Supplementary Information

Unexpected thermal decomposition of the "Alder carbene" (*i*Pr$_2$N)$_2$C

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Experimental Section

General

All reactions were carried out in an inert atmosphere by applying standard Schlenk or glovebox techniques. Bis(diisopropylamino)carbene (**1**)[S1] and diisopropylamino-*cis*-2,6-dimethylpiperidinocarbene (**4**)[S2] were prepared according to published procedures. NMR spectra were recorded in C_6D_6 solution with a Varian Unity Inova 500 MHz NMR spectrometer. The residual protio impurity of the deuterated solvent was used as internal standard (^{1}H NMR: δ = 7.16; ^{13}C NMR: 128.0 ppm). Mass spectra (ESI and APCI) were obtained with a quadrupole ion-trap spectrometer Finnigan LCQ^{DECA} (ThermoQuest, San José, USA). High-resolution mass spectra (HRMS) were measured with a time-of-flight mass spectrometer micrOTOF (Bruker Daltonics, Bremen, Germany) using an Apollo^{TM} Ion Funnel ESI ion-source.

Fragmentation experiments

A C_6D_6 solution of the respective carbene in a flame-sealed NMR tube was kept at a constant temperature by means of a thermostat (Thermo Haake B3, C10). The sample was periodically analysed by NMR spectroscopy. A detailed description is given below.

*Bis(diisopropylamino)carbene (**1**)*

The first-order kinetics of the fragmentation reaction was established by monitoring three samples of different concentration kept at 308 K. Fig. S1 exemplarily shows ^{1}H NMR spectra recorded after 0 h, 150 h and 450 h for one such sample. For determining the activation energy, samples of identical concentration which were kept at four different temperatures were monitored. All samples showed a gradual decrease of the carbene concentration and a

concomitant increase of the concentration of the fragmentation products, which were identified as propene and *N,N,N'*-triisopropylformamidine (**2**).

Bis(diisopropylamino)carbene (**1**):

^{1}H NMR: δ = 1.28 (br. d, 24 H); 3.70 (br. m, 4 H)

^{13}C NMR: δ = 24.2 (br.); 49.6 (br.); 255.5

Propene:

^{1}H NMR: δ = 1.55 (m, 3 H); 4.97 (m, 2 H); 5.72 (m, 1 H)

^{13}C NMR: δ = 19.4; 115.9; 133.7

N,N,N'-Triisopropylformamidine (**2**):

^{1}H NMR: δ = 1.00 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H); 1.32 (d, $^{3}J_{HH}$ = 6.5 Hz, 6 H); 3.30 (br. sept, 1 H); 3.80 (br. m, 2 H); 7.45 (s, 1 H)

^{13}C NMR: δ = 21.9 (br.); 26.6; 45.2; 57.7; 147.9

MS/APCI(+): *m/z* (%) = 171.13 (100) $[M + H]^+$

HRMS/ESI(+): *m/z* = 171.185443 $[M + H]^+$; 171.185575 calcd. for $[C_{10}H_{23}N_2]^+$.

For determining the concentrations of the carbene and the formamidine, integrals of diagnostic ^{1}H NMR signals were compared with respect to the initial concentration $[A]_0$ of the carbene. The following signals were used: carbene **1**: δ = 1.28 (br. d, 24 H); fomamidine **2**: δ = 1.00 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H). Experimental parameters and results of this kinetic study are collected in Table S1.

Table S1 Experimental parameters and results of fragmentation experiments performed with **1**

T [K]	**[A]$_0$** [mol/l]	$t_{½}$ [min]	***k*** [1/s]
295	0.13	14811	$7.8 \cdot 10^{-7}$
308	0.07	2712	$4.3 \cdot 10^{-6}$
308	0.13	2712	$4.3 \cdot 10^{-6}$
308	0.19	2712	$4.3 \cdot 10^{-6}$
323	0.13	431	$2.7 \cdot 10^{-5}$
338	0.13	76	$1.5 \cdot 10^{-4}$

