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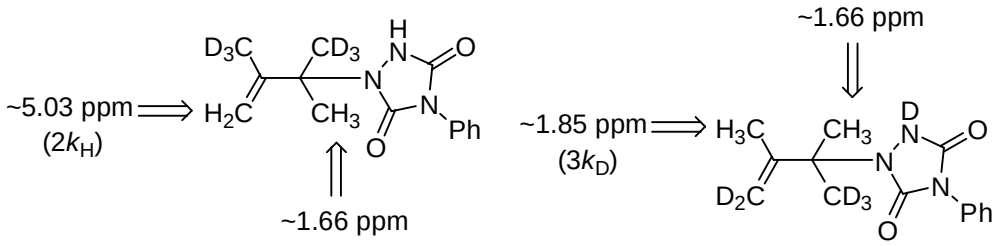
Supporting Information

Solvent-Dependent Changes in the Triazolinedione-Alkene Ene Reaction Mechanism

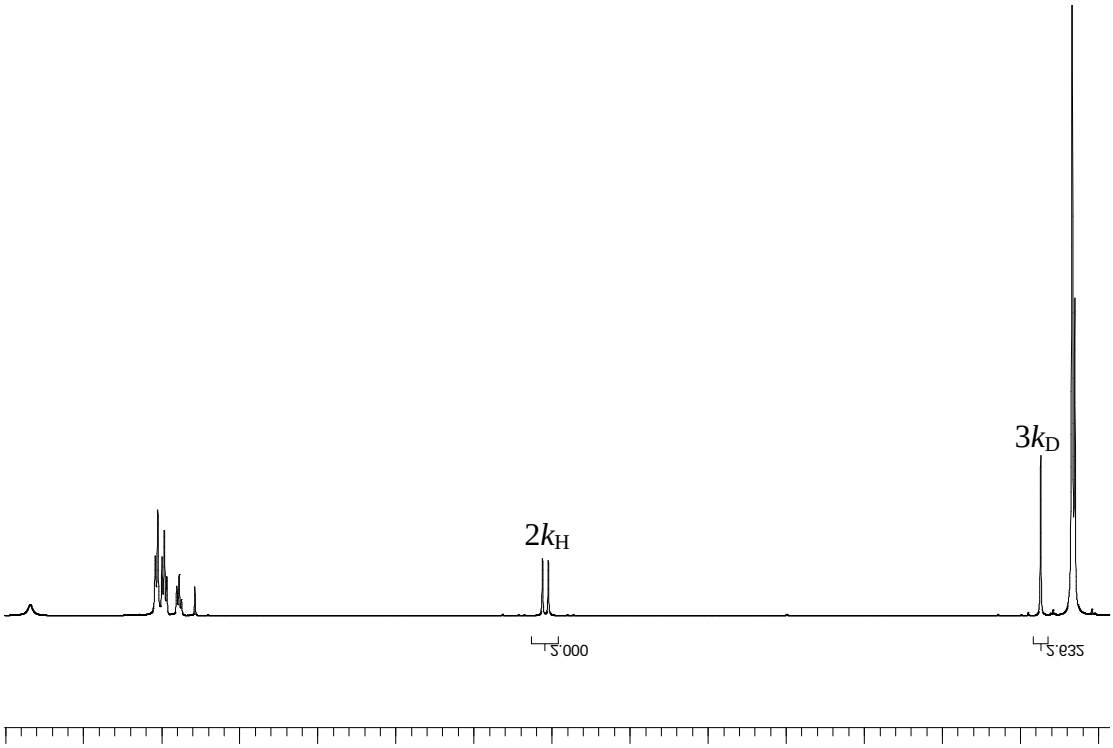
Georgios C. Vougioukalakis, Manolis M. Roubelakis, Mariza N. Alberti, and Michael Orfanopoulos*

Department of Chemistry, University of Crete, Heraklion, Voutes 71003, Crete, Greece

A)[1] H NMR spectra for the measurement of the KIEs in the reaction of *cis*-TME-d_6 with PTAD*

