

**Safe, simple and efficient approach to bicyclic phosphines
based on magnesium phosphide**

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List of contents

S1. Materials and methods.....	S1
S2. Synthesis of bicyclic phosphines	S2
S3. NMR spectra	S4
S4. DFT modeling	S8
References.....	S18

S1. Materials and methods

S1.1. Materials

Commercial forms of metal phosphides AlP (Fosfin, 56 wt.%, Agrofos, Russia) and Mg₃P₂ (Magtoxin, 66 wt.%, AgroServer, Russia) were used as purchased. Before loading to reactor, the tablets of metal phosphides were crushed to a size of 1–3 mm.

Cycloocta-1,5-diene **1**, (*R*)-limonene **2**, AIBN and toluene (Ruschim, Russia) were used as purchased.

S1.2. Analysis

CDCl₃ (Cambridge Isotope Laboratories, Inc., D 99.8 %) was used as purchased. DMSO-d₆ (Aldrich, ≥99.5 atom % ²H) was distilled over CaH₂ and stored over molecular sieves. The ¹H and ³¹P NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (400 MHz) at 20 °C. The chemical shifts are reported in ppm relative to the solvent residual peaks (¹H NMR) or using H₃PO₄ standard (³¹P NMR).

S2. Synthesis of bicyclic phosphines

S2.1. H-Phob 3

Syntheses of H-Phob **3** (mixture of 9-phosphabicyclo[3.3.1]nonane and 9-phosphabicyclo[4.2.1]nonane) were conducted using the methods described below.

Synthesis of H-Phob with separation by vacuum distillation

Cycloocta-1,5-diene **1** (18.5 mL, 0.15 mol), magtoxin (17.5 g, 80 mmol of Mg_3P_2), AIBN (0.5 g), toluene (45 mL) and H_2O (4 mL, excess) were placed into a glass reactor (100 mL). The mixture was heated with stirring to 65 °C within 1 h, and stirred at 70±5 °C within 12 h. The mixture was cooled and filtered, the filtrate was evaporated under reduced pressure and distilled *in vacuo* (bp 55–60 °C at 0.3 Torr). Distillation of the reaction product was complicated by its crystallization. The yield 17.3 g (81%), colorless crystalline solid. ^{31}P NMR (CDCl_3 , 20°C) δ : –48.26, –53.85. (Lit. ^{31}P NMR (CDCl_3) δ : –48.4 (*as*-isomer), –54.1 (*s*-isomer)^{S1}), see Figure S1.

The reaction of cycloocta-1,5-diene **1** with AIP and reactions of cycloocta-1,5-diene with Mg_3P_2 using different volumes of toluene were conducted in the same way.

Synthesis of H-Phob 3 with separation via adduct with CH_2O (6a/6b)

The reaction was conducted using the method described above. The filtrate was treated by excess of aq. CH_2O (15 mL), conc. HCl (20 mL) was added, the aqueous phase was separated and evaporated under reduced pressure, the residue was treated with Pr^iOH . White precipitate was filtered off, washed by cold Pr^iOH and dried *in vacuo*. The yield was 29.0 g (81%). ^1H NMR ($\text{DMSO}-d_6$, 20°C) δ : 4.71 (s), 4.65 (s), 4.39 (s) {4H, $-\text{CH}_2\text{O}-$ }, 3.08 (br, 1H), 2.60–1.68 (gr. m, 13H). ^{31}P { ^1H } NMR ($\text{DMSO}-d_6$, 20°C) δ : 55.47, 21.40. (Lit. ^{31}P NMR (H_2O) δ : 55.2, 23.4¹). NMR spectra of the reaction product are presented in Figures S2 and S3.

The mixture **6a/6b** was suspended in pentane (10 mL), aq. NaOH (4.6 mL of 1 M) and NaHSO_3 (3.5 g) were added. The mixture was stirred within 5 days at 20 °C, the organic phase was separated and evaporated under reduced pressure. The yield was 0.9 g (71%). ^{31}P NMR (CDCl_3 , 20°C) δ : –48.29, –53.87. (Lit. ^{31}P NMR (CDCl_3) δ : –48.4 (*as*-isomer), –54.1 (*s*-isomer)^{S1}), see Figure S4.

S2.2. H-Lim 4

(*R*)-Limonene **2** (24.2 mL, 0.15 mol), magtoxin (17.5 g, 80 mmol of Mg_3P_2), AIBN (0.5 g), toluene (45 mL) and H_2O (4 mL, excess) were placed into glass reactor (100 mL). The mixture was heated with stirring to 65 °C within 1 h, and stirred at 70±5 °C within 12 h. The mixture was cooled and filtered, the filtrate was evaporated under reduced pressure and distilled *in vacuo* (bp 60–65 °C at 0.3 Torr). The yield 21.5 g (84%). ^{31}P NMR (CDCl_3 , 20°C) δ : –73.8, –97.8 (Lit. ^{31}P NMR (toluene- d_8) δ : –72.4, –96.5^{S2}), see Figure S5.

S2.3. Tertiary phosphine 5

(*R*)-Limonene **2** (9.7 mL, 60 mmol), magtoxin (3.3 g, 15 mmol of Mg₃P₂), AIBN (0.5 g), toluene (45 mL) and H₂O (4 mL, excess) were placed into glass reactor (100 mL). The mixture was heated with stirring to 65 °C within 1 h, and stirred at 70±5 °C within 12 h. The mixture was cooled and filtered, the filtrate was evaporated under reduced pressure and distilled *in vacuo* (bp 145–155 °C at 0.3 Torr). The yield 3.2 g (27%), pale yellow oil. Found (%): C, 78.49; H, 11.59. Calc. for C₂₀H₃₅P (%): C, 78.38; H, 11.51; P, 10.11. ¹H NMR (CDCl₃, 20°C) δ: 5.56 (s, 1H), 2.08–1.88 (m, 6H), 1.75 (bs, 3H); 1.64–0.71 (groups m, >25H). ³¹P NMR (CDCl₃, 20°C) δ: –49.73, –50.35, –56.41, –56.49. NMR spectra are presented in Figs. S6 and S7.

