Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Cyclisation of biscarbenoids – a novel mode of cyclobutadiene stabilisation

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Materials and methods: Bis(piperidyl)acetylene was prepared according to a literature procedure.[1] Dimethyltin dichloride (Me_2SnCl_2) was purchased from Aldrich and used as received. Hexane was dried by distillation from sodium/potassium alloy; benzene was dried by distillation from metallic sodium. Solvents were then stored over activated molecular sieves under argon atmospheres. Deuterated solvents were dried under an argon atmosphere over activated molecular sieves and degassed by three *freeze-pump-thaw* cycles. Unless otherwise noted all manipulations were carried out either in an argon-filled glovebox or with Schlenk techniques as described by Shriver and Drezdzon.[2]

Physical Methods: All solution NMR spectra were acquired on a Bruker Avance I 500 spectrometer (^{1}H: 500.13 MHz, ^{11}B: 160.5 MHz, ^{13}C: 125.8 MHz, ^{119}Sn: 186.5 MHz). ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were referenced to external TMS via the residual protons of the solvent (^{1}H) or the solvent itself (^{13}C). ^{11}B{^{1}H} NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. ^{119}Sn spectra were referenced to external $SnMe_4$. Elemental analysis was conducted on an Elementar vario MICRO cube elemental analyser.

Synthesis of 2: Solid Me_2SnCl_2 (28.6 mg, 0.13 mmol) was added to a stirred benzene (2 mL) solution of bis(piperidyl)acetylene (**1**) (50.0 mg, 0.26 mmol) at room temperature. Over the course of 0.25 h a color change of the clear reaction solution to light yellow was observed. Hexane (2 mL) was added to the reaction solution, the mixture was filtered and the resulting residue discarded. After standing for 5 h, crystals of **2**, containing ca. 6% hexane (quantified by proton NMR) were obtained from the benzene/hexane solution (61.0 mg, 0.10 mmol, 78%). **^{1}H NMR** (500.13 MHz, C_6D_6) δ = 1.08-1.48, 1.63-1.95 (m, 24H, 3,4,5-NC_5H_{10}) 1.51 (s, 6H, $Sn(CH_3)_2$), 2.39-2.69 (m, 2H, 2,6-NC_5H_{10}), 2.77 (t, 4H, $^3J_{HH}$ = 5.03 Hz, 2,6-NC_5H_{10}), 3.03-3.38 (m, 4H, 2,6-NC_5H), 3.55-3.61 (m, 2H, 2,6-NC_5H), 3.61-3.69 (m, 2H, 2,6-NC_5H), 3.91-4.07 (m, 2H, 2,6-NC_5H); **^{13}C NMR** (125.7 MHz, C_6D_6) δ = 13.26 ($Sn(CH_3)_2$, $^1J_{C\text{-}Sn}$ = 630 Hz), 22.68, 24.04, 25.08, 25.54, 26.10, 26.19, 48.85, 51.22, 52.28, 52.32 (CH_2, NC_5H_{10}), 78.34 (C_q, $C{\rightarrow}Sn$, $^1J_{C\text{-}Sn}$ = 535 Hz), 112.83 (C_q, CNC_5H_{10}), 172.02 (C_q, CNC_5H_{10}); **^{119}Sn NMR** (186.5 MHz, C_6D_6) δ = −145.05 ppm. **Elemental Analysis:** calcd.: C, 52.42; H, 7.88; N, 9.06. found: C, 52.28; H, 7.99; N 8.88.

