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^{1}H NMR Chemical Shifts and Coupling Constants of Some 3-Monosubstituted 2-Methylpropenes

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^{1}H NMR chemical shifts and proton–proton coupling constants for some 3-substituted 2-methylpropenes [$YCH_2C(Me)CH_2$, Y = H, Cl, Br, I, OH, OMe, OEt, SH, SMe, SEt, NMe_2 and NEt_2] are reported. Resonances of the olefinic protons were assigned through lanthanide-induced shifts. Chemical shifts of the olefinic protons (H_A and H_B) showed a dependence on the substituent at C-3 of the allylic fragment. Long-range allylic coupling constants ($^4J_{cisoid}$ for H_A and CH_2 and H_B and Me; $^4J_{transoid}$ for H_B and CH_2 and H_A and Me) were determined by spectral expansion and simulation. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Despite numerous studies of the ^{1}H and ^{13}C NMR spectra of alkenes, relatively limited information is available on α-substituted propenes.[1] The majority is concerned with proton–proton coupling in 2-substituted propenes[2] and in mono- and polycyclic systems,[3] while simple methallyl derivatives have received little attention.[4]

In view of the lack of information concerning substituent effects on the NMR parameters of methallyl derivatives, which are the simplest allylic compounds which exhibit four-bond coupling (cisoid and transoid) between a hydrogen and both a methyl and a methylene group, complete assignments of the ^{1}H resonances were performed, and the coupling constants of these systems were determined.

In this paper we report a study of the substituent effects on the ^{1}H NMR parameters [δ and $^nJ_{H,H}$; $n = 2$ and 4] for some 3-substituted 2-methylpropenes [$YCH_2C(Me)CH_2$, Y = H, Cl, Br, I, OH, OMe, OEt, SH, SMe, SEt, NMe_2 and NEt_2] (**2**–**12**) with the unsubstituted 2-methylpropene (**1**) taken as a reference compound.

RESULTS AND DISCUSSION

^{1}H NMR chemical shifts and corresponding substituent-induced chemical shifts (SCS) for the 3-substituted 2-methylpropenes **2**–**12** and the parent compound 2-methylpropene[1] (**1**), are given in Table 1. Lanthanide-induced shifts for the 3-methoxy derivative **6** are given in Tables 2 and 3 and the corresponding plots in Fig. 1. Nuclear Overhauser enhancements are presented in Table 4. Interproton spin–spin coupling constants are given in Table 5 and depicted in Fig. 2. Experimental and simulated spectra for compounds **7** (Y = OEt) and **8** (Y = SH) are presented in Figs 3 and 4, respectively.

Chemical shift assignments

The olefinic protons of 3-substituted 2-methylpropenes are not magnetically equivalent because they are located either on the same side (H_{cis}), or on the opposite side (H_{trans}), of the substituted methylene group. In order to assign relative chemical shifts of the *cis* and *trans* protons for these compounds, lanthanide-induced shifts (LIS) were employed. A set of experiments with the methallyl compounds **5**, **6** and **12** (Y = OH, OMe and NEt_2), which have functional groups that are able to complex with the lanthanide reagent, were performed using $Eu(fod)_3$ and $Pr(fod)_3$ as shift reagents in CCl_4 solutions. LIS for the protons were obtained from the slope of plots of the induced shifts *vs.* the molar ratios

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Table 1. ^1H NMR chemical shifts (δ, ppm from TMS)[a] and substituent-induced shifts (ppm)[b] for some 3-substituted 2-methylpropenes [$YCH_2C(Me)CH_2$]