S3. NMR spectra

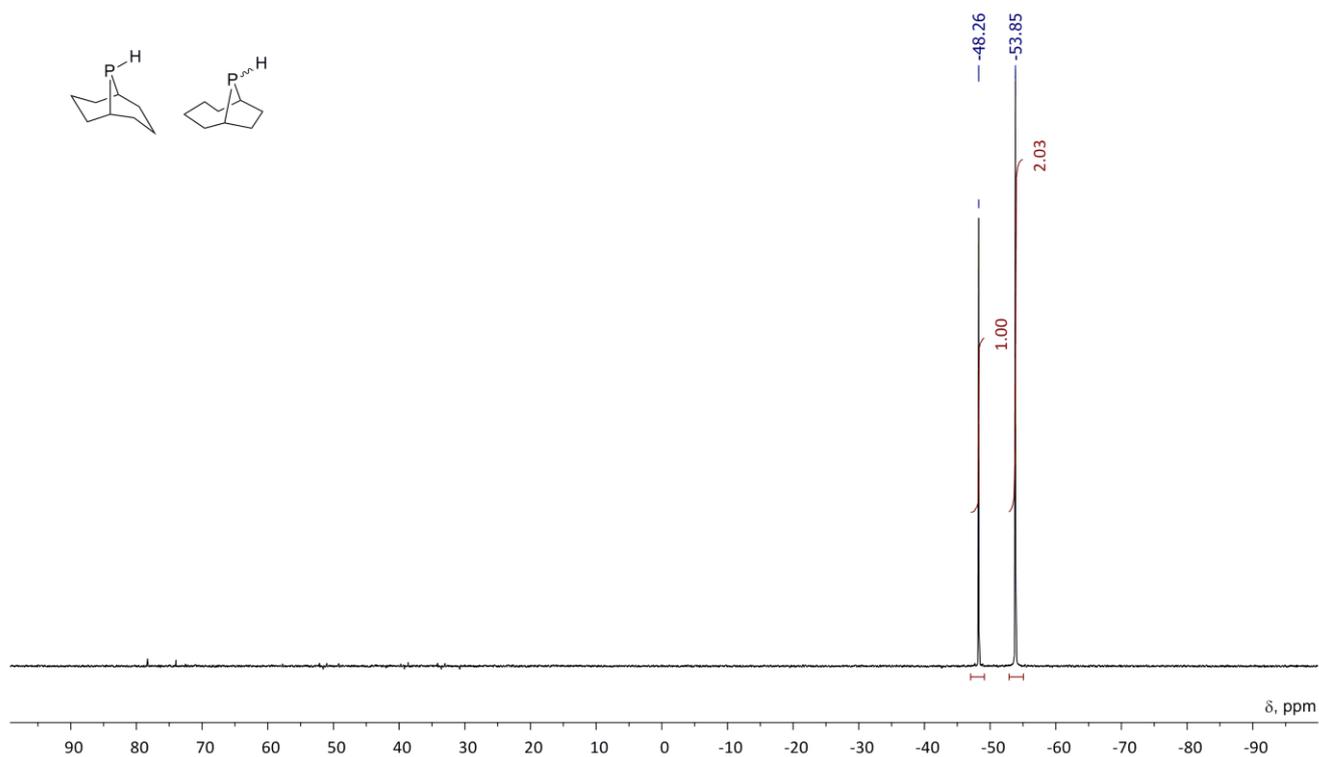


Figure S1 ^{31}P $\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 20 °C, 162 MHz) of H-Phob **3** obtained by distillation

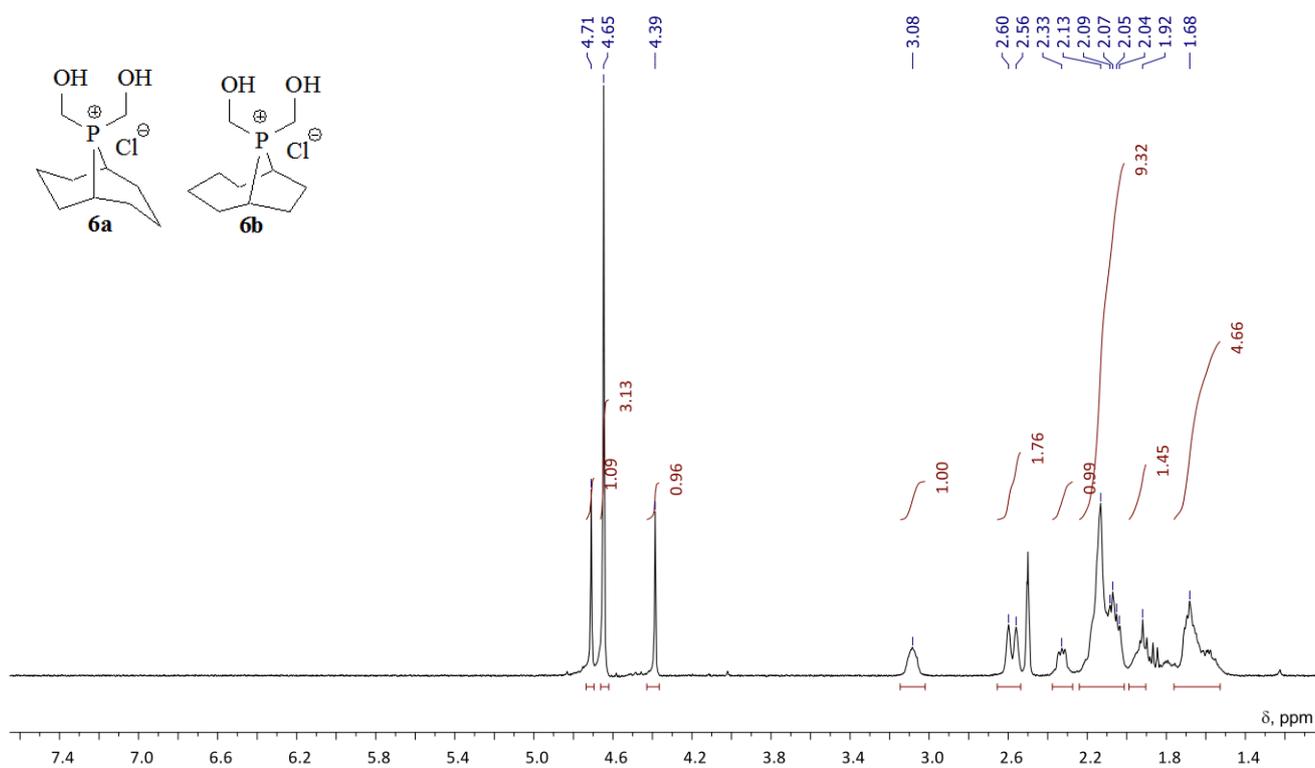


Figure S2 ^1H NMR spectrum (DMSO-d_6 , 20 °C, 400 MHz) of **6a/6b**

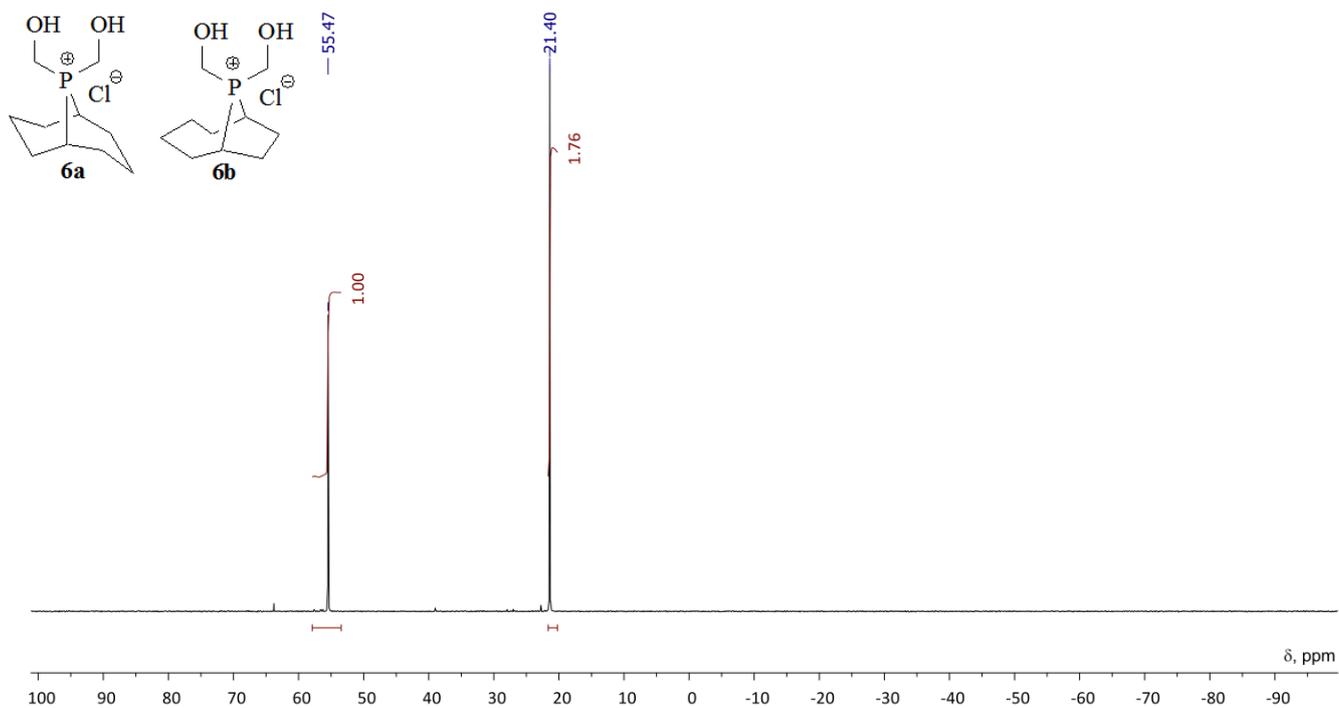


Figure S3 ^{31}P $\{^1\text{H}\}$ NMR spectrum (DMSO- d_6 , 20 °C, 162 MHz) of **6a/6b**

