Supporting Informations for:

# Stereospecific synthesis of chiral P-containing polyaromatics based on 7-membered P-rings

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Experimental part

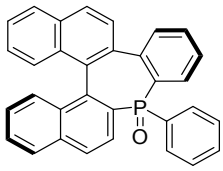
**General**

All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly purified using MBRAUN SPS-800 drying columns filled with $Al_2O_3$. Separations were performed on air by gravity column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063–0.200 mmm). $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on a Bruker AV III 400 MHz NMR spectrometer equipped with BBFO probehead. Assignment of H and C atoms is based on COSY, NOESY, edited-HSQC and HMBC experiments. Special $^{31}P$ decoupled experiments ($\{^{31}P\}^{1}H$, $\{^{31}P\text{-}^{1}H\}^{13}C$, $\{^{31}P\}$-HSQC, HMBC, COSY, NOESY) were performed on a Bruker Av III HD 500 MHz fitted with a triple inverse probehead ($^{1}H\text{-}^{31}P\text{-}X$), part of the PRISM core facility (Biogenouest©, UMS Biosit, Université de Rennes 1- Campus de Villejean- 35043 RENNES Cedex, FRANCE). $^{1}H$ and $^{13}C$ NMR chemical shifts were reported in parts per million (ppm) using the residual solvent signal as a reference. $^{31}P$ NMR downfield chemical shift were expressed with a positive sign, in ppm, relative to external 85% $H_3PO_4$. SEC purification was performed on a LC-9160 II NEXT system from the Japan Analytical Industry Co., Ltd. (JAI) equipped with coupled UV-vis 4Ch NEXT through a set of two JAIGEL-2H columns at an elution rate of chloroforme of 10 $mL.min^{-1}$ ($CHCl_3$). High-resolution mass spectra were obtained on Bruker Maxis 4G instrument at Scanmat (UMS 2001). UV-Visible spectra were recorded at room temperature on a JASCO V-630 spectrophotometer. The UV-Vis emission and excitation spectra measurements were recorded on an FL 920 Edimburgh Instrument and corrected for the response of the photomultiplier. Quantum yields were calculated relative to quinine sulfate ($\Phi$ = 0.54 in $H_2SO_4$ 0.1N, $\phi_{ref}$=0.55). The CD spectra measurements were recorded on Spectropolarimeter of circular dichroism J-815 (Jasco France) and the optical rotations measurements were carried out on Perkin Elmer 341 instrument with sodium light at 589 nm. The electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat for cyclic voltammetry with the three-electrode configuration: the working electrode was a platinum disk, the reference electrode was a saturated calomel electrode and the counter-electrode a platinum wire. All potentials were internally referenced to the ferrocene/ferrocenium couple. For the measurements,

concentrations of $10^{-3}$ M of the electroactive species were used in freshly distilled and degassed dichloromethane and 0.2 M tetrabutylammonium hexafluorophosphate. UV-vis-NIR spectroelectrochemical experiments were performed in DCM, under argon, with an Optically Transparent Thin-Layer Electrochemical (OTTLE) cell, path length = 0.2 mm, using a UV-Vis-NIR Jasco V770 spectrometer and an EG&G PAR model 362 potentiostat. A Pt mesh was used as the working electrode, a Pt wire as the counter electrode, and an Ag wire as a pseudo-reference electrode.

**BINAP-O** and rac-**1** were synthesized according to published procedure[1].

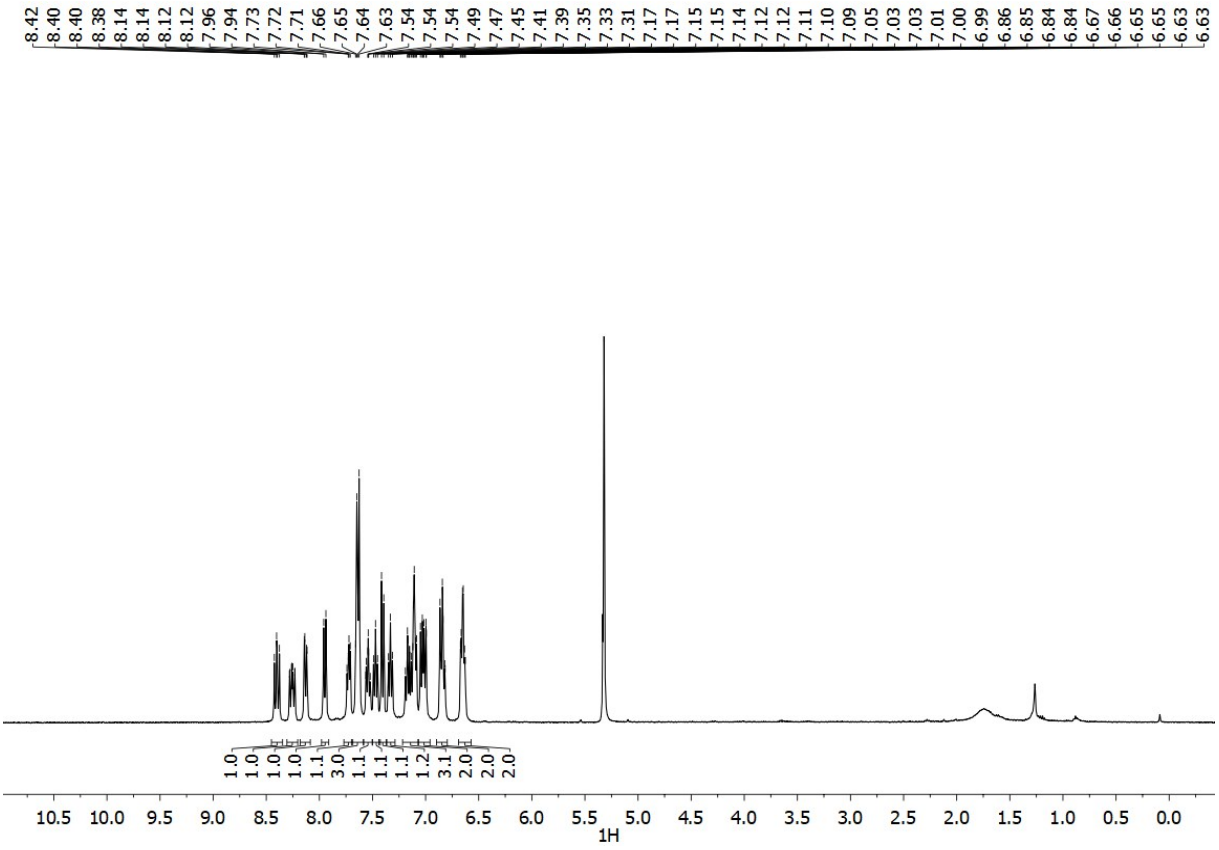
Synthetic procedure for rac-**1** (0.05 g, 70%), ($R_P$,*M*)-**1** ( 0.24 g, 54%) and ($S_P$,*P*)-**1** ( 0.22 g, 63%) (only the procedure for the rac-**1** is described)




To a degassed solution of rac-**BINAP-O** (0.65 g, 0.99 mmol) in 40 mL of THF, 2.0 M LDA solution in THF (2.00 mL, 4.01 mmol) was added at -15 °C under Ar. The dark brown solution formed was stirred for 15 h. The reaction was quenched by the addition of 10% aqueous HCl solution and the mixture was extracted with DCM. The organic layer was washed with water, dried on MgSO4, filtered and then the solvent was evaporated. The crude mixture was purified by silica gel chromatography (DCM/Acetone, 90/10) to afford ($R_P$,*M*)-**1** as a white powder (0.24 g, 54%). $^1$H NMR (400.16 MHz, $CD_2Cl_2$): δ (ppm) = 6.65 (td, *J*(H-H) = 7.9Hz, *J*(P-H) = 3.0 Hz, 2H); 6.80-6.84 (m, 2H); 6.98-7.06 (m, 2H); 7.10 (d, *J*(H-H) = 8.9 Hz, 1H); 7.12 (ddd, *J*(H-H) = 8.1 Hz, *J*(H-H) = 6.6 Hz, *J*(H-H) = 1.2Hz, 1H); 7.17 (dd, *J*(H-H) = 8.0 Hz, *J*(H-H) = 6.7 Hz, 1H); 7.33 (dd, *J*(H-H) = 8.0 Hz, *J*(H-H) = 6.9 Hz, 1H); 7.41 (d, *J*(H-H) = 8.6 Hz, 1H); 7.44-7.50 (m, 1H); 7.51- 7.57 (m, 1H); 7.61-7.66 (m, 3H); 7.70-7.74 (m, 1H); 7.95 (d, *J*(H-H) = 8.3 Hz, 1H); 8.13 (dd, *J*(H-H) = 8.4 Hz, J(H-H) = 1.7 Hz, 1H); 8.27 (dd, *J*(P-H) = 12.2 Hz, *J*(H-H) = 7.6 Hz, 1H); 8.41 (dd, *J*(P-H) = 10.6 Hz, *J*(H-H) = 8.5 Hz, 1H). $^{31}$P NMR (161.99 MHz, $CD_2Cl_2$): δ (ppm) = + 20.5 (s). $^{13}$C NMR (100.63 MHz, $CD_2Cl_2$): δ (ppm) = 126.2 (d, *J*(P-C) = 7.0 Hz, CH); 126.5 (CH); 126.8 (CH); 127.0 (CH); 127.6 (d, *J*(P-C) = 13.0 Hz, 2xCH); 127.9 (d, *J*(P-C) = 9.6 Hz, CH); 128.2 (CH); 128.4 (CH); 128.6 (CH); 128.9 (CH); 129.1 (d, *J*(P-C) = 10.9 Hz, CH); 129.4 (CH); 129.5 (d, *J*(P-C) = 11.8 Hz, 2xCH); 130.3 (d, *J*(P-C) = 9.7

[1] M. Widhalm, K. Mereiter *Bull. Chem. Soc. Jpn.* 76 (2003) 1233-1244

Hz, CH); 130.9 (d, *J*(P-C) = 2.8 Hz, CH); 131.4 (d, *J*(P-C) = 6.7 Hz, CH); 131.8 (d, *J*(P-C) = 108.3 Hz, $C_q$); 132.5 ($C_q$); 132.6 ($C_q$); 132.7 (d, *J*(P-C) = 2.3Hz, CH); 133.4 (d, *J*(P-C) = 3.6 Hz, $C_q$); 133.6 (d, *J*(P-C) = 11.7 Hz, $C_q$); 135.4 (d, *J*(P-C) = 2.2 Hz, $C_q$); 135.5 (d, *J*(P-C) = 102.7 Hz, $C_q$); 136.8 (d, *J*(P-C) = 101.5 Hz, $C_q$); 136.9 (d, *J*(P-C) = 10.6 Hz, $C_q$); 137.9 (d, *J*(P-C) = 1.7 Hz, $C_q$); 142.5 (d, *J*(P-C) = 9.5 Hz, $C_q$). HR-MS (m/z) $[M]^+$ calcd for $C_{32}H_{21}OP$: 452.1325; found: 452.1326.



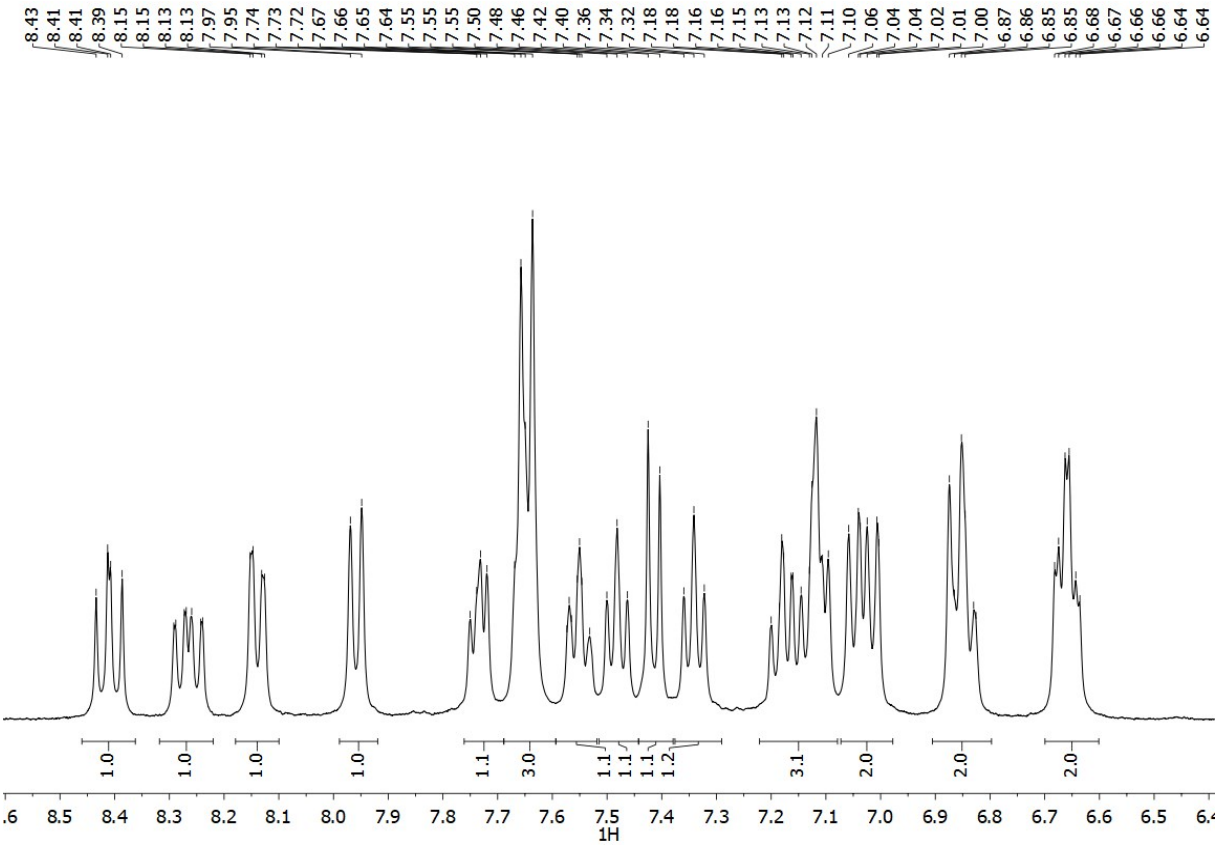



**Figure S1:** $^{1}H$ NMR (400 MHz, $CD_2Cl_2$) spectra of ($R_P$,*M*)-**1**

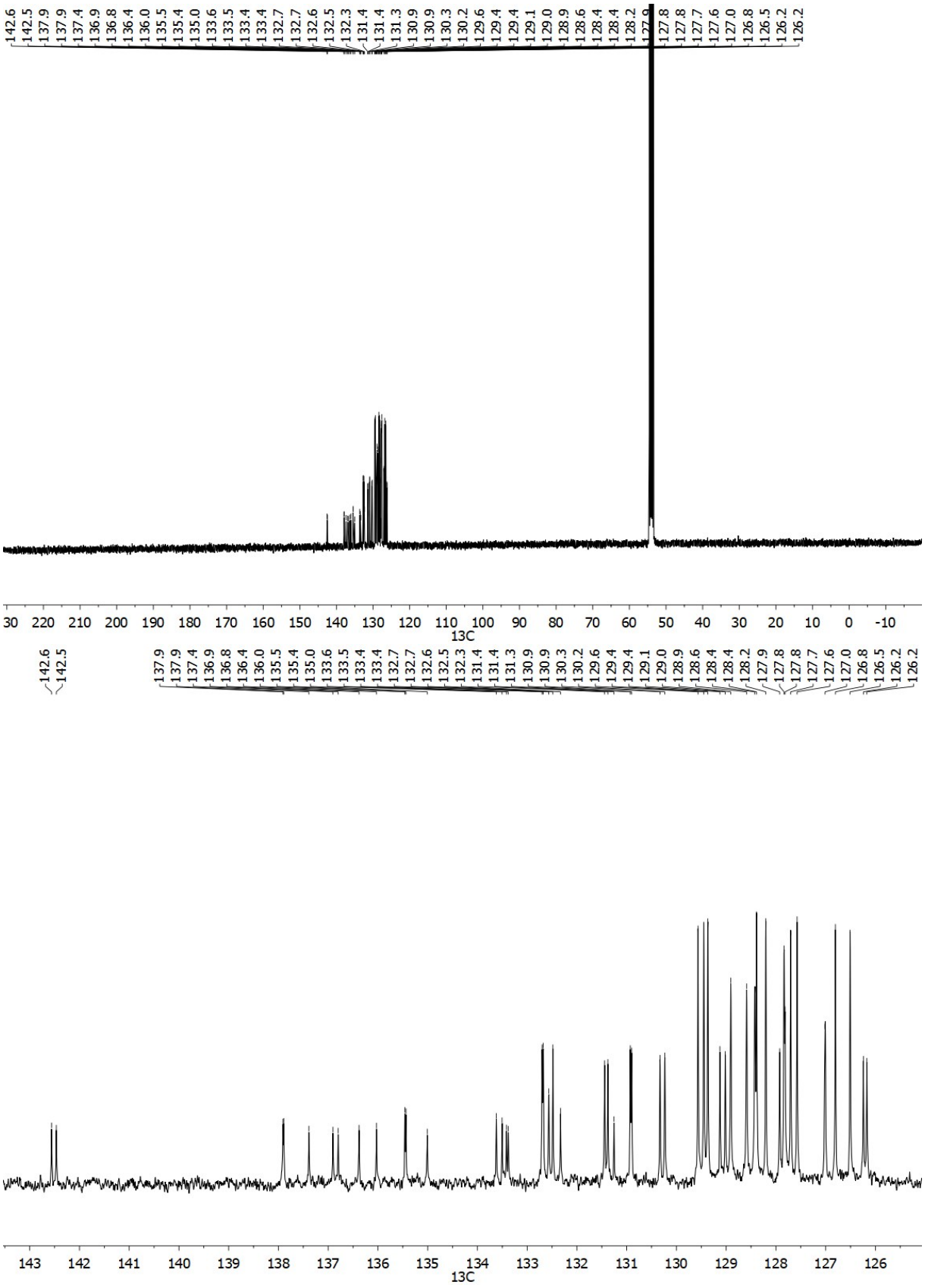



**Figure S1b:** $^{13}C$ NMR (100 MHz, $CD_2Cl_2$) spectra of ($R_P$,*M*)-**1**

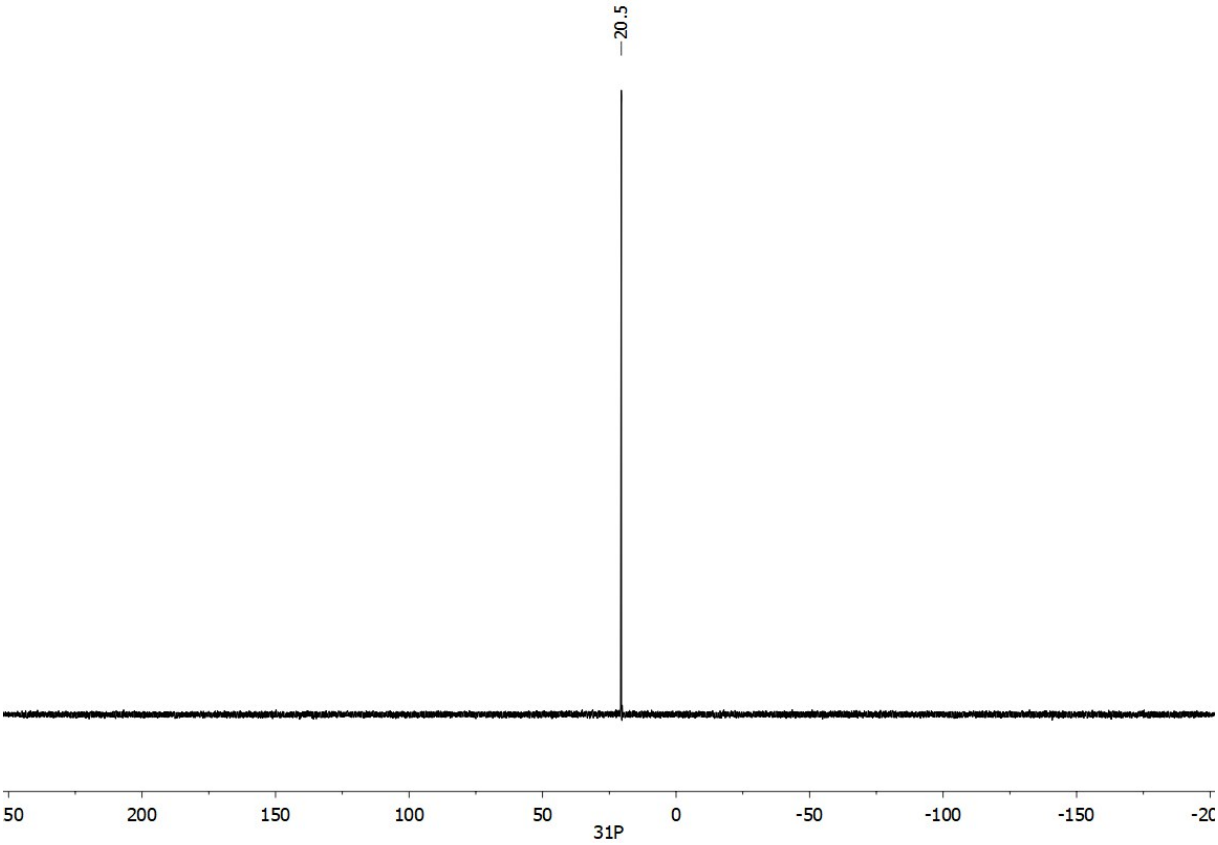
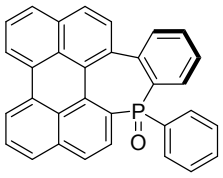



**Figure S1c:** $^{31}$P NMR (162 MHz, $CD_2Cl_2$) spectra of ($R_P$,*M*)-**1**

Synthetic procedure for rac-**2** (0.06 g, 63%), ($R_P$,*M*)-**2** (0.09 g, 61%) and ($S_P$,*P*)-**2** (0.11 g, 50%) (only the procedure for the rac-**2** is described)




In a Schlenk under Ar, $AlCl_3$ (0.35 g, 2.65 mmol) and NaCl (0.08 g, 1.33 mmol) are added to rac-**1** (0.10 g, 0.22 mmol) was added. The mixture was then heated to 140°Cfor 2,5 hours to give a black melt. The mixture was cooled down to room temperature (rt) and was quenched at 0°C with 10% HCl aqueous solution for 30 min. The resulting solution was then extracted with DCM, dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated. Then, DDQ (0.10 g, 0.44 mmol) and toluene (25mL) were added under inert atmosphere and the mixture was heated at 60°C for 2,5 hours. The reaction was cooled down to rt and quenched with saturated $NaHCO_3$ solution, extracted with DCM, dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated. The residue was purified by column chromatography on silica gel (DCM/Acetone, 100/0→85/15) and the product was purified SEC HPLC to give a yellow solid (0.06 g, 63 %). $^1$H NMR (500.15 MHz, $CD_2Cl_2$): δ (ppm) = 6.92 (td, *J*(H-H) = 7.9 Hz, *J*(P-H)

= 2.9 Hz, 2H); 7.03-7.09 (m, 2H); 7.11-7.16 (m, 1H); 7.28 (d, *J*(H-H) = 8.5 Hz, 2H); 7.33 (dd, *J*(H-H) = 7.6 Hz, *J*(P-H) = 4.8 Hz, 1H); 7.53-7.59 (m, 2H); 7.64 (t, *J*(H-H) =7.7 Hz, 1H); 7.70-7.78 (m, 3H); 7.94 (d, *J*(H-H) =8.0 Hz, 1H); 8.08-8.12 (m, 1H); 8.31-8.40 (m, 3H); 8.60 (dd, *J*(P-H) = 11.5 Hz, *J*(H-H) = 8.4 Hz, 1H). $^{31}$P NMR (202.46 MHz, $CD_2Cl_2$): δ (ppm) = +18.6 (s). $^{13}$C NMR (125.78 MHz, $CD_2Cl_2$): δ (ppm) = 121.9 (CH); 122.5 (CH); 127.2 (CH); 127.7 (CH); 127.9 (CH); 128.1 (CH); 128.2 (d, J(P-C) = 12.7 Hz, 2xCH); 128.3 (CH); 128.5 (d, *J*(P-C) = 10.6 Hz, CH); 128.6 ($C_q$); 128.7 (d, *J*(P-C) = 9.8 Hz, CH); 128.8 (d, *J*(P-C) = 6.9 Hz, CH); 129.0 (d, *J*(P-C) = 6.2 Hz, CH); 129.4-129.6 (m, 2x$C_q$); 129.9 (d, *J*(P-C) = 97.6 Hz, $C_q$); 130.6 (d, *J*(P-C) = 11.2 Hz, 2xCH); 130.8 ($C_q$); 131.4 (d, *J*(P-C) = 2.4 Hz, CH); 131.5 ($C_q$); 131.9 (CH); 131.9 (d, *J*(P-C) = 109.2 Hz, $C_q$); 132.0 (d, *J*(P-C) = 2.7 Hz, CH); 132.5 (d, *J*(P-C) = 11.3 Hz, CH); 132.9 ($C_q$); 133.7 (d, *J*(P-C) = 8.5 Hz, $C_q$); 135.6 (d, *J*(P-C) = 2.1 Hz, $C_q$); 136.6 (d, *J*(P-C) = 102.2 Hz, $C_q$); 139.9 (d, *J*(P-C) = 2.5 Hz, $C_q$); 141.3 (d, *J*(P-C) = 12.7 Hz, $C_q$). HR-MS (ESI, $CH_2Cl_2$/ $CH_3OH$: 80/20, m/z) $[M+Na]^+$ calcd for $C_{32}H_{19}ONaP$: 473.1066; found: 473.1067.

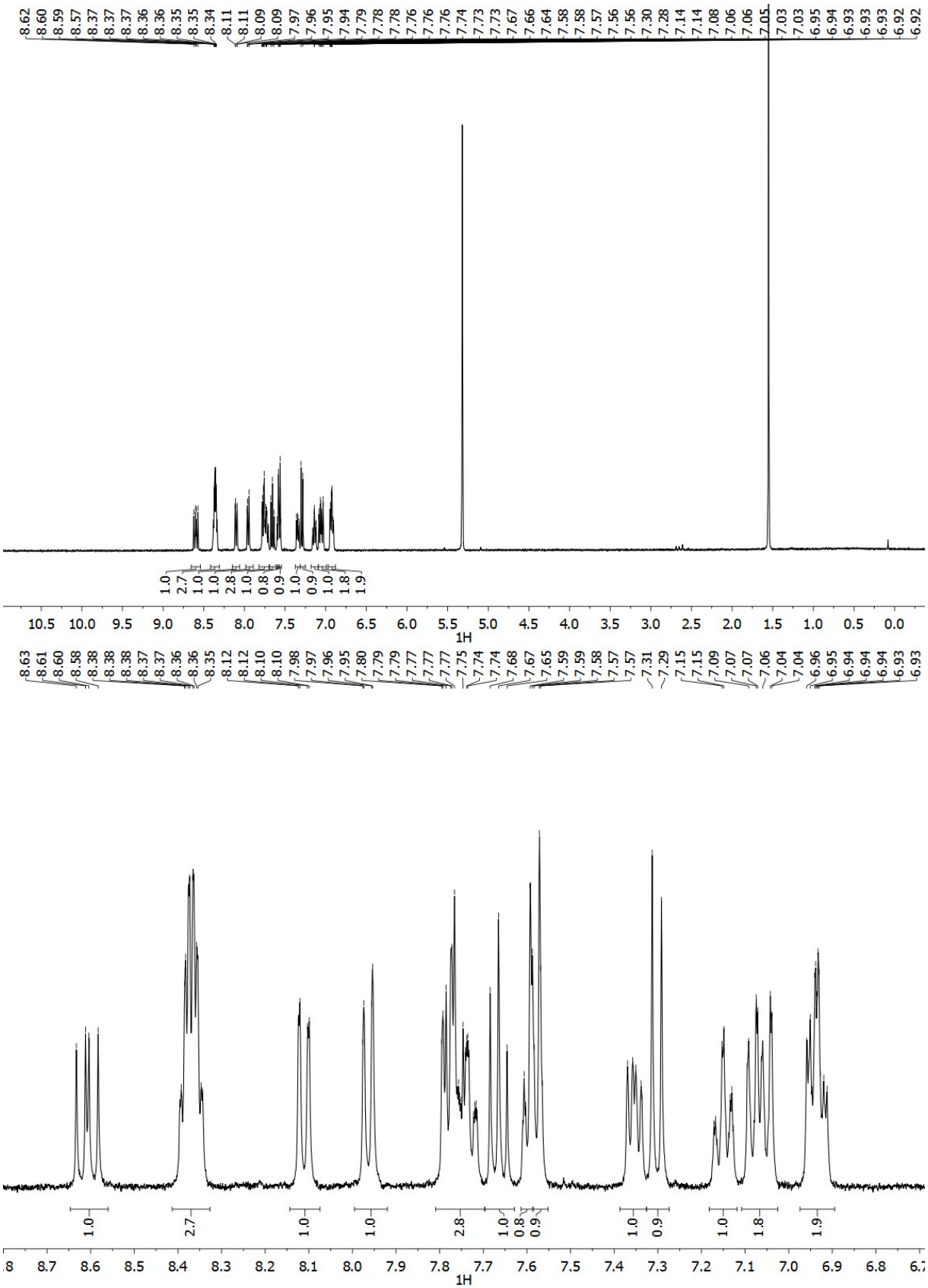


**Figure S2:** $^{1}H$ NMR (500 MHz, $CD_2Cl_2$) spectra of rac-**2**

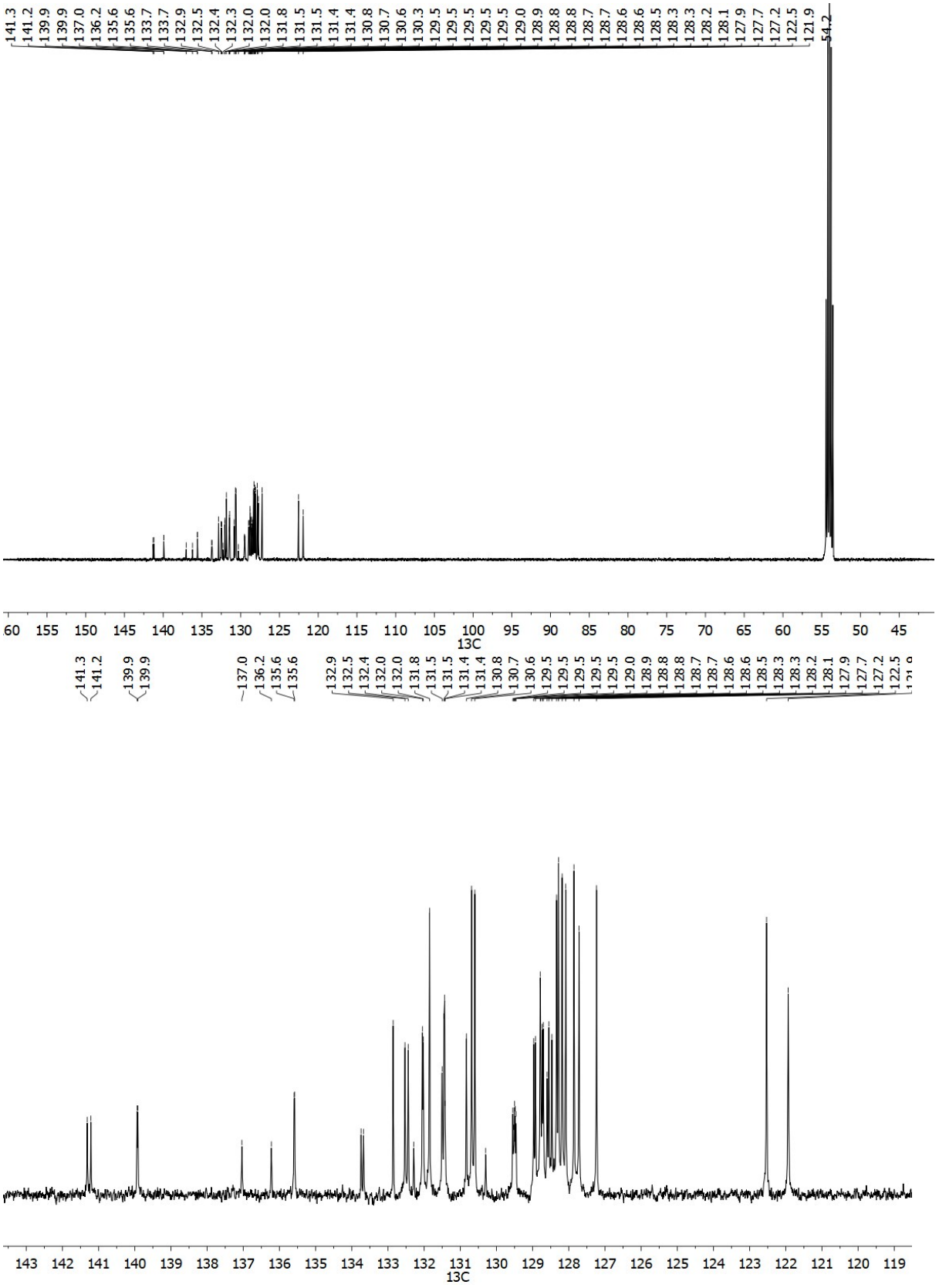


**Figure S2b:** $^{13}C$ NMR (125 MHz, $CD_2Cl_2$) spectra of rac-**2**

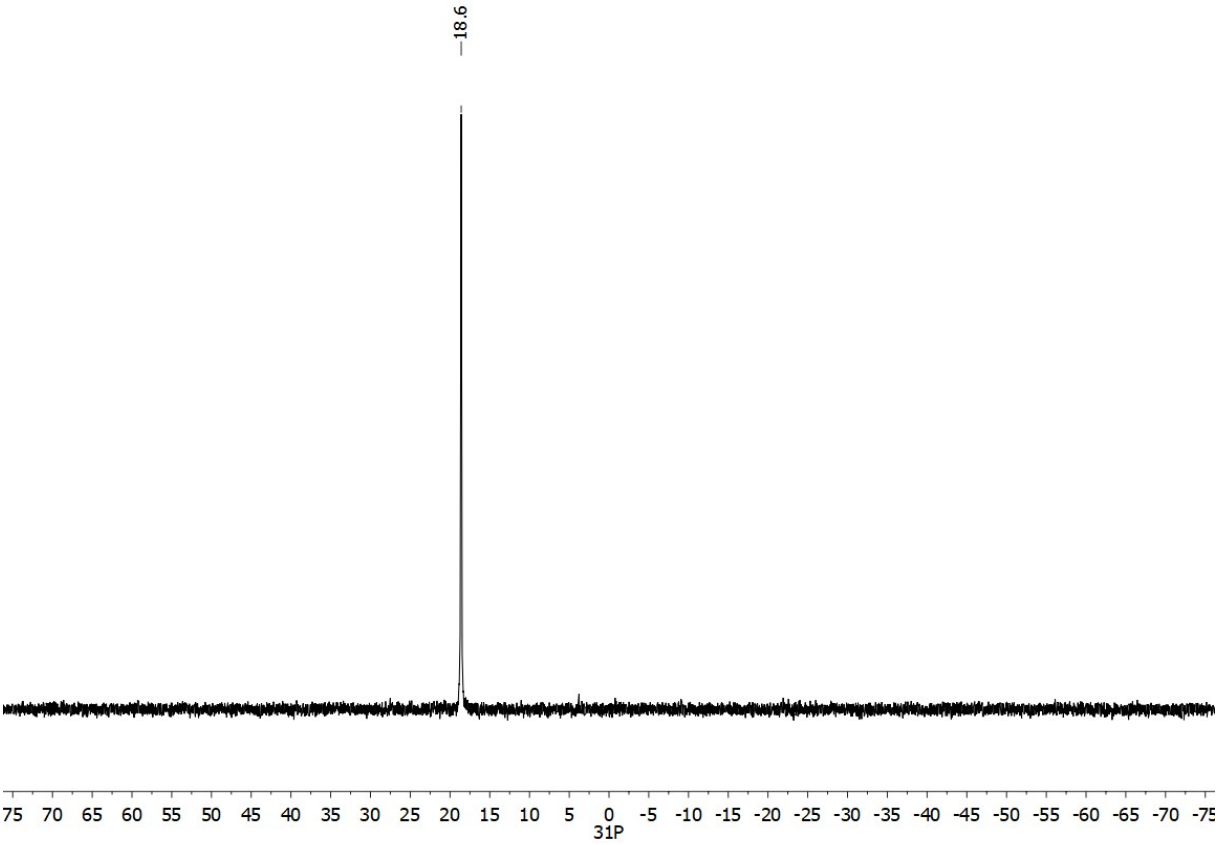
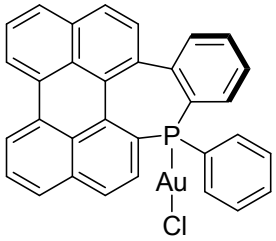



**Figure S2c:** $^{31}P$ NMR (202 MHz, $CD_2Cl_2$) spectra of rac-**2**

Synthetic procedure for rac-**3**(0.03 g, 41%), ($R_P$,*M*)-**3** (0.06 g, 43%) and ($S_P$,*P*)-**3** (0.08d g, 55%) (only the procedure for the rac-**3** is described)




To a degassed solution of rac-**1** (0.05 g, 0.11 mmol) in 5 mL of toluene was added $HSiCl_3$ (0.11 mL, 1.11 mmol) under inert atmosphere. The reaction mixture was refluxed for 90 minutes, then it was cooled down to rt. The solvent was evaporated and the residue was dissolved in DCM. The solution was filtered on basic alumina, then a part of the solvent was evaporated under vacuum. $Me_2SAuCl$ (0.03 g, 0.11 mmol) was added to the solution and the mixture was stirred for 1h at rt. The solution was filtered on celite/$MgSO_4$ and the solvent was evaporated. The crude was precipitated in DCM - pentane mixtures to afford white crystals (0.03 g, 41 %). $^1H$ NMR (300.13 MHz, $CD_2Cl_2$): δ (ppm) = 6.54-6.64 (m, 2H); 6.66-6.89 (m, 4H); 7.09-7.25 (m, 3H); 7.35 (t, *J*(H-H) =7.5 Hz, 1H); 7.42 (d, *J*(H-H) =8.6 Hz, 1H); 7.47-7.58 (m, 2H); 7.64

(d, *J*(H-H) =8.5 Hz, 2H); 7.61-7.74 (m, 1H); 7.78-7.85 (m, 1H); 7.96 (d, *J*(H-H) =8.2 Hz, 1H); 8.12 (dd, *J*(H-H) =8.1 Hz, *J*(H-H) =1.9 Hz, 1H); 8.47 (dd, *J*(H-H) =7.6 Hz, 1H); 8.56 (dd, *J*(H-H) =8.4 Hz, 1H). $^{31}$P NMR (121.50 MHz, $CD_2Cl_2$): δ (ppm) = +35.5 (s). $^{13}$C NMR (75.48 MHz, $CD_2Cl_2$): δ (ppm) = 126.8 (CH);127.0 (CH);127.5 (CH); 127.9 (CH); 128.0 (CH) 128.0 (CH); 128.2 (d, *J*(P-C) = 1.2 Hz, CH); 128.4 (CH); 128.7 (CH); 128.8 (CH); 128.9 (CH); 129.2 (d, *J*(P-C) = 15.6 Hz, CH); 129.6 (CH); 129.7 (CH); 131.5 (d, *J*(P-C) = 6.9 Hz, CH); 131.7 ($C_q$); 132.0 ($C_q$); 132.4 ($C_q$); 132.6 (CH); 132.9 ($C_q$); 133.0 (CH); 133.4 ($C_q$); 133.4 (d, *J*(P-C) = 2.9 Hz, $C_q$); 133.7 (d, *J*(P-C) = 2.9 Hz, CH); 134.2 (d, *J*(P-C) = 9.2 Hz, $C_q$); 135.6 (d, *J*(P-C) = 1.7 Hz, $C_q$); 137.9 (d, *J*(P-C) = 1.2 Hz, $C_q$); 138.5 (d, *J*(P-C) = 27.2 Hz, CH); 139.1 (d, *J*(P-C) = 2.3 Hz, $C_q$); 143.8 (d, *J*(P-C) = 2.3 Hz, $C_q$). HR-MS (ESI, $CH_2Cl_2$/ $CH_3OH$: 80/20, m/z) $[M+Na]^+$ calcd for $C_{32}H_{21}{}^{35}ClNaPAu$: 691.0627; found: 691.0636.