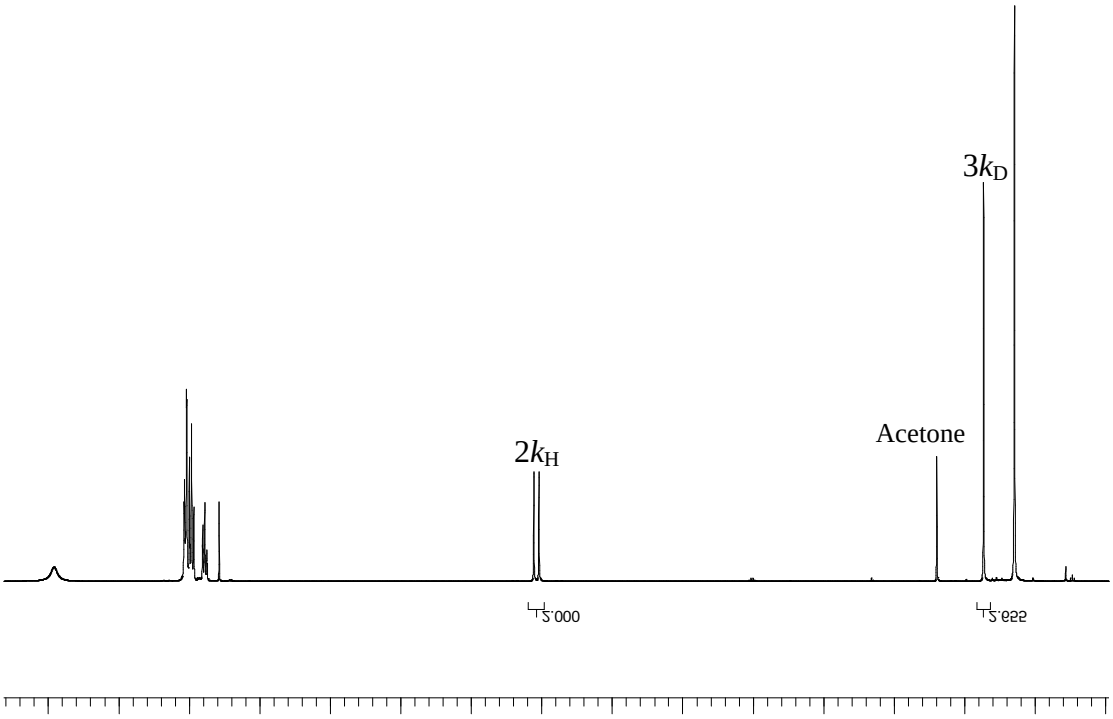


substrate	solvent	temperature	k_H/k_D
cis-TME-*d*6	$CDCl_3$	rt	1.14 ± 0.03

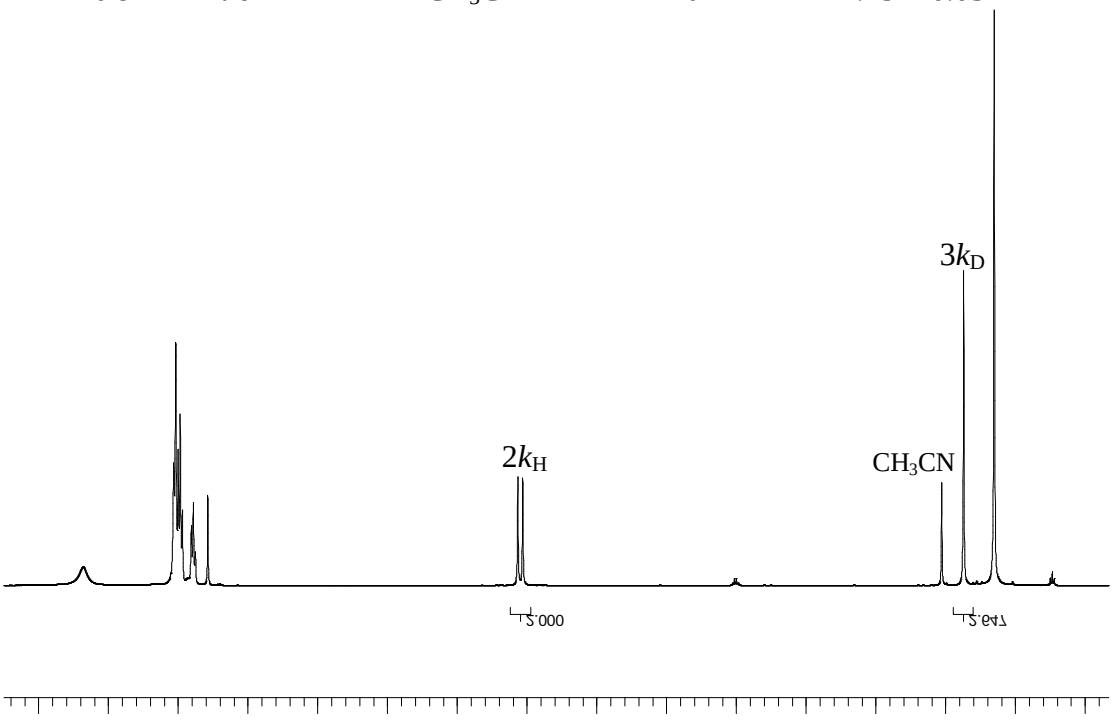


* In all ^{1}H NMR integrations a spin-lattice relaxation time T1 = 5sec was used.

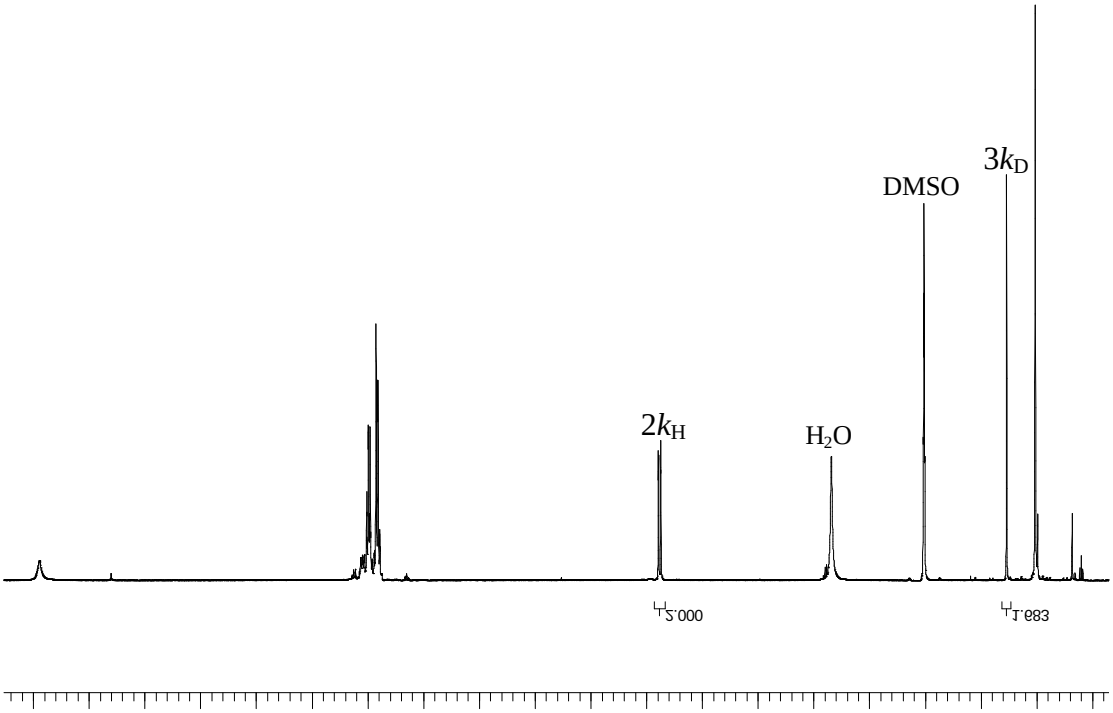
substrate	solvent	temperature	k_H/k_D
cis-TME-*d*6	acetone	rt	1.13 ± 0.03



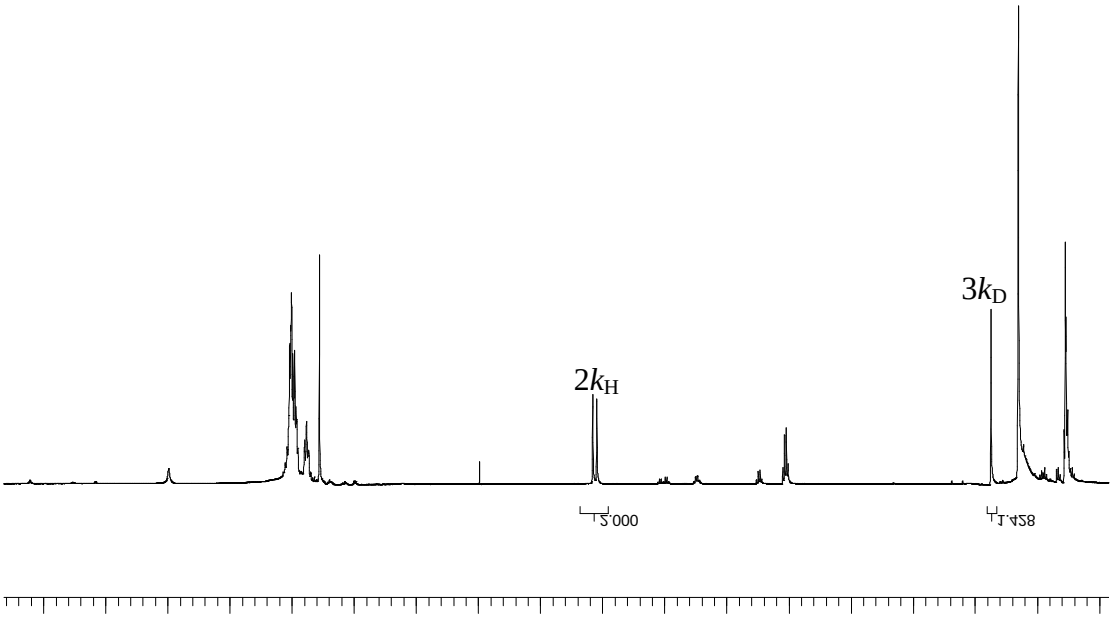
substrate	solvent	temperature	k_H/k_D
cis-TME-*d*6	CH_3CN	rt	1.13 ± 0.03