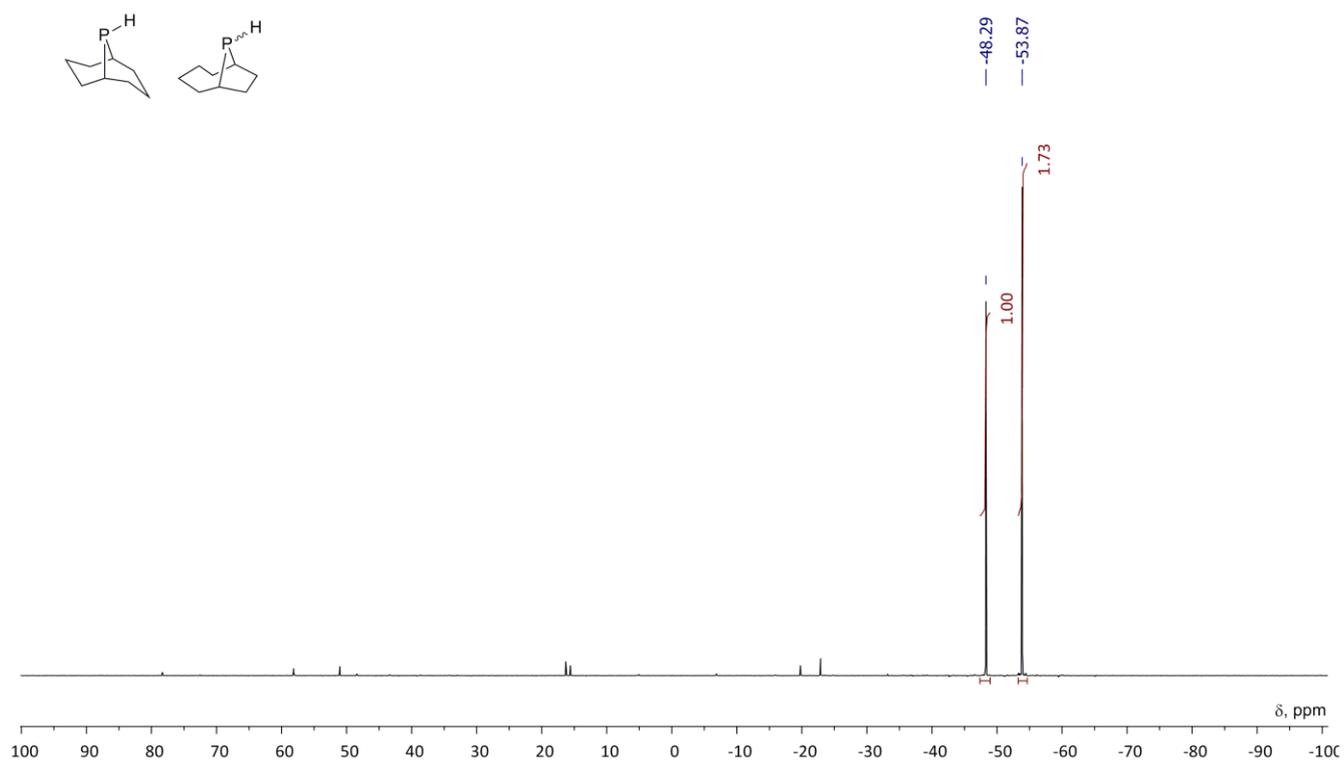


Figure S4 ^{31}P $\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 20 °C, 162 MHz) of H-Phob **3** obtained *via* adduct with CH_2O