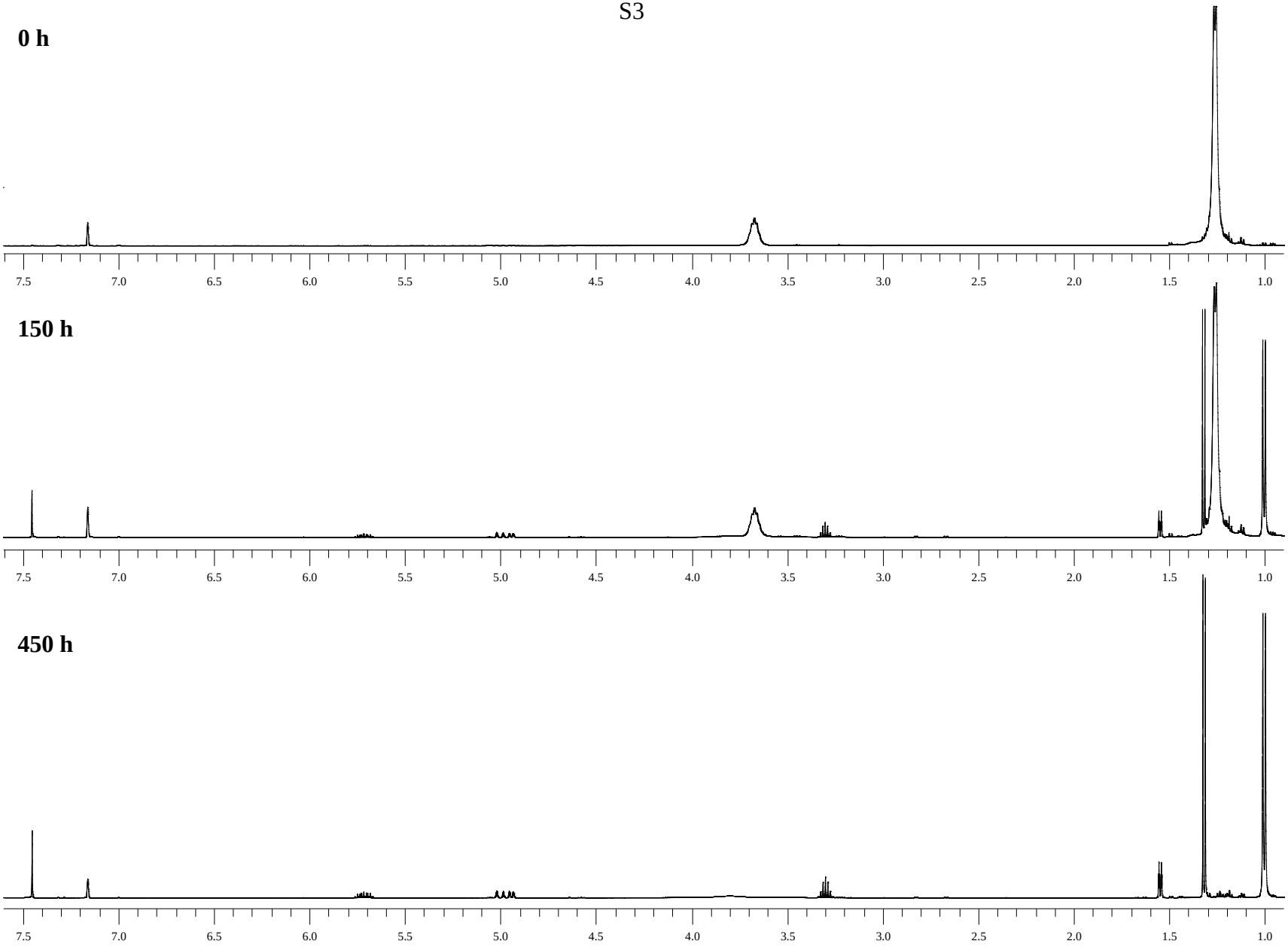

Fig. S1 ^{1}H-NMR spectra of (iPr$_2$N)$_2$C (**1**) (0.13 M; 308 K; C_6D_6) after 0 h (top; **1**), 150 h (middle; mixture of **1** and its fragmentation products) and 450 h (bottom: no **1** left, only fragmentation products present).

Reaction rate constants *k* were determined by plotting the logarithmic concentration of the carbene ln[A] *versus* time *t*. A typical result is shown in Fig. S2. For a first-order reaction, *k* is equal to the negative slope –*m* of the best-fit straight line (y = *m*x + *b*).

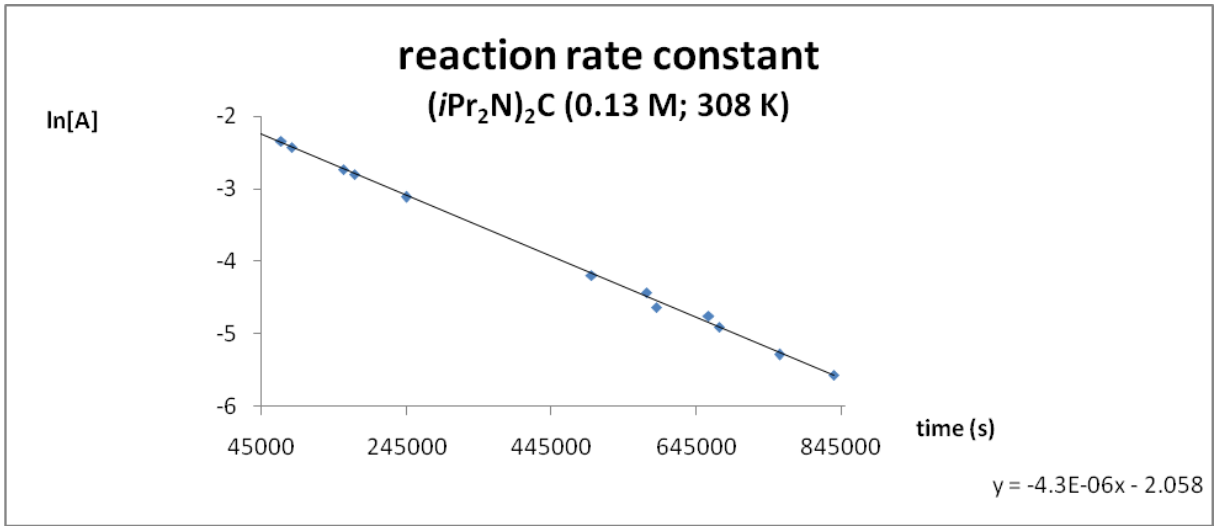

Fig. S2 Example for the determination of the reaction rate constant (k = 4.3•10^{-6} s^{-1}).

To determine the activation energy E_a, the logarithmic reaction rate constant ln*k* was plotted *versus* 1/*T*. This ARRHENIUS plot is shown in Fig. S3.

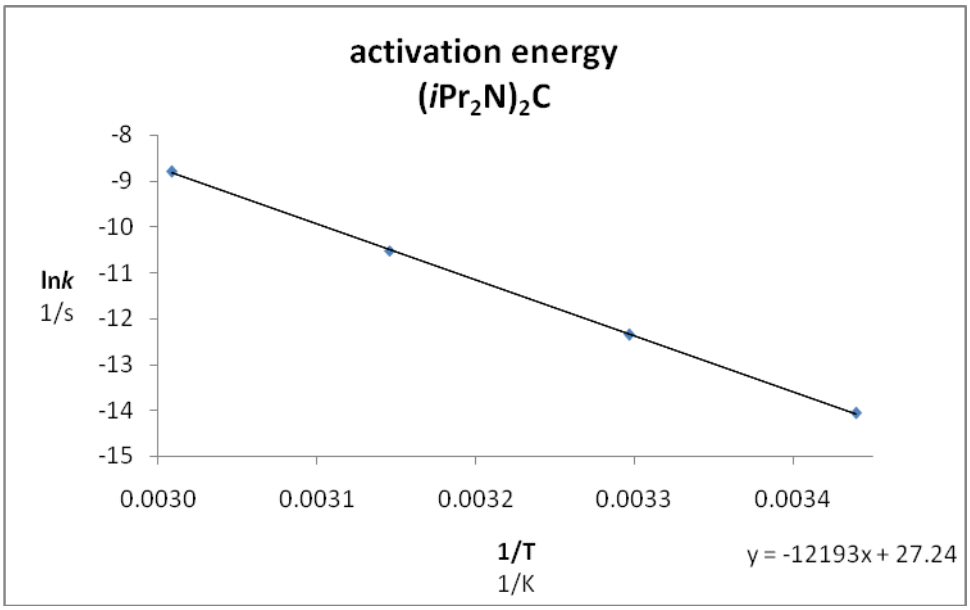

Fig. S3 ARRHENIUS plot for the fragmentation of **1**.

