# Applications of spin–spin coupling

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## 1. Introduction

The material in this chapter covers the period from 1 June 2006 to 31 May 2007. It has been arranged as was done previously,[1] *i.e.* according to (i) the increasing atomic number of the nuclei involved, and (ii) the number of the bonds separating them. We follow the IUPAC,[2] recommendations with one notable exception, namely, the nucleus with the smaller mass is given first. For the sake of simplicity the following symbols are used throughout the paper: H for $^{1}$H, D–$^{2}$H, T–$^{3}$H, Li–$^{6}$Li, Be–$^{9}$Be, B–$^{11}$B, C–$^{13}$C, N–$^{15}$N, O–$^{17}$O, F–$^{19}$F, Al–$^{27}$Al, Si–$^{29}$Si, P–$^{31}$P, S–$^{33}$S, V–$^{51}$V, Mn–$^{55}$Mn, Fe–$^{57}$Fe, Co–$^{59}$Co, Cu–$^{65}$Cu, As–$^{75}$As, Se–$^{77}$Se, Br–$^{79}$Br, Y–$^{89}$Y, Nb–$^{93}$Nb, Mo–$^{95}$Mo, Ru–$^{99}$Ru, Tc–$^{99}$Tc, Rh–$^{103}$Rh, Ag–$^{109}$Ag, Cd–$^{113}$Cd, In–$^{115}$In, Sn–$^{119}$Sn, Sb–$^{121}$Sb, Te–$^{125}$Te, I–$^{127}$I, Cs–$^{133}$Cs, W–$^{183}$W, Os–$^{187}$Os, Pt–$^{195}$Pt, Hg–$^{199}$Hg, Tl–$^{205}$Tl, Pb–$^{207}$Pb. All the other isotopes are described explicitly.

A historical review on the scientific life of Martin Karplus, a man who played the pivotal role in NMR couplings has been given by Karplus himself.[3]

Recent advances in theoretical calculations of indirect spin–spin couplings have been reviewed by Krivdin and Contreras.[4]

An application of vicinal–vicinal spin–spin couplings to study the stereochemistry of eight- and nine-membered medium ring *cis*-cycloalkenes has been discussed by Glaser *et al.*[5]

In a short review Fukushi[6] has presented several 2D methods to measure $^{2,3}J_{HC}$ values, which are useful for stereochemical assignment in detailed structure analysis of natural products.

The use of NMR spectroscopy to study tautomerism has been reviewed by Claramunt *et al.*[7]

A review on applications of chemical shifts $\delta(^{29}Si)$ and one-, two- and three-bond couplings, $J_{SiX}$, has been written by Wrackmeyer.[8] Also couplings across more than three bonds are briefly discussed.

$^{1}J_{PCu}$ couplings have been collected by Szymańska[9] in her review on application of the Cu and P NMR to characterize Cu(I) complexes with P-donor ligands.

An application of multinuclear NMR spectroscopy to study the action mechanism of Pt anticancer drugs has been reviewed by Berners-Price *et al.*,[10] and a critical review on the progress in Pt NMR over the last 25 years has been written by Still *et al.*[11] who collected, among others, Pt couplings with various nuclei.

The work on computational NMR recently carried out at the University of Padova has been reviewed by Bagno and Saielli.[12] It covers the calculations of chemical shifts and spin–spin couplings for a variety of compounds and interactions including hydrogen bonding and van der Waals CH-π forces.

Overviews on NMR techniques used for measurement of scalar and dipolar couplings applied in solution structure elucidation of very large proteins and RNAs have been written by Tzakos *et al.*[13] and by Foster and co-workers.[14] Al-Hashimi and co-workers[15] have reviewed the use of dipolar couplings in characterisation of structural plasticity and dynamics of RNA.

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Mittag and Forman-Kay[16] have described the use of RDCs among other data in atomic level characterisation of disordered proteins.

## 2. New methods

A satellite-selective 1D-TOCSY experiment that measures the sign and the magnitude of $^{n}J_{HC}$ in small organic molecules in a fast, sensitive and accurate way has been described by Parella and co-workers.[17]

Modifications of time-shared HSQC-like experiments originally developed by Griesienger and co-workers have been proposed by Nolis *et al.*[18] They have shown that simultaneous acquisition of $^{1}H,^{13}C$ and $^{1}H,^{15}N$ HSQC-TOCSY and HSQMBC experiments can afford experimental sensitivity enhancements of 20–40% with respect to the separate acquisition of individual $^{13}C$ or $^{15}N$ data. Among others, these modifications allow simultaneous measurements of long-range proton–carbon and proton–nitrogen couplings.

The knowledge of the true value of long-range couplings, which are usually rather small, is crucial for elucidation of torsion angle restraints in molecules of biological importance such as proteins and carbohydrates. It has been shown by Clore and co-workers[19] that cross-correlated relaxation may alter the apparent *J*-coupling through interference with passive longitudal relaxation, thereby counteracting the self-decoupling effect and bringing the measured *J*-coupling closer to its true value.

A $^{13}C$-detected IPAP-INADEQUATE experiment for simultaneous measurement of one-bond and long-range scalar or residual dipolar couplings has been designed by Jin and Uhrín.[20] The method gives accurate values of one-bond and long-range couplings and is illustrated by the measurement of interglycosidic $^{3}J_{CCOC}$ couplings in a disaccharide molecule providing important information on the conformation of the glycosidic linkage.

A 1D pulse sequence which converts double quantum coherence of *y* phase with optimal efficiency, relying on single transition selection has been designed by Ramesh and Chandrakumar.[21] Its application to 1D $^{13}C$ INADEQAUATE has been demonstrated by the use of a sucrose sample.

$^{13}C$ direct detected methods that improve detectability of scalar and residual dipolar couplings have been proposed by Bertini and co-workers[22] and by Piccoli and co-workers.[23] The first group[22] has applied protonless ReCACO and ReCON experiments for measurement of RDCs in the case when the proton spectrum of protein contains broad signals. The second group[23] has used the COCO-TOCSY experiment to measure $^{3}J_{C'C'}$ couplings in proteins that provide the first dihedral angle constraints obtained with protonless approach.

A Java applet that can be executed from a web page has been built by Evans *et al.*[24] It allows prediction of NOEs and NMR couplings, as well as easy visualization of three-dimensional molecular structures.

Two-dimensional[25] and three-dimensional through-bond homonuclear/heteronuclear[26] correlation experiments have been designed by Deschamps and co-workers for quadrupolar nuclei in solid-state NMR. The experiments can be realized between spins of type X, separated by four chemical bonds, in X–O–Y–O–X motifs provided a *J* coupling between X and Y exists. Both experiments have been tested and demonstrated on $AlPO_4$-14 samples where they allowed a detailed characterization of the Al–O–P–O–Al motives. These experiments open new possibilities for the characterization of complex chemical bond networks in perfectly crystalline, disordered or amorphous solids.

It has been shown by Fayon *et al.*[27] that simple pulse sequences based on scalar *J*-couplings and previously developed for liquid-state NMR, can be applied under MAS condition to obtain homonuclear triple-quantum-single-quantum correlation spectra of crystalline and disordered solids. The feasibility of these experiments in coupled spin-1/2 systems has been demonstrated for fully $^{13}C$-labelled L-alanine and

$Pb_3PO_4O_{13}$ crystalline compounds, used as models for three-spin and four-spin systems, respectively.

The experiments which select only the magnetization from $I$ nuclei bound to S nuclei have been designed by Iuga *et al.*[28] These methods can be applied for samples where the spin $I$ and the spin $S$ have spectra spread over a large frequency range. In order to show their feasibility the spectra of $(XeF^+)(AsF_6^-)$ have been recorded, where the $^{19}F$ isotropic chemical shift is *ca.* −278 ppm and $^1J_{FXe}$ is −6900 Hz.

A new analytical method based on the 2D HSQC NMR sequence, which can be applied for quantitative structural determination of complicated polymers, has been designed by Zhang and Gellerstedt.[29] It takes into account the influence of $T_1$ and $T_2$ relaxations, off-resonance effects, and homo- and heteronuclear couplings. The authors claim that the methodology developed by them can be widely applied in areas where a quantitative analysis of structurally complicated polymers is necessary.

The first two-dimensional correlation NMR (COSY) spectra have been obtained by Robinson *et al.*[30] at ultra low frequencies using the Earth's magnetic field. The spectra were measured for trifluoroethanol and *para*-difluorobenzene.

A method for the automatic multiplet analysis in weakly coupled systems which relies on a multistep procedure forming the automatic $J$ algorithm has been proposed by Prost *et al.*[31] To show its usefulness the spectrum of sucrose and a multiplet of the methine proton of 3-bromo-2-methyl-1-propanol have been simulated.

The P.E.HSQC experiment for simultaneous, sign-sensitive measurement of $D_{HH}$ and $D_{HC}$ couplings in small and medium sized molecules has been introduced by Luy and co-workers.[32] Kobzar and Luy[33] have compared three experimental schemes used for measuring $^nD_{HC}$ couplings at natural abundance. The aim of their work was the technical analysis and improvement of those sequences.

Several new methods have been introduced for accurate and precise measurement of scalar and dipolar spin–spin couplings in proteins. The 3D BEST-*J*comp-HMQC2 experiment for the measurement of $D_{HH}$ couplings between amide protons has been introduced by Schanda *et al.*[34] A modified version of the HACACO experiment has been presented by Bazzo and co-workers[35] as a sensitive and accurate method to measure $^1D_{H\alpha C\alpha}$ dipolar couplings. $^1J(^{15}N–H^N)$-modulated[$^1H–^{15}N$]-HSQC pulse schemes aimed for accurate measurement of $^1D_{HN}$ couplings in deuterated and non-deuterated proteins have been reported by de Alba and Tjandra.[36] Luy and co-workers[37] have applied the *J*-evolution spectroscopy with a $BIRD^{d,X}$ element during *J*-evolution (JE-N-$BIRD^{d,X}$-HSQC experiment) for accurate measurement of $^1D_{HN}$ couplings in small to medium sized biomolecules.

New methods for extracting information concerning multiplicities of different types in a single NMR experiment have been elaborated. Szyperski and co-workers[38] have presented G-matrix Fourier transform (GFT) NMR spectroscopy for mutually correlated nuclear couplings and implemented the constant-time *J*-GFT (6,2)D (HA–CA–CO)–N–HN experiment for simultaneous measurement of $^1D_{HC}$, $^1D_{HN}$, $^1D_{CC}$ and $^1D_{CN}$ couplings in proteins. TS–$^1H$,$^{13}C$/$^1H$,$^{15}N$–HSQC–F1(and F2)-IPAP experiments have been developed by Nolis and Parella[39] for simultaneous measurement of $^1D_{HC}$ and $^1D_{HN}$ couplings in $^{13}C$/$^{15}N$-labelled proteins. Liu and co-workers[40] have reported a new strategy, isotopomer-selective IS-TROESY, for the simultaneous assignment of backbone and side chain amides in large proteins.

Ying and Bax[41] have described a novel 3D constant-time HMQC-IPAP-NOESY experiment that permits measurement of $^3J_{HO–C}$ couplings in helical RNA through the E.COSY principle. A novel $S^3E$-$^{19}F$-α,β-edited NOESY experiment for quantitation of long-range scalar $J_{HF}$ couplings in 5-fluoropyrimidine-substituted RNA has been developed by Hennig and co-workers.[42] A quantitative adiabatic $J_{NN}$ HNN-COSY experiment that provides observations of hydrogen bonding interactions in oligonucleotides where donor and acceptor nitrogens are separated by up to 140 ppm has been reported by Hennig and co-workers.[43]

The new approaches for data collection in NMR experiments are constantly being developed. The 2D HIFI HNCO experiment for measuring small $^1D_{C'N}$ couplings in proteins has been proposed by Cornilescu *et al.*[44] In that method the approach called '*H*igh *R*esolution *I*terative *F*requency *I*dentification of couplings' is applied. Rovnyak and co-workers[45] have used maximum entropy reconstruction (MaxEnt) processing for nonuniformly sampled data in $^1D_{C'C\alpha}$ measurements for proteins. Both approaches offer a substantial shortening of the time of NMR experiments, which is important in the case of unstable proteins.

An enhanced CPMG-HSQMBC experiment has been presented by Köver and co-workers.[46] The method allows accurate measurement of long-range heteronuclear couplings. Merlet and co-workers[47] have demonstrated the $^{13}$C-*J*-resolved-BIRD and *J*-HSQC-BIRD experiments that make possible the visualization of enantiomers dissolved in chiral ordering solvent on the basis of the $^1D_{HC}$ couplings.

A program for simulation of splittings in the one-dimensional $^1$H NMR spectra has been designed by Constantino *et al.*[48]

## 3. One-bond couplings to hydrogen

Perera and Bartlett[49] have proposed a bond-parity model that predetermines signs of the Fermi-contact contributions to the NMR couplings and demonstrated its validity by numerical calculations which have been performed for $H_4$ and $CO_2$.

Partially deuterated samples of complexes $[(C_5Me_5)Os(H_2)H_2(L)][BHF_4]$, where L is $PPh_3$, $AsPh_3$ or $PCy_3$, have been prepared by Gross and Girolami[50] and H–H distances within the bound $H_2$ ligands have been deduced from the observed $^1J_{HD}$(av) couplings. A substantial $J_{HD}$ of 22.0 Hz has been measured by Dutta and Jagirdar[51] for the HD isotopomer of the $[Ru(\eta^2\text{-}H\cdots H)(PP)_2]$–$[OTf]_2$ complex, PP = $[(C_6H_5CH_2)_2PCH_2CH_2P(CH_2C_6H_5)_2]$, which corresponds to the H–H bond distance of 1.05 Å and corresponds to an elongated dihydrogen ligand.

The complex $OsCl(NH{=}C(Ph)C_6H_4)(P\text{-}i\text{-}Pr_3)_2(H_2)$ has been recently studied by Barea *et al.*[52] who assigned to it an elongated dihydrogen structure on the basis of $J_{HD}$ = 6.3 Hz observed in its $d_1$- isotopomer. However, the new low-temperature NMR results obtained by Schloerer *et al.*[53] provide evidence that rather quantum mechanical exchange takes place in this compound. Mixtures of deuterium labelled complexes $(p\text{-XPOCOP})IrH_{2-X}D_X$ where POCOP denotes $C_6H_2$-1,3-$[OP(t\text{-}Bu)_2]_2$ and X = MeO, Me, H, F, $C_6H_5$, 3,5-$(CF_3)_2$–$C_6H_3$, have been studied by Göttker-Schnetmann *et al.*[54] $J_{HD}$ of 3.8–9.0 Hz observed in the spectra of these compounds measured in toluene and pentane between 296 and 213 K suggest the presence of an elongated $H_2$ ligand.

The detection of one-bond hydrogen–boron coupling, $^1J_{HB}$ = 154 Hz, provided evidence of the existence of a nucleophilic, anionic organoboryl species synthesized recently by Segawa *et al.*[55]

The correct choice of exchange-correlation functional for computing NMR indirect spin–spin couplings has been the subject of studies conducted by Keal *et al.*;[56] modifications of standard basis sets for use in spin–spin coupling calculations have been analysed by Deng *et al.*[57]

Nuclear magnetic shielding and indirect spin–spin couplings including $^1J_{HC}$ in gaseous and liquid cyclopropane have been measured by Makulski and Wilczek.[58]

The $^1J_{HC}$ couplings in conformationally constrained sulfoxides, bissulfoxides, sulfoxide-sulfones and sulfilimines derived from 2-benzylidene-1,3-dithiane and 2-(2,2-dimethylpropylidene)-1,3-dithiolane have been measured by Wedel *et al.*;[59] the Perlin effects have been also calculated. It has been found that the relative configuration of S=X groups (X = O, Ntos) in these compounds exerts a strong influence on the magnitude of couplings for axial and equatorial C–H bonds.

An unprecedented large reverse Perlin effect ($^1J_{HaxC} > {}^1J_{HeqC}$) for all three methylene groups has been observed experimentally and calculated theoretically by Shainyan *et al.*[60] in 1-(methylsulfonyl)-3,5-bis(trifluoromethylsulfonyl)-1,3,5-

triazinane and interpreted in terms of the presence at the α-position of the nitrogen atom bearing a very strong electron-withdrawing group $CF_3SO_2$, which makes it almost positively charged.

The magnitudes of one-bond $^1J_{HC}$ and long-range ones ($^nJ_{HC}$, $n > 1$) have been applied by Katritzky *et al.*[61] for unambiguous differentiation between regioisomers of nitro-substituted five-membered heterocycles.

The increase of $^1J_{HC}$ occurring in $[Ti(N\text{-}t\text{-}Bu)(Me_3[9]aneN_3)Me]^+$ upon formation from $Ti(N\text{-}t\text{-}Bu)(Me_3[9]aneN_3)Me_2$, $Me_3[9]aneN_3$ = 1,4,7-trimethyltriazacyclononane, has been interpreted by Bolton *et al.*[62] in terms of intrinsic global changes in carbon 2s orbital contribution to the Ti–C and C–H bonds upon cation formation; 116 Hz has been observed for the cation and 111 Hz for its methyl precursor.

Theoretical and experimental studies on the molecular and electronic structures of cytosine and unsaturated keto-sparteines[63] as well as matrine-type alkaloids[64] have been performed by Galasso and co-workers. It has been found for both groups of compounds that hyperconjugative stereoelectronic effects on $\Delta\delta(H_{eq}/H_{ax})$ and $\Delta(^1J_{HCeq}/^1J_{HCax})$ of the >N–CO– groups are correctly accounted for by the DFT results.

The plane wave periodic DFT calculations of models of the Re based olefin metathesis catalyst, [(≡SiO)Re(≡C-*t*-Bu)(=CH-*t*-Bu)($CH_2$-*t*-Bu)] have been performed by Solans-Monfort *et al.*[65] The calculated low $^1J_{HC}$ (111 Hz) couplings for the key alkylidene group well reproduce those observed experimentally (109 Hz) for the *syn* isomers and are in agreement with agostic interactions suggested by other parameters. The $^1J_{HC}$ coupling in the *anti* isomer, where such interaction does not occur, is much higher (159 Hz).

A comparison of the analytical data of (≡SiO)Hf($CH_2$-*t*-Bu)$_3$-$SiO_2$ and (≡SiO)Zr($CH_2$-*t*-Bu)$_3$ complexes, which also included $^1J_{HC\alpha}$ couplings, has been made by Tosin *et al.*[66] during their studies on reactivity of tetraneopentylhafnium, Hf($CH_2$-*t*-Bu)$_4$ with silica surfaces. A lower value of $^1J_{HC\alpha}$ coupling observed for the hafnium complex has been interpreted in terms of a larger steric hindrance in the coordination sphere of the Hf metal.

Disappearance of the $^1J_{HC}$ coupling has been used by Tanaka *et al.*[67] as evidence that a metal-free acetylide anion is formed during the deprotonation of phenylacetylene when treated by the strong non-metallic base *t*-Bu-P4.

Proton–carbon and proton–nitrogen couplings across one and more bonds have been computed by Jimeno *et al.*[68] by the use of DFT with the B3LYP functional and *ab initio* EOM-CCSD method for the ten species in the two series of $X(CH_3)_nH_{4-n}$, where the central atom X is $^{13}C$ or $^{15}N$. Overall, good agreement between the computed couplings obtained from both methods and the experimental data has been found as well as between the total EOM-CCDD couplings and the FC terms.

Proton–carbon and proton–nitrogen couplings across one and more bonds have been used by Pazderski *et al.*[69] to investigate tautomerism and protonation patterns in bis(6-purinyl) disulfide and ionic forms of 6-mercaptopurine.

Effects of methyl substitution in 4-silathiane S-oxides on the stereochemistry and $^1J_{HC}$ couplings have been studied by Shainyan *et al.*[70] Almost all compounds have shown the normal Perlin effect except for 2,4,4-trimethyl-4-silathiane-S-oxide and S,S-dioxide possessing the axial S=O group and showing the reverse Perlin effect for the 3- and 5-$CH_2$ groups.

The scalar $^1J_{HC}$ and restored dipolar H–C dipolar couplings have been applied by Chaffee *et al.*[71] to study chloroform@cryptophane-A and chloroform@bis-cryptophane inclusion complexes oriented in thermotropic liquid crystals.

Indirect spin–spin couplings including those across one C–H bonds, experimental dipolar couplings and chemical shifts have been reported for 1,3-butadiene by Celebre *et al.*[72] who analysed its conformation in a nematic phase. The authors confirmed the presence of a small but significant percentage of the *s-cis* or *s-gauche* conformer (*ca.* 1–2%) as was previously found both experimentally and theoretically for an isolated molecule.

The one-bond $^{1}H–^{14}N$ coupling of 54 Hz has been observed by Helm *et al.*[73] in the spectrum of the $[Cd([18]aneS_4N_2)](PF_6)_2$ complex ($[Cd([18]aneS_4N_2)]$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane). The coupling is absent in dry samples and is temperature dependent. This is the first example of $^{1}H–^{14}N$ coupling observed in a coordinated $[18]aneS_4N_2$ ligand.

It has been demonstrated by Afonin *et al.*[74] that the bifurcated NH···N and N–H···O intramolecular hydrogen bond is present in 2-trifluoroacetyl-5-(2′-pirydyl)-pyrrole causing an increase in the absolute size of the $^{1}J_{HN}$ coupling by about 6 Hz.

