Supplementary information for

Small Ring Expansion by Consecutively Inserting Two Difunctional Organic Units: An Efficient Route for Synthesis of Phosphorus-Selenium Macro-Heterocycles

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Experimental Section

Unless otherwise stated, all reactions were carried out under on oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work up procedures were performed in air. ^{1}H (270 MHz), ^{13}C (67.9 MHz), ^{31}P-{^{1}H} (109 MHz) and ^{77}Se-{^{1}H} (51.4 MHz referenced to external Me_2Se) NMR spectra were recorded at 25 $^{\circ}$C (unless stated otherwise) on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000-250 cm^{-1} on a Perkin-Elmer 2000 FTIR/Raman spectrometer. Microanalysis was performed by the University of St-Andrews microanalysis service. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St Andrews Mass Spectrometry Service. X-ray crystal data for compounds **5** – **7**, **9** and **11a, 11b** were collected using Rigaku SCXMIni Mercury CCD system Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 by using the program SHELXTL. Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

General procedure for synthesis of heterocycles 4 – 9: A suspension of anhydrous diol (1.0 mmol) and sodium hydride (0.160 g, 60%, 4.0 mmol) in 100 mL of dry THF was heated at 60°C for 2 h leading to a grayish white suspension. Upon cooling to ambient temperature the suspension was filtered off to remove unreacted solid. The filtrate was added **WR** (0.540 g, 1.0 mmol) and the mixture was stirred at ambient temperature for 6 h. Then, the appropriate dibromide (1.0 mmol) was added to the mixture and the suspension was continued stirring at ambient temperature for another 24 h giving a grayish yellow mixture. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was

loaded onto a silica gel column (50% / 50% dichloromethane / hexane to 100% dichloromethane as eluent) to give products **4** – **9**. Characterizing spectroscopic data is provided in the supporting information.

2,6-Diphenyl-1,7,3,5,2,6-dioxadiselenadiphosphonane 2,6-diselenide (4). 0.265 g as an yellow paste. 43.4% isolated yield. Selected IR (KBr, cm^{-1}): 1434(m), 1102(s), 947(m), 742(m), 712(m), 685(m), 540(s), 493(m). ^{1}H NMR (CD_2Cl_2, δ), 8.04-7.95 (m, 4H, ArH), 7.56-7.48 (m, 6H, ArH), 5.21-5.10 (m, 4H, OCH_2), 4.22 (d, J(P,H) = 12.5 Hz, 2H, $SeCH_2$) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.1 (d, J(P,C) = 99.0 Hz, Ar-C), 133.0 (d, J(P,C) = 3.1 Hz, Ar-C), 130.4 (d, J(P,C) = 12.5 Hz, Ar-C), 128.5 (d, J(P,C) = 14.5 Hz, Ar-C), 66.1 (OCH_2), 29.8 ($SeCH_2$) ppm. ^{31}P NMR (CD_2Cl_2, δ), 67.6 (s, J(P,Se) = 446 Hz, J(P,Se) = 822 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 490.1 (d, J(P,Se) = 446 Hz), -75.3 (d, J(P,Se) = 822 Hz) ppm. Accurate mass measurement [CI^+, m/z]: 610.7359 $[M+H]^+$, calculated mass for $C_{15}H_{17}O_2P_2Se_4$: 610.7365.