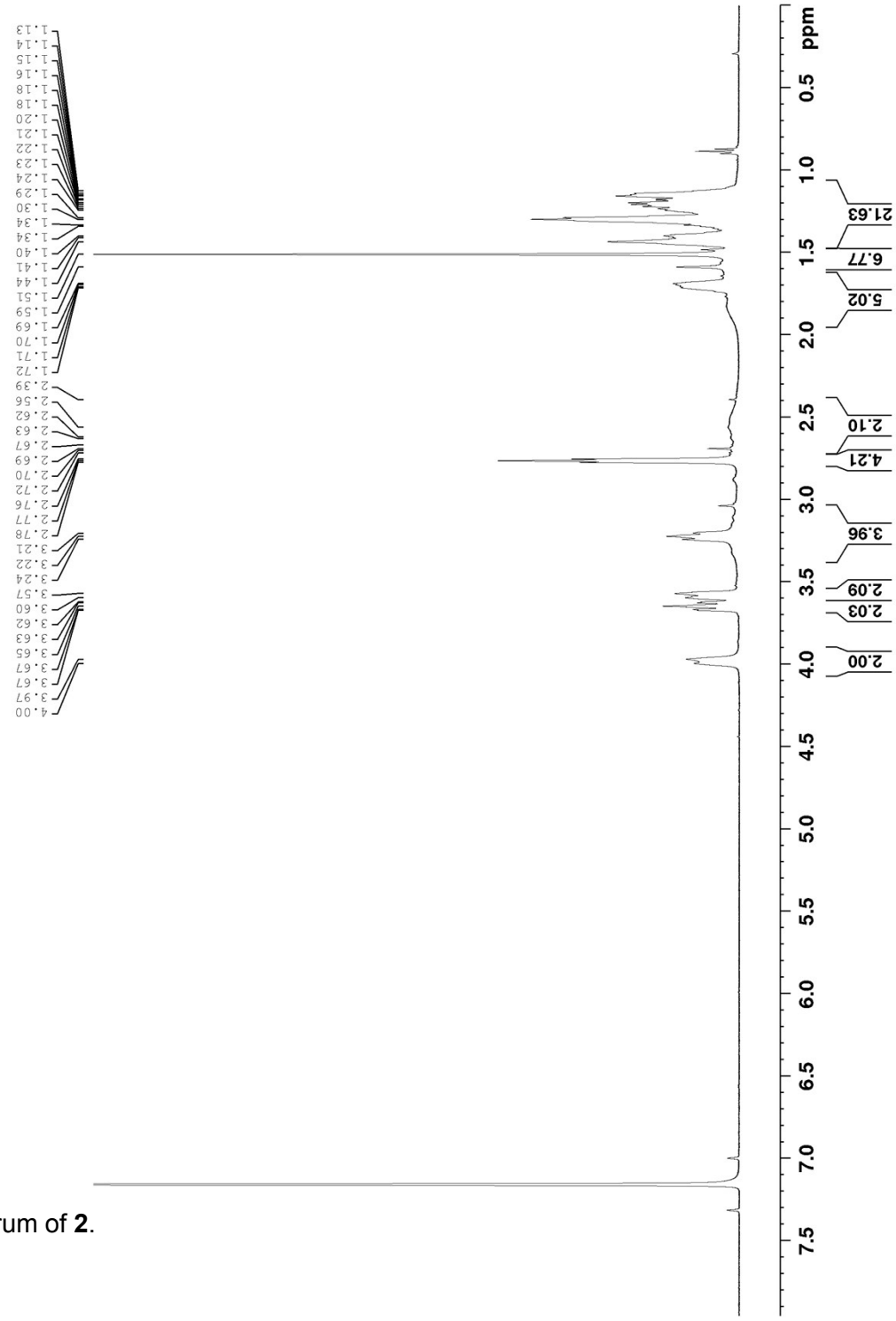


Figure S1: ^{1}H NMR spectrum of **2**.