$^{1}J_{HN}$ couplings have been applied by Przybylski *et al.*[75] to study some gossypol derivatives, and by Lyčka *et al.*[76] to establish the structure of 1-(indazol-3-yl)-1,2-dihydro-benzimidazol-2-one, the product of the reduction of 2-(3-oxo-3,4-dihydro-quinoxalin-2-yl)benzene.

$^{1}J_{HN}$ coupling has been calculated by Yan *et al.*[77] for the prototypical model system [imidazole–$(H_2O)_n$–imidazole]$^{+}$, $n$ = 1–9, in order to gain insight into the factors regulating the proton transfer along hydrogen-bonded water chains.

Effects of the relativistic treatment of parity violation contributions to the spin–spin couplings of $H_2O_2$ ($^{1}J_{HO}$, $^{1}J_{OO}$, $^{2}J_{HO}$, $^{3}J_{HH}$), $H_2S_2$ ($^{1}J_{HS}$, $^{1}J_{SS}$, $^{2}J_{HS}$, $^{3}J_{HH}$) and $H_2Se_2$ ($^{1}J_{HSe}$, $^{1}J_{SeSe}$, $^{2}J_{HSe}$, $^{3}J_{HH}$) have been studied by Weijo *et al.*[78]

$^{1}J_{HSi}$ couplings in $SiH_nCl_{4-n}$ ($n$ = 0–4) dissolved in THF-$d_8$ have been recorded by Thorshaug *et al.*[79] as a function of temperature and the experimental data has been compared with the DFT calculated $J$ values.

It has been observed by Vyboishchikov and Nikonov[80] that the magnitude of $J_{HSi}$ couplings in the family of the $[Fe(Cp)(L)(SiMe_nCl_{3-n})_2H]$ (L = CO, $PMe_3$; $n$ = 0–3) complexes primarily depends on the orientation of the silyl group rather than on the number of electron-withdrawing groups at a silicon atom.

Proton–phosphorous spin–spin couplings of hypophosphorous acid complexes with proton acceptors such as nitromethane, acetonitrile, acetone or pyridine have been measured by Golubev *et al.*[81] under slow exchange conditions. The formation and strengthening of the hydrogen bond by the OH bond results in a strong shielding of the phosphorous nucleus and decrease of $^{1}J_{HP}$ coupling.

The $\eta^2$-coordination of the Si-H bond to the tungsten atom takes place upon irradiation of $W(CO)_6$ and $HSiEt_3$ in cyclohexane-$d_{12}$ solution as has been reported by Gądek and Szymańska-Buzar[82] who found $^{1}J_{HSi}$ of 89 Hz and $^{1}J_{HW}$ of 35 Hz for this complex. For comparison, $^{1}J_{HSi}$ coupling in $Et_3SiH$ is of 179 Hz. Spectroscopic data including $^{1}J_{HSi}$ couplings and crystal structure has been reported by the same group of authors[83] for the bis{($\mu$-$\eta^2$-hydridodiethylsilyl)tetracarbonylmolybdenum(I)} complex, $[\{Mo(\mu\text{-}\eta^2\text{-H-SiEt}_2)(CO)_4\}_2]$.

$^{1}J_{HP}$ couplings have been measured by Paris *et al.*[84] for a series of Ru(II) complexes, $[(p\text{-cymene})RuCl(L)_2](PF_6)$ where L = $PH_2CH_2Fc$ and $PH(CH_2Fc)_2$ (*p*-cymene = *p*-*i*-$PrC_6H_4Me$, Fc (ferrocenyl) = $C_5H_5FeC_5H_5$) and *trans*-$[RuCl_2(L_4)]$ where L = $PH_2Fc$, $PH_2CH_2Fc$ and $PH(CH_2Fc)_2$. A significant increase of the $^{1}J_{HP}$ value has been observed for ruthenium(II)-bound phosphine complexes compared with the free phosphines. The data obtained seem to be generally consistent with a suggestion that the increase in $^{1}J_{HP}$ approximately correlates with the Lewis acidity of the complexed metal ion and hence with the σ-donor strength of the phosphine.

The presence of two diastereisomeric forms has been proved by the use of the NOE effect and $^{1}J_{HSn}$ couplings in (*R*,*S*)(*S*,*R*)-[2-(4-(*R*)-isopropyl-2-oxazoline)-5-phenyl]*t*-butylphenyltin and (*R*,*S*)(*S*,*R*)-[2-(4-(*R*)-isopropyl-2-oxazoline)-5-phenyl]*t*-butylmetyltin hydrides studied by Staliński and co-workers.[85] The $^{1}J_{H119Sn}$ couplings of 1549/1908 and 1444/1770 Hz, respectively have been observed for these two compounds. The $^{1}J_{H117Sn}$ couplings are correspondingly smaller: 1480/1823 and 1380/1692 Hz.

## 4. One-bond couplings not involving hydrogen

NMR spectral data including LiB coupling has been computed by Del Bene *et al.*[86] for Li-diazaborole, $(C_2H_4B_1N_2)Li$, and its complexes with one $H_2O$ or LiF molecule. Additionally, solvent effects on this coupling have been analysed.[87]

One-bond Li–C couplings, $^1J_{LiC}$ of *ca.* 4 Hz, have been measured by Fraenkel *et al.*[88] for three internally solvated allylic lithium compounds with different potential ligands tethered at $C_2$: $CH_3OCH_2CH_2NCH_3CH_2$-; 1-TMS, $(CH_3)_2NCH_2$-$CH_2NCH_3CH_2$-; 1-TMS and $((CH_3)_2NCH_2CH_2)_2NCH_2$-; 1-TMS. The coupling pattern observed (triplet) provided evidence that all three compounds are monomers.

The $^1J_{LiN}$ couplings of 20 different tetra- (3.7 to 4.6 Hz), 25 tri- (4.5 to 5.7 Hz) and 4 dicoordinated lithium atoms (6.5 Hz) in chiral lithium amides and their mixed complexes have been measured by Granander *et al.*[89] The results clearly show that the coordination number for a given lithium nucleus in a lithium amide or its mixed complex can be obtained directly from the magnitude of the $^1J_{LiN}$ coupling.

*Ab initio* EOM-CCSD calculations have been carried out by Del Bene *et al.*[90] on iminoboranes RBNH, HBNR, and RBNR, for R = H, $CH_3$, $NH_2$, OH, and F, to evaluate substituent effects on one- and two-bond $^{11}B$–$^{15}N$, $^1H$–$^{11}B$, and $^1H$–$^{15}N$ couplings. For comparison purposes, they have also performed calculations on corresponding isoelectronic acetylene derivatives RC≡CH and RC≡CR.

Both $^{11}B$ and $^{17}O$ are quadrupole nuclei which makes the measurements of the corresponding spin–spin coupling a difficult task. Experimental $^1J_{BO}$ coupling values have been determined for the first time by Wrackmeyer and Tok[91] for trimethoxyborane (22 Hz) and tetraethyldiboroxane (18 Hz) by the measurement of $^{17}O$ NMR spectra at high temperature (120° and 160° C, respectively); the magnitudes of these couplings have been found to be in reasonable agreement with the DFT calculated data.

The $^1J_{BP}$ couplings have been measured by Dornhaus *et al.*[92] for $BH_3(H)PPh_2$, $BH_3(CH_3)PPh_2$ and $[(BH_3)PPh_2]^-$, 42, 55 and 64 Hz, respectively. Basing on these results, the authors came to the conclusion that the phosphanylborohydride ligand $[BH_3PPh_2]^-$ possesses a higher Lewis basicity towards $[BH_3]$ than its neutral isoelectronic and isostructural congener $P(CH_3)Ph_2$.

Excellent linear correlation between experimental and DFT calculated $^nJ_{CC}$ values ($n$ = 1, 2, 3), has been found by Witanowski *et al.*[93] in a series of disubstituted benzenes; the range of the couplings studied was from about −3 to +83 Hz.

DFT and CCSD calculations of the nuclear shielding and $J$(CC) spin–spin couplings in *o*-benzyne have been performed by Helgaker *et al.*[94]

Several papers on application of carbon–carbon spin–spin couplings in structural studies have been written by Krivdin and co-workers. This included elucidation of the structure of 2,3,4,6-tetra(*O*-vinyl)methyl-α-D-glucopyranoside,[95] conformational study of 2-arylazo-1-vinylpyrroles[96] and pyrrolylpyridines,[97] and configurational assignment of carbon, silicon and germanium containing propynal oximes.[98] Lone-pair orientation effect of an α-oxygen atom on $^1J_{CC}$ couplings in *o*-substituted phenols has been studied by Taurian *et al.*[99]

The full $^1H$ and $^{13}C$ NMR spectral characterization of α- and γ-1,2,5,6,9,10-hexabromocyclodecane has been reported by Arsenault *et al.*[100] Among others, one- and two-bond carbon–carbon couplings have been measured for α-diastereoisomer.

One-, two- and three-bond carbon–carbon couplings have been measured for [18,19,21,22-$^{13}C_4$]—labelled tautomycin, the compound synthesized by Isobe *et al.*[101] and used as an NMR probe of protein phosphatase inhibitor.

A method based on *ab initio* calculations and first-order perturbation theory has been developed by Woodford and Harbison[102] to include thermal averaging in calculated magnetic properties, such as chemical shielding and $J$ couplings. Using this approach chemical shielding values and $J$ couplings including those across one C–C and H–C bonds have been calculated for 1′-imidazolyl-2′-deoxy-ribofuranose, a model compound for purine nucleosides in DNA.

Experimental and DFT studies on the transmission mechanisms of $^{n}J_{HC}$ and $^{n}J_{CC}$, $n$ = 1, 3, 4, have been performed by Contreras *et al.*[103] for 1-X- and 1-X-3-methylbicyclo[1.1.1]-pentanes.

The existence of inverse relationship between $^{1}J_{CC}$ and carbon–carbon bond length was suggested by Unkefer *et al.*[104] some time ago on the basis of the data obtained for derivatives of naphthalene. It has been invoked recently by White and co-workers[105] to interpret the mechanism of the Alder-Rickert ethylene extrusion reaction in the structures of bicyclo[2.2.2]octadiene and bicyclo[2.2.2]octane derivatives. However, the authors have not noticed the recent works[106,107] in light of which Unkefer's suggestions that $^{1}J_{CC}$ is directly related to the CC bond length can be questioned.

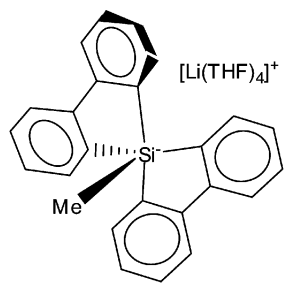
The $^{13}$C CPMAS spectra of oxybuprocaine hydrochloride, modification II° measured by Harris *et al.*[108] revealed crystallographic splittings arising from the fact that there are two molecules, with substantially different conformations, in the asymmetric unit. A 2D INADEQUATE spectrum has been used to link signals for the same independent molecule.

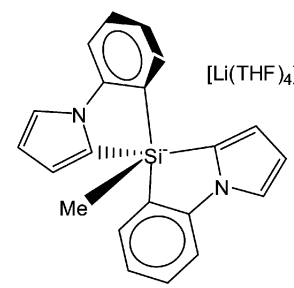
The one-bond $^{1}J_{CN}$ couplings have been reported by Schraml and co-workers[109] for the parent benzonitrile (X = H, $J$ = 17.59 Hz) and two *para* derivatives (X = 4-F, $J$ = 17.63 Hz and X = $OCH_3$, $J$ = 17.69 Hz).

$^{1}J_{CN}$, $^{2}J_{CN}$, $^{1}J_{HN}$ and $J_{HH}$ couplings measured by Sega *et al.*[110] for acetylcholine in a variety of solvents remain practically constant, which indicates that there are no solvent effects on the conformational equilibrium of this compound. The C–N couplings across one, two and three bonds have been reported by Langer *et al.*[111] for the Ni(II) complex of the Schiff base of (*S*)-*N*-(2-benzoyl-4-chlorophenyl)-1-benzylpyrrolidyne-2-carboxamide and glycine.

NMR spectra of 1,2-dibromo-1,1-difluoroethane and 1-bromo-2-iodo-tetrafluoroethane dissolved in nematic liquid crystalline solvents have been analysed by Emsley *et al.* [112] to yield the magnitudes and signs of the scalar couplings, $J$, and total anisotropic couplings, $T$, between all the $^{1}$H, $^{19}$F and $^{13}$C nuclei, except for those between $^{13}$C nuclei. This also included one- and two-bond carbon–fluorine couplings, $^{1,2}J_{CF}$. $^{n}J_{CF}$ couplings ($n$ = 1–4) have been measured by Laihia *et al.*[113] in order to characterize ten variously substituted 1,2-diaryl-(4*E*)-arylidene-2-imidazolin-5-ones. $^{1}J_{CF}$ and $^{2}J_{CF}$ couplings have been reported by Iriarte *et al.*[114] for 2-chloro-2,2-difluoroacetamide, $ClF_2CC(O)NH_2$.

Good agreement has been observed between experimental and DFT calculated $^{1}J_{CSi}$ coupling values in two exceptionally stable pentaorganosilicates studied by Couzijn *et al.*[115] (Fig. 1); the data obtained provided useful information on the electronic structure of these compounds.




| | exp. | DFT | exp. | DFT |
|---|---|---|---|---|
| $^{1}J_{CSi}$ (*ax*) [Hz] | 33.4 | 28.8 | 30 | 24.4 |
| $^{1}J_{CSi}$ (*eq*) [Hz] | 70.1 | 67.6 | 86 | 86.3 |
| $^{1}J_{CSi}$ (Me)[Hz] | 57.4 | 53.3 | 64 | 60.4 |

**Fig. 1**

The $^{13}C$ and $^{31}P$ DE (direct excitation) MAS spectra of the Pd/PDMP catalyst (PDMP = polydimethylphosphazene) have been measured by Panziera *et al.*[116] providing an interesting piece of information on the structural features of this compound. This included information on the conformation and mobility of the methyl side groups for which $^{1}J_{CP}$ coupling of 90 Hz has been determined.

Experimental NMR parameters, which included $^{1}J_{CFe}$ and $^{1}J_{NFe}$ couplings, have been reported by Wrackmeyer and Herberhold[117] for the tetrahedrane $[Fe_2(CO)_6$-($\mu$-SNH)] and compared with the DFT calculated data.

$^{1}J_{CSe}$ couplings have been measured and calculated by the DFT method at the B3LYP/6-311 + G(d,p) level of theory by Wrackmeyer *et al.*[118] for variously substituted 1-cyclohepta-2,4,6-trienyl-selanes, $Se(C_7H_7)_2$, R–Se–$C_7H_7$ with R = Bu, *t*-Bu, Ph and 4-F–$C_6H_4$, and relatively good agreement has been found between the experimental and computed data.

$^{1}J_{CPt}$, $^{2}J_{CPt}$ and $^{1}J_{PPt}$ couplings have been measured by Lind *et al.*[119] in order to characterize two Pt(II) complexes with thiophenyl and phenyl groups in the ligands, *trans*-$Pt(P(n\text{-}Bu)_3)_2(C{\equiv}C\text{–}Ar)_2$, where Ar = –$C_4H_2S$-C$\equiv$C-*p*-$C_6H_4$-*n*-$C_5H_{11}$ and –*p*-$C_6H_4$–C$\equiv$C–$C_4H_3S$, and to obtain information about the electronic coupling between Pt and the alkyne ligand.

The presence of the one-bond $^{15}N$–$^{117/119}Sn$ couplings of 112.6 and 116.3 Hz in major diastereoisomers of (*R*)-2-[(*R*,*S*)(*S*,*R*)-(2-iodo-*t*-butyl-phenylstannyl)-phenyl]-4-*iso*-propyl-4,5-dihydro-oxazole and (*R*)-2-[(*R*,*S*)(*S*,*R*)-(2-bromo-*t*-butyl-methyl-stannyl)-phenyl]-4-*iso*-propyl-4,5-dihydro-oxazole provided evidence that the Sn–N interaction takes place in these compounds.[85]

Two papers on computations of one-bond spin–spin couplings in $H_mX\text{-}YH_n$ molecules, where X = N, O, P, S, have been published by Del Bene and Elguero.[120,121]

$^{1}J_{OTc}$ coupling of 80 ± 5 Hz has been measured by Grundler *et al.*[122] for the *fac*-$[(CO)_3Tc(H_2O)_3]^+$ complex.

$^{1}J_{FP}$ coupling of −1045 ± 20 Hz has been determined by Weil *et al.*[123] for disilver(I) monofluorophosphate, $Ag_2PO_3F$, from the solid-state MAS NMR spectra, which is on the same order of magnitude as the $^{1}J_{FP}$ couplings reported earlier in the literature for other monofluorophosphates.[124]

$^{1}J_{FS}$ coupling of 242 Hz has been measured by Tervonen *et al.*[125] for gaseous $SF_6$ at 223 K and 3 atm; $^{1}J_{FS}$ about 254 Hz has been found in TLC (thermotropic liquid crystals) solution.

The non-relativistic Hartree-Fock and relativistic Dirac-Hartree-Fock calculations of $^{1}J_{FXe}$ couplings have been performed by Antušek *et al.*[126] for $XeF_n$, $n$ = 2, 4, 6. The calculations relatively well reproduced the experimental $J$ values reported for the first two compounds, whereas a dramatic discrepancy between the experiment and theory has been found for $XeF_6$; its possible causes are discussed by the authors.

The first example of quadrupolar effects from $^{127}I$ has been reported by Gerken *et al.*[127] who recorded the solid-state $^{19}F$ NMR spectrum of powdered, microcrystalline $[N(CH_3)_4][IO_2F_2]$. It showed broad lines that arise from residual dipolar coupling and result from the large quadrupole moment of the $^{127}I$ nucleus. The $^{19}F$ lineshape was simulated using $^{1}J_{FI}$ = −1000 Hz and a $^{127}I$ quadrupolar coupling of 5000 Hz as preliminary values.

A variety of 9-phospha-10-silatryptycenes and some derivatives, such as the phosphine selenides and *cis*-platinum complexes, has been synthesized by Tsuji *et al.*[128] The $^{1}J_{PSe}$ couplings have been measured for the phosphine selenides and $^{1}J_{CPt}$ couplings for the Pt complexes. The $^{1}J_{PSe}$ coupling values have been interpreted in terms of the large s-character of the lone pair orbital on the phosphorus atom.

Two new phospholanes, (3a*R*,4a*R*,7a*R*,7b*R*)-4-phenylperhydrofuro-[2′,3′:4,5]-phospholo[3,2-*b*]furan-2,6-dione and (3a*S*,4a*S*,7a*S*,7b*S*)-4-cyclohexylperhydrofuro-[2′,3′:4,5]phospholo[3,2-*b*]furan-2,6-dione have been synthesized by Bilenko *et al.*[129] and their σ-donor properties have been estimated by the use of $^{1}J_{PSe}$ in the corresponding phosphine selenides. $^{1}J_{PSe}$ couplings of *ca.* 850 Hz have been

measured by Anderson *et al.*[130] for (1-diphenylphosphanylselenido-1*H*-pyrrol-2-ylmethylene)phenylamine, (bis-(di-*iso*-propyloamino)phosphanylselenido-1*H*-pyrrol-2-ylmethylene)phenylamine and their derivatives and used to estimate the donor characteristics/basicity of the corresponding P–N chelating *N*-pyrrolylphosphino-*N*-arylaldimine ligands.

The $^{1}J_{PSe}$ couplings of a series of trisarylphosphine selenides derivatised with a variety of different perfluoroalkyl groups have been measured by Adams *et al.*,[131] which allowed the authors the direct comparison between phosphine ligands that is not possible *via* other spectroscopic methods. A linear correlation has been observed between $^{1}J_{PSe}$ and $^{1}J_{PPt}$ for both the *cis* and *trans*-$[PtCl_2L_2]$ complexes.

The $^{1}J_{PSe}$ couplings have been used by Hrib *et al.*[132] to characterize two complexes of bidendate phosphane selenide ligands with mesitylenetellurenyl iodide, $dppmSe_2[Te(I)Mes]_2$ and $dppeSe_2[Te(I)Mes]_2$; $^{1}J_{PSe}$ of 717.7 and 711.6 Hz have been found, respectively.

A reaction of $RuCl_2(PPh_3)_3$ with LiNN′, where NN′ = 2-[(2,6-diisopropylphenyl)imino]pyrrolide, yielded an α-pyrrolato complex, $[RuCl(\kappa^2\text{-}N,N'\text{-}ArN{=}CHC_4H_3N)(PPh_3)_2]_2$.[133] Its structure shown in Fig. 2 has been established by Foucault *et al.*[133] by the use of extensive NMR studies. $^{31}$P CP MAS NMR experiments yielded the largest $^{1}J_{PRu}$ coupling = 244 ± 20 Hz measured so far.

An inverse relationship between the $^{1}J_{PRh}$ coupling and the electronic parameter ($\chi$) of the phosphine has been observed by Tiburcio *et al.*[134] in the mononuclear complexes with the isosteric phosphines, $[RhCl(\eta^4\text{-COD})(PR_3)]$, where COD = 1,5-cyclooctadiene, R = 4-$(OCH_3)C_6H_4$, 4-$(CH_3)C_6H_4$, $C_6H_5$, 4-$FC_6H_4$, 4-$(CF_3)C_6H_4$ and 4-$ClC_6H_4$.

