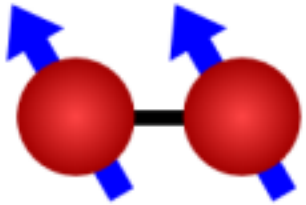
Mechanistic insight into heterogeneous hydrogenation of methylenecyclobutane with the use of parahydrogen

Oleg G. Salnikov[1,2], Dudari B. Burueva[1], Larisa M. Kovtunova[2], Kirill V. Kovtunov[1], Igor V. Koptyug[1]

[1]International Tomography Center SB RAS, Novosibirsk, Russia
[2]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

Spin isomers of hydrogen molecules

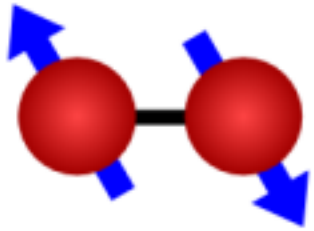


Orthohydrogen

I = 1

Triplet state

$$|\psi_o\rangle = \left\{ \begin{array}{c} |\alpha\alpha\rangle \\ \frac{1}{\sqrt{2}} \cdot \left(|\alpha\beta\rangle + |\beta\alpha\rangle \right) \\ |\beta\beta\rangle \end{array} \right\}$$

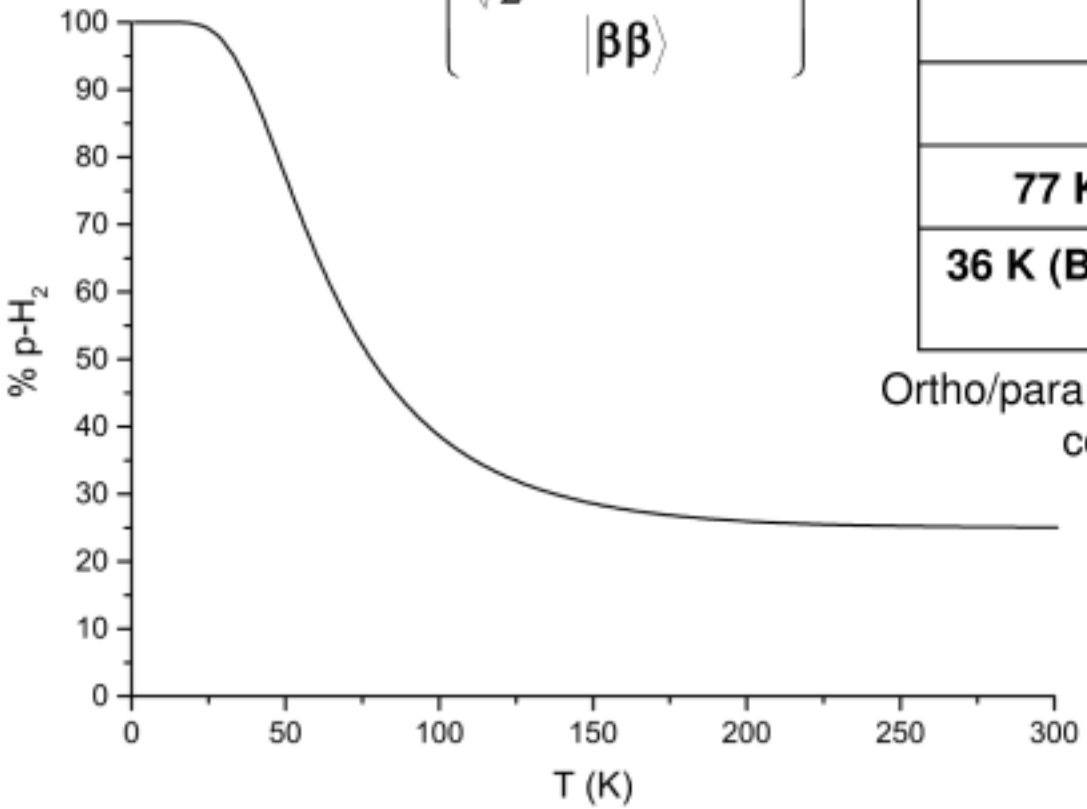


Parahydrogen

I = 0

Singlet state

$$|\psi_p\rangle = \frac{1}{\sqrt{2}} \cdot \left(|\alpha\beta\rangle - |\beta\alpha\rangle \right)$$

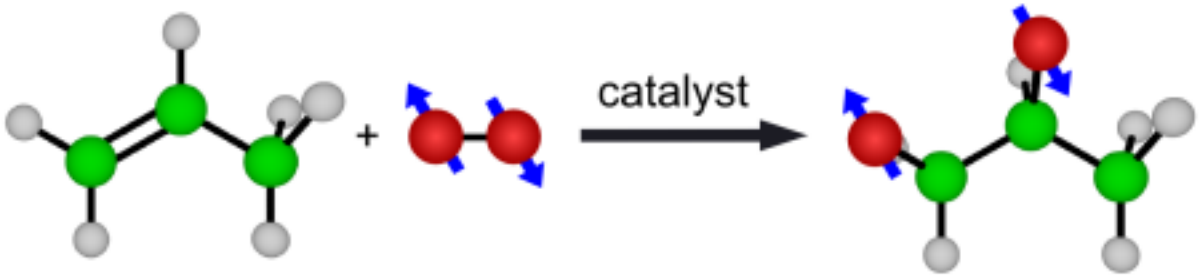


Temperature	p-H_2 fraction
298 K (room)	25%
77 K (liquid nitrogen)	50%
36 K (Bruker p-H_2 generator at its best)	93%

Ortho/para conversion is catalyzed by paramagnetic compounds (FeO(OH), charcoal)

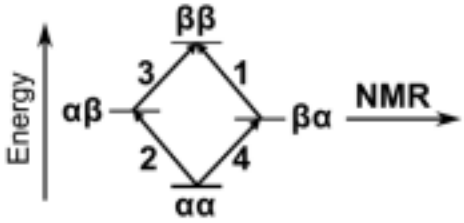
$$\frac{N_{ortho}}{N_{para}} = \frac{3 \cdot \sum_{j=1,3,\ldots}^{\infty} (2j+1) \cdot e^{-\Theta_r j(j+1)/T}}{\sum_{j=0,2,\ldots}^{\infty} (2j+1) \cdot e^{-\Theta_r j(j+1)/T}}$$

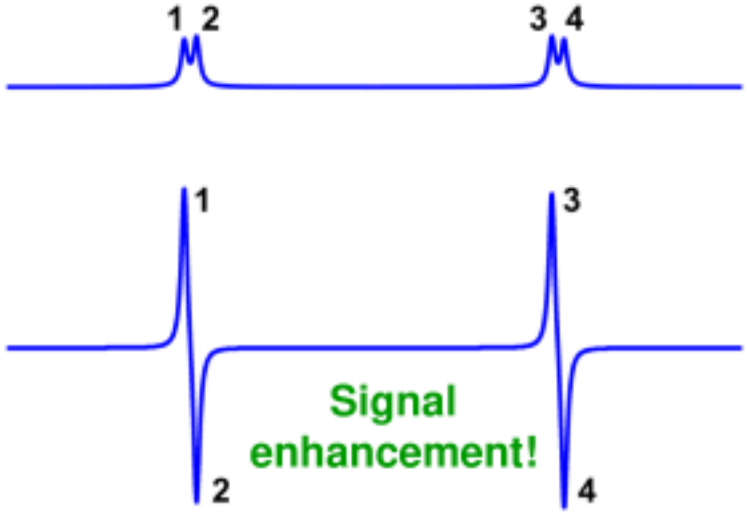
Parahydrogen-Induced Polarization (PHIP)



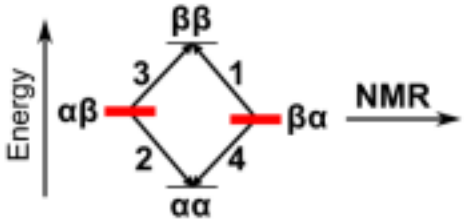
Pairwise addition of two H atoms from the same p-H_2 molecule is required for PHIP!

Normal hydrogen (ortho/para = 3:1) or non-pairwise addition



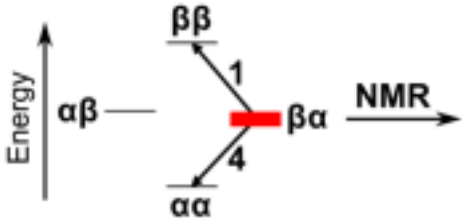


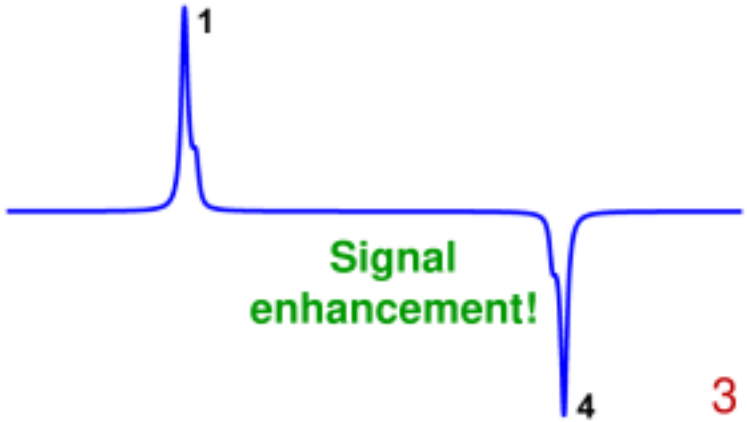
PASADENA
(hydrogenation in the high magnetic field)



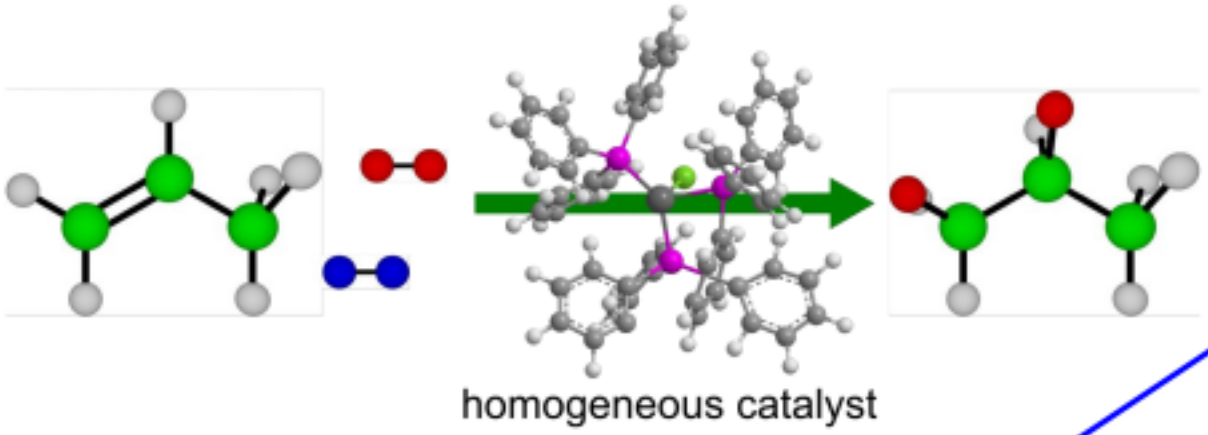
Parahydrogen (ortho/para < 3:1) and pairwise addition

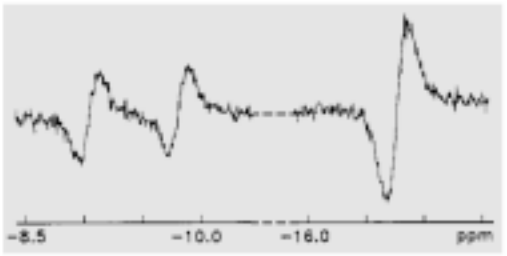
ALTADENA
(hydrogenation in the low magnetic field)