2,7-Diphenyl-1,8,3,6,2,7-dioxadiselenadiphosphecane 2,7-diselenide (5). 0.349 g as a pale yellow solid. 56.1% isolated yield. A pair of stereoisomers was found in *ca*. 3 : 2 intensity ratio. Selected IR (KBr, cm^{-1}): 1434(m), 1232(m), 1101(s), 1052(m), 1018(s), 923(s), 743(m), 710(m), 686(m), 547(s). ^{1}H NMR (CD_2Cl_2, δ), 8.32-7.93 (m, 4Hx2, ArH), 7.53-7.50 (m, 6Hx2, ArH), 4.90-4.17 (m, 4Hx2, OCH_2), 3.41-3.23 (d, 4Hx2, $SeCH_2$) ppm. ^{13}C NMR (CD_2Cl_2, δ), 135.9 (d, J(P,C) = 99.5 Hz, Ar-C), 135.8 (d, J(P,C) = 99.7 Hz, Ar-C), 132.7 (d, J(P,C) = 3.1 Hz, Ar-C), 132.6 (d, J(P,C) = 3.1 Hz, Ar-C), 130.3 (d, J(P,C) = 12.5 Hz, Ar-C), 130.0 (d, J(P,C) = 12.5 Hz, Ar-C), 128.8 (d, J(P,C) = 14.5 Hz, Ar-C), 128.7 (d, J(P,C) = 14.5 Hz, Ar-C), 66.5 (OCH_2), 66.1 (OCH_2), 31.2 ($SeCH_2$), 31.1 ($SeCH_2$) ppm. ^{31}P NMR (CD_2Cl_2, δ), 75.7 (s, J(P,Se) = 469 Hz, J(P,Se) = 824 Hz), 80.3 (s, J(P,Se) = 453 Hz, J(P,Se) = 828 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 341.8 (d, J(P,Se) = 469 Hz), 376.2 (d, J(P,Se) = 453 Hz), -71.8 (d, J(P,Se) = 824 Hz), -95.4 (d, J(P,Se) = 828 Hz) ppm. MS [CI^+, m/z]: 640 $[M+NH_4]^+$. Accurate mass measurement [CI^+, m/z]: 639.7791 $[M+NH_4]^+$, calculated mass for $C_{16}H_{18}O_2P_2Se_4NH_4$: 639.7799.

2,8-Diphenyl-1,9-dioxa-3,7-diselena-2,8-diphosphacycloundecane 2,8-diselenide (6). 0.275 g as an yellow paste. 43.2% isolated yield. A pair of stereoisomers was found in *ca.* 5 : 4 intensity ratio. Selected IR (KBr, cm^{-1}): 1434(m), 1215(m), 1102(s), 1056(m), 1019(m), 932(s), 744(m), 709(m), 687(m), 547(s). ^{1}H NMR (CD_2Cl_2, δ), 8.04-7.94 (m, 4Hx2, ArH), 7.57-7.7.51 (m, 6Hx2, NH), 4.83-4.76 (m, 4H, CH_2), 4.25-4.14 (m, 4H, CH_2), 3.30-3.25 (m, 2H, CH_2), 3.02-2.90 (m, 4H, CH_2), 2.79-2.67 (m, 4H, CH_2), 2.25-2.20 (m, 2H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.0 (d, J(P,C) = 96.5 Hz, Ar-C), 135.6 (d, J(P,C) = 96.5 Hz, Ar-C), 132.8 (d, J(P,C) = 3.1 Hz, Ar-C), 132.6 (d, J(P,C) = 3.1 Hz, Ar-C), 130.6 (Ar-C), 130.4 (Ar-C), 128.8 (Ar-C), 128.6 (Ar-C), 66.2 (dd, J(P,C) = 15.6 Hz, J(P,C) = 7.3 Hz, OCH_2), 65.9 (dd, J(P,C) = 15.6 Hz, J(P,C) = 7.3 Hz, OCH_2), 32.3 (d, J(P,C) = 14.6 Hz, $SeCH_2$), 31.7 (d, J(P,C) = 14.6 Hz, $SeCH_2$), 30.6 (s, $SeCH_2$) ppm. ^{31}P NMR (CD_2Cl_2, δ), 81.9 (s, J(P,Se) = 460 Hz, J(P,Se) = 826 Hz); 80.8 (s, J(P,Se)

= 469 Hz, *J*(P,Se) = 826 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, *δ*), 366.2 (d, *J*(P,Se) = 458 Hz); 365.3 (d, *J*(P,Se) = 467 Hz); -90.6 (d, *J*(P,Se) = 826 Hz); -103.9 (d, *J*(P,Se) = 826 Hz) ppm. MS [CI$^+$, m/z]: 637 $[M+H]^+$. Accurate mass measurement [EI$^+$, m/z]: 636.7683 $[M]^+$, calculated mass for $C_{17}H_{20}O_2P_2Se_4H$: 636.7690.