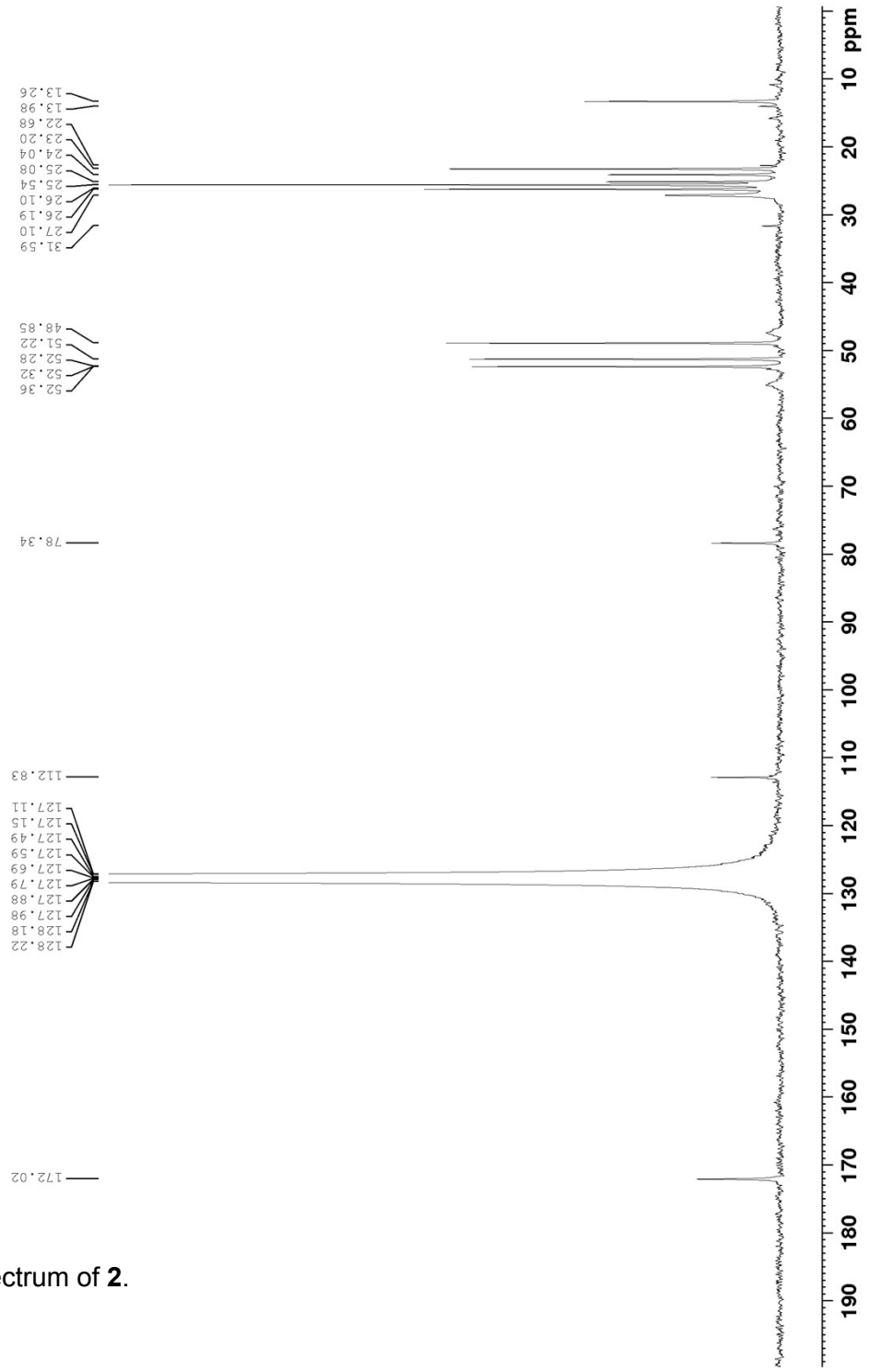


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

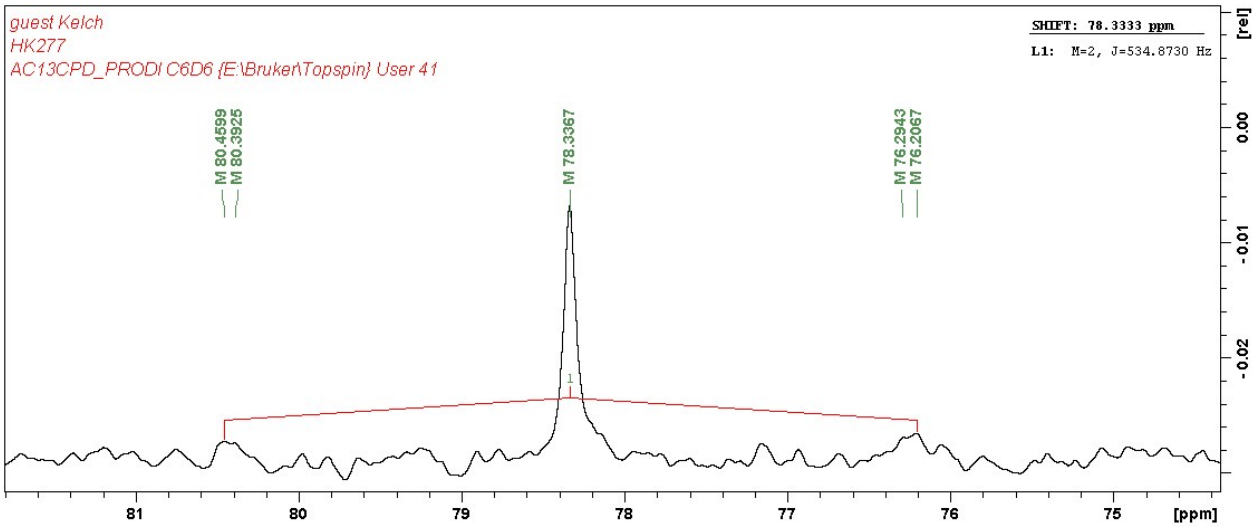


Figure S3: Expansion of the $^{13}C\{^{1}H\}$ NMR spectrum showing $^{1}J(^{13}C\text{-}^{119}Sn)$ satellites.