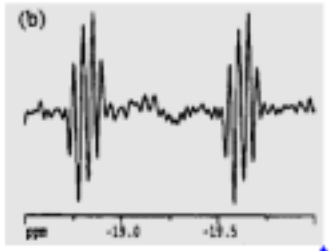


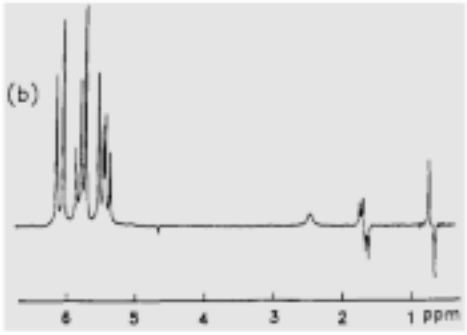


Homogeneous PHIP



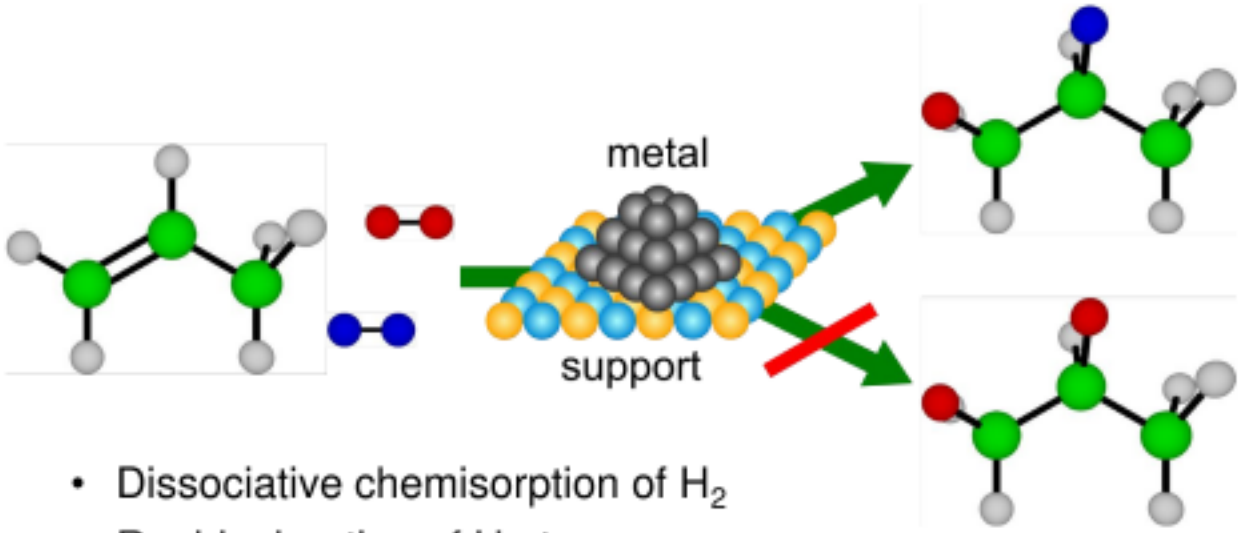






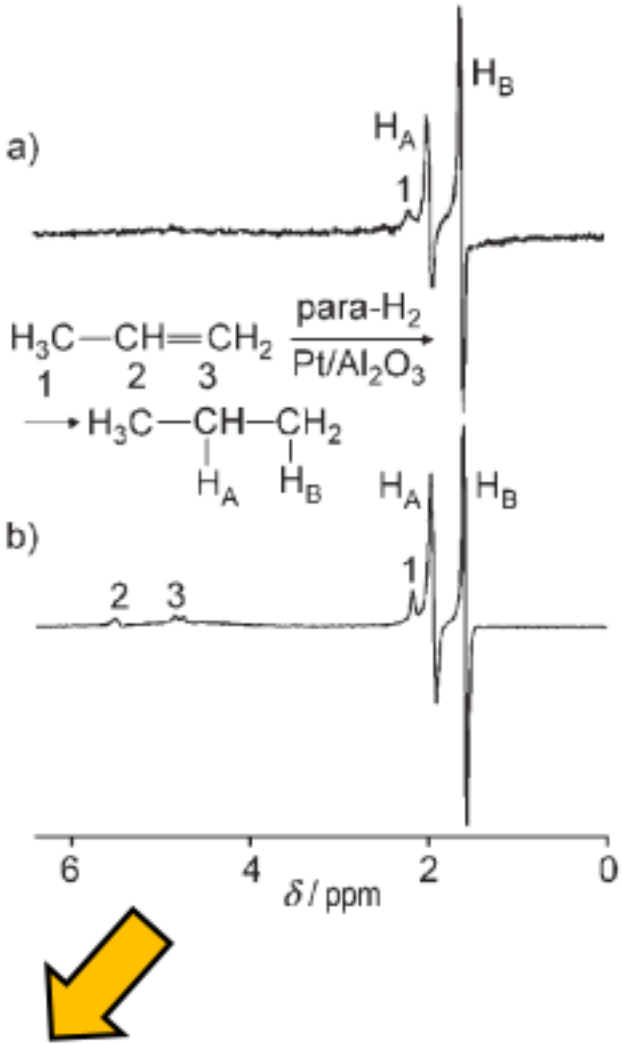
S. B. Duckett, C. L. Newell, R. Eisenberg, *J. Am. Chem. Soc.*, **1994**, 116, 10548-10556

Heterogeneous PHIP



- Dissociative chemisorption of H_2
- Rapid migration of H atoms

Pairwise addition of H_2 on metal catalysts <u>is impossible?</u>



Pairwise addition of H_2 on supported metal catalysts <u>is possible!</u>
(though it is not the main reaction pathway)

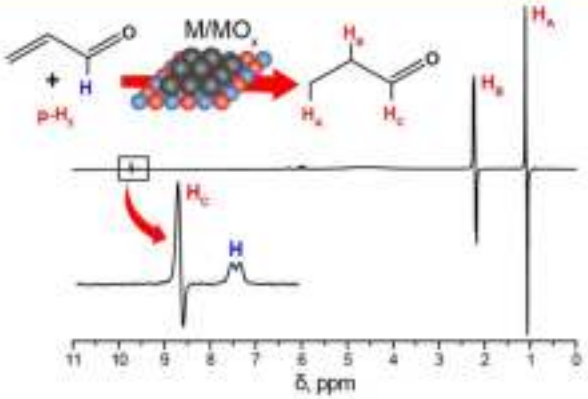
K.V. Kovtunov, I.E. Beck, V.I. Bukhtiyarov, I.V. Koptyug, *Angew. Chem., Int. Ed.*, **2008**, 47, 1492-1495

HET-PHIP for mechanistic studies of catalytic reactions

ACS Catalysis
Research Article
pubs.acs.org/acscatalysis

Evaluation of the Mechanism of Heterogeneous Hydrogenation of α,β-Unsaturated Carbonyl Compounds via Pairwise Hydrogen Addition

Oleg G. Salnikov,[†,‡] Kirill V. Kovtunov,[*,†,‡] Danila A. Barskiy,[†,‡] Alexander K. Khudorozhkov,[‡,§] Elizaveta A. Inozemtseva,[‡,§] Igor P. Prosvirin,[§] Valery I. Bukhtiyarov,[‡,§] and Igor V. Koptyug[†,‡]



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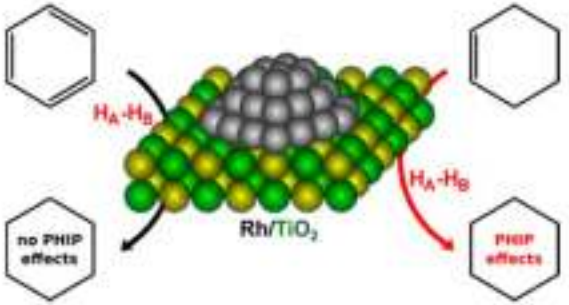
Hydrogenation of Unsaturated Six-Membered Cyclic Hydrocarbons Studied by the Parahydrogen-Induced Polarization Technique

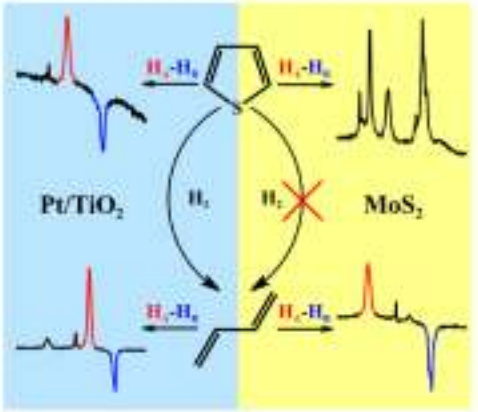
Dudari B. Burueva,[†,‡] Oleg G. Salnikov,[†,‡] Kirill V. Kovtunov,[*,†,‡] Alexey S. Romanov,[†,‡] Larisa M. Kovtunova,[§,‡] Alexander K. Khudorozhkov,[§,‡] Andrey V. Bukhtiyarov,[§,‡] Igor P. Prosvirin,[§,‡] Valerii I. Bukhtiyarov,[§,‡] and Igor V. Koptyug[†,‡]



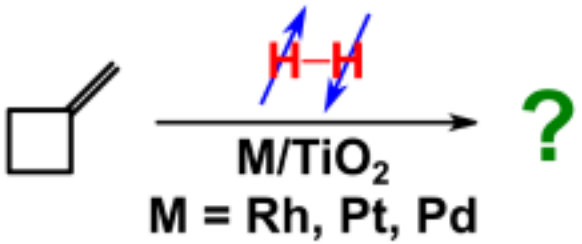
ChemPubSoc Europe
DOI: 10.1002/cctc.201500691
CHEMCATCHEM Full Papers

A Mechanistic Study of Thiophene Hydrodesulfurization by the Parahydrogen-Induced Polarization Technique

Oleg G. Salnikov,[a, b] Dudari B. Burueva,[a, b] Danila A. Barskiy,[a, b] Galina A. Bukhtiyarova,[c] Kirill V. Kovtunov,*[a, b] and Igor V. Koptyug[a, b]



Hydrogenation of methylenecyclobutane



Two types of unsaturated functional groups:

- C=C bond
- cyclobutane ring

Reaction products:

- cyclic, linear, branched?
- unsaturated, saturated?

What information can we get with the use of p-H_2?

ChemPhysChem

Research Article
doi.org/10.1002/cphc.202200072

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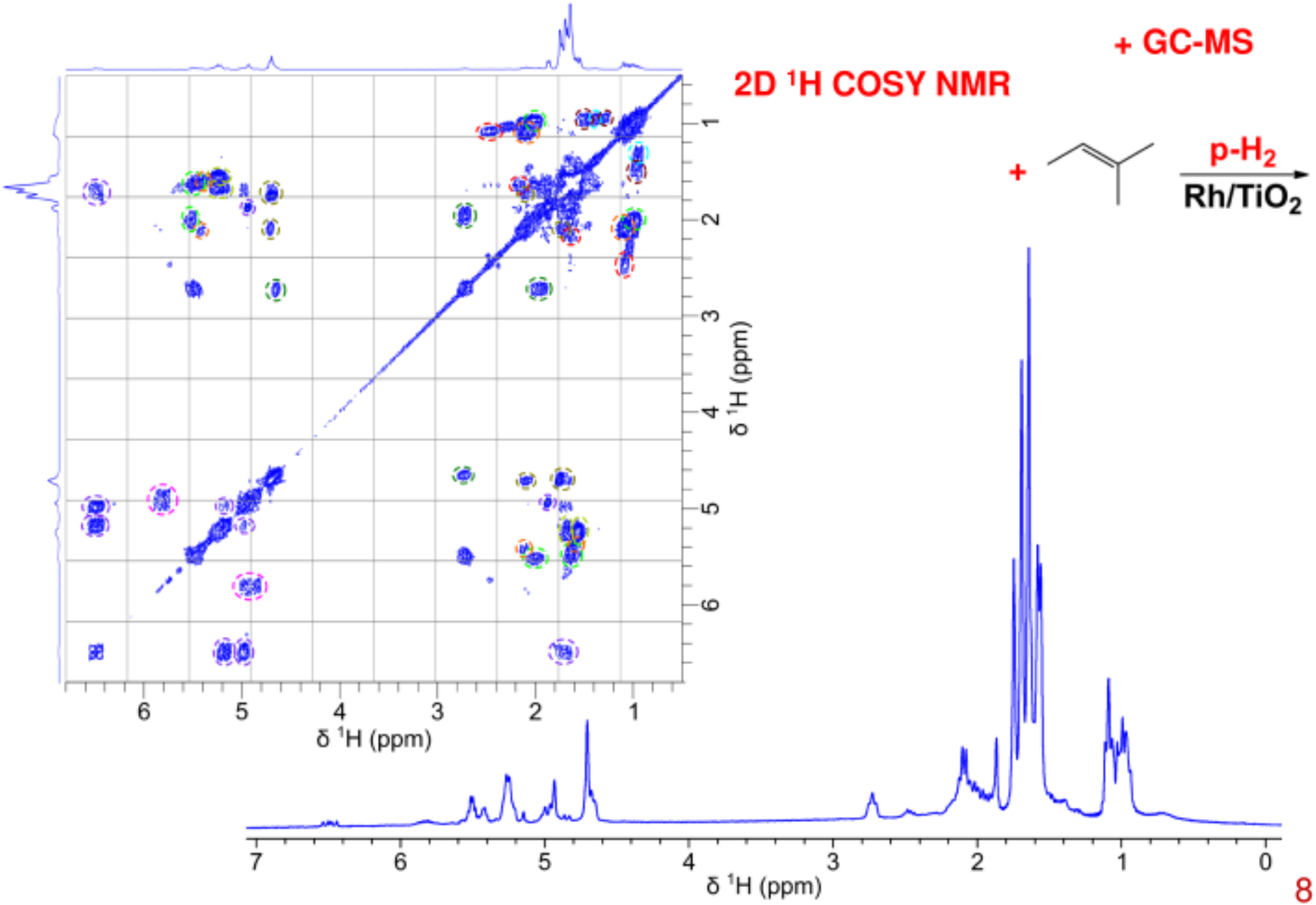
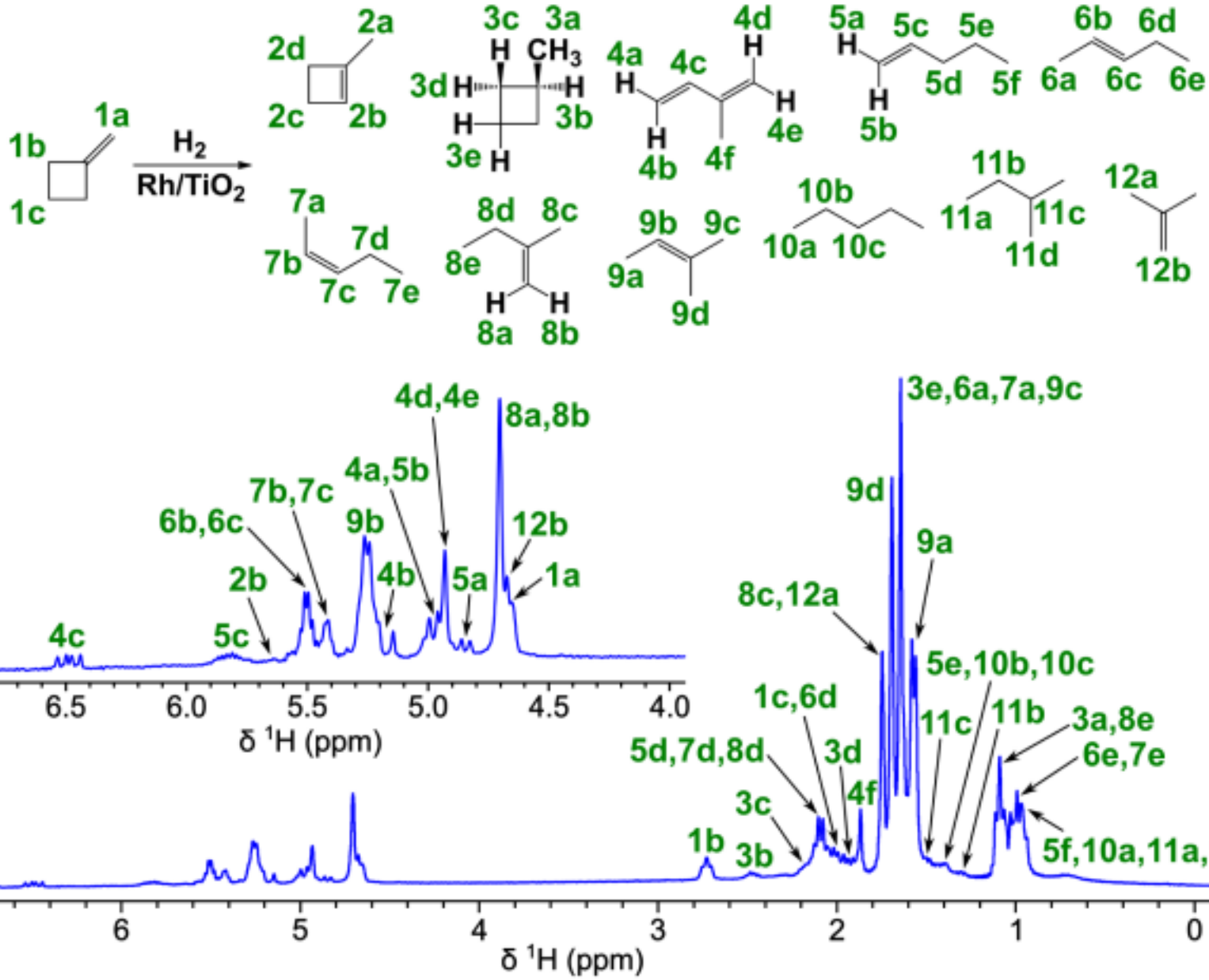
Mechanisms of Methylenecyclobutane Hydrogenation over Supported Metal Catalysts Studied by Parahydrogen-Induced Polarization Technique

