Supporting information available for

Ladderization of Polystyrene Derivatives by Palladium-Catalyzed Polymer Direct Arylation

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Table of contents

S1. Materials and instruments

Anhydrous THF (without stabilizer) and CH_2Cl_2 were purchased from Kanto Chemical Co. Toluene and *N*,*N*-dimethylacetamide (DMAc) were dried by standard methods, distilled, and kept under nitrogen before use. Other materials were obtained from commercial suppliers and used without purification. 2-Bromostyrene[1] and 1-(2'-bromophenyl)-3-phenylpropane[2] were prepared following to the previous reports. Microwave-assisted reactions were performed in a Biotage microwave reactor (Initiator) using microwave reaction vials.·^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectroscopies were obtained on a Bruker Avance III HD NanoBay 400 FT-NMR spectrometers using tetramethylsilane (^{1}H-NMR, δ 0.00) and solvent residual peaks as the internal standard (^{13}C-NMR). Gel permeation chromatography (GPC) analyses were carried out on a Shodex 104 system using tandem LF-404 columns (THF as an eluent, flow rate = 1.0 mL/min, 40 °C) equipped with an UV detector (Shimadzu SPP-20A). Number-averaged molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined on the basis of a calibration curve made from standard polystyrene samples and ethylbenzene. Ultraviolet-visible (UV-vis) and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1650 spectrophotometer and a Shimadzu RF-5300 spectrofluorometer, respectively, using a 10 mm quartz cell. Fluorescence quantum yields (QYs) in solution were determined relative to quinine sulfate in 0.05 M H_2SO_4 having a QY of 0.55. Thermogravimetric analyses (TGA) were performed on a Shimadzu DTG-60 in the nitrogen stream of 50 mL/min at the heating rate of 10 °C/min. Differential scanning calorimetry (DSC) were measured on a Seiko Instruments Inc. DSC 220C at the heating and cooling rate of 5 °C/min under the nitrogen flow (25 mL/min).

S2. Experimental details

S2-1. Free radical polymerization of 2-bromostyrene

A test tube containing 2-bromostyrene (2.49 g, 13.6 mmol), benzoyl peroxide (33 mg, 0.136 mmol), and toluene (27 mL) was degassed by freeze-pump-thaw cycle several times and back-filled with nitrogen, which was placed in an oil bath at 100 °C for 24 h. After cooling to room temperature, a polymer was precipitated into MeOH and dried under vacuum at 50 °C to obtain a colorless solid **Pre^{R}-Br** in 1.50 g (60% yield).

M_n = 7620, M_w/M_n = 1.7.

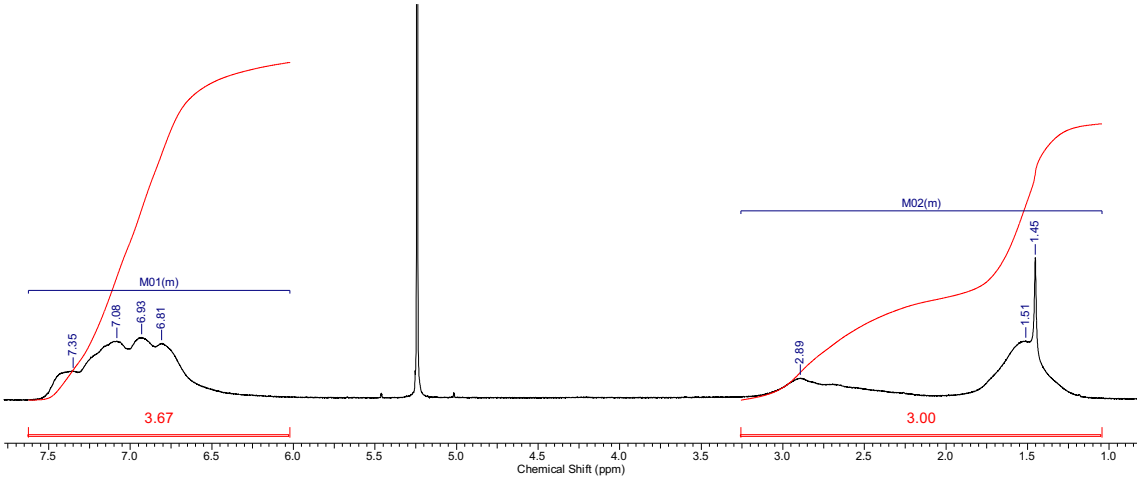

Figure S1. ^{1}H-NMR spectrum of **Pre^{R}-Br** in CD_2Cl_2.

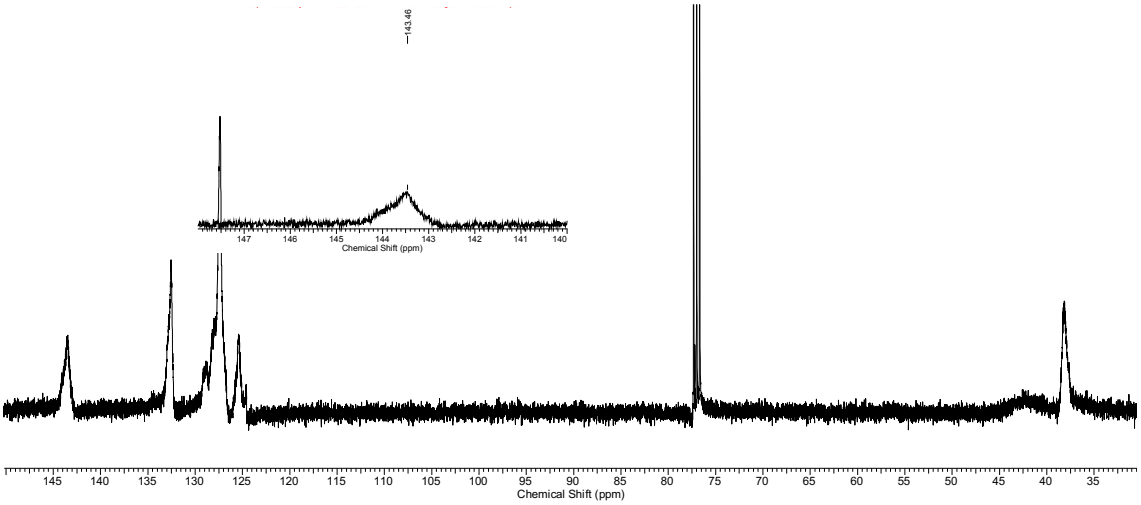

Figure S2. ^{13}C-NMR spectrum of **Pre^{R}-Br** in $CDCl_3$.

S2-2. Free radical polymerization of 2-chlorostyrene

This polymerization was carried out in a similar manner to that of 2-bromostyrene.

M_n = 6600 and M_w/M_n = 1.6.