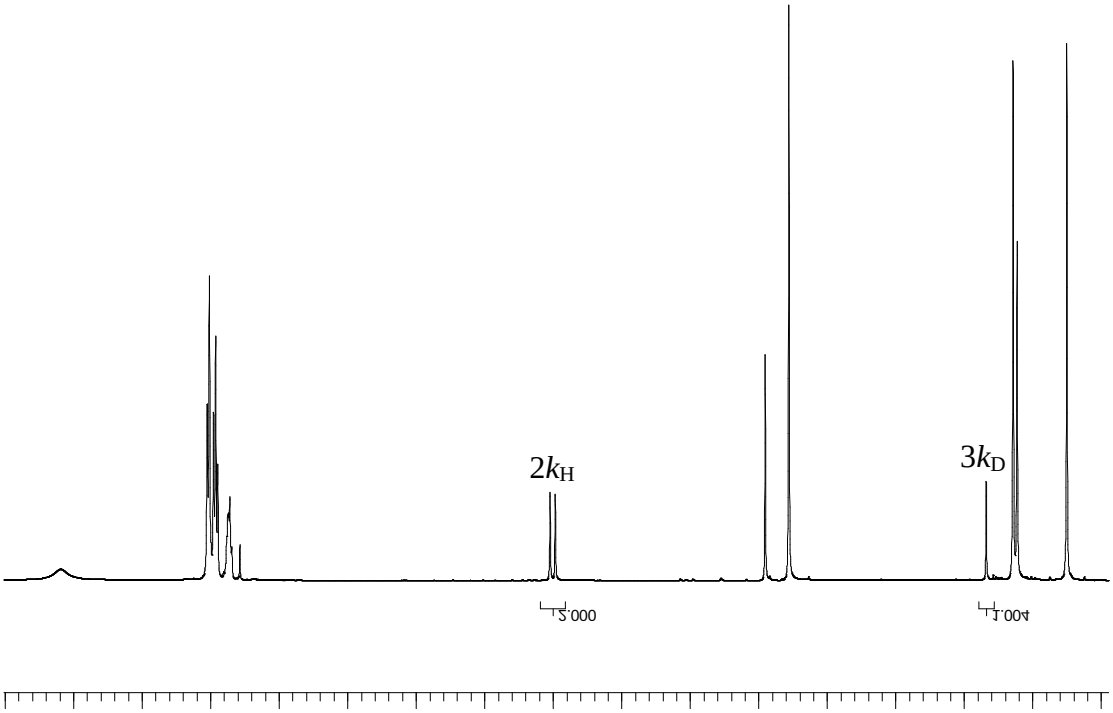
substrate	solvent	temperature	k_H/k_D
cis-TME-*d*6	DMSO	rt	1.78 ± 0.05



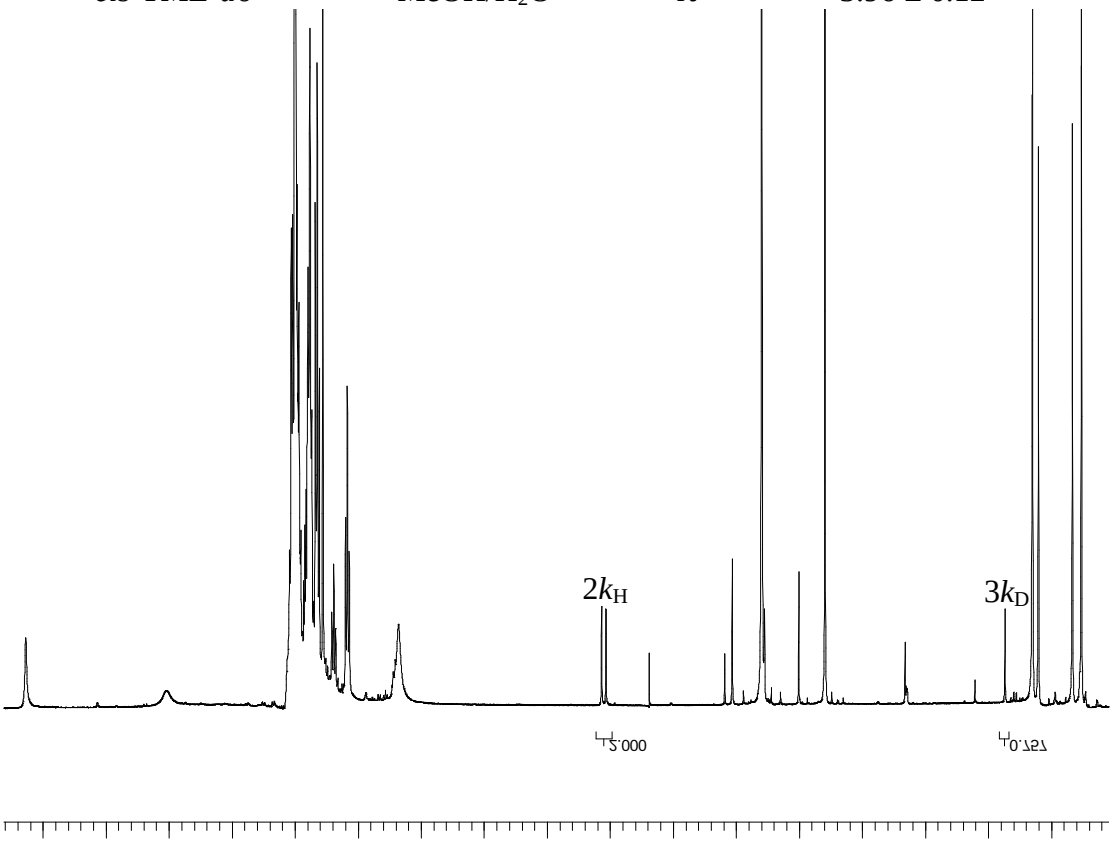
substrate	solvent	temperature	k_H/k_D
cis-TME-*d*6	EtOH	rt	2.10 ± 0.06



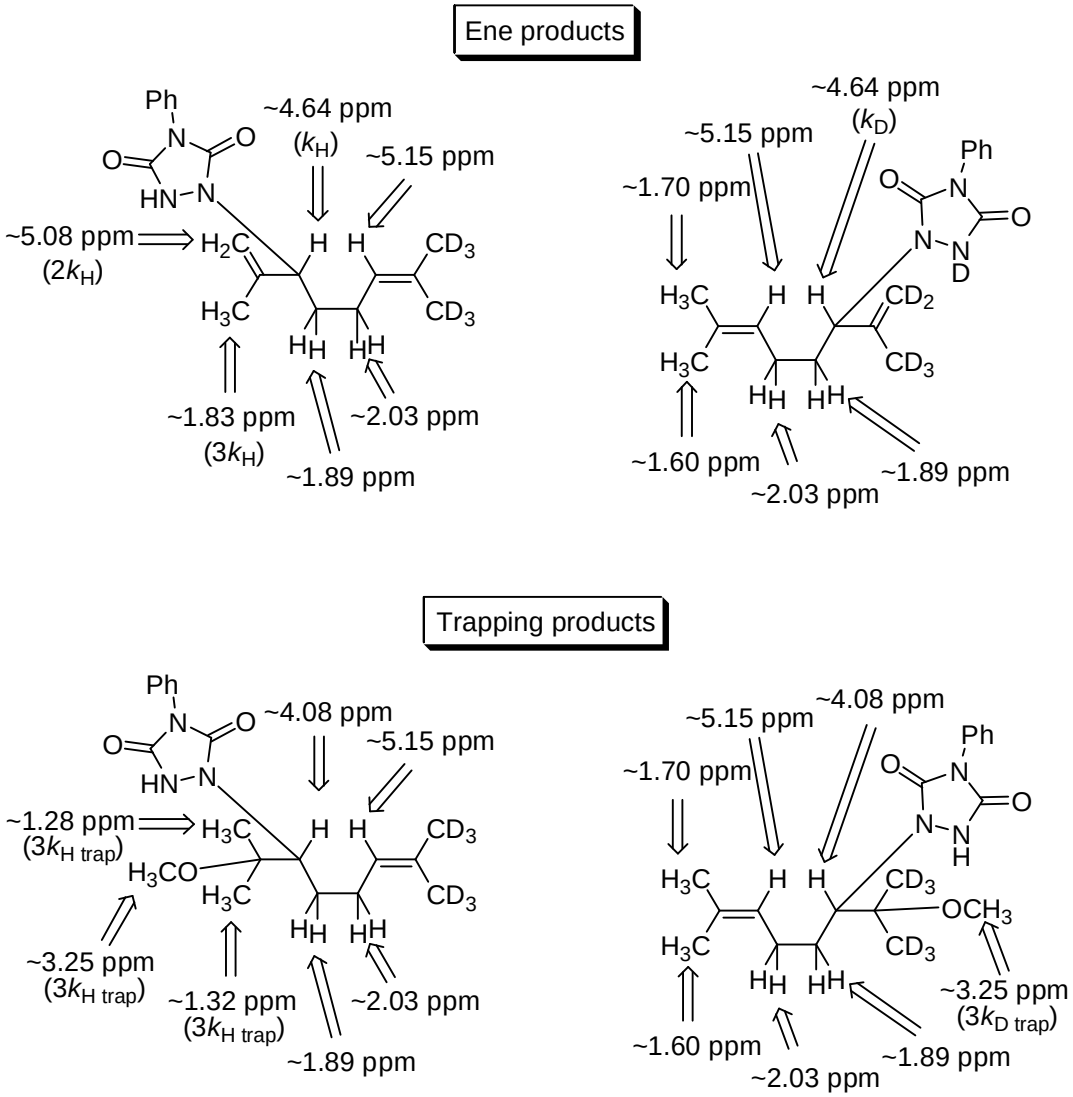
substrate	solvent	temperature	k_H/k_D
cis-TME-*d*6	MeOH	rt	2.99 ± 0.09