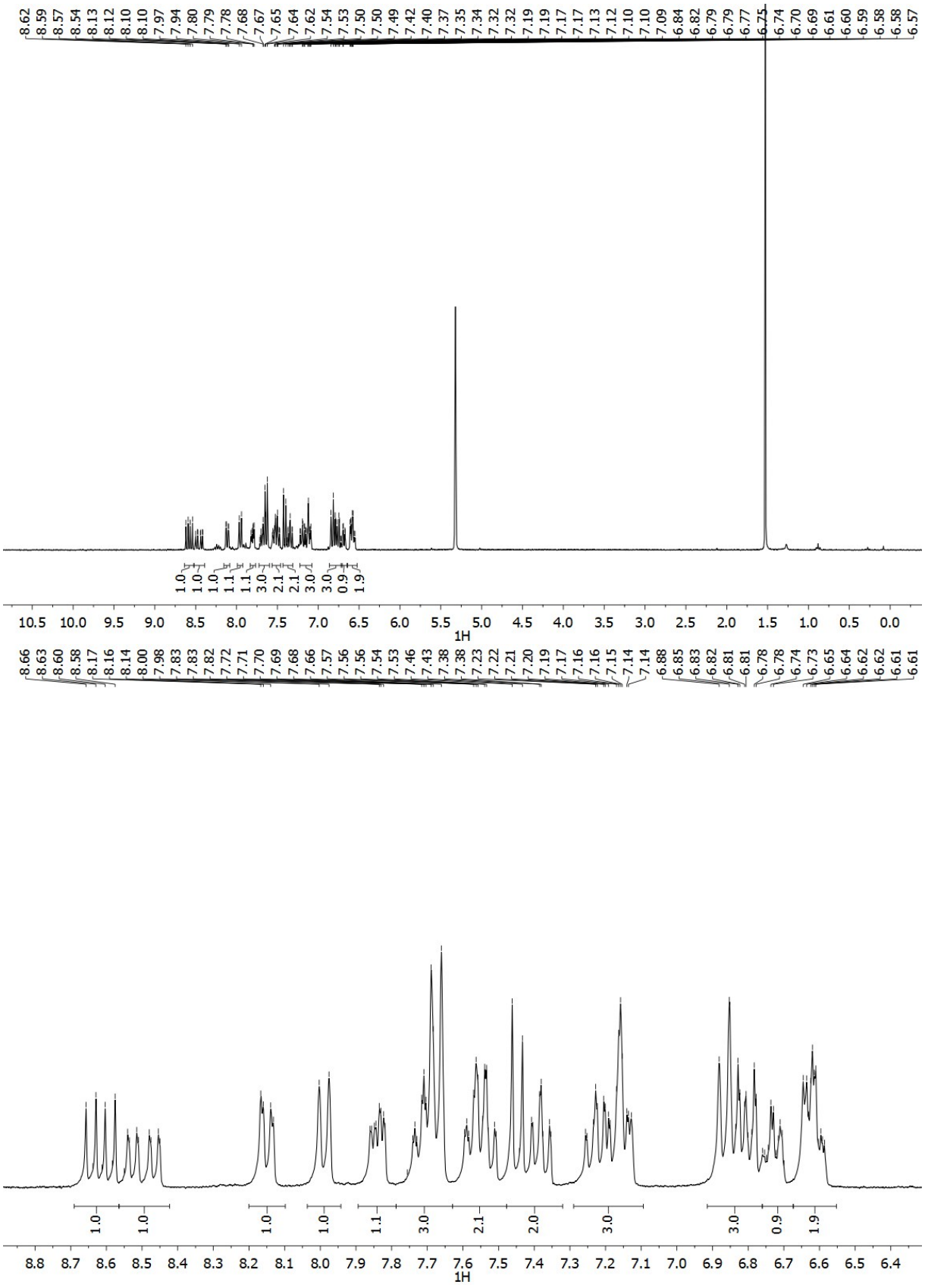


**Figure S3a:** $^{1}H$ NMR (300 MHz, $CD_2Cl_2$) spectra of rac-**3**

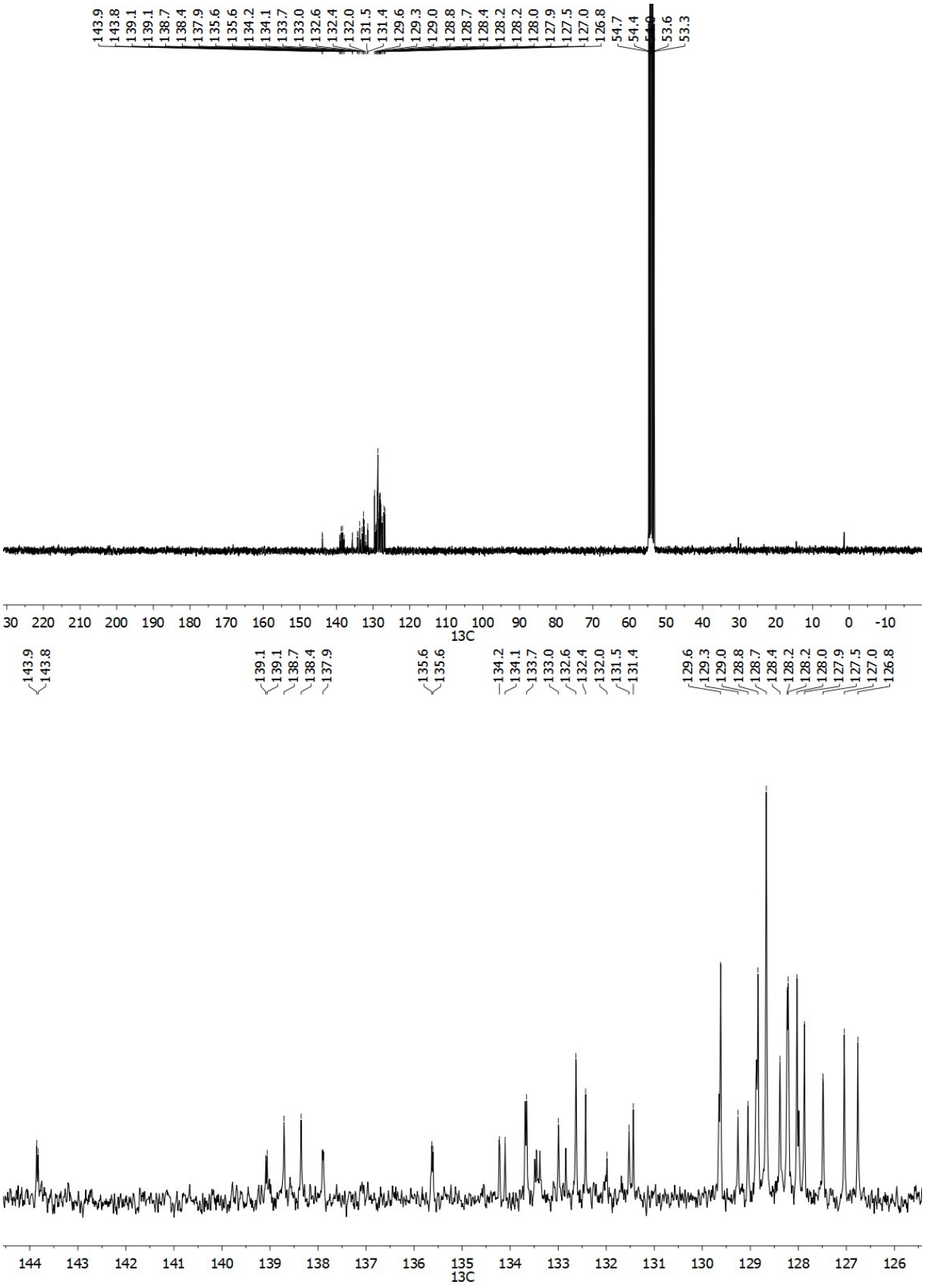



**Figure S3b:** $^{13}C$ NMR (75 MHz, $CD_2Cl_2$) spectra of rac-**3**

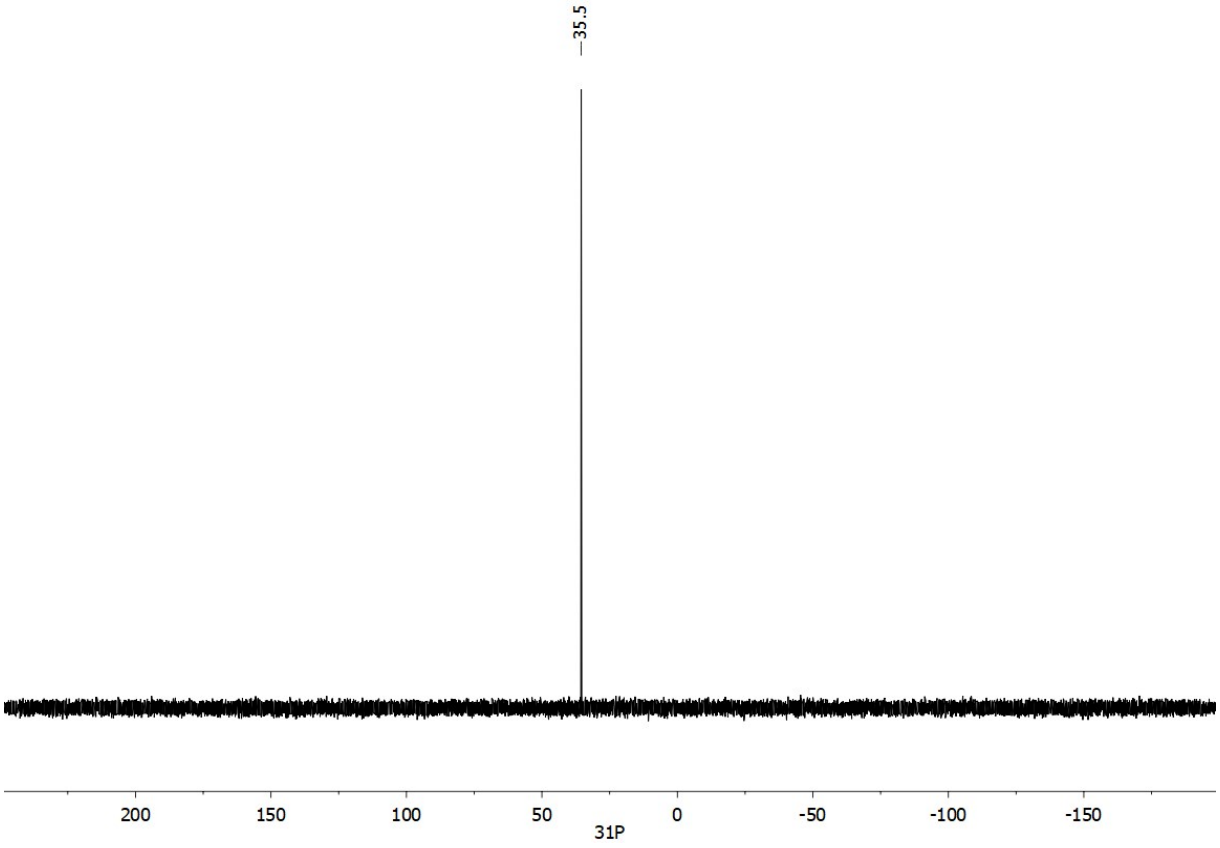



**Figure S3c:** $^{31}P$ NMR (121 MHz, $CD_2Cl_2$) spectra of rac-**3**

**X-ray Crystallographic Study:**

**Crystal structure determination**: Single crystals suitable for X-Ray crystal analysis were obtained by slow diffusion of vapors of pentane into a dichloromethane solution of the derivatives at room temperature. Single crystal data collection were performed at 150 K with an D8 Venture Bruker-AXS diffractometer with Mo-*K*α radiation ($\lambda$ = 0.71073 Å). The structure was solved by dual-space algorithm using the *SHELXT* program[2], and then refined with full-matrix least-squares methods based on $F^2$(*SHELXL*)[3]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters.

**Table S1:** Crystal data and structure refinement

[2] G. M. Sheldrick, *Acta Cryst*. A71 (2015) 3-8
[3] Sheldrick G.M., *Acta Cryst*. C71 (2015) 3-8

| **Compound** | **($R_P$,*M*)-1** | **($S_P$,*P*)-1** | **rac-2** | **($R_P$,*M*)-2** | **($S_P$,*P*)-2** |
|---|---|---|---|---|---|
| CCDC | 1921440 | 1921441 | 1921442 | 1921443 | 1921466 |
| Formula | $C_{32}H_{21}OP$ | $C_{32}H_{21}OP$ | $C_{32}H_{19}OP$ | $C_{33}H_{21}Cl_2OP$ | $C_{33}H_{21}Cl_2OP$ |
| MW | 452.46 | 452.46 | 450.44 | 535.37 | 535.37 |
| a (Å) | 8.3929(7) | 8.4045(5) | 8.6807(7) | 11.636(3) | 11.5367(12) |
| b (Å) | 15.4894(12) | 15.4654(8) | 9.5045(7) | 14.154(3) | 14.1314(16) |
| c (Å) | 17.3100(16) | 17.2962(11) | 13.79552(10) | 15.569(3) | 15.3922(19) |
| α (°) | 90 | 90 | 98.101(3) | 90 | 90 |
| β (°) | 90 | 90 | 97.742(2) | 90 | 90 |
| γ (°) | 90 | 90 | 103.706(3) | 90 | 90 |
| V (Å$^3$) | 2250.3(3) | 2248.1(2) | 1077.91(14) | 2564.0(9) | 2509.4(5) |
| Z | 4 | 4 | 2 | 4 | 4 |
| *D*c (g.cm$^{-3}$) | 1.335 | 1.337 | 1.388 | 1.387 | 1.417 |
| Crystal system | orthorhombic | orthorhombic | triclinic | orthorhombic | orthorhombic |
| Space group | P $2_1$ $2_1$ $2_1$ | P $2_1$ $2_1$ $2_1$ | P -1 | P $2_1$ $2_1$ $2_1$ | P $2_1$ $2_1$ $2_1$ |
| T (K) | 150 K | 150 K | 150 K | 293 K | 150 |
| Wavelength Mo-Kα (Å) | 0.71073 Å | 0.71073 Å | 0.71073 | 0.71073 | 0.71073 Å |
| μ (mm$^{-1}$) | 0.146 | 0.147 | 0.153 | 0.342 | 0.349 |
| *F* (000) | 944 | 944 | 468 | 1104 | 1104 |
| θ limit (°) | 3.001 to 27.484 | 3.380 to 27.472 | 3.030 to 27.478 | 2.986 to 27.479 | 2.206 to 27.466 |
| Index ranges *hkl* | -10 ≤ h ≤ 10 | -10 ≤ h ≤ 10 | -11 ≤ h ≤ 11 | -15 ≤ h ≤ 13 | -14 ≤ h ≤ 14 |
| | -20 ≤ k ≤ 20 | -19 ≤ k ≤ 20 | -12 ≤ k ≤ 12 | -18 ≤ k ≤ 17 | -14 ≤ k ≤ 18 |
| | -22 ≤ l ≤ 22 | -20 ≤ l ≤ 22 | -17 ≤ l ≤ 17 | -18 ≤ l ≤ 20 | -19 ≤ l ≤ 19 |
| Reflections collected | 42334 | 11309 | 25530 | 17033 | 13640 |
| Independant reflections | 5135 | 5042 | 4942 | 5854 | 5698 |
| Reflections [*I*>2σ(*I*)] | 4709 | 4434 | 4447 | 3824 | 5179 |
| Data / restraints / parameters | 5135 / 0 / 307 | 5042 / 0 / 307 | 4942 / 0 / 307 | 5854 / 0 / 322 | 5698 / 0 / 334 |
| Goodness-of-fit on $F^2$ | 1.040 | 1.035 | 1.025 | 1.043 | 1.062 |
| Final *R* indices [I>2σ(I)] | R1 = 0.0366 | R1 = 0.0410 | R1 = 0.0365 | R1 = 0.0794 | R1 = 0.0499 |
| | *wR2 =0.0847* | *wR2 =0.1021* | *wR2 = 0.0938* | *wR2 = 0.2281* | *wR2 =0.1316* |
| R indices (all data) | *R*1 = 0.0428 | *R*1 = 0.0513 | *R*1 = 0.0414 | *R*1 = 0.1225 | *R*1 = 0.0570 |
| | *wR*2 = 0.0881 | *wR*2 = 0.1083 | *wR*2 = 0.0971 | *wR*2 = 0.2668 | *wR*2 = 0.1393 |
| Largest diff peak and hole (e Å$^{-3}$) | 0.230, and -0.308 | 0.347, and -0.249 | 0.359, and -0.436 | 1.448, and -0.575 | 0.334, and -0.579 |

| **Compound** | **Rac-3** | **($R_P$,*M*)-3** |
|---|---|---|
| CCDC | 1921447 | 1921449 |
| Formula | $C_{32}H_{21}AuClP$ | $C_{32}H_{21}AuClP$ |
| MW | 668.87 | 668.87 |
| a (Å) | 9.0391(11) | 14.699(3) |
| b (Å) | 20.028(3) | 15.681(3) |
| c (Å) | 14.2025(19) | 24.869(4) |
| α (°) | 90 | 90 |
| β (°) | 108.406(4) | 90 |
| γ (°) | 90 | 90 |
| V (Å$^3$) | 2439.6(6) | 5732.2(19) |
| Z | 4 | 8 |
| *D*c (g.cm$^{-3}$) | 1.821 | 1.550 |
| Crystal system | monoclinic | orthorhombic |
| Space group | P $2_1$/c | P $2_1$ $2_1$ $2_1$ |
| T (K) | 150 K | 150 K |
| Wavelength Mo-Kα (Å) | 0.71073 Å | 0.71073 |
| μ (mm$^{-1}$) | 6.225 | 5.299 |
| *F* (000) | 1296 | 2592 |
| θ limit (°) | 2.034 to 27.485 | 2.068 to 27.503 |
| Index ranges *hkl* | -10 ≤ h ≤ 11 | -18 ≤ h ≤ 19 |
| | -22 ≤ k ≤ 25 | -18 ≤ k ≤ 20 |
| | -18 ≤ l ≤ 18 | -31 ≤ l ≤ 32 |
| Reflections collected | 18925 | 33629 |
| Independant reflections | 5536 | 13079 |
| Reflections [*I*>2σ(*I*)] | 5079 | 12599 |
| Data / restraints / parameters | 5536 / 0 / 316 | 13079 / 0 / 517 |
| Goodness-of-fit on $F^2$ | 1.093 | 1.065 |
| Final *R* indices [I>2σ(I)] | R1 = 0.0266 | R1 = 0.0438 |
| | wR2 =0.0635 | wR2 = 0.1123 |
| R indices (all data) | R1 = 0.0297 | R1 = 0.0454 |
| | wR2 = 0.0651 | wR2 = 0.1135 |
| Largest diff peak and hole (e Å$^{-3}$) | 1.215, and -1.917 | 1.929, and -3.555 |