According to the ARRHENIUS equation in its logarithmic form:

$$\ln k = -E_a/RT + \text{const.}$$

the activation energy E_a can be obtained from the slope of the best-fit straight line:

$$E_a = -mR$$

With R = 1.987 cal K^{-1} mol^{-1} the activation energy for the fragmentation of **1** is calculated as 24.2 kcal/mol. The standard deviation of this value is ±0.2 kcal/mol. According to a cautious estimation, the margin of total experimental error is ±1.0 kcal/mol.

*Diisopropylamino-cis-2,6-dimethylpiperidinocarbene (**4**)*

Fig. S4 exemplarily shows ^{1}H NMR spectra recorded at different stages of the fragmentation of **4** at room temperature. Fig. S5 shows the temporal development of selected characteristic ^{1}H NMR signals of a sample kept at 338 K. The gradual decrease of the concentration of **4** is accompanied by a concomitant increase of the concentration of the products, which were identified as propene, 1-*cis*-2,6-dimethylpiperidinoisopropylimine (**5**) and *N,N*-diisopropyl-*N*'-1-methylhex-5-enylformamidine (**6**).

Diisopropylamino-*cis*-2,6-dimethylpiperidinocarbene (**4**)

^{1}H NMR: δ = 1.24 (br. s, 6 H); 1.26 (br. d, 12 H); 1.36 (br. m, 2 H); 1.70 (br. m, 4 H); 3.74 (br. s, 2 H); 4.28 (br. m, 2 H)

^{13}C NMR: δ = 14.8; 23.0; 24.1 (br.); 31.8; 49.5 (br.); 56.2; 258.5

1-*cis*-2,6-Dimethylpiperidinoisopropylimine (**5**):

^{1}H NMR: δ = 1.08 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, NCH(CH_3)CH_2); 1.32 (d, $^3J_{HH}$ = 6.3 Hz, 6 H, CH(CH_3)$_2$); 1.20–1.55 (m, 6 H, $CH_2CH_2CH_2$); 3.31 (m, $^3J_{HH}$ = 6.3 Hz, 1 H, CH(CH_3)$_2$); 3.92 (m, 2 H, NCH(CH_3)CH_2); 7.17 (s, 1 H, NCHN)

^{13}C NMR: δ = 151.7 (N*C*HN); 57.2 (N*C*H(CH_3)$_2$); 48.2 (N*C*H(CH_3)CH_2); 26.8 (NCH(CH_3)*C*H_2); 26.5 (NCH(*C*H_3)$_2$); 20.9 (NCH(*C*H_3)CH_2); 15.3 (CH_2*C*H_2CH_2)

MS/APCI(+): *m/z* (%) = 183.2 (40) $[M + H]^+$

HRMS/ESI(+): *m/z* = 183.185395 $[M + H]^+$; 183.185575 calcd. for $[C_{11}H_{23}N_2]^+$.

N,N-diisopropyl-*N*'-1-methylhex-5-enylformamidine (**6**):

^{1}H NMR: δ = 1.00 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(CH_3)$_2$); 1.02 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH(CH_3)$_2$); 1.31 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, NCHCH_3); 1.56–1.68 (m, 4 H, CH_2CH_2); 2.07 (m, 2 H, CH_2CH_2CH=CH_2); 3.04 (m, 1 H, NC$H$$CH_3$); 3.78 (br. m, 2 H, C$H$($CH_3$)$_2$); 5.02 (dddd, 1 H_Z, $^3J_{trans}$ = 17.1 Hz, ^2J = 2.4 Hz, ^4J = 1.6 Hz, ^4J = 1.6 Hz; dddd, 1 H_E; $^3J_{cis}$ = 10.1 Hz, ^2J = 2.4 Hz, ^4J = 1.3 Hz, ^4J = 1.3 Hz; CH=CH_2); 5.85 (dddd, $^3J_{trans}$ = 17.0 Hz, $^3J_{cis}$ = 10.1 Hz, ^3J = 6.7 Hz, ^3J = 6.7 Hz, 1 H, CH=CH_2); 7.40 (s, 1 H, NCHN)

^{13}C NMR: δ = 148.4 (N*C*HN); 139.6 (CH_2*C*HCH_2); 114.3 (CH_2C*H*CH_2); 62.3 (NCH(CH_3)CH_2); 45.2 (NCH(CH_3)$_2$); 39.4 (NCH(CH_3)*C*H$_2$); 34.3 (*C*H$_2$CHCH$_2$); 30.4 (CH_2*C*H$_2$CH$_2$); 25.1 (NCH(*C*H$_3$)CH$_2$); 21.9 (NCH(*C*H$_3$)$_2$)

MS/APCI(+): *m/z* (%) = 225.2 (100) $[M + H]^+$

HRMS/ESI(+): *m/z* = 225.232048 $[M + H]^+$; 225.232525 calcd. for $[C_{14}H_{29}N_2]^+$.