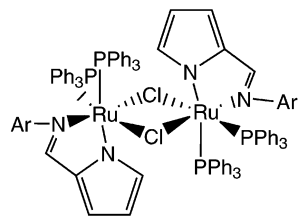
$^{1}J_{PPt}$ couplings have been used by Gallego *et al.*[135] to characterize the triphenylphosphine derivatives of the [Pt(II)Br(*C*$C_5H_4C_6H_4CH$*N*BzI)$(SMe_2)$] complex which contains a seven-membered cyclometalated ring.

An experimental and relativistic DFT investigation of one-bond spin–spin coupling, $^{1}J_{ClX}$, where X = C, Si, Sn and Pb, has been performed by Willans *et al.*;[136] it represents the first of this type study of spin–spin coupling involving spin-pairs containing quadrupolar nuclei.

A spin–spin coupling between chlorine and selenium, $^{1}J_{ClSe}$ = 110 Hz, has been measured by Demko *et al.*[137] for $Ph_2SeCl_2$ by the use of CP MAS spectra. This seems to be the first reported coupling between these nuclei.

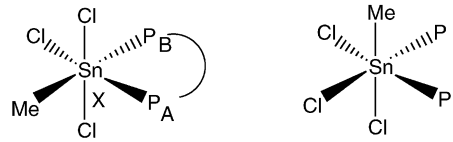
The hexacoordinated organotin(IV) complexes $[RSnCl_3(cis\text{-}Ph_2PCH{=}CHPPh_2)]$ (R = Me, *n*-Bu, Ph) synthesized by Ebrahim *et al.*[138] can adopt two configurations (I or II, see Fig. 3) but only in configuration I do the Sn and two P atoms represent an ABX type spectrum. An analysis of the low-temperature $^{31}$P NMR spectra of these compounds yielded two different $^{1}J_{PSn}$ couplings (for example 2419 and 1283 Hz for R = Me), which is consistent with structure I.

Very large $^{1}J_{PPt}$ couplings between 4689 and 5233 Hz have been found by Keglevich *et al.*[139] for a series of novel bis(dibenzo[c.e][1,2]oxaphosphorino)dichloroplatinum complexes, which confirmed the *cis* arrangement of the P-ligands




$^{1}J_{PRu}$ = 244 ± 20 Hz

**Fig. 2**




**I** **II**

$^{2}J_{P(A)P(B)}$ = 307 Hz
$^{1}J_{P(A)Sn}$ = 2419 Hz
$^{1}J_{P(B)Sn}$ = 1283 Hz

**Fig. 3**



(or that of the chloro atoms). For the *trans* isomers $^{1}J_{PPt}$ couplings of *ca.* 3000 Hz are expected.

$^{1}J_{PPt}$ couplings, which have been determined by Bortoluzzi *et al.*[140] for a series of square-planar bis(diphenylphosphinoethyl)phenylphosphine complexes of Pt(II) with pyridines and anilines, [Pt(L)(triphos)](ClO$_4$), revealed dependence upon the p*K*a of L (L are 4-substituted pyridines or anilines).

$^{1}J_{SePt}$ and $^{1}J_{TePt}$ couplings have been determined by Risto *et al.*[141] for a series of mononuclear arylchalcogenaloto-platinum(II) complexes: [Pt(MAr)$_2$(dppe)] where M = Se, Te; Ar = phenyl, 2-thienyl; dppe = 1,2-bis(diphenylphosphino)ethane. The couplings helped the authors to establish the structures of the studied compounds, in particular the information that the $^{1}J_{SePt}$ couplings of the *cis* isomers are larger than those of the *trans* isomers was important.

## 5. Two-bond couplings to hydrogen

An extensive study of the conformational/structural dependencies of the geminal proton–proton coupling, $^{2}J_{HH'}$, in substituted methanes has been presented by Barfield.[142]

The temperature dependence of two-bond couplings between protons of the methyl group has been observed by Czerski and Szymański[143] in 1,4-dibromo-9-methyltryptycene and invoked as a new argument that the DQR effect occurs in substituted 9-methyltryptycenes (DQR = damped quantum rotation; for the theory of this phenomenon see refs. 144–146).

A $^{2}J_{HH}$ coupling of 13.8 Hz, typical of geminal coupling of diastereotopic protons, has been observed by Hahn *et al.*[147] in the room-temperature spectra of three pincer-type complexes: [2,6-bis(*N*-alkyl-methylenebenzimidazolin-2-ylidene)phenylene]bromopalladium (alkyl = Et, *n*-Pr, *n*-Bu). The diastereotopic behaviour of the benzylic protons in these compounds differs significantly from the behaviour of the protons for the methylene bridges in the analogous complexes with lutidine-bridged bis-(benzimidazolin-2-ylidene) ligands studied earlier by the same group of authors[148] where the resonances for the methylene protons appear as broad singlets at room temperature.

Liu and co-workers[40] have measured $^{2}J_{HC'}$ couplings for *trans* and *cis* protons in amide groups of the side chains in proteins. The values found range from +2.5 to +5.0 Hz and −5.0 to −2.5 Hz; respectively.

The presence of all four optically isomeric conformers in hexamethylene triperoxide diamine has been detected by Harbison and co-workers.[149] The isomers, which coexist at slow equilibrium on the NMR timescale at room temperature, have been characterized by the use of $^{1}$H NMR including geminal proton–proton couplings.

Complete NMR analyses with full assignments of $^{1}$H and $^{13}$NMR data have been performed by Dillner and Traficante[150] for both epimers of menthane-1-carboxylic acid. This also included two- and three-bond proton–proton couplings.

An analysis of $^{2,3}J_{HH}$ couplings has been carried out by Krawczyk *et al.*[151] for five derivatives of creatinine yielding information on the conformation of these compounds in solution, by Krivoshey *et al.*[152] who studied the structure of (*Z*)-(5*R*)-methyl-2-(4-phenylbenzylidene)cyclohexanone as chiral component of liquid-crystalline systems and by Goodall *et al.*[153,154] who investigated a variety of derivatives of 3-azabicyclo[3.3.1]nonane including eight new 3-azabicyclo[3.3.1]nonanes with *N*-(3-phenylpropyl) substitution.

Tormena *et al.*[155] who studied the stereoelectronic behaviour of $^{2}J_{HH}$ in heterocyclohexanes containing either oxygen or sulfur came to the conclusion that these couplings can be applied instead of $^{2}J_{HC}$'s for structure elucidation of these compounds. $^{2}J_{HH}$'s have been found to be sensitive to the occupancy of the $\sigma_{CH}$* antibonding orbital and, as the authors indicate, are much easier to measure at low temperatures than the corresponding $^{2}J_{HC}$ couplings.

The method for assigning the configuration in natural products based on $^{2,3}J_{HC}$ and $^{3}J_{HH}$ couplings was proposed by Murata and co-workers[156] several years ago. It has been recently applied by Hassfeld *et al.*[157] for determination of the stereostructure of the structurally unique 24-membered myxobacterial macrolides, archazolid A and B, highly potent vacuolar-type ATPase inhibitors, by Oh *et al.*[158] in their studies on the new cyclic depsipetides emericellamides A and B from the marine-derived fungus *Emericella* sp., by Iranshahi *et al.*[159] to establish the configuration of stereocentres in a phenylpropanoid derivative, 2-epihelmanticine isolated from *Ferula szowitsiana,* and by Park *et al.*[160] who analysed the relative and absolute structure of versipelostatin, a down-regulator of molecular chaperone GRP78 expression.

The same approach has been applied by Matveeva *et al.*[161] to establish the structures of the benzylidene dichlorides and α-chlorocinnamic derivatives, the products of the reaction of aromatic aldehydes with triphenylphospine and ethyl trichloroacetate or trichloroacetonitrile, correspondingly.

Although *J*-based configuration analysis has been shown to be a powerful tool in solving stereochemical problems in acyclic structures, there are some cases when it does not give a clear solution. Such an example has been presented by Sharman[162] who studied a small molecule related to reboxetine by the use of this approach. However, the study was complicated by the fact that the molecule exists in the form of several conformers and only a quantitative fitting procedure in which the couplings and NOEs from all possible conformers were used allowed a clear indication of the stereochemistry of the compound studied.

$^{2}J_{HP}$ and $^{2}J_{PP}$ couplings have been applied by Kuznetsov *et al.*[163] to establish the structures of four isomers of $RuHCl[2,6\text{-}(CH_2P\text{-}(t\text{-}Bu)_2)_2C_6H_8]$ obtained upon heating of the starting $RuH_2Cl[2,6\text{-}(CH_2P\text{-}(t\text{-}Bu)_2)_2C_6H_9]$ complex.

$^{2}J_{HSn}$ coupling of 87 ± 3 Hz has been measured by Bagno *et al.*[164] for the D-ribonic acid-dimethyltin(IV) complex and used in the Lockhart-Manders equation[165] to obtain the value of *ca.* 141° for the C–Sn–C angle, which suggests a skewed octahedral geometry around tin.

$^{2}J_{HSn}$ of 83 Hz and $^{1}J_{CSn}$ of 675 Hz observed by Bertazzi *et al.*[166] in the $Me_2Sn$(IV)NANA complex correspond to a C–Sn–C angle of *ca.* 135° (NANA = *β*-*N*-acetyl-neuraminic acid = 5-amino-3,5-dideoxy-D-glycero-*β*-D-galactononulosic acid).

Two-bond H–$^{119}$Sn and H–$^{117}$Sn couplings of *ca.* 110 and 40 Hz, respectively have been measured by Gholivand *et al.*[167] for four novel organotin(IV) complexes of the formula $SnCl_2(CH_3)_2(X)_2$ where X = $C_6H_5C(O)NHP(O)(NC_4H_8)_2$, $C_6H_5C(O)NHP(O)(NC_5H_{10})_2$, $C_6H_5C(O)NHP(O)[N(CH_3)(C_6H_{11})]_2$ and $C_6H_5C(O)NHP(O)[NHC(CH_3)_3]_2$. However, the $^{2}J_{HSn}$ and $^{1}J_{CSn}$ coupling values reported in this paper are obviously erroneous; the ratio $J_{H119Sn}/J_{H117Sn}$ is far from 0.9558, which corresponds to the ratio of the gyromagnetic coefficients of $^{119}$Sn and $^{117}$Sn isotopes. The same applies to $J_{CSn}$ couplings.

## 6. Two-bond couplings not involving hydrogen

Values of the $^2J_{CN}$ and $^1J_{CN}$ couplings have been used by Schwalbe and co-workers[168] as the criteria for the identification of a protein in the random coil state.

$^2J_{CN}$ couplings have been applied by Šimůnek *et al.*[169] to establish the regiochemistry of some azo coupled cyclic β-enaminones formed by the reaction of 3-phenylamino-1*H*-inden-1-one with 4-methylbenzene- or benzenediazonium tetrafluoroborates. The compounds studied exist in solution as a mixture of three forms.

Two- and three-bond carbon-phosphorus couplings have been measured by Stockland *et al.*[170] for a large series of gold complexes of ethynyl-17β-hydroxyandros-4-en-3-one and related ethynyl steroids, $R_3P$–Au–steroid; correlations between common measures of phosphine donor ability and these couplings have been made.

Two- and three-bond proton–phosphorus and carbon–phosphorus couplings have been extensively applied by Gholivand and co-workers to establish the structures of some new phosporamidates,[171,172] several new phosphoramidates and the corresponding cyclophosphazanes,[173] novel carbacylamidophosphate derivatives,[174] novel phosphorictriamide derivatives with morpholine,[175] and several new 1,3,2-diazaphosphorinanes.[176] A dependency of these couplings on the ring size, hybridisation and substituents in new diazaphospholes and diazaphosphorinanes has also been studied by this group of authors.[177]

For the first time the $^2J_{NN}$ coupling of 2.4 Hz across $Hg^{II}$ has been reported by Ono and co-workers,[178] confirming the chemical structure of T–$Hg^{II}$–T pairs in a DNA duplex.

Two-bond Si–Si couplings have been determined for a large series of oligosiloxanes by Kurfürst and Schraml.[179] The couplings are small (0–5 Hz) and their values depend on the branching or on the number of electronegative substituents on the Si–O–Si moiety.

It has been shown by Emsley and co-workers[180] that incorporating a *z*-filter results in an efficient method for measuring pure *J*-coupling modulations between selected pairs of nuclei in an isotopically enriched spin system. In a combination with a selective double-quantum (DQ) filter it allows the measurement of $^2J_{SiOSi}$ couplings in isotopically enriched solids as has been demonstrated by the use of a 50% $^{29}Si$ enriched sample of surfactant-templated layered silicate lacking long-range 3D crystallinity. *J* coupling values of *ca.* 15 Hz have been obtained and their accuracy was sufficient enough to distinguish between different $^{29}Si$–O–$^{29}Si$ pairs, shedding insight on the local structure of the silicate framework.

It has been shown by Coelho *et al.*[181] that the Si–P MAS-*J*-INEPT experiment can be a useful tool in investigation of silicophosphate compounds. An analysis of the 1D Si–P MAS-*J*-INEPT build-up curves allowed the determination of the $^2J_{\mathbf{SiNP}}$ couplings in the crystalline $Si_5O(PO_4)_6$; the couplings have been found to be strongly dependent on the crystallographic path.

$^2J_{\mathbf{SiNP}}$ coupling across the N → Si dative bond of the range 5.1 through 14.0 Hz has been measured by Sivaramakrishna *et al.*[182] for a series of novel hypercoordinate silicon bis-chelate complexes with the phosphinimino-*N* ligand group. Their magnitudes increase with the increasing electron withdrawal by the monodendate ligands reflecting the increase in the strength of coordination.

The existence of *J* coupling distributions and their effects on the measurement of average *J* coupling values have been analysed and discussed by Emsley and co-workers.[183] Using a *z*-filtered spin-echo experiment they have demonstrated the existence of a pair-specific distribution of $^2J_{\mathbf{PNP}}$ couplings in a slightly disordered bis-phosphino amine sample.

Two-bond phosporus–phosphorus couplings have been measured by Bilge *et al.*[184] for a large series of novel spiro–ansa–spiro–, spiro–bino–spiro–, spiro-phosphazene derivatives, obtained *via* the condensation reaction of $N_2O_x$ ($x$ = 2, 3) donor-type aminopodand and dibenzo–diaza–crown ethers with hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$.

The first example of a two-bond P–Tl coupling and the first example of a P–Tl coupling in the solid state has been reported by Gave *et al.*[185] who observed them in the CP MAS spectra of $TlBiP_2S_7$ and $Tl_4Bi_2(PS_4)_2(P_2S_6)$; the coupling values varied from 481 to 1390 Hz.

Rarely observed two-bond Se–Se couplings through a transition atom metal have been measured by Hayes and co-workers[186] in the clusters $[Re_5OsSe_8(CN)_6]^{3-}$ and $[Re_4Os_2Se_8(CN)_6]^{2-}$ at natural abundance of $^{77}Se$ isotope.

## 7. Three-bond hydrogen–hydrogen couplings

Van Gunsteren and co-workers[187] have used $^3J_{HH}$ couplings as time-dependent restraints in molecular simulations in order to generate a conformational ensemble of molecules. Weinstock *et al.*[188] have applied $^3J_{HH}$ scalar couplings together with other NMR parameters to identify simulated ensembles of the GB1 peptide that best match the experimental data. Examples of peptides and proteins for which couplings have been used as structural parameters are given in Table 1.

The presence of the β-structures has been shown in urea-denaturated ubiquitin with the aid of $^3J_{HH}$ couplings: Avbelj and Grdadolnik[209] have proven the presence of the fluctuating β-strands and Grzesiek and co-workers[210] have observed β-hairpin. In the latter case the analysis of $D_{HH}$ couplings was also of importance. An analysis of $^3J_{HH}$ couplings allowed Forman-Kay and co-workers[211] to suggest that the drkN SH3 domain exists in the unfolded state as a compact ensemble with native-like and non-native structures.

**Table 1** Peptides and proteins for which the solution structure has been calculated with $^3J_{HH}$

| Name | [a] | [b] | Ref. |
|---|---|---|---|
| Proline zwitterion | 1 | 10 | 189 |
| H–(AAKA)–OH | 4 | 3 | 190 |
| Uperolein, amphibian tachykinin | 11 | 8 | 191 |
| A peptide from a respiratory syncitial vitrus fusion protein | 13 | 9 | 192 |
| GB1 peptide | 16 | 14 | 188 |
| [N] NWr6, NOWA cysteine-rich domain (647–671) | 25 | 14 | 193 |
| [N] Nwr1, NOWA cysteine rich domain repeat 1 (466–492) | 27 | 15 | 193 |
| [N] NWr8, NOWA cysteine-rich domain (720–747) | 28 | 19 | 193 |
| Magi 5, a spider *Macrothele gigas* toxin | 29 | 26 | 194 |
| [N] phospho-T30-ItchWW3 | 34 | —[c] | 195 |
| [N]ItchWW3 (399–432) complexed with PY peptide (54–62) | 34 + 9 | —[c] | 195 |
| [C/N] C-terminal SH3 domain of c-Crk-II | 58 | 49 | 196 |
| [C/N] PF1455 from *Pyrococcus furiosus* | 75 | 47 | 197 |
| [C/N]Parkin IBR (307–384) zinc loaded | 78 | 26 | 198 |
| [C/N] FecA TonB | 80 | 37 | 199 |
| [C/N] PupA TonB | 82 | 43 | 199 |
| [C/N] KIV8 module of apolipoprotein(a) | 85 | 43 | 200 |
| [C/N] Nrho, N-terminal domain of *P. aeruginosa* rhomboid | 87 | 48 | 201 |
| [C/N] pMSP, β-microseminoprotein | 91 | 59 | 202 |
| [C/N] domain III of *Langat flavivirus* E protein | 96 | 67 | 203 |
| [C/N] KSRP KH3 domain (317–418) | 102 | 27 | 204 |
| [C/N] KSRP KH4 domain (423–525) | 103 | 47 | 204 |
| [N] N-DCX (45–150) (refinement) | 106 | 93 | 205 |
| [D/N] [C/N] talin F3 domain (305–405) complexed with a chimeric β3 integrin-PIP kinase peptide (717–749) | 101 + 33 | 11 | 206 |
| [C/N] Mlc1p N-lobe (2–79) | 149 | 63 | 207 |
| [N] FADD (1–191) | 191 | 120 | 208 |

[a] The number of amino acid residues. [b] The total number of vicinal backbone and side chain proton–proton couplings measured. [c] Number not specified.

$^3J_{HH}$ couplings have been extensively used by Corzana *et al.*[212] to study the effect of β-D-O-glucosylation on L-serine and L-threonine diamides and by Gudasheva *et al.*[213] to perform a conformational analysis of retropeptide analogues of 4-cholecystokinin.

Relationship between structure and $^3J_{HH}$ couplings in glycosoaminoglycans has been studied by Hricovíni and Bizik,[214] and a conformational analysis of 5-thio-pyranose monosaccharides by the use of computed NMR chemical shifts and $^3J_{HH}$ couplings has been performed by Aguirre-Valderrama and Dobado.[215] Further examples include conformational analyses of galactose-derived bicyclic scaffolds,[216] methyl 5-*O*-methyl septanosides,[217] and aldonamides derived from D-glycero-D-gulo-heptono-1,4-lactone.[218]

The stereochemistry of guaiacylglycerol-8-*O*-4′-(sinapyl alcohol) ether, an 8-*O*-4′ neolignan which consists of coniferyl and sinapyl alcohol moieties in *Eucommia ulmoides*, as well as four synthetic 8-*O*-4′ neolignans, guaiacylglycerol-8-*O*-4′-(sinapyl alcohol) ether, syringylglycerol-8-*O*-4′(coniferyl alcohol) ether, guaiacylglycerol-8-*O*-4′(coniferyl alcohol) ether and syringylglycerol-8-*O*-4′-(sinapyl alcohol) ether have been investigated by Lourith *et al.*[219] by the use of $^1$H NMR spectroscopy. All of the *erythro*-acetonide derivatives of these compounds have larger couplings (*ca.* 9 Hz) for the C7–H bonds than those of the *threo* ones (1.5–2.0 Hz).

Table 2 lists the examples of carbohydrates and nucleic acids whose structures have been found with the aid of $^3J_{HH}$ couplings.

It has been shown by Seike *et al.*[226] that it is possible to assemble $^3J_{HH}$ profiles from NMR data collected on relevant, but not necessarily specific, NMR database compounds representing a given stereocluster. They have created the $^3J_{HH}$ profile for the contiguous tetraol peracetate cluster and showed the reliability and applicability for the peracetates derived from two heptoses.