2,9-Diphenyl-1,10-dioxa-3,8-diselena-2,9-diphosphacyclododecane 2,9-diselenide (7). 0.350 g as a purple yellow solid. 50.1% isolated yield. A pair of stereoisomers was found in *ca*. 1 : 1 intensity ratio. Selected IR (KBr, cm^{-1}): 1486(m), 1449(m), 1436(m), 1225(m), 1104(m), 1023(s), 939(m), 747(s), 687(m), 550(s), 495(m). ^{1}H NMR (CD_2Cl_2, *δ*), 8.07-7.96 (m, 4Hx2, ArH), 7.59-7.7.05 (m, 10Hx2, ArH), 4.58 (d, *J*(P,H) = 13.4 Hz, 4H, OCH_2), 4.50 (d, *J*(P,H) = 13.4 Hz, 4H, OCH_2), 4.00 (d, *J*(P,H) = 13.2 Hz, 4H, $SeCH_2$), 3.92 (d, *J*(P,H) = 13.2 Hz, 4H, $SeCH_2$) ppm. ^{13}C NMR (CD_2Cl_2, *δ*), 136.5 (d, *J*(P,C) = 96.8 Hz, Ar-C), 135.4 (d, *J*(P,C) = 96.8 Hz, Ar-C), 132.9 (Ar-C), 131.2 (Ar-C), 130.9 (Ar-C), 130.8 (Ar-C), 130.6 (Ar-C), 130.4 (Ar-C), 129.5 (Ar-C), 129.0 (Ar-C), 128.7 (Ar-C), 128.4 (Ar-C), 128.1 (Ar-C), 127.7 (Ar-C), 127.4 (Ar-C), 126.4 (Ar-C), 125.9 (Ar-C), 31.2 (OCH_2), 30.3 (OCH_2), 25.1 ($SeCH_2$), 24.3 ($SeCH_2$) ppm. ^{31}P NMR (CD_2Cl_2, *δ*), 79.7 (s, *J*(P,Se) = 451 Hz, *J*(P,Se) = 829 Hz); 77.3 (s, *J*(P,Se) = 470 Hz, *J*(P,Se) = 826 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, *δ*), 396.3 (d, *J*(P,Se) = 451 Hz); 375.5 (d, *J*(P,Se) = 470 Hz); -98.7 (d, *J*(P,Se) = 825 Hz), -108.4 (d, *J*(P,Se) = 825 Hz) ppm. MS [CI$^+$, m/z]: 716 $[M+NH_4]^+$. Accurate mass measurement [CI$^+$, m/z]: 715.8108 $[M+NH_4]^+$, calculated mass for $C_{22}H_{22}O_2P_2Se_4NH_4$: 715.8114.

2,8-Diphenyl-1,9-dioxa-3,7-diselena-2,8-diphosphacyclododecane 2,8-diselenide (8). 0.230 g as a pale yellow sticky oil in 36.1% isolated yield. Selected IR (KBr, cm^{-1}): 1435(m), 1398(m), 1208(s), 1103(m), 978(vs), 819(m), 740(m), 712(m), 689(m), 552(vs), 499(m). ^{1}H NMR (CD_2Cl_2, *δ*), 7.96-7.87 (m, 4H, ArH), 7.52-7.45 (m, 6H, ArH), 4.18--3.95 (m, 4H, CH_2), 3.40-3.26 (m, 4H, CH_2), 2.15-2.07 (m, 2H, CH_2), 1.81-1.71 (m, 2H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, *δ*), 136.7 (d, *J*(P,C) = 106.9 Hz, Ar-C), 132.3 (d, *J*(P,C) = 12.5 Hz, Ar-C), 130.2 (d, *J*(P,C) = 12.5 Hz, Ar-C), 128.5 (d, *J*(P,C) = 14.5 Hz, Ar-C), 68.4 (d, *J*(P,C) = 7.3 Hz, OCH_2), 32.9 (d, *J*(P,C) = 13.5 Hz, $SeCH_2$), 30.4 (d, *J*(P,C) = 4.2 Hz, CH_2), 23.3 (d, *J*(P,C) = 9.3 Hz, CH_2) ppm. ^{31}P NMR (CD_2Cl_2, *δ*), 80.6 (s, *J*(P,Se) = 436 Hz, *J*(P,Se) = 828 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, *δ*), 334.1 (d, *J*(P,Se) = 436 Hz), -100.6 (d, *J*(P,Se) = 828 Hz) ppm. Accurate mass measurement [EI$^+$, m/z]: 637.7599 $[M]^+$, calculated mass for $C_{17}H_{20}O_2P_2Se_4$: 637.7597.