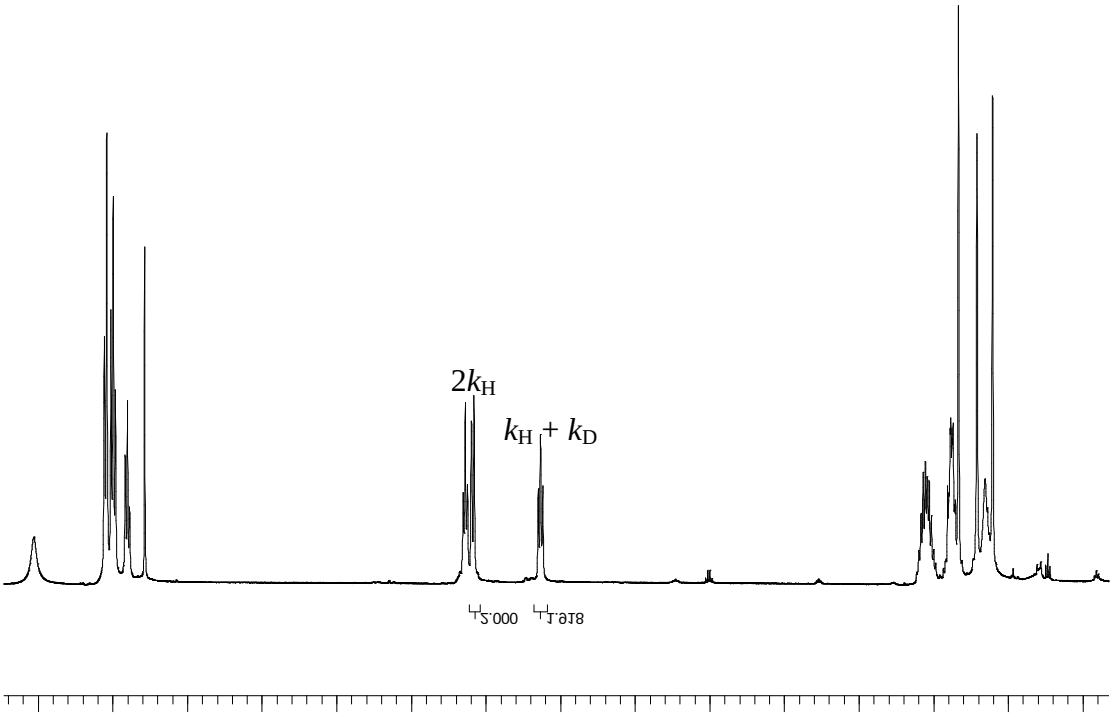
substrate	solvent	temperature	k_H/k_D
cis-TME-*d*6	MeOH/H_2O	rt	3.96 ± 0.12



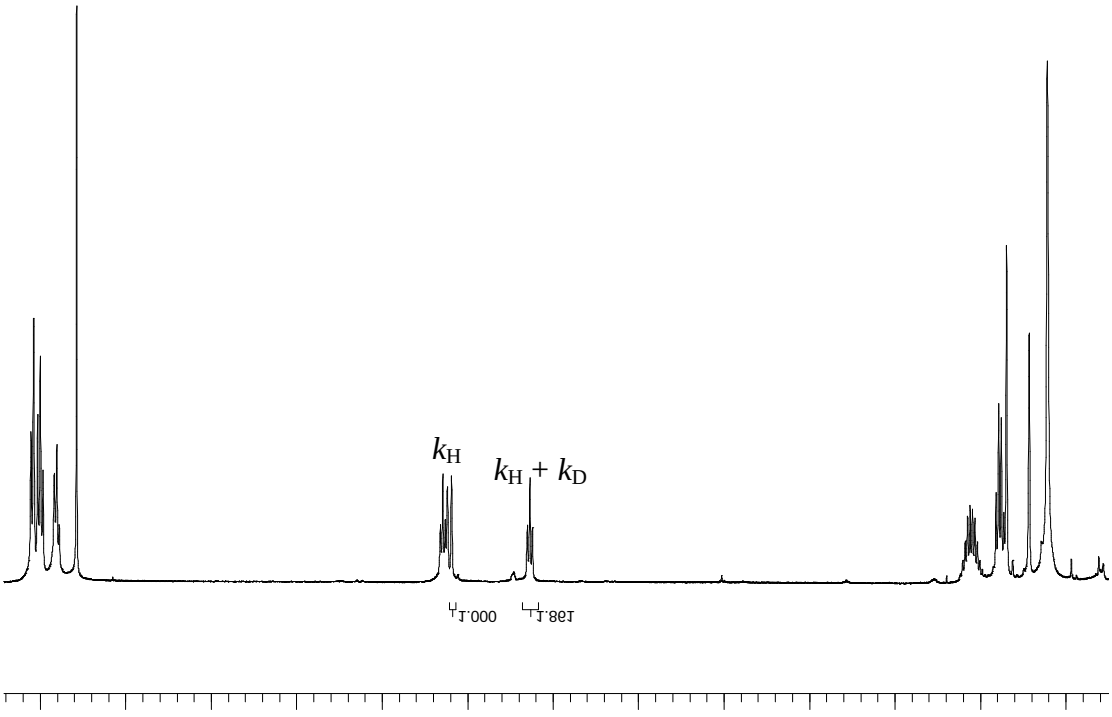
B) ^{1}H NMR spectra for the measurement of the KIEs in the reaction of DMOD-d_6 with PTAD



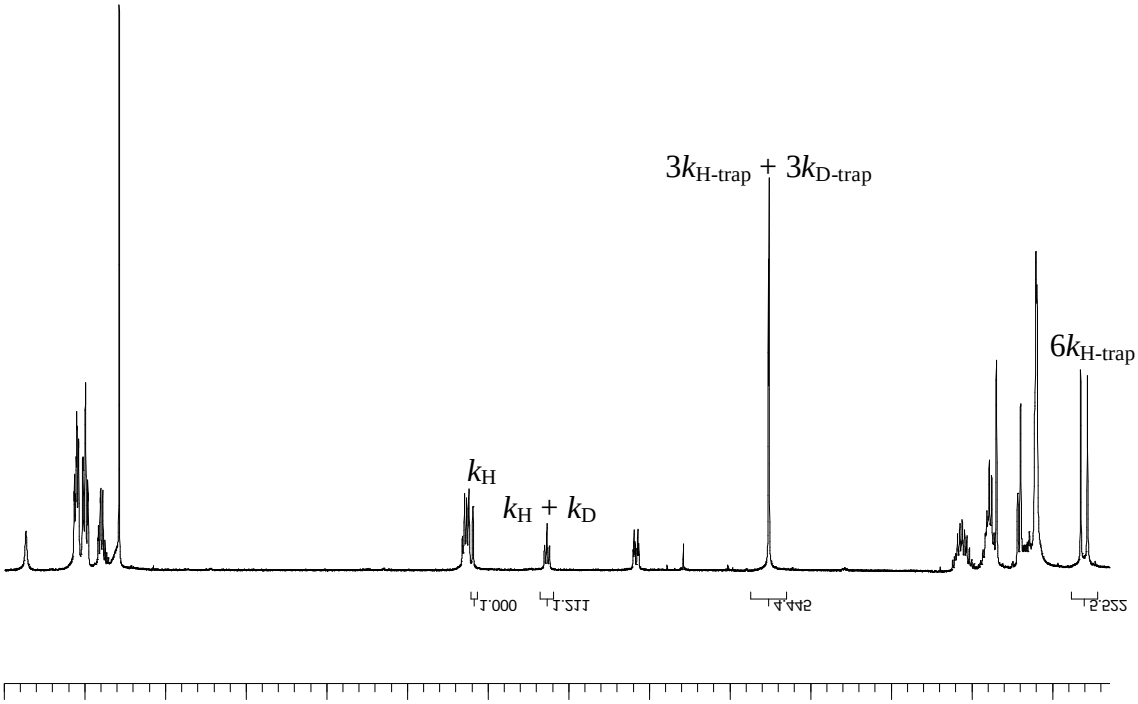
substrate	solvent	temperature	k_H/k_D
DMOD-d_6	CH_2Cl_2	rt	1.09 ± 0.03