Compound	Substituent Y	H_A[c]	H_B	YCH_2	2-CH_3	Y(H-α)	Y(H-β)
1	H[d]	4.63	4.63	1.68	1.68		
2	Cl	5.07	4.93	3.99	1.89		
		(0.44)	(0.30)	(2.31)	(0.21)		
3	Br	5.13	4.90	3.89	1.86		
		(0.50)	(0.27)	(2.21)	(0.18)		
4	I	5.22	4.90	3.89	1.94		
		(0.59)	(0.27)	(2.21)	(0.26)		
5	OH	4.94	4.79	3.94	1.72		
		(0.31)	(0.16)	(2.26)	(0.04)		
6	OMe	4.92	4.86	3.75	1.70	3.26	
		(0.29)	(0.23)	(2.07)	(0.02)		
7	OEt	4.93	4.84	3.82	1.72	3.40	1.18
		(0.30)	(0.21)	(2.14)	(0.04)		
8	SH	4.90	4.76	3.12	1.88		
		(0.27)	(0.13)	(1.44)	(0.20)		
9	SMe	4.92	4.90	3.03	1.84	1.95	
		(0.29)	(0.27)	(1.35)	(0.16)		
10	SEt	4.76	4.76	3.03	1.80	2.35	1.20
		(0.13)	(0.13)	(1.35)	(0.12)		
11	$N(Me)_2$	4.80	4.80	2.81	1.77	2.19	
		(0.17)	(0.17)	(1.13)	(0.09)		
12	$N(Et)_2$	4.84	4.77	2.88	1.71	2.58	0.98
		(0.21)	(0.14)	(1.20)	(0.03)		

[a] For CCl_4 solutions.
[b] In parentheses.
[c] H_A and H_B are *cis* and *trans* to the CH_2Y group, respectively (see Fig. 2).
[d] From Ref. 5.

[$Eu(fod)_3$ or $Pr(fod)_3$]/[methallyl compound] at a constant concentration of the methallyl compound. It is well known that the magnitude of the induced shifts is largest for protons that are closest to the binding site of the Lewis base (oxygen or nitrogen).[7] In the presence of these shift reagents for the compounds under investigation (**5**, **6** and **12**), the observed LIS was larger for H_A than H_B. Hence it was clear that H_A is *cis* to the substituted methylene group and H_B is *trans* to it. A typical example is presented in Fig. 1, which shows the variation of induced shifts with the corrected[6] molar ratios for the $Eu(fod)_3$–3-methoxy-2-methylpropene (**6**) complex [Fig. 1(a)] and for the corresponding $Pr(fod)_3$ complex [Fig. 1(b)]. The related experimental data are given in Tables 2 and 3, respectively.

Preliminary NOE experiments (100 MHz) with 3-hydroxy-2-methylpropene[8] through the irradiation of the 2-methyl protons led to an unexpected result: a positive enhancement for just the OH proton and no signals for both olefinic protons in the NOE difference spectrum. However, further experiments (400 MHz) supported the LIS studies in establishing olefinic proton assignments in spite of small enhancements for certain protons (Table 4).

Table 2. Lanthanide-induced shifts (Δν) for $Eu(fod)_3$–3-methoxy-2-methylpropene [$MeOCH_2C(Me)CH_2$] (6) solutions (CCl_4)

Sample	Molar ratio[a] ×10^3	H_A	H_B	Δν[b] CH_2	OCH_3	CH_3
1[c]	1.75	492	486	377	326	170
2	4.66	500	490	394	342	178
3	9.18	514	500	423	370	188
4	14.78	531	508	460	406	202
5	20.77	548	518	498	446	216
6	33.87	584	542	582	529	250
7	39.29	604	552	618	564	257
8	43.16	616	558	644	588	266

[a] [$Eu(fod)_3$]/[**6**] molar ratios. Compound **6** concentrations were corrected according to the procedure described in Ref. 6.
[b] In Hz, downfield from TMS.
[c] Initial sample, without the LSR.

Table 3. Lanthanide-induced shifts (Δν) for $Pr(fod)_3$–3-methoxy-2-methylpropene [$MeOCH_2C(Me)CH_2$] (6) solutions (CCl_4)

Sample	Molar ratio[a] ×10^3	H_A	H_B	Δν[b] CH_2	OCH_3	CH_3
1[c]	−0.48	492	486	377	326	170
2	3.35	483	483	364	315	165
3	6.69	479	479	351	302	160
4	12.05	471	471	334	287	154
5	16.81	464	467	317	269	149
6	23.64	452	460	294	247	140
7	30.18	439	453	268	233	130
8	36.63	431	449	247	204	123
9	45.61	417	441	215	173	112

[a] [$Pr(fod)_3$]/[**6**] molar ratios. Compound **6** concentrations were corrected according to the procedure described in Ref. 6.
[b] In Hz, downfield from TMS.
[c] Initial sample, without the LSR.