3,9-Diphenyl-5,6,7,11-tetrahydro-1H-benzo[e][1,10,3,8,2,9]dioxadiselenadiphosphacyclotridecine 3,9-diselenide (9). 0.353 g as an yellow sticky oil in 44.7% isolated yield. Selected IR (KBr, cm^{-1}): 1475(m), 1439(m), 1178(m), 1102(m), 1004(m), 960(m), 757(vs), 740(s), 553(s), 499(m). ^{1}H NMR (CD_2Cl_2, *δ*), 7.93-7.85 (m, 4H, ArH), 7.69-7.66 (m, 2H, ArH), 7.36-7.31 (m, 6H, ArH), 7.28-7.14 (m, 6H, ArH), 4.16-3.77 (m, 4H, OCH_2), 3.45 (d, *J*(P,H) = 11.6 Hz, 4H, $SeCH_2$), 0.87-0.83 (m, 2H, CH_2) ppm.

^{13}C NMR (CD_2Cl_2, δ), 136.9 (d, J(P,C) = 106.0 Hz, Ar-C), 132.6 (d, J(P,C) = 3.1 Hz, Ar-C), 130.7, 130.6, 130.5, 130.3, 130.1, 129.9, 128.9, 128.7, 128.5, 128.4, 128.1, 127.8, 127.5, 127.3, 126.7, 126.5, 62.6 (d, J(P,C) = 6.2 Hz), 34.4 (d, J(P,C) = 4.2 Hz, CH_2), 22.7 ppm. ^{31}P NMR (CD_2Cl_2, δ), 78.8 (s, J(P,Se) = 439 Hz, J(P,Se) = 831 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 420.4 (d, J(P,Se) = 439 Hz), -108.9 (d, J(P,Se) = 831 Hz) ppm. MS [EI^+, m/z]: 788 $[M]^+$, 710 $[M\text{-}Se]^+$. Accurate mass measurement [EI^+, m/z]: 787.8224 $[M]^+$, calculated mass for $C_{29}H_{28}O_2P_2Se_4$: 787.8233.

2,9-Diphenyl-1,8-dioxa-3,10-diselena-2,9-diphosphacyclo-tetra-decane 2,9-diselenide (11). 0.250 g as a reddish yellow sticky oil in 36.8% isolated yield. Two diastereomers were identified as **11a** and **11b**, along with a small amount of what we believe to be isomeric compound **10**. Selected IR (KBr, cm^{-1}): 1435(s), 1258(m), 1104(s), 991(s), 745(m), 711(m), 688(m), 552(s), 496(m). ^{1}H NMR (CD_2Cl_2, δ), 7.96-7.87 (m, 4Hx3, ArH), 7.54-7.47 (m, 6Hx3, ArH),4.36-4.23 (m, 2Hx3, OCH_2), 4.14-4.08 (m, 2Hx3, OCH_2), 3.35-3.30 (m, 2Hx3, CH_2), 2.83-2.77 (m, 2Hx3, CH_2), 2.00-1.91 (m, 4Hx3, CH_2), 1.86-1.73 (m, 4Hx3, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, δ), 136.7 (d, J(P,C) = 96.7 Hz, Ar-C), 136.6 (d, J(P,C) = 100.7 Hz, Ar-C), 132.3 (d, J(P,C) = 3.1 Hz, Ar-C), 130.3 (d, J(P,C) = 11.4 Hz, Ar-C), 130. (d, J(P,C) = 11.4 Hz, Ar-C), 128.6 (d, J(P,C) = 14.5 Hz, Ar-C), 128.5 (d, J(P,C) = 14.5 Hz, Ar-C), 66.1 (d, J(P,C) = 6.1 Hz, CH_2), 65.3 (d, J(P,C) = 7.3 Hz, CH_2), 34.2 (d, J(P,C) = 4.2 Hz, CH_2), 33.1, 32.6, 31.9 (d, J(P,C) = 3.1 Hz, CH_2), 30.4 (s, CH_2), 29.1 (d, J(P,C) = 3.1 Hz, CH_2) ppm. ^{31}P NMR (CD_2Cl_2, δ), 82.4 (s, J(P,Se) = 444 Hz, J(P,Se) = 829 Hz); 82.0 (s, J(P,Se) = 439 Hz, J(P,Se) = 829 Hz); 81.9 (s, J(P,Se) = 441 Hz, J(P,Se) = 829 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), 349.1 (d, J(P,Se) = 444 Hz); 343.3 (d, J(P,Se) = 439 Hz), 341.3 (d, J(P,Se) = 441 Hz); -101.5 (d, J(P,Se) = 829 Hz); -106.7 (d, J(P,Se) = 829 Hz), -115.3 (d, J(P,Se) = 829 Hz) ppm. MS [EI^+, m/z]: 680 $[M+H]^+$. Accurate mass measurement [EI^+, m/z]: 679.8070 $[M]^+$, calculated mass for $C_{20}H_{26}O_2P_2Se_4$: 679.8067.

