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Chemistry of nuclear spin isomers of symmetric molecules for new scientific and practical applications

Novosibirsk
September 7, 2022

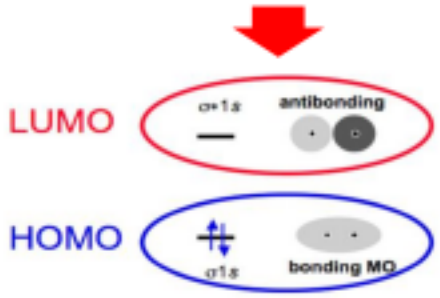
Nuclear spin isomers of symmetric molecules

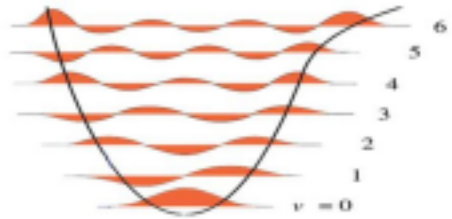
C_2H_2 H_2 H_2CO H_2O

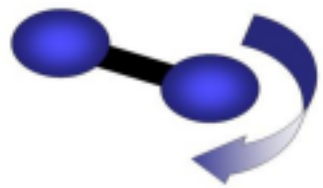
CH_4 C_2H_4 NH_3 CH_3OH

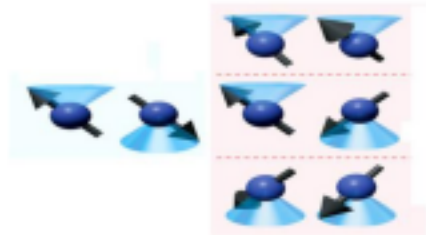
CH_3F $^{13}CH_4$ ……..

$\Psi = \Psi_{electronic} \times \Psi_{vibrational} \times \Psi_{rotational} \times \Psi_{nuclear\ spin}$





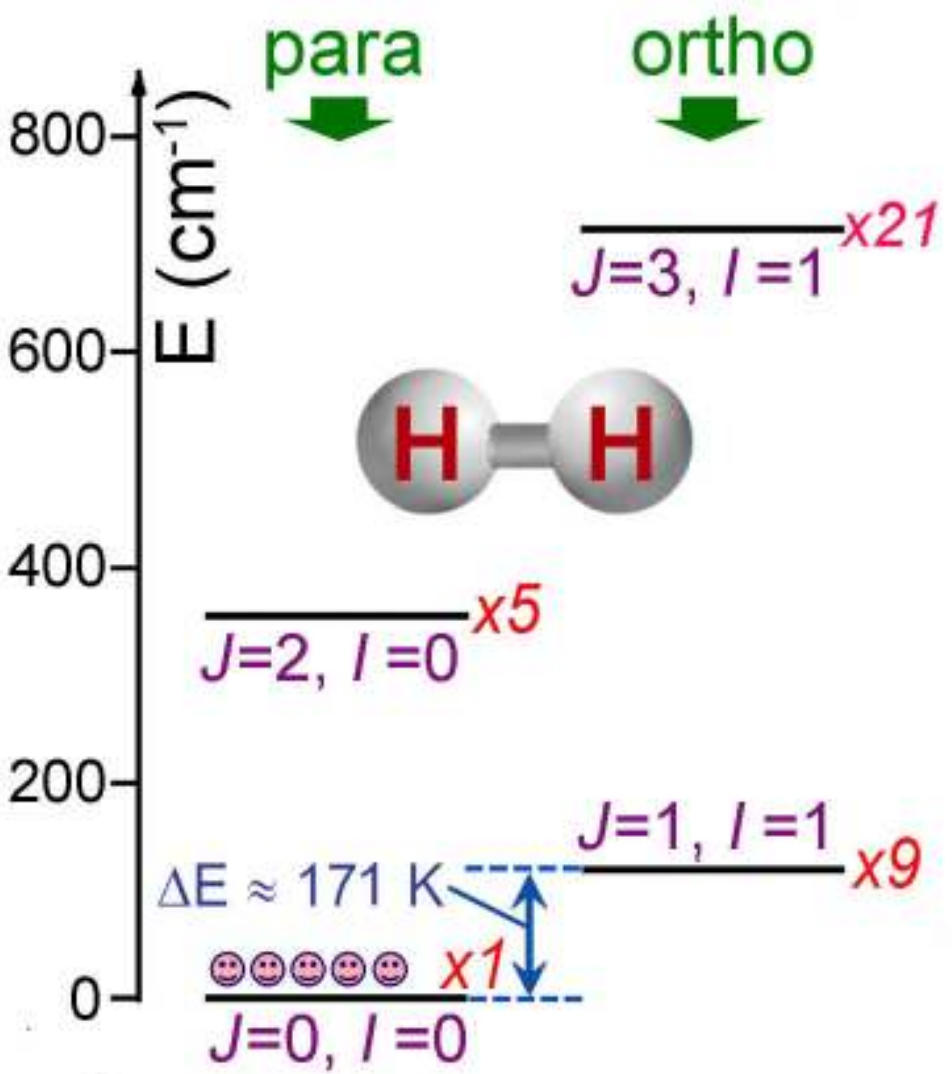




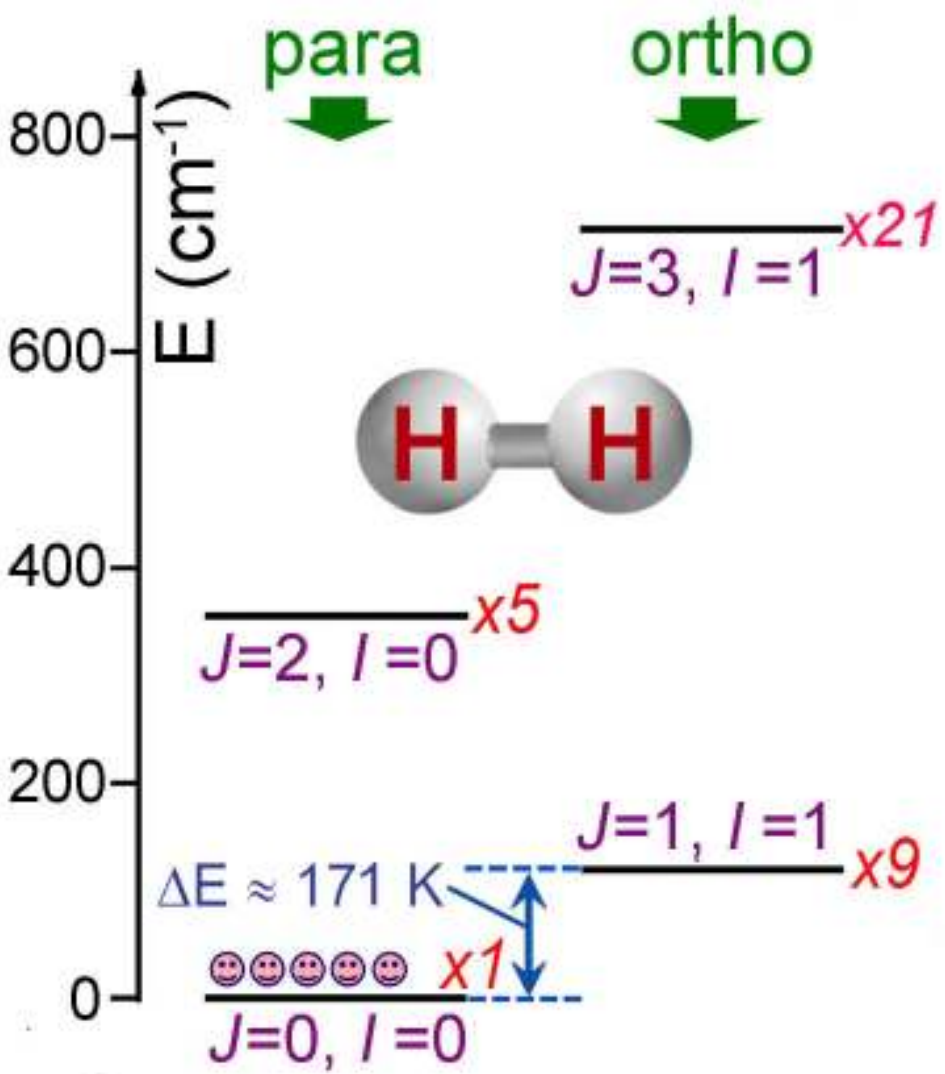
The Pauli principle (for Fermions):

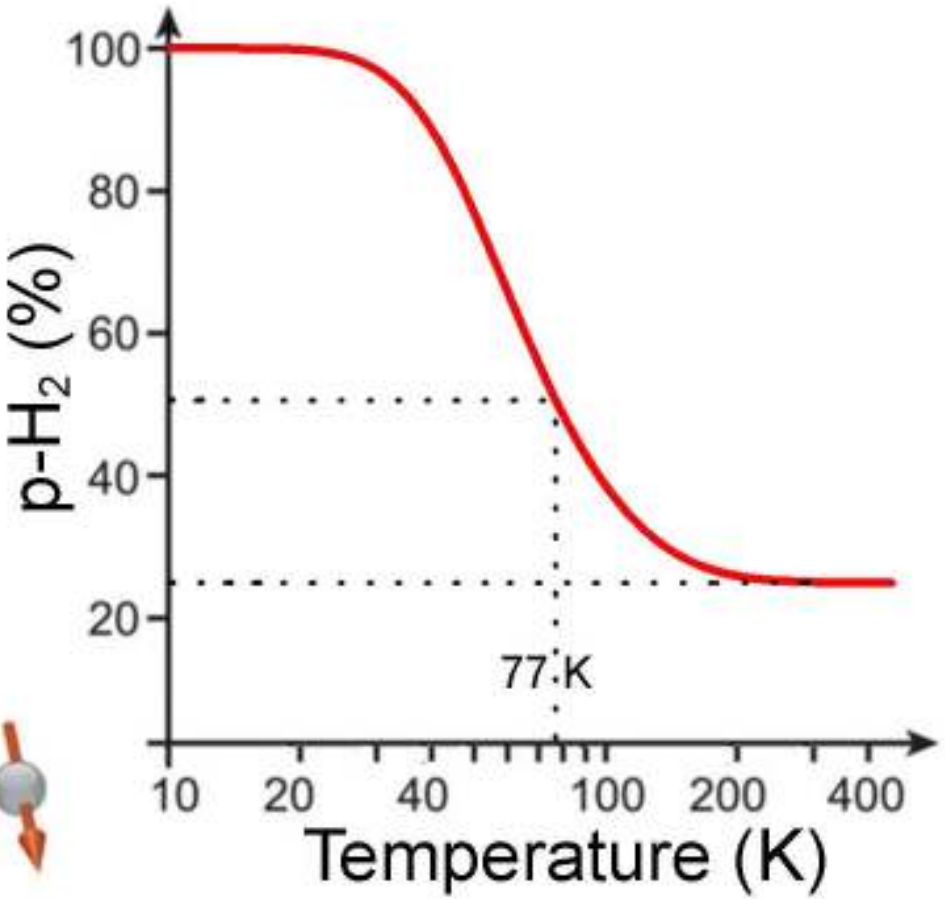
Ψ (Ha,Hb) = -Ψ (Hb,Ha)

Cryogenic spin isomer enrichment (for H_2 and D_2)