Vicinal H–H couplings have been also extensively applied to establish the structures of a variety of natural terpenoids such as: a new 2(3 → 20)*abeo*taxane[227] with an unusual 13*β*-substitution pattern and a new 6/8/-ring taxane isolated from the needles of *Taxus cuspidata*, three cucurbitane triterpenoids from *Momordica charantia*,[228] five eremophilanolides from *Psacalium paucicapitatum*,[229] a new eremophilanolide from *Senecio sinuatus* Gilib,[230] two new cucurbitane-type triterpenoids isolated from the fruits of *Cayaponia racemosa*,[231] and several clerodane diterpenoids of *Salvia splendens*.[232] Another example includes four briarane diterpenoids isolated from the gorgonian coral *Pachyclavularia violacea* whose structures have been determined by Uchio *et al.*[233] by the use of the experimental vicinal proton–proton couplings and the molecular mechanics calculations. It is worth noting that the authors did not resort to the aid of X-ray crystallographic studies and emphasised that the molecular mechanics calculation is a method of choice for the elucidation of the structure of highly flexible medium ring compounds. Proton–

**Table 2** Nucleosides, nucleotides, oligonucleotides and carbohydrates for which $^3J_{HH}$ has been used as a structural parameter

| Name | Ref. |
|---|---|
| A glyconucleoside with S-glycosidic linkage | 220 |
| The RNA hairpin with GCUA tetraloop | 221 |
| | |
| Carbohydrates | |
| β-D-furanurono-6,3-lactones | 222 |
| A series of 5-thio-pyranose monosaccharides | 215 |
| A series of glycosaminoglycans | 214 |
| *C*-glycosyl analogue of sulfatide | 223 |
| A series of hyaluronan oligosaccharides | 224 |
| [N] hyaluronan, $HA_4$ and $HA_6$ | 225 |

proton couplings have been measured by Kazmi *et al.*[234] for sorbinols A and B, new terpenes from *Sorbus cashmariana*, and by Zhou *et al.*[235] for two new triterpenoid saponins from *Ilex hainanensis* in order to assign their spectra and elucidate structures, by Macías *et al.*[236] for four saponins isolated from the *Agave brittoniana* Trel.spp. Brachypus leaves and by Santos *et al.*[237] for two new bidesmoside triterpenoid saponins isolated from *Cordia piauhiensis*. $^3J_{HH}$ couplings have been applied as crucial parameters in structure analysis of four new acyclic diterpene glycosides obtained from the fresh sweet pepper fruits of *Capsicum annuum L.* by Iorizzi and co-workers.[238]

Another group of natural products studied by the use of $^3J_{HH}$ couplings were alkaloids: a new chlorotryptamine alkaloid and its already known hallucinogenic analogues isolated from the Chinese shrub *Acacia confusa*[239] and four unusual alkaloids isolated from *Pseudoxandra cuspidata* by Roumy *et al.*[240]

The $^3J_{HH}$ couplings have been used to establish the structure of four dehydrotri- and dehydrotetraferulic acids isolated from insoluble maize bran fiber by Bunzel and co-workers[241] and the structure of new destruxins from the marine-derived fungus *Beauveria felina* by Berlinck and co-workers.[242] Sasaki and co-workers have used $^3J_{HH}$ couplings to confirm the stereochemistry of brevenal[243] which they soon revised.[244] Collison and co-workers[245] have traced with these couplings the first total synthesis of montiporyne E.

The axial or equatorial positions of the cyclohexanic protons in kallisteine A and B, two new coumarins from the roots of *Peucedanum paniculatum* L, have been assigned by Vellutini *et al.*[246] by taking into account the $^3J_{HH}$ coupling values and the NOESY correlations. It is worth noting that kallisteine B represents the first example of a furanocoumarin bearing a spiro substituent. Two novel angular-type furanocoumarin glycosides, peucedanoside A and peucedanoside B, along with a known compound apterin have been isolated from the roots of *Peucedanum praeruptorum* Dunn by Chang *et al.*[247] and their structures established by the use of vicinal proton–proton couplings. A furanocoumarin glycoside named turbinato-coumarin has been isolated by Ngameni *et al.*[248] from the twigs of *Dorstenia turbinata* and its structure established as 5-methoxy-3-[3-(β-glucopyranosyloxy)-2-hydroxy-3-methylbuthyl]psoralen by the use of an NMR method including proton–proton couplings.

Vicinal proton–proton couplings have been applied to perform a structural analysis of complex saponins from the mesocarp of *Balanites aegyptiaca* fruit,[249] to identify a new biophenolic secoiridoids with antioxidant activity from Australian olive mill waste[250] and to determine the structure and conformation of two native procyanidin trimers.[251]

$^3J_{HH}$ couplings have been measured by Bertazzi *et al.*[166] for two $R_2Sn(IV)$-*β*-*N*-acetyl-neuraminate (R = Me, Bu) complexes in $D_2O$ and DMSO-$d_6$, and their values compared with the corresponding dihedral angles for the pyranosidic ring.

Vicinal couplings $^3J_{HH}$ helped to assign the conformational arrangement of the cyclohexane ring of hexahydro-furo[3,2-*c*]benzofuran-2-one studied by Xie *et al.*[252]

A rapid method based on simple indirect determination of values and numbers of the $^3J_{HH}$ couplings involved in the pattern of the most deshielded proton signal which allows to identify and assign the diastereoisomers of 1-decalols and 2-decalols has been described by Solladié-Cavallo *et al.*[253] The compounds have been obtained by heterogeneous hydrogenation of 1-naphtol and 2-naphtol.

A conformational analysis by the use of $^3J_{HH}$ couplings has been performed by Reyes-Trejo *et al.*[254] for (-)[4.3.3]propellane obtained *via* the Wagner-Meerwein rearrangement of a [3.3.3]propellane.

$^3J_{HH}$ couplings have been reported for three monocyclic benzoannelated dilactam polyethers by Smith *et al.*[255] and for di-pentacyclo-undecane cyclic ether by Kruger *et al.*[256]

Vicinal proton–proton couplings and deuterium isotope effects on $^{13}C$ chemical shifts have been applied by Rozwadowski[257] to estimate the position of the

tautomeric equilibrium in a series of the optically active Schiff bases, derivatives of *ortho*-hydroxyaldehydes and their dirhodium adducts. Large $^{3}J_{NHH}$ coupling values of the range 11–14 Hz found for the most compounds studied indicate that they exist in the NH form. Another paper published by this author concerned an application of the $^{3}J_{HH}$ couplings to estimate the position of the proton transfer equilibrium in the tetrabutylammonium salts of Schiff bases amino acids.[258]

Structure elucidation of two novel spiro[2*H*-indol]-3(1*H*)-ones by the use of NMR including proton–proton spin–spin couplings has been performed by Košmrlj *et al.*[259] and by Matijević-Sosa[260] for 2-hydroxy-1-naphtylidene Schiff bases with chloro and hydroxyl substituted aniline moiety.

A complete $^{1}$H and $^{13}$C NMR assignment of *trans*,*trans*-2,3-divinylfuran derivatives has been performed by Škorić *et al.*;[261] the $^{3}J_{HH}$ coupling values across double bonds confirmed their *trans*,*trans* configuration.

$^{3}J_{HH}$ couplings can be also helpful in structure elucidation when NMR spectroscopy is coupled with high-performance liquid chromatography. Schefer and co-workers[262] have applied the HPLC-NMR method for separation and characterization of eight limonoids from *Switenia macrophylla*.

## 8. Three-bond couplings to hydrogen

Saielli and co-workers[263] have applied the $^{3}J_{H10B}$ and $^{3}J_{H11B}$ couplings to confirm the structure of the product in their mechanistic studies of Fries rearrangement of aryl formates.

Recently, Schmidt has published two papers[264,265] devoted to $^{3}J$ couplings that correspond to dihedral angles in peptides in proteins. In the first paper[264] incremental component couplings are proposed to account for substituent effect on each type of $^{3}J$ ($\varphi$ and $\chi_1$ related) arising from the peptide sequence. In the second paper[265] asymmetric Karplus curves have been proposed for the protein side-chain $^{3}J$ couplings. The asymmetry arises from two effects: the type of a particular substituent and its positioning, and the coupling path.

Time-average three-bond proton–carbon and proton–proton couplings DFT-calculated by Hricovíni[266] have agreed with the experimental data which led the author to the conclusion that only two chair forms contribute to the conformational equilibrium of methyl 2-*O*-sulfo-α-L-iduronate monosodium salt. The influence of the charged groups upon the magnitudes of spin–spin couplings has been also observed.

The conformational behaviour of 2-*O*- and 4-*O*-sulfated derivatives of linear (1 → 3)-linked di-, tri-, and tetrafucosides and 2,3-branched tetrafucosides has been studied by Grachev *et al.*[267] by the use of molecular modelling and *trans* glycosidic vicinal couplings $^{3}J_{HC}$. The $^{3}J_{HC}$ couplings have been applied by Borbás and co-workers[268] for determination of the anomeric configuration of a series of ketopyranosyl glycosides. The angular dependence of $^{3}J_{OH,C}$, $^{2}J_{OH,C}$ and $^{2}J_{OH,H}$ couplings have been calculated by Carlomagno and co-workers[269] using DFT to derive the Karplus-like relations essential for the accurate determination of the 2′-hydroxy group conformation in RNAs.

An analysis of the experimental and hybrid B3LYP DFT calculated $^{3}J_{HC}$ and $^{3}J_{HH}$ couplings of two epimers of antibiotic 2-hydroxymutilin has been performed by Vogt *et al.*[270] in order to obtain relative stereochemical assignments of the isomers.

A large set of three-bond proton–carbon couplings supplemented by numerous two-bond couplings has been obtained by Lacerda *et al.*[271] for eight different derivatives of cyclopentane. These $^{2,3}J_{HC}$ couplings have been shown to be useful in the determination of the relative stereochemistry of these compounds.

It has been emphasized by DiMichele *et al.*[272] that the measurements of the proton–carbon three-bond couplings have been necessary to establish the regiochemistry of the products of regioselective halogen/metal exchange reactions carried out on a series of 3-substituted-1,2-dibromoarenes.

$^3J_{HC}$ couplings have been applied by Grošelj *et al.*[273] to establish the configuration around double bonds in some *N*-substituted(1*R*,4*S*)-3-aminomethylidene-1,7,7-trimethylbicyclo[2.2.1]-heptan-2-ones, by Senior *et al.*[274] to obtain unambiguous structural characterization of hydantoin reaction products and by Sanz *et al.*[275] to prove the structure of 3-phenyl-5-(*R*)-7-trifluoromethylpyrazolo[1,5-*a*]pyrimidines. Proton–carbon couplings across one, two and three bonds have been measured by Larina *et al.*[276] for a large series of acetylation products of heterocyclic thiosemicarbazones in order to confirm their structures.

The effect of substituents on the acid assisted proton transfer in 4-[(4-*R*-phenylimino)methyl]pyridin-3-ols (R = H, $CH_3$, $OCH_3$, Br, Cl, $NO_2$) has been studied by Perona *et al.*[277] by the use of NMR and UV spectroscopies as well as by DFT calculations. Proton–carbon couplings across one and three bonds and proton–proton couplings have been reported for the compounds studied and their salts.

Three- and two-bond proton–carbon and proton–nitrogen couplings have been measured for a series of 7-substituted pyrazolo[3,4-*c*]pyridines by Kourafalos *et al.*[278] who studied the tautomerism of these compounds; for some compounds also low-temperature spectra have been recorded.

$^3J_{HN}$ couplings have been applied by Damberg and co-workers[279] to determine distribution of conformations of motilin in aqueous solution.

Coxon[280] has proposed a Karplus-like equation for $^3J_{HN}$ couplings in amino sugar derivatives: $^3J_{HCCN} = 3.1\cos^2\varphi - 0.6\cos\varphi + 0.4$. For other examples of carbohydrates and nucleic acids whose structure has been solved with heteronuclear couplings see Table 3.

$^3J_{HN}$ couplings have been measured by De Benassuti *et al.*[287] for a series of 1-(4-substituted)phenyl-3-methoxycarbonyl-5-ethoxycarbonyl-4,5-dihydropyrazoles at natural abundance of the $^{15}N$ isotope. The couplings encompass the range 5.7–6.4 Hz and are scarcely dependent on the nature of R (R = H, Me, OMe, Cl, $NO_2$).

Spectral assignments for $^1H$, $^{13}C$ and $^{15}N$ solution NMR spectra of *s*-tetrazine and dihydro-*s*-tetrazine derivatives which included proton–carbon and proton–nitrogen couplings have been reported by Palmas *et al.*[288]

The configuration of heptaene moiety has been determined by Oishi and co-workers[289] based on $^3J_{HF}$ and $^3J_{HH}$ values in the synthesis of 28-$^{19}$F-amphotericin B methyl ester.



**Table 3** Nucleosides, nucleotides, oligonucleotides and carbohydrates for which heteronuclear vicinal couplings have been used as a structural parameter

| Name | [a] | [b] | Ref. |
|---|---|---|---|
| d($TL_4T$) and d(TGLGLT) quadruplexes | 12 | $^3J_{HP}$ | 281 |
| [C/N] from helix-35 of *E.coli* 23S ribosomal RNA | 24 | $^3J_{HO-C}$ | 41 |
| $d(CGCGAATTCGCG)_2$ | 24 | $^3J_{HP}$ | 282 |
| Tel26 G-quadruplex, $K^+$ | 26 | $^3J_{HP}$ | 283 |
| The JunFos oligomer | 28 | $^3J_{HP}$ | 284 |
| 5-Fluoropyrimidine-substituted TAR RNA | 30 | $^5J_{HF}$ | 42 |
| [C/N] HJ1 RNA and HJ3 RNA | 35 | $^3J_{HP}$ | 285 |
| Carbohydrates | | | |
| α -L-Rha*p*-(1→2)-α-L-Rha*p*-OMe | | $^3J_{HC}$ | 286 |
| [N] a series of amino sugar derivatives | | $^3J_{HN}$ | 280 |
| Methyl 2-*O*-sulfo-α-L-iduronate monosodium salt | | $^3J_{HC}$ | 266 |
| A series of tetrafucosides | | $^3J_{HC}$ | 267 |

[a] The number of nucleotides. [b] Type of vicinal heteronuclear couplings measured; $^3J_{HH}$ homonuclear couplings have also been measured in most cases.

Conformational studies for a series of 2-fluoro-substituted 19β,28-epoxy-18α-oleanane triterpenoids have been performed by Tislerova *et al.*[290] by the use of vicinal proton–proton, proton–fluorine and carbon–fluorine couplings.

Vicinal H–Pt couplings have been helpful in differentiating species and assigning the metal oxidation states of a series of 2,2′-bipyridine complexes of Pt(II) and Pt(IV) studied by Nakabayashi *et al.*[291] $^{3}J_{\mathbf{CH3N,Pt}}$ of 29.8, 31.6 and 31.6 Hz have been observed for *mer*-[$PtCl_3$(2,2′-bpy)-($MeNH_2$)]Cl–$H_2O$, *trans*-[$PtCl_2$(2,2′-bpy)-($MeNH_2$)$_2$]$Cl_2$ and *trans*-[Pt(2,2′-bpy)($MeNH_2$)$_2$($OH)_2$]$Cl_2$, respectively. Analogous vicinal couplings between methyl resonances of the $MeNH_2$ ligand and Pt atom in [PtCl(2,2′-bpy)($MeNH_2$)]Cl and [PtCl(2,2′-bpy)($MeNH_2$)$_2$]$Cl_2$ were approximately 40 and 43 Hz, respectively.



## 9. Three-bond couplings not involving hydrogen

$^{3}J_{CC}$ and $^{3}J_{CN}$ scalar couplings together with RDCs have been used by Lee and co-workers to study side-chain rotamers of valines and threonines (and transmissions of structural changes) in multiple V to A mutations in protein eglin c[292] and for evaluation of energetic and dynamic coupling networks in a PDZ domain protein.[293]

For more examples of peptides and proteins for which heteronuclear couplings have been applied as structural restraints see Table 4.

The benzyl-substituted triazacycloheksane complexes of Ni(II) studied by Köhn *et al.*[298] revealed unusually broad *ortho*-C signals with apparently small vicinal C–F or H–C couplings. This phenomenon has been interpreted in terms of $T_1$ spin decoupling from much faster relaxing $^{1}H$ or $^{19}F$ nuclei in close proximity to the paramagnetic nickel centre. The authors suggest that quantitative treatment of this effect can provide improved relaxation data for the $^{13}C$ nucleus and attached to it $^{1}H$ and $^{19}F$ nuclei. It is noteworthy that this effect was already described over 30 years ago by Navon and Polak.[299]

It has been shown by Khudina *et al.*[300] that fluoroalkyl-containing 1,2,3-trione 2-arylhydrazones exist in $CDCl_3$ exclusively and in $(CD_3)_2CO$ preferentially as isomers in which the acyl or aryl group is involved in the intramolecular hydrogen bond. The structures of these compounds have been assigned, among others, on the basis of carbon–fluorine couplings across one, two, three and more bonds.

Theoretical studies on relationship between $^{2,3}J_{HC}$, $^{2,3}J_{HP}$, $^{2,3}J_{CP}$ and the backbone torsion angles of nucleic acids have been performed by Sychrovský *et al.*[301]

$^{3}J_{CP}$ and $^{3}J_{HP}$ couplings have been determined by Maghsoodlou *et al.*[302] for several phosphonato esters obtained by the reaction between triphenylphosphite and acetylenic esters in order to establish their configuration.

The relative configuration of diastereomers in electrophilic substitution of rigid 2-lithio-*N*-methylpyrrolidines has been established by Gawley and co-workes[303] with the help of $^{3}J_{CSn}$ and $^{3}J_{HH}$ couplings.

**Table 4** Peptides and proteins for which heteronuclear couplings have been used as a structural parameter in 3D structure calculations

| Name | [a] | [b] | [c] | Ref. |
|---|---|---|---|---|
| A series of alanine peptides, selectively labelled | 3 to 7 | Up to 40 | $^{3}J_{HC}$, $^{3}J_{CC}$, $^{1,2}J_{CN}$ | 294 |
| [C/N] Brk BDB-omb12T5 complex | 59 + | 30 | $^{3}J_{CC}$, $^{3}J_{CN}$ | 295 |
| [D/N] $\zeta\zeta_{TM}$ dimer | 33 × 2 | 21 | $^{3}J_{CC}$, $^{3}J_{CN}$ | 296 |
| [C/N] calbindin $D_{9K}$, $Ca_2Cb$ | 75 | 49 | $^{3}J_{CC}$ | 23 |
| [C/N] $Em^{LEM}$ (1–47) complexed with [C/N] $BAF_2$ selectively deuterated | 47 + 89 × 2 | 46 | $^{3}J_{CC}$, $^{3}J_{CN}$ | 297 |

[a] Number of residues. [b] Total number of vicinal couplings measured (homonuclear $^{3}J_{HH}$ couplings are also included if measured). [c] Types of heteronuclear couplings measured.

$^{2}J_{CSn}$ and $^{3}J_{CSn}$ couplings have been observed by Bordinhao *et al.*[304] for the olefinic carbons of 4,5-bis[(triphenyltin)thiolato]-1,3-dithiole-2-one and 4,5-bis[(triphenyltin)thiolato]-1,3-dithiole-2-thione compounds, but the authors have not been able to distinguish between these two types of couplings.

Several new papers devoted to investigation of a variety of Pt–amine complexes by the use of $^{2,3}J_{HPt}$ and $^{2,3}J_{CPt}$ couplings have been published by Rochon *et al.* This included characterization of $[Pt(amine)_4]I_2$ and *trans*-$[Pt(CH_3NH_2)_2(H_3C–N{=}C(CH_3)_2)_2]I_2$,[305] Pt(II) complexes containing amines and bidendate carboxylate ligands,[306] as well as Pt(II)–aromatic amines complexes of the types *cis*- and *trans*-$Pt(amine)_2I_2$ and $I(amine)Pt(\mu\text{-}I)_2Pt(amine)I$.[307]

An analysis of $^{3}J_{NF}$ and $^{4}J_{NF}$ couplings has allowed Kline and Cheatham unambiguous assignment of trifluoromethylpyrazole regioisomers.[308]

Vicinal couplings between ring attached fluorine atoms have been determined and analysed by Brey *et al.*[309] for a large series of variously substituted cyclopropanes. It has been found that the couplings display unusual behaviour and are not helpful in assigning the fluorine resonances.

The Si–P couplings across three and two bonds of 2.6, 4.5 and 15.0 Hz have been observed by Nakata *et al.*[310] for the hafnium-silylene phosphine complex, $(\eta\text{-}C_5H_4–Et)_2(PMe_3)Hf{=}Si(SiMe\text{-}t\text{-}Bu_2)_2$ and have been assigned by the authors to two *t*-$Bu_2MeSi$ groups and the silylene signal.

## 10. Couplings over more than three bonds and through space

It has been shown by Katrizky *et al.*[311] that the values of $^{n}J_{HH}$ ($n = 3, 4, 5$) and $^{n}J_{HC}$ ($n = 1, 2, 3, 4$) couplings can be correctly predicted using the larger 6-31 + G(d,p) and 6-311 + + G(d,p) basis sets at the B3LYP/6-31 + G(d,p) and B3LYP/6-311 + + G(d,p) levels of theory. The calculations have been performed for a large number of derivatives of five-membered aromatic heterocycles and the theoretical results have been compared with the experimental data.

Proton–proton couplings across three- and four bonds have been measured by Barros and Silva for 26 new aminoflavones.[312]

A paper devoted to the orientation of molecules by magnetic field as a new source of information on their structures has been published by Chertkov and co-workers [313] who measured and analysed a series of high resolution $^{1}H$ NMR spectra of 1,2,3-trichloronaphtalene on spectrometers operating at frequencies 200, 400, 500 and 600 MHz. This allowed them to determine with a high accuracy all possible proton–proton couplings in this molecule including that across six bonds.

The long-range couplings, $^{5,6}J_{HF}$ and the chemical shifts of trifluoromethyl groups in the $^{19}F$ NMR spectra have been used by Khudina *et al.*[314] for the determination of regio-isomeric structures of mono(trifluoromethyl)-substituted pyrazoles.

Long-range H–F couplings across two, four and seven bonds have been used by Prekupec *et al.*[315] to confirm the chemical structure of a series of novel C-6 fluorinated acyclic side chain pyrimidine derivatives.