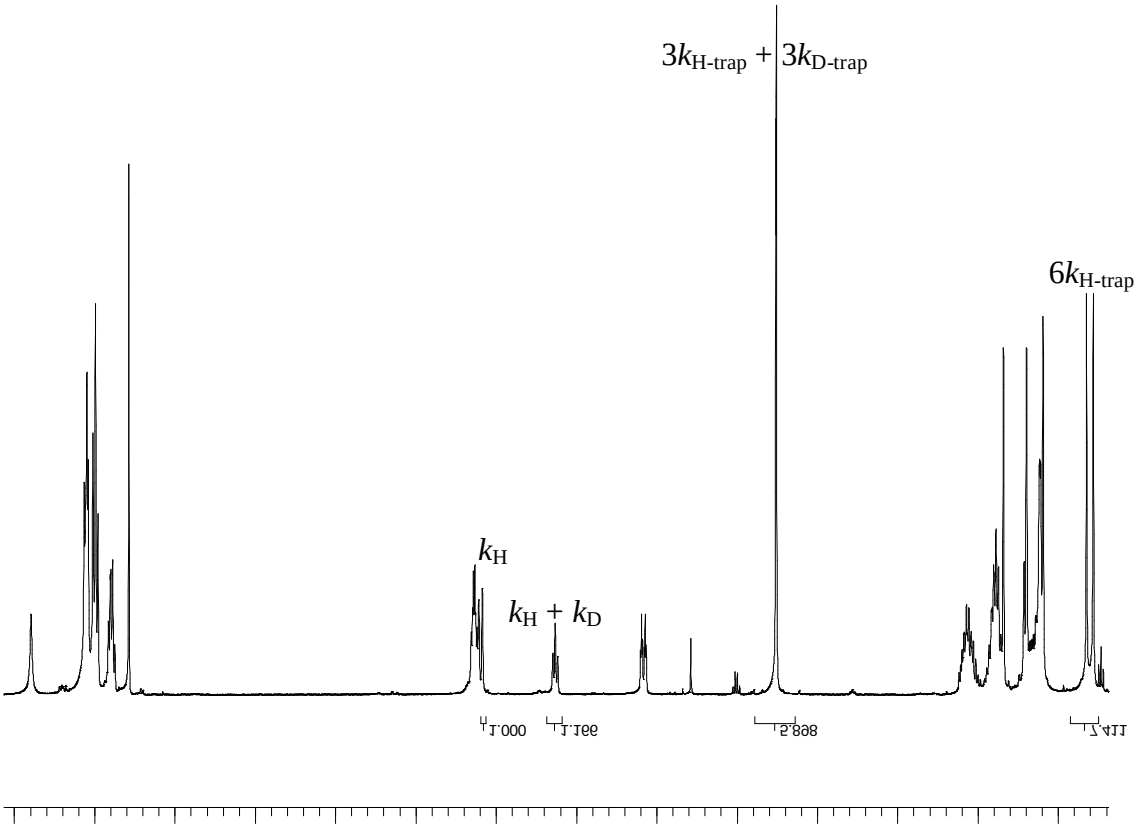
substrate	solvent	temperature	k_H/k_D
DMOD-d_6	CH_2Cl_2	0 °C	1.16 ± 0.03