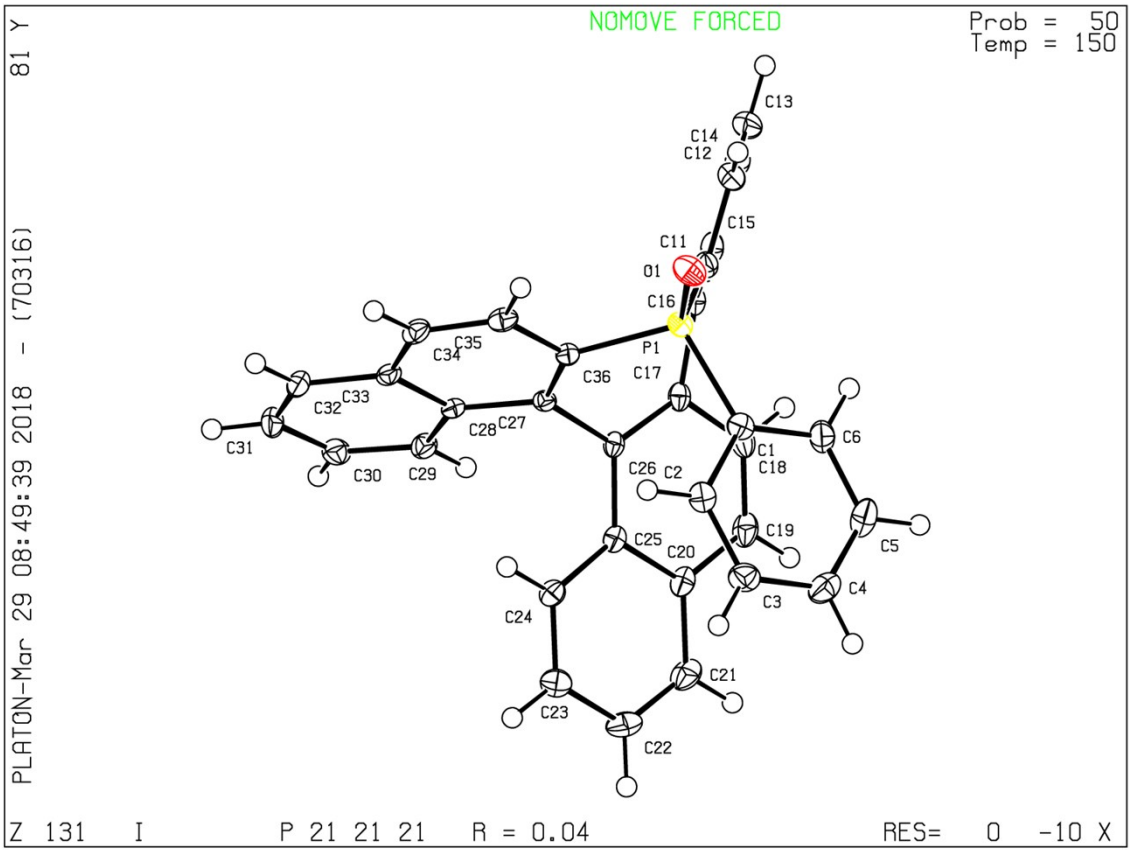



**Figure S4:** ORTEP representation of ($R_P$,*M*)-**1** with 50% probability ellipsoids

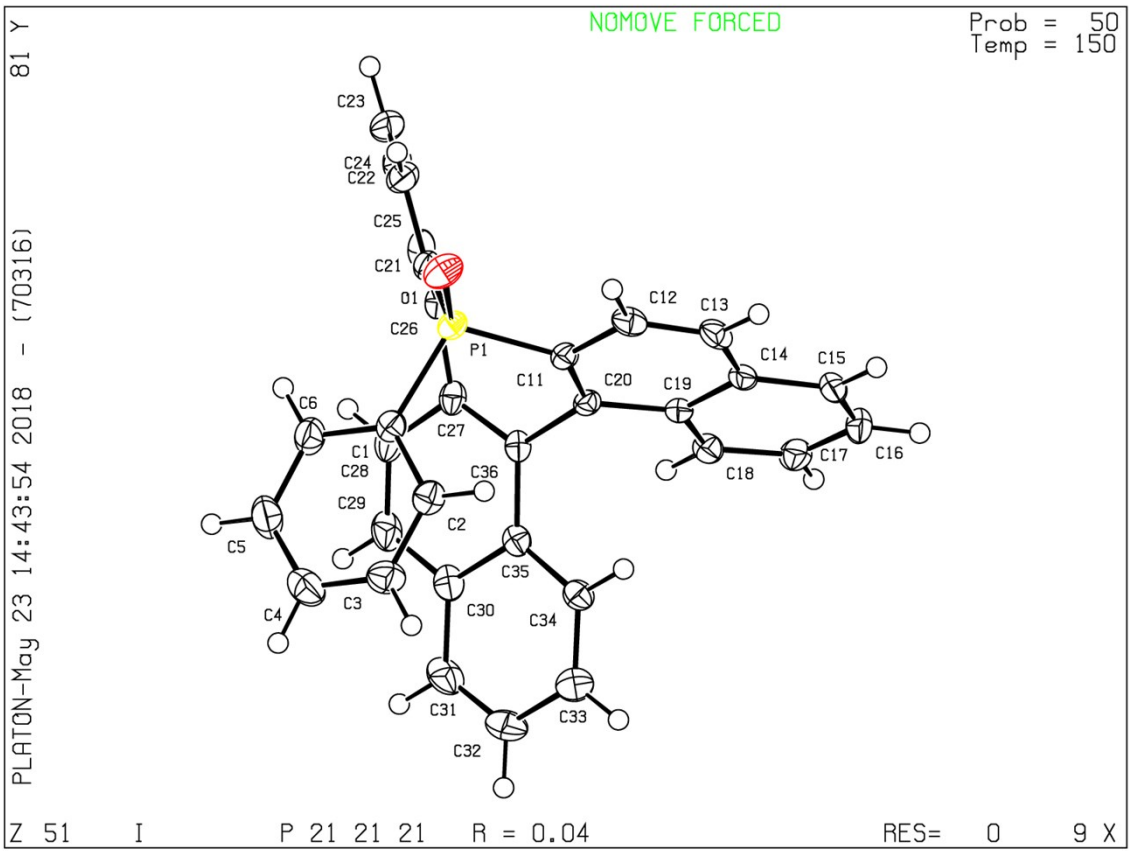



**Figure S5:** ORTEP representation of ($S_P$,*P*)-**2** with 50% probability ellipsoids

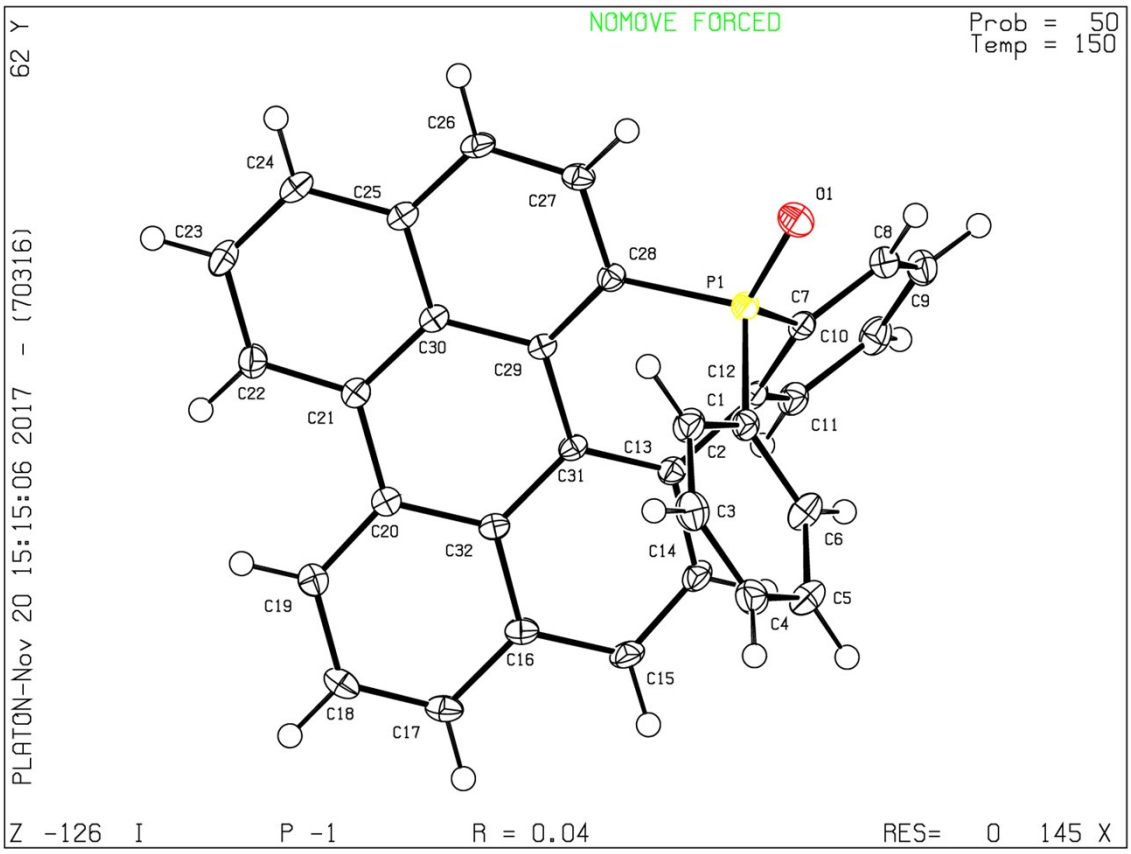



**Figure S6:** ORTEP representation of rac-**2** with 50% probability ellipsoids

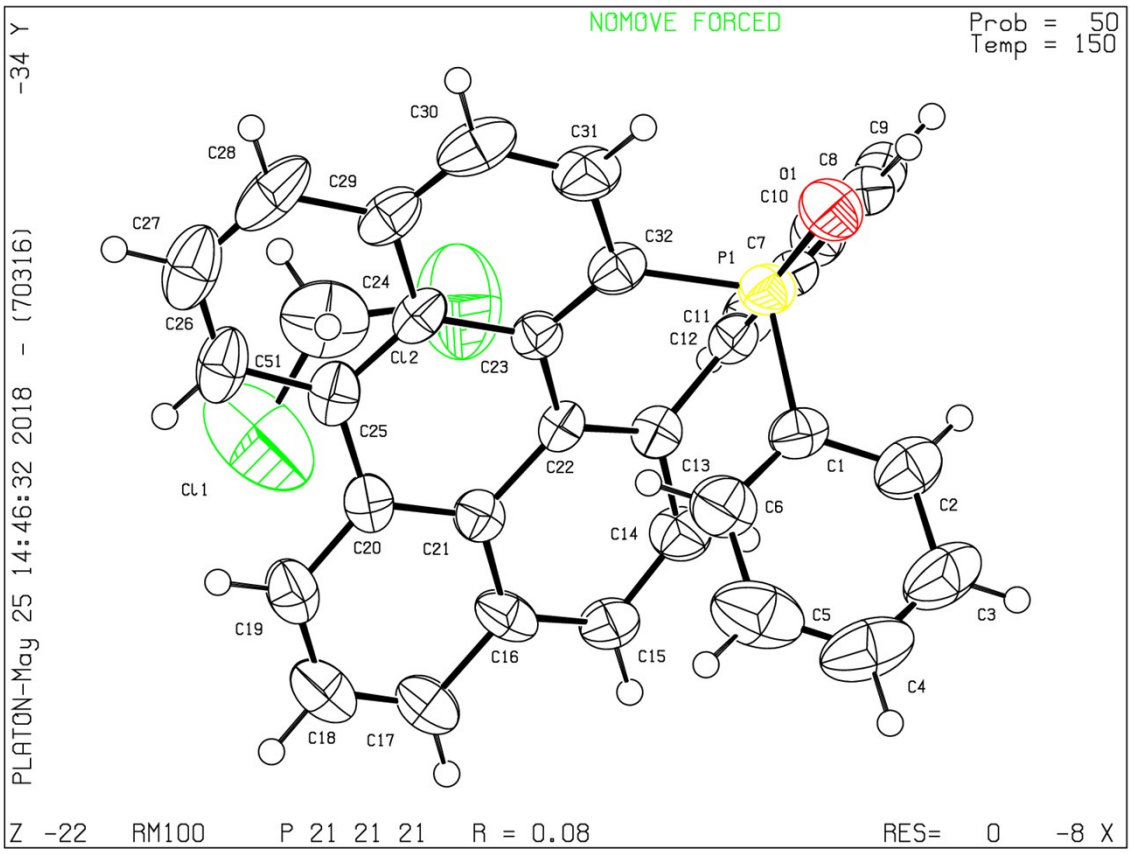



**Figure S7:** ORTEP representation of ($R_P$,*M*)-**2** with 50% probability ellipsoids

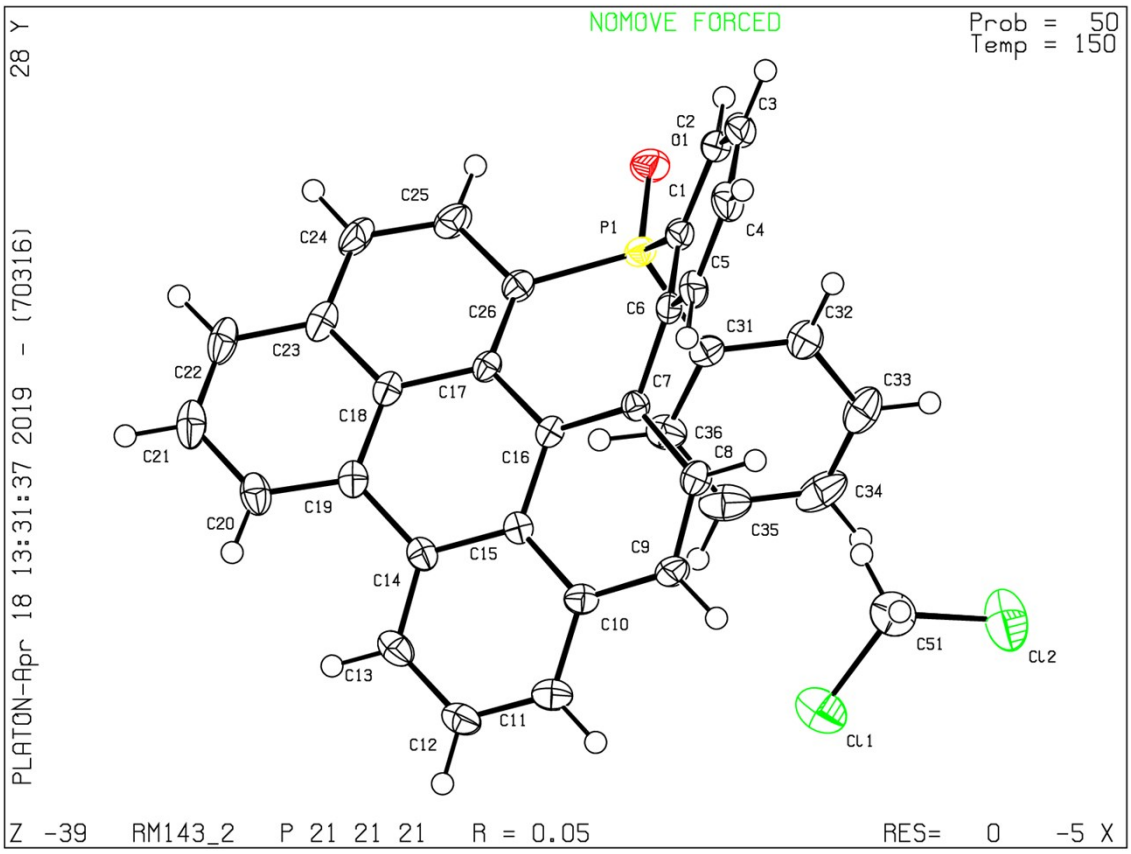



**Figure S8:** ORTEP representation of ($S_P$,*P*)-**2** with 50% probability ellipsoids

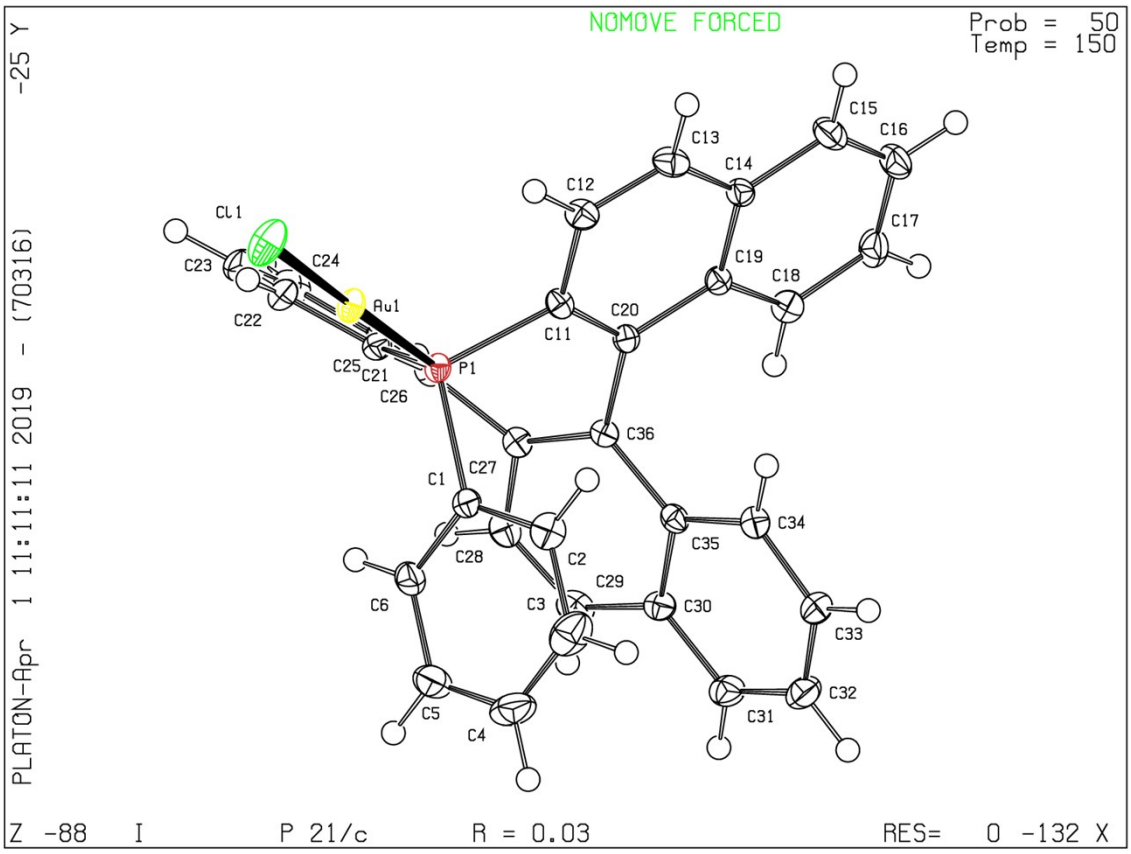



**Figure S9:** ORTEP representation of rac-**3** with 50% probability ellipsoids

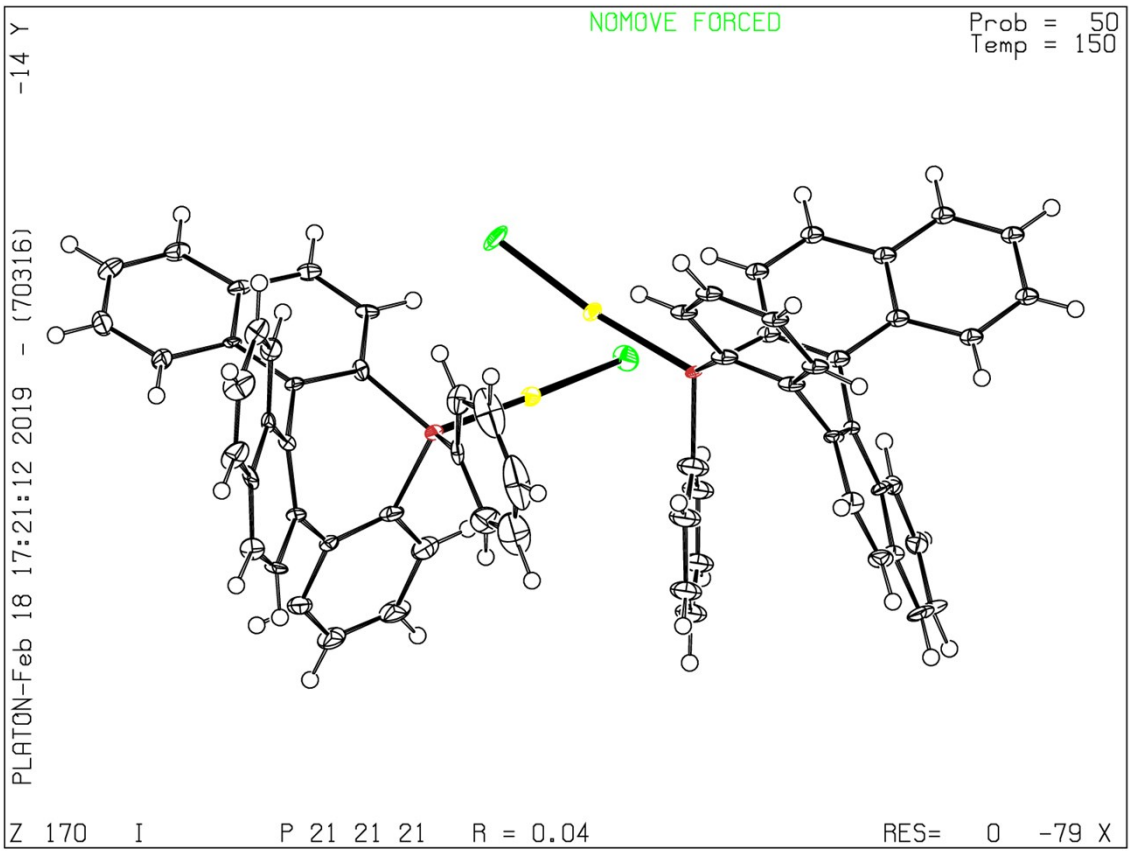



**Figure S10:** ORTEP representation of ($R_P$,*M*)-**3** with 50% probability ellipsoids

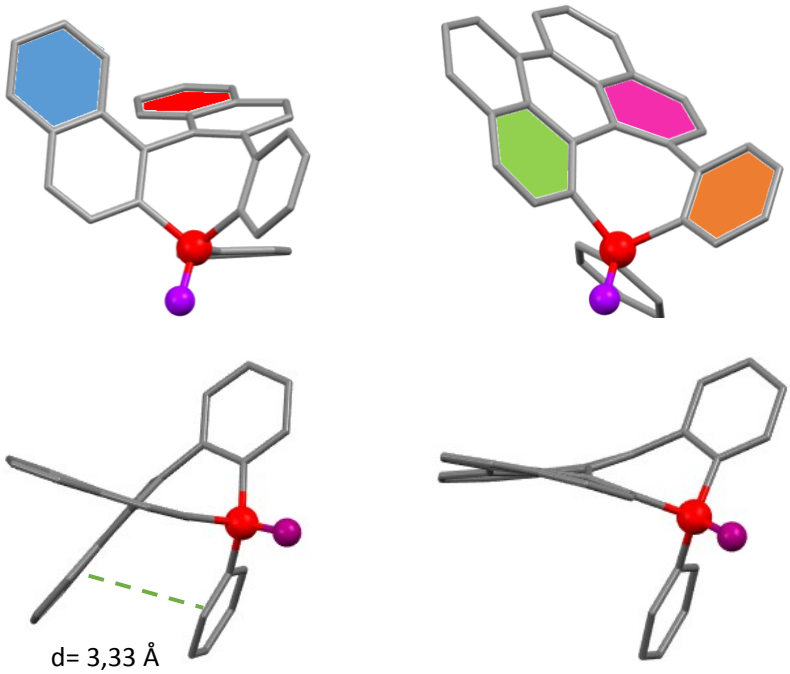



**Figure S11:** X-ray crystallographic structure of ($R_P$, *M*)-**1** (left) and ($R_P$, *M*)-**2** (right).

# Optical and electrochemical properties

**Table S2:** Optical and electrochemical properties

| | $\lambda_{abs}$[a] [nm] | log ε | $\lambda_{em}$[a] [nm] | Φ[b] [%] | $\lambda_{em}$[c] [nm] | Φ[d] [%] | $E_{ox}$[e] [V] | $E_{red}$[e] [V] | HOMO [eV] | LUMO [eV] |
|---|---|---|---|---|---|---|---|---|---|---|
| rac-**1** | 333 (331)[e] | 3.7 | 370 (397)[e] | 18 | 390 | x | - | - | -5.78[f] | -1.49[f] |
| ($R_P$,*M*)-**1** | 333 (331)[e] | 3.7 | 369 (397)[e] | 18 | 384 | x | - | - | -5.78[f] | -1.49[f] |
| ($S_P$,*P*)-**1** | 334 (331)[e] | 3.7 | 369 (397)[e] | 18 | 388 | x | - | - | -5.78[f] | -1.49[f] |
| rac-**2** | 444 (442)[e] | 4.3 | 462 (500)[e] | 79 | 540 | 10 | +0.84 | -1.98 | -5.23[f] | -2.18[f] |
| ($R_P$,*M*)-**2** | 443 (442)[e] | 4.3 | 461 (500)[e] | 80 | 538 | 10 | +0.80 | -1.96 | -5.23[f] | -2.18[f] |
| ($S_P$,*P*)-**2** | 444 (442)[e] | 4.2 | 462 (500)[e] | 76 | 537 | 10 | +0.83 | -1.97 | -5.23[f] | -2.18[f] |
| rac-**3** | 340 (344)[e] | 3.4 | 379 (398)[e] | <0.01 | 389 | x | - | - | -6.27[g] | -2.10[g] |

[a] In $CH_2Cl_2$ ($10^{-5}$M) [b] Measured relative to quinine sulfate ($H_2SO_4$, 0.1 M), Φ=55% [c] in powder [d]measured in powder in calibrated integration sphere [e]In $CH_2Cl_2$ with $Bu_4N^+PF_6^-$ (0.2M) at a scan rate of 100 $mVs^{-1}$. $E_{ox}(E_{red})=E_{pc}$ ($E_{pa}$). Potentials vs ferrocene/ferrocenium. [f] at the B3LYP/6-31G*//B3LYP/6-31+G* level [g] at the B3LYP/Def2-SVP level

Note that the integration sphere is not calibrated in the spectral range allowing the measurements of quantum yields for **1** and **3**.

**Redox properties**

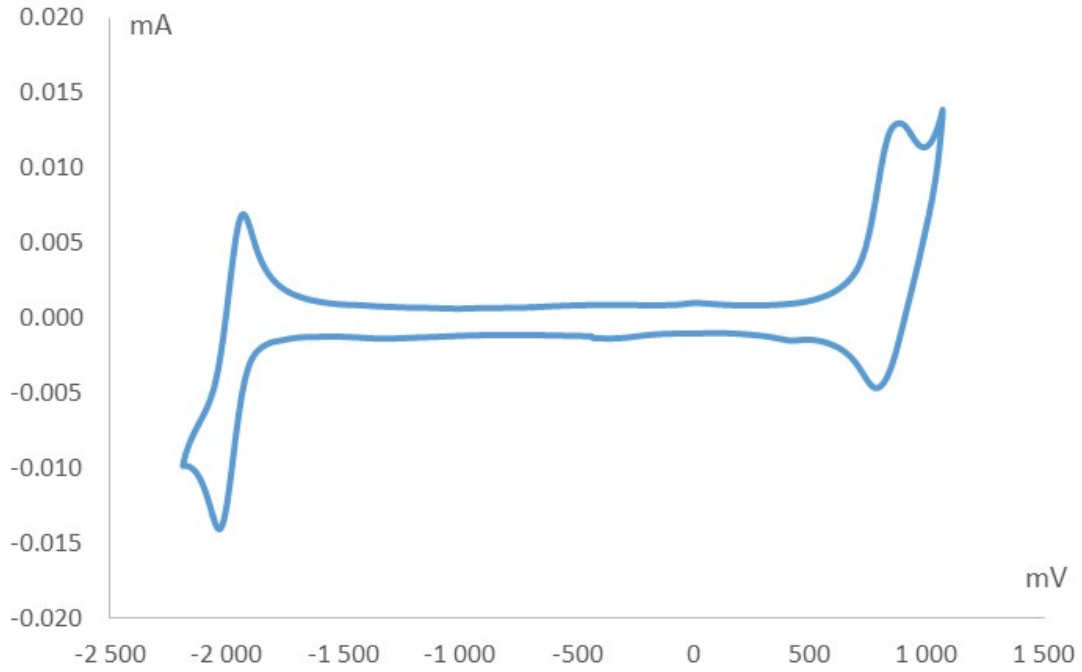



**Figure S12:** Cyclic voltammograms of rac-**2** recorded in DCM with $Bu_4N^+PF_6^-$ (0.2 M) at a scan rate of 100 $mVs^{-1}$. Potentials vs. Ferrocene/Ferrocenium

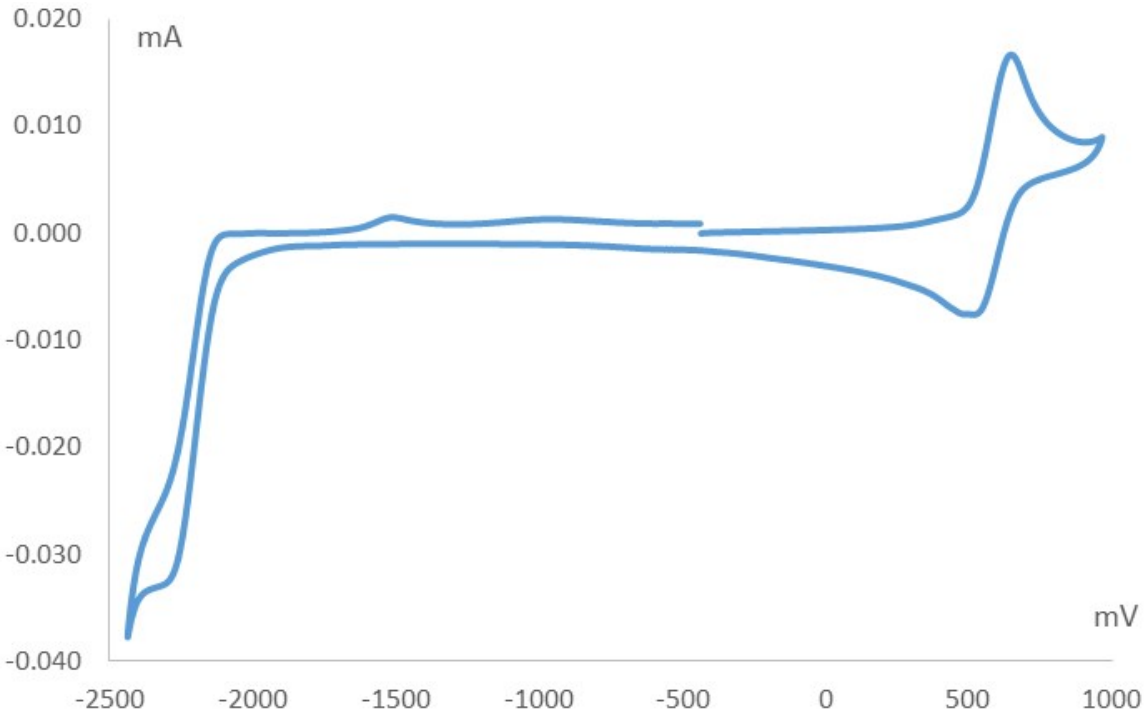



**Figure S13:** Cyclic voltammograms of perylene recorded in DCM with $Bu_4N^+PF_6^-$ (0.2 M) at a scan rate of 100 $mVs^{-1}$. Potentials vs. Ferrocene/Ferrocenium