It has been demonstrated by Chan *et al.*[316] that the proton–fluorine and carbon–fluorine couplings, $^{1h}J_{HF}$ of *ca.* 3 Hz and $^{2h}J_{CF}$ of *ca.* 6, observed in a series of group 4 postmetallocene catalysts, supported by fluorine-functionalized tridendate ligands with the fluorine substituent close to the metal centre (Fig. 4), occur through space rather than through bond or by M–F coordination.

Through-space $J_{HTl}$ and $J_{TlTl}$ couplings in the model $Tl_2(C_6H_6)^{2+}$ system have been calculated by Bagno and Saielli.[12] The computed data reasonably well reproduced the experimental data reported by Howarth *et al.*[317] for the dithallium(I) cryptate.

A series of substituted 3-phenoxy-3-perfluoroalkylprop-2-enals has been synthesized by El Kharrat *et al.*[318] and $^{4}J_{CF}$ coupling has been found to be a crucial parameter in determination of their configuration and conformation in solution.

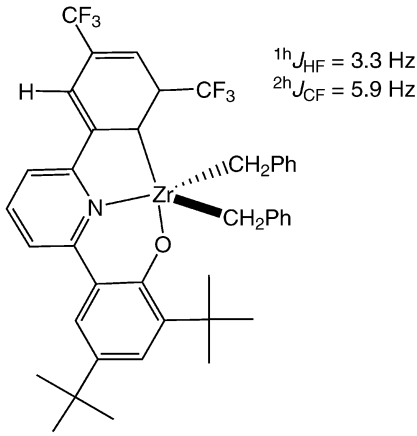



**Fig. 4**

A large set of $^{n}J_{CSi}$ couplings ($n$ = 2, 3, 4, 5) over Si–O–$C_{arom}$ link has been measured and calculated by Schraml and co-workers[319] in *para* substituted silylated phenols, $XC_6H_4$–O–$SiR^1R^2R^3$ where X = $NO_2$, $CF_3$, Cl, F, H, $CH_3$, $CH_3O$. The low sensitivity of these couplings to substitution both on the silicon atom and the benzene ring has been observed.

A through-space P–P coupling, $J_{PP}$ = 8 Hz has been observed by Kuhn *et al.*[320] in the large, unsymmetrical diphosphine 5,11,17,23-tetra-*t*-butyl-25,26-bis(diphenylphosphinomethoxy)-27(or 28)-benzyloxy-28(or 27)-hydroxycalix[4]arene in which the phosphorus atoms are separated by ten bonds.

Another example of a phosphorus–phosphorus coupling which at least in part occurs across through space has been reported by Hatnean *et al.*[321] who observed $J_{PP}$ of *ca.* 15 Hz across formally six bonds in three complexes: $[P(CH_2NPh)_3]_2Mg_3(THF)_3 \cdot 1.5THF$, $[P(CH_2N\text{-}3,5\text{-}(CF_3)_2C_6H_3)_3]_2Mg_3(THF)_3$ and $[P(CH_2N\text{-}3,5\text{-}Me_2C_6H_3)_3]_2Mg_3(THF)_3$.

## 11. Couplings through hydrogen bonds

The $^{4h}J_{HH}$ couplings through C–H···O hydrogen bonds in the C–H···O–C–H moieties have been investigated in three lariat ethers and their alkali-metal ionic complexes by Ding *et al.*[322]

OH···OH hydrogen mediated scalar couplings in *syn*- and *anti*-1,3-diols are usually too small to be observed directly as splittings in 1D NMR spectra. However, it has been recently shown by Loening *et al.*[323] that the cross-peaks due to these couplings can be readily observed in a 2D COSY experiment modified with a refocusing delay (COSYLR). Using this method the authors have measured $J_{OH\cdots OH}$ couplings for a series of *anti* and *syn*-polyacetate and polypropionate derivatives which covered a range of 0.16 through 0.42 Hz with the accuracy ±0.02 Hz.

The first example of a O–H···N hydrogen bond, $^{1h}J_{NOH}$ = 1.8 Hz, in a relatively small biologically active natural product, nocathiacin I, has been reported by Huang *et al.*[324] This observation afforded a restraint to further refine the 3D solution structure of this compound. The intramolecular C–H···N hydrogen bond has been identified in (*E*)-9-benzyl-6-[isobenzofuran-1(3*H*)-ylidene-methyl]-9*H*-purine by Gundersen and co-workers.[325]

The differences in hydrogen bond lengths between RNA and DNA found earlier with the help of $^{1h}J_{HN}$ and $^{2h}J_{NN}$ couplings have been confirmed now with the help of *trans*-hydrogen bond deuterium isotope shifts by Li Wang and co-workers.[326] Several examples of proteins and nucleic acids for which couplings through hydrogen bonds have been used in structural analysis are given in Table 5.

**Table 5** Compounds for which scalar couplings have been measured through the hydrogen bond

| Name | [a] | [b] | [c] | Ref. |
|---|---|---|---|---|
| *cyclo*-(-D-Pro-Ala$_4$-) | N–H···O=C | $^{3h}J_{CN}$ | 2 | 327 |
| [C/N] ScYLV RNA pseudoknot | N–H···N | $^{1h}J_{NH}$, $^{2h}J_{NN}$ | 18 | 43 |
| [C/N] the P4 element of RNase P | N–H···N | $^{2h}J_{NN}$ | 10 | 328 |

[a] Hydrogen bond type, symbols of nuclei involved are given in bold. [b] Type of couplings measured. [c] Number of couplings measured.



Sychrovský and co-workers[329] have used the DFT method to calculate $^{2h}J_{HP}$ and $^{3h}J_{CP}$ couplings across the C–H···O=P hydrogen bond between the nucleic acid backbone phosphate and the C–H group of a nucleic base and proposed application of these couplings for structure determination of nucleic acids.

The coupling between hydrogen and selenium nuclei in selones, $J_{HSe}$ = *ca.* 12–13 Hz which occurred through the N–H···Se=C hydrogen bond in these compounds was already observed some time ago by Wu *et al.*[330] A similar type of coupling, $J_{HSe}$ = 5.4 Hz, has been found recently by Okamura *et al.*[331] in the $(NEt_4)_2[Mo(IV)O(Se\text{-}2\text{-}t\text{-}BuCONHC_6H_4)_4]$ complex. The coupling of similar value, $J_{HSe}$ = 6 Hz occurring in the fragment NH···Se=P, has been observed by Mansfield *et al.*[332] in phospha(v)guanidine, $Ph_2P(Se)C\{NCy\}\{NHCy\}$. This interaction, although rather weak, is strong enough to slow rotation about the P–$C_{amidine}$ bond on the NMR time scale and to generate the conformation with intramolecular hydrogen bond.

A relatively large $J_{HCd}$ coupling of *ca.* 9.0 Hz has been observed by Chmielewski *et al.*[333] in *S*-confused thiaporphyrin 5,10,15,20-tetraphenyl-2-thia-21-carbaporphyrin providing evidence that the interaction takes place between the spin-active nucleus ($^{111}$Cd, $^{113}$Cd) and the proximate $^1$H nucleus despite the absence of a direct Cd–thiophene bond. Formally, these two nuclei are six bonds apart and the geometry of the coupling path is unfavourable.

Systematic *ab initio* studies of N–N and H–N spin–spin couplings across N–$H^+$–N hydrogen bonds have been performed by Del Bene and Elguero.[334] A CLOPPA analysis of the distance dependence of $^{2h}J_{FF}$ and $^{1h}J_{HF}$ in FH···FH has been performed by Giribet and de Azua.[335] *Ab initio* calculations have been performed by Del Bene *et al.*[336] in order to obtain structures, energies, P–P and H–P couplings of 22 open and 3 cyclic complexes formed from the $sp^2$ [$H_2C$=PH and HP=PH (*cis* and *trans*)] and $sp^3$ [$PH_2(CH_3)$ and $PH_3$] hybridised phosphorus bases and their corresponding protonated ions.

$^{3h}J_{C'N}$ couplings have been helpful in studying residual structures of urea-denaturated ubiquitin by Grzesiek and co-workers.[210] Vendruscolo and co-workers[337] have described a method of using this type of couplings as ensemble-averaged restraints in molecular dynamics simulations.

## 12. Residual dipolar couplings

An easy to use toolkit for RDC analysis, iDC has been created by Wei and Werner.[338] The program can perform most experimental RDC analyses including simultaneous estimation of tensor alignment of an entire structure family.

De Alba and Tjandra[339] have shown that the effect of cross-correlation is a source of error in quantitative *J* experiments. The authors found that in the case of methylene moieties the error of measured RDC values can amount to several Hz. Systematic studies on solvent effects exerted on RD and $^1J_{HC}$ couplings in acetonitrile have been performed by Gronenborn and co-workers.[340] No significant influence of alignment media on these parameters has been observed. The authors conclude that the structural features of small rigid molecules determined using

RDCs are in good agreement with the geometric parameters derived from other structural methods.

A new system for partial alignment of polar organic molecules to measure residual dipolar couplings has been proposed by Klochkov *et al.*[341] and as examples the H, C residual dipolar couplings for the amino acid methionine and for an α-methylene-γ-butyrolactone have been obtained.

Ramamoorthy and co-workers[342] have demonstrated the usefulness of a solid-state NMR approach that can be used to measure dipolar couplings between $^{1}H$, $^{13}C$ and $^{31}P$ nuclei in the structural studies of membrane-associated molecules without the need for isotopic enrichment. $^{1}D_{HN}$ couplings have been applied by Zweckstetter and co-workers[343] for characterisation of interaction of protein Tau with microtubules.

$^{1}D_{HN}$ residual dipolar couplings have been used by Shortle and co-workers[344] in their efforts to describe the residual structure in denaturated staphylococcal nuclease; by Ho and co-workers[345] for demonstration of spontaneous preferential orientation of deoxyhemoglobin in solution at high magnetic fields; by Gehring and co-workers[346] to compare the structure of BCL-$x_L$ dimer with the crystal structure of this protein; by McIntosh and co-workers[347] for direct demonstration of the flexibility of the glycosylated proline–threonine linker in the modular xylanase Cex; by Iwahara *et al.*[348] for structural and kinetic characterization of the HoxD9 homeodomain diffusing on non-specific DNA; by Wand and co-workers[349] to study the structure of several proteins in reverse micelles; by Zweckstetter and co-workers[350] to demonstrate that molecular alignment in unstructured proteins in charged nematic media strongly depends on electrostatic interactions between the protein and the alignment medium, and by Avbelj and Grdadolnik[209] to prove the presence of the fluctuating β-strands in denaturated proteins. The theoretical framework for residual dipolar couplings in unfolded proteins has been given by Obolensky and co-workers.[351]

$^{1}D_{HN}$ residual dipolar couplings induced by a rigid lanthanide-binding tag used for site-specific labelling of proteins have been applied for structural studies of N-terminal domain of *E.coli* arginine repressor by Otting and co-workers,[352] and for investigating global fold of the TM domain of outer membrane protein A by Johansson *et al.*[353]

$^{1}D_{HC}$ and $^{1}D_{HN}$ residual dipolar couplings have been used by Grzesiek and co-workers[354] to show that in short peptides individual amino acids reveal systematic conformational preferences, and by Ohnishi and co-workers[355] to prove that polyglycine in solution exhibits conformational preference to an elongate structure. Best *et al.*[356] have shown that experimentally measured residual dipolar couplings are well reproduced by their respective 'high-sequence similarity PDB ensembles'.

A polynomial-time algorithm for *de novo* protein backbone structure determination that utilizes residual dipole couplings as restraints has been formulated by Donald and co-workers.[357]

The list of proteins whose structures have been elucidated with the use of residual dipolar couplings is given in Table 6.

It has been shown by Lukavsky and co-workers[381] that complementary segmental labelling of large RNAs simplifies NMR spectra and doubles the number of measurable residual dipole couplings. Iverson and co-workers[382] have applied $^{1}D_{HC}$, $^{1}D_{HN}$, $^{1}D_{CN}$ and $^{3}D_{HH}$ couplings in their studies on the structure of the $d(CGGTACCG)_2$ complex with a new threading bisintercalator.

Several examples of nucleic acids and carbohydrates for which resiudal couplings have been measured and applied in structural analysis are listed in Table 7.

The $^{1}D_{CC}$ dipolar couplings between the labelled methyl and carbonyl carbons of the acetyl groups have been used for structural monitoring of oligosaccharides by Yu and Prestegard.[393]

**Table 6** Proteins for which the solution structure has been calculated with RDCs

| Name | [a] | [b] | [c] | Ref. |
|---|---|---|---|---|
| [C/N] TM domain (7–39) of the ζ chain of the T cell receptor complex | 33 | 46 | $^{1}D_{HC}$, $^{1}D_{HN}$ | 358 |
| [D/N] $\zeta\zeta_{TM}$ dimer | 33 × 2 | 35 | $^{1}D_{HC}$, $^{1}D_{HN}$ | 296 |
| [N] hTpoR (479–519) | 41 | 27 | $^{1}D_{HN}$ | 359 |
| [C/N] $Em^{LEM}$ (1–47) | 47 | 110 | $^{1}D_{HN}$, $^{1}D_{CN}$, $^{2}D_{HC}$ | 297 |
| GB3, immunoglobulin G-binding protein G precursor (298–352) | 55 | 750 | $^{1}D_{HN}$, $^{1}D_{CC}$, $^{1}D_{CN}$ | 360 |
| [D/C/N] GB1 | 56 | 352 | $D_{HH}$, $^{1}D_{HN}$, $^{2,3}D_{HC}$, $^{1}D_{CC}$, $^{1}D_{CN}$ | 361 |
| [C/N] Brk BDB (43–101) -omb12T5 complex | 59+ | 92 | $^{1}D_{HC}$, $^{1}D_{HN}$ | 295 |
| Conk-S1 and S2, conkunitzin-S1 and S2 | 60/65 | 190/138 | $^{1}D_{HC}$, $^{1}D_{HN}$, $^{1}D_{CC}$, $^{1}D_{CN}$ | 362 |
| [C/N] calbindin D9K, CaTmCb | 75 | 136 | $^{1}D_{HC}$, $^{1}D_{HN}$, $^{1}D_{CC}$ | 22 |
| [C/N] PF1455 from *Pyrococcus furiosus* | 75 | 178 | $^{1}D_{HN}$, $^{1}D_{HC}$, $^{2}D_{HH}$ | 197 |
| [C/N] Aα(406–483) αC-domain fragment of bovine fibrinogen | 78 | 71 | $^{1}D_{HN}$ | 363 |
| [C/N] FecA TonB | 80 | 42 | $^{1}D_{HN}$ | 199 |
| [C/N] PupA TonB | 82 | 54 | $^{1}D_{HN}$ | 199 |
| [C/N] HPV16 E2C (283–363) bound to DNA | 81+ | 102 | $^{1}D_{HN}$ | 364 |
| [C/N] the $^{2}F1^{3}F1$ module pair of the N-terminal of human fibronectin | 90 | 59 | $^{1}D_{HN}$ | 365 |
| [C/N] pMSP, β-microseminoproteins | 91 | 157 | $^{1}D_{HN}$, $^{1}D_{CN}$, $^{2}D_{HC}$ | 202 |
| [C/N] hMSP, β-microseminoprotein | 94 | 140 | $^{1}D_{HN}$, $^{1}D_{CN}$, $^{2}D_{HC}$ | 202 |
| [C/N] domain III of *Langat flavivirus* E protein | 96 | 80 | $^{1}D_{HN}$ | 203 |
| [N] N-DCX (45–150) (refinement) | 106 | 74 | $^{1}D_{HN}$ | 205 |
| [C/N] the CH domain of human MICAL-1 (506–614) | 109 | 74 | $^{1}D_{HN}$ | 366 |
| [C/N] GatB ($IIB^{gat}$), PTS system, galactitol-specific IIB component | 113 | 82 | $^{1}D_{HN}$ | 367 |
| [C/N] *Hs*Sen15 (36–157), a subunit of human tRNA splising endonuclease | 122 | 94 | $^{1}D_{HN}$ | 368 |
| [C/N] PACAP(6′-38′) complexed with [N] hPAC1-$R_S$ (21–122) | 33 + 102 | 23 | $^{1}D_{HC}$, $^{1}D_{HN}$ | 369 |
| [D/C/N] Ly49A NKD (127–262) | 136 | 104 | $^{1}D_{HN}$ | 370 |
| [D/C/N] the L11 protein from *Thermotoga maritima* complexed with 60 nt RNA and thiostrepton | 141+ | 120 | $^{1}D_{HN}$ | 371 |
| [C/N] C26S SAP18 (6–149) | 144 | 62 | $^{1}D_{HN}$ | 372 |
| [C/N] Wzb of *E.coli* | 147 | 97 | $^{1}D_{HN}$ | 373 |
| [C/N] Mlc1p N-lobe (2–79) + C-lobe (80–149) | 78 + 70 | 254 + 232 | $^{1}D_{HC}$, $^{1}D_{HN}$, $^{1}D_{CC}$ | 207 |
| [C/N] Spc24p/Spc25p globular domain of the yeast kinetochore | 89 + 76 | 173 | $^{1}D_{HN}$, $^{1}D_{CC}$ | 374 |
| [C/N] CaM/RYR1, calmodulin complexed with a ryanodine receptor target | 143 + 27 | 90 | $^{1}D_{HN}$ | 375 |
| [D/C/N] OmpA, the membrane protein | 177 | 434 | $^{1}D_{HN}$, $^{1}D_{CC}$, $^{1}D_{CN}$ | 376 |
| [N] FADD (1–191) | 191 | 137 | $^{1}D_{HN}$ | 208 |
| [N] the Ig doublet Z1Z2, N-terminus of titin | 194 | 53 | $^{1}D_{HN}$ | 377 |
| [C/N] Rv1980c, an antigen MPT64 from *Mycobacterium tuberculosis* | 205 | 253 | $^{1}D_{HN}$, $^{1}D_{CC}$ | 378 |
| [C/N] $Em^{LEM}$ (1–47) complexed with [C/N] $BAF_2$ selectively deuterated | 47 + 89 × 2 | 140 | $^{1}D_{HN}$ | 297 |
| [D/C/N] calbindin-$D_{28K}$, $Ca^{2+}$ loaded | 261 | 304 | $^{1}D_{HN}$, $^{1}D_{CN}$ | 379 |
| [D/N] ClC-0, a $Cl^{-}$ channel,[d] | 302 | 140 | $^{1}D_{HN}$ | 380 |

[a] Number of residues. [b] The total number of residual dipolar couplings measured. [c] Types of residual dipolar couplings measured. [d] Global fold only.

**Table 7** Oligonucleotides and carbohydrates for which the solution structure has been calculated with RDCs

| Name | [a] | [b] | [c] | Ref. |
|---|---|---|---|---|
| The RNA hairpin with GCUA tetraloop | 14 | 17 | $^1D_{HC}$ | 221 |
| Human U2 stem I RNA | 20 | 42 | $^1D_{HC}$, $^1D_{CC}$ | 383 |
| [C/N] yeast U2 stem I RNA | 20 | 71 | $^1D_{HC}$, $^1D_{CC}$ | 383 |
| [C/N] TER RNA SLIV | 21 | 17 | $^1D_{HC}$ | 384 |
| d(CGCGAATTCGCG)$_2$ | 24 | 964 | $^1D_{HC}$, $^1D_{HN}$, $^1D_{HP}$, $D_{HH}$ | 282 |
| [C/N] RNA hairpins Ycu and Yuu | 22/22 | 39/39 | $^1D_{HC}$ | 385 |
| [selective-uridine lab.] the pgRNA of HVB | 27 | 28 | $^1D_{HC}$ | 386 |
| [C/N] HRV-14 SLD | 27 | 66 | $^1D_{HC}$ | 387 |
| TAR RNA | 29 | 29 | $^1D_{HC}$ | 388 |
| [C/N] RNase P P4 | 29 | 43 | $^1D_{HC}$ | 328 |
| [C/N] the bulge-containing HIV-1 TAR RNA | 29 | 62 | $^1D_{HC}$, $^1D_{HN}$ | 389 |
| [C/N] SL1m HIV-1 RNA, free and $Mg^{2+}$ loaded | 36 | 52/52 | $^1D_{HC}$, $^1D_{HN}$ | 390 |
| The GAAA tetraloop-receptor RNA $Mn^{2+}$ and $Co(NH_3)_6^{3+}$ loaded | 43 | 24/24 | $^1D_{HN}$ | 391 |
| [C/N] SL1 RNA HIV-1 dimer initiation site | 35 × 2 | 65 × 2 | $^1D_{HC}$ | 392 |
| Carbohydrates | | | | |
| α -L-Rha*p*-(1 → 2)-α-L-Rha*p*-OMe | 2 | 10 | $^1D_{HC}$ | 286 |
| Doubly $^{13}$C-labeled N-acetyl O-butyl-chitobiose | 2 | 2 | $^1D_{CC}$ | 393 |
| Lactose bound to galectin-3 C251-CRD and S-propyl-C252-CRD | 2 | 11 | $^1D_{HC}$, $^2D_{HH}$ | 394 |

[a] The number of nucleotides or sugar units. [b] The total number of residual dipolar couplings measured. [c] Types of residual dipolar couplings measured.

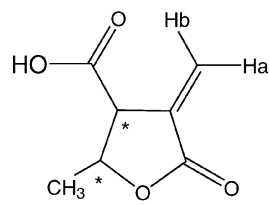



**Fig. 5**

Relative configuration of the stereogenic centres in a five-membered flexible lactone, α-methylene-γ-butyrolactone (Fig. 5) has been determined by Thiele and co-workers[395] with the aid of $^nD_{HC}$, $^1D_{CC}$ and $^3D_{HH}$ residual dipolar couplings.

