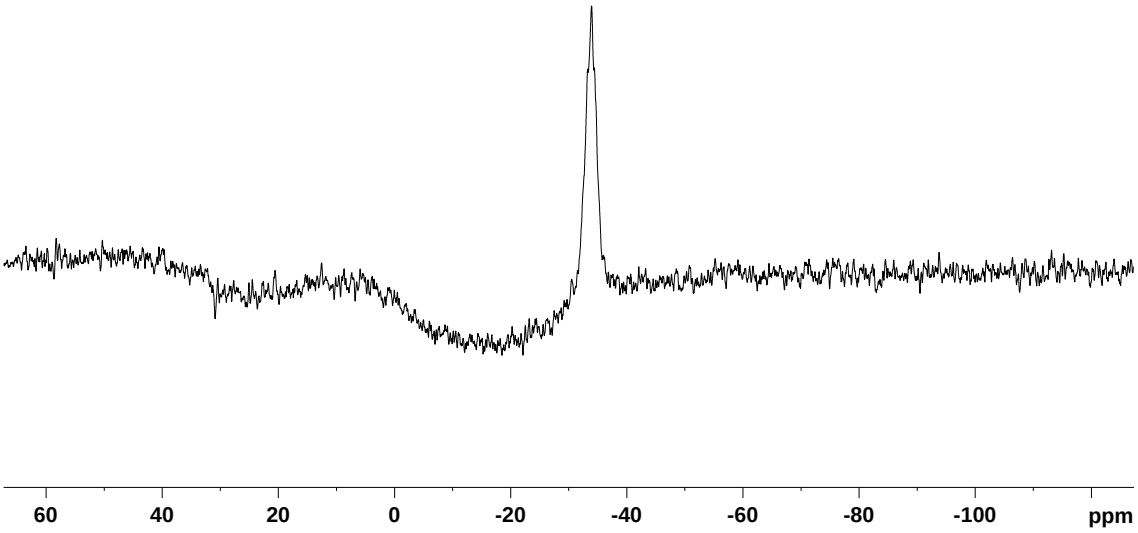
$^{31}P\{^{1}H\}$ NMR spectrum (Tol-d8, 293 K).



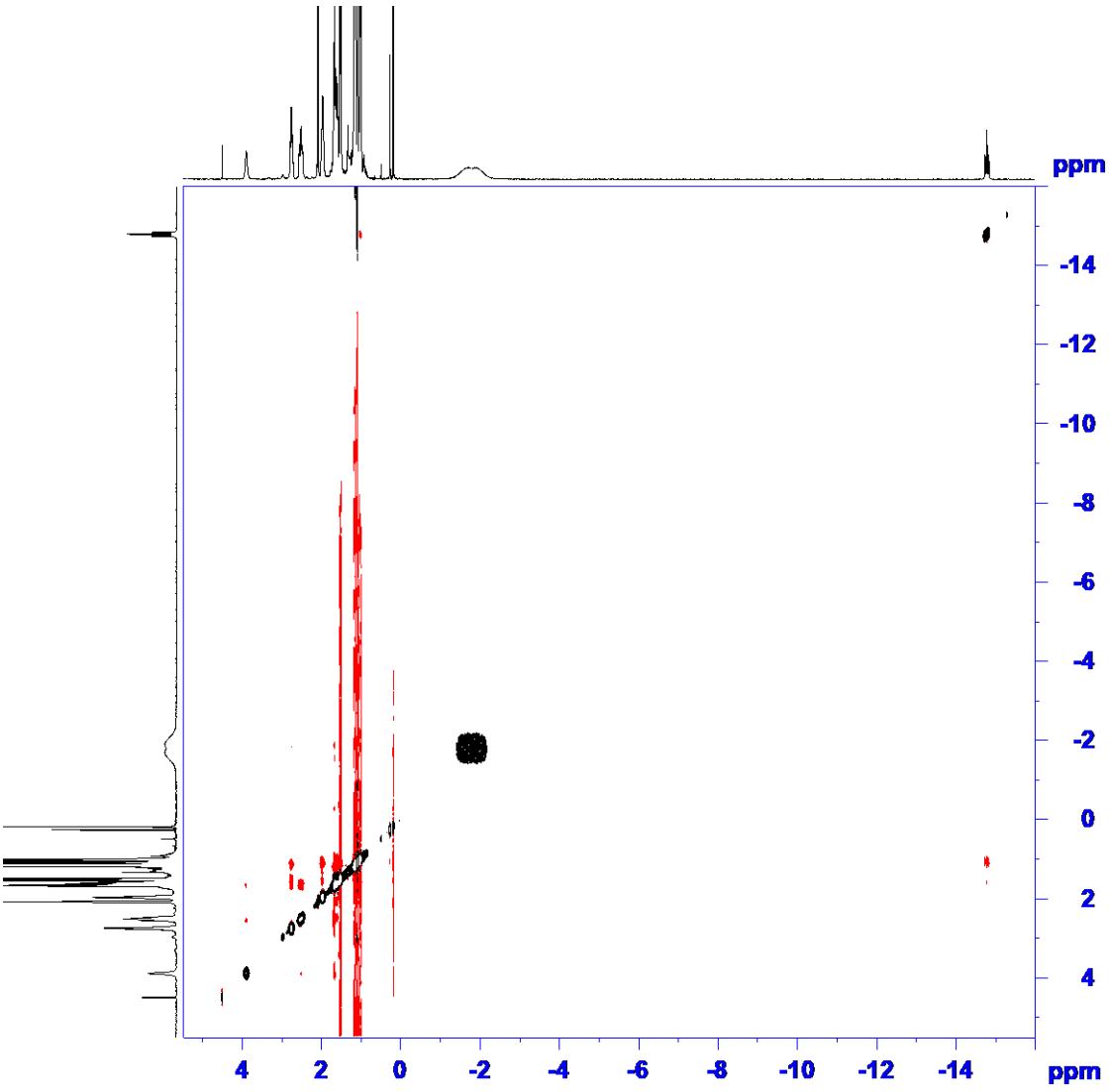
$^{11}B\{^{1}H\}$ NMR spectrum (Tol-d8, 293 K).



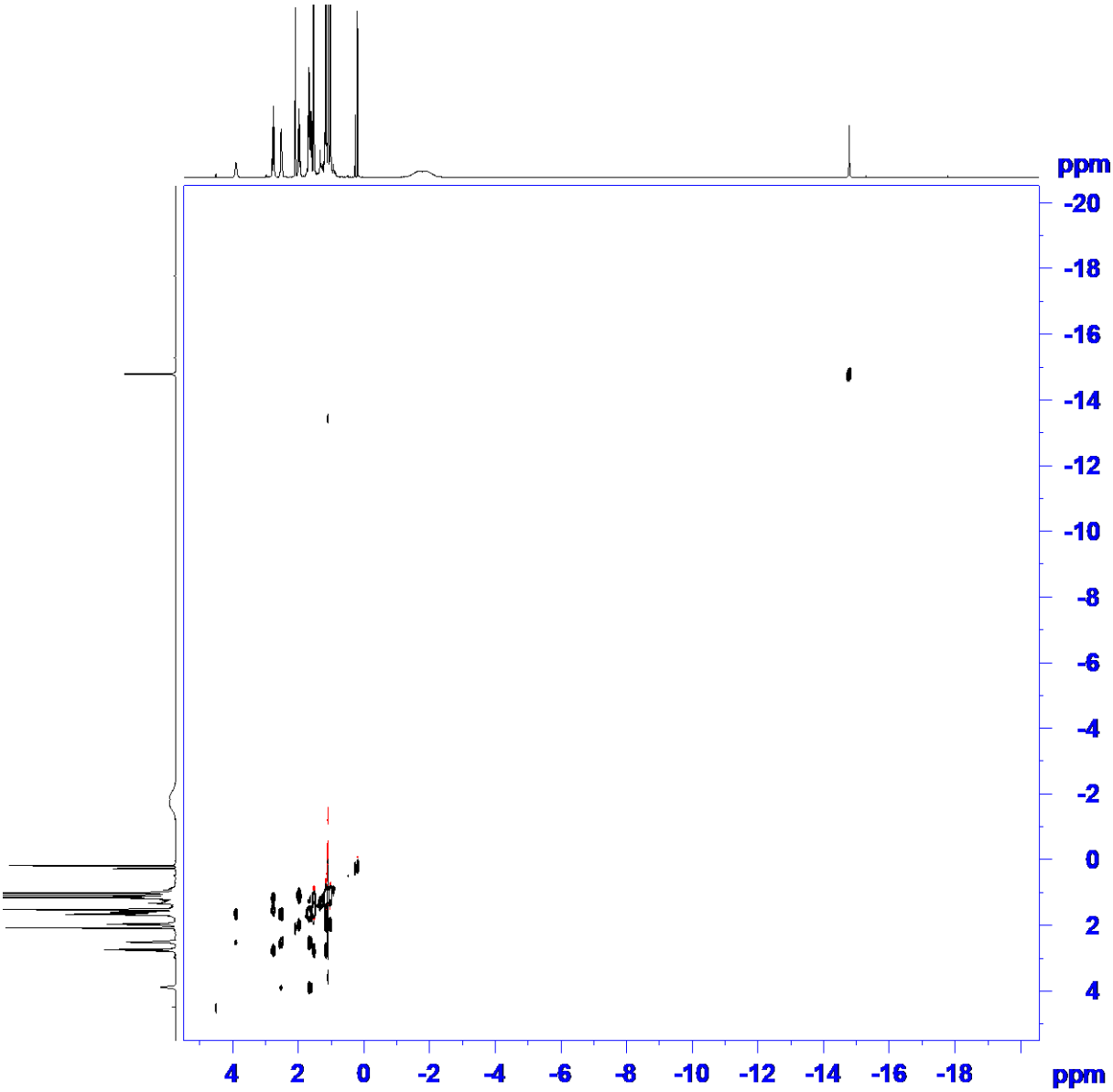
^{11}B NMR spectrum (Tol-d8, 293 K).



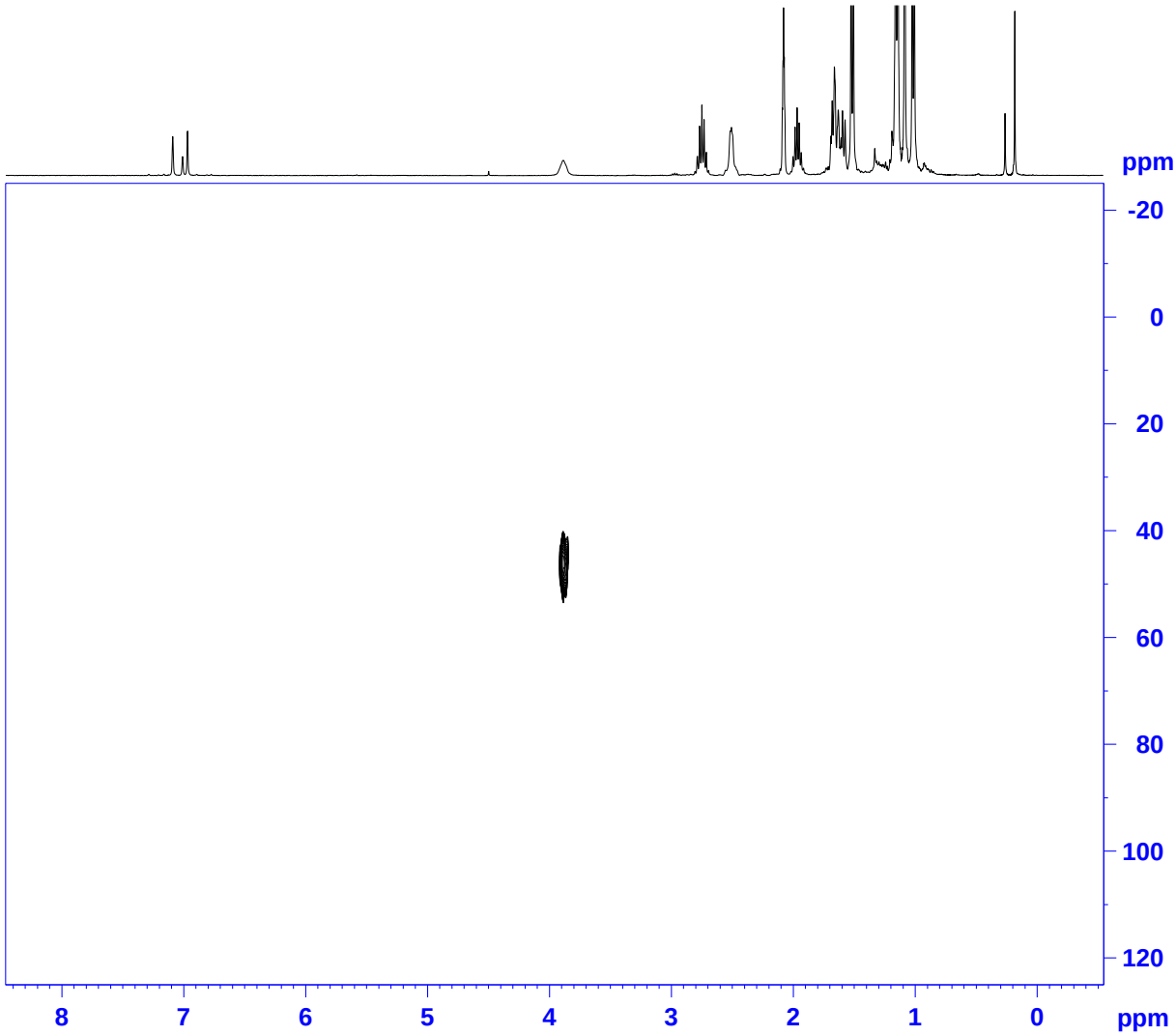
2D ^{1}H-^{1}H NOESY NMR spectrum (Tol-d8, 293 K).



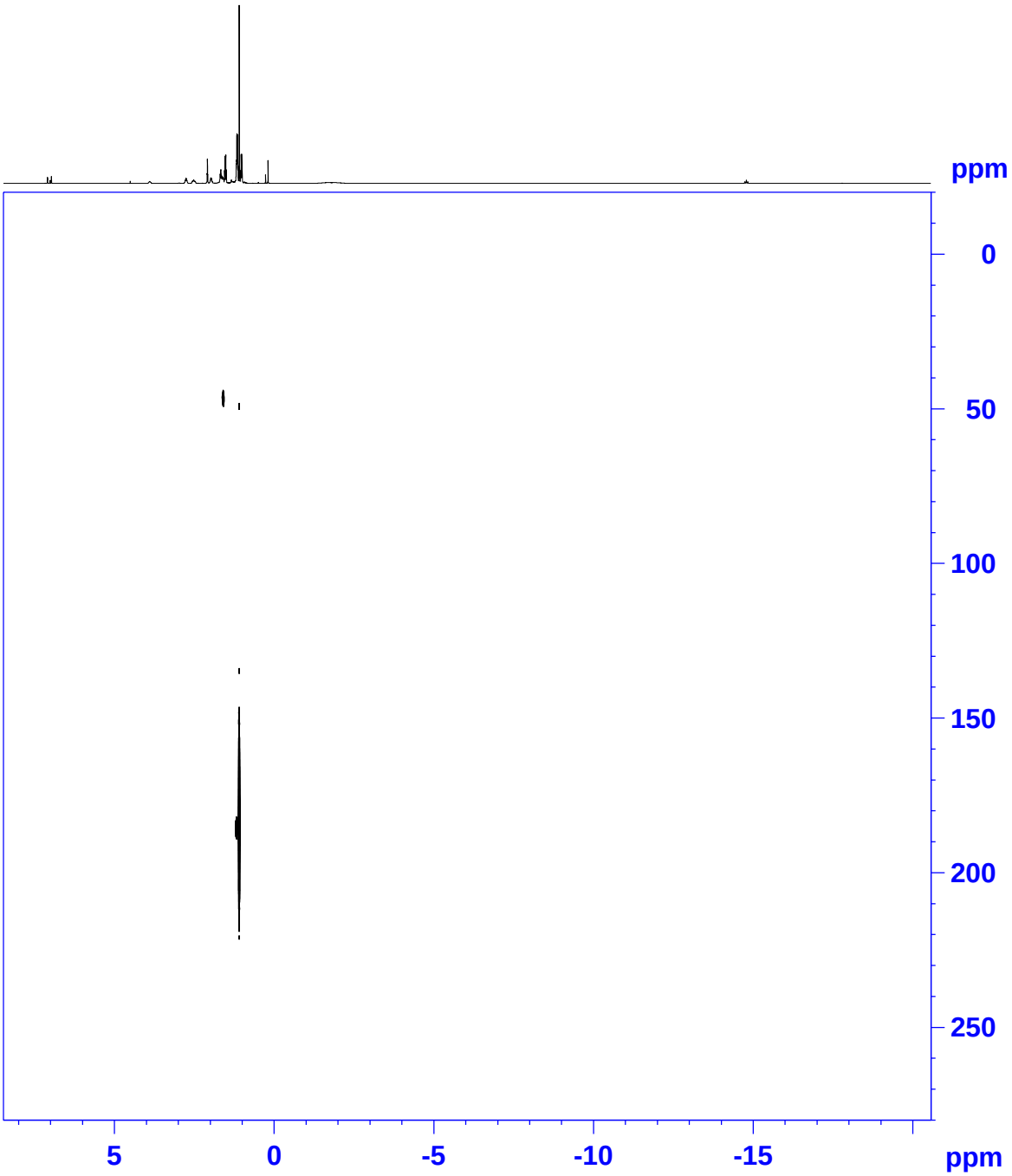
2D ^{1}H-^{1}H TOCSY NMR spectrum (Tol-d8, 293 K).



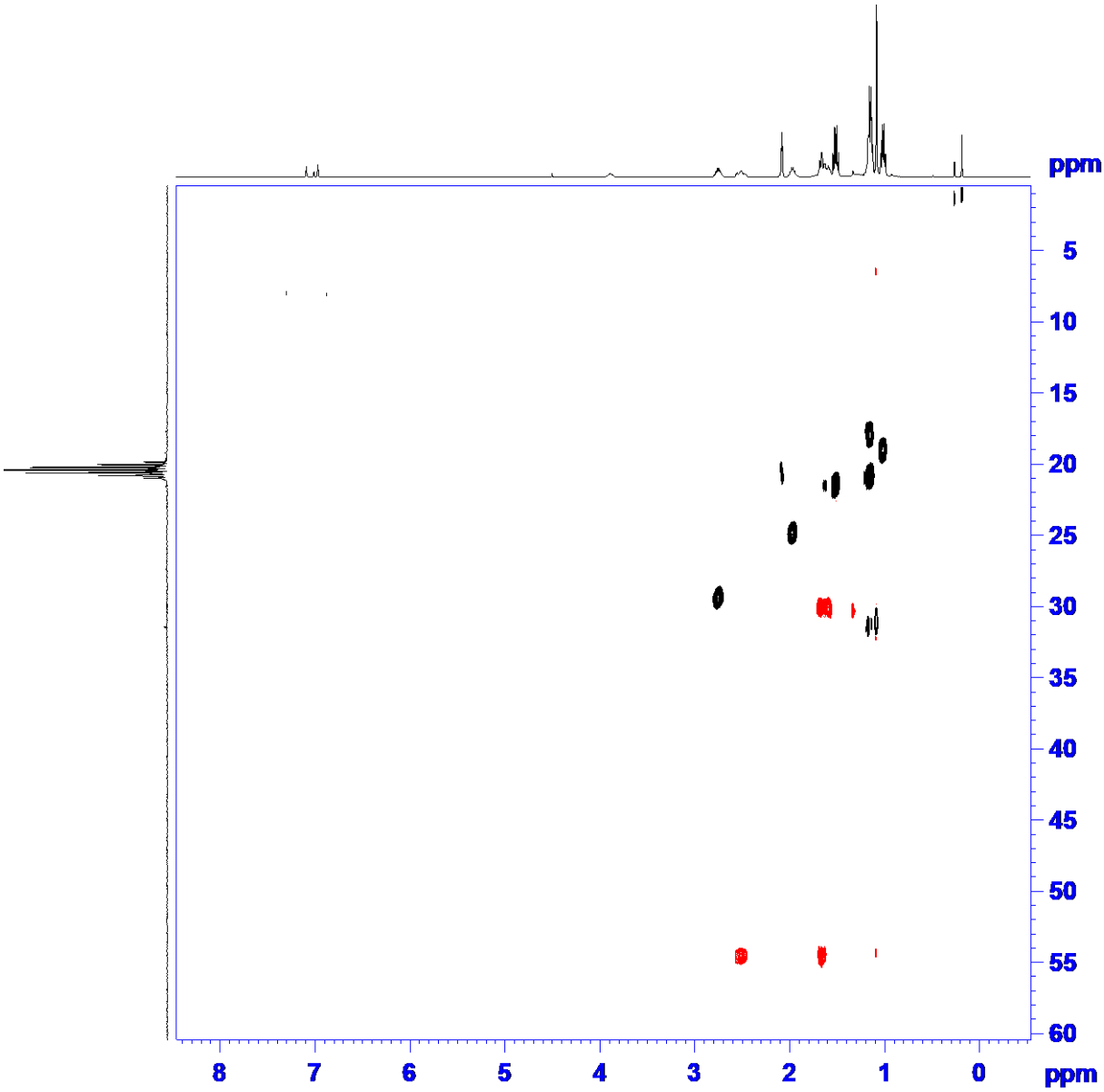
2D ^{1}H-^{15}N HSQC NMR spectrum (Tol-d8, 293 K).



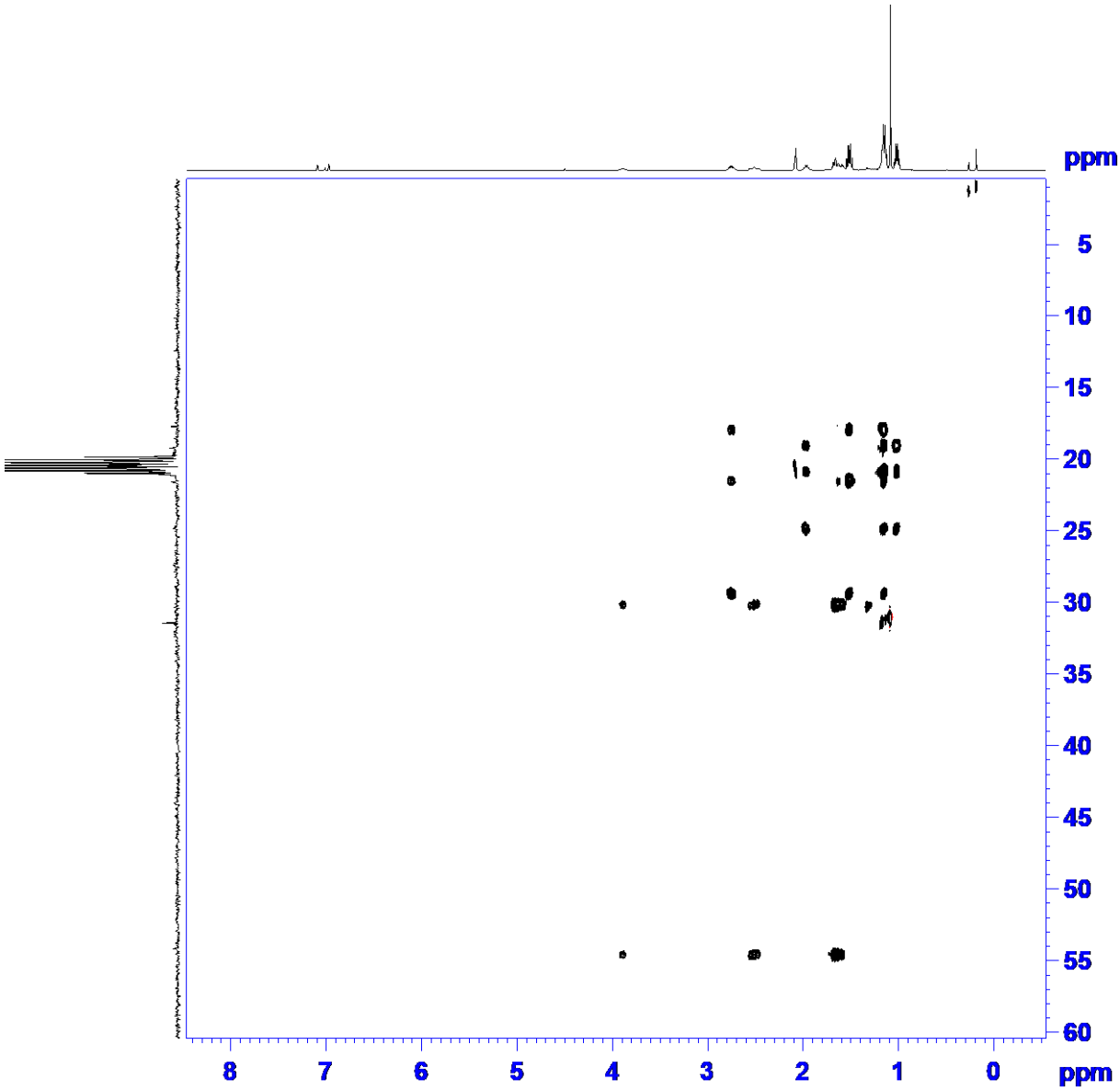
2D ^{1}H-^{15}N HMBC NMR spectrum (Tol-d8, 293 K).



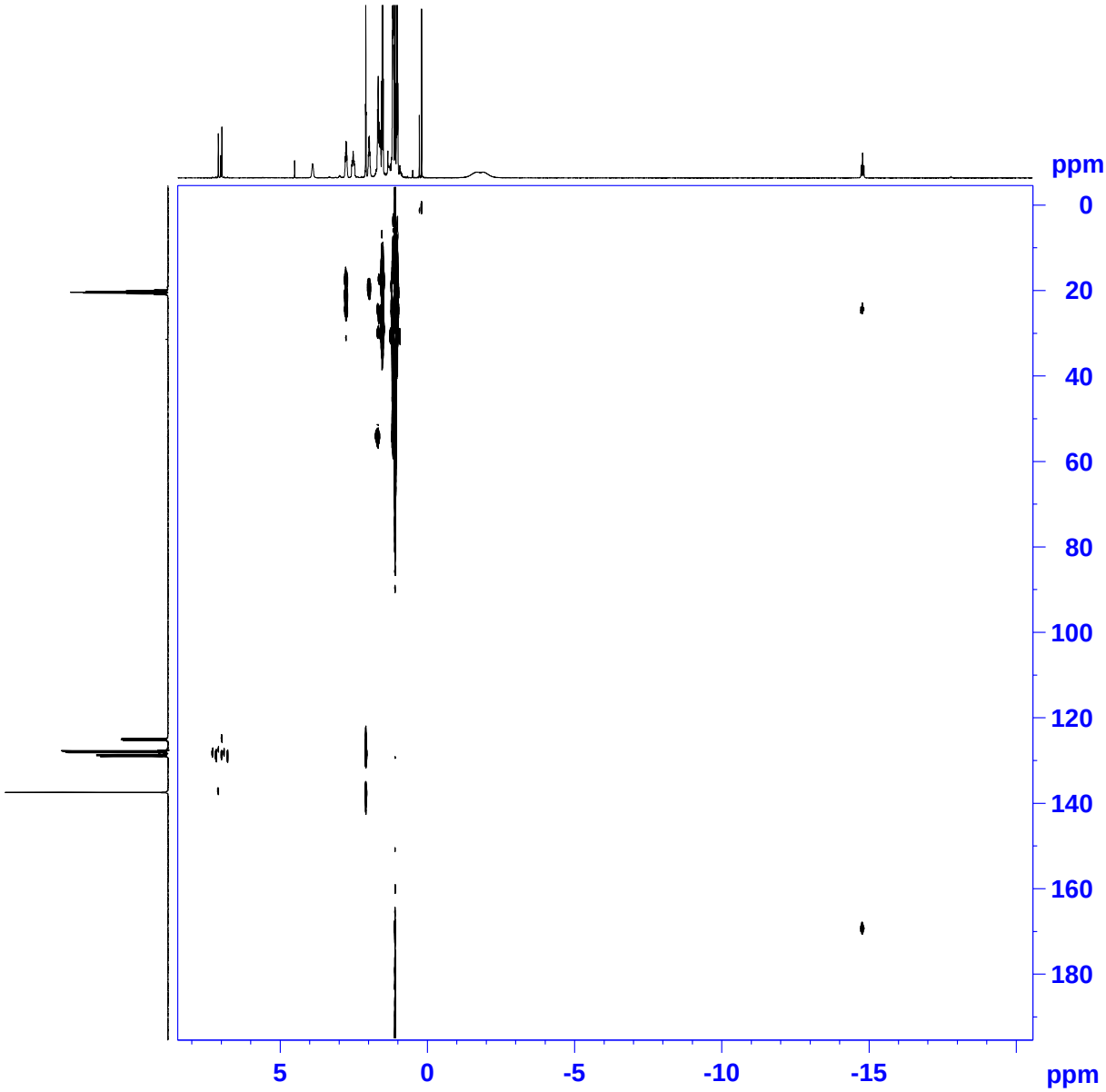
2D ^{1}H-^{13}C HSQC NMR spectrum (Tol-d8, 293 K).



2D ^{1}H-^{13}C HSQC TOCSY NMR spectrum (Tol-d8, 293 K).

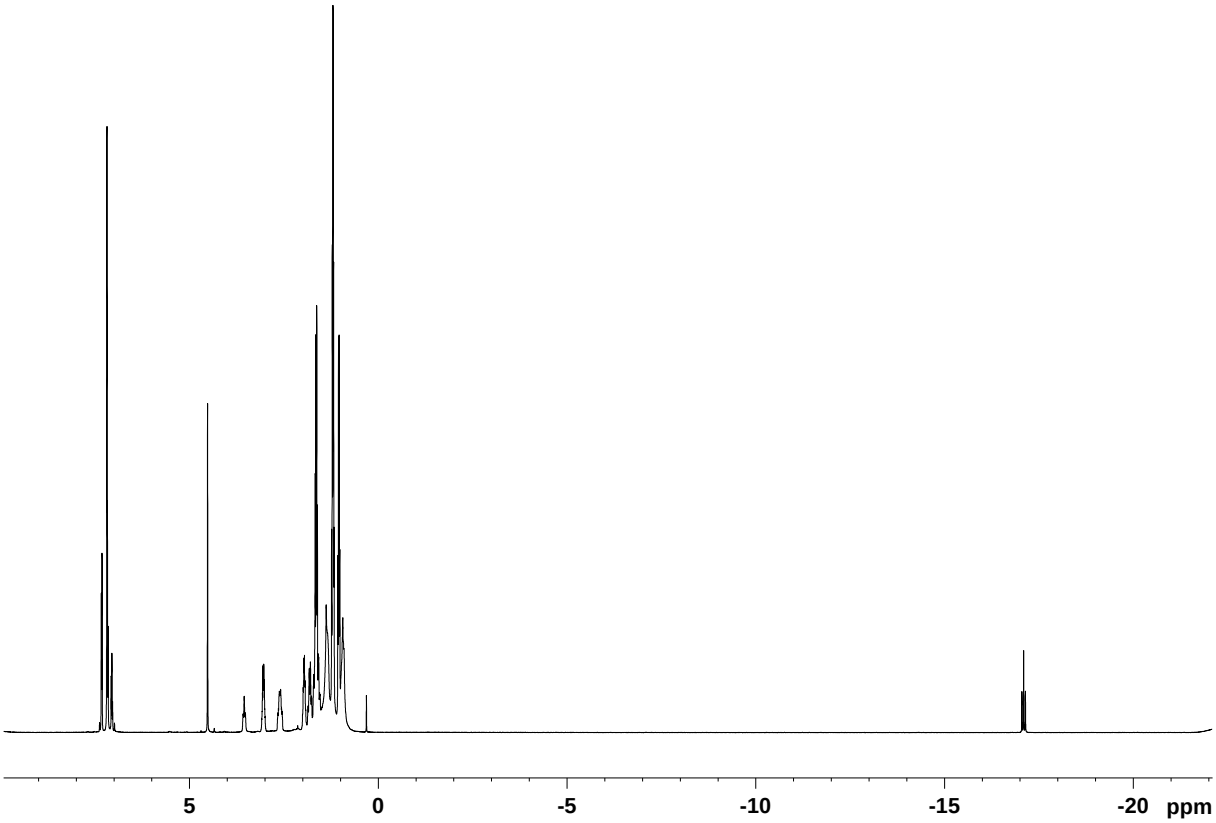


2D ^{1}H-^{13}C HMBC NMR spectrum (Tol-d8, 293 K).