Table 4. Nuclear Overhauser effects for H_A and H_B [a] of some 3-substituted 2-methylpropenes [$YCH_2C(Me)CH_2$]

Compound	Substituent Y	H_A (irr. YCH_2)	H_B (irr. CH_3)
2	Cl	5.4%	6%
3	Br	5%	5.5%
5	OH	4%	2.2%
7	OEt	2%	2.3%
12	$N(Et)_2$	2.7%	6.7%

[a] H_A and H_B are *cis* and *trans* to the CH_2Y group, respectively (see Fig. 2).

The olefinic proton signals for compounds **2**–**12** appear in the region between 5.22 and 4.76 ppm and are thus deshielded in relation to the corresponding protons of the parent compound **1** (Table 1). Although this deshielding effect might be ascribed to Y-substituent electronegativity, no correlation could be found between the substituent induced shifts and the following parameters: Inamoto *et al.*[9] inductive effects (Δi), Swain and Lupton's field effects (F) as proposed by Hansch and Leo,[10] Charton's inductive parameters[11] (σ_i) and Charton's steric parameters[12] (ν_{ef}). This lack of correlation may be attributed either to changes in conformational equilibria with the substituent or to anisotropic effects. It is suggested that the larger substituent deshielding effects on H_A of the halogen derivatives **2**–**4** (I>Br>Cl) are due to a contribution from steric shift effects since H_B, which is further from the substituents, shows very similar chemical shifts (4.90–4.93 ppm). H_A is also deshielded in relation to H_B for the two compounds bearing an acidic proton (**5**, OH; and **8**, SH), which suggests that potential hydrogen bonding may introduce changes in the conformational equilibria, with the eclipsed (*syn*) rotamer being favoured. For the

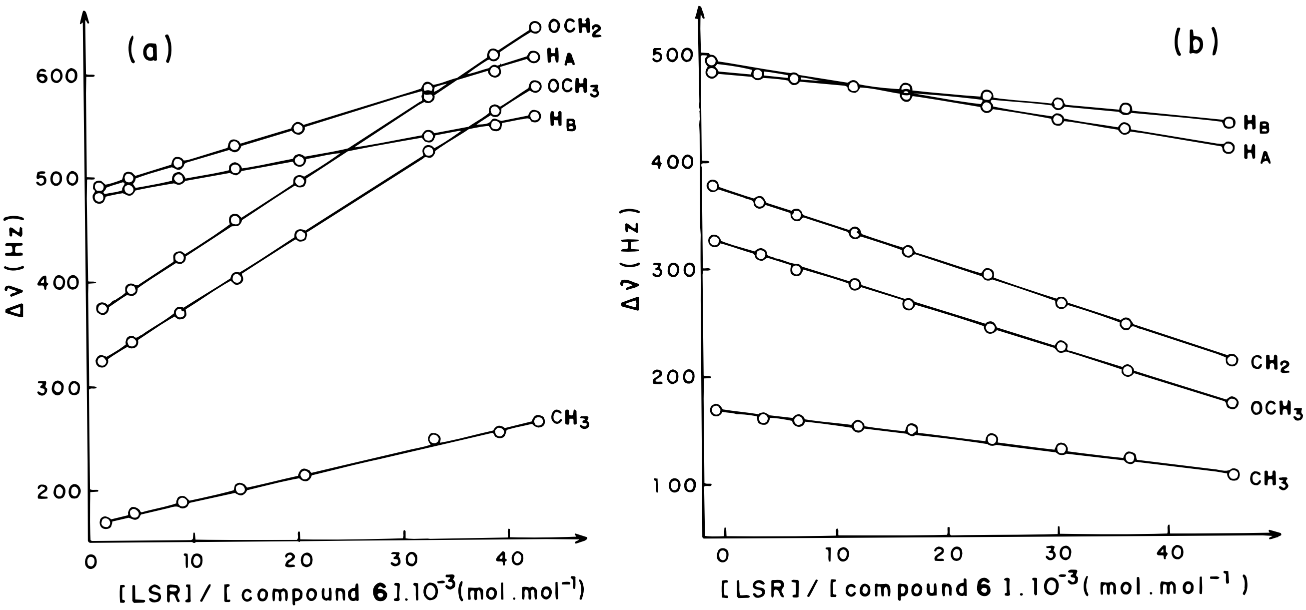

Figure 1. Correlation between the lanthanide-induced shifts $\Delta\nu$ and the molar ratio [LSR]/[**6**]: (a) $Eu(fod)_3$; (b) $Pr(fod)_3$. Compound **6** concentrations were corrected according to the procedure described in Ref. 6.