**Spectroscopic properties (UV-vis, fluorescence)**

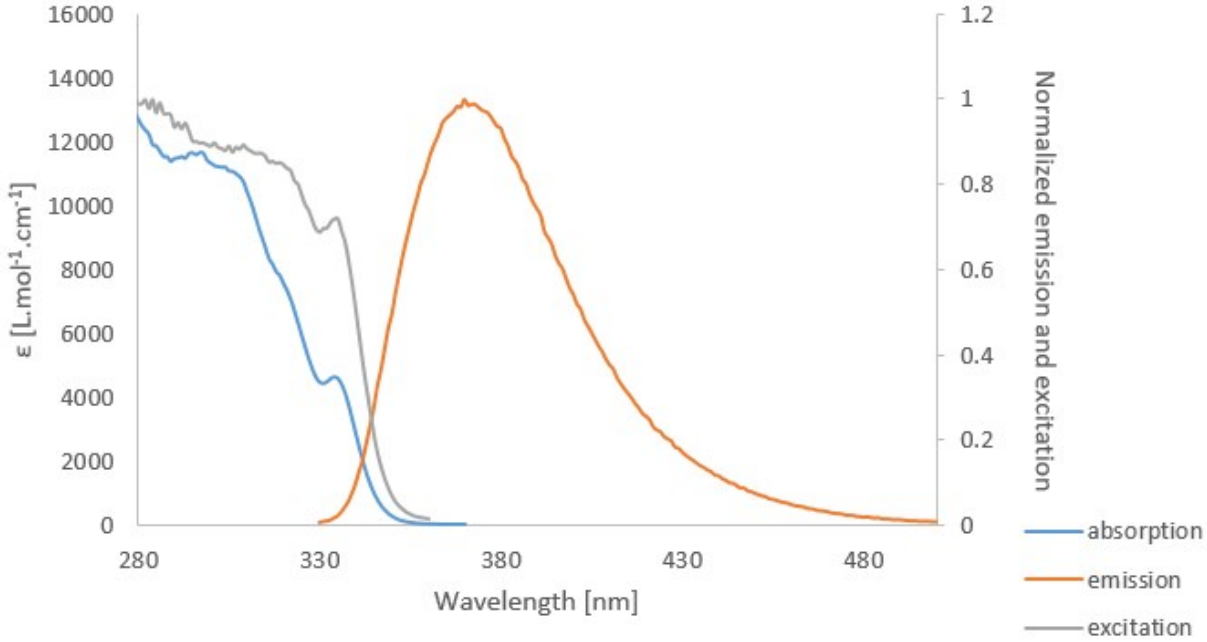



**Figure S14:** Absorption, emission and excitation spectra of rac-**1** in DCM at $6.10^{-5}$M

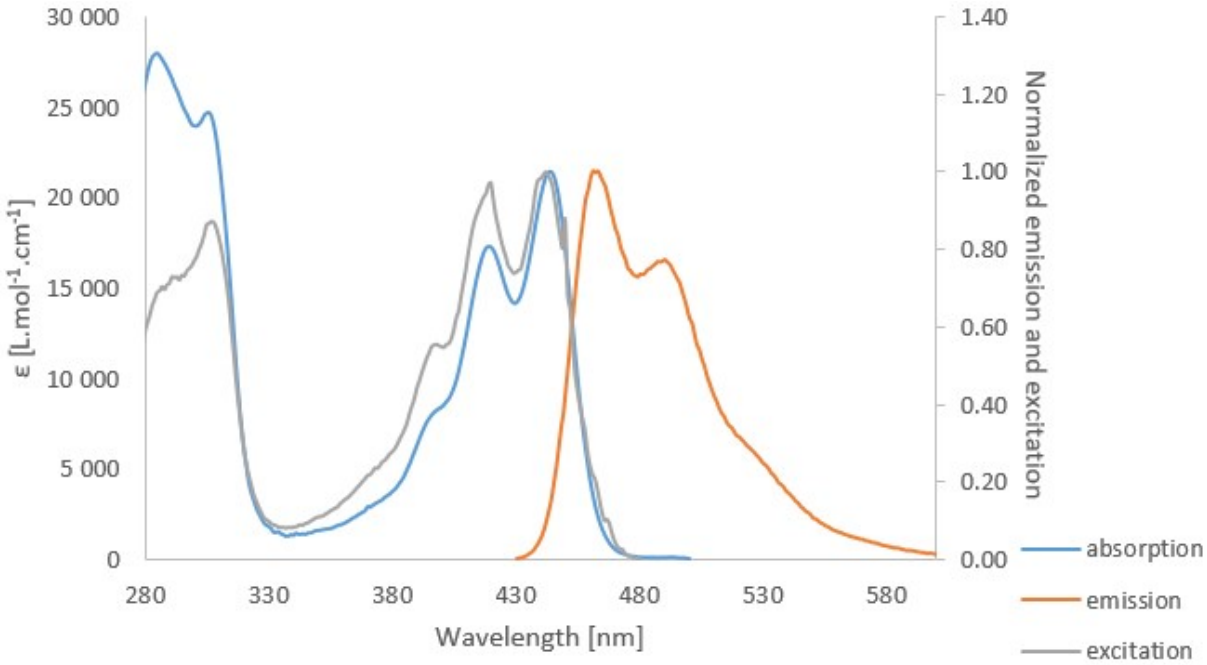



**Figure S15:** Absorption, emission and excitation spectra of rac-**2** in DCM at $4.10^{-6}$ M

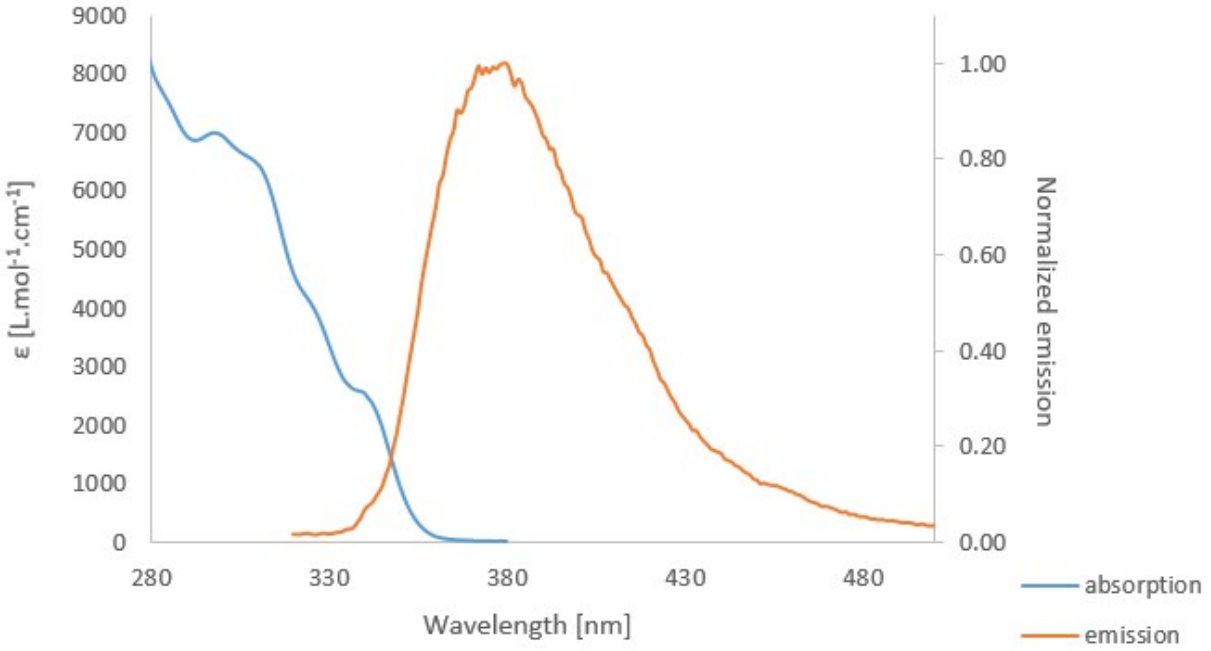



**Figure S16:** Absorption, emission and excitation spectra of rac-**3** in DCM at $1.10^{-4}$ M

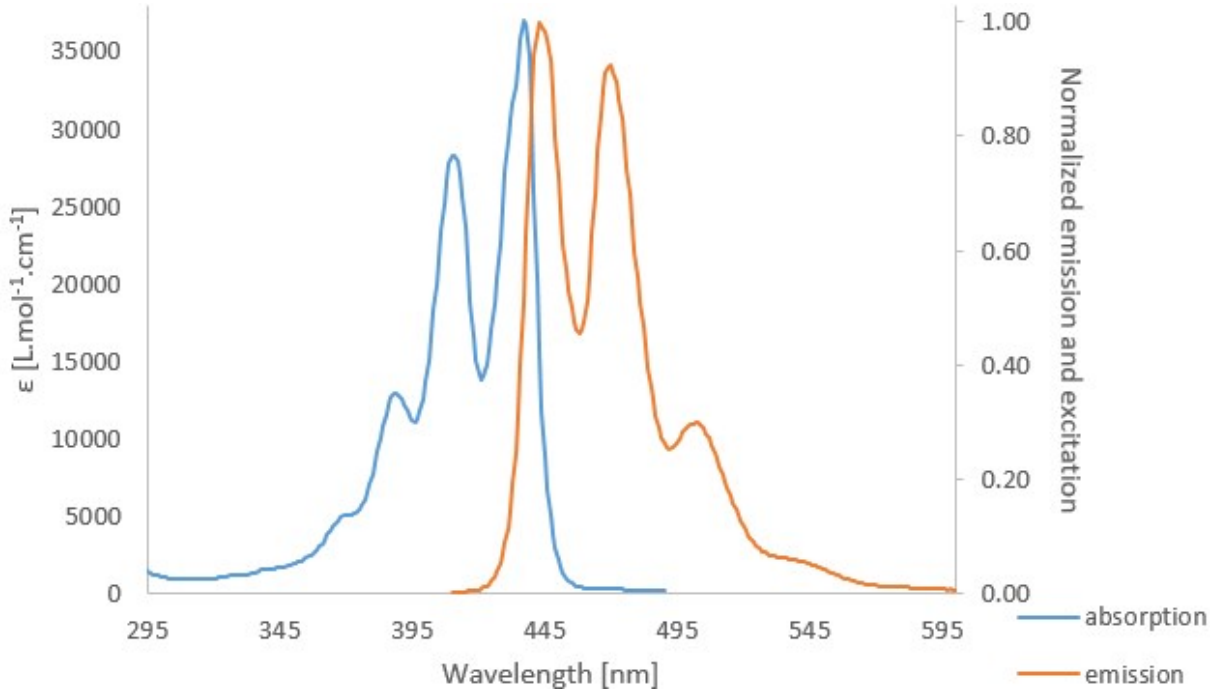



**Figure S17:** Absorption and emission spectra of perylene in DCM at $2.10^{-5}$ M

**Solid-state fluorescence**

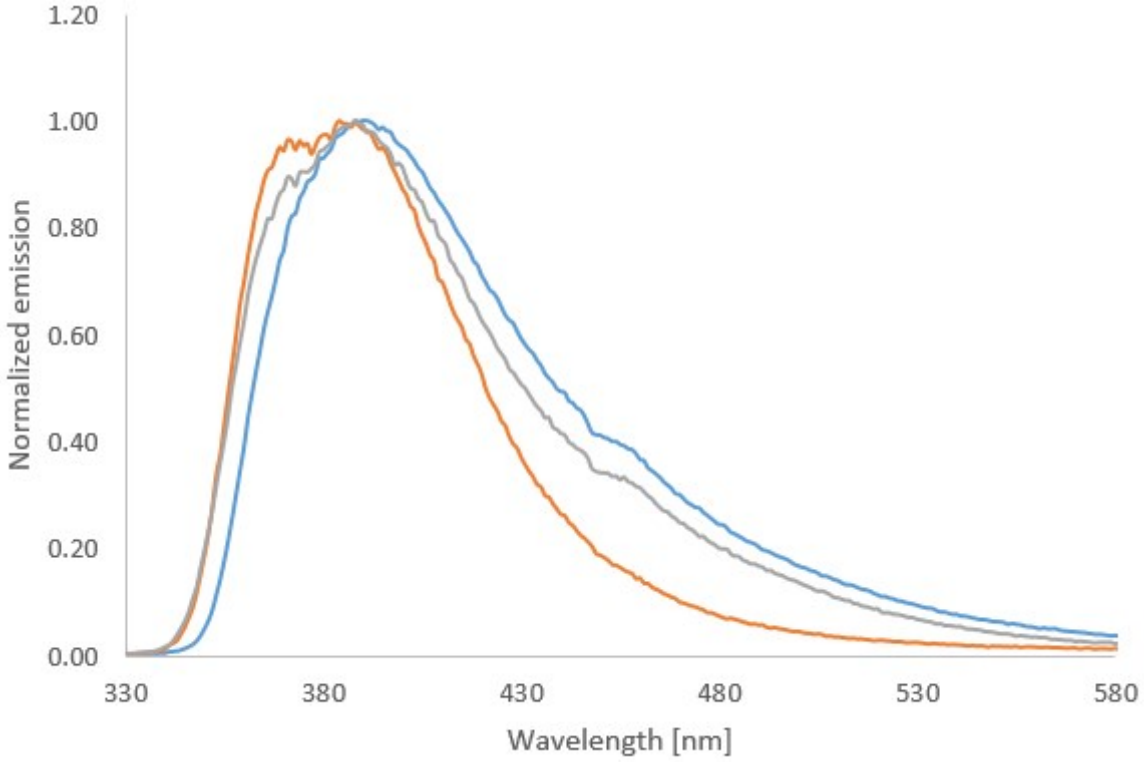



**Figure S18:** Emission of rac-**1** (blue), ($R_P$,*M*)-**1** (brown) and ($S_P$,*P*)-**1** (grey) in powder

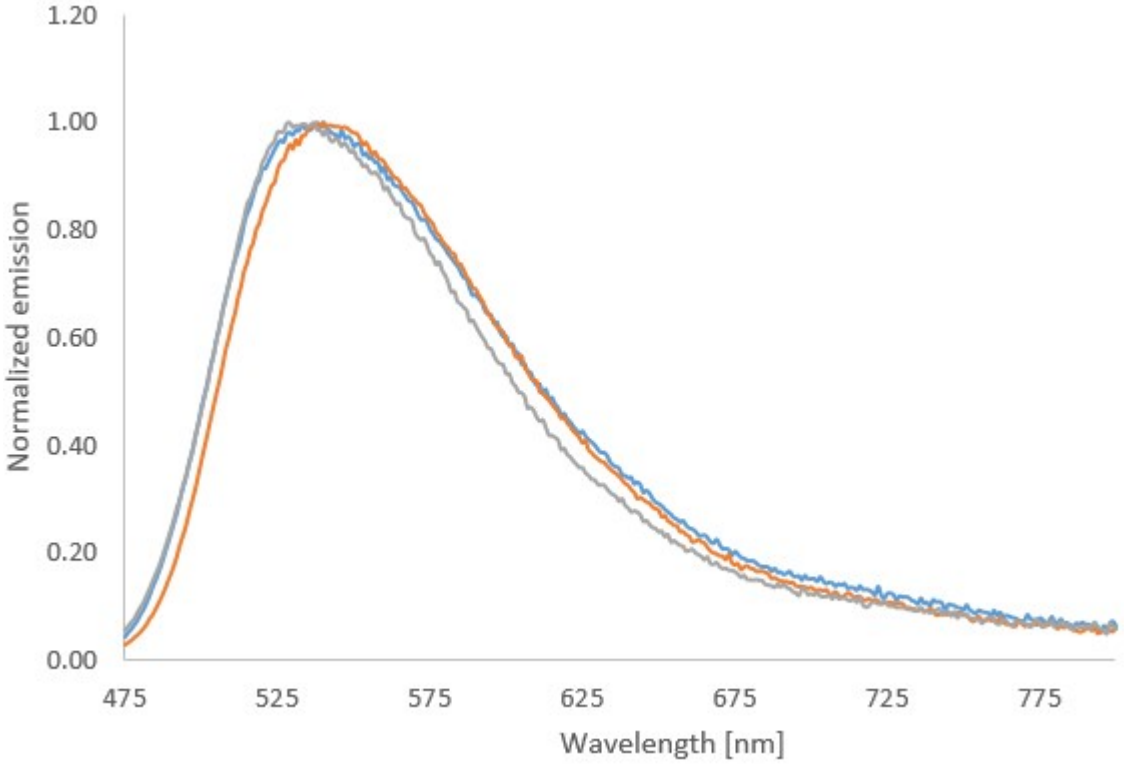



**Figure S19:** Emission of rac-**2** (blue), ($R_P$,*M*)-**2** (brown) and ($S_P$,*P*)-**2** (grey) in powder

**Low temperature fluorescence**

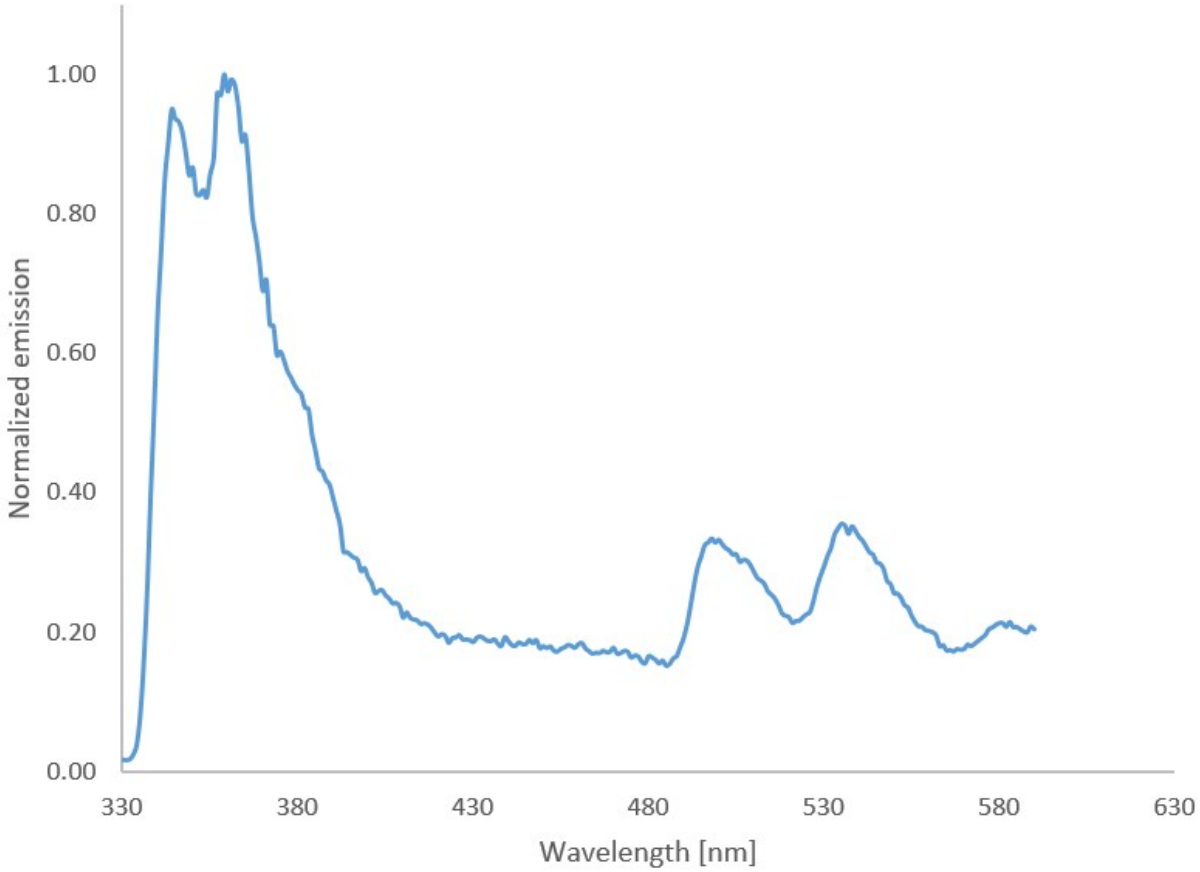



**Figure S20:** Emission of rac-**1** at 77K in 2-methyltetrahydrofuran

**Spectroelectrochemistry**

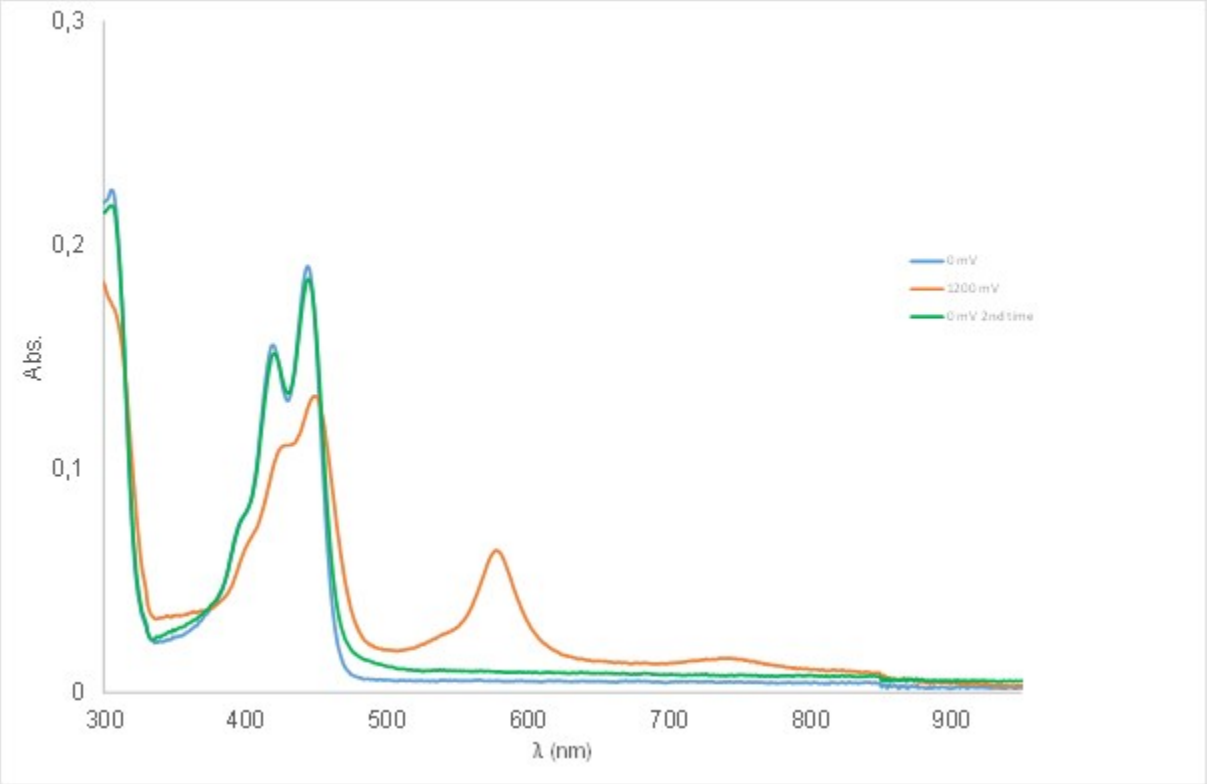



**Figure S21:** UV-Vis absorption upon electrochemical oxidation of rac-**2** in $CH_2Cl_2$

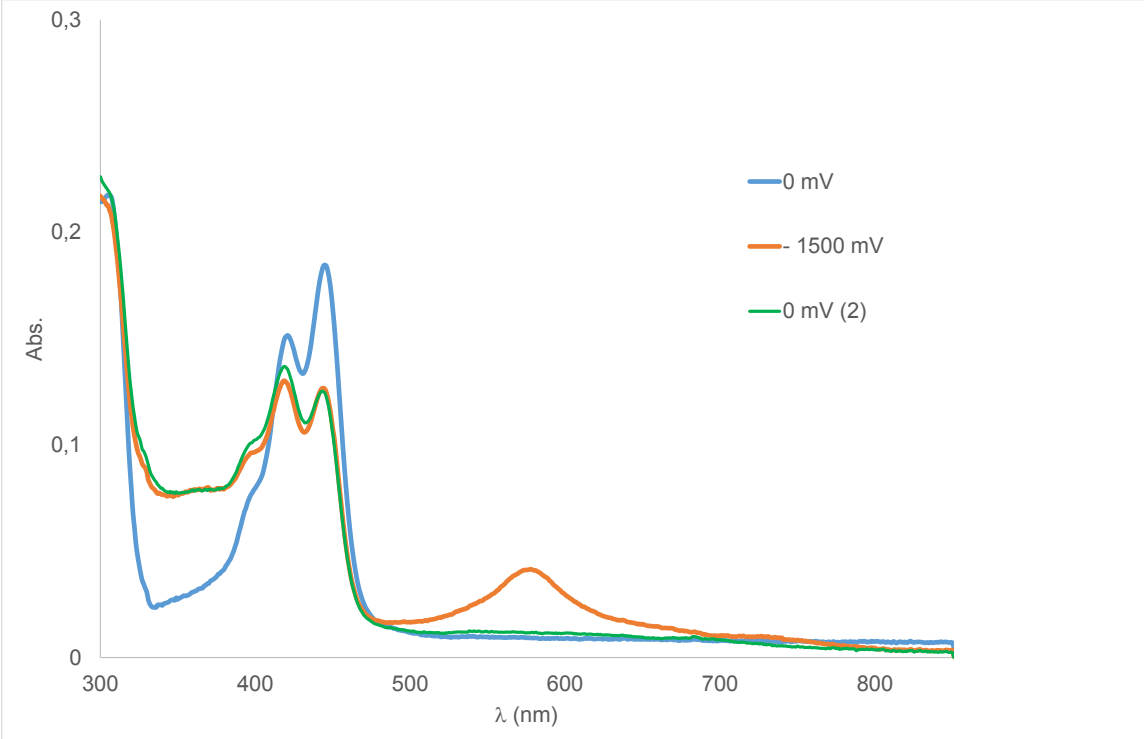



**Figure S22:** UV-Vis absorption upon electrochemical reduction of rac-**2** in $CH_2Cl_2$

**Chiroptical properties (CD, optical rotation)**

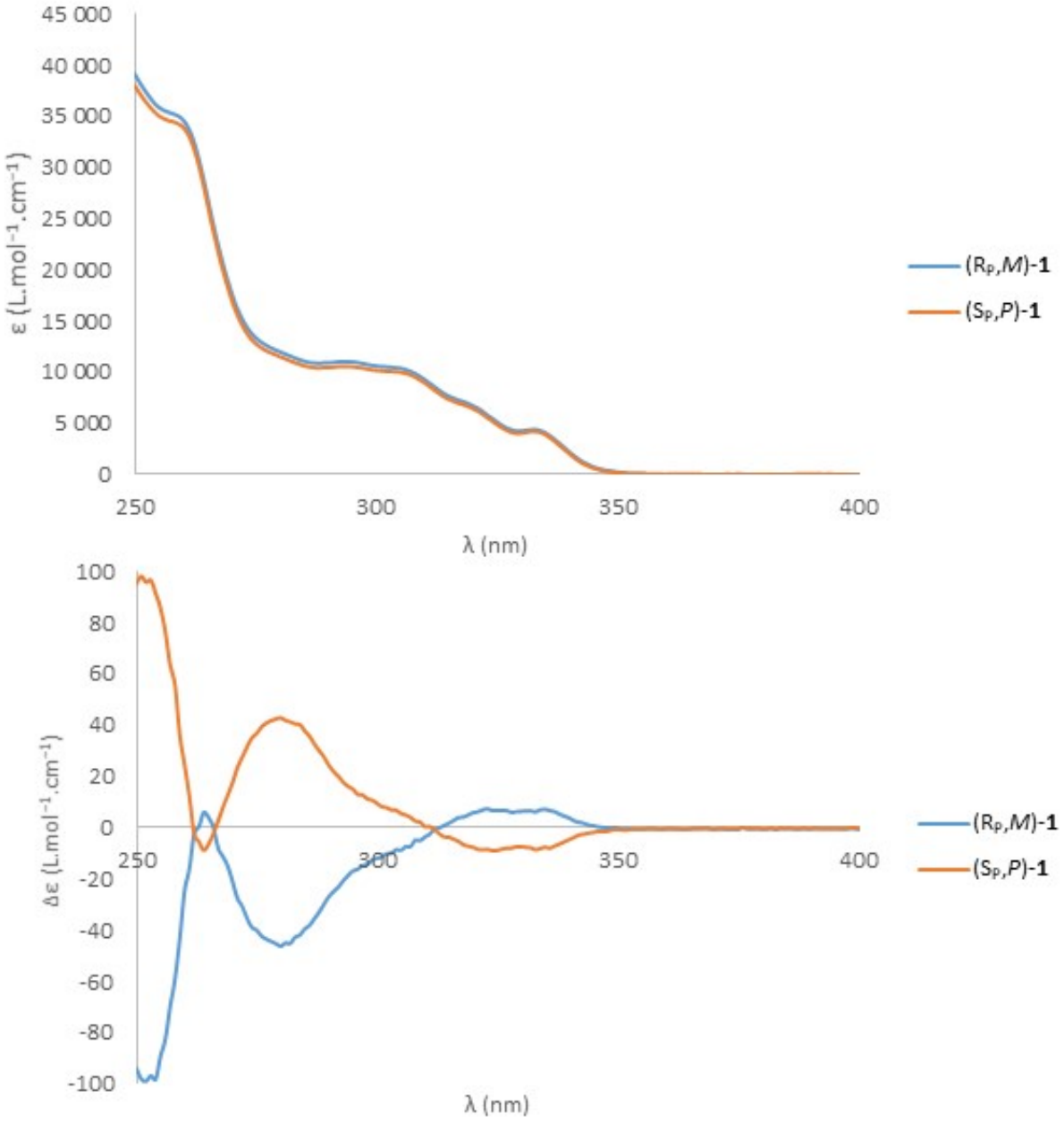



**Figure 23:** Absorption and ECD spectra of **1** in DCM at $5.10^{-5}$ M

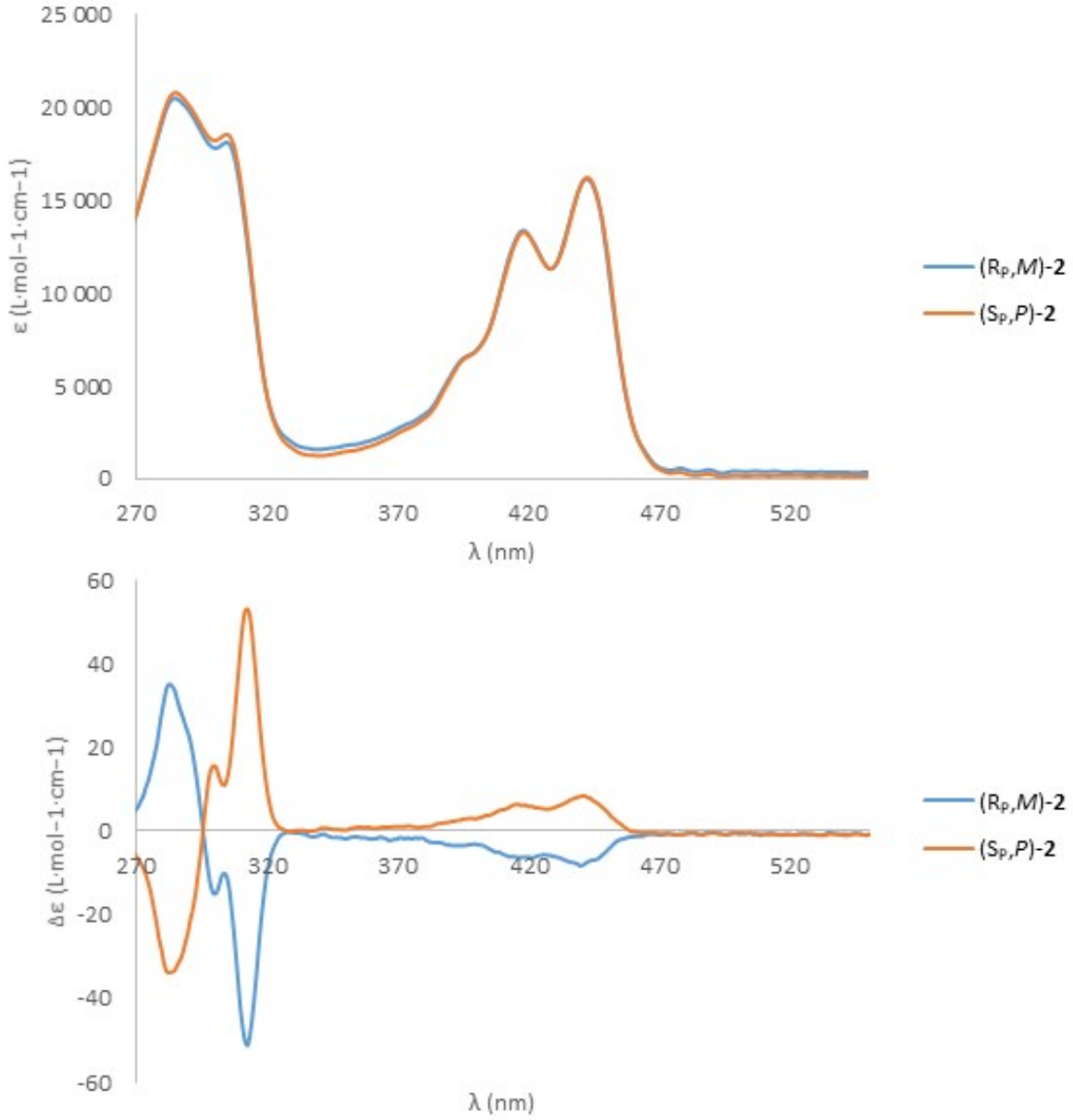



**Figure S24:** Absorption and ECD spectra of **2** in DCM at $4.10^{-5}$ M

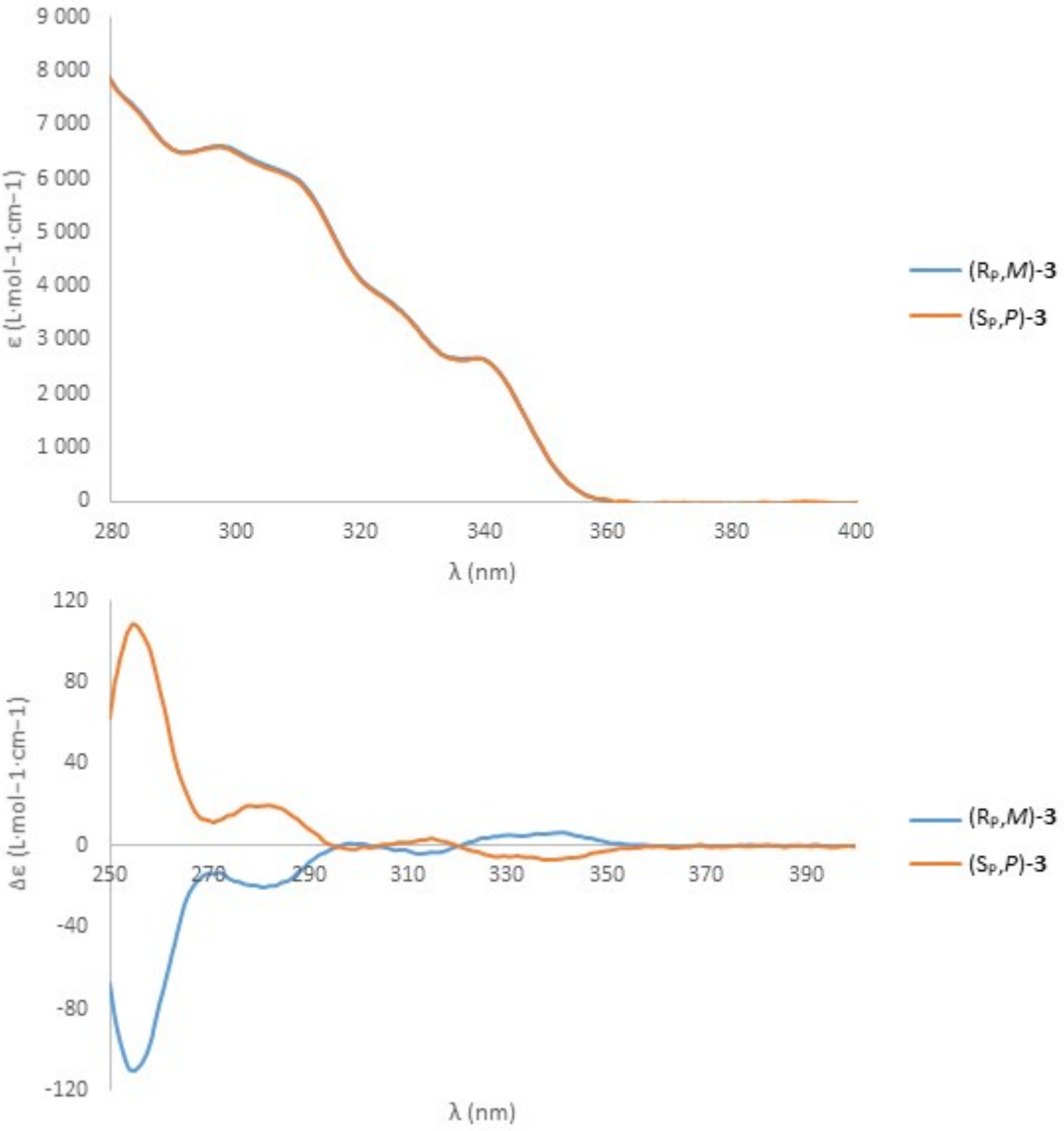



**Figure S25:** Absorption and ECD spectra of **3** in DCM at $4.10^{-5}$ M

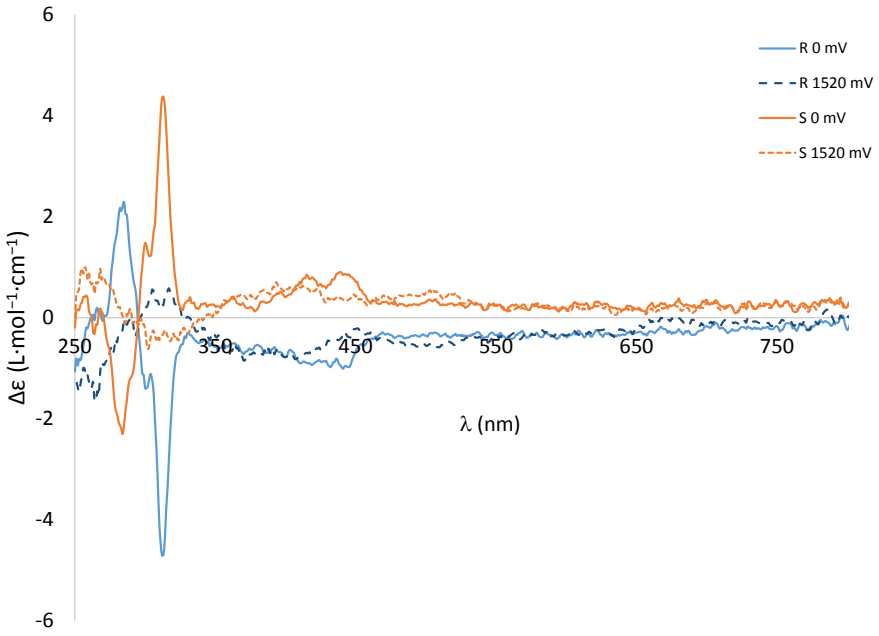



**Figure S26:** ECD spectra upon electrochemical reduction of **($S_P$, *P*)-2** and **($R_P$, *M*)-2** in $CH_2Cl_2$

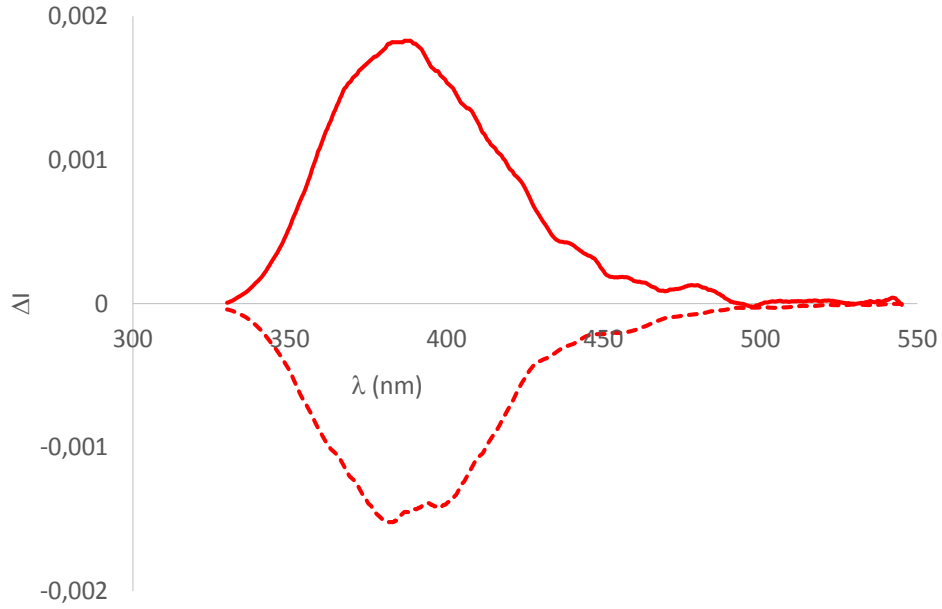



**Figure S27:** CPL spectra of ($R_P$, *M*)-**1** (red), ($S_P$, *P*)-**1** (red, dotted) (down) in diluted DCM at $10^{-5}$ M

## Optical rotation

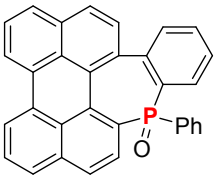
**Table S3:** Optical rotation data

| | $[\alpha]^{T}_{D}$ |
|---|---|
| R-**BINAP-O** | 225° (T=25.0 °C, c=7.03·10$^{-3}$ M) |
| S-**BINAP-O** | -199° (T=20.0 °C, c=4.12·10$^{-3}$ M) |
| ($R_P$,*M*)-**1** | -100° (T=20.0 °C, c=5.30·10$^{-3}$ M) |
| ($S_P$,*P*)-**1** | 113° (T=20.0 °C, c=6.52·10$^{-3}$ M) |
| ($R_P$,*M*)-**2** | -375° (T=20.0 °C, c=4.88·10$^{-3}$ M) |
| ($S_P$,*P*)-**2** | 396° (T=20.0 °C, c=4.22·10$^{-3}$ M) |
| ($R_P$,*M*)-**3** | -36° (T=20.0 °C, c=3.73·10$^{-3}$ M) |
| ($S_P$,*P*)-**3** | 35° (T=20.0 °C, c=3.59·10$^{-3}$ M) |

**SFC analysis (Supercritical Fluid Chromatography)**

Samples were analysed using a Shimadzu Nexera UC SFC/UHPLC system (Shimadzu Corporation, Japan) consisting of two LC-30AD quaternary modifier pumps and LC-30ADSF $CO_2$ pump. The Sil-30AC autosampler was composed of a sample loop of 5 µL and three needle-rinsing ports. The modifier pumps and needle rinsing were degassed with three degassing units (DGU-5AR and DGU-3AR). Two CTO-20AC column ovens were used. Eight chiral columns (Daicel Corporation, Japan) were installed for both ovens. Three valves were directly installed into these both ovens: one six port valve (FCV-32AH) to switch from SFC to UHPLC mode (or from UHPLC to SFC) and two seven port valves (FCV-34AH) to select one of these chiral columns for analysis. An adapted SPD-M20A diode array detector (DAD) with high-pressure cell and a Sedex LT-ELSD 85 detector (Sedere, France) were employed for detection. Internal pressure into the chromatographic system was regulated by a SFC-30A backpressure regulator (BPR). The entire system was driven by CBM-20A as system controller. The monitoring interface was the LabSolutions software. Analyses were automatically performed with the Nexera Method Scouting software to generate a large number of SFC/UHPLC methods by combining columns and modifiers.

**Enantiomeric excess determination**




Chemical Formula: $C_{32}H_{19}OP$
Molecular Weight: 450,4768

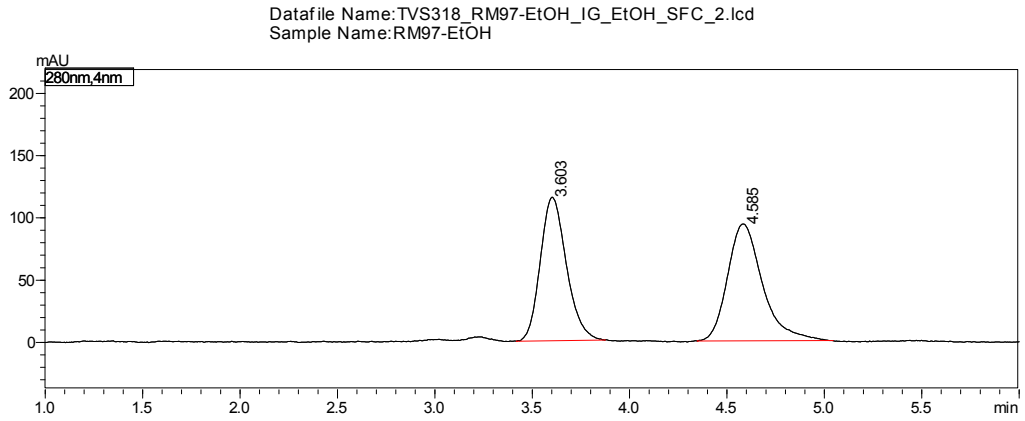
After screening of chromatographic conditions, enantiomeric purity was determined by SFC analysis in comparison with authentic racemic material (Chiralpack IG: 150 mm x 3 mm x 3 µm). Mobile phase (flow rate: 2 mL/min): solvent (A): $CO_2$ and solvent (B): EtOH with the following elution gradient program.

| Time | % solvent | %solvent |
|---|---|---|

| (min) | A | B |
|---|---|---|
| 0.00 | 55 | 45 |
| 7.00 | 55 | 45 |

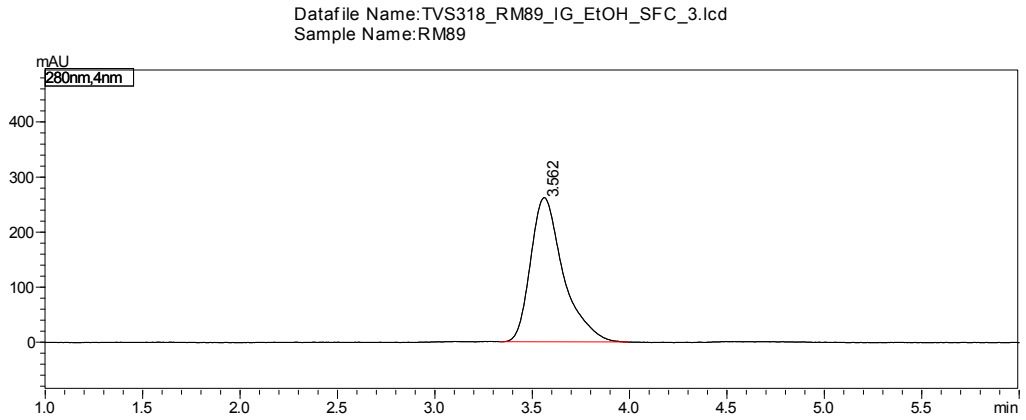
Column oven temperature: 40°C, back-pressure regulator (BPR): 150 bar, full loop injection (5 µL). DAD detector (200 nm - 450 nm, 3 Hz, cste : 0.32 sec). $t_{R1}$= 3.6 min, $t_{R2}$= 4.6 min.

rac-**2**:



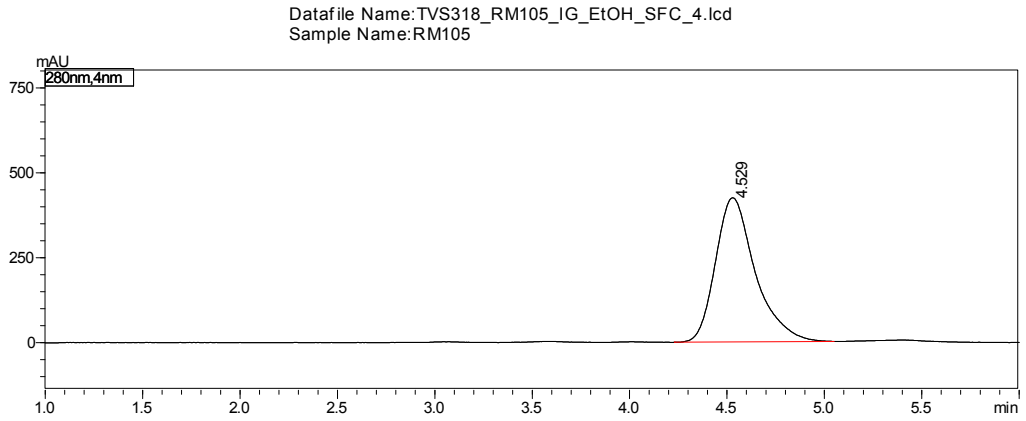

| Retention time | Area | Height | %Area | Resolution (USP) |
|---|---|---|---|---|
| 3.603 | 1074795 | 115214 | 47.870 | -- |
| 4.585 | 1170463 | 93962 | 52.130 | 3.489 |

($R_P$,*M*)-**2**:

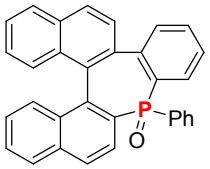



| Retention time | Area | Height | %Area | Resolution (USP) |
|---|---|---|---|---|
| 3.562 | 3051110 | 262111 | 100.000 | -- |
| | 3051110 | 262111 | 100.000 | |

($S_P$,*P*)-**2**:




| Retention time | Area | Height | %Area | Resolution (USP) |
|---|---|---|---|---|
| 4.529 | 6022142 | 424709 | 100.000 | -- |
| | 6022142 | 424709 | 100.000 | |



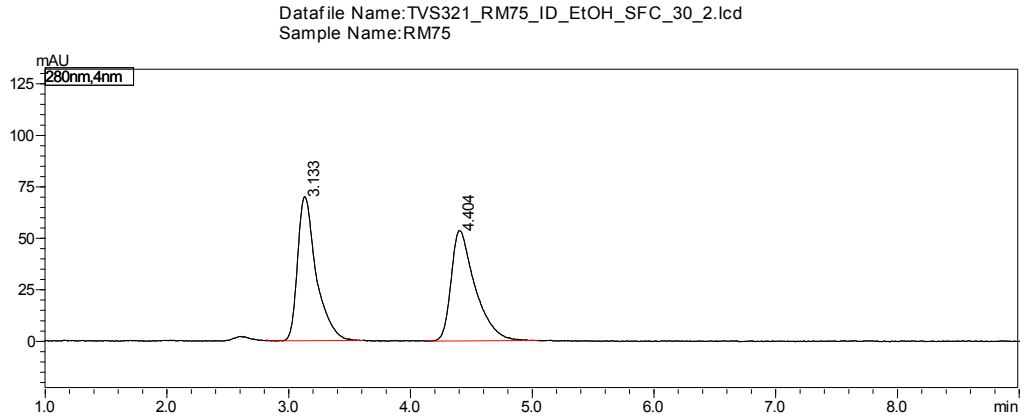

Chemical Formula: $C_{32}H_{21}OP$
Molecular Weight: 452,4928

After screening of chromatographic conditions, enantiomeric purity was determined by SFC analysis in comparison with authentic racemic material (Chiralpack ID: 150 mm x 3 mm x 3 µm). Mobile phase (flow rate: 2 mL/min): solvent (A): $CO_2$ and solvent (B): EtOH with the following elution gradient program.

| **Time (min)** | **% solvent A** | **%solvent B** |
|---|---|---|
| 0.00 | 70 | 30 |
| 10.00 | 70 | 30 |
| 10.01 | 50 | 50 |
| 13.00 | 50 | 50 |
| 13.01 | 70 | 30 |
| 15.00 | 70 | 30 |

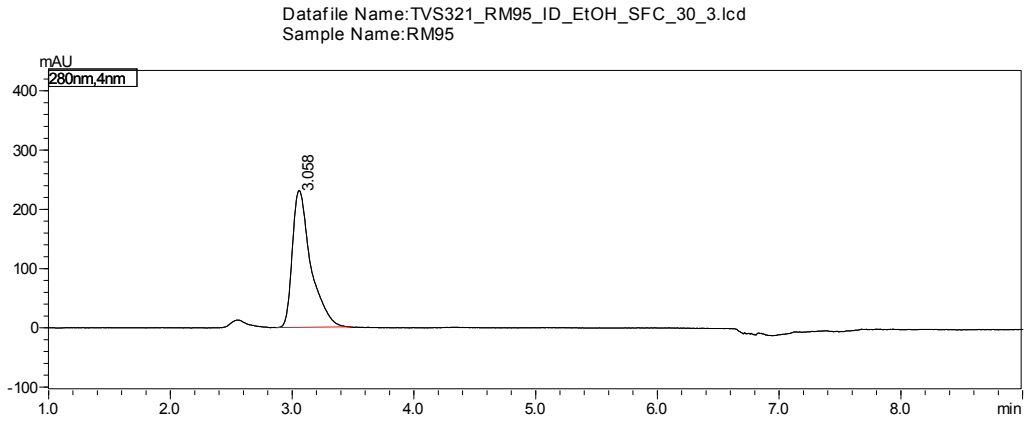
Column oven temperature: 40°C, back-pressure regulator (BPR): 150 bar, full loop injection (5 µL). DAD detector (200 nm - 450 nm, 3 Hz, cste : 0.32 sec). $t_{R1}$= 3.1 min, $t_{R2}$= 4.3 min.

rac-**1**:



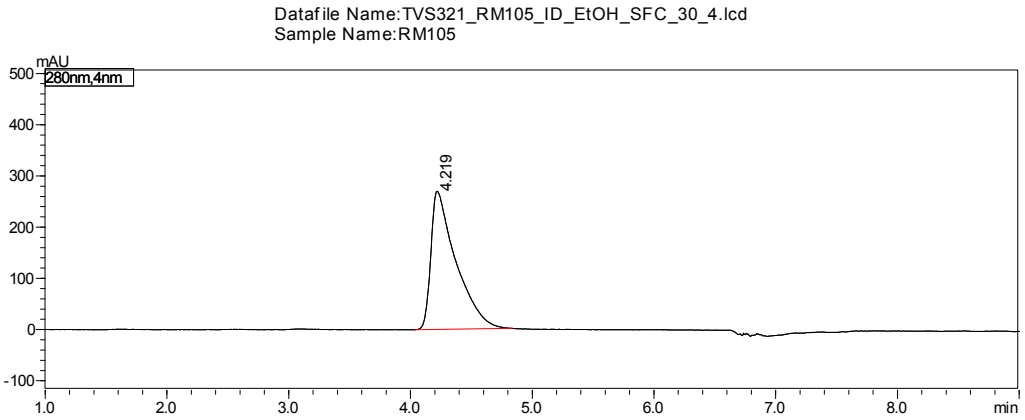

| Retention time | Area | Height | %Area | Resolution (USP) |
|---|---|---|---|---|
| 3.133 | 742809 | 69814 | 50.292 | -- |
| 4.404 | 734196 | 53273 | 49.708 | 4.239 |