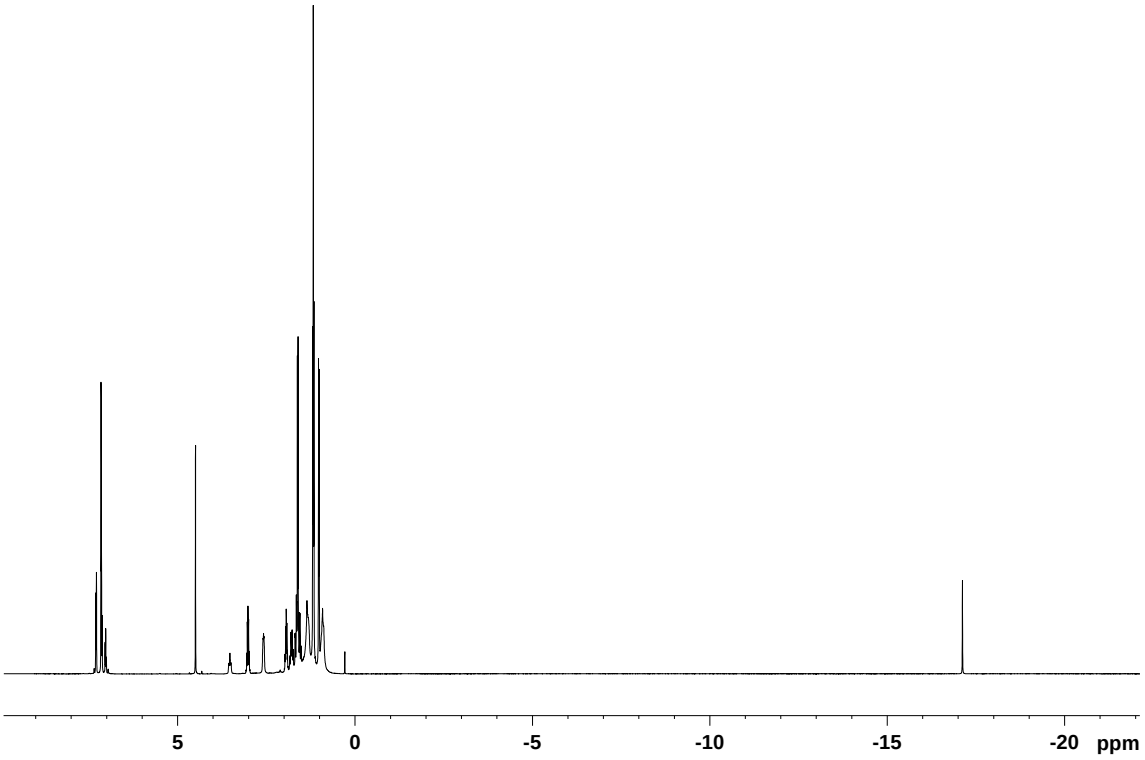


SX. NMR spectra and X-ray structure of [Ru(H)(Cl)(CN-CH_2Ph){NH($CH_2CH_2P(iPr)_2)_2$}] (4a)

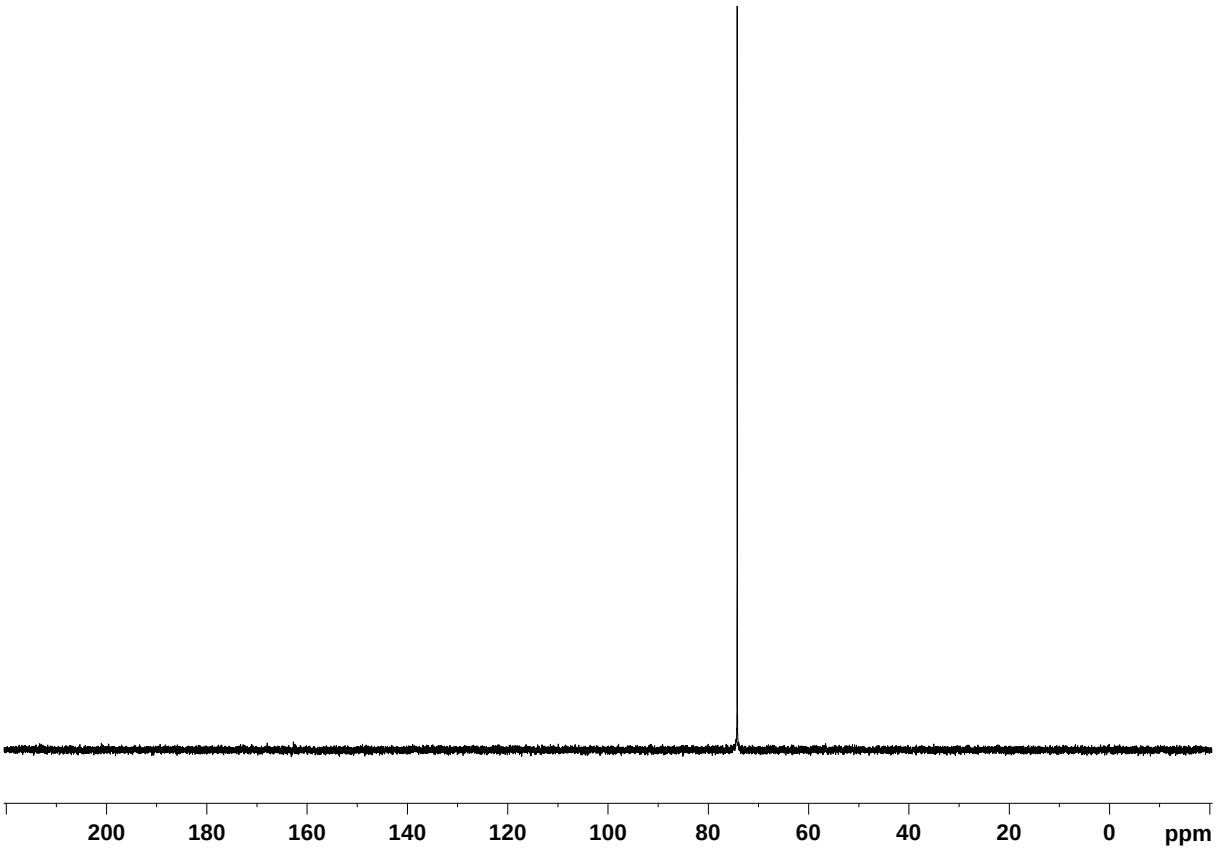
^{1}H NMR spectrum (C_6D_6, 300 K).



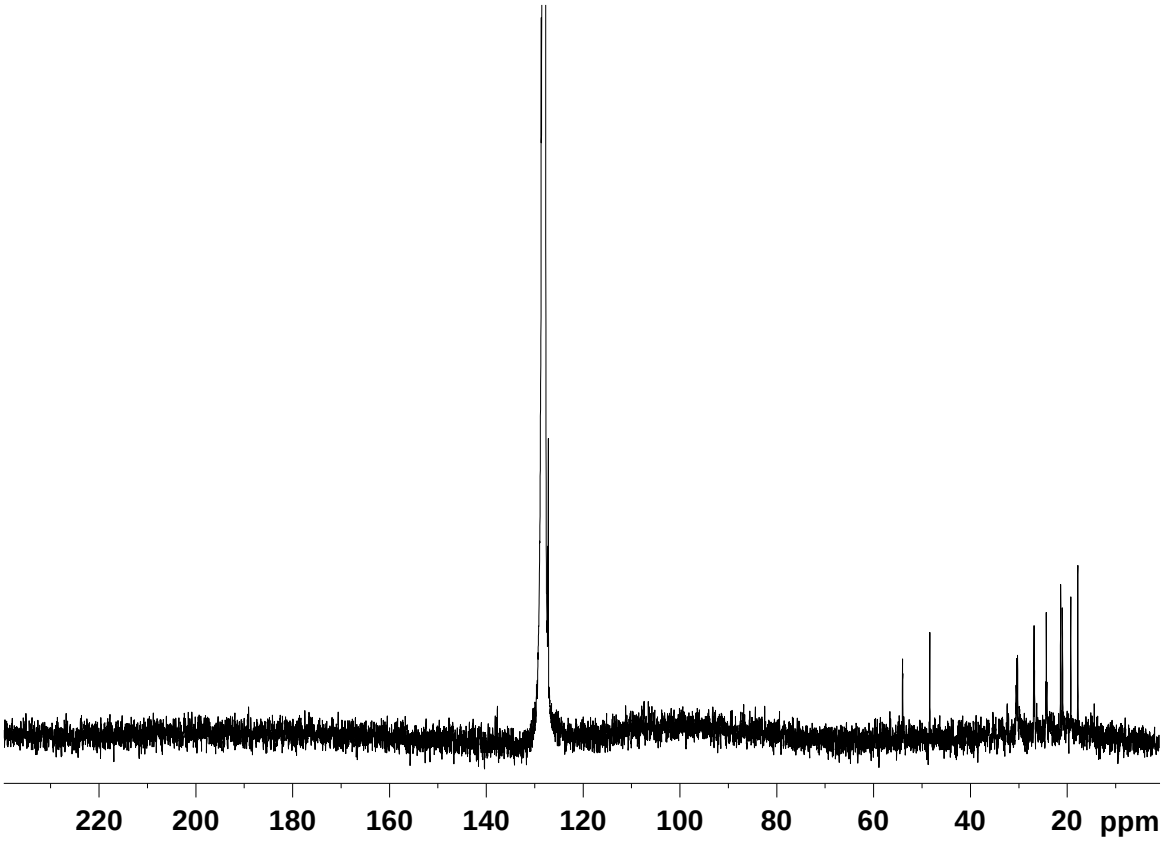
^{1}H{^{31}P} NMR spectrum (C_6D_6, 300 K).



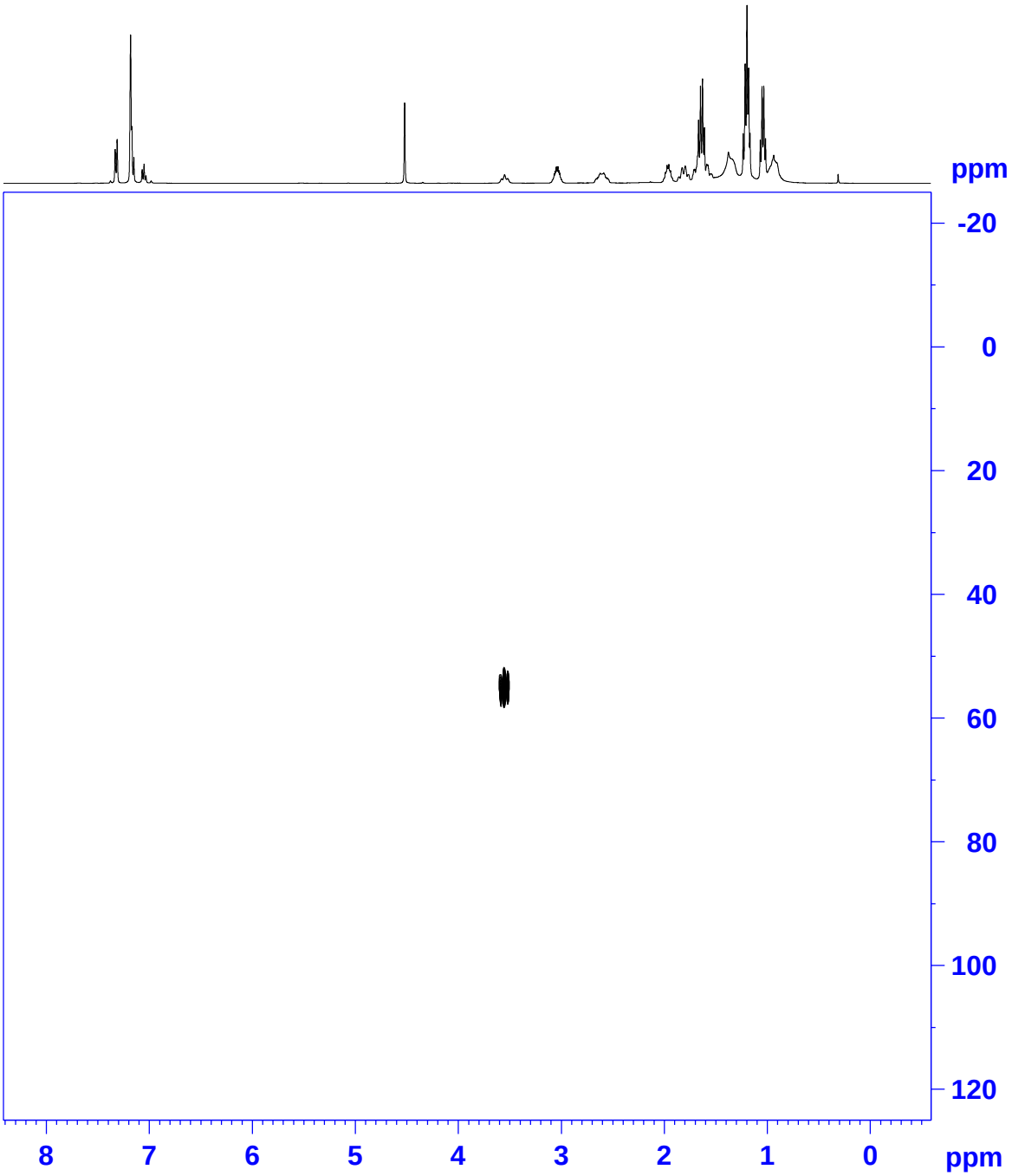
$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K).



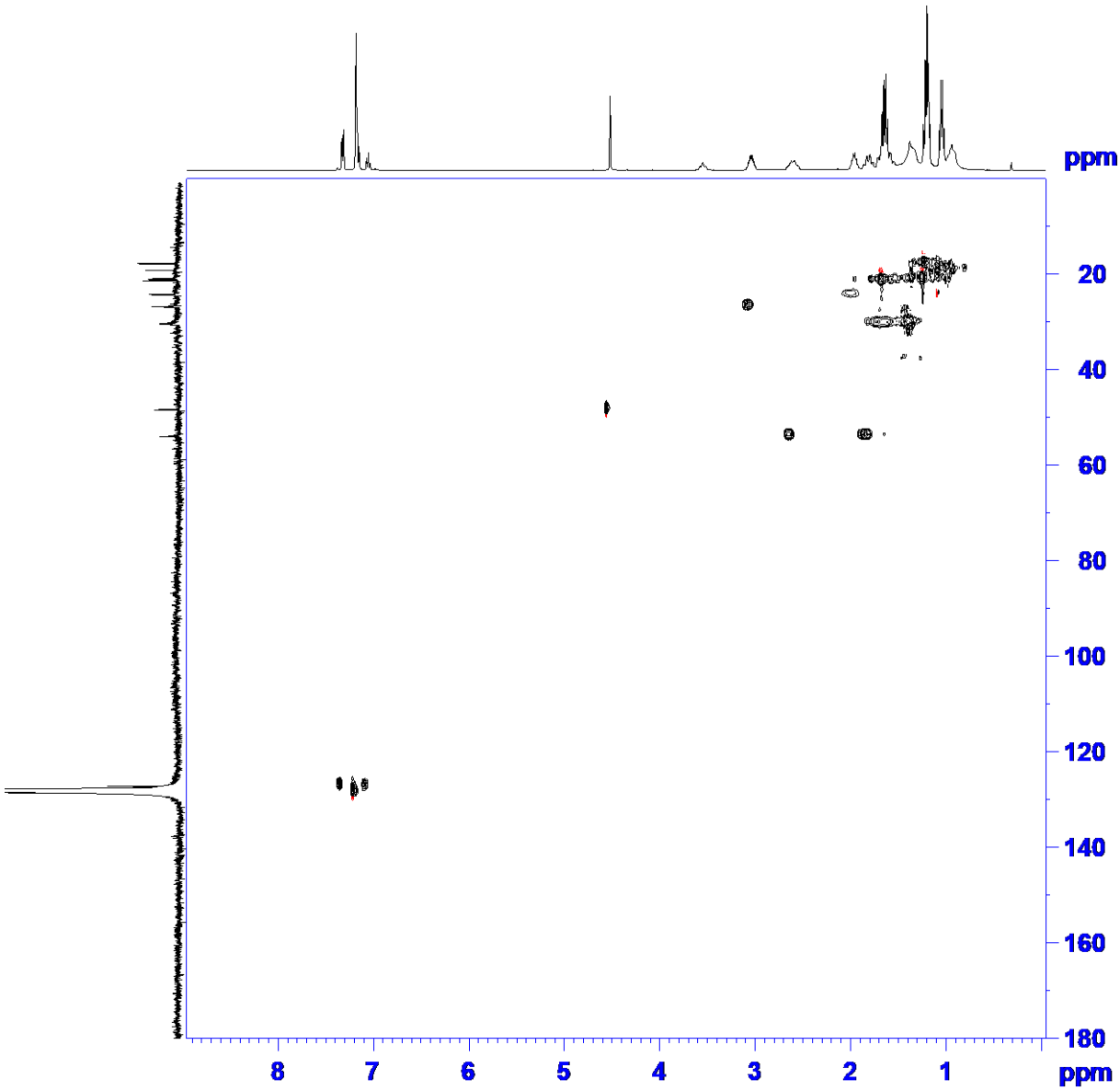
$^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K).



2D ^{1}H-^{15}N HSQC NMR spectrum (C_6D_6, 300 K).

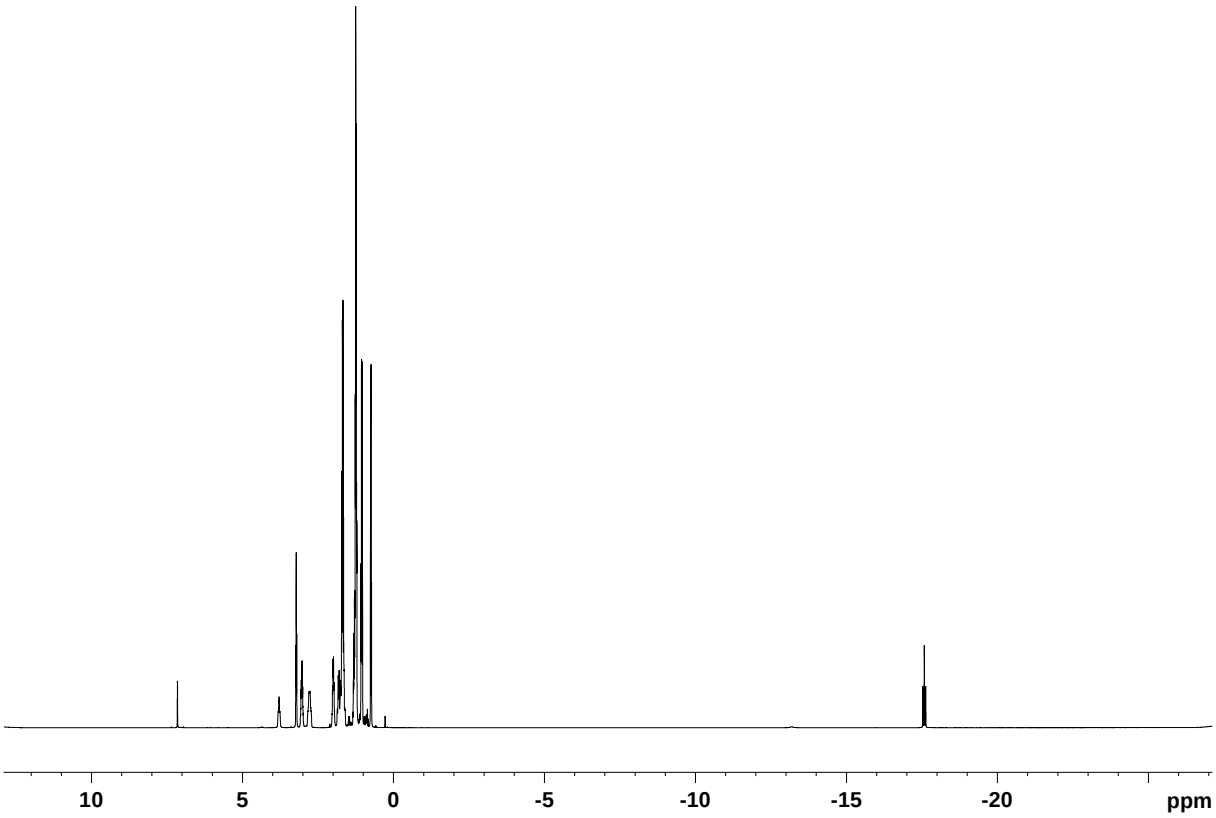


2D ^{1}H-^{13}C HSQC NMR spectrum (C_6D_6, 300 K).

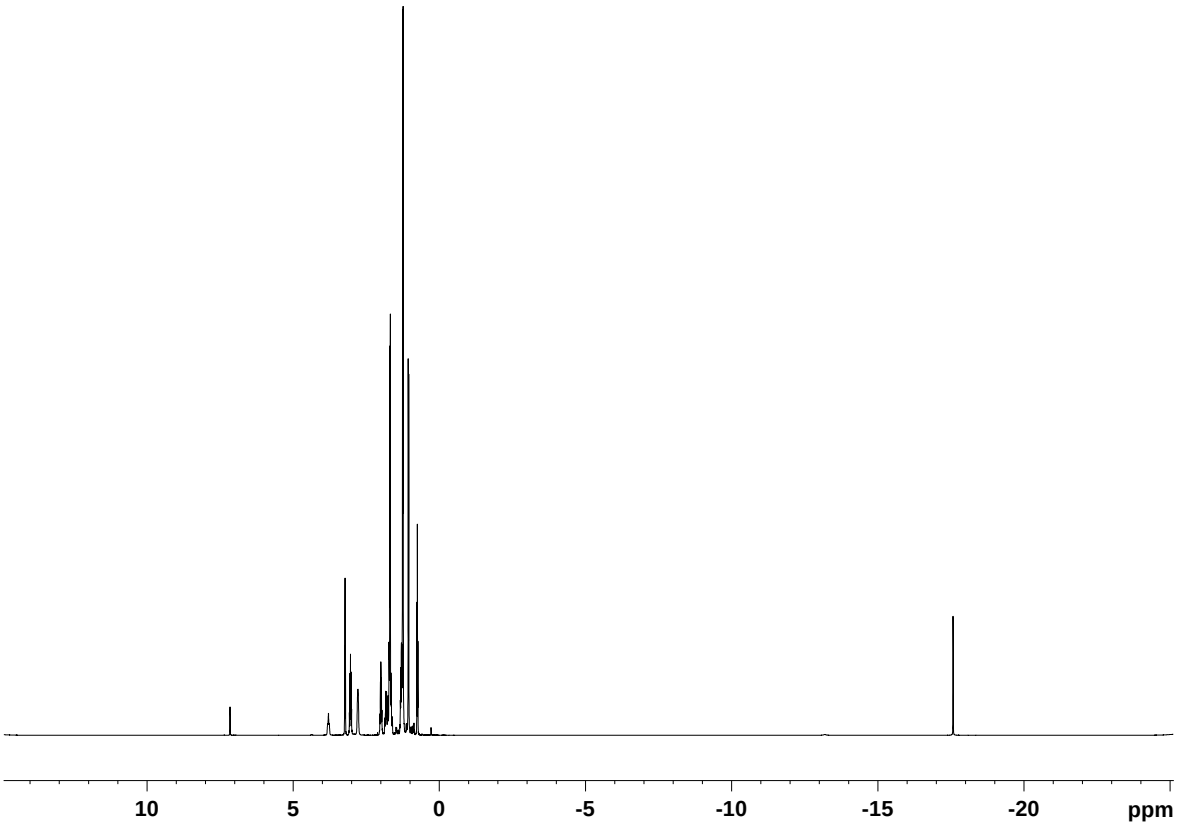


SXI. NMR spectra of [Ru(H)(Cl)(CN-*n*Bu){NH($CH_2CH_2P(iPr)_2)_2$}] (4b)

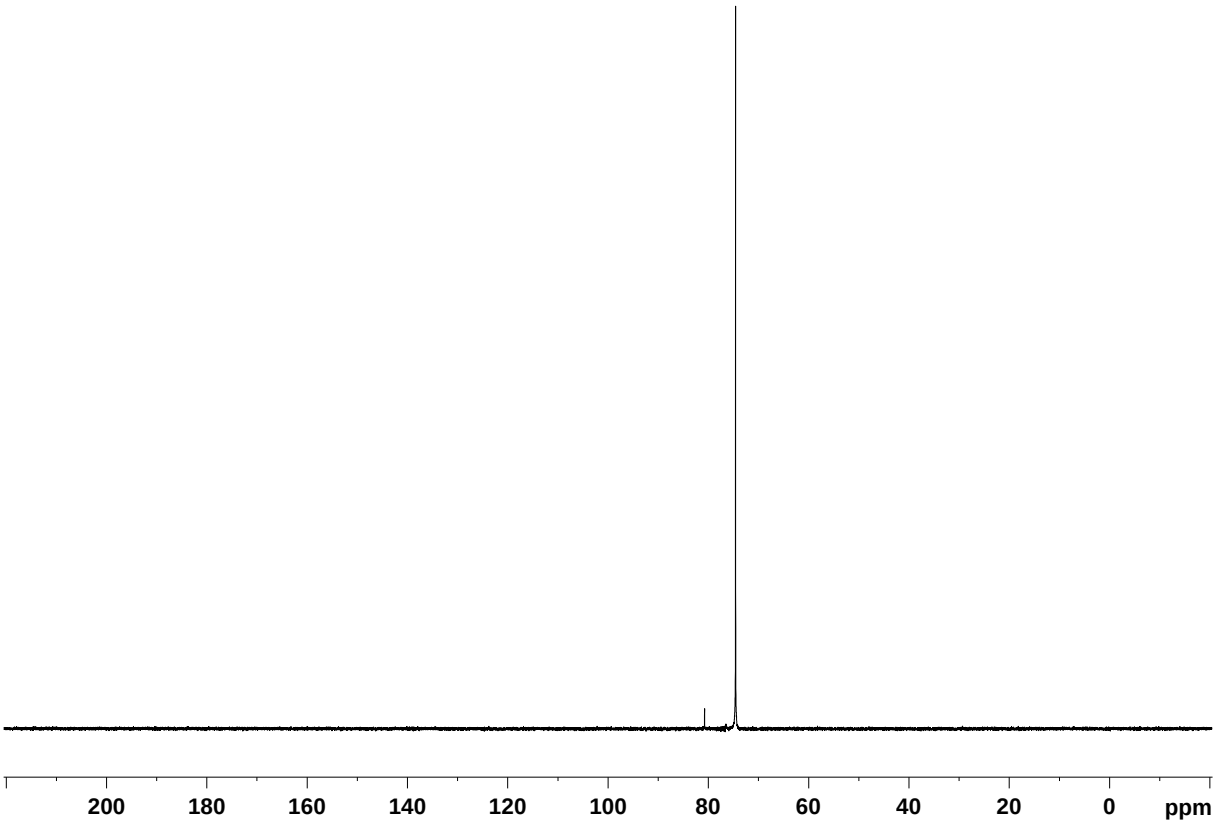
^1H NMR spectrum (C_6D_6, 300 K).



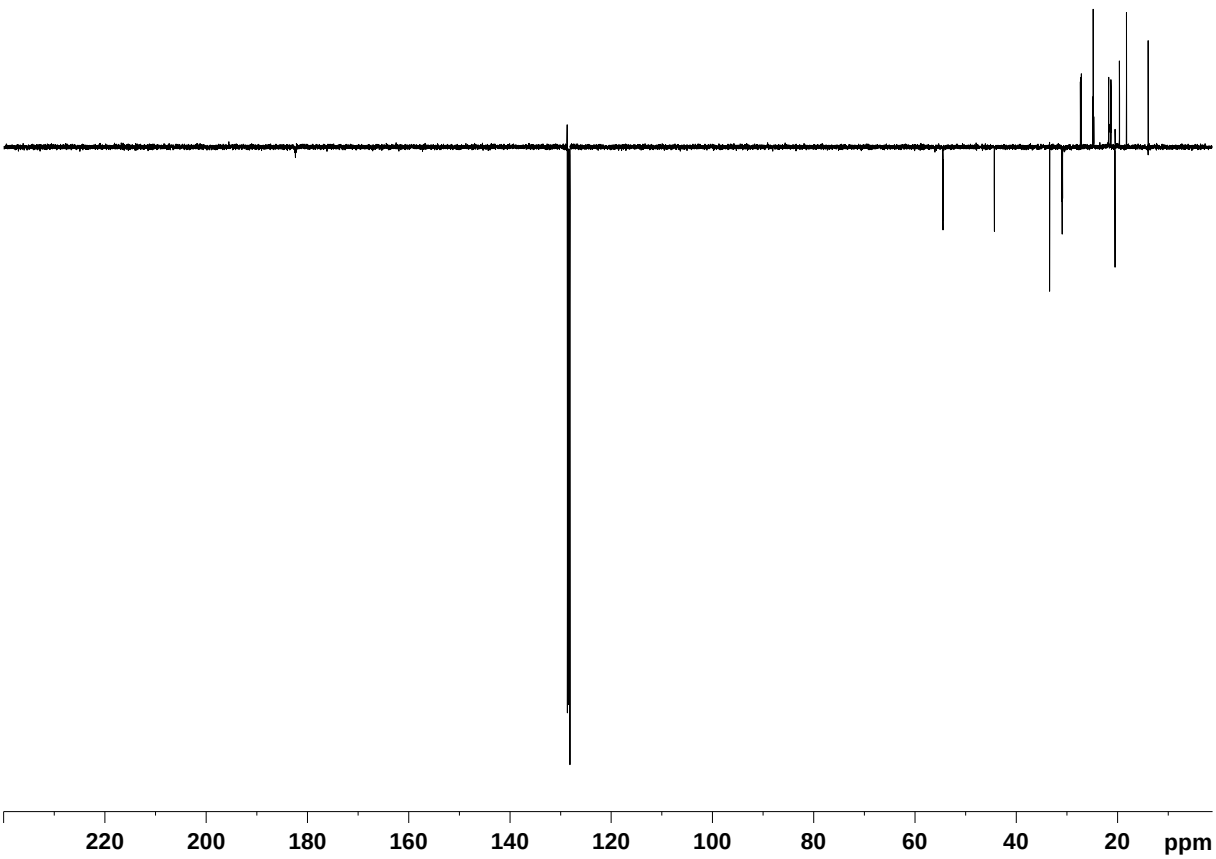
$^1H\{^{31}P\}$ NMR spectrum (C_6D_6, 300 K).