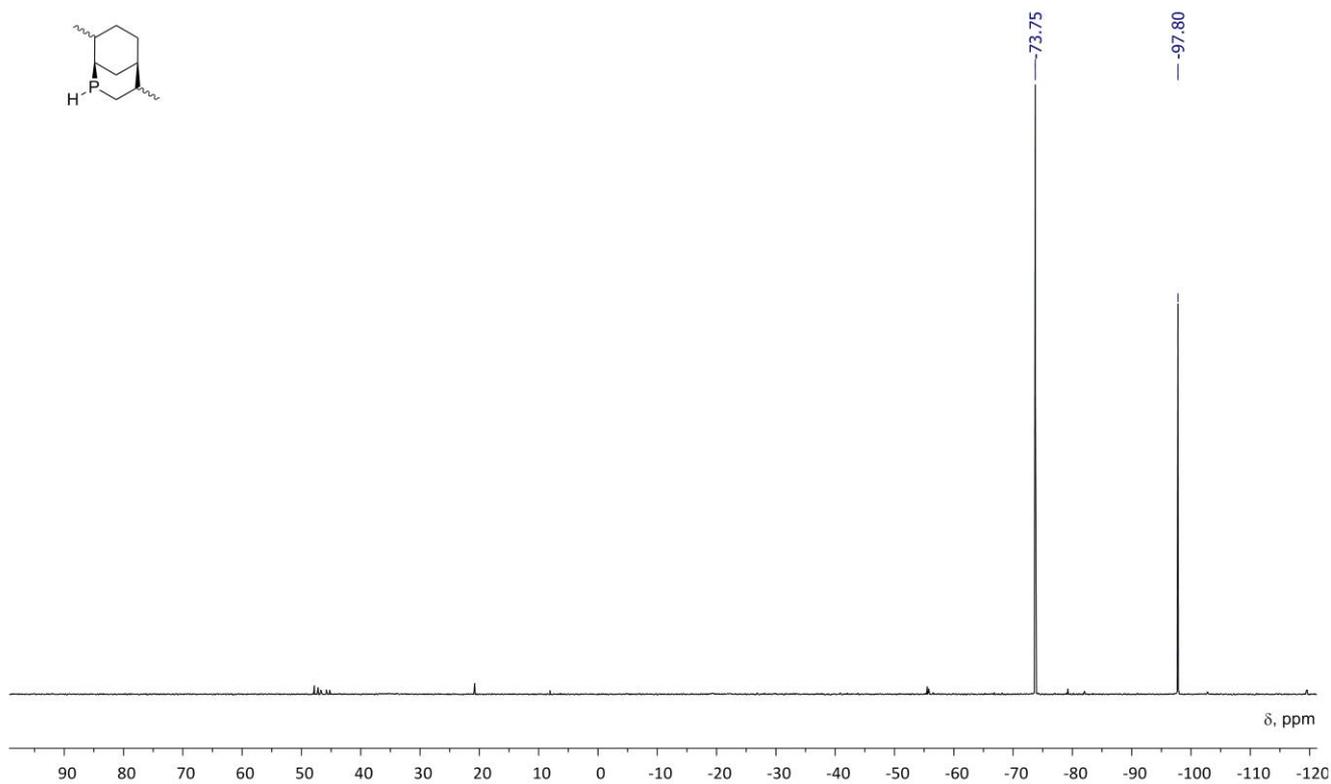


Figure S5 ^{31}P { ^1H } NMR spectrum (CDCl₃, 20 °C, 162 MHz) of H-Lim 4

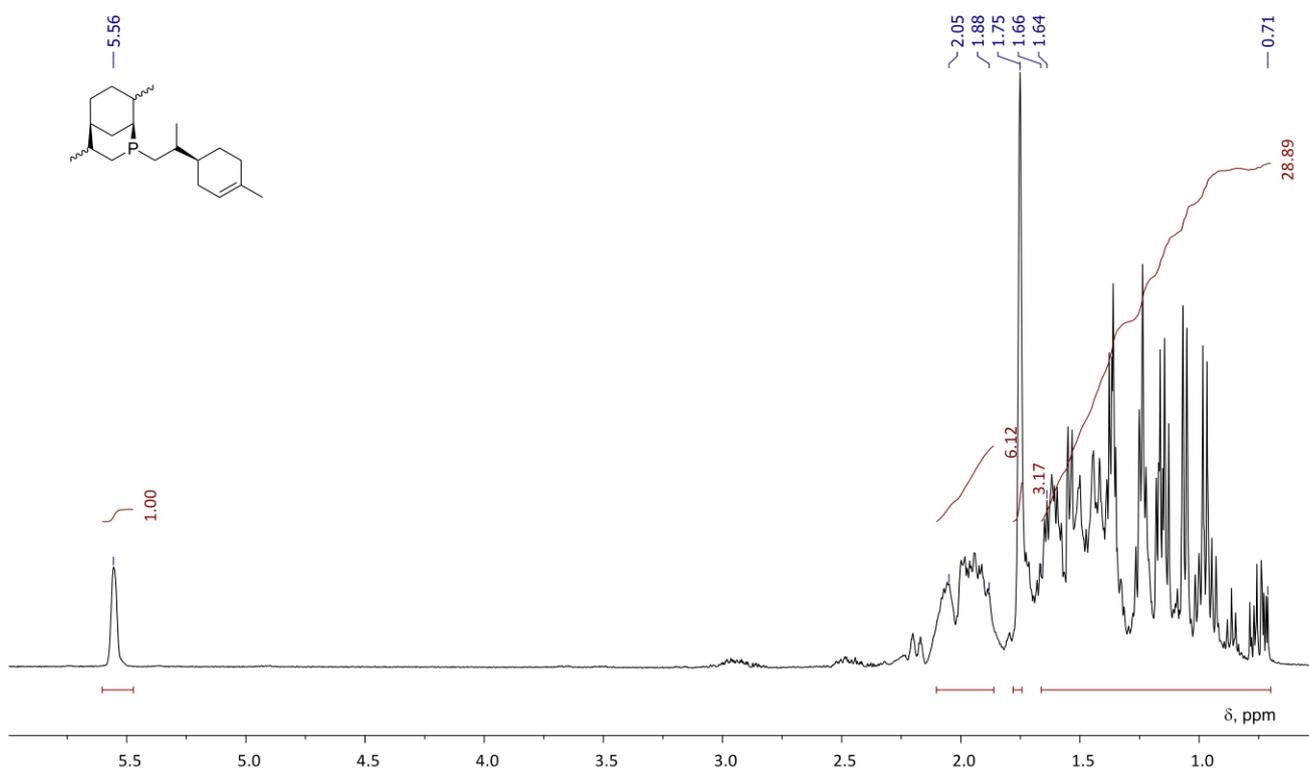


Figure S6 ^1H NMR spectrum (DMSO-d₆, 20 °C, 400 MHz) of 5

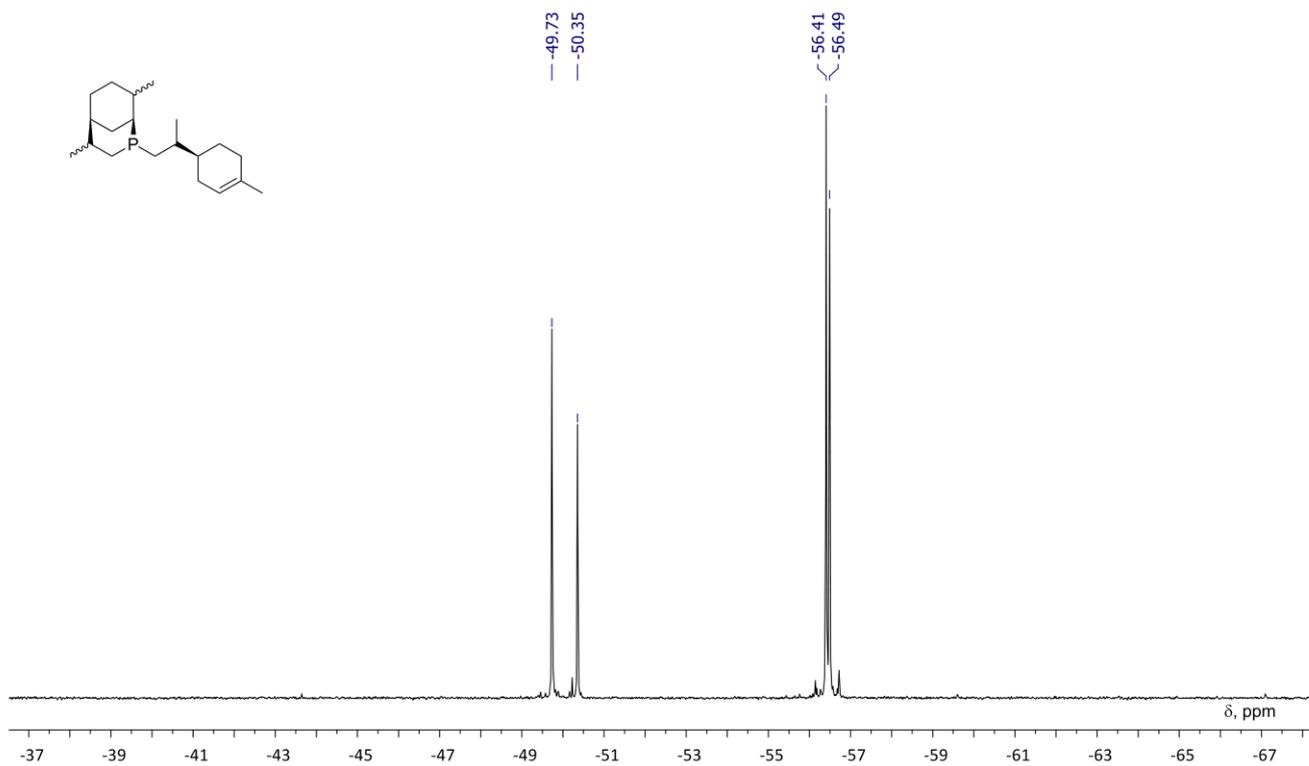


Figure S7 ^{31}P $\{^1\text{H}\}$ NMR spectrum (CDCl_3 , 20°C , 162 MHz) of **5**

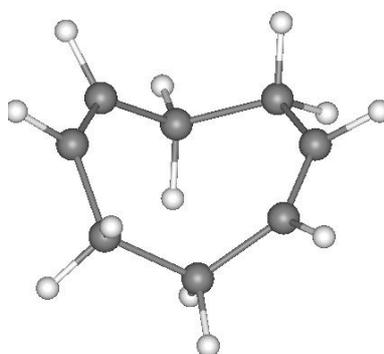
S4. DFT modeling

S4.1. Methods

The stationary points and transition states of the reactions under study had been found by PRIRODA program (version 4.0, M.V. Lomonosov Moscow University, Moscow, Russia)^{S3,S4} using the gradient-corrected PBE functional^{S5} and full-electron 3 ζ basis set for gas phase at 298.15 K. Transition states (TSs) were found by energy scanning with gradual changes of interatomic distances in increments of 0.01 Å. The geometries, corresponding to the energy maxima, were optimized with a calculation of Hessian, and subsequent optimization of the 1st order saddle points that correspond to the imaginary frequencies. The optimized geometries of the TSs were confirmed by intrinsic reaction coordinate simulations.

S4.2. Starting compounds, chain transfer

Cycloocta-1,5-diene (Cod) 1



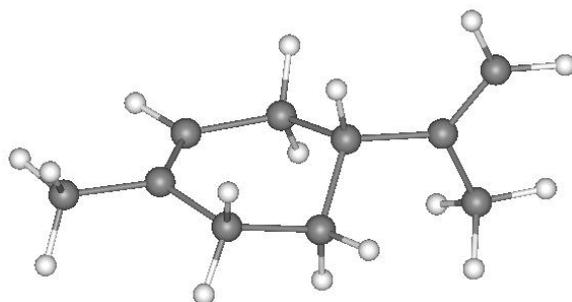
E = -311.709723 E₀ = -311.535090
ZPVE = 0.174633 a.u. = 109.5838 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	17.6028	39.9486	0.8887	1.4812	-10.4294
rotational	12.6218	28.0632	0.8887	0.8887	-7.4783
vibrational	3.3108	16.7888	112.6278	112.6278	107.6222
total	33.5355	84.8005	114.4053	14.9977	89.7145

Cartesian

6	0.00751783	1.10656929	1.70953834	1	-0.58432823	-0.76800573	2.57100677
6	-0.29913431	-0.39964092	1.57350278	1	0.61400735	-0.94488329	1.30733287
6	-1.42782629	-0.70783573	0.61611050	1	-0.62329912	-0.06308336	-2.54744172
6	-1.39955258	-0.80787331	-0.72252232	1	-0.03012874	-1.65406811	-2.12211108
6	-0.25769249	-0.65992504	-1.69348085	1	1.77084959	-0.03717422	-2.01629353
6	1.05418253	-0.02977596	-1.18060637	1	1.49734259	-0.66641849	-0.40587702
6	0.89899248	1.39652693	-0.70425254	1	0.43100512	2.93923140	0.59880751
6	0.46416530	1.85052490	0.48213711	1	-2.40587425	-0.84422976	1.08836257
1	0.76350695	1.24428654	2.50537491	1	-2.35396624	-1.03708792	-1.20890391
1	-0.89564592	1.61563706	2.08938169	1	1.15685451	2.15886021	-1.44625282