Residual dipolar couplings have been applied by Voda *et al.*[396] to analyse the morphology of thermoplastic polyurethanes, and homo- and heteronuclear residual dipolar couplings have been used by Bertmer *et al.*[397] to study segmental mobility in a series of short poly(dimethylsiloxane) chains grafted onto hydrophilic silica.

Orientational ordering of short and intermediate *n*-alkanes confined to silicon nanotubes has been studied by Valiulin and Khokhlov[398] by the use of $^1$H NMR. They established that the residual nuclear dipolar couplings characterizing the degree of molecular ordering depend on the pore size and the molecular length in a complex way.

## References

1 K. Kamieńska-Trela and J. Wójcik, *Nucl. Magn. Reson.*, 2007, **36**, 131.

2 K. J. Harris, J. Kowalewski and S. Cabral de Menezes, *Pure & Appl. Chem.*, 1997, **69**, 2489.
3 M. Karplus, *Annu. Rev. Biophys. Biomol. Struc.*, 2006, **35**, 1.
4 L. B. Krivdin and R. H. Contreras, *Ann. Rep. NMR Spectrosc.*, 2007, **61**, 133.
5 R. Glaser, I. Ergaz, G. Levi-Ruso, D. Shiftan, A. Novoselsky and S. Geresh, *Ann. Rep. NMR Spectrosc.*, 2005, **56**, 143.
6 E. Fukushi, *Biosci. Biotechnol. Biochem.*, 2006, **70**, 1803.
7 R. M. Claramunt, C. López, M. D. Santa María, D. Sanz and J. Elguero, *Progr. NMR Spectrosc.*, 2006, **49**, 169.
8 B. Wrackmeyer, *Ann. Rep. NMR Spectrosc.*, 2006, **57**, 1.
9 I. Szymańska, *Polish J. Chem.*, 2006, **80**, 1095.
10 S. J. Berners-Price, L. Ronconi and P. J. Sadler, *Progr. NMR Spectrosc.*, 2006, **49**, 65.
11 B. M. Still, P. G. A. Kumar, J. R. Aldrich-Wright and W. S. Price, *Chem. Soc. Rev.*, 2007, **36**, 665.
12 A. Bagno and G. Saielli, *Theor. Chem. Acc.*, 2007, **117**, 603.
13 A. G. Tzakos, C. R. R. Grace, P. J. Lukavsky and R. Riek, *Annu. Rev. Biophys. Biomol. Struc.*, 2006, **35**, 319.
14 M. P. Foster, C. A. McElroy and C. D. Amero, *Biochemistry*, 2007, **46**, 331.
15 M. Getz, X. Sun, A. Casiano-Negroni, Q. Zhang and H. M. Al-Hashimi, *Biopolymers*, 2007, **86**, 384.
16 T. Mittag and J. D. Forman-Kay, *Curr. Opin. Struct. Biol.*, 2007, **17**, 3.
17 P. Vidal, N. Esturau, T. Parella and J. F. Espinosa, *J. Org. Chem.*, 2007, **72**, 3166.
18 P. Nolis, M. Pérez and T. Parella, *Magn. Reson. Chem.*, 2006, **44**, 1031.
19 K. Hu, B. Vögeli and G. M. Clore, *Chem. Phys. Lett.*, 2006, **423**, 123.
20 L. Jin and D. Uhrín, *Magn. Reson. Chem.*, 2007, **245**, 628.
21 V. Ramesh and N. Chandrakumar, *Magn. Reson. Chem.*, 2006, **44**, 936.
22 S. Balayssac, I. Bertini, C. Luchinat, G. Parigi and M. Piccioli, *J. Am. Chem. Soc.*, 2006, **128**, 15042.
23 S. Balayssac, B. Jiménez and M. Piccioli, *J. Magn. Reson.*, 2006, **182**, 325.
24 D. A. Evans, M. J. Bodkin, S. R. Baker and G. J. Sharman, *Magn. Reson. Chem.*, 2007, **45**, 595.
25 M. Deschamps, F. Fayon, V. Montouillout and D. Massiot, *Chem. Commun.*, 2006, **1924**.
26 M. Deschamps and D. Massiot, *J. Magn. Reson.*, 2007, **184**, 15.
27 F. Fayon, C. Roiland, L. Emsley and D. Massiot, *J. Magn. Reson.*, 2006, **179**, 49.
28 A. Iuga, D. Iuga, A. R. Cross, M. Gerken and P. Hazendonk, *J. Chem. Phys.*, 2007, **126**, 054305.
29 L. Zhang and G. Gellerstedt, *Magn. Reson. Chem.*, 2007, **45**, 37.
30 J. N. Robinson, A. Coy, R. Dykstra, C. D. Eccles, M. W. Hunter and P. T. Callaghan, *J. Magn. Reson.*, 2006, **182**, 343.
31 E. Prost, S. Bourg and J.-M. Nuzillard, *C. R. Chimie*, 2006, **9**, 498.
32 P. Tzvetkova, S. Simova and B. Luy, *J. Magn. Reson.*, 2007, **186**, 193.
33 K. Kobzar and B. Luy, *J. Magn. Reson.*, 2007, **186**, 131.
34 P. Schanda, E. Lescop, M. Falge, R. Sounier, J. Boisbouvier and B. Brutscher, *J. Biomol. NMR*, 2007, **38**, 47.
35 D. O. Cicero, G. M. Contessa, M. Paci and R. Bazzo, *J. Magn. Reson.*, 2006, **180**, 222.
36 E. de Alba and N. Tjandra, *J. Magn. Reson.*, 2006, **183**, 160.
37 J. Furrer, M. John, H. Kessler and B. Luy, *J. Biomol. NMR*, 2007, **37**, 231.
38 H. S. Atreya, E. Garcia, Y. Shen and T. Szyperski, *J. Am. Chem. Soc.*, 2007, **129**, 680.
39 P. Nolis and T. Parella, *J. Biomol. NMR*, 2007, **37**, 65.
40 A. Z. Liu, Y. Li, L. S. Yao and H. G. Yan, *J. Biomol. NMR*, 2006, **36**, 205.
41 J. F. Ying and A. Bax, *J. Am. Chem. Soc.*, 2006, **128**, 8372.
42 M. Hennig, M. L. Munzarová, W. Bermel, L. G. Scott, V. Sklenár and J. R. Williamson, *J. Am. Chem. Soc.*, 2006, **128**, 5851.
43 P. V. Cornish, D. P. Giedroc and M. Hennig, *J. Biomol. NMR*, 2006, **35**, 209.
44 G. Cornilescu, A. Bahrami, M. Tonelli, J. L. Markley and H. R. Eghbalnia, *J. Biomol. NMR*, 2007, **38**, 341.
45 J. A. Kubat, J. J. Chou and D. Rovnyak, *J. Magn. Reson.*, 2007, **186**, 201.
46 K. E. Köver, G. Batta and K. Fehér, *J. Magn. Reson.*, 2006, **181**, 89.
47 L. Ziani, J. Courtieu and D. Merlet, *J. Magn. Reson.*, 2006, **183**, 60.
48 M. G. Constantino, G. V. J. da Silva, V. C. G. Heleno, I. A. Borin and I. P. de Arruda Campos, *Quim. Nova*, 2006, **29**, 160.
49 S. A. Perera and R. J. Bartlett, *Mol. Phys.*, 2006, **104**, 2403.
50 C. L. Gross and G. S. Girolami, *Organometallics*, 2007, **26**, 1658.
51 S. Dutta and B. R. Jagirdar, *Inorg. Chem.*, 2006, **45**, 7047.

52 G. Barea, M. A. Estereuelas, A. Lledos, A. M. Lopez, E. Onate and J. I. Tolosa, *Organometallics*, 1998, **17**, 4065.
53 N. Schloerer, V. Pons, D. G. Gusev and D. M. Heinekey, *Organometallics*, 2006, **25**, 3481.
54 I. Göttker-Schnetmann, D. M. Heinekey and M. Brookhart, *J. Am. Chem. Soc.*, 2006, **128**, 17114.
55 Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113.
56 T. W. Keal, T. Helgaker, P. Sałek and D. J. Tozer, *Chem. Phys. Lett.*, 2006, **425**, 163.
57 W. Deng, J. R. Cheeseman and M. J. Frisch, *J. Chem. Theory Comput.*, 2006, **2**, 1028.
58 W. Makulski and M. Wilczek, *Polish J. Chem.*, 2006, **80**, 1055.
59 T. Wedel, M. Müller, J. Podlech, H. Goesmann and C. Feldmann, *Chem. Eur. J.*, 2007, **13**, 4273.
60 B. A. Shainyan, I. A. Ushakov, A. Koch and E. Kleinpeter, *J. Org. Chem.*, 2006, **71**, 7638.
61 A. R. Katritzky, N. G. Akhmedov, J. Doskocz, C. D. Hall, R. G. Akhmedova and S. Majumder, *Magn. Reson. Chem.*, 2007, **45**, 5.
62 P. D. Bolton, E. Clot, N. Adams, S. R. Dubberley, A. R. Cowley and P. Mountford, *Organometallics*, 2006, **25**, 2806.
63 V. Galasso, A. K. Przybył, V. Christov, B. Kovač, F. Asaro and E. Zangrando, *Chem. Phys.*, 2006, **325**, 365.
64 V. Galasso, F. Asaro, F. Berti, B. Pergolese, B. Kovač and F. Pichierri, *Chem. Phys.*, 2006, **330**, 457.
65 X. Solans-Montfort, J.-S. Filhol, C. Copéret and O. Eisenstein, *New J. Chem.*, 2006, **30**, 842.
66 G. Tosin, C. C. Santini, M. Taoufik, A. De Mallmann and J.-M. Basset, *Organometallics*, 2006, **25**, 3324.
67 Y. Tanaka, M. Arakawa, Y. Yamaguchi, C. Hori, M. Ueno, T. Tanaka, T. Imahori and Y. Kondo, *Chem. Asian. J.*, 2006, **1**, 581.
68 M.-L. Jimeno, I. Alkorta, J. Elguero and J. E. Del Bene, *Magn. Reson. Chem.*, 2006, **44**, 698.
69 L. Pazderski, J. Toušek, J. Sitkowski, L. Kozerski and E. Szłyk, *Polish J. Chem.*, 2007, **81**, 193.
70 B. A. Shainyan, I. A. Ushakov and E. N. Suslova, *J. Sulfur Chem.*, 2006, **27**, 3.
71 K. E. Chaffee, M. Marjanska and B. M. Goodson, *Solid State NMR*, 2006, **29**, 104.
72 G. Celebre, M. Concistré, G. De Luca, M. Longeri and G. Pileio, *ChemPhysChem*, 2006, **7**, 1930.
73 M. L. Helm, L. L. Hill, J. P. Lee, D. G. Van Derveer and G. J. Grant, *Dalton Trans.*, 2006, 3534.
74 A. V. Afonin, I. A. Ushakov, A. I. Mikhaleva and B. A. Trofimov, *Magn. Reson. Chem.*, 2007, **45**, 220.
75 P. Przybylski, G. Bejcar, W. Schilf, B. Kamieński and B. Brzeziński, *J. Mol. Struct.*, 2007, **826**, 150.
76 A. Lyčka, I. Fryšová and J. Slouka, *Magn. Reson. Chem.*, 2007, **45**, 46.
77 S. Yan, L. Zhang, R. I. Cukier and Y. Bu, *ChemPhysChem*, 2007, **8**, 944.
78 V. Weijo, R. Bast, P. Manninen, T. Saue and J. Vaara, *J. Chem. Phys.*, 2007, **126**, 074107.
79 K. Thorshaug, O. Swang, I. M. Dahl and A. Olafsen, *J. Phys. Chem. A*, 2006, **110**, 9801.
80 S. F. Vyboishchikov and G. I. Nikonov, *Chem. Eur. J.*, 2006, **12**, 8518.
81 N. S. Golubev, R. E. Asfin, S. N. Smirnov and P. M. Tolstoy, *Russ. J. Gen. Chem.*, 2006, **76**, 915.
82 A. Gądek and Szymańska-Buzar, *Polyhedron*, 2006, **25**, 1441.
83 M. Stosur, A. Kochel, A. Keller and T. Szymańska-Buzar, *Organometallics*, 2006, **25**, 3791.
84 S. I. M. Paris, J. L. Petersen, E. Hey-Hawkins and M. P. Jensen, *Inorg. Chem.*, 2006, **45**, 5561.
85 K. Staliński, Z. Urbańczyk-Lipkowska, P. Cmoch, L. Rupnicki and A. Grachev, *J. Organomet. Chem.*, 2006, **691**, 2394.
86 J. E. Del Bene, J. Elguero, I. Alkorta, M. Yáñez and O. Mó, *J. Phys. Chem. A*, 2007, **111**, 419.
87 J. E. Del Bene and J. Elguero, *Magn. Reson. Chem.*, 2007, **45**, 484.
88 G. Fraenkel, J. Gallucci and H. Liu, *J. Am. Chem. Soc.*, 2006, **128**, 8211.
89 J. Granander, R. Sott and G. Hilmersson, *Chem. Eur. J.*, 2006, **12**, 4191.
90 J. E. Del Bene, J. Elguero, I. Alkorta, M. Yáñez and O. Mó, *J. Chem. Theory Comput.*, 2007, **3**, 549.
91 B. Wrackmeyer and O. Tok, *Z. Naturforsch.*, 2006, **61b**, 949.
92 F. Dornhaus, M. Bolte, H.-W. Lerner and M. Wagner, *Eur. J. Inorg. Chem.*, 2006, **1777**.

93 M. Witanowski, K. Kamieńska-Trela and Z. Biedrzycka, *J. Mol. Struct*., 2007, doi:10.1016/j.molstruc.2007.01.039.
94 T. Helgaker, O. B. Lutnaes and M. Jaszuński, *J. Chem. Theory Comput*., 2007, **3**, 86.
95 B. A. Trofimov, L. A. Oparina, L. B. Krivdin, N. K. Gusarova, K. A. Chernyshev, L. M. Sinegovskaya, L. V. Klyba, L. N. Parshina, A. P. Tantsyrev, O. N. Kazheva, G. G. Alexandrov and O. A. D'yachenko, *J. Mol. Struct*., 2006, **791**, 1.
96 Y. Y. Rusakov, L. B. Krivdin, E. Y. Senotrusova, E. Y. Schmidt, A. M. Vasiltsov, A. I. Mikhaleva, B. A. Trofimov, O. A. D'yachenko, A. N. Chekhlov and O. N. Kazheva, *Magn. Reson. Chem*., 2007, **45**, 142.
97 Y. Y. Rusakov, L. B. Krivdin, E. Y. Schmidt, A. I. Mikhaleva and B. A. Trofimov, *Magn. Reson. Chem*., 2006, **44**, 692.
98 K. A. Chernyshev, L. B. Krivdin, L. I. Larina, T. V. Konkova, M. M. Demina and A. S. Medvedeva, *Magn. Reson. Chem*., 2007, **45**, 661.
99 O. E. Taurian, R. H. Contreras, D. G. De Kowalewski, J. E. Pérez and C. F. Tormena, *J. Chem. Theory Comput*., 2007, **3**, 1284.
100 G. Arsenault, B. Chittim, A. McAlees and R. McCrindle, *Chemosphere*, 2007, **67**, 1684.
101 M. Isobe, M. Kurono, K. Tsuboi and A. Takai, *Chem. Asian J*., 2007, **2**, 377.
102 J. N. Woodford and G. S. Harbison, *J. Chem. Theory Comput*., 2006, **2**, 1464.
103 R. H. Contreras, A. L. Esteban, E. Díez, I. J. Lochert, E. W. Della and C. F. Tormena, *Magn. Reson. Chem*., 2007, **45**, 572.
104 C. J. Unkefer, R. E. London, T. W. Whaley and G. H. Daub, *J. Am. Chem. Soc*., 1983, **105**, 733.
105 Y. W. Goh, S. M. Danczak, T. K. Lim and J. M. White, *J. Org. Chem*., 2007, **72**, 2929.
106 K. Kamieńska-Trela, L. Kania and E. Bednarek, *Magn. Reson. Chem*., 1993, **31**, 268.
107 M. Witanowski and Z. Biedrzycka, *Magn. Reson. Chem*., 1994, **32**, 62.
108 R. K. Harris, S. Cadars, L. Emsley, J. R. Yates, C. J. Pickard, R. K. R. Jetti and U. J. Griesser, *Phys. Chem. Chem. Phys*., 2007, **9**, 360.
109 P. Žáček, A. Dransfeld, O. Exner and J. Schraml, *Magn. Reson. Chem*., 2006, **44**, 1073.
110 E. M. Sega, C. F. Tormena, P. R. de Oliveira, R. Rittner, L. W. Tinoco, J. D. Figueroa-Villar and N. F. Höehr, *J. Mol. Struct*., 2006, **797**, 44.
111 V. Langer, A. Popkov, M. Nádvorník and A. Lyčka, *Polyhedron*, 2007, **26**, 911.
112 J. W. Emsley, M. Longeri, D. Merlet, G. Pileio and N. Suryaprakash, *J. Magn. Reson*., 2006, **180**, 245.
113 K. Laihia, E. Kolehmainen, V. Nikiforov and S. Milsov, *Magn. Reson. Chem*., 2006, **44**, 895.
114 A. G. Iriarte, E. H. Cutin and C. O. Della Védova, *J. Mol. Struct*., 2006, **800**, 154.
115 E. P. A. Couzijn, A. W. Ehlers, M. Schakel and K. Lammertsma, *J. Am. Chem. Soc*., 2006, **128**, 13634.
116 N. Panziera, P. Pertici, L. Barazzone, A. M. Caporusso, G. Vitulli, P. Salvadori, S. Borsacchi, M. Geppi, C. A. Veracini, G. Martra and L. Bertinetti, *J. Catal*., 2007, **246**, 351.
117 B. Wrackmeyer and M. Herberhold, *Struct. Chem*., 2006, **17**, 79.
118 B. Wrackmeyer, Z. García Hernández and M. Herberhold, *Magn. Reson. Chem*., 2007, **45**, 198.
119 P. Lind, D. Boström, M. Calrsson, A. Eriksson, E. Glimsdal, M. Lindgren and B. Eliasson, *J. Phys. Chem. A*, 2007, **111**, 1598.
120 J. E. Del Bene and J. Elguero, *J. Phys. Chem. A*, 2006, **110**, 12543.
121 J. E. Del Bene and J. Elguero, *J. Phys. Chem. A*, 2007, **111**, 2517.
122 P. V. Grundler, L. Helm, R. Alberto and A. E. Merbach, *Inorg. Chem*., 2006, **45**, 10378.
123 M. Weil, M. Puchberger, E. Füglein, E. J. Baran, J. Vannahme, H. J. Jakobsen and J. Skibsted, *Inorg. Chem*., 2007, **46**, 801.
124 H. A. Prescott, S. I. Troyanov and E. Kemnitz, *Z. Kristallogr*., 2000, **215**, 240.
125 H. Tervonen, J. Saunavaara, L. P. Ingman and J. Jokisaari, *J. Phys. Chem. B*, 2006, **110**, 16232.
126 A. Antušek, M. Pecul and J. Sadlej, *Chem. Phys. Lett*., 2006, **427**, 281.
127 M. Gerken, P. Hazendonk, A. Iuga, J. P. Mack, H. P. A. Mercier and G. J. Schrobilgen, *J. Fluor. Chem*., 2006, **127**, 1328.
128 H. Tsuji, T. Inoue, Y. Kaneta, S. Sase, A. Kawachi and K. Tamao, *Organometallics*, 2006, **25**, 6142.
129 V. Bilenko, A. Spannenberg, W. Baumann, I. Komarov and A. Börner, *Tetrahedron: Asymmetry*, 2006, **17**, 2082.
130 C. E. Anderson, A. S. Batsanov, P. W. Dyer, J. Fawcett and J. A. K. Howard, *Dalton Trans*., 2006, 5362.
131 D. J. Adams, J. A. Bennett, D. Duncan, E. G. Hope, J. Hopewell, A. M. Stuart and A. J. West, *Polyhedron*, 2007, **26**, 1505.