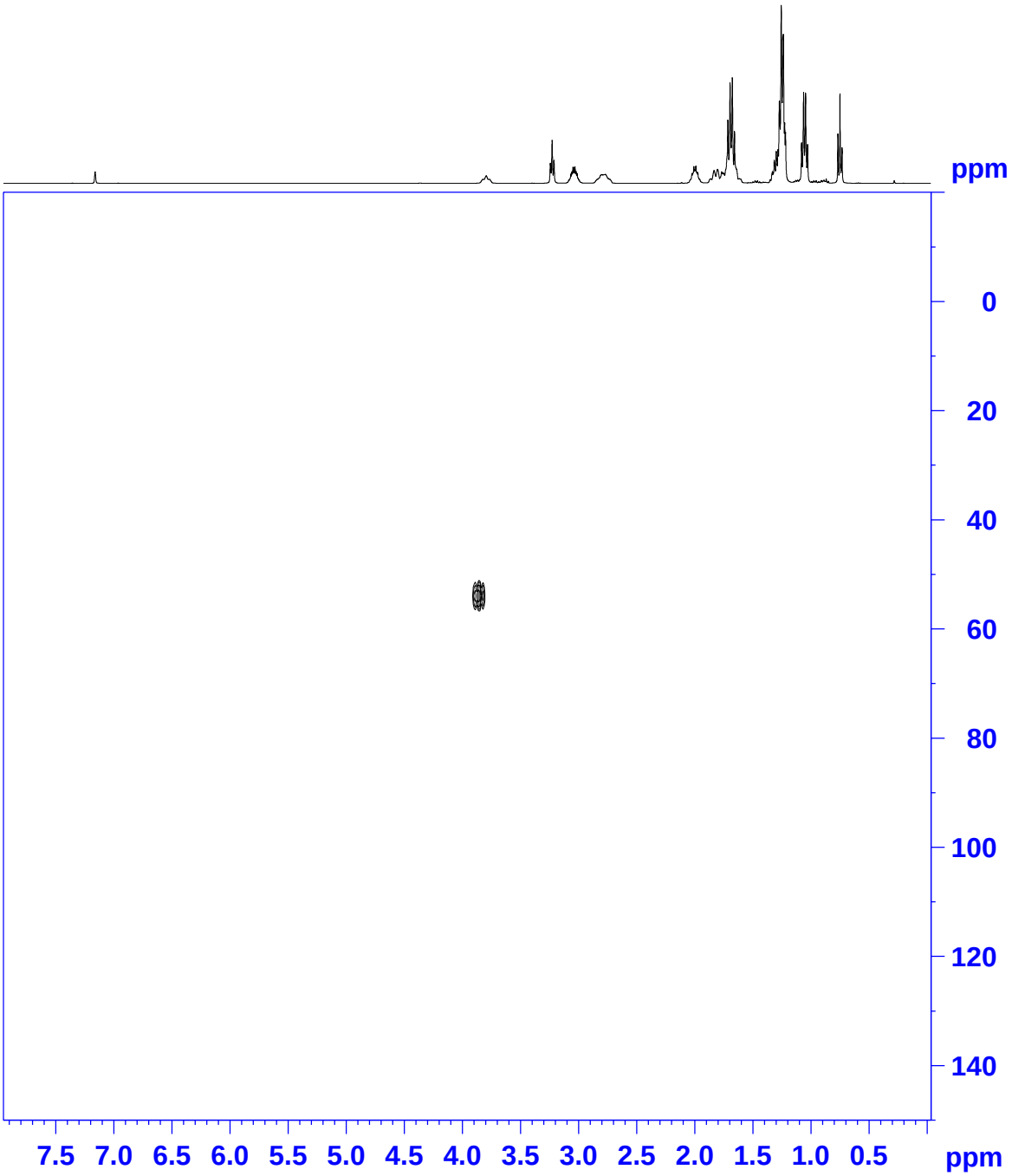
$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K).



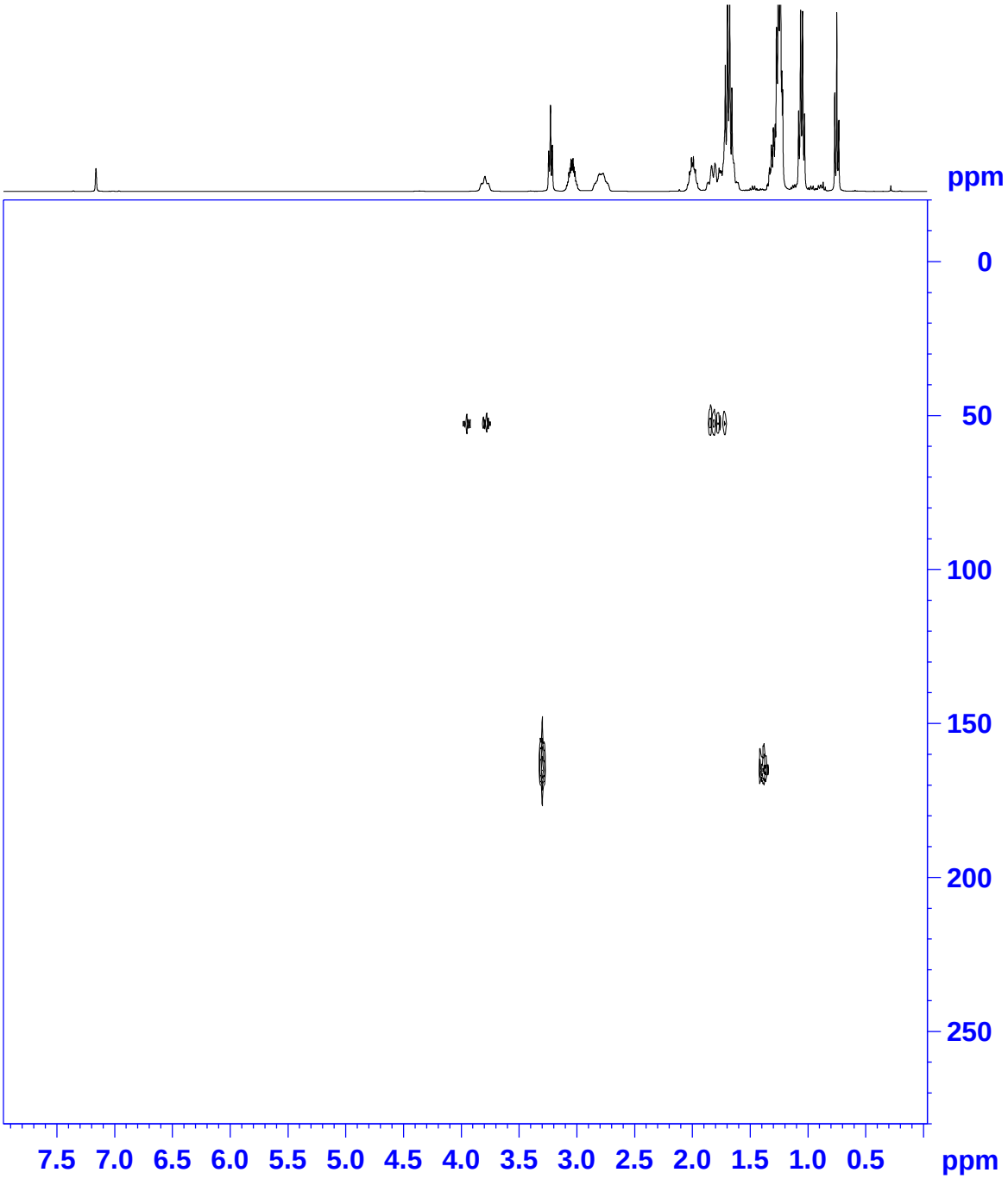
$^{13}C\{^{1}H\}$ JMOD NMR spectrum (C_6D_6, 300 K).



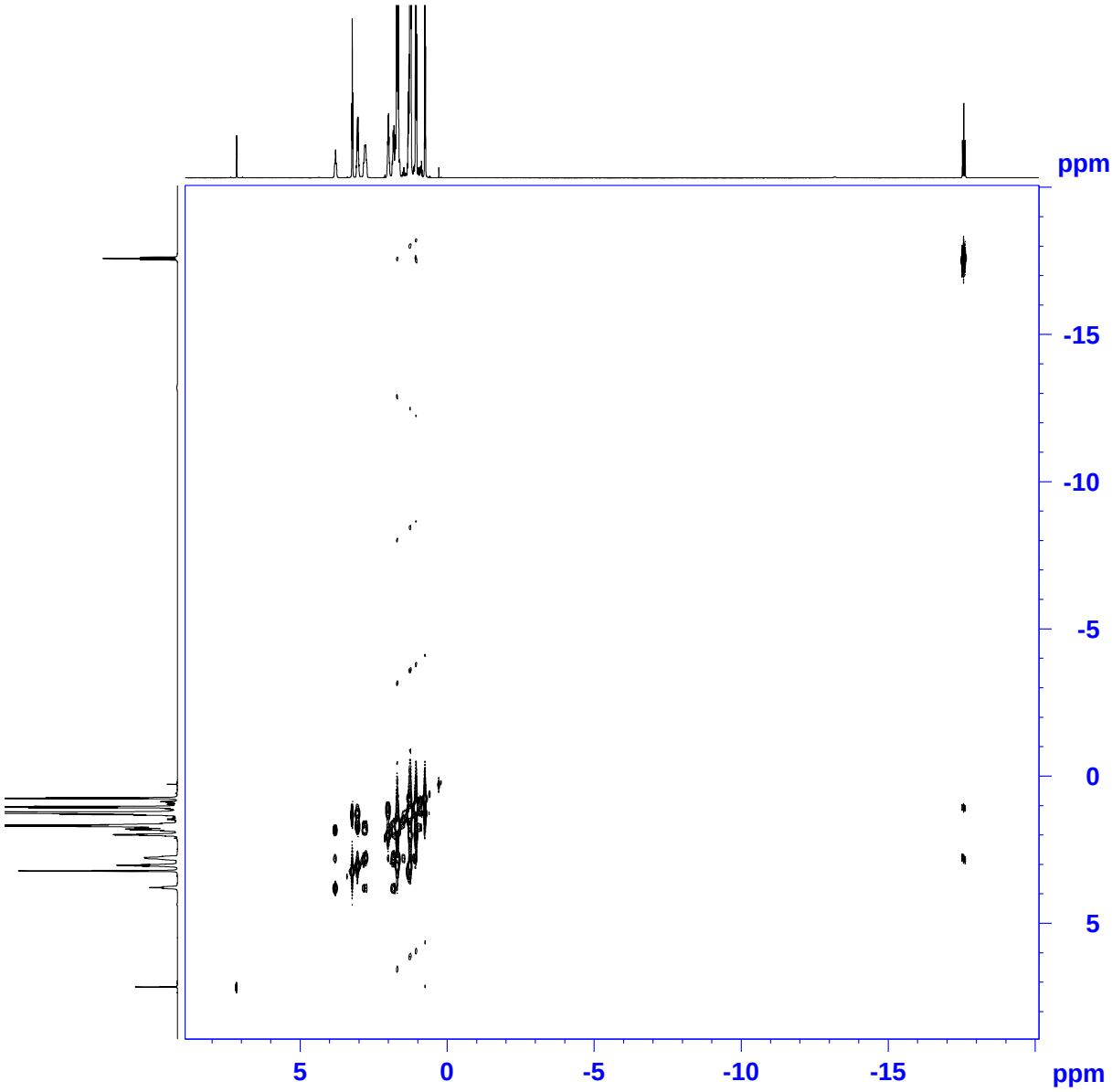
2D ^{1}H-^{15}N HSQC NMR spectrum (C_6D_6, 300 K).



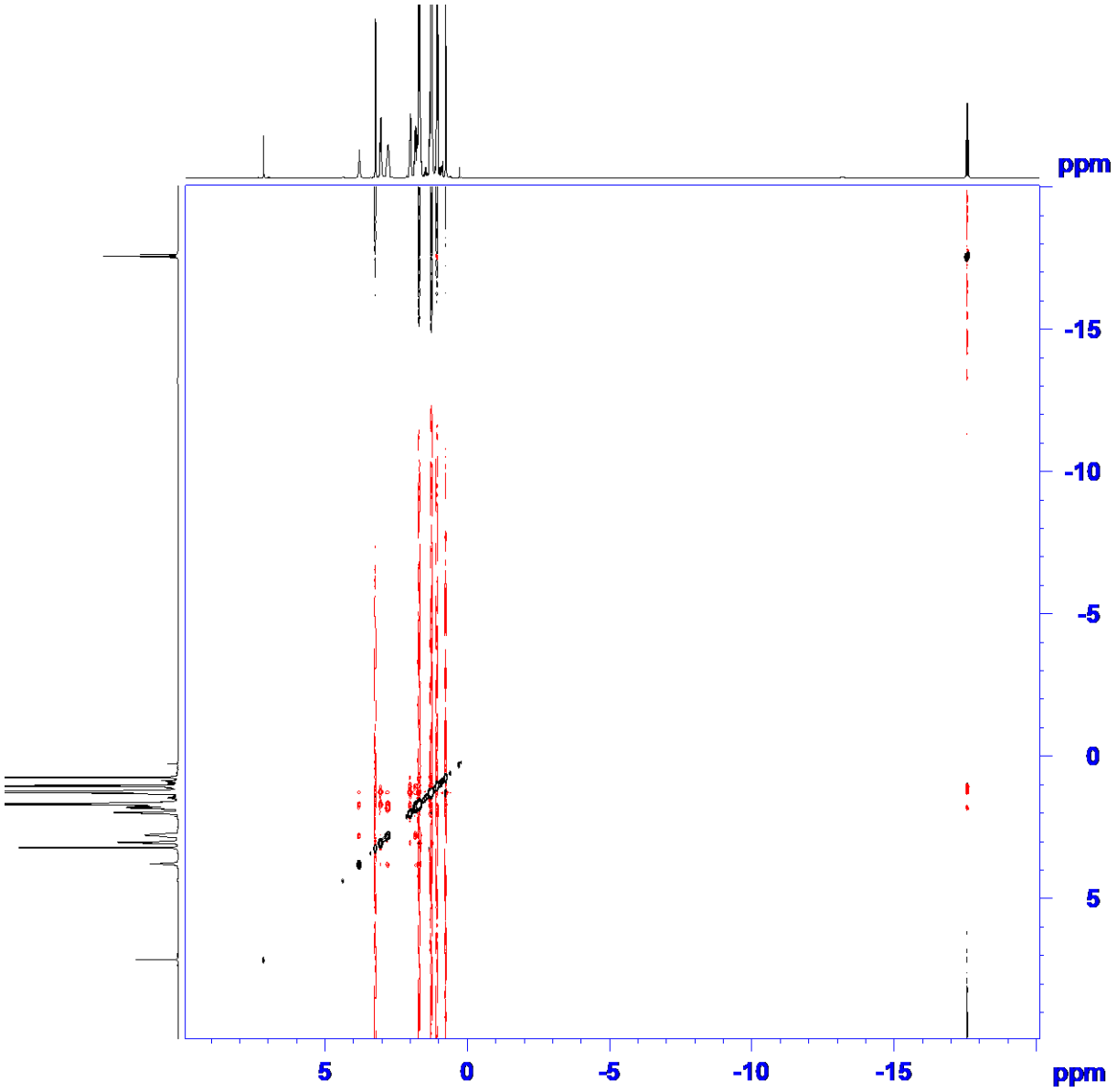
2D ^{1}H-^{15}N HMBC NMR spectrum (C_6D_6, 300 K).



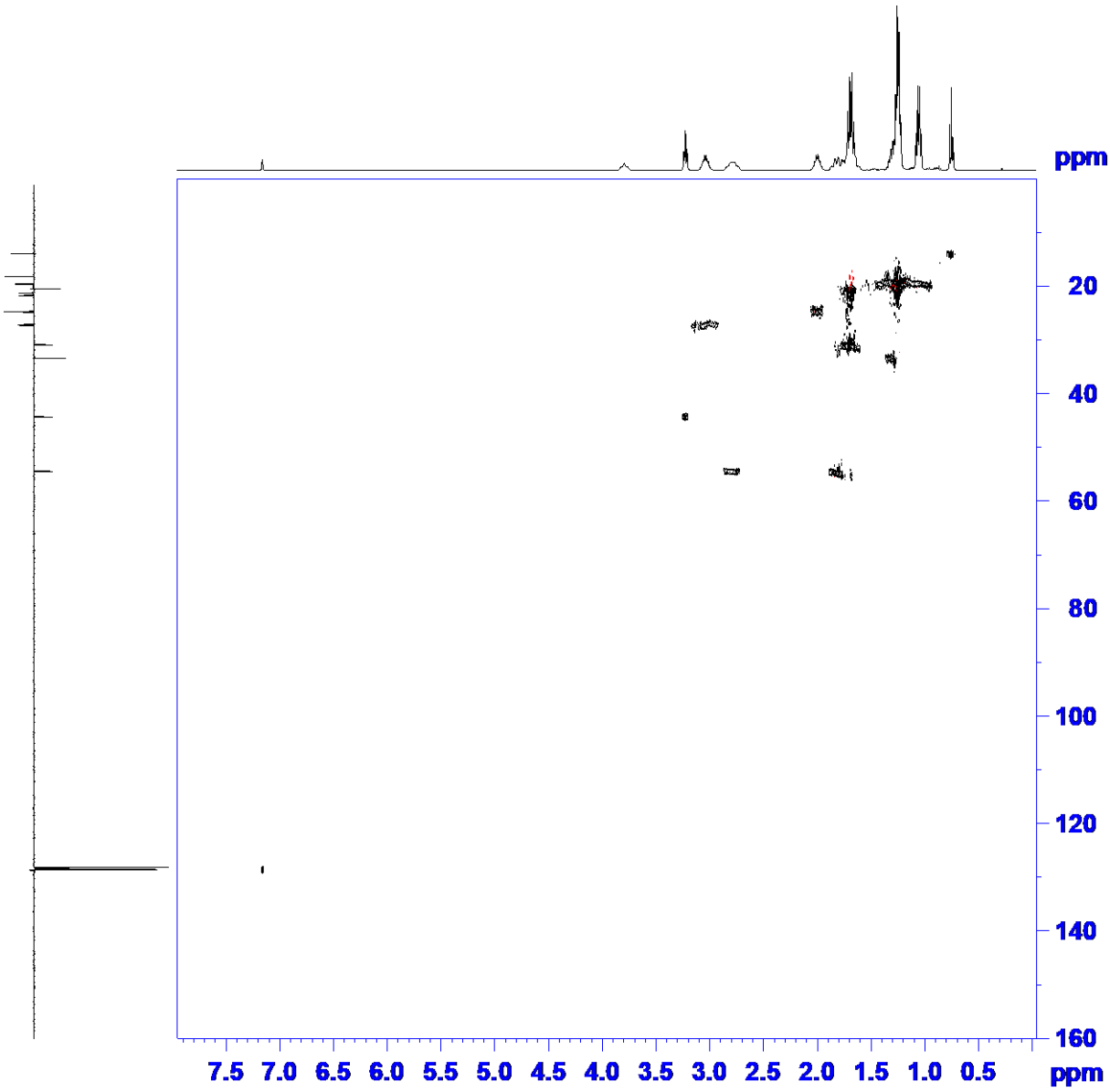
2D ^{1}H-^{1}H COSY NMR spectrum (C_6D_6, 300 K).



2D ^{1}H-^{1}H NOESY NMR spectrum (C_6D_6, 300 K).

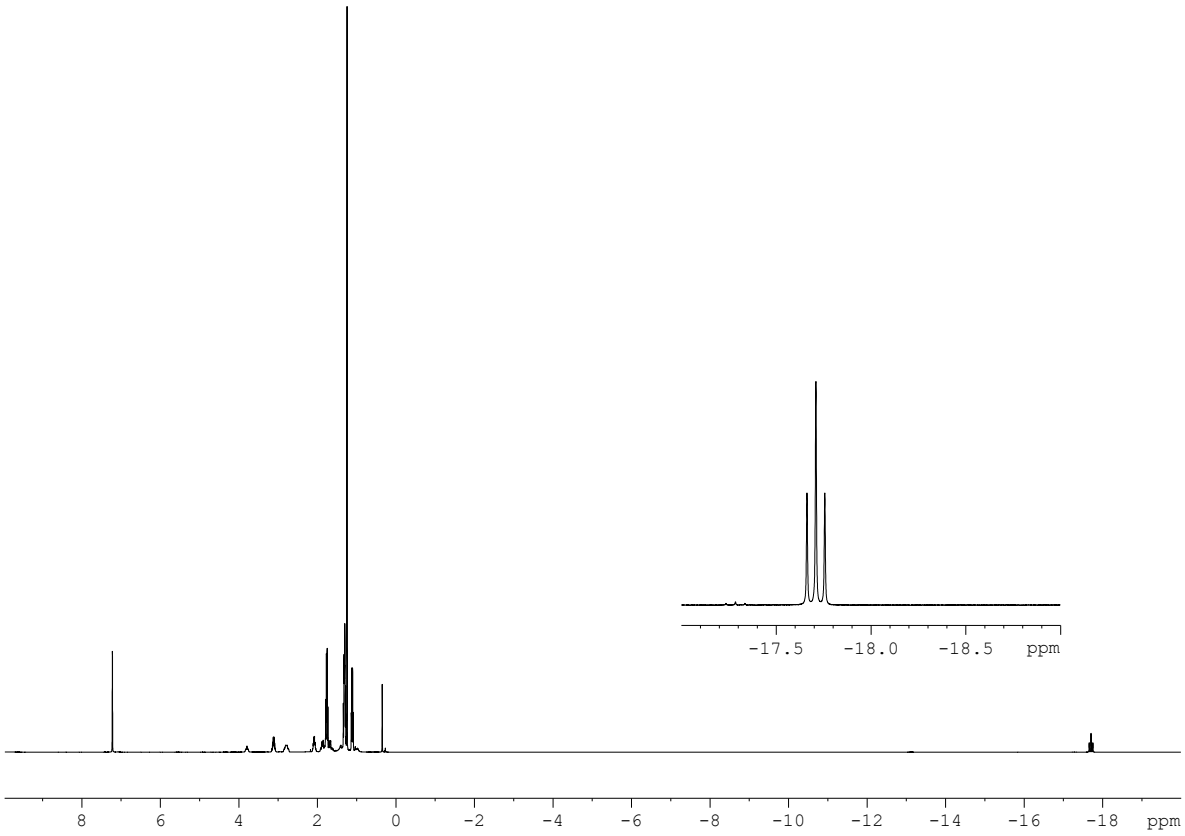


2D ^{1}H-^{1}H HSQC NMR spectrum (C_6D_6, 300 K).

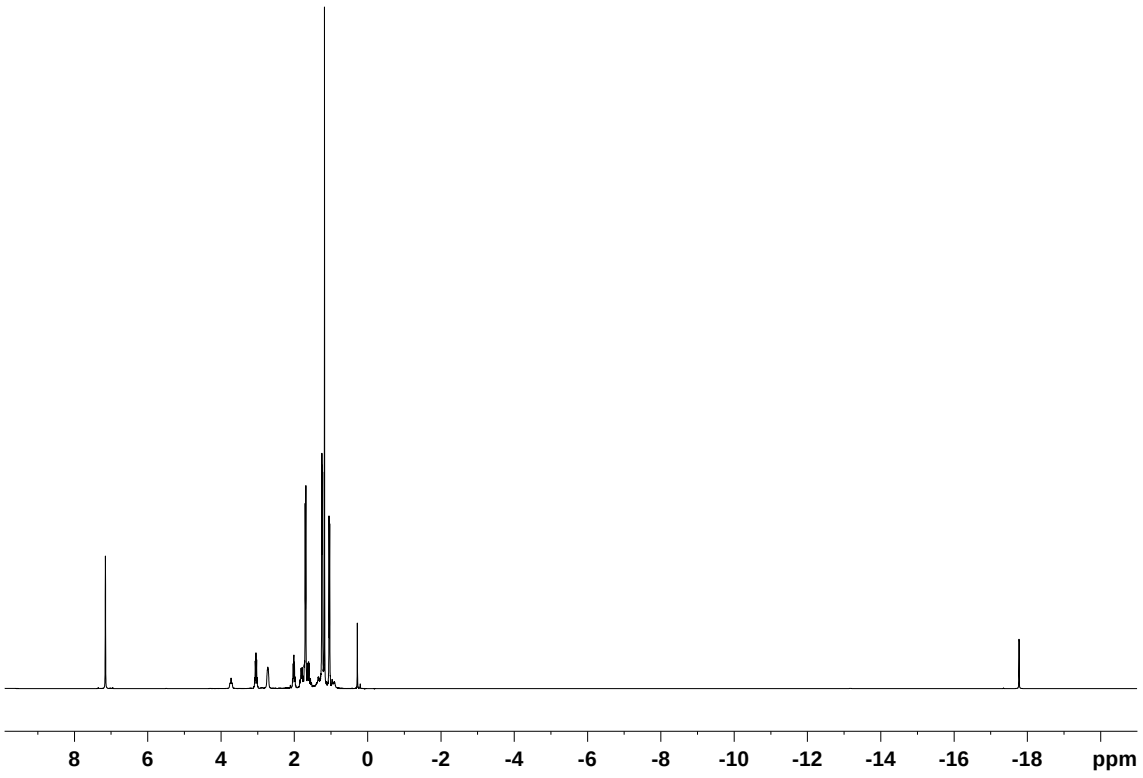


SXII. NMR spectra of [Ru(H)(Cl)(CN-*t*Bu){NH($CH_2CH_2P(iPr)_2)_2$}] (4c)

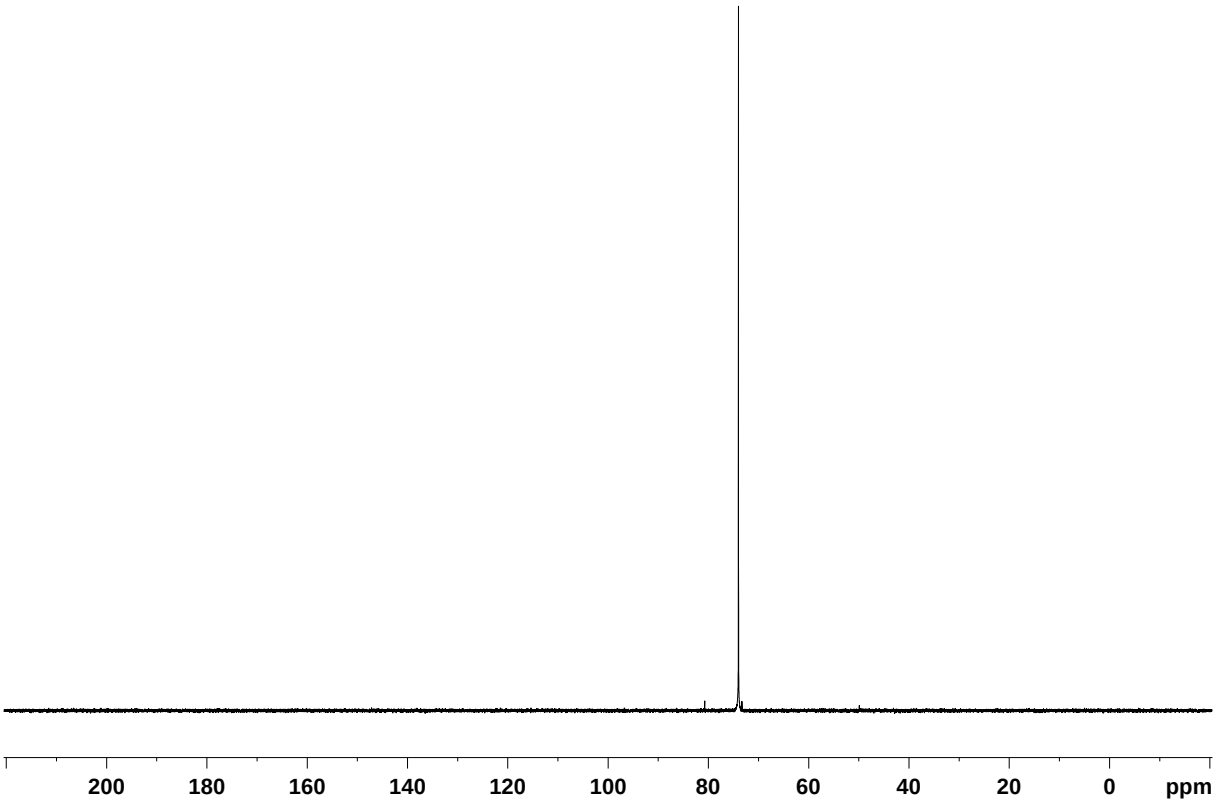
^1H NMR spectrum (C_6D_6, 298 K).



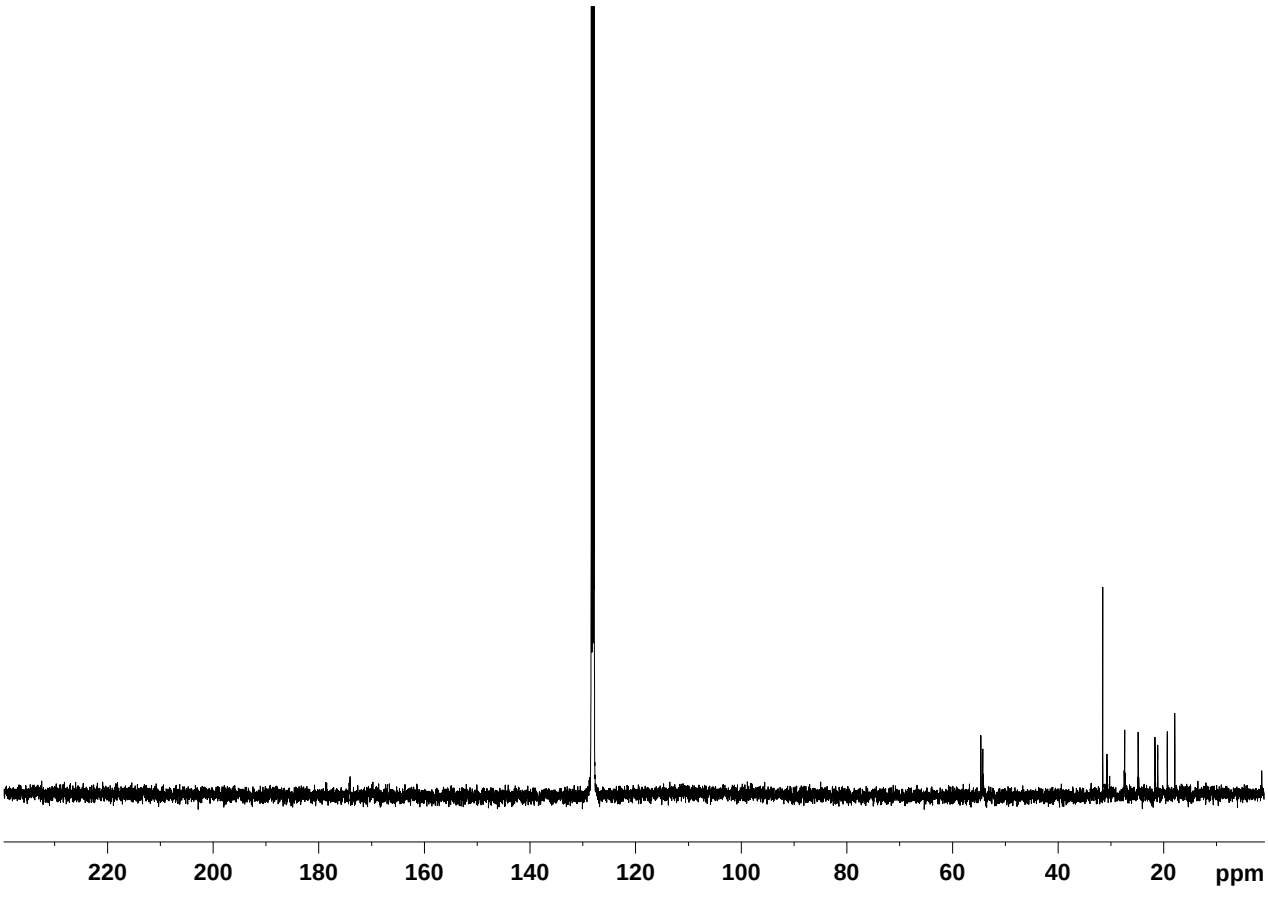
$^1H\{^{31}P\}$ NMR spectrum (C_6D_6, 298 K).