($R_P$,*M*)-**1**:

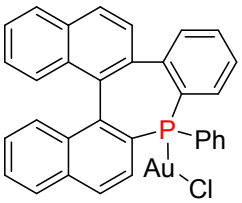



| Retention time | Area | Height | %Area | Resolution (USP) |
|---|---|---|---|---|
| 3.058 | 2422598 | 230815 | 100.000 | -- |

($S_P$,*P*)-**1**:




| Retention time | Area | Height | %Area | Resolution (USP) |
|---|---|---|---|---|
| 4.219 | 3853545 | 269847 | 100.000 | -- |



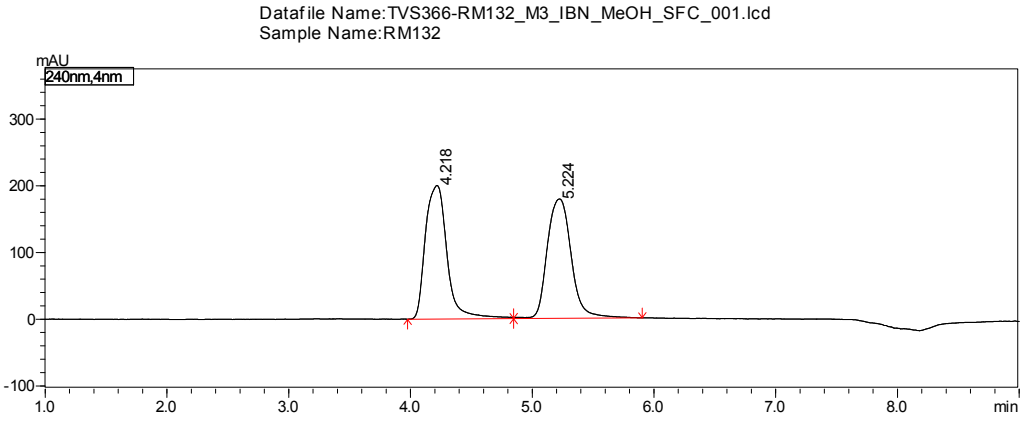

Chemical Formula: $C_{32}H_{21}AuClP$
Molecular Weight: 668.91

After screening of chromatographic conditions, enantiomeric purity was determined by SFC analysis in comparison with authentic racemic material (Chiralpack IBN: 150 mm x 3 mm x 3 µm). Mobile phase (flow rate: 2 mL/min): solvent (A): $CO_2$ and solvent (B): $CH_3OH$ with the following elution gradient program.

| **Time (min)** | **% solvent A** | **%solvent B** |
|---|---|---|
| 0.00 | 70 | 30 |
| 7.00 | 70 | 30 |
| 7.5 | 50 | 50 |
| 10.50 | 50 | 50 |
| 11.00 | 70 | 30 |
| 13.00 | 70 | 30 |

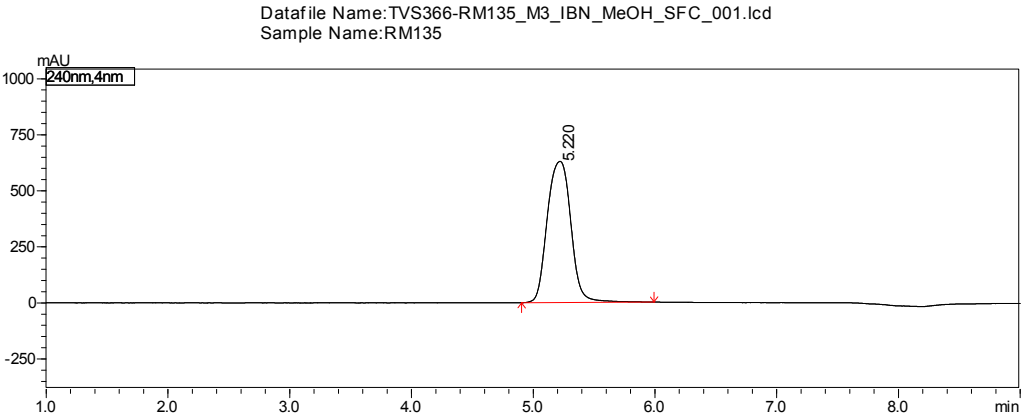
Column oven temperature: 40°C, back-pressure regulator (BPR): 150 bar, full loop injection (5 µL). DAD detector (200 nm - 450 nm, 3 Hz, cste : 0.32 sec). $t_{R1}$= 4.2 min, $t_{R2}$= 5.2 min.

rac-**3**:



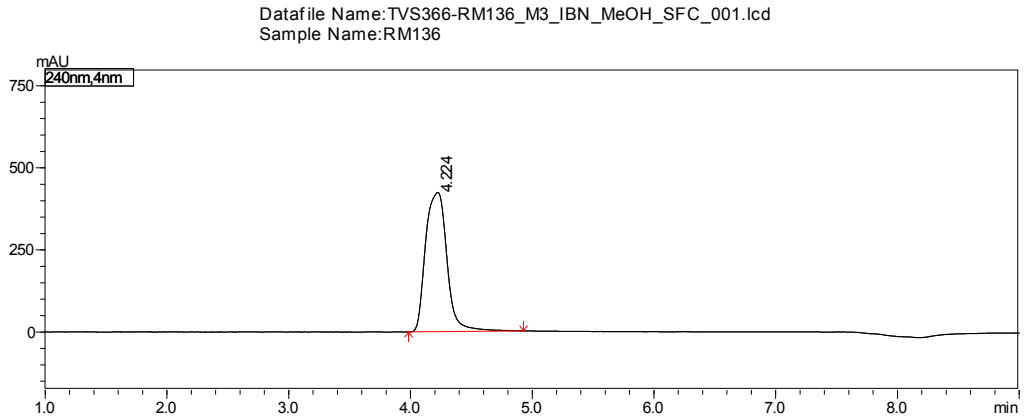

| Peak# | Ret. Time | Area | Height | Area% | Resolution(USP) |
|---|---|---|---|---|---|
| 1 | 4.218 | 2477877 | 200038 | 50.288 | -- |
| 2 | 5.224 | 2449530 | 178813 | 49.712 | 3.236 |

($R_P$,*M*)-**3**:




| Peak# | Ret. Time | Area | Height | Area% | Resolution(USP) |
|---|---|---|---|---|---|
| 1 | | | | | -- |
| 2 | 5.220 | 8519359 | 629551 | 100.000 | -- |

($S_p$,*P*)-**3**:




| Peak# | Ret. Time | Area | Height | Area% | Resolution(USP) |
|---|---|---|---|---|---|
| 1 | 4.224 | 5192364 | 423957 | 100.000 | -- |
| 2 | | | | | |

# Theoretical calculations

The computational results were obtained with the Gaussian 09[4] or with the MRRC[5] suite of programs. All structures were optimized using the B3LYP, B3LYP-D3, ωB97XD, M06-2X and cam-B3LYP functionals combined with the 6-31+G*, 6-31G*, cc-pVDZ and def2-SVP basis sets, and the ADC(2) method with def2-SVP basis set was also used In the case of all the optimized structures vibrational analysis was carried out to check whether the stationary point located is a minimum of the potential energy hypersurface (no imaginary frequencies were obtained) or a transition state (one imaginary frequency). For the TD-DFT calculations the first 20 excitations were considered. The geometries were plotted with the Molden program[6,7] and the molecular orbitals were visualized with the Avogadro program[8]. The CD spectra were plotted with the Gaussum program[9]. The spin densities were plotted with IQmol code[10].

[4] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[5] Mrcc, a quantum chemical program suite written by M. Kállay, P. R. Nagy, Z. Rolik, D. Mester, G. Samu, J. Csontos, J. Csóka, B. P. Szab´o, L. Gyevi-Nagy, I. Ladjánszki, L. Szegedy, B. Ladóczki, K. Petrov, M. Farkas, P. D. Mezei, and B. Hégely. See also Z. Rolik, L. Szegedy, I. Ladjánszki, B. Ladóczki, and M. Kállay, J. Chem. Phys. 139, 094105 (2013), as well as: www.mrcc.hu

[6] G. Schaftenaar, J. H. Noordik. J. Comput. Aided Mol. Des. 2000, 14. 123-134.

[7] G. Schaftenaar, E. Vlieg, G. Vriend. J. Comput. Aided. Mol. Des. 2017. 31, 789-800.

[8] https://avogadro.cc/

[9] N.M. O'Boyle, A.L. Tenderholt and K.M. Langner. J. Comp. Chem. 2008, 29, 839-845.

[10] iqmol.org

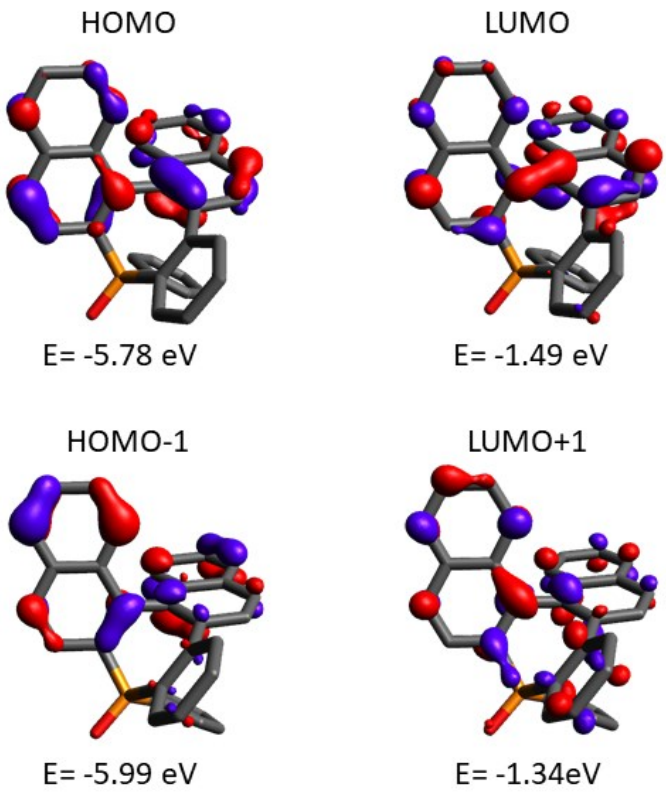



**Figure S28:** LUMO+1, LUMO, HOMO and HOMO-1 orbitals and their energies of **1** at the B3LYP/6-31G* level (Hydrogen atoms were omitted for clarity.)

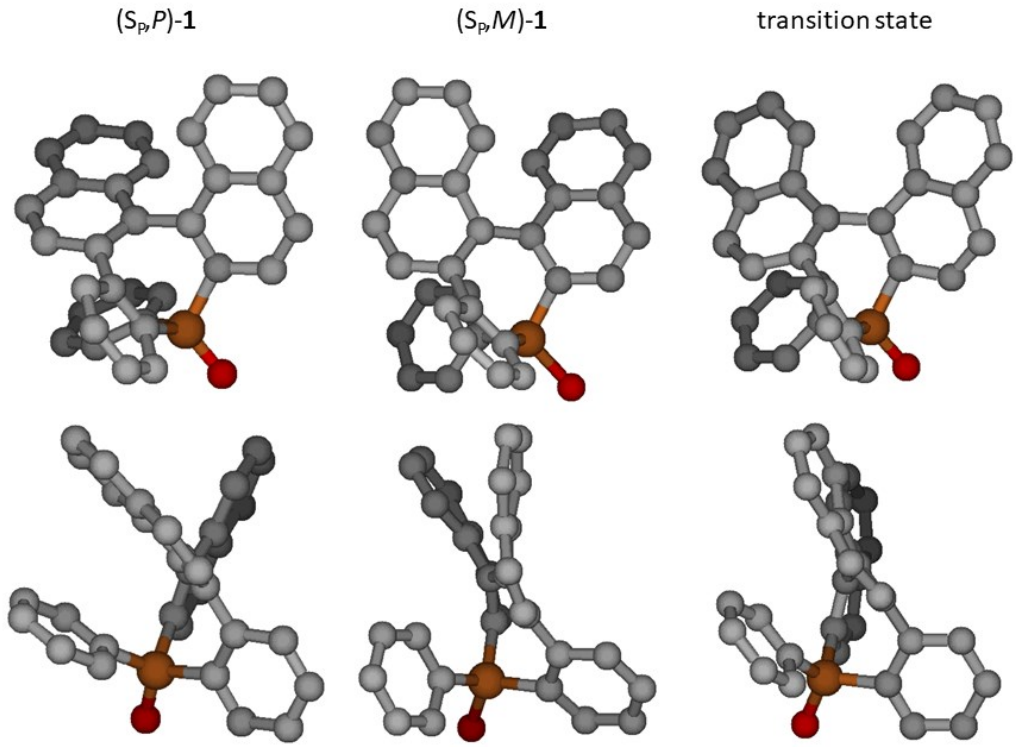



**Figure S29:** Side (up) and front (down) view of ($S_P$,*P*)-**1** and ($S_P$,M)-**1** and the transition state at the B3LYP-D3/cc-pVDZ level (Hydrogen atoms were omitted for clarity.)

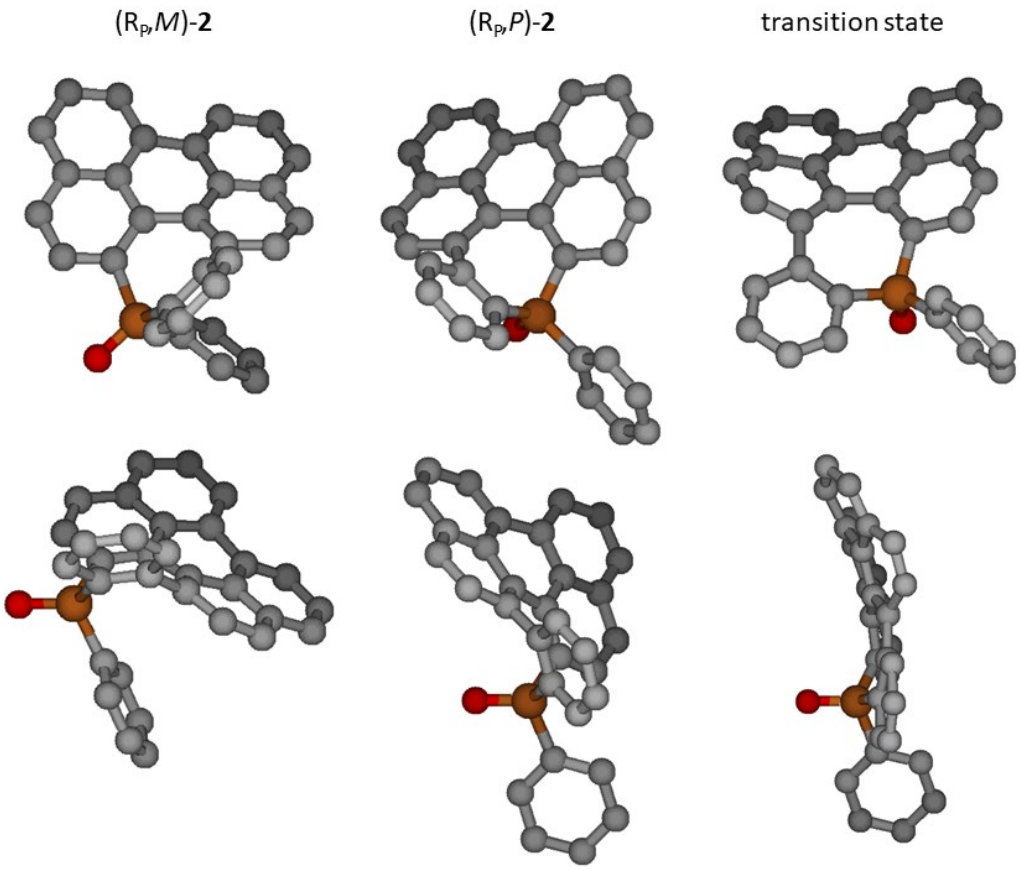



**Figure S30:** Side (up) and front (down) view of (R$_P$,*M*)-**2** and (R$_P$,*P*)-**2** and the transition state at the B3LYP-D3/cc-pVDZ level (Hydrogen atoms were omitted for clarity.)

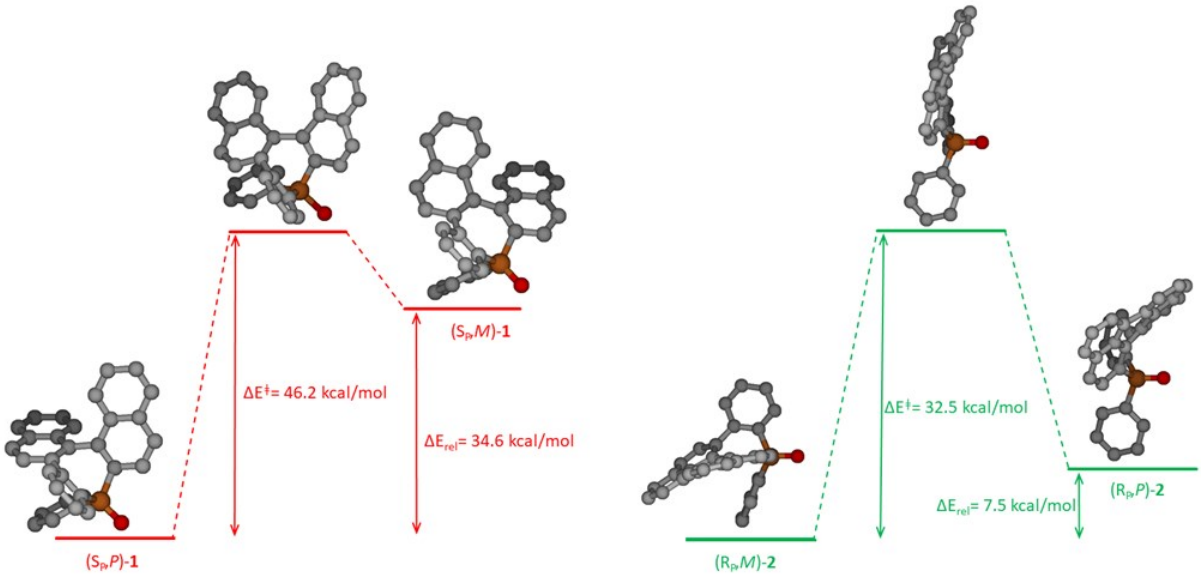



**Figure S31:** Inversion products and the corresponding activation barriers at the B3LYP-D3/cc-pVDZ level (Red and green curves denote compounds **1** and **2**, respectively.)

**Table S4:** Racemization barriers of **1** and **2** and the energy difference of the two isomers at the different level of theory

| Theory level | **ΔE (ΔG) between [kcal/mol]** | | | |
|---|---|---|---|---|
| | ($S_P$,*P*)-**1** and the transition state | ($S_P$,*P*)-**1** and ($S_P$,M)-**1** | ($R_P$,*M*)-**2** and the transition state | ($R_P$,*M*)-**2** and ($R_P$,*P*)-**2** |
| B3LYP/ 6-31+G* | 46.7 (46.8) | 33.2 (32.7) | 29.5 (30.8) | 4.9 (5.8) |
| B3LYP-D3/ cc-pVDZ | 46.2 (46.6) | 34.6 (33.8) | 32.5 (33.3) | 7.5 (8.0) |
| ωB97XD/ cc-pVDZ | 47.3 (47.5) | 37.1 (35.8) | 34.6 (35.8) | 8.2 (9.3) |

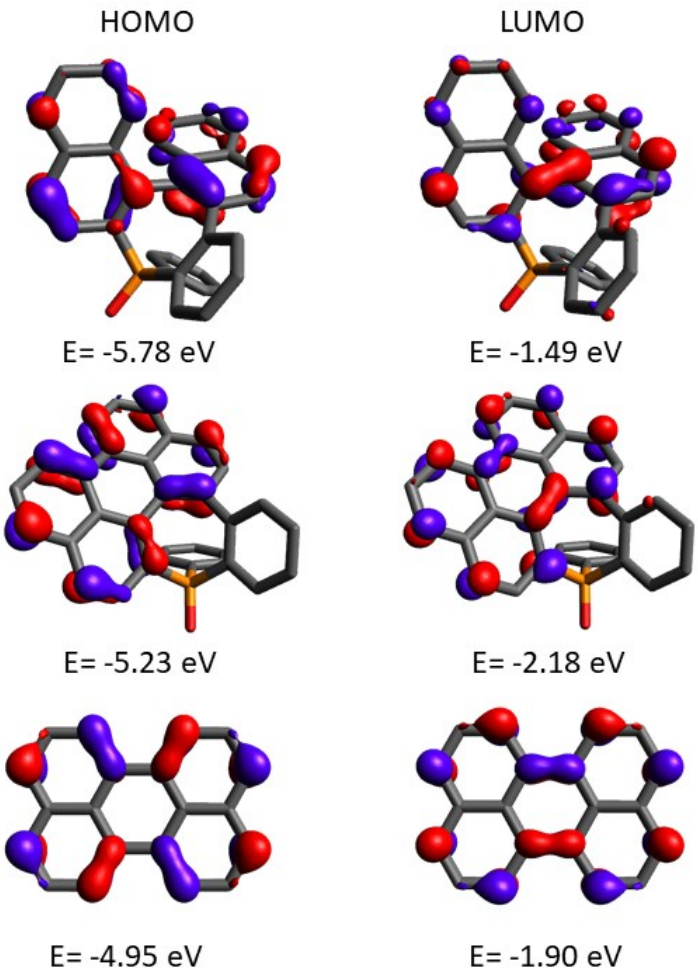
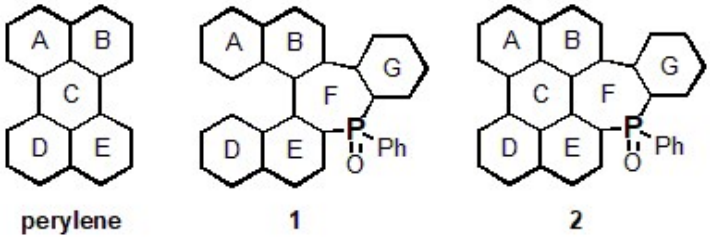
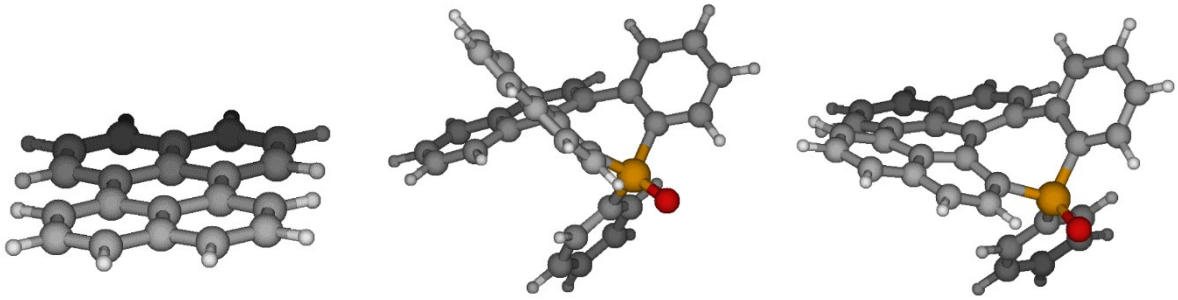



**Figure S32:** HOMO and LUMO of **1** (up) and **2** (middle) and perylene (down) calculated at the B3LYP/6-31G*//B3LYP/6-31+G* level

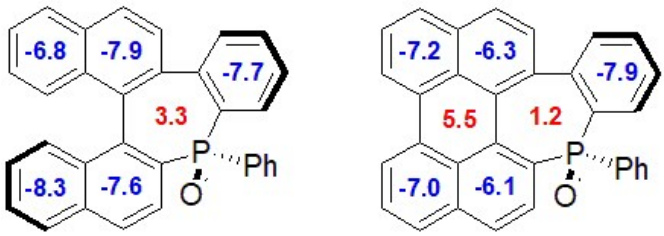
**Table S5:** NICS(-1), NICS(0) and NICS(1) values of **perylene**, **1** and **2** at the B3LYP/6-311+G**/B3LYP/6-31+G* level The NICS(-1) and NICS(1) values correspond to the direction depicted on stick representation, the NICS(1) value is calculated above the ring planes.



| | perylene | | | 1 | | | 2 | | |
|---|---|---|---|---|---|---|---|---|---|
| | NICS(n) | | | | | | | | |
| **n** | **-1** | **0** | **1** | **-1** | **0** | **1** | **-1** | **0** | **1** |
| **A** | -8.44 | -5.83 | -8.32 | -11.51 | -6.80 | -10.36 | -9.23 | -7.16 | -9.74 |
| **B** | -8.33 | -5.78 | -8.27 | -11.21 | -7.88 | -8.86 | -9.02 | -6.33 | -8.58 |
| **C** | 2.75 | 7.86 | 2.74 | - | - | - | 0.77 | 5.50 | 0.75 |
| **D** | -8.30 | -5.87 | -8.34 | -10.04 | -8.31 | -10.90 | -9.63 | -6.99 | -9.30 |
| **E** | -8.31 | -5.82 | -8.43 | -9.15 | -7.61 | -10.18 | -8.77 | -6.07 | -8.75 |
| **F** | - | - | - | -1.11 | 3.34 | -1.36 | -2.11 | 1.20 | -2.40 |
| **G** | - | - | - | -9.64 | -7.68 | -10.00 | -9.50 | -7.92 | -10.27 |

**Figure S33**. NICS(0) values of compound **1** and **2** at the B3LYP/6-311+G*//B3LYP/6-31+G* level



The aromaticity of compounds **1** and **2** has been investigated by nucleus independent chemical shift (NICS) calculations at the B3LYP/6-311+G*//B3LYP/6-31+G* level. Here we only discuss the NICS(0) values (see Fig. S27), which shows similar tendencies as NICS(1) and NICS(-1) (Table S5). The 7-membered rings in both compounds are slightly anti-aromatic, similarly to previously described phosphepines. In helicenoid **1,** all of the 6-membered rings are, as expected, aromatic, while in **2** the central ring in the middle of the perylene part is anti-aromatic, similarly to perylene itself (Table S5).

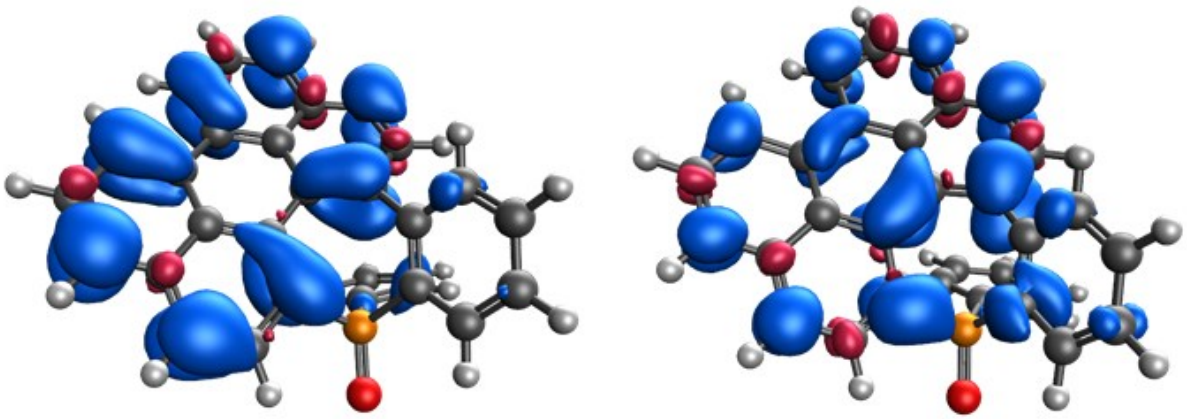


**Figure S34:** Spin density of the radical cation corresponding to the oxidation of **2** (left) and the radical anion corresponding to reduction of **2** (right) at the TD-B3LYP/6-31+G*(PCM)//B3LYP/6-31+G* level (PCM=dichloromethane)

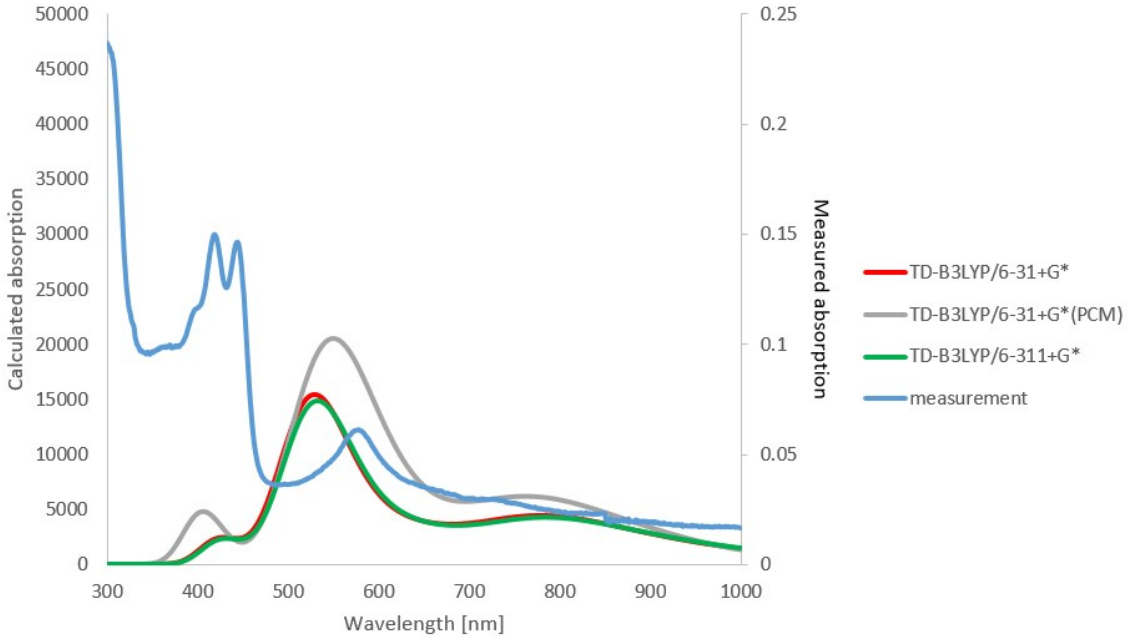



**Figure S35**: Experimental and simulated absorption spectra of the radical anion of **2** (PCM=dichloromethane)

**Table S6:** Vertical excitation energies (in eV), wavelengths (in nm) and oscillator strengths (f) of **perylene** at the TD-B3LYP/6-31G*//B3LYP/6-31+G* level

Excited State 1: Singlet-A 2.8959 eV 428.13 nm f=0.3615 <S**2>=0.000

66 -> 67 0.70451

Excited State 2: Singlet-A 3.7078 eV 334.38 nm f=0.0000 <S**2>=0.000

65 -> 67 -0.39631

66 -> 68 0.57116

66 -> 69 0.10672

Excited State 3: Singlet-A 4.0307 eV 307.60 nm f=0.0000 <S**2>=0.000

62 -> 67 -0.10668

65 -> 67 0.41655

66 -> 68 0.19678

66 -> 69 0.52208

Excited State 4: Singlet-A 4.0328 eV 307.44 nm f=0.0053 <S**2>=0.000

64 -> 67 0.54504

66 -> 71 0.43934

Excited State 5: Singlet-A 4.1128 eV 301.46 nm f=0.0000 <S**2>=0.000

62 -> 67 0.54306

65 -> 67 -0.19220

66 -> 68 -0.21480

66 -> 69 0.34704

Excited State 6: Singlet-A 4.2488 eV 291.81 nm f=0.0000 <S**2>=0.000

63 -> 67 0.52607

66 -> 70 0.47015

Excited State 7: Singlet-A 4.5971 eV 269.70 nm f=0.0000 <S**2>=0.000

63 -> 67 -0.44820

64 -> 68 -0.15056

65 -> 71 0.10955

66 -> 70 0.50634

Excited State 8: Singlet-A 4.6372 eV 267.37 nm f=0.0000 <S**2>=0.000

62 -> 67 0.42900

63 -> 71 0.11210

64 -> 70 0.11530

65 -> 67 0.35120

66 -> 68 0.28335

66 -> 69 -0.29495

Excited State 9: Singlet-A 4.8869 eV 253.71 nm f=0.2998 <S**2>=0.000

63 -> 68 0.19655

64 -> 67 -0.40172

65 -> 70 -0.17595

66 -> 71 0.51509

Excited State 10: Singlet-A 5.4716 eV 226.60 nm f=0.0006 <S**2>=0.000

60 -> 67 -0.10230

62 -> 68 0.51608

65 -> 69 0.46032

Excited State 11: Singlet-A 5.6504 eV 219.43 nm f=0.0235 <S**2>=0.000

63 -> 68 0.53590

64 -> 67 0.10129

65 -> 70 0.44385

Excited State 12: Singlet-A 5.6507 eV 219.41 nm f=0.0727 <S**2>=0.000

62 -> 69 -0.19200

64 -> 71 0.13806

65 -> 68 0.66014

Excited State 13: Singlet-A 5.7455 eV 215.79 nm f=0.0000 <S**2>=0.000

62 -> 71 -0.30943

64 -> 68 0.25480

64 -> 69 0.54528

65 -> 71 0.17440

Excited State 14: Singlet-A 5.7855 eV 214.30 nm f=0.0000 <S**2>=0.000

59 -> 67 0.70381

Excited State 15: Singlet-A 5.8151 eV 213.21 nm f=0.0000 <S**2>=0.000

62 -> 71 0.15388

64 -> 68 0.55491

64 -> 69 -0.26511

65 -> 71 0.29857

Excited State 16: Singlet-A 5.8253 eV 212.84 nm f=0.0000 <S**2>=0.000

58 -> 67 0.70222

Excited State 17: Singlet-A 5.8278 eV 212.75 nm f=0.0003 <S**2>=0.000

61 -> 67 0.34505

62 -> 70 -0.28976

63 -> 69 0.52848

66 -> 72 -0.11903

Excited State 18: Singlet-A 5.9519 eV 208.31 nm f=0.0286 <S**2>=0.000

60 -> 67 0.29957

62 -> 68 -0.35411

62 -> 69 0.20678

64 -> 71 0.13461

65 -> 69 0.46490

Excited State 19: Singlet-A 5.9645 eV 207.87 nm f=0.0000 <S**2>=0.000

63 -> 71 -0.44655

64 -> 70 0.54024

Excited State 20: Singlet-A 5.9863 eV 207.11 nm f=0.0000 <S**2>=0.000

61 -> 67 0.53654

62 -> 70 0.34253

63 -> 69 -0.21146

66 -> 72 -0.21307

**Table S7:** Vertical excitation energies (in eV), wavelengths (in nm) and oscillator strengths (f) of **1** at the TD-B3LYP/6-31G*//B3LYP/6-31+G* level