Oleg G. Salnikov,*[a, b, c] Dudari B. Burueva,[b, c] Larisa M. Kovtunova,[a, b, c] Valerii I. Bukhtiyarov,[a, c] Kirill V. Kovtunov+,[b, c] and Igor V. Koptyug[b]

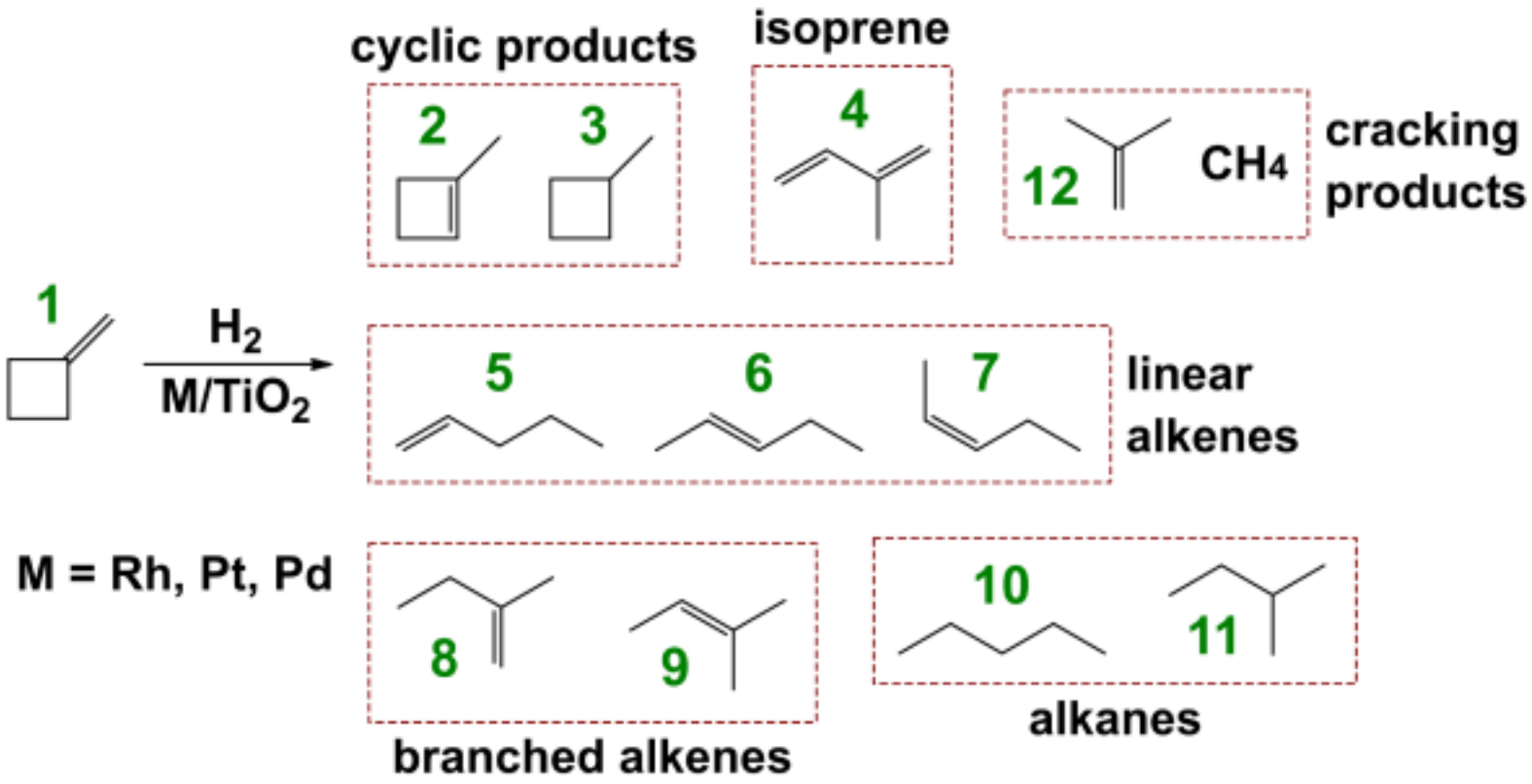
Identification of reaction products



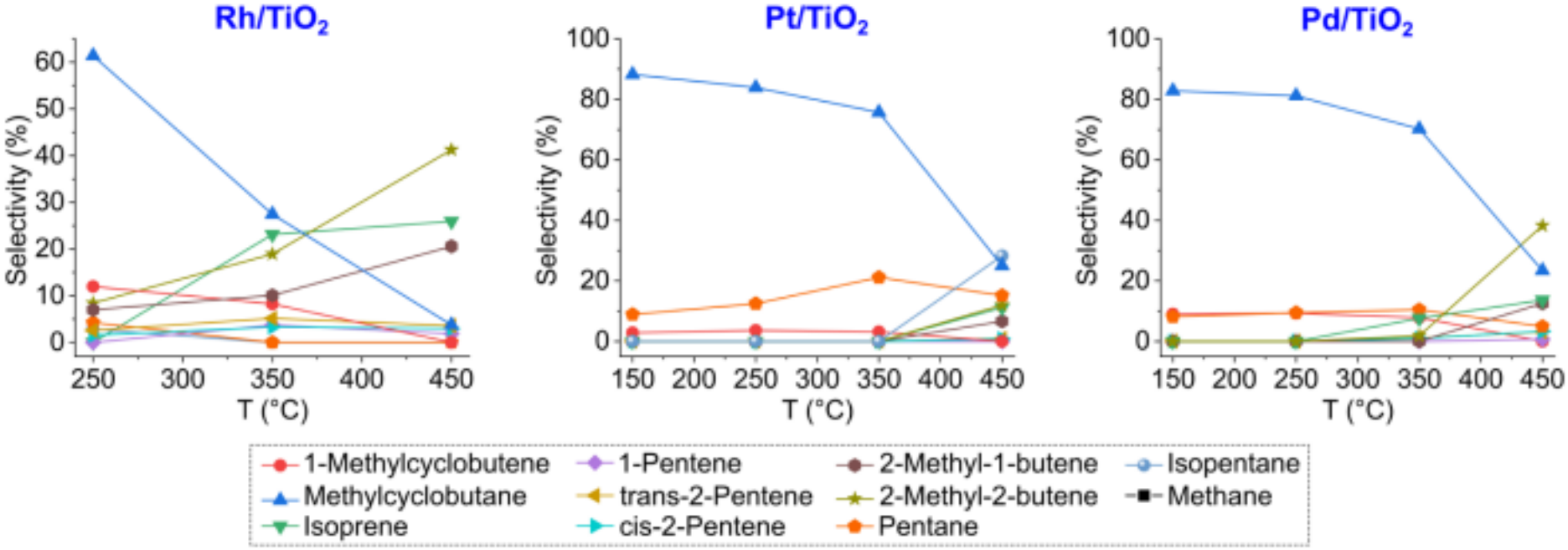
Identification of reaction products

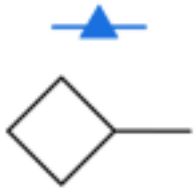


Identification of reaction products

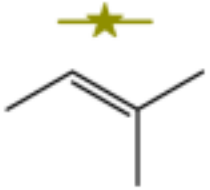


Temperature dependence of selectivity





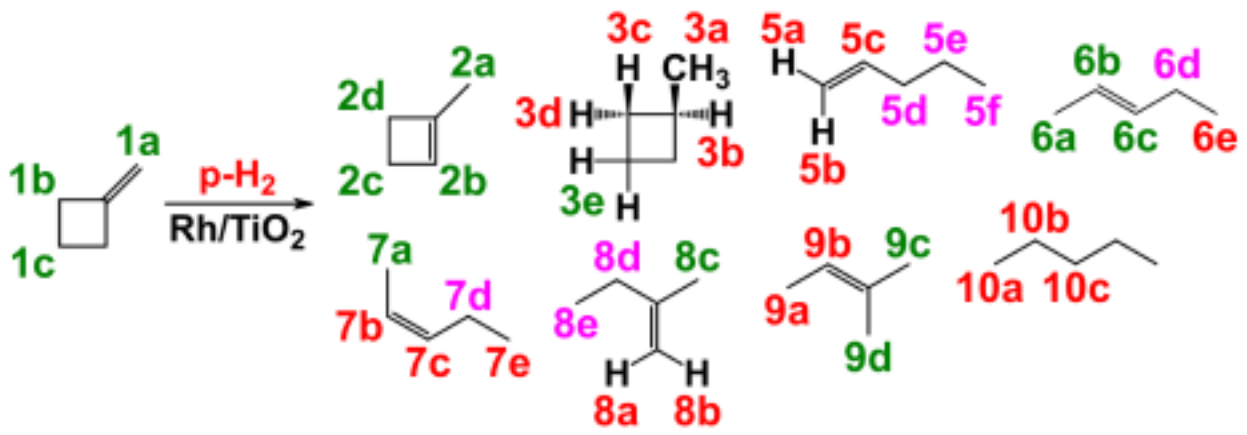
- Methylcyclobutane is the major product at T ≤ 350 °C



- 450 °C favors branched products, especially 2-methyl-2-butene

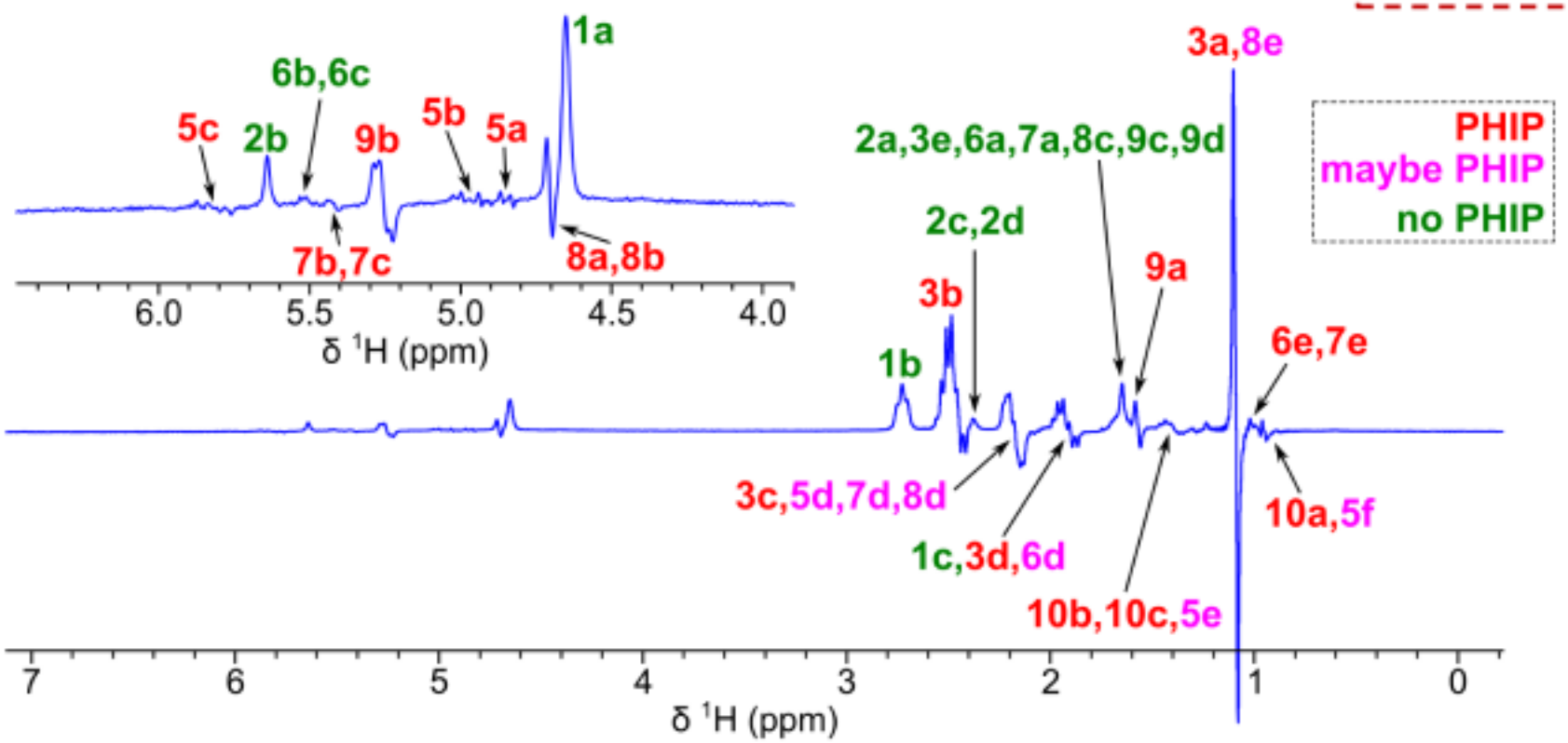
- Pt, Pd – more methylcyclobutane and alkanes
- Rh – more alkenes