Table 5. Coupling constants [$J_{H,H}$ (Hz)] for some 3-substituted 2-methylpropenes [$YCH_2C(Me)CH_2$]

Compound	Substituent Y	$^2J_{AB}$	$^4J_{csd}$ (H_A, CH_2Y)	$^4J_{csd}$ (H_B, Me)	$^4J_{trd}$ (H_B, CH_2Y)	$^4J_{trd}$ (H_A, Me)	^4J (CH_2Y, Me)
1	H[a]			1.2		1.2	
2	Cl	1.0	0.8	1.4	0.6	0.9	
3	Br	1.0	0.8	1.4	1.1	0.9	
4	I	1.0	0.8	1.4		0.8	
5	OH	2.0	1.6	1.5	1.1	0.9	
6	OMe	2.5	1.4	1.4	0.9	1.0	0.5
7	OEt	2.0	1.4	1.5	0.9	1.0	0.4
8	SH	1.0	1.1	1.4	1.2	0.8	0.5
9	SMe	1.0	1.2	1.4	0.8	0.8	
10	SEt	1.0	1.0	1.4	0.8	0.9	
11	$N(Me)_2$	2.1	1.0	1.2	0.8	1.0	
12	$N(Et)_2$	2.3	1.0	1.6	0.8	1.0	

[a] From Ref. 5.

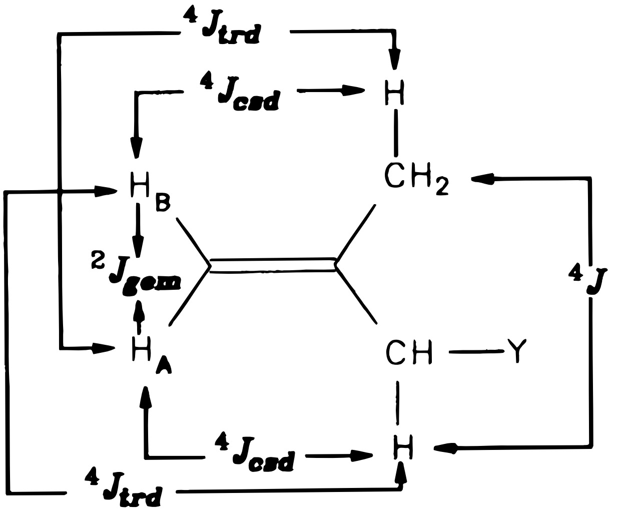

Figure 2. Notation for the coupling constants in 3-substituted 2-methylpropenes.

remaining compounds (**6**, OMe; **7**, OEt; **9**, SMe; **10**, SEt; **11**, NMe_2 and **12**, NEt_2), no significant difference was observed in the chemical shifts of H_A and H_B. The substituent effects can be visualized through the substituent induced shifts (SCS), which are also presented in Table 1.