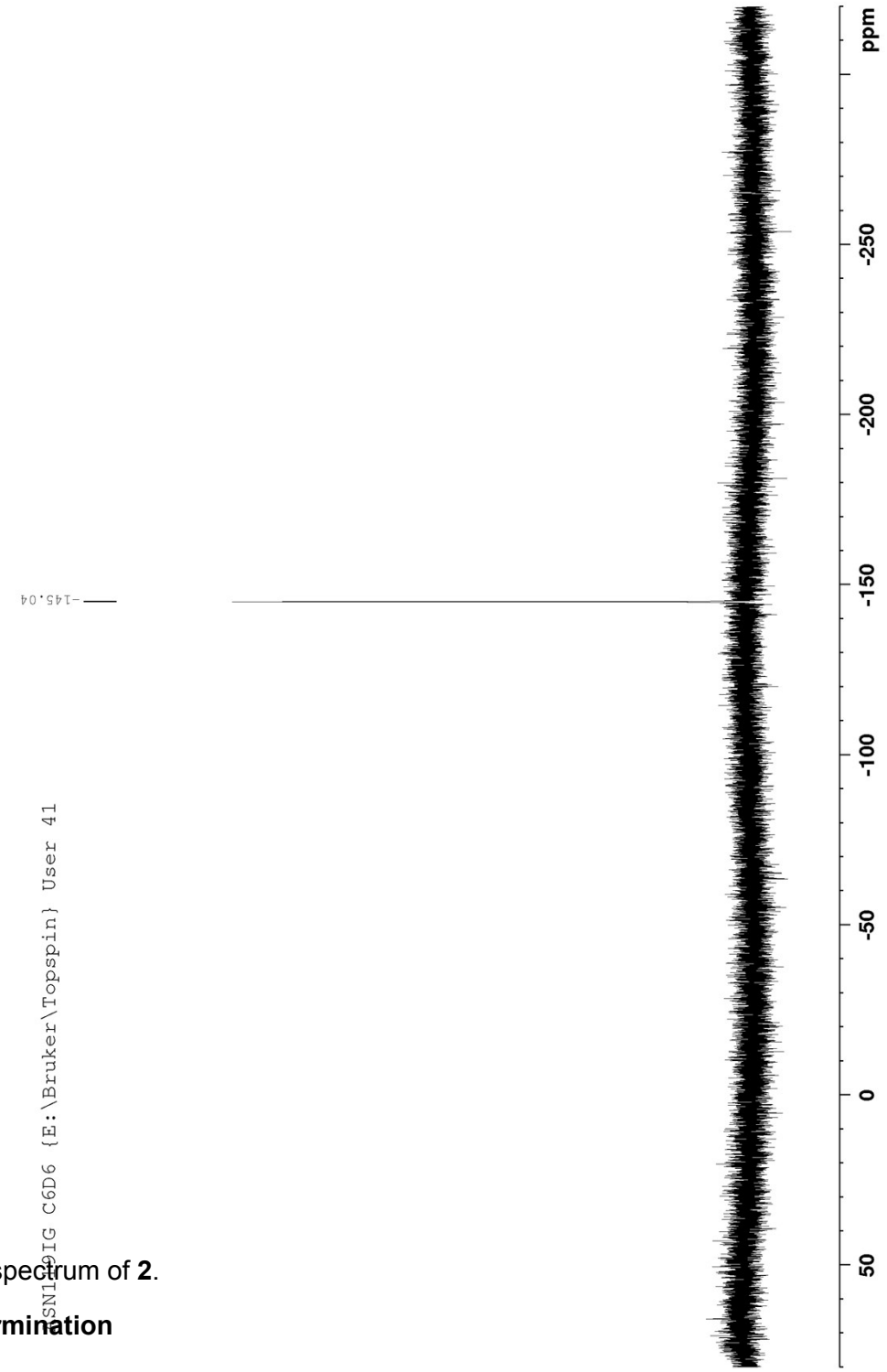


Figure S4: ^{119}Sn NMR spectrum of **2**.

Crystal structure determination

The crystal data of **2** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[3] refined with the SHELXL program[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystal data for **2**: $C_{26}H_{46}Cl_2N_4Sn$, M_r = 604.26, colourless block, 0.23×0.16×0.10 mm^3, monoclinic space group *Cc*, *a* = 10.291(3) Å, *b* = 21.844(7) Å, *c* = 12.742(5) Å, β = 106.679(18)°, *V* = 2743.9(16) $Å^3$, *Z* = 4, ρ_{calcd} = 1.463 $g \cdot cm^{-3}$, μ = 1.148 mm^{-1}, *F*(000) = 1256, *T* = 296(2) K, R_1 = 0.0137, wR^2 = 0.0346, 5604 independent reflections [$2\theta \leq 52.742°$] and 300 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1500452. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

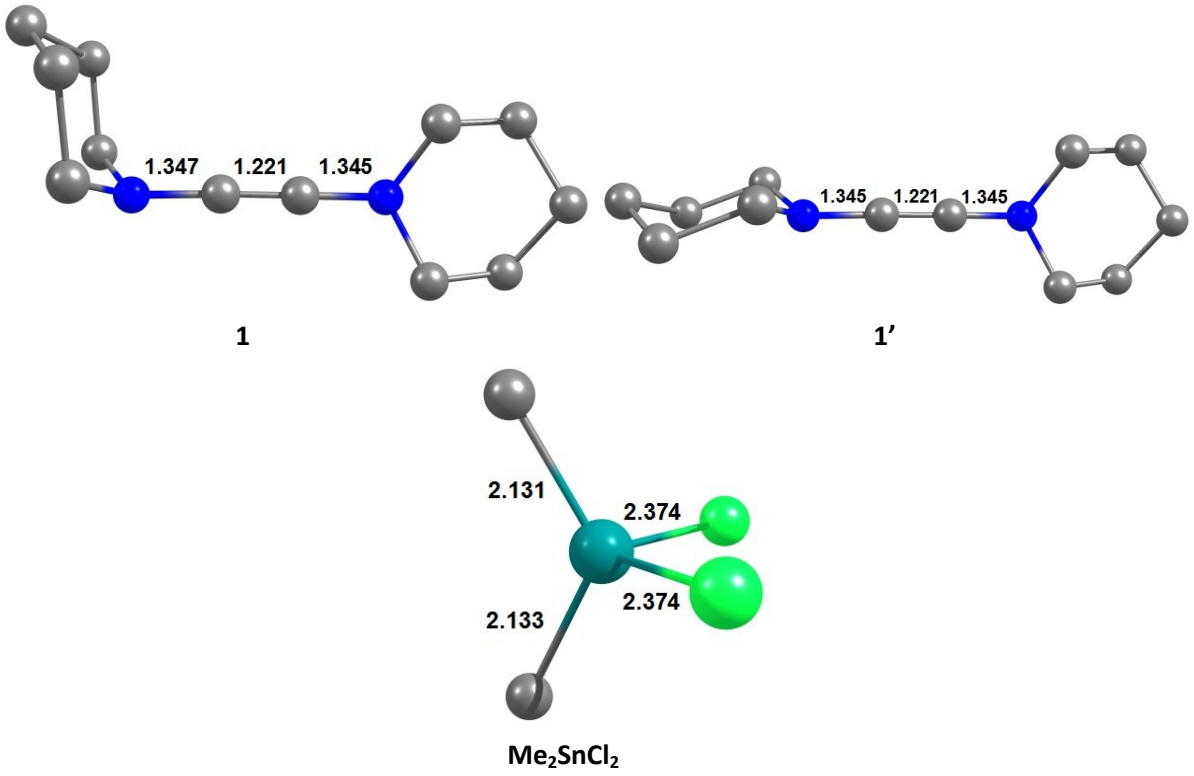


Figure S5. Optimized geometries of **R1**, **R2** and **R3** at the PCM-M05-2X/def2-SVP level.