PHIP effects observation

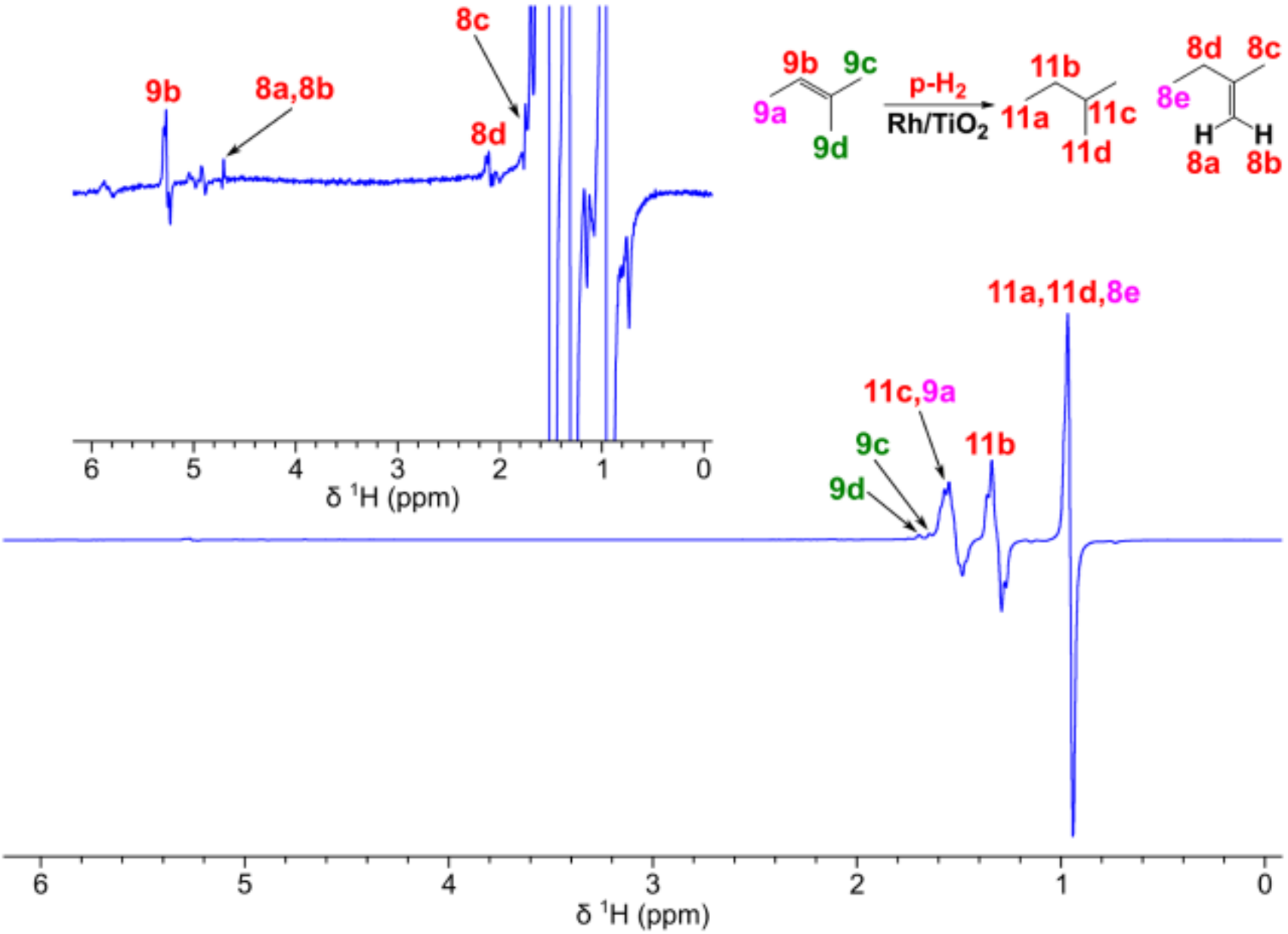


Pt and Pd catalysts showed qualitatively similar results

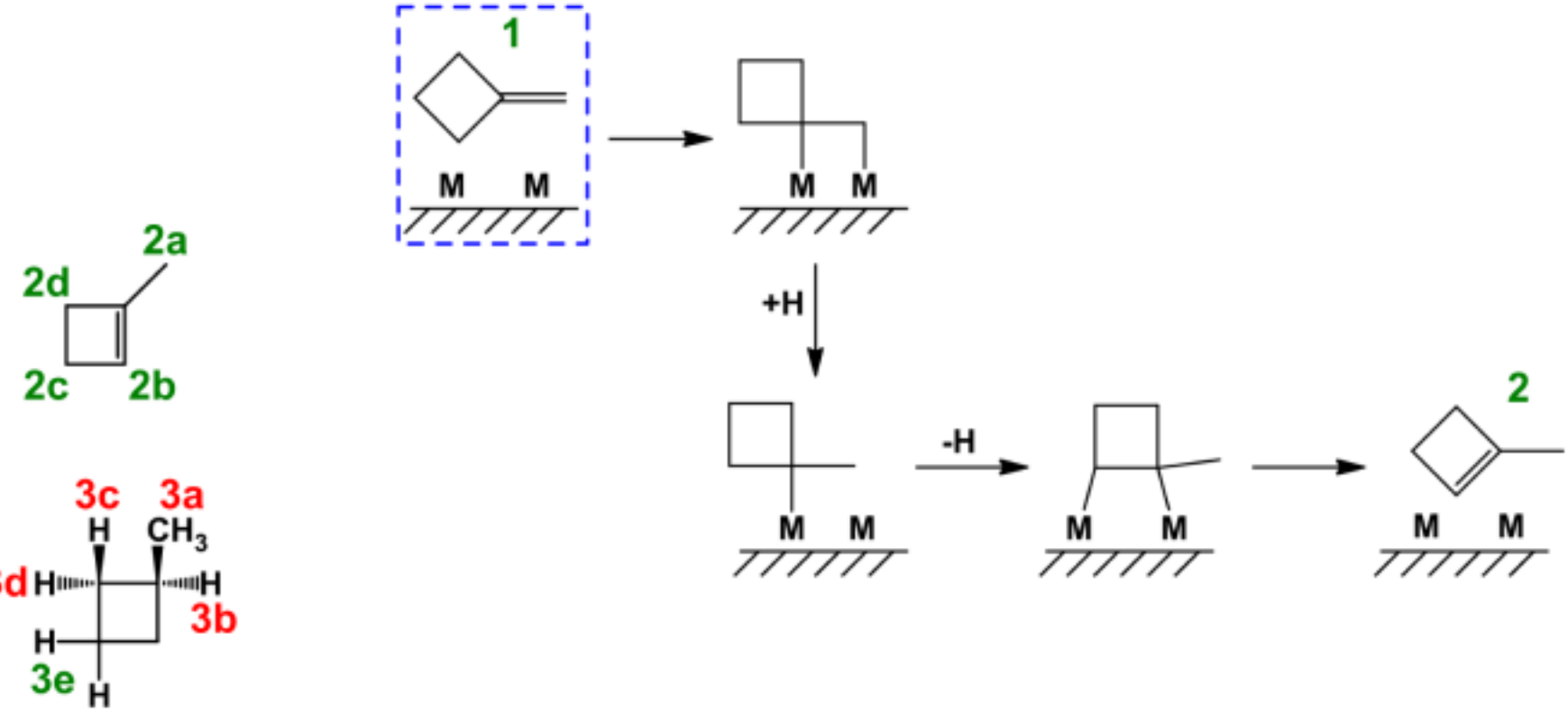
similar reaction mechanisms



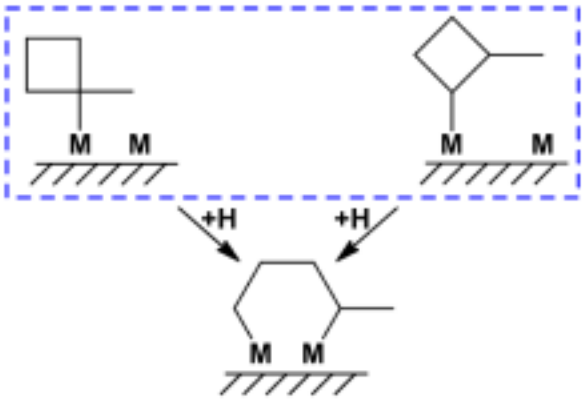
Additional data: hydrogenation of 2-methyl-2-butene

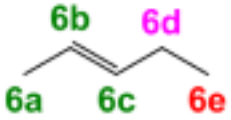


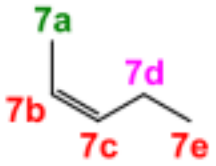
Formation of cyclic products from methylenecyclobutane