Limonene (Lim) 2



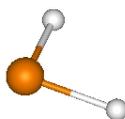
E = -390.270572 E₀ = -390.043044
 ZPVE = 0.227528 a.u. = 142.7761 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	17.9486	40.6359	0.8887	1.4812	-10.6344
rotational	13.4830	29.7744	0.8887	0.8887	-7.9885
vibrational	6.9699	31.1949	147.9472	147.9472	138.6465
total	38.4015	101.6052	149.7247	150.3172	120.0236

Cartesian

6	0.52252740	0.89794934	-0.26524445	1	2.81913638	1.13680804	-2.59793663
6	-0.17882033	-0.38461331	-0.62846887	6	-1.79244423	-2.20740724	-3.15870929
6	-0.10772613	-0.68669170	-2.14047790	6	0.16496730	-3.26722407	-2.05468488
6	1.33132887	-0.44572499	-2.63401771	1	-2.19243169	-3.19138050	-3.40747285
6	1.73320532	1.02053416	-2.43870735	1	-2.37215233	-1.34119678	-3.48188233
6	1.37154472	1.55664957	-1.07200587	1	-0.35460761	-4.20034695	-2.30633759
1	-1.23487544	-0.33074355	-0.31692216	1	1.15041220	-3.28237057	-2.54588890
1	0.25571111	-1.21980381	-0.04956432	1	0.35558155	-3.26389480	-0.97026557
1	-0.75709534	0.04742405	-2.64823103	1	0.30366981	1.31346309	0.72345638
6	-0.64021879	-2.06604815	-2.48502851	6	2.00891137	2.86138368	-0.67769730
1	1.42300236	-0.72681290	-3.69444656	1	1.76842880	3.65347838	-1.40633178
1	2.02569699	-1.08839631	-2.06854677	1	1.67310119	3.19476819	0.31308803
1	1.25681877	1.65235150	-3.21151233	1	3.10804057	2.77744937	-0.66129750

PH₂ radical



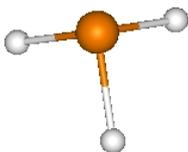
E = -342.356307 E₀ = -342.343348
 ZPVE = 0.012959 a.u. = 8.1321 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	15.8226	36.4109	0.8887	1.4812	-9.3747
rotational	5.7406	14.3886	0.8887	0.8887	-3.4012
vibrational	0.0054	0.0676	8.1490	8.1490	8.1289
total	21.5686	50.8671	9.9265	10.5190	-4.6471

Cartesian

15	-1.61801553	2.23006558	-0.47076476	1	-2.13173914	2.12117314	0.87022108
1	-2.65784264	1.36658859	-0.96793634				

PH₃



E = -342.990430 E₀ = -342.967292
ZPVE = 0.023138 a.u. = 14.5196 kcal/mol

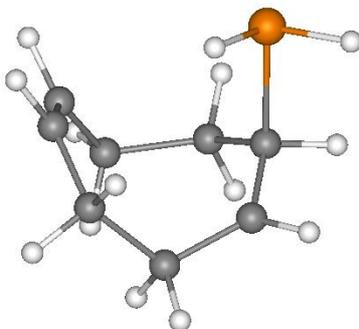
T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	15.8677	36.5006	0.8887	1.4812	-9.4014
rotational	6.4273	15.7532	0.8887	0.8887	-3.8081
vibrational	0.0190	0.2293	14.5767	14.5767	14.5083
total	22.3140	52.4831	16.3541	16.9466	1.2988

Cartesian

15	1.87411404	-1.58340204	1.23320842	1	0.93221503	-1.05202961	0.28970009
1	0.88161576	-1.68073356	2.26531696	1	2.28104568	-0.27496809	1.66002250

S4.3. Cycloalkenyl-phosphine radicals

Intermediate 8'



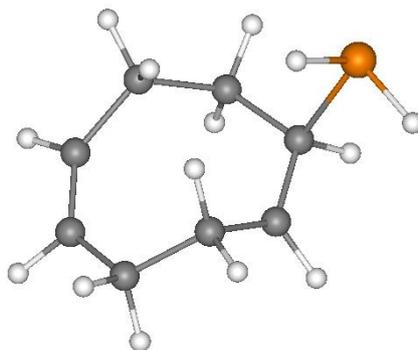
E = -654.072456 E₀ = -653.880917
ZPVE = 0.191539 a.u. = 120.1924 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.0023	40.7425	0.8887	1.4812	-10.6662
rotational	13.2955	29.4018	0.8887	0.8887	-7.8774
vibrational	5.9422	27.3863	124.8369	124.8369	116.6717
total	37.2400	97.5306	126.6144	127.2069	98.1281

Cartesian

6	-0.03616488	0.93436748	1.56662846	1	0.70379966	-1.09043026	1.28743708
6	-0.24446648	-0.59924686	1.53686845	1	-0.50550652	-0.69561881	-2.58737445
6	-1.33733511	-1.08764005	0.61950094	1	0.28121287	-2.11992669	-1.94202995
6	-1.25422764	-1.30751455	-0.70287472	1	1.82794452	-0.26787618	-2.05539989
6	-0.09872965	-1.12139308	-1.65373504	1	1.62869465	-0.75686949	-0.38531870
6	1.11346221	-0.25276652	-1.21814668	1	0.34515843	2.71593642	0.46317008
6	0.82706153	1.18145990	-0.88777453	1	-2.30879307	-1.27213860	1.08747661
6	0.00128274	1.69561970	0.22230095	1	-2.16228247	-1.67595077	-1.19240296
1	0.91304255	1.12981069	2.09306455	1	1.11984551	1.92428207	-1.63315487
1	-0.82753700	1.38925493	2.18254113	15	-1.80931818	2.14203811	-0.36770543
1	-0.47884521	-0.91617340	2.56464195	1	-1.41240764	3.26416492	-1.17551458
				1	-1.91971886	1.27952373	-1.50423408

Intermediate 8' conformer 2



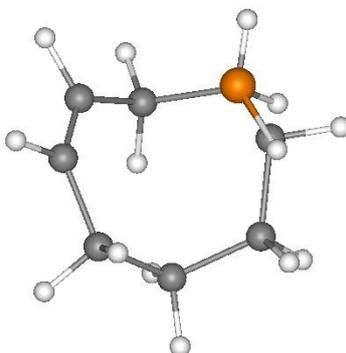
E = -654.074734 E₀ = -653.883520
 ZPVE = 0.191214 a.u. = 119.9885 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.0023	40.7425	0.8887	1.4812	-10.6662
rotational	13.4225	29.6543	0.8887	0.8887	-7.9527
vibrational	6.0034	27.8545	124.7364	124.7364	116.4316
total	37.4283	98.2513	126.5139	127.1063	97.8127

Cartesian

6	0.15480649	0.68541920	1.79301131	1	2.40595293	-2.05015969	-1.42091250
6	0.09964732	-0.85031915	1.60466170	1	3.39421868	-0.68813843	-0.93698072
6	1.45797908	-1.51864719	1.62746668	1	0.32856318	-0.69393212	-1.14802539
6	2.39213109	-1.63664877	0.66985488	1	1.47018862	-0.01524220	-2.29881787
6	2.41395211	-1.16434956	-0.75822115	1	0.55260605	2.56192207	0.83877152
6	1.30416369	-0.19385652	-1.22170055	1	1.72438753	-1.94659984	2.59934807
6	1.29415607	1.12133408	-0.50758737	1	3.30705333	-2.16527963	0.95976895
6	0.30337384	1.54158819	0.50738835	1	1.99684167	1.88015950	-0.86004853
1	1.00242150	0.91959530	2.45593119	15	-1.45706606	1.81070483	-0.25002947
1	-0.75462508	1.01998973	2.31815028	1	-1.02470863	2.46941185	-1.45079100
1	-0.46485847	-1.10348141	0.69701374	1	-1.58343077	0.54465514	-0.91704291
1	-0.48407310	-1.26808071	2.43808198				

Intermediate 8''