Excited State 1: Singlet-A 3.7511 eV 330.53 nm f=0.0864 <S**2>=0.000

117 ->120 0.15685

118 ->119 0.65336

118 ->120 0.17773

Excited State 2: Singlet-A 3.7786 eV 328.12 nm f=0.0042 <S**2>=0.000

117 ->119 0.42168

118 ->119 -0.18565

118 ->120 0.52511

Excited State 3: Singlet-A 4.0559 eV 305.69 nm f=0.0388 <S**2>=0.000

117 ->119 -0.29572

117 ->120 0.58247

118 ->119 -0.14462

118 ->120 0.17908

Excited State 4: Singlet-A 4.1003 eV 302.37 nm f=0.0150 <S**2>=0.000

116 ->119 0.12837

117 ->119 0.45248

117 ->120 0.33286

118 ->120 -0.33473

118 ->121 -0.11271

Excited State 5: Singlet-A 4.1483 eV 298.88 nm f=0.0065 <S**2>=0.000

116 ->119 0.44088

116 ->120 -0.16901

117 ->121 -0.18300

118 ->120 0.14660

118 ->121 -0.41522

Excited State 6: Singlet-A 4.3067 eV 287.89 nm f=0.0017 <S**2>=0.000

114 ->119 -0.26735

114 ->120 -0.19813

115 ->119 -0.18298

116 ->120 0.30391

117 ->121 0.25386

117 ->124 0.10099

118 ->120 0.10530

118 ->121 -0.19011

118 ->122 0.22916

118 ->123 -0.16039

118 ->124 -0.11475

Excited State 7: Singlet-A 4.4668 eV 277.57 nm f=0.0403 <S**2>=0.000

114 ->119 0.10191

114 ->120 0.14351

115 ->120 0.10068

116 ->119 0.41831

116 ->120 0.41327

118 ->121 0.29459

Excited State 8: Singlet-A 4.5188 eV 274.38 nm f=0.0155 <S**2>=0.000

115 ->119 0.60578

116 ->120 0.22061

117 ->121 0.11862

118 ->121 -0.16425

Excited State 9: Singlet-A 4.5658 eV 271.55 nm f=0.0419 <S**2>=0.000

114 ->119 -0.28678

115 ->119 0.24344

116 ->120 -0.18647

117 ->121 -0.26018

117 ->122 -0.16495

117 ->123 0.10825

118 ->121 0.28523

118 ->122 0.30300

118 ->124 -0.10846

Excited State 10: Singlet-A 4.6016 eV 269.44 nm f=0.0186 <S**2>=0.000

114 ->120 0.21003

115 ->120 0.11424

117 ->121 -0.15852

117 ->122 0.28725

117 ->123 -0.12162

118 ->121 -0.16106

118 ->122 0.48106

118 ->124 0.13113

Excited State 11: Singlet-A 4.6410 eV 267.15 nm f=0.0134 <S**2>=0.000

114 ->119 -0.32300

115 ->120 0.54938

116 ->120 -0.13214

117 ->121 0.17730

118 ->122 -0.11393

Excited State 12: Singlet-A 4.6889 eV 264.42 nm f=0.0171 <S**2>=0.000

112 ->119 -0.12381

114 ->119 -0.36020

114 ->120 0.39221

115 ->120 -0.24042

117 ->121 -0.12158

118 ->122 -0.21255

118 ->123 -0.16557

Excited State 13: Singlet-A 4.7105 eV 263.21 nm f=0.0056 <S**2>=0.000

112 ->119 0.25888

112 ->120 0.19882

113 ->119 0.58451

113 ->120 0.10011

114 ->120 0.11096

115 ->120 -0.10970

Excited State 14: Singlet-A 4.7162 eV 262.89 nm f=0.1371 <S**2>=0.000

113 ->119 -0.16475

113 ->120 0.10418

114 ->120 0.18698

115 ->120 -0.22613

116 ->119 0.15793

116 ->120 -0.21328

117 ->121 0.42155

118 ->122 0.12386

118 ->123 0.25217

Excited State 15: Singlet-A 4.8050 eV 258.03 nm f=0.0050 <S**2>=0.000

112 ->119 0.35059

112 ->120 0.23345

113 ->119 -0.29528

113 ->120 0.35737

118 ->123 -0.26138

Excited State 16: Singlet-A 4.8474 eV 255.78 nm f=0.1108 <S**2>=0.000

110 ->119 -0.18597

112 ->119 0.34438

113 ->119 -0.13215

114 ->119 -0.11798

116 ->119 -0.11568

116 ->120 0.16666

117 ->122 -0.11197

118 ->123 0.43971

Excited State 17: Singlet-A 4.8888 eV 253.61 nm f=0.0460 <S**2>=0.000

111 ->119 -0.14564

112 ->119 0.11002

113 ->120 -0.17736

117 ->122 0.47808

117 ->123 0.15464

118 ->124 -0.37407

Excited State 18: Singlet-A 4.8970 eV 253.18 nm f=0.0234 <S**2>=0.000

111 ->119 0.22631

112 ->119 -0.30270

112 ->120 0.13301

113 ->120 0.36678

114 ->120 -0.20154

117 ->122 0.17160

117 ->124 0.10513

118 ->123 0.19470

118 ->124 -0.16315

Excited State 19: Singlet-A 4.9375 eV 251.11 nm f=0.0322 <S**2>=0.000

110 ->119 0.13300

111 ->119 0.49016

111 ->120 -0.17380

112 ->119 0.18614

113 ->120 -0.18455

117 ->122 0.10008

117 ->123 0.13298

117 ->124 0.12890

118 ->124 0.16708

Excited State 20: Singlet-A 4.9812 eV 248.90 nm f=0.0018 <S**2>=0.000

110 ->119 0.37517

111 ->119 0.13247

112 ->120 -0.31027

113 ->120 0.15536

117 ->123 -0.22803

117 ->124 -0.13588

118 ->124 -0.27676

118 ->125 0.10711

**Table S8:** Vertical excitation energies (in eV), wavelengths (in nm) and oscillator strengths (f) of **2** at the TD-B3LYP/6-31G*//B3LYP/6-31+G* level

Excited State 1: Singlet-A 2.8078 eV 441.57 nm f=0.2384 <S**2>=0.000

117 ->118 0.70165

Excited State 2: Singlet-A 3.5638 eV 347.90 nm f=0.0033 <S**2>=0.000

116 ->118 0.51662

117 ->119 -0.45708

Excited State 3: Singlet-A 3.7207 eV 333.22 nm f=0.0014 <S**2>=0.000

111 ->118 -0.10993

114 ->118 0.45282

115 ->118 0.28659

117 ->120 -0.38394

117 ->122 0.16073

Excited State 4: Singlet-A 3.8809 eV 319.47 nm f=0.0092 <S**2>=0.000

114 ->118 -0.22825

115 ->118 0.58919

116 ->118 0.17549

117 ->119 0.11362

117 ->120 0.20879

Excited State 5: Singlet-A 3.9347 eV 315.10 nm f=0.0523 <S**2>=0.000

111 ->118 -0.18349

112 ->118 0.23177

114 ->118 0.24057

116 ->118 -0.26009

117 ->119 -0.31715

117 ->120 0.34336

117 ->121 -0.14985

117 ->122 -0.11823

Excited State 6: Singlet-A 3.9879 eV 310.90 nm f=0.1189 <S**2>=0.000

113 ->118 -0.26604

114 ->118 0.22167

115 ->118 -0.14095

116 ->118 0.21023
117 ->119 0.31462
117 ->120 0.28285
117 ->121 -0.30312
117 ->124 -0.10589
Excited State 7: Singlet-A 4.0167 eV 308.67 nm f=0.0511 <S**2>=0.000
111 ->118 0.32075
112 ->118 -0.22150
113 ->118 -0.29162
115 ->118 0.15855
116 ->118 -0.18000
117 ->119 -0.13843
117 ->120 -0.13774
117 ->121 -0.29618
117 ->122 -0.21882
Excited State 8: Singlet-A 4.0662 eV 304.91 nm f=0.0071 <S**2>=0.000
112 ->118 -0.27771
113 ->118 0.44411
117 ->121 -0.22693
117 ->123 0.35496
Excited State 9: Singlet-A 4.1285 eV 300.32 nm f=0.0066 <S**2>=0.000
110 ->118 0.18102
111 ->118 0.40424
112 ->118 0.43514
113 ->118 0.26098
117 ->121 -0.11415
Excited State 10: Singlet-A 4.1580 eV 298.18 nm f=0.0254 <S**2>=0.000
110 ->118 0.19952
111 ->118 0.12671
112 ->118 -0.19877
116 ->118 -0.10404
117 ->120 0.17087
117 ->122 0.55764
117 ->123 -0.10983

Excited State 11: Singlet-A 4.2171 eV 294.00 nm f=0.0048 <S**2>=0.000

108 ->118 0.23055

110 ->118 0.37817

111 ->118 -0.37169

114 ->118 -0.22000

117 ->120 -0.10960

117 ->121 -0.24430

Excited State 12: Singlet-A 4.2933 eV 288.79 nm f=0.0256 <S**2>=0.000

109 ->118 0.44897

110 ->118 0.21387

113 ->118 -0.19634

117 ->121 0.17729

117 ->122 0.10676

117 ->123 0.36665

Excited State 13: Singlet-A 4.3140 eV 287.40 nm f=0.0681 <S**2>=0.000

108 ->118 0.13425

109 ->118 0.39029

110 ->118 -0.32774

114 ->118 -0.12839

117 ->119 -0.11690

117 ->121 -0.25980

117 ->122 0.14095

117 ->124 0.21484

117 ->126 0.11734

Excited State 14: Singlet-A 4.3767 eV 283.28 nm f=0.0032 <S**2>=0.000

108 ->118 0.41076

109 ->118 -0.21879

110 ->118 -0.25788

112 ->118 0.14140

117 ->121 0.10408

117 ->122 0.14565

117 ->123 0.30124

117 ->124 -0.20701

Excited State 15: Singlet-A 4.4938 eV 275.90 nm f=0.0058 <S**2>=0.000

108 ->118 0.36233
109 ->118 0.24458
112 ->118 -0.18593
113 ->118 0.10932
117 ->120 0.11241
117 ->121 0.13040
117 ->122 -0.14316
117 ->123 -0.27754
117 ->124 -0.27100
Excited State 16: Singlet-A 4.6233 eV 268.17 nm f=0.0036 <S**2>=0.000
107 ->118 0.11201
108 ->118 -0.12157
117 ->124 -0.34002
117 ->125 0.57654
Excited State 17: Singlet-A 4.6314 eV 267.70 nm f=0.0522 <S**2>=0.000
107 ->118 0.50603
108 ->118 0.15501
117 ->124 0.22943
117 ->126 0.28173
Excited State 18: Singlet-A 4.7072 eV 263.39 nm f=0.0622 <S**2>=0.000
107 ->118 -0.22663
108 ->118 0.22552
114 ->118 0.12517
117 ->121 0.10515
117 ->124 0.34198
117 ->125 0.35577
117 ->126 -0.28448
Excited State 19: Singlet-A 4.9157 eV 252.22 nm f=0.0838 <S**2>=0.000
107 ->118 -0.35648
116 ->119 0.17459
116 ->123 0.10710
117 ->126 0.50207
Excited State 20: Singlet-A 4.9884 eV 248.54 nm f=0.0377 <S**2>=0.000
107 ->118 0.13437

115 ->119 0.17342

116 ->119 0.48499

116 ->120 0.37080

**Table S9:** Vertical excitation energies (in eV), wavelengths (in nm) and oscillator strengths (f) of the radical anion corresponding to reduction of **2** at the TD-B3LYP/6-31+G*(PCM)//B3LYP/6-31+G* level (PCM=dichloromethane)

Excited State 1: 2.030-A 1.4201 eV 873.10 nm f=0.0257 <S**2>=0.780

118A ->119A 0.38714

118A ->120A 0.90623

Excited State 2: 2.024-A 1.4717 eV 842.47 nm f=0.0047 <S**2>=0.774

118A ->119A 0.89395

118A ->120A -0.38225

118A ->121A -0.15469

118A ->122A -0.11866

Excited State 3: 2.033-A 1.6301 eV 760.58 nm f=0.0613 <S**2>=0.783

118A ->119A 0.14909

118A ->120A -0.11167

118A ->121A 0.92925

118A ->122A 0.20670

118A ->123A 0.12133

118A ->125A -0.11410

117B ->118B -0.10354

Excited State 4: 2.031-A 1.7489 eV 708.94 nm f=0.0015 <S**2>=0.781

118A ->122A 0.25612

118A ->123A 0.52190

118A ->124A 0.28312

118A ->125A 0.22276

117B ->118B 0.71410

Excited State 5: 2.032-A 1.8327 eV 676.51 nm f=0.0141 <S**2>=0.782

118A ->119A 0.12954

118A ->121A -0.12225

118A ->122A 0.64156

118A ->123A -0.45063

118A ->124A 0.52730

118A ->125A -0.24754

Excited State 6: 2.037-A 1.9947 eV 621.57 nm f=0.0376 <S**2>=0.788

118A ->121A -0.28121

118A ->122A 0.52453

118A ->123A 0.54698

118A ->124A -0.37716

118A ->125A -0.23323

117B ->118B -0.36455

Excited State 7: 2.037-A 2.1178 eV 585.45 nm f=0.0496 <S**2>=0.787

118A ->122A -0.41322

118A ->123A 0.42592

118A ->124A 0.61855

118A ->125A -0.41967

117B ->118B -0.27021

Excited State 8: 2.060-A 2.2501 eV 551.01 nm f=0.1898 <S**2>=0.810

118A ->122A 0.10812

118A ->123A 0.11255

118A ->124A 0.26448

118A ->125A 0.68355

118A ->127A -0.45408

117B ->118B -0.42009

Excited State 9: 2.082-A 2.4222 eV 511.86 nm f=0.0852 <S**2>=0.834

118A ->124A 0.15152

118A ->125A 0.38993

118A ->126A -0.17940

118A ->127A 0.81902

117B ->118B -0.22196

Excited State 10: 2.023-A 2.5409 eV 487.95 nm f=0.0047 <S**2>=0.773

118A ->126A 0.94052

118A ->127A 0.19051

118A ->128A 0.20580

118A ->129A -0.10775

Excited State 11: 2.023-A 2.8255 eV 438.81 nm f=0.0020 <S**2>=0.774

118A ->126A -0.22856

118A ->128A 0.91634
118A ->129A -0.26869
118A ->130A 0.11146
Excited State 12: 2.026-A 2.8682 eV 432.28 nm f=0.0012 <S**2>=0.776
118A ->128A -0.19771
118A ->129A -0.29484
118A ->130A 0.91911
Excited State 13: 2.025-A 2.9354 eV 422.37 nm f=0.0038 <S**2>=0.775
118A ->127A 0.11380
118A ->128A 0.21888
118A ->129A 0.88852
118A ->130A 0.32978
Excited State 14: 3.196-A 2.9906 eV 414.59 nm f=0.0127 <S**2>=2.304
117A ->119A -0.14983
117A ->120A -0.28023
117A ->121A 0.27257
117A ->123A 0.11762
118A ->127A -0.16696
115B ->118B 0.17259
116B ->118B 0.10514
117B ->119B 0.44143
117B ->120B 0.51811
117B ->121B 0.36361
117B ->123B -0.14724
117B ->124B -0.12862
Excited State 15: 3.029-A 3.0609 eV 405.05 nm f=0.0249 <S**2>=2.044
117A ->120A 0.17113
117B ->119B 0.77190
117B ->120B -0.56247
Excited State 16: 3.070-A 3.0851 eV 401.88 nm f=0.0220 <S**2>=2.106
117A ->121A -0.32619
117A ->123A -0.20211
117A ->124A 0.11697
114B ->118B 0.13517

115B ->118B -0.18976
116B ->118B -0.18586
117B ->119B 0.38061
117B ->120B 0.52386
117B ->121B -0.33487
117B ->123B 0.18560
117B ->124B 0.32819
Excited State 17: 2.052-A 3.1461 eV 394.08 nm f=0.0008 <S**2>=0.802
118A ->126A 0.11420
118A ->131A 0.70093
118A ->132A -0.58455
118A ->133A -0.26850
118A ->134A 0.10224
118A ->135A -0.14158
Excited State 18: 2.032-A 3.1768 eV 390.28 nm f=0.0007 <S**2>=0.782
118A ->129A -0.10244
118A ->131A 0.55110
118A ->132A 0.24213
118A ->133A 0.73402
118A ->134A -0.20126
118A ->135A 0.12992
Excited State 19: 2.027-A 3.1806 eV 389.82 nm f=0.0009 <S**2>=0.778
118A ->131A 0.39223
118A ->132A 0.74090
118A ->133A -0.49780
118A ->134A 0.15010
Excited State 20: 3.031-A 3.2183 eV 385.25 nm f=0.0031 <S**2>=2.046
117A ->120A -0.12203
117A ->122A -0.12812
117A ->123A -0.36152
117A ->124A -0.21767
117A ->125A -0.26841
118A ->147A -0.10463
113B ->118B 0.16697

114B ->118B 0.40658

116B ->118B 0.23666

117B ->120B -0.16120

117B ->121B 0.16119

117B ->123B 0.33189

117B ->125B -0.16154

117B ->126B 0.36580

**Table S10:** Vertical excitation energies (in eV), wavelengths (in nm) and oscillator strengths (f) of **1** at the ωB97xd/cc-pVDZ//ωB97xd/cc-pVDZ level

Excited State 1: Singlet-A 4.3322 eV 286.19 nm f=0.1499 <S**2>=0.000

116 ->121 0.10874

117 ->119 0.11941

117 ->120 0.29158

118 ->119 0.55786

118 ->120 -0.18646

Excited State 2: Singlet-A 4.4390 eV 279.31 nm f=0.0089 <S**2>=0.000

109 ->119 0.10920

116 ->119 0.39070

116 ->120 0.12070

117 ->119 0.16017

117 ->121 -0.15756

117 ->122 0.13062

118 ->119 -0.16680

118 ->120 -0.18342

118 ->121 -0.29774

Excited State 3: Singlet-A 4.4878 eV 276.27 nm f=0.0151 <S**2>=0.000

114 ->119 0.10693

114 ->120 -0.13576

115 ->119 -0.15689

115 ->120 0.12858

116 ->120 0.16171

117 ->119 0.29325

117 ->121 -0.15964

117 ->124 -0.10007
118 ->119 0.14285
118 ->120 0.39918
118 ->122 0.13782
118 ->123 0.10569
Excited State 4: Singlet-A 4.5937 eV 269.90 nm f=0.0084 <S**2>=0.000
114 ->119 -0.10343
114 ->120 0.16386
115 ->119 0.13610
115 ->120 -0.19676
116 ->120 -0.11016
117 ->119 0.32320
117 ->120 -0.21942
117 ->121 0.19007
117 ->122 0.11702
118 ->120 0.24128
118 ->121 -0.14047
118 ->122 -0.19307
Excited State 5: Singlet-A 4.8601 eV 255.10 nm f=0.0549 <S**2>=0.000
116 ->119 0.11618
117 ->119 -0.13892
117 ->120 0.48075
118 ->119 -0.16312
118 ->120 0.33252
Excited State 6: Singlet-A 4.9413 eV 250.91 nm f=0.0232 <S**2>=0.000
114 ->120 -0.10363
116 ->119 -0.10883
117 ->119 0.43685
117 ->120 0.27008
118 ->119 -0.26887
118 ->120 -0.21830
118 ->121 0.12170
Excited State 7: Singlet-A 5.1991 eV 238.47 nm f=0.1293 <S**2>=0.000
109 ->124 0.10371

110 ->120 0.13353
110 ->121 0.11139
110 ->124 -0.10727
111 ->119 -0.10210
111 ->120 -0.10843
112 ->119 -0.10555
114 ->119 0.14019
114 ->120 0.10096
116 ->120 0.22989
116 ->122 0.10163
116 ->124 -0.14624
117 ->119 0.10348
117 ->121 0.16907
117 ->124 -0.11288
118 ->120 -0.10061
118 ->121 0.24181
Excited State 8: Singlet-A 5.2714 eV 235.20 nm f=0.0247 <S**2>=0.000
113 ->119 0.11641
113 ->120 0.10460
113 ->121 -0.16551
113 ->122 0.23957
113 ->123 -0.21636
114 ->119 -0.12181
114 ->125 0.15358
115 ->119 -0.20232
115 ->120 -0.10818
115 ->122 -0.11768
115 ->123 0.12802
115 ->124 -0.12489
115 ->125 0.12714
Excited State 9: Singlet-A 5.2966 eV 234.08 nm f=0.2728 <S**2>=0.000
112 ->120 0.11310
113 ->123 0.10979
114 ->120 -0.10971

116 ->119 0.34080
116 ->120 0.15672
117 ->121 0.23869
118 ->121 0.16810
118 ->122 -0.16559
Excited State 10: Singlet-A 5.5068 eV 225.15 nm f=0.3623 <S**2>=0.000
112 ->119 -0.16934
112 ->120 0.30975
113 ->119 -0.11041
114 ->120 -0.12496
116 ->119 -0.25748
116 ->120 0.28800
118 ->121 -0.28572
Excited State 11: Singlet-A 5.5988 eV 221.45 nm f=0.0584 <S**2>=0.000
109 ->119 -0.15306
113 ->123 -0.10886
114 ->119 0.26982
114 ->121 -0.12089
114 ->122 0.11551
115 ->119 0.32020
115 ->120 0.17595
116 ->119 0.11115
116 ->121 -0.15959
116 ->122 0.11317
117 ->122 0.10290
117 ->123 -0.11769
118 ->123 -0.13990
Excited State 12: Singlet-A 5.6520 eV 219.36 nm f=0.3069 <S**2>=0.000
112 ->119 -0.21967
112 ->120 0.29314
114 ->119 -0.13235
114 ->120 0.15686
115 ->119 0.11162
115 ->120 -0.12347

117 ->121 -0.24446

118 ->121 0.31033

118 ->122 0.15582

Excited State 13: Singlet-A 5.7365 eV 216.13 nm f=0.0124 <S**2>=0.000

112 ->119 0.13489

113 ->119 -0.10627

113 ->120 -0.12263

114 ->119 -0.13602

115 ->120 -0.11145

117 ->121 0.11318

117 ->122 0.21901

117 ->123 -0.18401

118 ->122 0.41069

118 ->123 -0.23749

Excited State 14: Singlet-A 5.7466 eV 215.75 nm f=0.0682 <S**2>=0.000

112 ->120 -0.10056

113 ->119 -0.33488

113 ->120 -0.19264

114 ->122 -0.11251

115 ->119 0.34364

115 ->122 -0.14186

115 ->123 0.11325

117 ->121 -0.11667

117 ->124 -0.10616

Excited State 15: Singlet-A 5.7897 eV 214.14 nm f=0.0346 <S**2>=0.000

111 ->120 0.30726

111 ->121 0.11101

112 ->120 -0.13282

114 ->120 0.20257

115 ->120 0.13741

116 ->119 -0.17727

116 ->120 0.34137

Excited State 16: Singlet-A 5.7975 eV 213.86 nm f=0.0388 <S**2>=0.000

110 ->120 -0.19212

111 ->120 -0.12543
112 ->120 -0.16936
113 ->119 0.25411
114 ->119 0.12300
114 ->120 -0.23007
115 ->120 -0.20340
116 ->119 -0.10437
116 ->120 0.13252
116 ->121 -0.15218
117 ->121 -0.11210
117 ->122 0.16133
118 ->121 0.12710
118 ->122 -0.15167
Excited State 17: Singlet-A 5.8563 eV 211.71 nm f=0.2513 <S**2>=0.000
113 ->119 0.30329
115 ->119 0.21453
115 ->120 -0.20421
116 ->120 0.18567
116 ->121 0.22211
116 ->122 -0.11987
117 ->121 0.14500
117 ->122 -0.24344
118 ->122 0.21989
118 ->123 0.12269
Excited State 18: Singlet-A 5.8997 eV 210.15 nm f=0.0140 <S**2>=0.000
111 ->119 0.13113
111 ->120 0.10716
114 ->119 0.45040
115 ->119 -0.20586
115 ->120 -0.27351
116 ->120 -0.12261
Excited State 19: Singlet-A 5.9176 eV 209.52 nm f=0.0602 <S**2>=0.000
110 ->119 -0.24710
110 ->120 -0.11441

112 ->119 -0.19935

112 ->120 -0.10134

114 ->119 0.15368

114 ->123 0.10917

115 ->120 0.15877

115 ->121 0.15857

116 ->120 -0.10302

117 ->121 0.29658

118 ->122 0.12423

118 ->123 0.12513

Excited State 20: Singlet-A 5.9696 eV 207.69 nm f=0.0457 <S**2>=0.000

109 ->119 0.15531

111 ->121 -0.13939

112 ->119 0.31332

112 ->122 0.11828

112 ->123 -0.11863

113 ->119 -0.10370

114 ->121 -0.12487

114 ->123 -0.10927

115 ->122 0.10446

117 ->123 0.21231

118 ->121 0.13688

118 ->123 0.15290

**Table S11:** Vertical excitation energies (in eV), wavelengths (in nm) and oscillator strengths (f) of **1** at the M06-2X/def2-SVP//B3LYP/6-31+G* level

Excited State 1: Singlet-A 4.2470 eV 291.93 nm f=0.1719 <S**2>=0.000

117 ->120 0.17092

118 ->119 0.63940

118 ->120 -0.15065

Excited State 2: Singlet-A 4.3657 eV 283.99 nm f=0.0063 <S**2>=0.000

115 ->120 0.10698

116 ->119 0.30570

117 ->119 -0.15994

117 ->122 0.11196

117 ->123 -0.10033

118 ->119 0.15618

118 ->120 0.41948

118 ->121 -0.25670
Excited State 3: Singlet-A 4.4804 eV 276.72 nm f=0.0212 <S**2>=0.000
115 ->119 -0.19685
115 ->120 0.10055
116 ->119 -0.14184
116 ->120 -0.21855
117 ->119 0.31064
117 ->121 0.20268
118 ->119 0.10352
118 ->120 0.33208
118 ->121 0.15941
118 ->122 -0.14724
118 ->123 0.12876
Excited State 4: Singlet-A 4.5875 eV 270.27 nm f=0.0090 <S**2>=0.000
115 ->119 0.19548
115 ->120 -0.17909
116 ->119 0.11720
116 ->120 0.13775
117 ->119 0.44988
117 ->120 -0.14827
117 ->121 -0.19183
118 ->120 0.18091
118 ->122 0.17640
118 ->123 -0.10579
Excited State 5: Singlet-A 4.6591 eV 266.11 nm f=0.0281 <S**2>=0.000
115 ->119 0.10844
115 ->120 -0.15580
116 ->119 -0.16548
117 ->119 -0.17463
117 ->120 0.45791
117 ->122 -0.10464
118 ->119 -0.12264
118 ->120 0.28095
118 ->121 0.14411
Excited State 6: Singlet-A 4.7357 eV 261.81 nm f=0.0125 <S**2>=0.000
115 ->120 0.14188
116 ->119 0.14512
117 ->119 0.33257
117 ->120 0.44812
118 ->119 -0.14106
118 ->120 -0.21660
118 ->121 -0.18130
Excited State 7: Singlet-A 5.1352 eV 241.44 nm f=0.2828 <S**2>=0.000
111 ->120 -0.10896
112 ->119 0.13734
112 ->120 0.10014
112 ->126 0.10361
115 ->120 0.11347
116 ->119 0.12543
116 ->120 0.28257

116 ->122 -0.10057
116 ->124 -0.13775
117 ->121 0.16360
117 ->122 0.13338
118 ->121 0.34044
118 ->124 0.10077
Excited State 8: Singlet-A 5.2313 eV 237.00 nm f=0.3445 <S**2>=0.000
112 ->119 -0.11372
112 ->120 -0.14469
112 ->121 0.11121
114 ->120 0.14233
115 ->120 -0.10713
116 ->119 0.40382
117 ->121 0.16335
118 ->121 0.21965
118 ->122 -0.19439
Excited State 9: Singlet-A 5.3493 eV 231.78 nm f=0.1830 <S**2>=0.000
110 ->119 0.10684
110 ->120 -0.14152
112 ->120 -0.16199
114 ->120 0.11429
116 ->119 -0.24525
116 ->120 0.40374
117 ->121 0.21214
118 ->121 -0.23527
118 ->122 -0.13493
Excited State 10: Singlet-A 5.4000 eV 229.60 nm f=0.0051 <S**2>=0.000
113 ->120 -0.12127
113 ->121 -0.16870
113 ->122 0.30316
113 ->123 0.28713
114 ->119 0.16192
114 ->124 0.17801
114 ->125 -0.26164
115 ->125 -0.10296
Excited State 11: Singlet-A 5.4834 eV 226.11 nm f=0.1023 <S**2>=0.000
111 ->119 -0.11384
112 ->120 0.13849
115 ->119 0.21648
115 ->120 -0.10498
116 ->119 0.15455
116 ->120 -0.18521
117 ->121 0.39083
118 ->121 -0.28381
Excited State 12: Singlet-A 5.5569 eV 223.12 nm f=0.0481 <S**2>=0.000
110 ->120 -0.12220
112 ->120 -0.15749
115 ->119 -0.14871
117 ->121 0.17781
118 ->122 0.53556

Excited State 13: Singlet-A 5.6036 eV 221.26 nm f=0.0258 <S**2>=0.000
109 ->119 -0.11351
109 ->120 0.10718
110 ->119 -0.19379
110 ->120 0.20162
111 ->119 -0.18369
111 ->120 0.21342
112 ->119 -0.24257
112 ->120 0.12237
114 ->119 0.10178
115 ->119 -0.12645
116 ->119 -0.13439
116 ->120 0.26787
117 ->121 0.14729
118 ->122 0.18403
Excited State 14: Singlet-A 5.6357 eV 220.00 nm f=0.0012 <S**2>=0.000
112 ->120 -0.11195
114 ->119 0.10593
115 ->119 0.49375
115 ->120 0.33465
Excited State 15: Singlet-A 5.7075 eV 217.23 nm f=0.1063 <S**2>=0.000
109 ->120 -0.12000
114 ->119 0.51487
114 ->120 -0.13595
114 ->121 0.10855
116 ->121 -0.11836
117 ->121 0.10092
117 ->122 -0.16920
118 ->123 -0.25196
Excited State 16: Singlet-A 5.7263 eV 216.52 nm f=0.0416 <S**2>=0.000
109 ->119 -0.10166
109 ->120 0.10083
110 ->120 -0.23167
111 ->119 0.13554
111 ->120 0.13109
112 ->120 0.11867
113 ->119 -0.11844
114 ->120 0.31822
114 ->122 -0.12970
117 ->122 0.12100
118 ->123 -0.28342
Excited State 17: Singlet-A 5.7441 eV 215.85 nm f=0.5846 <S**2>=0.000
111 ->119 -0.12033
113 ->119 0.21211
114 ->119 -0.14942
114 ->120 0.13483
114 ->122 -0.11205
115 ->119 -0.14569
115 ->120 0.35363
116 ->121 -0.12556

117 ->122 -0.32125
118 ->123 -0.14899
Excited State 18: Singlet-A 5.7842 eV 214.35 nm f=0.0582 <S**2>=0.000
110 ->120 -0.11053
111 ->119 -0.17106
113 ->119 0.27422
113 ->120 0.11067
114 ->119 0.29646
114 ->120 0.22605
117 ->121 -0.15332
117 ->122 0.17653
117 ->123 0.10509
118 ->123 0.21736
Excited State 19: Singlet-A 5.8341 eV 212.52 nm f=0.0591 <S**2>=0.000
111 ->119 0.14503
113 ->119 -0.30453
116 ->121 -0.10917
117 ->122 -0.28699
117 ->123 0.16884
118 ->123 0.38324
Excited State 20: Singlet-A 5.8949 eV 210.33 nm f=0.1434 <S**2>=0.000
110 ->120 0.13695
111 ->119 0.16137
111 ->120 0.10821
113 ->119 0.21671
114 ->120 0.10743
115 ->120 -0.20669
116 ->121 -0.21765
117 ->123 -0.14346
118 ->123 0.11356
118 ->124 0.37699

**Table S12:** Vertical excitation energies (in eV), wavelengths (in nm) and oscillator strengths (f) of **1** at the cam-B3LYP/def2-SVP//B3LYP/6-31+G* level

Excited State 1: Singlet-A 4.2274 eV 293.29 nm f=0.1730 <S**2>=0.000
116 ->121 0.10395
117 ->120 0.22783
118 ->119 0.61843
118 ->120 -0.13647
Excited State 2: Singlet-A 4.3584 eV 284.47 nm f=0.0041 <S**2>=0.000
115 ->120 0.11346
116 ->119 0.33980
116 ->120 0.10825
117 ->119 -0.11814
117 ->121 -0.11033
117 ->122 0.12298
117 ->123 -0.11437
118 ->119 0.13784
118 ->120 0.36406
118 ->121 -0.27246

Excited State 3: Singlet-A 4.4461 eV 278.86 nm f=0.0175 <S**2>=0.000
115 ->119 -0.19308
116 ->119 -0.11167
116 ->120 -0.21473
117 ->119 0.30665
117 ->121 0.19968
118 ->119 0.10244
118 ->120 0.32282
118 ->121 0.14310
118 ->122 -0.14249
118 ->123 0.14396
Excited State 4: Singlet-A 4.5496 eV 272.52 nm f=0.0100 <S**2>=0.000
114 ->119 -0.11182
114 ->120 0.11798
115 ->119 0.18484
115 ->120 -0.18431
116 ->120 0.12432
117 ->119 0.39282
117 ->120 -0.12899
117 ->121 -0.18267
117 ->122 -0.10029
118 ->120 0.23379
118 ->121 0.13030
118 ->122 0.18370
118 ->123 -0.10875
Excited State 5: Singlet-A 4.7167 eV 262.86 nm f=0.0322 <S**2>=0.000
115 ->120 -0.11822
116 ->119 -0.16303
117 ->119 -0.25479
117 ->120 0.42872
118 ->119 -0.13402
118 ->120 0.32359
118 ->121 0.10297
Excited State 6: Singlet-A 4.8009 eV 258.25 nm f=0.0199 <S**2>=0.000
116 ->119 0.11260
117 ->119 0.35541
117 ->120 0.44680
118 ->119 -0.20466
118 ->120 -0.20445
118 ->121 -0.13727
Excited State 7: Singlet-A 5.1255 eV 241.90 nm f=0.1595 <S**2>=0.000
111 ->120 0.16450
111 ->121 -0.12322
112 ->119 0.12505
114 ->119 -0.11161
114 ->120 -0.14429
116 ->120 0.23568
116 ->122 -0.11460
116 ->124 -0.15635
117 ->121 0.13956

117 ->122 0.12992
117 ->124 0.10084
118 ->121 0.27457
Excited State 8: Singlet-A 5.2404 eV 236.59 nm f=0.4098 <S**2>=0.000
112 ->120 -0.13751
114 ->120 0.14668
116 ->119 0.36572
116 ->120 0.17435
116 ->126 0.10395
117 ->121 0.22222
118 ->121 0.23406
118 ->122 -0.17554
118 ->123 0.10889
Excited State 9: Singlet-A 5.3356 eV 232.37 nm f=0.0045 <S**2>=0.000
109 ->125 0.11823
110 ->125 -0.11124
113 ->120 -0.12413
113 ->121 -0.16333
113 ->122 0.30983
113 ->123 0.28292
114 ->124 0.13321
114 ->125 -0.21920
115 ->119 0.10203
115 ->124 0.12483
115 ->125 -0.17938
Excited State 10: Singlet-A 5.4163 eV 228.91 nm f=0.2801 <S**2>=0.000
112 ->119 0.15796
112 ->120 -0.21508
116 ->119 -0.29467
116 ->120 0.35515
117 ->121 0.17902
118 ->121 -0.27646
118 ->122 -0.11302
Excited State 11: Singlet-A 5.5389 eV 223.84 nm f=0.1438 <S**2>=0.000
111 ->119 -0.12641
112 ->119 0.17888
112 ->120 -0.18788
114 ->119 0.20369
115 ->119 -0.10614
116 ->119 -0.12817
116 ->120 0.12495
117 ->121 -0.30754
118 ->121 0.31227
Excited State 12: Singlet-A 5.6027 eV 221.29 nm f=0.0027 <S**2>=0.000
109 ->119 0.11060
111 ->120 0.12699
112 ->119 0.20366
112 ->120 -0.23648
113 ->120 -0.10388
114 ->119 0.10200

114 ->120 -0.16234
115 ->120 -0.23291
116 ->119 0.15509
116 ->120 -0.22325
117 ->121 0.13991
118 ->122 0.27254
Excited State 13: Singlet-A 5.6320 eV 220.14 nm f=0.0377 <S**2>=0.000
112 ->119 -0.11820
114 ->120 0.14687
115 ->119 -0.22198
115 ->120 0.15264
117 ->121 0.17772
117 ->122 0.12508
118 ->122 0.48304
Excited State 14: Singlet-A 5.6644 eV 218.88 nm f=0.0257 <S**2>=0.000
114 ->119 0.10544
114 ->122 -0.12548
114 ->123 -0.11500
115 ->119 0.44893
115 ->120 0.32237
116 ->120 -0.18475
117 ->121 0.12115
Excited State 15: Singlet-A 5.6760 eV 218.44 nm f=0.0367 <S**2>=0.000
110 ->120 0.15808
111 ->120 -0.23426
112 ->119 -0.15913
112 ->120 0.10500
113 ->119 -0.10981
113 ->120 0.12878
114 ->119 0.27467
114 ->120 -0.25710
114 ->122 0.10346
115 ->119 0.19641
115 ->120 -0.11781
116 ->119 -0.10490
116 ->120 0.18356
117 ->121 0.11391
Excited State 16: Singlet-A 5.7279 eV 216.46 nm f=0.2683 <S**2>=0.000
111 ->120 0.10084
114 ->119 0.39007
114 ->121 0.10622
115 ->119 -0.23077
115 ->122 -0.10245
116 ->121 -0.12824
117 ->121 0.10074
117 ->122 -0.21226
118 ->123 -0.26389
Excited State 17: Singlet-A 5.7818 eV 214.44 nm f=0.3069 <S**2>=0.000
110 ->119 -0.13483
110 ->120 -0.15907