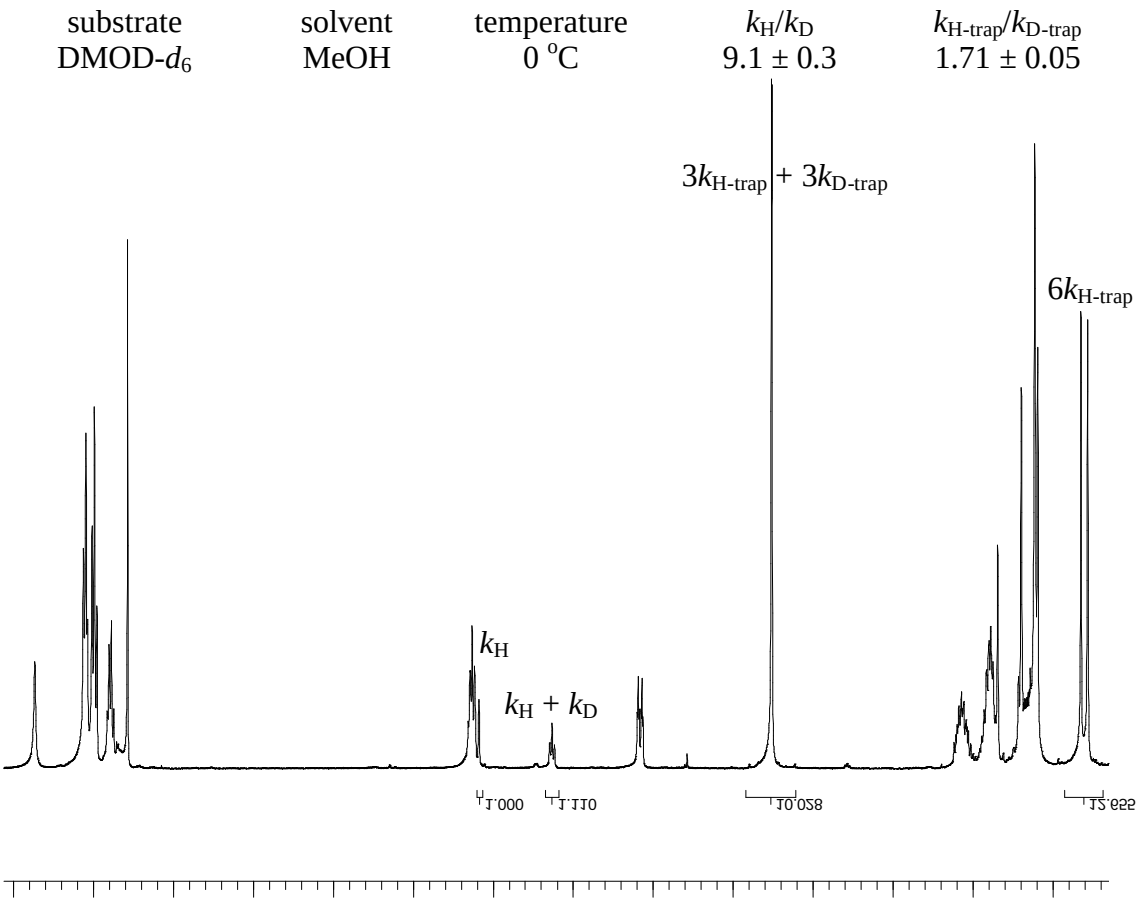


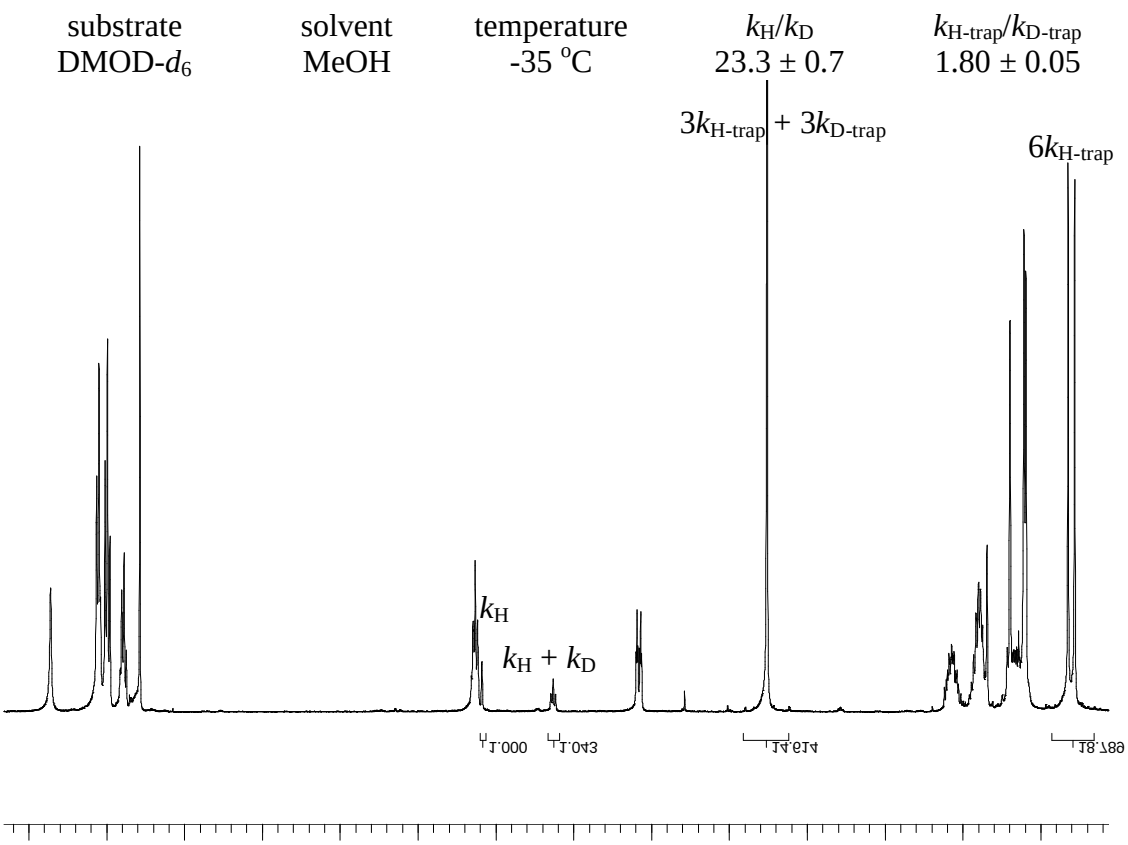
substrate	solvent	temperature	k_H/k_D	$k_{H\text{-trap}}/k_{D\text{-trap}}$
DMOD-d_6	MeOH	40 °C	4.7 ± 0.1	1.64 ± 0.05



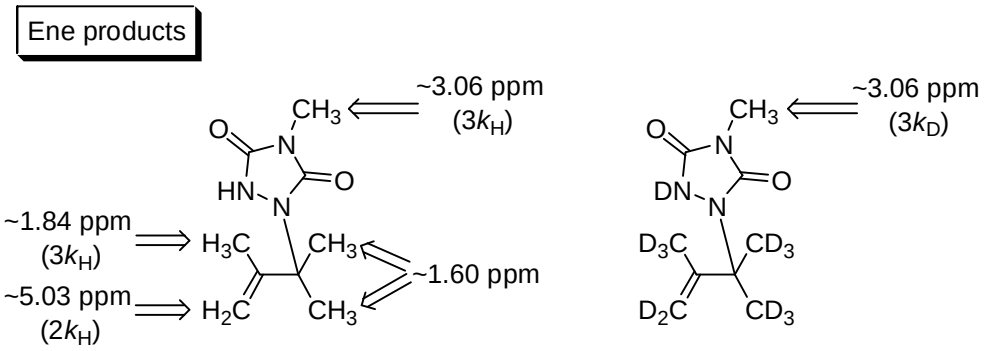
substrate	solvent	temperature	k_H/k_D	$k_{H\text{-trap}}/k_{D\text{-trap}}$
DMOD-d_6	MeOH	rt	6.0 ± 0.2	1.69 ± 0.05



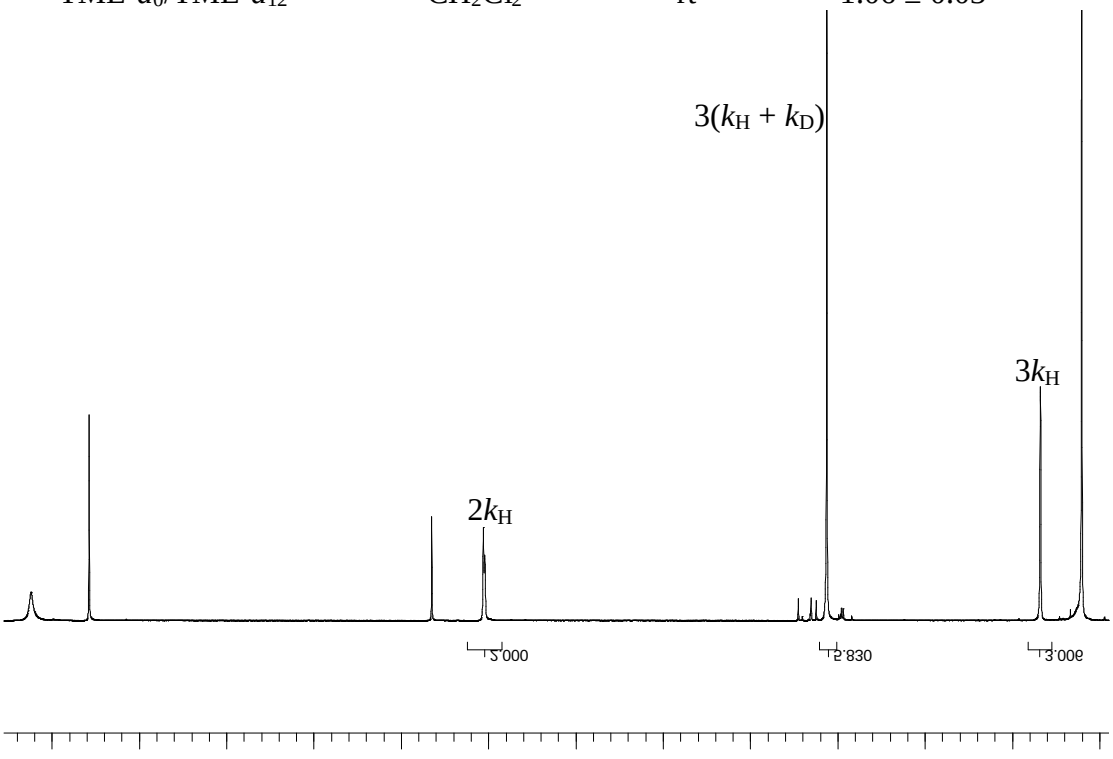

substrate
DMOD-d_6
solvent
MeOH
temperature
0 °C
k_H/k_D
9.1 ± 0.3
$k_{H\text{-trap}}/k_{D\text{-trap}}$
1.71 ± 0.05
$3k_{H\text{-trap}} + 3k_{D\text{-trap}}$
$6k_{H\text{-trap}}$
k_H
$k_H + k_D$


substrate
DMOD-d_6
solvent
MeOH
temperature
-35 °C
k_H/k_D
23.3 ± 0.7
$k_{H\text{-trap}}/k_{D\text{-trap}}$
1.80 ± 0.05
$3k_{H\text{-trap}} + 3k_{D\text{-trap}}$
$6k_{H\text{-trap}}$
k_H
$k_H + k_D$