Table S1 ^{31}P and ^{77}Se NMR data for compounds **4** – **9** and **11**

Product	$\delta_{(P)}$ [ppm]	$J_{(P–Se)}$ / $J_{(P=Se)}$ [Hz]	$\delta_{(Se\text{-}endo)}$ [ppm]	$J_{(Se–P)}$ [Hz]	$\delta_{(Se\text{-}exo)}$ [ppm]	$J_{(Se=P)}$ [Hz]
4	67.6	446 / 822	490.1	446	-75.3	822
5	75.7	469 / 824	341.8	469	-71.8	824
	80.3	453 / 828	376.2	453	-95.4	828
6	80.8	469 / 826	365.3	467	-90.6	826
	81.9	460 / 826	366.2	458	-103.9	826
7	77.3	470 / 826	375.5	470	-98.7	825
	79.7	451 / 829	396.3	451	-108.8	825
8	80.6	436 / 828	334.1	436	-100.6	828
9	78.8	439 / 831	420.4	439	-108.9	831
11	81.9	441 / 829	341.3	441	-101.5	829
	82.0	439 / 829	343.3	439	-106.7	829
	82.4	444 / 829	349.1	444	-115.3	829

Table S2 Details of the x-ray data collections and refinements for **5**, **6** and **7**

Compound	**5**	**6**	**7**
CCDC No	914879	914877	914878
Formula	$C_{16}H_{18}O_2P_2Se_4$	$C_{17}H_{20}O_2P_2Se_4$	$C_{22}H_{22}O_2P_2Se_4$
M	620.08	634.11	696.18
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C2/c*	*P2(1)/c*	*P2(1)2(1)2(1)*
a/Å	26.370(7)	8.935(3)	9.139(2)
b/Å	7.177(2)	21.352(8)	9.953(2)
c/Å	22.019(8)	11.253(4)	26.516(7)
α	90	90	90
β	99.462(8)	92.026(11)	90
γ	90	90	90
U/A^3	4110(2)	2145.6(13)	2411.9(10)
Z	8	4	4
μ/mm^{-1}	7.30	7.00	6.23
Reflections collected	12836	13246	24622
Independent reflections	3719	3846	4387
R_{int}	0.074	0.088	0.054
R1	0.038	0.043	0.027
wR2 [I > 2σ(I)]	0.074	0.099	0.063
GOOF	1.067	1.119	0.999

Table S**3** Details of the x-ray data collections and refinements for **9**, **11a** and **11b**

Compound	**9**	**11a**	**11b**
CCDC No	914880	914881	914882
Formula	$C_{29}H_{28}O_2P_2Se_4$	$C_{20}H_{26}O_2P_2Se_4$	$C_{20}H_{26}O_2P_2Se_4$
M	786.29	676.19	676.19
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P1*	*Pn*	*C2/c*
a/Å	11.234(3)	9.013(2)	22.920(12)
b/Å	11.774(3)	14.311(3)	9.231(3)
c/Å	12.298(4)	19.453(5)	15.919(9)
α	101.435(6)	90	90
β	106.641(6)	98.027(8)	133.807(7)
γ	96.727(4)	90	90
U/A^3	1501.2(7)	2487.5(11)	2431(2)
Z	2	4	4
μ/mm^{-1}	5.02	6.05	6.18
Reflections collected	9430	14626	7397
Independent reflections	5276	7174	2201
R_{int}	0.040	0.059	0.047
R1	0.041	0.065	0.050
wR2 [I > 2σ(I)]	0.072	0.191	0.133
GOOF	0.988	1.039	1.075