113 ->119 -0.21611
113 ->120 -0.10451
114 ->119 0.20755
114 ->120 0.22425
115 ->120 -0.22526
116 ->121 0.13794
117 ->122 0.28329
Excited State 18: Singlet-A 5.8187 eV 213.08 nm f=0.0402 <S**2>=0.000
109 ->119 0.11169
110 ->119 0.11481
111 ->119 0.15818
113 ->119 0.19128
113 ->120 0.13603
114 ->119 0.23480
114 ->120 0.10711
117 ->121 -0.23853
117 ->123 0.17972
118 ->121 -0.13082
118 ->123 0.31768
Excited State 19: Singlet-A 5.8873 eV 210.60 nm f=0.1652 <S**2>=0.000
110 ->120 0.10738
111 ->120 -0.15792
112 ->119 0.10918
113 ->119 0.26800
113 ->120 0.17777
113 ->125 -0.11098
114 ->122 -0.11715
115 ->120 -0.20212
115 ->121 0.15391
116 ->121 0.13565
117 ->122 0.22809
117 ->123 -0.12006
118 ->123 -0.15926
Excited State 20: Singlet-A 5.9297 eV 209.09 nm f=0.0161 <S**2>=0.000
109 ->119 -0.12999
110 ->119 -0.14754
111 ->119 -0.16804
111 ->120 -0.11008
112 ->119 0.24762
112 ->120 0.11670
113 ->119 -0.13030
114 ->120 0.11784
115 ->120 -0.10461
116 ->121 -0.13082
117 ->122 -0.16125
118 ->123 0.36105
118 ->124 0.14070

**Table S13:** Vertical excitation energies, wavelengths and oscillator strengths of **1** at the ADC(2)/def2-SVP//B3LYP/6-31+G* level

| Excited state | Excitation energy [eV] | Absorption wavelength [nm] | Oscillator strength |
|---|---|---|---|
| 1 | 4.2690 | 290.43 | 0.0020695 |
| 2 | 4.3233 | 286.78 | 0.0193908 |
| 3 | 4.5328 | 273.53 | 0.0654905 |
| 4 | 4.6897 | 264.38 | 0.0054483 |
| 5 | 4.7111 | 263.18 | 0.0256373 |
| 6 | 4.7111 | 263.18 | 0.0257625 |
| 7 | 4.7111 | 263.17 | 0.0261809 |
| 8 | 4.7837 | 259.18 | 0.0100450 |
| 9 | 5.0076 | 247.59 | 0.0126053 |
| 10 | 5.3380 | 232.27 | 0.2318871 |
| 11 | 5.4145 | 228.99 | 0.0221695 |
| 12 | 5.4686 | 226.72 | 0.0846498 |
| 13 | 5.5590 | 223.04 | 0.0010145 |
| 14 | 5.6440 | 219.67 | 0.0244885 |
| 15 | 5.6969 | 217.64 | 0.0007262 |
| 16 | 5.8002 | 213.76 | 0.3046052 |
| 17 | 5.8172 | 213.13 | 0.0394195 |
| 18 | 5.9973 | 206.73 | 0.0370365 |
| 19 | 6.7352 | 184.08 | 0.0138611 |

Total energies and Cartesian coordinates at the B3LYP/6-31+G* level
**perylene**

E(hartree): -769.428663

| | | | |
|---|---|---|---|
| C | 0.030196 | -0.087081 | -0.042494 |
| C | 0.043297 | -0.497862 | 1.288261 |
| C | 1.235387 | -0.574690 | 2.033544 |
| C | 2.439071 | -0.239460 | 1.454255 |
| C | 2.487943 | 0.186198 | 0.101192 |
| C | 1.274015 | 0.265927 | -0.662655 |
| C | 3.722995 | 0.533934 | -0.505478 |
| C | 3.759520 | 0.945783 | -1.819207 |
| C | 2.571912 | 1.025240 | -2.571323 |
| C | 1.331748 | 0.696803 | -2.029138 |
| C | 0.082925 | 0.778723 | -2.814986 |
| C | -1.160894 | 0.425781 | -2.194824 |
| C | -2.374815 | 0.505470 | -2.958684 |
| C | -2.325914 | 0.930925 | -4.311796 |
| C | -1.122193 | 1.265990 | -4.891133 |

| | | | |
|---|---|---|---|
| C | 0.069877 | 1.189252 | -4.145829 |
| C | -1.218654 | -0.005008 | -0.828298 |
| C | -2.458849 | -0.333201 | -0.286060 |
| C | -3.646467 | -0.253729 | -1.038177 |
| C | -3.609902 | 0.157893 | -2.351963 |
| H | -4.591195 | -0.520383 | -0.571420 |
| H | -4.521636 | 0.222521 | -2.941125 |
| H | -3.251951 | 0.986936 | -4.879126 |
| H | -1.082336 | 1.592091 | -5.927255 |
| H | 0.993986 | 1.462589 | -4.642636 |
| H | 2.648239 | 1.354380 | -3.601541 |
| H | 4.704231 | 1.212592 | -2.285910 |
| H | 4.634758 | 0.469290 | 0.083635 |
| H | 3.365139 | -0.295510 | 2.021532 |
| H | 1.195547 | -0.900980 | 3.069606 |
| H | -0.880781 | -0.771371 | 1.785033 |
| H | -2.535216 | -0.662140 | 0.744220 |

**1**

E(hartree): -1648.728635

| | | | |
|---|---|---|---|
| C | -0.376530 | -1.197565 | -1.248815 |
| C | -1.097923 | -0.515984 | -0.271524 |
| C | -2.517957 | -0.742157 | -0.176220 |
| C | -3.165107 | -1.573840 | -1.151572 |
| C | -2.390583 | -2.183003 | -2.174060 |
| C | -1.026106 | -2.025530 | -2.203013 |
| C | -4.567975 | -1.793599 | -1.060946 |
| C | -5.308243 | -1.243844 | -0.038503 |
| C | -4.668977 | -0.450474 | 0.945786 |
| C | -3.314577 | -0.204578 | 0.876204 |
| C | -0.429379 | 0.444334 | 0.664974 |
| C | 0.542790 | 0.035812 | 1.583102 |
| C | 1.051942 | 0.976821 | 2.528526 |
| C | 0.644127 | 2.285303 | 2.540022 |

| | | | |
|---|---|---|---|
| C | -0.278555 | 2.759178 | 1.571573 |
| C | -0.813087 | 1.836007 | 0.614559 |
| C | -1.684698 | 2.356135 | -0.385653 |
| C | -2.023974 | 3.692703 | -0.419281 |
| C | -1.516505 | 4.591013 | 0.549658 |
| C | -0.657918 | 4.128081 | 1.522033 |
| C | 1.139132 | -1.330678 | 1.632855 |
| C | 1.683633 | -1.958966 | 0.488771 |
| C | 2.332897 | -3.195903 | 0.601174 |
| C | 2.454065 | -3.825539 | 1.840954 |
| C | 1.908359 | -3.220496 | 2.975360 |
| C | 1.265339 | -1.986272 | 2.870061 |
| P | 1.450187 | -1.318515 | -1.212051 |
| C | 2.192319 | 0.345125 | -1.336865 |
| C | 1.679875 | 1.266961 | -2.261967 |
| C | 2.322308 | 2.488849 | -2.468699 |
| C | 3.484616 | 2.797946 | -1.756199 |
| C | 4.003443 | 1.881649 | -0.836930 |
| C | 3.361199 | 0.659423 | -0.628382 |
| O | 1.973634 | -2.272544 | -2.255945 |
| H | 0.778013 | 1.031717 | -2.821730 |
| H | 1.915146 | 3.198674 | -3.184147 |
| H | 3.984608 | 3.749718 | -1.917308 |
| H | 4.907867 | 2.117836 | -0.281912 |
| H | 3.770886 | -0.049495 | 0.086633 |
| H | 2.728482 | -3.656631 | -0.300011 |
| H | 2.960946 | -4.783838 | 1.917870 |
| H | 1.979174 | -3.708536 | 3.944268 |
| H | 0.838862 | -1.526696 | 3.758048 |
| H | 1.803785 | 0.641573 | 3.237032 |
| H | 1.051566 | 2.981765 | 3.269534 |
| H | -0.245229 | 4.807894 | 2.264359 |
| H | -1.796599 | 5.640711 | 0.517646 |
| H | -2.685688 | 4.059091 | -1.200042 |

| | | | |
|---|---|---|---|
| H | -2.082519 | 1.690476 | -1.143165 |
| H | -2.841526 | 0.400817 | 1.641423 |
| H | -5.250914 | -0.034366 | 1.764145 |
| H | -6.378221 | -1.425195 | 0.022750 |
| H | -5.044304 | -2.418822 | -1.812936 |
| H | -2.889557 | -2.803825 | -2.914921 |
| H | -0.414359 | -2.536264 | -2.941115 |

**2**

E(hartree): -1647.540285

| | | | |
|---|---|---|---|
| C | 1.644331 | 1.365867 | -0.648824 |
| C | 1.436377 | 2.737454 | -1.003137 |
| C | 0.161138 | 3.130275 | -1.481760 |
| C | -0.815912 | 2.190430 | -1.670989 |
| C | -0.655392 | 0.825981 | -1.282822 |
| C | 0.542984 | 0.431201 | -0.646587 |
| C | 2.977051 | 0.940771 | -0.345020 |
| C | 3.992305 | 1.892171 | -0.256136 |
| C | 3.755514 | 3.253298 | -0.514999 |
| C | 2.499661 | 3.668445 | -0.906012 |
| C | 0.779186 | -0.880701 | -0.001189 |
| C | 2.134333 | -1.360298 | 0.087861 |
| C | 3.241543 | -0.492721 | -0.166352 |
| C | 2.396399 | -2.711859 | 0.487054 |
| C | 3.726182 | -3.204332 | 0.466822 |
| C | 4.771013 | -2.377736 | 0.110435 |
| C | 4.529782 | -1.022992 | -0.183219 |
| C | -0.225205 | -1.678092 | 0.573610 |
| C | 0.056866 | -2.993297 | 1.029117 |
| C | 1.320117 | -3.521383 | 0.932525 |
| C | -1.776592 | -0.058786 | -1.723236 |
| C | -2.501805 | -0.922520 | -0.882400 |
| C | -3.581177 | -1.672813 | -1.369098 |
| C | -3.963683 | -1.569623 | -2.705450 |

| | | | |
|---|---|---|---|
| C | -3.251102 | -0.720639 | -3.557956 |
| C | -2.178720 | 0.026470 | -3.071905 |
| P | -1.967232 | -1.191824 | 0.825162 |
| C | -1.994063 | 0.414581 | 1.699354 |
| C | -1.017857 | 0.730205 | 2.655526 |
| C | -1.121207 | 1.902500 | 3.407411 |
| C | -2.202787 | 2.766300 | 3.214242 |
| C | -3.183973 | 2.453740 | 2.268579 |
| C | -3.080995 | 1.282953 | 1.515241 |
| O | -2.767922 | -2.260404 | 1.524955 |
| H | -0.174333 | 0.063696 | 2.814160 |
| H | -0.357000 | 2.140394 | 4.142935 |
| H | -2.282262 | 3.678645 | 3.800039 |
| H | -4.029121 | 3.120580 | 2.117409 |
| H | -3.848848 | 1.045927 | 0.782695 |
| H | -4.102922 | -2.335641 | -0.684043 |
| H | -4.802616 | -2.149616 | -3.080856 |
| H | -3.525332 | -0.643291 | -4.607139 |
| H | -1.625053 | 0.670570 | -3.749662 |
| H | -1.769792 | 2.488224 | -2.095569 |
| H | -0.016314 | 4.172966 | -1.734259 |
| H | 2.308518 | 4.709717 | -1.154316 |
| H | 4.570320 | 3.966977 | -0.426538 |
| H | 4.994736 | 1.585718 | 0.023307 |
| H | 5.375033 | -0.386892 | -0.424404 |
| H | 5.788258 | -2.759242 | 0.079971 |
| H | 3.905606 | -4.239768 | 0.746011 |
| H | 1.518231 | -4.545016 | 1.241588 |
| H | -0.761128 | -3.572447 | 1.447477 |

($S_P$,*P*)-**1**

E(hartree): -1648.728635

| | | | |
|---|---|---|---|
| C | 1.265496 | 1.986266 | 2.870023 |
| C | 1.139219 | 1.330713 | 1.632811 |

| | | | |
|---|---|---|---|
| C | 1.683648 | 1.959039 | 0.488701 |
| C | 2.332899 | 3.195974 | 0.601098 |
| C | 2.454133 | 3.825578 | 1.840892 |
| C | 1.908511 | 3.220502 | 2.975310 |
| C | 0.542902 | -0.035801 | 1.583071 |
| C | -0.429334 | -0.444301 | 0.665032 |
| C | -0.813010 | -1.835993 | 0.614590 |
| C | -0.278376 | -2.759180 | 1.571536 |
| C | 0.644404 | -2.285319 | 2.539904 |
| C | 1.052201 | -0.976835 | 2.528400 |
| C | -1.684681 | -2.356111 | -0.385561 |
| C | -2.023952 | -3.692684 | -0.419188 |
| C | -1.516422 | -4.590999 | 0.549707 |
| C | -0.657747 | -4.128076 | 1.522017 |
| C | -1.097974 | 0.515985 | -0.271433 |
| C | -0.376603 | 1.197518 | -1.248785 |
| C | -1.026233 | 2.025395 | -2.203023 |
| C | -2.390718 | 2.182814 | -2.174053 |
| C | -3.165202 | 1.573709 | -1.151503 |
| C | -2.518006 | 0.742109 | -0.176112 |
| C | -4.568069 | 1.793464 | -1.060828 |
| C | -5.308283 | 1.243781 | -0.038310 |
| C | -4.668982 | 0.450458 | 0.945996 |
| C | -3.314586 | 0.204564 | 0.876371 |
| P | 1.450106 | 1.318573 | -1.212087 |
| C | 2.192315 | -0.345039 | -1.336903 |
| O | 1.973400 | 2.272638 | -2.256034 |
| H | 2.728407 | 3.656746 | -0.300096 |
| H | 2.961020 | 4.783874 | 1.917809 |
| H | 1.979381 | 3.708527 | 3.944220 |
| H | 0.839069 | 1.526665 | 3.758021 |
| H | 1.804131 | -0.641588 | 3.236811 |
| H | 1.051927 | -2.981804 | 3.269349 |
| H | -0.245008 | -4.807905 | 2.264300 |

| | | | |
|---|---|---|---|
| H | -1.796539 | -5.640692 | 0.517736 |
| H | -2.685697 | -4.059062 | -1.199925 |
| H | -2.082557 | -1.690442 | -1.143036 |
| H | -2.841489 | -0.400782 | 1.641599 |
| H | -5.250902 | 0.034394 | 1.764385 |
| H | -6.378252 | 1.425159 | 0.023004 |
| H | -5.044443 | 2.418644 | -1.812826 |
| H | -2.889741 | 2.803528 | -2.914972 |
| H | -0.414520 | 2.536096 | -2.941173 |
| C | 3.360960 | -0.659570 | -0.628195 |
| C | 4.003144 | -1.881845 | -0.836763 |
| C | 3.484452 | -2.797938 | -1.756283 |
| C | 2.322336 | -2.488604 | -2.469033 |
| C | 1.679981 | -1.266703 | -2.262281 |
| H | 3.770548 | 0.049195 | 0.087035 |
| H | 4.907409 | -2.118176 | -0.281553 |
| H | 3.984364 | -3.749747 | -1.917416 |
| H | 1.915293 | -3.198297 | -3.184678 |
| H | 0.778303 | -1.031259 | -2.822251 |

($S_P$,*M*)-**1**

E(hartree): -1648.675768

| | | | |
|---|---|---|---|
| C | 2.311982 | 2.965961 | -0.845832 |
| C | 1.830698 | 1.667896 | -0.551202 |
| C | 2.571467 | 0.591603 | -1.070961 |
| C | 3.728456 | 0.795867 | -1.835931 |
| C | 4.185348 | 2.084905 | -2.101196 |
| C | 3.465615 | 3.171949 | -1.600358 |
| C | 0.540290 | 1.623390 | 0.208839 |
| C | -0.645227 | 0.897378 | -0.110146 |
| C | -1.879068 | 1.670648 | 0.071117 |
| C | -1.946437 | 2.729038 | 1.032738 |
| C | -0.753367 | 3.098807 | 1.705777 |
| C | 0.439538 | 2.632857 | 1.221211 |

| | | | |
|---|---|---|---|
| C | -3.012094 | 1.500469 | -0.775954 |
| C | -4.158757 | 2.251601 | -0.612856 |
| C | -4.258110 | 3.199499 | 0.431258 |
| C | -3.162615 | 3.435443 | 1.233269 |
| C | -0.749695 | -0.490945 | -0.623934 |
| C | 0.301132 | -1.226785 | -1.216097 |
| C | 0.028873 | -2.364566 | -2.020126 |
| C | -1.245074 | -2.862488 | -2.151854 |
| C | -2.261493 | -2.382428 | -1.288715 |
| C | -1.994991 | -1.244680 | -0.453154 |
| C | -3.498104 | -3.078150 | -1.170387 |
| C | -4.399490 | -2.759592 | -0.180878 |
| C | -4.077016 | -1.739171 | 0.744516 |
| C | -2.921315 | -0.999706 | 0.603412 |
| P | 2.072326 | -1.113475 | -0.793526 |
| C | 2.133046 | -1.391179 | 1.019952 |
| O | 2.905817 | -2.099818 | -1.571622 |
| H | 4.255429 | -0.076013 | -2.213461 |
| H | 5.083006 | 2.238733 | -2.693928 |
| H | 3.789402 | 4.188492 | -1.809615 |
| H | 1.746302 | 3.829615 | -0.511858 |
| H | 1.368900 | 3.030616 | 1.617887 |
| H | -0.784053 | 3.825325 | 2.514038 |
| H | -3.193254 | 4.205496 | 2.001007 |
| H | -5.176328 | 3.763706 | 0.571876 |
| H | -4.990559 | 2.111741 | -1.298297 |
| H | -2.964612 | 0.787177 | -1.590060 |
| H | -2.699948 | -0.237186 | 1.338952 |
| H | -4.741187 | -1.536773 | 1.580713 |
| H | -5.329238 | -3.313737 | -0.081813 |
| H | -3.689461 | -3.906340 | -1.849038 |
| H | -1.452285 | -3.698791 | -2.815142 |
| H | 0.870332 | -2.841776 | -2.514206 |
| C | 3.066705 | -0.707221 | 1.812883 |

| | | | |
|---|---|---|---|
| C | 3.191766 | -1.003272 | 3.172328 |
| C | 2.385874 | -1.986601 | 3.751808 |
| C | 1.456943 | -2.676922 | 2.967225 |
| C | 1.331923 | -2.382896 | 1.608285 |
| H | 3.697440 | 0.059836 | 1.371512 |
| H | 3.917456 | -0.465280 | 3.777140 |
| H | 2.481956 | -2.215869 | 4.810154 |
| H | 0.829505 | -3.444781 | 3.412560 |
| H | 0.608947 | -2.927754 | 1.007207 |

transition state of **1**

E(hartree): -1648.654157

| | | | |
|---|---|---|---|
| C | 3.554413 | 1.196181 | -0.396738 |
| C | 2.775226 | 0.005266 | -0.375068 |
| C | 3.533821 | -1.188889 | -0.653767 |
| C | 4.954877 | -1.181222 | -0.586988 |
| C | 5.659782 | -0.011394 | -0.421572 |
| C | 4.936904 | 1.198579 | -0.408640 |
| C | 1.308054 | -0.099778 | -0.233002 |
| C | 0.746858 | -1.199325 | -0.916578 |
| C | 1.538548 | -2.279589 | -1.410642 |
| C | 2.876777 | -2.341784 | -1.148207 |
| C | 0.365601 | 0.721714 | 0.660492 |
| C | -0.631660 | 0.013298 | 1.368235 |
| C | -1.776461 | 0.672259 | 1.916376 |
| C | -2.007851 | 1.999497 | 1.709873 |
| C | -0.969630 | 2.798064 | 1.174001 |
| C | 0.283976 | 2.188962 | 0.807798 |
| C | -1.137549 | 4.209265 | 1.137162 |
| C | -0.077616 | 5.052966 | 0.896095 |
| C | 1.203598 | 4.480961 | 0.768264 |
| C | 1.366427 | 3.108104 | 0.735867 |
| C | -0.739753 | -1.465317 | 1.616633 |
| C | -1.195070 | -2.324674 | 0.604940 |

| | | | |
|---|---|---|---|
| C | -1.496824 | -3.663170 | 0.872079 |
| C | -1.360339 | -4.154608 | 2.173053 |
| C | -0.901129 | -3.309820 | 3.188212 |
| C | -0.604614 | -1.969993 | 2.916564 |
| P | -1.024836 | -1.707659 | -1.093600 |
| O | -1.216784 | -2.793547 | -2.122188 |
| C | -2.118119 | -0.286291 | -1.423801 |
| C | -1.671044 | 0.816972 | -2.163826 |
| C | -2.571703 | 1.808067 | -2.561010 |
| C | -3.924601 | 1.700949 | -2.228126 |
| C | -4.377235 | 0.599116 | -1.495662 |
| C | -3.478823 | -0.391454 | -1.096857 |
| H | -1.810771 | -4.307655 | 0.055243 |
| H | -1.595856 | -5.193110 | 2.390792 |
| H | -0.774606 | -3.692416 | 4.197971 |
| H | -0.267653 | -1.313076 | 3.714772 |
| H | -2.519486 | 0.062205 | 2.420281 |
| H | -2.941638 | 2.464274 | 2.016367 |
| H | -2.124024 | 4.609024 | 1.361466 |
| H | -0.211228 | 6.131250 | 0.883995 |
| H | 2.083547 | 5.118618 | 0.730768 |
| H | 2.369932 | 2.734543 | 0.778365 |
| H | 3.062998 | 2.140211 | -0.536088 |
| H | 5.464403 | 2.148551 | -0.447599 |
| H | 6.745877 | -0.012159 | -0.388717 |
| H | 5.474955 | -2.124790 | -0.736295 |
| H | 3.459962 | -3.223593 | -1.402722 |
| H | 1.032539 | -3.090135 | -1.925139 |
| H | -3.838709 | -1.250797 | -0.535984 |
| H | -5.429756 | 0.508517 | -1.239004 |
| H | -4.624958 | 2.470994 | -2.541915 |
| H | -2.215632 | 2.661571 | -3.132150 |
| H | -0.622144 | 0.903769 | -2.433866 |

($R_P$,*M*)-**2**

E(hartree): -1647.540285

| | | | |
|---|---|---|---|
| C | -4.529829 | -1.022929 | 0.183057 |
| C | -3.241577 | -0.492683 | 0.166245 |
| C | -2.134368 | -1.360266 | -0.087943 |
| C | -2.396448 | -2.711822 | -0.487146 |
| C | -3.726239 | -3.204275 | -0.466962 |
| C | -4.771076 | -2.377664 | -0.110616 |
| C | -0.779211 | -0.880683 | 0.001128 |
| C | -0.543016 | 0.431211 | 0.646549 |
| C | -1.644357 | 1.365882 | 0.648774 |
| C | -2.977080 | 0.940808 | 0.344942 |
| C | -1.436406 | 2.737468 | 1.003096 |
| C | -0.161176 | 3.130287 | 1.481742 |
| C | 0.815859 | 2.190426 | 1.671005 |
| C | 0.655346 | 0.825980 | 1.282829 |
| C | -3.992334 | 1.892211 | 0.256076 |
| C | -3.755544 | 3.253331 | 0.514970 |
| C | -2.499686 | 3.668464 | 0.905984 |
| C | -1.320179 | -3.521369 | -0.932600 |
| C | -0.056921 | -2.993290 | -1.029188 |
| C | 0.225168 | -1.678092 | -0.573684 |
| C | 1.776521 | -0.058789 | 1.723263 |
| C | 2.501684 | -0.922589 | 0.882450 |
| C | 3.580969 | -1.672979 | 1.369187 |
| C | 3.963460 | -1.569802 | 2.705548 |
| C | 3.250949 | -0.720725 | 3.558020 |
| C | 2.178639 | 0.026463 | 3.071935 |
| P | 1.967196 | -1.191864 | -0.825154 |
| O | 2.767932 | -2.260440 | -1.524892 |
| C | 1.994119 | 0.414575 | -1.699284 |
| C | 1.017858 | 0.730544 | -2.655274 |
| C | 1.121418 | 1.902871 | -3.407086 |
| C | 2.203267 | 2.766357 | -3.214024 |

| | | | |
|---|---|---|---|
| C | 3.184527 | 2.453447 | -2.268549 |
| C | 3.081342 | 1.282628 | -1.515292 |
| H | 0.174109 | 0.064297 | -2.813805 |
| H | 0.357161 | 2.141044 | -4.142464 |
| H | 2.282897 | 3.678721 | -3.799769 |
| H | 4.029880 | 3.120044 | -2.117462 |
| H | 3.849253 | 1.045332 | -0.782901 |
| H | 4.102675 | -2.335860 | 0.684155 |
| H | 4.802323 | -2.149875 | 3.080980 |
| H | 3.525168 | -0.643370 | 4.607204 |
| H | 1.625007 | 0.670609 | 3.749675 |
| H | 1.769718 | 2.488217 | 2.095623 |
| H | 0.016310 | 4.172981 | 1.734198 |
| H | -2.308543 | 4.709729 | 1.154310 |
| H | -4.570347 | 3.967015 | 0.426535 |
| H | -4.994764 | 1.585761 | -0.023374 |
| H | -5.375073 | -0.386809 | 0.424210 |
| H | -5.788325 | -2.759159 | -0.080209 |
| H | -3.905676 | -4.239702 | -0.746169 |
| H | -1.518284 | -4.545011 | -1.241630 |
| H | 0.761057 | -3.572449 | -1.447564 |

($R_P$,*P*)-**2**

E(hartree): -1647.532405

| | | | |
|---|---|---|---|
| C | -3.962389 | -2.607257 | -0.771279 |
| C | -3.124273 | -1.585787 | -0.329341 |
| C | -1.709905 | -1.725361 | -0.490254 |
| C | -1.194659 | -2.987341 | -0.930597 |
| C | -2.085074 | -4.005379 | -1.356430 |
| C | -3.448110 | -3.803608 | -1.303890 |
| C | -0.813586 | -0.643412 | -0.172380 |
| C | -1.400693 | 0.697996 | 0.043151 |
| C | -2.780091 | 0.752199 | 0.465016 |
| C | -3.633869 | -0.389330 | 0.350375 |

| | | | |
|---|---|---|---|
| C | -3.343594 | 1.970234 | 0.962774 |
| C | -2.563754 | 3.152321 | 0.907193 |
| C | -1.333462 | 3.129082 | 0.307650 |
| C | -0.729586 | 1.922130 | -0.155361 |
| C | -4.930175 | -0.327745 | 0.859399 |
| C | -5.442271 | 0.848045 | 1.434572 |
| C | -4.667514 | 1.988853 | 1.466273 |
| C | 0.203768 | -3.206667 | -0.883022 |
| C | 1.037200 | -2.235199 | -0.387631 |
| C | 0.557458 | -0.944436 | -0.037442 |
| C | 0.544112 | 2.144651 | -0.901882 |
| C | 1.777498 | 1.533021 | -0.593611 |
| C | 2.946115 | 1.930199 | -1.261715 |
| C | 2.903731 | 2.896797 | -2.265144 |
| C | 1.680123 | 3.476207 | -2.610038 |
| C | 0.522340 | 3.113495 | -1.925276 |
| P | 1.724361 | 0.261487 | 0.706337 |
| O | 1.308702 | 0.763508 | 2.063620 |
| C | 3.386559 | -0.517871 | 0.777405 |
| C | 4.106395 | -1.004360 | -0.328011 |
| C | 5.376231 | -1.558691 | -0.156059 |
| C | 5.941791 | -1.633305 | 1.121597 |
| C | 5.234134 | -1.150561 | 2.224510 |
| C | 3.963012 | -0.593834 | 2.054209 |
| H | 3.680007 | -0.954605 | -1.326630 |
| H | 5.923170 | -1.931479 | -1.018506 |
| H | 6.930745 | -2.065179 | 1.253405 |
| H | 5.669678 | -1.204729 | 3.218953 |
| H | 3.405033 | -0.209383 | 2.903273 |
| H | 3.899167 | 1.490148 | -0.988599 |
| H | 3.817819 | 3.194337 | -2.772281 |
| H | 1.627166 | 4.216240 | -3.404537 |
| H | -0.424260 | 3.575884 | -2.190859 |
| H | -0.763654 | 4.048656 | 0.218102 |

| | | | |
|---|---|---|---|
| H | -2.967837 | 4.078949 | 1.307687 |
| H | -5.061515 | 2.919213 | 1.868389 |
| H | -6.453549 | 0.856048 | 1.832453 |
| H | -5.566517 | -1.205597 | 0.821875 |
| H | -5.039024 | -2.490948 | -0.704043 |
| H | -4.132465 | -4.576079 | -1.644921 |
| H | -1.673829 | -4.946638 | -1.713168 |
| H | 0.601653 | -4.171594 | -1.188435 |
| H | 2.088410 | -2.464159 | -0.264745 |

transition state of **2**

E(hartree): -1647.493352

| | | | |
|---|---|---|---|
| C | 0.862915 | 3.833471 | -0.320583 |
| C | 0.659680 | 2.420858 | -0.277014 |
| C | 1.822461 | 1.672138 | 0.044144 |
| C | 3.082456 | 2.298773 | 0.142530 |
| C | 3.248716 | 3.665414 | -0.022166 |
| C | 2.106114 | 4.440415 | -0.216841 |
| C | -0.750676 | 1.940328 | -0.482825 |
| C | -1.424370 | 0.710636 | -0.163046 |
| C | -2.871097 | 0.799714 | 0.017107 |
| C | -3.584163 | 2.031269 | -0.143190 |
| C | -2.923781 | 3.066148 | -0.844378 |
| C | -1.581313 | 2.975490 | -1.044103 |
| C | -0.842721 | -0.666558 | -0.129750 |
| C | -1.753505 | -1.796690 | -0.202283 |
| C | -3.142219 | -1.661076 | 0.094625 |
| C | -3.665149 | -0.331226 | 0.383542 |
| C | -1.280169 | -3.112801 | -0.531112 |
| C | 0.099638 | -3.317654 | -0.748954 |
| C | 0.973077 | -2.294869 | -0.501938 |
| C | 0.533100 | -0.989305 | -0.151598 |
| C | -3.988054 | -2.768165 | 0.020184 |
| C | -3.512922 | -4.040604 | -0.331417 |

| | | | |
|---|---|---|---|
| C | -2.174819 | -4.209234 | -0.608368 |
| C | -4.919976 | 2.175540 | 0.293642 |
| C | -5.577026 | 1.110435 | 0.875543 |
| C | -4.954652 | -0.145590 | 0.886057 |
| P | 1.790939 | -0.005147 | 0.703737 |
| O | 1.583311 | -0.032888 | 2.197073 |
| C | 3.421569 | -0.727101 | 0.250024 |
| C | 4.175130 | -1.299391 | 1.282962 |
| C | 5.427670 | -1.861457 | 1.012600 |
| C | 5.932176 | -1.853045 | -0.289728 |
| C | 5.184354 | -1.279898 | -1.325717 |
| C | 3.935412 | -0.718423 | -1.056958 |
| H | 3.361729 | -0.271739 | -1.866152 |
| H | 5.575511 | -1.269216 | -2.340021 |
| H | 6.905855 | -2.288528 | -0.500322 |
| H | 6.007163 | -2.302512 | 1.819683 |
| H | 3.771374 | -1.293037 | 2.291817 |
| H | 3.949881 | 1.695687 | 0.386262 |
| H | 4.233345 | 4.117279 | 0.059271 |
| H | 2.171076 | 5.524617 | -0.261825 |
| H | 0.016094 | 4.499746 | -0.386086 |
| H | -1.107995 | 3.747626 | -1.633571 |
| H | -3.488497 | 3.916239 | -1.219362 |
| H | -5.407650 | 3.139863 | 0.173676 |
| H | -6.583225 | 1.222682 | 1.270170 |
| H | -5.507254 | -0.997078 | 1.268106 |
| H | -5.049641 | -2.647035 | 0.202730 |
| H | -4.202729 | -4.878326 | -0.389988 |
| H | -1.777685 | -5.184580 | -0.878378 |
| H | 0.459660 | -4.301930 | -1.037616 |
| H | 2.035294 | -2.494671 | -0.556985 |

Total energies and Cartesian coordinates at the B3LYP-D3/cc-pVDZ level
($S_P$,*P*)-**1**

E(hartree): -1648.837998

| | | | |
|---|---|---|---|
| C | 1.203543 | 2.278307 | 2.708831 |
| C | 1.080707 | 1.562097 | 1.506105 |
| C | 1.466016 | 2.204015 | 0.305714 |
| C | 1.957949 | 3.515109 | 0.324227 |
| C | 2.077981 | 4.207076 | 1.531597 |
| C | 1.690623 | 3.587405 | 2.723166 |
| C | 0.672513 | 0.128878 | 1.525620 |
| C | -0.293364 | -0.424822 | 0.680804 |
| C | -0.447027 | -1.857144 | 0.624533 |
| C | 0.320162 | -2.691546 | 1.501425 |
| C | 1.220776 | -2.082218 | 2.414943 |
| C | 1.399075 | -0.722267 | 2.411996 |
| C | -1.295837 | -2.494810 | -0.326195 |
| C | -1.389558 | -3.869438 | -0.393508 |
| C | -0.646678 | -4.687334 | 0.492595 |
| C | 0.190400 | -4.105032 | 1.419656 |
| C | -1.159056 | 0.416653 | -0.205732 |
| C | -0.610786 | 1.161165 | -1.246028 |
| C | -1.425858 | 1.888431 | -2.151721 |
| C | -2.794106 | 1.872160 | -2.014284 |
| C | -3.404564 | 1.173036 | -0.936797 |
| C | -2.583412 | 0.444711 | -0.009709 |
| C | -4.815217 | 1.193392 | -0.746297 |
| C | -5.397335 | 0.542717 | 0.319410 |
| C | -4.587302 | -0.155453 | 1.250177 |
| C | -3.219193 | -0.204447 | 1.088849 |
| P | 1.193938 | 1.465745 | -1.355230 |
| C | 2.027377 | -0.164281 | -1.400151 |
| O | 1.561217 | 2.418310 | -2.483507 |
| H | 2.231316 | 3.977778 | -0.626798 |
| H | 2.464152 | 5.228681 | 1.541194 |
| H | 1.764819 | 4.125266 | 3.671154 |
| H | 0.899623 | 1.801576 | 3.643489 |

| | | | |
|---|---|---|---|
| H | 2.142942 | -0.270148 | 3.070239 |
| H | 1.800932 | -2.714636 | 3.091384 |
| H | 0.780216 | -4.723435 | 2.101103 |
| H | -0.733100 | -5.774507 | 0.433305 |
| H | -2.039994 | -4.330559 | -1.140067 |
| H | -1.867944 | -1.883927 | -1.023031 |
| H | -2.607033 | -0.741401 | 1.813155 |
| H | -5.051135 | -0.656071 | 2.102944 |
| H | -6.480833 | 0.569799 | 0.455001 |
| H | -5.429789 | 1.745754 | -1.461689 |
| H | -3.428710 | 2.417697 | -2.717368 |
| H | -0.932255 | 2.459752 | -2.940503 |
| C | 3.235607 | -0.370743 | -0.718652 |
| C | 3.878599 | -1.608225 | -0.793431 |
| C | 3.319135 | -2.644906 | -1.547534 |
| C | 2.118072 | -2.440744 | -2.233943 |
| C | 1.475662 | -1.203473 | -2.164223 |
| H | 3.664720 | 0.431911 | -0.114430 |
| H | 4.814972 | -1.766704 | -0.253636 |
| H | 3.817667 | -3.615709 | -1.596176 |
| H | 1.672554 | -3.251276 | -2.814440 |
| H | 0.528646 | -1.052106 | -2.686980 |