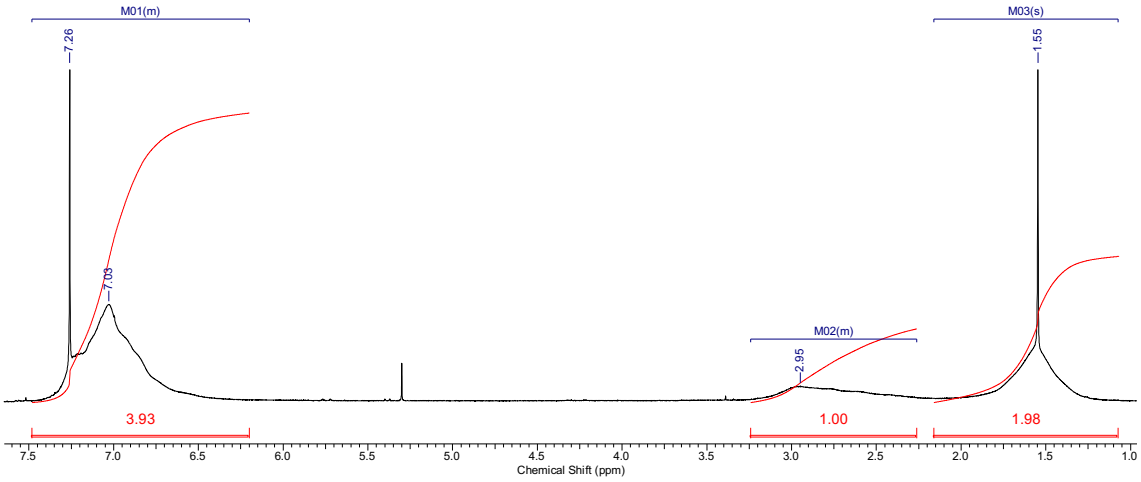

Figure S3. ^{1}H-NMR spectrum of **Pre^R-Cl** in $CDCl_3$.

S2-3. Synthesis of 2-bromo-4-octyloxystyrene

To a solution of *N*,*N*,*N*′-trimethylethylenediamine (3.05 mL, 23.5 mmol) in THF (50 mL) was added *n*-butyllithium solution in hexane (1.6 M, 14.0 mL, 22.4 mmol) at -20 °C, and the mixture was stirred for 25 min. 4-Octyloxybenzaldehyde (5.02 g, 21.4 mmol) was added and stirred for 25 min. Additional *n*-butyllithium solution in hexane (1.6 M, 40.0 mL, 64.0 mmol) was added and stirred for 40 min, and then the mixture was stirred at -7 °C for 22 h. The reaction system was again cooled to -78 °C, and CBr_4 (22.7 g, 68.3 mmol) was added and stirred at room temperature for 2 h. The reaction was quenched by adding 10% HCl solution, and aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, and solvents were removed by rotary evaporator. The obtained crude product was purified by SiO_2 column chromatography using hexane/ethyl acetate (9/1 in volume) (Rf = 0.45) as an eluent to obtain 2-bromo-4-octyloxybenzaldehyde as colorless oil in 3.30 g (49% yield). ^{1}H-NMR ($CDCl_3$) δ ppm 0.89 (t, J = 7.09 Hz, 3H), 1.22–1.51 (10H), 1.80

(m, 2H), 4.02 (t, J = 6.48 Hz, 2H), 6.92 (dd, J = 8.61 and 2.38 Hz, 1H), 7.13 (d, J = 2.38 Hz, 1H), 7.88 (d, J = 8.61 Hz, 1H), 10.2 (s, 1H).

To a solution of methyltriphenylphosphonium bromide (4.54 g, 12.7 mmol) in THF (56 mL) was added *n*-butyllithium solution in hexane (1.6 M, 7.95 mL, 12.7 mmol) at 0 °C, and the mixture was stirred at 30 min. After 2-bromo-4-octyloxybenzaldehyde (3.30 g, 10.6 mmol) was added, the temperature was gradually increased to room temperature and the reaction was conducted for 16 h. The reaction was quenched by adding saturated NH_4Cl solution, and aqueous phase was extracted with hexane. The combined organic phase was dried over $MgSO_4$, and solvents were removed by rotary evaporator. The obtained crude product was purified by SiO_2 column chromatography using hexane/ethyl acetate (19/1 in volume) (Rf = 0.70) as an eluent to obtain 2-bromo-4-octyloxystyrene as pale yellow oil in 1.82 g (55% yield). ^{1}H-NMR ($CDCl_3$) δ ppm 0.89 (t, J = 7.09 Hz, 3H), 1.22–1.50 (10H), 1.77 (m, 2H), 3.93 (t, J = 6.48 Hz, 2H), 5.24 (dd, J = 11.0 and 0.98 Hz, 1H), 5.58 (dd, J = 17.4 and 0.98 Hz, 1H), 6.83 (dd, J = 8.80 and 2.69 Hz, 1H), 6.98 (dd, J = 17.4 and 11.0 Hz, 1H), 7.08 (d, J = 2.69 Hz, 1H), 7.47 (d, J = 8.80 Hz, 1H).

S2-4. Free radical polymerization of 2-bromo-4-octyloxystyrene

This polymerization was carried out in a similar manner to that of 2-bromostyrene.

M_n = 8250, M_w/M_n = 1.7

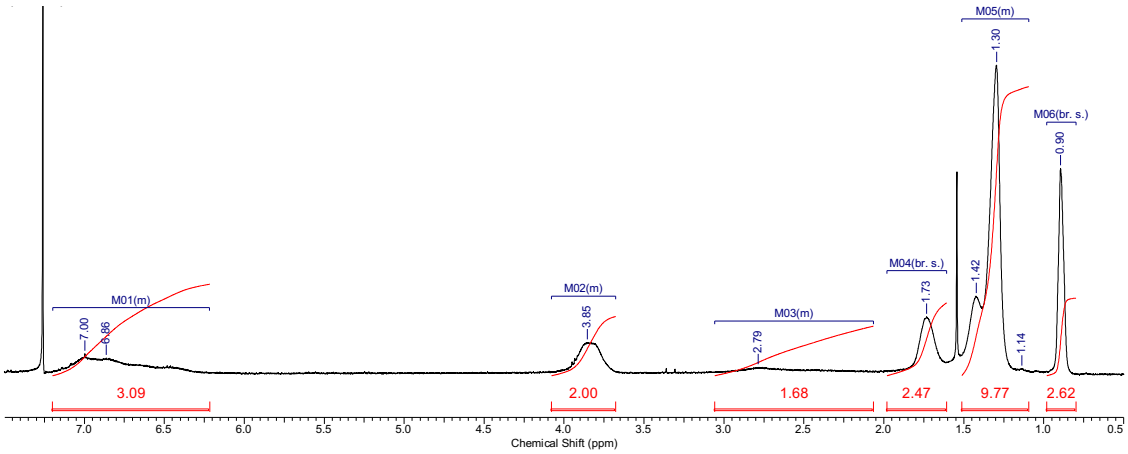

Figure S4. ^{1}H-NMR spectrum of **Pre^{R}OR-Br** in $CDCl_3$.