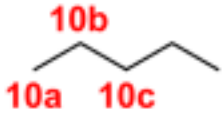


Formation of linear products from methylenecyclobutane

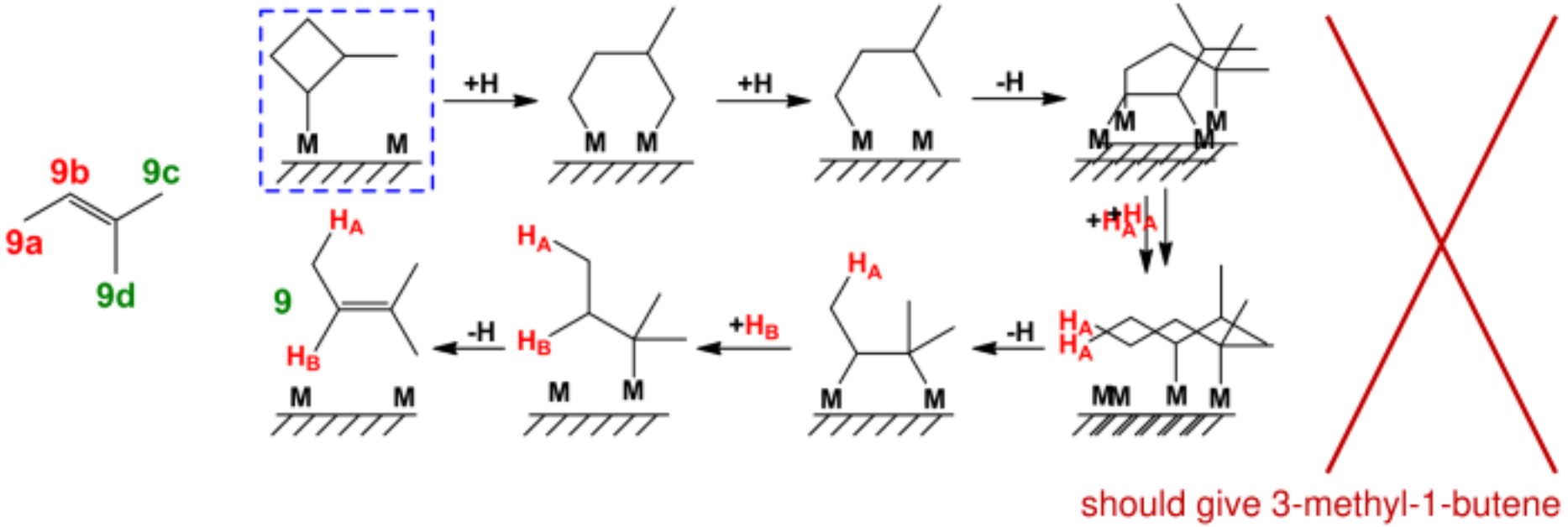




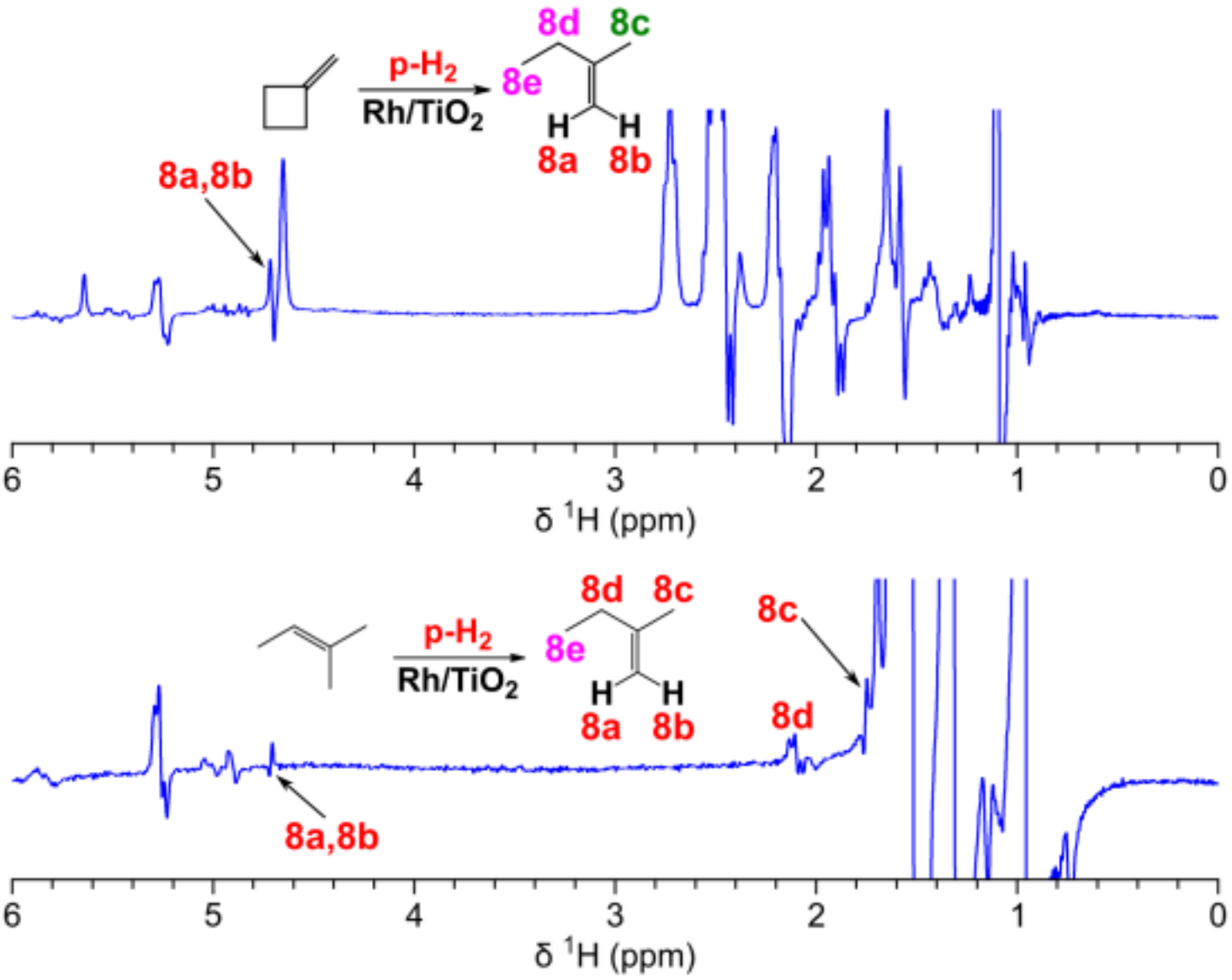




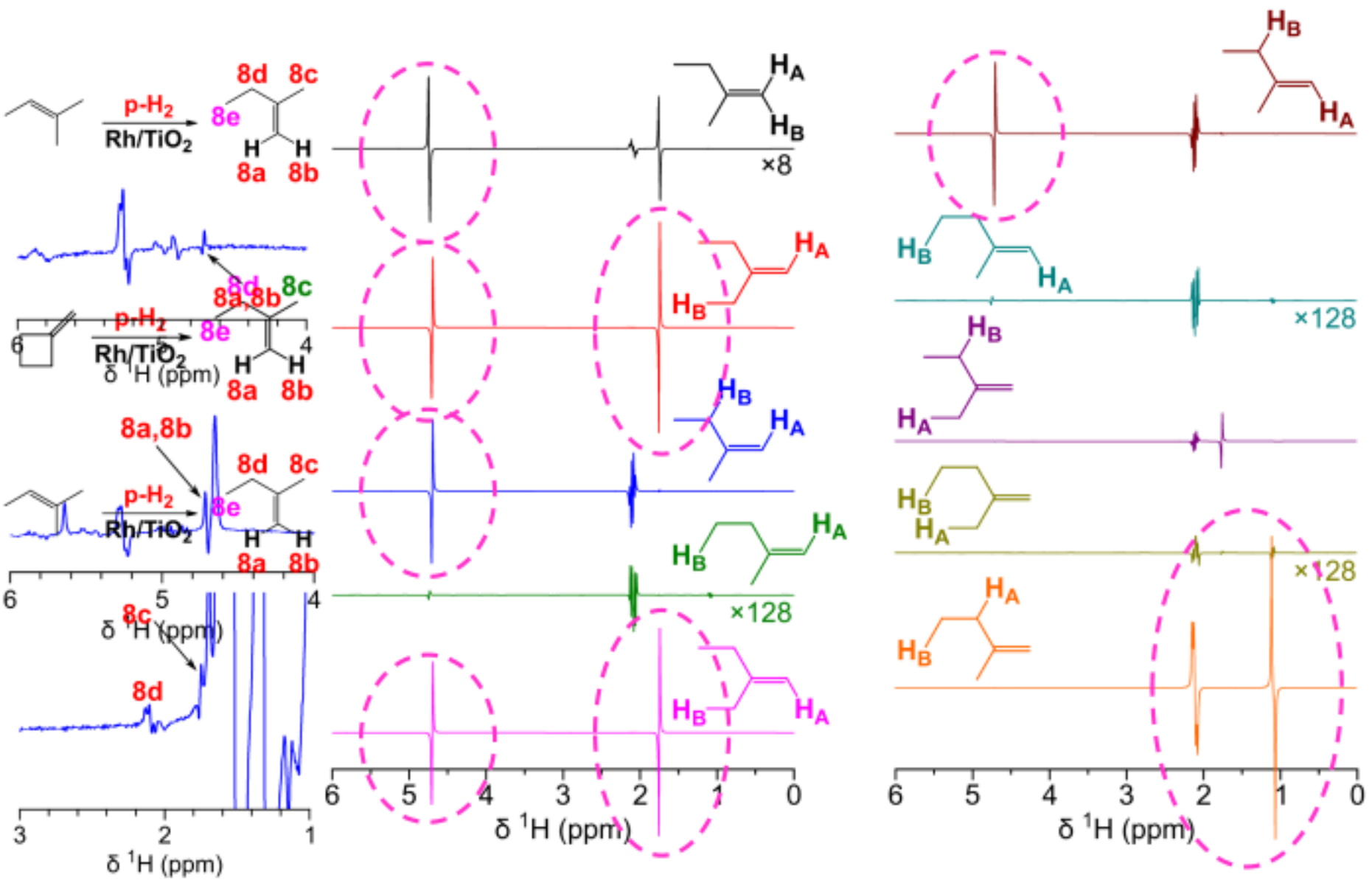
Formation of 2-methyl-2-butene from methylenecyclobutane



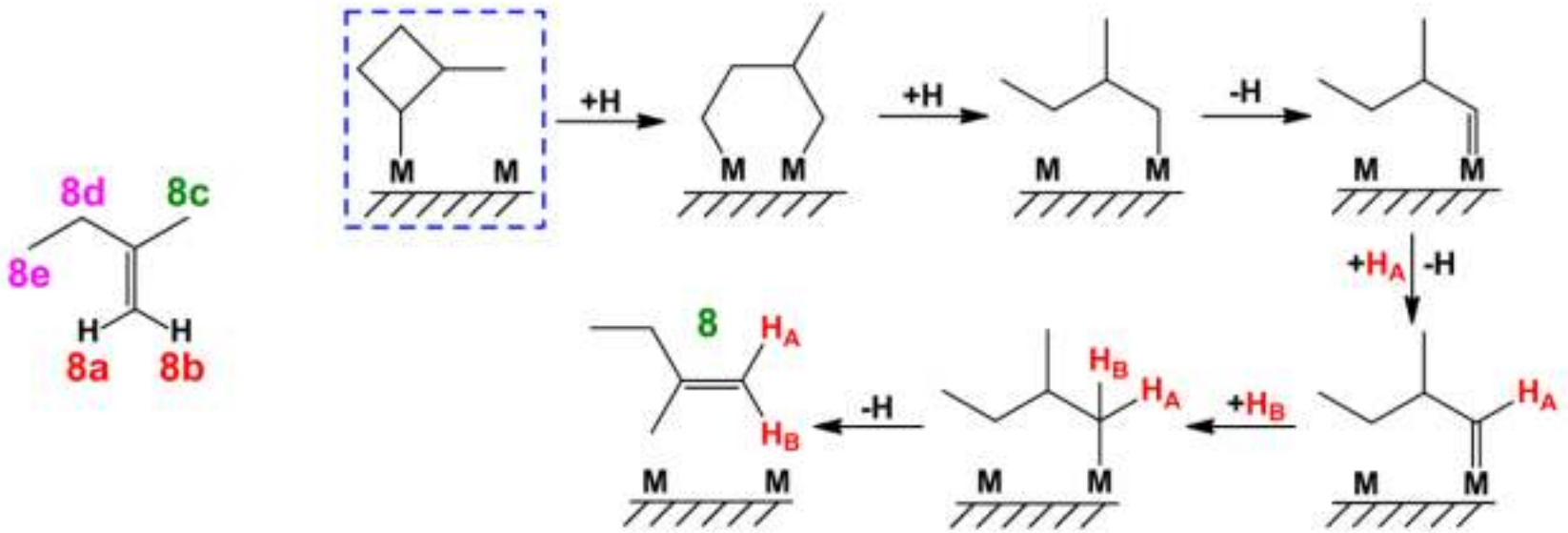
Lineshape of 2-methyl-1-butene PASADENA signal



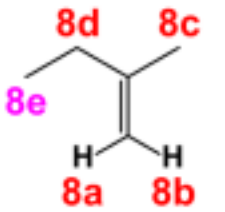
NMR spectra simulations for 2-methyl-1-butene

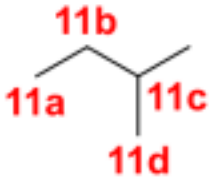


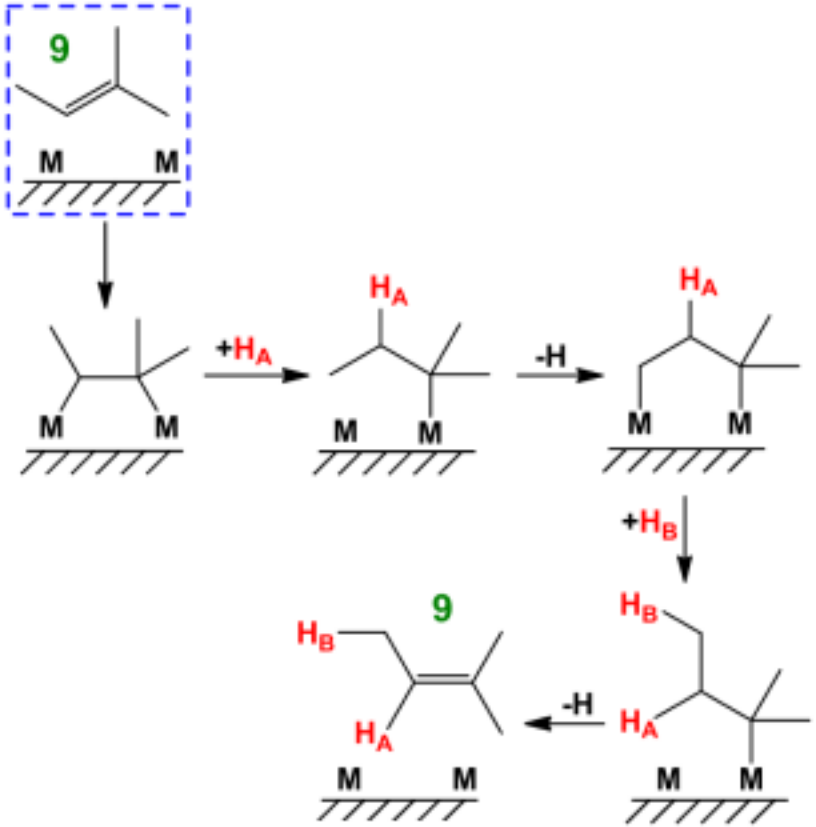
Formation of 2-methyl-1-butene from methylenecyclobutane



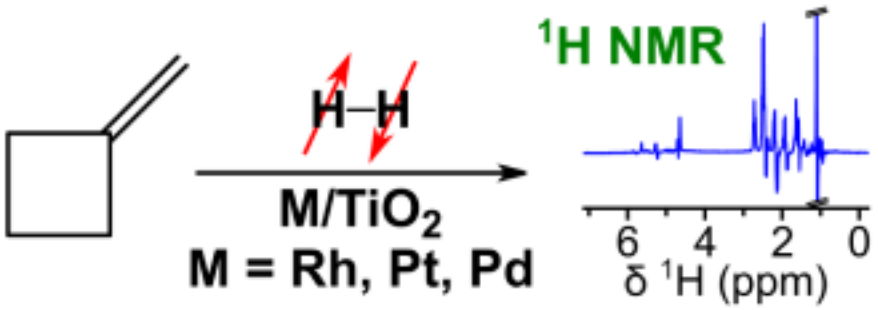
Mechanism of 2-methyl-2-butene hydrogenation







Conclusions



- 11 reaction products
- Reaction mechanisms proposed based on parahydrogen-induced polarization effects

- Methylenecyclobutane (MCB) hydrogenation over TiO_2-supported Rh, Pt and Pd leads to formation of up to 11 products.
- At T ≤ 350 °C the major reaction product is methylcyclobutane, at 450 °C – branched products isoprene, 2-methyl-1-butene and 2-methyl-2-butene.
- The use of PHIP technique allowed to propose mechanisms of formation of various reaction products.
- Altogether, the obtained results demonstrate the unique features of PHIP technique as a tool for mechanistic studies of hydrogenation reactions.

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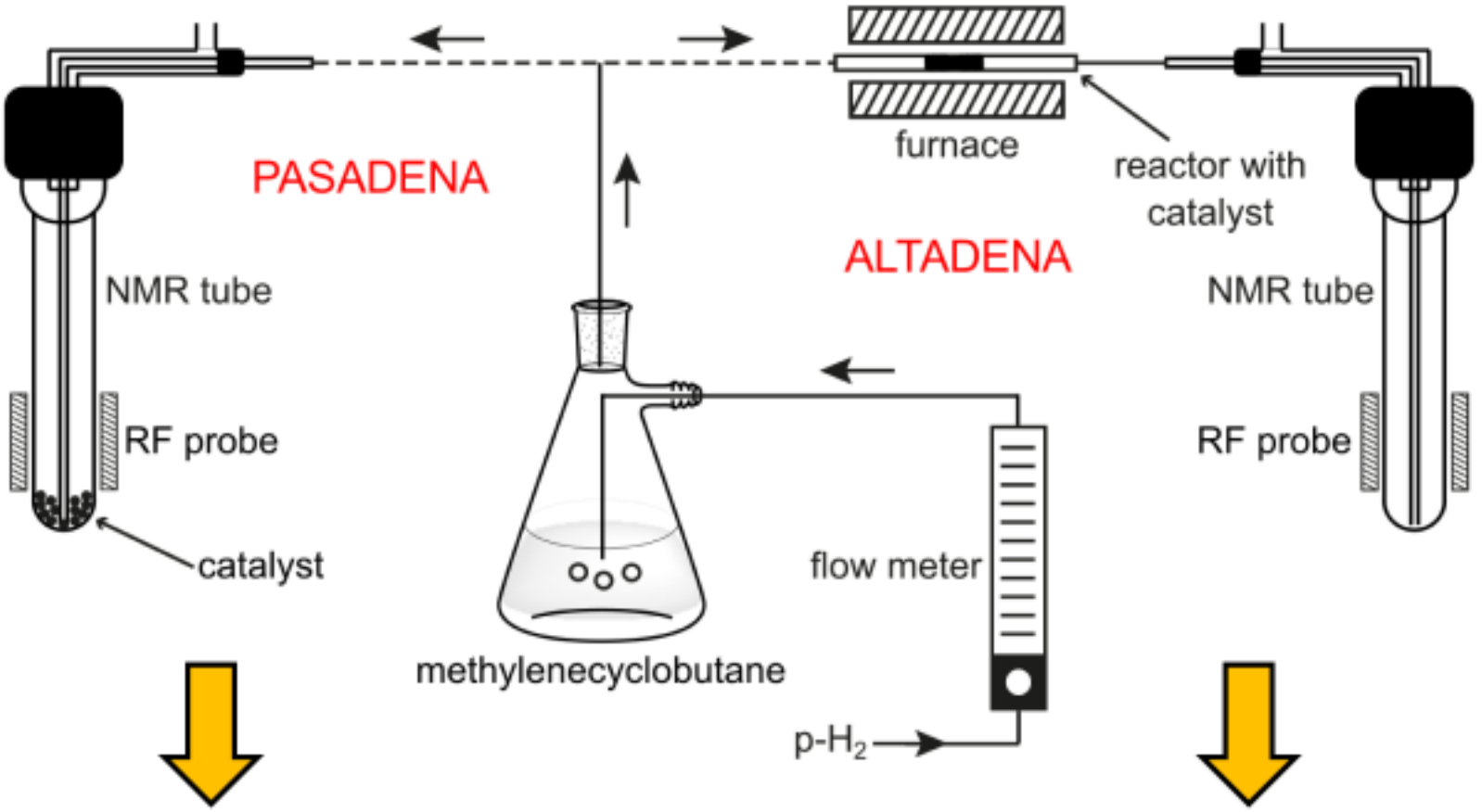
14.01.1983–19.05.2020