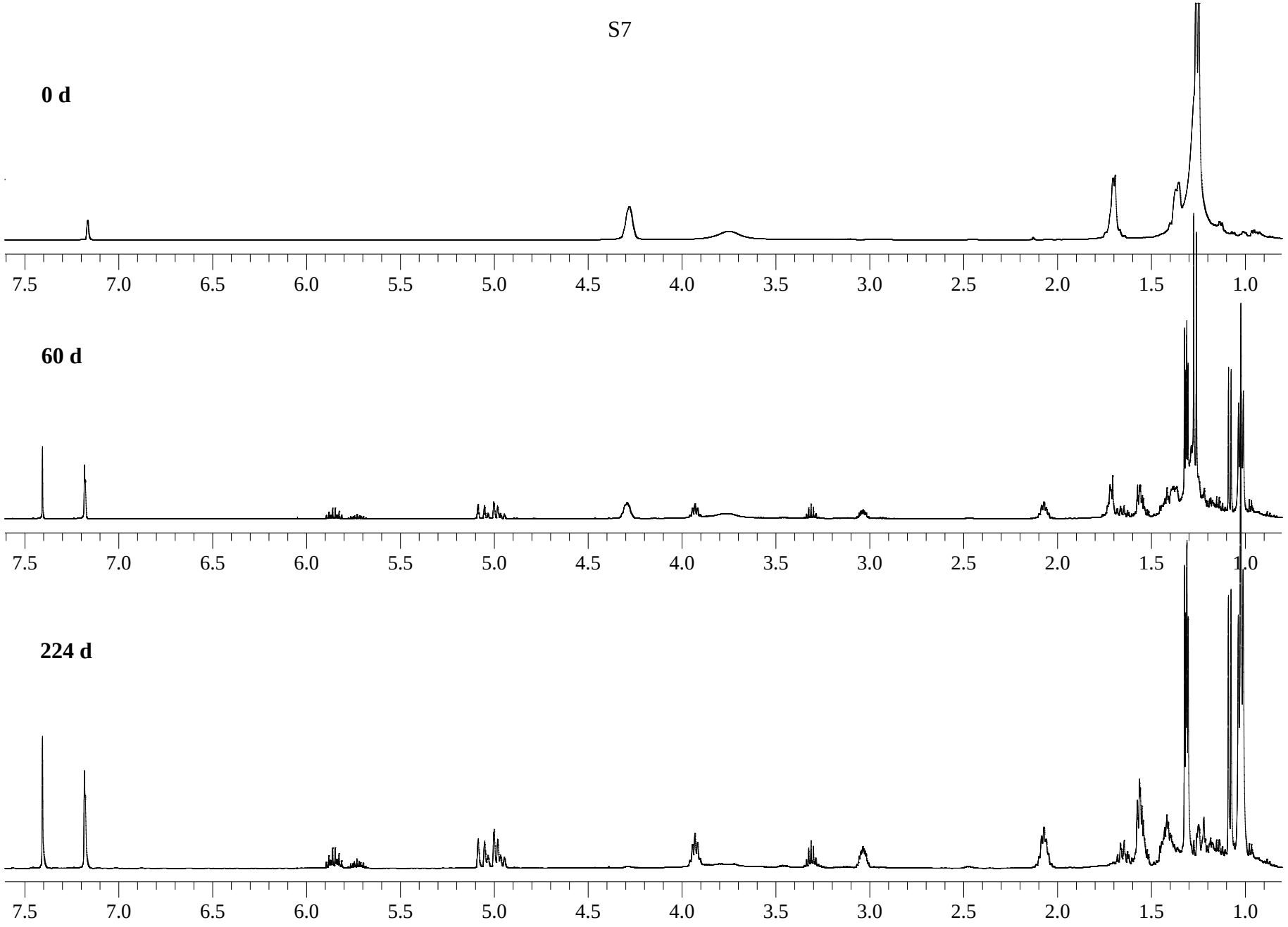

Fig. S4 ^{1}H-NMR spectra of (iPr$_2$N)C(PipMe$_2$) (**4**) (0.4 M; 295 K; C_6D_6) after 0 d (top; **4**), 60 d (middle; mixture of **4** and its fragmentation products) and 224 d (bottom; trace amounts of **4** left, essentially only fragmentation products present).

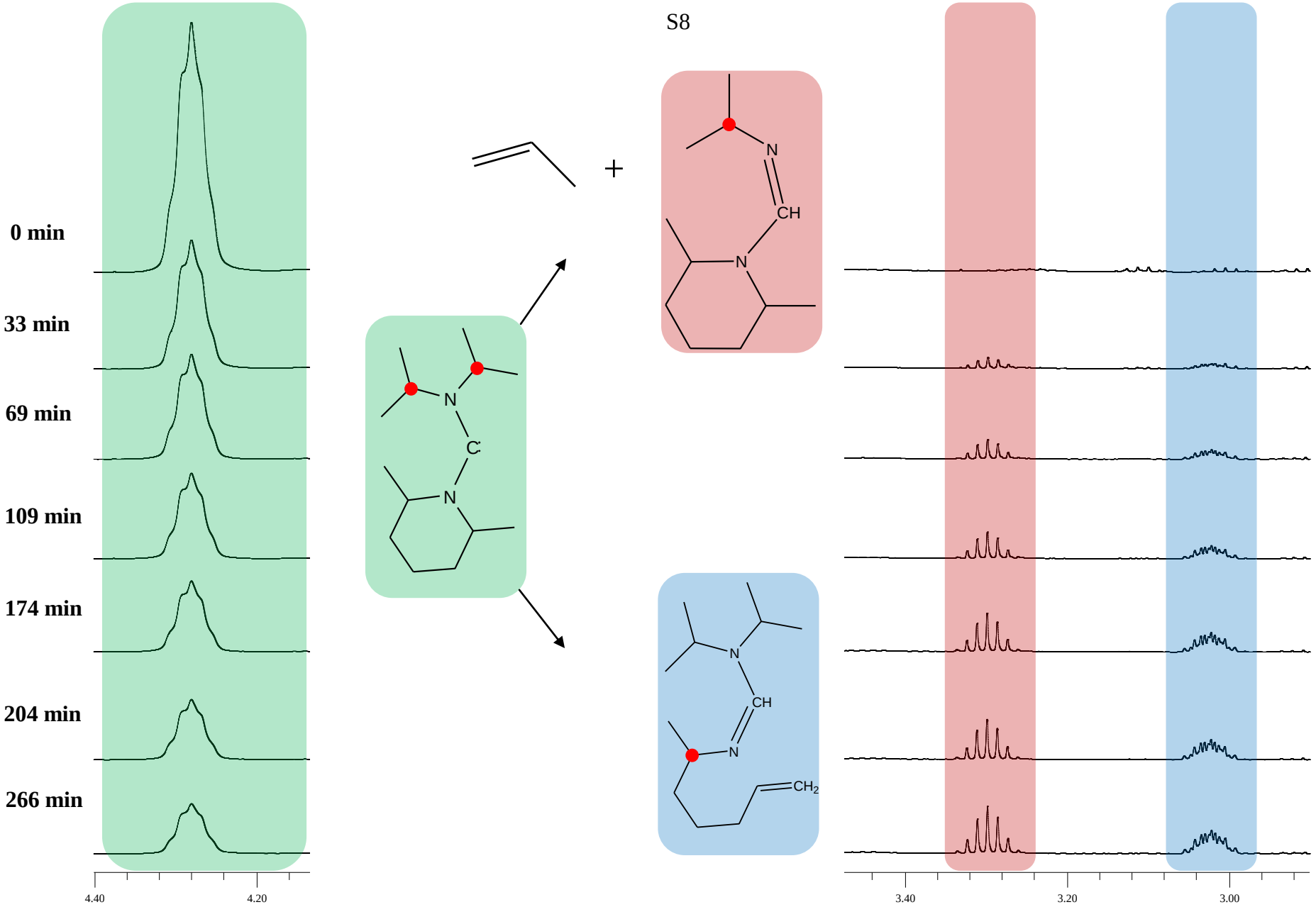

Fig. S5 Temporal development of selected characteristic ^{1}H NMR signals of a sample of (*i*Pr$_2$N)C(PipMe$_2$) (**4**) (0.4 M; C_6D_6; 338 K). Corresponding proton positions are marked with red dots.