Coupling constants

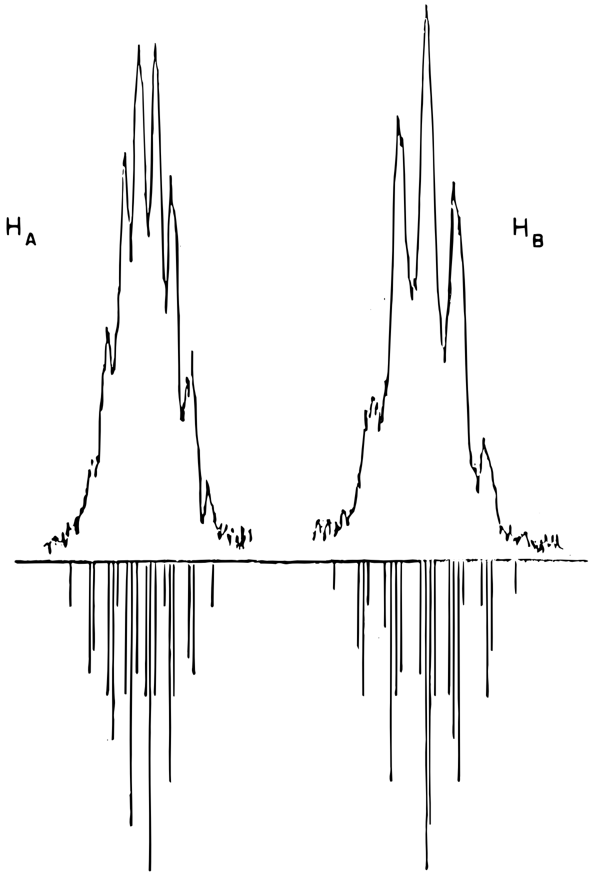

Figure 4. Expanded regions (olefinic protons only) of the ^{1}H NMR spectrum of 3-thio-2-methylpropene (**8**) (upper trace) in comparison with simulated spectra (inverted, lower trace) of the same regions via the UEAITR program.

3-Substituted 2-methylpropenes constitute an ABM_2X_3 spin system, where the AB part is related to the olefinic protons and M_2X_3 to the substituted methylene and methyl protons, respectively. Different coupling constants can be derived from the ^{1}H NMR spectra of these compounds: geminal coupling (J_{gem}) between the olefinic protons and allylic coupling between the olefinic protons and both the methylene ($^{4}J_{H,CH_2}$) and methyl protons ($^{4}J_{H,CH_3}$). Coupling through the four bonds

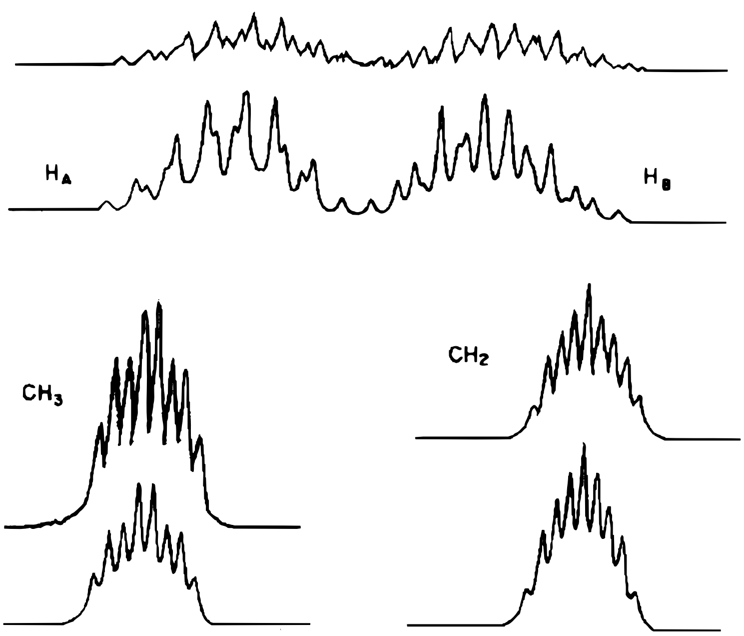

Figure 3. Expanded regions of the ^{1}H NMR spectrum of 3-ethoxy-2-methylpropene (**7**) (upper trace) in comparison with simulated spectra (lower trace) of the same regions via the NMRCAL program.