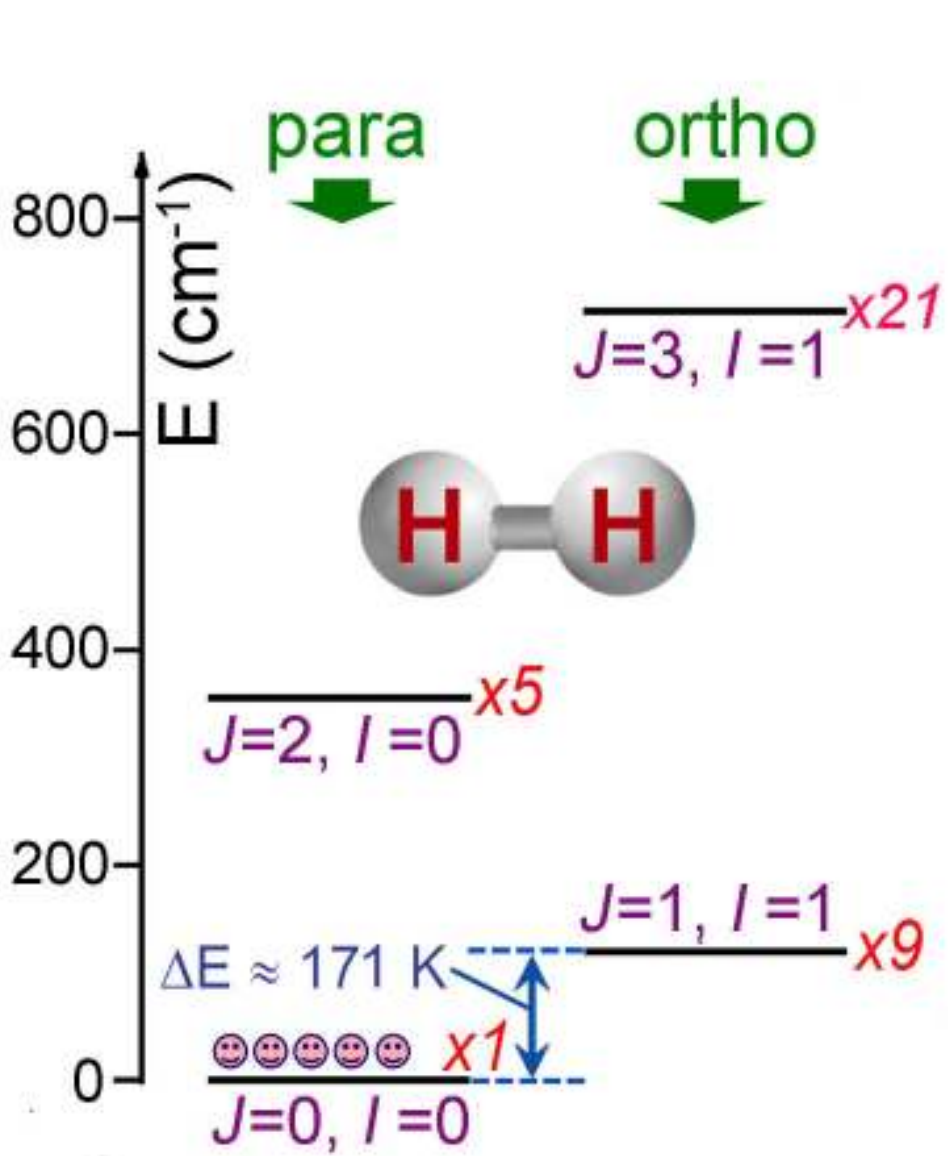


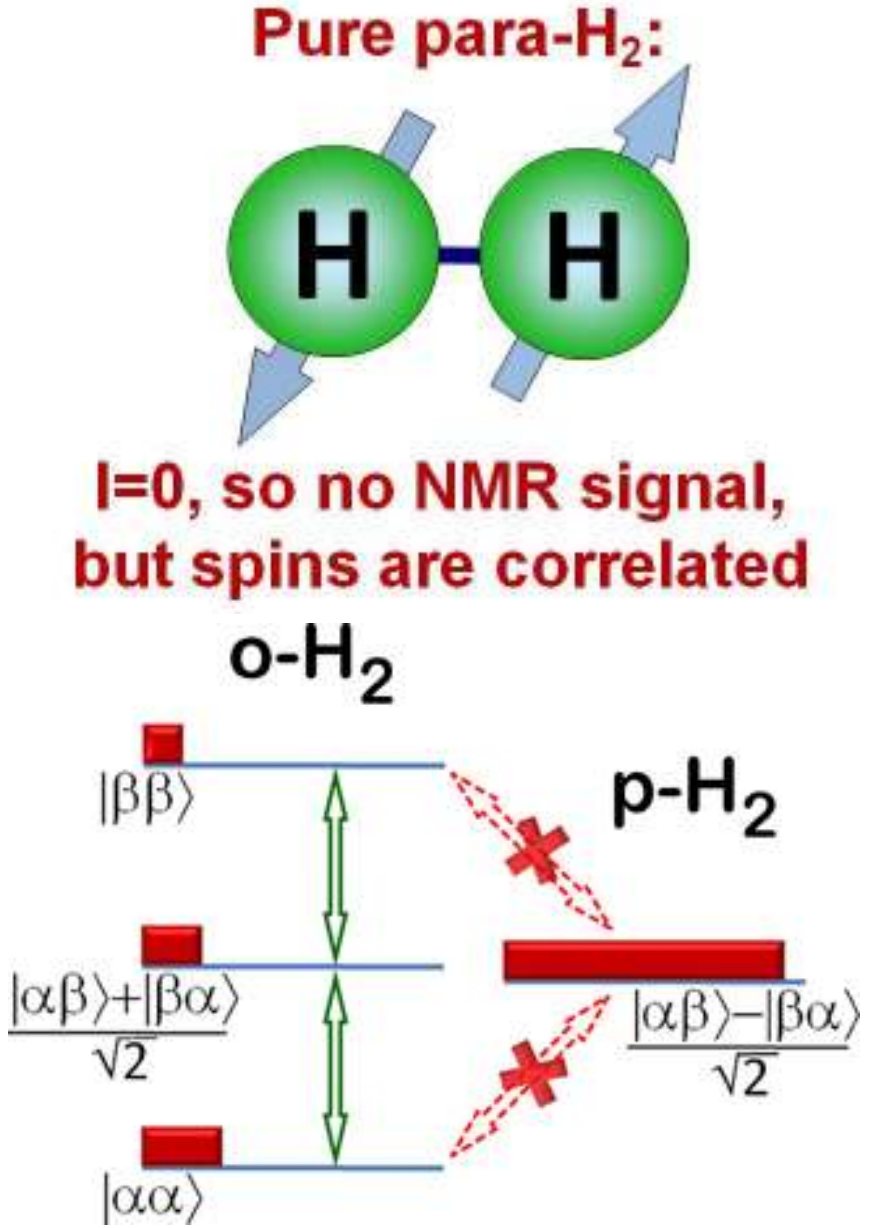
Cryogenic spin isomer enrichment (for H_2 and D_2)



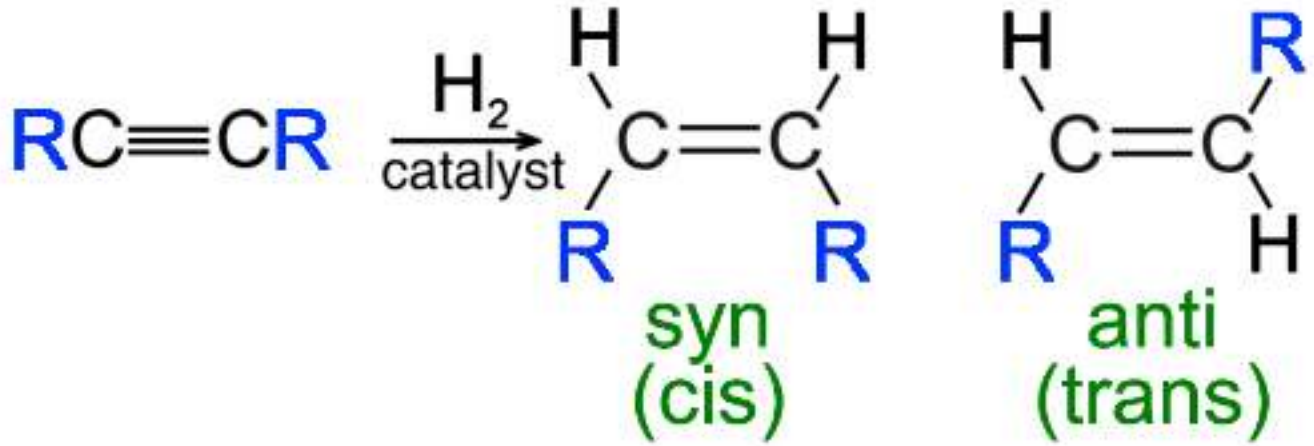


Cryogenic spin isomer enrichment (for H_2 and D_2)

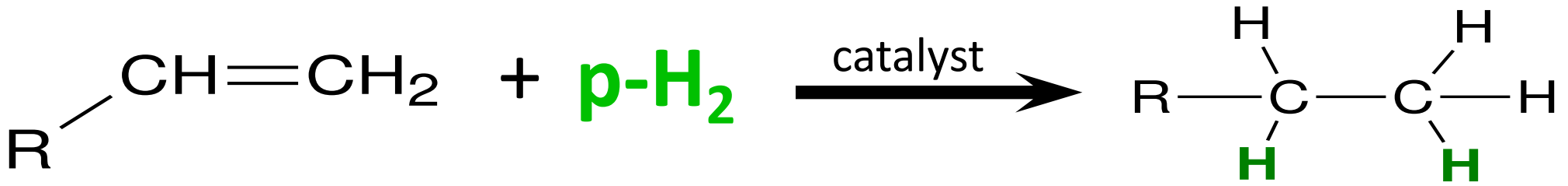




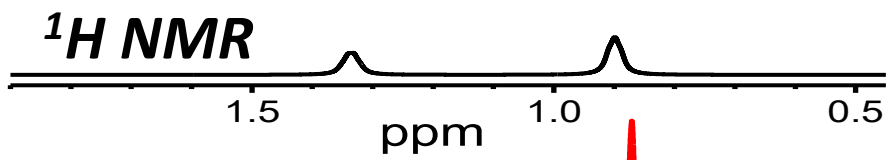
Selective semihydrogenation of alkynes with H_2



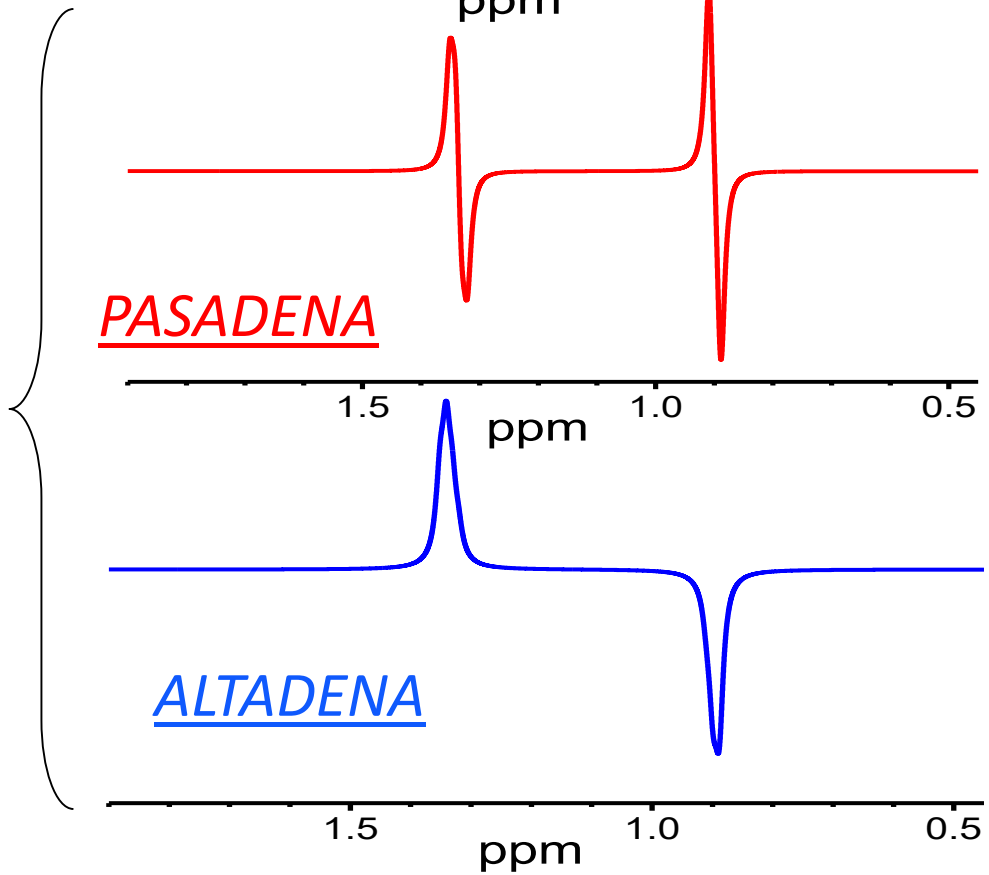
Hydrogenation with n-H_2 and with p-H_2



Non-pairwise H_2 addition



Pairwise H_2 addition



NMR signal enhancement by a factor of 10^4 and even more! (PHIP)

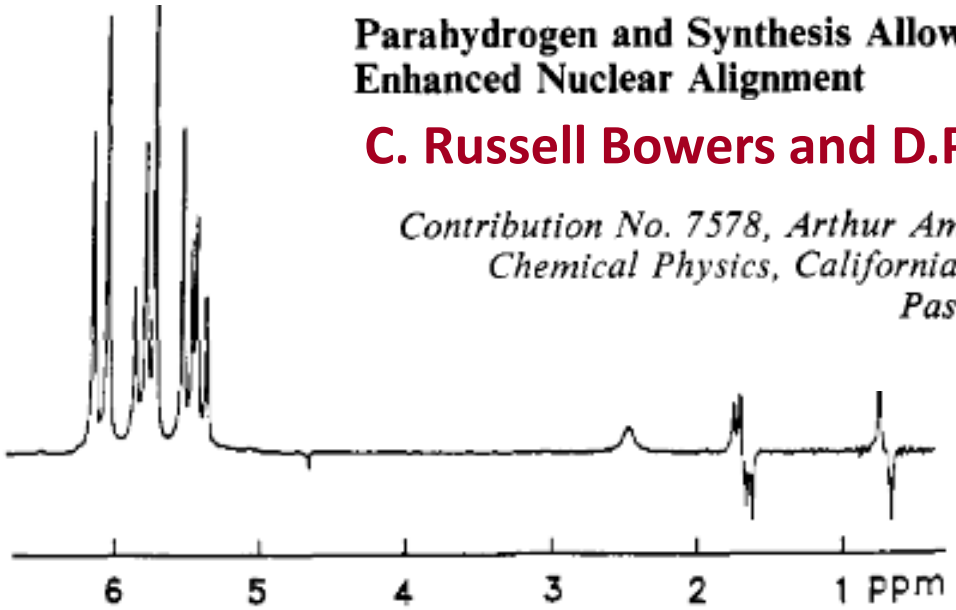
J. Am. Chem. SOC. ***1987, 109, 5541-5542***

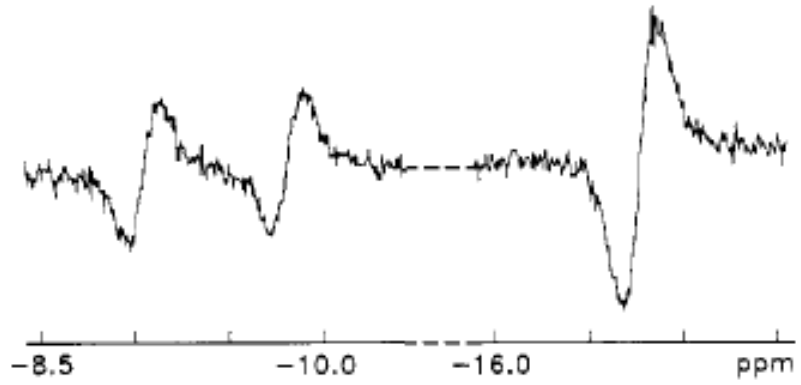
Parahydrogen and Synthesis Allow Dramatically Enhanced Nuclear Alignment

C. Russell Bowers and D.P. Weitekamp

Contribution No. 7578, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology Pasadena, California 91125