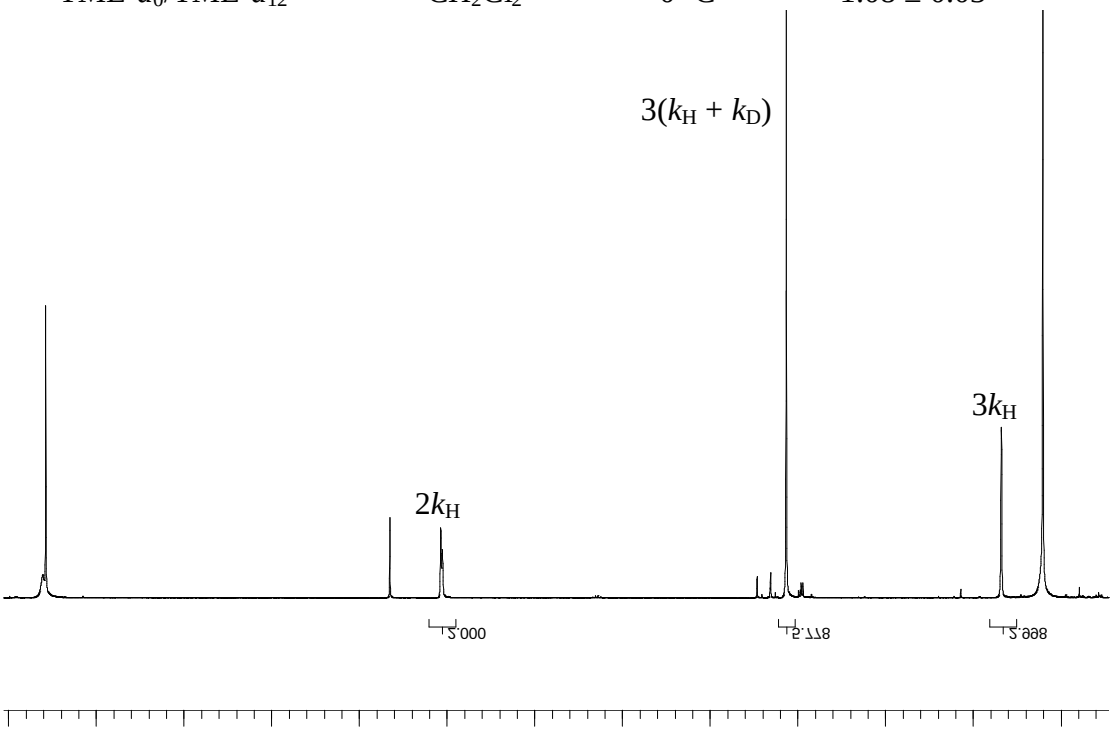
C) ^{1}H NMR spectra for the measurement of the KIEs in the reaction of TME-d_0/TME-d_{12} with MTAD



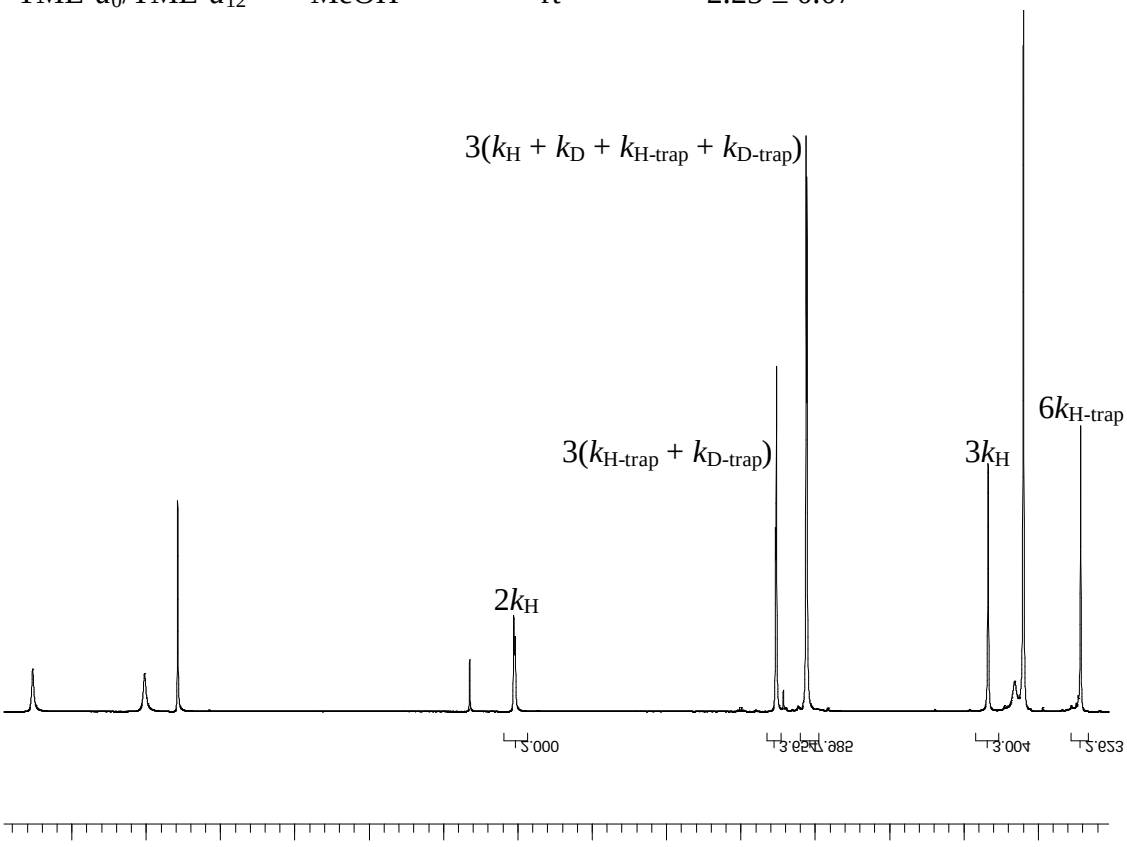
substrate: TME-d_0/TME-d_{12} | solvent: CH_2Cl_2 | temperature: rt | k_H/k_D: 1.06 ± 0.03