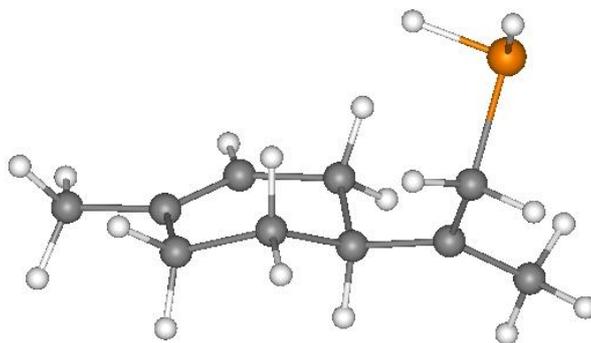
E = -654.095979 E₀ = -653.900675
 ZPVE = 0.195304 a.u. = 122.5552 kcal/mol

T = 298.150 K	ln(Q)	S cal/mol·K	U kcal/mol	H kcal/mol	G kcal/mol
translational	18.0023	40.7425	0.8887	1.4812	-10.6662
rotational	13.2404	29.2924	0.8887	0.8887	-7.8448
vibrational	5.5534	25.9527	127.0027	127.0027	119.2649
total	36.7961	95.9876	128.7802	129.3727	100.7540

Cartesian

6	0.18171930	0.76823550	1.74218822	1	-0.46014193	-0.52851468	-2.32565761
6	0.05934737	-0.77767158	1.72770524	1	0.27050295	-2.08458638	-2.02088404
6	-1.03934920	-1.31138194	0.84293520	1	2.00878978	-0.48083866	-1.94704592
6	-1.04700696	-1.42947066	-0.49777102	1	1.80455625	-1.05807221	-0.31359211
6	0.01339218	-1.12860787	-1.52765191	1	0.43358392	2.53883600	0.59984487
6	1.31857097	-0.45082837	-1.08791494	1	-1.96611810	-1.58648300	1.35480738
6	1.24122500	1.02687073	-0.64730418	1	-1.97198451	-1.81459737	-0.93975890
6	0.17539440	1.48521543	0.37707010	15	-1.58900321	1.69547105	-0.27741295
1	1.11496353	1.02315688	2.27316332	1	-1.17662978	2.33158588	-1.50823569
1	-0.63710135	1.18568051	2.35019135	1	1.11572146	1.64986587	-1.54749203
1	-0.12860949	-1.10365903	2.76176643	1	2.23291302	1.29314554	-0.23894432
1	1.02637362	-1.21418405	1.45112705				

Intermediate 7'



$E = -732.640574$ $E_0 = -732.396358$

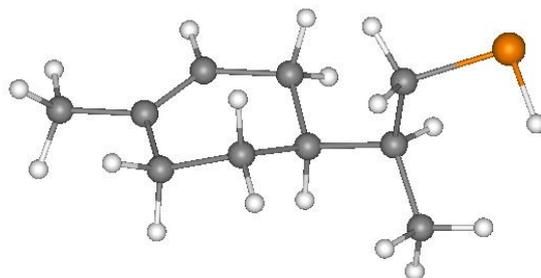
ZPVE = 0.244216 a.u. = 153.2478 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.2741	41.2827	0.8887	1.4812	-10.8272
rotational	14.1963	31.1919	0.8887	0.8887	-8.4111
vibrational	10.6789	44.3558	160.1454	160.1454	146.9207
total	43.1493	116.8305	161.9229	162.5154	127.6824

Cartesian

6	-0.04488903	1.29517794	1.42170882	6	-2.63820100	-1.89393210	-0.70580405
6	-0.72966802	0.00404645	1.05945957	1	-2.98615670	-2.63797426	-1.44086874
6	-0.60063893	-0.33708146	-0.45147589	1	-2.96106410	-2.27107787	0.28526846
6	0.85094696	-0.09743082	-0.89215994	1	-3.18215752	-0.95416832	-0.88207811
6	1.24549389	1.37270665	-0.70688862	1	-0.29916981	1.72988582	2.39376378
6	0.83320022	1.93744123	0.63339674	6	1.45669234	3.24997902	1.02387726
1	-1.79532242	0.06334143	1.33457148	1	1.24560702	4.02663565	0.27000326
1	-0.31761035	-0.82334799	1.66559708	1	1.08410525	3.60428381	1.99395931
1	-1.22981572	0.40498558	-0.98206371	1	2.55423832	3.16526771	1.08380115
6	-1.15661907	-1.69715822	-0.78342879	1	-0.78033352	-3.65472007	-1.54605711
1	0.98485851	-0.38942418	-1.94515836	1	0.69321662	-2.67603660	-1.31673002
1	1.52784967	-0.73007977	-0.29402775	15	-0.04553259	-3.83173370	0.77121818
1	0.80026084	1.98921597	-1.51000893	1	0.89553159	-4.80104542	0.27462813
1	2.33681583	1.48578453	-0.82658935	1	1.00249767	-2.98745322	1.27334750
6	-0.29863173	-2.89874506	-0.90570962				

Intermediate 7''



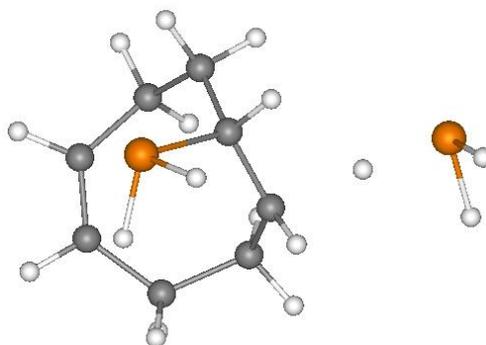
E = -732.660427 E₀ = -732.412117
 ZPVE = 0.248310 a.u. = 155.8170 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.2741	41.2827	0.8887	1.4812	-10.8272
rotational	14.2176	31.2343	0.8887	0.8887	-8.4238
vibrational	10.0929	42.3228	162.4556	162.4556	149.8371
total	42.5846	114.8398	164.2331	164.8256	130.5861

Cartesian

6	0.61649245	1.49127018	1.64142585	6	-2.09902525	-1.74587965	-1.17199266
6	-0.03702005	0.13763823	1.54434347	1	-2.54081893	-2.75023961	-1.21570444
6	-0.60014361	-0.15359551	0.14385898	1	-2.92224789	-1.02361929	-1.07491565
6	0.42627504	0.27223599	-0.91566771	1	-1.60013366	-1.56095684	-2.13527083
6	0.70418572	1.77843964	-0.83053988	1	0.82424152	1.86613619	2.64846897
6	0.93941069	2.25582147	0.58456582	6	1.54776347	3.62370276	0.73552382
1	-0.85029703	0.06975333	2.28727221	1	0.92717820	4.38798904	0.23867805
1	0.69042468	-0.64191949	1.83965337	1	1.65761960	3.90556407	1.79097712
1	-1.48621571	0.49645057	0.01759681	1	2.54048824	3.67146802	0.25854778
6	-1.11922240	-1.61179078	0.00166282	1	0.46665317	-2.62745452	-1.11239982
1	0.08038557	0.01606519	-1.92877841	1	0.84088641	-2.38188124	0.60054237
1	1.36976898	-0.27418312	-0.75186777	15	-0.42134112	-4.41095161	0.32162610
1	-0.13830180	2.34605598	-1.26808751	1	-1.68175733	-1.82757580	0.92788309
1	1.58069241	2.03490925	-1.45008385	1	-1.27287030	-4.63717175	-0.82002276
6	0.03342163	-2.64324427	-0.09928572				

Transition state TS-8'/8



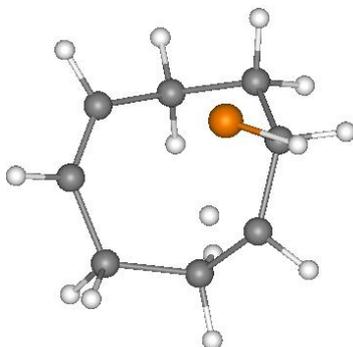
E = -997.061537 E₀ = -996.846545
 ZPVE = 0.214993 a.u. = 134.9100 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.3262	41.3861	0.8887	1.4812	-10.8580
rotational	14.2378	31.2744	0.8887	0.8887	-8.4357
vibrational	10.6262	43.0819	141.4590	141.4590	128.6141
total	43.1901	115.7423	143.2365	143.8290	109.3204