S2-5. Anionic polymerization of 2-bromostyrene

The anionic polymerization of this monomer is described in the other paper.[3]

$M_n = 7510$, $M_w/M_n = 1.8$

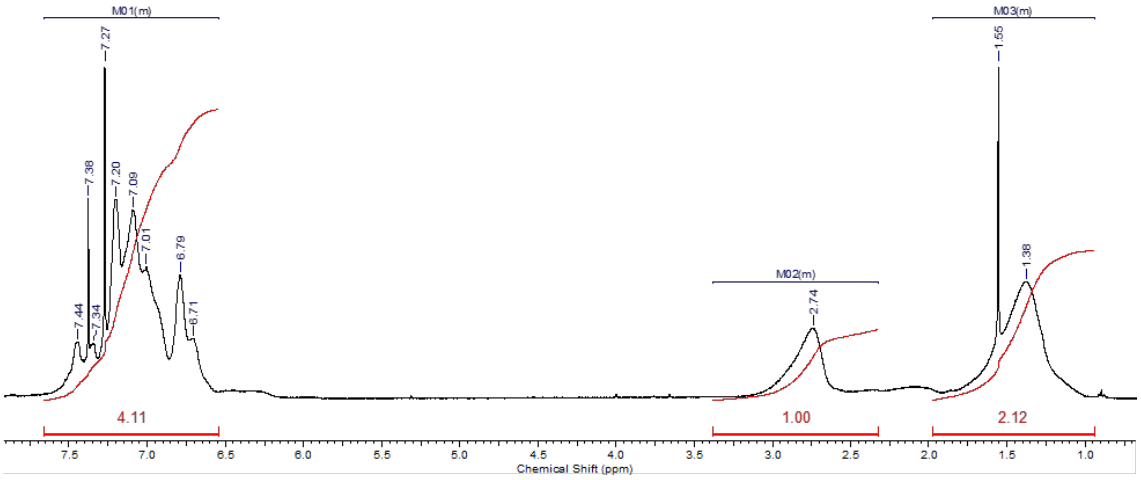

Figure S5. ^{1}H-NMR spectrum of **Pre^{A}-Br** in $CDCl_3$.

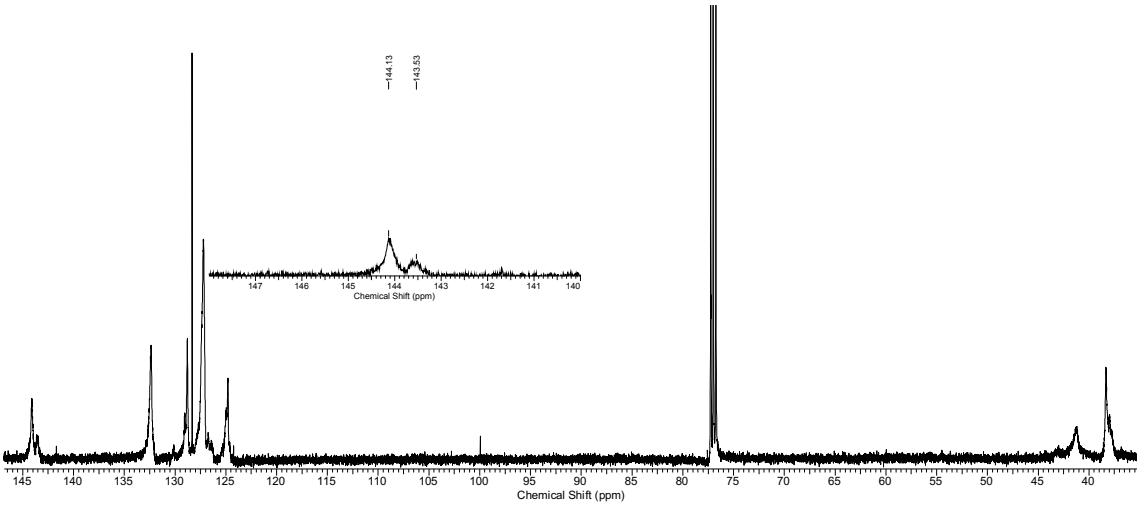

Figure S6. ^{13}C-NMR spectrum of **Pre^{A}-Br** in $CDCl_3$.

S2-6. Typical procedure of polymer direct arylation

A microwave vial containing **Pre^{R}-Br** (100 mg, 546 μmol), $Pd(OAc)_2$ (6.1 mg, 27 μmol), $PCy_3 \cdot HBF_4$ (20.1 mg, 54.6 μmol), pivalic acid (22.3 mg, 218 μmol), and K_2CO_3 (268 mg, 1.94 mmol) was evacuated and back-filled

with nitrogen several times. DMAc (3.5 mL) was added and the vial was heated to 145 °C for 24 h under the microwave heating. After the precipitate was removed, solution was concentrated to pour into MeOH/HCl. A polymer was recovered by filtration, dried under vacuum at 50 °C, and further purified by preparative GPC to obtain a ladderized polystyrene **LP^{R}-85** in 40 mg (81% yield).

M_n = 5100, M_w/M_n = 2.3

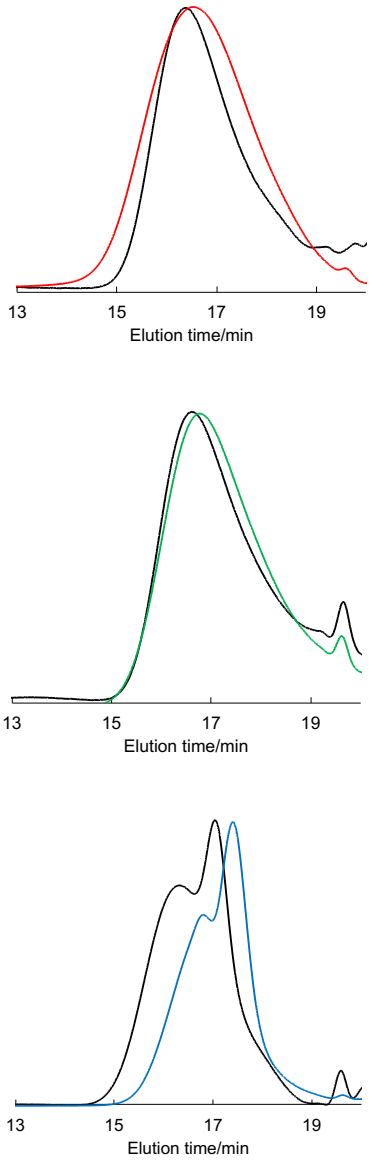

Figure S7. GPC profiles of polymers. (Top) **Pre^{R}-Br** (black line) and **LP^{R}-85** (red line). (Middle) **Pre^{R}-Br** (black line) and **LP^{R}-34** (green line). (Bottom) **Pre^{A}-Br** (black line) and **LP^{A}-79** (blue line).

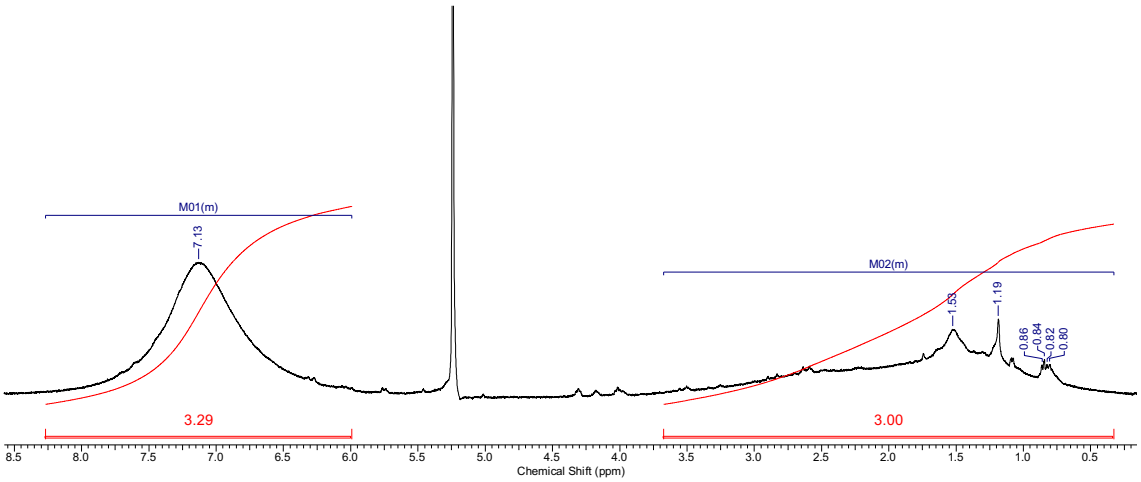

Figure S8. ^{1}H-NMR spectrum of **LP^{R}-85** in CD_2Cl_2.