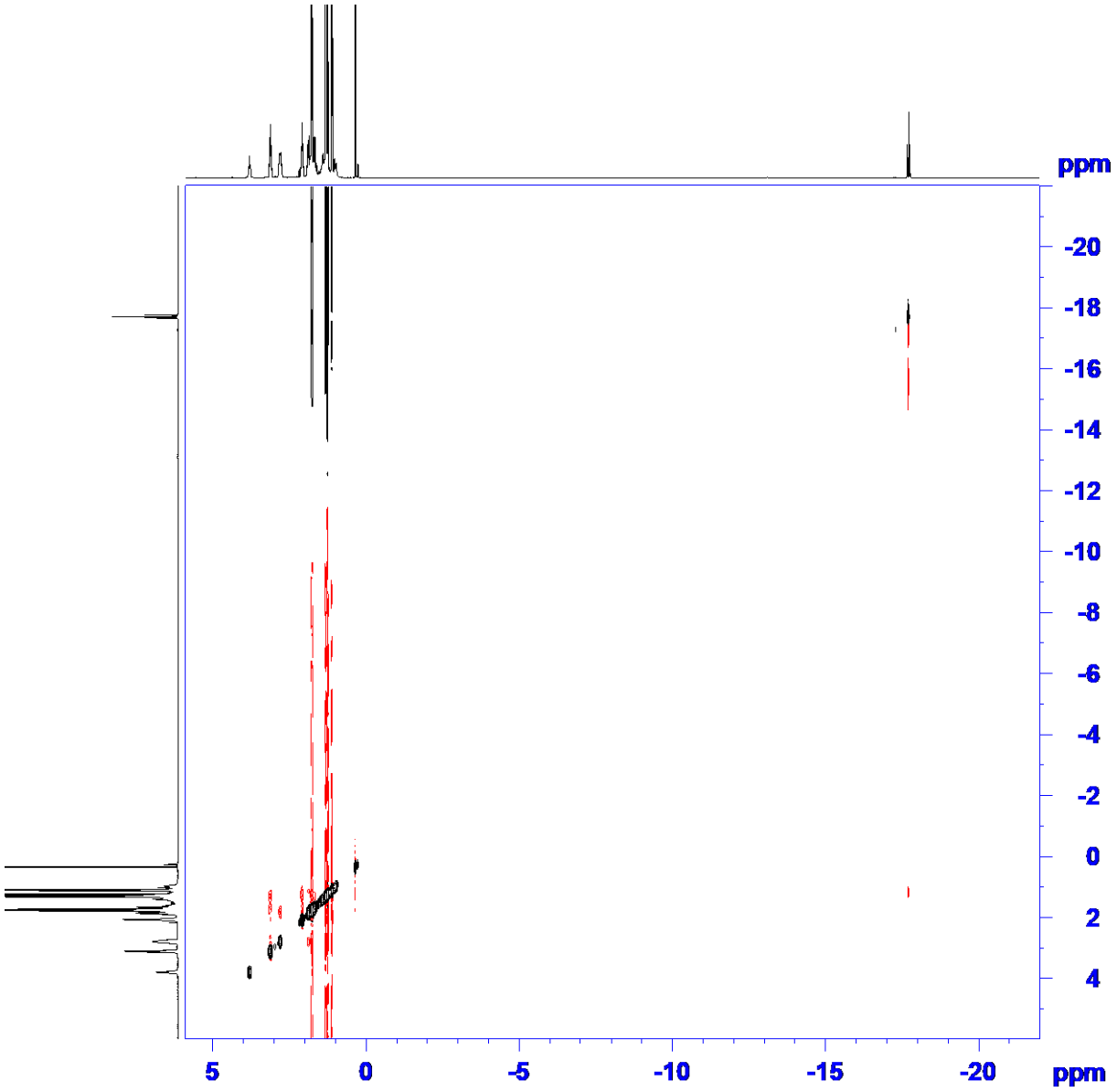
$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K).



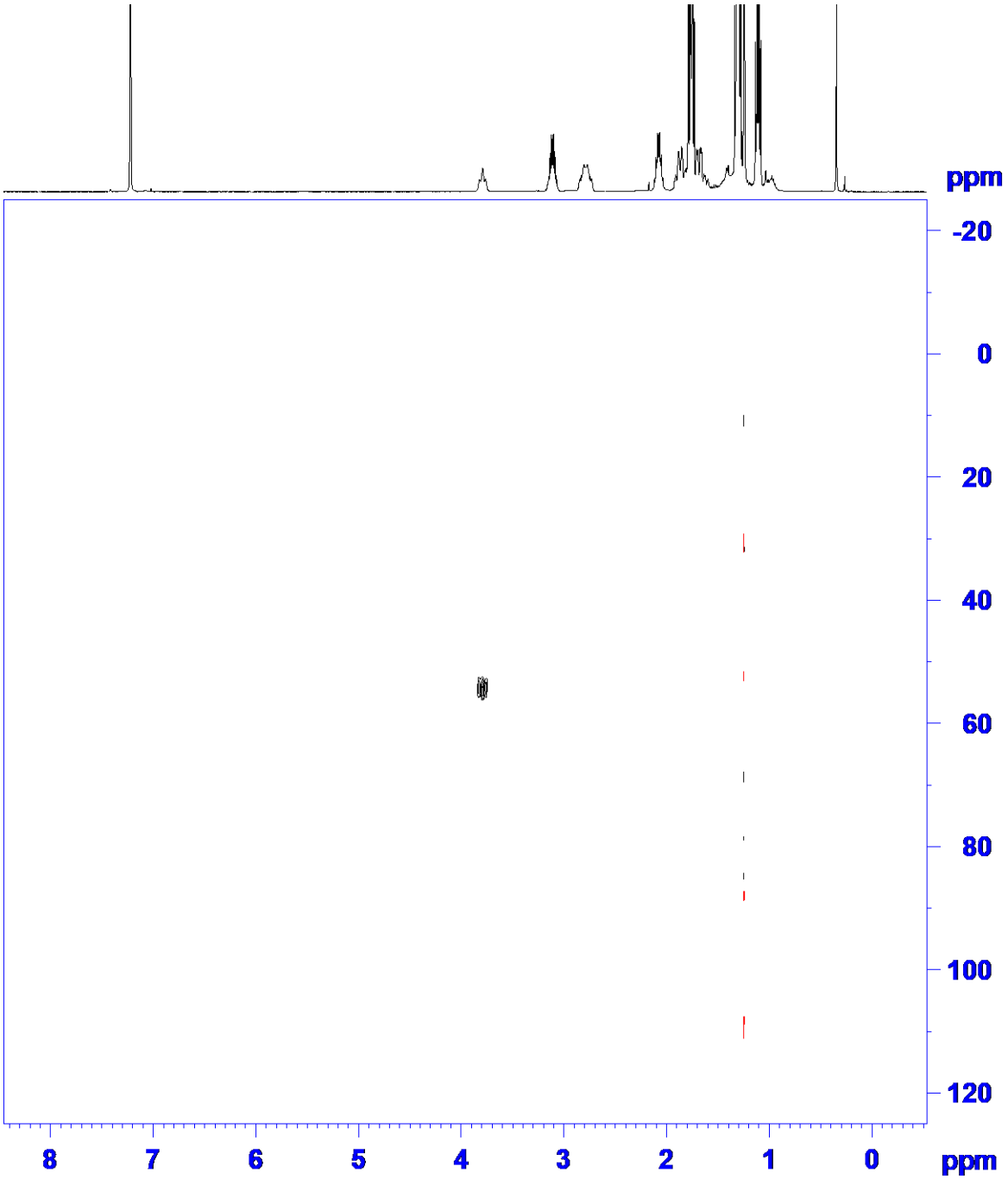
$^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K).



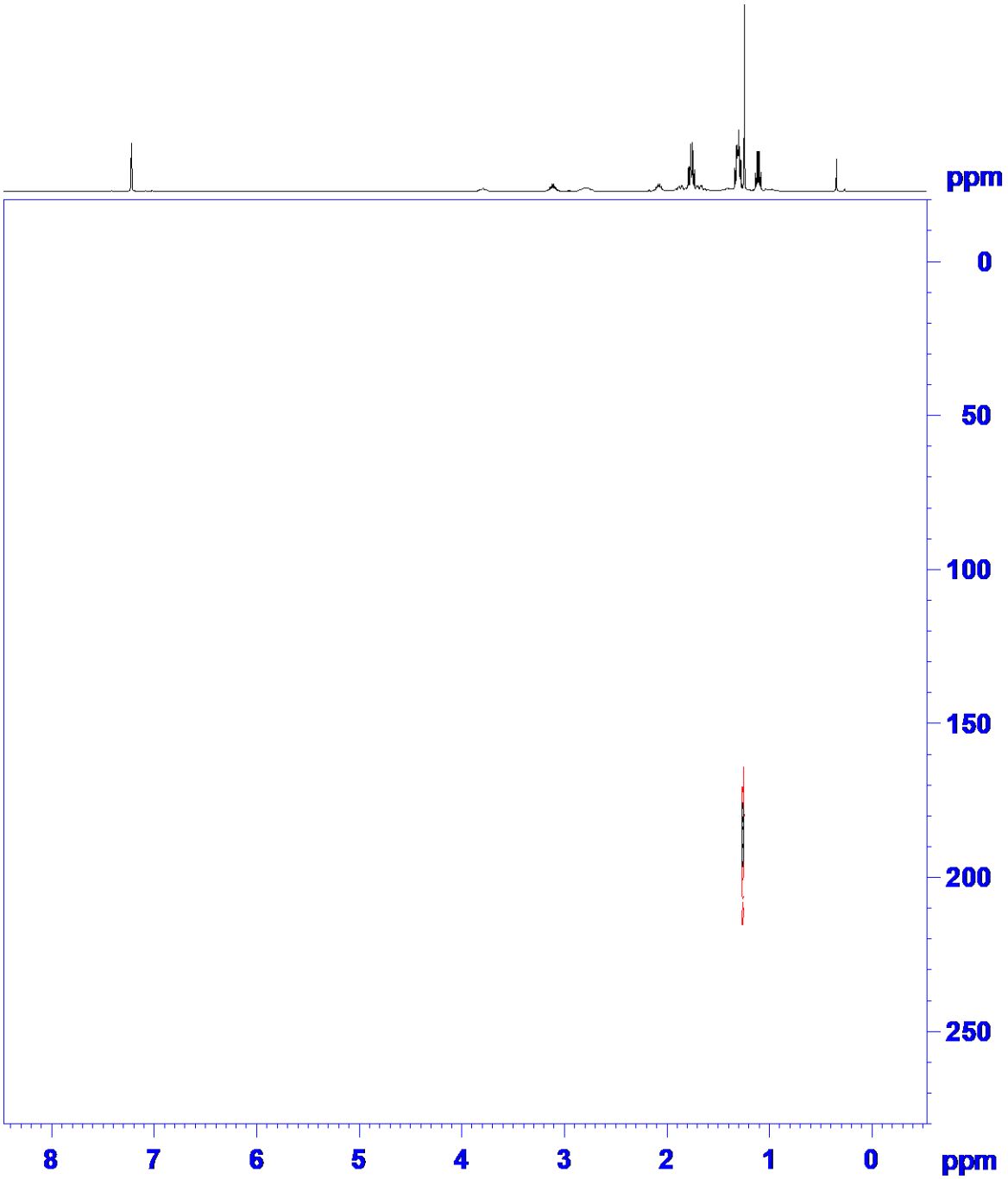
2D ^{1}H-^{1}H NOESY NMR spectrum (C_6D_6, 298 K).



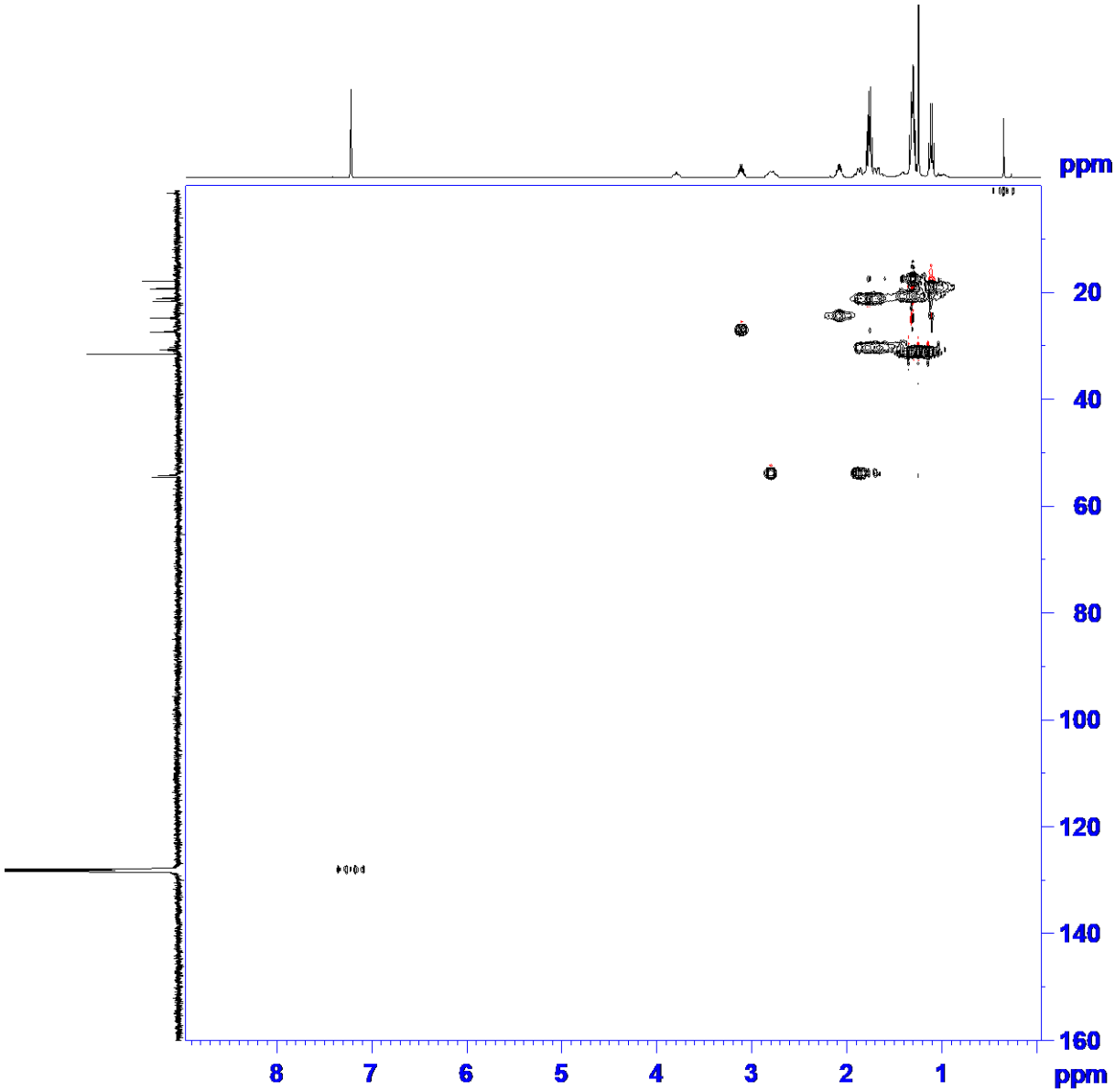
2D ^{1}H-^{15}N HSQC NMR spectrum (C_6D_6, 298 K).



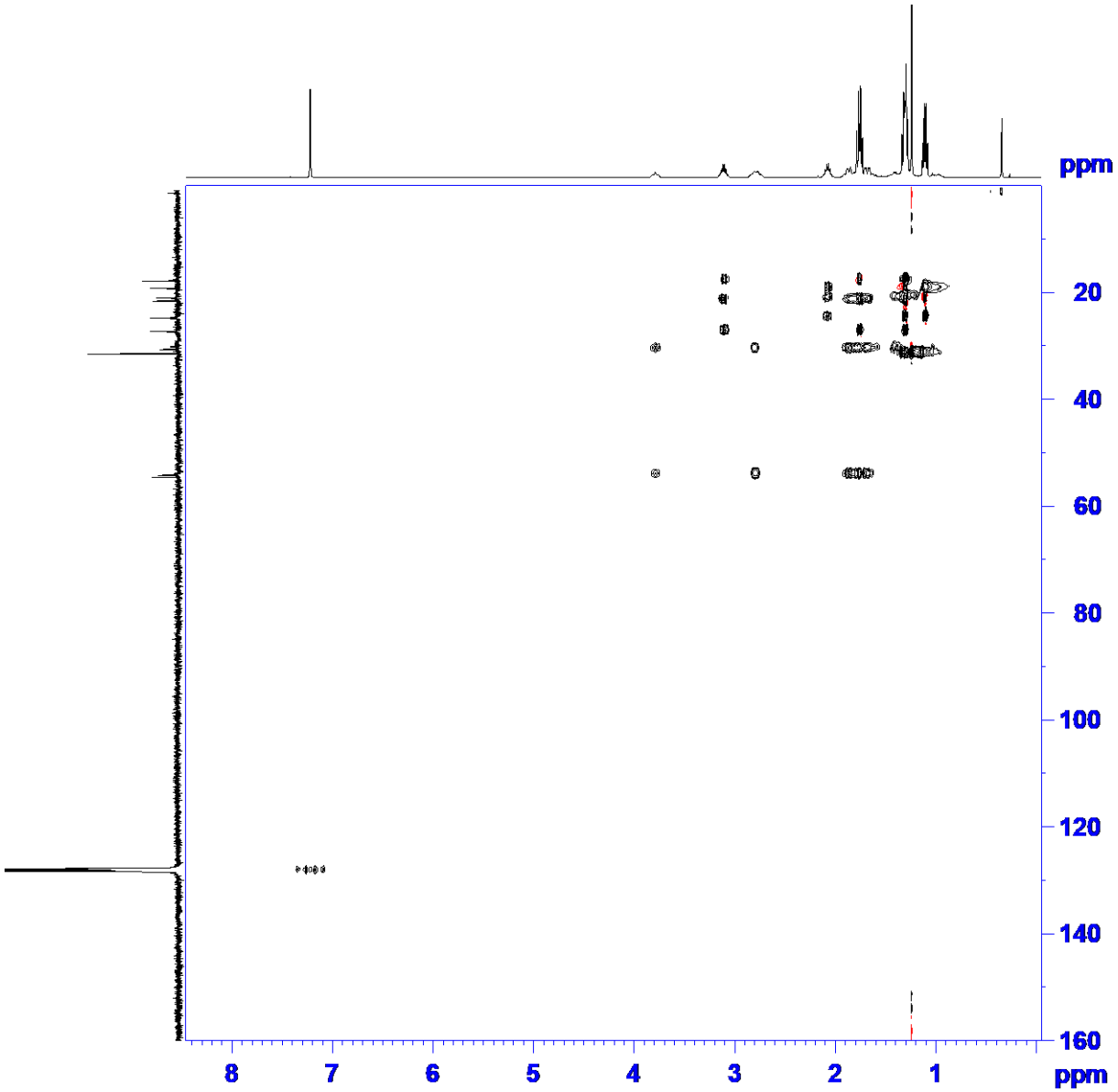
2D ^{1}H-^{15}N HMBC NMR spectrum (C_6D_6, 298 K).



2D ^{1}H-^{13}C HSQC NMR spectrum (C_6D_6, 298 K).

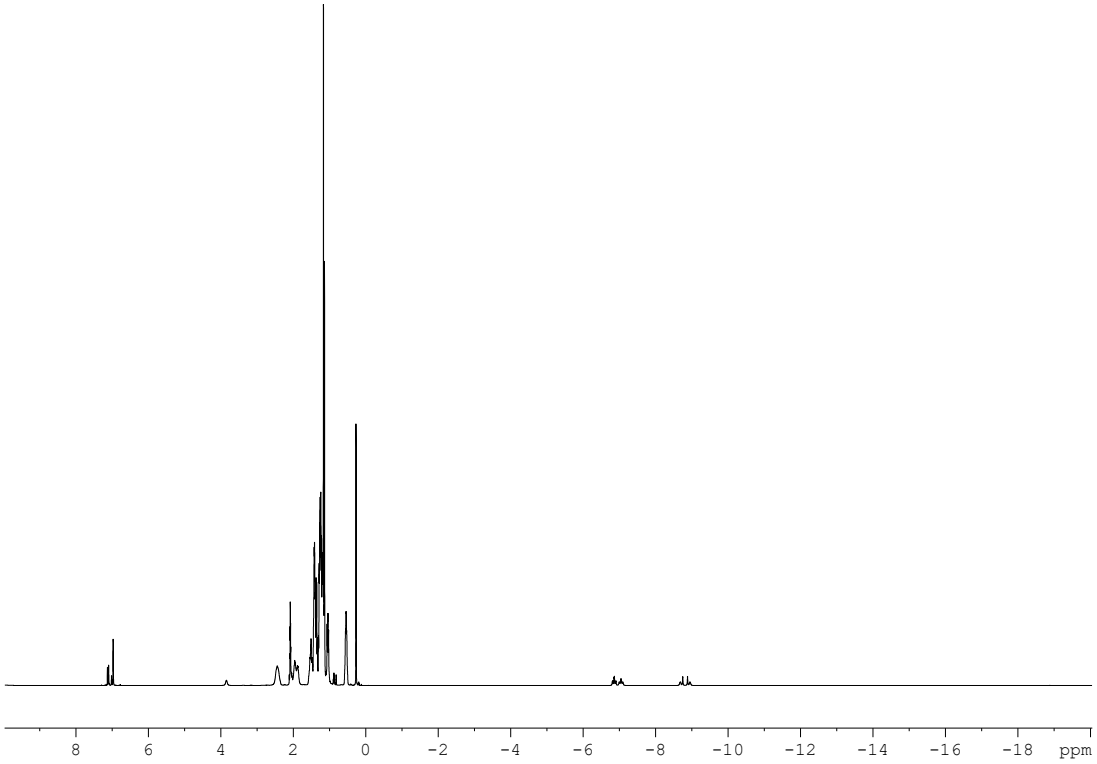


2D ^{1}H-^{13}C HSQC TOCSY NMR spectrum (C_6D_6, 298 K).

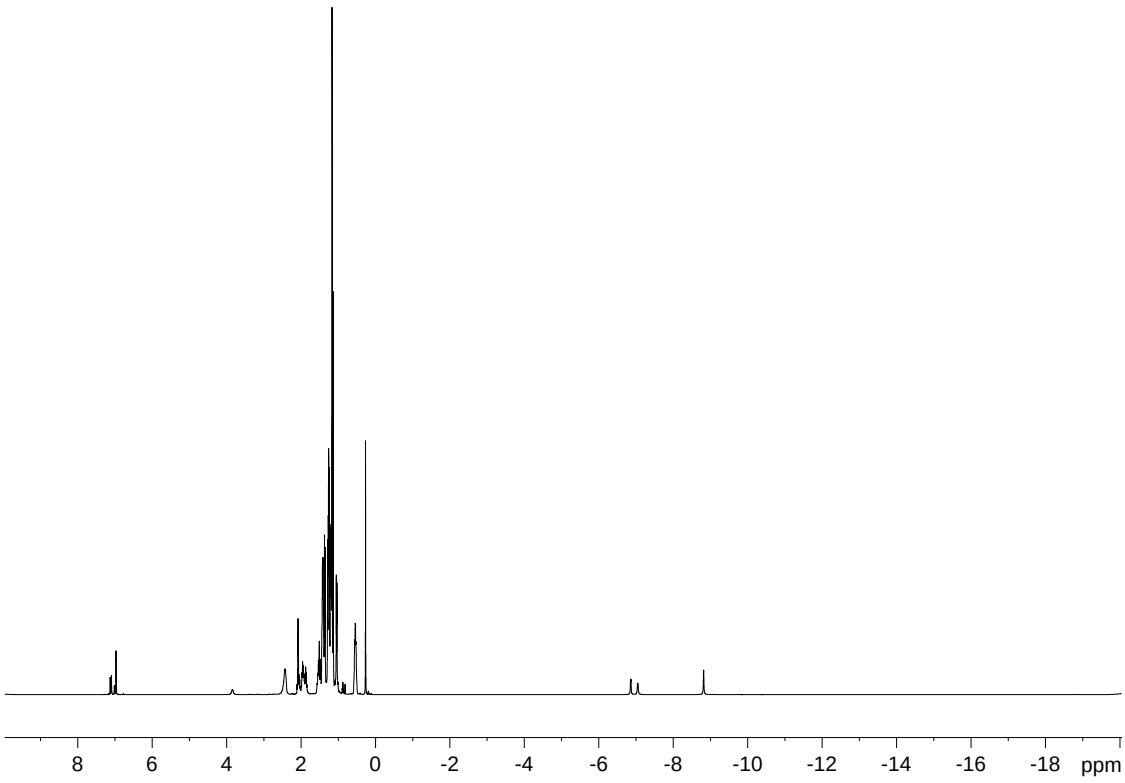


SXIII. NMR spectra of [Ru(H)$_2$(CN-*t*Bu){NH(CH$_2$CH$_2$P(*i*Pr)$_2$)$_2$}] (5c)

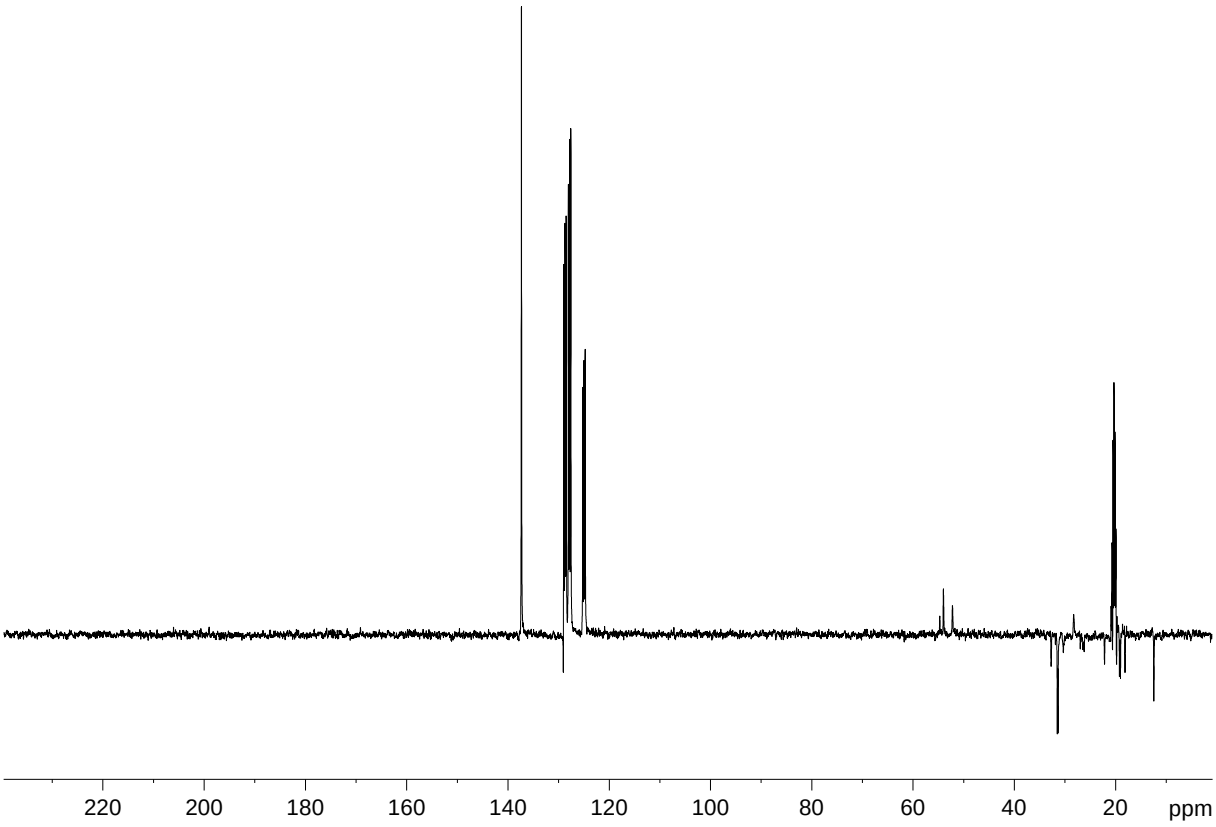
^{1}H NMR spectrum (C_7D_8, 285 K)



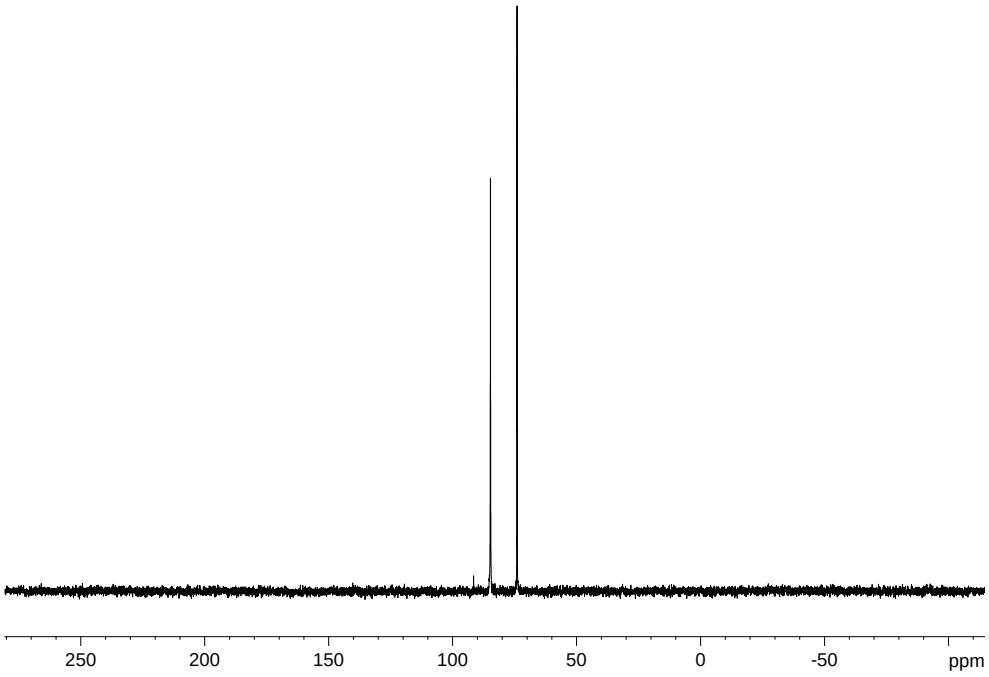
^{1}H{^{31}P} NMR spectrum (C_7D_8, 285 K).



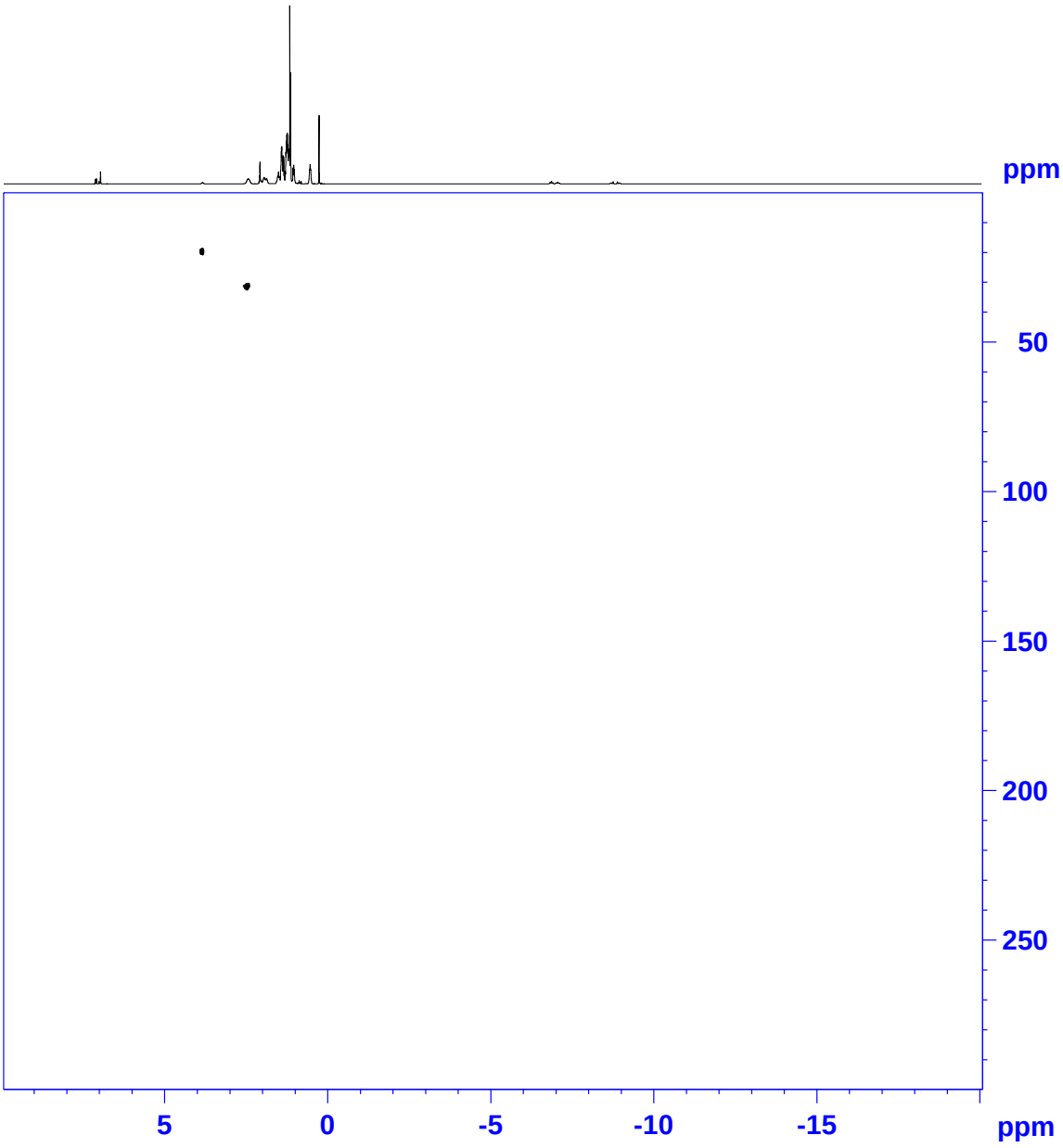
$^{13}C\{^{1}H\}$ JMOD NMR spectrum (C_7D_8, 285 K).