132 C. G. Hrib, P. G. Jones, W.-W. du Mont, V. Lippolis and F. A. Devillanova, *Eur. J. Inorg. Chem.*, 2006, 1294.
133 H. M. Foucault, D. L. Bryce and D. E. Fogg, *Inorg. Chem.*, 2006, **45**, 10293.
134 J. Tiburcio, S. Bernès and H. Torrens, *Polyhedron*, 2006, **25**, 1549.
135 C. Gallego, M. Martinez and V. S. Safont, *Organometallics*, 2007, **26**, 527.
136 M. J. Willans, B. A. Demko and R. E. Wasylishen, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2733.
137 B. A. Demko, K. Eichele and R. E. Wasylishen, *J. Phys. Chem. A*, 2006, **110**, 13537.
138 M. M. Ebrahim, H. Stoeckli-Evans and K. Panchanatheswaran, *J. Organomet. Chem.*, 2007, **692**, 2168.
139 G. Keglevich, A. Kerényi, H. Szelke and T. Imre, *Trans. Metal Chem.*, 2006, **31**, 306.
140 M. Bortoluzzi, G. Annibale, G. Marangoni, G. Paolucci and B. Pitteri, *Polyhedron*, 2006, **25**, 1979.
141 M. Risto, E. M. Jahr, M. S. Hannu-Kuure, R. Oilunkaniemi and R. S. Laitinen, *J. Organomet. Chem.*, 2007, **692**, 2193.
142 M. Barfield, *Magn. Reson. Chem.*, 2007, **45**, 634.
143 I. Czerski and S. Szymański, *Polish J. Chem.*, 2006, **80**, 1233.
144 S. Szymański, *J. Chem. Phys.*, 1996, **104**, 8216.
145 S. Szymański, *J. Chem. Phys.*, 1997, **106**, 3430.
146 T. Ratajczyk and S. Szymański, *J. Chem. Phys.*, 2005, **123**, 204509.
147 F. E. Hahn, M. C. Jahnke and T. Pape, *Organometallics*, 2007, **26**, 150.
148 F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales and T. Pape, *Organometallics*, 2005, **24**, 6458.
149 C. Guo, J. Persons and G. S. Harbison, *Magn. Reson. Chem.*, 2006, **44**, 832.
150 D. K. Dillner and D. D. Traficante, *Magn. Reson. Chem.*, 2007, **45**, 193.
151 H. Krawczyk, A. Pietras and A. Kraska, *Spectrochim. Acta A*, 2007, **66**, 9.
152 A. I. Krivoshey, N. S. Pivnenko, S. V. Shishkina, A. V. Turov, L. A. Kutulya and O. V. Shishkin, *Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 999.
153 K. J. Goodall, M. A. Brimble and D. Barker, *Magn. Reson. Chem.*, 2006, **44**, 980.
154 K. J. Goodall, M. A. Brimble and D. Barker, *Magn. Reson. Chem.*, 2007, **245**, 695.
155 C. F. Tormena, J. D. Vilcachagua, V. Karcher, R. Rittner and R. H. Contreras, *Magn. Reson. Chem.*, 2007, **45**, 590.
156 N. Matsumori, D. Kaneno, M. Murata, H. Nakamura and K. Tachibana, *J. Org. Chem.*, 1999, **64**, 866.
157 J. Hassfeld, C. Farès, H. Steinmetz, T. Carlomagno and D. Menche, *Org. Lett.*, 2006, **8**, 4751.
158 D.-C. Oh, C. A. Kauffman, P. R. Jensen and W. Fenical, *J. Nat. Prod.*, 2007, **70**, 515.
159 M. Iranshahi, P. Arfa, M. Ramezani, M. R. Jaafari, H. Sadeghian, C. Bassarello, S. Piacente and C. Pizza, *Phytochemistry*, 2007, **68**, 554.
160 H.-R. Park, S. Chijiwa, K. Furihata, Y. Hayakawa and K. Shin-ya, *Org. Lett.*, 2007, **9**, 1457.
161 E. D. Matveeva, A. S. Erin, A. G. Osetrov, I. F. Leshcheva and L. Kurts, *Russ J. Org. Chem.*, 2006, **42**, 388.
162 G. J. Sharman, *Magn. Reson. Chem.*, 2007, **45**, 317.
163 V. F. Kuznetsov, K. Abdur-Rashid, A. J. Lough and D. G. Gusev, *J. Am. Chem. Soc.*, 2006, **128**, 14388.
164 A. Bagno, N. Bertazzi, G. Casella, L. Pellerito, G. Saielli and I. D. Sciacca, *J. Phys. Org. Chem.*, 2006, **19**, 874.
165 T. P. Lockhart and W. F. Manders, *Inorg. Chem.*, 1986, **25**, 892.
166 N. Bertazzi, G. Casella, F. Ferrante, L. Pellerito, A. Rotondo and E. Rotondo, *Dalton Trans.*, 2007, 1440.
167 K. Gholivand and Z. Shariatinia, *J. Organomet. Chem.*, 2006, **691**, 4215.
168 J. Wirmer, W. Peti and H. Schwalbe, *J. Biomol. NMR*, 2006, **35**, 175.
169 P. Šimůnek, L. Lusková, M. Svobodová, V. Bertolasi, A. Lyčka and V. Macháček, *Magn. Reson. Chem.*, 2007, **45**, 330.
170 R. A. Stockland Jr, M. C. Kohler, I. A. Guzei, M. E. Kastner, J. A. Bawiec III, D. C. Labaree and R. B. Hochberg, *Organometallics*, 2006, **25**, 2475.
171 K. Gholivand, Z. Shariatinia and A. Tadjarodi, *Main Group Chem.*, 2005, **4**, 111.
172 K. Gholivand, Z. Hosseini, M. Pourayoubi and Z. Shariatinia, *Z. Anorg. Allg. Chem.*, 2005, **631**, 3074.
173 K. Gholivand, Z. Shariatinia, Z. A. Tabasi and A. Tadjarodi, *Heteroatom Chem.*, 2006, **17**, 337.
174 K. Gholivand, F. Mojahed, A. M. Alizadehgan and H. R. Bijanzadeh, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1570.
175 K. Gholivand, F. Mohajed and A. M. Alizadehgan, *Polish J. Chem.*, 2007, **81**, 393.

176 K. Gholivand, Z. Shariatinia, F. Yaghmaian and H. Faramarzpour, *Bull. Chem. Soc. Jpn*, 2006, **79**, 1604.
177 K. Gholivand, M. Pourayoubi and Z. Shariatinia, *Polyhedron*, 2007, **26**, 837.
178 Y. Tanaka, S. Oda, H. Yamaguchi, Y. Kondo, C. Kojima and A. Ono, *J. Am. Chem. Soc*., 2007, **129**, 244.
179 M. Kurfürst and J. Schraml, *Magn. Reson. Chem*., 2007, **245**, 685.
180 S. Cadars, A. Lesage, N. Hedin, B. F. Chmelka and L. Emsley, *J. Phys. Chem. B*, 2006, **110**, 16982.
181 C. Coelho, T. Azais, L. Bonhomme-Coury, G. Laurent and C. Bonhomme, *Inorg. Chem*., 2007, **46**, 1379.
182 A. Sivaramakrishna, I. Kalikhman, E. Kertsnus, A. A. Korlyukov and D. Kost, *Organometallics*, 2006, **25**, 3665.
183 S. Cadars, A. Lesage, M. Trierweiler, L. Heux and L. Emsley, *Phys. Chem. Chem. Phys*., 2007, **9**, 92.
184 S. Bilge, S. Demiriz, A. Okumuş, Z. Kiliç, B. Tercan, T. Hökelek and O. Büyükgüngör, *Inorg. Chem*., 2006, **45**, 8755.
185 M. A. Gave, C. D. Malliakas, D. P. Weliky and M. G. Kanatzidis, *Inorg. Chem*., 2007, **46**, 3632.
186 K. Ramaswamy, E. G. Tulsky, J. R. Long, J. L.-F. Kao and S. Hayes, *Inorg. Chem*., 2007, **46**, 1177.
187 B. Keller, M. Christen, C. Oostenbrink and W. F. van Gunsteren, *J. Biomol. NMR*, 2007, **37**, 1.
188 D. S. Weinstock, C. Narayanan, A. K. Felts, M. Andrec, R. M. Levy, K. P. Wu and J. Baum, *J. Am. Chem. Soc*., 2007, **129**, 4858.
189 J. Kapitán, V. Baumruk, V. Kopecký, R. Pohl and P. Bouř, *J. Am. Chem. Soc*., 2006, **128**, 13451.
190 R. Schweitzer-Stenner, T. Measey, L. Kakalis, F. Jordan, S. Pizzanelli, C. Forte and K. Griebenow, *Biochemistry*, 2007, **46**, 1587.
191 A. Dike and S. M. Cowsik, *J. Struct. Biol*., 2006, **156**, 442.
192 N. E. Shepherd, H. N. Hoang, V. S. Desai, E. Letouze, P. R. Young and D. P. Fairlie, *J. Am. Chem. Soc*., 2006, **128**, 13284.
193 S. Meier, P. R. Jensen, P. Adamczyk, H. P. Bächinger, T. W. Holstein, J. Engel, S. Özbek and S. Grzesiek, *J. Mol. Biol*., 2007, **368**, 718.
194 G. Corzo, J. K. Sabo, F. Bosmans, B. Billen, E. Villegas, J. Tygat and R. S. Norton, *J. Biol. Chem*., 2007, **282**, 4643.
195 B. Morales, X. Ramirez-Espain, A. Z. Shaw, P. Martin-Malpartida, F. Yraola, E. Sánchez-Tilló, C. Farrera, A. Celada, M. Royo and M. J. Macias, *Structure*, 2007, **15**, 473.
196 V. Muralidharan, K. Dutta, J. Cho, M. Vila-Perello, D. P. Raleigh, D. Cowburn and T. W. Muir, *Biochemistry*, 2006, **45**, 8874.
197 K. L. Mayer, Y. Qu, S. Bansal, P. D. LeBlond, F. E. Jenney Jr, P. S. Brereton, M. W. W. Adams, Y. Xu and J. H. Prestegard, *Proteins*, 2006, **65**, 480.
198 S. A. Beasley, V. A. Hristova and G. S. Shaw, *Proc. Nat. Acad. Sci. USA*, 2007, **104**, 3095.
199 A. D. Ferguson, C. A. Amezcua, N. M. Halabi, Y. Chelliah, M. K. Rosen, R. Ranganathan and J. Deisenhofer, *Proc. Nat. Acad. Sci. USA*, 2007, **104**, 513.
200 S. Chitayat, V. Kanelis, M. L. Koschinsky and S. P. Smith, *Biochemistry*, 2007, **46**, 1732.
201 A. Del Rio, K. Dutta, J. Chavez, I. Ubarretxena-Belandia and R. Ghose, *J. Mol. Biol*., 2007, **365**, 109.
202 H. Ghasriani, K. Teilum, Y. Johnsson, P. Fernlund and T. Drakenberg, *J. Mol. Biol*., 2006, **362**, 502.
203 M. Mukherjee, K. Dutta, M. A. White, D. Cowburn and R. O. Fox, *Protein Sci*., 2006, **15**, 1342.
204 M. F. García-Mayoral, D. Hollingworth, L. Masino, I. Díaz-Moreno, G. Kelly, R. Gherzi, C. F. Chou, C. Y. Chen and A. Ramos, *Structure*, 2007, **15**, 485.
205 T. Cierpicki, M. H. Kim, D. R. Cooper, U. Derewenda, J. H. Bushweller and Z. S. Derewenda, *Proteins*, 2006, **64**, 874.
206 K. L. Wegener, A. W. Partridge, J. Han, A. R. Pickford, R. C. Liddington, M. H. Ginsberg and I. D. Campbell, *Cell*, 2007, **128**, 171.
207 M. Pennestri, S. Melino, G. M. Contessa, E. C. Casavola, M. Paci, A. Ragnini-Wilson and D. O. Cicero, *J. Biol. Chem*., 2007, **282**, 667.
208 P. E. Carrington, C. Sandu, Y. F. Wei, J. M. Hill, G. Morisawa, T. Huang, E. Gavathiotis, Y. Wei and M. H. Werner, *Mol. Cell*, 2006, **22**, 599.
209 F. Avbelj and S. G. Grdadolnik, *Protein Sci*., 2007, **16**, 273.
210 S. Meier, M. Strohmeier, M. Blackledge and S. Grzesiek, *J. Am. Chem. Soc*., 2007, **129**, 754.

211 J. A. Marsh, C. Neale, F. E. Jack, W. Y. Choy, A. Y. Lee, K. A. Crowhurst and J. D. Forman-Kay, *J. Mol. Biol.*, 2007, **367**, 1494.
212 F. Corzana, J. H. Busto, S. B. Engelsen, J. Jiménez-Barbero, J. L. Asensio, J. M. Peregrina and A. Avenoza, *Chem. Eur. J.*, 2006, **12**, 7864.
213 O. A. Gudasheva, V. P. Lezina, E. P. Kir'yanova, V. S. Troitskaya, L. G. Kolik and S. B. Seredenin, *Pharm. Chem. J.*, 2006, **40**, 367.
214 M. Hricovíni and F. Bízik, *Carbohyd. Res.*, 2007, **342**, 779.
215 A. Aguirre-Valderrama and J. A. Dobado, *J. Carbohyd. Chem.*, 2006, **25**, 557.
216 S. Mari, F. J. Cañada, J. Jiménez-Barbero, A. Bernardi, G. Marcou, I. Motto, I. Velter, F. Nicotra and B. La Ferla, *Eur J. Org. Chem.*, 2006, 2925.
217 M. P. DeMatteo, S. Mei, R. Fenton, M. Morton, D. M. Baldiserri, C. M. Hadad and M. W. Peczuh, *Carbohyd. Res.*, 2006, **341**, 2927.
218 A. J. Metta-Mangaña, R. Reyes-Martínez and H. Tlahuext, *Carbohyd. Res.*, 2007, **342**, 243.
219 N. Lourith, T. Katayama and T. Suzuki, *J. Wood Sci.*, 2005, **51**, 370.
220 J. Buckingham, J. A. Brazier, J. Fisher and R. Cosstick, *Carbohyd. Res.*, 2007, **342**, 16.
221 W. J. G. Melchers, J. Zoll, M. Tessari, D. V. Bakhmutov, A. P. Gmyl, V. I. Agol and H. A. Heus, *RNA*, 2006, **12**, 1671.
222 B. Liberek, D. Tuwalska, I. do Santos-Zounon, A. Konitz, A. Sikorski and Z. Smiatacz, *Carbohyd. Res.*, 2006, **341**, 2275.
223 J. J. Hernandéz-Gay, L. Panza, F. Ronchetti, F. J. Cañada, F. Compostella and J. J. Jiménez-Barbero, *Carbohyd. Res.*, 2007, **342**, 1966.
224 C. D. Blundell, M. A. C. Reed and A. Almond, *Carbohyd. Res.*, 2006, **341**, 2803.
225 A. Almond, P. L. DeAngelis and C. D. Blundell, *J. Mol. Biol.*, 2006, **358**, 1256.
226 H. Seike, I. Ghosh and Y. Kishi, *Org. Lett.*, 2006, **8**, 3861.
227 C. Huo, X. Su, X. Li, X. Zhang, C. Li, Y. Wang, Q. Shi and H. Kiyota, *Magn. Reson. Chem.*, 2007, **45**, 527.
228 Q.-Y. Li, H.-B. Chen, Z.-M. Liu, B. Wang and Y.-Y. Zhao, *Magn. Reson. Chem.*, 2007, **45**, 451.
229 E. Burgueño-Tapia, B. Hernández-Carlos and P. Joseph-Nathan, *J. Mol. Struct.*, 2006, **825**, 115.
230 E. Burgueño-Tapia, S. López-Escobedo, M. González-Ledesma and P. Joseph-Nathan, *Magn. Reson. Chem.*, 2007, **45**, 457.
231 D. C. Chaves, J. C. C. Assunção, R. Braz-Filho, T. L. G. Lemos and F. J. Q. Monte, *Magn. Reson. Chem.*, 2007, **45**, 389.
232 G. Fontana, G. Savona and B. Rodríguez, *Magn. Reson. Chem.*, 2006, **44**, 962.
233 Y. Uchio, N. K. Kubota, T. Haino and Y. Fukazawa, *Bull. Chem. Soc. Jpn*, 2006, **79**, 914.
234 M. H. Kazmi, E. Ahmed, S. Hameed, A. Malik and M. Ashraf, *Magn. Reson. Chem.*, 2007, **45**, 416.
235 S. Zhou, J. Yang, F. Liu and P. Tu, *Magn. Reson. Chem.*, 2007, **45**, 179.
236 F. A. Macías, J. O. Guerra, A. M. Simonet and C. M. Nogueiras, *Magn. Reson. Chem.*, 2007, **45**, 615.
237 R. P. Santos, E. R. Silveira, D. E. de A. Uchôa, O. D. L. Pessoa, F. A. Viana and R. Braz-Filho, *Magn. Reson. Chem.*, 2007, **245**, 692.
238 S. De Marino, N. Borbone, F. Gala, F. Zollo, G. Fico, R. Pagiotti and M. Iorizzi, *J. Agric. Food Chem.*, 2006, **54**, 7508.
239 M. S. Buchanan, A. R. Carroll, D. Pass and R. J. Quinn, *Magn. Reson. Chem.*, 2007, **45**, 359.
240 V. Roumy, N. Fabre, F. Souard, S. Massou, G. Bourdy, S. Maurel, A. Valentin and C. Moulis, *Planta Med.*, 2006, **72**, 894.
241 M. Bunzel, J. Ralph, P. Brüning and H. Steinhart, *J. Agric. Food Chem.*, 2006, **54**, 6409.
242 S. P. Lira, A. M. Vita-Marques, M. H. R. Seleghim, T. S. Bugni, D. V. LaBarbera, L. D. Sette, S. R. P. Sponchiado, C. M. Ireland and R. G. S. Berlinck, *J. Antibiot.*, 2006, **59**, 553.
243 H. Fuwa, M. Ebine and M. Sasaki, *J. Am. Chem. Soc.*, 2006, **128**, 9648.
244 H. Fuwa, M. Ebine, A. J. Bourdelais, D. G. Baden and M. Sasaki, *J. Am. Chem. Soc.*, 2006, **128**, 16989.
245 C. G. Collison, J. Chen and R. Walvoord, *Synthesis*, 2006, 2319.
246 M. Vellutini, F. Tomi, P. Richomme and J. Casanova, *Magn. Reson. Chem.*, 2007, **45**, 355.
247 H. Chang, Y. Okada, T. Okuyama and P. Tu, *Magn. Reson. Chem.*, 2007, **45**, 611.
248 B. Ngameni, M. Touaibia, R. Patnam, A. Belkaid, P. Sonna, B. T. Ngadjui, B. Annabi and R. Roy, *Phytochemistry*, 2006, **67**, 2573.
249 D. Stærk, B. P. Chapagain, T. Lindin, Z. Wiesman and J. W. Jaroszewski, *Magn. Reson. Chem.*, 2006, **44**, 923.

250 H. K. Obied, P. Karuso, P. D. Prenzler and K. Robards, *J. Agric. Food Chem.*, 2007, **55**, 2848.
251 I. Tarascou, M.-A. Ducasse, E. J. Dufourc, D. Moskau, E. Fouquet, M. Laguerre and I. Pianet, *Magn. Reson. Chem.*, 2007, **45**, 157.
252 X. Xie, S. Tschan and F. Glorius, *Magn. Reson. Chem.*, 2007, **45**, 381.
253 A. Solladié-Cavallo, B. Ahmed, M. Schmitt and F. Garin, *C. R. Chimie*, 2005, **8**, 1975.
254 B. Reyes-Trejo, M. S. Morales-Rios and P. Joseph-Nathan, *Magn. Reson. Chem.*, 2007, **45**, 346.
255 G. N. L. Smith, S. S. Alguindigue, M. A. Khan, D. R. Powell and R. W. Taylor, *Magn. Reson. Chem.*, 2006, **44**, 901.
256 H. G. Kruger and R. Ramdhani, *Magn. Reson. Chem.*, 2006, **44**, 1058.
257 Z. Rozwadowski, *Magn. Reson. Chem.*, 2007, **45**, 605.
258 Z. Rozwadowski, *Magn. Reson. Chem.*, 2006, **44**, 881.
259 J. Košmrlj, S. Kafka, I. Leban and M. Grad, *Magn. Reson. Chem.*, 2007, **245**, 700.
260 J. Matijević-Sosa, M. Vinković and D. Vikić-Topić, *Croatica Chem. Acta*, 2006, **79**, 489.
261 I. Škorić, Z. Marinić, K. Molčanov, B. Kojić-Prodić and M. Šindler-Kulyk, *Magn. Reson. Chem.*, 2007, **45**, 680.
262 A. B. Schefer, U. Braumann, L. H. Tseng, M. Spraul, M. G. Soares, J. B. Fernandes, M. F. G. F. da Silva, P. C. Vieira and A. G. Ferreira, *J. Chromatogr. A*, 2006, **1128**, 152.
263 A. Bagno, W. Kantlehner, R. Kress, G. Saielli and E. Stoyanov, *J. Org. Chem.*, 2006, **71**, 9331.
264 J. M. Schmidt, *J. Magn. Reson.*, 2007, **186**, 34.
265 J. M. Schmidt, *J. Biomol. NMR*, 2007, **37**, 287.
266 M. Hricovíni, *Carbohyd. Res.*, 2006, **341**, 2575.
267 A. A. Grachev, A. G. Gerbst, N. E. Ustyuzhanina, A. S. Shashkov, A. I. Usov and N. E. Nifantiev, *J. Carbohyd. Chem.*, 2006, **25**, 315.
268 G. Májer, A. Borbás, T. Z. Illýs, L. Szilágyi, A. C. Bényei and A. Lipták, *Carbohyd. Res.*, 2007, **342**, 1393.
269 J. Fohrer, U. Reinscheid, M. Hennig and T. Carlomagno, *Angew. Chem. Int. Ed.*, 2006, **45**, 7033.
270 F. G. Vogt, G. P. Spoors, Q. Su, Y. W. Andemichael, H. Wang, T. C. Potter and D. J. Minick, *J. Mol. Struct.*, 2006, **797**, 5.
271 V. Lacerda Jr, G. V. J. da Silva, C. F. Tormena, R. T. Williamson and B. L. Marquez, *Magn. Reson. Chem.*, 2007, **45**, 82.
272 L. DiMichelle, K. Menzel, P. Mills, D. Frantz and T. Nelson, *Magn. Reson. Chem.*, 2006, **44**, 1041.
273 U. Grošelj, S. Rečnik, A. Meden, B. Stanovnik and J. Svete, *Acta Chim. Slov.*, 2006, **53**, 245.
274 M. M. Senior, T. M. Chan, G. Li, Y. Huang and A. Stamford, *Magn. Reson. Chem.*, 2007, **45**, 240.
275 D. Sanz, R. M. Claramunt, A. Saini, V. Kumar, R. Aggarwal, S. P. Singh, I. Alkorta and J. Elguero, *Magn. Reson. Chem.*, 2007, **45**, 513.
276 L. I. Larina, V. N. Elokhina, T. I. Yaroshenko, A. S. Nakhmanovich and G. V. Dolgushin, *Magn. Reson. Chem.*, 2007, **245**, 667.
277 A. Perona, D. Sanz, R. M. Claramunt, E. Pinilla, M. R. Torres and J. Elguero, *J. Phys. Org. Chem.*, 2007, **20**, 610.
278 V. N. Kourafalos, P. Marakos, E. Mikros, N. Pouli, J. Marek and R. Marek, *Tetrahedron*, 2006, **62**, 11987.
279 T. Massad, J. Jarvet, R. Tanner, K. Tomson, J. Smirnova, P. Palumaa, M. Sugai, T. Kohno, K. Vanatalu and P. Damberg, *J. Biomol. NMR*, 2007, **38**, 107.
280 B. Coxon, *Carbohyd. Res.*, 2007, **342**, 1044.
281 J. T. Nielsen, K. Arar and M. Petersen, *Nucleic Acids Res.*, 2006, **34**, 2006.
282 C. D. Schwieters and G. M. Clore, *Biochemistry*, 2007, **46**, 1152.
283 J. Dai, C. Punchihewa, A. Ambrus, D. Chen, R. A. Jones and D. Yang, *Nucleic Acids Res.*, 2007, **35**, 2440.
284 B. Heddi, N. Foloppe, N. Bouchemal, E. Hantz and B. Hartmann, *J. Am. Chem. Soc.*, 2006, **128**, 9170.
285 H. Jin, J. P. Loria and P. B. Moore, *Mol. Cell*, 2007, **26**, 205.
286 C. Landersjö, B. Stevensson, R. Eklund, J. Östervall, P. Söderman, G. Widmalm and A. Maliniak, *J. Biomol. NMR*, 2006, **35**, 89.
287 L. De Benassuti, T. Recca and G. Molteni, *Tetrahedron*, 2007, **63**, 3302.
288 P. Palmas, E. Girard, E. Pasquinet, T. Caron and D. Poullain, *Magn. Reson. Chem.*, 2007, **45**, 65.
289 H. Tsuchikawa, N. Matsushita, N. Matsumori, M. Murata and T. Oishi, *Tetrahedron Lett.*, 2006, **47**, 6187.