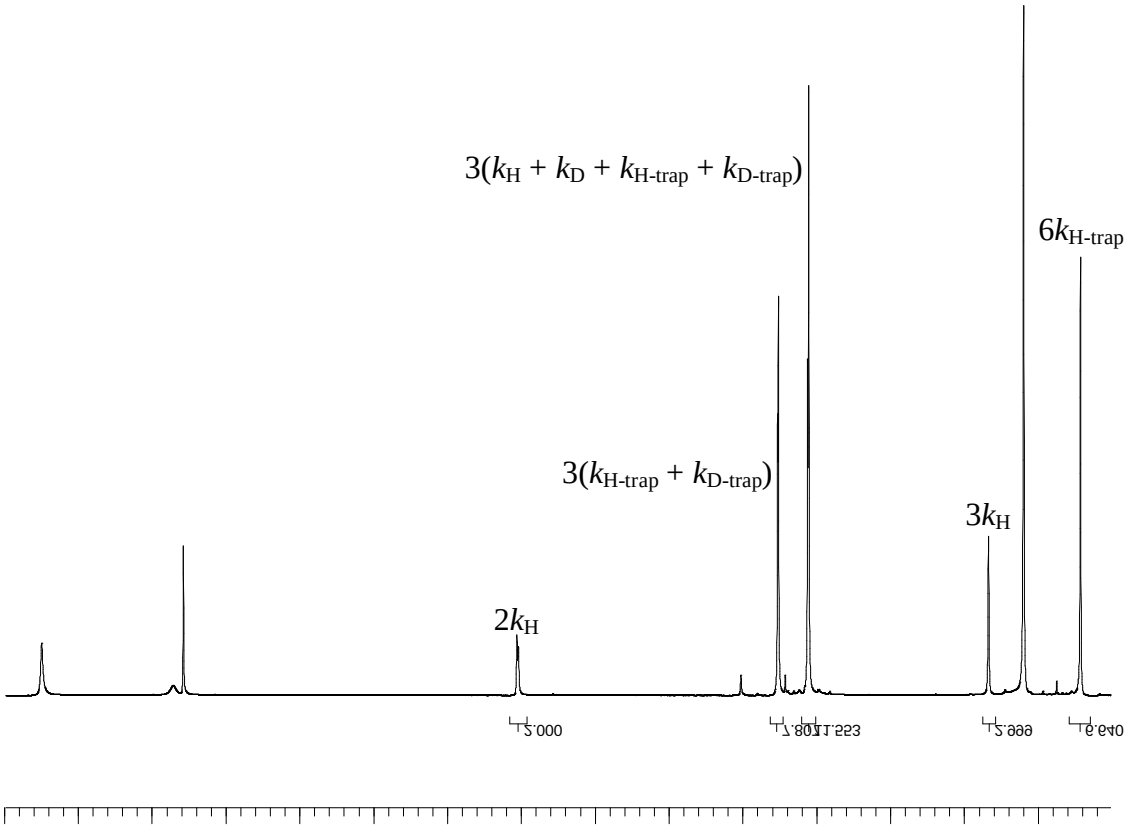
substrate	solvent	temperature	k_H/k_D
TME-d_0/TME-d_{12}	CH_2Cl_2	0 °C	1.08 ± 0.03



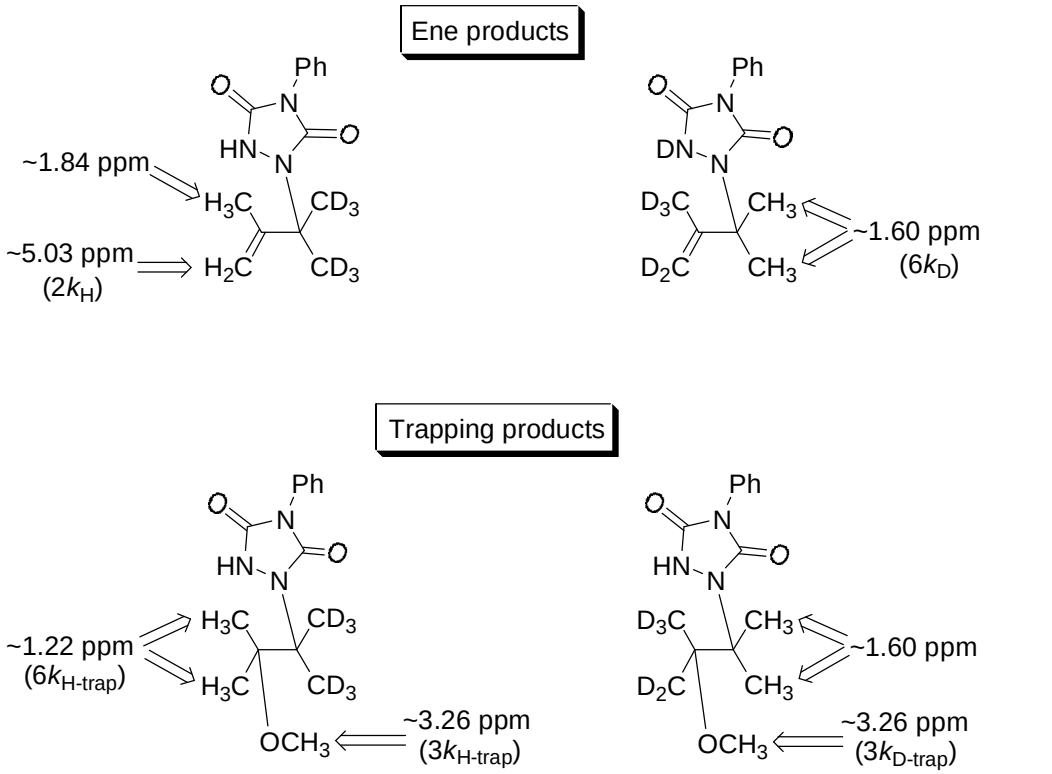
substrate	solvent	temperature	k_H/k_D
TME-d_0/TME-d_{12}	MeOH	rt	2.25 ± 0.07



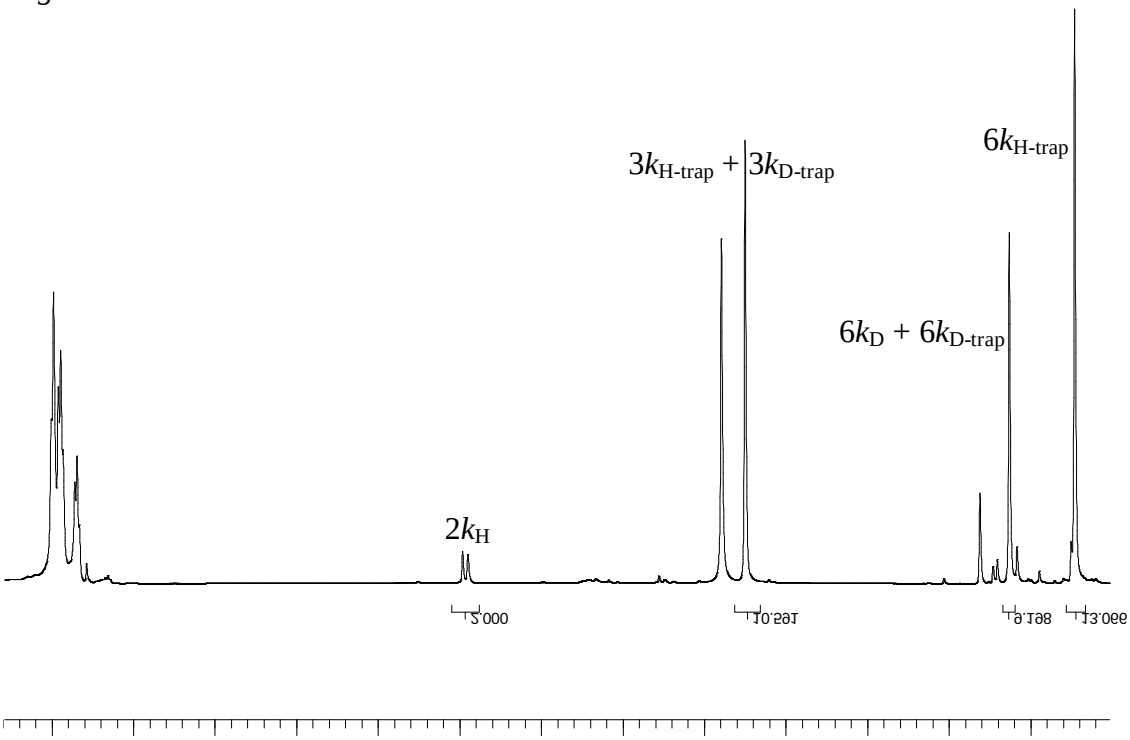
substrate	solvent	temperature	k_H/k_D
TME-d_0/TME-d_{12}	MeOH	0 °C	4.02 ± 0.12



D) ^{1}H NMR spectra for the measurement of the KIEs in the reaction of *gem*-TME-d_6 with PTAD



substrate	solvent	temperature	k_H/k_D	$k_{H\text{-}trap}/k_{D\text{-}trap}$
gem-TME-*d*6	MeOH	rt	5.5 ± 0.2	1.61 ± 0.05



substrate	solvent	temperature	k_H/k_D	$k_{H\text{-trap}}/k_{D\text{-trap}}$
gem-TME-*d*6	MeOH	0 °C	5.7 ± 0.2	1.64 ± 0.05