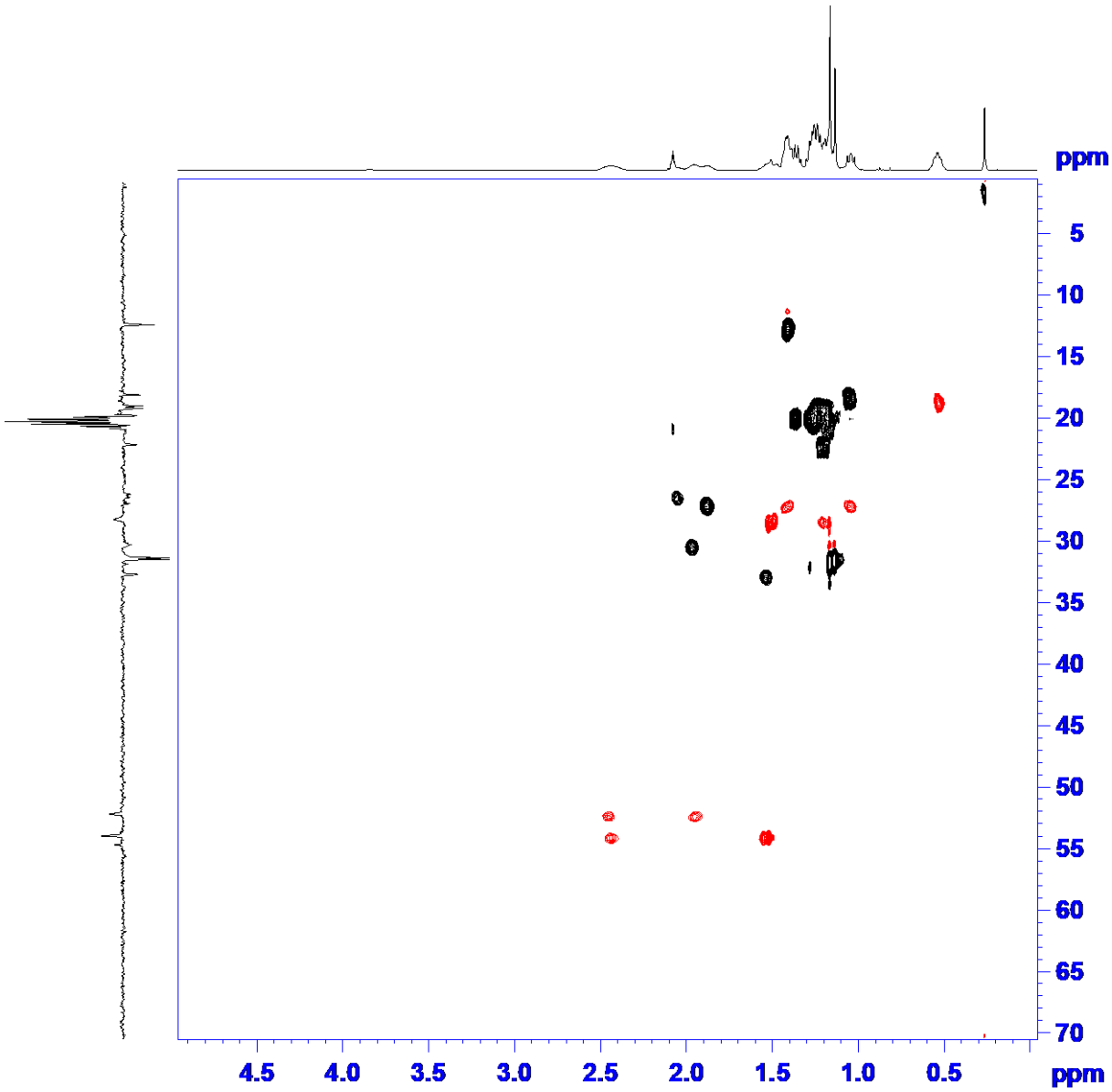
$^{31}P\{^{1}H\}$ NMR spectrum (C_7D_8, 285 K).



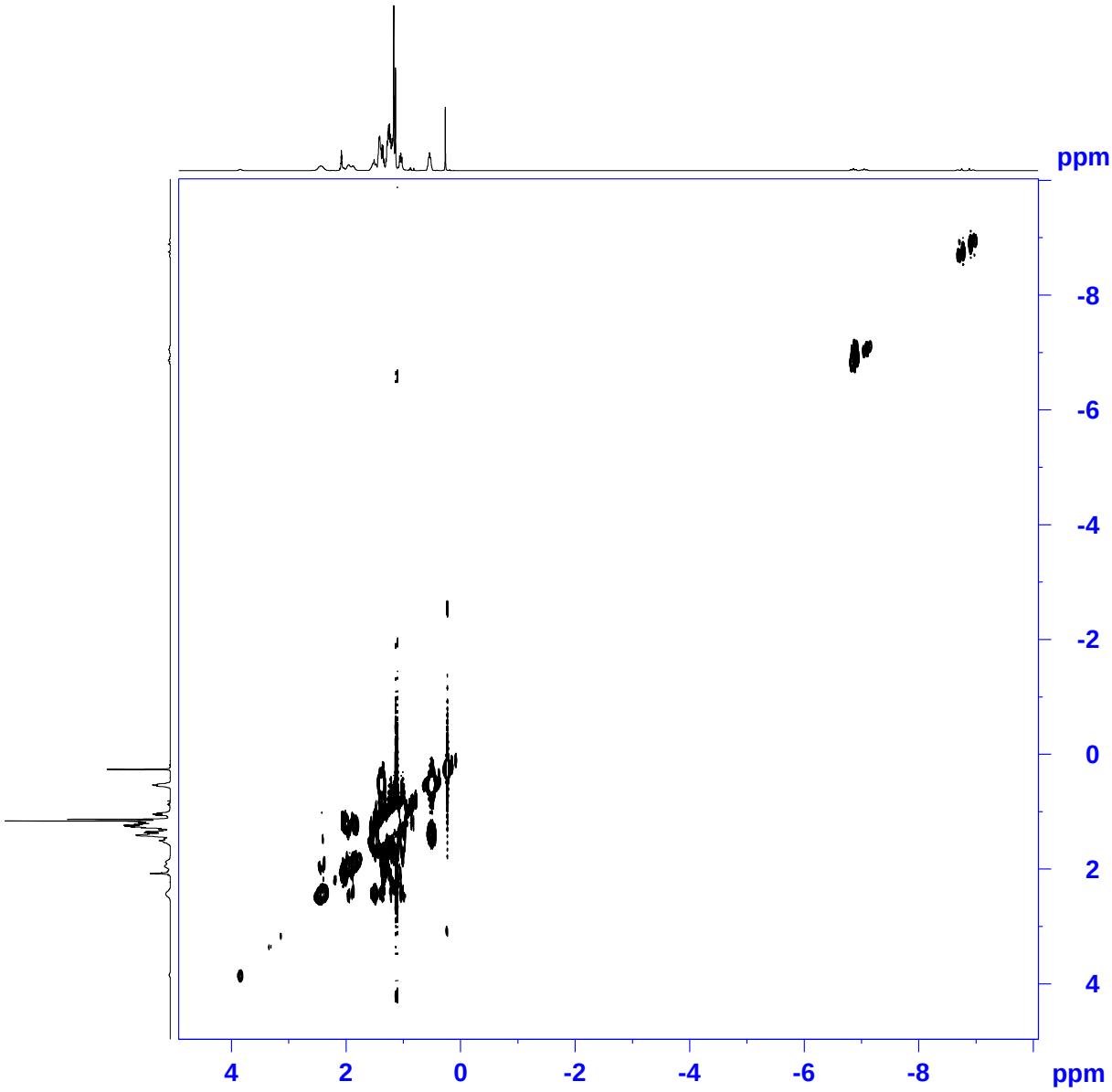
2D ^{15}N-^{1}H HSQC NMR spectrum (C_7D_8, 285 K).



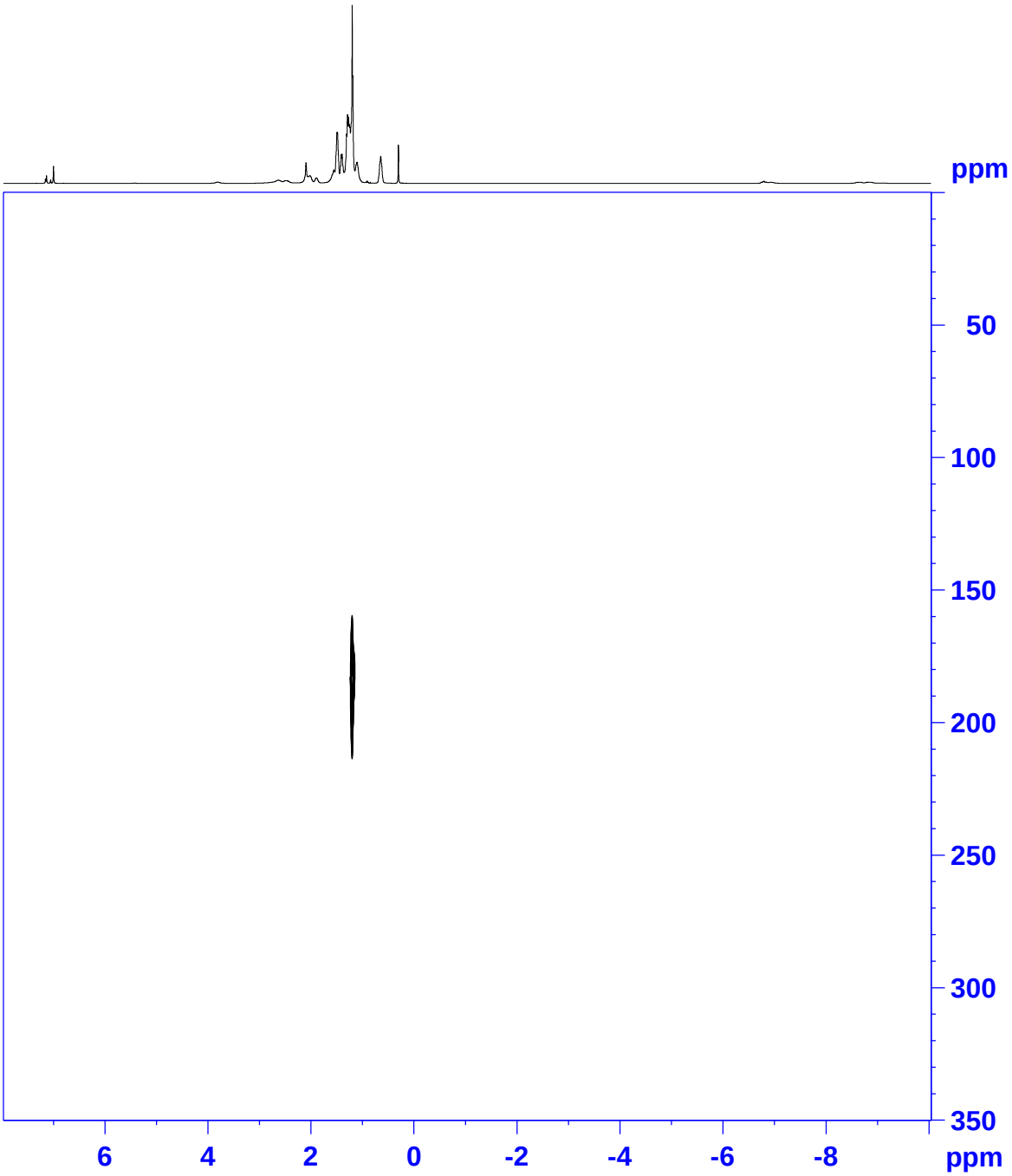
2D ^{13}C-^{1}H HSQC NMR spectrum (C_7D_8, 285 K).



2D ^{1}H-^{1}H COSY NMR spectrum (C_7D_8, 285 K).

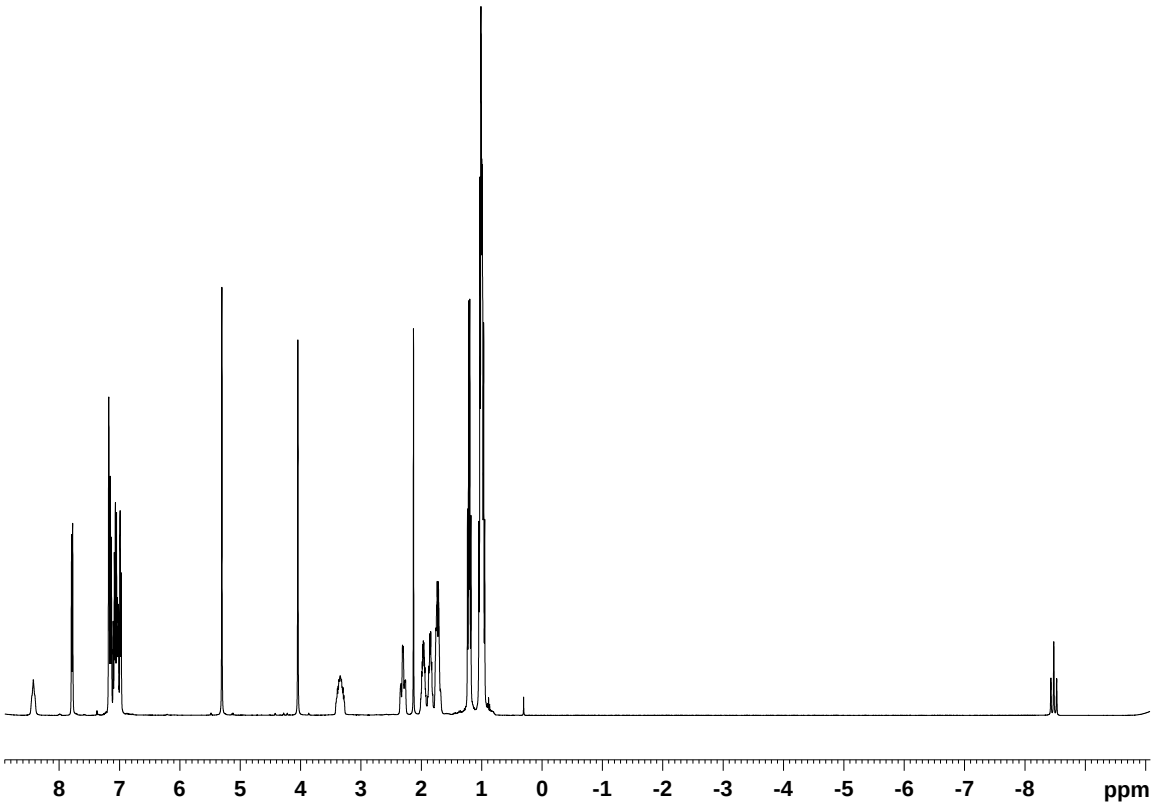


2D ^{15}N-^{1}H HMBC NMR spectrum (C_7D_8, 285 K)

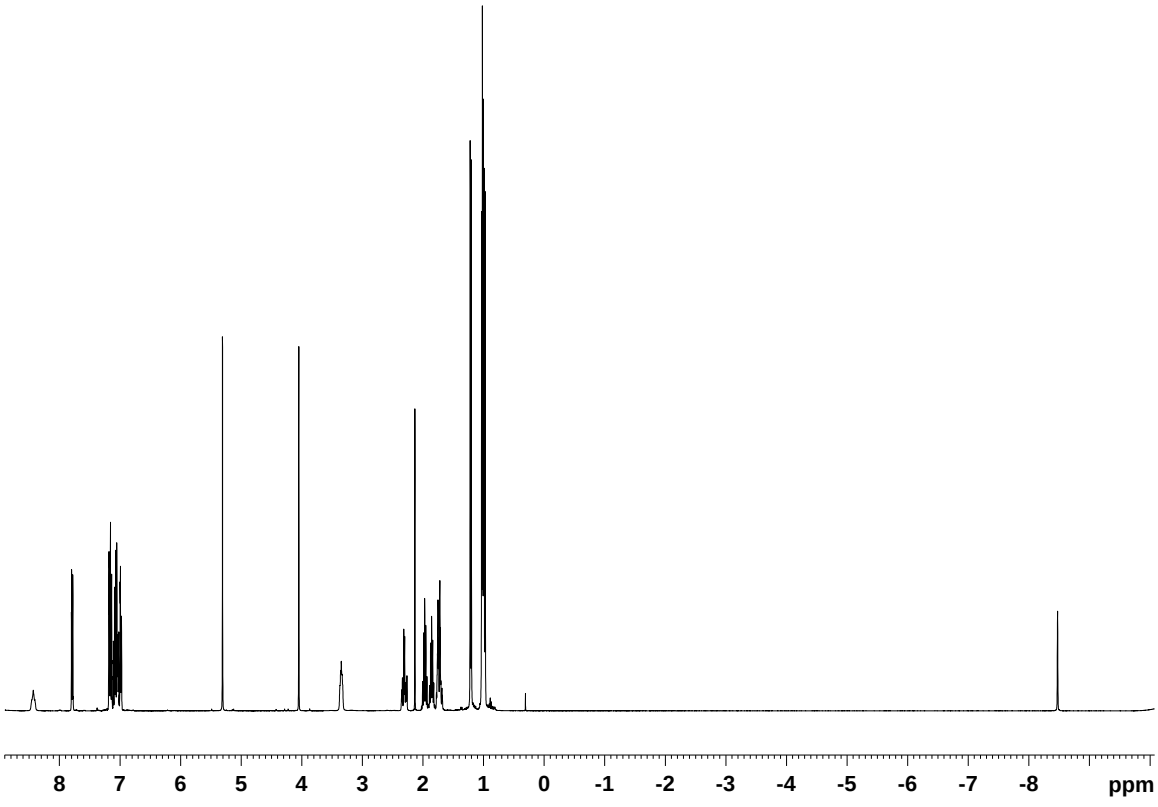


SXIV. NMR spectra of [Ru(H)(CN-CH_2Ph)$_2$(NH(CH_2CH_2P(*i*Pr)$_2$)$_2$)](Cl) (7)

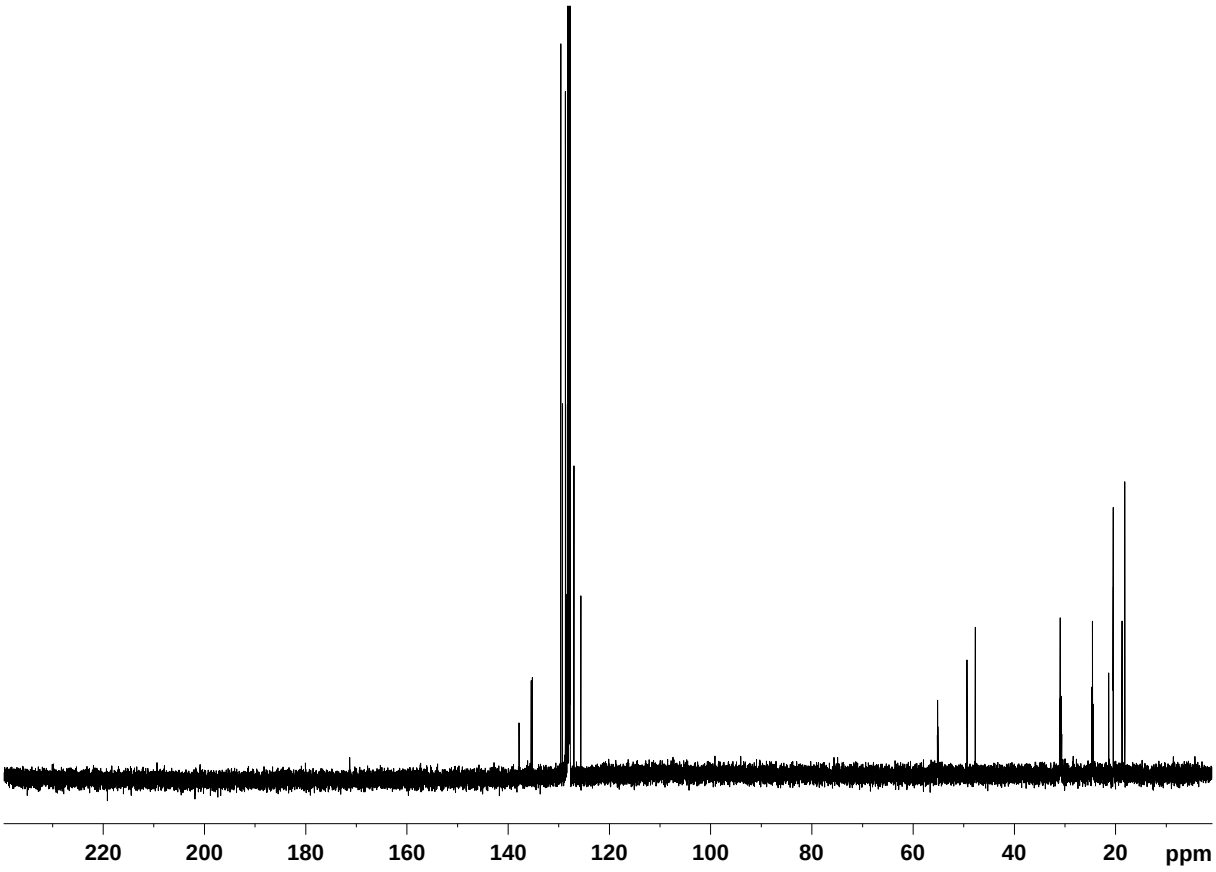
^{1}H NMR spectrum (C_6D_6, 300 K).



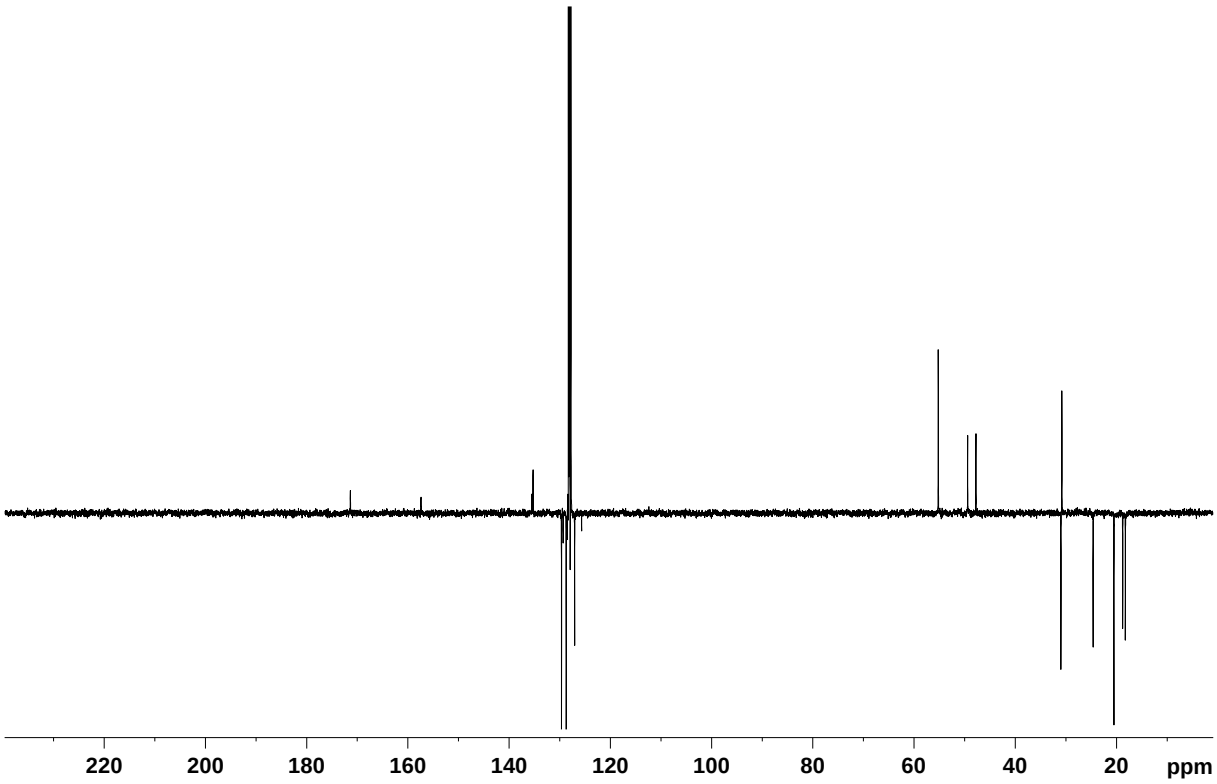
^{1}H{^{31}P} NMR spectrum (C_6D_6, 300 K).



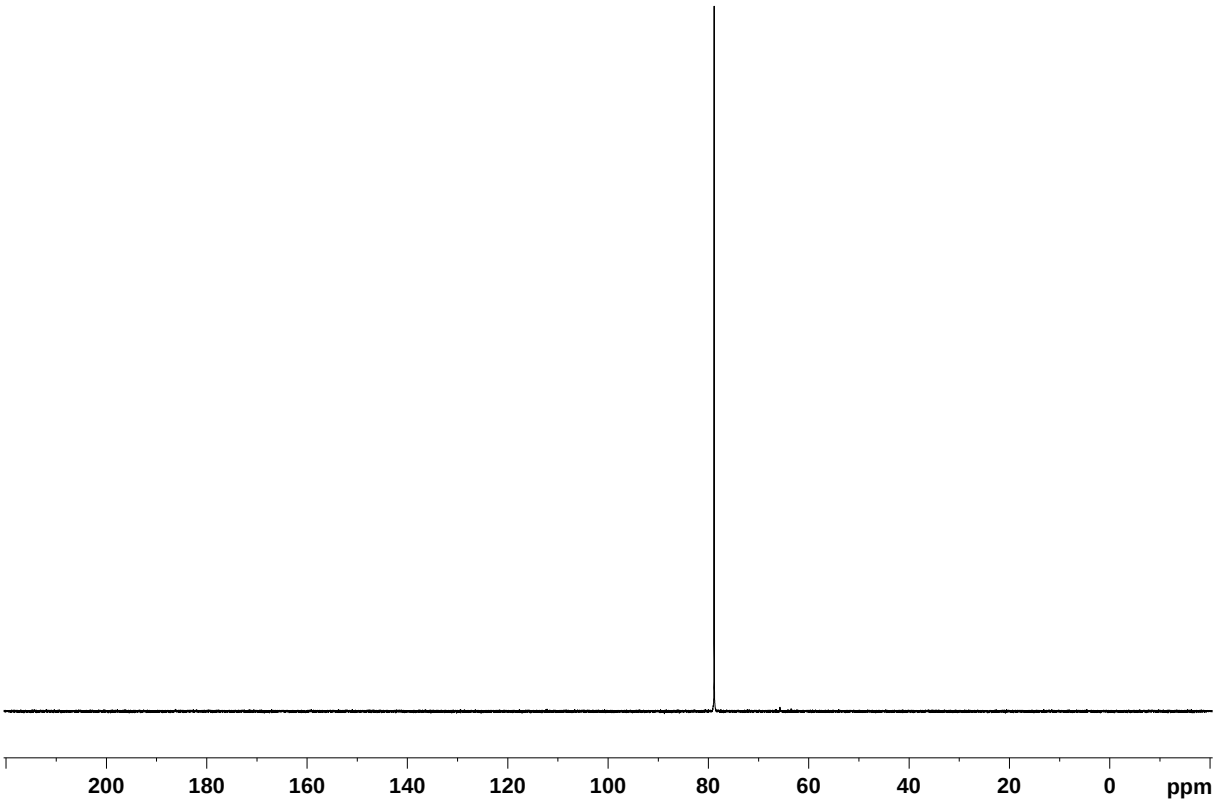
$^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K).



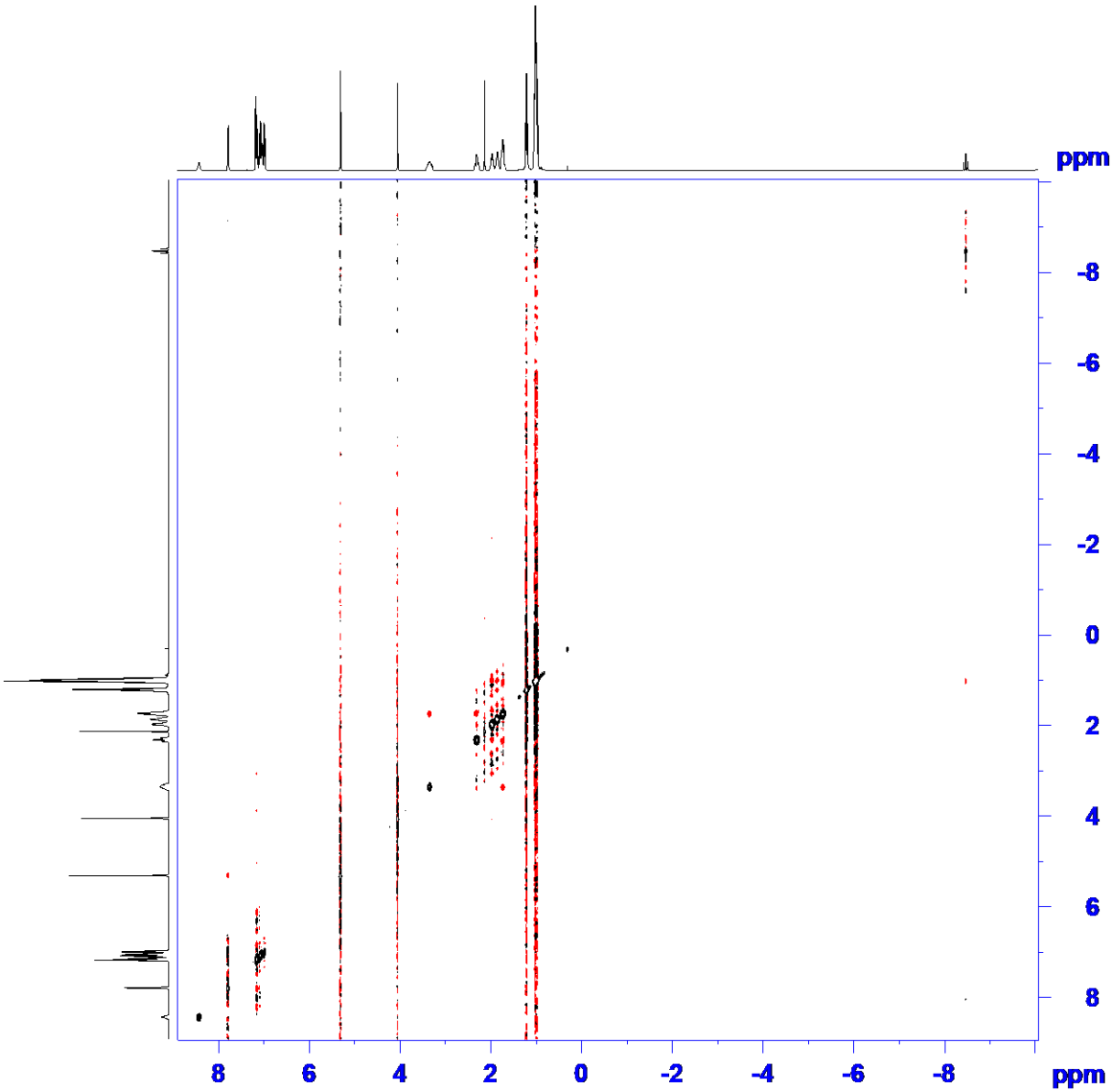
$^{13}C\{^{1}H\}$ JMOD NMR spectrum (C_6D_6, 300 K).