Prof. Igor Koptyug

Dr. Larisa Kovtunova

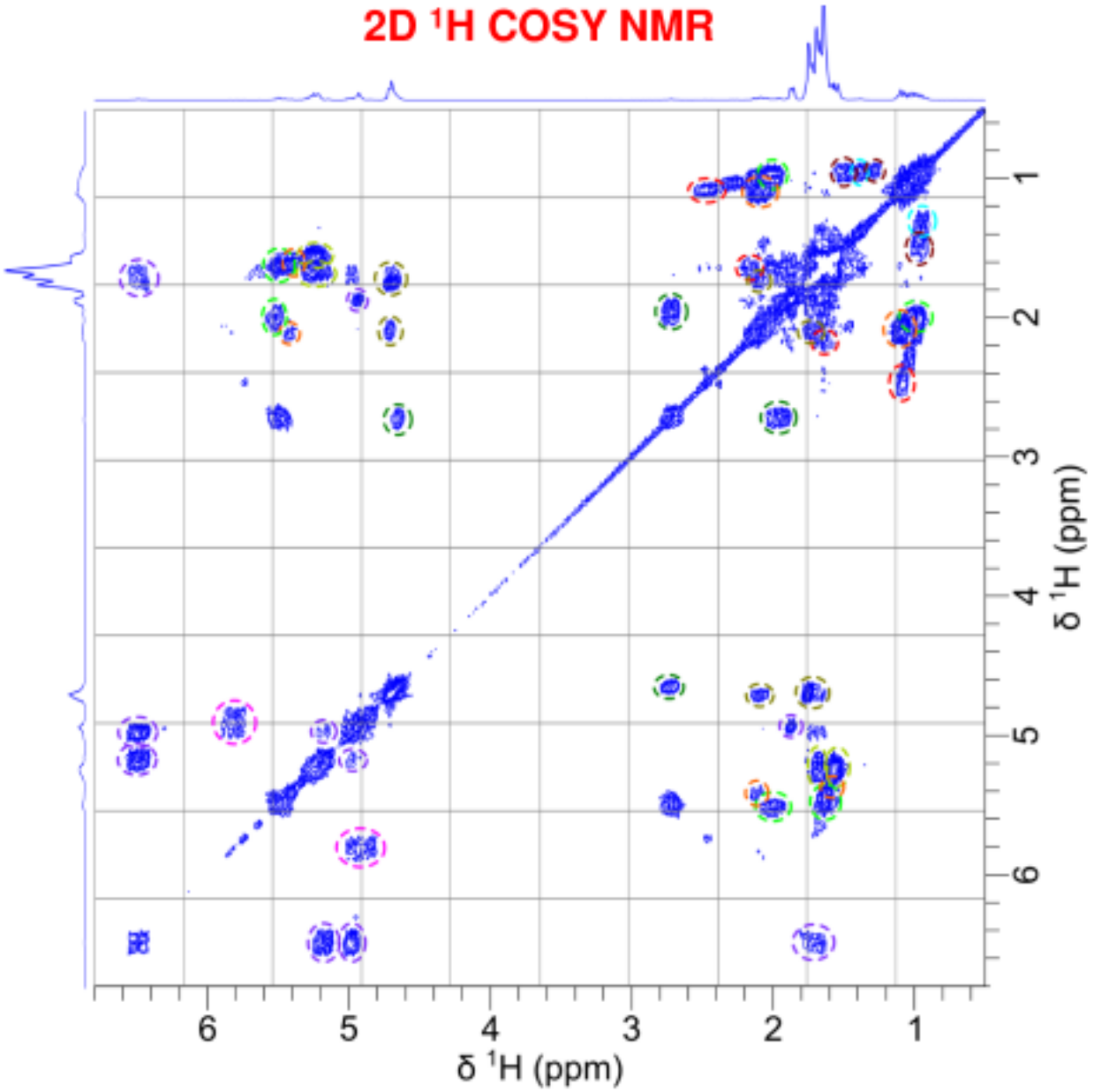
Thank you for kind attention!

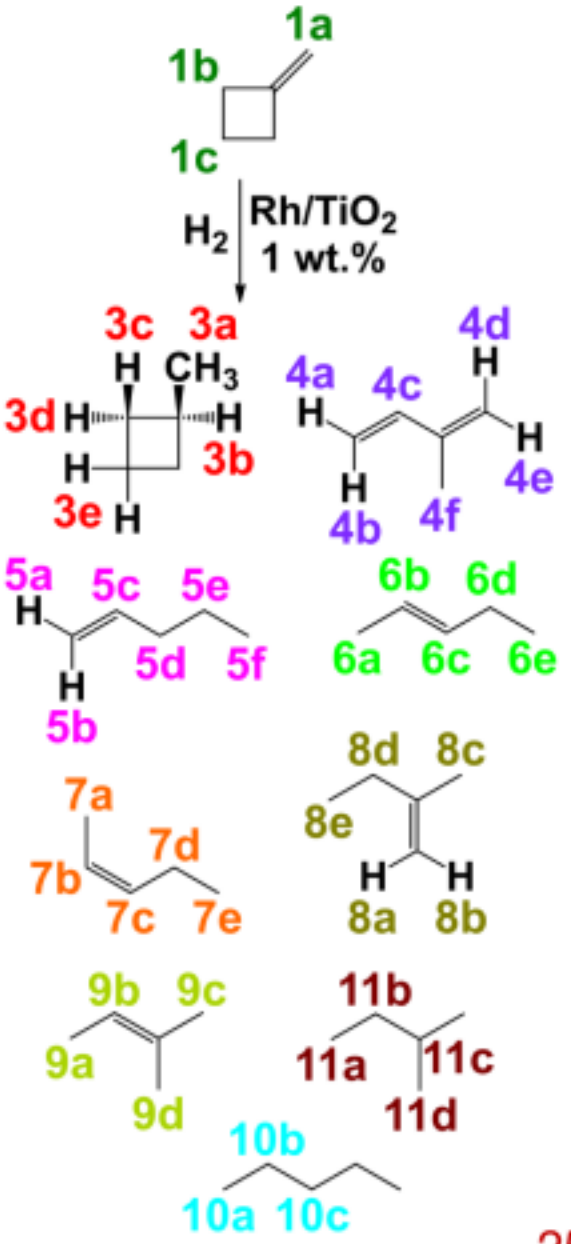
PASADENA vs. ALTADENA in gas-phase HET-PHIP



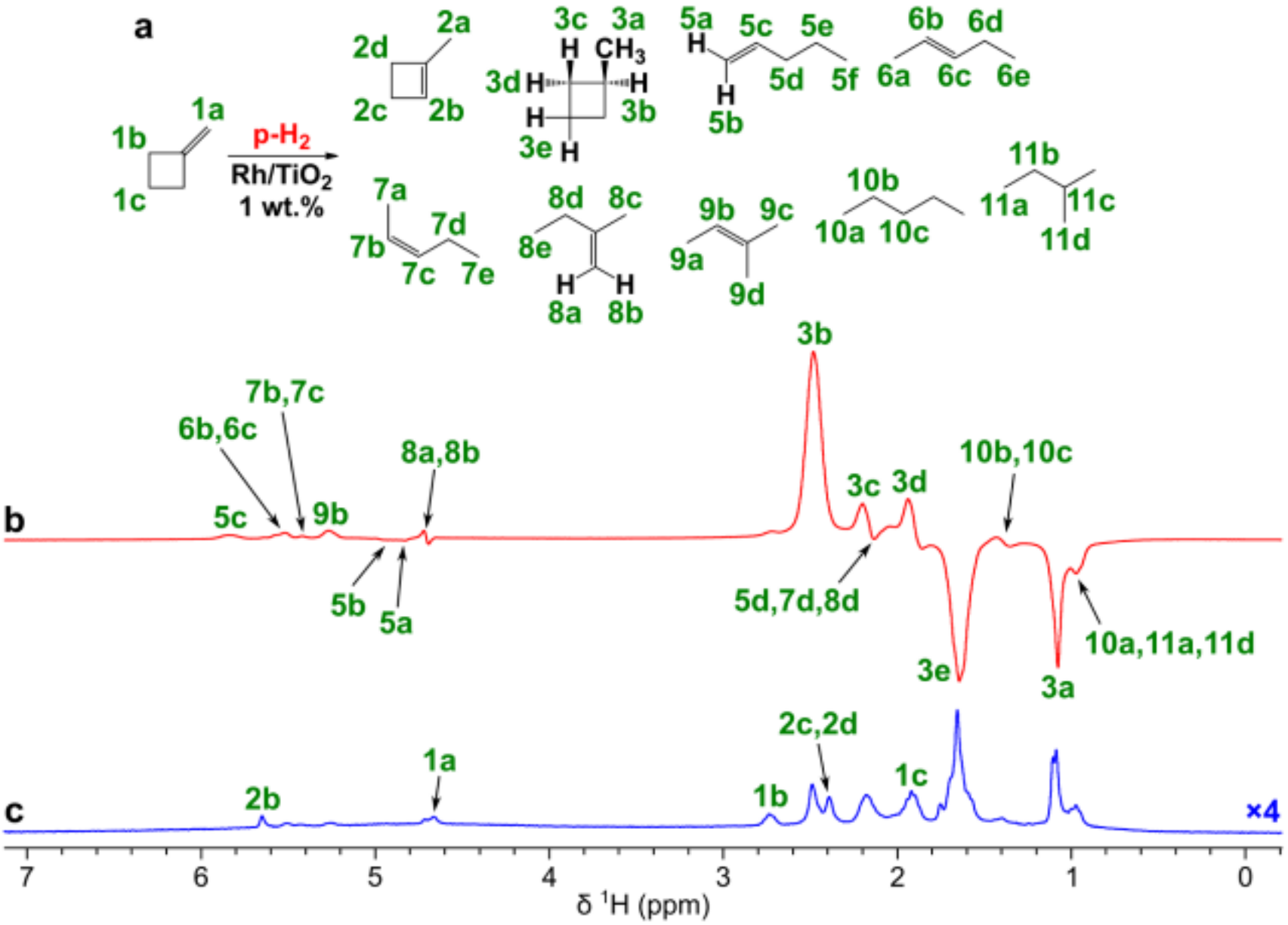
- Conversion measurements are problematic
- Conversion can be easily measured after gas flow is stopped
- PHIP effects correspond to protons originated from the same p-H_2 molecule
- PHIP effects are not informative due to spontaneous polarization transfer