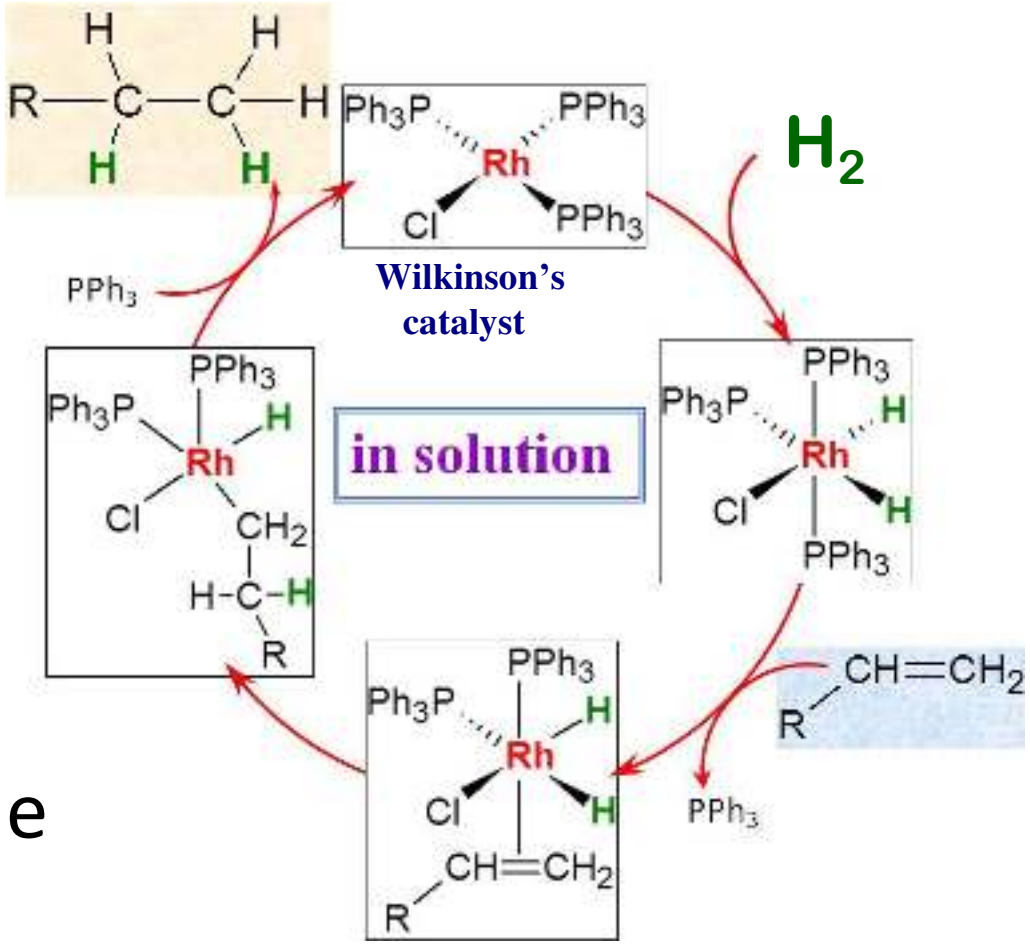
Received April 23, 1987



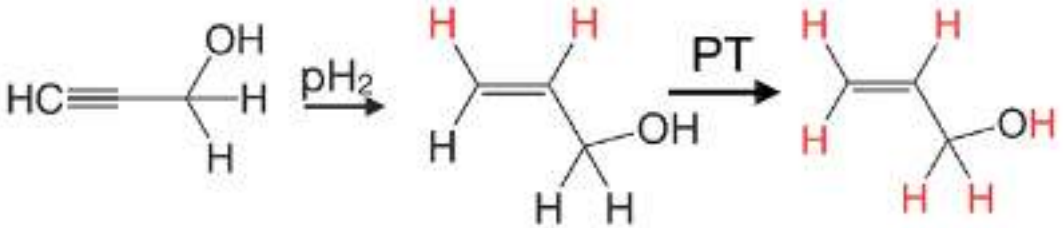


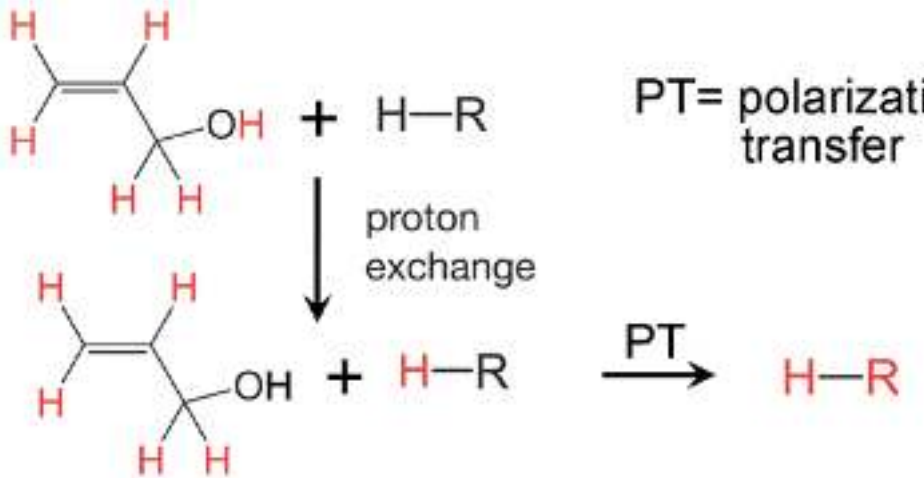
R is - C ≡ N
acrylonitrile
to propionitrile

S. Aime, J. Bargon, D. Canet ,
S.B. Duckett, R. Eisenberg,
K. Golman, H.-H. Limbach, …



PHIP-X (X is for exchange)

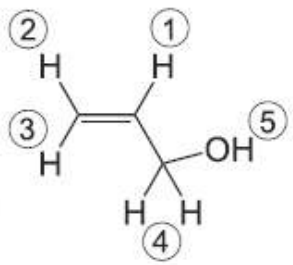


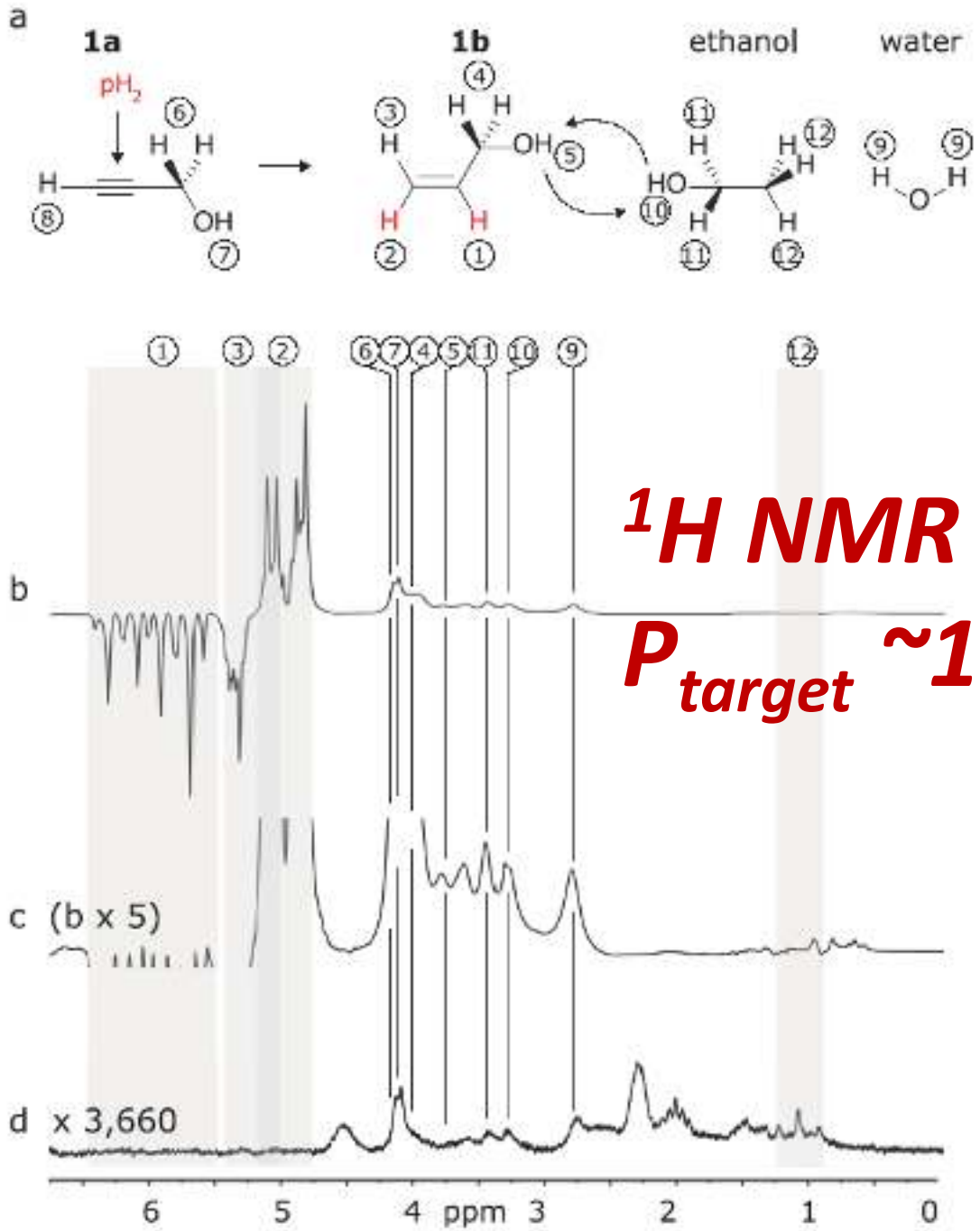


PT= polarization transfer

ID	Proton gr.	P_{HP} (%)	P'_{HP} (%)
H1	=CH-	12.6 ± 0.2	37.7
H2	H_2C=	13.3 ± 0.5	39.9
H3	H_2C=	8.9 ± 0.7	26.6
H4	-CH_2-	1.1 ± 0.1	3.4
H5	-OH	4.2 ± 0.3	12.4