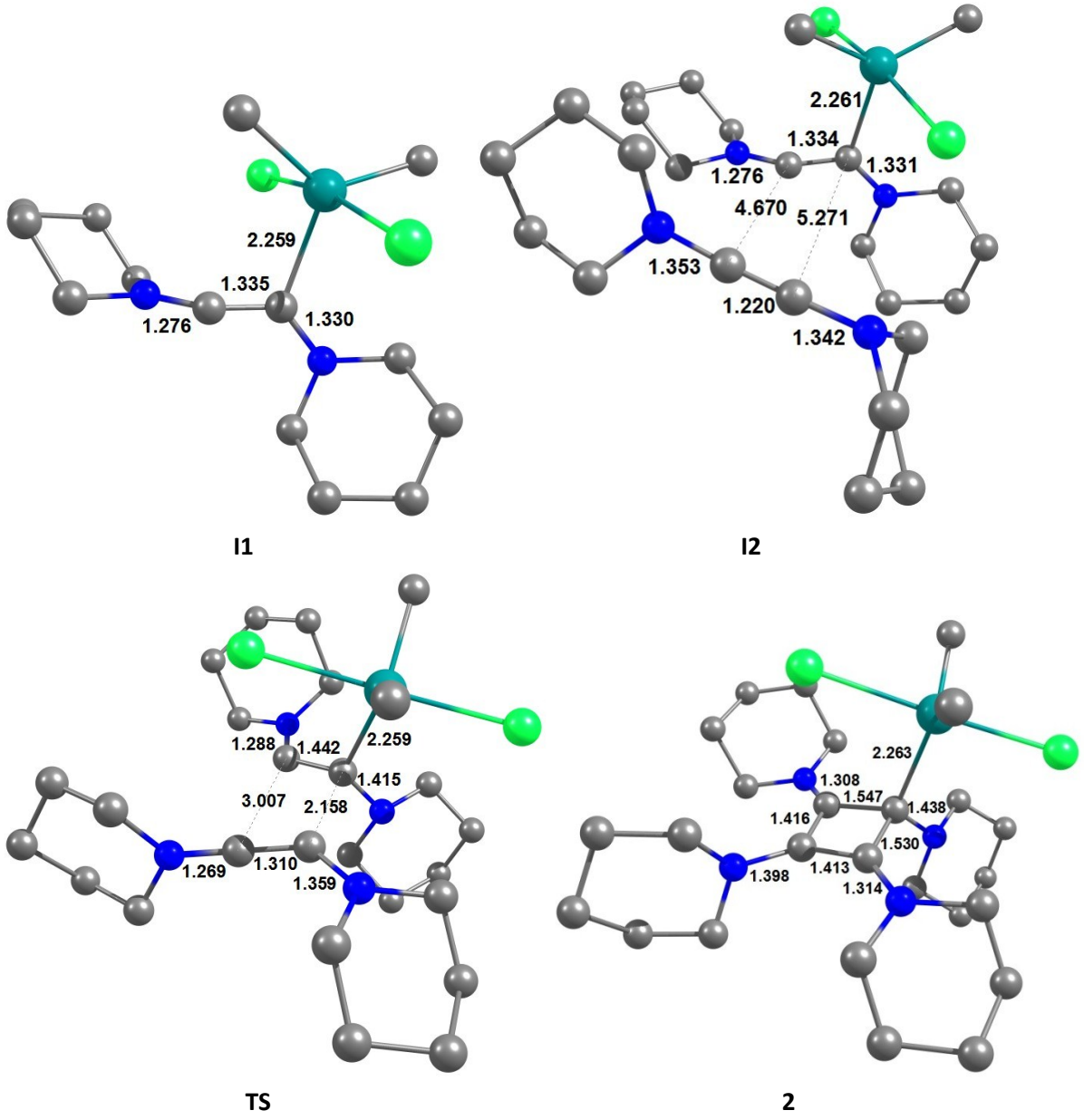
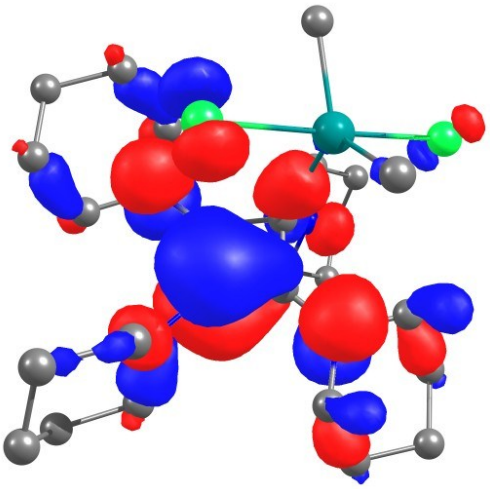
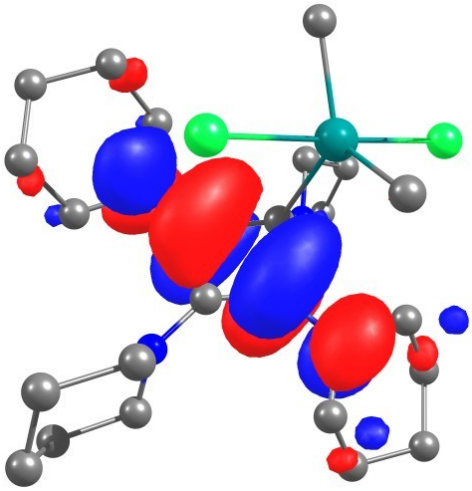


Figure S6. Optimized geometries of the stationary points and transition states of the addition reaction of **1**, **1'** and $\mathbf{Me_2SnCl_2}$ at the PCM-M05-2X/def2-SVP level. Interatomic distances are given in Å.