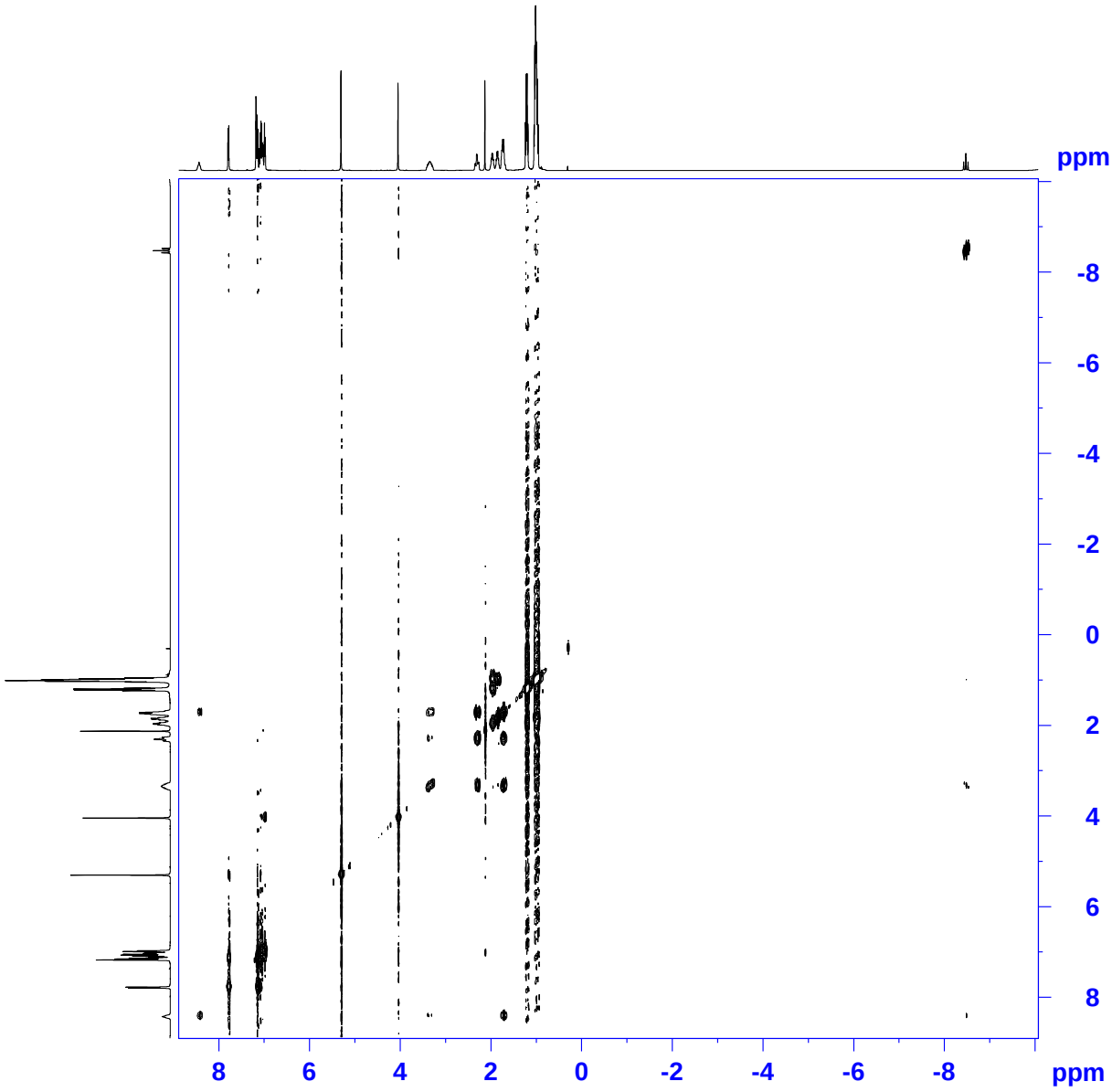
$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K).



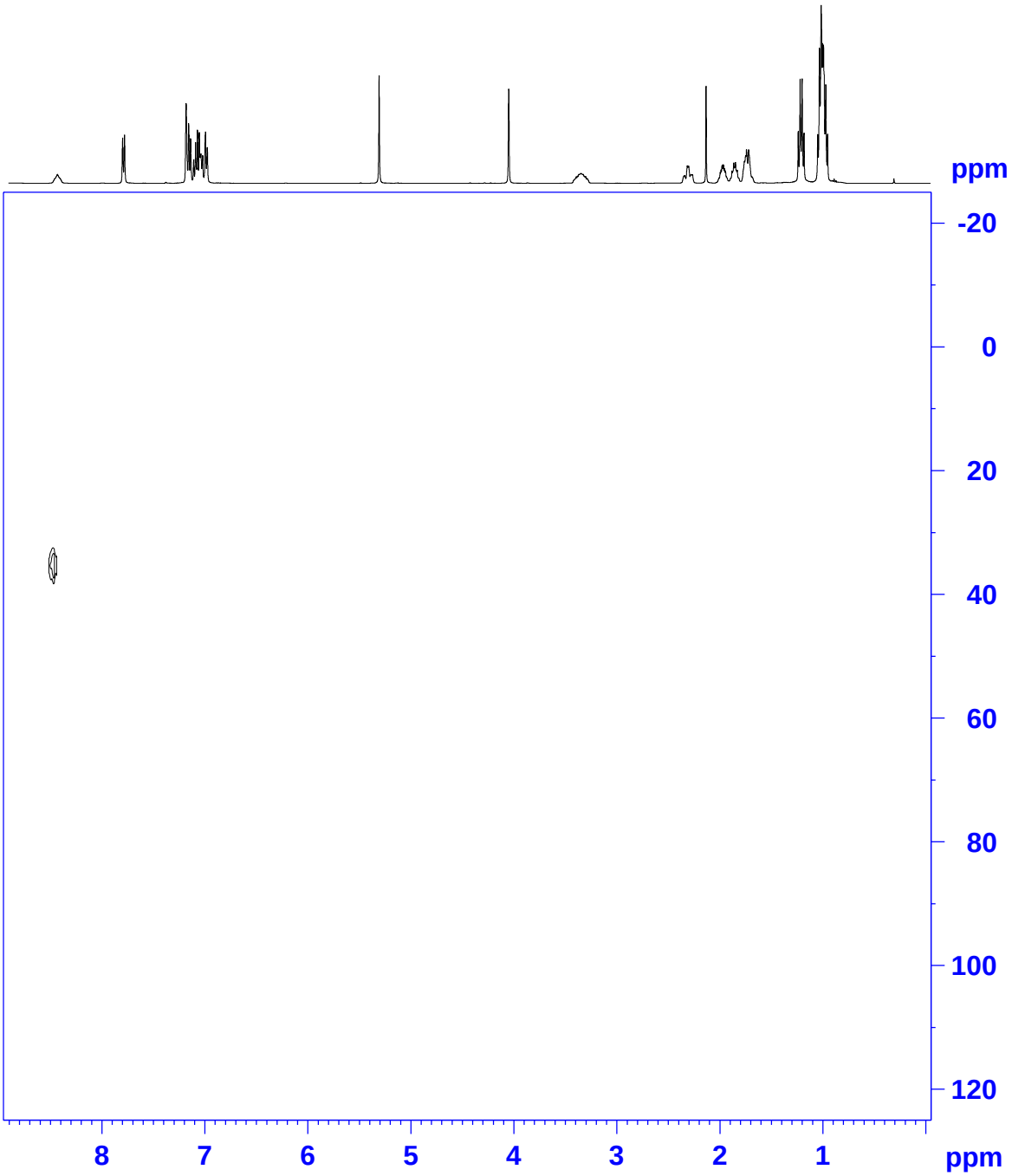
^{1}H-^{1}H 2D NOESY NMR spectrum (C_6D_6, 300 K).



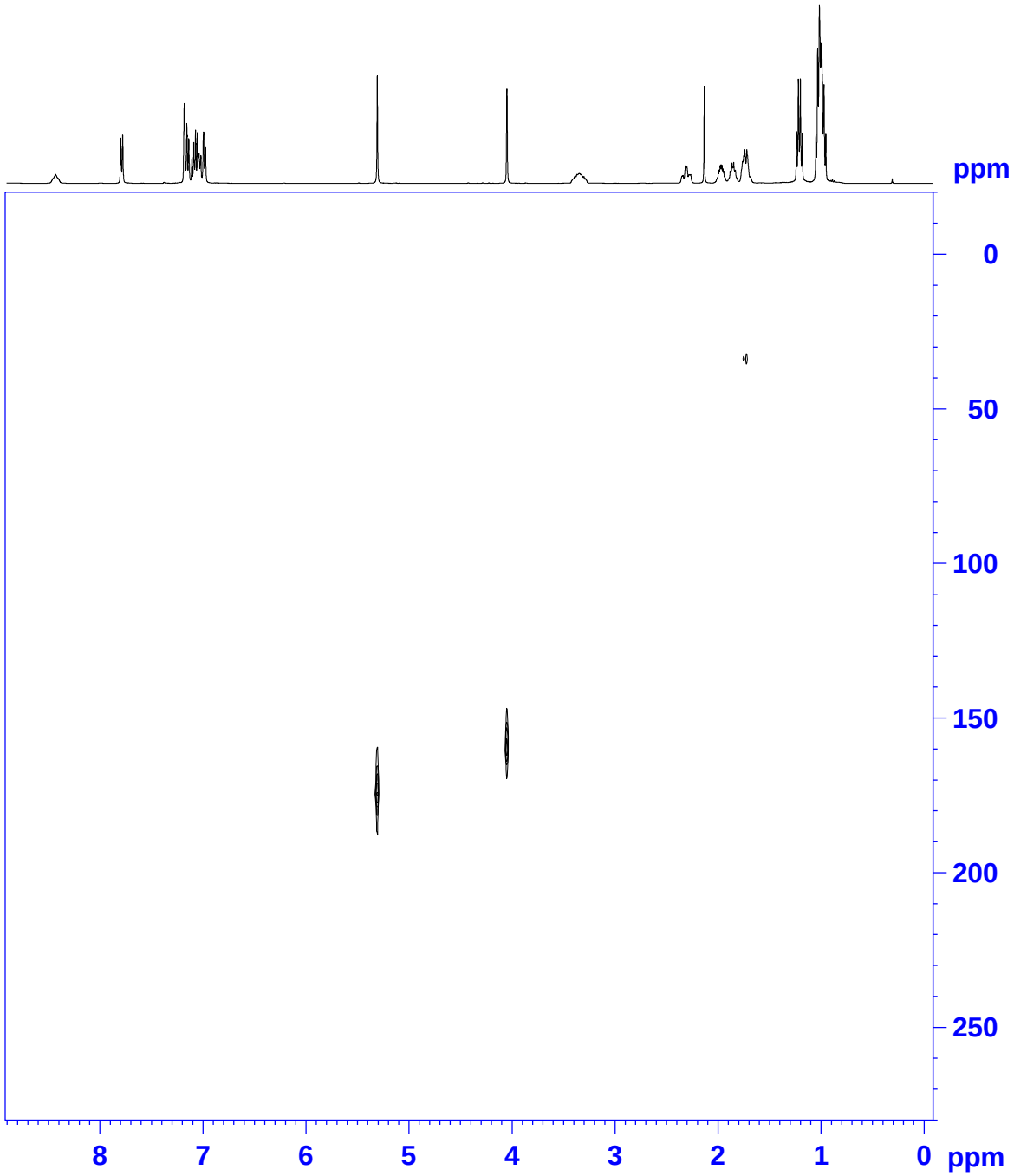
^{1}H-^{1}H 2D COSY NMR spectrum (C_6D_6, 300 K).



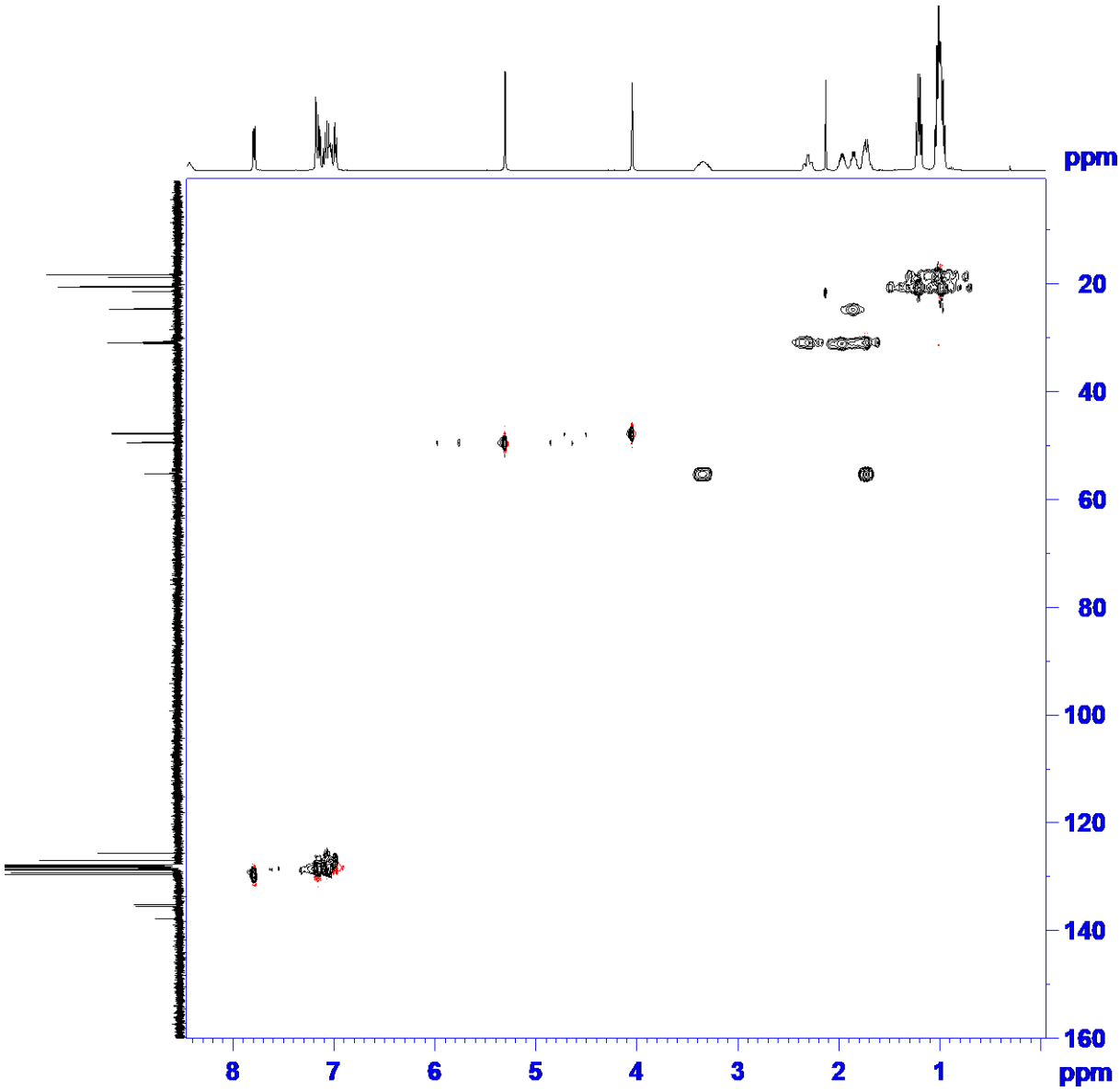
^{1}H-^{15}N 2D HSQC NMR spectrum (C_6D_6, 300 K).



2D ^{1}H-^{15}N HMBC NMR (C_6D_6, 300 K).

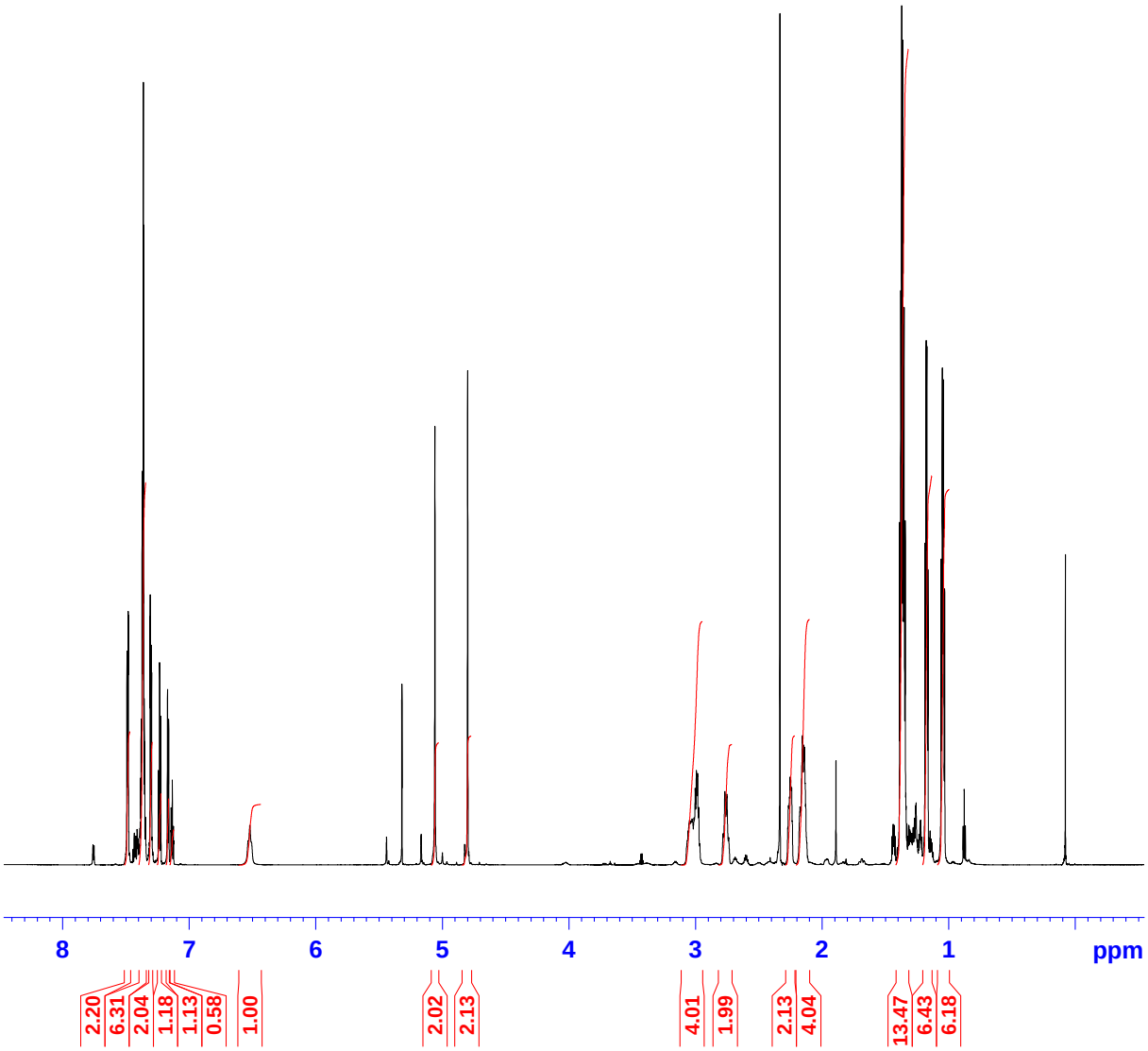


2D ^{1}H-^{13}C HSQC NMR (C_6D_6, 300 K).

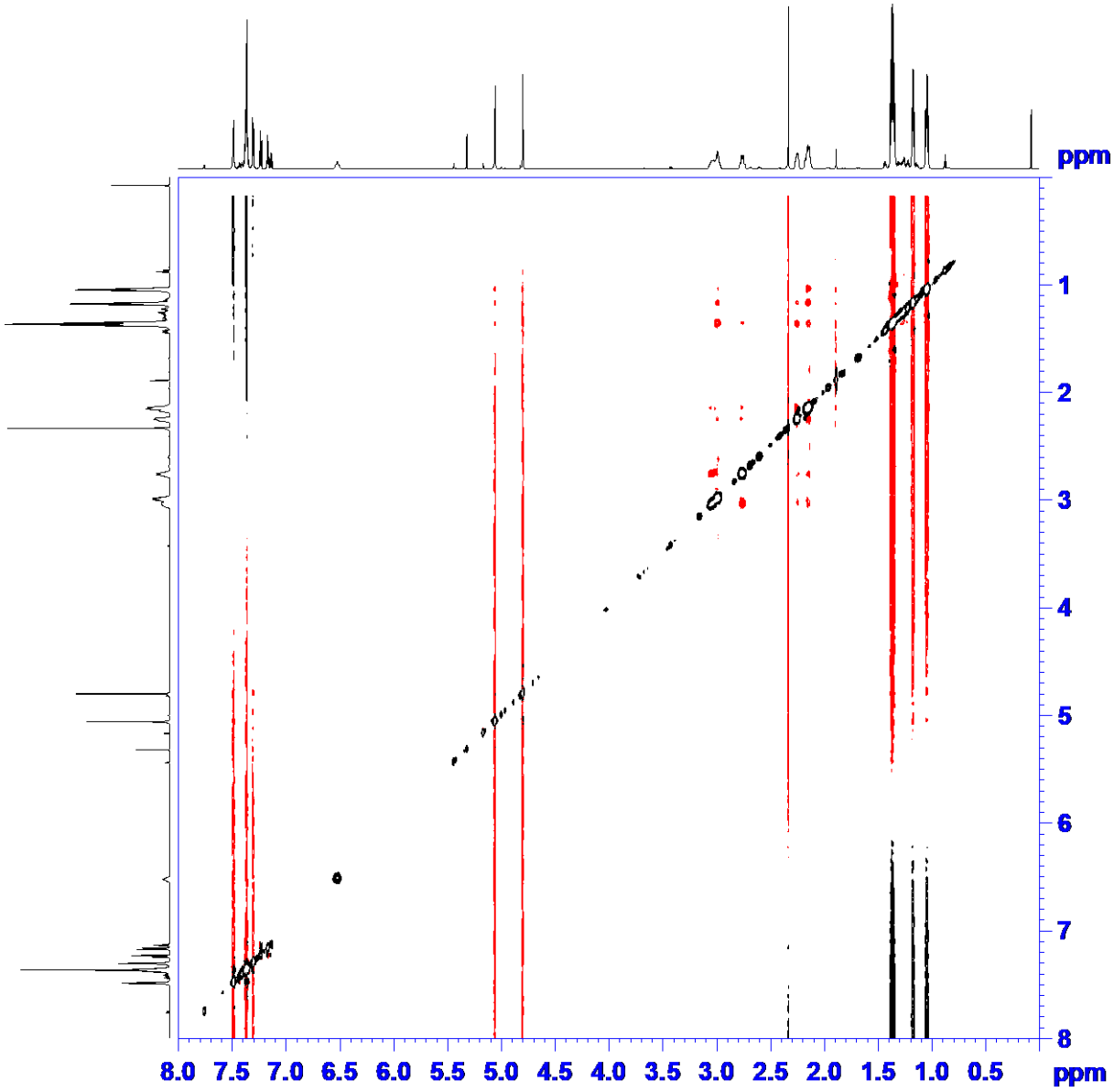


SXV. NMR spectra of [Fe(Br)(CN-CH_2Ph)$_2$(NH(CH_2CH_2P(*i*Pr)$_2$)$_2$)](Br) (8)

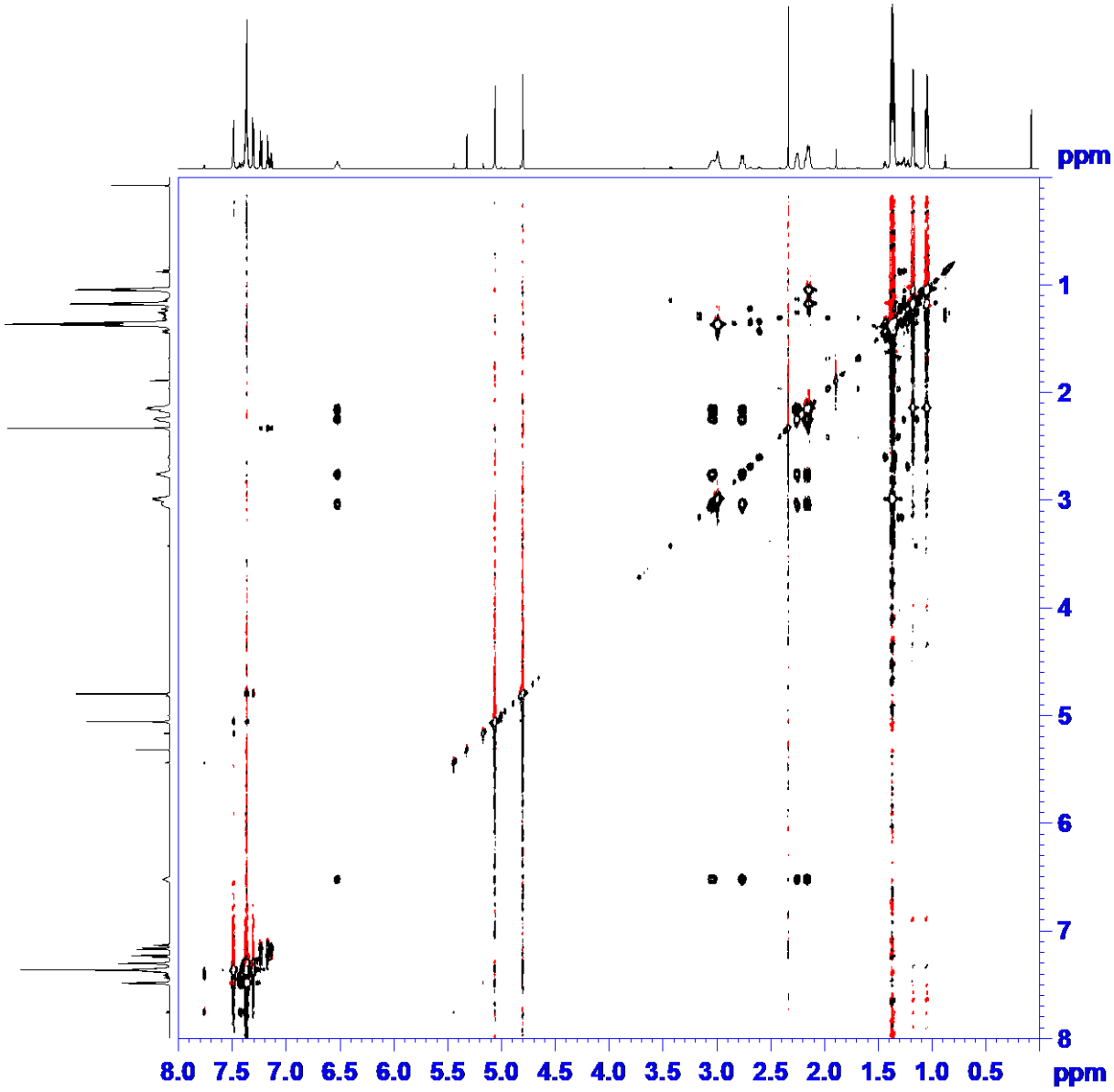
^{1}H NMR spectrum (CD_2Cl_2, 300 K, 800 MHz).



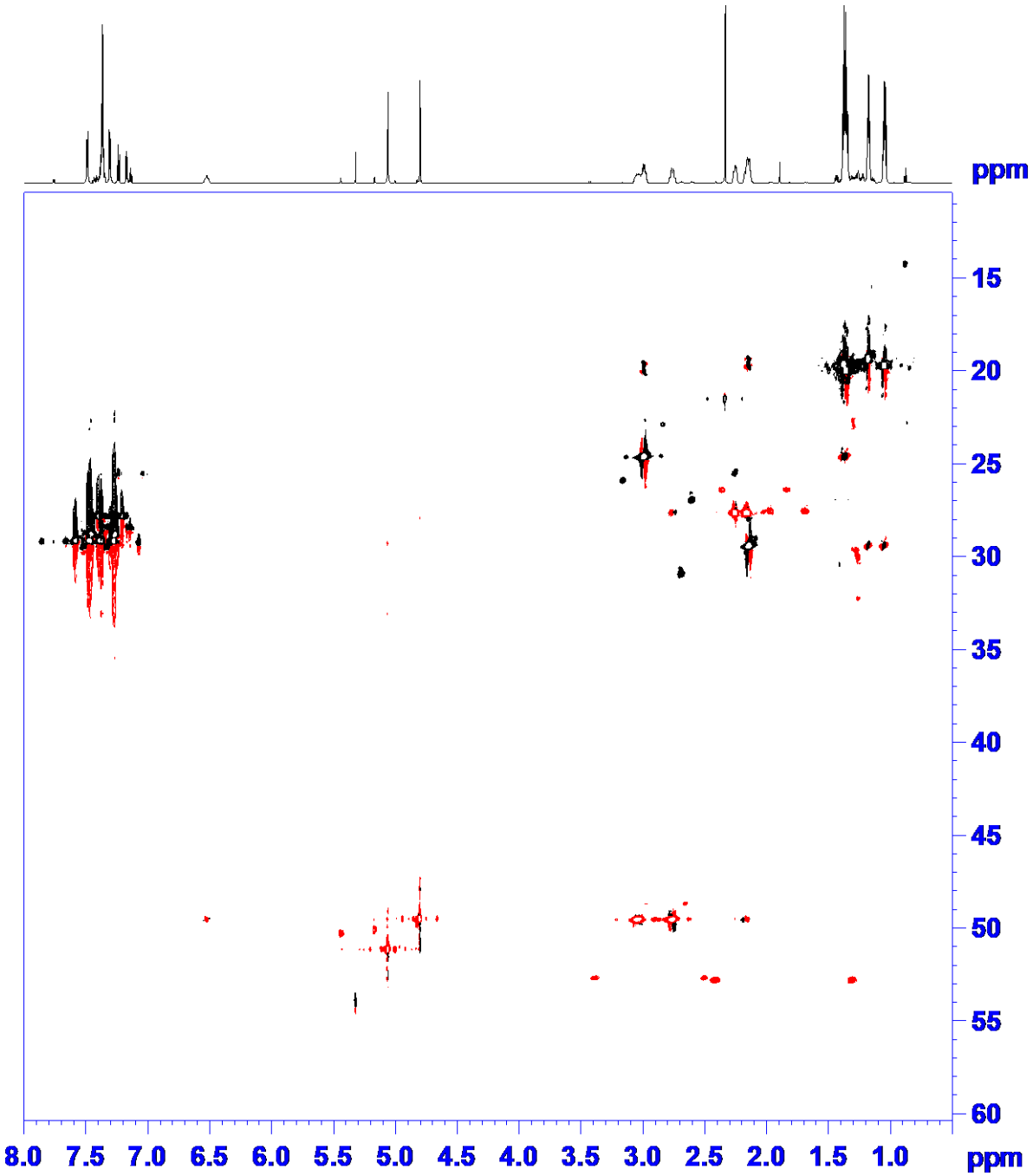
^{1}H-^{1}H 2D NOESY NMR spectrum (CD_2Cl_2, 300 K, 800 MHz).