Allyl alcohol

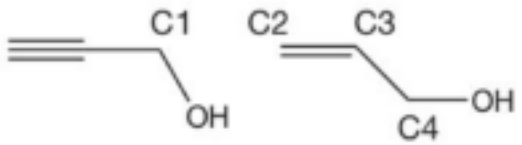




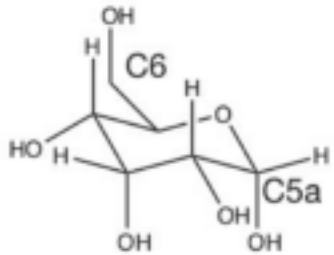
^{1}H NMR

P_{target} ~1%

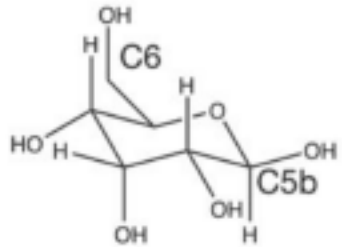
PHIP-X polarization of heteronuclei



1a 1b



α-D-Glucose

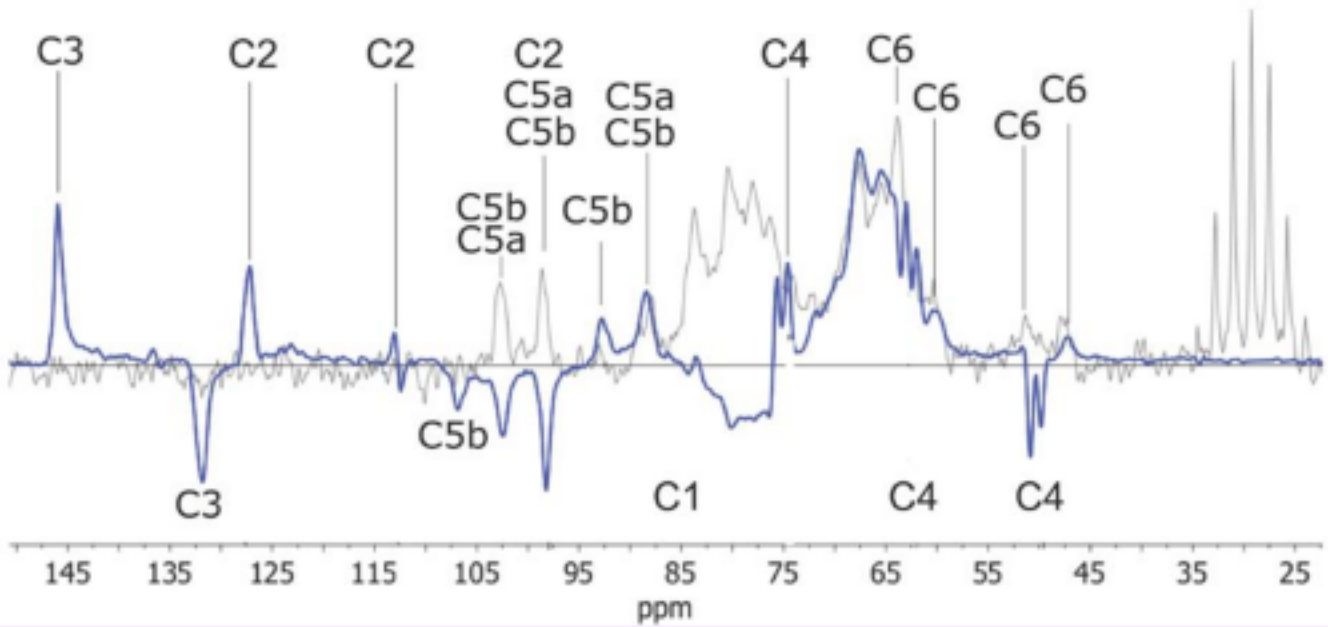


β-D-Glucose

^{13}C NMR

PHIP-X of $^{13}C_6$-D-glucose using **1b**

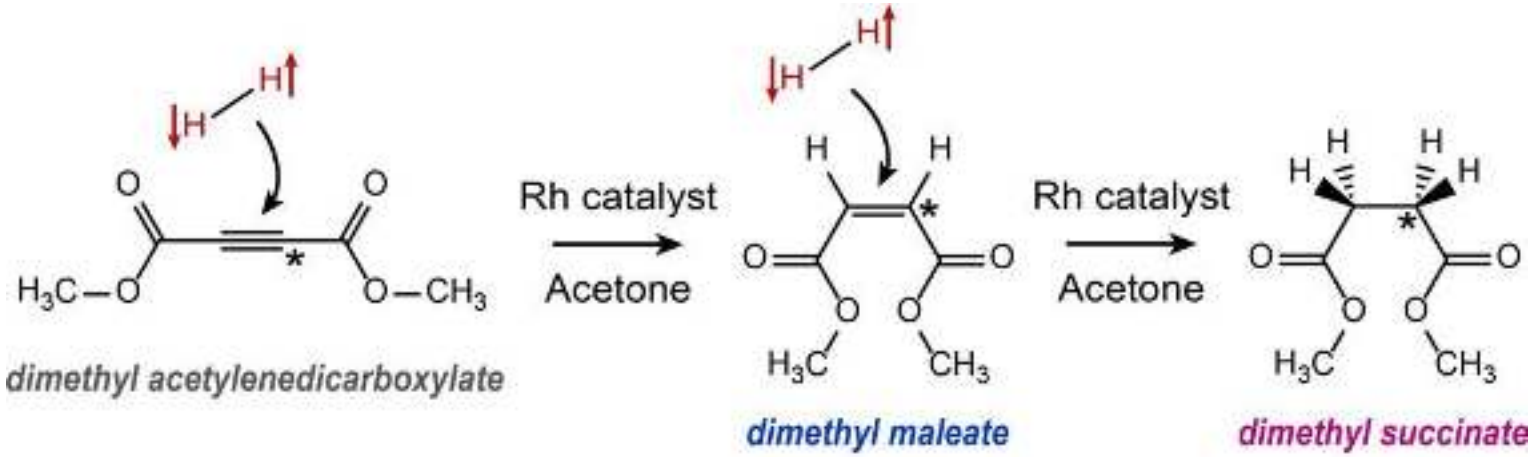
Thermal reference × 600 and 8000 scans

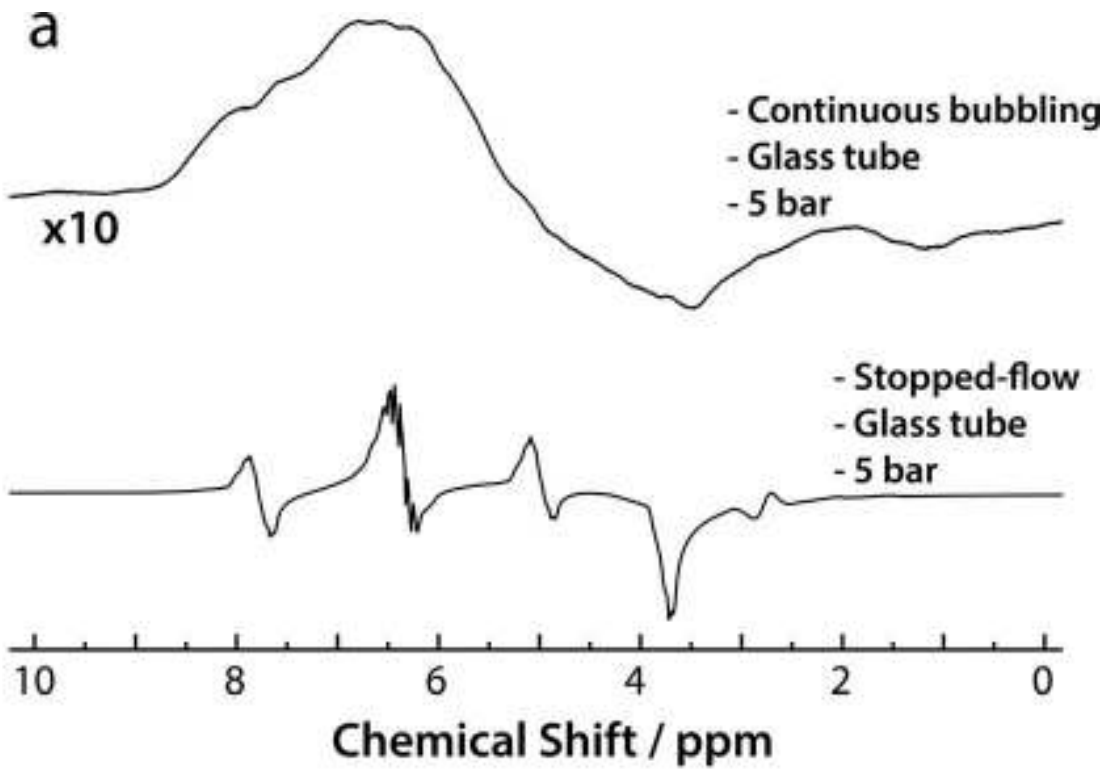


Hydrogenation
In Earth's field

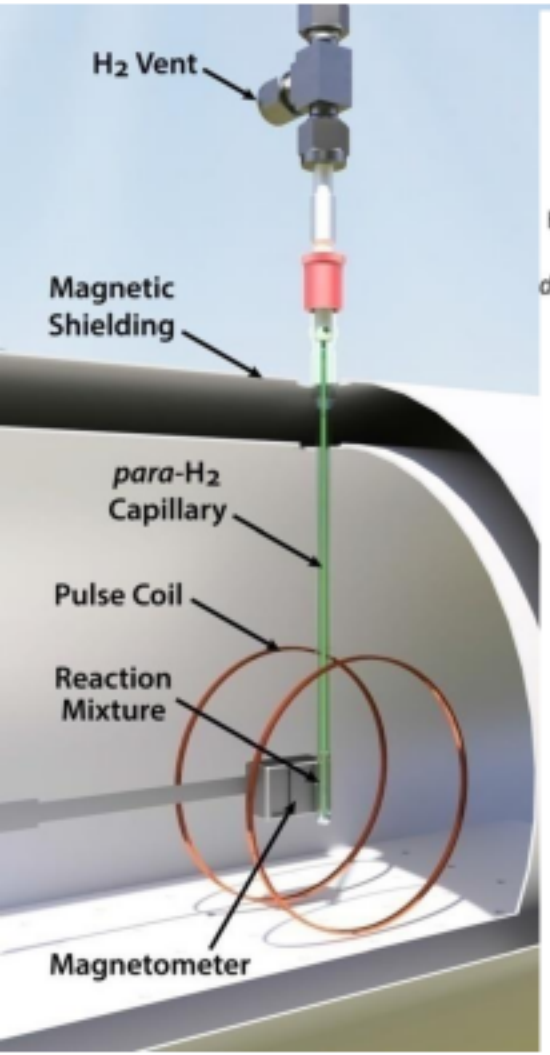
K. Them, F. Ellermann, A.N. Pravdivtsev, O.G. Salnikov, I.V. Skovpin, I.V. Koptyug, R. Herges, J.-B. Hovener. J. Am. Chem. Soc., 143, 13694-13700 (2021).

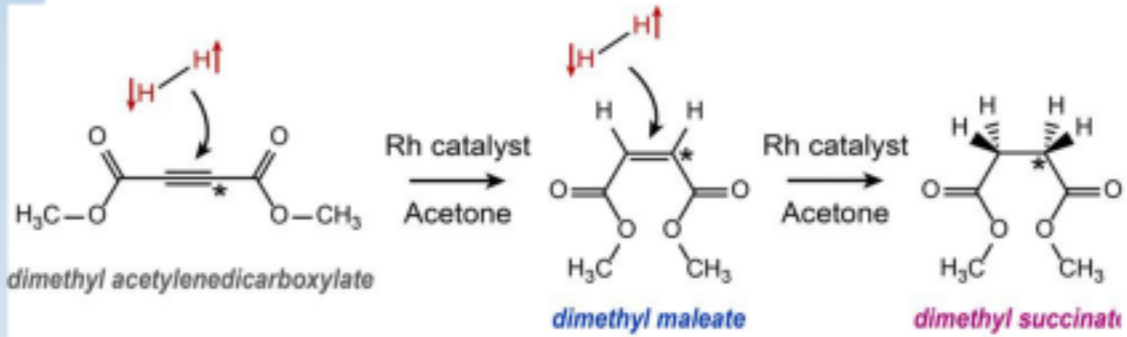
High-field NMR of homogeneous hydrogenations with H_2

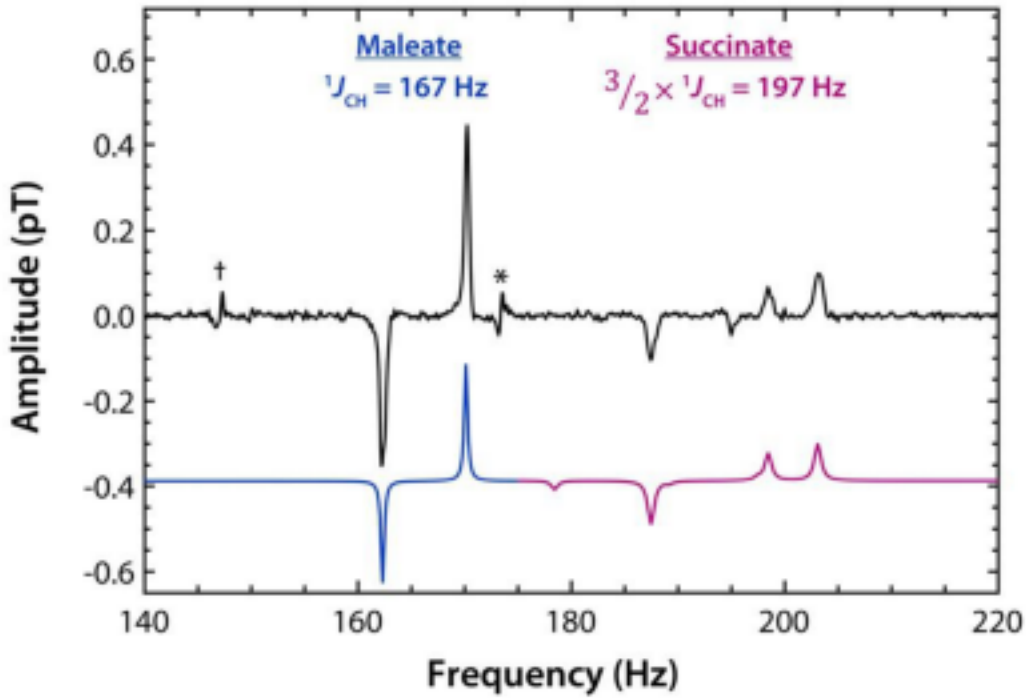




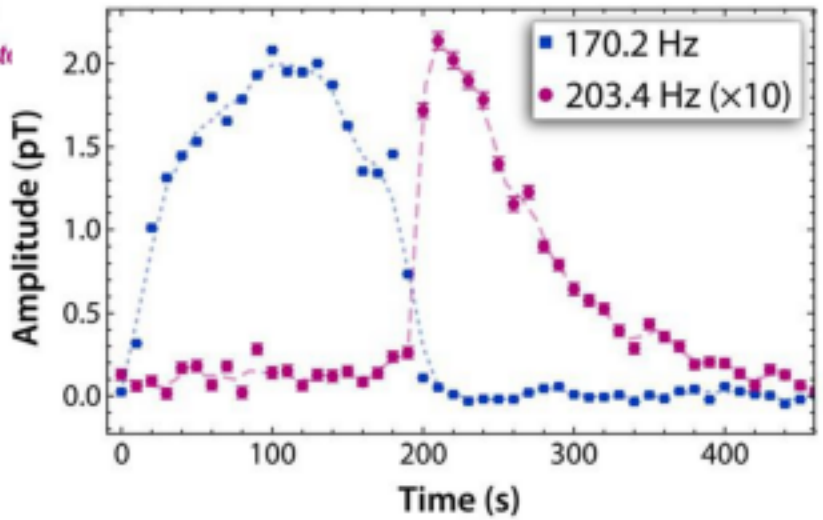
Zero-field NMR for monitoring catalytic processes







Monitoring reaction kinetics



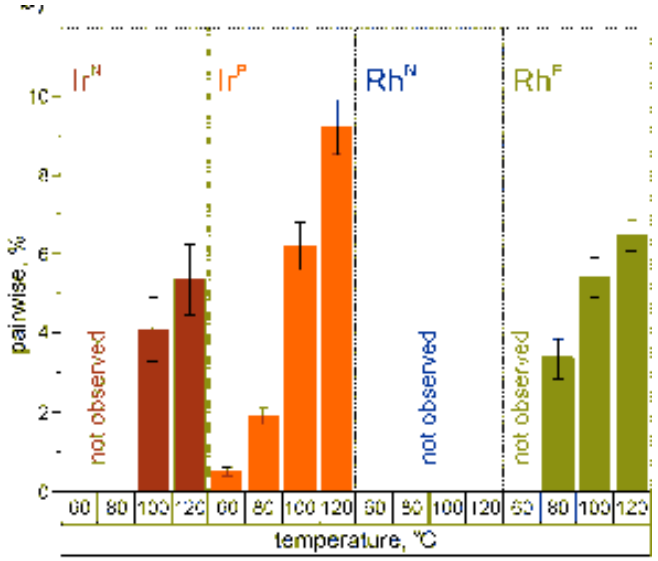
Reaction is carried out ***in a titanium tube*** (shown to the right); 5 bar p-H_2 pressure

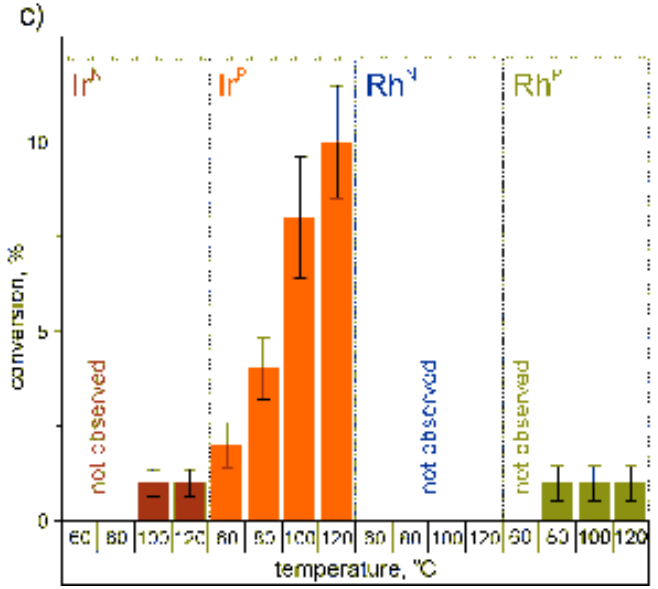
D.B. Burueva, J. Eills, J.W. Blanchard, A. Garcon, R. Picazo-Frutos, K.V. Kovtunov, I.V. Koptyug, D. Budker. Angew. Chem. Int. Ed., 59, 17026-17032 (2020)