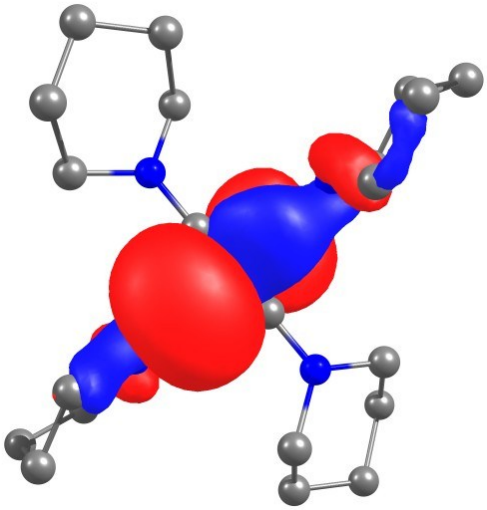
Figure S7. (top) Plot of the HOMO and LUMO of **2** and (bottom) the HOMO of the free cyclobutadiene (eV) at the PCM-MO5-2X/def2-SVP level.



HOMO (-7.20)



LUMO (0.02)



HOMO (-4.98)

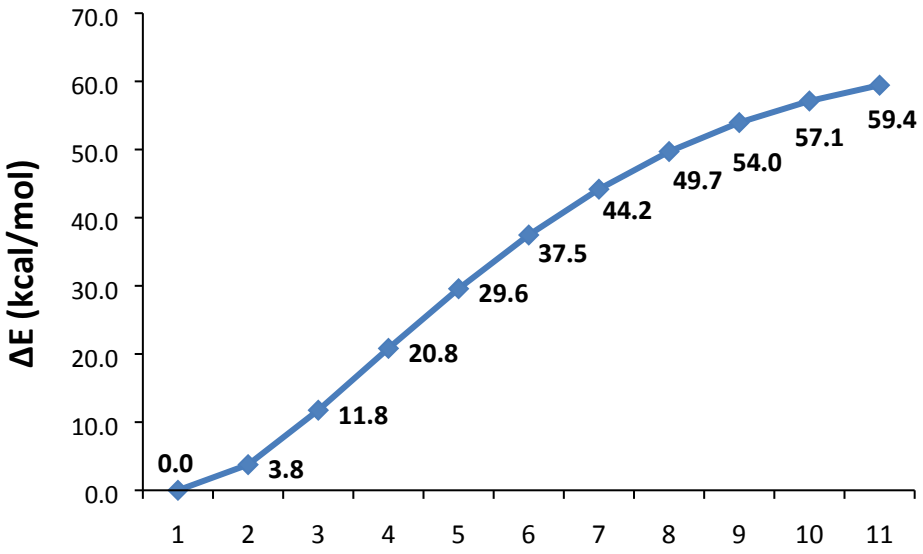


Figure S8. Systematic scan of the potential energy surface from **I1** to the reactants **1** and **Me_2SnCl_2**.

Computational Details

The geometries of **1**, **1'**, **Me_2SnCl_2**, **I1**, **I2**, **TS** and **2** have been optimized using the hybrid meta–GGA functional M05-2X[5] in conjunction with def2-SVP[6] basis set. The nature of stationary points were determined by calculating the vibrational frequencies. Minima have only positive eigenvalues whereas the transition states have only one negative eigenvalue. Intrinsic reaction coordinate (IRC) calculations[7] were carried out to ensure the connectivity of the reported minima and transition states. The solvent effects have been evaluated using the PCM[8] solvent model. Nucleus-independent chemical shifts (NICS)[9] were computed by employing the gauge-invariant atomic orbital[10] (GIAO) approach. The calculations were performed with the Gaussian 09, Revision D.01 program package.[11]

Table S1. Cartesian coordinates (Å) and energy (a.u.) of the complex at the PCM-M05-2X/def2-SVP level.

1

E=-578.2305832

C	0.77292700	-0.70893600	0.03305300
N	2.07818500	-1.04134700	0.03635400
C	-0.41974700	-0.44715300	0.04064900
N	-1.73371800	-0.16390900	0.07713300
C	-2.67280600	-1.22774500	-0.27391500
H	-2.26778100	-2.17125000	0.10705300
H	-2.75280500	-1.31504800	-1.37443500
C	-4.04897500	-0.94350500	0.31659000
H	-3.97691100	-0.98036600	1.41327800
H	-4.74897800	-1.72874400	0.00149500
C	-4.54657600	0.43497400	-0.11630400
H	-4.68957700	0.44204000	-1.20862100
H	-5.52168800	0.65412300	0.33789000
C	-3.52386100	1.50496200	0.26368600
H	-3.84334400	2.49448700	-0.08944200
H	-3.43304000	1.55384200	1.35853500
C	-2.15720000	1.17556600	-0.32567400
H	-2.20374500	1.24305700	-1.42960900
H	-1.39800600	1.88535900	0.02017000
C	2.83985600	-0.78469800	-1.18735100
H	2.21524700	-1.05747700	-2.04486600
H	3.71942900	-1.44701400	-1.18129100
C	3.28991600	0.67429100	-1.25906400
H	2.39429800	1.31051200	-1.33019500
H	3.88683300	0.84143200	-2.16614800
C	4.08901200	1.04524100	-0.00650800
H	4.36427400	2.10798100	-0.02703000