Computational Section

Computational Details

All structure optimisations and frequency calculations were performed with the Gaussian 09[S3] program package employing the B97-D functional (which includes empirical dispersion corrections)[S4] and the SVP[S5] basis set (B97-D/SVP). For improved computational efficiency, the resolution of the identity (RI) approximation[S6,S7] was used for these calculations in combination with the appropriate auxiliary basis set.[S8,S9] All stationary points localised were characterised as minima or first order saddle points by eigenvalue-analysis of computed Hessian matrices. The connectivities between minima and transition states implied in Figure 1 were validated by intrinsic reaction coordinate (IRC) calculations.[S10] Unscaled zero-point vibrational energies, as well as thermal and entropic corrections were obtained from Hessians computed at the B97-D/SVP level using the standard procedures implemented in Gaussian 09. Subsequent single-point calculations were performed with the ORCA program package[S11] employing the B2GP-PLYP[S12] double-hybrid functional in combination with the def2-QZVP[S13] basis set. For the SCF part the RI-JK algorithm and for the MP2 part the RI algorithm were used as implemented in ORCA[S14] in combination with the appropriate def2-QZVP/jk and def2-QZVP/c auxiliary basis sets,[S15,S16] respectively. Empirical dispersion[S17,S18] and free-energy corrections were added and relative energies discussed in the text refer to Gibbs free energy differences at 298.15 K obtained at the B2GP-PLYP-D/def2-QZVP//B97-D/SVP level of theory.

Following a reviewer's request we excluded the potential occurrence of competing low-energy pathways involving a biradical contamination of the wave functions, that is, broken-symmetry (BS) species or a two-state-reactivity scenario[S19] involving triplet species. To this end we first excluded the presence of RKS/UKS instabilities in the B97-D/SVP closed-shell singlet wave-functions for all stationary points identified, making use of the 'stable' keyword within the Gaussian 09 program package.[S20] All closed-shell singlet wave-functions were found stable at this level of DFT. Further, we computed B2GP-PLYP-D/def2-QZVP single-points to obtain (vertical) triplet state energies for all minima and transition structures localised at the B97-D/SVP level. The compilation of results in Table S2 illustrates that all triplet states are substantially higher in energy than the singlet ground state energies. Based on the triplet wave-functions obtained we tried to optimise BS singlet solutions employing the corresponding orbital transformation[S21] routines implemented in ORCA ('brokensym' keyword). In the DFT part of these double-hybrid calculations, however, we found that all but one wave-functions collapsed back into the closed-shell singlet solutions. Only for the carbene **1** we were able to obtain a BS solution – its energy, however, is even

above the corresponding triplet state (cf. Table S2). We thus feel safe to exclude any involvement of BS or triplet species in the course of the reaction studied.

Table S2. Vertical triplet (T) and broken symmetry (BS) energies (total energy differences given in kcal mol^{-1} relative to closed-shell singlet energies; B2GP-PLYP-D/def2-QZVP single-point calculations on B97-D/SVP optimized closed-shell singlet structures; $<S^2>$ values obtained for the corresponding Kohn-Sham wave-functions employed in the double-hybrid calculations).

	E_{rel}(T)	$<S^2>$	E_{rel}(BS)	$<S^2>$
1	72.0	2.0118	85.6	1.0118
TS1-2	91.2	2.0302	(0.0)[a]	0.0000
2	103.9	2.0206	(0.0)[a]	0.0001
TS1-3	35.1	2.0177	(0.0)[a]	0.0001
3	128.0	2.0120	(0.0)[a]	0.0000
TS3-2	28.1	2.0188	(0.0)[a]	0.0000

[a] BS wave function collapsed back to the closed-shell singlet solution.

Optimised Structures (Cartesian coordinates in Å obtained at the B97-D/SVP level of DFT)

1

C	-0.068850	0.203786	-0.124035
N	0.513180	0.570010	-1.285461
N	0.400965	0.585835	1.082259
C	-0.011387	-0.140272	-2.495513
H	0.565021	0.240709	-3.358543
C	-1.498887	0.157682	-2.734696
H	-1.666314	1.239899	-2.885380
H	-1.862880	-0.384870	-3.628400
H	-2.071562	-0.166998	-1.847250
C	-0.508900	0.275658	2.231190
H	-0.010255	0.659800	3.140038
C	-1.838242	1.031705	2.091305
H	-2.477345	0.854545	2.978486
H	-1.658577	2.119607	1.993243
H	-2.364517	0.681609	1.184623
C	0.260451	-1.648765	-2.401090
H	-0.292093	-2.066839	-1.539983
H	-0.065915	-2.157751	-3.329185
H	1.340196	-1.840829	-2.250429
C	1.419607	1.723285	-1.575232
H	1.540564	2.268675	-0.629768
C	-0.726576	-1.235445	2.397746
H	-1.408433	-1.436445	3.246432
H	-1.169090	-1.633487	1.466776
H	0.231299	-1.755164	2.582869
C	1.768545	1.050158	1.469087
H	2.376289	1.022674	0.554828
C	2.798588	1.265207	-2.075718
H	2.703506	0.722418	-3.035691
H	3.466801	2.133366	-2.240912
H	3.278275	0.583185	-1.348532
C	2.460030	0.067527	2.436248
H	3.507990	0.388132	2.592573

H	1.968717	0.034139	3.425778
H	2.464022	-0.953768	2.014116
C	1.758276	2.481805	2.027864
H	1.160967	2.531907	2.958407
H	2.786250	2.820067	2.265225
H	1.312398	3.187955	1.302200
C	0.772836	2.737978	-2.540153
H	0.636846	2.325507	-3.556543
H	-0.213354	3.060434	-2.159735
H	1.426209	3.627676	-2.623722