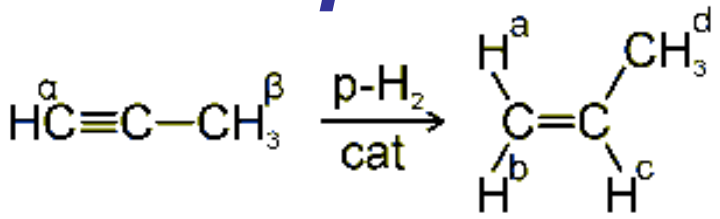
Immobilized metal complexes for PHIP

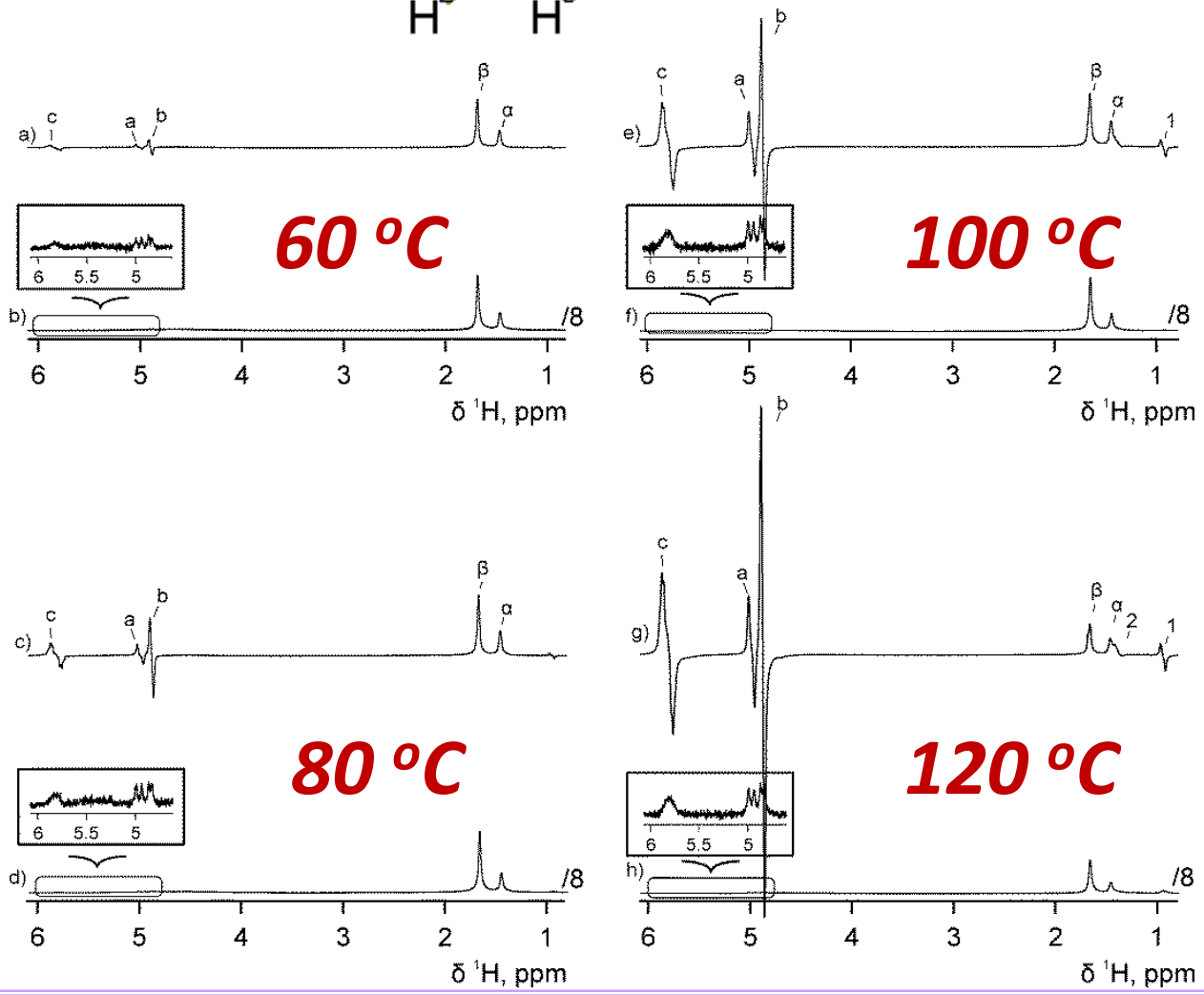
SiO_2

Rh and Ir complexes on diphenylphoshinoethyl-SiO_2 and 3-aminopropyl-SiO_2



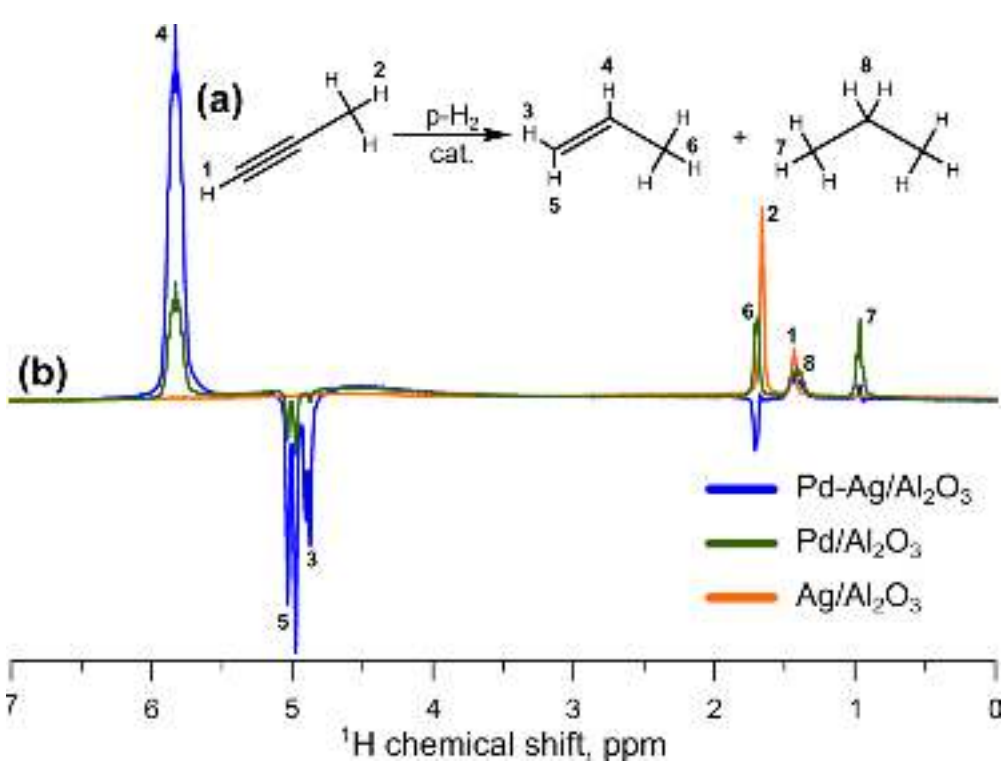






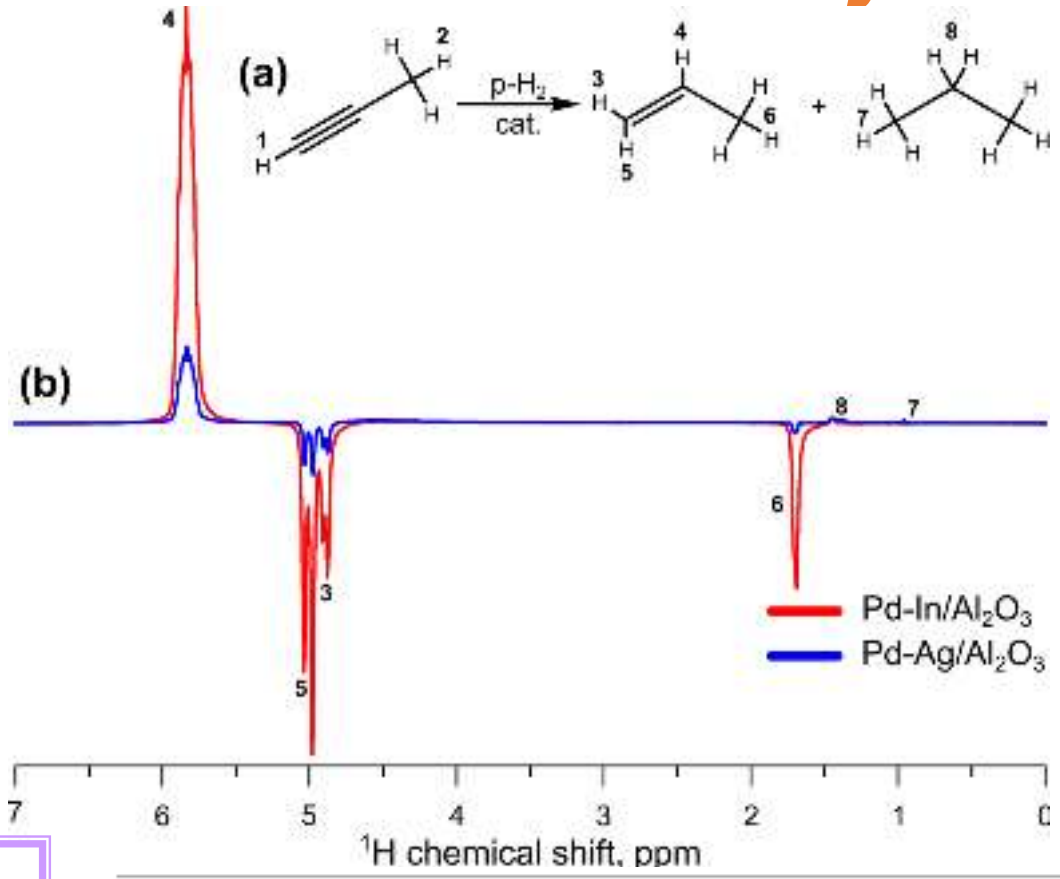
I. Skovpin, L. Kovtunova, A. Nartova, R. Kvon, V. Bukhtiyarov, I. Koptyug, Catal. Sci. Technol., 12, 3247 (2022).

HET-PHIP – monometallic vs. bimetallic catalysts



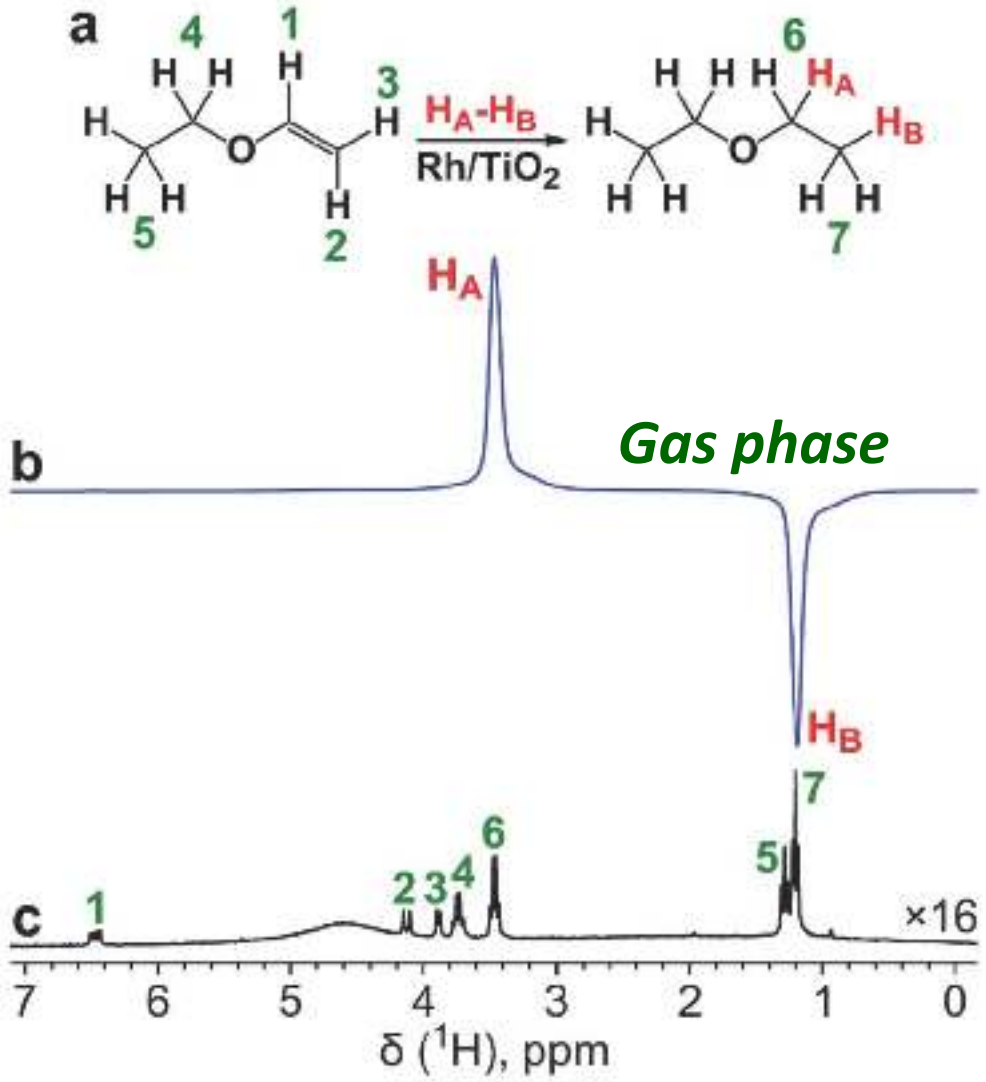
Catalyst	T (°C)	Flow rate (mL s^{-1})	X (%)	SE
Ag	200	1.3	0	–
		3.8	0	–
Pd	300	1.3	100	–
		3.8	96	3
Pd-Ag	300	1.3	96	–
		3.8	77	13

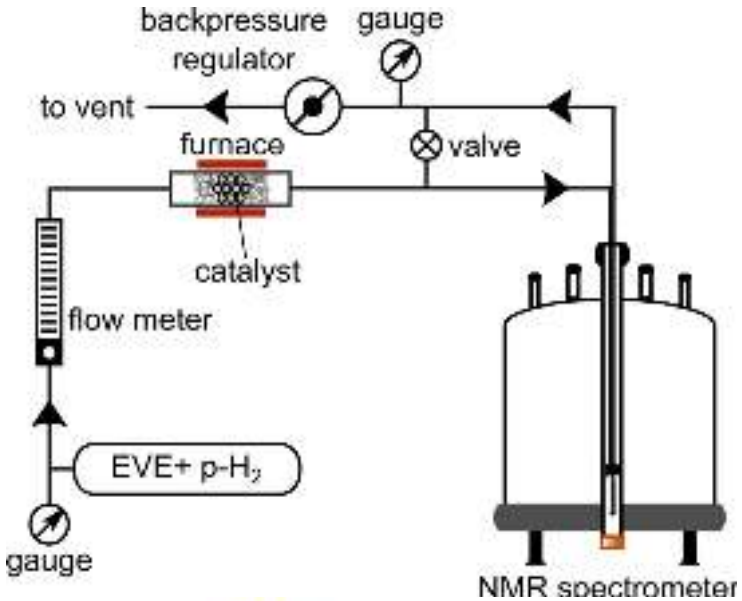
D.B. Burueva, A.Y. Stakheev, I.V. Koptyug. Magn. Reson., 2, 93-103 (2021)