290 I. Tislerova, V. Richtr and J. Klinot, *Coll. Czech. Chem. Comm.*, 2006, **71**, 368.
291 Y. Nakabayashi, A. Erxleben, U. Létinois, G. Pratviel, B. Meunier, L. Holland and B. Lippert, *Chem. Eur. J.*, 2007, **13**, 3980.
292 M. W. Clarkson, S. A. Gilmore, M. H. Edgell and A. L. Lee, *Biochemistry*, 2006, **45**, 7693.
293 E. J. Fuentes, S. A. Gilmore, R. V. Mauldin and A. L. Lee, *J. Mol. Biol.*, 2006, **364**, 337.
294 J. Graf, P. H. Nguyen, G. Stock and H. Schwalbe, *J. Am. Chem. Soc.*, 2007, **129**, 1179.
295 F. Cordier, B. Hartmann, M. Rogowski, M. Affolter and S. Grzesiek, *J. Mol. Biol.*, 2006, **361**, 659.
296 M. E. Call, J. R. Schnell, C. Q. Xu, R. A. Lutz, J. J. Chou and K. W. Wucherpfennig, *Cell*, 2006, **127**, 355.
297 M. Cai, Y. Huang, J. Y. Suh, J. M. Luis, R. Ghirlando, R. Craige and G. M. Clore, *J. Biol. Chem.*, 2007, **282**, 14525.
298 R. D. Köhn, M. Haufe and G. Kociok-Köhn, *J. Am. Chem. Soc.*, 2006, **128**, 10682.
299 G. Navon and M. Polak, *Chem. Phys. Lett.*, 1974, **25**, 239.
300 O. G. Khudina, E. V. Shchegol'kov, Y. V. Burgart, M. I. Kodess, V. I. Saloutin, O. N. Kazheva, G. V. Shilov, O. A. D'yachenko, M. A. Grishina, V. A. Potemkin and O. N. Chupakhin, *Russ. J. Org. Chem.*, 2007, **43**, 380.
301 V. Sychrovský, Z. Vokáčový, J. Šponer, N. Špačková and B. Schneider, *J. Phys. Chem. B*, 2006, **110**, 22894.
302 M. T. Maghsoodlou, N. Hazeri, S. M. Habibi-Khorassani, L. Saghatforoush, M. K. Rofouei and M. Rezaie, *ARKIVOC*, 2006, **117**.
303 R. E. Gawley, D. B. Eddings, M. Santiago and D. A. Vicic, *Org. Biomol. Chem.*, 2006, **4**, 4285.
304 J. Bordinhão, N. M. Comerlato, G. B. Ferreira, R. A. Howie, C. X. A. da Silva and J. L. Wardell, *J. Organomet. Chem.*, 2006, **691**, 1598.
305 F. D. Rochon, C. Tessier and V. Buculei, *Inorg. Chim. Acta*, 2007, **360**, 2255.
306 F. D. Rochon and G. Massarweh, *Inorg. Chim. Acta*, 2006, **359**, 4095.
307 F. D. Rochon and C. Bonnier, *Inorg. Chim. Acta*, 2007, **360**, 461.
308 M. Kline and S. Cheatham, *Magn. Reson. Chem.*, 2007, **45**, 76.
309 W. S. Brey, D. Richardson, B. Bechtel and A. Aksenov, *Magn. Reson. Chem.*, 2007, **45**, 205.
310 N. Nakata, T. Fujita and A. Sekiguchi, *J. Am. Chem. Soc.*, 2006, **128**, 16024.
311 A. R. Katrizky, N. G. Akhmedov, J. Doskocz, P. P. Mohapatra, C. D. Hall and A. Güven, *Magn. Reson. Chem.*, 2007, **45**, 532.
312 A. I. R. N. A. Barros and A. M. S. Silva, *Magn. Reson. Chem.*, 2006, **44**, 1122.
313 A. K. Shestakova, A. V. Makarkina, O. V. Smirnova, M. M. Shtern and V. A. Chertkov, *Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1359.
314 O. G. Khudina, E. V. Shchegol'kov, Y. V. Burgart, M. I. Kodess, O. N. Kazeva, A. N. Chekhlov, G. V. Shilov, O. A. D'yachenko, V. I. Saloutin and O. N. Chupakhin, *J. Fluor. Chem.*, 2005, **126**, 1230.
315 S. Prekupec, D. Makuc, J. Plavec, L. Šuman, M. Kralj, K. Pavelić, J. Balzarini, E. De Clercq, M. Mintas and S. Raić-Malić, *J. Med. Chem.*, 2007, **50**, 3037.
316 M. C. W. Chan, S. C. F. Kui, J. M. Cole, G. J. McIntyre, S. Matsui, N. Zhu and K.-H. Tam, *Chem. Eur. J.*, 2006, **12**, 2607.
317 O. W. Howarth, J. Nelson and V. McKee, *Chem. Commun.*, 2000, 21.
318 S. El Kharrat, P. Laurent and H. Blancou, *J. Org. Chem.*, 2006, **71**, 6742.
319 J. Sýkora, V. Blechta, V. Sychrovský, J. Hetflejš, S. Šabata, L. Soukupová and J. Schraml, *Magn. Reson. Chem.*, 2006, **44**, 669.
320 P. Kuhn, C. Jeunesse, D. Matt, J. Harrowfield and L. Ricard, *Dalton Trans.*, 2006, 3454.
321 J. A. Hatnean, R. Raturi, J. Lefebvre, D. B. Leznoff, G. Lawes and S. A. Johnson, *J. Am. Chem. Soc.*, 2006, **128**, 14992.
322 S. W. Ding, Y. W. Hong, C. Y. Chen and N. C. Chang, *Biophys. Chem.*, 2006, **121**, 75.
323 N. M. Loening, C. E. Anderson, W. S. Iskenderian, C. D. Anderson, S. D. Rychnovski, M. Barfield and D. J. O'Leary, *Org. Lett.*, 2006, **8**, 5321.
324 X. S. Huang, X. Liu, K. L. Constantine, J. E. Leet and V. Roongta, *Magn. Reson. Chem.*, 2007, **45**, 447.
325 T. C. Berg, V. Bakken, L. L. Gundersen and D. Petersen, *Tetrahedron*, 2006, **62**, 6121.
326 Y. I. Kim, M. N. Manalo, L. M. Peréz and A. Li Wang, *J. Biomol. NMR*, 2006, **34**, 229.
327 M. Heller, M. Sukopp, N. Tsomaia, M. John, D. F. Mierke, B. Reif and H. Kessler, *J. Am. Chem. Soc.*, 2006, **128**, 13806.
328 M. M. Getz, A. J. Andrews, C. A. Fierke and H. M. Al-Hashimi, *RNA*, 2007, **13**, 251.
329 V. Sychrovský, J. Šponer, L. Trantírek and B. Schneider, *J. Am. Chem. Soc.*, 2006, **128**, 6823.

330 R. Wu, C. Hernandez, J. D. Odom, R. B. Dunlap and L. A. Silks, *Chem. Commun.*, 1996, 1125.
331 T. Okamura, K. Taniuchi, K. Lee, H. Yamamoto, N. Ueyama and A. Nakamura, *Inorg. Chem.*, 2006, **45**, 9374.
332 N. E. Mansfield, J. Grundy, M. P. Coles, A. G. Avent and P. B. Hitchcock, *J. Am. Chem. Soc.*, 2006, **128**, 13879.
333 M. J. Chmielewski, M. Pawlicki, N. Sprutta, L. Szterenberg and L. Latos-Grażyński, *Inorg. Chem.*, 2006, **45**, 8664.
334 J. E. Del Bene and J. Elguero, *J. Phys. Chem. A*, 2006, **110**, 7496.
335 C. G. Giribet and M. C. R. de Azúa, *J. Phys. Chem. A*, 2006, **110**, 11575.
336 J. E. Del Bene, J. Elguero and I. Alkorta, *J. Phys. Chem. A*, 2007, **111**, 3416.
337 J. Gsponer, H. Hopearuoho, A. Cavalli, C. M. Dobson and M. Vendruscolo, *J. Am. Chem. Soc.*, 2006, **128**, 15127.
338 Y. F. Wei and M. H. Werner, *J. Biomol. NMR*, 2006, **35**, 17.
339 E. de Alba and N. Tjandra, *J. Biomol. NMR*, 2006, **35**, 1.
340 A. A. Shahkhatuni, A. G. Shahkhatuni, H. A. Panosyan, A. B. Sahakyan, I.-J. L. Byeon and A. M. Gronenborn, *Magn. Reson. Chem.*, 2007, **45**, 557.
341 V. V. Klochkov, A. V. Klochkov, C. M. Thiele and S. Berger, *J. Magn. Reson.*, 2006, **179**, 58.
342 S. Dvinskikh, U. Dürr, K. Yamamoto and A. Ramamoorthy, *J. Am. Chem. Soc.*, 2006, **128**, 6326.
343 M. D. Mukrasch, M. von Bergen, J. Biernat, D. Fischer, C. Griesinger, E. Mandelkow and M. Zweckstetter, *J. Biol. Chem.*, 2007, **282**, 12230.
344 E. B. Gebel, K. Ruan, J. R. Tolman and D. Shortle, *J. Am. Chem. Soc.*, 2006, **128**, 9310.
345 S. C. Sahu, V. Simplaceanu, Q. G. Gong, N. T. Ho, J. G. Glushka, J. H. Prestegard and C. Ho, *J. Am. Chem. Soc.*, 2006, **128**, 6290.
346 A. Y. Denisov, T. Sprules, J. Fraser, G. Kozlov and K. Gehring, *Biochemistry*, 2007, **46**, 734.
347 D. K. Y. Poon, S. G. Withers and L. P. McIntosh, *J. Biol. Chem.*, 2007, **282**, 2091.
348 J. Iwahara, M. Zweckstetter and G. M. Clore, *Proc. Nat. Acad. Sci. USA*, 2006, **103**, 15062.
349 K. G. Valentine, M. S. Pometun, J. M. Kielec, R. E. Baigelman, J. K. Staub, K. L. Owens and A. J. Wand, *J. Am. Chem. Soc.*, 2006, **128**, 15930.
350 L. Skora, M. K. Cho, H. Y. Kim, S. Becker, C. O. Fernandez, M. Blackledge and M. Zweckstetter, *Angew. Chem. Int. Ed.*, 2006, **45**, 7012.
351 O. I. Obolensky, K. Schlepckow, H. Schwalbe and A. V. Solov'yov, *J. Biomol. NMR*, 2007, **39**, 1.
352 X. C. Su, T. Huber, N. E. Dixon and G. Otting, *ChemBioChem*, 2006, **7**, 1599.
353 M. U. Johansson, S. Alioth, K. F. Hu, R. Walser, R. Koebnik and K. Pervushin, *Biochemistry*, 2007, **46**, 1128.
354 S. A. Dames, R. Aregger, N. Vajpai, P. Bernado, M. Blackledge and S. Grzesiek, *J. Am. Chem. Soc.*, 2006, **128**, 13508.
355 S. Ohnishi, H. Kamikubo, M. Onitsuka, M. Kataoka and D. Shortle, *J. Am. Chem. Soc.*, 2006, **128**, 16338.
356 R. B. Best, K. Lindorff-Larsen, M. A. DePristo and M. Vendruscolo, *Proc. Nat. Acad. Sci. USA*, 2006, **103**, 10901.
357 L. C. Wang, R. R. Mettu and B. R. Donald, *J. Comput. Biol.*, 2006, **13**, 1267.
358 S. M. Douglas, J. J. Chou and W. M. Shih, *Proc. Nat. Acad. Sci. USA*, 2007, **104**, 6644.
359 M. J. Kim, S. H. Park, S. J. Opella, T. H. Marsilje, P. Y. Michellys, H. M. Seidel and S. S. Tian, *J. Biol. Chem.*, 2007, **282**, 14253.
360 G. Bouvignies, P. Markwick, R. Brüscheweiler and M. Blackledge, *J. Am. Chem. Soc.*, 2006, **128**, 15100.
361 G. Bouvignies, S. Meier, S. Grzesiek and M. Blackledge, *Angew. Chem. Int. Ed.*, 2006, **45**, 8166.
362 J. Korukottu, M. Bayrhuber, P. Montaville, V. Vijayan, Y. S. Jung, S. Becker and M. Zweckstetter, *Angew. Chem. Int. Ed.*, 2007, **46**, 1176.
363 R. A. Burton, G. Tsurupa, R. R. Hantgan, N. Tjandra and L. Medved, *Biochemistry*, 2007, **46**, 8550.
364 D. O. Cicero, A. D. Nadra, T. Eliseo, M. Dellarole, M. Paci and G. de Prat-Gay, *Biochemistry*, 2006, **45**, 6551.
365 E. Rudiño-Piñera, R. B. G. Ravelli, G. M. Sheldrick, M. H. Nanao, V. V. Korostelev, J. M. Werner, U. Schwarz-Linek, J. R. Potts and E. F. Garman, *J. Mol. Biol.*, 2007, **368**, 833.
366 H. B. Sun, H. M. Dai, J. H. Zhang, X. J. Jin, S. M. Xiong, J. Xu, J. H. Wu and Y. Y. Shi, *J. Biomol. NMR*, 2006, **36**, 295.

367 L. Volpon, C. R. Young, A. Matte and K. Gehring, *Protein Sci.*, 2006, **15**, 2435.
368 J. Song and J. L. Markley, *J. Mol. Biol.*, 2007, **366**, 155.
369 C. Sun, D. Song, R. A. Davis-Taber, L. W. Barrett, V. E. Scott, P. L. Richardson, A. Pereda-Lopez, M. E. Uchic, L. R. Solomon, M. R. Lake, K. A. Walter, P. J. Hajduk and E. T. Olejniczak, *Proc. Nat. Acad. Sci. USA*, 2007, **104**, 7875.
370 J. Dam, J. Baber, A. Grishaev, E. L. Malchiodi, P. Schuck, A. Bax and R. A. Mariuzza, *J. Mol. Biol.*, 2006, **362**, 102.
371 H. R. A. Jonker, S. Ilin, S. K. Grimm, J. Wöhnert and H. Schwalbe, *Nucleic Acids Res.*, 2007, **35**, 441.
372 S. A. McCallum, J. F. Bazan, M. Merchant, J. P. Yin, B. Pan, F. J. de Sauvage and W. J. Fairbrother, *Biochemistry*, 2006, **45**, 11974.
373 E. Lescop, Y. F. Hu, H. M. Xu, W. Hu, J. Chen, B. Xia and C. W. Jin, *J. Biol. Chem.*, 2006, **281**, 19570.
374 R. R. Wei, J. R. Schnell, N. A. Larsen, P. K. Sorger, J. J. Chou and S. C. Harrison, *Structure*, 2006, **14**, 1003.
375 A. A. Maximciuc, J. A. Putkey, Y. Shamoo and K. R. MacKenzie, *Structure*, 2006, **14**, 1547.
376 T. Cierpicki, B. Y. Liang, L. K. Tamm and J. H. Bushweller, *J. Am. Chem. Soc.*, 2006, **128**, 6947.
377 M. Marino, P. J. Zou, D. Svergun, P. Garcia, C. Edlich, B. Simon, M. Wilmanns, C. Muhle-Goll and O. Mayans, *Structure*, 2006, **14**, 1437.
378 Z. Wang, B. M. Potter, A. M. Gray, K. A. Sacksteder, B. V. Geisbrecht and J. H. Laity, *J. Mol. Biol.*, 2007, **366**, 375.
379 D. J. Kojetin, R. A. Venters, D. R. Kordys, R. J. Thompson, R. Kumar and J. Cavanagh, *Nature Struct. Mol. Biol.*, 2006, **13**, 641.
380 S. Alioth, S. Meyer, R. Dutzler and K. Pervushin, *J. Mol. Biol.*, 2007, **369**, 1163.
381 A. G. Tzakos, L. E. Easton and P. J. Lukavsky, *J. Am. Chem. Soc.*, 2006, **128**, 13344.
382 Y. J. Chu, S. Sorey, D. W. Hoffman and B. L. Iverson, *J. Am. Chem. Soc.*, 2007, **129**, 1304.
383 D. G. Sashital, V. Venditti, C. G. Angers, G. Cornilescu and S. E. Butcher, *RNA*, 2007, **13**, 328.
384 R. J. Richards, H. Wu, L. Trantirek, C. M. O'Connor, K. Collins and J. Feigon, *RNA*, 2006, **12**, 1475.
385 J. Zoll, M. Tessari, F. J. M. Van Kuppeveld, W. J. G. Melchers and H. A. Heus, *RNA*, 2007, **13**, 781.
386 S. Flodell, M. Petersen, F. Girard, J. Zdunek, K. Kidd-Ljunggren, J. Schleucher and S. Wijmenga, *Nucleic Acids Res.*, 2006, **34**, 4449.
387 S. J. Headey, H. Huang, J. K. Claridge, G. A. Soares, K. Dutta, M. Schwalbe, D. Yang and S. M. Pascal, *RNA*, 2007, **13**, 351.
388 C. Musselman, S. W. Pitt, K. Gulati, L. L. Foster, I. Andricioaei and H. M. Al-Hashimi, *J. Biomol. NMR*, 2006, **36**, 235.
389 A. Casiano-Negroni, X. Sun and H. M. Al-Hashimi, *Biochemistry*, 2007, **46**, 6525.
390 X. Sun, Q. Zhang and H. M. Al-Hashimi, *Nucleic Acids Res.*, 2007, **35**, 1698.
391 J. H. Davis, T. R. Foster, M. Tonelli and S. E. Butcher, *RNA*, 2007, **13**, 76.
392 N. B. Ulyanov, A. Mujeeb, Z. H. Du, M. Tonelli, T. G. Parslow and T. L. James, *J. Biol. Chem.*, 2006, **281**, 16168.
393 F. Yu and J. H. Prestegard, *Biophys. J.*, 2006, **91**, 1952.
394 T. Zhuang, H. Leffler and J. H. Prestegard, *Protein Sci.*, 2006, **15**, 1780.
395 C. M. Thiele, A. Marx, R. Berger, J. Fischer, M. Biel and A. Giannis, *Angew. Chem. Int. Ed.*, 2006, **45**, 4455.
396 M. A. Voda, D. E. Demco, A. Voda, T. Schauber, M. Adler, T. Dabisch, A. Adams, M. Baias and B. Blümich, *Macromolecules*, 2006, **39**, 4802.
397 M. Bertmer, M. Wang, D. E. Demco and B. Blümich, *Solid State NMR*, 2006, **30**, 45.
398 R. Valiullin and A. Khokhlov, *Phys. Rev. E*, 2006, **73**, 051605.