between H_A (and H_B) and the methylene or methyl protons is characterized by the constants $^4J_{\text{cisoid}}$ and $^4J_{\text{transoid}}$ (see Fig. 2, data in Table 5). For similar compounds such as 2-substituted propenes[1] and 1-substituted 2-methylpropenes,[13] the signs of allylic coupling constants have been determined to be negative. Therefore, it is assumed that the signs of allylic coupling constants of methallyl compounds are also negative. In the NMR spectra of 3-substituted 2-methylpropenes, the A and B lines are frequently superpositions of several transitions, hence multiple irradiation techniques were used for the determination of coupling constants. Simultaneous and successive irradiation of resonance frequencies of the methylene and methyl groups was performed to achieve selective decoupling. In some instances, however, low signal-to-noise ratios, irregular forms and superposition of lines hindered spectral evaluation. Therefore, coupling constants were gradually adjusted, utilizing the NMRCAL program, to reproduce graphically the experimental spectra. Typical results are presented in Fig. 3, where the experimental and simulated spectra of compound **7** are shown. For compound **8**, the corresponding results were obtained via the UEAITR program and are given in Fig. 4. Substitution in the allylic fragment leads to variations in magnitude of the allylic coupling constants. The allylic coupling constants, $^4J_{BX}$ and $^4J_{AX}$, do not change considerably with the introduction of different substituents at C-3. The range of values is shown in Table 5. The small, general range of 1.4–1.6 Hz for $^4J^{\text{csd}}_{BX}$ and actual range of 0.8–1.0 Hz for $^4J^{\text{trd}}_{AX}$ is probably due to the influence of the methyl group in the allylic fragment H—C=C—CH_3 producing an average coupling value which is unaffected by conformational changes in the rest of the molecule. However, the allylic coupling to the methylene group, $^4J^{\text{trd}}_{BM}$ and $^4J^{\text{csd}}_{AM}$, is considerably affected by substituents. The values cover the ranges 0.8–1.2 and 0.8–1.6 Hz, respectively. These variations may be due to the fact that allylic coupling constants in acyclic compounds have average values for several rotamers and that rotamer populations vary depending on the substituent present. This situation makes it difficult to determine any intrinsic substituent effects. For the methallyl compounds it was found that $^4J_{\text{csd}}$ is larger than $^4J_{\text{trd}}$, as has been shown for 2-substituted propenes.[3] Furthermore, certain methallyl compounds exhibit long-range coupling through the σ-electron framework between the methyl (X_3) and the substituted methylene (X_2) groups. This effect was observed for compounds **6**, **7** and **8**. Its existence could be due to the fact that large substituents have one preferential conformation, with a considerable population, which favours the path of coupling. Recent studies of rotational isomerism of 3-chloro-2-methylpropene[14] and 3-bromo-2-methylpropene[15] reveal that the *gauche* conformer is the predominant one for both compounds.

EXPERIMENTAL

Materials

The methallyl derivatives **2–12** were prepared as described previously.[16] Both the NMR solvents and lanthanide shift reagents, Eu(fod)$_3$ and Pr(fod)$_3$, were used without further purification.

Spectra

^{1}H NMR spectra of 0.1 M solutions of compounds **2–12** in CCl_4 with 1% TMS as an internal reference in 5 mm o.d. sample tubes were recorded at 100.1 MHz using a Varian XL-100-15 spectrometer operating in the CW mode. The following experimental conditions were employed: ^{19}F external lock; temperature, *ca.* 31 °C; spinning rate, 30 rps; spectral width, 1000 Hz (and 50 Hz for *J* measurements); sweep time, 500 s and RF, 50 dB. LIS were obtained from nine experiments for each substrate: 2-methylpropen-3-ol, 3-diethylamino- and 3-methoxy-2-methylpropene, using [LSR]/[substrate] molar ratios in the range 0–0.20 in carbon tetrachloride solutions. The samples were prepared by addition of incremental amounts of shift reagent to a solution of the substrate (incremental weighing method).[17] The transfer operations were performed in a dry-box and the spectra recorded at the same conditions as above, but with a sweep time of 250 s and an RF of 60 dB. The 400 MHz spectra were recorded in $CDCl_3$ for compounds **2**, **3**, **5**, **7** and **12** using a Varian NMR Instruments VXR-400 spectrometer. The following experimental conditions were used: pulse width, 15 μs (tip angle 45°); acquisition time, *ca.* 4 s; spectral width, 4000 Hz; number of transients, 16; and number of data points, 32 K. Nuclear Overhauser and spin decoupling experiments were performed under essentially the same conditions but with pulse delay times of 30 s and second-irradiating frequency strengths of 20 dB (NOE) and 5 dB (decoupling).

Spectral simulation

Spectra were simulated for compounds **2–12** using the indicated (non-iterative) program at the following institutions: (i) **5–7** by NMRCAL at the Universidad de Buenos Aires on a laboratory-built, 100 MHz, CW NMR spectrometer, equipped for double- and triple-resonance experiments; (ii) **3**, **4** and **8–11** by UEAITR at UNICAMP; and (iii) **2**, **5**, **7** and **12** by NMRCAL at FDA for ABM_2X_3 and ABM_2 (X-decoupled) systems. NMR chemical shifts and coupling constants were gradually changed until the graphically produced spectra matched the experimental spectra. In order to ensure that coupling constants were correctly determined, the α-methyl and the α-methylene protons were successively and simultaneously irradiated in case (i).

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