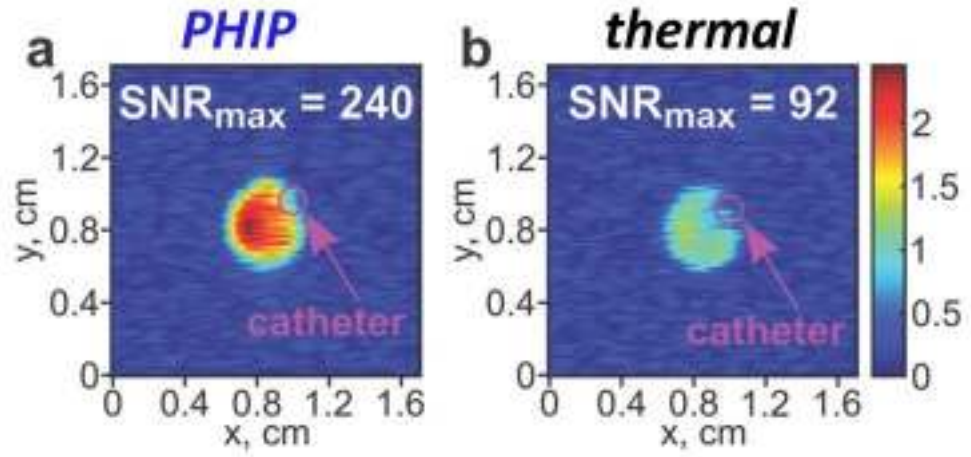


Catalyst	T (°C)	Flow rate (mL s^{-1})	X (%)	$S_{propene}$ (%)	SE
Pd-In	300	1.3	89	98	4
		3.8	45	96	89
	400	1.3	62	94	3
		3.8	19	91	**107**

HET-PHIP of diethyl ether, an inhalable contrast agent

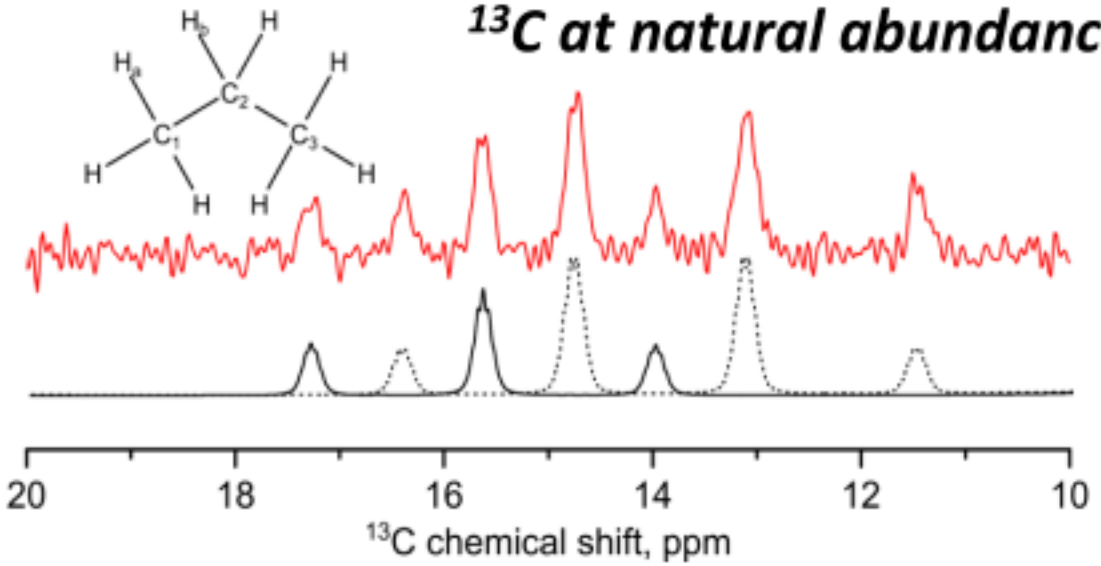




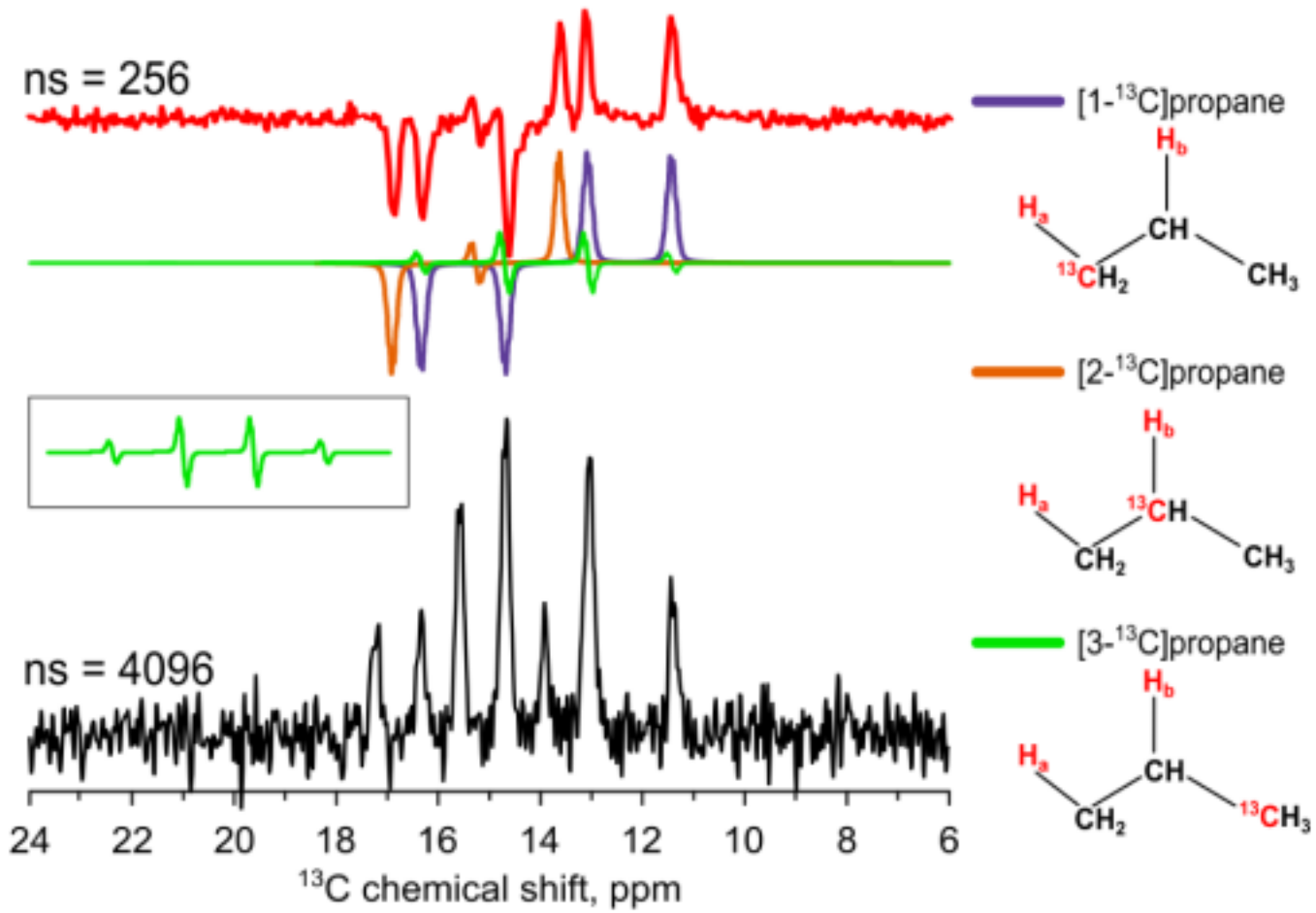


O.G. Salnikov, A. Svyatova, L.M. Kovtunova, N.V. Chukanov, V.I. Bukhtiyarov, K.V. Kovtunov, E.Y. Chekmenev, I.V. Koptyug. Chem. Eur. J., 27, 1316-1322 (2021). HOT PAPER

PH-INEPT: ^{13}C hyperpolarization of gases

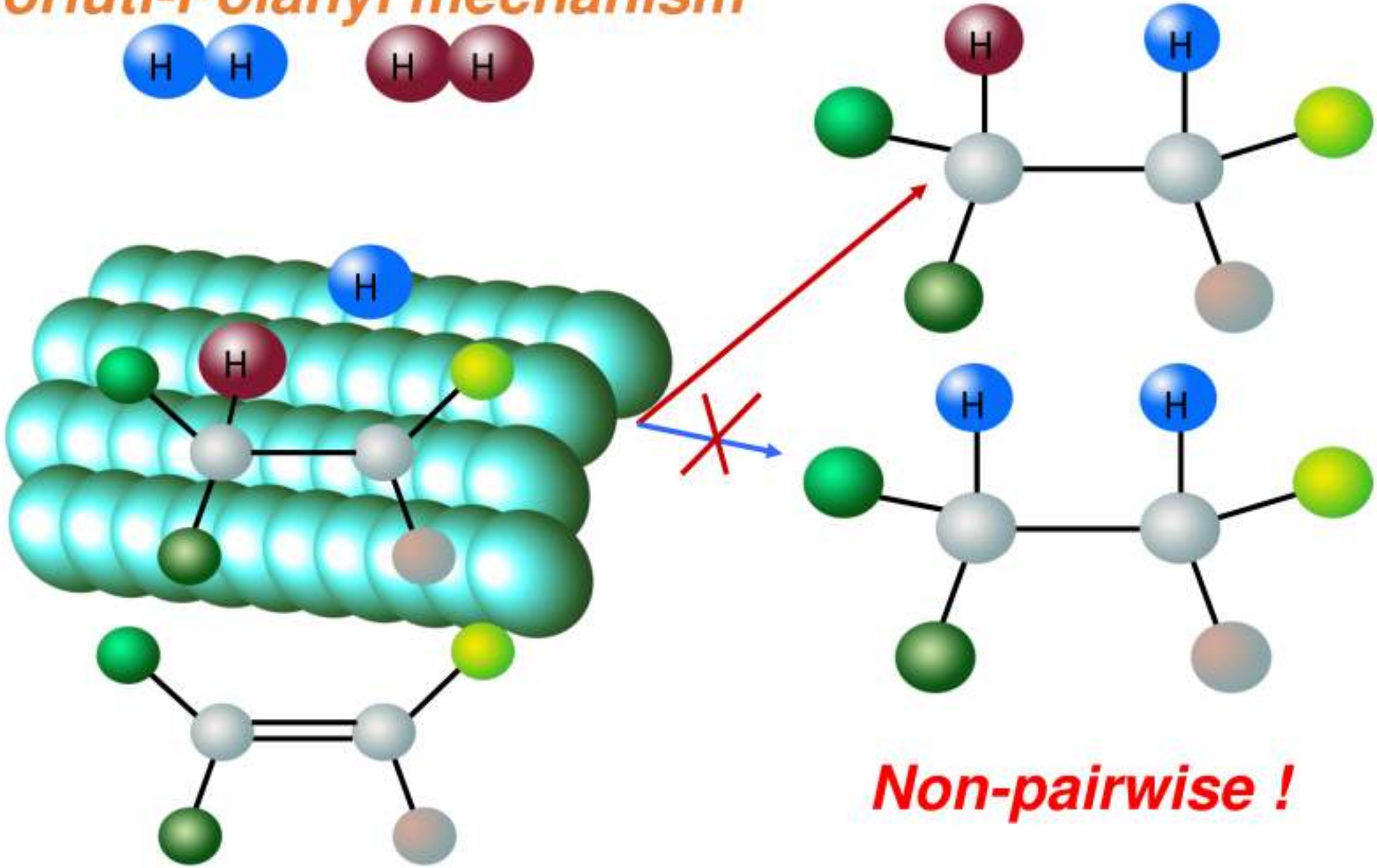


	^{13}C NMR	
	CH_2	CH_3
Enhancement	13	29
Polarization, %	0.030±0.006%	0.07±0.01%
T1, ms	140±10	149±8



D.B. Burueva, V.P. Kozinenko, S.V. Sviyazov, L.M. Kovtunova, V.I. Bukhtiyarov, E.Y. Chekmenev, O.G. Salnikov, K.V. Kovtunov, I.V. Koptyug. AMR 53, 653-669 (2022).

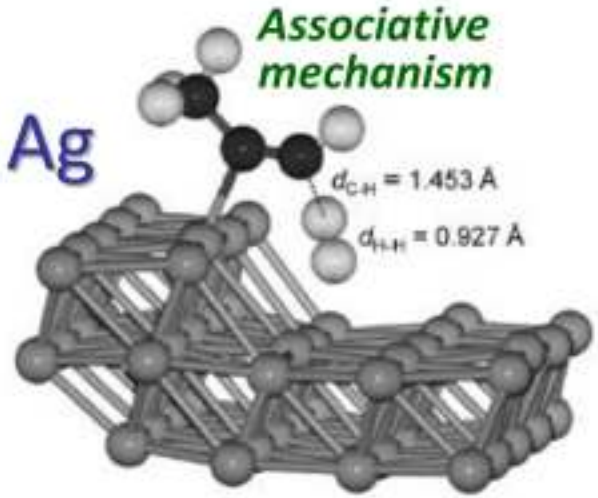
The Horiuti-Polanyi mechanism

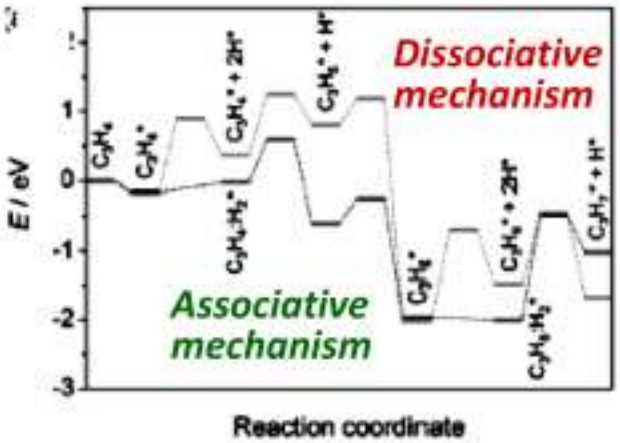


Non-pairwise !