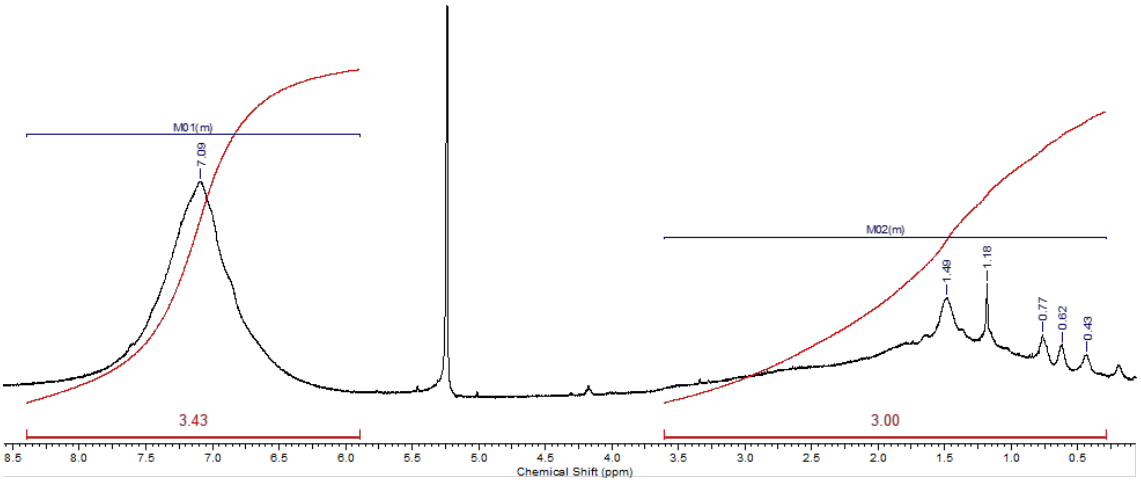

Figure S9. ^{1}H-NMR spectrum of **LP^{A}-78** in CD_2Cl_2.

S2-7. Direct arylation of model compound

1-(2'-bromophenyl)-3-phenylpropane (720 mg, 2.62 mmol), $Pd(OAc)_2$ (29.4 mg, 133 μmol), $PCy_3{\cdot}HBF_4$ (96.3 mg, 260 μmol), pivalic acid (107 mg, 1.04 mmol), and K_2CO_3 (1.26 g, 9.12 mmol) was evacuated and back-filled with nitrogen several times. DMAc (16.7 mL) was added and the vial was heated to 145 °C for 24 h under the microwave heating. After the precipitate was removed, solution was concentrated and purified by SiO_2 column chromatography using hexane (Rf = 0.55) as an eluent to obtain colorless oil. Judging from GPC analysis, the

product contained oligomers in addition to the debrominated product (18%) and cyclized product (23%) where the numbers in parentheses indicate the isolated yields.

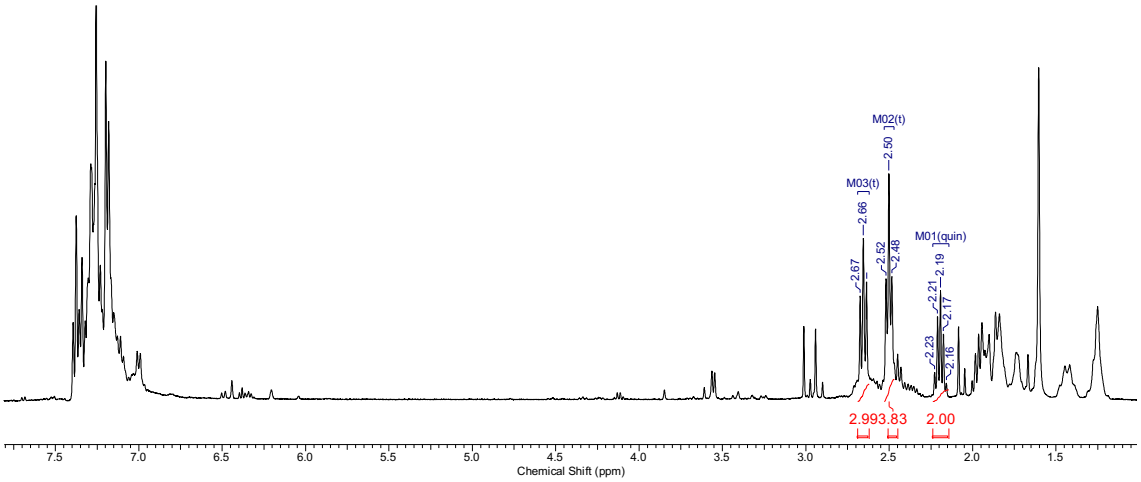

Figure S10. ^{1}H-NMR spectrum of crude mixture of model reaction in $CDCl_3$.

S3. UV spectra

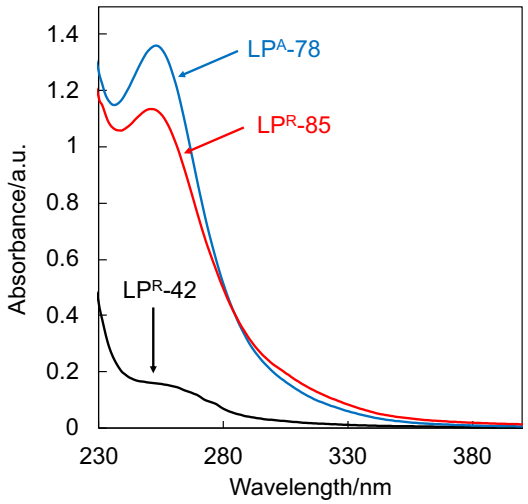

Figure S11. UV spectra of ladderized polystyrenes in CH_2Cl_2 (100 μM).

S4. Theoretical calculations

S4-1. Computational Detail

Density functional theory (DFT) calculations were performed using Gaussian 16 program package.[4] Geometry optimizations, vibrational analyses of all local equilibrium, and transition state structures were performed using B3LYP functionals together with effective core potentials (ECPs) with the LANL2DZ basis sets for Pd and 6-31G(d,p) basis sets for the other atom. All stationary points were optimized without any symmetry assumptions, and were characterized by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima and 1 for transition states). The intrinsic reaction coordinate (IRC) method[5–7] was used to track minimum energy paths from transition structures to the corresponding local minima. The values of electronic energies (ΔE) were evaluated by single-point energy calculations, which were performed at the B3LYP functionals together with ECPs with the SDD basis sets for Pd and 6-311++G(3d2f,3p2d) basis sets for the other atom. Cartesian coordinates and energies of the computed structures are listed in the Supporting information (pages S13–S33).