2

C	0.265088	0.348951	0.145964
N	0.288105	0.662788	-1.207713
C	1.177996	1.664279	-1.818926
N	0.626284	0.961609	1.214803
C	1.082531	2.338941	1.309319
C	-0.594000	-0.113919	-2.108834
C	-0.161026	-1.587018	-2.242088
H	-0.489446	0.350648	-3.105551
C	-2.074289	0.017463	-1.707154
H	-2.369066	1.082327	-1.662176
H	-2.720829	-0.501258	-2.440822
H	-2.253748	-0.431276	-0.712136
H	-0.176997	-0.654410	0.305925
C	0.380042	2.983606	2.521185
C	2.612649	2.383529	1.498967
H	0.814695	2.953198	0.419713
H	2.962356	3.424401	1.642928
H	2.889179	1.788069	2.389882
H	3.143960	1.949971	0.629452
H	0.705129	4.034997	2.649582
H	-0.717732	2.964355	2.385796
H	0.622217	2.415524	3.439753
H	-0.790800	-2.105260	-2.990517
H	0.894863	-1.656413	-2.560003
H	-0.269773	-2.122765	-1.280310
H	1.847463	2.011650	-1.021008
C	2.088583	1.041047	-2.897560
H	1.510414	0.674475	-3.766622
H	2.801177	1.802383	-3.267487
H	2.663706	0.195237	-2.477923
C	0.395308	2.872419	-2.363077
H	-0.194420	3.345556	-1.556192
H	1.084888	3.626717	-2.788182
H	-0.301650	2.558842	-3.164354

3

C	0.055295	-0.432752	-0.783703
N	-1.040601	0.086561	0.006766
N	1.420516	-0.001603	-0.418873
C	-2.343250	0.221800	-0.661496
H	-3.073660	0.448857	0.137724
C	-2.364804	1.417899	-1.632049
H	-1.619979	1.288706	-2.440559
H	-3.361142	1.519375	-2.104594
H	-2.128786	2.354227	-1.094434
C	1.837647	-1.333511	0.045797
H	1.848680	-1.426138	1.161093
C	0.536122	-1.914573	-0.570952
H	-0.088502	-2.520686	0.103377
H	0.705792	-2.467245	-1.513189
H	-0.190501	-0.195568	-1.838365
C	3.161120	-1.857491	-0.515060
H	4.024032	-1.294712	-0.114649
H	3.294980	-2.926320	-0.253259
H	3.162756	-1.755317	-1.617315

C	1.742632	1.248959	0.248113
H	1.248404	1.312897	1.249776
C	3.256819	1.351099	0.486108
H	3.495686	2.311719	0.980919
H	3.619616	0.532862	1.135372
H	3.800482	1.299250	-0.476950
C	1.236709	2.427924	-0.595414
H	1.730070	2.420542	-1.586980
H	0.145611	2.354949	-0.739726
H	1.463370	3.386747	-0.090482
C	-1.047058	-0.162782	1.454408
H	-0.007006	-0.420064	1.721278
C	-1.947126	-1.332154	1.920166
H	-1.694584	-2.275893	1.405392
H	-1.833686	-1.489861	3.010039
H	-3.013543	-1.110872	1.723962
C	-1.415386	1.123065	2.220494
H	-2.449917	1.437702	1.979810
H	-1.359028	0.962612	3.314684
H	-0.731766	1.945131	1.941979
C	-2.820736	-1.071551	-1.361669
H	-2.151609	-1.328773	-2.205184
H	-2.825365	-1.921847	-0.657019
H	-3.843406	-0.944254	-1.767381

4

C	0.093482	-0.607390	0.328928
N	-1.086592	-0.224107	-0.270300
N	1.270344	0.116614	0.074347
C	-0.935056	0.423938	-1.623566
H	0.156850	0.525128	-1.713113
C	-1.498424	1.849264	-1.665368
H	-1.094502	2.440664	-0.823776
H	-1.176528	2.329526	-2.609411
H	-2.600410	1.896370	-1.621057
C	2.478856	-0.667478	-0.234353
H	3.332089	0.036422	-0.202897
C	2.771157	-1.794989	0.781249
H	3.727125	-2.296844	0.535641
H	2.836575	-1.400134	1.811080
H	1.967207	-2.554972	0.750476
C	-1.393295	-0.494708	-2.764965
H	-2.489274	-0.569131	-2.865668
H	-0.989940	-0.101920	-3.718055
H	-0.983388	-1.510507	-2.615030
C	-2.308714	-0.402047	0.300487
H	0.001410	-1.227160	1.227629
C	2.386696	-1.236195	-1.660849
H	3.274908	-1.850232	-1.906069
H	1.485336	-1.874321	-1.741003
H	2.302227	-0.419908	-2.402920
C	1.437190	1.403285	0.790492
H	0.406309	1.786672	0.920215
C	-2.355726	-0.917598	1.707747
H	-3.369856	-0.778975	2.129143
H	-2.109543	-2.004231	1.800134
H	-1.612726	-0.387848	2.345655
C	2.199201	2.436321	-0.057247
H	2.197826	3.422645	0.445571
H	3.256188	2.141933	-0.205370
H	1.727418	2.543842	-1.051936
C	2.056575	1.253838	2.194373
H	3.108056	0.914365	2.126295
H	2.045423	2.219659	2.736949
H	1.487289	0.513488	2.787995
C	-3.586621	-0.468907	-0.492569
H	-4.439255	-0.274612	0.186270

H	-3.653687	0.256970	-1.318977
H	-3.765992	-1.476952	-0.941624

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C	-0.072352	-0.322781	-0.400781
N	-1.277231	0.106875	0.244871
N	1.154322	-0.212007	0.337696
C	-2.231153	1.090338	-0.284208
H	-1.851426	2.066962	0.084078
C	-3.593635	0.833082	0.375737
H	-3.487462	0.794766	1.475335
H	-4.314396	1.629293	0.109887
H	-4.007425	-0.134953	0.033269
C	2.297249	-0.921156	-0.255388
H	3.186816	-0.611275	0.322843
C	2.136908	-2.442937	-0.076955
H	3.013243	-2.979408	-0.489547
H	2.025063	-2.700586	0.991150
H	1.235656	-2.797296	-0.611765
C	-2.370202	1.226625	-1.815881
H	-2.918354	0.376894	-2.260501
H	-2.935891	2.150137	-2.045386
H	-1.383374	1.306047	-2.308817
C	-1.170578	-1.318192	-0.053047
H	0.002301	-0.121121	-1.490393
C	2.587492	-0.593207	-1.743171
H	3.546711	-1.053572	-2.048523
H	1.799735	-1.002269	-2.404316
H	2.651738	0.495235	-1.914739
C	1.386568	1.080258	1.001298
H	0.389390	1.375266	1.377981
C	-1.039969	-2.190107	1.187118
H	-2.026821	-2.304244	1.677926
H	-0.664350	-3.197461	0.922578
H	-0.335957	-1.720009	1.894950
C	1.891619	2.203123	0.067563
H	1.908587	3.175128	0.598816
H	2.919668	1.994890	-0.287310
H	1.233378	2.305433	-0.816625
C	2.297123	0.931819	2.231552
H	3.342200	0.698130	1.948197
H	2.317163	1.879217	2.803475
H	1.925148	0.124347	2.888910
C	-1.934151	-1.973523	-1.200396
H	-3.014675	-2.053930	-0.969461
H	-1.820528	-1.418968	-2.147304
H	-1.551381	-3.001053	-1.356337