Cartesian

6	-0.33742711	0.51844186	1.74797106	1	1.48287320	-0.95325178	-1.78164041
6	-0.76476896	-0.97026563	1.72030091	1	1.13184631	-1.39151847	-0.12324915
6	-1.87400818	-1.31179786	0.75619042	1	0.26198861	2.24025583	0.65454954
6	-1.77045202	-1.53806150	-0.56398940	1	-2.87831402	-1.37531531	1.18492019
6	-0.56840765	-1.49969113	-1.47374558	1	-2.69947267	-1.78581047	-1.08867431
6	0.73784834	-0.82713628	-0.98040152	1	0.84307569	1.30969512	-1.51357090
6	0.66480356	0.64531785	-0.66149992	15	-1.89065003	1.87637687	-0.26918688
6	-0.17908549	1.25928283	0.40298191	1	-1.35359550	2.98348331	-1.01584637
1	0.62298256	0.58068854	2.28608179	1	-2.01957631	1.06540406	-1.44082999
1	-1.06209123	1.08654475	2.35101247	15	3.64232230	1.05627787	0.51870012
1	-1.08841741	-1.23534346	2.73802519	1	3.79086161	2.27946973	-0.21974523
1	0.11263917	-1.59736395	1.52081990	1	2.20670009	0.85925418	-0.01341227
1	-0.87832379	-1.01014745	-2.41363692	1	4.18952894	0.27268842	-0.55354220
1	-0.32288054	-2.53747964	-1.76858211				

Transition state TS-8'/8''



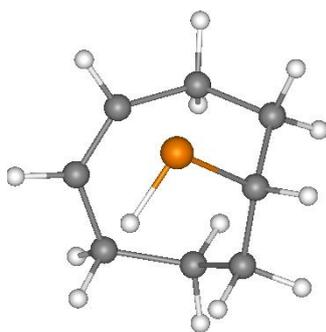
E = -654.046127 E₀ = -653.856300
 ZPVE = 0.189827 a.u. = 119.1180 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.0023	40.7425	0.8887	1.4812	-10.6662
rotational	13.2675	29.3463	0.8887	0.8887	-7.8609
vibrational	5.0866	24.1730	123.3114	123.3114	116.1043
total	36.3564	94.2618	125.0889	125.6814	97.5772

Cartesian

6	0.19327833	0.71770972	1.74670184	1	-0.28535146	-1.17292392	-2.44509816
6	0.00271529	-0.81721312	1.68012369	1	0.59516048	-2.40975785	-1.57169533
6	-1.12629580	-1.28456712	0.80214894	1	1.89200974	-0.35763291	-2.00881863
6	-1.05829656	-1.54424703	-0.51267922	1	1.85184968	-0.74332845	-0.29882720
6	0.11886990	-1.41928780	-1.44934297	1	0.57168567	2.52225494	0.68052614
6	1.22667360	-0.38214216	-1.13192463	1	-2.10024285	-1.40363276	1.28575766
6	0.76229125	1.03188252	-0.86440188	1	-1.97941315	-1.88225424	-0.99740165
6	0.16014010	1.53332448	0.43972665	1	1.29792213	1.81038785	-1.41460419
1	1.15928423	0.90610427	2.24611449	15	-1.57460070	1.84854531	-0.34635991
1	-0.57249504	1.14290524	2.41434407	1	-1.22537935	3.16292548	-0.82710260
1	-0.17570131	-1.16776240	2.70866489	1	-0.67537099	1.19894481	-1.50101912
1	0.94126588	-1.29023468	1.36516738				

Transition state *TS-8''/8'''-1*



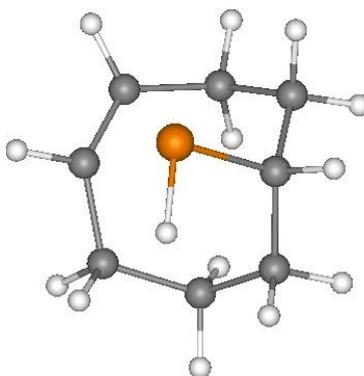
E = -654.094158 E₀ = -653.898734
 ZPVE = 0.195424 a.u. = 122.6303 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.0023	40.7425	0.8887	1.4812	-10.6662
rotational	13.1738	29.1601	0.8887	0.8887	-7.8053
vibrational	3.9495	20.4333	126.3825	126.3825	120.2903
total	35.1256	90.3359	128.1600	128.7525	101.8188

Cartesian

6	0.33820975	0.70193875	1.72223389	1	-0.24011211	-0.79342651	-2.52265620
6	-0.25993568	-0.73415226	1.64634383	1	0.42566264	-2.21903658	-1.76686358
6	-1.35805643	-0.95041054	0.61502820	1	2.03831148	-0.42132893	-1.79842055
6	-1.17259479	-1.29775214	-0.69477189	1	1.69545758	-0.83299404	-0.13536796
6	0.06638324	-1.19677734	-1.53989625	1	0.36427331	2.57278919	0.68519759
6	1.25301814	-0.36545259	-1.02666795	1	-2.35737300	-1.12561309	1.01763546
6	0.99775440	1.12756085	-0.75564760	1	-2.06869411	-1.59571505	-1.24760807
6	0.10751597	1.52689099	0.44422746	15	-1.76937461	1.56405449	0.21930504
1	1.41513836	0.64820707	1.95484924	1	-1.81321752	1.42155695	-1.21268153
1	-0.13159618	1.23643565	2.56184244	1	0.60491186	1.60318613	-1.66914248
1	-0.66757888	-0.99605083	2.63285851	1	1.98865354	1.58412135	-0.58323258
1	0.54324323	-1.45803058	1.45343554				

Transition state *TS-8''/8'''-2*



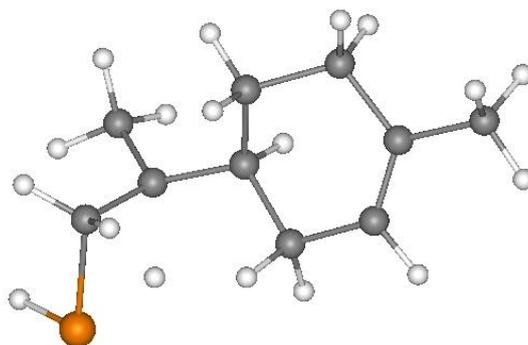
E = -654.092554 E₀ = -653.897148
 ZPVE = 0.195406 a.u. = 122.6194 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.0023	40.7425	0.8887	1.4812	-10.6662
rotational	13.1430	29.0988	0.8887	0.8887	-7.7871
vibrational	3.6008	19.5669	126.3198	126.3198	120.4860
total	34.7462	89.4082	128.0973	128.6898	102.0327

Cartesian

6	0.09286410	0.73005676	1.72491896	1	-0.50238305	-0.53513497	-2.44516754
6	-0.04232527	-0.82190007	1.70760262	1	0.08428455	-2.08202910	-1.86730909
6	-1.17553306	-1.27035248	0.83212352	1	1.89016593	-0.44396183	-1.98895192
6	-1.24851036	-1.11854458	-0.53107321	1	1.68913484	-1.03056622	-0.35656944
6	-0.12015924	-1.04320514	-1.54634178	1	0.17344052	2.51346350	0.57093072
6	1.21089172	-0.40577400	-1.12189496	1	-2.11730289	-1.49413931	1.34053040
6	1.13983071	1.05768633	-0.64778161	1	-2.20279217	-1.40443683	-0.98284429
6	0.03155364	1.43895090	0.35608816	15	-1.73268569	1.38310087	-0.34765771
1	1.04584920	0.98427272	2.21934700	1	-1.34820938	1.79601896	-1.67751312
1	-0.70601875	1.14424562	2.36086893	1	1.02302659	1.71058846	-1.52765679
1	-0.21537749	-1.16089737	2.73935986	1	2.11878705	1.31900990	-0.20676306
1	0.91146797	-1.26645148	1.39575350				

Transition state TS-7'/7''