S4-2. Theoretical reaction pathway with monophosphine ligand

Although the reaction might proceed through this process as shown in Figure S11, we consider that the reaction proceeds through **$INT_{RE}1$→$TS_{RE}(1\text{-}2)$→$INT_{RE}2$** in the main text due to the higher stabilization effect of two phosphine ligands in **$INT_{RE}2$**.

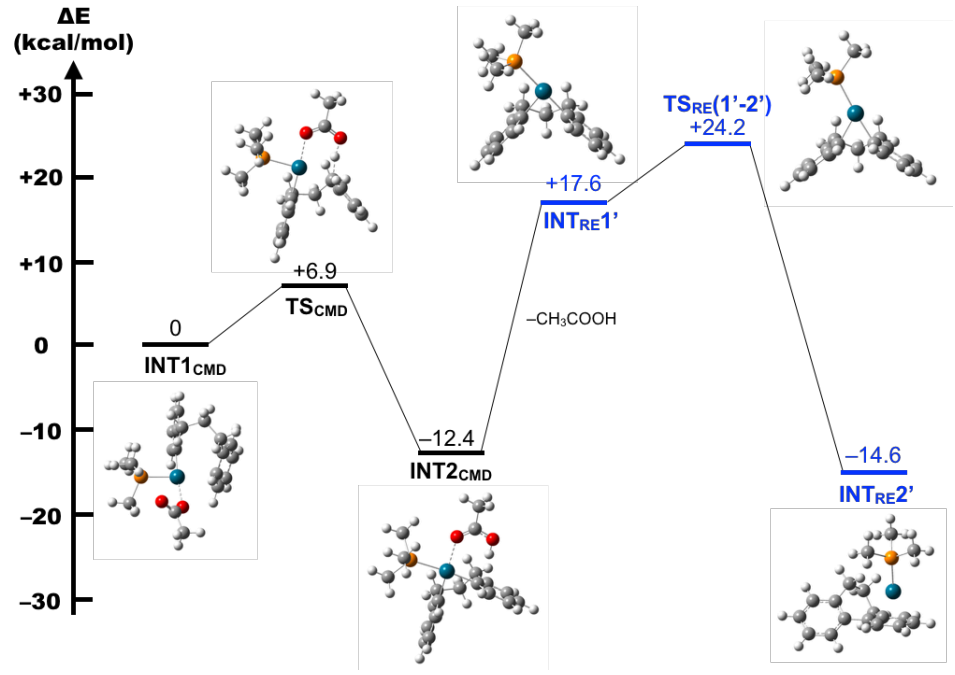

Figure S12. Theoretical reaction pathway for the formation of seven-membered cyclic structure (B3LYP/6-311++G(3d2f,3p2d)-ECP-SDD(Pd)//B3LYP/TZVP-ECP-LANL2DZ(Pd)). The geometries in inset are given by ball and stick type model (atom colour: red = oxygen, yellow = phosphine, silver = carbon, light green = Pd, white = hydrogen).

S5. References

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5) Fukui, K. *Acc. Chem. Res.* 1981, **14**, 363–368.

6) Ishida, K.; Morokuma, K.; Komornicki, A. *J. Chem. Phys.* 1977, **66**, 2153–2156.

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S6. Appendix

Cartesian Coordinates (in Å) and Energies

$INT_{CMD}1$

E (el) = -1397.3555129 a.u.

Sum of electronic and thermal free energy = -1396.992567 a.u.

C	-2.12693300	2.49021000	1.17641500
H	-1.21101000	3.08530800	1.13569600
C	-2.08803900	1.61150100	2.44378400
H	-3.06597400	1.14904700	2.60237500
H	-1.92720400	2.28302100	3.29235600
C	-0.99990600	0.51418200	2.46871200
H	-0.07737300	0.90759900	2.03403100
H	-0.77916600	0.28999500	3.51722900
C	-1.38985800	-0.77856300	1.77402400
C	-0.84798300	-1.18432200	0.54549800
C	-2.36167200	-1.58777900	2.37968600
C	-1.31421100	-2.36009300	-0.05097100
C	-2.81608800	-2.75662500	1.78383600
H	-2.77293100	-1.28689700	3.33856400
C	-2.29654800	-3.14021700	0.55185800
H	-0.90594500	-2.67719200	-1.00421500
H	-3.56668400	-3.36282700	2.27696100
H	-2.64390500	-4.04545500	0.06698100

C	-2.27464600	1.74093700	-0.12592500
C	-1.22179400	1.73252600	-1.05842400
C	-3.42974900	1.02955400	-0.43375400
C	-1.32379500	1.00939900	-2.25527600
H	-0.36901400	2.38252600	-0.90545000
C	-3.53702900	0.31470200	-1.62629200
H	-4.26013600	1.02612700	0.26306100
C	-2.48611100	0.28950500	-2.53244000
H	-0.51061500	1.05672700	-2.96753800
H	-4.44758900	-0.23212900	-1.83990200
H	-2.57258500	-0.26850900	-3.45633800
Pd	0.47480300	-0.05778800	-0.49138500
P	2.16685000	-1.30170500	0.44461900
C	2.81092700	-0.57646500	2.00644500
H	2.02429300	-0.57594300	2.76028500
H	3.65930700	-1.16014100	2.37046700
H	3.11845000	0.44464400	1.78760200
C	1.83224900	-3.06178300	0.88541600
H	2.74015600	-3.51354800	1.29042300
H	1.03335900	-3.11996000	1.62152300
H	1.52128500	-3.61553500	0.00029200
O	1.70103800	1.18136600	-1.75859500
C	2.71238000	1.85002600	-1.32119100
O	3.21051500	1.74221800	-0.19427300
C	3.31178800	2.81690200	-2.33708500

H	3.72139300	2.25276300	-3.17812900
H	2.53668100	3.47233600	-2.73781300
H	4.10082600	3.41011300	-1.87958200
C	3.64294500	-1.43256500	-0.64786800
H	3.35087300	-1.84237200	-1.61404400
H	4.05638100	-0.43669200	-0.78568900
H	4.38764800	-2.08422200	-0.18570800
H	-2.95310800	3.20085800	1.28275200

$INT_{CMD}2$

E (el) = -1397.3337793 a.u.

Sum of electronic and thermal free energy = -1396.974027 a.u.