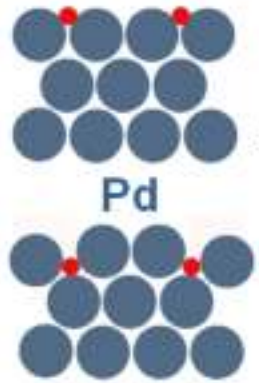
Mechanisms of heterogeneous hydrogenations

M. Garcia-Melchor, L. Bellarosa, N. Lopez, ACS Catal. 4, (2015) 4015





G. Vile, D. Baudouin, I.N. Remediakis, C. Coperet, N. Lopez, J. Perez-Ramirez, ChemCatChem, 5, 3750 (2013).

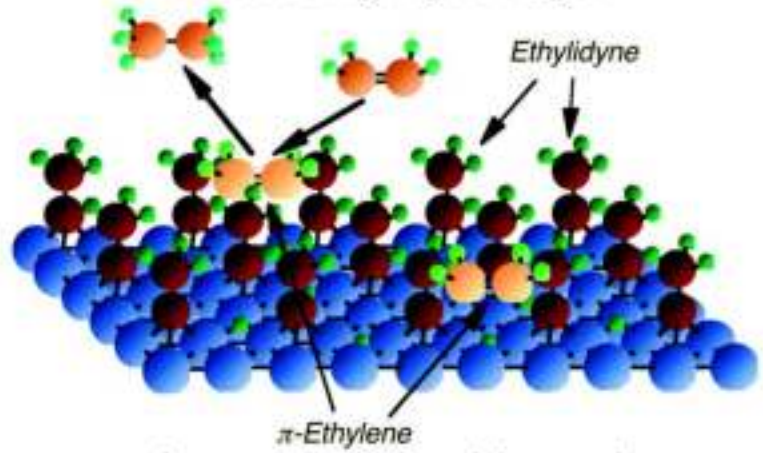


Surface H:
Selective
Less reactive

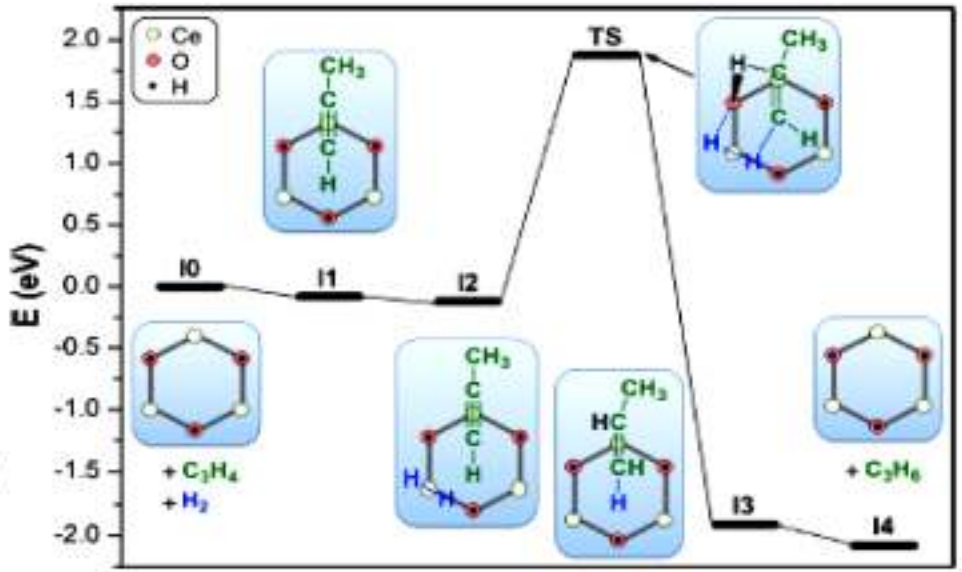
Subsurface H:
Non-selective
More reactive

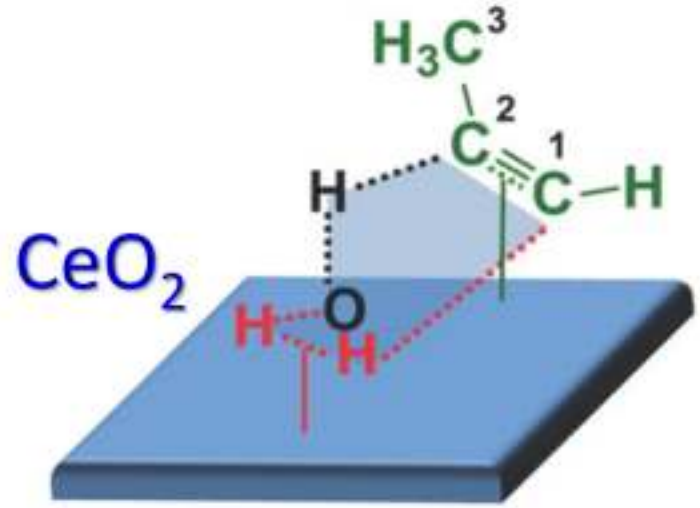
Ethylene Hydrogenation/Pt(111)

Role of Ethylidyne Layer



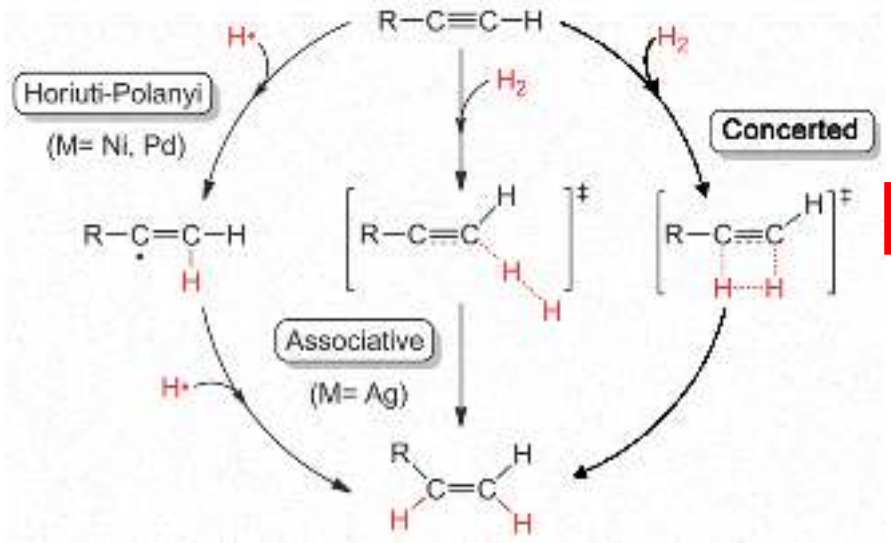
S.J. Thomson, G. Webb. J. Chem. Soc., Chem. Commun. 526 (1976).





Mechanisms of heterogeneous hydrogenations

M. Garcia-Melchor, L. Bellarosa, N. Lopez, ACS Catal. 4, (2015) 4015

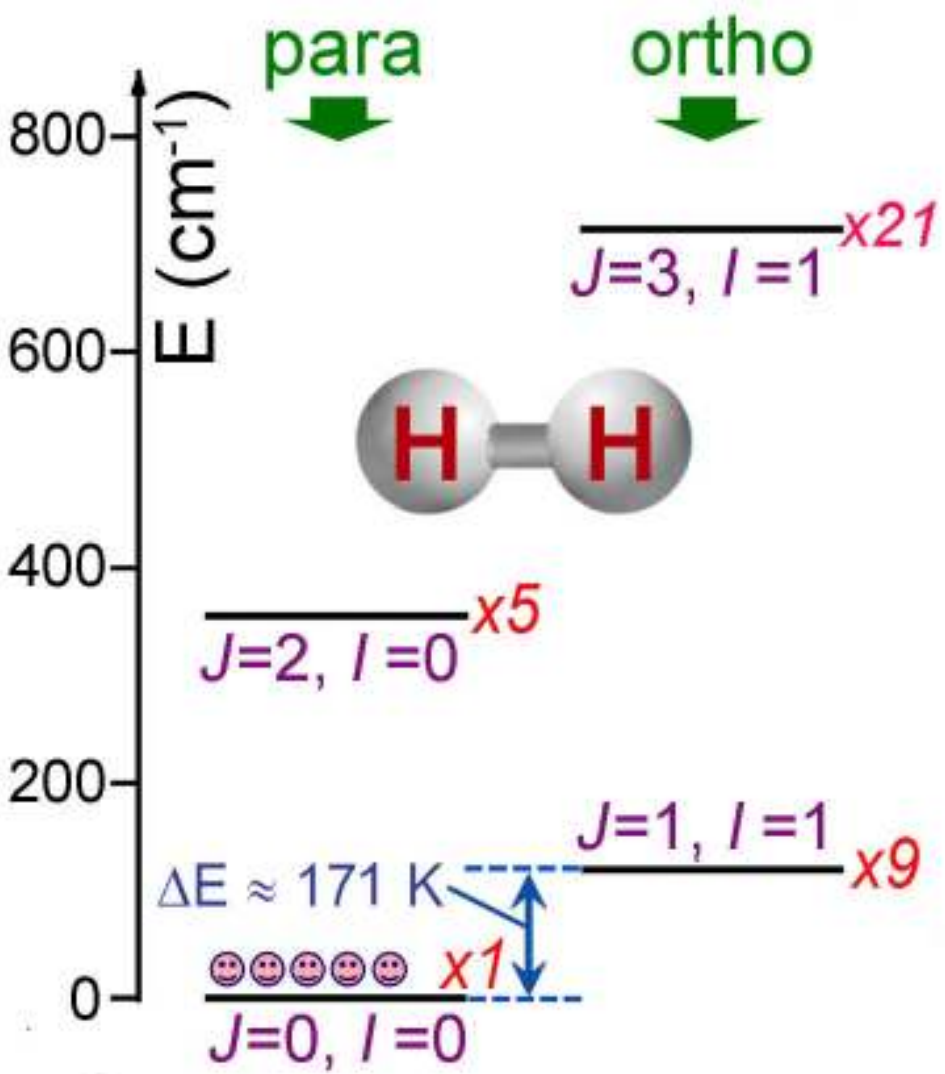


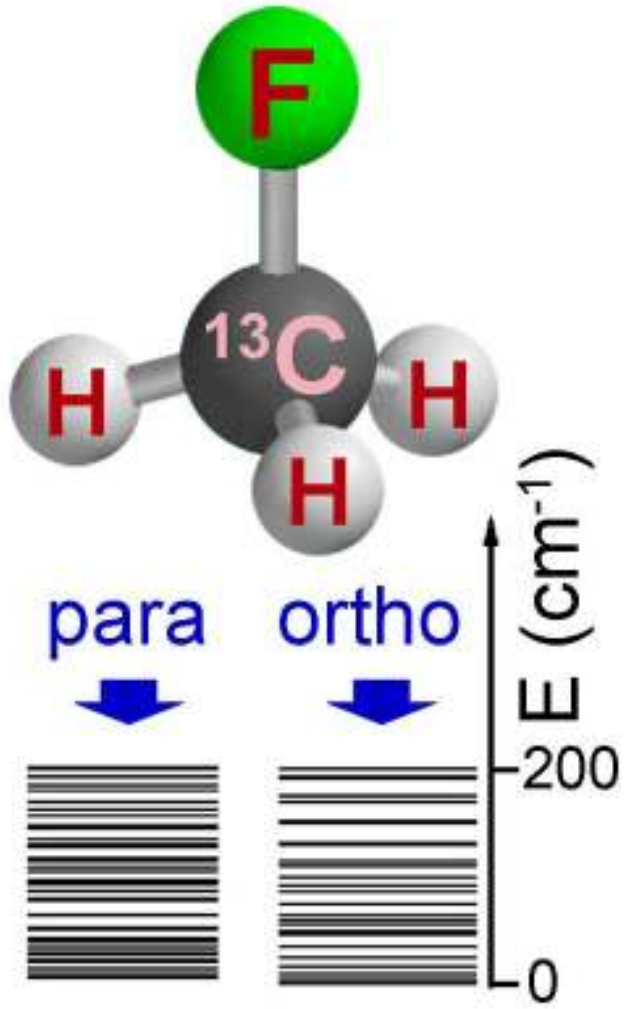
Horiuti-Polanyi ⟺

Non-Horiuti-Polanyi:

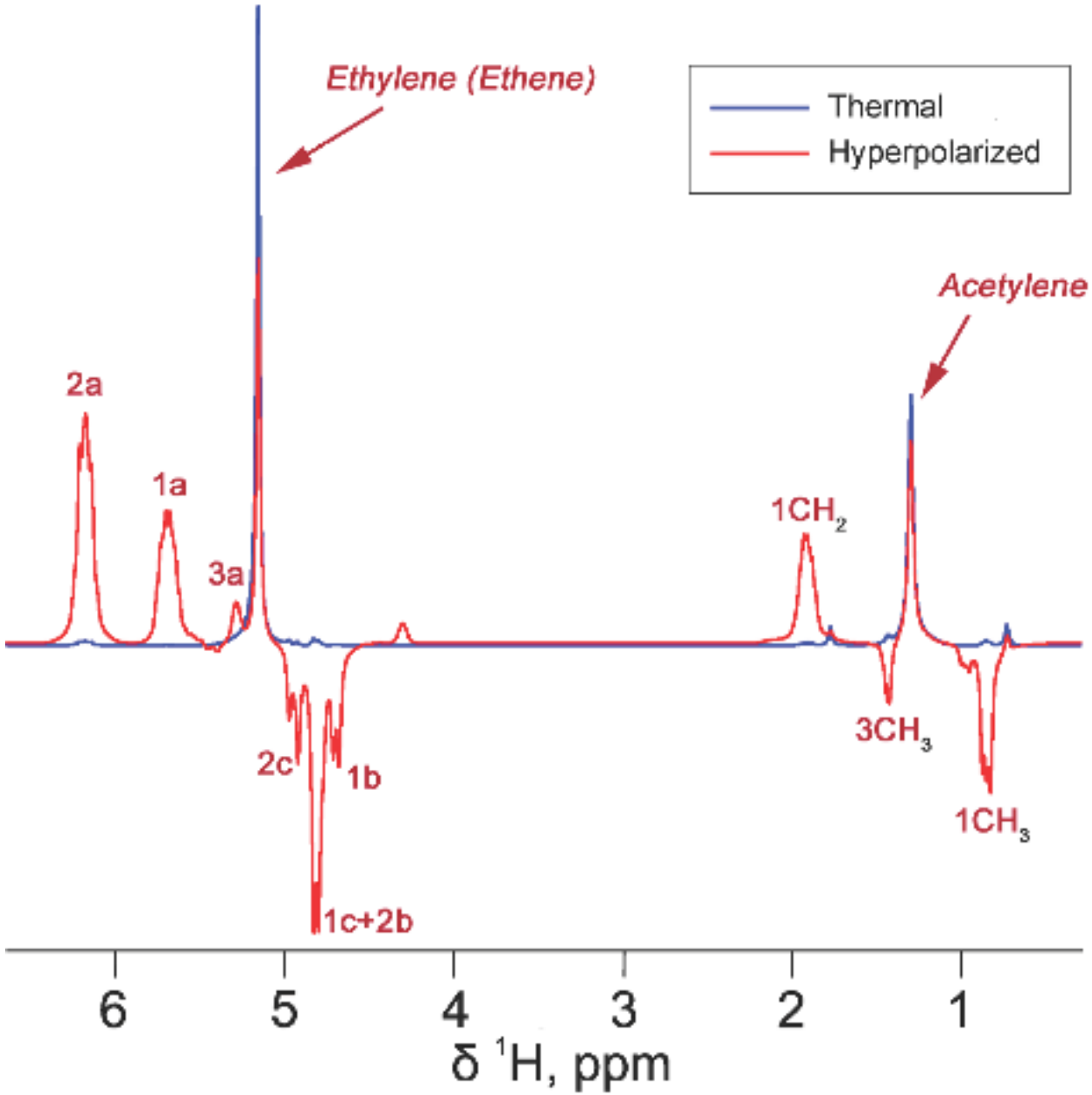
- **Associative**
- **Concerted**
- **Direct**
- **Eley-Rideal**
- **H transfer**
- **.....**
- **Pairwise**