Propene

C	-0.000820	0.150205	0.029191
H	0.300748	-0.531435	0.851839
H	0.915513	0.531352	-0.460487
C	-0.901654	-0.551236	-0.952347
H	-0.521890	1.005196	0.508606
C	-0.648163	-0.708205	-2.262528
H	-1.839628	-0.961885	-0.542125
H	-1.350828	-1.232495	-2.925055
H	0.275273	-0.315192	-2.715291

TS1-2

C	-0.006178	0.525200	0.078826
N	0.164663	0.761778	-1.232104
C	1.020318	1.809751	-1.848300
N	0.373395	1.093842	1.159685
C	1.102680	2.330399	1.426315
C	-0.554641	-0.149757	-2.168426
C	-0.022466	-1.587177	-2.062269

H	-0.344679	0.221572	-3.188318
C	-2.074420	-0.082323	-1.953240
H	-2.437611	0.957260	-2.058106
H	-2.595669	-0.717290	-2.695350
H	-2.327880	-0.440281	-0.938898
C	-0.288033	0.027283	2.664976
C	0.989618	-0.453842	3.321955
H	-0.798351	0.841167	3.198520
C	-1.116773	-0.936086	1.981759
H	-2.207648	-0.804530	2.081660
H	-0.797371	-0.556025	0.757064
H	-0.800699	-1.991160	2.063914
H	0.756253	-1.042560	4.233990
H	1.550673	-1.113446	2.631529
H	1.655900	0.375977	3.621219
C	0.656945	2.996353	2.740243
C	2.628443	2.103650	1.406051
H	0.850093	3.054257	0.622181
H	3.166994	3.065646	1.512997
H	2.929191	1.438217	2.235099
H	2.942635	1.627069	0.458831
H	1.150080	3.981799	2.838906
H	-0.437823	3.149154	2.748916
H	0.930818	2.386232	3.618931
H	-0.536545	-2.246026	-2.788351
H	1.064561	-1.619166	-2.262751
H	-0.202076	-1.974490	-1.042639
H	1.538954	2.310430	-1.020907
C	2.112848	1.202478	-2.747926
H	1.684028	0.699259	-3.634856
H	2.788690	2.001331	-3.108893
H	2.711126	0.462619	-2.184510
C	0.179867	2.864799	-2.586744
H	-0.559076	3.320685	-1.901611
H	0.830385	3.665077	-2.990116
H	-0.367937	2.413421	-3.435923

TS1-3

C	-4.264144	0.981068	0.657350
N	-5.372347	1.492407	1.233975
N	-2.985050	1.223586	0.976311
C	-2.705719	-1.131495	0.450892
H	-7.421774	1.822495	1.085242
C	-2.055108	0.219454	0.282534
C	-2.452750	2.388691	1.690801
C	-5.474481	1.894569	2.661715
C	-6.641209	1.335891	0.472185
H	-4.464542	1.782407	3.082060
H	-3.308378	3.038899	1.938415
H	-7.991197	-0.207670	-0.267502
C	-1.865769	0.560552	-1.212111
C	-1.510466	3.226758	0.804693
H	-6.264191	-0.690474	-0.288117
C	-6.562037	2.088094	-0.865249
C	-5.915648	3.358473	2.807705
H	-1.070635	0.398523	0.788562
C	-6.380815	0.935956	3.456289
H	-7.153891	-0.643916	1.259319
C	-7.034342	-0.141043	0.283967
C	-1.754575	1.958844	2.995646
H	-5.785891	1.636259	-1.511176
H	-7.532573	2.035253	-1.393662
H	-6.301777	3.150539	-0.700621
H	-6.933023	3.506741	2.397763
H	-5.935721	3.649633	3.874999
H	-5.227532	4.036152	2.268644
H	-7.434144	0.997118	3.124999

H	-6.033785	-0.106913	3.341960
H	-6.348550	1.203592	4.529489
H	-2.280983	-1.902570	-0.219645
H	-2.713077	-1.471524	1.506630
H	-4.320653	0.081552	-0.012374
H	-1.135940	-0.143585	-1.654430
H	-2.825096	0.429024	-1.749982
H	-1.499226	1.590668	-1.375699
H	-1.194932	4.133639	1.355617
H	-0.608303	2.649344	0.535945
H	-2.018900	3.536610	-0.126323
H	-0.899577	1.295334	2.769816
H	-1.373337	2.843578	3.540203
H	-2.447828	1.404797	3.655494

TS1-4

C	0.228639	-0.823972	-0.362175
N	-0.949025	-0.129979	-0.615372
N	1.352565	-0.155290	0.006219
C	-1.166056	0.987932	-1.535083
H	-0.169456	1.429376	-1.721869
C	-2.070255	2.060784	-0.908368
H	-1.637955	2.445893	0.034101
H	-2.210591	2.908439	-1.606270
H	-3.064385	1.635504	-0.677205
C	2.602775	-0.954862	0.106465
H	3.396888	-0.248950	0.411166
C	2.492478	-2.042070	1.187147
H	3.451239	-2.587270	1.280701
H	2.241425	-1.595040	2.166620
H	1.697870	-2.760646	0.917158
C	-1.710246	0.510865	-2.898615
H	-2.737215	0.118286	-2.798996
H	-1.728816	1.353570	-3.617156
H	-1.066886	-0.290530	-3.305858
C	-1.894786	-0.900071	0.146732
H	-0.630015	-1.719231	0.201964
C	2.994697	-1.536305	-1.261076
H	3.953812	-2.084218	-1.186209
H	2.206998	-2.230131	-1.607651
H	3.103000	-0.729608	-2.010456
C	1.414668	1.265874	0.431627
H	0.375976	1.630817	0.388155
C	-2.111462	-0.413047	1.576209
H	-2.801765	0.462239	1.633446
H	-2.555210	-1.214603	2.201830
H	-1.152295	-0.109852	2.041177
C	2.278669	2.108554	-0.520578
H	2.251415	3.175538	-0.226635
H	3.334378	1.776361	-0.491552
H	1.921306	2.020056	-1.563253
C	1.876114	1.402901	1.894410
H	2.921230	1.066320	2.028502
H	1.822544	2.464289	2.204373
H	1.227272	0.807782	2.562597
C	-3.154631	-1.367425	-0.557071
H	-3.878000	-0.540506	-0.757362
H	-2.922409	-1.851187	-1.525375
H	-3.686721	-2.103862	0.076670