C	-1.57405400	2.14809600	1.28218300
H	-0.48497800	2.23921500	1.33648400
C	-2.04265200	1.22359700	2.42753100
H	-3.09203300	0.95326000	2.27690300
H	-2.00598700	1.81443900	3.34898000
C	-1.20915000	-0.05239700	2.67823800
H	-0.14869600	0.21392100	2.62651400
H	-1.40160200	-0.36928100	3.70794700
C	-1.47623400	-1.23491100	1.77130000
C	-0.84639600	-1.39365200	0.52770900
C	-2.38106800	-2.21567300	2.19758300

C	-1.15390000	-2.50998800	-0.25444000
C	-2.67392700	-3.33047400	1.42103900
H	-2.86243000	-2.09957800	3.16386500
C	-2.05476900	-3.47747100	0.18550000
H	-0.69358500	-2.62906200	-1.22869300
H	-3.37823300	-4.07305200	1.77682000
H	-2.27243300	-4.33690100	-0.43878100
C	-1.97580400	1.74453800	-0.12078800
C	-1.19733200	0.85760900	-0.89304700
C	-3.15225500	2.28056800	-0.65854100
C	-1.65522200	0.53543500	-2.18067900
H	0.01907400	2.28491400	-1.64990900
C	-3.58043000	1.95395600	-1.94003300
H	-3.74059100	2.97058500	-0.06148400
C	-2.82429300	1.07768500	-2.70939800
H	-1.08647200	-0.15961900	-2.78986600
H	-4.49402900	2.38357200	-2.33407400
H	-3.14310800	0.81233100	-3.71110700
Pd	0.51419900	-0.07220700	-0.15626300
P	2.40242500	-1.33009100	0.69598100
C	3.71712700	-0.33294800	1.53807600
H	3.30269800	0.12464000	2.43696600
H	4.57669600	-0.94754000	1.81402900
H	4.03771900	0.46366700	0.86727400
C	2.07787700	-2.68108300	1.91366600

H	2.99900500	-3.19798700	2.19011900
H	1.61752100	-2.25972000	2.80738000
H	1.37289300	-3.39166000	1.48314100
O	2.09611000	1.43051400	-0.97870400
C	1.91327900	2.46636600	-1.60770100
O	0.72268400	2.91534600	-1.95705100
C	3.03597200	3.35601200	-2.05917400
H	3.98958400	2.94720200	-1.73739700
H	3.01595900	3.44702400	-3.14643400
H	2.89903300	4.35700800	-1.64702000
C	3.36517200	-2.20629300	-0.62234000
H	2.71515200	-2.92234200	-1.12576600
H	3.70642300	-1.47829100	-1.35857100
H	4.22770400	-2.73421100	-0.20963400
H	-1.98066800	3.14493200	1.47885200

TS_{CMS}(1-2)

E (el) = -1397.3233075 a.u.

Sum of electronic and thermal free energy = -1396.965633 a.u.

C	-1.33379300	2.36532500	1.02498200
H	-0.26084800	2.57416200	1.00787700
C	-1.65102600	1.50981800	2.26837400
H	-2.70641100	1.22079600	2.25925200

H	-1.51473000	2.15123300	3.14546200
C	-0.77921600	0.25391800	2.47154600
H	0.26984400	0.53382400	2.33431700
H	-0.88828800	-0.05787900	3.51510800
C	-1.10822300	-0.92913600	1.58542600
C	-0.49261000	-1.13709500	0.34346200
C	-2.07292100	-1.84715600	2.02073600
C	-0.86939300	-2.23674000	-0.43102800
C	-2.43716000	-2.94545600	1.25172700
H	-2.54510300	-1.69293900	2.98631300
C	-1.83265000	-3.13898500	0.01495600
H	-0.41566500	-2.39324400	-1.40314400
H	-3.18543900	-3.64039000	1.61381100
H	-2.10785900	-3.98555000	-0.60399900
C	-1.74681200	1.78816000	-0.31088300
C	-0.79255000	1.24664400	-1.19979600
C	-3.09402300	1.82927100	-0.67906300
C	-1.25076500	0.76500500	-2.44119000
H	0.31614300	2.11985300	-1.38332000
C	-3.51804100	1.33003700	-1.90433500
H	-3.82272200	2.26067700	0.00007500
C	-2.59111000	0.79754500	-2.79738900
H	-0.53121000	0.36897000	-3.15097500
H	-4.56860200	1.36883000	-2.16872200
H	-2.91442700	0.42109800	-3.76101400

Pd	0.92701800	0.11115600	-0.36902100
P	2.63216700	-1.25835100	0.48522300
C	3.89787700	-0.31372300	1.44265700
H	3.44365900	0.08437400	2.35019300
H	4.74543400	-0.94693200	1.71323600
H	4.23929800	0.52064000	0.83146200
C	2.22824800	-2.67821700	1.58869800
H	3.13393600	-3.21521700	1.87708100
H	1.72252300	-2.31175500	2.48160700
H	1.54587400	-3.35488300	1.07598300
O	2.59047100	1.39525200	-1.14167200
C	2.31125400	2.52836800	-1.59741400
O	1.12236500	2.98428500	-1.69683500
C	3.41812200	3.43770300	-2.07532100
H	4.39180600	2.98680300	-1.89969000
H	3.28781800	3.63169100	-3.14141000
H	3.35002600	4.39731300	-1.56114500
C	3.62808800	-2.03134000	-0.86498400
H	2.99548000	-2.70793800	-1.43964900
H	3.98553300	-1.24408800	-1.52812600
H	4.47828800	-2.58737200	-0.46409100
H	-1.83720900	3.32930200	1.15344400

$INT_{RE}1'$

E (el) = -1168.191996 a.u.

Sum of electronic and thermal free energy = -1167.887003 a.u.

C	-2.95672500	1.41279000	1.30294000
H	-3.27587700	2.41521000	1.59634800
C	-2.38016600	0.67875200	2.52976000
H	-3.20676700	0.42259500	3.19930600
H	-1.71615000	1.34573500	3.08738800
C	-1.59061200	-0.59023100	2.15240900
H	-0.60102300	-0.28786400	1.79700600
H	-1.43349700	-1.19850800	3.04597000
C	-2.24509300	-1.42403700	1.07783500
C	-2.26842400	-0.96459400	-0.25558600
C	-2.80141200	-2.66818900	1.37365400
C	-2.84200900	-1.77345300	-1.24245800
C	-3.37393900	-3.46060900	0.38442800
H	-2.77413700	-3.02593500	2.39720000
C	-3.39256800	-3.01043500	-0.93060400
H	-2.87315300	-1.41684400	-2.26512500
H	-3.80051500	-4.42319000	0.63958500
H	-3.83822400	-3.61606800	-1.71040300
C	-1.99868500	1.50363000	0.14001100
C	-1.68683900	0.35649600	-0.60921500
C	-1.42416500	2.73010200	-0.21585900

C	-0.82776500	0.47252100	-1.72130400
C	-0.56974000	2.84427600	-1.30118600
H	-1.66472600	3.61107200	0.36871500
C	-0.27842100	1.71416600	-2.08534700
H	-0.66594600	-0.39194800	-2.35221500
H	-0.15428500	3.80737900	-1.56952100
H	0.25041800	1.82385700	-3.02529800
Pd	1.47425100	0.78634000	-0.94486900
P	3.43477200	0.06193100	-0.02742500
C	4.98752900	0.90670000	-0.60239200
H	4.92340200	1.97128600	-0.37632300
H	5.87682100	0.48955500	-0.12248800
H	5.07784600	0.79712500	-1.68326600
C	3.63604500	0.18722500	1.81608600
H	4.61126100	-0.18227700	2.14418400
H	3.52559900	1.22848600	2.11977100
H	2.85086900	-0.39087600	2.30377100
C	3.88410600	-1.71938000	-0.30600200
H	3.10210700	-2.35604400	0.10815900
H	3.94136200	-1.91174300	-1.37753100
H	4.84076000	-1.97408100	0.15793600
H	-3.85505700	0.88222800	0.97491600

$INT_{RE}2'$

E (el) = -1168.1313835 a.u.