Identification of reaction products

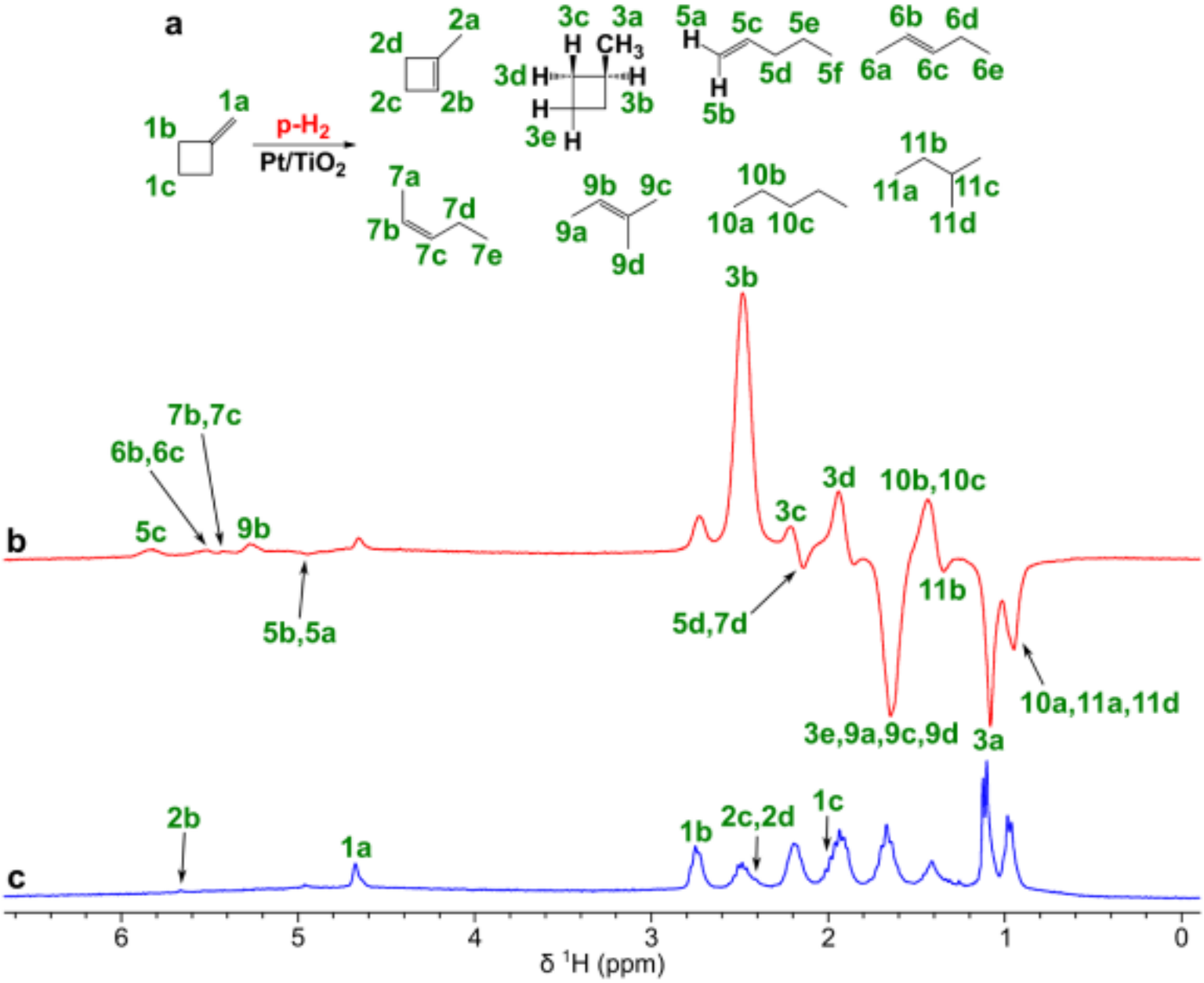




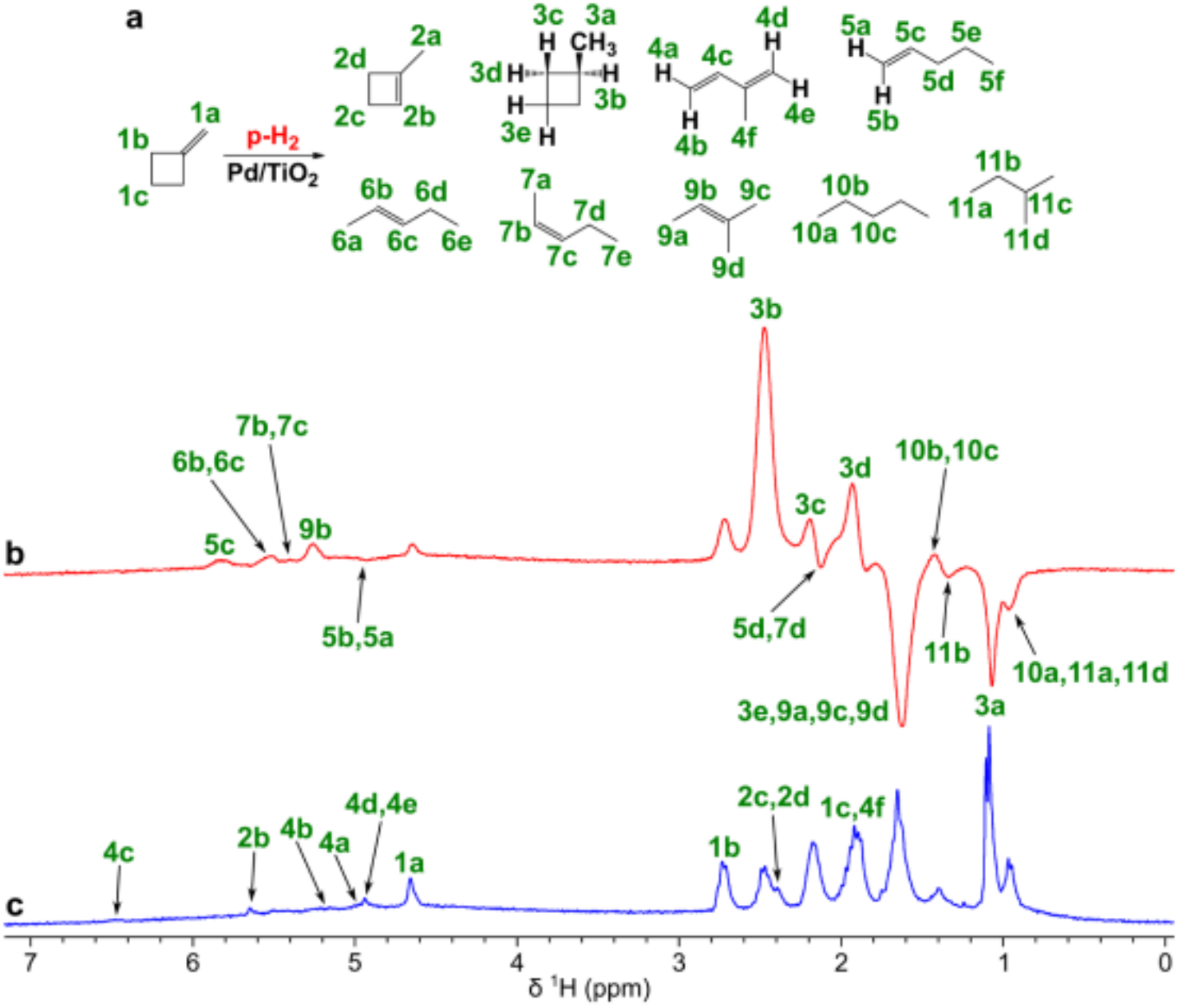
ALTADENA spectrum: Rh



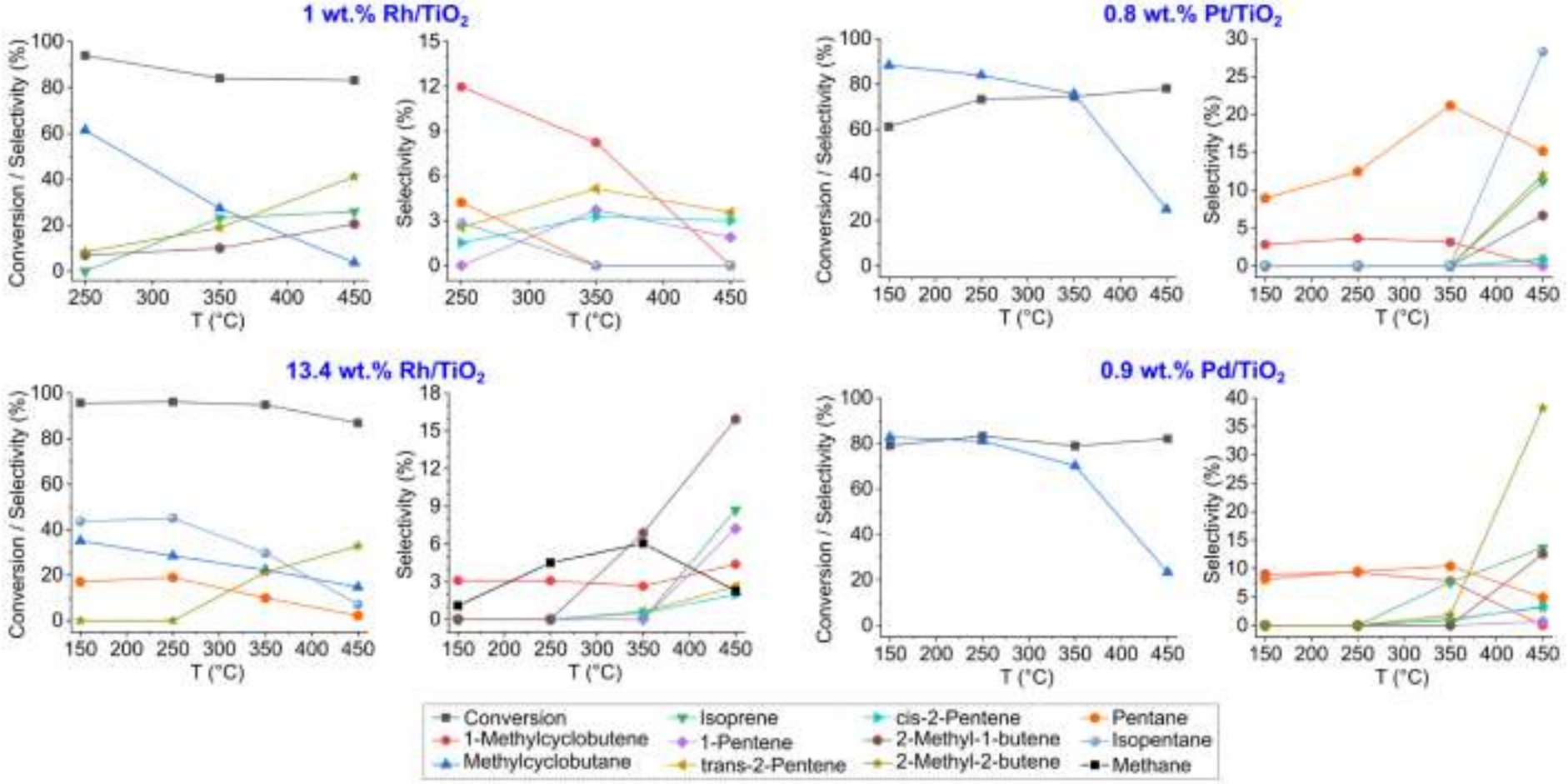
ALTADENA spectrum: Pt



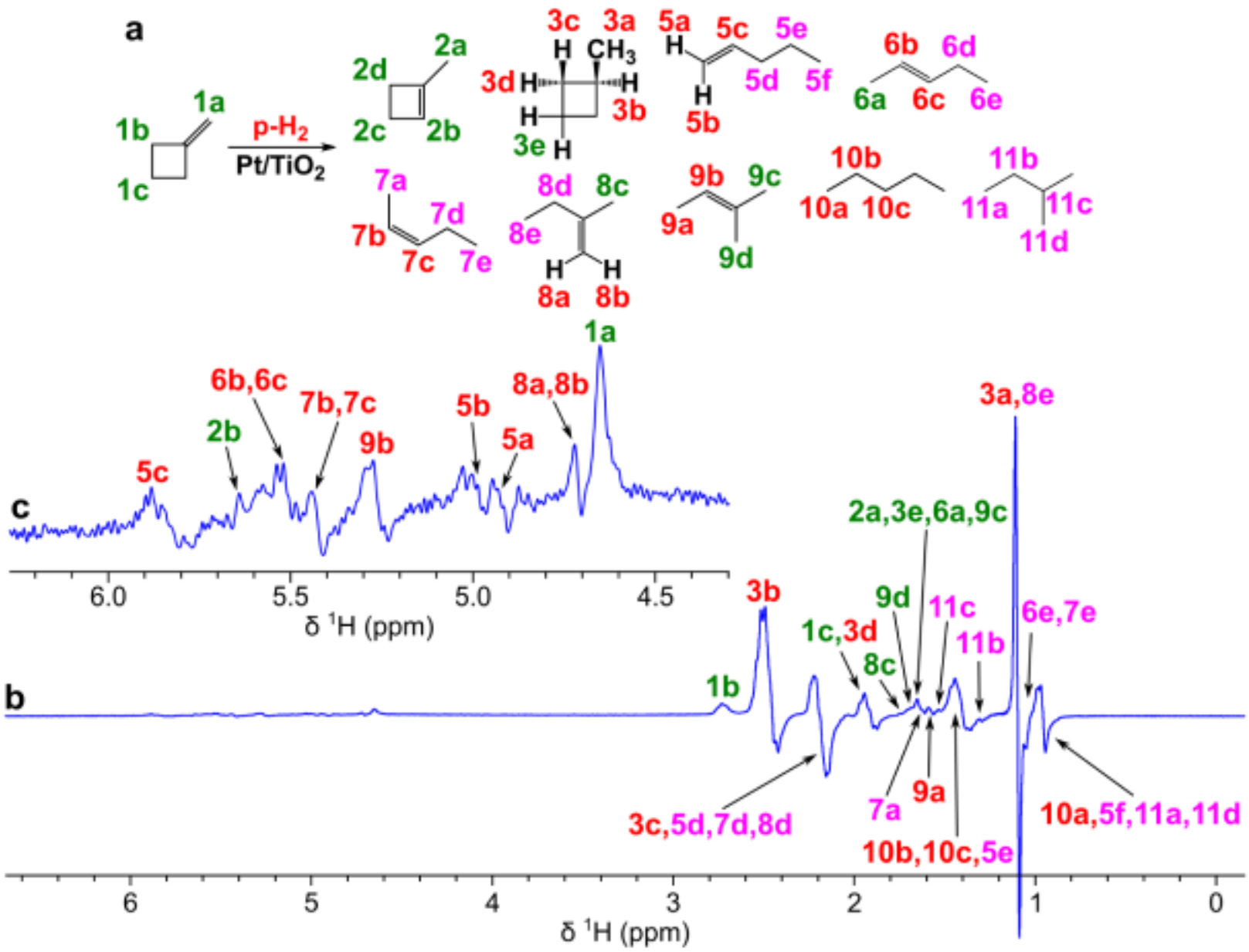
ALTADENA spectrum: Pd



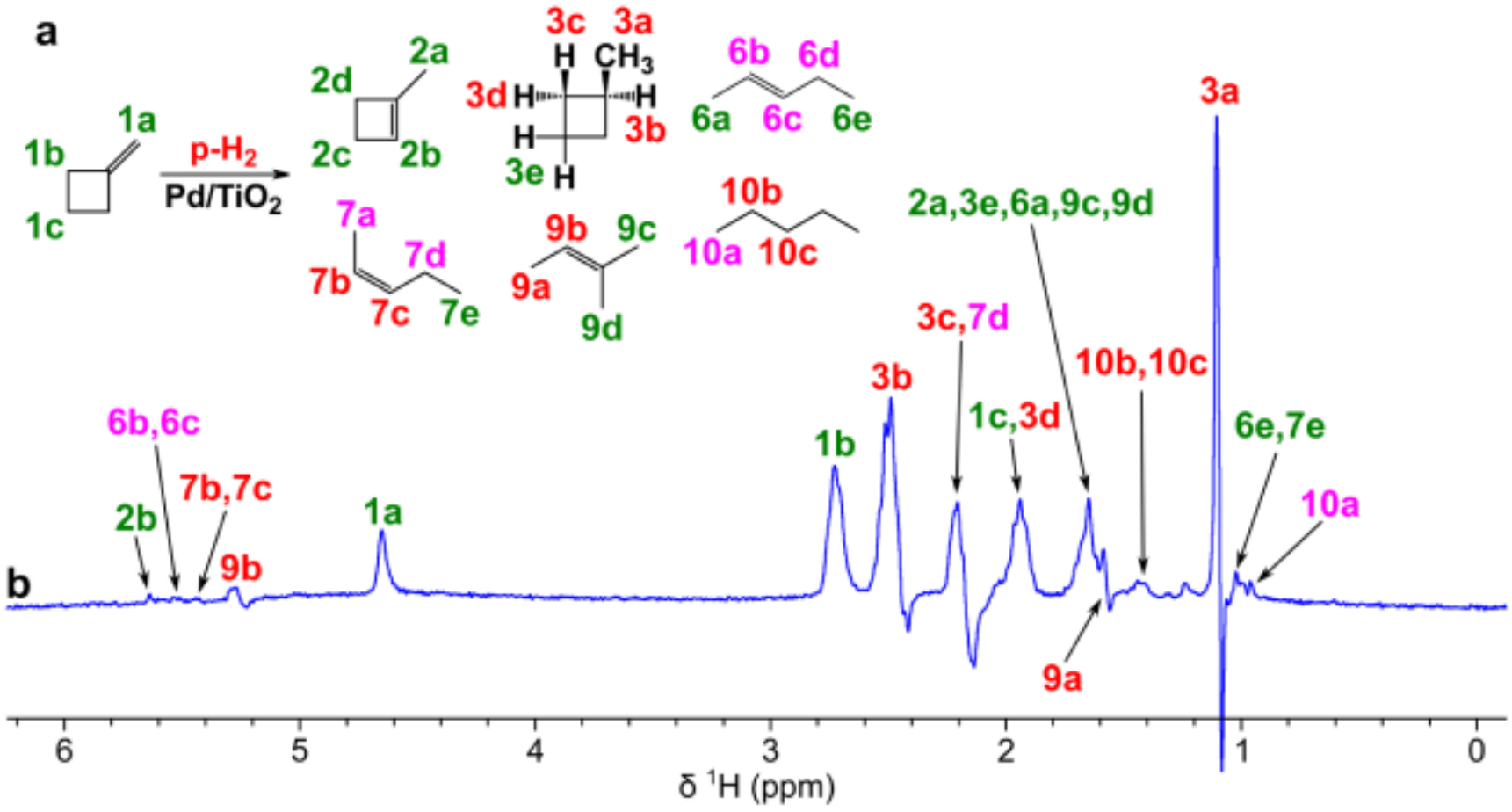
Temperature dependence of conversion & selectivity