TS3-2

C	-0.027975	-0.634054	-0.254760
N	-1.137582	-0.019849	0.206471
N	1.210578	-0.501631	0.283647
C	-2.312247	0.039792	-0.700464
H	-3.097710	0.582121	-0.143105
C	-1.984083	0.859150	-1.958126

H	-1.170562	0.372074	-2.527755
H	-2.874296	0.936268	-2.610337
H	-1.654084	1.878689	-1.684542
C	2.146488	-1.625208	-0.323164
H	2.956163	-1.693137	0.433032
C	1.300392	-2.842198	-0.491439
H	1.223689	-3.507840	0.384478
H	1.408238	-3.371225	-1.451880
H	-0.098935	-1.454147	-1.002530
C	2.763250	-1.154282	-1.652598
H	3.335767	-0.213262	-1.548088
H	3.447530	-1.931522	-2.041054
H	1.966875	-0.996120	-2.406720
C	1.716140	0.824090	0.714205
H	1.064469	1.179875	1.531406
C	3.127717	0.716158	1.309428
H	3.414336	1.694829	1.737788
H	3.160532	-0.043200	2.112102
H	3.873664	0.445330	0.541134
C	1.650077	1.889155	-0.402034
H	2.340219	1.644642	-1.228923
H	0.626127	1.952749	-0.812816
H	1.927715	2.881909	0.002679
C	-1.343581	0.330961	1.634855
H	-0.409298	0.042625	2.144574
C	-2.464158	-0.512636	2.269827
H	-2.263713	-1.590351	2.129388
H	-2.513195	-0.302112	3.355089
H	-3.453705	-0.275976	1.835733
C	-1.581347	1.837739	1.812861
H	-2.523127	2.145605	1.318954
H	-1.664636	2.092090	2.886351
H	-0.753266	2.421816	1.372252
C	-2.852619	-1.360332	-1.043038
H	-2.094239	-1.959120	-1.579940
H	-3.131602	-1.907955	-0.125841
H	-3.746276	-1.272148	-1.689229

TS4-5

C	0.161527	-0.769702	-0.691626
N	-1.128429	-0.439999	-0.414572
N	1.254663	-0.125290	-0.129112
C	-1.757631	0.873653	-0.707268
H	-0.922488	1.599092	-0.747670
C	-2.714015	1.268072	0.424146
H	-2.185029	1.296845	1.395319
H	-3.159073	2.262502	0.230624
H	-3.533071	0.530255	0.505834
C	2.596546	-0.446877	-0.638428
H	3.297982	0.211436	-0.094080
C	2.998224	-1.903985	-0.331276
H	4.035507	-2.096466	-0.665834
H	2.930528	-2.103454	0.753590
H	2.332511	-2.615610	-0.854461
C	-2.444451	0.875104	-2.084122
H	-3.321008	0.201438	-2.087241
H	-2.788789	1.894389	-2.348052
H	-1.735577	0.529751	-2.860328
C	-1.715024	-1.598634	0.082482
H	0.369404	-1.686231	-1.256669
C	2.727974	-0.118487	-2.137980
H	3.761843	-0.304679	-2.486377
H	2.039541	-0.746500	-2.733545
H	2.472537	0.941265	-2.323666
C	1.122856	0.823161	0.982781
H	0.049406	0.836151	1.237416
C	-1.333832	-2.090638	1.458997

H	-2.105121	-1.835276	2.233345
H	-1.221258	-3.197024	1.499362
H	-0.375959	-1.648874	1.792053
C	1.541722	2.247795	0.572005
H	1.365278	2.960266	1.400395
H	2.619649	2.283387	0.320564
H	0.970675	2.585374	-0.312577
C	1.884670	0.351779	2.237538
H	2.975381	0.307785	2.055323
H	1.711633	1.055504	3.074476
H	1.540173	-0.652666	2.544315
C	-2.993349	-2.118533	-0.519706
H	-3.913899	-1.607840	-0.133638
H	-3.006397	-2.005988	-1.622400
H	-3.126614	-3.195694	-0.288240

TS5-2

C	-0.270134	0.361390	0.203745
N	-1.198992	-0.576475	-0.217948
N	1.114930	0.021442	-0.070417
C	-2.498586	-0.665433	0.425082
H	-2.718933	-1.755983	0.482640
C	-3.605781	-0.068604	-0.482465
H	-3.554539	-0.536217	-1.482696
H	-4.609626	-0.254583	-0.052489
H	-3.490029	1.023951	-0.602779
C	2.115272	0.477023	0.891158
H	3.092084	0.125808	0.508635
C	2.190163	2.017323	0.950189
H	3.023715	2.348826	1.599120
H	2.337211	2.437008	-0.063068
H	1.258044	2.439560	1.376850
C	-2.612684	-0.126997	1.871210
H	-2.528890	0.974982	1.909770
H	-3.593535	-0.404775	2.302261
H	-1.819160	-0.555566	2.513922
C	-0.762122	1.606922	-0.681468
H	-0.346898	0.716937	1.258825
C	1.950984	-0.109051	2.316250
H	2.789975	0.207527	2.966747
H	1.013444	0.244194	2.787851
H	1.924521	-1.211571	2.284231
C	1.435035	-1.112176	-0.944737
H	0.502165	-1.318434	-1.496296
C	1.788081	-2.404574	-0.179008
H	1.942836	-3.245836	-0.883204
H	2.718628	-2.283407	0.409946
H	0.963694	-2.667521	0.508531
C	2.534601	-0.750063	-1.961568
H	3.501650	-0.542656	-1.461375
H	2.701843	-1.587717	-2.666643
H	2.249785	0.149179	-2.539779
C	-1.543248	2.675706	-0.114695
H	-2.196054	3.313380	-0.728889
H	-1.549133	2.819845	0.974781
H	-0.119817	2.573768	-0.322760
C	-0.734193	1.453392	-2.191122
H	-0.007501	0.674463	-2.473924
H	-1.727754	1.171037	-2.582726
H	-0.441783	2.411778	-2.663307

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