Sum of electronic and thermal free energy = -1167.825756 a.u.

C	-1.56416600	2.29256700	1.30034400
H	-0.50510200	2.43734000	1.53515100
C	-2.09849900	1.12492500	2.15876200
H	-3.07895700	0.81136800	1.78901700
H	-2.26206500	1.52089700	3.16637900
C	-1.17873700	-0.10817500	2.31002900
H	-0.14924500	0.24257000	2.43006400
H	-1.44916800	-0.60766800	3.24492200
C	-1.23147800	-1.14206200	1.20701000
C	-0.51020200	-1.02614300	0.01262000
C	-2.03202100	-2.27894200	1.38309500
C	-0.62579100	-2.00125400	-0.97738100
C	-2.13365400	-3.26472300	0.40883600
H	-2.58674900	-2.38679000	2.30978800
C	-1.42669300	-3.12432500	-0.77908500
H	-0.09709400	-1.88951400	-1.91603100
H	-2.76369000	-4.13028600	0.57489300
H	-1.49939900	-3.87774800	-1.55507500
C	-1.73927600	2.17974600	-0.19987000
C	-0.89002300	1.39913100	-1.00420400
C	-2.77616400	2.89571300	-0.80859900
C	-1.13198600	1.33417200	-2.38063700

C	-2.99051500	2.84463000	-2.18205100
H	-3.42371900	3.51244600	-0.19310500
C	-2.16248800	2.05961800	-2.97466600
H	-0.51000100	0.70479400	-3.00824000
H	-3.80225100	3.40905800	-2.62592700
H	-2.31910600	2.00460200	-4.04606700
Pd	0.78760500	0.49283900	-0.29261200
P	2.83917500	-0.59515400	0.45657600
C	4.40261900	0.40203400	0.53987300
H	4.26713800	1.23524700	1.23039600
H	5.24839300	-0.20251900	0.87422600
H	4.62721700	0.81154900	-0.44571300
C	2.76685100	-1.34795500	2.14587700
H	3.68487000	-1.88917500	2.38407800
H	2.61062300	-0.56371700	2.88701300
H	1.92032900	-2.03308500	2.19273600
C	3.35122300	-2.03500500	-0.58801500
H	2.52910300	-2.74945500	-0.63281200
H	3.55931300	-1.69180200	-1.60185500
H	4.23848300	-2.52892100	-0.18640500
H	-2.07685700	3.20128600	1.62884700

TS_{RE} (1'-2')

E (el) = -1168.1240682 a.u.

Sum of electronic and thermal free energy = -1167.819521 a.u.

C	-1.57797600	1.97016600	1.48154100
H	-0.51578500	2.02603900	1.73872700
C	-2.23184100	0.88693000	2.35314900
H	-3.25796000	0.70654700	2.01897300
H	-2.30184500	1.28694700	3.36979200
C	-1.46650700	-0.44401800	2.43504100
H	-0.40655800	-0.22414600	2.59982300
H	-1.81400100	-0.98178700	3.32116400
C	-1.60192800	-1.37216300	1.24989900
C	-0.98136100	-1.13728200	0.00927300
C	-2.35104400	-2.54384000	1.40881700
C	-1.12490100	-2.08330900	-1.01207300
C	-2.48701000	-3.48016700	0.39161700
H	-2.82705200	-2.72749000	2.36650300
C	-1.85828100	-3.24896200	-0.82575800
H	-0.65973600	-1.91384700	-1.97383600
H	-3.07415900	-4.37664700	0.54958300
H	-1.93879200	-3.96759100	-1.63318100
C	-1.72258000	1.81552400	-0.01741500
C	-1.06576300	0.81525500	-0.76296700
C	-2.51432000	2.74414500	-0.70102700
C	-1.21969700	0.79756500	-2.15455900
C	-2.65628300	2.71891000	-2.08359400

H	-3.01789800	3.51780000	-0.13086000
C	-1.99204100	1.74440900	-2.81718700
H	-0.73533700	0.02611500	-2.73901300
H	-3.27739200	3.45498300	-2.57975900
H	-2.07910500	1.71157100	-3.89693000
Pd	0.73696300	0.04733500	-0.08686400
P	2.90439500	-0.71447400	0.56178400
C	4.32888700	0.46973600	0.42906900
H	4.13885000	1.33931500	1.05897900
H	5.26871800	0.00506500	0.73590400
H	4.42068500	0.81311100	-0.60180300
C	3.07950500	-1.31176100	2.30813400
H	4.08635600	-1.68618000	2.50724200
H	2.85884200	-0.49395900	2.99455400
H	2.35708900	-2.10821500	2.48724900
C	3.53730200	-2.16903600	-0.39674100
H	2.82540300	-2.98995700	-0.31012000
H	3.61569200	-1.90008200	-1.45036200
H	4.51455300	-2.49711100	-0.03494200
H	-2.01047500	2.93527700	1.75803700

$INT_{RE}1$

E (el) = -1629.3318496 a.u.

Sum of electronic and thermal free energy = -1628.919639 a.u.

C	-1.66397400	2.19289400	1.19342800
H	-0.73984300	1.91686100	1.71240500
C	-2.77781700	1.22198500	1.64337800
H	-3.65452100	1.34666200	1.00101300
H	-3.08499500	1.53166200	2.64835800
C	-2.40392900	-0.27457600	1.72673500
H	-1.41590400	-0.35508800	2.19074400
H	-3.11112500	-0.74993300	2.41401700
C	-2.41569900	-1.05262400	0.42739800
C	-1.29836000	-1.10739500	-0.42331200
C	-3.58513400	-1.73568500	0.07051700
C	-1.40999100	-1.82670000	-1.61753700
C	-3.67479700	-2.46127300	-1.11205000
H	-4.44214300	-1.69746600	0.73652300
C	-2.57759900	-2.50449700	-1.96375300
H	-0.57460300	-1.85160500	-2.30984600
H	-4.59127400	-2.98114900	-1.36548300
H	-2.62913900	-3.05561200	-2.89646700
C	-1.39684300	2.28608000	-0.29436600
C	-0.53251000	1.40022000	-0.95733900
C	-2.03181300	3.29900200	-1.02435100
C	-0.35389800	1.55083000	-2.33601700
C	-1.83392000	3.44689800	-2.39235600
H	-2.69263300	3.98743100	-0.50579900

C	-0.98779800	2.56382900	-3.05291200
H	0.28691300	0.85964200	-2.87413400
H	-2.33676100	4.23936700	-2.93417300
H	-0.82457400	2.65668800	-4.12114400
Pd	0.47600000	-0.12034300	0.02667600
P	2.40672700	1.32582100	0.32133800
C	2.18382500	3.10339600	-0.13664600
H	1.40864300	3.54470500	0.48914900
H	3.11526300	3.65915600	-0.01015600
H	1.84709400	3.17305300	-1.16985800
C	3.15413500	1.49330300	2.01382500
H	3.99281000	2.19279300	2.00980700
H	2.39408200	1.85713200	2.70604500
H	3.50241300	0.52451100	2.36901300
C	3.88607700	0.87105300	-0.70405000
H	4.22769800	-0.13082200	-0.44307200
H	3.60062700	0.86848500	-1.75636000
H	4.70722100	1.57650200	-0.55989500
H	-1.93680700	3.19042200	1.55250900
P	1.31905700	-2.21080600	0.95522400
C	0.14620400	-3.12490800	2.05711000
H	-0.01775500	-2.55178300	2.97017400
H	-0.80961100	-3.23296300	1.54671700
H	0.53820500	-4.10993000	2.31852500
C	1.65085200	-3.46091500	-0.37032500

H	2.43822000	-3.09484800	-1.03015300
H	1.95533600	-4.41955900	0.05479800
H	0.74489000	-3.59726000	-0.95947300
C	2.88577300	-2.32938400	1.95260900
H	3.10212100	-3.36436100	2.22580800
H	3.72687200	-1.93696700	1.38016000
H	2.78586300	-1.74117300	2.86537500

$INT_{RE}2$

E (el) = -1629.3867463 a.u.