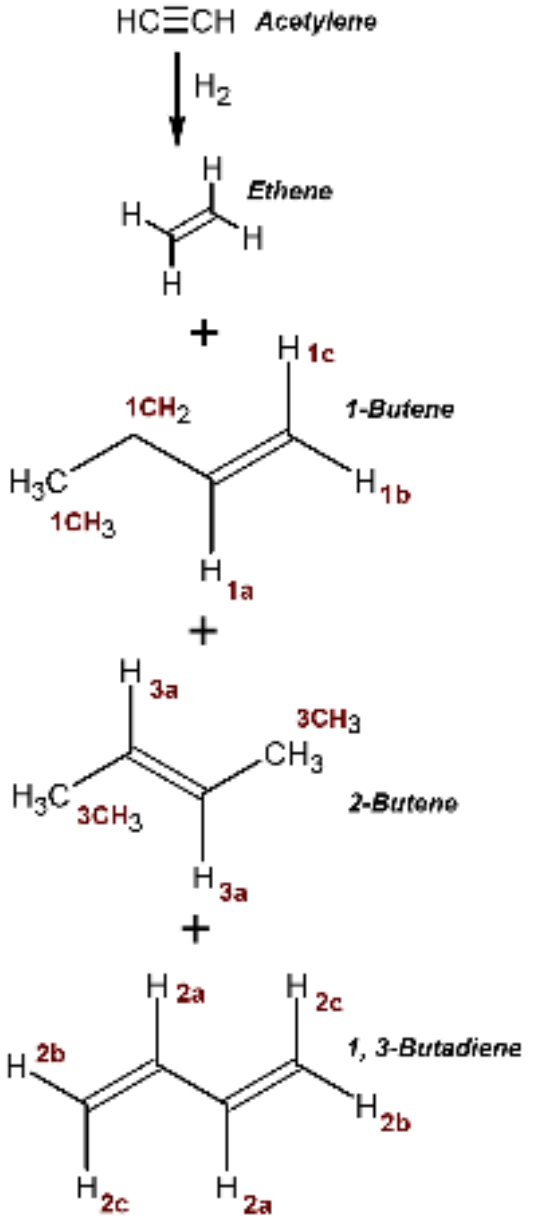
Cryogenic spin isomer enrichment (for H_2





PHIP in acetylene oligomerization over supported Pd





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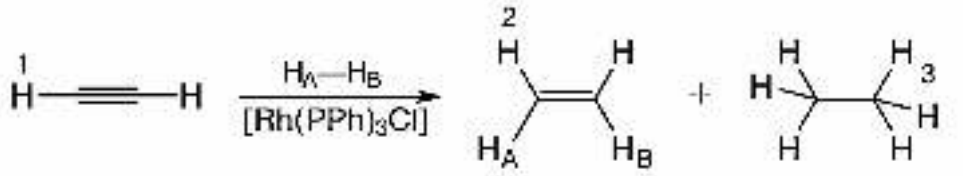
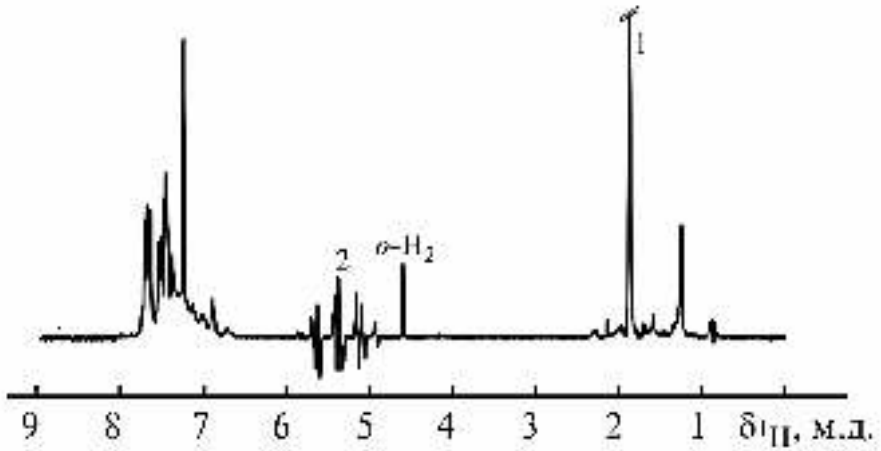
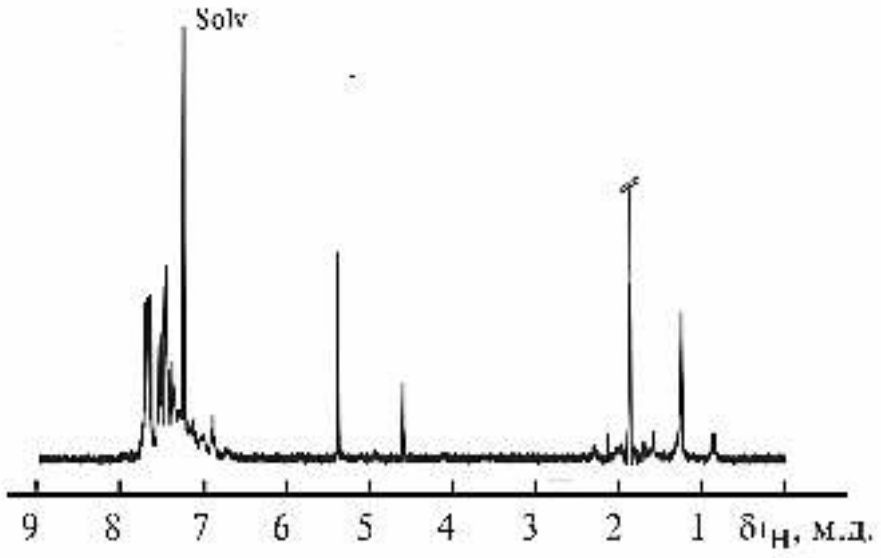
PHIP in homogeneous acetylene hydrogenation







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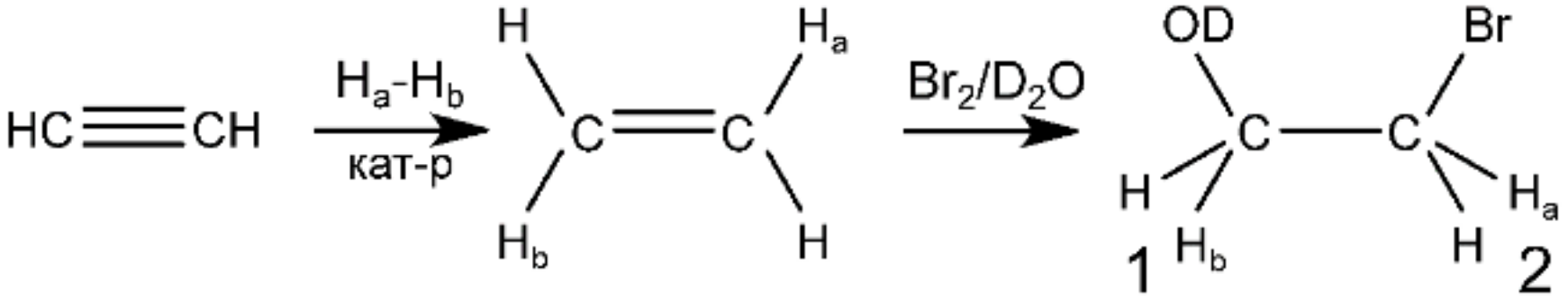
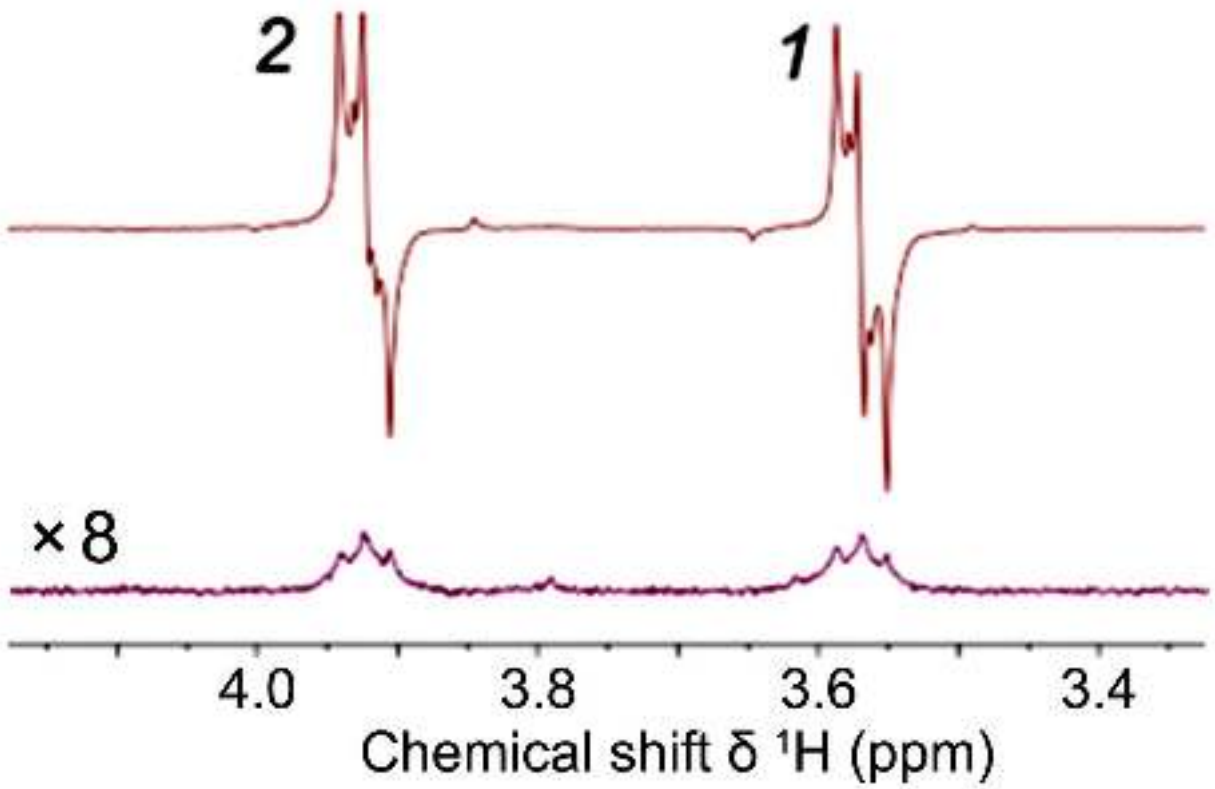
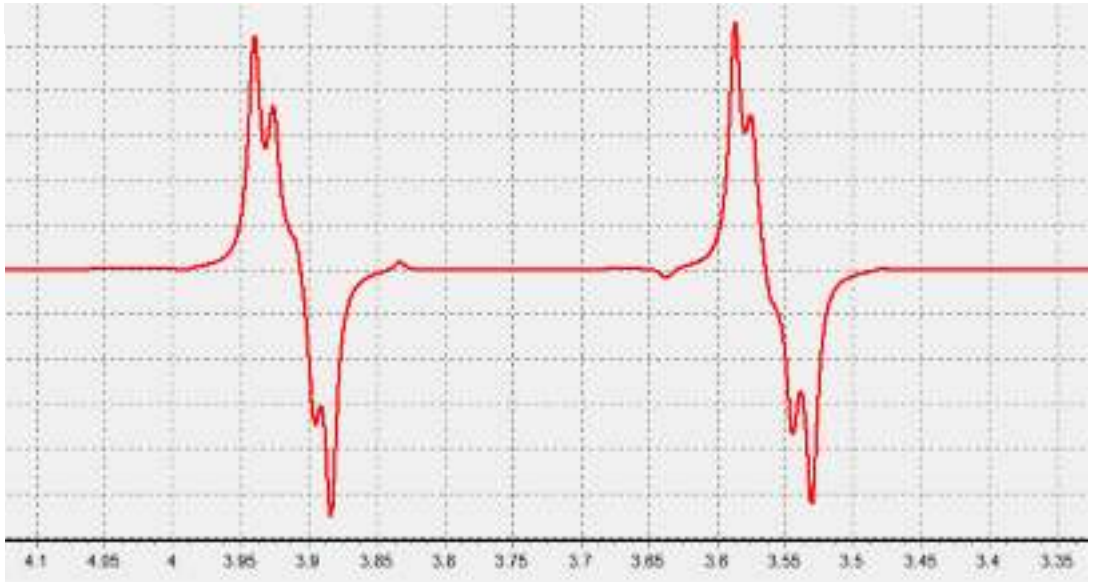
Hyperpolarization based on spin isomers of ethylene







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