H	5.02967500	0.47115800	0.00233800
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H	2.39944700	1.35980600	1.31304800
C	2.84470400	-0.73918000	1.24689600
H	3.72424900	-1.40139100	1.26202600
H	2.22343700	-0.97954200	2.11636800

1‘

E=-578.2309873

N	1.95438200	0.06491400	0.04258300
C	0.61026700	0.03635300	0.01001600
N	-1.95437700	0.06516600	-0.04164800
C	-0.61026200	0.03640700	-0.00930800
C	2.65253100	0.67536700	-1.08738100
H	2.05892300	1.53150700	-1.42518600
H	2.71610300	-0.04311000	-1.92703500
C	4.05573500	1.10835000	-0.67878700
H	4.57805700	1.51994200	-1.55268500
H	3.97352200	1.90979100	0.06969400
C	2.64881400	-1.07391300	0.64001600
H	2.71246600	-1.90468500	-0.08877500
H	2.05256600	-1.42126200	1.49053600
C	-4.05580100	1.10167900	0.68938600
H	-3.97335600	1.91039900	-0.05119700
H	-4.57829900	1.50473700	1.56714900
C	-4.83086800	-0.06796600	0.08414300
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H	3.96951700	0.06476000	1.89170700
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H	5.82861200	0.25342600	0.24168500
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C	-4.05174400	-0.66327500	-1.08792800
H	-3.96904000	0.08320400	-1.89118800
H	-4.57132600	-1.53936800	-1.49834000
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H	-2.05912300	1.51738300	1.44033000
H	-2.71654100	-0.06200100	1.92664900

Me_2SnCl_2

E=-1214.1871305

Sn	-2.66140700	0.73923400	-1.50195000
Cl	-2.89375200	2.54384900	0.02298300
Cl	-1.95543800	-1.07020100	-0.13727100
C	-4.61916900	0.26191900	-2.19566700
H	-4.64412800	-0.78874500	-2.50192100
H	-4.87882100	0.90685000	-3.04141700
H	-5.32049300	0.42724500	-1.37190400
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H	-0.12290600	0.77955600	-2.36309200
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H	-1.20999600	0.82130000	-3.78891700

I1

E=-1792.4412307

Sn	-1.51316400	-1.67443400	0.64286700
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N	1.45280100	-2.17208300	1.75303000
C	0.43882000	-1.31191300	1.71965800
Cl	-0.14987000	-1.52005200	-1.49034600
N	0.07339900	0.80795600	3.01073200
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C	1.48776000	-3.42549300	1.00427100
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H	2.33524300	-2.65428400	-0.79561900
C	2.71535700	-1.82914200	2.40474800
H	2.94203900	-2.60658200	3.15107100
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H	0.94335200	2.65054900	3.45965400

I2

E=-2370.6789958

Sn	-1.83792300	-1.89606000	1.05048300
Cl	-2.38260000	-1.71914500	3.55740900
N	1.28275100	-2.45682400	1.60106500
C	0.30239100	-1.56246400	1.69860900
Cl	-0.89828000	-2.15718700	-1.29487200
N	0.26487100	0.65954200	2.85169700
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N	1.41271200	0.27689100	-3.44531000
C	0.57218800	2.20686100	-1.98477400
N	0.03838100	3.19805600	-1.23508000
C	1.12513500	-3.78931800	1.02566100
H	0.08306500	-3.92520000	0.72652600
H	1.36595700	-4.53105400	1.80431600
C	2.04315400	-3.97346600	-0.18038100
H	1.95586300	-5.00758500	-0.53881800
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H	2.97183000	-2.81459100	2.77736700
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H	-1.79780500	2.45063000	2.66357000
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H	-3.69914300	-3.81719800	1.33464800
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H	-1.50752600	3.99476400	-2.43768200
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H	-1.93607700	3.74694200	0.58460100
H	-3.00953700	4.55506800	-0.56918300
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H	-1.25712000	6.23039500	-1.08187900
H	-1.53779800	6.20577400	0.66376200
C	0.32823400	5.28695000	0.03308000
H	0.92705800	6.20607700	0.08317100
H	0.45959500	4.75686800	0.98760800
C	0.85298200	4.40627900	-1.09413900
H	0.84667600	4.97753200	-2.04236200
H	1.88550800	4.09380900	-0.90246000
C	1.90986900	0.58263000	-4.78457300
H	1.31516300	1.40616100	-5.19425200
H	1.74577400	-0.30393500	-5.41692800
C	3.39965700	0.92328700	-4.75176700
H	3.53307900	1.84873400	-4.17061600
H	3.76653300	1.11562700	-5.76947900
C	4.18556400	-0.21653500	-4.09822900