Full Computational Details

Geometries were fully optimised at the B3LYP/6-31G* level[1] with Curtis and Binning's 962(d) basis[2] on Se. Stationary points were characterised by computation of the harmonic vibrational frequencies (zero and one imaginary frequency for minima and transition states, respectively). These calculations were performed with the Gaussian 09 program.[3] Empirical dispersion corrections according to Grimme[4] were evaluated for the gas-phase B3LYP geometries (denoted B3LYP-D3, cf. Figure S1).

To obtain representative structures of **10**, we used the optimized geometries of **11** and switched the bridging Se and O atoms at one of the phosphorus stereocentres. Allowing for symmetry, this led to a total of six minimized structures (Figure S2). Relative energies were refined at the B3LYP-D3/6-311+G*

level (using the same 962(s) basis on Se) using a polarisable continuum using the default settings in Gaussian 09 and the parameters of THF (Table S4).

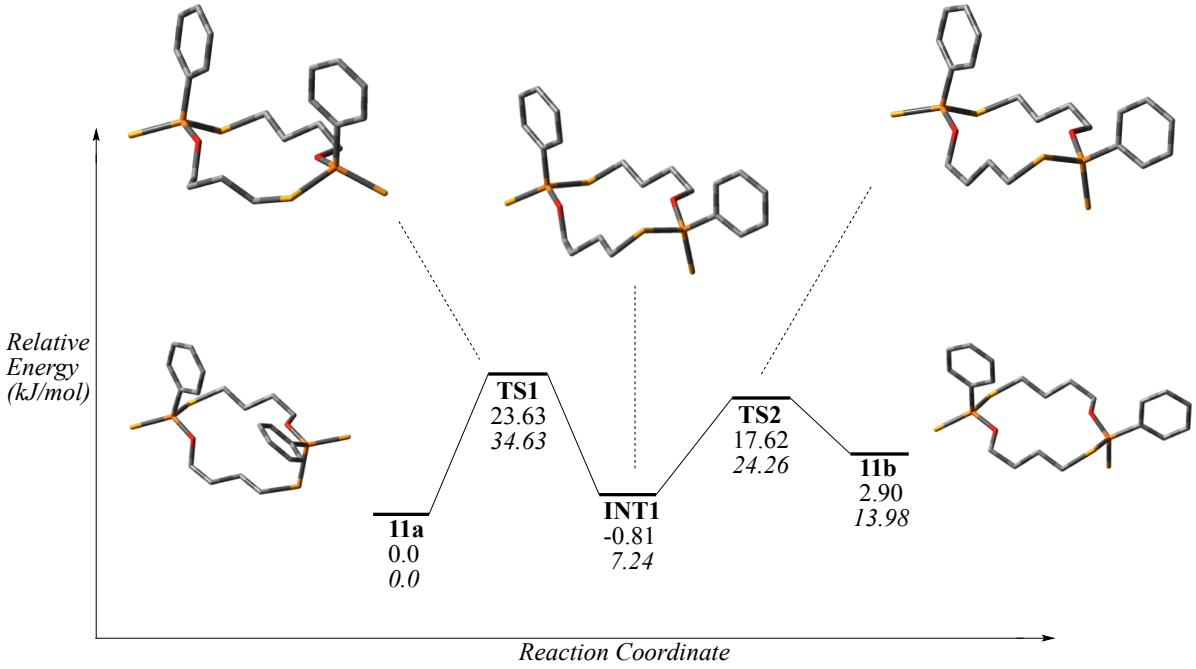

Figure S1 Reaction profile for the interconversion of (*S,S*)-**11a** to (*S,S*)-**11b**. Energies given are ZPE corrected in plain type while DFT-D3 corrected values are given in italics. B3LYP/6-31G geometries