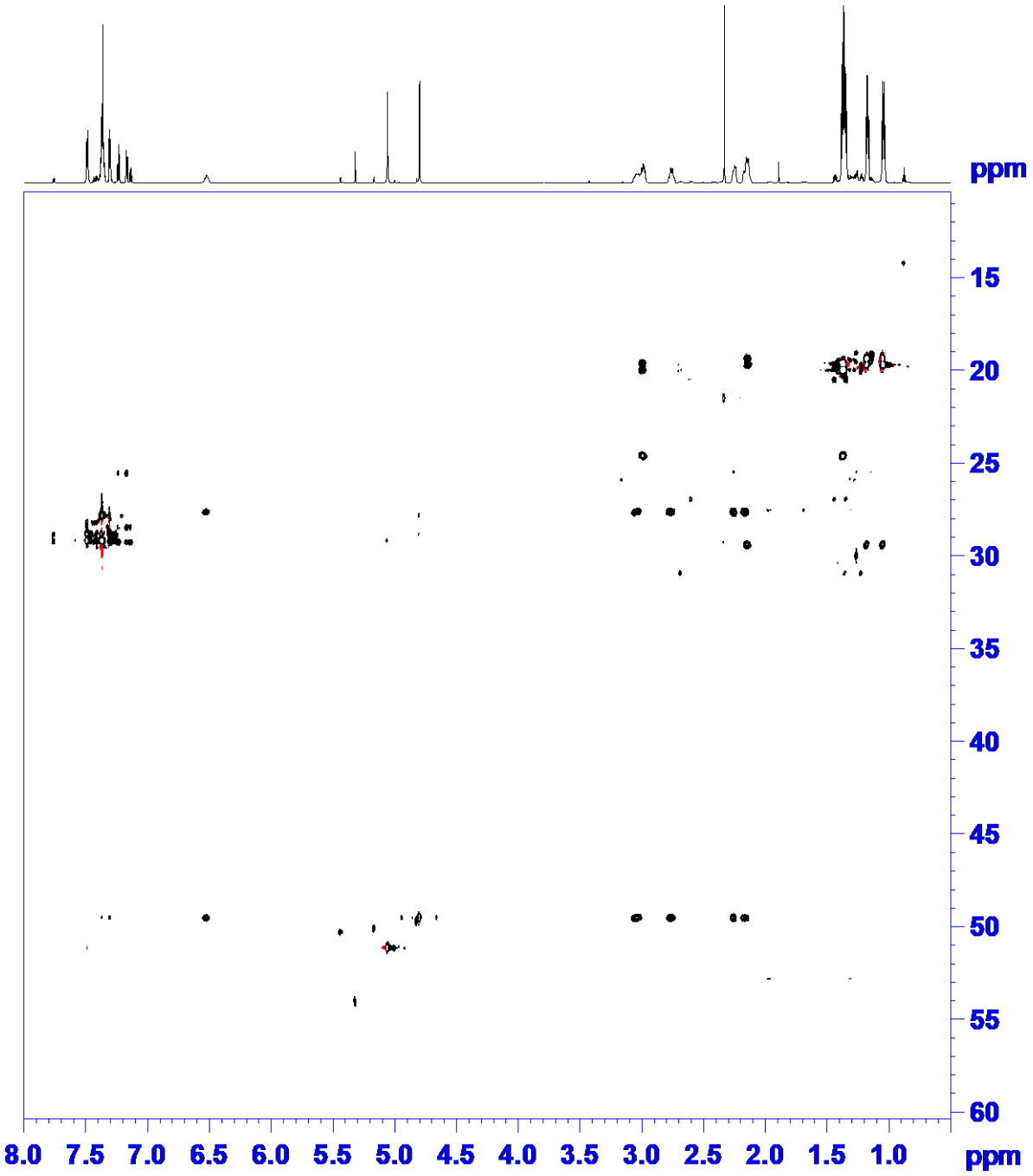
^{1}H-^{1}H 2D TOCSY NMR spectrum (CD_2Cl_2, 300 K, 800 MHz).



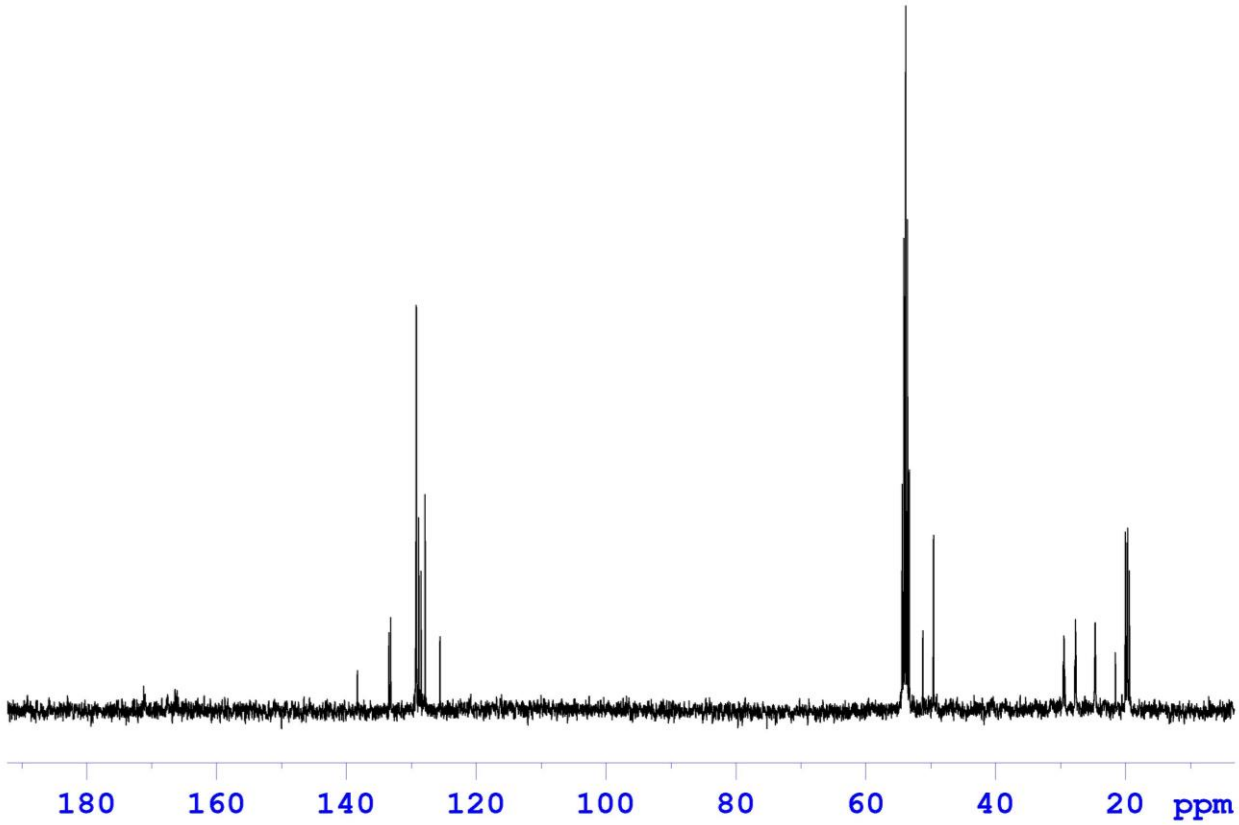
^{13}C-^{1}H 2D HSQC NMR spectrum (CD_2Cl_2, 300 K).



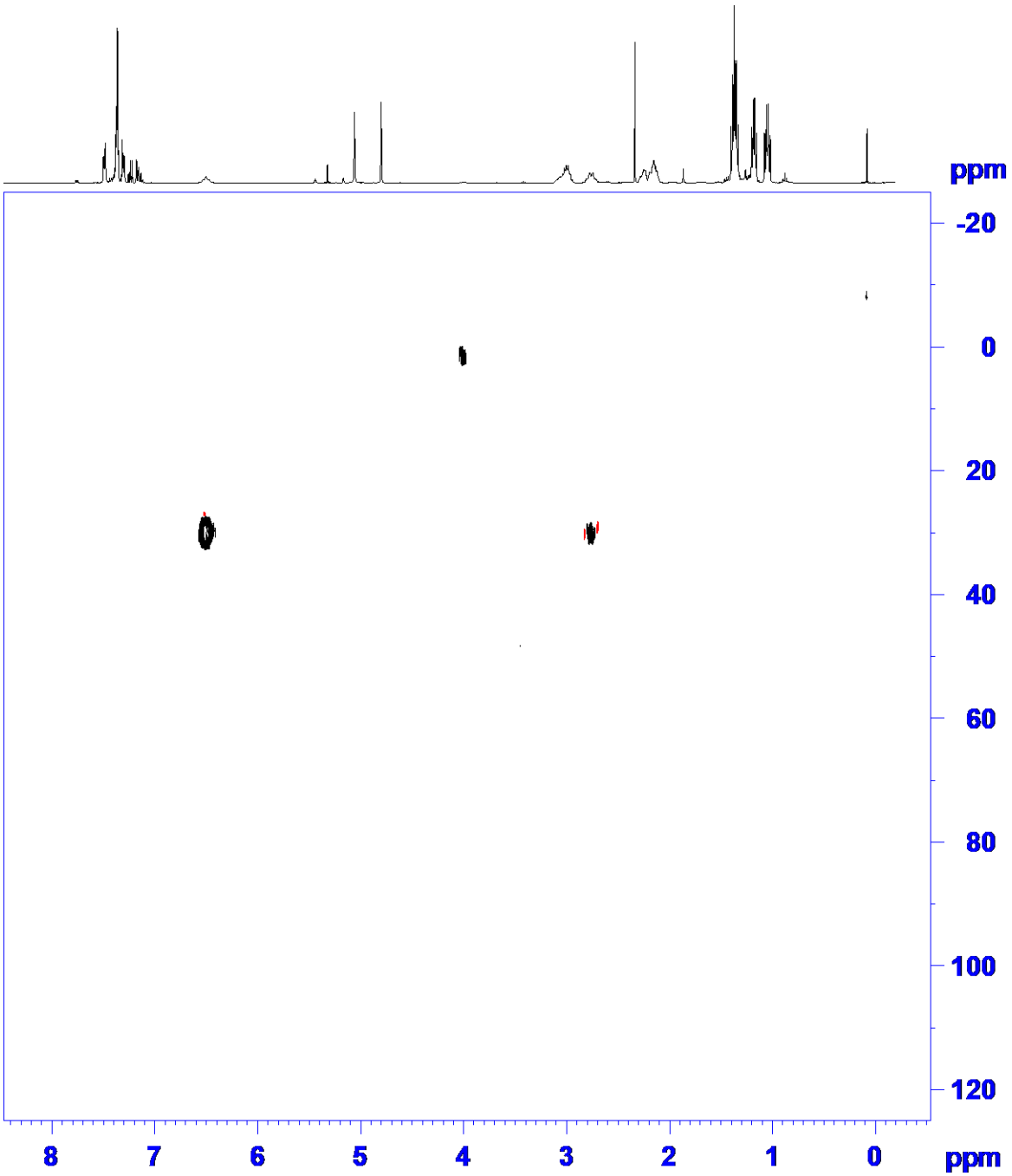
^{13}C-^{1}H 2D HSQC-TOCSY NMR spectrum (CD_2Cl_2, 300 K).



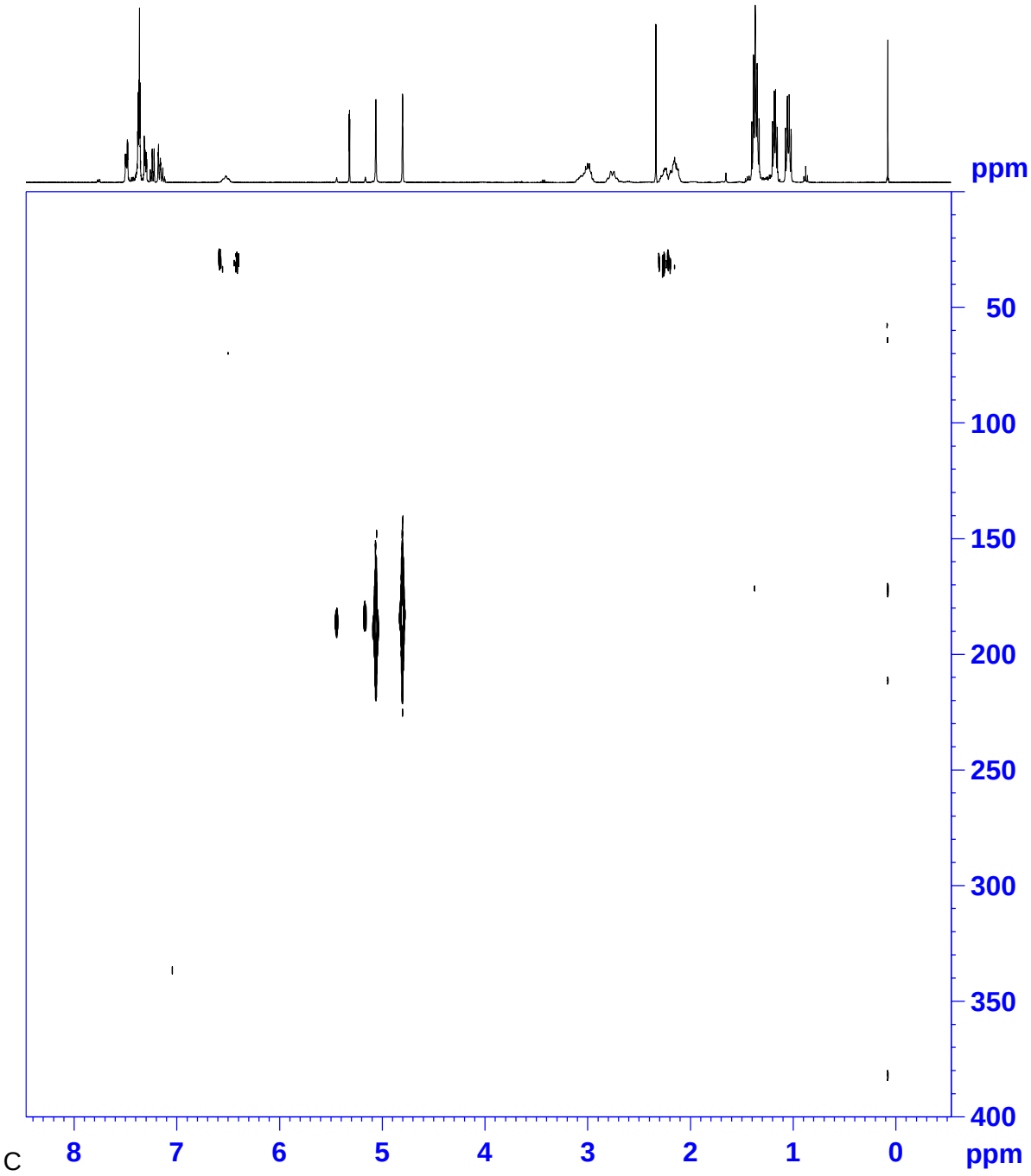
$^{13}C\{^{1}H/^{31}P\}$ UDEFT NMR spectrum (CD_2Cl_2, 300 K)



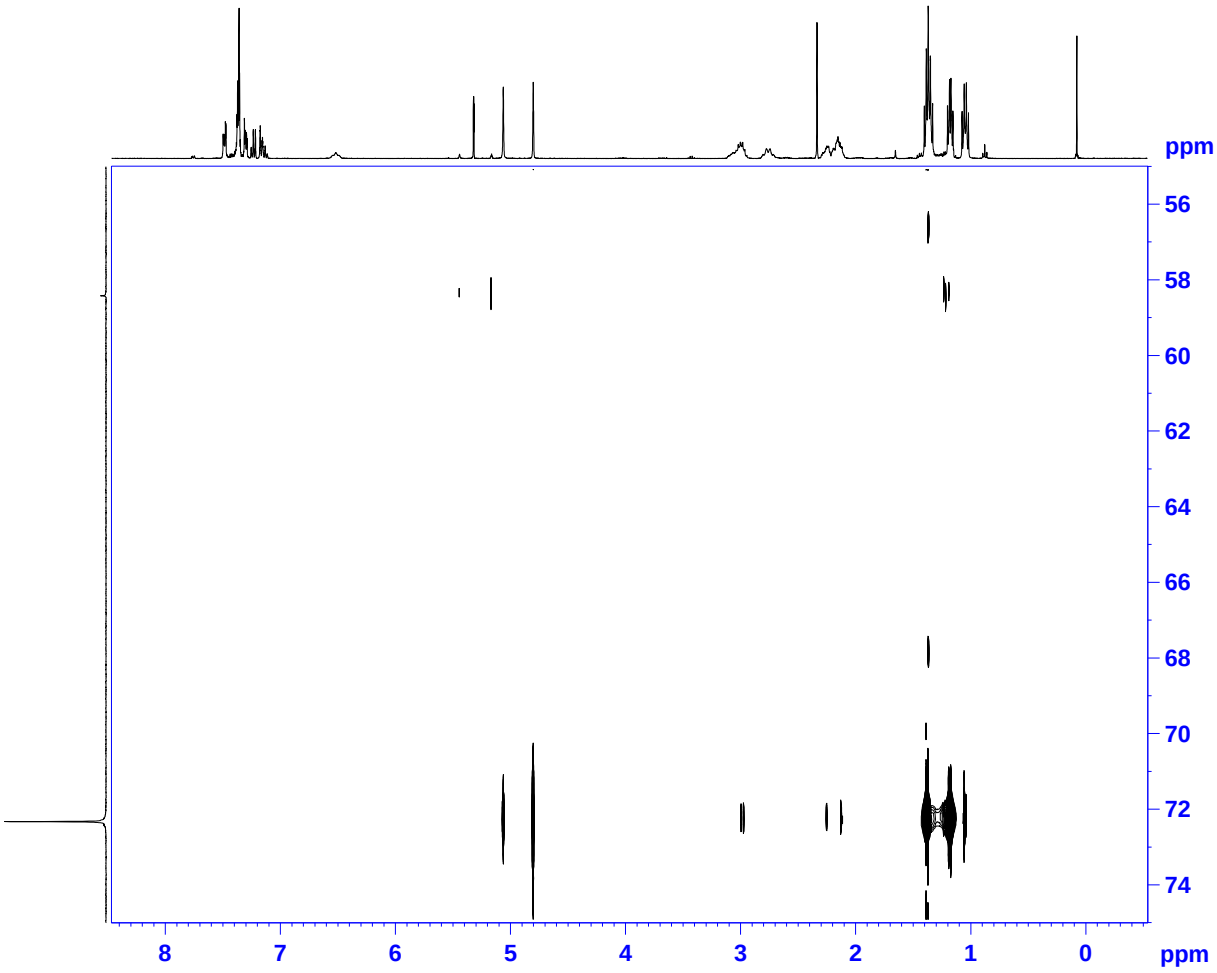
^{15}N-^{1}H 2D HSQC NMR spectrum (CD_2Cl_2, 300 K).



^{15}N-^{1}H 2D HMBC NMR spectrum (CD_2Cl_2, 300 K).

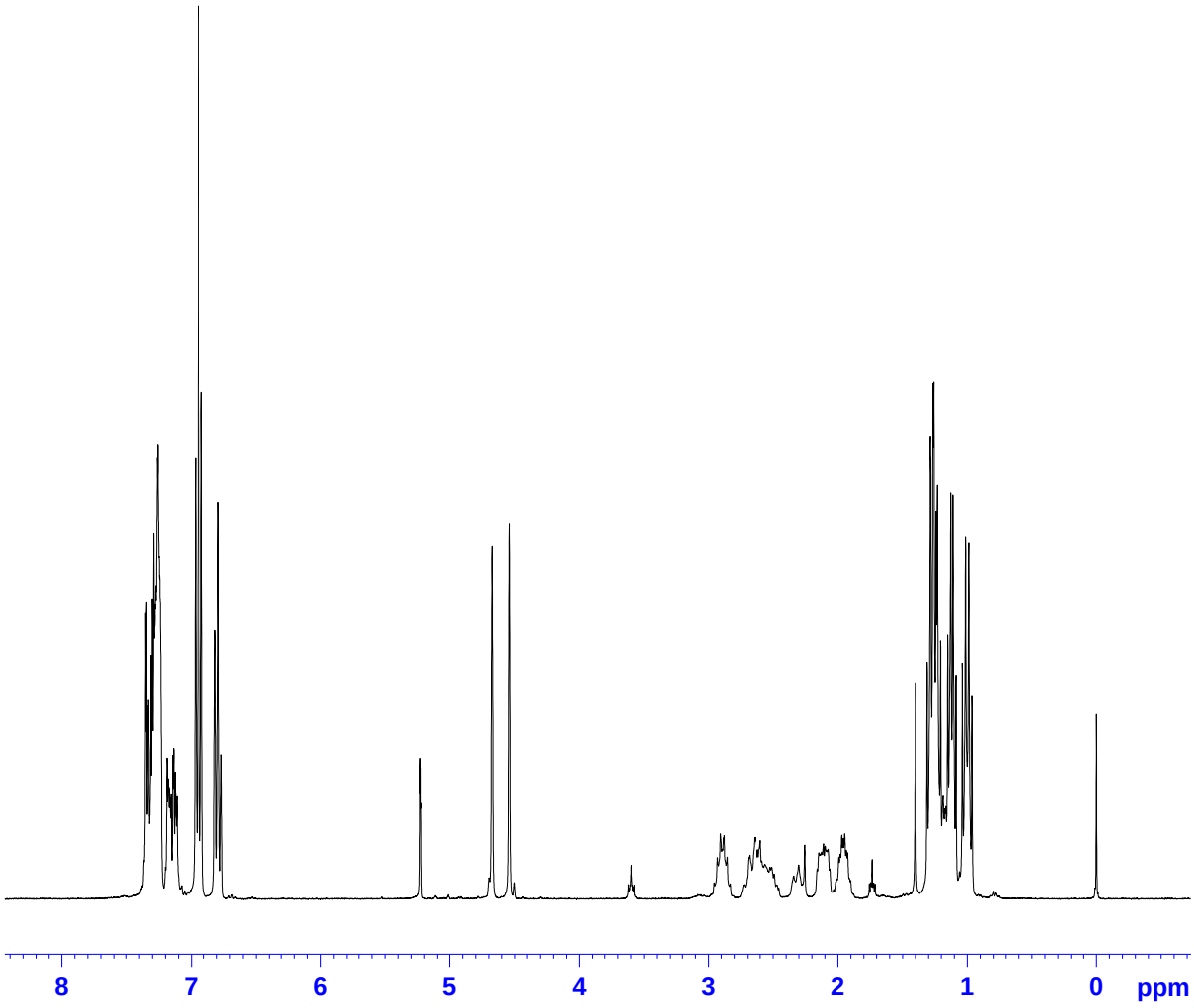


^{31}P-^{1}H 2D HSQC NMR spectrum (CD_2Cl_2, 300 K).

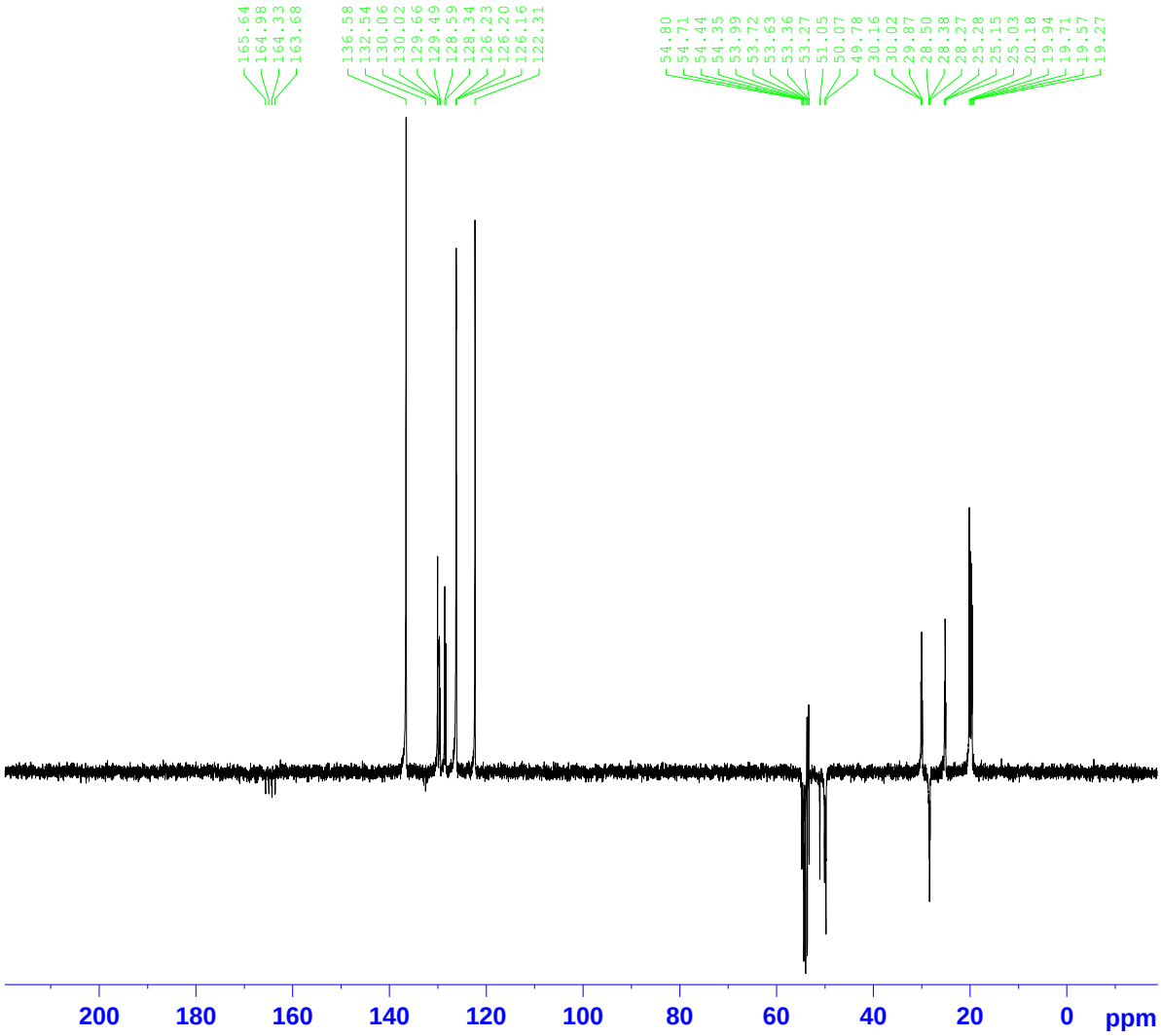


SXVI. NMR spectra of [Fe(Br)(CN-$CH_2Ph)_2$($NH(CH_2CH_2P(iPr)_2)_2$)]BPh_4 (9)

^1H NMR spectrum (300.13 MHz, CD_2Cl_2, 300 K).

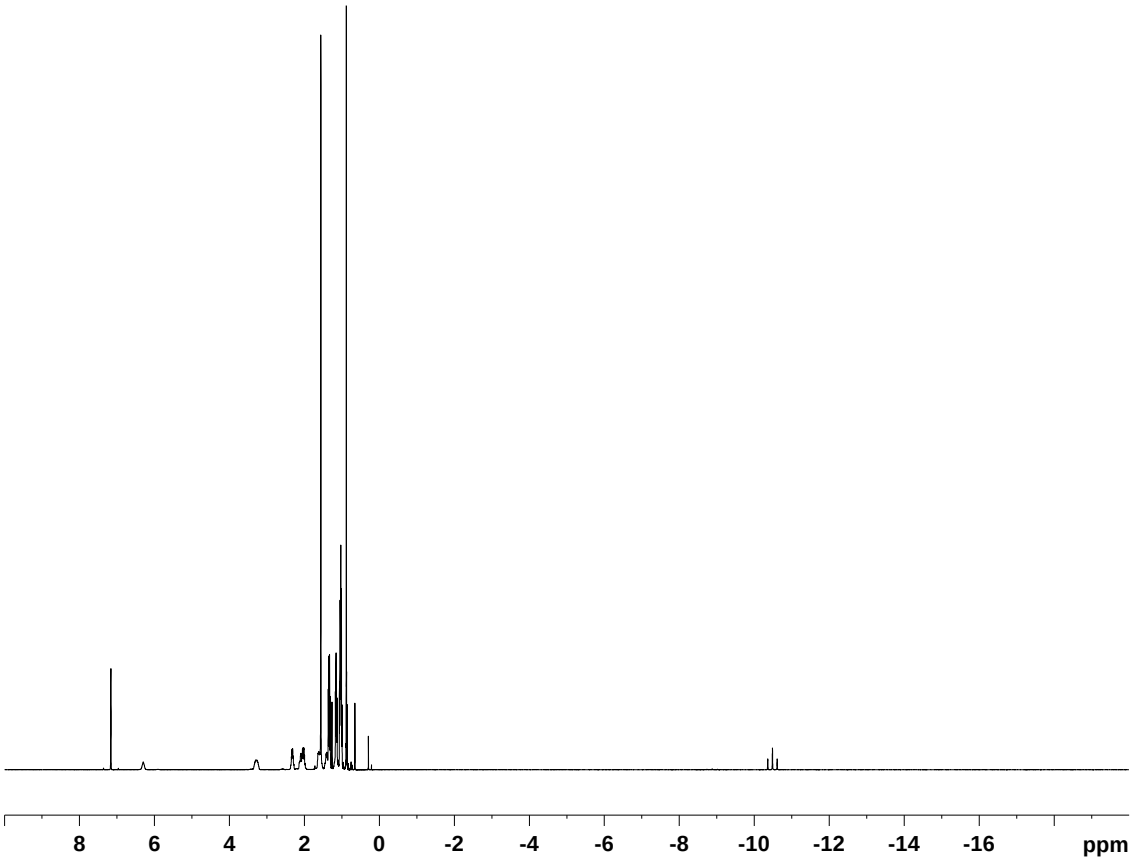


$^{13}C\{^{1}H\}$ NMR spectrum (75.468 MHz, CD_2Cl_2, 300 K).