($S_P$,*M*)-**1**

E(hartree): -1648.782878

| | | | |
|---|---|---|---|
| C | 2.593555 | 2.676502 | -1.050269 |
| C | 2.013103 | 1.448787 | -0.653044 |
| C | 2.693987 | 0.280890 | -1.036581 |
| C | 3.888883 | 0.321103 | -1.765963 |
| C | 4.445947 | 1.545092 | -2.133331 |
| C | 3.786466 | 2.723744 | -1.772313 |
| C | 0.708843 | 1.552348 | 0.075479 |
| C | -0.520163 | 0.893922 | -0.226904 |
| C | -1.700137 | 1.755043 | -0.106065 |

| | | | |
|---|---|---|---|
| C | -1.710342 | 2.858652 | 0.806367 |
| C | -0.499828 | 3.191135 | 1.469516 |
| C | 0.666280 | 2.624938 | 1.024367 |
| C | -2.835478 | 1.609835 | -0.955775 |
| C | -3.943407 | 2.422996 | -0.827266 |
| C | -3.994924 | 3.419179 | 0.175923 |
| C | -2.888707 | 3.636769 | 0.969143 |
| C | -0.715253 | -0.510727 | -0.658789 |
| C | 0.296584 | -1.360563 | -1.158605 |
| C | -0.021483 | -2.533733 | -1.888363 |
| C | -1.324819 | -2.946677 | -2.040566 |
| C | -2.333827 | -2.333311 | -1.253755 |
| C | -2.012113 | -1.165284 | -0.479963 |
| C | -3.624563 | -2.925271 | -1.138767 |
| C | -4.530510 | -2.476823 | -0.204471 |
| C | -4.158908 | -1.430642 | 0.674120 |
| C | -2.945094 | -0.791290 | 0.533224 |
| P | 2.041601 | -1.344083 | -0.614744 |
| C | 1.893935 | -1.362406 | 1.220147 |
| O | 2.850120 | -2.489423 | -1.206525 |
| H | 4.361090 | -0.628002 | -2.028246 |
| H | 5.379083 | 1.580602 | -2.699372 |
| H | 4.193912 | 3.693842 | -2.066437 |
| H | 2.079030 | 3.610284 | -0.819623 |
| H | 1.621173 | 2.985089 | 1.410718 |
| H | -0.491741 | 3.963936 | 2.241300 |
| H | -2.880188 | 4.444960 | 1.704847 |
| H | -4.888588 | 4.036341 | 0.290792 |
| H | -4.784749 | 2.295450 | -1.511653 |
| H | -2.820886 | 0.854646 | -1.739602 |
| H | -2.682630 | -0.002419 | 1.234321 |
| H | -4.833947 | -1.128655 | 1.477680 |
| H | -5.508704 | -2.952985 | -0.108219 |
| H | -3.859195 | -3.781598 | -1.775937 |

| | | | |
|---|---|---|---|
| H | -1.571743 | -3.815783 | -2.654745 |
| H | 0.811206 | -3.111593 | -2.294406 |
| C | 2.795062 | -0.636854 | 2.013763 |
| C | 2.718955 | -0.706527 | 3.407222 |
| C | 1.743385 | -1.501346 | 4.016593 |
| C | 0.845747 | -2.231067 | 3.229879 |
| C | 0.919972 | -2.164147 | 1.837231 |
| H | 3.551806 | -0.006081 | 1.542067 |
| H | 3.420654 | -0.134282 | 4.018481 |
| H | 1.680924 | -1.551178 | 5.106196 |
| H | 0.081656 | -2.852484 | 3.702376 |
| H | 0.209976 | -2.729065 | 1.229712 |

transition state of **1**

E(hartree): -1648.764346

| | | | |
|---|---|---|---|
| C | -1.633977 | 0.869264 | -1.930421 |
| C | -2.068524 | -0.355820 | -1.408956 |
| C | -3.435953 | -0.567044 | -1.172063 |
| C | -4.357293 | 0.446881 | -1.437982 |
| C | -3.918729 | 1.675434 | -1.944358 |
| C | -2.558552 | 1.883916 | -2.191119 |
| P | -0.929733 | -1.759750 | -1.137350 |
| C | -1.097151 | -2.393428 | 0.559424 |
| C | -0.730684 | -1.508407 | 1.584237 |
| C | -0.612790 | -2.001636 | 2.889387 |
| C | -0.838546 | -3.359183 | 3.148658 |
| C | -1.203275 | -4.231265 | 2.116987 |
| C | -1.323661 | -3.748780 | 0.810070 |
| C | -0.684136 | -0.032452 | 1.313950 |
| C | 0.331443 | 0.701014 | 0.664354 |
| C | 0.183079 | 2.163237 | 0.786434 |
| C | -1.129835 | 2.721373 | 0.983476 |
| C | -2.187318 | 1.884517 | 1.422722 |
| C | -1.909767 | 0.582840 | 1.722794 |

| | | | |
|---|---|---|---|
| C | 1.235439 | 3.116765 | 0.857569 |
| C | 1.019416 | 4.483303 | 0.839073 |
| C | -0.289575 | 5.003420 | 0.769346 |
| C | -1.343470 | 4.123836 | 0.886563 |
| C | 1.327461 | -0.076477 | -0.200864 |
| C | 0.822273 | -1.177543 | -0.928838 |
| C | 1.662691 | -2.198344 | -1.462242 |
| C | 3.005786 | -2.199296 | -1.210570 |
| C | 3.603811 | -1.038779 | -0.659867 |
| C | 2.784915 | 0.097949 | -0.313403 |
| C | 5.023192 | -0.960282 | -0.582542 |
| C | 5.664530 | 0.230143 | -0.325873 |
| C | 4.880445 | 1.398507 | -0.220954 |
| C | 3.500352 | 1.324615 | -0.225551 |
| O | -1.082071 | -2.855983 | -2.182478 |
| H | -1.567351 | -4.406133 | -0.027553 |
| H | -1.380731 | -5.287788 | 2.330003 |
| H | -0.728348 | -3.737305 | 4.167749 |
| H | -0.344624 | -1.321171 | 3.700675 |
| H | -2.671770 | -0.055900 | 2.170424 |
| H | -3.180158 | 2.306490 | 1.590025 |
| H | -2.369386 | 4.491380 | 0.969146 |
| H | -0.460951 | 6.080185 | 0.711068 |
| H | 1.874116 | 5.159181 | 0.917111 |
| H | 2.238768 | 2.770236 | 1.054164 |
| H | 2.951808 | 2.251093 | -0.276898 |
| H | 5.361540 | 2.378109 | -0.170688 |
| H | 6.754333 | 0.282532 | -0.282986 |
| H | 5.596659 | -1.867075 | -0.790725 |
| H | 3.635219 | -3.041801 | -1.506837 |
| H | 1.184873 | -3.015283 | -2.004916 |
| H | -3.778032 | -1.525346 | -0.773718 |
| H | -5.420022 | 0.279265 | -1.248517 |
| H | -4.639017 | 2.471316 | -2.147821 |

| | | | |
|---|---|---|---|
| H | -2.211789 | 2.843606 | -2.580126 |
| H | -0.572164 | 1.038864 | -2.116135 |

($R_P$,*M*)-**2**

E(hartree): -1647.645101

| | | | |
|---|---|---|---|
| C | -4.493677 | -1.054163 | 0.312172 |
| C | -3.204729 | -0.525702 | 0.256517 |
| C | -2.109408 | -1.395502 | -0.042481 |
| C | -2.385324 | -2.743672 | -0.447328 |
| C | -3.715424 | -3.234189 | -0.382239 |
| C | -4.745639 | -2.407915 | 0.018515 |
| C | -0.752773 | -0.917320 | 0.000351 |
| C | -0.487861 | 0.388708 | 0.643908 |
| C | -1.582243 | 1.329132 | 0.680226 |
| C | -2.928167 | 0.907646 | 0.427652 |
| C | -1.350380 | 2.702928 | 1.013538 |
| C | -0.052612 | 3.090993 | 1.436332 |
| C | 0.924301 | 2.144724 | 1.600109 |
| C | 0.736691 | 0.778395 | 1.231985 |
| C | -3.942104 | 1.864662 | 0.376489 |
| C | -3.686288 | 3.226855 | 0.615651 |
| C | -2.412538 | 3.639460 | 0.950294 |
| C | -1.326025 | -3.547084 | -0.947890 |
| C | -0.068660 | -3.013388 | -1.095076 |
| C | 0.224733 | -1.705131 | -0.630241 |
| C | 1.867864 | -0.116048 | 1.622253 |
| C | 2.554190 | -0.967562 | 0.737413 |
| C | 3.647022 | -1.735755 | 1.157613 |
| C | 4.084900 | -1.660279 | 2.479778 |
| C | 3.414782 | -0.821524 | 3.377529 |
| C | 2.326483 | -0.057060 | 2.953988 |
| P | 1.948118 | -1.185878 | -0.958010 |
| O | 2.740040 | -2.215909 | -1.749532 |
| C | 1.872209 | 0.487872 | -1.704614 |

| | | | |
|---|---|---|---|
| C | 0.792888 | 0.877944 | -2.510340 |
| C | 0.784564 | 2.140775 | -3.107206 |
| C | 1.855243 | 3.017946 | -2.908099 |
| C | 2.938871 | 2.628936 | -2.113741 |
| C | 2.948454 | 1.368029 | -1.514166 |
| H | -0.051107 | 0.201465 | -2.659250 |
| H | -0.063895 | 2.442294 | -3.725520 |
| H | 1.844787 | 4.007060 | -3.371868 |
| H | 3.776865 | 3.311900 | -1.956550 |
| H | 3.790589 | 1.070900 | -0.884447 |
| H | 4.132529 | -2.386663 | 0.427095 |
| H | 4.939420 | -2.253971 | 2.811671 |
| H | 3.737564 | -0.765066 | 4.419724 |
| H | 1.805338 | 0.583165 | 3.668837 |
| H | 1.902191 | 2.438598 | 1.984102 |
| H | 0.143714 | 4.140141 | 1.668708 |
| H | -2.204961 | 4.686853 | 1.181402 |
| H | -4.504184 | 3.947798 | 0.555399 |
| H | -4.961491 | 1.559624 | 0.139599 |
| H | -5.333042 | -0.413825 | 0.584433 |
| H | -5.766598 | -2.790297 | 0.081655 |
| H | -3.908040 | -4.271492 | -0.665570 |
| H | -1.537902 | -4.571635 | -1.262897 |
| H | 0.740090 | -3.577677 | -1.563472 |

($R_P$,*P*)-**2**

E(hartree): -1647.633082

| | | | |
|---|---|---|---|
| C | -3.963569 | -2.606001 | -0.755361 |
| C | -3.121612 | -1.582709 | -0.321667 |
| C | -1.707775 | -1.723120 | -0.496334 |
| C | -1.194569 | -2.983593 | -0.946464 |
| C | -2.089661 | -4.001306 | -1.366346 |
| C | -3.452851 | -3.800568 | -1.297393 |
| C | -0.809018 | -0.643426 | -0.179519 |

| | | | |
|---|---|---|---|
| C | -1.391576 | 0.697597 | 0.046585 |
| C | -2.766633 | 0.754046 | 0.479614 |
| C | -3.624861 | -0.385917 | 0.364656 |
| C | -3.321486 | 1.973479 | 0.986713 |
| C | -2.535792 | 3.153253 | 0.932304 |
| C | -1.309125 | 3.128220 | 0.322767 |
| C | -0.716113 | 1.920300 | -0.151112 |
| C | -4.920203 | -0.319520 | 0.878242 |
| C | -5.423720 | 0.856712 | 1.462150 |
| C | -4.643732 | 1.994611 | 1.497381 |
| C | 0.205985 | -3.201404 | -0.913686 |
| C | 1.044108 | -2.232003 | -0.418839 |
| C | 0.563520 | -0.944393 | -0.057943 |
| C | 0.542224 | 2.132052 | -0.926344 |
| C | 1.778484 | 1.519847 | -0.630146 |
| C | 2.936693 | 1.890690 | -1.330695 |
| C | 2.877389 | 2.835304 | -2.355432 |
| C | 1.650456 | 3.418169 | -2.685449 |
| C | 0.503312 | 3.079675 | -1.968947 |
| P | 1.721698 | 0.271907 | 0.700988 |
| O | 1.277525 | 0.799059 | 2.054774 |
| C | 3.385141 | -0.504952 | 0.797967 |
| C | 4.116791 | -1.005792 | -0.293787 |
| C | 5.384489 | -1.557195 | -0.094741 |
| C | 5.930699 | -1.612181 | 1.193025 |
| C | 5.207928 | -1.113826 | 2.280422 |
| C | 3.939170 | -0.560065 | 2.085078 |
| H | 3.698420 | -0.968181 | -1.301933 |
| H | 5.947907 | -1.944581 | -0.946736 |
| H | 6.922569 | -2.044024 | 1.346099 |
| H | 5.632972 | -1.154648 | 3.285911 |
| H | 3.358099 | -0.159364 | 2.918284 |
| H | 3.897043 | 1.448882 | -1.064886 |
| H | 3.786029 | 3.115987 | -2.892461 |

| | | | |
|---|---|---|---|
| H | 1.586399 | 4.145037 | -3.498301 |
| H | -0.450571 | 3.545674 | -2.223923 |
| H | -0.733929 | 4.050089 | 0.226983 |
| H | -2.935834 | 4.083756 | 1.341404 |
| H | -5.033658 | 2.928935 | 1.907970 |
| H | -6.438410 | 0.867576 | 1.865363 |
| H | -5.564145 | -1.198115 | 0.836971 |
| H | -5.044542 | -2.490389 | -0.674030 |
| H | -4.143365 | -4.576723 | -1.634152 |
| H | -1.679621 | -4.945319 | -1.732600 |
| H | 0.603196 | -4.168628 | -1.230608 |
| H | 2.101201 | -2.462961 | -0.302563 |

transition state of **2**

E(hartree): -1647.593246

| | | | |
|---|---|---|---|
| C | 3.913187 | -0.689293 | -1.086144 |
| C | 3.419101 | -0.730106 | 0.227692 |
| C | 4.180496 | -1.321884 | 1.242613 |
| C | 5.429896 | -1.877290 | 0.945023 |
| C | 5.918068 | -1.840258 | -0.363976 |
| C | 5.159170 | -1.245053 | -1.380412 |
| P | 1.792522 | -0.020845 | 0.722610 |
| O | 1.605971 | -0.086541 | 2.231602 |
| C | 1.824334 | 1.668797 | 0.082085 |
| C | 0.668330 | 2.417995 | -0.258357 |
| C | 0.875496 | 3.830578 | -0.306026 |
| C | 2.117570 | 4.435788 | -0.175350 |
| C | 3.254859 | 3.659562 | 0.052149 |
| C | 3.083568 | 2.292617 | 0.213505 |
| C | -0.739233 | 1.939164 | -0.484657 |
| C | -1.420705 | 0.712220 | -0.168076 |
| C | -2.868845 | 0.808090 | 0.000864 |
| C | -3.577126 | 2.042024 | -0.173653 |
| C | -2.905225 | 3.074611 | -0.869236 |

| | | | |
|---|---|---|---|
| C | -1.560373 | 2.977980 | -1.054465 |
| C | -3.670745 | -0.318716 | 0.368092 |
| C | -3.148610 | -1.654261 | 0.099677 |
| C | -1.758049 | -1.796278 | -0.190717 |
| C | -0.844888 | -0.667203 | -0.125639 |
| C | -4.966205 | -0.124645 | 0.855149 |
| C | -5.584854 | 1.133619 | 0.829568 |
| C | -4.917800 | 2.193466 | 0.248321 |
| C | -1.286176 | -3.117463 | -0.506724 |
| C | 0.094305 | -3.327177 | -0.725108 |
| C | 0.970210 | -2.302996 | -0.489048 |
| C | 0.530325 | -0.993420 | -0.150559 |
| C | -2.183111 | -4.214093 | -0.571008 |
| C | -3.521299 | -4.040426 | -0.294386 |
| C | -3.995477 | -2.762905 | 0.041935 |
| H | 3.322857 | -0.221114 | -1.877979 |
| H | 5.542647 | -1.213210 | -2.402935 |
| H | 6.893990 | -2.273267 | -0.596182 |
| H | 6.023374 | -2.337988 | 1.738177 |
| H | 3.777134 | -1.331857 | 2.257618 |
| H | 3.946925 | 1.681408 | 0.476676 |
| H | 4.242338 | 4.113104 | 0.156025 |
| H | 2.186745 | 5.524652 | -0.227221 |
| H | 0.025980 | 4.498921 | -0.400493 |
| H | -1.073533 | 3.755543 | -1.635538 |
| H | -3.464837 | 3.931794 | -1.250007 |
| H | -5.402519 | 3.163251 | 0.115509 |
| H | -6.599858 | 1.251707 | 1.213963 |
| H | -5.527467 | -0.976538 | 1.238297 |
| H | -5.061705 | -2.637564 | 0.225777 |
| H | -4.215122 | -4.882192 | -0.341751 |
| H | -1.785890 | -5.197419 | -0.832341 |
| H | 0.453893 | -4.319122 | -1.006919 |
| H | 2.038301 | -2.503370 | -0.541442 |

Total energies and Cartesian coordinates at the ωB97XD/cc-pVDZ level
($S_P$,*P*)-**1**

E(hartree): -1648.337612

| | | | |
|---|---|---|---|
| C | 0.698882 | 2.597926 | 2.611961 |
| C | 0.727958 | 1.827428 | 1.444588 |
| C | 0.966059 | 2.478529 | 0.217481 |
| C | 1.168414 | 3.859145 | 0.175924 |
| C | 1.141116 | 4.609701 | 1.349080 |
| C | 0.896936 | 3.976417 | 2.565641 |
| C | 0.646134 | 0.341760 | 1.517585 |
| C | -0.173283 | -0.429569 | 0.706259 |
| C | 0.021398 | -1.853714 | 0.653248 |
| C | 0.999552 | -2.463801 | 1.486062 |
| C | 1.742641 | -1.652803 | 2.382877 |
| C | 1.575396 | -0.297321 | 2.387907 |
| C | -0.681063 | -2.679482 | -0.268960 |
| C | -0.424301 | -4.025771 | -0.353639 |
| C | 0.542589 | -4.628372 | 0.484362 |
| C | 1.236313 | -3.860441 | 1.385290 |
| C | -1.218793 | 0.174037 | -0.176545 |
| C | -0.867524 | 0.984714 | -1.240954 |
| C | -1.837894 | 1.492435 | -2.139524 |
| C | -3.160580 | 1.182760 | -1.966048 |
| C | -3.577697 | 0.393911 | -0.860437 |
| C | -2.605740 | -0.108238 | 0.053820 |
| C | -4.952447 | 0.106226 | -0.636849 |
| C | -5.350896 | -0.630039 | 0.449571 |
| C | -4.388892 | -1.110645 | 1.370955 |
| C | -3.053945 | -0.858173 | 1.178306 |
| P | 0.828888 | 1.638989 | -1.403783 |
| C | 1.942865 | 0.195514 | -1.414936 |
| O | 0.981126 | 2.593616 | -2.569278 |
| H | 1.333231 | 4.328739 | -0.796114 |

| | | | |
|---|---|---|---|
| H | 1.301700 | 5.688353 | 1.311416 |
| H | 0.859099 | 4.557566 | 3.488914 |
| H | 0.509839 | 2.107689 | 3.569310 |
| H | 2.198011 | 0.326640 | 3.031469 |
| H | 2.479606 | -2.121679 | 3.038286 |
| H | 1.990999 | -4.310262 | 2.034301 |
| H | 0.736339 | -5.699629 | 0.408059 |
| H | -0.968942 | -4.635149 | -1.076850 |
| H | -1.420264 | -2.232209 | -0.932648 |
| H | -2.321270 | -1.226934 | 1.896465 |
| H | -4.712890 | -1.682578 | 2.242097 |
| H | -6.409507 | -0.839899 | 0.612047 |
| H | -5.688412 | 0.490190 | -1.346839 |
| H | -3.913950 | 1.557174 | -2.662638 |
| H | -1.498249 | 2.134470 | -2.954393 |
| C | 3.109544 | 0.163084 | -0.647124 |
| C | 3.923235 | -0.967122 | -0.662533 |
| C | 3.578603 | -2.065929 | -1.448195 |
| C | 2.426881 | -2.029462 | -2.232892 |
| C | 1.612911 | -0.900597 | -2.219040 |
| H | 3.369697 | 1.013169 | -0.012230 |
| H | 4.825632 | -0.993528 | -0.049114 |
| H | 4.209897 | -2.956465 | -1.447770 |
| H | 2.152703 | -2.889357 | -2.846068 |
| H | 0.698166 | -0.882688 | -2.816177 |

($S_P$,*M*)-**1**

E(hartree): -1648.278512

| | | | |
|---|---|---|---|
| C | 2.619365 | 2.711951 | -0.886077 |
| C | 2.029566 | 1.475095 | -0.558066 |
| C | 2.707035 | 0.326128 | -0.982157 |
| C | 3.914802 | 0.394059 | -1.679883 |
| C | 4.486442 | 1.626517 | -1.972959 |
| C | 3.826095 | 2.786750 | -1.574434 |

| | | | |
|---|---|---|---|
| C | 0.705406 | 1.561610 | 0.138630 |
| C | -0.503676 | 0.917423 | -0.204490 |
| C | -1.688235 | 1.764584 | -0.093180 |
| C | -1.722762 | 2.852939 | 0.820312 |
| C | -0.531858 | 3.178429 | 1.519799 |
| C | 0.639436 | 2.618102 | 1.103304 |
| C | -2.803164 | 1.617347 | -0.967749 |
| C | -3.910640 | 2.422603 | -0.859993 |
| C | -3.986920 | 3.412221 | 0.145451 |
| C | -2.904689 | 3.626944 | 0.961522 |
| C | -0.695166 | -0.480290 | -0.681171 |
| C | 0.306232 | -1.303177 | -1.212169 |
| C | -0.016969 | -2.465843 | -1.955923 |
| C | -1.313659 | -2.884333 | -2.086153 |
| C | -2.309161 | -2.288157 | -1.271922 |
| C | -1.983746 | -1.134873 | -0.497298 |
| C | -3.591818 | -2.891229 | -1.141190 |
| C | -4.480919 | -2.459253 | -0.192468 |
| C | -4.103180 | -1.418148 | 0.687340 |
| C | -2.902245 | -0.772937 | 0.533527 |
| P | 2.042139 | -1.309416 | -0.666391 |
| C | 1.863943 | -1.429004 | 1.152402 |
| O | 2.846082 | -2.420690 | -1.308200 |
| H | 4.387251 | -0.543196 | -1.979947 |
| H | 5.432550 | 1.682586 | -2.513238 |
| H | 4.245214 | 3.766351 | -1.811315 |
| H | 2.103204 | 3.636605 | -0.625841 |
| H | 1.583371 | 2.965131 | 1.526292 |
| H | -0.544502 | 3.940956 | 2.300429 |
| H | -2.916821 | 4.426657 | 1.705217 |
| H | -4.884528 | 4.024842 | 0.243798 |
| H | -4.735182 | 2.296954 | -1.563454 |
| H | -2.769947 | 0.867137 | -1.755879 |
| H | -2.634214 | 0.009615 | 1.239706 |

| | | | |
|---|---|---|---|
| H | -4.767472 | -1.127572 | 1.502701 |
| H | -5.453181 | -2.942722 | -0.083745 |
| H | -3.832600 | -3.740184 | -1.784772 |
| H | -1.567571 | -3.746352 | -2.706270 |
| H | 0.812399 | -3.025110 | -2.392666 |
| C | 2.697290 | -0.700534 | 2.006127 |
| C | 2.578360 | -0.839345 | 3.387900 |
| C | 1.629220 | -1.708331 | 3.922495 |
| C | 0.800304 | -2.443594 | 3.074921 |
| C | 0.916597 | -2.305739 | 1.694872 |
| H | 3.437500 | -0.012284 | 1.592310 |
| H | 3.227475 | -0.261892 | 4.048497 |
| H | 1.532776 | -1.813740 | 5.004716 |
| H | 0.056567 | -3.125882 | 3.490062 |
| H | 0.259232 | -2.878634 | 1.036958 |

transition state of **1**

E(hartree): -1648.262302

| | | | |
|---|---|---|---|
| C | 3.469737 | 1.368220 | -0.234853 |
| C | 2.775111 | 0.129498 | -0.305994 |
| C | 3.602564 | -0.991010 | -0.635515 |
| C | 5.018403 | -0.895668 | -0.552355 |
| C | 5.640380 | 0.300784 | -0.307032 |
| C | 4.842470 | 1.459397 | -0.224845 |
| C | 1.323012 | -0.062199 | -0.203180 |
| C | 0.836084 | -1.159521 | -0.928342 |
| C | 1.690222 | -2.174029 | -1.451184 |
| C | 3.023474 | -2.162026 | -1.183721 |
| C | 0.314379 | 0.702014 | 0.660337 |
| C | -0.682094 | -0.040439 | 1.304584 |
| C | -1.916952 | 0.556403 | 1.713492 |
| C | -2.211239 | 1.846267 | 1.409017 |
| C | -1.163227 | 2.695917 | 0.970101 |
| C | 0.146144 | 2.158746 | 0.776385 |

| | | | |
|---|---|---|---|
| C | -1.394807 | 4.092831 | 0.875144 |
| C | -0.355574 | 4.981506 | 0.759772 |
| C | 0.957462 | 4.478261 | 0.833670 |
| C | 1.188596 | 3.120587 | 0.852627 |
| C | -0.711567 | -1.515967 | 1.567825 |
| C | -1.065190 | -2.399142 | 0.543894 |
| C | -1.272203 | -3.753536 | 0.790534 |
| C | -1.144498 | -4.236603 | 2.092304 |
| C | -0.789938 | -3.365288 | 3.121989 |
| C | -0.583288 | -2.008294 | 2.867284 |
| P | -0.897498 | -1.760308 | -1.142891 |
| O | -1.026754 | -2.844592 | -2.192560 |
| C | -2.051846 | -0.378915 | -1.404668 |
| C | -1.641615 | 0.846145 | -1.933438 |
| C | -2.579448 | 1.847893 | -2.175341 |
| C | -3.927824 | 1.624207 | -1.903296 |
| C | -4.342907 | 0.394208 | -1.392156 |
| C | -3.407588 | -0.605911 | -1.144834 |
| H | -1.508021 | -4.413521 | -0.046771 |
| H | -1.307151 | -5.295124 | 2.301881 |
| H | -0.671686 | -3.745418 | 4.138504 |
| H | -0.320770 | -1.327243 | 3.679215 |
| H | -2.670587 | -0.093694 | 2.158689 |
| H | -3.207571 | 2.257961 | 1.577743 |
| H | -2.424709 | 4.447808 | 0.955358 |
| H | -0.539317 | 6.055195 | 0.700802 |
| H | 1.801865 | 5.164987 | 0.916473 |
| H | 2.194501 | 2.784083 | 1.056157 |
| H | 2.910199 | 2.287118 | -0.312161 |
| H | 5.311508 | 2.444395 | -0.190956 |
| H | 6.728171 | 0.368319 | -0.258429 |
| H | 5.602674 | -1.798072 | -0.745244 |
| H | 3.665452 | -2.997554 | -1.469577 |
| H | 1.223173 | -2.998327 | -1.991762 |

| | | | |
|---|---|---|---|
| H | -3.731617 | -1.567773 | -0.740620 |
| H | -5.399443 | 0.214244 | -1.185960 |
| H | -4.660547 | 2.410819 | -2.093606 |
| H | -2.251477 | 2.809448 | -2.573603 |
| H | -0.585543 | 1.027672 | -2.141516 |

($R_P$,*M*)-**2**

E(hartree): -1647.143505

| | | | |
|---|---|---|---|
| C | -4.471687 | -1.043172 | 0.349609 |
| C | -3.190319 | -0.524278 | 0.271625 |
| C | -2.107240 | -1.395234 | -0.051571 |
| C | -2.390943 | -2.726911 | -0.467146 |
| C | -3.719131 | -3.215227 | -0.378926 |
| C | -4.732599 | -2.394656 | 0.052028 |
| C | -0.752217 | -0.924090 | -0.022671 |
| C | -0.474941 | 0.371728 | 0.637996 |
| C | -1.555411 | 1.321842 | 0.674964 |
| C | -2.902700 | 0.911204 | 0.435248 |
| C | -1.306115 | 2.683752 | 0.997529 |
| C | -0.002708 | 3.057223 | 1.413792 |
| C | 0.955919 | 2.101882 | 1.583334 |
| C | 0.744705 | 0.739940 | 1.217988 |
| C | -3.903198 | 1.868851 | 0.386416 |
| C | -3.631553 | 3.229929 | 0.614756 |
| C | -2.357423 | 3.630139 | 0.935650 |
| C | -1.344580 | -3.521741 | -1.004394 |
| C | -0.096081 | -2.987893 | -1.168320 |
| C | 0.208146 | -1.691234 | -0.680482 |
| C | 1.866952 | -0.172418 | 1.589583 |
| C | 2.539548 | -1.007383 | 0.688109 |
| C | 3.618860 | -1.795650 | 1.090449 |
| C | 4.054216 | -1.754464 | 2.411006 |
| C | 3.396117 | -0.930000 | 3.323706 |
| C | 2.320043 | -0.145630 | 2.917748 |

| | | | |
|---|---|---|---|
| P | 1.925121 | -1.173792 | -1.003432 |
| O | 2.701311 | -2.177695 | -1.829071 |
| C | 1.856549 | 0.520481 | -1.679942 |
| C | 0.752190 | 0.978035 | -2.403656 |
| C | 0.737013 | 2.276132 | -2.907887 |
| C | 1.828375 | 3.118648 | -2.701816 |
| C | 2.940032 | 2.660574 | -1.995633 |
| C | 2.954186 | 1.365316 | -1.485213 |
| H | -0.110301 | 0.326554 | -2.557213 |
| H | -0.134591 | 2.632621 | -3.459167 |
| H | 1.812551 | 4.137118 | -3.094380 |
| H | 3.796817 | 3.317419 | -1.835626 |
| H | 3.819325 | 1.013566 | -0.918147 |
| H | 4.097761 | -2.437416 | 0.348168 |
| H | 4.899456 | -2.366265 | 2.730504 |
| H | 3.719591 | -0.899472 | 4.365848 |
| H | 1.806082 | 0.486762 | 3.644333 |
| H | 1.938828 | 2.380747 | 1.965448 |
| H | 0.207830 | 4.104506 | 1.638523 |
| H | -2.138763 | 4.676685 | 1.157319 |
| H | -4.441904 | 3.958159 | 0.557792 |
| H | -4.928251 | 1.572654 | 0.163481 |
| H | -5.304249 | -0.401506 | 0.638835 |
| H | -5.751777 | -2.775409 | 0.135040 |
| H | -3.920439 | -4.248815 | -0.667077 |
| H | -1.563368 | -4.539833 | -1.332559 |
| H | 0.704064 | -3.543821 | -1.660344 |

($R_P$,*P*)-**2**

E(hartree): -1647.130494

| | | | |
|---|---|---|---|
| C | -3.939404 | -2.596353 | -0.774090 |
| C | -3.105277 | -1.582851 | -0.332761 |
| C | -1.693469 | -1.721817 | -0.493625 |
| C | -1.177800 | -2.973790 | -0.930442 |

| | | | |
|---|---|---|---|
| C | -2.065860 | -3.990765 | -1.362607 |
| C | -3.422835 | -3.789918 | -1.313088 |
| C | -0.801548 | -0.642639 | -0.169939 |
| C | -1.392373 | 0.700135 | 0.039278 |
| C | -2.765479 | 0.753552 | 0.469209 |
| C | -3.615513 | -0.387647 | 0.357054 |
| C | -3.322515 | 1.964957 | 0.963227 |
| C | -2.544779 | 3.148286 | 0.899204 |
| C | -1.323205 | 3.123120 | 0.293856 |
| C | -0.726594 | 1.912415 | -0.165327 |
| C | -4.902207 | -0.330760 | 0.868282 |
| C | -5.412069 | 0.844766 | 1.447687 |
| C | -4.643423 | 1.982457 | 1.473313 |
| C | 0.219981 | -3.193651 | -0.870183 |
| C | 1.045071 | -2.226825 | -0.366606 |
| C | 0.559131 | -0.935729 | -0.026865 |
| C | 0.542684 | 2.122985 | -0.921543 |
| C | 1.771845 | 1.528493 | -0.594720 |
| C | 2.938168 | 1.909300 | -1.267468 |
| C | 2.890729 | 2.843267 | -2.296601 |
| C | 1.667639 | 3.403563 | -2.660296 |
| C | 0.512030 | 3.056204 | -1.970010 |
| P | 1.708985 | 0.280869 | 0.725430 |
| O | 1.282793 | 0.792146 | 2.082568 |
| C | 3.363312 | -0.495921 | 0.792852 |
| C | 4.070501 | -0.986400 | -0.314239 |
| C | 5.333267 | -1.546884 | -0.144964 |
| C | 5.898752 | -1.621050 | 1.129529 |
| C | 5.201250 | -1.132499 | 2.231788 |
| C | 3.936249 | -0.569254 | 2.064832 |
| H | 3.632920 | -0.934531 | -1.313914 |
| H | 5.878151 | -1.928531 | -1.010165 |
| H | 6.888392 | -2.062982 | 1.260671 |
| H | 5.643316 | -1.189277 | 3.227990 |

| | | | |
|---|---|---|---|
| H | 3.372002 | -0.174837 | 2.912206 |
| H | 3.896555 | 1.479201 | -0.976157 |
| H | 3.807334 | 3.132945 | -2.812811 |
| H | 1.613725 | 4.124449 | -3.477910 |
| H | -0.441148 | 3.509895 | -2.247699 |
| H | -0.750665 | 4.045585 | 0.190896 |
| H | -2.950513 | 4.079420 | 1.299226 |
| H | -5.038699 | 2.916075 | 1.878743 |
| H | -6.424945 | 0.850907 | 1.852945 |
| H | -5.541828 | -1.212596 | 0.829474 |
| H | -5.020799 | -2.481888 | -0.700313 |
| H | -4.109652 | -4.564122 | -1.658652 |
| H | -1.650866 | -4.933703 | -1.724124 |
| H | 0.622216 | -4.162554 | -1.172529 |
| H | 2.099839 | -2.456146 | -0.228294 |

transition state of **2**

E(hartree): -1647.088330

| | | | |
|---|---|---|---|
| C | 3.867830 | -0.698870 | -1.097236 |
| C | 3.401193 | -0.726239 | 0.222575 |
| C | 4.178914 | -1.305598 | 1.225451 |
| C | 5.418620 | -1.864116 | 0.910877 |
| C | 5.879103 | -1.840768 | -0.403562 |
| C | 5.103591 | -1.256845 | -1.408678 |
| P | 1.791823 | -0.016380 | 0.735935 |
| O | 1.627802 | -0.064191 | 2.239860 |
| C | 1.822916 | 1.659920 | 0.080068 |
| C | 0.676167 | 2.406278 | -0.262591 |
| C | 0.880711 | 3.811859 | -0.313395 |
| C | 2.120412 | 4.414510 | -0.182032 |
| C | 3.252656 | 3.640774 | 0.049454 |
| C | 3.079543 | 2.278857 | 0.214300 |
| C | -0.737200 | 1.925558 | -0.484014 |
| C | -1.413729 | 0.714469 | -0.164670 |

| | | | |
|---|---|---|---|
| C | -2.861522 | 0.811332 | -0.006315 |
| C | -3.561822 | 2.037953 | -0.178078 |
| C | -2.889246 | 3.069543 | -0.871536 |
| C | -1.550725 | 2.966683 | -1.054966 |
| C | -3.662639 | -0.309985 | 0.361865 |
| C | -3.142484 | -1.647633 | 0.086633 |
| C | -1.751711 | -1.793982 | -0.181776 |
| C | -0.837087 | -0.670658 | -0.103395 |
| C | -4.947932 | -0.119406 | 0.849487 |
| C | -5.564035 | 1.140176 | 0.828127 |
| C | -4.900322 | 2.192518 | 0.246406 |
| C | -1.284218 | -3.109105 | -0.481809 |
| C | 0.097781 | -3.330019 | -0.663752 |
| C | 0.968322 | -2.312758 | -0.418705 |
| C | 0.526393 | -0.997070 | -0.107926 |
| C | -2.183642 | -4.200500 | -0.565767 |
| C | -3.520350 | -4.020102 | -0.324320 |
| C | -3.992542 | -2.739791 | 0.004177 |
| H | 3.262231 | -0.239745 | -1.882690 |
| H | 5.467622 | -1.235667 | -2.437535 |
| H | 6.848582 | -2.278075 | -0.649775 |
| H | 6.026297 | -2.317131 | 1.696264 |
| H | 3.794026 | -1.305769 | 2.247503 |
| H | 3.941553 | 1.667918 | 0.483169 |
| H | 4.239014 | 4.093685 | 0.155950 |
| H | 2.191126 | 5.502110 | -0.238248 |
| H | 0.034115 | 4.483142 | -0.410577 |
| H | -1.059209 | 3.737017 | -1.640951 |
| H | -3.445500 | 3.926467 | -1.255239 |
| H | -5.381447 | 3.163908 | 0.117764 |
| H | -6.576224 | 1.260120 | 1.216712 |
| H | -5.510266 | -0.971689 | 1.229620 |
| H | -5.061171 | -2.606006 | 0.165288 |
| H | -4.218684 | -4.855719 | -0.388557 |

| | | | |
|---|---|---|---|
| H | -1.784021 | -5.185360 | -0.814421 |
| H | 0.458070 | -4.325635 | -0.927975 |
| H | 2.036444 | -2.516235 | -0.453594 |