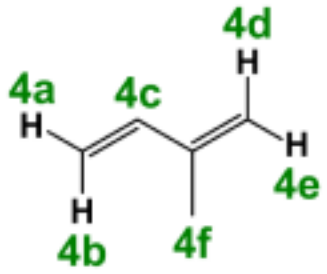
PASADENA spectrum: Pt



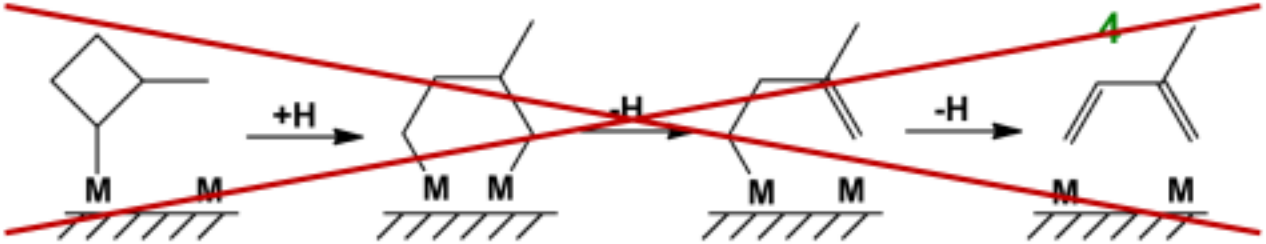
PASADENA spectrum: Pd



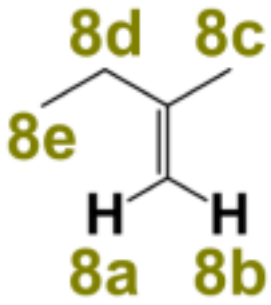
Mechanism of formation of isoprene



similar to mechanisms for alkenes 5-9, should give PHIP effects

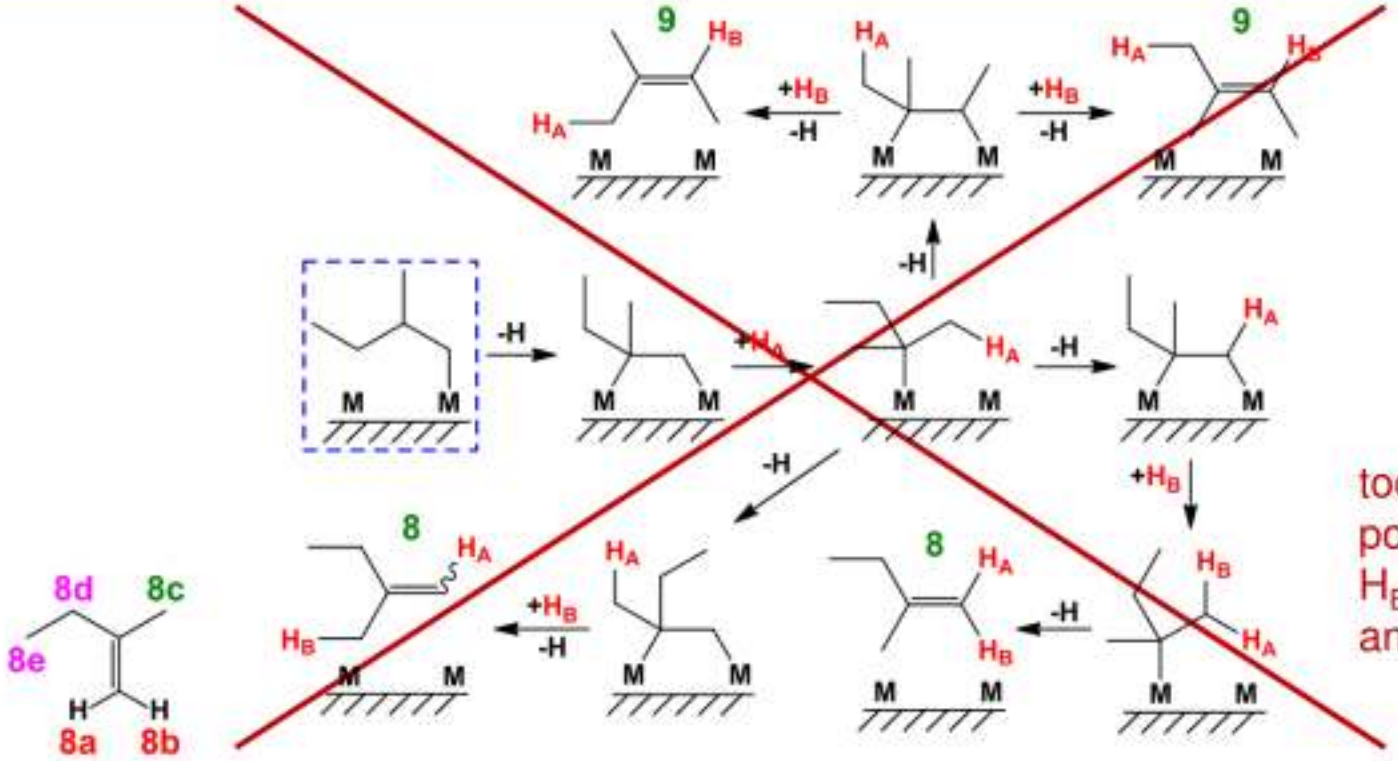


Parameters for spectral simulations of 2-methyl-1-butene



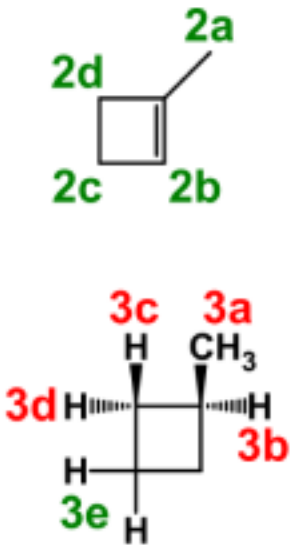
Signal	δ ^{1}H, ppm	J, Hz				
		8a	8b	8c	8d	8e
8a	4.70	X	2.5	–1.2	–1.7	0
8b	4.70		X	–1.7	–1.2	0
8c	1.75			X	–0.43	0
8d	2.10				X	7.3
8e	1.08					X

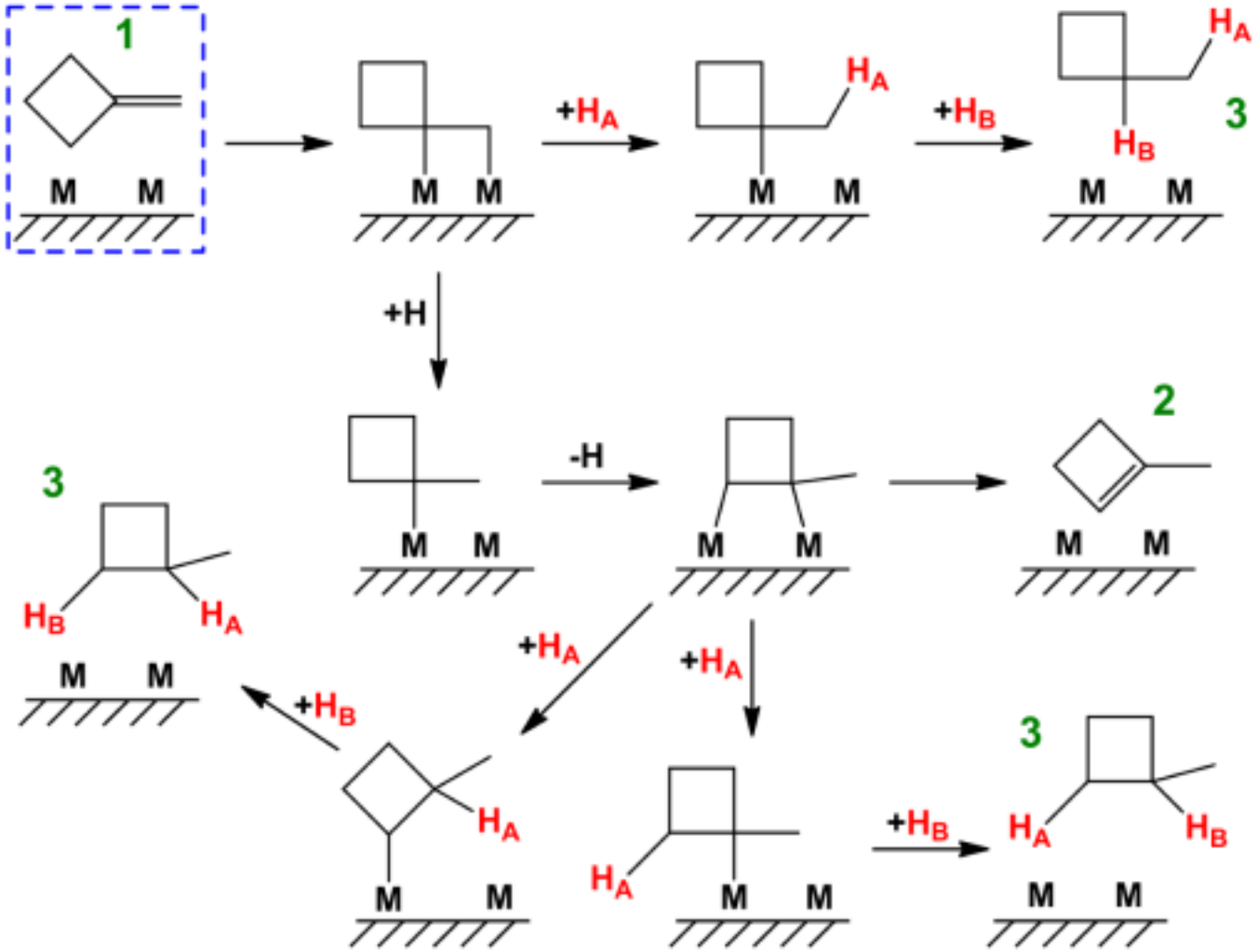
Mechanism of formation of 2-methyl-1-butene



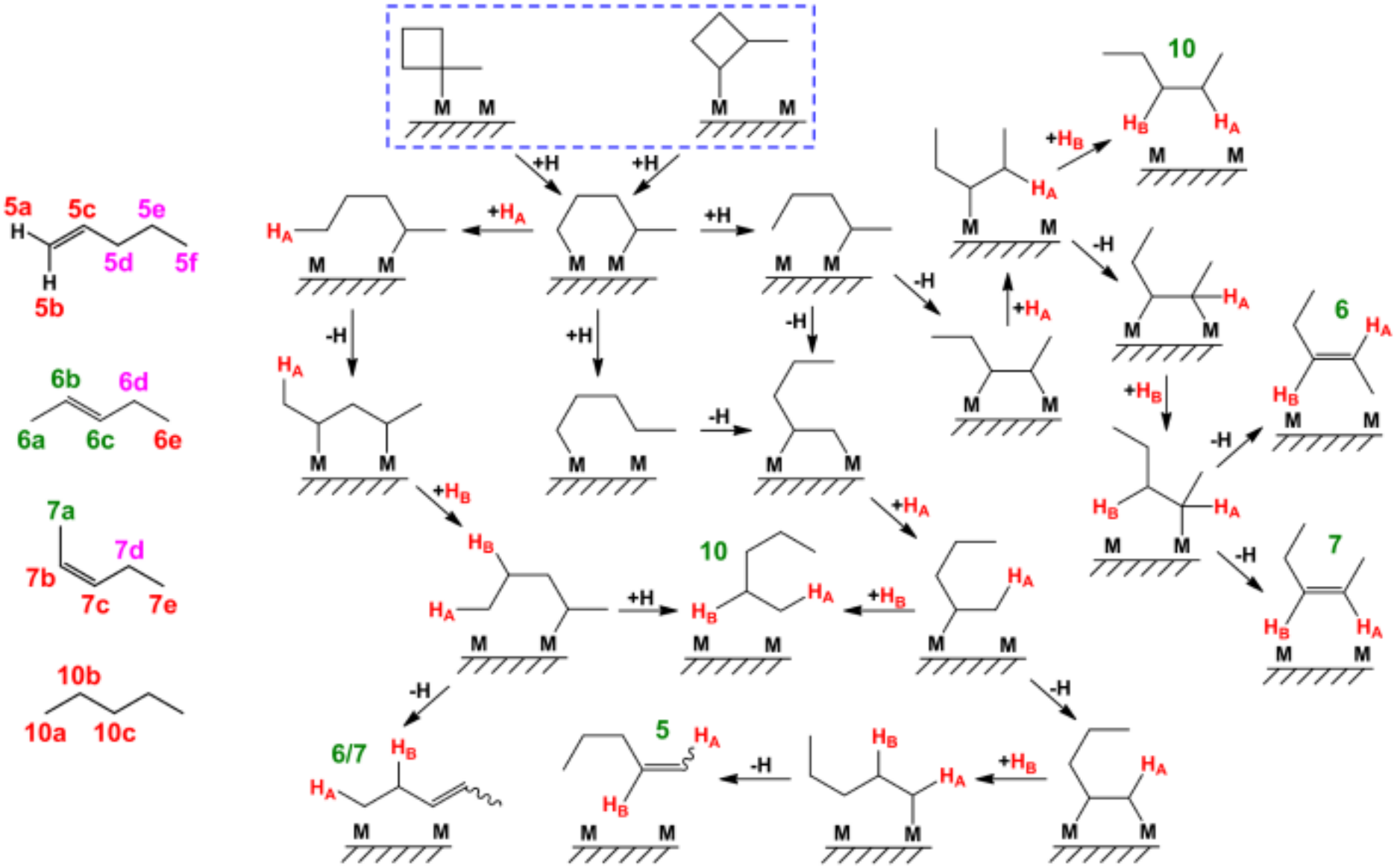
too many possible positions of H_A and H_B in products 8 and 9

Mechanism of formation of cyclic products





Mechanism of formation of linear products



Mechanism of formation of branched products