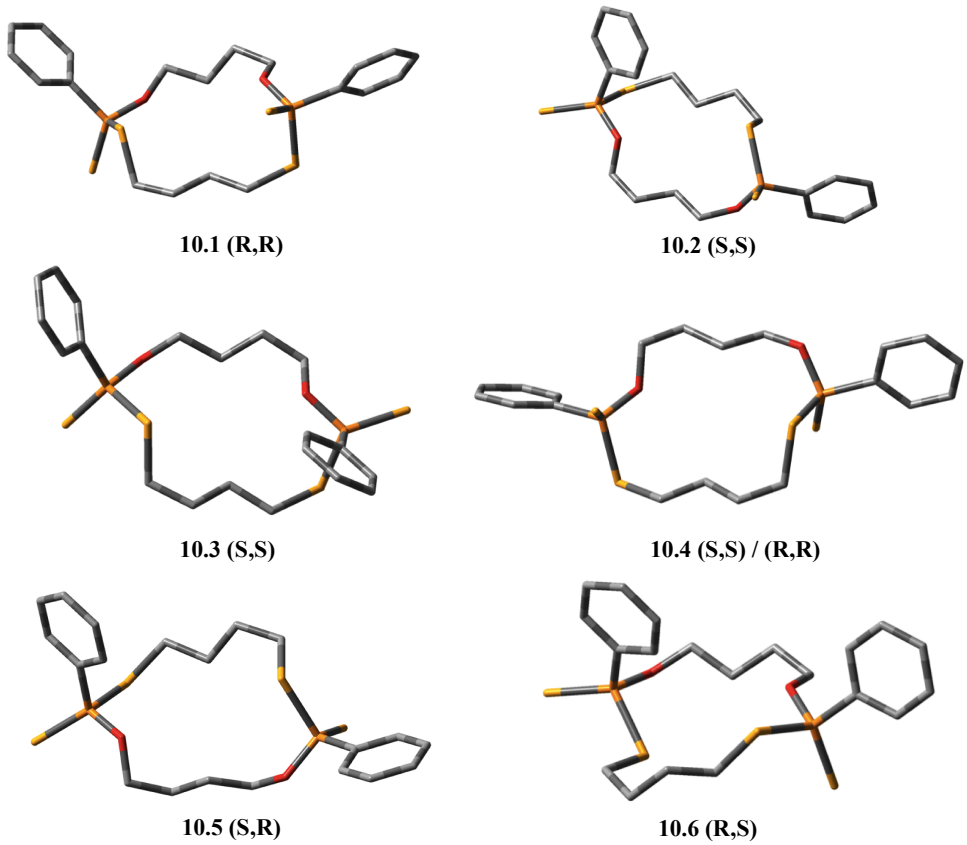

Figure S2 Selected isomers of **10** , (B3LYP/6-31G* optimised, H atoms omitted for clarity)

Table S4 Relative energies against (*R,S*)-**11b** at B3LYP and B3LYP-D3 levels (kJ/mol)

Basis	Level[a]	**11a** (S,S)	**11a** (R,S)	**11b** (S,S)	**10.1** (R,R)	**10.2** (S,S)	**10.3** (R,S)	**10.4** (S,S)	**10.5** (S,R)	**10.6** (R,S)
6-31G*	ΔE	4.39	13.24	8.22	41.75	14.43	28.14	9.03	13.51	54.43
	ΔE_{ZPE}	4.52	13.46	7.42	41.26	14.43	28.22	9.08	13.61	54.75
	$\Delta E_{ZPE\text{-}D3}$	-8.42	-1.03	5.56	34.77	3.85	21.75	6.65	9.55	35.56
6-311+G*	ΔE	3.81	12.17	8.10	39.49	12.72	25.80	8.34	11.61	54.25
	$\Delta E_{ZPE\text{-}D3}$	-9.00	-2.11	5.45	32.24	4.02	19.14	5.88	7.65	35.30
	$\Delta E_{ZPE\text{-}D3\text{-}PCM}$	-13.41	-4.40	2.42	24.30	0.94	12.86	8.63	8.42	30.36

[a]ZPE: including zero-point energy; D3: B3LYP-D3; PCM: polarisable continuum (THF).

1. (a) A. D. Becke, J. *Chem. Phys*. **1993**, *98*, 5648; (b) C. Lee, W. Yang R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
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