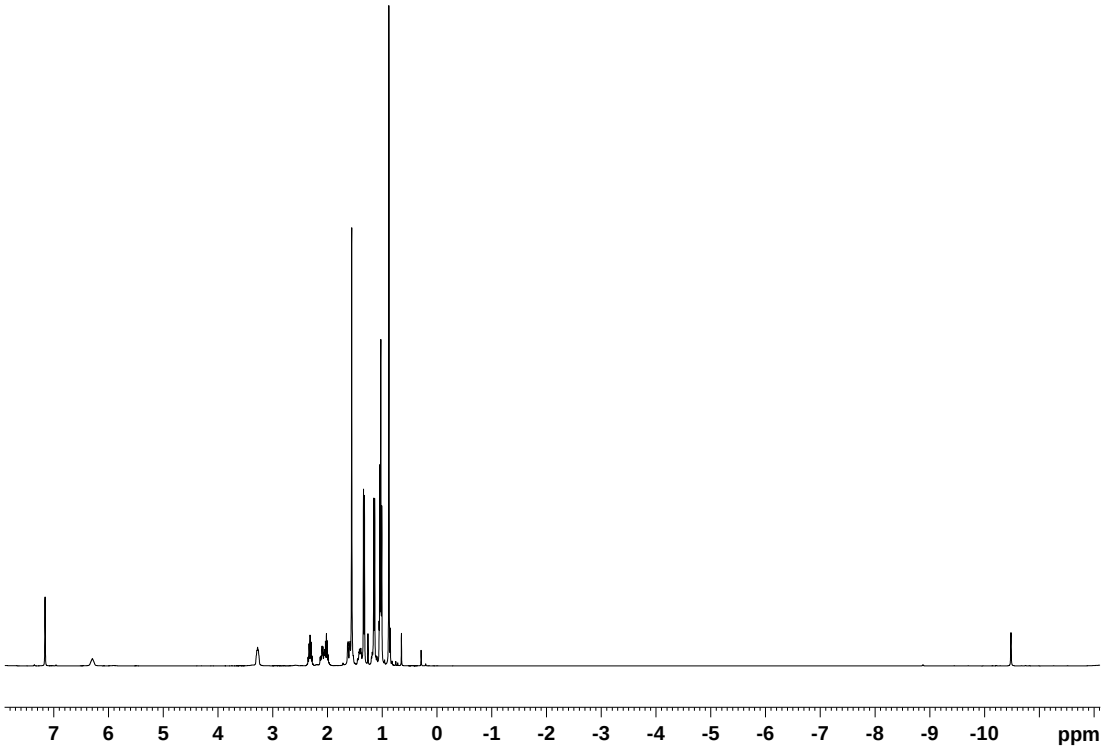


SXVII. NMR spectra of [Fe(H)(CN-*t*Bu)$_2$(NH(CH$_2$CH$_2$P(*i*Pr)$_2$)$_2$)](BH$_4$) (10)

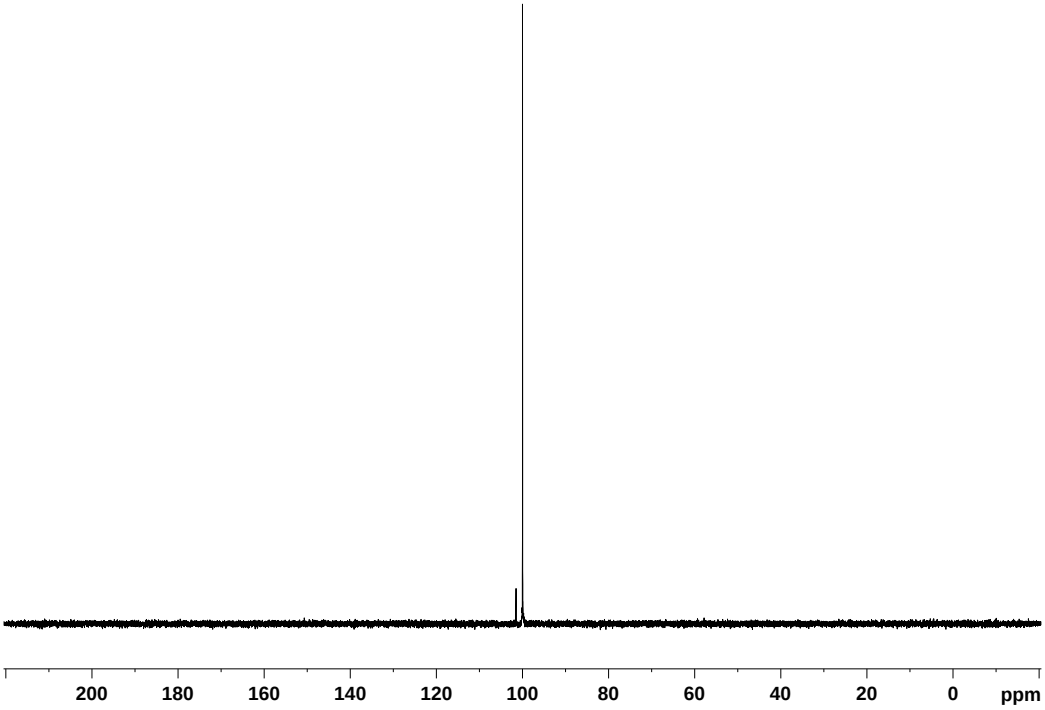
^{1}H NMR spectrum (C_6D_6, 400 MHz, 300 K).



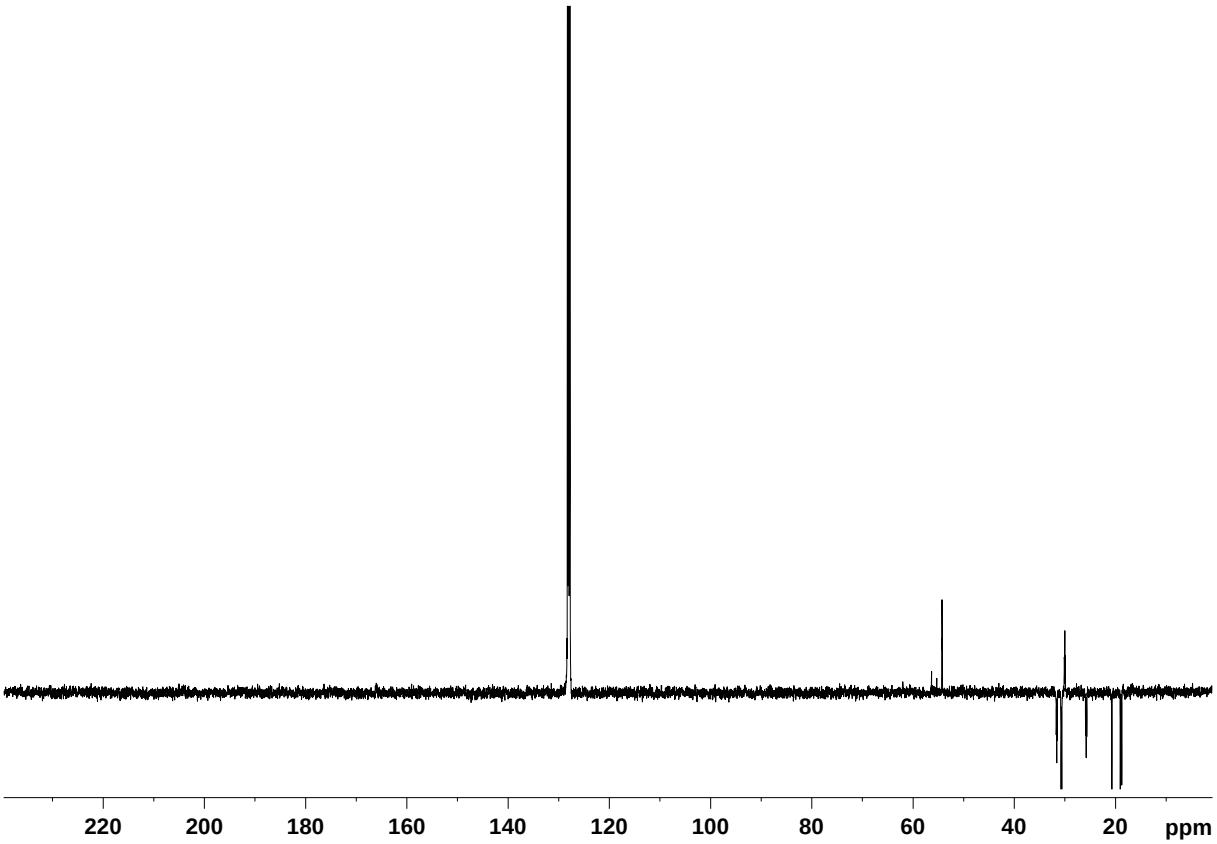
^{1}H{^{31}P} NMR spectrum (C_6D_6, 400 MHz, 300 K).



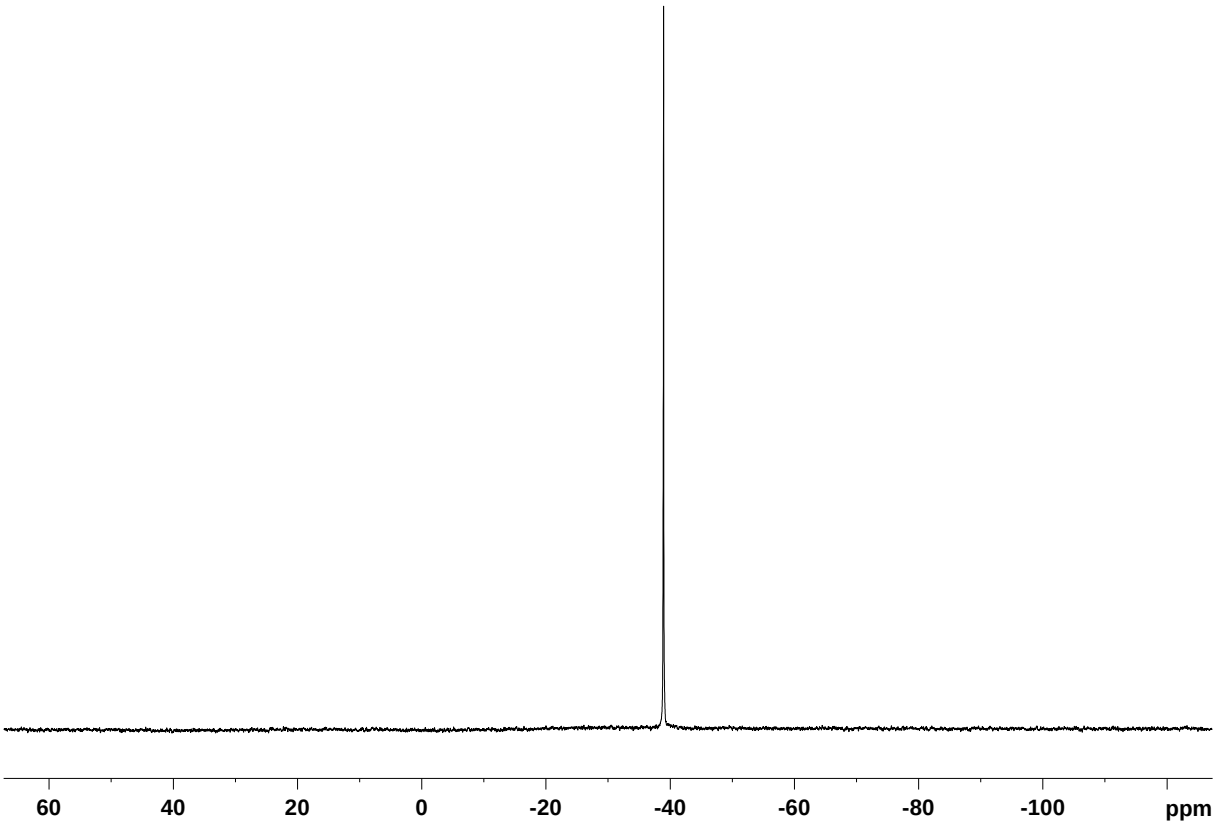
$^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K)



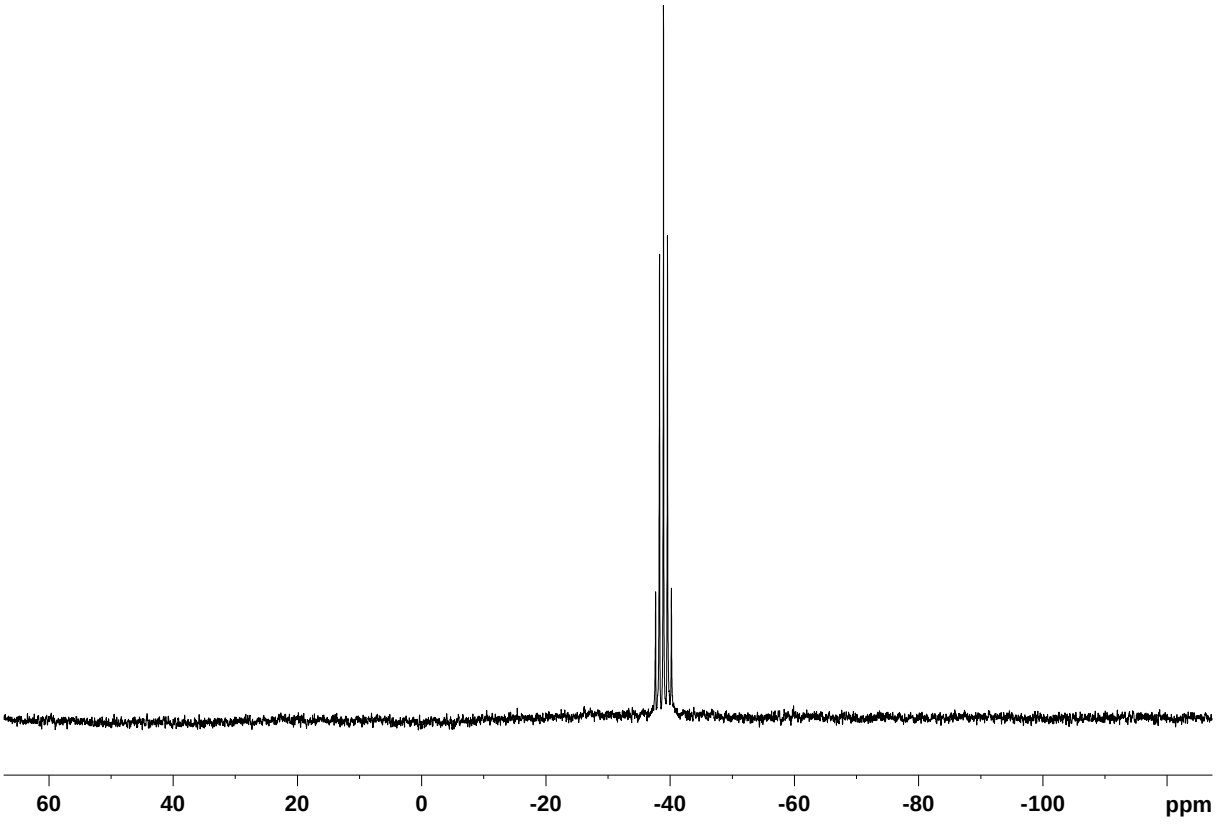
$^{13}C\{^{1}H\}$ JMOD NMR spectrum (C_6D_6, 298 K).



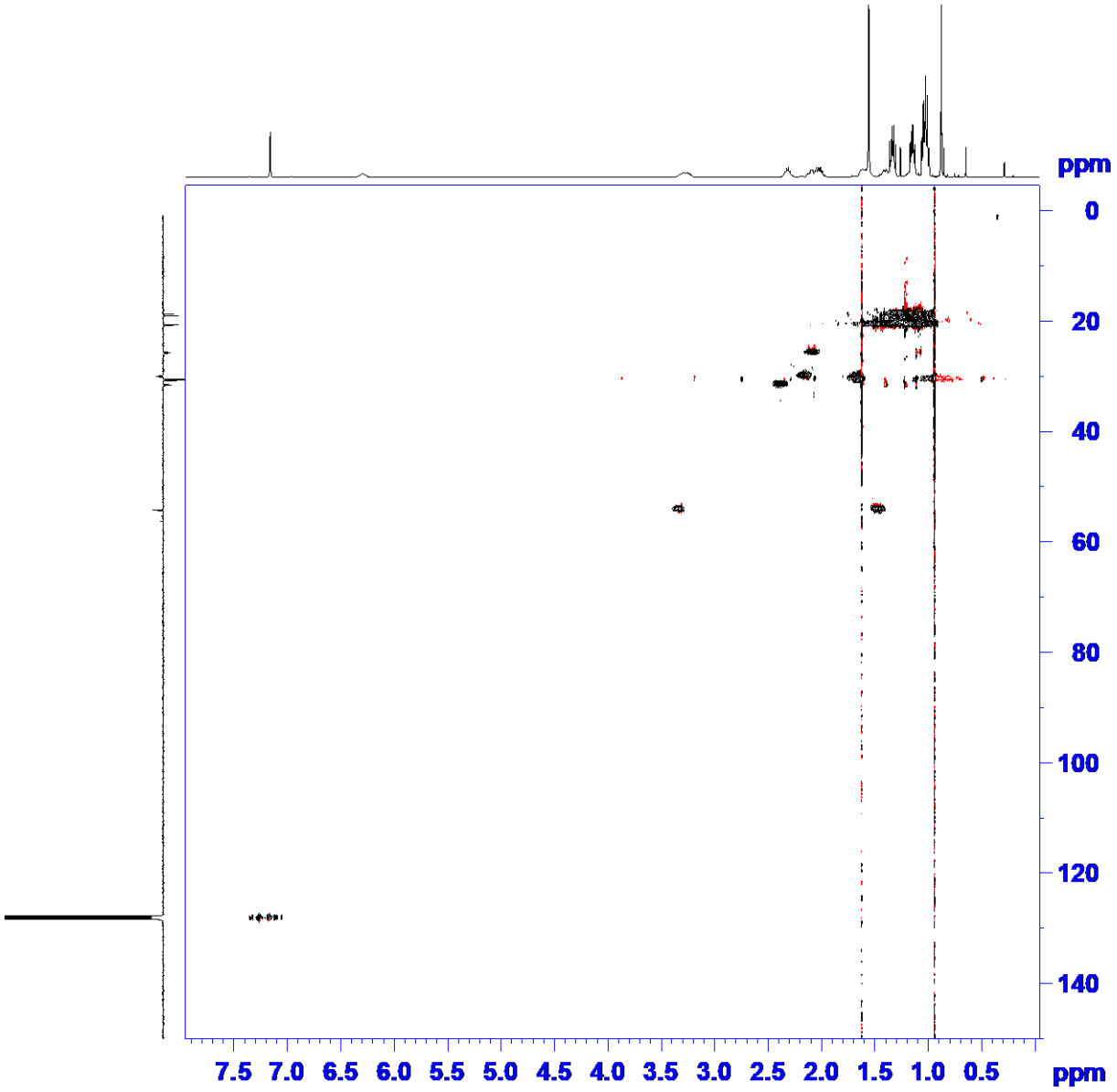
$^{11}B\{^{1}H\}$-NMR spectrum (C_6D_6, 298 K)



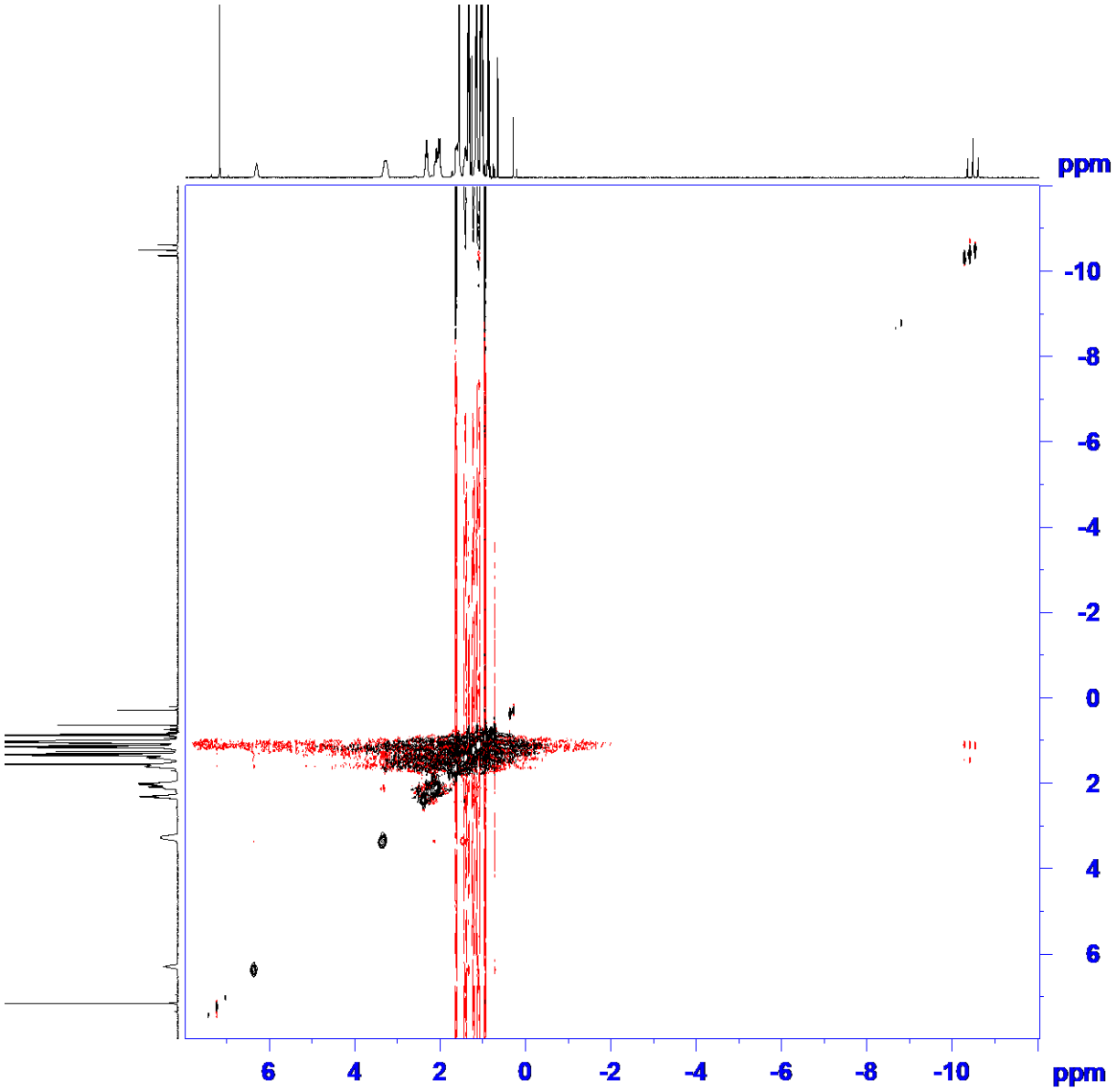
^{11}B NMR spectrum (C_6D_6, 298 K)



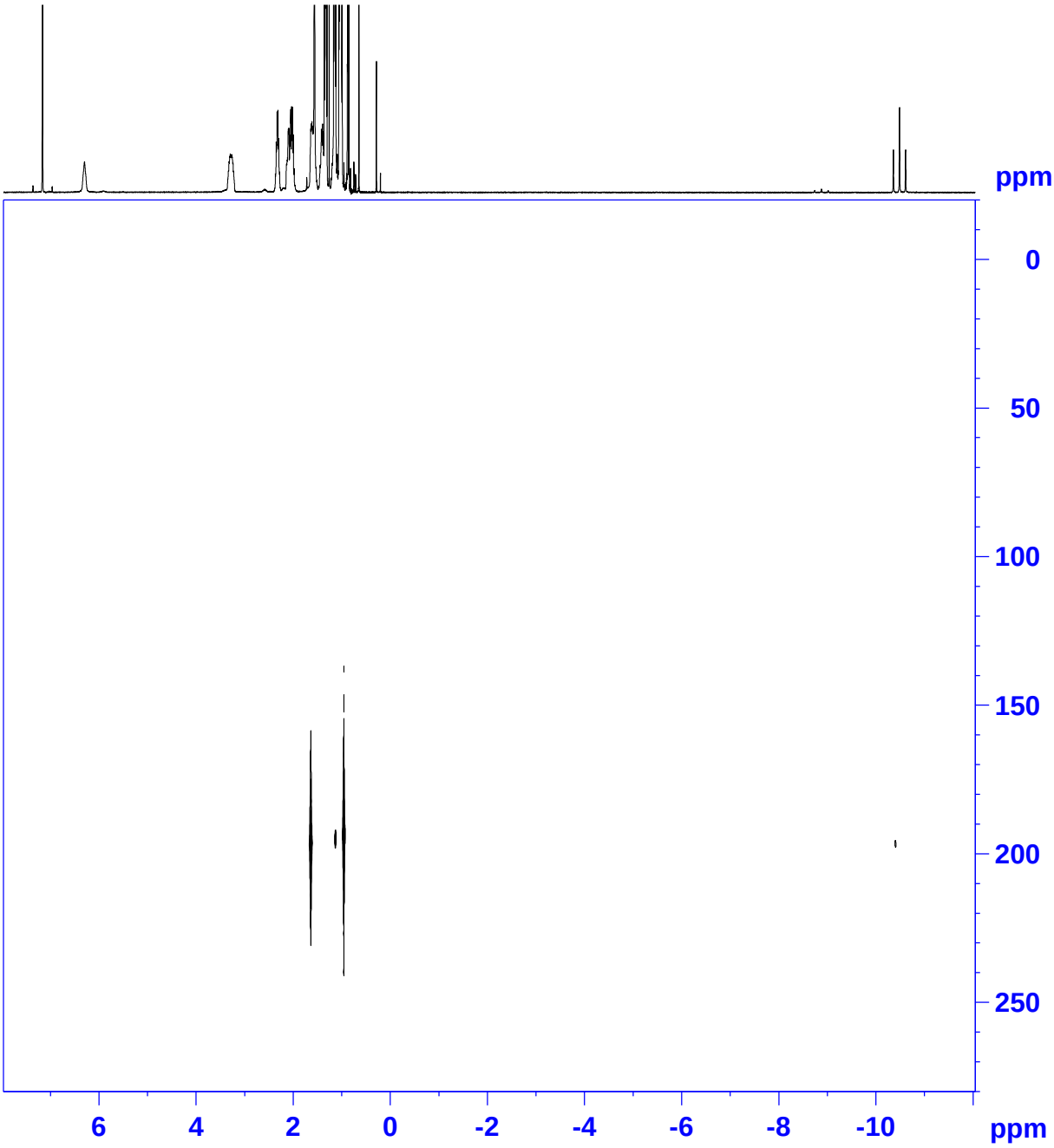
^{1}H-$^{13}C\{^{1}H\}$ 2D HSQC NMR spectrum (C_6D_6, 298 K)



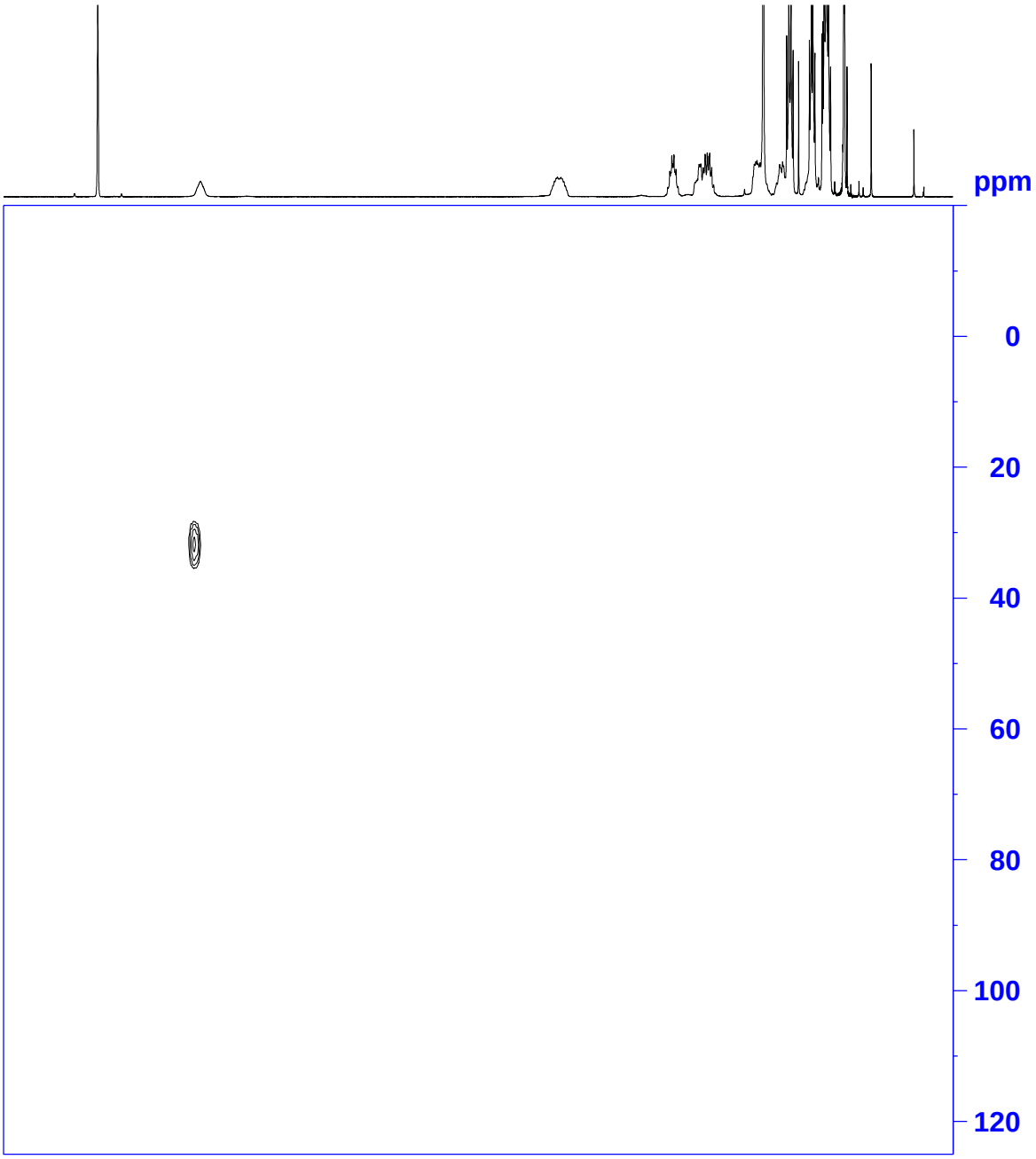
^{1}H-$^{13}C\{^{1}H\}$ 2D NOESY NMR spectrum (C_6D_6, 298 K).



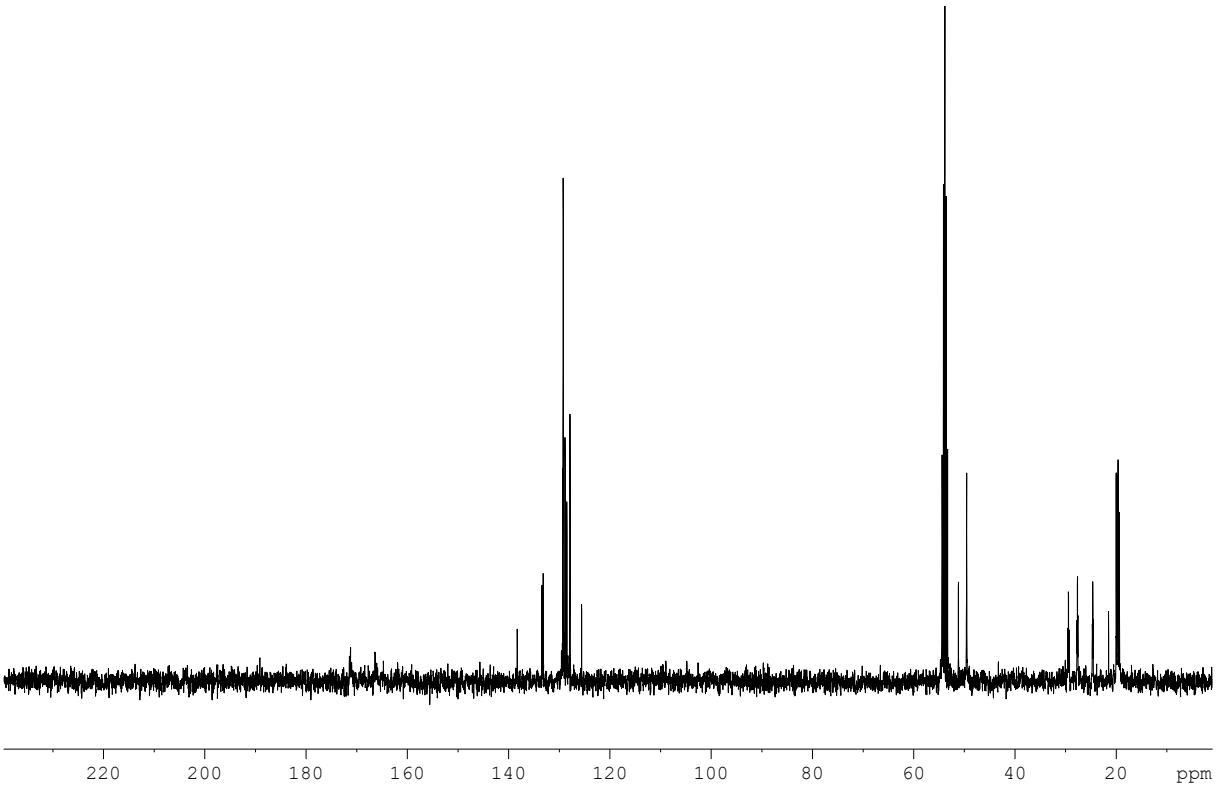
^{1}H-^{15}N 2D HMBC NMR spectrum (C_6D_6, 298 K).



^{1}H-^{15}N 2D HSQC NMR spectrum (C_6D_6, 298 K).



$^{13}C\{^{31}P\text{-}^{1}H\}$ NMR spectrum (CD_2Cl_2, 298 K).



SXVIII. Connectivity scheme for $[Ru(Cl)_2(CN\text{-}CH_2Ph)(NH(CH_2CH_2P(iPr)_2)_2)]$ (1a)