Sum of electronic and thermal free energy = -1628.984838 a.u.

C	-3.12092100	2.14097400	-0.06840100
H	-3.39895700	3.17304400	0.15631200
C	-2.69090900	1.43250000	1.23051200
H	-3.58287900	1.26746600	1.84235800
H	-2.02831500	2.08209200	1.80992000
C	-1.96485300	0.09552600	0.98290700
H	-0.92135400	0.29949000	0.72497600
H	-1.93991700	-0.47620200	1.91294300
C	-2.57605100	-0.74431800	-0.11239000
C	-2.45790700	-0.34902500	-1.46153300
C	-3.23211200	-1.93929100	0.18419200
C	-2.99251500	-1.17054700	-2.45985500

C	-3.76435700	-2.74496700	-0.81702700
H	-3.31806000	-2.24701300	1.22068700
C	-3.64133400	-2.35881500	-2.14645200
H	-2.91377000	-0.86019400	-3.49491600
H	-4.27056900	-3.66749700	-0.55934000
H	-4.05387700	-2.97463100	-2.93641000
C	-2.07502100	2.12193700	-1.15660100
C	-1.77237400	0.91913500	-1.82790900
C	-1.42031900	3.29254600	-1.53914500
C	-0.82783800	0.93659600	-2.85938400
C	-0.48150900	3.29662600	-2.56550800
H	-1.66328100	4.21998400	-1.03196900
C	-0.18462200	2.11162900	-3.22870500
H	-0.58226400	0.01021700	-3.36437100
H	0.01178900	4.21954800	-2.84591000
H	0.54768400	2.09925300	-4.02682800
Pd	2.35683500	-0.53367400	1.32692600
P	2.97950100	1.70276400	1.31414900
C	1.83766200	2.93114500	2.11519400
H	1.68603500	2.65525000	3.15905600
H	2.23530200	3.94827800	2.06583000
H	0.87082200	2.90054700	1.61250300
C	4.58509100	2.12332300	2.15040100
H	4.80943900	3.19142600	2.08691700
H	4.53245000	1.82867600	3.19878000

H	5.39185500	1.55815100	1.68321800
C	3.22889800	2.49053600	-0.34901500
H	3.99285400	1.93718300	-0.89581900
H	2.29972300	2.43280500	-0.91625700
H	3.53496200	3.53651400	-0.26184700
H	-4.02271300	1.65044100	-0.44616200
P	1.85389900	-2.80115800	1.30970100
C	0.73620900	-3.44777800	2.64656000
H	1.17686900	-3.23104200	3.61998900
H	-0.22420200	-2.93519900	2.58990800
H	0.57380500	-4.52503400	2.55617800
C	1.01855000	-3.47709200	-0.20511100
H	1.64275100	-3.27763700	-1.07651500
H	0.84404500	-4.55340200	-0.12651700
H	0.06508200	-2.96900600	-0.35059100
C	3.29376100	-3.96556700	1.46760000
H	2.97538900	-5.01122500	1.44739700
H	3.99098000	-3.78643000	0.64883600
H	3.81670800	-3.76656000	2.40328400

TS_{RE}(1-2)

E (el) = -1629.3103923 a.u.

Sum of electronic and thermal free energy = -1628.902390 a.u.

C	-1.52402400	1.48137800	1.49306600
H	-0.59725700	1.24108100	2.02717300
C	-2.62897600	0.55167000	2.00831000
H	-3.53971900	0.69192000	1.41790600
H	-2.86956800	0.85599200	3.03223600
C	-2.24954700	-0.93378800	2.03818000
H	-1.27262200	-1.03024200	2.52477500
H	-2.96519100	-1.45886200	2.67654900
C	-2.21273200	-1.64109500	0.70175300
C	-1.19222100	-1.42361600	-0.25895700
C	-3.20791500	-2.58797800	0.44447800
C	-1.21612900	-2.23690700	-1.41029800
C	-3.22159300	-3.36145600	-0.71023200
H	-3.98460800	-2.73543200	1.18817300
C	-2.19782600	-3.18940300	-1.63609400
H	-0.44976400	-2.11235000	-2.16378300
H	-4.00821300	-4.08695200	-0.87712400
H	-2.16538100	-3.78973000	-2.53840200
C	-1.25567400	1.45723500	0.00471900
C	-0.62705500	0.36773100	-0.65006700
C	-1.58552400	2.59999000	-0.72878600
C	-0.30705300	0.53906600	-2.01236800
C	-1.28356700	2.73385600	-2.07880300
H	-2.07435500	3.42074100	-0.21360800
C	-0.61594400	1.69299300	-2.71597700

H	0.19064200	-0.26060300	-2.54491900
H	-1.55252400	3.63509400	-2.61583700
H	-0.34180500	1.77339700	-3.76188800
Pd	0.76582800	-0.85725300	0.43571200
P	2.64875800	0.67655800	0.64480400
C	2.28881900	2.46669500	0.31508000
H	1.61493800	2.84823200	1.08255500
H	3.20097900	3.06791600	0.30814700
H	1.78201300	2.56004800	-0.64535600
C	3.62581600	0.80467900	2.22363400
H	4.43964400	1.52909300	2.14081100
H	2.96225200	1.10895300	3.03407800
H	4.04239900	-0.17032000	2.47737700
C	4.00833600	0.36502700	-0.58463100
H	4.42610800	-0.62968800	-0.42570800
H	3.59198200	0.39991700	-1.59178800
H	4.80758400	1.10559000	-0.50329500
H	-1.78230700	2.50696400	1.77037500
P	1.50480100	-3.00795300	1.32372600
C	0.26703900	-3.93900700	2.34730600
H	0.09455400	-3.40643800	3.28342100
H	-0.67800300	-3.98635400	1.80619300
H	0.60869500	-4.95223300	2.57139900
C	1.83909100	-4.23824600	-0.02639300
H	2.66709600	-3.88730300	-0.64344900

H	2.08411300	-5.22433500	0.37513700
H	0.95379300	-4.31655600	-0.65773300
C	3.03419500	-3.21470600	2.36618700
H	3.20563100	-4.25966200	2.63554500
H	3.90239900	-2.84632200	1.81795000
H	2.93436700	-2.62641100	3.27928100