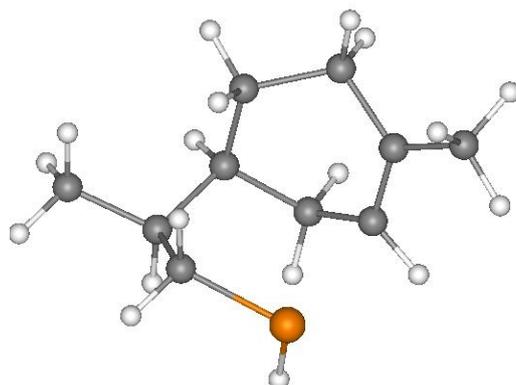
E = -732.615807 E₀ = -732.372972
 ZPVE = 0.242835 a.u. = 152.3811 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.2741	41.2827	0.8887	1.4812	-10.8272
rotational	14.1619	31.1236	0.8887	0.8887	-8.3908
vibrational	8.6995	38.3968	158.6747	158.6747	147.2267
total	41.1356	110.8031	160.4521	161.0446	128.0087

Cartesian

6	0.70086920	1.36519897	1.58883393	6	-1.95349979	-1.77070522	-1.43327856
6	0.09764828	0.00290871	1.37132990	1	-2.32038760	-2.80681539	-1.46936047
6	-0.48991206	-0.17174909	-0.04136600	1	-2.81299877	-1.10777557	-1.25888324
6	0.50427598	0.40662855	-1.07631147	1	-1.55686915	-1.53600991	-2.43980956
6	0.73230827	1.90433764	-0.84095901	1	0.91156381	1.64532912	2.62559986
6	0.97637564	2.24456739	0.61110252	6	1.53562939	3.61296773	0.89128190
1	-0.69241077	-0.17261894	2.11977959	1	0.87697142	4.39892530	0.48565930
1	0.86027896	-0.77301234	1.56953371	1	1.65609956	3.78990769	1.96810615
1	-1.40512800	0.44503784	-0.09373490	1	2.51611376	3.74798751	0.40575036
6	-0.89467907	-1.59669304	-0.37586841	1	0.21714026	-3.34013414	-1.16632807
1	0.13663135	0.24034394	-2.10013485	1	1.14672303	-2.35623193	-0.00205908
1	1.46447170	-0.12762721	-0.98782986	15	-0.66401350	-3.58244729	1.20593607
1	-0.13615100	2.48259878	-1.20785367	1	-1.49546134	-2.22545028	0.96714479
1	1.58888507	2.25151658	-1.44465184	1	-1.64304936	-4.27167177	0.40810966
6	0.14257494	-2.69931364	-0.27973866				

Transition state *TS-7''/7'''-1*



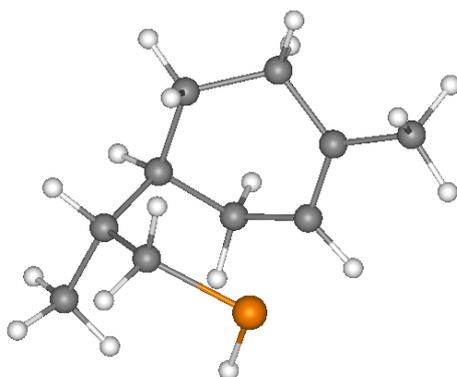
E = -732.648794 E₀ = -732.400397
 ZPVE = 0.248397 a.u. = 155.8717 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.2741	41.2827	0.8887	1.4812	-10.8272
rotational	13.8957	30.5947	0.8887	0.8887	-8.2331
vibrational	7.3762	34.1353	161.6789	161.6789	151.5014
total	39.5461	106.0127	163.4563	164.0488	132.4411

Cartesian

6	0.52884364	0.90979189	1.43604577	6	-1.54158270	-2.34599304	-1.34725916
6	-0.89725405	0.42482328	1.34200311	1	-1.35045922	-3.42872214	-1.36583495
6	-1.23059034	-0.18230388	-0.04427700	1	-2.63135648	-2.19456005	-1.33576965
6	-0.60170662	0.64945346	-1.19902611	1	-1.15312636	-1.92579353	-2.28734517
6	0.06620106	1.96243346	-0.73890293	1	1.01732540	0.92928582	2.41194296
6	0.96936417	1.76054358	0.44882107	6	2.29520965	2.45037770	0.49266231
1	-1.56895006	1.28654492	1.51339316	1	2.18636727	3.53920054	0.35394931
1	-1.12505889	-0.30381048	2.13253188	1	2.81624889	2.27132154	1.44223070
1	-2.32750964	-0.13463055	-0.14528172	1	2.95004320	2.09937310	-0.32469541
6	-0.87654924	-1.69085097	-0.12524082	1	0.75019604	-3.11156154	-0.11158710
1	-1.36109626	0.87847728	-1.96087360	1	1.09650755	-1.68306375	-1.06735718
1	0.16792072	0.05251479	-1.71004188	15	1.72393858	-1.35060942	1.24939442
1	-0.72195083	2.69225359	-0.46608850	1	-1.30879056	-2.15852165	0.77762556
1	0.61695832	2.41426444	-1.57839882	1	0.88011712	-1.79518569	2.33267283
6	0.63073844	-2.01505113	-0.12529320				

Transition state *TS-7''/7'''-2*



E = -732.646459 E₀ = -732.398035
 ZPVE = 0.248424 a.u. = 155.8883 kcal/mol

T = 298.150 K	ln(Q)	S	U	H	G
		cal/mol·K	kcal/mol	kcal/mol	kcal/mol
translational	18.2741	41.2827	0.8887	1.4812	-10.8272
rotational	13.8629	30.5293	0.8887	0.8887	-8.2136
vibrational	7.4084	34.1618	161.6843	161.6843	151.4990
total	39.5454	105.9738	163.4618	164.0542	132.4582

Cartesian

6	0.52243179	0.98175442	1.11812675	1	-1.14590073	-2.01004100	-1.41096509
6	-0.90151525	0.48605573	1.03659403	1	1.00023389	1.05427408	2.09669185
6	-1.22171807	-0.18177184	-0.32417297	6	2.28832912	2.48981690	0.12343883
6	-0.61799383	0.62748706	-1.50941479	1	2.17125320	3.57276917	-0.05084391
6	0.06896559	1.94741762	-1.10106528	1	2.80598044	2.34601784	1.08082294
6	0.96794987	1.78841007	0.09639578	1	2.94997406	2.11846876	-0.67915344
1	-1.57837963	1.35245275	1.15665853	1	0.84878534	-3.05442476	-0.34449217
1	-1.13427985	-0.19438396	1.86560559	1	1.18671620	-1.59561515	-1.25551665
1	-2.31931496	-0.16692521	-0.42632067	15	1.73562622	-1.27266359	1.06139195
6	-0.82656592	-1.68093622	-0.40346837	6	-1.60296130	-2.54455304	0.60001826
1	-1.39996243	0.84294772	-2.25284863	1	0.87847799	-1.68978369	2.14318609
1	0.13013355	0.01113404	-2.02911830	1	-1.44712448	-3.61271977	0.39096108
1	-0.70877516	2.69899607	-0.85853004	1	-1.28613508	-2.36610842	1.63695323
1	0.62503153	2.35837722	-1.95796788	1	-2.68288755	-2.34394479	0.53909183
6	0.69362473	-1.96250820	-0.34205800				

References

- S1. M. Carreira, M. Charernsuk, M. Eberhard, N. Fey, R. van Ginkel, A. Hamilton, W. P. Mul, A. Guy Orpen, H. Phetmung and P. G. Pringle, *J. Am. Chem. Soc.*, 2009, **131**, 3078;
<https://doi.org/10.1021/ja808807s>.
- S2. C. Crause, L. Bennie, L. Damoense, C. L. Dwyer, C. Grove, N. Grimmer, W. J. van Rensburg, M. M. Kirk, K. M. Mokheseng, S. Otto and P. J. Steynberg, *Dalton Trans.*, 2003, 2036;
<https://doi.org/10.1039/b210650g>.
- S3. D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151; [https://doi.org/10.1016/s0009-2614\(97\)01206-2](https://doi.org/10.1016/s0009-2614(97)01206-2).
- S4. D. N. Laikov and Yu. A. Ustynyuk, *Russ. Chem. Bull.*, 2005, **54**, 820;
<https://doi.org/10.1007/s11172-005-0329-x>.
- S5. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865;
<https://doi.org/10.1103/PhysRevLett.77.3865>.