H	5.25017800	0.04243700	-4.02428400
H	4.11688500	-1.11097800	-4.73818500
C	3.61647800	-0.54987400	-2.71591000
H	4.13782100	-1.41630500	-2.28464800
H	3.77153500	0.30222700	-2.03561900
C	2.11654000	-0.83346000	-2.80647700
H	1.94139100	-1.73635200	-3.41251600
H	1.65871900	-1.00446200	-1.82697300

TS

E=-2370.6358765

Sn	1.82299200	13.54205100	5.81558200
Cl	0.64690700	15.61440700	6.90529600
N	4.91263800	13.57665500	6.81524100
C	3.83416800	14.35730000	6.51710500
Cl	2.57686800	11.38623800	4.60697000
N	3.53056200	15.56412400	8.52383100
C	3.77476600	15.61042700	7.24839400
C	4.15086300	15.11172300	4.47005000
N	4.20556100	14.20337200	3.46225800
C	3.93804900	16.36886700	4.53652600
N	3.64349700	17.59326700	4.78477900
C	4.81396600	12.13393300	7.05679900
H	3.98396700	11.72908000	6.47267000
H	4.59483400	11.98306800	8.13052000
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C	2.29711900	17.04958400	10.07752100
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H	2.39801000	17.97494500	10.65998900
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H	1.00901700	16.02565300	11.49654400
C	7.38033200	13.47897100	6.97460800
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C	7.31051900	12.01062200	7.37990800
H	8.22907900	11.48256100	7.09360900
H	7.22169700	11.93797700	8.47560600
C	0.94442500	12.26112000	7.30754700
H	0.51446800	12.85341400	8.11925700

H	1.70167200	11.56273200	7.68002600
H	0.16060300	11.68283400	6.80521100
C	0.96341500	14.23172000	3.97829700
H	1.23875100	13.53454900	3.18353800
H	1.34042600	15.23760500	3.77225600
H	-0.12187100	14.27405900	4.11967200
C	1.88446900	14.59847700	10.12341600
H	1.05756900	14.69950100	9.40976800
H	1.70292000	13.70937600	10.74180000
C	3.17106000	14.37809800	9.32834300
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H	3.06148800	13.52271700	8.65766300
C	3.60183300	16.78765800	9.33394700
H	3.85929900	17.60145300	8.65312700
H	4.42273000	16.66142100	10.05875900
C	2.26364300	18.07579400	4.97078000
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H	2.02578100	18.73898000	4.12411000
C	2.13767900	18.82139500	6.29331800
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H	1.12069600	19.22763700	6.37000200
C	3.18370800	19.92913800	6.41516900
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C	4.58932000	19.36589700	6.20151700
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C	5.34040600	15.18225000	1.49955200
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2

E=-2370.7918357

Sn	-1.40748000	-1.79493700	-0.13661900
Cl	-2.72970400	0.30415500	0.70587800
N	1.67853000	-1.50441200	0.50262700
C	0.52164700	-0.68391600	0.26842000
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N	0.96870600	0.14770600	-2.12997200
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N	0.27444200	2.82651700	-0.18308700
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C	2.67906900	-3.61528700	1.23251500
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C	-2.23060400	-1.39324400	-2.08009400
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H	-1.88783400	-0.40484200	-2.40816200
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H	-1.58463200	-0.82725200	4.81138900
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C	0.10721500	2.14932500	2.95245400
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H	-1.47876300	4.63772600	0.85419500
H	-2.22242400	5.06427300	-0.69849300
C	-0.13411900	5.64513700	-0.50962900
H	-0.01301700	5.75494100	-1.59938900
H	-0.34210000	6.64567100	-0.10834500
C	1.16174900	5.09040100	0.08254800
H	2.01284400	5.73884500	-0.16568600
H	1.07937500	5.05721600	1.17936600
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H	2.29800500	3.23600600	0.06203300
C	1.03056000	1.25758200	-3.07726300
H	0.79091500	2.17949900	-2.54503300
H	0.25244300	1.09055700	-3.83840500
C	2.40265600	1.31816900	-3.74139200
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H	2.40898200	2.12980900	-4.48036400
C	2.73511200	-0.02353000	-4.39511700
H	3.73927400	0.00392100	-4.83662100
H	2.02613100	-0.20985100	-5.21662300
C	2.63078500	-1.15332000	-3.37070000
H	2.80373800	-2.12959400	-3.84082100
H	3.40033900	-1.02051900	-2.59658700
C	1.25863300	-1.16966900	-2.70099900
H	0.47896700	-1.39417300	-3.44439100
H	1.20441600	-1.92247100	-1.90967200

Benzene

E= -232.0422279

C	-1.02485200	0.79372500	-0.01335500
C	0.37037700	0.79366000	-0.01292500
C	1.06804400	2.00175800	-0.01344100
C	0.37044700	3.21001300	-0.01446100
C	-1.02468700	3.21007800	-0.01492000

C	-1.72240200	2.00189900	-0.01434300
H	-1.56948600	-0.14983700	-0.01292200
H	0.91490900	-0.14996300	-0.01215600
H	2.15750500	2.00177400	-0.01310000
H	0.91520100	4.15350500	-0.01489500
H	-1.56933700	4.15363400	-0.01569000
H	-2.81186300	2.00201600	-0.01468700

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